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Supporting Information

A Regio- and Stereodivergent Synthesis of Homoallylic Amines by a One-Pot Cooperative-Catalysis-Based Allylic Alkylation/Hofmann Rearrangement Strategy

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Supporting Information

General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry N_2 in flame or oven dried glassware with standard vacuum-line techniques. All reactions were carried out in Teflon screw cap reaction vials with magnetic stirring unless otherwise indicated. Dichloromethane, tetrahydrofuran, dioxane, and acetonitrile were purified under a positive pressure of dry argon by passage through two columns of activated alumina. Toluene was purified under a positive pressure of dry argon by passage through columns of activated alumina and Q5 (Grubbs apparatus). All workup and purification procedures were carried out with reagent grade solvents (purchased from Sigma-Aldrich) in air. Standard column chromatography techniques using ZEOprep 60/40-63 μm silica gel were used for purification. Liquids and solutions were transferred via syringe or cannula. Pentafluorophenyl esters were obtained from group's inventory and verified pure before use.

^{1}H and ^{13}C NMR spectra were recorded at room temperature (25 °C) on Varian Inova-instrumentation: Varian I400 (^{1}H NMR at 400MHz and ^{13}C NMR at 100 MHz), Varian VXR400 (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz), Varian I500 (^{1}H NMR at 500 MHz and ^{13}C NMR at 126 MHz) and Varian I600 (^{1}H NMR at 600 MHz and ^{13}C NMR at 151 MHz) using deuterium lock. Data for ^{1}H NMR spectra are quoted relative to chloroform as an internal standard (7.26 ppm) and data for ^{13}C NMR spectra are quoted relative to chloroform or as an internal standard (77.16 ppm) and are reported in terms of chemical shift (δ ppm). Carbon signals of aryl pentafluorophenyl esters in ^{13}C NMR not observed due to fluorine splitting. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. Infrared spectra (IR) were obtained on the Bruker TENSOR II FTIR Spectrometer and recorded in wavenumbers (cm^{-1}). Melting points were obtained on a Thomas Hoover capillary melting point apparatus without correction. High Resolution Mass (HRMS) analysis was obtained using Electron Impact Ionization (EI), Chemical Ionization (CI), Electrospray (ESI) and Atmospheric Pressure Chemical Ionization (APCI) and reported as m/z (relative intensity) for the $[M]^+$, $[M+H]^+$ or $[M+Na]^+$ molecular ion. Chiral HPLC analyses were performed on an Agilent 1200 Series system.

Experimental Section

Catalysts

(*R*)-(+)-Benzotetramisole, [(+)-BTM, CAS: 885051-07-0] and **(*S*)-(–)-Benzotetramisole** [(–)-BTM, CAS: 950194-37-3] were prepared from (*R*)-(–)-2-phenylglycinol or (*S*)-(+)-2-phenylglycinol, respectively, by the procedure of Smith and co-workers.[2]

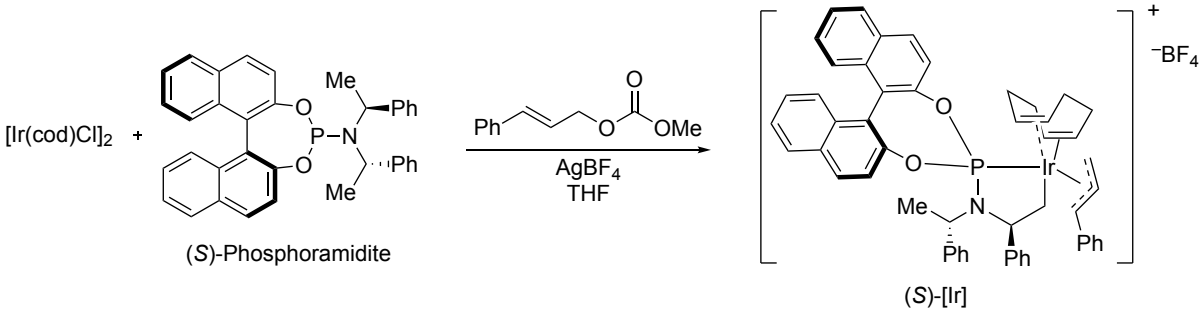
Pd_2dba_3 [CAS: 51364-51-3] was obtained from Oakwood Chemical and used without further purification.

Pd Xantphos G3 was prepared by the procedure of Buchwald and co-workers.[3]

$P(2\text{-thienyl})_3$ [CAS: 24171-89-9] was obtained from Alfa Aesar and used without further purification.

Tris[tri(2-thienyl)phosphine]palladium was prepared following the procedure of Bo and co-workers.[4]

[Ir] complex was prepared using a variation of the procedures from You,[5] Hartwig,[6] and Lundgren.[7] **(*R*)-[Ir]** was prepared using (*R*)-phosphoramidite and (*R*)-BINOL. **(*S*)-[Ir]** was prepared using (*S*)-phosphoramidite and (*S*)-BINOL as follows:



To a flame dried 100 mL 2-necked round bottom flask equipped with stirrer bar and nitrogen inlet were added $[Ir(cod)Cl]_2$ (1.0 g, 1.5 mmol, 1.0 equiv.) and (*S*)-Phosphoramidite (1.4 g, 3 mmol, 2 equiv.). The flask was then sealed with a rubber septa and purged with N_2 three times before adding THF (30 mL, 0.05 M). The reaction mixture was then stirred at room temperature for 30 mins before removing the septa adding cinnamyl methyl carbonate (578 mg, 3 mmol, 2 equiv.) and $AgBF_4$ (773 mg, 3 mmol, 2 equiv.) under a concurrent flow of nitrogen, affording a dark brown slurry. The flask was resealed with a rubber septa and continued stirring at room temperature for a further 2 h. The reaction mixture was then taken up in a 5 mL syringe via a 12 G wide bore needle. This needle was then exchanged for a 13 mm, 0.2 μm syringe filter and 20 G needle and the reaction mixture was added dropwise to stirred HPLC grade pentane, affording a beige precipitate. This process was repeated for the entire reaction mixture, using a fresh syringe filter each time. The crude complex was then collected by filtration and purified by trituration. The beige solid was added to a beaker and dissolved in a minimal quantity of DCM (5-10 mL) before adding Et_2O (20 mL) and pentane (20 mL). The resulting beige solid

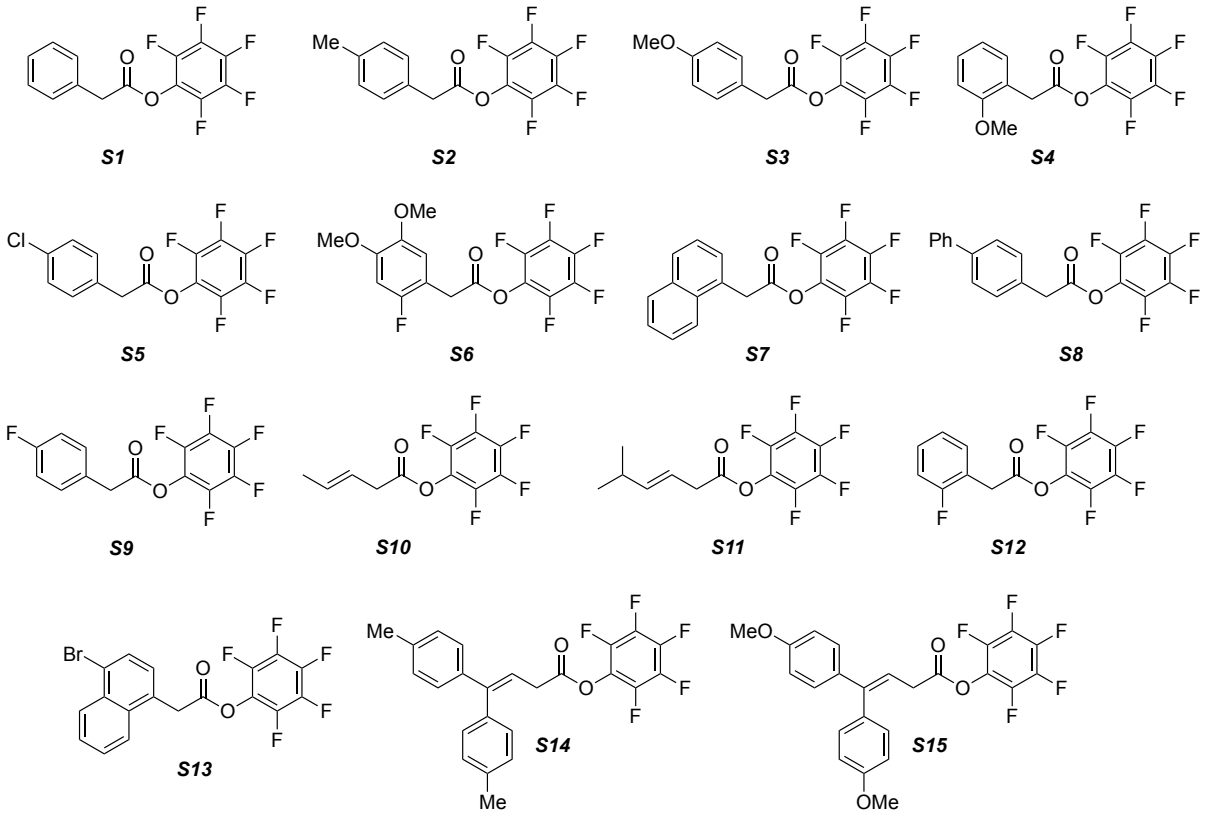
was crushed against the walls of the beaker. The supernatant was then removed, additional Et_2O (10 mL) was then added and the solid crushed again. The supernatant was again removed and the solid was redissolved in DCM and the above trituration steps were repeated. The resulting beige solid was then collected by filtration and dried under high vacuum to afford the desired Ir complex (2.07 g, 66%). Characterisation is consistent with these types of complexes reported previously.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.8 Hz, 1H), 8.22 (d, *J* = 8.9 Hz, 1H), 8.05 (dd, *J* = 12.3, 8.2 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.56 (ddd, *J* = 7.8, 5.0, 2.4 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.40 – 7.35 (m, 10H), 7.34 – 7.28 (m, 4H), 7.11 – 7.07 (m, 2H), 5.77 (t, *J* = 12.1 Hz, 1H), 5.30 – 5.21 (m, 1H), 4.77 (td, *J* = 11.6, 7.3 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.96 – 3.85 (m, 3H), 2.93 – 2.83 (m, 3H), 2.80 – 2.70 (m, 1H), 2.53 (q, *J* = 12.0, 10.4 Hz, 1H), 2.44 (d, *J* = 11.1 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.18 – 2.12 (m, 1H), 2.08 (dd, *J* = 12.7, 5.5 Hz, 1H), 1.83 – 1.72 (m, 1H), 1.64 – 1.52 (m, 6H), 1.11 (t, *J* = 12.3 Hz, 1H), 0.61 (d, *J* = 7.4 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 120.13.

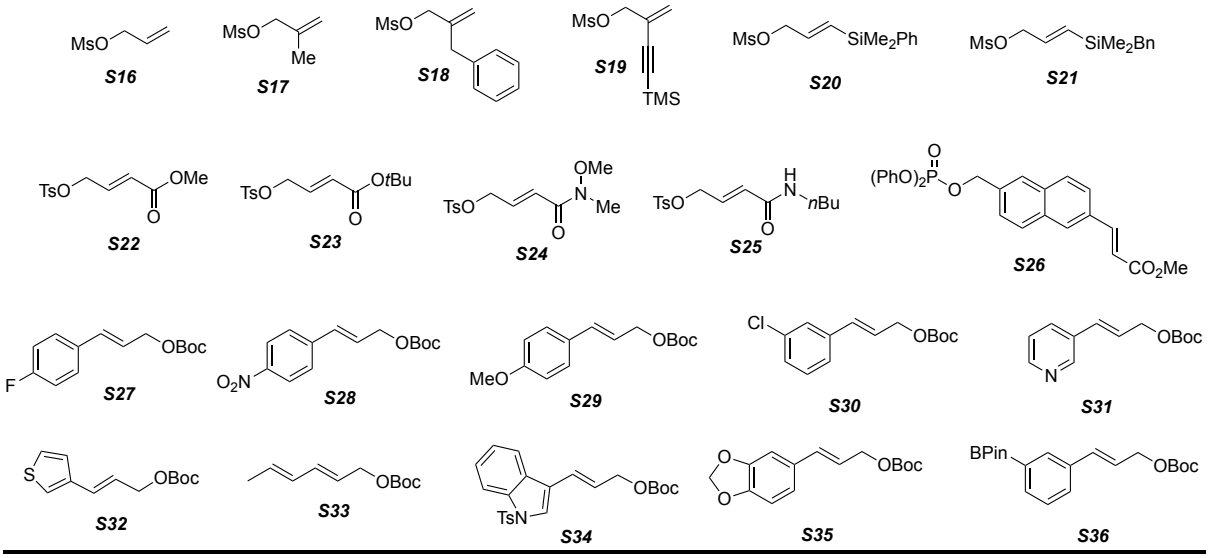
Aryl/Vinyl Acetic Acid Pentafluorophenyl Esters

Aryl/vinyl acetic acid Pentafluorophenyl esters **S1**–**S8** were prepared from the corresponding aryl/vinyl acetic acids according to previously published procedures.[8] Esters **S9**–**S11**,[9] **S12**,[10] **S13**,[11] and **S14**–**S15**[12] were prepared according to previously published procedures.



Electrophilic Partners

2-Substituted allyl mesylates **S17**–**S19** were prepared according to previously published procedures.[9] Silyl allyl mesylates **S20**–**S21** were prepared according to previously published procedures.[13] Electron withdrawing substituted allyl tosylates **S22**–**S25** were prepared according to previously published procedures.[14] Naphthyl phosphate **S26** was prepared according to previously published procedure.[12] Cinnamyl/vinyl carbonates **S27**–**S37** were prepared according to previously published procedures.[8,10,15]



(*E*)-*tert*-butyl (3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)allyl) carbonate (S36): Prepared according to previously published procedure,[8] the *title compound* was obtained as a white solid (432 mg, 30%) following purification by column chromatography (SiO_2, 10% Et_2O/petroleum ether).

IR (neat): 2978, 2934, 1739, 1425, 1359, 1273, 1254, 1145, 966, 853 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.70 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 6.68 (d, J = 16.0 Hz, 1H), 6.47 – 6.24 (m, 1H), 4.71 (d, J = 5.4 Hz, 2H), 1.50 (s, 9H), 1.35 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.5, 135.7, 134.5, 134.4, 133.3, 129.5, 128.1, 123.2, 84.0, 82.3, 67.6, 28.0, 25.0. Carbon bearing boron not observed.

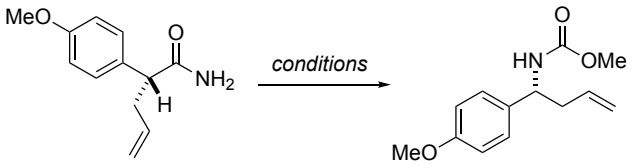
HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{20}H_{29}O_5BNa$: 383.2004 Found: 383.2003.

Reaction Optimization

General Procedure for Optimization of Hofmann Rearrangement

To an oven dried 1 dram vial was added (*R*)-2-(4-methoxyphenyl)pent-4-enamide (20.5 mg, 0.1 mmol, 1 equiv. 96:4 er) along with specified oxidant and base. The vial was then sealed and added solvent (1 mL, 0.1 M) and stirred at room temperature overnight. The reaction mixture was then diluted with EtOAC, washed with H_2O and brine, dried with Na_2SO_4 and concentrated under vacuum before adding durene (0.1 mL, 0.25 M, 0.025 mmol, 0.25 equiv) as a solution in $CDCl_3$. The reaction mixture was then diluted with $CDCl_3$ and analyzed by ^1H NMR.

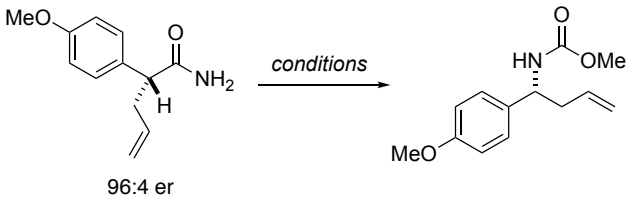
Table S1: Oxidant Screen



96:4 er

Entry	Oxidant	Base	Solvent	Yield [%]
1	PIFA (65 mg, 1.5 equiv.)	KOH (14 mg, 2.5 equiv.)	MeOH	90 (96:4 er)
2	PIDA (48 mg, 1.5 equiv.)	KOH (14 mg, 2.5 equiv.)	MeOH	80
3	PhI (20 mg, 1 equiv.) Oxone (123 mg, 2 equiv.)	-	MeOH	-
4	$Pb(OAc)_4$ (67 mg, 1.5 equiv.)	-	MeOH	89
5	NBS (27 mg, 1.5 equiv.)	DBU (45 μL, 3 equiv.)	MeOH	76

Table S2: Solvent Screen



96:4 er

Entry	Oxidant	Base	Solvent	Yield [%]
1	PIFA (65 mg, 1.5 equiv.)	KOH (14 mg, 2.5 equiv.)	THF/MeOH (20:1)	43
2	PIFA (65 mg, 1.5 equiv.)	KOH (14 mg, 2.5 equiv.)	Toluene/MeOH (20:1)	76
3	PIFA (65 mg, 1.5 equiv.)	KOH (14 mg, 2.5 equiv.)	MeCN/MeOH (20:1)	38
4	PIFA (65 mg, 1.5 equiv.)	KOH (14 mg, 2.5 equiv.)	THF/MeOH (2:1)	66
5	PIFA (65 mg, 1.5 equiv.)	KOH (14 mg, 2.5 equiv.)	Toluene/MeOH (2:1)	88
6	PIFA (65 mg, 1.5 equiv.)	KOH (14 mg, 2.5 equiv.)	MeCN/MeOH (2:1)	67
7	PIFA (65 mg, 1.5 equiv.)	-	THF/MeOH (2:1)	80
8[a]	PIFA (65 mg, 1.5 equiv.)	-	THF/MeOH (2:1)	99 (96:4 er)

[a] Reaction run at 60 °C overnight.

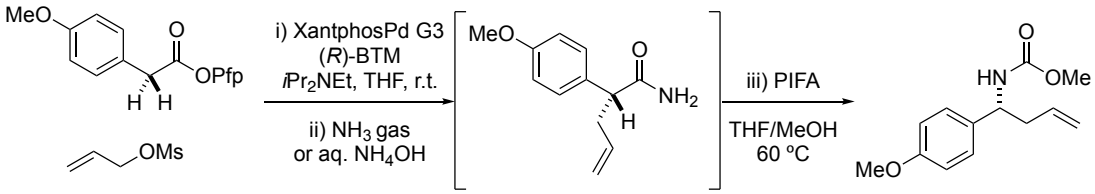
General Procedure for One-Pot allylation/Hofmann rearrangement with Palladium

To an oven dried 1 dram was added 4-methoxyphenyl acetic acid pentafluorophenyl ester (33 mg, 0.1 mmol, 1 equiv.) allyl mesylate (17 mg, 0.125 mmol, 1.25 equiv.), Xantphos Pd G3 (4.8 mg, 5 mol%) and (*R*)-BTM (5 mg, 20 mol%). The vial was then sealed and purged with N_2 × 3 before adding THF (1 mL, 0.1 M) and DIPEA (23 µL, 0.125 mmol, 1.25 equiv.). The reaction mixture was then stirred at room temperature for 24 h.

For reactions with NH_3 gas: A vent needle was then added and a balloon of NH_3 gas was bubbled through the reaction mixture while stirring continued. This was followed by a balloon of Ar gas in order to purge the NH_3 from solution. The reaction mixture was refilled to 1 mL with THF, replacing any solvent blown off during the bubbling process.

For reactions with aq. NH_4OH: aq. NH_4OH (1 mL) was added and the reaction mixture was stirred for 10 mins at room temperature. The reaction mixture was then diluted with EtOAc, washed with H_2O, 1 M HCl and brine before being dried with Na_2SO_4 and concentrated under vacuum. The crude mixture was then diluted with 1 mL THF.

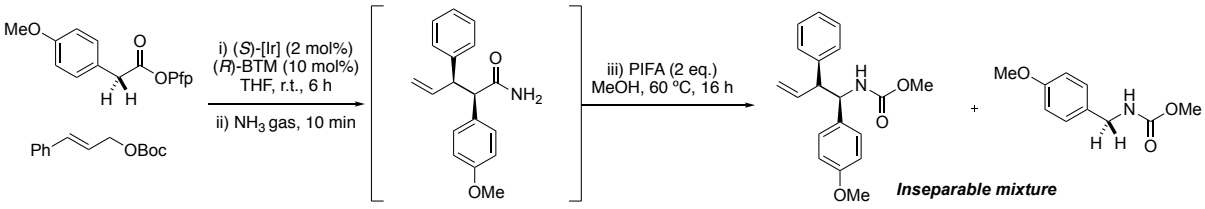
The cap was removed, MeOH (0.5 mL) was added followed by PIFA (65 mg, 0.15 mmol, 1.5 equiv.). The vial was then resealed and heated to 60 °C overnight. The reaction mixture was then diluted with EtOAC, washed with H_2O and brine, dried with Na_2SO_4 and concentrated under vacuum before adding durene (0.1 mL, 0.25 M, 0.025 mmol, 0.25 equiv) as a solution in $CDCl_3$. The reaction mixture was then diluted with $CDCl_3$ and analyzed by ^1H NMR.



Entry	**NH_3 Source**	**Oxidant**	Yield [%]
1	NH_3 gas	PIFA (65 mg, 1.5 equiv.)	67
2	NH_3 gas	PIFA (86 mg, 2 equiv.)	74 (97:3 er)
3	aq. NH_4OH (1 mL)	PIFA (86 mg, 2 equiv.)	73 (97:3 er)

Note: The reaction could also be performed using aqueous NH_4OH as an NH_3 source in identical yield and enantioselectivity however this does require an aqueous workup prior to oxidative rearrangement.

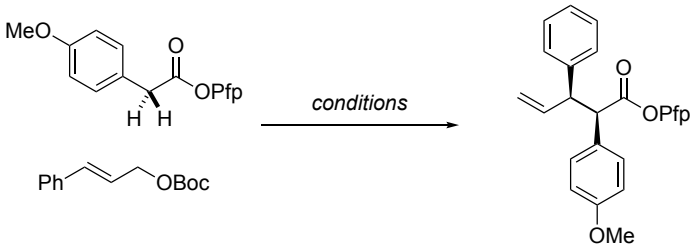
Optimization of one-Pot allylation/Hofmann rearrangement with Iridium



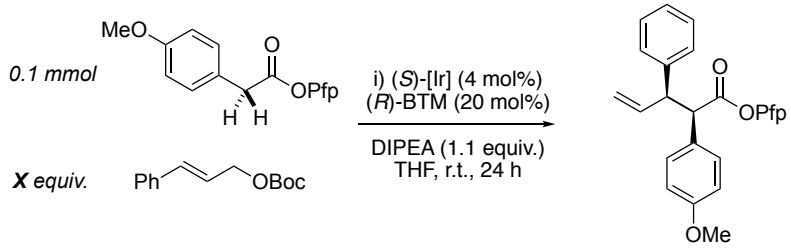
Initial attempts to directly transfer the conditions for oxidative rearrangement to a one-pot protocol based on the allylation conditions reported by Hartwig and coworkers[10] resulted in a large quantity of methyl (4-methoxybenzyl)carbamate which was inseparable from the desired product. Suspecting that this arose from incomplete consumption of the starting Pfp ester during the allylation step, screening was undertaken to optimize this step in isolation.

General Procedure for Optimization of Iridium Catalyzed Allylation

To an oven dried 1 dram was added *t*-butyl cinnamyl carbonate (23.4 mg, 0.1 mmol, 1 equiv.), 4-methoxyphenyl acetic acid pentafluorophenyl ester (34.7 mg, 0.105 mmol, 1.05 equiv.) (*S*)-[Ir] and (*R*)-BTM. The vial was then sealed and purged with N_2 × 3 before adding THF (0.5 mL, 0.2 M) and DIPEA (where required). The reaction mixture was then stirred at room temperature for the specified time. The reaction mixture was then diluted with petroleum ether and passed through a plug of silica. The vial was then rinsed with 1:1 EtOAc/petroleum ether and passed through silica plug. The crude reaction mixture was then concentrated under vacuum before adding durene (0.1 mL, 0.25 M, 0.025 mmol, 0.25 equiv) as a solution in $CDCl_3$. The reaction mixture was then diluted with $CDCl_3$ and analyzed by ^1H NMR.



Entry	(*S*)-[Ir]	(*R*)-BTM	DIPEA	Time	Yield [%]
1	2 mol% (2.1 mg)	10 mol% (2.5 mg)	-	6 h	23
2	2 mol% (2.1 mg)	10 mol% (2.5 mg)	-	24 h	34
3	2 mol% (2.1 mg)	10 mol% (2.5 mg)	1.1 equiv. (20 μL)	6 h	48
4	2 mol% (2.1 mg)	10 mol% (2.5 mg)	1.1 equiv. (20 μL)	24 h	42
5	4 mol% (4.2 mg)	10 mol% (2.5 mg)	-	6 h	64
6	2 mol% (2.1 mg)	20 mol% (5.0 mg)	-	6 h	20
7	4 mol% (4.2 mg)	20 mol% (5.0 mg)	-	6 h	71
8	4 mol% (4.2 mg)	10 mol% (2.5 mg)	1.1 equiv. (20 μL)	6 h	74
9	4 mol% (4.2 mg)	10 mol% (2.5 mg)	1.1 equiv. (20 μL)	24 h	70
10	4 mol% (4.2 mg)	20 mol% (5.0 mg)	1.1 equiv. (20 μL)	6 h	67
11	4 mol% (4.2 mg)	20 mol% (5.0 mg)	-	24 h	68
12	4 mol% (4.2 mg)	20 mol% (5.0 mg)	1.1 equiv. (20 μL)	24 h	83



Entry	*t*-butyl cinnamyl carbonate	Yield [%]
1	1.0 equiv. (23.4 mg)	73
2	1.1 equiv. (25.7 mg)	77
3	1.2 equiv. (28.1 mg)	81
4	1.5 equiv. (35.1 mg)	94

General Procedures-Preparation of homoallylic amine products

General Procedure A for linear homoallylic amines with palladium

To an oven dried 2 dram equipped with stirrer bar was added the specified acetic acid pentafluorophenyl ester (0.25 mmol, 1 equiv.), electrophile (0.3125 mmol, 1.25 equiv.), Pd catalyst (5 mol%) and (*R*)-BTM (12.5 mg, 20 mol%). The vial was then sealed and purged with N_2 × 3 before adding THF (2.5 mL, 0.1 M) and DIPEA (57 μL, 0.3125 mmol, 1.25 equiv.). The reaction mixture was then stirred at room temperature for 24 h. A vent needle was then added and a balloon of NH_3 gas was bubbled through the reaction mixture while stirring continued. This was followed by a balloon of Ar gas in order to purge the NH_3 from solution. The reaction mixture was refilled to 2.5 mL with THF, replacing any solvent blown off during the bubbling process. The cap was removed, the specified alcohol (1.25 mL) was added followed by PIFA (215 mg, 0.5 mmol, 2.0 equiv.). The vial was then resealed and heated to 60 °C overnight. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and washed twice with 2 M Na_2CO_3 before being dried (Na_2SO_4) and concentrated under vacuum. The crude material was then dry loaded on silica and purified by column chromatography (SiO_2, specified eluent).

General Procedure B for Hiyama-Denmark cross-coupling

To an oven dried 2 dram vial equipped with stirrer bar was added methyl (*R*,*E*)-(4-(benzyldimethylsilyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (96 mg, 0.25 mmol, 1 equiv.). The vial was then capped and purged with N_2 before adding THF (0.45 mL, 0.56 M) and H_2O (13.5 μL, 0.75 mmol, 3 equiv.) and cooling to 0 °C. Tetrabutylammonium fluoride (0.55 mL, 1 M in THF, 0.55 mmol, 2.2 equiv.) was then added and the reaction mixture was stirred at 0 °C for 5 minutes before the addition of the specified iodide (0.375 mmol, 1.5 equiv.) and Pd_2dba_3 (5.7 mg, 2.5 mol%). The reaction mixture was then warmed to room temperature and stirred for 24 h before being quenched with H_2O (2 mL) and extracted with Et_2O (4 mL). The organics were then dried (Na_2SO_4) and concentrated under vacuum before being purified by column chromatography (SiO_2, specified eluent).

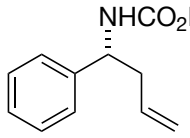
General Procedure C for branched homoallylic amines with iridium

To an oven dried 2 dram vial equipped with stirrer bar was added the specified acetic acid pentafluorophenyl ester (0.25 mmol, 1 equiv.) specified *t*-butyl carbonate (0.375 mmol, 1.5 equiv.), [Ir] (10.5 mg, 4 mol%) and BTM (12.5 mg, 20 mol%). The vial was then sealed and purged with N_2 × 3 before adding THF (1.25 mL, 0.2 M) and DIPEA (50 μL, 0.275 mmol, 1.1 equiv.). The reaction mixture was then stirred at room temperature for 24 h before being diluted with petroleum ether and passed through a plug of silica. The vial was then rinsed with 1:1 EtOAc/petroleum ether and passed through silica plug and the solvent removed under vacuum. The crude reaction mixture was then dissolved in THF (2.5 mL) and returned to the original 2 dram vial. A vent needle was then added and a balloon of NH_3 gas was bubbled through the reaction mixture while stirring continued. This was followed by a balloon of Ar gas in order to purge the NH_3 from solution. The reaction mixture was refilled to 2.5 mL with THF, replacing any solvent blown off during the bubbling process. The cap was removed, the specified alcohol (1.25 mL) was added followed by PIFA (215 mg, 0.5 mmol, 2.0 equiv.). The vial was then resealed and heated to 60 °C overnight. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and washed twice with 2 M Na_2CO_3 before being

dried (Na_2SO_4) and concentrated under vacuum. The crude material was then dry loaded on silica and purified by column chromatography (SiO_2, specified eluent).

Products from Scheme 1

Scope of Nucleophile



Methyl (*R*)-(1-phenylbut-3-en-1-yl)carbamate (1): Prepared according to General Procedure A using phenyl acetic acid pentafluorophenyl ester (76 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a colourless oil (39 mg, 76%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (93:7) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +41.2° (*c* = 1.0, $CHCl_3$).

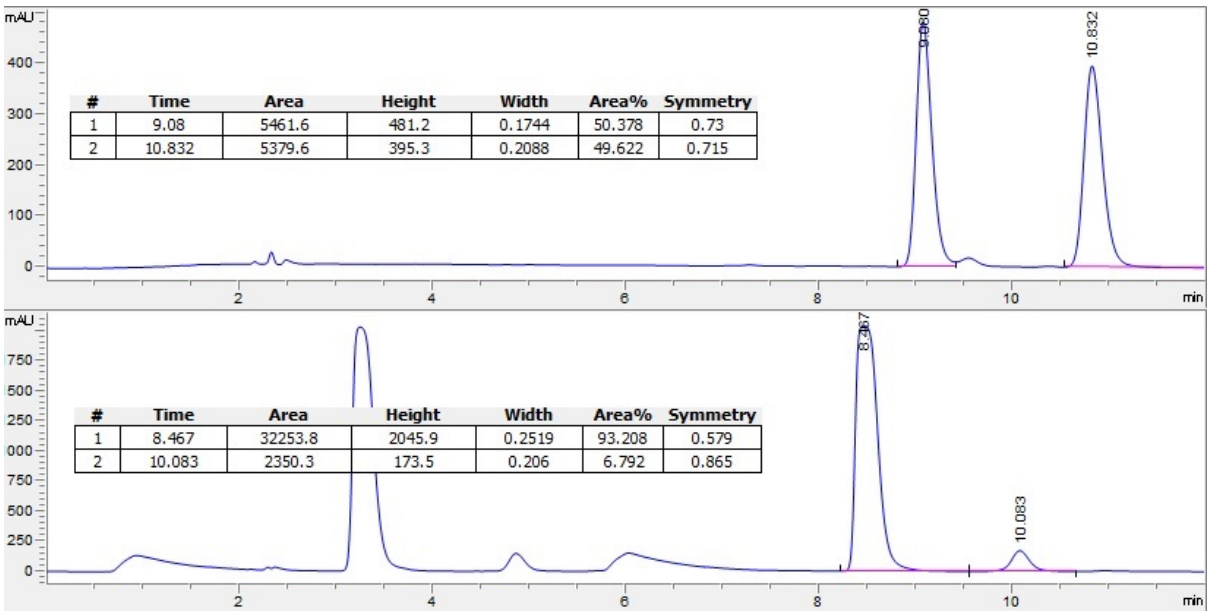
IR (neat): 3313, 2949, 1692, 1515, 1251, 917 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, *J* = 7.4 Hz, 2H), 7.23 – 7.14 (m, 3H), 5.61 (tt, *J* = 14.4, 5.1 Hz, 1H), 5.20 – 4.89 (m, 3H), 4.72 (s, 1H), 3.58 (s, 3H), 2.47 (s, 2H).

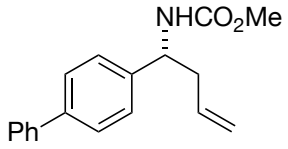
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.5, 142.1, 133.9, 128.7, 127.4, 126.3, 118.5, 54.5, 52.3, 41.1.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{25}H_{18}F_5NO_3Na$: 228.0995 Found: 228.0996.

HPLC analysis using a chiral column (Chiralpak IA 3µ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{major} = 8.467, t_{minor} = 10.083 min).



Methyl (*R*)-(1-([1,1'-biphenyl]-4-yl)but-3-en-1-yl)carbamate (2): Prepared according to General Procedure A using 2-([1,1'-biphenyl]-4-yl)acetic acid pentafluorophenyl ester (95 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white solid (51 mg, 73%) following purification by column chromatography (SiO_2, 10–20% EtOAc/petroleum ether). The enantiomeric ratio (92:8) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +92.5° (*c* = 1.0, $CHCl_3$).

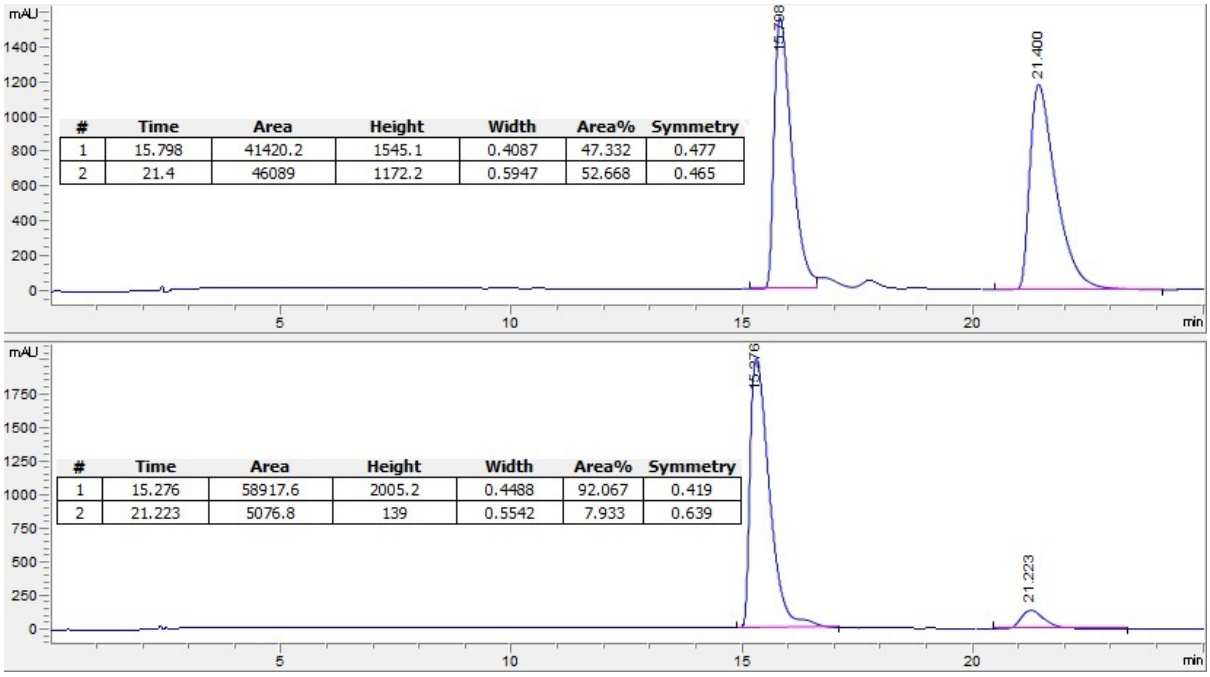
IR (neat): 3366, 2948, 1693, 1518, 1263, 1043, 778 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 8.0, 6.4 Hz, 4H), 7.44 (s, 2H), 7.41 – 7.31 (m, 3H), 5.81 – 5.71 (m, 1H), 5.27 – 5.06 (m, 3H), 4.86 (s, 1H), 3.68 (s, 3H), 2.59 (q, *J* = 6.5 Hz, 2H).

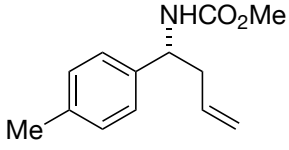
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.5, 141.3, 140.8, 140.3, 133.9, 128.8, 127.4, 127.3, 127.1, 126.8, 54.3, 52.3, 41.1.

HRMS (APCl): *m/z* calcd for $[M+H]^+$ $C_{25}H_{19}F_5NO_3$: 282.1489 Found: 282.1491.

HPLC analysis using a chiral column (Chiralpak IA 3µ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{major} = 15.276 min, t_{minor} = 21.223 min).



Methyl (*R*)-(1-(*p*-tolyl)but-3-en-1-yl)carbamate (3): Prepared according to General Procedure A using *p*-tolylacetic acid pentafluorophenyl ester (79 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a colourless oil (43 mg, 74%) following purification by column chromatography (SiO_2, 10%



EtOAc/petroleum ether). The enantiomeric ratio (96:4) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +74.2° (*c* = 1.0, $CHCl_3$).

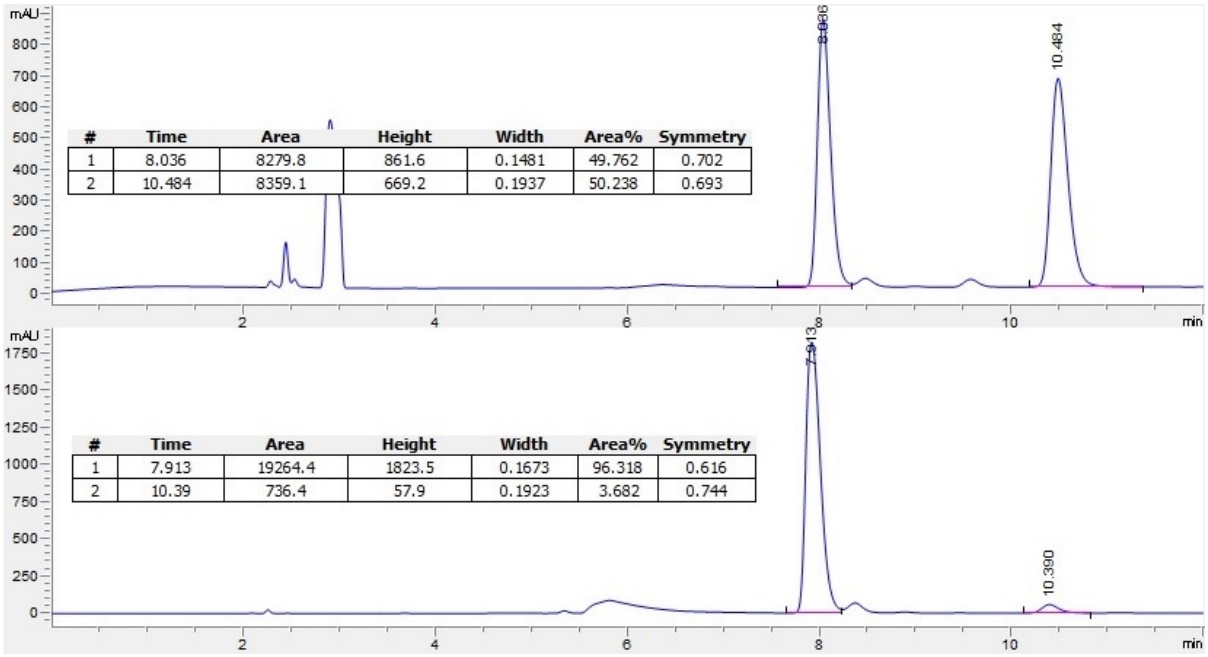
IR (neat): 3318, 2948, 1695, 1515, 1253, 1046 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, *J* = 4.4 Hz, 4H), 5.78 – 5.59 (m, 1H), 5.23 – 5.01 (m, 3H), 4.75 (s, 1H), 3.64 (s, 3H), 2.53 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 156.2, 138.9, 136.8, 133.8, 129.1, 126.0, 118.1, 54.1, 52.0, 40.9, 20.9.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{25}H_{18}F_5NO_3Na$: 242.1152 Found: 242.1152.

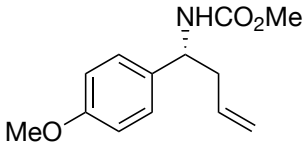
HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{major} = 7.913 min, t_{minor} = 10.390 min).



#	Time	Area	Height	Width	Area%	Symmetry
1	8.036	8279.8	861.6	0.1481	49.762	0.702
2	10.484	8359.1	669.2	0.1937	50.238	0.693

#	Time	Area	Height	Width	Area%	Symmetry
1	7.913	19264.4	1823.5	0.1673	96.318	0.616
2	10.39	736.4	57.9	0.1923	3.682	0.744

Methyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (4): Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white solid (43 mg, 73%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (97:3) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +31.7° (*c* = 1.0, $CHCl_3$).

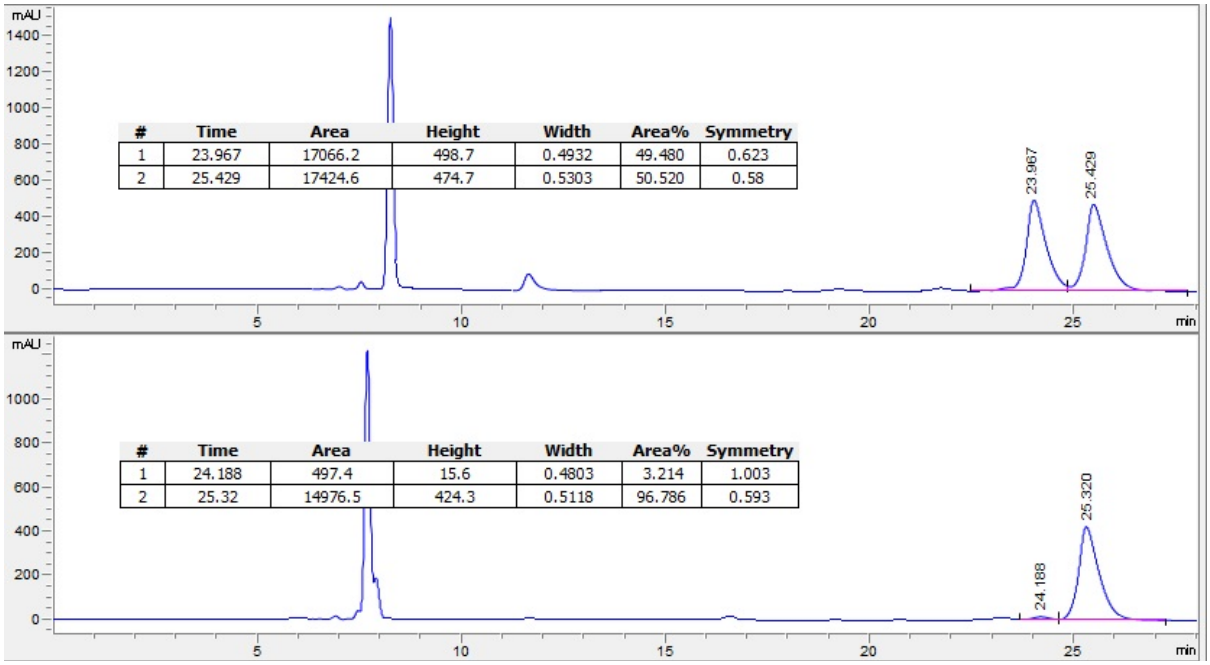
IR (neat): 3354, 2957, 1691, 1530, 1270, 1253, 1029 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.86 – 5.51 (m, 1H), 5.17 – 5.02 (m, 2H), 4.94 (s, 1H), 4.73 (s, 1H), 3.79 (s, 3H), 3.64 (s, 3H), 2.54 – 2.50 (m, 2H).

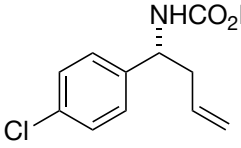
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.9, 156.4, 134.3, 134.1, 127.5, 118.3, 114.0, 55.4, 54.0, 52.2, 41.1.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{13}H_{17}O_3NNa$: 258.1101 Found: 258.1099.

HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 0.5 mL/min, 95:5 hexane:isopropanol, 210 nm, t_{minor} = 24.188 min, t_{major} = 25.320 min).



Methyl (*R*)-(1-(4-chlorophenyl)but-3-en-1-yl)carbamate (5): Prepared according to General Procedure A using 4-chlorophenylacetic acid pentafluorophenyl ester (84 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a colourless oil (39 mg, 66%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (90:10) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +59.4° (*c* = 1.0, $CHCl_3$).

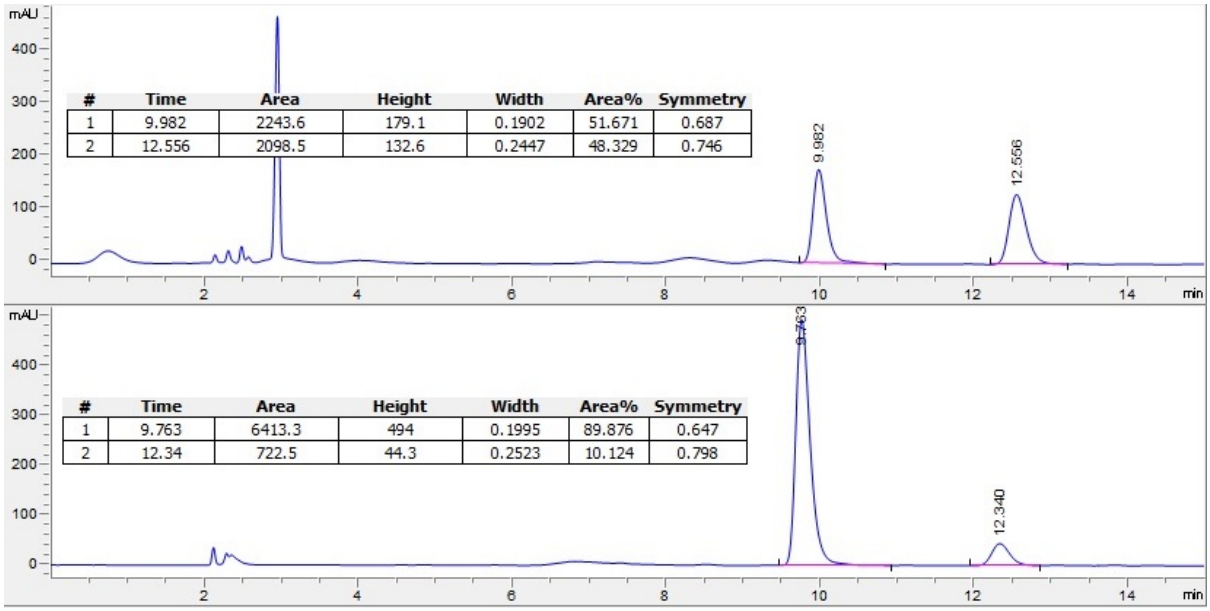
IR (neat): 3338, 2952, 1690, 1529, 1265, 1045 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.64 (ddt, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.20 – 5.06 (m, 3H), 4.73 (s, 1H), 3.63 (s, 3H), 2.49 (t, *J* = 6.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 156.4, 140.8, 133.5, 133.1, 128.8, 127.7, 118.8, 54.0, 52.3, 41.0.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{12}H_{14}ClNO_2Na$: 262.0605 Found: 262.0607.

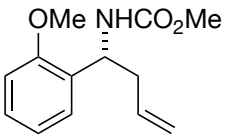
HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{major} = 9.763 min, t_{minor} = 12.340 min).



#	Time	Area	Height	Width	Area%	Symmetry
1	9.982	2243.6	179.1	0.1902	51.671	0.687
2	12.556	2098.5	132.6	0.2447	48.329	0.746

#	Time	Area	Height	Width	Area%	Symmetry
1	9.763	6413.3	494	0.1995	89.876	0.647
2	12.34	722.5	44.3	0.2523	10.124	0.798

Methyl (*R*)-(1-(2-methoxyphenyl)but-3-en-1-yl)carbamate (6): Prepared according to General Procedure A using 2-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a colourless oil (38 mg, 66%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (97:3) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +44.7° (*c* = 1.0, $CHCl_3$).

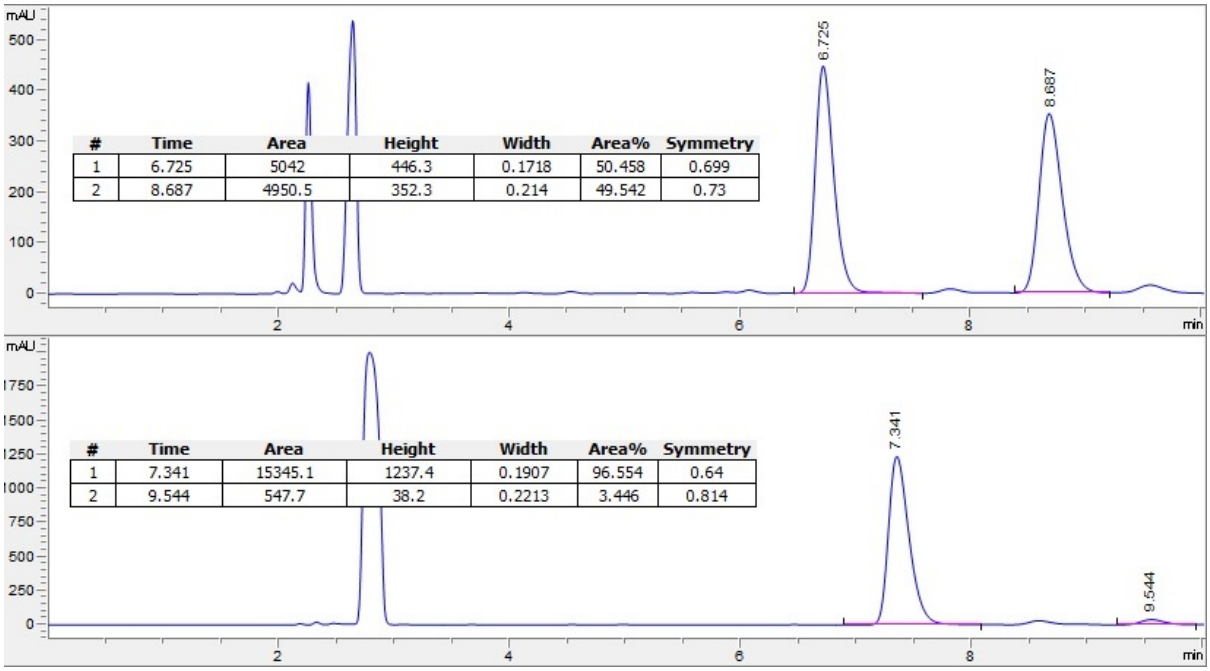
IR (neat): 3339, 2946, 1688, 1534, 1462, 1046 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.92 (m2H), 5.80 – 5.56 (m, 2H), 5.06 (m, 2H), 4.96 (t, *J* = 8.1 Hz, 1H), 3.89 (s, 3H), 3.67 (s, 3H), 2.57 (s, 2H).

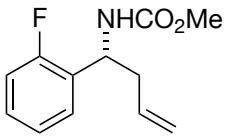
^{13}C NMR (126 MHz, $CDCl_3$): 157.0, 134.9, 129.6, 128.5, 120.7, 117.5, 111.0, 55.4, 52.9, 52.1, 39.9, 29.8.

HRMS (ESI): *m/z* calcd for $[M]^+$ $C_{13}H_{17}NO_3Na$: 258.1101 Found: 258.1101.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{major} = 7.341 min, t_{minor} = 9.544 min).



Methyl (*R*)-(1-(2-fluorophenyl)but-3-en-1-yl)carbamate (7): Prepared according to General Procedure A using 2-fluorophenylacetic acid pentafluorophenyl ester (80 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a colourless oil (39 mg, 70%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (89:11) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +52.9° (*c* = 1.0, $CHCl_3$).

IR (neat): 3316, 2951, 1693, 1531, 1255, 1045, 756 cm^{-1}.

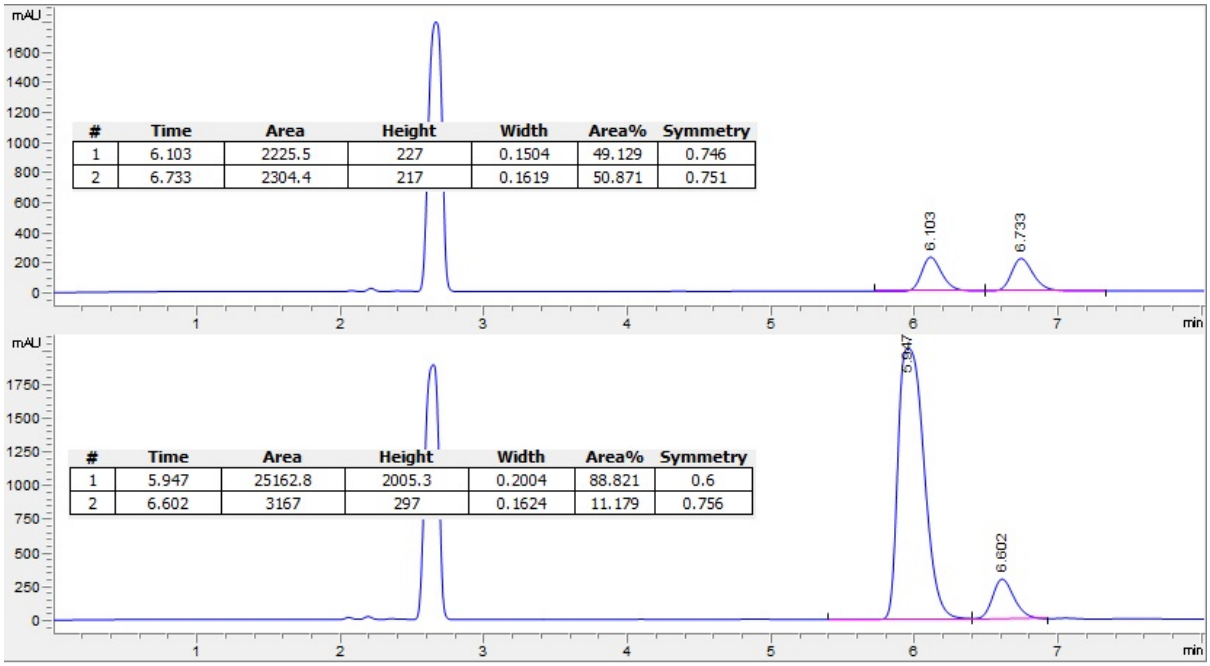
^1H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.18 (m, 2H), 7.11 – 7.07 (m, 1H), 7.06 – 7.00 (m, 1H), 5.67 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.30 (s, 1H), 5.14 – 5.03 (m, 2H), 4.97 (t, *J* = 7.8 Hz, 1H), 3.63 (s, 3H), 2.55 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.6 (d, $^1J_{C\text{-}F}$ = 244.1 Hz), 156.3, 133.8, 129.0 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 128.4, 124.2 (d, $J_{C\text{-}F}$ = 3.4 Hz), 118.5, 115.8 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 52.2, 50.8, 40.1. Quaternary carbon *ortho* to fluorine not observed.

^{19}F (376 MHz, $CDCl_3$): -118.5.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{12}H_{14}FNO_2Na$: 246.0901 Found: 246.0902.

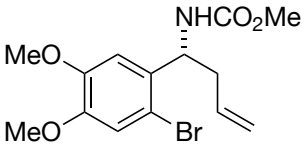
HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{major} = 5.947 min, t_{minor} = 6.602 min).



#	Time	Area	Height	Width	Area%	Symmetry
1	6.103	2225.5	227	0.1504	49.129	0.746
2	6.733	2304.4	217	0.1619	50.871	0.751

#	Time	Area	Height	Width	Area%	Symmetry
1	5.947	25162.8	2005.3	0.2004	88.821	0.6
2	6.602	3167	297	0.1624	11.179	0.756

Methyl (*R*)-(1-(2-bromo-4,5-dimethoxyphenyl)but-3-en-1-yl)carbamate (8): Prepared



according to General Procedure A using 2-bromo-4,5-dimethoxyphenylacetic acid pentafluorophenyl ester (110 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white solid (65 mg, 76%) following purification by column chromatography (SiO_2, 30% EtOAc/petroleum ether). The enantiomeric ratio (93:7) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +32.7° (*c* = 1.0, $CHCl_3$).

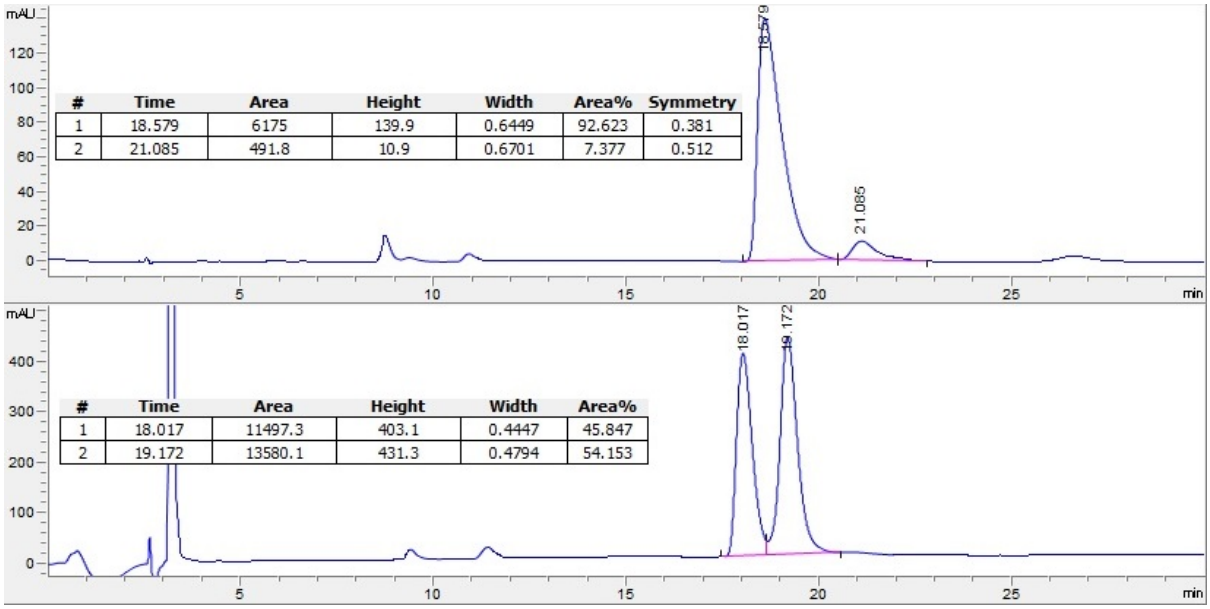
IR (neat): 3324, 2951, 1696, 1502, 1439, 1252, 911 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 6.97 (s, 1H), 6.74 (s, 1H), 5.68 (tt, *J* = 14.5, 5.1 Hz, 1H), 5.31 (d, *J* = 6.9 Hz, 1H), 5.18 – 5.06 (m, 2H), 4.99 (t, *J* = 7.1 Hz, 1H), 3.81 (s, 6H), 3.61 (s, 3H), 2.60 – 2.40 (m, 2H).

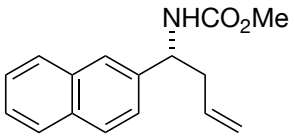
^{13}C NMR (126 MHz, $CDCl_3$): 156.3, 148.6, 133.7, 133.1, 118.6, 115.9, 112.6, 110.4, 56.2, 54.1, 52.3, 39.7, 29.7.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{14}H_{18}NO_4BrNa$: 366.0311 Found: 366.0314.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 95:5 hexane:isopropanol, 210 nm, t_{major} = 18.579 min, t_{minor} = 21.085 min).



Methyl (*R*)-(1-(naphthalen-2-yl)but-3-en-1-yl)carbamate (9): Prepared according to General Procedure A using napthalen-2-ylacetic acid pentafluorophenyl ester (88 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white solid (53 mg, 80%) following purification by column chromatography (SiO_2, 10–15% EtOAc/petroleum ether). The enantiomeric ratio (93:7) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +84.2° (*c* = 1.0, $CHCl_3$).

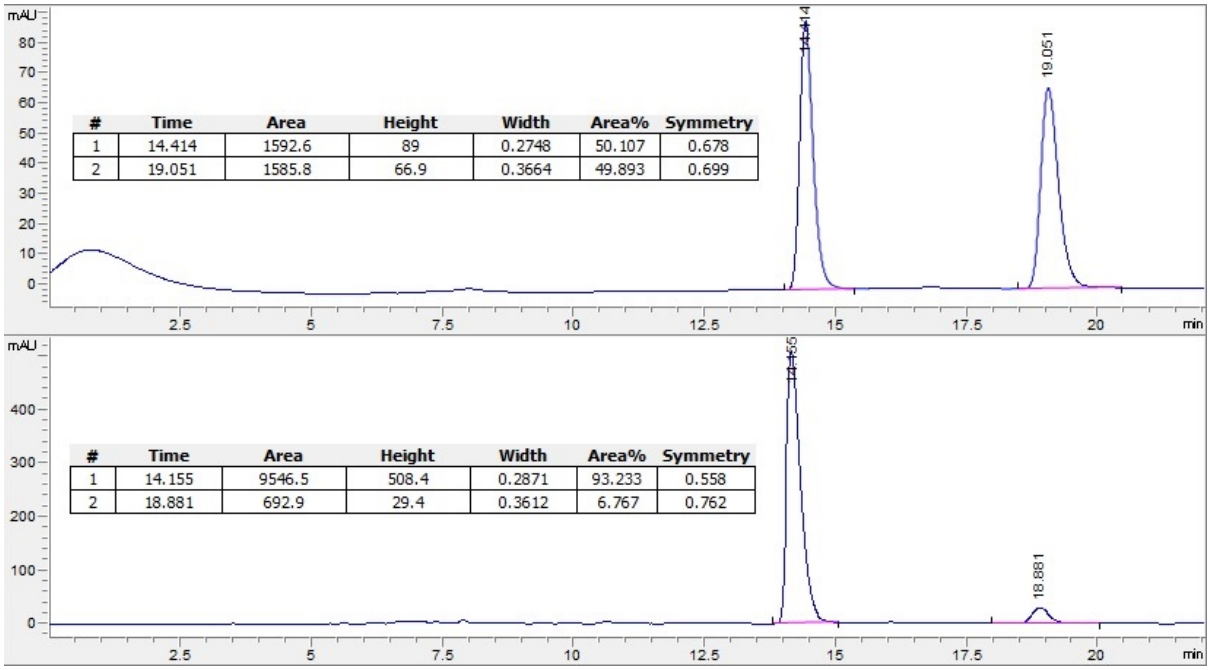
IR (neat): 3315, 2949, 1693, 1508, 1256, 1044, 730 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.90 – 7.77 (m, 3H), 7.74 (s, 1H), 7.47 (ddd, *J* = 6.6, 4.4, 1.9 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 1H), 5.79 – 5.65 (m, 1H), 5.33 (s, 2H), 5.20 – 5.08 (m, 2H), 4.98 (s, 1H), 3.68 (s, 3H), 2.63 (d, *J* = 7.0 Hz, 2H).

