Cobalt-Catalyzed Regio- and Enantioselective Allylic Alkylation of Malononitriles

Samir Ghorai, Sajid Ur Rehman, Wen-Bin Xu, Wen-Yu Huang, Changkun Li*

Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, China 200240

E-mail: chkli@sjtu.edu.cn

Context

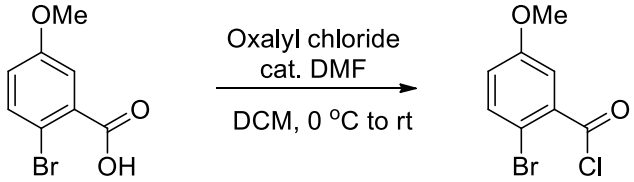
1. General information:

All air and moisture sensitive manipulations were carried out with standard Schlenk technique or in a nitrogen-filled glove box. Dried and oxygen free solvents were obtained from solvent purification system (Vigor YJC-7) and used thereafter. Column chromatography was performed on a column of silica gels (200-300 mesh) using either petroleum ether (PE)/ethyl acetate (EA) or dichloromethane (DCM)/MeOH as an eluent. The NMR spectra were recorded on a Bruker-400/500 MHz instrument and chemical shifts are reported in ppm relative to the residual deuterated solvents. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University with electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Enantiomers ratio were determined by Shimadzu HPLC-16 and Shimadzu HPLC-2030 instrument using DAICEL chiral column at 40 °C. Melting points were measured with Hanon MP100 melting point apparatus. Optical rotations were measured on an Anton Paar MCP100 automatic polarimeter using a 100 mm path-length cell at 589 nm. $Co(BF_4)_2{\cdot}6H_2O$ was purchased from Sigma-Aldrich. All other chemicals were purchased from TCI, Energy Chemical, Macklin or Alfa Aesar. Magnesium monoperoxyphthalate hexahydrate (MMPP) 80% analytical grade was obtained from Bide Pharmatech, China. Solvents were obtained from tansoole, China. Liquid substrates were distilled and degassed prior to use.

2. Synthesis of (*S*)-2-(2-bromo-5-methoxyphenyl)-4-methyl-4,5-dihydrooxazole (LS1):

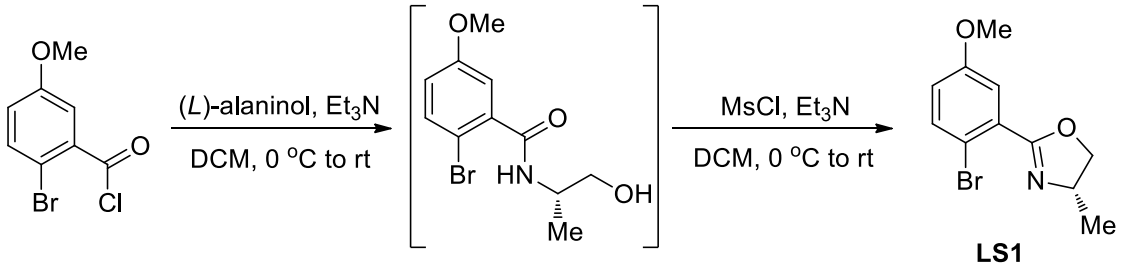
LS1 compound was prepared in two steps as below:

Step 1:



A suspension of 2-bromo-5-methoxybenzoic acid (4.620 g, 20 mmol) in DCM (40 mL) was carefully treated with oxalyl chloride (5.080 g, 40 mmol, 2 eq) in the presence of 2 drops of DMF at 0 °C under inert atmosphere. After stirring at room temperature for 4-5 hours, a clear solution was obtained. The reaction mixture was concentrated under vacuo to get the corresponding benzoyl chloride as light yellowish liquid. The crude product was directly used in the next step.

Step 2:



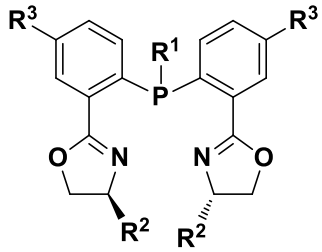
To a solution of (*L*)-alaninol (1.577 g, 21 mmol) and Et_3N (8.8 mL, 3 eq) in DCM (40 mL) was added 2-bromo-5-methoxybenzoyl chloride (diluted in 10 mL of DCM) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 12 hours. After that, it was cooled at 0 °C. Methanesulfonyl chloride (MsCl) (3.3 mL, 2 eq) and Et_3N (8.8 mL, 3 eq) were added carefully. The reaction mixture was stirred at room temperature for 4-5 hours. Then, it was washed with water twice and with brine twice. Organic layer was dried by Na_2SO_4, and concentrated. The residue was purified by column chromatography (PE/EA, 6:1) to get **LS1** as a colorless oil (4.590 g, 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 3.1 Hz, 1H), 6.82 (dd, J = 8.8, 3.1 Hz, 1H), 4.51 (dd, J = 9.4, 8.0 Hz, 1H), 4.39 (tt, J = 13.4, 6.6 Hz, 1H), 3.97 (t, J = 7.8 Hz, 1H), 3.78 (s, 3H), 1.37 (d, J = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 158.7, 134.7, 130.7, 118.5, 116.2, 112.3, 74.4, 62.5, 55.8, 21.6.

HRMS (ESI): calculated *m/z* for $C_{11}H_{12}BrNO_2$ $[M + H]^+$ = 270.0124, found 270.0131.

3. General procedure for the ligand synthesis:

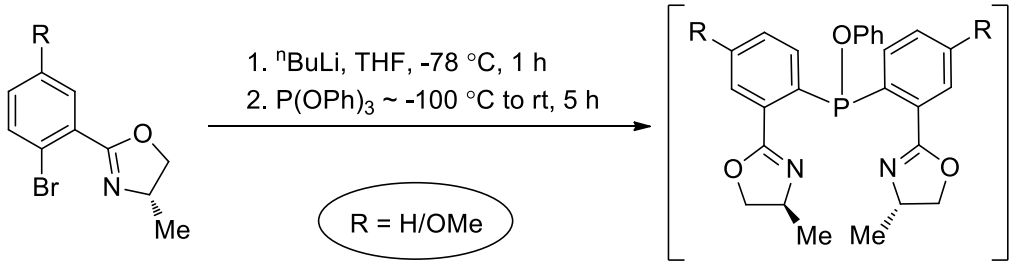


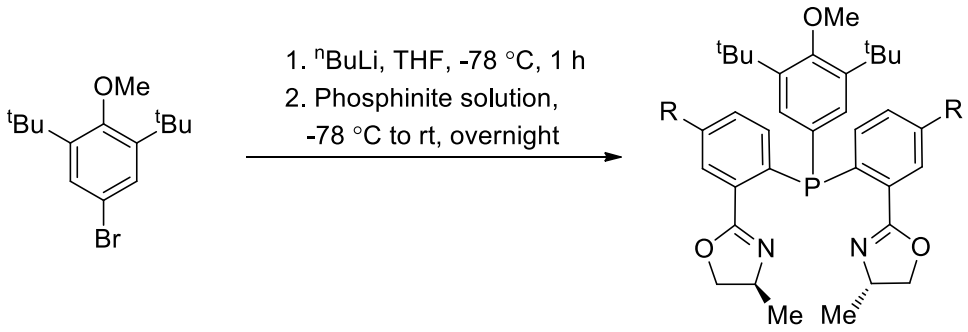
L1 [R^1 = Ph, R^2 = Ph, R^3 = H]; **L2** [R^1 = Ph, R^2 = ^{i}Pr, R^3 = H]; **L3** [R^1 = Ph, R^2 = ^{t}Bu, R^3 = H]; **L4** [R^1 = Ph, R^2 = Bn, R^3 = H]; **L5** [R^1 = Ph, R^2 = Me, R^3 = H] were synthesizd according to the reported literature procedure.[1]

L6 [R^1 = 4-OMe-3,5-^{t}Bu$_2$C$_6$H$_2$, R^2 = Me, R^3 = H], and **L7** [R^1 = 4-OMe-3,5-^{t}Bu$_2$C$_6$H$_2$, R^2 = Me, R^3 = OMe] were prepared according to the procedure **General Method 1**, reported in literature.[1]

L8 [R^1 = Me, R^2 = Me, R^3 = H]; **L9** [R^1 = Me, R^2 = Me, R^3 = OMe] were prepared according to the procedure **General Method 2**.

General Method 1:



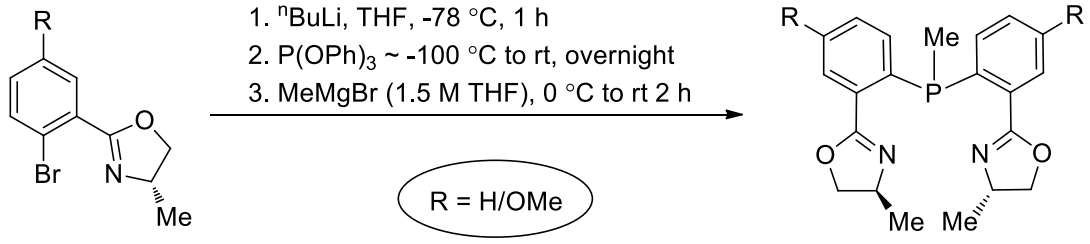


In a flame dried Schlenk tube, 2-bromooxazoline substrate (6 mmol, 2.0 eq) was dissolved in THF (12 mL) under an argon atmosphere and the reaction mixture was cooled down to -78 °C. ^{n}BuLi (2.2 eq, 1.6 M in hexane) was added dropwise and the mixture was stirred for 1 hour at this temperature. The reaction mixture was further

cooled to ~ -100 °C and was added triphenylphosphite (0.931 g, 3 mmol, 1 eq) in 2 mL of THF in one portion under vigorous stirring. The reaction was slowly warmed up to room temperature and stirred for 5 hours. Phosphinite reaction mixture was used *in situ* for further substitution to get the desired ligand.

In another flame dried Schlenk tube, lithiation of the 5-bromo-1,3-di-*tert*-butyl-2-methoxybenzene (1.077 g, 3.6 mmol, 1.2 eq) was carried out using ^{n}BuLi (1.32 eq, 1.6 M in hexane) at -78 °C. Then the reaction mixture was added the phosphinite solution via syringe over 10 minutes at -78 °C. Combined reaction mixture was allowed to warm to room temperature slowly and stirred overnight. The reaction mixture was quenched with water and extracted with ethyl acetate. The solvent was removed and the residue was purified by flash column chromatography on silica gels using PE/EA as an eluent to obtain the pure product.

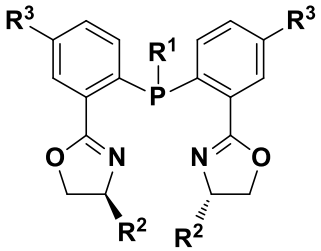
General Method 2:



In a flame dried Schlenk tube, 2-bromooxazoline substrate (6 mmol, 2 eq) was dissolved in THF (12 mL) under an argon atmosphere and cooled down to -78 °C. ^{n}BuLi (2.2 eq, 1.6 M in hexane) was added dropwise and the mixture was stirred for 1 hour at this temperature. The reaction mixture was further cooled down to ~ -100 °C and was added triphenylphosphite (0.931 g, 3 mmol, 1 eq) in 2 mL of THF in one portion under vigorous stirring. The reaction was slowly warmed up to room temperature and stirred overnight. Then, 1.5 mL of MeMgBr (3 M in THF) was added dropwise to the reaction mixture at 0 °C. The ice-bath was removed and the reaction mixture was stirred for two hours further at room temperature. The recation mixture was quenced with 2 mL of degassed water and filtered to remove the solid. Filtrate was dried over Na_2SO_4 and solvent was removed under reduced pressure. Crude product was purified by flash column chromatography on silica gels using PE/EA as an eluent to obtain the pure product.

L6 [R^1 = 4-OMe-3,5-^{t}Bu$_2$C$_6$H$_2$, R^2 = Me, R^3 = H]:

White solid; Yield 0.670 g, 39%.



R^1 = 4-OMe-3,5-^{t}Bu$_2$-C$_6$H$_2$
R^2 = Me; R^3 = H

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 5.5, 3.1 Hz, 2H), 7.34 – 7.24 (m, 6H), 7.01 – 6.93 (m, 2H), 4.34 – 4.30 (m, 1H), 4.27 – 4.15 (m, 3H), 3.75 (t, J = 7.6 Hz, 1H), 3.68 (s, 3H), 3.64 (t, J = 7.7 Hz, 1H), 1.33 (s, 18H), 1.10 (d, J = 6.5 Hz, 3H), 1.06 (d, J = 6.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1 (d, J = 9.5 Hz), 160.3 (s), 143.4 (d, J = 8.0 Hz), 140.6 (dd, J = 24.9, 14.1 Hz), 133.9 (d, J = 5.8 Hz), 133.6 (d, J = 13.0 Hz), 132.4 (dd, J = 82.0, 22.0 Hz), 130.8 (d, J = 10.6 Hz), 130.3 (d, J = 13.7 Hz), 129.9 (dd, J = 16.5, 3.7 Hz), 127.8 (d, J = 22.0 Hz), 73.9 (d, J = 4.5 Hz), 64.4 (s), 62.1 (d, J = 18.9 Hz), 36.0 (s), 32.2 (s), 21.29 (d, J = 16.9 Hz).

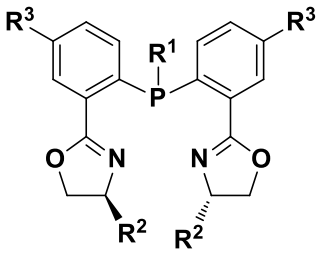
^{31}P NMR (162 MHz, $CDCl_3$) δ –5.70.

$[\alpha]_D^{25}$ = –26.0 (*c* 0.25, $CHCl_3$).

HRMS (ESI): *m/z* $[M + H]^+$ Calcd for $C_{35}H_{44}N_2O_3P$ 571.3084; found 571.3094.

L7 [R^1 = 4-OMe-3,5-^{t}Bu$_2$C$_6$H$_2$, R^2 = Me, R^3 = OMe]:

White solid; Yield 0.700 g, 37%.



R^1 = 4-OMe-3,5-^{t}Bu$_2$-C$_6$H$_2$
R^2 = Me; R^3 = OMe

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dt, J = 8.5, 2.6 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.92 – 6.83 (m, 4H), 4.34 (dd, J = 9.2, 8.1 Hz, 1H), 4.27 – 4.15 (m, 3H), 3.82 (s, 6H), 3.77 (t, J = 7.7 Hz, 1H), 3.70 – 3.67 (m, 4H), 1.33 (s, 18H), 1.15 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4 (s), 160.2 (s), 159.3 (d, J = 15.7 Hz), 143.4 (d, J = 7.8 Hz), 135.4 (d, J = 44.3 Hz), 134.3 – 133.4 (m), 133.3 (d, J = 24.1 Hz), 131.8 – 131.7 (m), 131.7 – 131.5 (m), 116.9 (d, J = 7.0 Hz), 114.7 (dd, J = 8.3, 4.4 Hz), 74.0 (d, J = 6.8 Hz), 64.4 (s), 62.1 (d, J = 15.6 Hz), 55.6 (d, J = 1.8 Hz), 36.0 (s), 32.3 (s), 21.3 (d, J = 21.2 Hz).

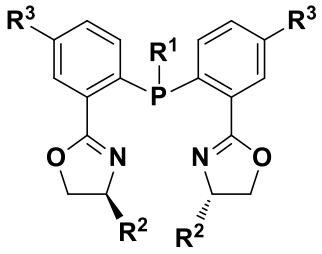
^{31}P NMR (202 MHz, $CDCl_3$) δ –9.32.

$[\alpha]_D^{25}$ = –15.6 (*c* 0.25, $CHCl_3$).

HRMS (ESI): *m/z* $[M + H]^+$ Calcd for $C_{37}H_{48}N_2O_5P$ 631.3295; found 631.3307.

L8 [R^1 = Me, R^2 = Me, R^3 = H]:

White solid; Yield 0.418 g, 38%.



R^1 = Me; R^2 = Me; R^3 = H

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.38 – 7.26 (m, 6H), 4.35 – 4.29 (m, 2H), 4.24 – 4.13 (m, 2H), 3.82 (dd, *J* = 7.9, 7.0 Hz, 1H), 3.65 (t, *J* = 8.2 Hz, 1H), 1.62 (d, *J* = 5.4 Hz, 3H), 1.16 (dd, *J* = 9.2, 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (d, *J* = 16.1 Hz), 142.5 (t, *J* = 24.7 Hz), 132.3 (dd, *J* = 40.8, 22.3 Hz), 131.6 (d, *J* = 28.4 Hz), 130.6 (d, *J* = 7.9 Hz), 129.8 – 129.7 (m), 127.8 (d, *J* = 15.6 Hz), 74.0 (d, *J* = 9.5 Hz), 62.2 (d, *J* = 16.6 Hz), 21.4 (d, *J* = 13.9 Hz), 14.3 (d, *J* = 17.3 Hz).

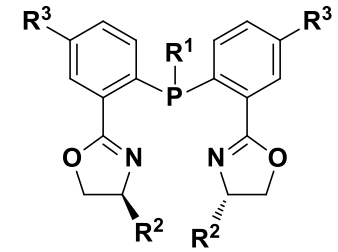
^{31}P NMR (162 MHz, $CDCl_3$) δ –26.51.

$[\alpha]_D^{25}$ = –25.2 (*c* 0.25, $CHCl_3$).

HRMS (ESI): *m/z* $[M + H]^+$ Calcd for $C_{21}H_{24}N_2O_2P$ 367.1570; found 367.1575.

L9 [R^1 = Me, R^2 = Me, R^3 = OMe]:

Colorless sticky oil; Yield 0.460 g, 36%.



R^1 = Me; R^2 = Me; R^3 = OMe

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 5.4, 2.7 Hz, 2H), 7.23 – 7.17 (m, 2H), 6.92 (ddd, *J* = 8.8, 6.3, 2.7 Hz, 2H), 4.39 – 4.34 (m, 2H), 4.29 – 4.17 (m, 2H), 3.85 (t, *J* = 6.0 Hz, 1H), 3.81 (d, *J* = 0.6 Hz, 6H), 3.73 (t, *J* = 8.2 Hz, 1H), 1.57 (d, *J* = 5.5 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.19 (d, *J* = 6.6 Hz, 3H).

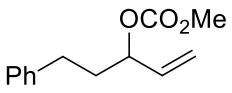
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (d, *J* = 10.9 Hz), 159.2 (d, *J* = 10.3 Hz), 134.0 – 133.2 (m), 133.2 (s), 132.9 (s), 117.0 (d, *J* = 5.6 Hz), 114.6 (dd, *J* = 9.2, 4.7 Hz), 74.1 (d, *J* = 6.6 Hz), 62.1 (d, *J* = 12.1 Hz), 55.5 (d, *J* = 1.5 Hz), 21.4 (d, *J* = 15.5 Hz), 14.5 (d, *J* = 17.0 Hz).

^{31}P NMR (202 MHz, $CDCl_3$) δ –30.91.

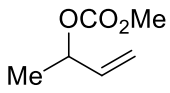
$[\alpha]_D^{25}$ = –6.4 (*c* 0.25, $CHCl_3$).

HRMS (ESI): *m/z* $[M + H]^+$ Calcd for $C_{23}H_{28}N_2O_4P$ = 427.1781; found 427.1789.

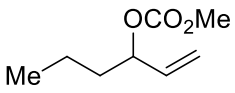
4. List of substrates:



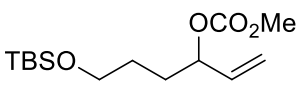
[**1a**]



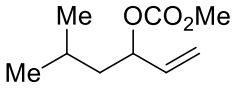
[**1b**]



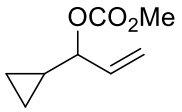
[**1c**]



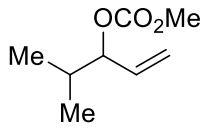
[**1d**]



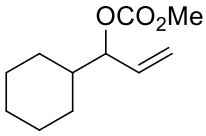
[**1e**]



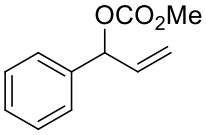
[**1f**]



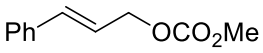
[**1g**]



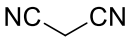
[**1h**]



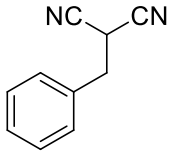
[**1i**]



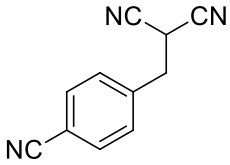
[**1j**]



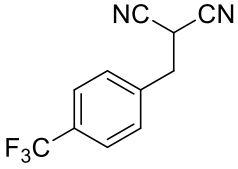
[**2a**]



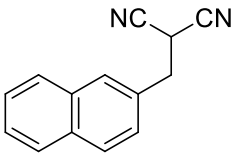
[**2b**]



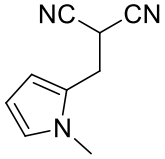
[**2c**]



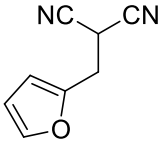
[**2d**]



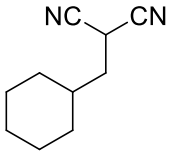
[**2e**]



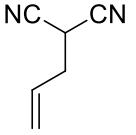
[**2f**]



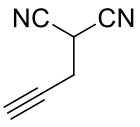
[**2g**]



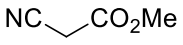
[**2h**]



[**2i**]



[**2j**]

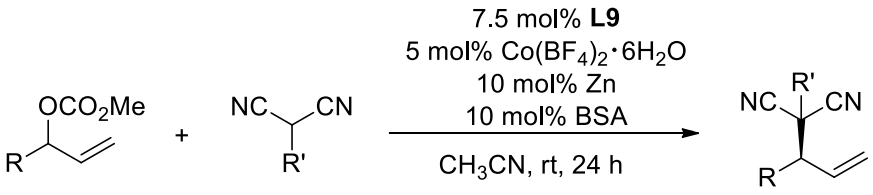


[**2k**]

[**2l**]

All the allylic carbonates were synthesized according to the known literature reported procedure.[2] **2a**, **2k** and **2l** were purchased from commercial source directly. Compounds **2b** to **2h** were also prepared accordingly to the known literature procedure.[3] **2i** and **2j** were known compounds and prepared from malononitrile (2 eq) and corresponding bromide (1 eq) in the presence of Hünig's base (1 eq) in dichloromethane (0.2 M) solvent.[4]

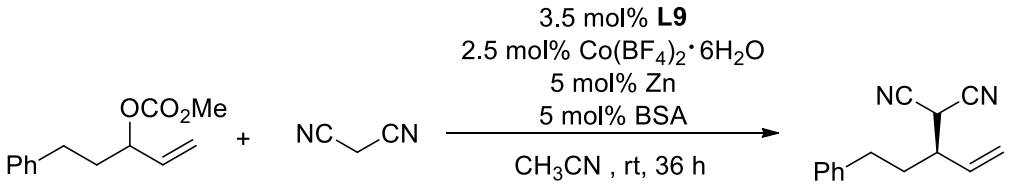
5. Representative procedure of cobalt-catalyzed allylic alkylation of malonitrile:



rac-**1** 0.25 mmol | **2** 0.5 mmol | **3**

In an N_2 filled glove box, **L9** (8.0 mg, 18.8 ×10^{-3} mmol, 7.5 mol%) and $Co(BF_4)_2{\cdot}6H_2O$ (4.3 mg, 12.6×10^{-3} mmol, 5 mol%) in 0.2 mL acetonitrile was transferred into a 10 mL reaction tube equipped with a Teflon stopcock and a stir bar. Zn dust (1.7 mg, 26.0×10^{-3} mmol, 10 mol%) was added followed by addition of 0.5 mL acetonitrile to complete transfer of zinc. The mixture was allowed to stir for 20 minutes. Afterward, allylic carbonate (0.25 mmol), malonitrile derivatives (0.5 mmol, 2 eq), bis(trimethylsilyl)acetamide (BSA) (6 μL, 25×10^{-3} mmol, 10 mol%), and 0.3 mL of acetonitrile were added sequentially to the reaction mixture. The reaction tube was sealed and brought out from the glove box. The reaction mixture was then stirred for 24 hours at room temperature. Then, solvent was removed and column chromatography was run on a column of silica gels (200-300 mesh) using PE/EA as an eluent to get the desired product.

6. Large scale synthesis of 3aa using 2.5 mol% catalyst:



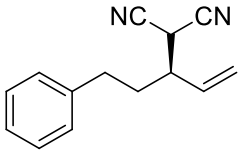
rac-**1a** 5 mmol | **2a** 10 mmol | **3aa** Yield 89%, *ee* 99%

In an N_2 filled glove box, a reaction tube equipped with a Teflon stopcock and a stir bar was charged with 3.5 mol% of **L9** (75 mg, 0.18 mmol), and 2.5 mol% of $Co(BF_4)_2{\cdot}6H_2O$ (43 mg, 0.126 mmol) in 1 mL of acetonitrile. Zn dust (16.4 mg, 0.25 mmol, 5 mol%) was added followed by addition of 1 mL acetonitrile to complete transfer of zinc. The mixture was stirred for 20 minutes. Then, *rac*-**1a** (1.102 g, 5 mmol) and **2a** (0.660 g, 10 mmol), bis(trimethylsilyl)acetamide (BSA) (60 μL, 5 mol%) were added to the reaction mixture sequentially. Then, the reaction was monitored by TLC and stopped after 36 hours. The reaction tube was removed from the glove box and solvent was removed under reduced pressure. The residue was purified by flash column chromatography using PE/EA as an eluent. Yield: 0.930 g, 89%; *ee*: 99%.

7. Spectral data of allylic alkylation of malonitrile products:

(*R*)-2-(5-phenylpent-1-en-3-yl)malononitrile (3aa):[5,6]

Clear oil; Yield: 47 mg, 89%.



TLC R*f* = 0.5 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.20 – 7.18 (m, 2H), 5.79 – 5.70 (m, 1H), 5.45 (dd, *J* = 32.7, 13.5 Hz, 2H), 3.68 (d, *J* = 5.4 Hz, 1H), 2.79 (ddd, *J* = 14.0, 8.8, 5.3 Hz, 1H), 2.68 – 2.55 (m, 2H), 2.08 – 1.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 133.8, 128.9, 128.5, 126.7, 122.3, 111.9, 111.7, 44.4, 33.3, 32.8, 28.8.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 10.0:90.0, 1.0 mL/min), R*t* = 12.95 min (major) and 16.04 min (minor), 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{25}}$ = –21.6 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + K]^+$ Calcd for $C_{14}H_{14}N_2K$ = 249.0794; found 249.0710.

Assignment of absolute configuration:

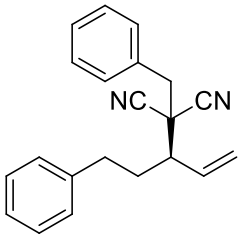
Literature data[4] for (*R*)-enantiomer: $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{24}}$ –8.05 (*c* = 0.77, $CHCl_3$), 82% *ee*

Literature data[5] for (*S*)-enantiomer: $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{25}}$ +21.7 (*c* = 1.28, $CHCl_3$), 88% *ee*

By comparing the literature reported data, the absolute configuration of the product **3aa** was assigned as (***R***) and all other compounds were assigned by analogy.

(*R*)-2-benzyl-2-(5-phenylpent-1-en-3-yl)malononitrile (3ab):[5]

White solid; Yield: 65 mg, 87%; M.P. 79-81 °C.



TLC R*f* = 0.6 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 7H), 7.29 – 7.22 (m, 3H), 5.82 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.61 (dd, *J* = 10.2, 1.1 Hz, 1H), 5.41 (d, *J* = 17.0 Hz, 1H), 3.22 (d, *J* = 13.7 Hz, 1H), 3.04 (d, *J* = 13.8 Hz, 1H), 2.88 (ddd, *J* = 13.8, 9.1, 4.6 Hz, 1H), 2.62 – 2.52 (m, 2H), 2.38 – 2.30 (m, 1H), 2.07 – 1.98 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.3, 133.4, 132.5, 130.3, 129.0, 128.8, 128.6, 126.5, 123.5, 115.0, 114.3, 50.2, 44.4, 41.7, 32.9, 32.4.

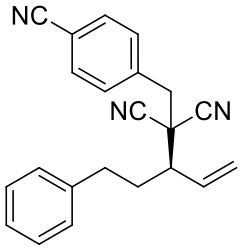
HPLC (Shimadzu LC-16) (Daicel Chiralpak IG Column, ^{i}PrOH:*n*-Hexane = 1.0:99.0, 1.0 mL/min), R*t* = 17.25 min (minor) and 20.31 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{25}}$ = –26.4 (*c* 0.05, $CHCl_3$). Literature data[4] for (*R*)-enantiomer: $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{26}}$ –2.4 (*c* = 0.5, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{21}H_{20}N_2Na$ 323.1524; found 323.1525.

(*R*)-2-(4-cyanobenzyl)-2-(5-phenylpent-1-en-3-yl)malononitrile (3ac):

White solid; Yield: 71 mg, 87%; M.P. 131-132 °C.



TLC R*f* = 0.3 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.18 (d, *J* = 7.1 Hz, 2H), 5.77 (dt, *J* = 16.8, 9.9 Hz, 1H), 5.61 (dd, *J* = 10.2, 0.9 Hz, 1H), 5.40 (d, *J* = 16.7 Hz, 1H), 3.23 (d, *J* = 13.7 Hz, 1H), 3.03 (d, *J* = 13.7 Hz, 1H), 2.86 (ddd, *J* = 13.6, 8.7, 4.6 Hz, 1H), 2.54 (dt, *J* = 22.3, 10.2 Hz, 2H), 2.33 – 2.25 (m, 1H), 2.05 – 1.95 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 137.7, 133.0, 132.8, 131.2, 128.9, 128.6, 126.7, 124.1, 118.4, 114.5, 113.8, 113.1, 50.4, 44.0, 41.7, 32.8, 32.5.

