Cr-Catalyzed Chiral Allenone Synthesis via Sequential Radical-Polar Crossover and Oppenauer Oxidation

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Supporting Information

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I. General Information

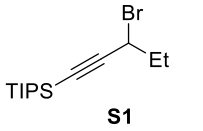
Unless otherwise noted, reagents were used as received from Sigma-Aldrich, Alfa, TCI, Energy Chemical, J&K. The aldehydes used for the reaction had been purified by reduced pressure distillation or recrystallization. All reactions were performed under an atmosphere of dry nitrogen gas. Anhydrous THF was purchased from J&K and stored under nitrogen gas. Other solvents were purified with activated aluminum oxide using a solvent-purification system.

NMR spectra were recorded on a Bruker spectrometer with a Prodigy broadband cryoprobe (500 MHz and 600 MHz); chemical shifts (δ) are reported in ppm downfield from tertramethylsilane, using the solvent resonance as the internal standard. Optical rotation data were obtained with a Jasco P-2000 polarimeter at 589 nm, using a 50 mm path-length cell in the solvent and at the concentration indicated. High resolution mass spectrometric analysis was performed on ultra-performance liquid chromatography-time-of-flight mass spectrometer (Synapt-G2-Si, Waters, USA) with electron spray ionization (ESI) resource and atmosphere pressure chemical ionization (APCI) resource. SFC analysis was carried out on an Agilent 1260 series system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 3 μm). HPLC analysis was carried out on Waters Arc HPLC system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 3 μm).

II. Preparation of Coupling Partners

Ligand Preparation: The ligand (*R*,*S*)-**L1** and (*S*,*R*)-**L1** were prepared according to a reported literature procedure, and all the analytical data matched the report (1).

The structures of propargyl bromides



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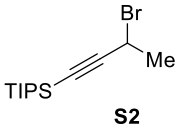

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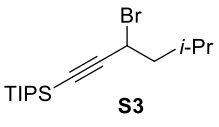

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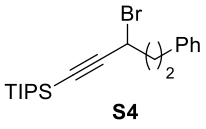

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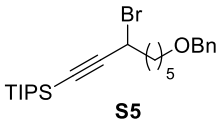

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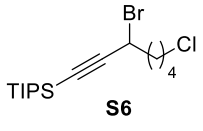

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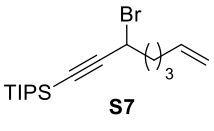

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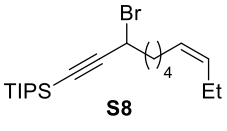

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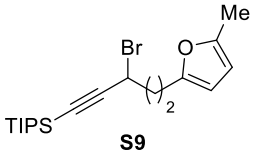

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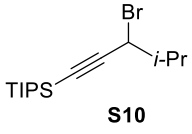

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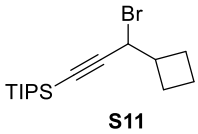

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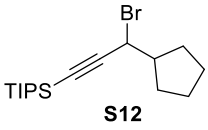

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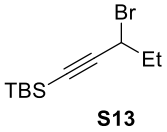

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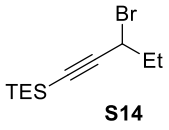

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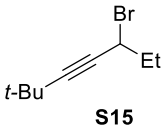

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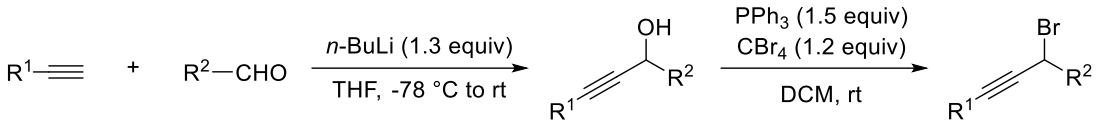
Propargyl Bromides Preparation:



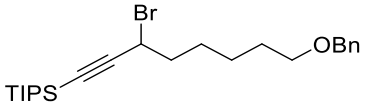
General Procedure 1 (GP-1): Preparation of propargyl bromides

A solution of the corresponding alkyne (20 mmol, 1.0 equiv) in 100 mL THF was cooled to –78 °C, *n*-butyl lithium in *n*-hexane (26 mmol, 1.3 equiv) was added dropwise under nitrogen atmosphere. The mixture was stirred at –78 °C for 20 minutes, followed by the dropwise addition of the corresponding aldehyde (24 mmol, 1.2 equiv). The resulting mixture was stirred at –78 °C for 1 h, and then warmed to room temperature slowly and stirred overnight. Saturated NH_4Cl aqueous solution (30 mL) was added cautiously at 0 °C. The resulting mixture was extracted with EtOAc (2×50 mL), and the organic phase was combined, washed with brine (60 mL), dried with anhydrous $MgSO_4$, and concentrated. The resulting mixture was purified by flash chromatography (hexanes/ethyl acetate) to provide propargyl alcohols.

To the cooled solution of the propargyl alcohols (20 mmol, 1.0 equiv) in 50 mL DCM at 0 °C, CBr_4 (8.0 g, 24 mmol, 1.2 equiv) was added under under air in one portion. The mixture was stirred at rt for 10 minutes, and then triphenylphosphine (7.9 g, 30 mmol, 1.5 equiv) in 20 mL DCM was added dropwise at 0 °C. The resulting mixture was stirred at rt for overnight. After completion of the reaction, the mixture was concentrated, purified by flash chromatography (hexanes/ethyl acetate), and further distilled under reduced pressure, which furnished the desired propargyl bromides.

Compound **S5**, **S6, S8** were prepared according to the **GP-1.**

Compound **S1**-**S4**, **S7**, **S9**-**S15** were prepared according to reported literature procedure, and all the analytical data matched the reports (2,3).

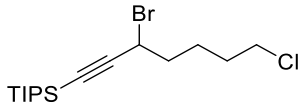


(8-(benzyloxy)-3-bromooct-1-yn-1-yl)triisopropylsilane (S5). The title compound was prepared according to the **GP-1**, using ethynyltriisopropylsilane and 6-(benzyloxy)hexanal, purified by flash column chromatography: 100% hexanes, 63% yield over 2 steps, colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.26 (m, 1H), 4.52 (t, *J* = 6.7 Hz, 1H), 4.49 (s, 2H), 3.46 (t, *J* = 6.5 Hz, 2H), 2.00 (dd, *J* = 15.5, 6.8 Hz, 2H), 1.63 (m, 2H), 1.57 (m, 2H), 1.42 (m, 2H), 1.07 (d, *J* = 2.1 Hz, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 128.3, 127.5, 127.4, 105.9, 88.6, 72.9, 70.1, 39.7, 37.3, 29.5, 27.1, 25.3, 18.5, 11.1.

HRMS (APCI) m/z $[M - Br]^+$ calcd for $C_{24}H_{39}OSi$: 371.2770, found: 371.2766.

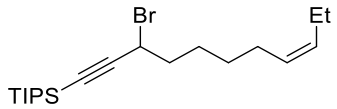


(3-bromo-7-chlorohept-1-yn-1-yl)triisopropylsilane (S6). The title compound was prepared according to the **GP-1**, using ethynyltriisopropylsilane and 5-chloropentanal, purified by flash column chromatography: 100% hexanes, 63% yield over 2 steps, colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.56 (t, *J* = 6.6 Hz, 1H), 3.54 (t, *J* = 6.5 Hz, 2H), 2.07 – 2.01 (m, 2H), 1.86 – 1.79 (m, 2H), 1.77 – 1.70 (m, 2H), 1.07 (s, 21H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 105.4, 89.2, 44.5, 38.9, 36.8, 31.7, 24.7, 18.5, 11.1.

HRMS (APCI) m/z $[M - Br]^+$ calcd for $C_{16}H_{30}ClSi$: 285.1805, found: 285.1810.



(Z)-(3-bromoundec-8-en-1-yn-1-yl)triisopropylsilane (S8). The title compound was prepared according to the **GP-1**, using ethynyltriisopropylsilane and (Z)-non-6-enal, purified by flash column chromatography: 100% hexanes, 57% yield over 2 steps, colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 – 5.27 (m, 2H), 4.54 (t, *J* = 6.7 Hz, 1H), 2.08 – 1.98 (m, 6H), 1.61 – 1.54 (m, 2H), 1.43 – 1.36 (m, 2H), 1.08 (s, 21H), 0.96 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.0, 128.5, 105.9, 88.7, 39.7, 37.3, 28.8, 27.0, 26.8, 20.5, 18.5, 14.3, 11.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{37}BrSi$: 305.2664, found: 305.2656.

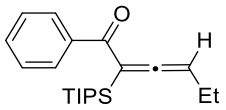
III. Catalytic Asymmetric Allenylation Reactions

General procedure 2 (GP-2): Catalytic Allenylation Reactions.

Preparation of the catalyst solution: In a nitrogen-filled glovebox, an oven-dried 20 mL vial with a magnetic stir bar, was charged the $CrCl_2$ (4.9 mg, 0.04 mmol, 10 mol% for product **1**-**27**, 2.5 mg, 0.02 mmol, 5 mol% for product **28**-**41**) and (*R,S*)-**L1** (29.0 mg, 0.06 mmol, 15 mol% for product **1**-**27**, 13.5 mg, 0.028 mmol, 7 mol% for product **28**-**41,**). Then 8.0 mL THF was added and the vial was closed with a PTFE septum cap. The mixture was stirred at room temperature for 2 h.

Catalytic asymmetric allenylation: In a nitrogen-filled glovebox, to the prepared catalyst solution was added the propargyl bromide (0.4 mmol, 1.0 equiv), the LiBr (35 mg, 0.4 mmol, 1.0 equiv), the aldehyde (0.8 mmol, 2.0 equiv), the dissociation reagent TESCl (135 μL, 0.8 mmol, 2.0 equiv), and Mn powder (44 mg, 0.8 mmol, 2.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. The reaction mixture was stirred at 40 °C for 8 h.

Work-up: The reaction mixture was run through a short silica gel pad with hexanes/EtOAc (5:1) as the eluent. Then the solvent was removed the under reduced pressure, and the residue was purified by flash chromatography to provide the desired product.



1-phenyl-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 1). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 96 mg, 73% yield, 92% ee; (*S,R*)-**L1**: 96 mg, 73% yield, 92% ee.

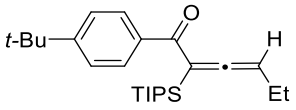
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.2 min (major), 4.5 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.53 – 7.48 (m, 1H), 7.43 – 7.39 (m, 2H), 5.01 (t, *J* = 7.2 Hz, 1H), 2.10 (p, *J* = 7.4 Hz, 2H), 1.41 – 1.32 (m, 3H), 1.11 (dd, *J* = 7.5, 4.1 Hz, 18H), 0.97 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.3, 196.5, 138.4, 132.1, 129.3, 128.0, 98.0, 88.9, 21.5, 18.7 (two carbons), 14.0, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{33}OSi$: 329.2301, found: 329.2290.

$[\alpha]^{24}_D$ = -6.4 (*c* = 0.5, $CHCl_3$); 92% ee, from (*R,S*)-**L1**.



1-(4-(*tert*-butyl)phenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 2). The title compound was prepared according to the **GP-2** from 4-(*tert*-butyl)benzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 108 mg, 70% yield, 90% ee; (*S,R*)-**L1**: 107 mg, 69% yield, 90% ee.

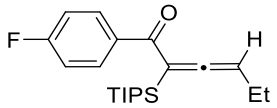
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.4 min (major), 4.9 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.45 – 7.40 (m, 2H), 5.01 (t, *J* = 7.2 Hz, 1H), 2.12 (p, *J* = 7.3 Hz, 2H), 1.40 – 1.33 (m, 12H), 1.15 – 1.09 (m, 18H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.5, 195.8, 155.7, 135.5, 129.4, 124.9, 97.8, 88.7, 35.0, 31.1, 21.6, 18.7 (two carbons), 14.0, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{41}OSi$: 385.2927, found: 385.2925.

$[\alpha]^{24}_D$ = +9.2 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



1-(4-fluorophenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 3). The title compound was prepared according to the **GP-2** from 4-fluorobenzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 97 mg, 70% yield, 93% ee; (*S,R*)-**L1**: 97 mg, 70% yield, 93% ee.

HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.1 min (major), 4.4 min (minor).

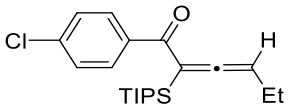
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.11 – 7.05 (m, 2H), 5.02 (t, *J* = 7.2 Hz, 1H), 2.10 (p, *J* = 7.4 Hz, 2H), 1.39 – 1.32 (m, 3H), 1.11 (dd, *J* = 7.5, 2.6 Hz, 18H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.9 (s), 194.8 (s), 165.2 (d, *J* = 253.3 Hz), 134.6 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 9.1 Hz), 115.0 (d, *J* = 21.7 Hz), 98.0 (s), 89.0 (s), 21.5 (s), 18.7 (s, two carbons), 14.1 (s), 11.6 (s).

^{19}F NMR (471 MHz, $CDCl_3$) δ -106.89.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{32}FOSi$: 347.2206, found: 347.2193.

$[\alpha]^{24}_D$ = +1.6 (*c* = 0.5, $CHCl_3$); 93% ee, from (*R,S*)-**L1**.



1-(4-chlorophenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 4). The title compound was prepared according to the **GP-2** from 4-chlorobenzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane,

colorless liquid.

(*R,S*)-**L1**: 94 mg, 65% yield, 90% ee; (*S,R*)-**L1**: 98 mg, 67% yield, 90% ee.

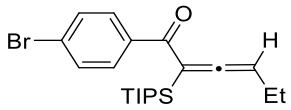
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.3 min (major), 4.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.40 – 7.35 (m, 2H), 5.03 (t, *J* = 7.2 Hz, 1H), 2.09 (p, *J* = 7.4 Hz, 2H), 1.39 – 1.31 (m, 3H), 1.10 (dd, *J* = 7.7, 2.8 Hz, 18H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.2, 195.0, 138.4, 136.6, 130.7, 128.3, 98.0, 89.1, 21.5, 18.7, 18.6, 14.0, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{32}ClOSi$: 363.1911, found: 363.1906.

$[\alpha]^{24}_D$ = +13.6 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



1-(4-bromophenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 5). The title compound was prepared according to the **GP-2** from 4-bromobenzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 110 mg, 67% yield, 90% ee; (*S,R*)-**L1**: 118 mg, 72% yield, 90% ee.

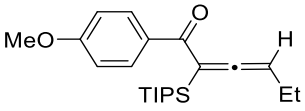
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.7 min (major), 5.3 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 7.57 – 7.52 (m, 2H), 5.03 (t, *J* = 7.2 Hz, 1H), 2.09 (p, *J* = 7.4 Hz, 2H), 1.38 – 1.32 (m, 3H), 1.10 (dd, *J* = 7.6, 2.7 Hz, 18H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.2, 195.2, 137.0, 131.2, 130.8, 127.1, 98.0, 89.2, 21.5, 18.7 (two carbons), 14.0, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{32}BrOSi$: 409.1388, found: 409.1399.

$[\alpha]^{24}_D$ = +13.6 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



1-(4-methoxyphenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 6). The title compound was prepared according to the **GP-2** from 4-methoxybenzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 90 mg, 63% yield, 93% ee; (*S,R*)-**L1**: 89 mg, 62% yield, 93% ee.

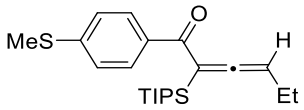
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 6.7 min (major), 7.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 6.92 – 6.88 (m, 2H), 5.00 (t, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 2.11 (p, *J* = 7.4 Hz, 2H), 1.38 – 1.31 (m, 3H), 1.11 (dd, *J* = 7.6, 2.9 Hz, 18H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.6, 194.6, 162.9, 131.7, 131.0, 113.2, 97.7, 88.4, 55.3, 21.6, 18.7 (two carbons), 14.1, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{35}O_2Si$: 359.2406, found: 359.2409.

$[\alpha]^{24}_D$ = +26.0 (*c* = 0.5, $CHCl_3$); 93% ee, from (*R,S*)-**L1**.



1-(4-(methylthio)phenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 7). The title compound was prepared according to the **GP-2** from 4-(methylthio)benzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 108 mg, 72% yield, 93% ee; (*S,R*)-**L1**: 108 mg, 72% yield, 93% ee.

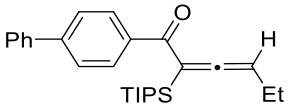
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 7.4 min (major), 8.2 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.25 – 7.21 (m, 2H), 5.01 (t, *J* = 7.2 Hz, 1H), 2.51 (s, 3H), 2.10 (p, *J* = 7.4 Hz, 2H), 1.38 – 1.31 (m, 3H), 1.11 (dd, *J* = 7.6, 2.6 Hz, 18H), 0.99 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.2, 195.1, 144.7, 134.5, 129.9, 124.6, 97.7, 88.7, 21.5, 18.7 (two carbons), 14.8, 14.1, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{35}OSSi$: 375.2178, found: 375.2177.

$[\alpha]^{24}_D$ = +16.0 (*c* = 0.5, $CHCl_3$); 93% ee, from (*R,S*)-**L1**.



1-([1,1'-biphenyl]-4-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 8). The title compound was prepared according to the **GP-2** from [1,1'-biphenyl]-4-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 127 mg, 78% yield, 91% ee; (*S,R*)-**L1**: 124 mg, 76% yield, 91% ee.

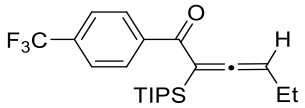
HPLC analysis: The ee was determined on a CHIRALCEL: OD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.9 min (major), 5.2 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.69 – 7.63 (m, 4H), 7.50 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 5.07 (t, *J* = 7.2 Hz, 1H), 2.16 (p, *J* = 7.4 Hz, 2H), 1.46 – 1.38 (m, 3H), 1.17 (dd, *J* = 7.7, 4.1 Hz, 18H), 1.03 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.9, 195.8, 144.8, 140.1, 137.0, 129.9, 128.8, 128.0, 127.2, 126.6, 98.0, 88.9, 21.5, 18.7 (two carbons), 14.0, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{37}OSi$: 405.2614, found: 405.2603.

$[\alpha]^{24}_D$ = +4.8 (*c* = 0.5, $CHCl_3$); 91% ee, from (*R,S*)-**L1**.



1-(4-(trifluoromethyl)phenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 9). The title compound was prepared according to the **GP-2** from 4-(trifluoromethyl)benzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 101 mg, 64% yield, 82% ee; (*S,R*)-**L1**: 98 mg, 62% yield, 82% ee.

HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 3.8 min (major), 4.1 min (minor).

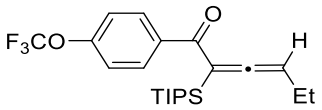
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.70 – 7.65 (m, 2H), 5.06 (t, *J* = 7.2 Hz, 1H), 2.10 (p, *J* = 7.4 Hz, 2H), 1.41 – 1.34 (m, 3H), 1.12 (dd, *J* = 7.8, 2.8 Hz, 18H), 0.97 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 216.3 (s), 195.5 (s), 141.5 (s), 133.3 (q, *J* = 32.5 Hz), 129.4 (s), 125.0 (q, *J* = 3.7 Hz), 123.8 (d, *J* = 272.5 Hz), 98.4 (s), 89.6 (s), 21.4 (s), 18.7 (s, two carbons), 13.9 (s), 11.6 (s).

^{19}F NMR (471 MHz, $CDCl_3$) δ -63.00.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{32}F_3OSi$: 397.2174, found: 397.2170.

$[\alpha]^{24}_D$ = +4.0 (*c* = 0.5, $CHCl_3$); 82% ee, from (*R,S*)-**L1**.



1-(4-(trifluoromethoxy)phenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 10). The title compound was prepared according to the **GP-2** from 4-(trifluoromethoxy)benzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 93 mg, 56% yield, 84% ee; (*S,R*)-**L1**: 94 mg, 57% yield, 84% ee.

HPLC analysis: The ee was determined on a CHIRALCEL: OD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 3.5 min (major), 3.6 min (minor).

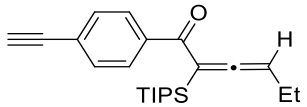
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.26 – 7.21 (m, 2H), 5.04 (t, *J* = 7.2 Hz, 1H), 2.10 (p, *J* = 7.4 Hz, 2H), 1.40 – 1.32 (m, 3H), 1.11 (dd, *J* = 7.5, 2.6 Hz, 18H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.5 (s), 194.8 (s), 151.9 (d, J = 1.7 Hz), 136.6 (s), 131.1 (s), 120.2 (d, J = 258.3 Hz), 119.8 (s), 98.1 (s), 89.3 (s), 21.5 (s), 18.7 (s, two carbons), 14.0 (s), 11.6 (s).

^{19}F NMR (471 MHz, $CDCl_3$) δ -57.63.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{32}F_3O_2Si$: 413.2124, found: 413.2119.

$[\alpha]^{24}_D$ = +6.8 (*c* = 0.5, $CHCl_3$); 84% ee, from (*R,S*)-**L1**.



1-(4-ethynylphenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 11). The title compound was prepared according to the **GP-2** from 4-ethynylbenzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 80 mg, 56% yield, 87% ee; (*S,R*)-**L1**: 77 mg, 54% yield, 87% ee.

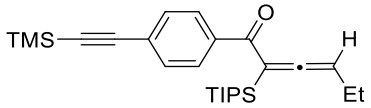
HPLC analysis: The ee was determined on a CHIRALCEL: OD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.0 min (major), 4.1 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 5.02 (t, *J* = 7.2 Hz, 1H), 3.20 (s, 1H), 2.09 (p, *J* = 7.4 Hz, 2H), 1.35 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.11 (dd, *J* = 7.6, 3.3 Hz, 18H), 0.97 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.5, 195.6, 138.3, 131.7, 129.1, 125.8, 98.1, 89.2, 83.0, 79.7, 21.5, 18.7 (two carbons), 14.0, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{33}OSi$: 353.2301, found: 353.2294.

$[\alpha]^{24}_D$ = -37.6 (*c* = 0.5, $CHCl_3$); 87% ee, from (*R,S*)-**L1**.



2-(triisopropylsilyl)-1-(4-((trimethylsilyl)ethynyl)phenyl)hexa-2,3-dien-1-one (Scheme 2, entry 12). The title compound was prepared according to the **GP-2** from 4-((trimethylsilyl)ethynyl)benzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 90 mg, 53% yield, 87% ee; (*S,R*)-**L1**: 91 mg, 53% yield, 88% ee.

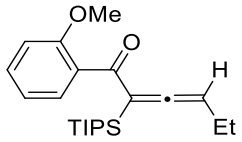
HPLC analysis: The ee was determined on a CHIRALCEL: OD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 3.4 min (major), 3.4 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.51 – 7.46 (m, 2H), 5.01 (t, *J* = 7.2 Hz, 1H), 2.08 (p, *J* = 7.4 Hz, 2H), 1.35 (dt, *J* = 11.3, 7.5 Hz, 3H), 1.10 (dd, *J* = 7.6, 3.7 Hz, 18H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.25 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.3, 195.6, 137.9, 131.5, 129.1, 126.8, 104.3, 98.1, 97.2, 89.1, 21.5, 18.7 (two carbons), 14.0, 11.6, -0.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{41}OSi_2$: 425.2696, found: 425.2691.

$[\alpha]^{24}_D$ = +18.8 (*c* = 0.5, $CHCl_3$); 88% ee, from (*R,S*)-**L1**.



1-(2-methoxyphenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 13). The title compound was prepared according to the **GP-2** from 2-methoxybenzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 58 mg, 40% yield, 77% ee; (*S,R*)-**L1**: 65 mg, 45% yield, 77% ee.

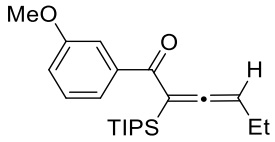
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 8.0 min (major), 9.8 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 1H), 7.27 – 7.22 (m, 1H), 6.94 – 6.89 (m, 1H), 6.88 – 6.84 (m, 1H), 4.92 (t, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 1.92 (p, *J* = 7.3 Hz, 2H), 1.42 – 1.34 (m, 3H), 1.12 (d, *J* = 7.8 Hz, 18H), 0.81 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 219.2, 198.9, 156.6, 131.1, 130.7, 128.6, 119.7, 110.7, 101.1, 89.3, 55.3, 20.9, 18.7 (two carbons), 13.9, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{35}O_2Si$: 359.2406, found: 359.2397.

$[\alpha]^{24}_D$ = -8.0 (*c* = 0.5, $CHCl_3$); 77% ee, from (*R,S*)-**L1**.



1-(3-methoxyphenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 14). The title compound was prepared according to the **GP-2** from 3-methoxybenzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 98 mg, 68% yield, 90% ee; (*S,R*)-**L1**: 100 mg, 69% yield, 90% ee.

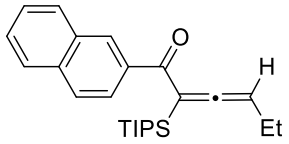
HPLC analysis: The ee was determined on a CHIRALCEL: OD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.4 min (major), 4.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.06 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.02 (t, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 2.11 (p, *J* = 7.4 Hz, 2H), 1.39 – 1.32 (m, 3H), 1.11 (dd, *J* = 7.5, 4.4 Hz, 18H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.0, 196.1, 159.4, 139.7, 128.8, 122.2, 118.7, 113.5, 98.0, 88.9, 55.3, 21.6, 18.7 (two carbons), 14.1, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{35}O_2Si$: 359.2406, found: 359.2407.

$[\alpha]^{24}_D$ = -0.8 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



1-(naphthalen-2-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 15). The title compound was prepared according to the **GP-2** from 2-naphthaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 111 mg, 73% yield, 93% ee; (*S,R*)-**L1**: 107 mg, 71% yield, 93% ee.

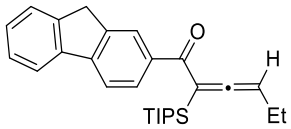
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 6.3 min (major), 7.3 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.99 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.60 – 7.51 (m, 2H), 5.06 (t, *J* = 7.2 Hz, 1H), 2.17 (p, *J* = 7.4 Hz, 2H), 1.47 – 1.40 (m, 3H), 1.23 – 1.15 (m, 18H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.1, 196.1, 135.5, 135.2, 132.3, 130.9, 129.4, 127.9, 127.8, 127.7, 126.4, 125.3, 98.1, 88.8, 21.5, 18.7 (two carbons), 14.1, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{35}OSi$: 379.2457, found: 379.2454.

$[\alpha]^{24}_D$ = -10.4 (*c* = 0.5, $CHCl_3$); 93% ee, from (*R,S*)-**L1**.



1-(9H-fluoren-2-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 16). The title compound was prepared according to the **GP-2** from 9H-fluorene-2-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, white solid.

(*R,S*)-**L1**: 102 mg, 61% yield, 92% ee; (*S,R*)-**L1**: 105 mg, 63% yield, 92% ee.

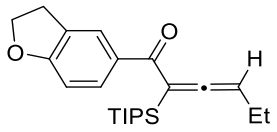
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.9 min (major), 6.5 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.43 – 7.34 (m, 2H), 5.04 (t, *J* = 7.2 Hz, 1H), 3.95 (s, 2H), 2.15 (p, *J* = 7.4 Hz, 2H), 1.44 – 1.37 (m, 3H), 1.18 – 1.14 (m, 18H), 1.01 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.6, 196.1, 145.6, 144.4, 142.8, 140.7, 136.8, 128.9, 127.7, 126.9, 126.0, 125.2, 120.7, 119.1, 98.2, 88.7, 36.9, 21.6, 18.8, 18.7, 14.1, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{28}H_{37}OSi$: 417.2614, found: 417.2610.

$[\alpha]^{24}_D$ = +8.0 (*c* = 0.5, $CHCl_3$); 92% ee, from (*R,S*)-**L1**.



1-(2,3-dihydrobenzofuran-5-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 17). The title compound was prepared according to the **GP-2** from 2,3-dihydrobenzofuran-5-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 92 mg, 62% yield, 90% ee; (*S,R*)-**L1**: 93 mg, 62% yield, 89% ee.

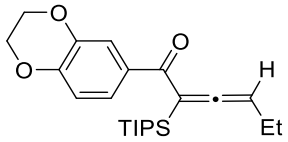
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 7.2 min (major), 8.0 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (m, 2H), 6.76 (d, *J* = 8.3 Hz, 1H), 4.98 (t, *J* = 7.2 Hz, 1H), 4.63 (t, *J* = 10.0, 7.6 Hz, 2H), 3.23 (t, *J* = 8.7 Hz, 2H), 2.11 (p, *J* = 7.4 Hz, 2H), 1.34 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.11 (dd, *J* = 7.6, 4.6 Hz, 18H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.4, 194.5, 163.9, 131.6, 131.2, 127.2, 126.5, 108.4, 97.7, 88.3, 72.0, 29.1, 21.6, 18.7 (two carbons), 14.1, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{35}O_2Si$: 371.2406, found: 371.2404.

$[\alpha]^{24}_D$ = +9.2 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 18). The title compound was prepared according to the **GP-2** from 2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 92 mg, 59% yield, 91% ee; (*S,R*)-**L1**: 90 mg, 58% yield, 91% ee.

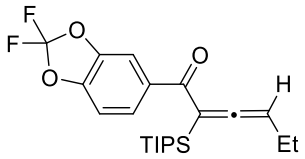
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 6.0 min (major), 6.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 1H), 5.00 (t, *J* = 7.2 Hz, 1H), 4.28 (dd, *J* = 14.8, 4.4 Hz, 4H), 2.12 (p, *J* = 7.3 Hz, 2H), 1.33 (dt, *J* = 14.8, 7.4 Hz, 3H), 1.10 (dd, *J* = 7.4, 3.9 Hz, 18H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.8, 194.4, 147.4, 142.8, 131.7, 123.5, 119.0, 116.7, 97.5, 88.5, 64.6, 64.1, 21.6, 18.7 (two carbons), 14.1, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{35}O_3Si$: 387.2355, found: 387.2351.

$[\alpha]^{24}_D$ = +14.0 (*c* = 0.5, $CHCl_3$); 91% ee, from (*R,S*)-**L1**.



1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 19). The title compound was prepared according to the **GP-2** from 2,2-difluorobenzo[d][1,3]dioxole-5-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 90 mg, 55% yield, 92% ee; (*S,R*)-**L1**: 85 mg, 52% yield, 91% ee.

HPLC analysis: The ee was determined on a CHIRALCEL: OD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 3.7 min (major), 4.2 min (minor).

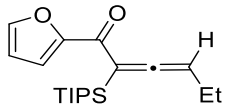
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.60 (d, *J* = 1.5 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 5.06 (t, *J* = 7.2 Hz, 1H), 2.11 (p, *J* = 7.4 Hz, 2H), 1.38 – 1.31 (m, 3H), 1.11 (dd, *J* = 7.7, 1.9 Hz, 18H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.7 (s), 193.7 (s), 146.5 (s), 143.7 (s), 134.6 (s), 131.7 (t, J = 256.8 Hz), 126.4 (s), 110.4 (s), 108.6 (s), 97.8 (s), 89.2 (s), 21.5 (s), 18.7 (s), 18.6 (s), 14.0 (s), 11.6 (s).

^{19}F NMR (471 MHz, $CDCl_3$) δ -49.79.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{31}F_2O_3Si$: 409.2010, found: 409.2008.

$[\alpha]^{24}_D$ = +16.0 (*c* = 0.5, $CHCl_3$); 92% ee, from (*R,S*)-**L1**.



1-(furan-2-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 20). The title compound was prepared according to the **GP-2** from furan-2-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 63 mg, 49% yield, 66% ee; (*S,R*)-**L1**: 64 mg, 50% yield, 67% ee.

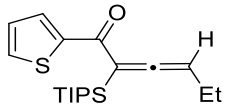
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.1 min (major), 5.4 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 0.9 Hz, 1H), 7.16 (d, *J* = 3.5 Hz, 1H), 6.47 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.14 (t, *J* = 7.1 Hz, 1H), 2.17 (p, *J* = 7.4 Hz, 2H), 1.35 – 1.29 (m, 3H), 1.10 – 1.04 (m, 21H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.4, 182.7, 152.2, 146.2, 118.4, 111.6, 97.4, 89.0, 21.6, 18.6 (two carbons), 14.0, 11.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{31}O_2Si$: 319.2093, found: 319.2090.

$[\alpha]^{24}_D$ = -30.8 (*c* = 0.5, $CHCl_3$); 66% ee, from (*R,S*)-**L1**.



1-(thiophen-2-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 21). The title compound was prepared according to the **GP-2** from thiophene-2-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 74 mg, 55% yield, 91% ee; (*S,R*)-**L1**: 75 mg, 56% yield, 90% ee.

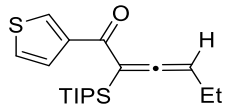
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.2 min (major), 4.4 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 1H), 7.59 – 7.55 (m, 1H), 7.10 – 7.06 (m, 1H), 5.15 (t, *J* = 7.2 Hz, 1H), 2.19 (p, *J* = 7.4 Hz, 2H), 1.34 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.12 – 1.04 (m, 21H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.7, 187.1, 144.1, 133.1, 132.9, 127.6, 98.5, 89.6, 21.8, 18.6 (two carbons), 14.0, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{31}OSSi$: 335.1865, found: 335.1859.

$[\alpha]^{24}_D$ = +31.6 (*c* = 0.5, $CHCl_3$); 91% ee, from (*R,S*)-**L1**.



1-(thiophen-3-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 22). The title compound was prepared according to the **GP-2** from thiophene-3-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 81 mg, 60% yield, 91% ee; (*S,R*)-**L1**: 82 mg, 61% yield, 91% ee.

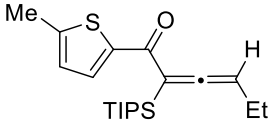
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.6 min (major), 5.0 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.52 (d, *J* = 4.8 Hz, 1H), 7.28 – 7.24 (m, 1H), 5.09 (t, *J* = 7.0 Hz, 1H), 2.15 (p, *J* = 7.1 Hz, 2H), 1.38 – 1.31 (m, 3H), 1.10 (d, *J* = 7.9 Hz, 18H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.2, 189.3, 142.4, 132.4, 128.0, 125.4, 99.0, 89.0, 21.8, 18.7, 18.6, 14.0, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{30}OSSi$: 335.1865, found: 335.1859.

$[\alpha]^{24}_D$ = +31.2 (*c* = 0.5, $CHCl_3$); 91% ee, from (*R,S*)-**L1**.



1-(5-methylthiophen-2-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 23). The title compound was prepared according to the **GP-2** from 5-methylthiophene-2-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 67 mg, 48% yield, 93% ee; (*S,R*)-**L1**: 70 mg, 50% yield, 93% ee.

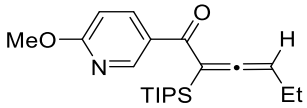
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.4 min (major), 4.8 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 6.76 (s, 1H), 5.10 (t, *J* = 7.1 Hz, 1H), 2.51 (s, 3H), 2.17 (p, *J* = 7.2 Hz, 2H), 1.32 (dt, *J* = 14.7, 7.3 Hz, 3H), 1.11 – 1.04 (m, 21H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.1, 186.8, 149.1, 141.9, 133.6, 126.4, 98.1, 89.3, 21.9, 18.6 (two carbons), 15.9, 14.0, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{33}OSSi$: 349.2021, found: 349.2016.

$[\alpha]^{24}_D$ = +42.4 (*c* = 0.5, $CHCl_3$); 93% ee, from (*R,S*)-**L1**.



1-(6-methoxypyridin-3-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 24). The title compound was prepared according to the **GP-2** from 6-methoxynicotinaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 107 mg, 74% yield, 94% ee; (*S,R*)-**L1**: 108 mg, 75% yield, 94% ee.

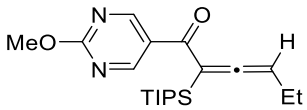
HPLC analysis: The ee was determined on a CHIRALCEL: OD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.6 min (major), 4.9 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 2.3 Hz, 1H), 8.05 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 5.06 (t, *J* = 7.2 Hz, 1H), 3.97 (s, 3H), 2.10 (p, *J* = 7.4 Hz, 2H), 1.32 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.08 (d, *J* = 7.9 Hz, 18H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.5, 193.5, 166.2, 150.1, 139.3, 127.6, 110.7, 97.9, 89.1, 53.9, 21.5, 18.7, 18.6, 14.1, 11.8, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{34}NO_2Si$: 360.2359, found: 360.2358.

$[\alpha]^{24}_D$ = -48.4 (*c* = 0.5, $CHCl_3$); 94% ee, from (*S,R*)-**L1**.



1-(2-methoxypyrimidin-5-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 25). The title compound was prepared according to the **GP-2** from 2-methoxypyrimidine-5-carbaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 95 mg, 65% yield, 90% ee; (*S,R*)-**L1**: 96 mg, 66% yield, 90% ee.

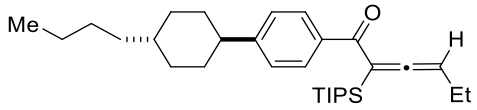
HPLC analysis: The ee was determined on a CHIRALCEL: OD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 8.9 min (major), 12.5 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 2H), 5.13 (t, *J* = 7.2 Hz, 1H), 4.05 (s, 3H), 2.15 – 2.08 (m, 2H), 1.32 (dt, *J* = 14.9, 7.4 Hz, 3H), 1.07 (d, *J* = 7.7 Hz, 18H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.9, 191.8, 166.6, 160.8, 125.7, 98.3, 90.0, 55.5, 21.5, 18.6 (two carbons), 13.9, 11.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{33}N_2O_2Si$: 361.2311, found: 361.2308.

$[\alpha]^{24}_D$ = +29.6 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



1-(4-(4-butylcyclohexyl)phenyl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 26). The title compound was prepared according to the **GP-2** from 4-(4-butylcyclohexyl)benzaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 110 mg, 59% yield, 90% de; (*S,R*)-**L1**: 112 mg, 60% yield, 90% de.

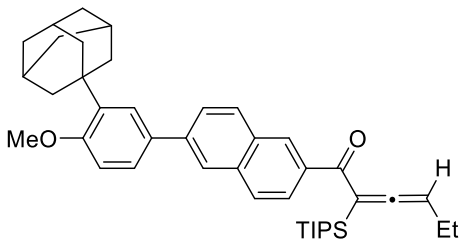
HPLC analysis: The de was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.0 min (major), 5.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 4.99 (t, *J* = 7.2 Hz, 1H), 2.50 (dd, *J* = 16.7, 7.5 Hz, 1H), 2.11 (p, *J* = 7.4 Hz, 2H), 1.89 (t, *J* = 11.2 Hz, 4H), 1.46 (dd, *J* = 22.8, 12.3 Hz, 2H), 1.39 – 1.23 (m, 10H), 1.14 – 1.08 (m, 20H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.5, 195.8, 152.6, 136.0, 129.6, 126.5, 97.8, 88.6, 44.7, 37.2, 37.1, 34.0, 33.5, 29.2, 23.0, 21.6, 18.7 (two carbons), 14.1 (two carbons), 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{31}H_{51}OSi$: 467.3709, found: 467.3706.

$[\alpha]^{24}_D$ = +6.0 (*c* = 0.5, $CHCl_3$); 90% de, from (*R,S*)-**L1**.



1-(6-(3-(adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 27). The title compound was prepared according to the **GP-2** from 6-(3-(adamantan-1-yl)-4-methoxyphenyl)-2-naphthaldehyde and (3-bromopent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, white solid.

(*R,S*)-**L1**: 119 mg, 48% yield, 91% ee; (*S,R*)-**L1**: 117 mg, 47% yield, 90% ee.

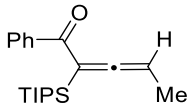
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.4 min (major), 6.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.03 (s, 1H), 8.01 – 7.97 (m, 2H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.56 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 5.08 (t, *J* = 7.2 Hz, 1H), 3.91 (s, 3H), 2.24 – 2.11 (m, 11H), 1.87 – 1.80 (m, 6H), 1.45 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.19 (t, *J* = 7.5 Hz, 18H), 1.03 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.9, 196.0, 158.8, 141.2, 138.9, 135.7, 135.1, 132.6, 131.0, 130.8, 129.8, 127.9, 126.3, 125.9, 125.7 (two carbons), 124.7, 112.1, 98.1, 88.8, 55.1, 40.6, 37.2, 37.1, 29.1, 21.6, 18.8, 18.7, 14.1, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{42}H_{55}O_2Si$: 619.3972, found: 619.3968.

$[\alpha]^{24}_D$ = -3.6 (*c* = 0.5, $CHCl_3$); 91% ee, from (*R,S*)-**L1**.



1-phenyl-2-(triisopropylsilyl)penta-2,3-dien-1-one (Scheme 3, entry 28). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromobut-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 80 mg, 63% yield, 87% ee; (*S,R*)-**L1**: 83 mg, 66% yield, 87% ee.

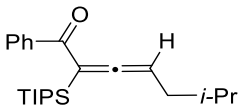
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.3 min (major), 4.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.54 – 7.49 (m, 1H), 7.45 – 7.39 (m, 2H), 5.00 (q, *J* = 7.2 Hz, 1H), 1.70 (d, *J* = 7.3 Hz, 3H), 1.40 – 1.33 (m, 3H), 1.15 – 1.10 (m, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 216.1, 196.3, 138.4, 132.2, 129.3, 128.0, 97.1, 81.7, 18.7 (two carbons), 12.7, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{31}OSi$: 315.2144, found: 315.2136.

$[\alpha]^{24}_D$ = -21.6 (*c* = 0.5, $CHCl_3$); 87% ee, from (*R,S*)-**L1**.



6-methyl-1-phenyl-2-(triisopropylsilyl)hepta-2,3-dien-1-one (Scheme 3, entry 29). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromo-5-methylhex-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 90 mg, 63% yield, 92% ee; (*S,R*)-**L1**: 91 mg, 63% yield, 93% ee.

HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in

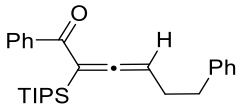
hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.0 min (major), 4.2 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.52 – 7.47 (m, 1H), 7.43 – 7.37 (m, 2H), 4.98 (t, *J* = 7.7 Hz, 1H), 2.05 – 1.90 (m, 2H), 1.55 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.41 – 1.33 (m, 3H), 1.12 (d, *J* = 7.6 Hz, 18H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.9, 196.6, 138.5, 132.0, 129.3, 128.0, 97.1, 86.0, 37.2, 28.8, 22.1, 21.89, 18.7 (two carbons), 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{37}OSi$: 357.2614, found: 357.2606.

$[\alpha]^{24}_D$ = +14.0 (*c* = 0.5, $CHCl_3$); 92% ee, from (*R,S*)-**L1**.



1,6-diphenyl-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 3, entry 30). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromo-5-phenylpent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 104 mg, 64% yield, 90% ee; (*S,R*)-**L1**: 107 mg, 66% yield, 90% ee.

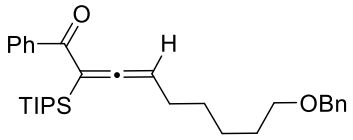
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.2 min (major), 5.8 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.54 – 7.48 (m, 1H), 7.44 – 7.39 (m, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.14 (m, 1H), 7.10 – 7.05 (m, 2H), 4.99 (t, *J* = 7.5 Hz, 1H), 2.68 – 2.56 (m, 2H), 2.42 – 2.36 (m, 2H), 1.37 – 1.29 (m, 3H), 1.10 (dd, *J* = 7.5, 3.7 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.1, 196.2, 141.0, 138.4, 132.2, 129.3, 128.4 (two carbons), 128.0, 126.1, 97.8, 86.5, 35.9, 30.1, 18.7, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{37}OSi$: 405.2614, found: 405.2608.

$[\alpha]^{24}_D$ = +6.4 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



9-(benzyloxy)-1-phenyl-2-(triisopropylsilyl)nona-2,3-dien-1-one (Scheme 3, entry 31). The title compound was prepared according to the **GP-2** from benzaldehyde and (8-(benzyloxy)oct-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 116 mg, 60% yield, 91% ee; (*S,R*)-**L1**: 117 mg, 61% yield, 90% ee.

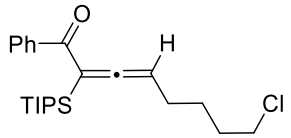
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 7.6 min (major), 8.9 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.24 (m, 7H), 4.97 (t, *J* = 7.5 Hz, 1H), 4.47 (s, 2H), 3.37 (t, *J* = 6.6 Hz, 2H), 2.13 – 2.03 (m, 2H), 1.57 – 1.50 (m, 2H), 1.40 – 1.24 (m, 7H), 1.11 (dd, *J* = 7.6, 2.3 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.5, 196.4, 138.6, 138.4, 132.1, 129.3, 128.3, 127.9, 127.6, 127.5, 97.6, 87.2, 72.9, 70.2, 29.5, 29.4, 28.0, 25.6, 18.7 (two carbons), 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{31}H_{45}O_2Si$: 477.3189, found: 477.3181.

$[\alpha]^{24}_D$ = +5.6 (*c* = 0.5, $CHCl_3$); 91% ee, from (*R,S*)-**L1**.



8-chloro-1-phenyl-2-(triisopropylsilyl)octa-2,3-dien-1-one (Scheme 3, entry 32). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromo-7-chlorohept-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 104 mg, 66% yield, 90% ee; (*S,R*)-**L1**: 102 mg, 65% yield, 90% ee.

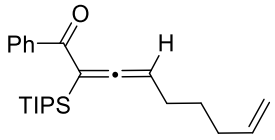
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.5 min (major), 6.5 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.53 – 7.48 (m, 1H), 7.44 – 7.39 (m, 2H), 4.98 (t, *J* = 7.5 Hz, 1H), 3.41 (t, *J* = 6.5 Hz, 2H), 2.15 – 2.05 (m, 2H), 1.66 – 1.59 (m, 2H), 1.53 – 1.43 (m, 2H), 1.37 (dt, *J* = 20.2, 7.5 Hz, 3H), 1.12 (d, *J* = 7.6 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.4, 196.3, 138.4, 132.2, 129.2, 128.0, 98.0, 86.7, 44.6, 31.7, 27.3, 26.7, 18.7 (two carbons), 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{36}ClOSi$: 391.2224, found: 391.2222.

$[\alpha]^{24}_D$ = +24.8 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



1-phenyl-2-(triisopropylsilyl)nona-2,3,8-trien-1-one (Scheme 3, entry 33). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromooct-7-en-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 68 mg, 46% yield, 91% ee; (*S,R*)-**L1**: 72 mg, 48% yield, 91% ee.

HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.2 min (major), 4.5 min (minor).

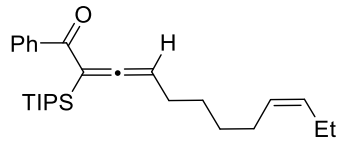
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H), 7.53 – 7.48 (m, 1H), 7.44 – 7.37 (m, 2H), 5.76 – 5.66 (m, 1H), 4.99 (t, *J* = 7.5 Hz, 1H), 4.96 – 4.89 (m, 2H), 2.13 – 2.04 (m, 2H), 1.94 (q, *J* = 7.3 Hz,

2H), 1.46 – 1.33 (m, 5H), 1.12 (d, *J* = 7.7 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.5, 196.4, 138.4, 138.1, 132.1, 129.3, 128.0, 114.8, 97.7, 87.0, 33.0, 28.7, 27.4, 18.7 (two carbons), 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{36}OSi$: 369.2614, found: 369.2614.

$[\alpha]^{24}_D$ = +15.2 (*c* = 0.5, $CHCl_3$); 91% ee, from (*R,S*)-**L1**.



(Z)-1-phenyl-2-(triisopropylsilyl)dodeca-2,3,9-trien-1-one (Scheme 3, entry 34). The title compound was prepared according to the **GP-2** from benzaldehyde and (Z)-(3-bromoundec-8-en-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 104 mg, 63% yield, 90% ee; (*S,R*)-**L1**: 106 mg, 64% yield, 90% ee.

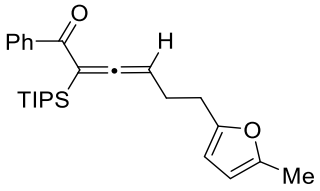
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.0 min (major), 4.3 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.3 Hz, 2H), 7.53 – 7.46 (m, 1H), 7.43 – 7.37 (m, 2H), 5.43 – 5.19 (m, 2H), 4.99 (t, *J* = 7.5 Hz, 1H), 2.13 – 1.92 (m, 6H), 1.41 – 1.31 (m, 5H), 1.28 – 1.23 (m, 2H), 1.12 (dd, *J* = 7.6, 2.6 Hz, 18H), 0.94 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.6, 196.4, 138.4, 132.1 (two carbons), 131.8, 129.3, 128.8, 128.7, 127.9, 97.6, 87.3, 87.2, 29.1, 29.0, 27.9, 26.7, 20.5, 18.7 (two carbons), 14.3, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{43}OSi$: 411.3083, found: 411.3070.

$[\alpha]^{24}_D$ = +11.2 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



6-(5-methylfuran-2-yl)-1-phenyl-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 3, entry 35). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromo-5-(5-methylfuran-2-yl)pent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 106 mg, 64% yield, 88% ee; (*S,R*)-**L1**: 109 mg, 66% yield, 88% ee.

HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.7 min (major), 5.0 min (minor).

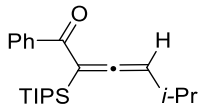
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.54 – 7.49 (m, 1H), 7.45 – 7.39 (m, 2H), 5.79 (d, *J* = 1.9 Hz, 1H), 5.76 (d, *J* = 2.9 Hz, 1H), 5.03 (t, *J* = 7.4 Hz, 1H), 2.63 – 2.56 (m, 2H), 2.40 (ddd, *J*

= 15.0, 7.4, 2.8 Hz, 2H), 2.23 (s, 3H), 1.39 – 1.32 (m, 3H), 1.12 (dd, *J* = 7.6, 3.0 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.0, 196.1, 152.7, 150.5, 138.3, 132.2, 129.3, 128.0, 106.0, 105.8, 97.9, 86.3, 28.1, 27.0, 18.7 (two carbons), 13.5, 11.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{37}O_2Si$: 409.2563, found: 409.2563.

$[\alpha]^{24}_D$ = +10.4 (*c* = 0.5, $CHCl_3$); 88% ee, from (*R,S*)-**L1**.



5-methyl-1-phenyl-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 3, entry 36). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromo-4-methylpent-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 57 mg, 41% yield, 92% ee; (*S,R*)-**L1**: 78 mg, 57% yield, 92% ee.

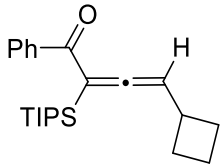
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.1 min (major), 4.3 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.52 – 7.47 (m, 1H), 7.42 – 7.38 (m, 2H), 4.95 (d, *J* = 7.8 Hz, 1H), 2.46 – 2.38 (m, 1H), 1.40 – 1.34 (m, 3H), 1.12 (dd, *J* = 7.5, 4.2 Hz, 18H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.6, 196.6, 138.5, 132.0, 129.3, 127.9, 99.1, 94.7, 28.6, 22.9 (two carbons), 18.8 (two carbons), 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{35}OSi$: 343.2457, found: 343.2444.

$[\alpha]^{24}_D$ = +5.2 (*c* = 0.5, $CHCl_3$); 92% ee, from (*R,S*)-**L1**.



4-cyclobutyl-1-phenyl-2-(triisopropylsilyl)buta-2,3-dien-1-one (Scheme 3, entry 37). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromo-3-cyclobutylprop-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 74 mg, 52% yield, 90% ee; (*S,R*)-**L1**: 83 mg, 58% yield, 90% ee.

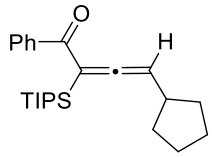
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.3 min (major), 4.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.52 – 7.47 (m, 1H), 7.43 – 7.38 (m, 2H), 5.13 (d, *J* = 7.9 Hz, 1H), 3.04 – 2.96 (m, 1H), 2.19 – 2.08 (m, 2H), 1.90 – 1.74 (m, 4H), 1.36 (dt, *J* = 15.0, 7.5 Hz, 3H), 1.12 (dd, *J* = 7.6, 2.9 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.8, 196.3, 138.3, 132.0, 129.3, 127.9, 98.6, 92.5, 34.2, 29.5 29.3, 18.7 (three carbons), 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{35}OSi$: 355.2457, found: 355.2461.

$[\alpha]^{24}_D$ = +0.8 (*c* = 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



4-cyclopentyl-1-phenyl-2-(triisopropylsilyl)buta-2,3-dien-1-one (Scheme 3, entry 38). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromo-3-cyclopentylprop-1-yn-1-yl)triisopropylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 101 mg, 68% yield, 96% ee; (*S,R*)-**L1**: 102 mg, 69% yield, 96% ee.

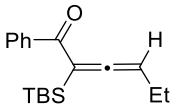
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.2 min (major), 4.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.52 – 7.46 (m, 1H), 7.43 – 7.37 (m, 2H), 5.00 (d, *J* = 8.1 Hz, 1H), 2.60 – 2.52 (m, 1H), 1.88 – 1.79 (m, 1H), 1.77 – 1.69 (m, 1H), 1.58 – 1.49 (m, 4H), 1.41 – 1.33 (m, 3H), 1.28 – 1.25 (m, 1H), 1.21 – 1.17 (m, 1H), 1.12 (dd, *J* = 7.5, 5.5 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.4, 196.5, 138.4, 132.0, 129.3, 127.9, 98.5, 92.5, 39.2, 33.3, 33.1, 24.9, 18.8, 18.7, 11.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{37}OSi$: 369.2614, found: 369.2619.

$[\alpha]^{24}_D$ = -5.6 (*c* = 0.5, $CHCl_3$); 96% ee, from (*R,S*)-**L1**.



2-(*tert*-butyldimethylsilyl)-1-phenylhexa-2,3-dien-1-one (Scheme 3, entry 39). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromopent-1-yn-1-yl)(*tert*-butyl)dimethylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 79 mg, 52% yield, 74% ee; (*S,R*)-**L1**: 72 mg, 48% yield, 74% ee.

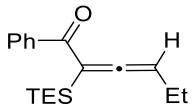
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.3 min (major), 4.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H), 7.53 – 7.48 (m, 1H), 7.44 – 7.38 (m, 2H), 5.07 (t, *J* = 7.0 Hz, 1H), 2.13 – 2.05 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.97 (s, 9H), 0.21 (d, *J* = 5.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.5, 196.0, 138.3, 132.2, 129.3, 128.0, 100.2, 88.9, 26.9, 21.2, 18.0, 13.9, -5.1, -5.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{27}OSi$: 287.1831, found: 287.1831.

$[\alpha]^{24}_D$ = +1.6 (*c* = 0.5, $CHCl_3$); 74% ee, from (*R,S*)-**L1**.



1-phenyl-2-(triethylsilyl)hexa-2,3-dien-1-one (Scheme 3, entry 40). The title compound was prepared according to the **GP-2** from benzaldehyde and (3-bromopent-1-yn-1-yl)triethylsilane, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 68 mg, 59% yield, 70% ee; (*S,R*)-**L1**: 65 mg, 55% yield, 70% ee.

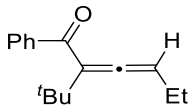
HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.6 min (major), 5.0 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.53 – 7.48 (m, 1H), 7.43 – 7.38 (m, 2H), 5.08 (t, *J* = 6.9 Hz, 1H), 2.13 – 2.05 (m, 2H), 1.03 – 0.96 (m, 12H), 0.80 – 0.74 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.7, 196.3, 138.3, 132.1, 129.2, 127.9, 99.3, 88.6, 21.2, 13.9, 7.4, 3.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{26}OSi$: 287.1831, found: 287.1826.

$[\alpha]^{24}_D$ = +15.6 (*c* = 0.5, $CHCl_3$); 70% ee, from (*R,S*)-**L1**.



2-(*tert*-butyl)-1-phenylhexa-2,3-dien-1-one (Scheme 3, entry 41). The title compound was prepared according to the **GP-2** from benzaldehyde and 5-bromo-2,2-dimethylhept-3-yne, purified by flash column chromatography on silica gel: hexane, colorless liquid.

(*R,S*)-**L1**: 20 mg, 21% yield, 95% ee; (*S,R*)-**L1**: 17 mg, 18% yield, 95% ee.

HPLC analysis: The ee was determined on a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.6 min (major), 4.8 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 5.35 (t, *J* = 6.7 Hz, 1H), 2.04 (qd, *J* = 7.5, 1.5 Hz, 2H), 1.27 (s, 9H), 0.95 (t, *J* = 7.4 Hz, 3H).

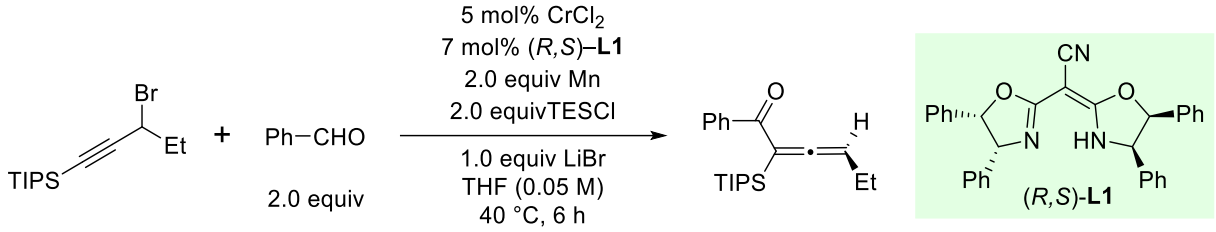
^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 196.0, 139.8, 131.8, 129.0, 127.8, 115.9, 97.3, 30.9, 29.7, 21.9, 13.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{20}O$: 229.1592, found: 229.1590.

$[\alpha]^{24}_D$ = +10.20 (*c* = 0.5, $CHCl_3$); 95% ee, from (*R,S*)-**L1**.

IV. Effect of Reaction Parameters

General procedure 3 (GP-3): Catalytic Allenylation Reactions.

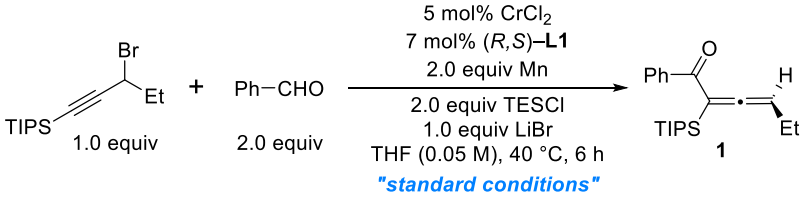


Preparation of the catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial with a magnetic stir bar, were charged the $CrCl_2$ (0.6 mg, 0.005 mmol, 5 mol%) and (*R,S*)-**L1** (3.4 mg, 0.007 mmol, 7 mol%). Then 2.0 mL THF was added and the vial was closed with a PTFE septum cap. The mixture was stirred at room temperature for 1 h.

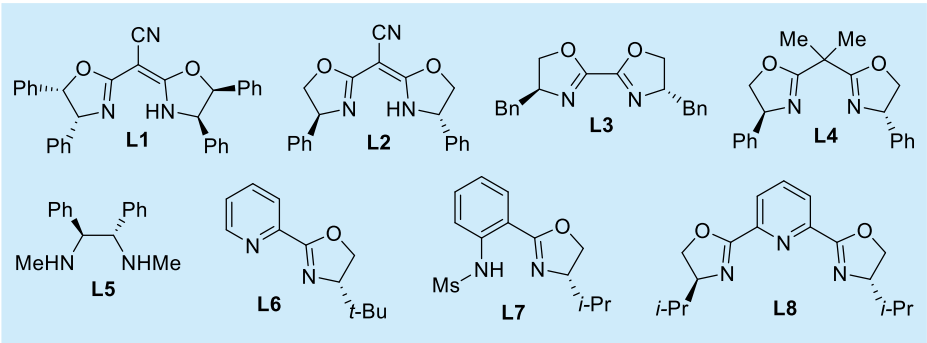
Catalytic asymmetric allenylation: In a nitrogen-filled glovebox, to the prepared catalyst solution were added the propargyl bromide (30 mg, 0.1 mmol, 1.0 equiv), the LiBr (8.7 mg, 0.1 mmol, 1.0 equiv), the aldehyde (20 μL, 0.2 mmol, 2.0 equiv), the dissociation reagent TESCl (34 μL, 0.2 mmol, 2.0 equiv), and Mn powder (11 mg, 0.2 mmol, 2.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. The reaction mixture was stirred at 40 °C for 6 h.

Work-up: The reaction mixture was run through a short silica gel pad with hexanes/EtOAc (10:1) as the eluent. Then the solvent was removed the under reduced pressure. The yield was determined via ^{1}H NMR analysis of the crude reaction mixture. The ee was determined via HPLC analysis after further purification by prep-TLC.

Table S1. Effect of Reaction Parameters.