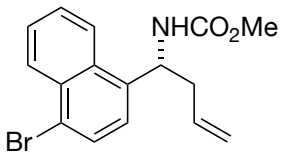
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.5, 139.5, 133.9, 133.4, 132.8, 128.5, 128.0, 127.7, 126.3, 125.9, 125.0, 124.5, 118.5, 54.7, 52.3, 41.0.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{16}H_{17}NO_2Na$: 278.1152 Found: 278.1154.

HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 270 nm, t_{major} = 14.155 min, t_{minor} = 18.881 min).



Methyl (*R*)-(1-(4-bromonaphthalen-1-yl)but-3-en-1-yl)carbamate (10): Prepared according to General Procedure A using 4-bromonaphthalen-1-ylacetic acid pentafluorophenyl ester (108 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.) Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white solid (48 mg, 58%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (92:8) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +37.8° (*c* = 1.0, $CHCl_3$).

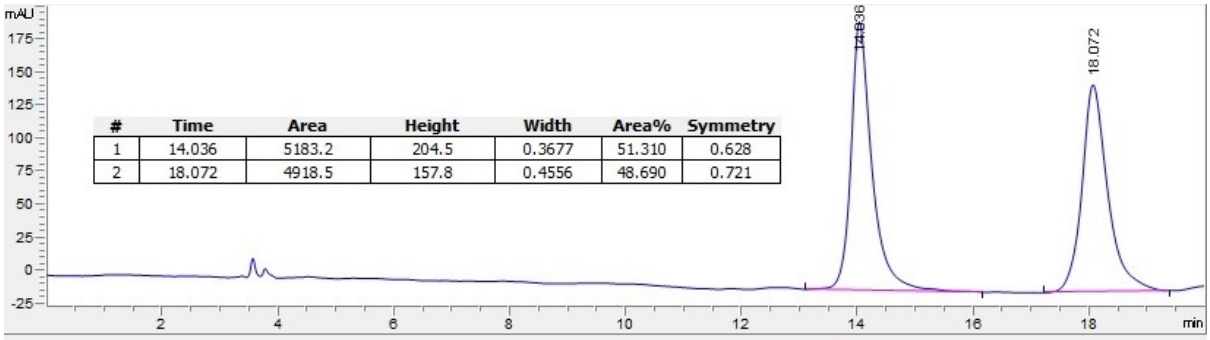
IR (neat): 3313, 2948, 1691, 1508, 1249, 1046, 904 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 8.57 – 8.49 (m, 1H), 8.36 (d, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 5.95 (dd, *J* = 16.7, 9.0 Hz, 1H), 5.92 – 5.80 (m, 2H), 5.51 (d, *J* = 7.9 Hz, 1H), 5.41 – 5.34 (m, 2H), 3.88 (s, 3H), 2.99 – 2.71 (m, 2H).

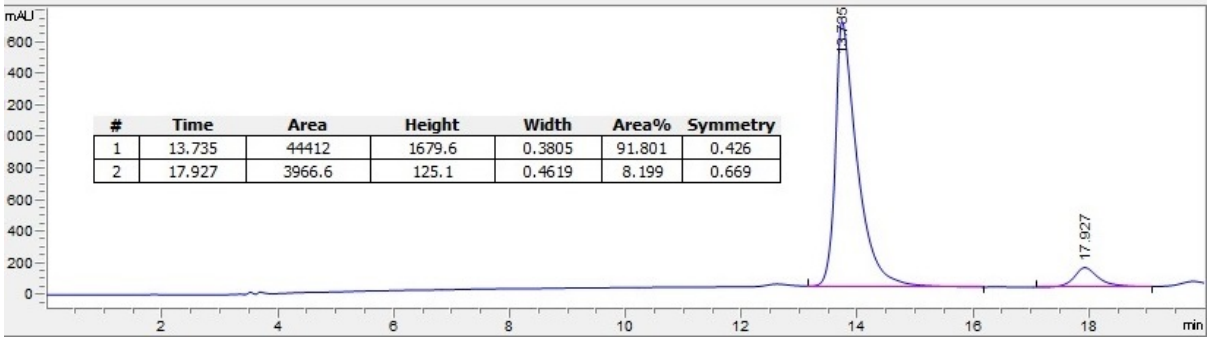
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.3, 137.9, 133.6, 132.2, 132.0, 129.4, 128.2, 127.22, 127.16, 123.3, 123.2, 122.7, 118.7, 52.3, 50.2, 40.2.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{16}H_{16}NO_2BrNa$: 356.0257 Found: 356.0259.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.0 mL/min, 99:1 hexane:isopropanol, 210 nm, t_{major} = 13.735 min, t_{minor} = 17.927 min).

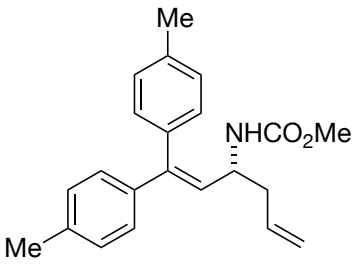


#	Time	Area	Height	Width	Area%	Symmetry
1	14.036	5183.2	204.5	0.3677	51.310	0.628
2	18.072	4918.5	157.8	0.4556	48.690	0.721



#	Time	Area	Height	Width	Area%	Symmetry
1	13.735	44412	1679.6	0.3805	91.801	0.426
2	17.927	3966.6	125.1	0.4619	8.199	0.669

Methyl (*R*)-(1,1-di-*p*-tolylhexa-1,5-dien-3-yl)carbamate (11): Prepared according to General Procedure A using 4,4-di-*p*-tolylbut-3-enoic acid pentafluorophenyl ester (108 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.), Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a colourless oil (45 mg, 51%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (92:8) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ -12.6° (*c* = 1.0, $CHCl_3$).

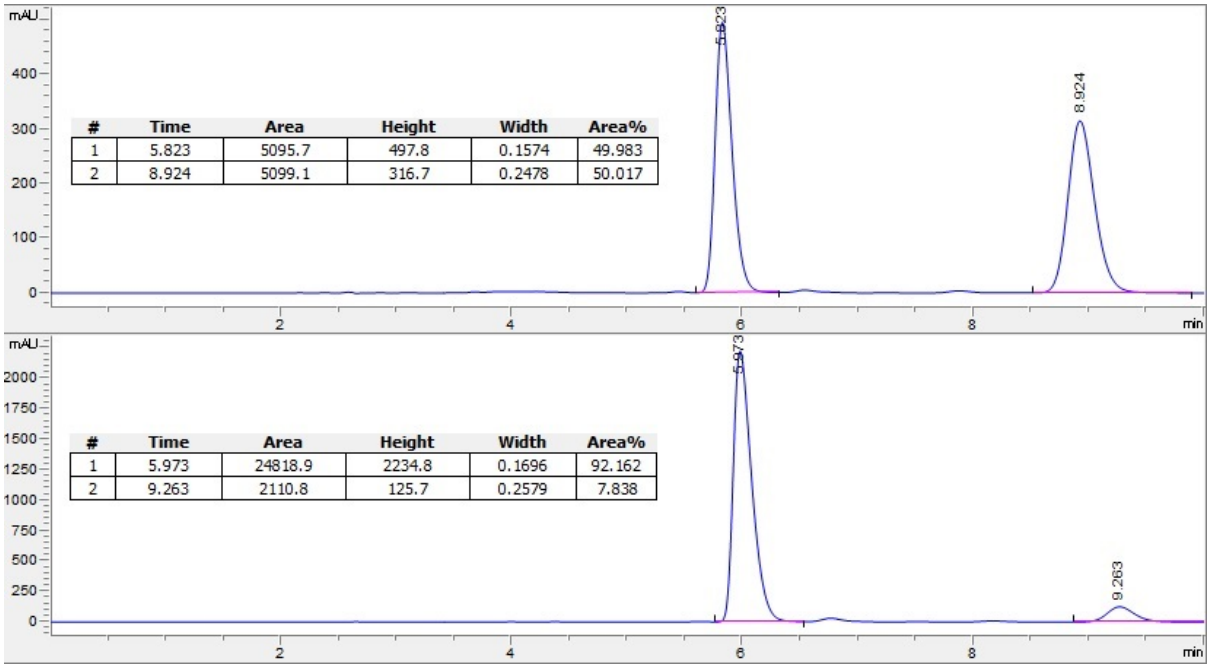
IR (neat): 3322, 2920, 1697, 1514, 1234, 1037, 817 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, *J* = 7.7 Hz, 2H), 7.15 – 7.10 (m, 4H), 7.07 (d, *J* = 8.1 Hz, 2H), 5.85 (d, *J* = 9.4 Hz, 1H), 5.73 (ddt, *J* = 17.1, 9.5, 7.2 Hz, 1H), 5.13 – 5.07 (m, 2H), 4.78 (s, 1H), 4.33 (s, 1H), 3.64 (s, 3H), 2.38 (s, 3H), 2.33 (s, 5H).

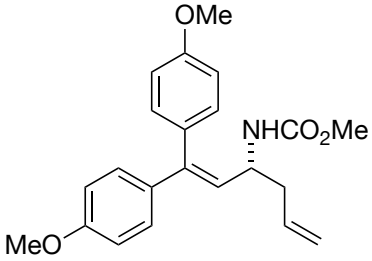
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.5, 139.3, 137.4, 137.1, 136.4, 133.9, 129.6, 129.1, 128.9, 127.5, 127.4, 118.4, 52.2, 50.2, 40.5, 21.4, 21.2.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{22}H_{25}NO_2Na$: 358.1778 Found: 358.1780.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 254 nm, t_{major} = 5.973 min, t_{minor} = 9.263 min).



Methyl (*R*)-(1,1-bis(4-methoxyphenyl)hexa-1,5-dien-3-yl)carbamate (12): Prepared according to General Procedure A using 4,4-bis(4-methoxyphenyl)but-3-enoic acid pentafluorophenyl ester (116 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.), Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a colourless oil (76 mg, 80%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (94:6) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ -23.6° (*c* = 1.0, $CHCl_3$).

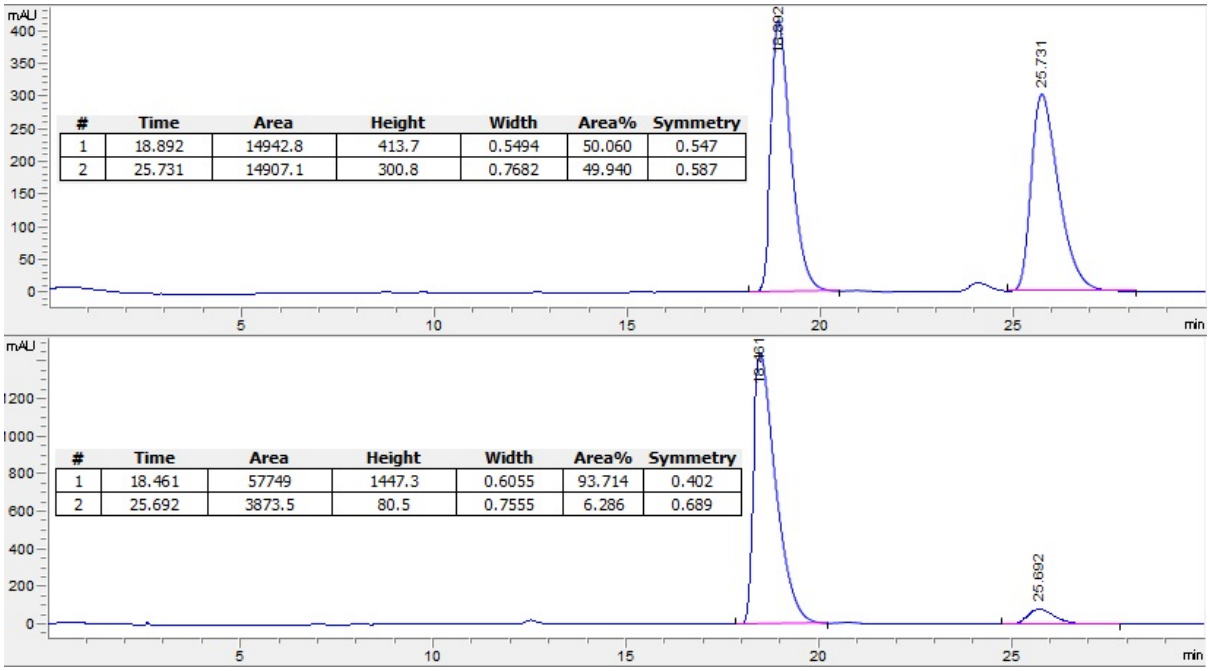
IR (neat): 2952, 2836, 1698, 1508, 1240, 1031 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.15 (td, *J* = 10.0, 8.7, 4.7 Hz, 4H), 6.91 (dd, *J* = 8.5, 1.7 Hz, 2H), 6.85 – 6.73 (m, 2H), 5.77 (dd, *J* = 9.4, 1.5 Hz, 1H), 5.72 (m, 1H), 5.14 – 5.04 (m, 2H), 4.80 (s, 1H), 4.33 (s, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.63 (s, 3H), 2.32 (m, 2H).

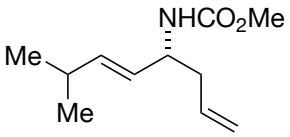
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2, 158.9, 156.1, 142.6, 134.9, 133.8, 131.7, 130.8, 128.6, 126.6, 118.2, 113.7, 113.5, 55.2, 52.0, 50.2, 40.5.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{22}H_{25}NO_4Na$: 390.1676: Found: 390.1679.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 254 nm, t_{major} = 18.461 min, t_{minor} = 25.692 min).



Methyl (*R*,*E*)-(7-methylocta-1,5-dien-4-yl)carbamate (13): Prepared according to General Procedure A using (*E*)-5-methylhex-3-enoic acid pentafluorophenyl ester (74 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.), Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a colourless oil (34 mg, 70%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (91:9) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +12.8° (*c* = 1.0, $CHCl_3$).

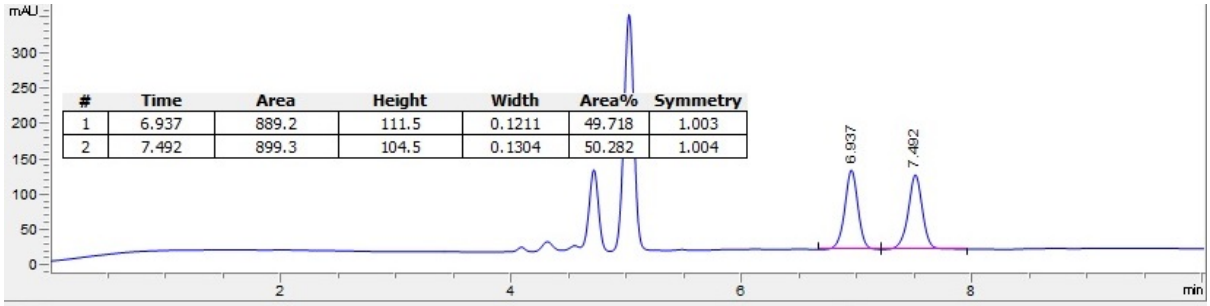
IR (neat): 3321, 2958, 1699, 1533, 1463, 1256 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 5.78 – 5.67 (m, 1H), 5.53 (ddd, *J* = 15.6, 6.6, 1.4 Hz, 1H), 5.34 – 5.25 (m, 1H), 5.11 – 5.00 (m, 2H), 4.70 (s, 1H), 4.18 (s, 1H), 3.64 (s, 3H), 2.25 (d, *J* = 6.6 Hz, 6H).

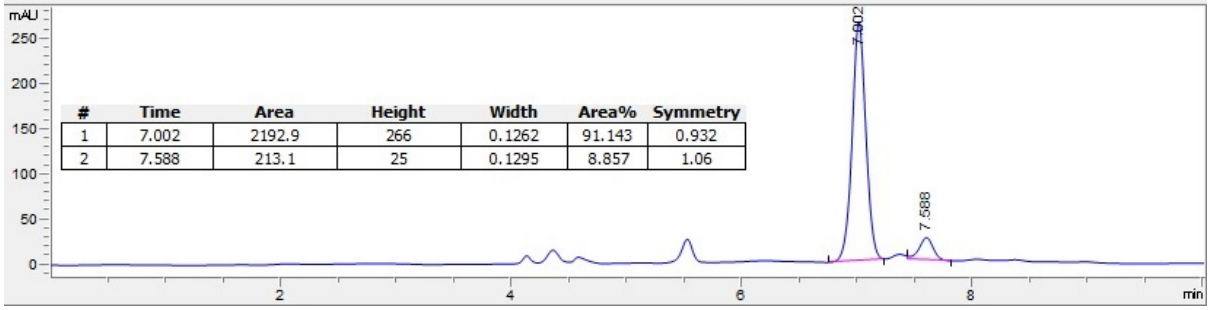
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.5, 138.6, 134.1, 126.7, 118.1, 52.1, 40.1, 30.8, 29.8, 22.4.

HRMS (APCI): *m/z* calcd for $[M]^+$ $C_{11}H_{20}NO_2$: 198.1489 Found: 198.1489.

HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.0 mL/min, 99:1 hexane:isopropanol, 210 nm, t_{minor} = 7.588 min, t_{major} = 7.002 min).

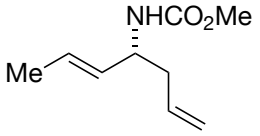


#	Time	Area	Height	Width	Area%	Symmetry
1	6.937	889.2	111.5	0.1211	49.718	1.003
2	7.492	899.3	104.5	0.1304	50.282	1.004



#	Time	Area	Height	Width	Area%	Symmetry
1	7.002	2192.9	266	0.1262	91.143	0.932
2	7.588	213.1	25	0.1295	8.857	1.06

Methyl (*R*,*E*)-hepta-1,5-dien-4-ylcarbamate (14): Prepared according to General Procedure A using (*E*)-pent-3-enoic acid pentafluorophenyl ester (67 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.), Xantphos Pd G3 (11.8 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a colourless oil (21 mg, 50%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (91:9) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +10.3° (*c* = 1.0, $CHCl_3$).

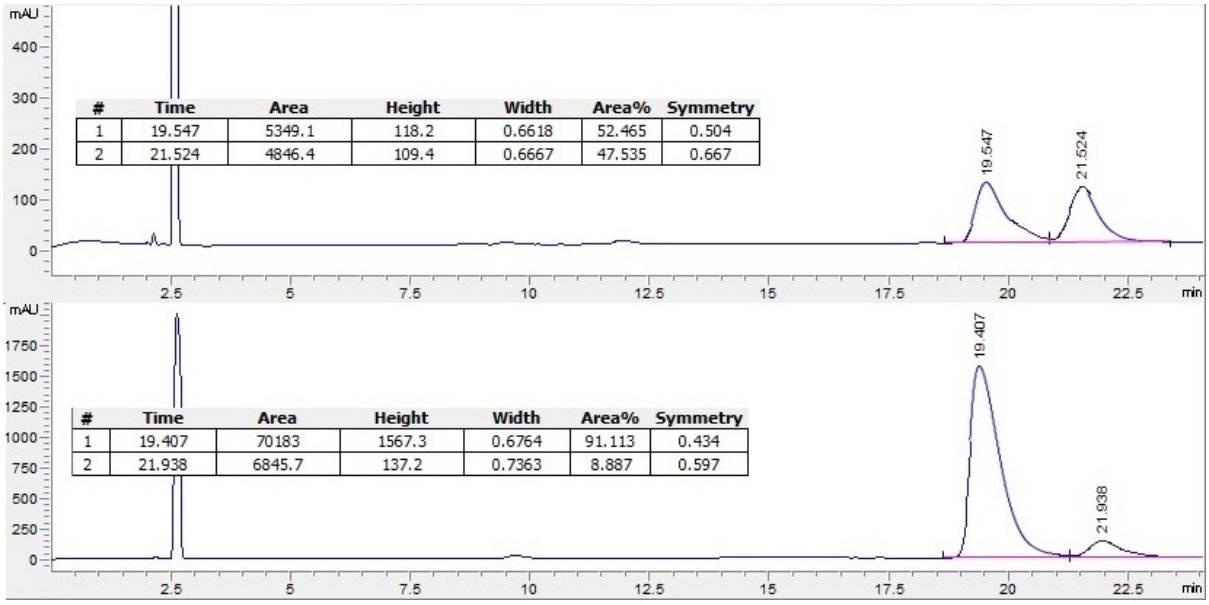
IR (neat): 3321, 2944, 1699, 1517, 1352, 1243, 966 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 5.72 (ddt, *J* = 18.4, 9.3, 7.1 Hz, 1H), 5.58 (dtd, *J* = 12.3, 6.7, 3.5 Hz, 1H), 5.36 (ddd, *J* = 15.4, 6.1, 1.8 Hz, 1H), 5.12 – 5.01 (m, 2H), 4.72 (s, 1H), 4.17 (s, 1H), 3.64 (s, 3H), 2.32 – 2.20 (m 2H), 1.66 (dt, *J* = 6.4, 1.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 156.3, 133.8, 130.7, 126.1, 117.8, 51.8, 39.6, 17.5.

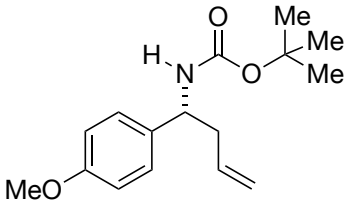
HRMS (APCl): *m/z* calcd for $[M]^+$ $C_9H_{16}NO_2$: 170.1176 Found: 170.1176.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{major} = 19.407 min, t_{minor} = 21.938 min.



Scope of N-substitution

***tert*-Butyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (15):** Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.), Xantphos Pd G3 (11.8 mg, 5 mol%) and *tert*-butanol (1.25 mL). The *title compound* was obtained as a white solid (42 mg, 61%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (97:3) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +54.6° (*c* = 1.0, $CHCl_3$).

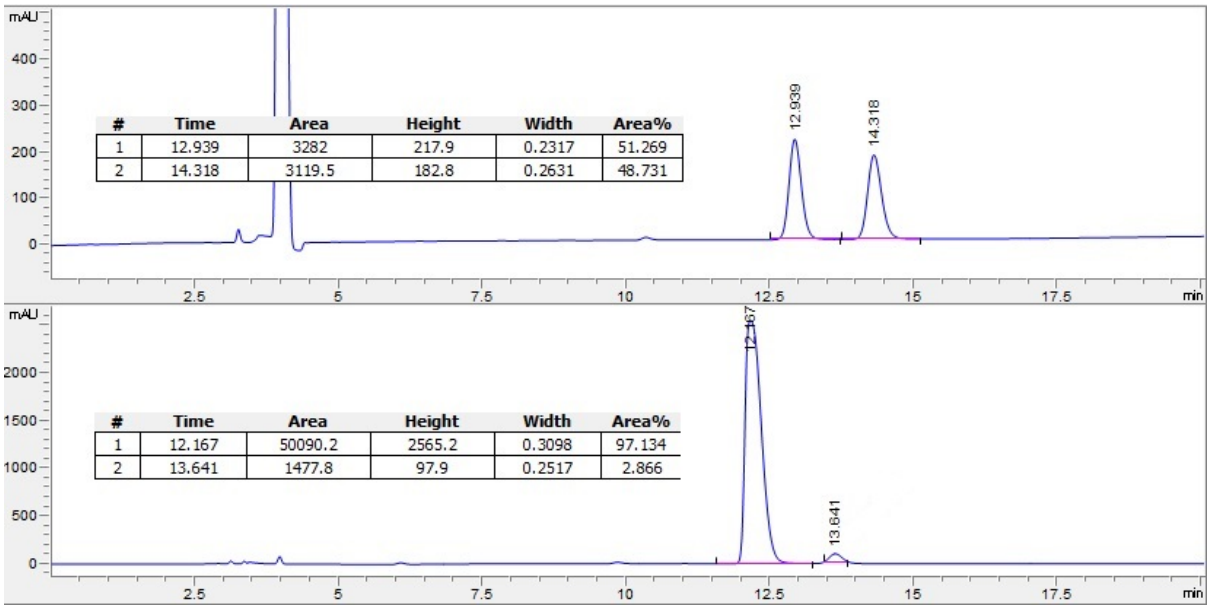
IR (neat): 3358, 2976, 1686, 1612, 1510, 1243, 1163, 1035, 828 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, *J* = 6.5 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.73 – 5.58 (m, 1H), 5.15 – 4.99 (m, 2H), 4.89 – 4.78 (m, 1H), 4.67 (s, 1H), 3.78 (s, 3H), 2.49 (t, *J* = 6.8 Hz, 2H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.8, 155.3, 134.3, 127.5, 118.1, 114.0, 79.5, 55.4, 53.7, 41.3, 29.8, 28.5.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{16}H_{23}NO_3Na$: 300.1570 Found: 300.1573.

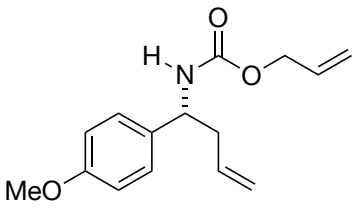
HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.00 mL/min, 98:2 hexane:isopropanol, 210 nm, t_{major} = 12.167 min, t_{minor} = 13.641 min)



#	Time	Area	Height	Width	Area%
1	12.939	3282	217.9	0.2317	51.269
2	14.318	3119.5	182.8	0.2631	48.731

#	Time	Area	Height	Width	Area%
1	12.167	50090.2	2565.2	0.3098	97.134
2	13.641	1477.8	97.9	0.2517	2.866

Allyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (16): Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.), Xantphos Pd G3 (11.8 mg, 5 mol%) and allyl alcohol (1.25 mL). The *title compound* was obtained as a colourless oil (40 mg, 63%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (98:2) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +49.6° (*c* = 1.0, $CHCl_3$).

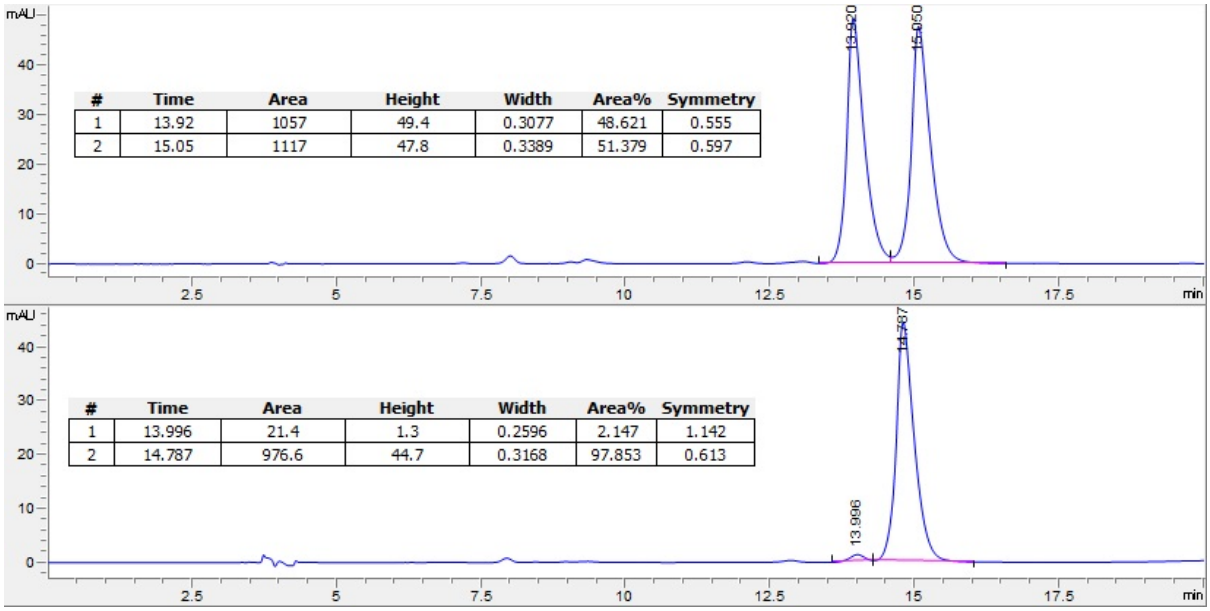
IR (neat): 3323, 2934, 1691, 1511, 1240, 1033, 829 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 5.8 Hz, 2H), 6.85 (dd, *J* = 8.7, 3.2 Hz, 2H), 5.88 (s, 1H), 5.67 (ddtd, *J* = 17.0, 10.0, 6.7, 3.0 Hz, 1H), 5.35 – 5.00 (m, 5H), 4.73 (s, 1H), 4.53 (d, *J* = 4.2 Hz, 2H), 3.78 (d, *J* = 3.2 Hz, 3H), 2.51 (d, *J* = 7.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.9, 155.7, 134.1, 132.9, 127.5, 118.3, 117.8, 114.0, 65.7, 55.3, 54.0, 41.1.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{15}H_{19}NO_3Na$: 284.1257 Found: 284.1260

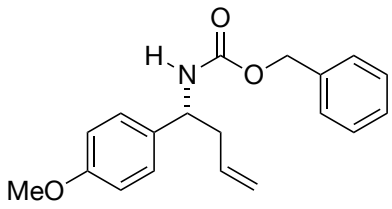
HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.00 mL/min, 98:2 hexane:isopropanol, 270 nm, t_{major} = 13.996 min, t_{minor} = 14.787 min).



#	Time	Area	Height	Width	Area%	Symmetry
1	13.92	1057	49.4	0.3077	48.621	0.555
2	15.05	1117	47.8	0.3389	51.379	0.597

#	Time	Area	Height	Width	Area%	Symmetry
1	13.996	21.4	1.3	0.2596	2.147	1.142
2	14.787	976.6	44.7	0.3168	97.853	0.613

Benzyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (17): Prepared according to



General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.), Xantphos Pd G3 (11.8 mg, 5 mol%) and benzyl alcohol (1.25 mL). The crude reaction mixture was placed in an oil bath at 75 °C under high vacuum overnight to remove excess benzyl alcohol prior to chromatography. The *title compound* was obtained as a white solid (54 mg, 69%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (97:3) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +28.5° (*c* = 1.0, $CHCl_3$).

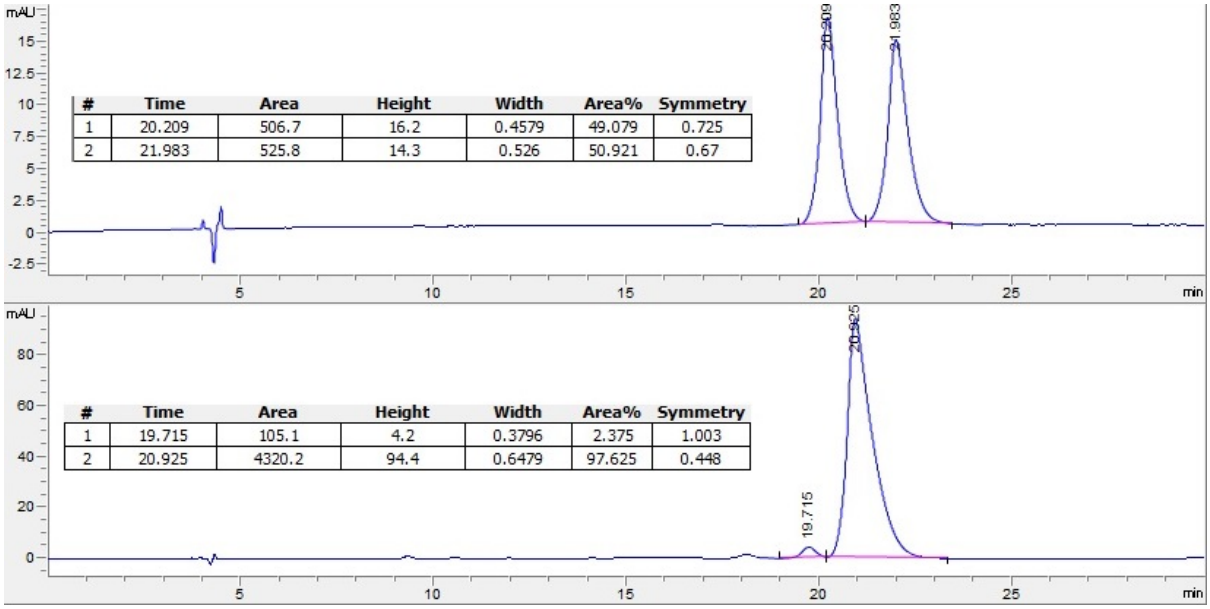
IR (neat): 3323, 2932, 1692, 1510, 1239, 1027, 829 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.34 (s, 5H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.76 – 5.60 (m, 1H), 5.22 – 4.99 (m, 5H), 4.77 (s, 1H), 3.80 (s, 3H), 2.54 (s, 2H).

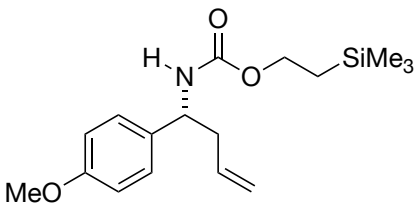
^{13}C NMR (126 MHz, $CDCl_3$): 158.9, 155.7, 136.6, 134.2, 134.0, 128.6, 128.2, 127.5, 118.3, 114.0, 66.8, 55.3, 54.1, 41.1, 29.8.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{19}H_{21}NO_3Na$: 334.1414 Found: 334.1417.

HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.00 mL/min, 97:3 hexane:isopropanol, 280 nm, t_{major} = 19.715 min, t_{minor} = 20.925 min).



2-(Trimethylsilyl)ethyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (18): Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), allyl mesylate (43 mg, 0.3125 mmol, 1.25 equiv.), Xantphos Pd G3 (11.8 mg, 5 mol%) and 2-(trimethylsilyl)ethanol (1.25 mL). The crude reaction mixture was placed under high vacuum overnight to remove excess 2-(trimethylsilyl)ethanol prior to chromatography. The *title compound* was obtained as a colourless oil (60 mg, 75%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (98:2) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +43.8° (*c* = 1.0, $CHCl_3$).

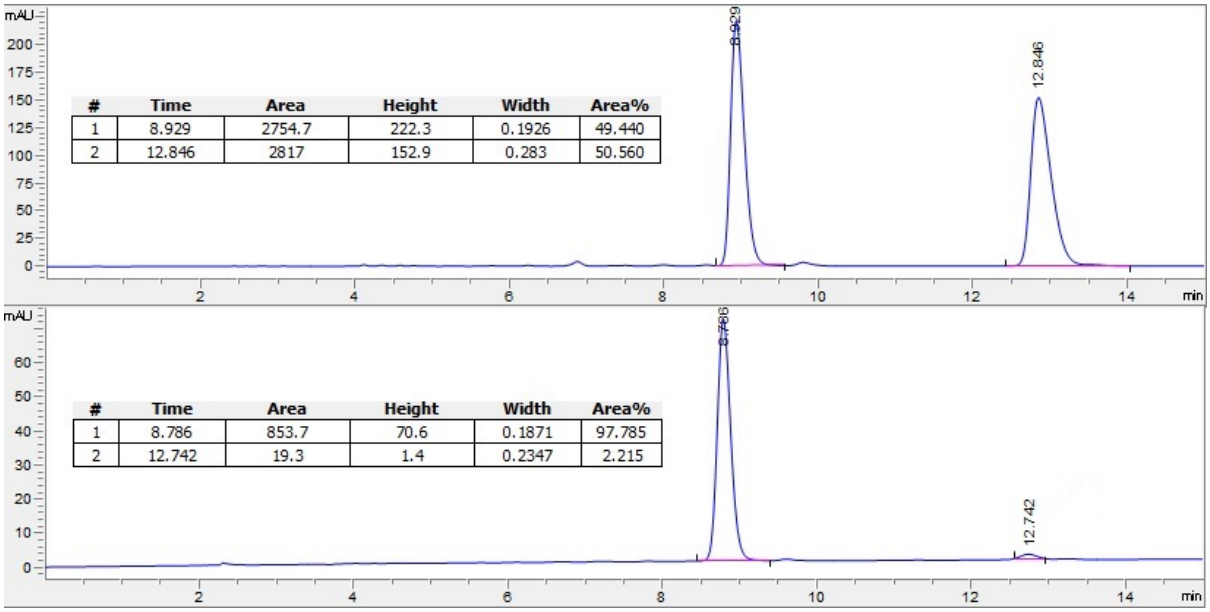
IR (neat): 3320, 2953, 1687, 1512, 1245, 1176, 1035, 830 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.67 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.14 – 5.01 (m, 3H), 4.72 (s, 1H), 4.13 (q, *J* = 6.8 Hz, 2H), 3.78 (s, 3H), 2.51 (t, *J* = 7.0 Hz, 2H), 0.95 (t, *J* = 8.6 Hz, 2H), 0.01 (s, 9H).

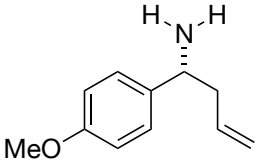
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.6, 156.1, 134.1, 133.8, 127.2, 118.0, 113.7, 63.1, 55.1, 53.7, 40.9, 17.5, -1.7.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{17}H_{27}NO_3SiNa$: 344.1652 Found: 344.1656.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 98:2 hexane:isopropanol, 280 nm, t_{major} = 8.786 min, t_{minor} = 12.742 min).



(*R*)-1-(4-Methoxyphenyl)but-3-en-1-amine (19): Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (332 mg, 1.0 mmol, 1 equiv.), allyl mesylate (170 mg, 1.25 mmol, 1.25 equiv.) Xantphos Pd G3 (47.2 mg, 5 mol%). Following bubbling with NH_3 the THF was removed under vacuum and MeCN/H_2O (3:1, 5.0 mL) was added. The *title compound* was obtained as a brown oil (72 mg, 42%) following purification by column chromatography (SiO_2, 5% MeOH/CH_2Cl_2). The enantiomeric ratio (97:3) was determined by chiral HPLC in comparison with the racemate following conversion to the corresponding methyl carbamate (Compound **4** in this SI). Characterization consistent with previously reported data.[16]

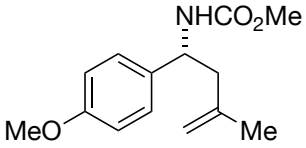


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, *J* = 7.5, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.81 – 5.62 (m, 1H), 5.23 – 4.96 (m, 2H), 4.04 – 3.95 (m, 1H), 3.79 (s, 3H), 2.56 – 2.31 (m, 2H), 2.15 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.7, 137.2, 135.3, 127.4, 117.7, 113.8, 55.3, 54.8, 43.8.

Scope of electrophile

Methyl (*R*)-(1-(4-methoxyphenyl)-3-methylbut-3-en-1-yl)carbamate (20): Prepared



according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), 2-methylallyl mesylate (47 mg, 0.3125 mmol, 1.25 equiv.), tris(tri-2-thienylphosphine)palladium(0) (11.9 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as an off-white solid (45 mg, 72%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (96:4) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +30.2° (*c* = 1.0, $CHCl_3$).

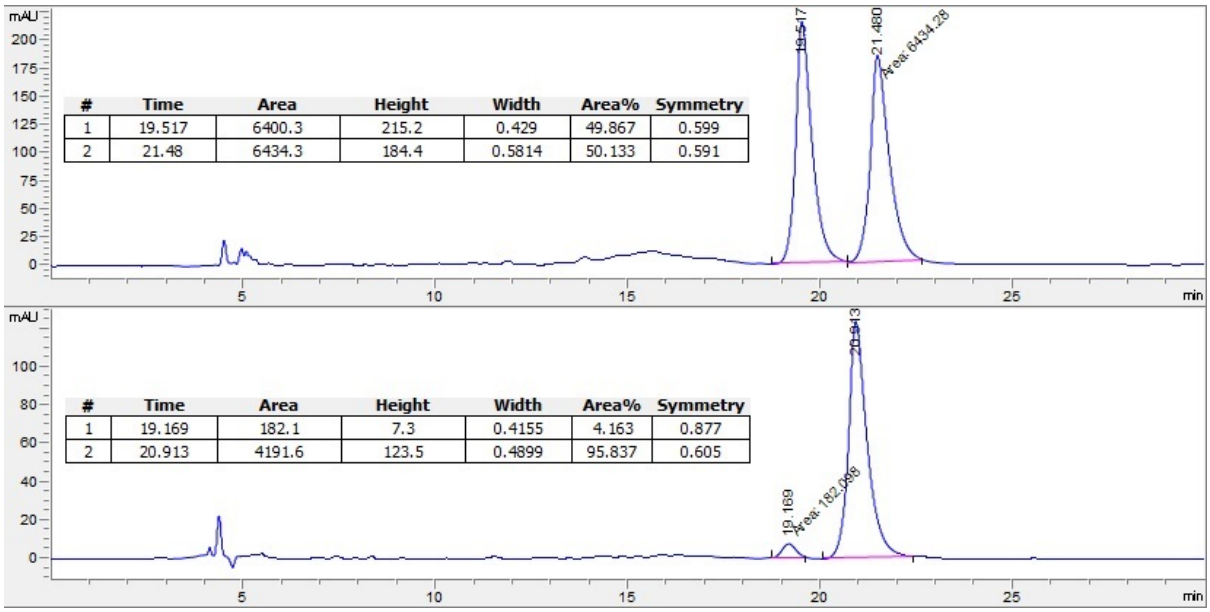
IR (neat): 3344, 2958, 1686, 1536, 1516, 1269, 1250 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.90 (s, 1H), 4.86 – 4.67 (m, 3H), 3.79 (s, 3H), 3.63 (s, 3H), 2.56 – 2.27 (m, 2H), 1.72 (s, 3H).

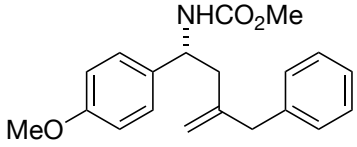
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.9, 156.5, 142.0, 135.0, 127.4, 114.0, 55.4, 52.7, 52.2, 45.6, 22.1.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{14}H_{19}NO_3Na$: 273.1290 Found: 273.1288.

HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.00 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{minor} = 19.169 min, t_{major} = 20.913 min).



Methyl (*R*)-(3-benzyl-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (21): Prepared



according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), 2-benzylallyl mesylate (77 mg, 0.3125 mmol, 1.5 equiv.), tris(tri-2-thienylphosphine)palladium(0) (11.9 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white

solid (56 mg, 79%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (94:6) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +32.7° (*c* = 1.0, $CHCl_3$).

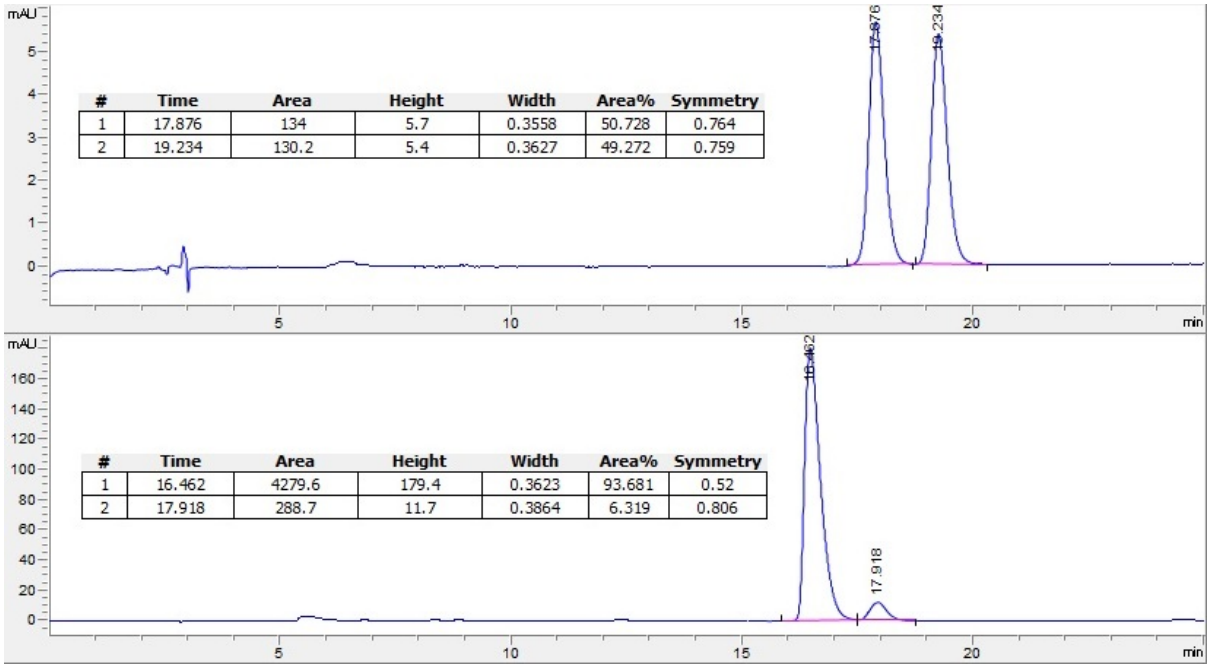
IR (neat): 3322, 2950, 1694, 1510, 1241, 1031, 827 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.19 – 7.13 (m, 4H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.99 (s, 1H), 4.92 – 4.81 (m, 3H), 3.78 (s, 3H), 3.65 (s, 3H), 3.32 (q, *J* = 15.1 Hz, 2H), 2.39 (t, *J* = 8.4 Hz, 2H).

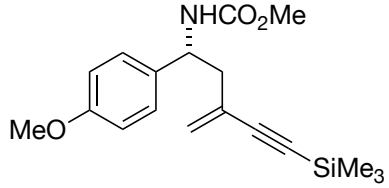
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.8, 156.4, 145.0, 139.0, 134.7, 129.1, 128.4, 127.3, 126.3, 115.0, 113.9, 55.3, 52.7, 52.1, 42.9, 42.5.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{20}H_{23}NO_3Na$: 348.1570 Found: 348.1574.

HPLC analysis using a chiral column (Chiralpak IA 3µ column, 22 °C, 1.00 mL/min, 97:3 hexane:isopropanol, 270 nm, t_{major} = 16.462 min, t_{minor} = 17.918 min).



Methyl (*R*)-(1-(4-methoxyphenyl)-3-methylene-5-(trimethylsilyl)pent-4-yn-1-yl)carbamate (22): Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (332 mg, 1.00 mmol, 1 equiv.), 2-methylene-4-(trimethylsilyl)but-3-yn-1-yl mesylate (349 mg, 1.50 mmol, 1.25 equiv.), tris(tri-2-thienylphosphine)palladium(0) (47.6 mg, 5 mol%) and methanol (5 mL). The *title compound* was obtained as a white solid (100 mg, 30%) following purification by column chromatography (SiO_2, 10% EtOAc/petroleum ether). The enantiomeric ratio (95:5) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +14.9° (*c* = 1.0, $CHCl_3$).

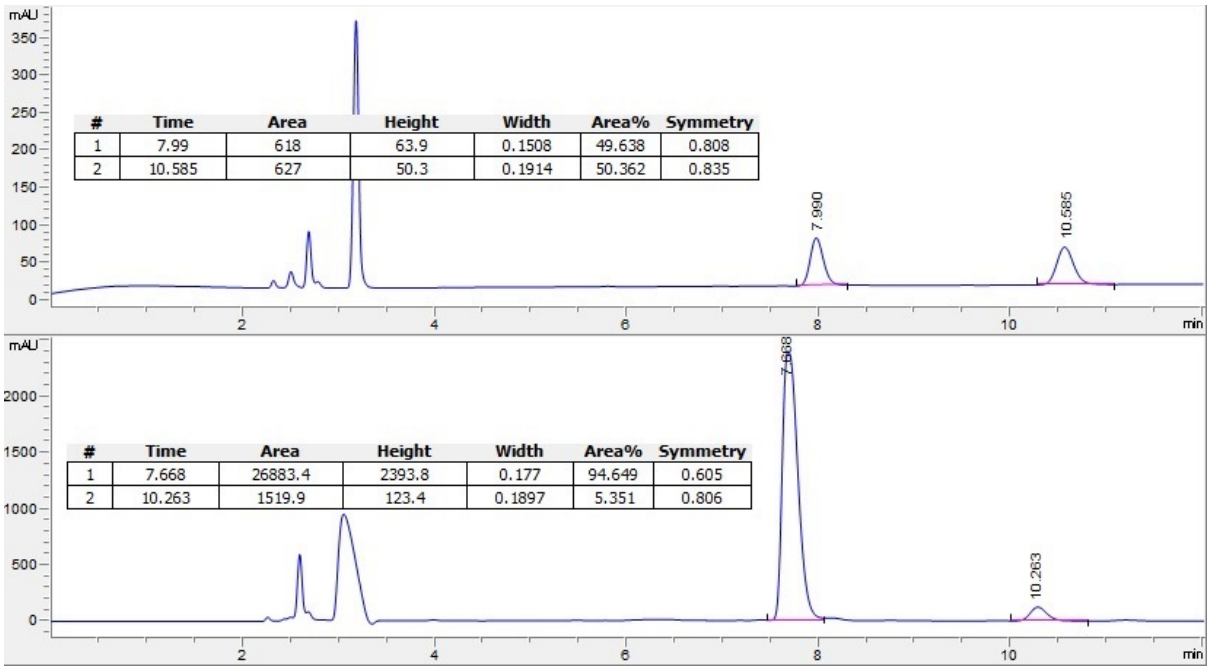
IR (neat): 3333, 2957, 1702, 1514, 1249, 1036, 842 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.44 – 5.33 (m, 2H), 5.19 (s, 1H), 4.89 (t, *J* = 7.3 Hz, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 0.20 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.9, 156.4, 134.0, 127.5, 125.2, 113.9, 105.0, 95.6, 55.3, 54.1, 52.2, 44.0, 29.8, -0.1.

HRMS (El): *m/z* calcd for $[M]^+$ $C_{18}H_{25}NO_3$: 331.1604: Found: 331.1596.

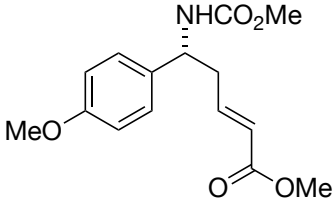
HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.00 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{major} = 7.668 min, t_{minor} = 10.263 min).



#	Time	Area	Height	Width	Area%	Symmetry
1	7.99	618	63.9	0.1508	49.638	0.808
2	10.585	627	50.3	0.1914	50.362	0.835

#	Time	Area	Height	Width	Area%	Symmetry
1	7.668	26883.4	2393.8	0.177	94.649	0.605
2	10.263	1519.9	123.4	0.1897	5.351	0.806

Methyl (*R*,*E*)-5-((methoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-2-enoate (23):



Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (104 mg, 0.3125 mmol, 1.25 equiv.), methyl (*E*)-4-(tosyloxy)but-2-enoate (68 mg, 0.25 mmol, 1 equiv.), tris(tri-2-thienylphosphine)palladium(0) (11.9 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a beige solid (41 mg, 56%) following purification by column chromatography (SiO_2, 10–20% EtOAc/petroleum ether). The enantiomeric ratio (95:5) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +31.8° (*c* = 1.0, $CHCl_3$).

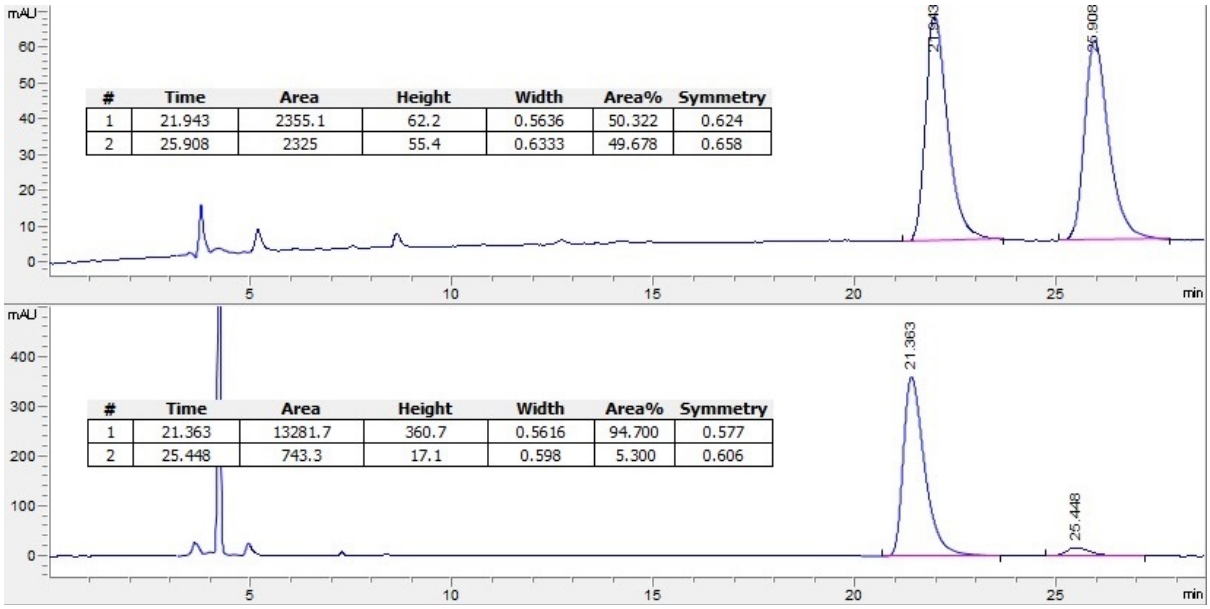
IR (neat): 3332, 3018, 2953, 1722, 1514, 1248, 1214, 1036, 747, 667 cm^{-1}.

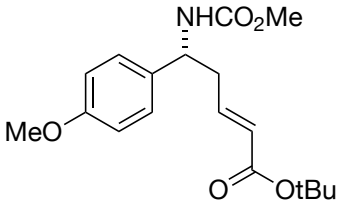
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.81 (dt, *J* = 15.0, 7.3 Hz, 1H), 5.86 (d, *J* = 15.7 Hz, 1H), 5.01 (s, 1H), 4.79 (s, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.64 (s, 3H), 2.82 – 2.55 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): 166.6, 159.2, 156.3, 144.3, 133.2, 127.6, 124.0, 114.3, 55.4, 53.8, 52.3, 51.7, 39.1, 29.8.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{15}H_{19}O_5NNa$: 316.1155 Found: 316.1160.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 90:10 hexane:isopropanol, 210 nm, t_{major} = 21.363 min, t_{minor} = 25.448 min).





***Tert*-butyl (*R*,*E*)-5-((methoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-2-enoate (24):** Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (104 mg, 0.3125 mmol, 1.25 equiv.), *tert*-butyl (*E*)-4-(tosyloxy)but-2-enoate (78 mg, 0.25 mmol, 1 equiv.), tris(tri-2-thienylphosphine)palladium(0) (11.9 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a beige solid (41 mg, 58%) following purification by column chromatography (SiO_2, 10–20% EtOAc/petroleum ether). The enantiomeric ratio (95:5) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +18.8° (*c* = 1.0, $CHCl_3$).

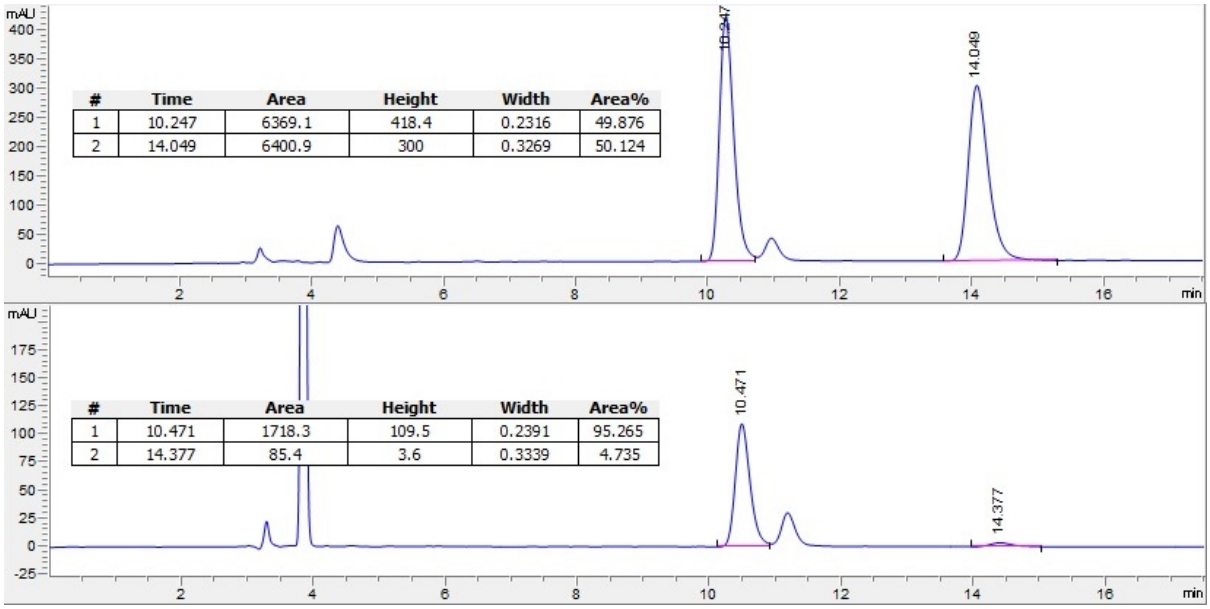
IR (neat): 3340, 3010, 2954, 1709, 1514, 1247, 1153, 1036, 756 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.70 (dt, *J* = 15.6, 7.2 Hz, 1H), 5.78 (d, *J* = 15.6 Hz, 1H), 5.06 (s, 1H), 4.77 (s, 1H), 3.78 (d, *J* = 0.9 Hz, 3H), 3.63 (s, 3H), 2.78 – 2.49 (m, 2H), 1.45 (s, 9H).

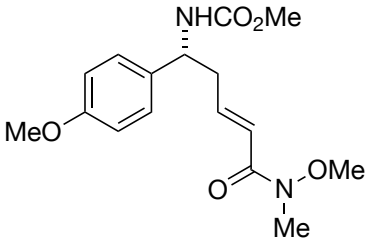
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 159.1, 142.7, 129.0, 127.5, 126.1, 114.2, 114.1, 80.5, 55.4, 53.8, 52.3, 44.7, 28.2.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{18}H_{25}O_5NNa$: 358.1625 Found: 358.1627.

HPLC analysis using a chiral column (Chiralpak IA 3µ column, 22 °C, 1.5 mL/min, 90:10 hexane:isopropanol, 210 nm, t_{major} = 10.471 min, t_{minor} = 14.377 min).



Methyl (*R*,*E*)-(5-(methoxy(methyl)amino)-1-(4-methoxyphenyl)-5-oxopent-3-en-1-yl)carbamate (25): Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (104 mg, 0.3125 mmol, 1.25 equiv.), (*E*)-4-(methoxy(methyl)amino)-4-oxobut-2-en-1-yl 4-methylbenzenesulfonate (75 mg, 0.25 mmol, 1 equiv.), tris(tri-2-thienylphosphine)palladium(0) (11.9 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a brown oil (50 mg, 62%) following purification by column chromatography (SiO_2, 50–100% EtOAc/petroleum ether). The enantiomeric ratio (95:5) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +22.3° (*c* = 1.0, $CHCl_3$).

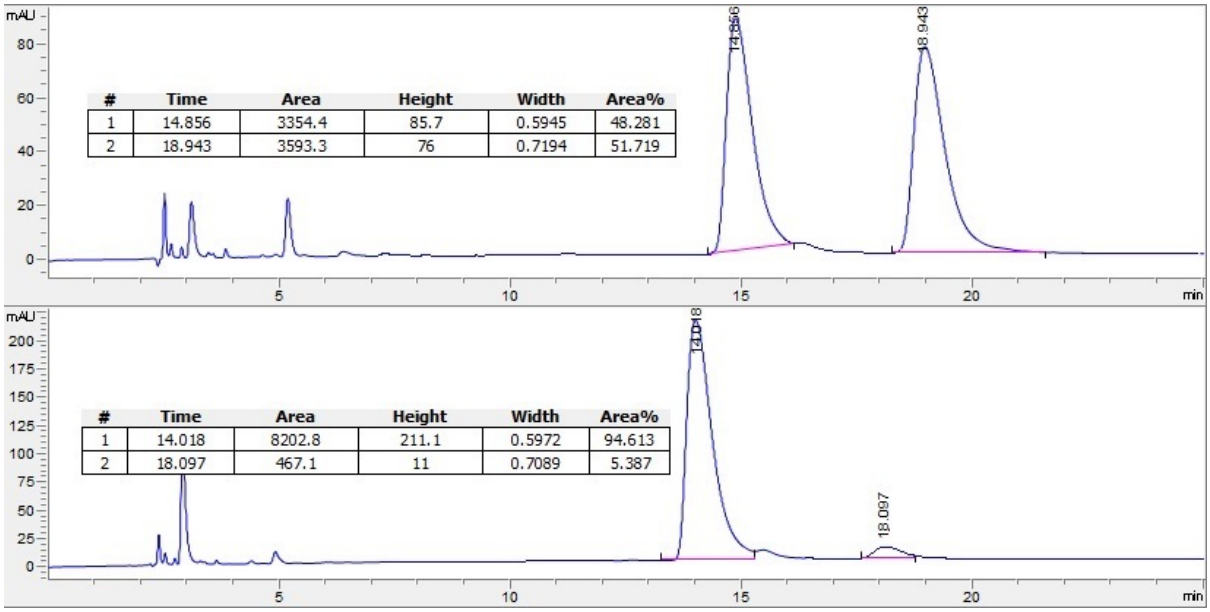
IR (neat): 3306, 2940, 1703, 1613, 1534, 1515, 1247, 1180 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 15.4 Hz, 1H), 5.00 (s, 1H), 4.81 (s, 1H), 3.78 (s, 3H), 3.64 (d, *J* = 5.4 Hz, 6H), 3.21 (s, 3H), 2.96 – 2.55 (m, 2H).

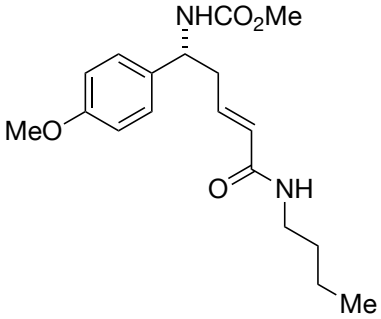
^{13}C NMR (126 MHz, $CDCl_3$): δ 166.3, 159.0, 156.3, 142.4, 133.4, 127.5, 121.6, 114.1, 61.7, 55.3, 53.8, 52.2, 39.1, 32.3.

HRMS (APCI): *m/z* calcd for $[M+H]^+$ $C_{16}H_{23}O_5N_2$: 323.1604 Found: 323.1601.

HPLC analysis using a chiral column (Chiralpak IA 3µ column, 22 °C, 1.5 mL/min, 85:15 hexane:isopropanol, 210 nm, t_{major} = 14.018 min, t_{minor} = 18.097 min).



Methyl (*R*,*E*)-(5-(butylamino)-1-(4-methoxyphenyl)-5-oxopent-3-en-1-yl)carbamate (26):



Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (104 mg, 0.3125 mmol, 1.25 equiv.), (*E*)-4-(butylamino)-4-oxobut-2-en-1-yl 4-methylbenzenesulfonate (78 mg, 0.25 mmol, 1 equiv.), tris(tri-2-thienylphosphine)palladium(0) (11.9 mg, 5 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white solid (31 mg, 37%) following purification by column chromatography (SiO_2, 30–50% EtOAc/petroleum ether). The enantiomeric ratio (92:8) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +35.1° (*c* = 1.0, $CHCl_3$).