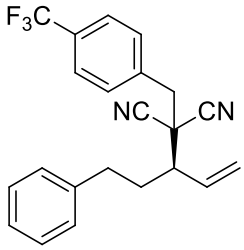
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 2.0:98.0, 1.0 mL/min), R*t* = 49.73 min (minor) and 53.14 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –2.6 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{22}H_{19}N_3Na$ 348.1477; found 348.1474.

(*R*)-2-(5-phenylpent-1-en-3-yl)-2-(4-(trifluoromethyl)benzyl)malononitrile (3ad):

White solid; Yield: 80 mg, 87%; M.P. 120-122 °C.



TLC R*f* = 0.7 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.18 (m, 3H), 5.78 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.61 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.39 (dd, *J* = 16.9, 0.6 Hz, 1H), 3.23 (d, *J* = 13.7 Hz, 1H), 3.04 (d, *J* = 13.7 Hz, 1H), 2.86 (ddd, *J* = 13.7, 8.8, 4.6 Hz, 1H), 2.60 – 2.48 (m, 2H), 2.34 – 2.26 (m, 1H), 2.05 – 1.95 (m, 1H).

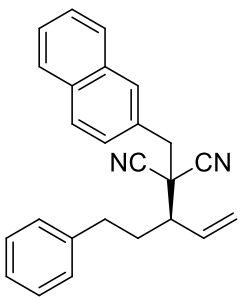
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 136.5, 133.2, 131.6 – 130.8 (m), 130.8, 128.9, 128.6, 126.7, 126.1 (q, *J* = 3.7 Hz), 127.3 – 120.8 (m), 124.0, 114.7, 114.0, 50.4, 44.1, 41.5, 32.8, 32.5.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 0.1:99.9, 0.5 mL/min), R*t* = 57.50 min (minor) and 61.26 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –1.0 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{22}H_{19}F_3N_2Na$ 391.1398; found 391.1387.

(*R*)-2-(naphthalen-2-ylmethyl)-2-(5-phenylpent-1-en-3-yl)malononitrile (3ae):



White solid; Yield: 80 mg, 91%; M.P. 103-105 °C.

TLC R*f* = 0.3 (PE:EA, 9:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 9.2, 3.8 Hz, 4H), 7.52 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.18 (m, 2H), 5.81 (dt, *J* = 16.9, 10.0 Hz, 1H), 5.60 (dd, *J* = 10.2, 1.0 Hz, 1H), 5.40 (d, *J* =

16.9 Hz, 1H), 3.35 (d, *J* = 13.8 Hz, 1H), 3.17 (d, *J* = 13.8 Hz, 1H), 2.84 (ddd, *J* = 13.8, 9.2, 4.6 Hz, 1H), 2.58 – 2.52 (m, 2H), 2.35 – 2.30 (m, 1H), 2.04 – 1.97 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 133.5, 133.4, 133.3, 130.0, 129.8, 128.9 (2C), 128.6, 128.2, 127.9, 127.7, 126.8, 126.7, 126.6, 123.7, 115.1, 114.4, 50.4, 44.5, 42.0, 32.9, 32.5.

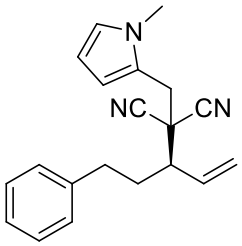
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 8.0:92.0, 1.0 mL/min), R*t* = 14.82 min (minor) and 24.01 min (major), 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –2.6 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{25}H_{22}N_2Na$ 373.1681; found 373.1682.

(*R*)-2-((1-methyl-1*H*-pyrrol-2-yl)methyl)-2-(5-phenylpent-1-en-3-yl)malononitrile (3af):

Clear oil; Yield: 65 mg, 86%.



TLC R*f* = 0.4 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.18 (m, 3H), 6.62 (dd, *J* = 2.5, 1.9 Hz, 1H), 6.24 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.12 – 6.10 (m, 1H), 5.76 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.58 (dd, *J* = 10.2, 1.1 Hz, 1H), 5.39 (d, *J* = 17.0 Hz, 1H), 3.63 (s, 3H), 3.26 (d, *J* = 15.2 Hz, 1H), 3.09 (d, *J* = 15.2 Hz, 1H), 2.83 (ddd, *J* = 13.9, 9.3, 4.7 Hz, 1H), 2.59 – 2.51 (m, 2H), 2.32 – 2.23 (m, 1H), 2.02 – 1.92 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 133.4, 128.9, 128.6, 126.6, 124.1, 123.7, 123.0, 115.3, 114.6, 111.1, 107.9, 49.8, 43.8, 34.3, 32.9, 32.7, 32.5.

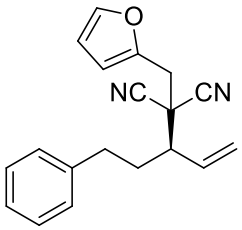
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 18.29 min (major) and 21.90 min (minor), 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –9.6 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + H]^+$ Calcd for $C_{20}H_{22}N_3$ 304.1808; found 304.1815.

(*R*)-2-(furan-2-ylmethyl)-2-(5-phenylpent-1-en-3-yl)malononitrile (3ag):

Clear oil; Yield: 60 mg, 83%.



TLC R*f* = 0.5 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.18 (m, 3H), 6.40 – 6.37 (m, 2H), 5.74 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.58 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.40 (dd, *J* = 16.9, 0.7 Hz, 1H), 3.28 (dd, *J* = 46.9, 15.1 Hz, 2H), 2.83 (ddd, *J* = 13.9, 9.3, 4.6 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.32 – 2.23 (m, 1H), 2.01 – 1.92 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 143.6, 140.4, 133.1, 128.8, 128.6, 126.5, 123.9, 114.7, 114.2, 111.0, 110.8, 49.3, 42.4, 34.7 32.9, 32.3.

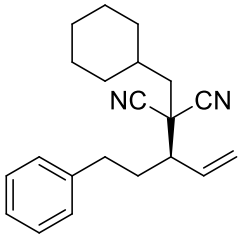
HPLC (Shimadzu LC-16) (Daicel Chiralpak IC Column, ^{i}PrOH:*n*-Hexane = 0.5:99.5, 1.0 mL/min), R*t* = 20.69 min (minor) and 22.48 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –6.3 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{19}H_{18}N_2ONa$ 313.1317; found 313.1321.

(*R*)-2-(cyclohexylmethyl)-2-(5-phenylpent-1-en-3-yl)malononitrile (3ah):

Clear oil; Yield: 67.5 mg, 88%.



TLC R*f* = 0.7 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.20 (dd, *J* = 20.4, 7.2 Hz, 3H), 5.66 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.49 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.30 (dd, *J* = 16.9, 0.8 Hz, 1H), 2.82 (ddd, *J* = 13.8, 9.0, 4.6 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.40 – 2.34 (m, 1H), 2.27 – 2.19 (m, 1H), 1.97 – 1.85 (m, 3H), 1.81 – 1.63 (m, 6H), 1.31 – 1.24 (m, 2H), 1.18 – 1.12 (m, 1H), 1.09 – 0.98 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.5, 133.5, 128.8, 128.6, 126.6, 123.2, 115.8, 115.3, 51.4, 43.0, 40.4, 35.9, 33.7, 33.5, 32.9, 32.1, 26.1, 26.1, 26.0.

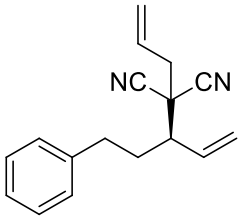
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 1.0:99.0, 1.0 mL/min), R*t* = 6.88 min (major) and 7.66 min (minor), 96 % *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –14.1 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{21}H_{26}N_2Na$ 329.1994; found 329.1992.

(*R*)-2-allyl-2-(5-phenylpent-1-en-3-yl)malononitrile (3ai):[5]

Clear oil; Yield: 53 mg, 85%.



TLC R*f* = 0.6 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.19 (m, 3H), 5.92 – 5.81 (m, 1H), 5.70 (dt, *J* = 16.8, 9.9 Hz, 1H), 5.54 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.41 – 5.32 (m, 3H), 2.87 – 2.80 (m, 1H), 2.69 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.59 – 2.43 (m, 3H), 2.28 – 2.20 (m, 1H), 2.00 – 1.91 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 133.1, 128.8, 128.6, 126.5, 123.4, 123.2, 114.9, 114.3, 49.2, 42.2, 40.1, 32.8, 32.3.

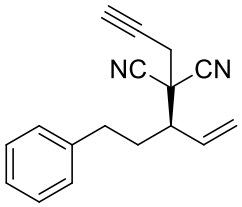
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0 :95.0, 1.0 mL/min), R*t* = 11.66 min (minor) and 12.65 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –6.3 (*c* 0.05, $CHCl_3$). Literature data[4] for (*R*)-enantiomer: $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{26}}$ = –2.78 (*c* = 0.5, $CHCl_3$), 71% *ee.*

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{18}N_2Na$ 273.1368; found 273.1370.

(*R*)-2-(5-phenylpent-1-en-3-yl)-2-(prop-2-yn-1-yl)malononitrile (3aj):

Clear oil; Yield: 47 mg, 76%.



TLC R*f* = 0.6 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.3 Hz, 2H), 7.22 (dd, *J* = 18.6, 7.2 Hz, 3H), 5.71 – 5.62 (m, 1H), 5.55 (dd, *J* = 10.1, 1.5 Hz, 1H), 5.43 (dd, *J* = 16.7, 1.2 Hz, 1H), 2.97 – 2.77 (m, 3H), 2.68 (ddd, *J* = 12.0, 9.6, 2.7 Hz, 1H), 2.60 – 2.52 (m, 1H), 2.34 (t, *J* = 2.6 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.01 – 1.91 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 132.4, 128.8, 128.6, 128.6, 126.6, 124.1, 114.3, 113.7, 75.3, 74.7, 48.6, 41.3, 32.9, 32.3, 27.3.

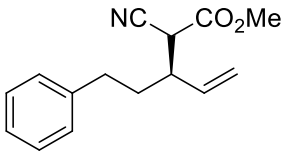
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 8.32 min (minor) and 10.60 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –11.1 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{16}N_2Na$ 271.1211; found 271.1210.

(*R*)-methyl 2-cyano-3-phenethylpent-4-enoate (3ak):

Clear oil; Yield: 34 mg, 56%.



TLC R*f* = 0.3 (PE:EA, 9:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.16 (m, 3H), 5.79 – 5.69 (m, 1H), 5.31 – 5.20 (m, 2H), 3.77 (s, 3H), {3.59 (d, *J* = 4.8 Hz, 0.6H), 3.52 (d, *J* = 6.0 Hz, 0.4H); *d/r* = 1.0:1.5.}, 2.81 – 2.69 (m, 2H), 2.55 (ddd, *J* = 25.8, 15.2, 8.4 Hz, 1H), 1.97 – 1.80 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 165.8, 141.0, 140.9, 136.3, 135.4, 128.7, 128.7, 128.5, 126.4, 126.3, 120.2, 119.7, 115.4, 115.1, 53.5, 53.5, 44.2, 44.1, 43.5, 43.5, 34.4, 33.2, 33.1, 33.0.

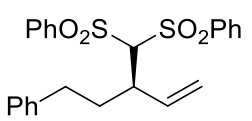
HPLC (Shimadzu LC-2030) (Daicel Chiralpak IC Column, ^{i}PrOH:*n*-Hexane = 0.1:99.1, 1.0 mL/min), *d/r* = 1.0:1.5. R*t* = 40.78 min (minor) and 46.95 min (major), > 99% *ee* for the major diastereomer.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –5.3 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{17}NO_2Na$ 266.1157; found 266.1158.

(*R*)-(2-vinylpentane-1,1-diyldisulfonyl)dibenzene (3al):

White solid; Yield: 58 mg, 61%; M.P. 91-93 ℃.



TLC R*f* = 0.2 (PE:EA, 9:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (t, *J* = 8.1 Hz, 4H), 7.70 – 7.64 (m, 2H), 7.54 (dd, *J* = 17.3, 8.0 Hz, 4H), 6.12 (dt, *J* = 17.2, 9.5 Hz, 1H), 5.07 (d, *J* = 10.1 Hz, 1H), 4.92 (d, *J* = 17.1 Hz, 1H), 4.60 (s, 1H), 3.06 – 3.01 (m, 1H), 1.90 (ddd, *J* = 23.8, 10.3, 4.8 Hz, 1H), 1.63 – 1.56 (m, 1H), 1.34 – 1.28 (m, 1H), 1.11 – 1.04 (m, 1H), 0.80 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 139.0, 137.7, 134.7, 134.4, 129.8, 129.5, 129.3, 129.2, 118.4, 88.0, 44.5, 32.7, 21.5, 13.7.

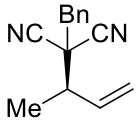
HPLC (Shimadzu LC-2030) (Daicel Chiralpak IG Column, ^{i}PrOH:*n*-Hexane = 3.0:97.0, 0.5 mL/min), R*t* = 86.38 min (major) and 90.37 min (minor), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +7.6 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{19}H_{22}O_4S_2Na$ 401.0857; found 401.0856.

(*R*)-2-benzyl-2-(but-3-en-2-yl)malononitrile (3bb):

White solid; Yield: 49 mg, 93%; M.P. 40-42 °C.



TLC R*f* = 0.4 (PE:EA, 9:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 5H), 5.89 (ddd, *J* = 17.0, 10.3, 8.8 Hz, 1H), 5.40 (dd, *J* = 22.5, 13.6 Hz, 2H), 3.20 (d, *J* = 13.7 Hz, 1H), 3.08 (d, *J* = 13.8 Hz, 1H), 2.77 – 2.71 (m, 1H), 1.46 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0, 132.6, 130.3, 129.1, 128.9, 121.0, 114.9, 114.4, 45.2, 44.9, 41.6, 17.2.

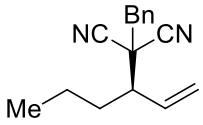
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OJ-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 9.75 min (major) and 15.05 min (minor), 90 % *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –22.0 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{14}N_2Na$ 233.1055; found 233.1054.

(*R*)-2-benzyl-2-(hex-1-en-3-yl)malononitrile (3cb):

White solid; Yield: 52 mg, 87%; M.P. 42-43 °C.



TLC R*f* = 0.5 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 5H), 5.71 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.49 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.35 (dd, *J* = 16.9, 0.6 Hz, 1H), 3.23 (d, *J* = 13.7 Hz, 1H), 3.05 (d, *J* = 13.7 Hz, 1H), 2.54 – 2.48 (m, 1H), 1.94 – 1.86 (m, 1H), 1.71 – 1.65 (m, 1H), 1.55 – 1.44 (m, 1H), 1.34 – 1.23 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7, 132.6, 130.4, 129.1, 128.8, 122.8, 115.2, 114.5, 50.9, 44.6, 41.9, 33.1, 20.3, 13.8.

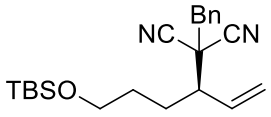
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 6.27 min (minor) and 7.15 min (major), 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –29.9 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{18}N_2Na$ 261.1368; found 261.1368.

(*R*)-2-benzyl-2-(6-((*tert*-butyldimethylsilyl)oxy)hex-1-en-3-yl)malononitrile (3db):

White solid; Yield: 68 mg, 74%; M.P. 43-44 °C.



TLC R*f* = 0.7 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 5H), 5.76 – 5.67 (m, 1H), 5.51 (d, *J* = 10.2 Hz, 1H), 5.36 (d, *J* = 16.9 Hz, 1H), 3.65 (t, *J* = 6.0 Hz, 2H), 3.23 (d, *J* = 13.7 Hz, 1H), 3.06 (d, *J* = 13.8 Hz, 1H), 2.54 (t, *J* = 10.2 Hz, 1H), 2.11 – 2.04 (m, 1H), 1.74 – 1.64 (m, 2H), 1.55 – 1.44 (m, 1H), 0.91 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7, 132.6, 130.4, 129.1, 128.8, 123.0, 115.0, 114.5, 62.5, 50.8, 44.6, 41.9, 30.2, 27.5, 26.1, 18.5, -5.1.

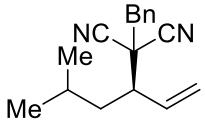
HPLC (Shimadzu LC-2030) (Daicel Chiralpak AD-H Column, ^{i}PrOH:*n*-Hexane = 2.0:98.0, 1.0 mL/min), R*t* = 10.40 min (major) and 11.84 min (minor), 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –15.3 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + H]^+$ Calcd for $C_{22}H_{33}N_2OSi$ 369.2357; found 369.2361; and $[M + Na]^+$ Calcd for $C_{22}H_{32}N_2OSiNa$ 391.2182; found 391.2168.

(*R*)-2-benzyl-2-(5-methylhex-1-en-3-yl)malononitrile (3eb):

White solid; Yield: 55.5 mg, 88%; M.P. 80-81 °C.



TLC R*f* = 0.6 (PE:EA, 9:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 5H), 5.74 – 5.66 (m, 1H), 5.49 (d, *J* = 10.2 Hz, 1H), 5.36 (d, *J* = 17.0 Hz, 1H), 3.22 (d, *J* = 13.7 Hz, 1H), 3.04 (d, *J* = 13.8 Hz, 1H), 2.60 (t, *J* = 10.5 Hz, 1H), 1.74 – 1.60 (m, 3H), 0.99 (d, *J* = 5.6 Hz, 3H), 0.89 (d, *J* = 5.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.8, 132.7, 130.4, 129.1, 128.8, 122.7, 115.2, 114.5, 49.4, 44.8, 41.9, 40.0, 25.3, 24.0, 20.7.

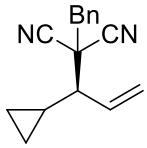
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 5.25 min (minor) and 6.28 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –14.5 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{20}N_2Na$ 275.1524; found 275.1525.

(*S*)-2-benzyl-2-(1-cyclopropylallyl)malononitrile (3fb):

White solid; Yield: 56 mg, 95%; M.P. 51-53 °C.



TLC R*f* = 0.4 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 5H), 5.95 – 5.86 (m, 1H), 5.45 (dd, *J* = 10.3, 0.9 Hz, 1H), 5.33 (d, *J* = 16.9 Hz, 1H), 3.24 – 3.12 (m, 2H), 2.00 (t, *J* = 9.0 Hz, 1H), 1.21 – 1.13 (m, 1H), 0.89 – 0.83 (m, 1H), 0.70 – 0.58 (m, 2H), 0.32 – 0.25 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.1, 132.7, 130.4, 129.0, 128.8, 121.7, 114.9, 114.8, 54.8, 44.8, 42.0, 12.6, 6.7, 3.1.

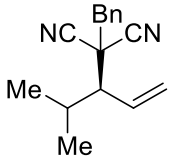
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 9.04 min (minor) and 9.74 min (major), 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –11.5 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{16}N_2Na$ 259.1211; found 259.1211.

(*R*)-2-benzyl-2-(4-methylpent-1-en-3-yl)malononitrile (3gb):

White solid; Yield: 40 mg, 67%; M.P. 82-83 °C.



TLC R*f* = 0.4 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 5H), 5.89 (dt, *J* = 16.8, 10.1 Hz, 1H), 5.56 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.34 (d, *J* = 16.9 Hz, 1H), 3.27 (d, *J* = 13.7 Hz, 1H), 3.03 (d, *J* = 13.7 Hz, 1H), 2.38 (dd, *J* = 7.3, 3.7 Hz, 2H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.5, 130.6, 130.5, 129.0, 128.9, 124.1, 115.1, 115.0, 55.9, 43.4, 42.6, 30.4, 22.7, 17.1.

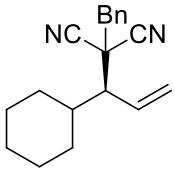
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 6.07 min (minor) and 7.83 min (major), 98% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –11.5 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{18}N_2Na$ 261.1368; found 261.1363.

(*S*)-2-benzyl-2-(1-cyclohexylallyl)malononitrile (3hb):

White solid; Yield: 49 mg, 70%; M.P. 130-132 °C.



TLC R*f* = 0.5 (PE:EA, 9:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 5H), 5.94 – 5.87 (m, 1H), 5.52 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.31 (dd, *J* = 16.9, 1.1 Hz, 1H), 3.26 (d, *J* = 13.7 Hz, 1H), 3.02 (d, *J* = 13.7 Hz, 1H), 2.34 (dd, *J* = 10.2, 3.4 Hz, 1H), 2.11 (d, *J* = 12.7 Hz, 1H), 2.01 – 1.95 (m, 1H), 1.82 – 1.75 (m, 2H), 1.68 (d, *J* = 13.0 Hz, 1H), 1.39 – 1.06 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.5, 131.7, 130.6, 129.0, 128.9, 123.5, 115.1, 115.1, 56.2, 43.4, 42.3, 40.5, 32.8, 28.0, 26.5, 26.3, 26.2.

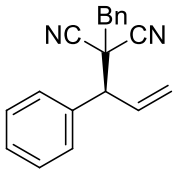
HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 5.68 min (minor) and 6.77 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –20.3 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$Calcd for $C_{19}H_{22}N_2Na$ 301.1681; found 301.1669.

(*S*)-2-benzyl-2-(1-phenylallyl)malononitrile (3ib):

White solid; Yield: 60.5 mg, 89%; M.P. 73-74 °C.



TLC R*f* = 0.3 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.35 (m, 10H), 6.40 (ddd, *J* = 16.8, 10.0, 9.3 Hz, 1H), 5.52 (d, *J* = 10.2 Hz, 1H), 5.46 (d, *J* = 16.8 Hz, 1H), 3.75 (d, *J* = 9.2 Hz, 1H), 3.19 (d, *J* = 13.7 Hz, 1H), 2.98 (d, *J* = 13.7 Hz, 1H).

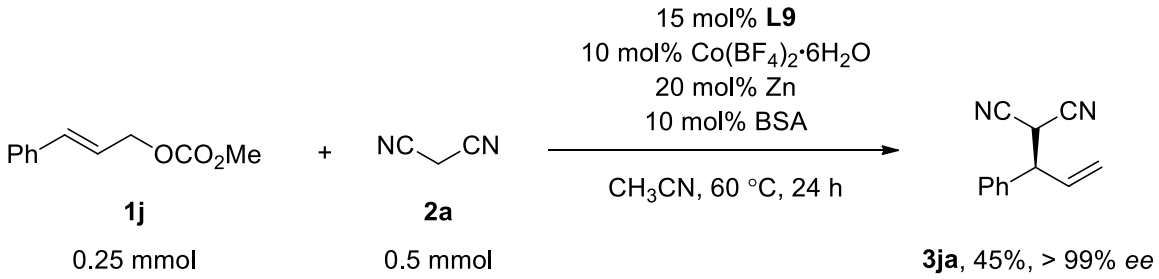
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1, 133.3, 132.4, 130.4, 129.4, 129.2, 129.1, 128.9, 122.2, 114.9, 114.5, 56.5, 45.6, 42.5.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 9.23 min (minor) and 10.30 min (major), 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +19.8 (*c* 0.05, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{19}H_{16}N_2Na$ 295.1211; found 295.1211.

8. Synthesis of (R)-2-(1-phenylallyl)malononitrile (3ja):[6]



In an N_2 filled glove box, **L9** (16 mg, 37.5 ×10^{-3} mmol, 15 mol%) and $Co(BF_4)_2{\cdot}6H_2O$ (8.6 mg, 25.2×10^{-3} mmol, 10 mol%) in 0.2 mL acetonitrile was taken into a 10 mL reaction tube equipped with a Teflon stopcock and a stir bar. Zn dust (3.3 mg, 50.5×10^{-3} mmol, 20 mol%) and 0.5 mL acetonitrile to complete transfer of zinc were added to it. The mixture was allowed to stir for 20 minutes. Afterward, (*E*)-cinnamyl methyl carbonate (**1j**) (48.2 mg, 0.25 mmol, 1 eq), malonitrile (**2a**) (33 mg, 0.5 mmol, 2 eq), bis(trimethylsilyl)acetamide (BSA) (6 μL, 25×10^{-3} mmol, 10 mol%), and 0.3 mL of acetonitrile were added sequentially to the reaction mixture. The reaction tube was sealed and brought out from the glove box. The reaction mixture was then stirred for 24 hours at 60 °C in oil bath. Then, it was cooled to room temperature. and solvent was removed under reduced pressure. The desired pure product was obtained by silica gels (200-300 mesh) column chromatography using PE/EA as an eluent.

Clear oil; Yield: 20.5 mg, 45%.

TLC R*f* = 0.2 (PE:EA, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 6.17 (ddd, *J* = 17.0, 10.3, 7.7 Hz, 1H), 5.49 (d, *J* = 10.3 Hz, 1H), 5.43 (dd, *J* = 17.0, 0.8 Hz, 1H), 4.01 (d, *J* = 6.6 Hz, 1H), 3.94 (t, *J* = 7.2 Hz, 1H).

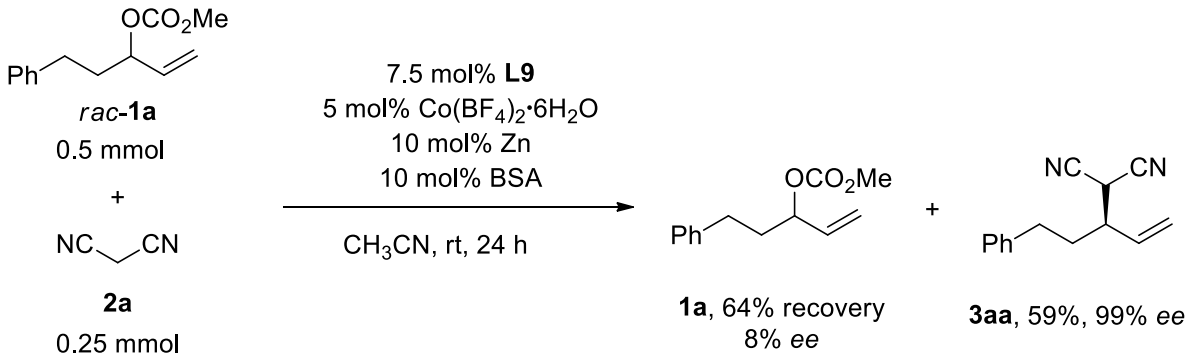
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3, 133.3, 129.6, 129.1, 128.0, 121.1, 111.8, 111.8, 50.3, 29.9.

HPLC (Shimadzu LC-16) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 10.0:90.0, 1.0 mL/min), R*t* = 17.01 min (minor) and 22.55 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +6.1 (*c* 0.05, $CHCl_3$). Literature report: $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{24}}$ = +41.4 (*c* 0.54, $CHCl_3$), 91% *ee*.

HRMS (ESI): *m/z* $[M + K]^+$ calculated for $C_{12}H_{10}N_2K$ 221.0481; found 221.0396.

9. Kinetic resolution study:



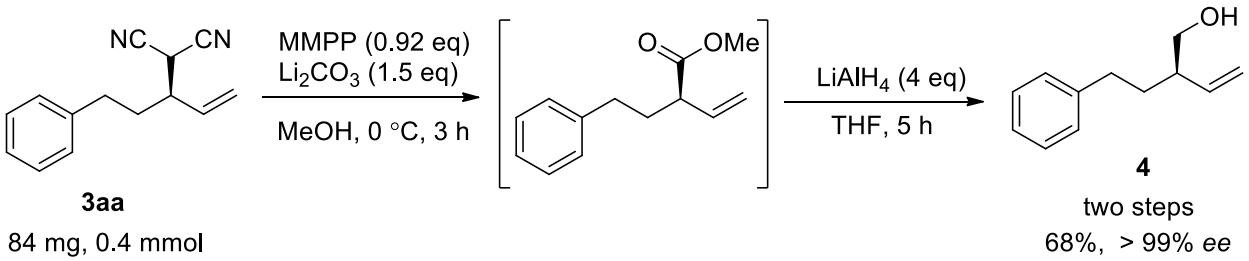
In an N_2 filled glove box, a reaction tube contains **L9** (8 mg, 18.8 ×10^{-3} mmol, 7.5 mol%) and $Co(BF_4)_2{\cdot}6H_2O$ (4.3 mg, 12.6×10^{-3} mmol, 5 mol%) in 0.2 mL acetonitrile was added Zn dust (1.7 mg, 26.0×10^{-3} mmol, 10 mol%). Additionally, 0.5 mL of acetonitrile was added to complete transfer of zinc. The mixture was allowed to stir for 20 minutes. Afterward, *rac*-**1a** (110 mg, 0.5 mmol, 2 eq), malonitrile (**2a**) (17 mg, 0.25 mmol, 1 eq), bis(trimethylsilyl)acetamide (BSA) (6 μL, 25×10^{-3} mmol, 10 mol%), and 0.3 mL of acetonitrile were added sequentially to the reaction mixture. The reaction tube was sealed with Teflon stopcock and brought out from the glove box. The reaction mixture was then stirred for 16 hours at room temperature. Then, solvent was removed and column chromatography was run on a column of silica gels (200-300 mesh) using PE/EA as an eluent to get the desired product.

The amount of recovery **1a** was 70 mg, 64% yield; *ee* 8%.

The amount of product **3aa** was 31 mg, 30% yield; *ee* 99%.

Enantiomeric excess of recovered **1a** was determined by **HPLC** (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 5.0:95.0, 1.0 mL/min), R*t* = 4.65 min (minor) and 4.92 min (major), 6% *ee*.