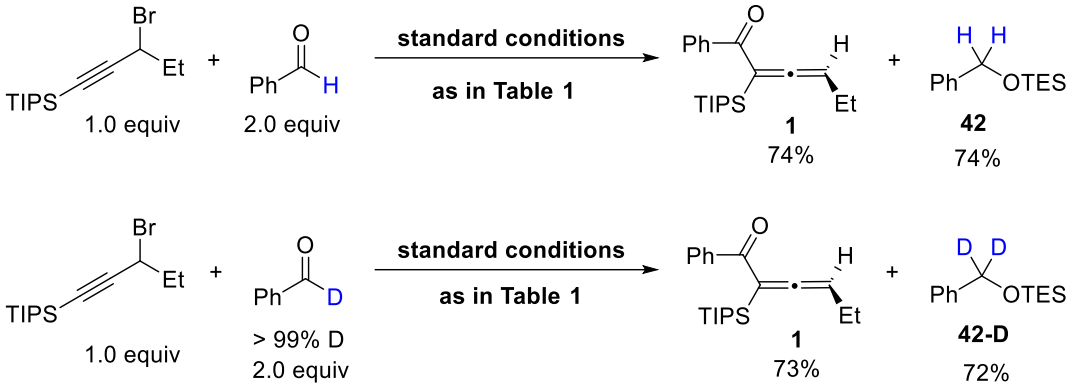
entry	variation from the "*standard conditions*"	Yield[a] (%)	ee[b] (%)
1	None	83	91
2	No $CrCl_2$, No **L1**	<1	–
3	No $CrCl_2$	<1	–
4	No **L1**	13	0
5	**L2**, instead of **L1**	40	88
6	**L3**, instead of **L1**	14	<2
7	**L4**, instead of **L1**	13	18
8	**L5**, instead of **L1**	11	20
9	**L6**, instead of **L1**	10	11
10	**L7**, instead of **L1**	14	21
11	**L8**, instead of **L1**	<1	–
12	Zn, instead of Mn	<1	–
13	No TESCl	<1	–
14	TMSCl, instead of TESCl	73	81
15	0.1 M, instead of 0.05 M, in THF	85	86
16	$CrCl_3(THF)_3$, instead of $CrCl_2$	74	88
17	No LiBr	36	82
18	0.5 equiv LiBr	66	90
19	2 mol% $CrCl_2$, 3 mol% **L1**	42	89
20	1.5 equiv aldehyde	59	89
21	1.5 equiv Mn	73	89
22	1.5 equiv TESCl	58	88
23	DME, instead of THF	56	88
24	rt, instead of 40 °C	42	87
25	1.0 equiv H_2O was added	21	87
26	1 mL air, added via syringe	<1	–
27[c]	1.0 equiv aldehyde	40	76



[a] All datas are the average of two experiments. [b] Yield and dr were determined via ^{1}H NMR analysis. [c] ee was determined via HPLC analysis.[c] The corresponding allenol was obtained with 21% yield, 5:1 dr and 92% ee.

V. Preliminary Mechanistic Study

Deuterium labelling experiment



This reaction was conducted according to the **GP-3**.

Data for product **42**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 5H), 4.74 (s, 2H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.66 (q, *J* = 8.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 128.2, 126.9, 126.2, 64.7, 6.8, 4.5.

Data for product 4**2-D**:

^{1}H NMR (500 MHz, $CDCl_3$) δ7.36 – 7.21 (m, 5H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 128.2, 127.0, 126.3, 64.2, 6.8, 4.5.

General procedure 4 (GP-4): Catalytic Allenylation Reactions.

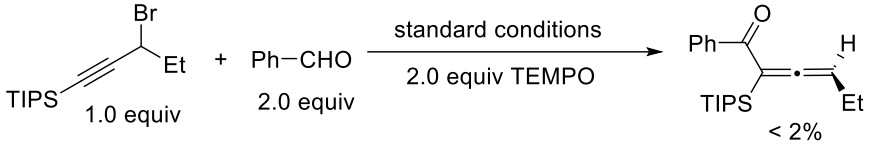
Preparation of the catalyst solution: In a nitrogen-filled glovebox, and oven-dried 20 mL vial with a magnetic stir bar, were charged the $CrCl_2$ (2.5 mg, 0.02 mmol, 5 mol%) and (*R,S*)-**L1** (13.5 mg, 0.028 mmol, 7 mol%). Then 8.0 mL THF was added and the vial was closed with a PTFE septum cap, and then stirred at room temperature for 2 h.

Catalytic asymmetric allenylation: In a nitrogen-filled glovebox, to the prepared catalyst solution were added the propargyl bromide (121 mg, 0.4 mmol, 1.0 equiv), the LiBr (35 mg, 0.4 mmol, 1.0 equiv), benzaldehyde (85 mg, 0.8 mmol, 2.0 equiv), TESCl (135 μL, 0.8 mmol, 2.0 equiv), Mn powder (44 mg, 0.8 mmol, 2.0 equiv) and radical scavenger (0.8 mmol, 2.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. The reaction mixture was stirred at 40 °C for 8 h.

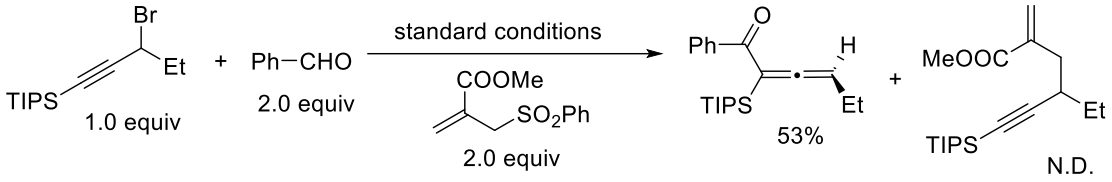
Work-up: The reaction mixture was run through a short silica gel pad with hexanes/EtOAc (5:1) as the eluent. Then the solvent was removed the under reduced pressure, and the residue was purified by flash chromatography to provide the desired product.

Radical trapping experiments

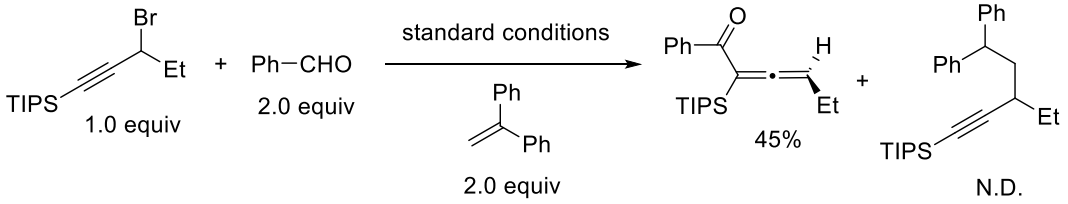
a)



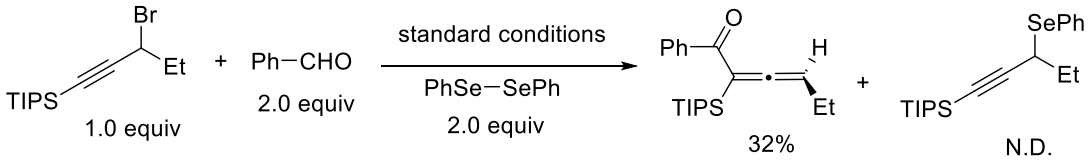
b)



c)

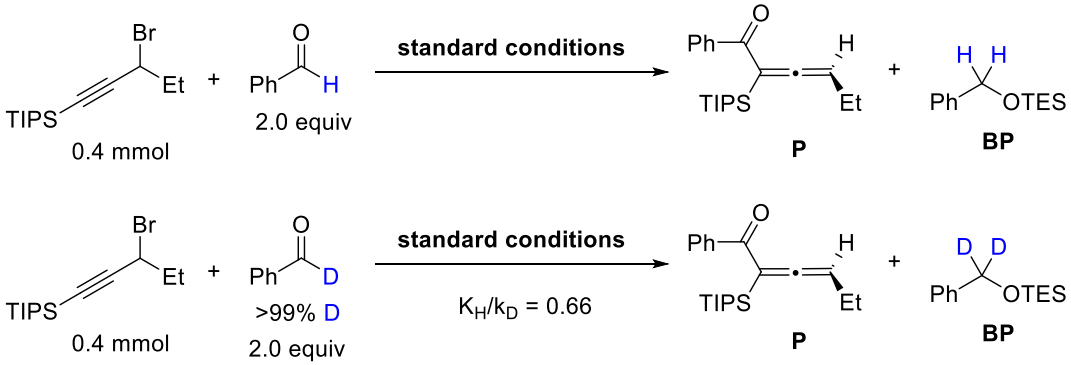


d)

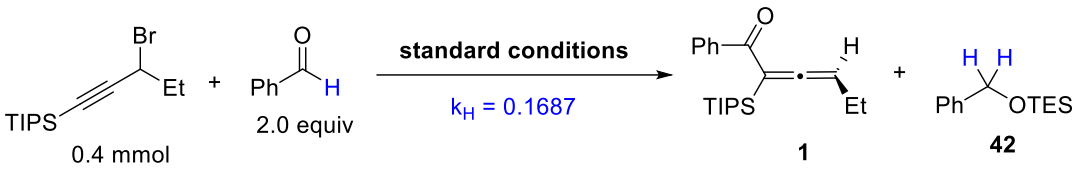


According to the **GP-4**, the reaction was proceeded with **a)** TEMPO (125 mg, 0.8 mmol, 2.0 equiv), **b)** methyl 2-((phenylsulfonyl)methyl)acrylate (192 mg, 0.8 mmol, 2.0 equiv), **c)** ethene-1,1-diyldibenzene (144 mg, 0.8 mmol, 2.0 equiv), **d)** 1,2-diphenyldiselane (249 mg, 0.8 mmol, 2.0 equiv) as radical scavenger respectively.

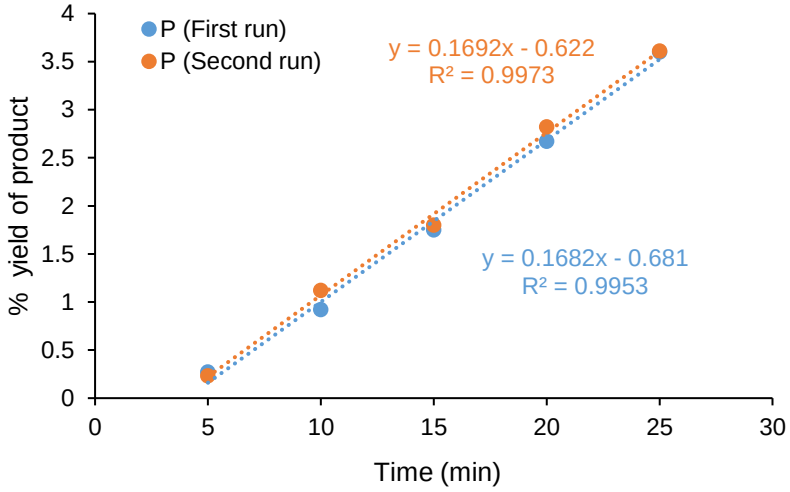
Secondary isotope effect



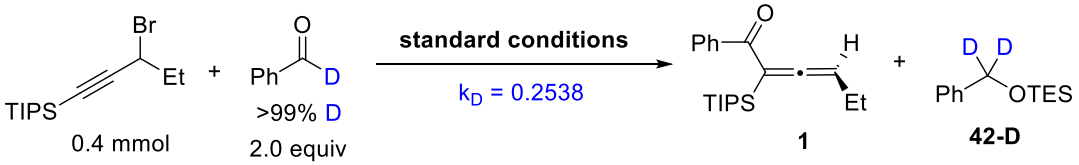
This reaction was conducted according to the **GP-2** with 1,3,5-trimethoxybenzene as an internal standard. In a nitrogen-filled glovebox, 200 μL of reaction mixture was taken every 5 minutes and the reaction mixture was run through a short silica gel pad with hexanes/EtOAc (3:1) as the eluent immediately. Then the solvent was removed the under reduced pressure. The yield was determined by ^{1}H NMR analysis of the crude product. Each experiment was repeated 2 times. The reactions were repeated with benzaldehyde-α-d_1 under otherwise identical conditions.



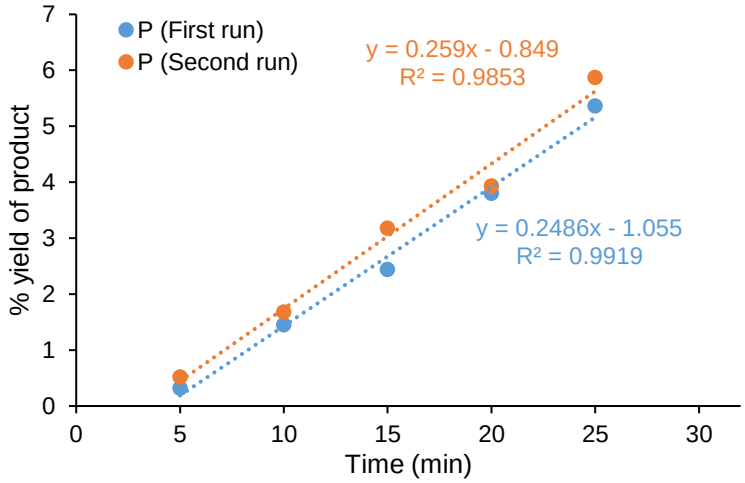
Time	**1** (%, First run)	**1** (%, Second run)
5 min	0.27	0.23
10 min	0.92	1.12
15 min	1.75	1.80
20 min	2.67	2.82
25 min	3.60	3.61



Scheme S1. Representative initial data of **42**



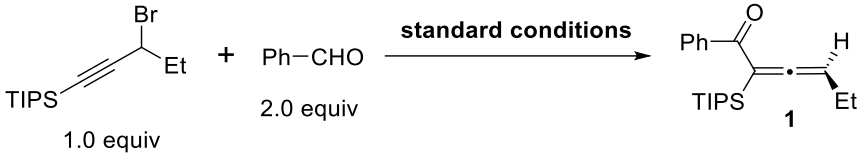
Time	**1** (%, First run)	**1** (%, Second run)
5 min	0.32	0.52
10 min	1.45	1.68
15 min	2.44	3.18
20 min	3.80	3.93
25 min	5.36	5.87



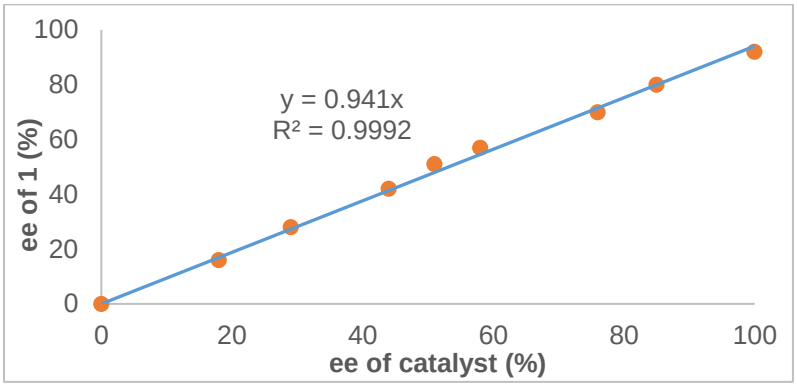
Scheme S2. Representative initial data of **42-D**

KIE= k_H /k_D = 0.1687/0.2538= 0.66

Non-linear effect study

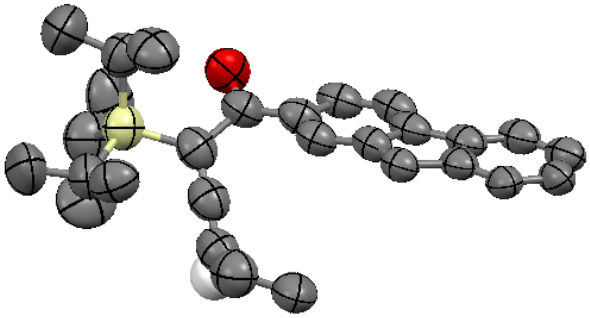


According to the **GP-3**, the reaction was proceeded in 9 times with chiral ligands (*S,R*)-**L1** and (*R,S*)-**L1** mixed in different proportions. The ee value of product **1** was determined by HPLC analysis: a CHIRALPAK: AD-3 column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.2 min (major), 4.5 min (minor). And the ee value of catalyst was determined by SFC analysis: a CHIRALCEL IG-3 column (20% MeOH in CO_2, 2.0 mL/min); retention times for catalyst: 3.6 min and 5.5 min.

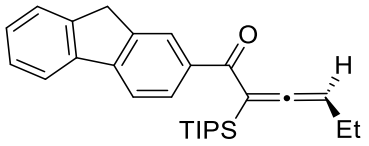


Scheme S3. Non-linear effect study of **1**

VI. Assignment of the Absolute Configuration



Scheme S4. Thermal ellipsoid plot at the 50% probability level. Hydrogen atoms are omitted for clarity.



(*R*)-1-(9H-fluoren-2-yl)-2-(triisopropylsilyl)hexa-2,3-dien-1-one (Scheme 2, entry 16). X-ray quality crystals were obtained by slow evaporation of a saturated solution in MeCN of a sample synthesized with (*R,S*)-**L1**. A single crystal of $C_{28}H_{36}OSi$ was selected and mounted in a nylon loop in parabar oil. All measurements were performed on a Bruker Photon III diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2 (*4*), the structure was solved with the ShelXS structure solution program (*5*) using Direct Methods and refined with the ShelXL refinement package (*6*) using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter. Crystal data, data collection parameters, and structure refinement details are given in **Table S2** and **Table S3**.

Table S2. Sample and crystal data.

Identification code	CU-ORTH-FULL4-NO14_a_a	
Chemical formula	$C_{28}H_{36}OSi$	
Formula weight	416.66 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.2879(5) Å	α = 90°
	b = 8.1290(6) Å	β = 90°
	c = 41.692(3) Å	γ = 90°

Volume	2470.0(3) Å^3
Z	4
Density (calculated)	1.120 g/cm^3
Absorption coefficient	0.942 mm^{-1}
F(000)	904
Crystal size	0.100 x 0.100 x 0.080 mm^3

Table S3. Data collection and structure refinement.

Theta range for data collection	4.241 to 74.907°
Index ranges	-8<=h<=9, -10<=k<=9, -52<=l<=52
Reflections collected	60775
Independent reflections	5059 [R(int) = 0.0732]
Completeness to theta = 67.679°	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.927 and 0.910
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5059 / 849 / 498
Goodness-of-fit on F^2	0.977
Final R indices [I>2sigma(I)]	R1 = 0.0666, wR2 = 0.1704
R indices (all data)	R1 = 0.0891, wR2 = 0.1909
Absolute structure parameter	0.01(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.257 and -0.280 e.Å^{-3}

VII. References

(1) Nolin, K. A.; Ahn, R. W.; Kobayashi, Y.; Kennedy-Smith, J. J.; Toste, F. D., Enantioselective Reduction of Ketones and Imines Catalyzed by (CN-Box)Re^{V}–Oxo Complexes. *Chem. Eur. J.* **2010**, *16*, 9555.

(2) Zhang, F.-H.; Guo, X.; Zeng, X.; Wang, Z., Catalytic Enantioconvergent Allenylation of Aldehydes with Propargyl Halides. *Angew. Chem., Int. Ed.* **2022**, e202117114.

(3) Wang, P.-F.; Yu, J.; Guo, K.-X.; Jiang, S.-P.; Chen, J.-J.; Gu, Q.-S.; Liu, J.-R.; Hong, X.; Li, Z.-L.; Liu, X.-Y., Design of Hemilabile N,N,N-Ligands in Copper-Catalyzed Enantioconvergent Radical Cross-Coupling of Benzyl/Propargyl Halides with Alkenylboronate Esters. *J. Am. Chem. Soc.* **2022**, *144*, 6442.

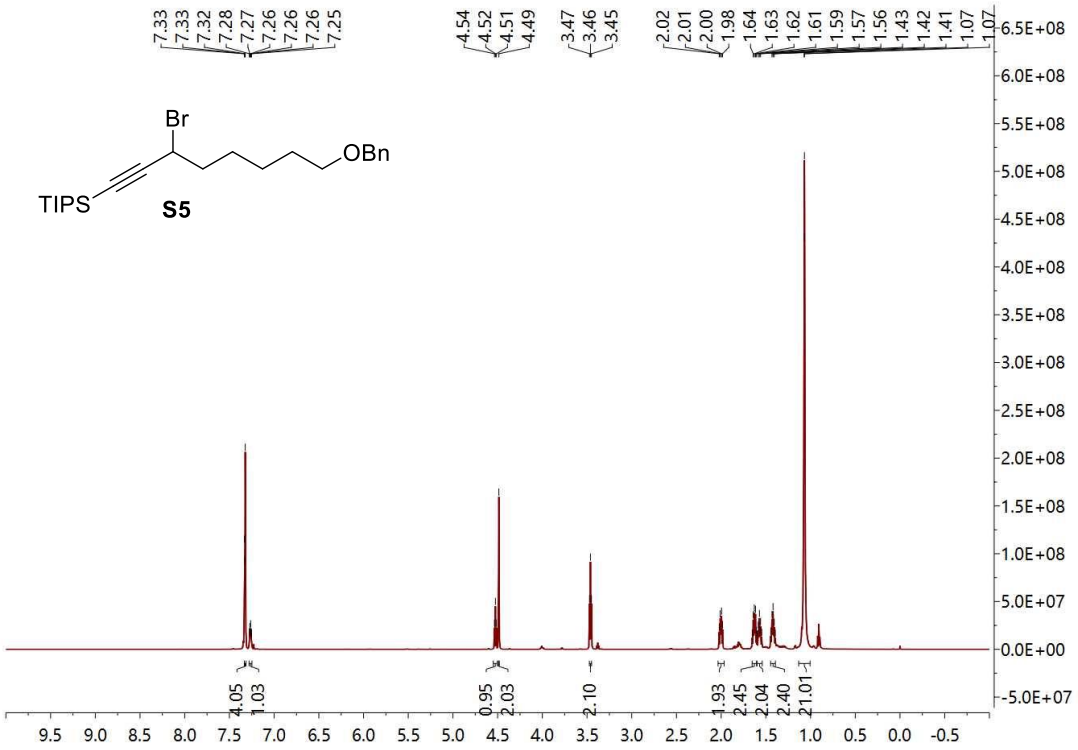
(4) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a Complete Structure Solution, Refinement, and Analysis Program. *J. Appl. Cryst.* **2009,** *42*, 339.

(5) Sheldrick, G., SHELXT - Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst. A* **2015,** *71*, 3.

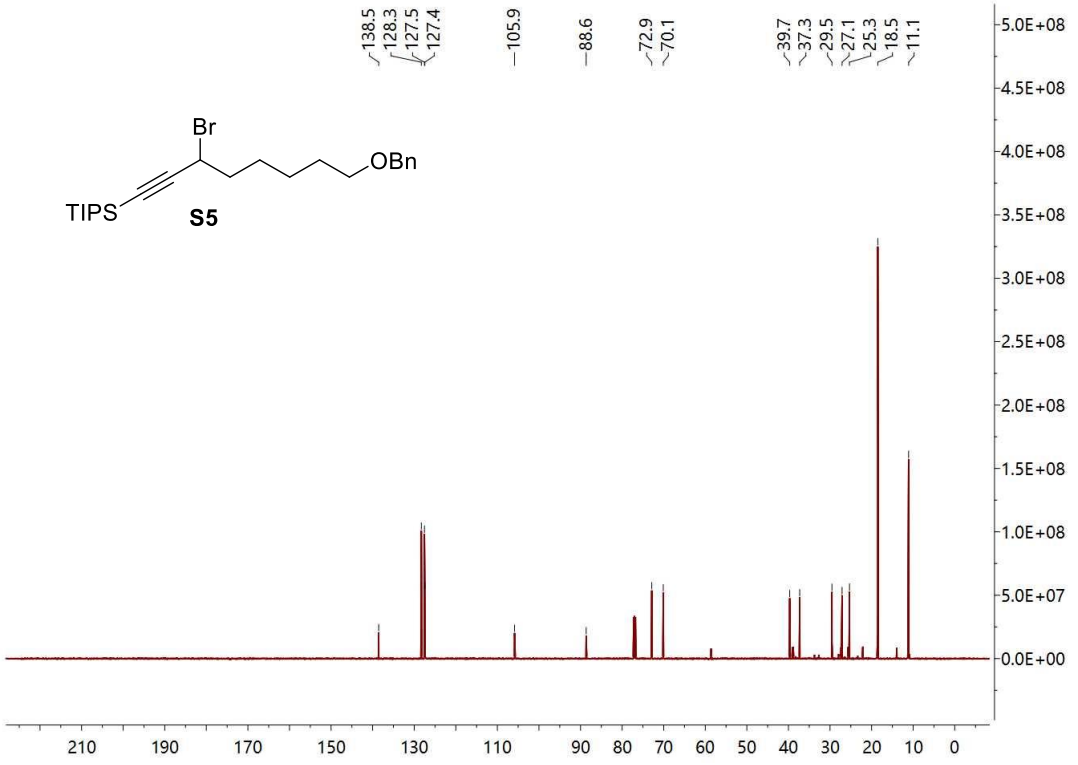
(6) Sheldrick, G., Crystal Structure Refinement with SHELXL. *Acta Cryst. C* **2015,** *71*, 3.

VIII. NMR Spectra

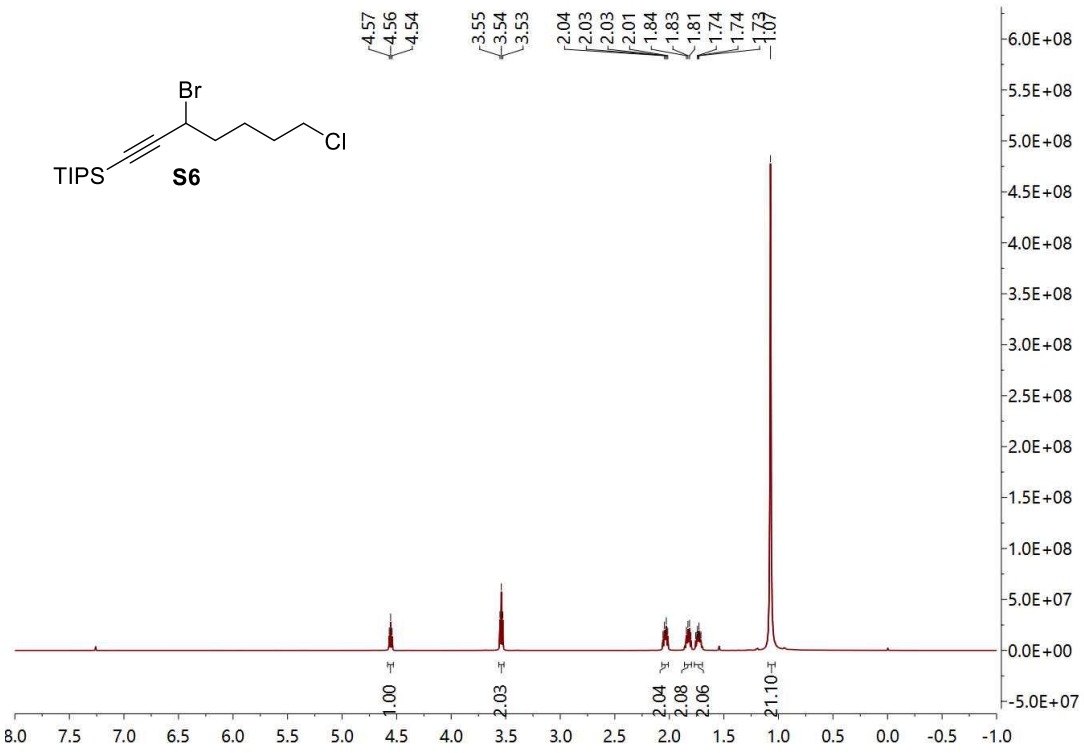
^{1}H NMR (600 MHz, $CDCl_3$)



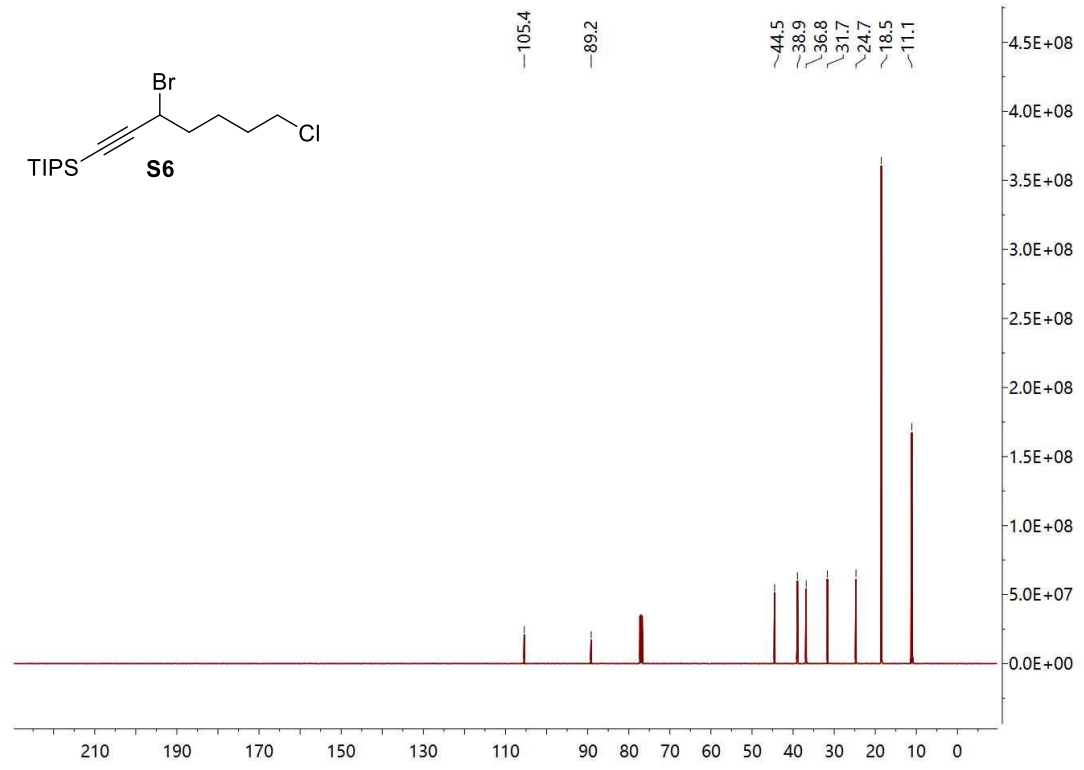
^{13}C NMR (151 MHz, $CDCl_3$)



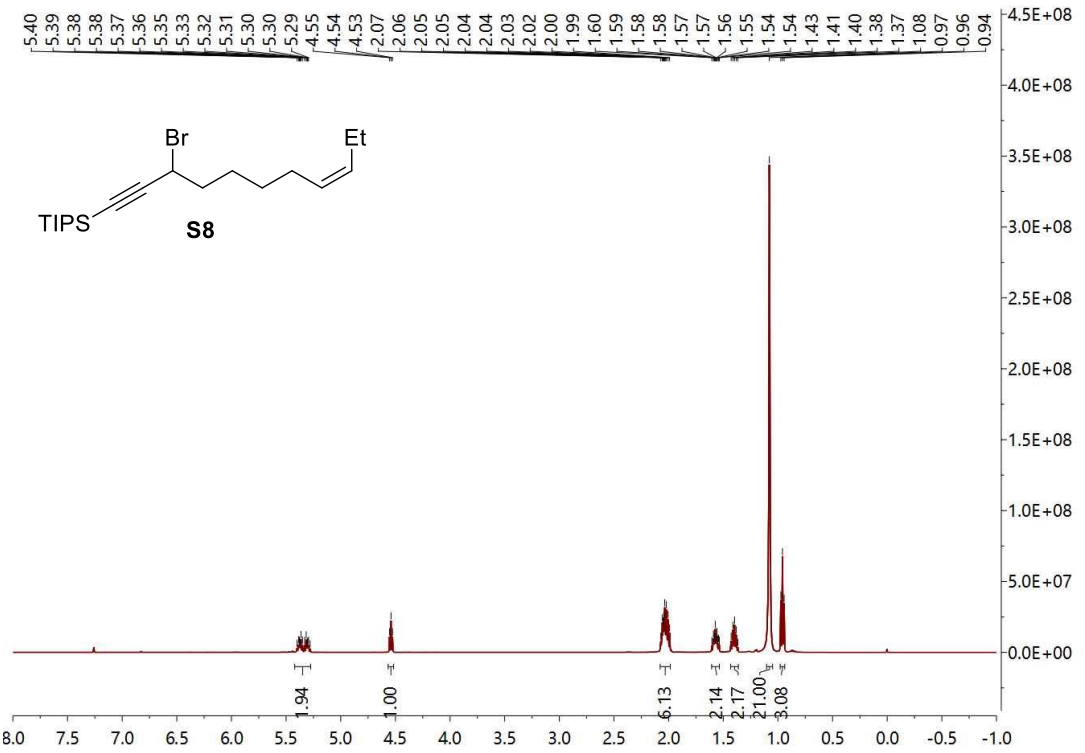
^{1}H NMR (500 MHz, $CDCl_3$)



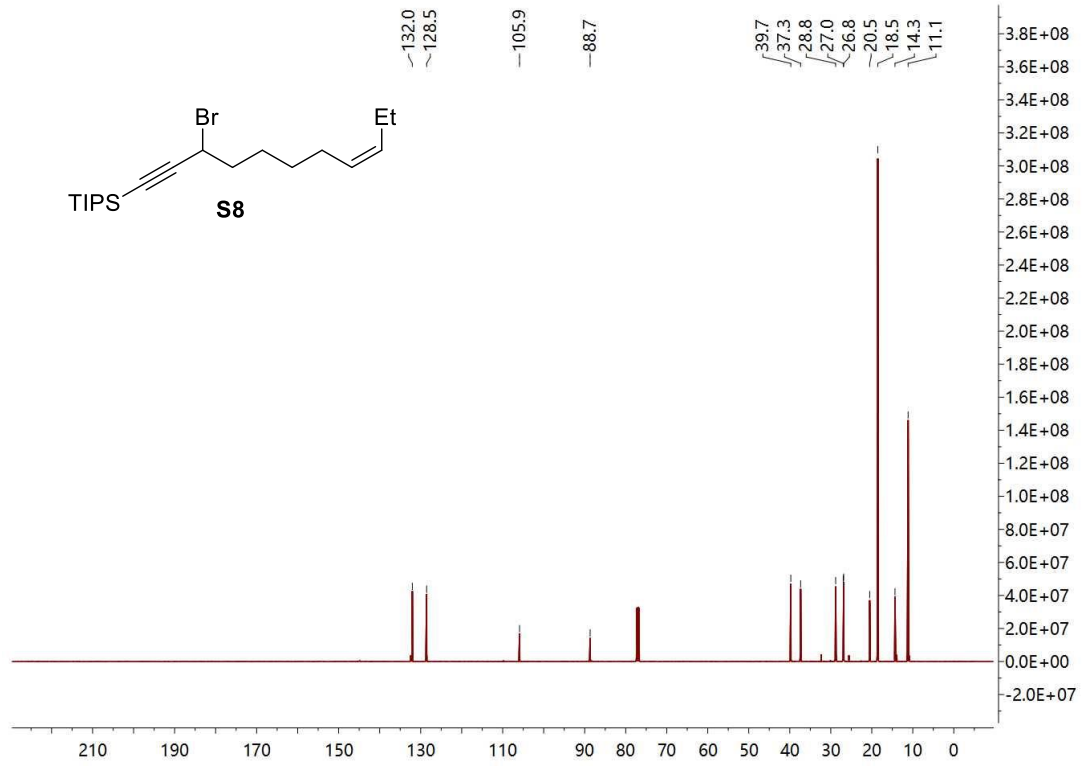
^{13}C NMR (126 MHz, $CDCl_3$)



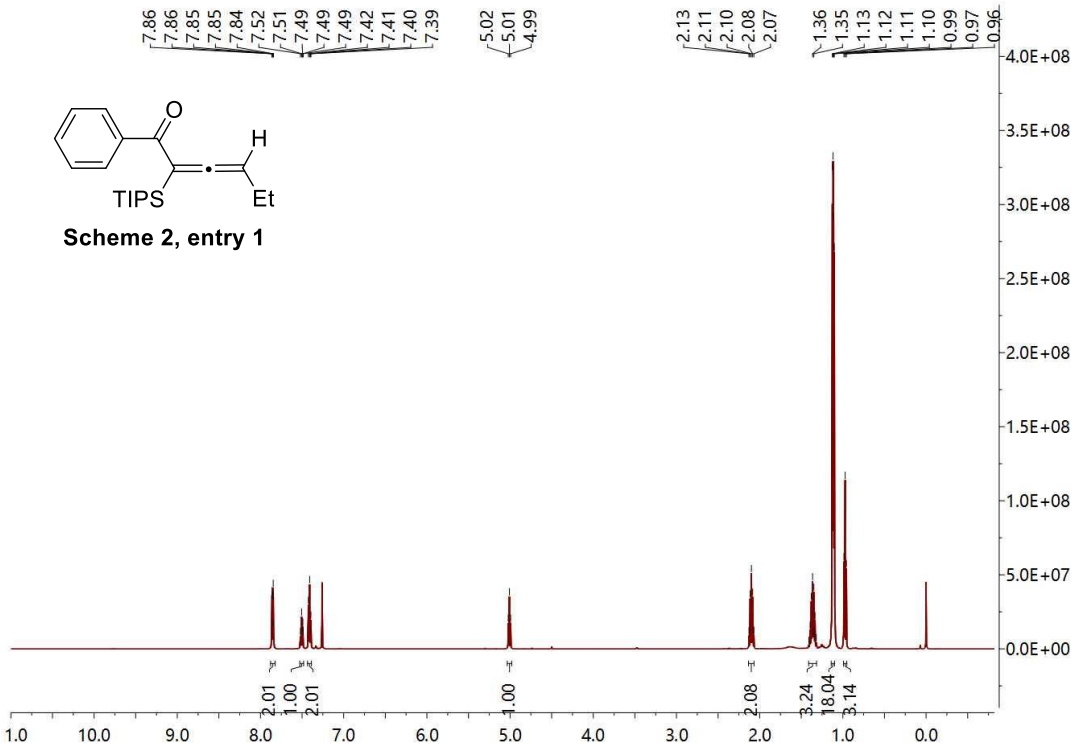
^{1}H NMR (500 MHz, $CDCl_3$)



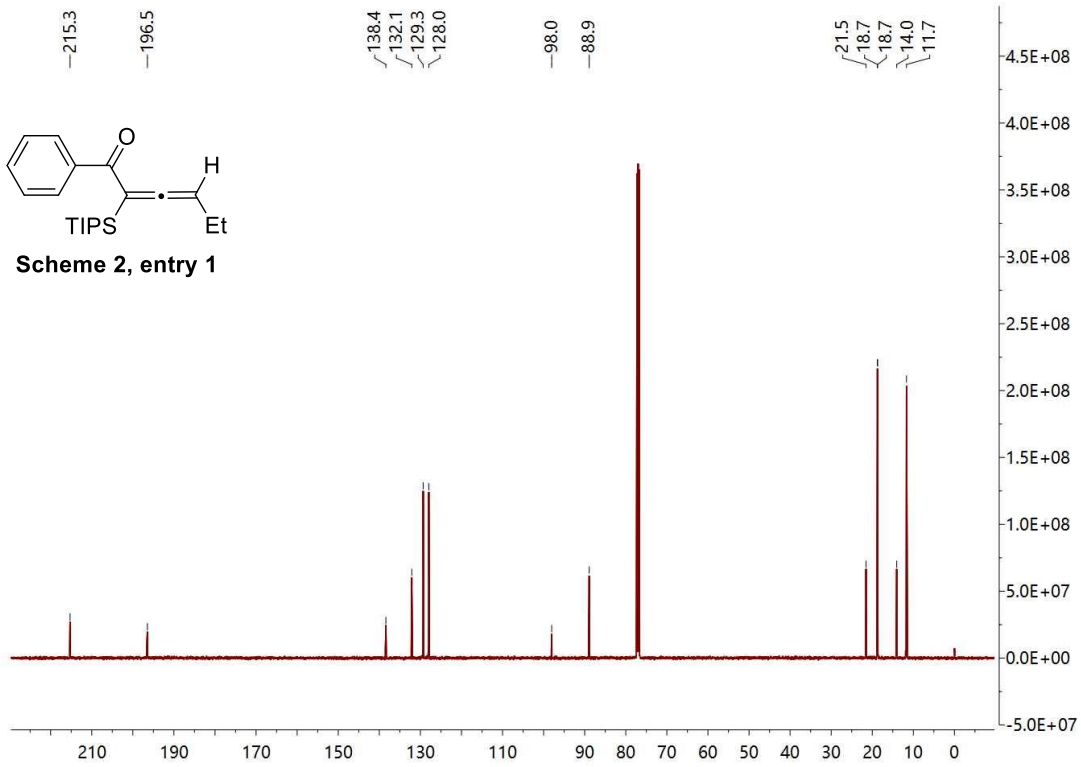
^{13}C NMR (126 MHz, $CDCl_3$)



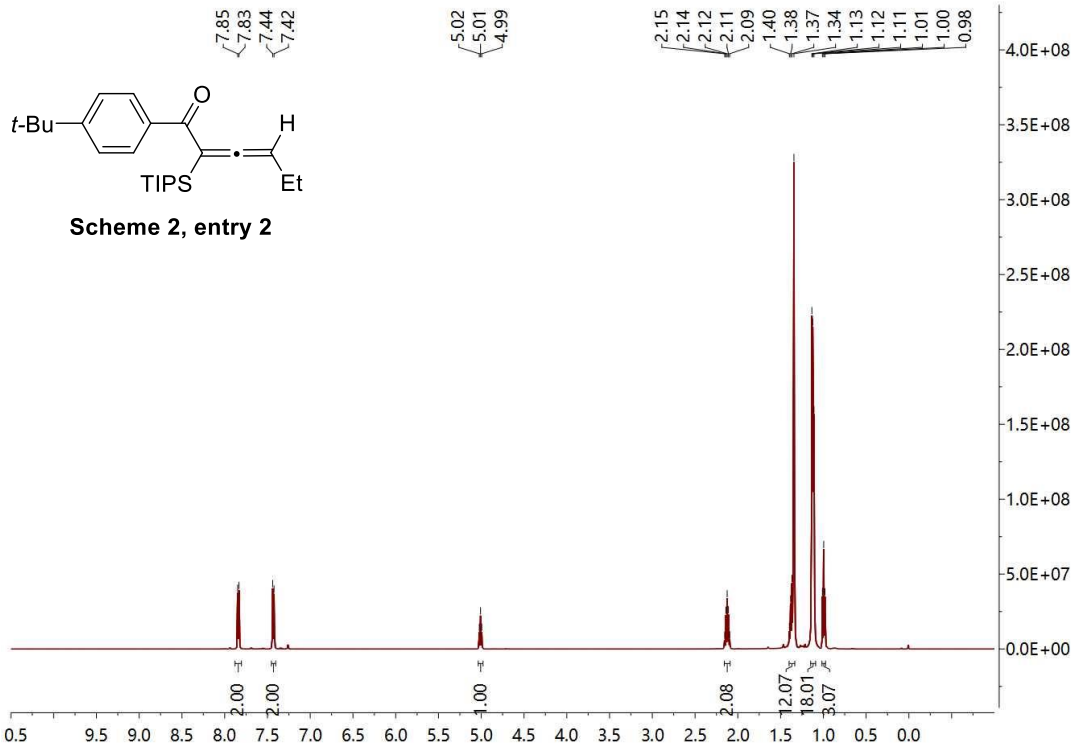
^{1}H NMR (500 MHz, $CDCl_3$)



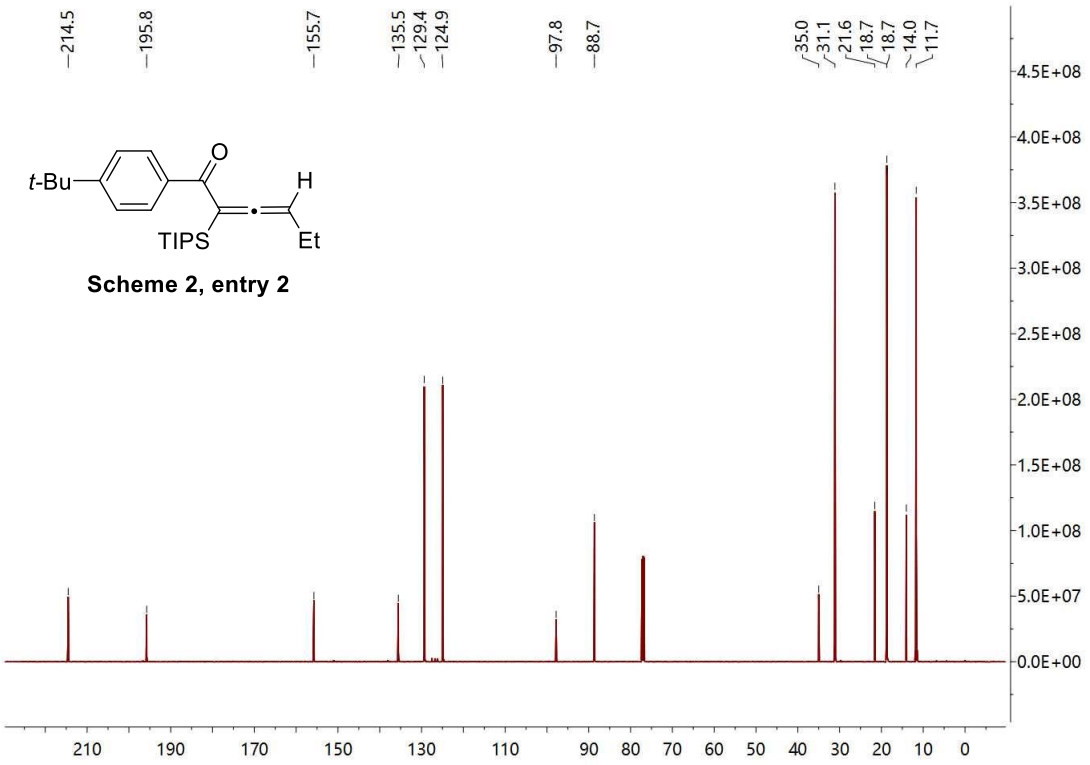
^{13}C NMR (126 MHz, $CDCl_3$)



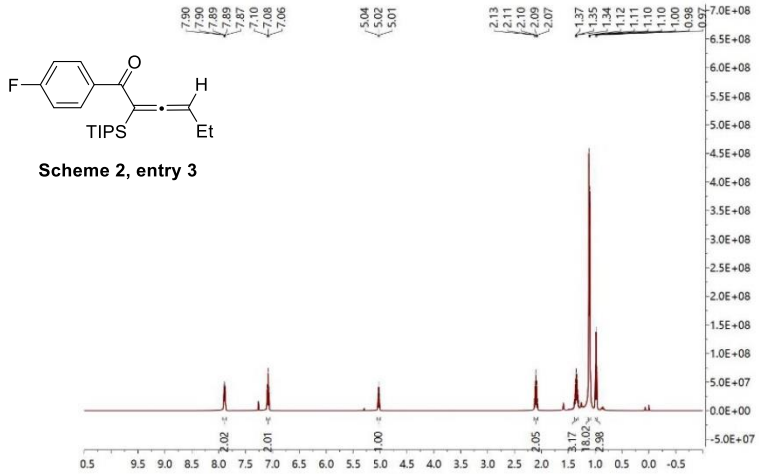
^{1}H NMR (500 MHz, $CDCl_3$)



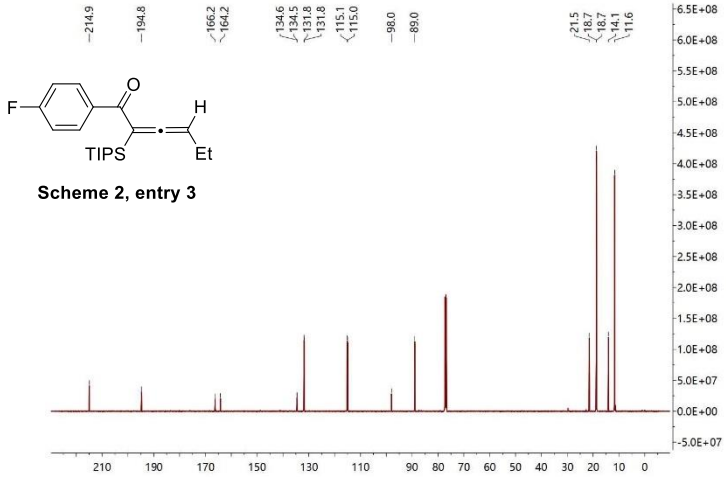
^{13}C NMR (126 MHz, $CDCl_3$)



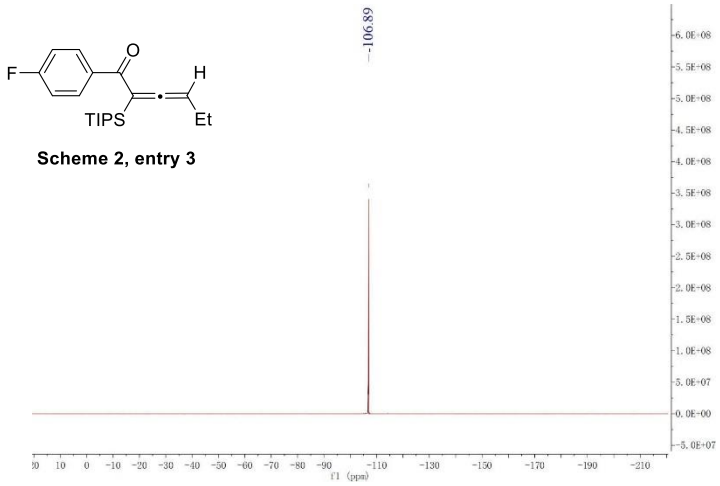
^{1}H NMR (500 MHz, $CDCl_3$)



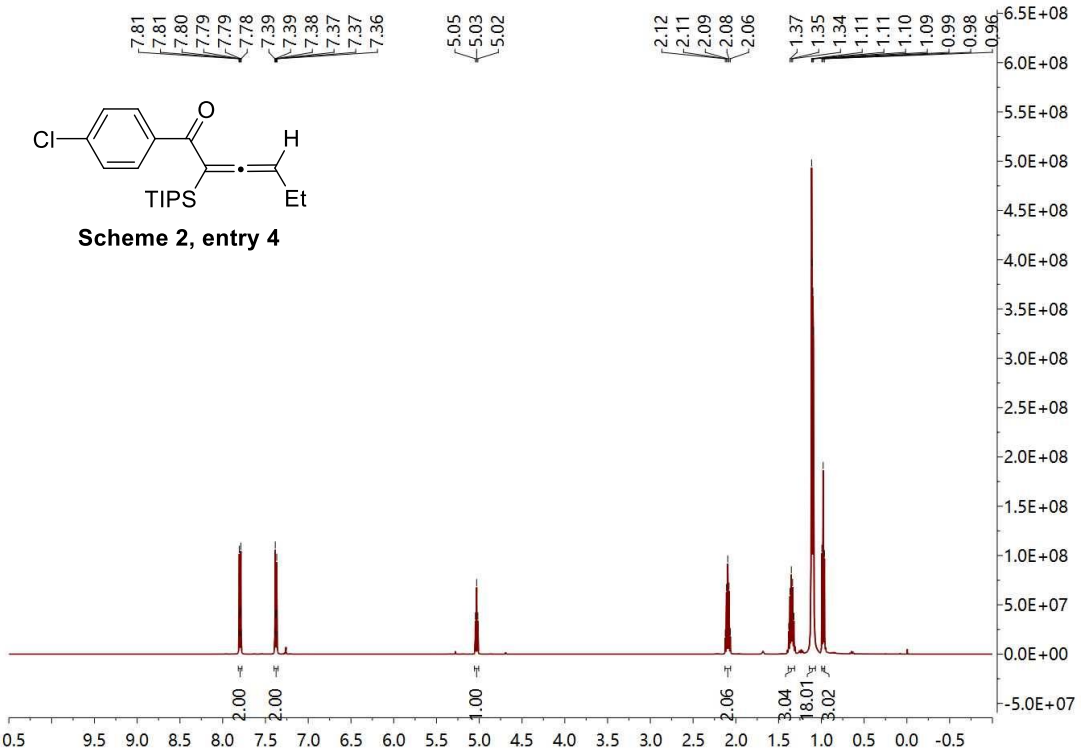
^{13}C NMR (126 MHz, $CDCl_3$)



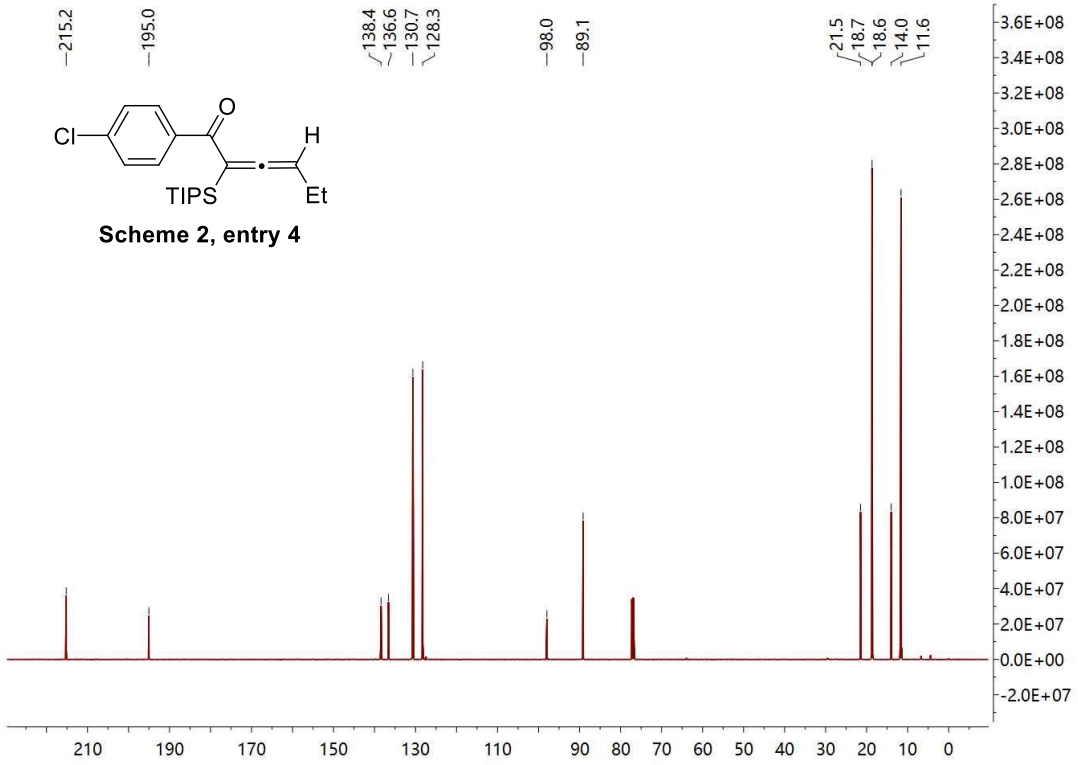
^{19}F NMR (471 MHz, $CDCl_3$)



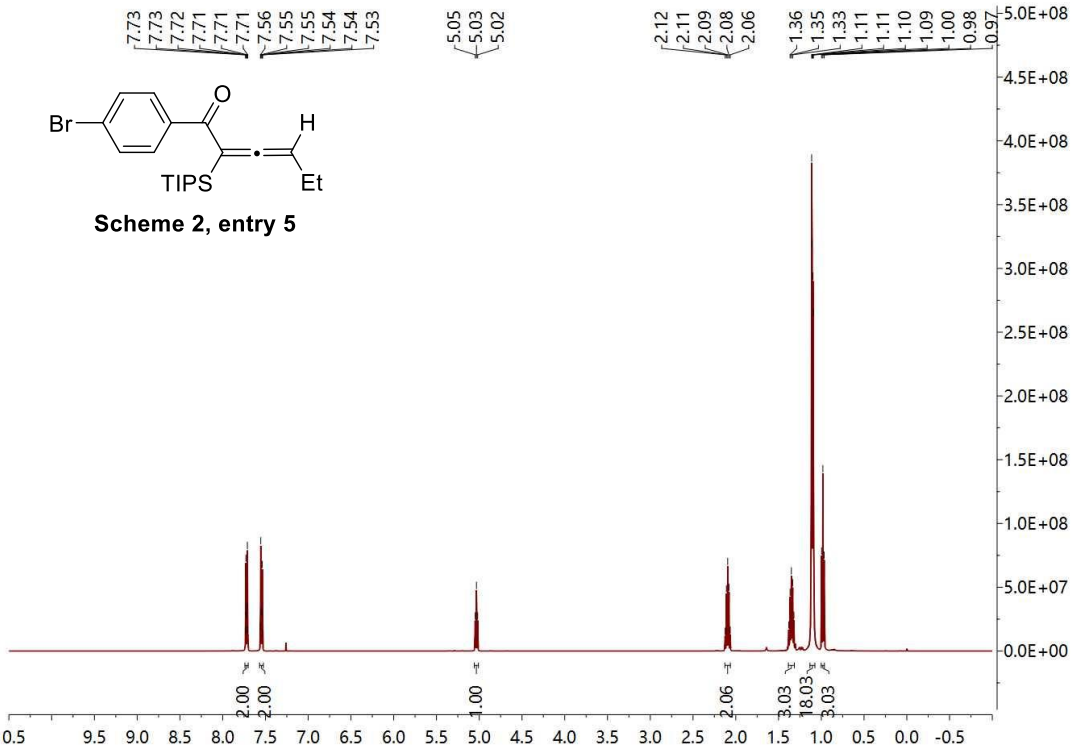
^{1}H NMR (500 MHz, $CDCl_3$)



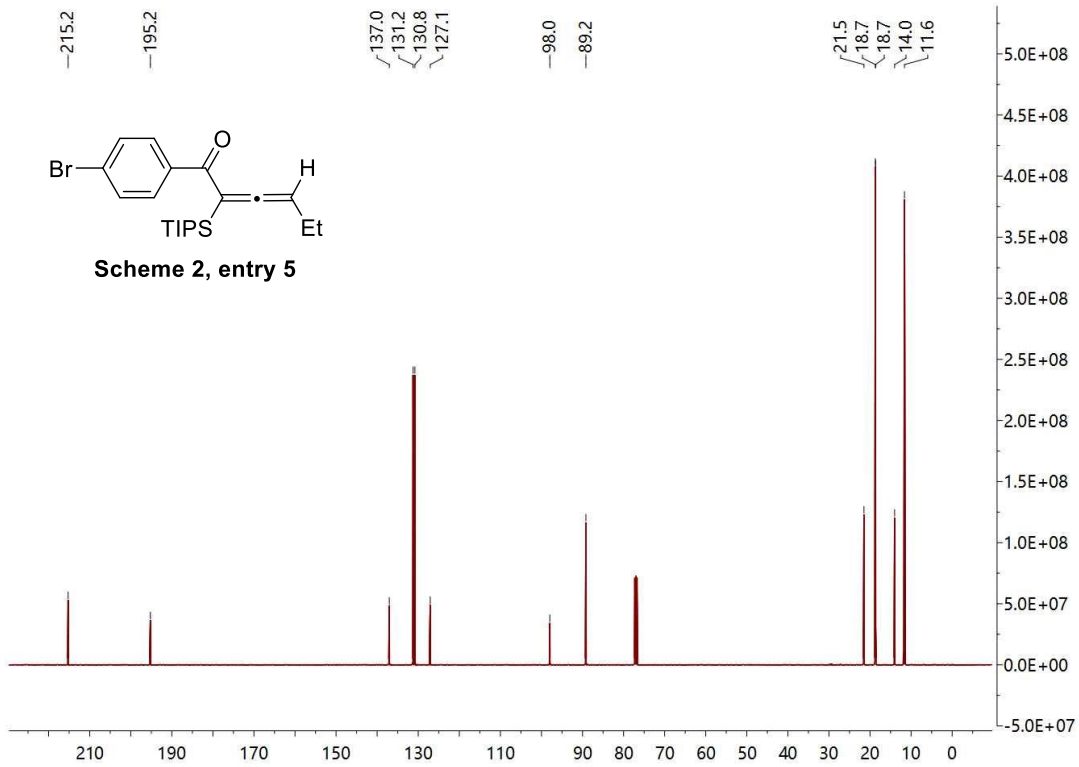
^{13}C NMR (126 MHz, $CDCl_3$)



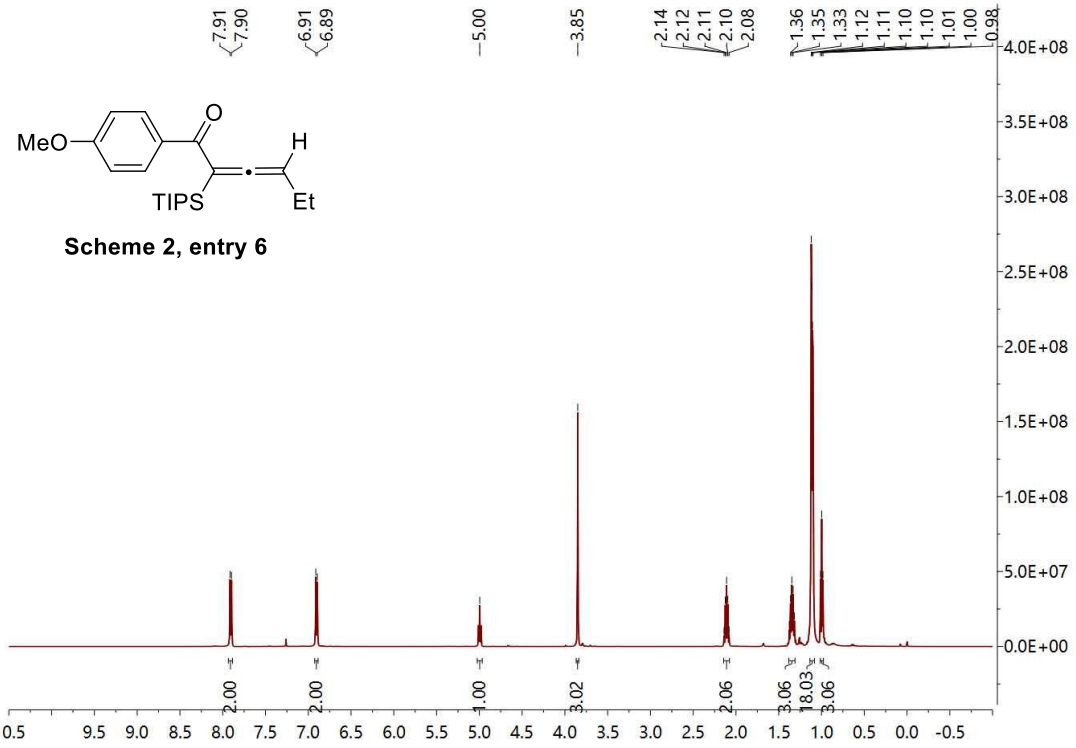
^{1}H NMR (500 MHz, $CDCl_3$)



