Supporting Information

Design of Hemilabile N,N,N-Ligands in Copper-Catalyzed Enantioconvergent Radical Cross-Coupling of Benzyl/Propargyl Halides with Alkenylboronate Esters

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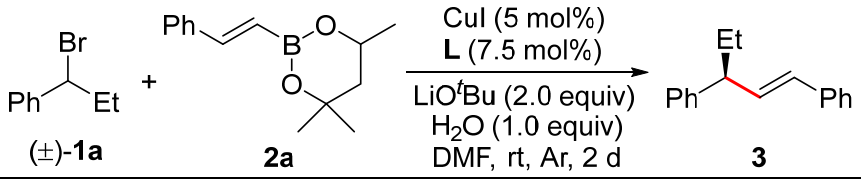
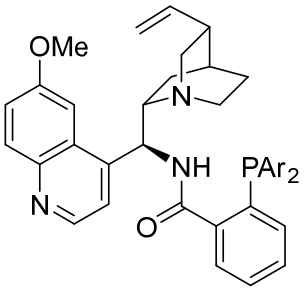
General information

All reactions were carried out under argon atmosphere using Schlenk techniques, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Cuprous iodide (99.999%) was purchased from Sigma-Aldrich. Lithium tert-butoxide (99%) was purchased from Macklin, which was dry at 90 ^{o}C for 3 h under reduced pressure. *N, N*-dimethylformamide (DMF) was purchased from Titan, which was distilled over CaH_2 prior to use. NMR spectra were recorded for ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) using TMS as an internal standard and Bruker AV 400 as an instrument. The chemical shifts are expressed in ppm and coupling constants are given in Hertz (Hz). Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s = singlet; d = doublet; dd = doublet of doublets; t = triplet; td = triplet of doublets; q = quarter; m = multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectroscopy (HRMS) was obtained on Thermo Scientific Q Exactive mass spectrometer using ESI and APCI ion source by TOF and orbitrap mass analyzer. Enantiomeric excess (ee) was determined by Agilent and Shimadzu high-performance liquid chromatography (HPLC) with a Hatachi detector (at appropriate wavelength).

The optimization of reaction conditions

Table S1. Screening of other NNP-Ligands[a]



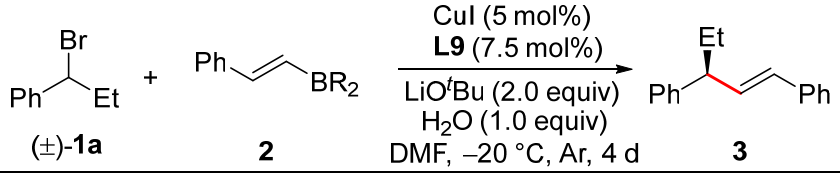


L12, Ar = 3,5-$(CF_3)_2C_6H_3$
L13, Ar = 3,5-$(MeO)_2C_6H_3$
L14, Ar = 3,5-^{i}Pr$_2C_6H_3$
L15, Ar = 3-MeC_6H_4
L16, Ar = 3-$MeOC_6H_4$
L17, Ar = 2-Naphthyl
L18, Ar = 2,3,4,5,6-Me_5C_6

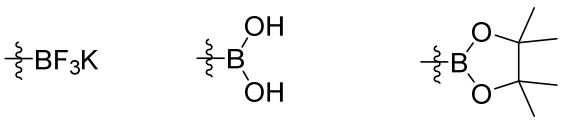
entry	L	yield of 3 (%)	ee of 3 (%)
1	**L12**	17	31
2	**L13**	30	38
3	**L14**	30	40
4	**L15**	23	28
5	**L16**	20	36
6	**L17**	16	28
7	**L18**	18	35

[a]Reaction conditions: (±)-**1a** (0.30 mmol), **2a** (0.20 mmol), CuI (5 mol%), **L** (7.5 mol%), LiO^{t}Bu (2.0 equiv) and H_2O (1.0 equiv) in DMF (2.0 mL) at room temperature for 2 d under argon. Yield was based on ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard. Ee values were based on HPLC analysis.

Table S2. Screening of different boronate esters[a]



BR$_2$ =



2a1 **2a2** **2a3**

entry	2	yield of 3 (%)	ee of 3 (%)
1	**2a1**	4	50
2	**2a2**	8	59
3	**2a3**	65	93

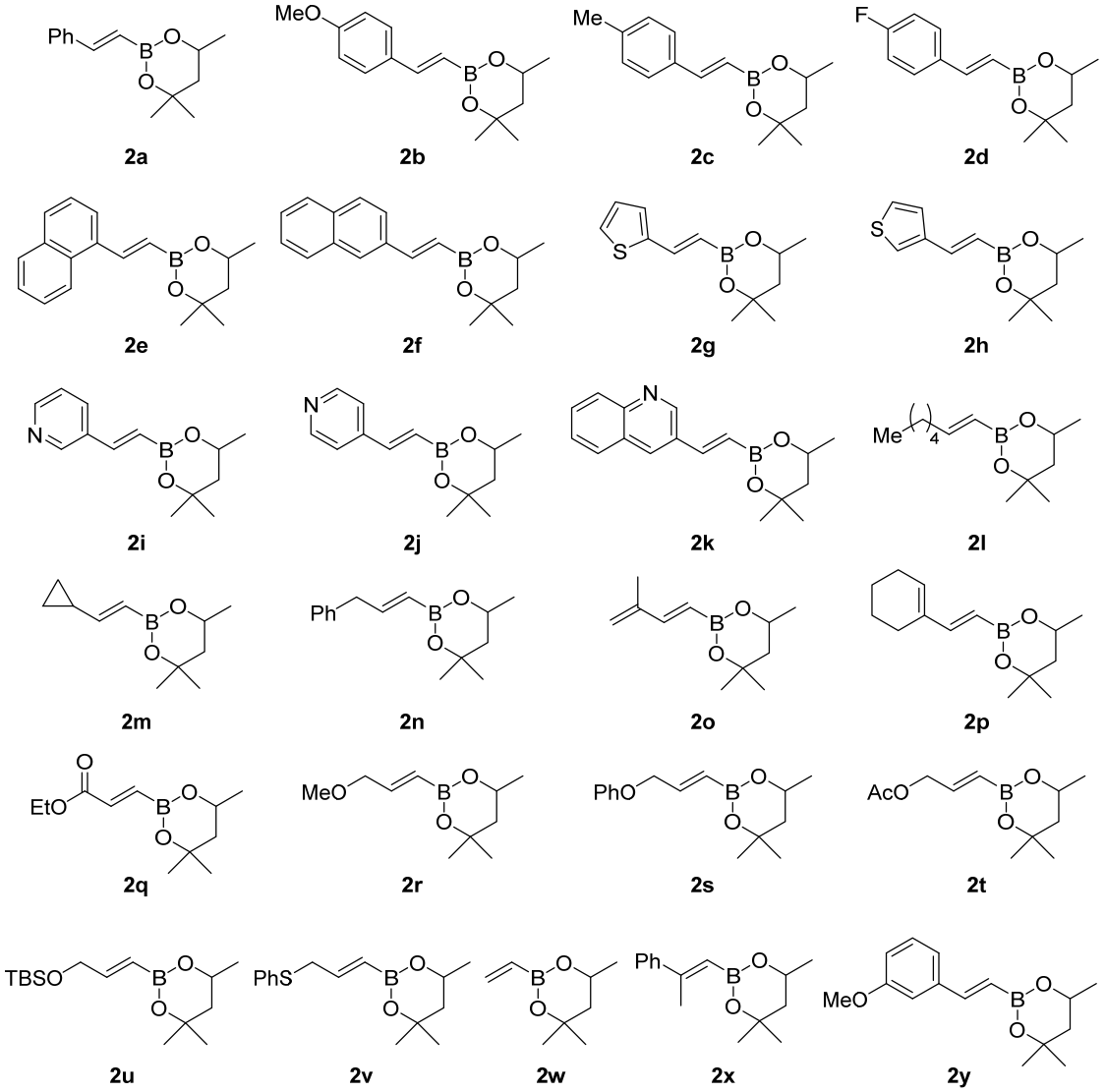
[a]Reaction conditions: (±)-**1a** (0.30 mmol), **2** (0.20 mmol), CuI (5 mol%), **L9** (7.5 mol%), LiO^{t}Bu (2.0 equiv) and H_2O (1.0 equiv) in DMF (2.0 mL) at –20 °C for 4 d under argon. Yield was based on ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard. Ee values were based on HPLC analysis.

Scheme S1. Investigation of protodeboronation side products[a]

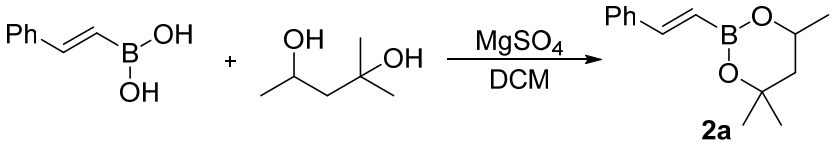
entry	base	yield of 8 (%)	yield of 8' (%)	ee of 8 (%)
1	LiO^{t}Bu	45	5	89
2	Cs_2CO_3	6	30	18
3[b]	LiO^{t}Bu	78	trace	94

[a]Reaction conditions: (±)-**1a** (0.30 mmol), **2f** (0.20 mmol), CuI (5 mol%), **L9** (7.5 mol%), base (2.0 equiv) and H_2O (1.0 equiv) in DMF (2.0 mL) at room temperature for 2 d under argon. [b]The reaction was conducted at –20 °C for 4 d. Yield was based on ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard. Ee values were based on HPLC analysis. mp = methylpentanediol.

The structures and synthesis of alkenylboronate esters

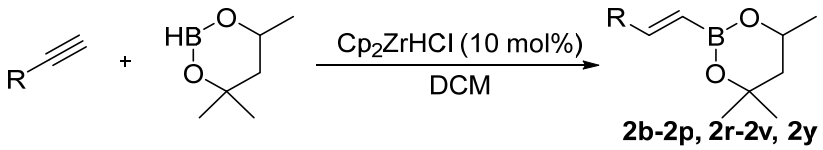


2a was prepared from (*E*)-styrylboronic acid



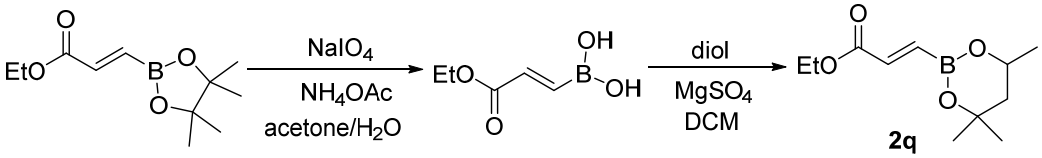
Under an argon atmosphere, (*E*)-styrylboronic acid (3.551 g, 24 mmol) was dissolved in dry dichloromethane (24.0 mL), followed by the addition of 2-methylpentane-2,4-diol (3.121 g, 26.4 mmol, 1.1 equiv) and magnesium sulfate (19.2 g). The reaction mixture was stirred at room temperature overnight. After completion of the reaction, the reaction mixture was filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford the desired product **2a** as a colorless oil (4.3958 g, 80% yield).

2b-2p, 2r-2v, 2y were prepared according to previously reported procedure and slightly modified from the corresponding alkyne.[1]



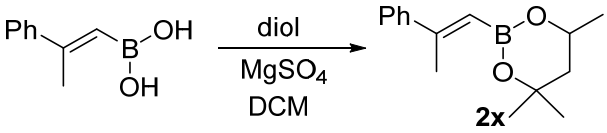
Under an argon atmosphere, to a solution of bis(cyclopentadienyl)zirconium chloride hydride Cp_2ZrHCl (10 mol%) in CH_2Cl_2 (1 M) was added alkynes (1 equiv) and 4,4,6-trimethyl-1,3,2-dioxaborinane MPBH (1.1 equiv) at ice water bath. The reaction mixture was stirred at room temperature overnight. After completion of the reaction, water was poured into the above reaction mixture, and the mixture was extracted with CH_2Cl_2 at three times. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to provide the desired product.

2q was from boronic acid, which was obtained by hydrolysis of commercial boronic acid pinacol ester according to previously reported hydrolysis procedure.[2]



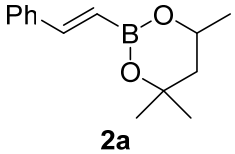
2w was prepared according to previously reported procedure.[3]

2x was prepared from boronic acid, which was obtained according to previously reported procedure.[4]



Characterization data for alkenylboronate esters

(*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane (2a)

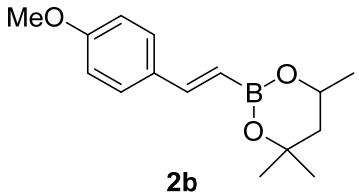


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.35 – 7.21 (m, 4H), 6.11 (d, *J* = 18.3 Hz, 1H), 4.33 – 4.23 (m, 1H), 1.86 – 1.79 (m, 1H), 1.61 – 1.51 (m, 1H), 1.38 – 1.29 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 138.0, 128.4, 128.3, 126.9 70.9, 64.8, 46.0, 31.3, 28.1, 23.2.

HRMS (ESI) m/z calcd. for $C_{14}H_{20}BO_2$ $[M+H]^+$ 231.1551, found 231.1545.

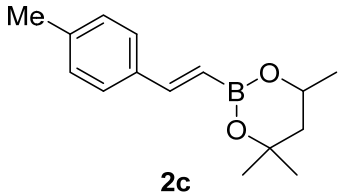
(*E*)-2-(4-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2b)



2b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.26 (d, *J* = 18.2 Hz, 1H), 6.85 – 6.80 (m, 2H), 5.95 (d, *J* = 18.2 Hz, 1H), 4.29 – 4.19 (m, 1H), 3.75 (s, 3H), 1.80 – 1.73 (m, 1H), 1.56 – 1.45 (m, 1H), 1.35 – 1.25 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 145.9, 130.8, 128.1, 113.7, 70.6, 64.6, 55.0, 45.9, 31.2, 28.0, 23.1.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}BO_3$ $[M+H]^+$ 261.1657, found 261.1660.

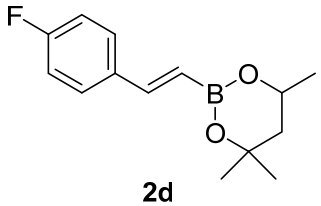
(*E*)-4,4,6-trimethyl-2-(4-methylstyryl)-1,3,2-dioxaborinane (2c)



2c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 18.0 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.05 (d, *J* = 18.2 Hz, 1H), 4.33 – 4.21 (m, 1H), 2.33 (s, 1H), 1.86 – 1.78 (m, 1H), 1.60 – 1.49 (m, 1H), 1.37 – 1.27 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 138.2, 135.3, 129.3, 126.9, 70.8, 64.8, 46.0, 31.3, 28.1, 23.2, 21.3.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}BO_2$ $[M+H]^+$ 245.1707, found 245.1710.

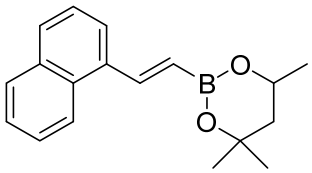
(*E*)-2-(4-fluorostyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2d)



2d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.25 (d, *J* = 18.2 Hz, 1H), 7.03 – 6.95 (m, 2H), 6.01 (d, *J* = 18.2 Hz, 1H), 4.31 – 4.21 (m, 1H), 1.84 – 1.77 (m, 1H), 1.58 – 1.49 (m, 1H), 1.35 – 1.28 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, J_{C-F} = 247.7 Hz), 145.1, 134.2 (d, J_{C-F} = 3.2 Hz), 128.5 (d, J_{C-F} = 8.0 Hz), 115.3 (d, J_{C-F} = 21.5 Hz), 70.9, 64.8, 46.0, 31.2, 28.1, 23.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.48.
HRMS (ESI) m/z calcd. for $C_{14}H_{19}BFO_2$ $[M+H]^+$ 249.1457, found 249.1457.

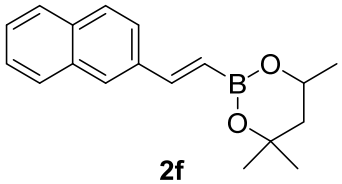
(*E*)-4,4,6-trimethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborinane (2e)



2e

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.9 Hz, 1H), 8.11 (d, *J* = 17.9 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.55 – 7.40 (m, 3H), 6.19 (d, *J* = 17.9 Hz, 1H), 4.37 – 4.27 (m, 1H), 1.89 – 1.81 (m, 1H), 1.65 – 1.55 (m, 1H), 1.42 – 1.31 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 135.9, 133.6, 131.2, 128.41, 128.42, 125.9, 125.6, 123.90, 123.86, 70.9, 64.9, 46.0, 31.3, 28.2, 23.2.
HRMS (ESI) m/z calcd. for $C_{18}H_{22}BO_2$ $[M+H]^+$ 281.1707, found 281.1705.

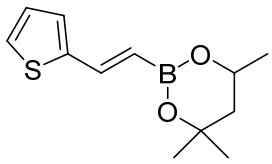
(*E*)-4,4,6-trimethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborinane (2f)



2f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 4H), 7.70 (m, 1H), 7.51 – 7.41 (m, 3H), 6.23 (d, *J* = 18.2 Hz, 1H), 4.36 – 4.25 (m, 1H), 1.87 – 1.80 (m, 1H), 1.63– 1.51 (m, 1H), 1.40 – 1.30 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 135.5, 133.54, 133.49, 128.3, 128.1, 127.6, 127.5, 126.12, 126.05, 123.7, 70.9, 64.9, 46.0, 31.3, 28.2, 23.2.
HRMS (ESI) m/z calcd. for $C_{18}H_{22}BO_2$ $[M+H]^+$ 281.1707, found 281.1707.

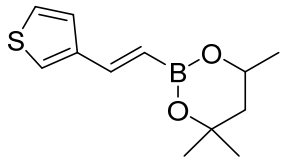
(*E*)-4,4,6-trimethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborinane (2g)



2g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 17.9 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.04 (d, *J* = 2.9 Hz, 1H), 6.98 – 6.94 (m, 1H), 5.86 (d, *J* = 17.9 Hz, 1H), 4.31 – 4.20 (m, 1H), 1.84 – 1.78 (m, 1H), 1.59 – 1.49 (m, 2H), 1.35 – 1.28 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 138.9, 127.4, 126.8, 125.5, 70.9, 64.8, 46.0, 31.2, 28.1, 23.2.
HRMS (ESI) m/z calcd. for $C_{12}H_{18}BO_2S$ $[M+H]^+$ 237.1115, found 237.1117.

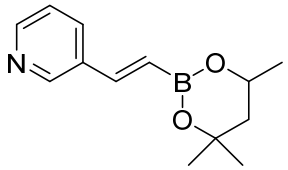
(*E*)-4,4,6-trimethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborinane (2h)



2h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 4H), 5.89 (d, *J* = 18.1 Hz, 1H), 4.31 – 4.21 (m, 1H), 1.84 – 1.77 (m, 1H), 1.58 – 1.49 (m, 1H), 1.35 – 1.27 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 140.2, 125.7, 125.2, 123.8, 70.8, 64.8, 46.0, 31.2, 28.1, 23.2.
HRMS (ESI) m/z calcd. for $C_{12}H_{18}BO_2S$ $[M+H]^+$ 237.1115, found 237.1117.

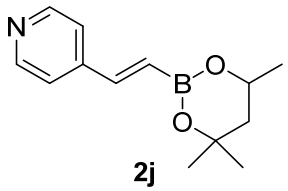
(*E*)-3-(2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)pyridine (2i)



2i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 2.3 Hz, 1H), 8.47 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.31 – 7.21 (m, 2H), 6.19 (d, *J* = 18.3 Hz, 1H), 4.33 – 4.23 (m, 1H), 1.87 – 1.79 (m, 1H), 1.60 – 1.50 (m, 1H), 1.37 – 1.28 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.9, 142.5, 133.3, 132.9, 123.3, 70.9, 64.8, 45.8, 31.1, 28.0, 23.0.
HRMS (ESI) m/z calcd. for $C_{13}H_{19}BNO_2$ $[M+H]^+$ 232.1503, found 232.1505.

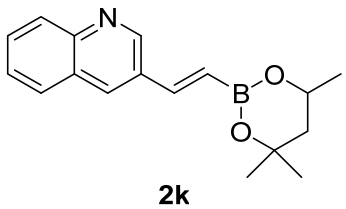
(*E*)-4-(2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)pyridine (2j)



2j

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.53 (m, 2H), 7.35 – 7.29 (m, 2H), 7.20 (d, *J* = 18.2 Hz, 1H), 6.32 (d, *J* = 18.2 Hz, 1H), 4.34 – 4.24 (m, 1H), 1.88 – 1.81 (m, 1H), 1.61 – 1.51 (m, 1H), 1.38 – 1.30 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 145.0, 143.6, 121.2, 71.2, 65.1, 45.9, 31.2, 28.1, 23.1.
HRMS (ESI) m/z calcd. for $C_{13}H_{19}BNO_2$ $[M+H]^+$ 232.1503, found 232.1505.

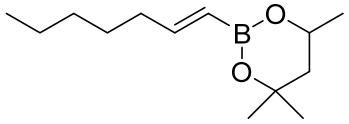
(*E*)-3-(2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)quinoline (2k)



2k

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 2.2 Hz, 1H), 8.14 (d, *J* = 2.2 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.57 – 7.49 (m, 1H), 7.45 (d, *J* = 18.3 Hz, 1H), 6.36 (d, *J* = 18.3 Hz, 1H), 4.36 – 4.27 (m, 1H), 1.90 – 1.81 (m, 1H), 1.63 – 1.57 (m, 1H), 1.41 – 1.31 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 147.9, 142.9, 133.3, 130.7, 129.4, 129.2, 128.1, 128.0, 126.9, 71.1, 65.0, 46.0, 31.2, 28.2, 23.2.
HRMS (ESI) m/z calcd. for $C_{17}H_{21}BNO_2$ $[M+H]^+$ 282.1660, found 282.1662.

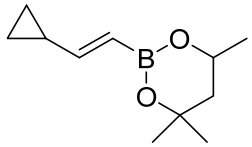
(*E*)-2-(hept-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2l)



2l

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 – 6.46 (m, 1H), 5.34 (d, *J* = 17.7 Hz, 1H), 4.26 – 4.15 (m, 1H), 2.17 – 2.06 (m, 2H), 1.82 –1.77 (m, 1H), 1.55 – 1.36 (m, 3H), 1.35 – 1.21 (m, 13H), 0.88 (t, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 70.5, 64.5, 46.0, 35.4, 31.5, 31.2, 28.1, 23.2, 22.5, 14.0.
HRMS (ESI) m/z calcd. for $C_{13}H_{26}BO_2$ $[M+H]^+$ 225.2020, found 225.2024.

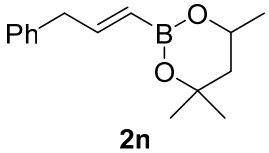
(*E*)-2-(2-cyclopropylvinyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2m)



2m

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (dd, *J* = 17.6, 9.1 Hz, 1H), 5.40 (d, *J* = 17.4 Hz, 1H), 4.24 – 4.14 (m, 1H), 1.80 – 1.72 (m, 1H), 1.53 – 1.43 (m, 2H), 1.33 – 1.21 (m, 9H), 0.80 – 0.72 (m, 2H), 0.54 – 0.46 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 70.5, 64.5, 46.0, 31.2, 28.0, 23.2, 16.5, 7.6.
HRMS (ESI) m/z calcd. for $C_{11}H_{20}BO_2$ $[M+H]^+$ 195.1551, found 195.1554.

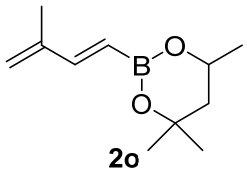
(*E*)-4,4,6-trimethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane (2n)



2n

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 6.65 (td, *J* = 17.6, 6.4 Hz, 1H), 5.37 (td, *J* = 17.6, 1.6 Hz, 1H), 4.25 – 4.14 (m, 1H), 3.44 (dd, *J* = 6.4, 1.6 Hz, 2H), 1.79 – 1.72 (m, 1H), 1.52 – 1.44 (m, 1H), 1.30 – 1.22 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 139.7, 128.9, 128.4, 126.0, 70.6, 64.6, 45.9, 42.0, 31.2, 28.1, 23.1.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}BO_2$ $[M+H]^+$ 245.1707, found 245.1711.

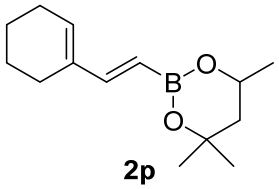
(*E*)-4,4,6-trimethyl-2-(3-methylbuta-1,3-dien-1-yl)-1,3,2-dioxaborinane (2o)



2o

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 18.0 Hz, 1H), 5.49 (d, *J* = 18.0 Hz, 1H), 5.12 – 5.08 (m, 2H), 4.29 – 4.18 (m, 1H), 1.84 (s, 3H), 1.82 – 1.76 (m, 1H), 1.56 – 1.46 (m, 1H), 1.35 – 1.25 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 143.3, 118.7, 70.7, 64.7, 46.0, 31.2, 28.1, 23.1, 18.0.
HRMS (ESI) m/z calcd. for $C_{11}H_{20}BO_2$ $[M+H]^+$ 195.1551, found 195.1546.

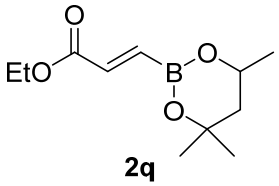
(*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2p)



2p

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 18.0 Hz, 1H), 5.94 – 5.86 (m, 1H), 5.36 (d, *J* = 18.0 Hz, 1H), 4.28 – 4.17 (m, 1H), 2.19 – 2.10 (m, 4H), 1.82 – 1.74 (m, 1H), 1.69 – 1.41 (m, 5H), 1.35 – 1.23 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 137.3, 132.7, 70.6, 64.6, 46.0, 31.3, 28.1, 26.1, 24.0, 23.2, 22.50, 22.45.
HRMS (ESI) m/z calcd. for $C_{14}H_{24}BO_2$ $[M+H]^+$ 235.1864, found 235.1866.

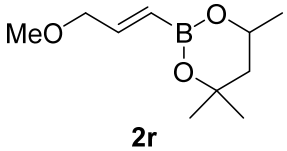
Ethyl (*E*)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate (2q)



2q

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 18.0 Hz, 1H), 6.54 (d, *J* = 18.0 Hz, 1H), 4.30 – 4.15 (m, 3H), 1.86 –1.79 (m, 1H), 1.57 – 1.47 (m, 1H), 1.34 – 1.23 (m, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 136.0, 71.3, 65.1, 60.3, 45.8, 31.0, 28.0, 22.9, 14.2.
HRMS (ESI) m/z calcd. for $C_{11}H_{20}BO_4$ $[M+H]^+$ 227.1449, found 227.1451.

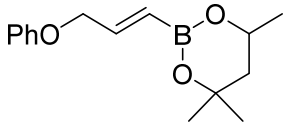
(*E*)-2-(3-methoxyprop-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2r)



2r

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (td, *J* = 17.9, 5.1 Hz, 1H), 5.58 (td, *J* = 17.9, 1.6 Hz, 1H), 4.27 – 4.17 (m, 1H), 3.98 (dd, *J* = 5.1, 1.6 Hz, 2H), 3.34 (s, 3H), 1.82 – 1.75 (m, 1H), 1.54 – 1.45 (m, 1H), 1.31 – 1.23 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 74.5, 70.7, 64.7, 58.1, 45.9, 31.2, 28.1, 23.1.
HRMS (ESI) m/z calcd. for $C_{10}H_{20}BO_3$ $[M+H]^+$ 199.1500, found 199.1503.

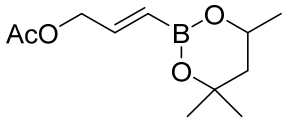
(*E*)-4,4,6-trimethyl-2-(3-phenoxyprop-1-en-1-yl)-1,3,2-dioxaborinane (2s)



2s

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 6.96 – 6.87 (m, 3H), 6.66 (td, *J* = 17.9, 4.7 Hz, 1H), 5.73 (td, *J* = 17.9, 1.7 Hz, 1H), 4.58 (dd, *J* = 4.8, 1.8 Hz, 2H), 4.27 – 4.17 (m, 1H), 1.82 – 1.74 (m, 1H), 1.55 – 1.45 (m, 1H), 1.34 – 1.23 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 143.9, 129.4, 120.6, 114.7, 70.8, 69.5, 64.8, 45.9, 31.2, 28.1, 23.1.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}BO_3$ $[M+H]^+$ 261.1657, found 261.1661.

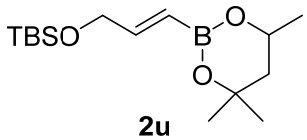
(*E*)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)allyl acetate (2t)



2t

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 – 6.41 (m, 1H), 5.59 (m, 1H), 4.62 (m, 2H), 4.27 – 4.16 (m, 1H), 2.08 (d, *J* = 1.7 Hz, 3H), 1.83 –1.76 (m, 1H), 1.55 – 1.45 (m, 1H), 1.33 – 1.23 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 142.5, 70.8, 65.8, 64.8, 45.9, 31.1, 28.0, 23.0, 20.8.
HRMS (ESI) m/z calcd. for $C_{11}H_{20}BO_4$ $[M+H]^+$ 227.1449, found 227.1450.

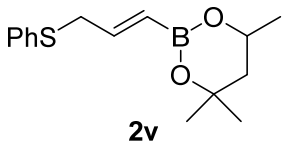
(*E*)-tert-butyldimethyl((3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)allyl)oxy)silane (2u)



2u

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (td, *J* = 17.7, 4.1 Hz, 1H), 5.61 (td, *J* = 17.7, 2.0 Hz, 1H), 4.27 – 4.14 (m, 3H), 1.82 – 1.74 (m, 1H), 1.53 – 1.44 (m, 1H), 1.32 – 1.23 (m, 9H), 0.91 (s, 9H), 0.06 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 70.6, 64.9, 64.6, 46.0, 31.2, 28.1, 26.0, 23.2, 18.4, -5.3.
HRMS (ESI) m/z calcd. for $C_{15}H_{32}BO_3Si$ $[M+H]^+$ 299.2208, found 299.2210.

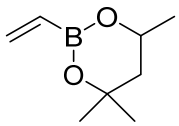
(*E*)-4,4,6-trimethyl-2-(3-(phenylthio)prop-1-en-1-yl)-1,3,2-dioxaborinane (2v)



2v

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 4H), 7.19 – 7.11 (m, 1H), 6.52 (td, *J* = 17.4, 6.6 Hz, 1H), 5.52 (td, *J* = 17.4, 1.4 Hz, 1H), 4.24 – 4.14 (m, 1H), 3.61 (dd, *J* = 6.6, 1.4 Hz, 2H), 1.80 – 1.73 (m, 1H), 1.52 – 1.43 (m, 1H), 1.30 – 1.21 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 136.6, 128.8, 128.7, 125.7, 70.8, 64.7, 45.9, 38.2, 31.2, 28.1, 23.1.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}BO_2S$ $[M+H]^+$ 277.1428, found 277.1432.

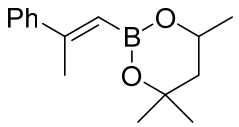
4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane (2w)



2w

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 – 5.99 (m, 1H), 5.91 – 5.72 (m, 2H), 4.28 – 4.17 (m, 1H), 1.83 – 1.75 (m, 1H), 1.56 – 1.46 (m, 1H), 1.32 – 1.24 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.8, 70.7, 64.7, 45.9, 31.2, 28.1, 23.1.
HRMS (ESI) m/z calcd. for $C_8H_{16}BO_2$ $[M+H]^+$ 155.1238, found 155.1240.

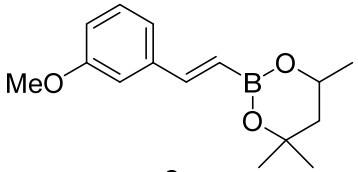
(*E*)-4,4,6-trimethyl-2-(2-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane (2x)



2x

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.35 – 7.19 (m, 3H), 5.66 (s, 1H), 4.34 – 4.24 (m, 1H), 2.38 (s, 3H), 1.86 – 1.78 (m, 1H), 1.61 – 1.52 (m, 2H), 1.37 – 1.28 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 144.7, 128.0, 127.4, 125.8, 70.9, 64.8, 45.9, 31.4, 28.3, 23.3, 19.3.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}BO_2$ $[M+H]^+$ 245.1707, found 245.1712.

(*E*)-2-(3-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane

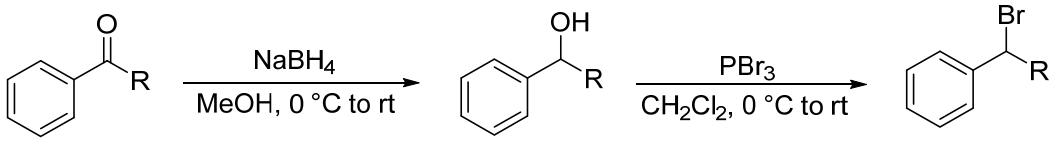


2y

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 2H), 7.10 – 7.02 (m, 2H), 6.84 – 6.79 (m, 1H), 6.10 (d, J = 18.2 Hz, 1H), 4.37 – 4.19 (m, 1H), 3.80 (s, 3H), 1.85 – 1.78 (m, 1H), 1.59 – 1.50 (m, 1H), 1.37 – 1.28 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 146.3, 139.4, 129.3, 119.8, 114.4, 111.4, 70.8, 64.8, 55.1, 45.9, 31.2, 28.1, 23.1.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}BO_3$ $[M+H]^+$ 261.1657, found 261.1651.

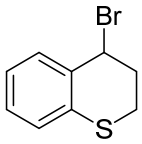
The synthesis of benzyl/propargyl halides
The synthesis of benzyl bromides



To a solution of ketone (3.0 mmol) in MeOH (9.0 mL) was added $NaBH_4$ (136.2 mg, 3.6 mmol) at ice bath and the reaction mixture was stirred at room temperature for 0.5–2 h. After completion of reaction (monitored by TLC), the reaction was quenched by water, and the mixture was extracted with CH_2Cl_2 three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the corresponding alcohol. The crude product was purified by flash chromatography on silica gel to provide the desired product.

To a solution of the residue obtained above in CH_2Cl_2 (9.0 mL) was added PBr_3 (0.20 mL, 2.1 mmol) under an argon atmosphere at ice water bath and the resulting reaction mixture was stirred at room temperature. After completion of reaction (monitored by TLC), the mixture was quenched by water at ice water bath, and the mixture was extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the corresponding crude benzyl bromides, which was directly used in the next step without further purification or stored in a refridgerator.
S58, **S59** were prepared according to the above procedure.
Benzyl bromide **1d** was purchased form Bide Pharmatech.
Other benzyl bromides were prepared according to previously reported procedure.[5,6]

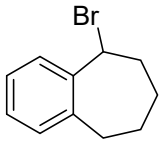
4-bromothiochromane (S58):



S58

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 7.7 Hz, 1H), 7.12 – 6.87 (m, 3H), 3.70 (t, J = 12.8 Hz, 1H), 2.92 – 2.87 (m, 1H), 2.65 – 2.59 (m, 1H), 2.35 – 2.27 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.4, 128.8, 126.6, 124.1, 49.7, 31.4, 22.6.
HRMS (APCI) *m/z* calcd. for C_9H_9S $[M-Br]^+$ 149.0420, found 149.0418.

5-bromo-6,7,8,9-tetrahydro-5H-benzo[7]annulene (S59):

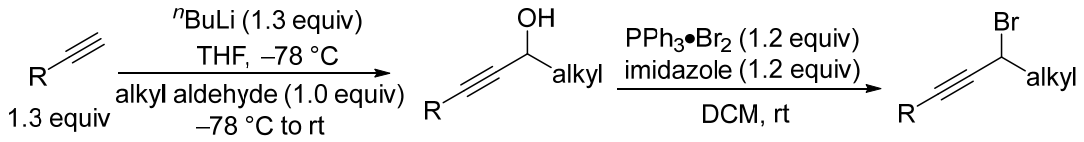


S59

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 2H), 7.12 – 7.06 (m, 2H), 5.47 – 5.45 (m, 1H), 3.30 – 3.23 (m, 1H), 2.77 – 2.69 (m, 1H), 2.39 – 2.21 (m, 2H), 2.07 – 1.99 (m, 1H), 1.98 – 1.85 (m, 2H), 1.49 – 1.38 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 130.8, 128.9, 128.6, 126.0, 60.1, 36.4, 35.7, 28.0, 27.3.
HRMS (APCI) *m/z* calcd. for $C_{11}H_{13}$ $[M\text{-}Br]^+$ 145.1012, found 145.1009.

The synthesis of propargyl bromides

The propargyl bromides were prepared according to previously reported procedure.[7]



^{n}BuLi (2.4 M in hexane, 1.3 equiv) was added dropwise into a solution of alkynes (1.3 equiv) in anhydrous THF (1 M) at −78 °C. The mixture was stirred at room temperature for 30 min and cooled to −78 °C. Aldehyde (1.0 equiv) was added dropwise. Then the mixture was warmed up to room temperature and stirred for overnight. The mixture was quenched by a saturated NH_4Cl aqueous solution, extracted with EtOAc, and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure and then subjected to flash chromatography to afford the desired product.

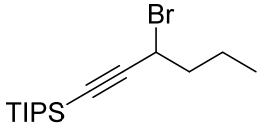
Under an argon atmosphere, to a solution of imidazole (1.2 equiv) in dry CH_2Cl_2 (1 M) was added propargyl alcohol (1.0 equiv). The solution was stirred for 15 min, followed by the addition of dibromotriphenylphosphorane (1.2 equiv). The reaction mixture was stirred at room temperature overnight. Then the reaction was quenched by the addition of silica gel. The solvent was removed under reduced pressure, and then the plug of silica gel was subjected to flash chromatography to afford the desired product.

S65, **S70, S71**, **S74**, **S75**, **S77**, **S80**, **S82, S83, S84** were prepared according to the above procedure.

Other propargyl bromides were prepared according to previously reported procedure.[5,7-10]

Propargyl chloride was prepared according to previously reported procedure.[7]

(3-bromohex-1-yn-1-yl)triisopropylsilane (S65):

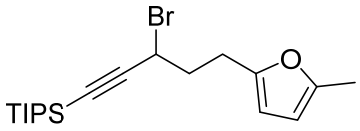


S65

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 (t, *J* = 6.8 Hz, 1H), 2.06 – 1.92 (m, 2H), 1.63 –

1.53 (m, 2H), 1.07 (s, 21H), 0.96 (t, J = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 106.0, 88.6, 41.8, 37.3, 20.7, 18.5, 13.2, 11.2.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{30}BrSi$ $[M+H]^+$ 317.1295, found 317.1296.

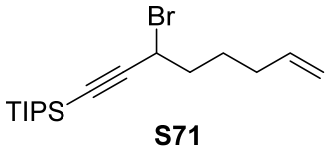
(3-bromo-5-(5-methylfuran-2-yl)pent-1-yn-1-yl)triisopropylsilane (S70):



S70

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 – 5.80 (m, 2H), 4.51 – 4.37 (m, 1H), 2.81 (t, J = 7.6 Hz, 2H), 2.27 (s, 3H), 2.15 – 2.00 (m, 2H), 1.08 – 1.07 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 150.5, 108.3, 105.79, 105.76, 85.9, 62.2, 36.3, 23.8, 18.5, 13.5, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{32}BrOSi$ $[M+H]^+$ 383.1400, found 383.1393.

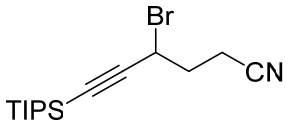
(3-bromooct-7-en-1-yn-1-yl)triisopropylsilane (S71):



S71

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 – 5.74 (m, 1H), 5.11 – 4.93 (m, 2H), 4.55 (t, J = 6.7 Hz, 1H), 2.15 – 1.95 (m, 4H), 1.74 – 1.60 (m, 2H), 1.07 (s, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 115.1, 105.8, 88.8, 39.2, 37.2, 32.7, 26.5, 18.6, 11.2.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{31}Si$ $[M-Br]^+$ 263.2190, found 263.2186.

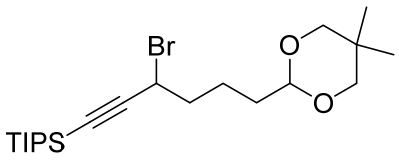
4-bromo-6-(triisopropylsilyl)hex-5-ynenitrile (S74):



S74

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (t, J = 6.1 Hz, 1H), 2.72 – 2.62 (m, 2H), 2.38 – 2.33 (m, 2H), 1.08 – 1.07 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 118.3, 103.2, 91.2, 35.0, 34.2, 18.5, 15.1, 11.0.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{27}BrNSi$ $[M+H]^+$ 328.1091, found 328.1086.

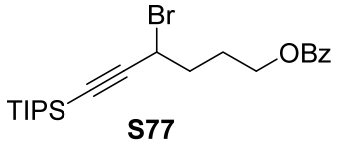
(3-bromo-6-(5,5-dimethyl-1,3-dioxan-2-yl)hex-1-yn-1-yl)triisopropylsilane (S75):



S75

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (t, *J* = 6.7 Hz, 1H), 4.42 (t, *J* = 4.4 Hz, 1H), 3.58 (d, *J* = 10.9 Hz, 2H), 3.41 (d, *J* = 10.9 Hz, 2H), 2.14 – 1.94 (m, 2H), 1.82 – 1.59 (m, 4H), 1.18 (s, 3H), 1.07 (s, 21H), 0.72 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 105.8, 101.7, 88.8, 77.2, 39.6, 37.2, 33.7, 30.1, 23.0, 21.9, 21.8, 18.5, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{40}BrO_2Si$ $[M+H]^+$ 431.1975, found 431.1969.

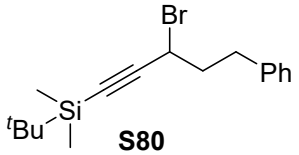
4-bromo-6-(triisopropylsilyl)hex-5-yn-1-yl benzoate (S77):



S77

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.62 – 7.53 (m, 1H), 7.49 – 7.41 (m, 2H), 4.65 (t, *J* = 6.4 Hz, 1H), 4.40 – 4.36 (m, 2H), 2.23 – 2.17 (m, 2H), 2.12 – 2.02 (m, 2H), 1.07 (s, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 133.0, 130.1, 129.6, 128.4, 105.2, 89.4, 63.9, 36.6, 26.6, 18.5, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{34}BrO_2Si$ $[M+H]^+$ 437.1506, found 437.1499.

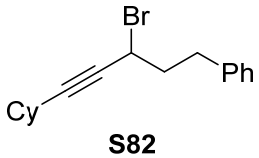
(3-bromo-5-phenylpent-1-yn-1-yl)(tert-butyl)dimethylsilane (S80):



S80

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.17 (m, 3H), 4.45 (t, *J* = 6.8 Hz, 1H), 2.91 – 2.81 (m, 2H), 2.37 – 2.22 (m, 2H), 0.96 (s, 9H), 0.13 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 128.6, 126.3, 104.2, 90.9, 41.2, 36.4, 33.4, 26.0, 16.6, -4.8.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{25}Si$ $[M-Br]^+$ 257.1720, found 257.1718.

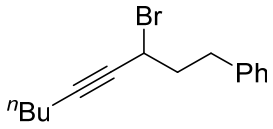
(3-bromo-5-cyclohexylpent-4-yn-1-yl)benzene (S82):



S82

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 4.51 (td, *J* = 6.7, 2.0 Hz, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.50 – 2.43 (m, 1H), 2.35 – 2.24 (m, 2H), 1.83 – 1.66 (m, 4H), 1.54 – 1.40 (m, 3H), 1.35 – 1.26 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 128.52, 128.48, 126.2, 92.7, 79.1, 41.8, 37.8, 33.5, 32.33, 32.31, 29.1, 25.8, 24.7.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{21}$ $[M-Br]^+$ 225.1638, found 225.1634.

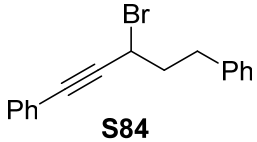
(3-bromonon-4-yn-1-yl)benzene (S83):



S83

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 4.52 – 4.47 (m, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.32 – 2.25 (m, 4H), 1.60 – 1.33 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 128.5, 128.5, 126.2, 88.8, 79.0, 41.7, 37.8, 33.5, 30.5, 21.9, 18.6, 13.6.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{19}$ $[M\text{-}Br]^+$ 199.1481, found 199.1479.

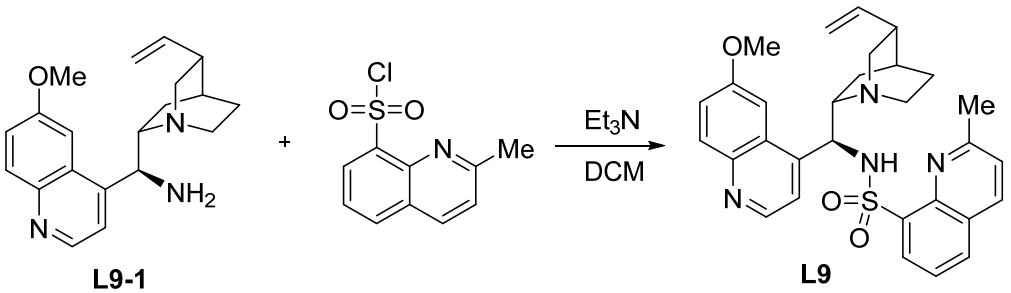
(3-bromopent-1-yne-1,5-diyl)dibenzene (S84):



S84

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.37 – 7.27 (m, 5H), 7.25 – 7.19 (m, 3H), 4.71 (t, *J* = 6.7 Hz, 1H), 2.95 – 2.91 (m, 2H), 2.45 – 2.39 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 131.8, 128.8, 128.6, 128.3, 126.3, 87.7, 87.26. 41.3, 37.1, 33.5.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{15}$ $[M\text{-}Br]^+$ 219.1168, found 219.1165.

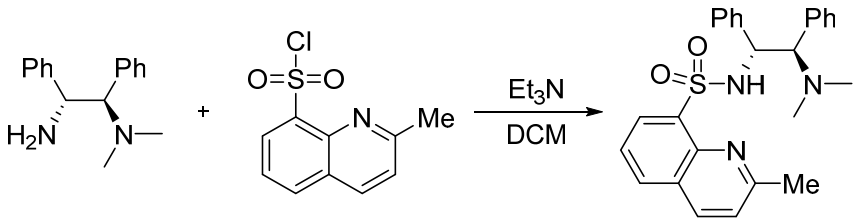
The synthesis of optimal chiral ligand L9 and L11.



L9-1 **L9**

Quinine-derived chiral amine **L9-1** was prepared from quinine according to the previously reported literature procedure.[11] Under an argon atmosphere, chiral amine **L9-1** (857.1 mg, 2.65 mmol) was dissolved in CH_2Cl_2 (6.0 mL), followed by the addition of triethylamine (402.2 mg, 3.98 mmol) and 2-methylquinoline-8-sulfonyl chloride (672.5 mg, 2.78 mmol) at ice water bath. The reaction mixture was allowed to warm up to room temperature and stirred overnight. After completion of the reaction, water was poured to above mixture, and the mixture was extracted with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 to ethyl acetate as eluent to provide the product **L9** as a white solid (1.064 g, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 – 8.55 (m, 0.72H+0.27H), 8.25 – 8.07 (m, 0.72H×2+0.27H×2), 8.03 – 7.98 (m, 0.72H×2+0.27H×3), 7.65 (d, *J* = 5.0 Hz, 0.72H), 7.54 – 7.31 (m, 0.72H×3+0.27H×3), 7.09 (s, 0.72H), 5.70 – 5.47 (m, 1H), 4.89 (d, *J* = 16.1 Hz, 2H), 4.65 (d, *J* = 10.4 Hz, 0.72H), 4.00 – 3.75 (m, 0.72H×3+0.27H×4),3.42 (0.27H) 3.20 – 2.62 (m, 72H×6+0.27H×5), 2.10 (s, 1H), 1.69 (d, *J* = 43.5 Hz, 2H), 1.54 – 1.39(s, 1H), 1.31 – 1.07 (m, 3H), 0.68 – 0.50 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 157.5, 157.0, 147.6, 146.7, 145.1, 144.8, 144.2, 142.8, 141.7, 141.1, 136.4, 135.0, 133.0, 132.9, 131.7, 131.1, 130.7, 128.3, 127.2, 126.7, 124.3, 124.1, 123.0, 121.1, 120.7, 119.8, 114.4, 103.8, 100.9, 62.9, 61.3, 56.8, 55.7, 55.2, 52.8, 39.3, 38.8, 27.6, 27.1, 25.5, 24.8.
HRMS (ESI) m/z calcd. for $C_{30}H_{33}N_4O_3S$ $[M+H]^+$ 529.2268, found: 529.2278.

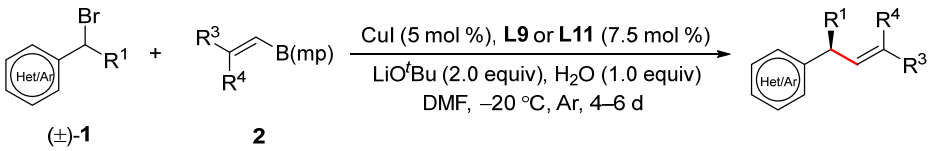


L11

Under an argon atmosphere, commercial (1*R*,2*R*)-*N,N*-dimethyl-1,2-diphenylethane-1,2-diamine (432.6 mg, 1.8 mmol) was dissolved in dichloromethane (5.0 mL), followed by the addition of triethylamine (273.2 mg, 2.7 mmol) and 2-methylquinoline-8-sulfonyl chloride (456.8 mg, 1.9 mmol) at an ice water bath. The reaction mixture was allowed to warm up to room temperature and stirred overnight. After completion of the reaction, water was poured to above mixture, and the mixture was extracted with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 to ethyl acetate as eluent to provide the product **L11** as a white solid (641.7 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 7.3, 1.5 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.96 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.10 – 7.05 (m, 3H), 7.04 – 6.93 (m, 3H), 6.84 – 6.77 (m, 2H), 4.47 (d, *J* = 10.8 Hz, 1H), 3.63 (d, *J* = 10.8 Hz, 1H), 2.88 (s, 3H), 1.58 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 143.2, 140.5, 136.4, 136.1, 132.6, 131.4, 130.5, 129.7, 128.0, 127.5, 127.4, 127.3, 126.84, 126.78, 124.5, 122.9, 73.8, 58.3, 40.1, 25.8.
HRMS (ESI) m/z calcd. for $C_{26}H_{28}N_3O_2S$ $[M+H]^+$ 446.1897, found: 446.1904

Experimental procedures

Copper-Catalyzed Enantioconvergent Radical Cross-Coupling of Benzyl/Propargyl Halides with Alkenylboronate Esters



General procedure A:

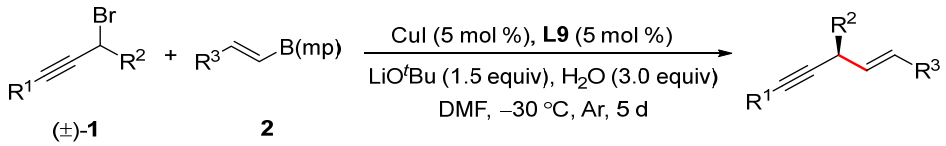
An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI (1.90 mg, 5 mol%), chiral ligand (7.5 mol%), LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv). The tube was evacuated and backfilled with argon three times. Then DMF (2.0 mL) and H_2O (3.6 mg, 1.0 equiv) were added under a counter flow of argon. Finally, alkenylboronate esters (0.2 mmol, 1.0 equiv) and benzyl bromides (0.3 mmol, 1.5 equiv) were added by microsyringe under a counter flow of argon. The tube was sealed and the reaction mixture was allowed to stir at −20 °C for 4−6 d. Upon completion of the reaction (monitored by TLC), the mixture was quenched with water. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the desired product.

General procedure B:

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI (1.90 mg, 5 mol%), chiral ligand (7.5 mol%), LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv) and alkenylboronate esters (0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with argon three times. Then DMF (2.0 mL) and H_2O (3.6 mg, 1.0 equiv) were added under a counter flow of argon. Finally, benzyl bromides (0.3 mmol, 1.5 equiv) was added by microsyringe under a counter flow of argon. The tube was sealed and the mixture was allowed to stir at −20 °C for 4−6 d. Upon completion of the reaction (monitored by TLC), the mixture was quenched with water. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the desired product.

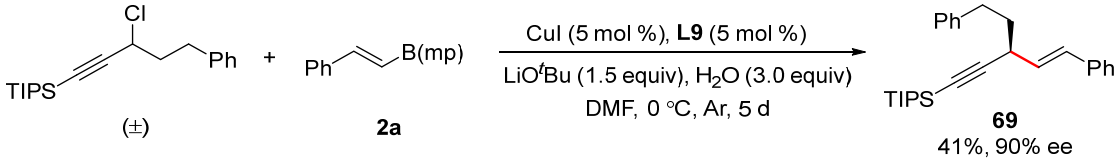
General procedure C:

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI (1.90 mg, 5 mol%), chiral ligand (7.5 mol%), LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv) and benzyl bromides (0.3 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon three times. Then DMF (2.0 mL) and H_2O (3.6 mg, 1.0 equiv) were added under a counter flow of argon. Finally, alkenyl boronates (0.2 mmol, 1.0 equiv) was added by microsyringe under a counter flow of argon. The tube was sealed and the mixture was allowed to stir at −20 °C for 4−6 d. Upon completion of the reaction (monitored by TLC), the mixture was quenched with water. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the desired product.



General procedure D:

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI (1.90 mg, 5 mol%), chiral ligand **L9** (5 mol%), LiO^{t}Bu (24.2 mg, 0.3 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon three times. Then DMF (1.0 mL) and H_2O (10.8 mg, 3.0 equiv) were added by syringe and microsyringe under a counter flow of argon. Finally, alkenyl boronates (0.2 mmol, 1.0 equiv) and propargyl bromides (0.25 mmol, 1.25 equiv) were added by microsyringe under a counter flow of argon. The tube was sealed and the mixture was allowed to stir at –30 °C for 5 d. Upon completion of the reaction (monitored by TLC), the mixture was quenched with water. The mixture was extracted with dichloromethane (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the desired product.



General procedure E:

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI (1.90 mg, 5 mol%), chiral ligand **L9** (5 mol%), LiO^{t}Bu (24.2 mg, 0.3 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon three times. Then DMF (1.0 mL) and H_2O (10.8 mg, 3.0 equiv) were added by syringe and microsyringe under a counter flow of argon. Finally, alkenyl boronates **2a** (0.2 mmol, 1.0 equiv) and propargyl chloride (0.25 mmol, 1.25 equiv) were added by microsyringe under a counter flow of argon. The tube was sealed and the mixture was allowed to stir at 0 °C for 5 d. Upon completion of the reaction (monitored by TLC), the mixture was quenched with water. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the desired product **69** (33.0 mg, 41% yield, 90% ee).

Determination of absolute configuration

The absolute configuration of **3** was determined by comparing the HPLC spectrum and specific rotation with those reported in literature.[5] Measured specific rotation of **3**: $[\alpha]_D^{22}$ = –40.30 (c 0.71 CH_2Cl_2, 95% ee), Reported specific optical rotation of **3**: $[\alpha]_D^{27}$ = –24 (c 0.71 CH_2Cl_2, 96% ee).[5] The product **3** was determined to be of an *S* absolute configuration according to the reported data.

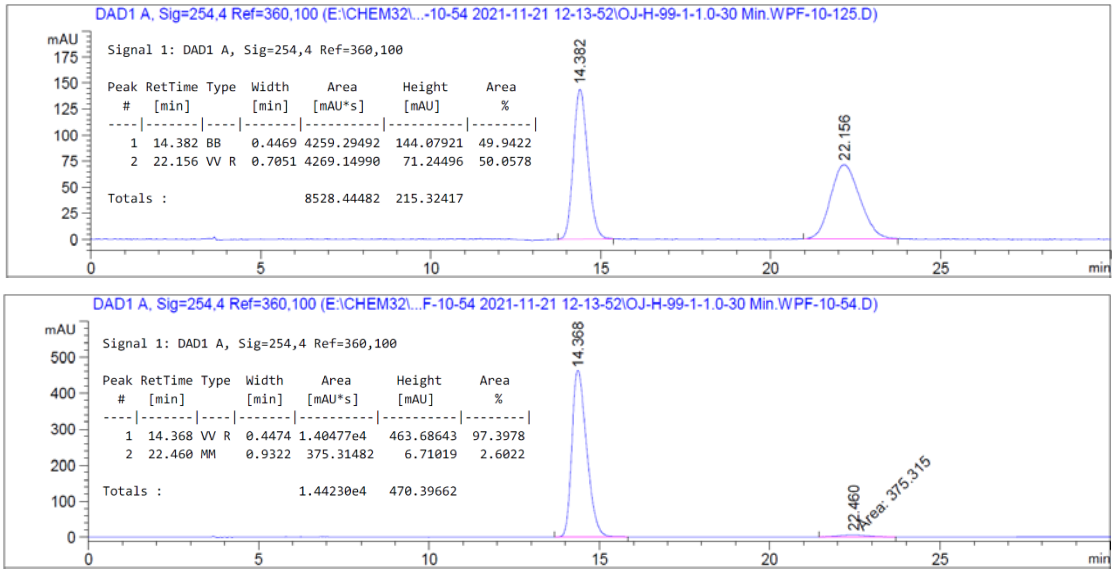
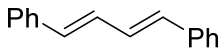


Figure S1. Determination of absolute stereochemistry

Characteristic data of side products and products

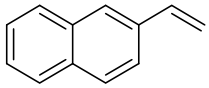
(1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (3')[12]



3'

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 4H), 7.38 – 7.29 (m, 4H), 7.28 – 7.19 (m, 2H), 7.01 – 6.90 (m, 2H), 6.73 – 6.62 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 132.8, 129.2, 128.7, 127.6, 126.4.

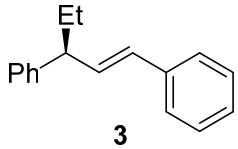
2-vinylnaphthalene (8')[13]



8'

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 3H), 7.75 (s, 1H), 7.64 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.49 – 7.40 (m, 2H), 6.93 – 6.83 (m, 1H), 5.87 (d, *J* = 17.6 Hz, 1H), 5.37 – 5.31 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 135.0, 133.5, 133.1, 128.1, 128.0, 127.7, 126.4, 126.2, 125.9, 123.2, 114.2.

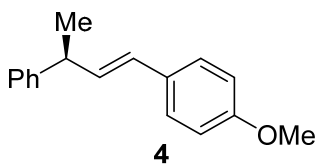
(*S*,*E*)-pent-1-ene-1,3-diyldibenzene (3)



3

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) for 4 d. the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **3** as a colorless oil (35.4 mg, 80% yield, 95% ee).
HPLC analysis: Chiralcel OJ-H (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 14.36 min, t_R (minor) = 22.46 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.13 (m, 10H), 6.45 – 6.26 (m, 2H), 3.31 (q, *J* = 7.3 Hz, 1H), 1.90 –1.76 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 137.6, 134.2, 129.4, 128.4, 127.7, 127.0, 126.2, 126.1, 51.0, 28.8, 12.3.
HRMS (APCI) m/z calcd. for $C_{17}H_{19}$ $[M+H]^+$ 223.1481, found: 223.1480.

(*S*,*E*)-1-methoxy-4-(3-phenylbut-1-en-1-yl)benzene (4)



4

According to **general produce A** with (1-bromoethyl)benzene **1d** (55.5 mg, 0.30 mmol, 1.5 equiv) and (*E*)-2-(4-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2b** (52.0 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **4** as a colorless oil (34.2 mg, 72% yield, 89% ee).

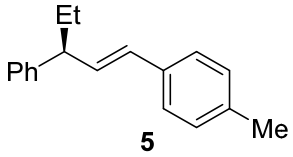
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 14.29 min, t_R(major) = 17.78 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 6H), 7.22 – 7.18 (m, 1H), 6.89 – 6.78 (m, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.24 (dd, *J* = 15.9, 6.7 Hz, 1H), 3.79 (s, 3H), 3.65 – 3.58 (m, 1H), 1.45 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 145.9, 133.1, 130.4, 128.4, 127.8, 127.3, 127.2, 126.1, 113.9, 55.3, 42.5, 21.3.

HRMS (APCI) *m/z* calcd. for $C_{17}H_{19}O$ $[M + H]^+$ 239.1430, found 239.1425.

(*S*,*E*)-1-methyl-4-(3-phenylpent-1-en-1-yl)benzene (5)



5

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-(4-methylstyryl)-1,3,2-dioxaborinane **2c** (48.8 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **5** as a colorless oil (38.3 mg, 81% yield, 95% ee).

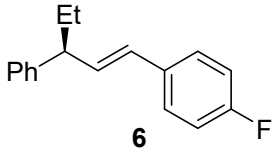
HPLC analysis: Chiralcel OJ-3 (n-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 19.33 min, t_R (minor) = 30.26 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.26 – 7.16 (m, 5H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.42 – 6.22 (m, 2H), 3.29 (q, *J* = 7.4 Hz, 1H), 2.30 (s, 3H), 1.88 – 1.74 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 136.7, 134.8, 133.2, 129.3, 129.1, 128.4, 127.7, 126.1, 126.0, 50.9, 28.8, 21.1, 12.3.

HRMS (APCI) m/z calcd. for $C_{18}H_{21}$ $[M+H]^+$ 237.1638, found: 237.1633.

(*S*,*E*)-1-fluoro-4-(3-phenylpent-1-en-1-yl)benzene (6)

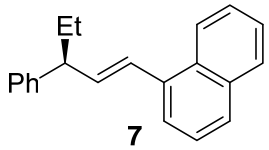


6

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-2-(4-fluorostyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2d** (49.6 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **6** as a colorless oil (36.4 mg, 76% yield, 93% ee).

HPLC analysis: Chiralcel OJ-3 (n-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 20.06 min, t_R (minor) = 29.48 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 4H), 7.25 – 7.17 (m, 3H), 7.00 – 6.92 (m, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.8, 7.7 Hz, 1H), 3.29 (q, *J* = 7.5 Hz, 1H), 1.88 – 1.76 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, J_{C-F} = 245.8 Hz), 144.4, 134.0 (d, J_{C-F} = 2.2 Hz), 133.7 (d, J_{C-F} = 3.3 Hz), 128.5, 128.3, 127.7, 127.5 (d, J_{C-F} = 7.8 Hz), 126.2, 115.3 (d, J_{C-F} = 21.5 Hz), 50.9, 28.8, 12.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.47.
HRMS (APCI) m/z calcd. for $C_{17}H_{18}F$ $[M+H]^+$ 241.1387, found: 241.1383.

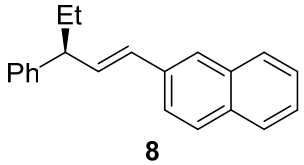
(*S*,*E*)-1-(3-phenylpent-1-en-1-yl)naphthalene (7)



7

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborinane **2e** (56.0 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **7** as a colorless oil (37.8 mg, 69% yield, 93% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 11.37 min, t_R (minor) = 15.60 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.51 – 7.26 (m, 7H), 7.26 – 7.19 (m, 1H), 7.13 (d, *J* = 15.6 Hz, 1H), 6.39 – 6.31 (m, 1H), 3.44 (q, *J* = 7.6 Hz, 1H), 1.97 – 1.82 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 137.5, 135.5, 133.6, 131.2, 128.5, 128.4, 127.7, 127.4, 126.8, 126.2, 125.8, 125.6, 125.6, 123.9, 123.7, 51.3, 29.0, 12.4.
HRMS (APCI) m/z calcd. for $C_{21}H_{21}$ $[M+H]^+$ 273.1638, found: 273.1637.

(*S*,*E*)-2-(3-phenylpent-1-en-1-yl)naphthalene (8)

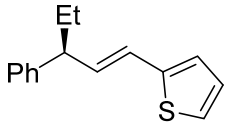


8

According to the **general procedure B** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborinane **2f** (56.0 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **8** as a white solid (39.7 mg, 73% yield, 94% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 33.50 min, t_R (minor) = 39.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 8.3 Hz, 3H), 7.67 (s, 1H), 7.60 – 7.52 (m 1H), 7.46 – 7.36 (m, 2H), 7.36 – 7.25 (m, 4H), 7.21 (m, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.46 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.36 (q, *J* = 7.4 Hz, 1H), 1.95 – 1.79 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 135.1, 134.7, 133.7, 132.7, 129.6, 128.5, 128.00, 127.8, 127.7, 127.6, 126.2, 126.1, 125.7, 125.5, 123.6, 51.1, 28.8, 12.3.
HRMS (APCI) m/z calcd. for $C_{21}H_{21}$ $[M+H]^+$ 273.1638, found: 273.1631.

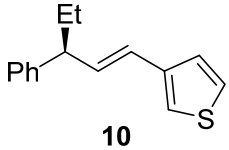
(*S*,*E*)-2-(3-phenylpent-1-en-1-yl)thiophene (9)



9

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborinane **2g** (47.2 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **9** as a colorless oil (32.3 mg, 71% yield, 95% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.25 mL/min, λ = 254 nm), t_R (major) = 58.31 min, t_R (minor) = 62.88 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.27 – 7.17 (m, 3H), 7.08 (d, *J* = 5.1 Hz, 1H), 6.93 – 6.90 (m, 1H), 6.87 (d, *J* = 3.6 Hz, 1H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.18 (dd, *J* = 15.7, 7.7 Hz, 1H), 3.26 (q, *J* = 7.5 Hz, 1H), 1.90 – 1.73 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 142.8, 134.1, 128.5, 127.7, 127.2, 126.2, 124.7, 123.4, 122.7, 50.8, 28.7, 12.3.
HRMS (ESI) m/z calcd. for $C_{15}H_{17}S$ $[M+H]^+$ 229.1045, found: 229.1047.

(*S*,*E*)-3-(3-phenylpent-1-en-1-yl)thiophene (10)

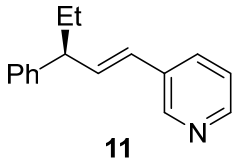


10

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborinane **2h** (47.2 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **10** as a colorless oil (36.9 mg, 81% yield, 95% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 25.67 min, t_R (minor) = 30.15 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.15 (m, 5H), 7.05 (d, *J* = 1.7 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.18 (dd, *J* = 15.9, 7.7 Hz, 1H), 3.26 (q, *J* = 7.6 Hz, 1H), 1.89 – 1.73 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 140.2, 134.2, 128.4, 127.7, 126.2, 125.7, 125.0, 123.7, 120.9, 50.8, 28.7, 12.3.
HRMS (ESI) m/z calcd. for $C_{15}H_{17}S$ $[M+H]^+$ 229.1045, found: 229.1047.

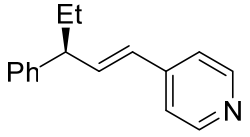
(*S*,*E*)-3-(3-phenylpent-1-en-1-yl)pyridine (11)



11

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-3-(2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)pyridine **2i** (46.2 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to yield the product **11** as a colorless oil (39.0 mg, 87% yield, 89% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 27.19 min, t_R (minor) = 30.06 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.42 (d, *J* = 4.6 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.37 – 7.29 (m, 2H), 7.28 – 7.16 (m, 4H), 6.47 – 6.31 (m, 2H), 3.33 (q, *J* = 7.2 Hz, 1H), 1.91 – 1.79 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.09, 148.05, 143.9, 136.7, 133.1, 132.5, 128.6, 127.6, 126.4, 125.9, 123.3, 51.1, 28.6, 12.2.
HRMS (ESI) m/z calcd. for $C_{16}H_{18}N$ $[M+H]^+$ 224.1434, found: 224.1435.

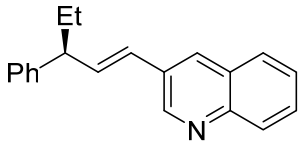
(*S*,*E*)-4-(3-phenylpent-1-en-1-yl)pyridine (12)



12

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4-(2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)pyridine **2j** (46.2 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to yield the product **12** as a colorless oil (33.8 mg, 76% yield, 89% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 14.04 min, t_R (minor) = 27.16 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.15 (m, 5H), 6.58 (dd, *J* = 15.9, 7.8 Hz, 1H), 6.32 (d, *J* = 15.9 Hz, 1H), 3.34 (q, *J* = 7.6 Hz, 1H), 1.91 – 1.79 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 144.9, 143.4, 139.3, 128.6, 127.7, 127.3, 126.5, 120.8, 51.0, 28.5, 12.2.
HRMS (ESI) m/z calcd. for $C_{16}H_{18}N$ $[M+H]^+$ 224.1434, found: 224.1435.

(*S*,*E*)-3-(3-phenylpent-1-en-1-yl)quinoline (13)



13

According to the **general procedure B** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-3-(2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)quinoline **2k** (56.2 mg, 0.20 mmol, 1.0 equiv) for 5.5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to yield the product **13** as a colorless oil (43.7 mg, 80% yield, 86% ee).

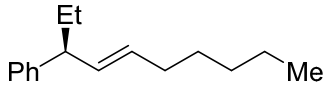
HPLC analysis: Chiralcel AD-3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 28.38 min, t_R (major) = 41.66 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 2.2 Hz, 1H), 8.10 – 7.95 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.58 (m, 1H), 7.53 – 7.43 (m, 1H), 7.39 – 7.31 (m, 2H), 7.31 – 7.20 (m, 3H), 6.63 – 6.48 (m, 2H), 3.38 (q, *J* = 7.2 Hz, 1H), 1.96 – 1.83 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 147.2, 143.9, 136.9, 131.8, 130.4, 129.1, 128.9, 128.6, 128.1, 127.7, 127.6, 126.8, 126.4, 126.3, 51.2, 28.6, 12.3.

HRMS (ESI) m/z calcd. for $C_{20}H_{20}N$ $[M+H]^+$ 274.1590, found: 274.1592.

(*S*,*E*)-dec-4-en-3-ylbenzene (14)



14

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-2-(hept-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2l** (44.8 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **14** as a colorless oil (22.7 mg, 52% yield, 91% ee).

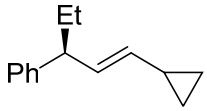
HPLC analysis: Chiralcel OJ (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.3 mL/min, λ = 214 nm), t_R (minor) = 13.74 min, t_R (major) = 14.59 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 5.57 – 5.38 (m, 2H), 3.08 (q, *J* = 7.4 Hz, 1H), 2.03 – 1.95 (m, 2H), 1.74 – 1.64 (m, 2H), 1.39 – 1.20 (m, 6H), 0.90 – 0.82 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 133.7, 130.4, 128.3, 127.5, 125.8, 50.7, 32.6, 31.4, 29.2, 29.0, 22.5, 14.1, 12.2.

HRMS (APCI) m/z calcd. for $C_{16}H_{25}$ $[M+H]^+$ 217.1951, found: 217.1947.

(*S*,*E*)-(1-cyclopropylpent-1-en-3-yl)benzene (15)



15

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-2-(2-cyclopropylvinyl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2m** (38.4 mg, 0.20 mmol, 1.0 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **15** as a colorless oil (23.9 mg, 64% yield, 92% ee).

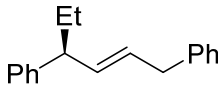
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 214 nm), t_R (major) = 18.41 min, t_R (minor) = 19.34 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 5.69 – 5.58 (m, 1H), 5.30 – 4.92 (m, 1H), 3.06 (q, *J* = 7.5 Hz, 1H), 1.74 – 1.63 (m, 2H), 1.39 – 1.30 (m, 1H), 0.84 (t, *J* = 7.4 Hz, 3H), 0.69 – 0.60 (m, 2H), 0.36 – 0.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 133.7, 131.7, 128.3, 127.6, 125.9, 50.6, 29.1, 13.6, 12.2, 6.54, 6.48.

HRMS (APCI) m/z calcd. for $C_{14}H_{19}$ $[M+H]^+$ 187.1481, found: 187.1477.

(*S*,*E*)-hex-2-ene-1,4-diyldibenzene (16)



16

According to the **general procedure B** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane **2n** (48.9 mg, 0.20 mmol, 1.0 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **16** as a colorless oil (33.5 mg, 71% yield, 92% ee).

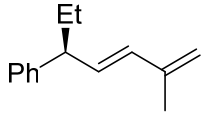
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 13.52 min, t_R (minor) = 20.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.18 (m, 6H), 5.73 – 5.55 (m, 2H), 3.35 (d, *J* = 5.9 Hz, 2H), 3.14 (q, *J* = 7.3 Hz, 1H), 1.77 – 1.66 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 140.8, 135.5, 128.6, 128.5, 128.33, 128.32, 127.6, 126.0, 125.9, 50.6, 39.0, 28.9, 12.3.

HRMS (APCI) m/z calcd. for $C_{18}H_{21}$ $[M+H]^+$ 237.1638, found: 237.1633.

(*S*,*E*)-(6-methylhepta-4,6-dien-3-yl)benzene (17)



17

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-(3-methylbuta-1,3-dien-1-yl)-1,3,2-

dioxaborinane **2o** (38.8 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **17** as a colorless oil (23.5 mg, 63% yield, 93% ee).

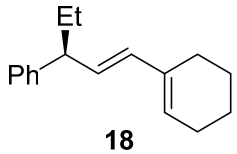
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.4 mL/min, λ = 230 nm), t_R (major) = 12.08 min, t_R (minor) = 14.20 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 6.15 (d, *J* = 15.7 Hz, 1H), 5.76 (dd, *J* = 15.6, 7.9 Hz, 1H), 4.88 (s, 2H), 3.19 (q, *J* = 7.6 Hz, 1H), 1.85 – 1.80 (s, 3H), 1.80 – 1.71 (m, 2H), 0.90 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 142.0, 134.1, 132.4, 128.4, 127.6, 126.1, 115.0, 50.8, 28.9, 18.7, 12.2.

HRMS (APCI) m/z calcd. for $C_{14}H_{19}$ $[M+H]^+$ 187.1481, found: 187.1477.

(*S*,*E*)-(1-(cyclohex-1-en-1-yl)pent-1-en-3-yl)benzene (18)



18

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2p** (46.8 mg, 0.20 mmol, 1.0 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **18** as a colorless oil (32.1 mg, 71% yield, 92% ee).

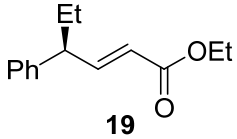
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 16.09 min, t_R (minor) = 21.05 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 6.03 (d, *J* = 15.7 Hz, 1H), 5.70 – 5.60 (m, 2H), 3.16 (q, *J* = 7.6 Hz, 1H), 2.18 – 2.03 (m, 4H), 1.80 – 1.69 (m, 2H), 1.69 – 1.55 (m, 4H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 135.6, 133.1, 130.0, 128.3, 128.0, 127.6, 125.9, 50.9, 29.0, 25.8, 24.6, 22.6, 22.5, 12.3.

HRMS (APCI) m/z calcd. for $C_{17}H_{23}$ $[M+H]^+$ 227.1794, found: 227.1787.

Ethyl (*S*,*E*)-4-phenylhex-2-enoate (19)



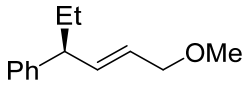
19

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and Ethyl (*E*)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate **2q** (45.2 mg, 0.20 mmol, 1.0 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **19** as a colorless oil (31.8 mg, 73% yield, 86% ee).

HPLC analysis: Chiralcel OD-H (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 214 nm), t_R (major) = 9.00 min, t_R (minor) = 12.79 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.26 – 7.14 (m, 3H), 7.07 (dd, *J* = 15.7, 7.9 Hz, 1H), 5.79 (dd, *J* = 15.7, 1.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.29 (q, *J* = 7.5 Hz, 1H), 1.91 – 1.72 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 151.7, 142.1, 128.6, 127.8, 126.7, 120.8, 60.2, 50.2, 27.9, 14.2, 12.1.
HRMS (ESI) m/z calcd. for $C_{14}H_{19}O_2$ $[M+H]^+$ 219.1380, found: 219.1381.

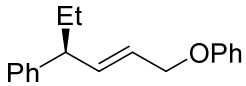
(*S*,*E*)-(6-methoxyhex-4-en-3-yl)benzene (20)



20

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-2-(3-methoxyprop-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2r** (39.6 mg, 0.20 mmol, 1.0 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **20** as a colorless oil (31.0 mg, 81% yield, 90% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 8.60 min, t_R (minor) = 10.26 min
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.22 – 7.11 (m, 3H), 5.90 – 5.78 (m, 1H), 5.61 – 5.49 (m, 1H), 3.88 (d, *J* = 6.2 Hz, 2H), 3.30 (s, 3H), 3.16 (q, *J* = 7.5 Hz, 1H), 1.80-1.68 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 137.8, 128.4, 127.6, 126.1, 125.9, 73.1, 57.7, 50.4, 28.5, 12.2.
HRMS (ESI) m/z calcd. for $C_{13}H_{18}ONa$ $[M+Na]^+$ 213.1250, found: 213.1251.

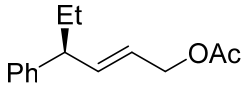
(*S*,*E*)-(6-phenoxyhex-4-en-3-yl)benzene (21)



21

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-(3-phenoxyprop-1-en-1-yl)-1,3,2-dioxaborinane **2s** (52.0 mg, 0.20 mmol, 1.0 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to yield the product **21** as a colorless oil (38.4 mg, 76% yield, 86% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 24.87 min, t_R (minor) = 33.36 min
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 4H), 7.22 – 7.14 (m, 3H), 6.96 – 6.86 (m, 3H), 6.01 – 5.91 (m, 1H), 5.77 – 5.65 (m, 1H), 4.49 (d, *J* = 5.7 Hz, 2H), 3.20 (q, *J* = 7.5 Hz, 1H), 1.82 – 1.67 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 144.1, 138.3, 129.4, 128.4, 127.7, 126.2, 124.8, 120.7, 114.8, 68.6, 50.4, 28.5, 12.2.
HRMS (ESI) m/z calcd. fo $C_{18}H_{21}O$ $[M+H]^+$ 253.1587, found: 253.1589.

(*S,E*)-4-phenylhex-2-en-1-yl acetate (22)



22

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)allyl acetate **2t** (45.2 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **22** as a colorless oil (32.7 mg, 75% yield, 89% ee).

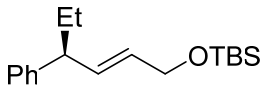
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 16.22 min, t_R (minor) = 23.00 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.23 – 7.14 (m, 3H), 5.94 – 5.84 (m, 1H), 5.63 – 5.62 (m, 1H), 4.58 – 4.47 (m, 2H), 3.16 (q, *J* = 7.5 Hz, 1H), 2.05 (s, 3H), 1.82-1.67 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 143.9, 139.3, 128.4, 127.6, 126.2, 123.6, 65.1, 50.3, 28.5, 21.0, 12.1.

HRMS (ESI) m/z calcd. for $C_{14}H_{18}NaO_2$ $[M+Na]^+$ 241.1199, found: 241.1199.

(*S,E*)-tert-butyldimethyl((4-phenylhex-2-en-1-yl)oxy)silane (23)



23

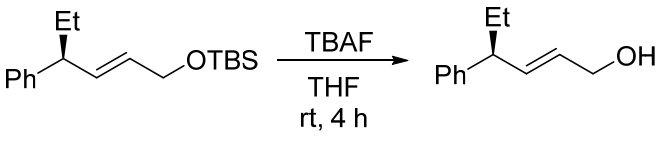
According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-tert-butyldimethyl((3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)allyl)oxy)silane **2u** (59.7 mg, 0.20 mmol, 1.0 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **23** as a colorless oil (46.3 mg, 80% yield, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.20 – 7.13 (m, 3H), 5.84 – 5.73 (m, 1H), 5.58 – 5.49 (m, 1H), 4.14 (d, *J* = 5.2 Hz, 2H), 3.14 (q, *J* = 7.5 Hz, 1H), 1.80 – 1.64 (m, 2H), 0.87 (d, *J* = 15.8 Hz, 12H), 0.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 134.4, 129.1, 128.3, 127.7, 126.0, 63.9, 50.2, 28.8, 26.0, 18.4, 12.2, -5.10.

HRMS (APCI) m/z calcd. for $C_{18}H_{30}OSiNa$ $[M+Na]^+$ 313.1958, found: 313.1948.

*Note: The ee value (91%) of product **23** was determined by chiral HPLC analysis of **(S,E)-4-phenylhex-2-en-1-ol (23')**, which was obtained by transformation of product **23**.*



23 **23'**, 85%, 91% ee

Under an argon atmosphere, to a solution of product **23** (23.3 mg, 0.115 mmol) in anhydrous THF (2.0 mL) was added tetrabutylammonium fluoride (TBAF, 0.23 mL, 2.0 equiv, 1M in THF) at ice bath. The reaction mixture was allowed to stir at room temperature for 4 h, and then quenched with water. The reaction mixture was extracted with ethyl acetate three times. The organic layers were combined and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate = 5/1 as eluent to provide the product **23'** as a colorless oil (17.2 mg, 85% yield, 91% ee).

(S,E)-4-phenylhex-2-en-1-ol (23')：

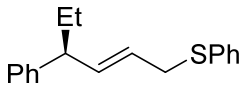
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 23.12 min, t_R (minor) = 26.49 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 5.88 – 5.76 (m, 1H), 5.69 – 5.58 (m, 1H), 4.10 (d, *J* = 5.8 Hz, 2H), 3.15 (q, *J* = 7.5 Hz, 1H), 1.80 – 1.68 (m, 2H), 1.33 (s, 1H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 136.4, 128.7, 128.4, 127.6, 126.2, 63.7, 50.4, 28.6, 12.2.

HRMS (APCI) m/z calcd. for $C_{12}H_{17}O$ $[M+H]^+$ 177.1274, found: 177.1269.

(*S,E*)-phenyl(4-phenylhex-2-en-1-yl)sulfane (24)



24

According to the **general procedure B** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv) and (*E*)-4,4,6-trimethyl-2-(3-(phenylthio)prop-1-en-1-yl)-1,3,2-dioxaborinane **2v** (55.2 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **24** as a colorless oil (44.1 mg, 82% yield, 88% ee).

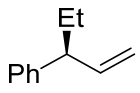
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 19.78 min, t_R (minor) = 29.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.28 – 7.19 (m, 4H), 7.19 – 7.12 (m, 2H), 7.06 (d, *J* = 7.1 Hz, 2H), 5.67 – 5.58 (m, 1H), 5.55 – 5.45 (m, 1H), 3.57 – 3.44 (m, 2H), 3.07 (q, *J* = 7.5 Hz, 1H), 1.69 – 1.57 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 137.6, 135.8, 130.3, 128.7, 128.3, 127.5, 126.2, 126.0, 125.0, 50.2, 36.7, 28.5, 12.0.

HRMS (APCI) m/z calcd. for $C_{18}H_{21}S$ $[M+H]^+$ 269.1358, found: 269.1351.

(*S*)-pent-1-en-3-ylbenzene (25)



25

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg,

0.30 mmol, 1.5 equiv) and 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane **2w** (32.8 mg, 0.20 mmol, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **25** as a colorless oil (14.5 mg, 50% yield, 92% ee).

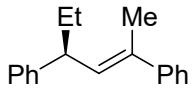
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.4 mL/min, λ = 214 nm), t_R (minor) = 12.15 min, t_R (major) = 12.85 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 6.01 – 5.89 (m, 1H), 5.06 – 4.99 (m, 2H), 3.13 (q, *J* = 7.5 Hz, 1H), 1.80 – 1.66 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 142.3, 128.4, 127.6, 126.1, 114.0, 51.7, 28.3, 12.2.

HRMS (APCI) m/z calcd. for $C_{11}H_{15}$ $[M+H]^+$ 147.1168, found: 147.1165.

(*S*,*E*)-hex-2-ene-2,4-diyldibenzene (26)



26

According to the **general procedure A** with (1-bromopropyl)benzene **1a** (59.7 mg, 0.30 mmol, 1.5 equiv.) and (*E*)-4,4,6-trimethyl-2-(2-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane **2x** (48.8 mg, 0.20 mmol, 1.0 equiv.), CuI (3.81 mg, 10 mol%), chiral ligand **L9** (15.86 mg, 15 mol%) and LiO^tBu (32.0 mg, 2.0 equiv) for 6 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **26** as a colorless oil (18.9 mg, 40% yield, 44% ee).

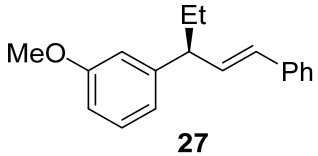
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 15.41 min, t_R (major) = 18.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.15 (m, 8H), 5.94 – 5.88 (m, 1H), 3.55 (q, *J* = 8.1 Hz, 1H), 2.07 (d, *J* = 1.4 Hz, 3H), 1.88 – 1.68 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 143.9, 134.8, 132.3, 128.4, 128.1, 127.5, 126.6, 125.9, 125.8, 46.6, 30.3, 16.3, 12.2.

HRMS (APCI) m/z calcd. for $C_{18}H_{21}$ $[M+H]^+$ 237.1638, found: 237.1635.

(*S*,*E*)-1-methoxy-3-(1-phenylpent-1-en-3-yl)benzene (27)

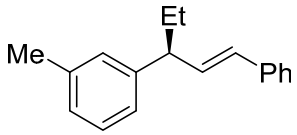


27

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 1-(1-bromopropyl) -3-methoxybenzenee **S27** (68.7 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **27** as a colorless oil (46.9 mg, 93% yield, 94% ee).

HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 16.84 min, t_R (minor) = 23.96 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.30 – 7.14 (m, 4H), 6.87 – 6.71 (m, 3H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.79 (s, 3H), 3.28 (q, *J* = 7.4 Hz, 1H), 1.87 – 1.76 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 146.3, 137.6, 134.1, 129.5, 129.4, 128.5, 127.0, 126.2, 120.2, 113.7, 111.2, 55.2, 51.1, 28.8, 12.3.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}O$ $[M+H]^+$ 253.1587, found 253.1589.

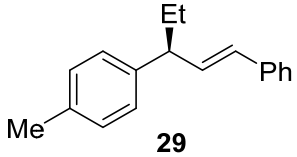
(*S*,*E*)-1-methyl-3-(1-phenylpent-1-en-3-yl)benzene (28)



28

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 1-(1-bromopropyl)-3-methylbenzene **S28** (63.9 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **28** as a colorless oil (35.3 mg, 75% yield, 95% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.64 min, t_R (minor) = 10.08 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.30 – 7.23 (m, 2H), 7.22 – 7.14 (m, 2H), 7.08 – 6.97 (m, 3H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.32 (dd, *J* = 15.8, 7.4 Hz, 1H), 3.26 (q, *J* = 7.4 Hz, 1H), 2.33 (s, 3H), 1.88 – 1.73 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 138.0, 137.7, 134.3, 129.3, 128.4, 128.3, 126.94 , 126.92 , 126.1, 124.6, 51.0, 28.8, 21.5, 12.3.
HRMS (APCI) *m/z* calcd. for $C_{18}H_{21}$ $[M+H]^+$ 237.1638, found 237.1634.

(*S*,*E*)-1-methyl-4-(1-phenylpent-1-en-3-yl)benzene (29)

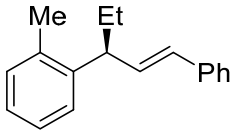


29

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 1-(1-bromopropyl)-4-methylbenzene **S29** (63.9 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **29** as a colorless oil (39.6 mg, 84% yield, 93% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.50 min, t_R (minor) = 12.01 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.29 – 7.23 (m, 2H), 7.20 – 7.10 (m, 5H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.9, 7.3 Hz, 1H), 3.27 (q, *J* = 7.4 Hz,

1H), 2.32 (s, 3H), 1.87 – 1.75 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 137.7, 135.6, 134.4, 129.2, 129.1, 128.4, 127.5, 126.9, 126.1, 50.5, 28.8, 21.0, 12.3.
HRMS (APCI) *m/z* calcd. for $C_{18}H_{21}$ $[M+H]^+$ 237.1638, found 237.1633.

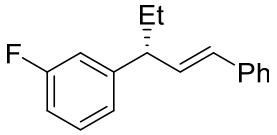
(*S*,*E*)-1-methyl-2-(1-phenylpent-1-en-3-yl)benzene (30)



30

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 1-(1-bromopropyl)-2-methylbenzene **S30** (63.9 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **30** as a colorless oil (31.2 mg, 66% yield, 90% ee).
HPLC analysis: Chiralcel OJ-H (*n*-hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 17.37 min, t_R (minor) = 25.01 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.30 – 7.20 (m, 4H), 7.20 – 7.07 (m, 3H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.27 (dd, *J* = 15.8, 7.2 Hz, 1H), 3.56 (q, *J* = 7.3 Hz, 1H), 2.36 (s, 3H), 1.90 – 1.76 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 137.6, 136.0, 133.8, 130.4, 129.4, 128.4, 126.9, 126.4, 126.2, 126.1, 125.9, 46.1, 28.4, 19.7, 12.3.
HRMS (APCI) *m/z* calcd. for $C_{18}H_{21}$ $[M+H]^+$ 237.1638, found 237.1631.

(*R*,*E*)-1-fluoro-3-(1-phenylpent-1-en-3-yl)benzene (31)

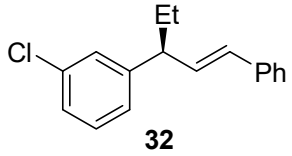


31

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv), 1-(1-bromopropyl)-3-fluorobenzene **S31** (65.1 mg, 0.30 mmol, 1.5 equiv) and chiral ligand **L11** (6.68 mg, 7.5 mol%) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **31** as a colorless oil (29.4 mg, 61% yield, 93% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.47 min, t_R (major) = 10.38 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.24 (m, 3H), 7.22 – 7.17 (m, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.97 – 6.86 (m, 2H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 15.8, 7.7 Hz, 1H), 3.31 (q, *J* = 7.5 Hz, 1H), 1.89 – 1.74 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 245.4 Hz), 147.2 (d, *J* = 6.8 Hz), 137.3,

133.4, 129.9, 129.8 (d, J = 8.3 Hz), 128.5, 127.2, 126.1, 123.4 (d, J = 2.6 Hz), 114.4 (d, J = 21.2 Hz), 113.0 (d, J = 21.1 Hz), 50.7, 50.7, 28.7, 12.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.45.
HRMS (APCI) *m/z* calcd. for $C_{17}H_{18}F$ $[M+H]^+$ 241,1387, found 241.1378.

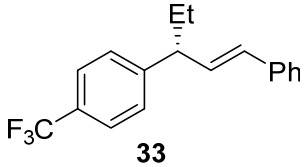
(*S,E*)-1-chloro-3-(1-phenylpent-1-en-3-yl)benzene (32)



32

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 1-(1-bromopropyl)-3-chlorobenzene **S32** (70.0 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **32** as a colorless oil (36.3 mg, 71% yield, 91% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.97 min, t_R (minor) = 11.90 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 4H), 7.14 – 7.10 (m, 1H), 6.40 (d, J = 15.9 Hz, 1H), 6.27 (dd, J = 15.9, 7.7 Hz, 1H), 3.29 (q, J = 7.5 Hz, 1H), 1.90 – 1.73 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 137.3, 134.2, 133.3, 130.0, 129.7, 128.5, 127.79 , 127.2, 126.4, 126.2, 125.9, 50.7, 28.7, 12.2.
HRMS (APCI) *m/z* calcd. for $C_{17}H_{18}Cl$ $[M+H]^+$ 257.1092, found 257.1089.

(*R,E*)-1-(1-phenylpent-1-en-3-yl)-4-(trifluoromethyl)benzene (33)

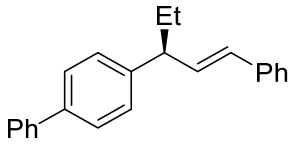


33

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv), 1-(1-bromopropyl)-4-(trifluoromethyl)benzene **S33** (80.1 mg, 0.30 mmol, 1.5 equiv) and chiral ligand **L11** (6.68 mg, 7.5 mol%) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **33** as a colorless oil (45.2 mg, 78% yield, 88% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.38 min, t_R (minor) = 9.87 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.32 – 7.26 (m, 2H), 7.23 – 7.18 (m, 1H), 6.41 (d, J = 15.8 Hz, 1H), 6.29 (dd, J = 15.8, 7.7 Hz, 1H), 3.38 (q, J = 7.5 Hz, 1H), 1.93 – 1.76 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 137.2, 133.1, 130.3, 128.6, 128.5 (q, J_{C-F} = 32.0 Hz), 128.0, 127.3, 126.2, 125.4 (q, J_{C-F} = 3.7 Hz), 124.3 (q, J_{C-F} = 272.7 Hz), 50.8, 28.7, 12.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.30 .
HRMS (APCI) *m/z* calcd. for $C_{18}H_{18}F_3$ $[M+H]^+$ 291.1355, found 291.1348.

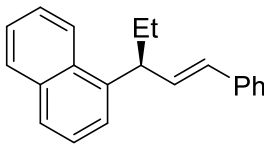
(*S*,*E*)-4-(1-phenylpent-1-en-3-yl)-1,1'-biphenyl (34)



34

According to **general produce C** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 4-(1-bromopropyl)-1,1'-biphenyl **1c** (82.5 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **34** as a colorless oil (48.6 mg, 81% yield, 93% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.00 min, t_R (major) = 9.40 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 4H), 7.46 – 7.39 (m, 2H), 7.38 – 7.25 (m, 7H), 7.21 – 7.15 (m, 1H), 6.51 – 6.29 (m, 2H), 3.36 (q, *J* = 7.4 Hz, 1H), 1.94 – 1.79 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 141.0, 139.1, 137.6, 134.0, 129.6, 128.7, 128.5, 128.1, 127.2, 127.02 , 127.00 , 126.1, 50.6, 28.8, 12.3.
HRMS (APCI) *m/z* calcd. for $C_{23}H_{23}$ $[M+H]^+$ 299.1794, found 299.1788.

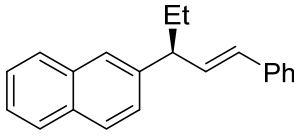
(*S*,*E*)-1-(1-phenylpent-1-en-3-yl)naphthalene (35)



35

According to **general produce C** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 1-(1-bromopropyl)naphthalene **S35** (74.7 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **35** as a colorless oil (42.4 mg, 78% yield, 99% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.79 min, t_R (major) = 6.36 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.53 – 7.43 (m, 4H), 7.36 – 7.31 (m, 2H), 7.29 – 7.22 (m, 2H), 7.20 – 7.14 (m, 1H), 6.47 (d, *J* = 3.2 Hz, 2H), 4.22 – 4.13 (m, 1H), 2.09 – 1.94 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 137.6, 134.0, 133.9, 131.8, 129.9, 128.9, 128.4, 127.0, 126.7, 126.1, 125.8, 125.6, 125.3, 124.1, 123.5, 45.3, 28.6, 12.5.
HRMS (APCI) *m/z* calcd. for $C_{21}H_{21}$ $[M+H]^+$ 273.1638, found 273.1637.

(*S*,*E*)-2-(1-phenylpent-1-en-3-yl)naphthalene (36)



36

According to **general produce C** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 2-(1-bromopropyl)naphthalene **S36** (74.7 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **36** as a colorless oil (42.8 mg, 79% yield, 95% ee).

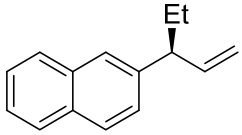
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 26.93 min, t_R (minor) = 30.87 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 3H), 7.67 (d, *J* = 1.7 Hz, 1H), 7.47 – 7.32 (m, 5H), 7.30 – 7.24 (m, 2H), 7.21 – 7.15 (m, 1H), 6.48 – 6.35 (m, 2H), 3.53 – 3.43 (m, 1H), 2.00 – 1.87 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 137.6, 134.1, 133.6, 132.3, 129.7, 128.5, 128.1, 127.6, 127.6, 127.0, 126.4, 126.1, 126.0, 125.9, 125.3, 51.0, 28.6, 12.3.

HRMS (APCI) *m/z* calcd. for $C_{21}H_{21}$ $[M+H]^+$ 273.1638, found 273.1642.

(*S*)-2-(pent-1-en-3-yl)naphthalene (37)[14]



37

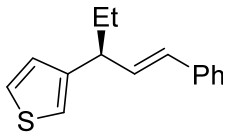
According to **general produce C** with 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane **2w** (154.0 mg, 1.00 mmol, 1.0 equiv), 2-(1-bromopropyl)naphthalene **S36** (373.7 mg, 1.50 mmol, 1.5 equiv), CuI (9.5 mg, 5 mol%), chiral ligand **L9** (39.7 mg, 7.5 mol %) and LiO^{t}Bu (160.0 mg, 2.0 equiv) in DMF (10.0 mL) and H_2O (18.0 mg, 1.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **37** as a colorless oil (131 mg, 67% yield, 90% ee).

HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.93 min, t_R (major) = 8.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 3H), 7.62 (d, *J* = 1.7 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.10 – 5.94 (m, 1H), 5.13 – 5.02 (m, 2H), 3.31 (q, *J* = 7.4 Hz, 1H), 1.90 – 1.77 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 141.8, 133.6, 132.2, 128.0, 127.59, 127.56, 126.3, 125.9, 125.8, 125.2, 114.3, 51.7, 28.2, 12.2.

(*S*,*E*)-3-(1-phenylpent-1-en-3-yl)thiophene (38)



38

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv), 3-(1-bromopropyl)thiophene **S38** (61.5 mg, 0.30 mmol, 1.5 equiv), CuI (3.81 mg, 10 mol%), chiral ligand **L9** (15.86 mg, 15 mol%) and LiO′Bu (32.0 mg, 2.0 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to yield the product **38** as a colorless oil (26.3 mg, 58% yield, 92% ee).

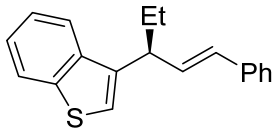
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.01 min, t_R (major) = 14.47 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.32 – 7.25 (m, 3H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.04 – 6.95 (m, 2H), 6.47 – 6.17 (m, 2H), 3.43 (q, *J* = 7.5 Hz, 1H), 1.90 – 1.70 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 137.5, 133.5, 129.7, 128.5, 127.3, 127.0, 126.1, 125.3, 119.9, 46.3 , 28.6, 12.2.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{17}S$ $[M+H]^+$ 229.1045, found 229.1047.

(*S*,*E*)-3-(1-phenylpent-1-en-3-yl)benzo[b]thiophene (39)



39

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 3-(1-bromopropyl)benzo[b] thiophene **S39** (76.5 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to yield the product **39** as a colorless oil (41.2 mg, 74% yield, 92% ee).

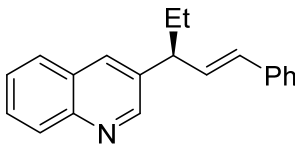
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.65 min, t_R (major) = 6.20 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 2H), 7.37 – 7.31 (m, 4H), 7.31 – 7.26 (m, 2H), 7.21 – 7.16 (m, 2H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.34 (dd, *J* = 15.9, 7.8 Hz, 1H), 3.76 (q, *J* = 7.5 Hz, 1H), 2.08 – 1.88 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 139.0, 138.7, 137.4, 132.6, 130.3, 128.5, 127.1, 126.2, 124.2, 123.8, 122.9, 122.2, 121.0, 44.5, 27.8, 12.4.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}S$ $[M+H]^+$ 279.1202, found 279.1204.

(*S*,*E*)-3-(1-phenylpent-1-en-3-yl)quinoline (40)



40

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 3-(1-bromopropyl)quinoline **S40** (75.0 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to yield the product **40** as a colorless oil (32.9 mg, 60% yield, 88% ee).

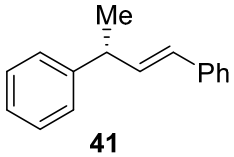
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.41 min, t_R (minor) = 7.95 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 2.3 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 2.2 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.55 – 7.48 (m, 1H), 7.38 – 7.16 (m, 5H), 6.50 – 6.33 (m, 2H), 3.54 (q, *J* = 7.4 Hz, 1H), 1.98 – 1.94 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 147.0, 137.1, 137.0, 133.6, 132.7, 130.6, 129.1, 128.8, 128.5, 128.2, 127.5, 127.3, 126.6, 126.2, 48.4, 28.5, 12.2.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{20}N$ $[M+H]^+$ 274.1590, found 274.1592.

(*R*,*E*)-but-1-ene-1,3-diyldibenzene (41)



41

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv), (1-bromoethyl)benzene **1d** (55.5 mg, 0.30 mmol, 1.5 equiv) and chiral ligand **L11** (6.68 mg, 7.5 mol%) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **41** as a colorless oil (30.4 mg, 73% yield, 93% ee)

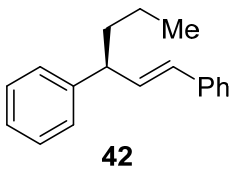
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 17.24 min, t_R (major) = 18.60 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 8H), 7.24 – 7.16 (m, 2H), 6.45 – 6.34 (m, 2H), 3.69 – 3.59 (m, 1H), 1.47 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 137.5, 135.2, 128.5, 127.3, 127.0, 126.2, 126.1, 42.5, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{17}$ $[M+H]^+$ 209.1325, found 209.1325.

(*S*,*E*)-hex-1-ene-1,3-diyldibenzene (42)



42

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (1-bromobutyl)benzene **S42** (63.9 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **42** as a colorless oil (34.6 mg, 73% yield, 94% ee)

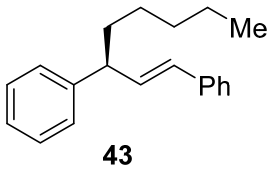
HPLC analysis: Chiralcel OD-H (*n*-hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.52 min, t_R (minor) = 9.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 8H), 7.22 – 7.14 (m, 2H), 6.43 – 6.28 (m, 2H), 3.42 (q, *J* = 7.4 Hz, 1H), 1.84 – 1.70 (m, 2H), 1.40 – 1.24 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 137.6, 134.4, 129.2, 128.5, 128.4, 127.6, 127.0, 126.1, 126.1, 48.9, 38.1, 20.7, 14.0.

HRMS (APCI) *m/z* calcd. for $C_{18}H_{21}$ $[M+H]^+$ 237.1638, found 237.1636.

(*S*,*E*)-oct-1-ene-1,3-diyldibenzene (43)



43

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (1-bromohexyl)benzene **S43** (72.3 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **43** as a colorless oil (34.8 mg, 66% yield, 94% ee)

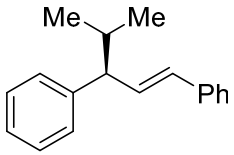
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.84 min, t_R (major) = 10.26 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 8H), 7.22 – 7.15 (m, 2H), 6.43 – 6.26 (m, 2H), 3.39 (q, *J* = 7.4 Hz, 1H), 1.84 – 1.73 (m, 2H), 1.39 – 1.19 (m, 6H), 0.91 – 0.80 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 129.2, 128.5, 128.4, 127.6, 127.0, 126.1, 126.1, 49.2, 35.9, 31.8, 27.3, 22.6, 14.1.

HRMS (APCI) *m/z* calcd. for $C_{20}H_{25}$ $[M+H]^+$ 265.1951, found 265.1945.

(*S*,*E*)-(4-methylpent-1-ene-1,3-diyl)dibenzene (44)

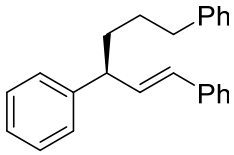


44

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (1-bromo-2-methylpropyl) benzene **S44** (63.9 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **44** as a

colorless oil (32.5 mg, 69% yield, 98% ee)
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.49 min, t_R (major) = 9.60 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 6H), 7.24 – 7.15 (m, 4H), 6.45 – 6.33 (m, 2H), 3.09 – 2.99 (m, 1H), 2.09 – 1.99 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 137.6, 133.2, 130.3, 128.41, 128.38, 127.9, 127.0, 126.1, 126.0, 57.6, 33.2, 21.2, 20.9.
HRMS (APCI) *m/z* calcd. for $C_{18}H_{21}$ $[M+H]^+$ 237.1638, found 237.1633.

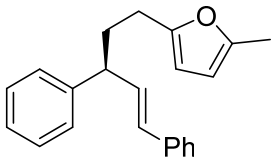
(*S*,*E*)-hex-1-ene-1,3,6-triyltribenzene (45)



45

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (1-bromobutane-1,4-diyl) dibenzene **S45** (86.7 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **45** as a colorless oil (40.2 mg, 64% yield, 90% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 25.00 min, t_R (major) = 32.39 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.09 (m, 15H), 6.41 – 6.26 (m, 2H), 3.42 (q, *J* = 7.3 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.89 – 1.80 (m, 2H), 1.73 – 1.57 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.4, 137.5, 134.1, 129.4, 128.5, 128.44, 128.40, 128.3, 127.6, 127.0, 126.2, 126.1, 125.7, 49.1, 35.9, 35.4, 29.4
HRMS (APCI) *m/z* calcd. for $C_{24}H_{25}$ $[M+H]^+$ 313.1951, found 313.1941.

(*S*,*E*)-2-(3,5-diphenylpent-4-en-1-yl)-5-methylfuran (46)

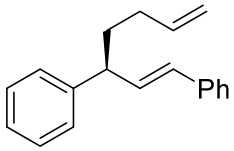


46

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 2-(3-bromo-3-phenylpropyl)-5-methylfuran **S46** (83.7 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to yield the product **46** as a colorless oil (37.0 mg, 61% yield, 94% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.36 min, t_R (minor) = 6.13 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 10H), 6.45 – 6.28 (m, 2H), 5.84 (s, 2H), 3.45 (q, *J* = 7.5 Hz, 1H), 2.67 – 2.48 (m, 2H), 2.24 (s, 3H), 2.20 – 2.06 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 150.3, 143.9, 137.4, 133.6, 129.8, 128.6, 128.4, 127.7, 127.1, 126.4, 126.1, 105.8, 105.5, 48.4, 34.0, 26.1, 13.5.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{23}O$ $[M+H]^+$ 303.1743, found 303.1747.

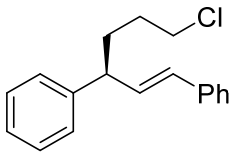
(*S*,*E*)-hepta-1,6-diene-1,3-diyldibenzene (47)



47

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (1-bromopent-4-en-1-yl) benzene **S47** (67.5 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **47** as a colorless oil (26.0 mg, 52% yield, > 99% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.37 min, t_R (major) = 10.69 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 7H), 7.25 – 7.16 (m, 3H), 6.44 – 6.27 (m, 2H), 5.89 – 5.76 (m, 1H), 5.06 – 4.94 (m, 2H), 3.45 (q, *J* = 7.5 Hz, 1H), 2.14 – 1.98 (m, 2H), 1.94 – 1.86 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 138.4, 137.5, 134.0, 129.6, 128.52, 128.45, 127.7, 127.1, 126.3, 126.1, 114.8, 48.4, 34.9, 31.6
HRMS (APCI) *m/z* calcd. for $C_{19}H_{21}$ $[M+H]^+$ 249.1638, found 249.1630.

(*S*,*E*)-(6-chlorohex-1-ene-1,3-diyl)dibenzene (48)

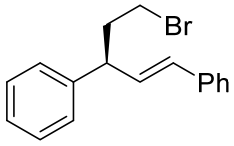


48

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (1-bromo-4-chlorobutyl) benzene **S48** (74.1 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **48** as a colorless oil (43.8 mg, 81% yield, 94% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 22.98 min, t_R (minor) = 27.70 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.14 (m, 10H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.32 (dd, *J* = 15.8, 7.6 Hz, 1H), 3.54 (t, *J* = 6.5 Hz, 2H), 3.43 (q, *J* = 7.5 Hz, 1H), 2.05 – 1.90 (m, 2H), 1.90 – 1.66 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 137.3, 133.5, 129.8, 128.6, 128.5, 127.5, 127.2, 126.5, 126.2, 48.5, 45.0, 33.0, 30.7.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{20}Cl$ $[M+H]^+$ 271.1248, found 271.1241.

(*S*,*E*)-(5-bromopent-1-ene-1,3-diyl)dibenzene (49)



49

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (1,3-dibromopropyl)benzene **S49** (83.1 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **49** as a colorless oil (48.3 mg, 80% yield, 96% ee).

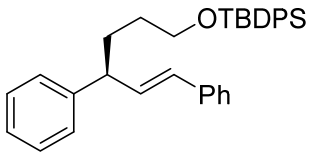
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 14.98 min, t_R (minor) = 20.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.17 (m, 10H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.29 (dd, *J* = 15.8, 7.9 Hz, 1H), 3.71 (q, *J* = 7.6 Hz, 1H), 3.45 – 3.26 (m, 2H), 2.39 – 2.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 137.1, 132.1, 130.4, 128.7, 128.5, 127.6, 127.3, 126.7, 126.2, 47.1, 38.4, 31.8.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{18}Br$ $[M+H]^+$ 301.0586, found 301.0586.

(*S*,*E*)-tert-butyl((4,6-diphenylhex-5-en-1-yl)oxy)diphenylsilane (50)



50

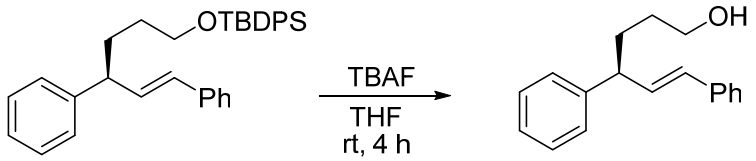
According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (4-bromo-4-phenylbutoxy) (tert-butyl)diphenylsilane **S50** (140.0 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **50** as a colorless oil (65.4 mg, 67% yield, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.59 (m, 4H), 7.43 – 7.26 (m, 12H), 7.23 – 7.16 (m, 4H), 6.41 – 6.24 (m, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 3.39 (q, *J* = 7.4 Hz, 1H), 1.94 – 1.85 (m, 2H), 1.67 – 1.46 (m, 2H), 1.04 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 137.6, 135.6, 134.3, 134.0, 129.5, 129.3, 128.5, 128.4, 127.7, 127.6, 127.0, 126.2, 126.1, 63.7, 48.7, 31.9, 30.5, 26.9, 19.2.

HRMS (APCI) *m/z* calcd. for $C_{34}H_{39}OSi$ $[M+H]^+$ 491.2765, found 491.2764.

*Note: The ee value (90%) of product **50** was determined by chiral HPLC analysis of **(S,E)-4,6-diphenylhex-5-en-1-ol (50')**, which was obtained by transformation of product **50**.*



50 **50'**, 66%, 90% ee

Under an argon atmosphere, to a solution of product **50** (45.2 mg, 0.092 mmol) in anhydrous THF (5.0 mL) was added tetrabutylammonium fluoride (TBAF, 0.18 mL, 2.0 equiv, 1M in THF) at ice water bath. The reaction mixture was allowed to stir at room temperature for 4 h, and then quenched with water. The reaction mixture was extracted with EtOAc three times. The organic layers were combined and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate = 5/1 as eluent to provide the product **50'** as a colorless oil (15.2 mg, 66% yield, 90% ee).

(S,E)-4,6-diphenylhex-5-en-1-ol (50')

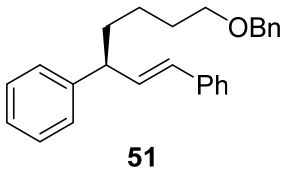
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 13.55 min, t_R (minor) = 19.30 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 3H), 7.30 – 7.23 (m, 5H), 7.23 – 7.16 (m, 2H), 6.47 – 6.27 (m, 2H), 3.64 (t, *J* = 6.5 Hz, 2H), 3.42 (q, *J* = 7.5 Hz, 1H), 1.94 – 1.82 (m, 2H), 1.73 – 1.43 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 137.4, 133.9, 129.5, 128.5, 128.4, 127.6, 127.1, 126.3, 126.1, 62.8, 48.9, 31.9, 30.8.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}O$ $[M+H]^+$ 253.1587, found 253.1588.

(*S,E*)-(7-(benzyloxy)hept-1-ene-1,3-diyl)dibenzene (51)



51

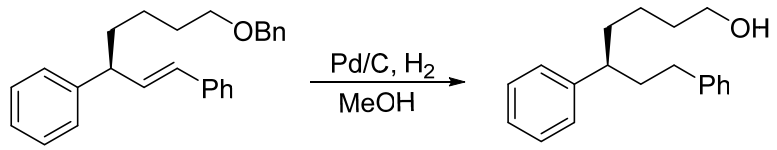
According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (5-(benzyloxy)-1-bromopentyl) benzene **S51** (100.0 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **51** as a colorless oil (43.5 mg, 61% yield, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.11 (m, 15H), 6.44 – 6.26 (m, 2H), 4.47 (s, 2H), 3.50 – 3.35 (m, 3H), 1.88 – 1.75 (m, 2H), 1.71 – 1.59 (m, 2H), 1.49 – 1.29 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 138.6, 137.5, 134.2, 129.4, 128.5, 128.4, 128.3, 127.61, 127.59, 127.46, 127.0, 126.2, 126.1, 72.8, 70.2, 49.1, 35.7, 29.7, 24.3.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{29}O$ $[M+H]^+$ 357.2213, found 357.2212.

*Note: The ee value (91%) of product **51** was determined by chiral HPLC analysis of **(S)-5,7-diphenylheptan-1-ol (51')**, which was obtained by transformation of product **51**.*



51 **51'**, 99%, 91% ee

To mixture of Pd/C (1.0 mg, 10% w/t Pd on carbon) in THF (5.0 mL) was added **51** (9.0 mg, 0.025 mmol, 1.0 equiv.) under argon atmosphere. Then, the reaction flask was evacuated and refilled with hydrogen through a balloon. The resulting reaction mixture was stirred under the hydrogen atmosphere at room temperature for 12 h. After completion, the reaction mixture was filtered and rinsed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to afford **51'** as a colorless oil (6.6 mg, 99% yield, 91% ee)

(S)-5,7-diphenylheptan-1-ol (51')

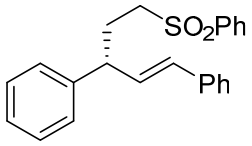
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 210 nm), t_R (minor) = 14.41 min, t_R (major) = 15.96 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.28 – 7.20 (m, 3H), 7.20 – 7.12 (m, 3H), 7.12 – 7.07 (m, 2H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.60 – 2.48 (m, 1H), 2.48 – 2.39 (m, 2H), 2.08 – 1.83 (m, 2H), 1.74 – 1.40 (m, 4H), 1.36 – 1.10 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 142.5, 128.4, 128.2, 127.7, 126.1, 125.6, 62.9, 45.6, 38.5, 36.8, 33.8, 32.8, 23.7.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{25}O$ $[M+H]^+$ 269.1900, found 269.1901.

(*R,E*)-(5-(phenylsulfonyl)pent-1-ene-1,3-diyl)dibenzene (52)



52

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv), (1-bromo-3-(phenylsulfonyl) propyl)benzene **S52** (101.8 mg, 0.30 mmol, 1.5 equiv) and chiral ligand **L11** (6.68 mg, 7.5 mol%) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to yield the product **52** as a colorless oil (48.6 mg, 67% yield, 93% ee).

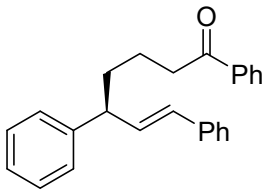
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 25.81 min, t_R (major) = 30.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.70 – 7.61 (m, 1H), 7.60 – 7.51 (m, 2H), 7.34 – 7.27 (m, 6H), 7.25 – 7.18 (m, 2H), 7.18 – 7.13 (m, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.8, 7.8 Hz, 1H), 3.47 (q, *J* = 7.7 Hz, 1H), 3.18 – 3.08 (m, 1H), 3.07 – 2.95 (m, 1H), 2.30 – 2.16 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 139.0, 136.7, 133.7, 131.7, 130.7, 129.3, 128.9, 128.5, 128.0, 127.5, 127.4, 127.0, 126.2, 54.5, 47.6, 28.3.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}O_2S$ $[M+H]^+$ 363.1413, found 363.1416.

(*S*,*E*)-1,5,7-triphenylhept-6-en-1-one (53)



53

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 5-bromo-1,5-diphenylpentan-1-one **S53** (95.1 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to yield the product **53** as a colorless oil (47.6 mg, 70% yield, 90% ee).

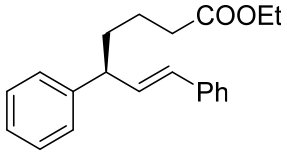
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 35.20 min, t_R (major) = 47.06 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.55 – 7.48 (m, 1H), 7.41 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.29 – 7.23 (m, 5H), 7.22 – 7.14 (m, 2H), 6.45 – 6.25 (m, 2H), 3.46 (q, *J* = 7.3 Hz, 1H), 2.96 (t, *J* = 7.0 Hz, 2H), 1.93 – 1.86 (m, 2H), 1.85 – 1.77 (m, 1H), 1.75 – 1.64 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 144.1, 137.4, 136.9, 133.8, 132.9, 129.5, 128.52, 128.49, 128.4, 128.0, 127.6, 127.0, 126.3, 126.1, 49.1, 38.4, 35.3, 22.4.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}O$ $[M+H]^+$ 341.1900, found 341.1904.

Ethyl (*S*,*E*)-5,7-diphenylhept-6-enoate (54)



54

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and ethyl 5-bromo-5-phenylpentanoate **S54** (85.5 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to yield the product **54** as a colorless oil (42.6 mg, 69% yield, 92% ee).

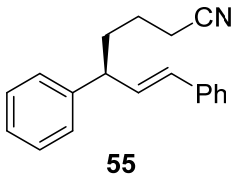
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 14.75 min, t_R (minor) = 16.82 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.20 (m, 10H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.42 (q, *J* = 7.4 Hz, 1H), 2.31 (t, *J* = 7.3 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.76 – 1.60 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 144.1, 137.4, 133.7, 129.6, 128.6, 128.4, 127.6, 127.1, 126.3, 126.1, 60.3, 48.9, 35.2, 34.2, 23.1, 14.2.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}O_2$ $[M+H]^+$ 309.1849, found 309.1852.

(*S*,*E*)-5,7-diphenylhept-6-enenitrile (55)



55

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 5-bromo-5-phenylpentanenitrile **S55** (71.4 mg, 0.30 mmol, 1.5 equiv) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to yield the product **55** as a colorless oil (36.8 mg, 70% yield, 93% ee).

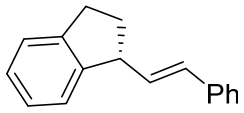
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 19.51 min, t_R (minor) = 21.87 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 6H), 7.25 – 7.17 (m, 4H), 6.47 – 6.25 (m, 2H), 3.43 (q, *J* = 7.6 Hz, 1H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.03 – 1.87 (m, 2H), 1.77 – 1.58 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 137.1, 133.0, 130.0, 128.7, 128.5, 127.5, 127.3, 126.6, 126.2, 119.5, 48.5, 34.6, 23.6, 17.1.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{20}N$ $[M+H]^+$ 262.1590, found 262.1594.

(*R,E*)-1-styryl-2,3-dihydro-1H-indene (56)



56

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv), 1-bromo-2,3-dihydro-1H-indene **S56** (59.1 mg, 0.30 mmol, 1.5 equiv) and chiral ligand **L11** (6.68 mg, 7.5 mol%) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **56** as a colorless oil (33.2 mg, 75% yield, 87% ee)

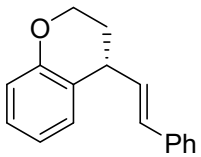
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 13.60 min, t_R (major) = 14.30 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.32 – 7.23 (m, 3H), 7.23 – 7.14 (m, 4H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.7, 8.5 Hz, 1H), 3.91 (q, *J* = 8.3 Hz, 1H), 3.04 – 2.81 (m, 2H), 2.45 – 2.34 (m, 1H), 2.00 – 1.85 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 143.9, 137.4, 133.0, 130.3, 128.5, 127.1, 126.7, 126.3, 126.2, 124.5, 49.1, 33.5, 31.7.

HRMS (APCI) *m/z* calcd. for $C_{17}H_{17}$ $[M+H]^+$ 221.1325, found 221.1321.

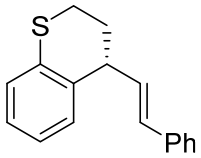
(*R,E*)-4-styrylchromane (57)



57

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv), 4-bromochromane **S57** (63.9 mg, 0.30 mmol, 1.5 equiv) and chiral ligand **L11** (6.68 mg, 7.5 mol%) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **57** as a white solid (28.6 mg, 61% yield, 93% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 27.07 min, t_R (minor) = 29.56 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.24 – 7.18 (m, 1H), 7.15 – 7.09 (m, 2H), 6.91 – 6.77 (m, 2H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.24 (dd, *J* = 15.7, 8.0 Hz, 1H), 4.31 – 4.13 (m, 2H), 3.67 (q, *J* = 7.0 Hz, 1H), 2.23 – 2.10 (m, 1H), 2.03 – 1.90 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 137.0, 133.1, 131.6, 130.2, 128.5, 127.9, 127.3, 126.2, 123.7, 120.2, 116.8, 64.0, 38.5, 29.0.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}O$ $[M+H]^+$ 237.1274, found 237.1275.

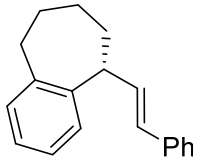
(*R,E*)-4-styrylthiochromane (58)



58

According to **general produce C** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv), 4-bromothiochromane **S58** (68.7 mg, 0.30 mmol, 1.5 equiv) and chiral ligand **L11** (6.68 mg, 7.5 mol%) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **58** as a colorless oil (23.7 mg, 47% yield, 88% ee).
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 12.06 min, t_R (minor) = 14.35 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.18 (m, 1H), 7.16 – 7.06 (m, 3H), 7.02 – 6.96 (m, 1H), 6.35 – 6.22 (m, 2H), 3.72 (q, *J* = 5.4 Hz, 1H), 3.19 – 3.06 (m, 1H), 3.02 – 2.91 (m, 1H), 2.27 – 2.16 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 134.6, 132.9, 132.7, 131.8, 130.7, 128.5, 127.3, 126.9, 126.6, 126.2, 123.9, 41.7, 28.7, 24.0.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}S$ $[M+H]^+$ 253.1045, found 253.1047.

(*R,E*)-5-styryl-6,7,8,9-tetrahydro-5H-benzo[7]annulene (59)



59

According to **general produce A** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2–dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv), 5-bromo-6,7,8,9-tetrahydro-5H-

benzo[7] annulene **S59** (67.5 mg, 0.30 mmol, 1.5 equiv) and chiral ligand **L11** (6.68 mg, 7.5 mol%) for 4 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **59** as a colorless oil (30.8 mg, 62% yield, 88% ee).