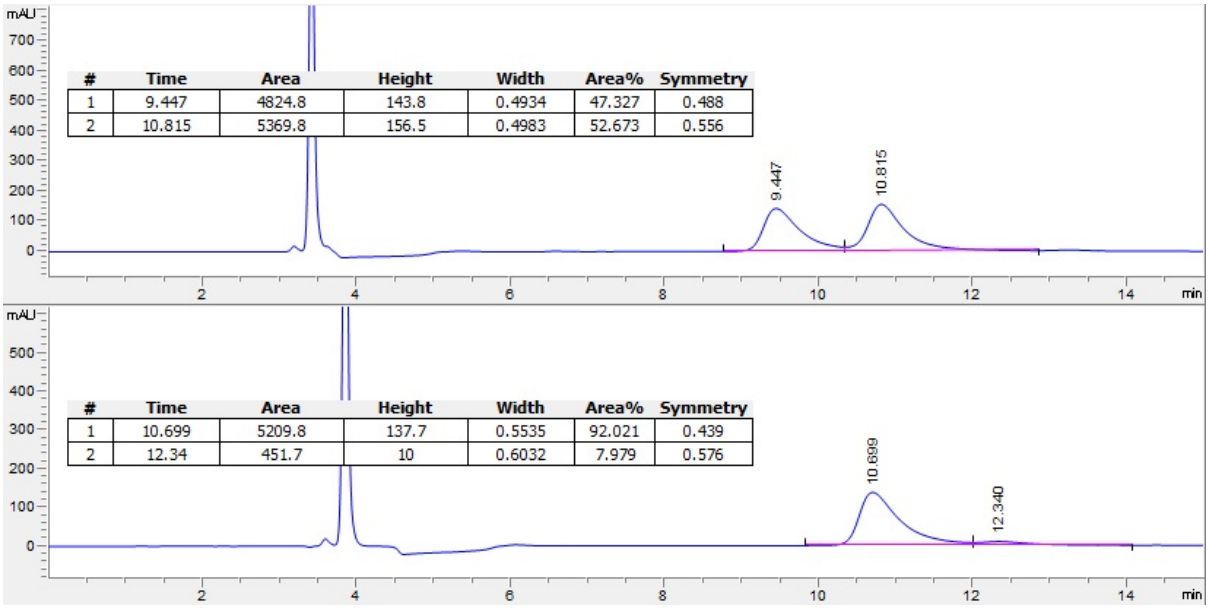
IR (neat): 3309, 2957, 2931, 1688, 1626, 1538, 1516, 1273, 1251, 1032 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.66 (dt, *J* = 14.8, 7.1 Hz, 1H), 5.80 (d, *J* = 15.4 Hz, 1H), 5.50 (t, *J* = 5.8 Hz, 1H), 5.02 (s, 1H), 4.78 (s, 1H), 3.79 (s, 3H), 3.64 (s, 3H), 3.29 (td, *J* = 7.2, 5.8 Hz, 2H), 2.73 – 2.54 (m, 2H), 1.54 – 1.45 (m, 2H), 1.35 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

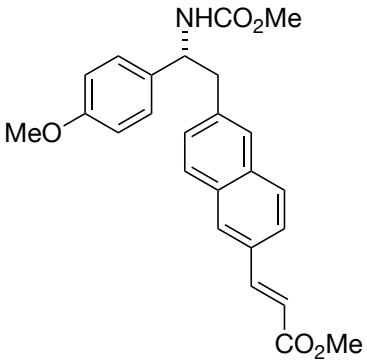
^{13}C NMR (151 MHz, $CDCl_3$): δ 165.5, 159.1, 156.4, 139.1, 133.5, 127.6, 126.8, 114.2, 55.4, 54.0, 52.3, 39.4, 31.8, 29.8, 20.2, 13.8.

HRMS (APCI): *m/z* calcd for $[M+H]^+$ $C_{18}H_{27}O_4N_2$: 335.1965 Found: 335.1967.

HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.5 mL/min, 80:20 hexane:isopropanol, 210 nm, t_{major} = 10.699 min, t_{minor} = 12.340 min).



Methyl (*R*,*E*)-3-(6-(2-((methoxycarbonyl)amino)-2-(4-methoxyphenyl)ethyl)naphthalen-2-yl)acrylate (27): Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (50 mg, 0.15 mmol, 1 equiv.), methyl (*E*)-3-(6-((diphenoxyphosphoryl)methyl)naphthalen-2-yl)acrylate (89 mg, 0.1875 mmol, 1.25 equiv.), Xantphos Pd G3 (14.3 mg, 10 mol%) and methanol (0.75 mL). The *title compound* was obtained as a beige solid (43 mg, 68%) following purification by column chromatography (SiO_2, 10–30% EtOAc/petroleum ether). The enantiomeric ratio (>99:1) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ -17.7° (*c* = 1.0, $CHCl_3$).

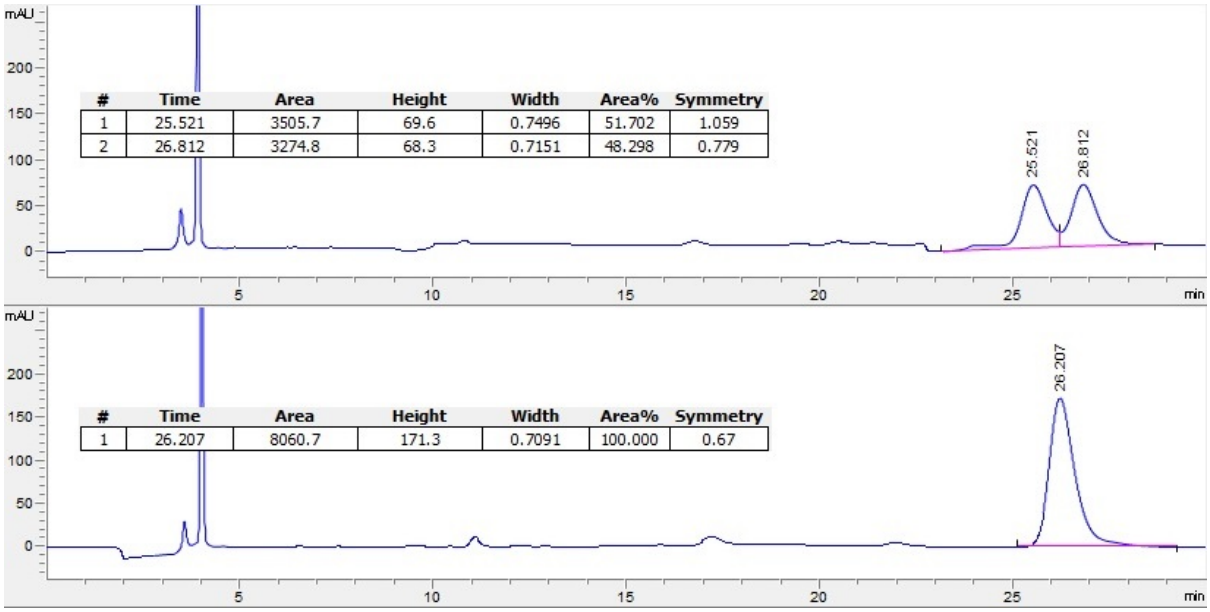
IR (neat): 3341, 3015, 2951, 1710, 1629, 1513, 1436, 1246, 1176, 1036, 755 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 7.88 – 7.86 (m, 1H), 7.83 (d, *J* = 15.9 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.63 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.50 (s, 1H), 7.21 – 7.17 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 5.00 (s, 2H), 3.83 (s, 3H), 3.78 (s, 3H), 3.60 (s, 3H), 3.31 – 3.17 (m, 2H).

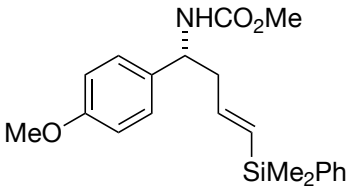
^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 159.0, 156.3, 145.0, 136.9, 134.3, 133.8, 132.1, 131.6, 129.8, 128.7, 128.6, 128.5, 128.0, 127.7, 123.7, 117.8, 114.1, 56.0, 55.3, 52.2, 51.8, 29.8.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{25}H_{25}O_5NNa$: 442.1625 Found: 442.1625.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 80:20 hexane:isopropanol, 210 nm, t_{major} = 26.207 min).



Methyl (*R*,*E*)-(4-(dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (28): Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), (*E*)-3-(dimethyl(phenyl)silyl)allyl mesylate (85 mg, 0.3125 mmol, 1.25 equiv.), Pd_2dba_3 (11.3 mg, 5 mol%), P(2-furyl)$_3$ (5.8 mg, 10 mol%) and methanol (1.25 mL). The *title compound* was obtained as a yellow oil (61 mg, 66%) following purification by column chromatography (SiO_2, 5–10% Et_2O/petroleum ether). The enantiomeric ratio (90:10) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +22.4° (*c* = 1.0, $CHCl_3$).

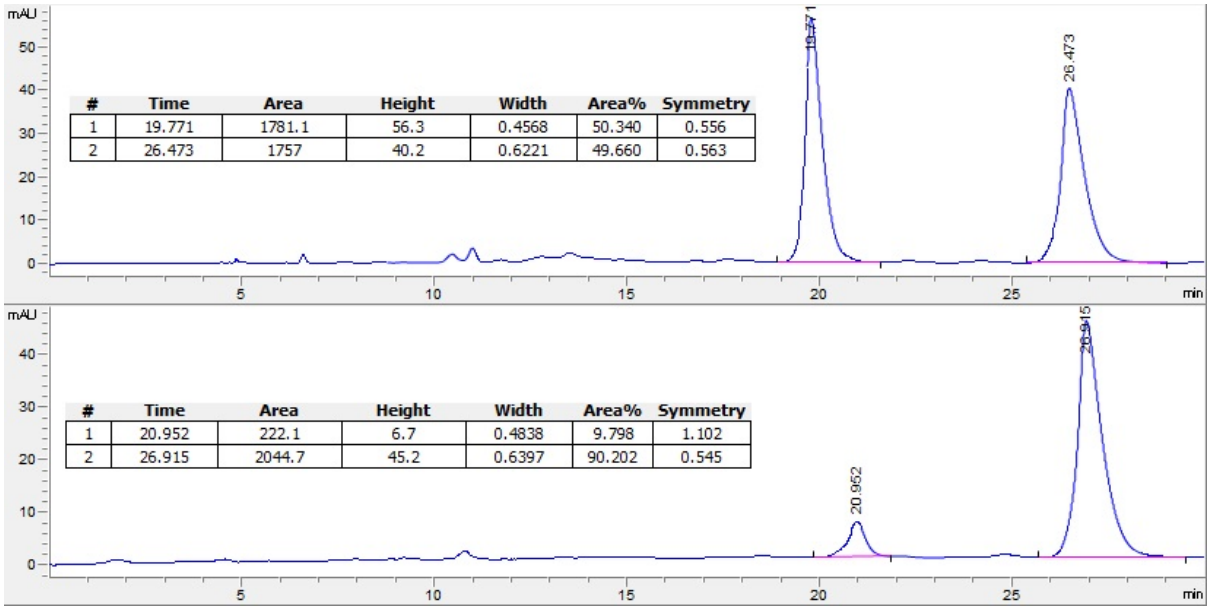
IR (neat): 3327, 2955, 1709, 1513, 1247, 1038, 831, 756 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.41 (m, 2H), 7.38 – 7.29 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.04 – 5.94 (m, 1H), 5.86 (d, *J* = 18.6 Hz, 1H), 5.03 (s, 1H), 4.77 (s, 1H), 3.80 (s, 3H), 3.65 (s, 3H), 2.62 (t, *J* = 6.8 Hz, 2H), 0.31 (s, 6H).

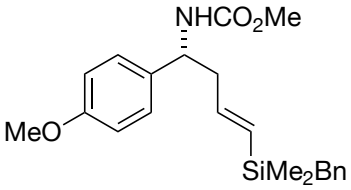
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.4, 158.9, 146.5, 141.3, 136.8, 136.4, 134.9, 131.5, 130.3, 130.0, 57.9, 56.6, 54.7, 46.7, 0.02, 0.00.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{21}H_{27}O_3NNaSi$: 392.1652 Found: 392.1656.

HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.00 mL/min, 97:3 hexane:isopropanol, 270 nm, t_{minor} = 20.952 min, t_{major} = 26.915 min).



Methyl (*R*,*E*)-(4-(benzyldimethylsilyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (29): Prepared according to General Procedure A using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), (*E*)-3-(benzyldimethylsilyl)allyl mesylate (89 mg, 0.3125 mmol, 1.25 equiv.), Pd_2dba_3 (11.3 mg, 5 mol%), P(2-furyl)$_3$ (5.8 mg, 10 mol%) and methanol (1.25 mL). The *title compound* was obtained as a yellow oil (75 mg, 78%) following purification by column chromatography (SiO_2, 10–20% Et_2O/petroleum ether). The enantiomeric ratio (91:9) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +28.9° (*c* = 1.0, $CHCl_3$).

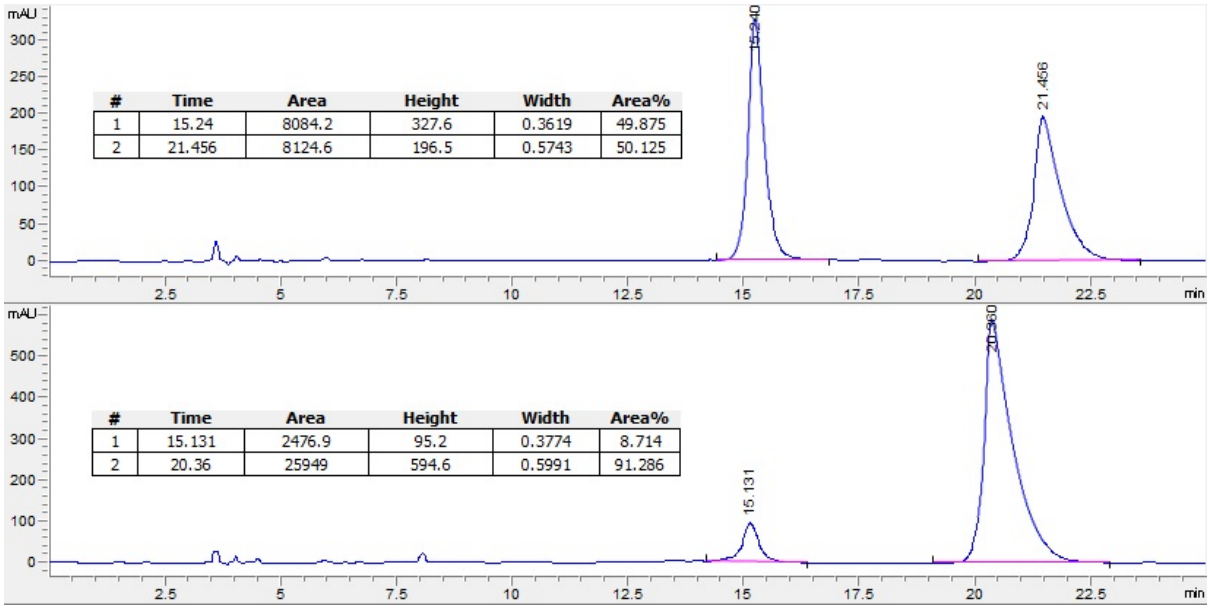
IR (neat): 3327, 3023, 2954, 1704, 1613, 1513, 1247, 1037, 832, 757 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.11 – 7.06 (m, 1H), 6.98 (d, *J* = 6.8 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.86 (dt, *J* = 18.6, 6.5 Hz, 1H), 5.70 (d, *J* = 18.6 Hz, 1H), 5.05 (s, 1H), 4.75 (s, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 2.56 (t, *J* = 6.6 Hz, 2H), 2.11 (s, 2H), 0.03 (d, *J* = 3.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.8, 156.4, 143.2, 140.0, 134.3, 132.6, 128.3, 128.2, 124.1, 113.9, 55.3, 53.9, 52.2, 44.1, 26.1, -3.2, -3.4.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{22}H_{29}O_3NNaSi$: 406.1809 Found: 406.1813.

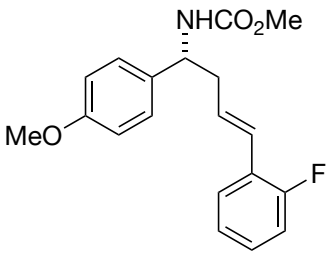
HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.00 mL/min, 97:3 hexane:isopropanol, 210 nm, t_{minor} = 15.131 min, t_{major} = 20.36 min).



For preparation on scale: To an oven dried 250 mL round bottomed flask equipped with stirrer bar was added 4-methoxyphenylacetic acid pentafluorophenyl ester (1.96 g, 5.9 mmol, 1 equiv.), (*Z*)-3-(benzyldimethylsilyl)allyl mesylate (2.1 g, 7.38 mmol, 1.25 equiv.), Pd_2dba_3 (271 mg, 5 mol%), P(2-furyl)$_3$ (138 mg, 10 mol%) and (*R*)-BTM (298 mg, 20 mol%). The flask was then sealed and purged with N_2 × 3 before adding THF (60 mL, 0.1 M) and DIPEA (1.29 mL, 7.38 mmol, 1.25 equiv.). Aq. NH_4OH (60 mL) was added and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was then diluted with EtOAc, washed H_2O, 1M HCl and brine before being dried with Na_2SO_4 and concentrated under vacuum. The crude mixture was then diluted with 60 mL THF before adding methanol (30 mL) followed by PIFA (5.1 g, 11.8 mmol, 2.0 equiv.). The flask was then resealed and heated to 60 °C overnight. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and washed twice with 2 M Na_2CO_3 before being dried (Na_2SO_4) and concentrated under vacuum. The *title compound* was obtained as a yellow oil (1.7 g, 75%) following purification by column chromatography (SiO_2, 5–20% Et_2O/petroleum ether). The enantiomeric ratio (90:10) was determined by chiral HPLC in comparison with the racemate.

Products from Hiyama-Denmark cross-coupling

Methyl (*R*,*E*)-(4-(2-fluorophenyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (30):



Prepared according to General Procedure B using 2-fluoroiodobenzene (44 µL, 0.375 mmol, 1.5 equiv.). The *title compound* was obtained as a white solid (60 mg, 73%) following purification by column chromatography (SiO_2, 15% EtOAc/petroleum ether). The enantiomeric ratio (92:8) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +35.0° (*c* = 1.0, $CHCl_3$).

IR (neat): 3322, 2952, 1696, 1512, 1245, 1035, 755 cm^{-1}.

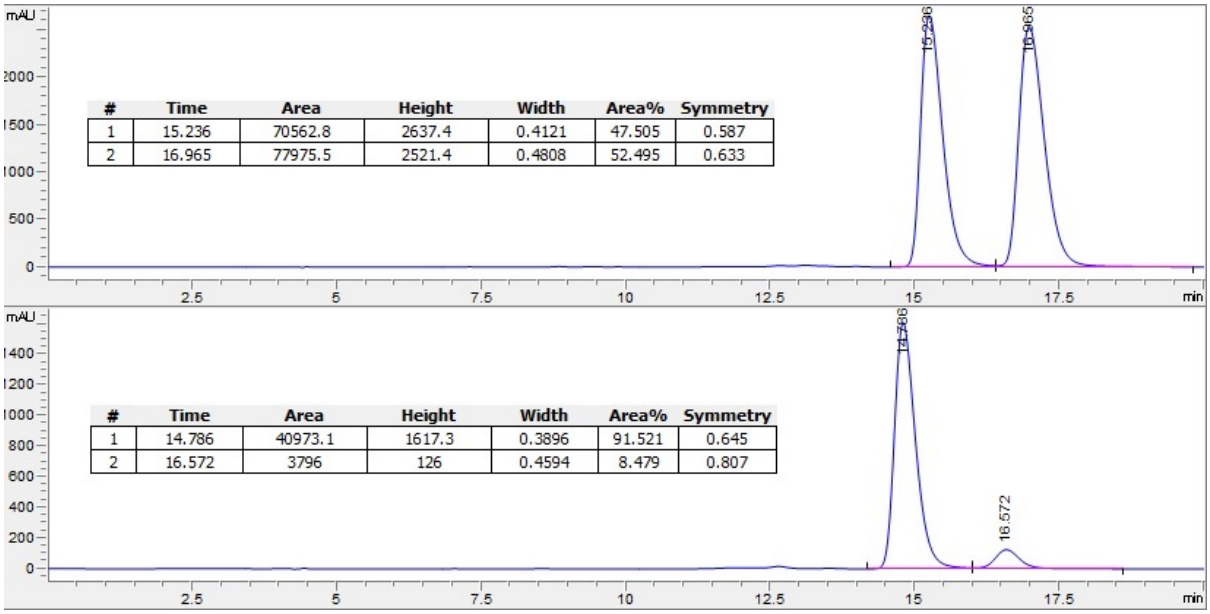
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (td, *J* = 7.7, 1.7 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.18 (tdd, *J* = 7.4, 5.0, 1.6 Hz, 1H), 7.08 – 6.98 (m, 2H), 6.91 – 6.86 (m, 2H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.14 (dt, *J* = 15.3, 7.2 Hz, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 2.71 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.0 (d, $^{1}J_{C\text{-}F}$ = 248.8 Hz), 158.9, 156.3, 134.0, 128.6 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 128.3, 127.4, 127.2 (d, $J_{C\text{-}F}$ = 3.8 Hz), 125.5, 124.9 (d, $^{3}J_{C\text{-}F}$ = 12.3 Hz), 124.0 (d, $J_{C\text{-}F}$ = 3.3 Hz), 115.6 (d, $^{2}J_{C\text{-}F}$ = 22.2 Hz), 114.0, 55.3, 54.3, 52.1, 40.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ -118.4.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{19}H_{20}FNO_3Na$: 352.1325 Found: 352.1322.

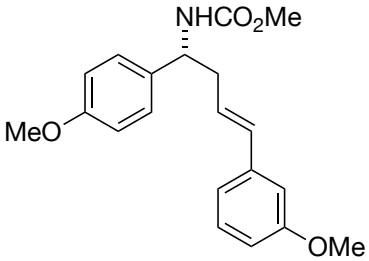
HPLC analysis using a chiral column (Cellulose 4 column, 22 °C, 1.0 mL/min, 85:15 hexane:isopropanol, 254 nm, t_{major} = 14.786 min, t_{minor} = 16.572 min).



#	Time	Area	Height	Width	Area%	Symmetry
1	15.236	70562.8	2637.4	0.4121	47.505	0.587
2	16.965	77975.5	2521.4	0.4808	52.495	0.633

#	Time	Area	Height	Width	Area%	Symmetry
1	14.786	40973.1	1617.3	0.3896	91.521	0.645
2	16.572	3796	126	0.4594	8.479	0.807

Methyl (*R*,*E*)-(4-(3-methoxyphenyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (31):



Prepared according to General Procedure B using 3-iodoanisole (45 µL, 0.375 mmol, 1.5 equiv.). The *title compound* was obtained as a yellow oil (57 mg, 67%) following purification by column chromatography (SiO_2, 15% EtOAc/petroleum ether). The enantiomeric ratio (90:10) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +29.0° (*c* = 1.0, $CHCl_3$).

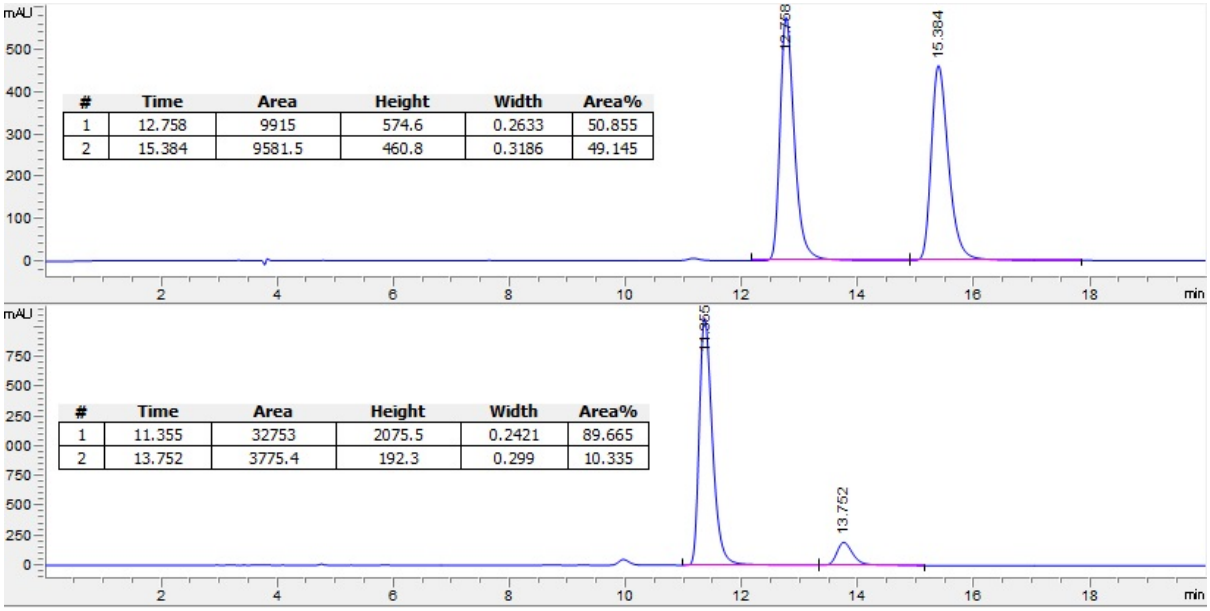
IR (neat): 3331, 3017, 2954, 1704, 1512, 1246, 752 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.18 (m, 3H), 6.92 – 6.83 (m, 4H), 6.78 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.06 (dt, *J* = 15.2, 7.2 Hz, 1H), 5.11 (br s, 1H), 4.81 (s, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 2.68 (t, *J* = 7.1 Hz, 2H).

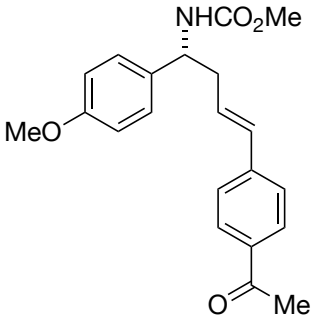
^{13}C NMR (126 MHz, $CDCl_3$): 159.8, 158.8, 156.3, 138.6, 134.1, 133.1, 129.5, 127.4, 125.9, 118.8, 114.0, 112.9, 111.7, 55.28, 55.22, 54.3, 52.1, 40.2.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{20}H_{23}NO_4Na$: 364.1519 Found: 364.1521.

HPLC analysis using a chiral column (Chiralpak IA 3µ column, 22 °C, 1.5 mL/min, 85:15 hexane:isopropanol, 254 nm, t_{major} = 11.355 min, t_{minor} = 13.752 min).



Methyl (*R*,*E*)-(4-(4-acetylphenyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (32):



Prepared according to General Procedure B using 4-iodoacetophenone (92 mg, 0.375 mmol, 1.5 equiv.). The *title compound* was obtained as a white solid (59 mg, 67%) following purification by column chromatography (SiO_2, 20–40% EtOAc/petroleum ether). The enantiomeric ratio (90:10) was determined by chiral HPLC in comparison with the racemate.

$[\alpha]_D^{23}$ +32.2° (*c* = 1.0, $CHCl_3$).

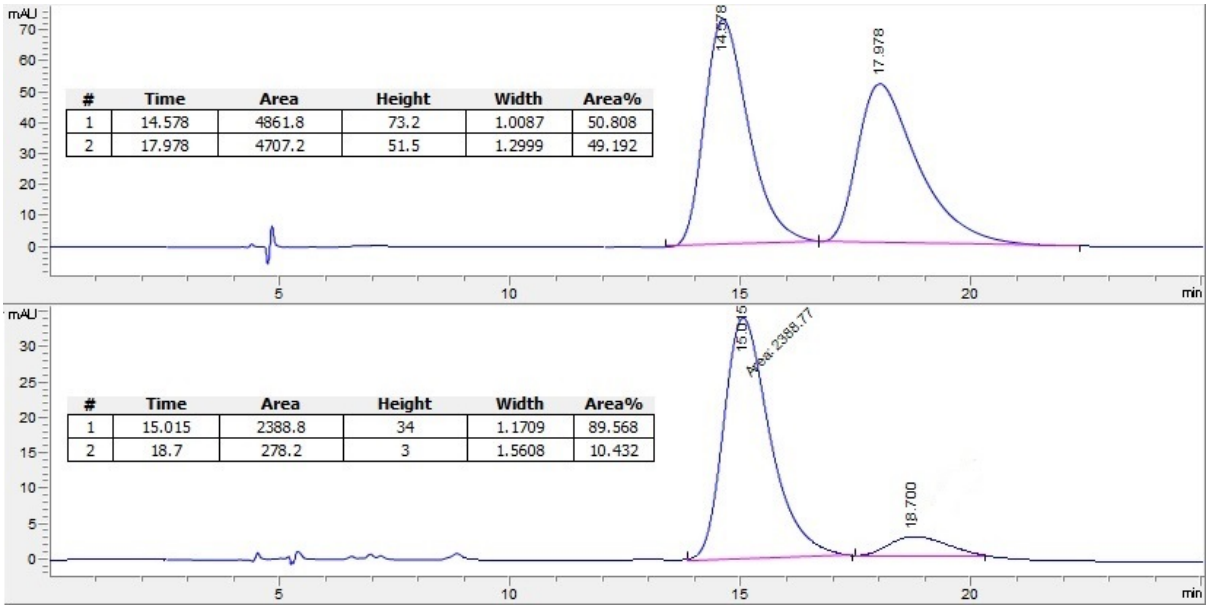
IR (neat): 3330, 1701, 1678, 1602, 1513, 1267, 1180 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H) 6.48 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.2, 7.2 Hz, 0H), 5.02 (s, 1H), 4.83 (s, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 2.71 (d, *J* = 9.0 Hz, 2H), 2.58 (s, 3H).

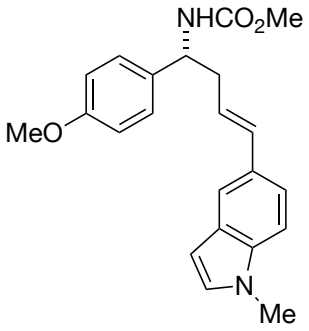
^{13}C NMR (126 MHz, $CDCl_3$): δ 197.5, 158.9, 156.3, 141.8, 135.8, 133.9, 132.1, 129.0, 128.7, 127.4, 126.2, 114.1, 55.3, 54.3, 52.1, 40.3, 26.6.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{21}H_{23}NO_4Na$: 376.1519 Found: 376.1524.

HPLC analysis using a chiral column (Cellulose 3µ column, 22 °C, 1.5 mL/min, 40:60 hexane:isopropanol, 210 nm, t_{major} = 15.015 min, t_{minor} = 18.700 min).



Methyl (*R*,*E*)-(1-(4-methoxyphenyl)-4-(1-methyl-1*H*-indol-5-yl)but-3-en-1-yl)carbamate (33): Prepared according to General Procedure B using 5-iodo-1-methyl-1*H*-indole (96 mg, 0.375 mmol, 1.5 equiv.). The *title compound* was obtained as a white solid (59 mg, 65%) following purification by column chromatography (SiO_2, 30% EtOAc/petroleum ether). The enantiomeric ratio (90:10) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +27.7° (*c* = 1.0, $CHCl_3$).

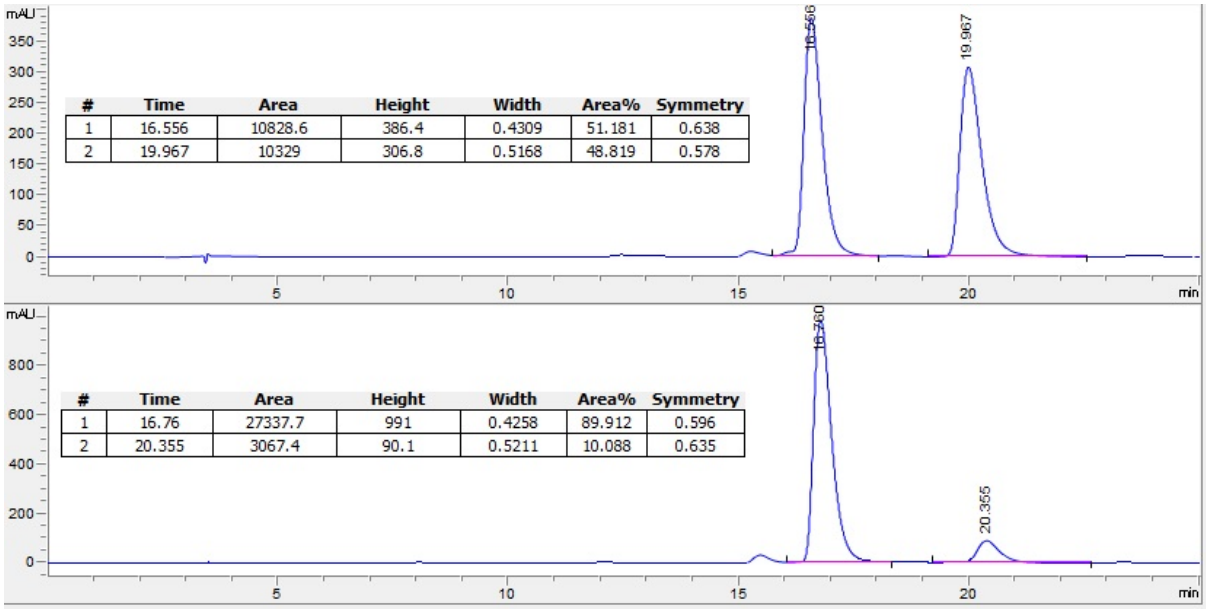
IR (neat): 3323, 2949, 2835, 1701, 1512, 1245, 1034 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 1.4 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.23 (d, *J* = 3.1 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 15.7 Hz, 1H), 6.66 (d, *J* = 3.1 Hz, 1H), 6.21 (dt, *J* = 15.1, 7.2 Hz, 1H), 5.37 (s, 1H), 5.04 (s, 1H), 4.01 (s, 3H), 3.96 (s, 3H), 3.85 (s, 3H), 2.90 (t, *J* = 7.0 Hz, 2H).

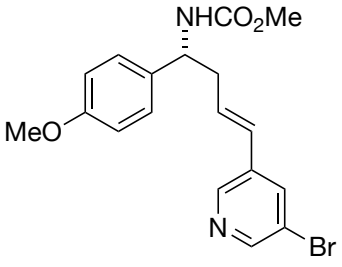
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.8, 156.5, 136.4, 134.5, 129.4, 128.8, 128.7, 127.5, 122.3, 120.0, 119.1, 114.0, 109.3, 101.3, 55.3, 54.5, 52.1, 40.5, 32.9.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{22}H_{24}N_2O_3Na$: 387.1679 Found: 387.1681.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 85:15 hexane:isopropanol, 280 nm, t_{major} = 16.760 min, t_{minor} = 20.355 min).



Methyl (*R*,*E*)-(1-(4-methoxyphenyl)-4-(1-methyl-1*H*-indol-5-yl)but-3-en-1-yl)carbamate (34): Prepared according to General Procedure B using 3-bromo-5-iodopyridine (106 mg, 0.375 mmol, 1.5 equiv.). The *title compound* was obtained as a white solid (65 mg, 67%) following purification by column chromatography (SiO_2, 30% EtOAc/petroleum ether). The enantiomeric ratio (90:10) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +17.2° (*c* = 1.0, $CHCl_3$).

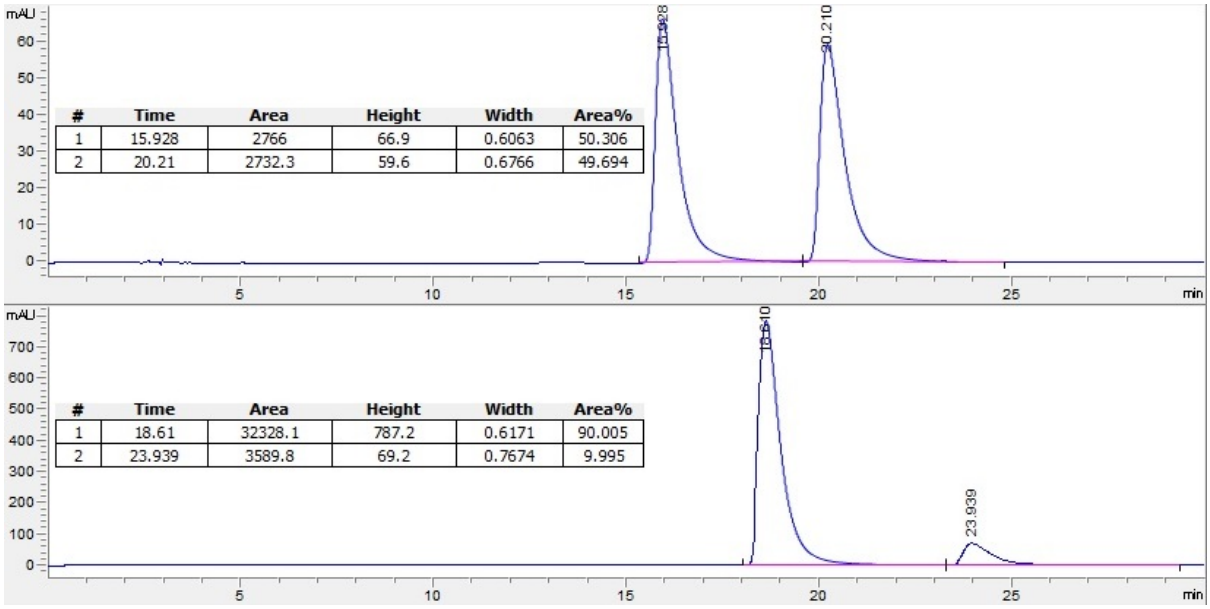
IR (neat): 3317, 2951, 1701, 1513, 1246, 1036 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 8.46 (d, *J* = 2.2 Hz, 1H), 8.37 (d, *J* = 1.9 Hz, 1H), 7.72 (s, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.38 – 6.27 (m, 1H), 6.14 (dt, *J* = 15.8, 7.1 Hz, 1H), 5.19 (d, *J* = 8.1 Hz, 1H), 4.80 (s, 1H), 3.78 (s, 3H), 3.63 (s, 3H), 2.81 – 2.54 (m, 2H).

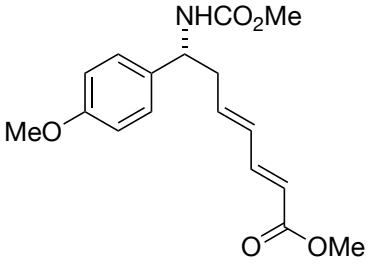
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1, 156.4, 149.2, 146.1, 135.2, 134.5, 133.6, 130.3, 128.1, 127.5, 120.9, 114.2, 55.4, 54.4, 52.3, 40.3.

HRMS (ESI): *m/z* calcd for $[M+H]^+$ $C_{18}H_{20}N_2O_3Br$: 391.0652 Found: 391.0656.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 85:15 hexane:isopropanol, 254 nm, t_{major} = 18.610 min, t_{minor} = 23.939 min).



Methyl (*R*,2*E*,4*E*)-7-((methoxycarbonyl)amino)-7-(4-methoxyphenyl)hepta-2,4-dienoate (35): Prepared according to General Procedure B using methyl (*E*)-3-iodoacrylate (132 mg, 0.375 mmol, 2.5 equiv.) at 50 °C. The *title compound* was obtained as a yellow oil (36 mg, 46%) following purification by column chromatography (SiO_2, 25% EtOAc/petroleum ether). The enantiomeric ratio (90:10) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ +15.9° (*c* = 1.0, $CHCl_3$).

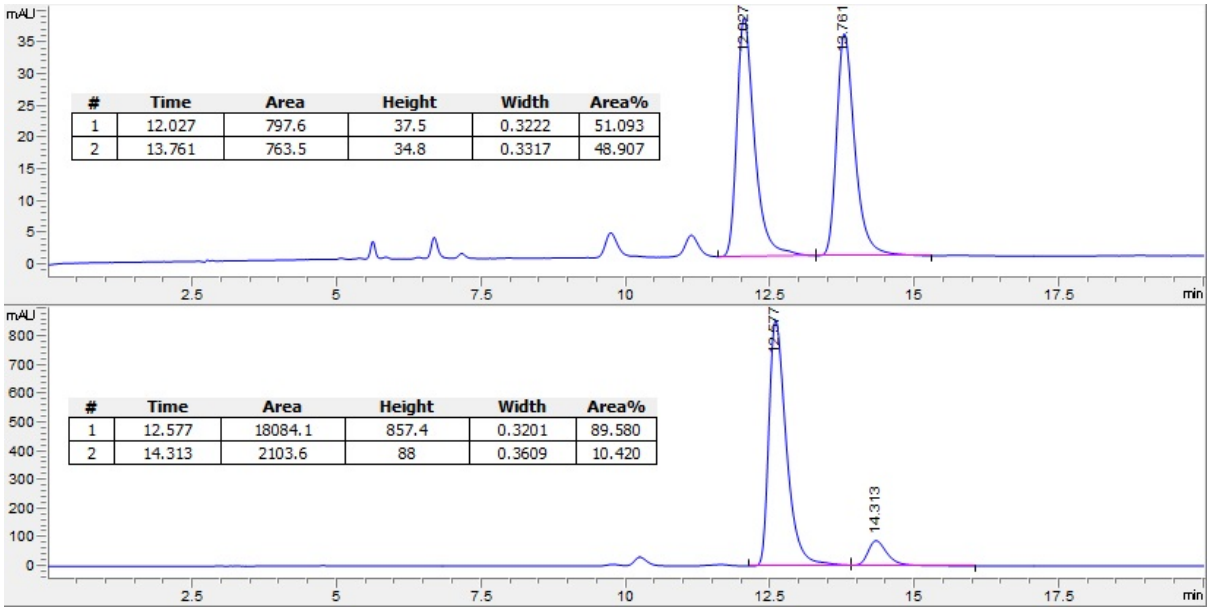
IR (neat): 3333, 2952, 1716, 1513, 1247, 1035 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 7.21 – 7.11 (m, 3H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.19 (dd, *J* = 15.2, 11.0 Hz, 1H), 5.94 (dt, *J* = 14.9, 7.3 Hz, 1H), 5.79 (d, *J* = 15.4 Hz, 1H), 5.06 (d, *J* = 8.2 Hz, 1H), 4.75 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.63 (s, 3H), 2.62 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 167.5, 159.1, 156.3, 144.5, 139.0, 133.6, 131.3, 127.5, 120.2, 114.2, 55.4, 54.2, 52.3, 51.6, 40.0.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{17}H_{21}NO_5Na$: 342.1317 Found: 342.1314.

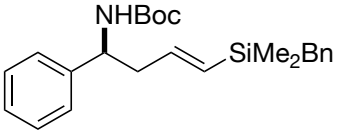
HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 85:15 hexane:isopropanol, 270 nm, t_{major} = 12.577 min, t_{minor} = 14.313 min).



#	Time	Area	Height	Width	Area%
1	12.027	797.6	37.5	0.3222	51.093
2	13.761	763.5	34.8	0.3317	48.907

#	Time	Area	Height	Width	Area%
1	12.577	18084.1	857.4	0.3201	89.580
2	14.313	2103.6	88	0.3609	10.420

***tert*-Butyl (*S*,*E*)-(4-(benzyldimethylsilyl)-1-phenylbut-3-en-1-yl)carbamate (36):** Prepared according to General Procedure A using phenylacetic acid pentafluorophenyl ester (604 mg, 2 mmol, 1 equiv.), (*Z*)-3-(benzyldimethylsilyl)allyl mesylate (711 mg, 2.5 mmol, 1.25 equiv.), Pd_2dba_3 (90.5 mg, 5 mol%), P(2-furyl)$_3$ (46.5 mg, 10 mol%), (*S*)-BTM (100 mg, 20 mol%), DIPEA (0.46 mL, 2.5 mmol, 1.25 equiv.), THF (20 mL, 0.1 M) and *t*-butanol (10 mL). The *title compound* was obtained as a yellow oil (418 mg, 53%) following purification by column chromatography (SiO_2, 5% Et_2O/petroleum ether). The enantiomeric ratio (91:9) was determined by chiral HPLC in comparison with the racemate.



$[\alpha]_D^{23}$ -14.0° (*c* = 1.0, $CHCl_3$).

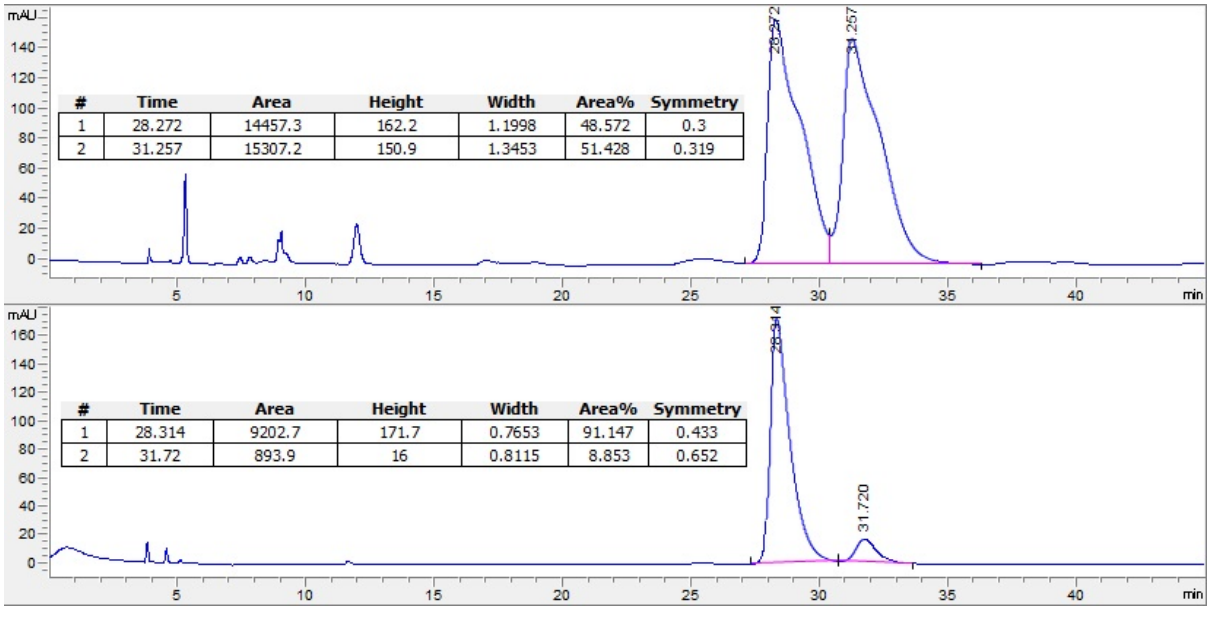
IR (neat): 3349, 2977, 1702, 1493, 1366, 1248, 1169, 833, 699 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 2H), 5.83 (dt, *J* = 18.6, 6.6 Hz, 1H), 5.68 (d, *J* = 18.6 Hz, 1H), 4.84 (s, 1H), 4.75 (s, 1H), 2.54 (s, 2H), 2.09 (s, 2H), 1.44 (s, 9H), -0.00 (d, *J* = 10.0 Hz, 6H).

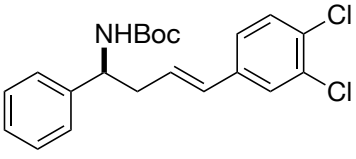
^{13}C NMR (126 MHz, $CDCl_3$): δ 155.3, 143.3, 140.1, 132.5, 129.7, 129.1, 129.0, 128.5, 128.3, 128.3, 127.2, 126.3, 124.1, 79.7, 54.0, 44.3, 28.5, 26.2, -3.1, -3.4.

HRMS (APCI): *m/z* calcd for $[M+H]^+$ $C_{24}H_{34}O_2NSi$: 396.2353 Found: 396.2351.

HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.5 mL/min, 600:1 hexane:isopropanol, 210 nm, t_{major} = 28.314 min, t_{minor} = 31.720 min).



***tert*-Butyl (*S*,*E*)-(4-(3,4-dichlorophenyl)-1-phenylbut-3-en-1-yl)carbamate (37):** Prepared according to General Procedure B using *tert*-butyl (*S*,*E*)-(4-(benzyldimethylsilyl)-1-phenylbut-3-en-1-yl)carbamate (X) (296 mg, 0.75 mmol, 1 equiv.), 3,4-dichloroiodobenzene (307 mg, 1.125 mmol, 1.5 equiv.) Pd_2dba_3 (17.3 mg, 2.5 mol%),

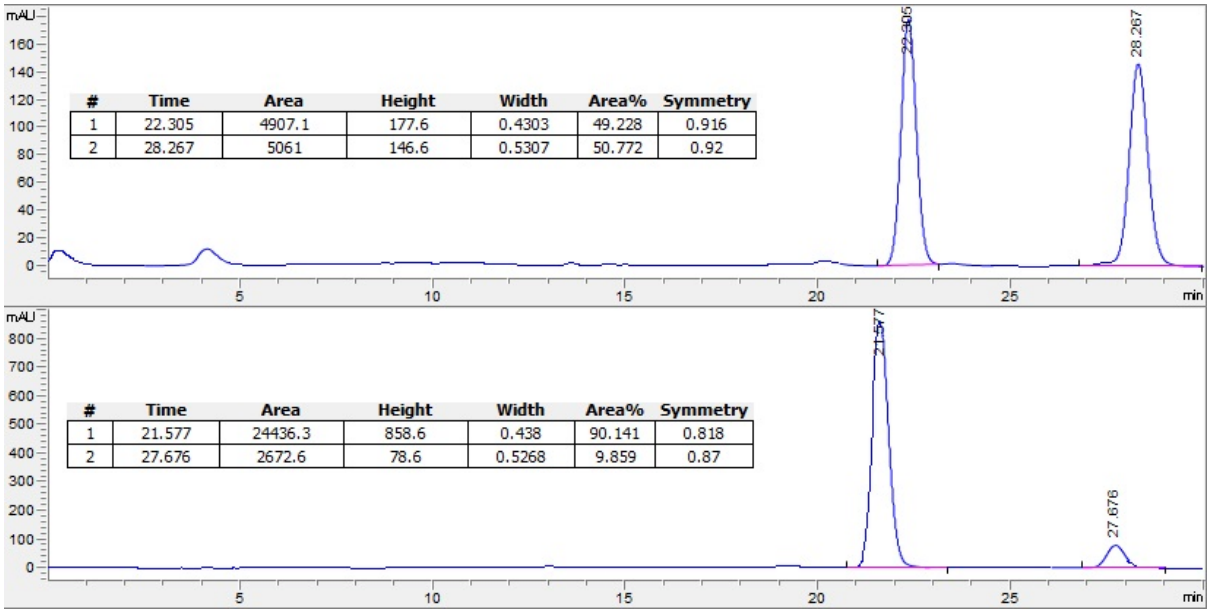


TBAF (1.65 mL, 1 M in THF, 1.65 mmol, 2.2 equiv.), H_2O (45 µL, 2.25 mmol, 3 equiv.) and THF (1.5 mL, 0.5 M). The *title compound* was obtained as a white solid (207 mg, 70%) following purification by column chromatography (SiO_2, 5–20% Et_2O/petroleum ether). The enantiomeric ratio (90:10) was determined by chiral HPLC in comparison with the racemate. Characterization consistent with previously reported data.[15]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.30 (m, 4H), 7.31 – 7.24 (m, 3H), 7.15 – 7.05 (m, 1H), 6.34 (d, *J* = 16.6 Hz, 1H), 6.16 – 5.99 (m, 1H), 4.84 (s, 2H), 2.68 (s, 2H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 155.3, 142.0, 137.5, 132.7, 131.0, 130.8, 130.5, 128.8, 128.1, 128.0, 127.5, 126.4, 125.5, 79.9, 54.5, 40.6, 28.5.

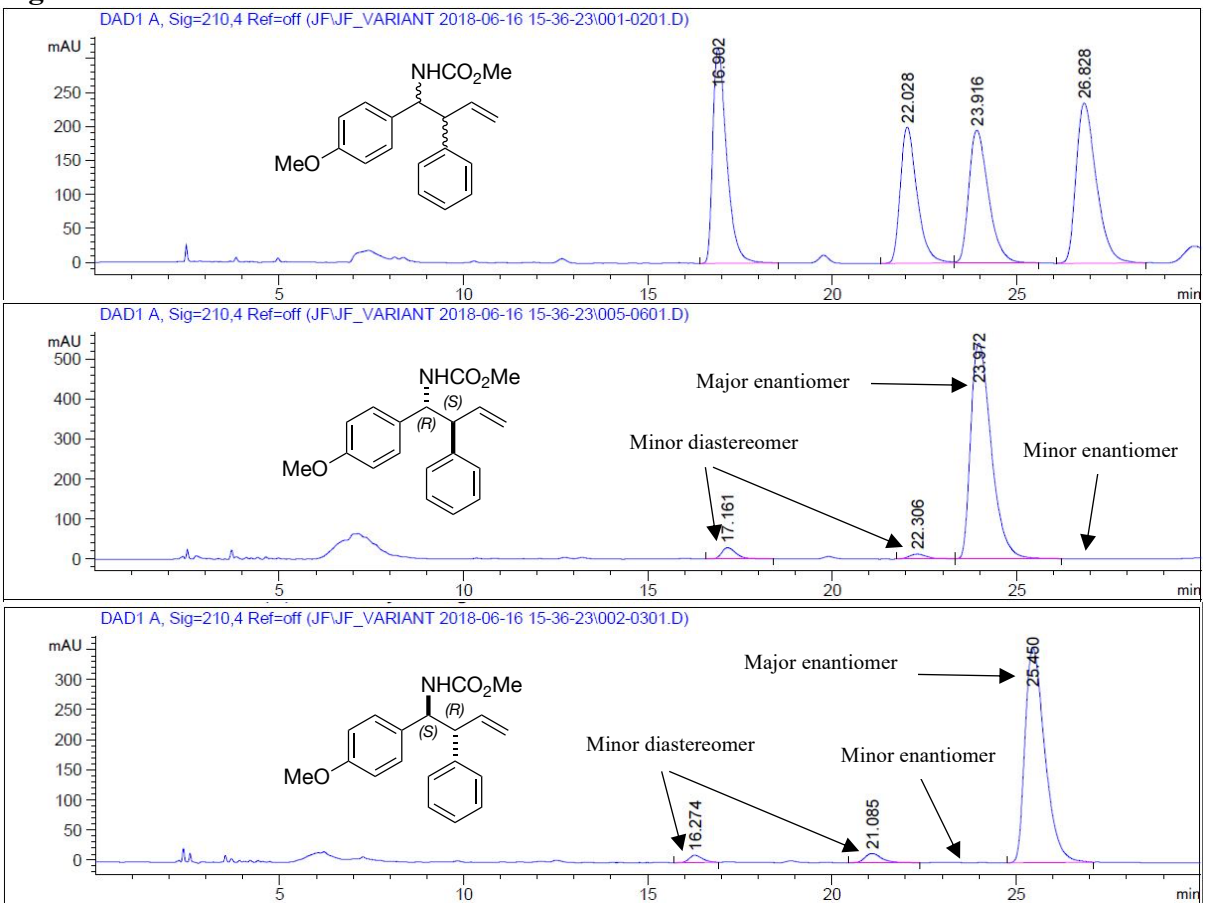
HPLC analysis using a chiral column (Chiralpak IA 3µ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 254 nm, t_{major} = 21.577 min, t_{minor} = 27.676 min).



Products from Scheme 2

*The diastereomeric and enantiomeric ratios of the following compounds were assigned by HPLC analysis of the product against both a racemic sample and the opposite enantiomer. Racemic samples were obtained by performing the reaction with (rac)-[Ir] and (rac)-BTM to afford ~1:1:1:1 mixture of all 4 stereoisomers (Figure S1, top). The reaction was then run using the reported catalyst pairing, eg. (S)-[Ir] and (R)-BTM in the case of (1R,2S)-**X** (Figure S1, middle), as well as the opposite catalyst pairing, eg. (R)-[Ir] and (S)-BTM to afford the opposite enantiomer (Figure S1, bottom). Comparison of HPLC traces of these 2 compounds with the racemic sample enabled the determination of peaks corresponding to pairs of diastereoisomers and pairs of enantiomers. In most cases the minor diastereomer was found to have significantly lower er.*

Figure S1:

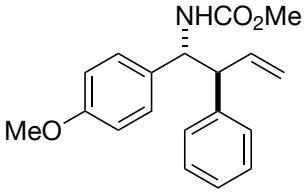


In all cases the isolated yield is of the mixture of diastereoisomers, with the shifts of the major diastereoisomer reported for ^{1}H and ^{13}C NMR.

The descriptors "t_{major}" and "t_{minor}" in the characterization section refer to the HPLC retention times of the major and minor enantiomers of the major diastereoisomer. Other retention times refer to the minor diastereomer. This is consistent with other reports of this type of diastereo- and enantioselective catalysis from Carreira et al, Science, 2013, 340, 1065–1068.

All stereoisomers of 39

Methyl ((1*R*,2*S*)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)carbamate ((1*R*,2*S*)-39):



Prepared according to General Procedure C using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), *t*-butyl cinnamyl carbonate (88 mg, 0.375 mmol, 1.5 equiv.), (*S*)-[Ir] (10.5 mg, 4 mol%), (*R*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a beige solid (64 mg, 83%) following purification by column chromatography (SiO_2, 1–5% Et_2O/toluene). The enantiomeric ratio (>99:1 er, 95:5 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ +39.6° (*c* = 1.0, $CHCl_3$).

IR (neat): 3322, 2953, 1695, 1535, 1514, 1246, 1033, 701 cm^{-1}.

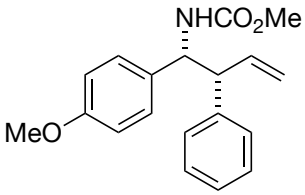
^1H NMR (600 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.09 (dt, *J* = 18.1, 9.5 Hz, 1H), 5.21 – 5.11 (m, 2H), 5.09 (s, 1H), 4.91 (s, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 3.56 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.7, 156.4, 140.4, 138.6, 132.9, 128.5, 128.2, 126.8, 117.5, 113.6, 58.7, 57.0, 55.2, 52.3.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{19}H_{21}O_3NNa$: 334.1414 Found: 334.1417.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 98:2 hexane:isopropanol, 210 nm, t = 16.902 min, t = 22.028 min, t_{major} = 23.916 min, t_{minor} = 26.828 min).

Methyl ((1*R*,2*R*)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)carbamate ((1*R*,2*R*)-39):



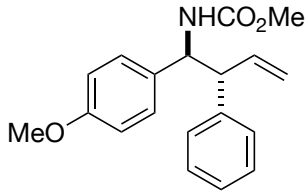
Prepared according to General Procedure C using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), *t*-butyl cinnamyl carbonate (88 mg, 0.375 mmol, 1.5 equiv.), (*R*)-[Ir] (10.5 mg, 4 mol%), (*R*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a beige solid (60 mg, 78%) following purification by column chromatography (SiO_2, 2–5% Et_2O/toluene). The enantiomeric ratio (>99:1 er, 95:5 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ -23.7° (*c* = 1.0, $CHCl_3$).

^1H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 1H), 5.94 (ddd, *J* = 16.9, 10.3, 8.3 Hz, 1H), 5.13 – 5.05 (m, 2H), 5.03 (d, *J* = 17.1 Hz, 1H), 4.98 (s, 1H), 3.78 (s, 3H), 3.67 (t, *J* = 8.1 Hz, 1H), 3.57 (s, 1H).

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 98:2 hexane:isopropanol, 210 nm, t_{major} = 16.902 min, t_{minor} = 22.028 min, t = 23.916 min, t = 26.828 min).

Methyl ((1*S*,2*R*)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)carbamate ((1*S*,2*R*)-39):



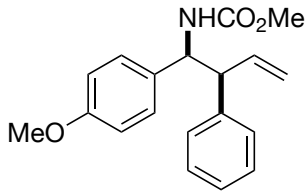
Prepared according to General Procedure C using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), *t*-butyl cinnamyl carbonate (88 mg, 0.375 mmol, 1.5 equiv.), (*R*)-[Ir] (10.5 mg, 4 mol%), (*S*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a beige solid (58 mg, 75%) following purification by column chromatography (SiO_2, 2–5% Et_2O/toluene). The enantiomeric ratio (>99:1 er, 95:5 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ -38.2° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.19 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.16 – 7.09 (m, 1H), 7.02 – 6.97 (m, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.10 (dt, *J* = 16.9, 9.5 Hz, 1H), 5.25 – 5.13 (m, 2H), 5.10 (s, 1H), 4.91 (s, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 3.58 – 3.52 (m, 1H).

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 98:2 hexane:isopropanol, 210 nm, t = 16.902 min, t = 22.028 min, t_{minor} = 23.916 min, t_{major} = 26.828 min).

Methyl ((1*S*,2*S*)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)carbamate ((1*S*,2*S*)-39):



Prepared according to General Procedure C using 4-methoxyphenylacetic acid pentafluorophenyl ester (83 mg, 0.25 mmol, 1 equiv.), *t*-butyl cinnamyl carbonate (88 mg, 0.375 mmol, 1.5 equiv.), (*S*)-[Ir] (10.5 mg, 4 mol%), (*S*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a beige solid (64 m

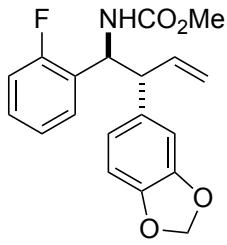
g, 83%) following purification by column chromatography (SiO_2, 2–5% Et_2O/toluene). The enantiomeric ratio (98:2 er, 94:6 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ +10.8° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.94 (ddd, *J* = 17.0, 10.3, 8.3 Hz, 1H), 5.21 – 5.05 (m, 2H), 5.03 (d, *J* = 17.1 Hz, 1H), 4.97 (s, 1H), 3.78 (s, 3H), 3.70 – 3.65 (m, 1H), 3.57 (s, 3H).

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 98:2 hexane:isopropanol, 210 nm, t_{minor} = 16.902 min, t_{major} = 22.028 min, t = 23.916 min, t = 26.828 min).

Scope of Branched Homoallylic Amines

Methyl ((1*S*,2*R*)-2-(benzo[*d*][1,3]dioxol-5-yl)-1-(2-fluorophenyl)but-3-en-1-yl)carbamate (*anti*-40): 

Prepared according to General Procedure C using 2-(2-fluorophenyl)acetic acid pentafluorophenyl ester (80 mg, 0.25 mmol, 1 equiv.), (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)allyl *tert*-butyl carbonate (105 mg, 0.375 mmol, 1.5 equiv.), (*R*)-[Ir] (10.5 mg, 4 mol%), (*S*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a brown gum (65 mg, 75%) following purification by column chromatography (SiO_2, 1–2% Et_2O/toluene). The enantiomeric ratio (>99:1 er, 90:10 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ -5.8° (*c* = 1.0, $CHCl_3$).

IR (neat): 3324, 3019, 1703, 1518, 1490, 1236, 1215, 1040, 755, 668 cm^{-1}.