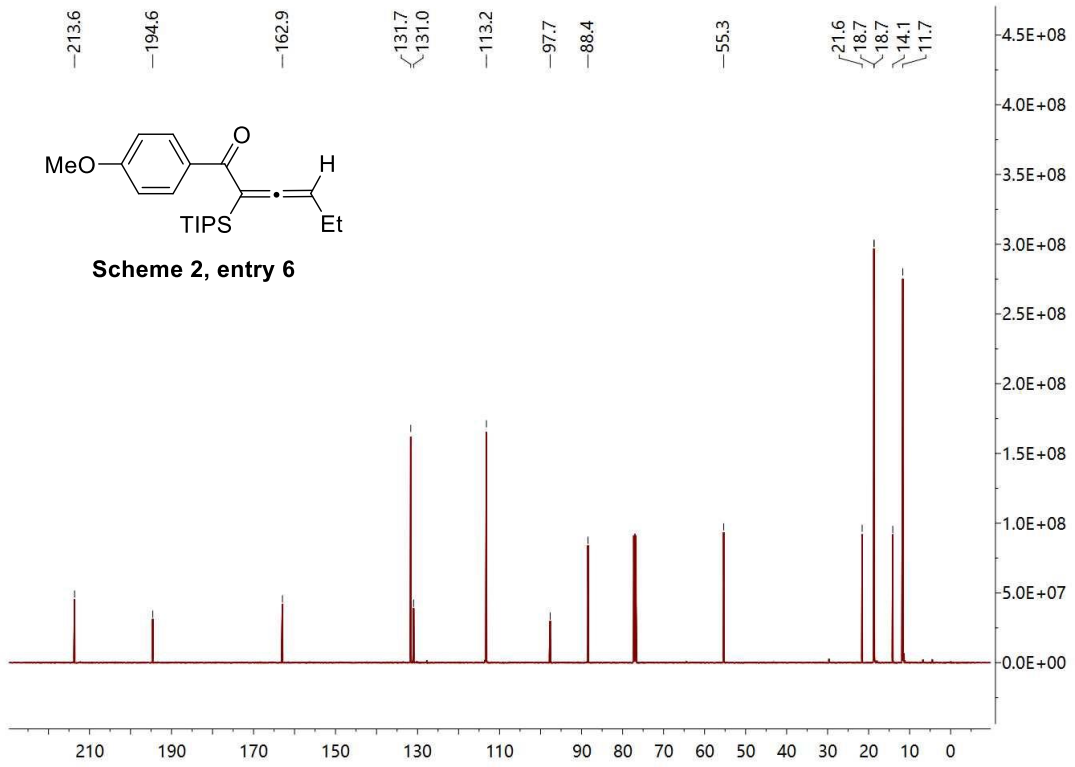
^{13}C NMR (126 MHz, $CDCl_3$)



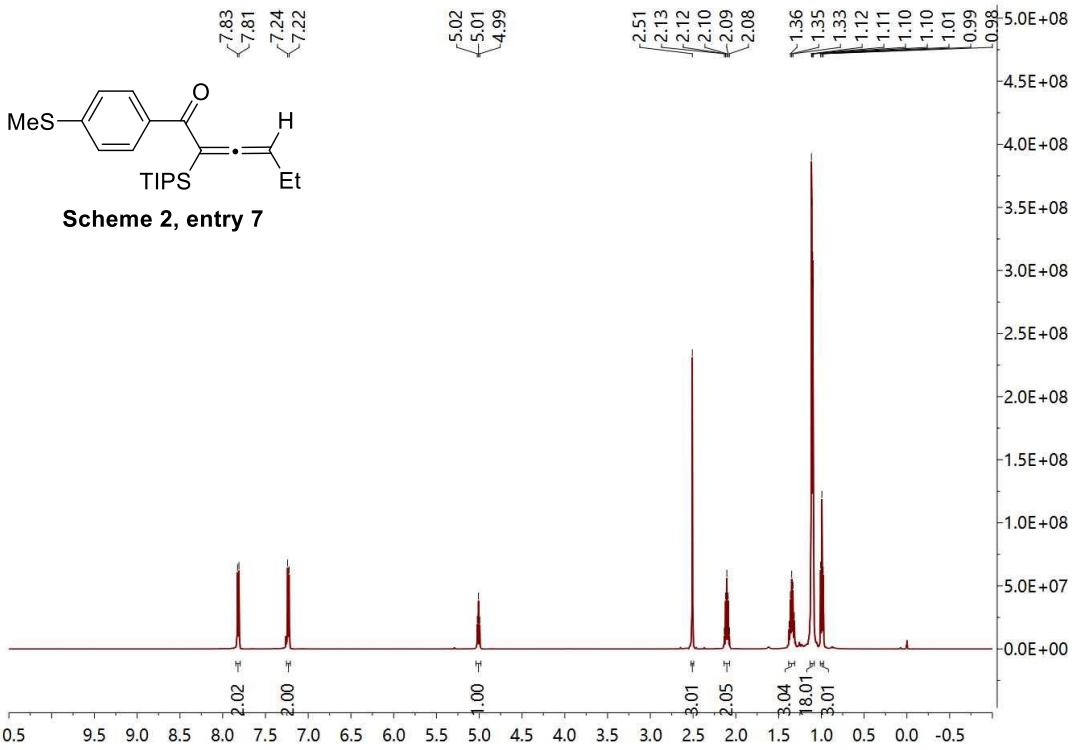
^{1}H NMR (500 MHz, $CDCl_3$)



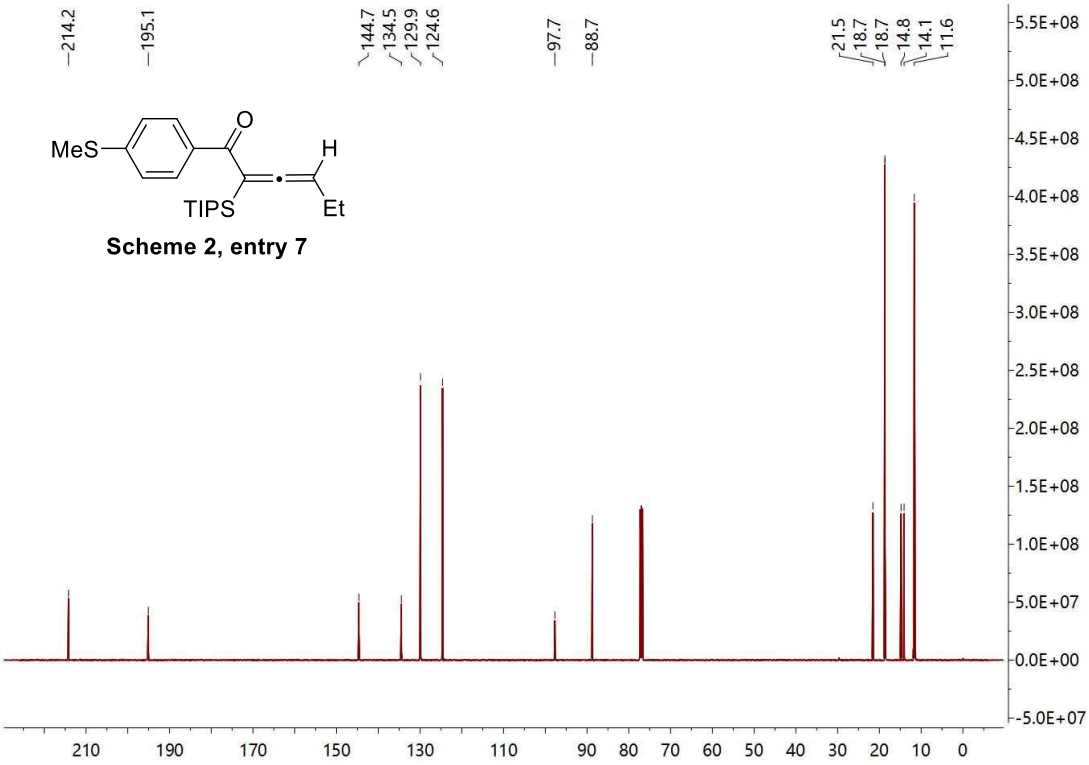
^{13}C NMR (126 MHz, $CDCl_3$)



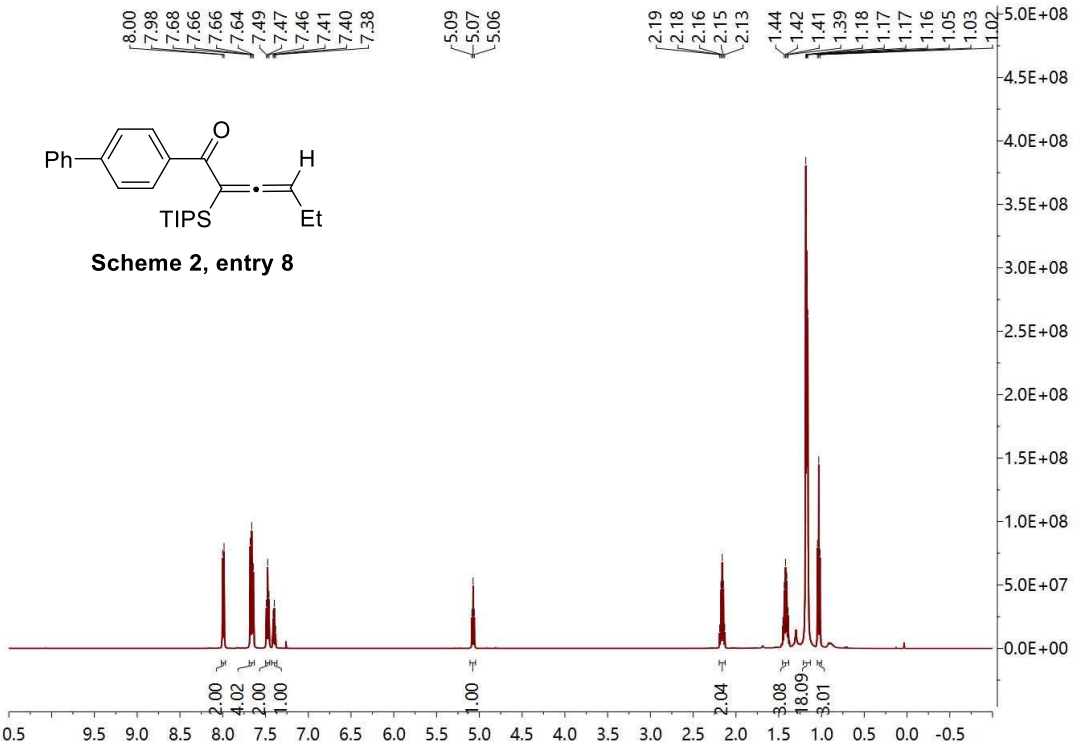
^{1}H NMR (500 MHz, $CDCl_3$)



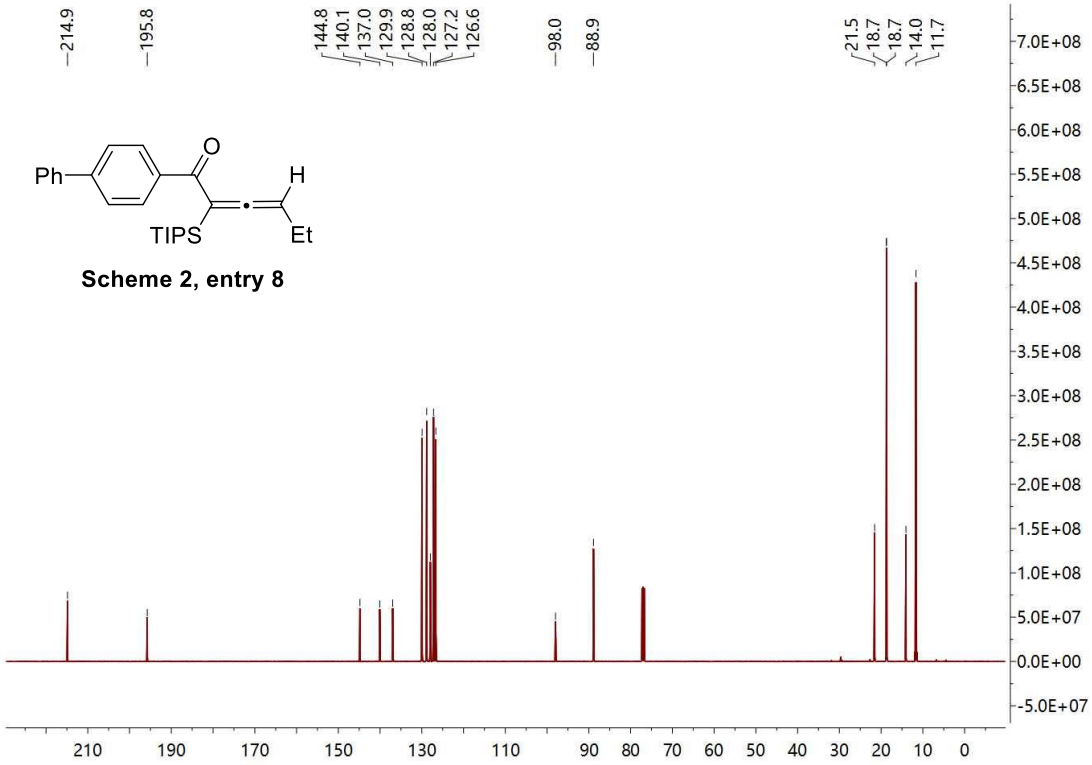
^{13}C NMR (126 MHz, $CDCl_3$)



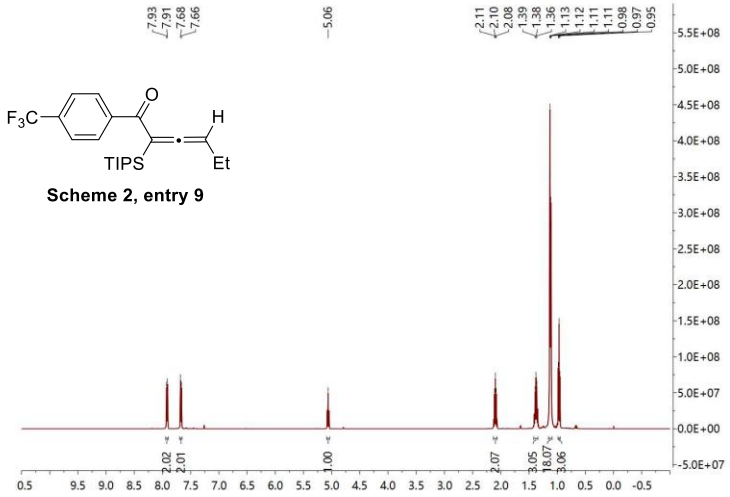
^{1}H NMR (500 MHz, $CDCl_3$)



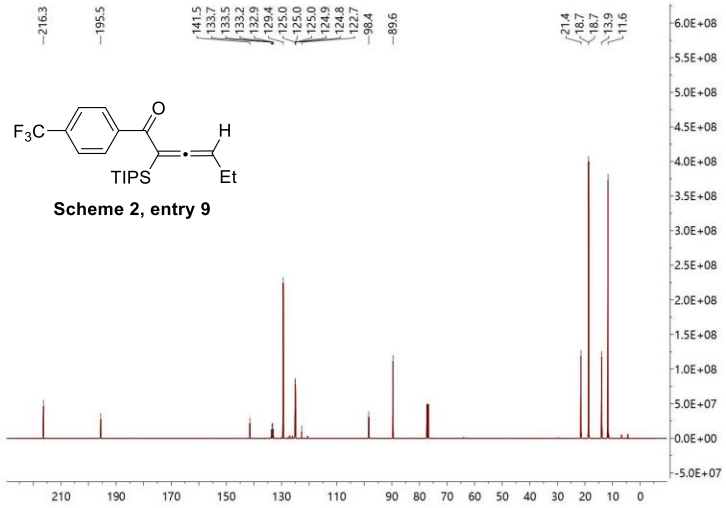
^{13}C NMR (126 MHz, $CDCl_3$)



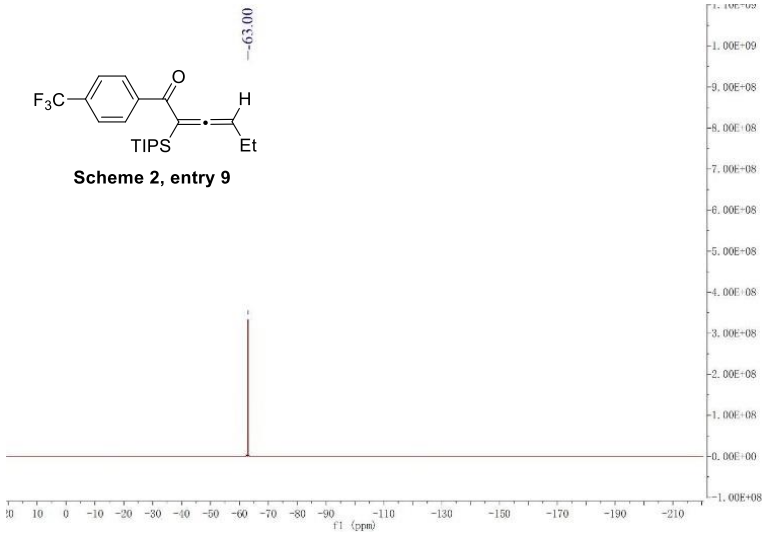
^{1}H NMR (500 MHz, $CDCl_3$)



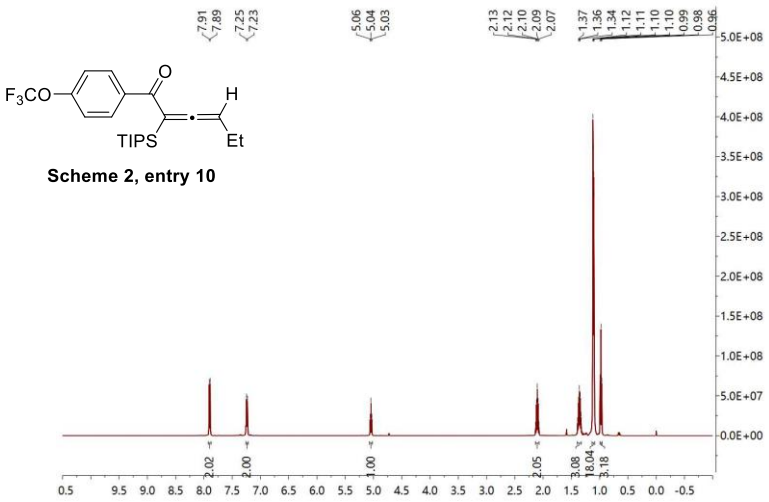
^{13}C NMR (126 MHz, $CDCl_3$)



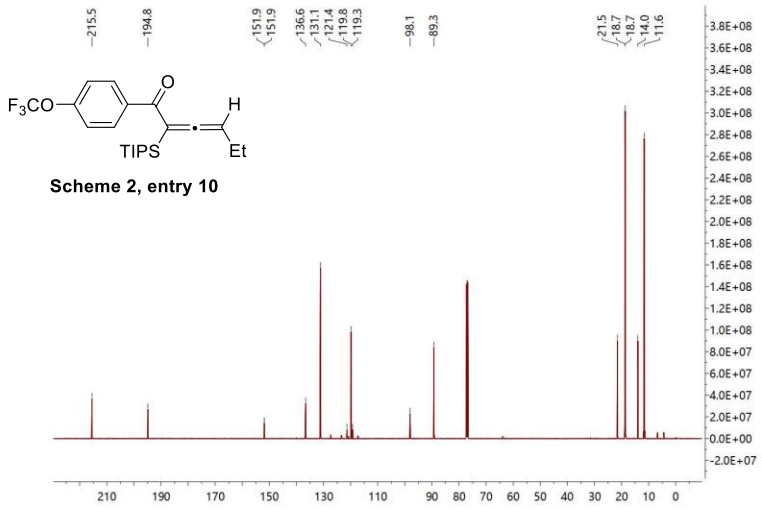
^{19}F NMR (471 MHz, $CDCl_3$)



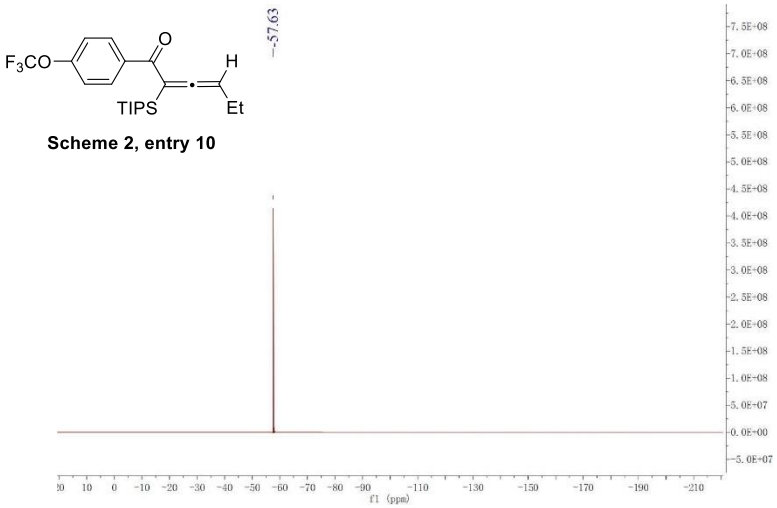
^{1}H NMR (500 MHz, $CDCl_3$)



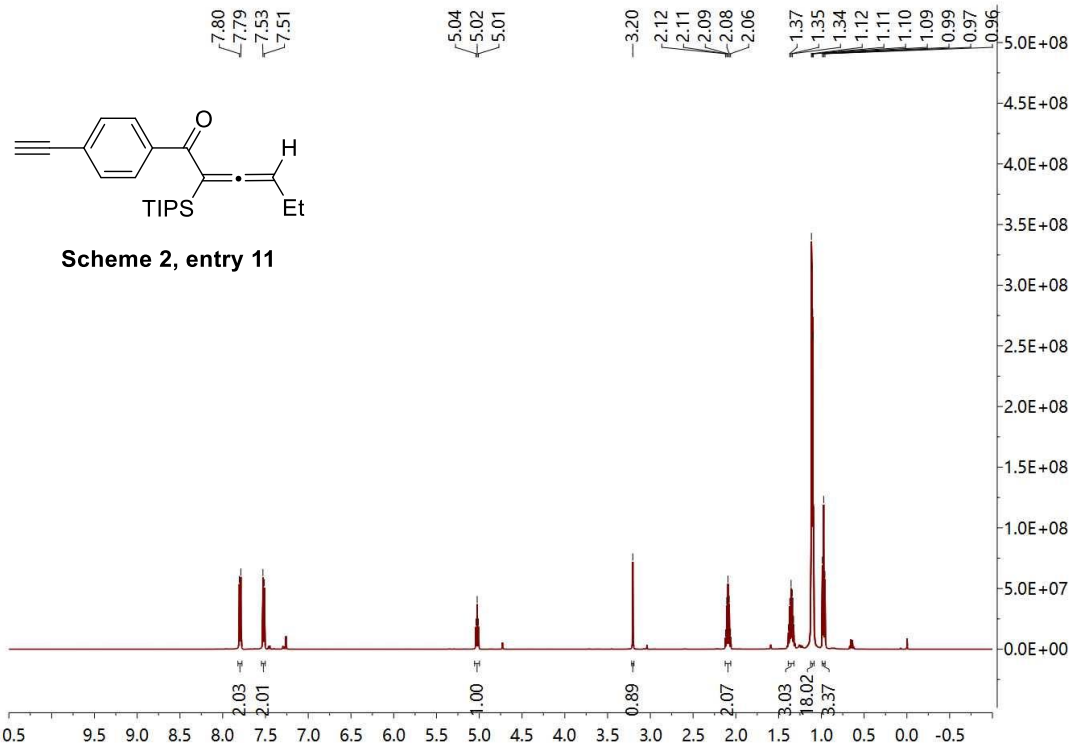
^{13}C NMR (126 MHz, $CDCl_3$)



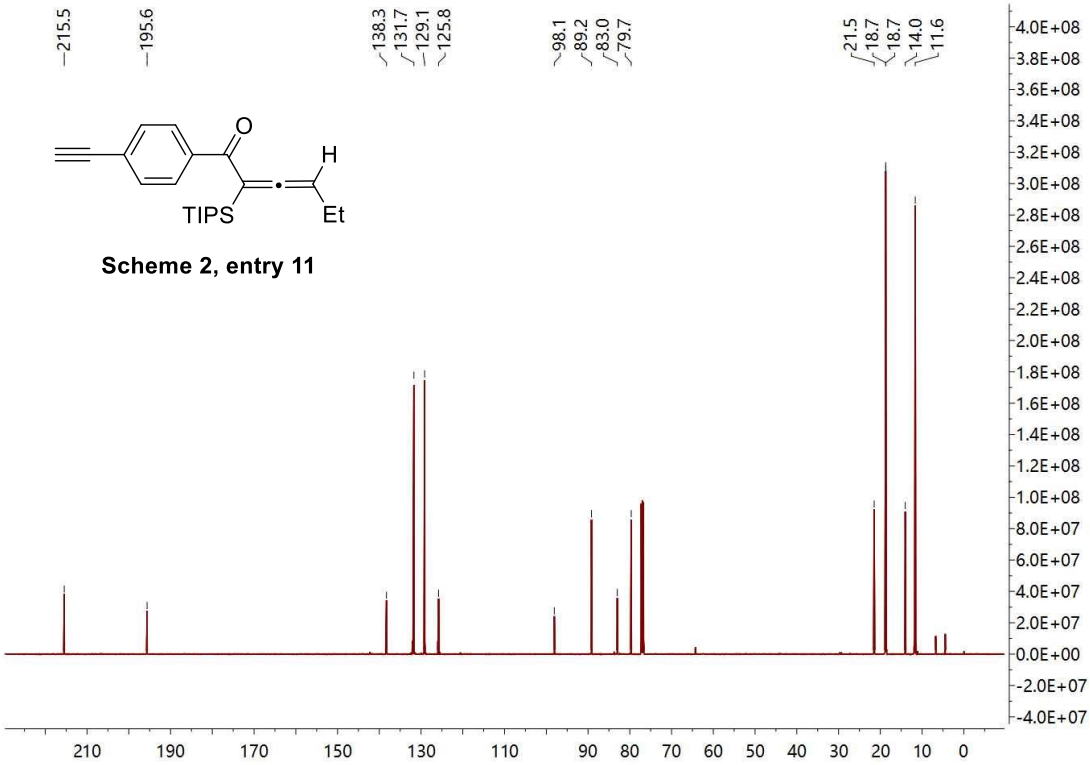
^{19}F NMR (471 MHz, $CDCl_3$)



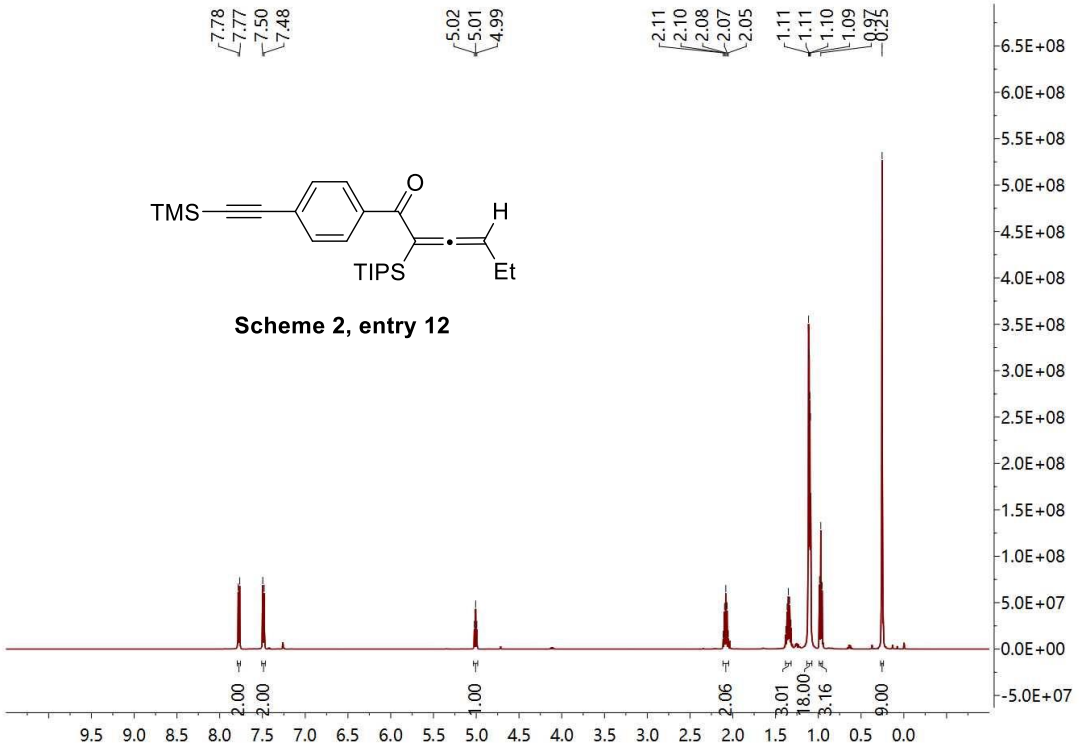
^{1}H NMR (500 MHz, $CDCl_3$)



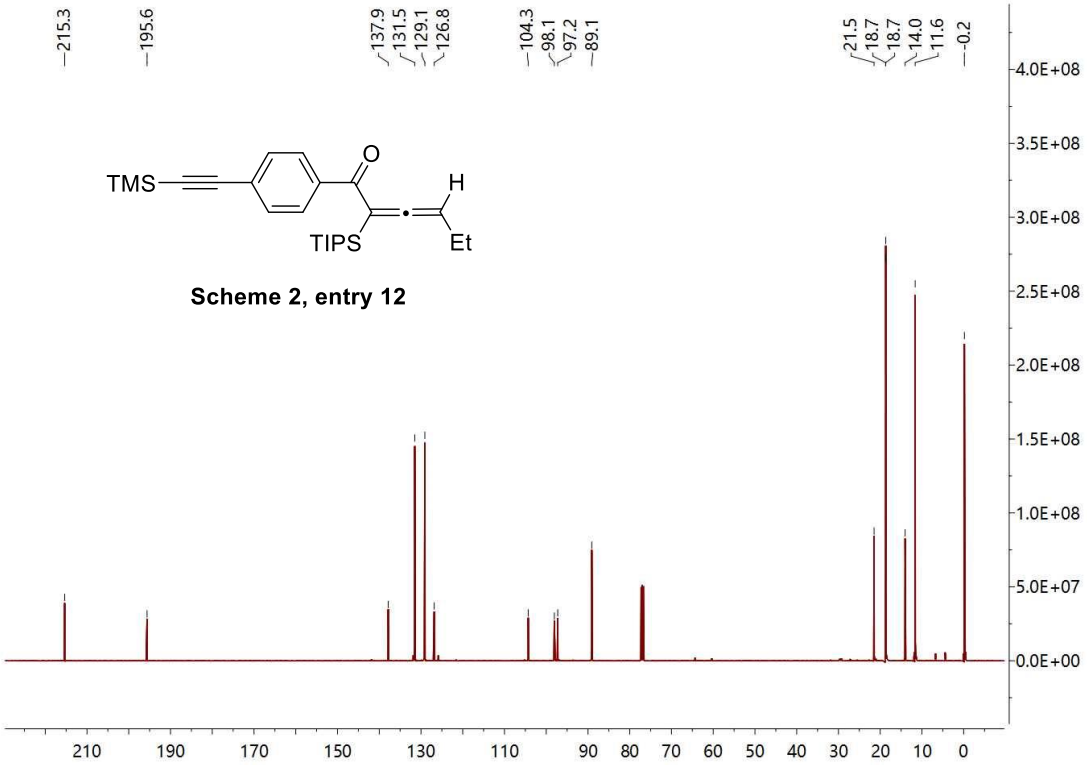
^{13}C NMR (126 MHz, $CDCl_3$)



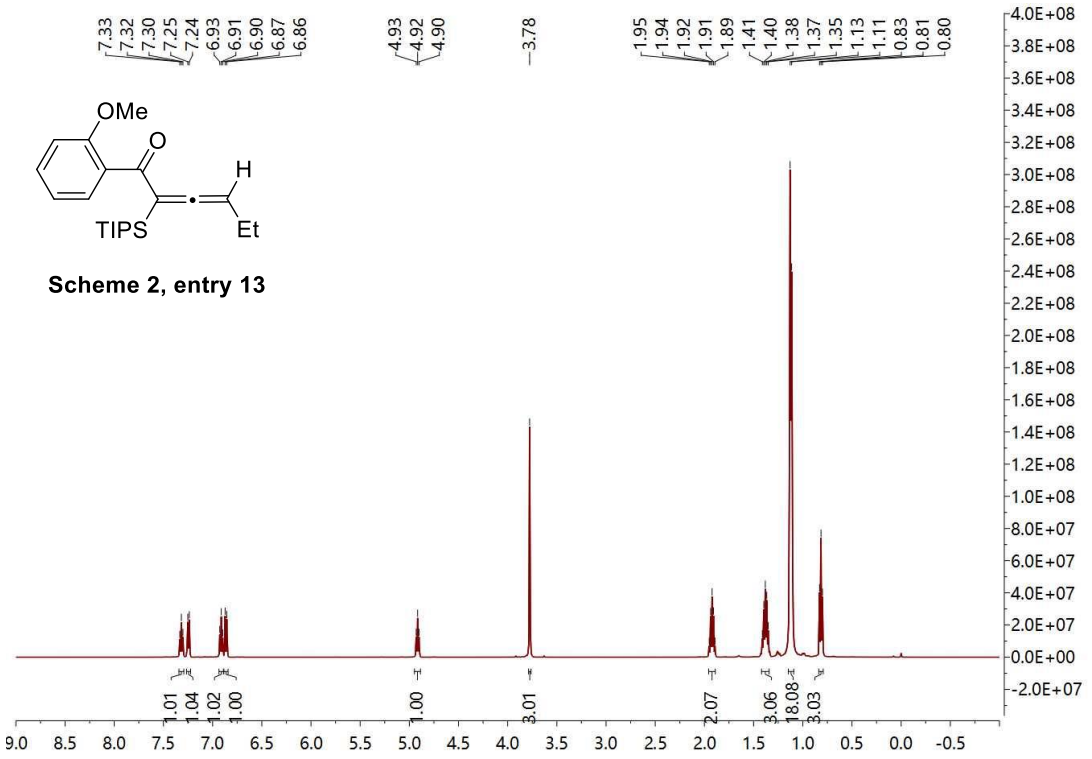
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

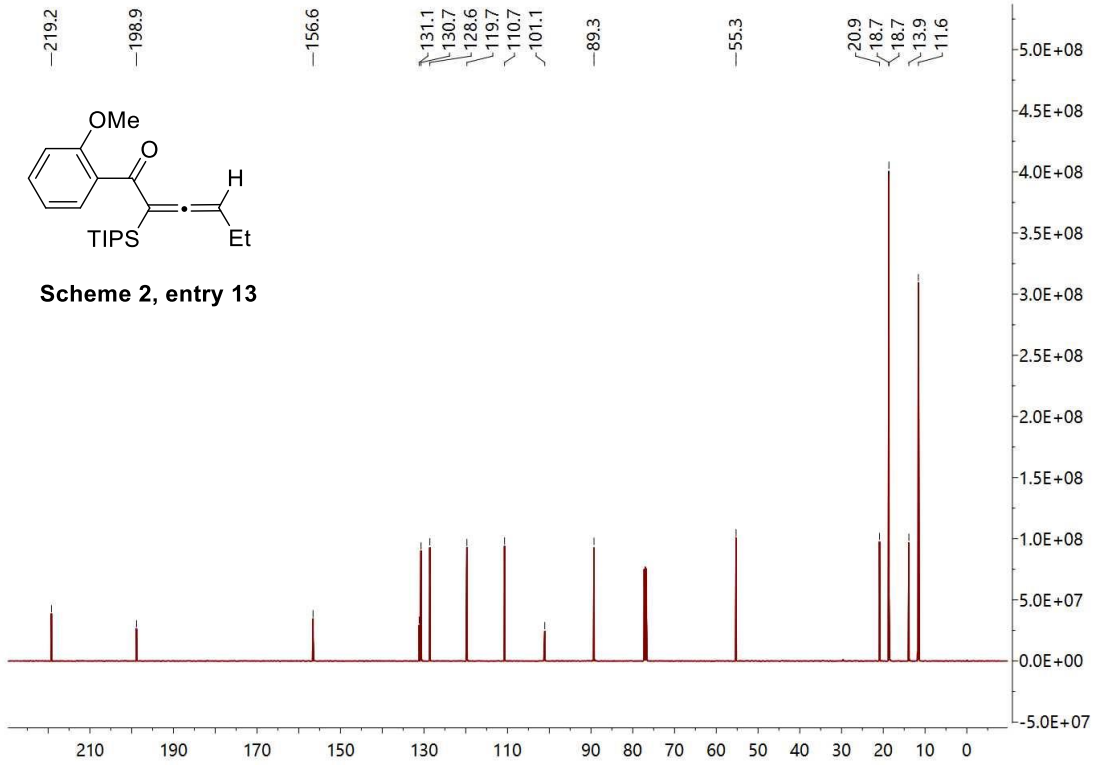


^{1}H NMR (500 MHz, $CDCl_3$)



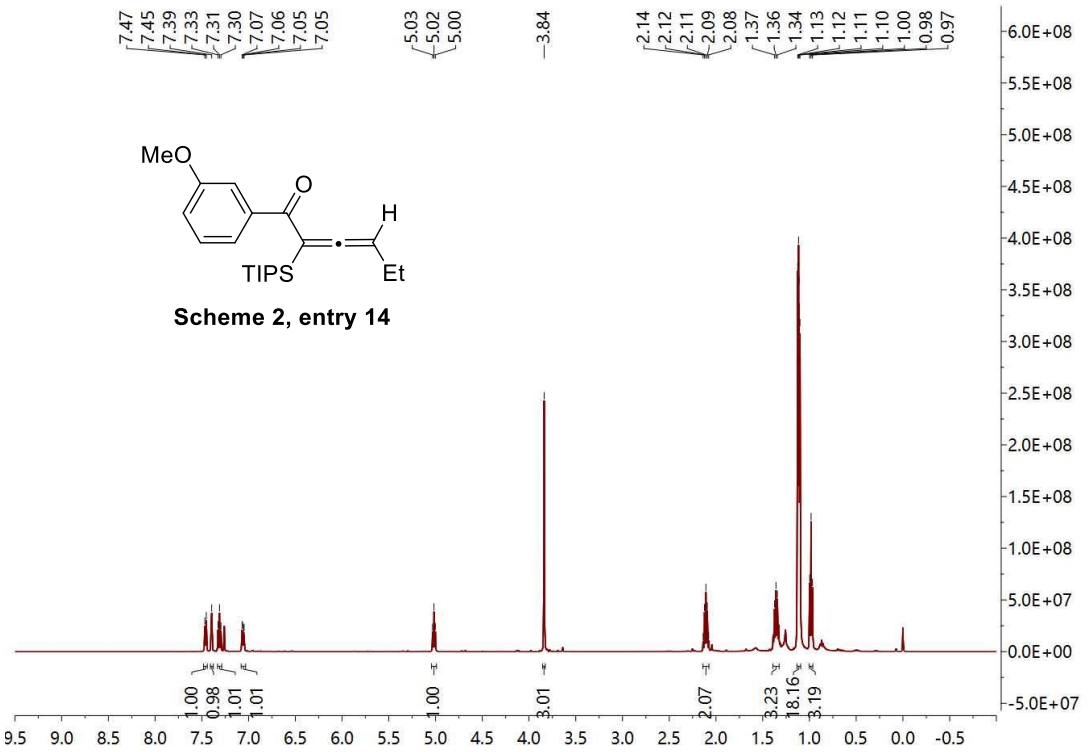
Scheme 2, entry 13

^{13}C NMR (126 MHz, $CDCl_3$)

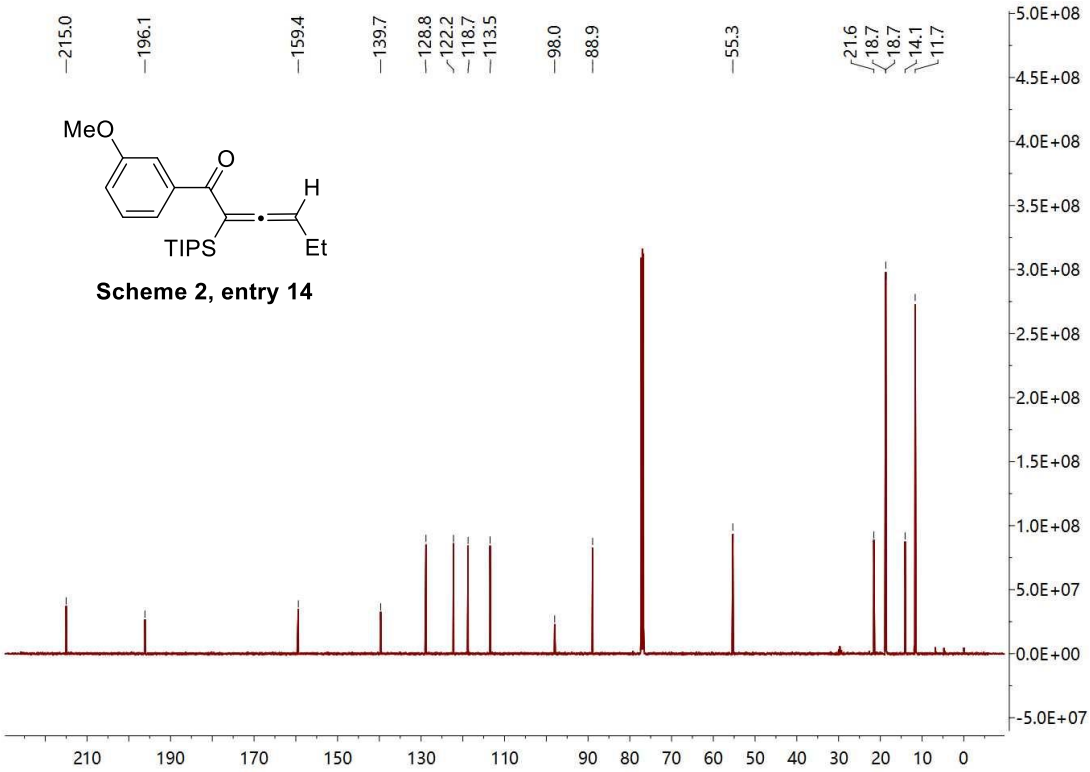


Scheme 2, entry 13

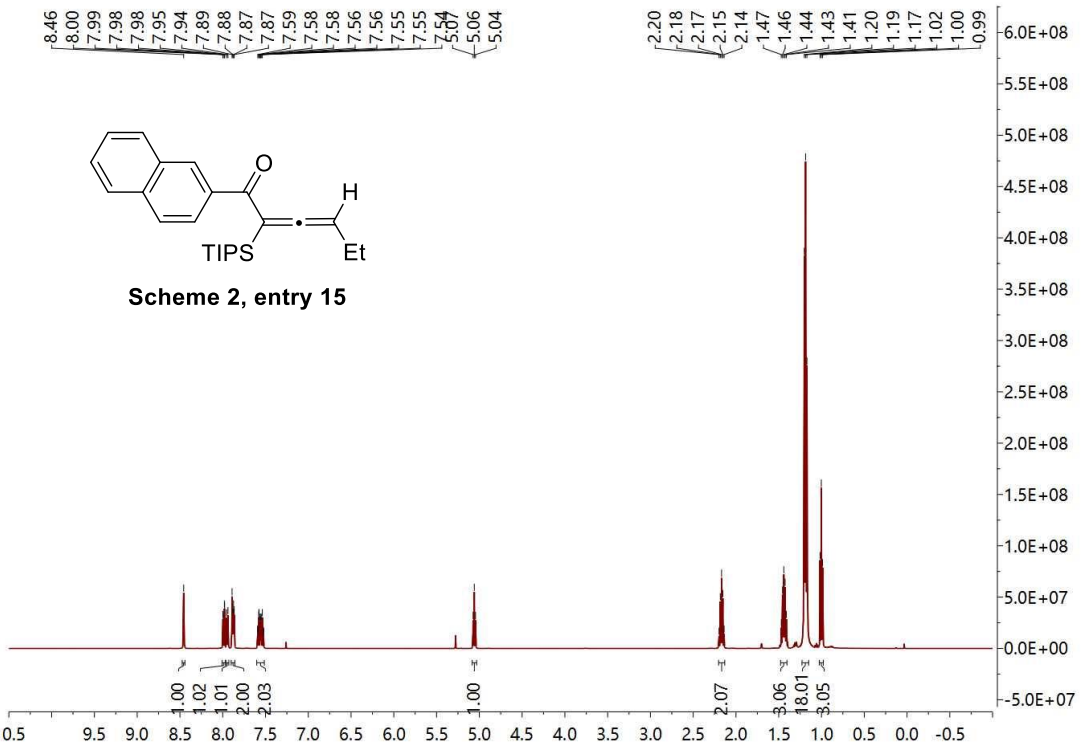
^{1}H NMR (500 MHz, $CDCl_3$)



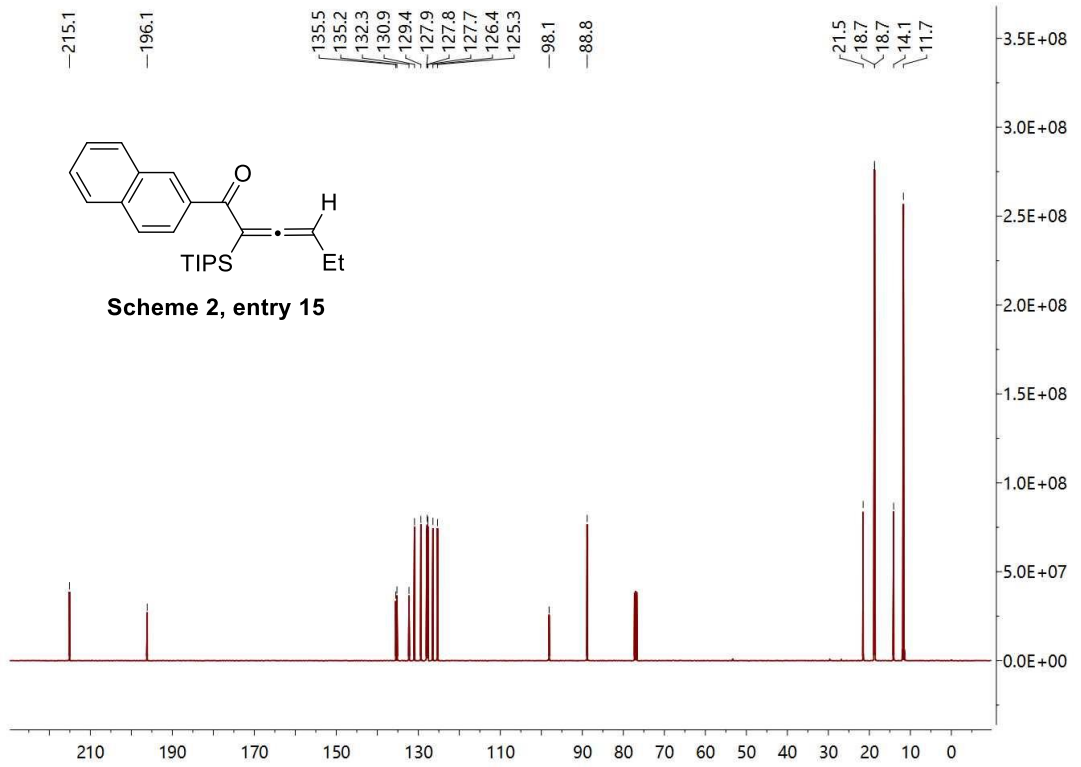
^{13}C NMR (126 MHz, $CDCl_3$)



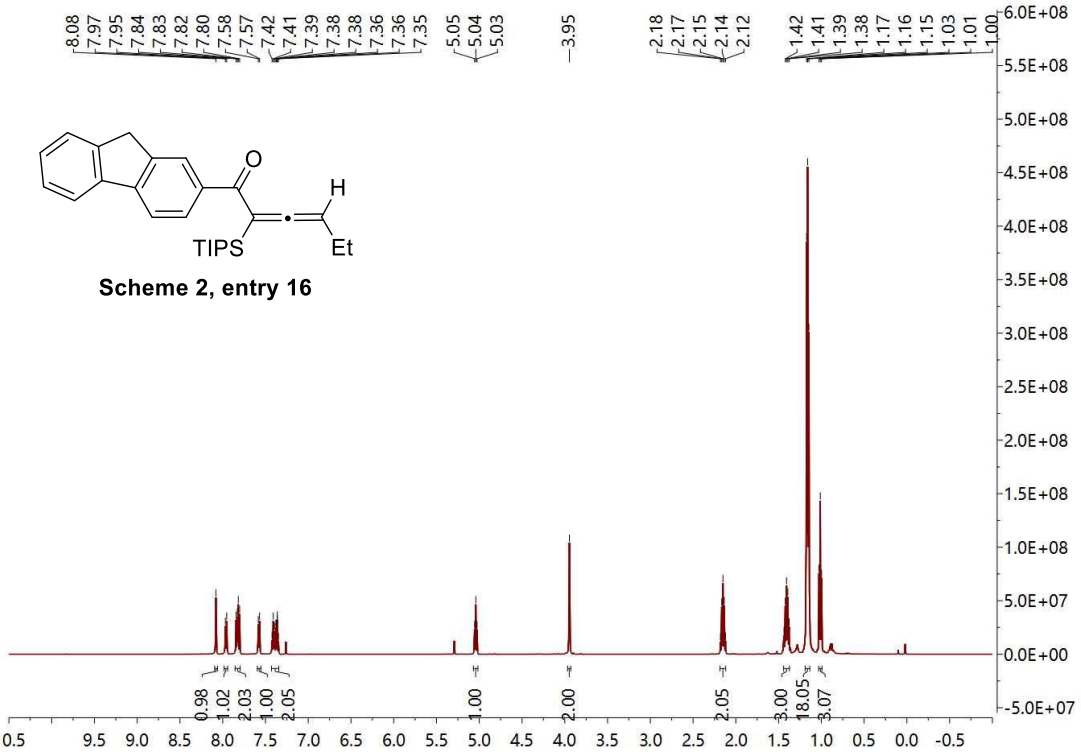
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

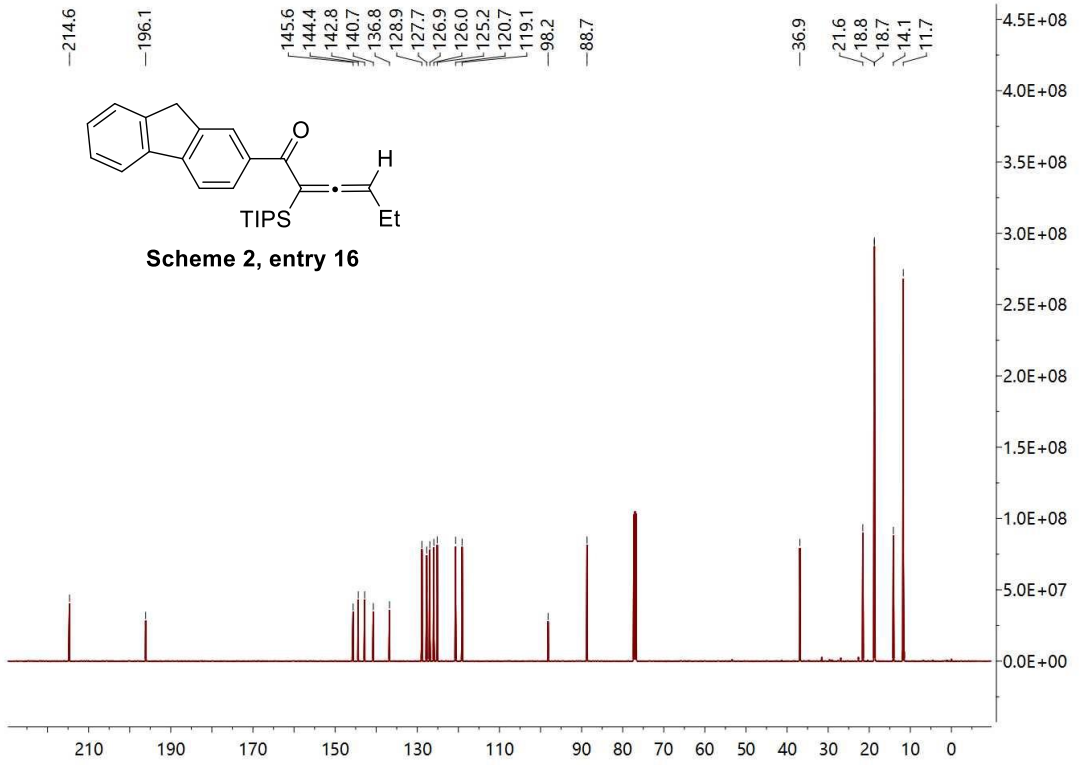


^{1}H NMR (500 MHz, $CDCl_3$)



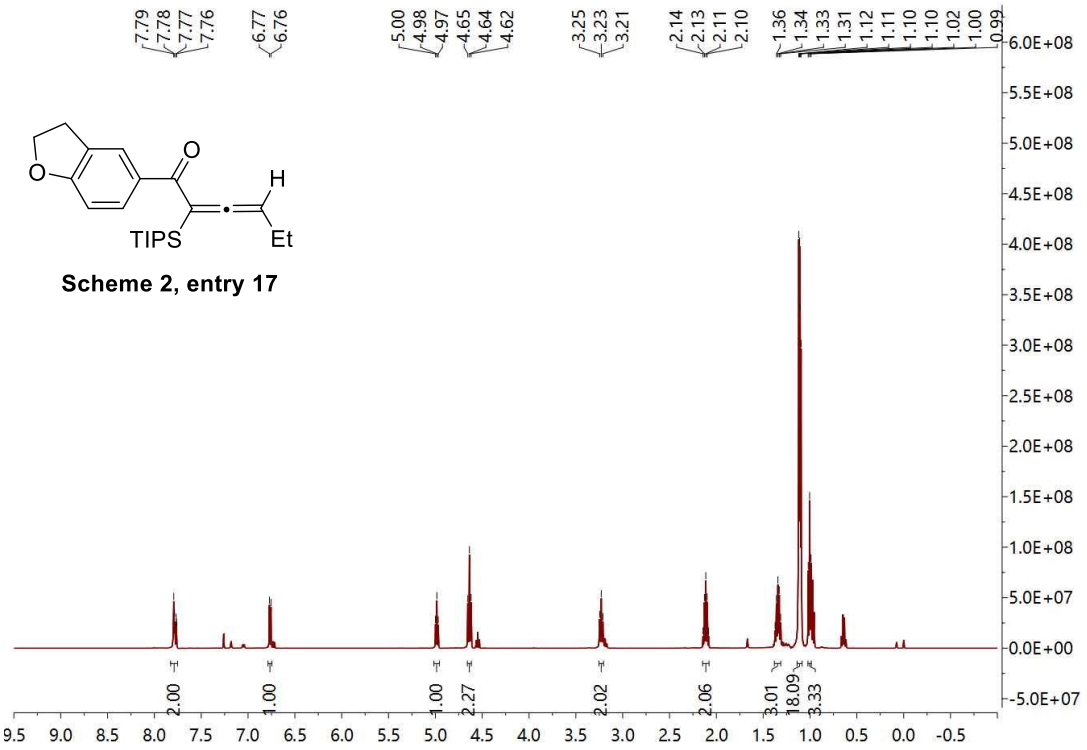
Scheme 2, entry 16

^{13}C NMR (126 MHz, $CDCl_3$)



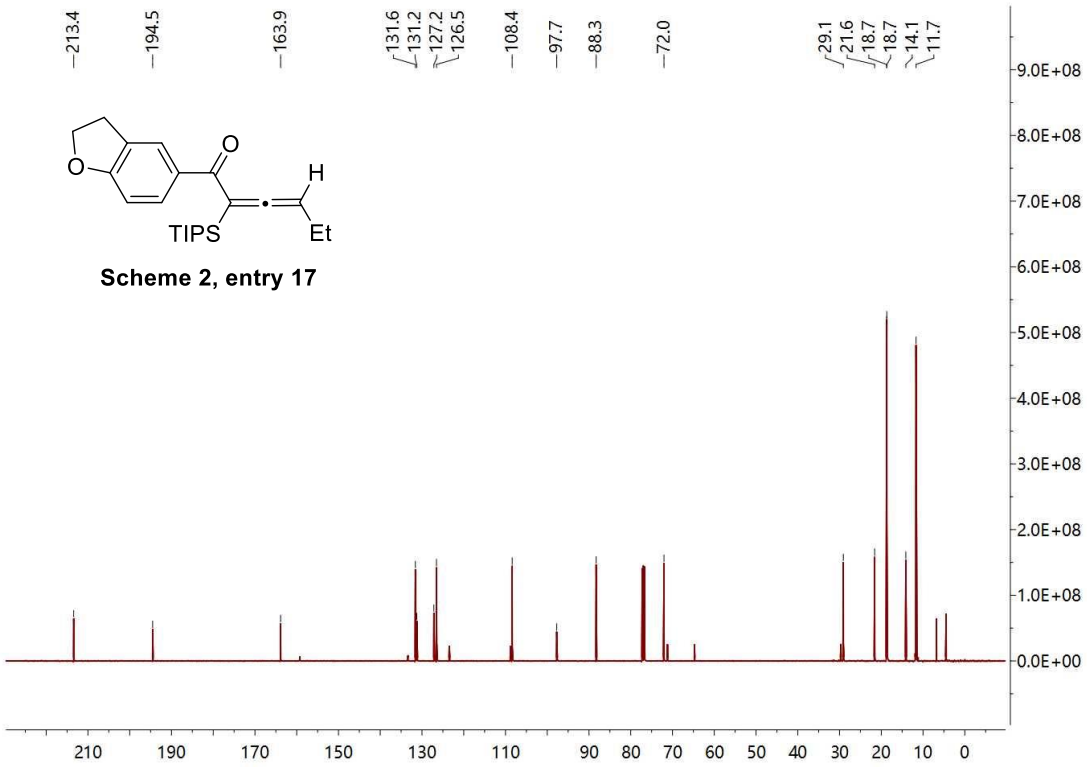
Scheme 2, entry 16

^{1}H NMR (500 MHz, $CDCl_3$)



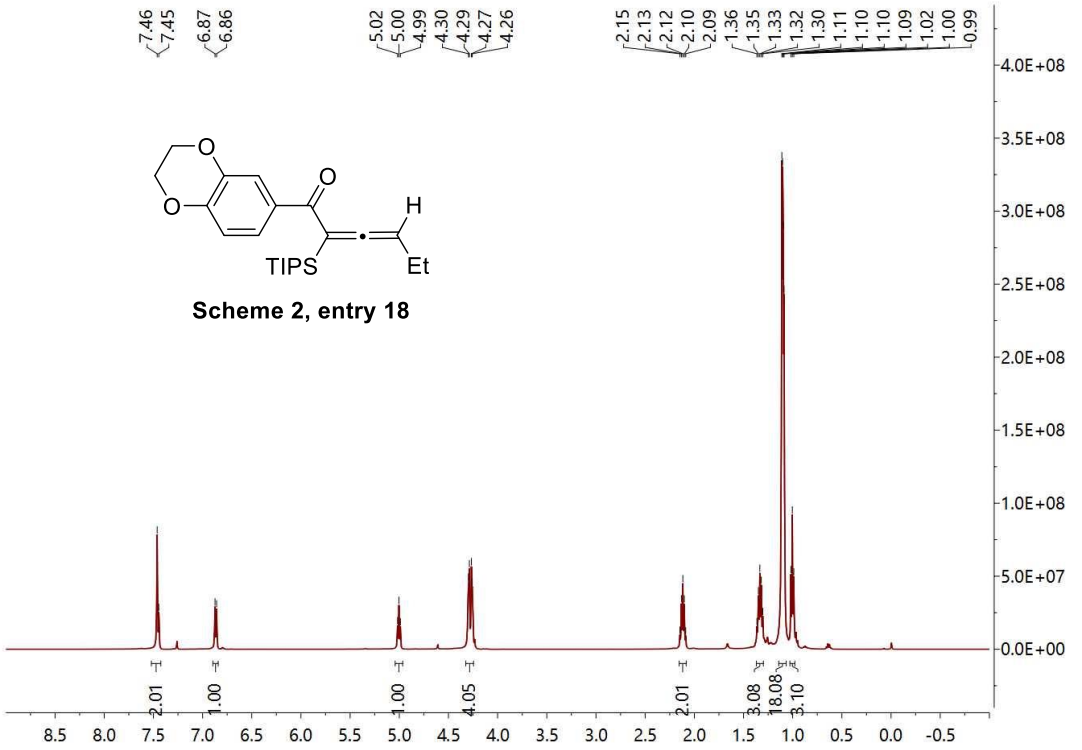
Scheme 2, entry 17

^{13}C NMR (126 MHz, $CDCl_3$)