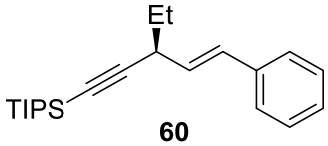
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 17.09 min, t_R (major) = 21.86 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.14 (m, 2H), 7.14 – 7.09 (m, 3H), 6.55 (dd, *J* = 16.0, 6.7 Hz, 1H), 6.30 – 6.21 (m, 1H), 3.85 – 3.74 (m, 1H), 2.95 – 2.74 (m, 2H), 2.00 – 1.90 (m, 2H), 1.88 – 1.75 (m, 2H), 1.72 – 1.59 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 142.7, 137.7, 133.2, 129.8, 129.6, 128.5, 128.3, 127.0, 126.3, 126.1, 126.0, 48.1, 36.3, 33.7, 29.0, 28.0.

HRMS (APCI) *m/z* calcd. for $C_{19}H_{21}$ $[M+H]^+$ 249.1638, found 249.1637.

(*S*,*E*)-(3-ethyl-5-phenylpent-4-en-1-yn-1-yl)triisopropylsilane (60)



60

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromopent-1-yn-1-yl) triisopropylsilane **S60** (75.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **60** as a colorless oil (56.0 mg, 86% yield, 97% ee).

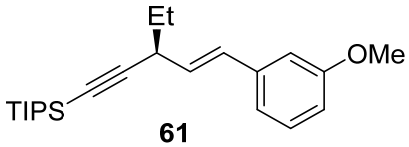
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 10.72 min, t_R (major) = 11.27 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.34 – 7.26 (m, 2H), 7.25 – 7.16 (m, 1H), 6.75 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.13 (dd, *J* = 15.7, 5.8 Hz, 1H), 3.30 – 3.20 (m, 1H), 1.77 – 1.64 (m, 1H), 1.66 – 1.53 (m, 1H), 1.15 – 1.08 (m, 21H), 1.06 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 130.4, 129.7, 128.5, 127.1, 126.2, 108.9, 83.7, 37.2, 29.0, 18.6, 11.34, 11.31.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{35}Si$ $[M+H]^+$ 327.2503, found 327.2499.

(*S*,*E*)-(3-ethyl-5-(3-methoxyphenyl)pent-4-en-1-yn-1-yl)triisopropylsilane (61)

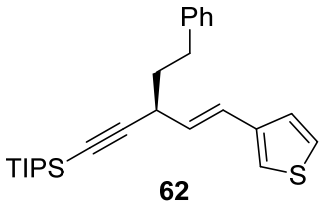


61

According to **general produce D** with (*E*)-2-(3-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2y** (52.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromopent-1-yn-1-yl) triisopropylsilane **S60** (75.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to yield the product **61** as a colorless oil (64.4 mg, 90% yield, 99% ee).

HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 12.91 min, t_R (major) = 18.30 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.18 (m, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.81 – 6.74 (m, 1H), 6.73 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.13 (dd, *J* = 15.7, 5.8 Hz, 1H), 3.81 (s, 3H), 3.31 – 3.20 (m, 1H), 1.80 – 1.63 (m, 1H), 1.66 – 1.51 (m, 1H), 1.13 – 1.08 (m, 21H), 1.05 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 138.7, 130.3, 130.0, 129.4, 118.9, 112.6, 111.7, 108.8, 83.8, 55.1, 37.2, 28.9, 18.6, 11.3, 11.2.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{37}OSi$ $[M+H]^+$ 357.2608, found 357.2604.

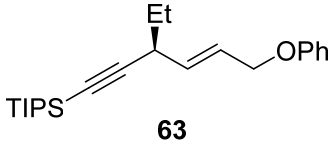
(*S*,*E*)-triisopropyl(3-phenethyl-5-(thiophen-3-yl)pent-4-en-1-yn-1-yl)silane (62)



62

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborinane **2h** (47.2 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-5-phenylpent-1- yn-1-yl)triisopropylsilane **S69** (94.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **62** as a colorless oil (70.1 mg, 86% yield, 99% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 22.85 min, t_R (minor) = 30.87 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.15 (m, 7H), 7.10– 7.07 (m, 1H), 6.77 (d, *J* = 15.7 Hz, 1H), 5.99 (dd, *J* = 15.7, 5.8 Hz, 1H), 3.32 – 3.23 (m, 1H), 2.92 – 2.76 (m, 2H), 2.00 – 1.81 (m, 2H), 1.16 – 1.07 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 139.7, 129.4, 128.5, 128.4, 125.91, 125.86, 125.0, 124.8, 121.5, 108.6, 84.4, 37.8, 35.1, 33.3, 18.7, 11.3.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{37}SSi$ $[M+H]^+$ 409.2380, found 409.2379.

(*S*,*E*)-(3-ethyl-6-phenoxyhex-4-en-1-yn-1-yl)triisopropylsilane (63)

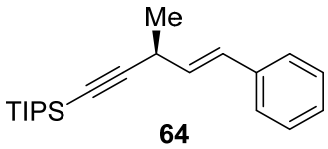


63

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-(3-phenoxyprop-1- en-1-yl)-1,3,2-dioxaborinane **2s** (52.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromopent- 1-yn-1-yl)triisopropylsilane **S60** (75.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to yield the product **63** as a colorless oil (58.6 mg, 82% yield, 98% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 6.02 min, t_R (major) = 6.69 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 2H), 6.98 – 6.87 (m, 3H), 6.09 – 5.97

(m, 1H), 5.84 – 5.71 (m, 1H), 4.54 (d, J = 5.7 Hz, 2H), 3.17 – 3.07 (m, 1H), 1.70 – 1.56 (m, 1H), 1.59 – 1.46 (m, 1H), 1.11 – 1.03 (m, 21H), 1.01 (t, J = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 133.6, 129.3, 125.7, 120.7, 114.7, 108.6, 83.5, 68.0, 36.7, 28.7, 18.6, 11.29, 11.25.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{37}OSi$ $[M+H]^+$ 357.2608, found 357.2603.

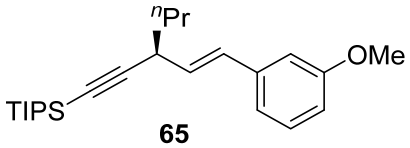
(*S*,*E*)-triisopropyl(3-methyl-5-phenylpent-4-en-1-yn-1-yl)silane (64)



64

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromobut-1-yn-1-yl) triisopropylsilane **S64** (72.3 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **64** as a colorless oil (33.0 mg, 53% yield, 97% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 7.31 min, t_R (major) = 7.91 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.35 – 7.26 (m, 2H), 7.26 – 7.17 (m, 1H), 6.73 (dd, J = 15.7, 1.4 Hz, 1H), 6.16 (dd, J = 15.7, 5.6 Hz, 1H), 3.43 – 3.31 (m, 1H), 1.36 (d, J = 7.1 Hz, 3H), 1.14 – 1.03 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 131.0, 129.5, 128.5, 127.2, 126.2, 110.2, 82.6, 29.9, 22.0, 18.6, 11.2.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{33}Si$ $[M+H]^+$ 313.2346, found 313.2344.

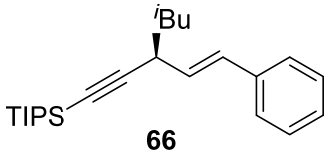
(*S*,*E*)-triisopropyl(3-(3-methoxystyryl)hex-1-yn-1-yl)silane (65)



65

According to **general produce D** with (*E*)-2-(3-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2y** (52.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromohex-1-yn-1-yl) triisopropylsilane **S65** (79.4 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **65** as a colorless oil (56.0 mg, 76% yield, 96% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 6.14 min, t_R (major) = 6.35 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.9 Hz, 1H), 6.95 (d, J = 7.7 Hz, 1H), 6.92 – 6.86 (m, 1H), 6.81 – 6.73 (m, 1H), 6.71 (dd, J = 15.7, 1.6 Hz, 1H), 6.13 (dd, J = 15.7, 5.9 Hz, 1H), 3.81 (s, 3H), 3.39 – 3.22 (m, 1H), 1.69 – 1.42 (m, 4H), 1.15 – 1.05 (m, 21H), 0.94 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 138.7, 130.3, 130.0, 129.4, 118.9, 112.6, 111.7, 109.0, 83.6, 55.1, 38.0, 35.5, 20.2, 18.6, 13.8, 11.2.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{39}OSi$ $[M+H]^+$ 371.2765, found 371.2764.

(*S*,*E*)-triisopropyl(5-methyl-3-styrylhex-1-yn-1-yl)silane (66)



66

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-5-methylhex-1-yn- 1-yl)triisopropylsilane **S66** (82.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **66** as a colorless oil (58.0 mg, 82% yield, 96% ee).

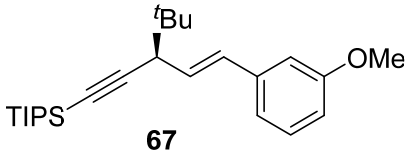
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 13.20 min, t_R (major) = 13.69 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 15.7 Hz, 1H), 6.13 (dd, *J* = 15.7, 6.0 Hz, 1H), 3.43 – 3.24 (m, 1H), 2.05 – 1.82 (m, 1H), 1.62 – 1.49 (m, 1H), 1.47 – 1.36 (m, 1H), 1.16 – 1.01 (m, 21H), 0.95 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 130.2, 129.9, 128.5, 127.1, 126.2, 109.1, 83.4, 45.1, 33.9, 25.9, 23.0, 21.8, 18.6, 11.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{39}Si$ $[M+H]^+$ 355.2816, found 355.2813.

(*R*,*E*)-(3-(tert-butyl)-5-(3-methoxyphenyl)pent-4-en-1-yn-1-yl)triisopropylsilane (67)



67

According to **general produce D** with (*E*)-2-(3-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2y** (52.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-4,4-dimethylpent-1-yn-1-yl)triisopropylsilane **S67** (82.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **67** as a colorless oil (55.0 mg, 72% yield, 98% ee).

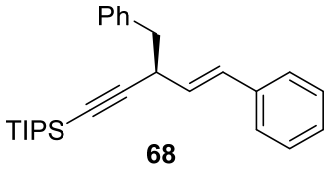
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 10.36 min, t_R (major) = 11.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.93 – 6.88 (m, 1H), 6.81 – 6.75 (m, 1H), 6.70 (dd, *J* = 15.7, 1.4 Hz, 1H), 6.22 (dd, *J* = 15.7, 6.8 Hz, 1H), 3.81 (s, 3H), 3.05 (dd, *J* = 6.8, 1.4 Hz, 1H), 1.14 – 1.07 (m, 21H), 1.04 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 138.9, 132.0, 129.4, 127.5, 118.9, 112.5, 111.9, 107.9, 84.7, 55.1, 47.7, 34.8, 27.5, 18.7, 11.3.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{41}OSi$ $[M+H]^+$ 385.2921, found 385.2921.

(*S*,*E*)-(3-benzyl-5-phenylpent-4-en-1-yn-1-yl)triisopropylsilane (68)



68

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-4-phenylbut-1- yn-1-yl)triisopropylsilane **S68** (91.4 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **68** as a colorless oil (68.0 mg, 88% yield, 98% ee).

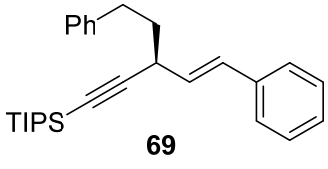
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 13.08 min, t_R (major) = 18.66 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 8H), 7.23 – 7.17 (m, 2H), 6.76 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.16 (dd, *J* = 15.7, 5.7 Hz, 1H), 3.69 – 3.48 (m, 1H), 2.93 (s, 1H), 2.91 (s, 1H), 1.13 – 1.01 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.1, 130.8, 129.4, 128.9, 128.5, 128.1, 127.3, 126.3, 108.2, 84.9, 42.5, 37.8, 18.6, 11.2.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{37}Si$ $[M+H]^+$ 389.2659, found 389.2658.

(*S*,*E*)-triisopropyl(3-phenethyl-5-phenylpent-4-en-1-yn-1-yl)silane (69)



69

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-5-phenylpent-1- yn-1-yl)triisopropylsilane **S69** (94.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **69** as a colorless oil (79.0 mg, 98% yield, 98% ee).

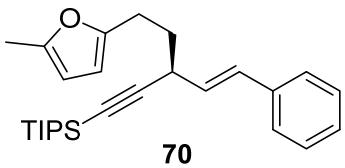
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 33.63 min, t_R (major) = 35.92 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 6H), 7.24 – 7.16 (m, 4H), 6.77 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.14 (dd, *J* = 15.7, 5.8 Hz, 1H), 3.40 – 3.23 (m, 1H), 2.97 – 2.74 (m, 2H), 2.09 – 1.77 (m, 2H), 1.20 – 1.03 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 137.1, 130.6, 129.4, 128.56, 128.52, 128.3, 127.2, 126.3, 125.8, 108.6, 84.4, 37.7, 35.2, 33.2, 18.7, 11.3.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{39}Si$ $[M+H]^+$ 403.2816, found 403.2813.

(*S*,*E*)-triisopropyl(3-(2-(5-methylfuran-2-yl)ethyl)-5-phenylpent-4-en-1-yn-1-yl)silane (70)



70

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-5-(5-methylfuran- 2-yl)pent-1-yn-1-yl)triisopropylsilane **S70** (95.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **70** as a colorless oil (71.0 mg, 87% yield, 98% ee).

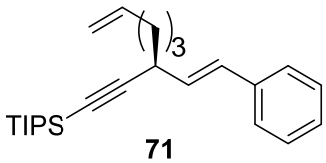
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 17.30 min, t_R (major) = 20.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.24 – 7.17 (m, 1H), 6.77 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.13 (dd, *J* = 15.7, 5.9 Hz, 1H), 5.88 (d, *J* = 3.0 Hz, 1H), 5.85 – 5.81 (m, 1H), 3.46 – 3.29 (m, 1H), 2.80 (t, *J* = 7.7 Hz, 2H), 2.24 (s, 3H), 2.05 – 1.94 (m, 1H), 1.93 – 1.82 (m, 1H), 1.18 – 1.04 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 150.4, 137.1, 130.7, 129.2, 128.5, 127.2, 126.3, 108.3, 105.8, 105.7, 84.3, 35.1, 34.3, 25.5, 18.6, 13.4, 11.2.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{39}OSi$ $[M+H]^+$ 407.2765, found 407.2760.

(*S*,*E*)-triisopropyl(3-styryloct-7-en-1-yn-1-yl)silane (71)



71

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromooct-7-en-1-yn-1-yl) triisopropylsilane **S71** (85.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **71** as a colorless oil (57.0 mg, 78% yield, 97% ee).

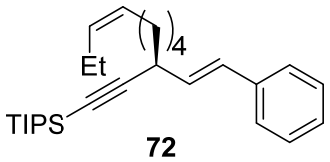
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 7.89 min, t_R (major) = 8.25 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 7.23 – 7.17 (m, 1H), 6.74 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.13 (dd, *J* = 15.7, 5.9 Hz, 1H), 5.87 – 5.74 (m, 1H), 5.05 – 4.93 (m, 2H), 3.35 – 3.27 (m, 1H), 2.23 – 2.01 (m, 2H), 1.75 – 1.55 (m, 4H), 1.19 – 1.00 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 137.2, 130.3, 129.8, 128.5, 127.2, 126.2, 114.5, 108.9, 83.8, 35.6, 35.3, 33.4, 26.2, 18.6, 11.3.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{39}Si$ $[M+H]^+$ 367.2816, found 367.2814.

Triisopropyl((*S*,*Z*)-3-((*E*)-styryl)undec-8-en-1-yn-1-yl)silane (72)



72

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromooct-7-en-1-yn-1-yl) triisopropylsilane **S72** (96.4 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **72** as a colorless oil (73.0 mg, 89% yield, 98% ee).

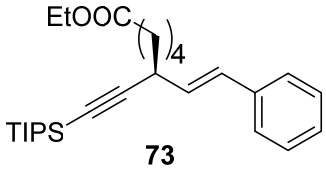
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 8.25 min, t_R (major) = 9.12 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 6.74 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.13 (dd, *J* = 15.7, 5.9 Hz, 1H), 5.41 – 5.27 (m, 2H), 3.36 – 3.24 (m, 1H), 2.13 – 1.94 (m, 4H), 1.73 – 1.47 (m, 4H), 1.45 – 1.32 (m, 2H), 1.17 – 1.03 (m, 21H), 0.95 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 131.7, 130.2, 129.9, 128.9, 128.5, 127.1, 126.2, 109.0, 83.7, 35.8, 35.7, 29.4, 27.0, 26.6, 20.5, 18.6, 14.3, 11.3.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{45}Si$ $[M+H]^+$ 409.3285, found 409.3285.

Ethyl (*S*,*E*)-8-phenyl-6-((triisopropylsilyl)ethynyl)oct-7-enoate (73)



73

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and ethyl 6-bromo-8-(triisopropylsilyl)oct-7-ynoate **S73** (100.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **73** as a colorless oil (67.0 mg, 79% yield, 98% ee).

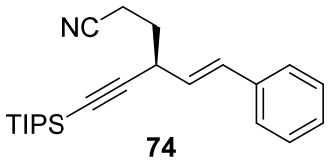
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 6.63 min, t_R (major) = 8.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 6.74 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.12 (dd, *J* = 15.7, 5.9 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.26 (m, 1H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.77 – 1.48 (m, 6H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.13 – 1.06 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 137.1, 130.4, 129.6, 128.4, 127.2, 126.2, 108.7, 83.8, 60.1, 35.5, 35.5, 34.2, 26.5, 24.7, 18.6, 14.2, 11.2.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{43}O_2Si$ $[M+H]^+$ 427.3027, found 427.3025.

(*S*,*E*)-6-phenyl-4-((triisopropylsilyl)ethynyl)hex-5-enenitrile (74)



74

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 4-bromo-6-(triisopropylsilyl) hex-5-ynenitrile **S74** (82.1 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **74** as a colorless oil (57.0 mg, 81% yield, 97% ee).

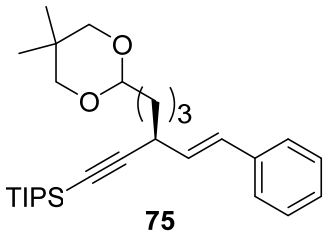
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 11.76 min, t_R (major) = 13.48 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.28 – 7.21 (m, 1H), 6.80 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.07 (dd, *J* = 15.7, 5.8 Hz, 1H), 3.59 – 3.42 (m, 1H), 2.65 – 2.46 (m, 2H), 2.19 – 2.00 (m, 1H), 1.98 – 1.82 (m, 1H), 1.17 – 1.03 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 132.1, 128.5, 127.7, 127.0, 126.3, 119.3, 105.9, 86.2, 34.7, 31.2, 18.6, 14.5, 11.1.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{34}NSi$ $[M+H]^+$ 352.2455, found 352.2451.

(*S*,*E*)-(6-(5,5-dimethyl-1,3-dioxan-2-yl)-3-styrylhex-1-yn-1-yl)triisopropylsilane (75)



75

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-6-(5,5-dimethyl- 1,3-dioxan-2- yl)hex-1-yn-1-yl)triisopropylsilane **S75** (107.9 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **75** as a colorless oil (84.0 mg, 92% yield, 98% ee).

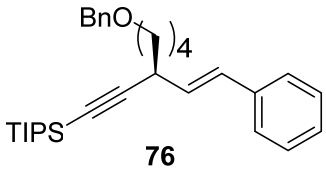
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 10.58 min, t_R (major) = 22.95 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 6.74 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.13 (dd, *J* = 15.7, 5.9 Hz, 1H), 4.42 – 4.38 (m, 1H), 3.58 (d, *J* = 11.3 Hz, 2H), 3.40 (d, *J* = 10.7 Hz, 2H), 3.34 – 3.26 (m, 1H), 1.78 – 1.58 (m, 6H), 1.18 (s, 3H), 1.14 – 1.03 (m, 21H), 0.70 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 130.3, 129.7, 128.4, 127.1, 126.2, 108.8, 102.0, 83.8, 77.1, 35.8, 35.7, 34.5, 30.0, 22.9, 21.8, 21.5, 18.6, 11.2.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{47}O_2Si$ $[M+H]^+$ 455.3340, found 455.3339.

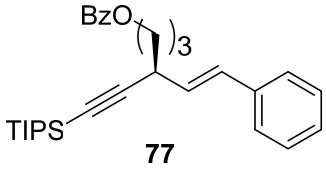
(*S*,*E*)-(7-(benzyloxy)-3-styrylhept-1-yn-1-yl)triisopropylsilane (76)



76

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (7-(benzyloxy)-3-bromohept-1-yn-1-yl)triisopropylsilane **S76** (109.4 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to yield the product **76** as a colorless oil (66.0 mg, 72% yield, 98% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 7.37 min, t_R (major) = 14.31 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.17 (m, 10H), 6.74 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.13 (dd, *J* = 15.7, 5.9 Hz, 1H), 4.49 (s, 2H), 3.47 (t, *J* = 6.0 Hz, 2H), 3.34 – 3.26 (m, 1H), 1.73 – 1.57 (m, 6H), 1.16 – 1.01 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 137.2, 130.3, 129.7, 128.4, 128.3, 127.5, 127.4, 127.2, 126.2, 108.9, 83.7, 72.8, 70.2, 35.74, 35.70, 29.4, 23.6, 18.6, 11.2.
HRMS (ESI) *m/z* calcd. for $C_{31}H_{45}OSi$ $[M+H]^+$ 461.3234, found 461.3232.

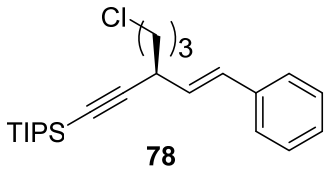
(*S*,*E*)-6-phenyl-4-((triisopropylsilyl)ethynyl)hex-5-en-1-yl benzoate (77)



77

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and 4-bromo-6-(triisopropylsilyl) hex-5-yn-1-yl benzoate **S77** (109.4 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to yield the product **77** as a colorless oil (72.0 mg, 78% yield, 98% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 8.37 min, t_R (major) = 10.20 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 7.60 – 7.50 (m, 1H), 7.46 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.18 (m, 1H), 6.78 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.15 (dd, *J* = 15.7, 5.8 Hz, 1H), 4.42 – 4.33 (m, 2H), 3.45 – 3.36 (m, 1H), 2.10 – 1.93 (m, 2H), 1.91 – 1.80 (m, 1H), 1.80 – 1.69 (m, 1H), 1.15 – 1.05 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 137.0, 132.8, 130.7, 130.3, 129.5, 129.2, 128.5, 128.2, 127.3, 126.3, 108.2, 84.4, 64.6, 35.4, 32.4, 26.2, 18.6, 11.2.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{41}O_2Si$ $[M+H]^+$ 461.2870, found 461.2868.

(*S*,*E*)-(6-chloro-3-styrylhex-1-yn-1-yl)triisopropylsilane (78)



78

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-6-chlorohex-1- yn-1-yl)triisopropylsilane **S78** (88.0 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **78** as a colorless oil (66.0 mg, 88% yield, 99% ee).

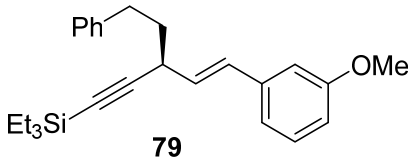
HPLC analysis: Chiralcel OD-H connected with Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.35 mL/min, λ = 254 nm), t_R (minor) = 52.87 min, t_R (major) = 54.87 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 4H), 7.26 – 7.18 (m, 1H), 6.77 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.12 (dd, *J* = 15.7, 5.8 Hz, 1H), 3.59 (t, *J* = 6.5 Hz, 2H), 3.42 – 3.31 (m, 1H), 2.11 – 1.92 (m, 2H), 1.91 – 1.80 (m, 1H), 1.78 – 1.64 (m, 1H), 1.20 – 1.01 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 130.8, 129.0, 128.5, 127.3, 126.3, 108.0, 84.5, 44.7, 35.0, 32.9, 29.9, 18.6, 11.2.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{36}ClSi$ $[M+H]^+$ 375.2269, found 375.2257.

(*S*,*E*)-triethyl(5-(3-methoxyphenyl)-3-phenethylpent-4-en-1-yn-1-yl)silane (79)



79

According to **general produce D** with (*E*)-2-(3-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2y** (52.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-5-phenylpent- 1-yn-1-yl)triethylsilane **S79** (84.4 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to yield the product **79** as a colorless oil (58.0 mg, 74% yield, 98% ee).

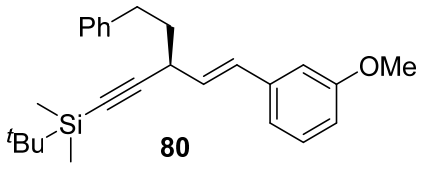
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 7.76 min, t_R (major) = 8.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.25 – 7.12 (m, 4H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.90 – 6.86 (m, 1H), 6.82 – 6.72 (m, 1H), 6.67 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.12 (dd, *J* = 15.7, 6.1 Hz, 1H), 3.80 (s, 3H), 3.33 – 3.22 (m, 1H), 2.92 – 2.74 (m, 2H), 2.07 – 1.77 (m, 2H), 1.05 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 141.7, 138.6, 130.5, 129.7, 129.4, 128.5, 128.3, 125.8, 119.0, 112.8, 111.7, 108.0, 85.6, 55.1, 37.5, 35.2, 33.2, 7.5, 4.5.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{35}OSi$ $[M+H]^+$ 391.2452, found 391.2452.

(*S*,*E*)-tert-butyl(5-(3-methoxyphenyl)-3-phenethylpent-4-en-1-yn-1-yl)dimethylsilane (80)



80

According to **general produce D** with (*E*)-2-(3-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2y** (52.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-5-phenylpent- 1-yn-1-yl)(tert-butyl)dimethylsilane **S80** (84.4 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to yield the product **80** as a colorless oil (63.0 mg, 81% yield, 98% ee).

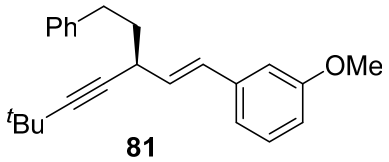
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 7.72 min, t_R (major) = 9.05 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.26 – 7.14 (m, 4H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.91 – 6.86 (m, 1H), 6.82 – 6.71 (m, 1H), 6.65 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.12 (dd, *J* = 15.7, 6.2 Hz, 1H), 3.80 (s, 3H), 3.36 – 3.18 (m, 1H), 2.96 – 2.67 (m, 2H), 2.04 – 1.83 (m, 2H), 0.99 (s, 9H), 0.15 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 141.7, 138.5, 130.6, 129.6, 129.4, 128.5, 128.3, 125.8, 119.0, 112.8, 111.7, 107.5, 86.5, 55.1, 37.4, 35.1, 33.2, 26.1, 16.5, -4.39.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{35}OSi$ $[M+H]^+$ 391.2452, found 391.2449.

(*S*,*E*)-1-(6,6-dimethyl-3-phenethylhept-1-en-4-yn-1-yl)-3-methoxybenzene (81)



81

According to **general produce D** with (*E*)-2-(3-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2y** (52.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-6,6-dimethylhept- 4-yn-1-yl)benzene **S81** (69.8 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to yield the product **81** as a colorless oil (56.0 mg, 84% yield, 97% ee).

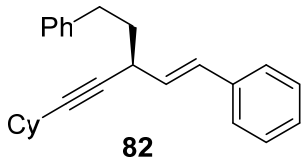
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 7.71 min, t_R (major) = 8.75 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.24 – 7.14 (m, 4H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.91 – 6.88 (m, 1H), 6.81 – 6.71 (m, 1H), 6.59 (dd, *J* = 15.6, 1.5 Hz, 1H), 6.12 (dd, *J* = 15.6, 6.3 Hz, 1H), 3.80 (s, 3H), 3.23 – 3.11 (m, 1H), 2.89 – 2.70 (m, 2H), 1.98 – 1.77 (m, 2H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 142.0, 138.7, 130.9, 129.9, 129.4, 128.5, 128.3, 125.7, 119.0, 112.7, 111.6, 93.1, 78.5, 55.1, 37.7, 34.1, 33.2, 31.4, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{29}O$ $[M+H]^+$ 333.2213, found 333.2210.

(*S*,*E*)-(3-(cyclohexylethynyl)pent-1-ene-1,5-diyl)dibenzene (82)



82

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromo-5-cyclohexylpent- 4-yn-1-yl)benzene **S82** (76.3 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **82** as a colorless oil (56.0 mg, 85% yield, 97% ee).

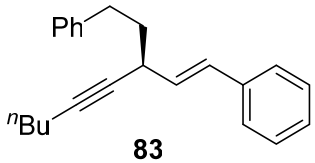
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 54.92 min, t_R (major) = 57.51 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.32 – 7.25 (m, 4H), 7.24 – 7.15 (m, 4H), 6.64 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.14 (dd, *J* = 15.7, 6.3 Hz, 1H), 3.31 – 3.14 (m, 1H), 2.93 – 2.71 (m, 2H), 2.55 – 2.41 (m, 1H), 1.98 – 1.80 (m, 4H), 1.79 – 1.70 (m, 2H), 1.56 – 1.45 (m, 3H), 1.39 – 1.26 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 137.2, 130.5, 130.0, 128.5, 128.4, 128.3, 127.1, 126.2, 125.7, 88.6, 80.2, 37.7, 34.3, 33.2, 33.1, 29.1, 25.9, 24.8.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{29}$ $[M+H]^+$ 329.2264, found 329.2261.

(*S*,*E*)-(3-(hex-1-yn-1-yl)pent-1-ene-1,5-diyl)dibenzene (83)



83

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromonon-4-yn-1-yl) benzene **S83** (69.8 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **83** as a colorless oil (54.0 mg, 89% yield, 94% ee).

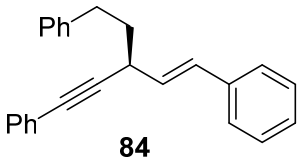
HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 14.81 min, t_R (major) = 16.63 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.24 (m, 4H), 7.24 – 7.14 (m, 4H), 6.63 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.13 (dd, *J* = 15.7, 6.4 Hz, 1H), 3.33 – 3.12 (m, 1H), 2.91 – 2.67 (m, 2H), 2.34 – 2.17 (m, 2H), 1.98 – 1.80 (m, 2H), 1.62 – 1.40 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 137.2, 130.5, 130.1, 128.5, 128.4, 128.3, 127.1, 126.2, 125.7, 84.2, 80.3, 37.7, 34.3, 33.2, 31.2, 21.9, 18.5, 13.6.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{27}$ $[M+H]^+$ 303.2107, found 303.2105.

(*S*,*E*)-(3-phenethylpent-1-en-4-yne-1,5-diyl)dibenzene (84)



84

According to **general produce D** with (*E*)-4,4,6-trimethyl-2-styryl-1,3,2-dioxaborinane **2a** (46.0 mg, 0.20 mmol, 1.0 equiv) and (3-bromopent-1-yne-1,5-diyl) dibenzene **S84** (74.8 mg, 0.25 mmol, 1.25 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **84** as a colorless oil (51.0 mg, 79% yield, 96% ee).

HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 15.20 min, t_R (major) = 16.81 min.

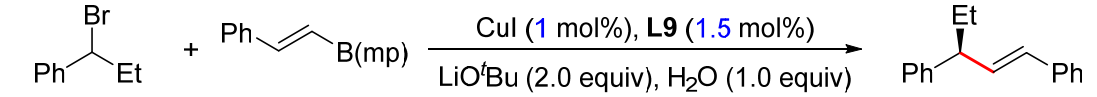
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.27 (m, 7H), 7.26 – 7.17 (m, 4H), 6.70 (dd, *J* = 15.7, 1.3 Hz, 1H), 6.20 (dd, *J* = 15.7, 6.6 Hz, 1H), 3.54 – 3.38 (m, 1H), 2.98 – 2.80 (m, 2H), 2.03 (q, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 137.0, 131.6, 130.6, 129.5, 128.56, 128.51, 128.4, 128.2, 127.8, 127.3, 126.3, 125.9, 123.6, 90.1, 84.1, 37.3, 34.8, 33.3.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{23}$ $[M+H]^+$ 323.1794, found 323.1792.

Synthetic utility

Gram-scale reaction

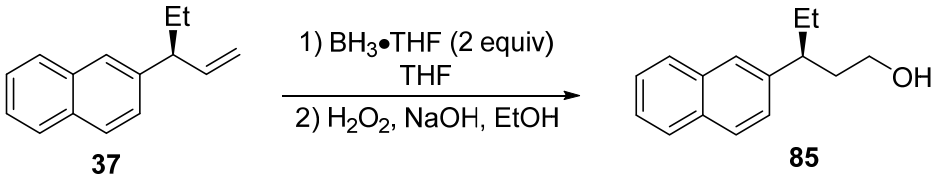


1a (1.5 equiv) **2a**, 1.15 g **3**, 73%, 94% ee

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI (9.5 mg, 1 mol%), chiral ligand **L9** (39.7 mg, 1.5 mol%), LiO^{t}Bu (800.5 mg, 2.0 equiv). The tube was evacuated and backfilled with argon three times. Then DMF (25.0 mL) and H_2O (90.0 mg, 1.0 equiv) were added under a counter flow of argon. Finally alkenylboronate esters **2a** (1.15 g, 5.0 mmol), and benzyl bromide **1a** (1.493 g, 7.5 mmol, 1.5 equiv) were added by syringe under a counter flow of argon. The tube was sealed and the mixture was allowed to stir at –20 °C for 8 d. Upon completion of the reaction, water was poured into the mixture. The mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the desired product **3** as a colorless oil (812.3 mg, 73% yield, 94% ee).

Synthesis of chiral building blocks

(*S*)-3-(naphthalen-2-yl)pentan-1-ol (85)[15]



37 **85**

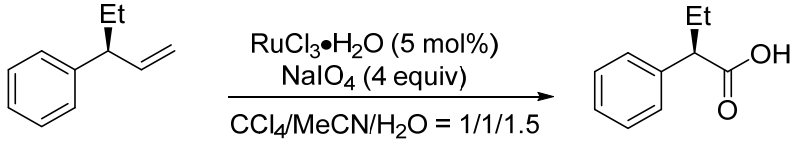
To a cooled solution of **37** (40 mg, 0.2 mmol) in THF (2.0 mL) was added a solution of BH_3·THF (1M in THF, 0.4 mL, 0.4 mmol) at ice water bath. The reaction mixture was stirred for 0.5 h, then it was allowed to reach room temperature. EtOH (2.5 mL), aq NaOH (1 M, 2.5 mL) and aq H_2O_2 (30%, 1.0 mL) were added sequentially. The resulting mixture was stirred vigorously overnight at room temperature, and then quenched with aq $Na_2S_2O_3$ (10 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **85** as a colorless oil. (38.0 mg, 89% yield, 90% ee)

HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 11.23 min, t_R (minor) = 12.48 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 3H), 7.59 (s, 1H), 7.49 – 7.38 (m, 2H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.58 – 3.40 (m, 2H), 2.82 – 2.68 (m, 1H), 2.06 – 1.95 (m, 1H), 1.94 – 1.84 (m, 1H), 1.80 – 1.62 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 133.5, 132.3, 128.1, 127.6, 127.5, 126.4, 125.9, 125.7, 125.2, 61.2, 44.3, 39.1, 29.7, 12.1.

(*R*)-2-phenylbutanoic acid (86)[16]



25 **86**

To a solution of **25** (29 mg, 0.2 mmol) and $NaIO_4$ (170 mg, 0.8 mmol) in CCl_4/MeCN/H_2O (1:1:1.5, 1.4 mL) was added $RuCl_3$·H_2O (2.3 mg, 0.01 mmol). The reaction mixture was stirred vigorously overnight. Afterward, CH_2Cl_2 (10 mL) and H_2O (5 mL) were added, and the organic layer was separated. The aqueous layer was further extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was dissolved in EtOAc (10 mL) and extracted with sat. aq $NaHCO_3$ (3 × 5 mL). The combined aqueous phase was acidified and extracted with CH_2Cl_2 (3 × 10 mL), dried over $MgSO_4$, filtered and concentrated in vacuo to afford the crude product. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1 – 3/1) to give the corresponding product **86** as a white solid (20.0 mg, 61% yield).

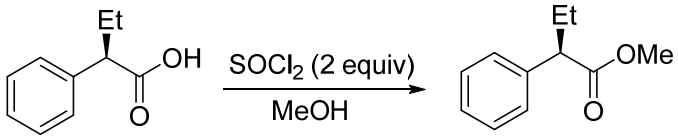
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.28 – 7.23 (m, 1H), 3.45 (t, *J* = 7.7 Hz, 1H), 2.18 – 2.02 (m, 1H), 1.88 – 1.73 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 138.4, 128.6, 128.1, 127.4, 53.3, 26.3, 12.1.

*Note: The ee value (92%) of product **86** was determined by chiral HPLC analysis of*

***methyl (R)-2-phenylbutanoate (87)**, which was obtained by transformation of product **86**.*

Methyl (*R*)-2-phenylbutanoate (87)[16]



86 **87**

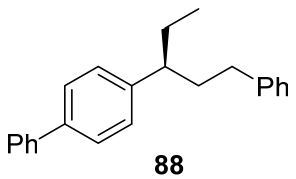
To a solution of **86** (21 mg, 0.13 mmol) in MeOH (5 mL) was added $SOCl_2$ (30.9 mg, 0.26 mmol). This mixture was heated to reflux for 3 h before evaporation. The residue was dissolved in DCM (30 mL), washed sequentially with aqueous $NaHCO_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated to give the crude residue. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to give the corresponding product **87** as a white solid (18.0 mg, 78% yield, 92% ee).

HPLC analysis: Chiralcel AS-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 4.40 min, t_R (major) = 4.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 5H), 3.65 (s, 3H), 3.45 (t, *J* = 7.7 Hz, 1H), 2.18 – 2.02 (m, 1H), 1.87 – 1.72 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 139.1, 128.5, 127.9, 127.2, 53.4, 51.9, 26.7, 12.1.

(*S*)-4-(1-phenylpentan-3-yl)-1,1'-biphenyl (88)[17]



88

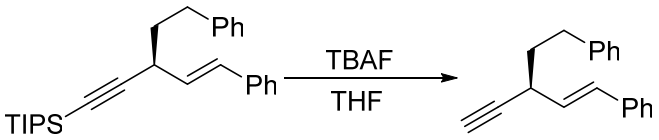
The procedure is followed the **general produce C**, except the following changes: After completion of the reaction, the reaction mixture was filtered by a short pad of silica gel (petroleum ether/ethyl acetate = 10/1) and concentrated under reduced pressure. Then crude product was dissolved in MeOH (5 mL) and followed by the addition of 10 mg Pd/C as solid (10 wt.%, wetted with ca. 55% water). Then a hydrogen-filled balloon was attached. The reaction was stirred at room temperature for 5 h. The resulting mixture was filtered and concentrated, and the residue was purified by column chromatography on silica gel as a colorless oil (39.0 mg, 65% yield, 93% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 15.34 min, t_R (minor) = 25.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.66 – 7.59 (m, 2H), 7.54 – 7.46 (m, 2H), 7.43 – 7.36 (m, 1H), 7.36 – 7.28 (m, 4H), 7.27 – 7.16 (m, 3H), 2.65 – 2.50 (m, 3H), 2.15 – 1.92 (m, 2H), 1.87 – 1.61 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 142.6, 128.7, 128.4, 128.2, 127.0, 126.9, 125.6, 47.0, 38.1, 33.9, 29.8, 12.1.

(*S,E*)-(3-ethynylpent-1-ene-1,5-diyl)dibenzene (89-1):



69, 98% ee **89-1**

The (*S,E*)-triisopropyl(3-phenethyl-5-phenylpent-4-en-1-yn-1-yl)silane **69** (80.5 mg, 0.20 mmol, 1.0 equiv) was dissolved in anhydrous THF (1 mL) under argon atmosphere in a 10 mL Schlenk flask. Then TBAF (0.72 mL, 0.72 mmol, 3.6 equiv**,** 1 M in THF**)** were added into the solution in three batches, and the mixture was stirred for 3 h at –10 °C. Upon completion of the reaction. The reaction mixture was poured into water (10 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to yield the product **89-1** as a colorless oil (35.0 mg, 71% yield, 98% ee).

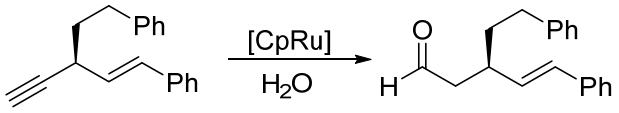
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 10.25 min, t_R (major) = 11.32 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.26 (m, 4H), 7.25 – 7.16 (m, 4H), 6.66 (dd, *J* = 15.8, 1.4 Hz, 1H), 6.13 (dd, *J* = 15.8, 6.5 Hz, 1H), 3.30 – 3.18 (m, 1H), 2.94 – 2.71 (m, 2H), 2.33 (d, *J* = 2.4 Hz, 1H), 2.03 – 1.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 136.9, 130.8, 128.9, 128.52, 128.51, 128.3, 127.4, 126.3, 125.9, 84.6, 71.8, 37.1, 33.9, 33.0.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}$ $[M+H]^+$ 247.1481, found 247.1478.

(*R,E*)-3-phenethyl-5-phenylpent-4-enal (89):



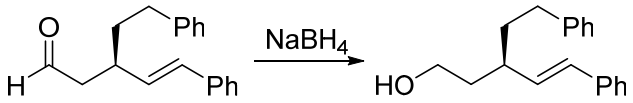
89-1 **89**

In a nitrogen-filled drybox, a 10-mL vial was charged sequentially with 5,5'-bis(trifluoromethyl)-2,2'-bipyridine (1.31 mg, 45 μmol, 0.045 equiv), tris(acetonitrile) (η^5-cyclopentadienyl)ruthenium hexafluorophosphate (1.95 mg, 45 μmol, 0.045 equiv), a mixture of water–*N*-methyl-2-pyrrolidinone (20% v/v, 0.5 mL), and (*S,E*)-(3-ethynylpent-1-ene-1,5-diyl)dibenzene (**89-1**, 24.6 mg, 0.1 mmol, 1.0 equiv). The vial was sealed with a Teflon-lined cap and the sealed vial was removed from the drybox. The mixture was stirred for 24 h at 25 ºC. Upon completion of the reaction. The reaction mixture was poured into water (10 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to yield the product **89** as a colorless oil (22.2 mg, 84% yield). The ee value of **89** was determined by converting it to the corresponding alcohol **90**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 2.2 Hz, 1H), 7.40 – 7.14 (m, 10H), 6.45 (d,

J = 15.8 Hz, 1H), 6.07 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.89 – 2.77 (m, 1H), 2.76 – 2.67 (m, 1H), 2.65 – 2.58 (m, 1H), 2.54 (dd, *J* = 6.9, 2.2 Hz, 2H), 1.91 – 1.68 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 141.7, 136.9, 132.1, 131.4, 128.5, 128.4, 128.4, 127.4, 126.2, 125.9, 49.1, 37.4, 36.7, 33.3.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}O$ $[M+H]^+$ 265.1587, found 265.1587.

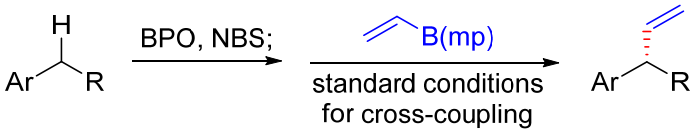
(*R*,*E*)-3-phenethyl-5-phenylpent-4-en-1-ol (90):



89 **90**

To an ordinary vial equipped with a magnetic stirring bar was added aldehyde **89** (13.2 mg, 0.05 mmol, 1 equiv) in CH_2Cl_2 (0.5 mL) at ambient temperature. MeOH (0.1 mL) and $NaBH_4$ (9.5 mg, 0.25 mmol, 5 equiv) was added, and the reaction was run until determined complete by TLC (CH_2Cl_2 as eluent). The reaction was quenched by addition of NH_4Cl and extracted with CH_2Cl_2 followed by drying with $MgSO_4$. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to yield the product **90** as a colorless oil (12.9 mg, 97% yield, 98% ee).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 12.03 min, t_R (major) = 13.27 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.35 – 7.12 (m, 8H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.01 (dd, *J* = 15.8, 9.3 Hz, 1H), 3.73 – 3.62 (m, 2H), 2.73 – 2.66 (m, 1H), 2.62 – 2.54 (m, 1H), 2.40 – 2.33 (m, 1H), 1.86 – 1.74 (m, 2H), 1.75 – 1.66 (m, 1H), 1.65 – 1.56 (m, 1H), 1.32 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 137.3, 134.1, 130.9, 128.5, 128.4, 128.3, 127.1, 126.1, 125.7, 61.1, 40.0, 38.3, 37.4, 33.6.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}O$ $[M+H]^+$ 267.1743, found 267.1740.

The general procedures for late-stage

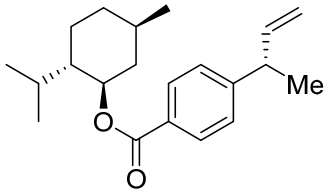


Under an argon atmosphere, alkane (0.3 mmol, 1.0 equiv) was dissolved in tetrachloromethane (2.0 mL), followed by the addition of N-bromosuccinimide (58.7 mg, 1.1 equiv) and benzoyl peroxide (3.6 mg, 5 mol%). The reaction mixture was stirred at 80 °C for 6 h. Upon completion of the reaction, the reaction mixture was cooled to room temperature, and then filtered. The filtrate was washed with sodium thiosulfate aqueous solution (1 M), and the mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was used directly for the next

step without further purification.

The crude product was transferred to a schlenk tube. The tube was evacuated and backfilled with argon three times. DMF (1.0 mL) was added via syringe, followed by the addition of CuI (1.90 mg), Chiral ligand **L9** (7.93 mg, 7.5 mol%) and LiO^{t}Bu (32.0 mg, 2.0 equiv). Then DMF (1.0 mL) and H_2O (3.6 mg, 1.0 equiv) were added under a counter flow of argon. Finally, alkenylboronate esters **2w** (32.8 mg, 0.2 mmol) was added by microsyringe. The mixture was allowed to stir at −20 ºC for 4 d. Upon completion of the reaction (monitored by TLC), water was poured into the reaction mixture. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the desired product.

(*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-((*S*)-but-3-en-2-yl)benzoate (91)



91

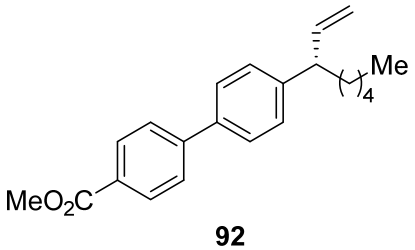
According to the general procedure, (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-ethylbenzoate was employed to yield the product **91** as a colorless oil (30.0 mg, 48% yield, dr>20:1). Dr value was based on ^{1}H NMR analysis of the crude product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.31 – 7.23 (m, 2H), 6.04 – 5.94 (m, 1H), 5.11 – 5.03 (m, 2H), 4.97– 4.87 (m, 1H), 3.58 – 3.47 (m, 1H), 2.16 – 2.08 (m, 1H), 2.00 – 1.90 (m, 1H), 1.77 – 1.68 (m, 2H), 1.62 – 1.50 (m, 3H), 1.37 (d, J = 7.0 Hz, 3H), 1.23 – 1.04 (m, 2H), 0.97 – 0.87 (m, 6H), 0.79 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 150.7, 142.3, 129.8, 128.8, 127.2, 113.8, 74.6, 47.3, 43.2, 41.0, 34.3, 31.4, 26.5, 23.6, 22.0, 20.8, 20.6, 16.5.

HRMS (ESI) m/z calcd. for $C_{21}H_{30}O_2Na$ $[M+Na]^+$ 337.2138, found 337.2144.

Methyl (*S*)-4'-(oct-1-en-3-yl)-[1,1'-biphenyl]-4-carboxylate (92)



92

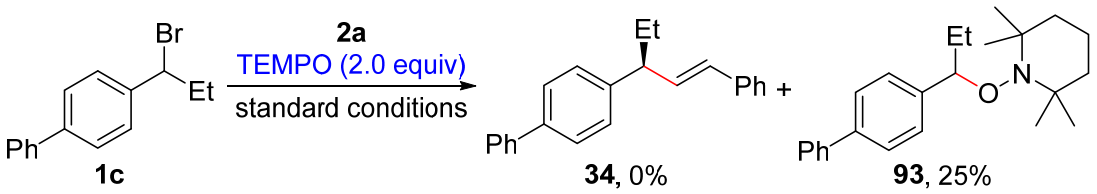
According to the general procedure, methyl 4'-hexyl-[1,1'-biphenyl]-4-carboxylate was employed to yield the product **92** as a white solid (30.3 mg, 47% yield, 87% ee).

HPLC analysis: Chiralcel OJ-3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 22.14 min, t_R (major) = 24.70 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 2H), 7.67 – 7.62 (m, 2H), 7.59 – 7.53 (m, 2H), 7.31 – 7.26 (m, 2H), 6.03 – 5.91 (m, 1H), 5.10 – 5.00 (m, 2H), 3.93 (s, 3H), 3.29 (q, *J* = 7.5 Hz, 1H), 1.80 – 1.68 (m, 2H), 1.39 – 1.19 (m, 6H), 0.91 – 0.82 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 145.5, 144.9, 142.2, 137.7, 130.0, 128.6, 128.1, 127.3, 126.8, 114.1, 52.1, 49.6, 35.3, 31.8, 27.2, 22.5, 14.1.
HRMS (ESI) m/z calcd. for $C_{22}H_{27}O_2$ $[M+H]^+$ 323.2006, found: 323.2005.

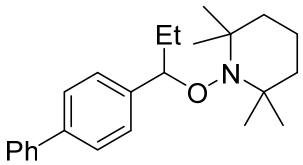
Mechanism studies

Scheme S2: TEMPO-trapped product



An oven-dried Schlenk equipped with a magnetic stirring bar was charged with CuI (1.90 mg, 5 mol%), chiral ligand **L9** (7.93 mg, 7.5mol%), LiO^tBu (32.0 mg, 2.0 equiv.), **1c** (82.6 mg, 0.3 mmol) and TEMPO (62.5 mg, 0.4 mmol). The tube was evacuated and backfilled with argon three times. Then DMF (2.0 mL) and H_2O (3.6 mg, 1.0 equiv.) were added under a counter flow of argon. Finally, **2a** (46 mg, 0.2 mmol) was added by microsyringe under a counter flow of argon. The tube was sealed and the mixture was allowed to stir at –20 ºC for 4 d. Upon completion of the reaction, water was poured into the reaction mixture. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product.

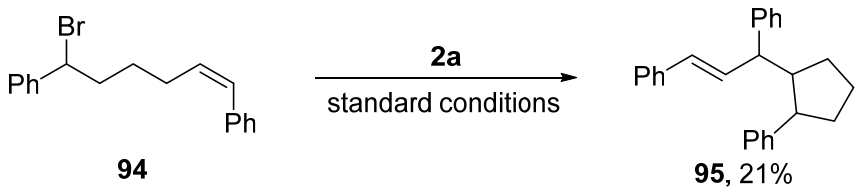
1-(1-([1,1'-biphenyl]-4-yl)propoxy)-2,2,6,6-tetramethylpiperidine (93):



93

The reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **93** as a white solid (26.1 mg, 25% yield based on **1c**).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.58 – 7.51 (m, 2H), 7.47 – 7.38 (m, 2H), 7.37 – 7.28 (m, 3H), 4.59 (dd, *J* = 9.5, 3.9 Hz, 1H), 2.22 – 2.07 (m, 1H), 1.91 – 1.75 (m, 1H), 1.60 – 0.96 (m, 16H), 0.71 (t, *J* = 7.5 Hz, 3H), 0.65 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 141.1, 139.5, 128.7, 128.1, 127.00, 126.97, 126.4, 88.3, 59.7, 40.4, 34.2, 28.7, 20.4, 17.2, 9.7.
HRMS (APCI) *m/z* calcd. for $C_{24}H_{34}ON$ $[M+H]^+$ 352.2635, found 352.2625.

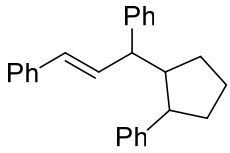
Radical clock experiment



94 **95**, 21%

An oven-dried Schlenk equipped with a magnetic stirring bar was charged with CuI (1.90 mg, 5 mol%), chiral ligand **L9** (7.93 mg, 7.5 mol%) and LiO^{t}Bu (32.0 mg, 2.0 equiv). The tube was evacuated and backfilled with argon three times. Then DMF (2.0 mL) and H_2O (3.6 mg, 1.0 equiv) were added under a counter flow of argon. Finally, **94** (94.5 mg, 0.3 mmol) and **2a** (46 mg, 0.2 mmol) were added by microsyringe in turn under a counter flow of argon. The tube was sealed and the mixture was allowed to stir at –20 °C for 4 d. Upon completion of the reaction, water was poured into the reaction mixture. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to afford **95** (21% yield, **95** containing inseparable impurities **95'** and an NMR yield is given. **95'** was produced via cross-coupling of **94** and **2a**).

(*E*)-(3-(2-phenylcyclopentyl)prop-1-ene-1,3-diyl)dibenzene (95):

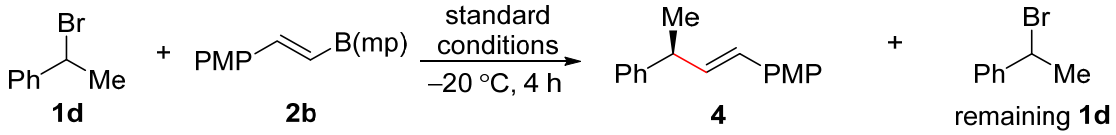


95

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 7.25 – 7.10 (m, 10H), 6.46 – 6.29 (m, 2H), 3.41 – 3.31 (m, 1H), 2.61 – 2.53 (m, 1H), 2.10 – 1.99 (m, 1H), 1.84 – 1.65 (m, 4H), 1.39 – 1.29 (m, 2H).

HRMS (ESI) *m/z* calcd. for $C_{26}H_{27}$ $[M+H]^+$ 339.2107, found 339.2102.

Experiments with racemic and enantioenriched alkyl bromide 1d:

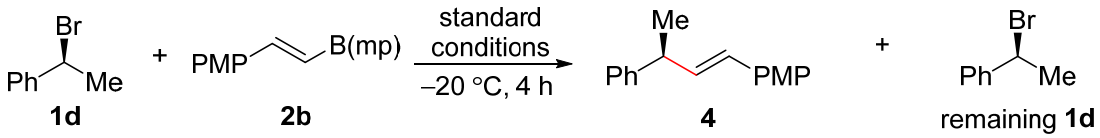


1d **2b** **4** remaining **1d**

(±)-**1d**, 0% ee 21%, 82% ee 0% ee

According to general procedure with (1-bromoethyl)benzene (±)-**1d** (55.5 mg, 0.30 mmol, 1.5 equiv), (*E*)-2-(4-methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane **2b** (52.0 mg, 0.20 mmol, 1.0 equiv), and for facile determination of yield by isolated, **4** (10.0 mg, 21% yield, 82% ee) was obtained.

Reaction time	Yield of **4**	ee of remaining **1d**	ee of **4**
4 h	21%	0%	82%



(*S*)-**1d**, 67% ee

22%, 82% ee

67% ee

The procedure for the reaction with (*S*)-(1-bromoethyl)benzene[6] (*S*)-**1d** was the same with that for (±)-**1d** described above except that (*S*)-**1d** (55.5 mg, 67% ee, 0.30 mmol, 2.0 equiv.) was used instead of (±)-**S1-1**.

Reaction time	Yield of **4**	ee of remaining **1d**	ee of **4**
4 h	22%	67%	82%

We speculate that the reaction temperature may not be easily controlled at –20 °C at the early stage of the reaction. The benzyl halide and **2b** may react a little at temperature above –20 °C and this may lead to the drop of ee in the coupling product especially when the product is formed in a small amount.

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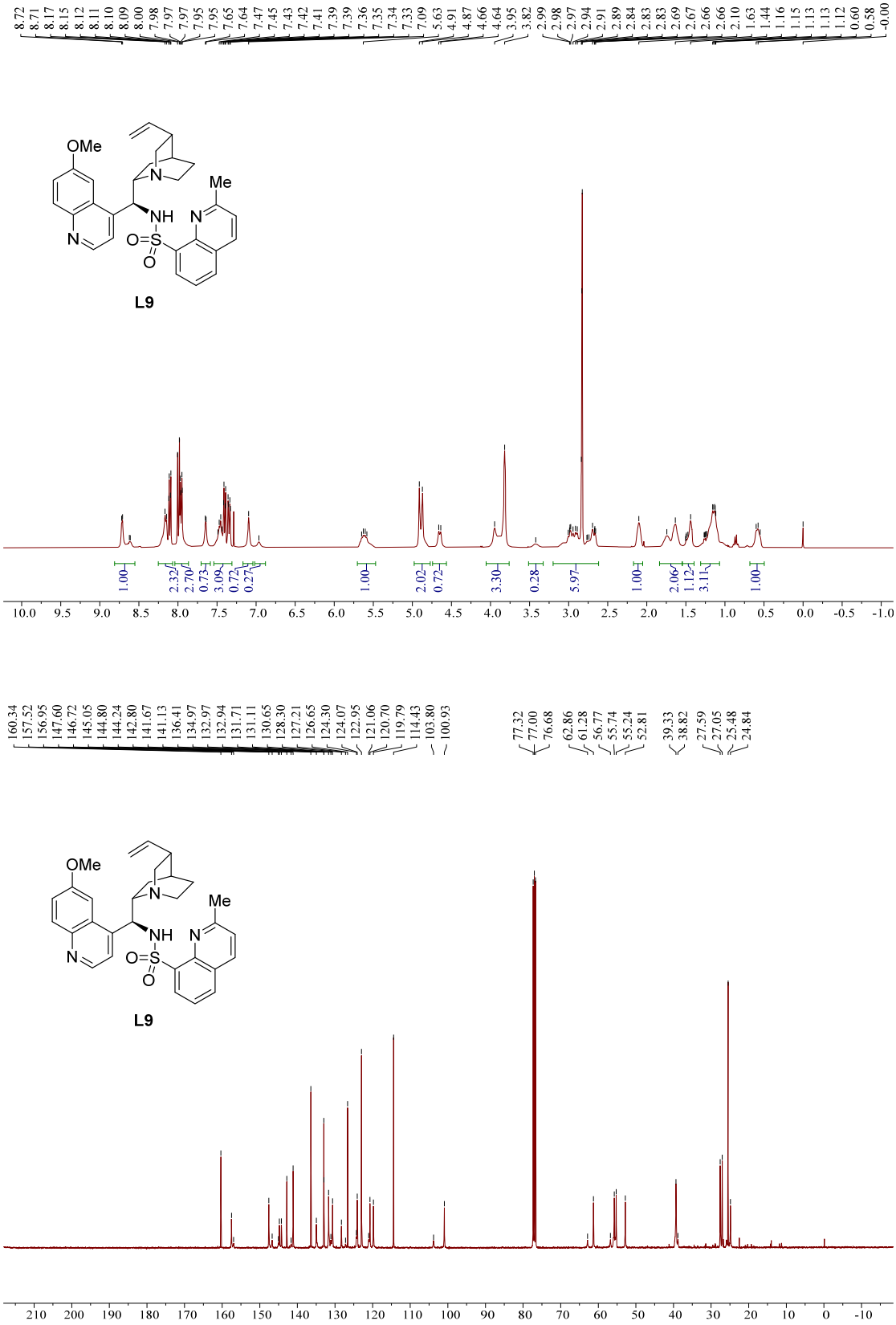
NMR spectra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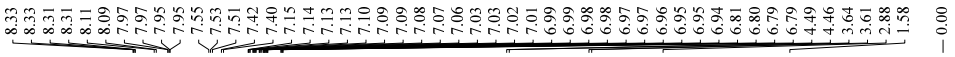
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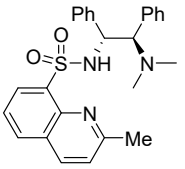
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f1 (ppm)


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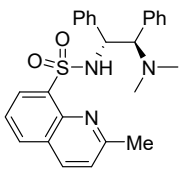
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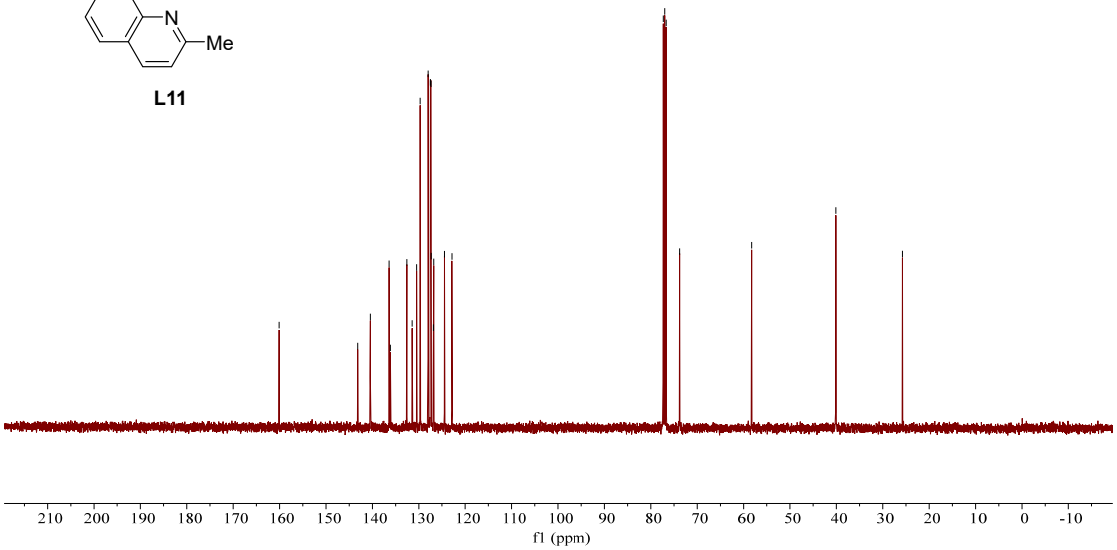
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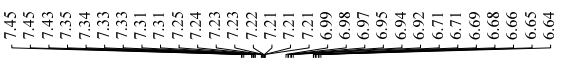
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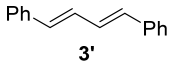
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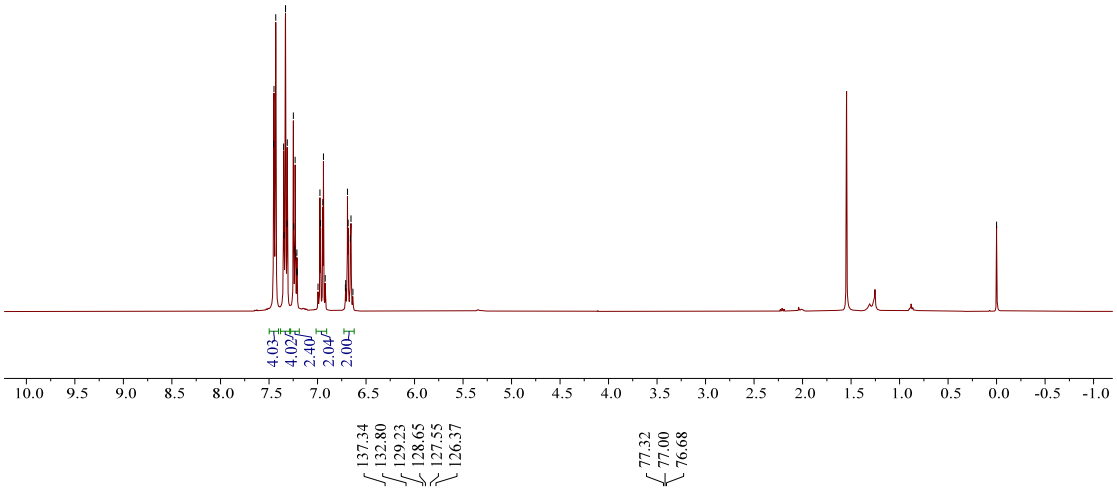
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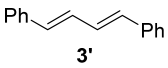
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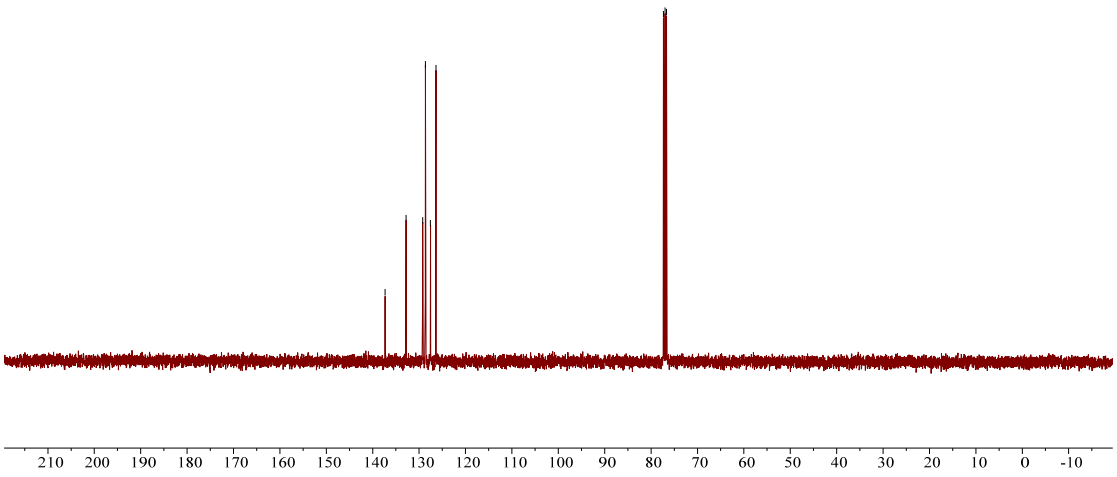
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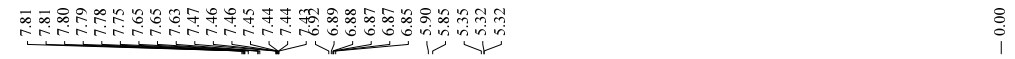
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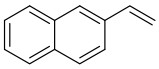

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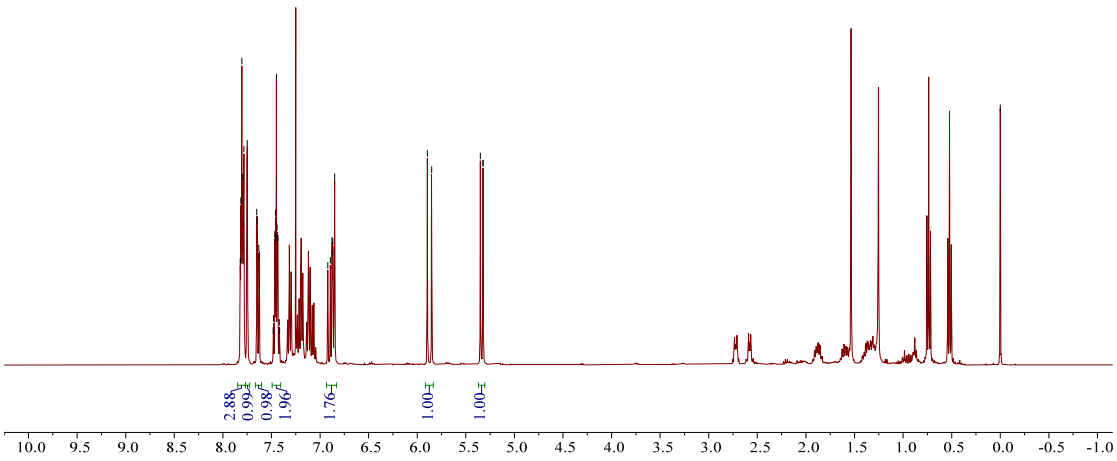
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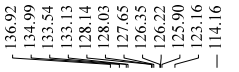
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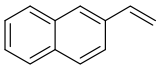

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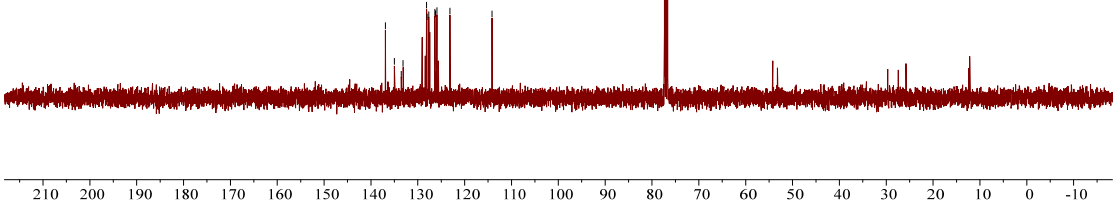
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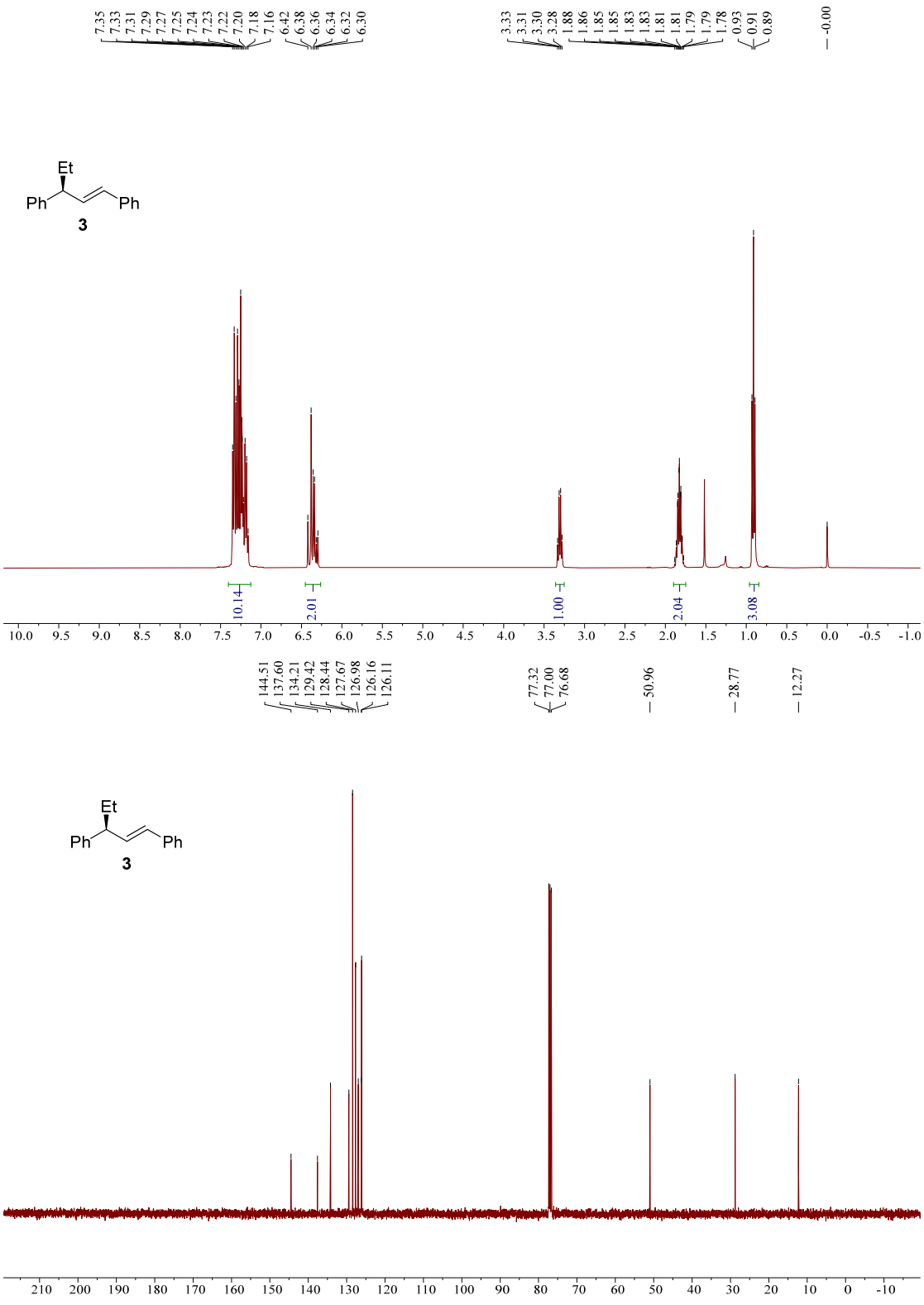
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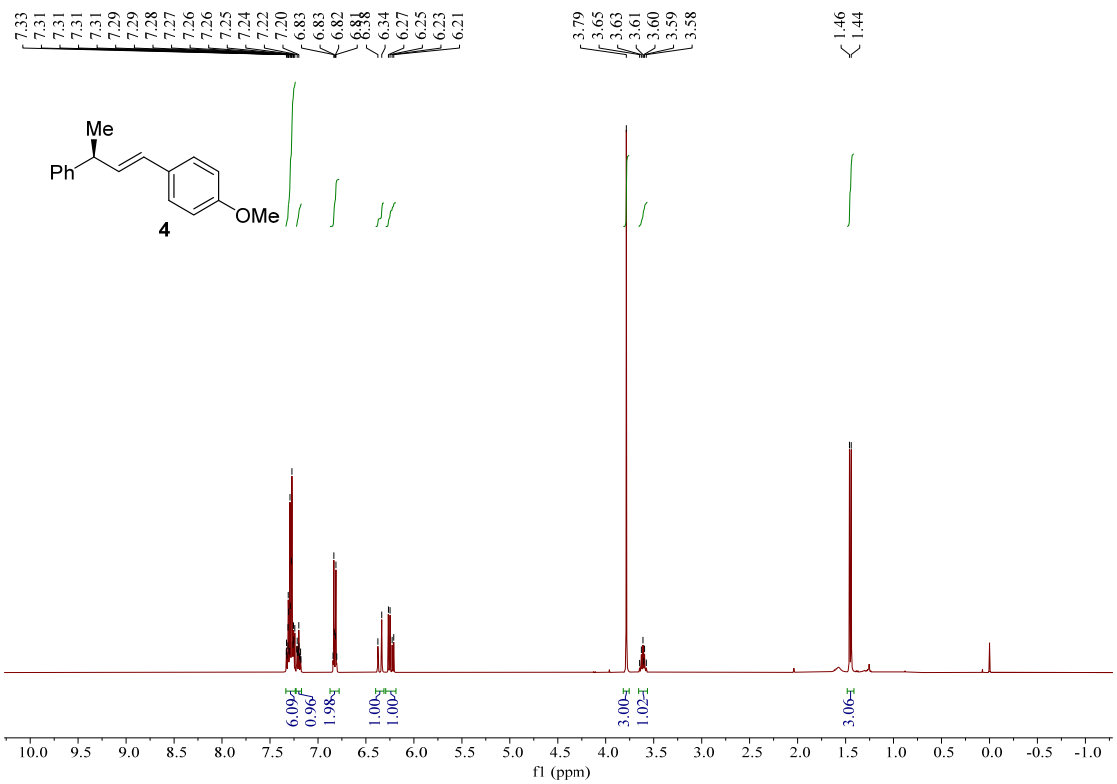
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3.06
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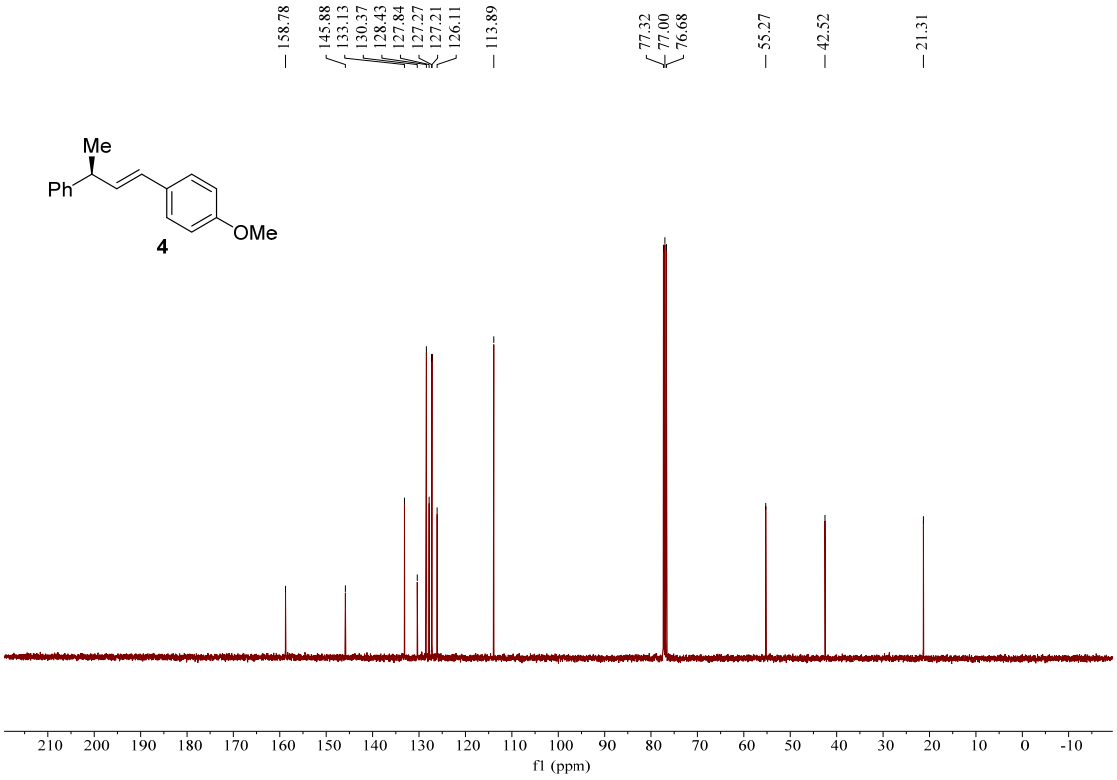
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OMe
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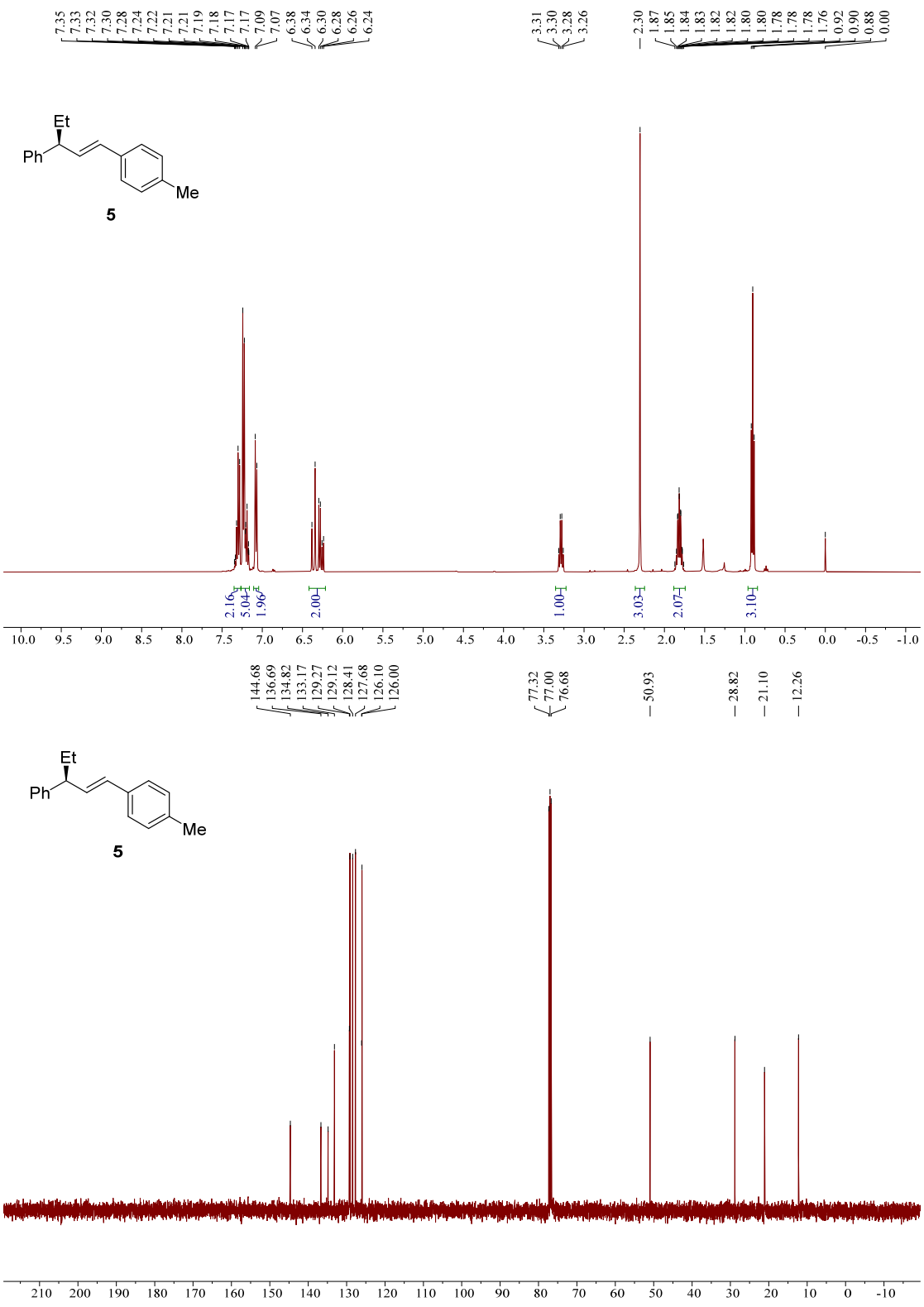
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0.00
Et
Ph
Me
5
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1.96
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1.00
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2.07
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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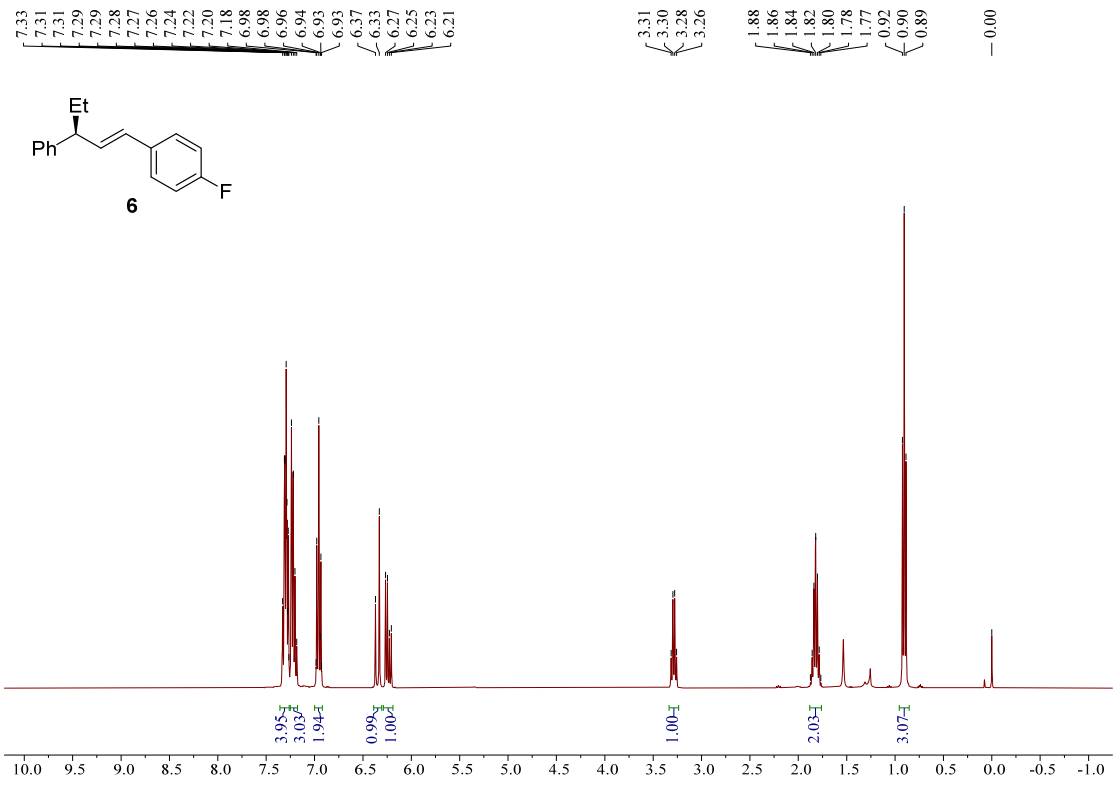
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6.93
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6.27
6.25
6.23
6.21
3.31
3.30
3.28
3.26
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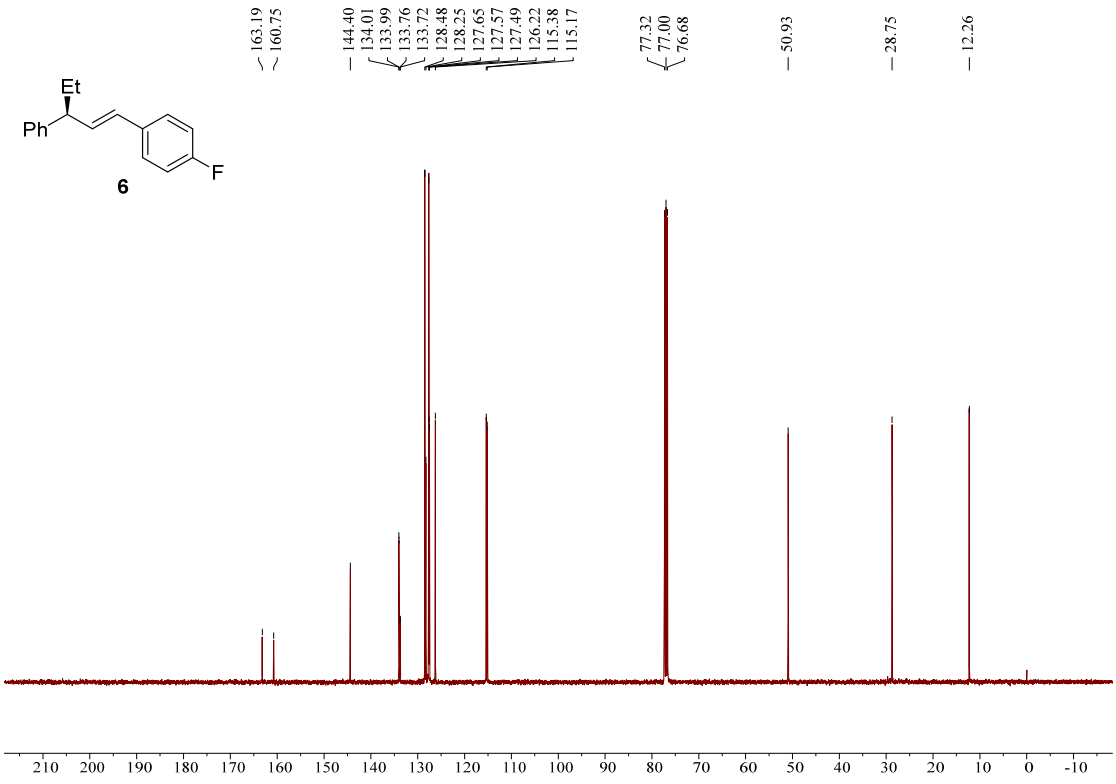
1.86
1.84
1.82
1.80
1.78
1.77
0.92
0.90
0.89
0.00
Et
Ph
F
6
3.95
3.03
1.94
0.99
1.00
1.00
2.03
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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Et
Ph
F
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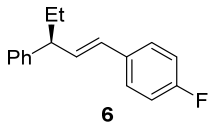
Et
Ph
F

6

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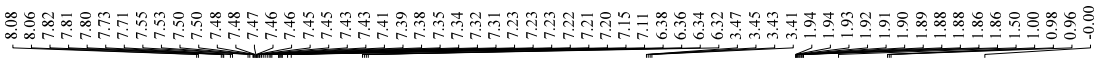
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3.41
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1.94
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1.92
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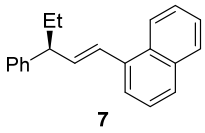
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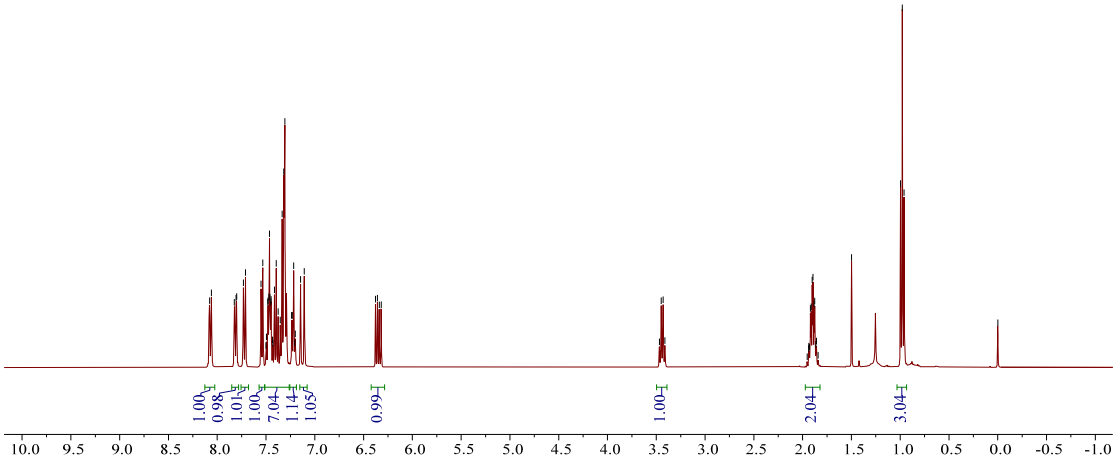
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6.0
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5.0
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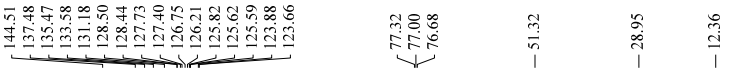
-1.0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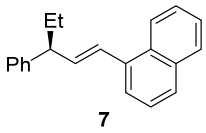
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Ph