10. Synthesis of (*R*)-2-phenethylbut-3-en-1-ol (4):



Compound **3aa** (84 mg, 0.4 mmol) was dissolved in MeOH (3 mL) in a 10 mL round bottom flask at 0 °C. Li_2CO_3 (45 mg, 0.6 mmol, 1.5 eq) and Magnesium monoperoxyphthalate hexahydrate (MMPP) 80% analytical grade (144 mg, 0.92 eq) were added sequentially to it. The reaction mixture was stirred for 3 hours at 0 °C. Then, it was diluted with EA (20 mL) and filtered through a pad of celite to remove solid residues and concentrated in vacuo. The crude product was further dissolved in EA (20 mL) and filtered through a pad of celite to get the clear oily product. The crude oily product was treated with $LiAlH_4$ (66 mg, 4 eq) in 8 mL THF at 0 °C and stirred continue at room temperature for 5 hours. The reaction mixture was quenched with water (5 mL) carefully and 5 mL of dil. HCl (1 M) was added and extracted with EA. The organic phase was dried on Na_2SO_4 and chromatographed on a column of silica gels (PE/EA as an eluent).

Clear oil; Yield: 48 mg, 68%.

TLC R*f* = 0.3 (PE:EA, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 5.66 (ddd, *J* = 17.2, 10.3, 8.8 Hz, 1H), 5.22 (ddd, *J* = 18.3, 13.8, 1.4 Hz, 2H), 3.59 (dd, *J* = 10.6, 5.2 Hz, 1H), 3.47 (dd, *J* = 10.6, 8.0 Hz, 1H), 2.72 (ddd, *J* = 15.0, 10.0, 5.3 Hz, 1H), 2.58 (ddd, *J* = 13.8, 9.8, 6.9 Hz, 1H), 2.32 – 2.23 (m, 1H), 1.82 – 1.73 (m, 1H), 1.67 (s, 1H), 1.64 – 1.55 (m, 1H).

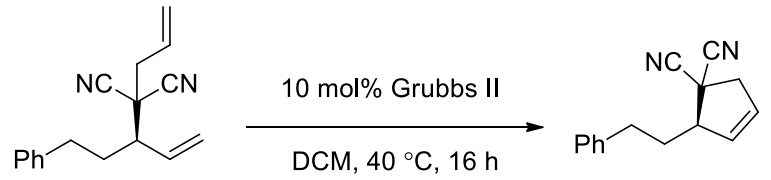
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 139.8, 128.6, 128.5, 125.9, 118.0, 65.7, 46.6, 33.4, 32.6.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +5.6 (*c* 0.25, $CHCl_3$).

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OJ-H Column, ^{i}PrOH:*n*-Hexane = 1.0 : 99.0, 1.0 mL/min), R*t* = 22.97 min (minor) and 24.04 min (major), > 99% *ee*.

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{12}H_{16}ONa$ 199.1099; found 199.1096.

11. Synthesis (*R*)-2-phenethylcyclopent-3-ene-1,1-dicarbonitrile (5):



3ai
53 mg, 0.21 mmol

5
77%, > 99% *ee*

In a Schlenk tube equipped with Teflon stop cock and stir bar, **3ai** (53 mg, 0.21 mmol) and Grubbs II (18 mg, 0.021 mmol, 10 mol%) were mixed in DCM (5 mL) under argon atmosphere. The reaction mixture was heated at 40 °C in oil bath for 16 hours. Then solvent was removed and column chromatography was performed on silica gels using PE/EA as an eluent.

Clear oil; Yield: 36 mg, 77%.

TLC R*f* = 0.3 (PE:EA, 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.24 – 7.21 (m, 3H), 5.82 – 5.76 (m, 2H), 3.31 (ddd, *J* = 8.4, 3.7, 1.8 Hz, 1H), 3.24 – 3.12 (m, 2H), 2.81 (dd, *J* = 11.7, 4.8 Hz, 2H), 2.15 (tt, *J* = 14.0, 7.2 Hz, 1H), 2.00 (ddd, *J* = 12.2, 7.9, 6.2 Hz, 1H).

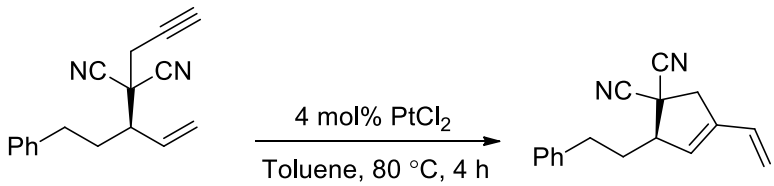
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.3, 132.4, 128.9, 128.5, 127.2, 126.6, 116.9, 115.0, 54.7, 44.9, 37.9, 33.6.

HPLC (Shimadzu LC-16) (Daicel Chiralpak AD-H Column, ^{i}PrOH:*n*-Hexane = 2.0:98.0, 0.5 mL/min), R*t* = 16.92 min (minor) and 18.11 min (major), > 99% *ee*.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –92.8 (*c* 0.25, $CHCl_3$).

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{14}N_2Na$ 245.1055; found 245.1059.

12. Synthesis (*R*)-2-phenethyl-4-vinylcyclopent-3-ene-1,1-dicarbonitrile (6):



3aj
0.124 g, 0.5 mmol

6
88%, > 99% *ee*

Under Argon atmosphere, a Schlenk tube equipped with Teflon stop cock and stir bar was charged with **3aj** (0.124 g, 0.5 mmol) and $PtCl_2$ (5.5 mg, 0.02 mmol, 4 mol%) in Toluene (5 mL). The reaction mixture was heated

at 80 °C in oil bath for 4 hours. Then, solvent was removed and column chromatography was performed on silica gels using PE/EA as an eluent.

Clear oil; Yield: 109 mg, 88%.

TLC R*f* = 0.3 (PE:EA, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.21 (m, 3H), 6.47 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.67 (s, 1H), 5.27 (d, *J* = 10.8 Hz, 1H), 5.15 (d, *J* = 17.6 Hz, 1H), 3.37 (t, *J* = 7.7 Hz, 1H), 3.34 – 3.19 (m, 2H), 2.81 (t, *J* = 7.9 Hz, 2H), 2.17 (dt, *J* = 14.5, 7.8 Hz, 1H), 2.00 (dq, *J* = 13.7, 8.1 Hz, 1H).

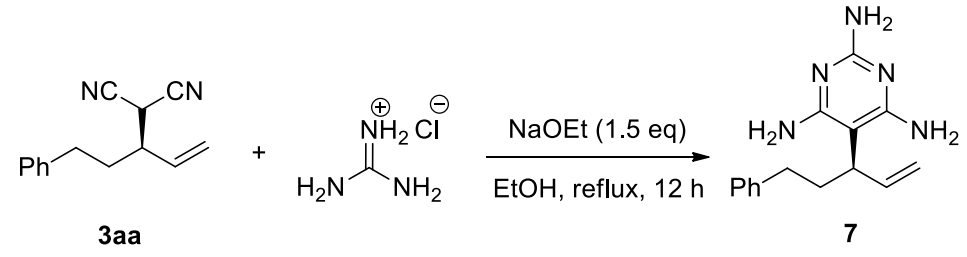
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.3, 139.1, 131.0, 129.3, 128.9, 128.5, 126.6, 118.2, 116.7, 114.9, 54.4, 43.2, 37.9, 33.7, 33.5.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –133.2 (*c* 0.25, $CHCl_3$).

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH:*n*-Hexane = 1.0 : 99.0, 0.5 mL/min), R*t* = 45.73 min (minor) and 47.24 min (major), > 99% *ee*

HRMS (ESI): *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{16}N_2Na$ 271.1211; found 271.1215.

13. Synthesis (*R*)-5-(5-phenylpent-1-en-3-yl)pyrimidine-2,4,6-triamine (7):



3aa — 63 mg, 0.3 mmol

36 mg, 0.38 mmol

7 — Yield: 82%

To an ethanolic solution of **3aa** (63 mg, 0.3 mmol) and guanidine hydrochloride (36 mg, 0.38 mmol, 1.25 eq), was added NaOEt (32 mg, 0.45 mmol, 1.5 eq) and the reaction mixture was refluxed in oil bath for 12 hours. Then, solvent was removed and column chromatography was performed on silica gels using DCM/MeOH as an eluent.

Light yellow solid; Yield: 66 mg, 82%; M.P. 63-64 °C.

TLC R*f* = 0.3 (PE:EA, 4:1).

^{1}H NMR (400 MHz, MeOD) δ 7.21 (dd, *J* = 10.1, 4.7 Hz, 2H), 7.14 – 7.10 (m, 3H), 6.07 – 5.99 (m, 1H), 5.17 (d, *J* = 2.3 Hz, 1H), 5.13 (dt, *J* = 3.6, 1.5 Hz, 1H), 4.93 (s, 6H), 3.46 (dtt, *J* = 11.1, 4.4, 2.3 Hz, 1H), 2.64 – 2.48 (m, 2H), 2.10 – 2.04 (m, 2H).

^{13}C NMR (126 MHz, MeOD) δ 163.5, 161.4, 143.8, 141.0, 129.5, 129.5, 126.9, 115.1, 88.0, 39.1, 35.2, 33.8.

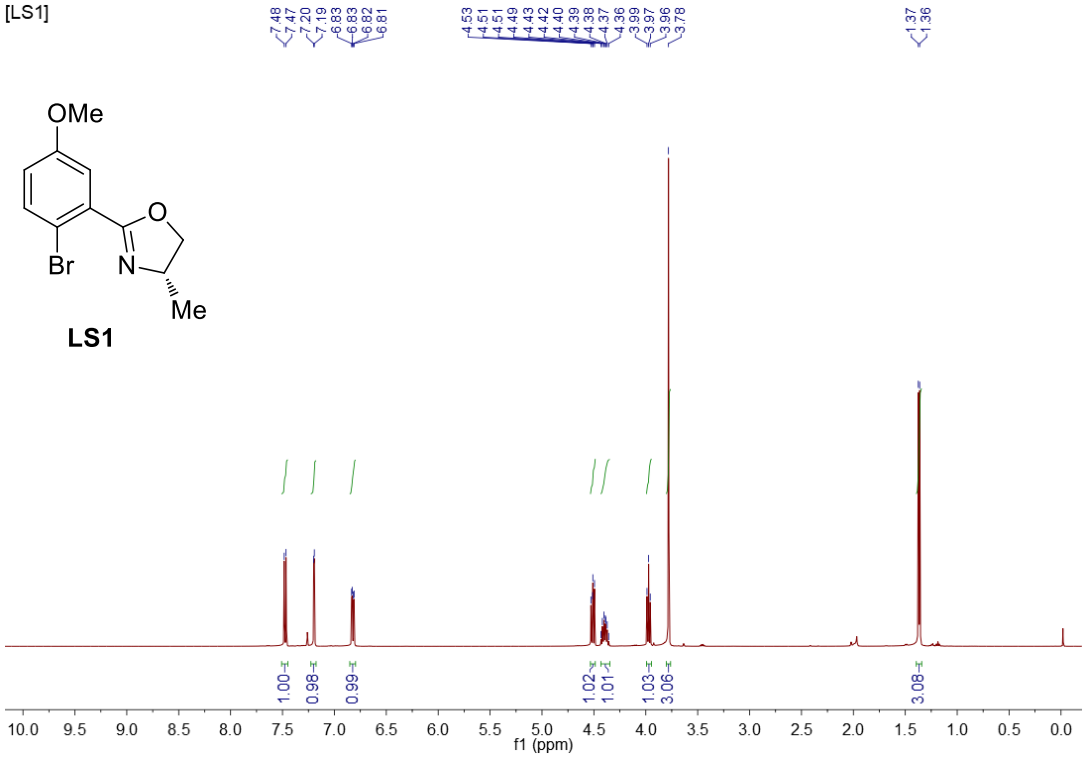
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = –35.6 (*c* 0.25, MeOH).

HRMS (ESI): *m/z* $[M + H]^+$ Calcd for $C_{15}H_{20}N_5$ 270.1713; found 270.1714.

14. NMR spectra of new compounds:

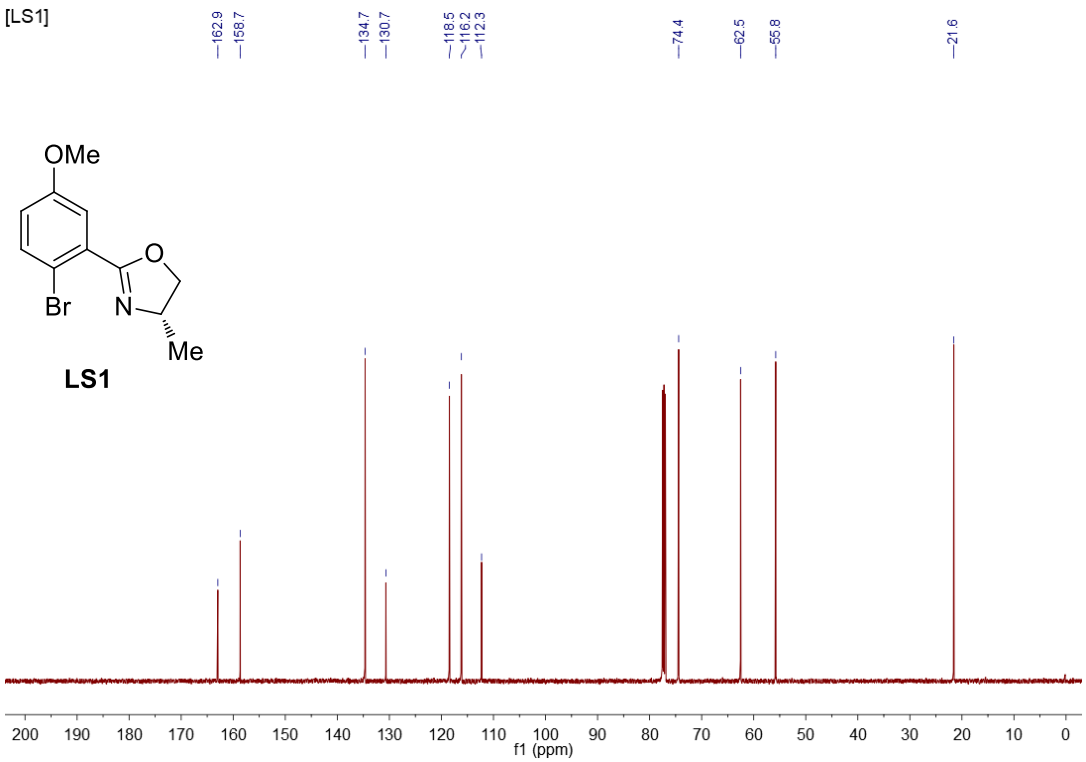
500 MHz, $CDCl_3$

[LS1]



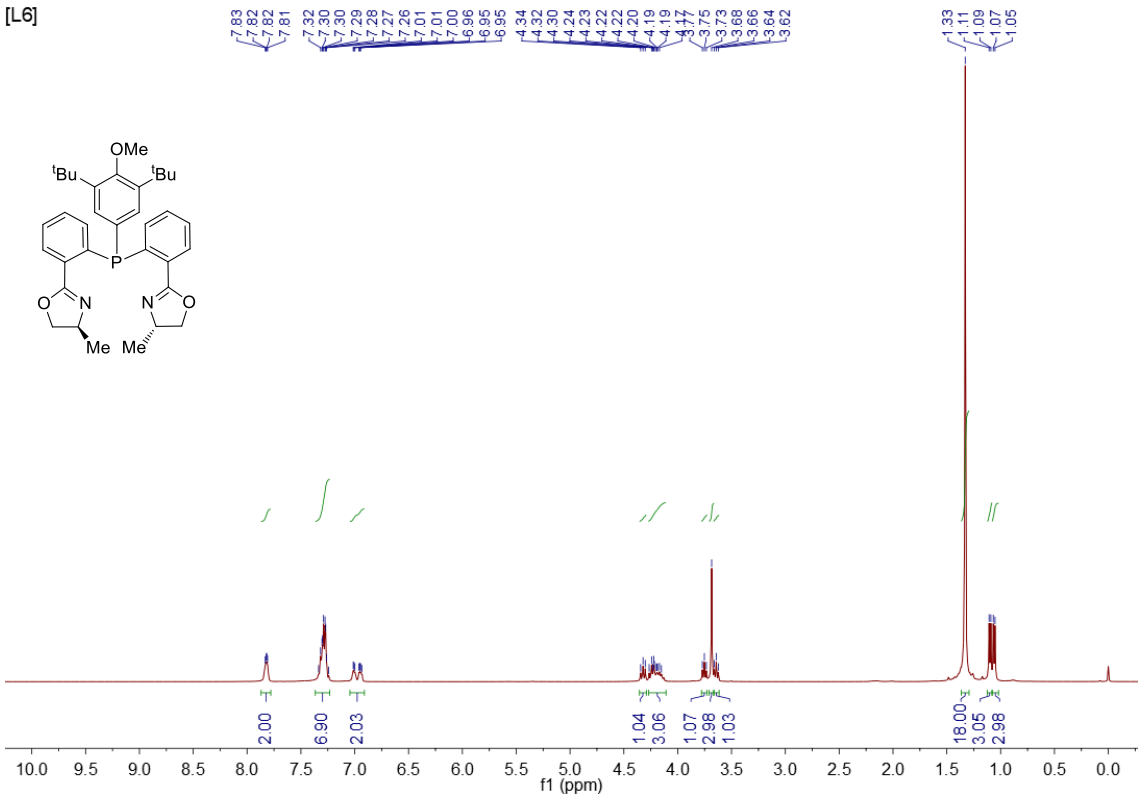
126 MHz, $CDCl_3$

[LS1]



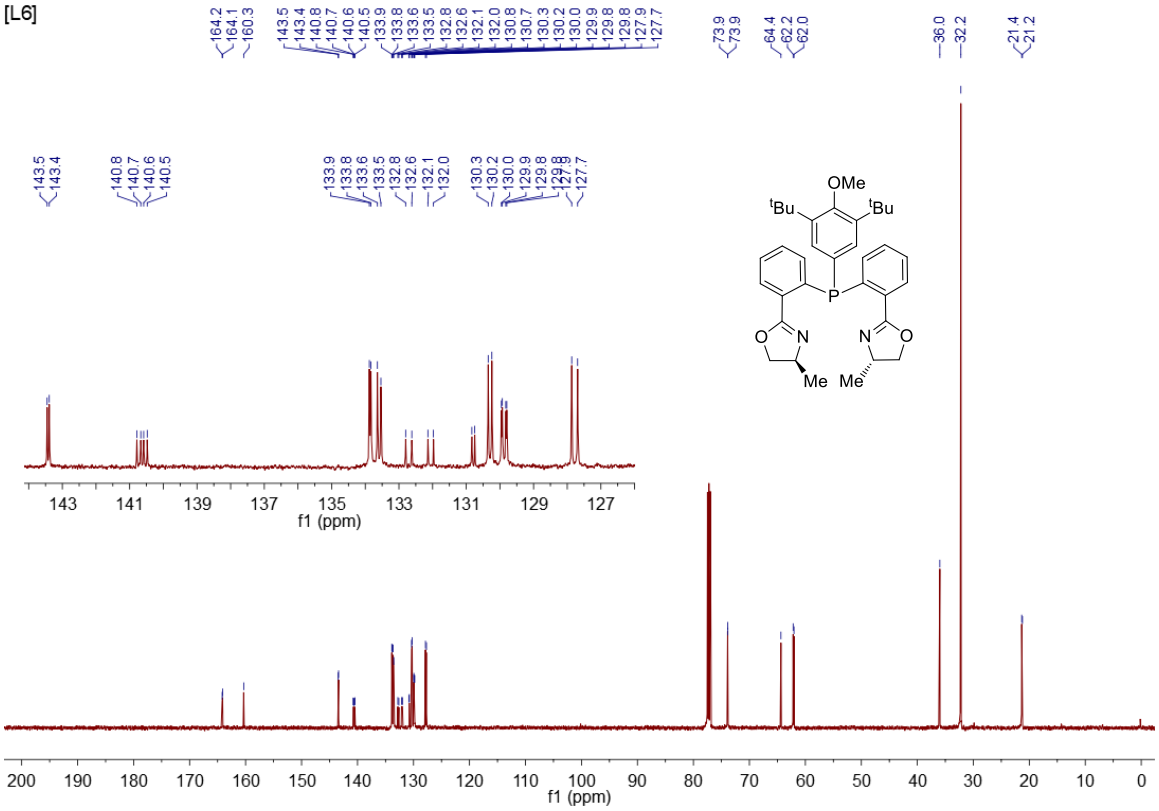
400 MHz, $CDCl_3$

[L6]



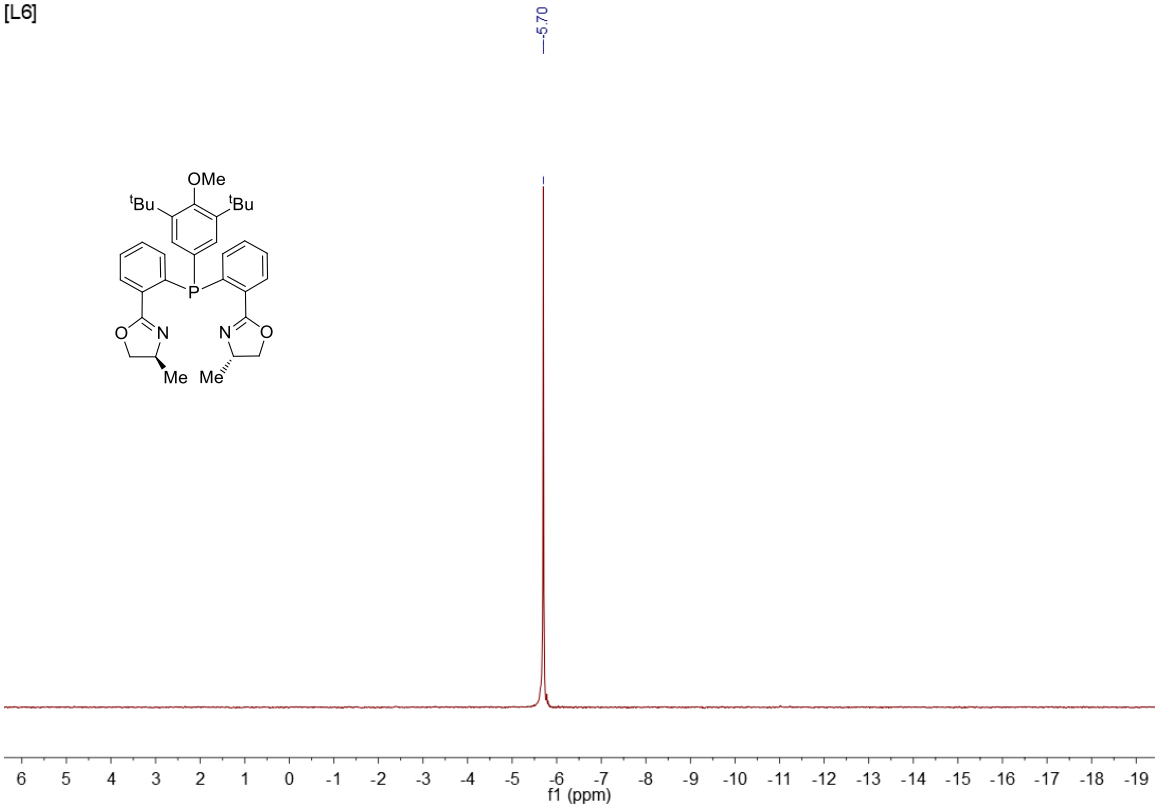
126 MHz, $CDCl_3$

[L6]



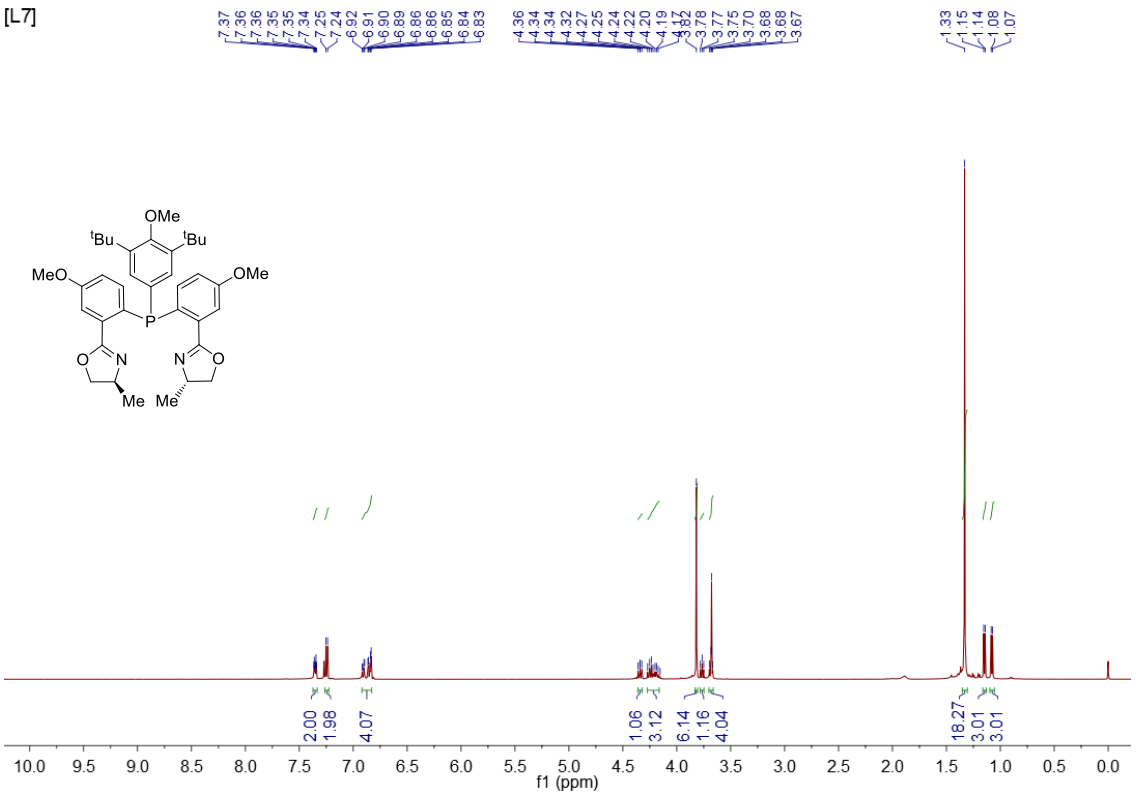
162 MHz, $CDCl_3$

[L6]



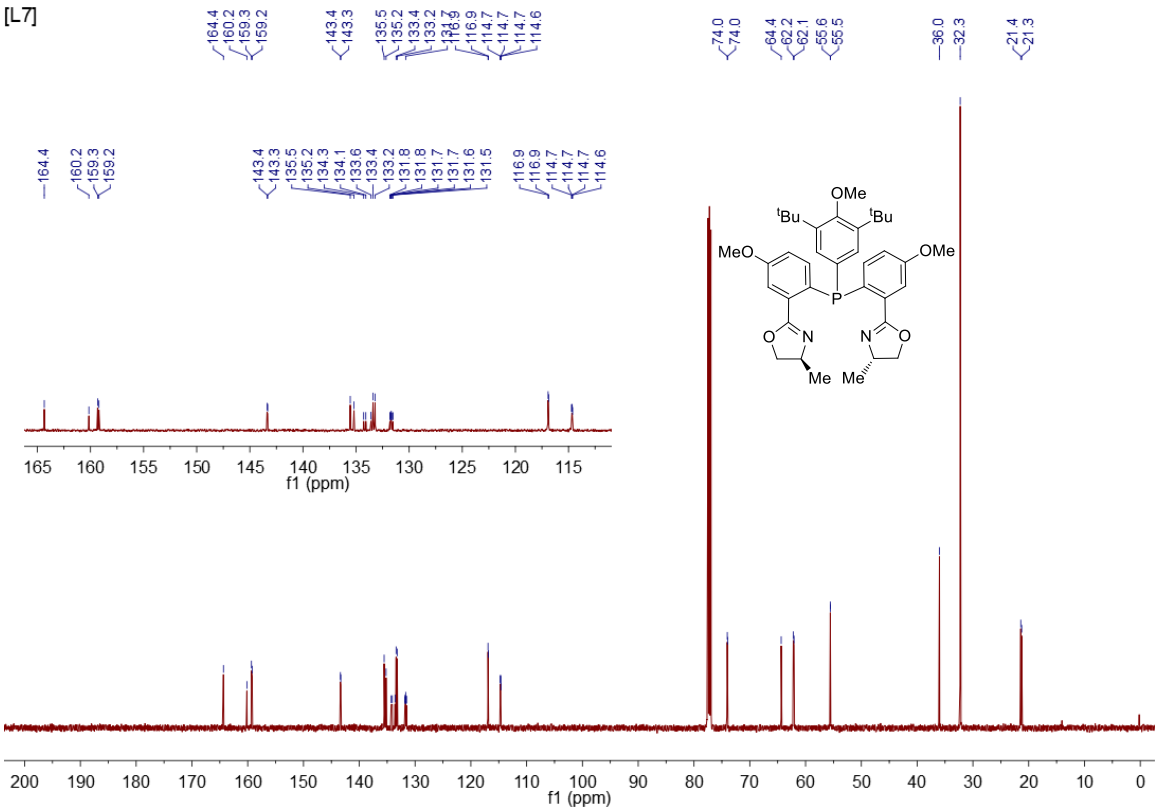
500 MHz, $CDCl_3$

[L7]