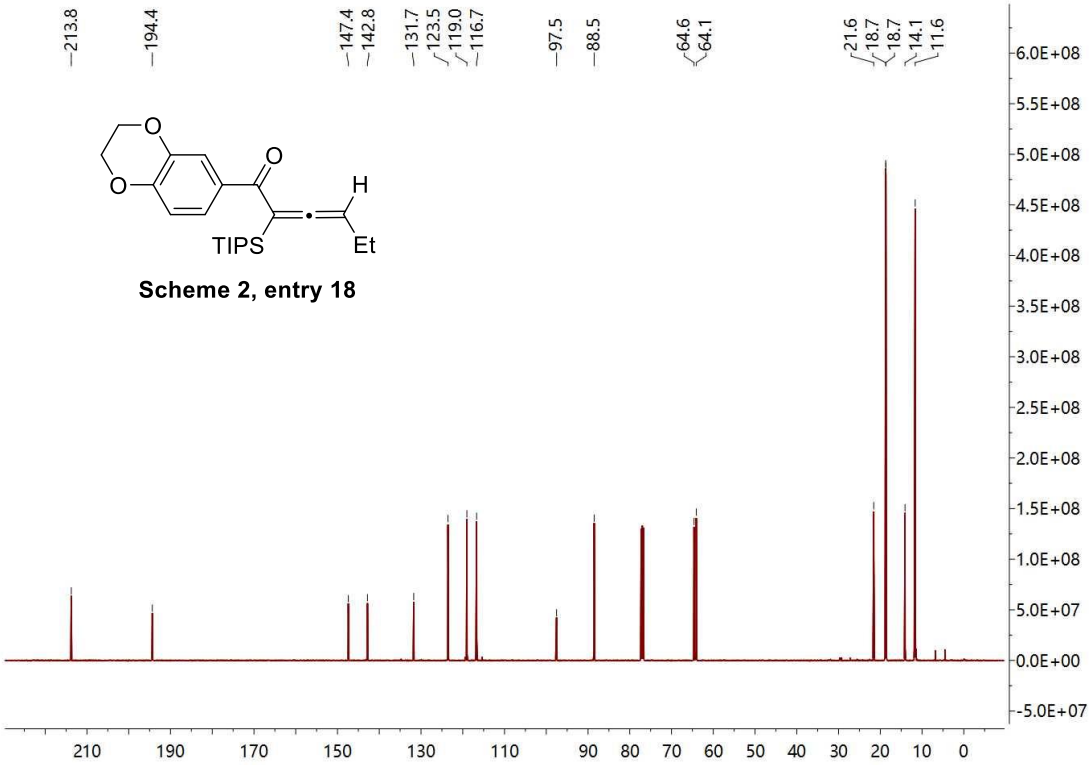


Scheme 2, entry 17

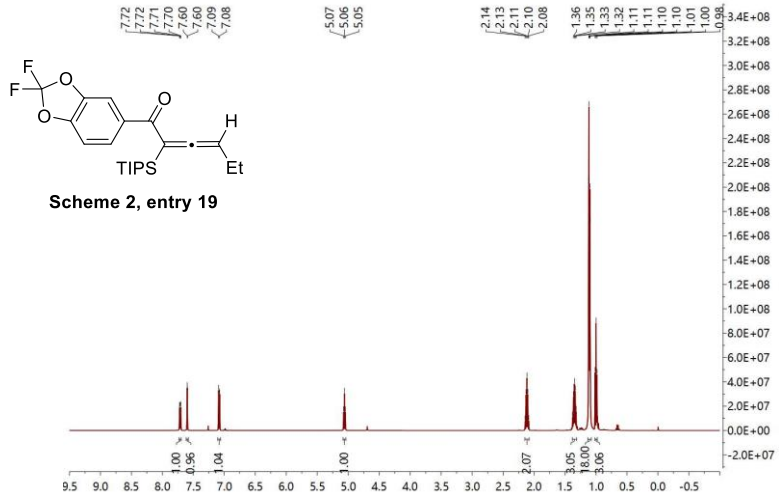
^{1}H NMR (500 MHz, $CDCl_3$)



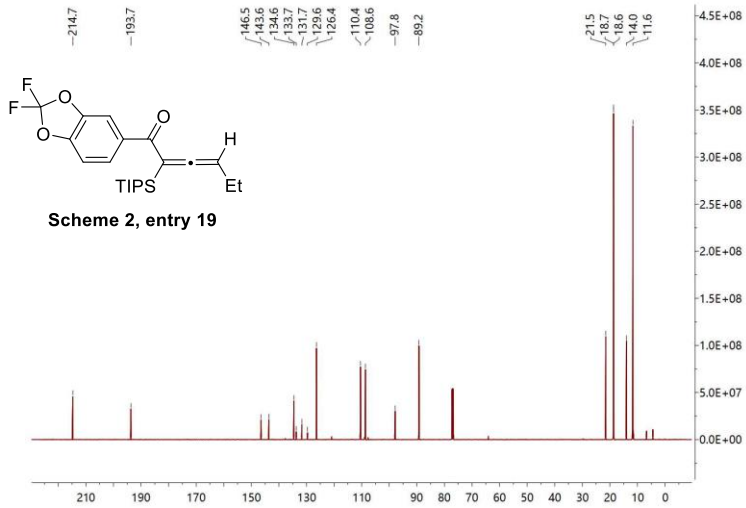
^{13}C NMR (126 MHz, $CDCl_3$)



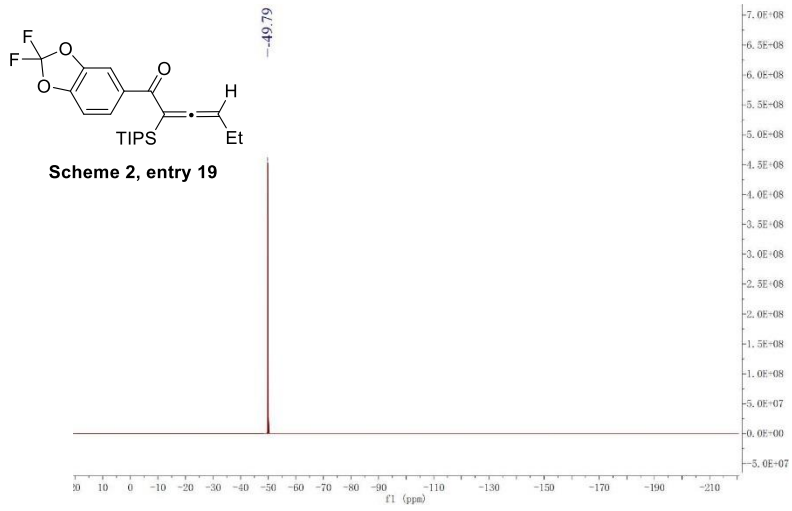
^{1}H NMR (500 MHz, $CDCl_3$)



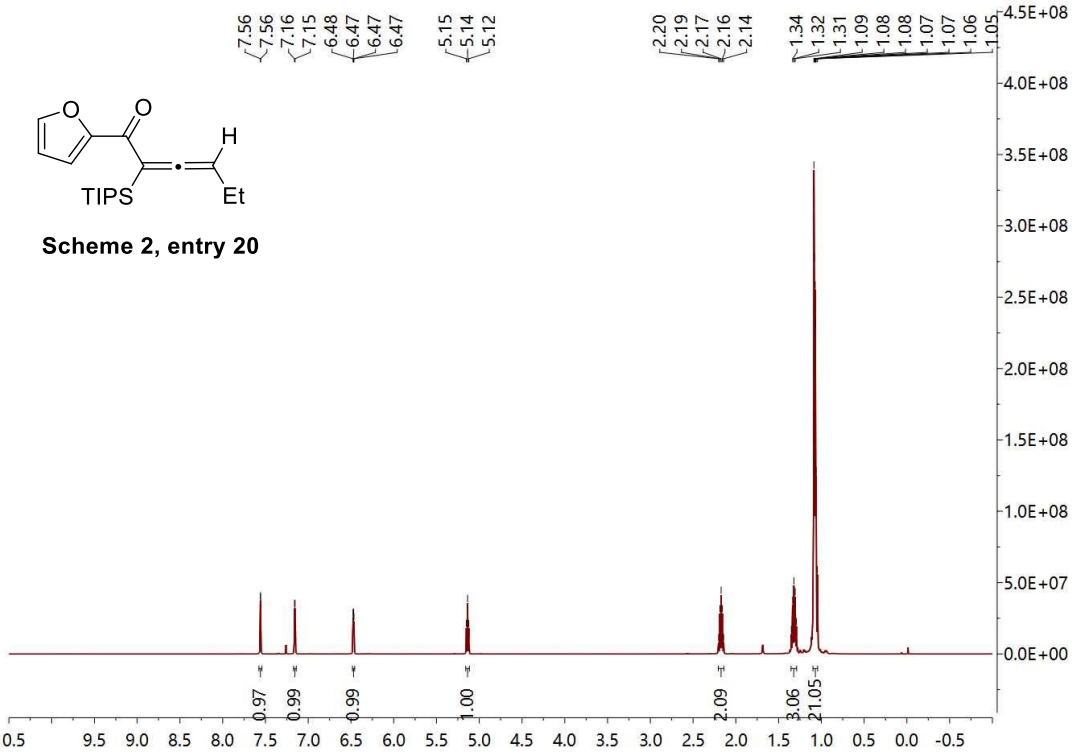
^{13}C NMR (126 MHz, $CDCl_3$)



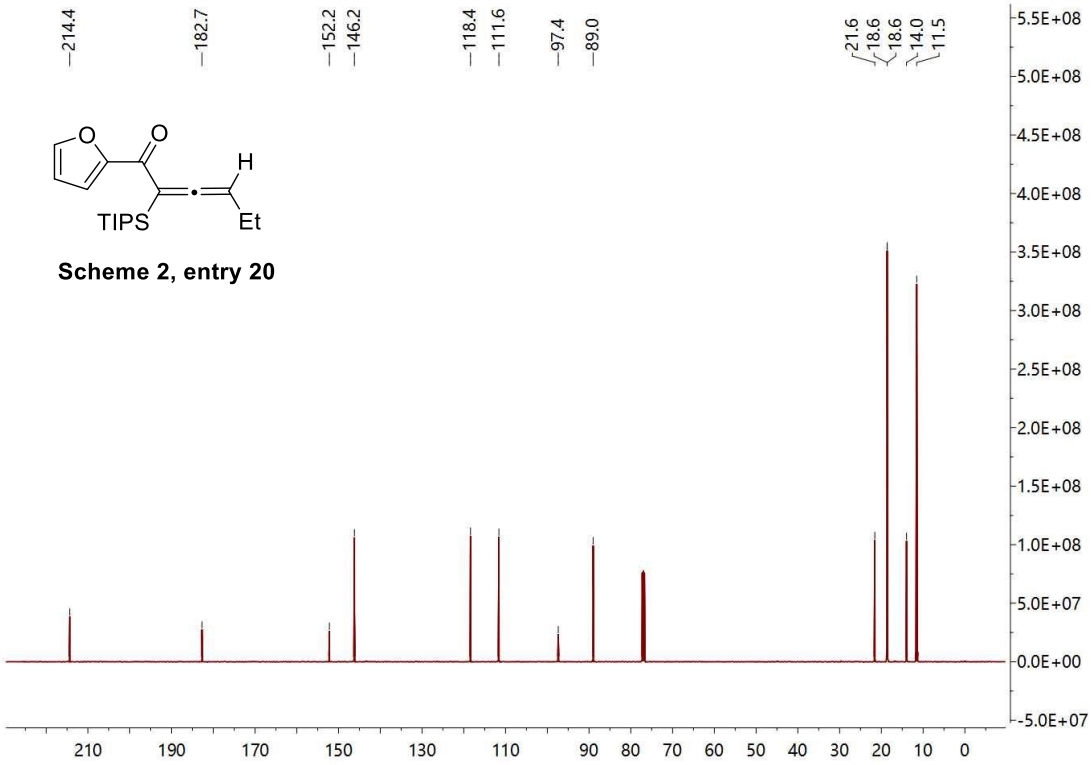
^{19}F NMR (471 MHz, $CDCl_3$)



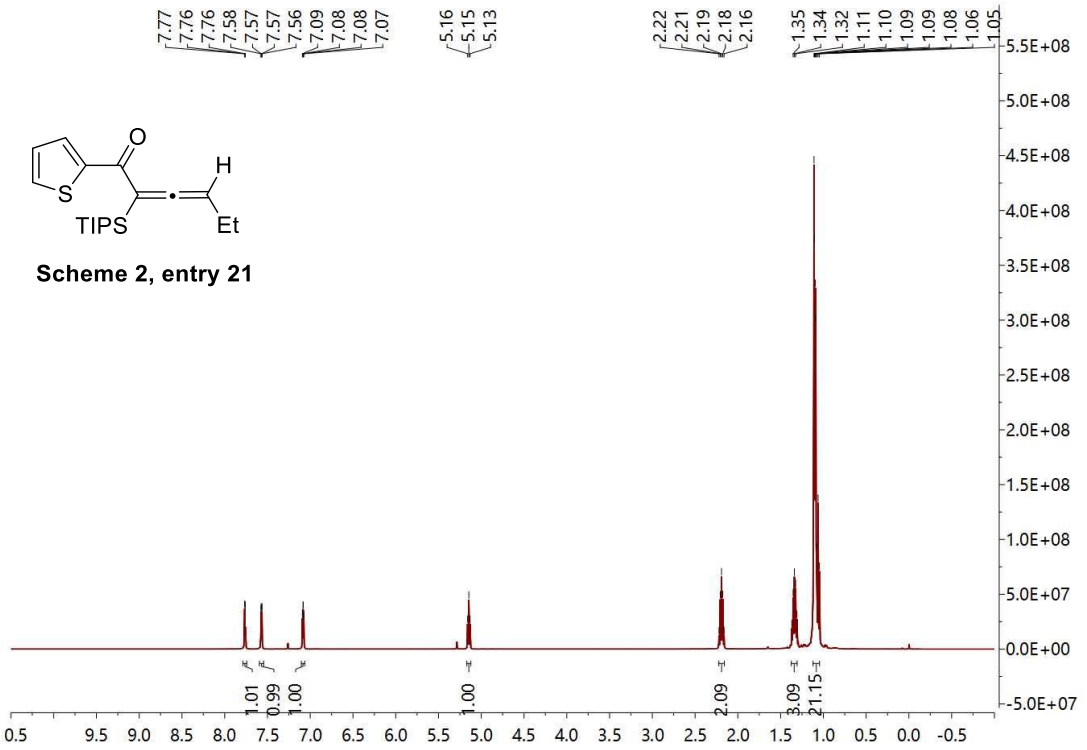
^{1}H NMR (500 MHz, $CDCl_3$)



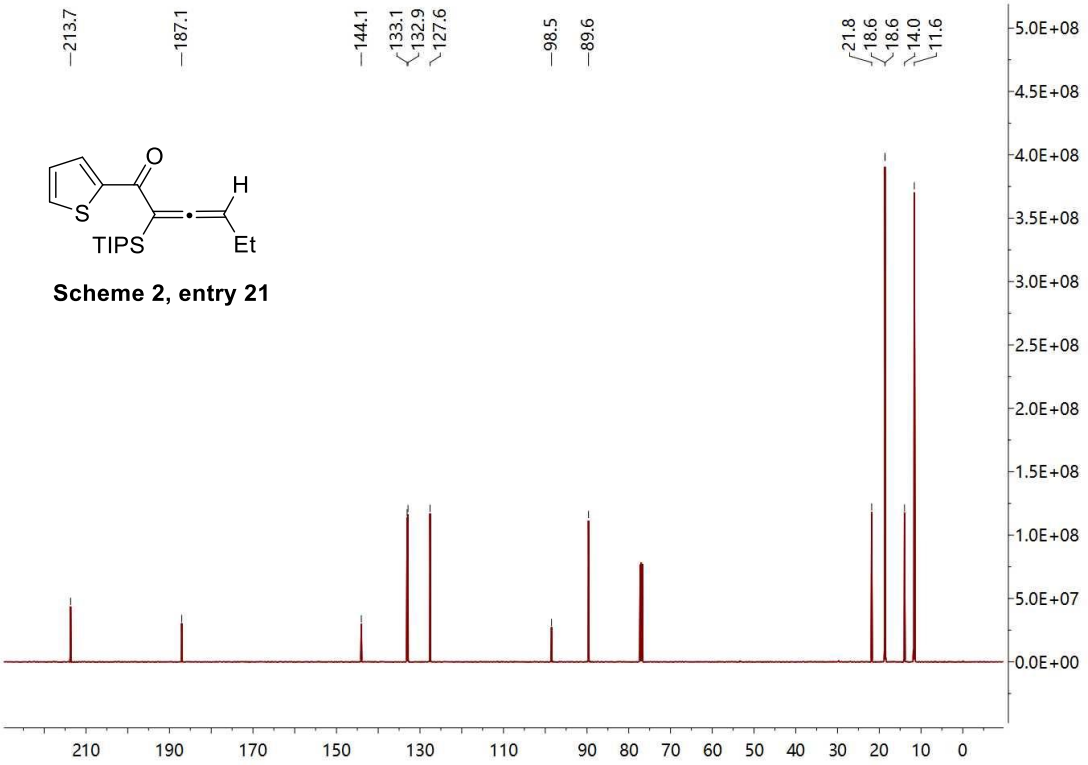
^{13}C NMR (126 MHz, $CDCl_3$)



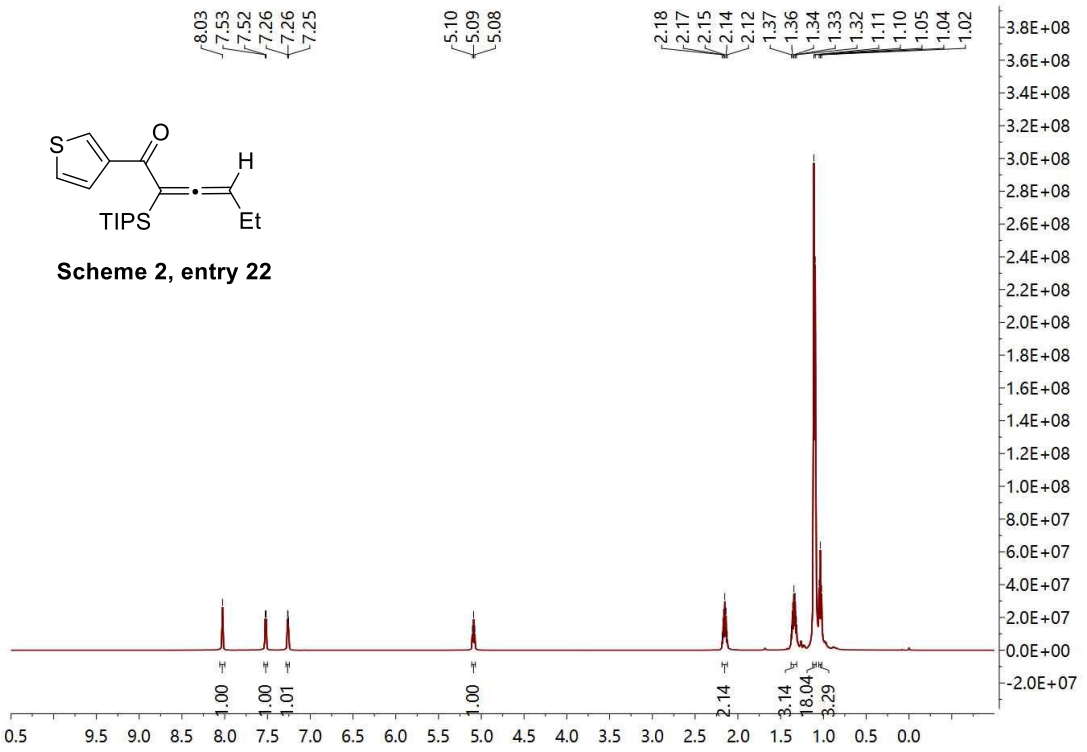
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

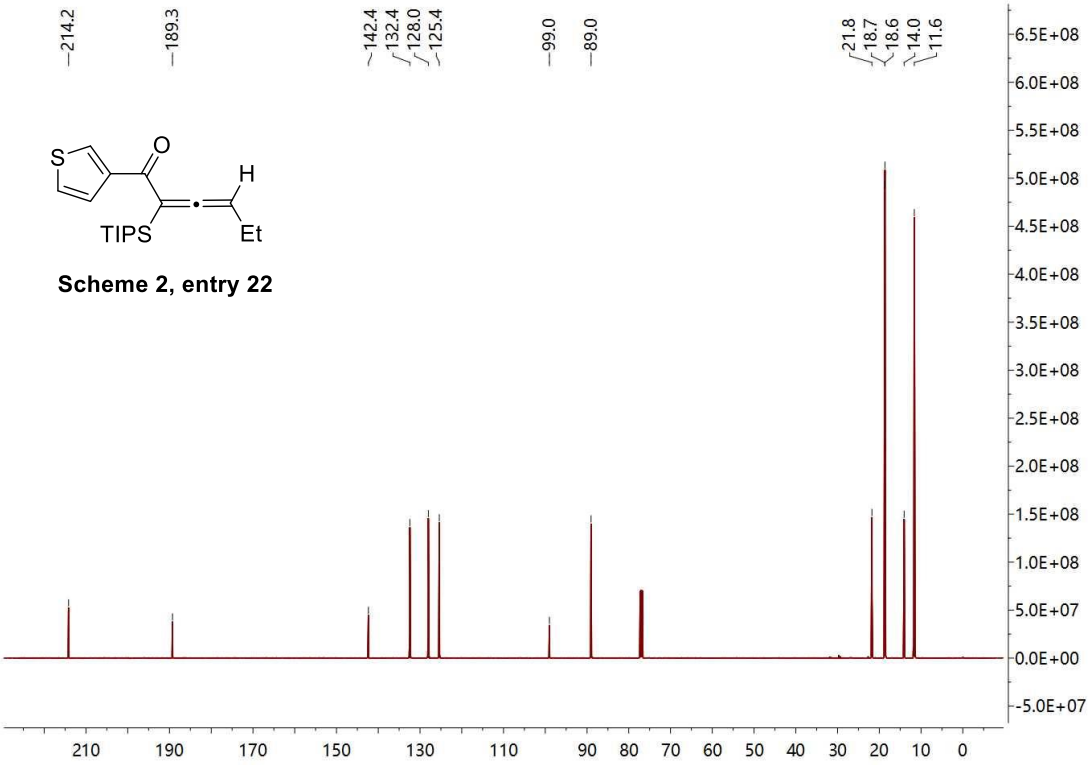


^{1}H NMR (500 MHz, $CDCl_3$)



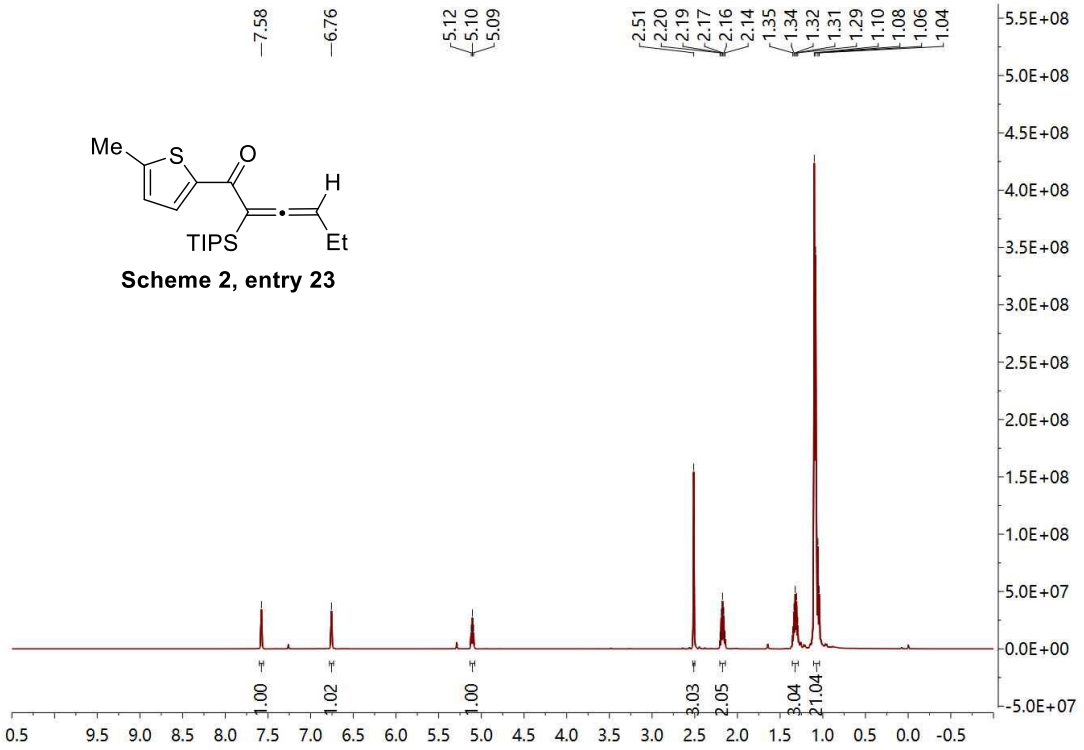
Scheme 2, entry 22

^{13}C NMR (126 MHz, $CDCl_3$)



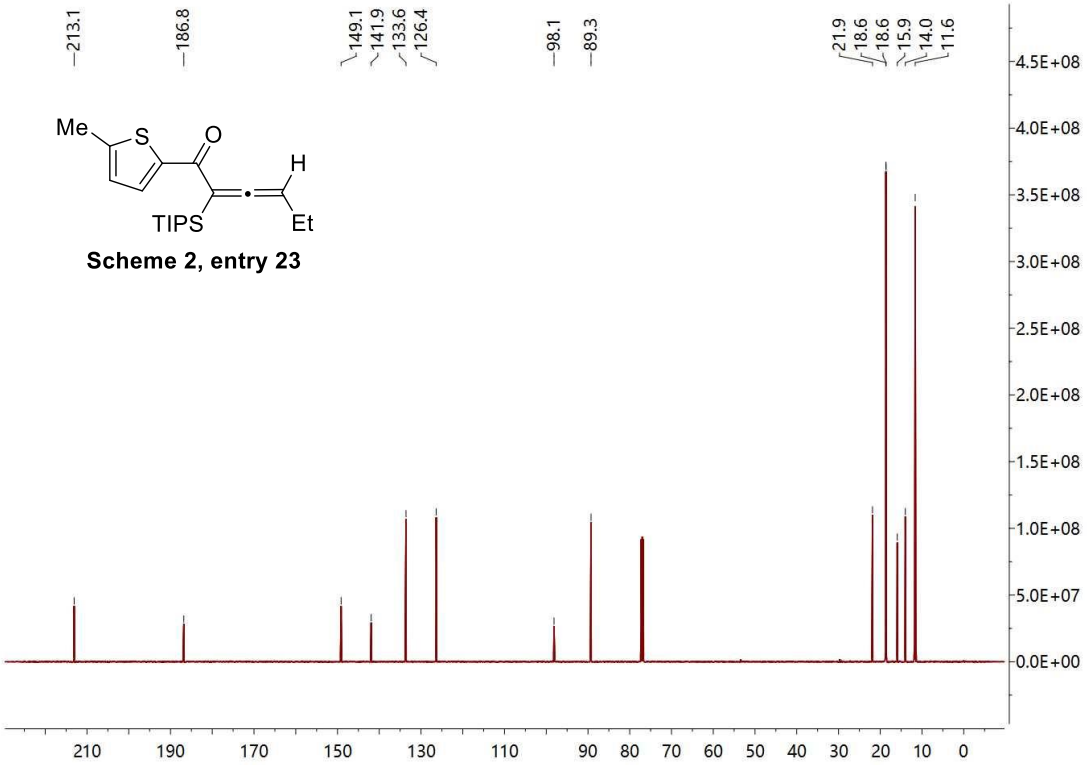
Scheme 2, entry 22

^{1}H NMR (500 MHz, $CDCl_3$)



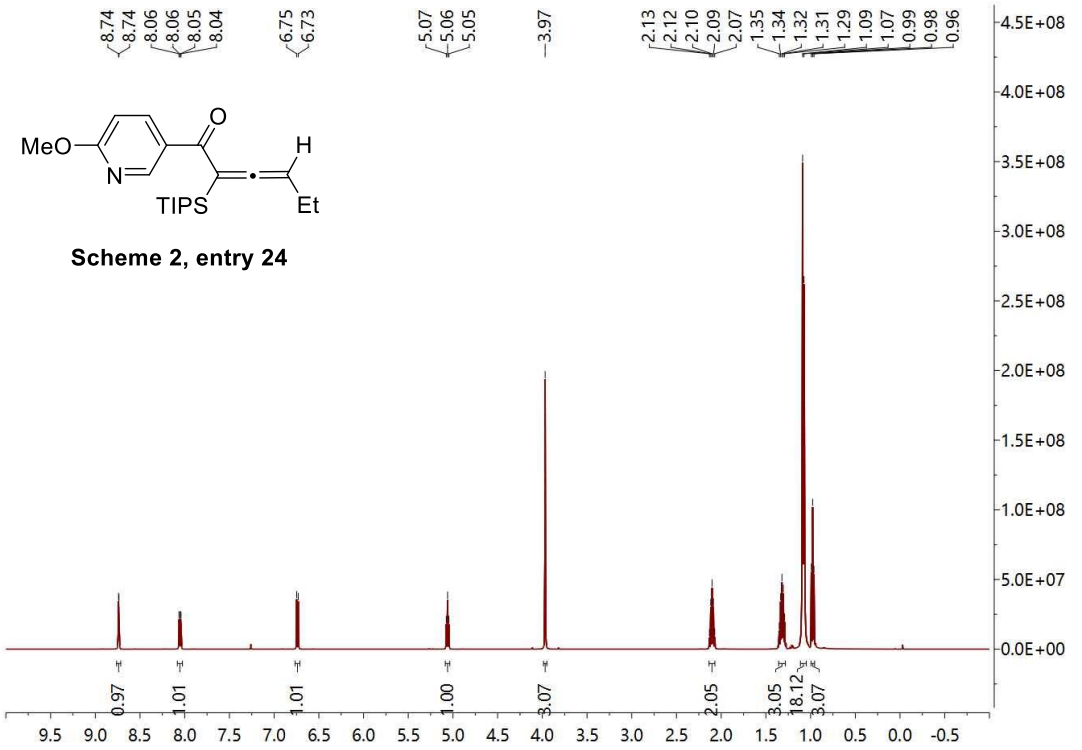
Scheme 2, entry 23

^{13}C NMR (126 MHz, $CDCl_3$)

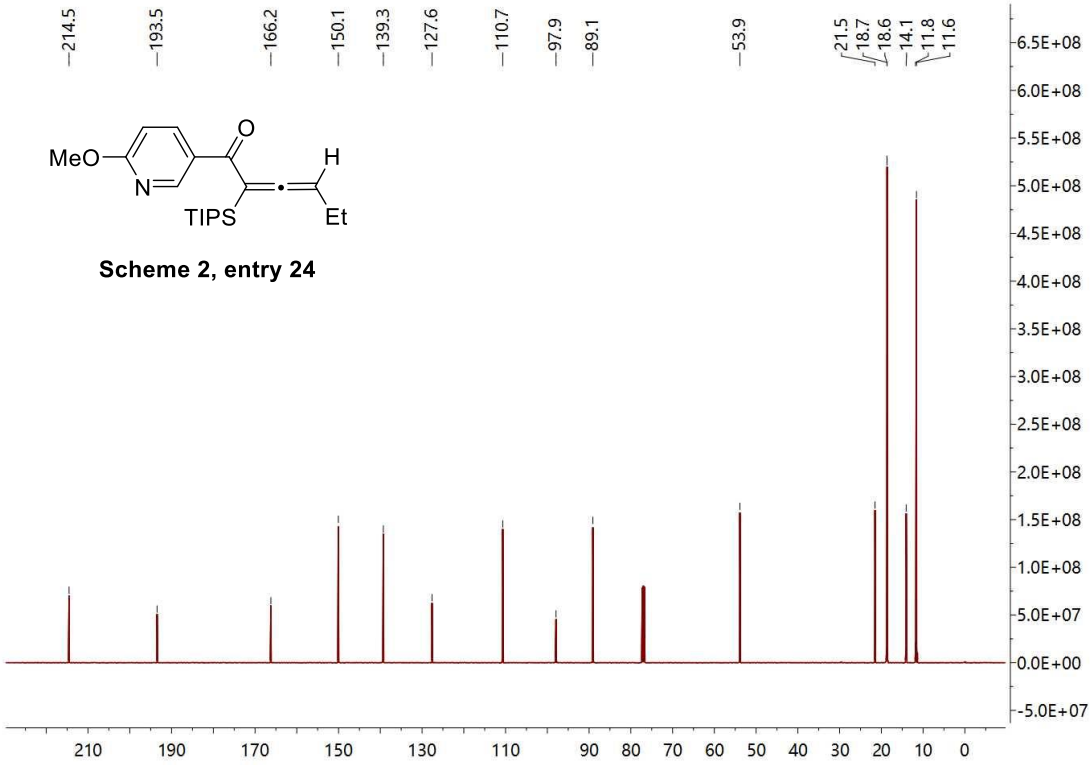


Scheme 2, entry 23

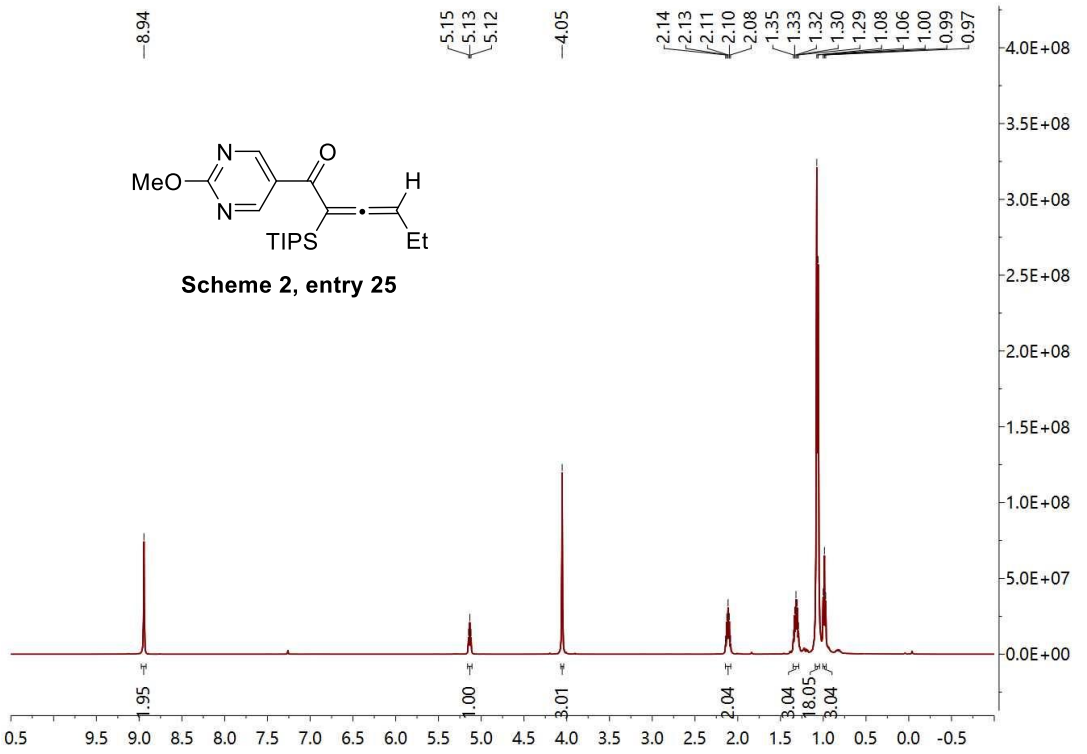
^{1}H NMR (500 MHz, $CDCl_3$)



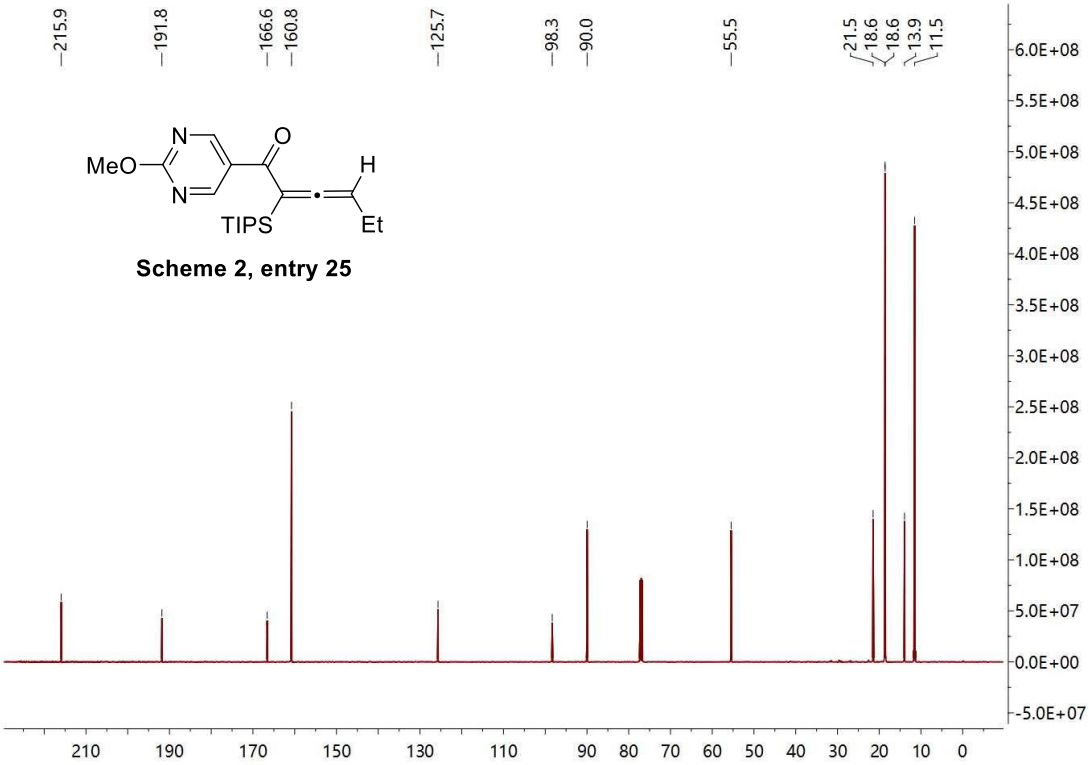
^{13}C NMR (126 MHz, $CDCl_3$)



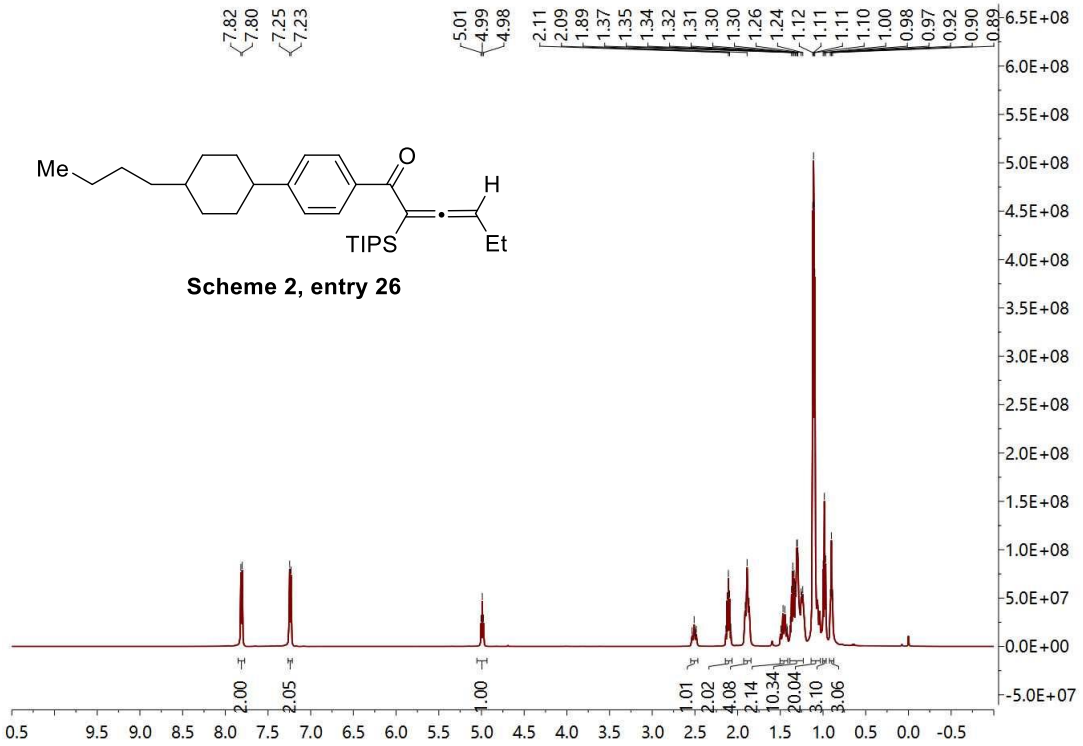
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

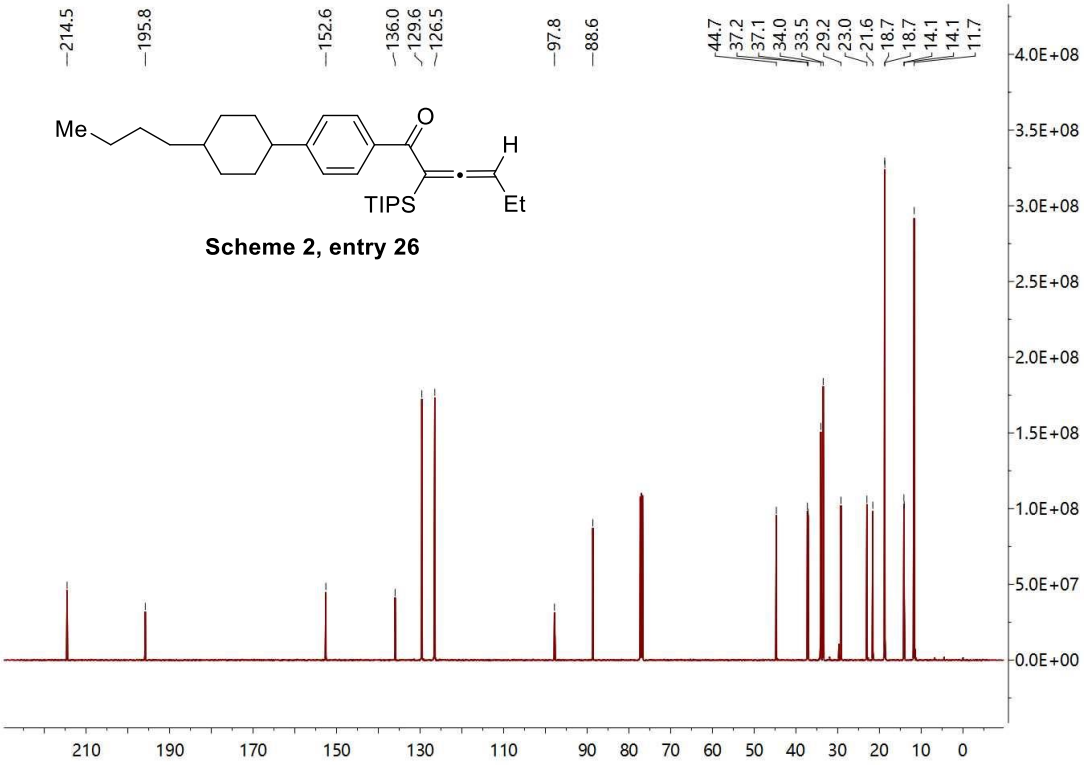


^{1}H NMR (500 MHz, $CDCl_3$)



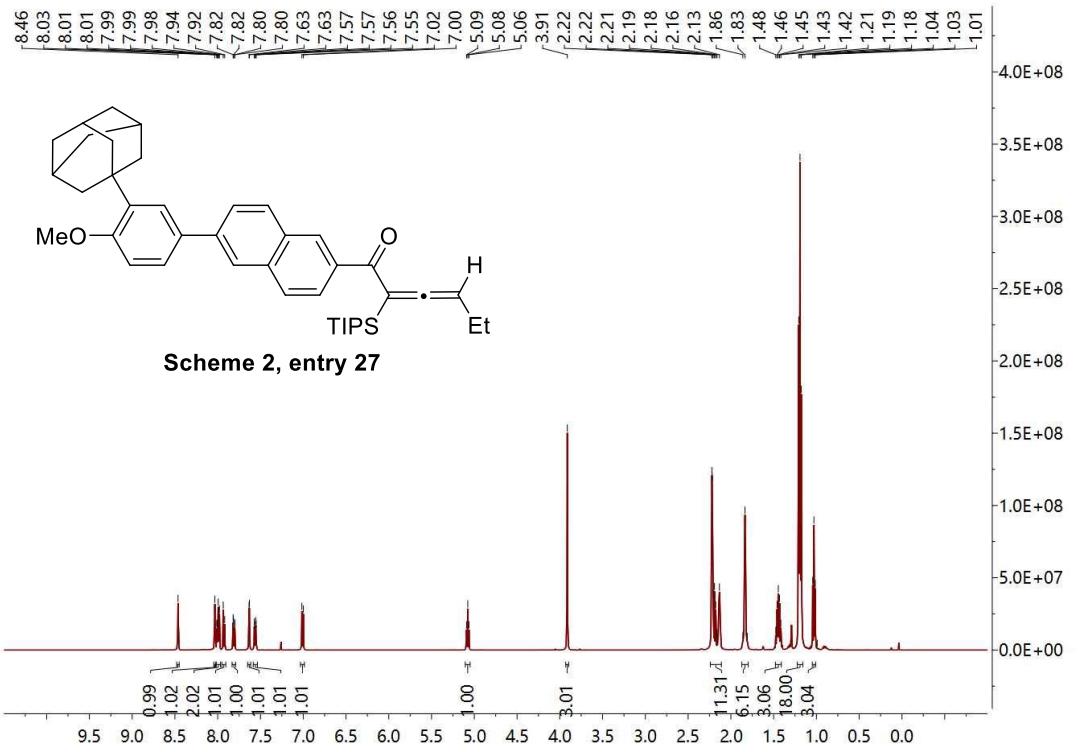
Scheme 2, entry 26

^{13}C NMR (126 MHz, $CDCl_3$)

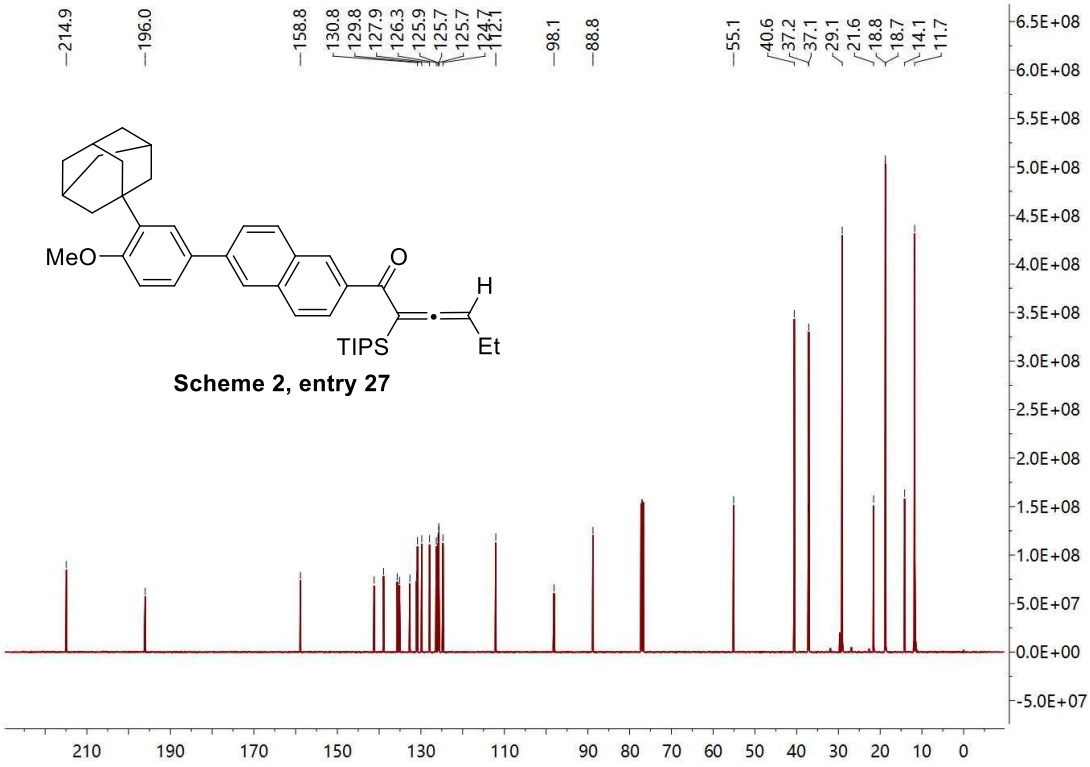


Scheme 2, entry 26

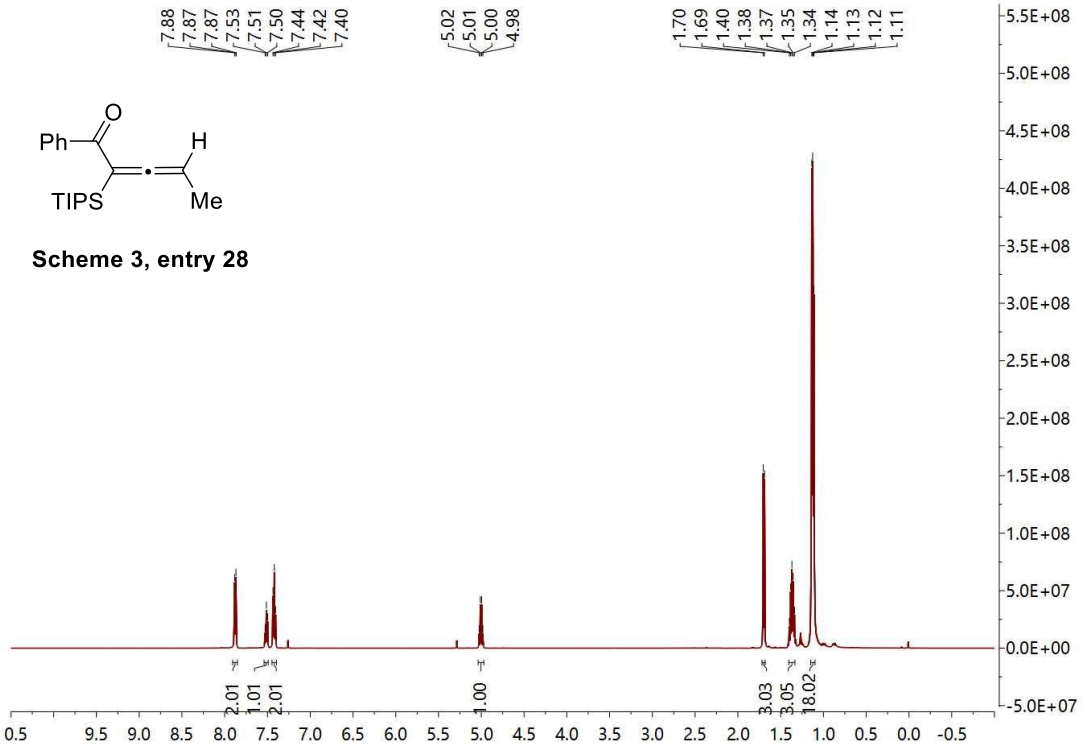
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

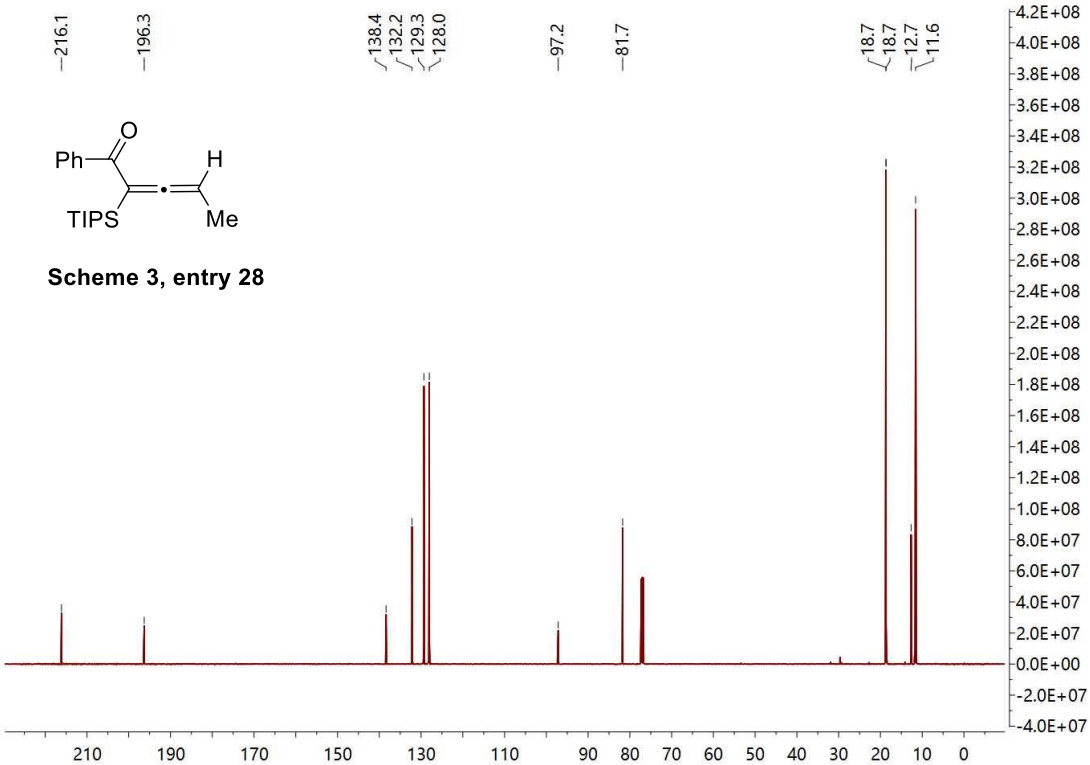


^{1}H NMR (500 MHz, $CDCl_3$)



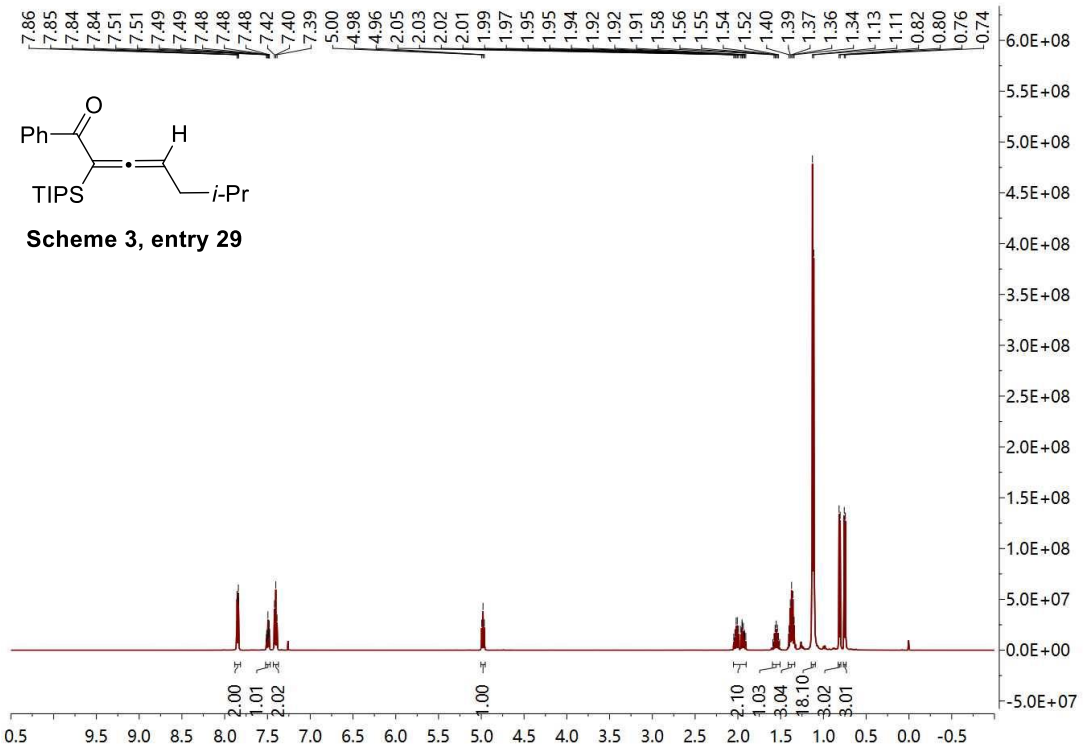
Scheme 3, entry 28

^{13}C NMR (126 MHz, $CDCl_3$)

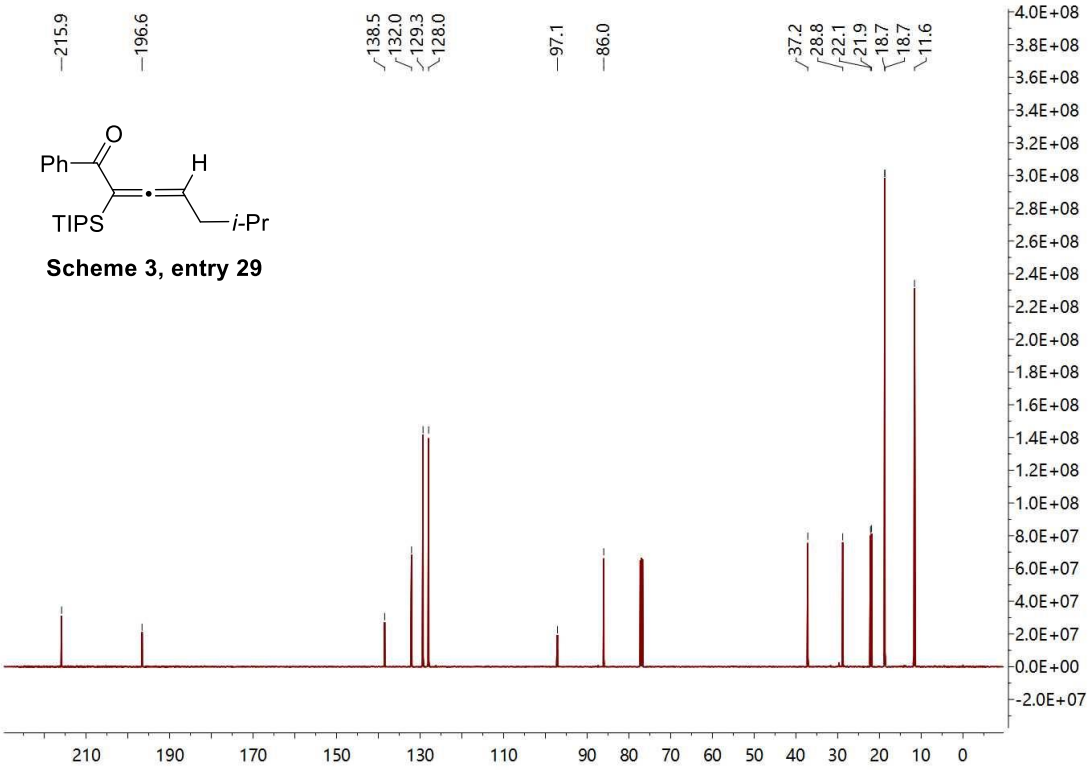


Scheme 3, entry 28

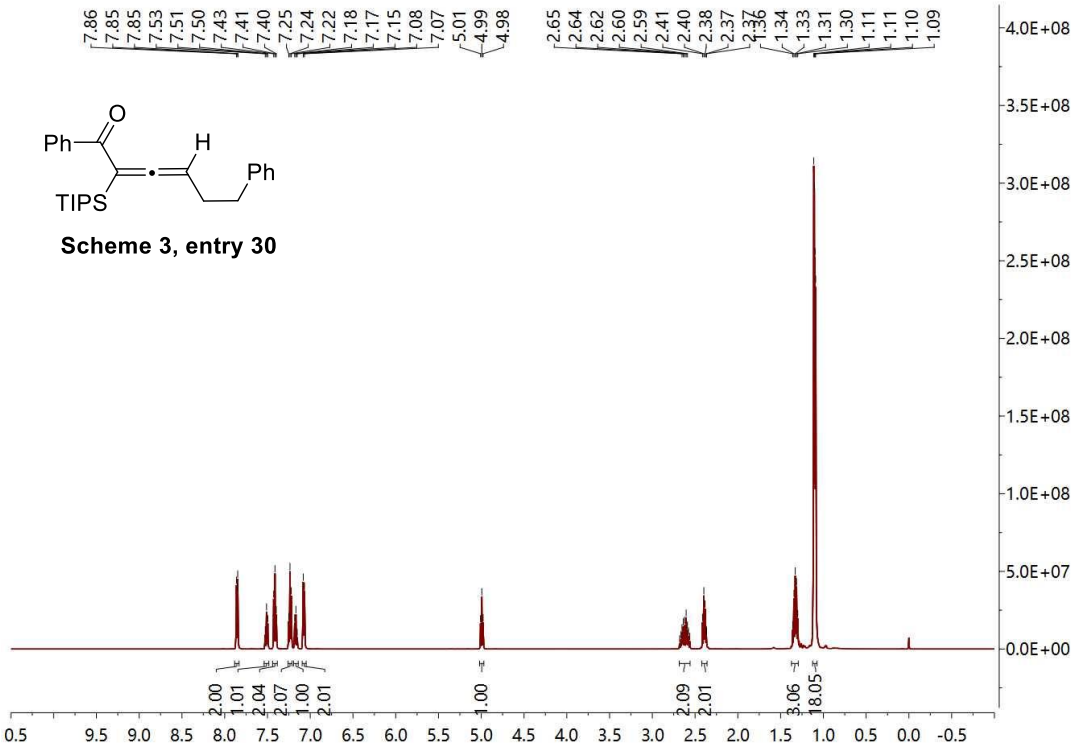
^{1}H NMR (500 MHz, $CDCl_3$)



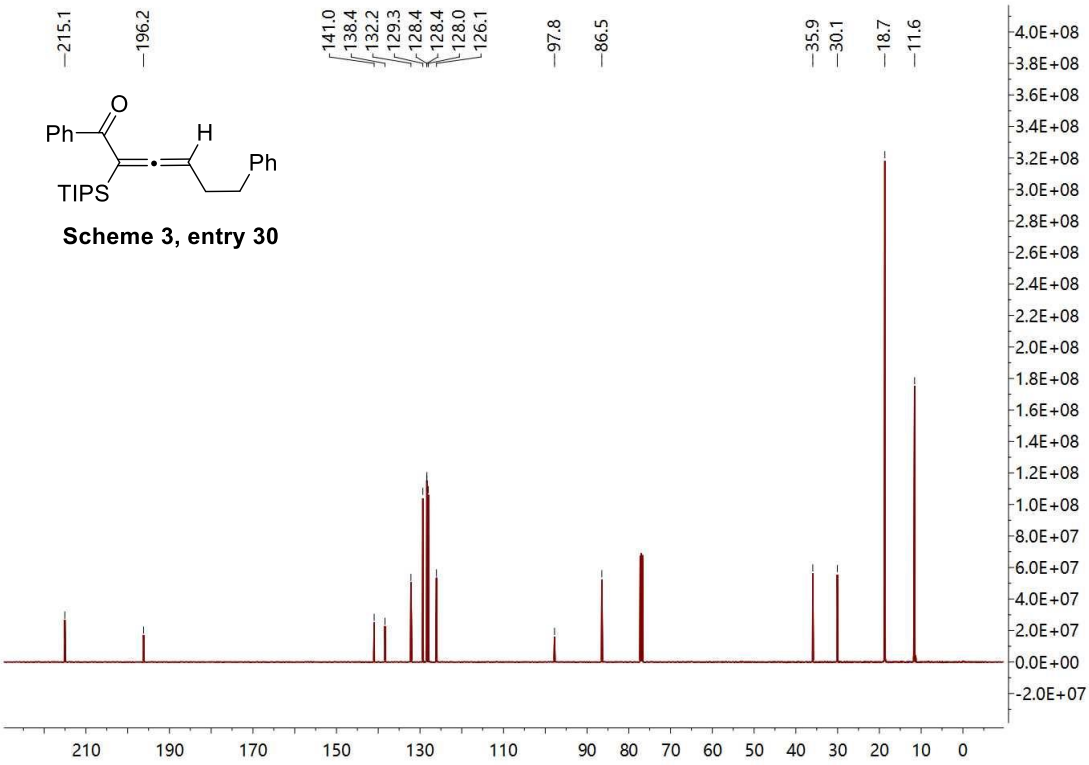
^{13}C NMR (126 MHz, $CDCl_3$)