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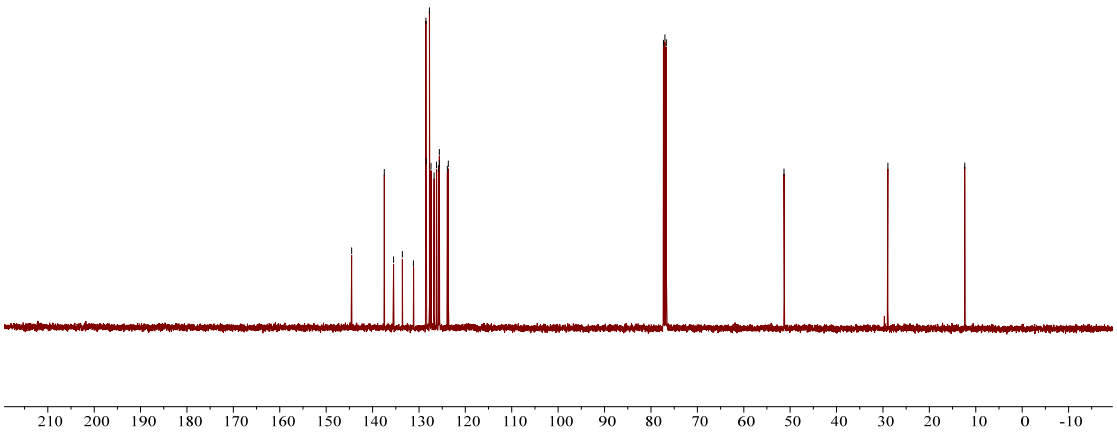
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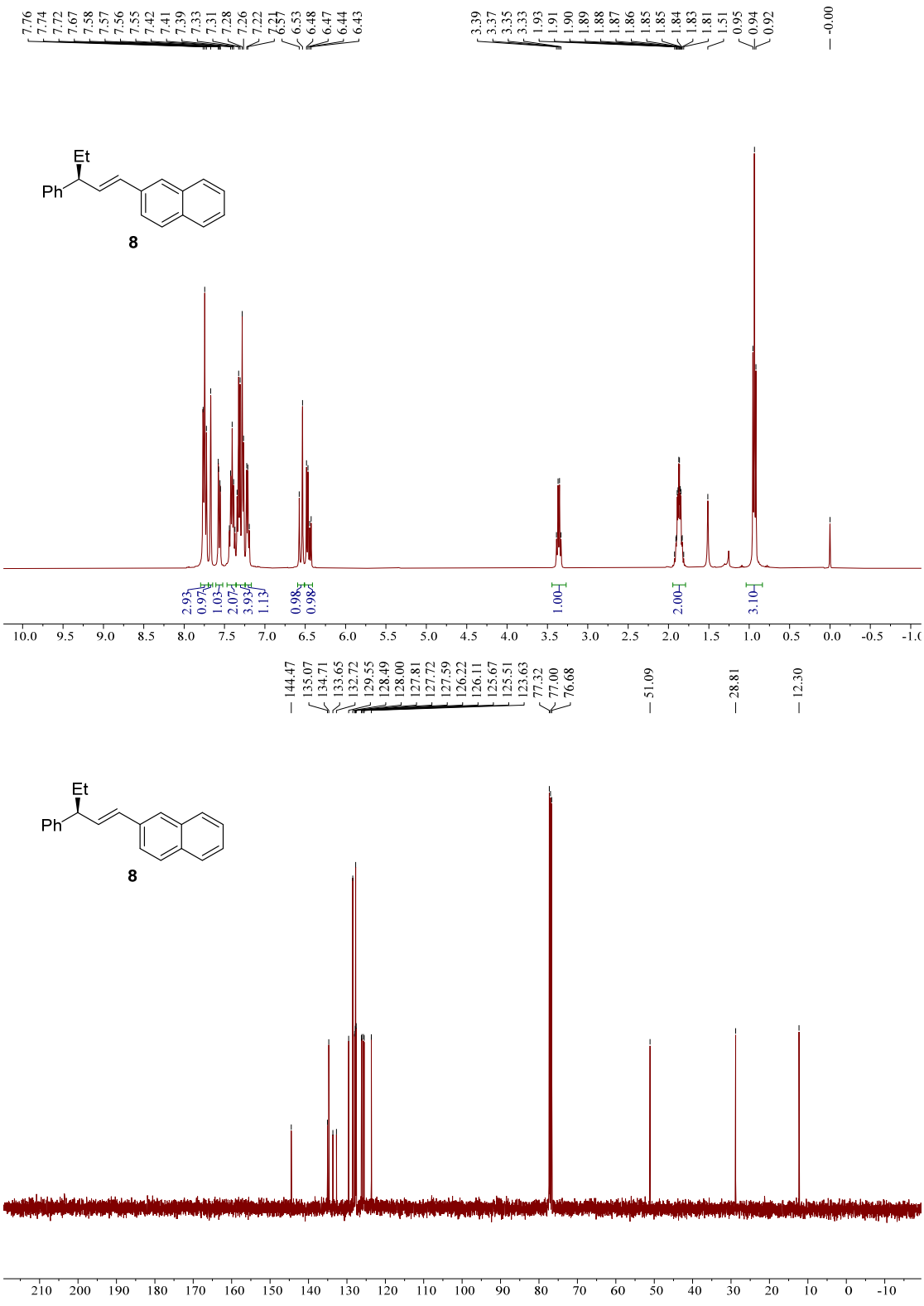
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Et
Ph
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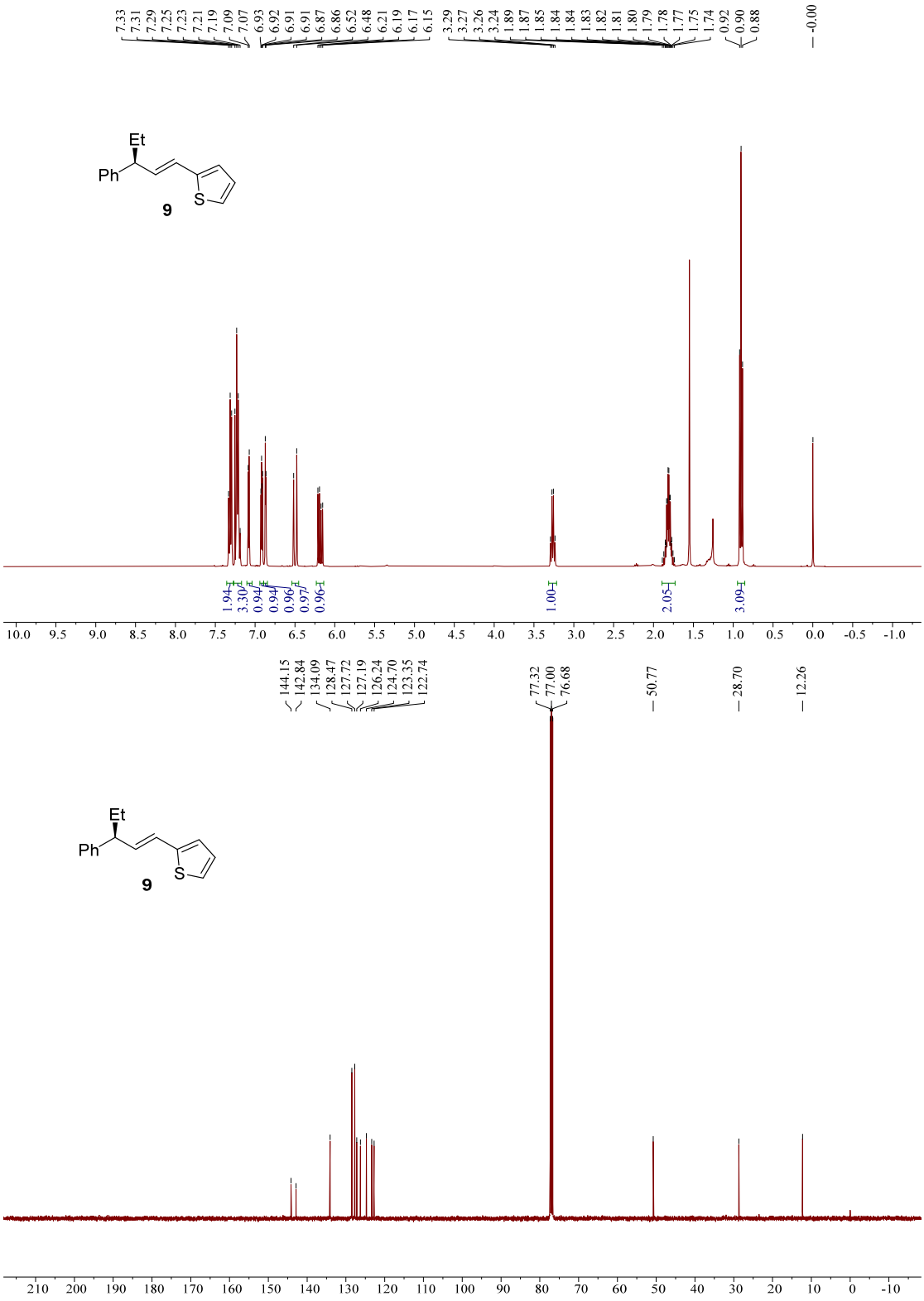
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1.74
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0.88
-0.00
Et
Ph
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3.30
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0.96
0.97
0.96
1.00
2.05
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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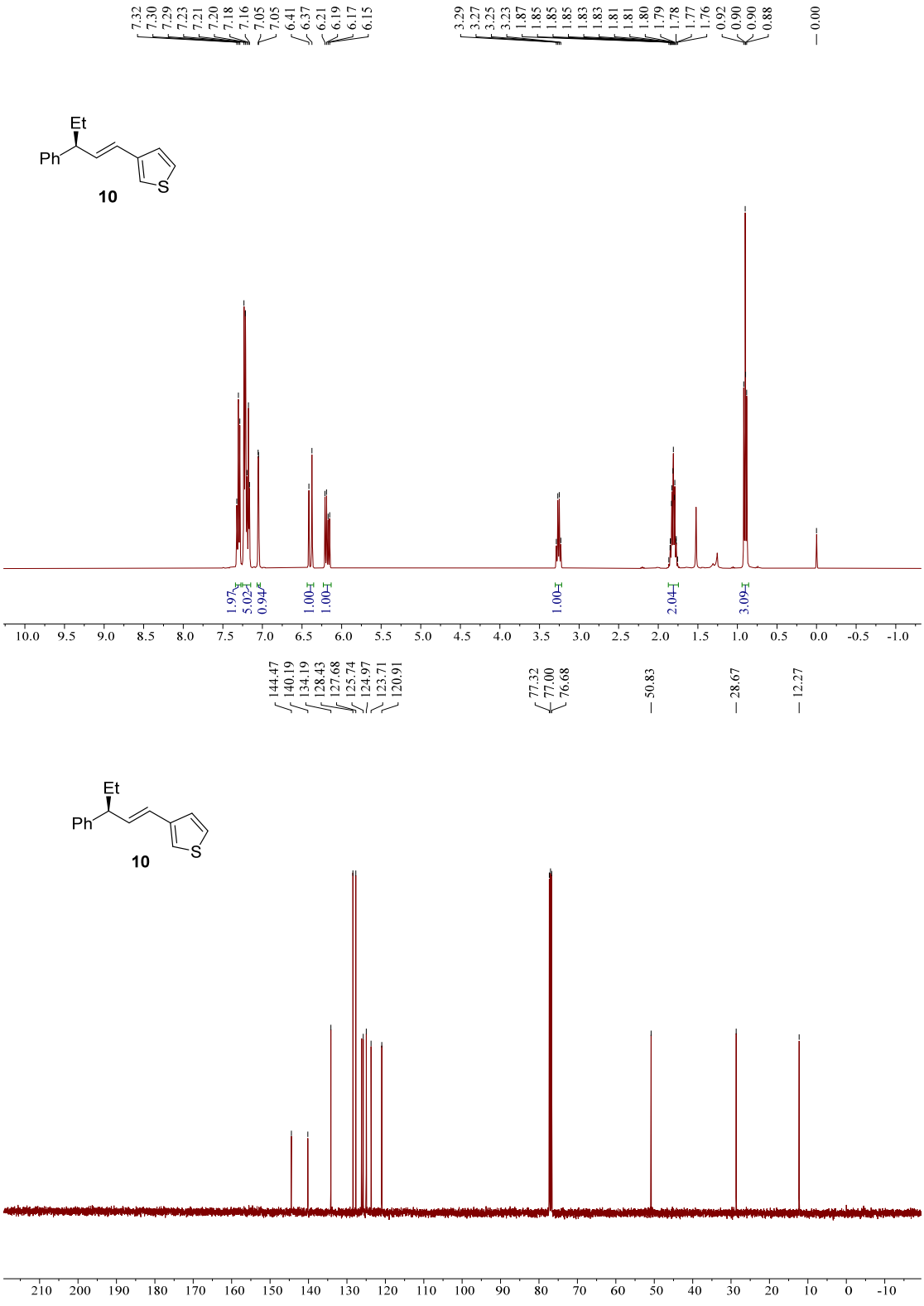
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0.90
0.88
0.00
Et
Ph
S
10
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5.02
0.94
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1.00
1.00
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3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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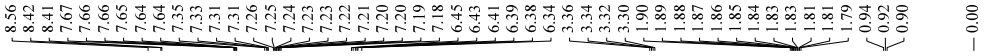
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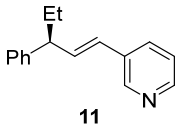
Et
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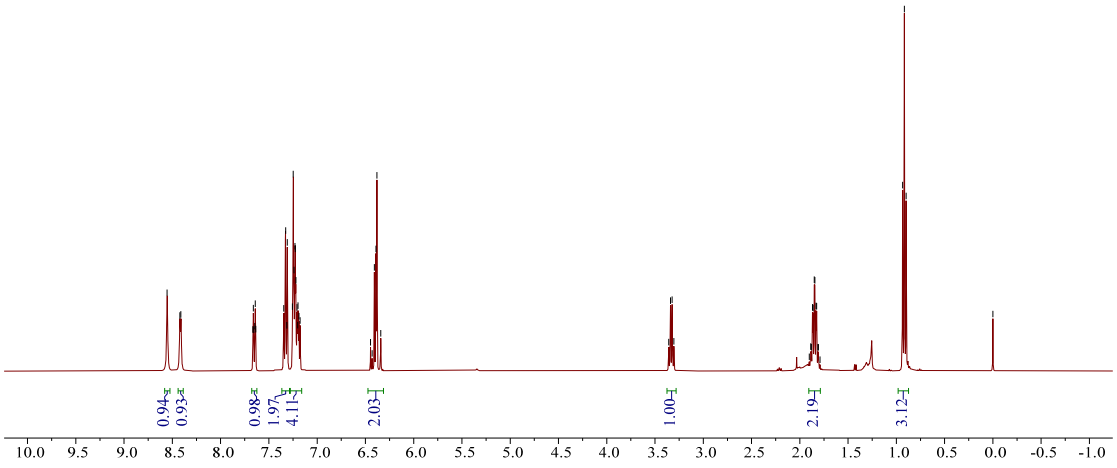
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7.5
7.0
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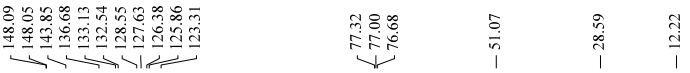
-1.0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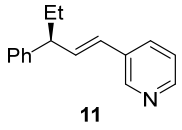
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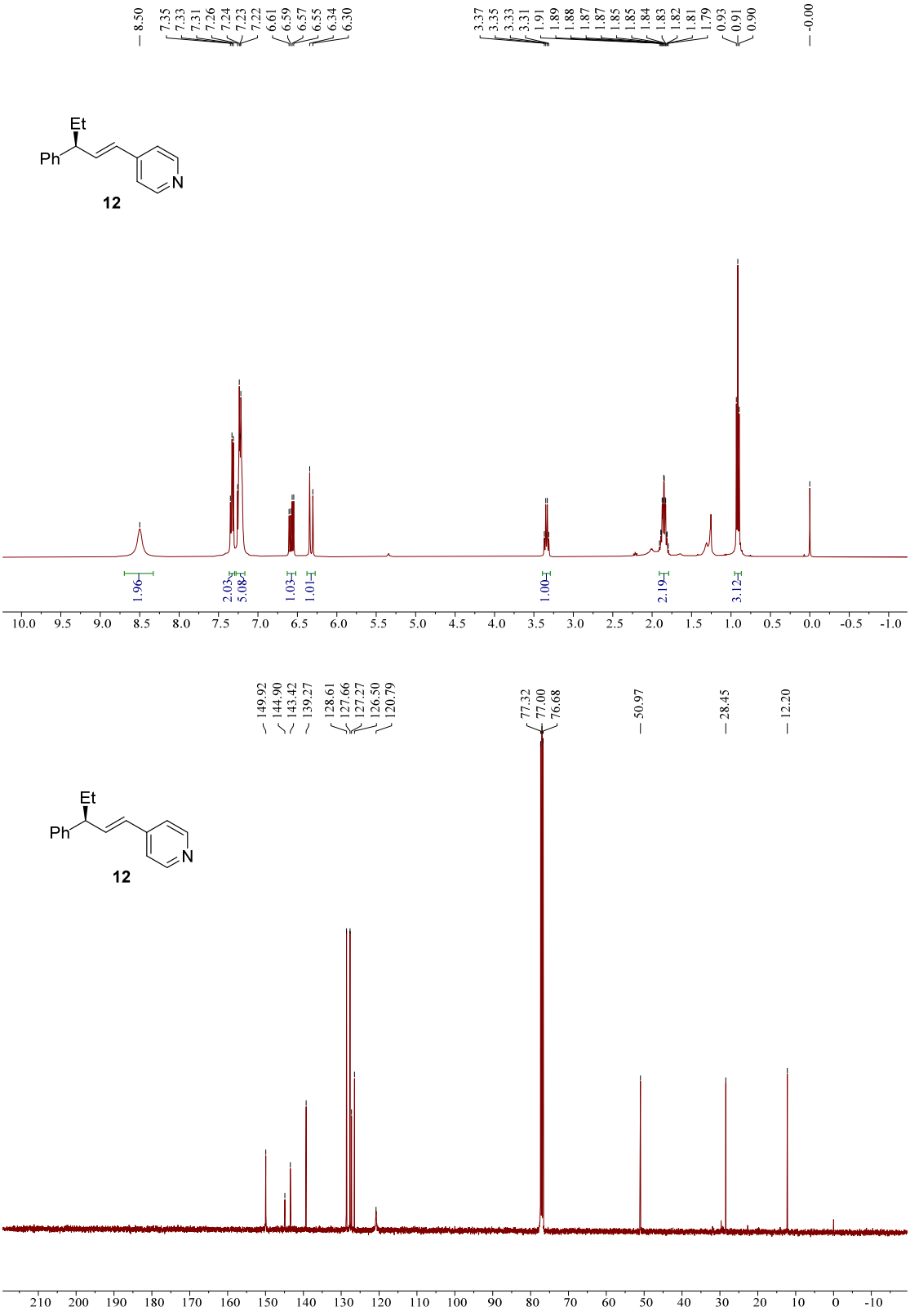
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Ph
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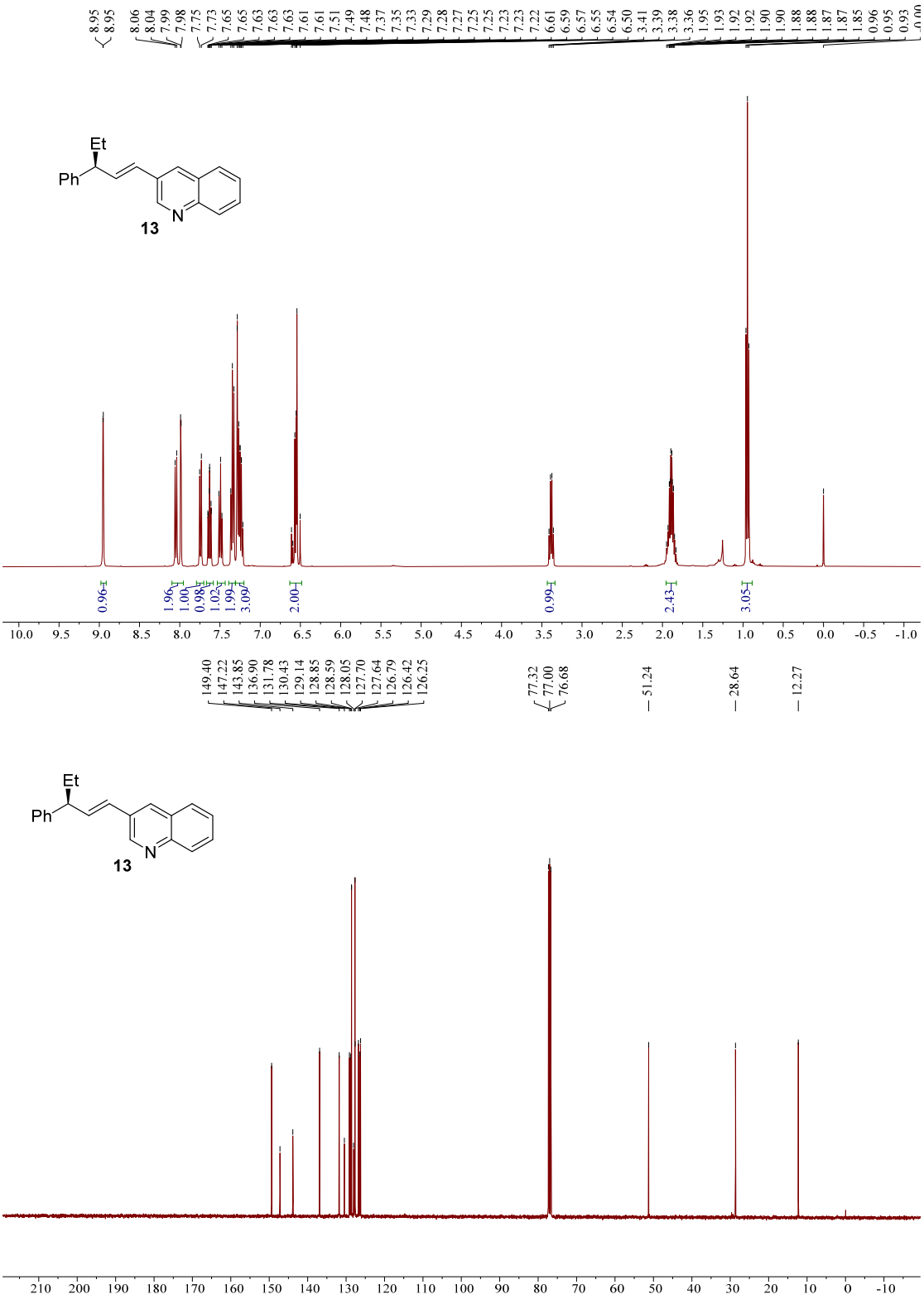
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0.96 1.96 1.00 0.98 1.02 1.99 3.09 2.00 0.99 2.43 3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
149.40 147.22 143.85 136.90 131.78 130.43 129.14 128.85 128.59 128.05 127.70 127.64 126.79 126.42 126.25
77.32 77.00 76.68
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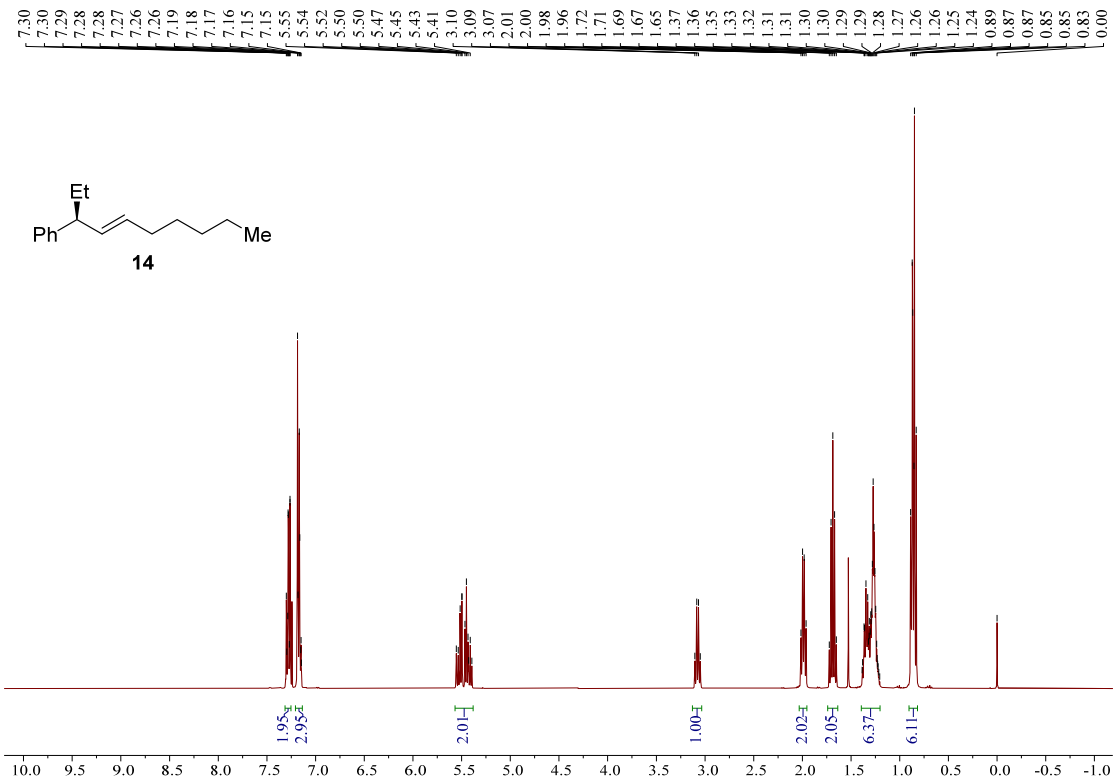
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Et
Ph
Me
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6.37
6.11
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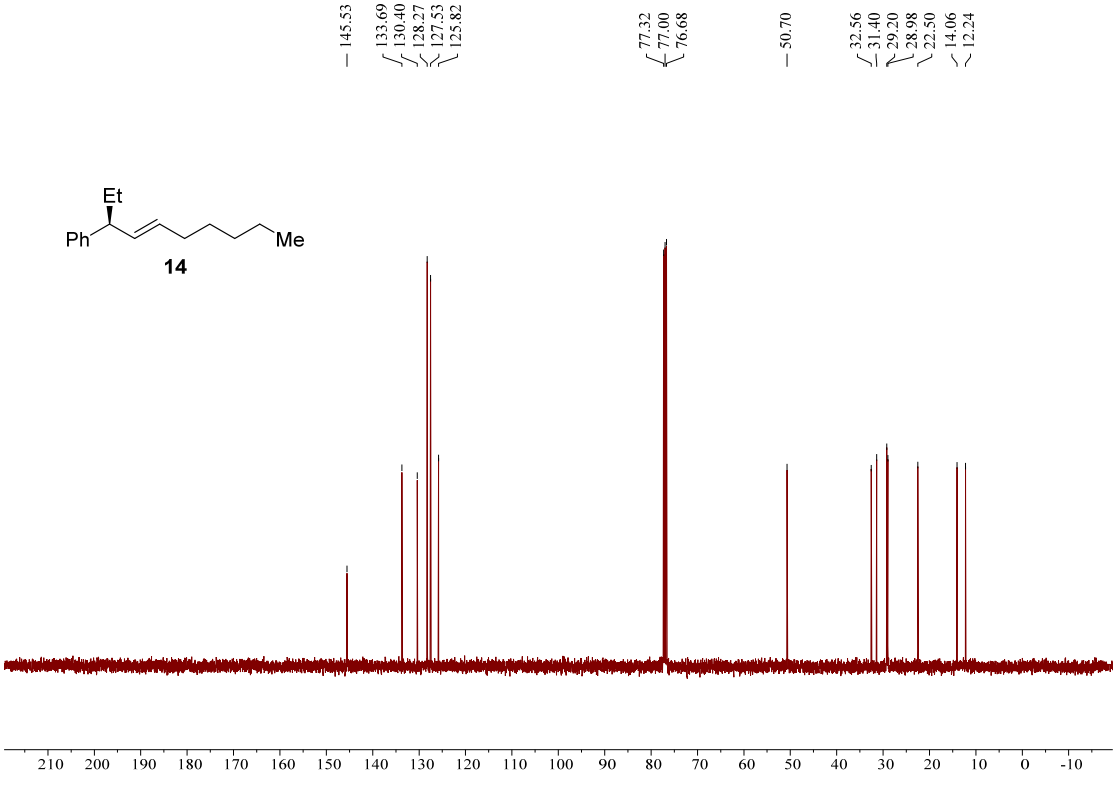
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14.06
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Et
Ph
Me
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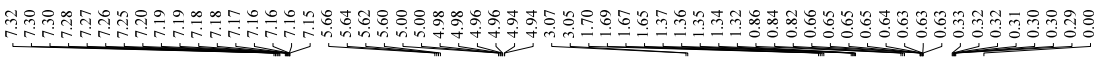
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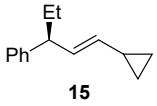
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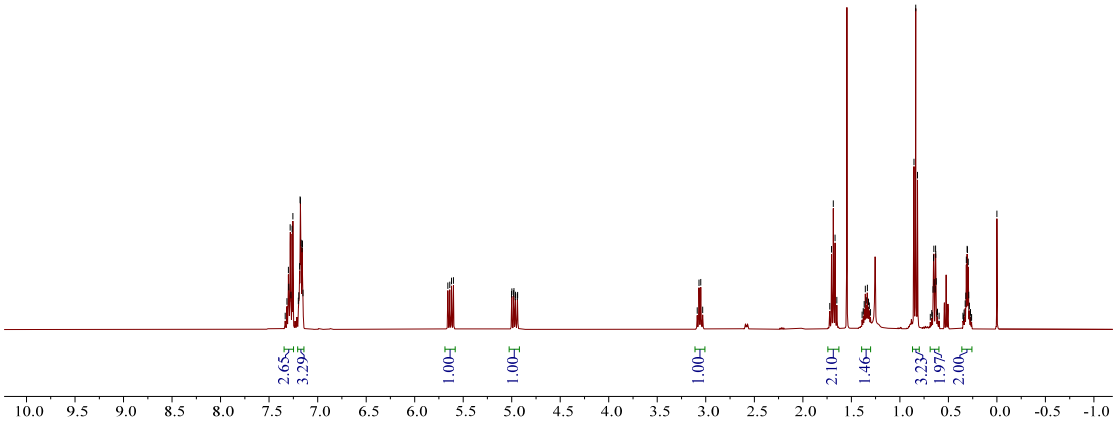
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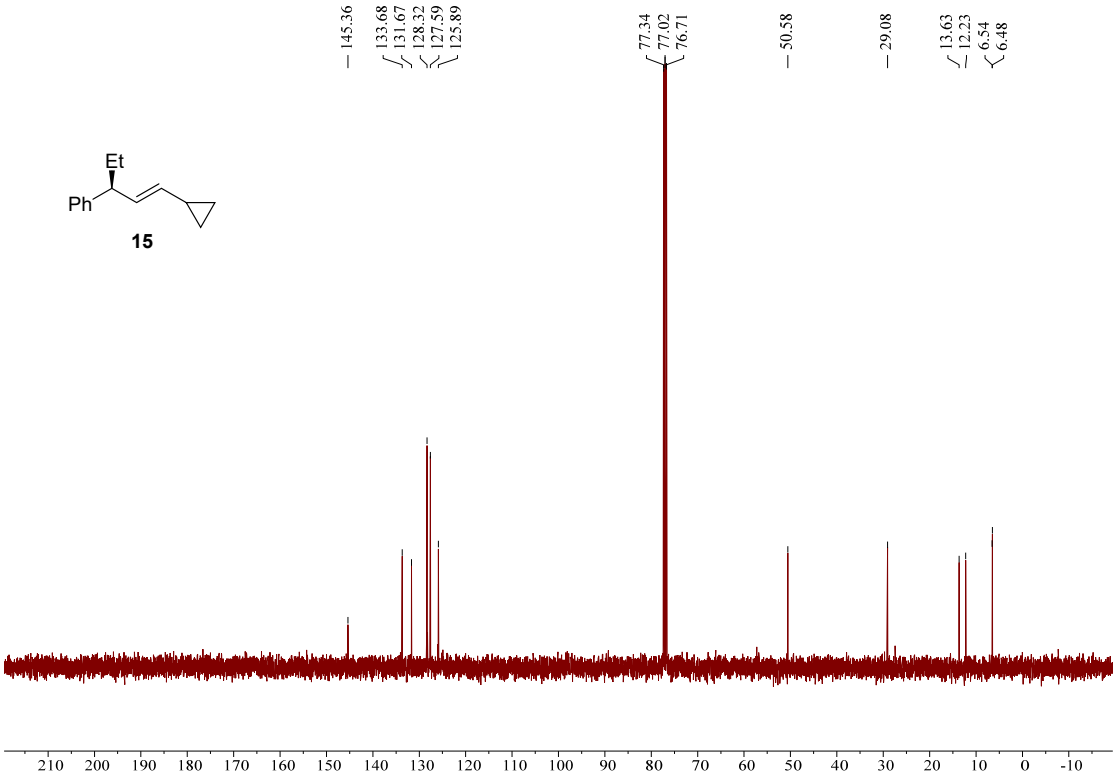
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Et
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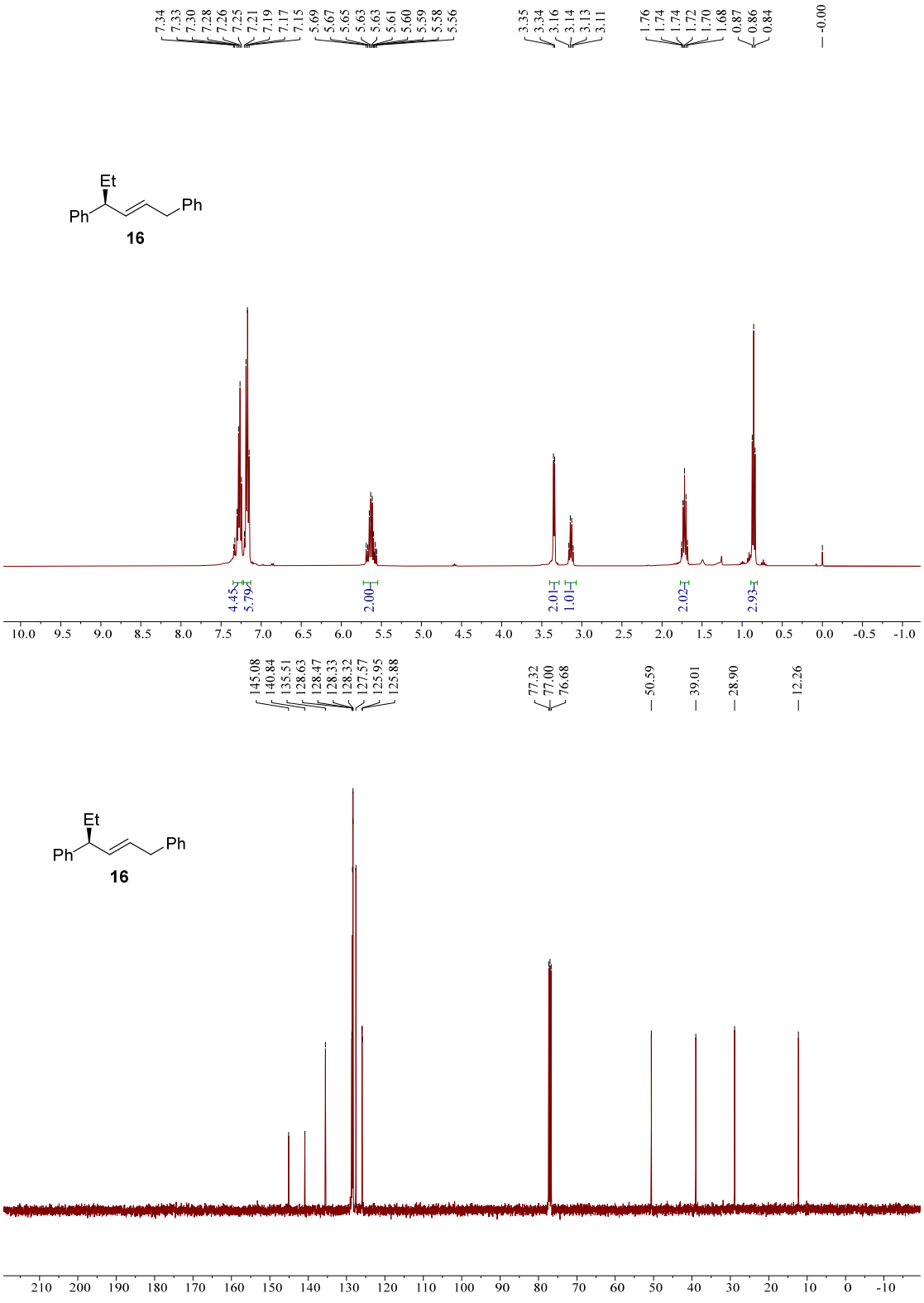
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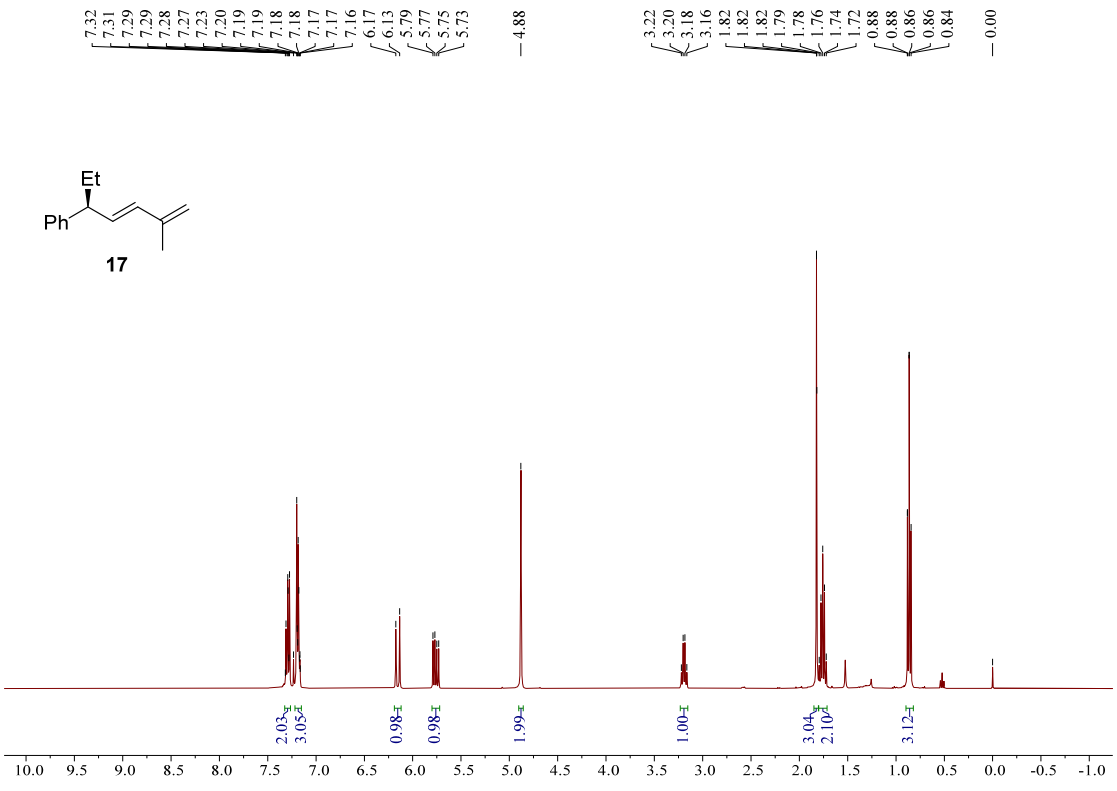
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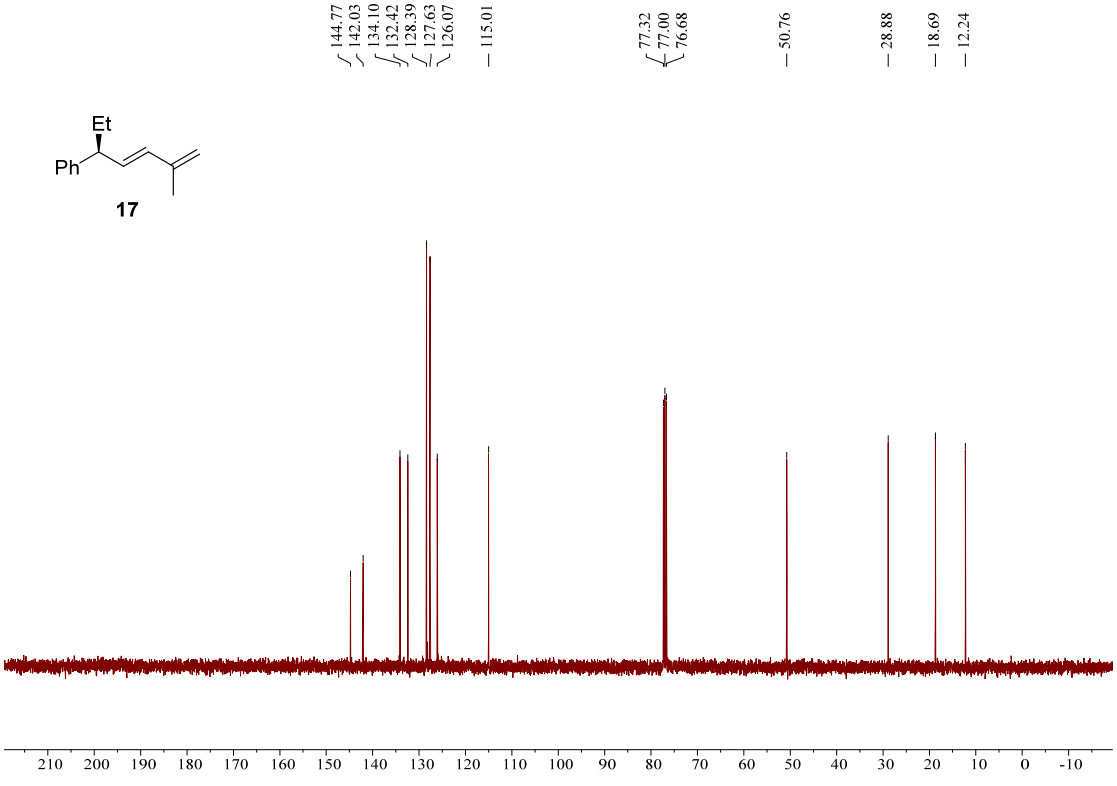
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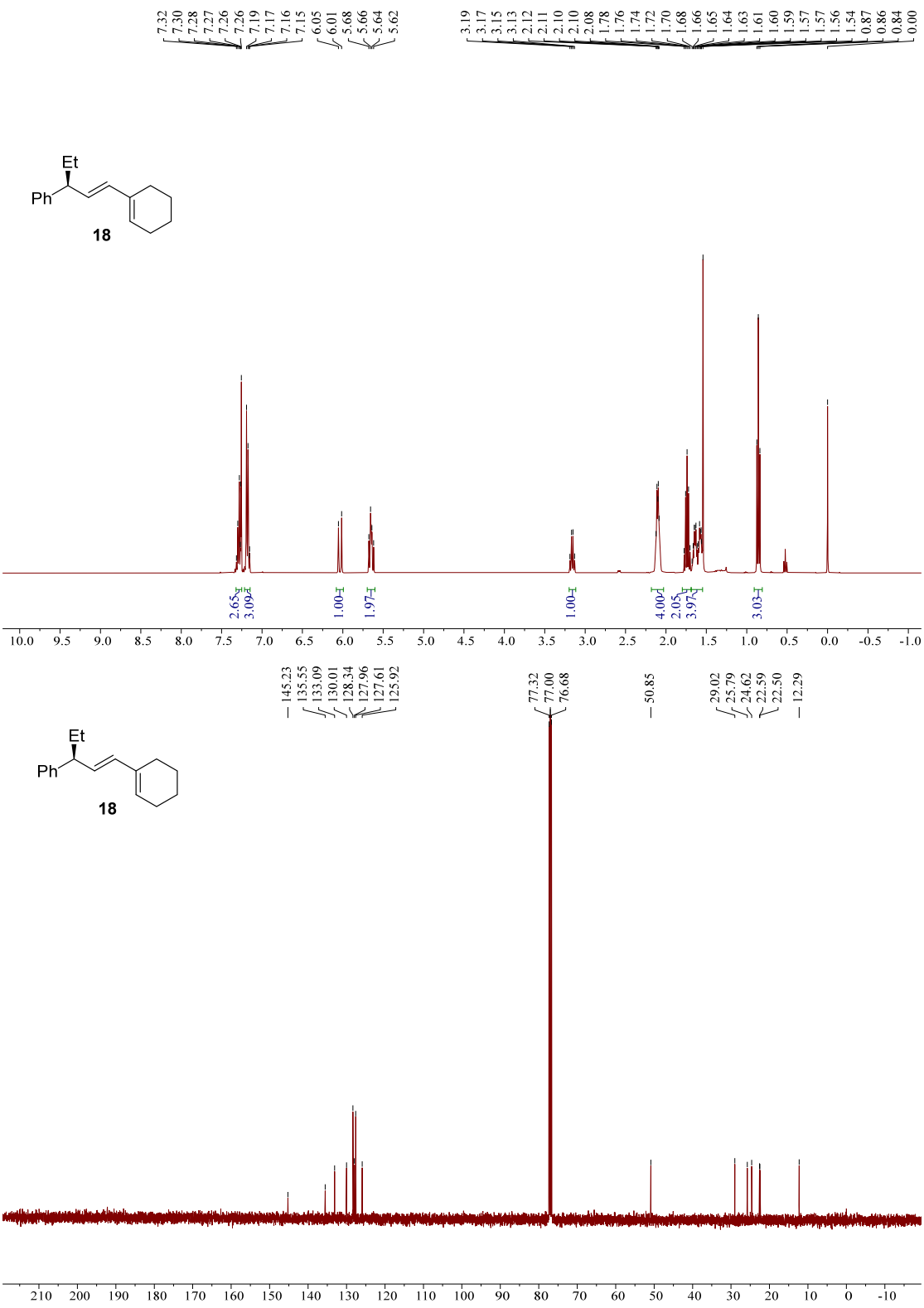
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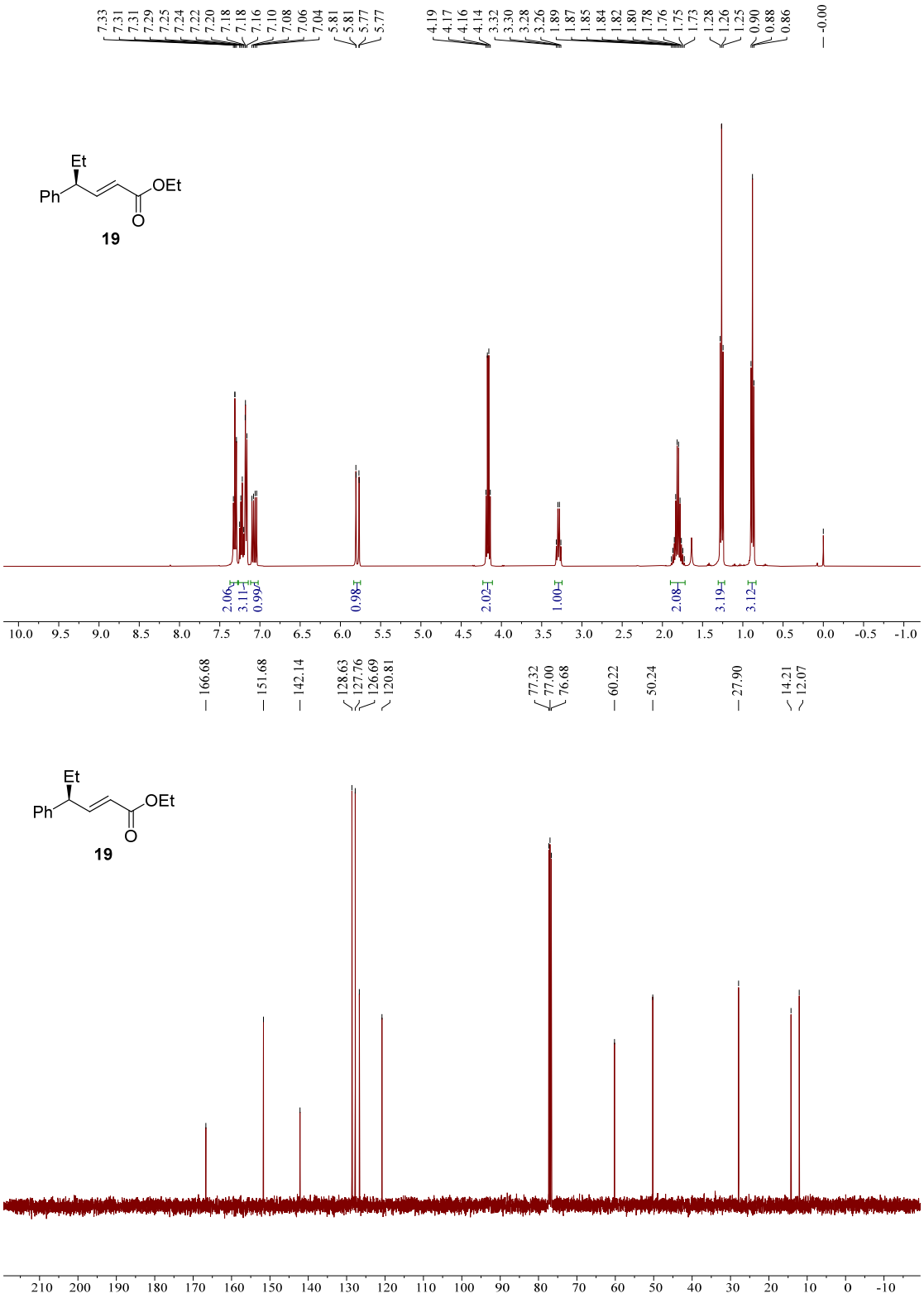
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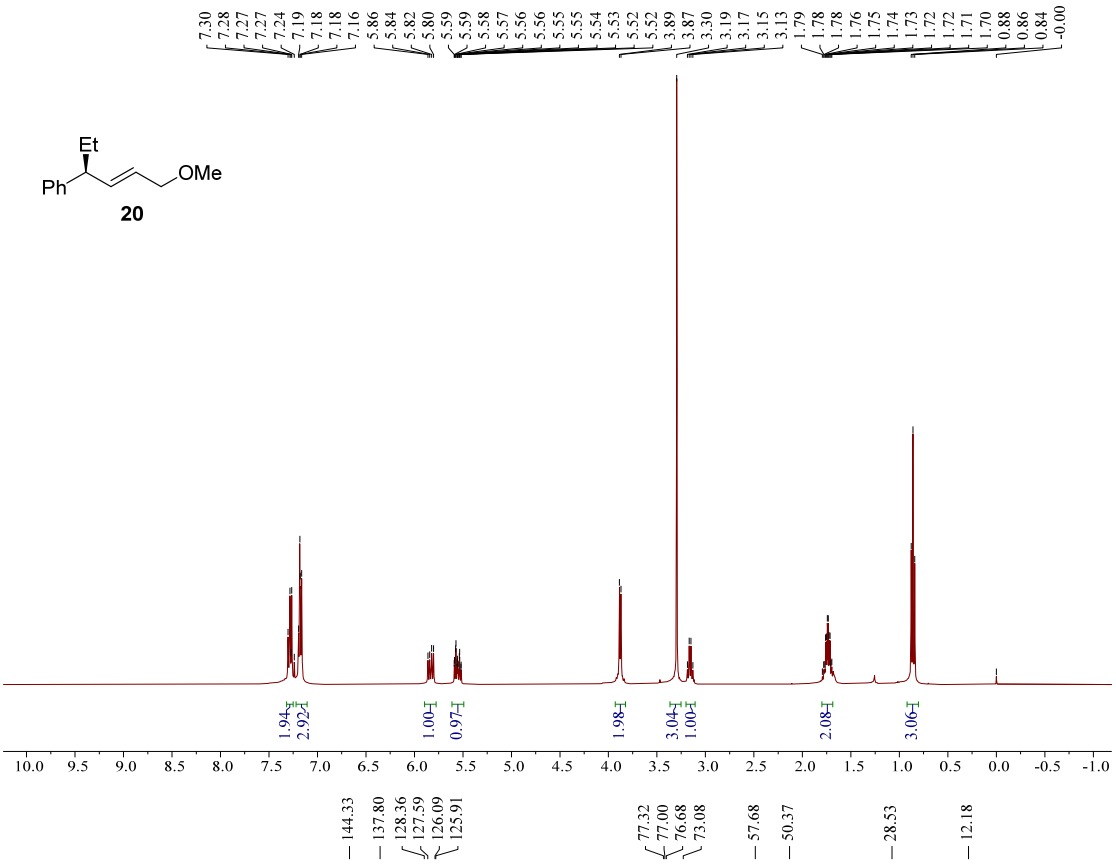
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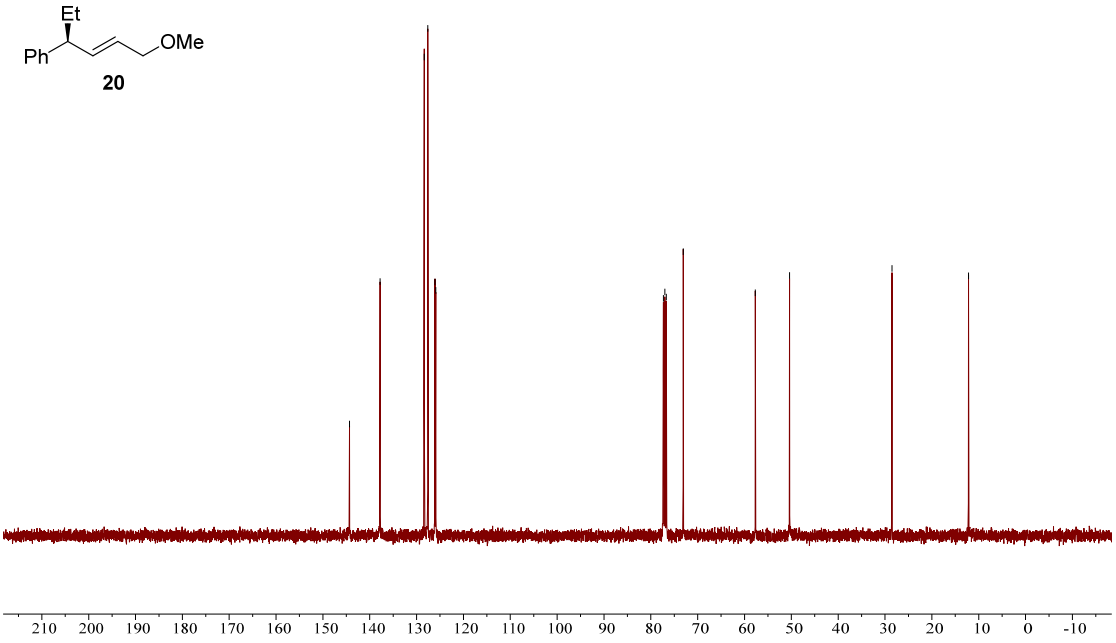
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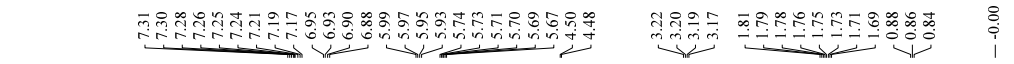
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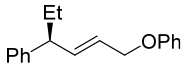
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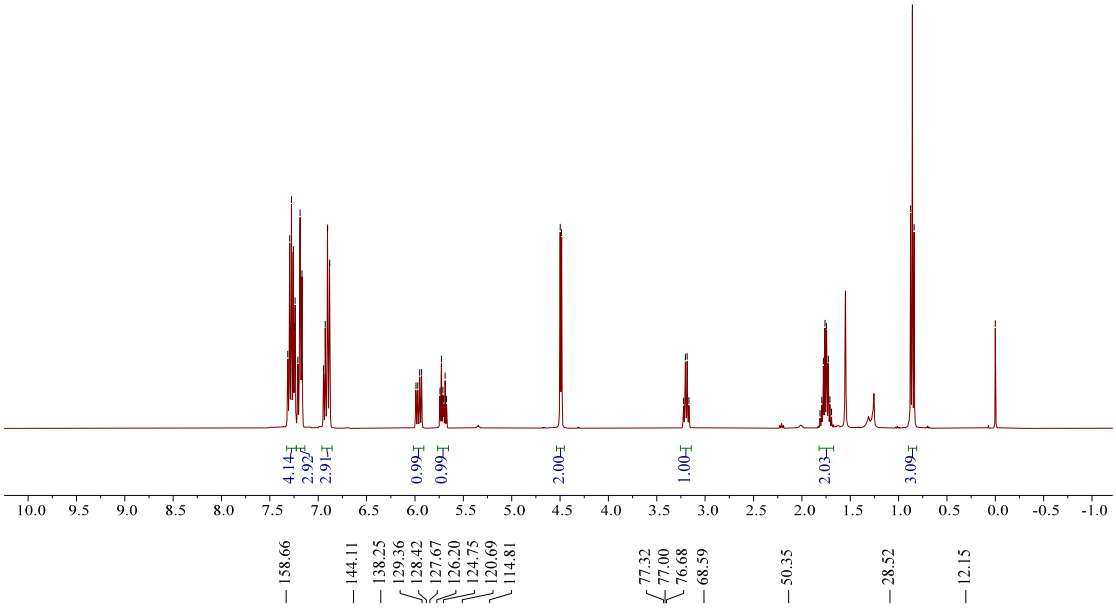
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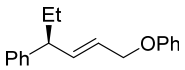
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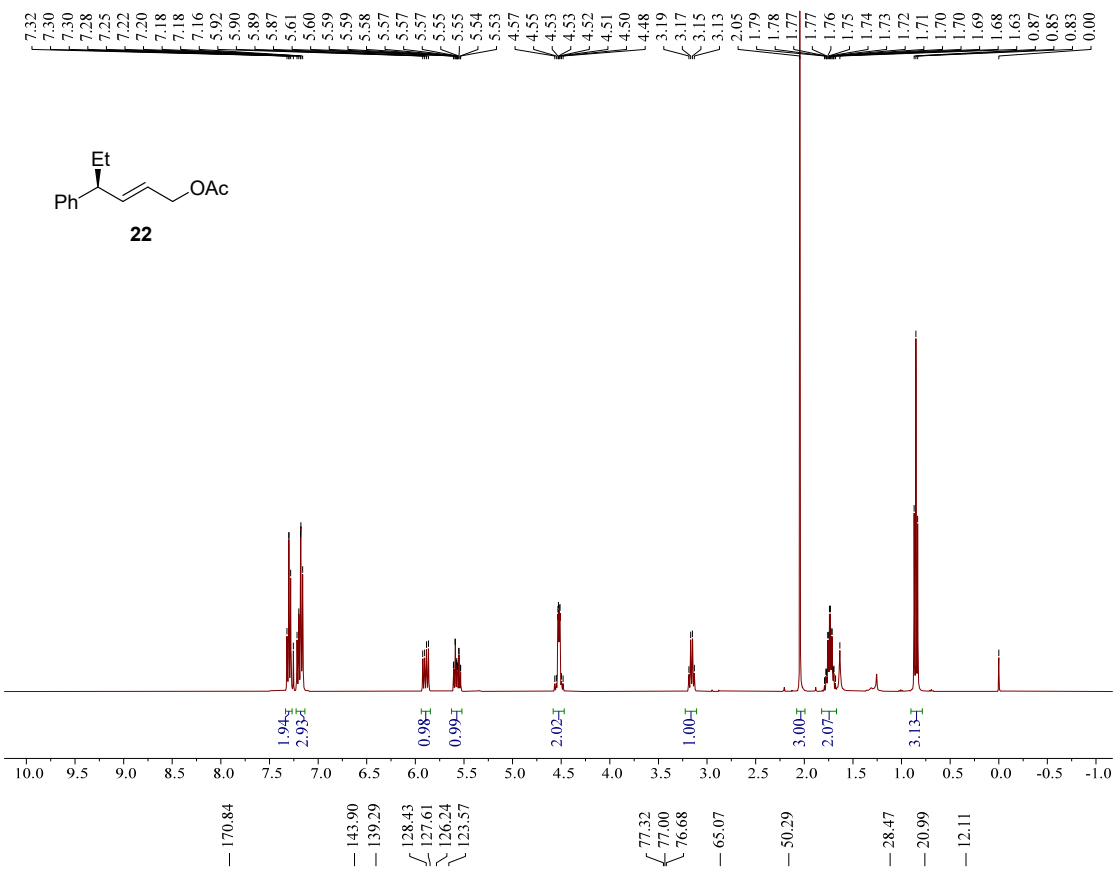
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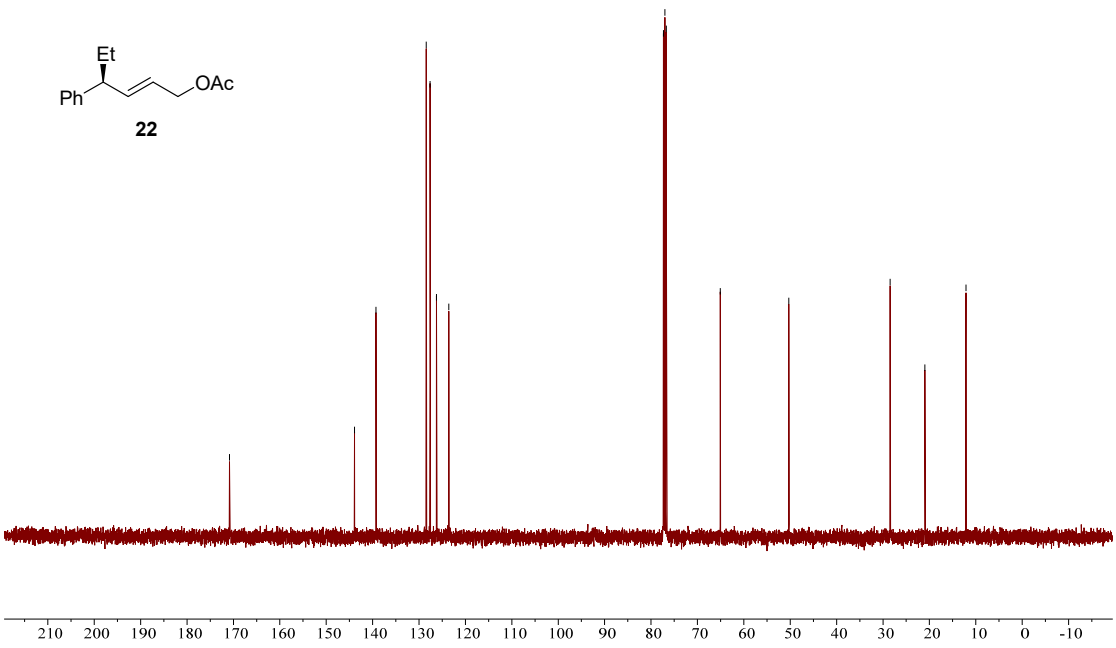
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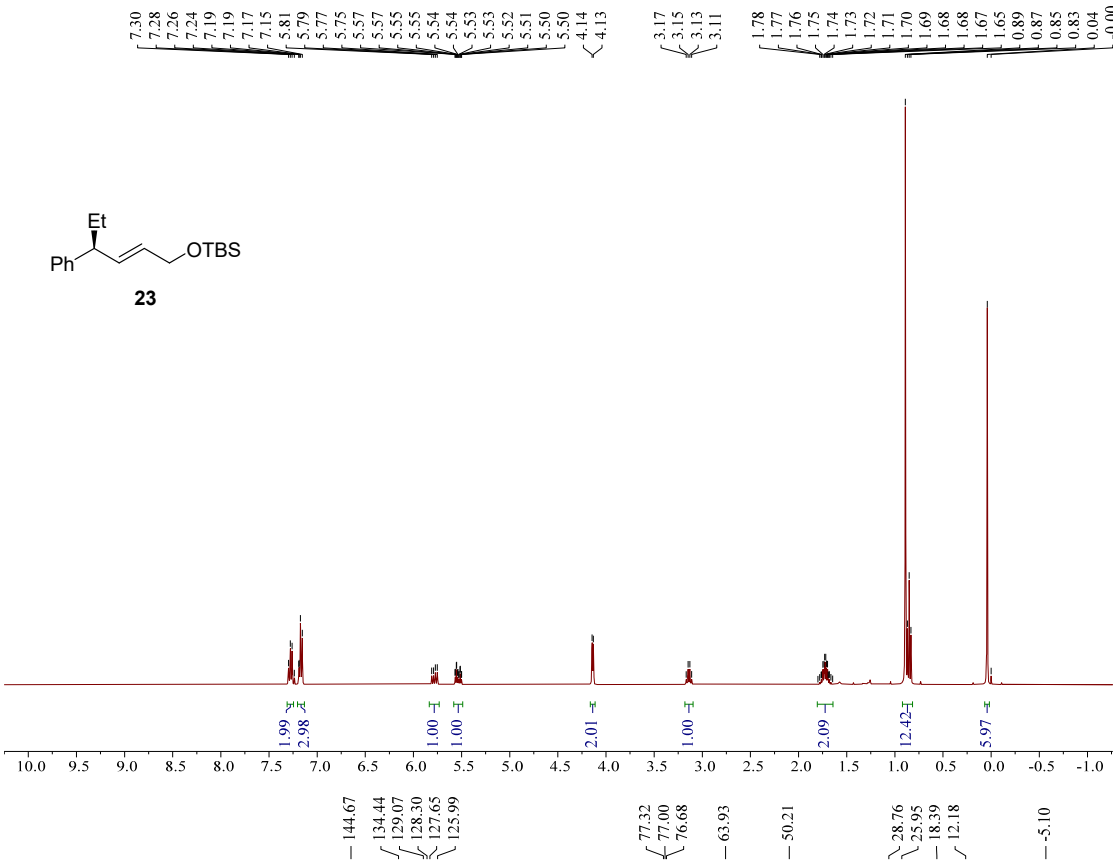
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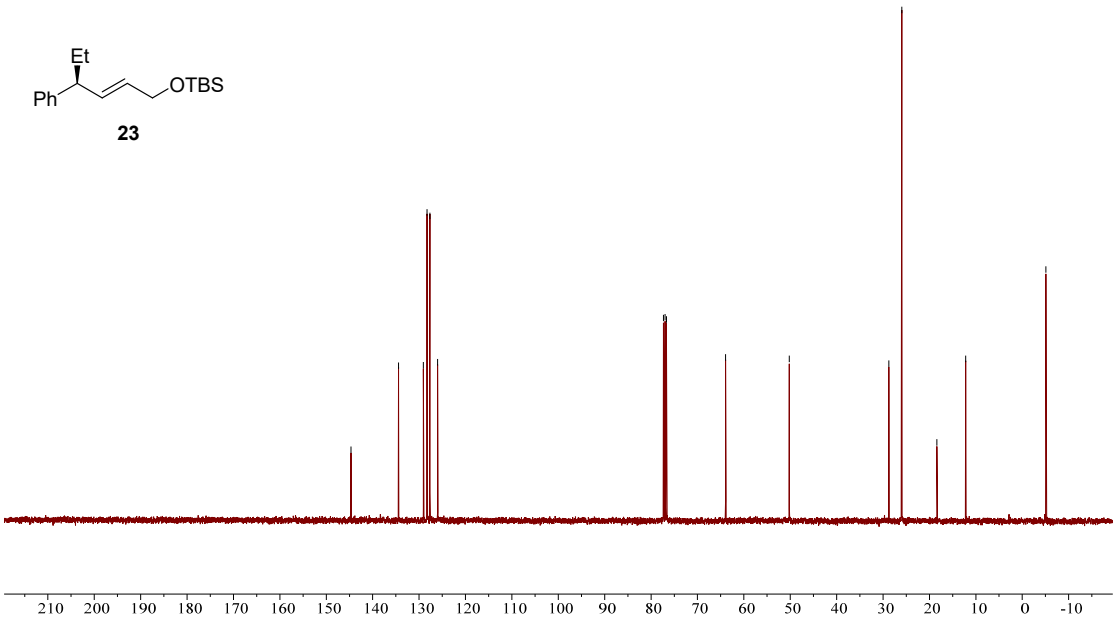
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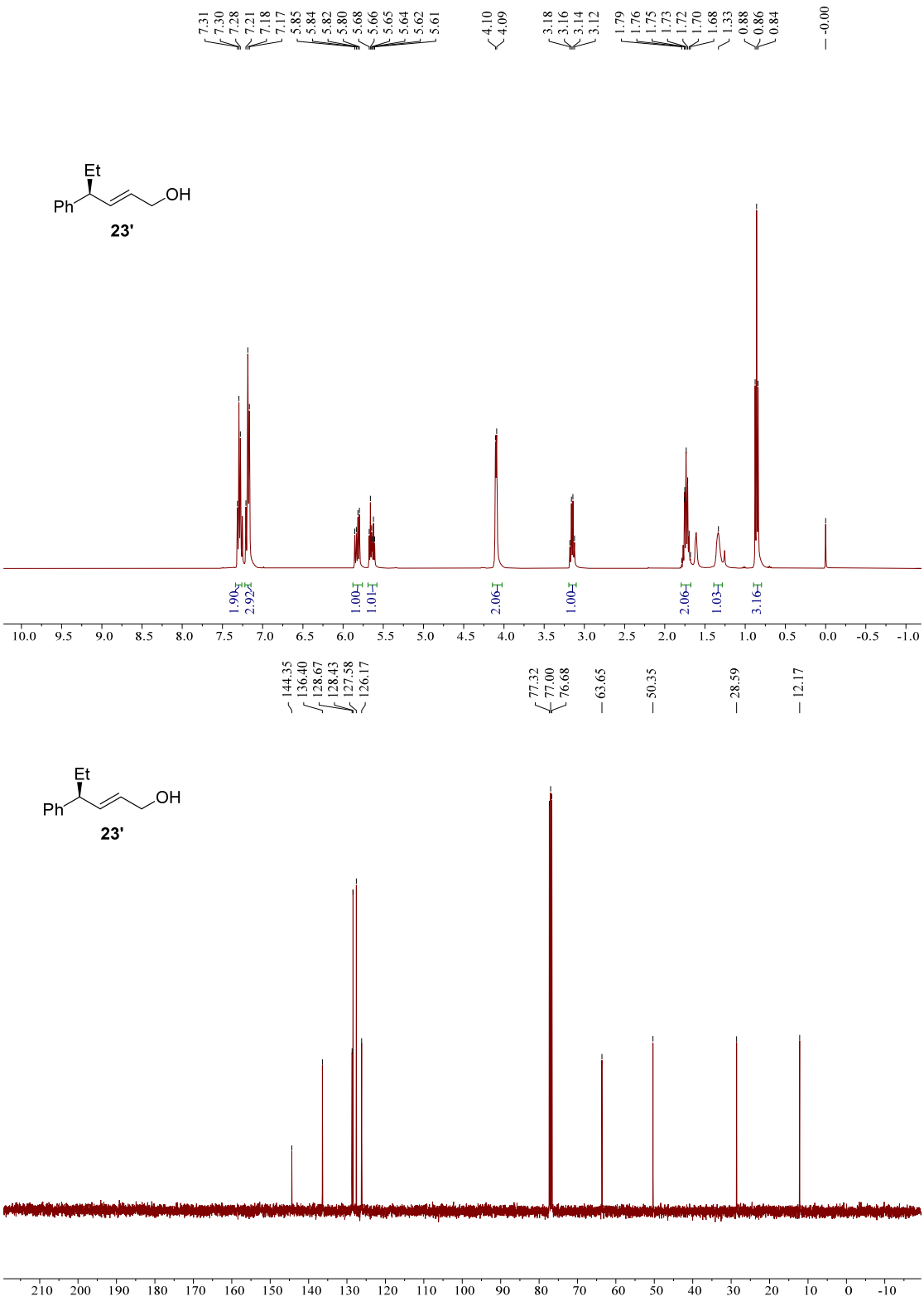
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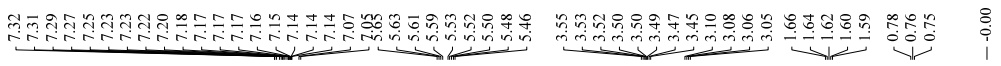
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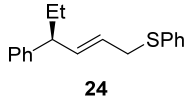
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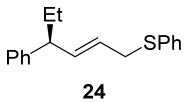
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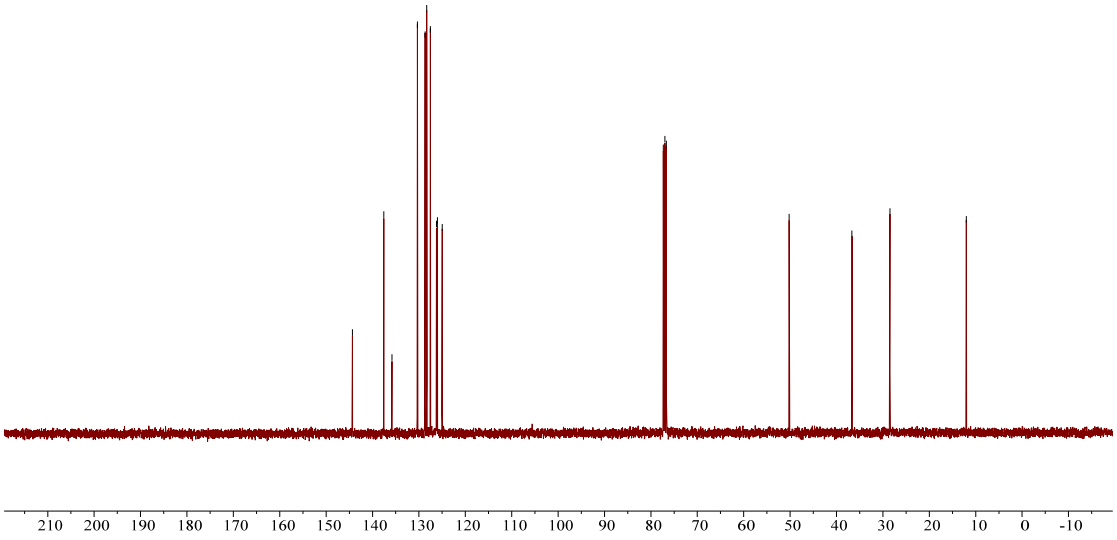
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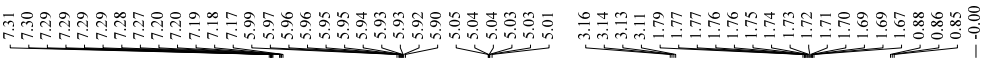
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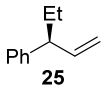
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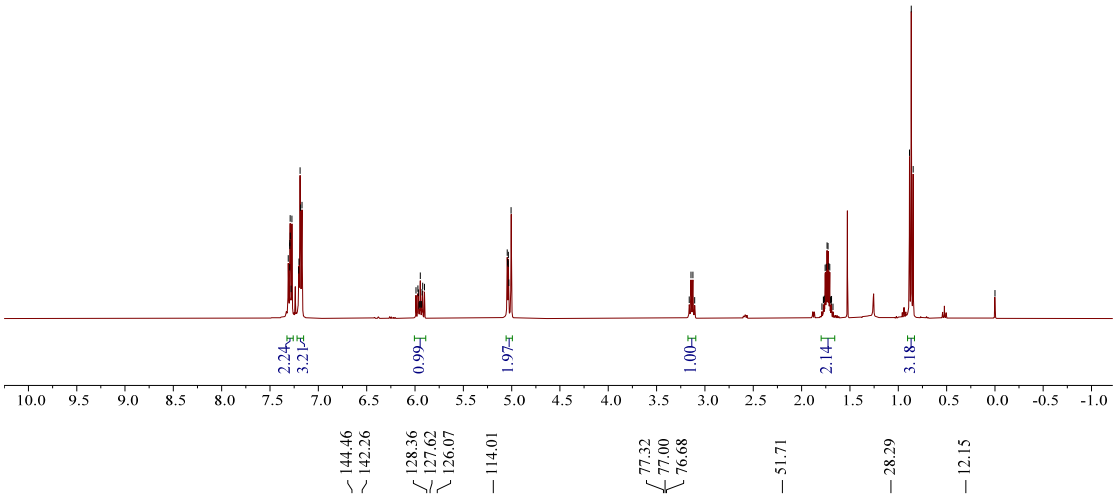
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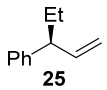
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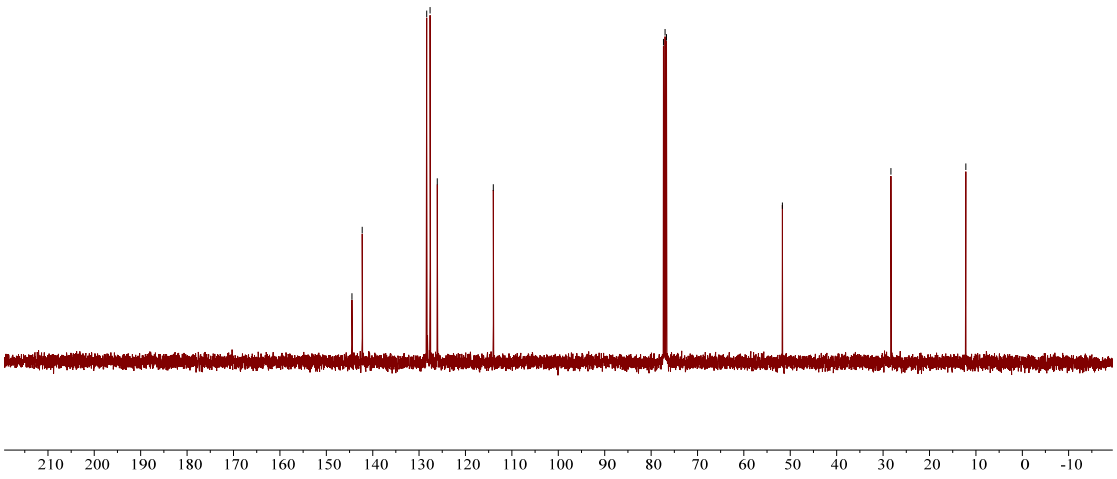
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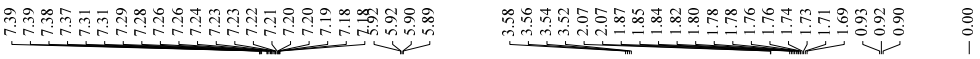
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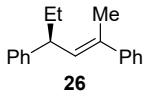
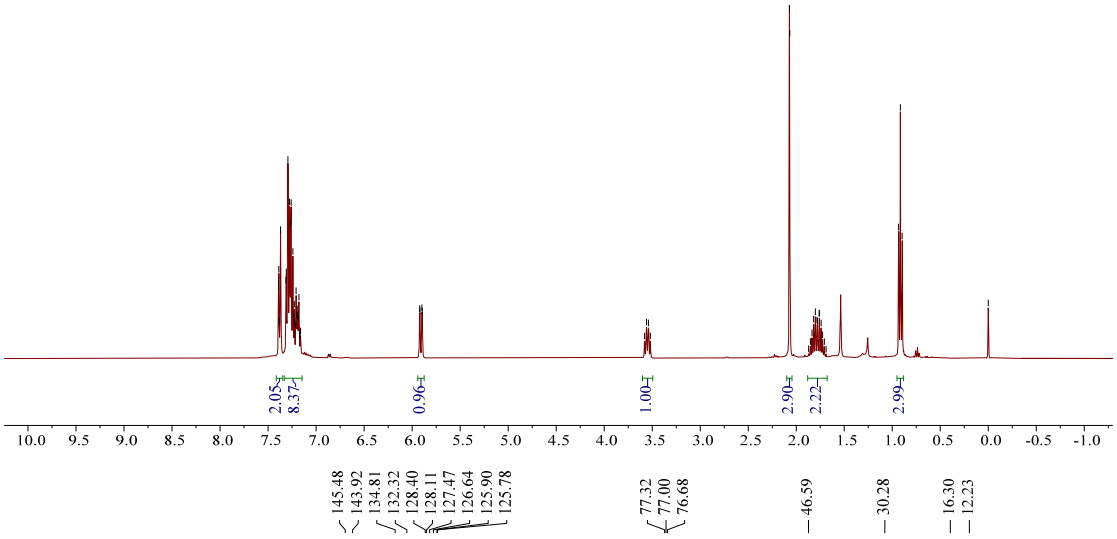

Et
Me
Ph
Ph

26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8.37
0.96
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2.22
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
145.48
143.92
134.81
132.32
128.40
128.11
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126.64
125.90
125.78
77.32
77.00
76.68
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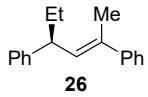
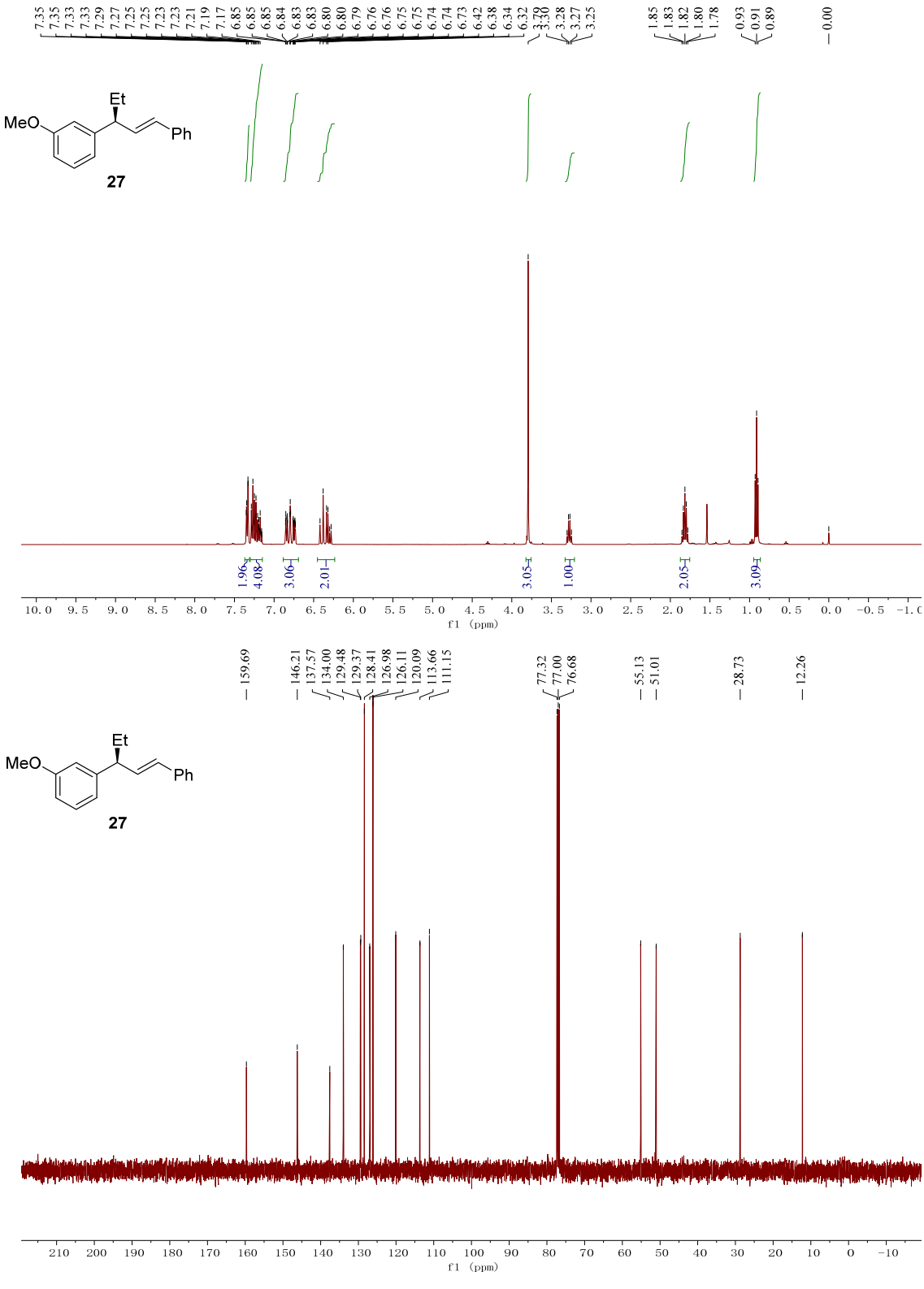
16.30
12.23


Et
Me
Ph
Ph

26

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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6.85
6.85
6.84
6.83
6.83
6.80
6.80
6.79
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6.75
6.75
6.74
6.74
6.73
6.42
6.38
6.34
6.32
3.30
3.28
3.27
3.25
1.85
1.83
1.82
1.80
1.78
0.93
0.91
0.89
0.00
Et
MeO
Ph
27
1.96
4.08
3.06
2.01
3.05
1.00
2.05
3.09
f1 (ppm)
159.69
146.21
137.57
134.00
129.48
129.37
128.41
126.98
126.11
120.09
113.66
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77.00
76.68
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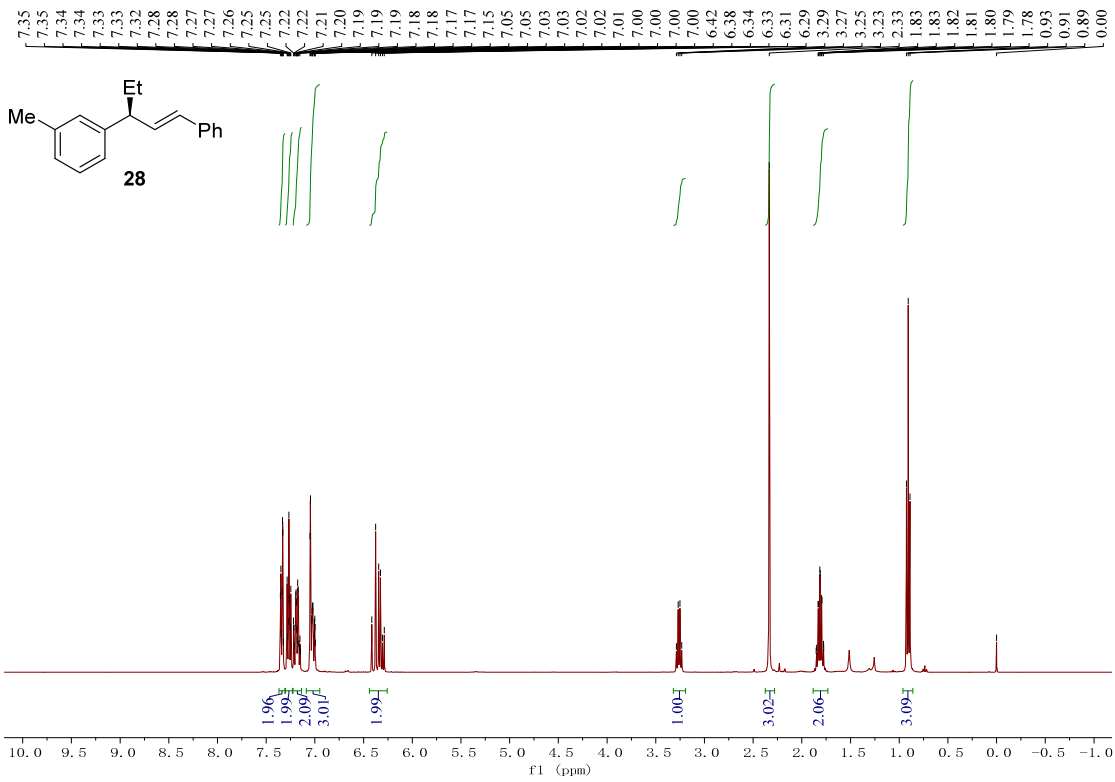
51.01
28.73
12.26
Et
MeO
Ph
27
f1 (ppm)


Et
Me
Ph
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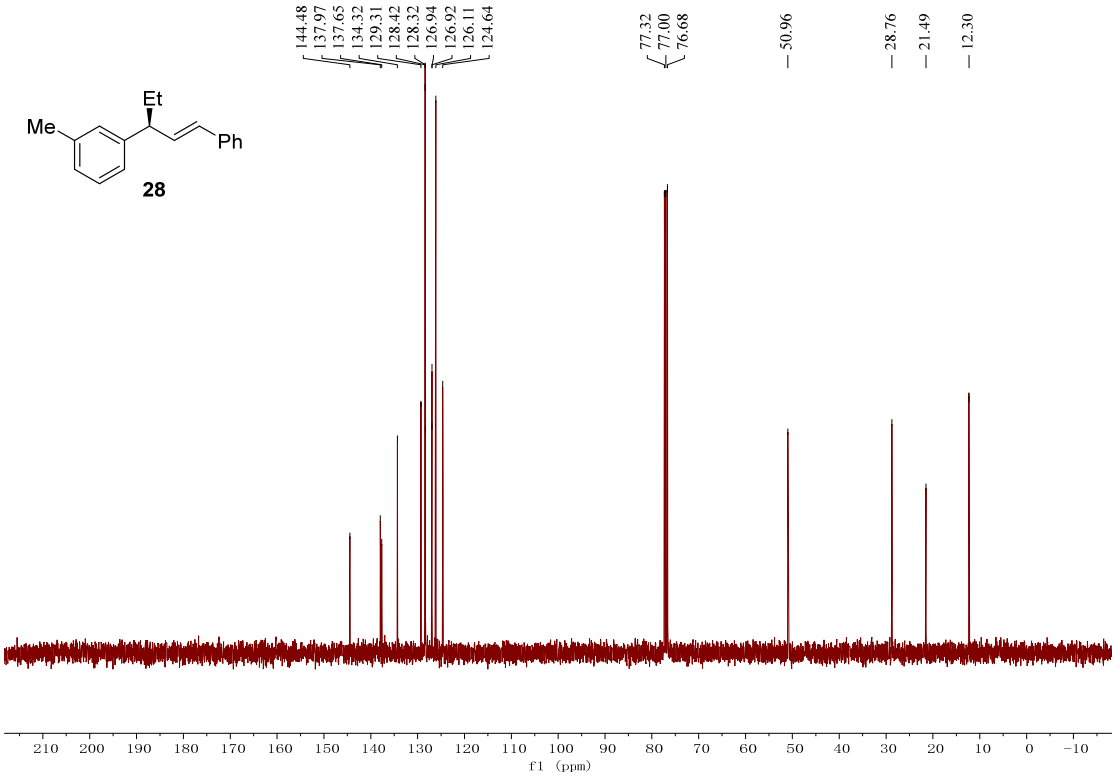
f1 (ppm)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Ph
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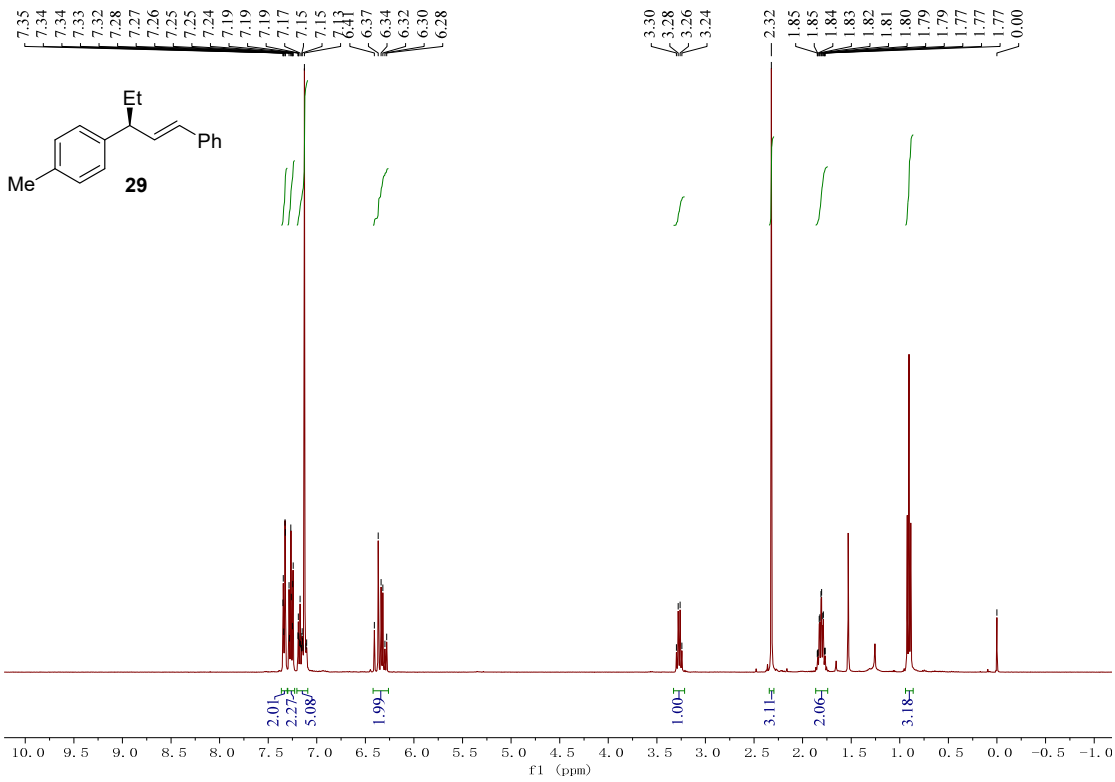
f1 (ppm)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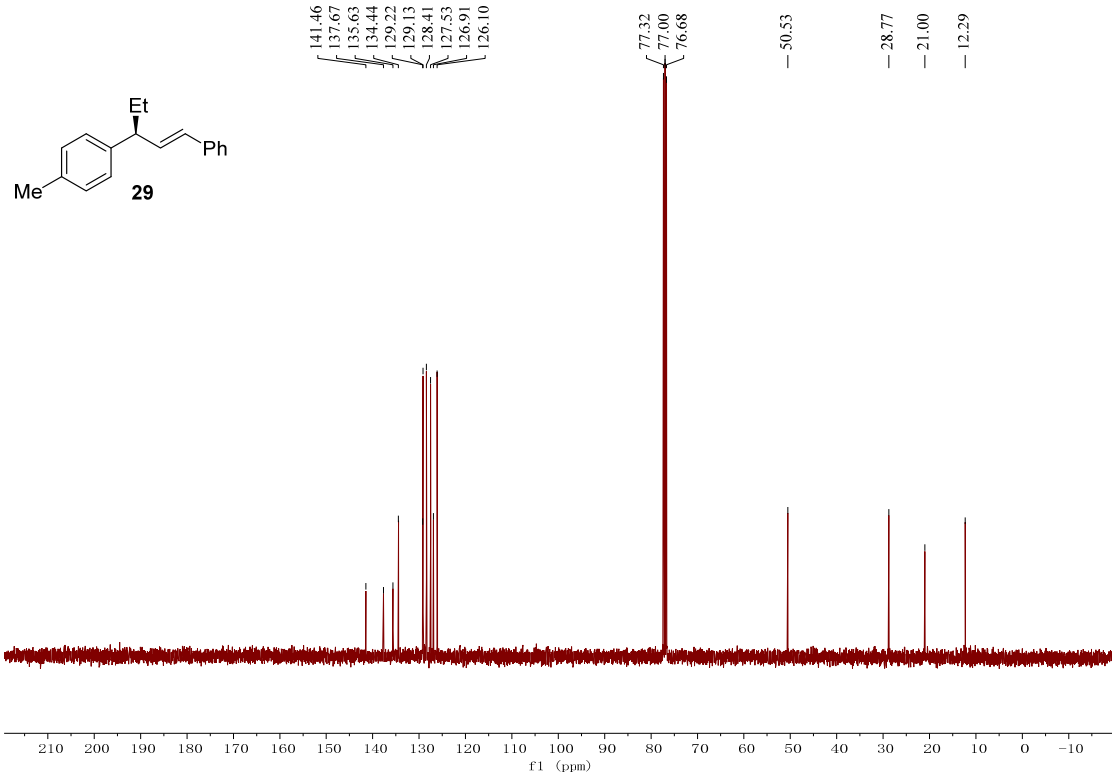
7.15
7.13
6.41
6.37
6.34
6.32
6.30
6.28
3.30
3.28
3.26
3.24
2.32
1.85
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.79
1.77
1.77
1.77
0.00
Et
Ph
Me
29
2.01
2.27
5.08
1.99
1.00
3.11
2.06
3.18
f1 (ppm)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129.13
128.41
127.53
126.91
126.10
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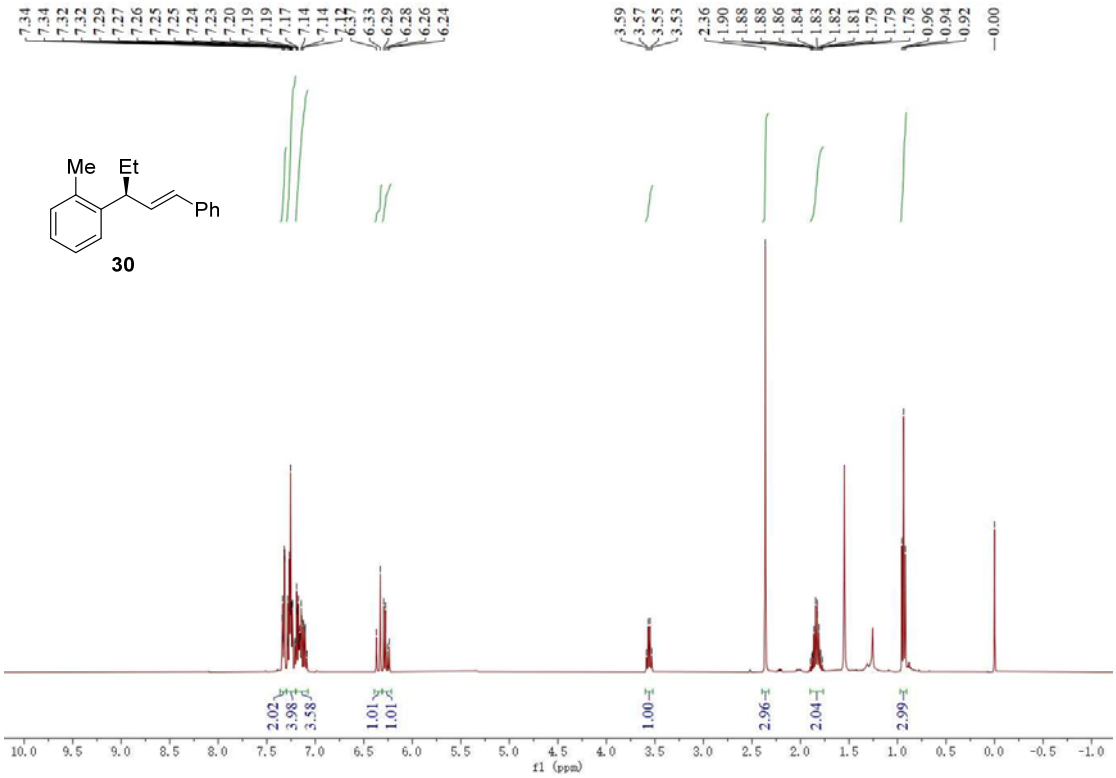
77.00
76.68
50.53
28.77
21.00
12.29
Et
Ph
Me
29
f1 (ppm)


Me
Et
Ph
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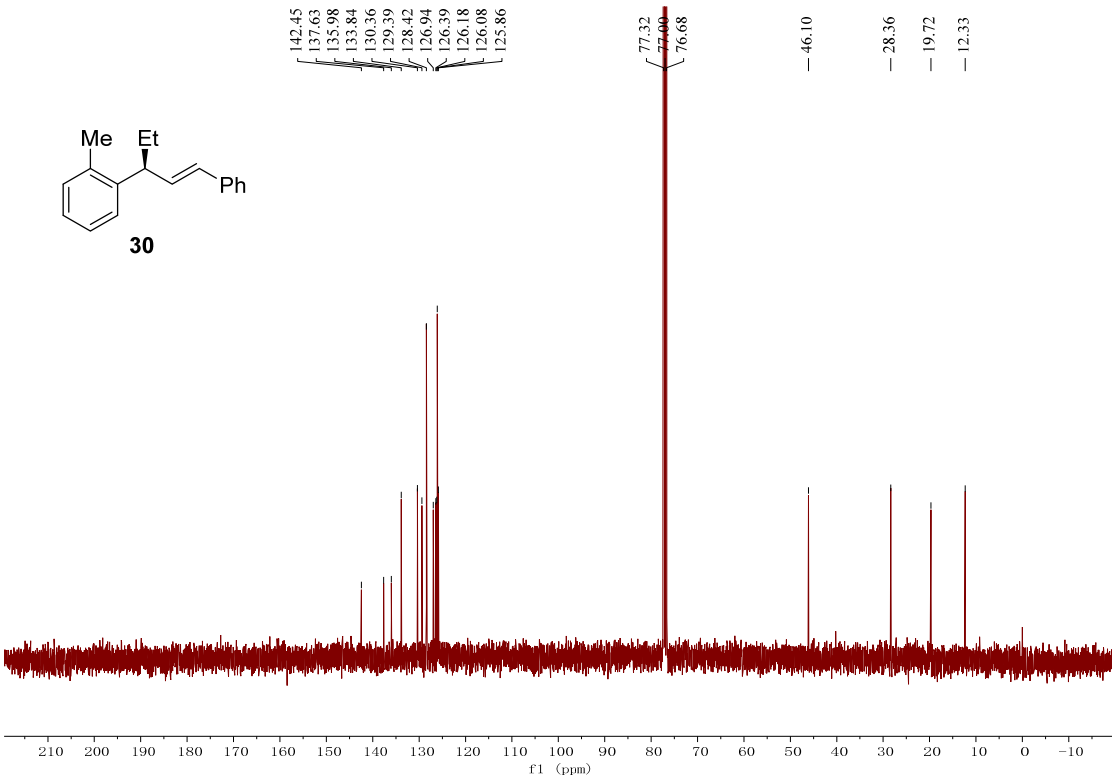
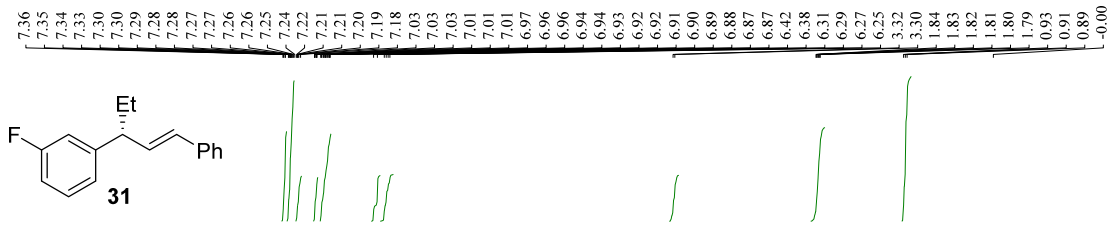
f1 (ppm)


Me
Et
Ph
30
f1 (ppm)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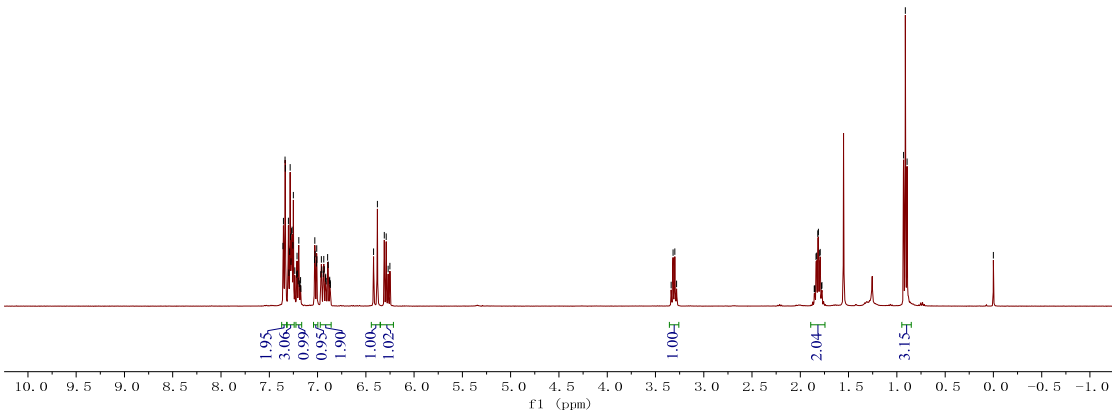
Et
F
Ph
31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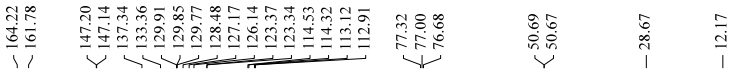
0.99
0.95
1.90
1.00
1.02
1.00
2.04
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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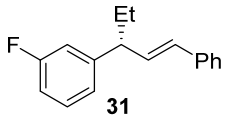
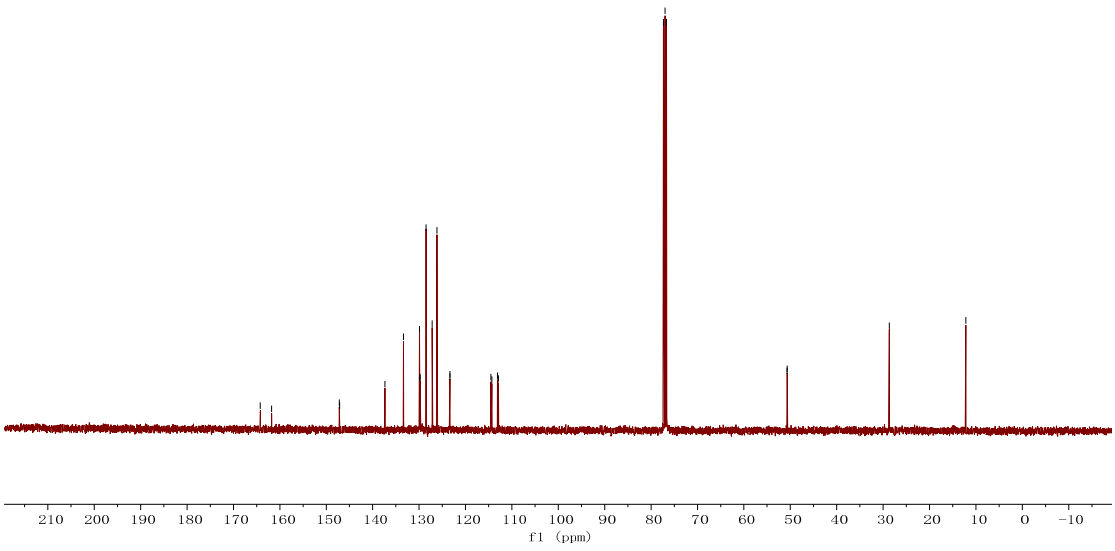
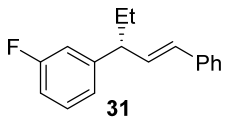
161.78
147.20
147.14
137.34
133.36
129.91
129.85
129.77
128.48
127.17
126.14
123.37
123.34
114.53
114.32
113.12
112.91
77.32
77.00
76.68
50.69
50.67
28.67
12.17


Et
F
Ph
31


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Et
F
Ph

31

-113.45
-30
-40
-50
-60
-70
-80
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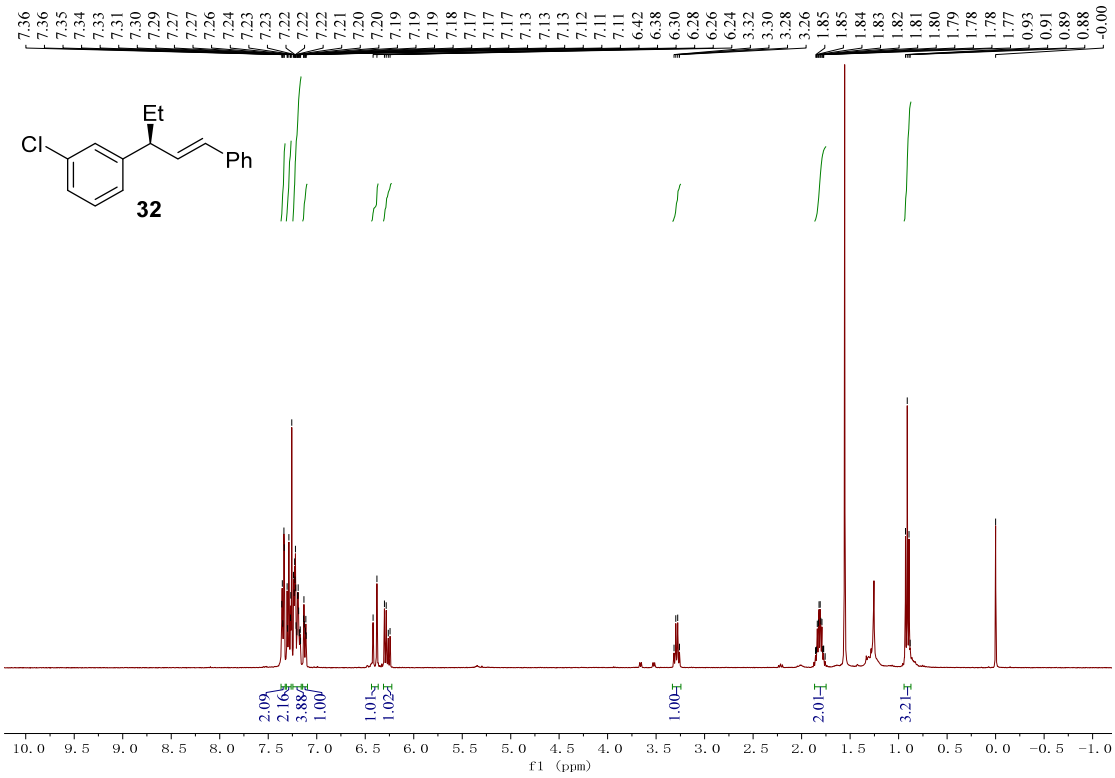
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)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Cl
Ph
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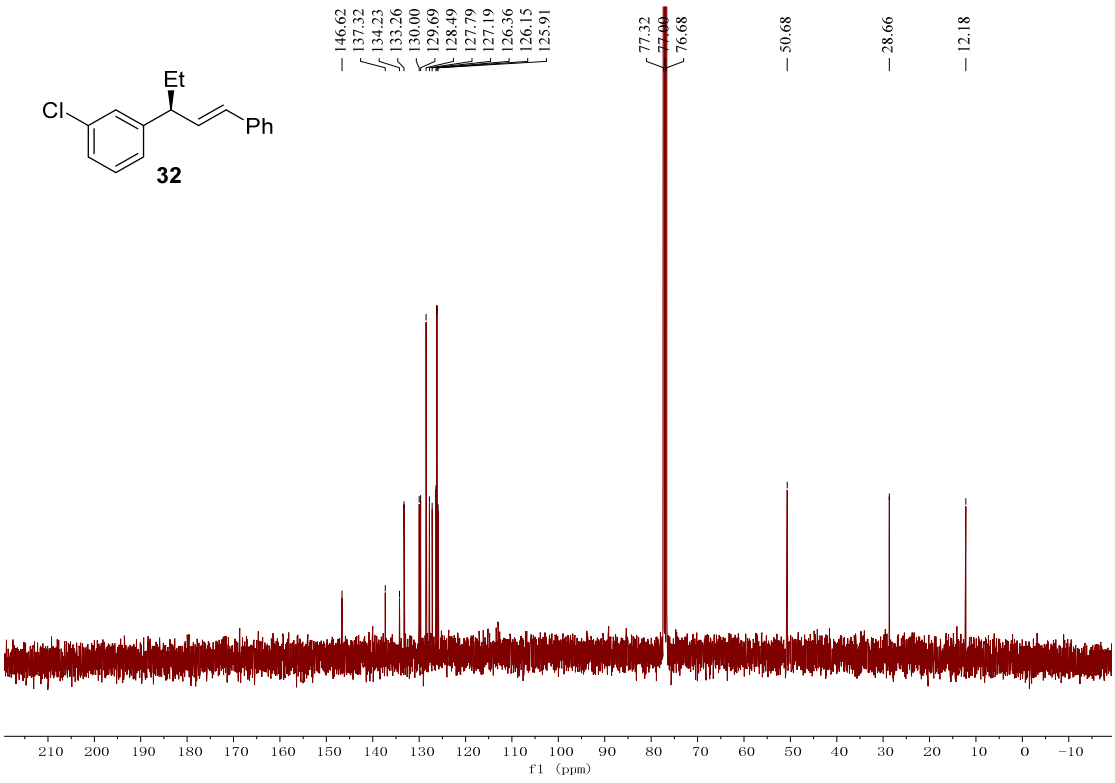
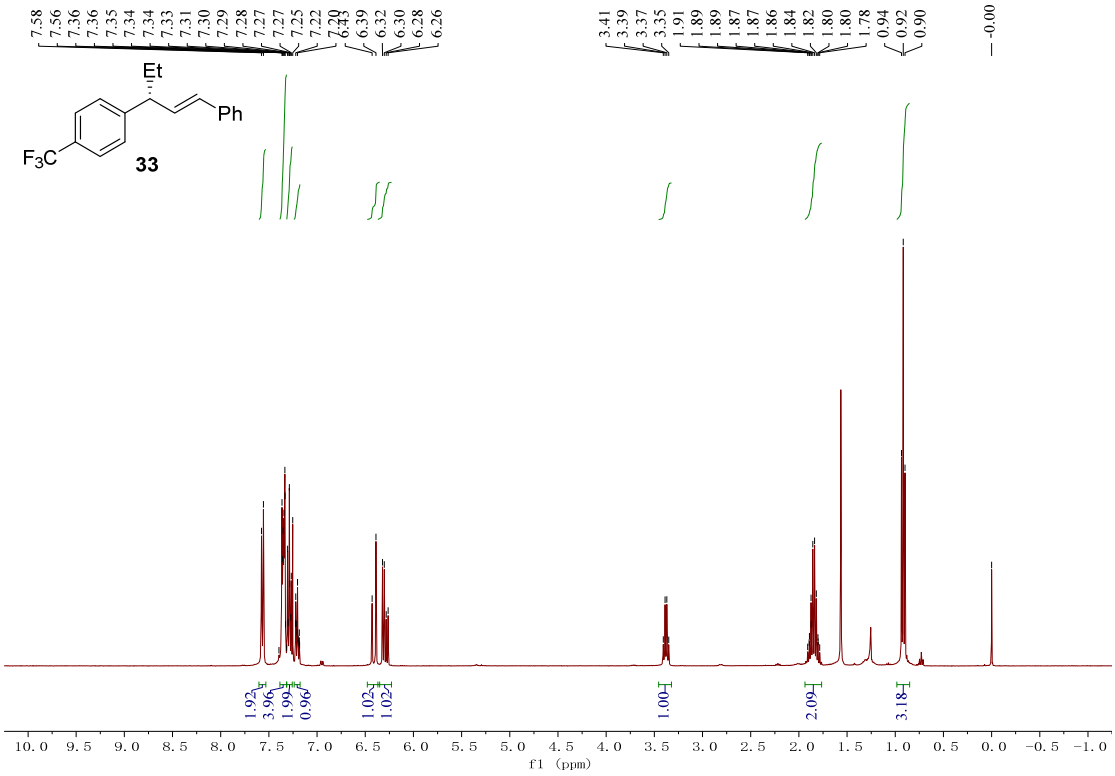
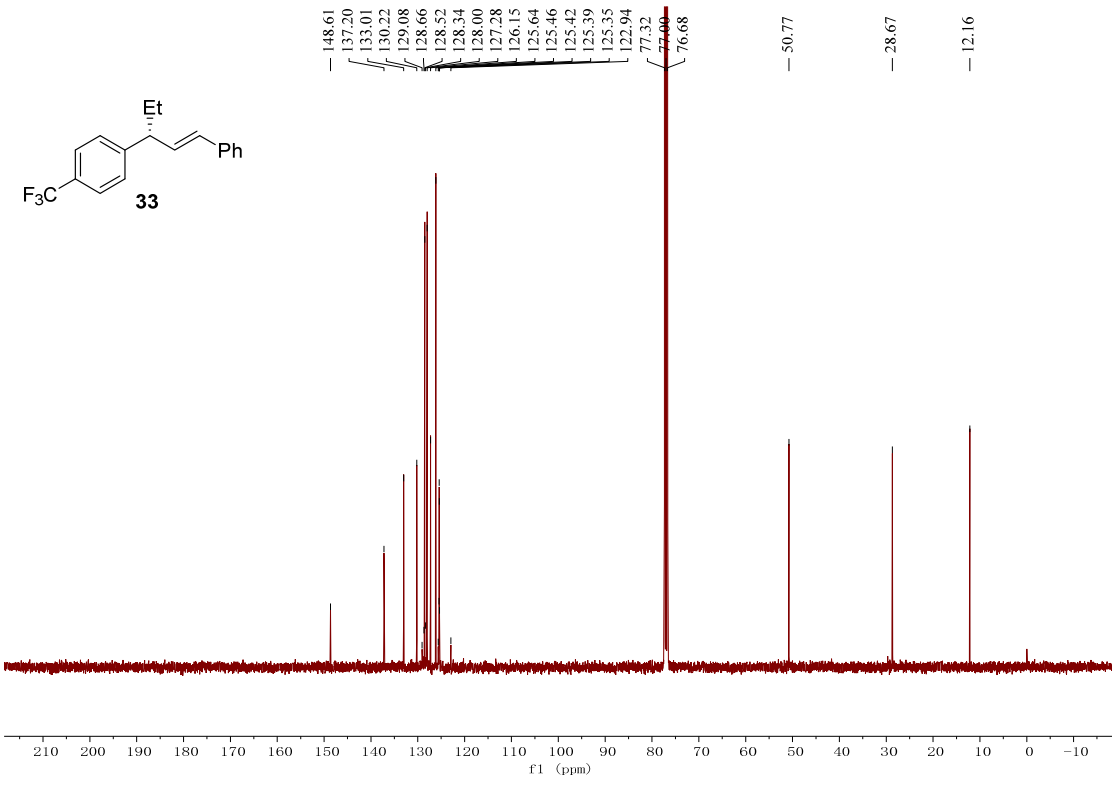
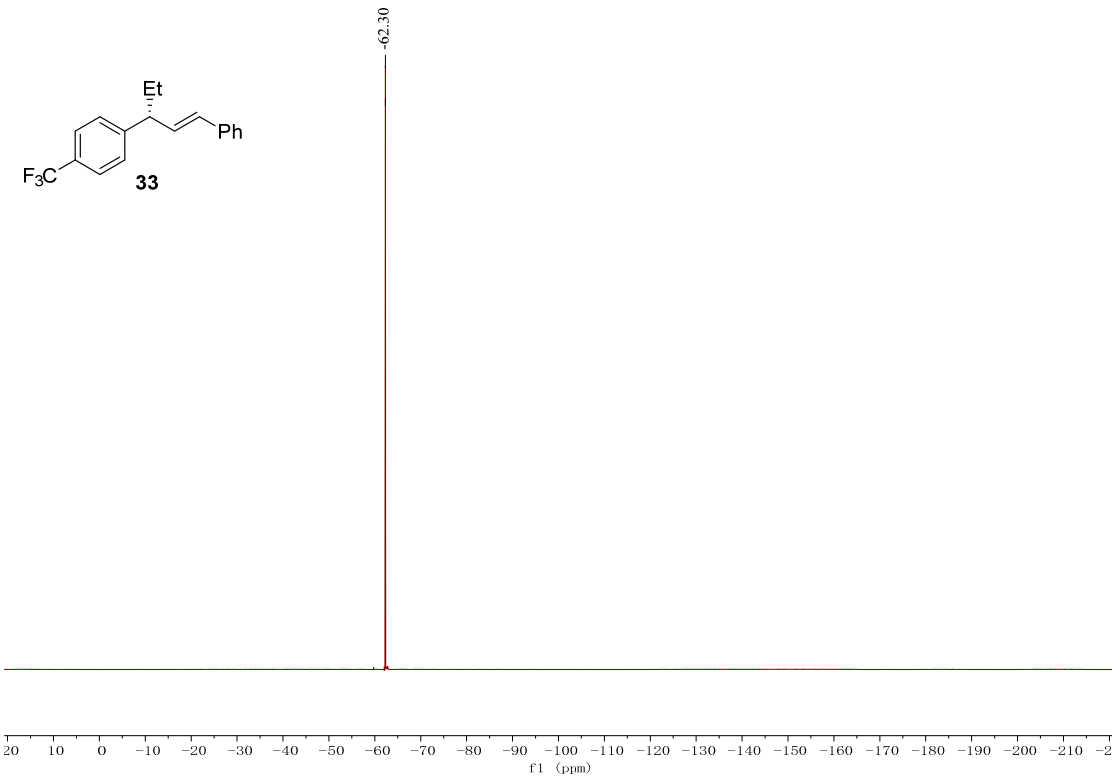
f1 (ppm)


Et
Cl
Ph
32
f1 (ppm)


Et
Ph
F3C
33
f1 (ppm)


Et
Ph
F3C
33
f1 (ppm)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Et
Ph
F3C
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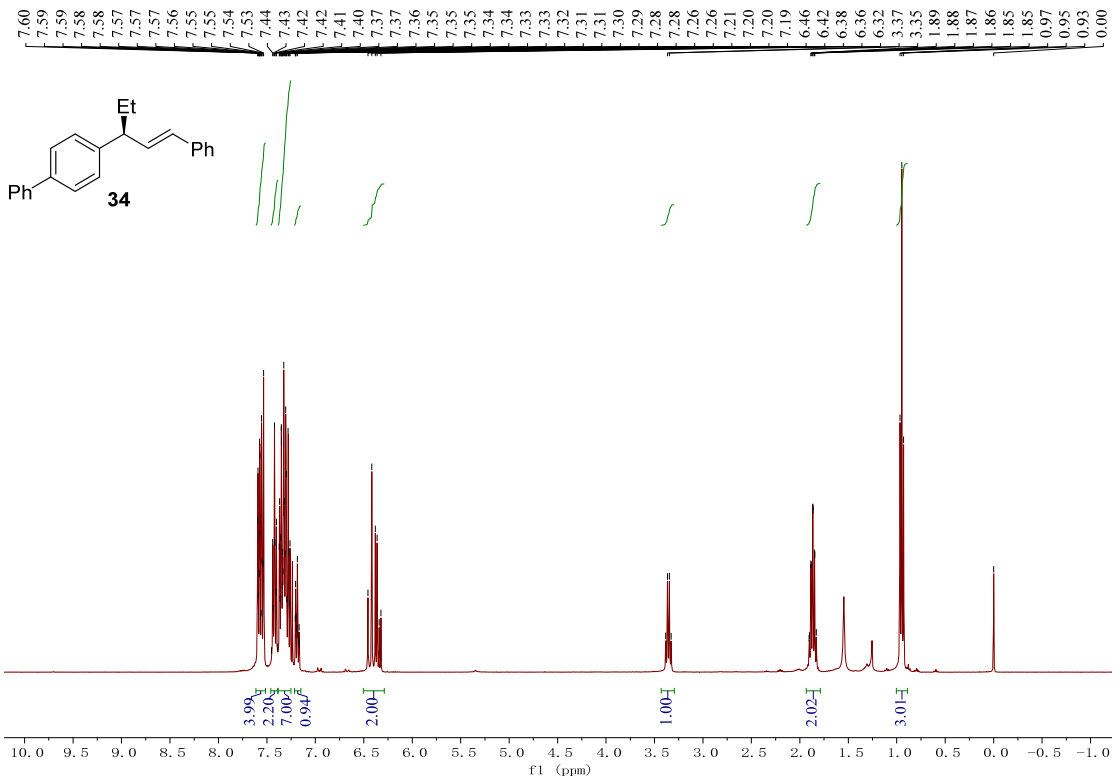
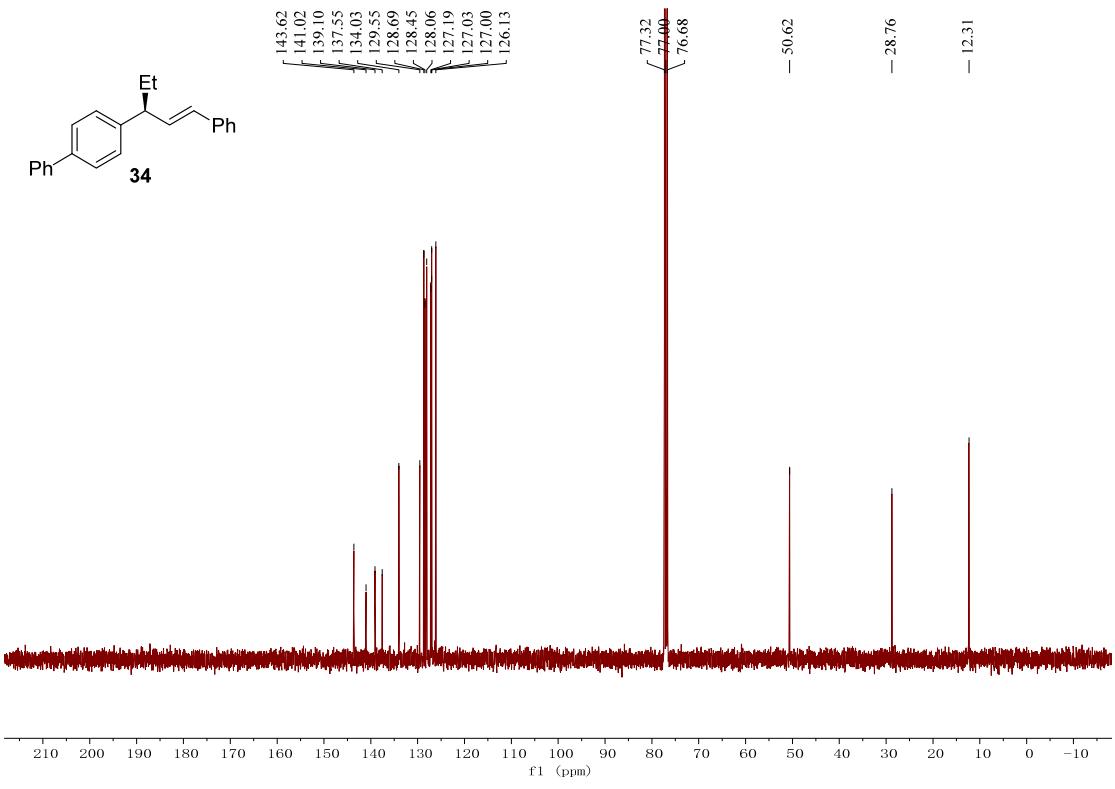
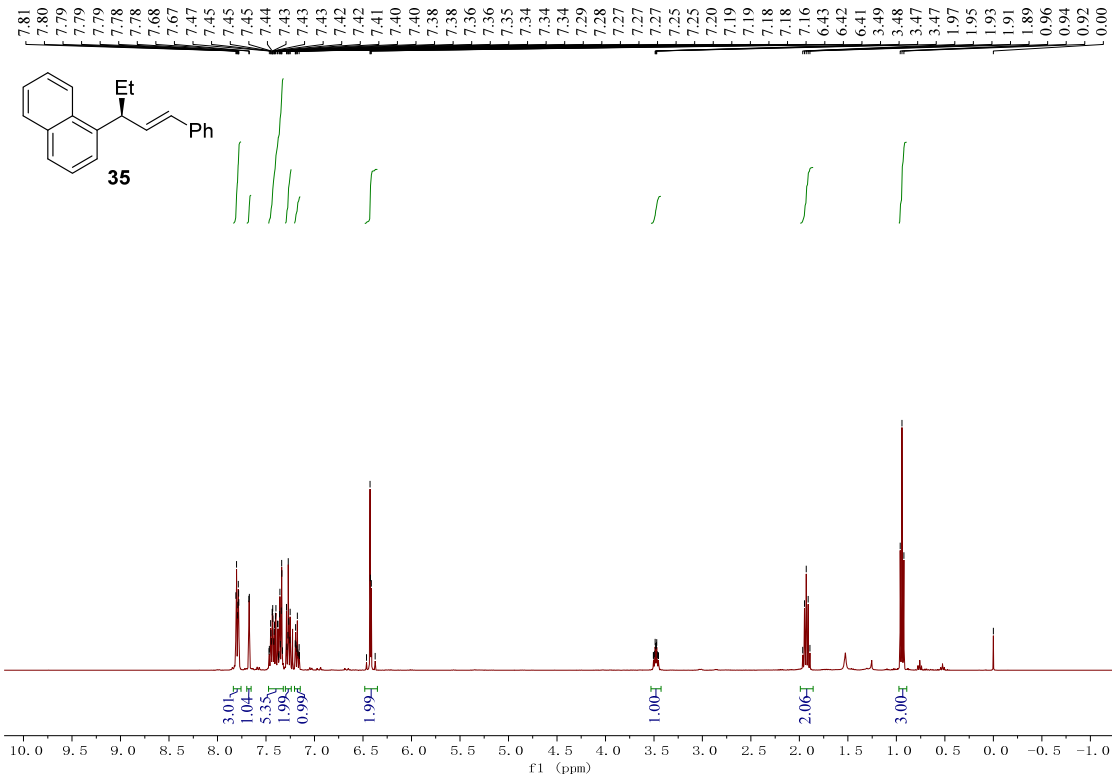
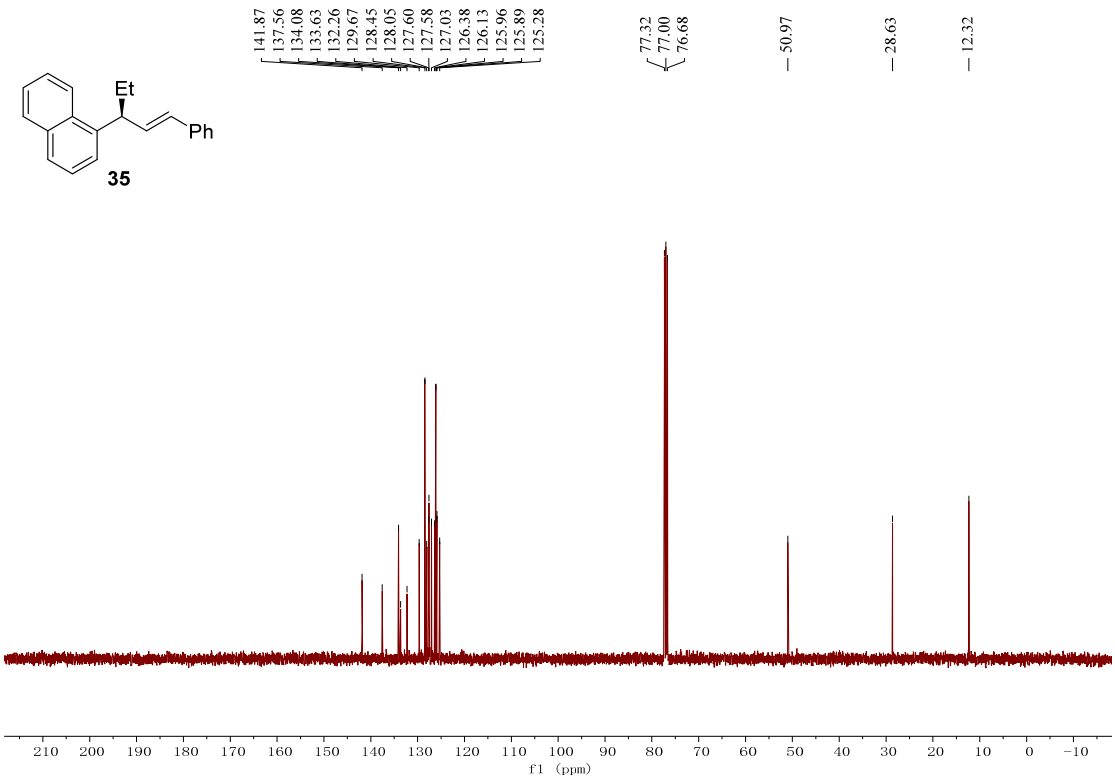
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)


Et
Ph
Ph
34
7.60 7.59 7.59 7.58 7.58 7.57 7.57 7.57 7.56 7.55 7.55 7.54 7.53 7.44 7.43 7.42 7.42 7.41 7.40 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.26 7.26 7.21 7.20 7.20 7.19 6.46 6.42 6.38 6.36 6.32 3.37 3.35 1.89 1.88 1.87 1.86 1.85 1.85 0.97 0.95 0.93 0.00
3.99 2.20 7.00 0.94 2.00 1.00 2.02 3.01
f1 (ppm)


Et
Ph
Ph
34
143.62 141.02 139.10 137.55 134.03 129.55 128.69 128.45 128.06 127.19 127.03 127.00 126.13
77.32 77.00 76.68
50.62
28.76
12.31
f1 (ppm)


Et
Ph
35
f1 (ppm)


Et
Ph
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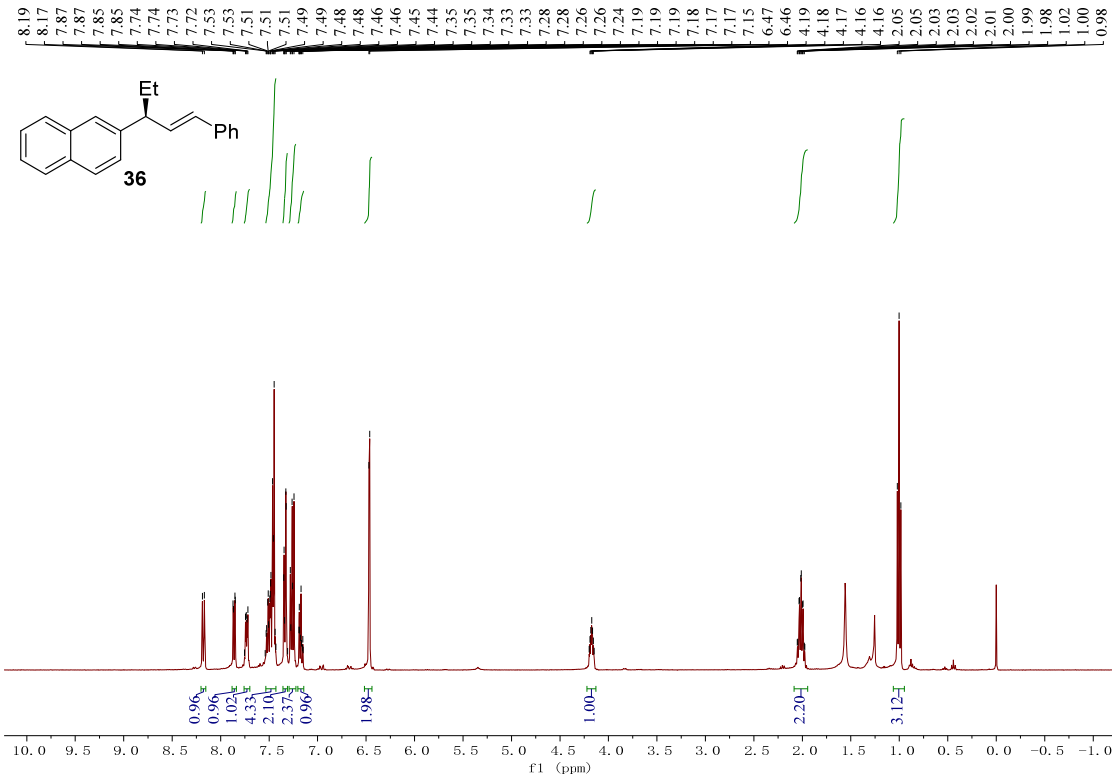
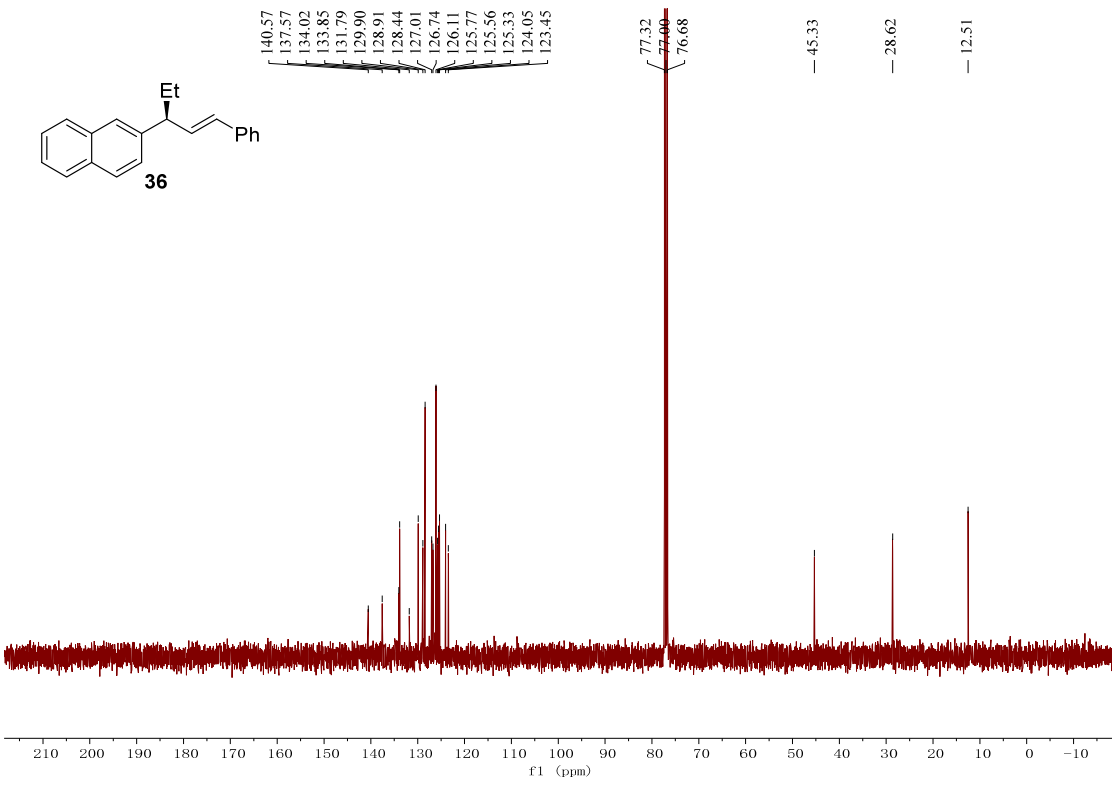
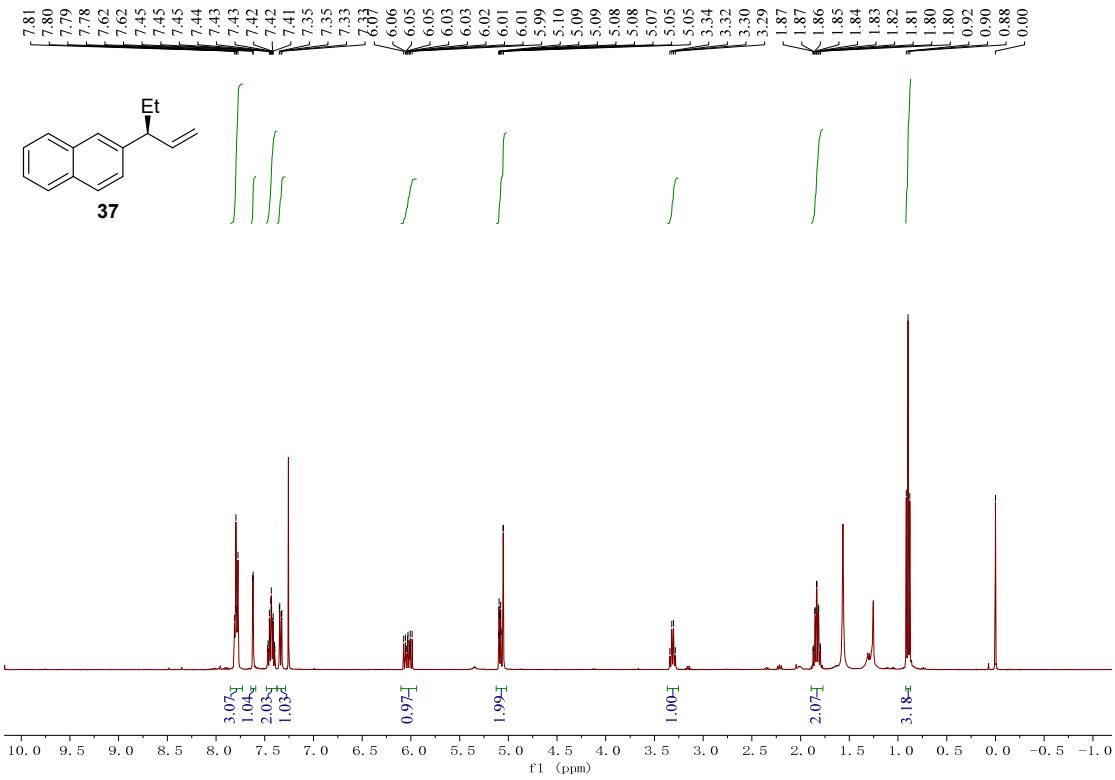
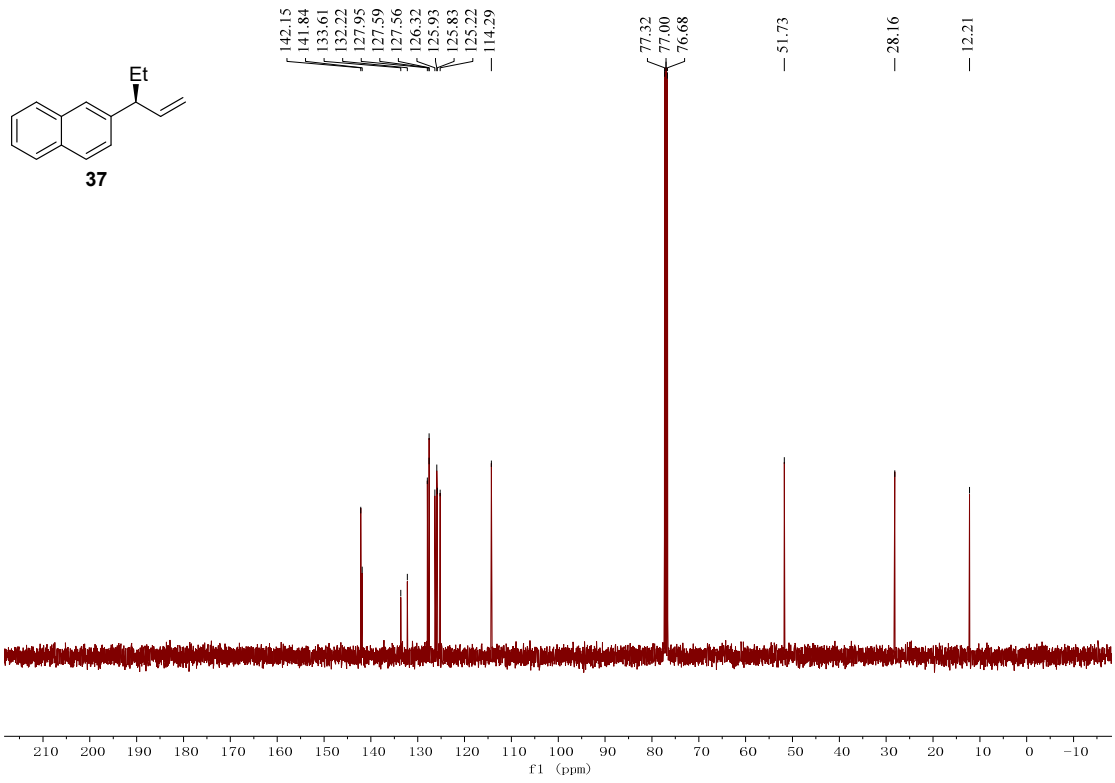
f1 (ppm)


8.19 8.17 7.87 7.87 7.85 7.85 7.74 7.74 7.73 7.72 7.53 7.53 7.51 7.51 7.51 7.49 7.49 7.48 7.48 7.46 7.46 7.45 7.44 7.35 7.35 7.34 7.33 7.33 7.28 7.28 7.26 7.26 7.24 7.19 7.19 7.19 7.18 7.17 7.17 7.15 6.47 6.46 4.19 4.18 4.17 4.16 4.16 2.05 2.05 2.03 2.03 2.02 2.01 2.00 1.99 1.98 1.02 1.00 0.98
Et
Ph
36
0.96 0.96 1.02 4.33 2.10 2.37 0.96 1.98 1.00 2.20 3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


140.57 137.57 134.02 133.85 131.79 129.90 128.91 128.44 127.01 126.74 126.11 125.77 125.56 125.33 124.05 123.45
77.32 77.00 76.68
45.33
28.62
12.51
Et
Ph
36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.81 7.80 7.79 7.78 7.62 7.62 7.45 7.45 7.45 7.44 7.43 7.43 7.42 7.42 7.41 7.35 7.35 7.33 7.33 6.07 6.06 6.05 6.05 6.03 6.03 6.02 6.01 6.01 5.99 5.10 5.09 5.09 5.08 5.08 5.07 5.05 5.05 3.34 3.32 3.30 3.29 1.87 1.87 1.86 1.85 1.84 1.83 1.82 1.81 1.80 1.80 0.92 0.90 0.88 0.00
Et
37
3.07 1.04 2.03 1.03 0.97 1.99 1.00 2.07 3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


142.15 141.84 133.61 132.22 127.95 127.59 127.56 126.32 125.93 125.83 125.22 114.29 77.32 77.00 76.68 51.73 28.16 12.21
Et
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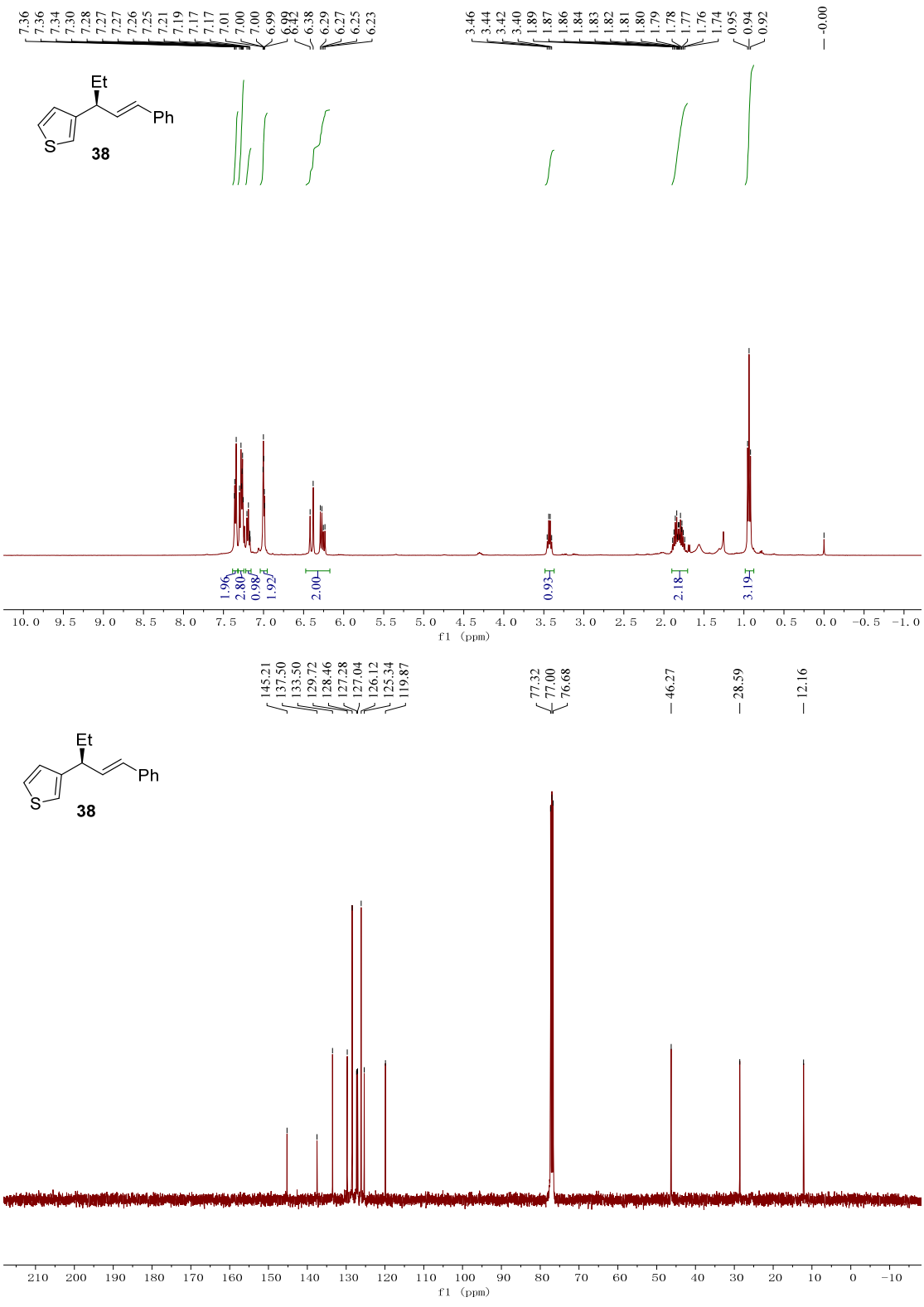
f1 (ppm)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7.19
7.17
7.17
7.01
7.00
7.00
6.99
6.99
6.42
6.38
6.29
6.27
6.25
6.23
3.46
3.44
3.42
3.40
1.89
1.87
1.86
1.84
1.83
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.74
0.95
0.94
0.92
-0.00
Et
Ph
S
38
1.96
2.80
0.98
1.92
2.00
0.93
2.18
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
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137.50
133.50
129.72
128.46
127.28
127.04
126.12
125.34
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77.32
77.00
76.68
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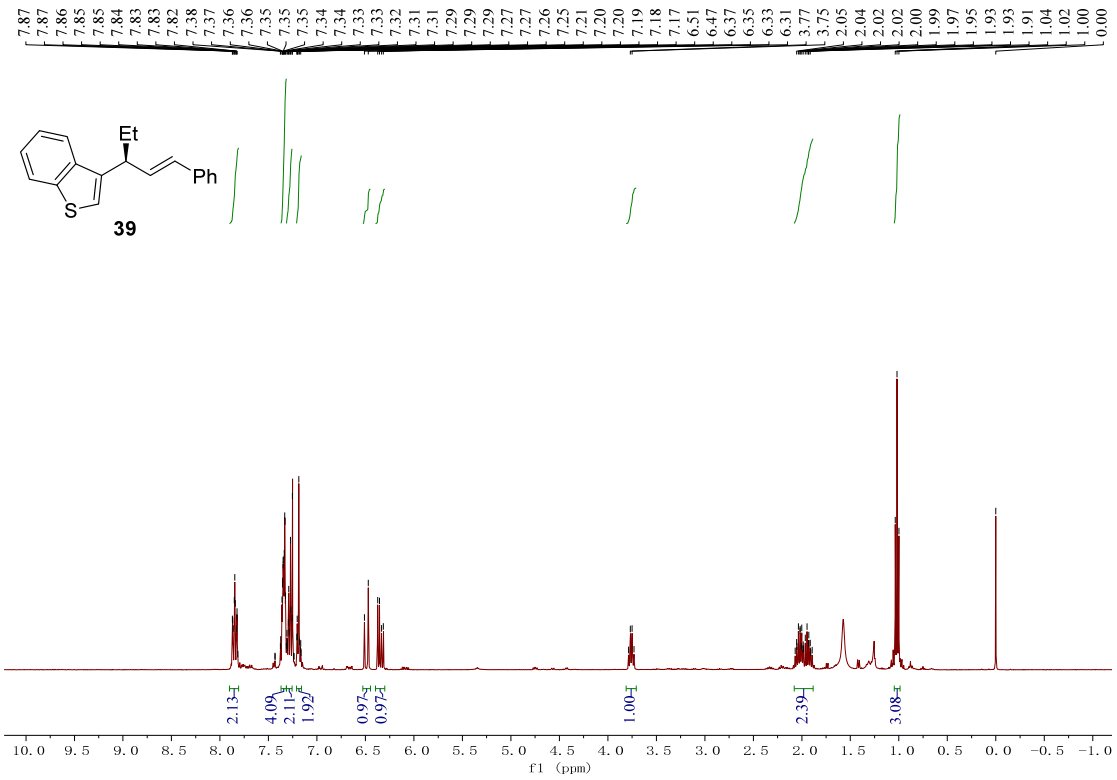
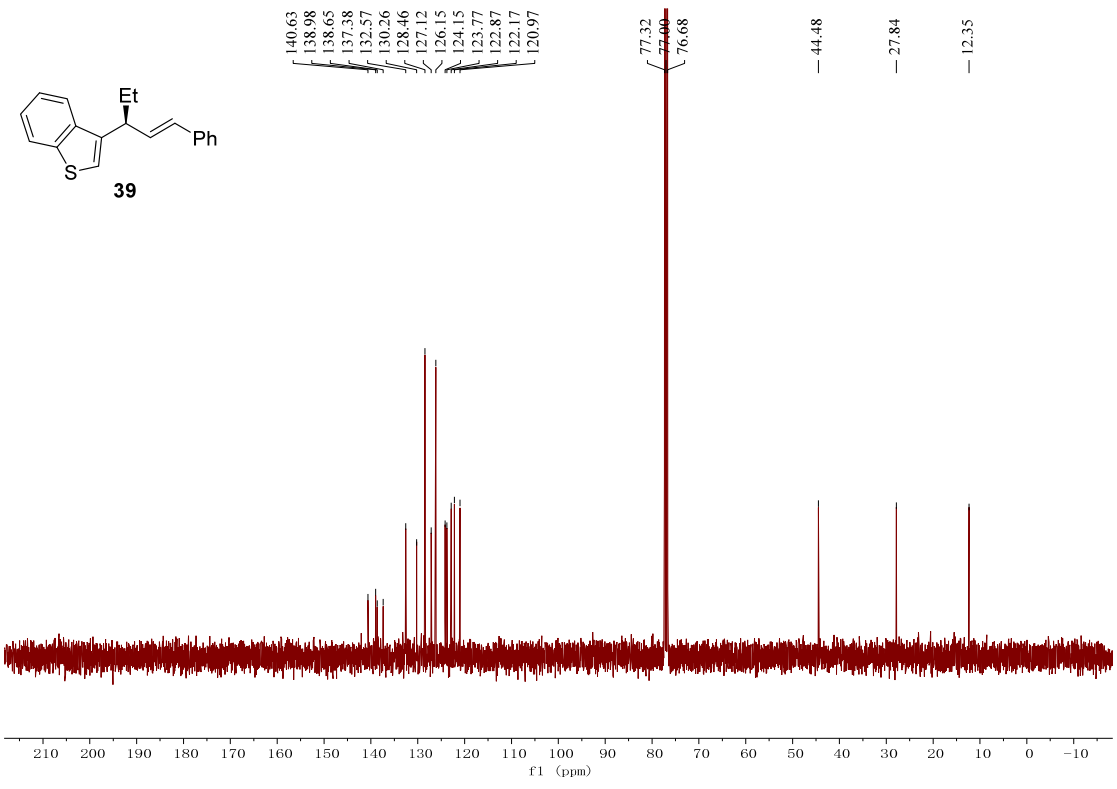
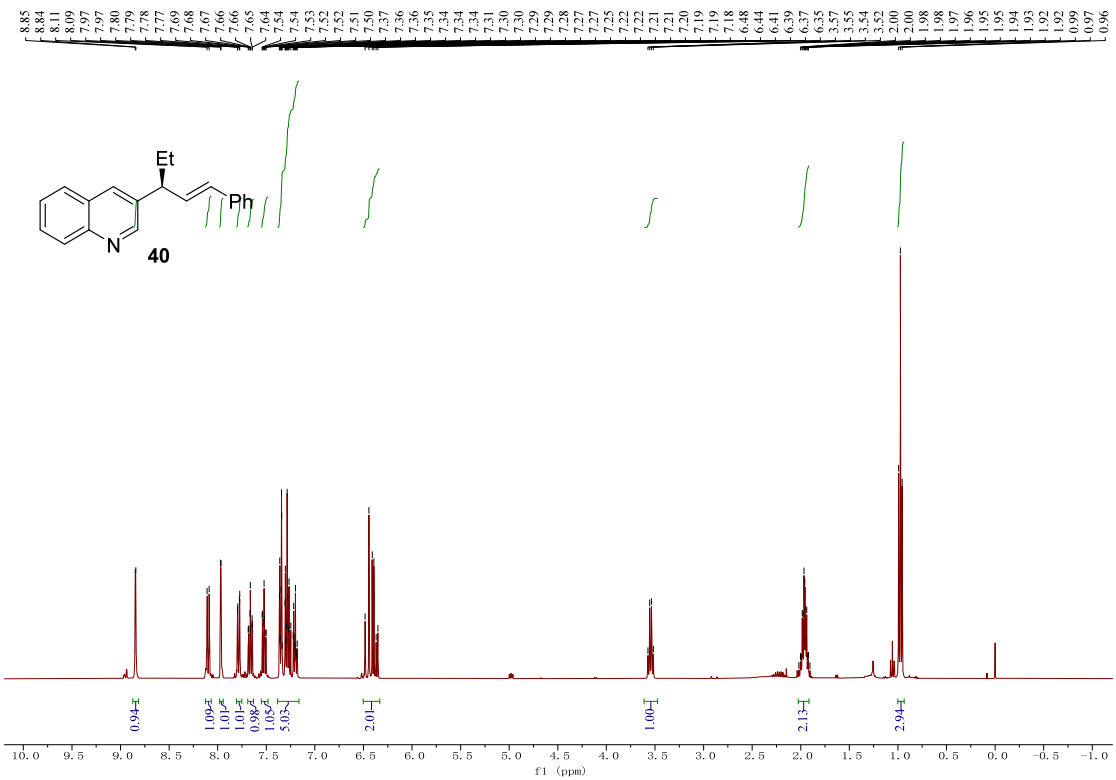
12.16
Et
Ph
S
38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Et
Ph
S
39