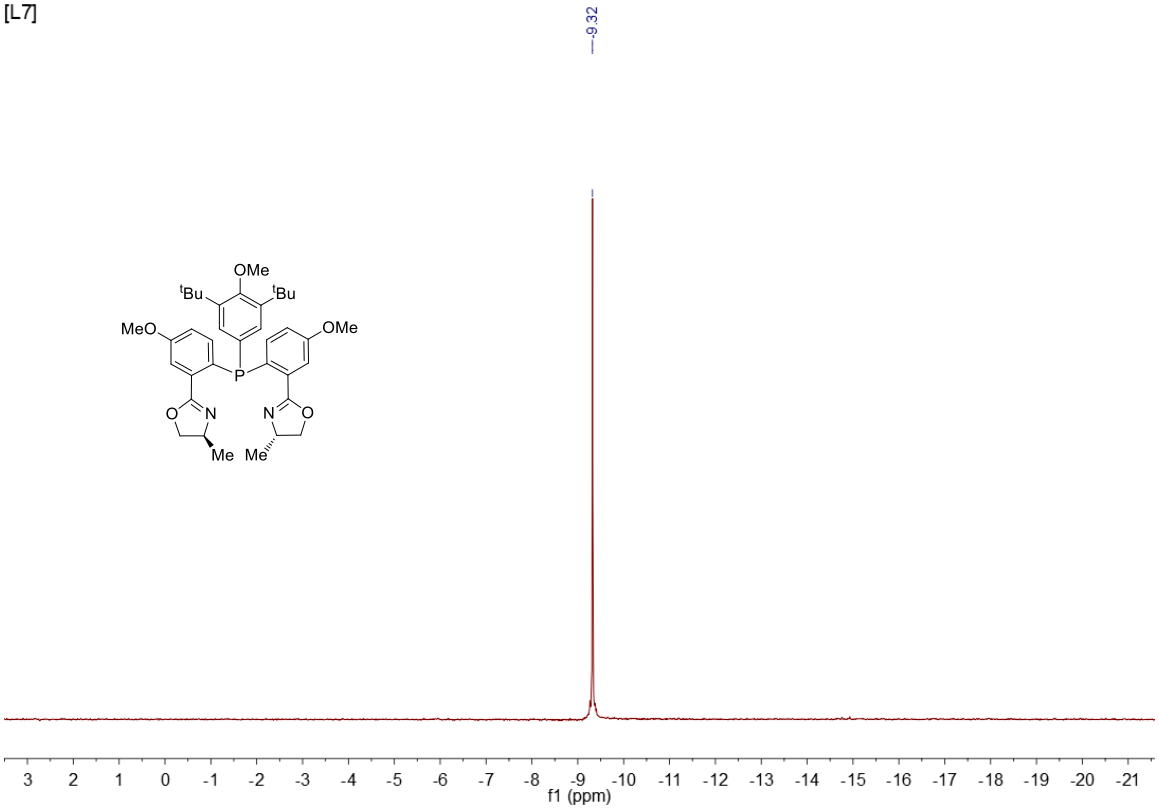
126 MHz, $CDCl_3$

[L7]

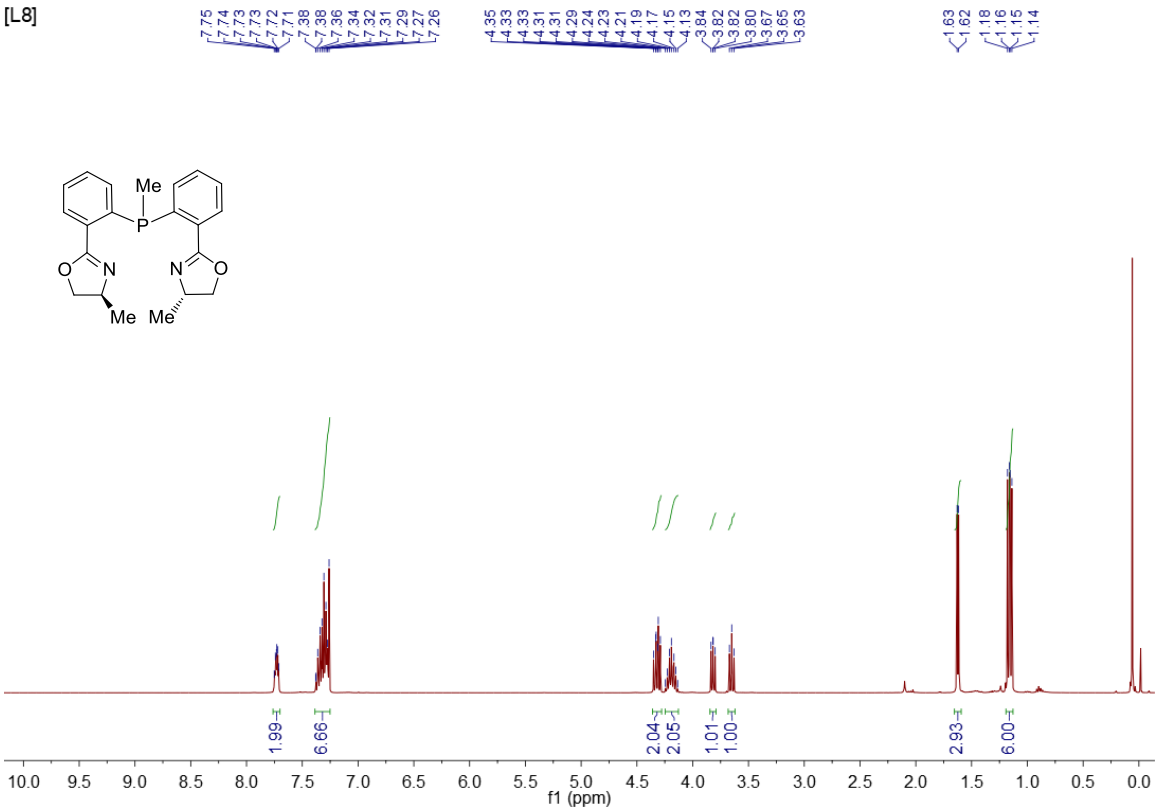


202 MHz, $CDCl_3$

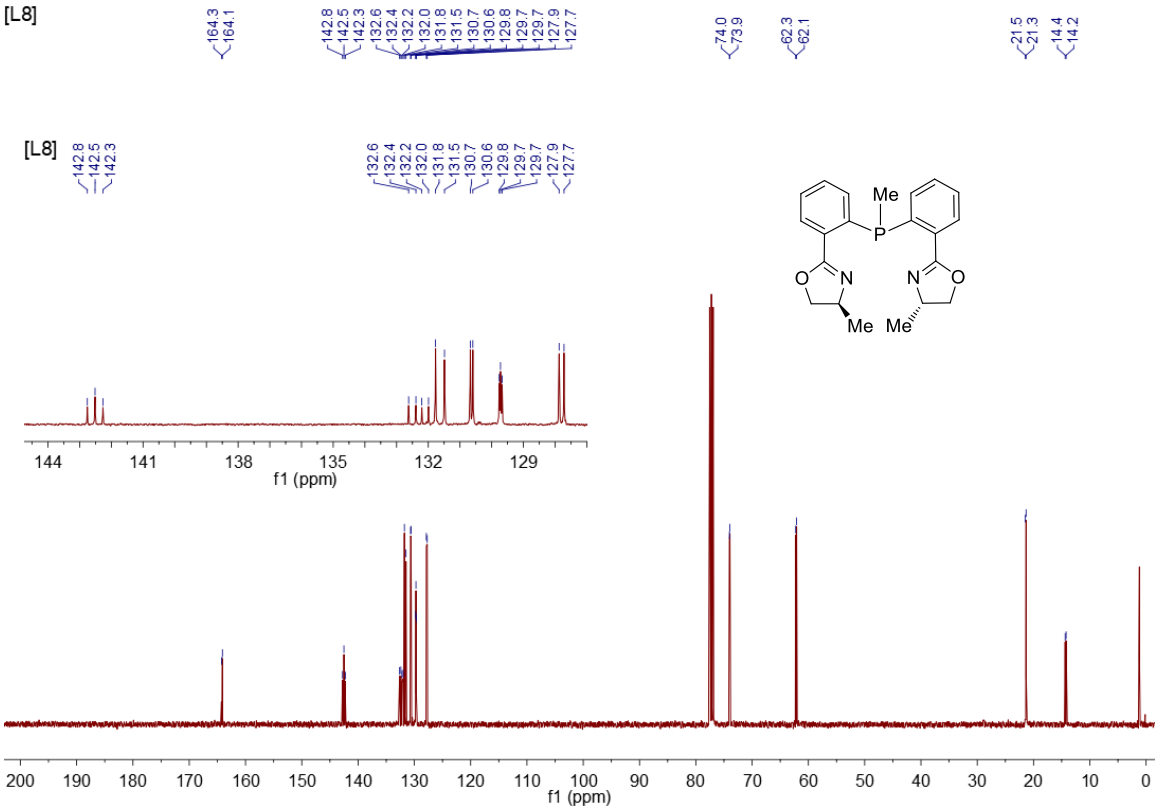
[L7]



400 MHz, $CDCl_3$

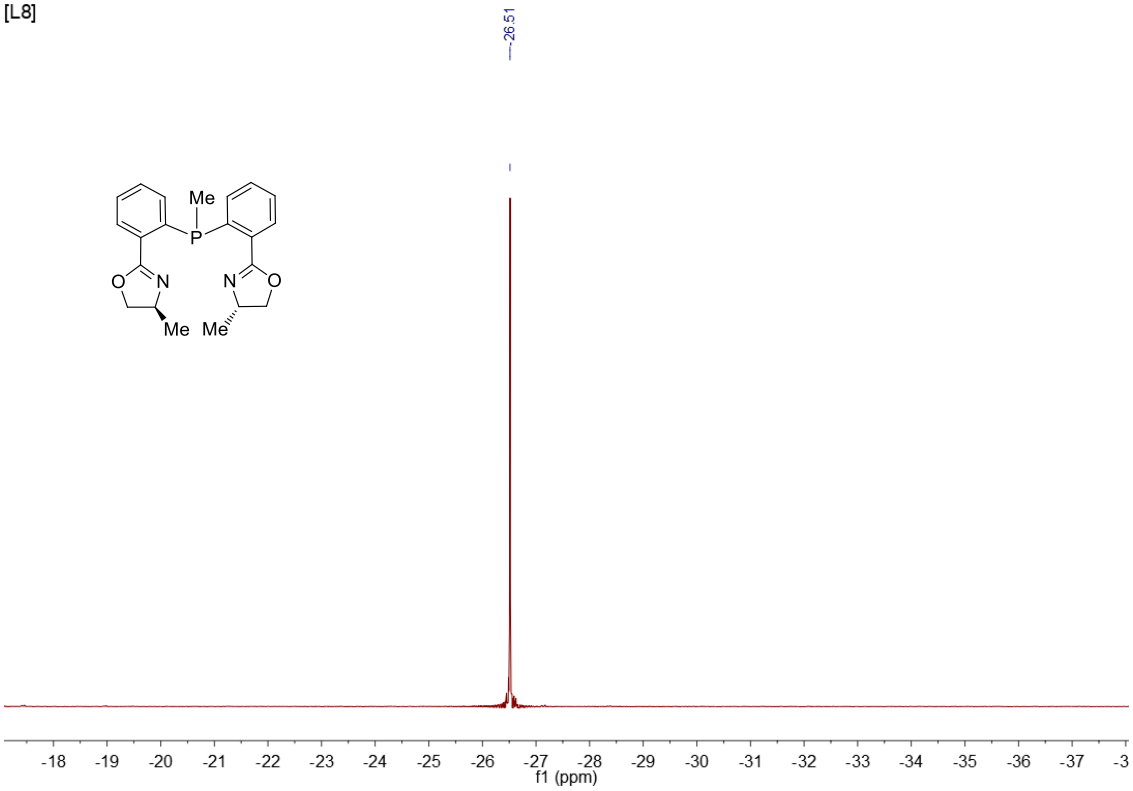


101 MHz, $CDCl_3$



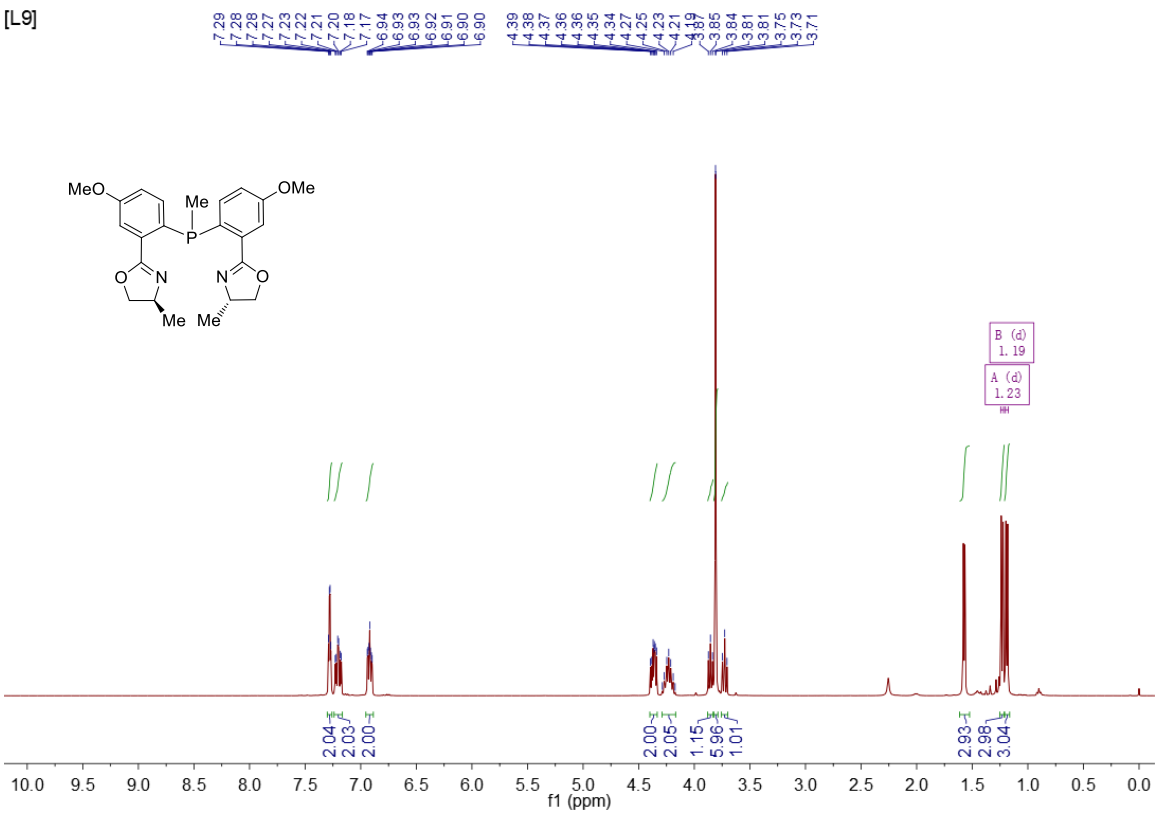
162 MHz, $CDCl_3$

[L8]



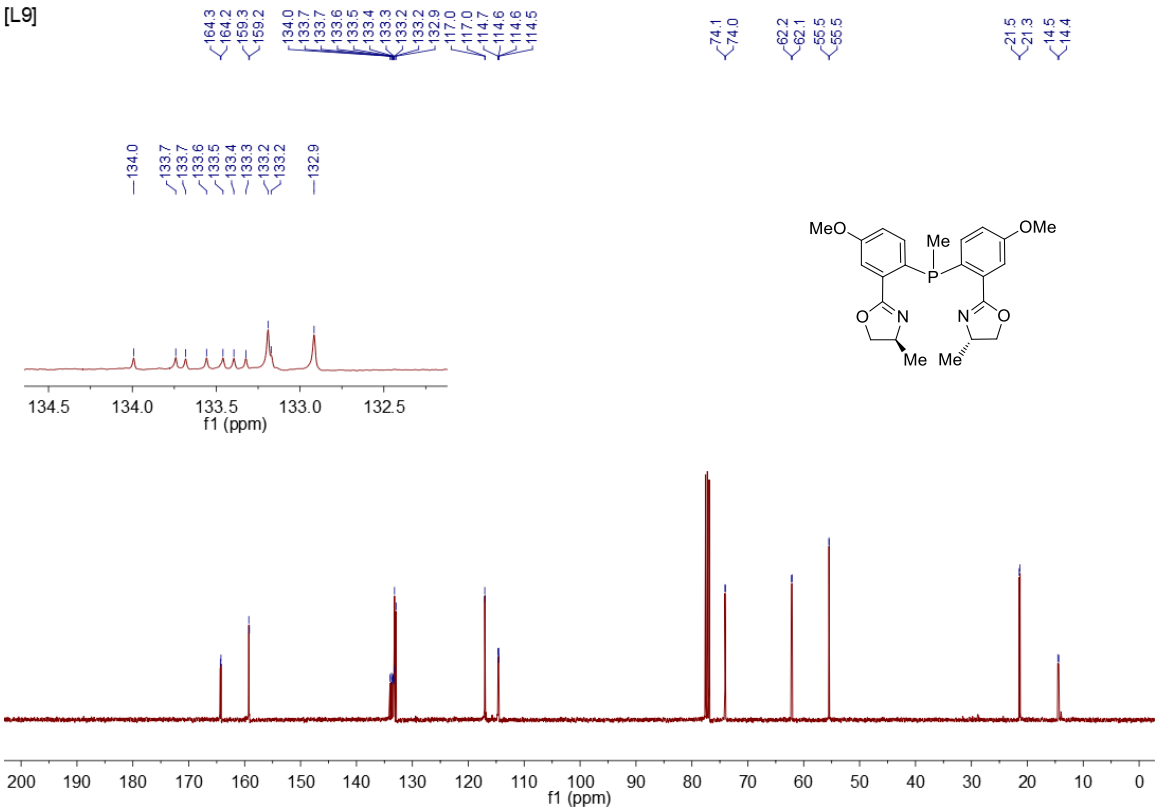
400 MHz, $CDCl_3$

[L9]



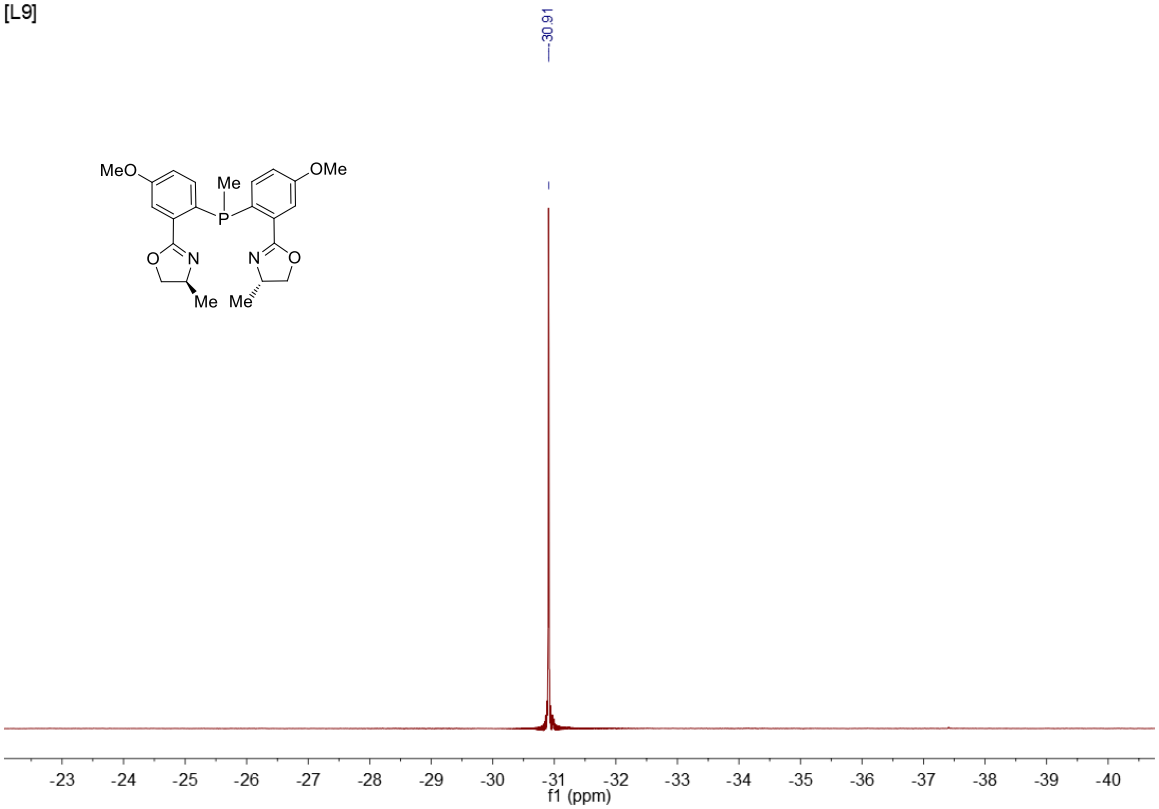
101 MHz, $CDCl_3$

[L9]



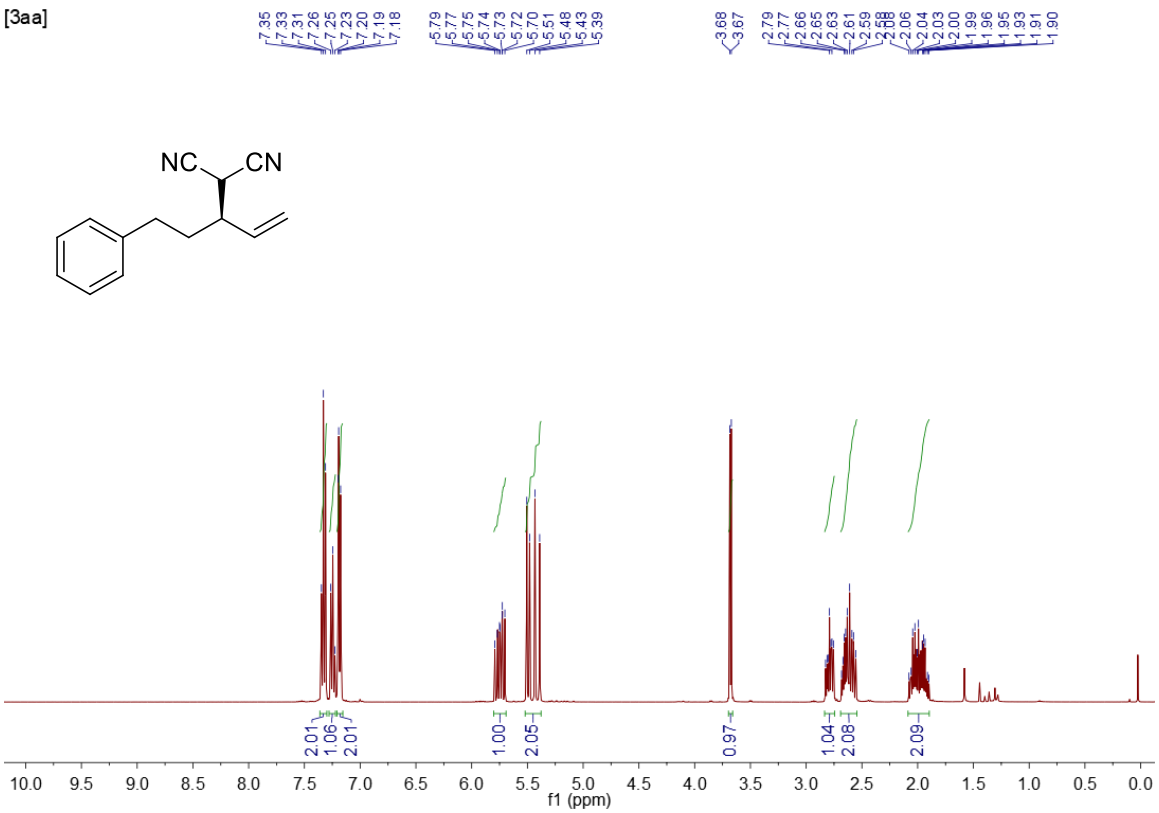
202 MHz, $CDCl_3$

[L9]



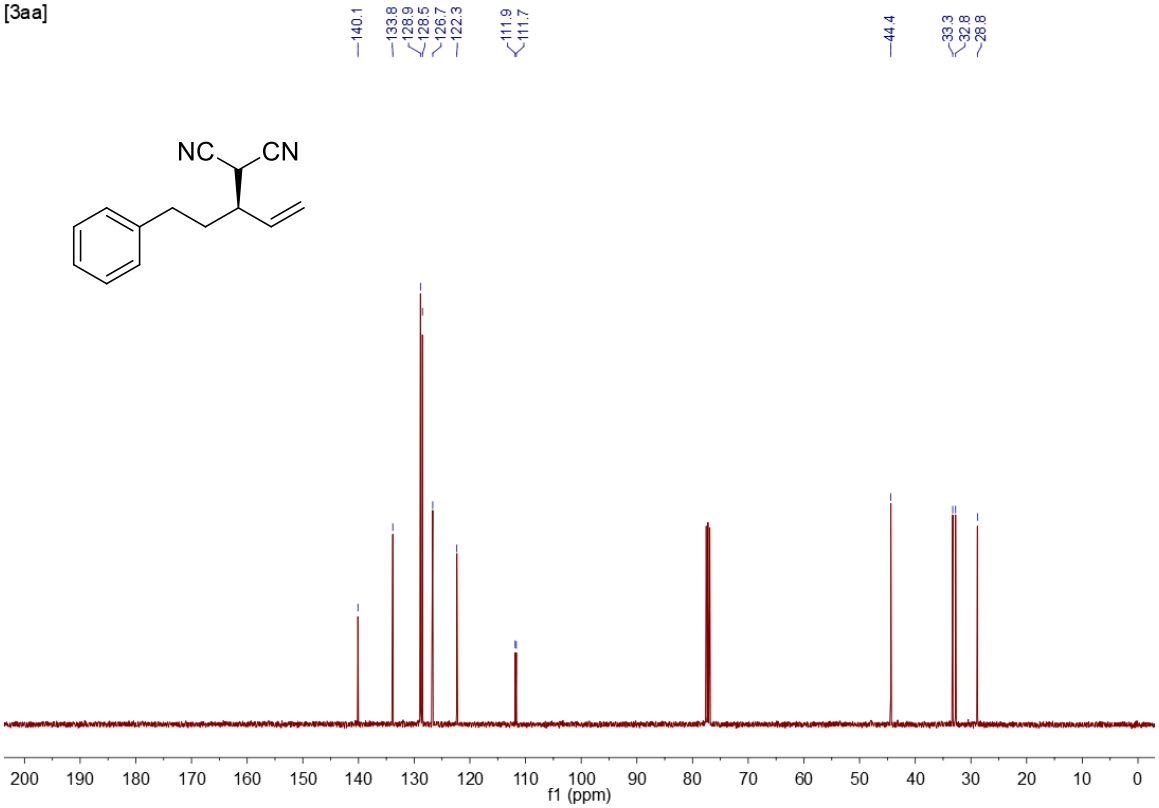
400 MHz, $CDCl_3$

[3aa]



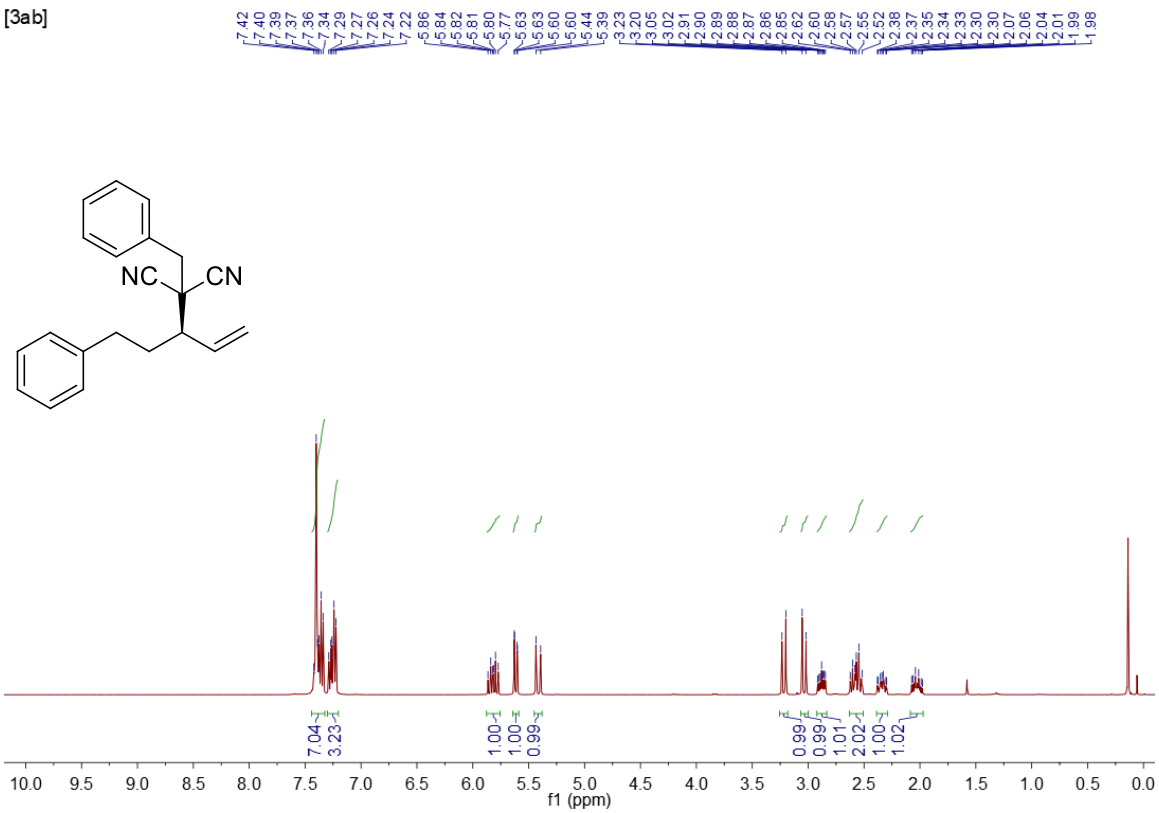
101 MHz, $CDCl_3$

[3aa]