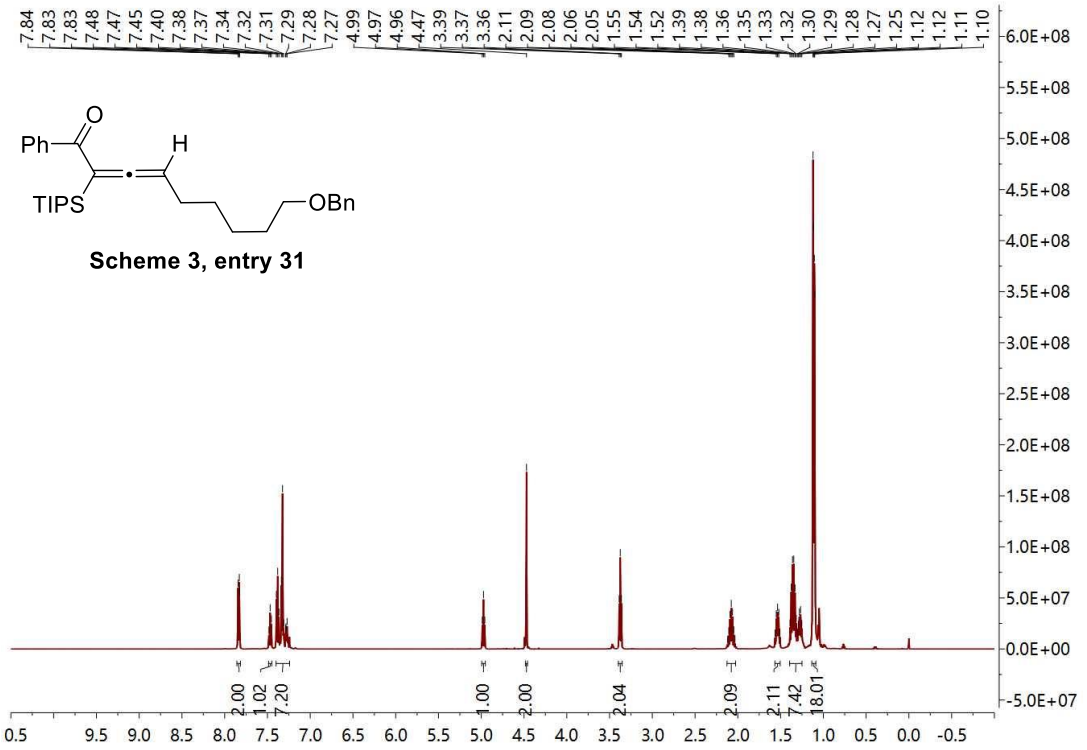
^{1}H NMR (500 MHz, $CDCl_3$)



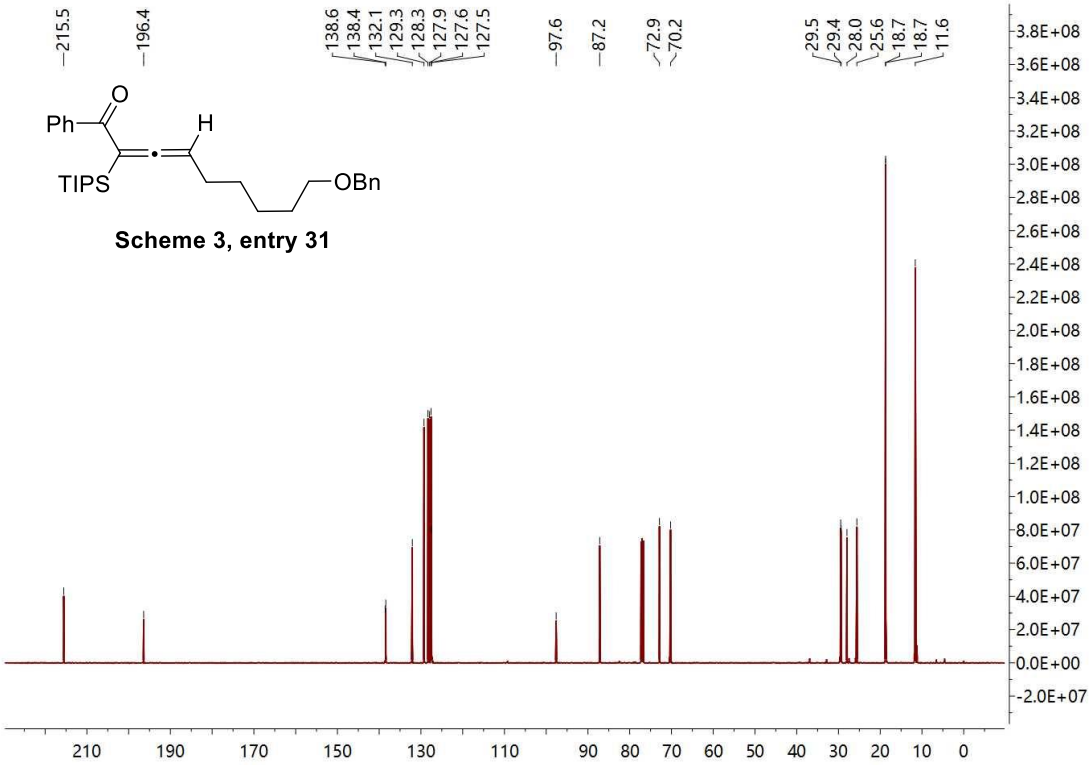
^{13}C NMR (126 MHz, $CDCl_3$)



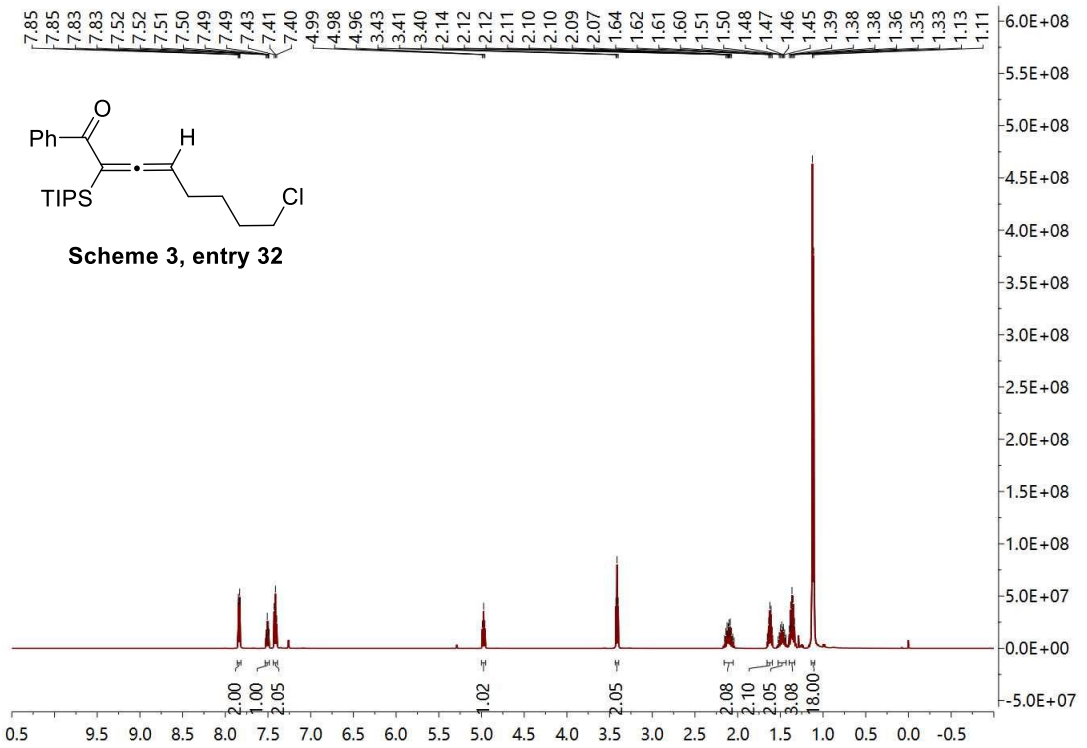
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

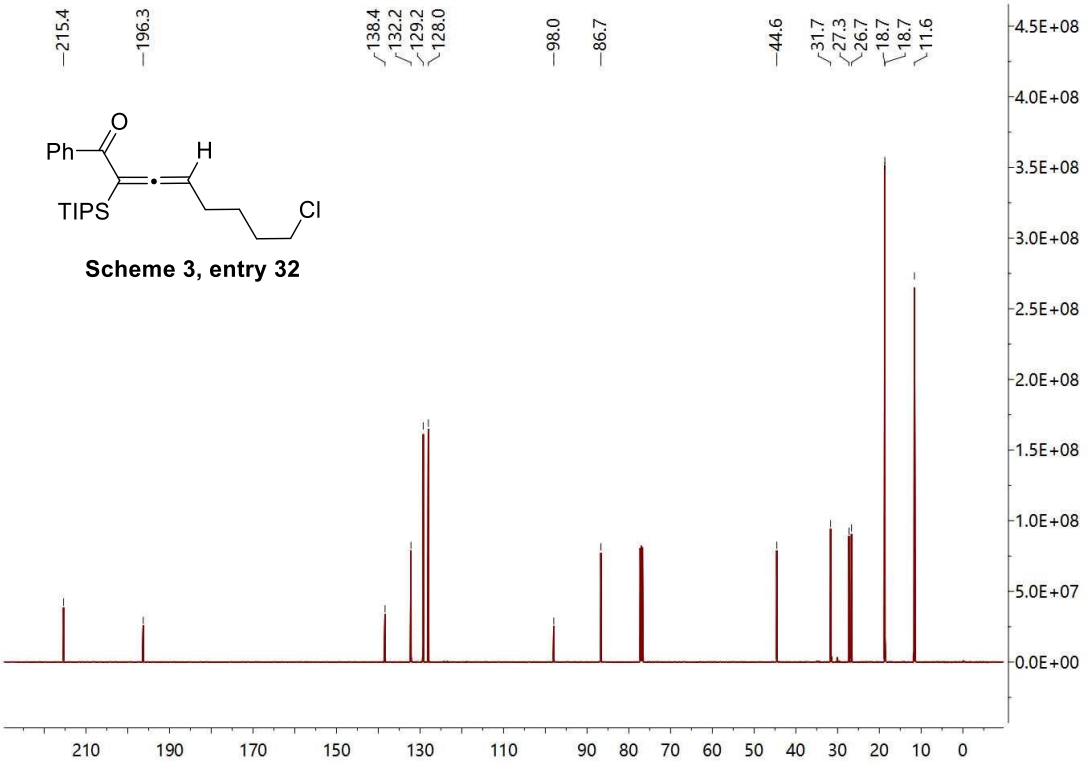


^{1}H NMR (500 MHz, $CDCl_3$)



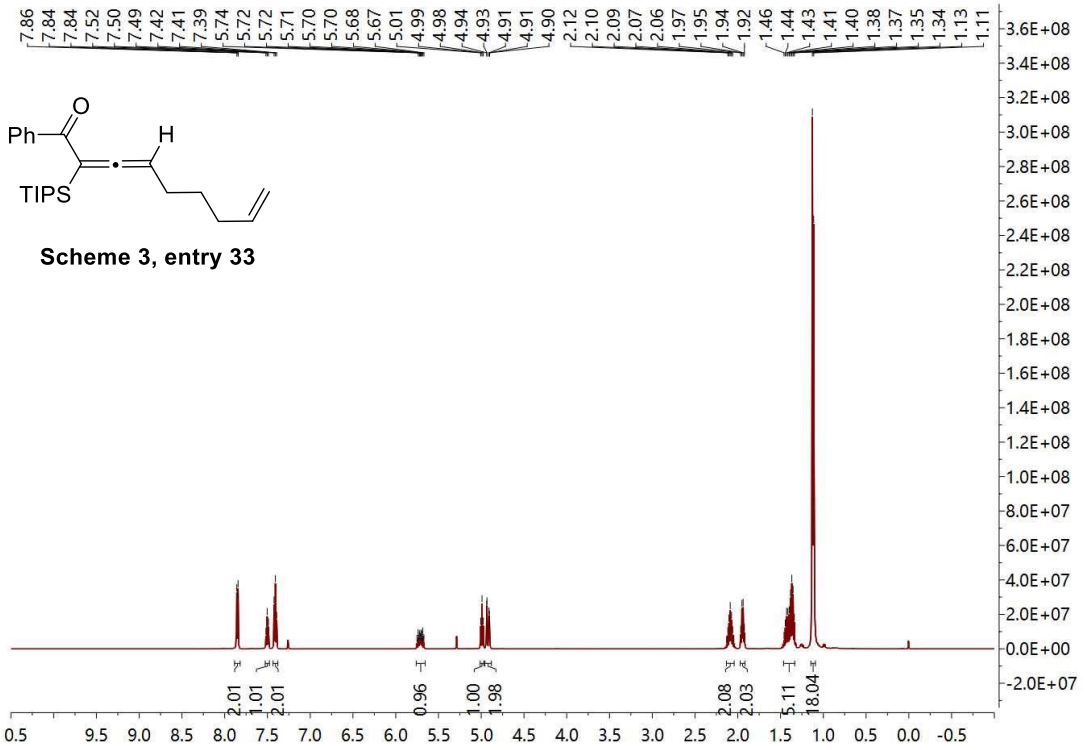
Scheme 3, entry 32

^{13}C NMR (126 MHz, $CDCl_3$)



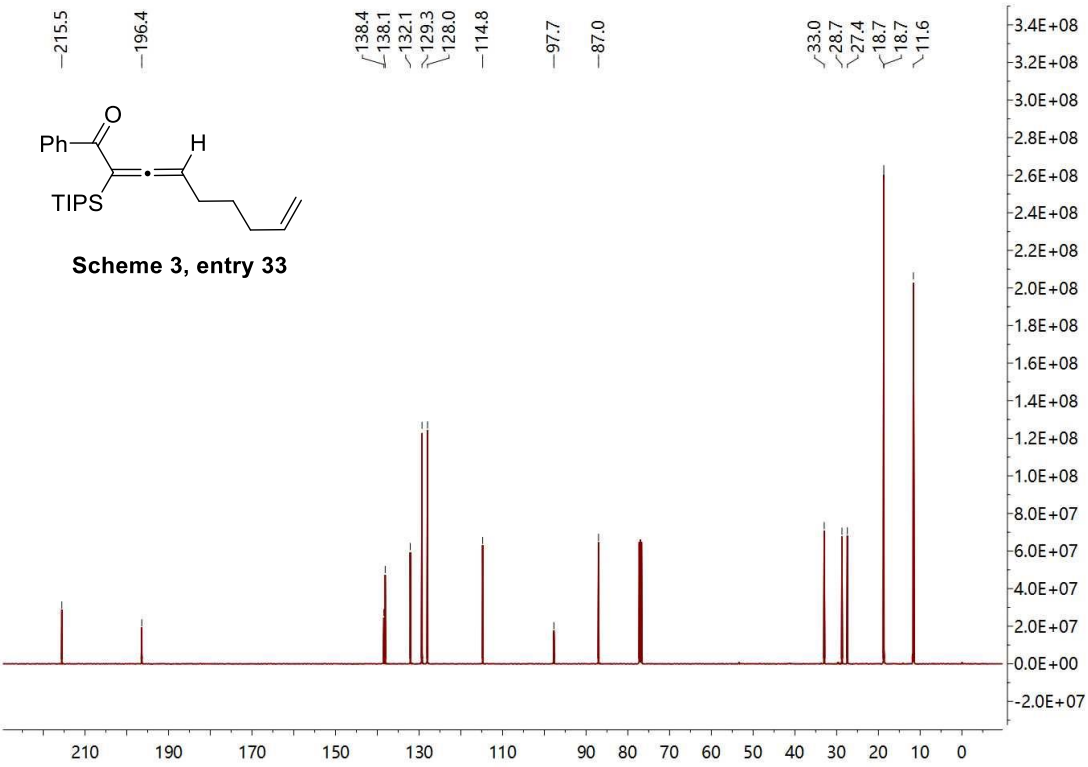
Scheme 3, entry 32

^{1}H NMR (500 MHz, $CDCl_3$)



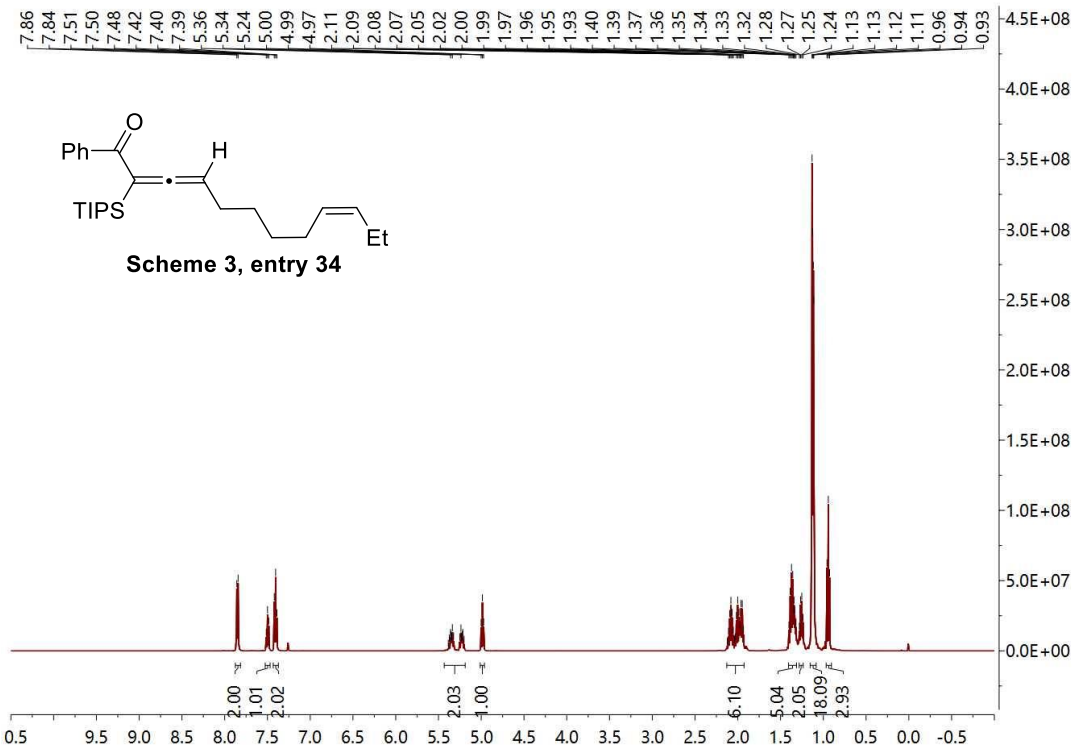
Scheme 3, entry 33

^{13}C NMR (126 MHz, $CDCl_3$)

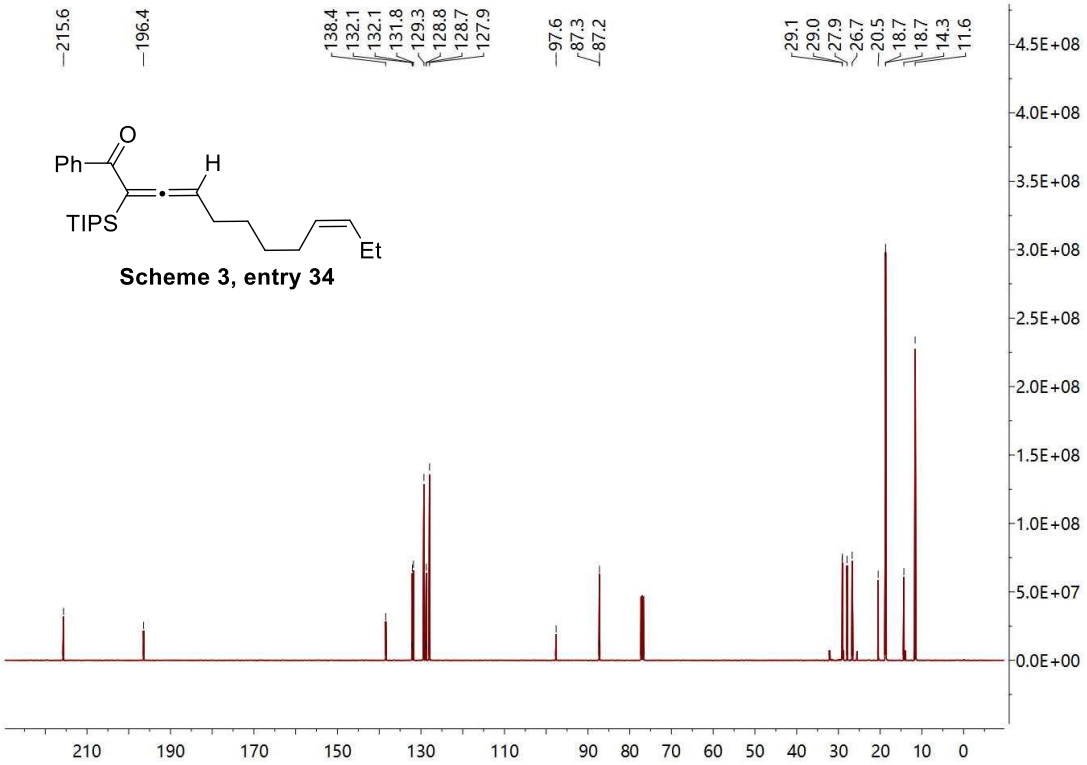


Scheme 3, entry 33

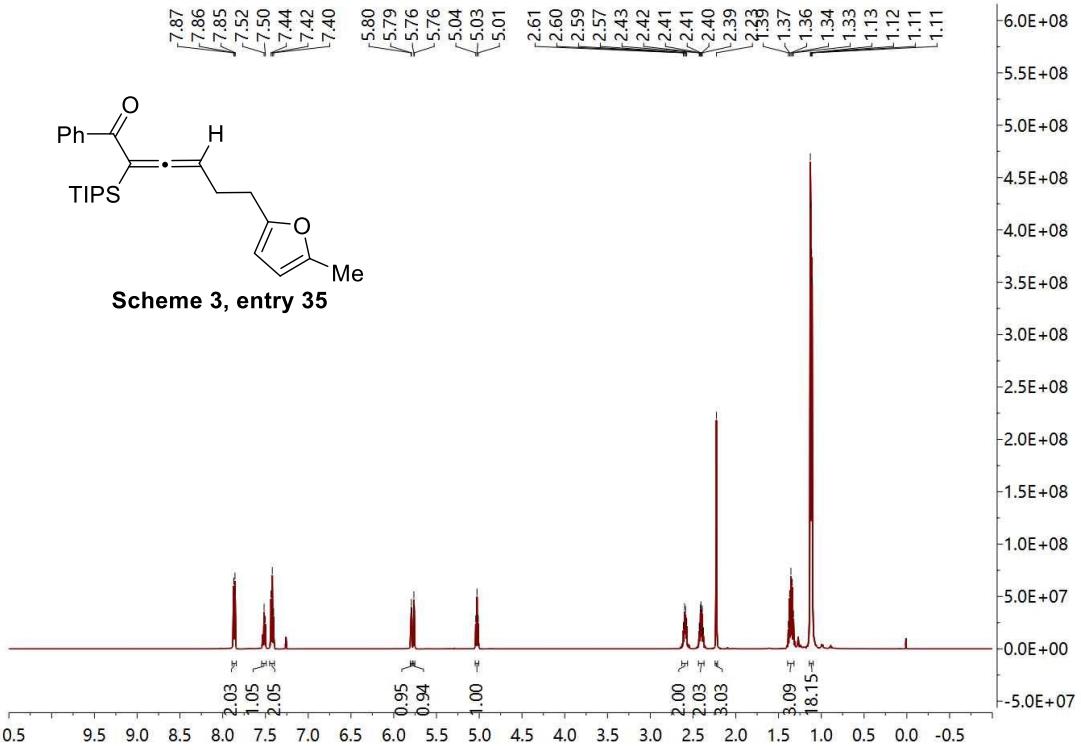
^{1}H NMR (500 MHz, $CDCl_3$)



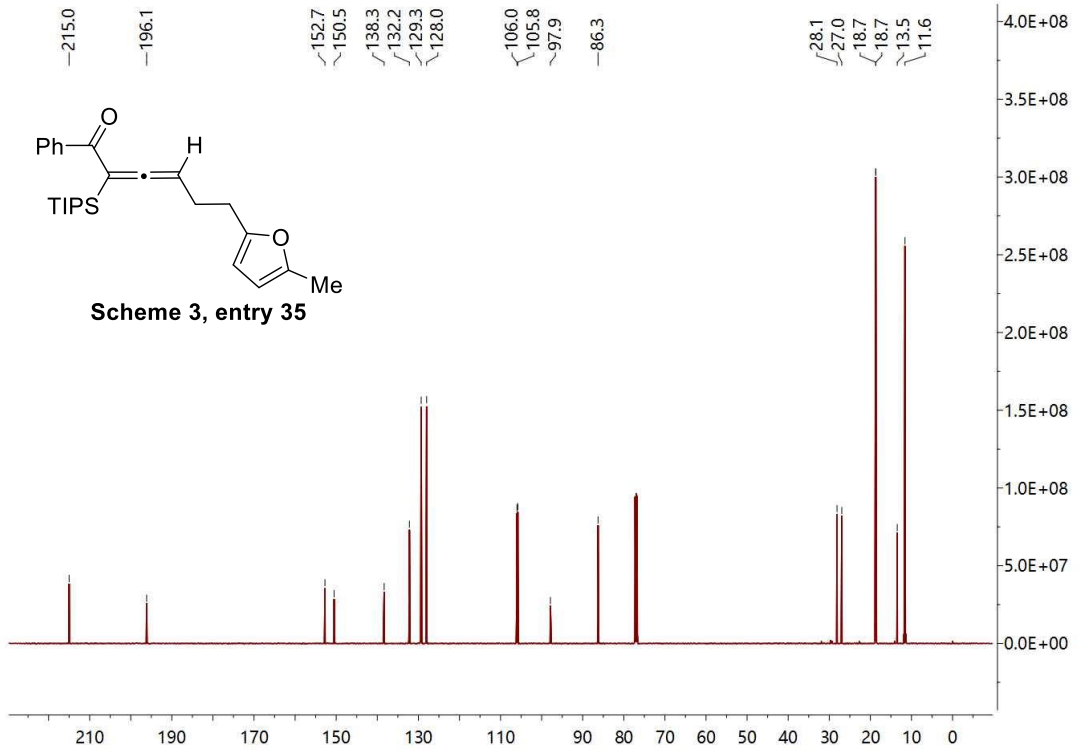
^{13}C NMR (126 MHz, $CDCl_3$)



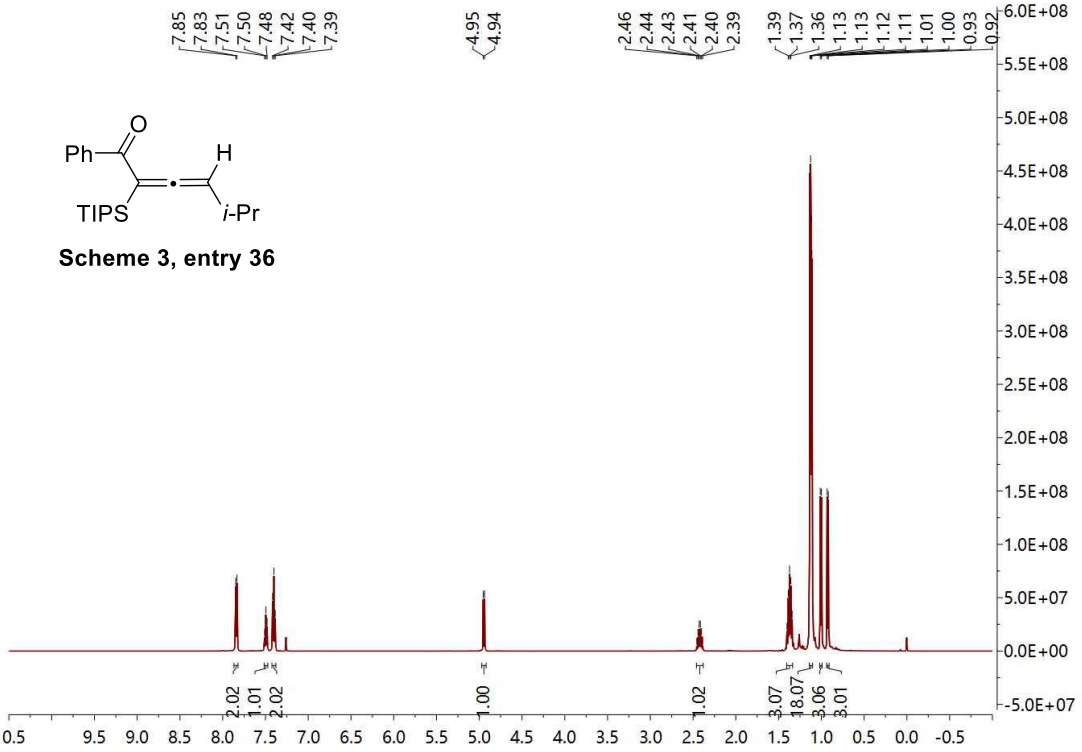
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

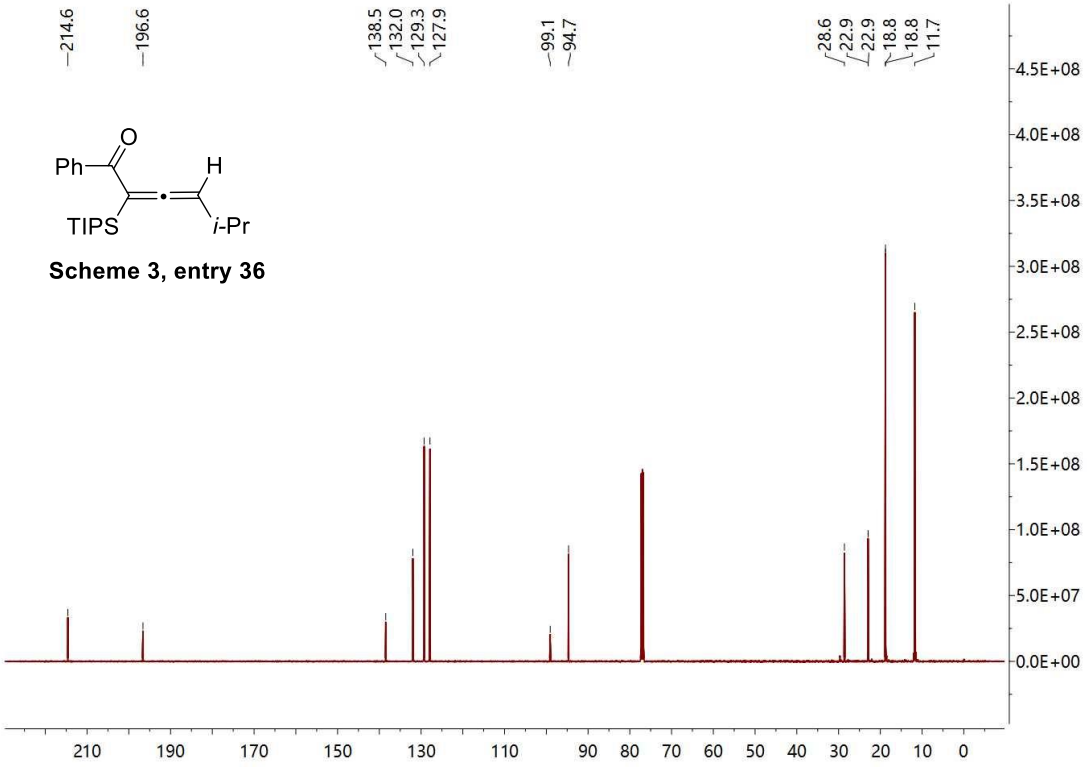


^{1}H NMR (500 MHz, $CDCl_3$)



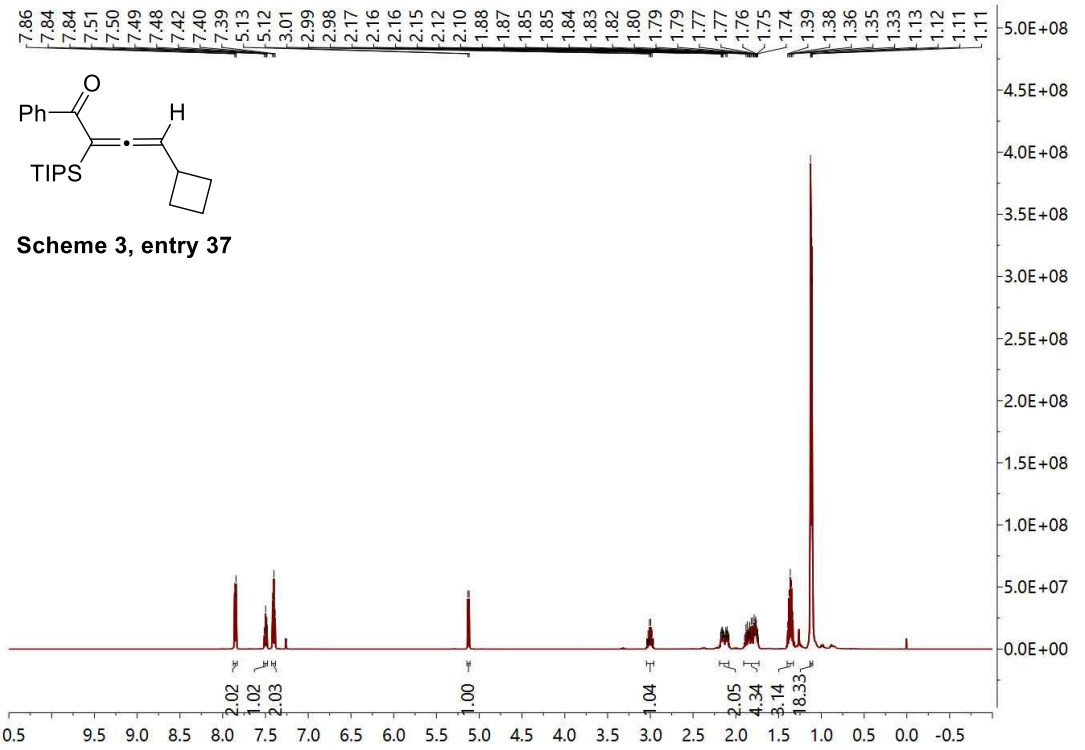
Scheme 3, entry 36

^{13}C NMR (126 MHz, $CDCl_3$)

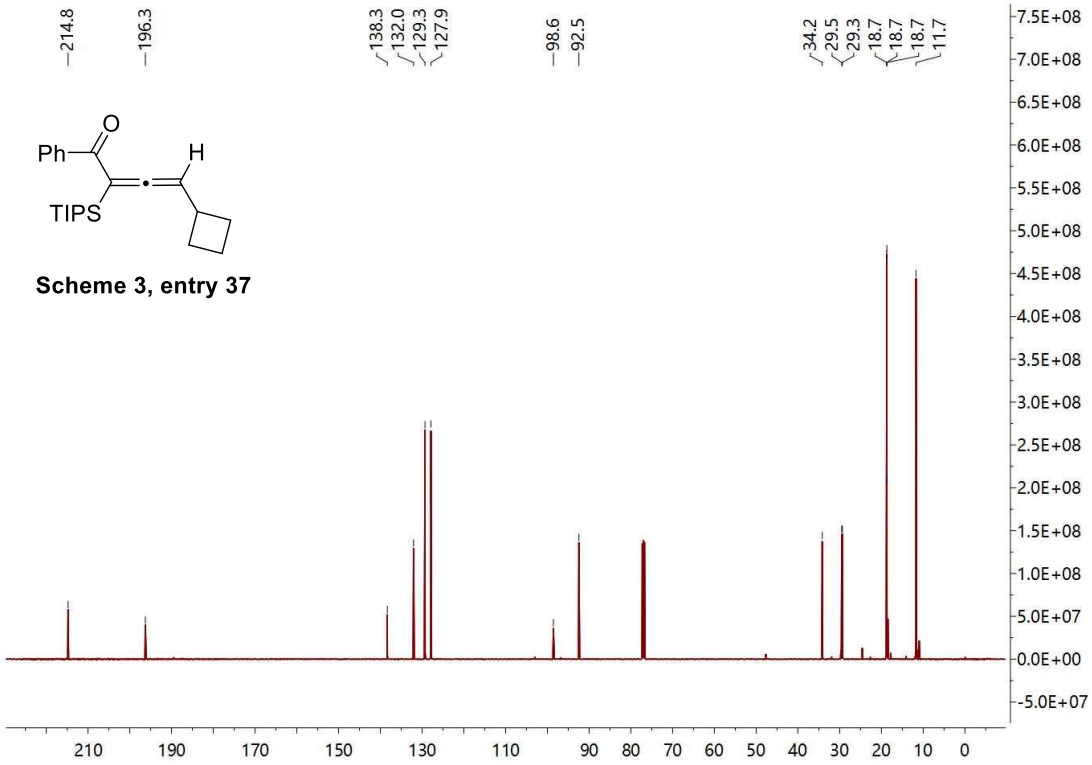


Scheme 3, entry 36

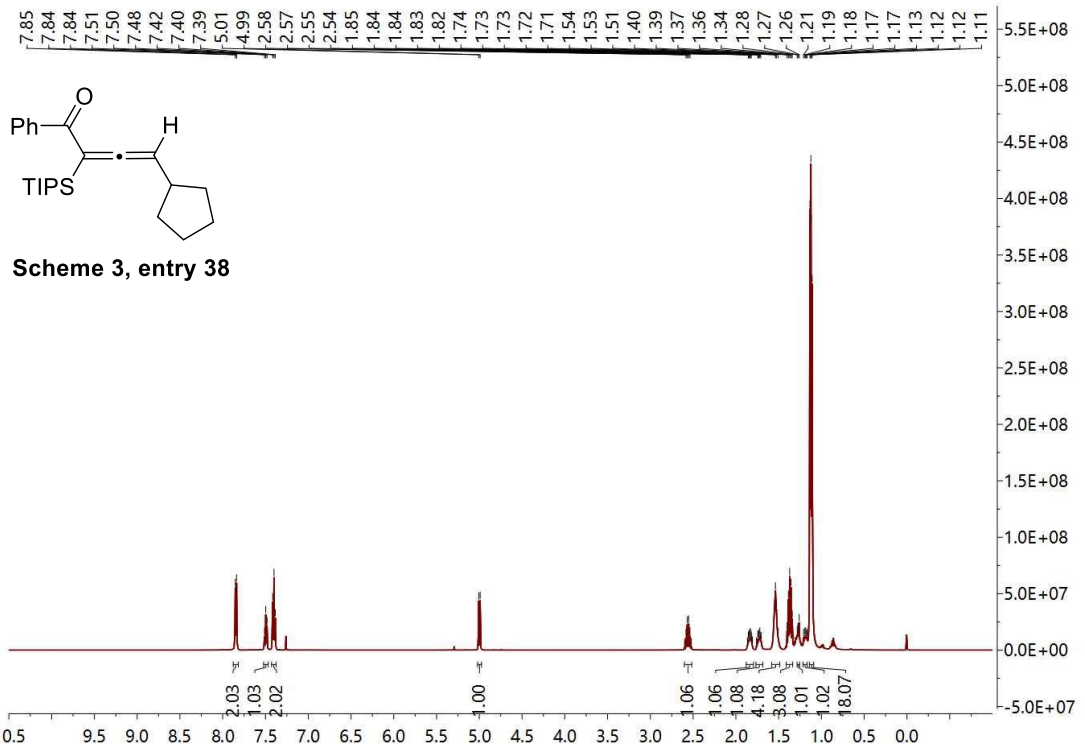
^{1}H NMR (500 MHz, $CDCl_3$)



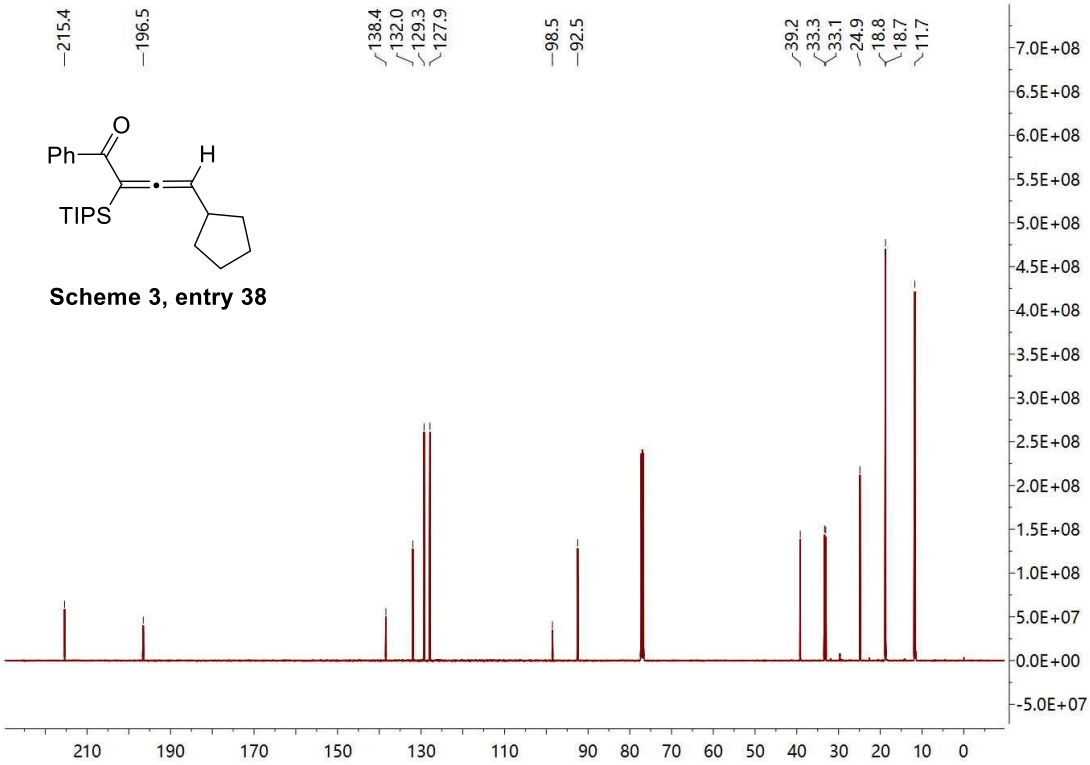
^{13}C NMR (126 MHz, $CDCl_3$)



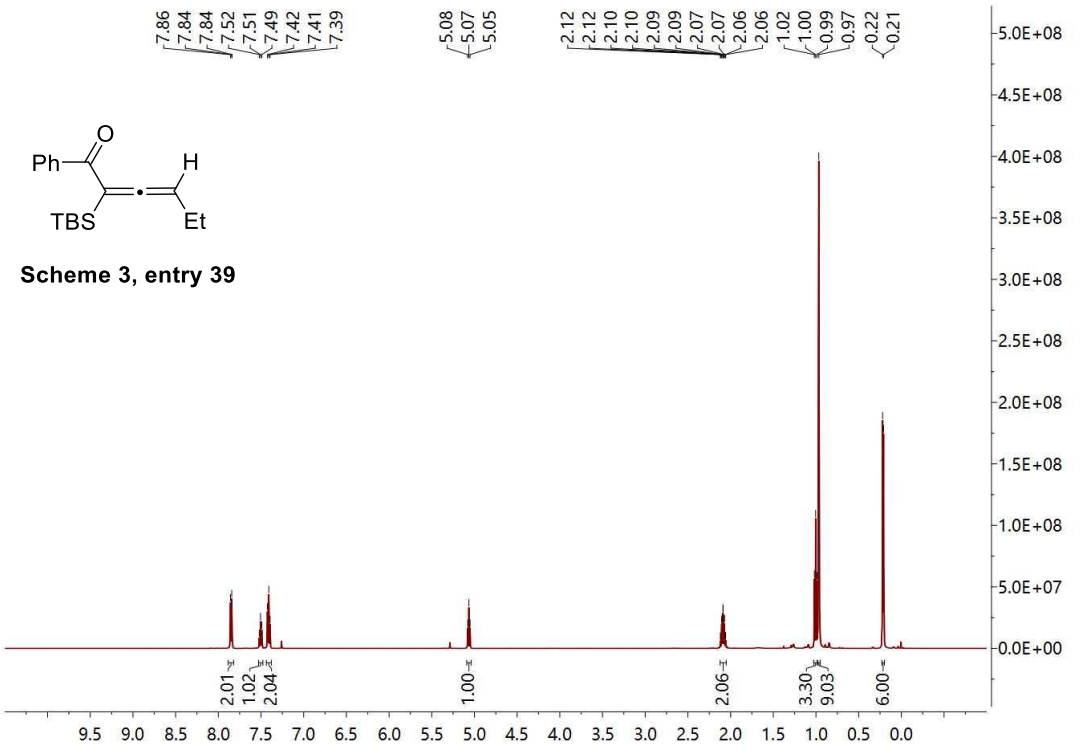
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

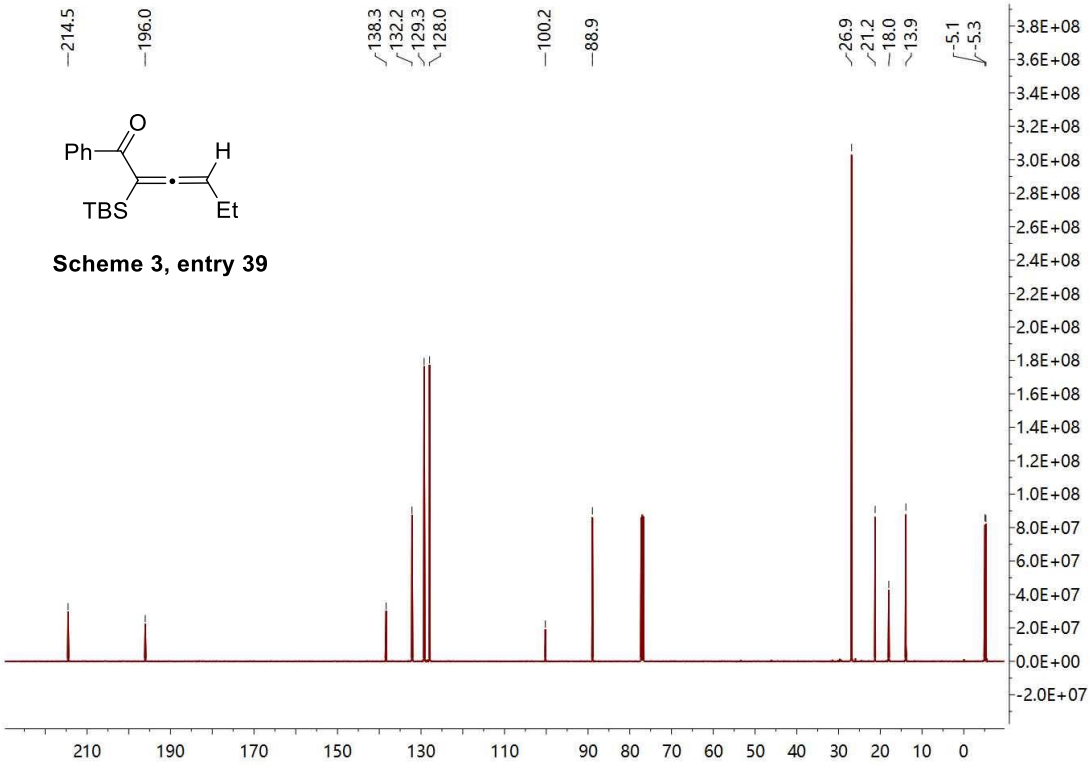


^{1}H NMR (500 MHz, $CDCl_3$)



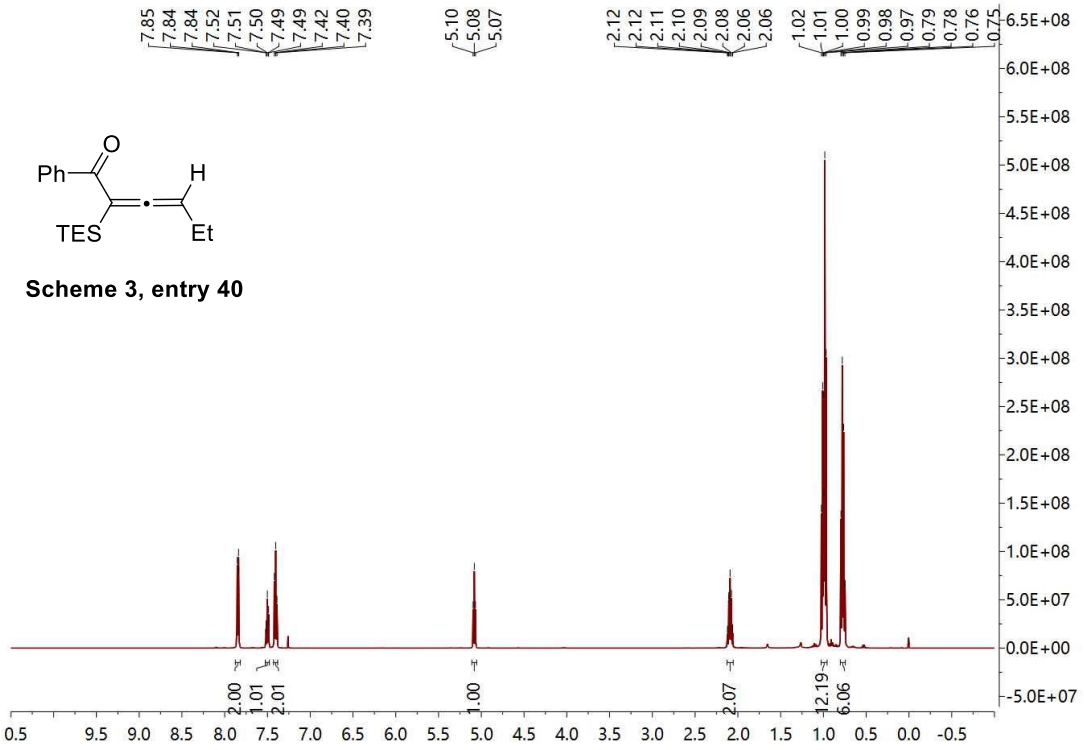
Scheme 3, entry 39

^{13}C NMR (126 MHz, $CDCl_3$)



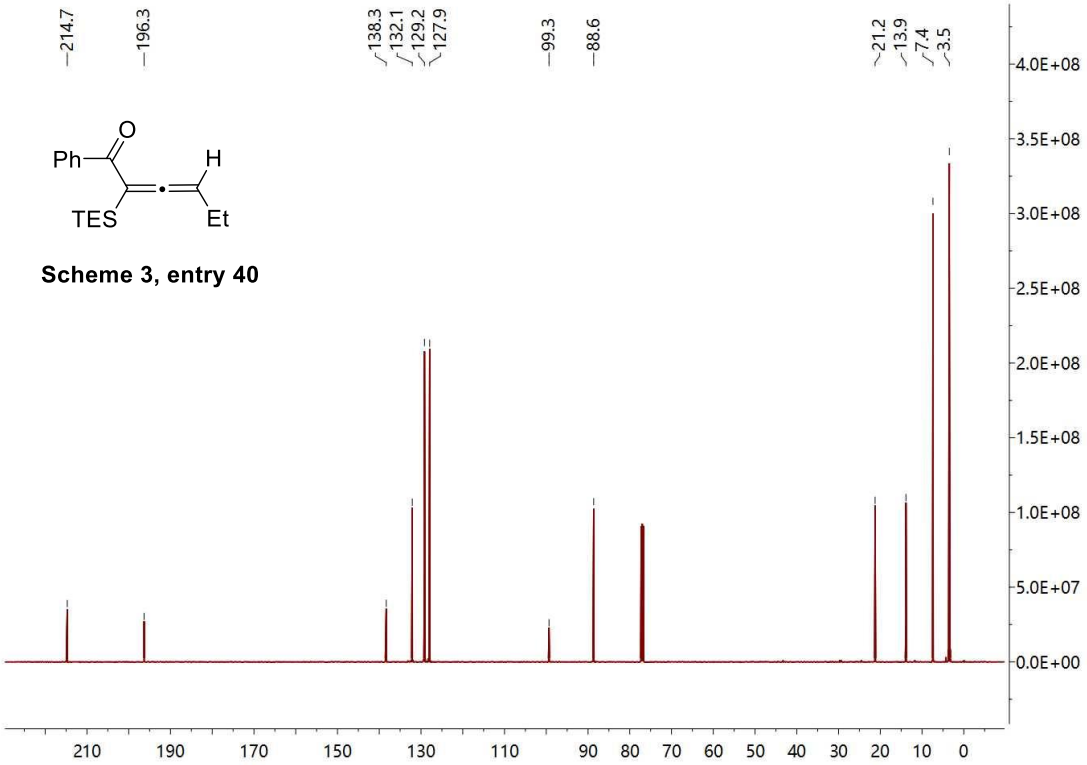
Scheme 3, entry 39

^{1}H NMR (500 MHz, $CDCl_3$)



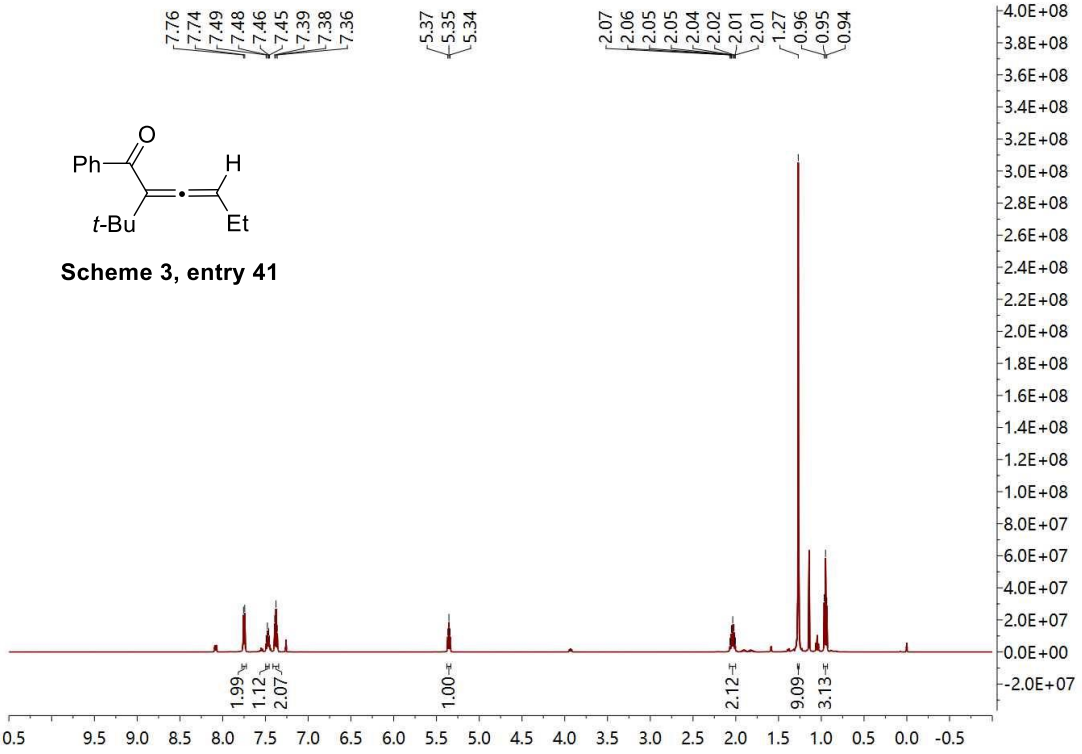
Scheme 3, entry 40

^{13}C NMR (126 MHz, $CDCl_3$)



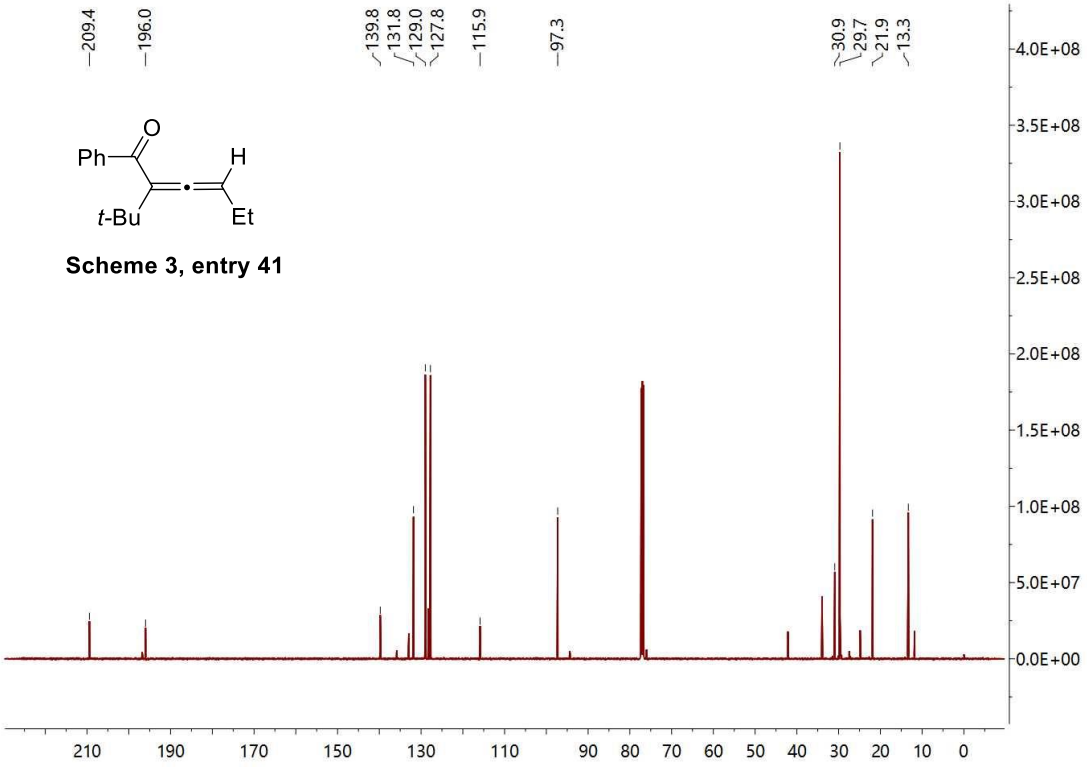
Scheme 3, entry 40

^{1}H NMR (500 MHz, $CDCl_3$)



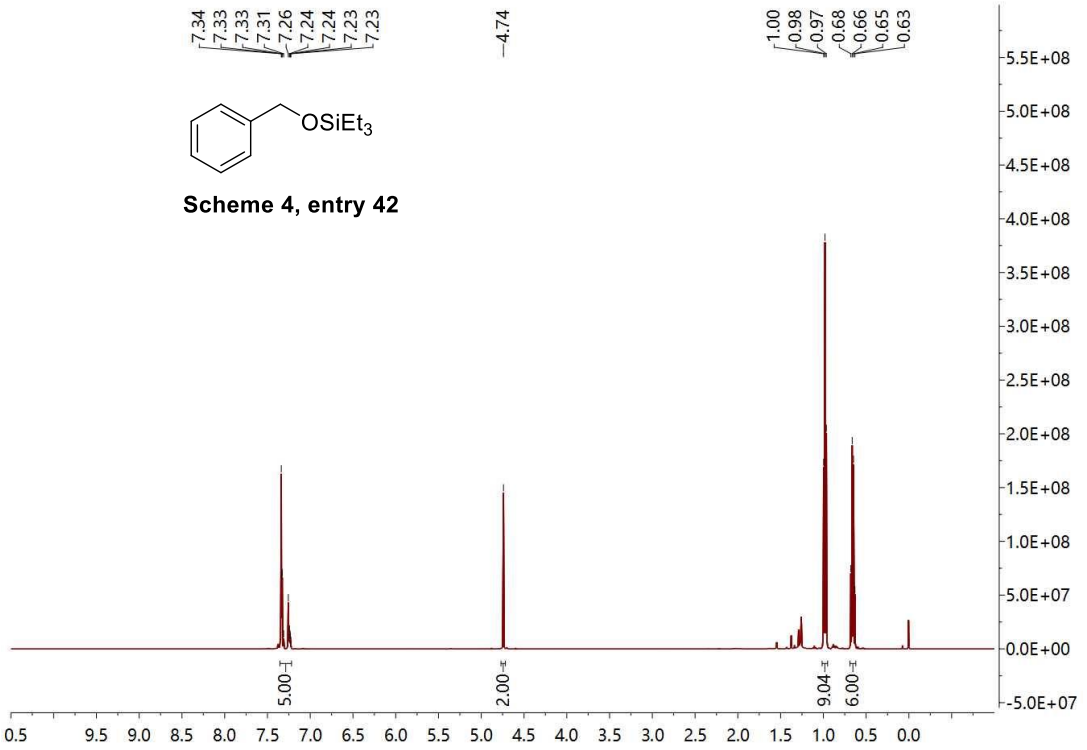
Scheme 3, entry 41

^{13}C NMR (126 MHz, $CDCl_3$)