2.13
4.09
2.11
1.92
0.97
0.97
1.00
2.39
3.08
f1 (ppm)


Et
Ph
S
39
f1 (ppm)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Ph
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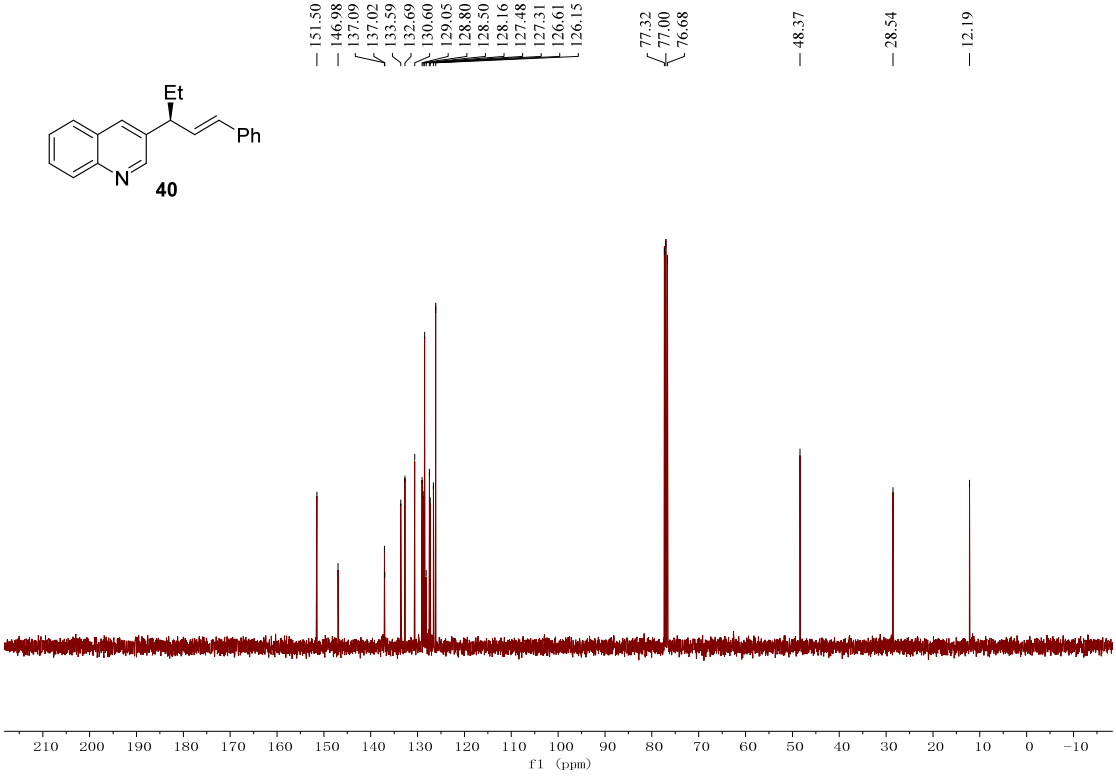
f1 (ppm)


Et
Ph
N
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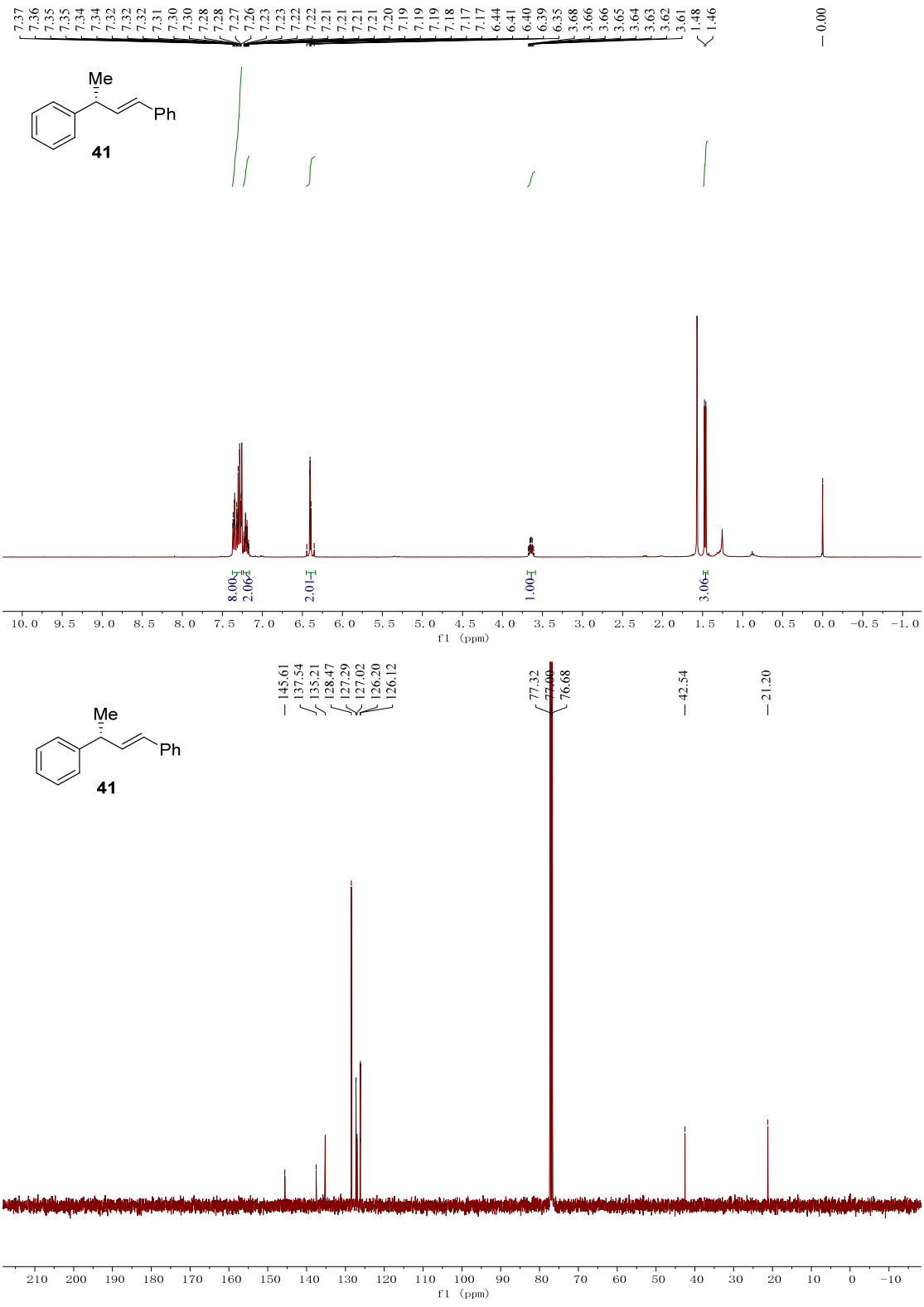
f1 (ppm)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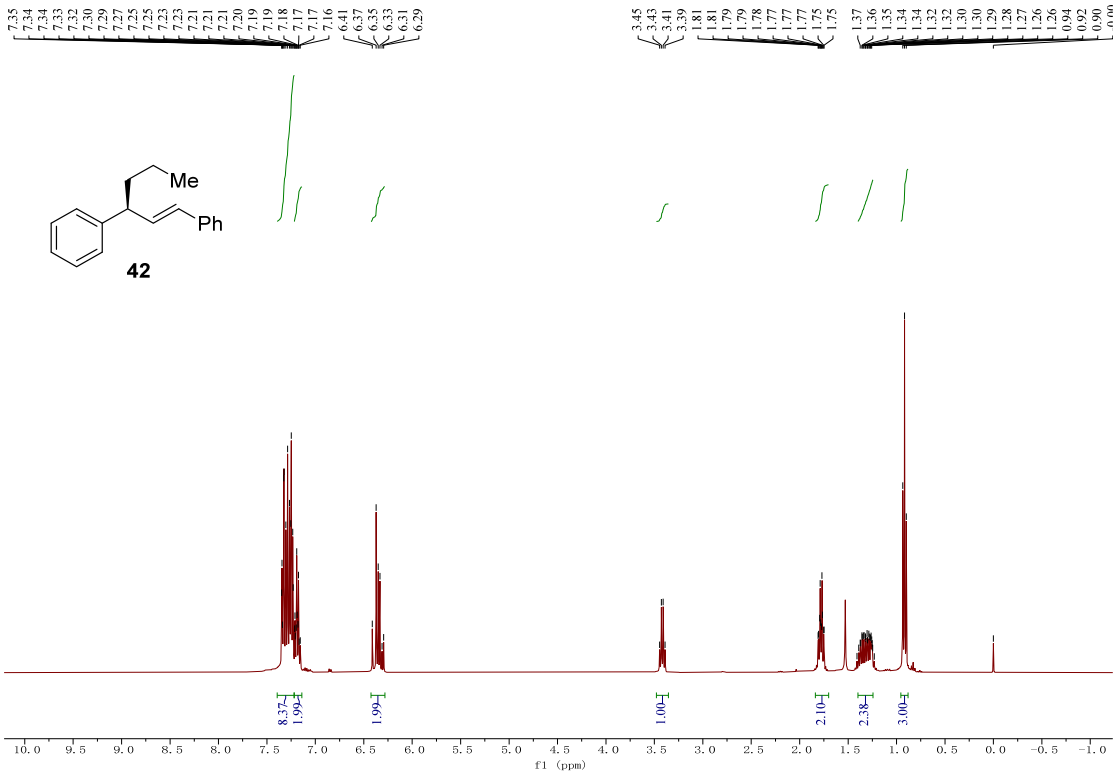
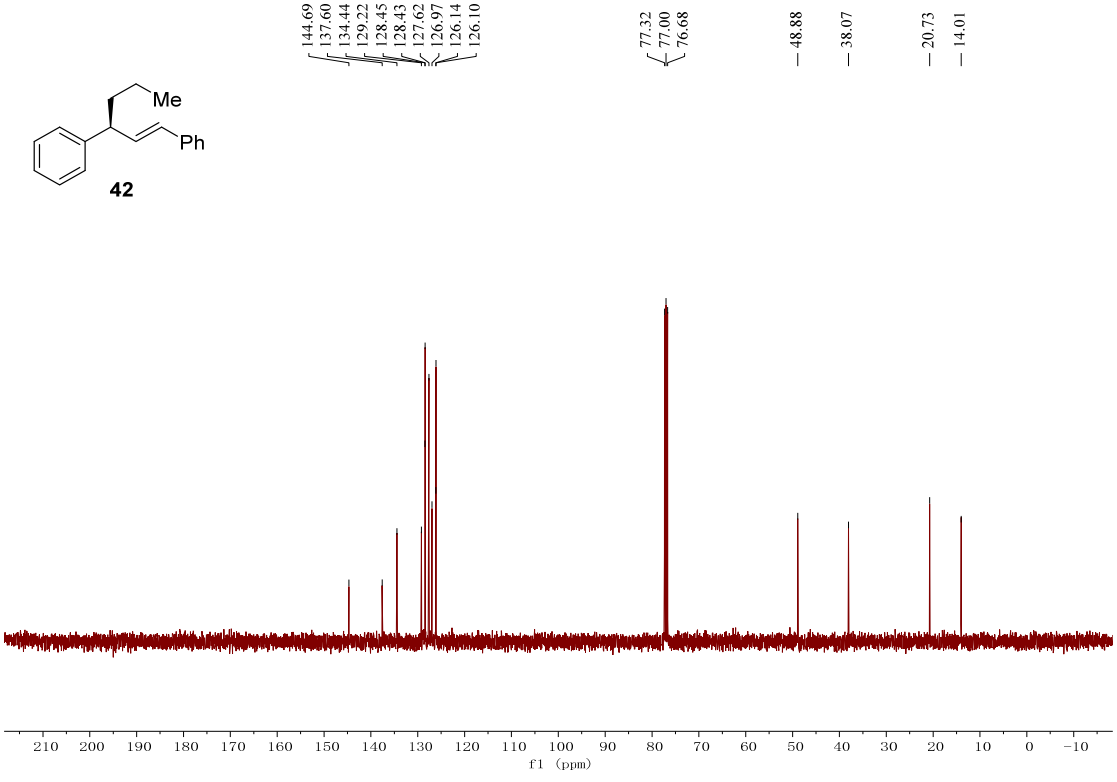
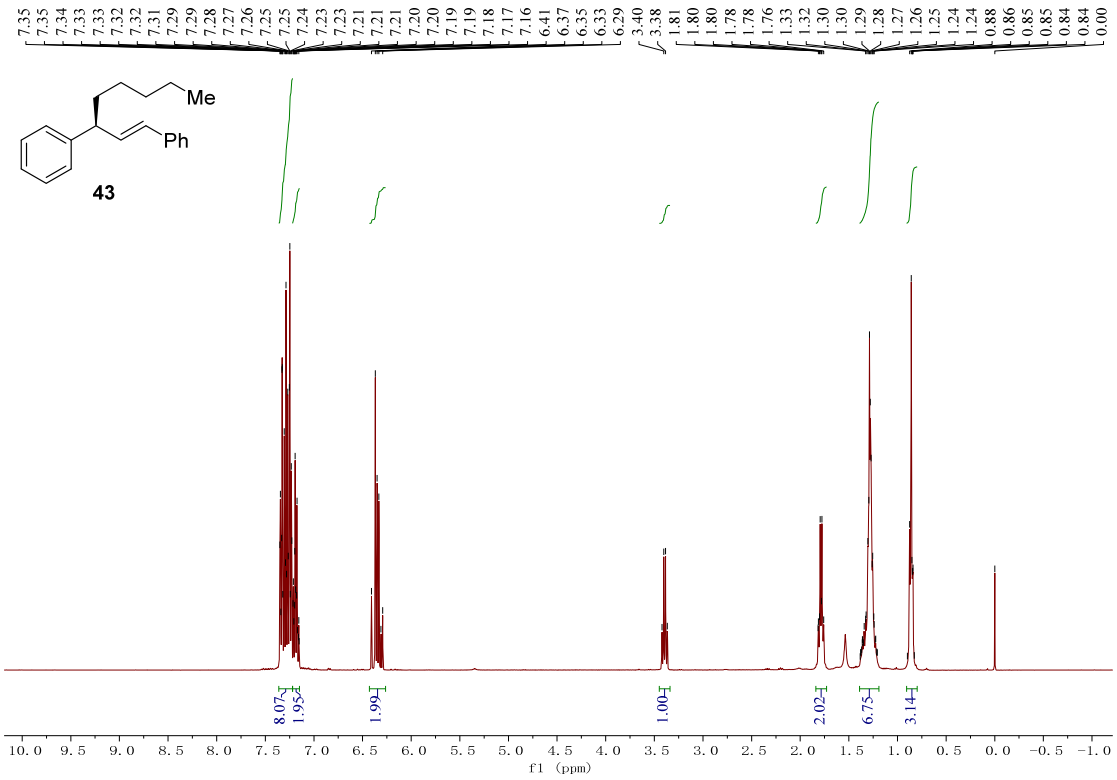
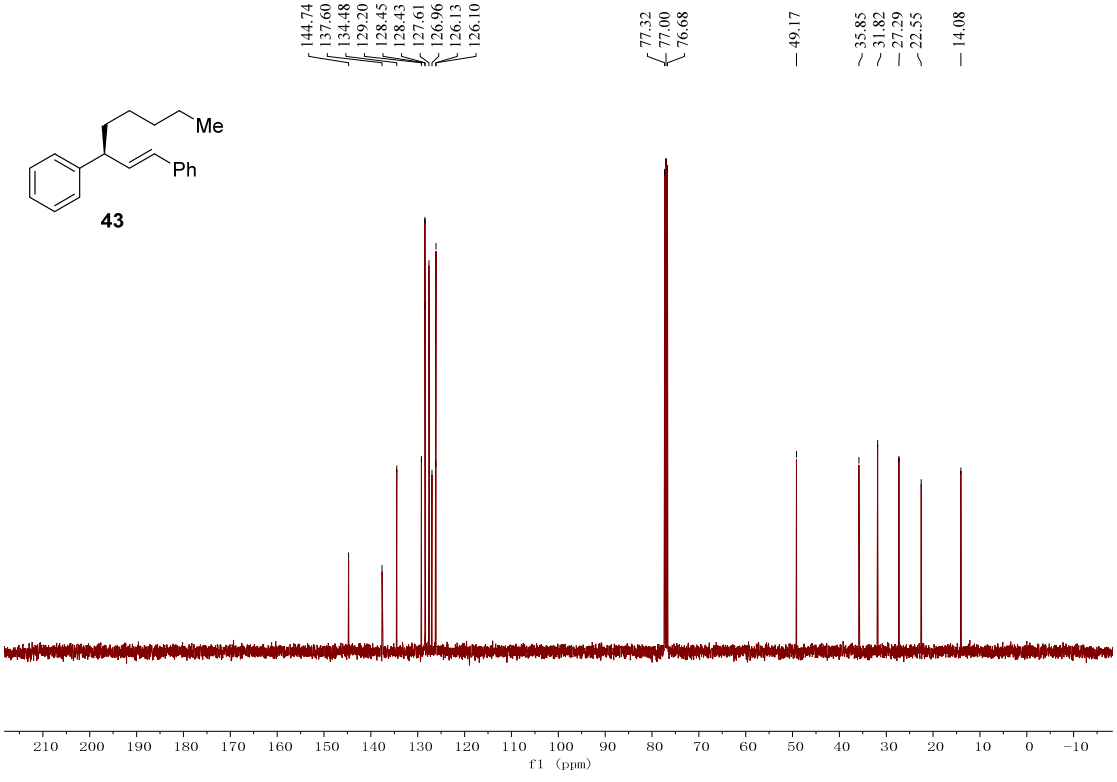
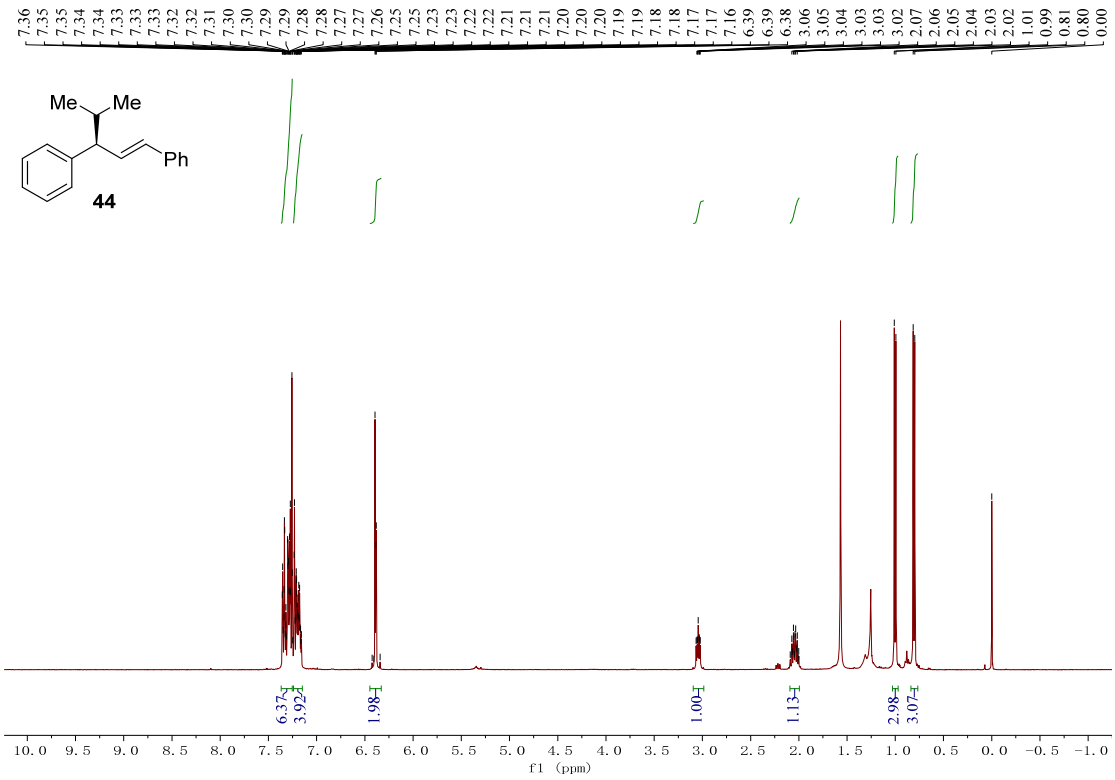
7.32
7.32
7.31
7.30
7.30
7.28
7.28
7.27
7.26
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.21
7.20
7.19
7.19
7.19
7.18
7.17
7.17
6.44
6.41
6.40
6.39
6.35
3.68
3.66
3.66
3.65
3.64
3.63
3.62
3.61
1.48
1.46
0.00
Me
Ph
41
8.00
2.06
2.01
1.00
3.06
f1 (ppm)
145.61
137.54
135.21
128.47
127.29
127.02
126.20
126.12
77.32
77.00
76.68
42.54
21.20
Me
Ph
41
f1 (ppm)

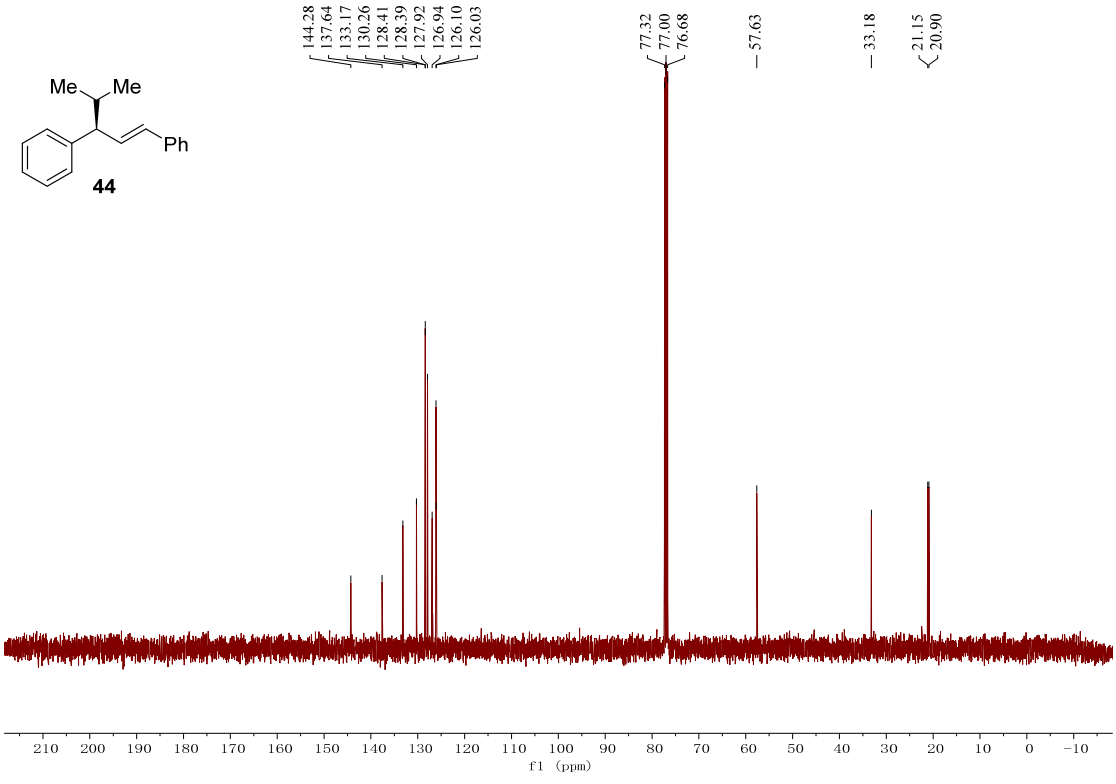

Me
Ph
42
8.37
1.99
1.99
1.00
2.10
2.38
3.00
f1 (ppm)

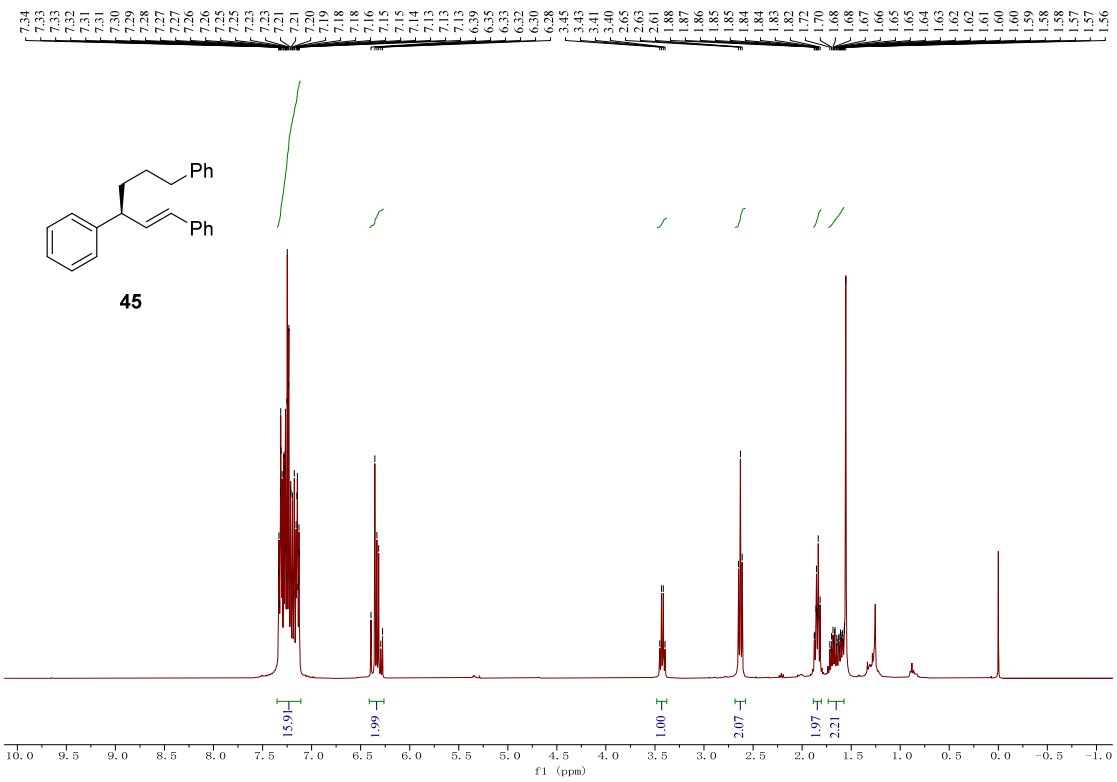

Me
Ph
42
144.69
137.60
134.44
129.22
128.45
128.43
127.62
126.97
126.14
126.10
77.32
77.00
76.68
48.88
38.07
20.73
14.01
f1 (ppm)

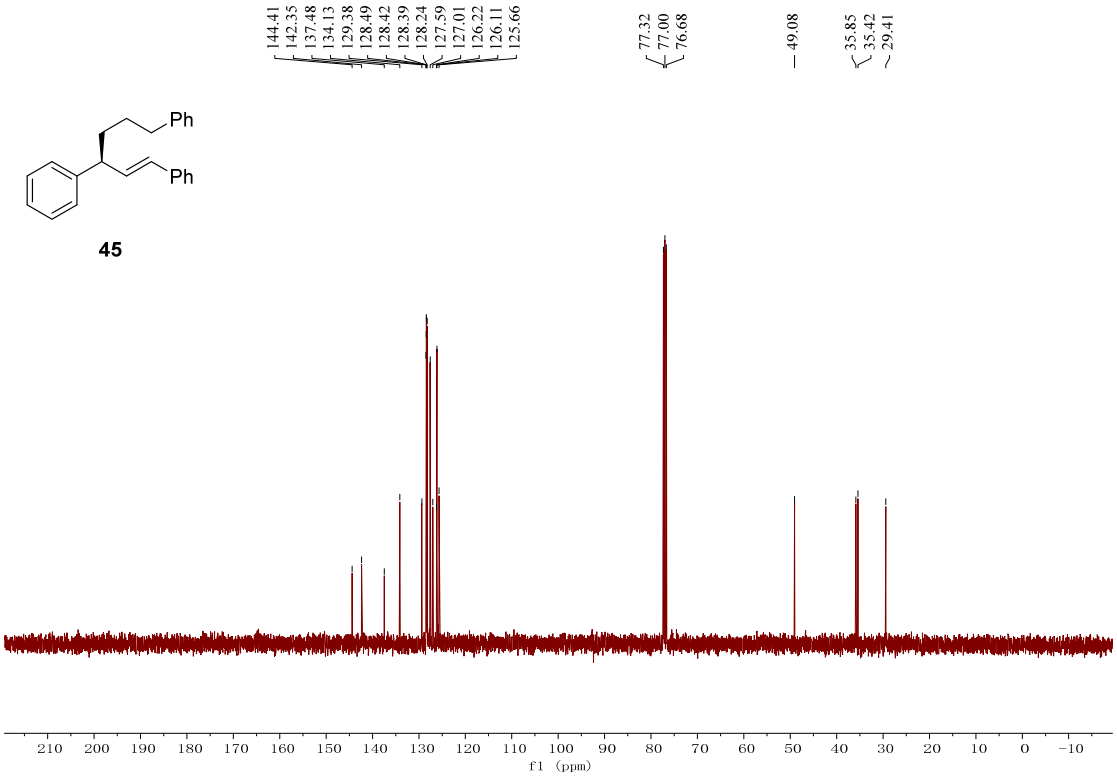

Me
Ph
43
f1 (ppm)

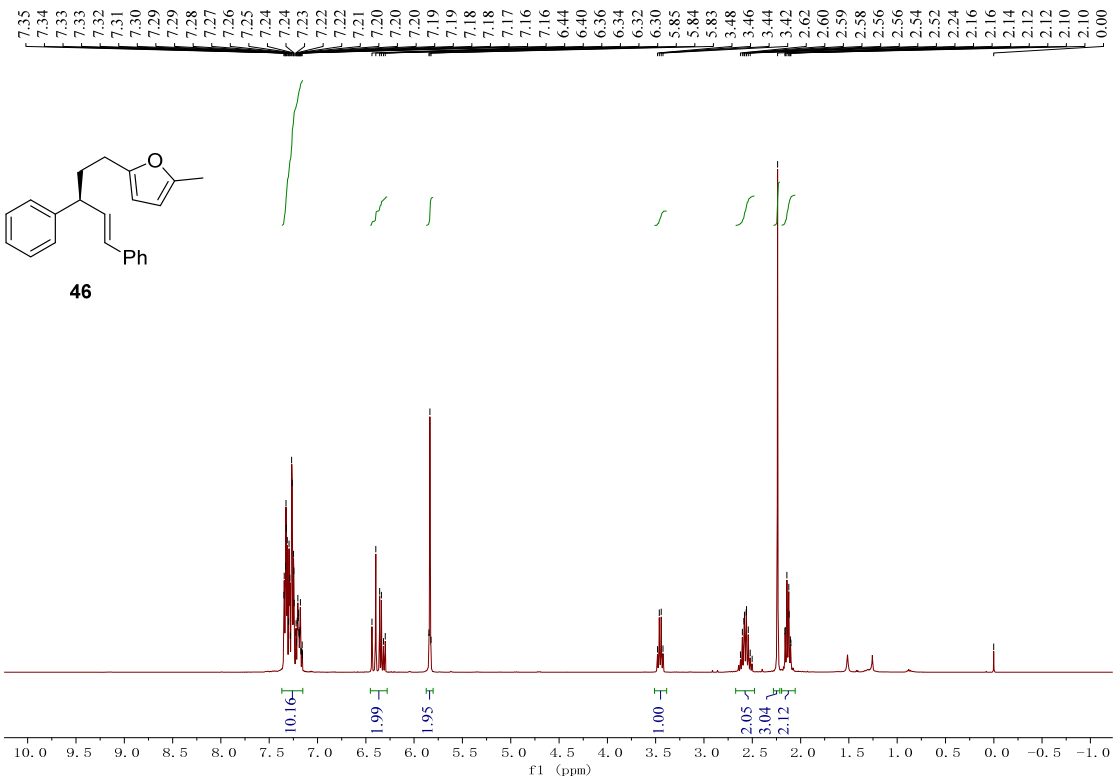

Me
Ph
43
f1 (ppm)

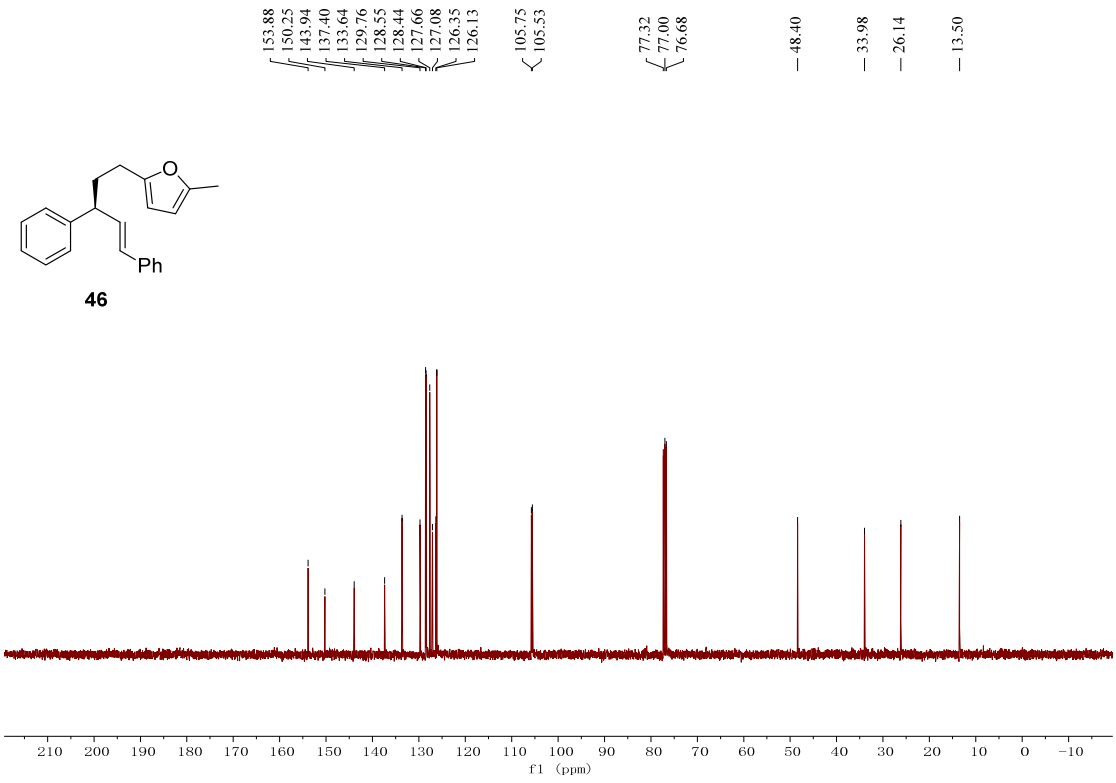

Me
Me
Ph
44
6.37
3.92
1.98
1.00
1.13
2.98
3.07
f1 (ppm)

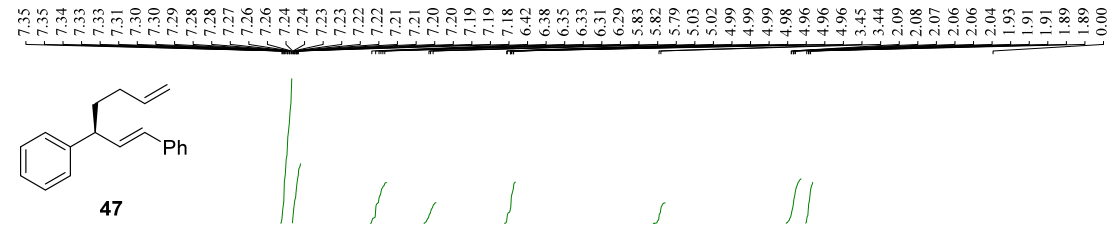

Me
Me
Ph
44
144.28
137.64
133.17
130.26
128.41
128.39
127.92
126.94
126.10
126.03
77.32
77.00
76.68
57.63
33.18
21.15
20.90
f1 (ppm)


Ph
Ph
45
15.91
1.99
1.00
2.07
1.97
2.21
f1 (ppm)


Ph
Ph
45
144.41
142.35
137.48
134.13
129.38
128.49
128.42
128.39
128.24
127.59
127.01
126.22
126.11
125.66
77.32
77.00
76.68
49.08
35.85
35.42
29.41
f1 (ppm)

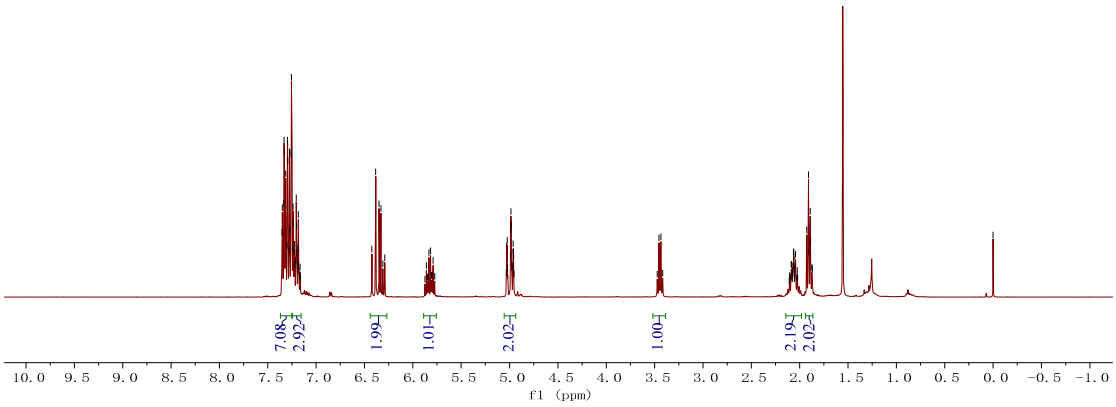

7.35 7.34 7.33 7.33 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.26 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.16 7.16 6.44 6.40 6.36 6.34 6.32 6.30 5.85 5.84 5.83 3.48 3.46 3.44 3.42 2.62 2.60 2.59 2.58 2.56 2.56 2.54 2.52 2.24 2.16 2.16 2.14 2.12 2.12 2.10 2.10 0.00
O
Ph
46
10.16
1.99
1.95
1.00
2.05
3.04
2.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

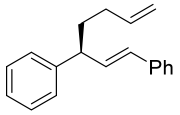

153.88 150.25 143.94 137.40 133.64 129.76 128.55 128.44 127.66 127.08 126.35 126.13 105.75 105.53 77.32 77.00 76.68 48.40 33.98 26.14 13.50
O
Ph
46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.35 7.35 7.34 7.33 7.33 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 6.42 6.38 6.35 6.33 6.31 6.29 5.83 5.82 5.79 5.03 5.02 4.99 4.99 4.99 4.98 4.96 4.96 4.96 3.45 3.44 2.09 2.08 2.07 2.06 2.06 2.04 1.93 1.91 1.91 1.89 1.89 0.00

Ph

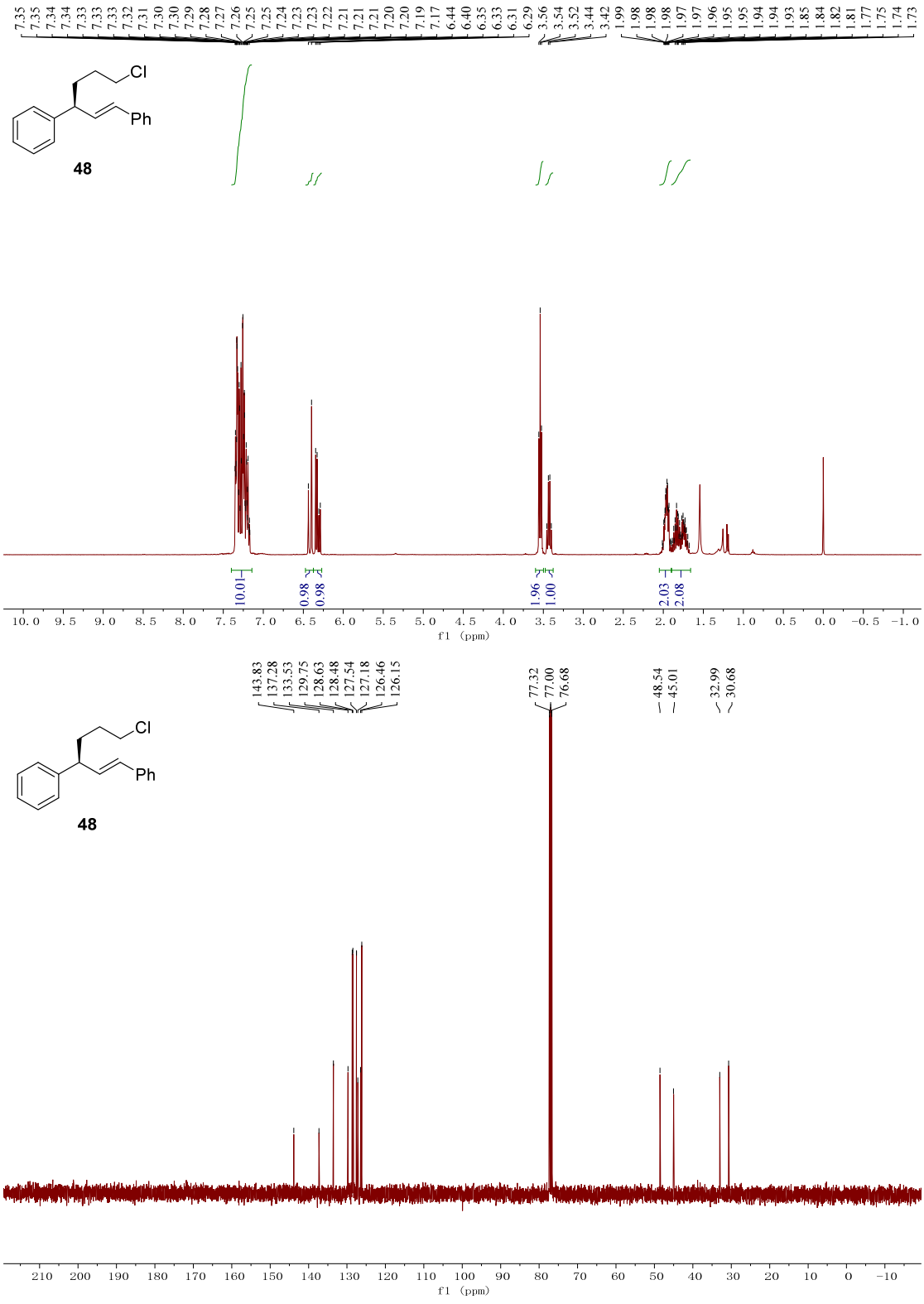
47

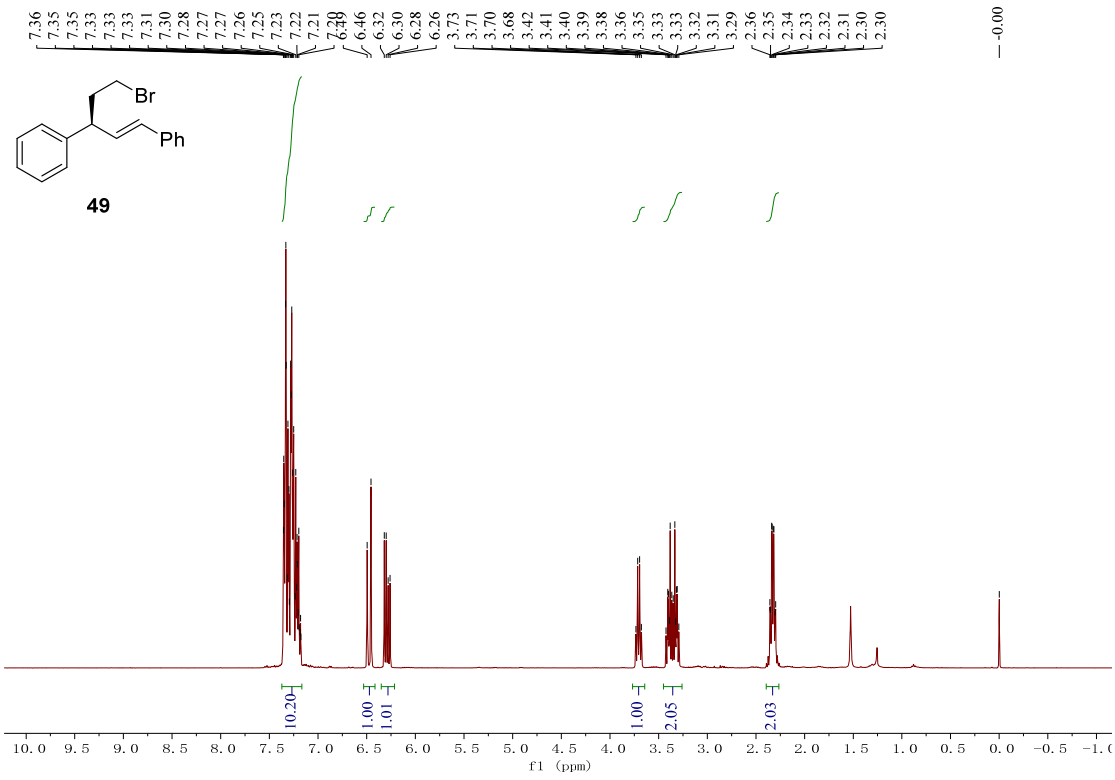

7.08
2.92
1.99
1.01
2.02
1.00
2.19
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

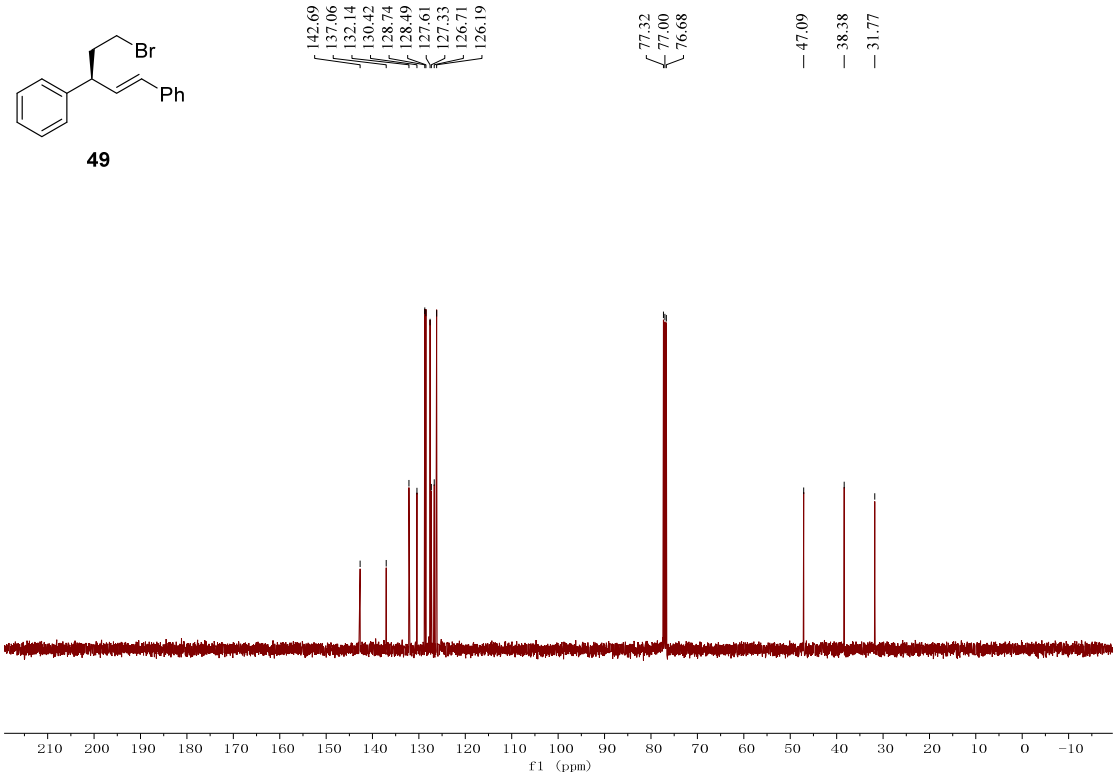

Ph

47

144.28
138.40
137.49
133.99
129.55
128.52
128.45
127.65
127.05
126.27
126.12
114.81
77.32
77.00
76.68
48.44
34.91
31.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.30 7.30 7.29 7.28 7.27 7.26 7.25 7.25 7.24 7.23 7.23 7.22 7.21 7.21 7.21 7.20 7.20 7.19 7.17 6.44 6.40 6.35 6.33 6.31 6.29 3.56 3.54 3.52 3.44 3.42 1.99 1.98 1.98 1.98 1.97 1.97 1.96 1.95 1.95 1.94 1.94 1.93 1.85 1.84 1.82 1.81 1.77 1.75 1.74 1.73
Cl
Ph
48
10.01
0.98
0.98
1.96
1.00
2.03
2.08
f1 (ppm)
143.83 137.28 133.53 129.75 128.63 128.48 127.54 127.18 126.46 126.15
77.32 77.00 76.68
48.54 45.01
32.99 30.68
Cl
Ph
48
f1 (ppm)


7.36
7.35
7.35
7.33
7.33
7.33
7.31
7.30
7.28
7.27
7.27
7.26
7.25
7.23
7.22
7.21
7.20
6.46
6.32
6.30
6.28
6.26
3.73
3.71
3.70
3.68
3.42
3.41
3.40
3.39
3.38
3.36
3.35
3.33
3.33
3.32
3.31
3.29
2.36
2.35
2.34
2.33
2.32
2.31
2.30
2.30
-0.00
Br
Ph
49
10.20
1.00
1.01
1.00
2.05
2.03
f1 (ppm)


142.69
137.06
132.14
130.42
128.74
128.49
127.61
127.33
126.71
126.19
77.32
77.00
76.68
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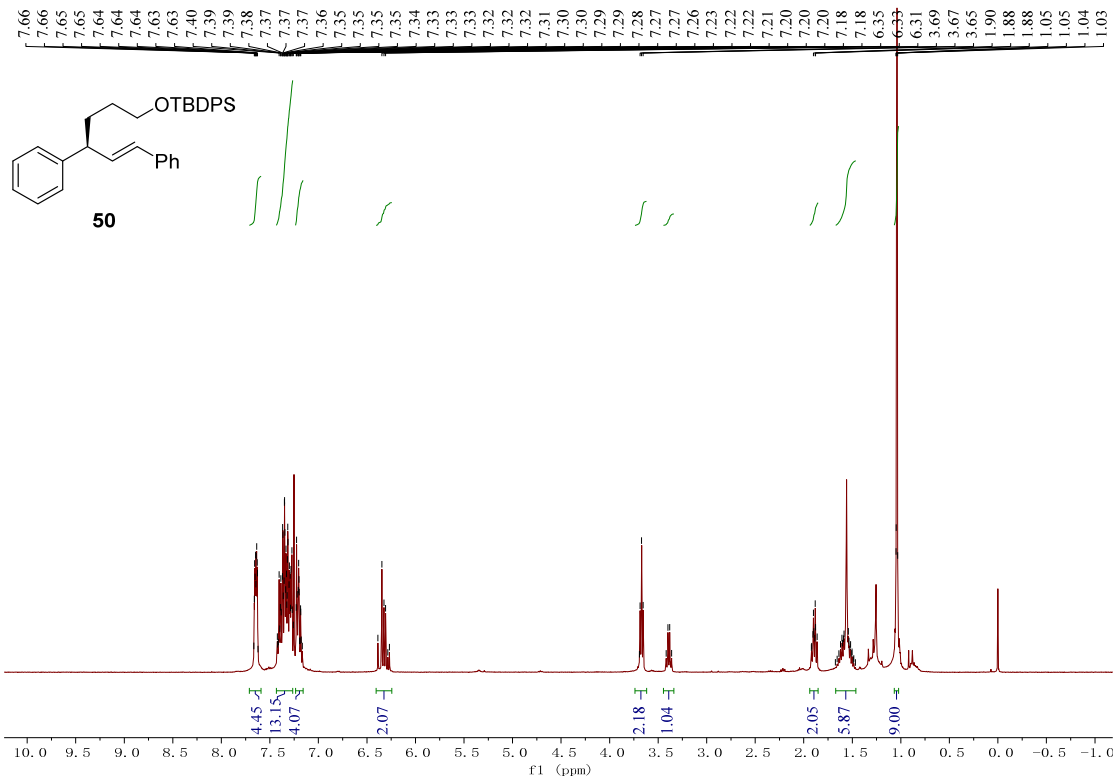
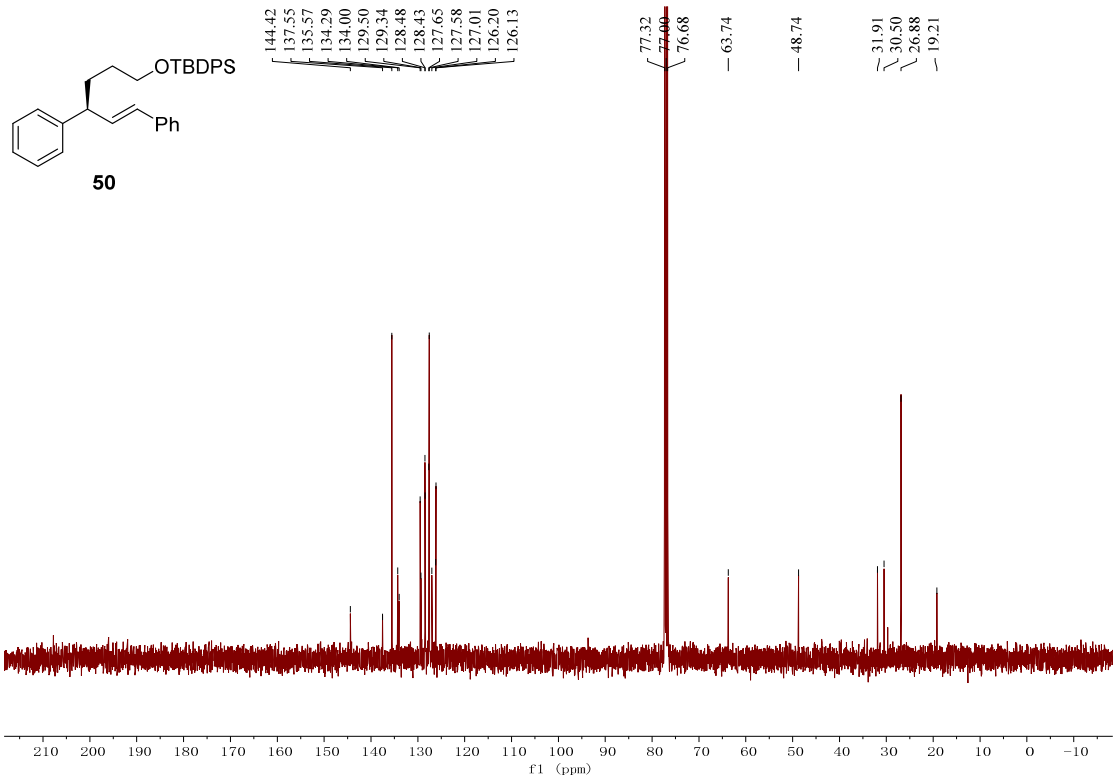
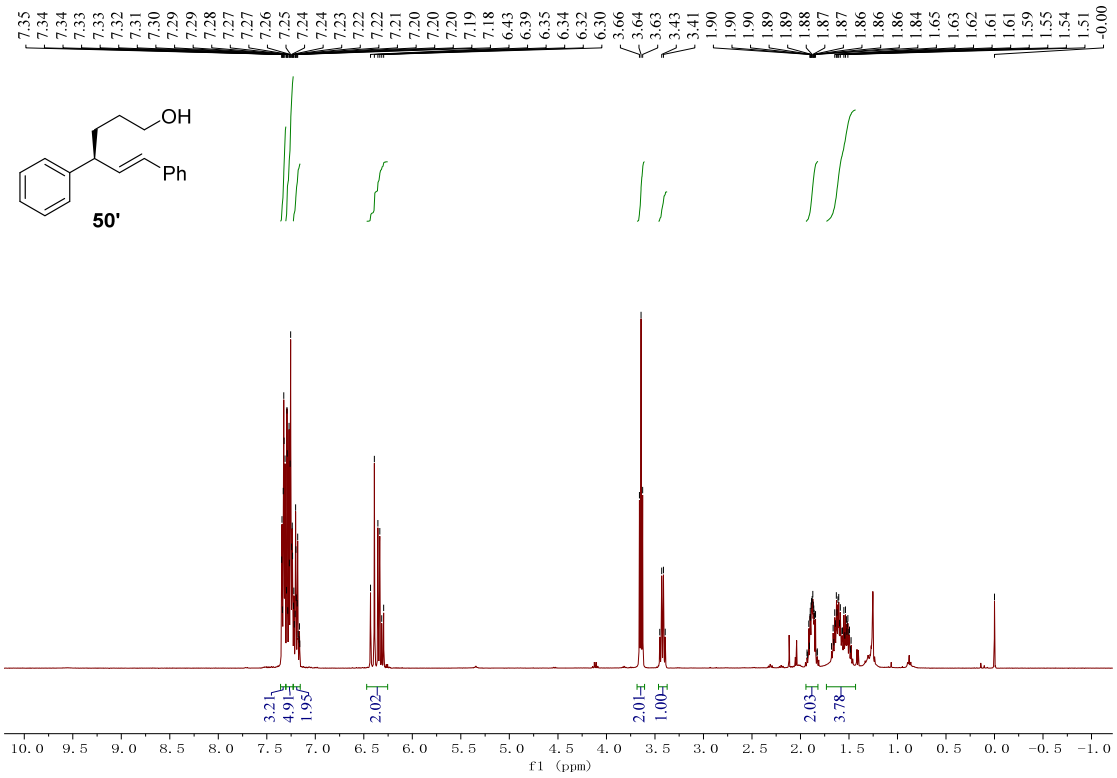
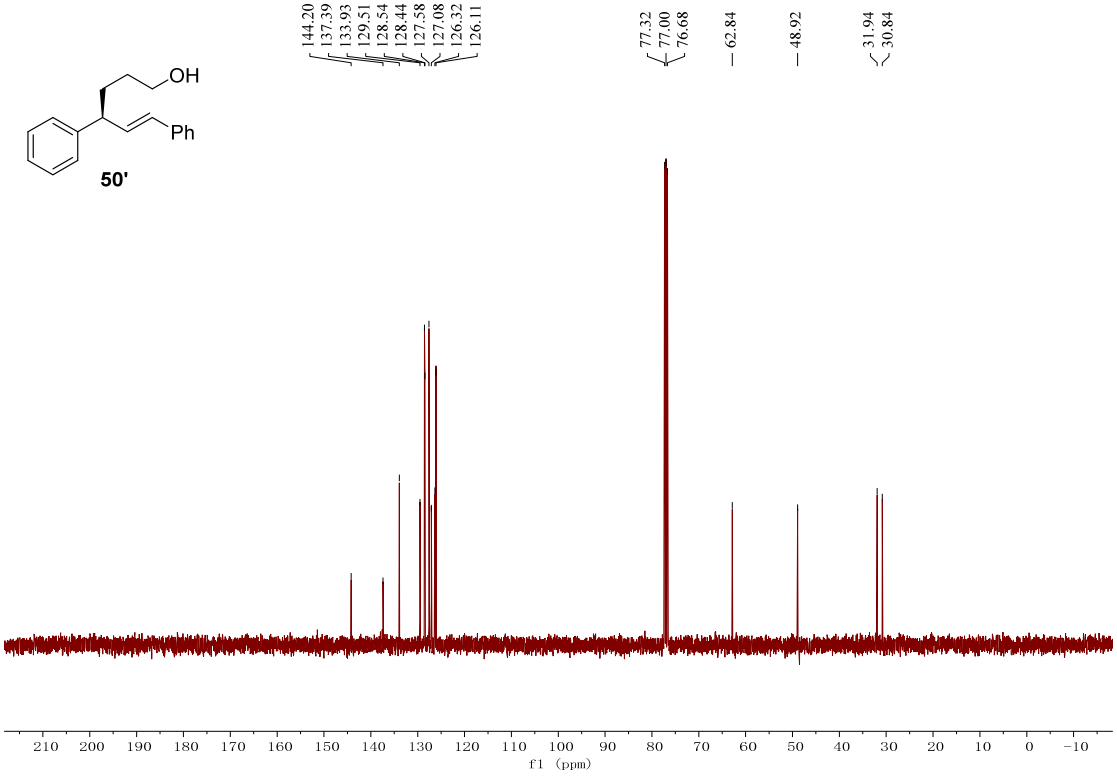
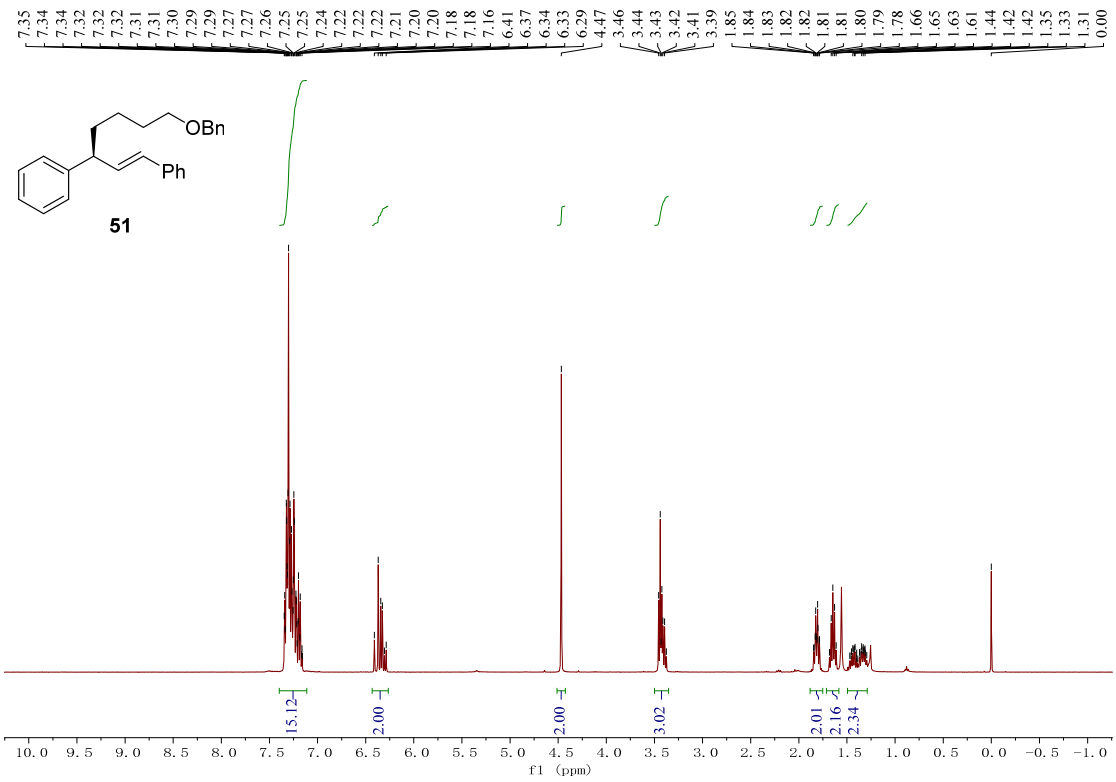
38.38
31.77
Br
Ph
49
f1 (ppm)

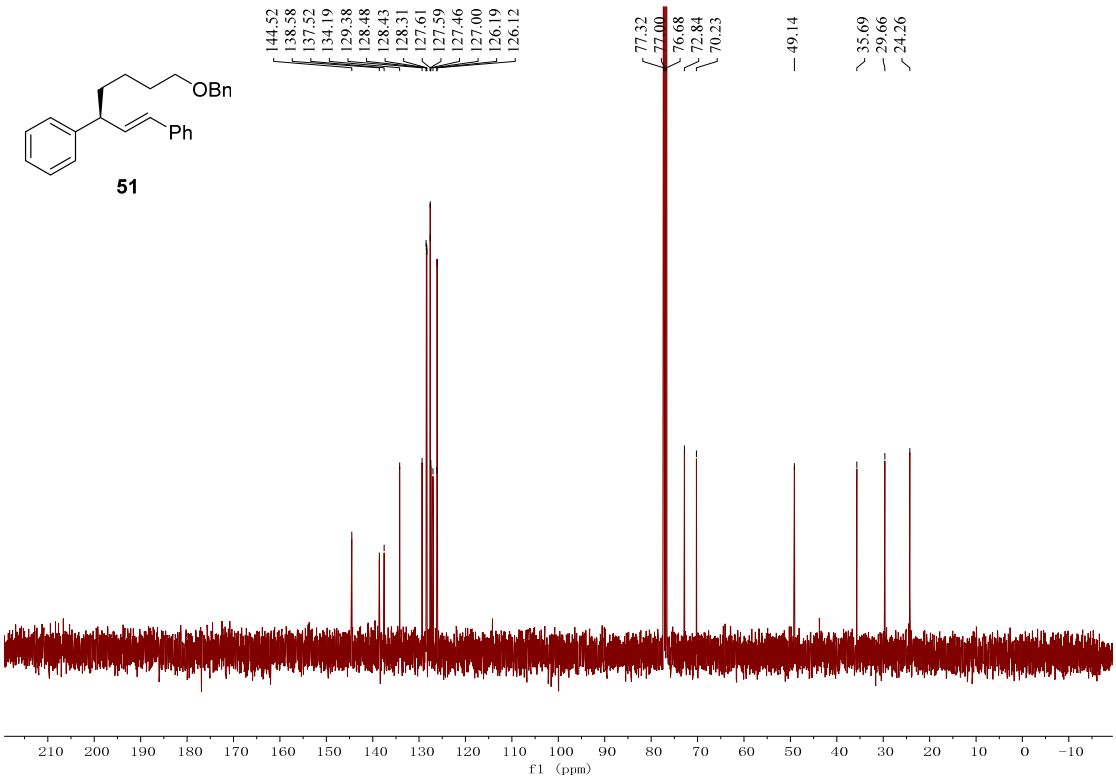

OTBDPS
Ph
50
f1 (ppm)

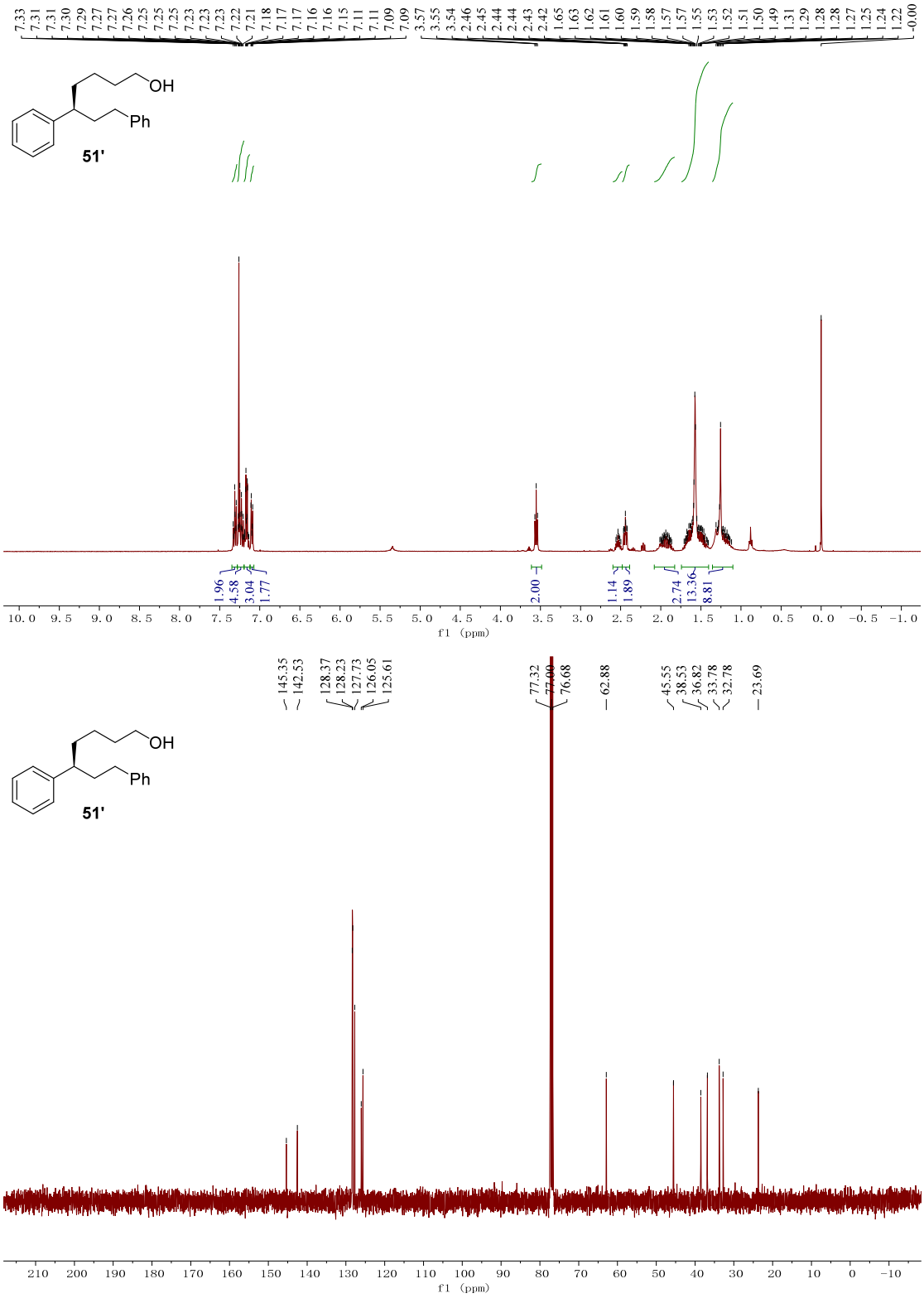

OTBDPS
Ph
50
f1 (ppm)

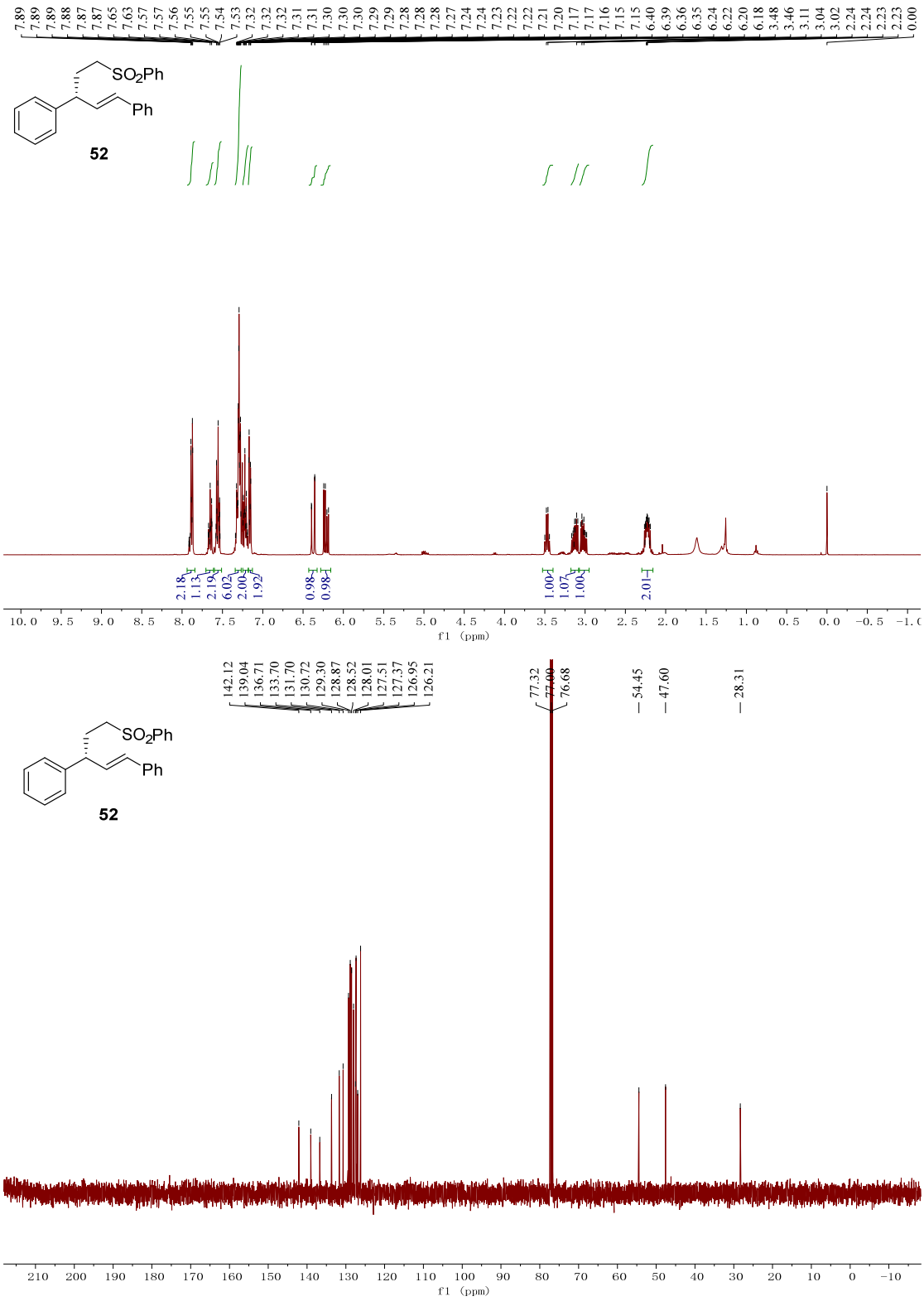

OH
Ph
50'
f1 (ppm)

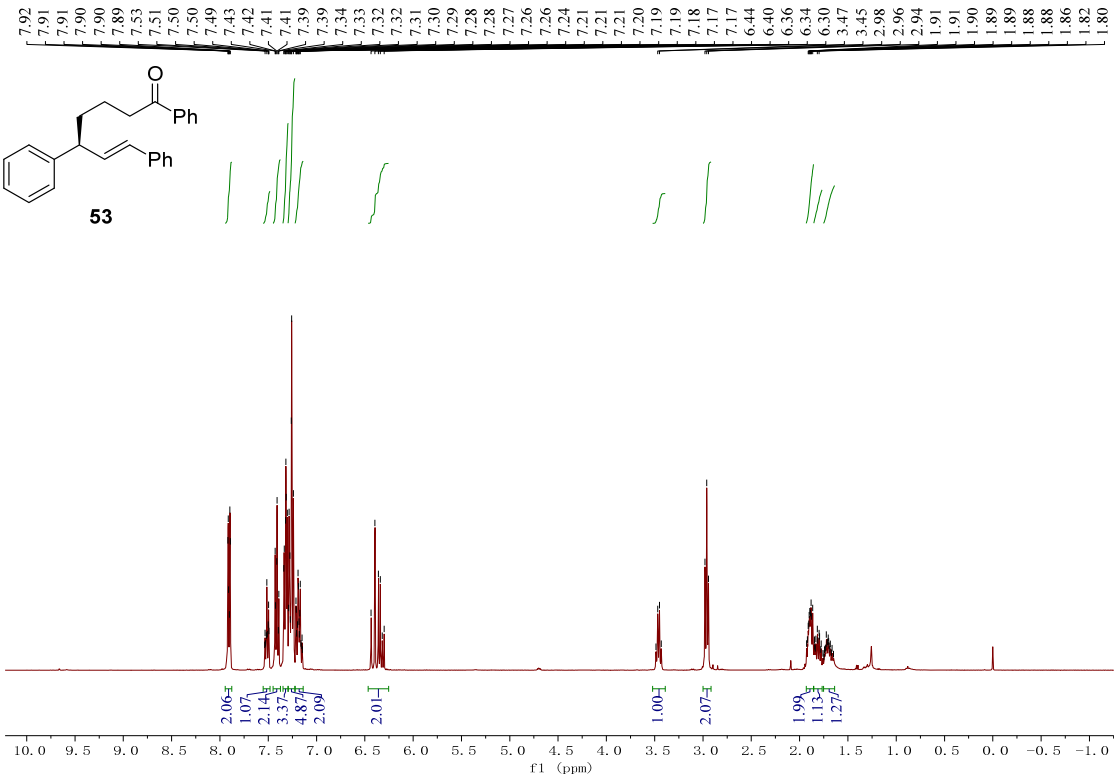

OH
Ph
50'
f1 (ppm)

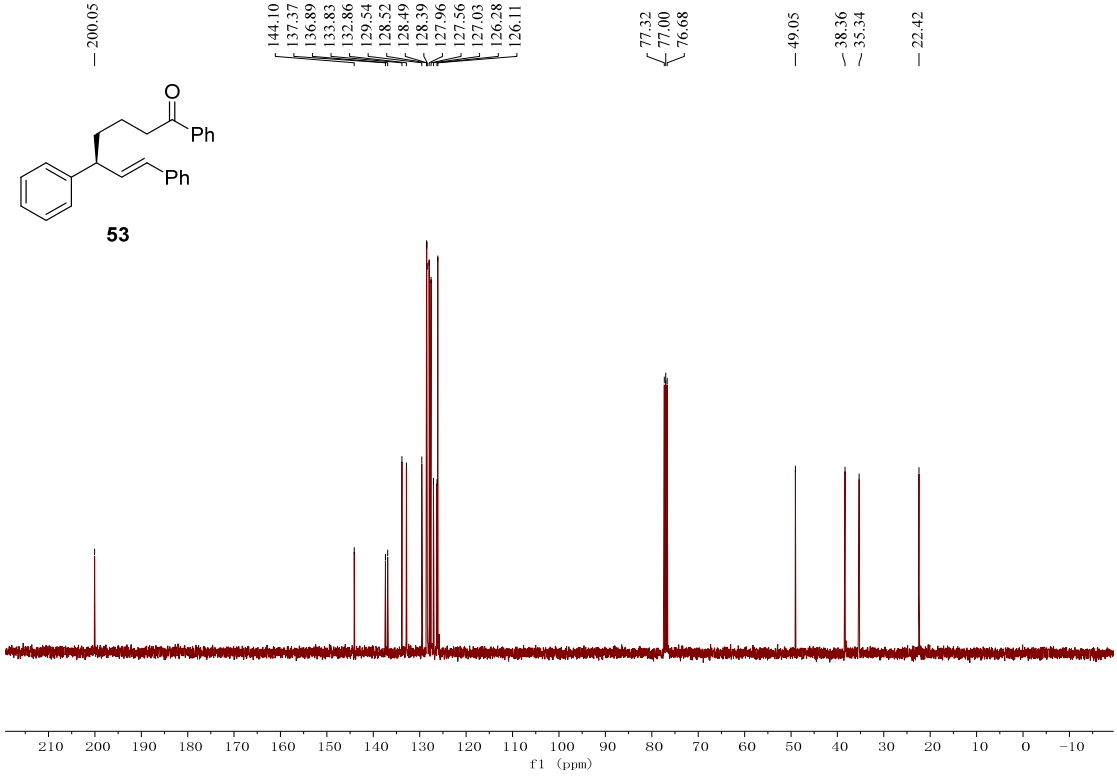

OBn
Ph
51
15.12
2.00
2.00
3.02
2.01
2.16
2.34
f1 (ppm)

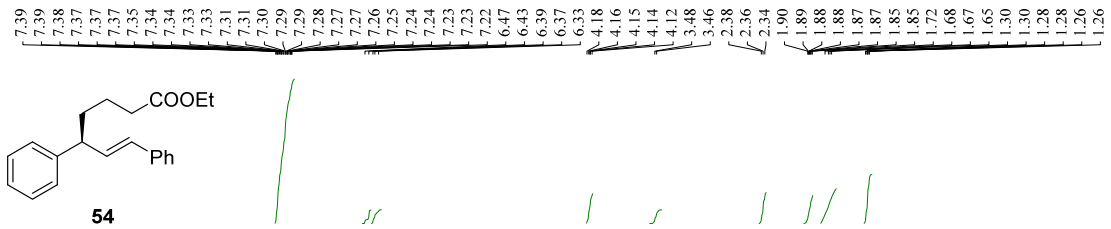

OBn
Ph
51
f1 (ppm)


7.33 7.31 7.31 7.30 7.29 7.27 7.27 7.26 7.25 7.25 7.25 7.23 7.23 7.23 7.22 7.21 7.18 7.17 7.17 7.16 7.16 7.15 7.11 7.11 7.09 7.09
3.57 3.55 3.54 2.46 2.45 2.44 2.44 2.43 2.42 1.65 1.63 1.62 1.61 1.60 1.59 1.58 1.57 1.57 1.55 1.53 1.52 1.51 1.50 1.49 1.31 1.29 1.28 1.28 1.27 1.25 1.24 1.22 -0.00
OH
Ph
51'
1.96 4.58 3.04 1.77 2.00 1.14 1.89 2.74 13.36 8.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
145.35 142.53 128.37 128.23 127.73 126.05 125.61 77.32 77.00 76.68 62.88 45.55 38.53 36.82 33.78 32.78 23.69
OH
Ph
51'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


SO2Ph
Ph
52
f1 (ppm)
SO2Ph
Ph
52
f1 (ppm)

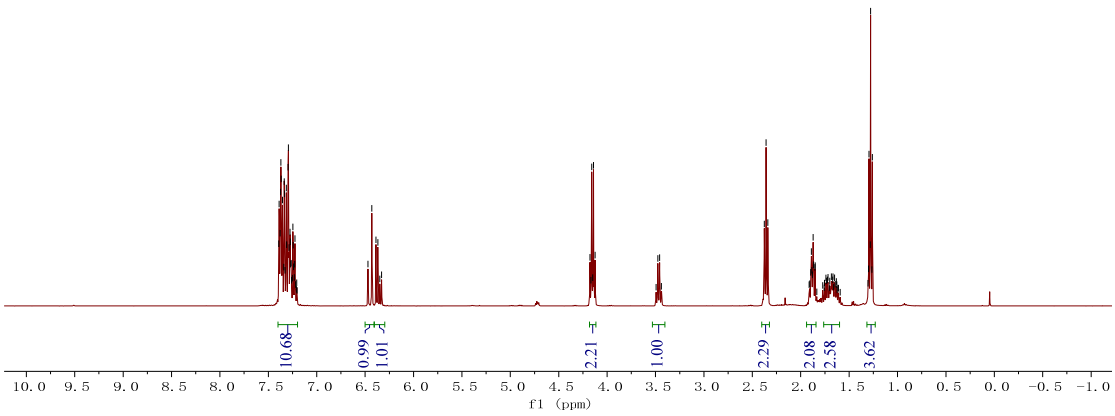

7.92 7.91 7.91 7.90 7.90 7.89 7.53 7.51 7.50 7.50 7.49 7.43 7.42 7.41 7.41 7.39 7.39 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.24 7.21 7.21 7.21 7.20 7.19 7.19 7.18 7.17 7.17 6.44 6.40 6.36 6.34 6.30 3.47 3.45 2.98 2.96 2.94 1.91 1.91 1.90 1.89 1.89 1.88 1.88 1.86 1.82 1.80
O
Ph
Ph
53
2.06 1.07 2.14 3.37 4.87 2.09 2.01 1.00 2.07 1.99 1.13 1.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

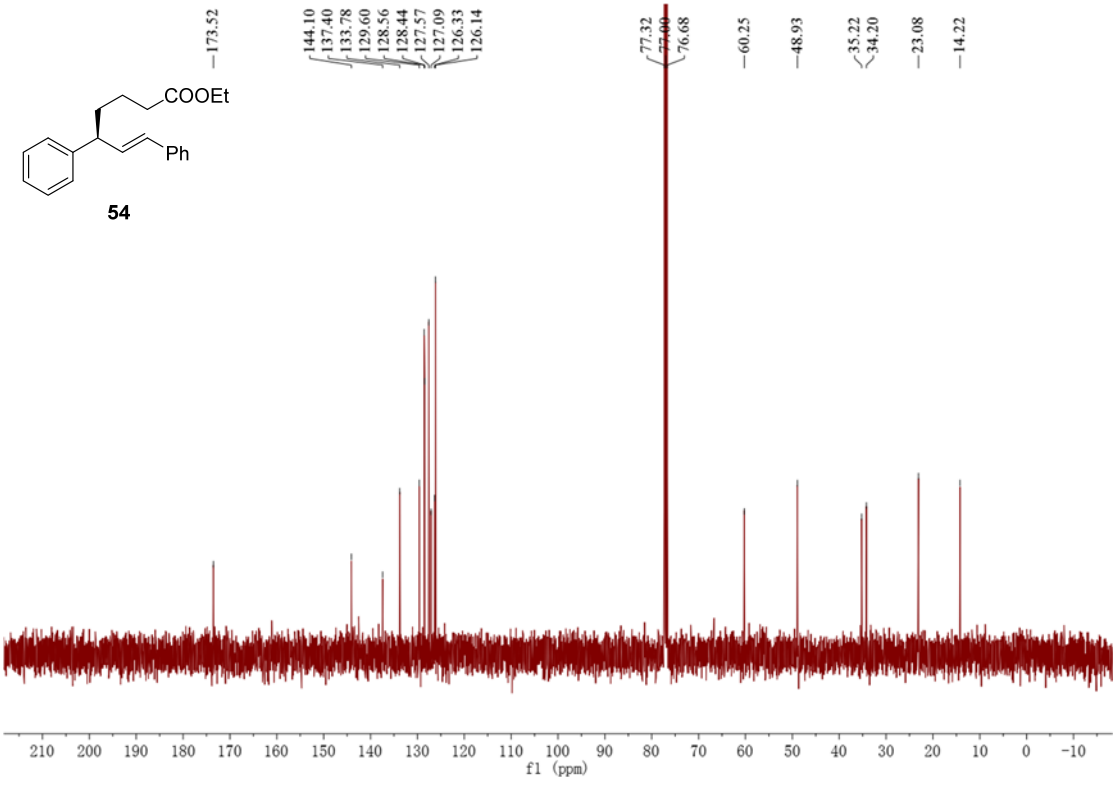

200.05
144.10 137.37 136.89 133.83 132.86 129.54 128.52 128.49 128.39 127.96 127.56 127.03 126.28 126.11
77.32 77.00 76.68
49.05
38.36 35.34
22.42
O
Ph
Ph
53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.39 7.39 7.38 7.37 7.37 7.37 7.35 7.34 7.34 7.33 7.33 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.24 7.24 7.23 7.23 7.22 6.47 6.43 6.39 6.37 6.33 4.18 4.16 4.15 4.14 4.12 3.48 3.46 2.38 2.36 2.34 1.90 1.89 1.88 1.88 1.87 1.87 1.85 1.85 1.72 1.68 1.67 1.65 1.30 1.28 1.28 1.26 1.26

COOEt
Ph

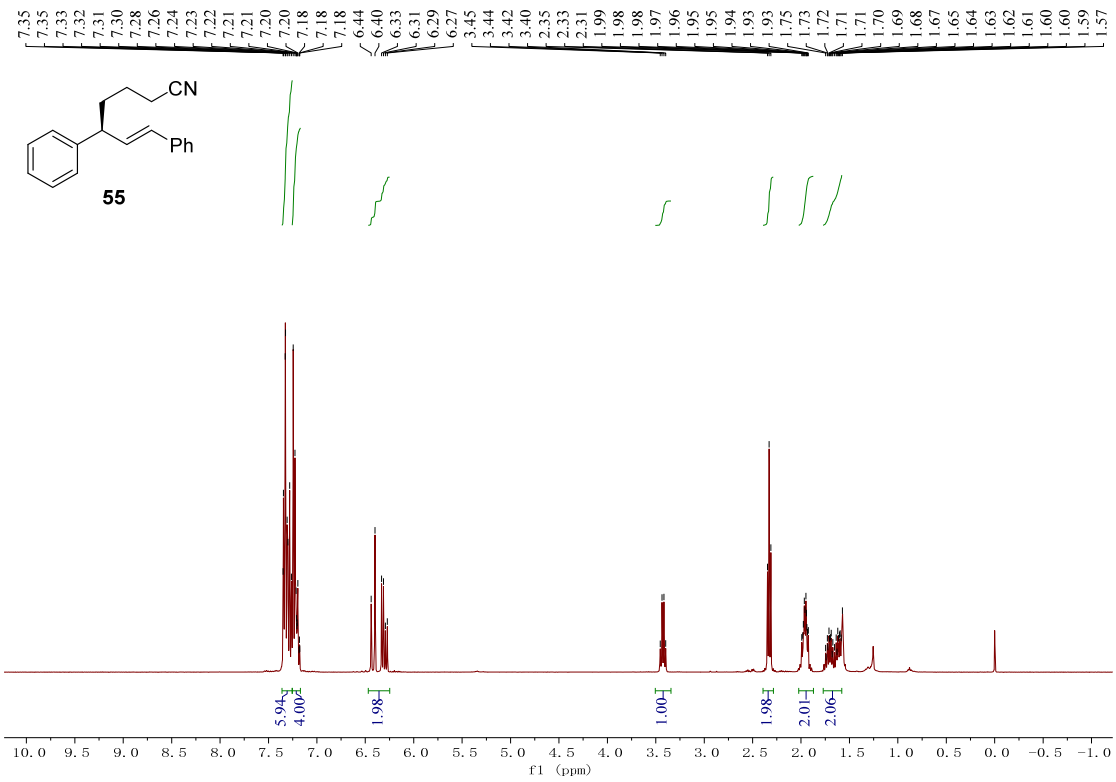
54

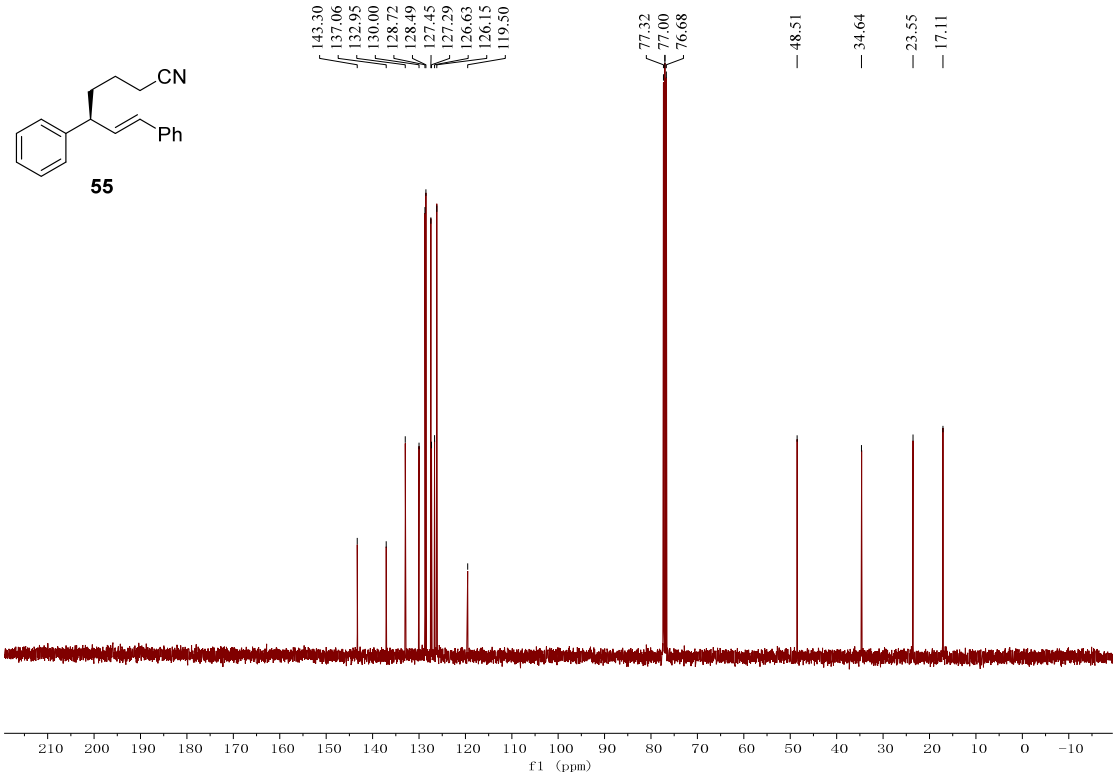

10.68
0.99
1.01
2.21
1.00
2.29
2.08
2.58
3.62
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

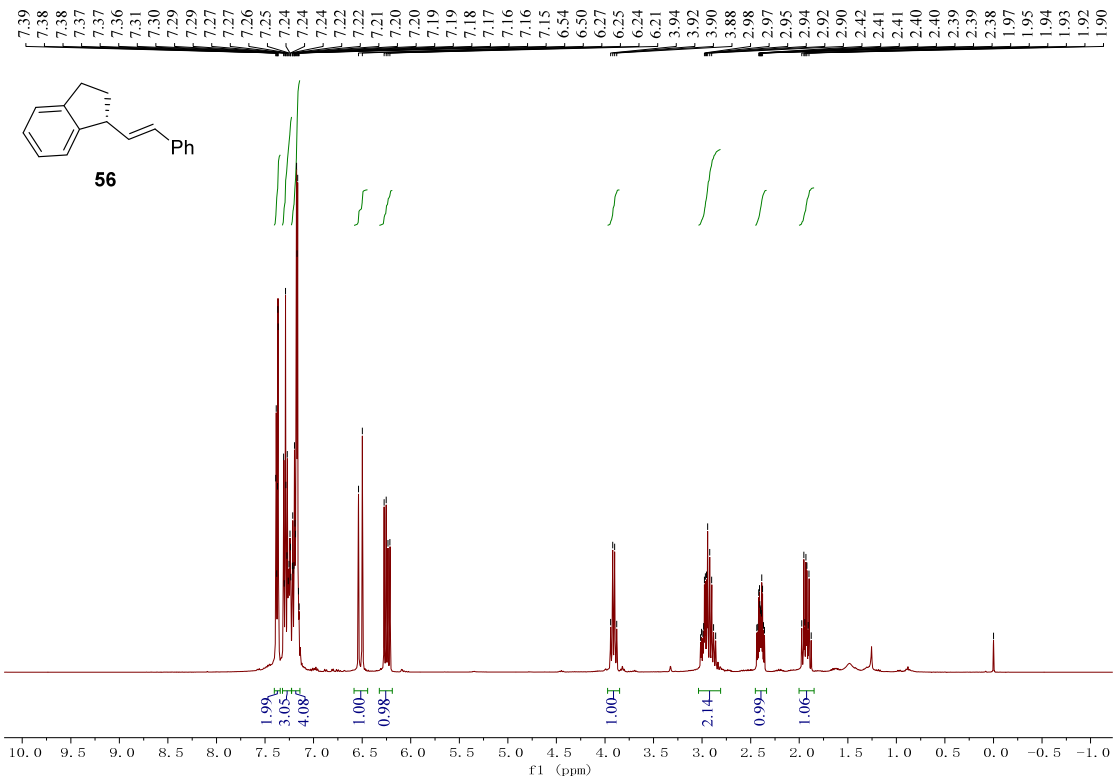

173.52
144.10
137.40
133.78
129.60
128.56
128.44
127.57
127.09
126.33
126.14
77.32
77.00
76.68
60.25
48.93
35.22
34.20
23.08
14.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

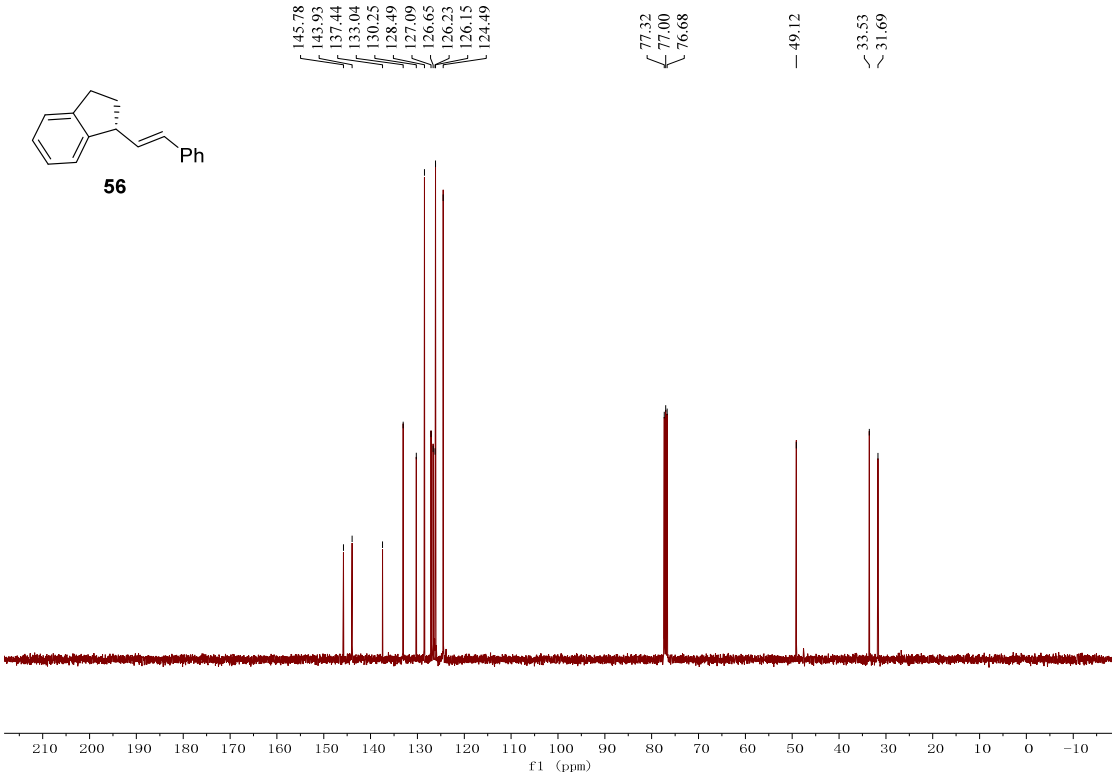
COOEt
Ph

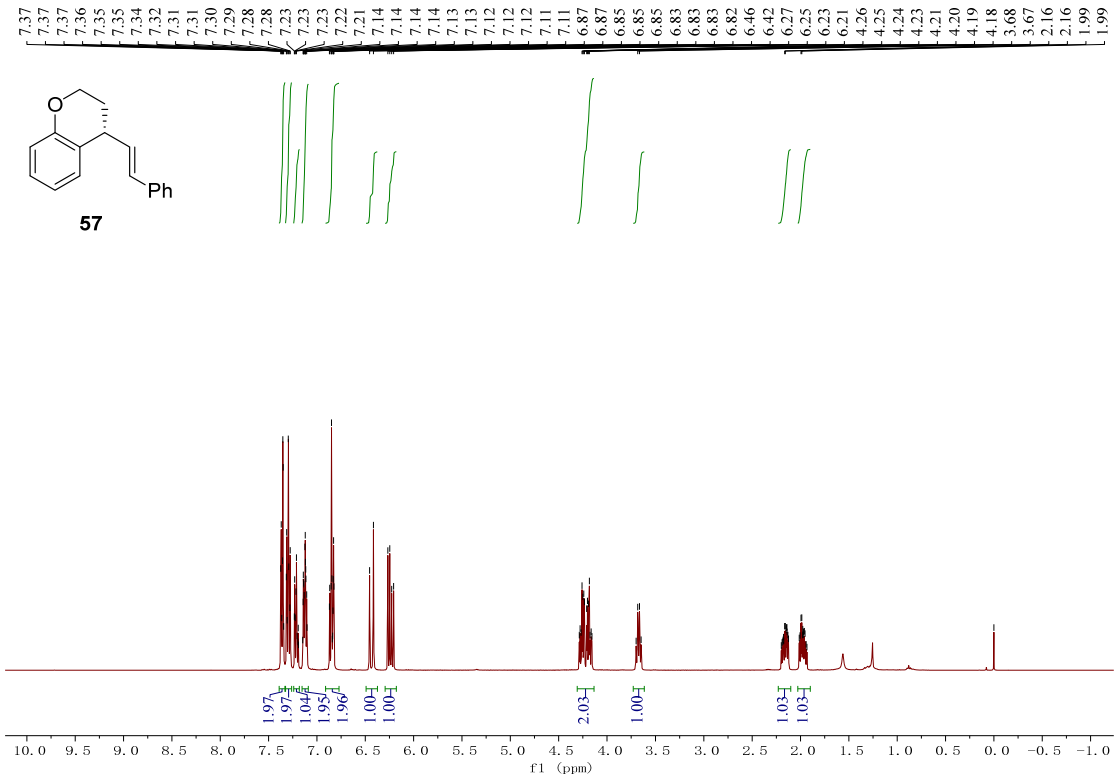
54

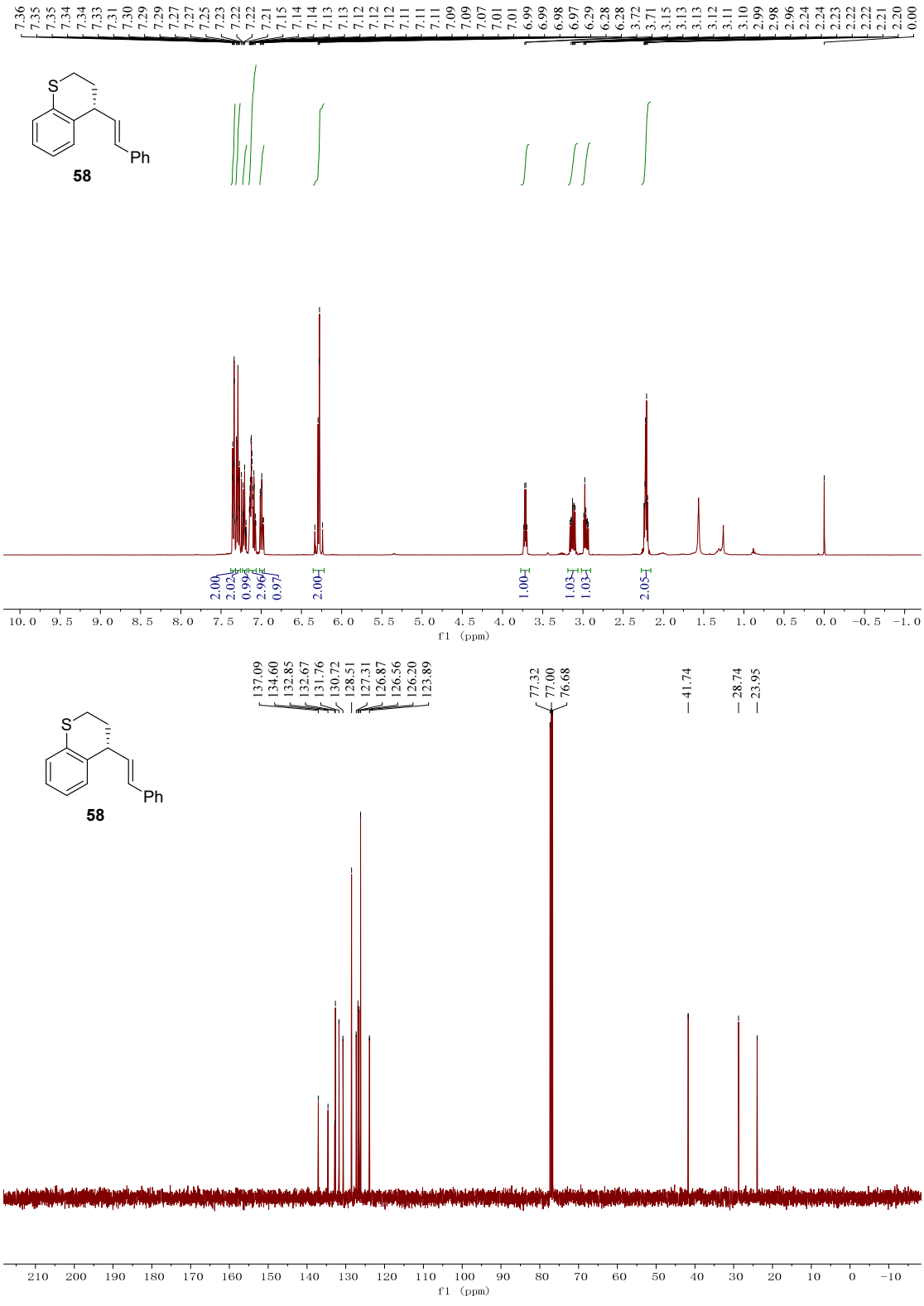

7.35 7.35 7.33 7.32 7.31 7.30 7.28 7.26 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.18 7.18 7.18 6.44 6.40 6.33 6.31 6.29 6.27 3.45 3.44 3.42 3.40 2.35 2.33 2.31 1.99 1.98 1.98 1.97 1.96 1.95 1.95 1.94 1.93 1.93 1.75 1.73 1.72 1.71 1.71 1.70 1.69 1.68 1.67 1.65 1.64 1.63 1.62 1.61 1.60 1.60 1.59 1.57
CN
Ph
55
5.94
4.00
1.98
1.00
1.98
2.01
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

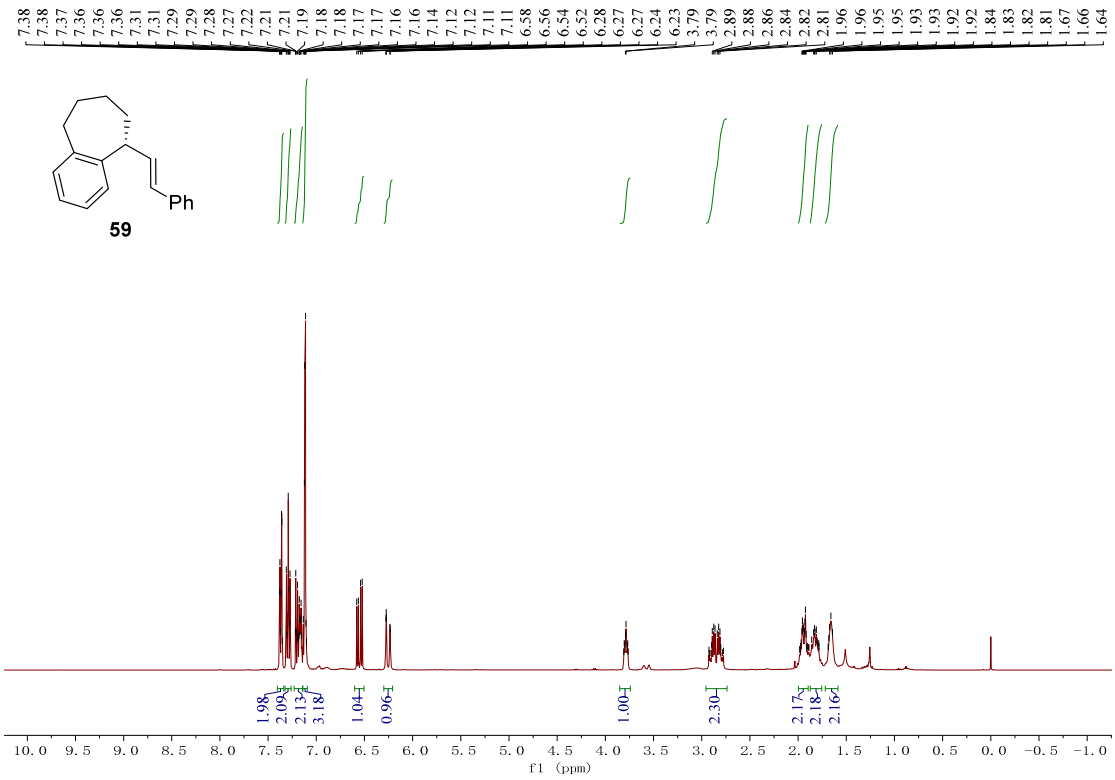

143.30 137.06 132.95 130.00 128.72 128.49 127.45 127.29 126.63 126.15 119.50
77.32 77.00 76.68
48.51
34.64
23.55
17.11
CN
Ph
55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

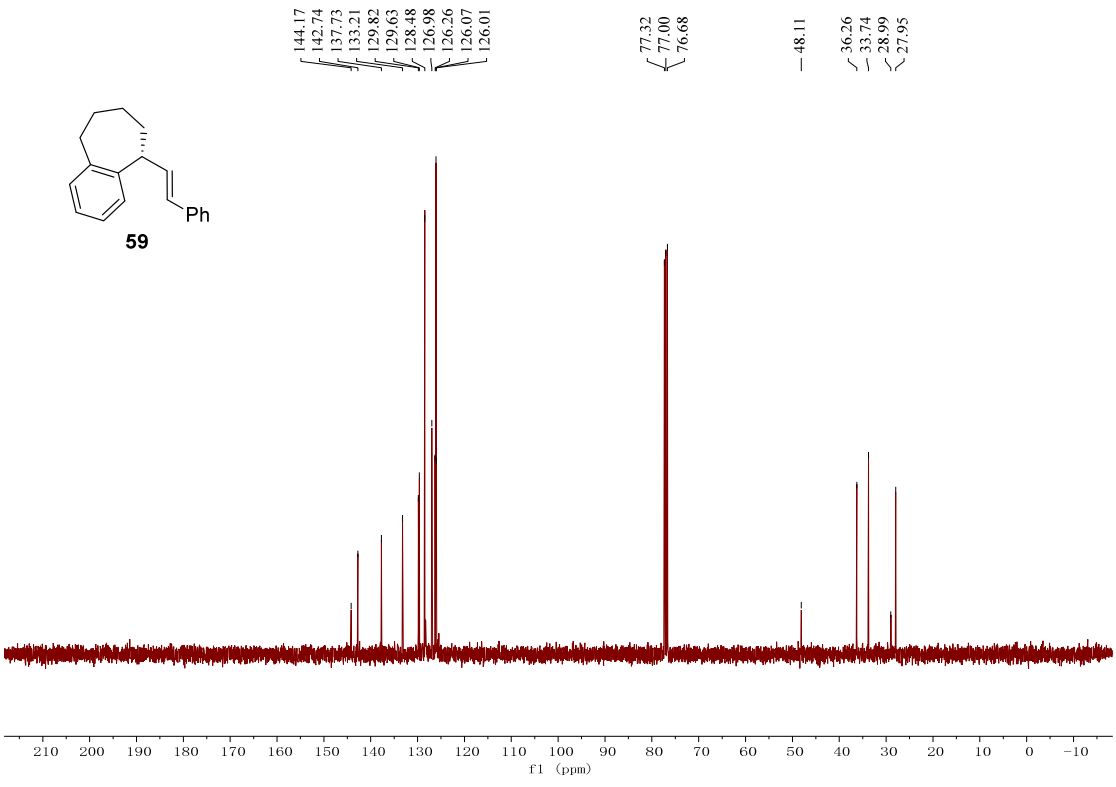

7.39 7.38 7.38 7.37 7.37 7.36 7.31 7.30 7.29 7.29 7.27 7.27 7.26 7.25 7.24 7.24 7.24 7.22 7.22 7.21 7.20 7.20 7.19 7.19 7.18 7.17 7.16 7.16 7.15 6.54 6.50 6.27 6.25 6.24 6.21 3.94 3.92 3.90 3.88 2.98 2.97 2.95 2.94 2.92 2.90 2.42 2.41 2.41 2.40 2.40 2.39 2.39 2.38 1.97 1.95 1.94 1.93 1.92 1.90
Ph
56
1.99
3.05
4.08
1.00
0.98
1.00
2.14
0.99
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

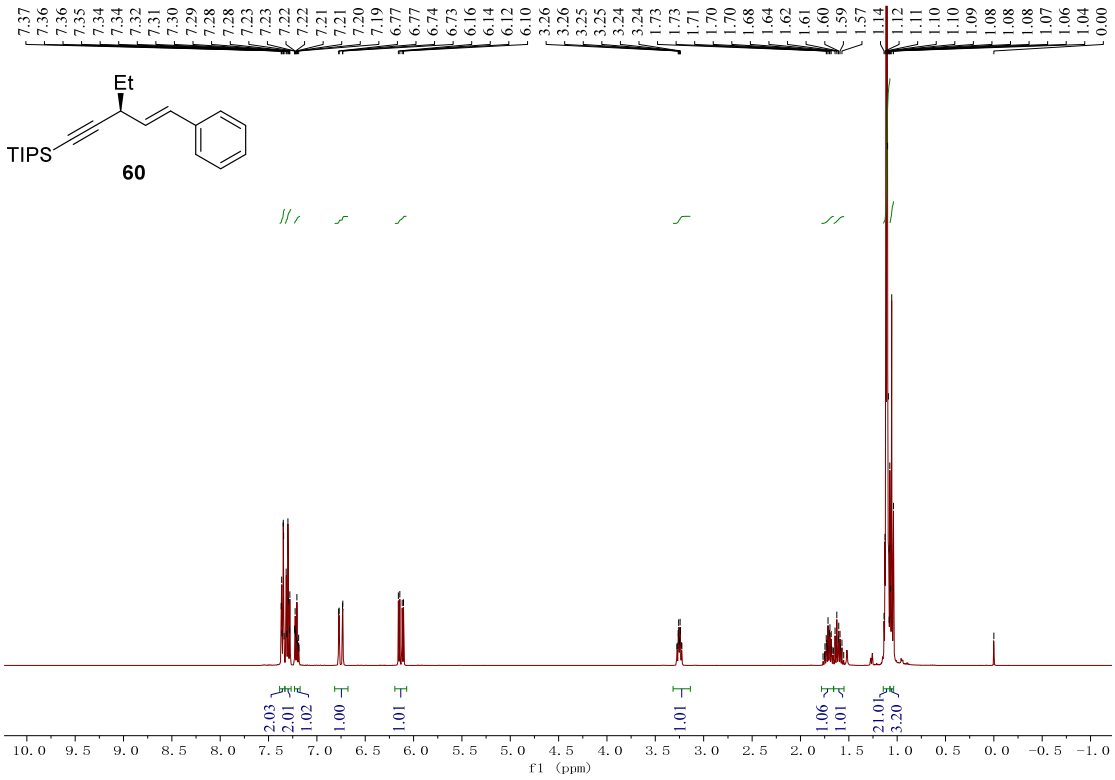

145.78
143.93
137.44
133.04
130.25
128.49
127.09
126.65
126.23
126.15
124.49
77.32
77.00
76.68
49.12
33.53
31.69
Ph
56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

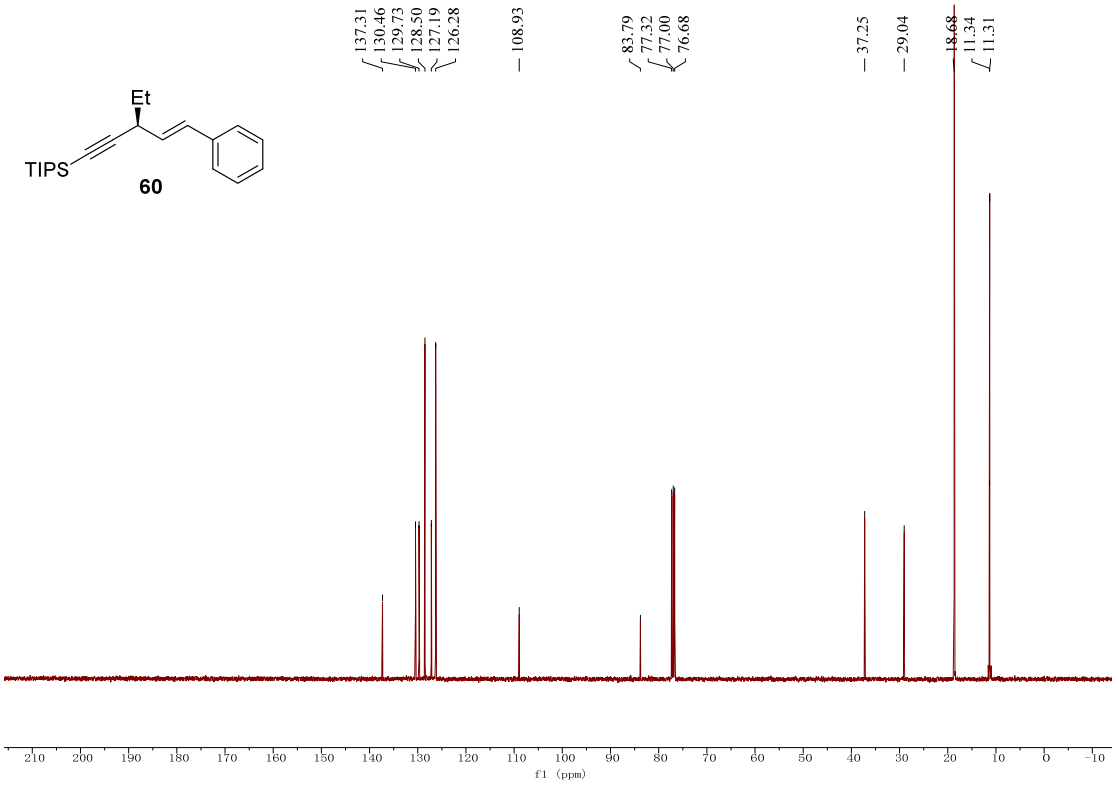

7.37 7.37 7.37 7.36 7.35 7.35 7.34 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.23 7.23 7.23 7.22 7.21 7.14 7.14 7.14 7.14 7.13 7.13 7.12 7.12 7.12 7.11 7.11 6.87 6.87 6.85 6.85 6.85 6.83 6.83 6.83 6.82 6.46 6.42 6.27 6.25 6.23 6.21 4.26 4.25 4.24 4.23 4.21 4.20 4.19 4.18 3.68 3.67 2.16 2.16 1.99 1.99
O
Ph
57
1.97 1.97 1.04 1.95 1.96 1.00 1.00 2.03 1.00 1.03 1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)
154.53 137.04 133.11 131.61 130.15 128.53 127.90 127.34 126.18 123.73 120.22 116.82 77.32 77.00 76.68 64.04 38.51 29.00
O
Ph
57
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

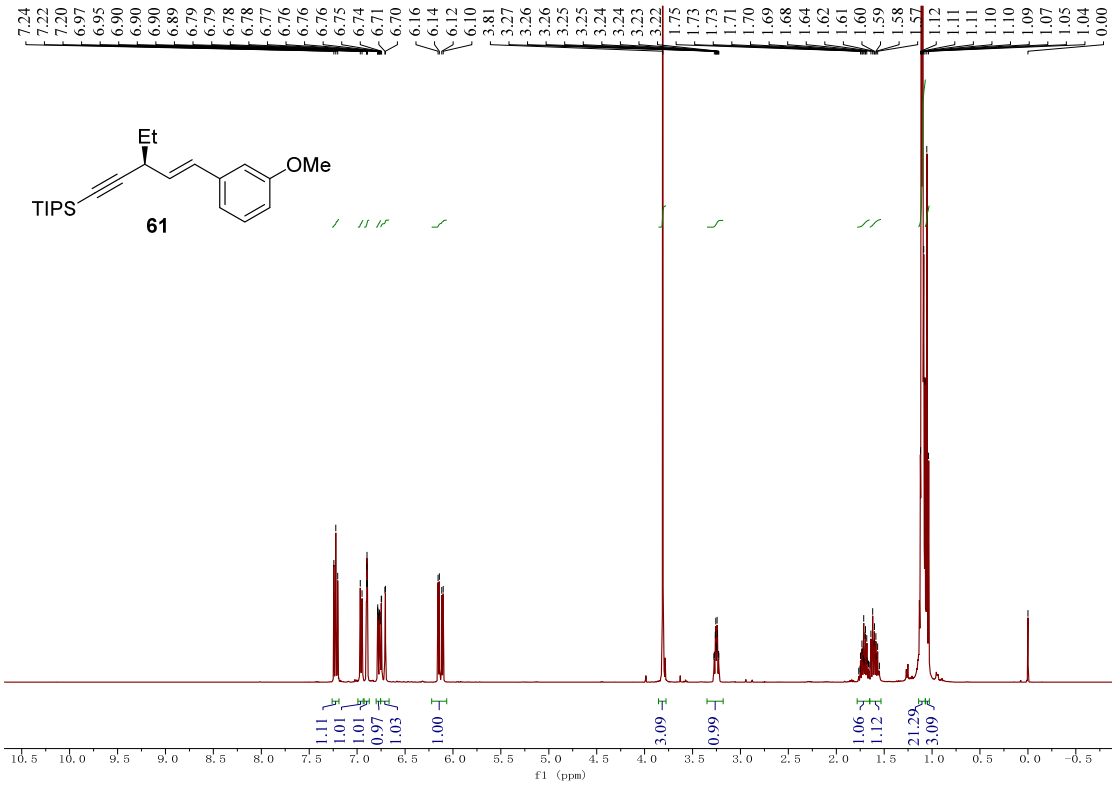

7.36 7.35 7.35 7.34 7.34 7.33 7.31 7.30 7.29 7.29 7.27 7.27 7.25 7.23 7.22 7.22 7.21 7.15 7.14 7.14 7.13 7.13 7.12 7.12 7.11 7.11 7.11 7.09 7.09 7.07 7.01 7.01 6.99 6.99 6.98 6.97 6.29 6.28 6.28 3.72 3.71 3.15 3.13 3.13 3.12 3.11 3.10 2.99 2.98 2.96 2.24 2.24 2.23 2.22 2.22 2.21 2.20 0.00
S
Ph
58
2.00 2.02 0.99 2.96 0.97 2.00 1.00 1.03 1.03 2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)
137.09 134.60 132.85 132.67 131.76 130.72 128.51 127.31 126.87 126.56 126.20 123.89
77.32 77.00 76.68
41.74
28.74 23.95
S
Ph
58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