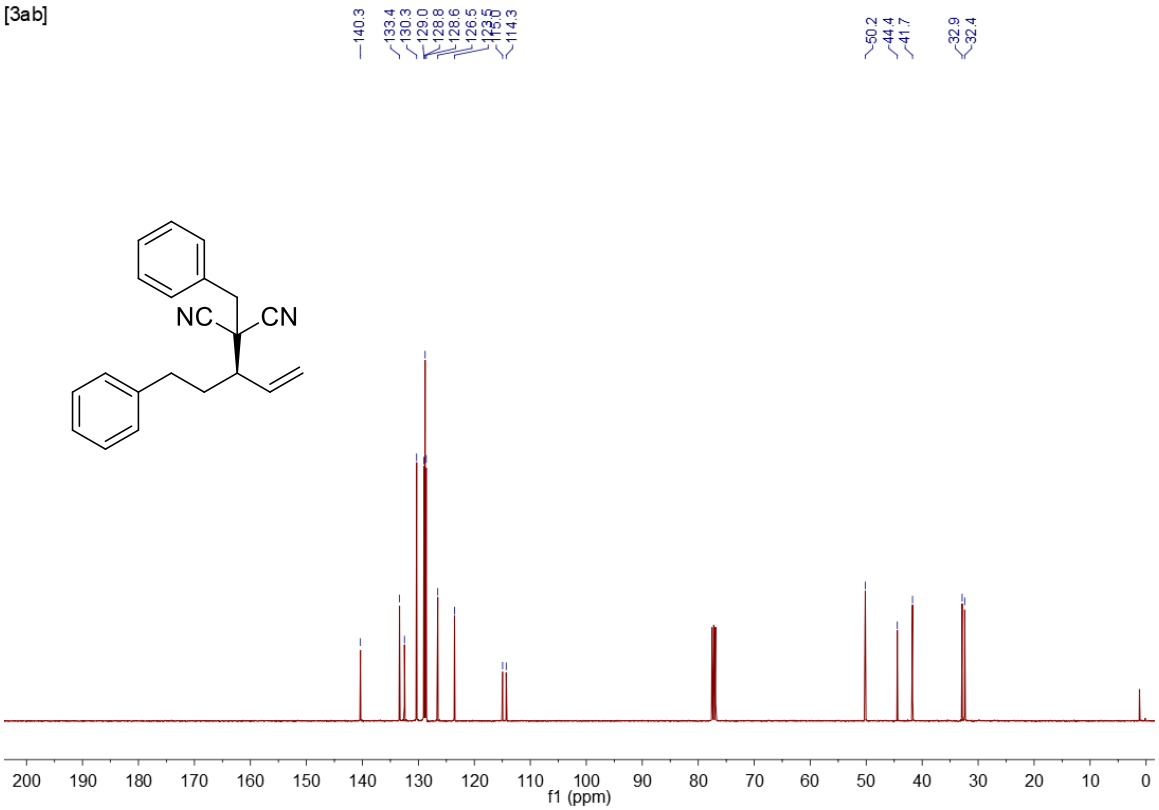
400 MHz, $CDCl_3$

[3ab]



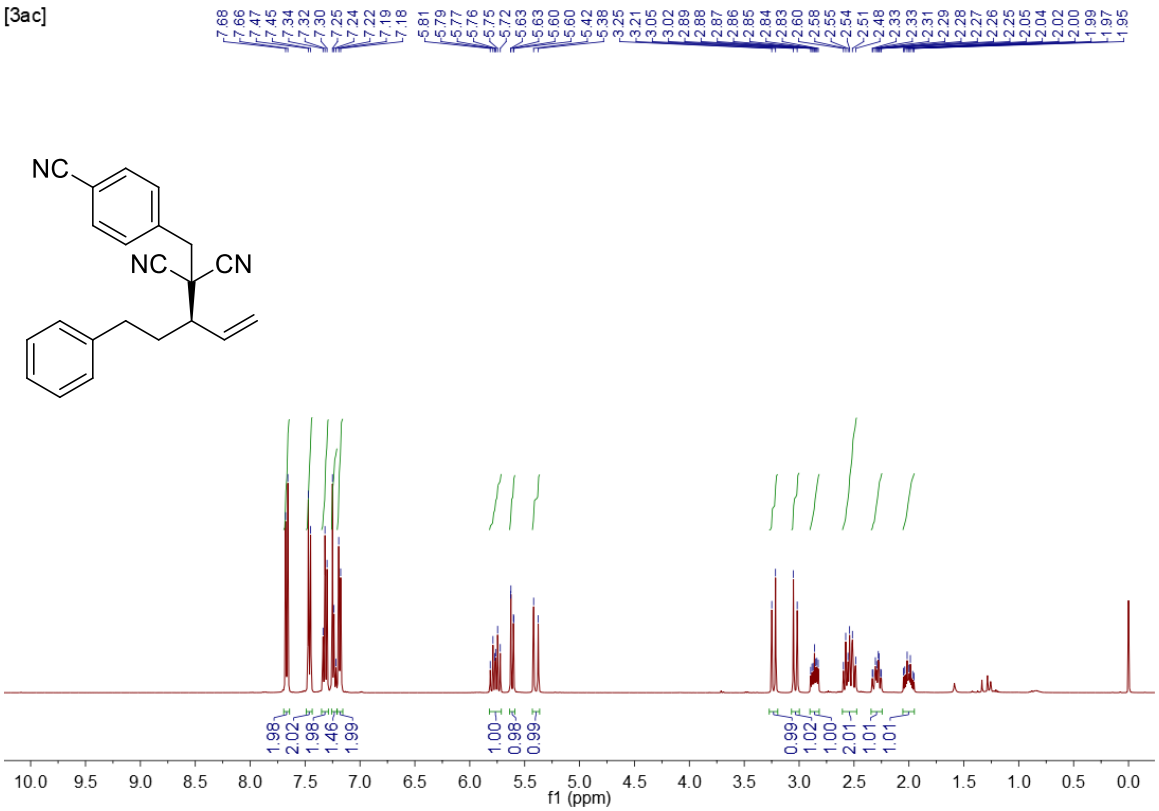
126 MHz, $CDCl_3$

[3ab]



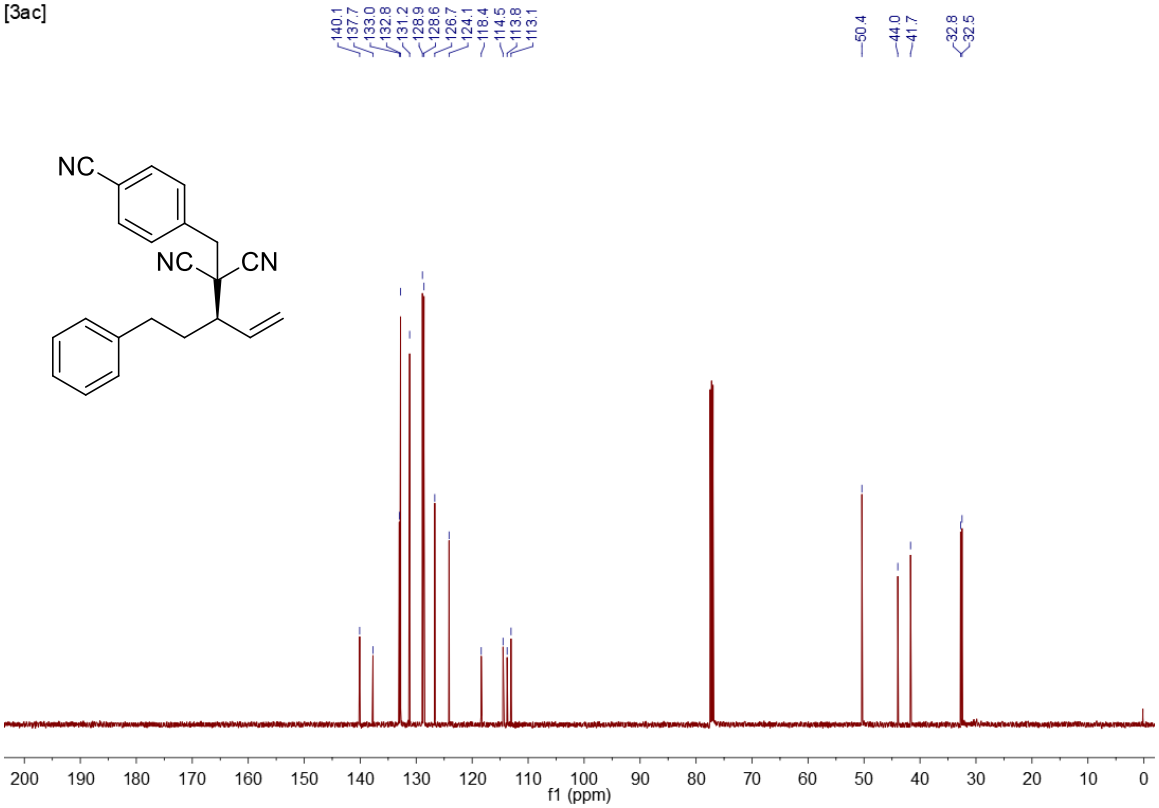
400 MHz, $CDCl_3$

[3ac]



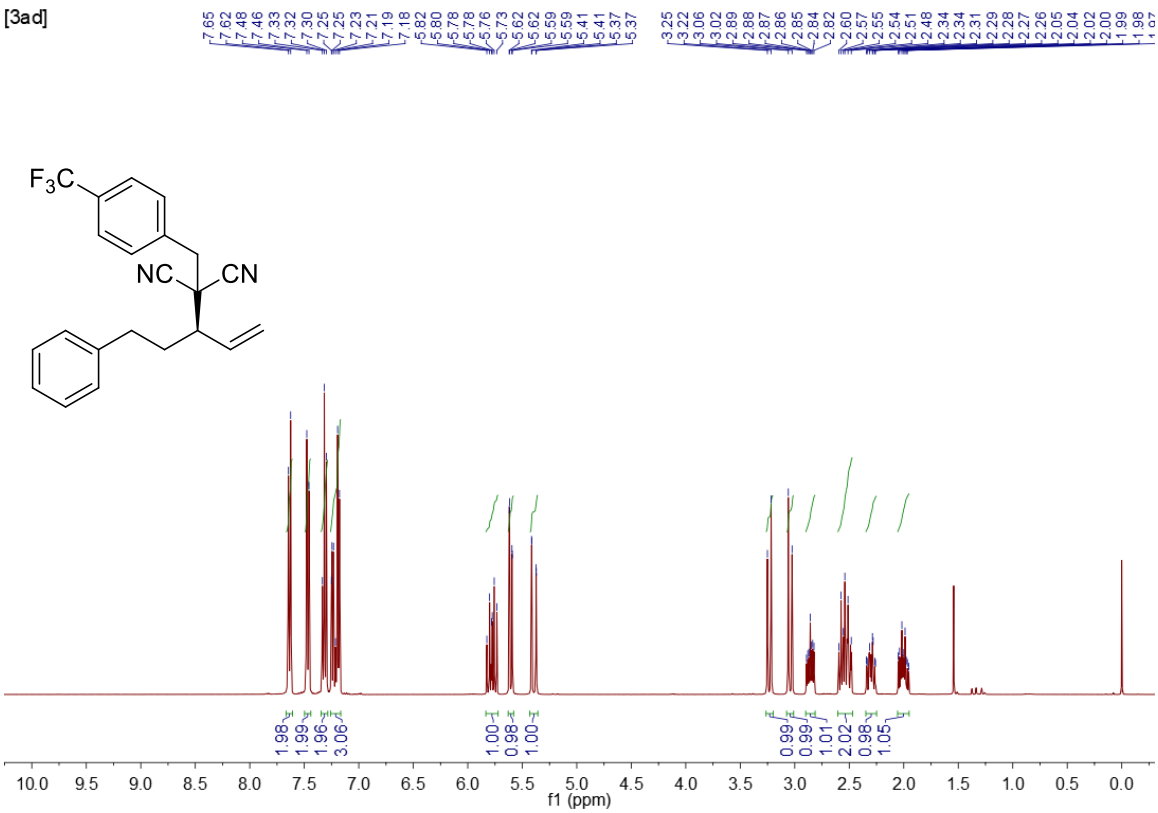
126 MHz, $CDCl_3$

[3ac]



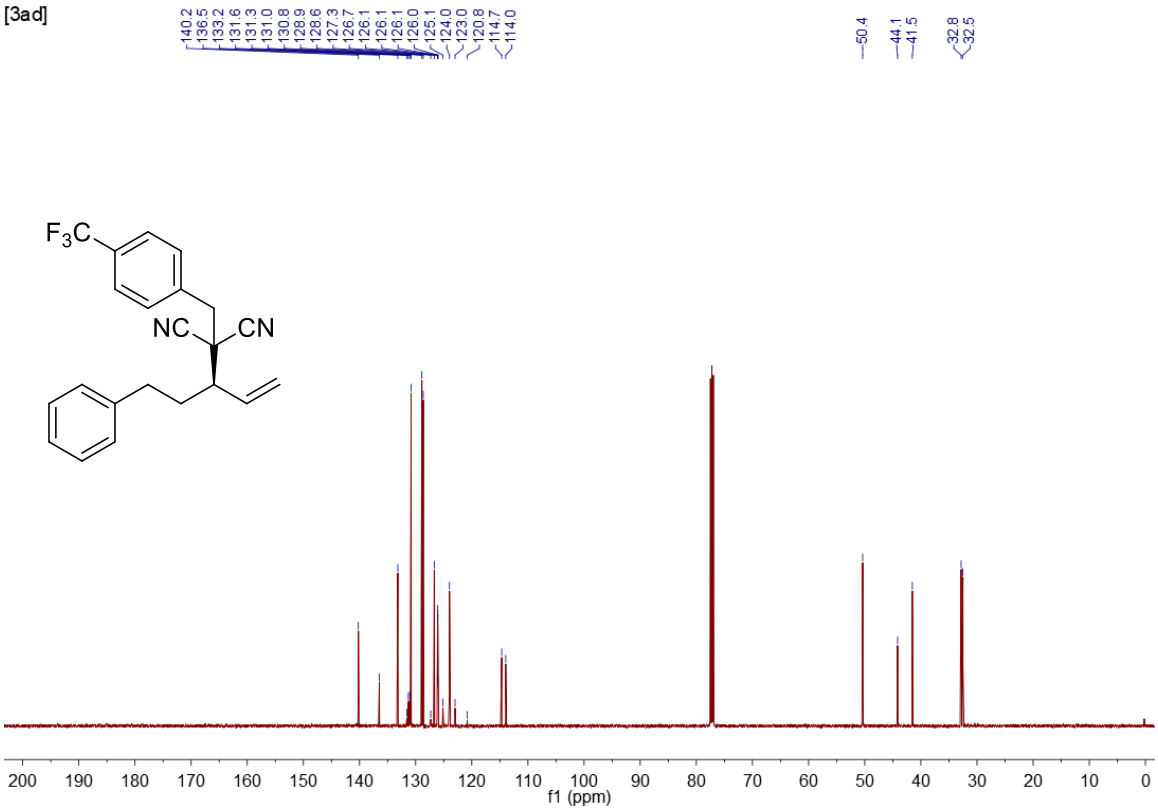
400 MHz, $CDCl_3$

[3ad]



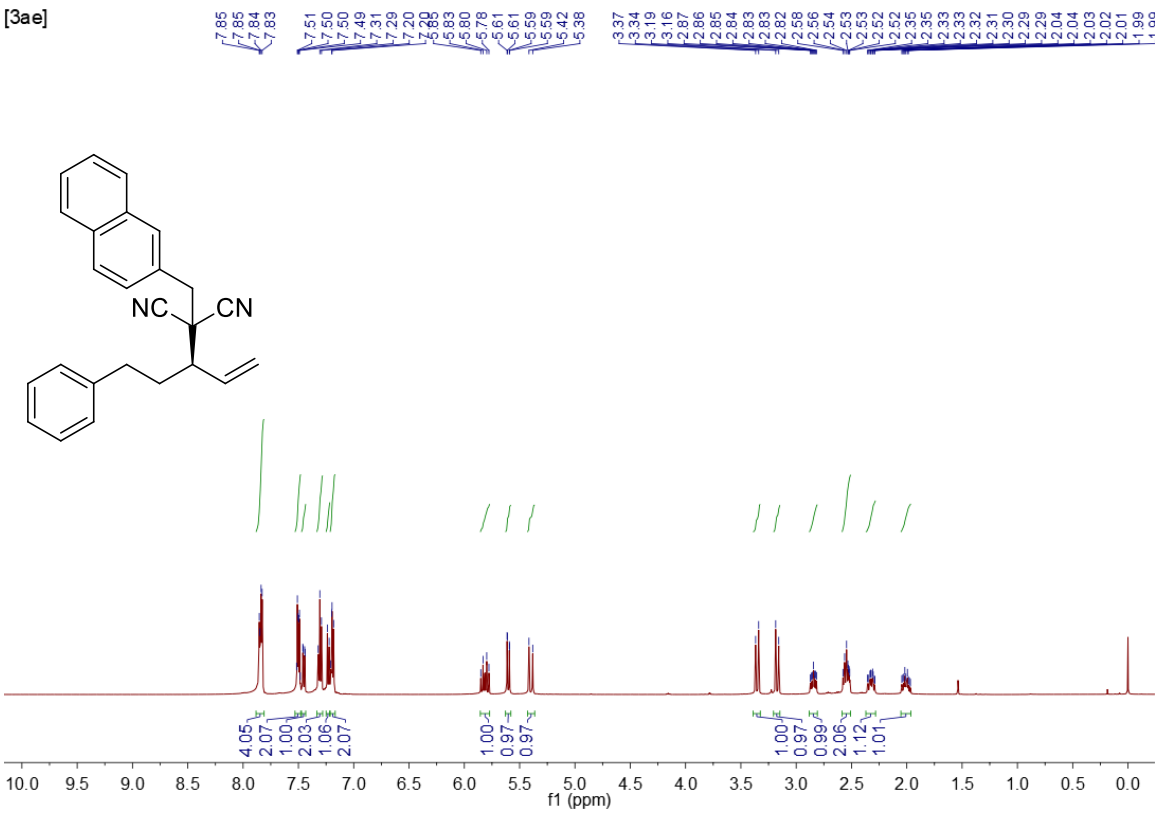
126 MHz, $CDCl_3$

[3ad]



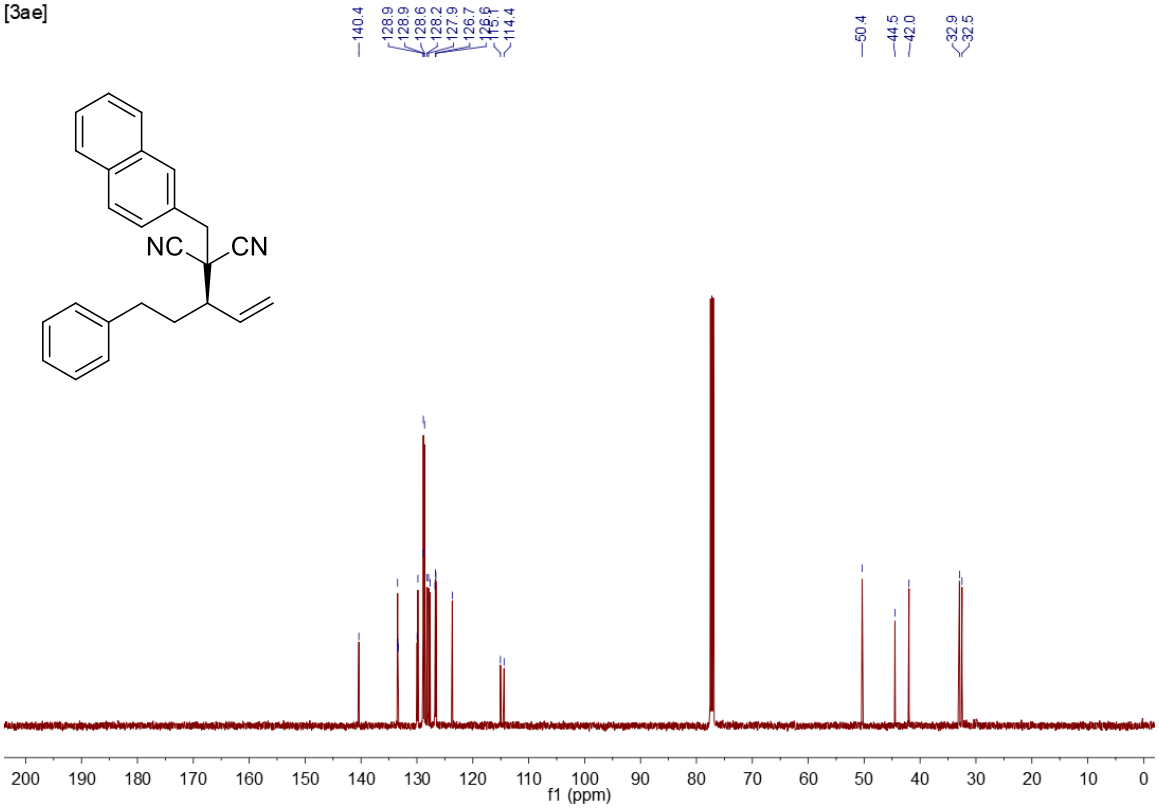
500 MHz, $CDCl_3$

[3ae]



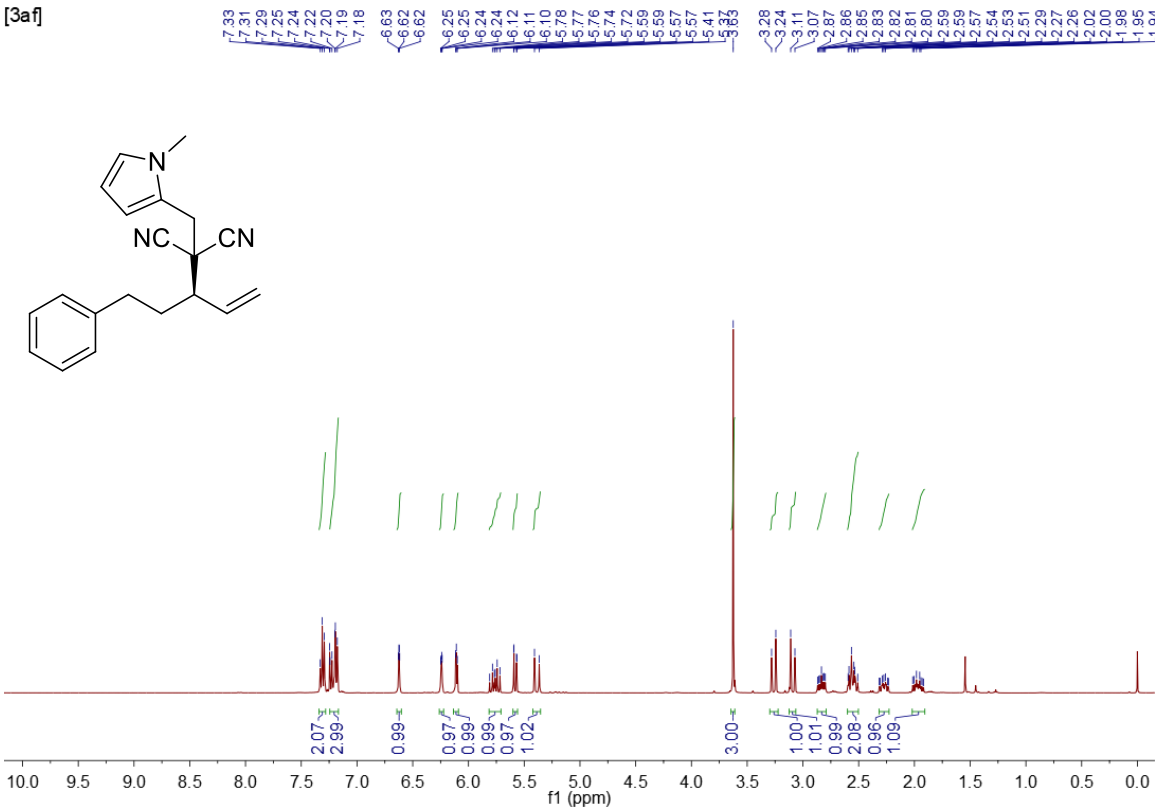
126 MHz, $CDCl_3$

[3ae]



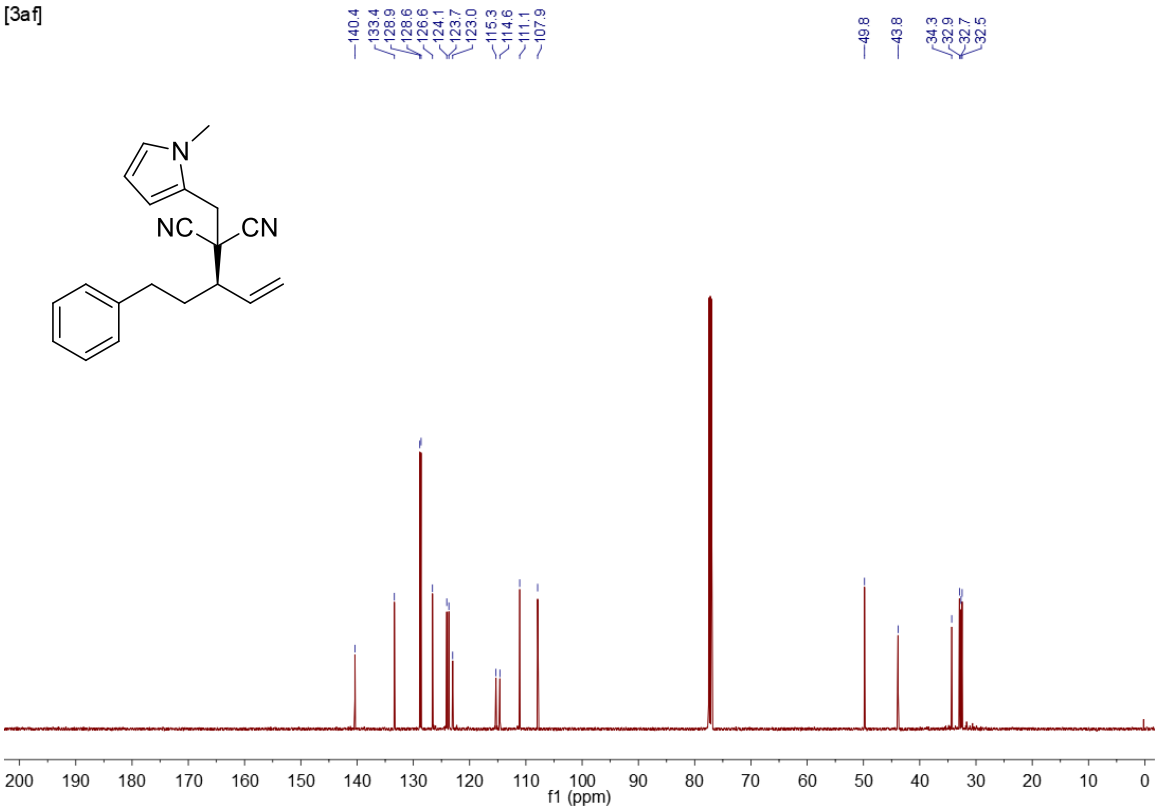
400 MHz, $CDCl_3$

[3af]



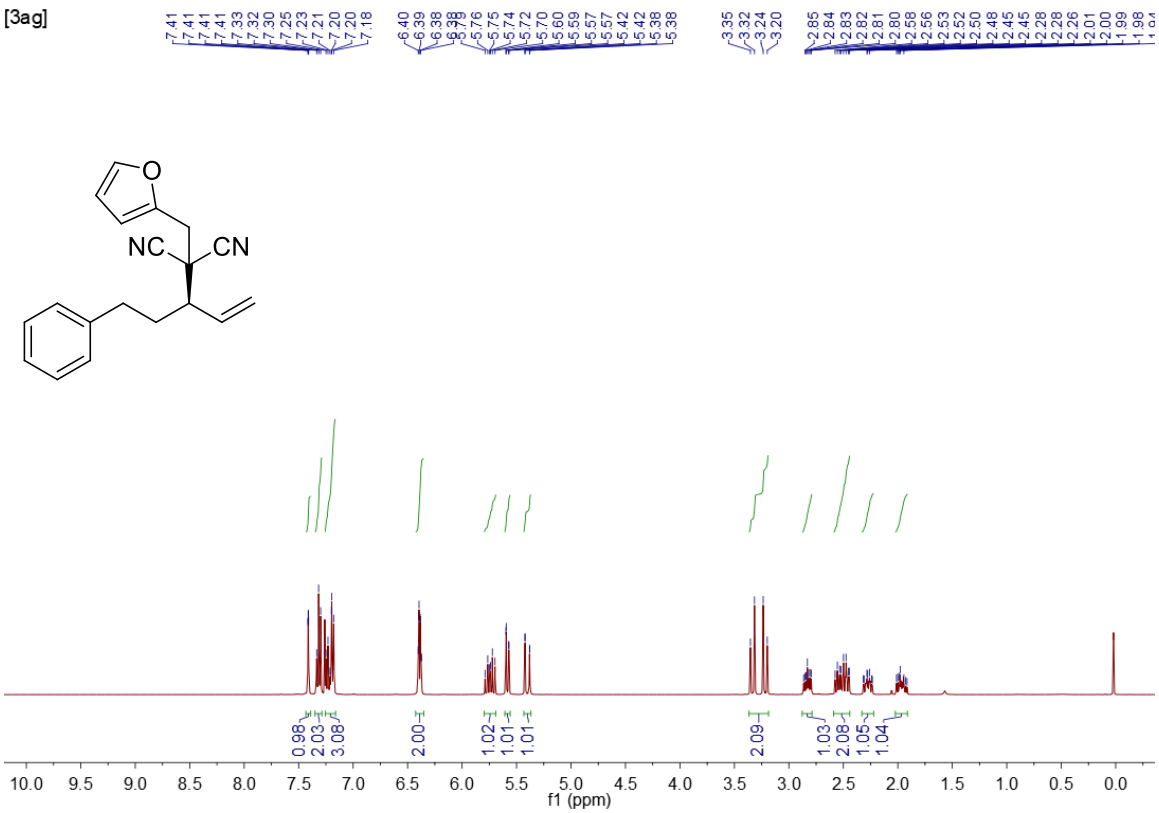
126 MHz, $CDCl_3$

[3af]