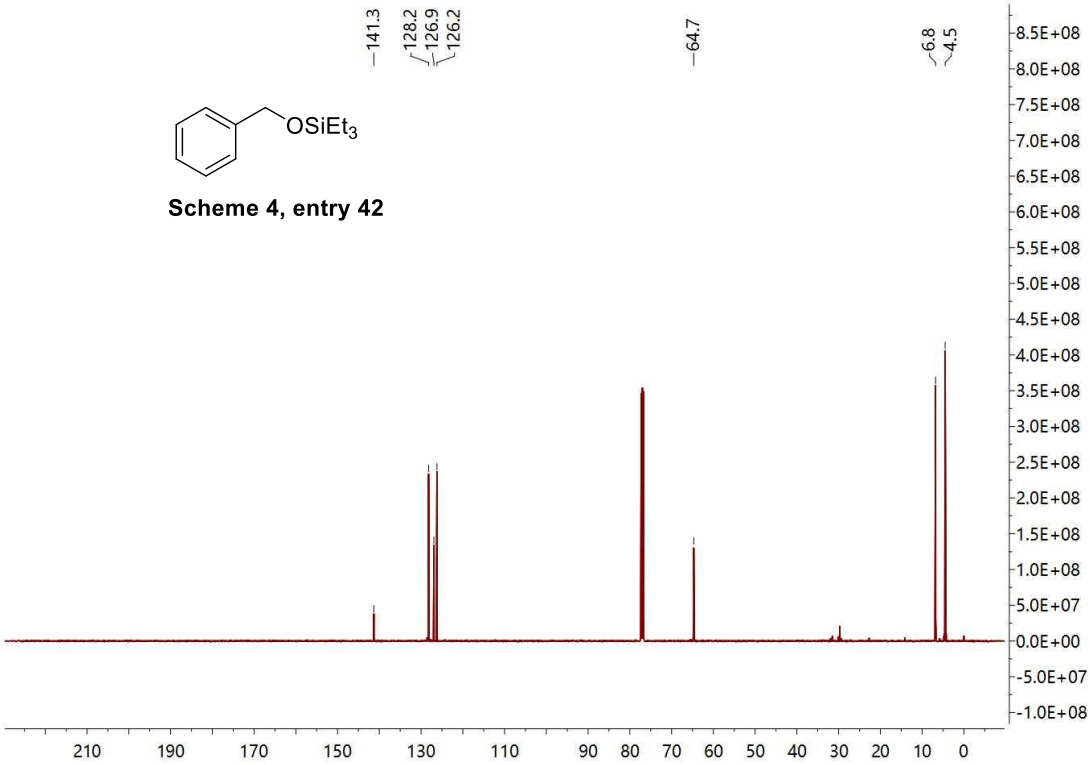
Scheme 3, entry 41

^{1}H NMR (500 MHz, $CDCl_3$)



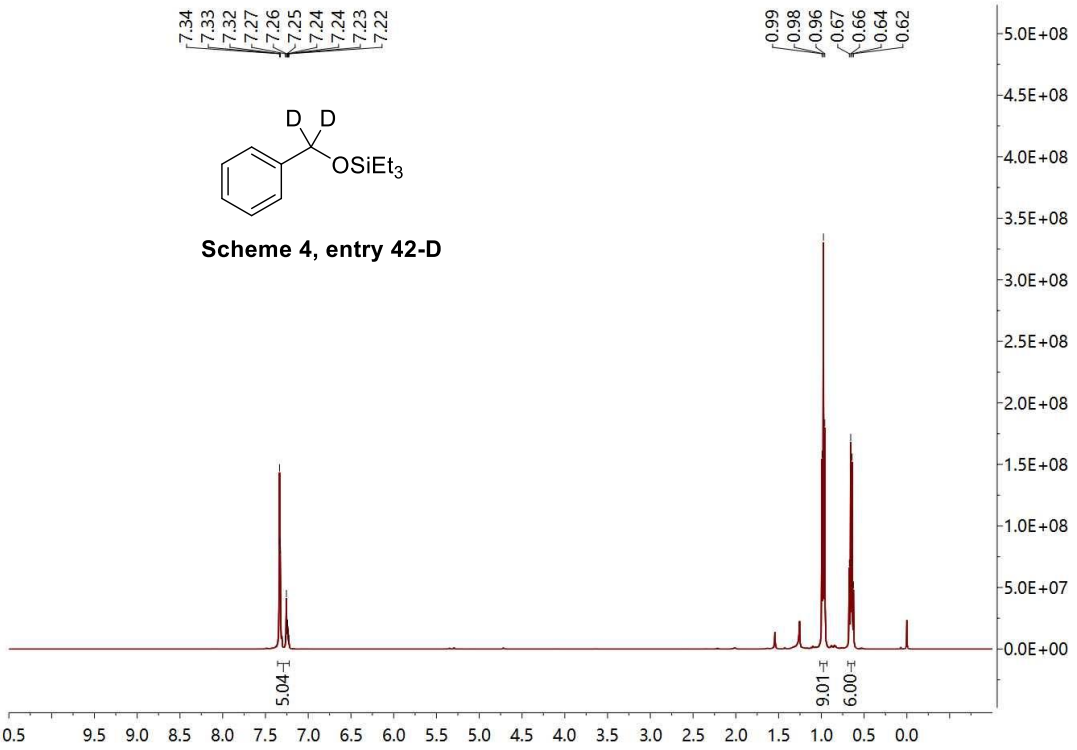
Scheme 4, entry 42

^{13}C NMR (126 MHz, $CDCl_3$)



Scheme 4, entry 42

^{1}H NMR (500 MHz, $CDCl_3$)



Scheme 4, entry 42-D

^{13}C NMR (126 MHz, $CDCl_3$)

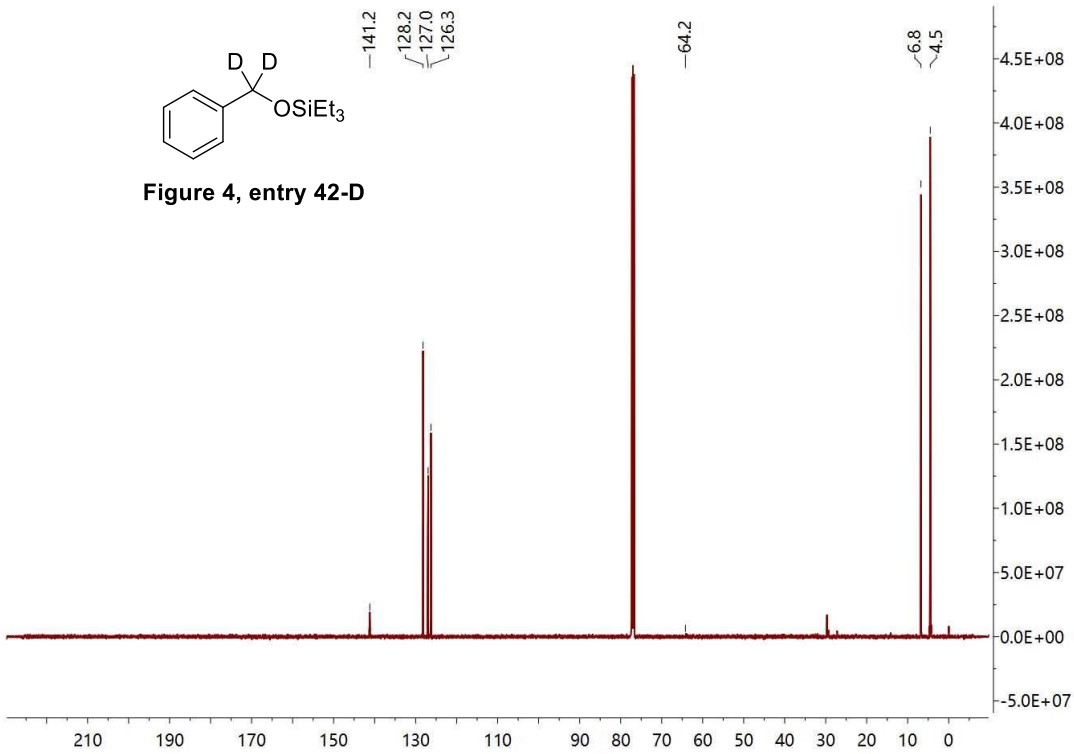
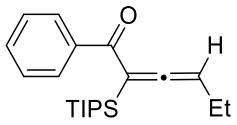
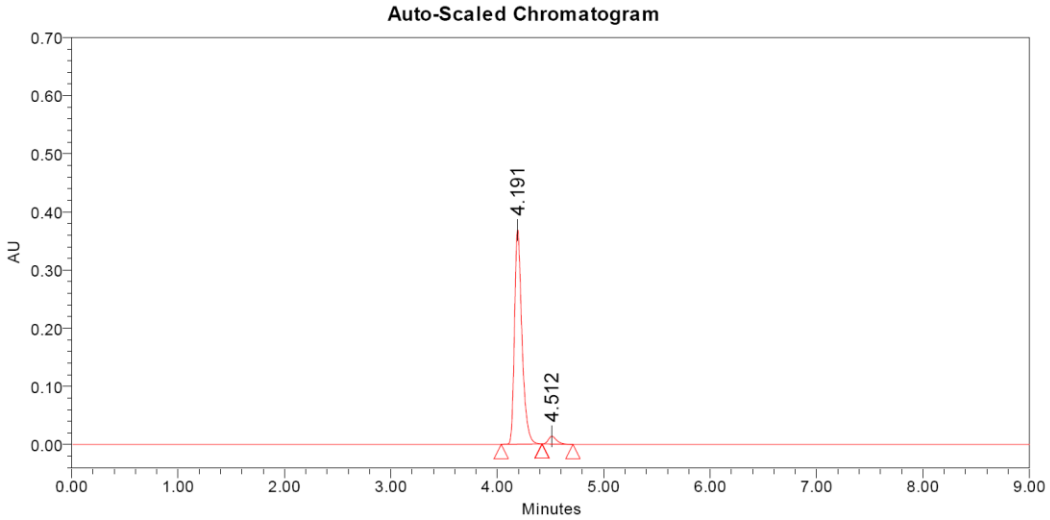


Figure 4, entry 42-D

IX. Stereoselectivity Analysis

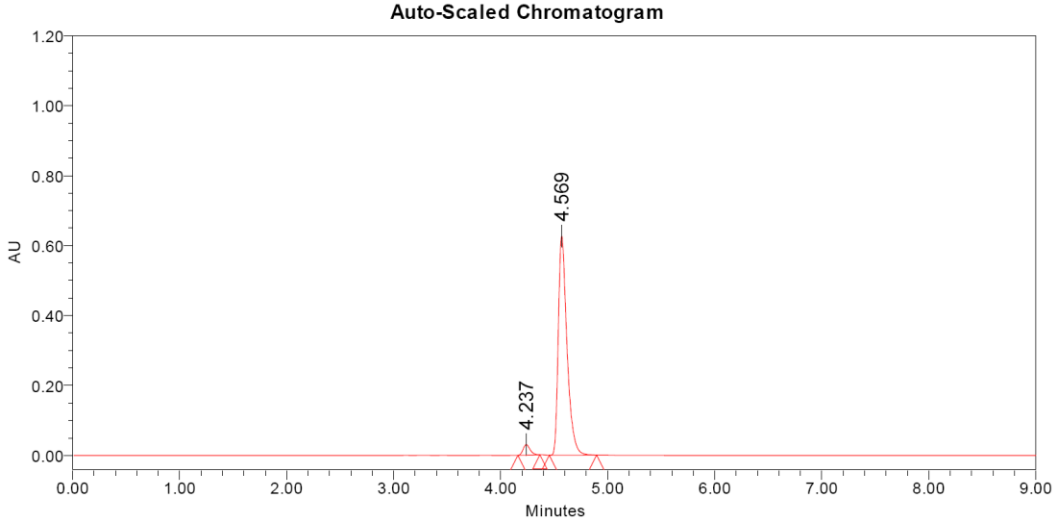


Scheme 2, entry 1
(*R*,*S*)-**L1**: 92% ee; (*S*,*R*)-**L1**: 92% ee



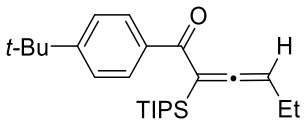
Peak Results

	Name	RT	Area	Height	% Area
1		4.191	1796482	368960	96.15
2		4.512	71877	13403	3.85

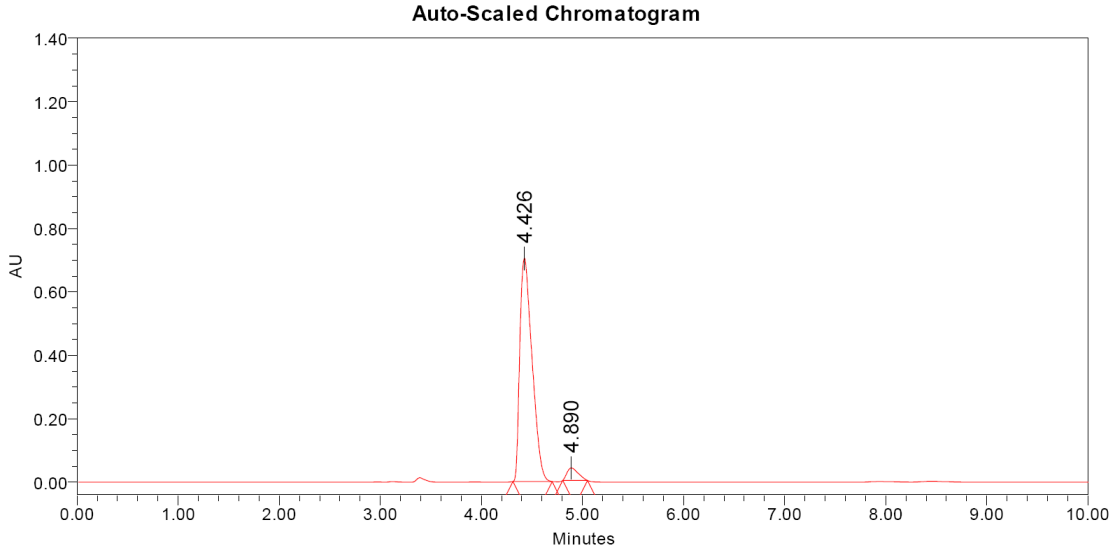


Peak Results

	Name	RT	Area	Height	% Area
1		4.237	134946	30019	3.68
2		4.569	3530125	626499	96.32

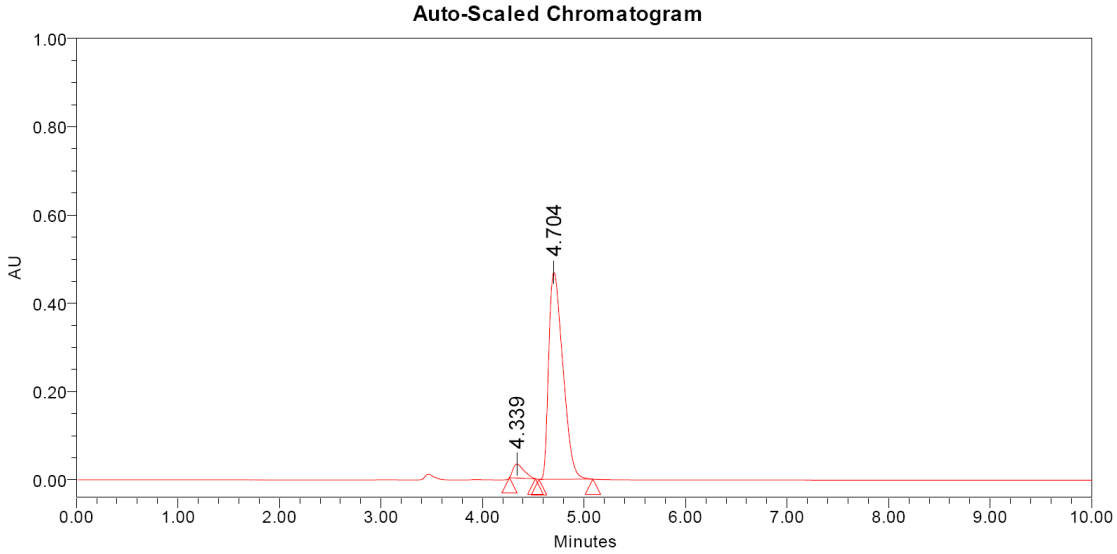


Scheme 2, entry 2
(*R*,*S*)-**L1**: 90% ee; (*S*,*R*)-**L1**: 90% ee



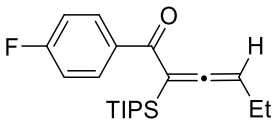
Peak Results

	Name	RT	Area	Height	% Area
1		4.426	5917058	704198	95.15
2		4.890	301622	39129	4.85

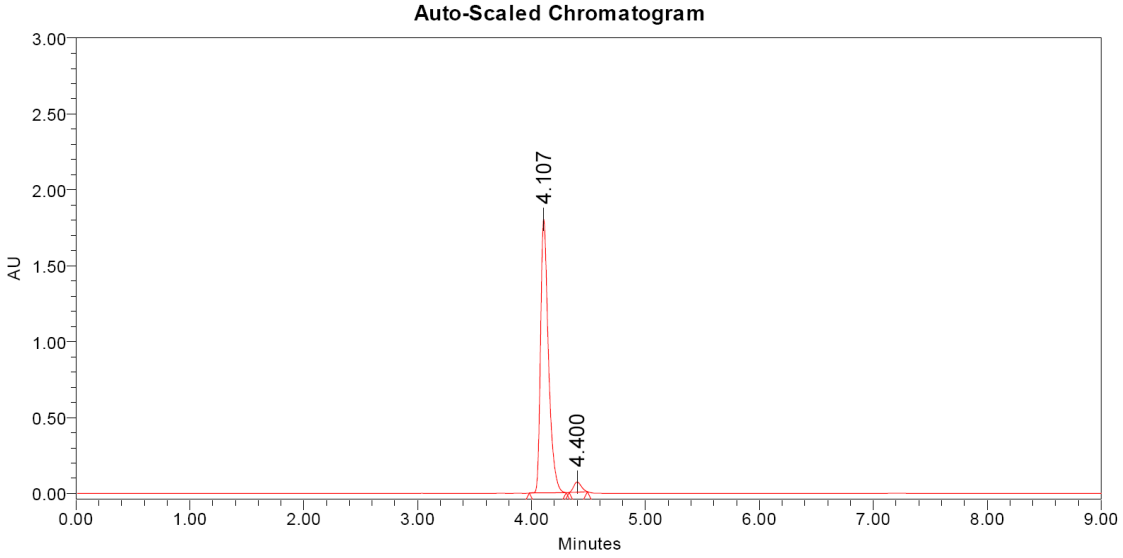


Peak Results

	Name	RT	Area	Height	% Area
1		4.339	236757	31530	4.95
2		4.704	4543441	469727	95.05

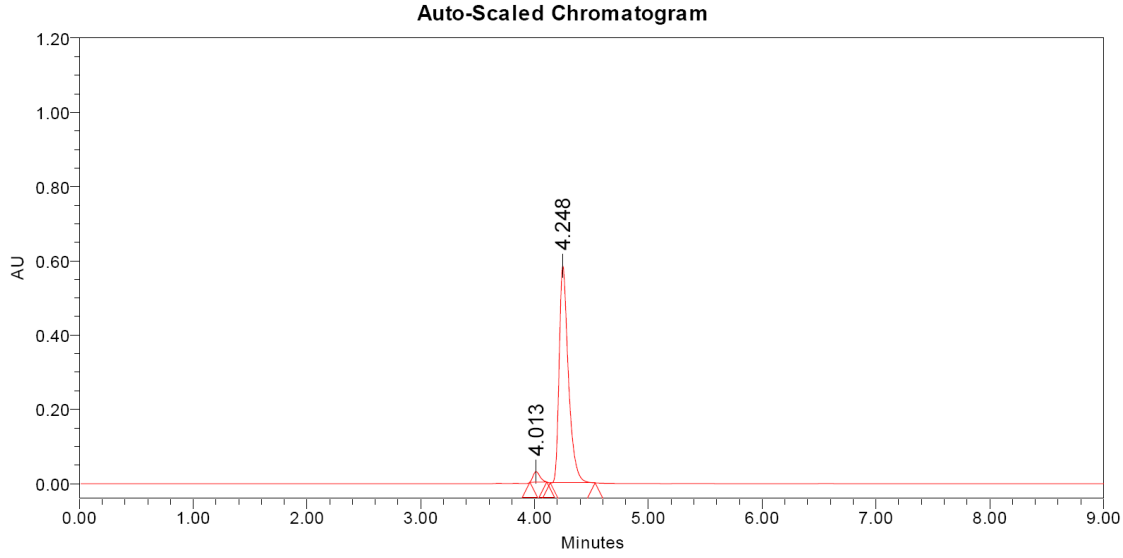


Scheme 2, entry 3
(*R,S*)-**L1**: 93% ee; (*S,R*)-**L1**: 93% ee



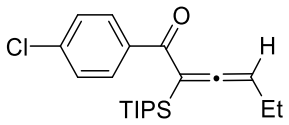
Peak Results

	Name	RT	Area	Height	% Area
1		4.107	8671829	1803111	96.61
2		4.400	304472	66695	3.39

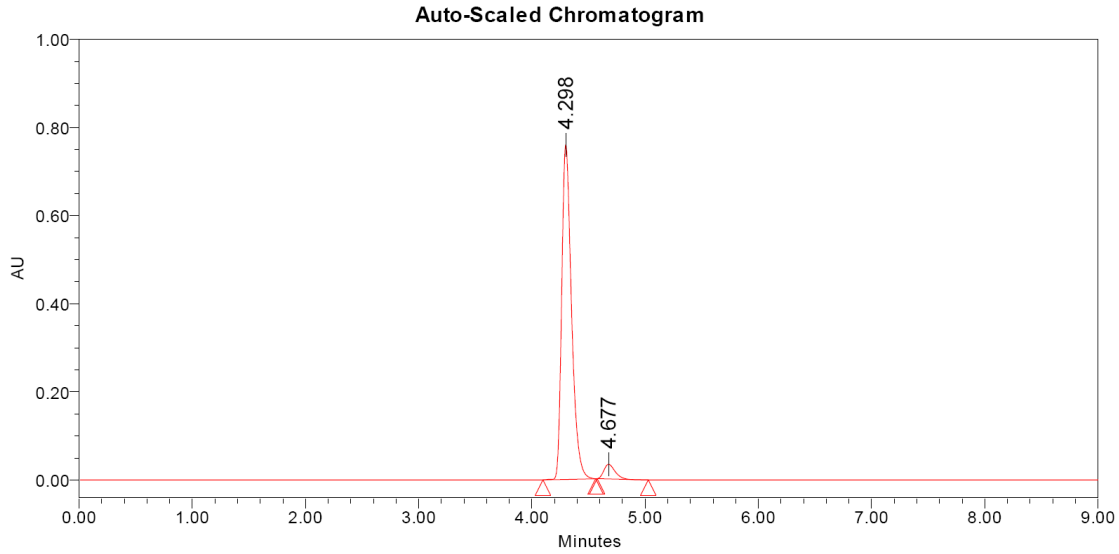


Peak Results

	Name	RT	Area	Height	% Area
1		4.013	117556	28229	3.45
2		4.248	3287456	584515	96.55

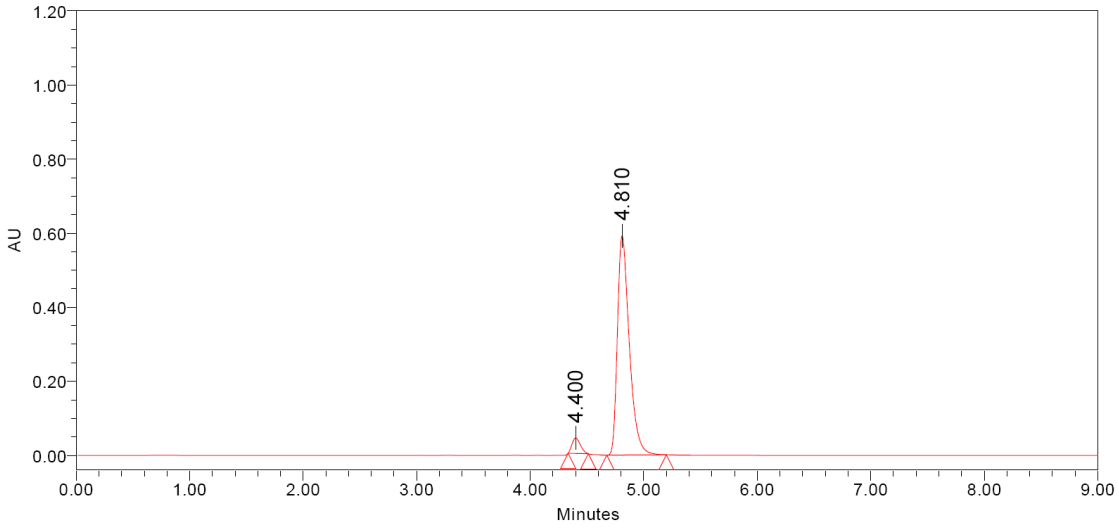


Scheme 2, entry 4
(*R*,*S*)-**L1**: 90% ee; (*S*,*R*)-**L1**: 90% ee



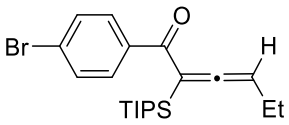
Peak Results

	Name	RT	Area	Height	% Area
1		4.298	4562321	759526	95.21
2		4.677	229330	33241	4.79



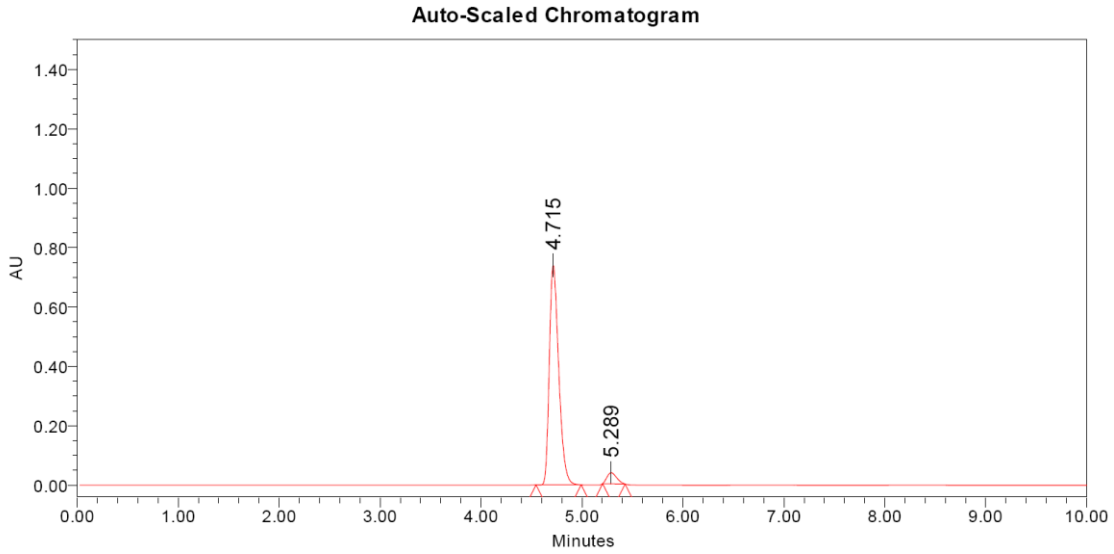
Peak Results

	Name	RT	Area	Height	% Area
1		4.400	214420	41867	4.74
2		4.810	4307473	592514	95.26



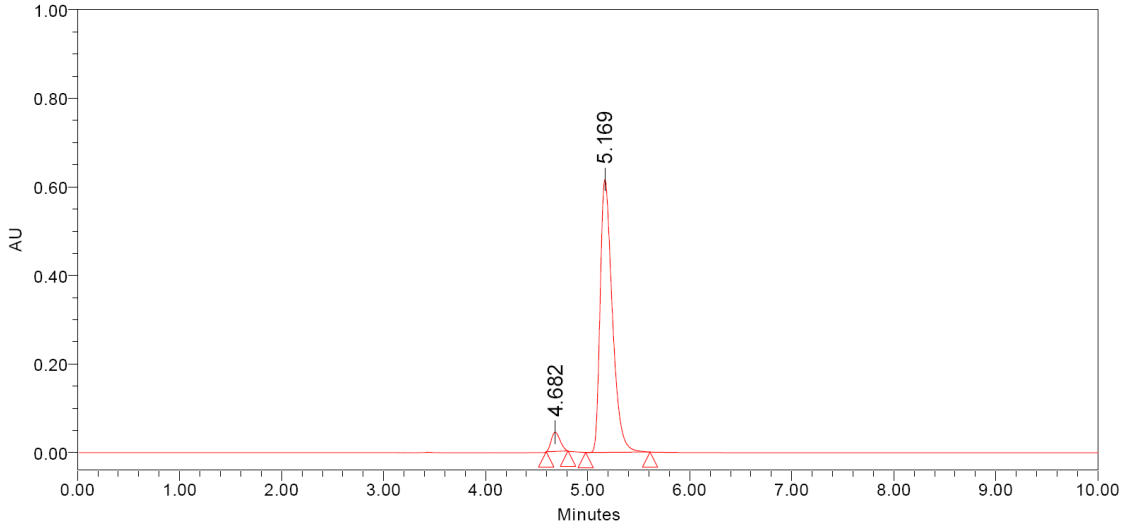
Scheme 2, entry 5

(*R*,*S*)-**L1**: 90% ee; (*S*,*R*)-**L1**: 90% ee



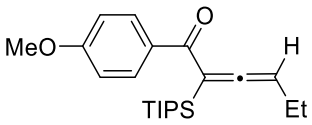
Peak Results

	Name	RT	Area	Height	% Area
1		4.715	4773449	739356	95.07
2		5.289	247273	37243	4.93



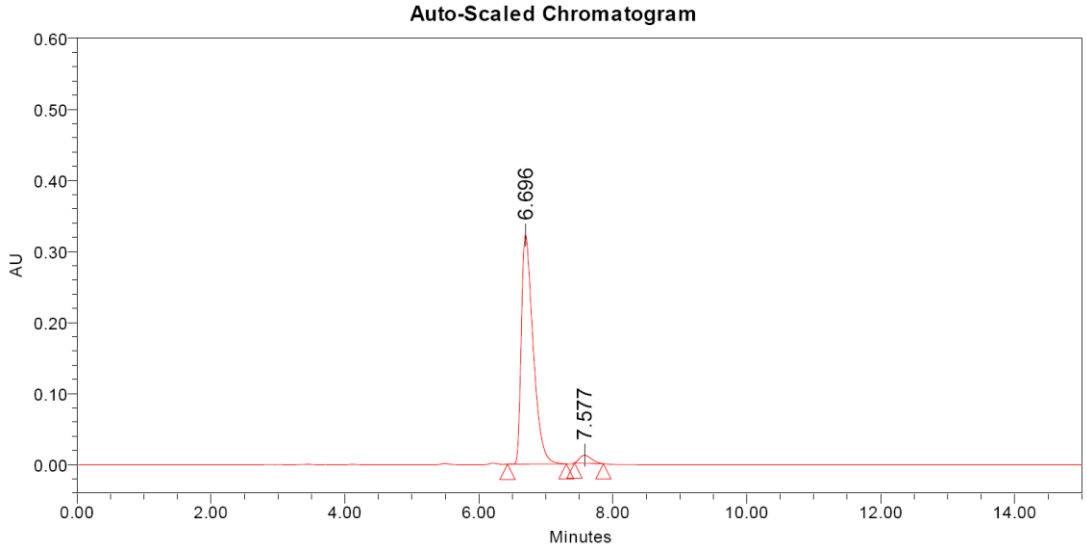
Peak Results

	Name	RT	Area	Height	% Area
1		4.682	262132	43525	4.90
2		5.169	5090827	616535	95.10



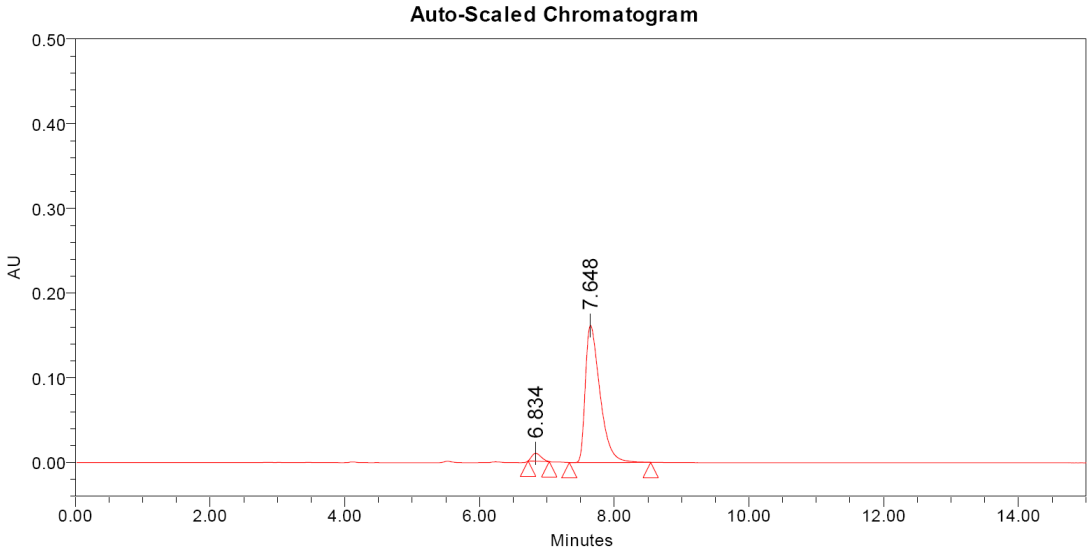
Scheme 2, entry 6

(*R*,*S*)-**L1**: 93% ee; (*S*,*R*)-**L1**: 93% ee



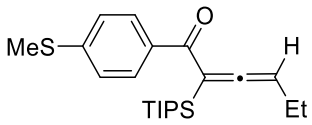
Peak Results

	Name	RT	Area	Height	% Area
1		6.696	3952762	322321	96.56
2		7.577	140699	11274	3.44

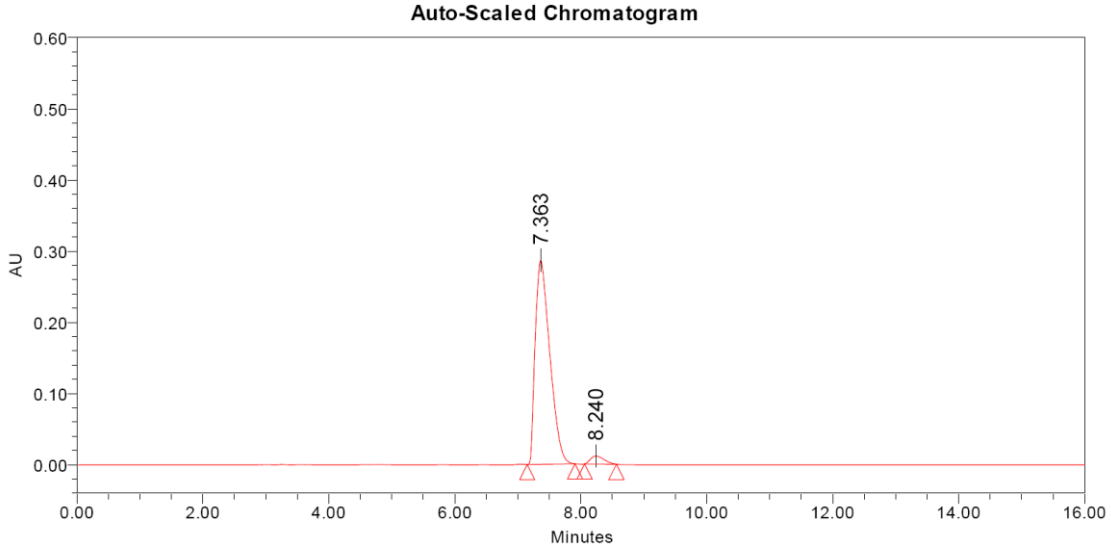


Peak Results

	Name	RT	Area	Height	% Area
1		6.834	88570	9344	3.50
2		7.648	2440233	161736	96.50

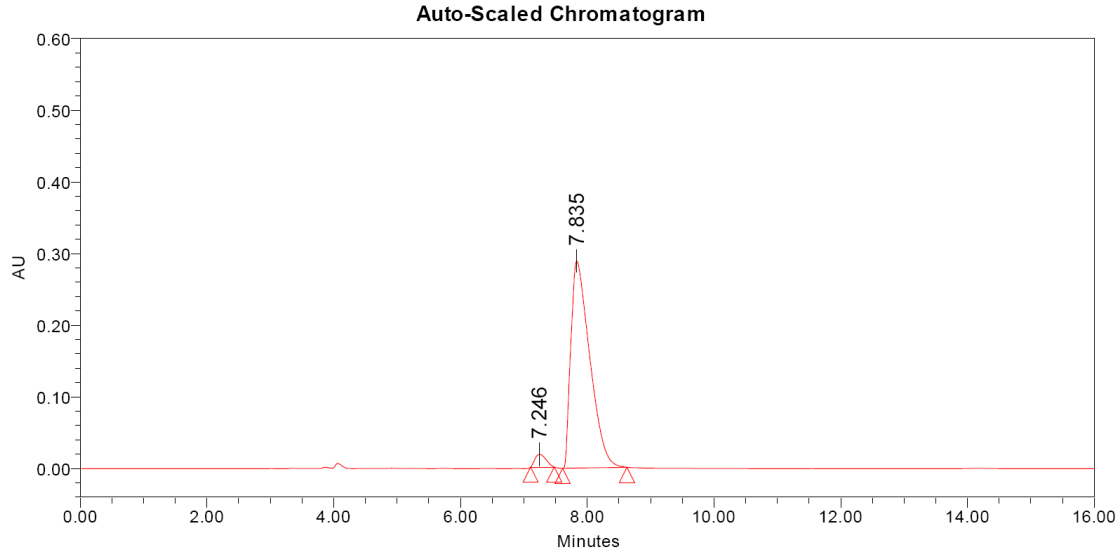


Scheme 2, entry 7
(*R*,*S*)-**L1**: 93% ee; (*S*,*R*)-**L1**: 93% ee



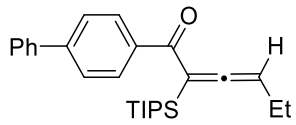
Peak Results

	Name	RT	Area	Height	% Area
1		7.363	4608514	286286	96.52
2		8.240	166178	11180	3.48

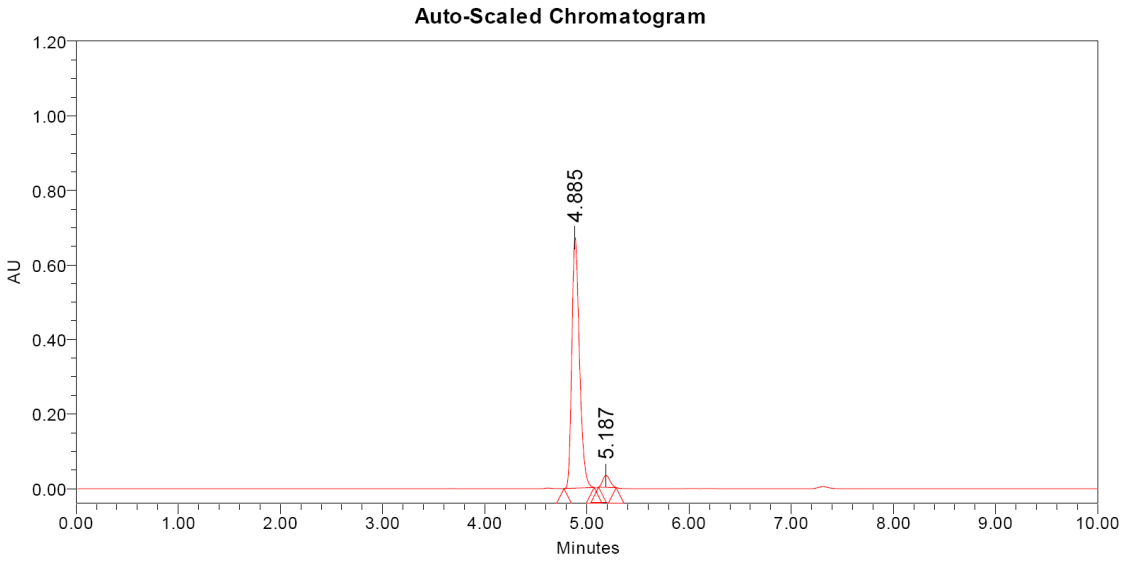


Peak Results

	Name	RT	Area	Height	% Area
1		7.246	215281	17752	3.47
2		7.835	5992505	288925	96.53

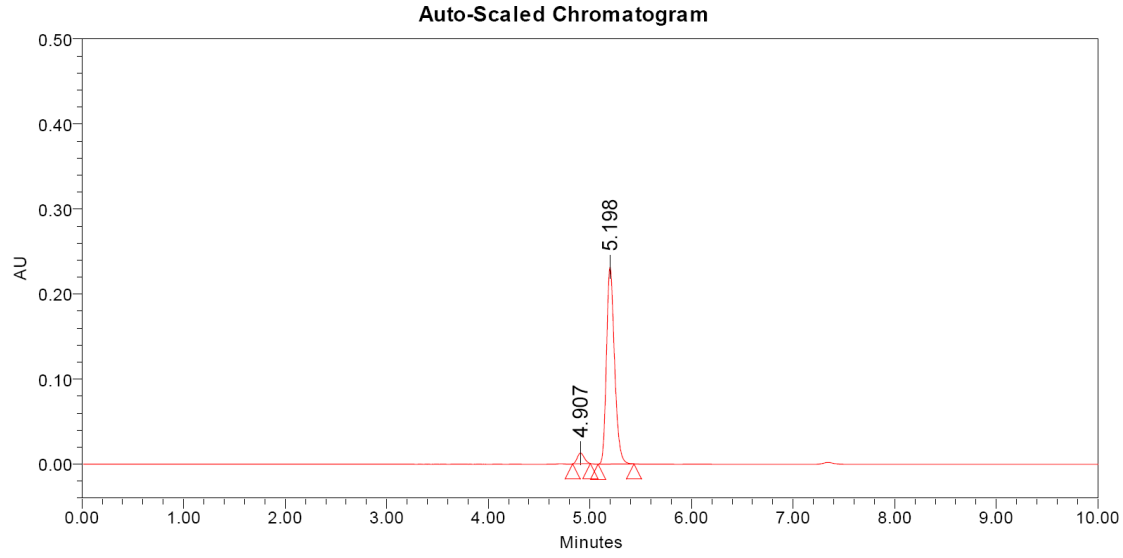


Scheme 2, entry 8
(*R,S*)-**L1**: 91% ee; (*S,R*)-**L1**: 91% ee



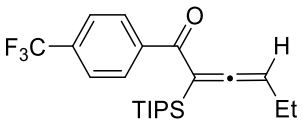
Peak Results

	Name	RT	Area	Height	% Area
1		4.885	3493897	672208	95.70
2		5.187	156955	32120	4.30

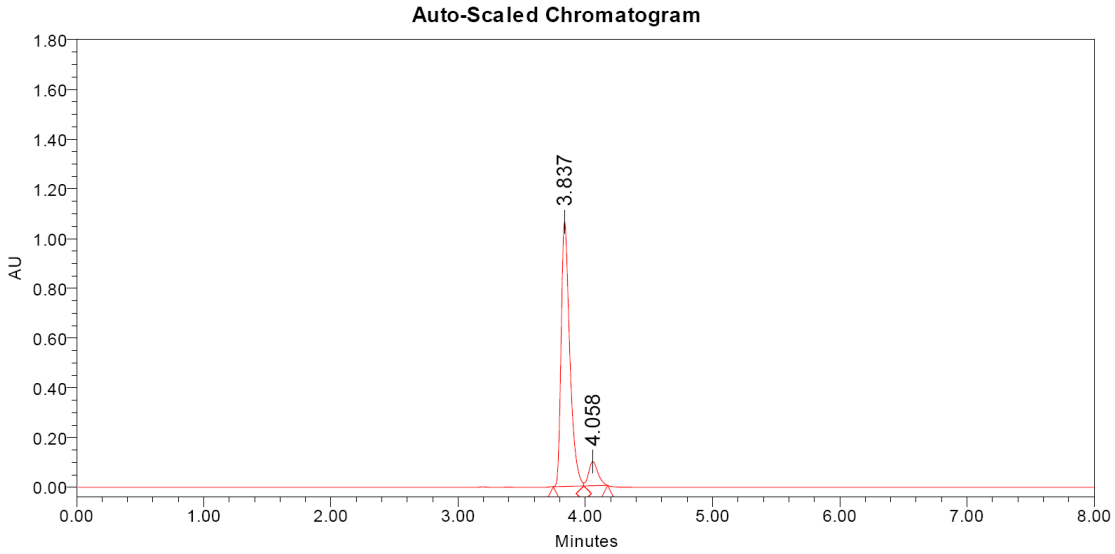


Peak Results

	Name	RT	Area	Height	% Area
1		4.907	59540	12571	4.46
2		5.198	1275438	231776	95.54

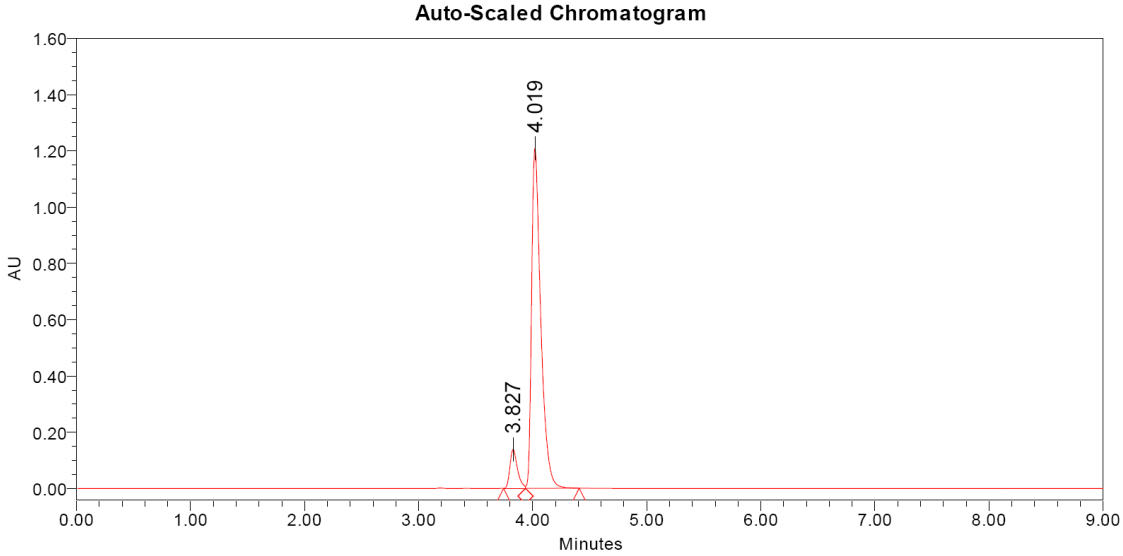


Scheme 2, entry 9
(*R,S*)-**L1**: 82% ee; (*S,R*)-**L1**: 82% ee



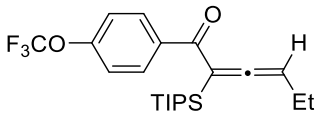
Peak Results

	Name	RT	Area	Height	% Area
1		3.837	5011917	1064174	91.07
2		4.058	491266	97469	8.93



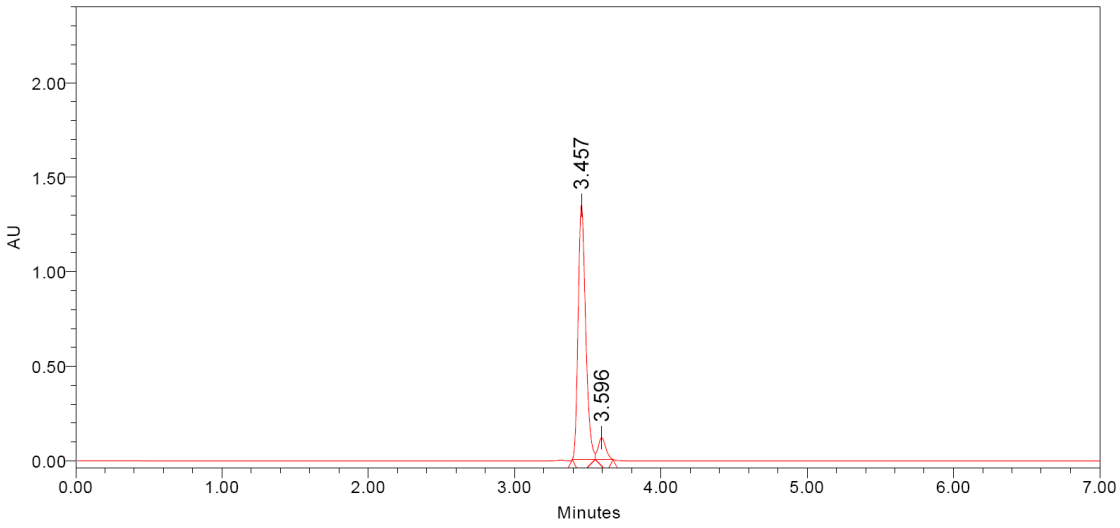
Peak Results

	Name	RT	Area	Height	% Area
1		3.827	632027	138374	8.56
2		4.019	6747930	1208675	91.44



Scheme 2, entry 10
(*R,S*)-**L1**: 84% ee; (*S,R*)-**L1**: 84% ee

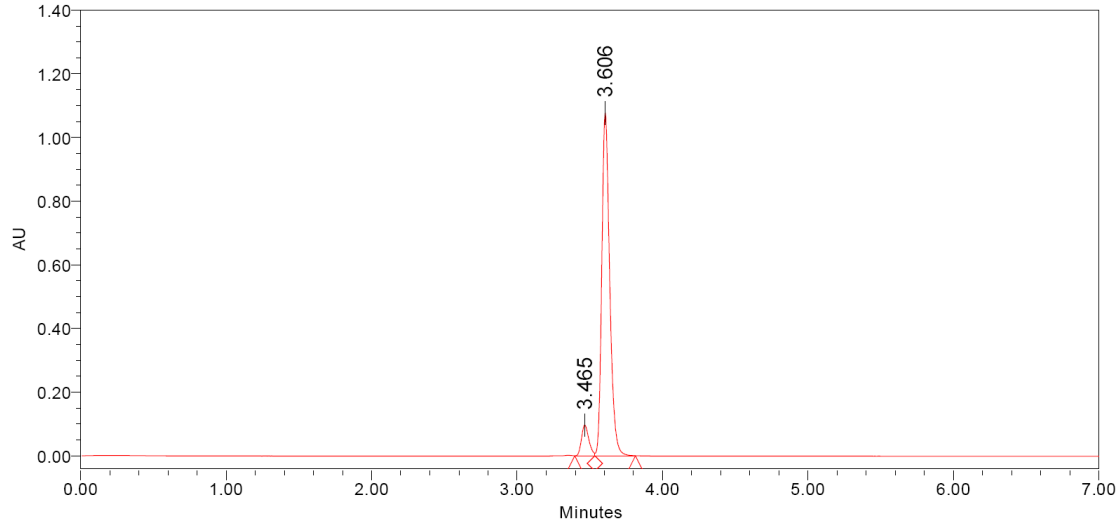
Auto-Scaled Chromatogram



Peak Results

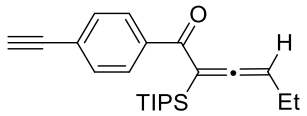
	Name	RT	Area	Height	% Area
1		3.457	4804307	1346829	92.03
2		3.596	416175	114893	7.97

Auto-Scaled Chromatogram



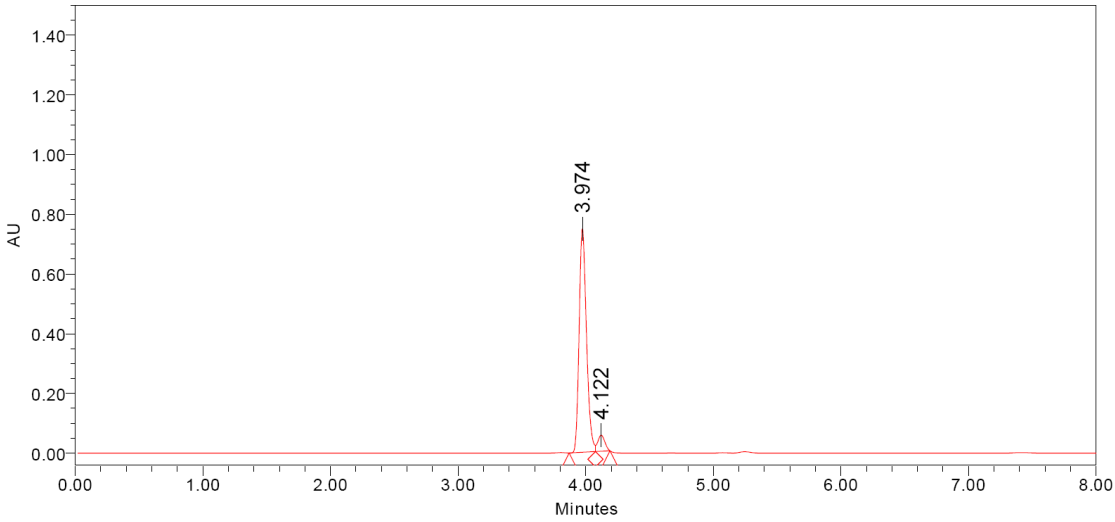
Peak Results

	Name	RT	Area	Height	% Area
1		3.465	338206	96578	7.68
2		3.606	4063196	1076982	92.32



Scheme 2, entry 11
(*R,S*)-**L1**: 87% ee; (*S,R*)-**L1**: 87% ee

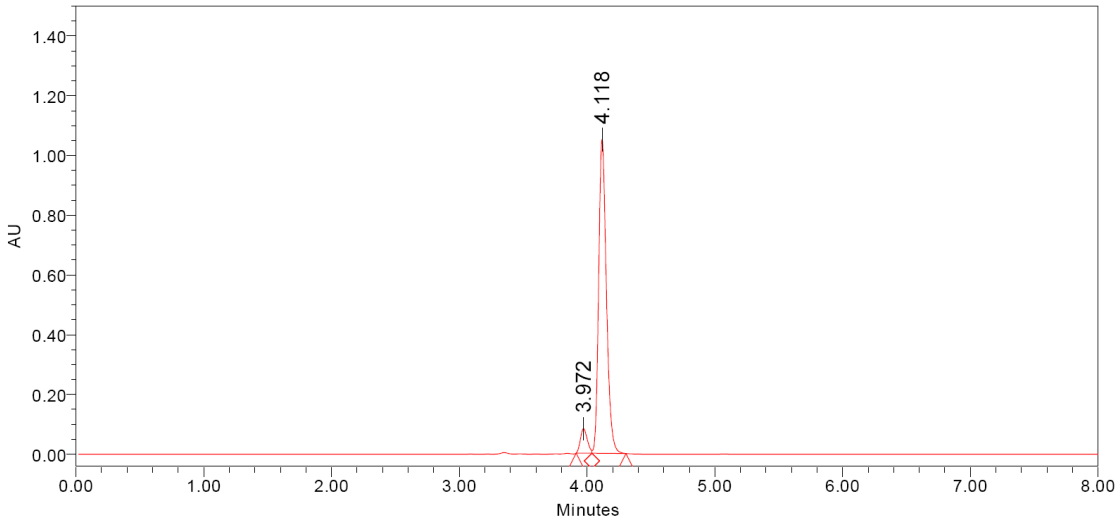
Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		3.974	2991541	748639	93.51
2		4.122	207728	54005	6.49

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		3.972	305797	82040	6.49
2		4.118	4404321	1052301	93.51

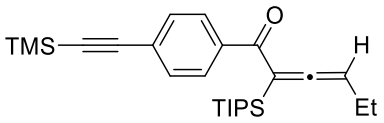
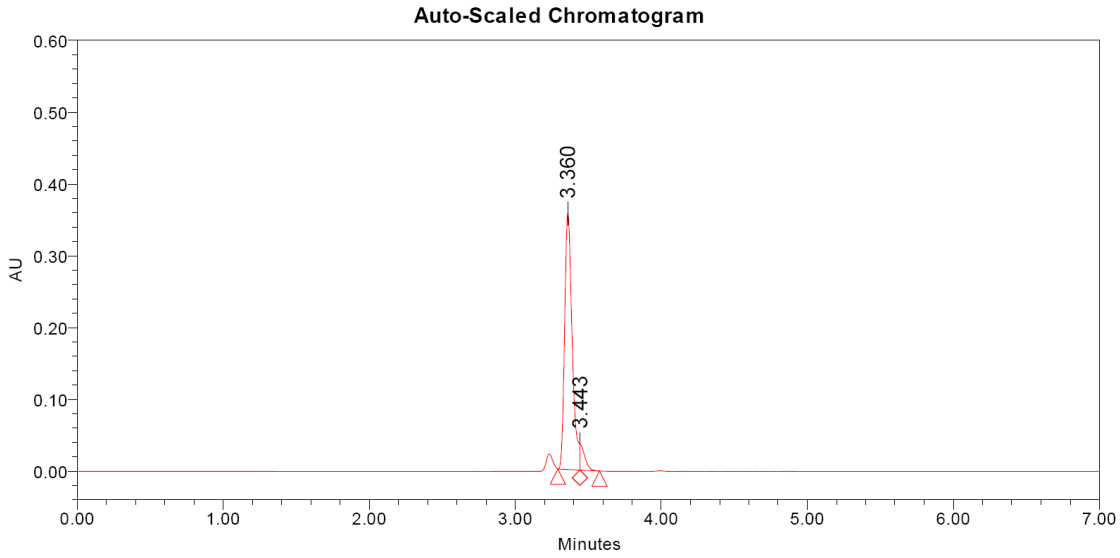
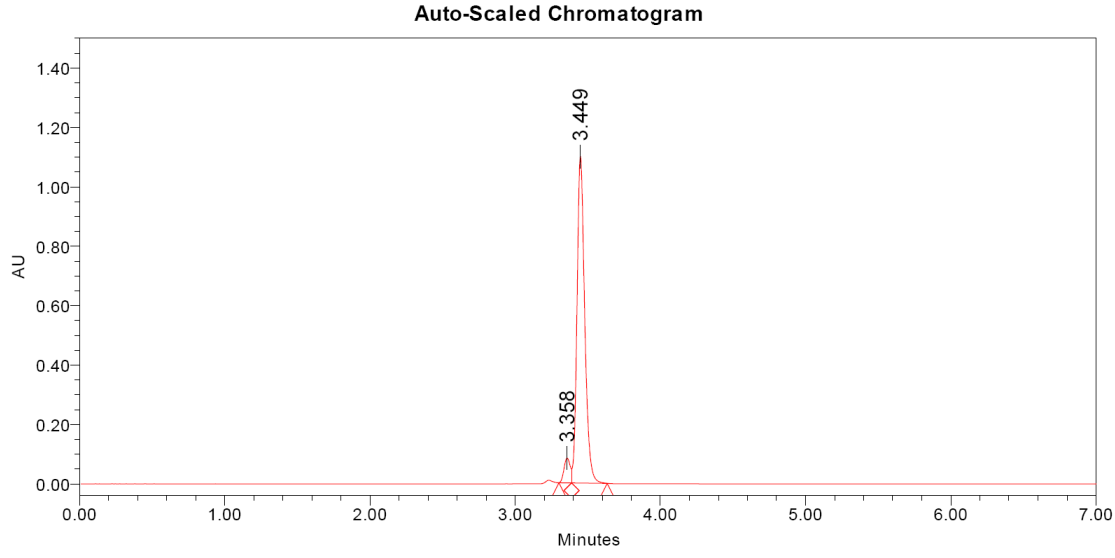


Figure 2, entry 12
(*R,S*)-**L1**: 88% ee; (*S,R*)-**L1**: 88% ee



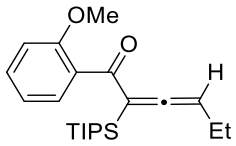
Peak Results

	Name	RT	Area	Height	% Area
1		3.360	1275510	356754	93.92
2		3.443	82584	36465	6.08

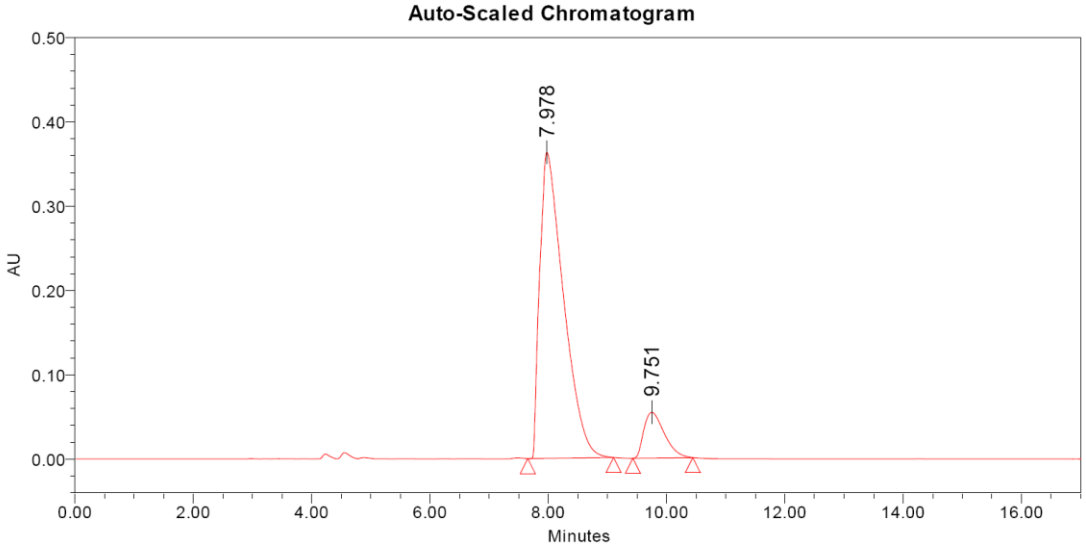


Peak Results

	Name	RT	Area	Height	% Area
1		3.358	244408	83277	5.69
2		3.449	4051460	1099956	94.31