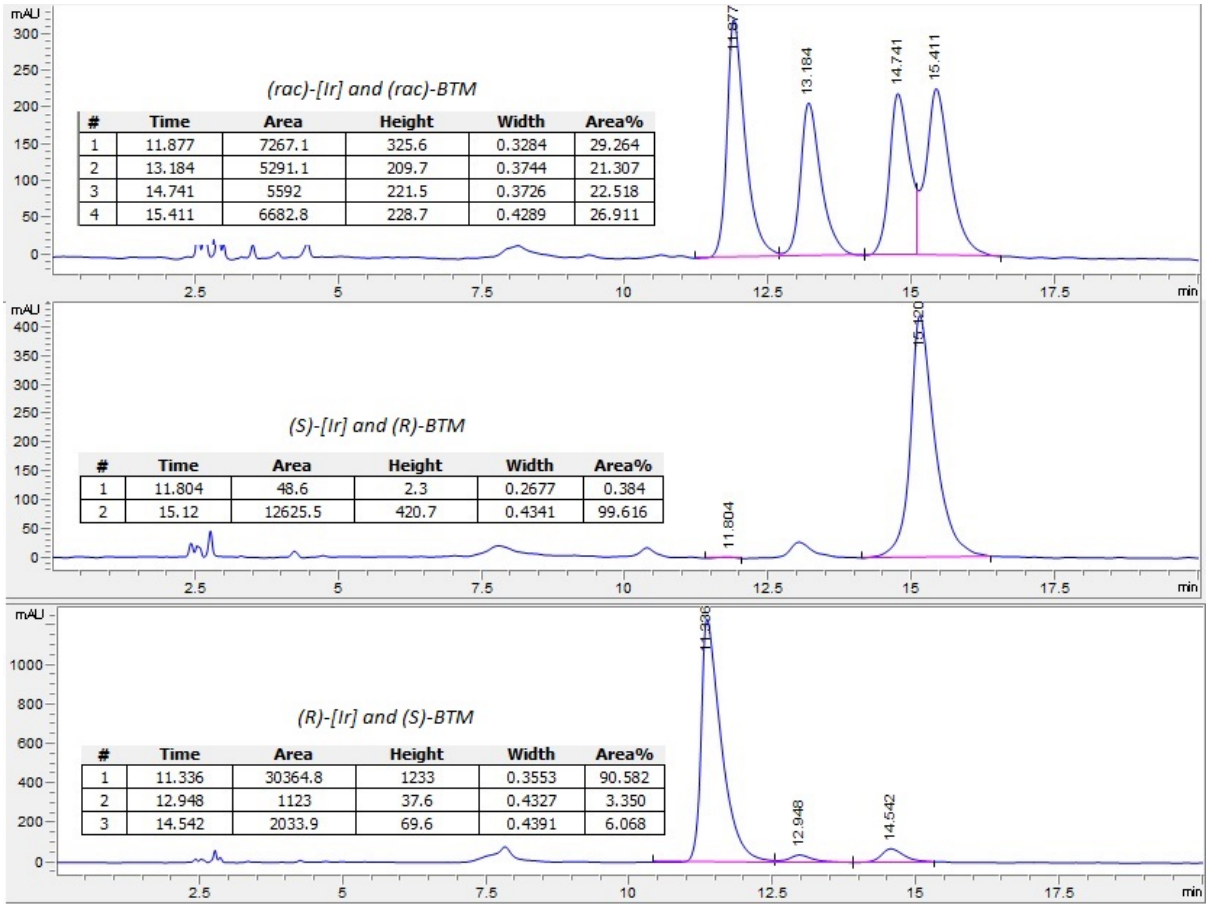
^1H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.09 (m, 1H), 7.03 – 6.87 (m, 3H), 6.66 – 6.56 (m, 2H), 6.52 – 6.47 (m, 1H), 6.08 (dt, *J* = 17.9, 9.4 Hz, 1H), 5.85 (d, *J* = 8.3 Hz, 1H), 5.40 (s, 1H), 5.19 – 5.11 (m, 2H), 5.05 (t, *J* = 9.7 Hz, 1H), 3.65 – 3.63 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.7 (d, $^1J_{C\text{-}F}$ = 244.7 Hz), 156.5, 147.6, 146.2, 138.2, 134.3, 129.9, 129.0, 123.9 (d, $J_{C\text{-}F}$ = 3.1 Hz), 121.1, 117.5, 115.6 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 108.2 (d, $^3J_{C\text{-}F}$ = 6.1 Hz), 100.9, 56.4, 55.3 (d, $J_{C\text{-}F}$ = 2.4 Hz), 52.3, 29.7.

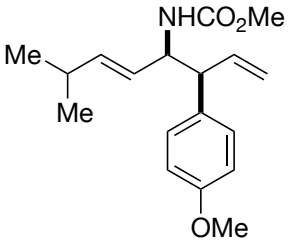
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.5.

HRMS (EI): *m/z* calcd for $[M]^+$ $C_{19}H_{18}FNO_4$: 343.1214 Found: 343.1211.

HPLC analysis using a chiral column (Chiralpak IB 3μ column, 22 °C, 1.5 mL/min, 99:1 hexane:isopropanol, 210 nm, t_{major} =11.877, t = 13.184, t = 14.741 min, t_{minor} = 15.411 min).



Methyl ((3*S*,4*R*,*E*)-3-(4-methoxyphenyl)-7-methylocta-1,5-dien-4-yl)carbamate (*syn*-41):



Prepared according to General Procedure C using (*E*)-5-methylhex-3-enoic acid pentafluorophenyl ester (74 mg, 0.25 mmol, 1 equiv.), (*E*)-*tert*-butyl (3-(4-methoxyphenyl)allyl) carbonate (99 mg, 0.375 mmol, 1.5 equiv.), (*S*)-[Ir] (10.5 mg, 4 mol%), (*S*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a yellow solid (50 mg, 66%) following purification by column chromatography (SiO_2, 1% Et_2O/toluene). The enantiomeric ratio (>99:1 er, 95:5 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ +52.0° (*c* = 1.0, $CHCl_3$).

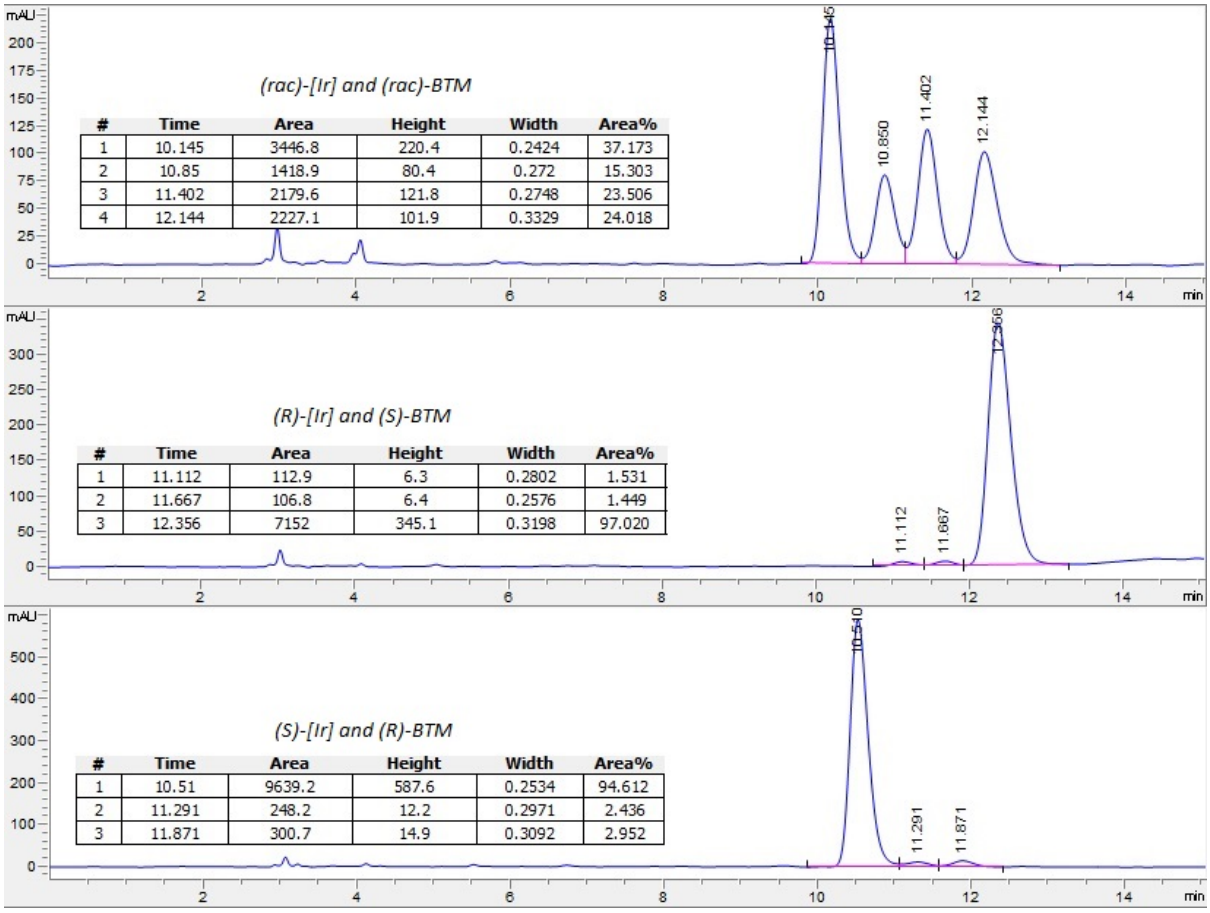
IR (neat): 3019, 1713, 1511, 1214, 748, 668 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 6.9 Hz, 2H), 6.02 (dddd, *J* = 17.0, 10.2, 8.6, 1.6 Hz, 1H), 5.42 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.26 (dd, *J* = 15.5, 6.2 Hz, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 4.63 (s, 1H), 4.44 (s, 1H), 3.79 (d, *J* = 1.6 Hz, 3H), 3.69 – 3.62 (m, 3H), 3.45 (t, *J* = 7.5 Hz, 1H), 2.24 (dt, *J* = 13.5, 6.8 Hz, 1H), 0.93 (d, *J* = 6.8 Hz, 6H).

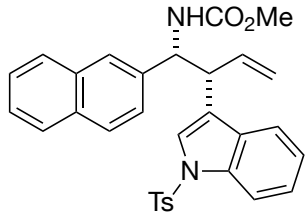
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.4, 156.4, 139.6, 137.3, 132.4, 129.4, 124.6, 117.7, 113.9, 56.3, 55.3, 54.0, 52.2, 30.9, 22.5, 22.4.

HRMS (APCI): *m/z* calcd for $[M+H]^+$ $C_{18}H_{26}O_3N$: 304.1907 Found: 304.1908.

HPLC analysis using a chiral column (Cellulose-4 3µ column, 22 °C, 1.5 mL/min, 99:1 hexane:isopropanol, 210 nm, t = 9.948 min, t_{major} = 10.651 min, t = 11.185 min, t_{minor} = 11.906 min).



Methyl ((1*R*,2*R*)-1-(naphthalen-2-yl)-2-(1-tosyl-1*H*-indol-3-yl)but-3-en-1-yl)carbamate (*syn*-42): Prepared according to General Procedure C using 2-(naphthalen-2-yl)acetic acid pentafluorophenyl ester (88 mg, 0.25 mmol, 1 equiv.), (*E*)-*tert*-butyl (3-(1-tosyl-1*H*-indol-3-yl)allyl) carbonate (160 mg, 0.375 mmol, 1.5 equiv.), (*R*)-[Ir] (10.5 mg, 4 mol%), (*R*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a yellow solid (100 mg, 77%) following purification by column chromatography (SiO_2, 1–5% Et_2O/toluene). The enantiomeric ratio (97:3 er, 93:7 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.



$[\alpha]_D^{23}$ +2.5° (*c* = 1.0, $CHCl_3$).

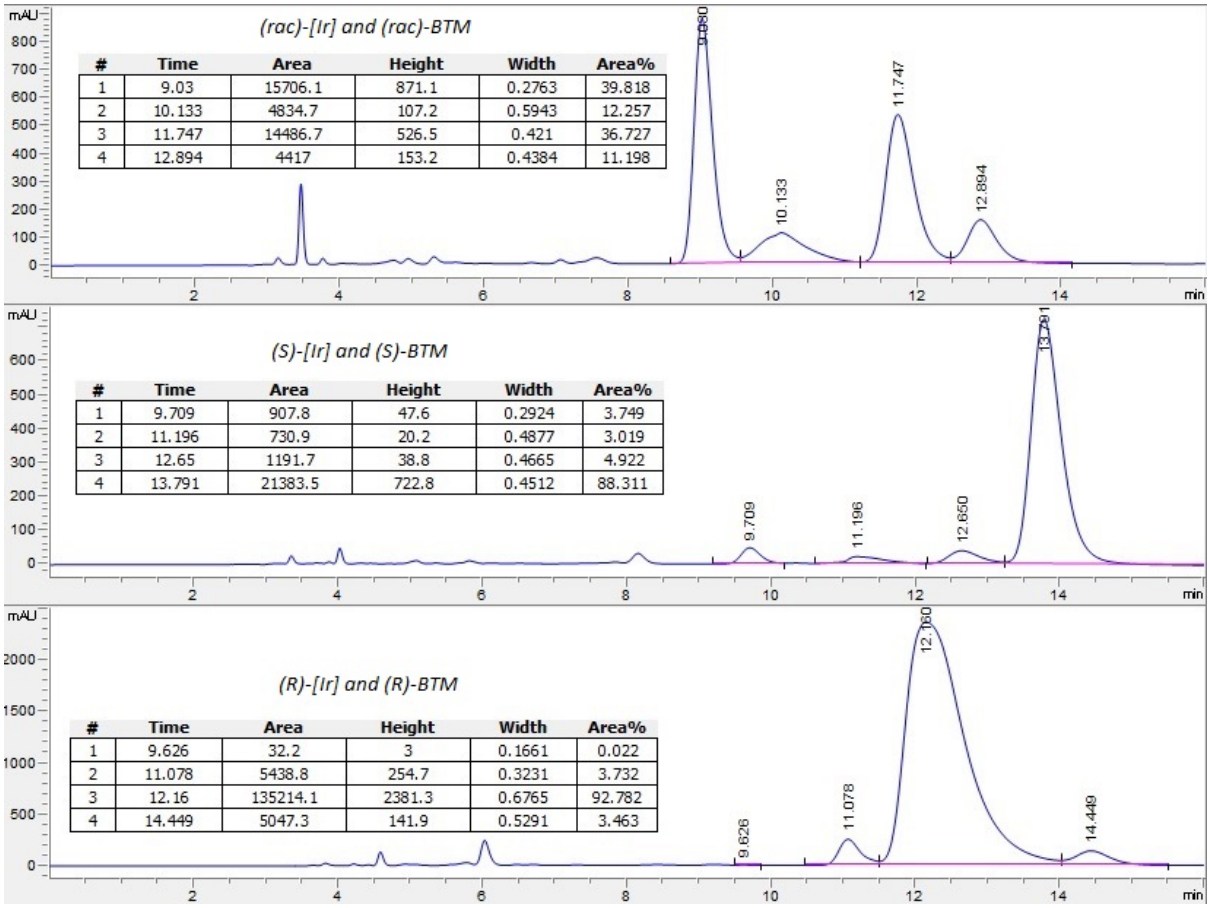
IR (neat): 3404, 3331, 1709, 1517, 1448, 1369, 1174, 747 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.59 (dd, *J* = 8.4, 4.9 Hz, 3H), 7.53 – 7.41 (m, 4H), 7.34 – 7.28 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.09 (m, 3H), 6.96 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.92 (dt, *J* = 17.8, 9.4 Hz, 1H), 5.36 (s, 2H), 5.30 – 5.01 (m, 2H), 4.09 (s, 1H), 3.65 (s, 3H), 2.36 (s, 3H).

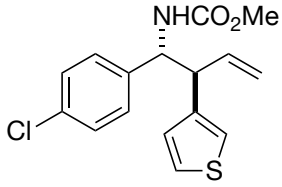
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.4, 144.9, 139.0, 136.9, 135.3, 133.1, 132.8, 130.2, 130.0, 129.2, 128.4, 128.1, 127.9, 127.7, 126.9, 126.3, 126.1, 125.4, 125.2, 125.1, 124.1, 121.0, 120.1, 118.8, 113.9, 57.5, 52.5, 46.9, 21.7.

HRMS (APCI): *m/z* calcd for $[M+H]^+$ $C_{31}H_{29}O_4N_2S$: 525.1843 Found: 525.1842.

HPLC analysis using a chiral column (Cellulose-1 3μ column, 22 °C, 1.5 mL/min, 70:30 hexane:isopropanol, 210 nm, t = 9.03 min, t_{major} = 10.133 min, t = 11.747 min, t_{minor} = 12.894 min).



Methyl ((1*R*,2*S*)-1-(4-chlorophenyl)-2-(thiophen-3-yl)but-3-en-1-yl)carbamate (*anti*-43):



Prepared according to General Procedure C using 4-chlorophenylacetic acid pentafluorophenyl ester (85 mg, 0.25 mmol, 1 equiv.), (*E*)-*tert*-butyl (3-(thiophen-3-yl)allyl) carbonate (90 mg, 0.375 mmol, 1.5 equiv.), (*S*)-[Ir] (10.5 mg, 4 mol%), (*R*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white solid (58 mg, 72%) following purification by column chromatography (SiO_2, 1% Et_2O/toluene). The enantiomeric ratio (>99:1 er, 90:10 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ +47.0° (*c* = 1.0, $CHCl_3$).

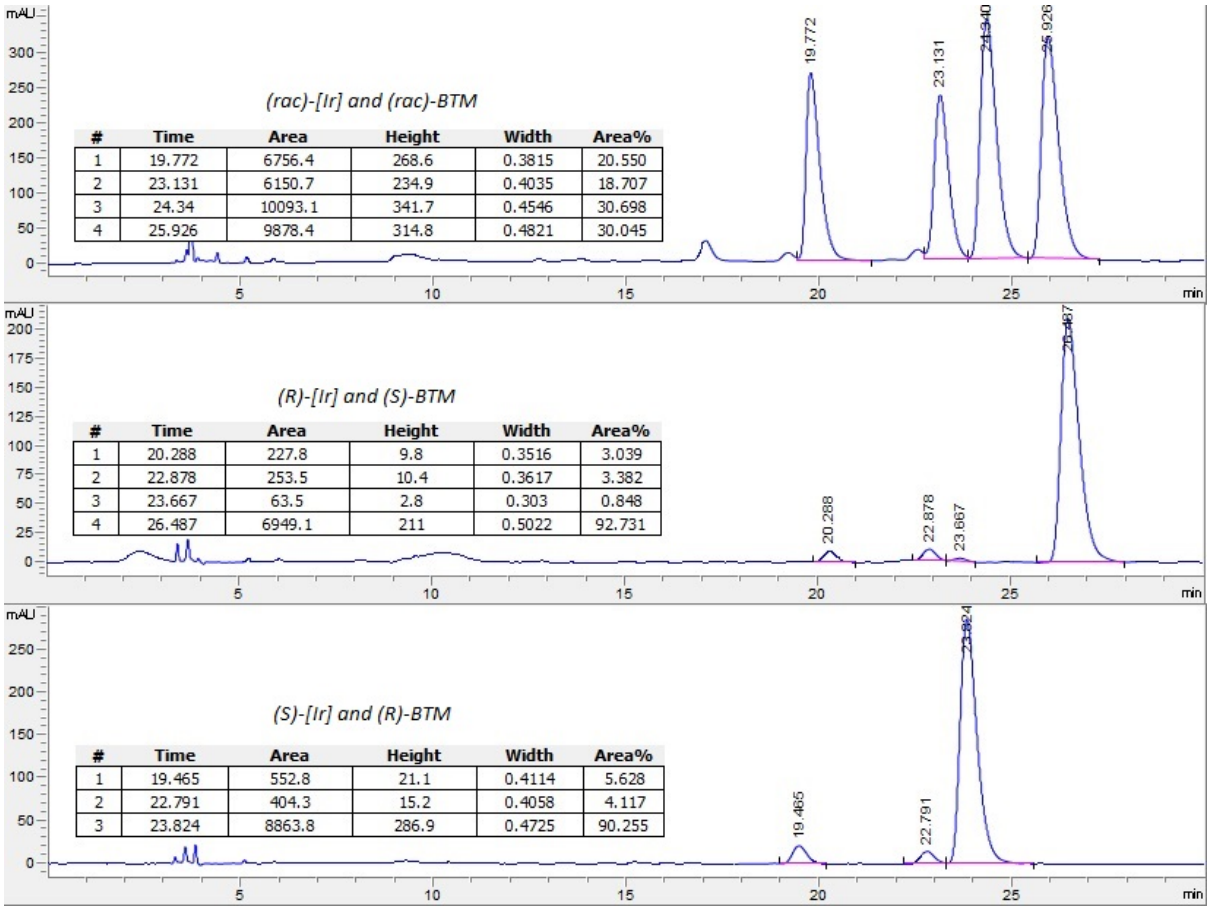
IR (neat): 3320, 2951, 1697, 1532, 1493, 1279, 1252, 1091, 779 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.4 Hz, 3H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 2.8 Hz, 1H), 6.76 (d, *J* = 5.0 Hz, 1H), 5.96 (ddd, *J* = 16.9, 10.2, 8.5 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 5.17 – 5.12 (m, 2H), 4.91 (s, 1H), 3.74 (t, *J* = 8.2 Hz, 1H), 3.64 (s, 3H).

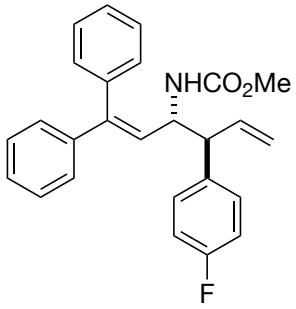
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.3, 140.1, 139.4, 137.0, 133.1, 128.4, 127.3, 125.8, 122.0, 118.3, 58.4, 52.4, 51.7.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{16}H_{16}ClNO_2SNa$: 344.0482 Found: 344.0484.

HPLC analysis using a chiral column (Chiralpak IA 3µ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 210 nm, t = 19.722 min, t = 23.131 min, t_{major} = 24.34 min, t_{minor} = 25.926 min).



Methyl ((3*S*,4*S*)-4-(4-fluorophenyl)-1,1-diphenylhexa-1,5-dien-3-yl)carbamate (*anti*-44):



Prepared according to General Procedure C using 4,4-diphenylbut-3-enoic acid pentafluorophenyl ester (100 mg, 0.25 mmol, 1 equiv.), (*E*)-*tert*-butyl (3-(4-fluorophenyl)allyl) carbonate (95 mg, 0.375 mmol, 1.5 equiv.), (*S*)-[Ir] (10.5 mg, 4 mol%), (*R*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white solid (83 mg, 83%) following purification by column chromatography (SiO_2, 1% Et_2O/toluene). The enantiomeric ratio (>99:1 er, 85:15 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ -112.7° (*c* = 1.0, $CHCl_3$).

IR (neat): 3326, 3022, 1704, 1509, 1224, 758, 701 cm^{-1}.

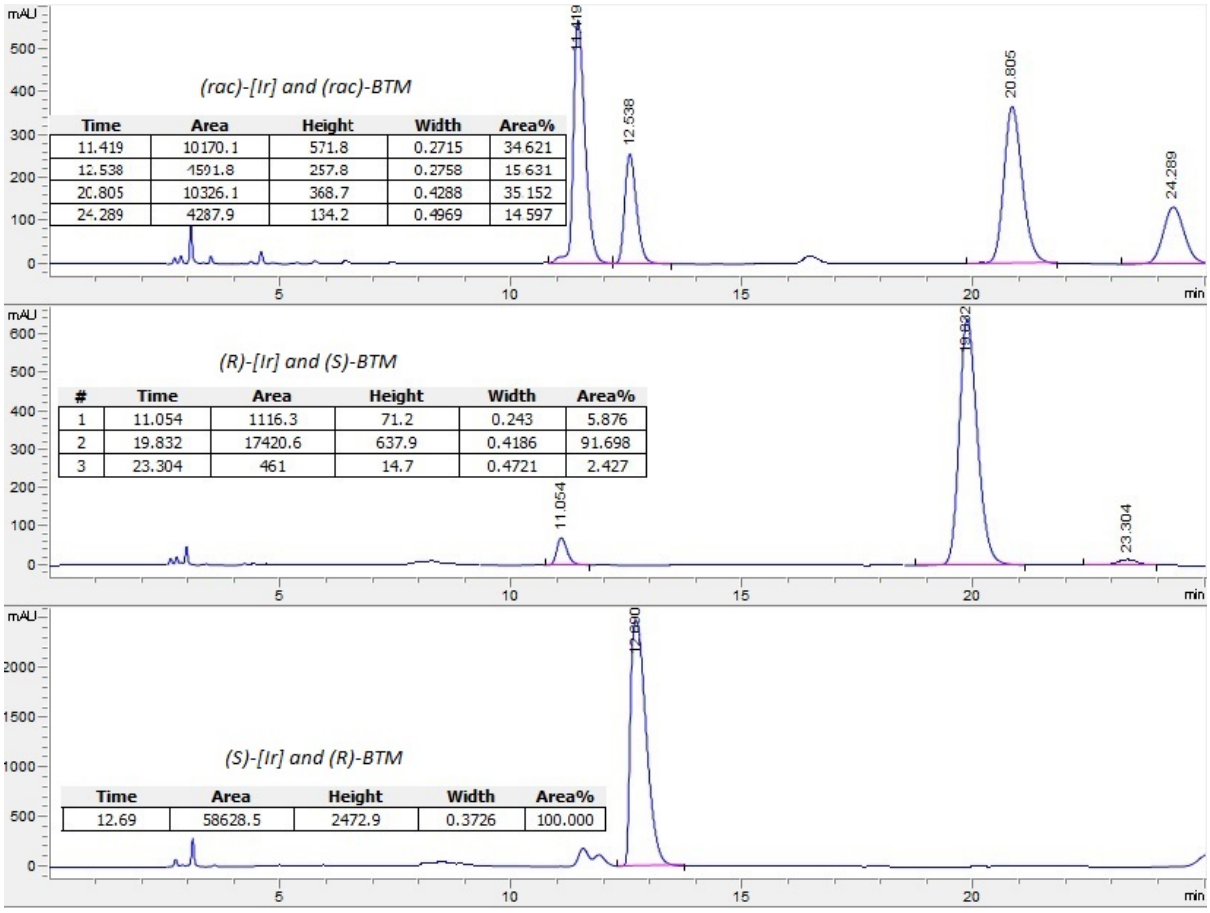
^1H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 4H), 7.24 – 7.18 (m, 2H), 7.11 – 6.78 (m, 8H), 5.95 (dt, *J* = 17.9, 9.5 Hz, 1H), 5.77 (d, *J* = 9.7 Hz, 1H), 5.11 (d, *J* = 9.9 Hz, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 4.73 (s, 1H), 4.53 (s, 1H), 3.65 (s, 3H), 3.44 (t, *J* = 8.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.8 (d, $^1J_{C\text{-}F}$ = 245.0 Hz), 156.2, 144.6, 142.2, 139.0, 137.8, 136.3 (d, $J_{C\text{-}F}$= 3.2 Hz), 130.0, 129.9, 129.8, 129.6, 128.2 (d, $^3J_{C\text{-}F}$ = 4.9 Hz), 127.7, 127.5, 127.1, 117.6, 115.4 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 55.4, 54.4, 52.3.

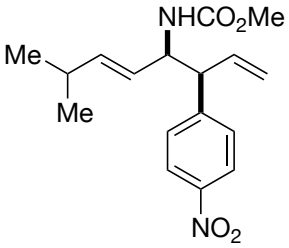
^{19}F NMR (376 MHz, $CDCl_3$): δ -116.2.

HRMS (APCI): *m/z* calcd for $[M+H]^+$ $C_{26}H_{25}O_2NF$: 402.1864 Found: 402.1865.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 98:2 hexane:isopropanol, 210 nm, t = 11.419 min, t_{major} = 12.538 min, t_{minor} = 20.806 min, t = 24.289 min).



Methyl ((3*S*,4*R*,*E*)-7-methyl-3-(4-nitrophenyl)octa-1,5-dien-4-yl)carbamate (*syn*-45):



Prepared according to General Procedure C using (*E*)-5-methylhex-3-enoic acid pentafluorophenyl ester (74 mg, 0.25 mmol, 1 equiv.), (*E*)-*tert*-butyl (3-(4-nitrophenyl)allyl) carbonate (105 mg, 0.375 mmol, 1.5 equiv.), (*S*)-[Ir] (10.5 mg, 4 mol%), (*S*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a white solid (50 mg, 63%) following purification by column chromatography (SiO_2, 1% Et_2O/toluene). The enantiomeric ratio (98:2 er, 81:19 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ +42.3° (*c* = 1.0, $CHCl_3$).

IR (neat): 3324, 2959, 1707, 1519, 1346, 1215, 754, 668 cm^{-1}.

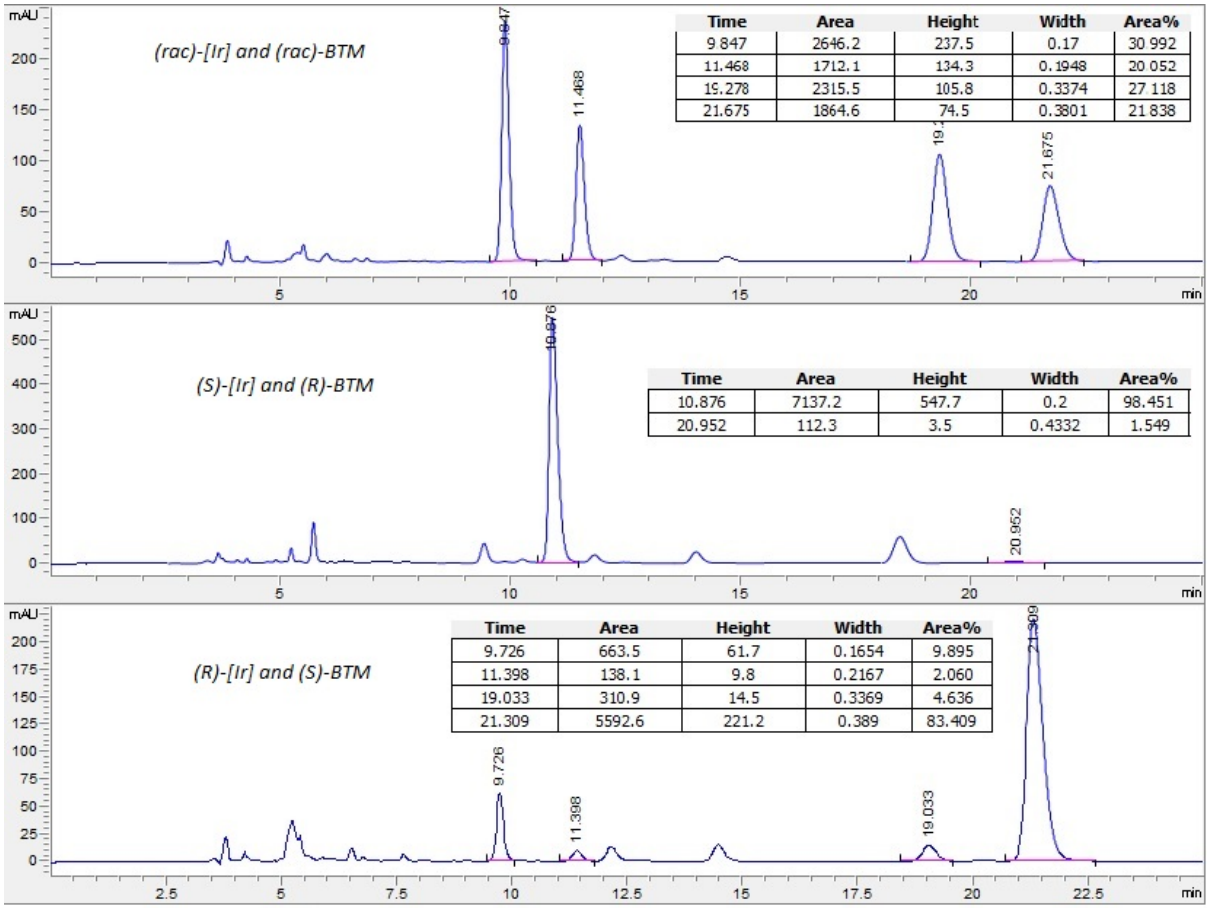
^1H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.03 (ddd, *J* = 17.0, 10.2, 8.9 Hz, 1H), 5.44 (ddd, *J* = 15.5, 6.6, 1.2 Hz, 1H), 5.30 – 5.21 (m, 2H), 5.18 (d, *J* = 17.1 Hz, 1H), 4.65 (s, 1H), 4.4 (s, 1H), 3.68 – 3.64 (m, 4H), 2.25 (q, *J* = 6.7 Hz, 1H), 0.93 (dd, *J* = 6.8, 2.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 156.2, 148.6, 146.9, 141.1, 135.5, 129.3, 126.7, 123.6, 119.5, 56.5, 54.9, 52.3, 31.0, 22.4, 22.3.

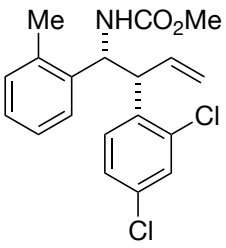
HRMS (APCI): *m/z* calcd for $[M+H]^+$ $C_{17}H_{23}O_4N_2$: 319.1652 Found: 319.1654.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 90:10 hexane:isopropanol, 210 nm, t = 9.391 min, t_{major} = 10.876 min, t = 18.417 min, t_{minor} = 20.952 min).

Note: Analysis of the crude reaction mixture following the initial allylation showed that the lower dr observed with electron withdrawing substituents is a product of the allylation itself and not epimerization during subsequent steps. The Pfp intermediate was isolated in 86% yield and 4.3:1 dr. Additionally this was not a factor of time for the allylation as when the reaction was stopped after 2 h the intermediate Pfp was isolated in 4.3:1 dr however in drastically reduced yield (24%).



Methyl ((1*R*,2*R*)-2-(2,4-dichlorophenyl)-1-(*o*-tolyl)but-3-en-1-yl)carbamate (*syn*-46):



Prepared according to General Procedure C using 2-(*o*-tolyl)acetic acid pentafluorophenyl ester (79 mg, 0.25 mmol, 1 equiv.), (*E*)-*tert*-butyl (3-(2,4-dichlorophenyl)allyl) carbonate (113 mg, 0.375 mmol, 1.5 equiv.), (*R*)-[Ir] (10.5 mg, 4 mol%), (*R*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a yellow solid (56 mg, 62%) following purification by column chromatography (SiO_2, 1% Et_2O/toluene). The enantiomeric ratio (99:1 er, 80:20 dr) was determined by chiral HPLC in comparison with racemate and opposite enantiomer.

$[\alpha]_D^{23}$ -26.7° (*c* = 1.0, $CHCl_3$).

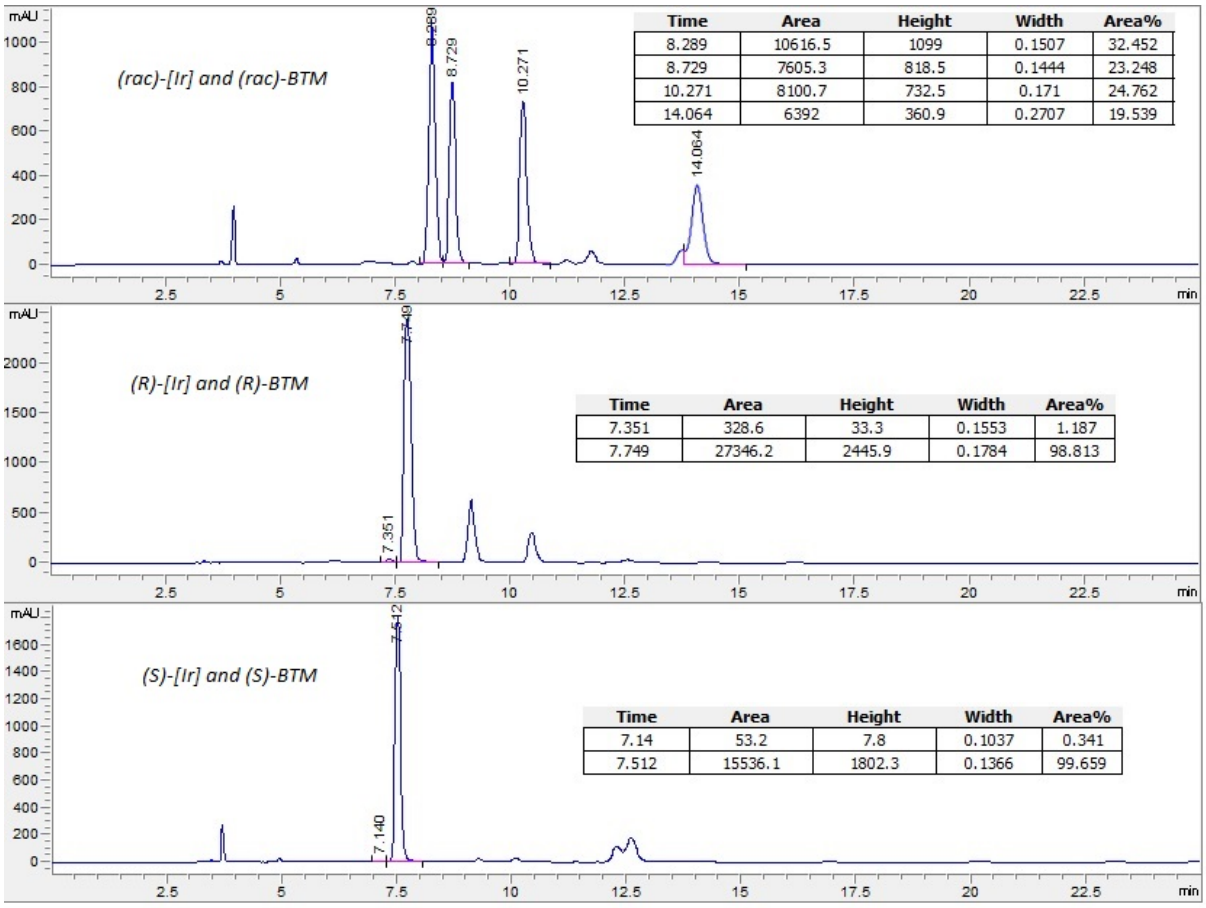
IR (neat): 3322, 2954, 1699, 1517, 1473, 1245, 1045, 752 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 2.1 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.20 – 7.14 (m, 2H), 7.15 – 7.07 (m, 1H), 5.79 (ddd, *J* = 17.5, 10.3, 7.7 Hz, 1H), 5.35 (t, *J* = 9.3 Hz, 1H), 5.14 (d, *J* = 9.2 Hz, 1H), 5.04 (d, *J* = 10.3 Hz, 1H), 4.89 (d, *J* = 17.1 Hz, 1H), 4.32 (t, *J* = 8.8 Hz, 1H), 3.51 (s, 3H), 2.32 (s, 3H).

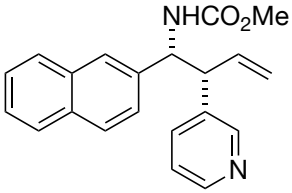
^{13}C NMR (151 MHz, $CDCl_3$): δ 156.1, 139.0, 136.5, 135.5, 135.3, 133.2, 130.6, 130.2, 129.4, 127.5, 127.4, 127.3, 126.4, 126.0, 118.7, 53.5, 52.2, 50.6, 19.7.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{19}H_{19}O_2NCl_2Na$: 386.0685 Found: 386.0688.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 95:5 hexane:isopropanol, 210 nm, t_{minor} = 7.389, t_{major} = 7.781, t = 9.166 min, t = 12.568 min).



Methyl ((1*R*,2*R*)-1-(naphthalen-2-yl)-2-(pyridin-3-yl)but-3-en-1-yl)carbamate (*syn*-47):



Prepared according to General Procedure C using 2-(naphthalen-2-yl)acetic acid pentafluorophenyl ester (88 mg, 0.25 mmol, 1 equiv.), (*E*)-*tert*-butyl (3-(pyridin-3-yl)allyl) carbonate (88 mg, 0.375 mmol, 1.5 equiv.), (*R*)-[Ir] (10.5 mg, 4 mol%), (*R*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a yellow gum (53 mg, 64%) following purification by column chromatography (SiO_2, 10–40% EtOAc/petroleum with 2% triethylamine). The enantiomeric ratio (>99:1 er,

88:12 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ -7.9° (*c* = 1.0, $CHCl_3$).

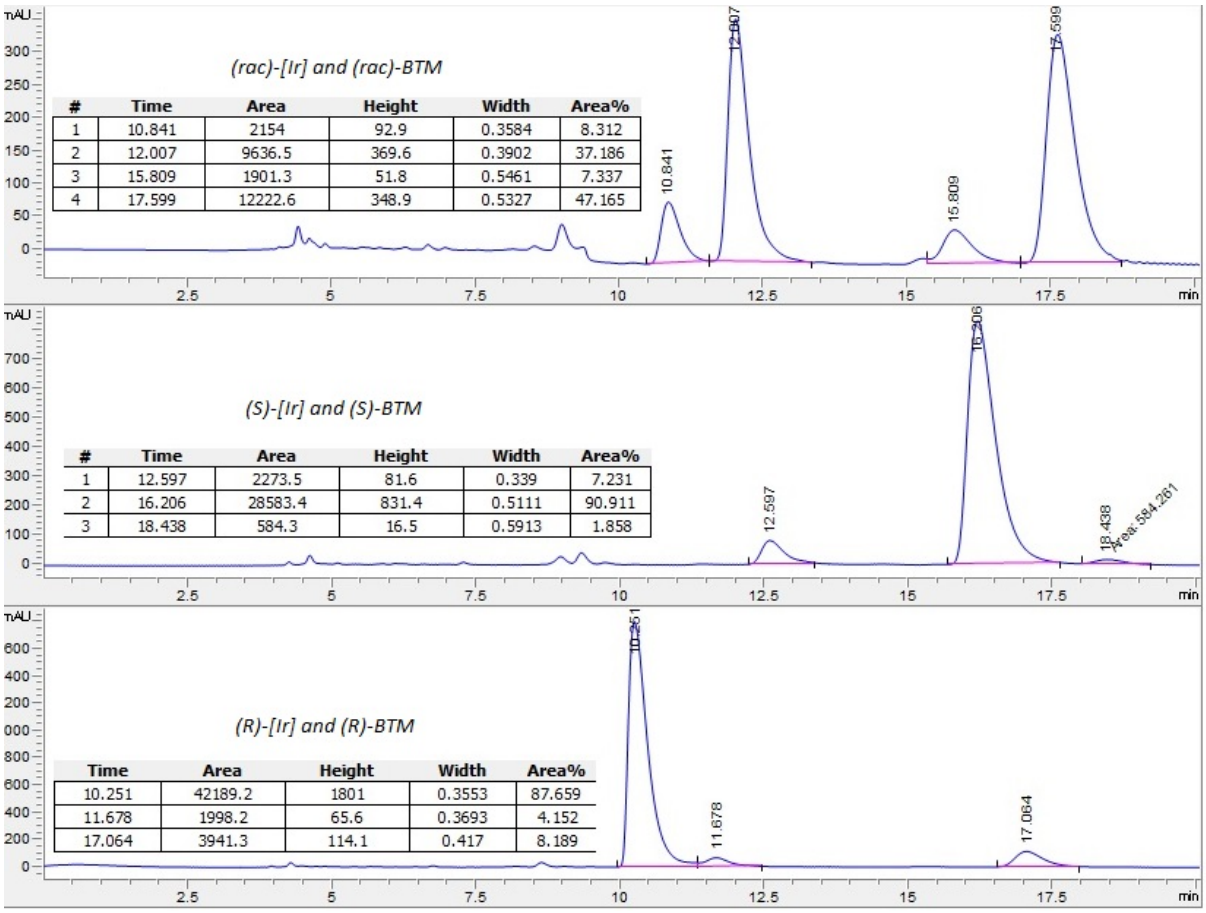
IR (neat): 3313, 3018, 1710, 1536, 1510, 1215, 751 cm^{-1}.

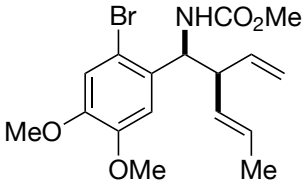
^1H NMR (500 MHz, $CDCl_3$): δ 8.48 (dd, *J* = 4.5, 2.3 Hz, 1H), 8.39 (s, 1H), 7.84 – 7.72 (m, 3H), 7.57 (s, 1H), 7.46 (dt, *J* = 7.4, 2.3 Hz, 2H), 7.43 – 7.40 (m, 1H), 7.25 (dd, *J* = 9.6, 5.3 Hz, 1H), 7.22 – 7.17 (m, 1H), 5.93 (dtd, *J* = 17.0, 9.1, 8.0, 2.2 Hz, 1H), 5.43 (d, *J* = 8.9 Hz, 1H), 5.28 – 5.15 (m, 1H), 5.11 (d, *J* = 9.9 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 3.88 (t, *J* = 8.0 Hz, 1H), 3.54 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 156.2, 150.1, 148.4, 137.2, 136.3, 135.9, 135.8, 133.1, 132.9, 128.4, 128.0, 127.7, 126.5, 126.4, 126.2, 125.0, 123.5, 118.8, 53.1, 52.3, 29.8.

HRMS (APCI): *m/z* calcd for $[M+H]^+$ $C_{21}H_{21}O_2N_2$: 333.1598 Found: 333.1600.

HPLC analysis using a chiral column (Cellulose-1 3μ column, 22 °C, 1.0 mL/min, 80:20 hexane:isopropanol, 210 nm, t_{major} = 10.841 min, t = 12.007 min, t_{minor} = 15.809 min, t = 17.599 min).



Methyl ((1*S*,2*S*,*E*)-1-(2-bromo-4,5-dimethoxyphenyl)-2-vinylpent-3-en-1-yl)carbamate (*syn*-48): 

Prepared according to General Procedure C using 2-(2-bromo-4,5-dimethoxyphenyl)acetic acid pentafluorophenyl ester (110 mg, 0.25 mmol, 1 equiv.), (*tert*-butyl ((2*E*,4*E*)-hexa-2,4-dien-1-yl) carbonate (75 mg, 0.375 mmol, 1.5 equiv.), (*S*)-[Ir] (10.5 mg, 4 mol%), (*S*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a yellow gum (64 mg, 67%) following purification by column chromatography (SiO_2, 1–10% Et_2O/toluene). The enantiomeric ratio (99:1 er, 80:20 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ -5.8° (*c* = 1.0, $CHCl_3$).

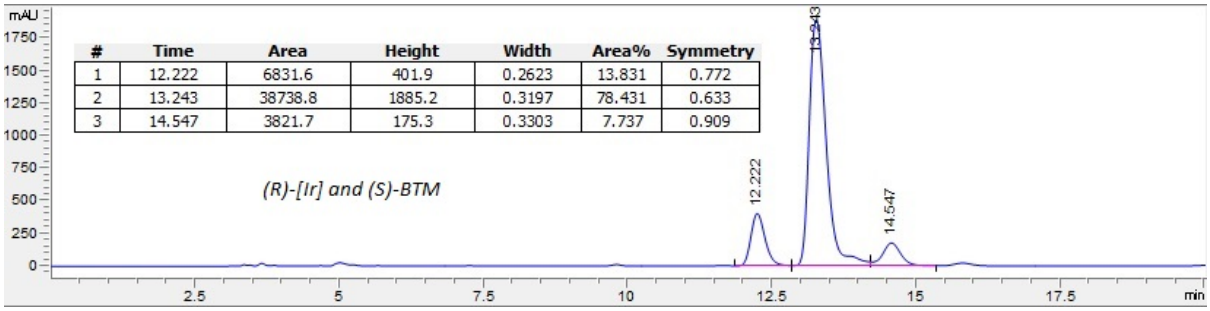
IR (neat): 3331, 3018, 1709, 1506, 1256, 1215, 1165, 1031, 755 cm^{-1}.

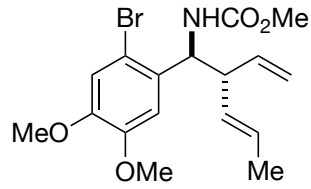
^1H NMR (600 MHz, $CDCl_3$): δ 6.99 (s, 1H), 6.65 (s, 1H), 5.76 (dt, *J* = 18.0, 9.2 Hz, 1H), 5.49 (dt, *J* = 12.9, 6.5 Hz, 1H), 5.43 – 5.31 (m, 1H), 5.27 – 5.14 (m, 1H), 5.14 – 5.01 (m, 2H), 4.97 (d, *J* = 7.4 Hz, 1H), 3.85 (d, *J* = 4.7 Hz, 6H), 3.63 (s, 3H), 3.18 (s, 1H), 1.70 (dd, *J* = 6.4, 1.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.3, 148.5, 148.3, 137.1, 129.6, 129.4, 128.3, 116.7, 115.6, 113.4, 111.4, 57.4, 56.1, 56.1, 52.3, 51.2, 18.2.

HRMS (APCI): *m/z* calcd for $[M+H]^+$ $C_{17}H_{23}O_4NBr$: 384.0805 Found: 384.0805.

HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 90:10 hexane:isopropanol, 210 nm, t = 10.376 min, t_{minor} = 10.9 min, t = 11.923 min, t_{major} = 13.051 min).



Methyl ((1*S*,2*R*,*E*)-1-(2-bromo-4,5-dimethoxyphenyl)-2-vinylpent-3-en-1-yl)carbamate (*anti*-48): 

Prepared according to General Procedure C using 2-(2-bromo-4,5-dimethoxyphenyl)acetic acid pentafluorophenyl ester (110 mg, 0.25 mmol, 1 equiv.), (*tert*-butyl ((2*E*,4*E*)-hexa-2,4-dien-1-yl) carbonate (75 mg, 0.375 mmol, 1.5 equiv.), (*R*)-[Ir] (10.5 mg, 4 mol%), (*S*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a yellow gum (78 mg, 81%) following purification by column chromatography (SiO_2, 1–10% Et_2O/toluene). The enantiomeric ratio (99:1 er, 77:23 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.

$[\alpha]_D^{23}$ -12.5° (*c* = 1.0, $CHCl_3$).

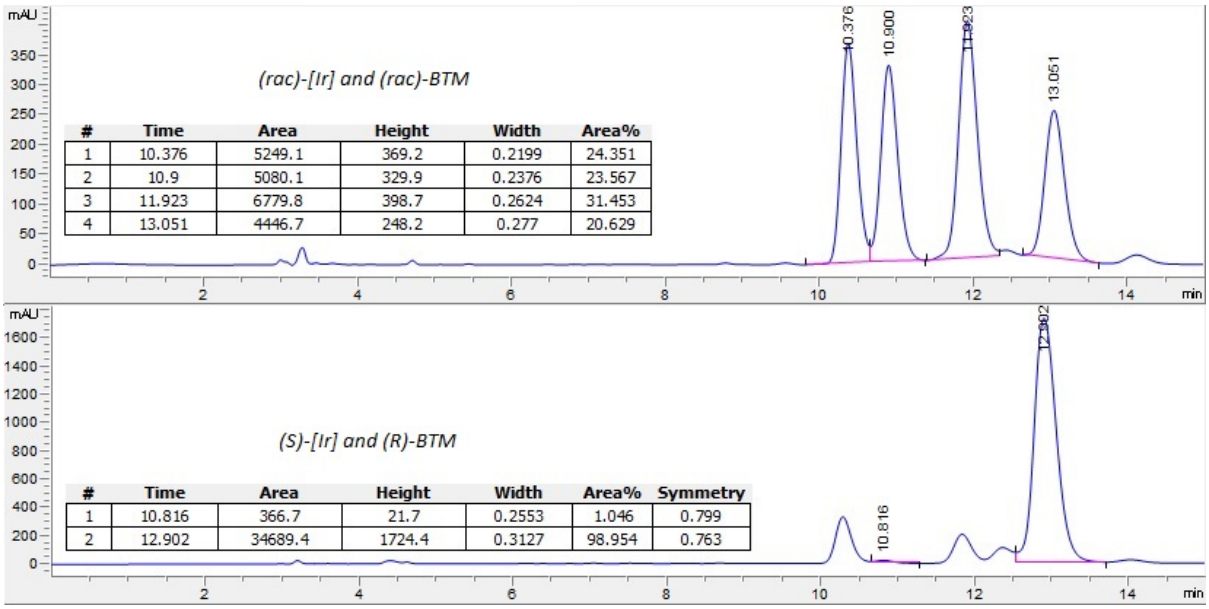
IR (neat): 3336, 3016, 2959, 1708, 1506, 1463, 1257, 1209, 1165, 1030, 754 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.99 (s, 1H), 6.66 (s, 1H), 5.82 – 5.68 (m, 1H), 5.54 – 5.44 (m, 1H), 5.42 – 5.36 (m, 1H), 5.27 – 5.13 (m, 2H), 5.10 (d, *J* = 17.0 Hz, 1H), 4.96 (t, *J* = 7.3 Hz, 1H), 3.85 (d, *J* = 2.3 Hz, 6H), 3.63 (s, 3H), 3.19 (s, 2H), 1.64 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.9, 156.2, 148.5, 148.2, 136.6, 128.8, 128.0, 117.8, 115.6, 113.4, 111.4, 57.4, 56.10, 56.07, 51.1, 18.0.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{17}H_{22}O_4NBrNa$: 406.0624 Found: 406.0627.

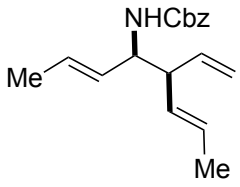
HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 90:10 hexane:isopropanol, 210 nm, t_{minor} =10.376 min, t = 10.9 min, t_{major} = 11.923 min, t = 13.051 min).



#	Time	Area	Height	Width	Area%
1	10.376	5249.1	369.2	0.2199	24.351
2	10.9	5080.1	329.9	0.2376	23.567
3	11.923	6779.8	398.7	0.2624	31.453
4	13.051	4446.7	248.2	0.277	20.629

#	Time	Area	Height	Width	Area%	Symmetry
1	10.816	366.7	21.7	0.2553	1.046	0.799
2	12.902	34689.4	1724.4	0.3127	98.954	0.763

Benzyl ((2*E*,4*R*,5*S*,6*E*)-5-vinylocta-2,6-dien-4-yl)carbamate (*syn*-49):



Prepared according to General Procedure C using (*E*)-pent-3-enoic acid pentafluorophenyl ester (67 mg, 0.25 mmol, 1 equiv.), *tert*-butyl ((2*E*,4*E*)-hexa-2,4-dien-1-yl) carbonate (75 mg, 0.375 mmol, 1.5 equiv.), (*S*)-[Ir] (10.5 mg, 4 mol%), (*S*)-BTM (12.5 mg, 20 mol%) and benzyl alcohol (1.25 mL). The crude reaction mixture was placed in an oil bath at 75 °C under high vacuum overnight to remove excess benzyl alcohol prior to chromatography. The *title compound* was obtained as a white solid (29 mg, 40%) following purification by column chromatography (SiO_2, 2% Et_2O/toluene). The diastereomeric ratio (85:15 dr) was determined by chiral HPLC. The enantiomeric ratio could not be obtained for this compound.

$[\alpha]_D^{23}$ +9.2° (*c* = 1.0, $CHCl_3$).

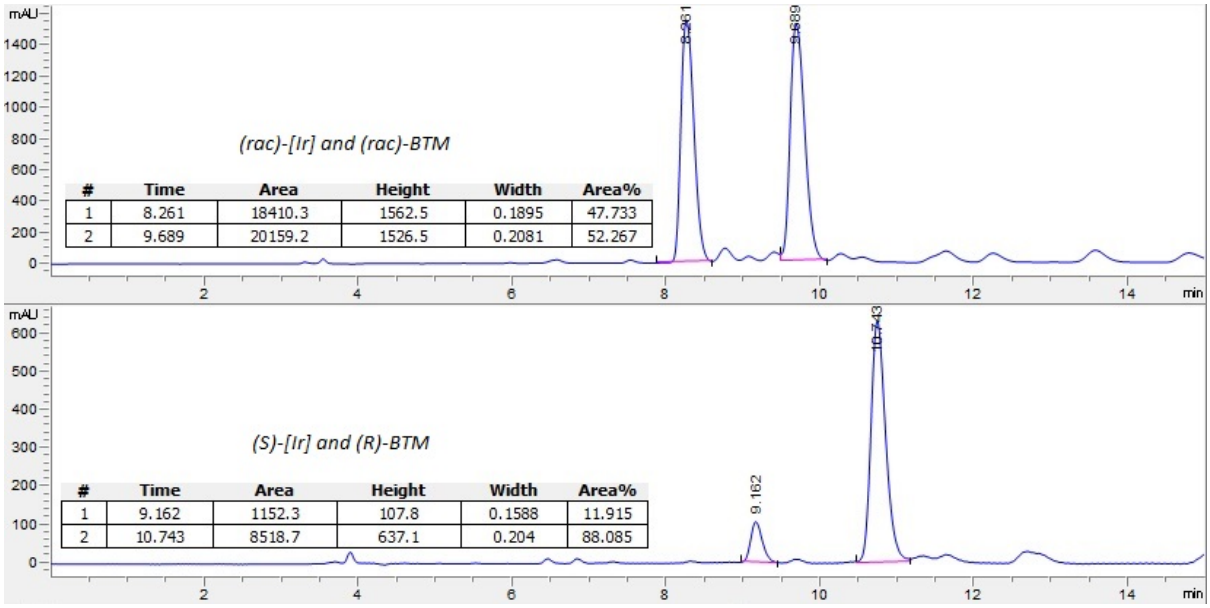
IR (neat): cm^{-1} 3328, 3031, 2936, 2918, 1709, 1503, 1231, 967, 755.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.27 (m, 5H), 5.82 – 5.66 (m, 1H), 5.64 – 5.54 (m, 1H), 5.55 – 5.46 (m, 1H), 5.43 – 5.31 (m, 2H), 5.16 – 5.00 (m, 4H), 4.78 (s, 1H), 4.19 (s, 1H), 2.86 (d, *J* = 8.4 Hz, 1H), 1.79 – 1.62 (m, 6H).

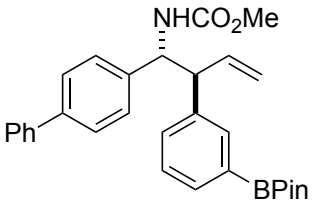
^{13}C NMR (151 MHz, $CDCl_3$): δ 155.8, 137.3, 136.7, 129.6, 128.6, 128.2, 127.5, 127.4, 66.8, 55.9, 51.8, 18.3, 17.9.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{18}H_{23}O_2NNa$: 308.1621 Found: 308.1622.

HPLC analysis using a chiral column (Cellulose-1 3μ column, 22 °C, 1.0 mL/min, 99:1 hexane:isopropanol, 210 nm, t_{major}= 8.91, t_{minor} = 10.455 min).



Methyl ((1*R*,2*S*)-1-([1,1'-biphenyl]-4-yl)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-1-yl)carbamate (*anti*-50): Prepared according to General Procedure C using 2-([1,1'-biphenyl]-4-yl)acetic acid pentafluorophenyl ester (95 mg, 0.25 mmol, 1 equiv.), (*E*)-*tert*-butyl (3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)allyl) carbonate (135 mg, 0.375 mmol, 1.5 equiv.), (*S*)-[Ir] (10.5 mg, 4 mol%), (*R*)-BTM (12.5 mg, 20 mol%) and methanol (1.25 mL). The *title compound* was obtained as a brown gum (45 mg, 38%) following purification by column chromatography (SiO_2, 1–10% Et_2O/toluene). The enantiomeric ratio (>99:1 er, 94:6 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.



$[\alpha]_D^{23}$ +10.2° (*c* = 1.0, $CHCl_3$).

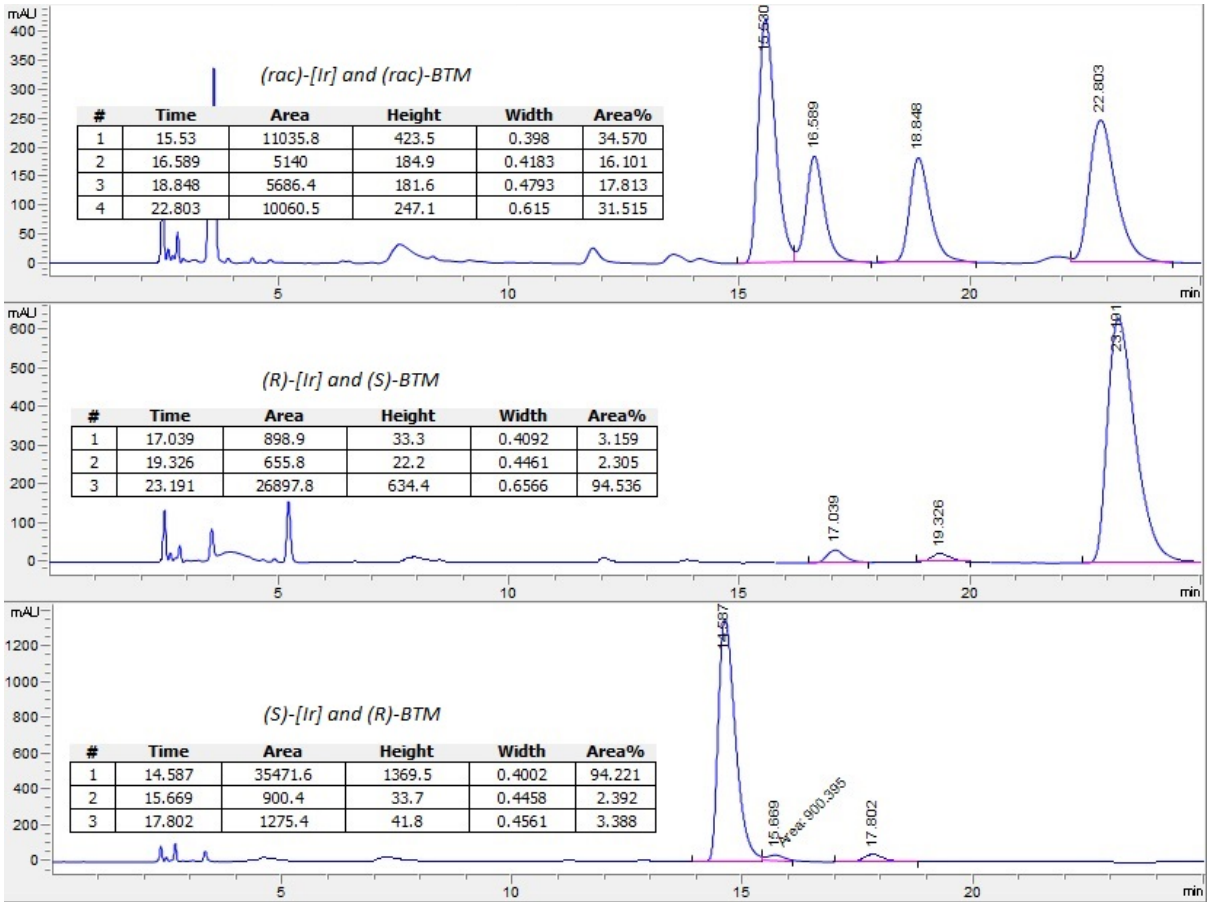
IR (neat): 3019, 1713, 1517, 1359, 1214, 1144, 750, 668 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.4 Hz, 1H), 7.51 (s, 3H), 7.44 – 7.35 (m, 4H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 3H), 6.16 (dt, *J* = 16.9, 9.5 Hz, 1H), 5.24 (s, 1H), 5.22 – 5.14 (m, 2H), 5.02 (s, 1H), 3.66 – 3.62 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.5, 140.8, 140.0, 139.6, 134.8, 133.4, 131.3, 128.8, 127.9, 127.6, 127.3, 127.1, 126.9, 83.9, 59.1, 57.0, 52.4, 25.0. Carbon bearing boron not observed.

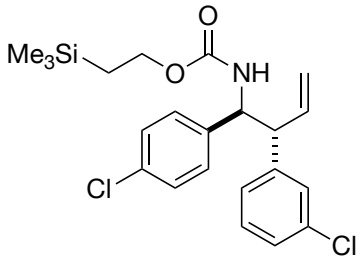
HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{30}H_{34}O_4NBNa$: 506.2478 Found: 506.2473.