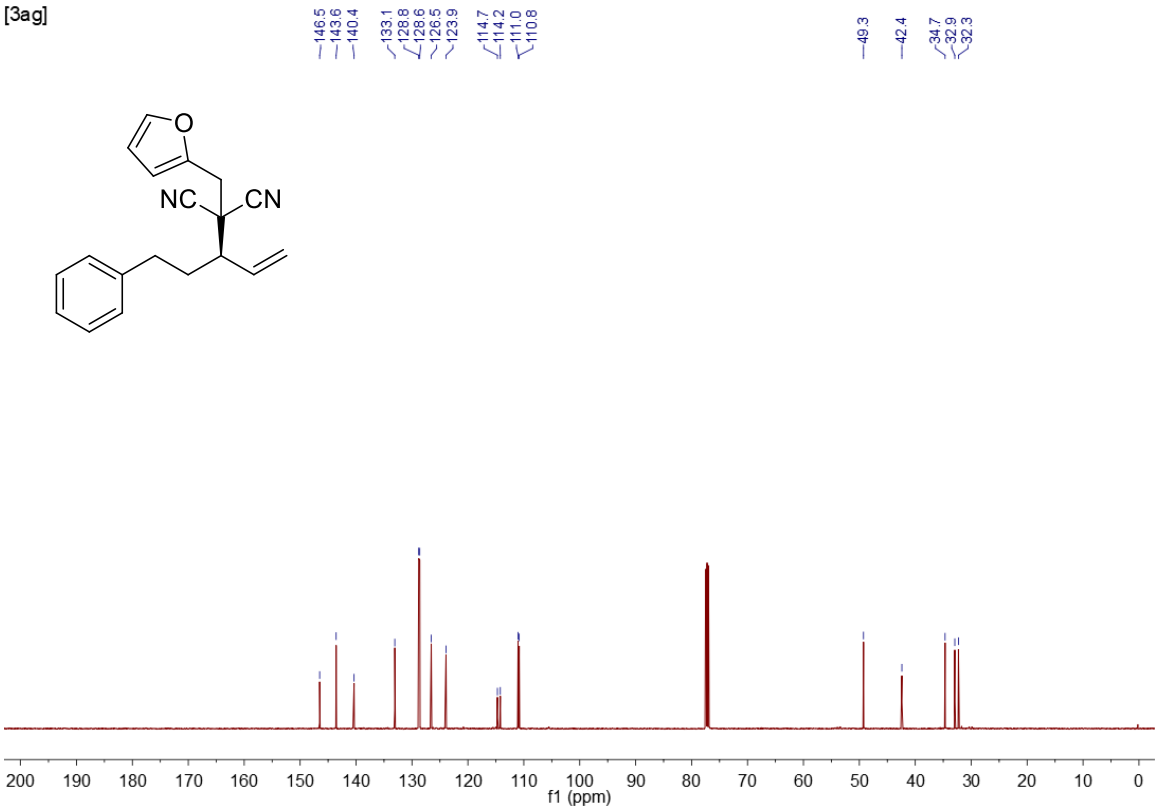
400 MHz, $CDCl_3$

[3ag]



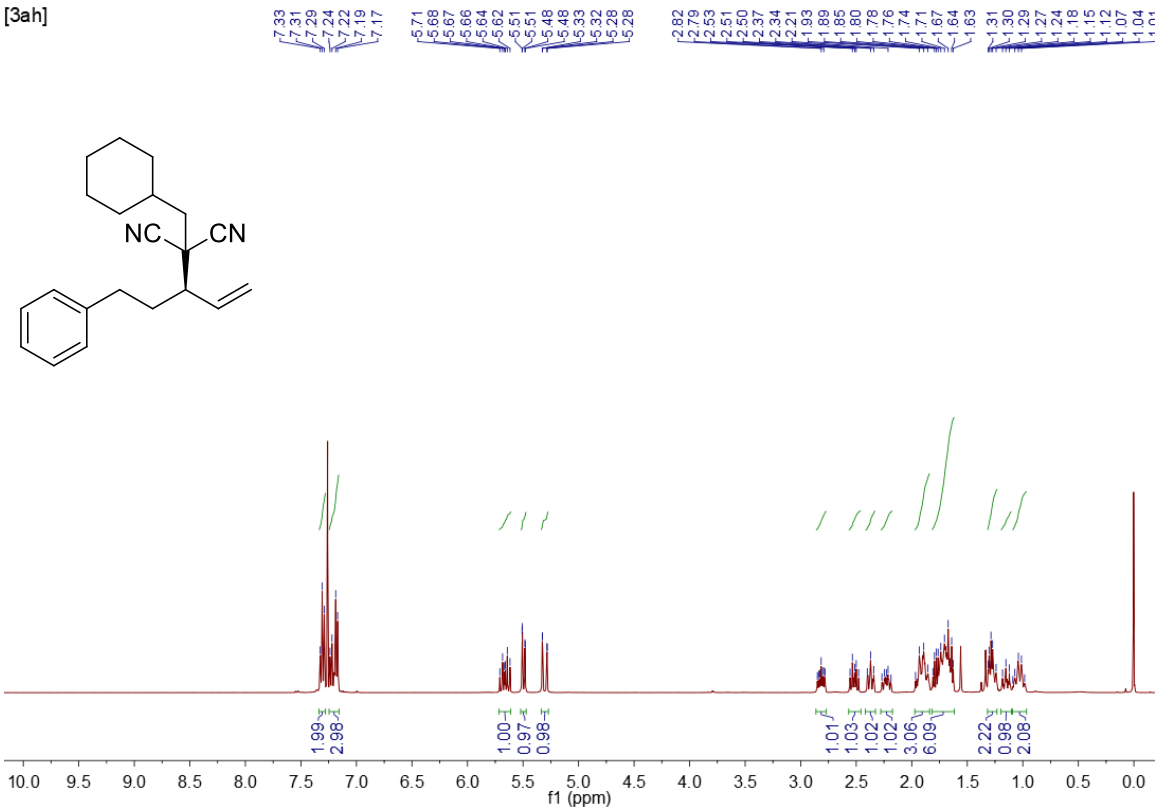
126 MHz, $CDCl_3$

[3ag]



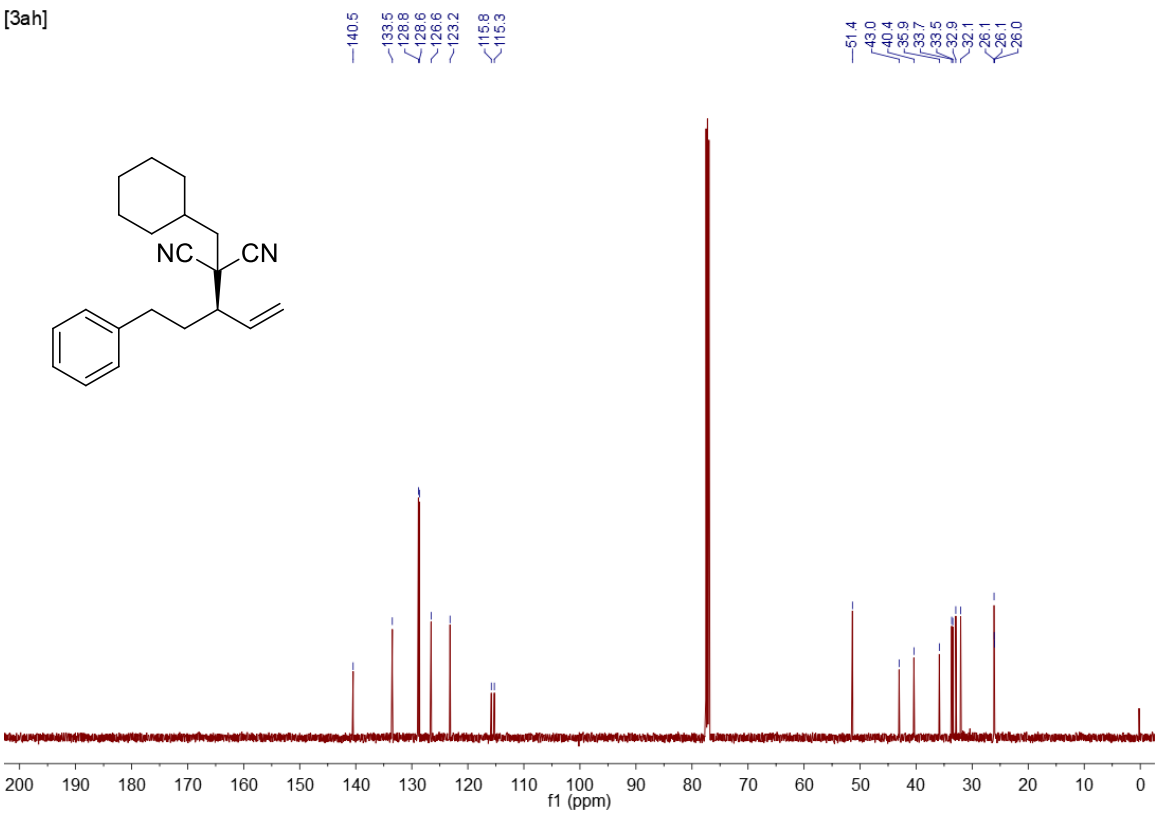
400 MHz, $CDCl_3$

[3ah]



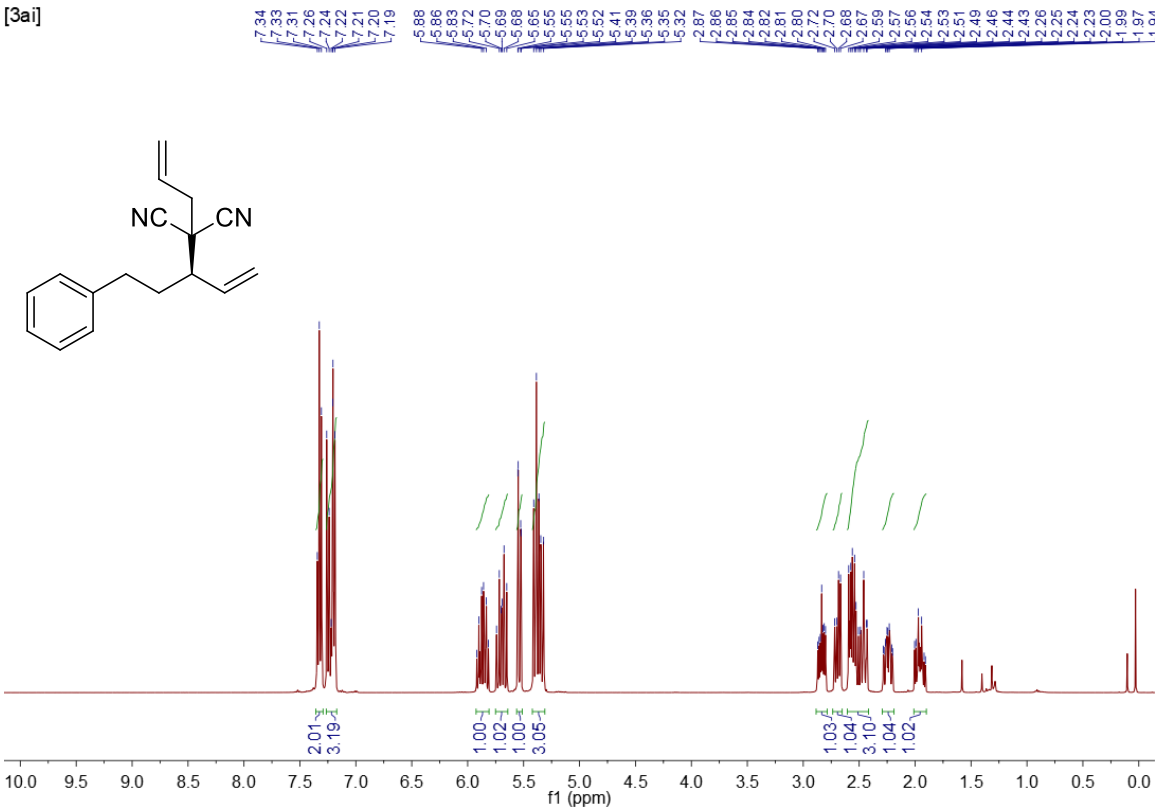
126 MHz, $CDCl_3$

[3ah]



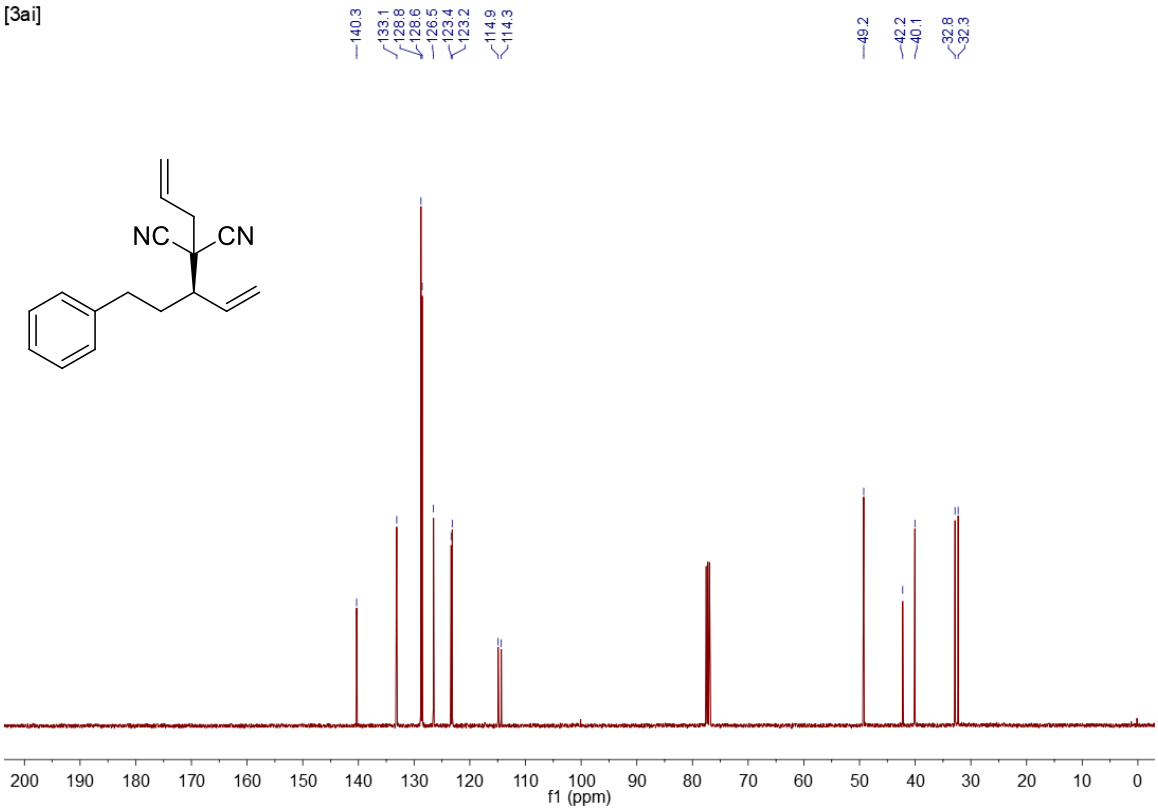
400 MHz, $CDCl_3$

[3ai]



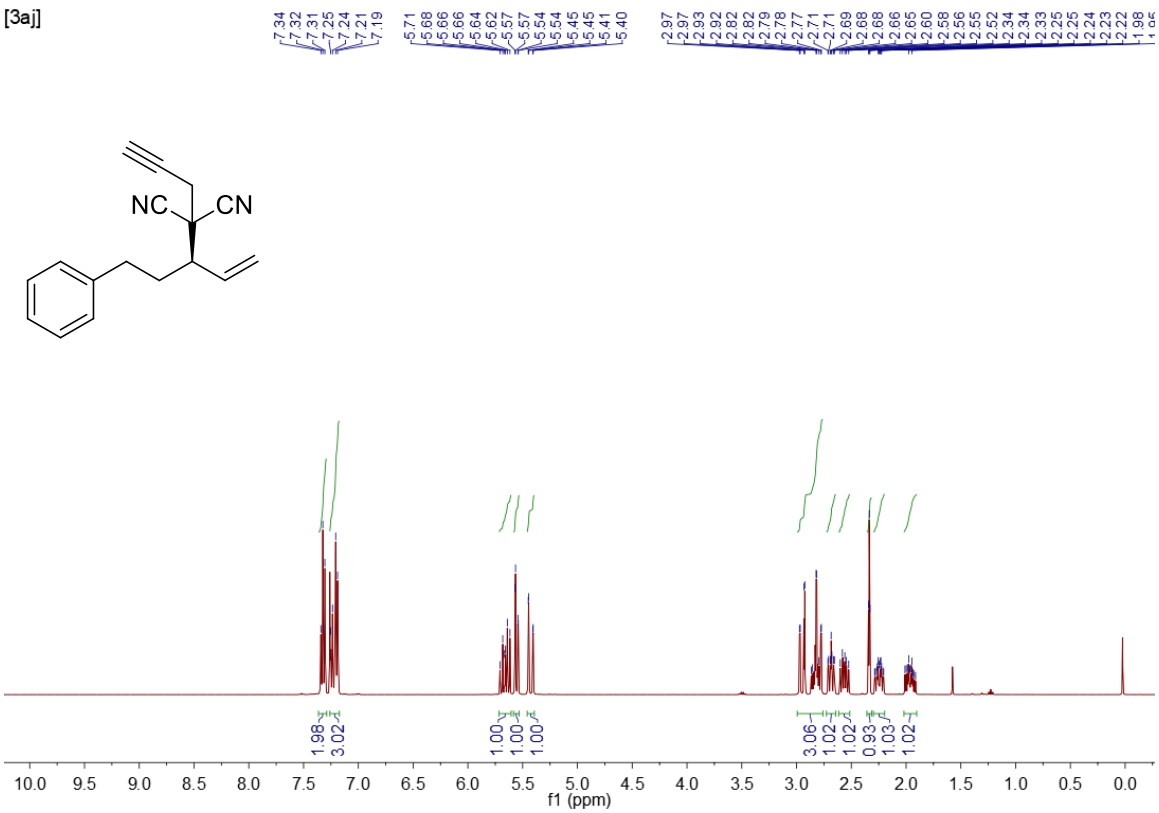
101 MHz, $CDCl_3$

[3ai]



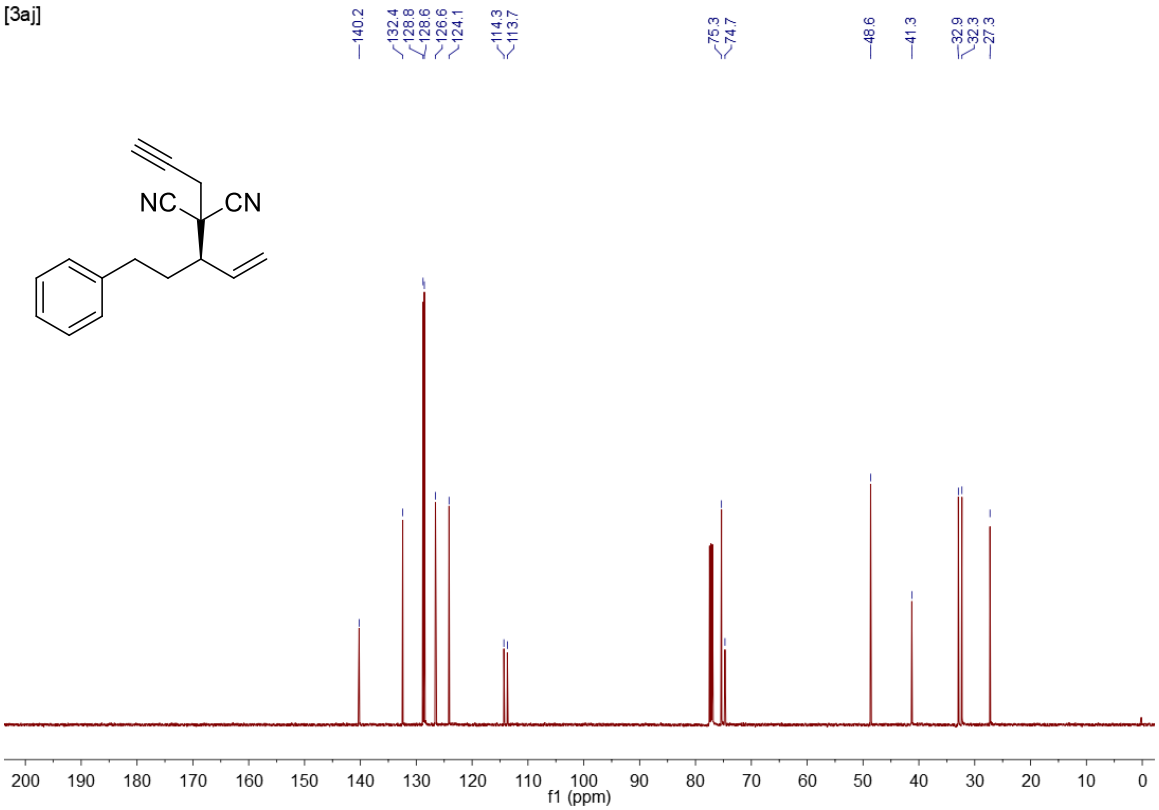
400 MHz, $CDCl_3$

[3aj]



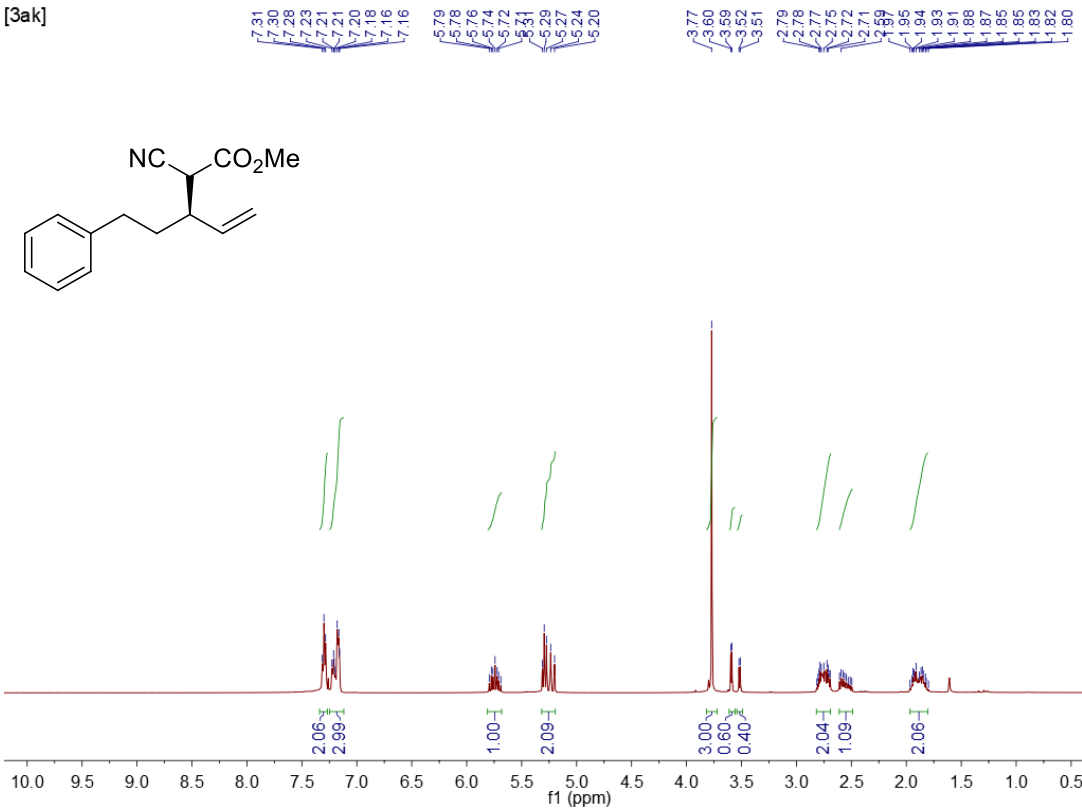
126 MHz, $CDCl_3$

[3aj]



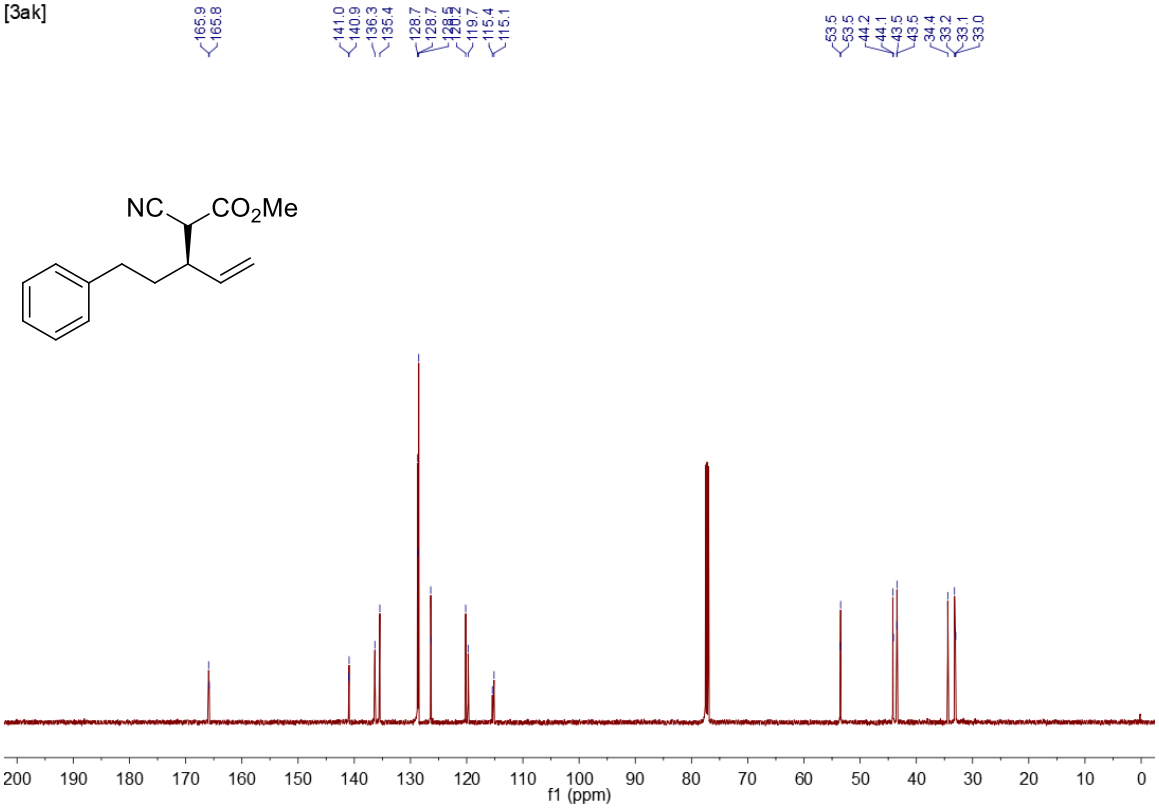
500 MHz, $CDCl_3$

[3ak]



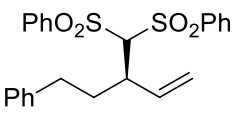
126 MHz, $CDCl_3$

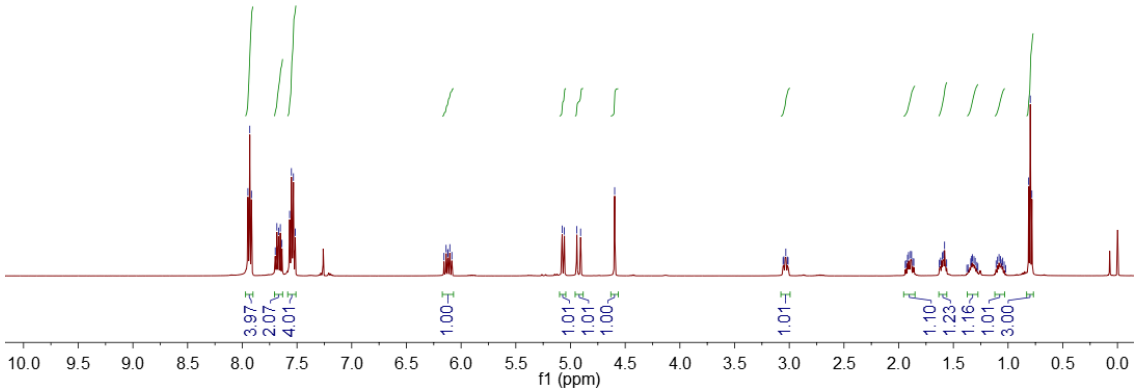
[3ak]



500 MHz, $CDCl_3$

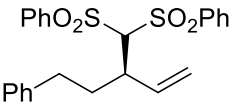
[3al]

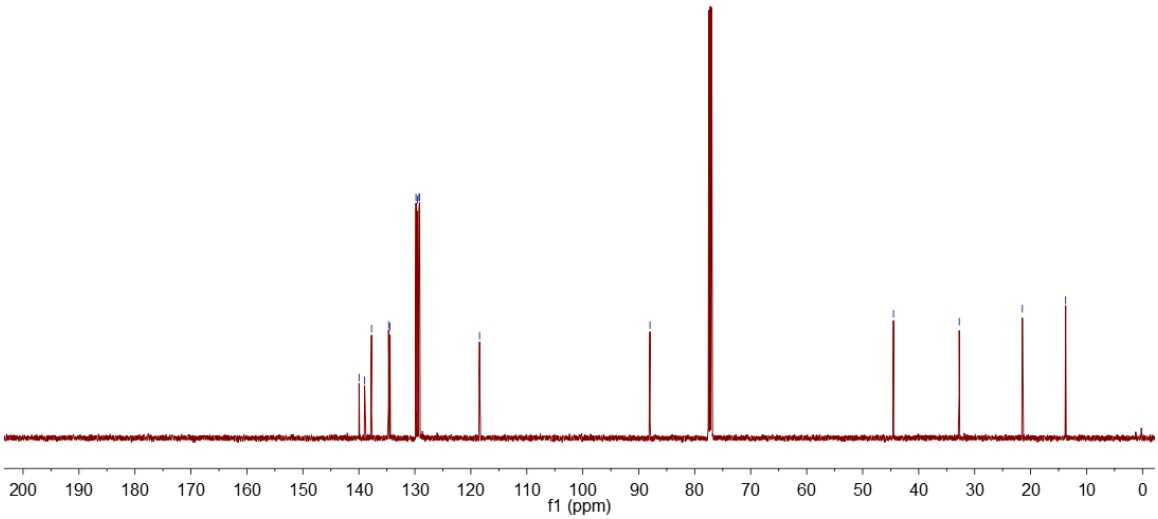




126 MHz, $CDCl_3$

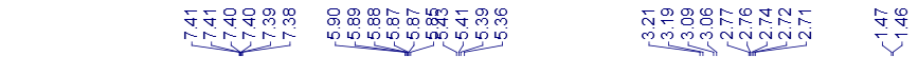
[3al]