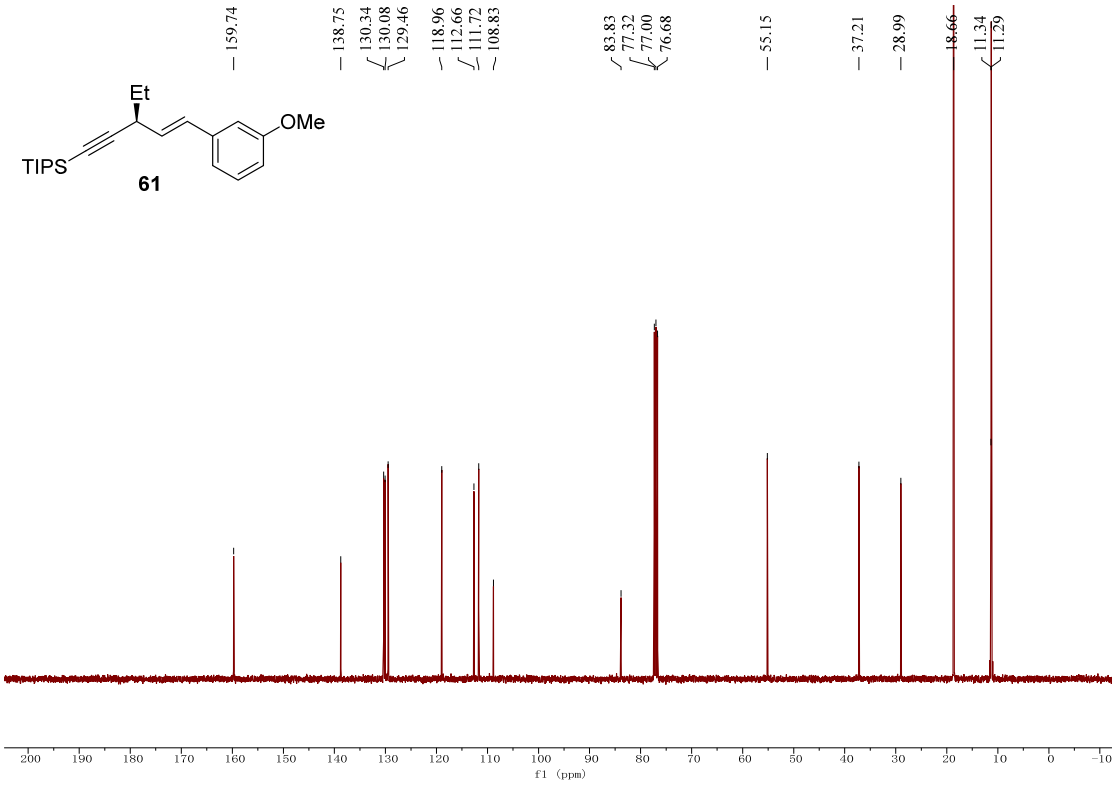

7.38 7.38 7.37 7.36 7.36 7.36 7.31 7.31 7.29 7.29 7.28 7.27 7.22 7.21 7.21 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.14 7.12 7.12 7.11 7.11 6.58 6.56 6.54 6.52 6.28 6.27 6.27 6.24 6.23 3.79 3.79 2.89 2.88 2.86 2.84 2.82 2.81 1.96 1.96 1.95 1.95 1.93 1.92 1.92 1.84 1.83 1.82 1.81 1.67 1.66 1.64
Ph
59
1.98 2.09 2.13 3.18 1.04 0.96 1.00 2.30 2.17 2.18 2.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

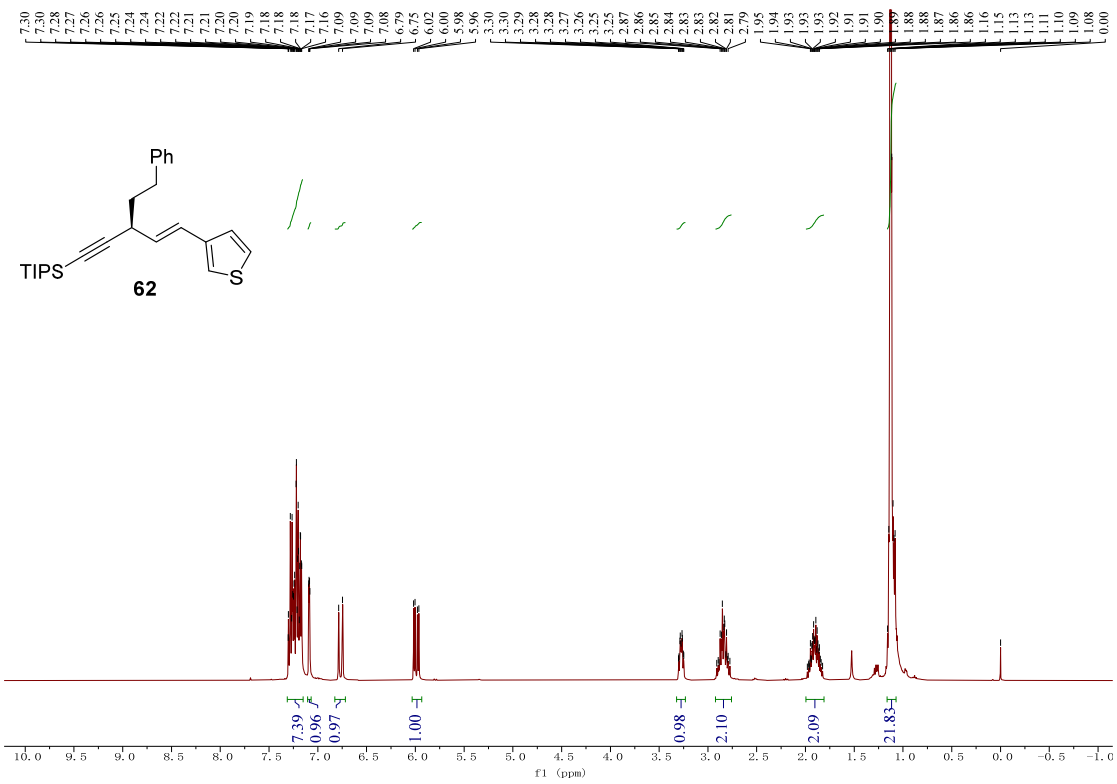

144.17 142.74 137.73 133.21 129.82 129.63 128.48 126.98 126.26 126.07 126.01
77.32 77.00 76.68
48.11
36.26 33.74 28.99 27.95
Ph
59
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

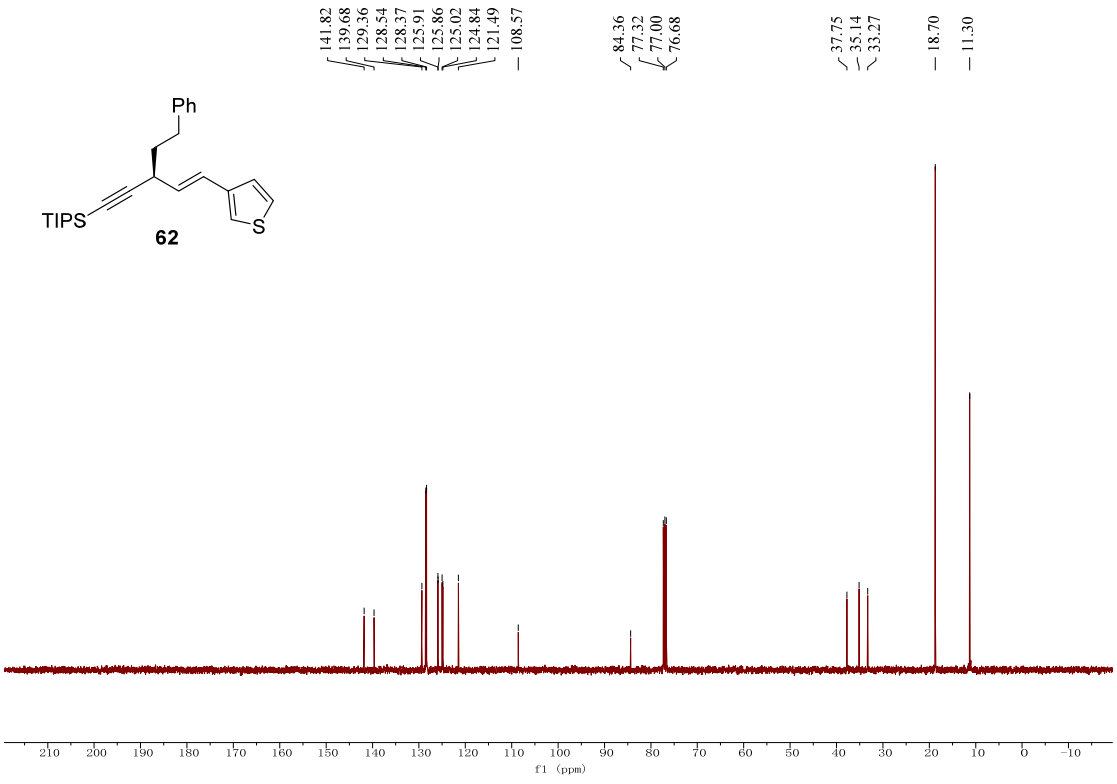

Et
TIPS
60
f1 (ppm)

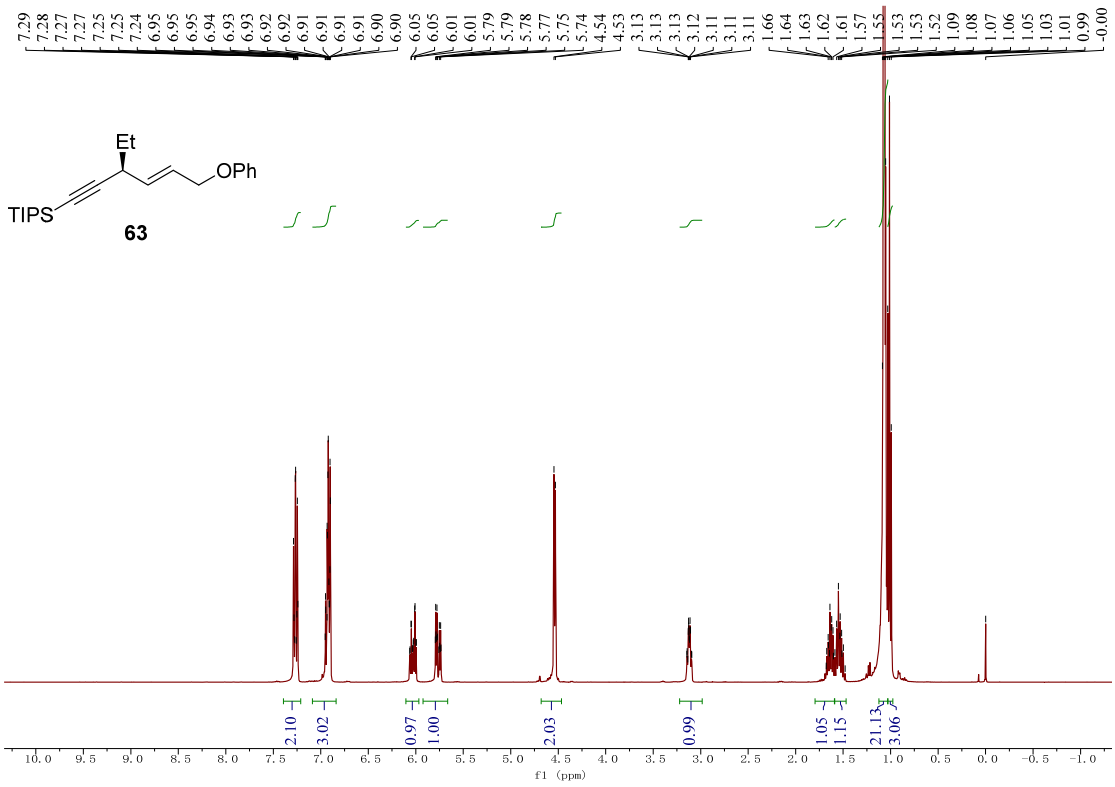

Et
TIPS
60
f1 (ppm)

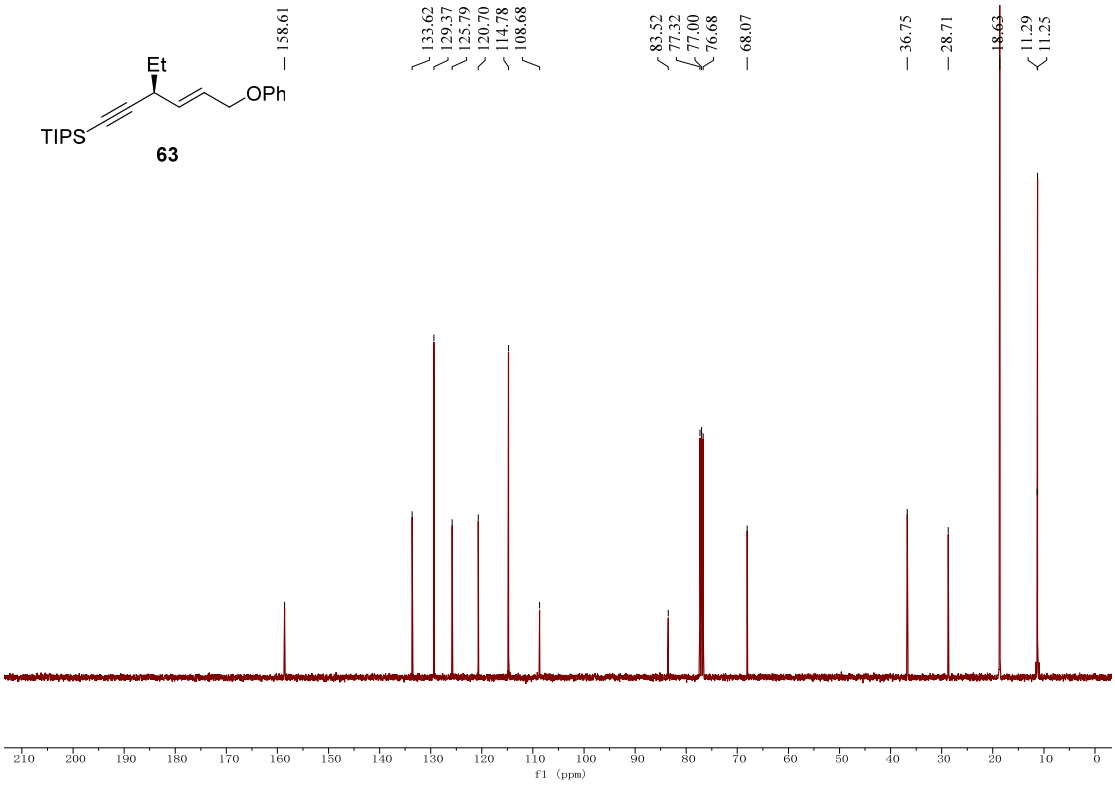

Et
OMe
TIPS
61
f1 (ppm)

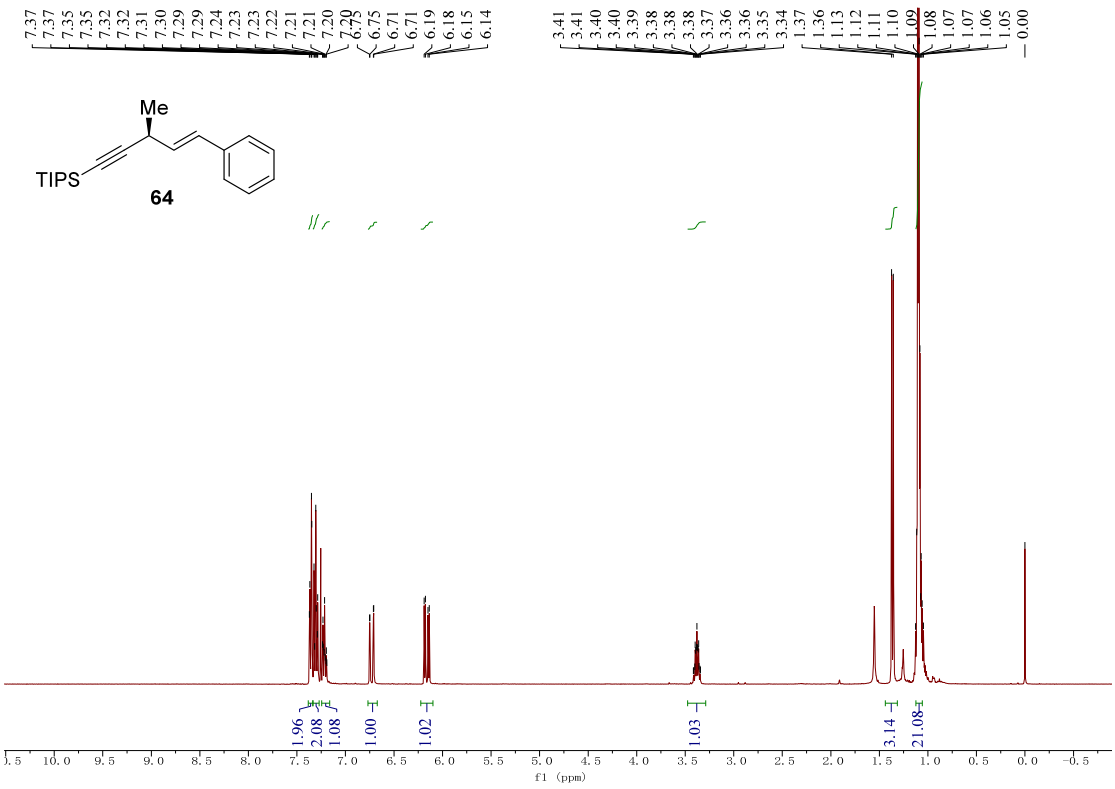

Et
OMe
TIPS
61
f1 (ppm)

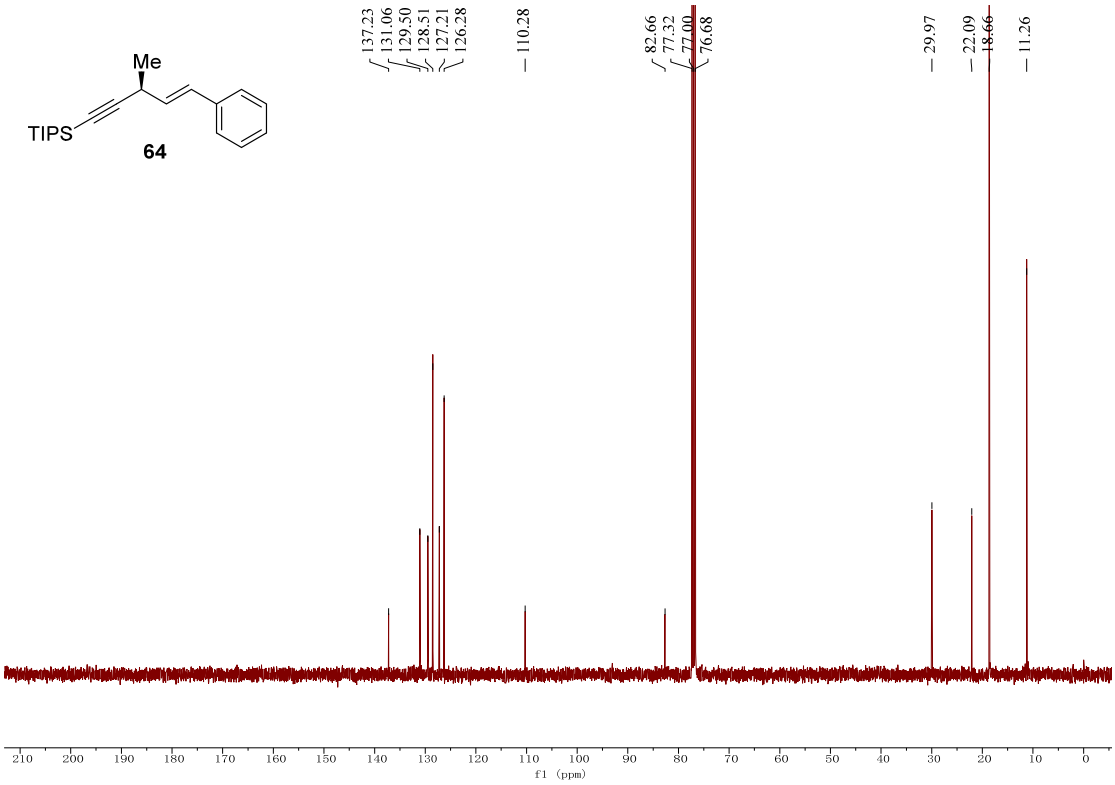

Ph
TIPS
S
62
f1 (ppm)

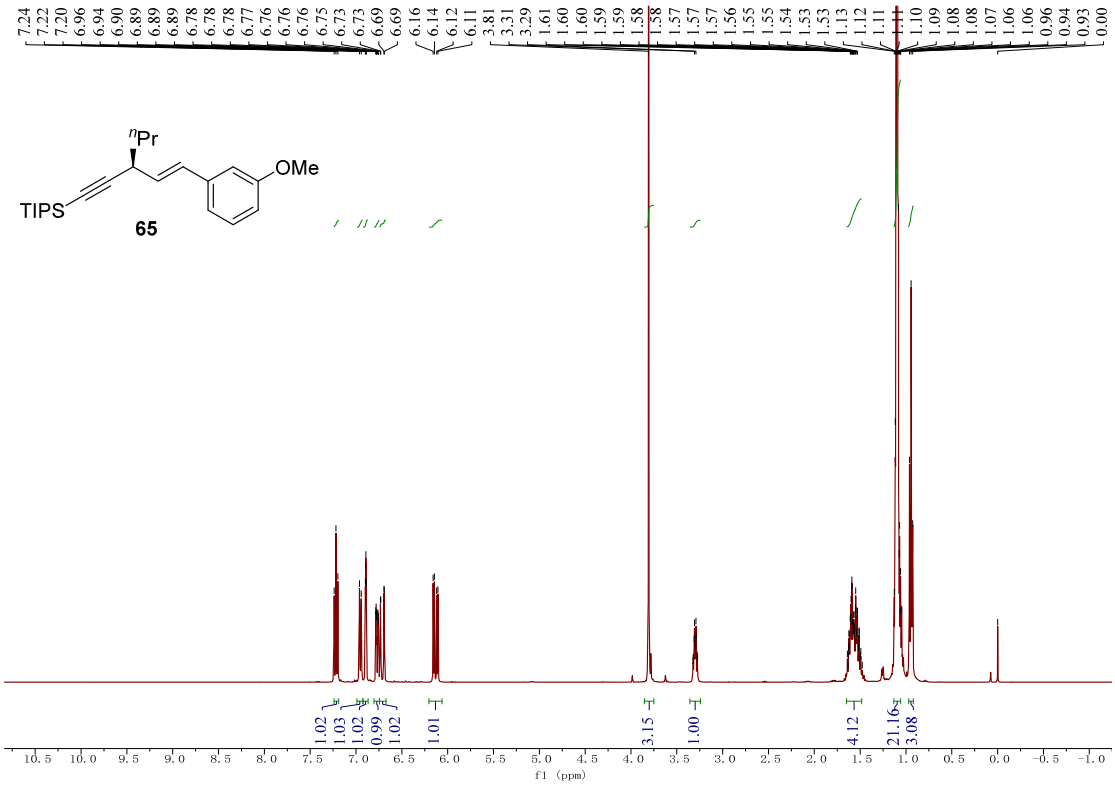

Ph
TIPS
S
62
f1 (ppm)

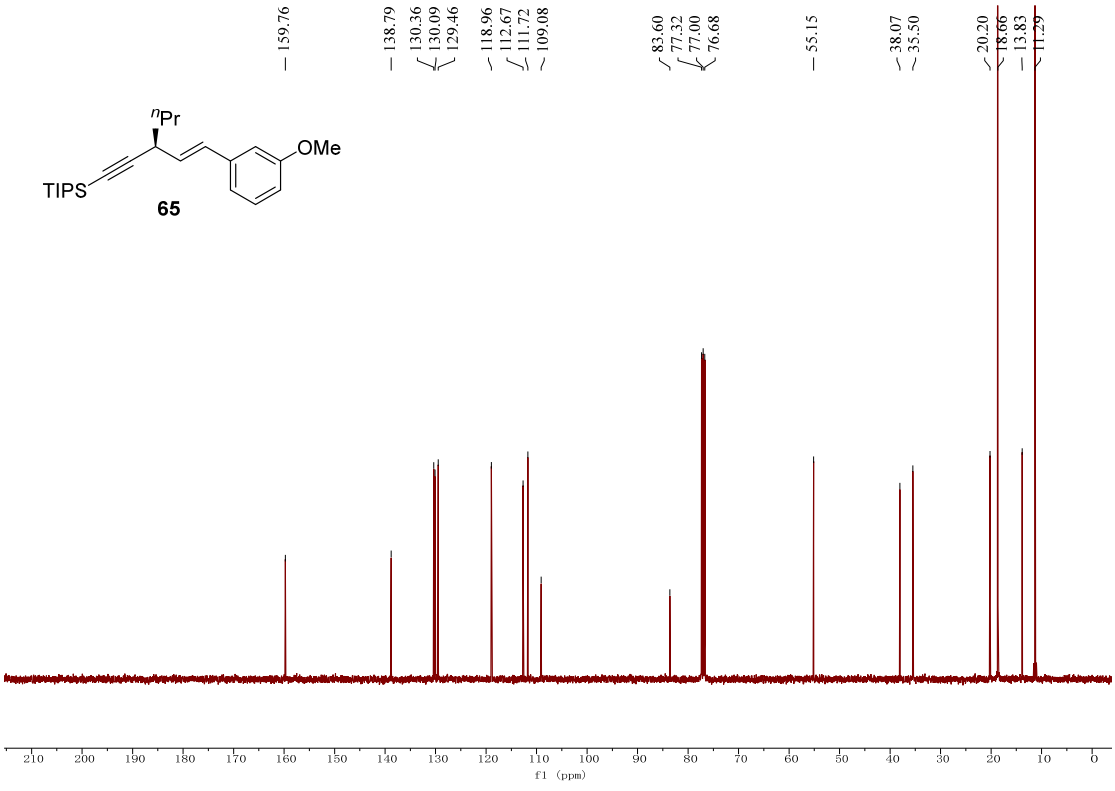

Et
OPh
TIPS
63
f1 (ppm)

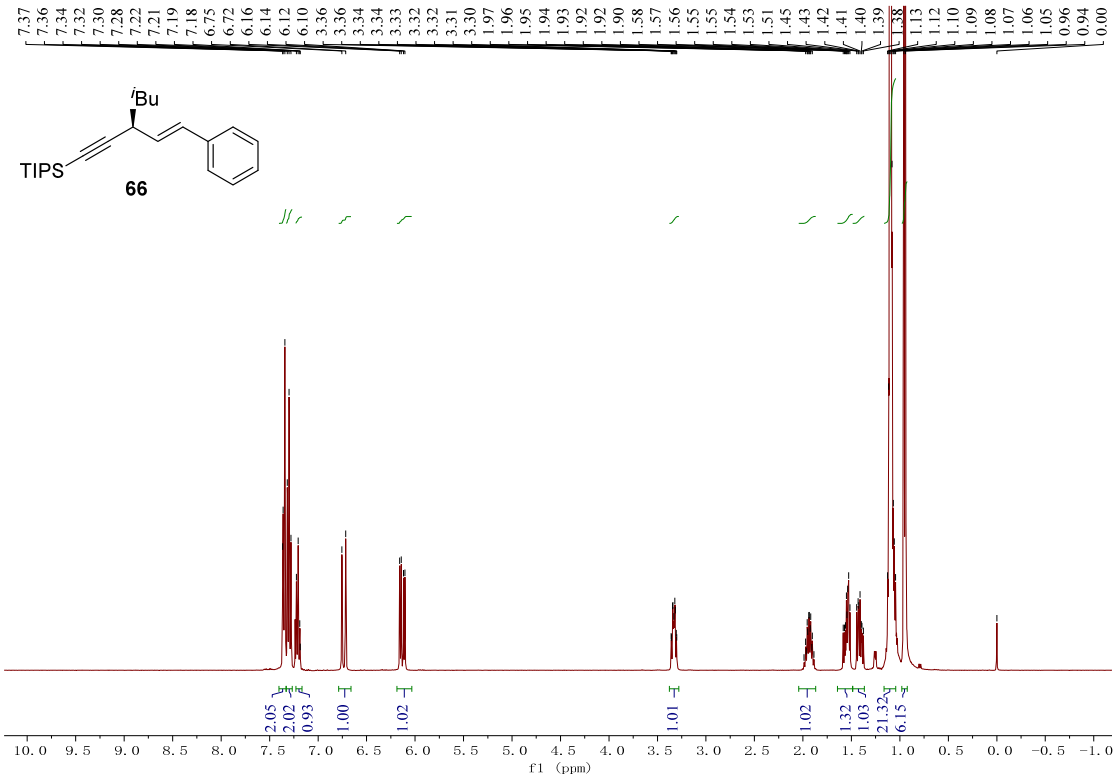

Et
OPh
TIPS
63
f1 (ppm)

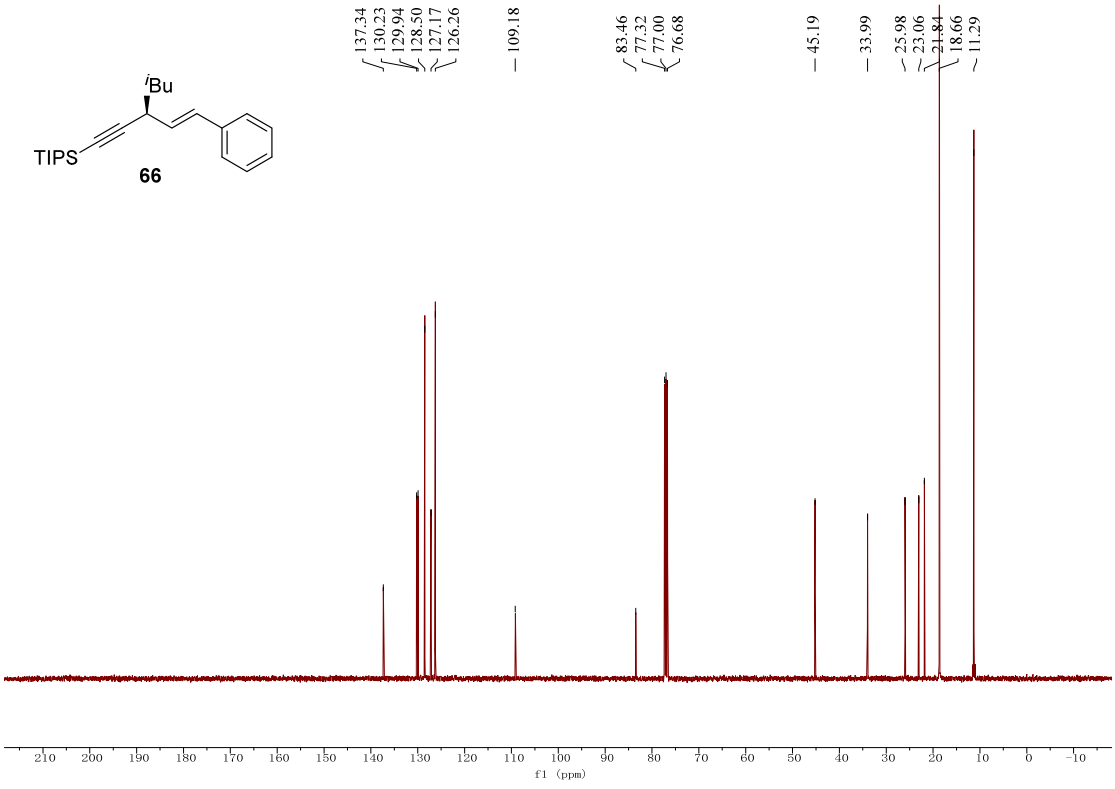

Me
TIPS
64
f1 (ppm)

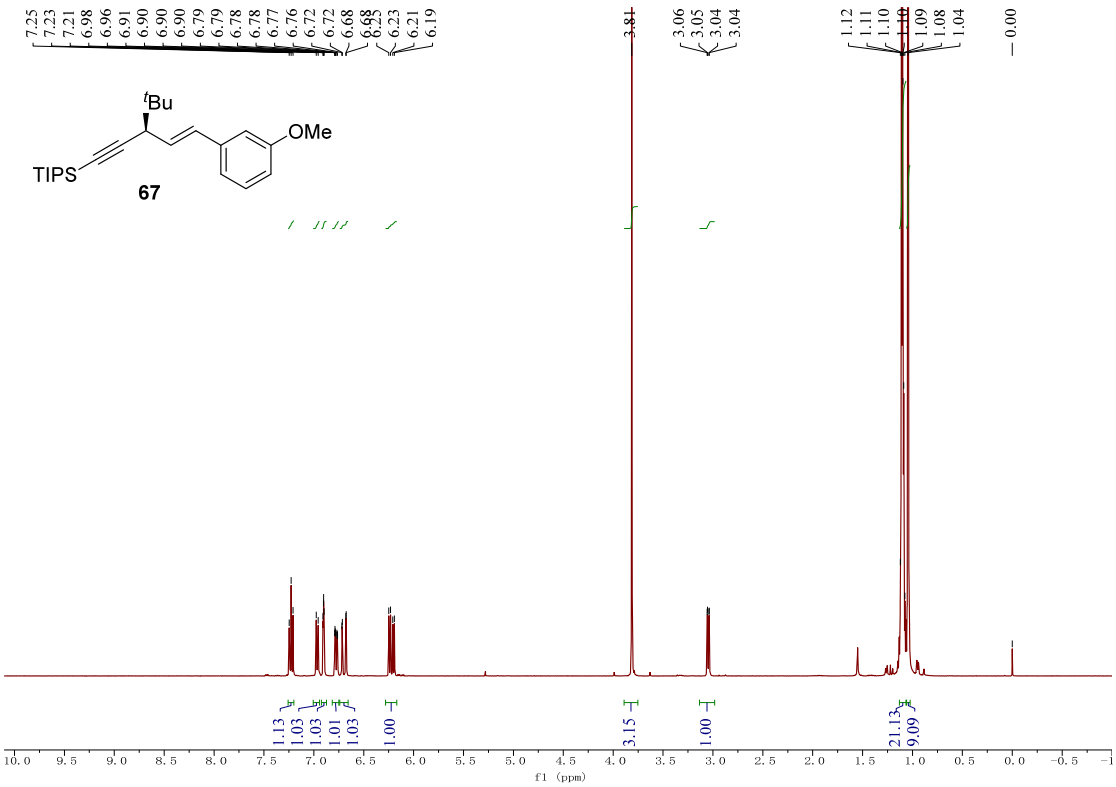

Me
TIPS
64
f1 (ppm)


7.24 7.22 7.20 6.96 6.94 6.90 6.89 6.89 6.89 6.78 6.78 6.78 6.77 6.76 6.76 6.76 6.75 6.73 6.69 6.69 6.16 6.14 6.12 6.11 3.81 3.31 3.29 1.61 1.60 1.60 1.59 1.59 1.58 1.58 1.57 1.57 1.57 1.56 1.55 1.55 1.54 1.53 1.53 1.13 1.12 1.11 1.11 1.10 1.09 1.08 1.08 1.07 1.06 1.06 0.96 0.94 0.93 0.00
nPr
OMe
TIPS
65
1.02 1.03 1.02 0.99 1.02 1.01 3.15 1.00 4.12 21.16 3.08
f1 (ppm)


159.76 138.79 130.36 130.09 129.46 118.96 112.67 111.72 109.08 83.60 77.32 77.00 76.68 55.15 38.07 35.50 20.20 18.66 13.83 11.29
nPr
OMe
TIPS
65
f1 (ppm)


7.37 7.36 7.34 7.32 7.30 7.28 7.22 7.21 7.19 7.18 6.75 6.72 6.16 6.14 6.12 6.10 3.36 3.36 3.34 3.34 3.33 3.32 3.32 3.31 3.30 1.97 1.96 1.95 1.94 1.93 1.92 1.92 1.90 1.58 1.57 1.56 1.55 1.55 1.54 1.53 1.51 1.45 1.43 1.42 1.41 1.40 1.39 1.38 1.13 1.12 1.10 1.09 1.08 1.07 1.06 1.05 0.96 0.94 0.00
iBu
TIPS
66
2.05 2.02 0.93 1.00 1.02 1.01 1.02 1.32 1.03 21.32 6.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


137.34 130.23 129.94 128.50 127.17 126.26 109.18 83.46 77.32 77.00 76.68 45.19 33.99 25.98 23.06 21.84 18.66 11.29
iBu
TIPS
66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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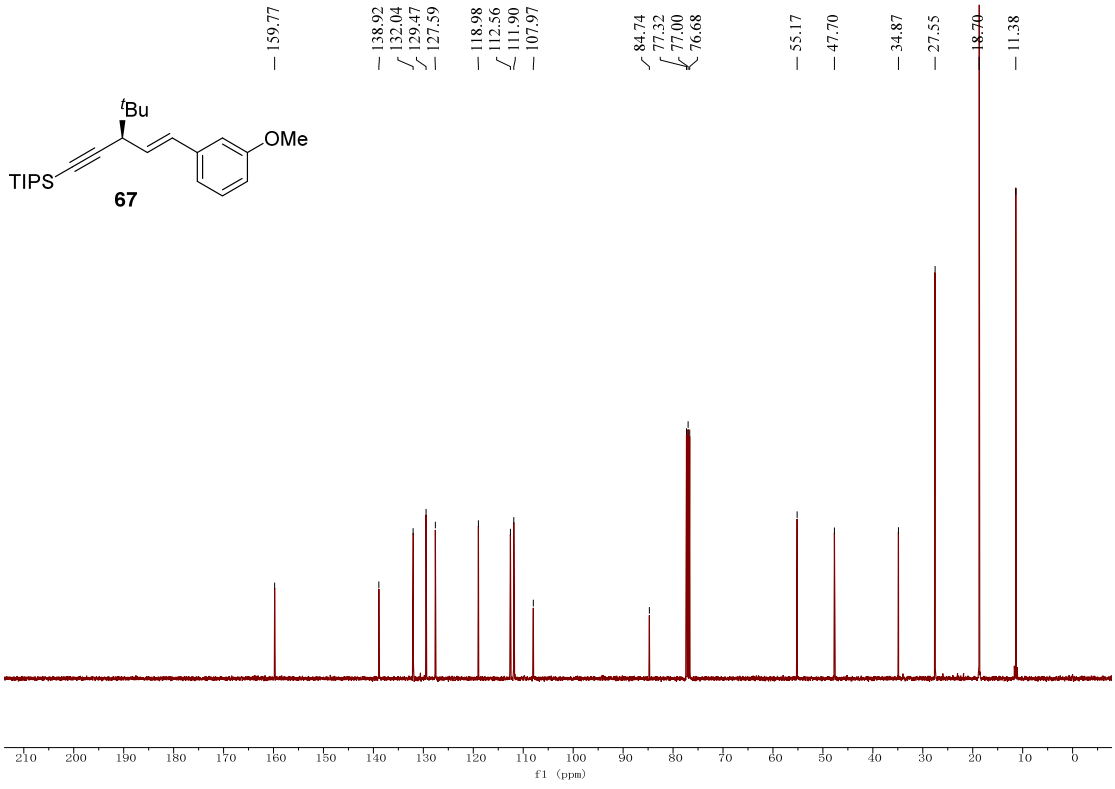
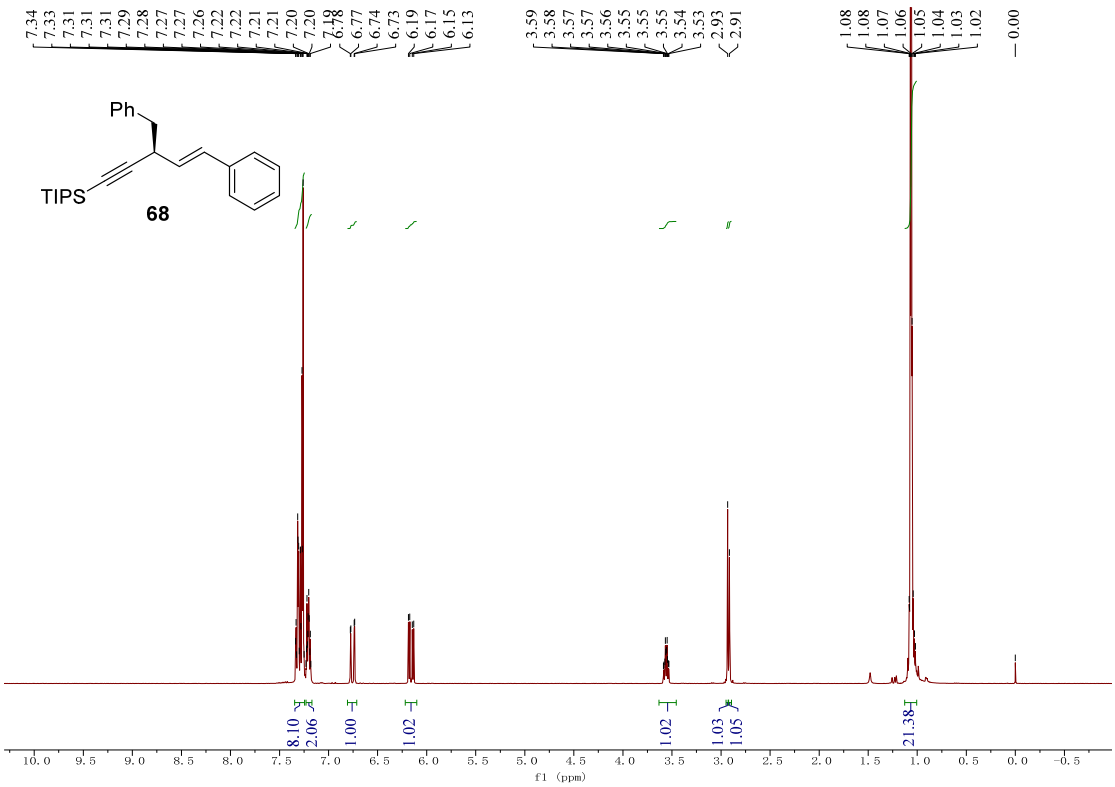
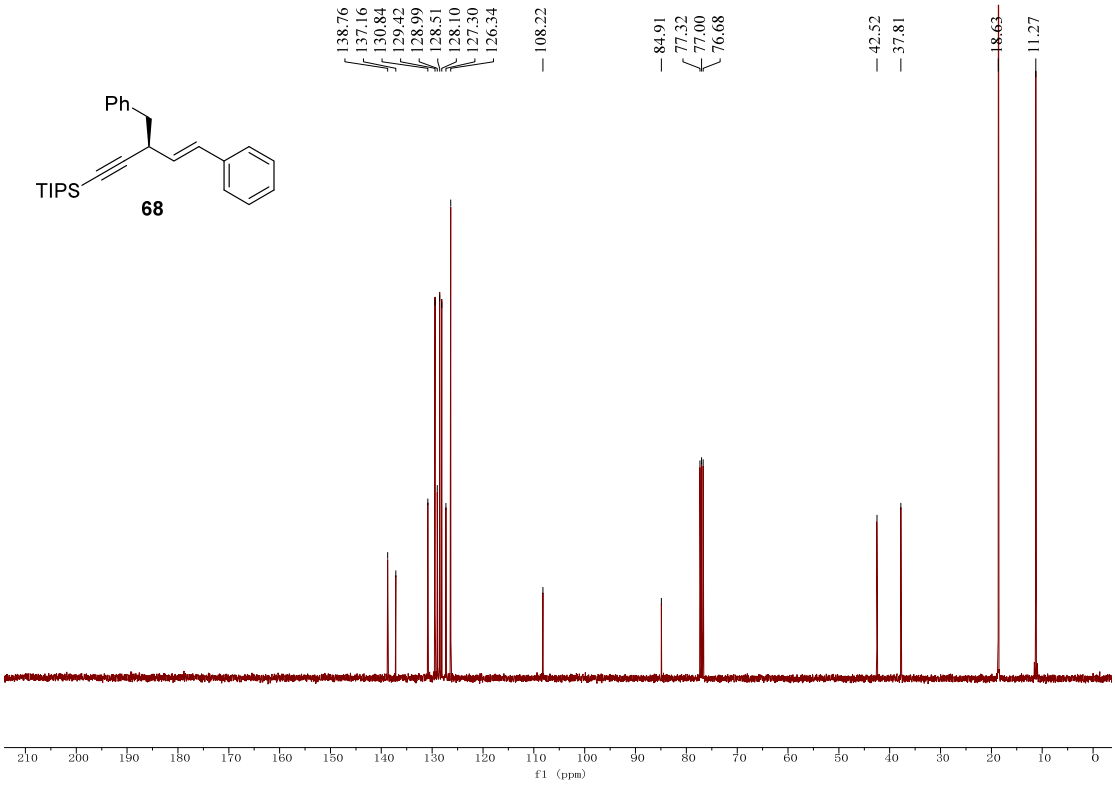
7.23
7.21
6.98
6.96
6.91
6.90
6.90
6.90
6.79
6.79
6.78
6.78
6.77
6.76
6.72
6.72
6.68
6.68
6.23
6.21
6.19
3.81
3.06
3.05
3.04
3.04
1.12
1.11
1.10
1.10
1.09
1.08
1.04
0.00
tBu
OMe
TIPS
67
1.13
1.03
1.03
1.01
1.03
1.00
3.15
1.00
21.13
9.09
f1 (ppm)


159.77
138.92
132.04
129.47
127.59
118.98
112.56
111.90
107.97
84.74
77.32
77.00
76.68
55.17
47.70
34.87
27.55
18.70
11.38
tBu
OMe
TIPS
67
f1 (ppm)


7.34
7.33
7.31
7.31
7.31
7.29
7.28
7.27
7.27
7.26
7.22
7.22
7.21
7.21
7.20
7.20
6.78
6.77
6.74
6.73
6.19
6.17
6.15
6.13
3.59
3.58
3.57
3.57
3.56
3.55
3.55
3.55
3.54
3.53
2.93
2.91
1.08
1.08
1.07
1.06
1.05
1.04
1.03
1.02
0.00
Ph
TIPS
68
8.10
2.06
1.00
1.02
1.02
1.03
1.05
21.38
f1 (ppm)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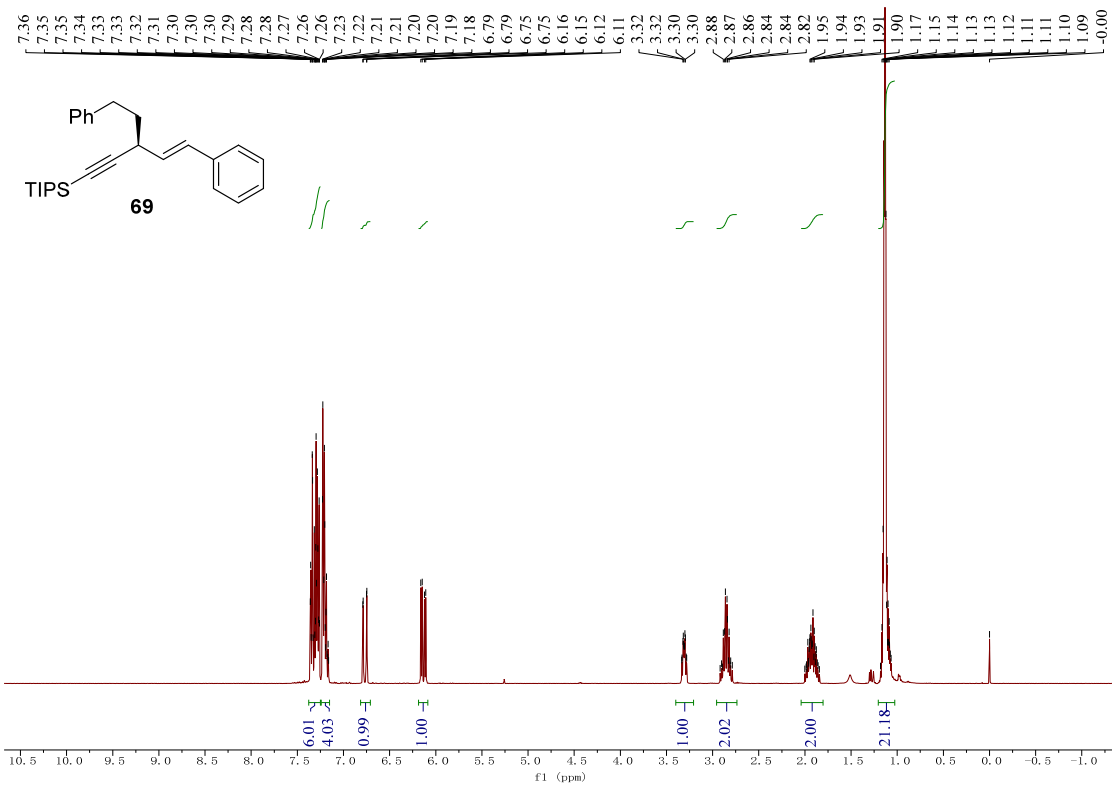
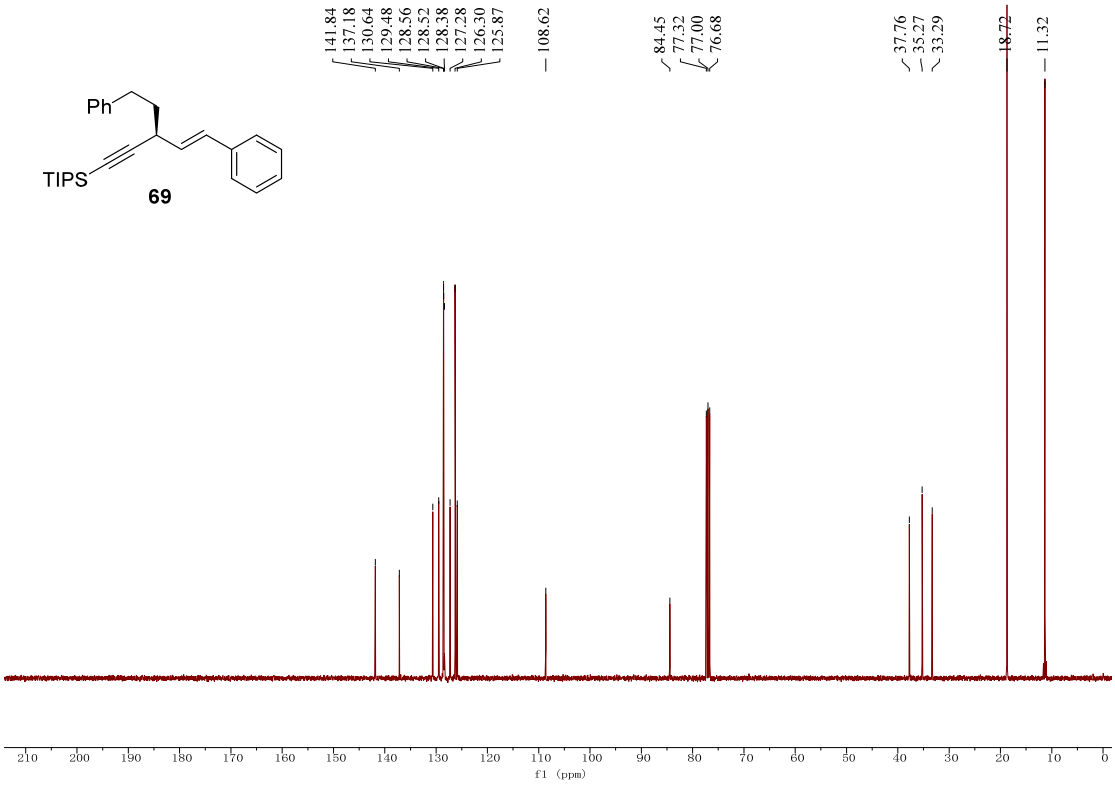
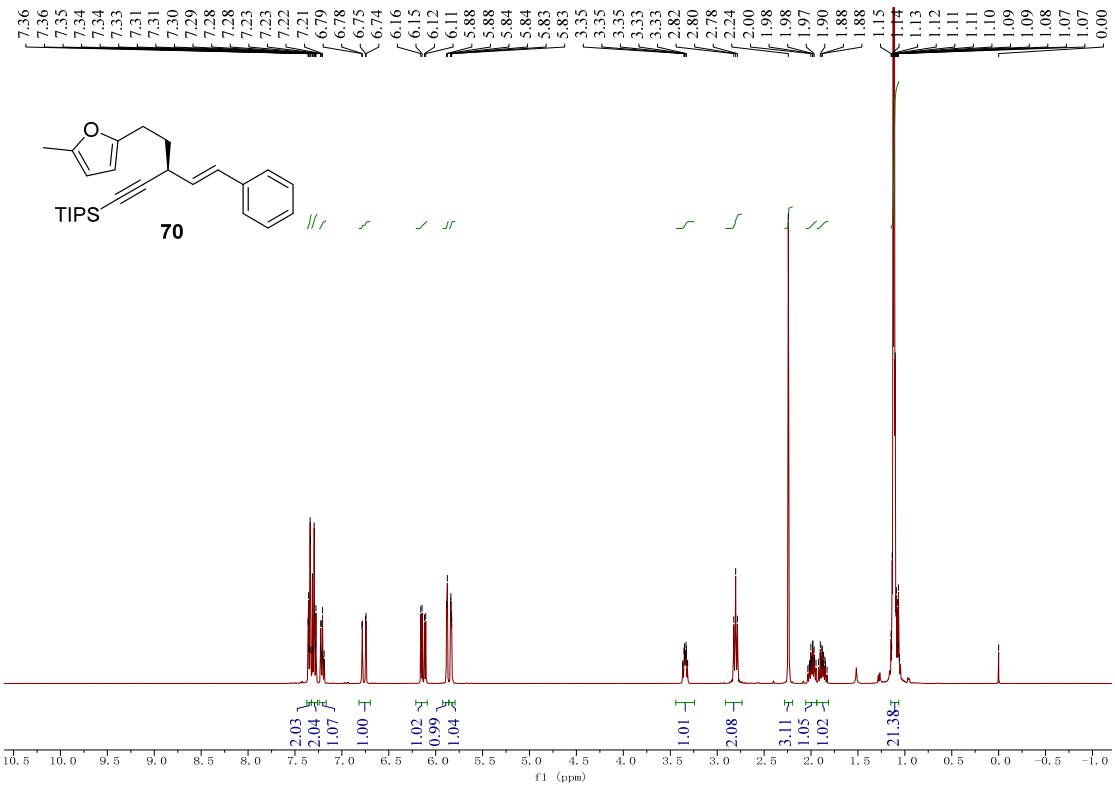
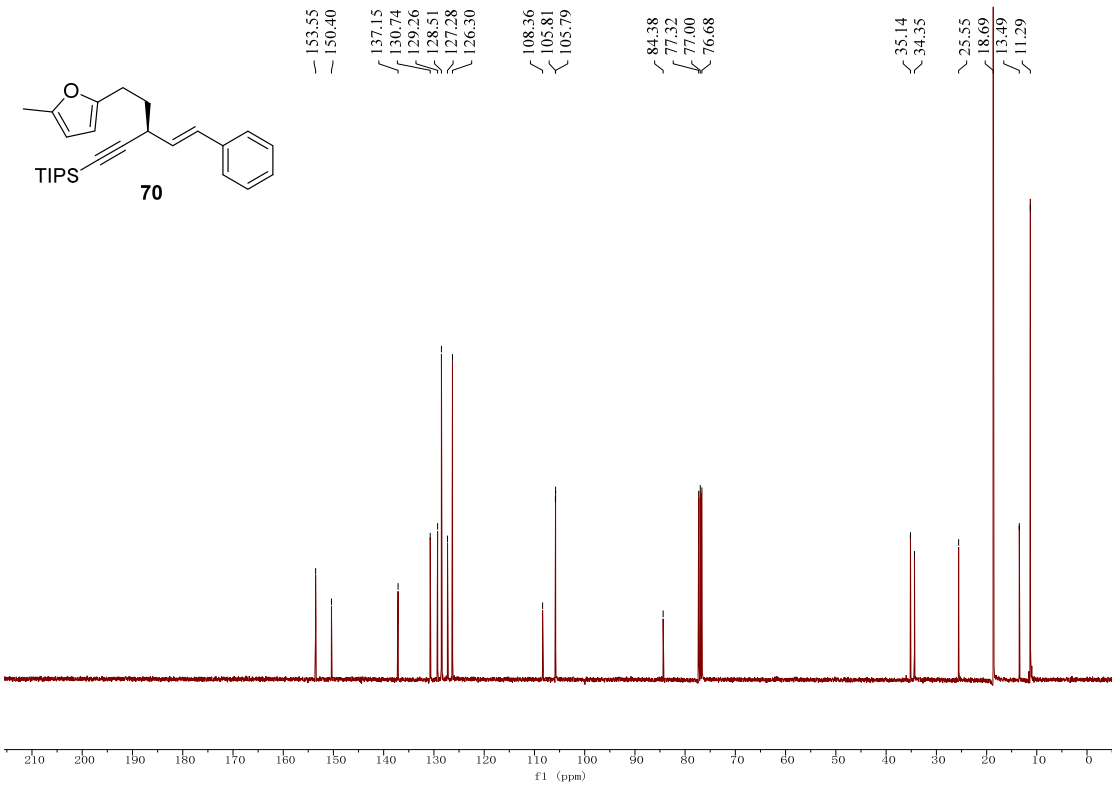
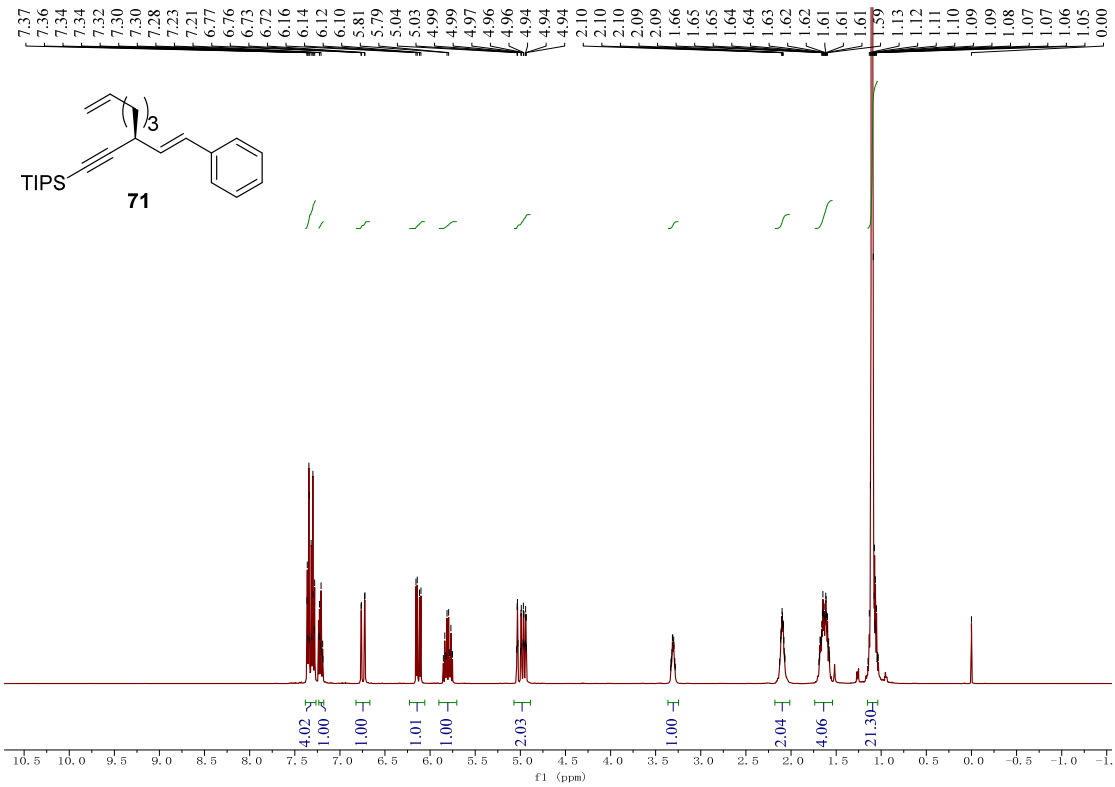
137.16
130.84
129.42
128.99
128.51
128.10
127.30
126.34
108.22
84.91
77.32
77.00
76.68
42.52
37.81
18.63
11.27
Ph
TIPS
68
f1 (ppm)

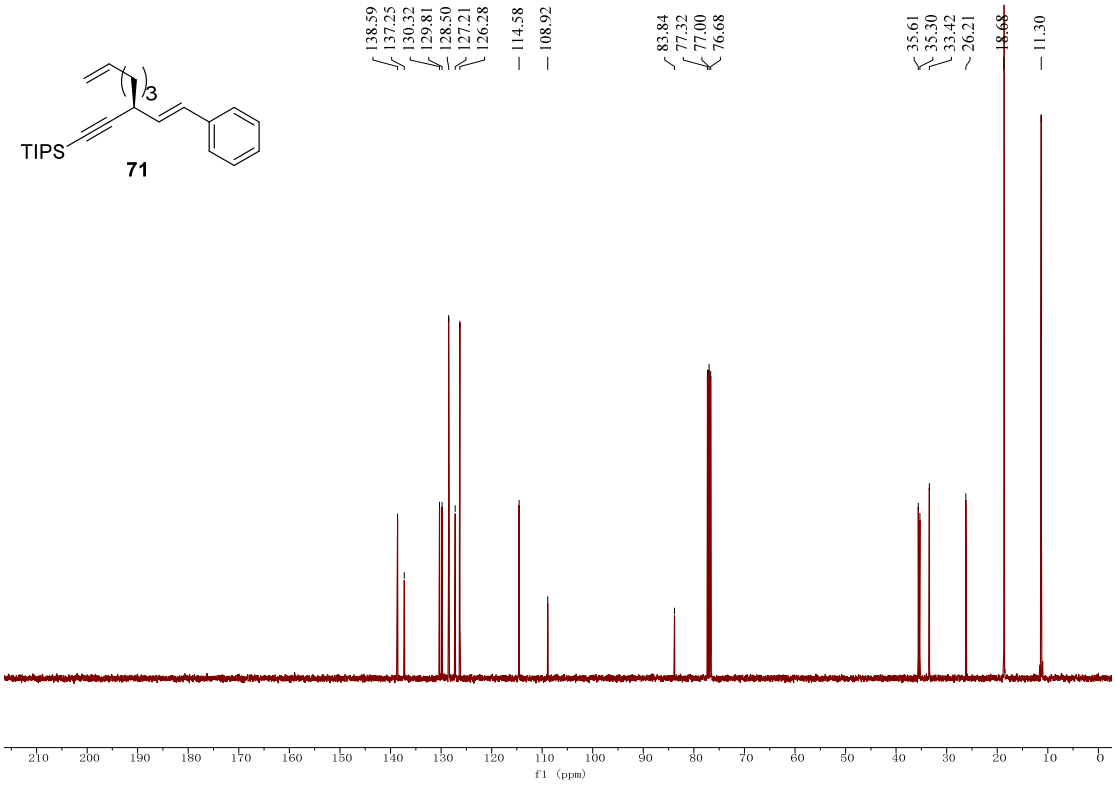

Ph
TIPS
69
f1 (ppm)

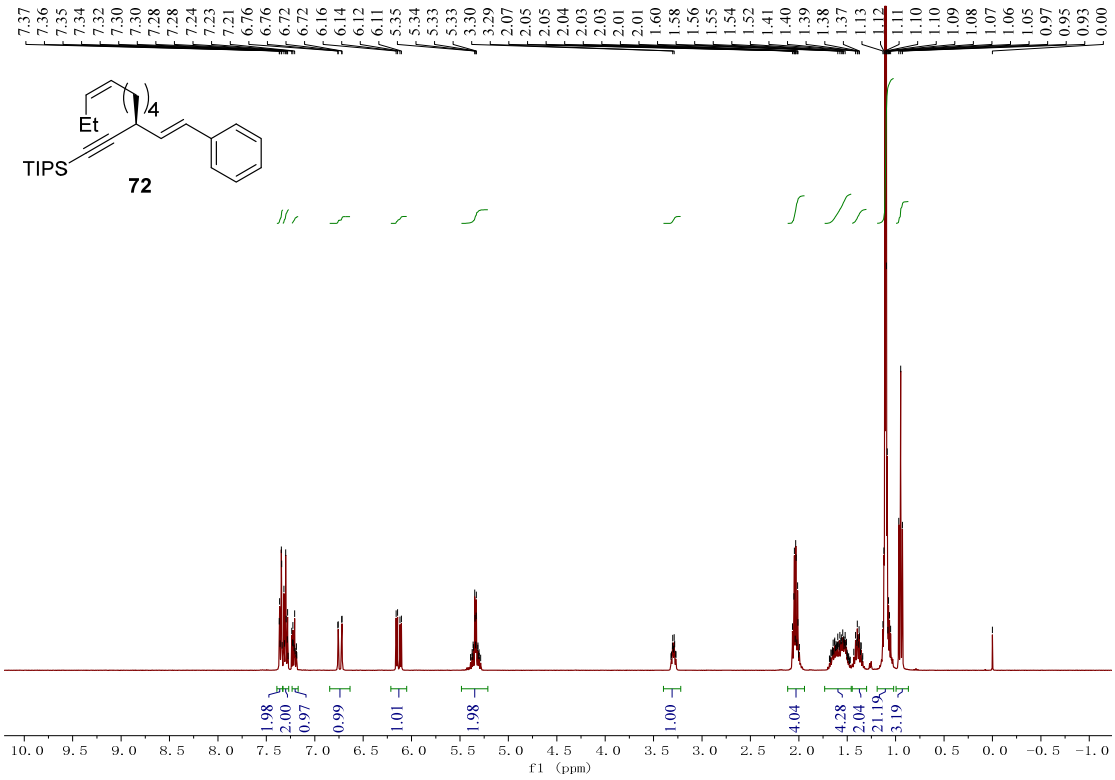

Ph
TIPS
69
f1 (ppm)

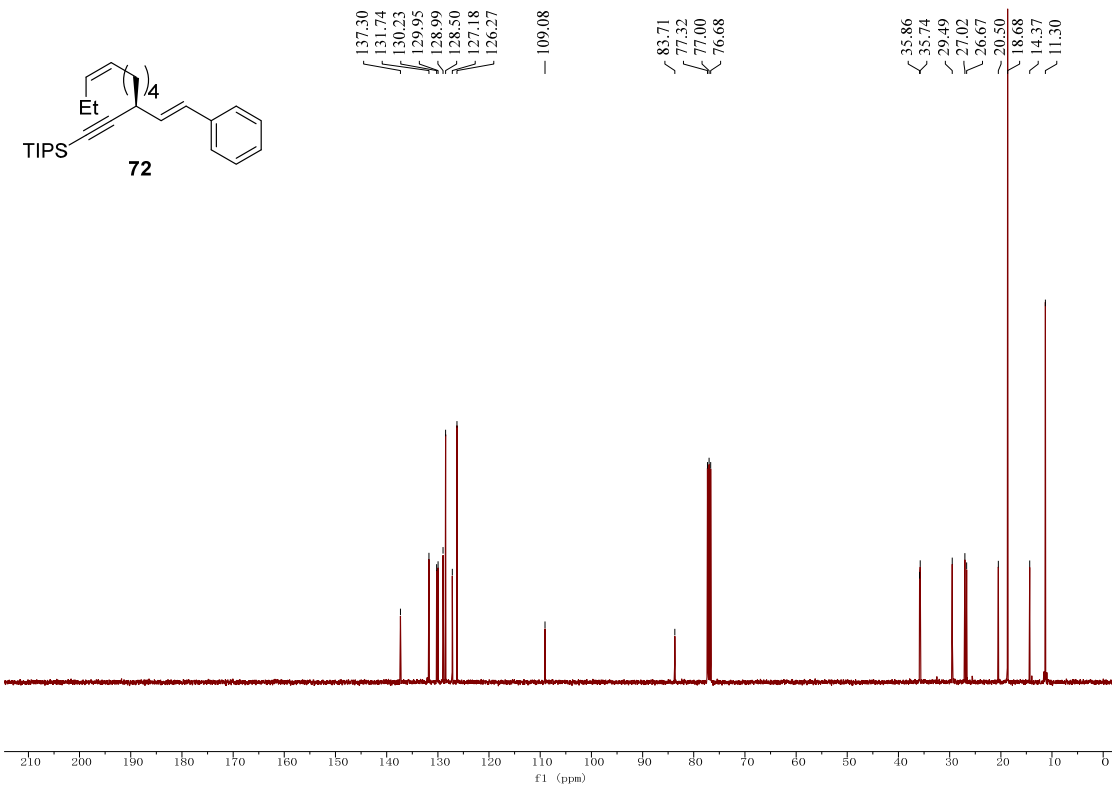

7.36 7.36 7.35 7.34 7.34 7.33 7.31 7.31 7.30 7.29 7.28 7.28 7.23 7.23 7.22 7.21 6.79 6.78 6.75 6.74 6.16 6.15 6.12 6.11 5.88 5.88 5.84 5.84 5.83 5.83 3.35 3.35 3.35 3.33 3.33 2.82 2.80 2.78 2.24 2.00 1.98 1.98 1.97 1.90 1.88 1.88 1.15 1.14 1.13 1.12 1.11 1.11 1.10 1.09 1.09 1.08 1.07 1.07 0.00
O
TIPS
70
2.03 2.04 1.07 1.00 1.02 0.99 1.04 1.01 2.08 3.11 1.05 1.02 21.38
f1 (ppm)

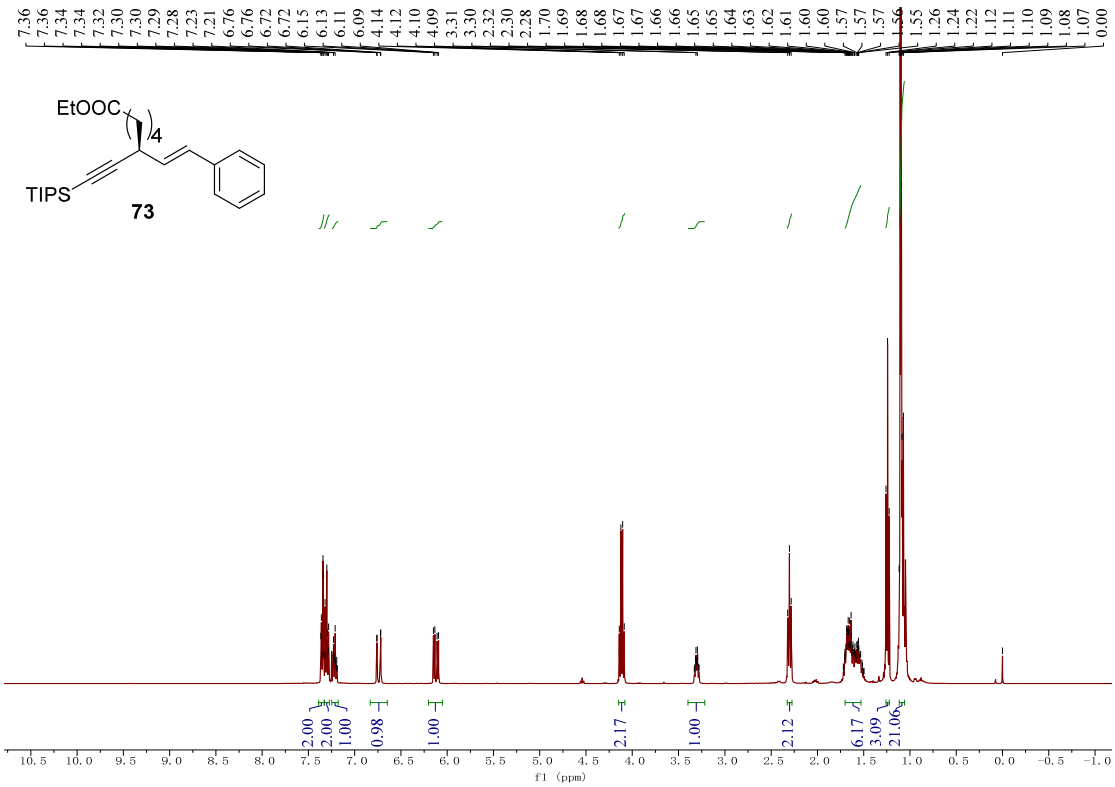

153.55 150.40 137.15 130.74 129.26 128.51 127.28 126.30 108.36 105.81 105.79 84.38 77.32 77.00 76.68 35.14 34.35 25.55 18.69 13.49 11.29
O
TIPS
70
f1 (ppm)

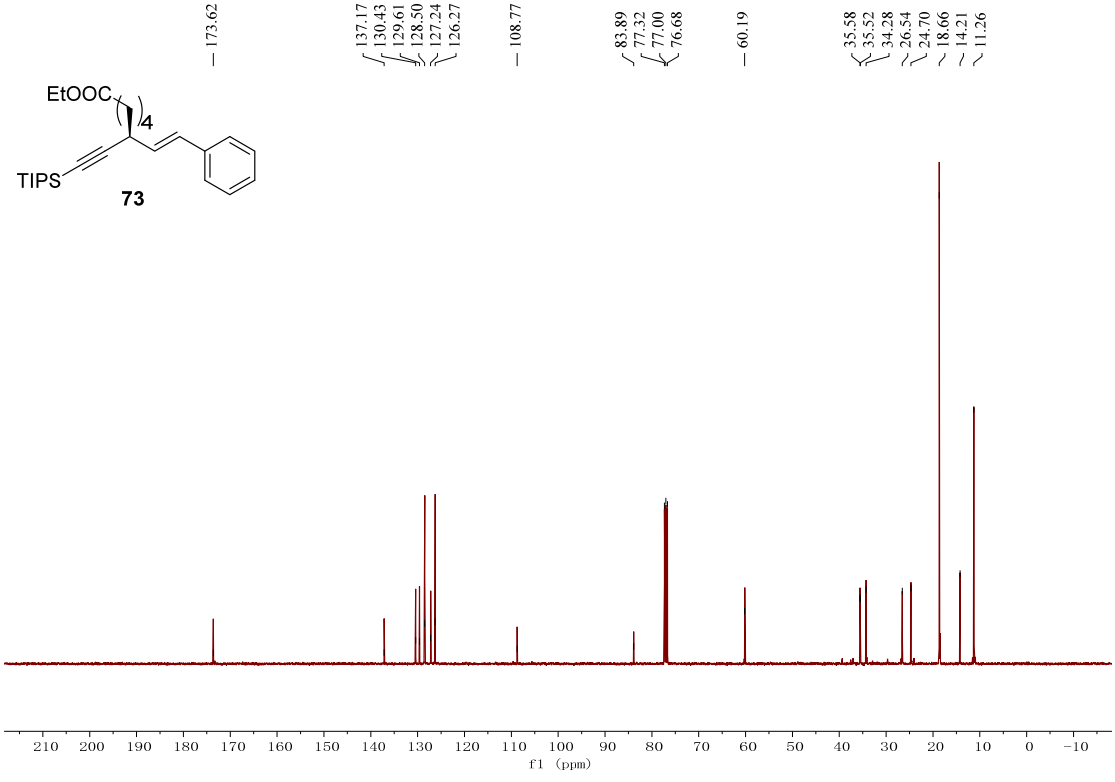

TIPS
71
f1 (ppm)

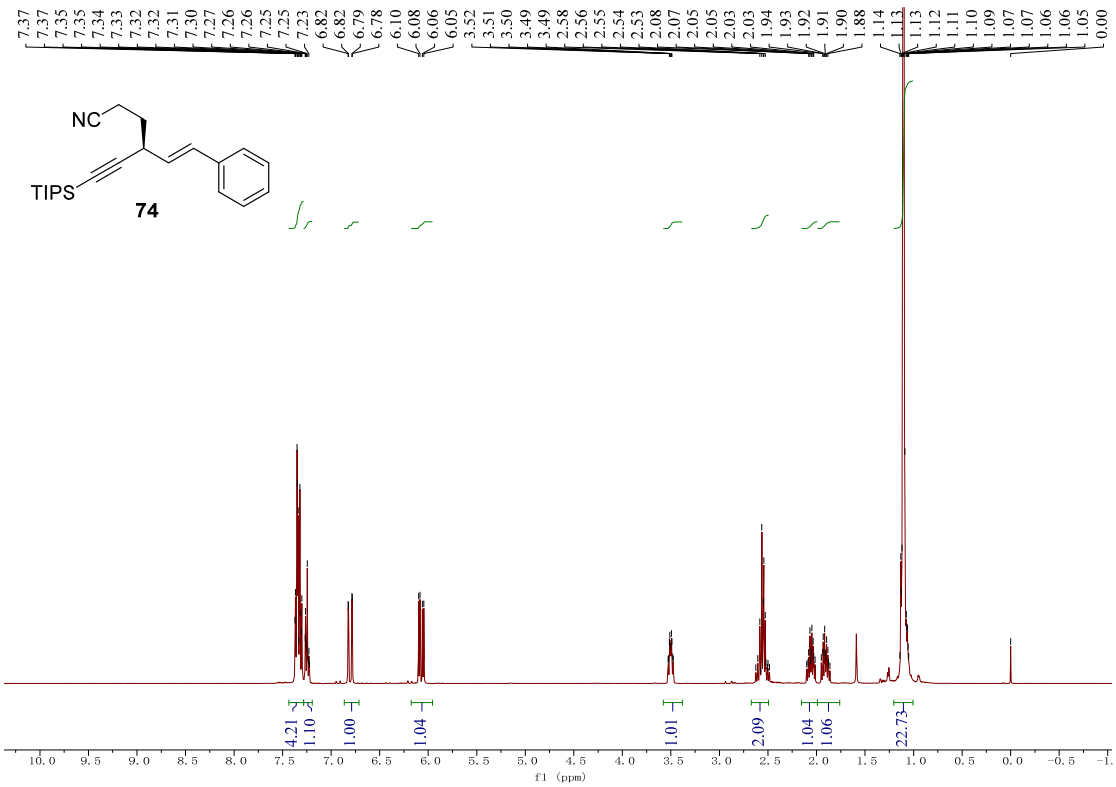

TIPS
71
f1 (ppm)

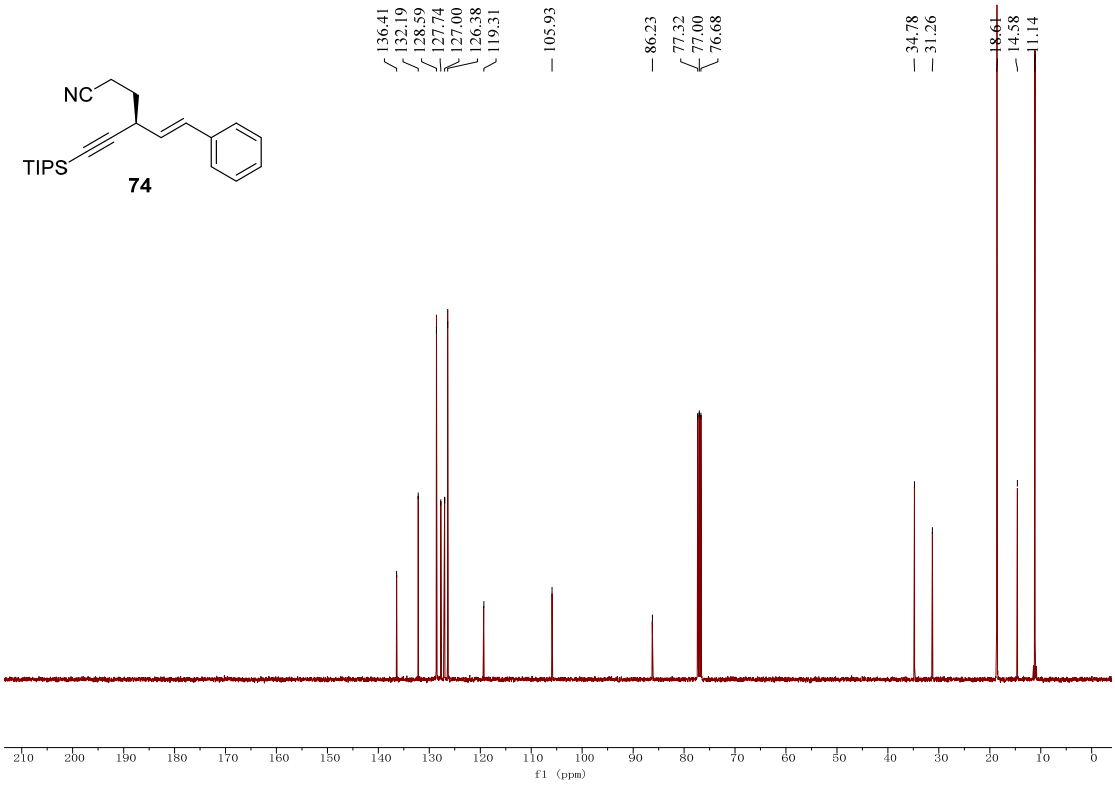

7.37 7.36 7.35 7.34 7.32 7.30 7.30 7.28 7.28 7.24 7.23 7.21 6.76 6.76 6.72 6.72 6.16 6.14 6.12 6.11 5.35 5.34 5.33 5.33 3.30 3.29 2.07 2.05 2.05 2.04 2.03 2.03 2.01 2.01 1.60 1.58 1.56 1.55 1.54 1.52 1.41 1.40 1.39 1.38 1.37 1.13 1.12 1.11 1.10 1.10 1.09 1.08 1.07 1.06 1.05 0.97 0.95 0.93 0.00
Et
TIPS
4
72
1.98 2.00 0.97 0.99 1.01 1.98 1.00 4.04 4.28 2.04 21.19 3.19
f1 (ppm)

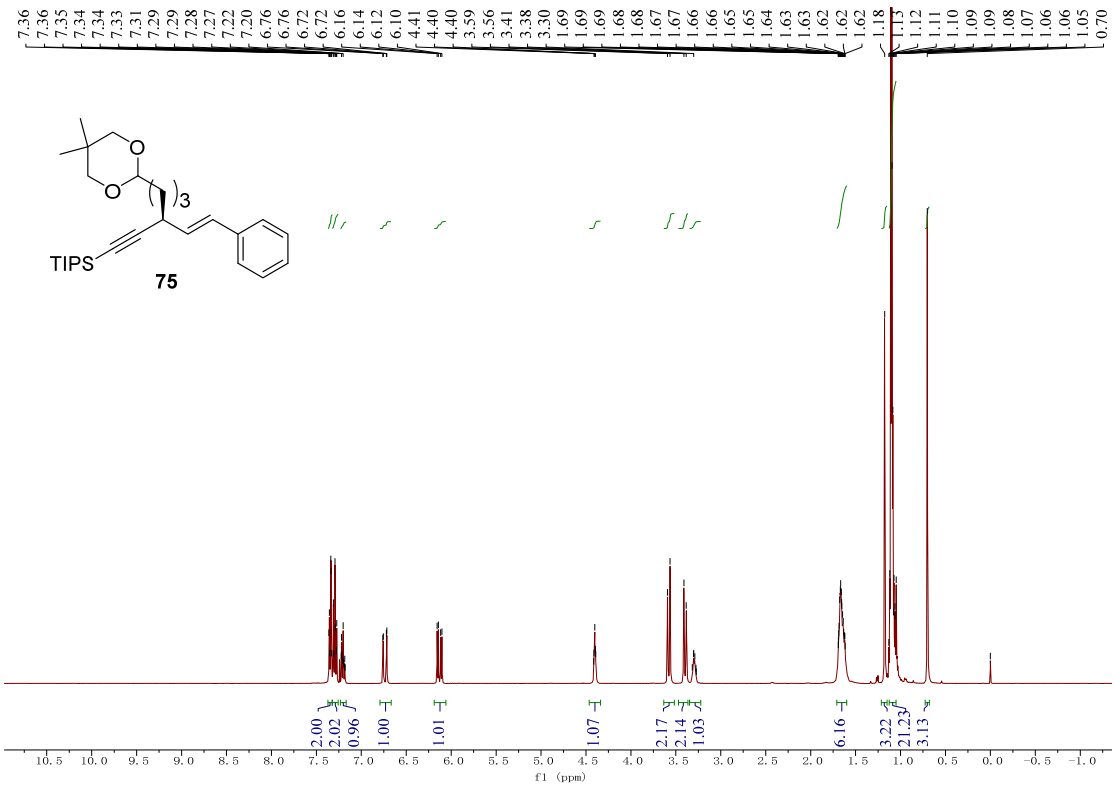

137.30 131.74 130.23 129.95 128.99 128.50 127.18 126.27 109.08 83.71 77.32 77.00 76.68 35.86 35.74 29.49 27.02 26.67 20.50 18.68 14.37 11.30
Et
TIPS
4
72
f1 (ppm)

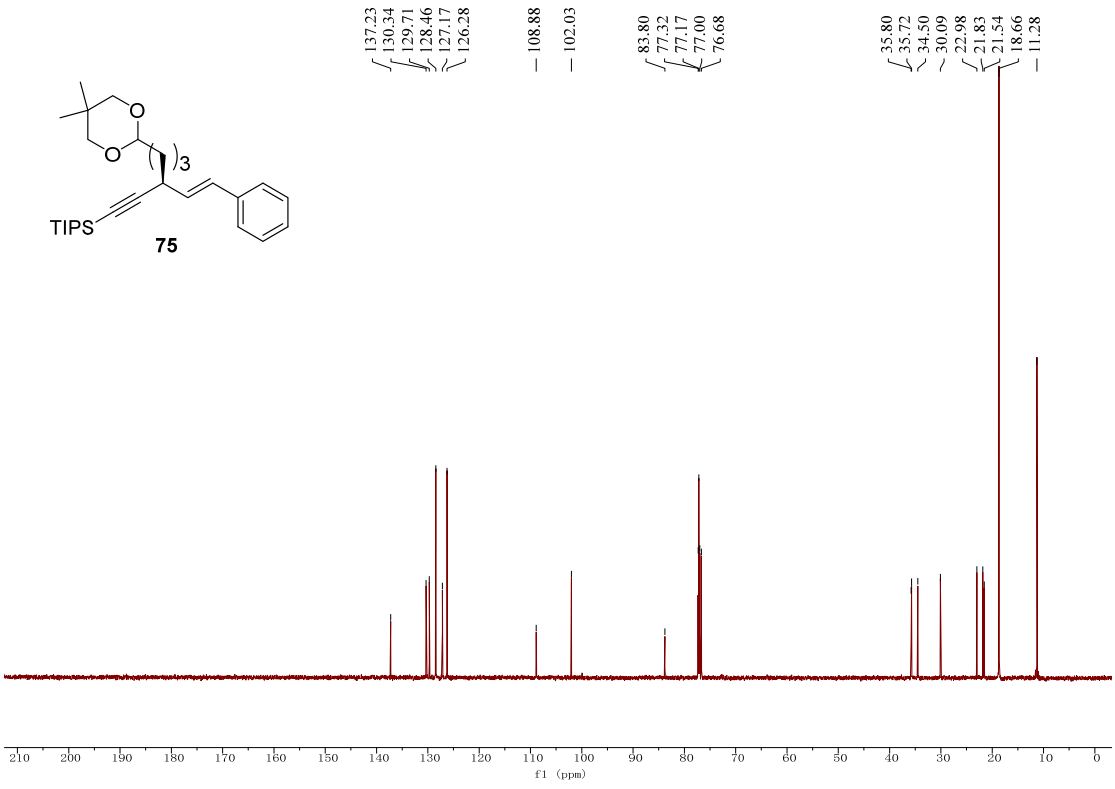

EtOOC
4
TIPS
73

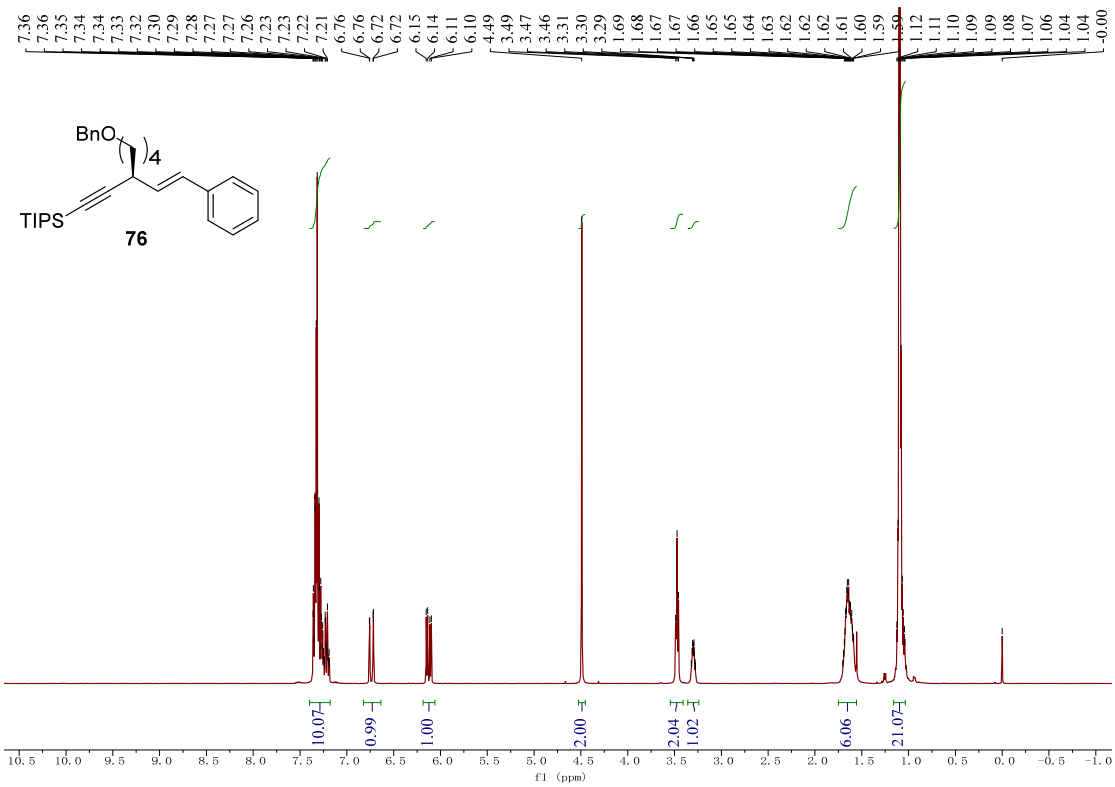

EtOOC
4
TIPS
73

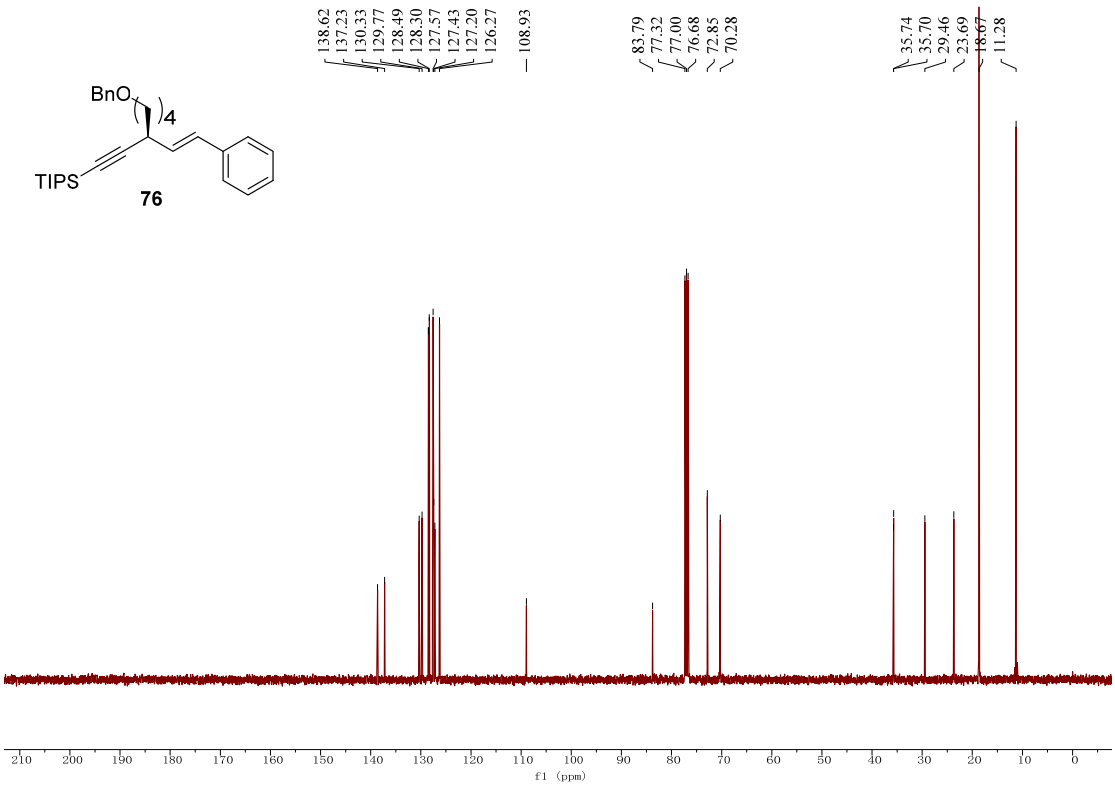

NC
TIPS
74
f1 (ppm)

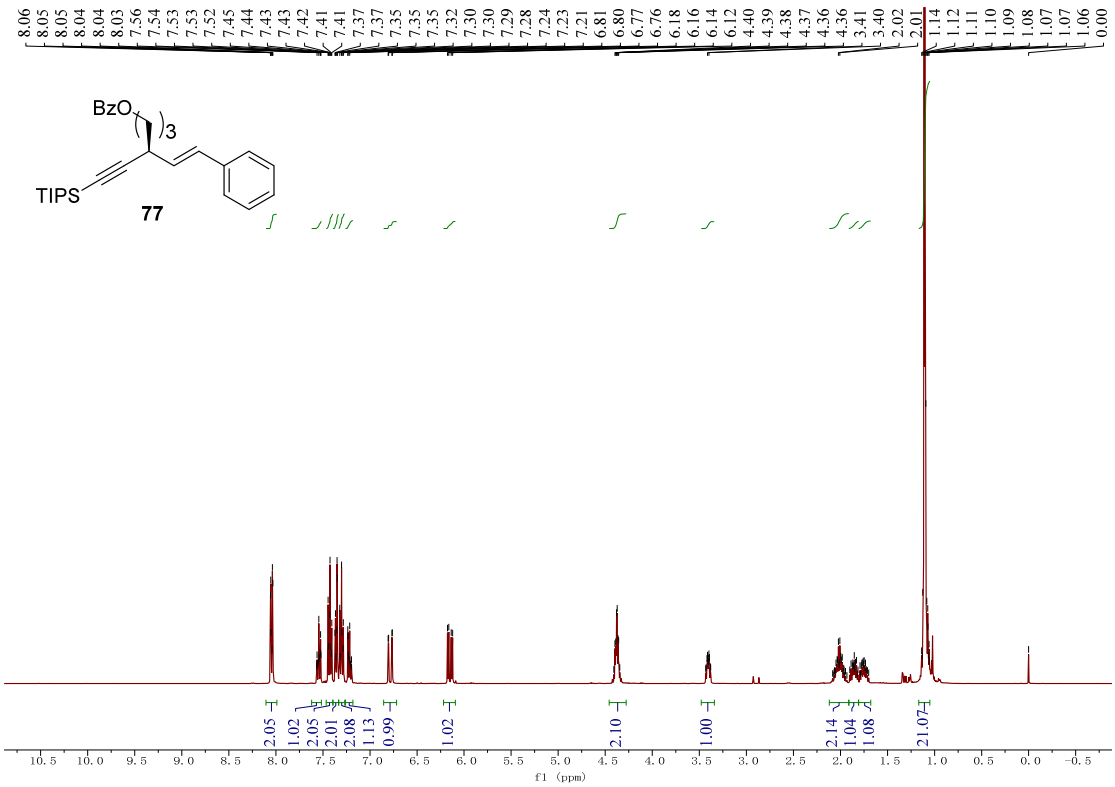

NC
TIPS
74
f1 (ppm)

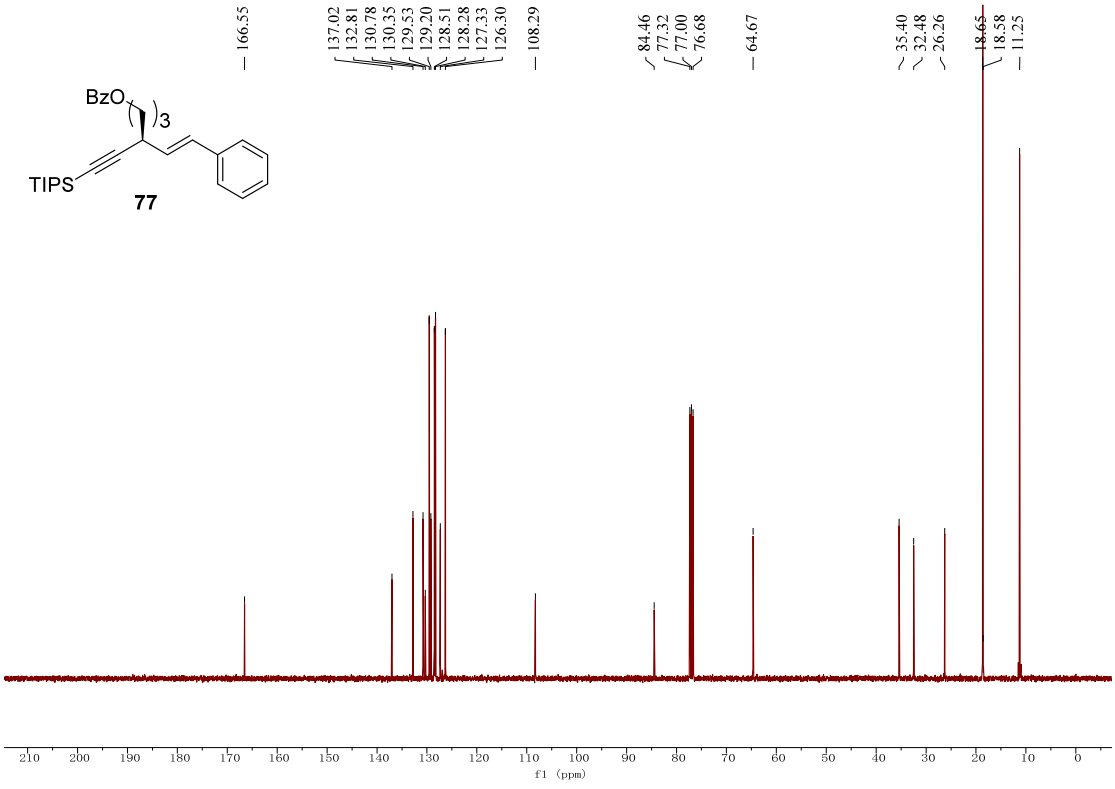

7.36 7.36 7.35 7.34 7.34 7.33 7.31 7.29 7.29 7.28 7.27 7.22 7.20 6.76 6.76 6.72 6.72 6.16 6.14 6.12 6.10 4.41 4.40 4.40 3.59 3.56 3.41 3.38 3.30 1.69 1.69 1.69 1.68 1.68 1.67 1.67 1.66 1.66 1.65 1.65 1.64 1.63 1.63 1.62 1.62 1.62 1.18 1.15 1.12 1.11 1.10 1.09 1.09 1.08 1.07 1.06 1.06 1.05 0.70
O
O
)3
TIPS
75
2.00 2.02 0.96 1.00 1.01 1.07 2.17 2.14 1.03 6.16 3.22 21.23 3.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

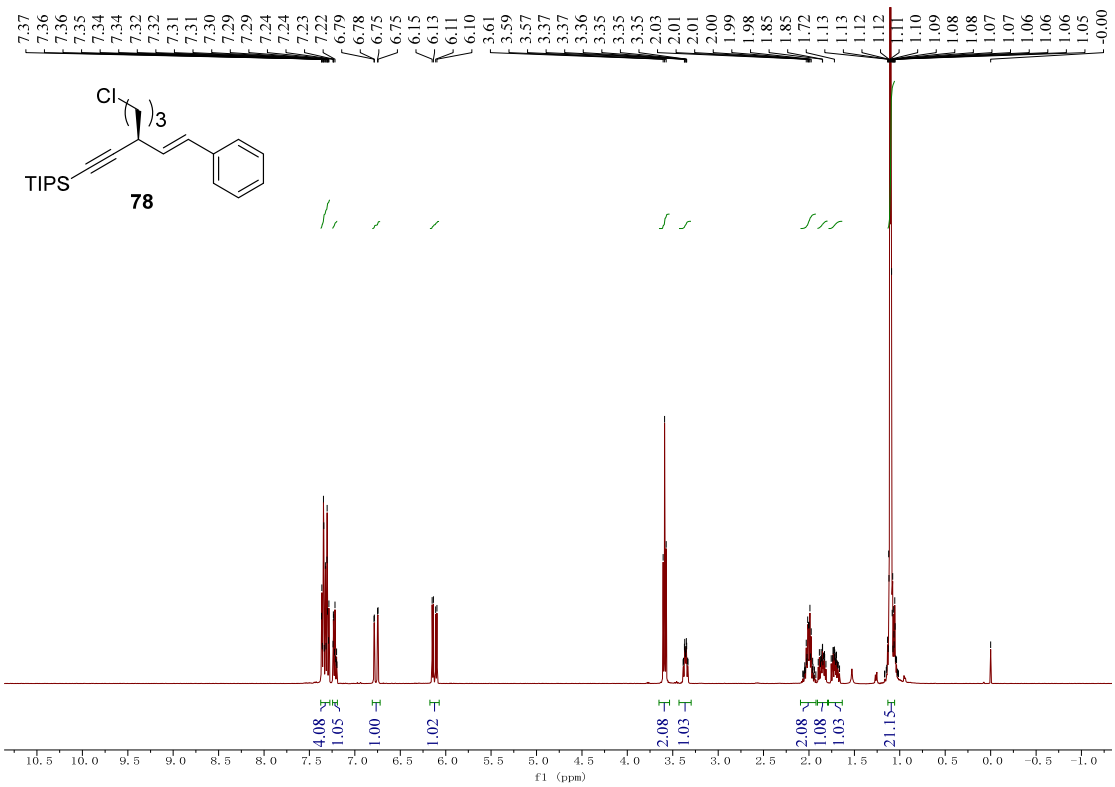

137.23 130.34 129.71 128.46 127.17 126.28 108.88 102.03 83.80 77.32 77.17 77.00 76.68 35.80 35.72 34.50 30.09 22.98 21.83 21.54 18.66 11.28
O
O
)3
TIPS
75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

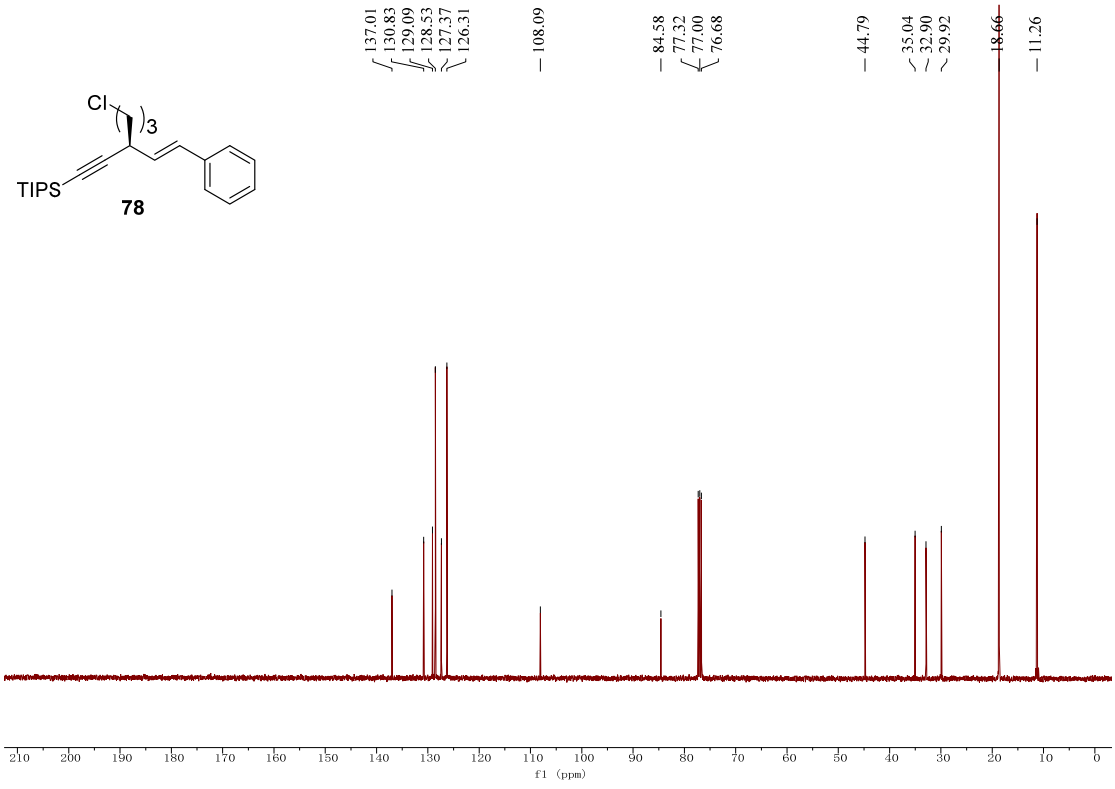

BnO
4
TIPS
76
7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.30 7.29 7.28 7.27 7.27 7.26 7.23 7.23 7.22 7.21 6.76 6.76 6.72 6.72 6.15 6.14 6.11 6.10 4.49 3.49 3.47 3.46 3.31 3.30 3.29 1.69 1.68 1.67 1.67 1.66 1.65 1.65 1.64 1.63 1.62 1.62 1.62 1.61 1.60 1.59 1.59 1.12 1.11 1.10 1.09 1.09 1.09 1.08 1.07 1.06 1.04 1.04 -0.00
10.07 0.99 1.00 2.00 2.04 1.02 6.06 21.07
f1 (ppm)

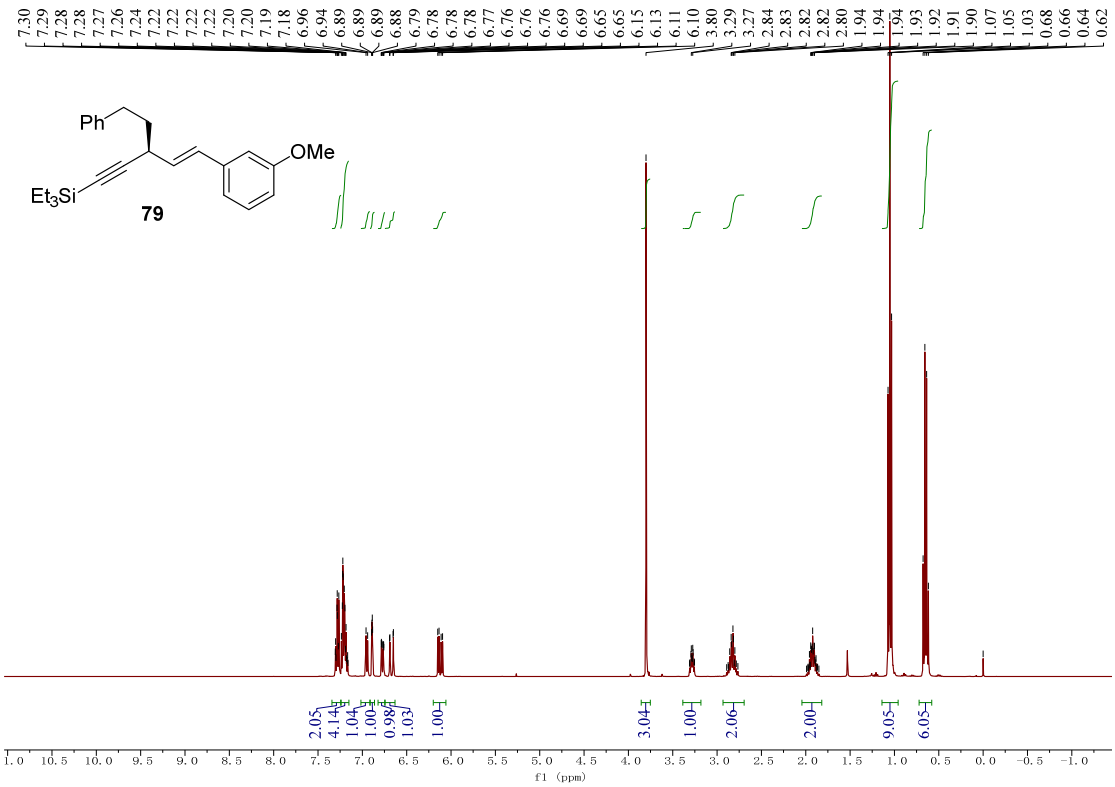

BnO
4
TIPS
76
138.62 137.23 130.33 129.77 128.49 128.30 127.57 127.43 127.20 126.27 108.93 83.79 77.32 77.00 76.68 72.85 70.28 35.74 35.70 29.46 23.69 18.67 11.28
f1 (ppm)

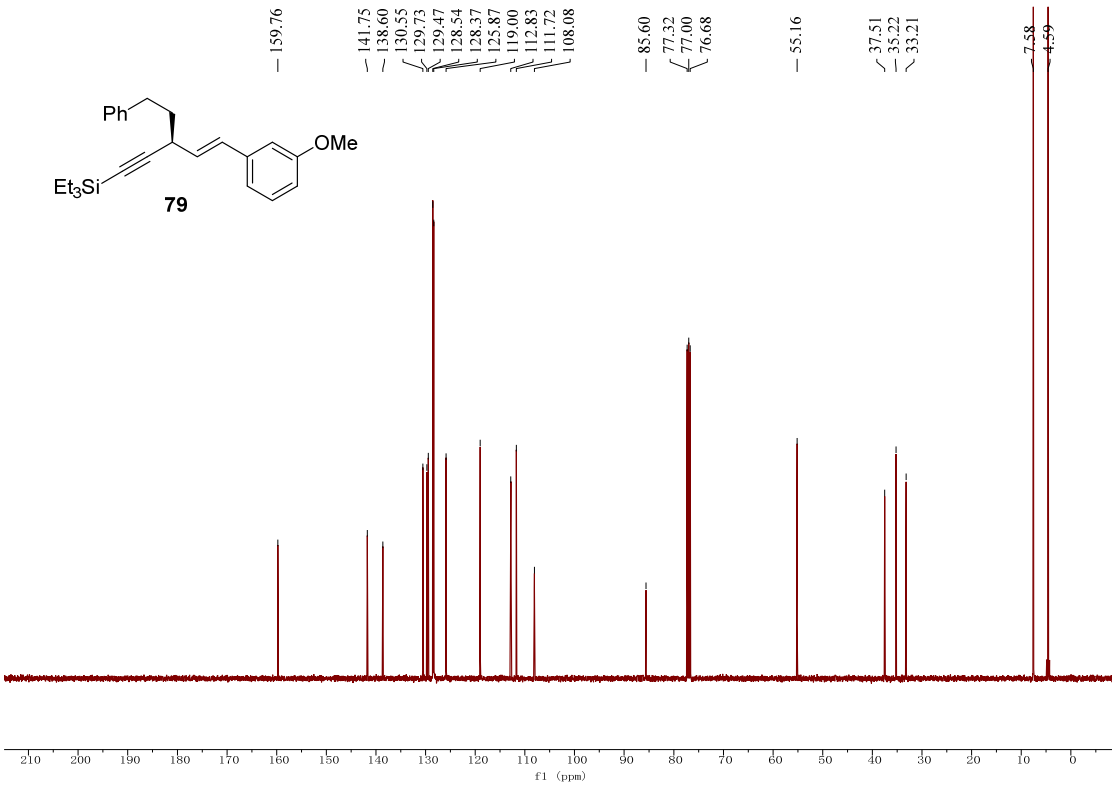

BzO
3
TIPS
77

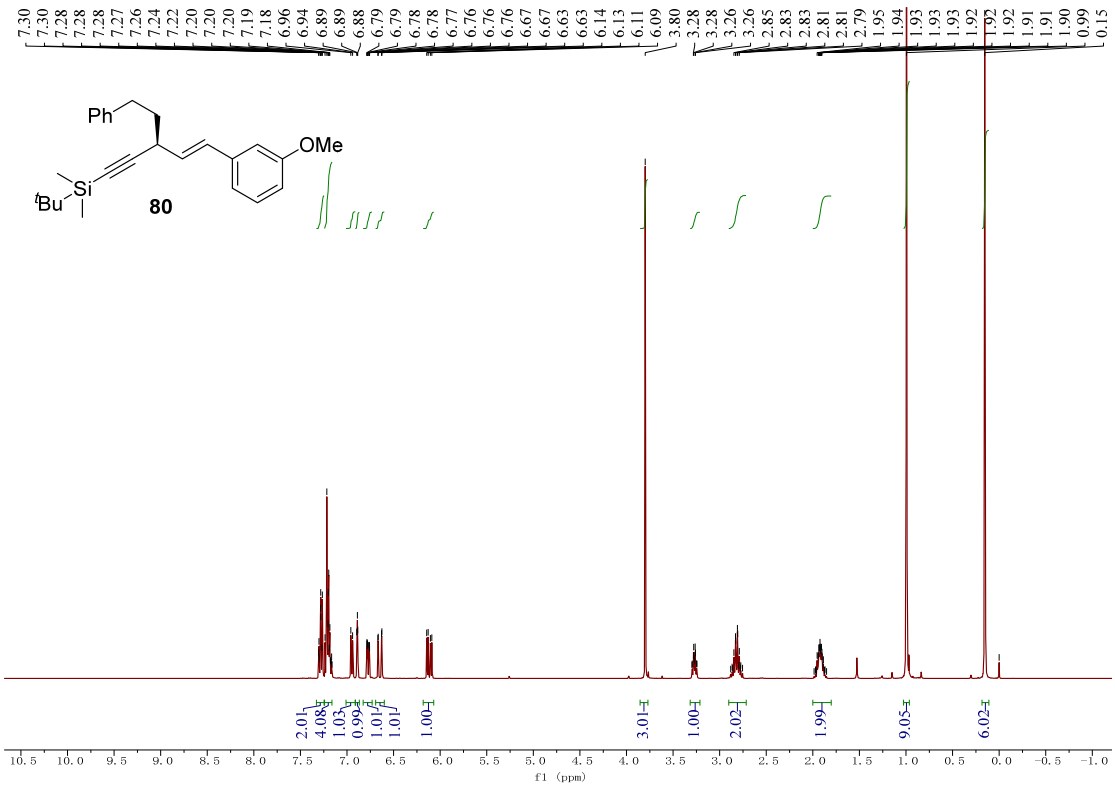

BzO
3
TIPS
77

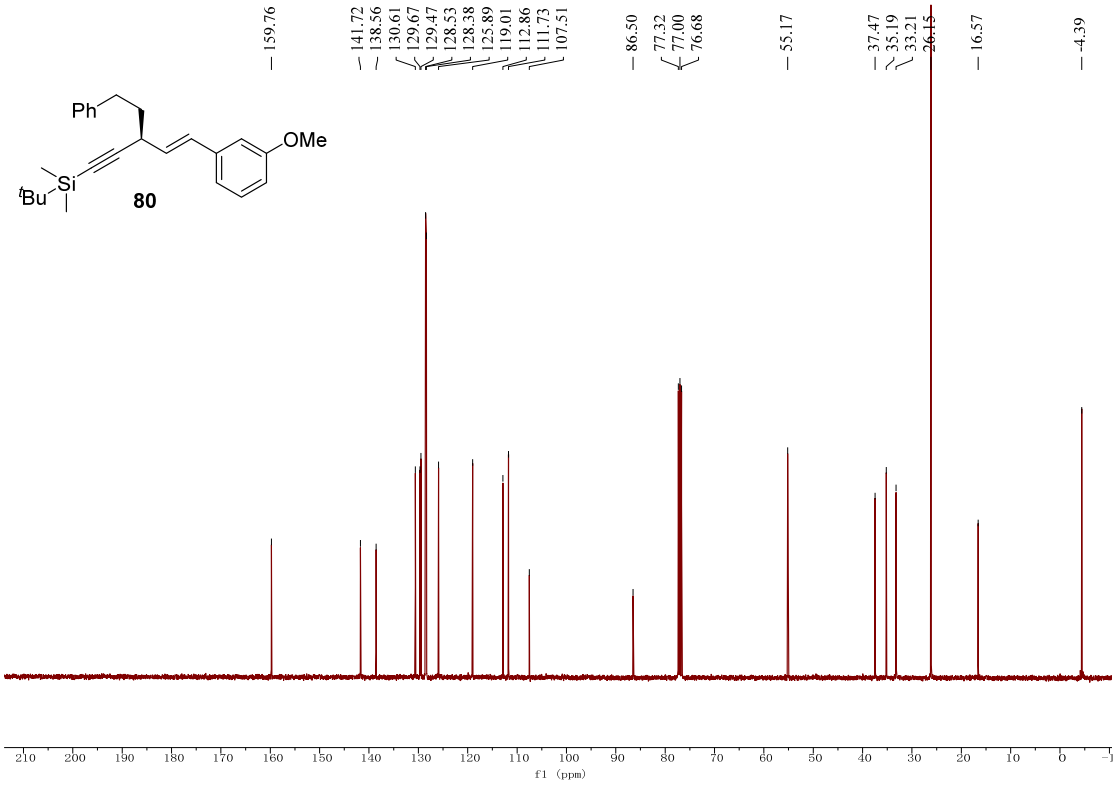

Cl
3
TIPS
78
f1 (ppm)

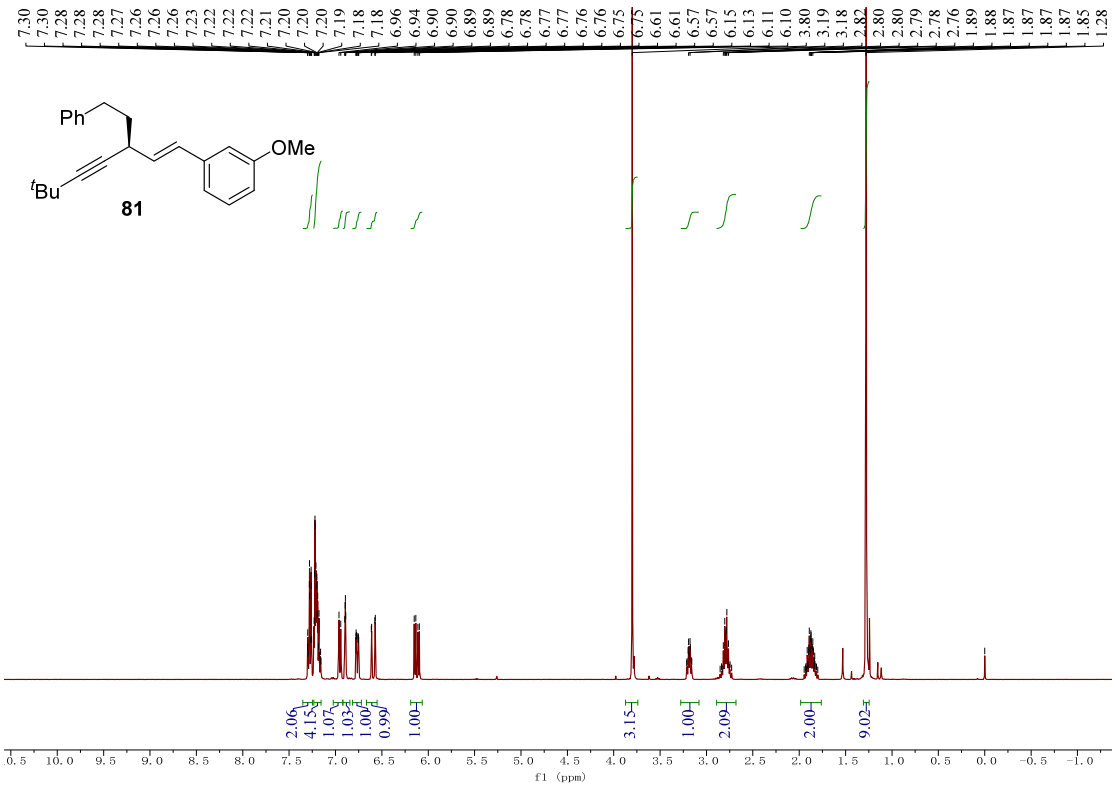

Cl
3
TIPS
78
f1 (ppm)