HPLC analysis using a chiral column (Chiralpak IA 3µ column, 22 °C, 1.5 mL/min, 99:1 hexane:isopropanol, 210 nm, t_{major} =15.53 min, t = 16.589 min, t = 18.848 min, t_{minor} = 22.803 min).



Application toward MDM2 inhibitor

2-(Trimethylsilyl)ethyl ((1*S*,2*R*)-2-(3-chlorophenyl)-1-(4-chlorophenyl)but-3-en-1-yl)carbamate (53): Prepared according to General Procedure C using 4-chlorophenylacetic acid pentafluorophenyl ester (85 mg, 0.25 mmol, 1 equiv.), (*E*)-*tert*-butyl (3-(3-chlorophenyl)allyl) carbonate (100 mg, 0.375 mmol, 1.5 equiv.), (*R*)-[Ir] (10.5 mg, 4 mol%), (*S*)-BTM (12.5 mg, 20 mol%) and trimethylsilyl ethanol (1.25 mL). The crude reaction mixture was laced under high vacuum overnight to remove excess trimethylsilyl ethanol. The *title compound* was obtained as a colorless oil (75 mg, 68%) following purification by column chromatography (SiO_2, 2% Et_2O/toluene). The enantiomeric ratio (>99:1 er, 91:9 dr) was determined by chiral HPLC in comparison with the racemate and opposite enantiomer.



$[\alpha]_D^{23}$ -5.7° (*c* = 1.0, $CHCl_3$).

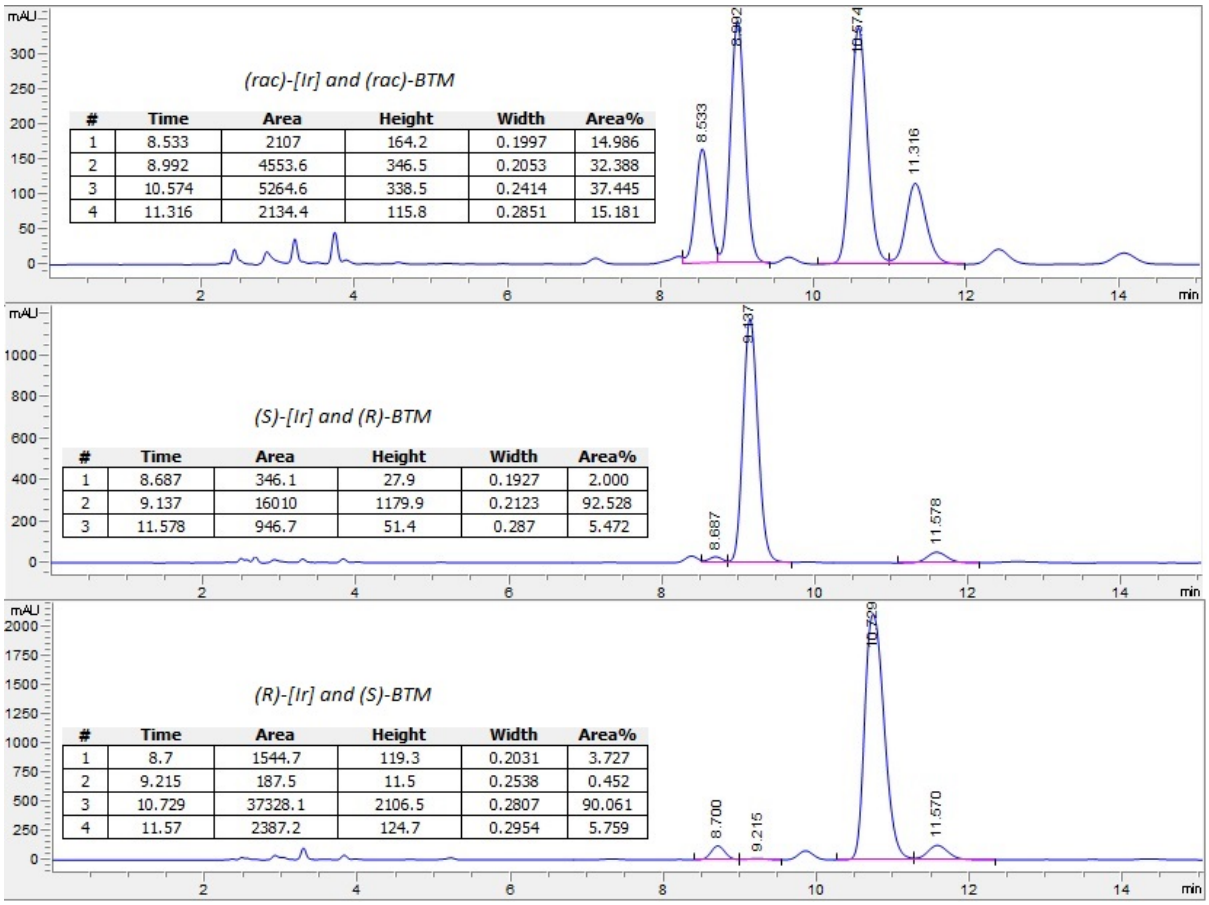
IR (neat): 3019, 1705, 1493, 1214, 750, 668 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 6.3 Hz, 2H), 7.02 (s, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.91 – 6.82 (m, 1H), 6.04 (ddd, *J* = 16.9, 10.2, 8.7 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.17 (d, *J* = 17.0 Hz, 1H), 5.08 (d, *J* = 7.7 Hz, 1H), 4.89 (s, 1H), 4.26 – 3.98 (m, 2H), 3.51 (t, *J* = 8.9 Hz, 1H), 0.94 (s, 2H), 0.02 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.0, 142.2, 139.2, 137.3, 134.4, 133.2, 129.9, 128.53, 128.48, 127.3, 126.6, 118.7, 63.6, 58.6, 56.5, 17.8, -1.4.

HRMS (ESI): *m/z* calcd for $[M+Na]^+$ $C_{22}H_{27}O_2NCl_2NaSi$: 458.1080 Found: 458.1080.

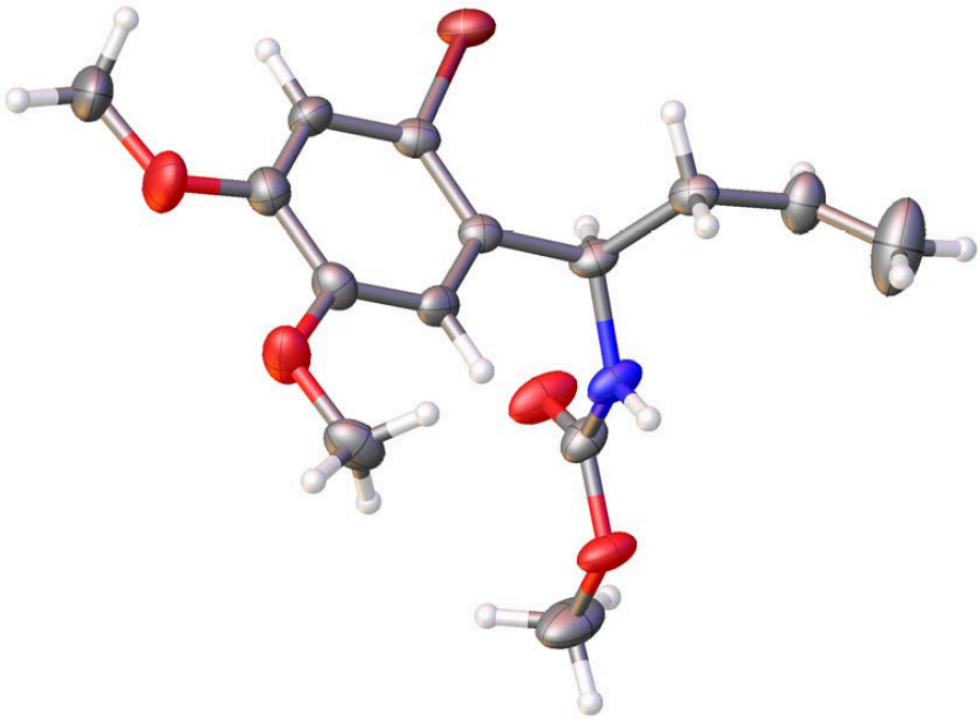
HPLC analysis using a chiral column (Chiralpak IA 3μ column, 22 °C, 1.5 mL/min, 97:3 hexane:isopropanol, 210 nm, t =8.533 min, t_{minor} = 8.992 min, t_{major} = 10.574 min, t = 11.316 min).



Confirmation of absolute stereochemistry via X-ray analysis of (*R*)-8. X-Ray

Single crystals of sufficient quality were obtained by slow diffusion of pentane into a saturated solution of **(*R*)-8** in Et_2O. Single crystal analysis confirmed the absolute stereochemistry as (*R*) and is derived from (*R*)-BTM. Thus, we have assigned all stereochemistry in analogy to this.

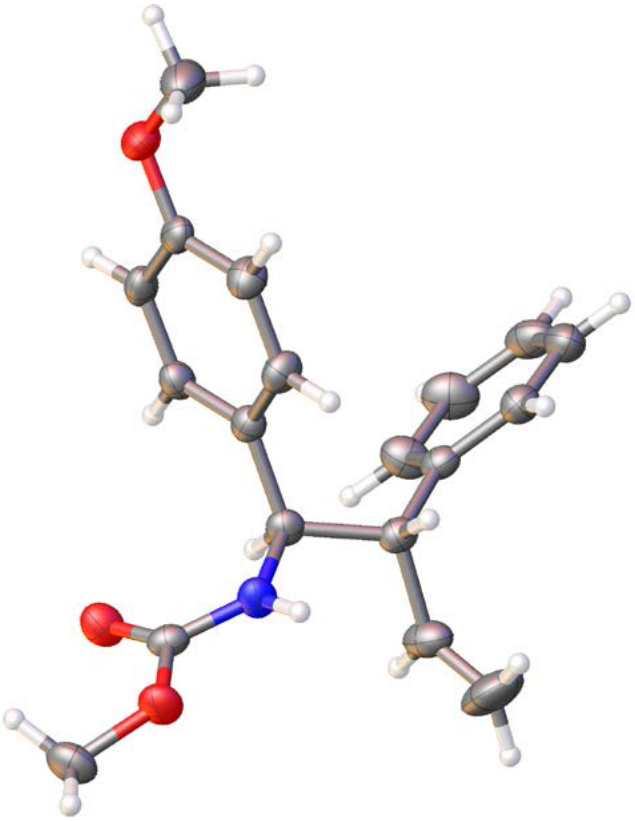
This structure has been deposited at the Cambridge Crystallographic Data Center and can be found under the deposition number: 1883569.



Confirmation of absolute stereochemistry via X-ray analysis of (1*R*,2*S*)-39. X-Ray

Single crystals of sufficient quality were obtained by slow diffusion of pentane into a saturated solution of **(1*R*,2*S*)-39** in Et_2O. Single crystal analysis confirmed the absolute stereochemistry as (1*R*,2*S*) and is derived from (*R*)-BTM and (*S*)-[Ir]. Thus, we have assigned all stereochemistry in analogy to this.

This structure has been deposited at the Cambridge Crystallographic Data Center and can be found under the deposition number: 1883135.



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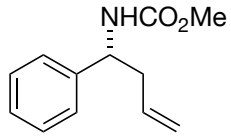
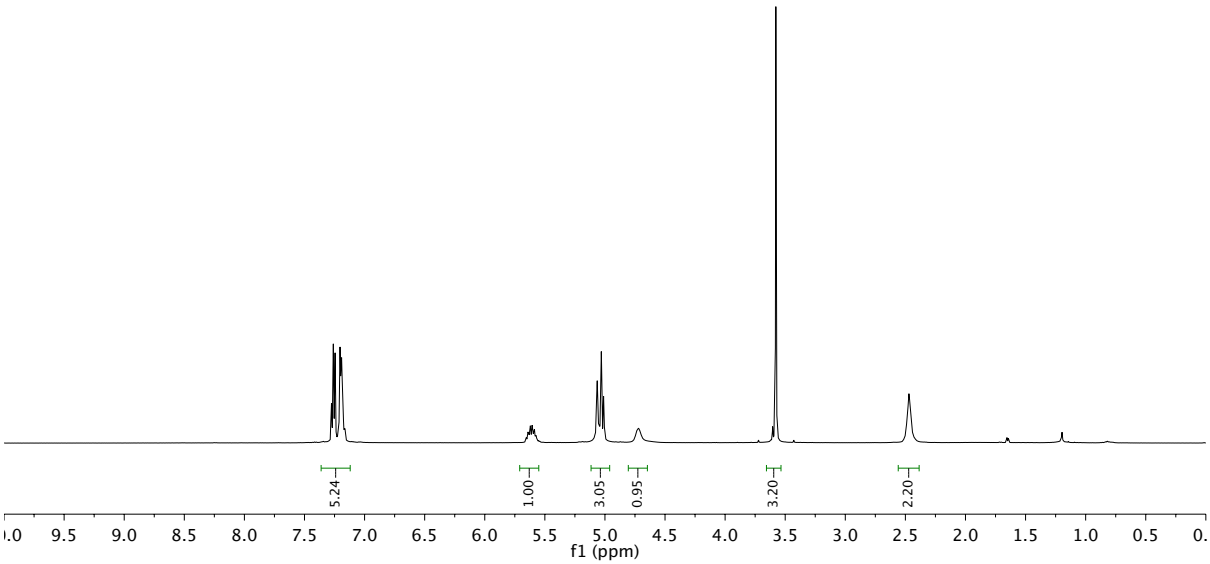
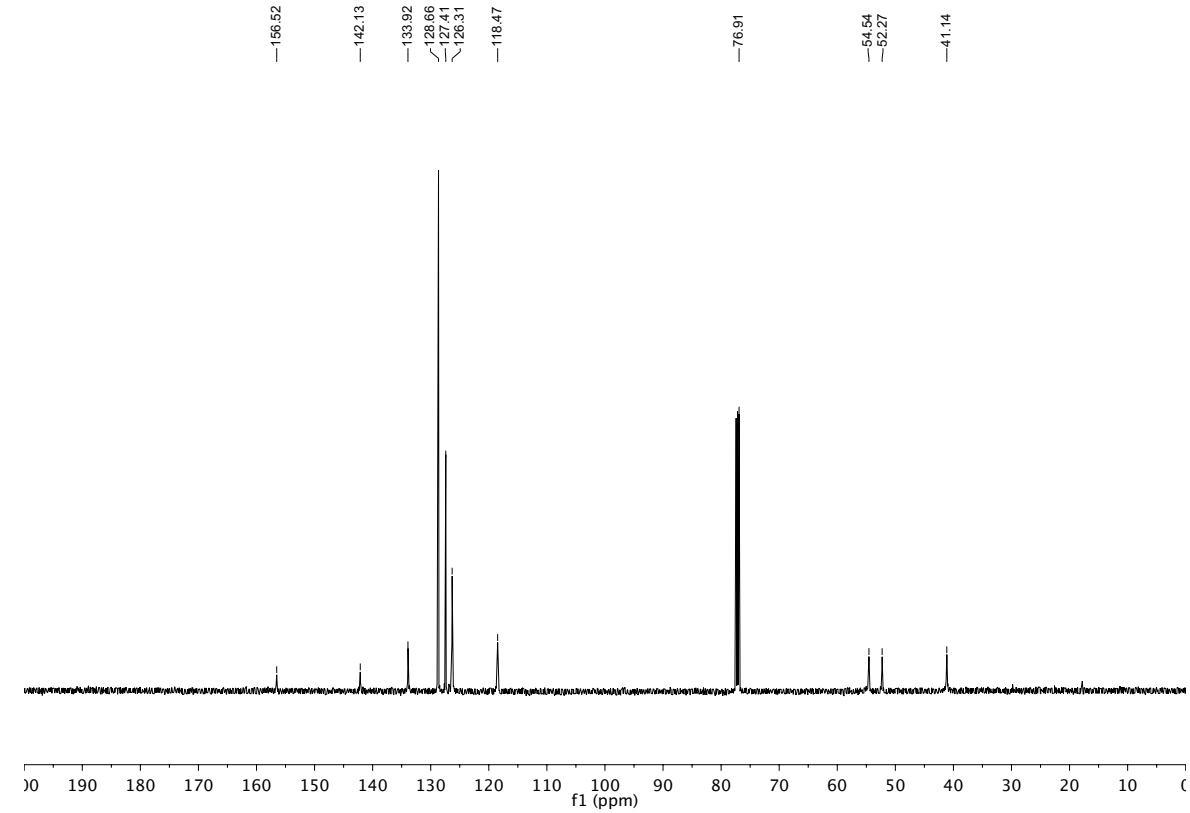
NMR Spectra

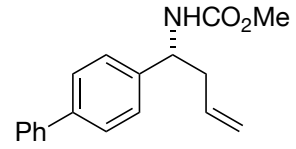
Methyl (*R*)-(1-phenylbut-3-en-1-yl)carbamate (1)

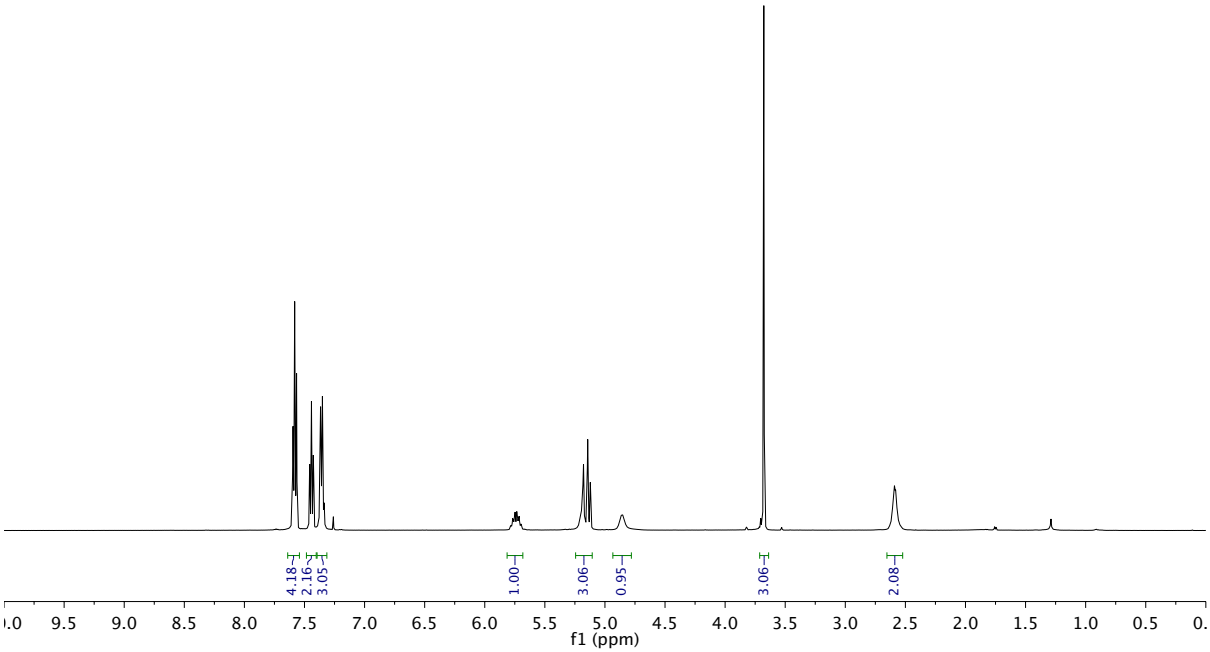


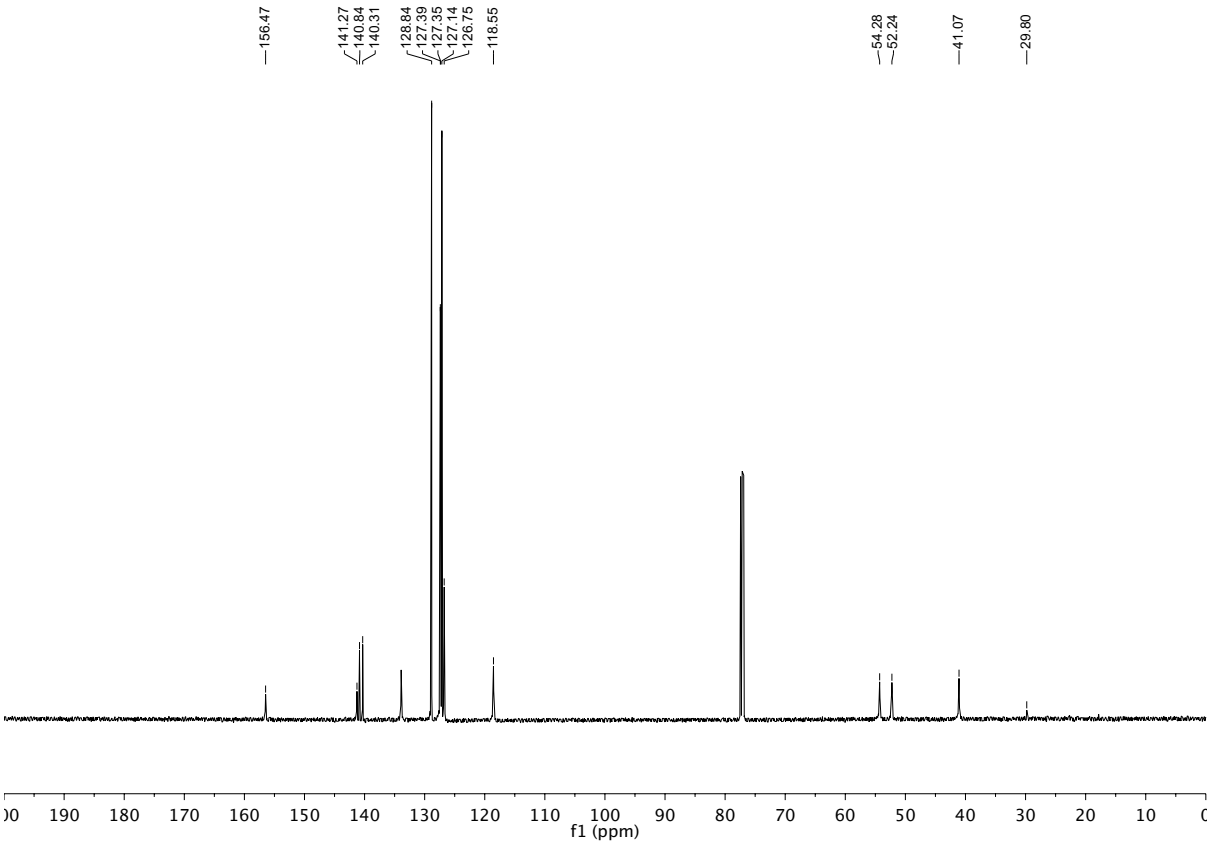




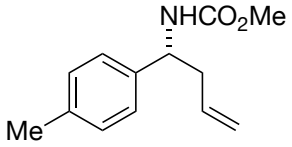
Methyl (*R*)-(1-([1,1'-biphenyl]-4-yl)but-3-en-1-yl)carbamate (2)

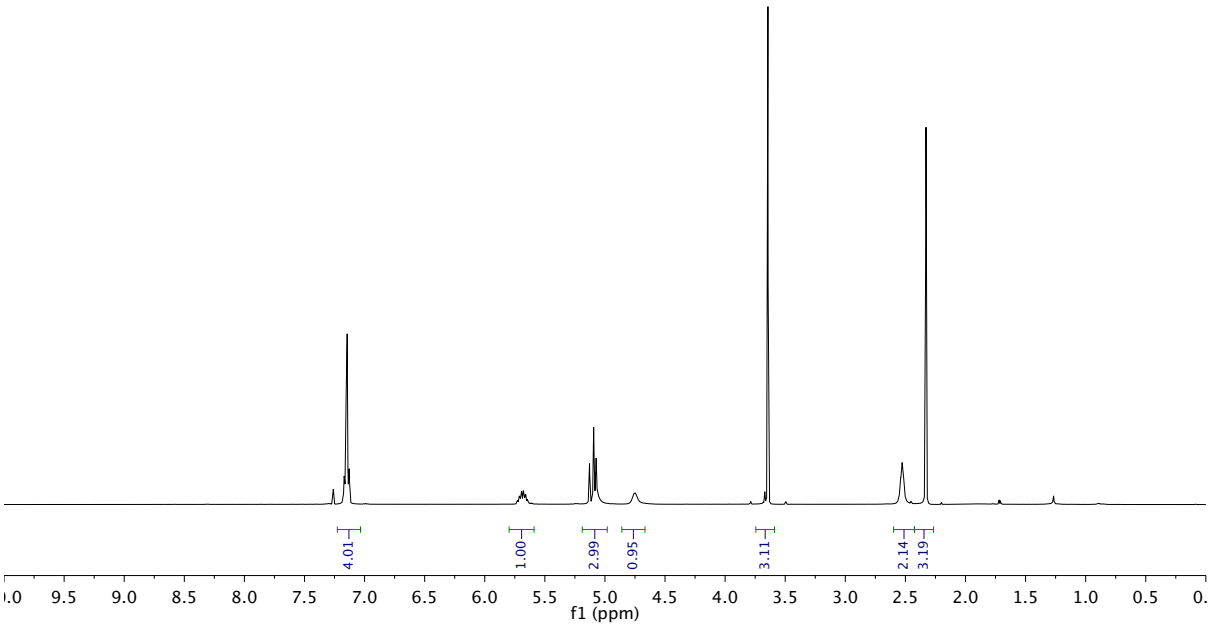


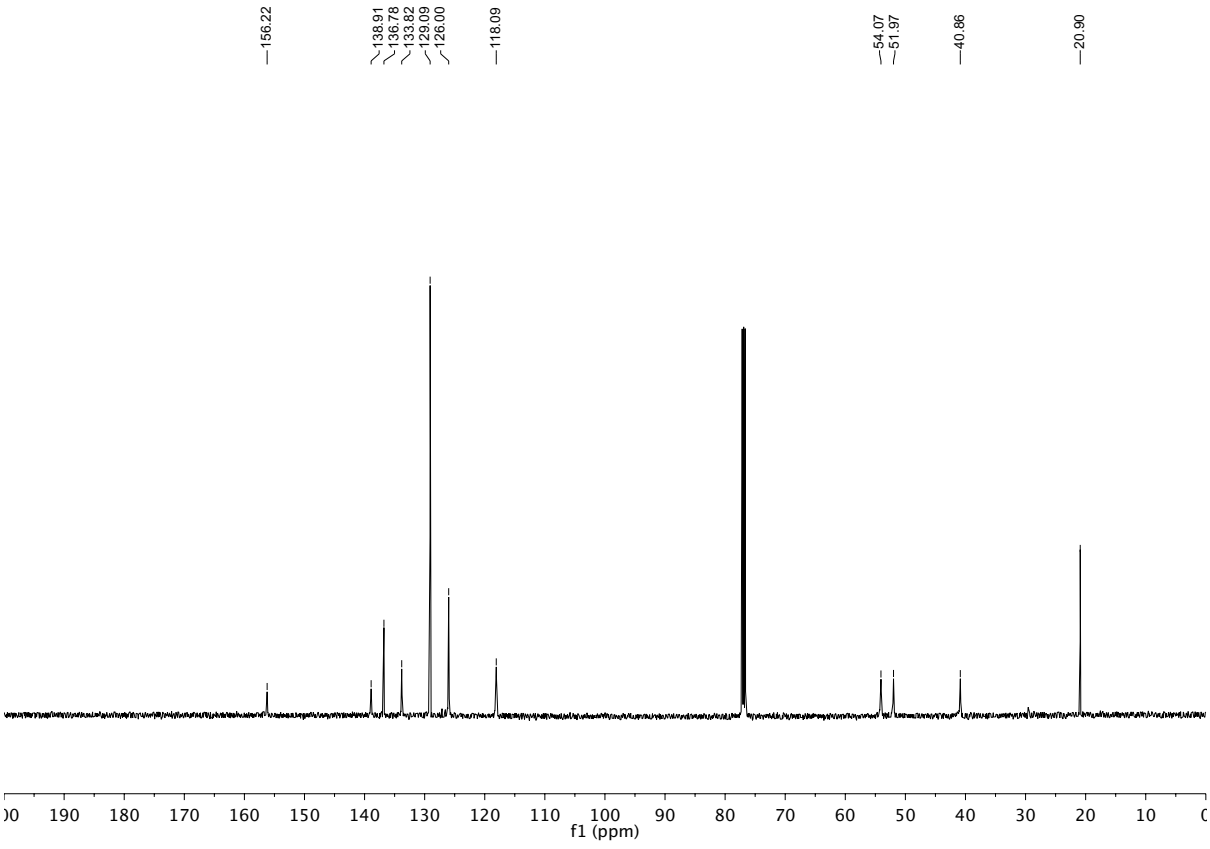




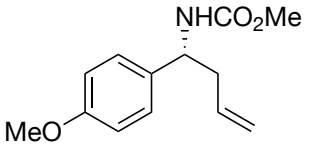
Methyl (*R*)-(1-(*p*-tolyl)but-3-en-1-yl)carbamate (3)

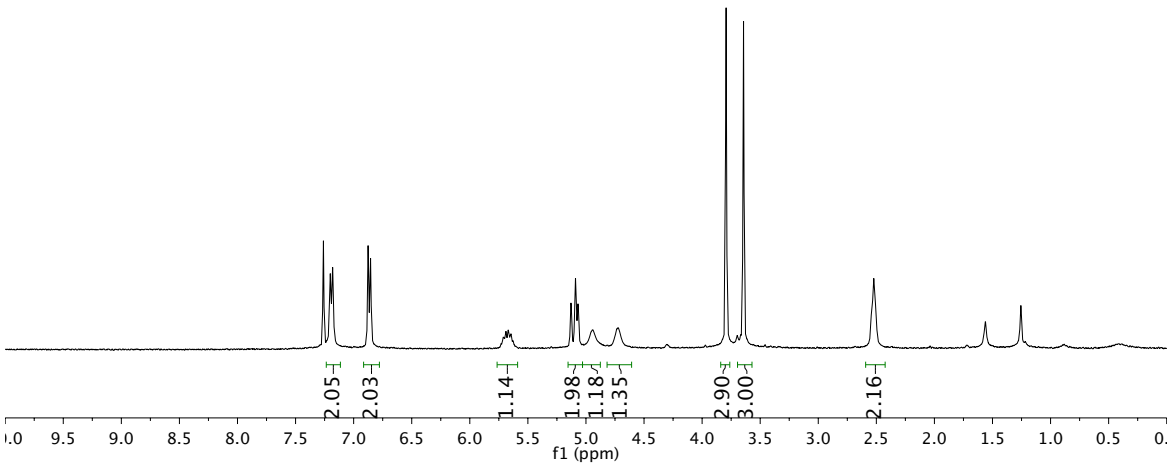


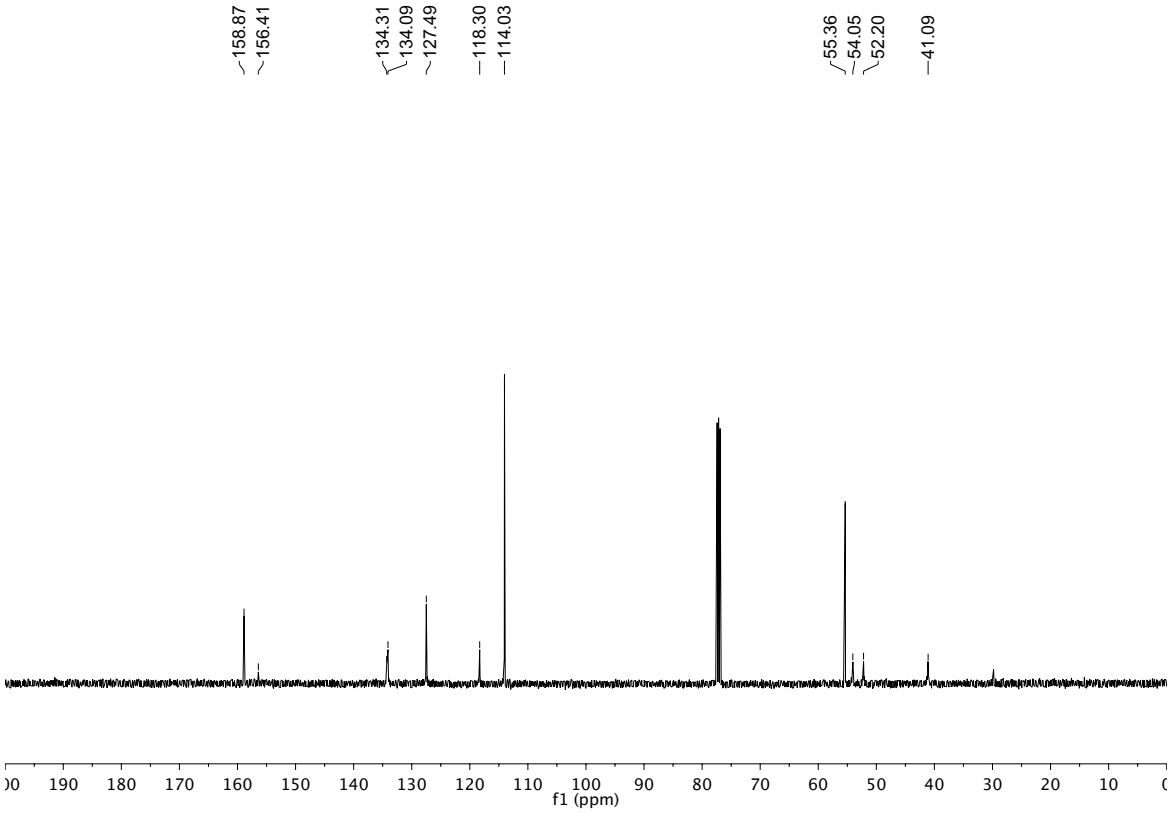




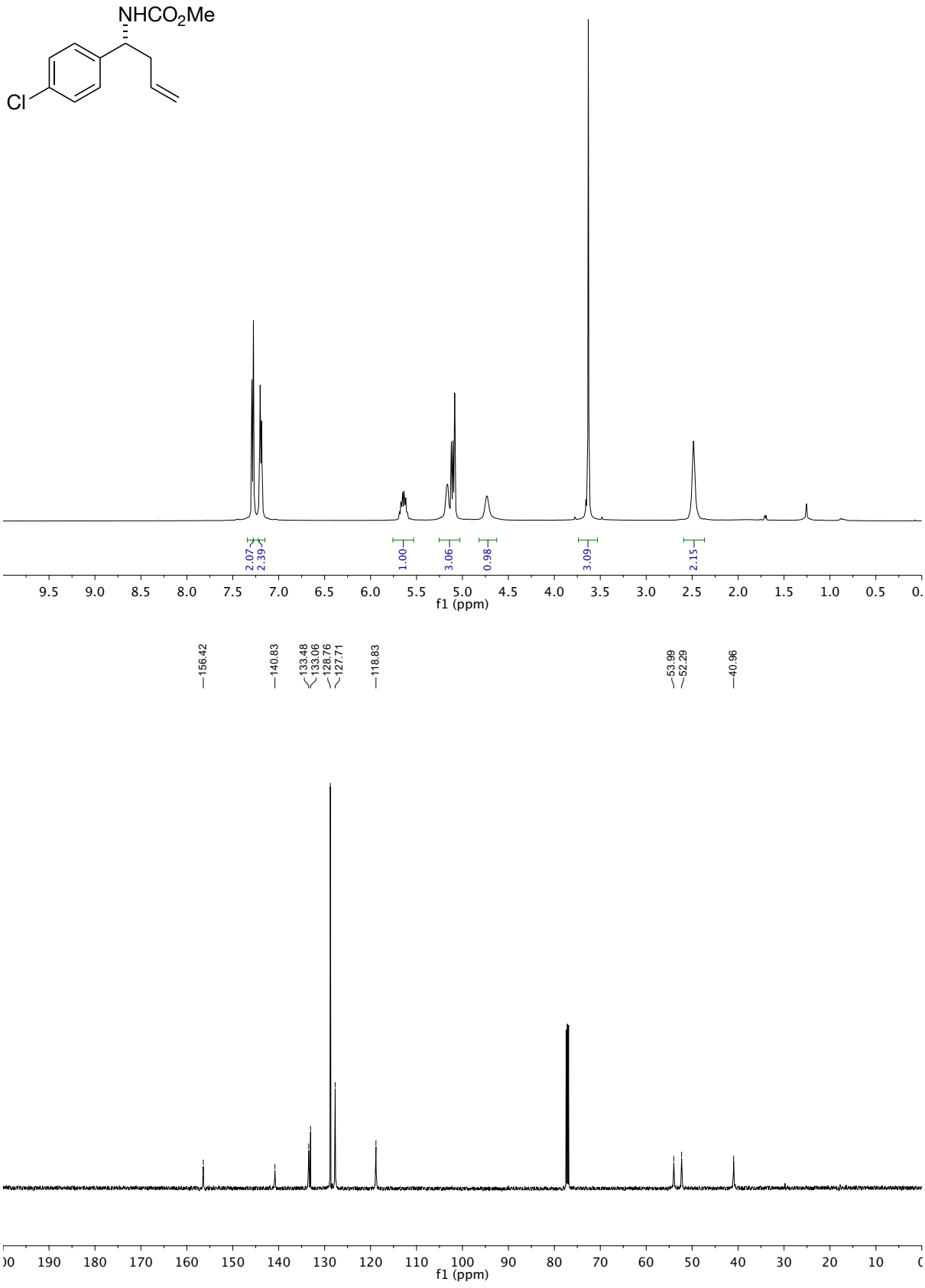
Methyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (4)



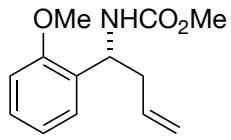


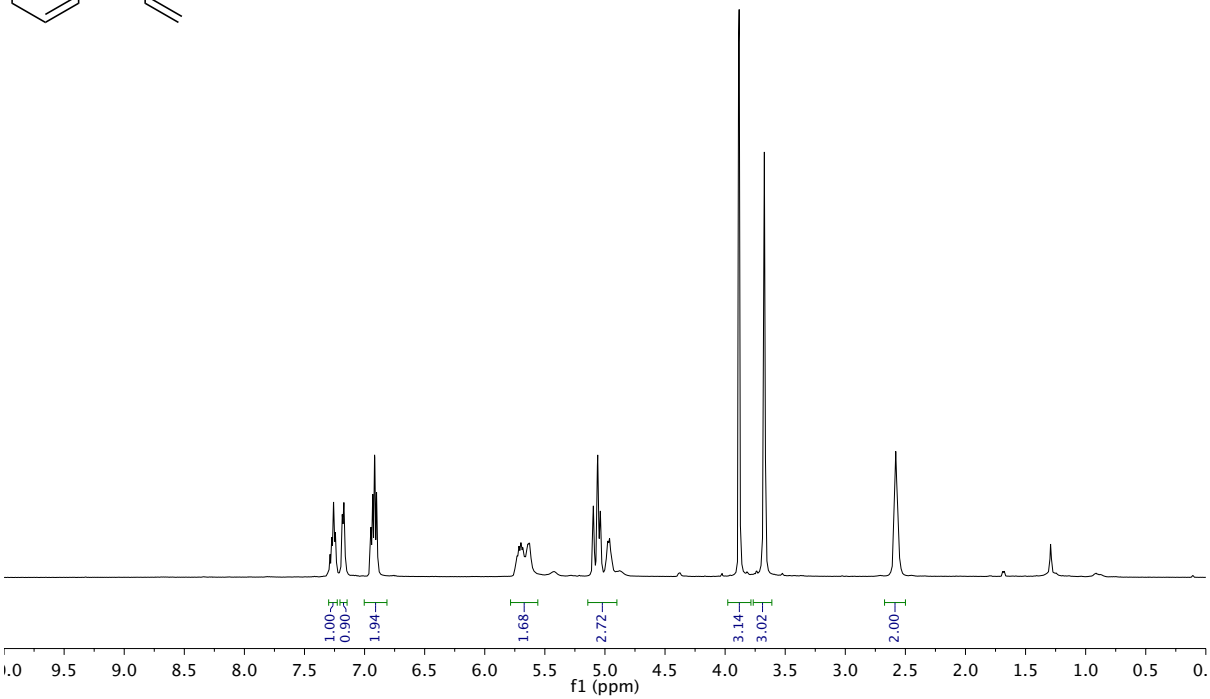


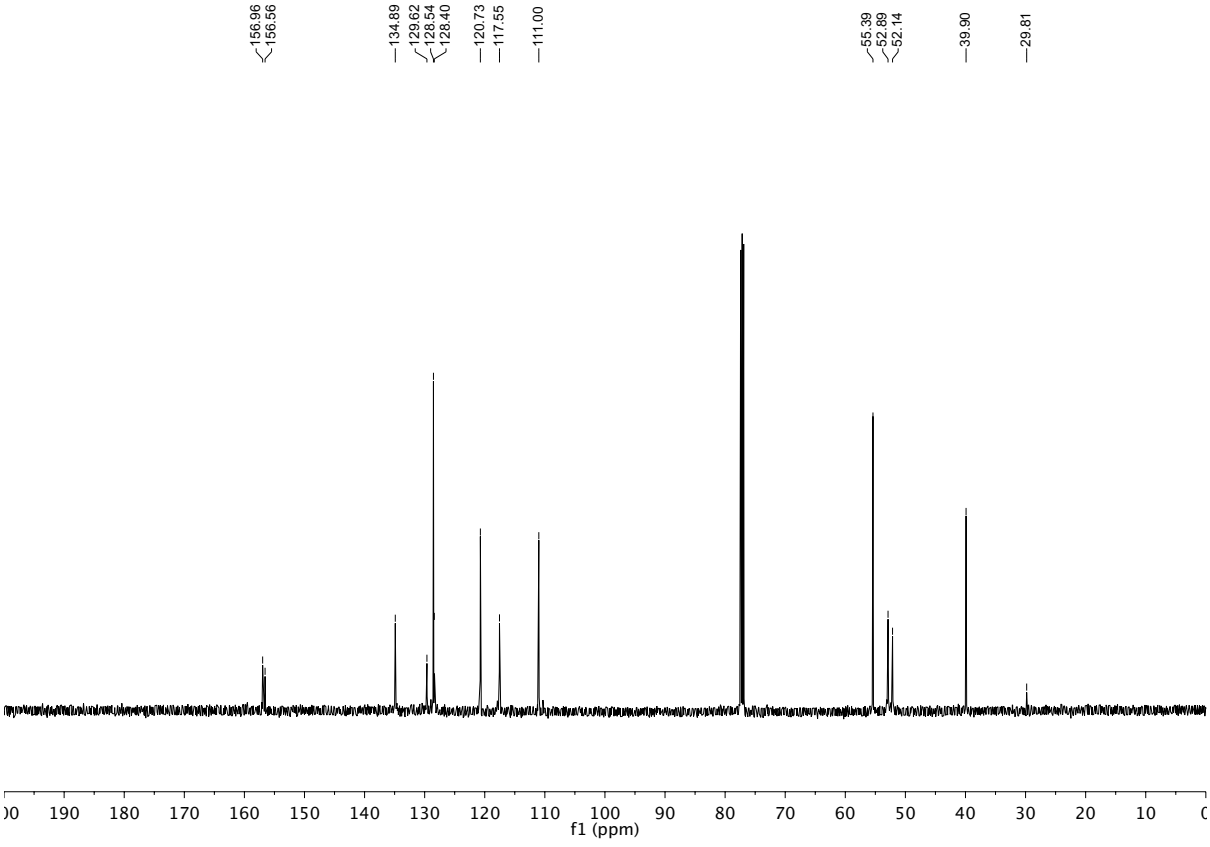
Methyl (*R*)-(1-(4-chlorophenyl)but-3-en-1-yl)carbamate (5)



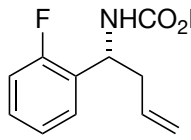
Methyl (*R*)-(1-(2-methoxyphenyl)but-3-en-1-yl)carbamate (6)

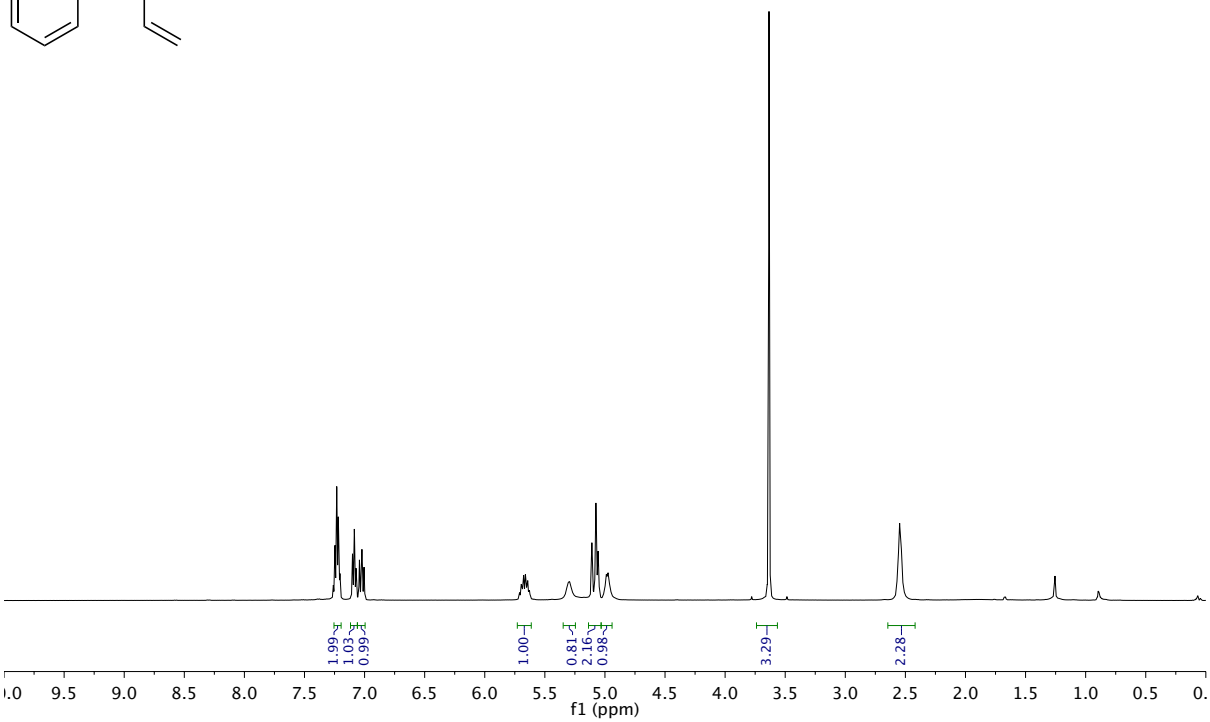


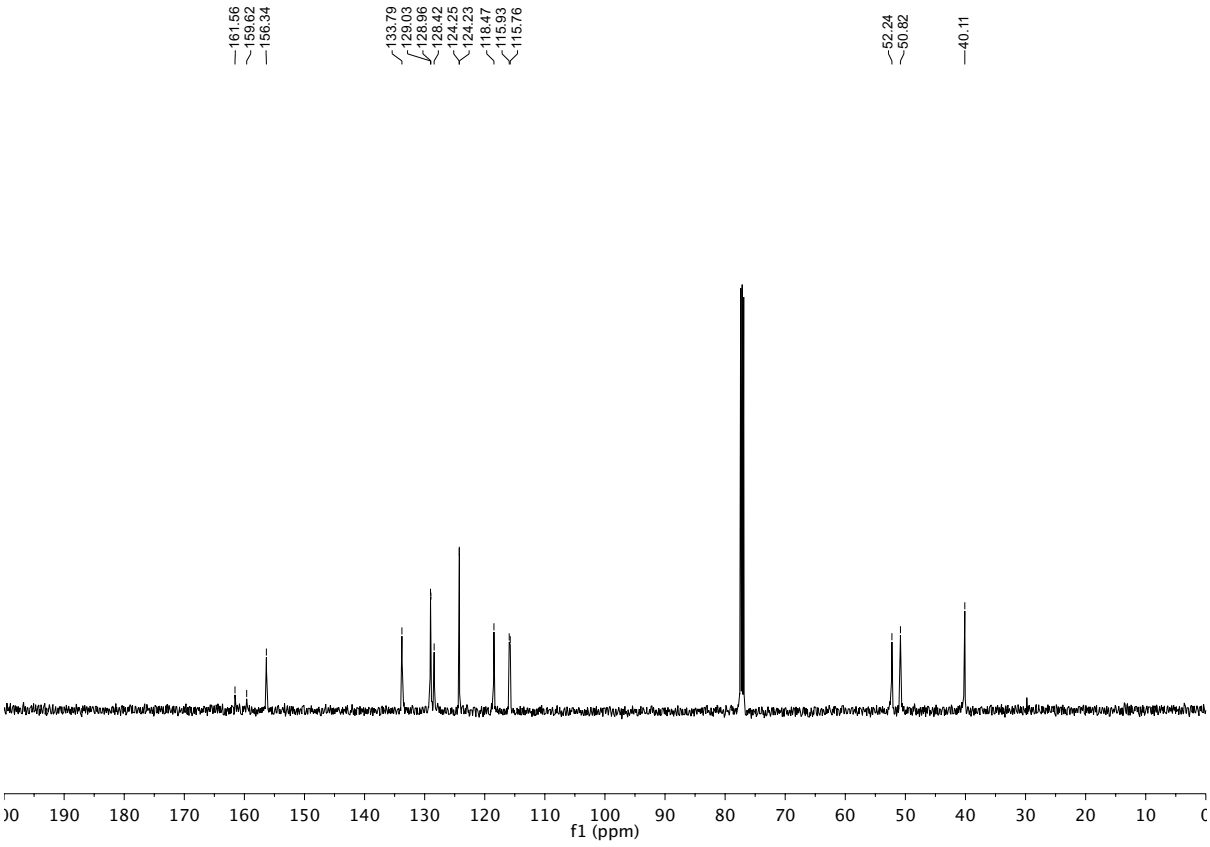




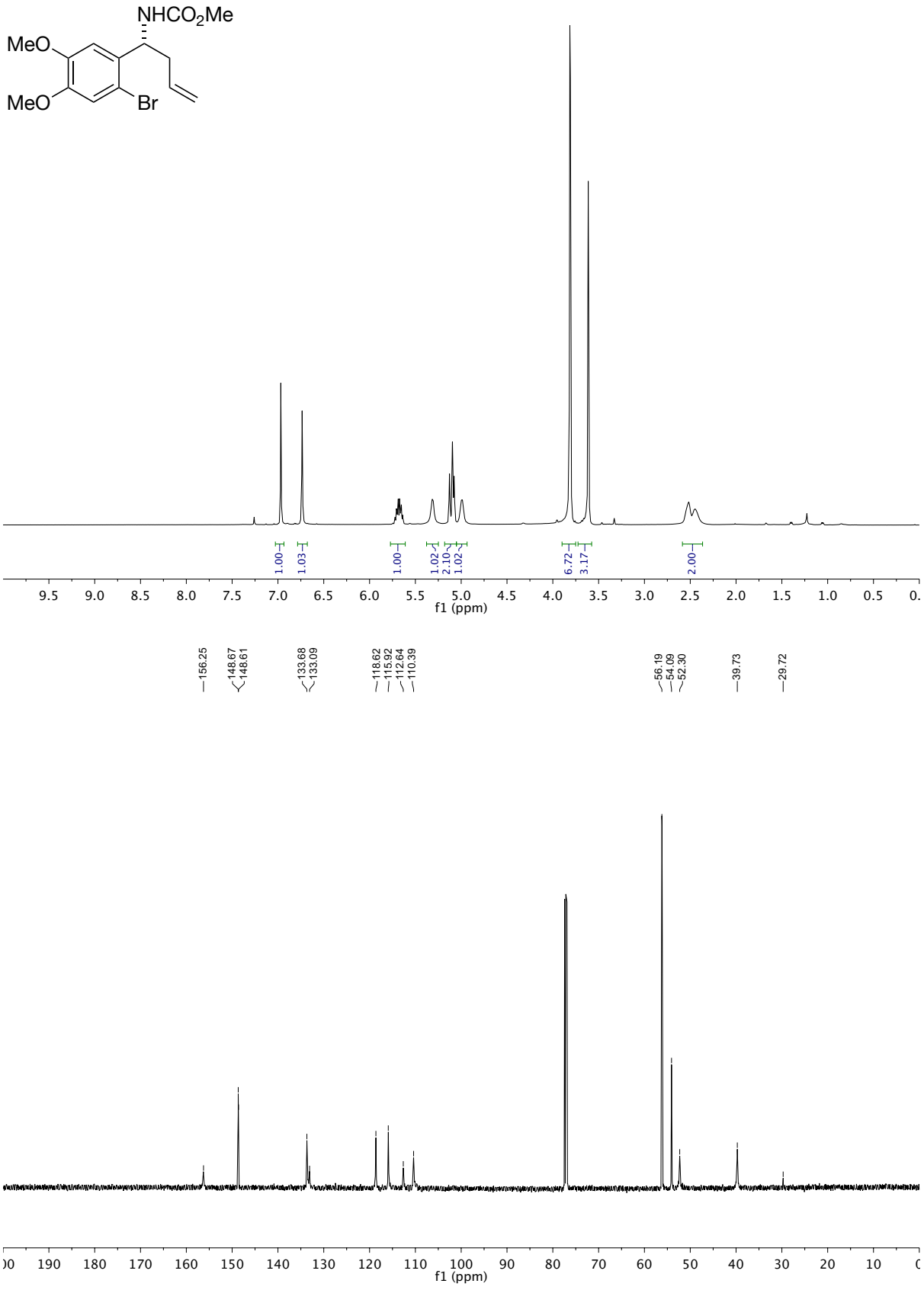
Methyl (*R*)-(1-(2-fluorophenyl)but-3-en-1-yl)carbamate (7)



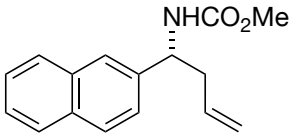


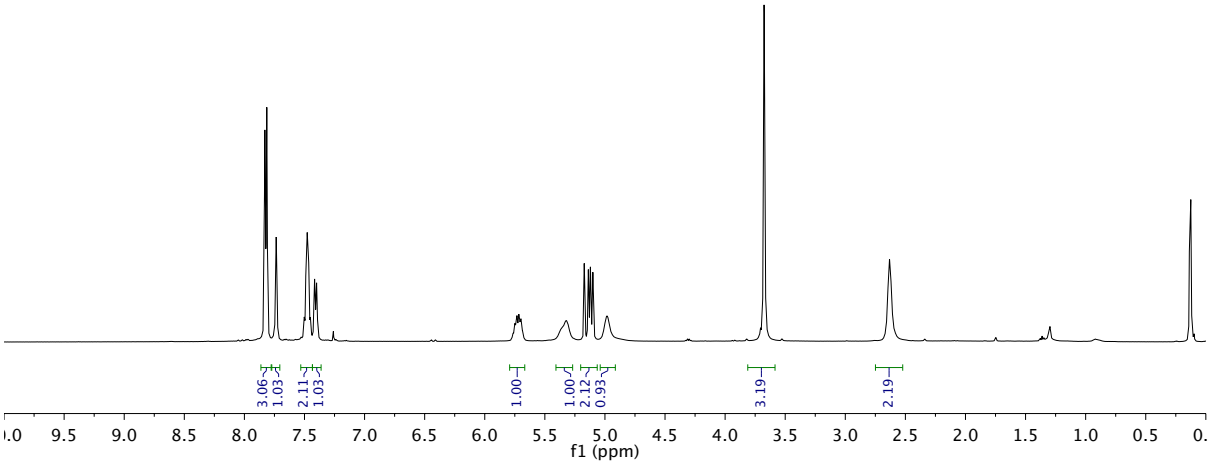


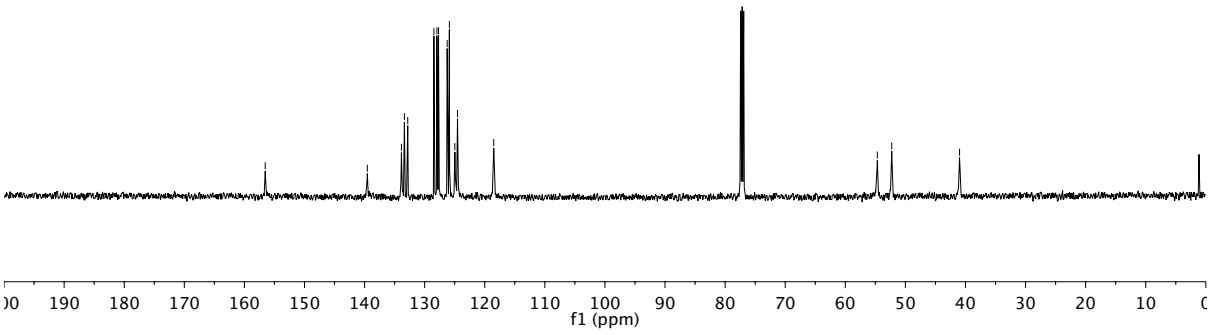
Methyl (*R*)-(1-(2-bromo-4,5-dimethoxyphenyl)but-3-en-1-yl)carbamate (8)



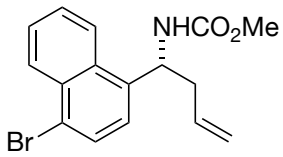
Methyl (*R*)-(1-(naphthalen-2-yl)but-3-en-1-yl)carbamate (9)

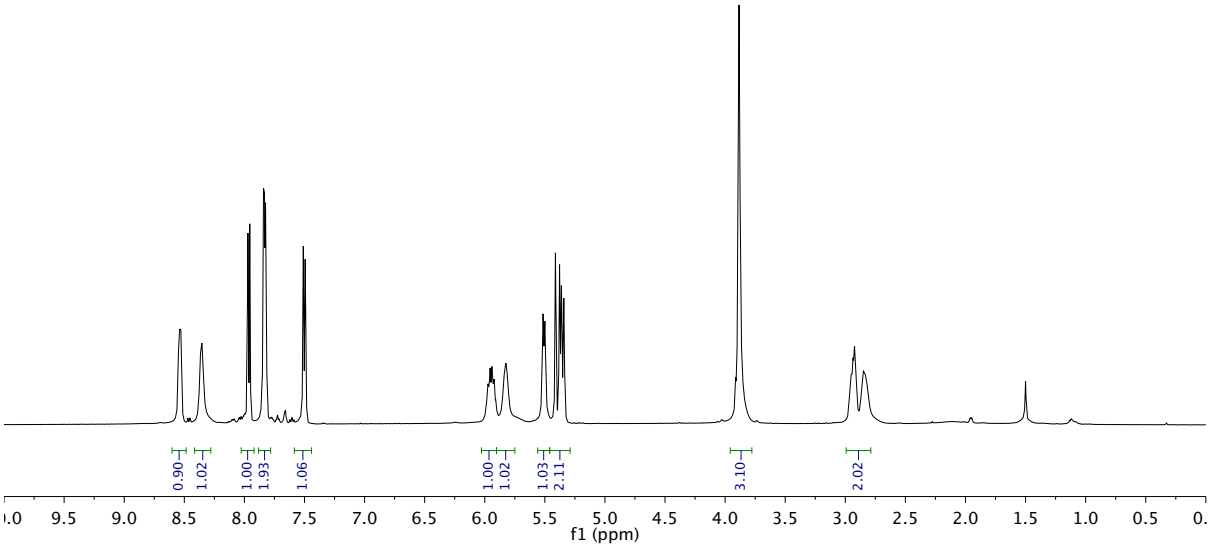


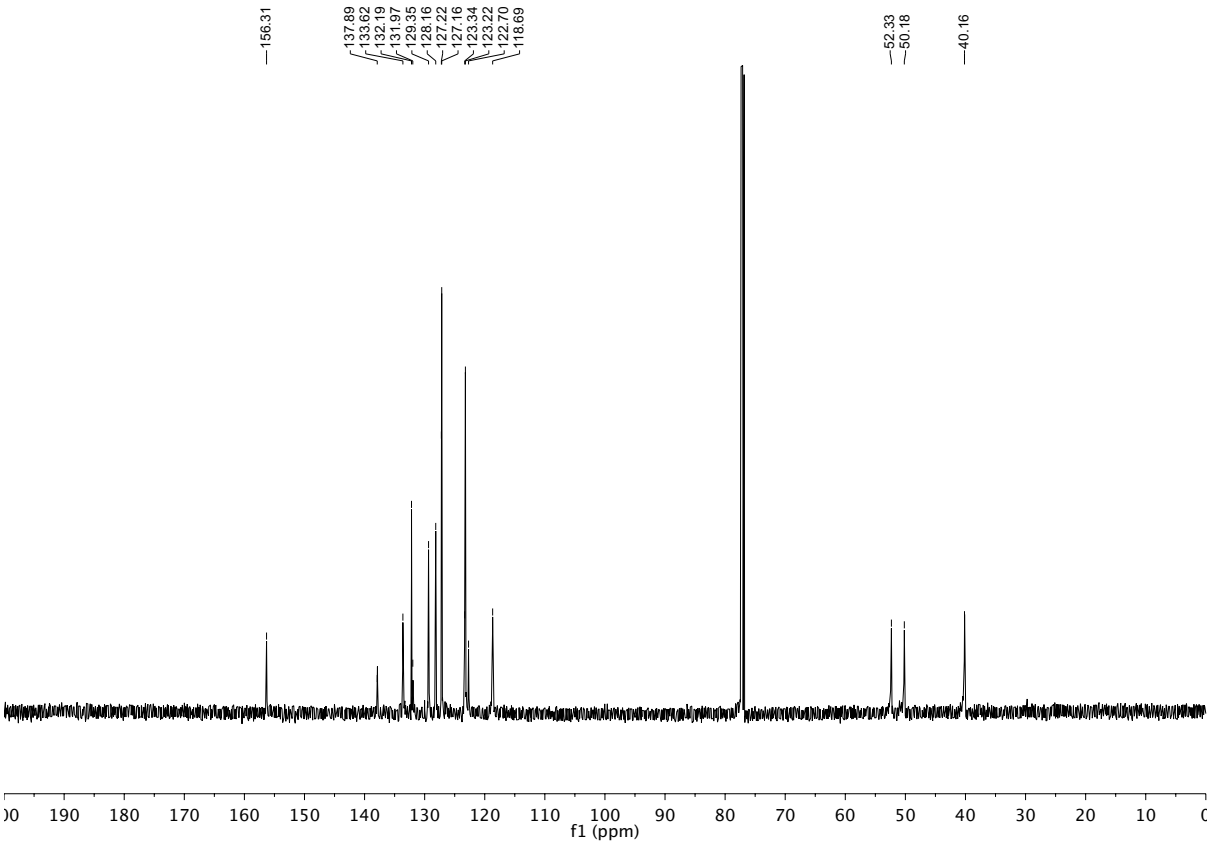




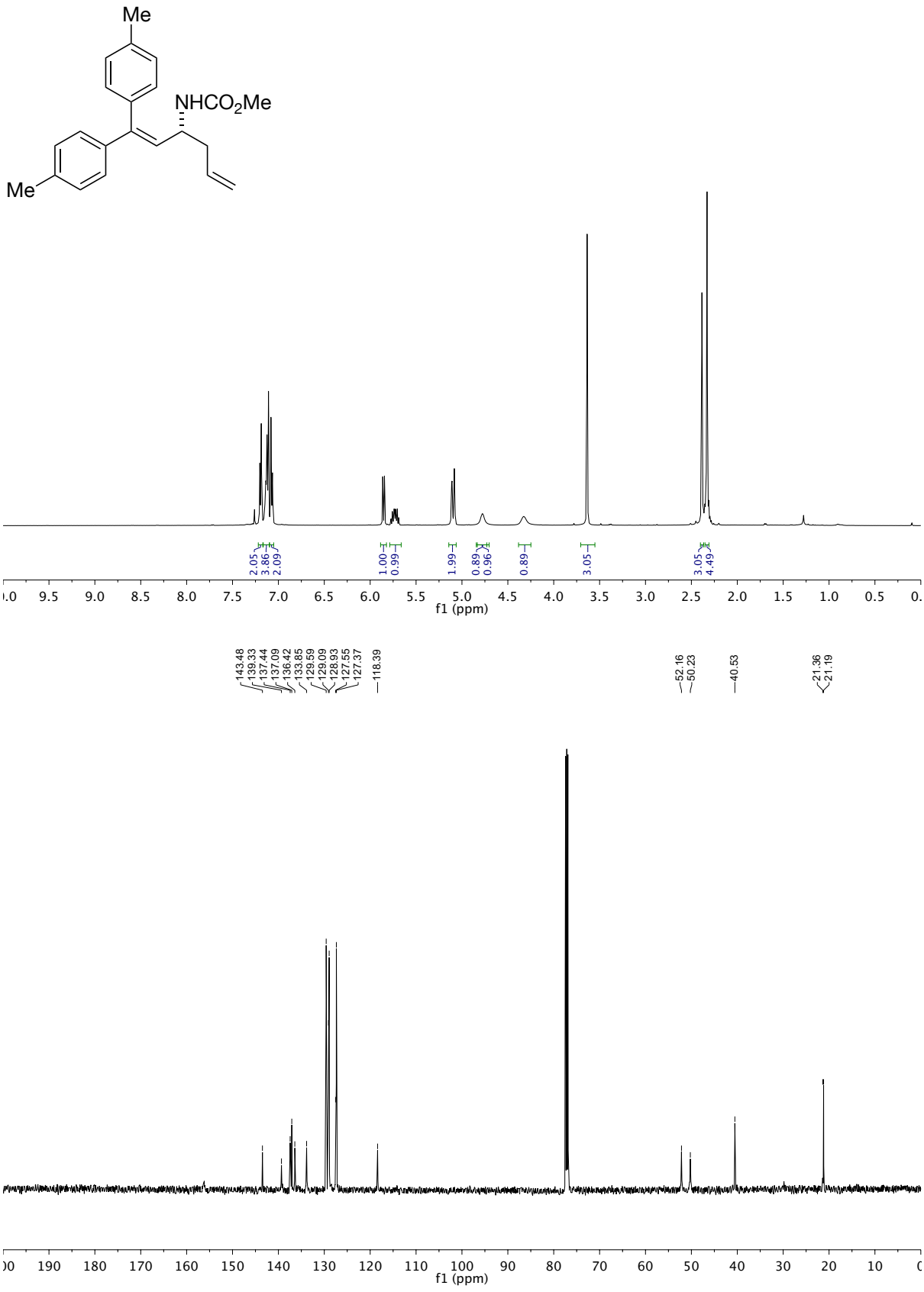
Methyl (*R*)-(1-(4-bromonaphthalen-1-yl)but-3-en-1-yl)carbamate (10)