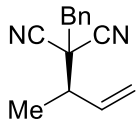


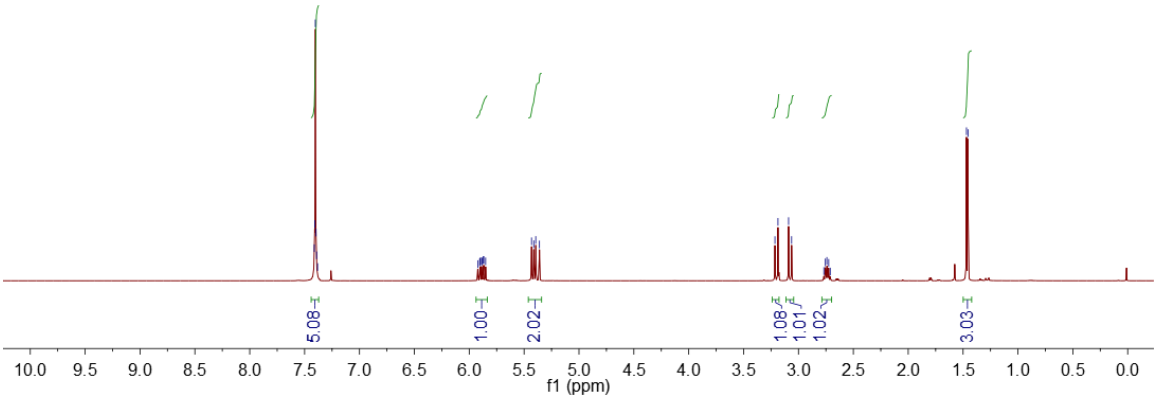


500 MHz, $CDCl_3$

[3bb]

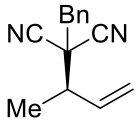


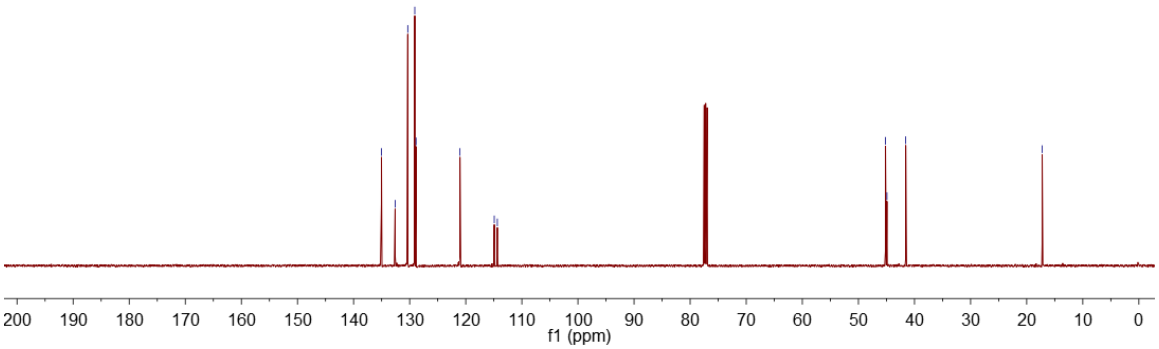




126 MHz, $CDCl_3$

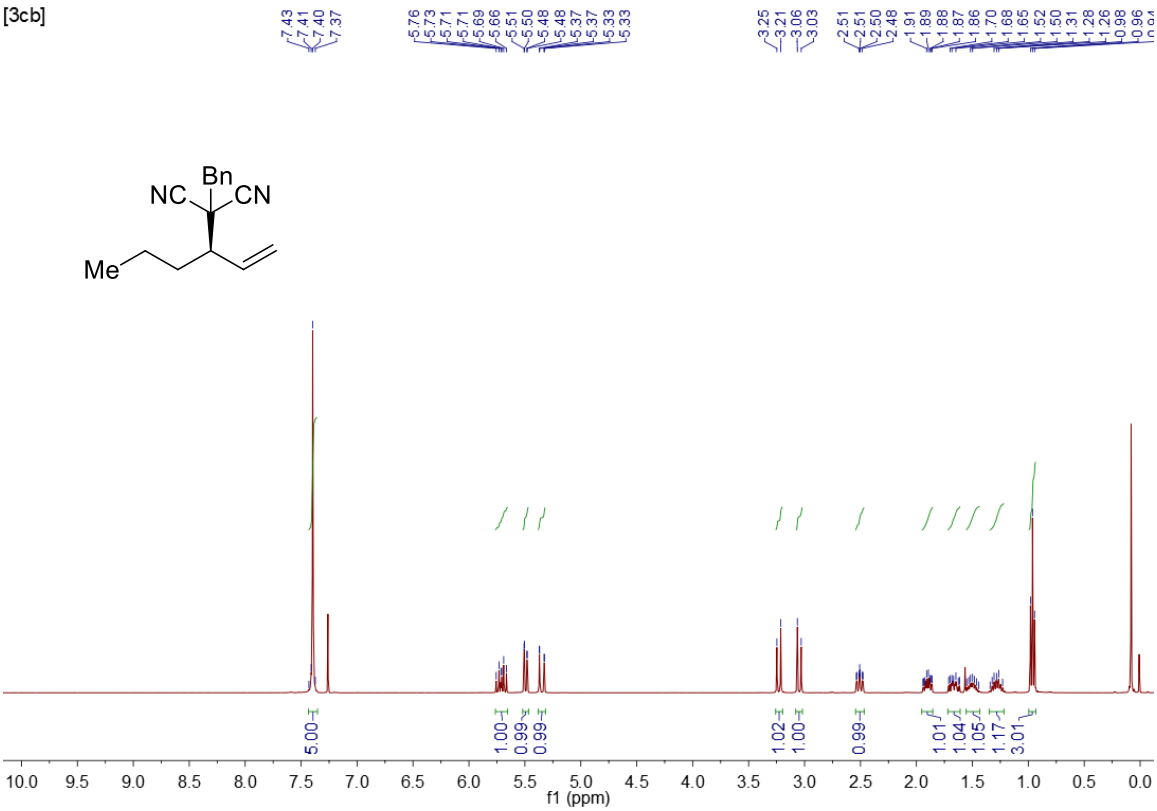
[3bb]





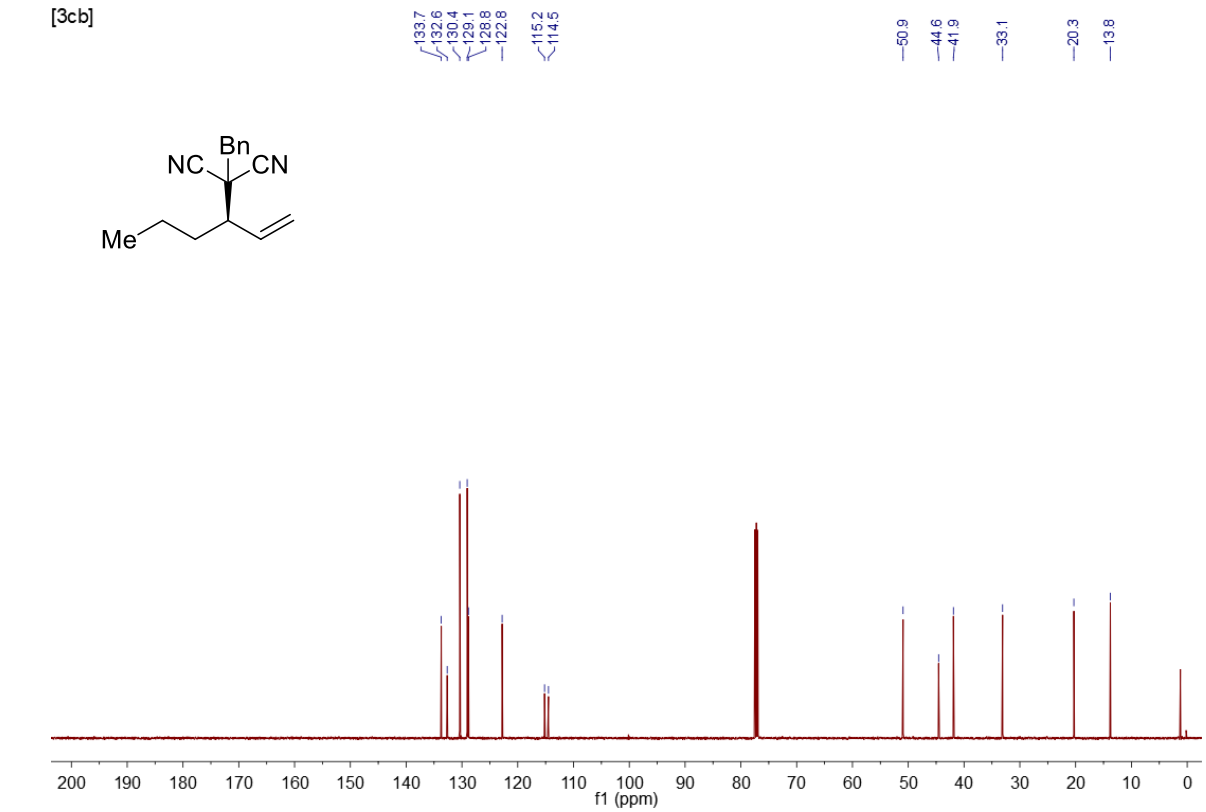
400 MHz, $CDCl_3$

[3cb]

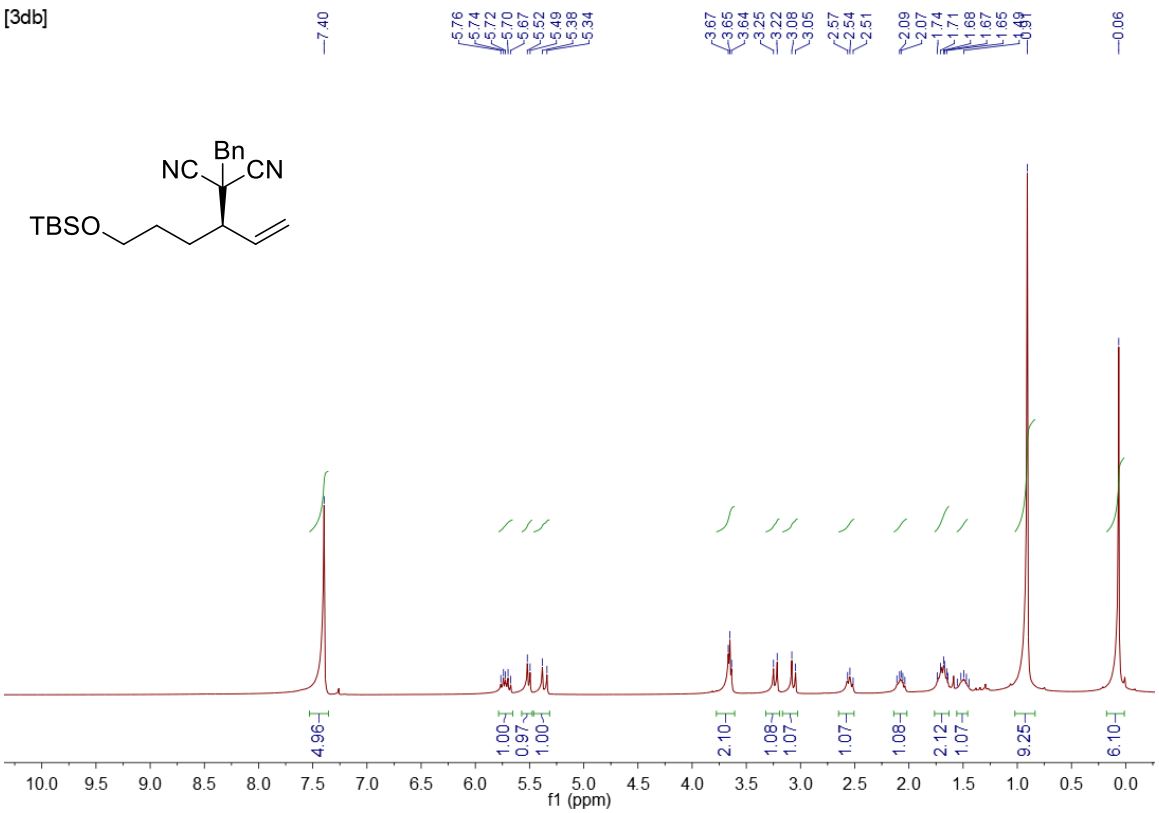


126 MHz, $CDCl_3$

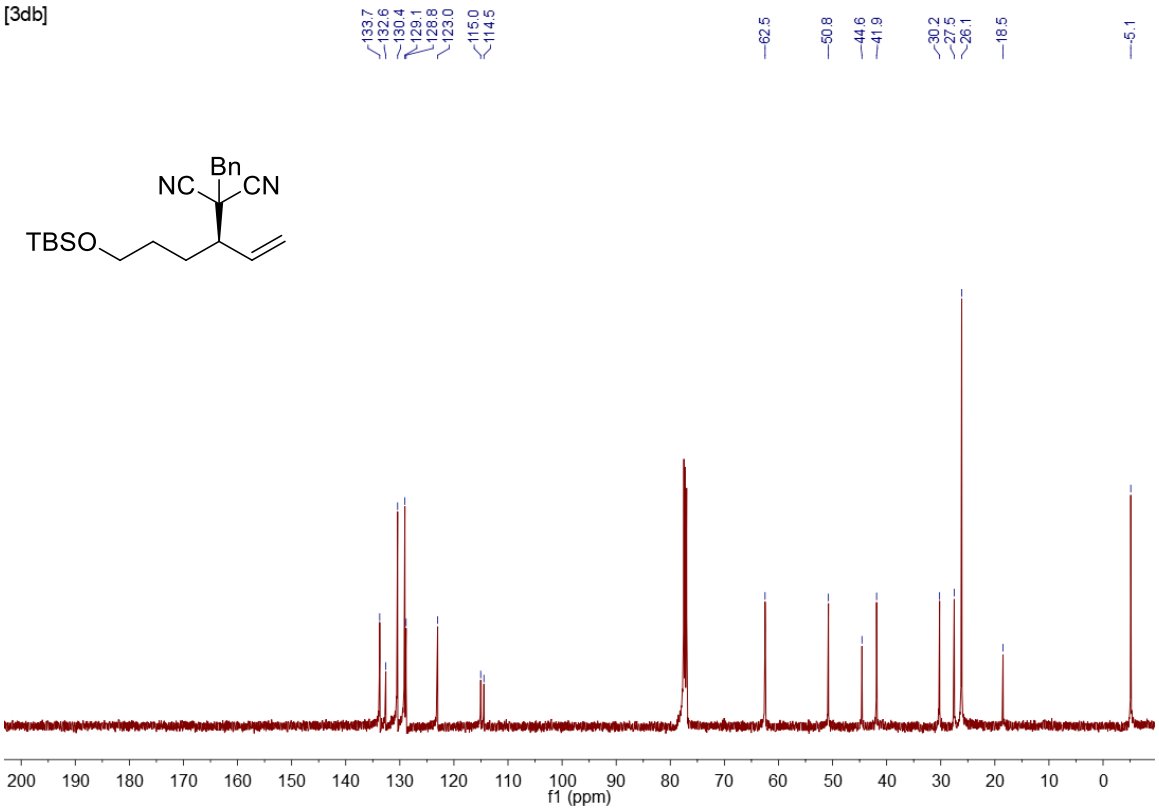
[3cb]



400 MHz, $CDCl_3$

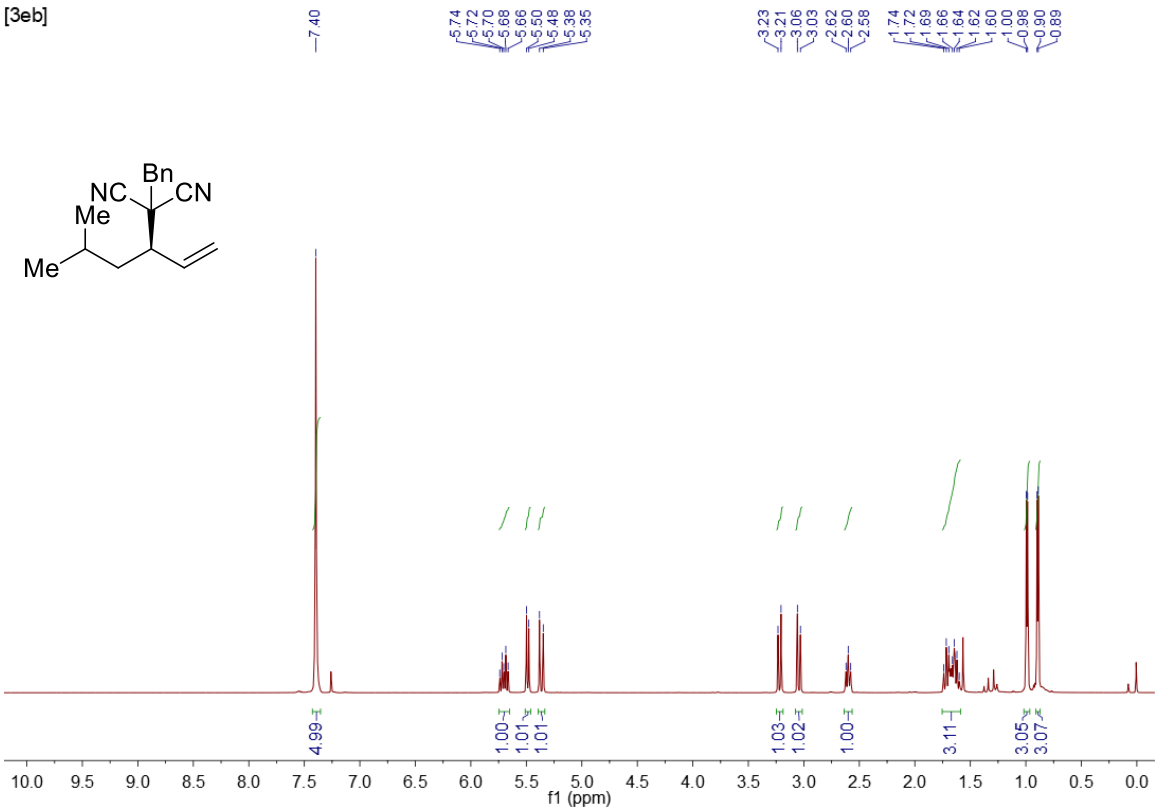


126 MHz, $CDCl_3$



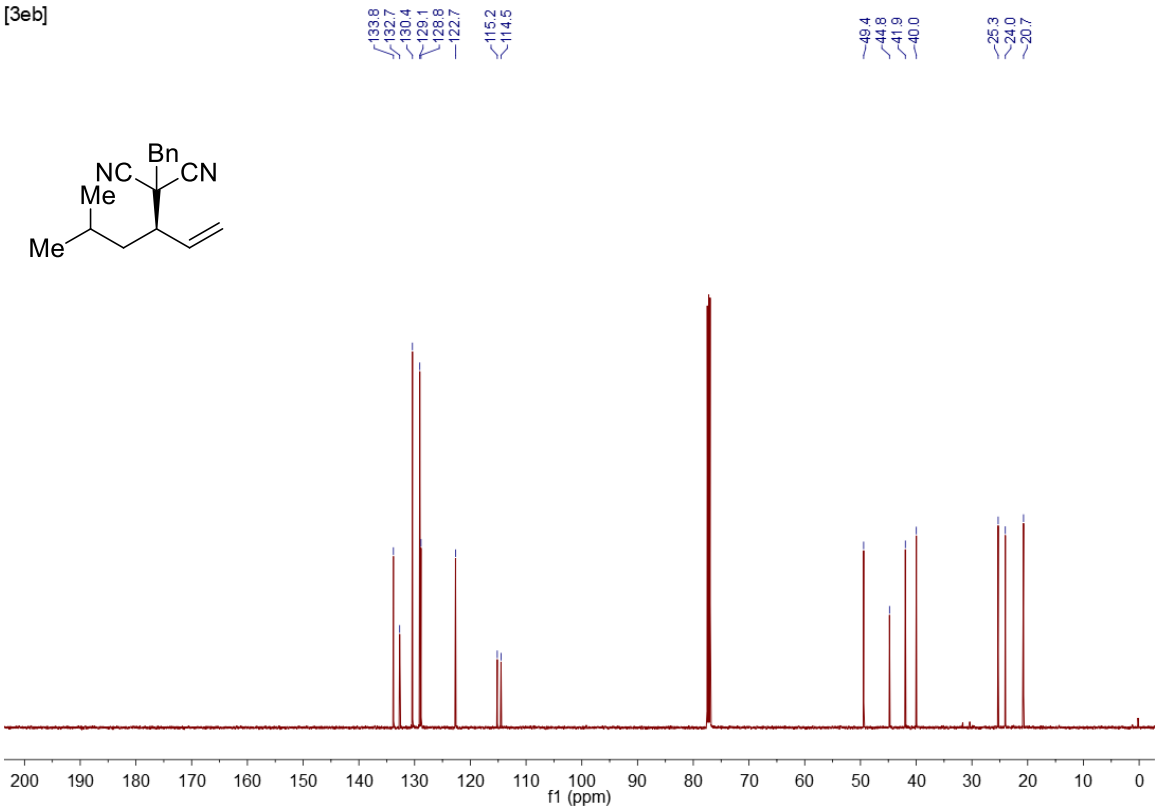
500 MHz, $CDCl_3$

[3eb]



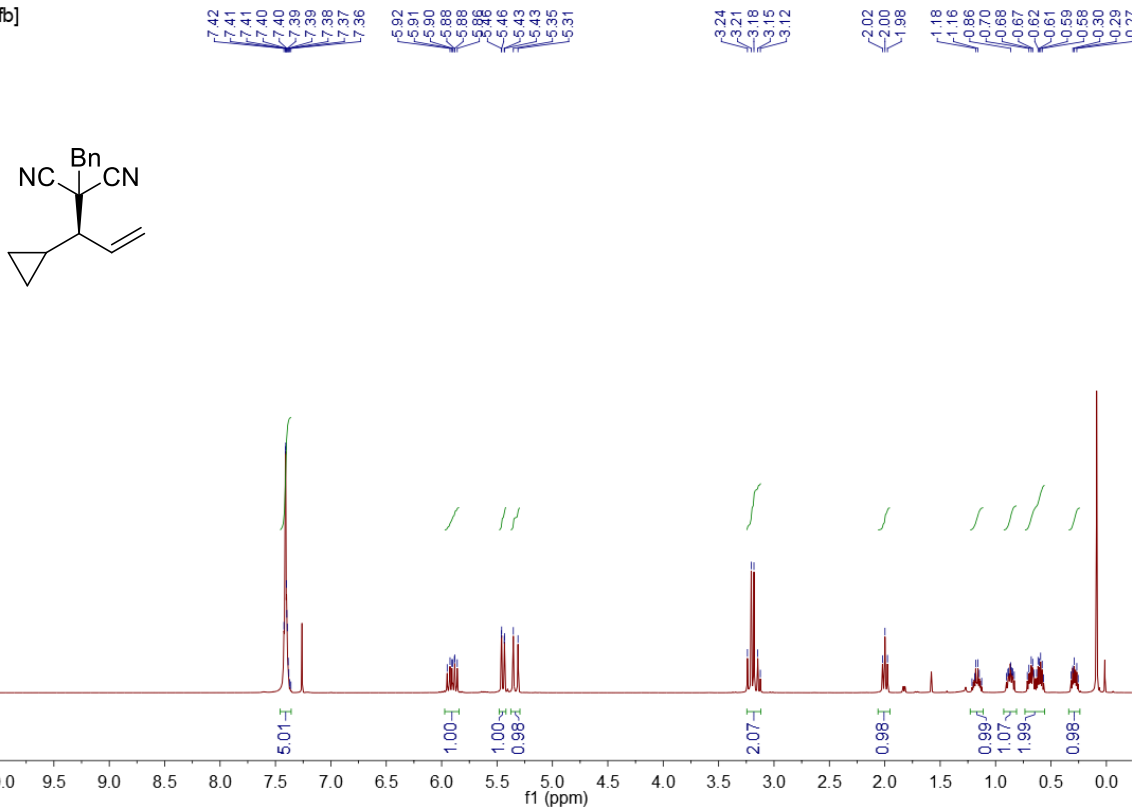
126 MHz, $CDCl_3$

[3eb]



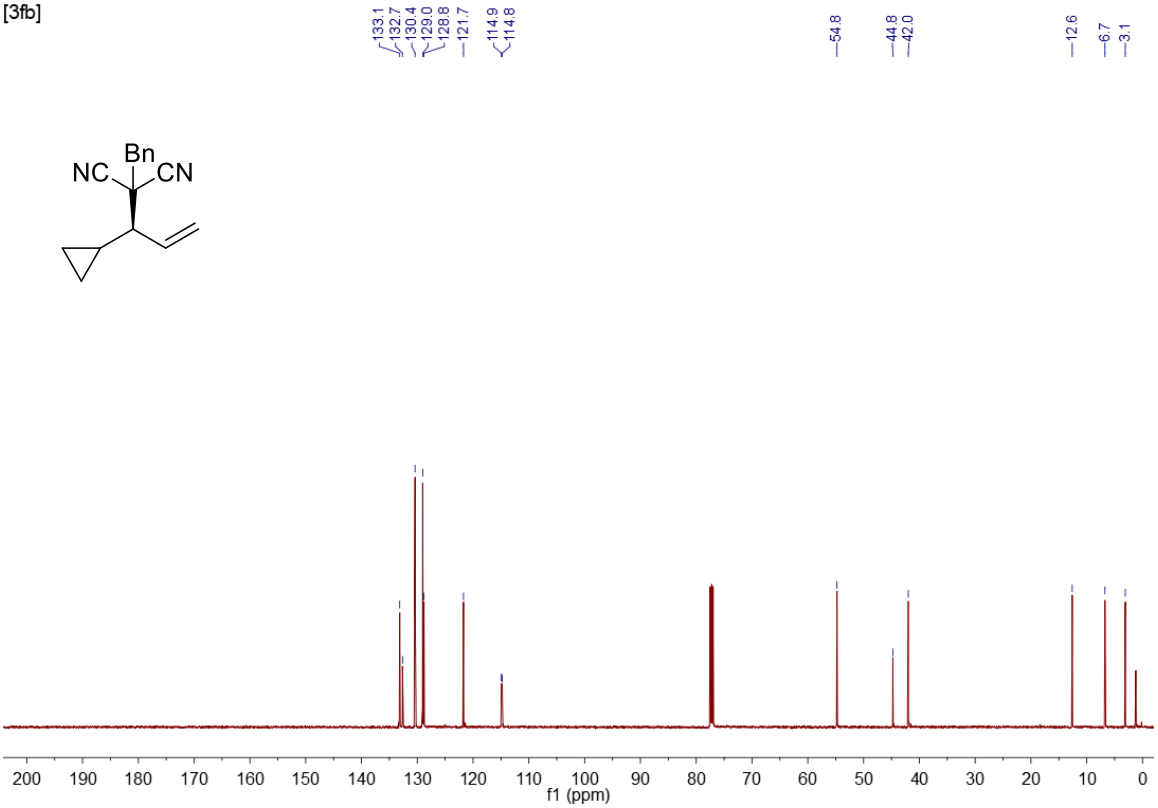
400 MHz, $CDCl_3$

[3fb]



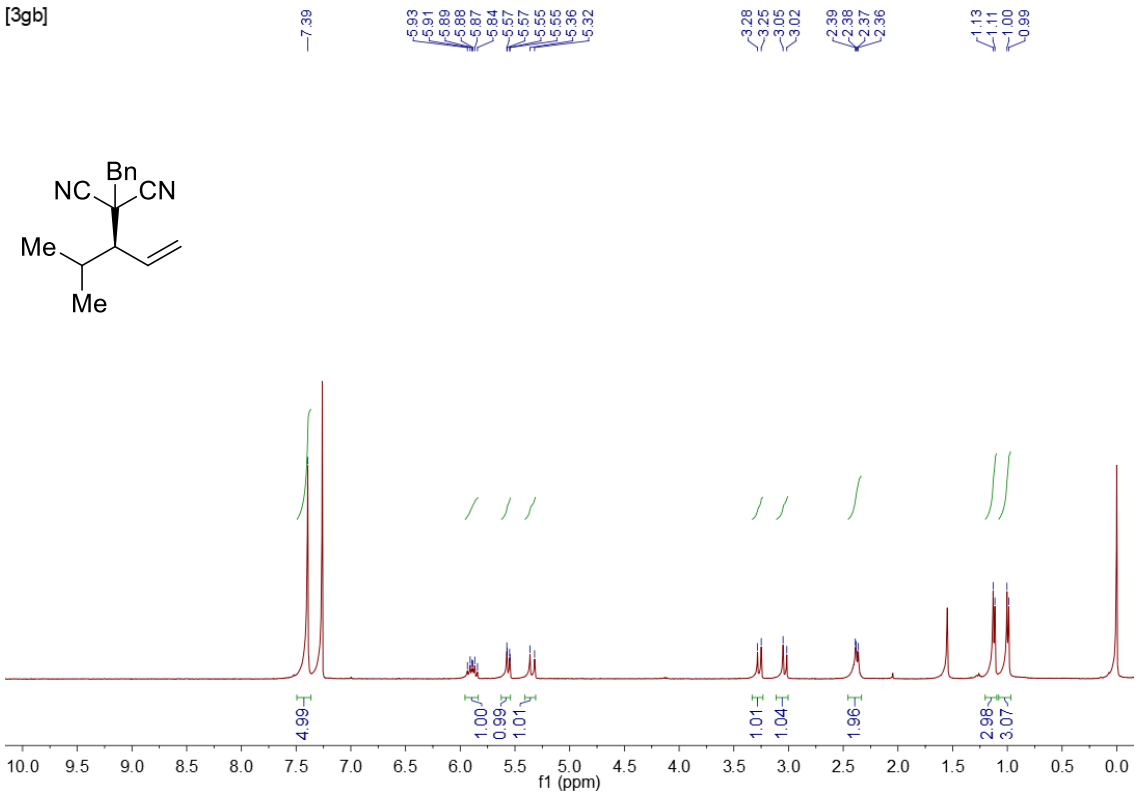
126 MHz, $CDCl_3$

[3fb]