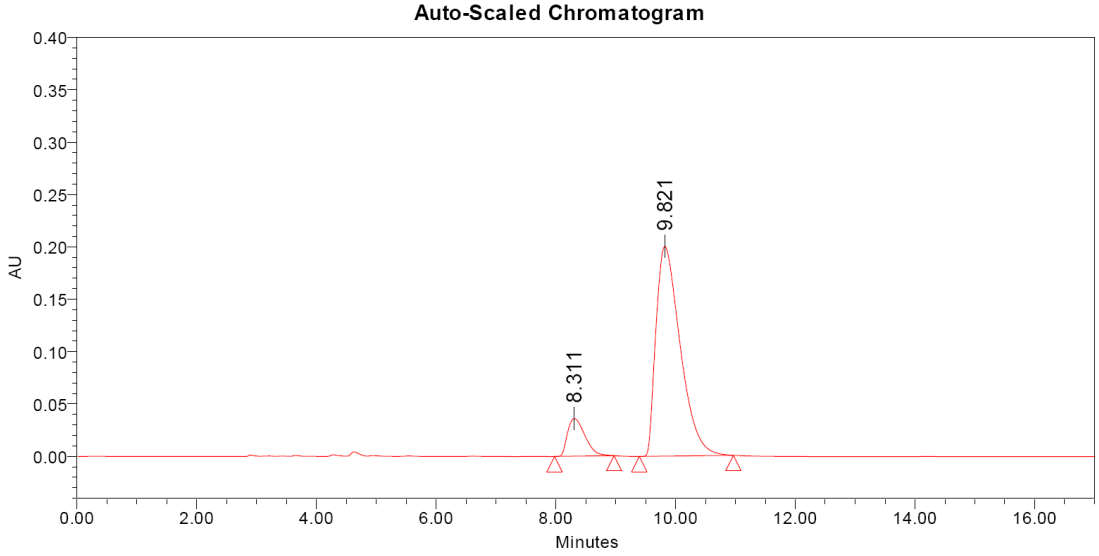


Scheme 2, entry 13
(*R*,*S*)-**L1**: 77% ee; (*S*,*R*)-**L1**: 77% ee



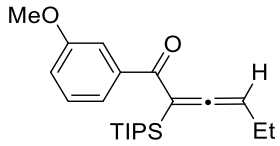
Peak Results

	Name	RT	Area	Height	% Area
1		7.978	10113266	363111	88.54
2		9.751	1308629	54293	11.46

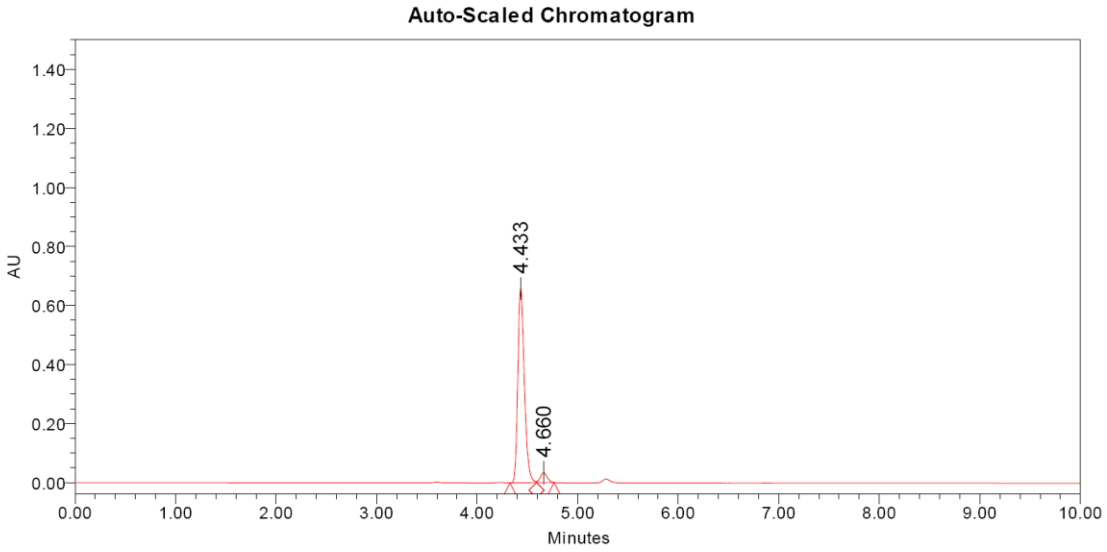


Peak Results

	Name	RT	Area	Height	% Area
1		8.311	729234	35966	11.45
2		9.821	5640463	200370	88.55

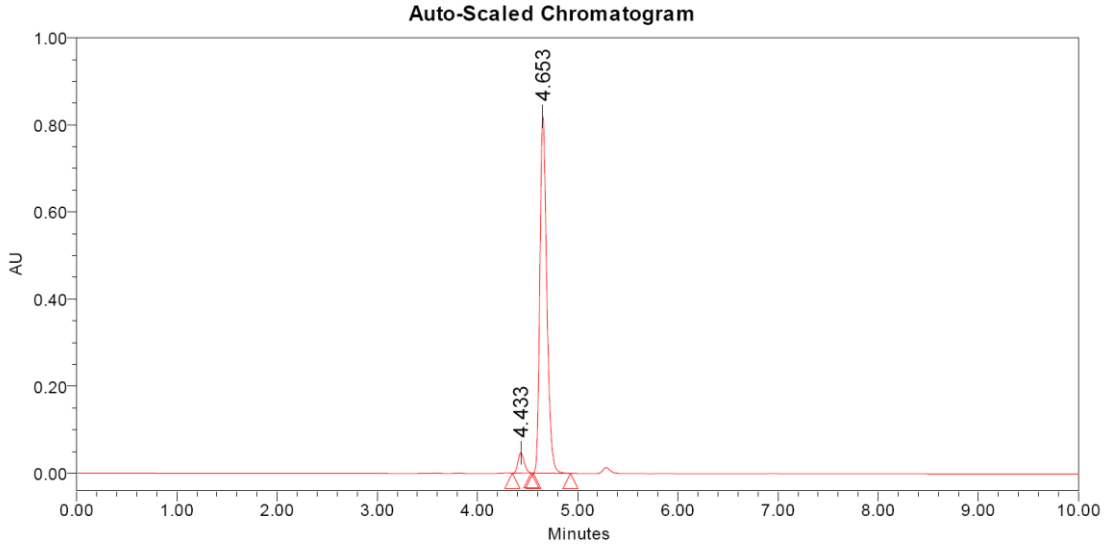


Scheme 2, entry 14
(*R*,*S*)-**L1**: 90% ee; (*S*,*R*)-**L1**: 90% ee



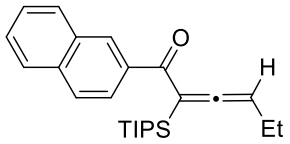
Peak Results

	Name	RT	Area	Height	% Area
1		4.433	2978510	658874	95.03
2		4.660	155615	33532	4.97



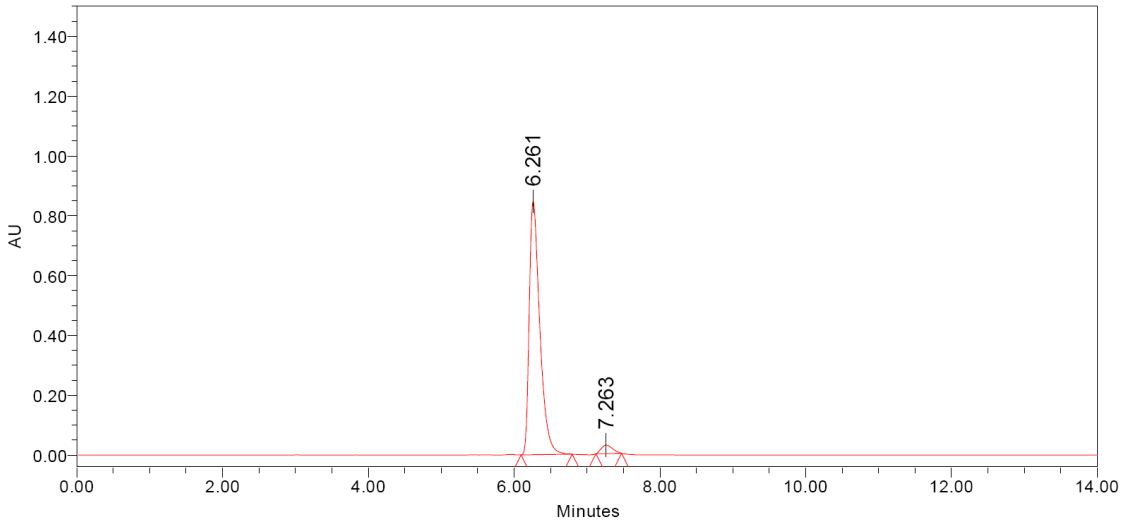
Peak Results

	Name	RT	Area	Height	% Area
1		4.433	200843	46679	4.87
2		4.653	3926407	819496	95.13



Scheme 2, entry 15
(*R*,*S*)-**L1**: 93% ee; (*S*,*R*)-**L1**: 93% ee

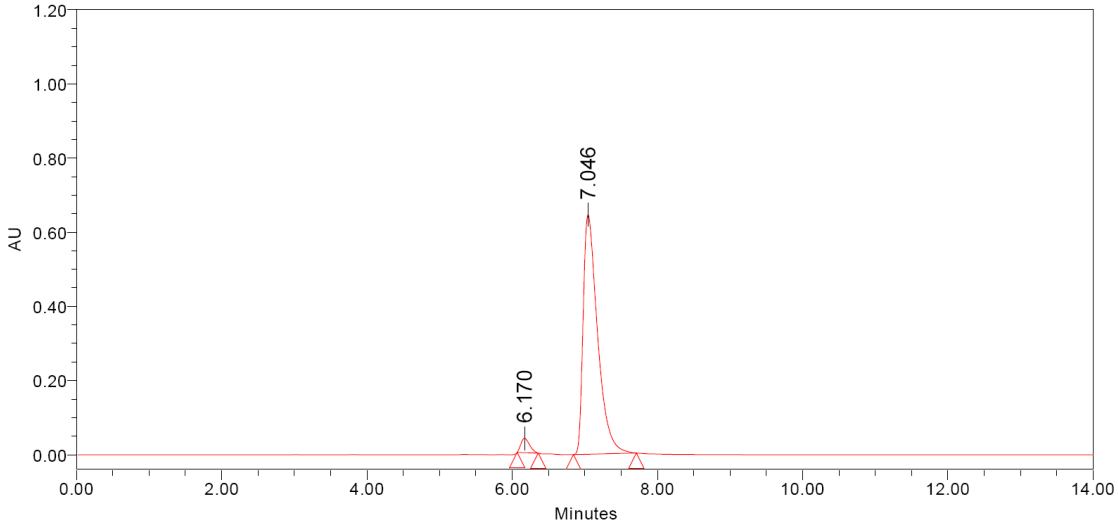
Auto-Scaled Chromatogram



Peak Results

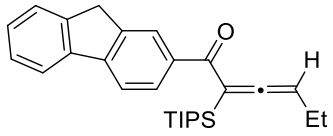
	Name	RT	Area	Height	% Area
1		6.261	8528704	847436	96.53
2		7.263	306200	28246	3.47

Auto-Scaled Chromatogram



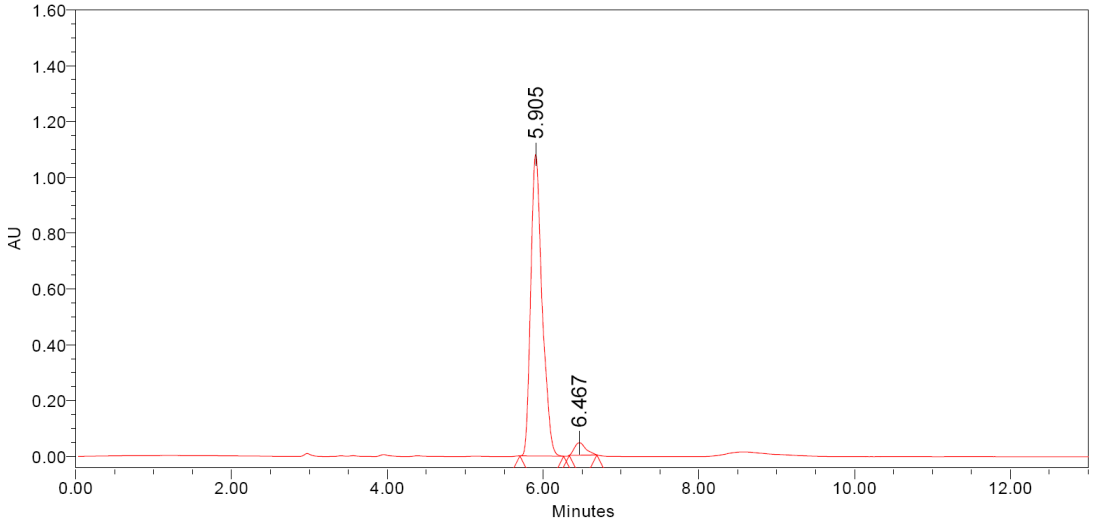
Peak Results

	Name	RT	Area	Height	% Area
1		6.170	322552	38846	3.50
2		7.046	8892007	645891	96.50



Scheme 2, entry 16
(*R,S*)-**L1**: 92% ee; (*S,R*)-**L1**: 92% ee

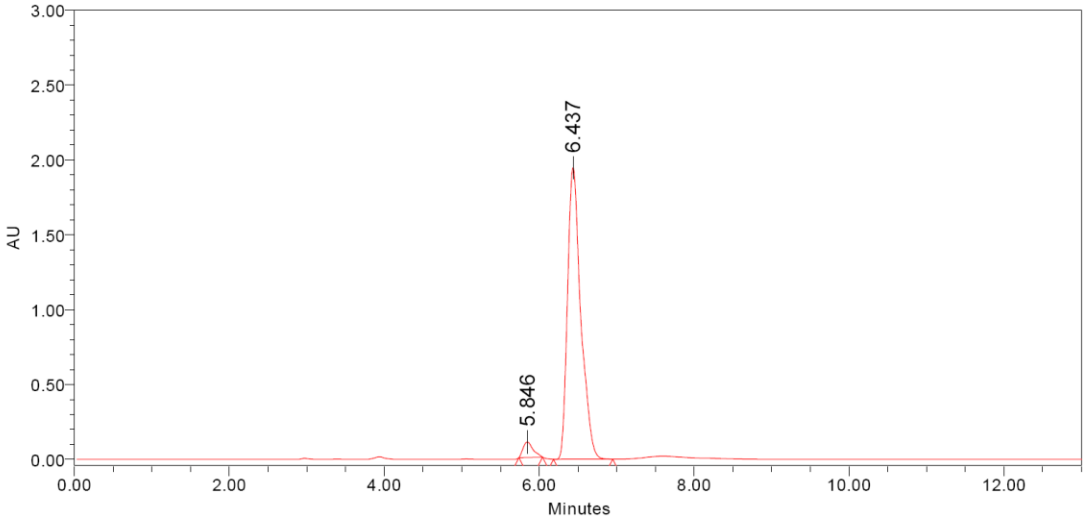
Auto-Scaled Chromatogram



Peak Results

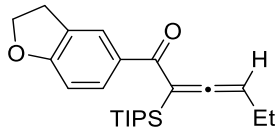
	Name	RT	Area	Height	% Area
1		5.905	10952617	1080482	96.04
2		6.467	451330	44860	3.96

Auto-Scaled Chromatogram

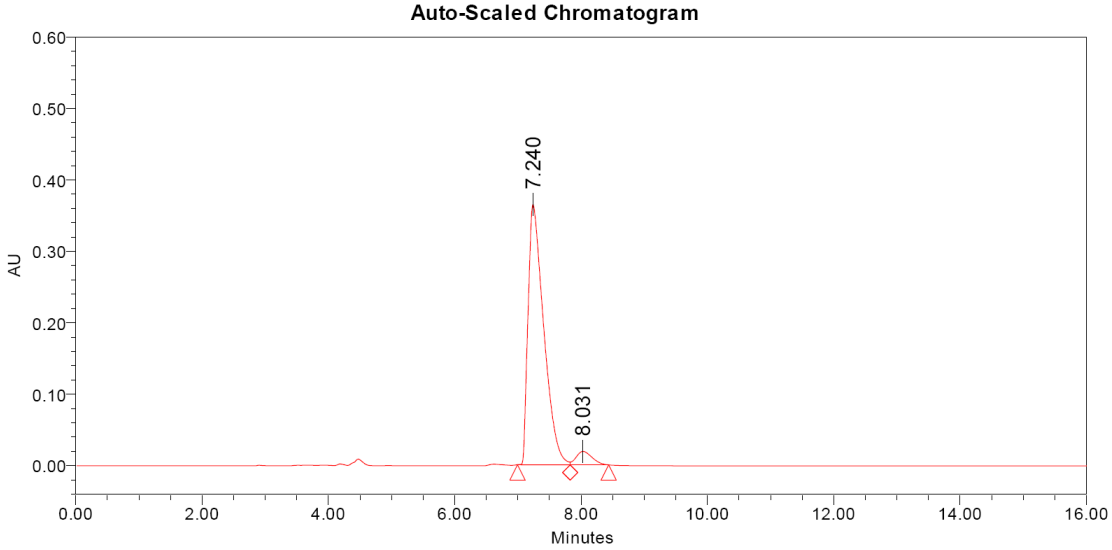


Peak Results

	Name	RT	Area	Height	% Area
1		5.846	915763	103138	3.81
2		6.437	23110238	1947391	96.19

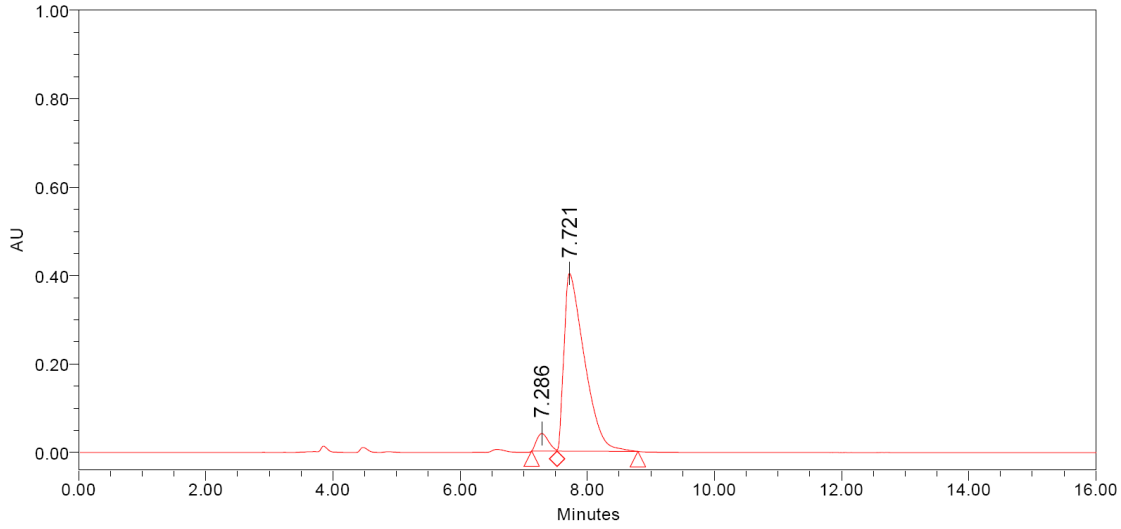


Scheme 2, entry 17
(*R*,*S*)-**L1**: 90% ee; (*S*,*R*)-**L1**: 89% ee



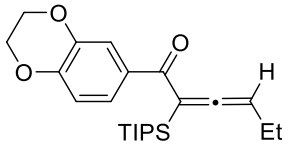
Peak Results

	Name	RT	Area	Height	% Area
1		7.240	6273708	364633	95.00
2		8.031	330167	18849	5.00

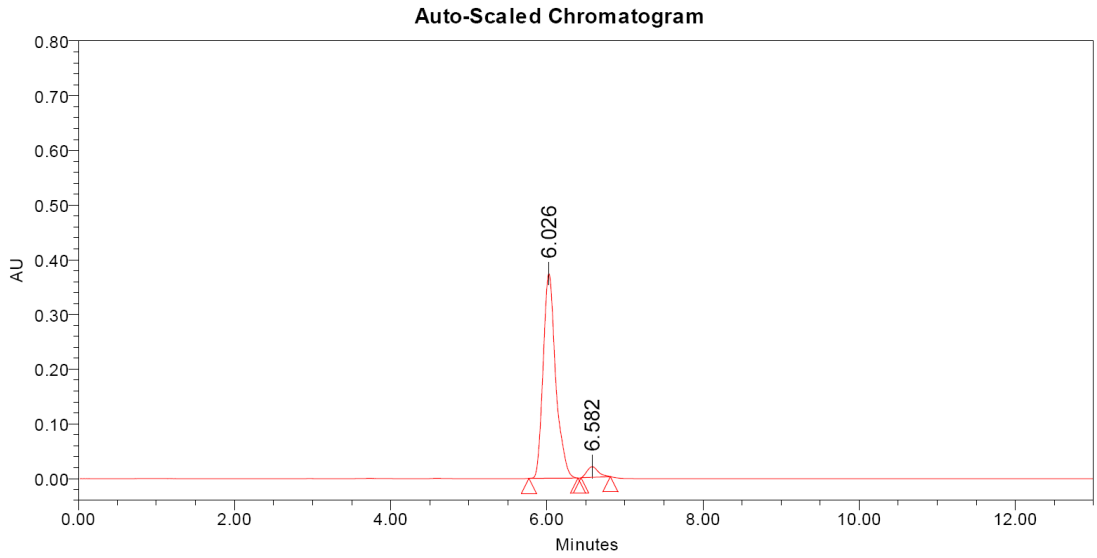


Peak Results

	Name	RT	Area	Height	% Area
1		7.286	509762	39591	5.39
2		7.721	8950682	401953	94.61

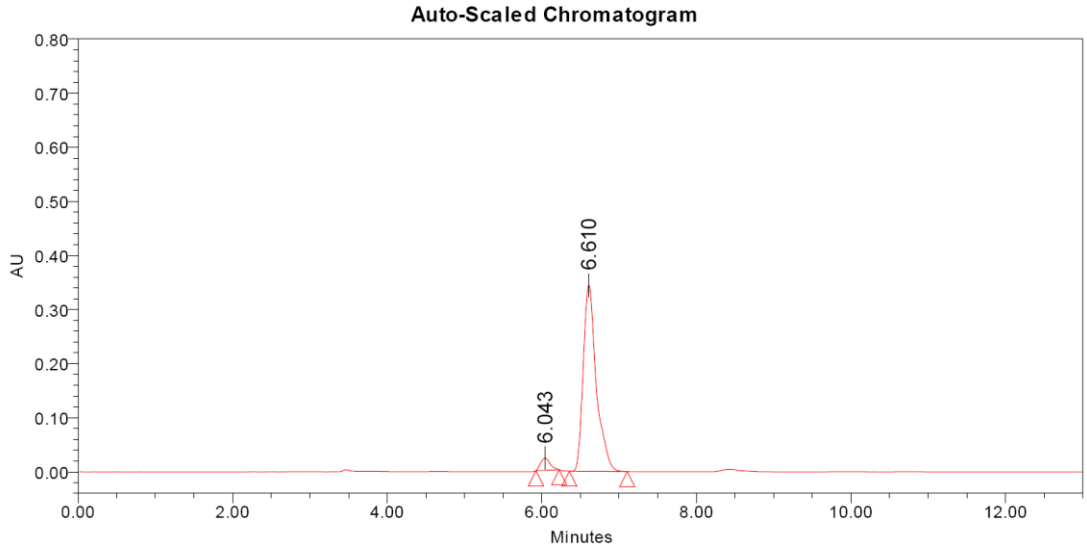


Scheme 2, entry 18
(*R,S*)-**L1**: 91% ee; (*S,R*)-**L1**: 91% ee



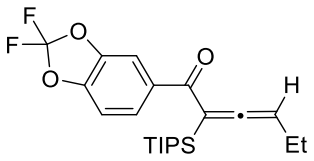
Peak Results

	Name	RT	Area	Height	% Area
1		6.026	4183805	374108	95.57
2		6.582	193884	19391	4.43

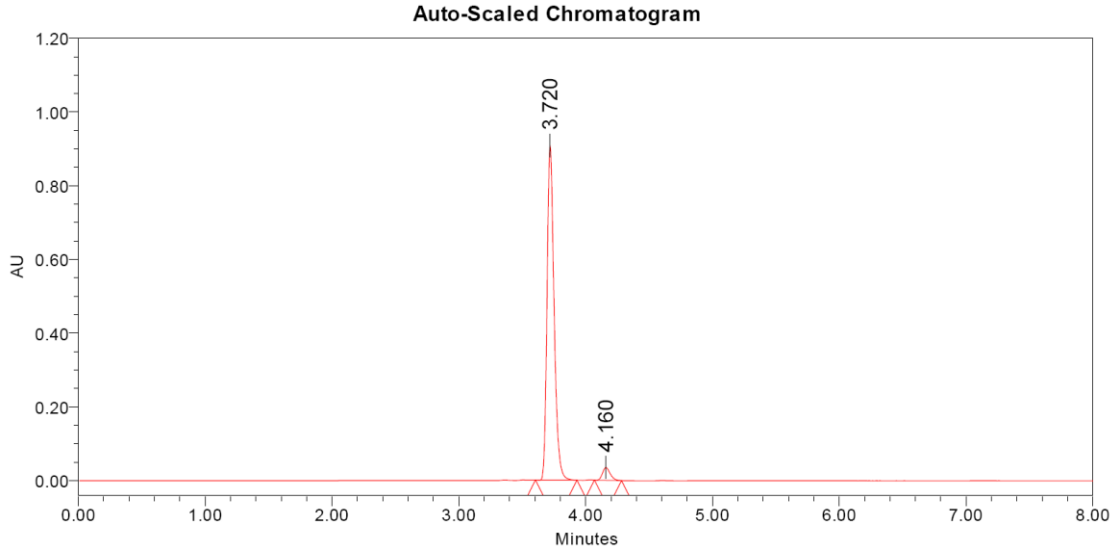


Peak Results

	Name	RT	Area	Height	% Area
1		6.043	190671	22355	4.50
2		6.610	4043977	344228	95.50

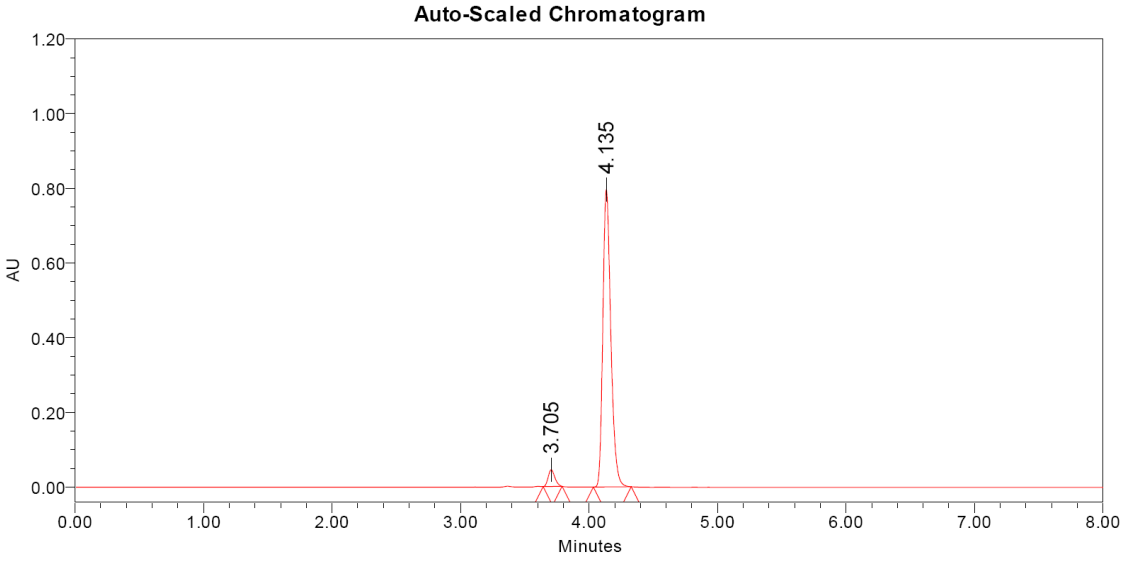


Scheme 2, entry 19
(*R,S*)-**L1**: 92% ee; (*S,R*)-**L1**: 91% ee



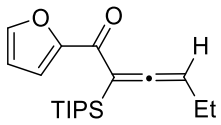
Peak Results

	Name	RT	Area	Height	% Area
1		3.720	3486715	906960	96.01
2		4.160	145070	34687	3.99



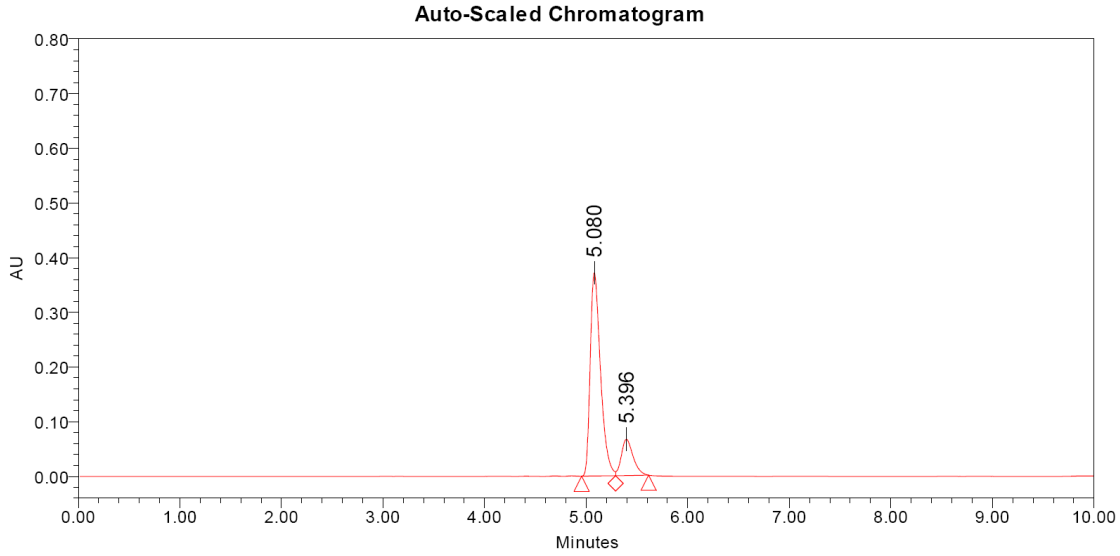
Peak Results

	Name	RT	Area	Height	% Area
1		3.705	161431	44850	4.50
2		4.135	3424146	796354	95.50



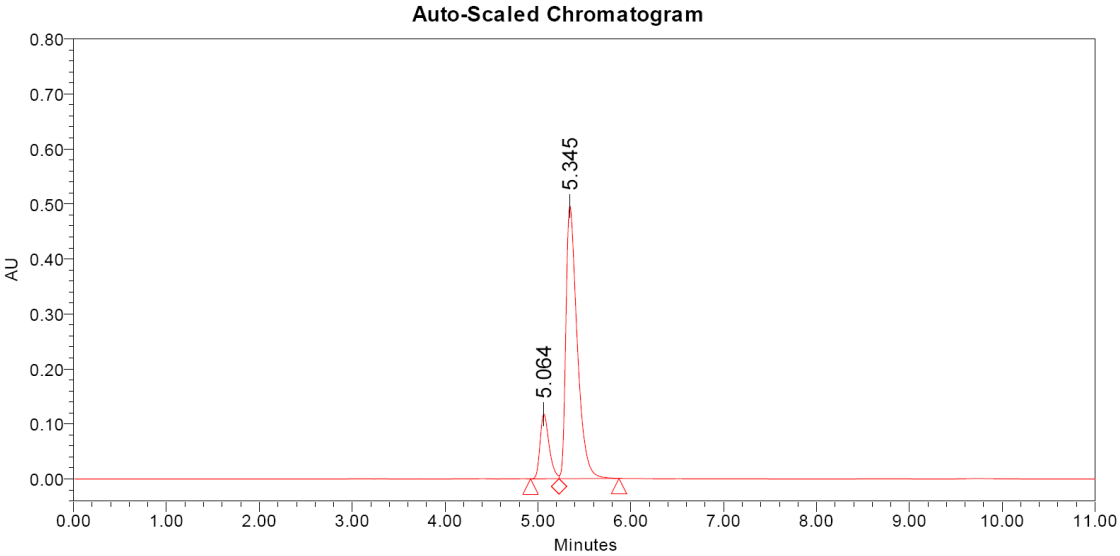
Scheme 2, entry 20

(*R*,*S*)-**L1**: 66% ee; (*S*,*R*)-**L1**: 67% ee



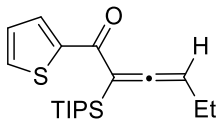
Peak Results

	Name	RT	Area	Height	% Area
1		5.080	2615441	371473	83.07
2		5.396	533161	66272	16.93



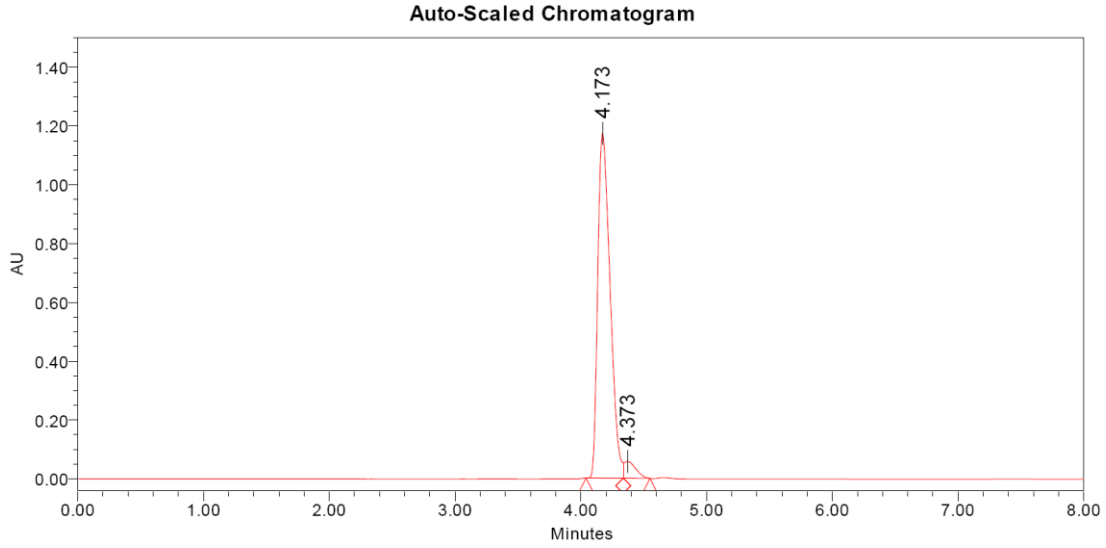
Peak Results

	Name	RT	Area	Height	% Area
1		5.064	802919	117646	16.03
2		5.345	4206192	495859	83.97



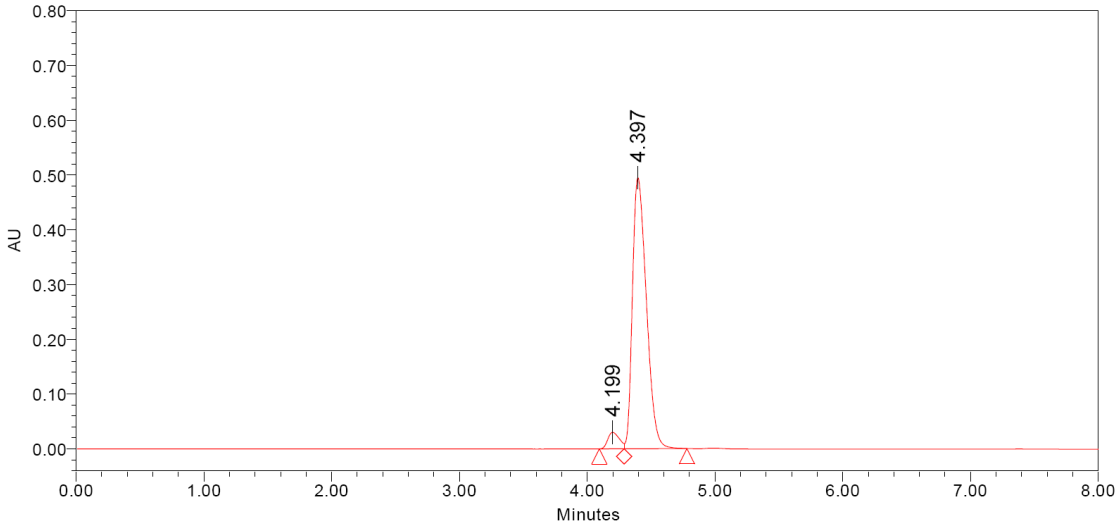
Scheme 2, entry 21

(*R*,*S*)-**L1**: 91% ee; (*S*,*R*)-**L1**: 90% ee



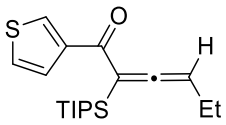
Peak Results

	Name	RT	Area	Height	% Area
1		4.173	7985057	1171895	95.54
2		4.373	373123	57042	4.46

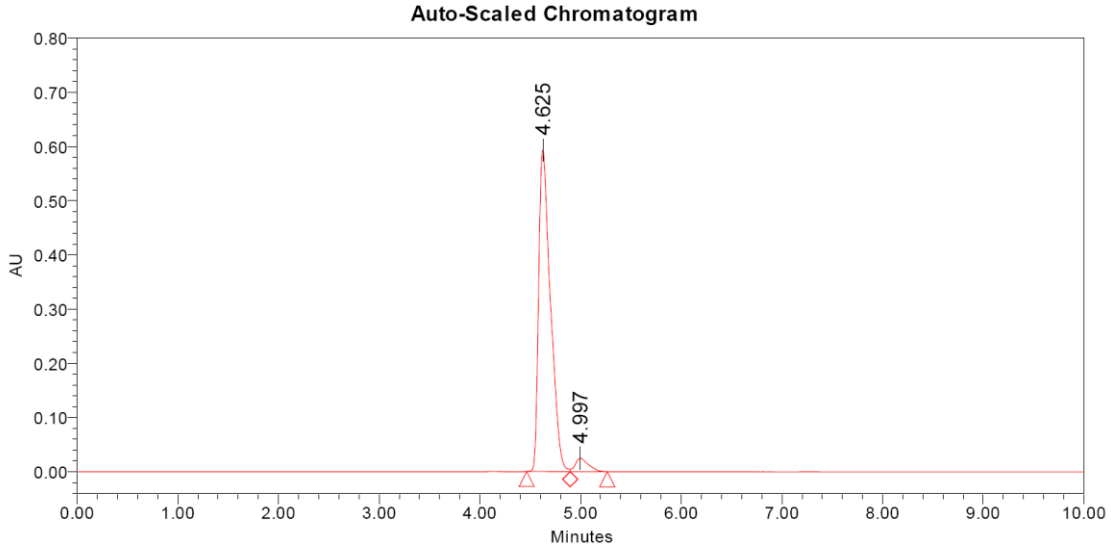


Peak Results

	Name	RT	Area	Height	% Area
1		4.199	187193	30027	4.76
2		4.397	3742689	494906	95.24

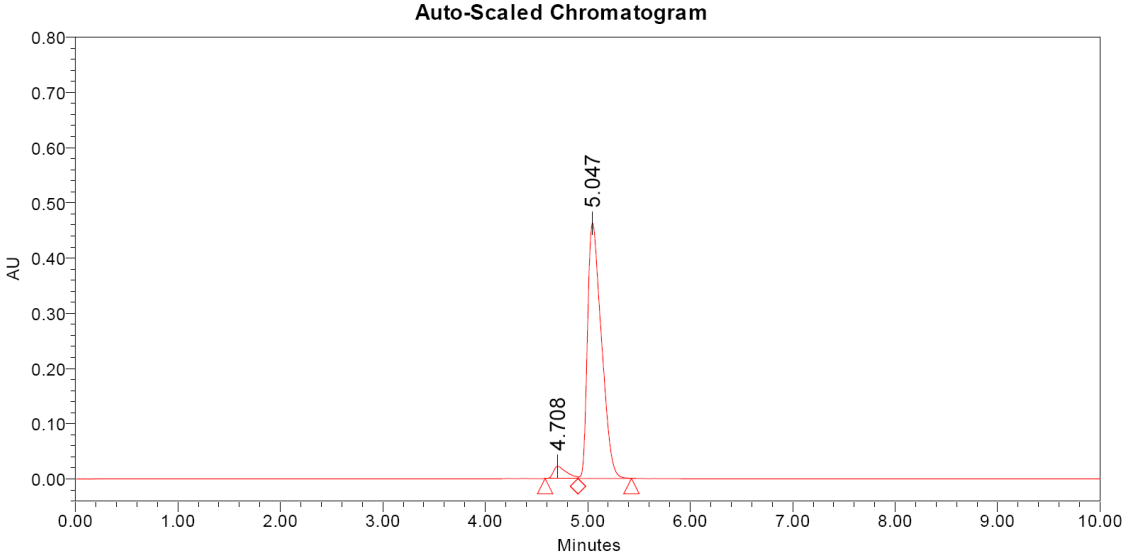


Scheme 2, entry 22
(*R*,*S*)-**L1**: 91% ee; (*S*,*R*)-**L1**: 91% ee



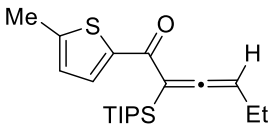
Peak Results

	Name	RT	Area	Height	% Area
1		4.625	4815257	592547	95.61
2		4.997	220985	24682	4.39

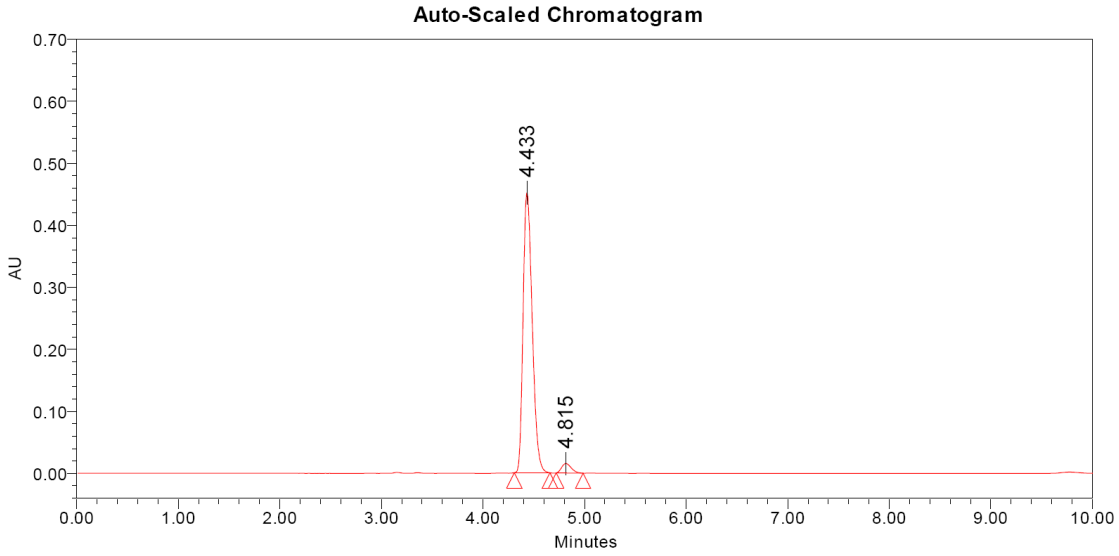


Peak Results

	Name	RT	Area	Height	% Area
1		4.708	194663	22203	4.28
2		5.047	4349428	462462	95.72

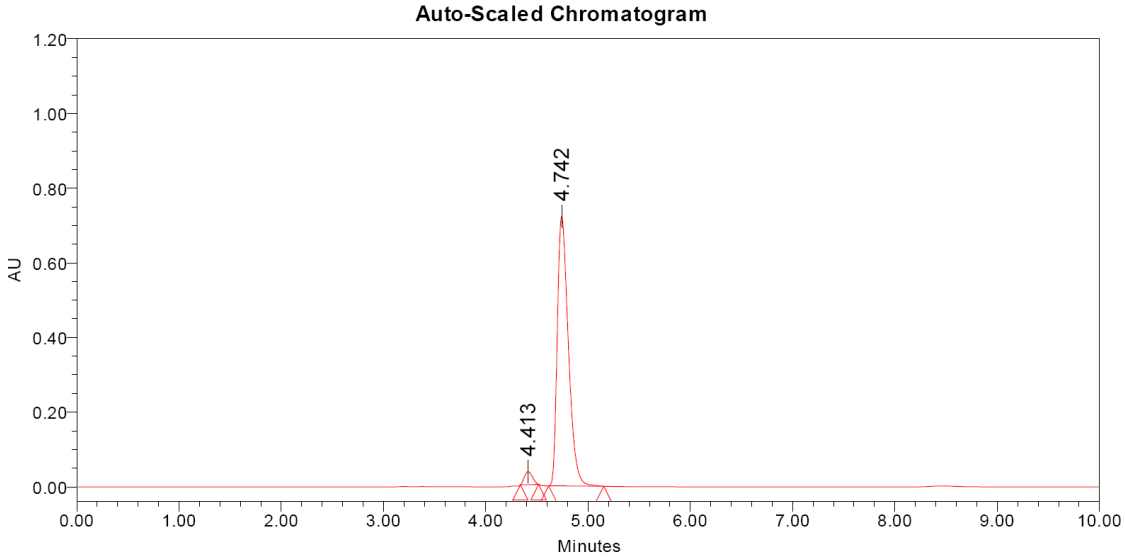


Scheme 2, entry 23
(*R,S*)-**L1**: 93% ee; (*S,R*)-**L1**: 93% ee



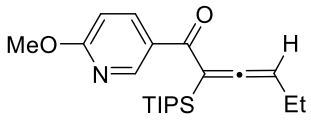
Peak Results

	Name	RT	Area	Height	% Area
1		4.433	2818561	451485	96.59
2		4.815	99561	15186	3.41



Peak Results

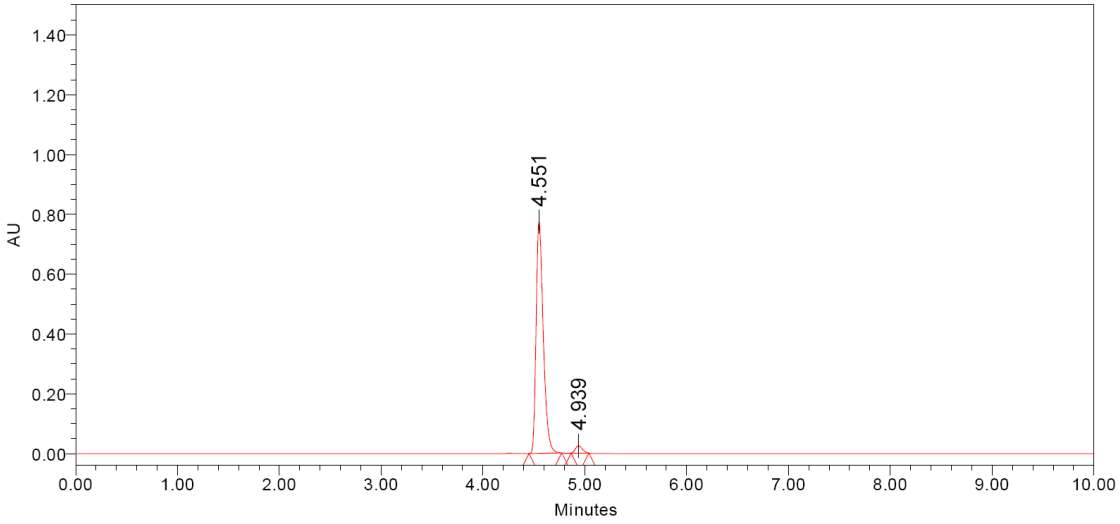
	Name	RT	Area	Height	% Area
1		4.413	191769	35083	3.41
2		4.742	5425684	722588	96.59



Scheme 2, entry 24

(*R,S*)-**L1**: 94% ee; (*S,R*)-**L1**: 94% ee

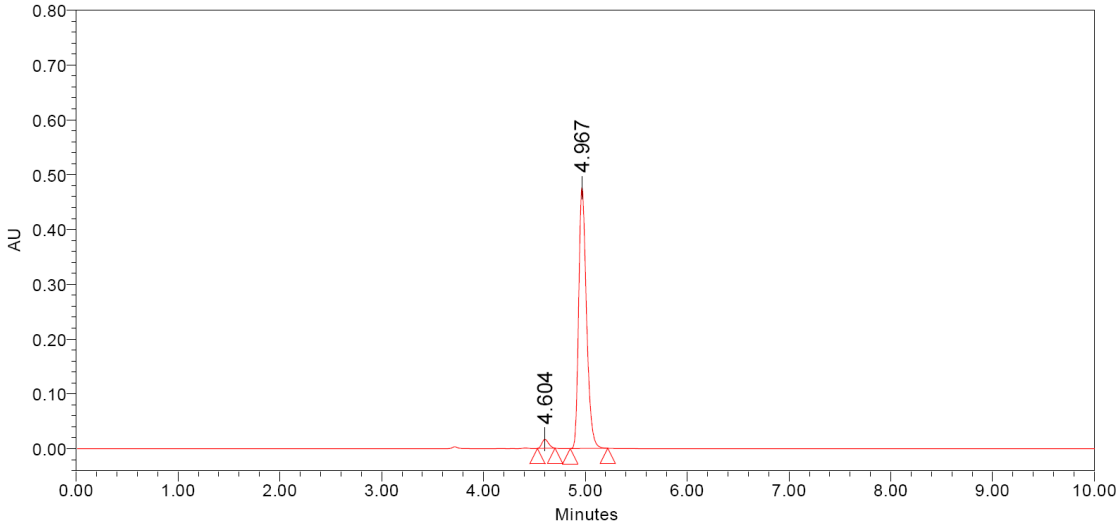
Auto-Scaled Chromatogram



Peak Results

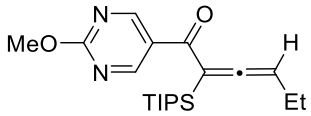
	Name	RT	Area	Height	% Area
1		4.551	3798140	775842	97.05
2		4.939	115476	24155	2.95

Auto-Scaled Chromatogram



Peak Results

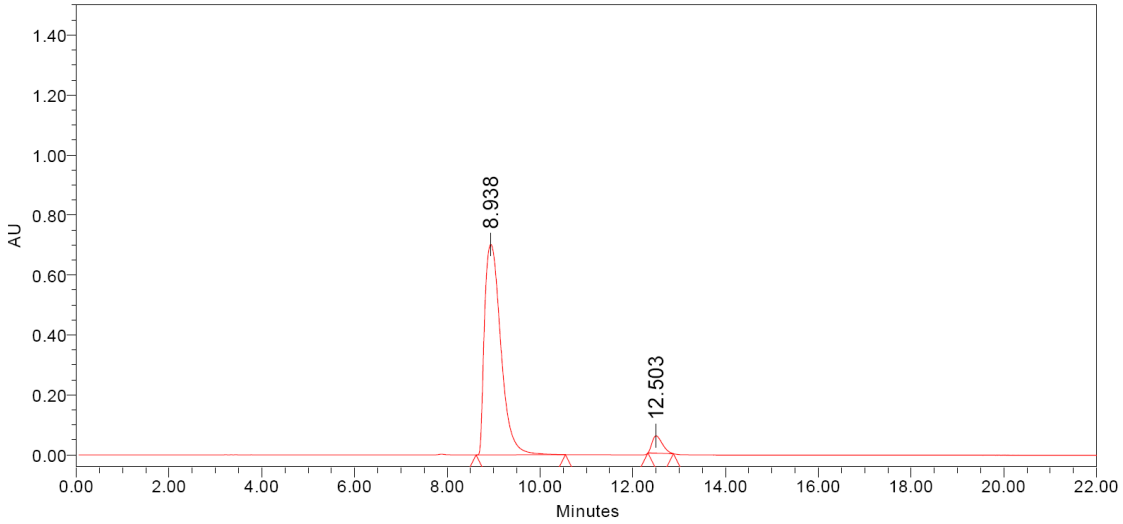
	Name	RT	Area	Height	% Area
1		4.604	74337	16372	2.85
2		4.967	2538507	476264	97.15



Scheme 2, entry 25

(*R,S*)-**L1**: 90% ee; (*S,R*)-**L1**: 90% ee

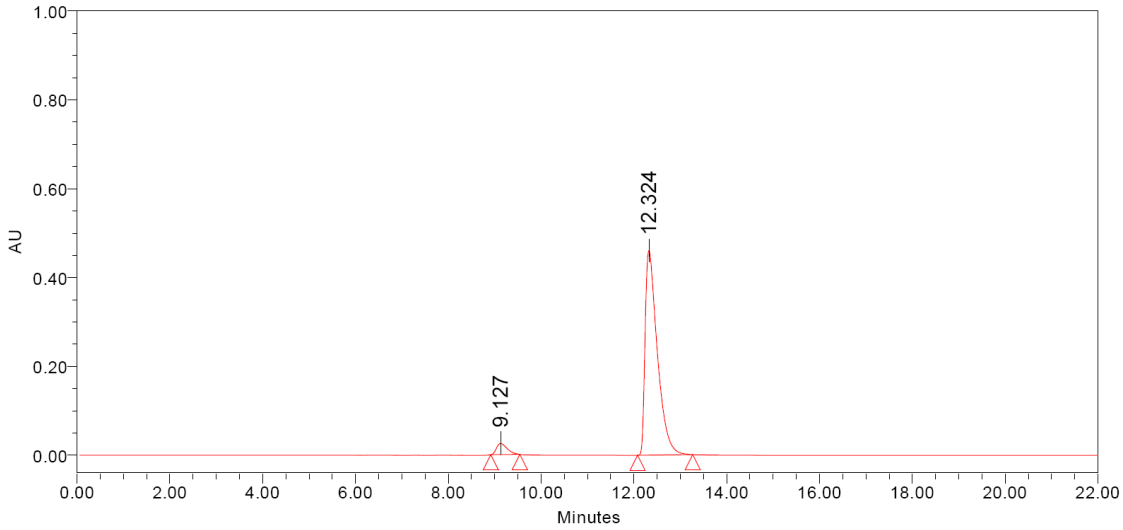
Auto-Scaled Chromatogram



Peak Results

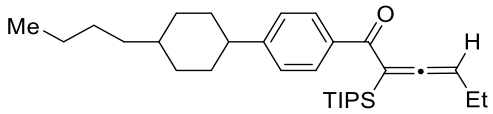
	Name	RT	Area	Height	% Area
1		8.938	17135701	702360	95.07
2		12.503	888190	57897	4.93

Auto-Scaled Chromatogram



Peak Results

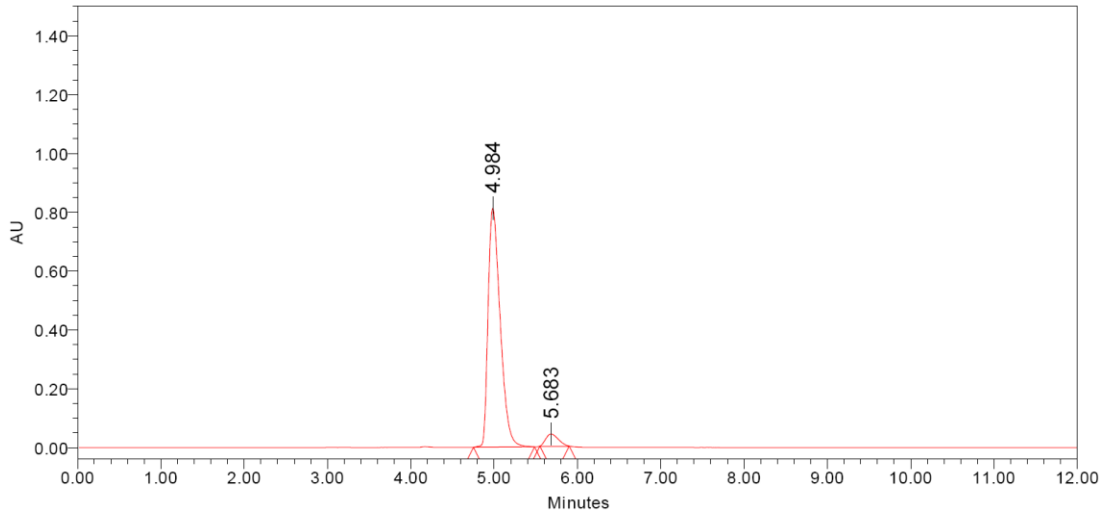
	Name	RT	Area	Height	% Area
1		9.127	397671	25044	4.52
2		12.324	8404586	460693	95.48



Scheme 2, entry 26

(*R,S*)-**L1**: 90% ee; (*S,R*)-**L1**: 90% ee

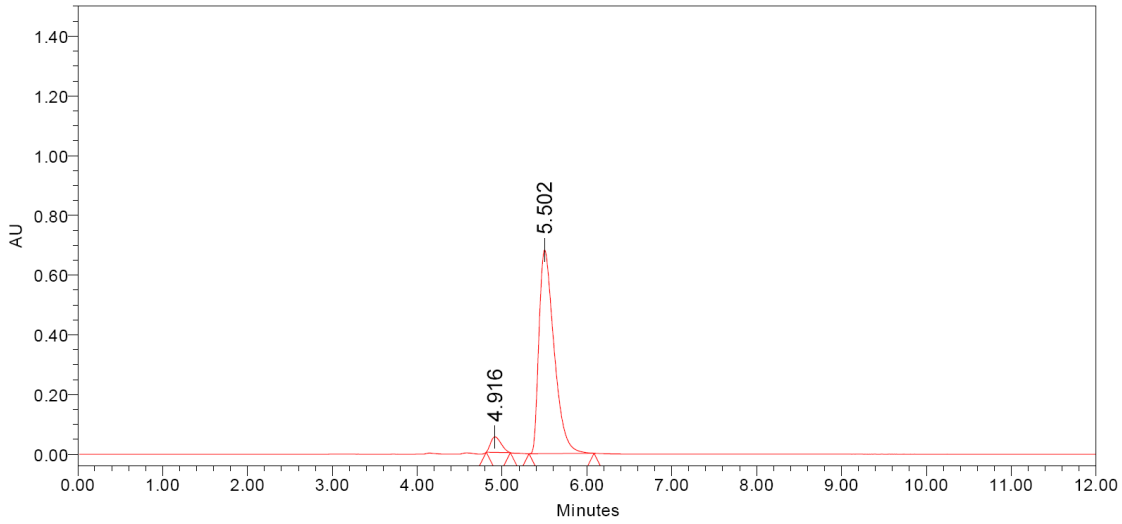
Auto-Scaled Chromatogram



Peak Results

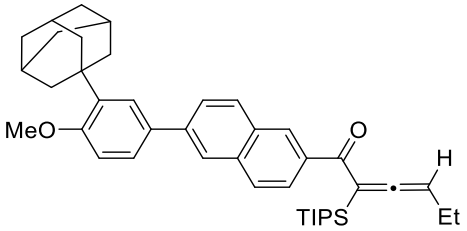
	Name	RT	Area	Height	% Area
1		4.984	8200535	812700	95.06
2		5.683	426281	40814	4.94

Auto-Scaled Chromatogram

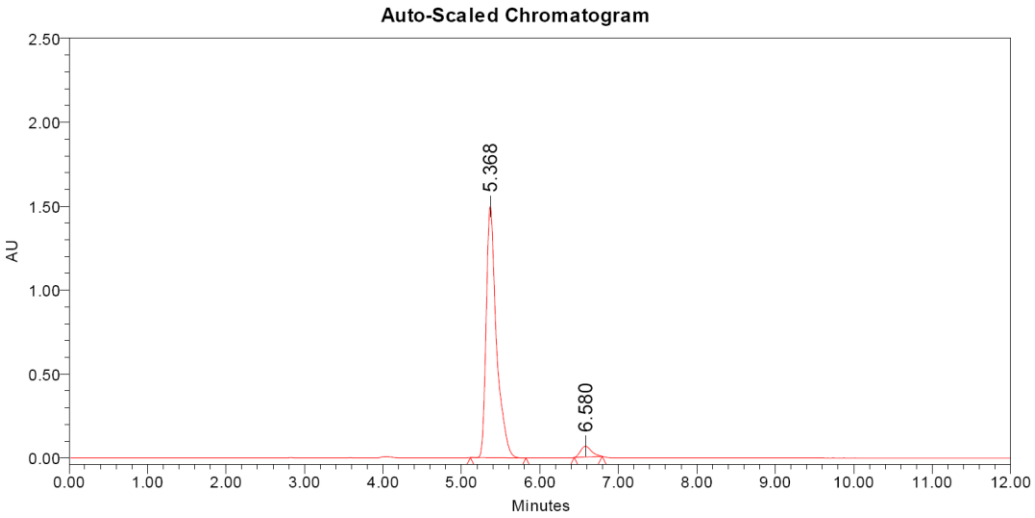


Peak Results

	Name	RT	Area	Height	% Area
1		4.916	440618	51893	4.97
2		5.502	8427256	682419	95.03