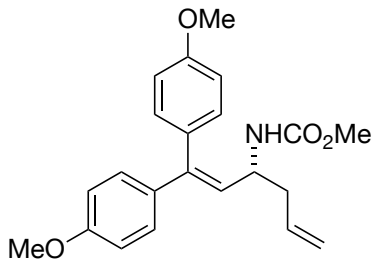


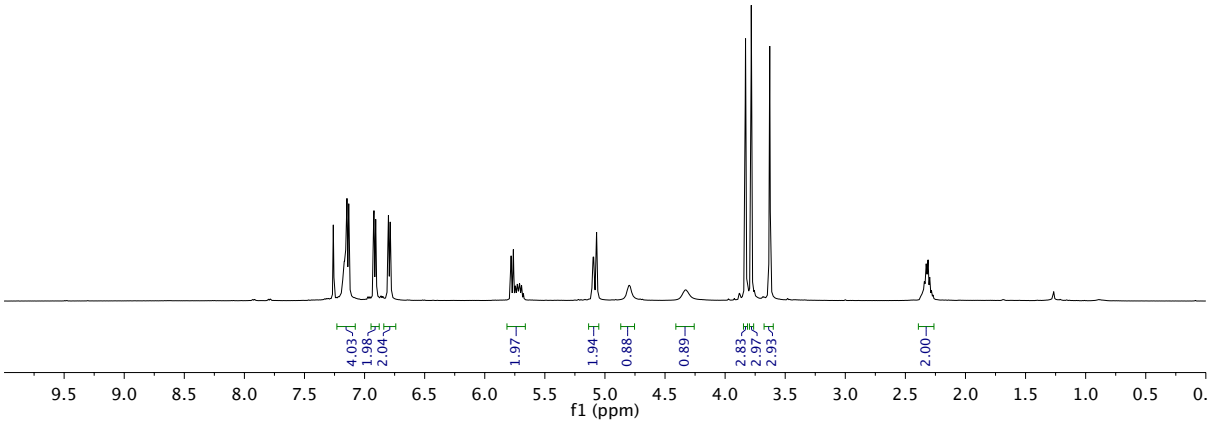


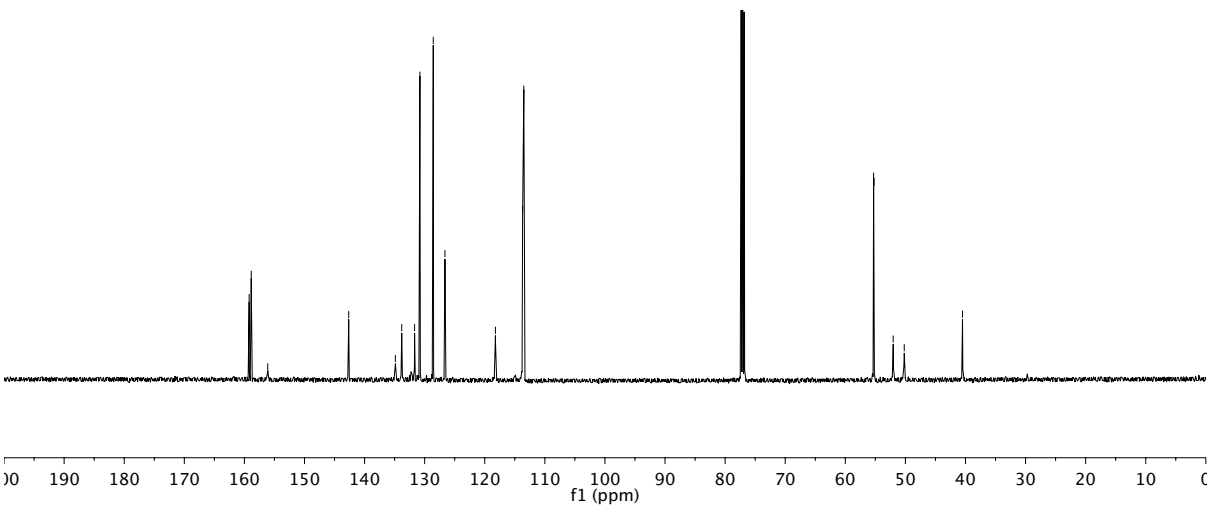
Methyl (*R*)-(1,1-di-*p*-tolylhexa-1,5-dien-3-yl)carbamate (11)



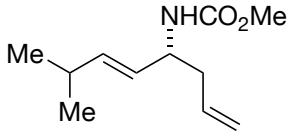
Methyl (*R*)-(1,1-bis(4-methoxyphenyl)hexa-1,5-dien-3-yl)carbamate (12)

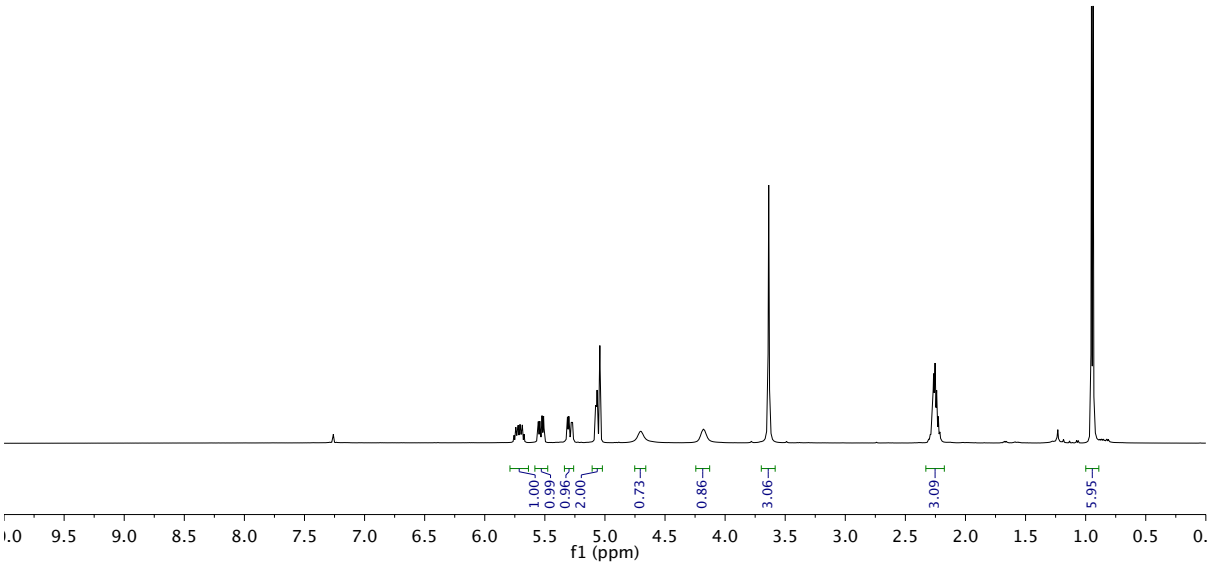


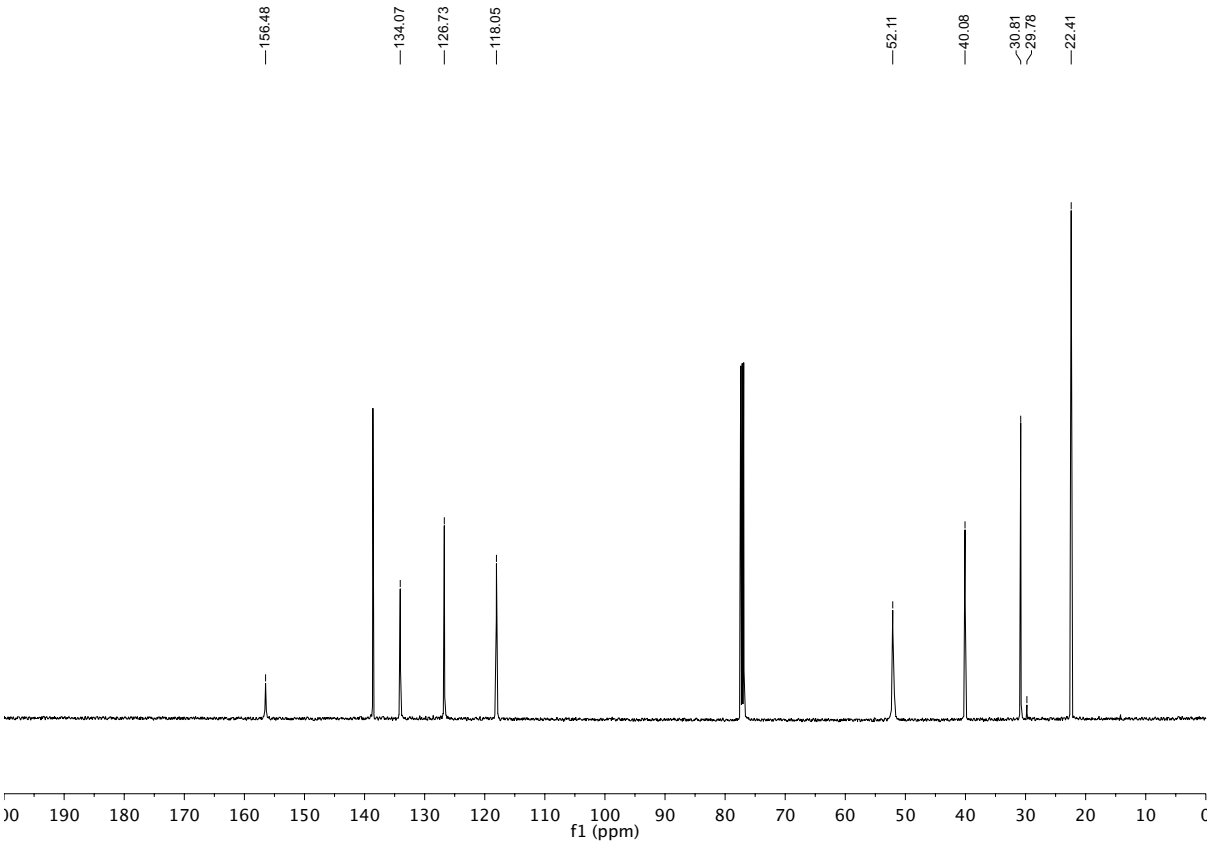




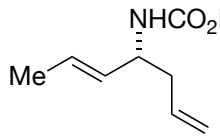
Methyl (*R*,*E*)-(7-methyloctа-1,5-dien-4-yl)carbamate (13)

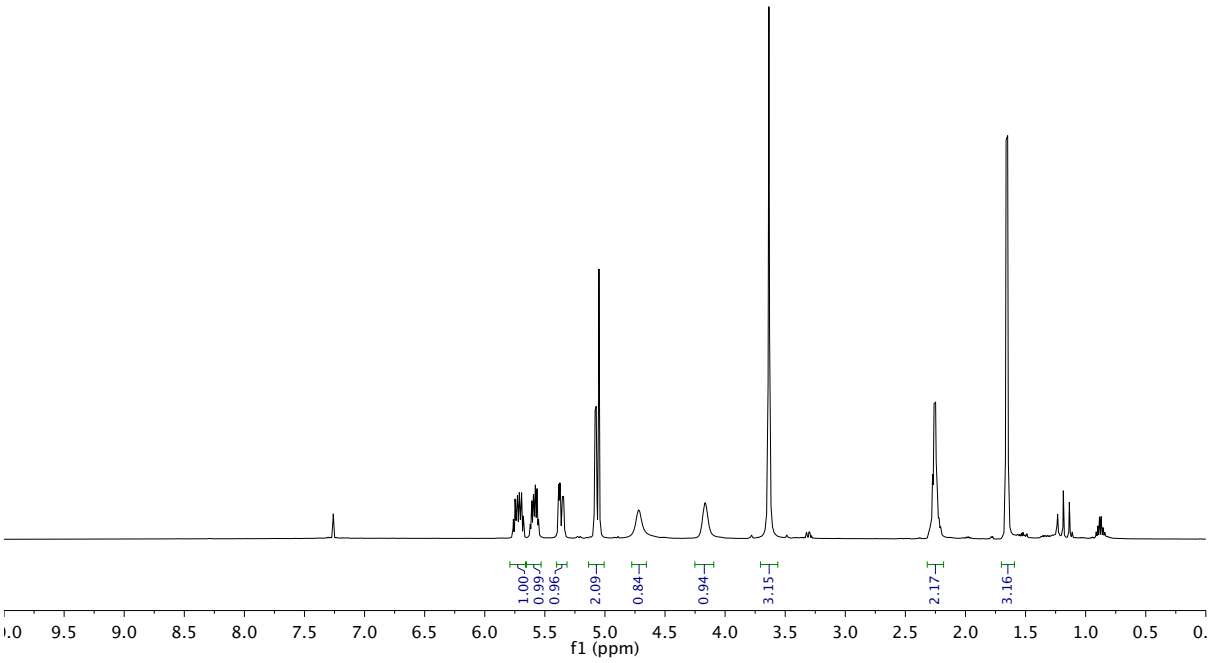




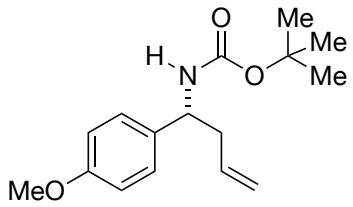


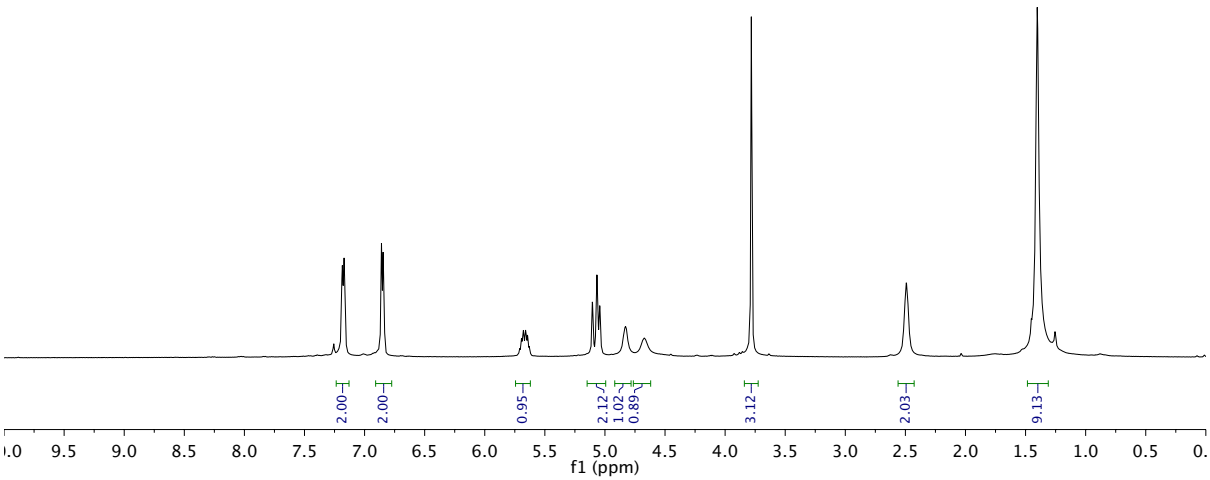
Methyl (*R*,*E*)-hepta-1,5-dien-4-ylcarbamate (14)

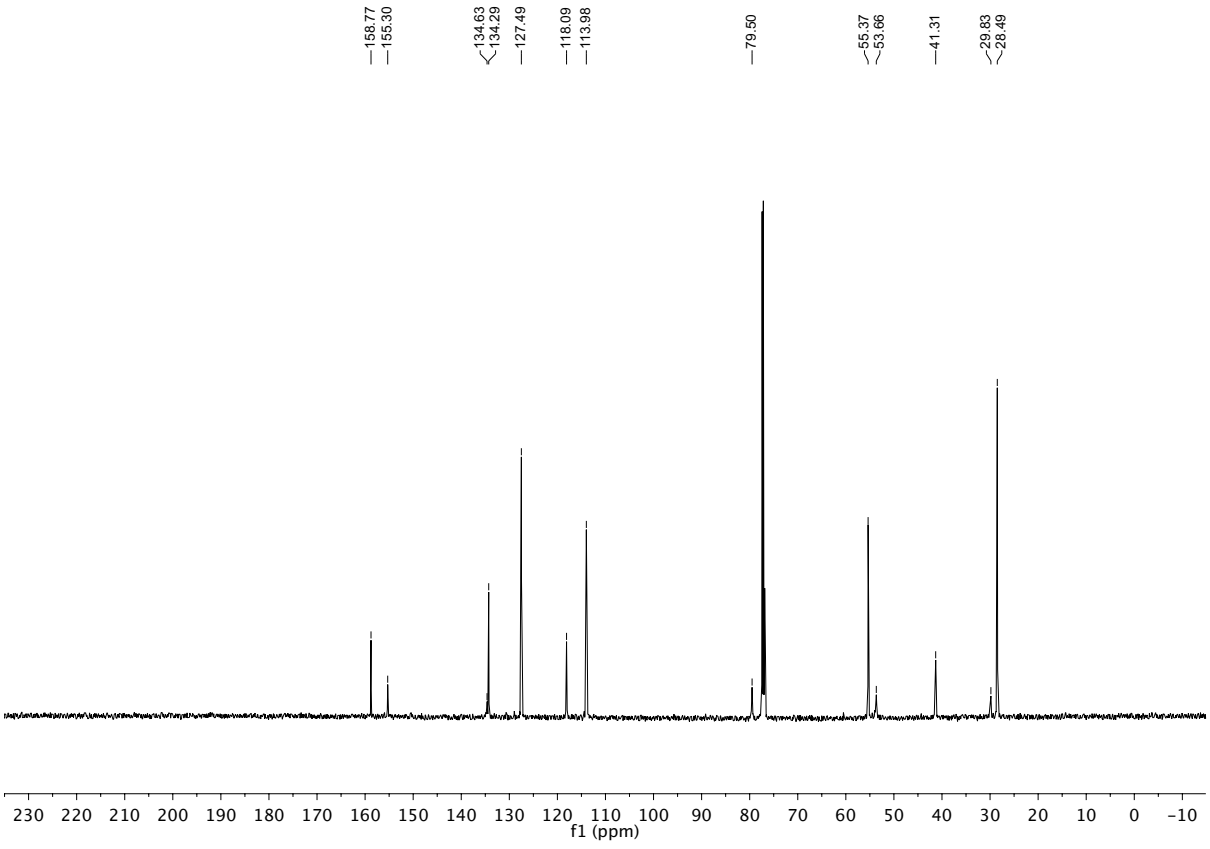




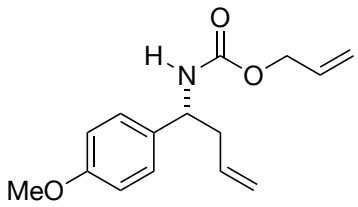
***Tert*-butyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (15)**

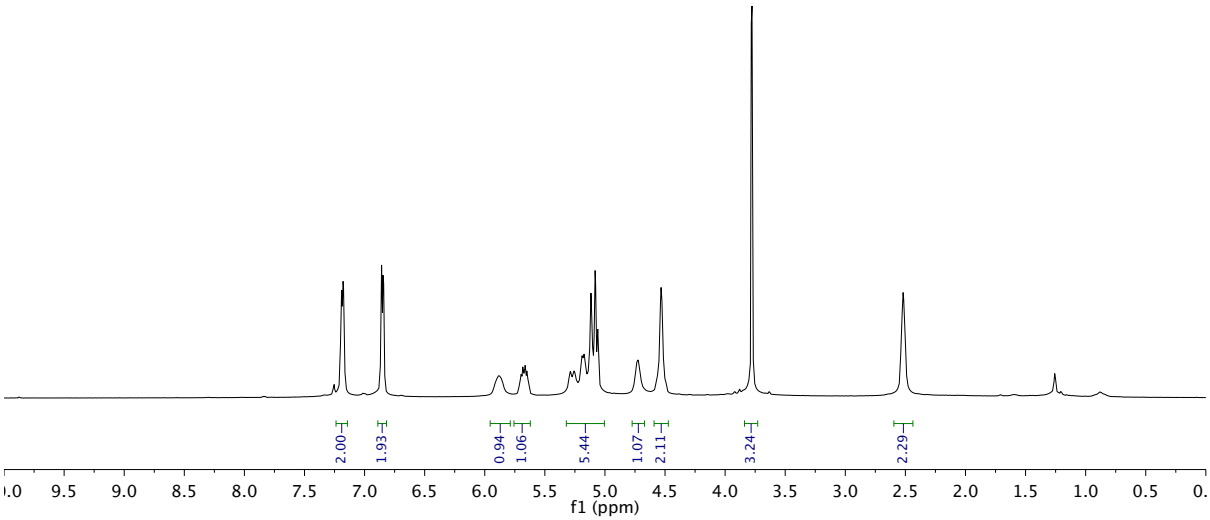


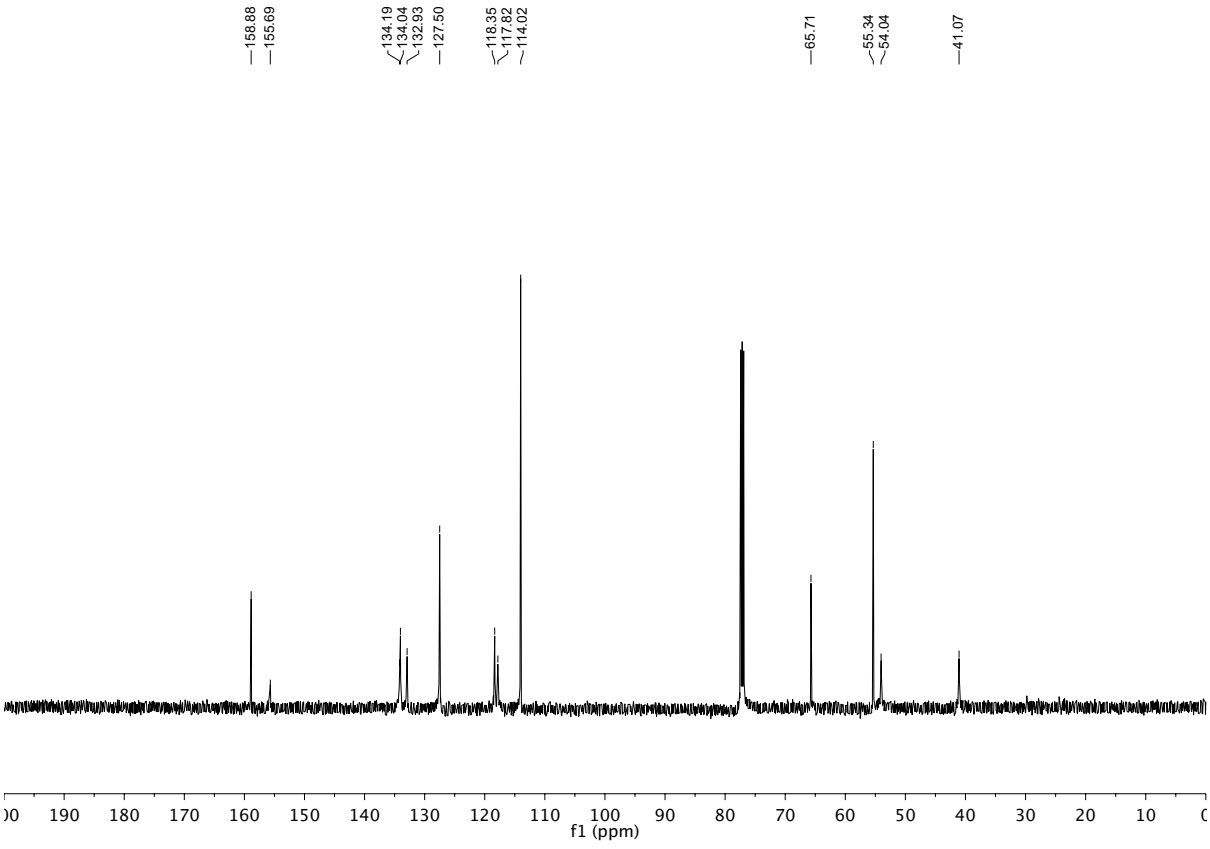




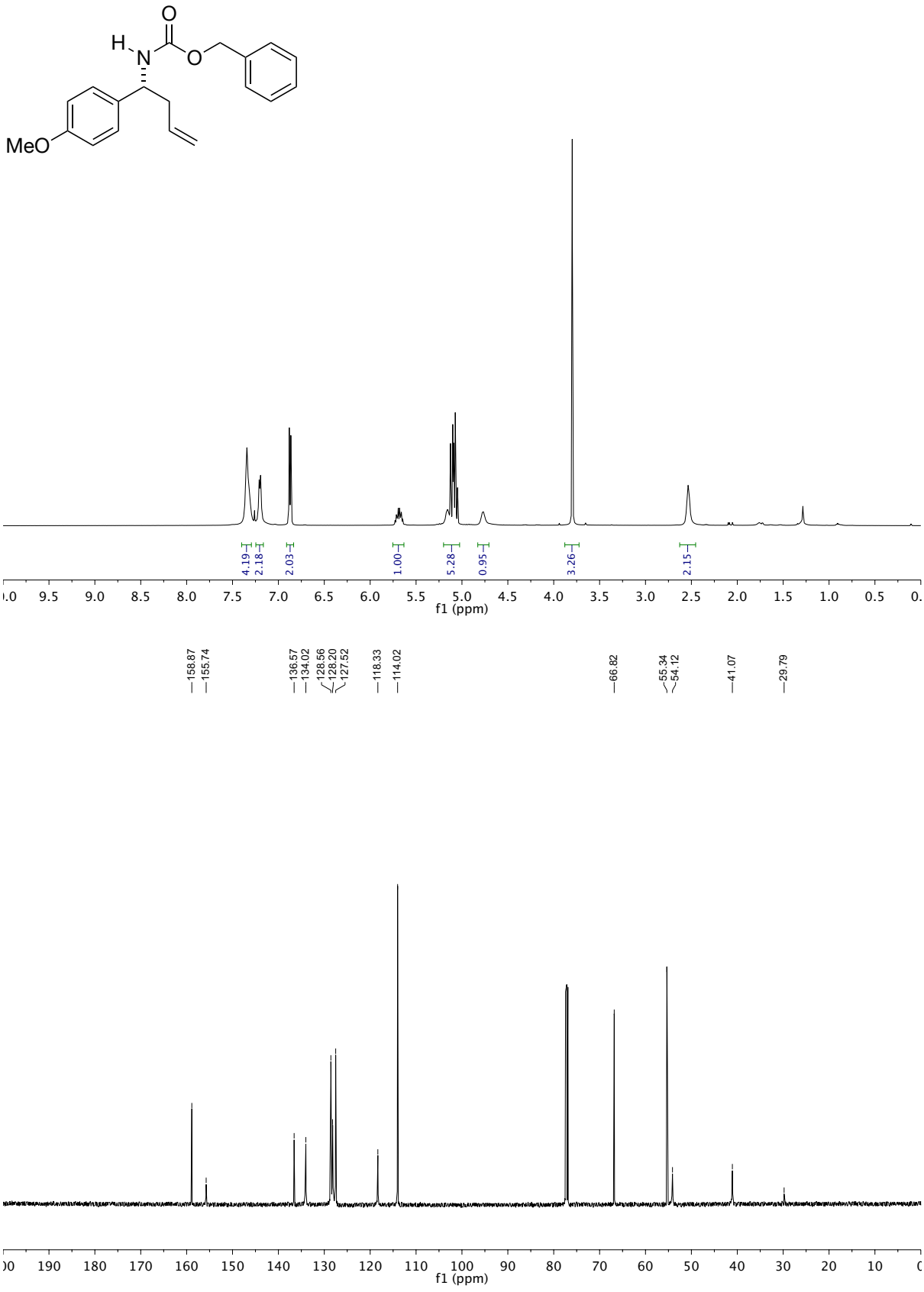
Allyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (16)



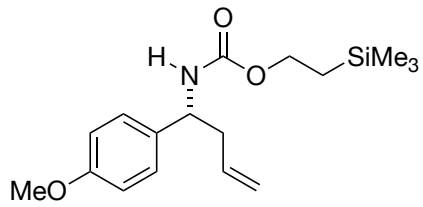


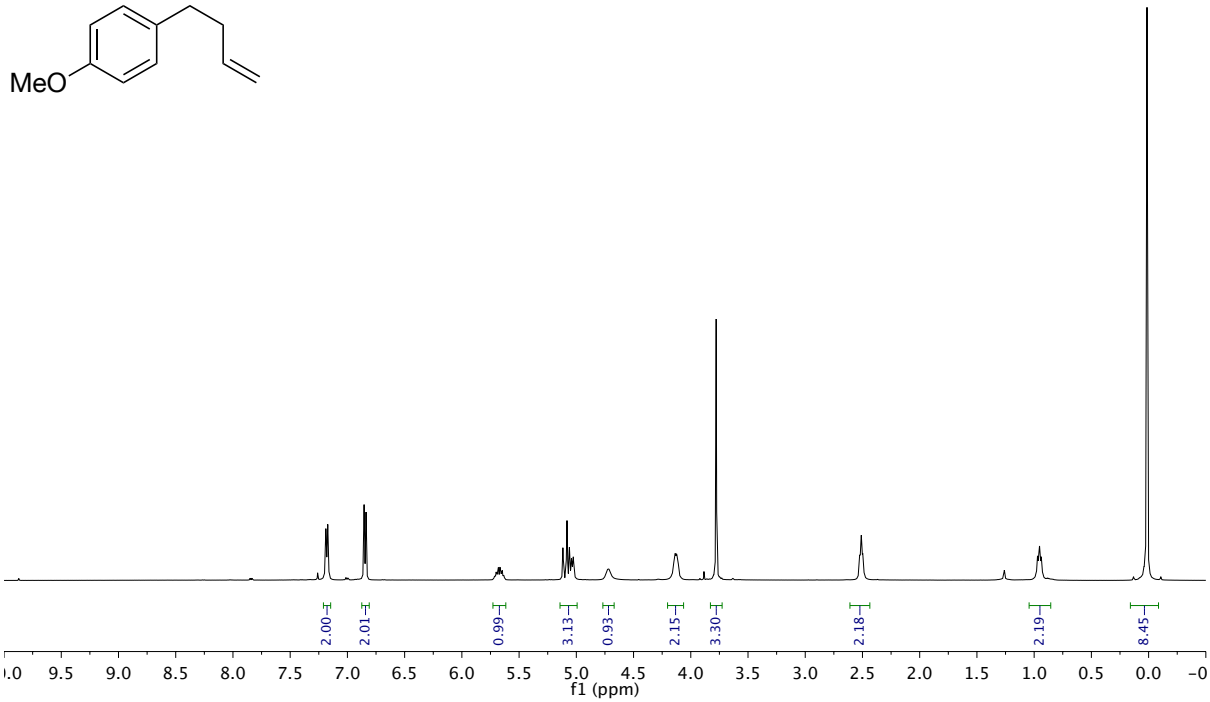


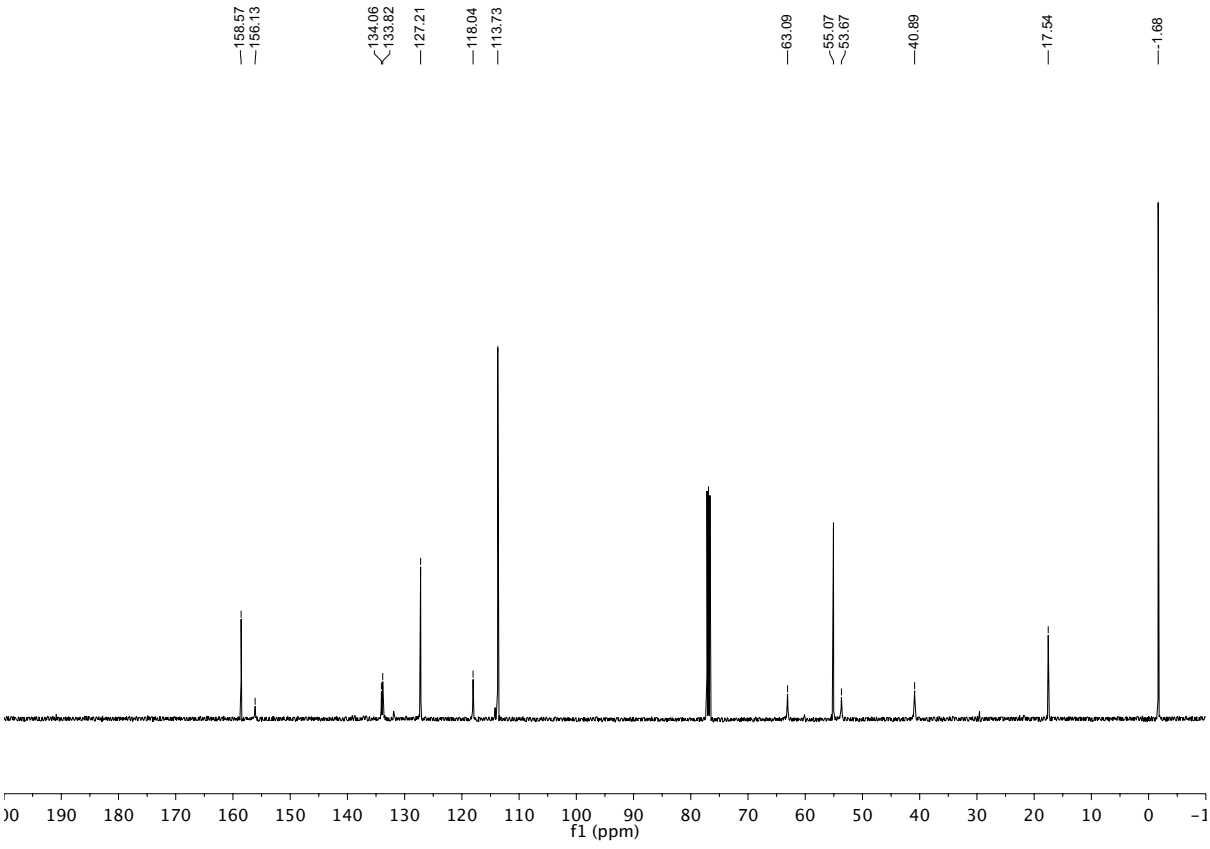
Benzyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (17)



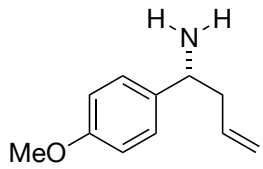
2-(Trimethylsilyl)ethyl (*R*)-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (18)

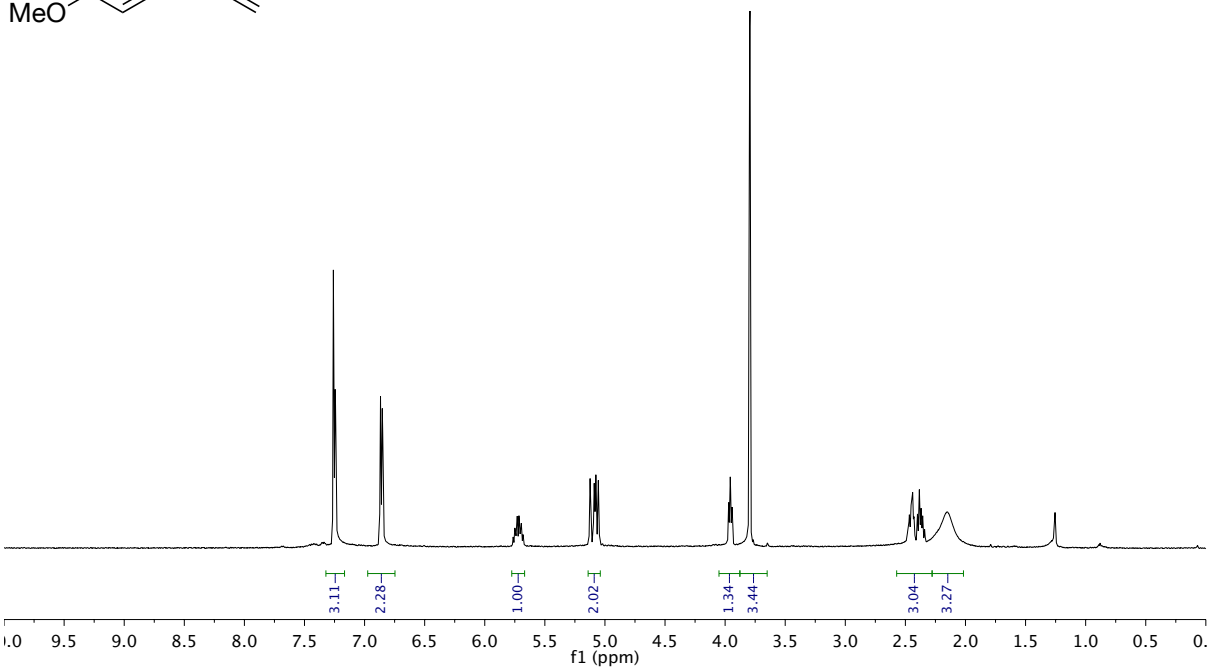


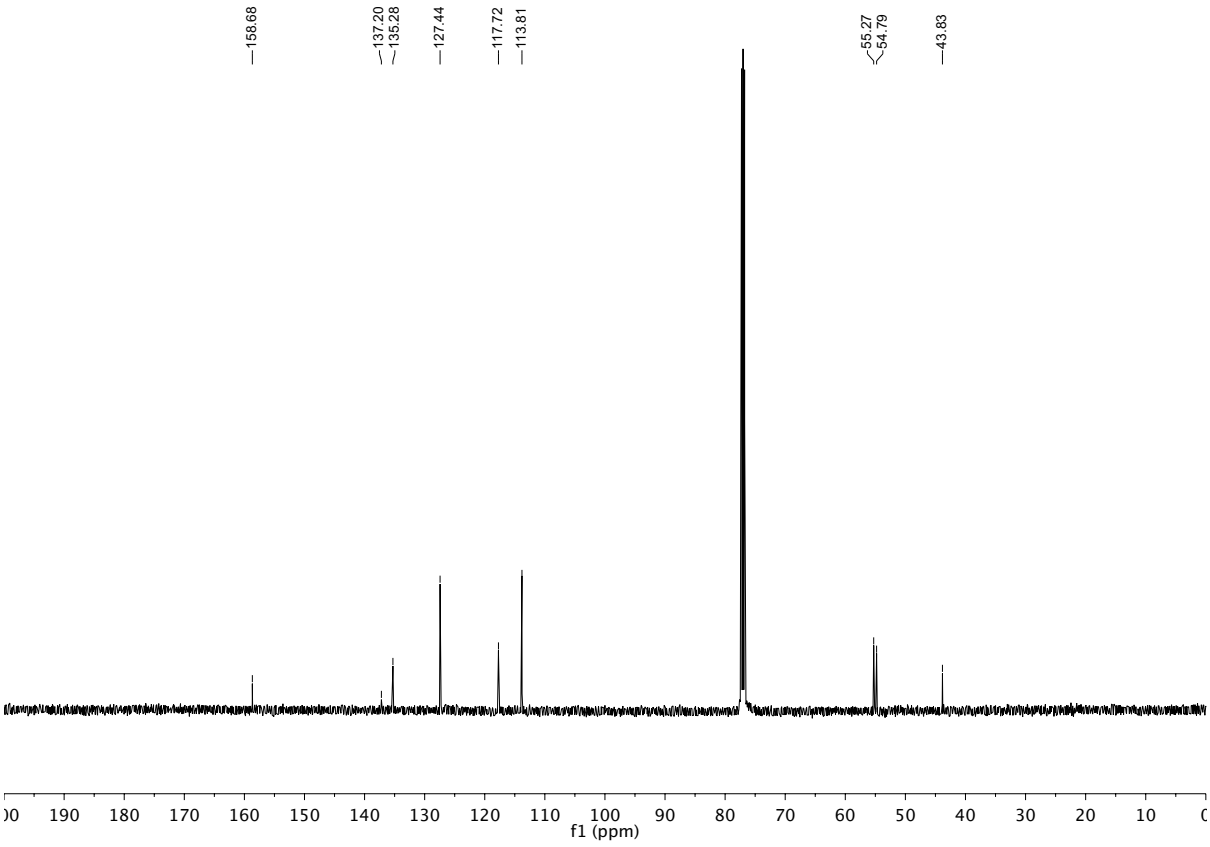




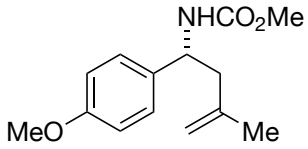
(*R*)-1-(4-Methoxyphenyl)but-3-en-1-amine (19)

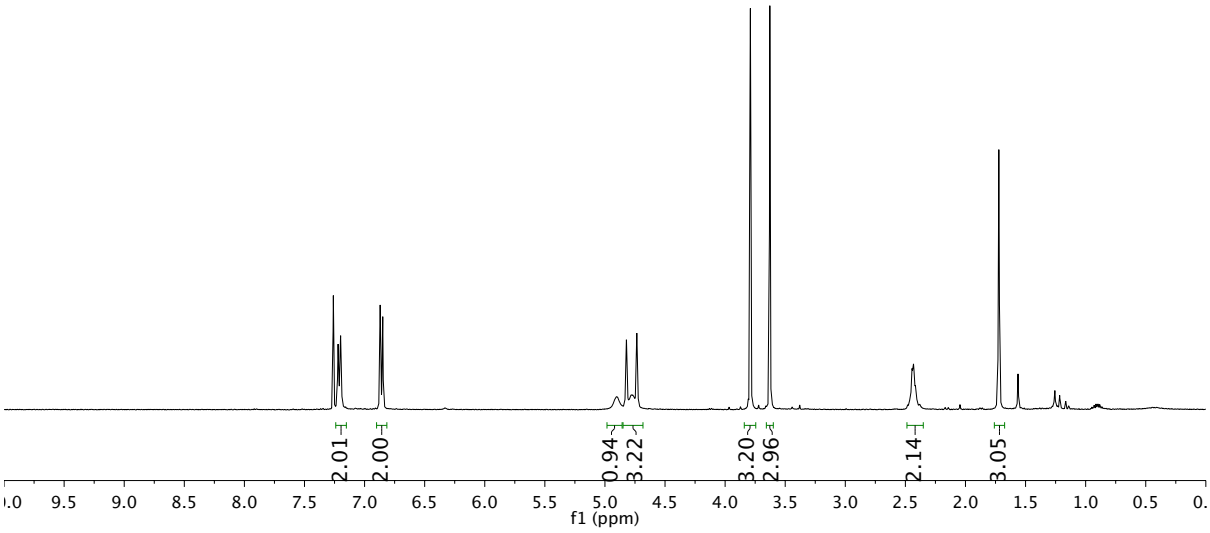


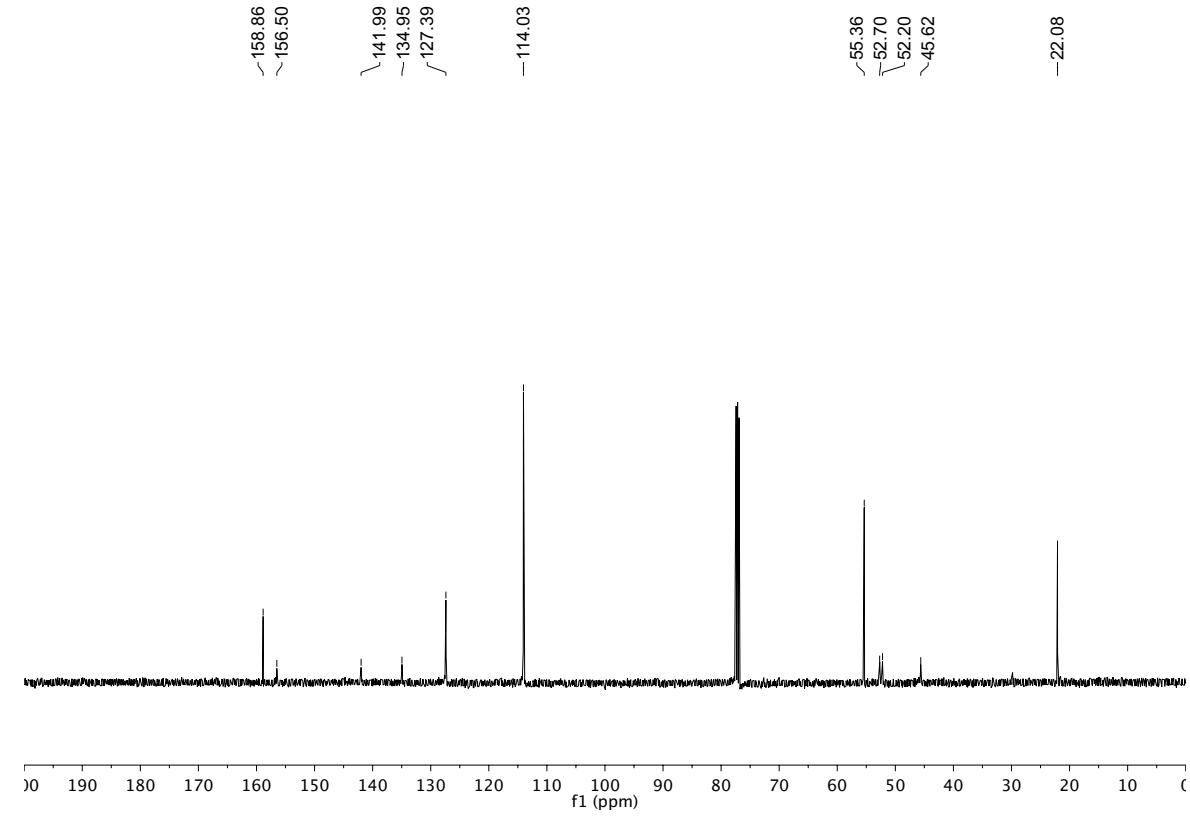




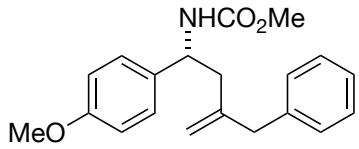
Methyl (*R*)-(1-(4-methoxyphenyl)-3-methylbut-3-en-1-yl)carbamate (20)

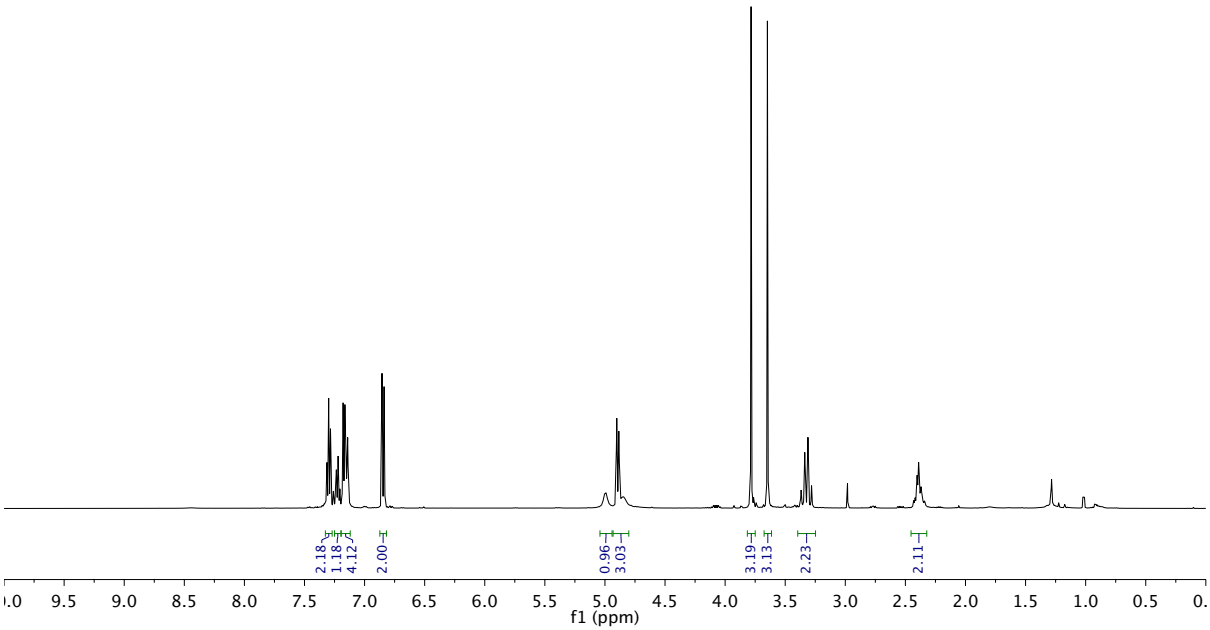


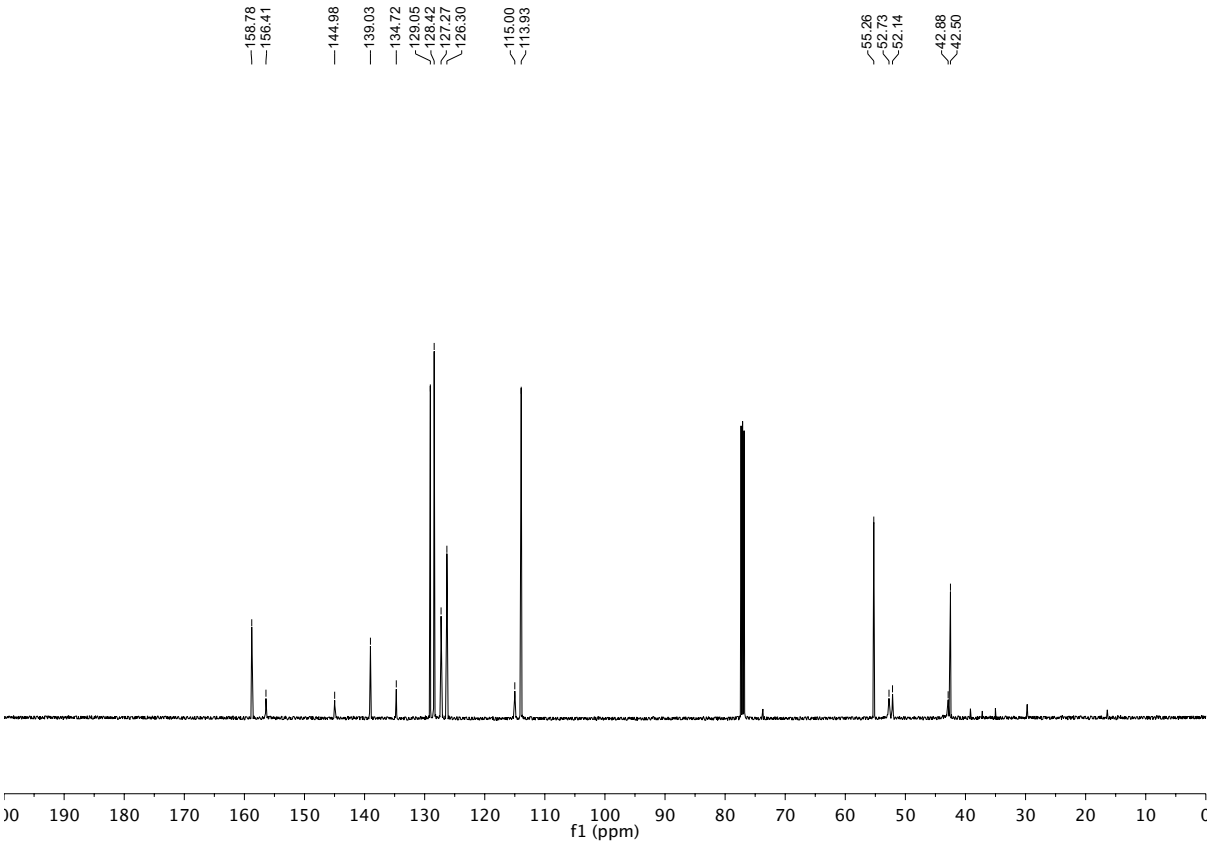




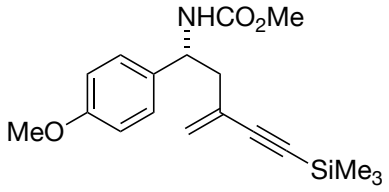
Methyl (*R*)-(3-benzyl-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (21)

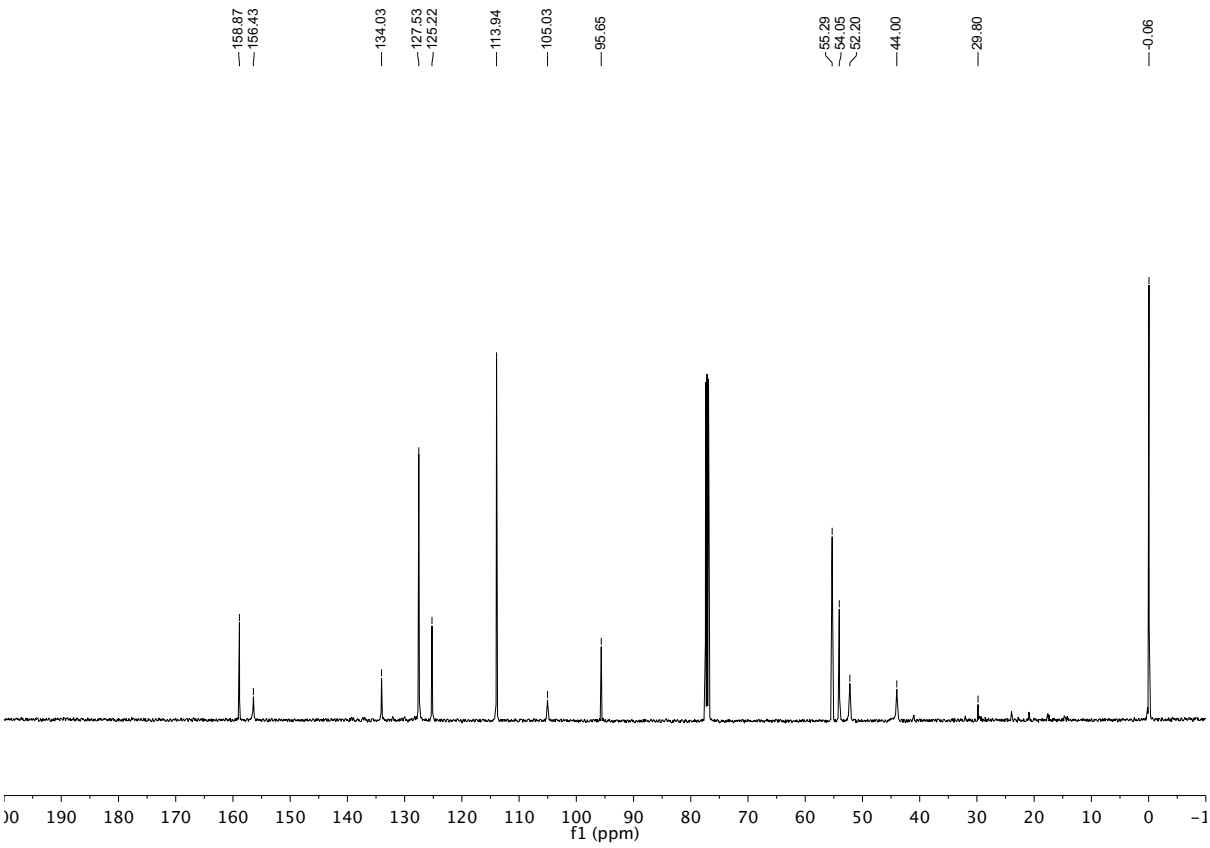




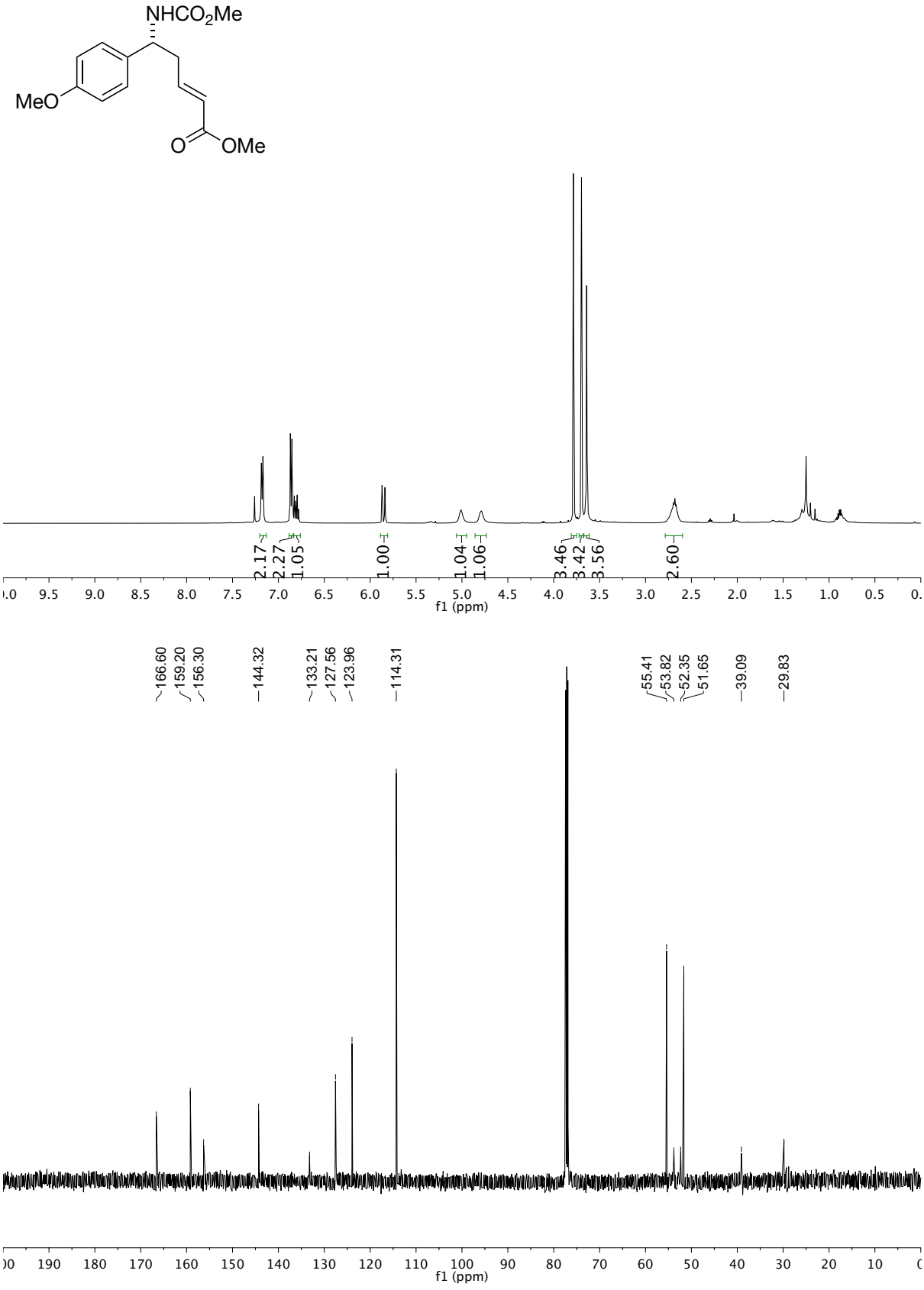


Methyl (*R*)-(1-(4-methoxyphenyl)-3-methylene-5-(trimethylsilyl)pent-4-yn-1-yl)carbamate (22)