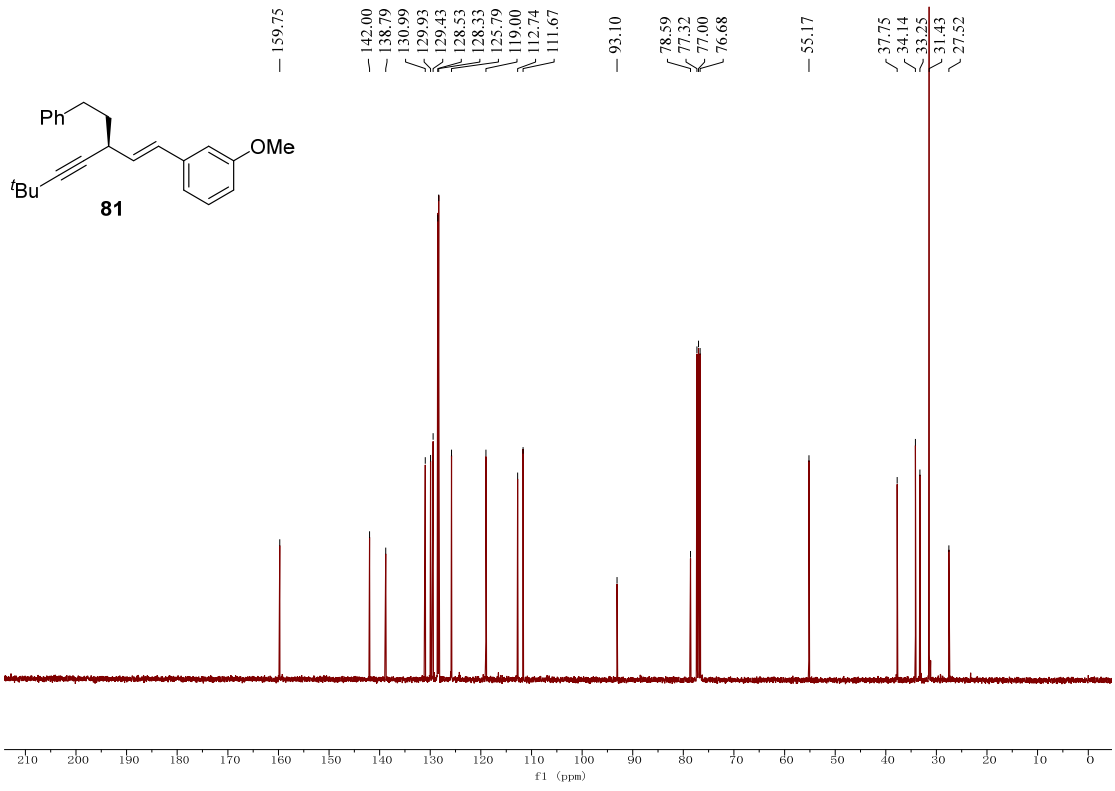

Ph
OMe
Et3Si
79

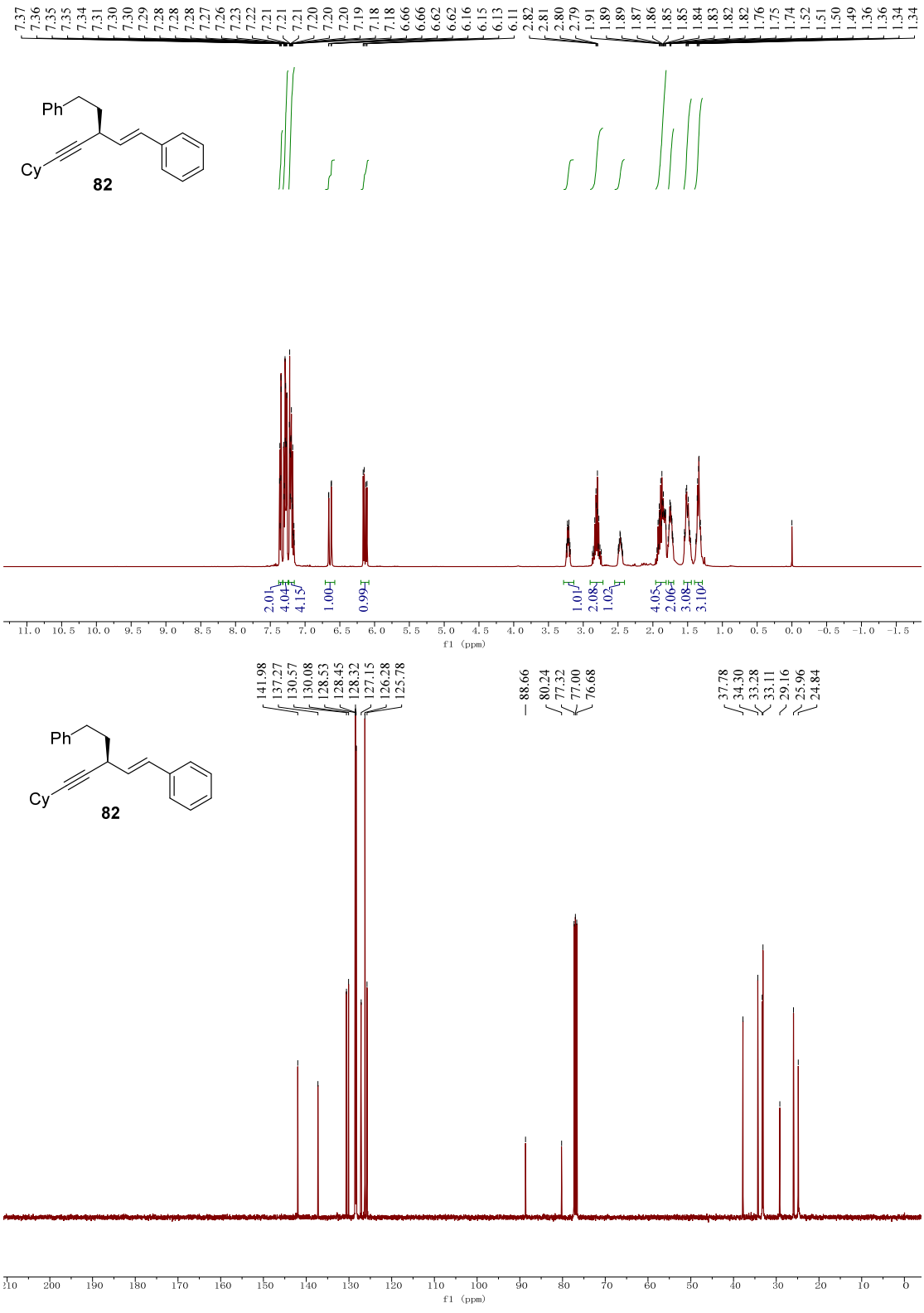

Ph
OMe
Et3Si
79

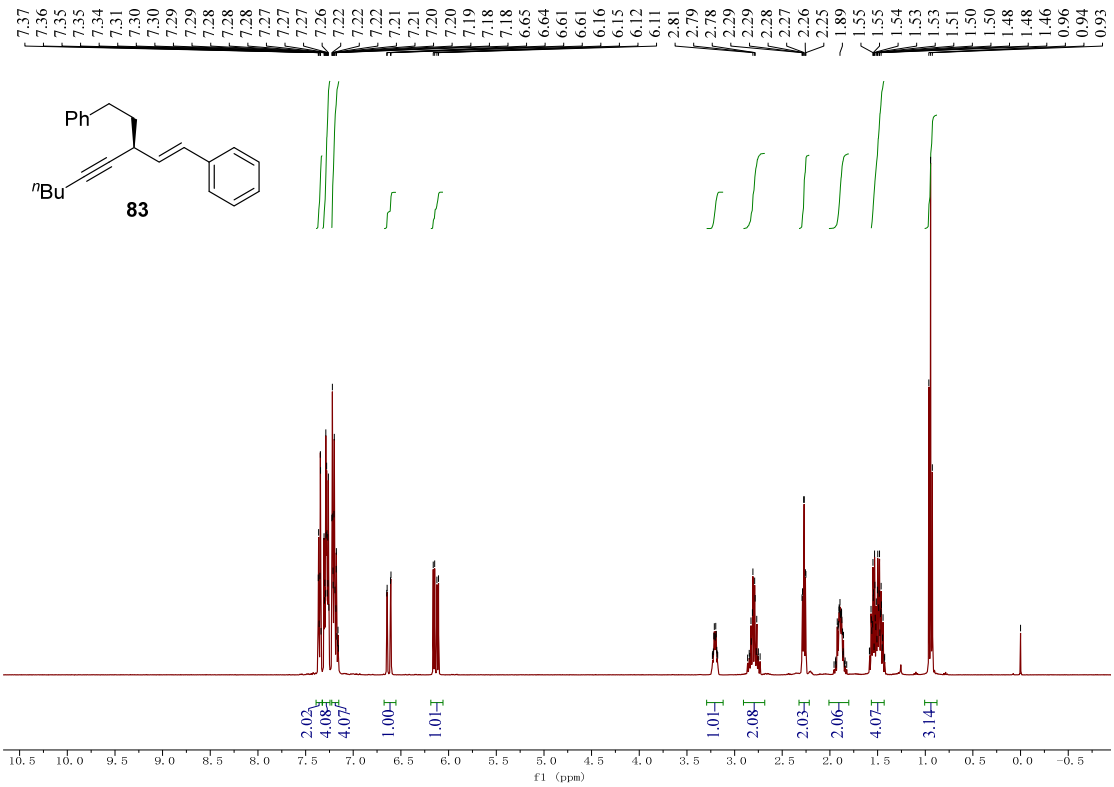

Ph
OMe
tBu
Si
80
f1 (ppm)

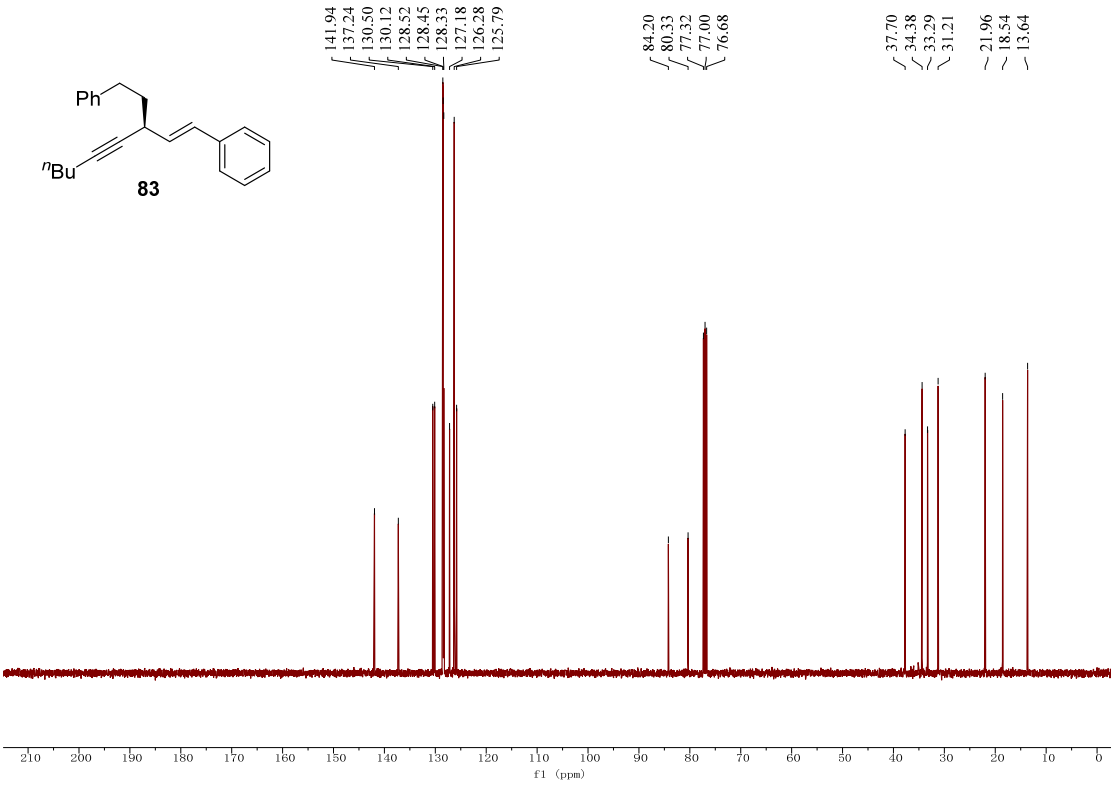

Ph
OMe
tBu
Si
80
f1 (ppm)

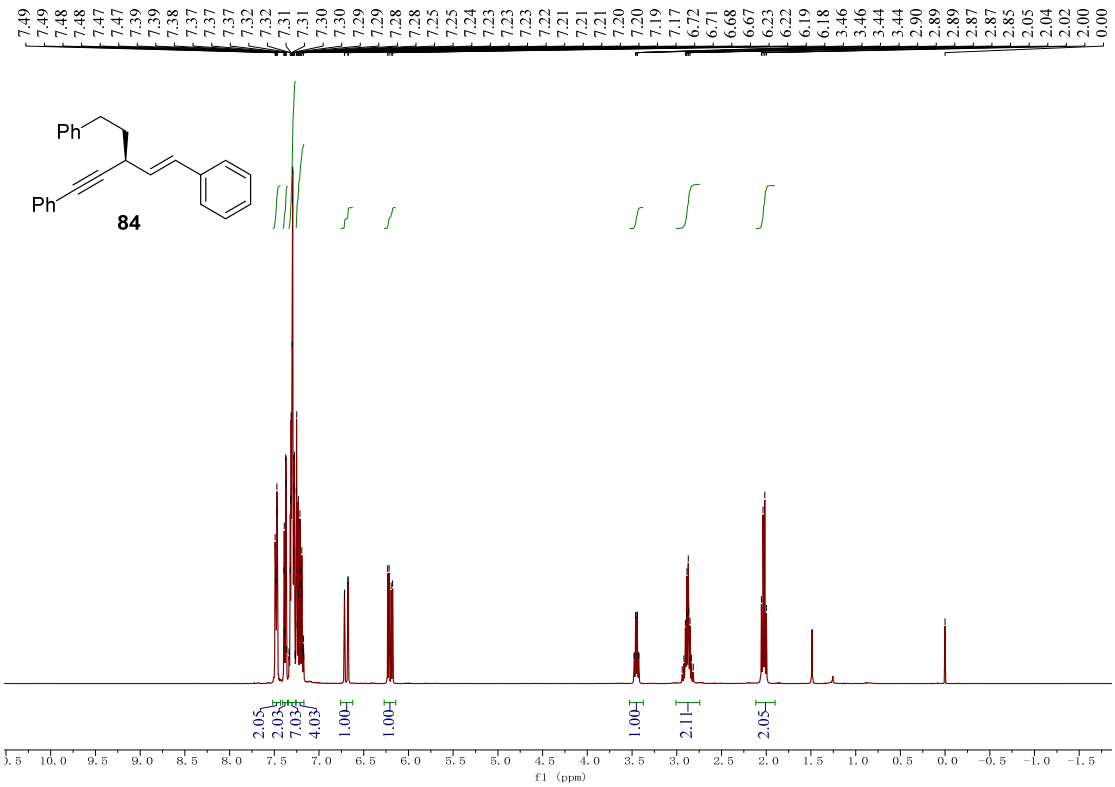

Ph
OMe
tBu
81
f1 (ppm)

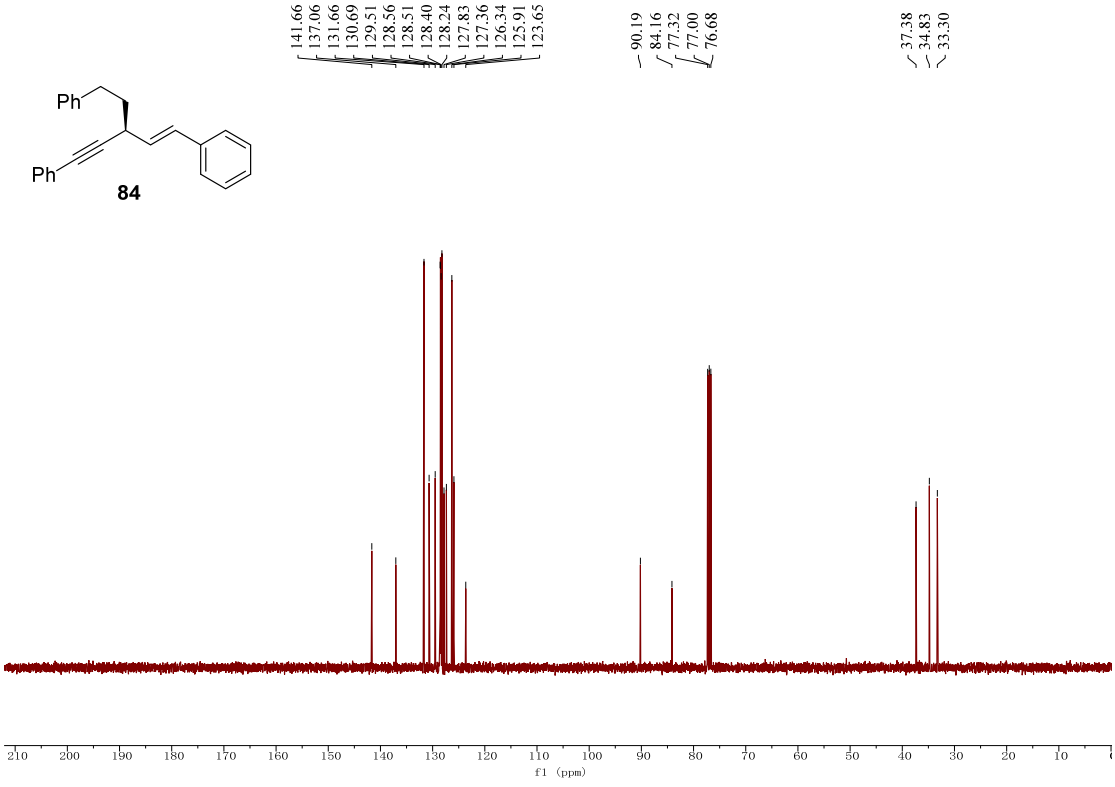

Ph
OMe
tBu
81
f1 (ppm)

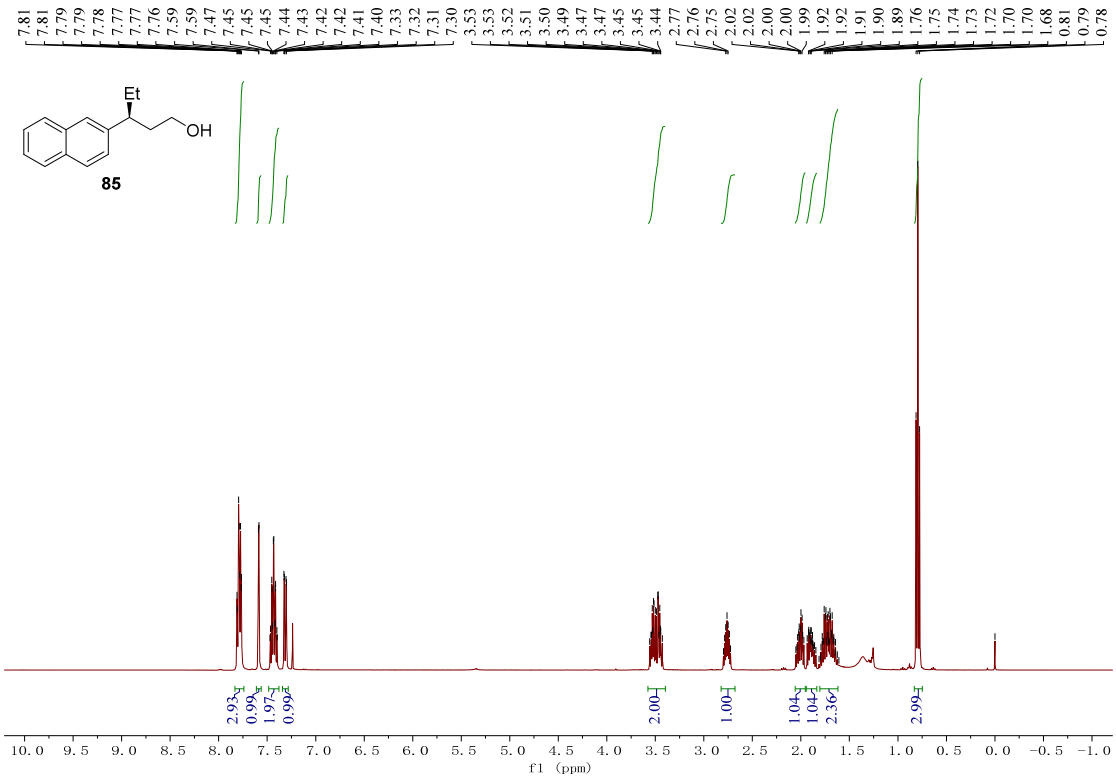

Ph
Cy
82
f1 (ppm)
f1 (ppm)

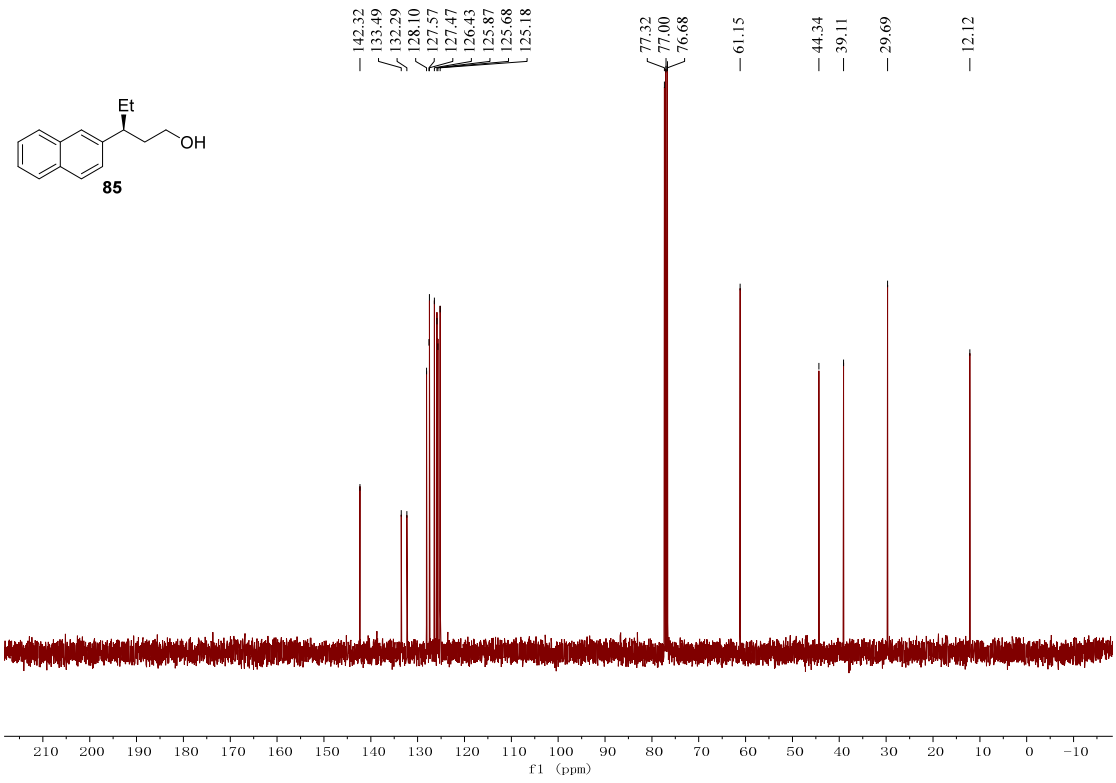

Ph
nBu
83
f1 (ppm)

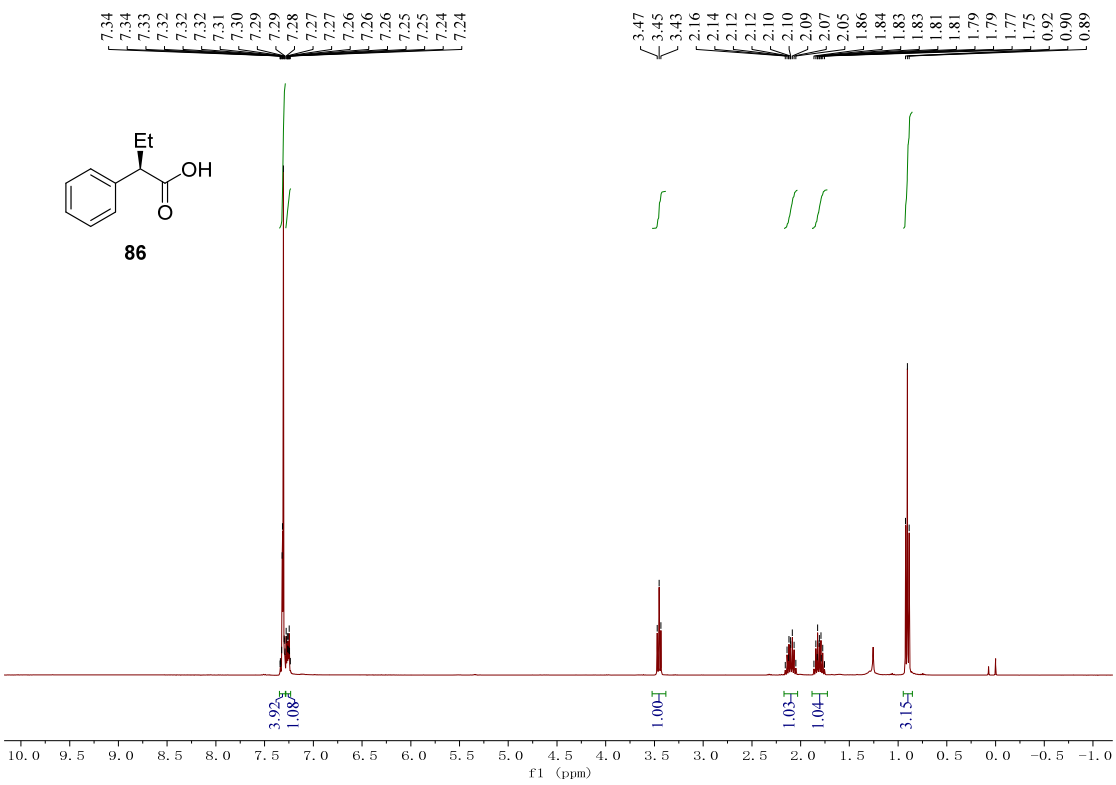

Ph
nBu
83
f1 (ppm)

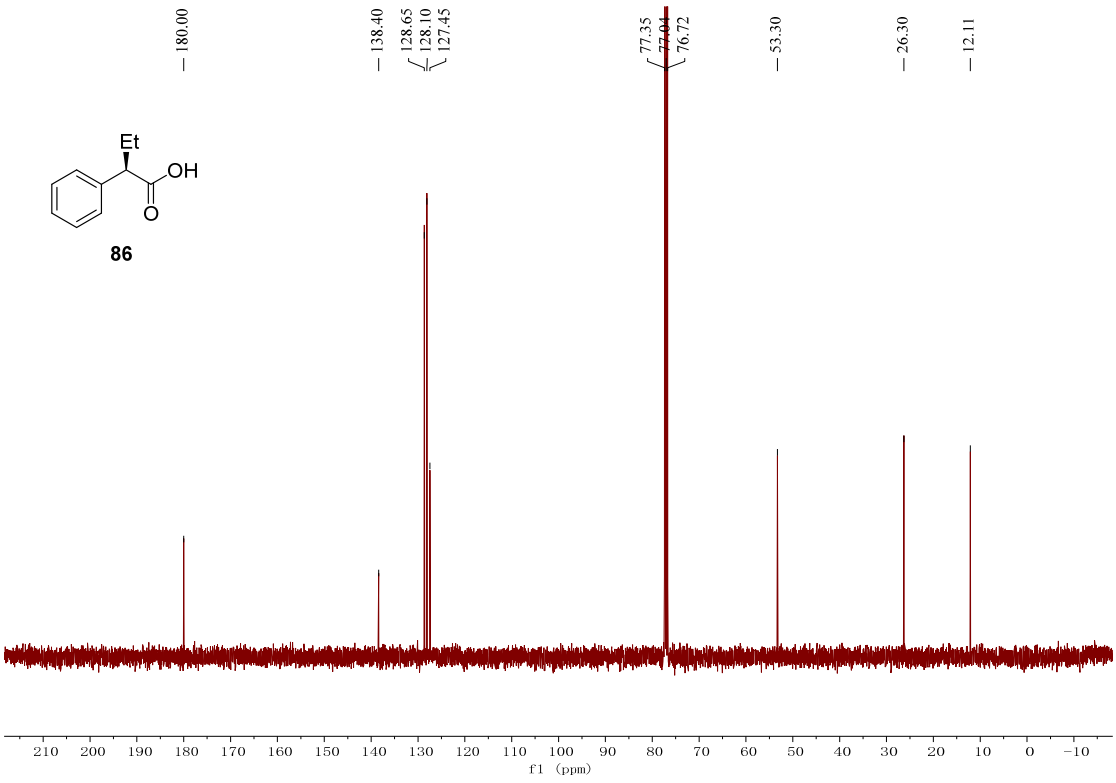

Ph
Ph
84
f1 (ppm)

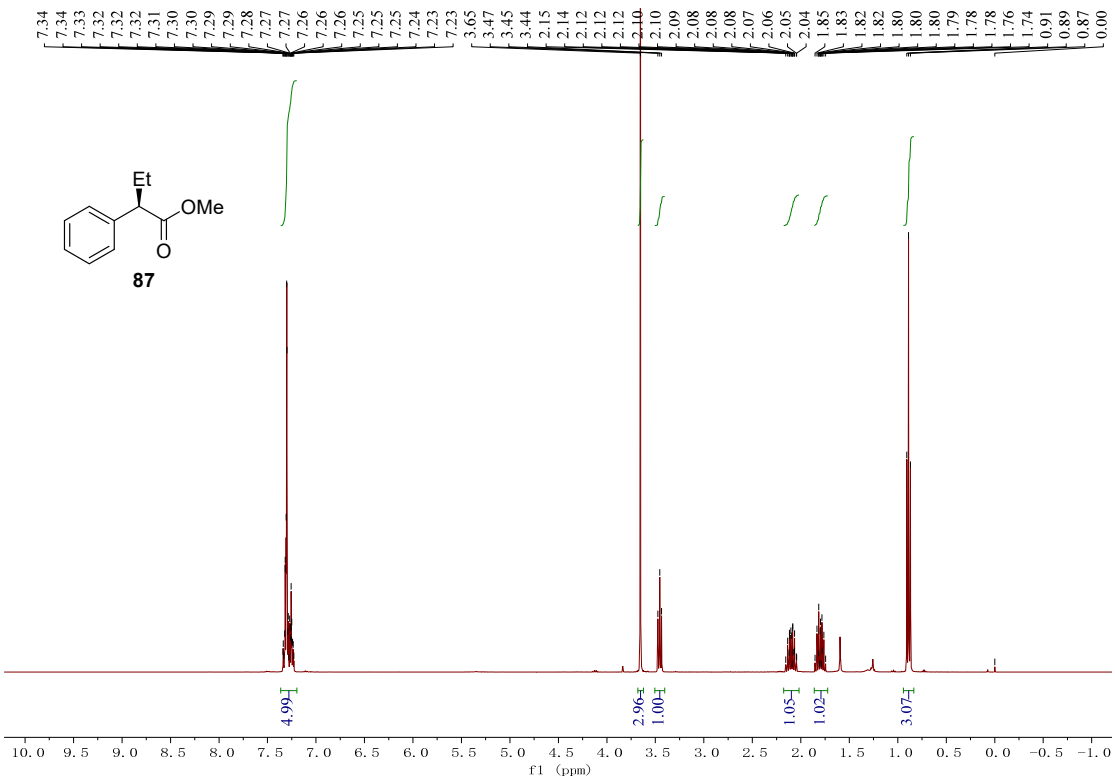

Ph
Ph
84
f1 (ppm)

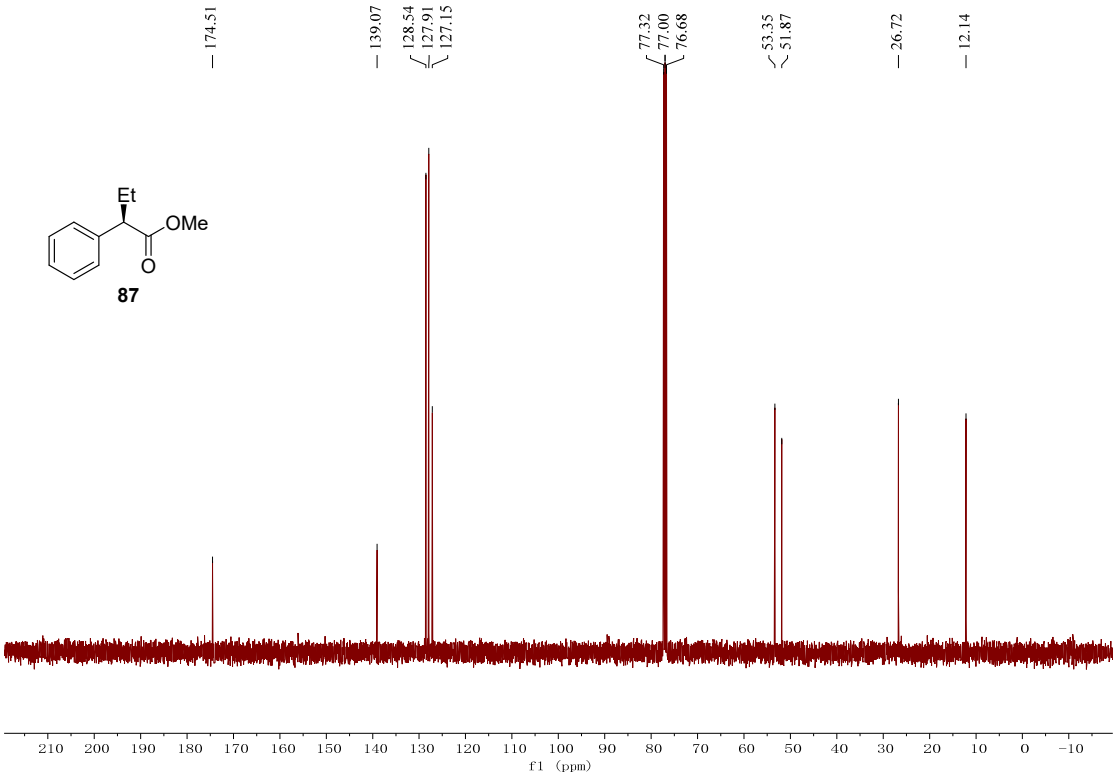

7.81 7.81 7.79 7.79 7.78 7.77 7.77 7.76 7.59 7.59 7.47 7.45 7.45 7.45 7.44 7.43 7.42 7.42 7.41 7.40 7.33 7.32 7.31 7.30
3.53 3.53 3.52 3.51 3.50 3.49 3.47 3.47 3.45 3.45 3.44
2.77 2.76 2.75 2.02 2.02 2.00 2.00 1.99 1.92 1.92 1.91 1.90 1.89 1.76 1.75 1.74 1.73 1.72 1.70 1.70 1.68 0.81 0.79 0.78
Et
OH
85
2.93 0.99 1.97 0.99
2.00 1.00 1.04 1.04 2.36 2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

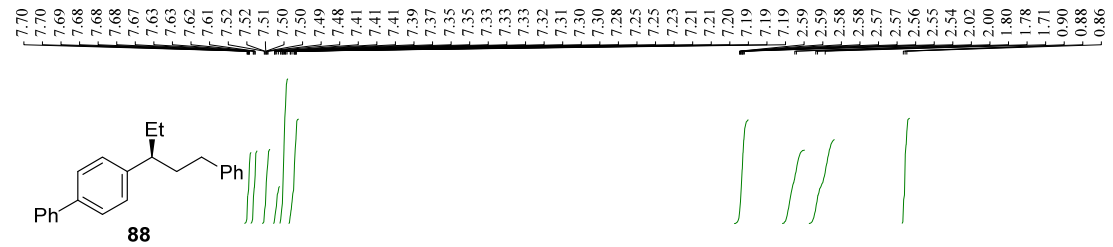

142.32 133.49 132.29 128.10 127.57 127.47 126.43 125.87 125.68 125.18
77.32 77.00 76.68
61.15
44.34 39.11
29.69
12.12
Et
OH
85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
3.47
3.45
3.43
2.16
2.14
2.12
2.12
2.10
2.10
2.09
2.07
2.05
1.86
1.84
1.83
1.83
1.81
1.81
1.79
1.79
1.77
1.75
0.92
0.90
0.89
Et
OH
O
86
3.92
1.08
1.00
1.03
1.04
3.15
f1 (ppm)


180.00
138.40
128.65
128.10
127.45
77.35
77.04
76.72
53.30
26.30
12.11
Et
OH
O
86
f1 (ppm)

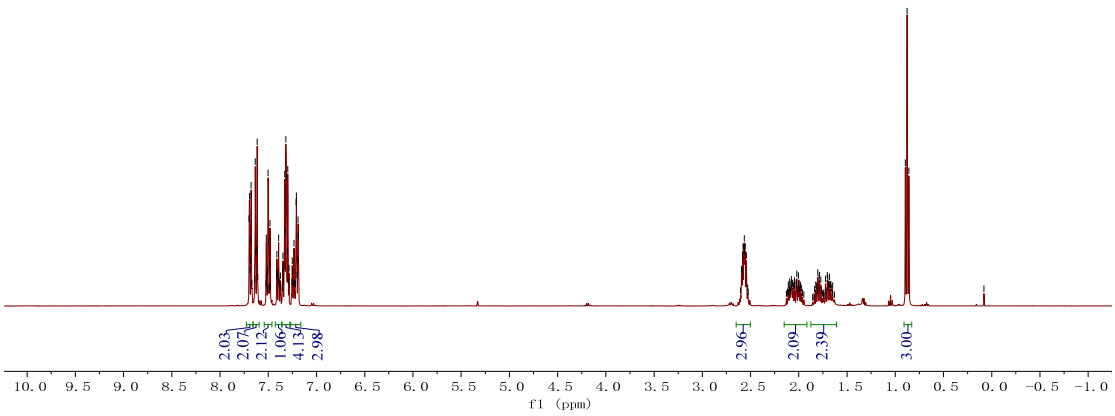

Et
OMe
O
87
4.99
2.96
1.00
1.05
1.02
3.07
f1 (ppm)

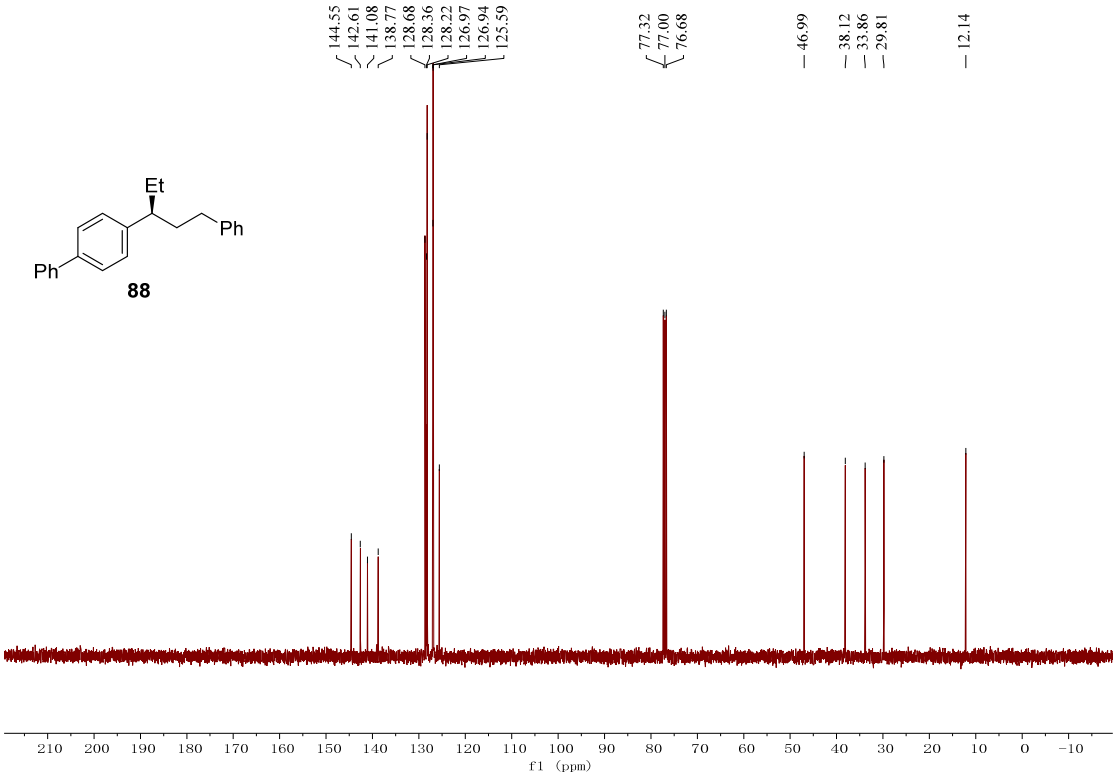

174.51
139.07
128.54
127.91
127.15
77.32
77.00
76.68
53.35
51.87
26.72
12.14
Et
OMe
O
87
f1 (ppm)


7.70 7.70 7.69 7.68 7.68 7.68 7.67 7.63 7.63 7.62 7.61 7.52 7.52 7.51 7.50 7.50 7.49 7.48 7.41 7.41 7.41 7.39 7.37 7.35 7.35 7.33 7.33 7.32 7.31 7.30 7.30 7.28 7.25 7.25 7.23 7.21 7.21 7.20 7.19 7.19 7.19 2.59 2.59 2.58 2.58 2.57 2.57 2.56 2.55 2.54 2.02 2.00 1.80 1.78 1.71 0.90 0.88 0.86

Et
Ph
Ph

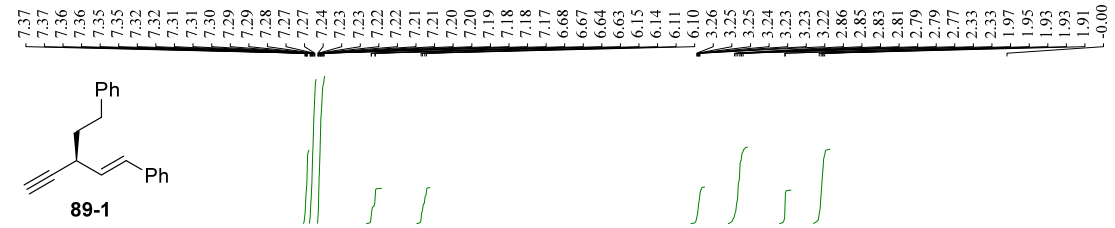
88


2.03 2.07 2.12 1.06 4.13 2.98 2.96 2.09 2.39 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


144.55 142.61 141.08 138.77 128.68 128.36 128.22 126.97 126.94 125.59 77.32 77.00 76.68 46.99 38.12 33.86 29.81 12.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Et
Ph
Ph

88


7.37
7.37
7.36
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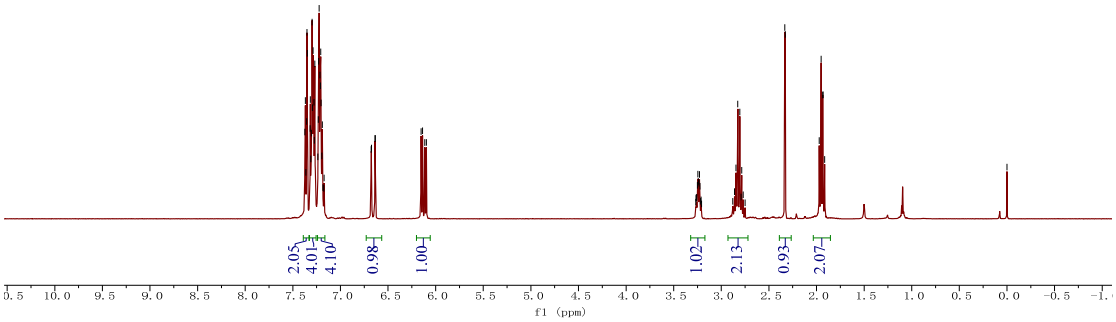
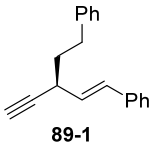
7.35
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.17
6.68
6.67
6.64
6.63
6.15
6.14
6.11
6.10
3.26
3.25
3.25
3.24
3.23
3.23
3.22
2.86
2.85
2.83
2.81
2.79
2.79
2.77
2.33
2.33
1.97
1.95
1.93
1.93
1.91
-0.00

Ph
Ph

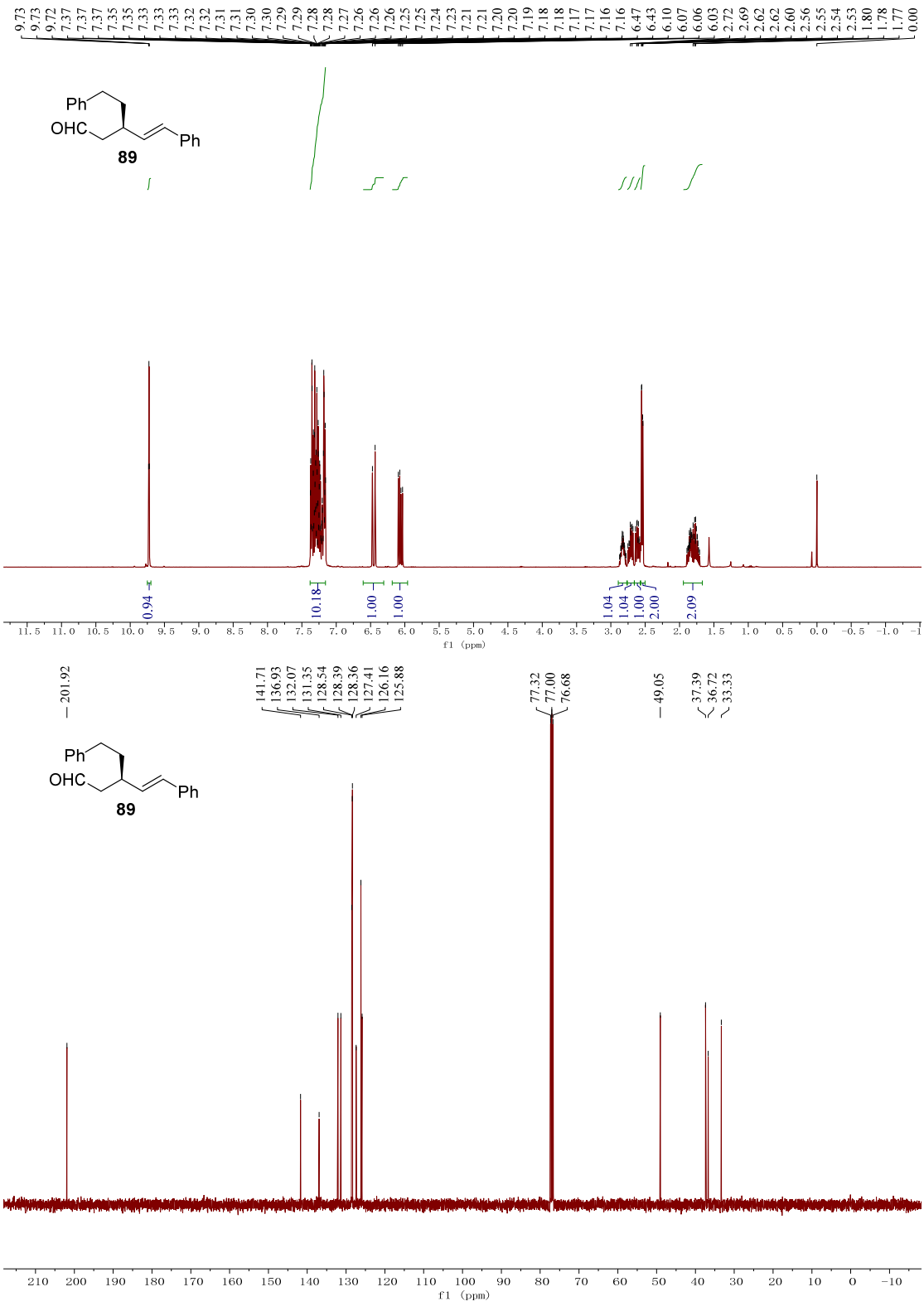
89-1


2.05
4.01
4.10
0.98
1.00
1.02
2.13
0.93
2.07
f1 (ppm)


Ph
Ph

89-1

141.49
136.90
130.81
128.92
128.51
128.51
128.39
127.41
126.31
125.93
84.67
77.32
77.00
76.68
71.83
37.14
33.92
33.05
f1 (ppm)


9.73 9.73 9.72 7.37 7.37 7.37 7.35 7.35 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.26 7.26 7.25 7.25 7.24 7.23 7.21 7.21 7.20 7.20 7.19 7.18 7.18 7.17 7.17 7.16 7.16 6.47 6.43 6.10 6.07 6.06 6.03 2.72 2.69 2.62 2.62 2.60 2.56 2.55 2.54 2.53 1.80 1.78 1.77 0.00
Ph
OHC
Ph
89
0.94
10.18
1.00
1.00
1.04
1.04
1.00
2.00
2.09
f1 (ppm)
201.92
141.71
136.93
132.07
131.35
128.54
128.39
128.36
127.41
126.16
125.88
77.32
77.00
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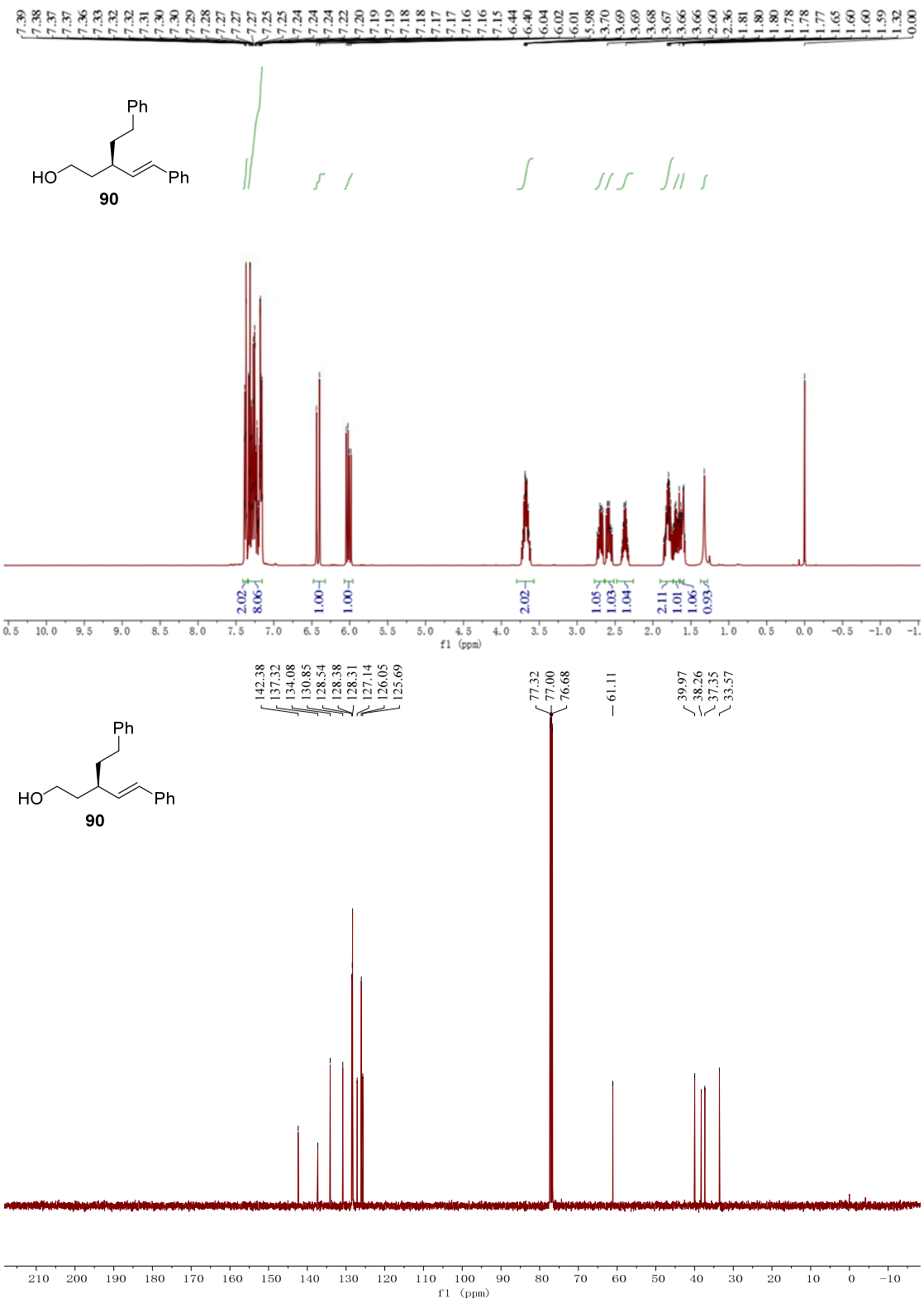
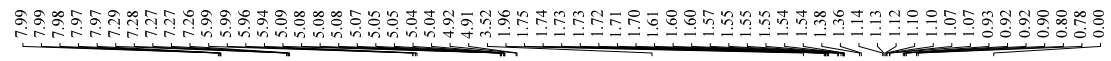
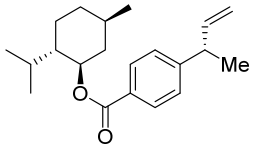
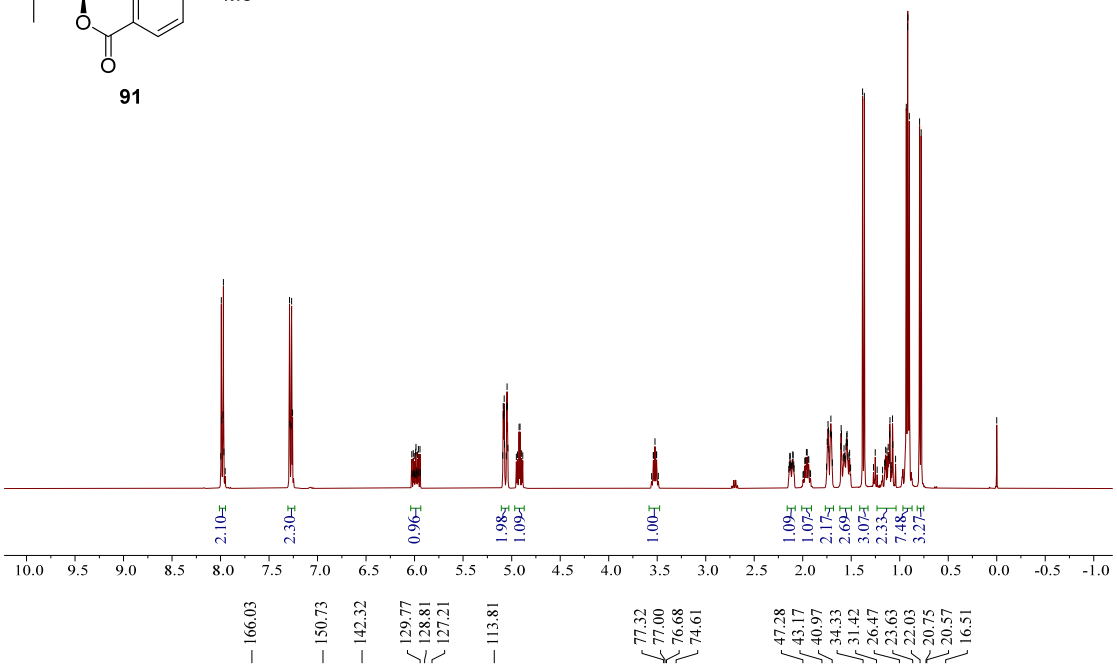
36.72
33.33
Ph
OHC
Ph
89
f1 (ppm)


Ph
HO
Ph
90
f1 (ppm)
Ph
HO
Ph
90
f1 (ppm)


7.99
7.99
7.98
7.97
7.97
7.29
7.28
7.27
7.27
7.26
5.99
5.99
5.96
5.94
5.09
5.08
5.08
5.08
5.07
5.05
5.05
5.04
5.04
4.92
4.91
3.52
1.96
1.75
1.74
1.73
1.73
1.72
1.71
1.70
1.61
1.60
1.60
1.57
1.55
1.55
1.55
1.54
1.54
1.38
1.36
1.14
1.13
1.12
1.10
1.10
1.07
1.07
0.93
0.92
0.92
0.90
0.80
0.78
0.00


Me
O
O

91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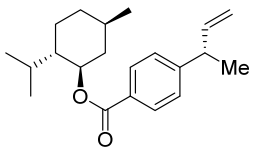
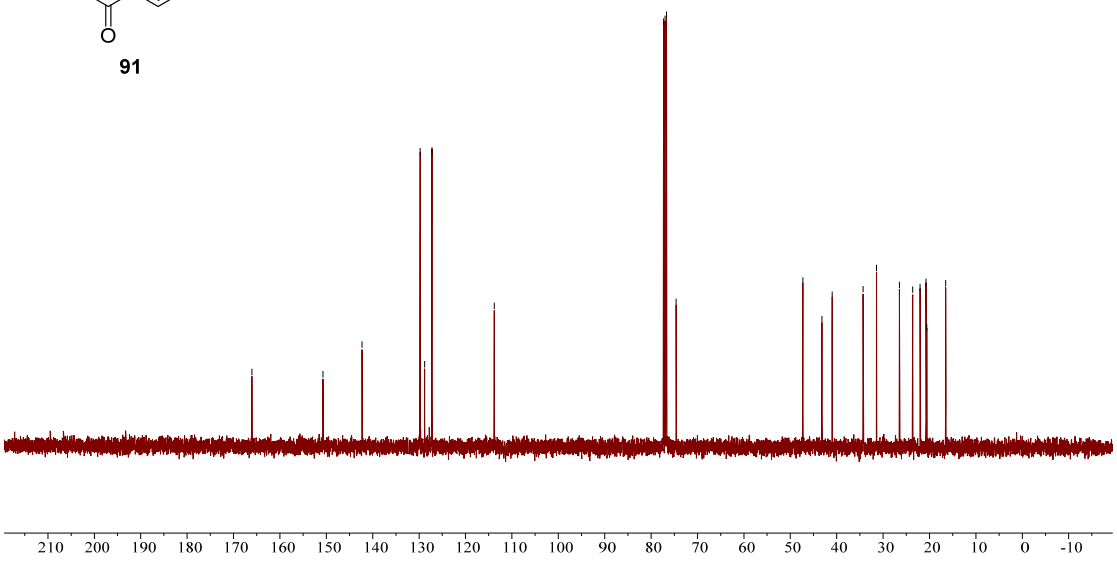
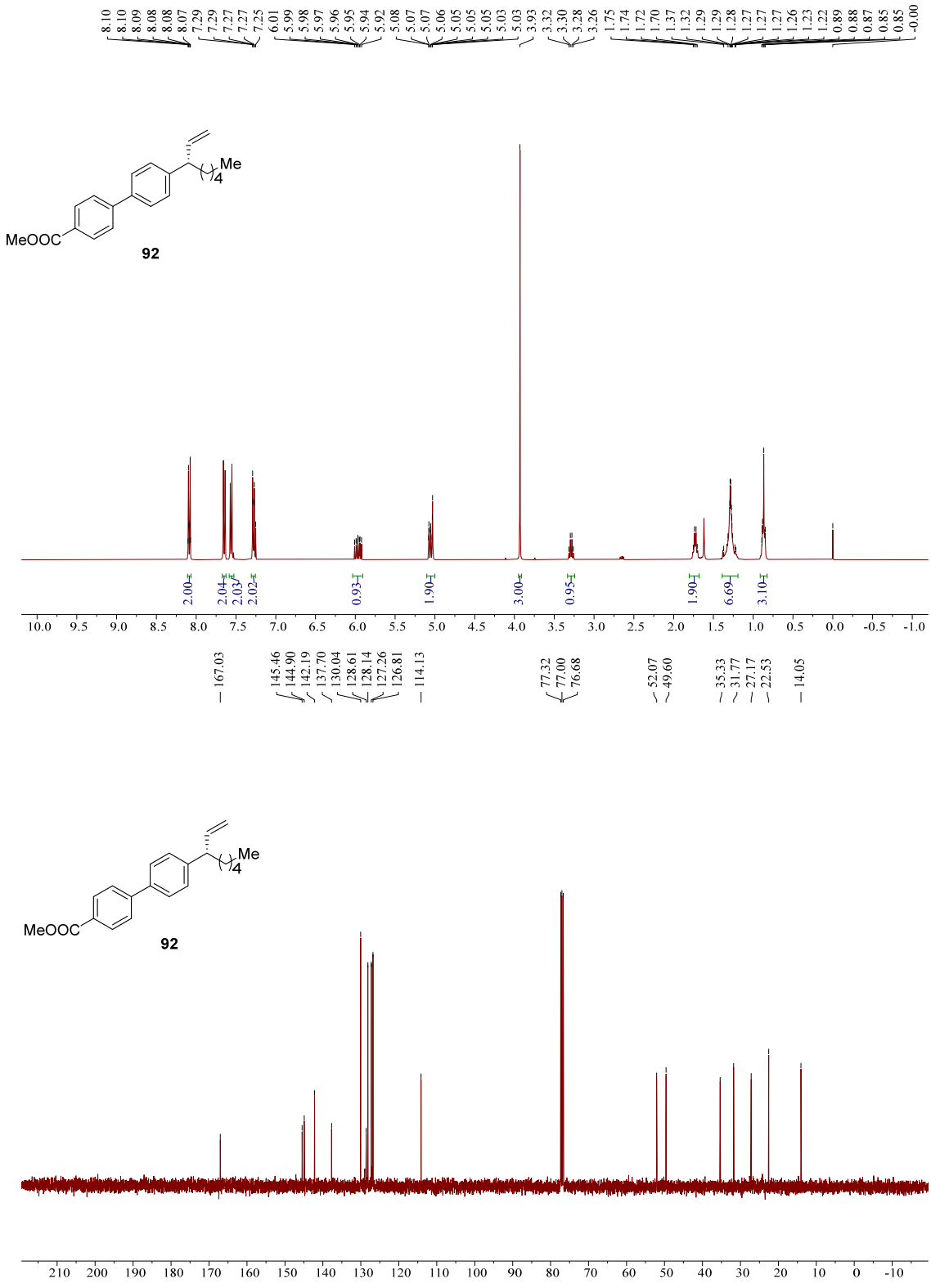
2.30
0.96
1.98
1.09
1.00
1.09
1.07
2.17
2.69
3.07
2.33
7.48
3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

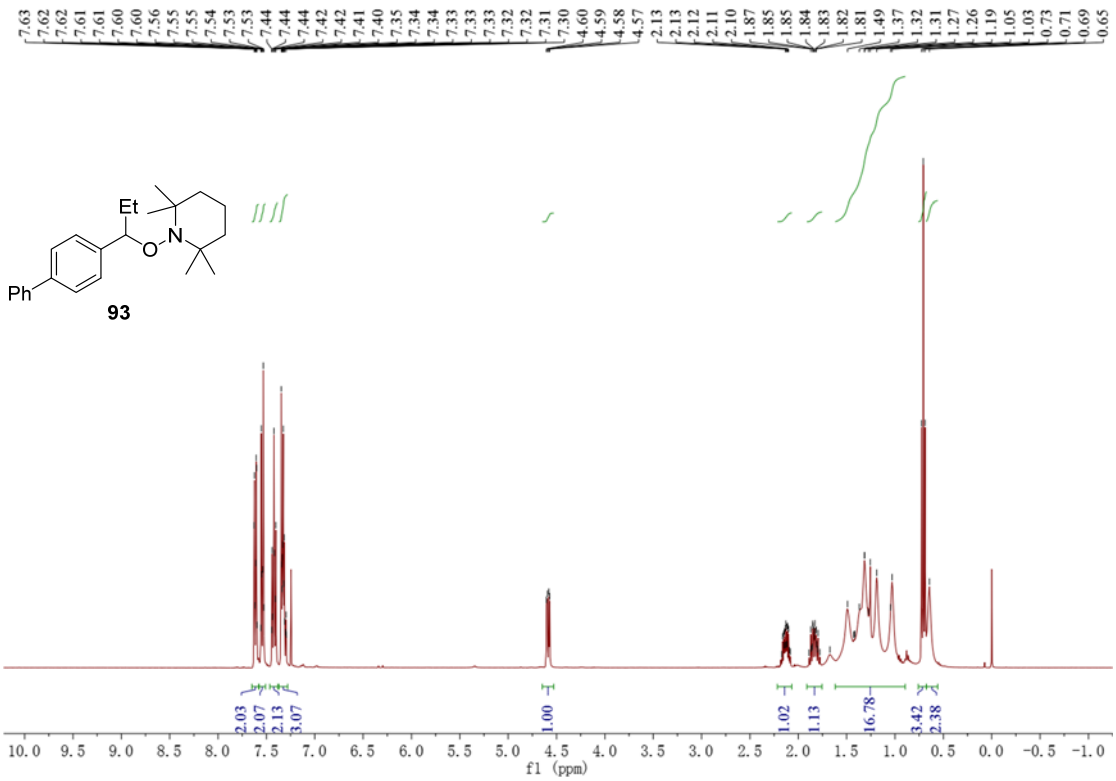
166.03
150.73
142.32
129.77
128.81
127.21
113.81
77.32
77.00
76.68
74.61
47.28
43.17
40.97
34.33
31.42
26.47
23.63
22.03
20.75
20.57
16.51

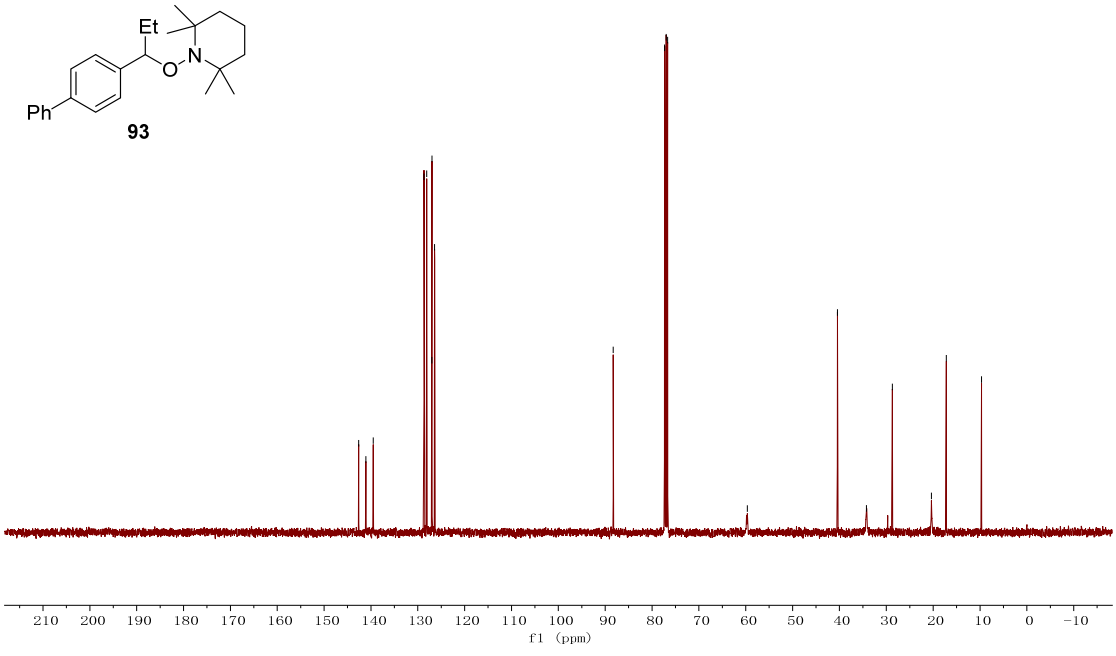

Me
O
O

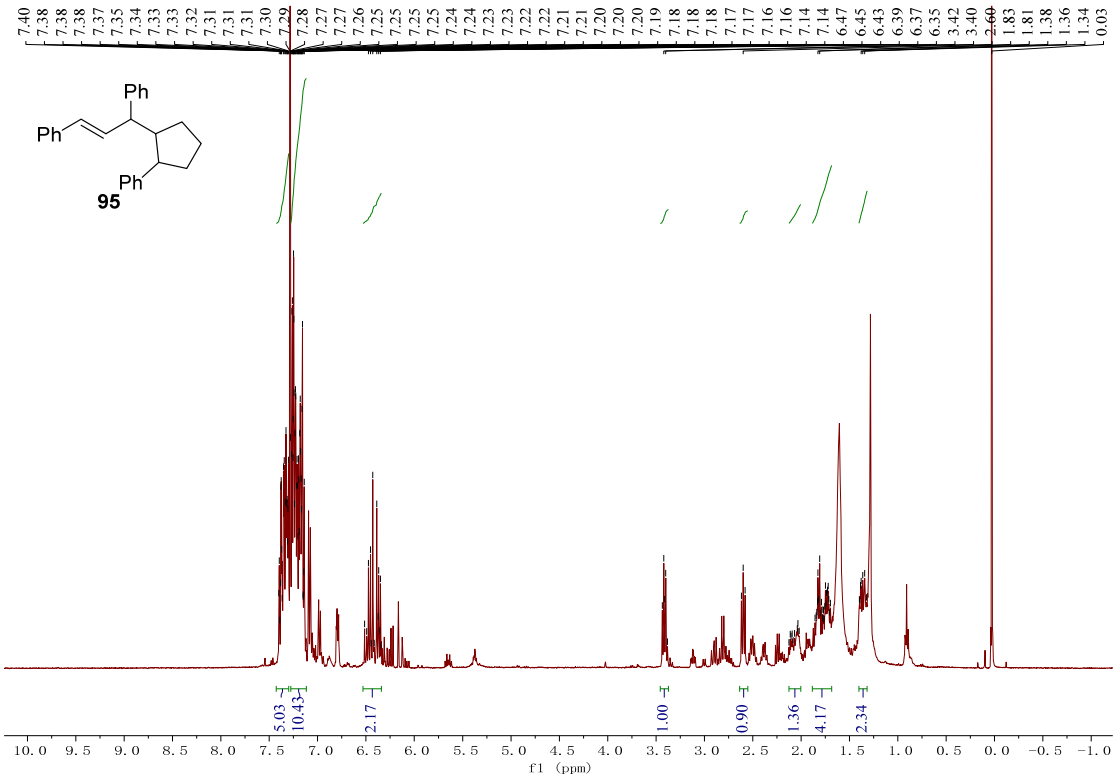
91

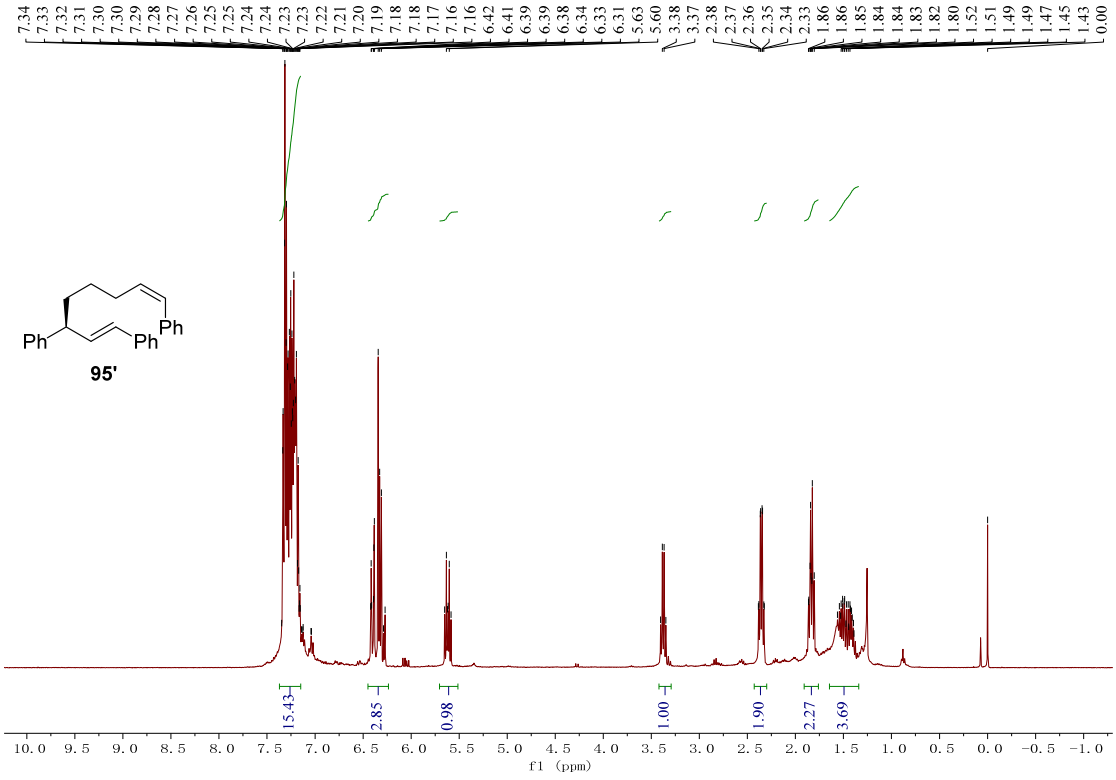

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


8.10 8.10 8.09 8.08 8.08 8.07 7.29 7.29 7.27 7.27 7.25 6.01 5.99 5.98 5.97 5.96 5.95 5.94 5.92 5.08 5.07 5.07 5.06 5.05 5.05 5.05 5.03 5.03 3.93 3.32 3.30 3.28 3.26 1.75 1.74 1.72 1.70 1.37 1.32 1.29 1.29 1.28 1.27 1.27 1.27 1.26 1.23 1.22 0.89 0.88 0.87 0.85 0.85 -0.00
Me
4
MeOOC
92
2.00 2.04 2.03 2.02 0.93 1.90 3.00 0.95 1.90 6.69 3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
167.03
145.46 144.90 142.19 137.70 130.04 128.61 128.14 127.26 126.81
114.13
77.32 77.00 76.68
52.07 49.60
35.33 31.77 27.17 22.53
14.05
Me
4
MeOOC
92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

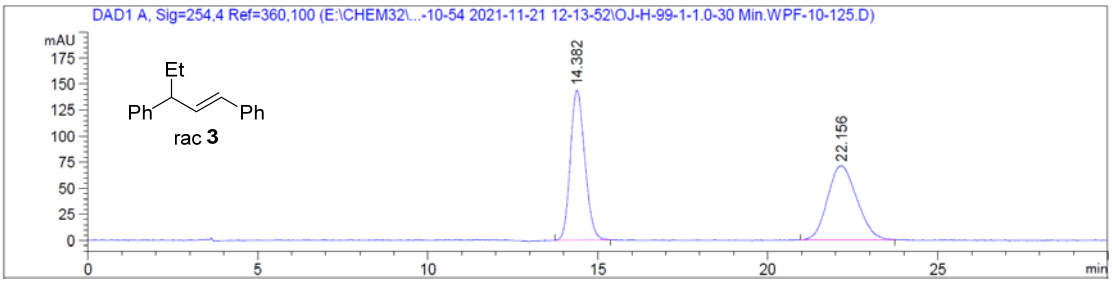

Et
N
O
Ph
93
f1 (ppm)


Et
N
O
Ph
93
f1 (ppm)


Ph
Ph
Ph
95
f1 (ppm)

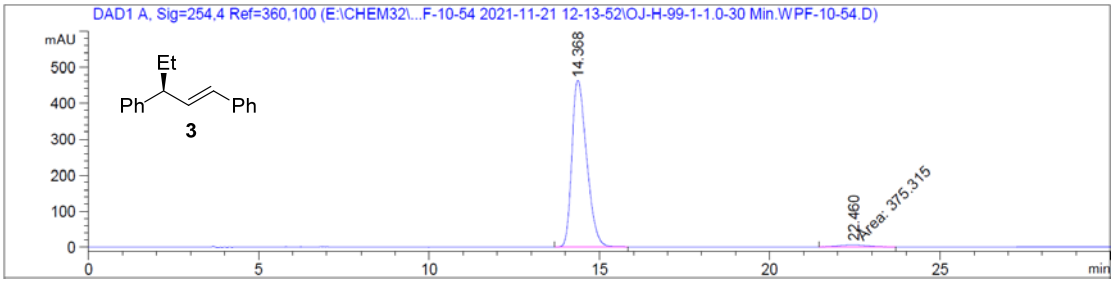

Ph
Ph
Ph
95'
f1 (ppm)

HPLC spectra



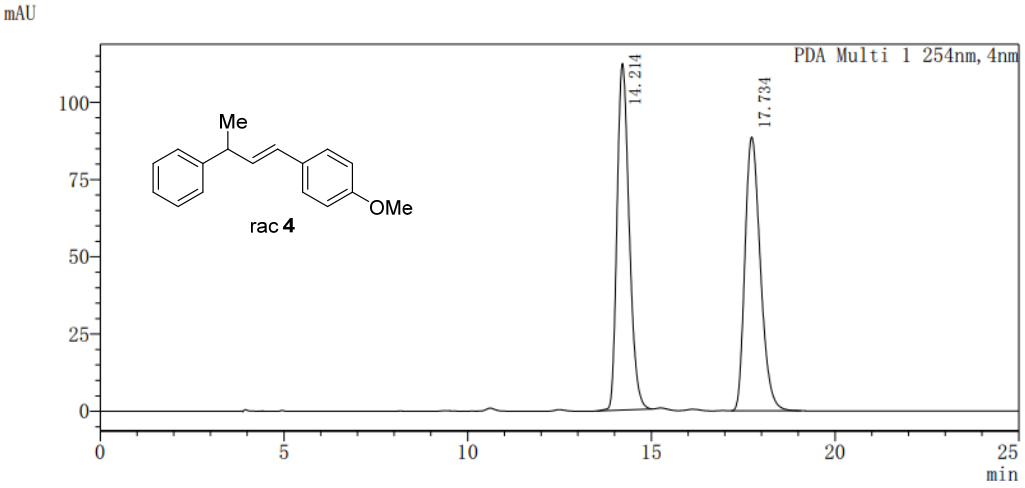
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.382	BB	0.4469	4259.29492	144.07921	49.9422
2	22.156	VV R	0.7051	4269.14990	71.24496	50.0578
Totals :				8528.44482	215.32417	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

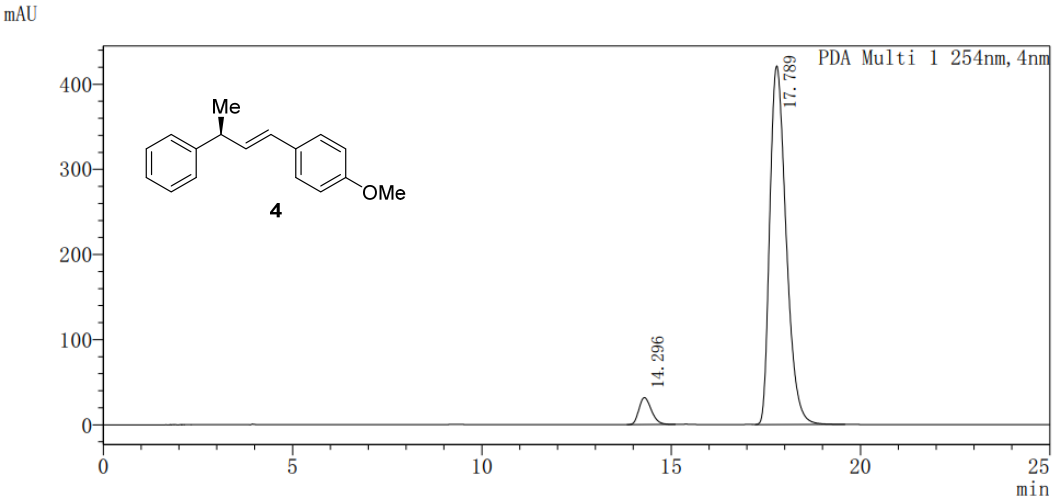
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.368	VV R	0.4474	1.40477e4	463.68643	97.3978
2	22.460	MM	0.9322	375.31482	6.71019	2.6022
Totals :				1.44230e4	470.39662	



Peak Table

PDA Ch1 254nm

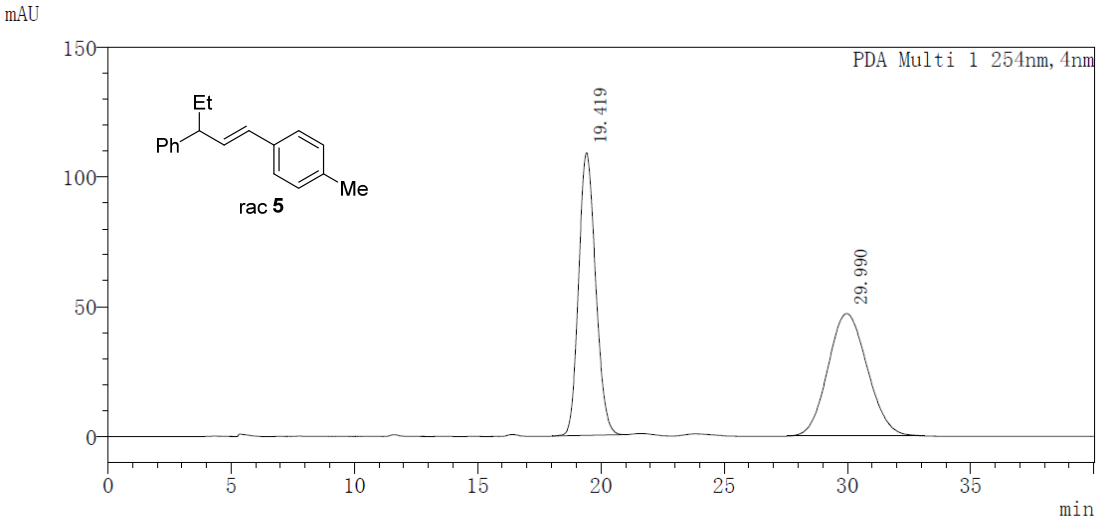
Peak#	Ret. Time	Area	Area%
1	14.214	2577394	49.850
2	17.734	2592879	50.150



Peak Table

PDA Ch1 254nm

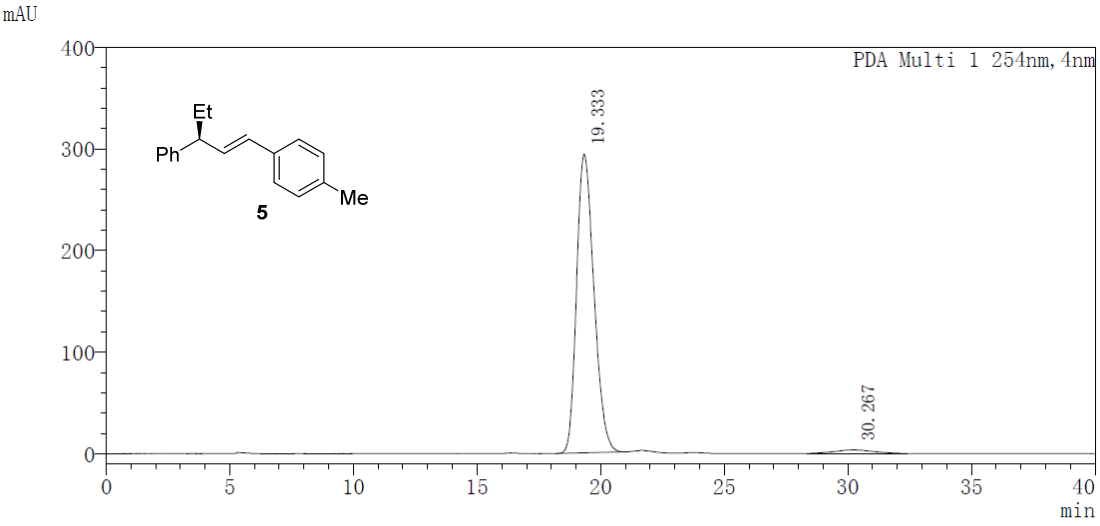
Peak#	Ret. Time	Area	Area%
1	14.296	724322	5.413
2	17.789	12657920	94.587



Peak Table

PDA Ch1 254nm

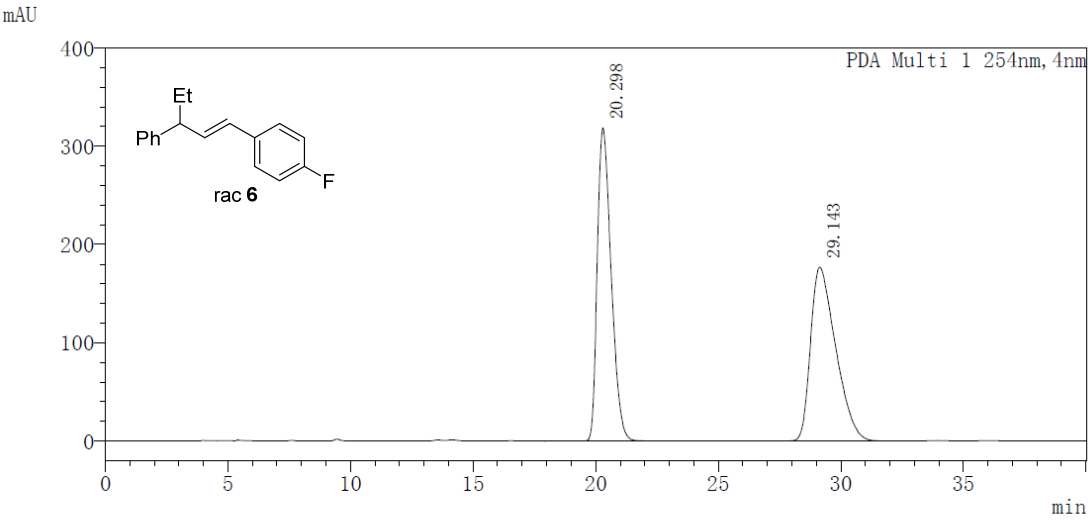
Peak#	Ret. Time	Area	Area%
1	19.419	5236929	49.933
2	29.990	5250877	50.067



Peak Table

PDA Ch1 254nm

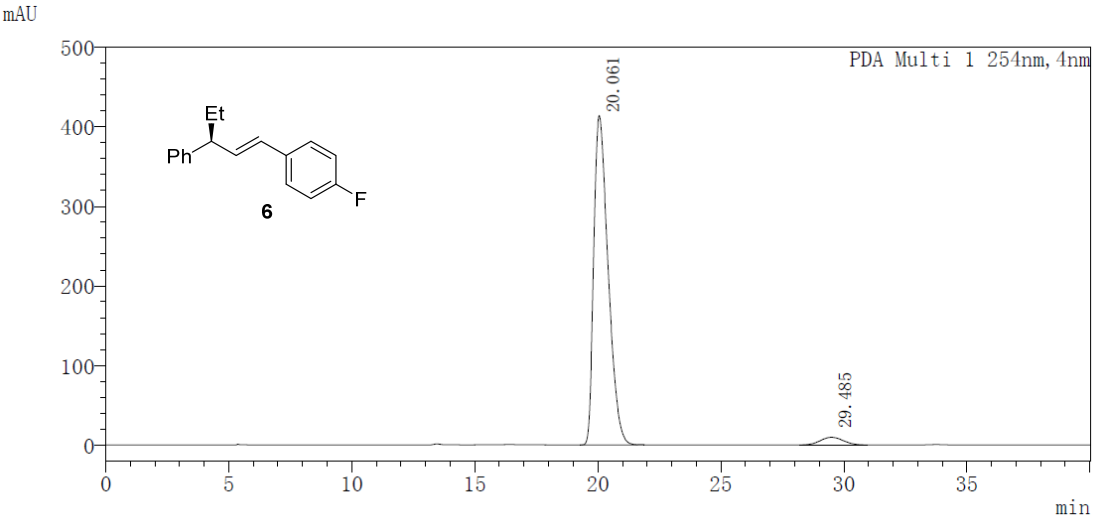
Peak#	Ret. Time	Area	Area%
1	19.333	14384788	97.442
2	30.267	377594	2.558



Peak Table

PDA Ch1 254nm

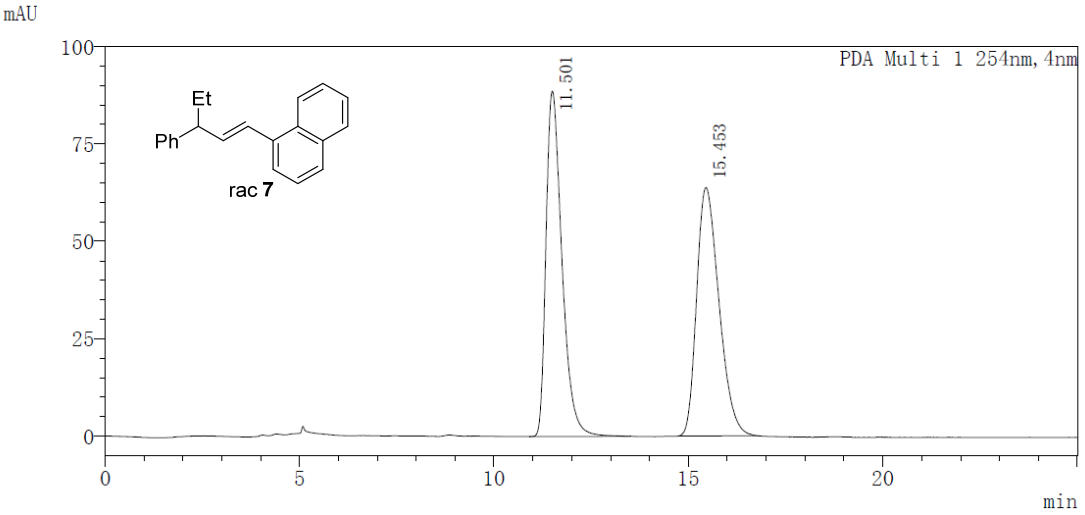
Peak#	Ret. Time	Area	Area%
1	20.298	12531163	49.903
2	29.143	12579794	50.097



Peak Table

PDA Ch1 254nm

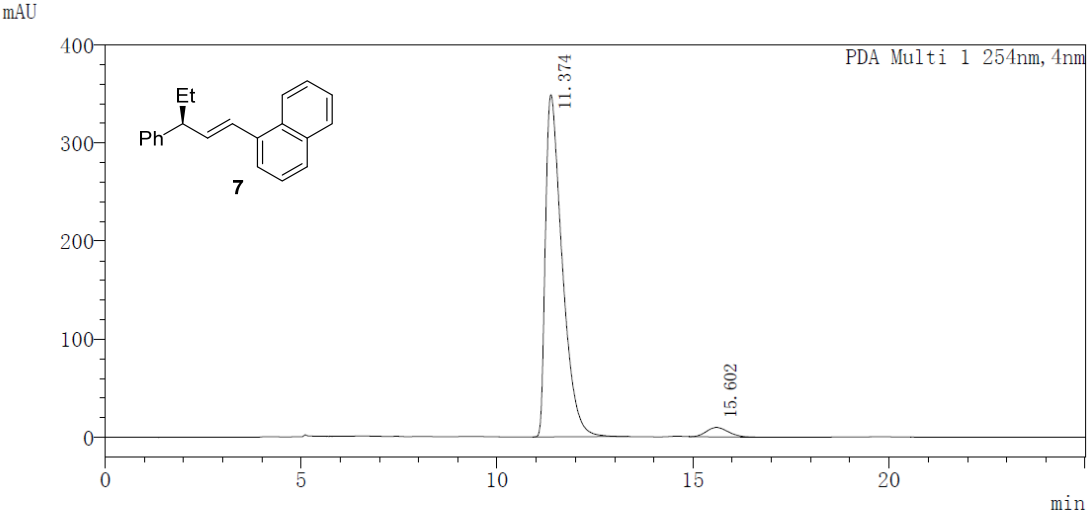
Peak#	Ret. Time	Area	Area%
1	20.061	16816474	96.328
2	29.485	641119	3.672



Peak Table

PDA Ch1 254nm

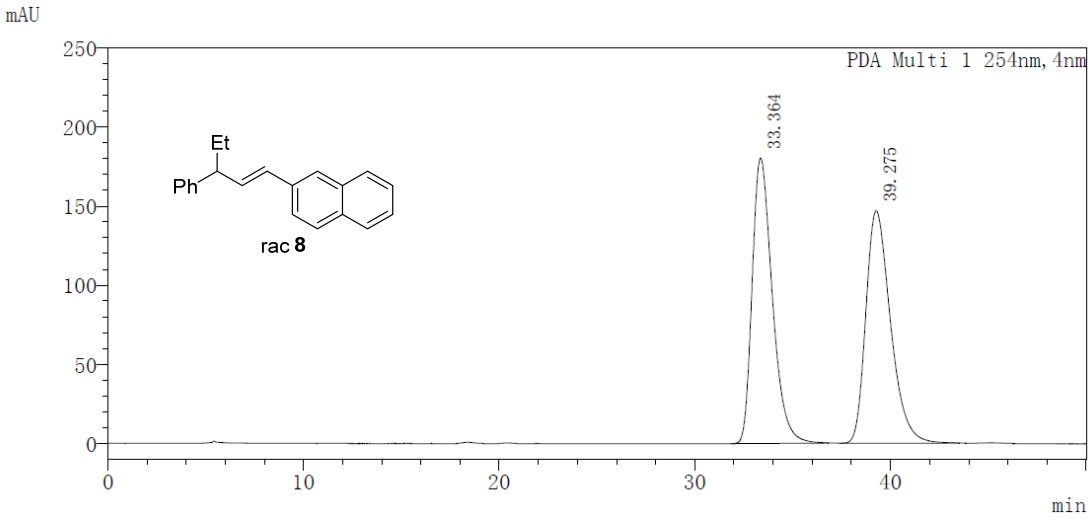
Peak#	Ret. Time	Area	Area%
1	11.501	2531146	49.829
2	15.453	2548493	50.171



Peak Table

PDA Ch1 254nm

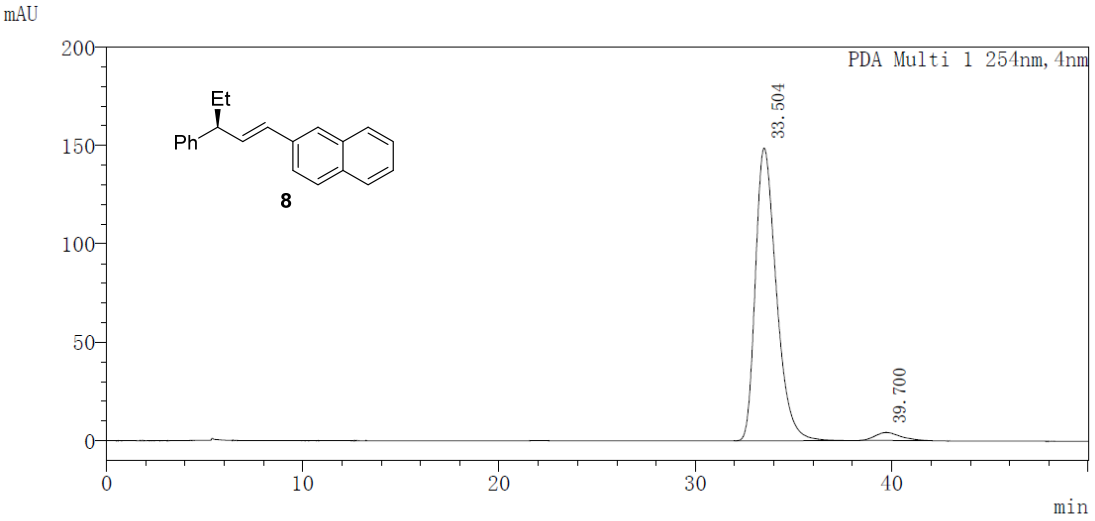
Peak#	Ret. Time	Area	Area%
1	11.374	10362269	96.570
2	15.602	368003	3.430



Peak Table

PDA Ch1 254nm

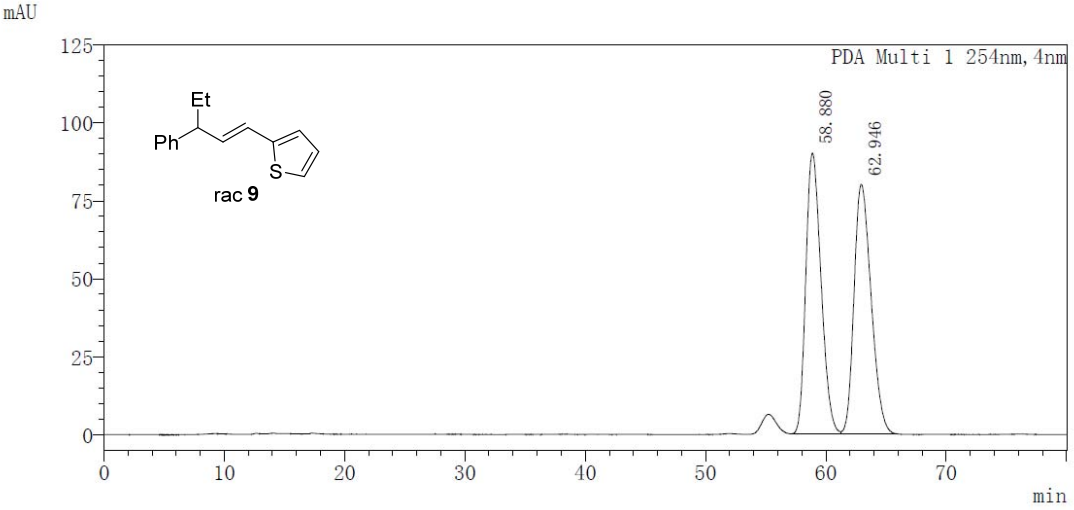
Peak#	Ret. Time	Area	Area%
1	33.364	12924408	50.058
2	39.275	12894276	49.942



Peak Table

PDA Ch1 254nm

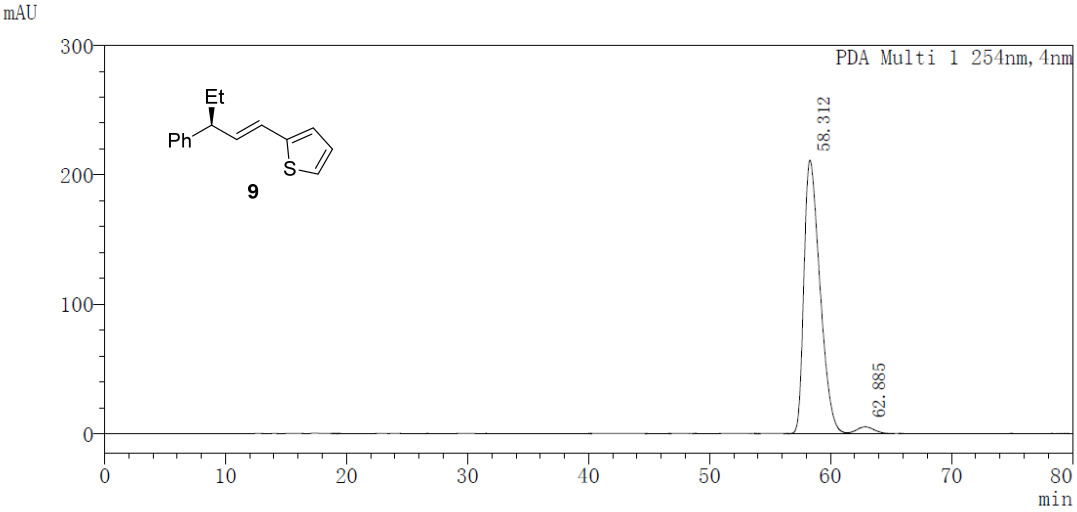
Peak#	Ret. Time	Area	Area%
1	33.504	11023930	96.760
2	39.700	369169	3.240



Peak Table

PDA Ch1 254nm

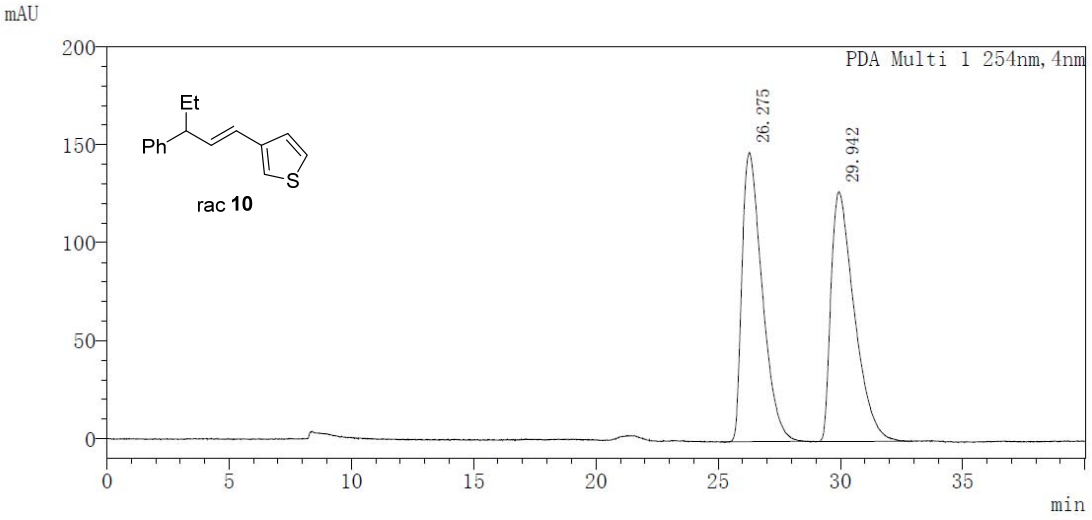
Peak#	Ret. Time	Area	Area%
1	58.880	7920281	50.026
2	62.946	7912176	49.974



Peak Table

PDA Ch1 254nm

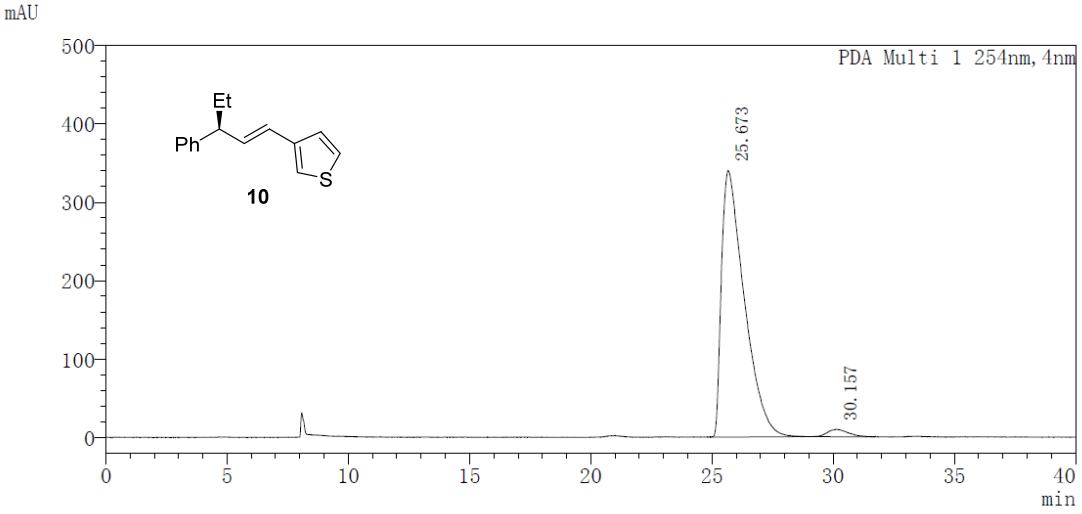
Peak#	Ret. Time	Area	Area%
1	58.312	19454816	97.436
2	62.885	511934	2.564



Peak Table

PDA Ch1 254nm

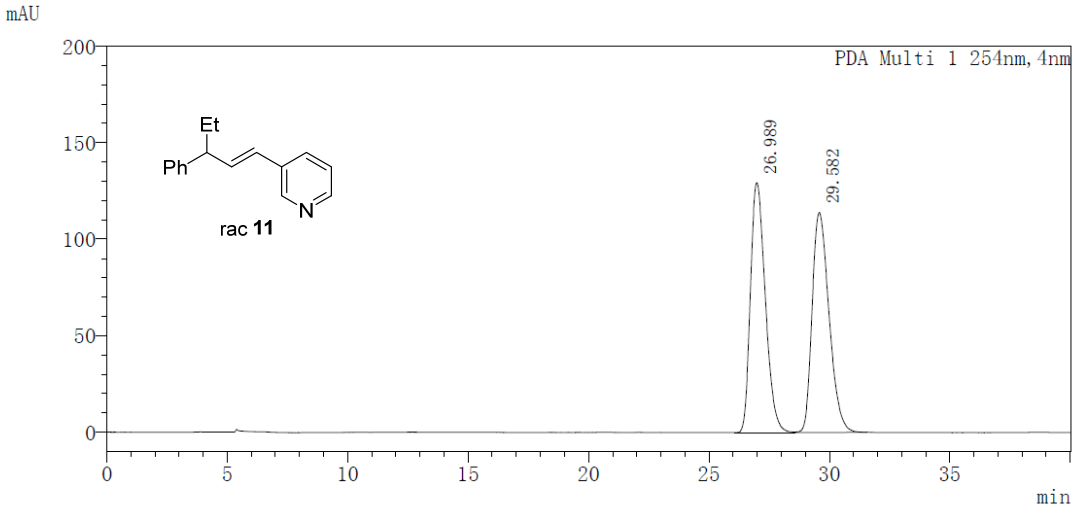
Peak#	Ret. Time	Area	Area%
1	26.275	8496280	50.029
2	29.942	8486277	49.971



Peak Table

PDA Ch1 254nm

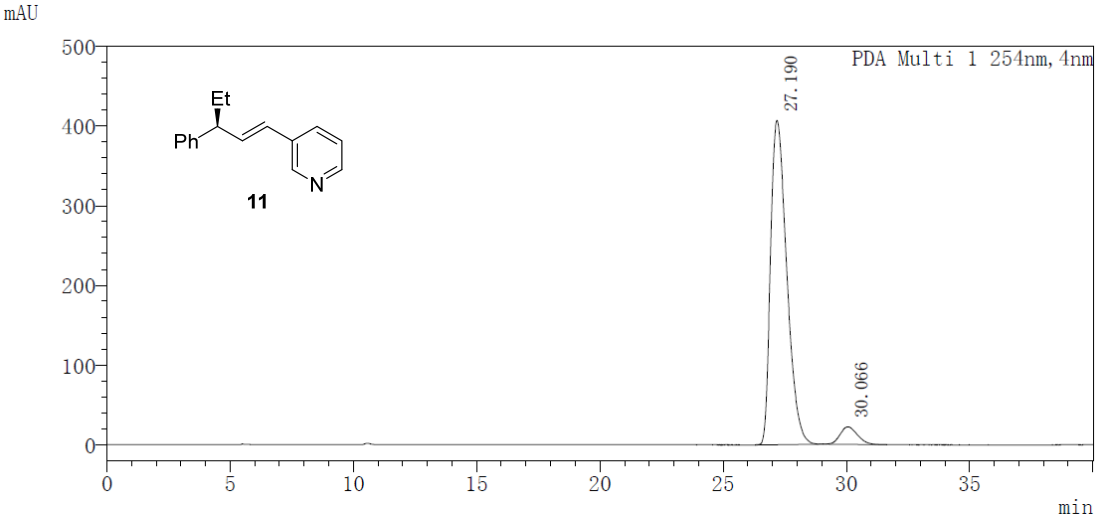
Peak#	Ret. Time	Area	Area%
1	25.673	22295426	97.559
2	30.157	557783	2.441



Peak Table

PDA Ch1 254nm

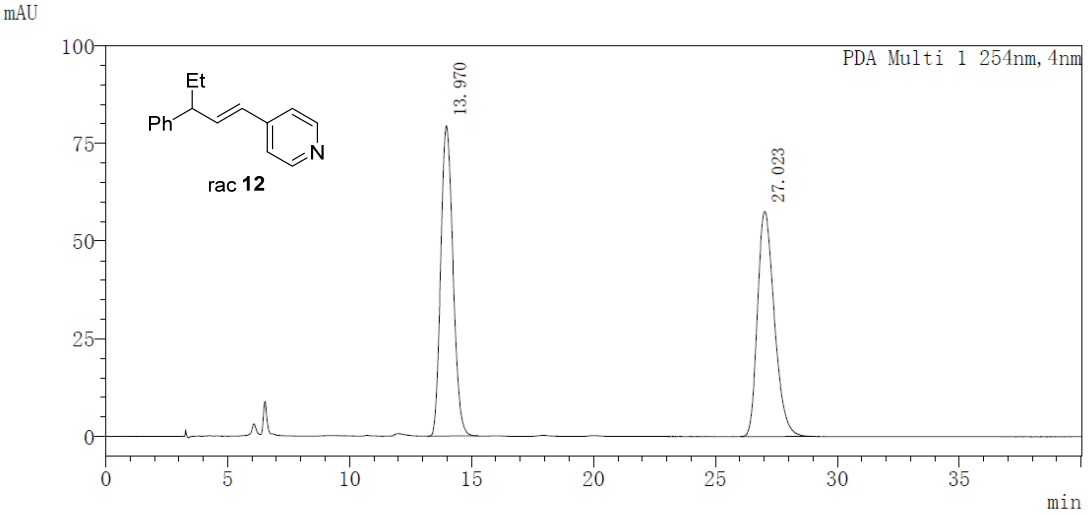
Peak#	Ret. Time	Area	Area%
1	26.989	5566183	49.932
2	29.582	5581449	50.068



Peak Table

PDA Ch1 254nm

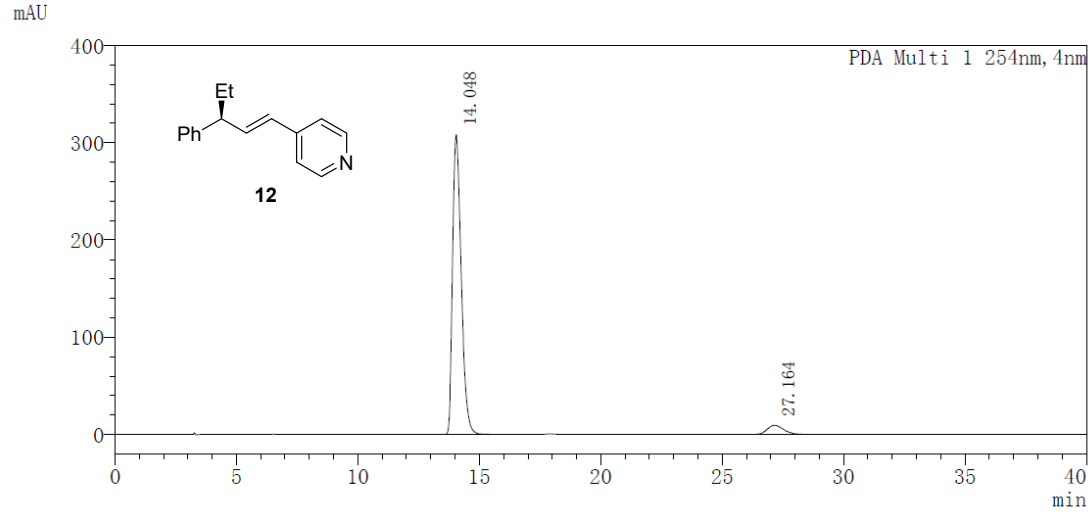
Peak#	Ret. Time	Area	Area%
1	27.190	18591119	94.458
2	30.066	1090787	5.542



Peak Table

PDA Ch1 254nm

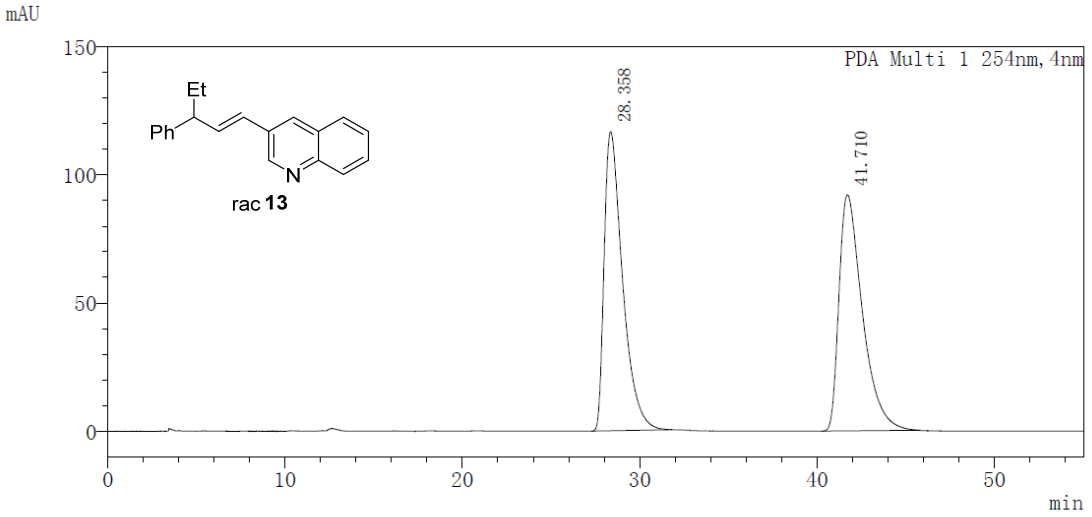
Peak#	Ret. Time	Area	Area%
1	13.970	2773915	50.042
2	27.023	2769303	49.958



Peak Table

PDA Ch1 254nm

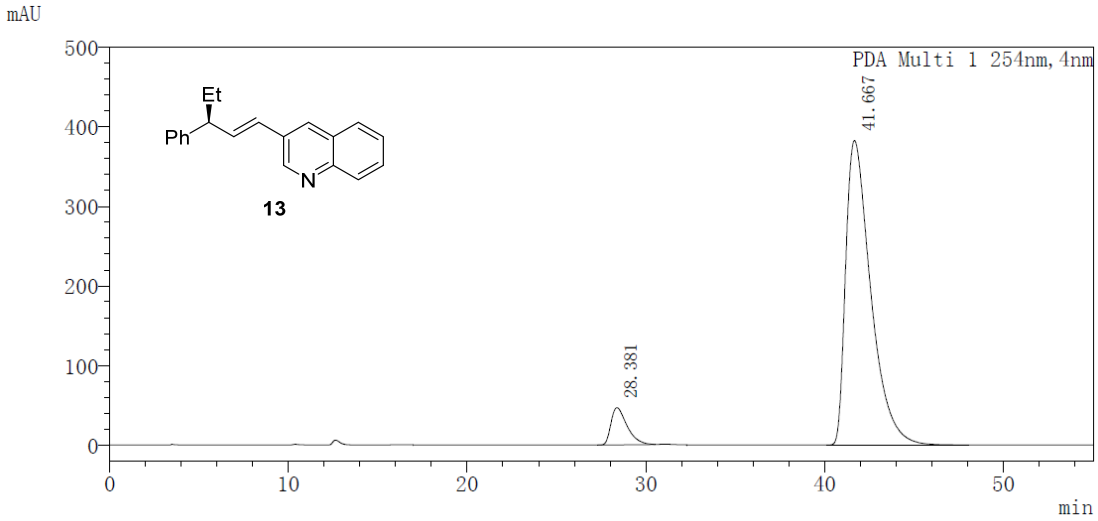
Peak#	Ret. Time	Area	Area%
1	14.048	7663201	94.584
2	27.164	438814	5.416



Peak Table

PDA Ch1 254nm

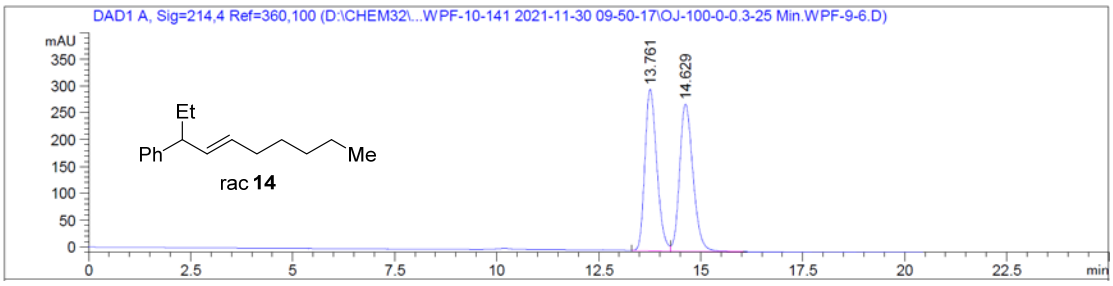
Peak#	Ret. Time	Area	Area%
1	28.358	8422308	49.912
2	41.710	8451944	50.088



Peak Table

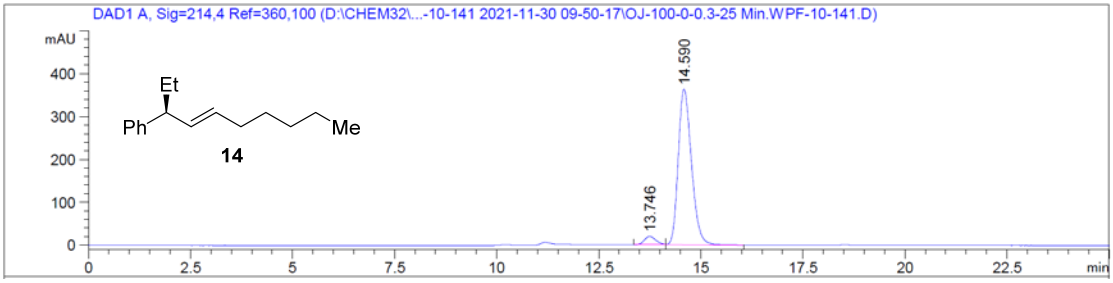
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.381	2919971	7.246
2	41.667	37377632	92.754



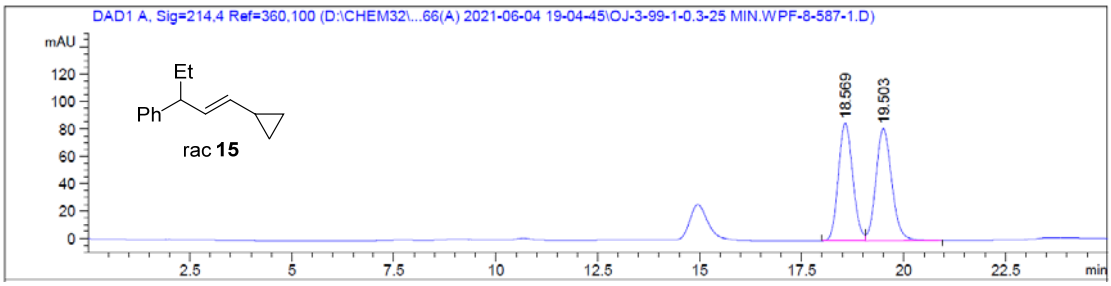
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.761	BV	0.3143	6093.77441	300.86780	49.3990
2	14.629	VB	0.3516	6242.06104	274.18552	50.6010
Totals :				1.23358e4	575.05331	



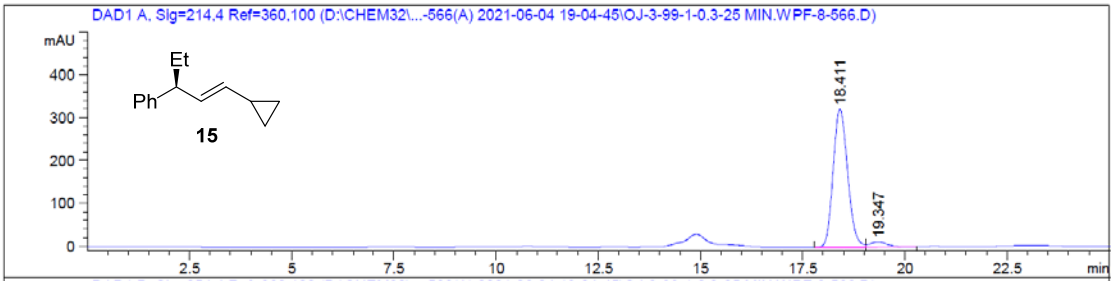
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.746	BV	0.3023	381.19427	19.30851	4.4636
2	14.590	VB	0.3506	8158.77734	362.40811	95.5364
Totals :				8539.97162	381.71663	



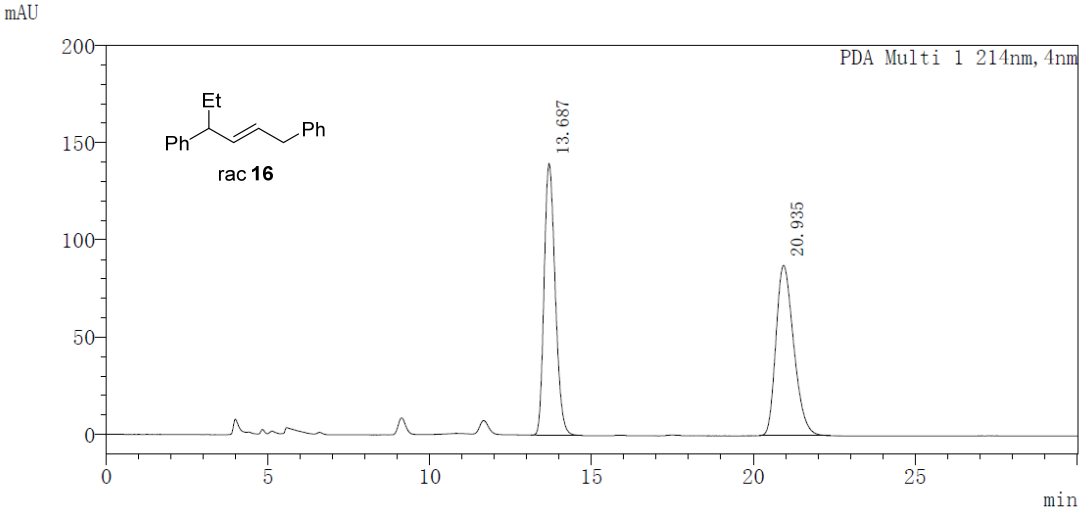
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.569	BV	0.3858	2101.98364	85.80315	48.7623
2	19.503	VB	0.4171	2208.68994	81.78945	51.2377
Totals :				4310.67358	167.59261	



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

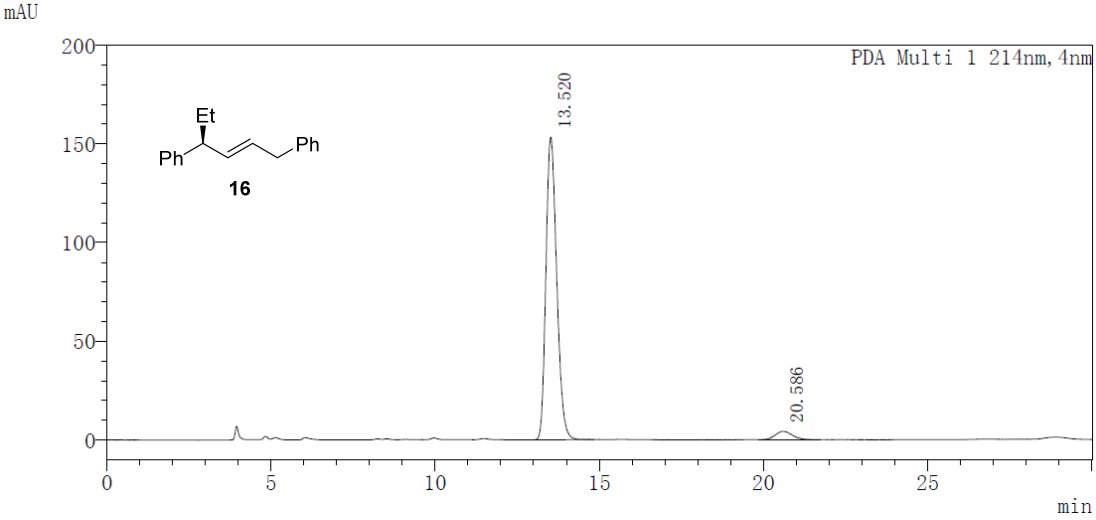
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.411	BV	0.3825	7887.74170	321.24454	95.9495
2	19.347	VB	0.4193	332.98212	11.86956	4.0505
Totals :				8220.72382	333.11409	