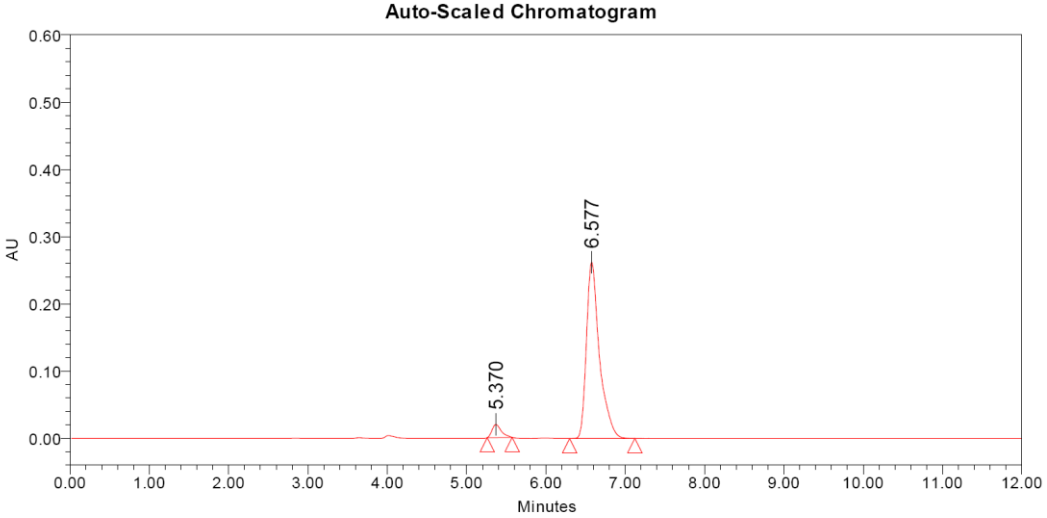


Scheme 2, entry 27
(*R,S*)-**L1**: 91% ee; (*S,R*)-**L1**: 90% ee



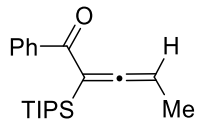
Peak Results

	Name	RT	Area	Height	% Area
1		5.368	13552058	1496556	95.61
2		6.580	622755	64837	4.39



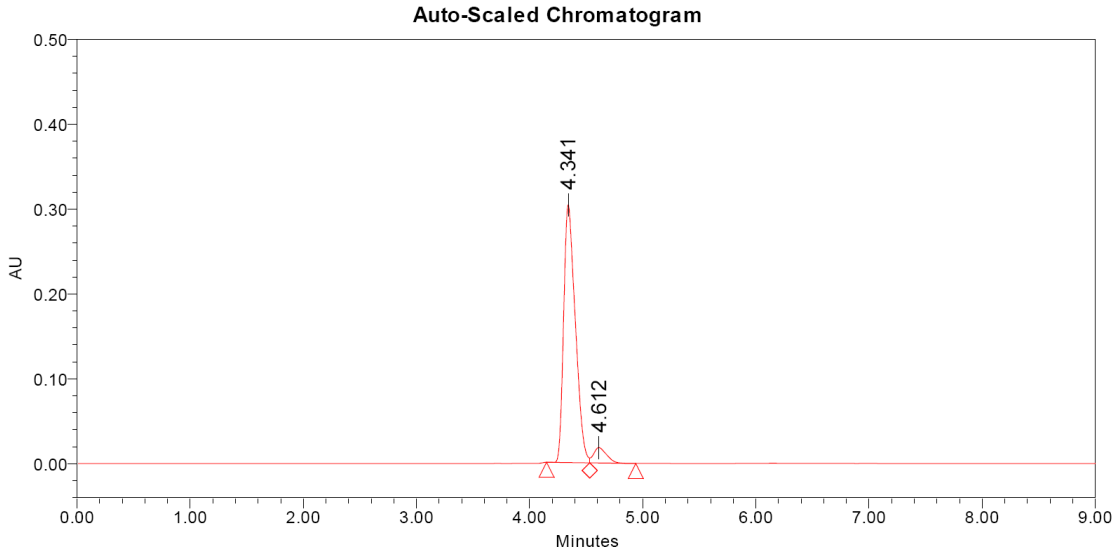
Peak Results

	Name	RT	Area	Height	% Area
1		5.370	156707	19478	4.99
2		6.577	2985312	262054	95.01



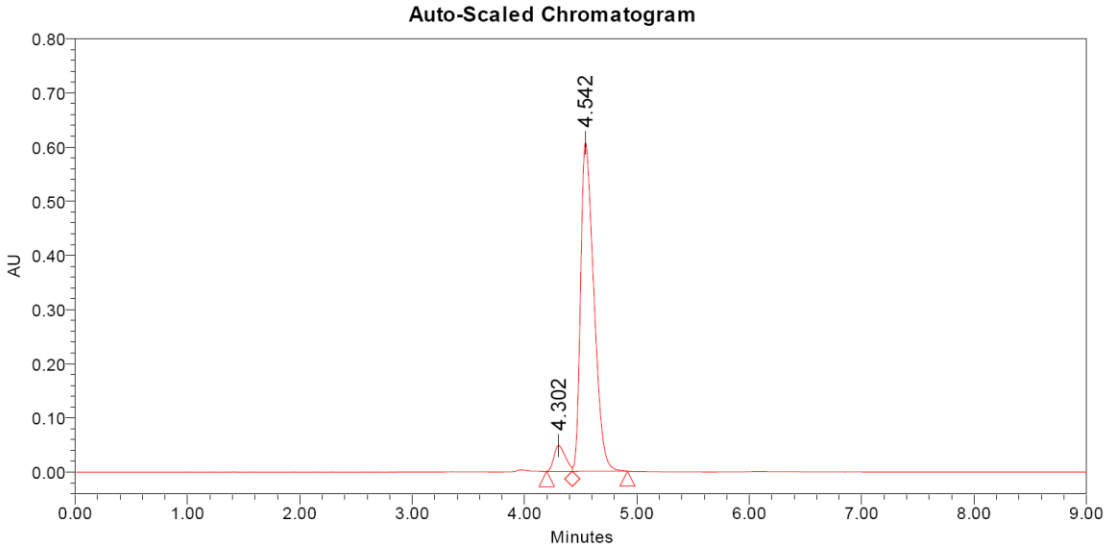
Scheme 3, entry 28

(*R,S*)-**L1**: 87% ee; (*S,R*)-**L1**: 87% ee



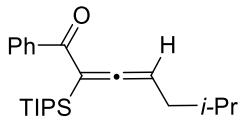
Peak Results

	Name	RT	Area	Height	% Area
1		4.341	2172067	303749	93.81
2		4.612	143299	18158	6.19

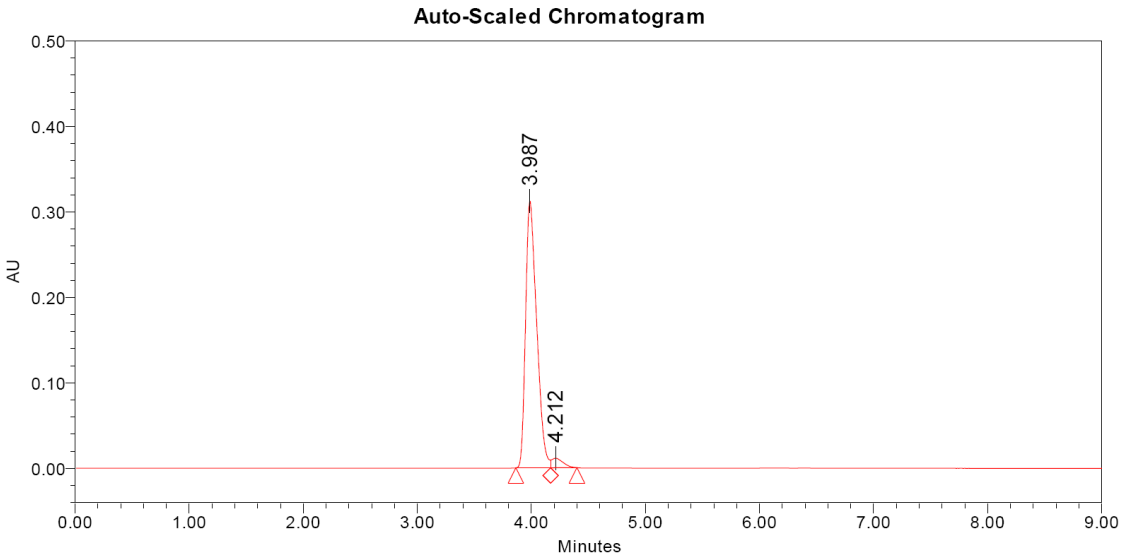


Peak Results

	Name	RT	Area	Height	% Area
1		4.302	331422	47499	6.25
2		4.542	4970801	606740	93.75

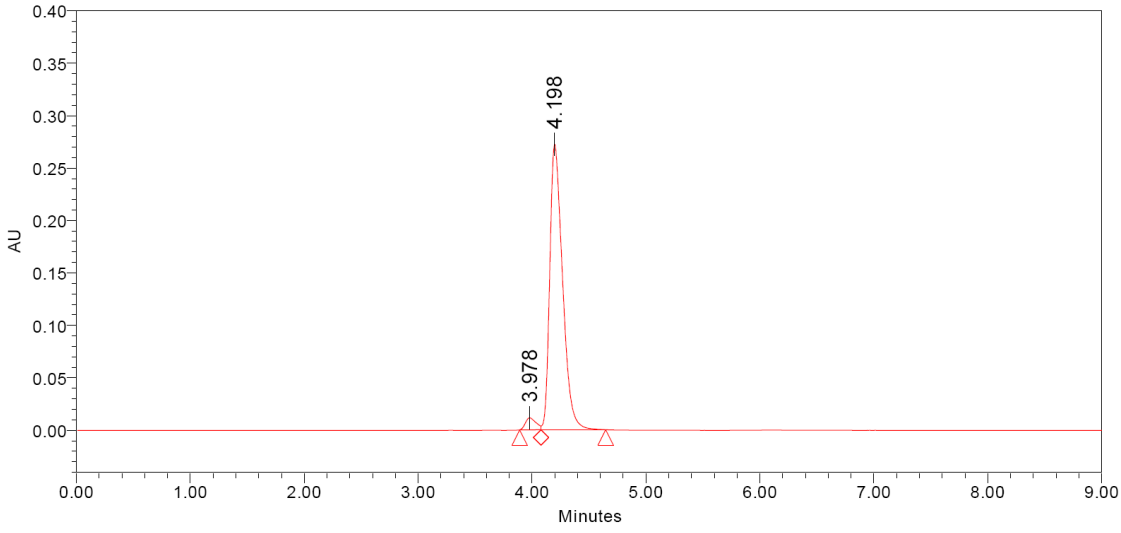


Scheme 3, entry 29
(*R*,*S*)-**L1**: 92% ee; (*S*,*R*)-**L1**: 93% ee



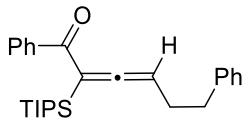
Peak Results

	Name	RT	Area	Height	% Area
1		3.987	2100192	312113	96.45
2		4.212	77385	11118	3.55

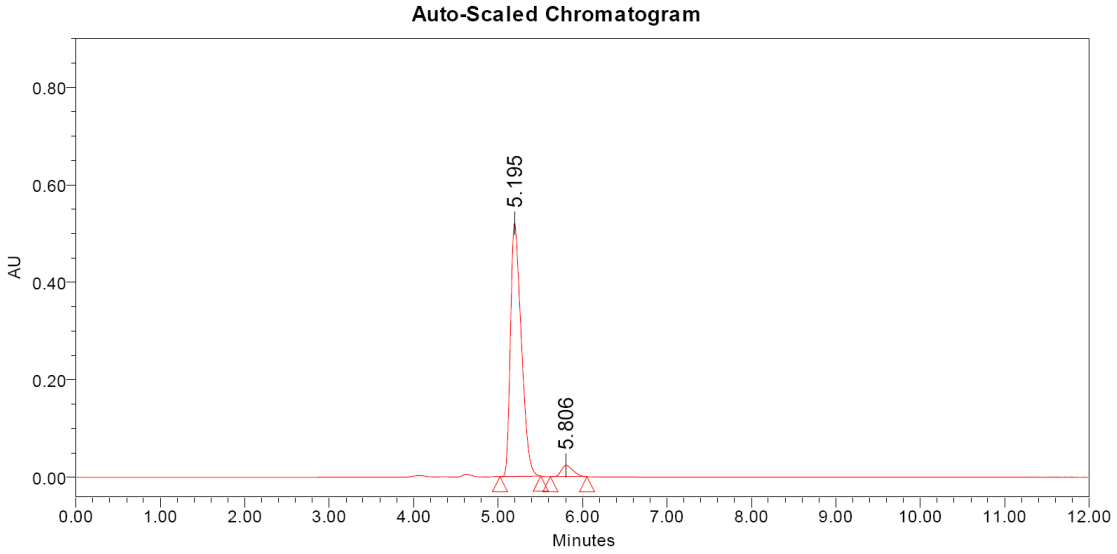


Peak Results

	Name	RT	Area	Height	% Area
1		3.978	74429	11531	3.39
2		4.198	2118301	272210	96.61

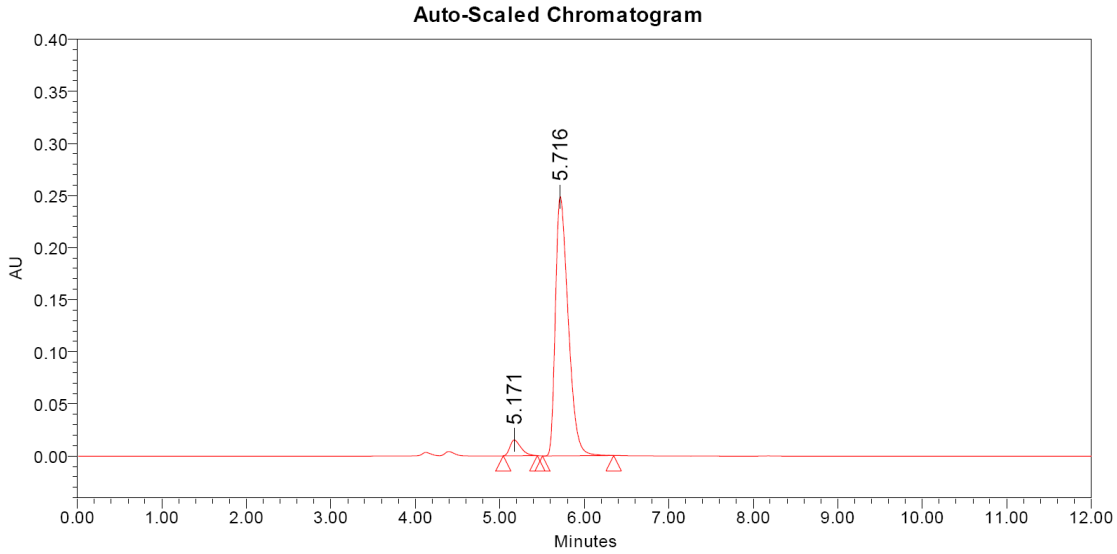


Scheme 3, entry 30
(*R*,*S*)-**L1**: 90% ee; (*S*,*R*)-**L1**: 90% ee



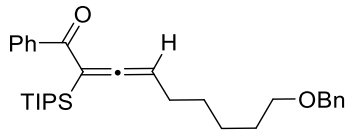
Peak Results

	Name	RT	Area	Height	% Area
1		5.195	4610551	519758	95.35
2		5.806	224917	23237	4.65



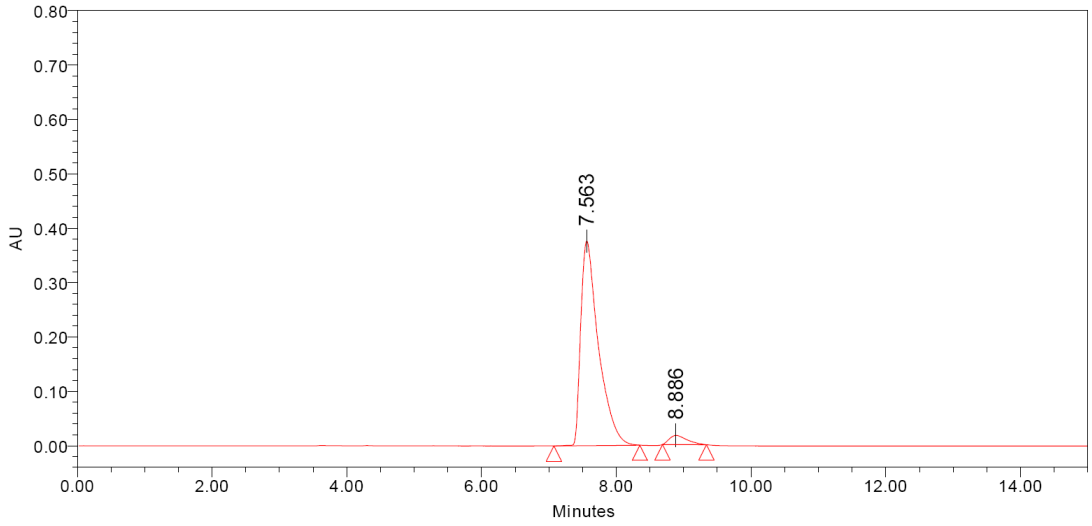
Peak Results

	Name	RT	Area	Height	% Area
1		5.171	137205	15249	4.99
2		5.716	2610188	248732	95.01



Scheme 3, entry 31
(*R*,*S*)-**L1**: 91% ee; (*S*,*R*)-**L1**: 90% ee

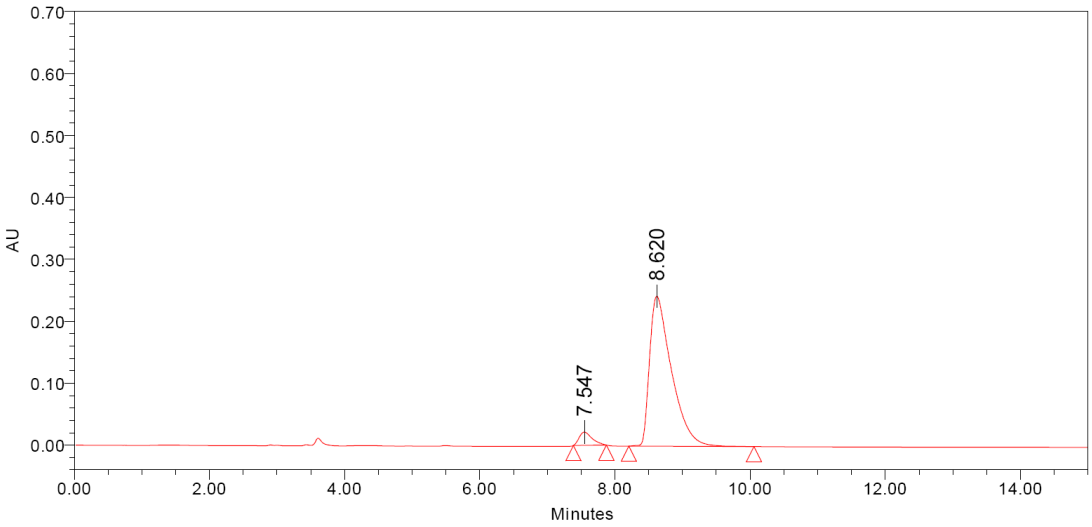
Auto-Scaled Chromatogram



Peak Results

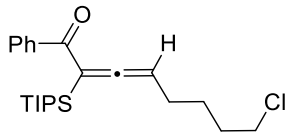
	Name	RT	Area	Height	% Area
1		7.563	6858144	376116	95.71
2		8.886	307518	16684	4.29

Auto-Scaled Chromatogram

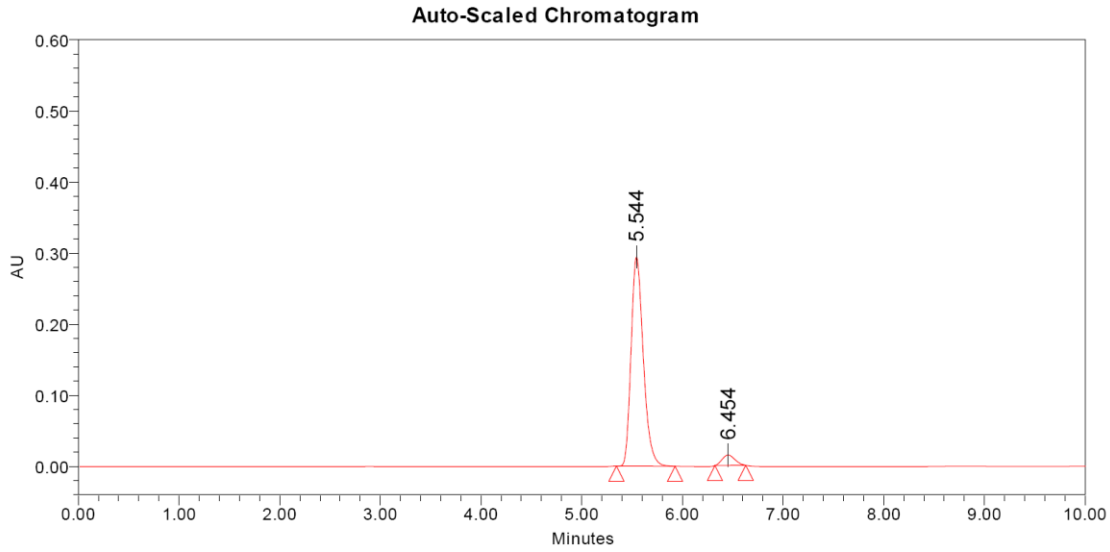


Peak Results

	Name	RT	Area	Height	% Area
1		7.547	284631	21410	4.97
2		8.620	5446835	242179	95.03

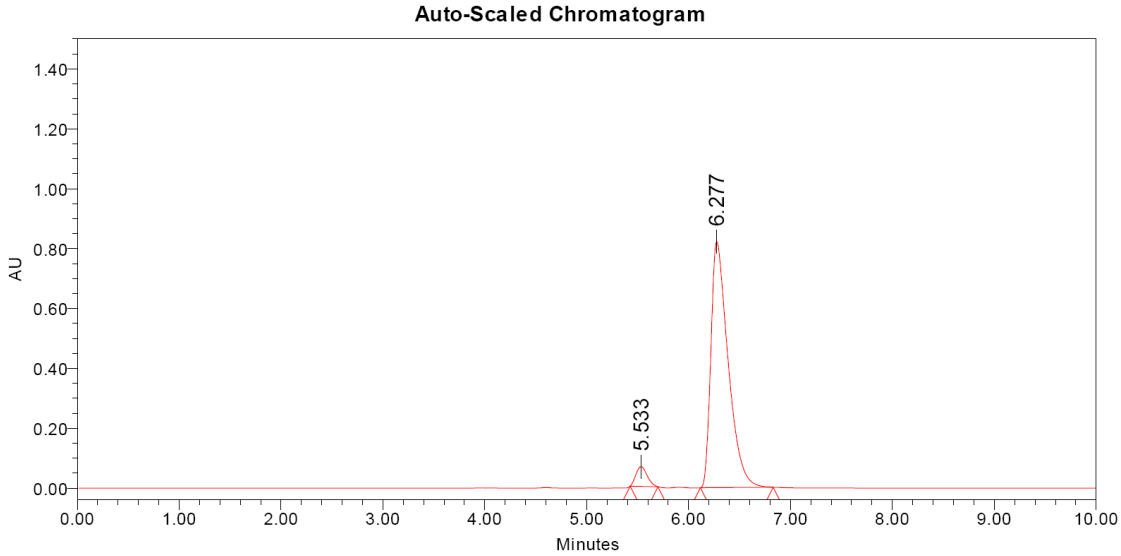


Scheme 3, entry 32
(*R*,*S*)-**L1**: 90% ee; (*S*,*R*)-**L1**: 90% ee



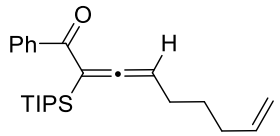
Peak Results

	Name	RT	Area	Height	% Area
1		5.544	2483157	294121	95.02
2		6.454	130271	14662	4.98



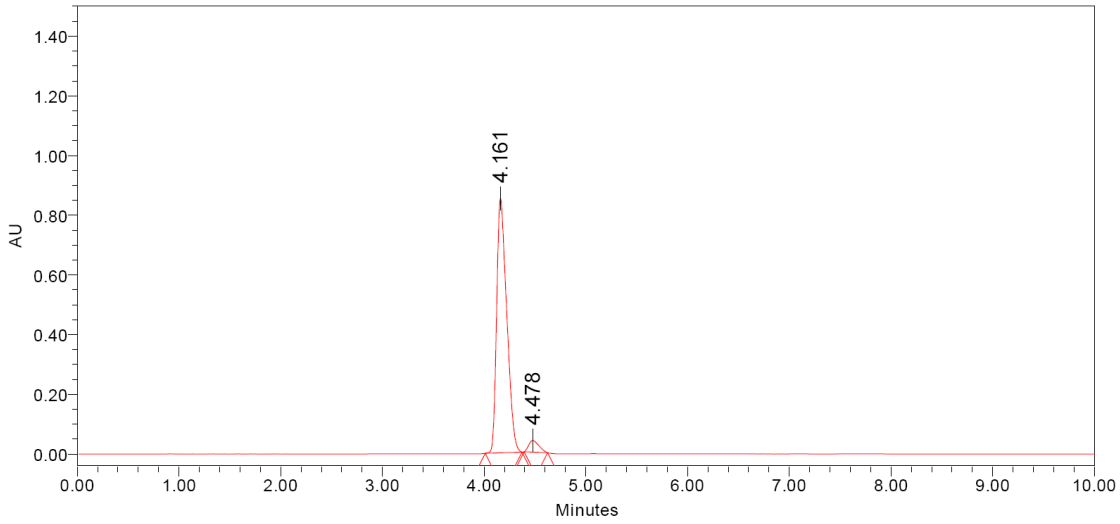
Peak Results

	Name	RT	Area	Height	% Area
1		5.533	504178	65986	4.97
2		6.277	9631943	821966	95.03



Scheme 3, entry 33
(*R*,*S*)-**L1**: 91% ee; (*S*,*R*)-**L1**: 91% ee

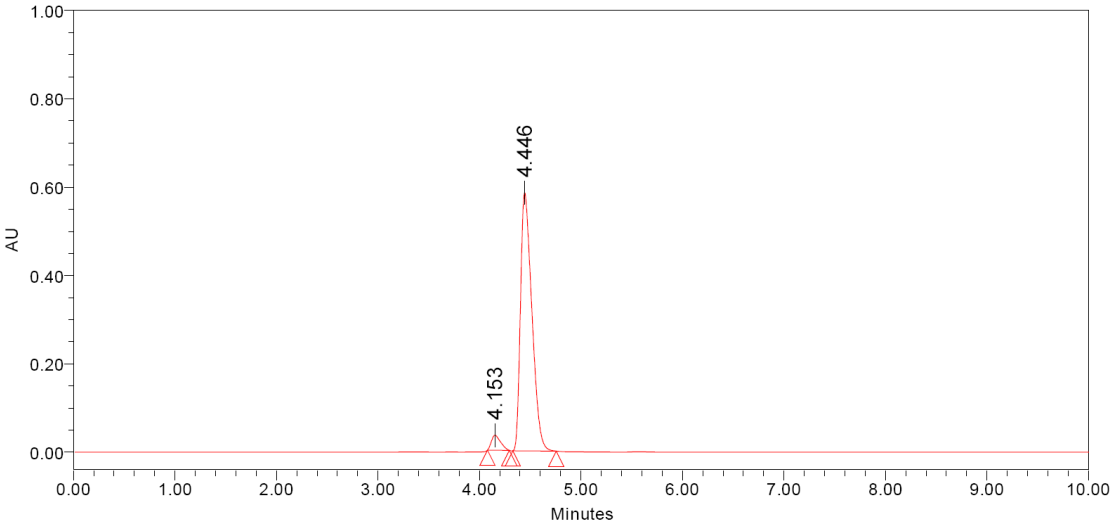
Auto-Scaled Chromatogram



Peak Results

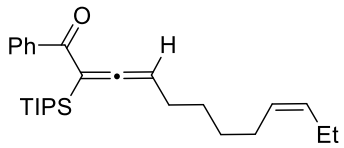
	Name	RT	Area	Height	% Area
1		4.161	5852807	853216	95.63
2		4.478	267574	38935	4.37

Auto-Scaled Chromatogram

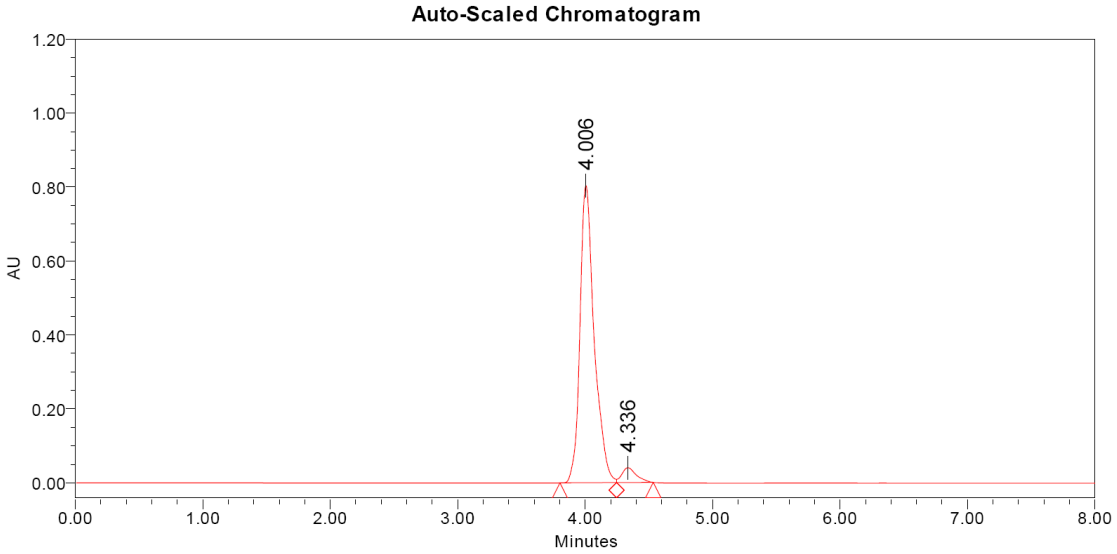


Peak Results

	Name	RT	Area	Height	% Area
1		4.153	211273	34034	4.44
2		4.446	4548746	584859	95.56

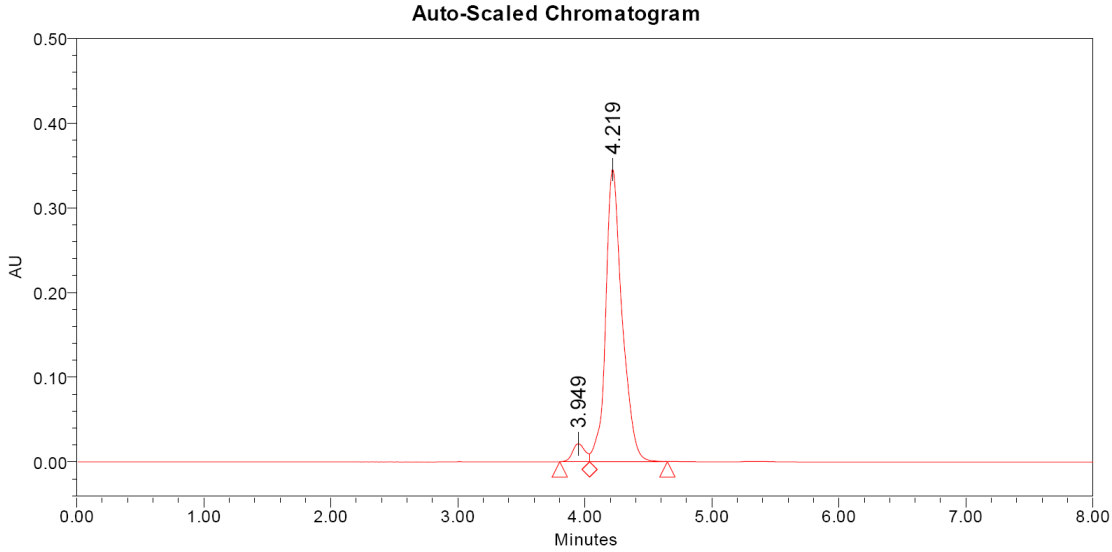


Scheme 3, entry 34
(*R*,*S*)-**L1**: 90% ee; (*S*,*R*)-**L1**: 90% ee



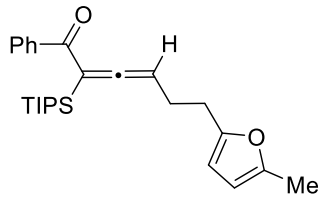
Peak Results

	Name	RT	Area	Height	% Area
1		4.006	6247588	803850	95.16
2		4.336	317553	40061	4.84



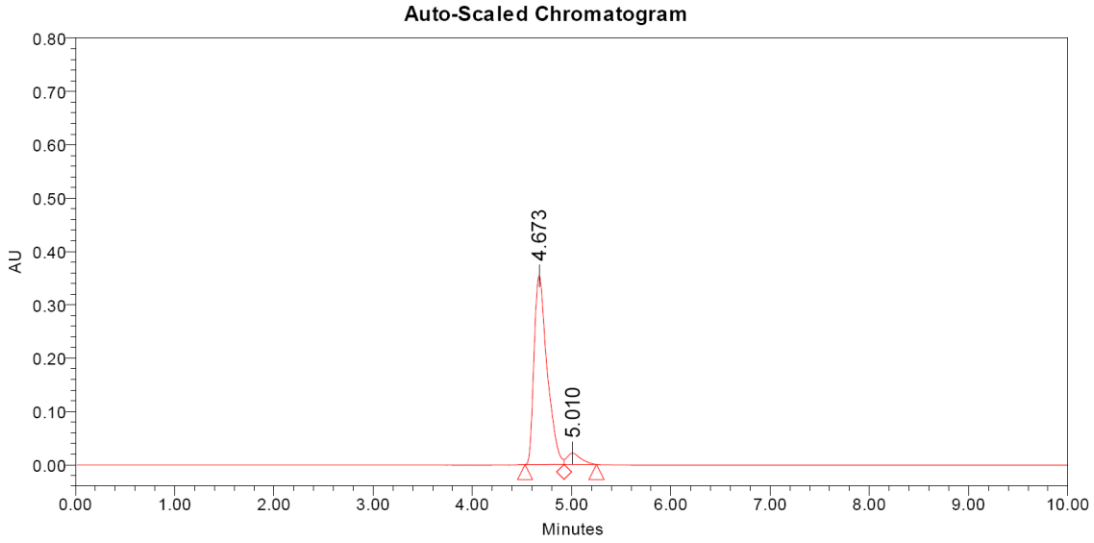
Peak Results

	Name	RT	Area	Height	% Area
1		3.949	147552	21379	4.53
2		4.219	3108114	345019	95.47



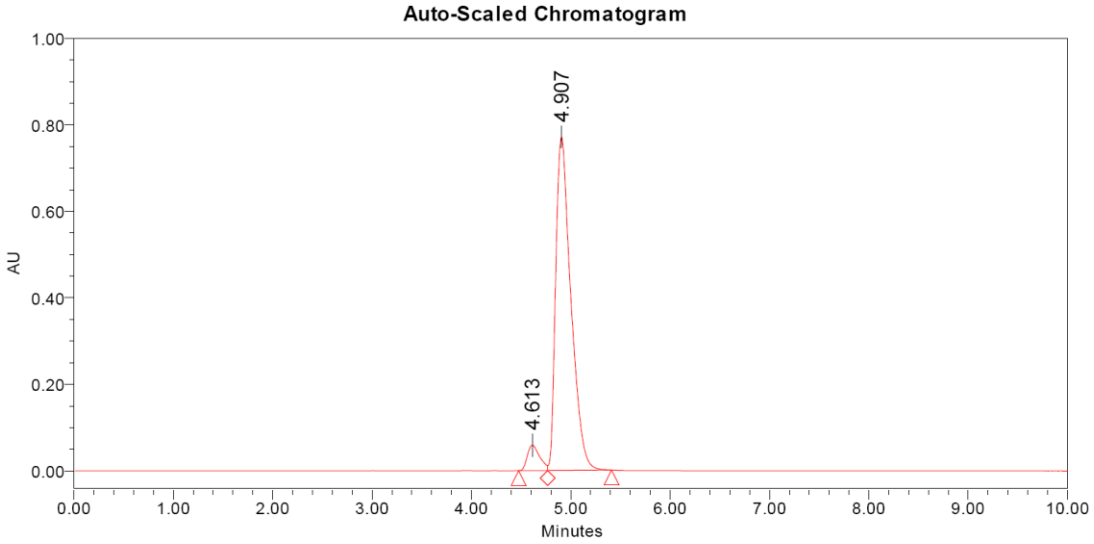
Scheme 3, entry 35

(*R,S*)-**L1**: 88% ee; (*S,R*)-**L1**: 88% ee



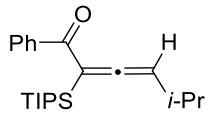
Peak Results

	Name	RT	Area	Height	% Area
1		4.673	3228482	353464	94.01
2		5.010	205572	21195	5.99



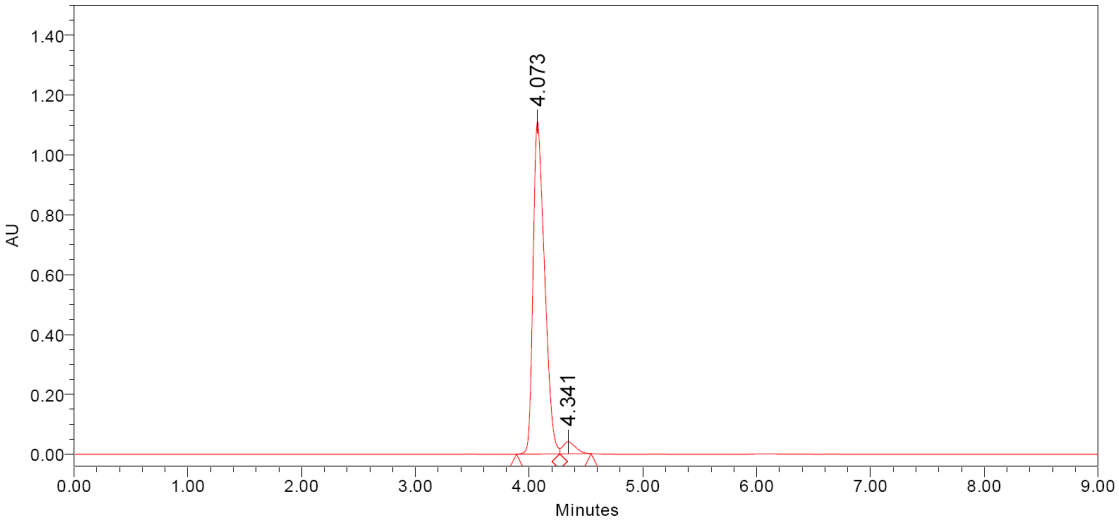
Peak Results

	Name	RT	Area	Height	% Area
1		4.613	512414	59022	5.90
2		4.907	8166799	770890	94.10



Scheme 3, entry 36
(*R,S*)-**L1**: 92% ee; (*S,R*)-**L1**: 92% ee

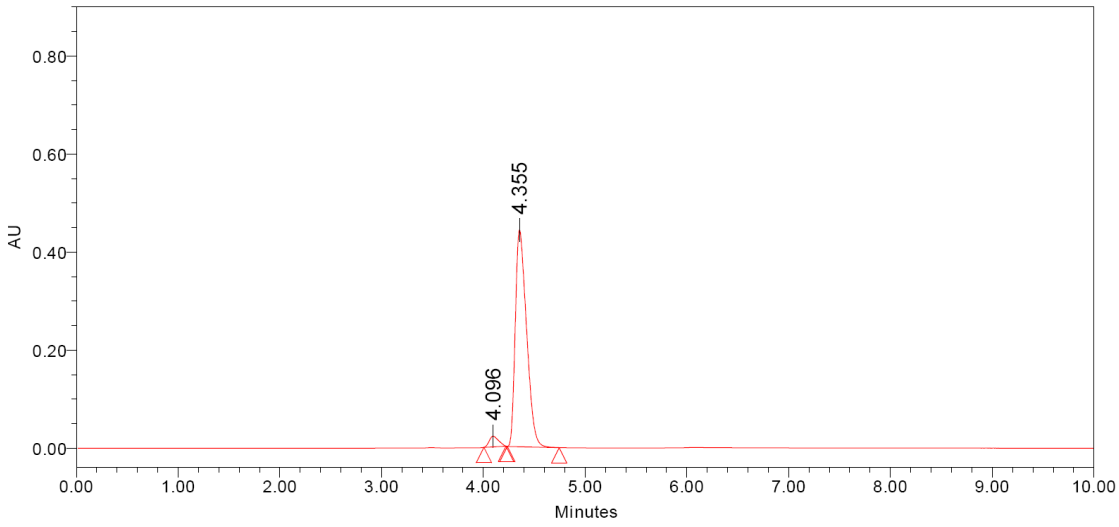
Auto-Scaled Chromatogram



Peak Results

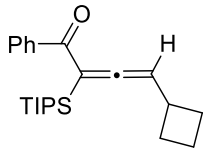
	Name	RT	Area	Height	% Area
1		4.073	7802582	1110994	96.14
2		4.341	313486	40361	3.86

Auto-Scaled Chromatogram



Peak Results

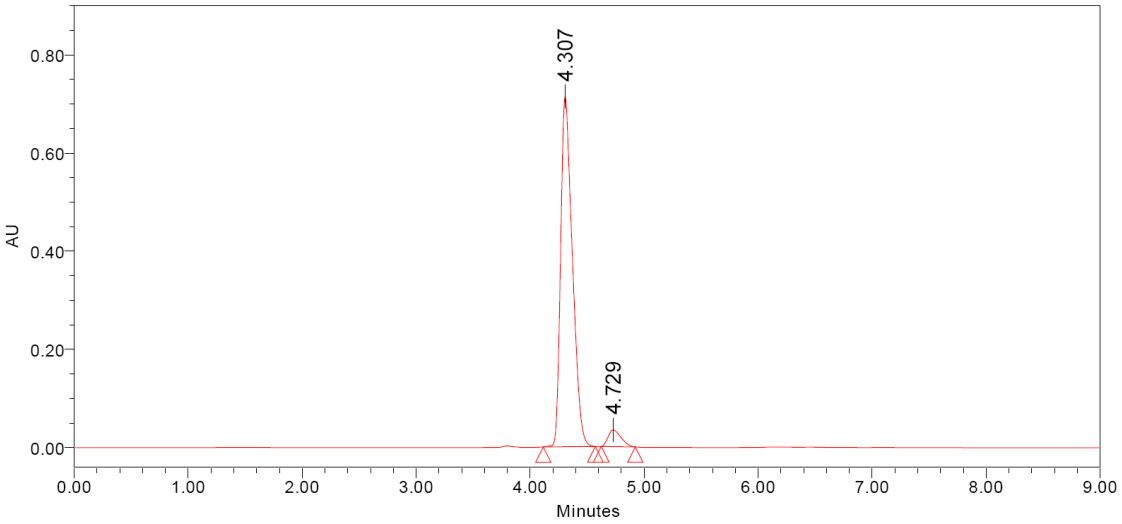
	Name	RT	Area	Height	% Area
1		4.096	138205	21925	3.92
2		4.355	3386768	442599	96.08



Scheme 3, entry 37

(*R,S*)-**L1**: 90% ee; (*S,R*)-**L1**: 90% ee

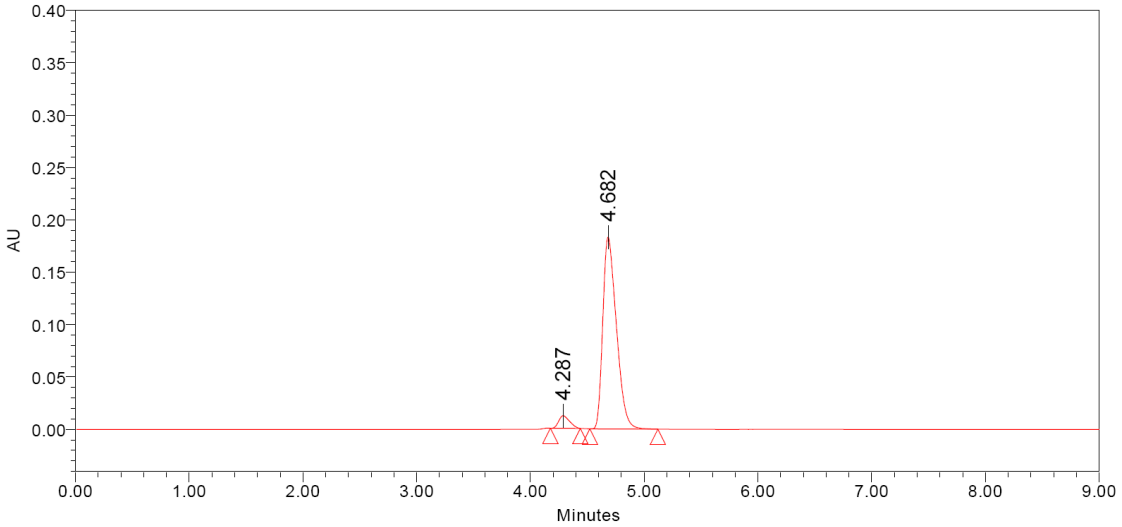
Auto-Scaled Chromatogram



Peak Results

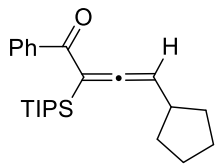
	Name	RT	Area	Height	% Area
1		4.307	5088991	713257	95.04
2		4.729	265382	34106	4.96

Auto-Scaled Chromatogram

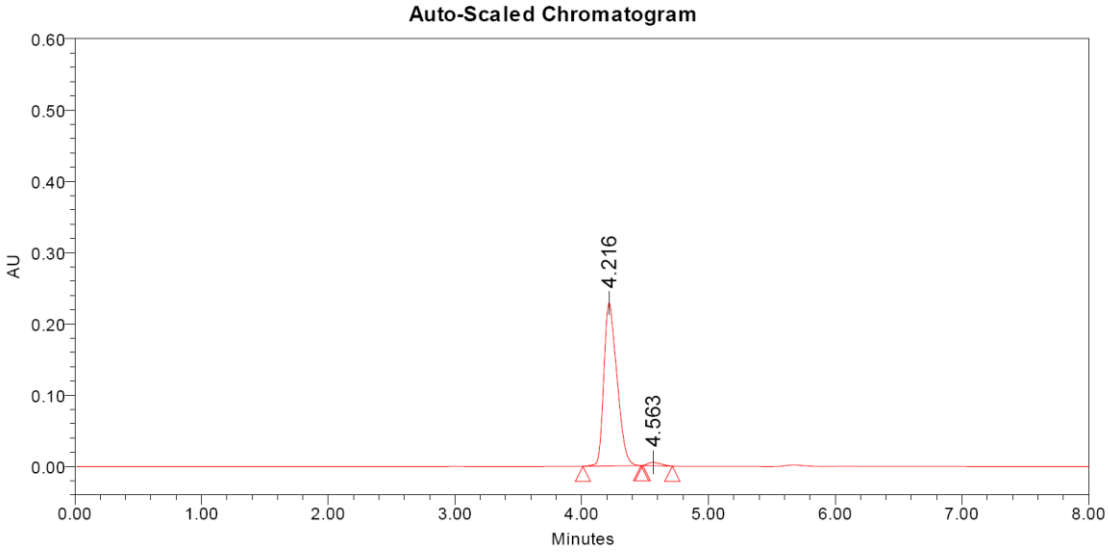


Peak Results

	Name	RT	Area	Height	% Area
1		4.287	79247	12044	4.96
2		4.682	1518238	183135	95.04

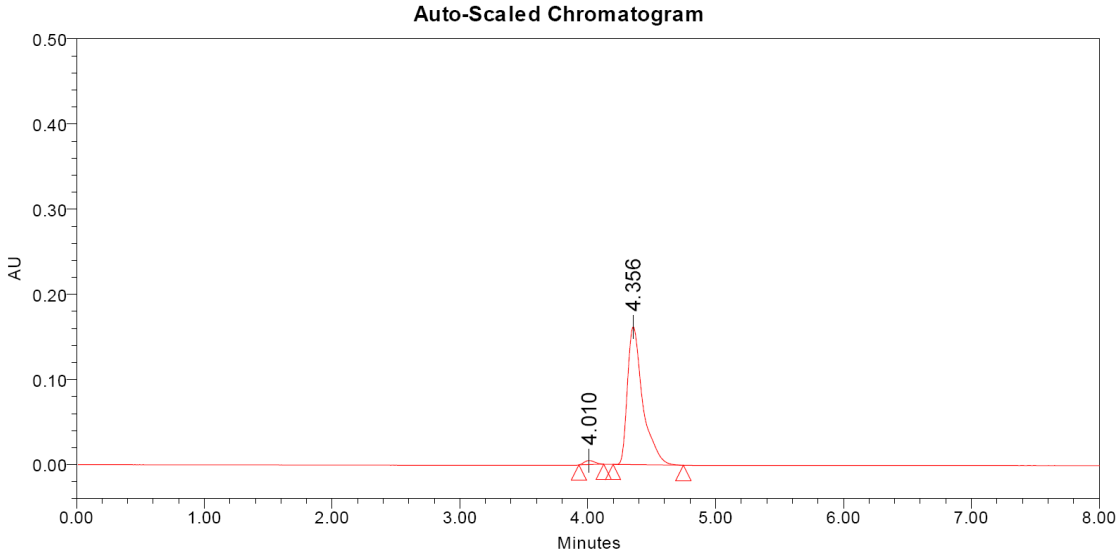


Scheme 3, entry 38
(*R*,*S*)-**L1**: 96% ee; (*S*,*R*)-**L1**: 96% ee



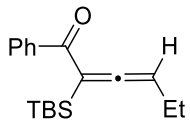
Peak Results

	Name	RT	Area	Height	% Area
1		4.216	1646406	228576	98.07
2		4.563	32410	4615	1.93



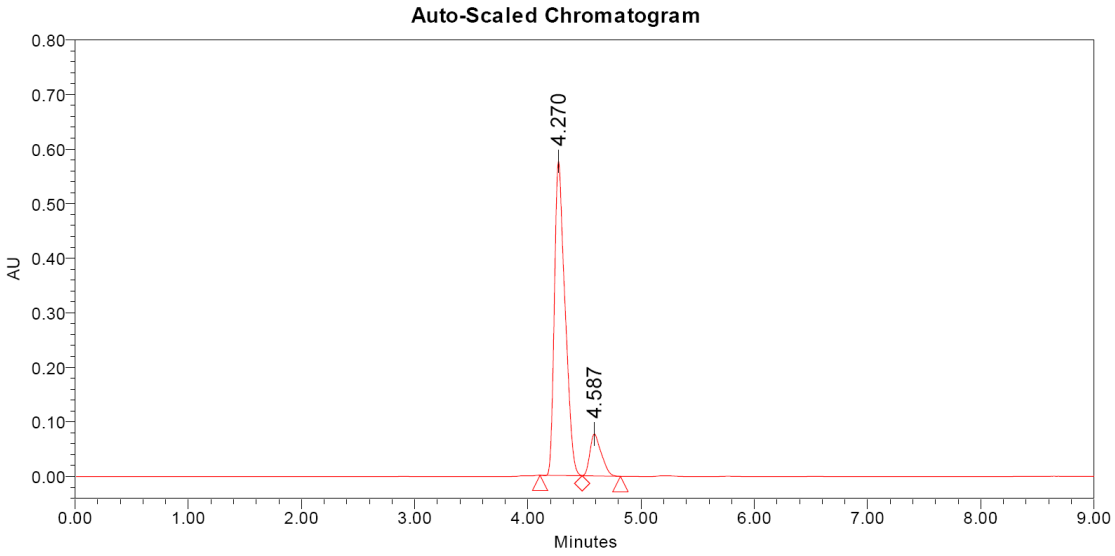
Peak Results

	Name	RT	Area	Height	% Area
1		4.010	27483	4760	2.00
2		4.356	1346537	161782	98.00



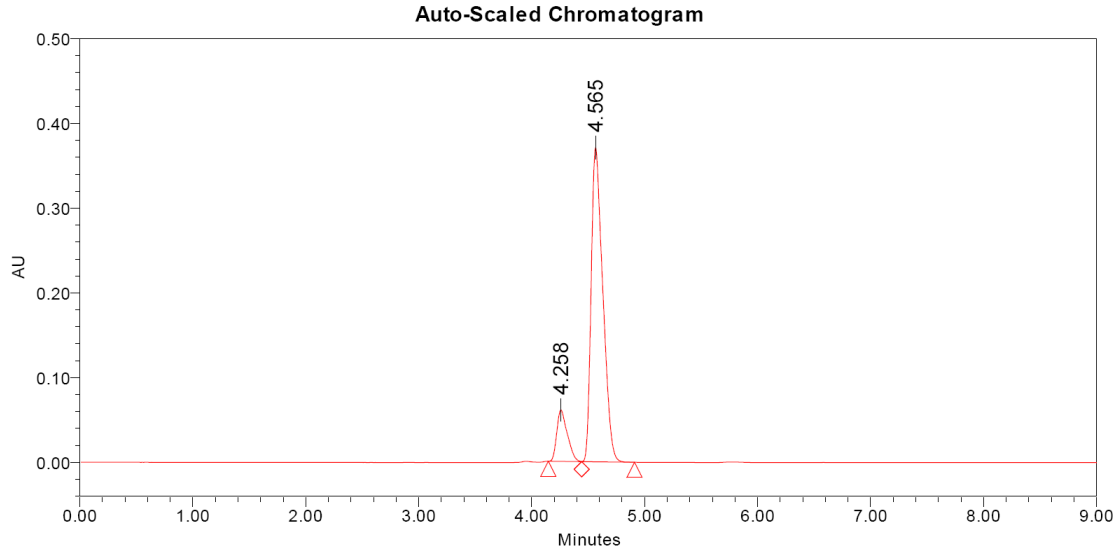
Scheme 3, entry 39

(*R*,*S*)-**L1**: 74% ee; (*S*,*R*)-**L1**: 74% ee



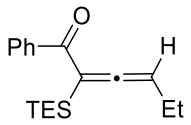
Peak Results

	Name	RT	Area	Height	% Area
1		4.270	3756330	575733	87.48
2		4.587	537686	76924	12.52



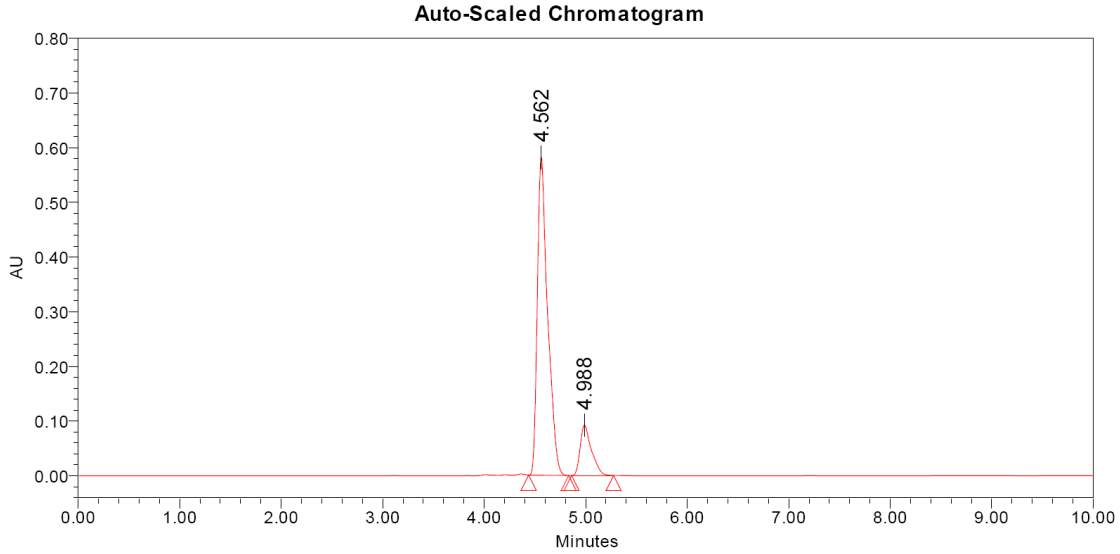
Peak Results

	Name	RT	Area	Height	% Area
1		4.258	391975	60781	12.86
2		4.565	2656167	370944	87.14



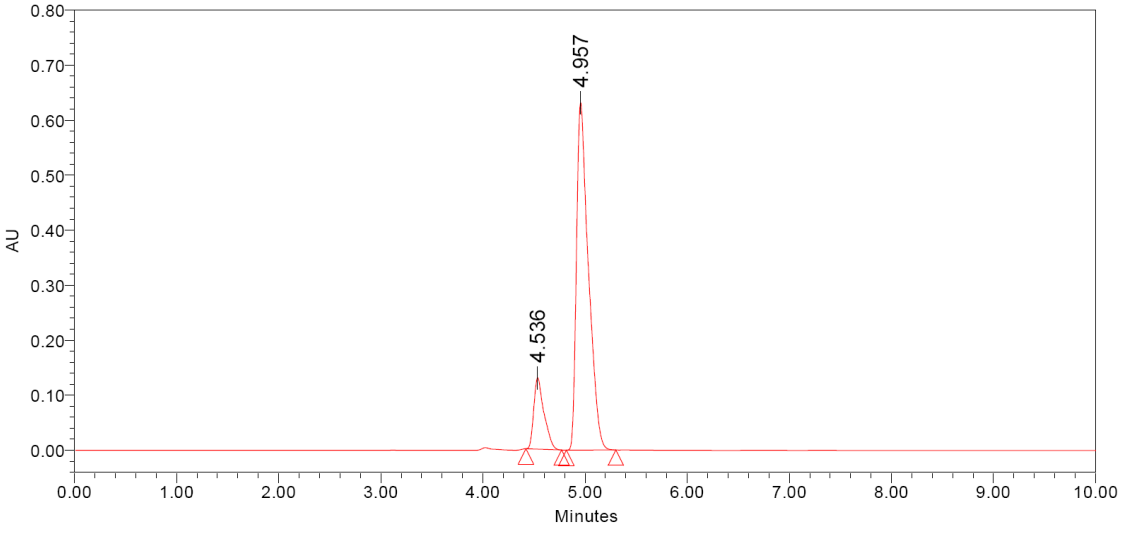
Scheme 3, entry 40

(*R*,*S*)-**L1**: 70% ee; (*S*,*R*)-**L1**: 70% ee



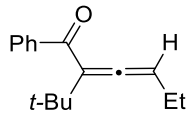
Peak Results

	Name	RT	Area	Height	% Area
1		4.562	4097632	581463	85.16
2		4.988	714131	92270	14.84



Peak Results

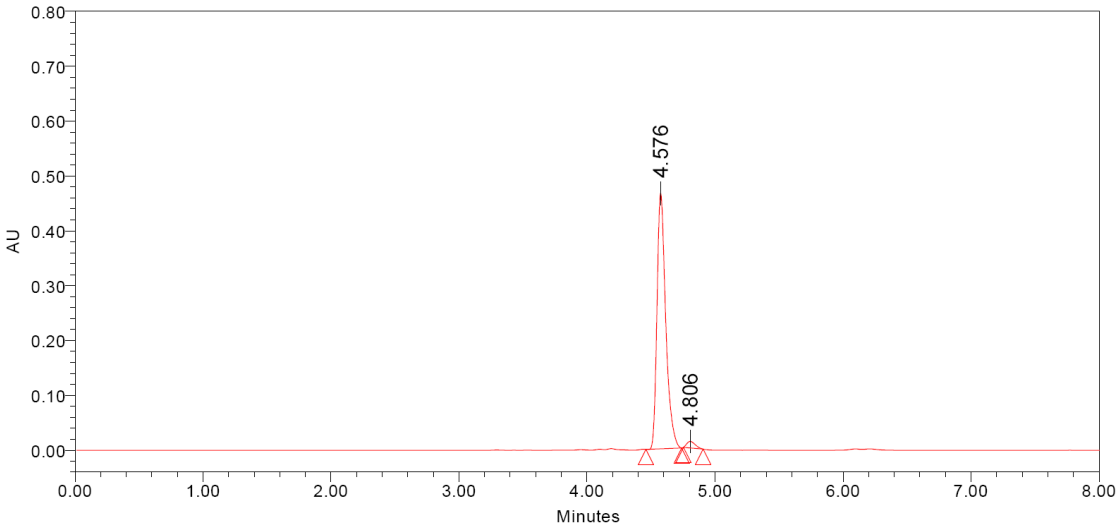
	Name	RT	Area	Height	% Area
1		4.536	900145	129629	14.93
2		4.957	5128051	631638	85.07



Scheme 3, entry 41

(*R,S*)-**L1**: 95% ee; (*S,R*)-**L1**: 95% ee

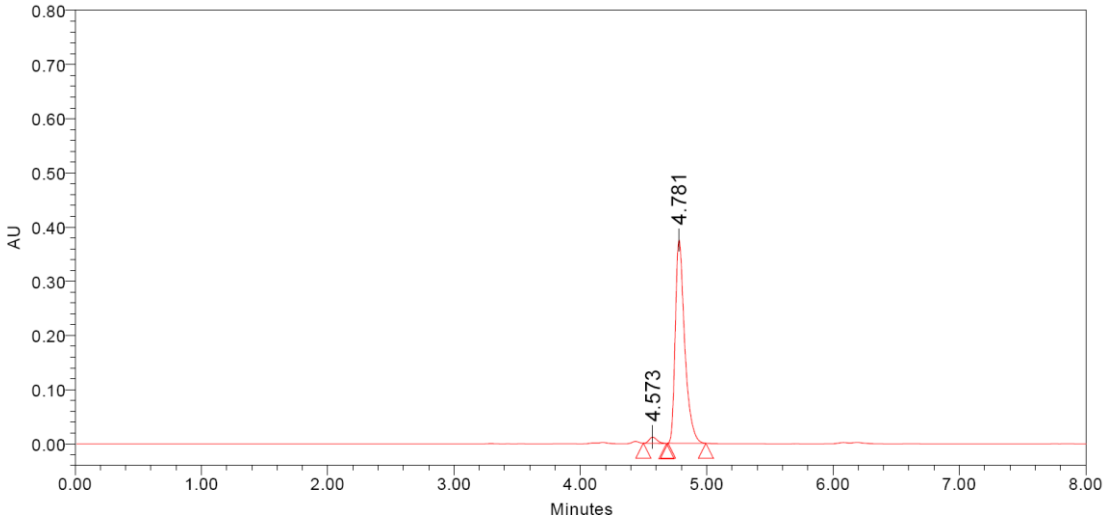
Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		4.576	2208734	466059	97.58
2		4.806	54861	12026	2.42

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		4.573	49362	11475	2.48
2		4.781	1940290	375245	97.52