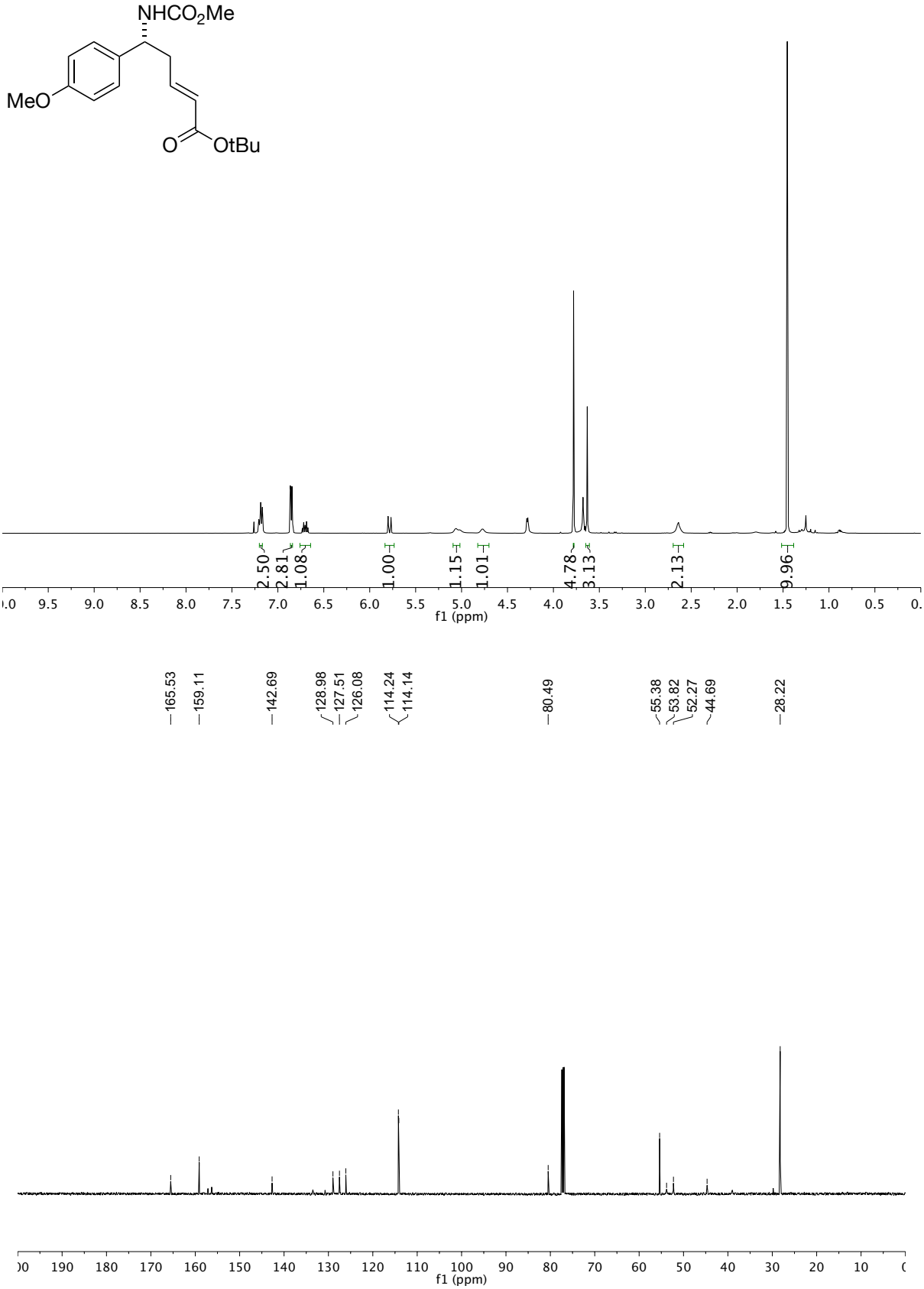




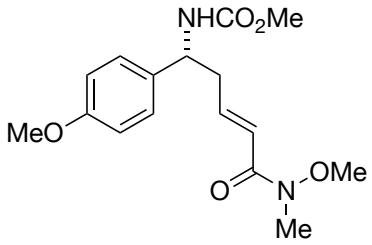
Methyl (*R*,*E*)-5-((methoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-2-enoate (23)

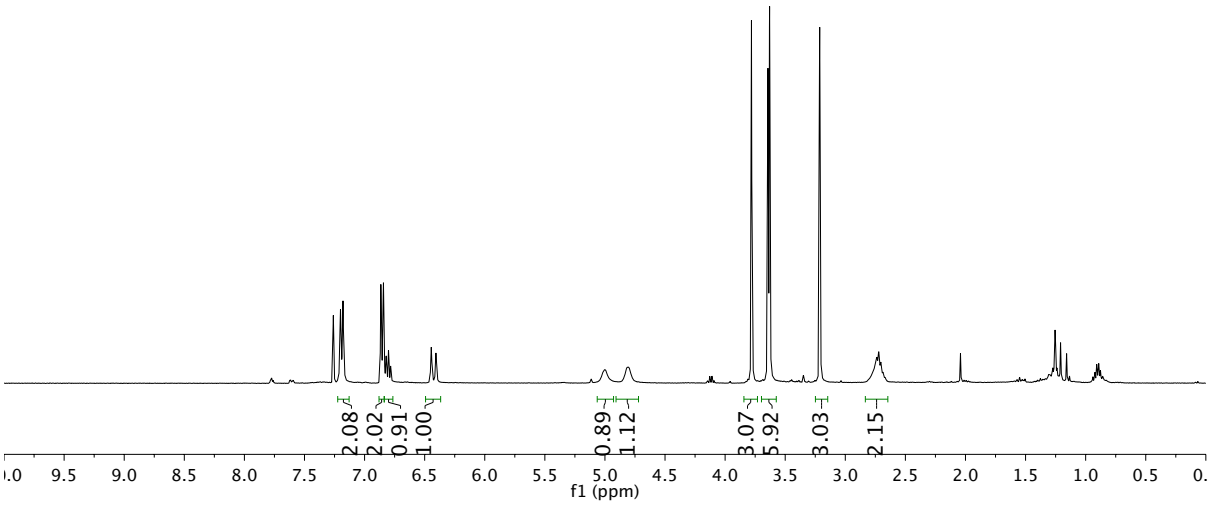


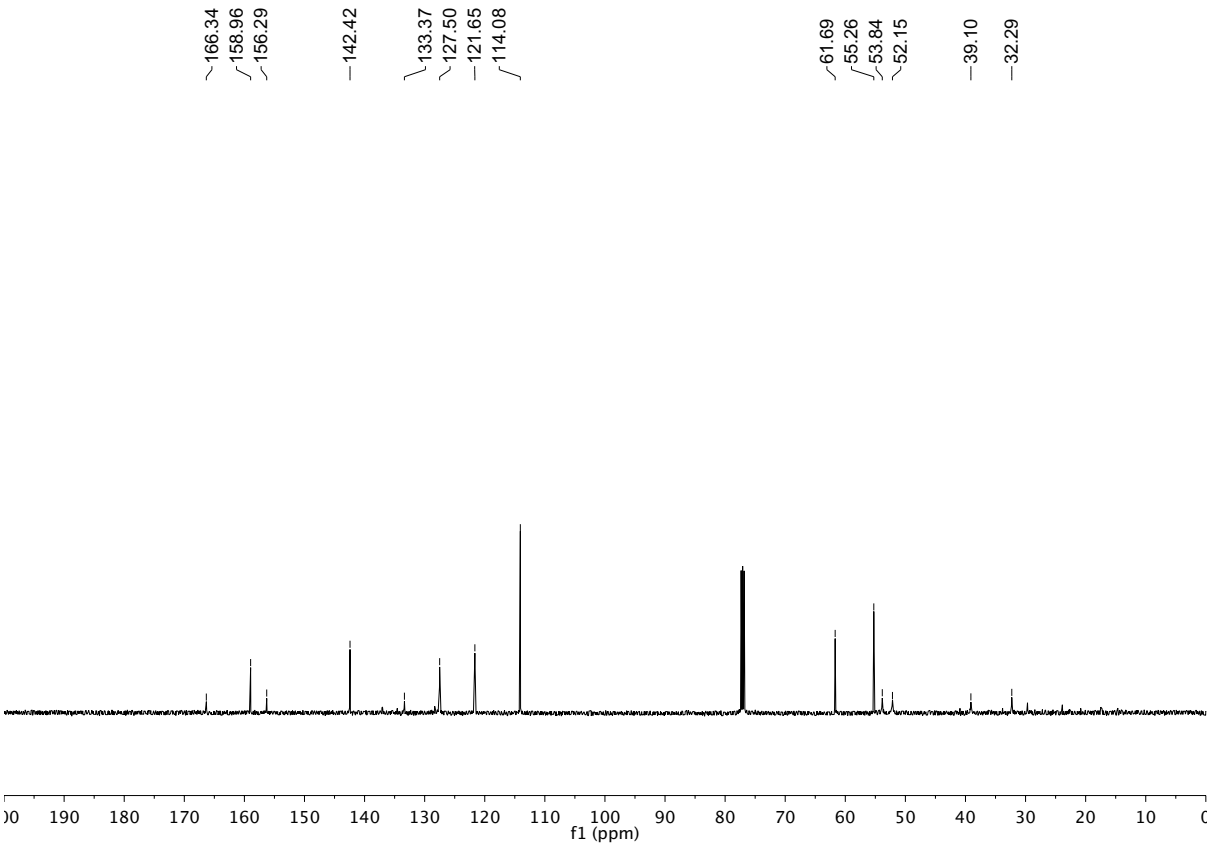
***tert*-Butyl (*R*,*E*)-5-((methoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-2-enoate (24)**



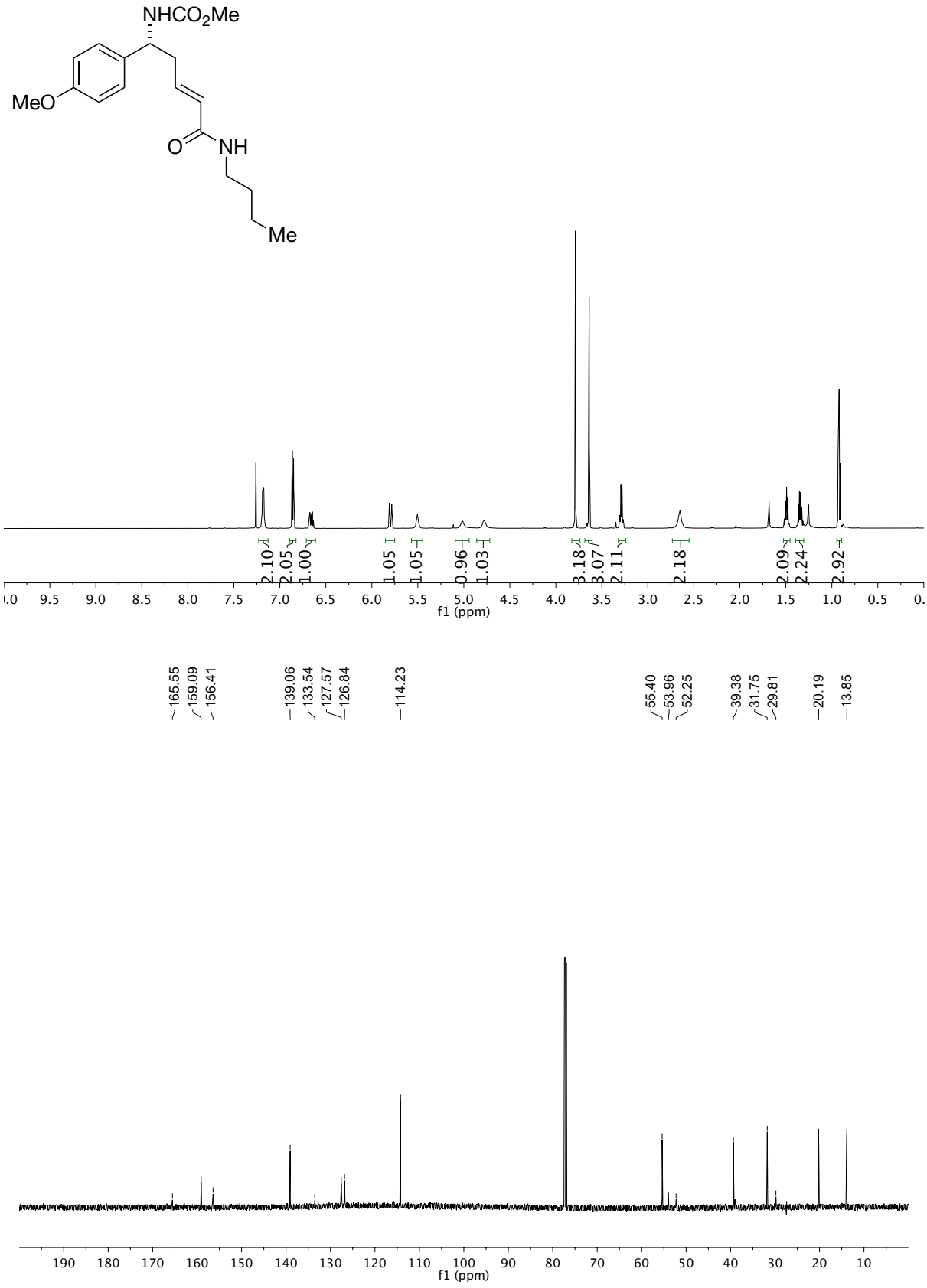
Methyl (*R*,*E*)-(5-(methoxy(methyl)amino)-1-(4-methoxyphenyl)-5-oxopent-3-en-1-yl)carbamate (25)



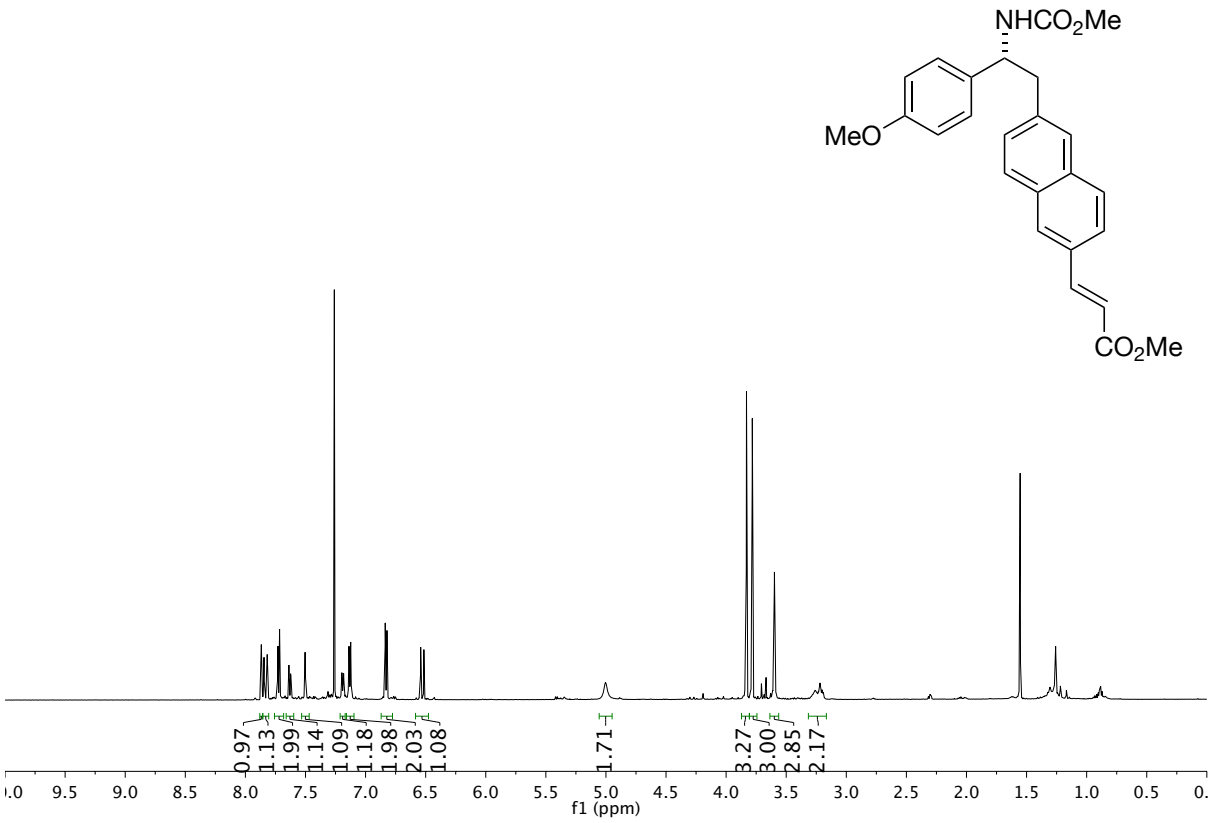


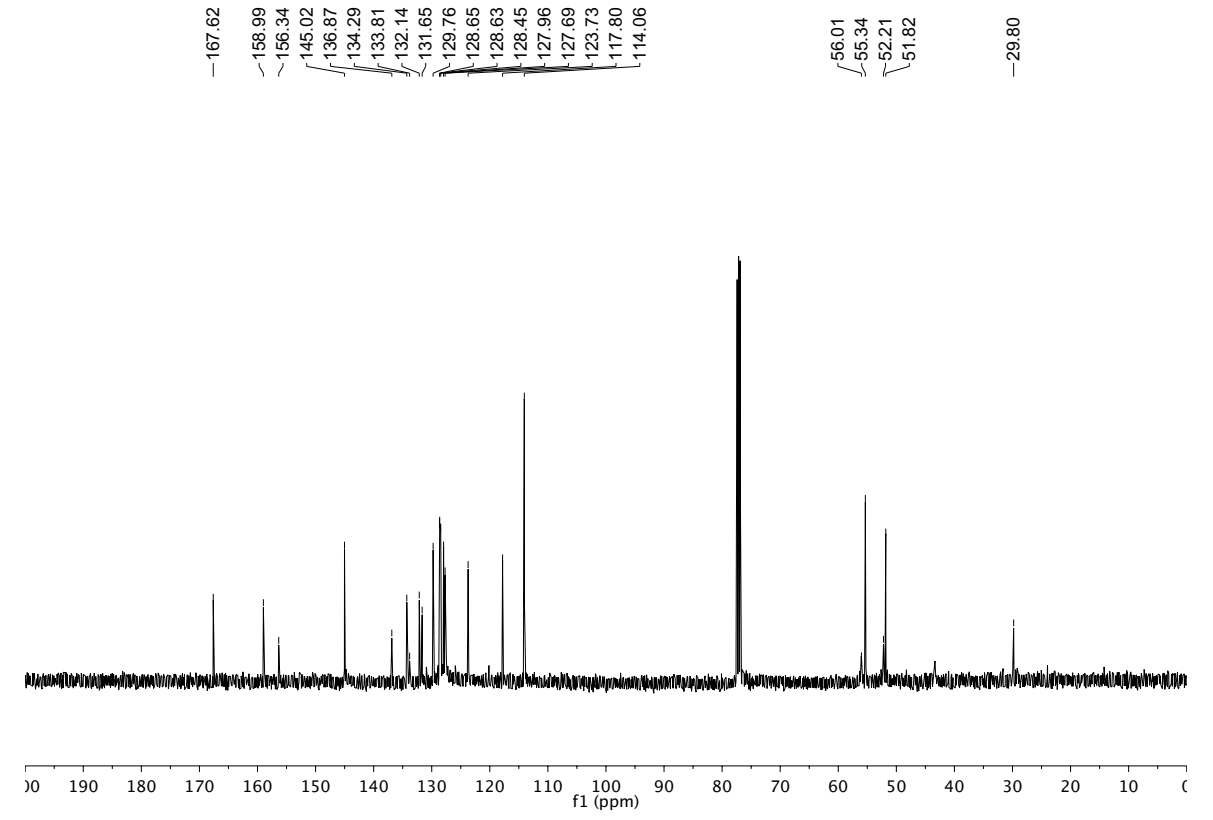


Methyl (*R*,*E*)-(5-(butylamino)-1-(4-methoxyphenyl)-5-oxopent-3-en-1-yl)carbamate (26)

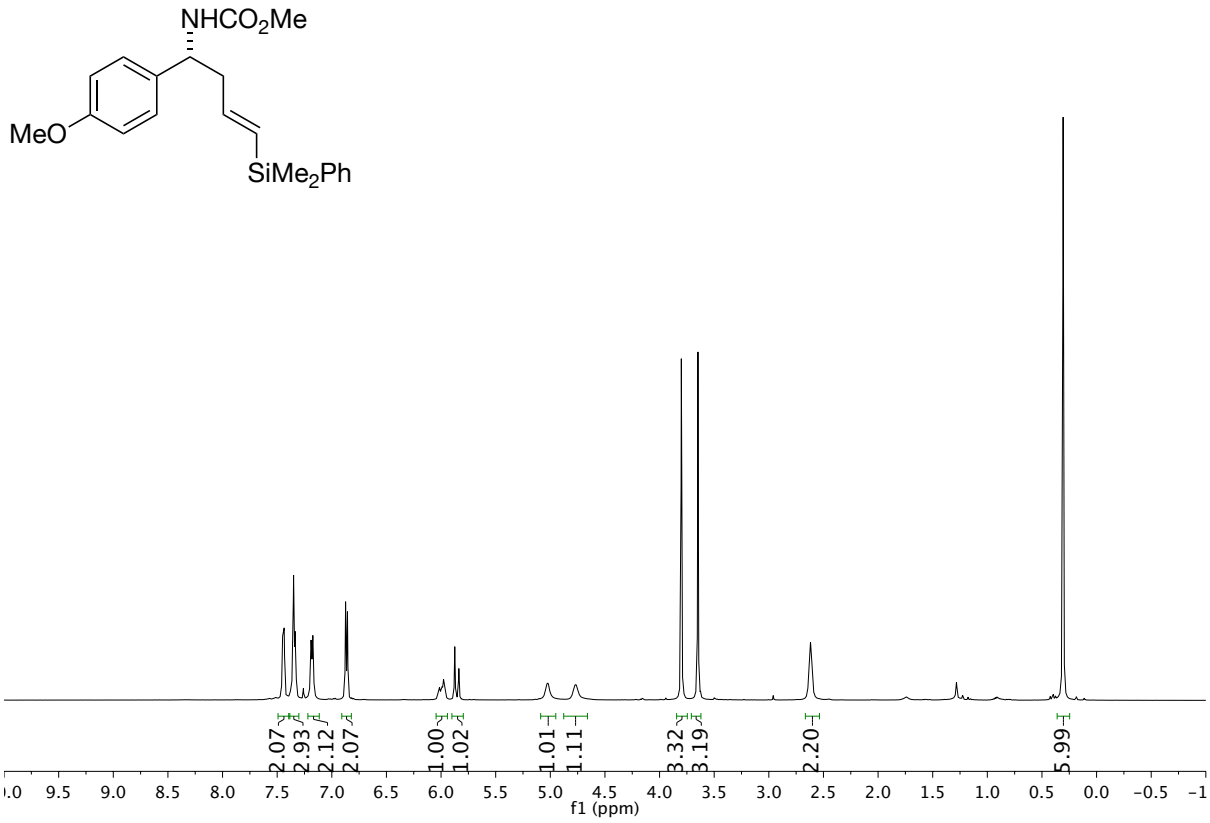


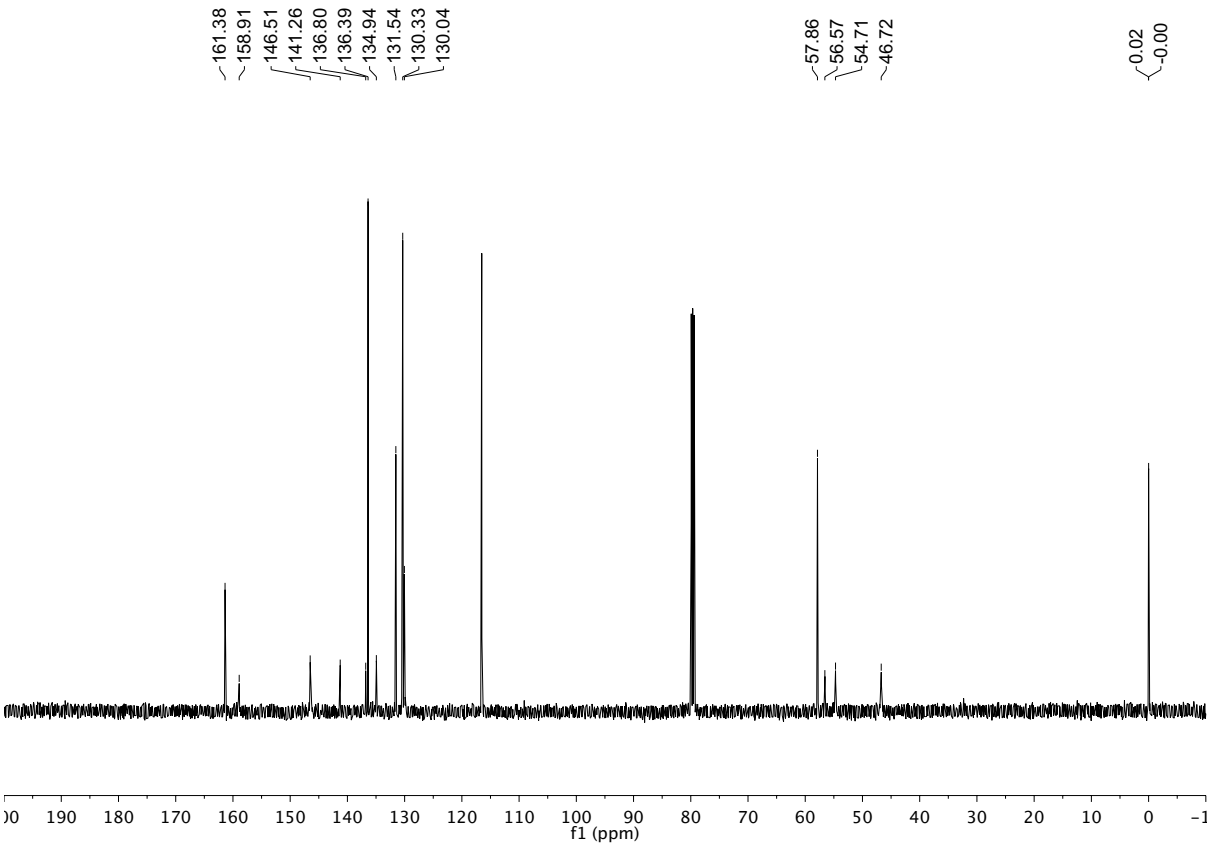
Methyl (*R*,*E*)-3-(6-(2-((methoxycarbonyl)amino)-2-(4-methoxyphenyl)ethyl)naphthalen-2-yl)acrylate (27)



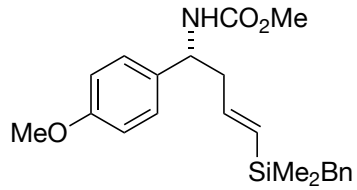


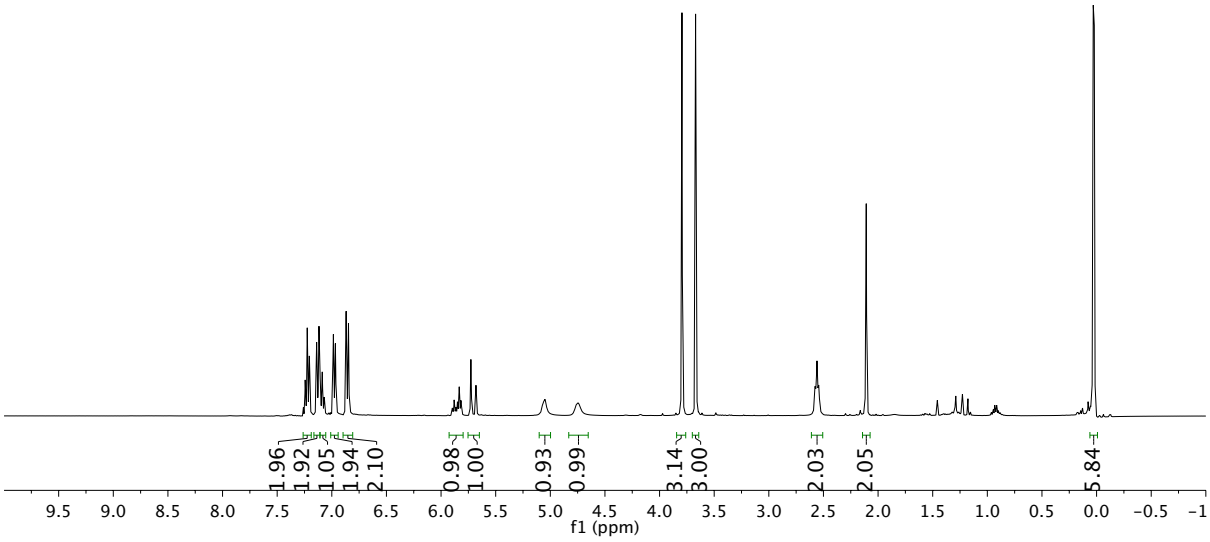
Methyl (*R*,*E*)-(4-(dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (28)

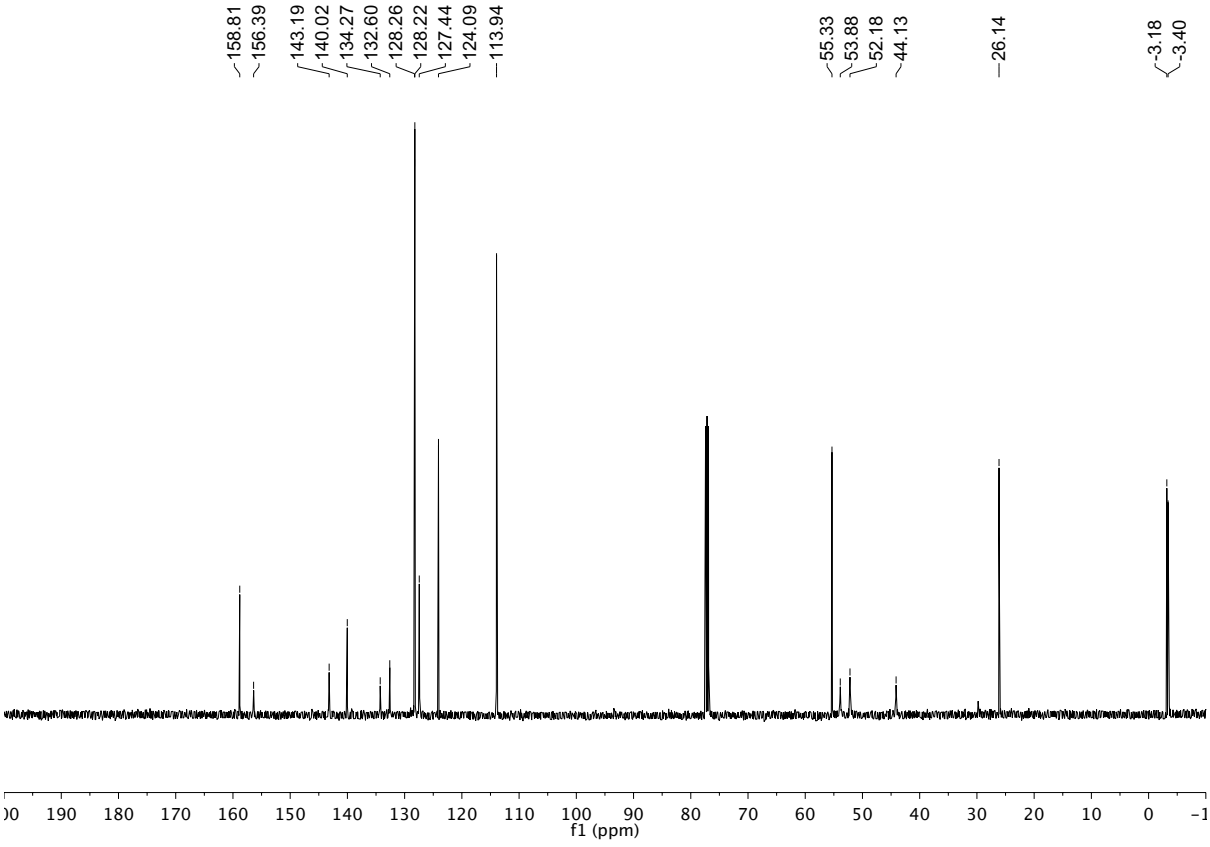




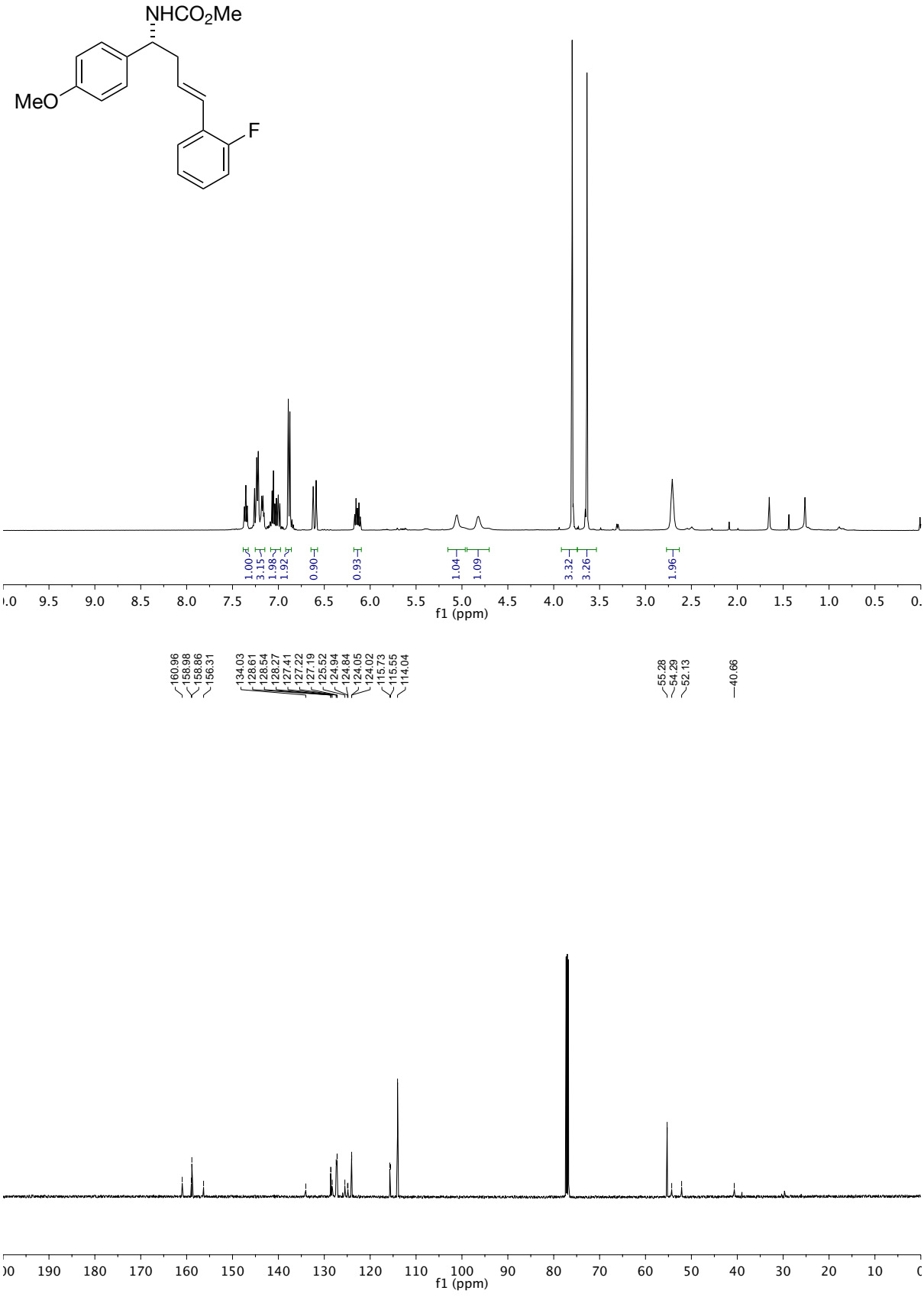
Methyl (*R*,*E*)-(4-(benzyldimethylsilyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (29)



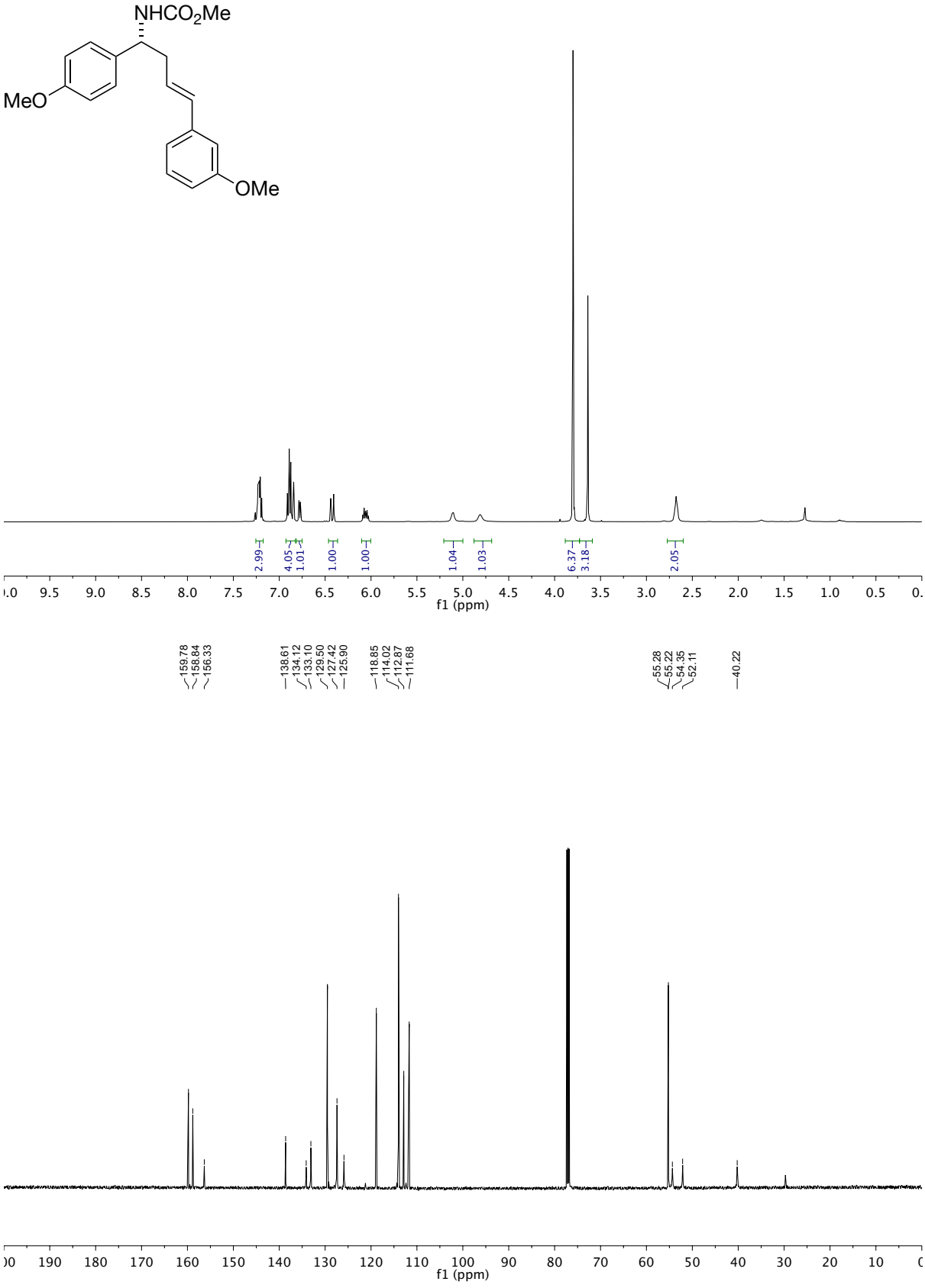




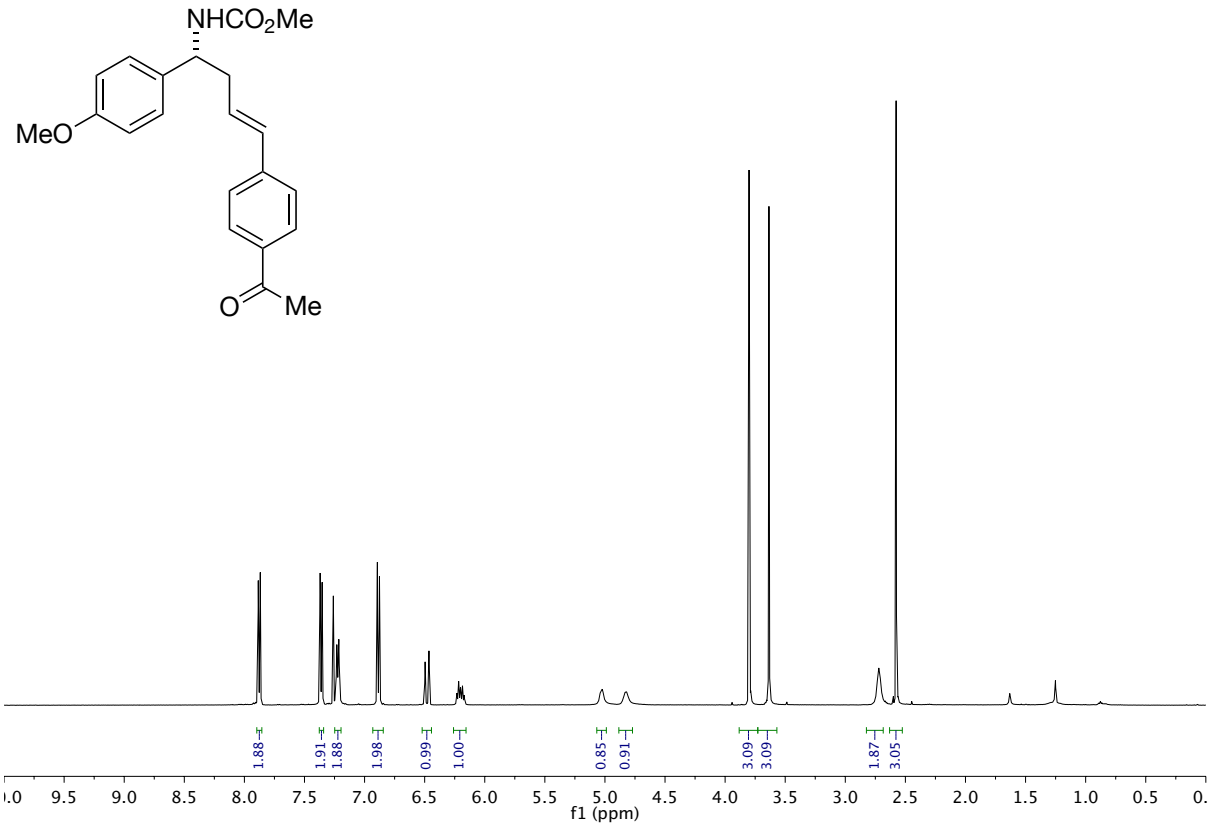
Methyl (*R*,*E*)-(4-(2-fluorophenyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (30)

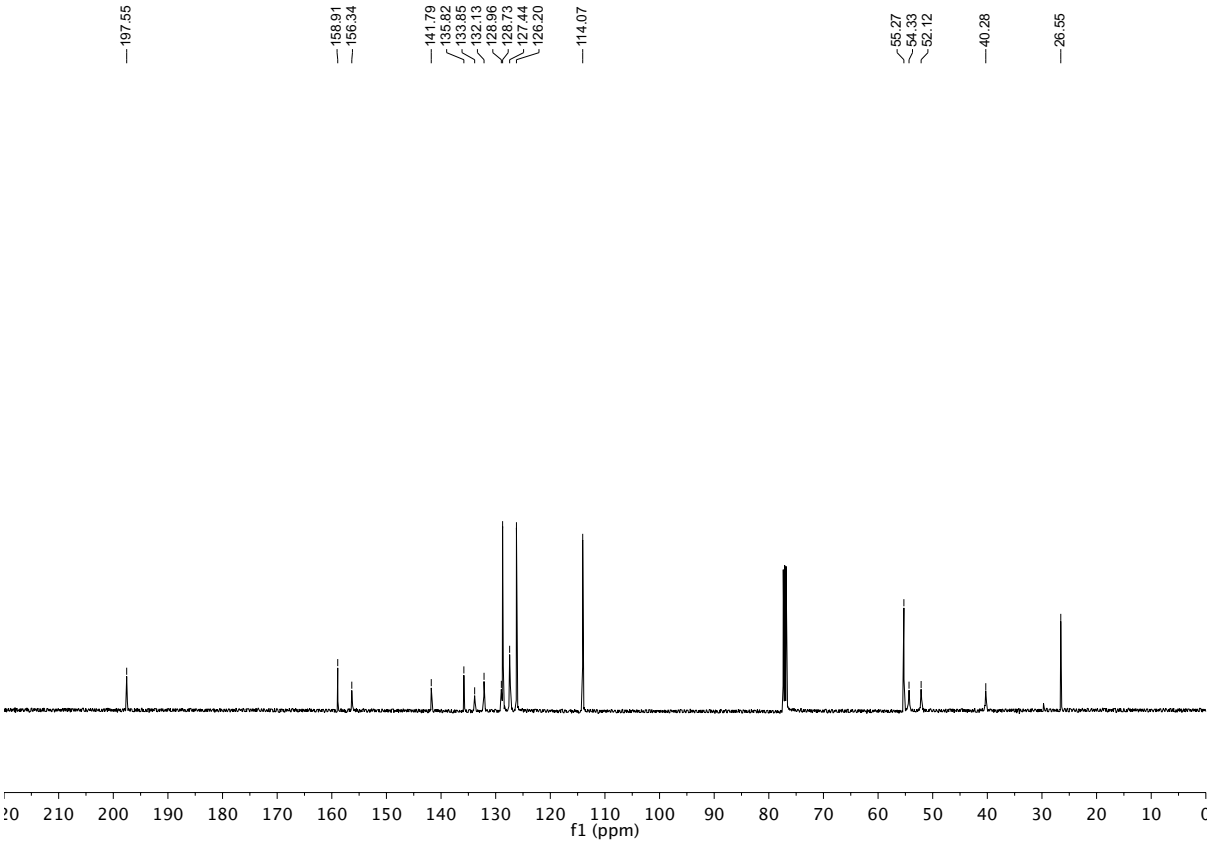


Methyl (*R*,*E*)-(4-(3-methoxyphenyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (31)

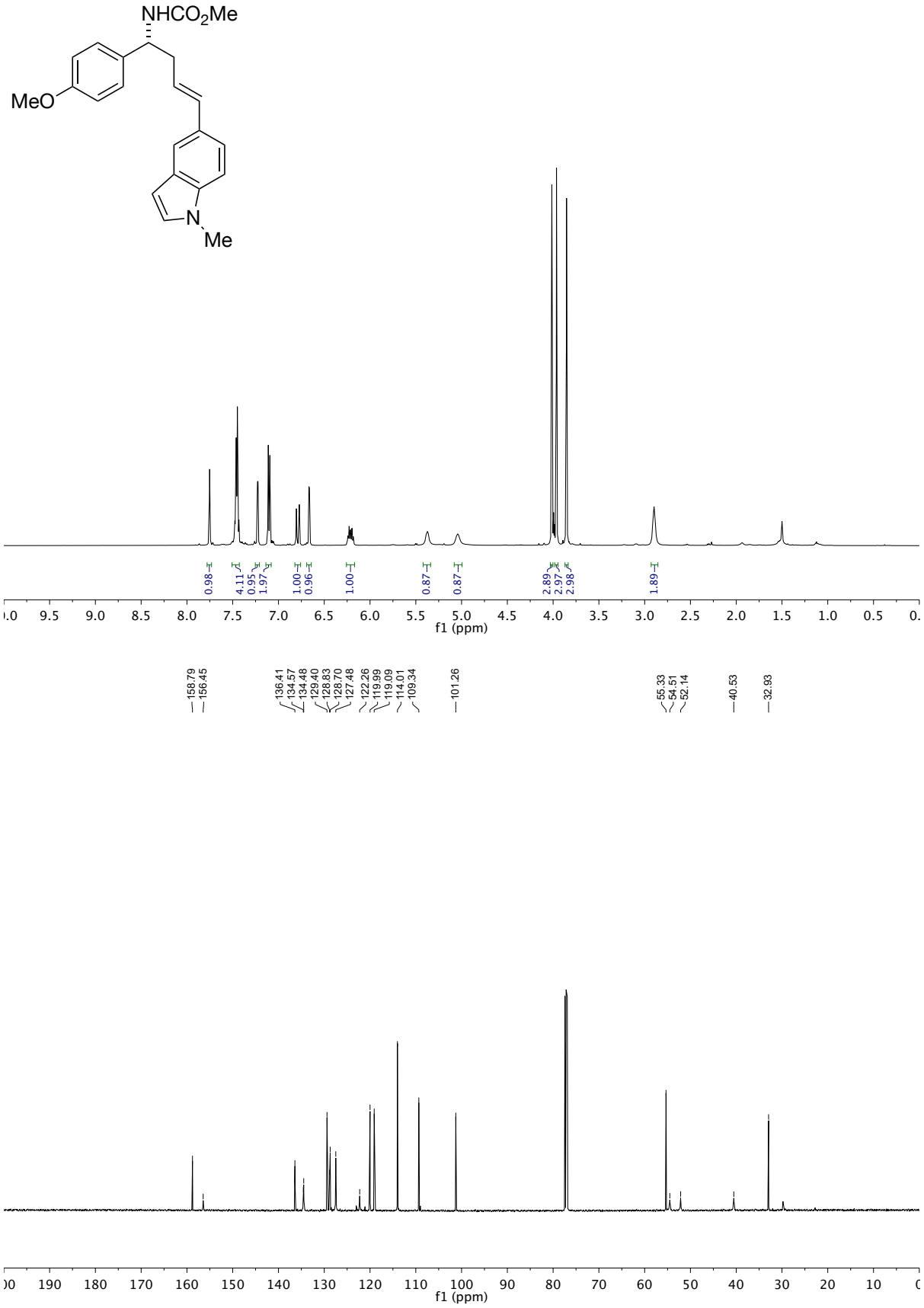


Methyl (*R*,*E*)-(4-(4-acetylphenyl)-1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (32)

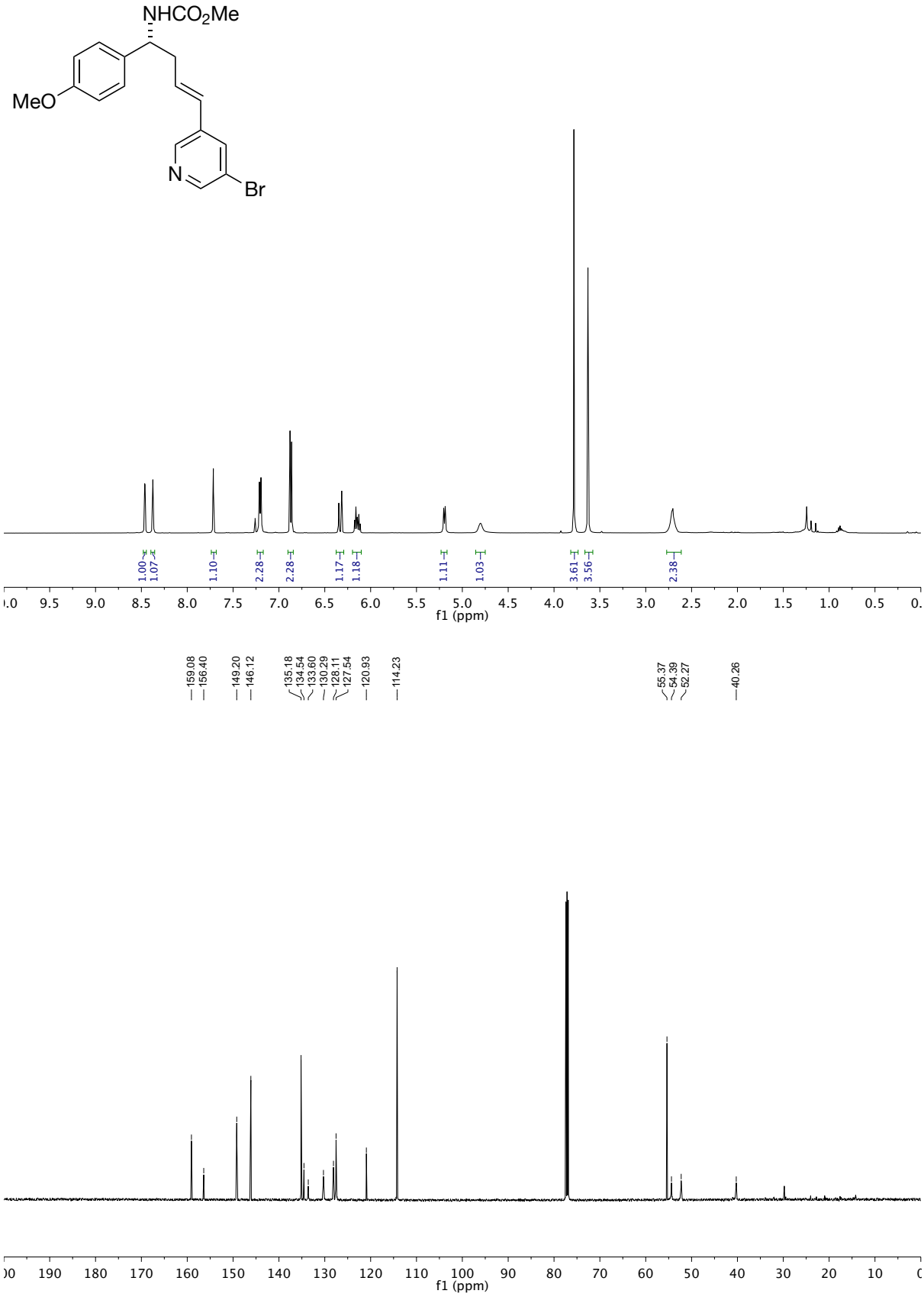




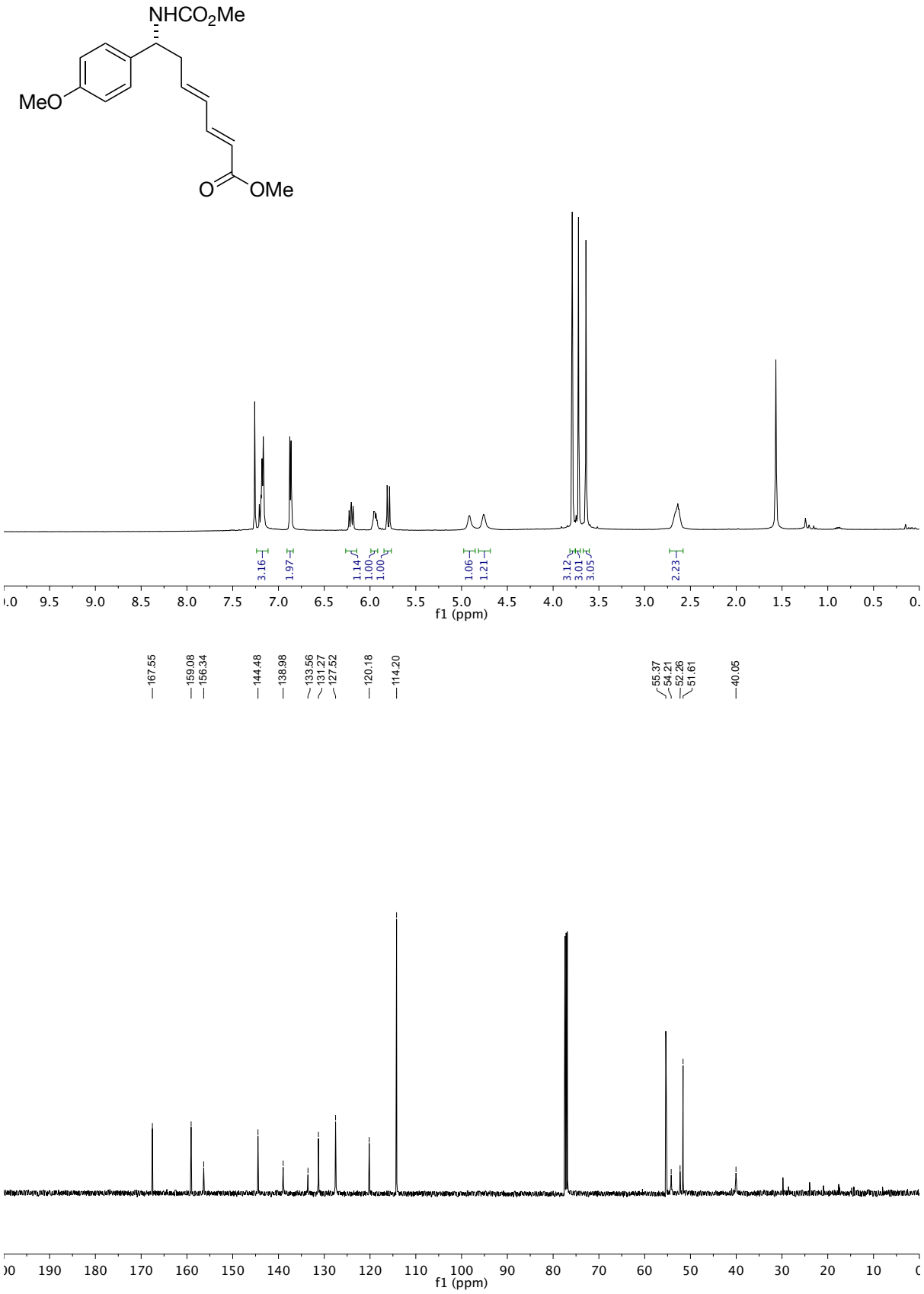
Methyl (*R*,*E*)-(1-(4-methoxyphenyl)-4-(1-methyl-1*H*-indol-5-yl)but-3-en-1-yl)carbamate (33)



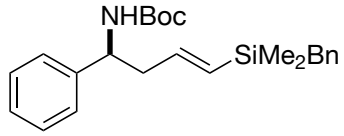
Methyl (*R*,*E*)-(1-(4-methoxyphenyl)-4-(1-methyl-1*H*-indol-5-yl)but-3-en-1-yl)carbamate (34)

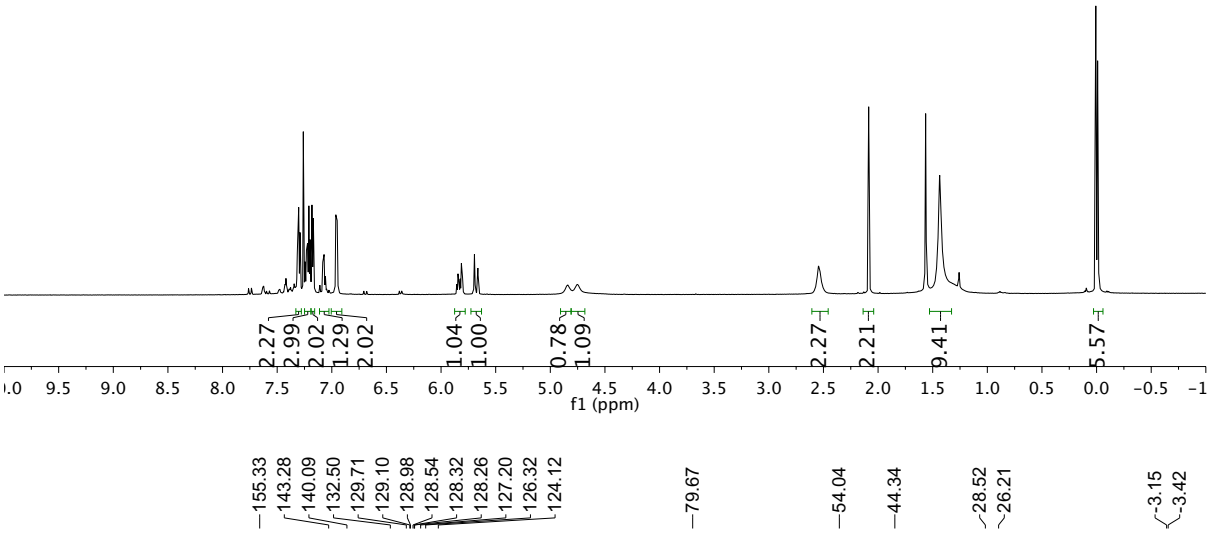


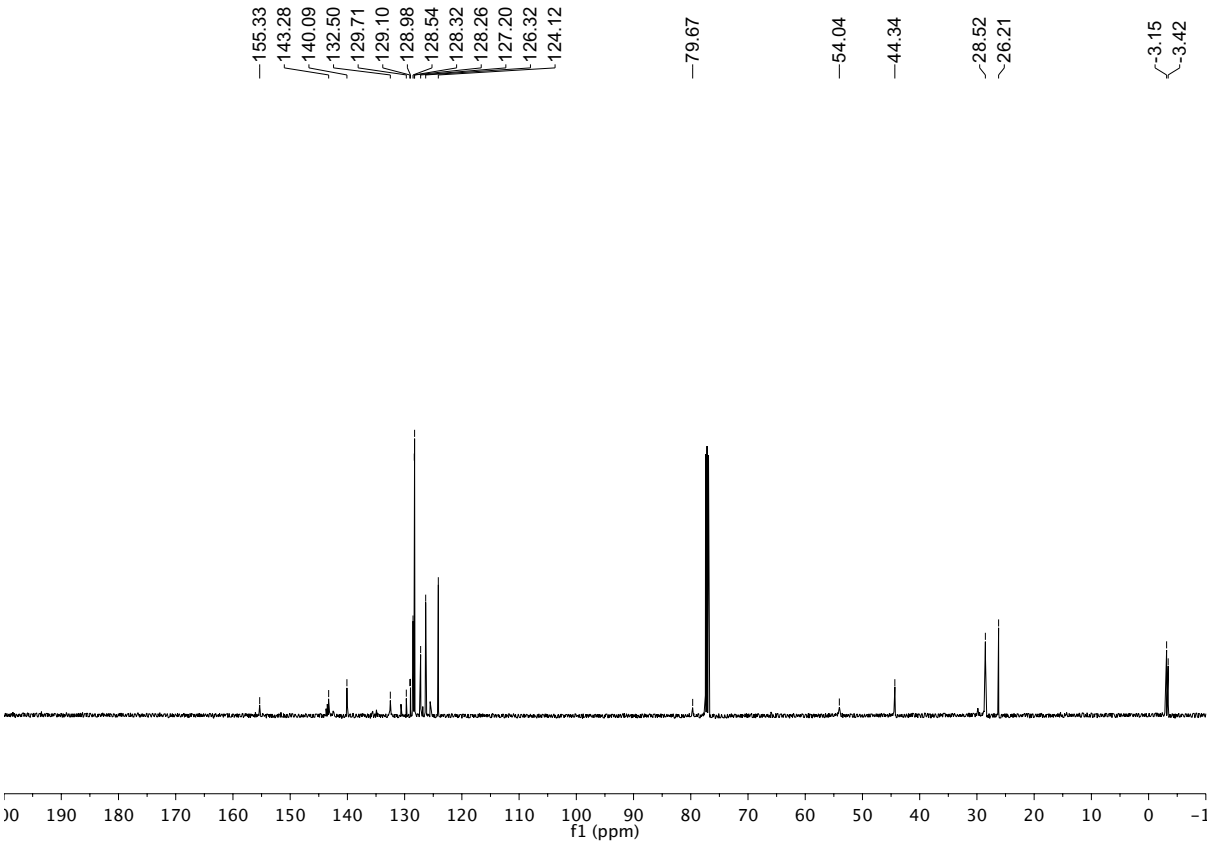
Methyl (*R*,2*E*,4*E*)-7-((methoxycarbonyl)amino)-7-(4-methoxyphenyl)hepta-2,4-dienoate (35)



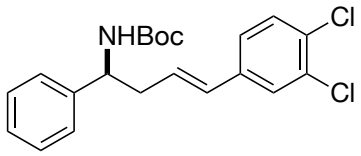
***tert*-Butyl (*S*,*E*)-(4-(benzyldimethylsilyl)-1-phenylbut-3-en-1-yl)carbamate (36)**