Peak Table

PDA Ch1 214nm

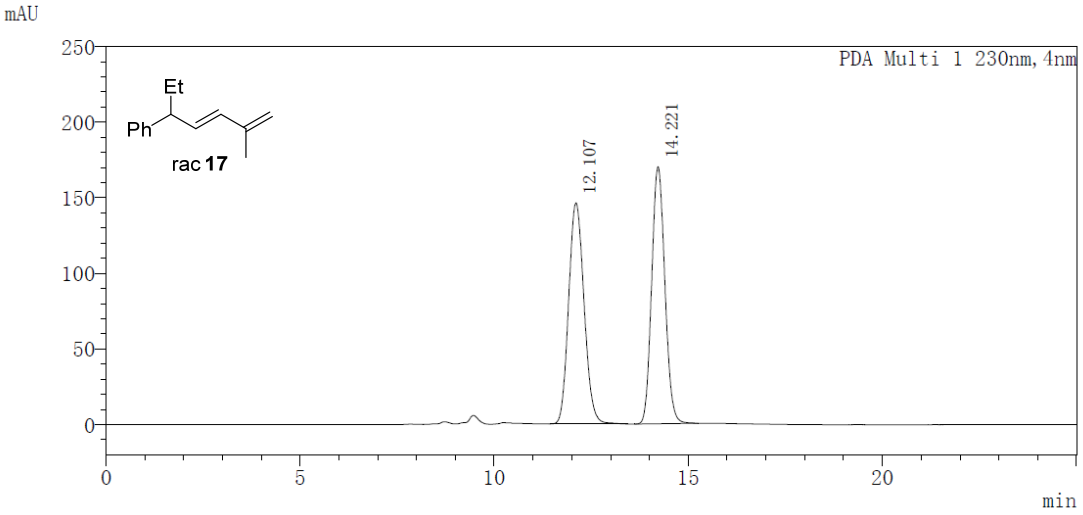
Peak#	Ret. Time	Area	Area%
1	13.687	3334125	49.891
2	20.935	3348751	50.109



Peak Table

PDA Ch1 214nm

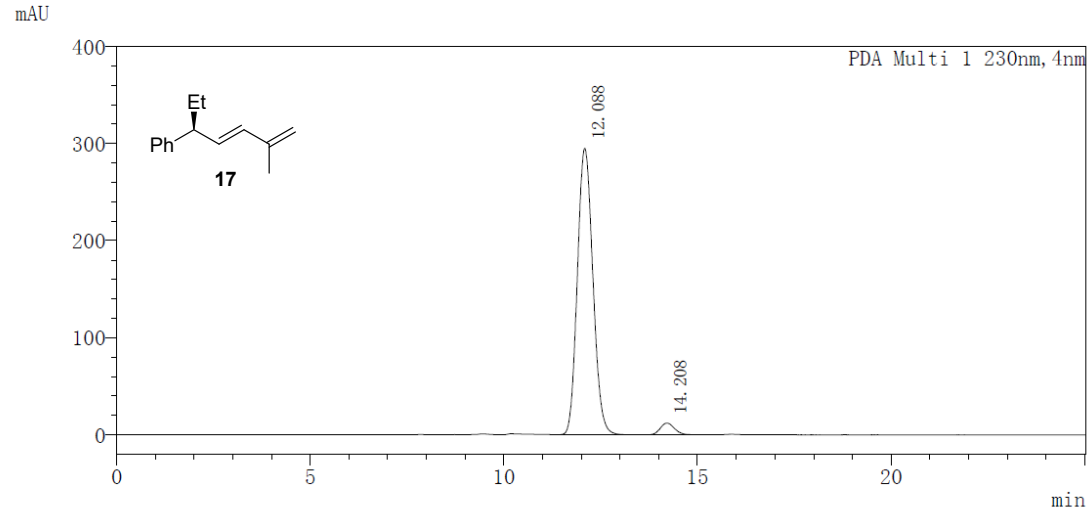
Peak#	Ret. Time	Area	Area%
1	13.520	3505032	95.847
2	20.586	151857	4.153



Peak Table

PDA Ch1 230nm

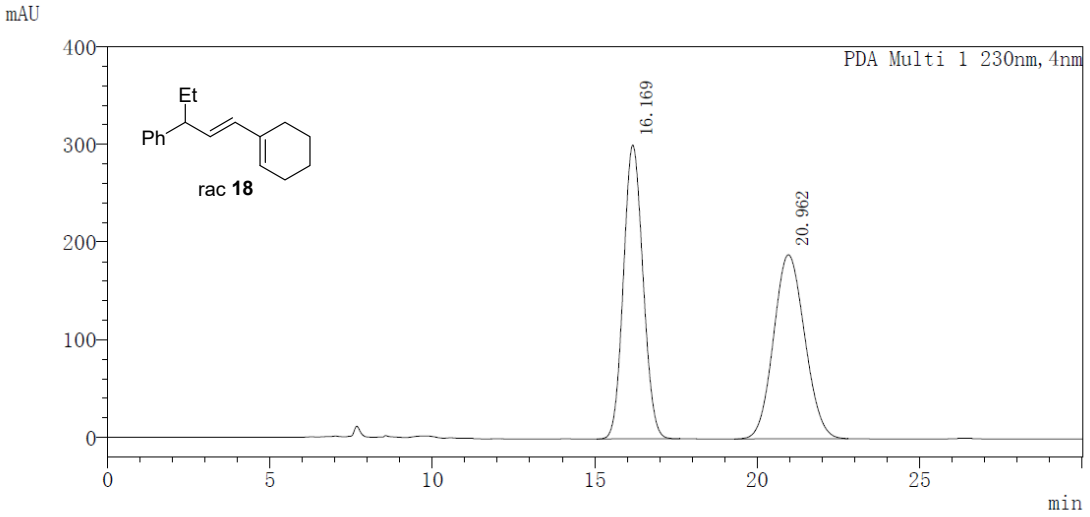
Peak#	Ret. Time	Area	Area%
1	12.107	4039529	50.154
2	14.221	4014672	49.846



Peak Table

PDA Ch1 230nm

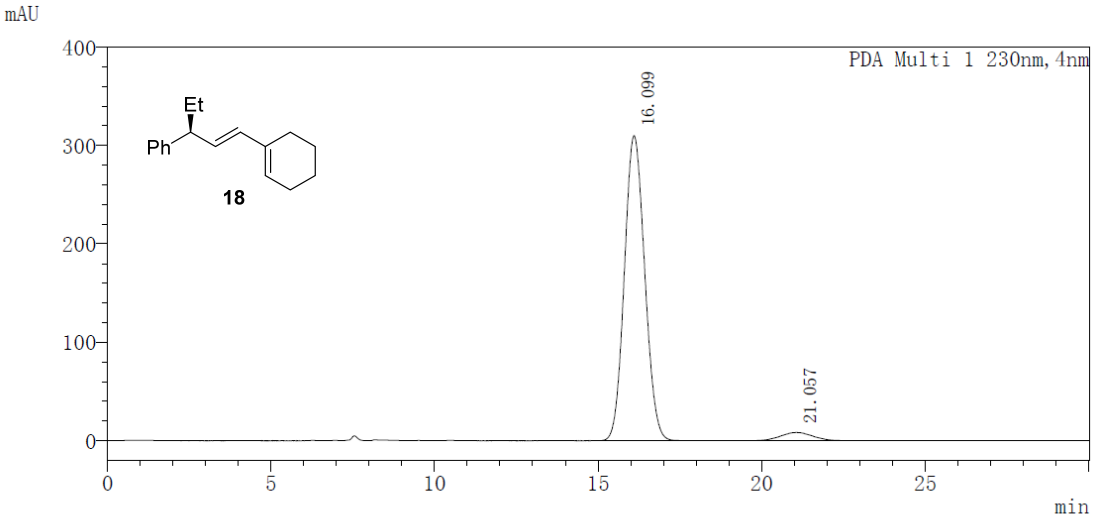
Peak#	Ret. Time	Area	Area%
1	12.088	8222229	96.422
2	14.208	305143	3.578



Peak Table

PDA Ch1 230nm

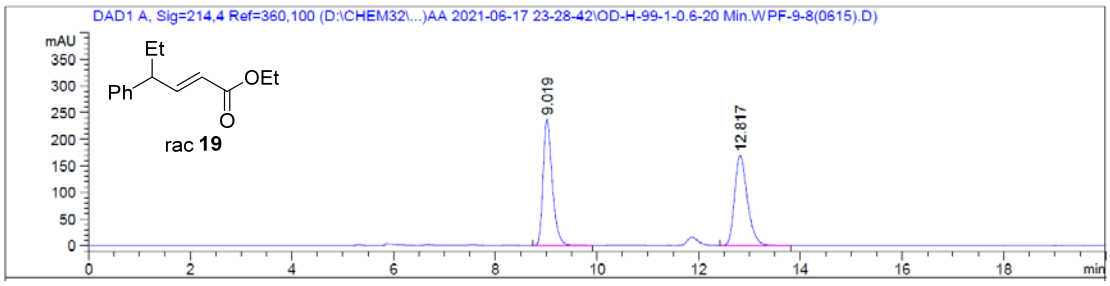
Peak#	Ret. Time	Area	Area%
1	16.169	12611418	50.062
2	20.962	12580262	49.938



Peak Table

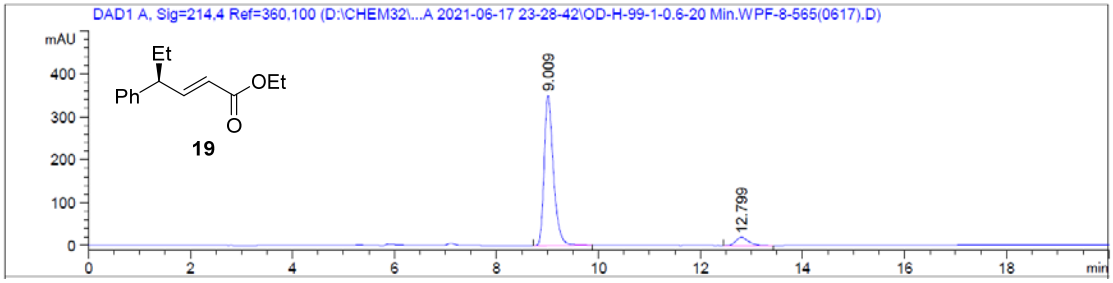
PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	16.099	13395331	96.029
2	21.057	553967	3.971



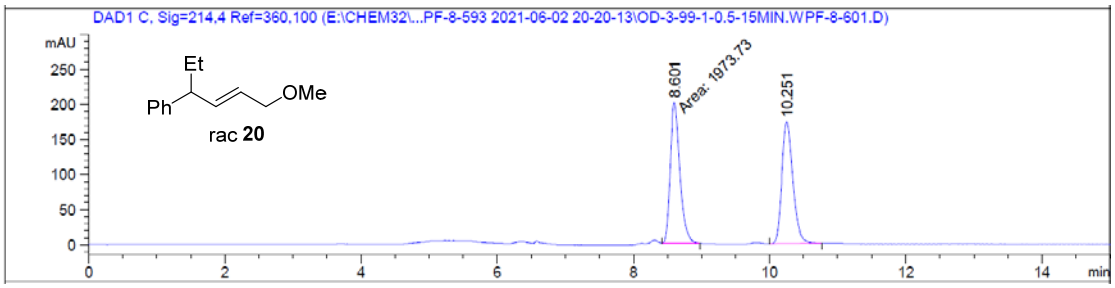
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.019	BB	0.1899	2969.22778	237.44185	50.1620
2	12.817	BB	0.2646	2950.04590	169.84706	49.8380
Totals :				5919.27368	407.28891	



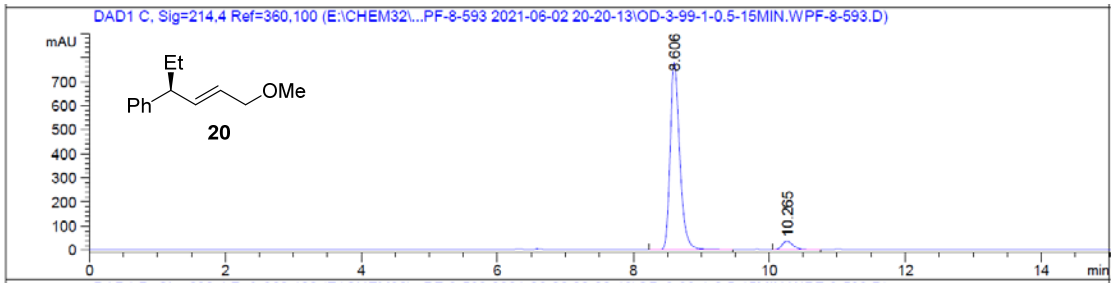
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.009	BB	0.1907	4403.69189	350.16611	93.0148
2	12.799	BB	0.2639	330.70566	19.11171	6.9852
Totals :				4734.39755	369.27781	



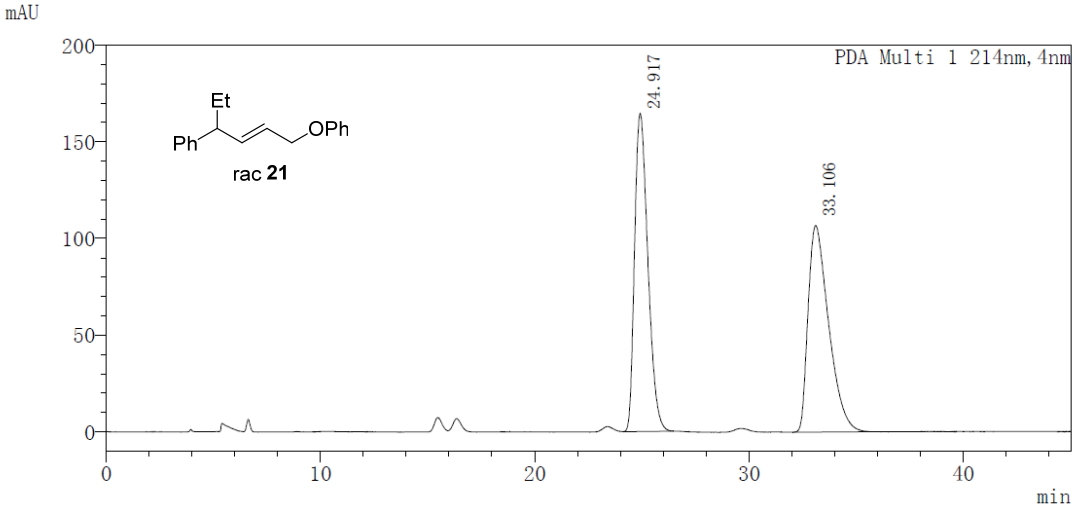
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.601	MM	0.1635	1973.73047	201.19806	50.1654
2	10.251	BB	0.1715	1960.71582	173.97925	49.8346
Totals :				3934.44629	375.17731	



Signal 3: DAD1 C, Sig=214,4 Ref=360,100

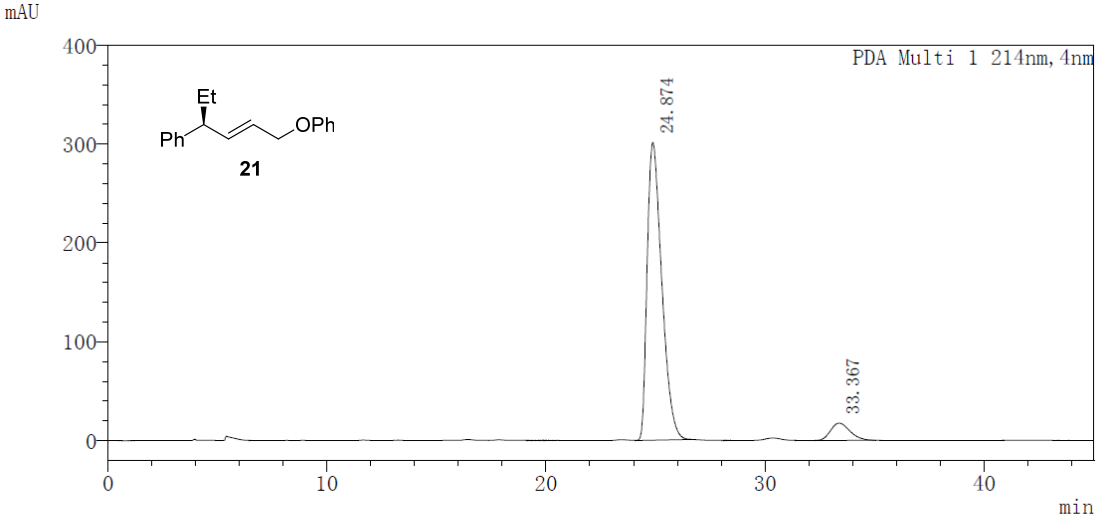
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.606	VV R	0.1522	7730.57520	776.23688	94.8136
2	10.265	BV R	0.1760	422.87125	37.38622	5.1864
Totals :				8153.44644	813.62309	



Peak Table

PDA Ch1 214nm

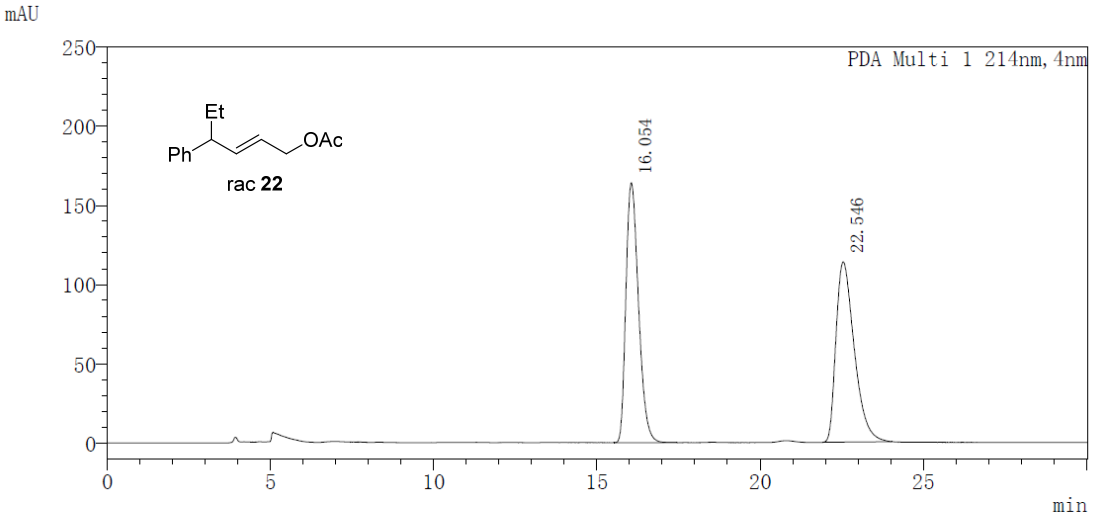
Peak#	Ret. Time	Area	Area%
1	24.917	7102190	49.854
2	33.106	7143716	50.146



Peak Table

PDA Ch1 214nm

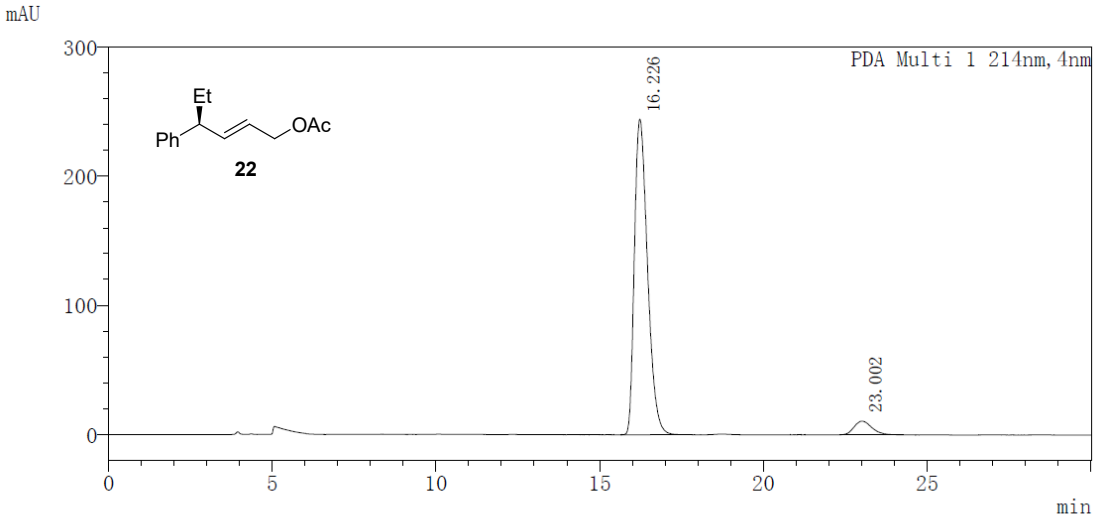
Peak#	Ret. Time	Area	Area%
1	24.874	13944820	92.850
2	33.367	1073874	7.150



Peak Table

PDA Ch1 214nm

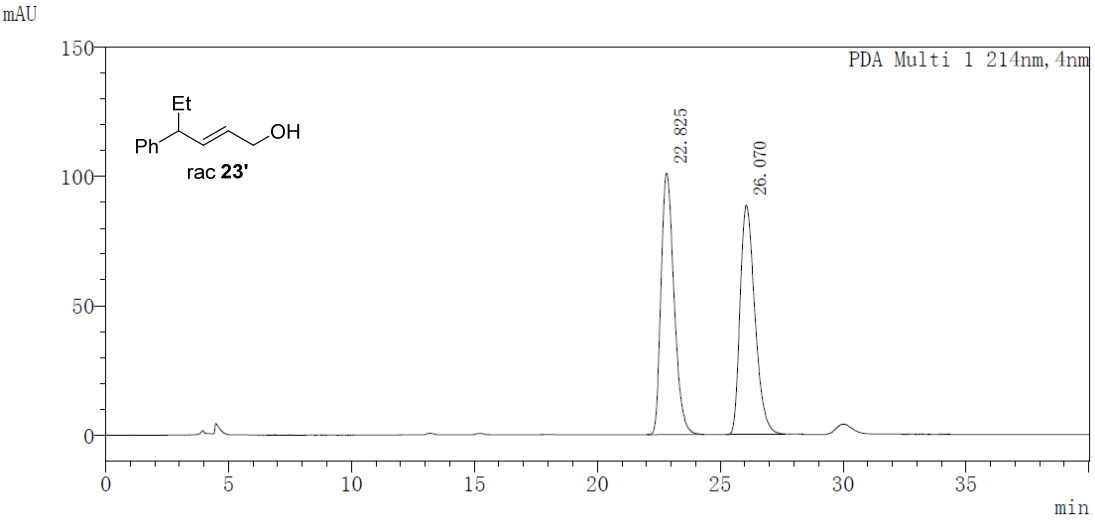
Peak#	Ret. Time	Area	Area%
1	16.054	4403116	49.876
2	22.546	4425062	50.124



Peak Table

PDA Ch1 214nm

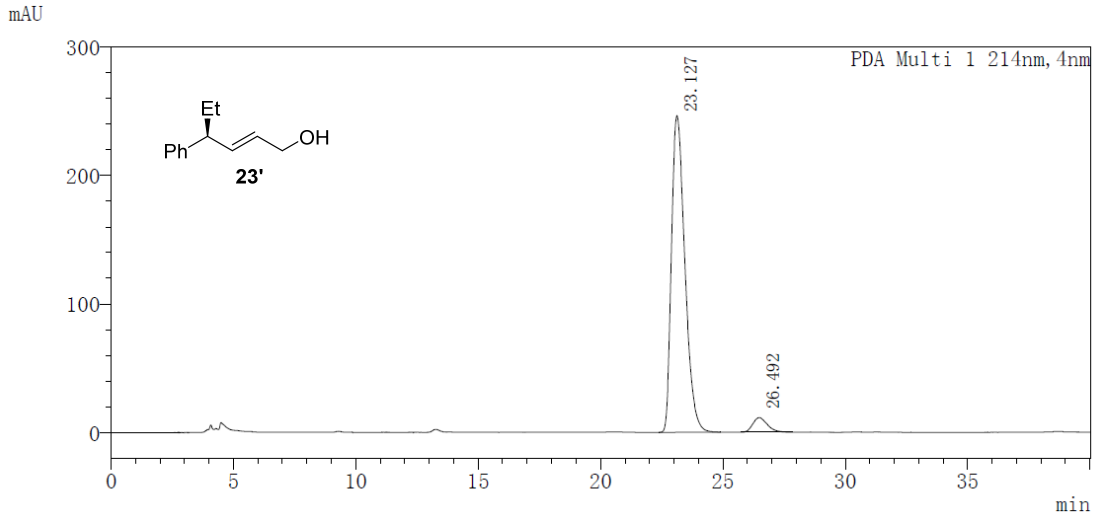
Peak#	Ret. Time	Area	Area%
1	16.226	6809918	94.379
2	23.002	405552	5.621



Peak Table

PDA Ch1 214nm

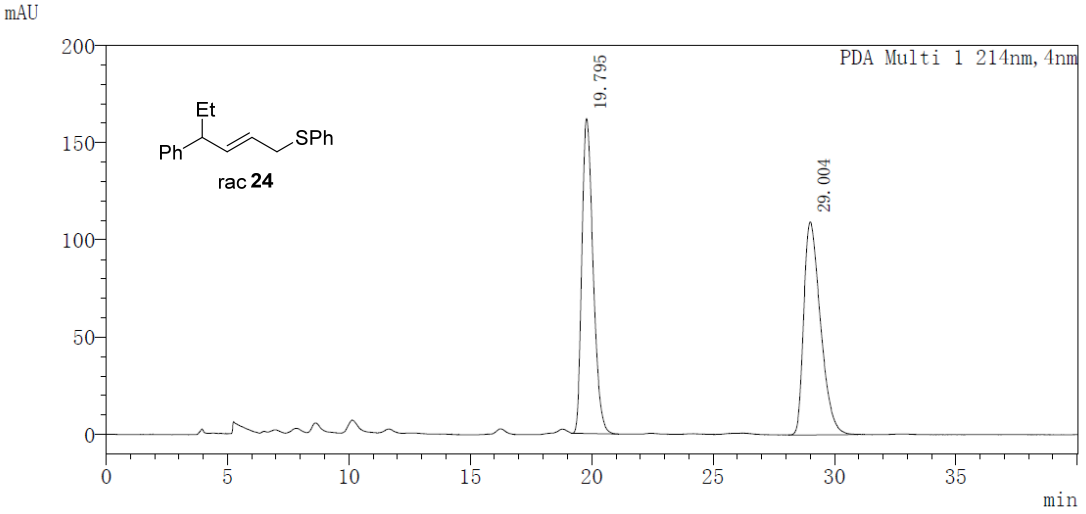
Peak#	Ret. Time	Area	Area%
1	22.825	3715738	50.048
2	26.070	3708579	49.952



Peak Table

PDA Ch1 214nm

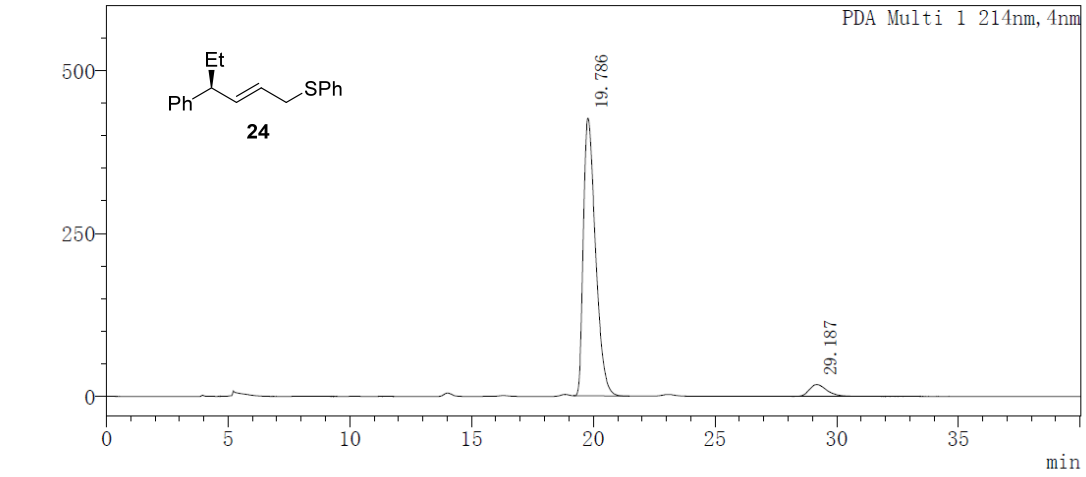
Peak#	Ret. Time	Area	Area%
1	23.127	9400691	95.283
2	26.492	465389	4.717



Peak Table

PDA Ch1 214nm

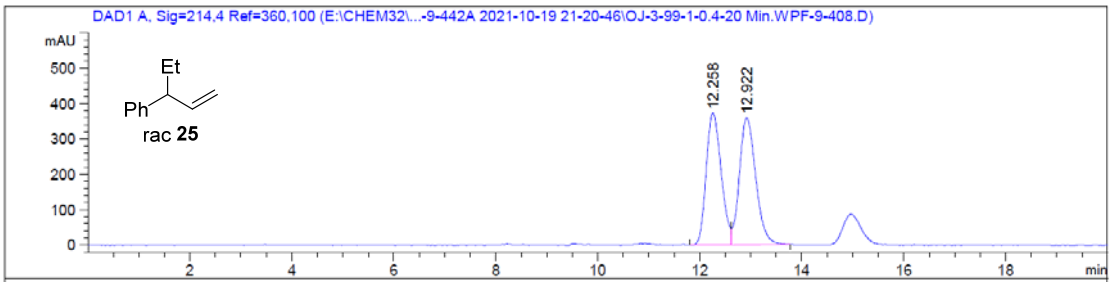
Peak#	Ret. Time	Area	Area%
1	19.795	5201816	49.773
2	29.004	5249169	50.227



Peak Table

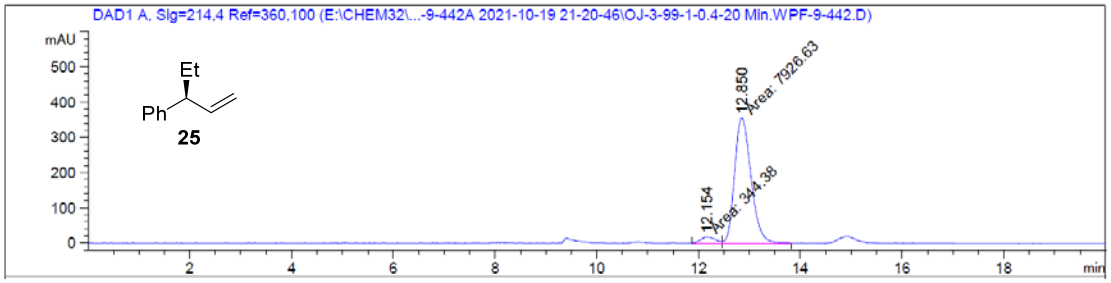
PDA Ch1 214nm

Peak#	Ret. Time	Area	Area%
1	19.786	14882116	94.242
2	29.187	909258	5.758



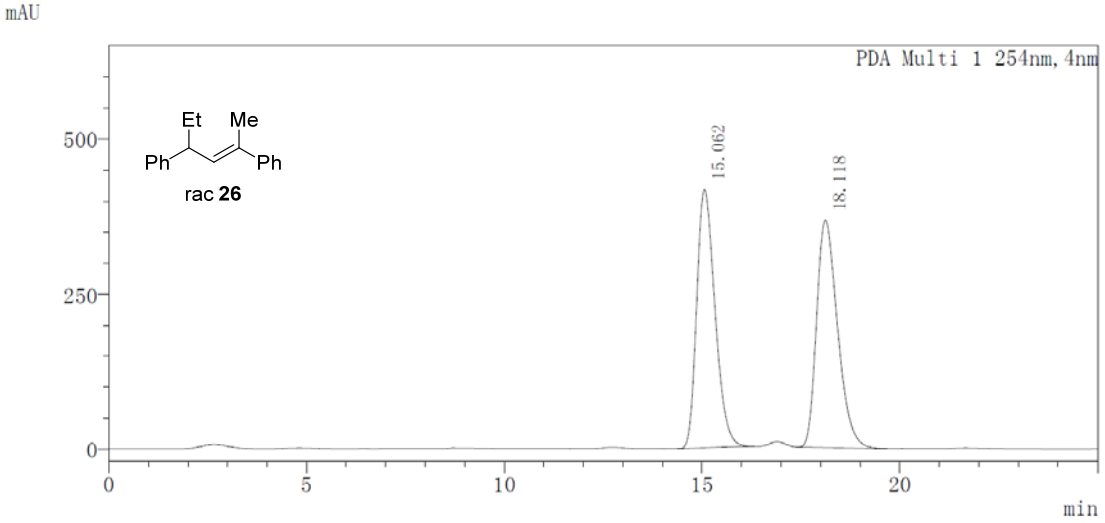
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.258	BV	0.3180	7588.28662	372.04517	48.6869
2	12.922	VV R	0.3398	7997.59375	359.17606	51.3131
Totals :				1.55859e4	731.22122	



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

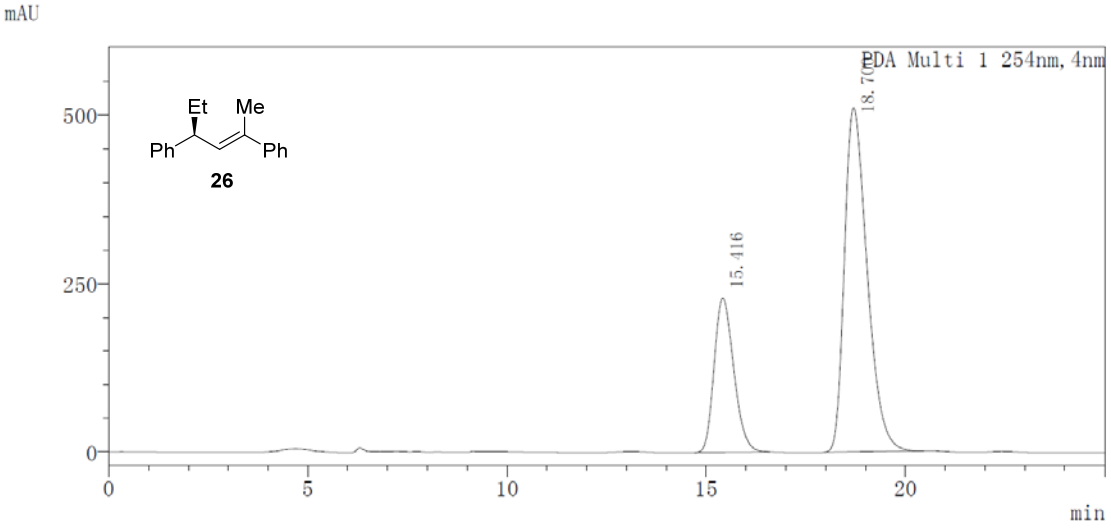
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.154	MF	0.3210	344.37976	17.87811	4.1637
2	12.850	FM	0.3710	7926.62891	356.12936	95.8363
Totals :				8271.00867	374.00747	



Peak Table

PDA Ch1 254nm

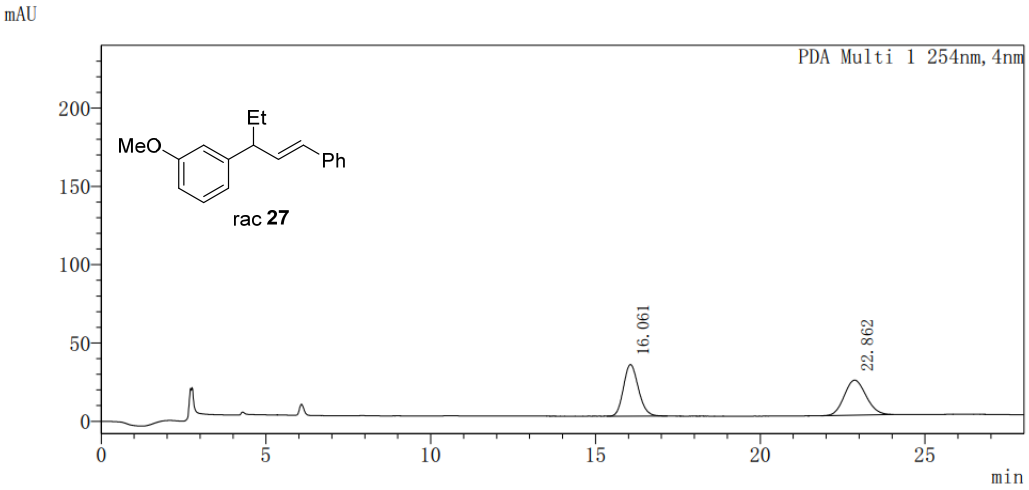
Peak#	Ret. Time	Area	Area%
1	15.062	13414412	49.761
2	18.118	13543295	50.239



Peak Table

PDA Ch1 254nm

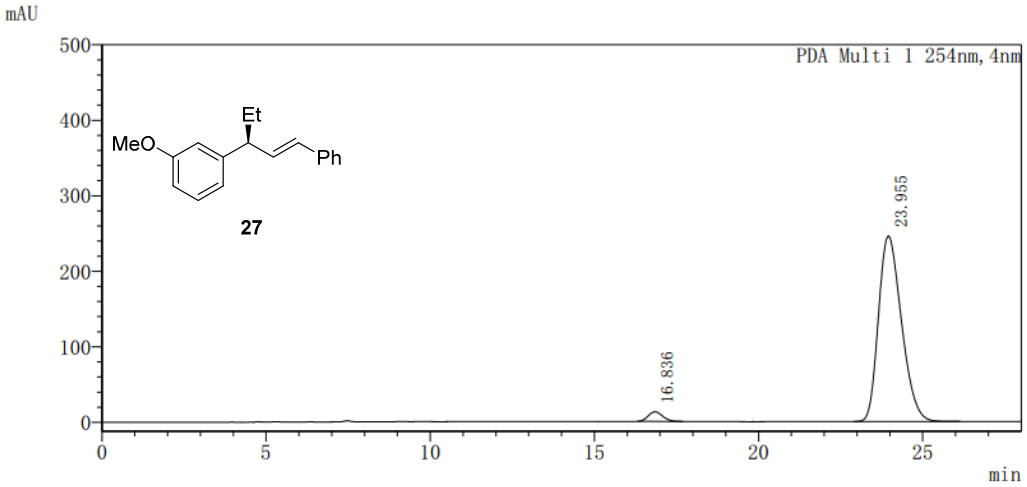
Peak#	Ret. Time	Area	Area%
1	15.416	7892607	27.991
2	18.700	20304271	72.009



Peak Table

PDA Ch1 254nm

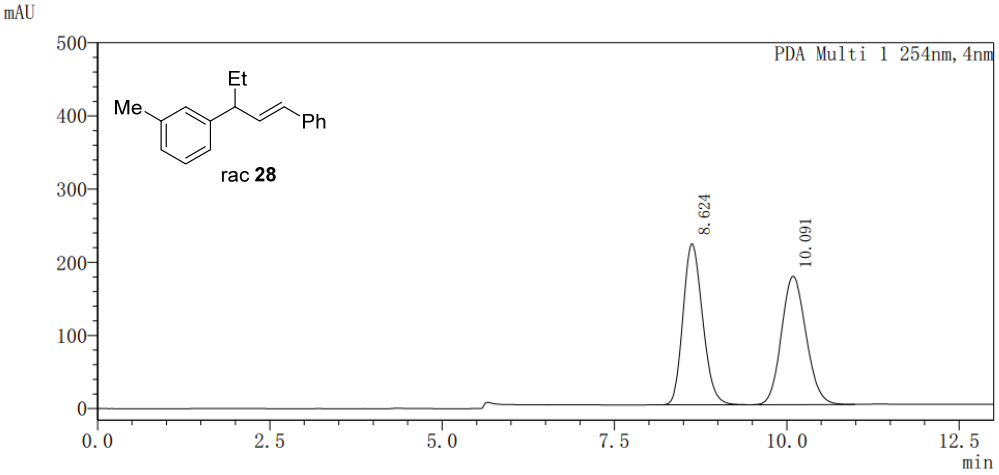
Peak#	Ret. Time	Area	Area%
1	16.061	1038976	50.267
2	22.862	1027948	49.733



Peak Table

PDA Ch1 254nm

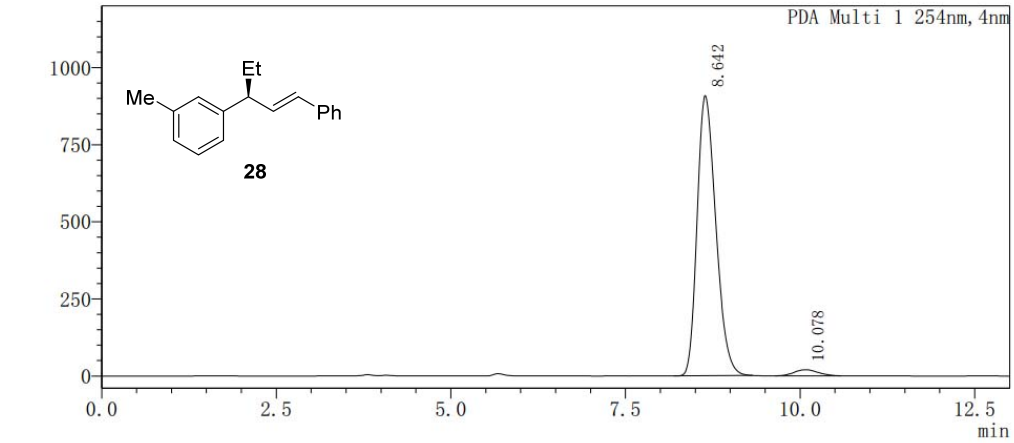
Peak#	Ret. Time	Area	Area%
1	16.836	389878	3.155
2	23.955	11966735	96.845



Peak Table

PDA Ch1 254nm

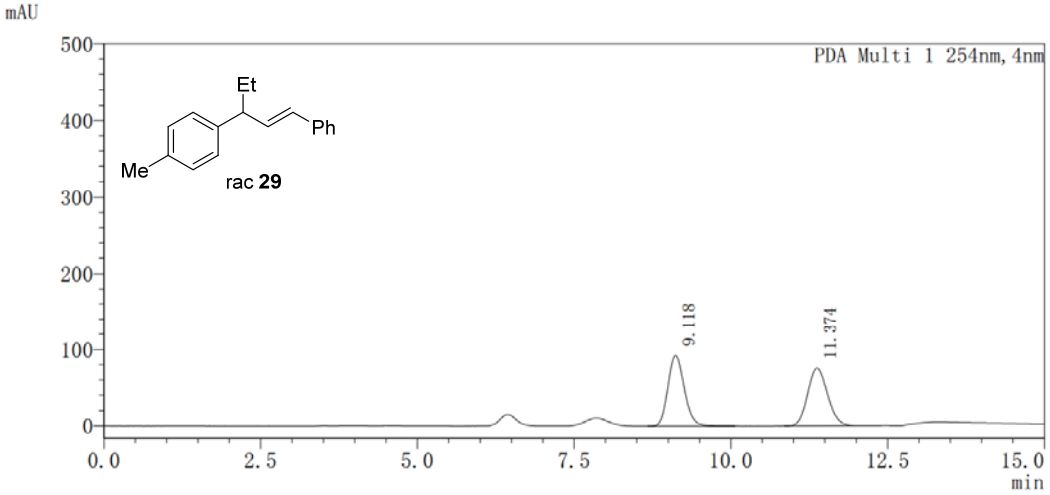
Peak#	Ret. Time	Area	Area%
1	8.624	4361865	49.940
2	10.091	4372373	50.060



Peak Table

PDA Ch1 254nm

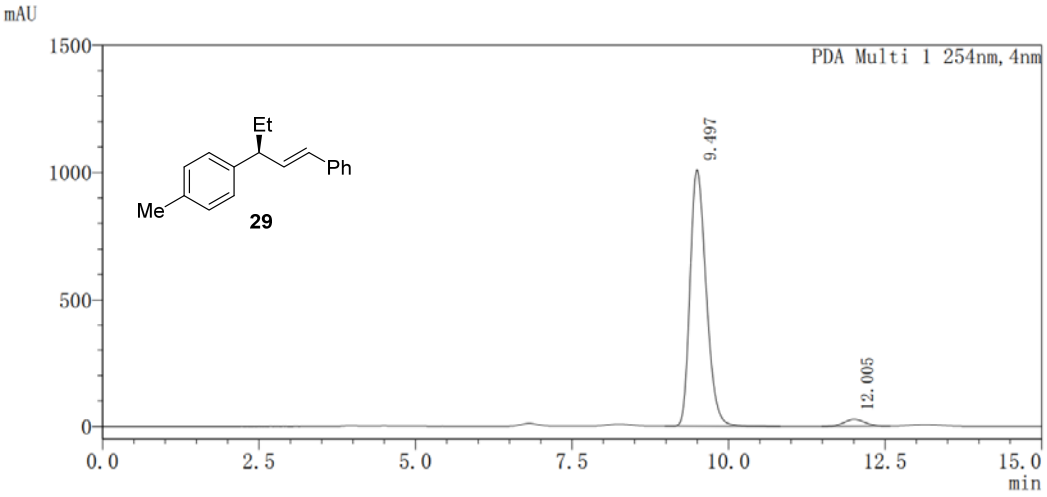
Peak#	Ret. Time	Area	Area%
1	8.642	16957985	97.277
2	10.078	474684	2.723



Peak Table

PDA Ch1 254nm

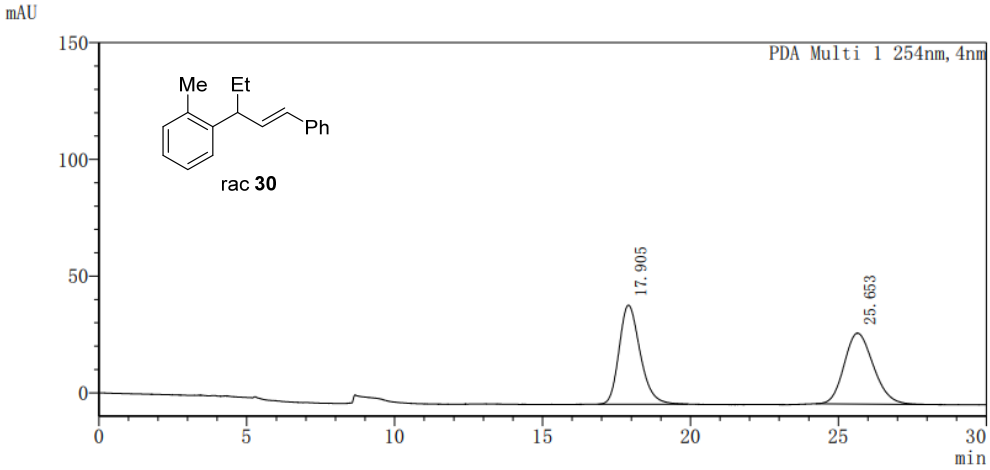
Peak#	Ret. Time	Area	Area%
1	9.118	1678981	50.250
2	11.374	1662290	49.750



Peak Table

PDA Ch1 254nm

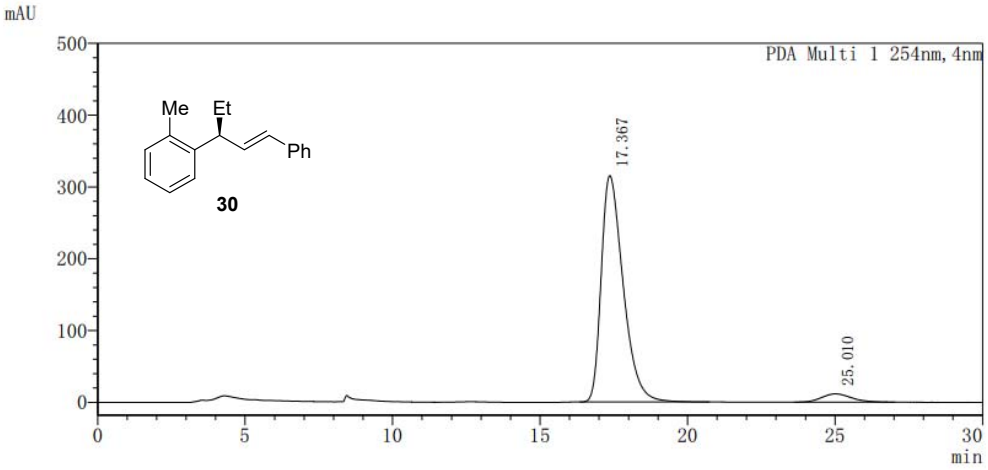
Peak#	Ret. Time	Area	Area%
1	9.497	18075205	96.664
2	12.005	623820	3.336



Peak Table

PDA Ch1 254nm

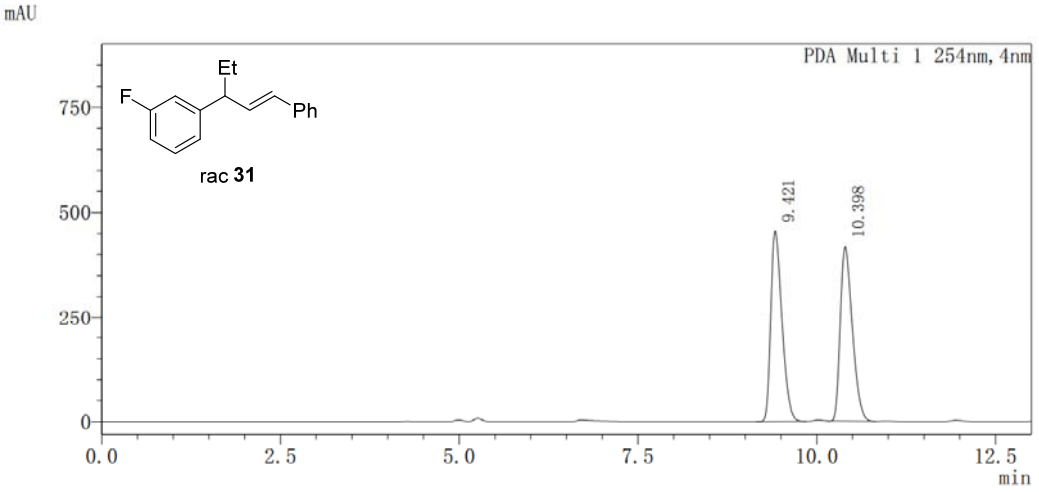
Peak#	Ret. Time	Area	Area%
1	17.905	2103237	50.249
2	25.653	2082373	49.751



Peak Table

PDA Ch1 254nm

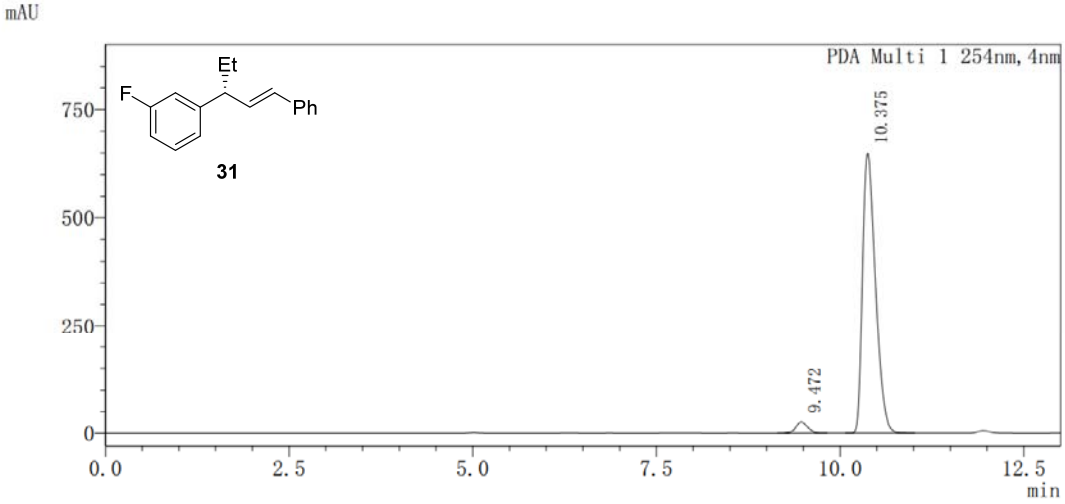
Peak#	Ret. Time	Area	Area%
1	17.367	16311862	95.165
2	25.010	828703	4.835



Peak Table

PDA Ch1 254nm

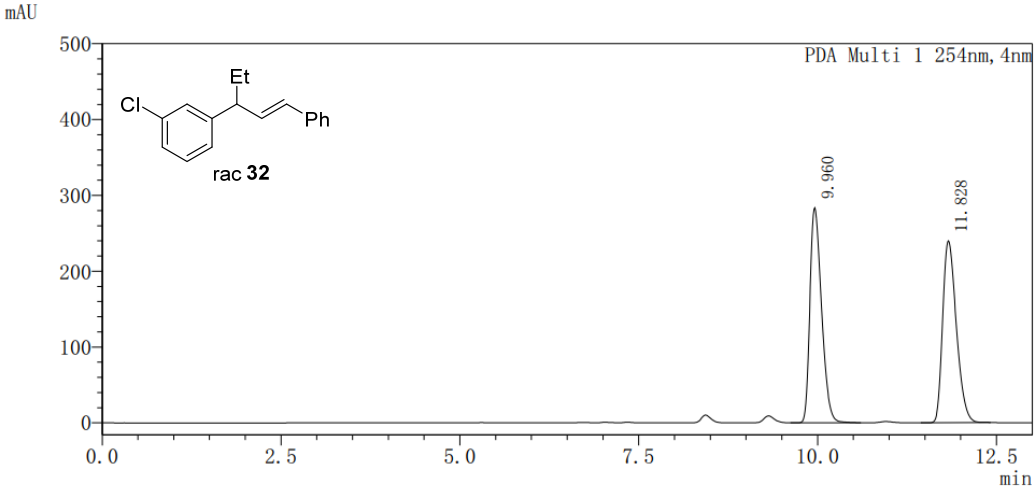
Peak#	Ret. Time	Area	Area%
1	9.421	4964212	50.286
2	10.398	4907827	49.714



Peak Table

PDA Ch1 254nm

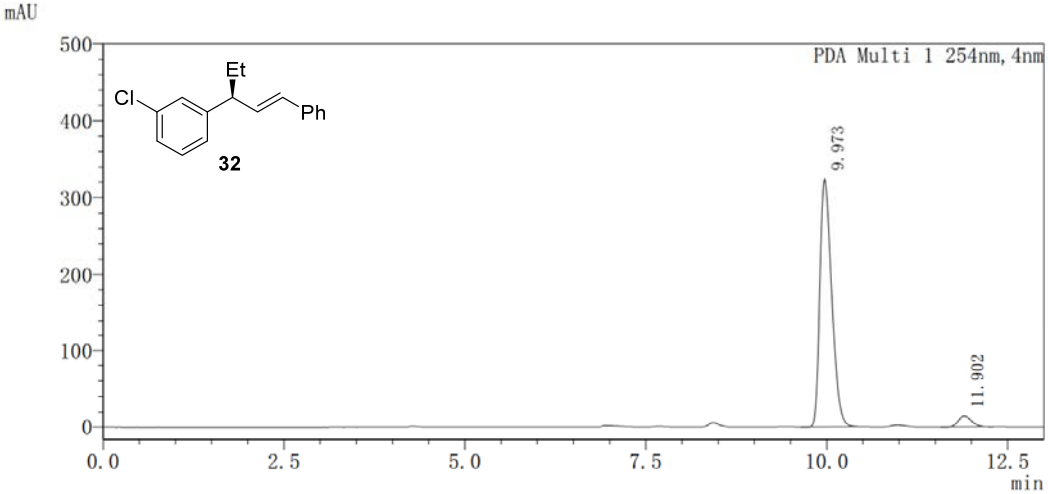
Peak#	Ret. Time	Area	Area%
1	9.472	284347	3.440
2	10.375	7980755	96.560



Peak Table

PDA Ch1 254nm

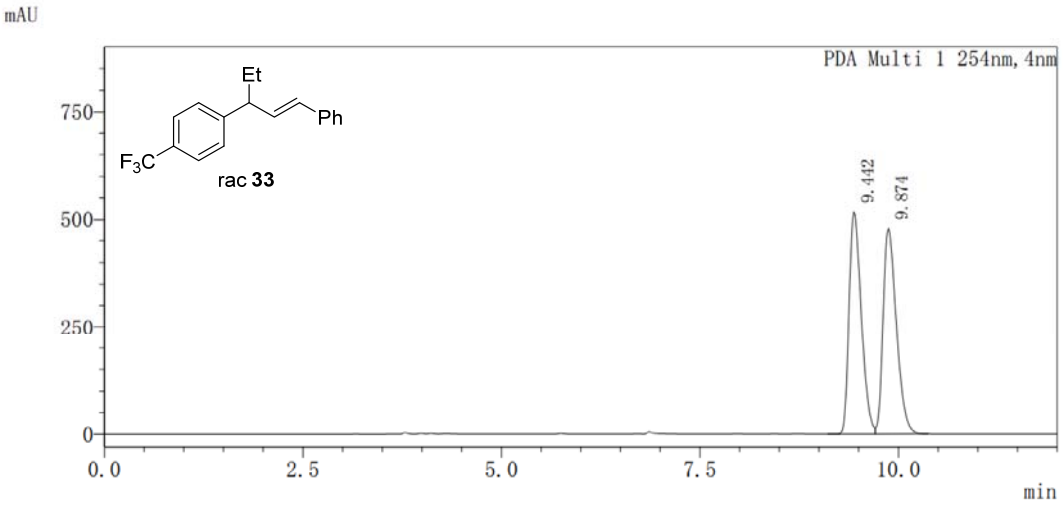
Peak#	Ret. Time	Area	Area%
1	9.960	3204825	50.163
2	11.828	3184054	49.837



Peak Table

PDA Ch1 254nm

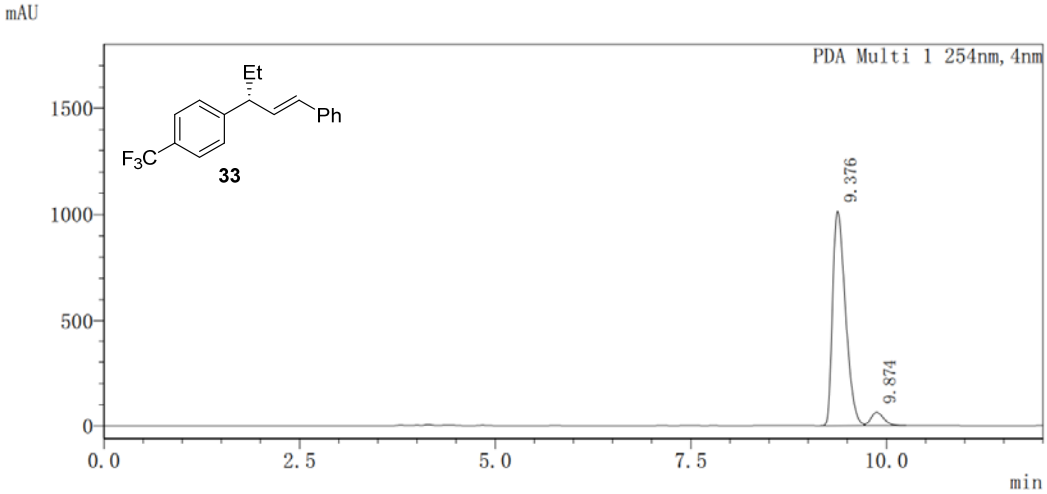
Peak#	Ret. Time	Area	Area%
1	9.973	3686023	95.334
2	11.902	180401	4.666



Peak Table

PDA Ch1 254nm

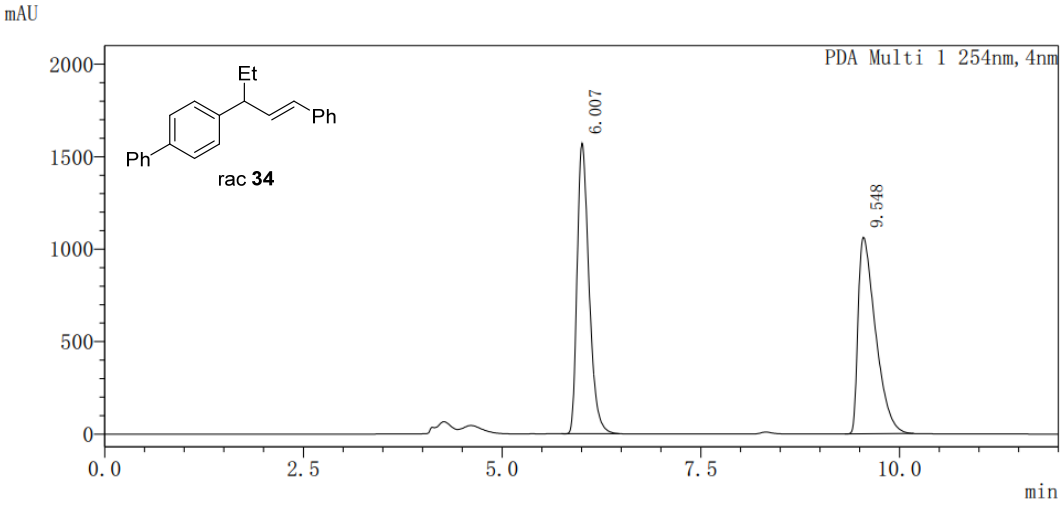
Peak#	Ret. Time	Area	Area%
1	9.442	5529223	49.830
2	9.874	5566926	50.170



Peak Table

PDA Ch1 254nm

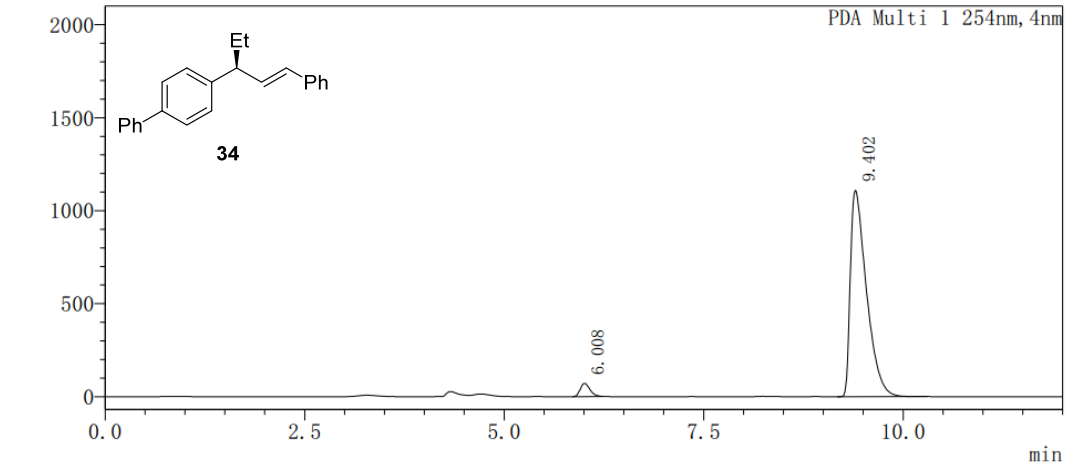
Peak#	Ret. Time	Area	Area%
1	9.376	11659397	94.104
2	9.874	730566	5.896



Peak Table

PDA Ch1 254nm

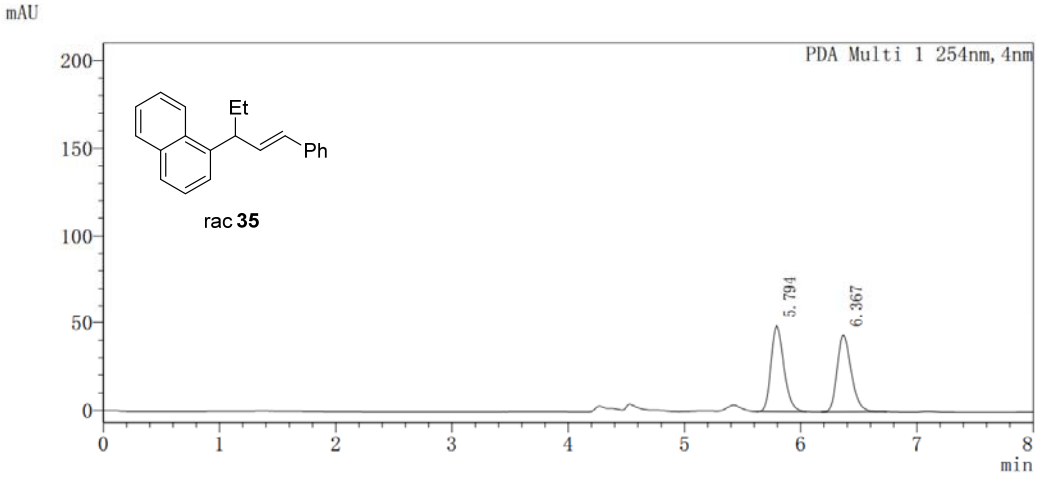
Peak#	Ret. Time	Area	Area%
1	6.007	16347870	50.177
2	9.548	16232232	49.823



Peak Table

PDA Ch1 254nm

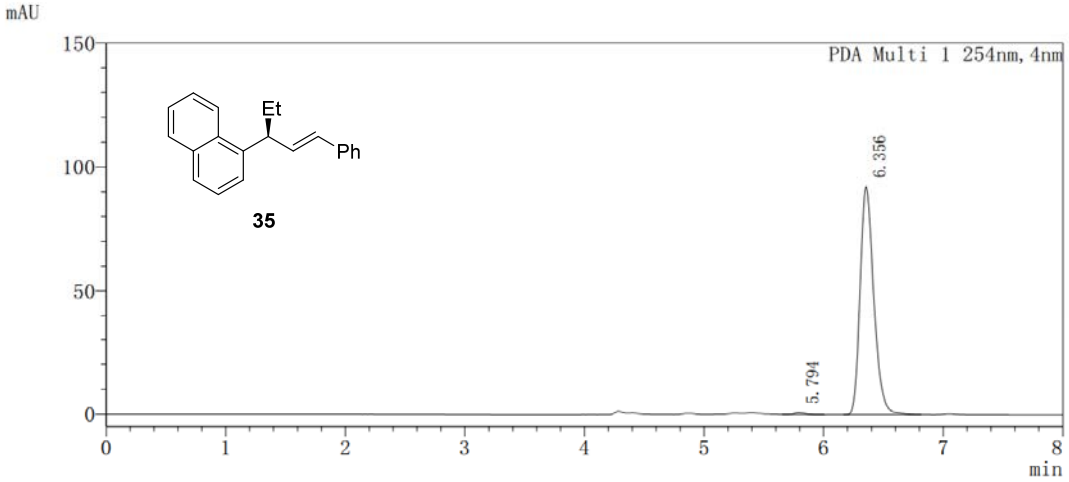
Peak#	Ret. Time	Area	Area%
1	6.008	598732	3.688
2	9.402	15637633	96.312



Peak Table

PDA Ch1 254nm

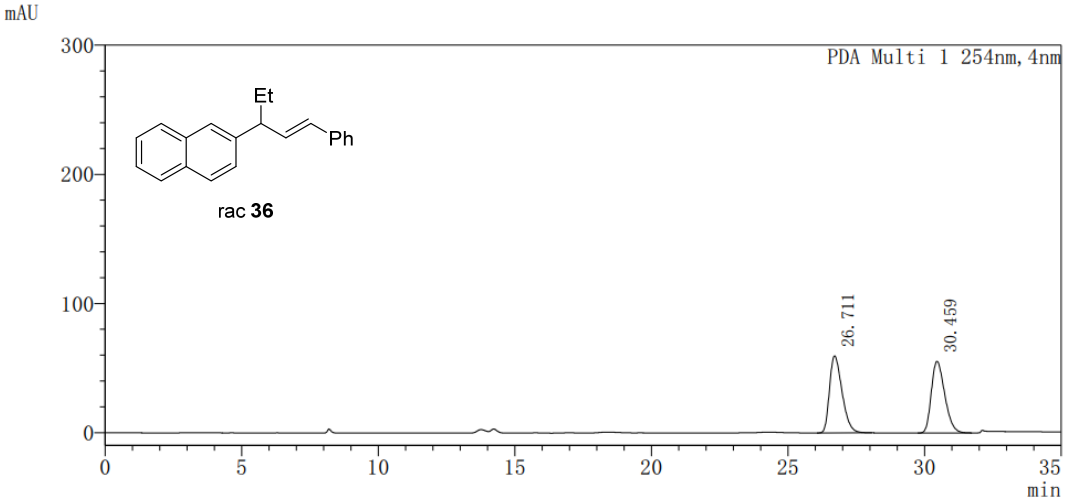
Peak#	Ret. Time	Area	Area%
1	5.794	373442	50.459
2	6.367	366643	49.541



Peak Table

PDA Ch1 254nm

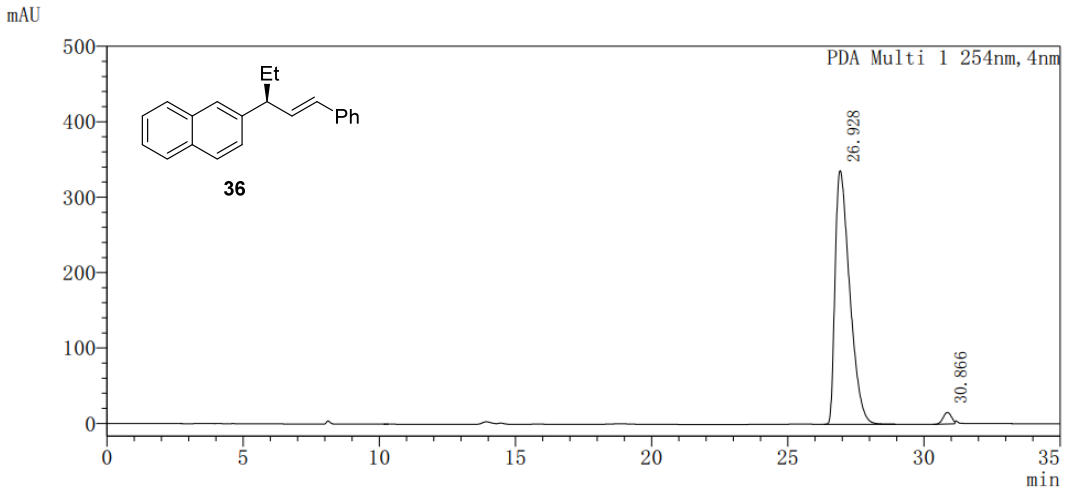
Peak#	Ret. Time	Area	Area%
1	5.794	5112	0.692
2	6.356	733061	99.308



Peak Table

PDA Ch1 254nm

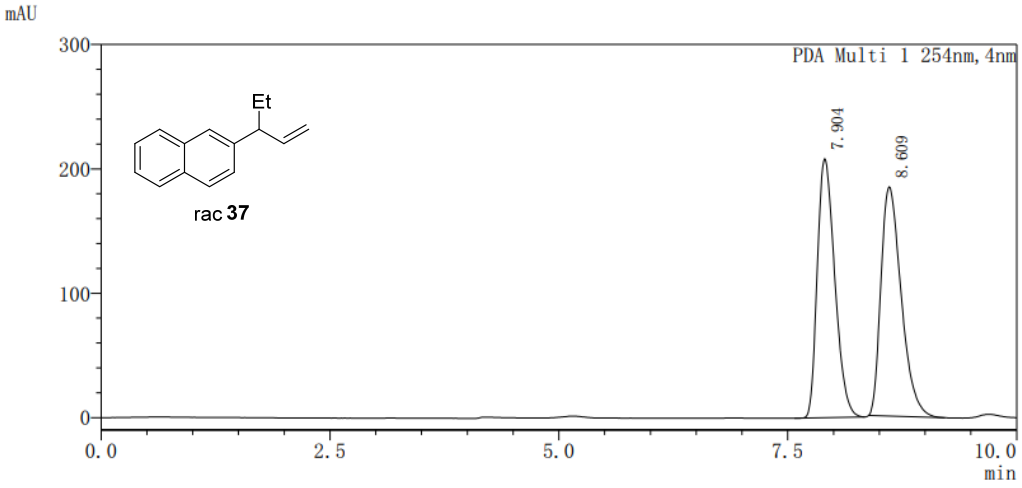
Peak#	Ret. Time	Area	Area%
1	26.711	1911917	50.176
2	30.459	1898528	49.824



Peak Table

PDA Ch1 254nm

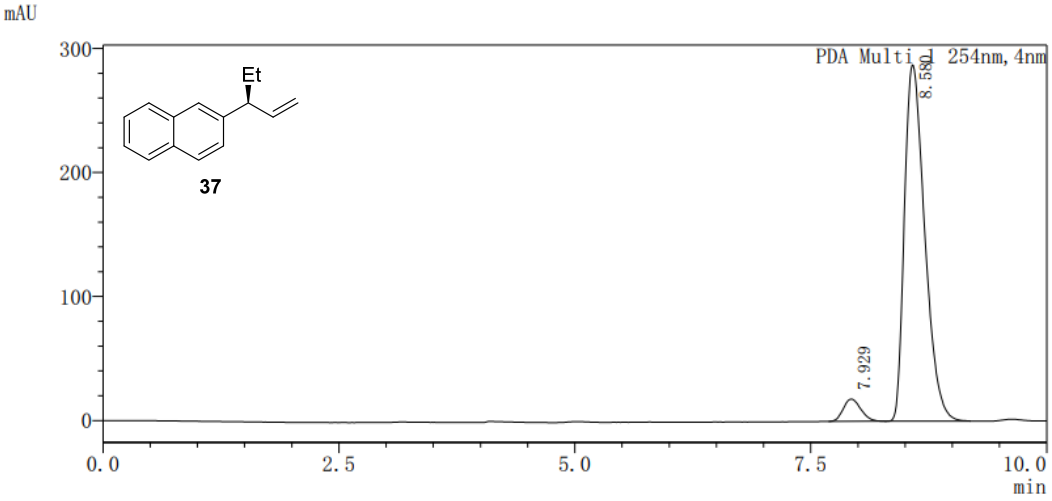
Peak#	Ret. Time	Area	Area%
1	26.928	12555528	97.450
2	30.866	328478	2.550



Peak Table

PDA Ch1 254nm

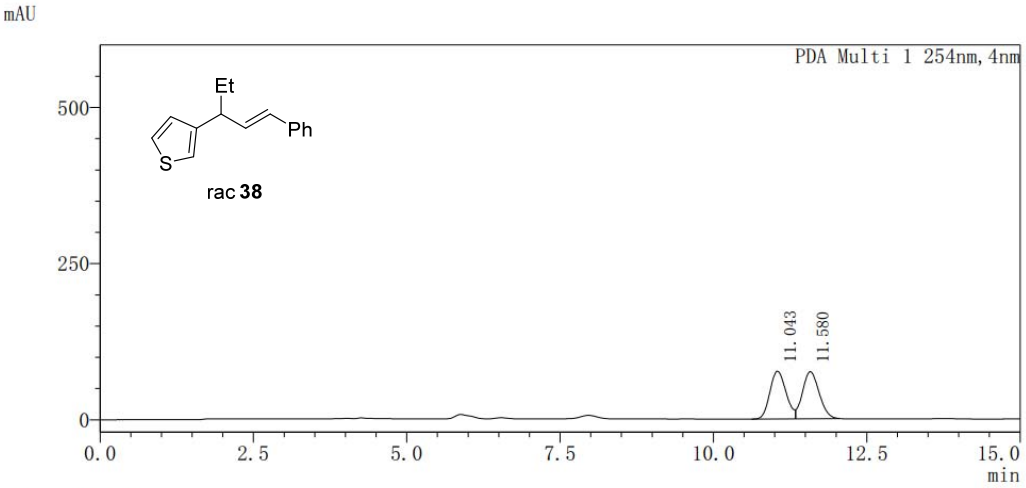
Peak#	Ret. Time	Area	Area%
1	7.904	2759268	49.229
2	8.609	2845713	50.771



Peak Table

PDA Ch1 254nm

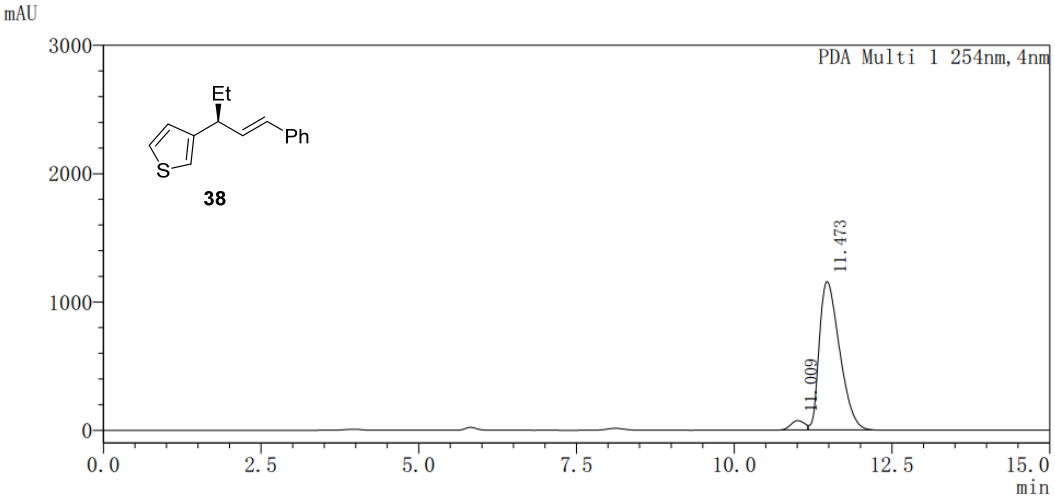
Peak#	Ret. Time	Area	Area%
1	7.929	231583	5.111
2	8.580	4299310	94.889



Peak Table

PDA Ch1 254nm

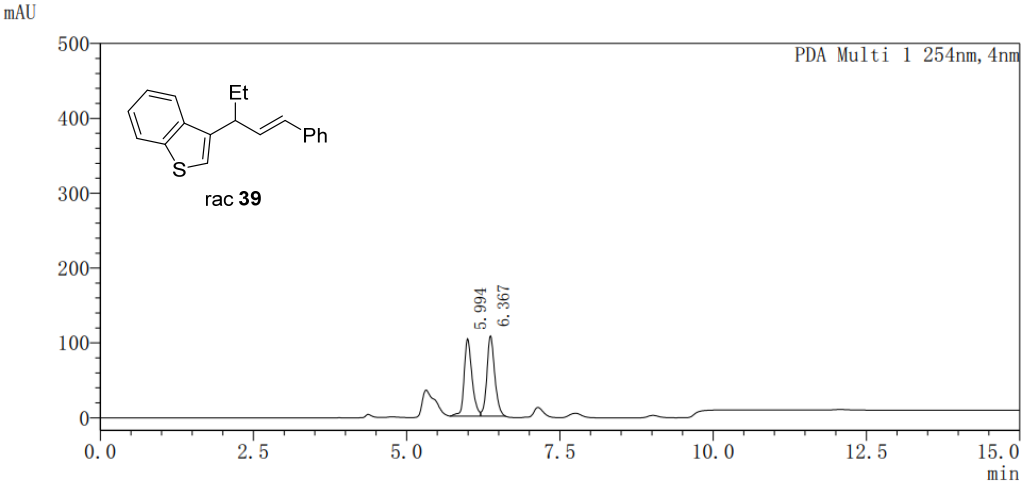
Peak#	Ret. Time	Area	Area%
1	11.043	1404322	49.794
2	11.580	1415966	50.206



Peak Table

PDA Ch1 254nm

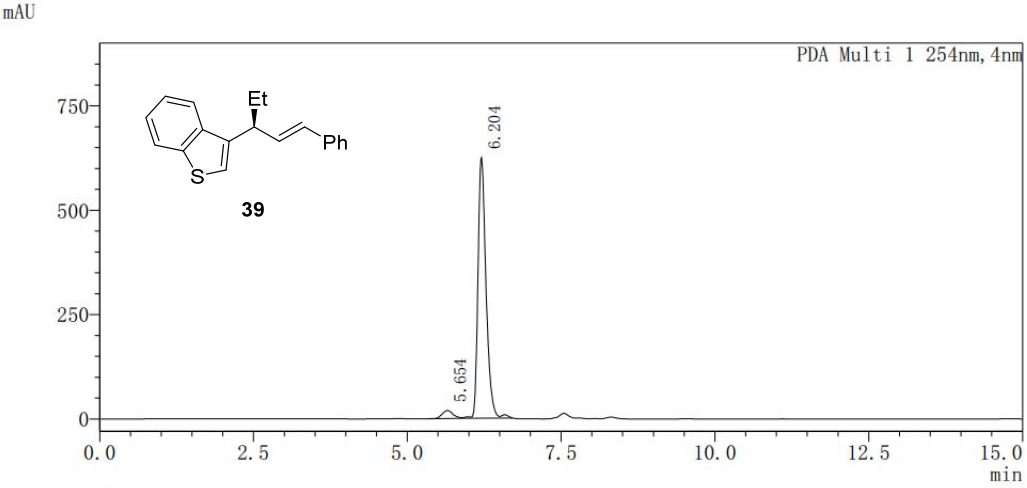
Peak#	Ret. Time	Area	Area%
1	11.009	1114859	4.128
2	11.473	25889175	95.872



Peak Table

PDA Ch1 254nm

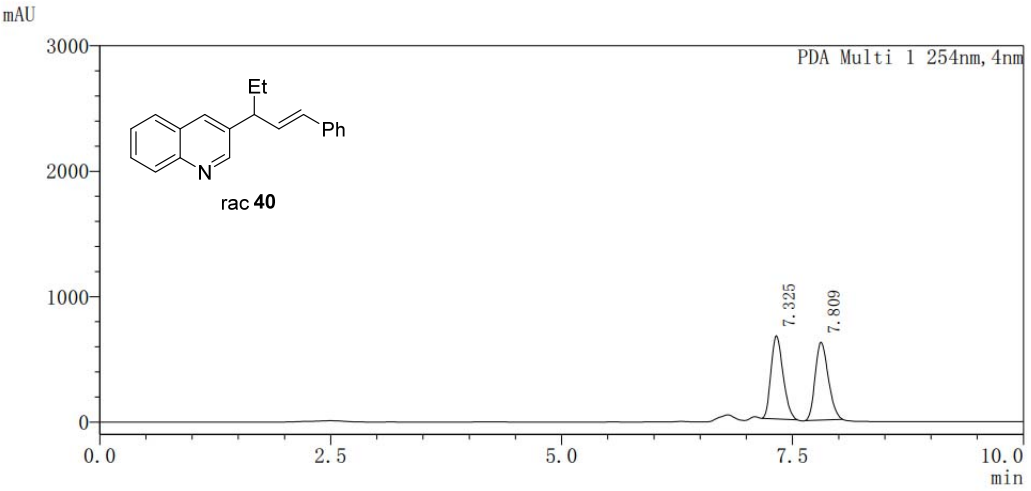
Peak#	Ret. Time	Area	Area%
1	5.994	924523	49.117
2	6.367	957760	50.883



Peak Table

PDA Ch1 254nm

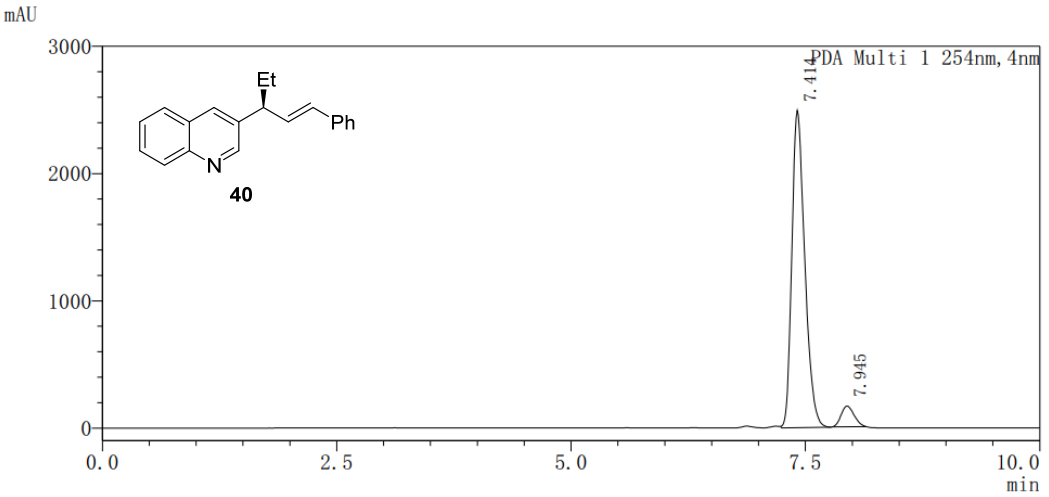
Peak#	Ret. Time	Area	Area%
1	5.654	239892	4.034
2	6.204	5707033	95.966



Peak Table

PDA Ch1 254nm

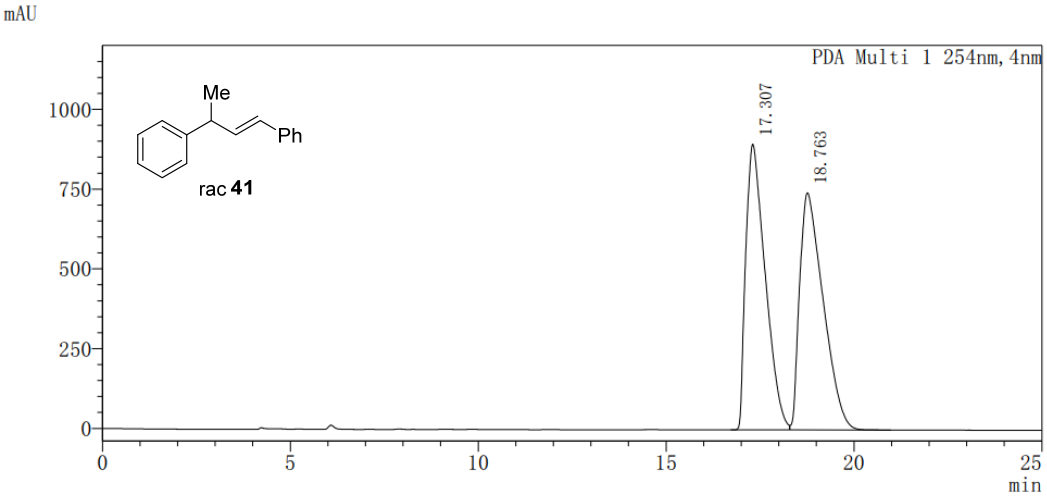
Peak#	Ret. Time	Area	Area%
1	7.325	6029450	49.600
2	7.809	6126663	50.400



Peak Table

PDA Ch1 254nm

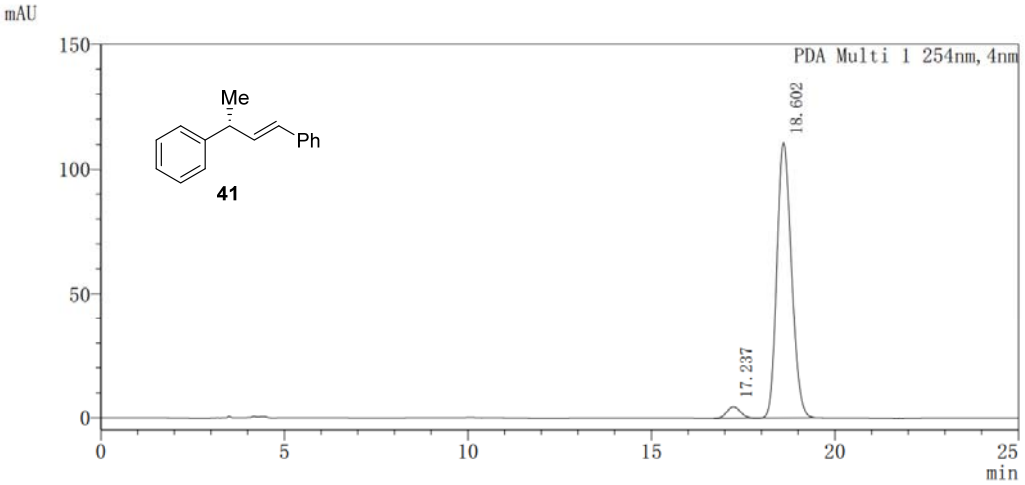
Peak#	Ret. Time	Area	Area%
1	7.414	23905984	93.796
2	7.945	1581173	6.204



Peak Table

PDA Ch1 254nm

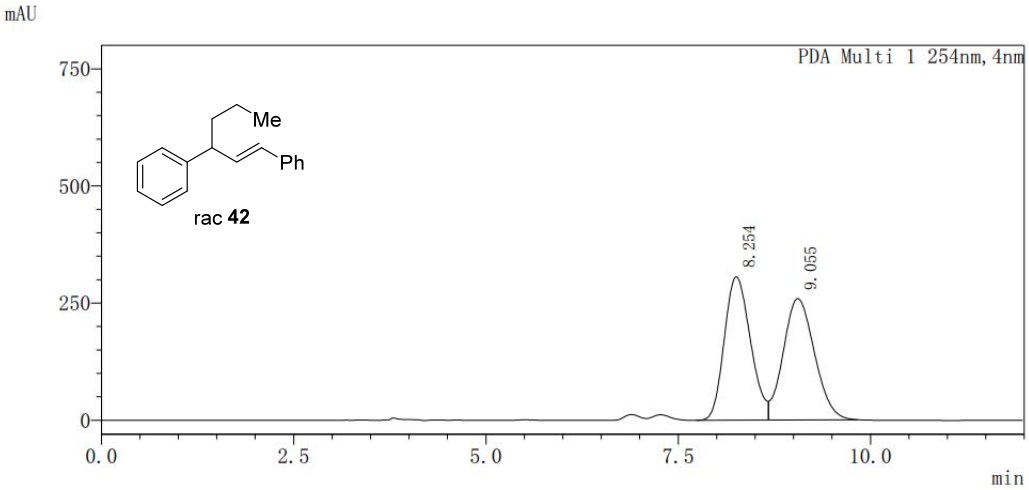
Peak#	Ret. Time	Area	Area%
1	17.307	32263624	49.895
2	18.763	32399268	50.105



Peak Table

PDA Ch1 254nm

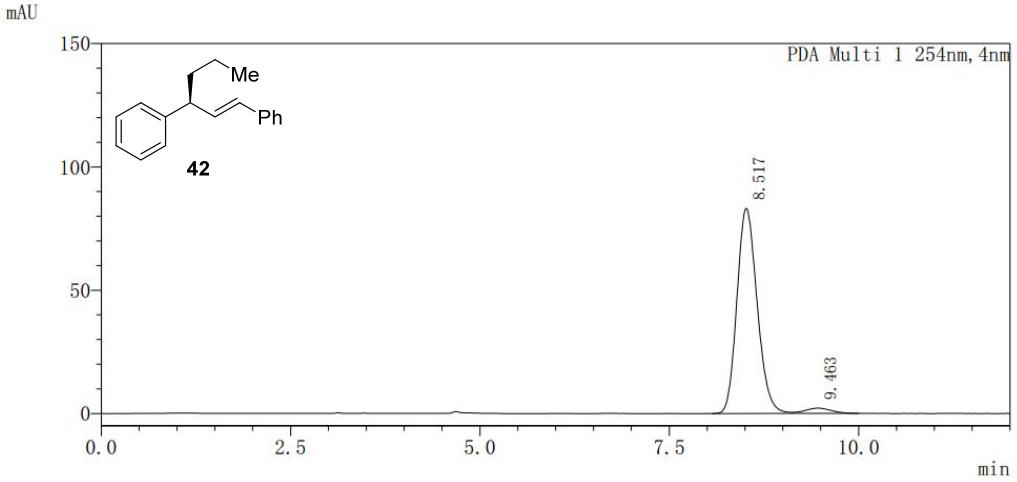
Peak#	Ret. Time	Area	Area%
1	17.237	116326	3.650
2	18.602	3070298	96.350



Peak Table

PDA Ch1 254nm

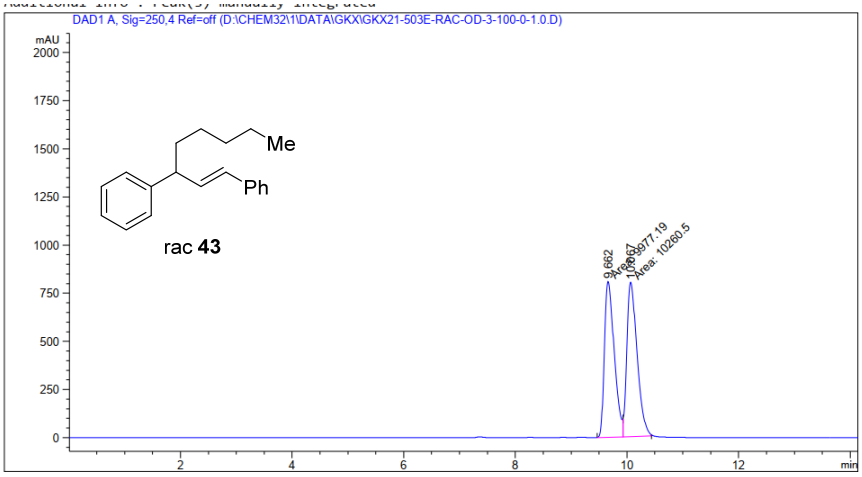
Peak#	Ret. Time	Area	Area%
1	8.254	7265842	49.789
2	9.055	7327479	50.211



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.517	1547199	96.759
2	9.463	51826	3.241



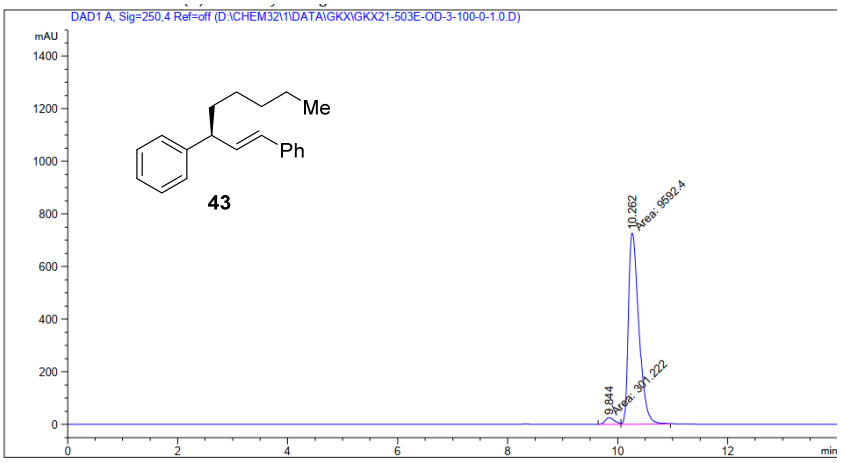
Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.662	MF	0.2056	9977.19434	808.80878	49.3000
2	10.067	FM	0.2137	1.02605e4	800.17621	50.7000

HPLC-5 8/16/2021 8:43:09 PM SYSTEM

Data File D:\CHEM32\1\DATA\GKX\GKX21-503E-RAC-OD-3-100-0-1.0.D
Sample Name: GKX21-503E-RAC-OD-3-100-0-1.0-1

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
Totals :				2.02377e4	1608.98499	



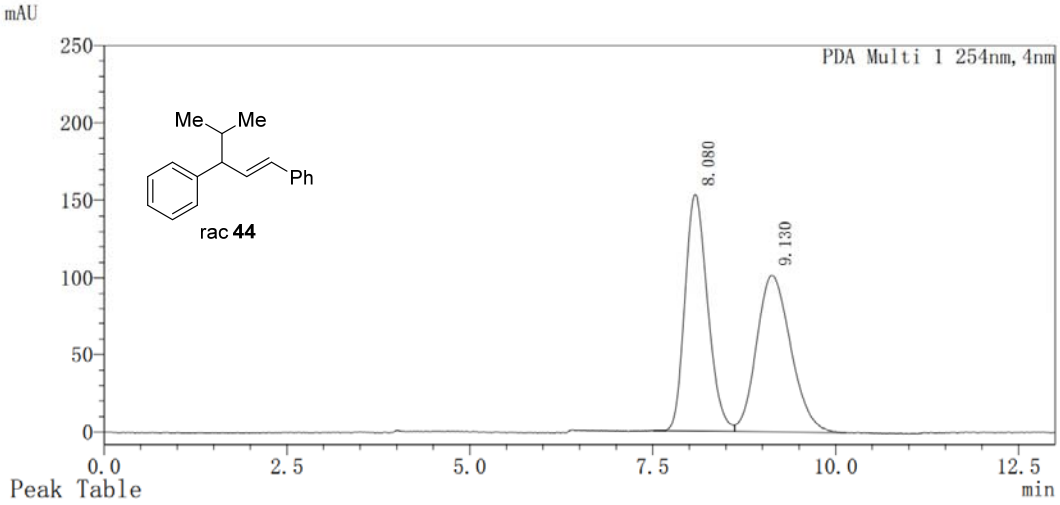
Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.844	MF	0.1979	301.22202	25.36960	3.0446
2	10.262	FM	0.2201	9592.39746	726.44775	96.9554

HPLC-5 8/16/2021 8:45:50 PM SYSTEM

Data File D:\CHEM32\1\DATA\GKX\GKX21-503E-OD-3-100-0-1.0.D
Sample Name: GKX21-503E-OD-3-100-0-1.0-1

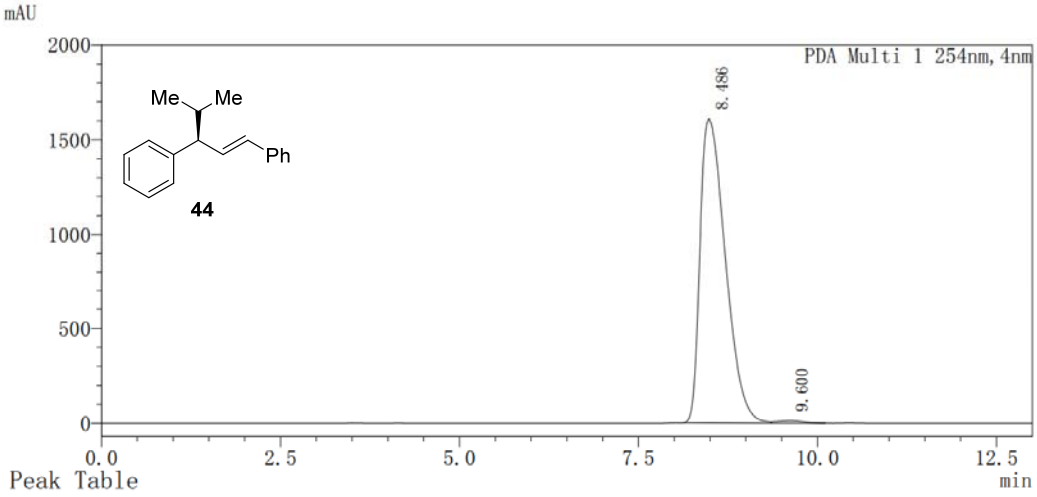
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
Totals :				9893.61948	751.81735	



Peak Table

PDA Ch1 254nm

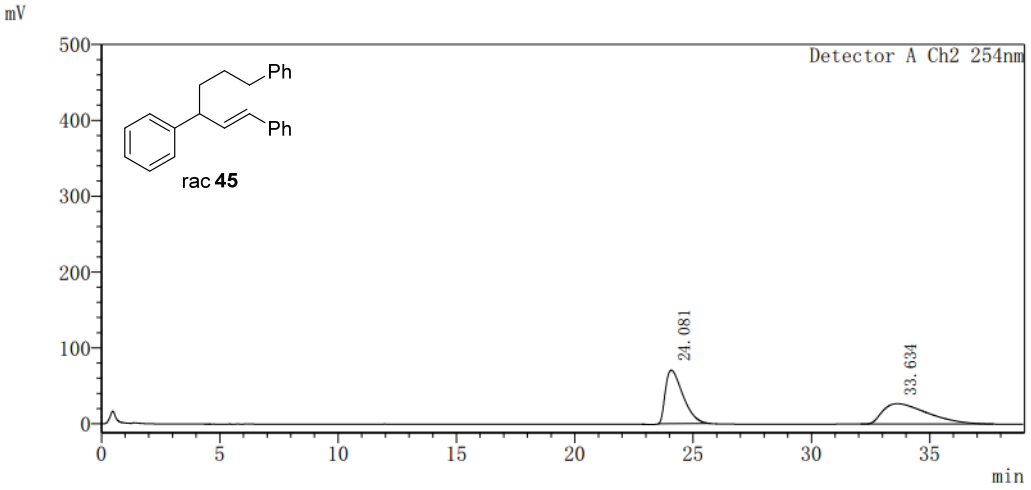
Peak#	Ret. Time	Area	Area%
1	8.080	3310903	50.154
2	9.130	3290614	49.846



Peak Table

PDA Ch1 254nm

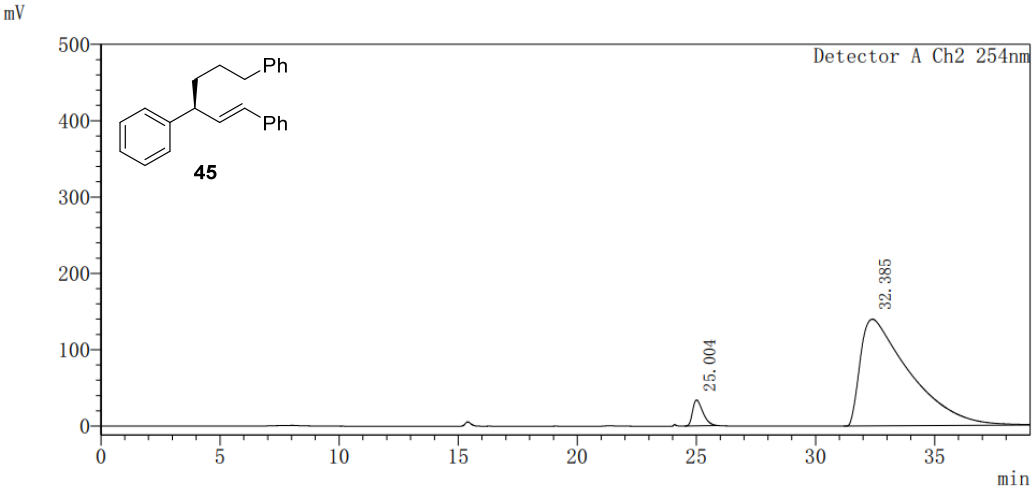
Peak#	Ret. Time	Area	Area%
1	8.486	39373981	99.227
2	9.600	306740	0.773



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	24.081	3632361	50.567
2	33.634	3550965	49.433

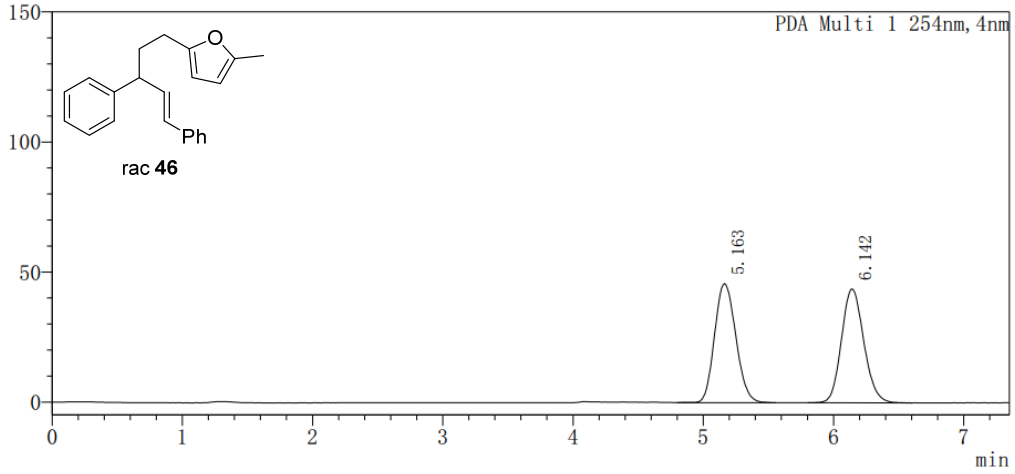


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.006	1033876	4.880
2	32.387	20153083	95.120

mAU

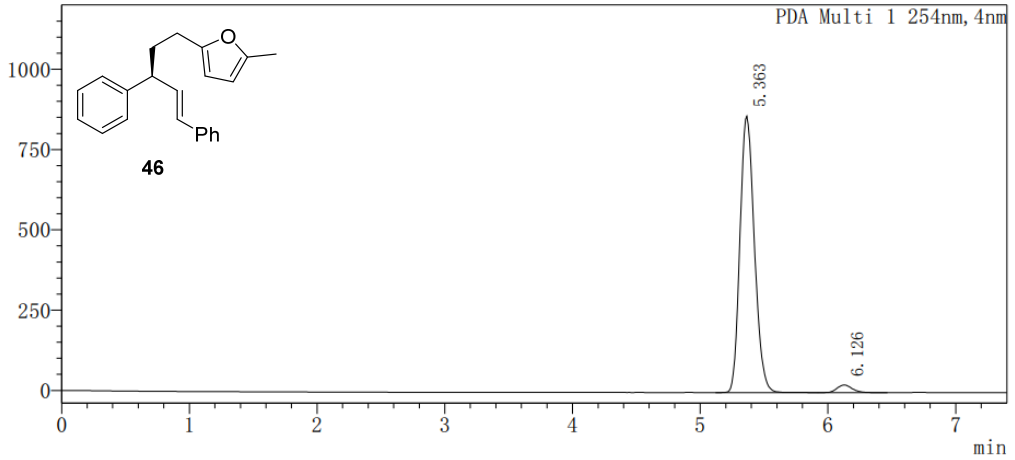


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.163	521088	49.946
2	6.142	522208	50.054

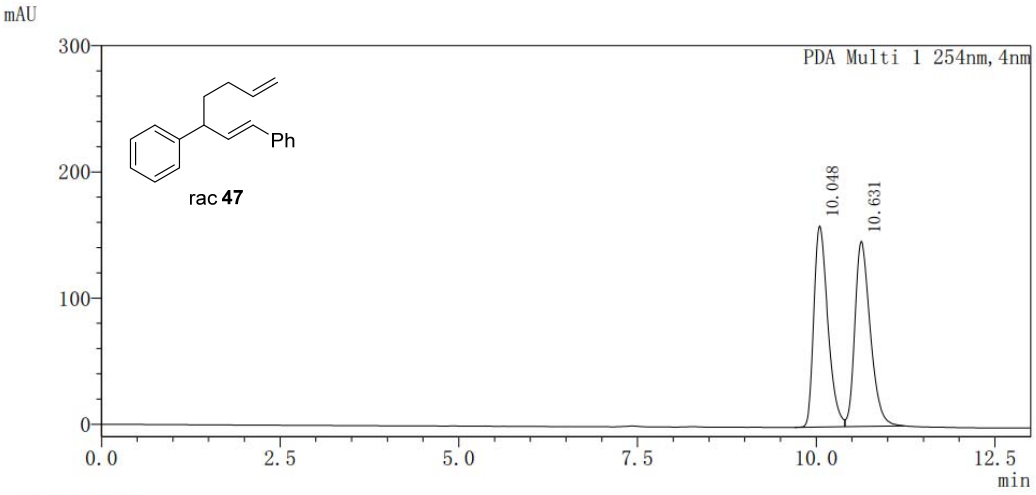
mAU



Peak Table

PDA Ch1 254nm

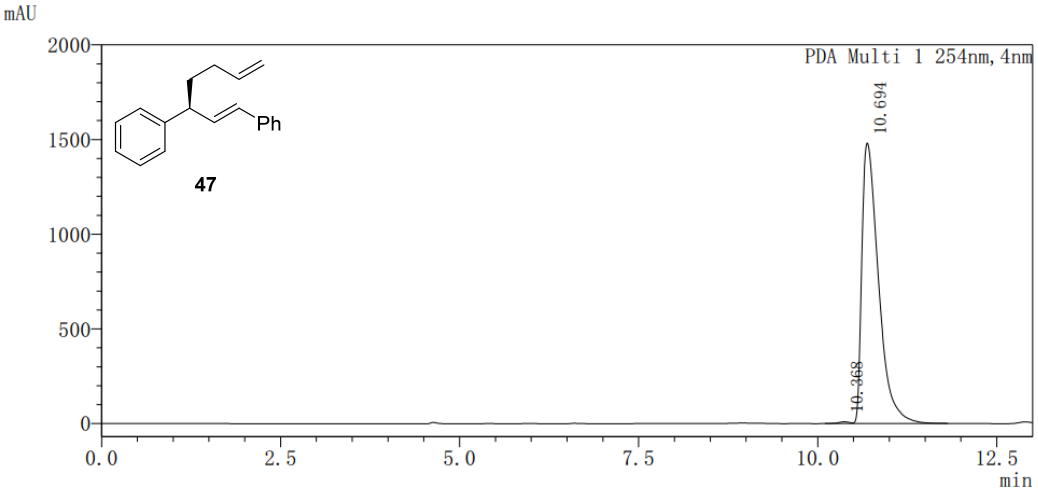
Peak#	Ret. Time	Area	Area%
1	5.363	6773865	97.201
2	6.126	195087	2.799



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.048	2172552	49.654
2	10.631	2202853	50.346

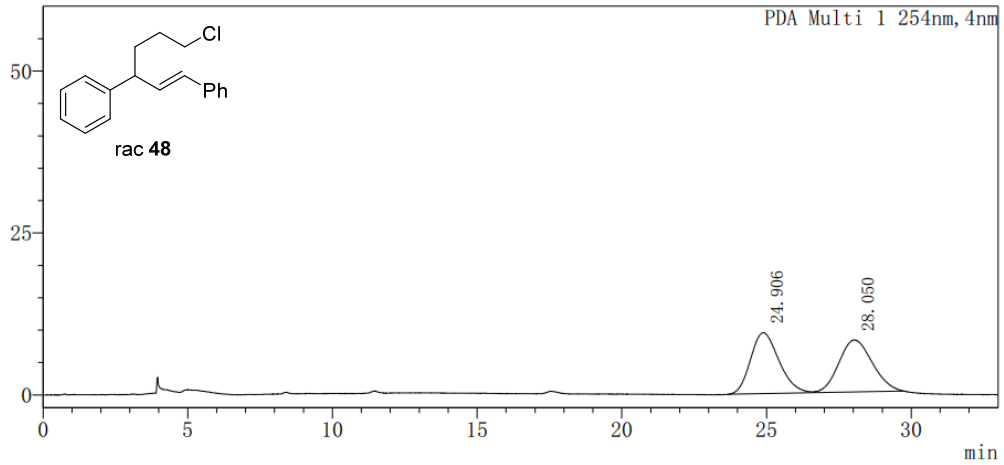


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.368	93122	0.386
2	10.694	24024473	99.614

mAU

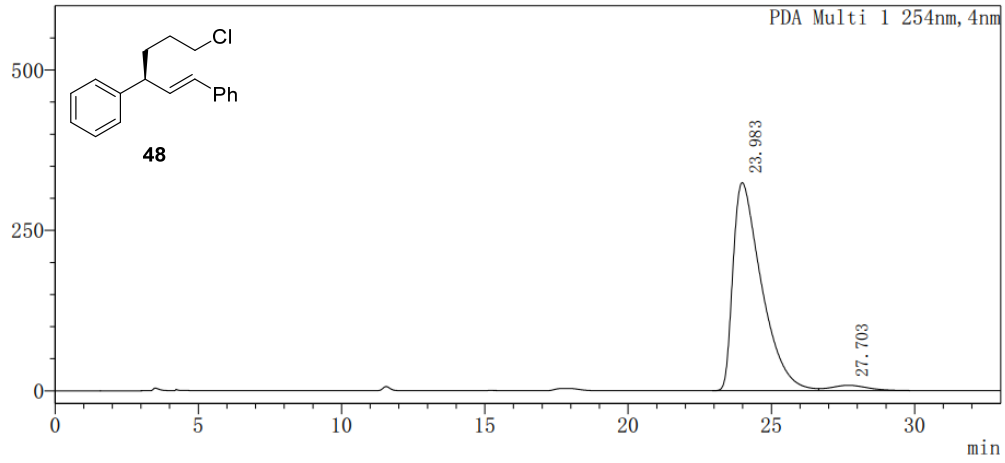


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.906	643914	49.972
2	28.050	644639	50.028

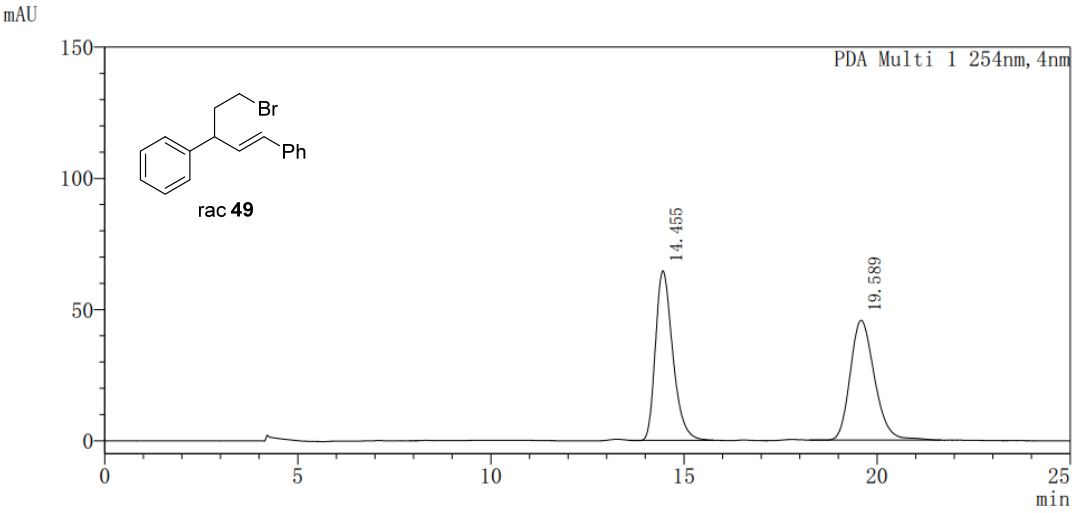
mAU



Peak Table

PDA Ch1 254nm

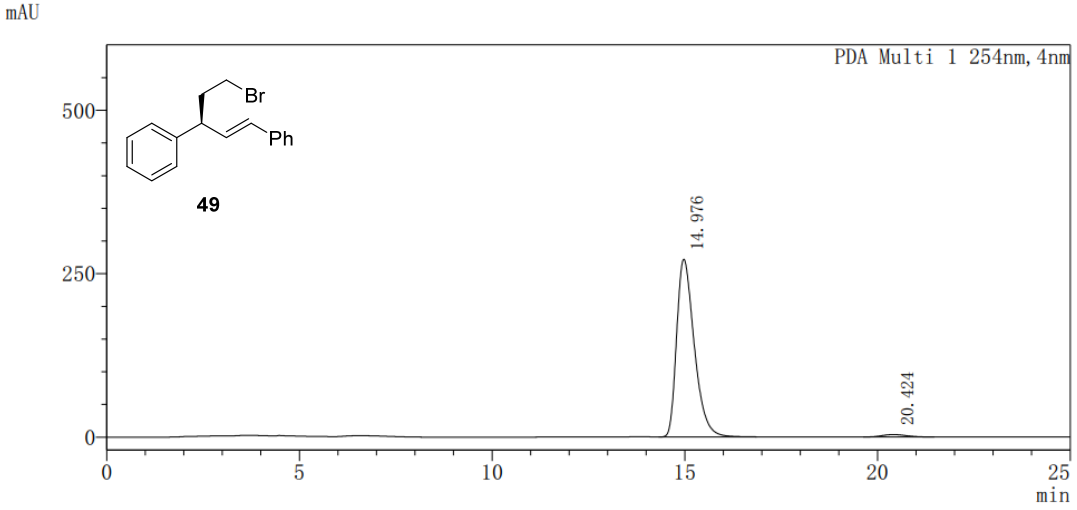
Peak#	Ret. Time	Area	Area%
1	23.983	22504279	96.855
2	27.703	730640	3.145



Peak Table

PDA Ch1 254nm

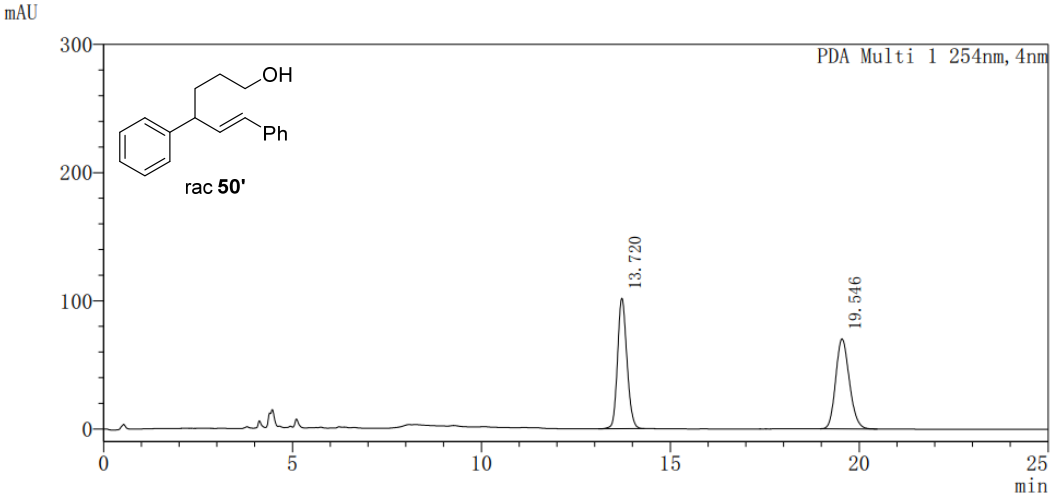
Peak#	Ret. Time	Area	Area%
1	14.455	2005914	50.091
2	19.589	1998614	49.909



Peak Table

PDA Ch1 254nm

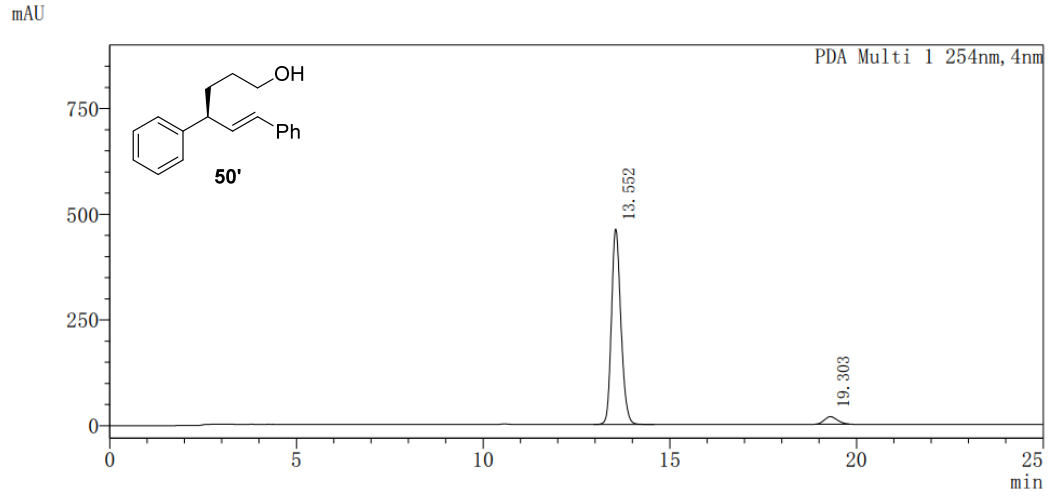
Peak#	Ret. Time	Area	Area%
1	14.976	8663351	98.134
2	20.424	164741	1.866



Peak Table

PDA Ch1 254nm

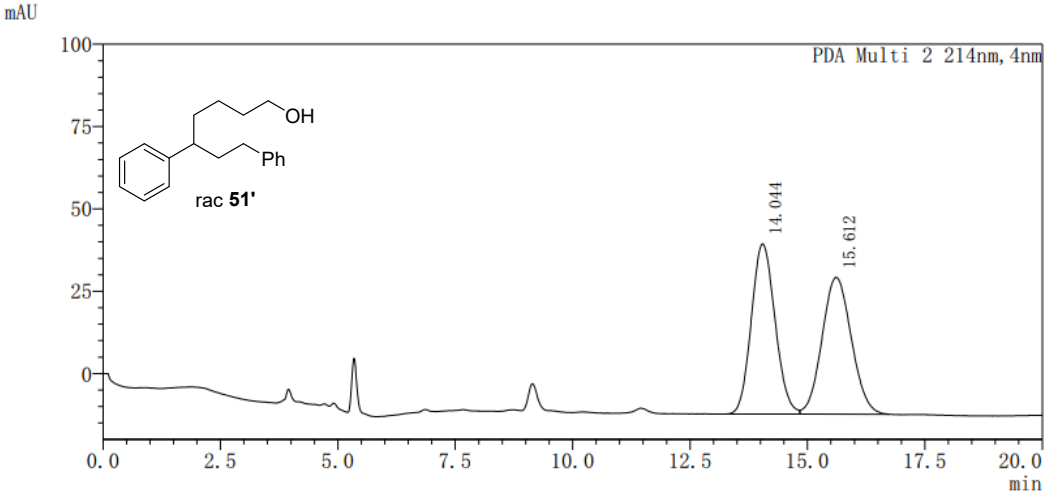
Peak#	Ret. Time	Area	Area%
1	13.720	1761082	49.925
2	19.546	1766351	50.075