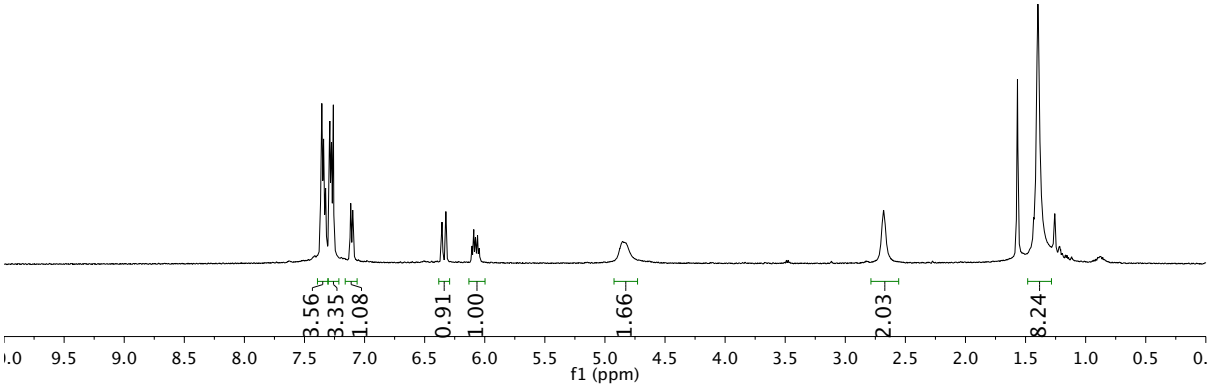


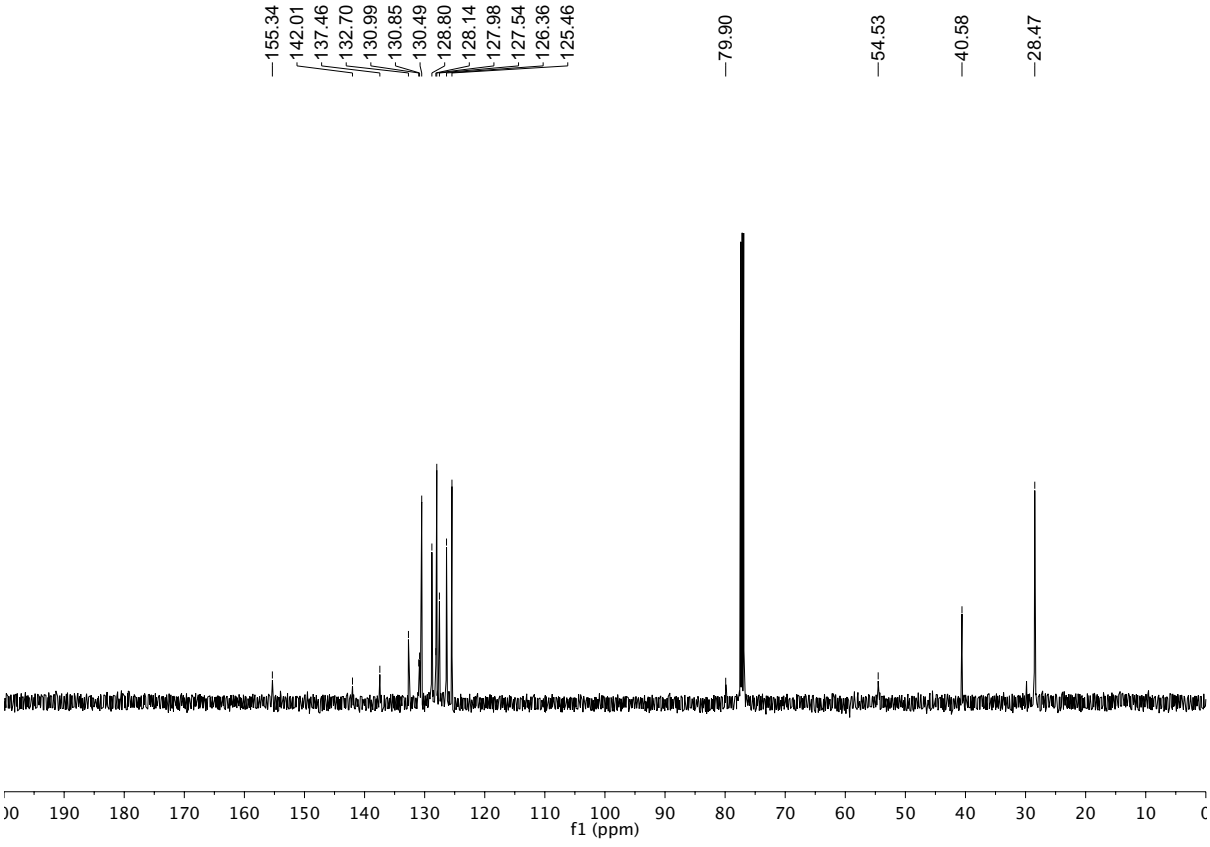




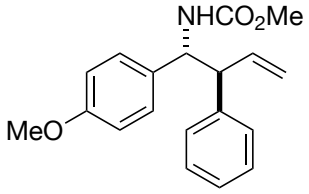
***tert*-Butyl (*S*,*E*)-(4-(3,4-dichlorophenyl)-1-phenylbut-3-en-1-yl)carbamate (37)**

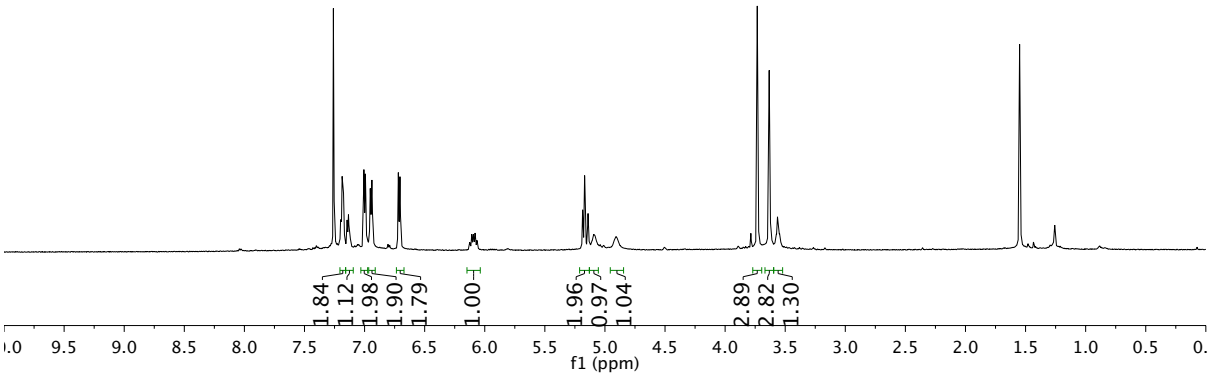


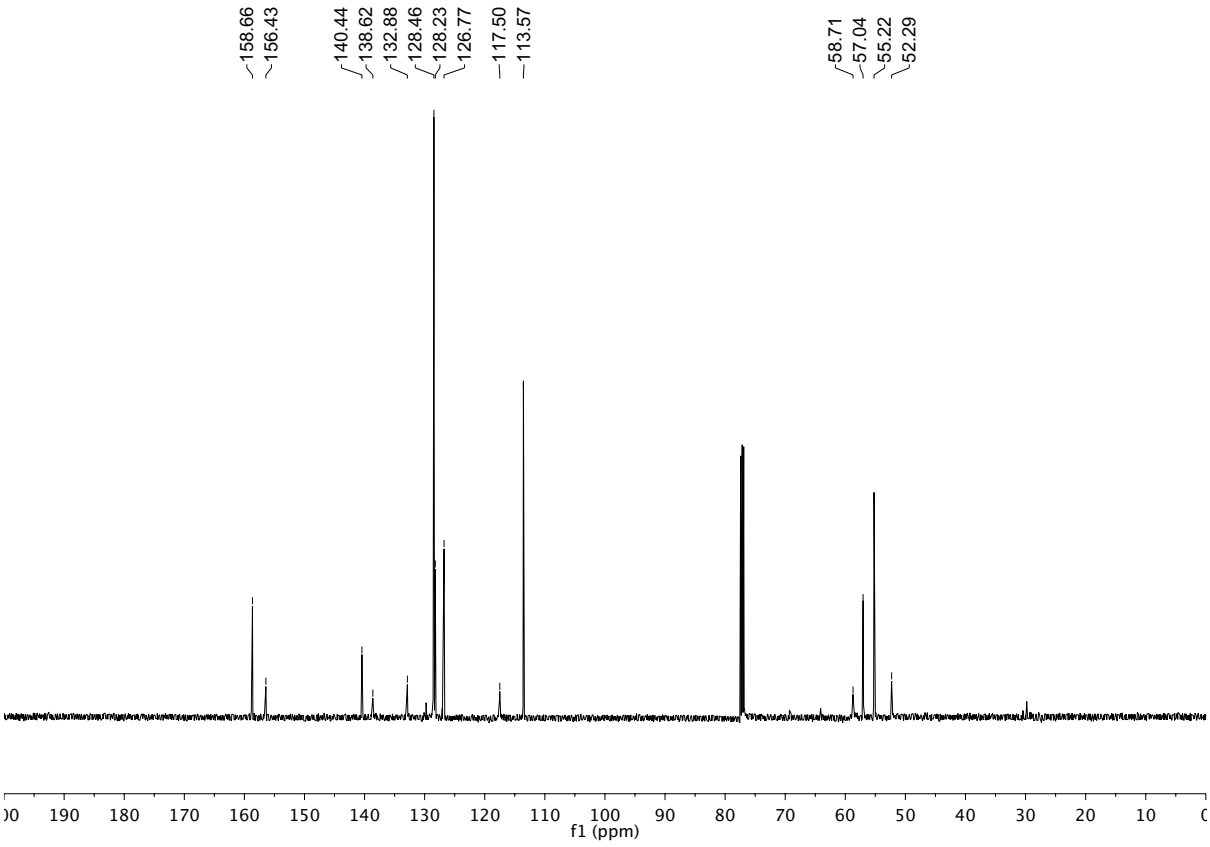




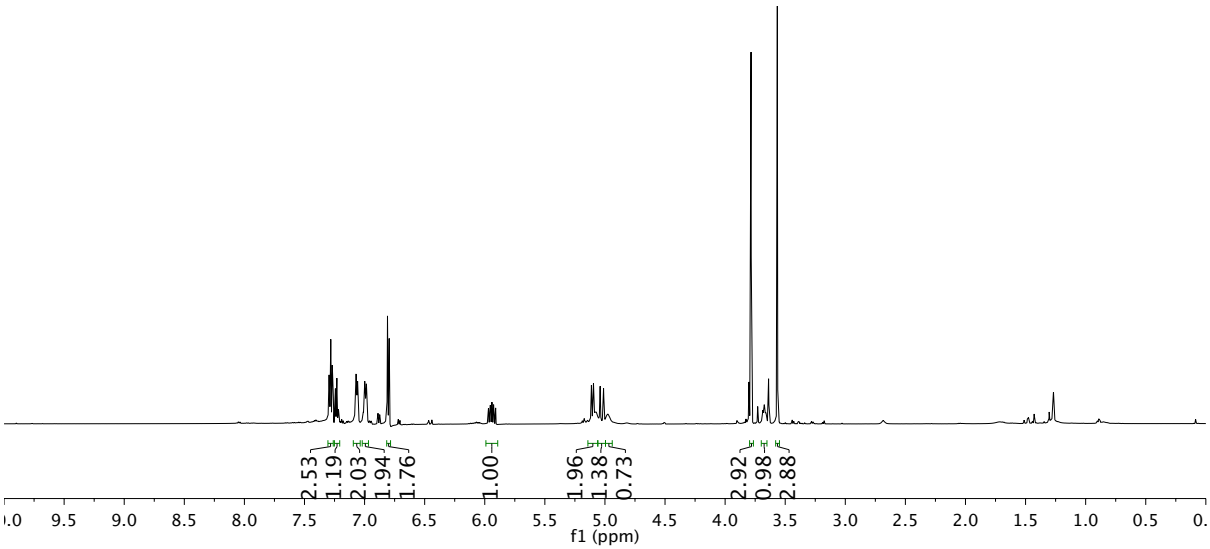
Methyl ((1*R*,2*S*)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)carbamate ((1*R*,2*S*)-39)



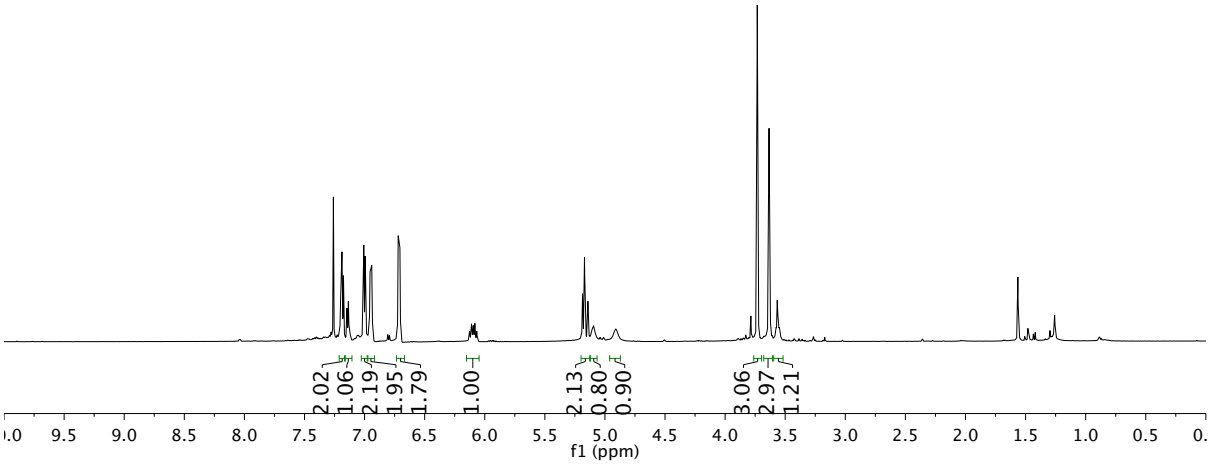




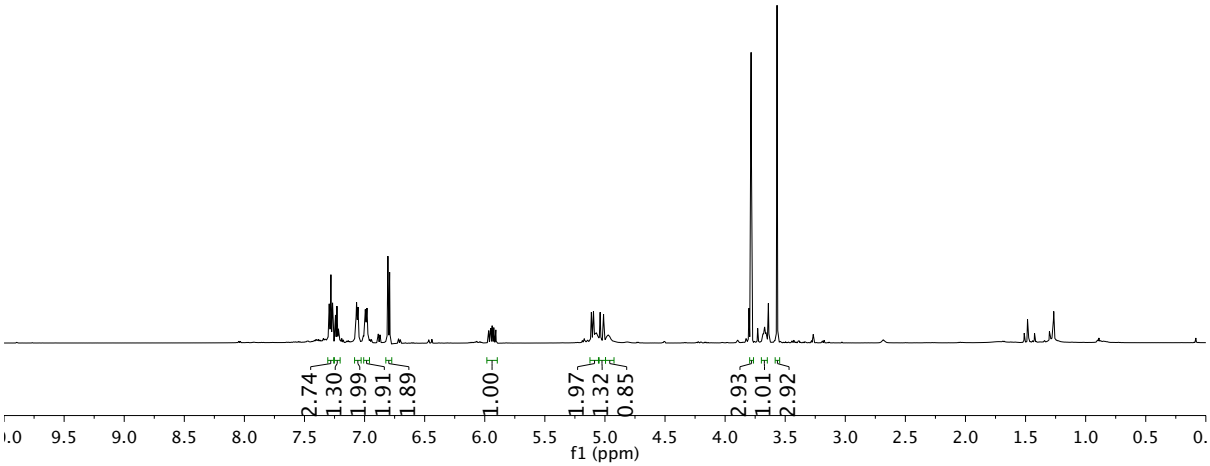
Methyl ((1*R*,2*R*)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)carbamate ((1*R*,2*R*)-39)



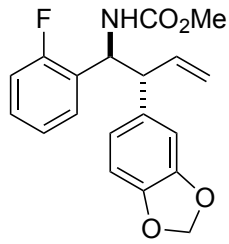
Methyl ((1*S*,2*R*)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)carbamate ((1*S*,2*R*)-39)

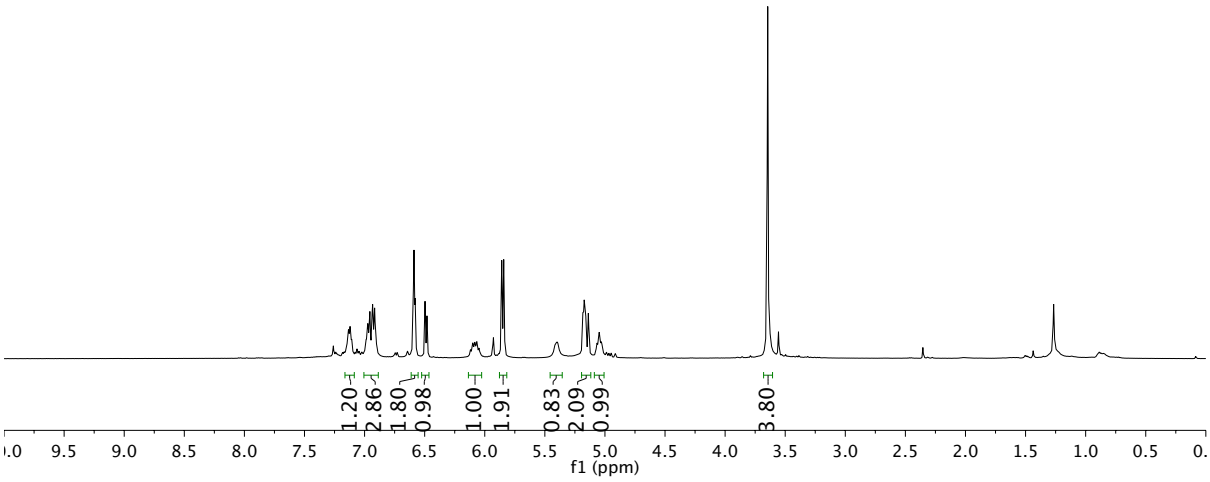


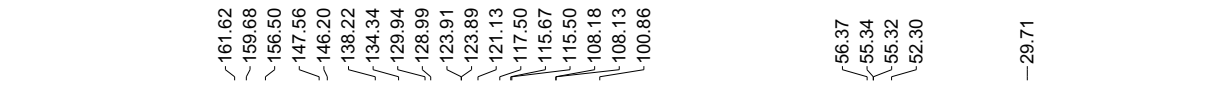
Methyl ((1*S*,2*S*)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)carbamate ((1*S*,2*S*)-39)

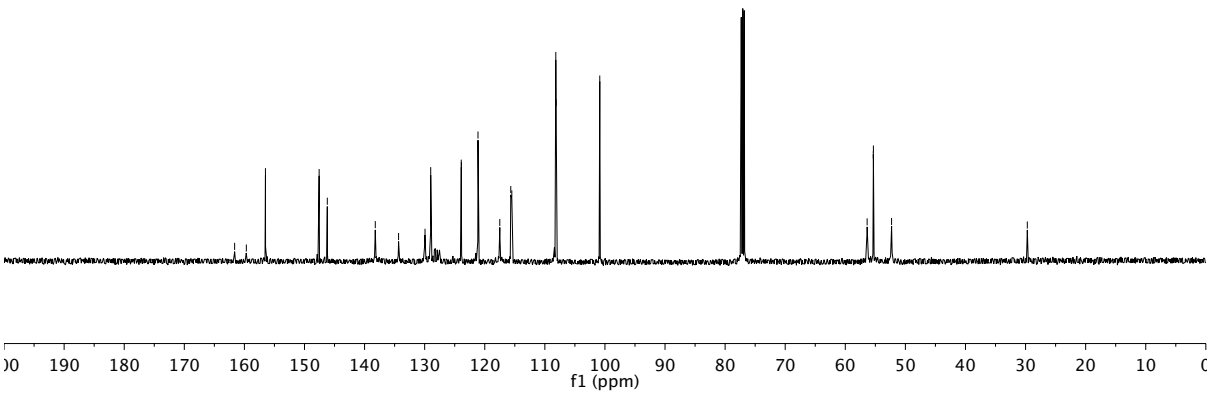


Methyl ((1*S*,2*R*)-2-(benzo[*d*][1,3]dioxol-5-yl)-1-(2-fluorophenyl)but-3-en-1-yl)carbamate (*anti*-40)

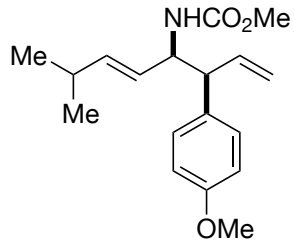


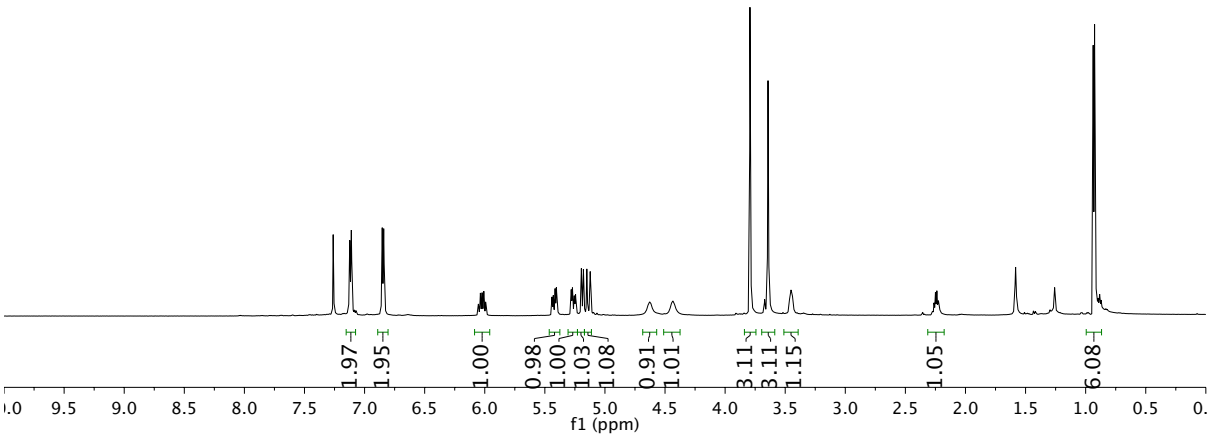


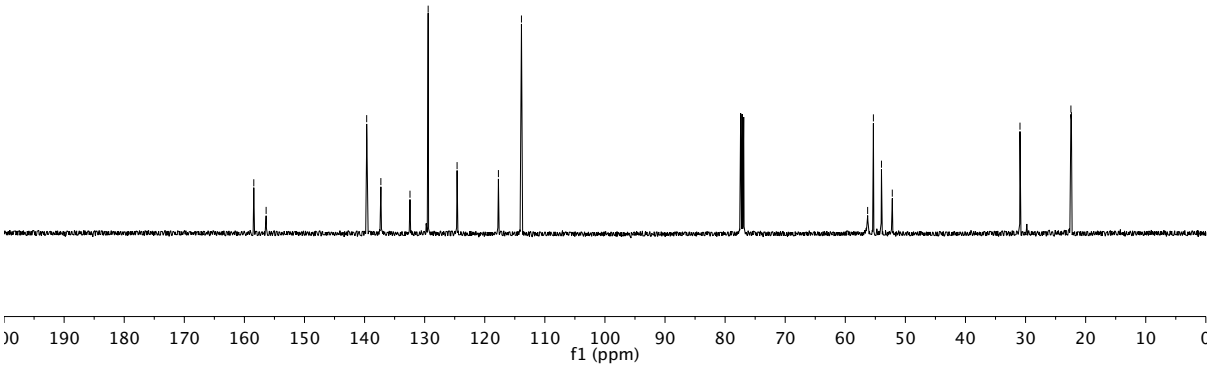




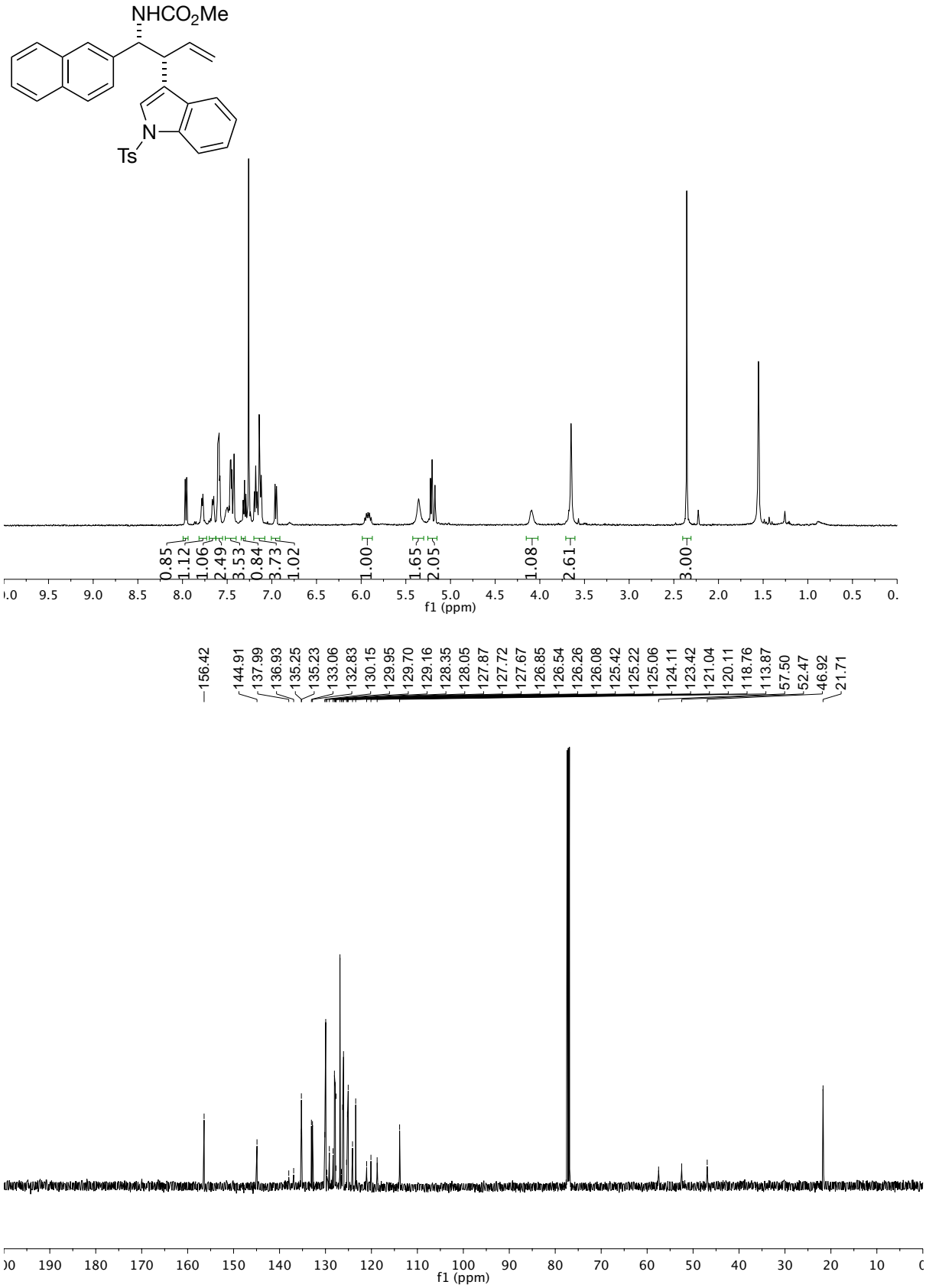
Methyl ((3*S*,4*R*,*E*)-3-(4-methoxyphenyl)-7-methylocta-1,5-dien-4-yl)carbamate (*syn*-41)



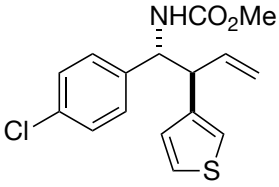


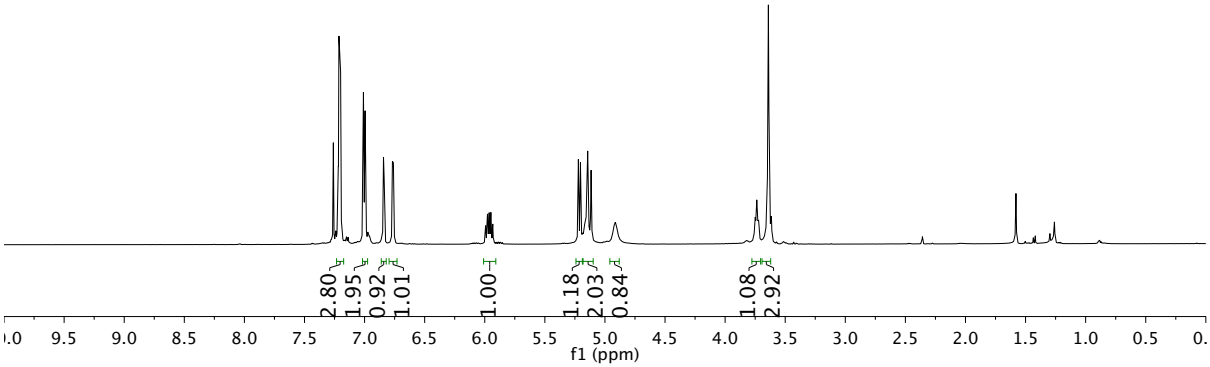


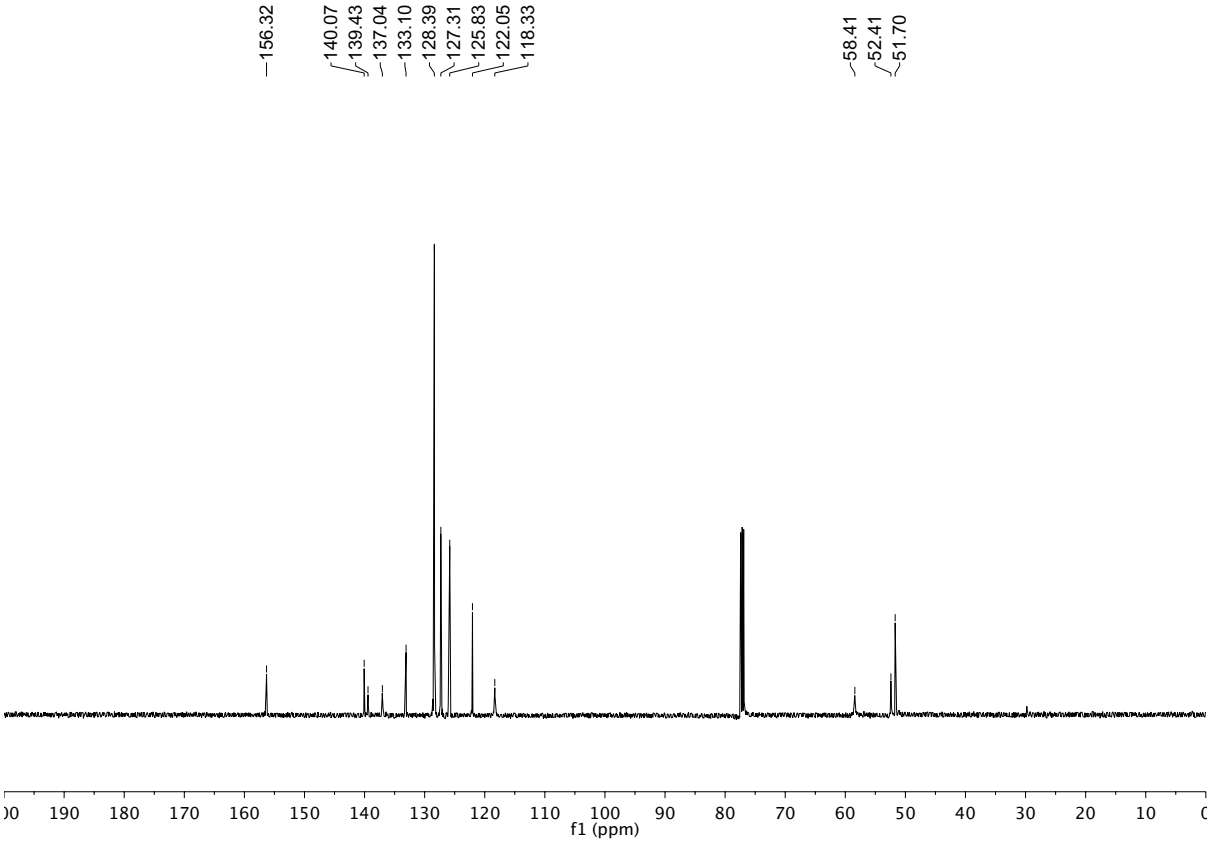
Methyl ((1*R*,2*R*)-1-(naphthalen-2-yl)-2-(1-tosyl-1*H*-indol-3-yl)but-3-en-1-yl)carbamate (*syn*-42)



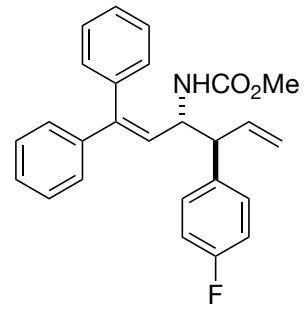
Methyl ((1*R*,2*S*)-1-(4-chlorophenyl)-2-(thiophen-3-yl)but-3-en-1-yl)carbamate (*anti*-43)

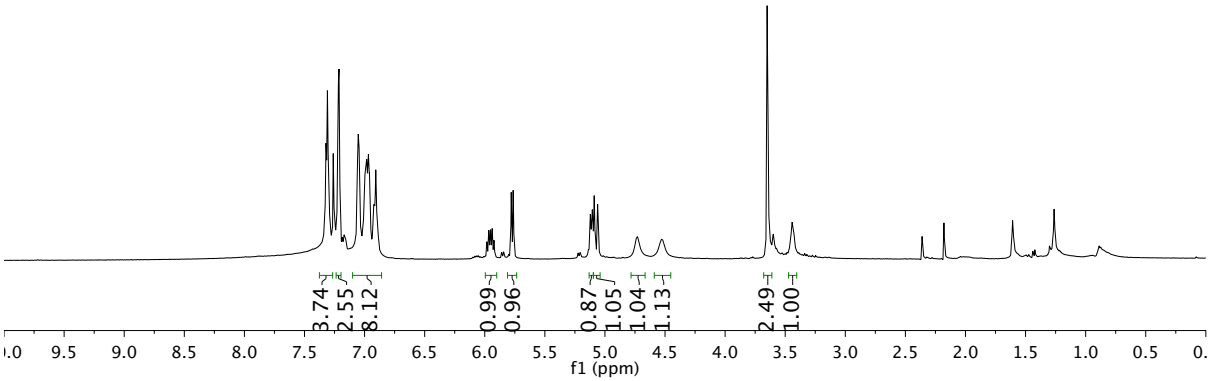


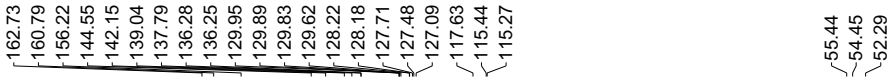


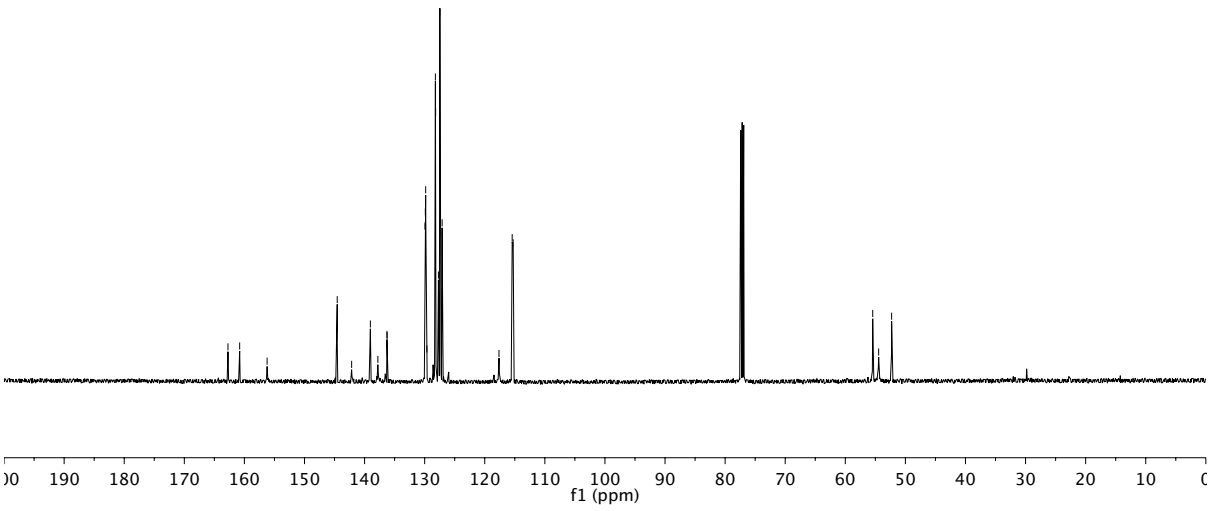


Methyl ((3*S*,4*S*)-4-(4-fluorophenyl)-1,1-diphenylhexa-1,5-dien-3-yl)carbamate (*anti*-44)

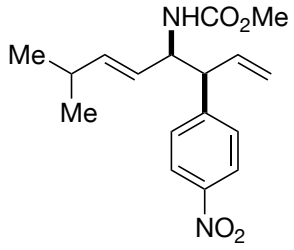


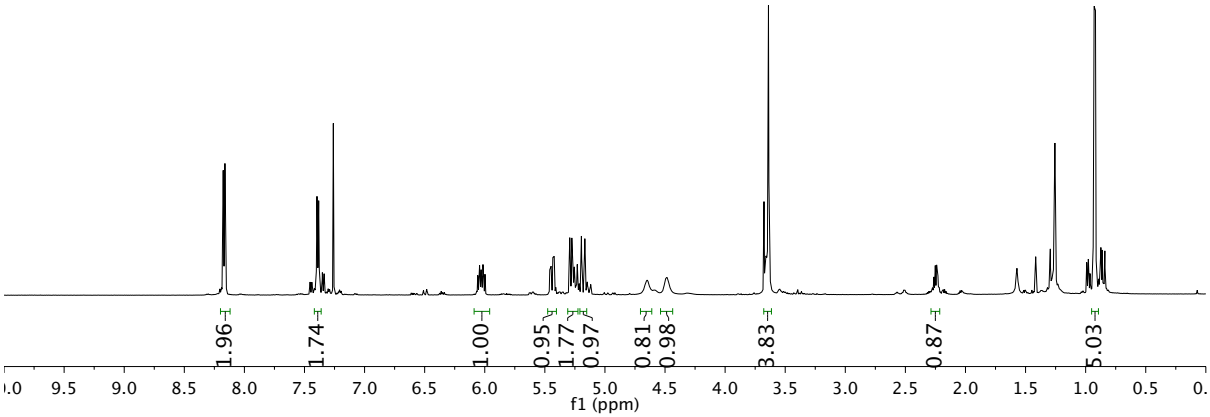


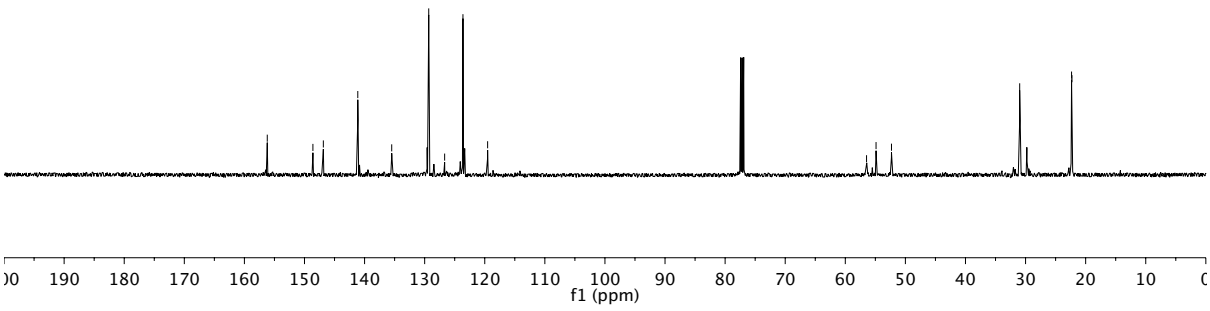




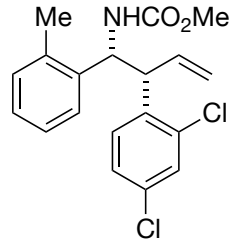
Methyl ((3*S*,4*R*,*E*)-7-methyl-3-(4-nitrophenyl)octa-1,5-dien-4-yl)carbamate (*syn*-45)

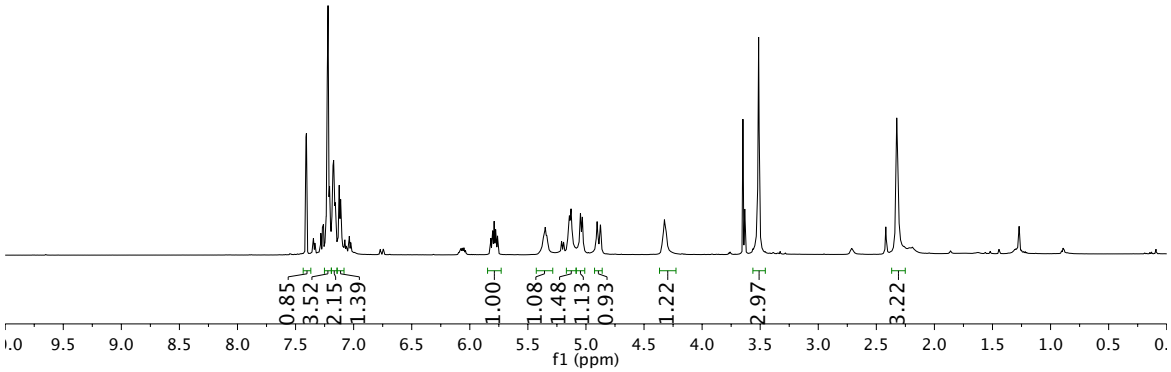


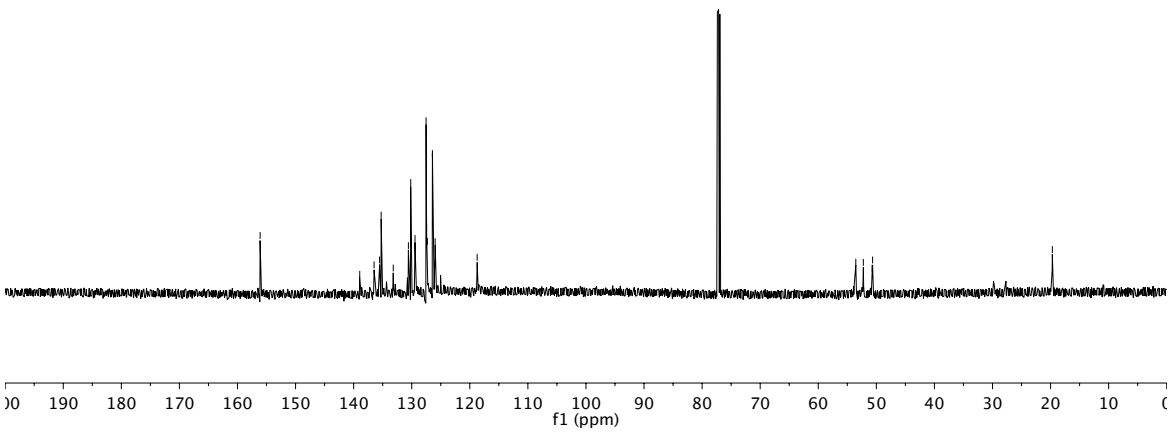




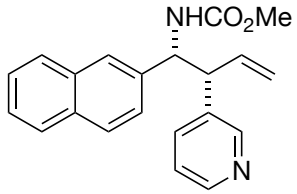
Methyl ((1*R*,2*R*)-2-(2,4-dichlorophenyl)-1-(*o*-tolyl)but-3-en-1-yl)carbamate (*syn*-46)

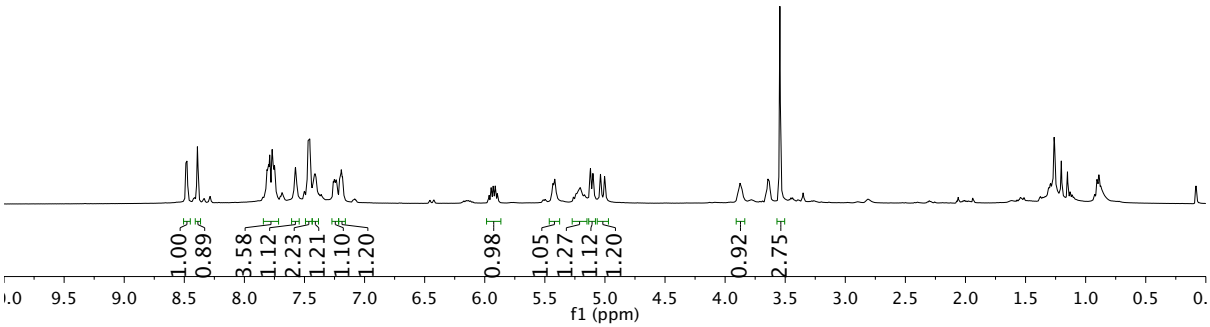


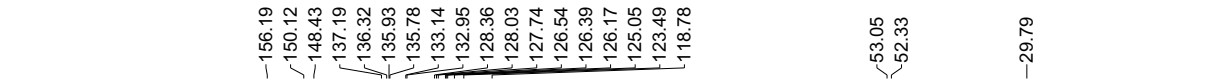


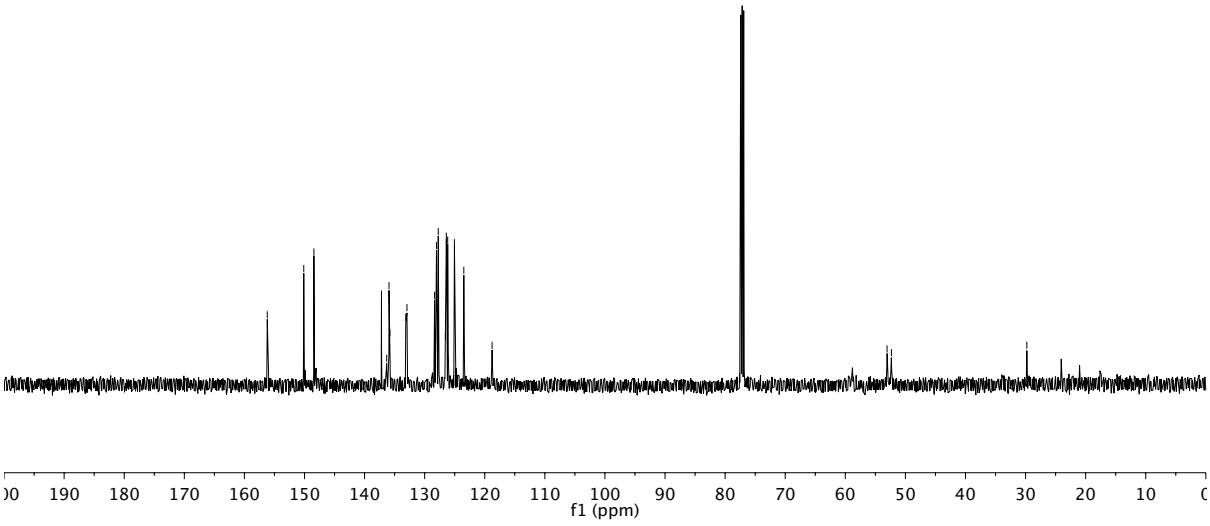


Methyl ((1*R*,2*R*)-1-(naphthalen-2-yl)-2-(pyridin-3-yl)but-3-en-1-yl)carbamate (*syn*-47)

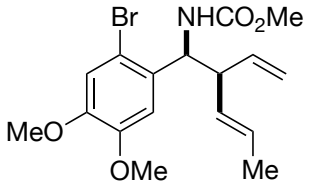


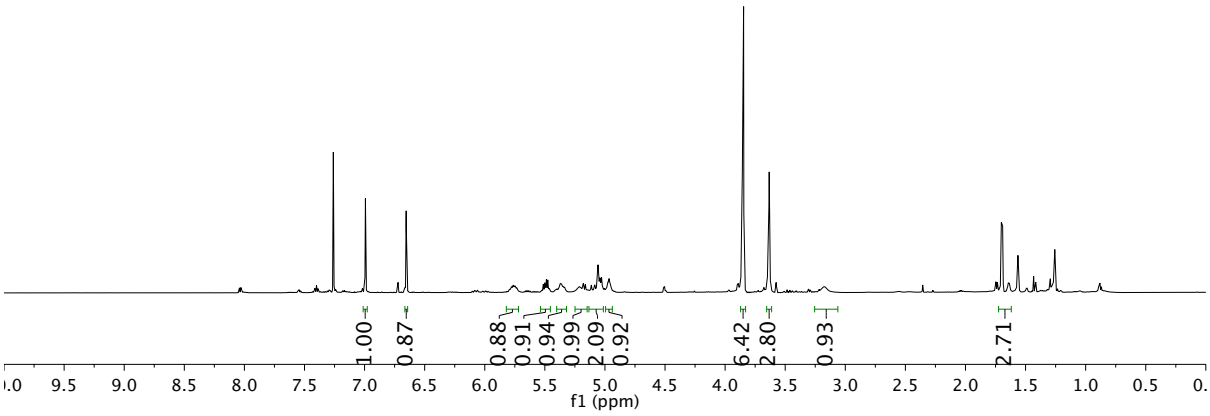


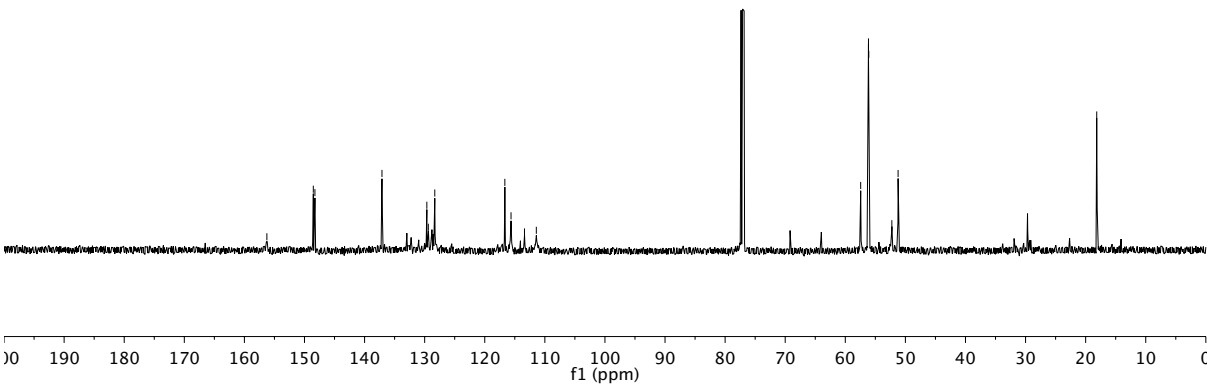




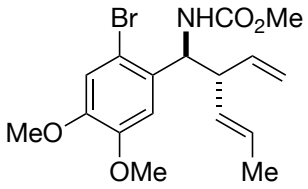
Methyl ((1*S*,2*S*,*E*)-1-(2-bromo-4,5-dimethoxyphenyl)-2-vinylpent-3-en-1-yl)carbamate (*syn*-48)

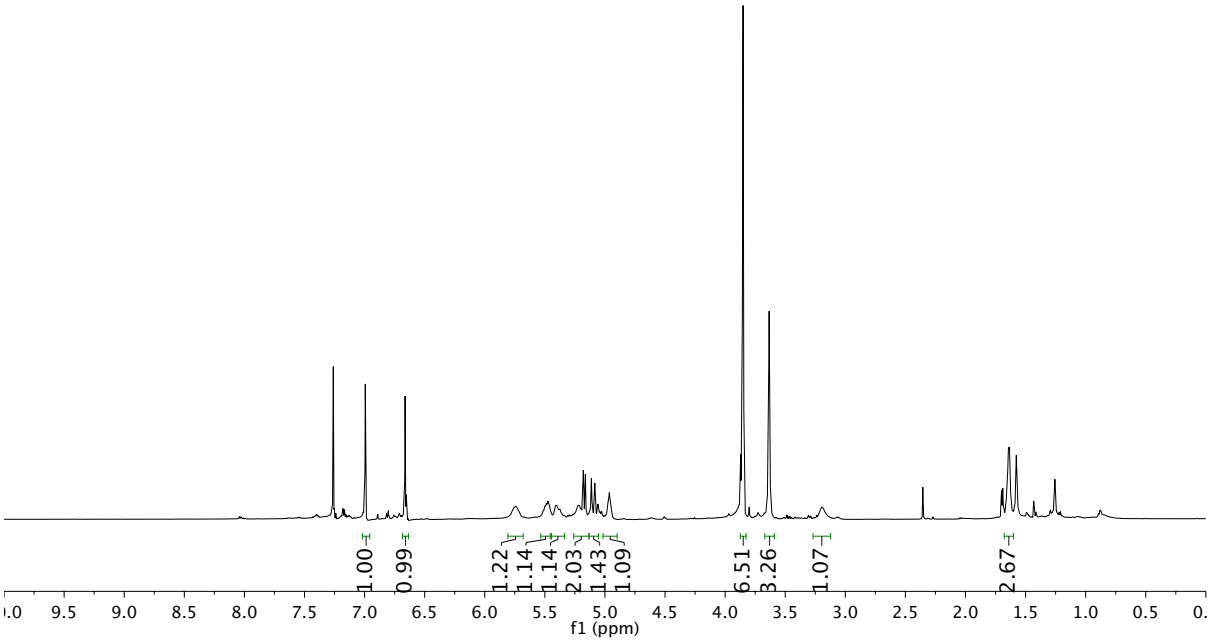


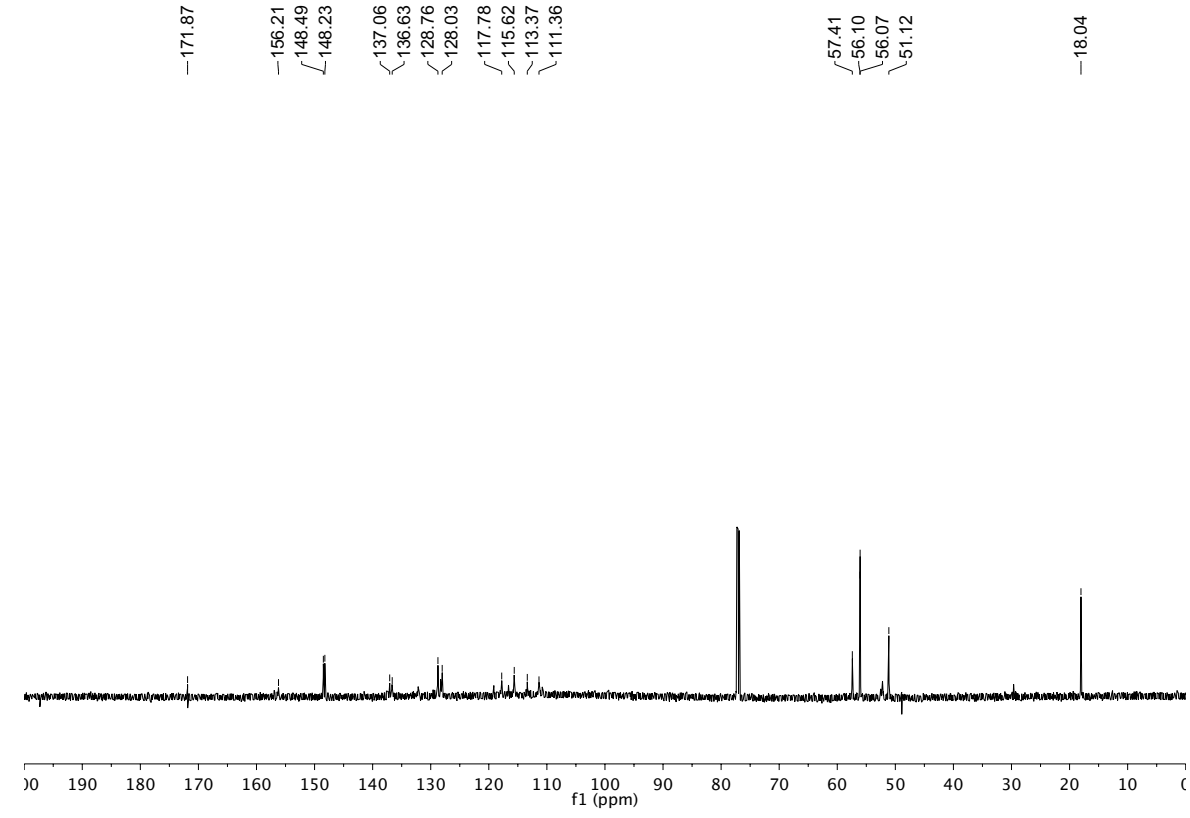




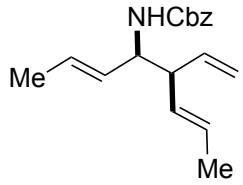
Methyl ((1*S*,2*R*,*E*)-1-(2-bromo-4,5-dimethoxyphenyl)-2-vinylpent-3-en-1-yl)carbamate (*anti*-48)

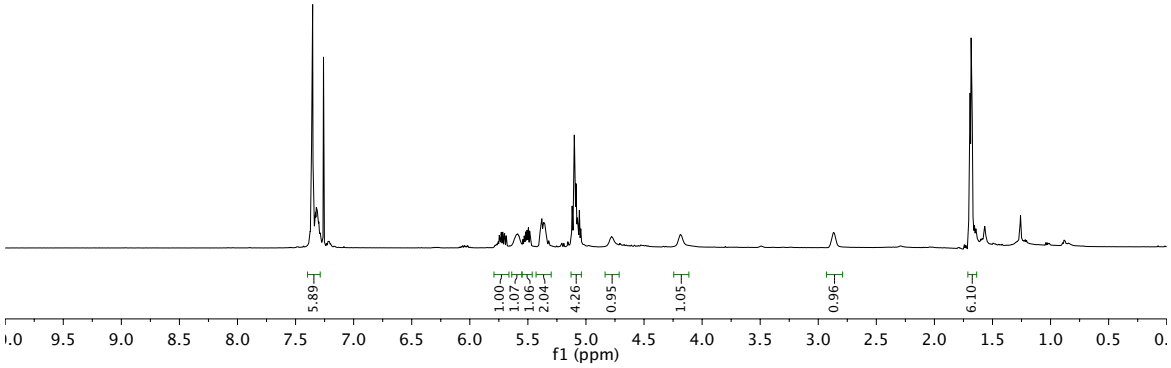


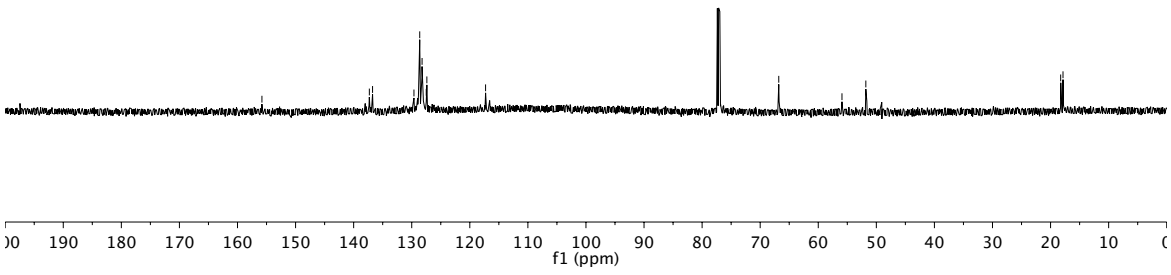




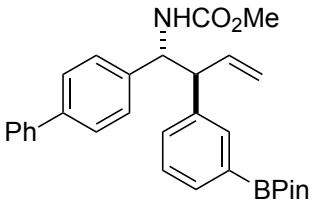
Benzyl ((2*E*,4*R*,5*S*,6*E*)-5-vinylocta-2,6-dien-4-yl)carbamate (*syn*-49)

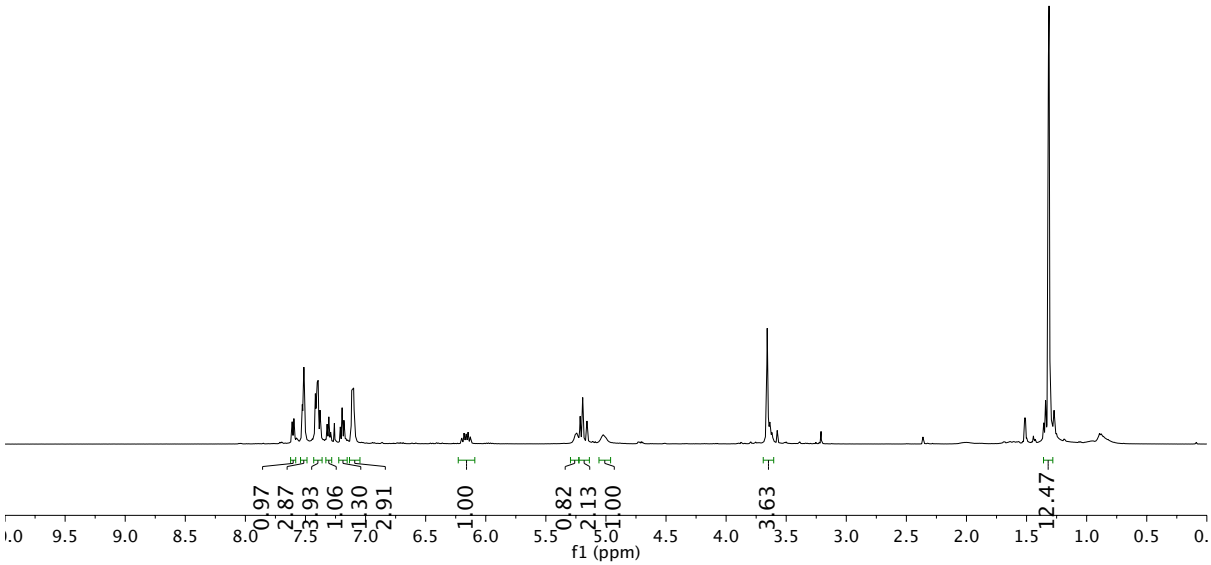


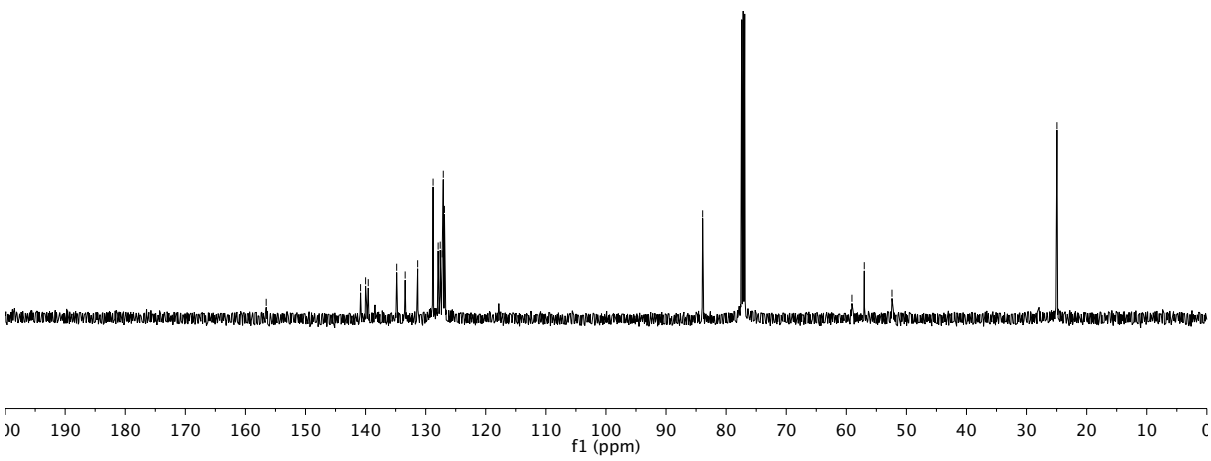




Methyl ((1*R*,2*S*)-1-([1,1'-biphenyl]-4-yl)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-1-yl)carbamate (*anti*-50)







2-(Trimethylsilyl)ethyl ((1*S*,2*R*)-2-(3-chlorophenyl)-1-(4-chlorophenyl)but-3-en-1-yl)carbamate (53)