Peak Table

PDA Ch1 254nm

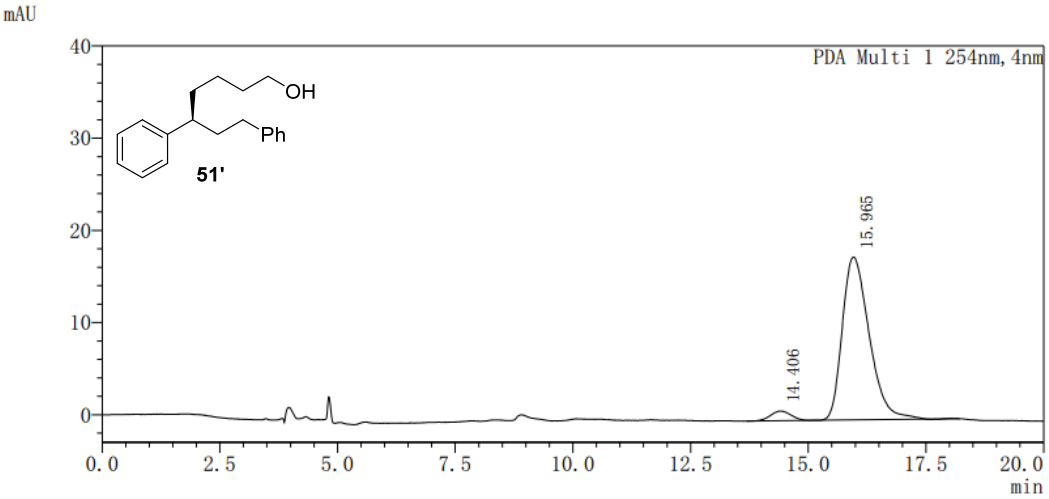
Peak#	Ret. Time	Area	Area%
1	13.552	8145168	94.991
2	19.303	429547	5.009



Peak Table

PDA Ch2 214nm

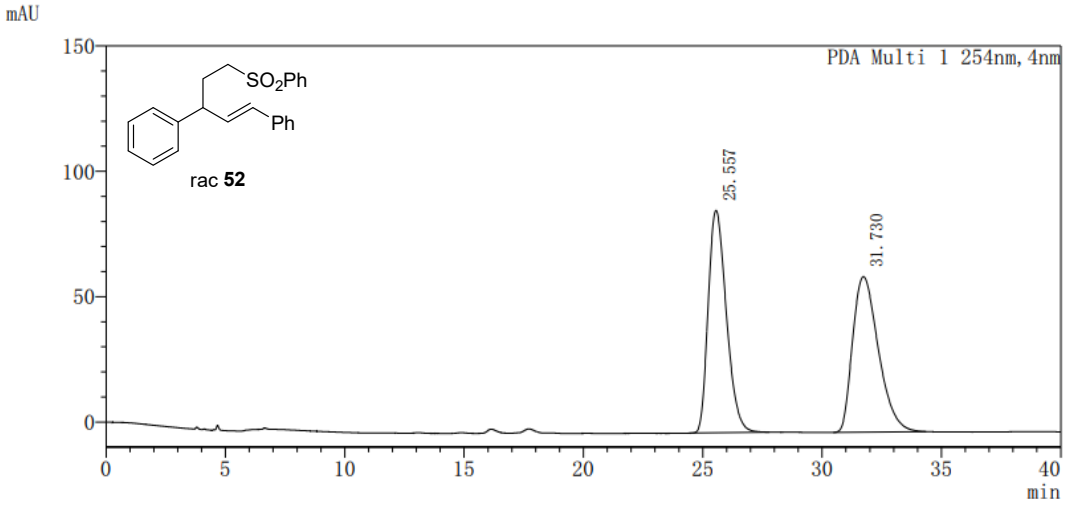
Peak#	Ret. Time	Area	Area%
1	14.044	1818042	50.178
2	15.612	1805109	49.822



Peak Table

PDA Ch2 214nm

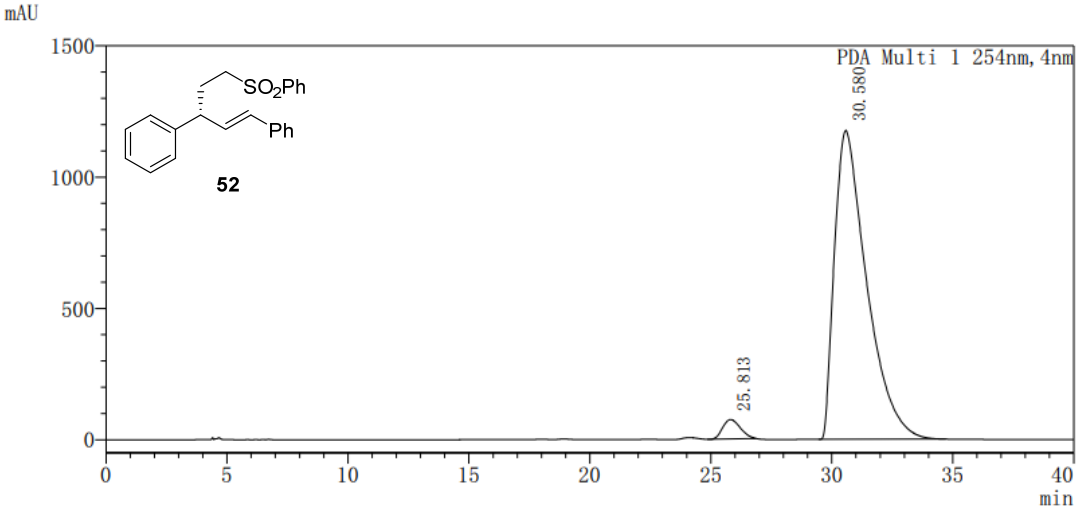
Peak#	Ret. Time	Area	Area%
1	14.407	1031494	4.524
2	15.961	21768930	95.476



Peak Table

PDA Ch1 254nm

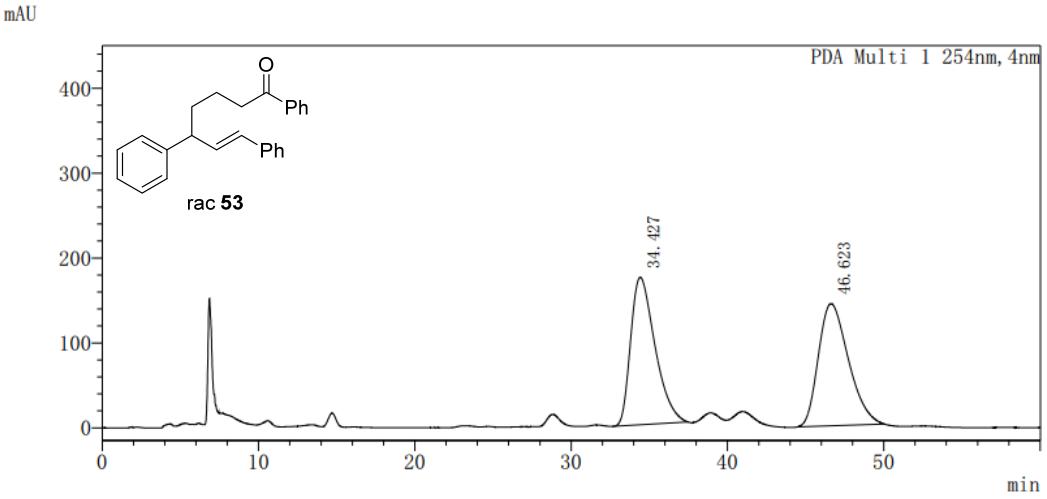
Peak#	Ret. Time	Area	Area%
1	25.557	4702934	50.197
2	31.730	4666071	49.803



Peak Table

PDA Ch1 254nm

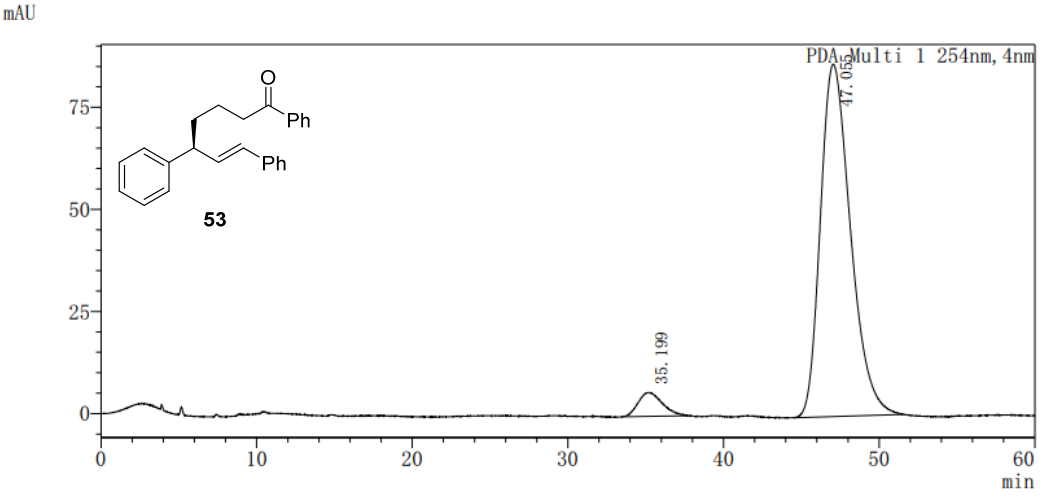
Peak#	Ret. Time	Area	Area%
1	25.813	3752170	3.326
2	30.580	109064753	96.674



Peak Table

PDA Ch1 254nm

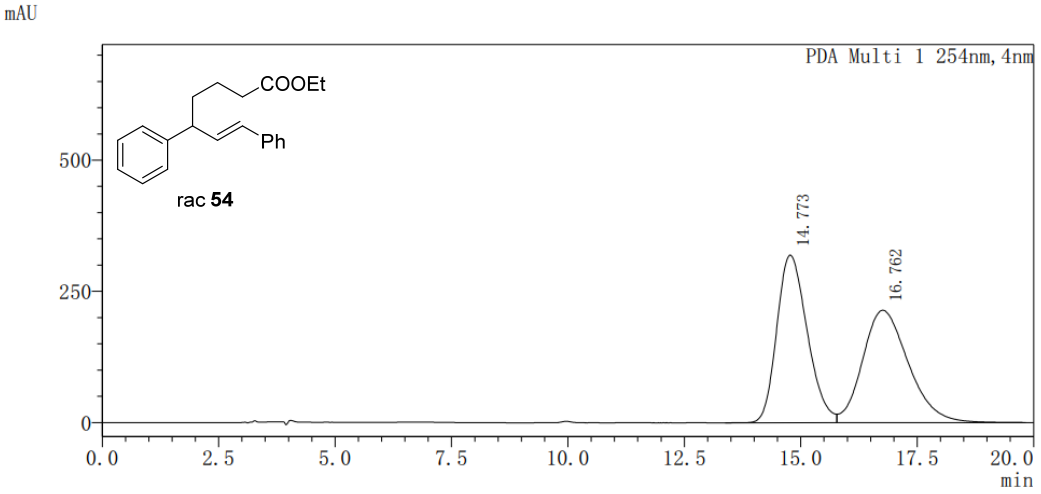
Peak#	Ret. Time	Area	Area%
1	34.427	18828969	49.483
2	46.623	19222355	50.517



Peak Table

PDA Ch1 254nm

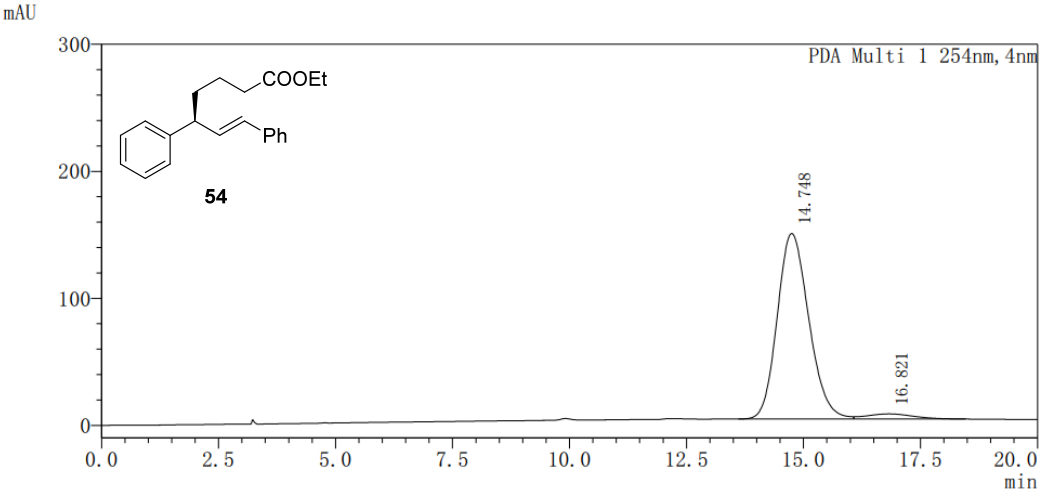
Peak#	Ret. Time	Area	Area%
1	35.199	634985	5.190
2	47.055	11598765	94.810



Peak Table

PDA Ch1 254nm

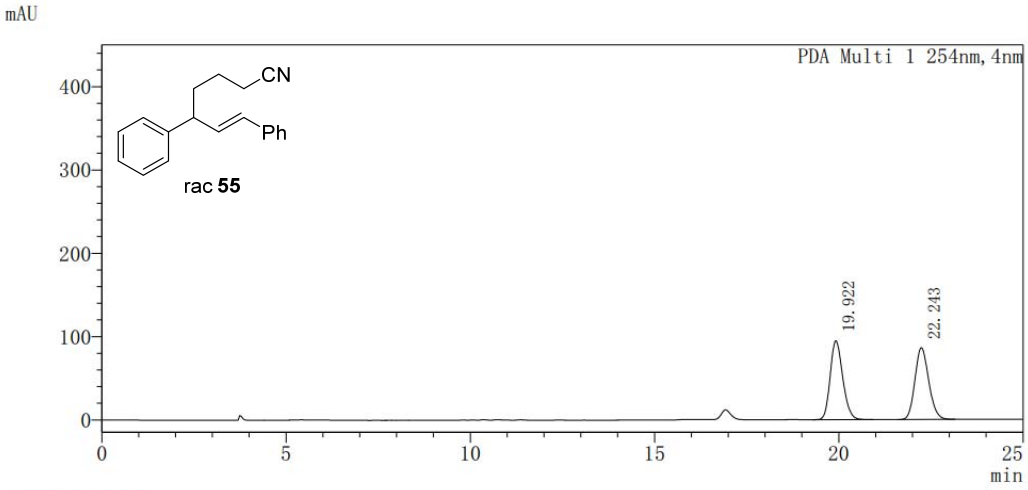
Peak#	Ret. Time	Area	Area%
1	14.773	14554352	49.806
2	16.762	14667924	50.194



Peak Table

PDA Ch1 254nm

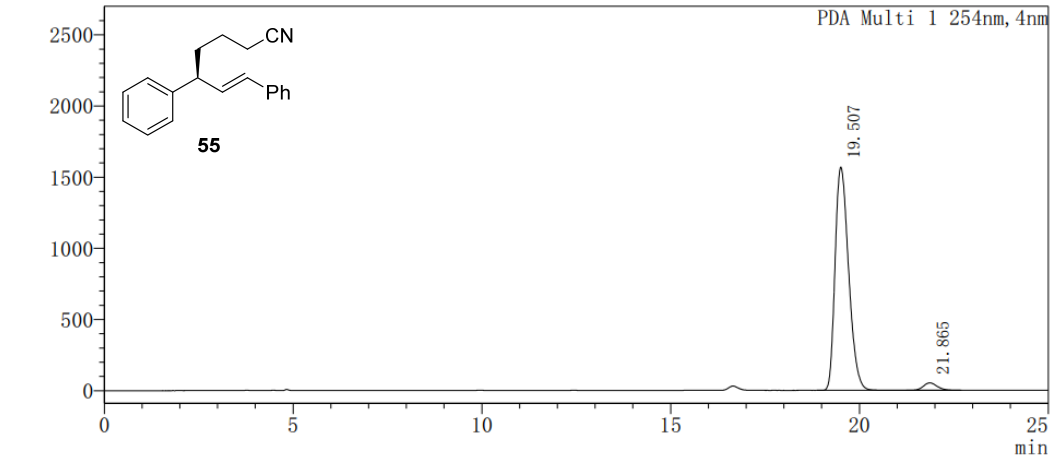
Peak#	Ret. Time	Area	Area%
1	14.748	6855409	96.042
2	16.821	282543	3.958



Peak Table

PDA Ch1 254nm

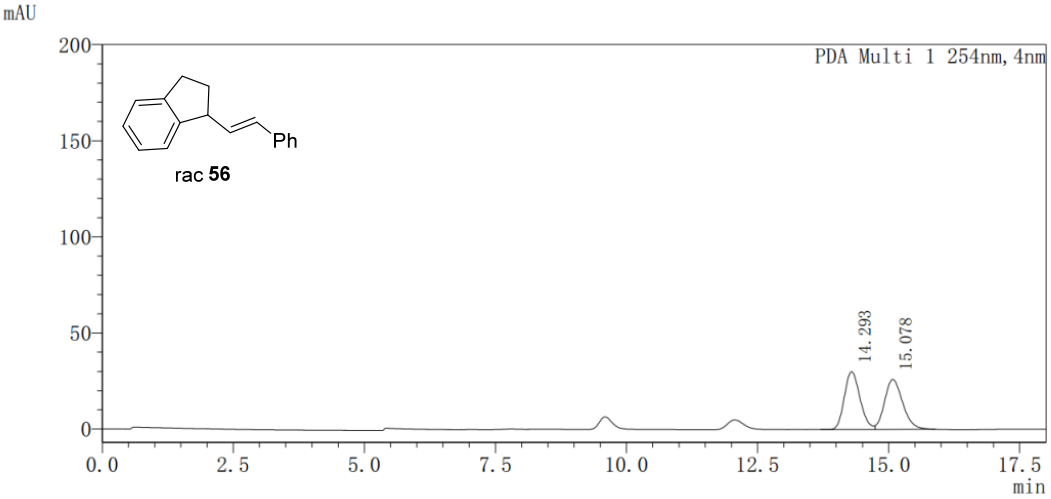
Peak#	Ret. Time	Area	Area%
1	19.922	2250440	50.055
2	22.243	2245473	49.945



Peak Table

PDA Ch1 254nm

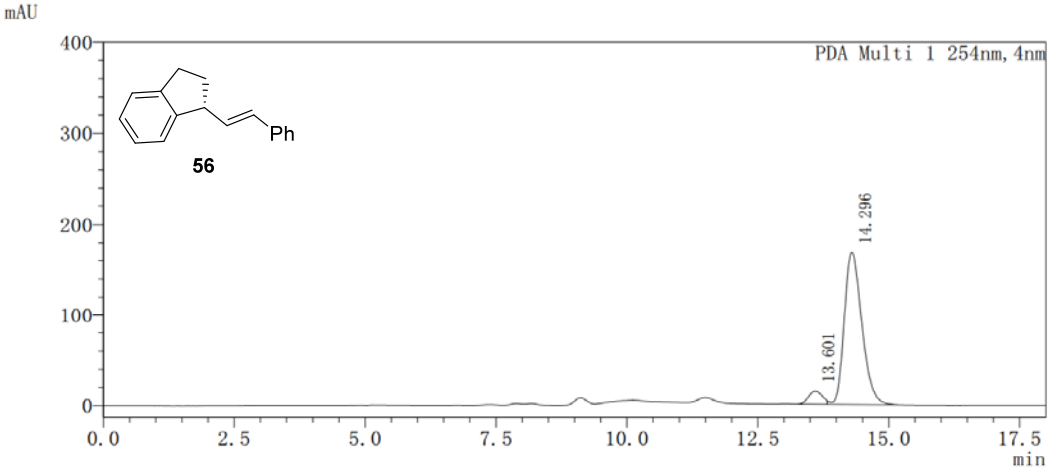
Peak#	Ret. Time	Area	Area%
1	19.507	39151548	96.705
2	21.865	1333831	3.295



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.293	625508	50.135
2	15.078	622129	49.865

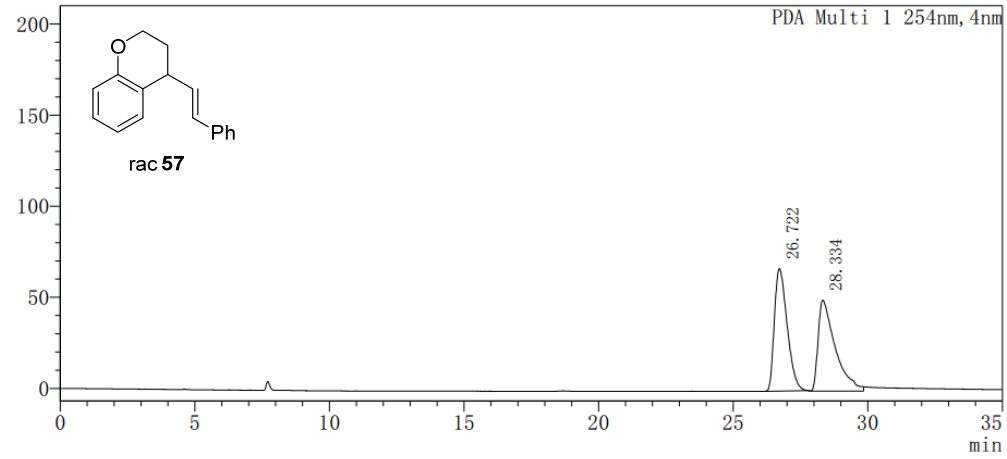


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.601	266561	6.350
2	14.296	3931166	93.650

mAU

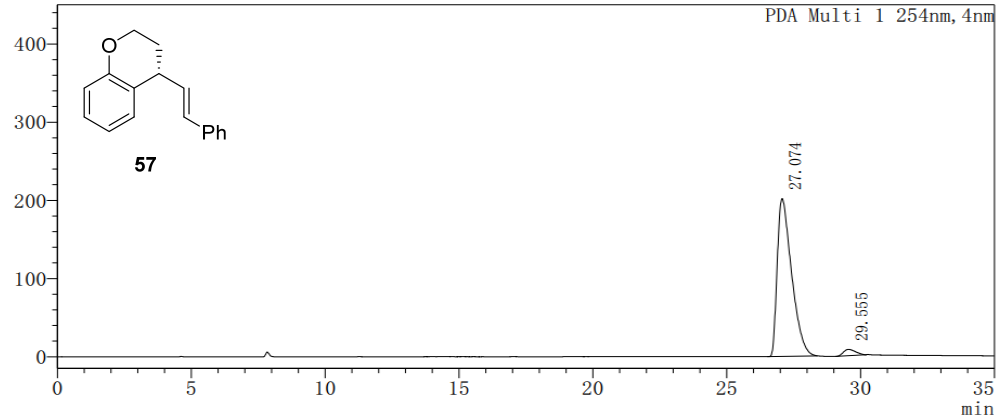


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	26.722	2219168	50.031
2	28.334	2216389	49.969

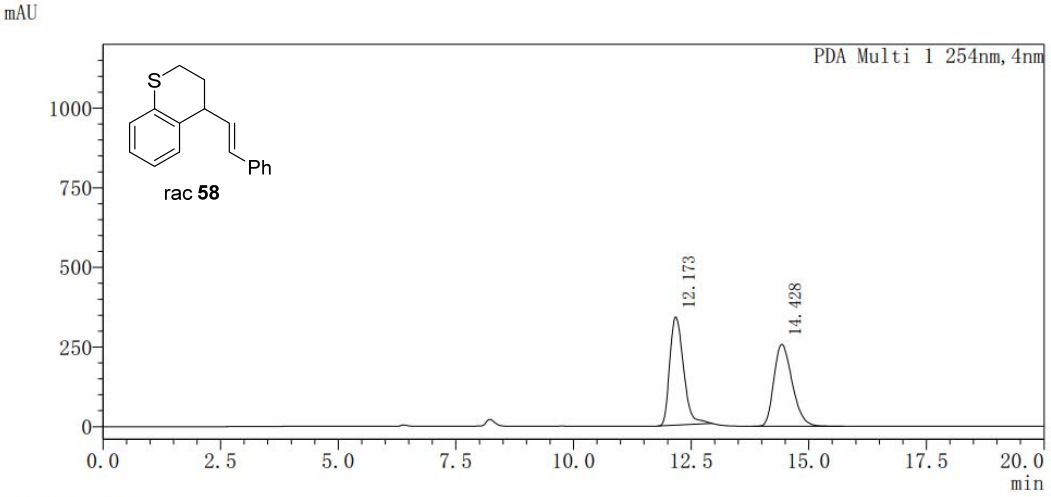
mAU



Peak Table

PDA Ch1 254nm

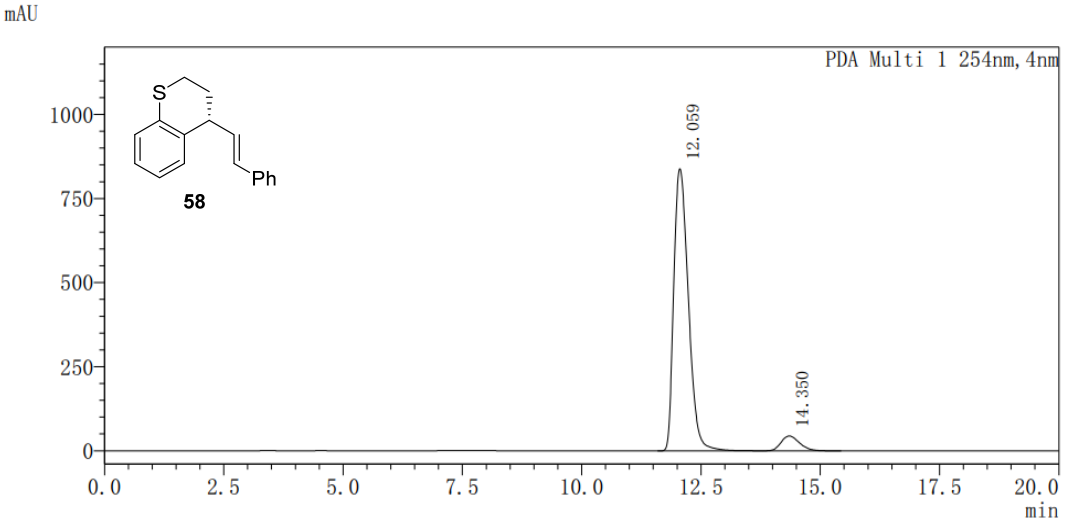
Peak#	Ret. Time	Area	Area%
1	27.074	7533281	96.747
2	29.555	253264	3.253



Peak Table

PDA Ch1 254nm

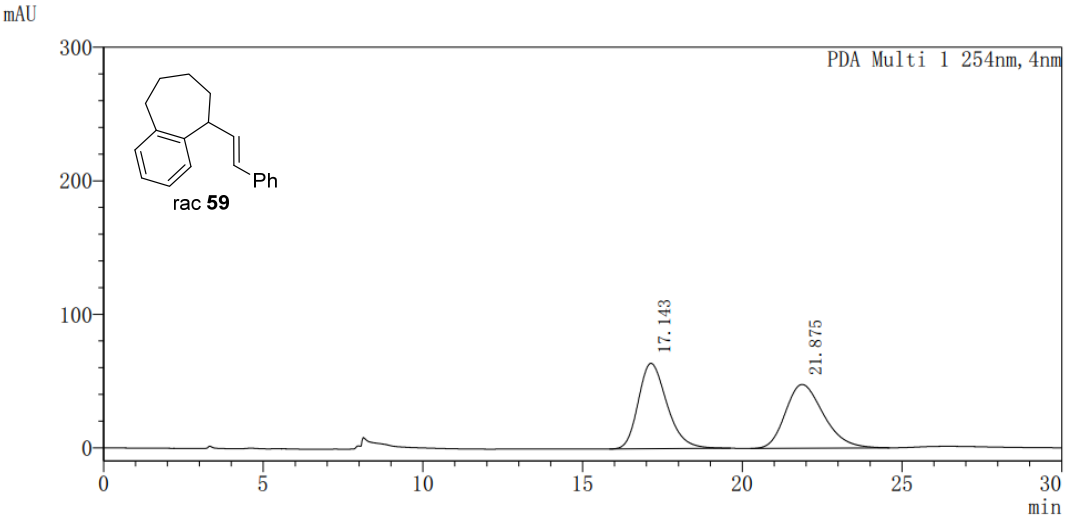
Peak#	Ret. Time	Area	Area%
1	12.173	6966010	50.009
2	14.428	6963500	49.991



Peak Table

PDA Ch1 254nm

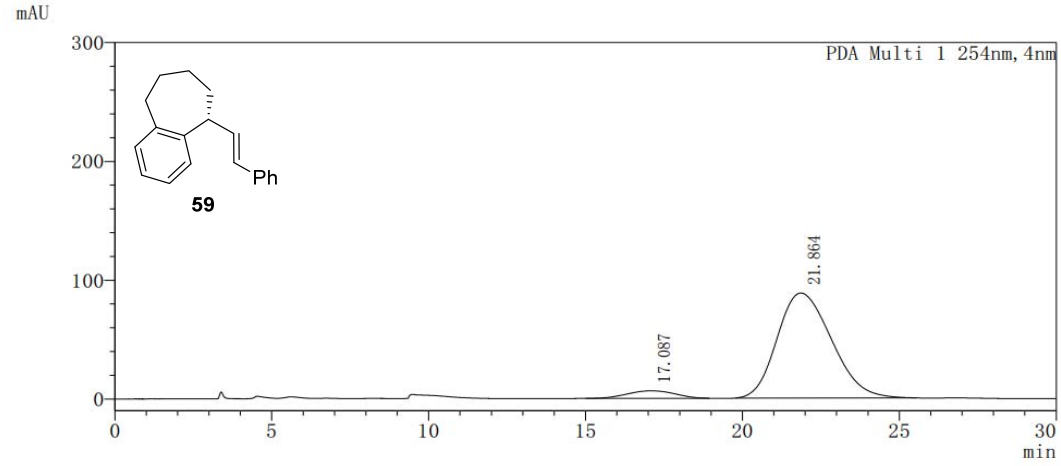
Peak#	Ret. Time	Area	Area%
1	12.059	17881032	93.754
2	14.350	1191276	6.246



Peak Table

PDA Ch1 254nm

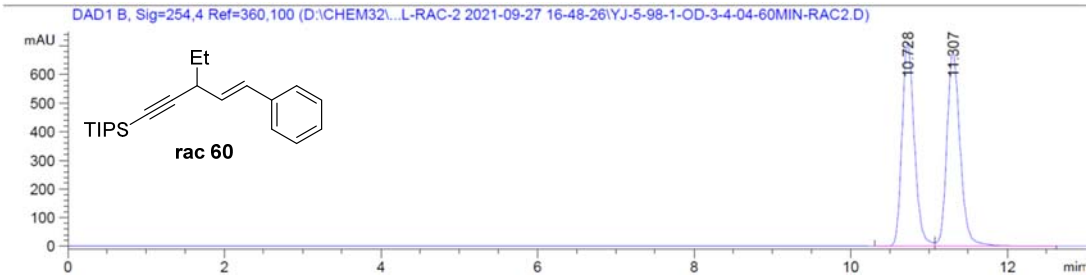
Peak#	Ret. Time	Area	Area%
1	17.143	4001531	50.252
2	21.875	3961431	49.748



Peak Table

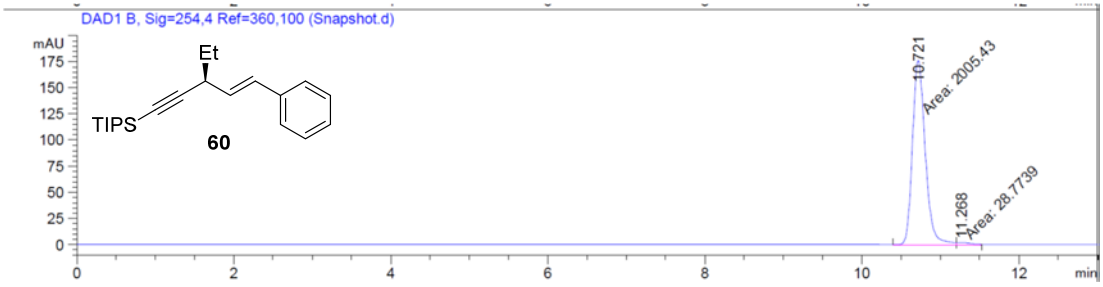
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.087	673338	5.954
2	21.864	10635750	94.046



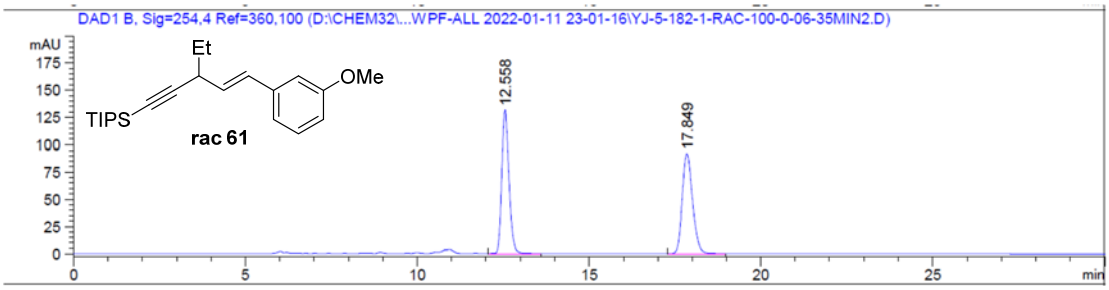
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.728	BV	0.1694	7758.53613	710.60760	49.2949
2	11.307	VB	0.1795	7980.49170	677.35522	50.7051
Totals :				1.57390e4	1387.96283	



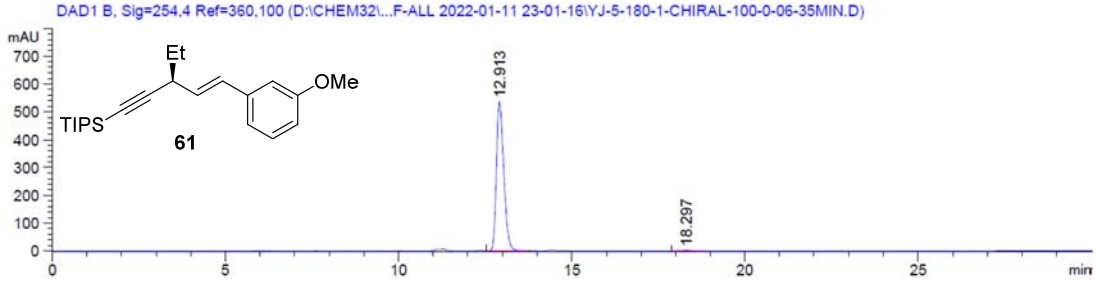
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.721	MF	0.1894	2005.42590	176.46976	98.5855
2	11.268	FM	0.2083	28.77394	2.30180	1.4145
Totals :				2034.19984	178.77156	



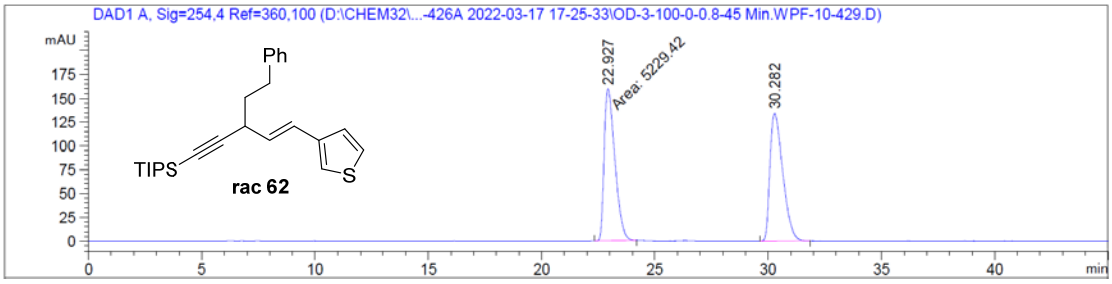
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.558	BB	0.2235	1921.15015	132.22681	49.9494
2	17.849	BB	0.3259	1925.03870	92.09118	50.0506
Totals :				3846.18884	224.31799	



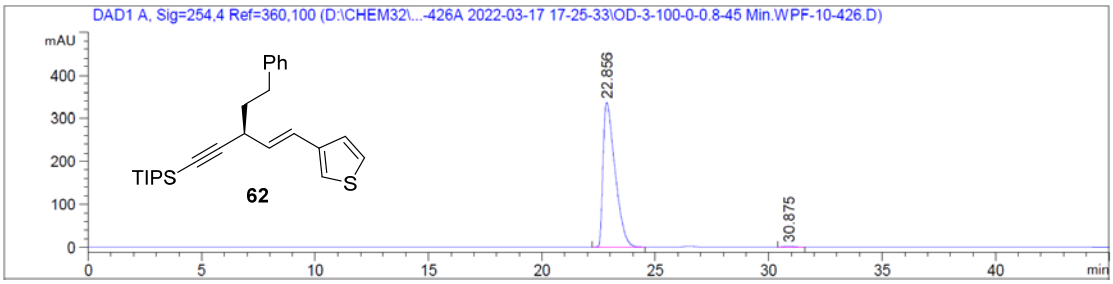
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.913	BB	0.2282	7887.58545	534.48438	99.2593
2	18.297	BB	0.2927	58.85534	2.87658	0.7407
Totals :				7946.44079	537.36096	



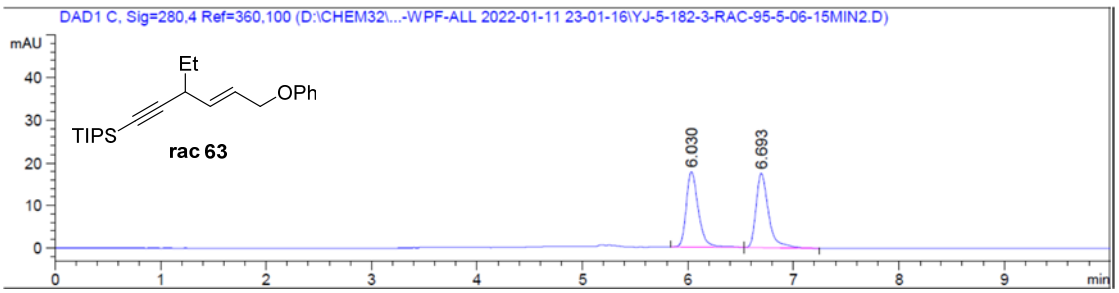
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.927	MM	0.5480	5229.42383	159.03575	49.7320
2	30.282	BB	0.5599	5285.78711	134.09586	50.2680
Totals :				1.05152e4	293.13161	



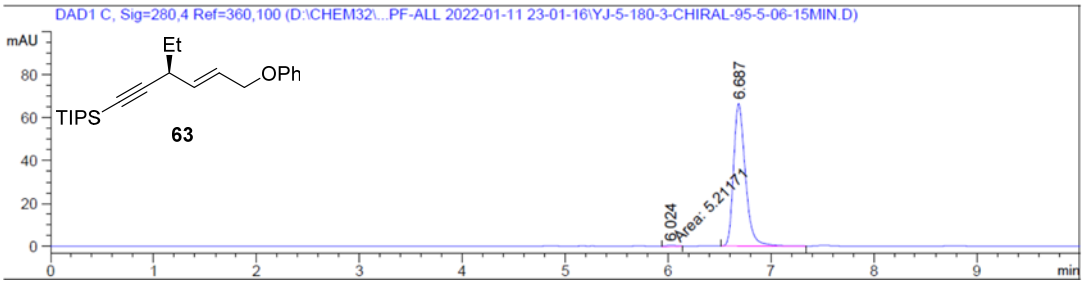
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.856	BB	0.5324	1.23905e4	335.88403	99.3735
2	30.875	BB	0.3933	78.11899	2.39010	0.6265
Totals :				1.24686e4	338.27413	



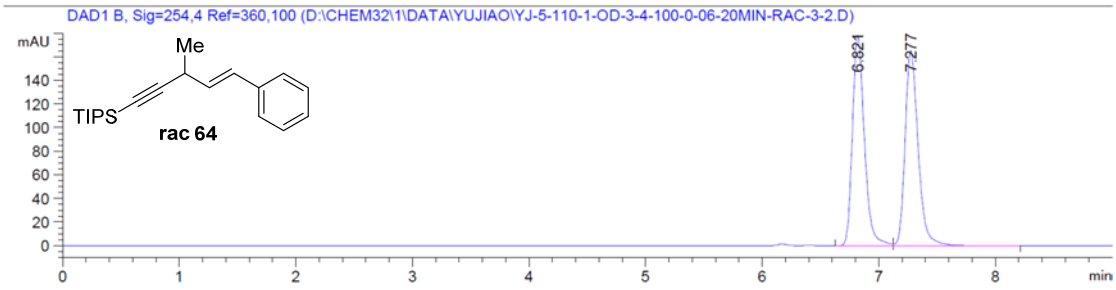
Signal 3: DAD1 C, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.030	BB	0.1212	141.65086	17.73513	49.7204
2	6.693	BB	0.1232	143.24402	17.55613	50.2796
Totals :				284.89488	35.29126	



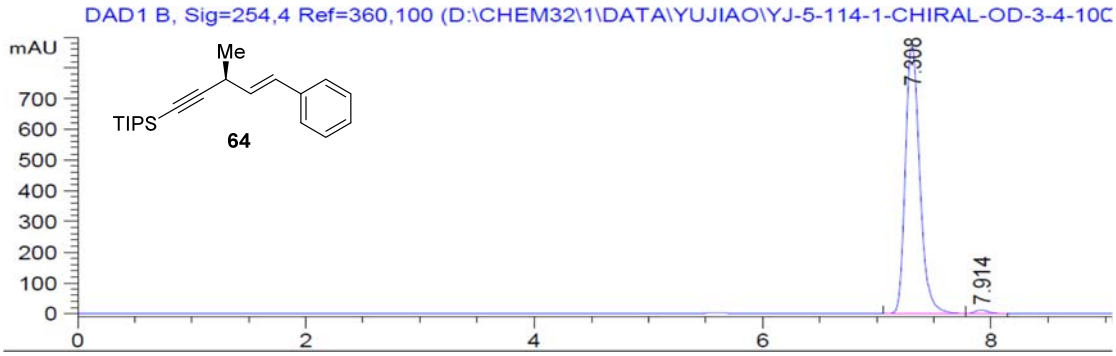
Signal 3: DAD1 C, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.024	MM	0.1383	5.21171	6.27988e-1	0.9729
2	6.687	BB	0.1213	530.45245	66.33139	99.0271
Totals :				535.66416	66.95938	



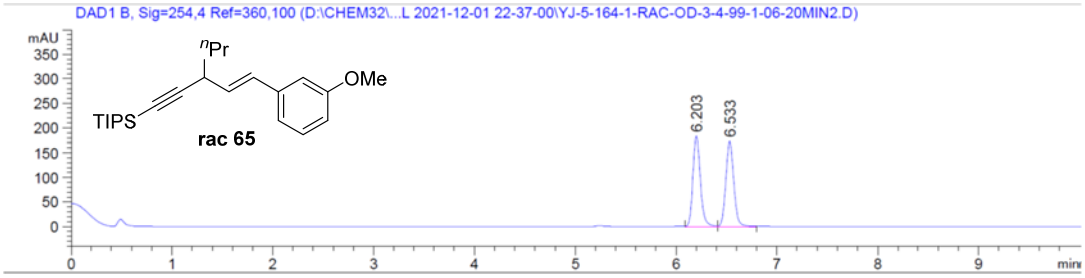
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.821	BV	0.1093	1272.74963	178.21114	49.7486
2	7.277	VB	0.1186	1285.61194	165.59537	50.2514
Totals :				2558.36157	343.80650	



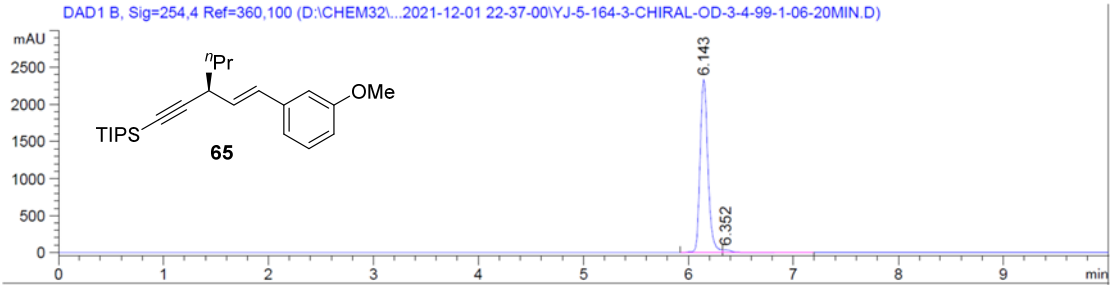
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.308	BV	0.1360	7616.53271	871.12329	98.7050
2	7.914	VV	0.1297	99.93106	11.68954	1.2950
Totals :				7716.46378	882.81283	



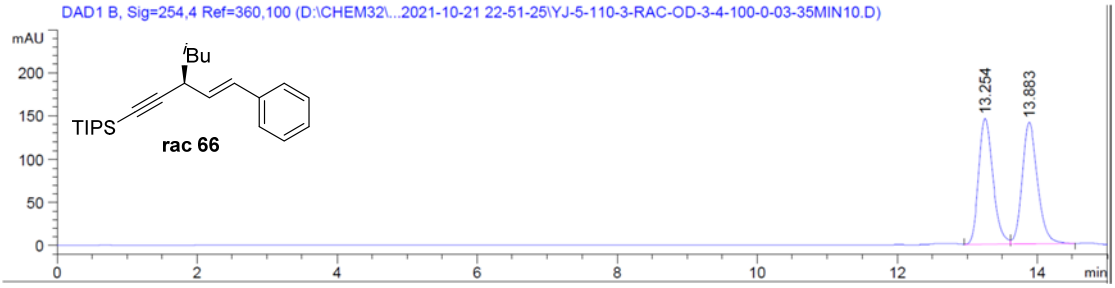
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.203	VV	0.0786	954.57391	183.78426	49.8168
2	6.533	VV	0.0848	961.59570	173.15106	50.1832
Totals :				1916.16962	356.93532	



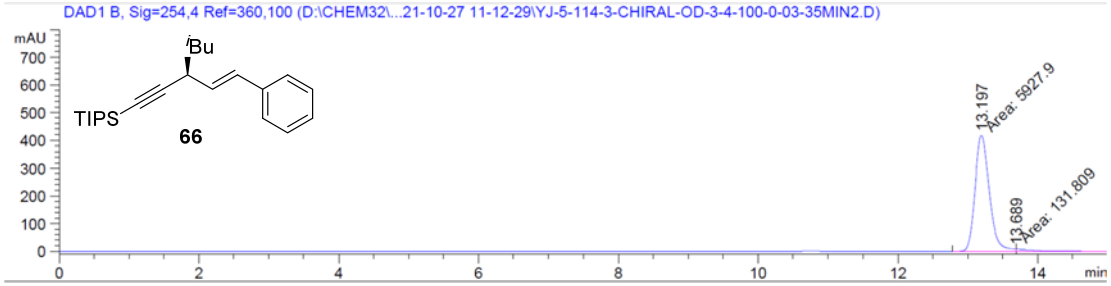
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.143	BV	0.0785	1.20891e4	2331.49658	98.0457
2	6.352	VB	0.0911	240.97211	37.44248	1.9543
Totals :				1.23301e4	2368.93906	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

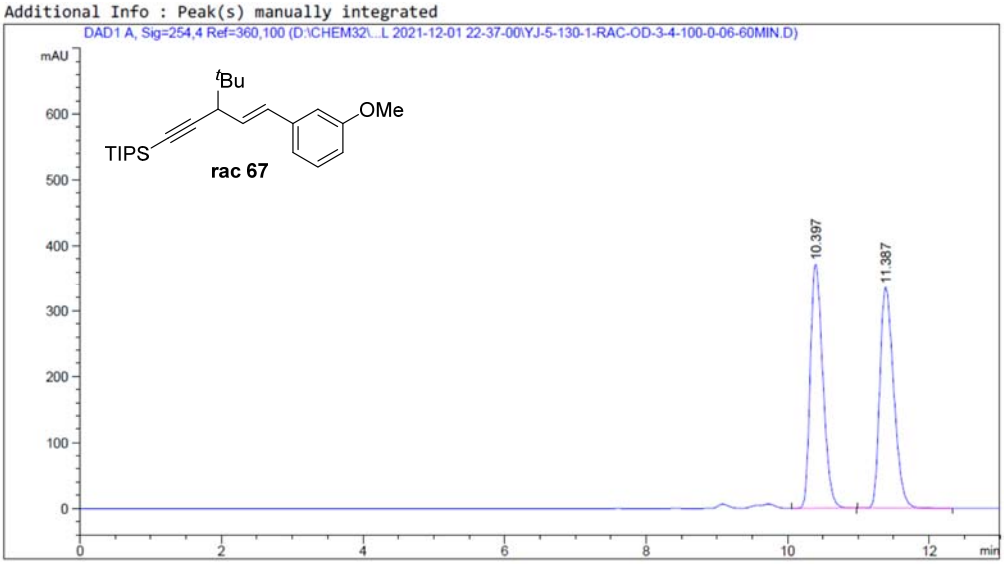
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.254	VV	0.2201	2065.76147	145.08989	49.0277
2	13.883	VB	0.2346	2147.70044	140.31886	50.9723
Totals :				4213.46191	285.40875	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.197	MF	0.2366	5927.89941	417.64941	97.8248
2	13.689	FM	0.2654	131.80870	8.27800	2.1752
Totals :				6059.70811	425.92741	

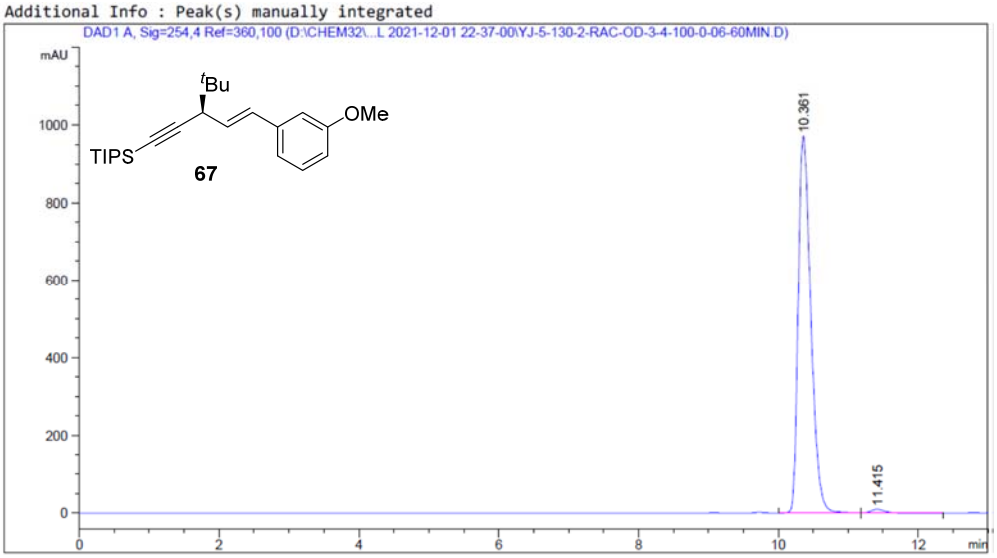
Additional Info : Peak(s) manually integrated



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.397	BB	0.1916	4575.04883	371.81555	49.9363
2	11.387	BB	0.2117	4586.72363	335.17880	50.0637
Totals :				9161.77246	706.99435	

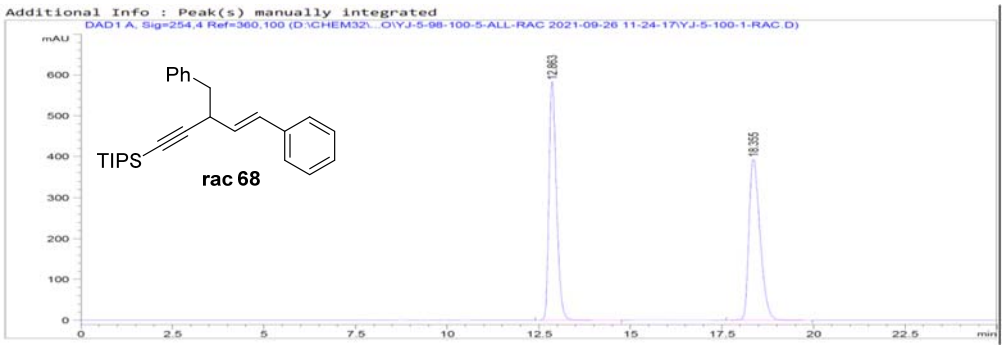
Additional Info : Peak(s) manually integrated



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

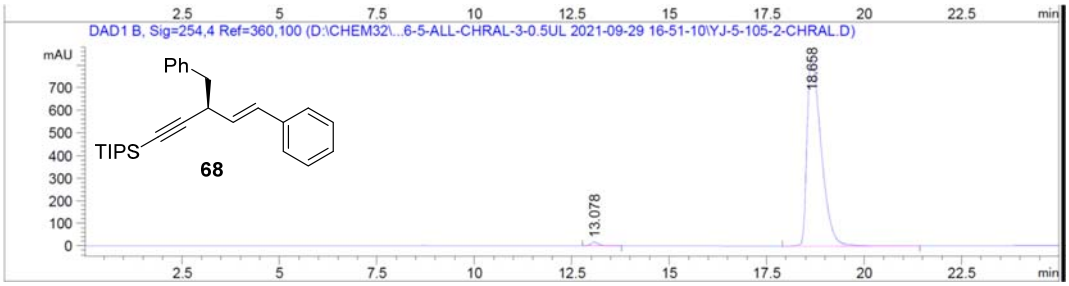
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.361	BV	0.1941	1.21641e4	971.04169	98.8745
2	11.415	VB	0.2193	138.46420	9.54380	1.1255
Totals :				1.23025e4	980.58549	

Additional Info : Peak(s) manually integrated



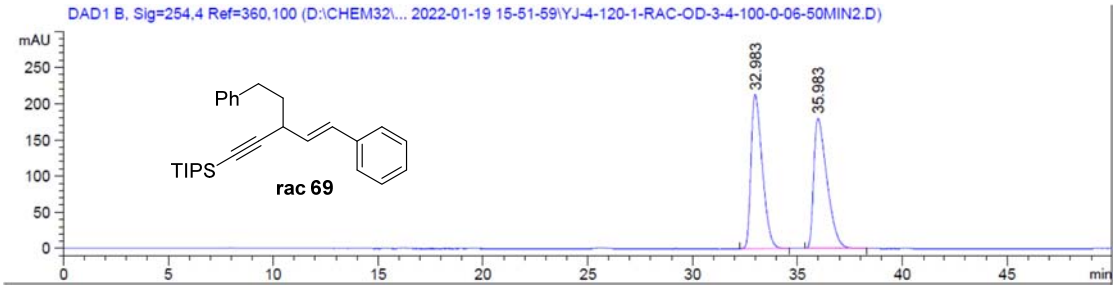
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.863	BB	0.2208	8336.70508	582.99634	50.0502
2	18.355	BB	0.3289	8319.99316	393.18613	49.9498
Totals :				1.66567e4	976.18246	



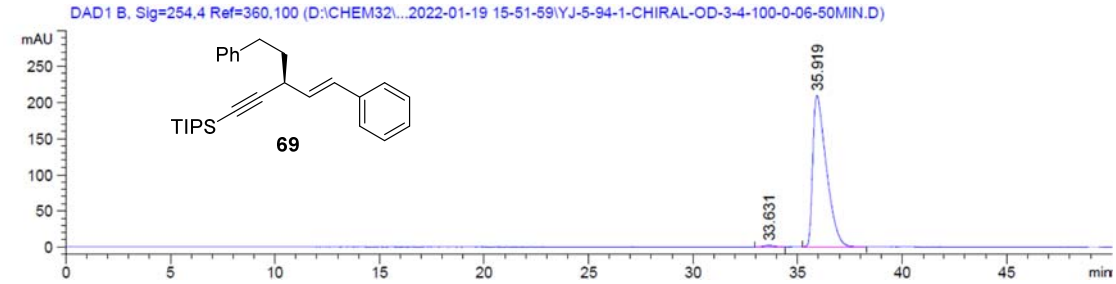
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.078	BB	0.2188	244.84978	17.12787	1.1411
2	18.658	BB	0.3866	2.12124e4	840.04626	98.8589
Totals :				2.14572e4	857.17414	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

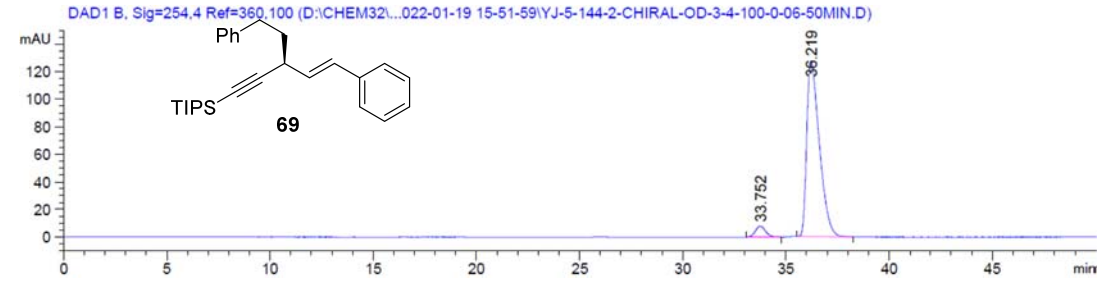
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.983	BB	0.5726	7917.22656	212.51578	50.1815
2	35.983	BB	0.6614	7859.96729	179.31242	49.8185
Totals :				1.57772e4	391.82820	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

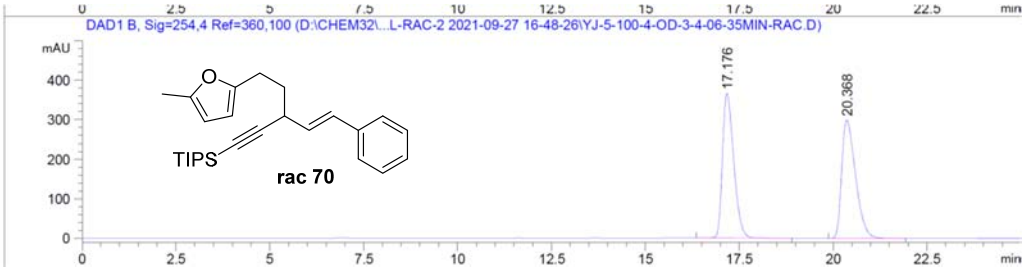
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.631	BB	0.4071	81.55185	2.40823	0.8558
2	35.919	BB	0.6676	9447.74316	209.70064	99.1442
Totals :				9529.29501	212.10887	

From Cl-Substrate



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.752	BB	0.4572	275.35962	7.96677	4.8406
2	36.219	BB	0.6398	5413.16357	127.37505	95.1594
Totals :				5688.52319	135.34182	

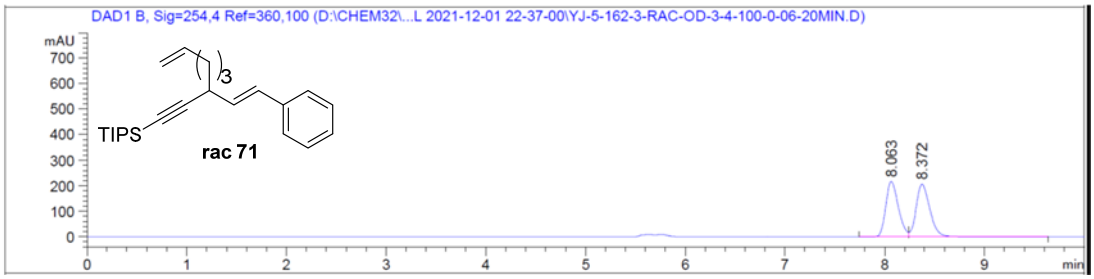


Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.176	BB	0.3241	7635.30469	364.89963	50.0061
2	20.368	BB	0.3968	7633.43994	298.04480	49.9939
Totals :				1.52687e4	662.94443	

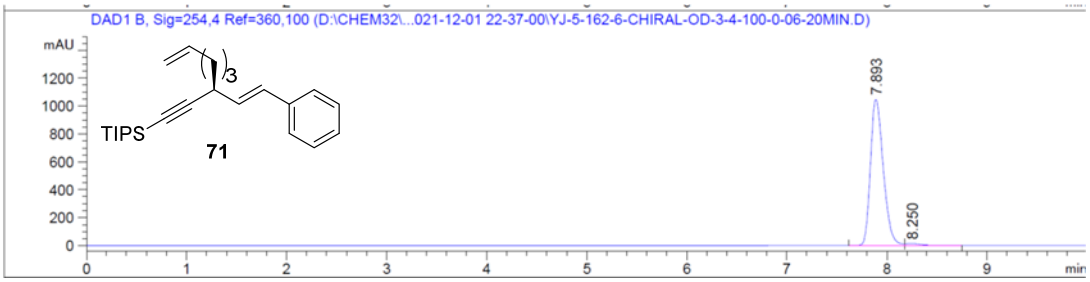
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.298	BB	0.3449	1.58994e4	705.55365	98.9003
2	20.808	BB	0.3731	176.78403	7.23323	1.0997
Totals :				1.60762e4	712.78688	



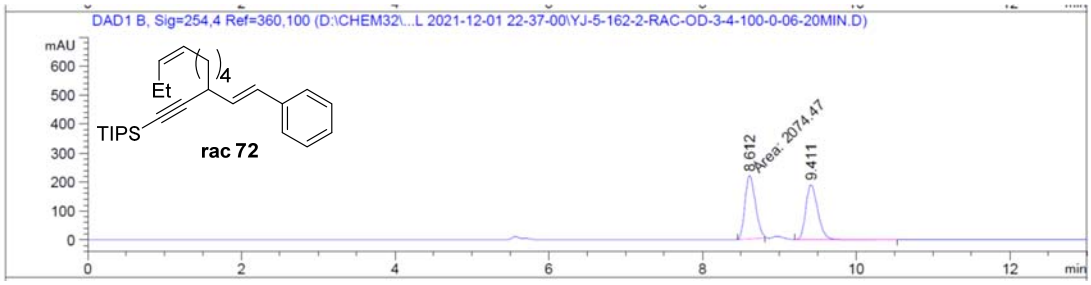
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.063	BV	0.1361	1903.42468	217.41853	49.0046
2	8.372	VB	0.1477	1980.74841	206.81711	50.9954
Totals :				3884.17310	424.23564	



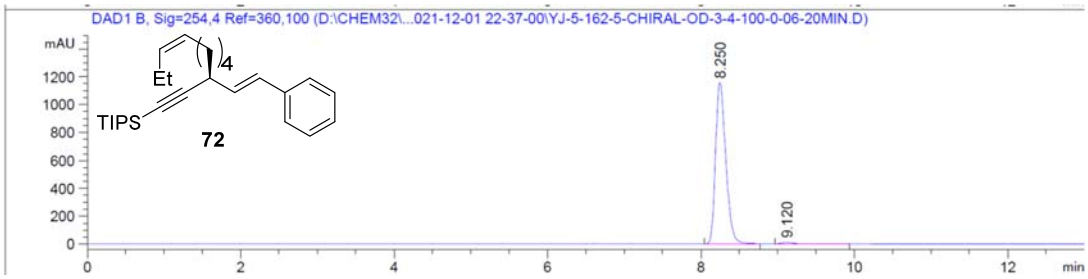
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.893	BV	0.1375	9307.23730	1048.64697	98.4109
2	8.250	VB	0.1491	150.28944	14.71640	1.5891
Totals :				9457.52675	1063.36337	



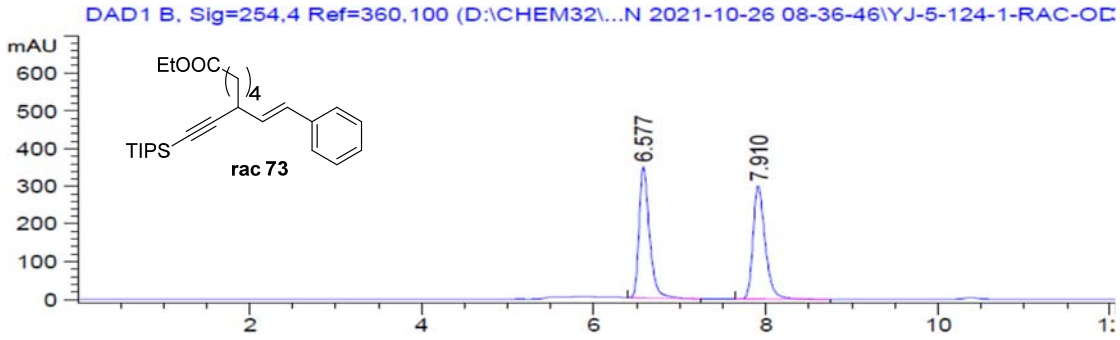
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.612	MM	0.1576	2074.46729	219.40526	49.9922
2	9.411	VB	0.1686	2075.11499	191.17545	50.0078
Totals :				4149.58228	410.58070	



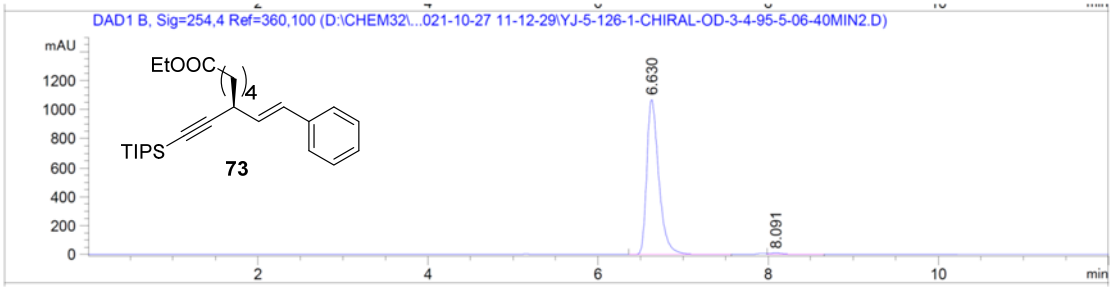
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.250	VV	0.1443	1.07383e4	1157.31067	98.9762
2	9.120	VB	0.1656	111.07938	10.15638	1.0238
Totals :				1.08494e4	1167.46705	



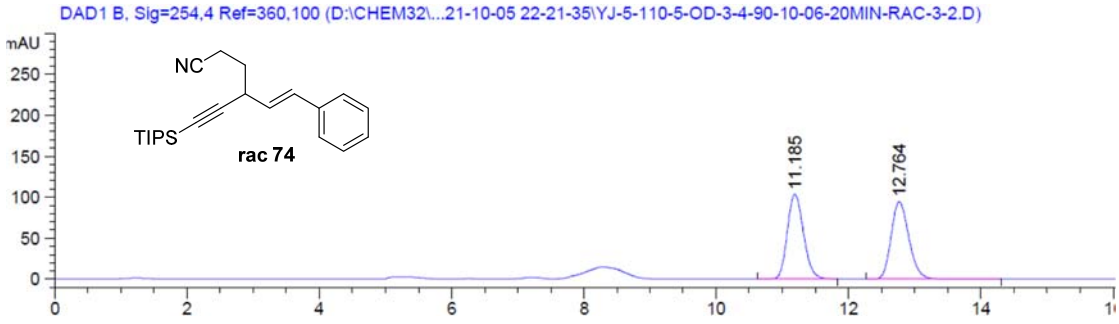
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.577	BB	0.1259	2919.25903	347.95065	49.5534
2	7.910	BB	0.1516	2971.87988	299.81003	50.4466
Totals :				5891.13892	647.76068	



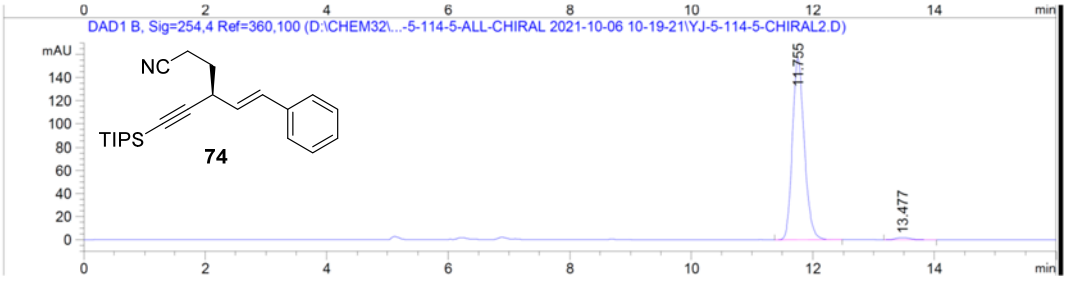
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.630	BB	0.1483	1.04873e4	1070.08130	98.8753
2	8.091	VB	0.1647	119.29053	10.64615	1.1247
Totals :				1.06065e4	1080.72745	



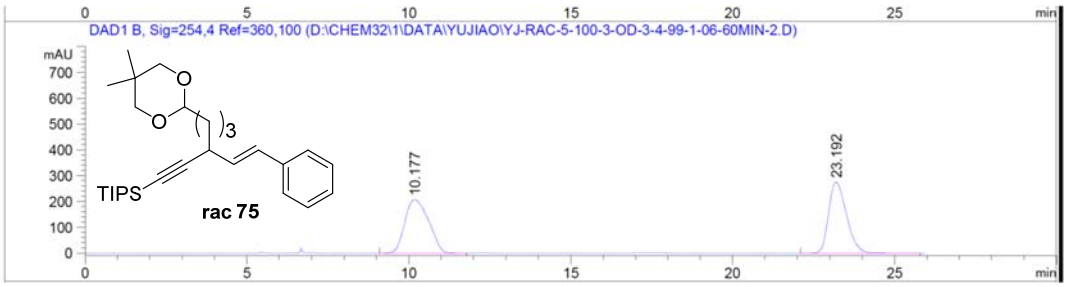
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.185	BB	0.2670	1762.65808	103.33720	49.9249
2	12.764	BB	0.2926	1767.95801	94.37234	50.0751
Totals :				3530.61609	197.70954	



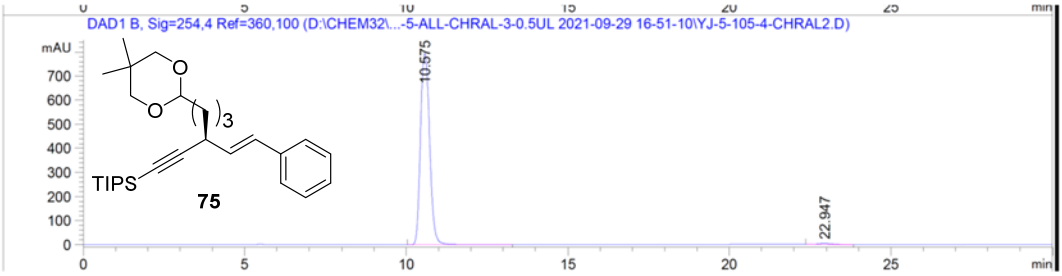
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.755	BB	0.2096	2139.99561	156.39520	98.6000
2	13.477	BB	0.2380	30.38511	1.90603	1.4000
Totals :				2170.38072	158.30123	



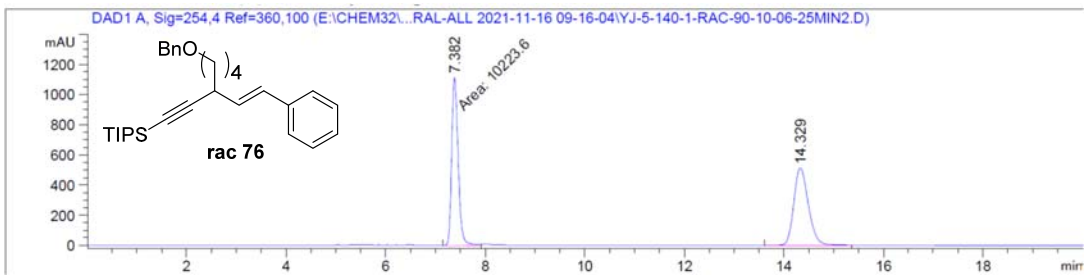
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.177	BB	0.8769	1.04890e4	206.41016	49.9353
2	23.192	BB	0.5987	1.05161e4	274.63007	50.0647
Totals :				2.10051e4	481.04022	



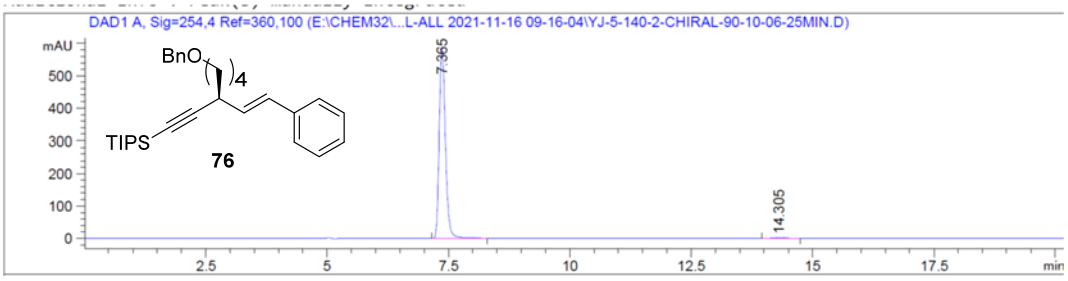
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.575	BB	0.3155	1.56205e4	794.19183	99.0976
2	22.947	BB	0.4662	142.23900	4.55583	0.9024
Totals :				1.57627e4	798.74767	



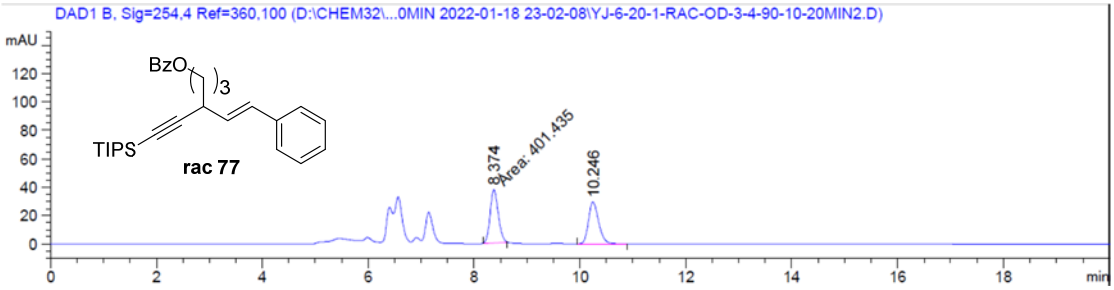
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.382	MM	0.1525	1.02236e4	1116.98584	49.5975
2	14.329	VV R	0.3119	1.03895e4	513.79761	50.4025
Totals :				2.06131e4	1630.78345	



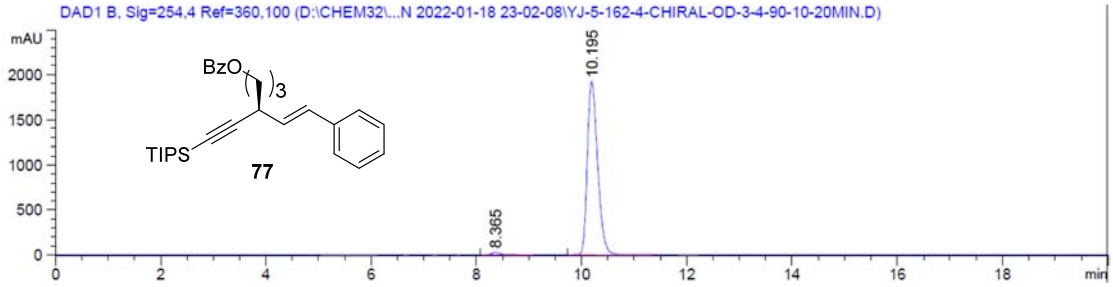
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.365	BV R	0.1359	5238.53711	586.85236	98.9338
2	14.305	VB	0.2397	56.45603	2.86703	1.0662
Totals :				5294.99314	589.71939	



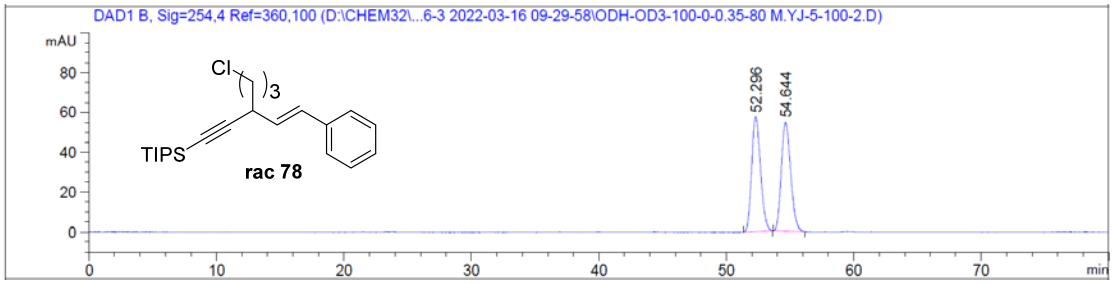
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.374	MM	0.1777	401.43509	37.65586	50.4019
2	10.246	BB	0.2054	395.03384	29.66517	49.5981
Totals :				796.46893	67.32104	



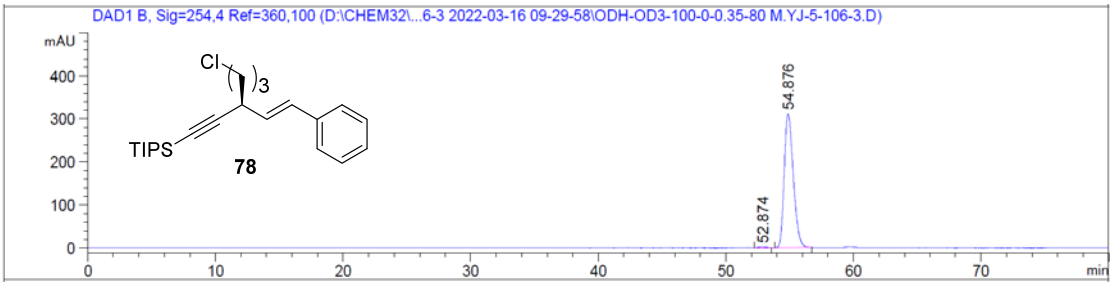
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.365	BB	0.1664	268.32065	24.38925	1.0159
2	10.195	BB	0.2107	2.61432e4	1922.08508	98.9841
Totals :				2.64115e4	1946.47433	



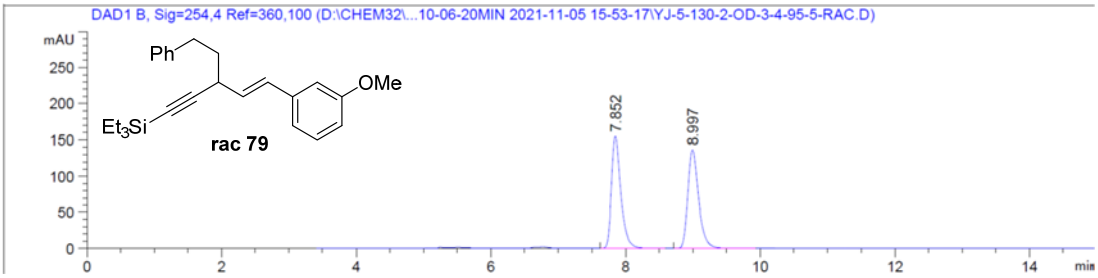
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.296	BB	0.5788	2787.01831	57.56633	49.9850
2	54.644	BB	0.6168	2788.69043	54.70142	50.0150
Totals :				5575.70874	112.26774	



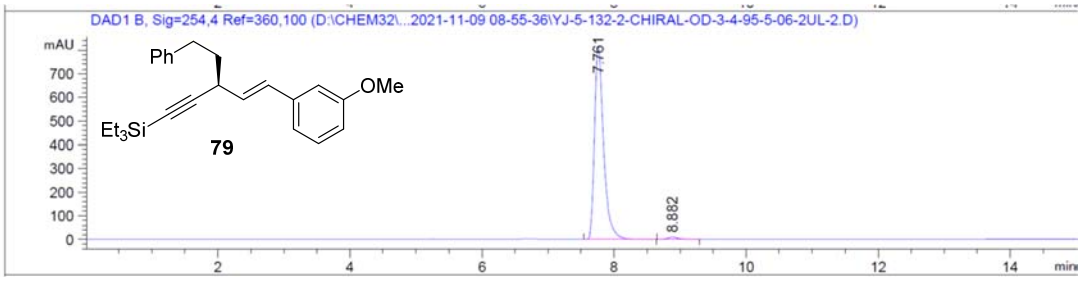
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.874	BB	0.4779	97.19391	2.43381	0.6244
2	54.876	BB	0.7296	1.54681e4	311.34787	99.3756
Totals :				1.55653e4	313.78168	



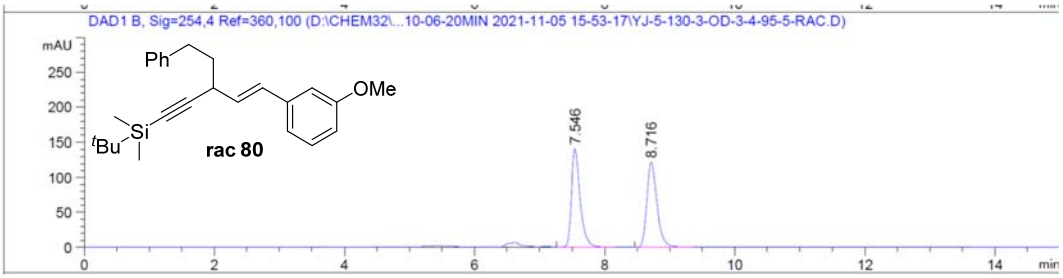
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.852	BB	0.1445	1494.11255	154.95773	49.8917
2	8.997	BB	0.1664	1500.59631	136.36746	50.1083
Totals :				2994.70886	291.32520	



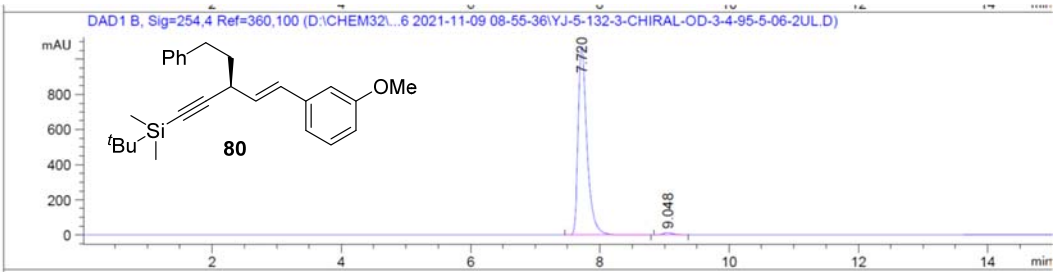
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.761	BB	0.1418	7699.46875	818.01874	98.7634
2	8.882	BB	0.1613	96.40506	9.11997	1.2366
Totals :				7795.87381	827.13870	



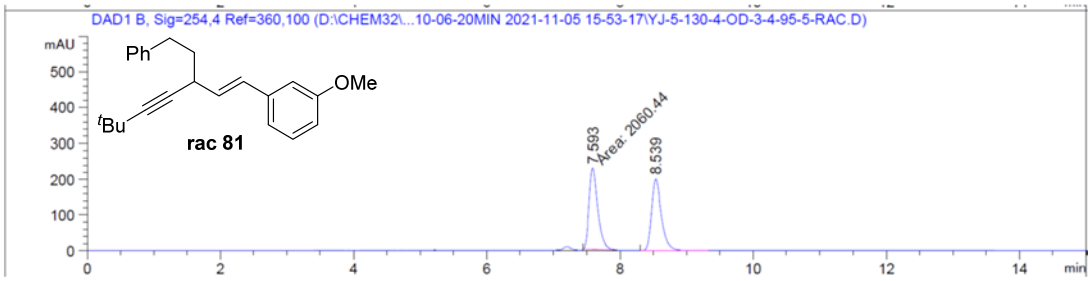
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.546	BB	0.1401	1301.17322	140.46347	50.0266
2	8.716	BB	0.1626	1299.78992	121.72453	49.9734
Totals :				2600.96313	262.18800	



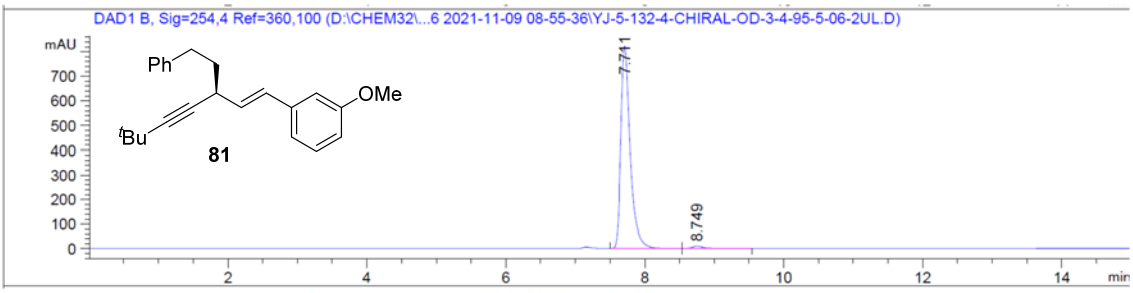
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.720	BB	0.1400	1.01261e4	1073.75610	98.7597
2	9.048	BB	0.1621	127.17579	11.95376	1.2403
Totals :				1.02532e4	1085.70986	



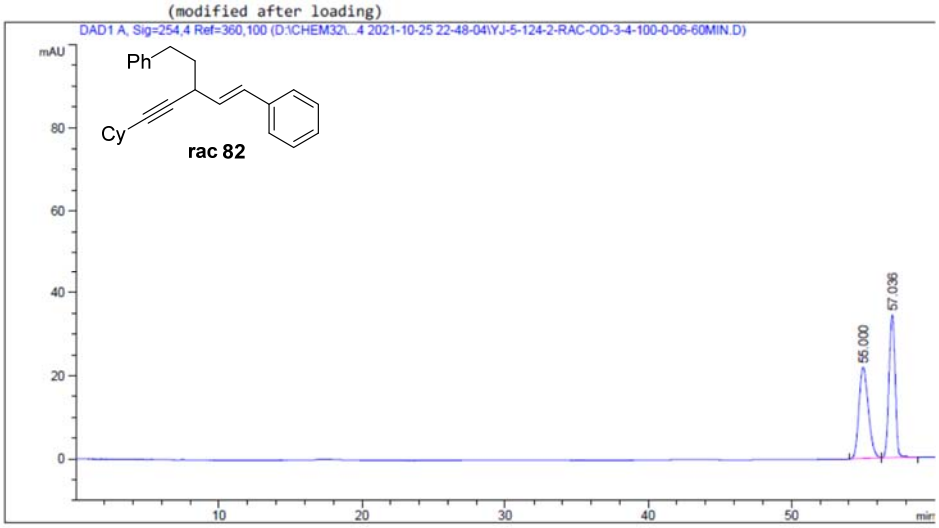
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.593	MM	0.1502	2060.43799	228.56219	50.0808
2	8.539	BB	0.1554	2053.79199	200.66583	49.9192
Totals :				4114.22998	429.22803	



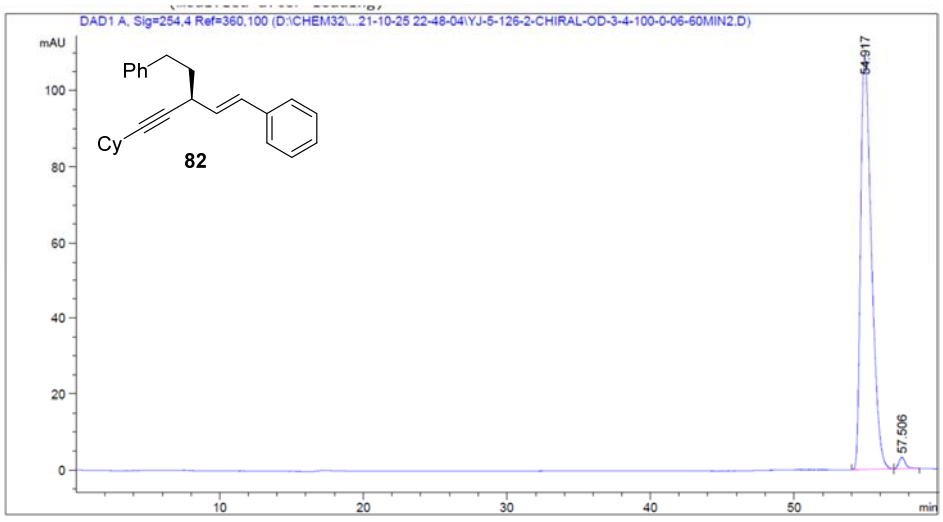
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.711	BB	0.1380	7630.13770	824.57373	98.6254
2	8.749	BB	0.1603	106.34670	9.98296	1.3746
Totals :				7736.48440	834.55669	



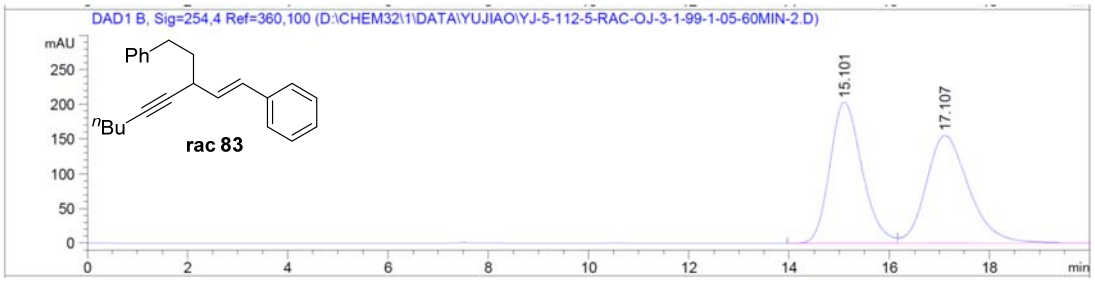
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.000	BB	0.6957	1004.69342	21.96265	49.3786
2	57.036	BB	0.4714	1029.97961	34.39271	50.6214
Totals :				2034.67303	56.35536	



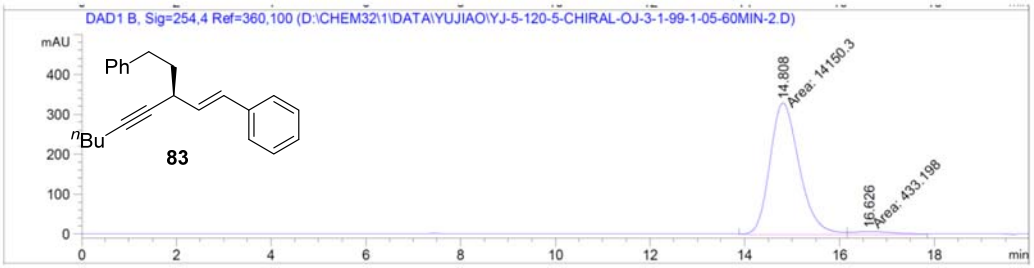
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	54.917	BB	0.8073	5725.44922	108.90945	98.3717
2	57.506	BB	0.4452	94.76952	3.01128	1.6283
Totals :				5820.21874	111.92074	



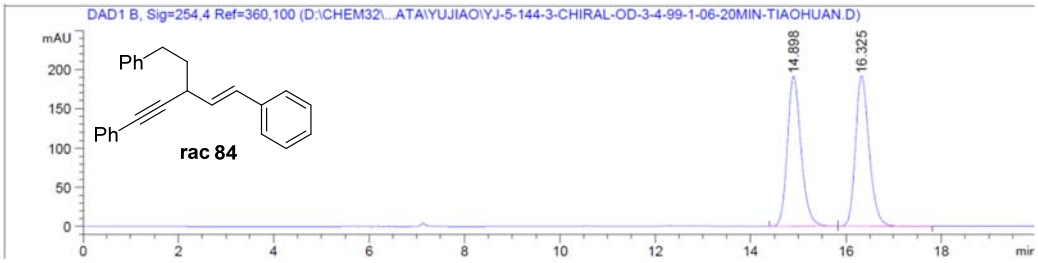
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.101	BV	0.6890	9077.45898	203.25929	49.6070
2	17.107	VBA	0.9036	9221.29004	155.09615	50.3930
Totals :				1.82987e4	358.35544	



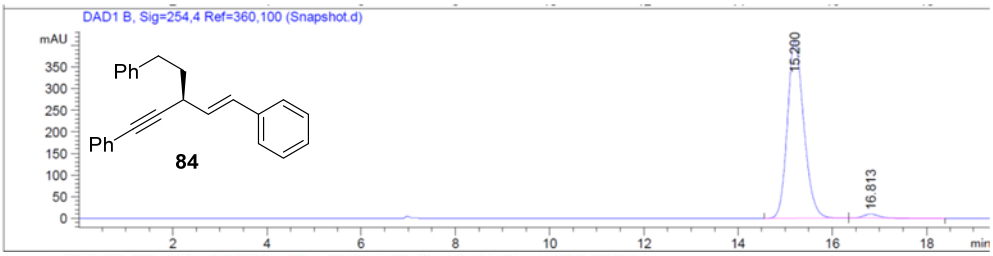
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.808	MF	0.7171	1.41503e4	328.88361	97.0295
2	16.626	FM	1.0646	433.19785	6.78197	2.9705
Totals :				1.45835e4	335.66558	



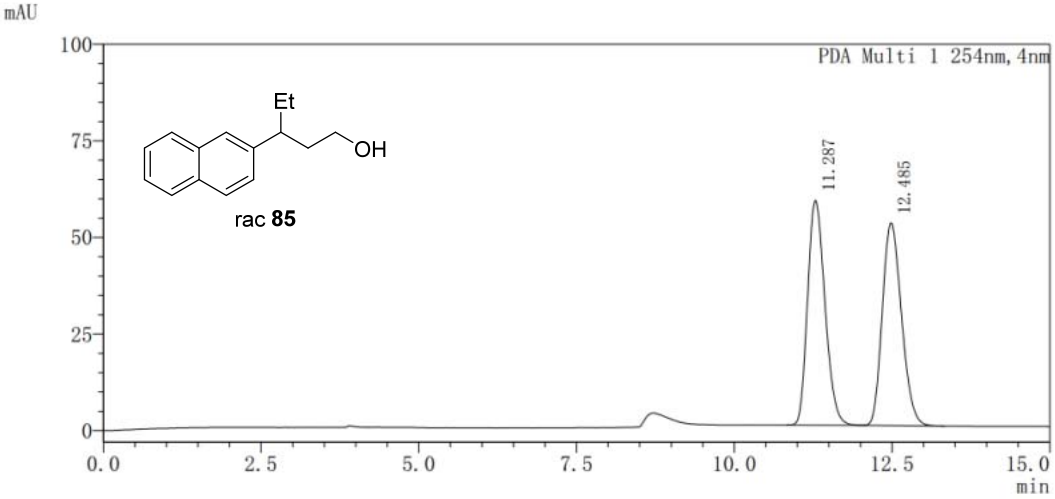
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.898	BB	0.3053	3820.65552	191.04643	50.1060
2	16.325	BB	0.3039	3804.48804	191.37062	49.8940
Totals :				7625.14355	382.41705	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

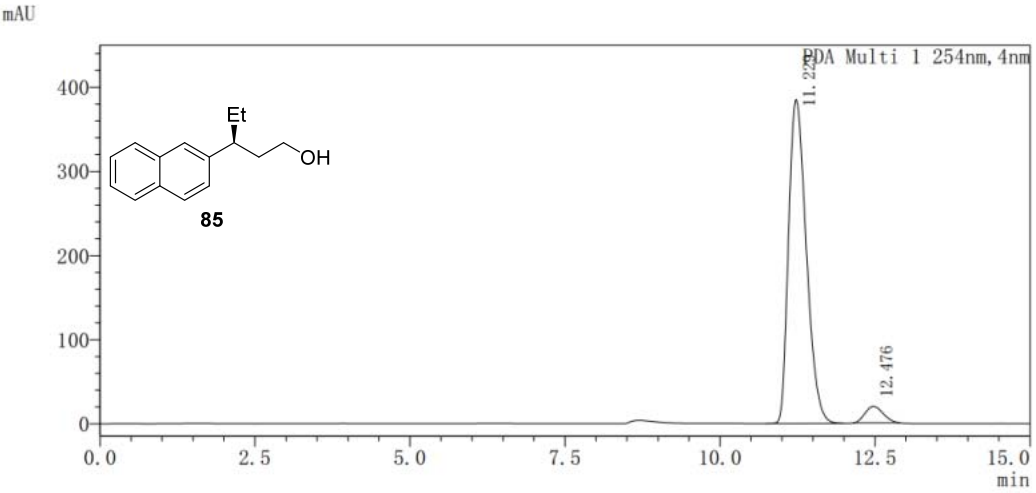
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.200	BB	0.3702	9950.61230	411.34973	97.9162
2	16.813	BB	0.3386	211.76567	9.40683	2.0838
Totals :				1.01624e4	420.75656	



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.287	1114967	50.049
2	12.485	1112805	49.951

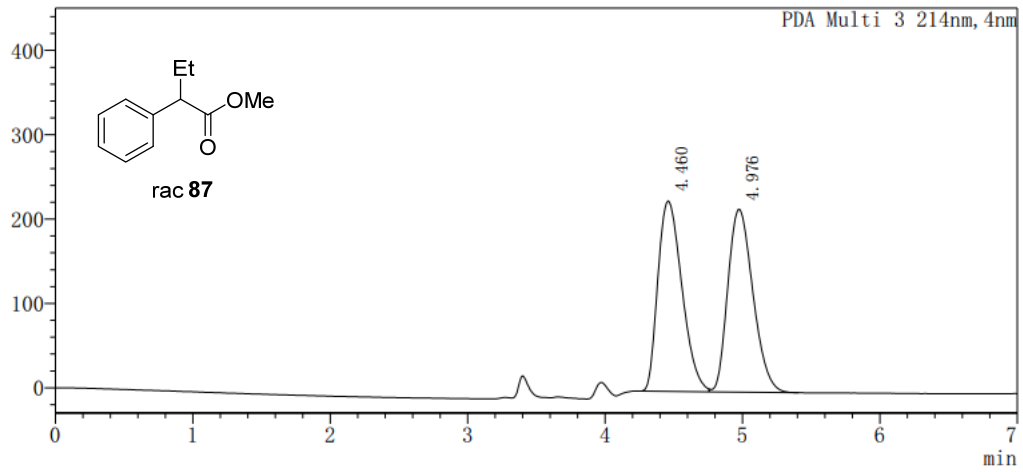


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.229	7654771	95.010
2	12.476	402014	4.990

mAU

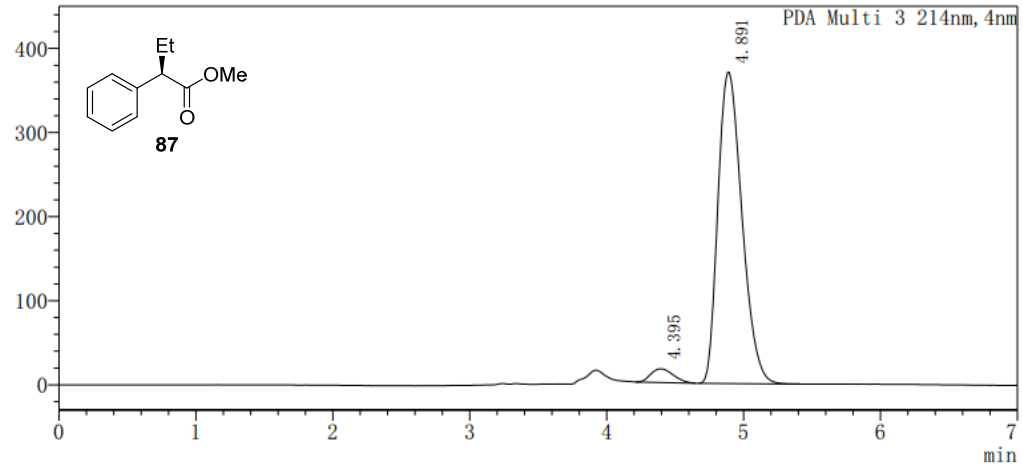


Peak Table

PDA Ch3 214nm

Peak#	Ret. Time	Area	Area%
1	4.460	2746792	49.912
2	4.976	2756504	50.088

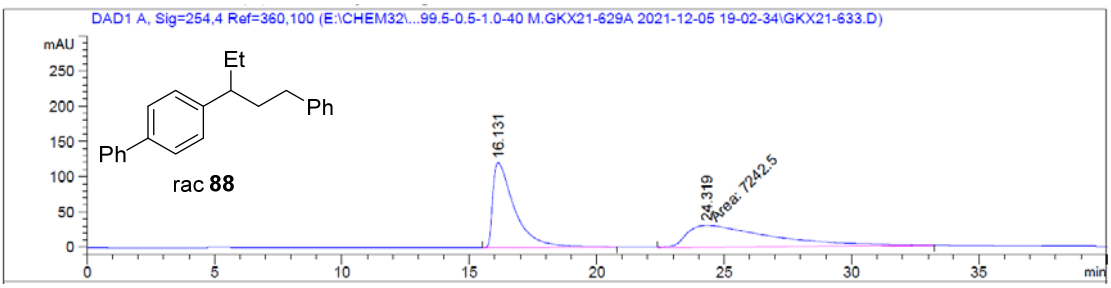
mAU



Peak Table

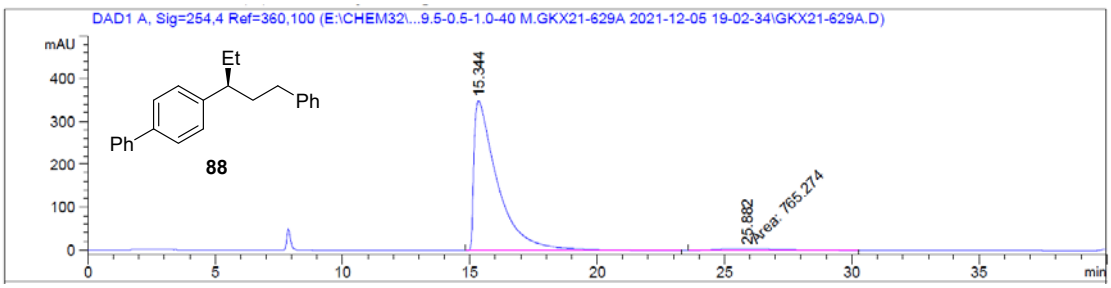
PDA Ch3 214nm

Peak#	Ret. Time	Area	Area%
1	4.395	185547	3.937
2	4.891	4527035	96.063



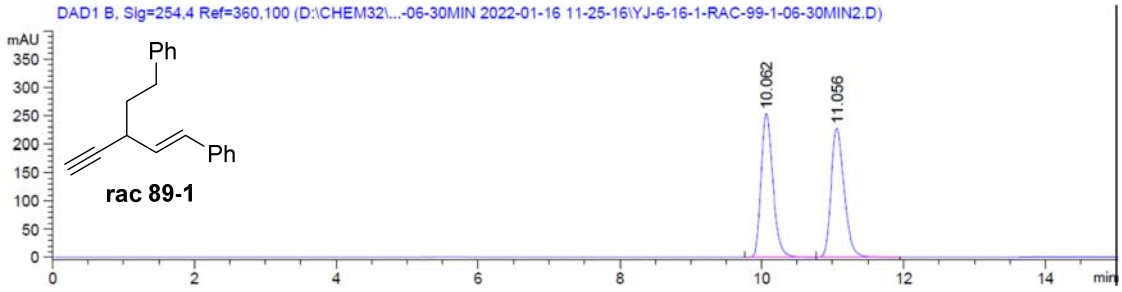
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.131	BV R	0.7939	7103.76855	120.13342	49.5165
2	24.319	MM	3.8751	7242.49609	31.14961	50.4835
Totals :				1.43463e4	151.28303	



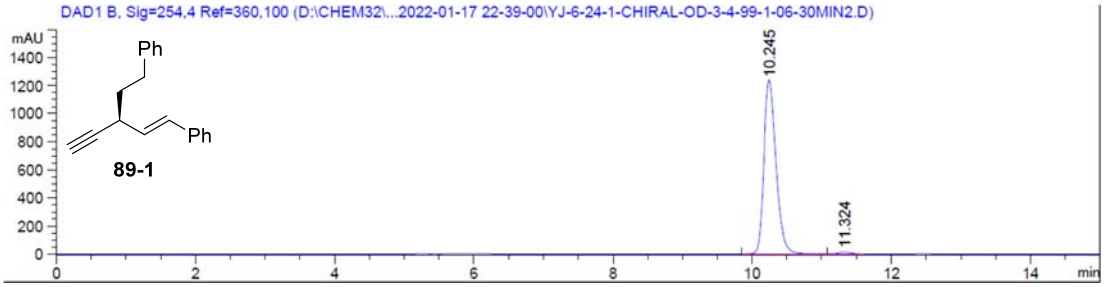
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.344	BB	0.9145	2.24337e4	348.75208	96.7013
2	25.882	MM	3.3980	765.27399	3.75354	3.2987
Totals :				2.31990e4	352.50561	



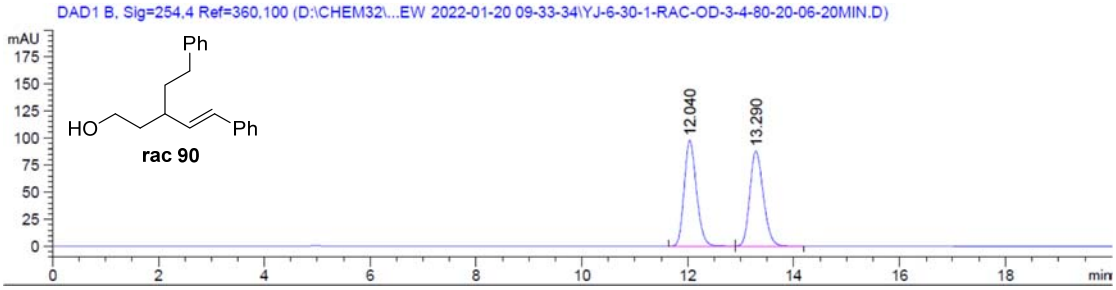
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.062	BB	0.1763	2919.31445	253.52602	50.0374
2	11.056	BB	0.1975	2914.94751	227.43668	49.9626
Totals :				5834.26196	480.96269	



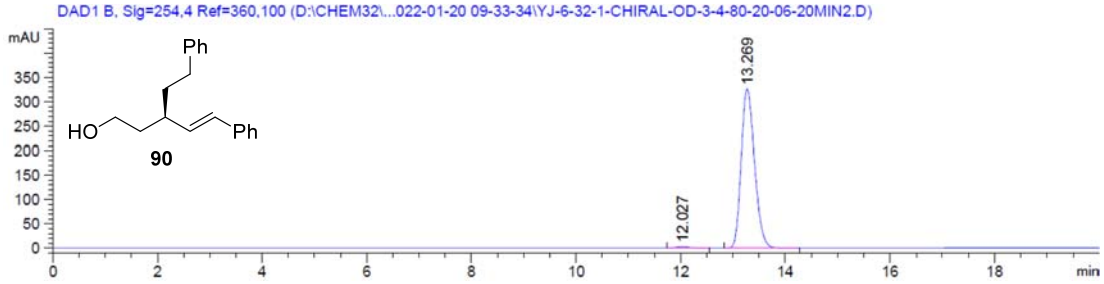
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.245	BV	0.1846	1.49814e4	1242.71680	98.9208
2	11.324	VB	0.2032	163.43704	12.28293	1.0792
Totals :				1.51448e4	1254.99973	



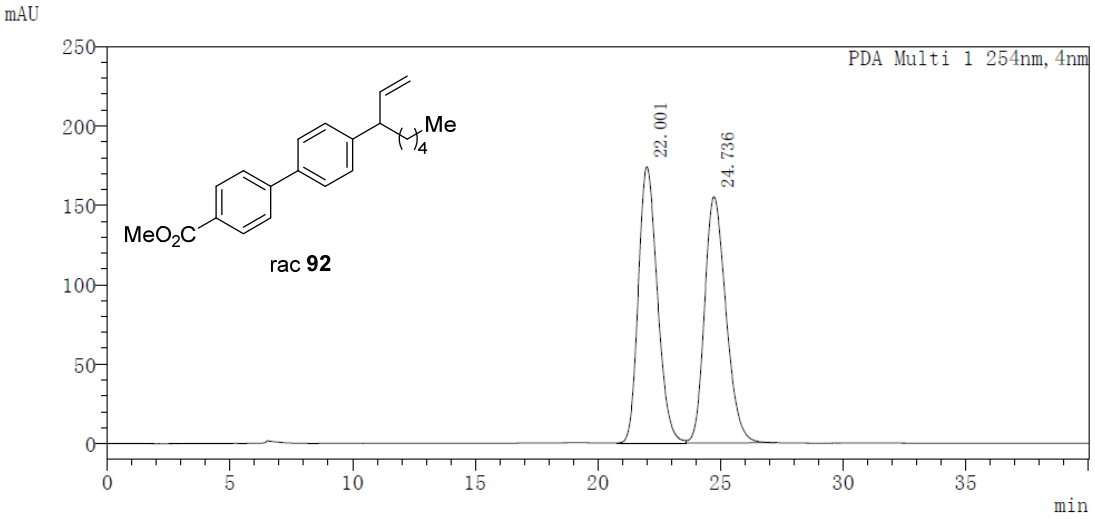
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.040	BB	0.2477	1563.53821	97.16304	50.0884
2	13.290	BB	0.2744	1558.01758	88.07980	49.9116
Totals :				3121.55579	185.24284	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

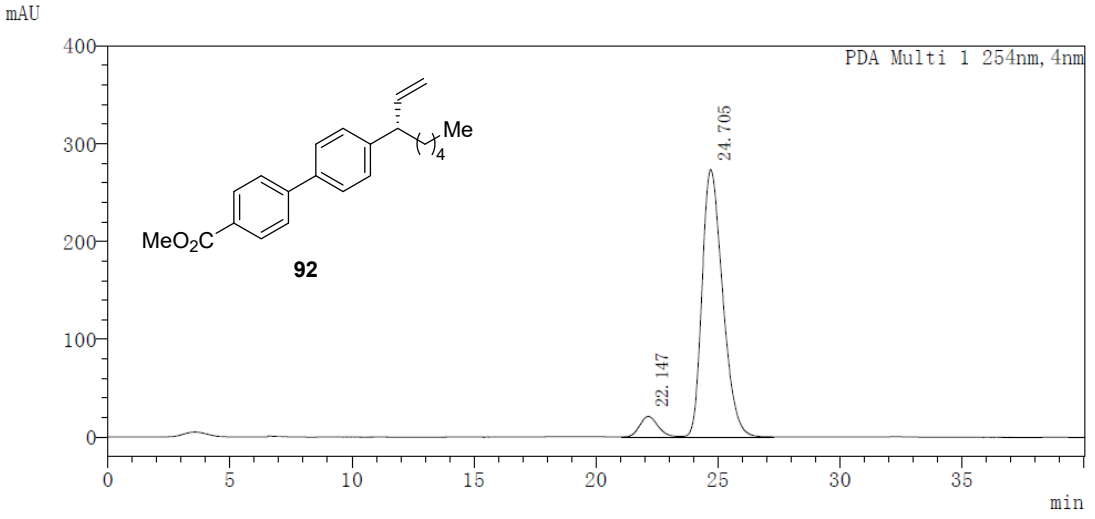
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.027	BB	0.2384	57.69463	3.61100	0.9886
2	13.269	BB	0.2748	5778.45703	325.91531	99.0114
Totals :				5836.15166	329.52631	



Peak Table

PDA Ch1 254nm

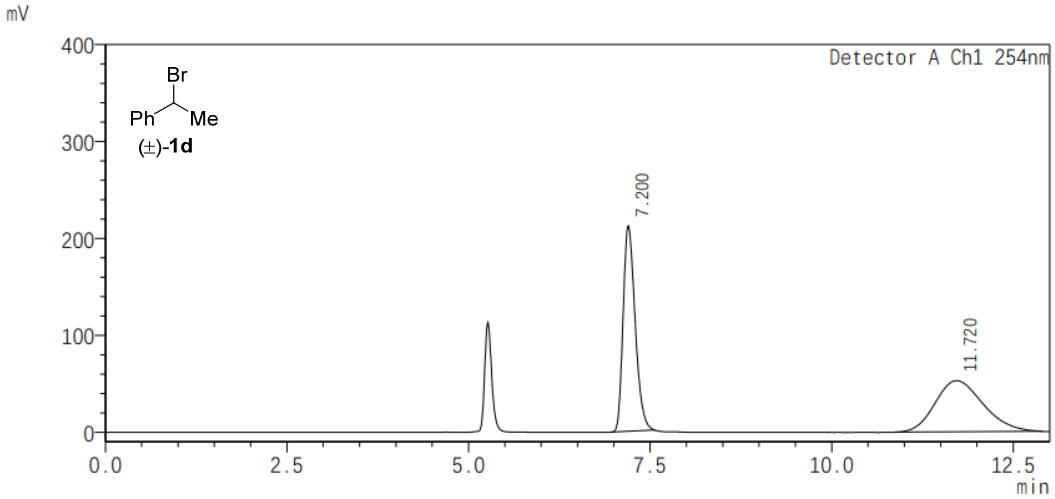
Peak#	Ret. Time	Area	Area%
1	22.001	9402283	49.937
2	24.736	9425888	50.063



Peak Table

PDA Ch1 254nm

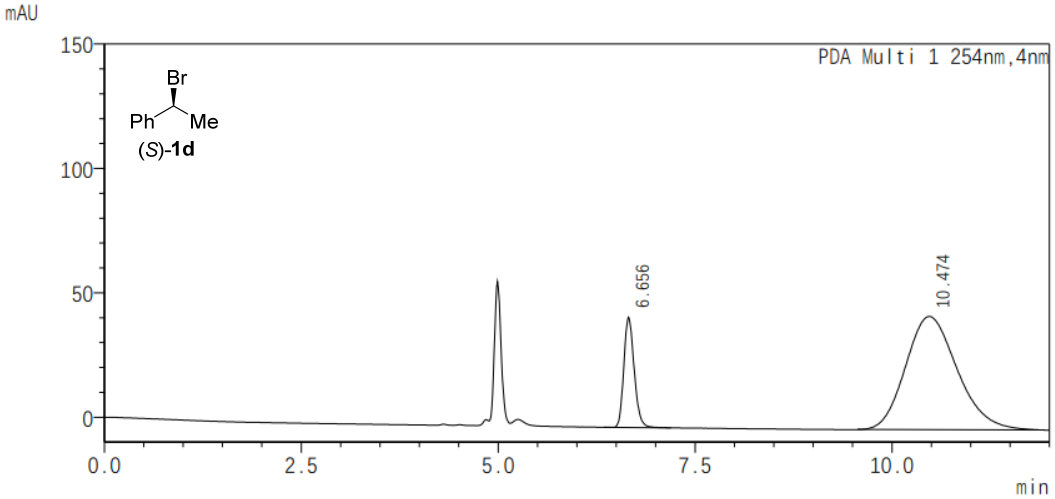
Peak#	Ret. Time	Area	Area%
1	22.147	1111182	6.465
2	24.705	16077459	93.535



Peak Table

Detector A Ch1 254nm

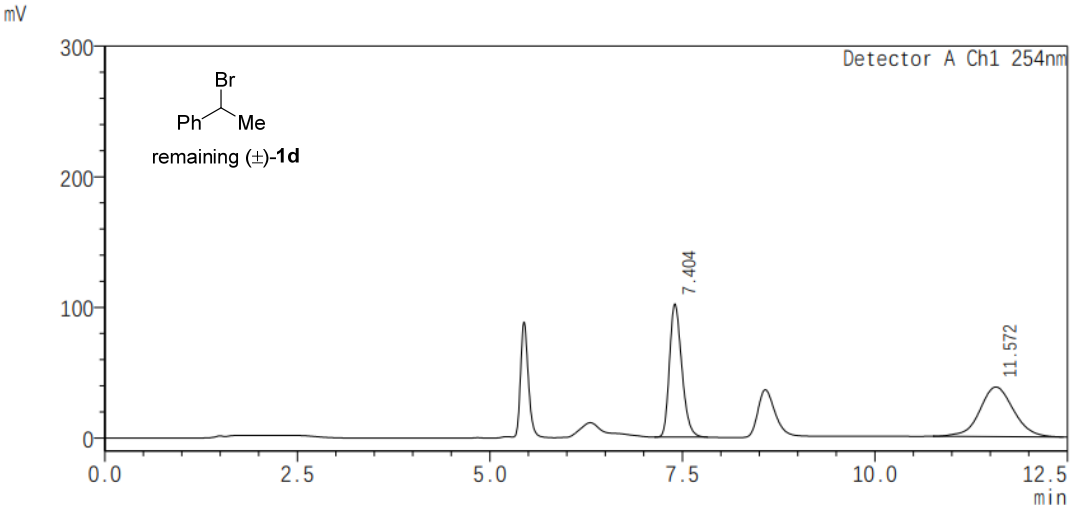
Peak#	Ret. Time	Area	Area%
1	7.200	2442319	50.171
2	11.720	2425633	49.829



Peak Table

PDA Ch1 254nm

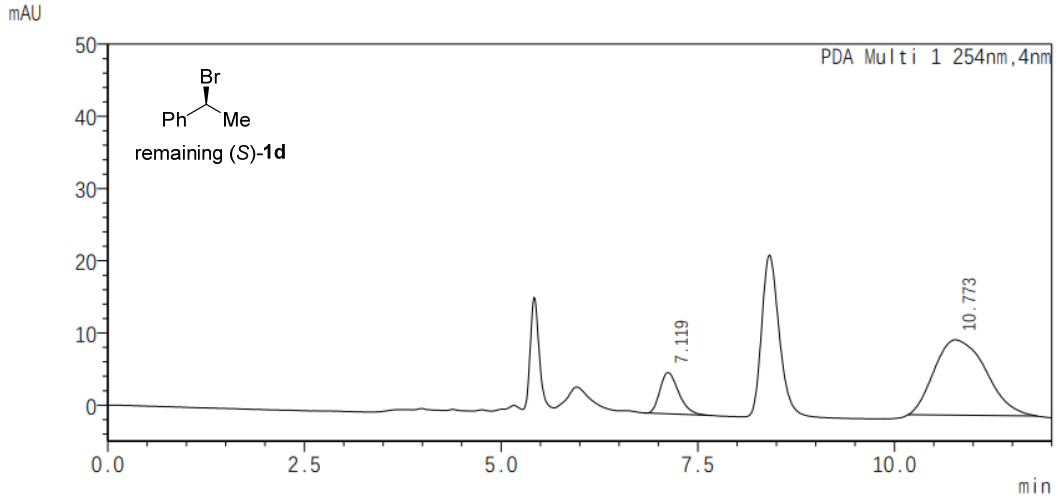
Peak#	Ret. Time	Area	Area%
1	6.656	405103	16.305
2	10.474	2079408	83.695



Peak Table

Detector A Ch1 254nm

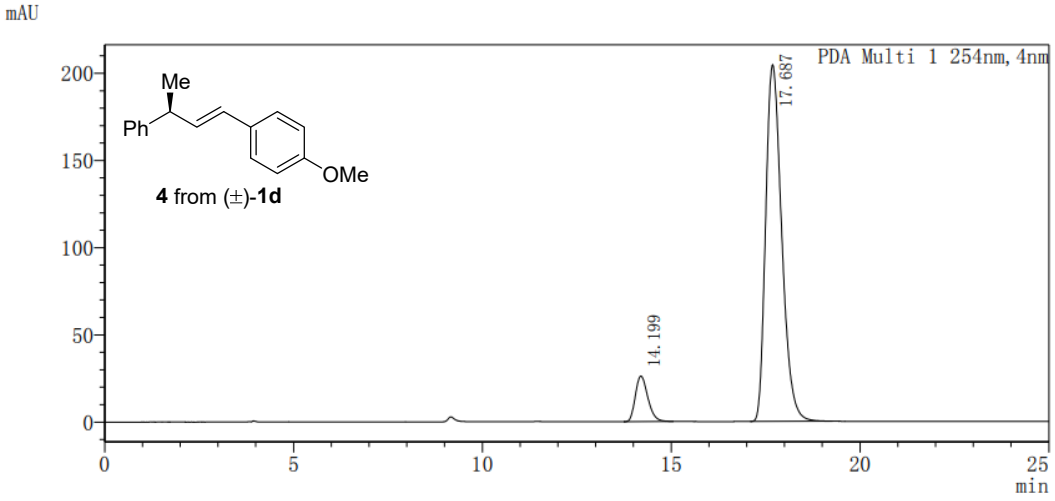
Peak#	Ret. Time	Area	Area%
1	7.404	1136429	49.450
2	11.572	1161705	50.550



Peak Table

PDA Ch1 254nm

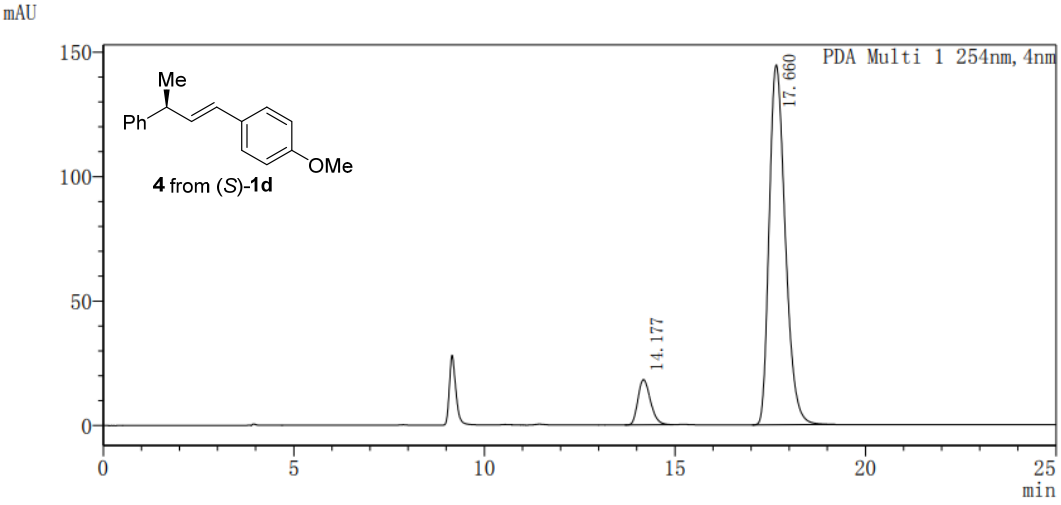
Peak#	Ret. Time	Area	Area%
1	7.119	94491	16.579
2	10.773	475458	83.421



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.199	599548	9.036
2	17.687	6035663	90.964



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.177	415502	8.923
2	17.660	4240983	91.077