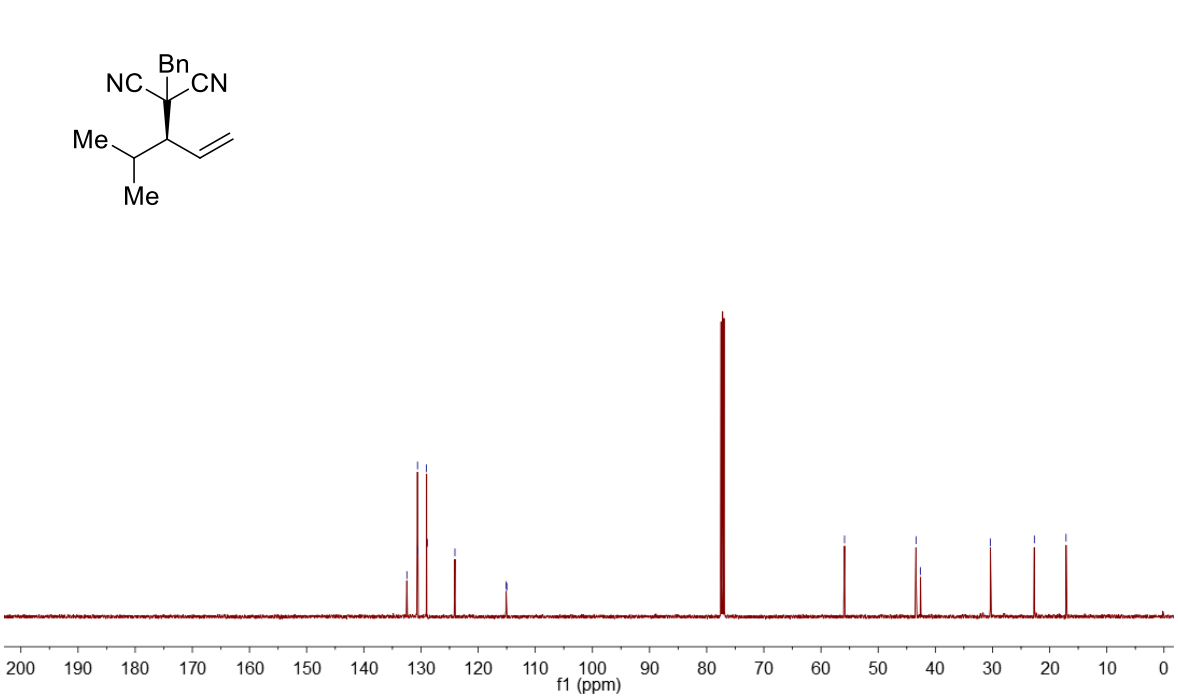
400 MHz, $CDCl_3$

[3gb]



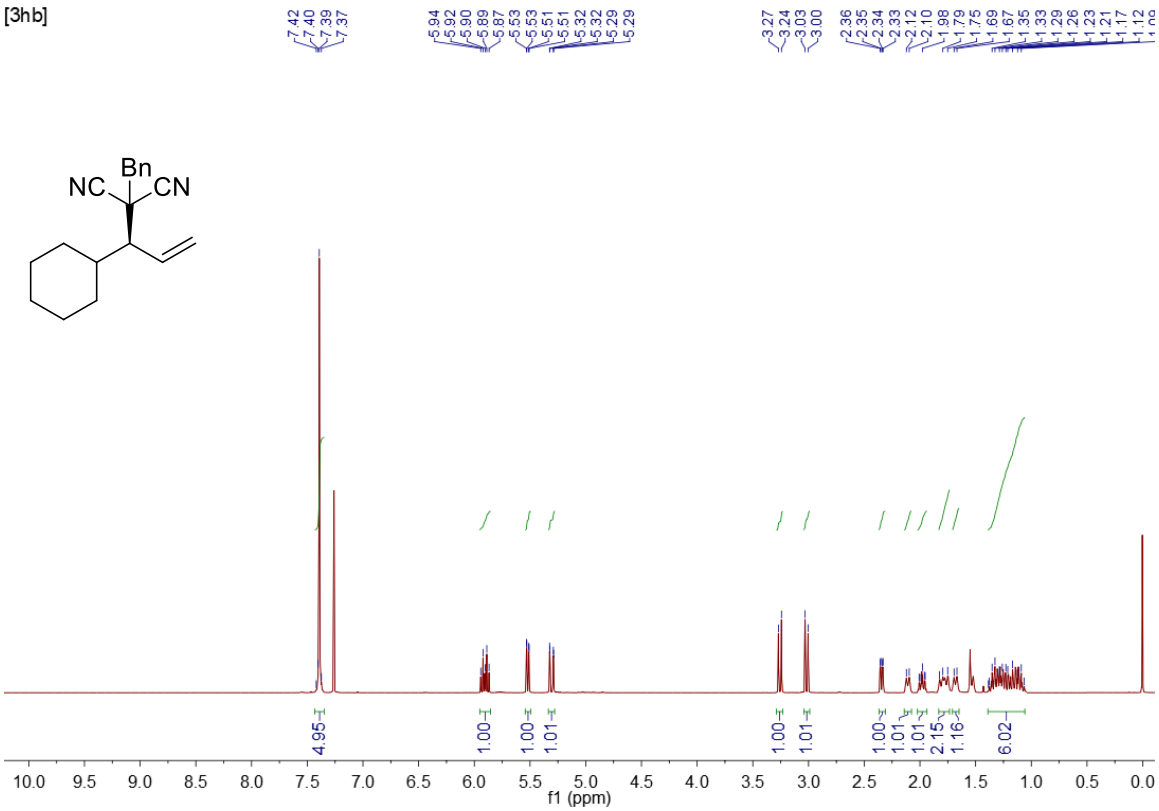
126 MHz, $CDCl_3$

[3gb]



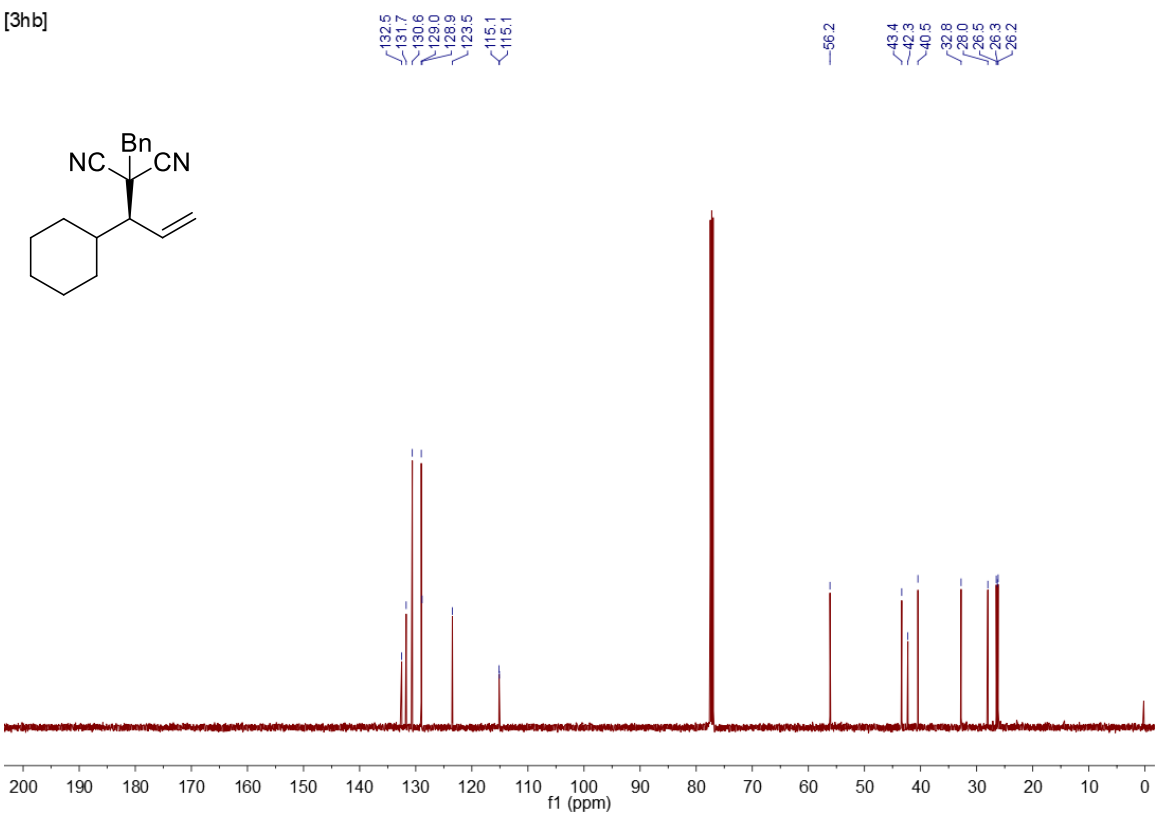
500 MHz, $CDCl_3$

[3hb]



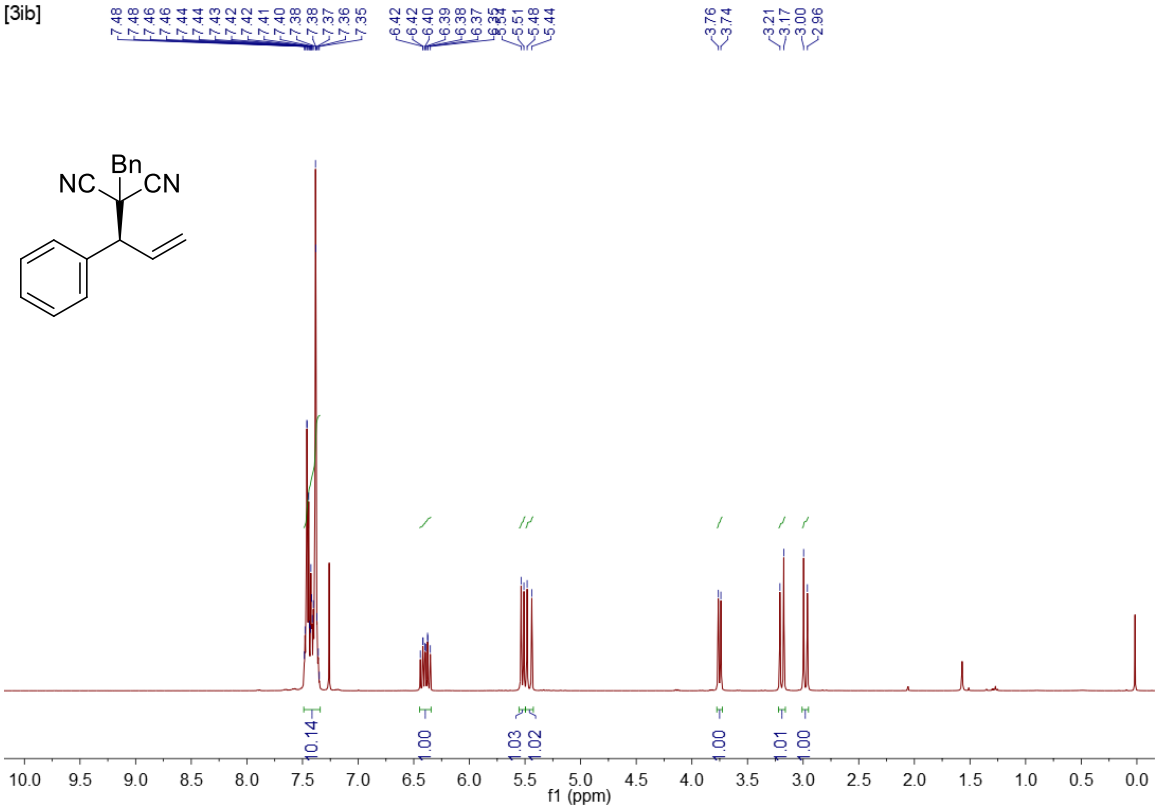
126 MHz, $CDCl_3$

[3hb]



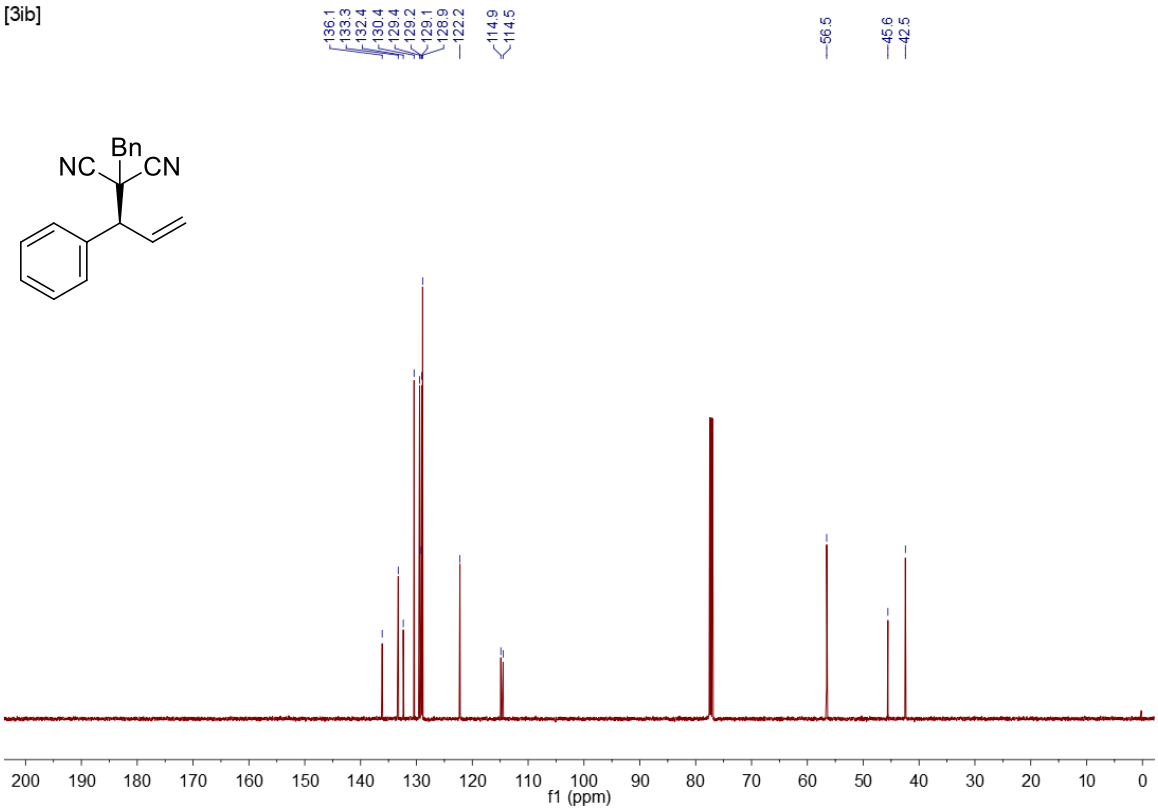
500 MHz, $CDCl_3$

[3ib]



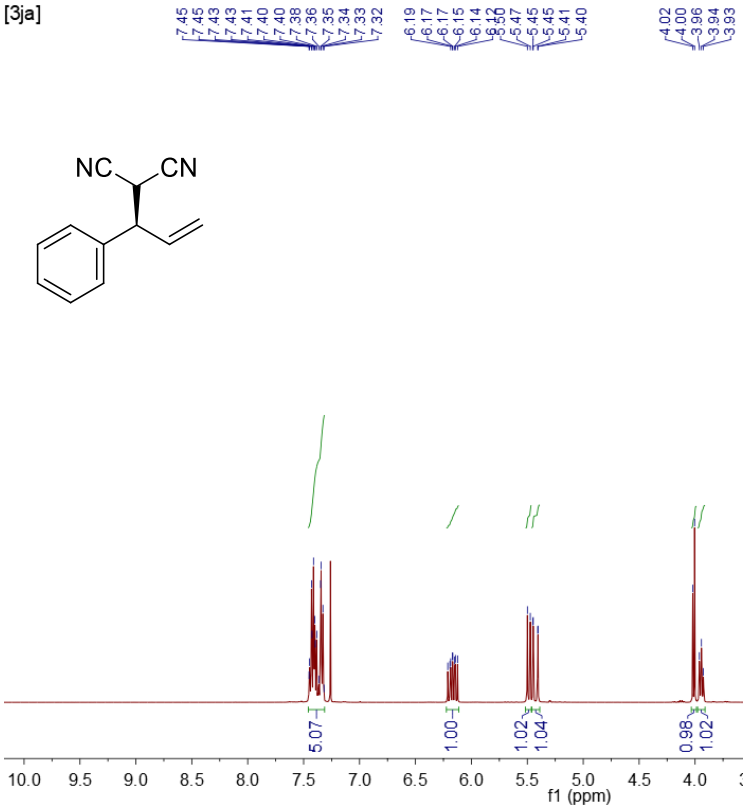
126 MHz, $CDCl_3$

[3ib]



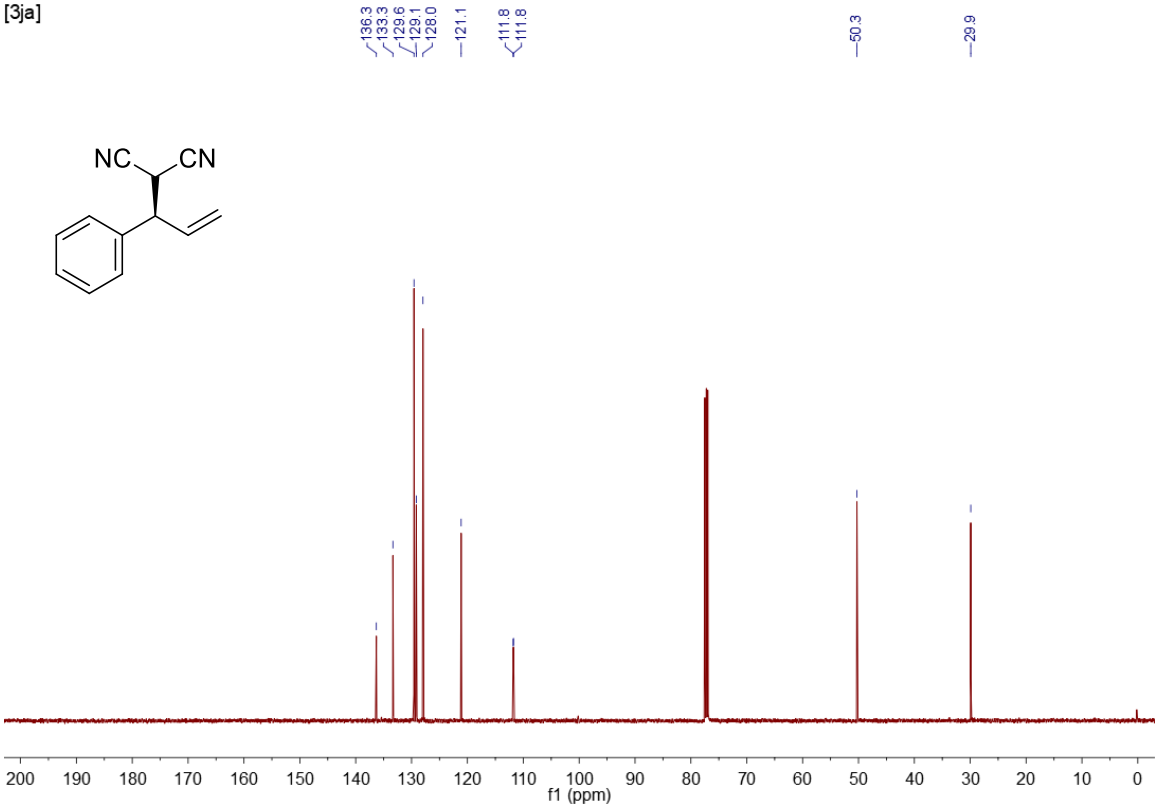
400 MHz, $CDCl_3$

[3ja]



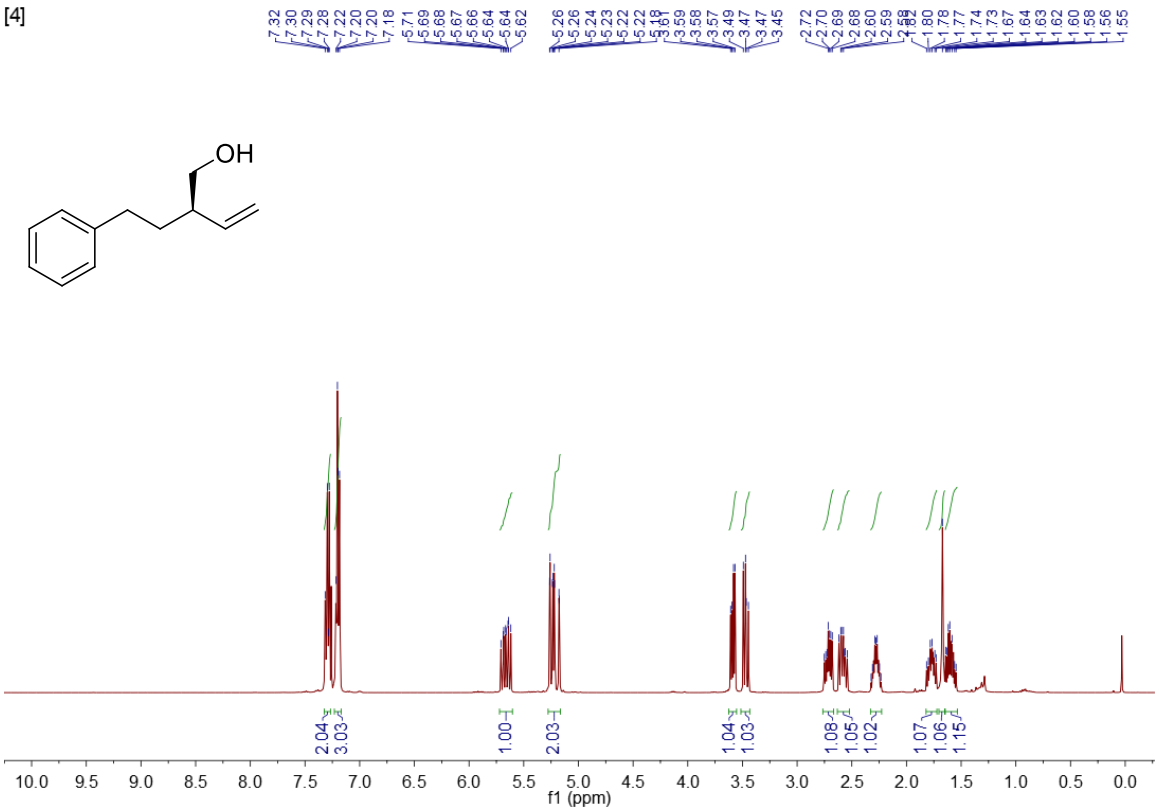
126 MHz, $CDCl_3$

[3ja]



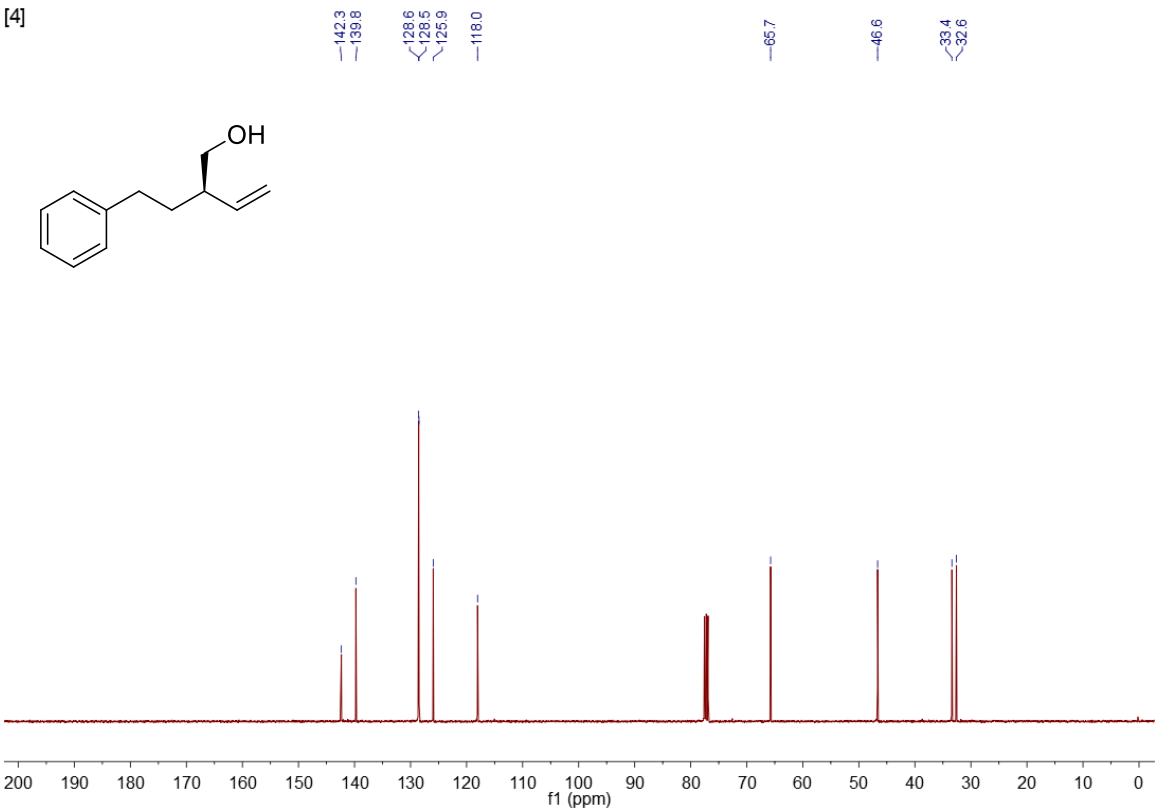
400 MHz, $CDCl_3$

[4]



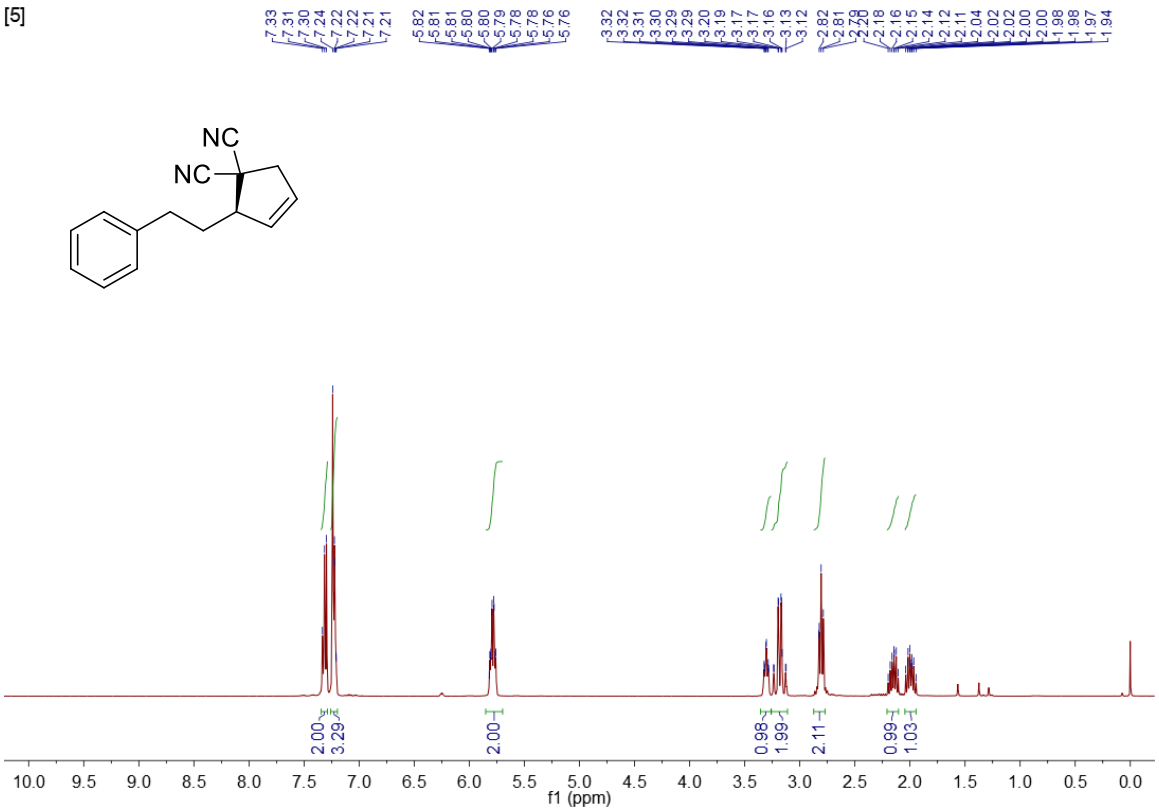
101 MHz, $CDCl_3$

[4]



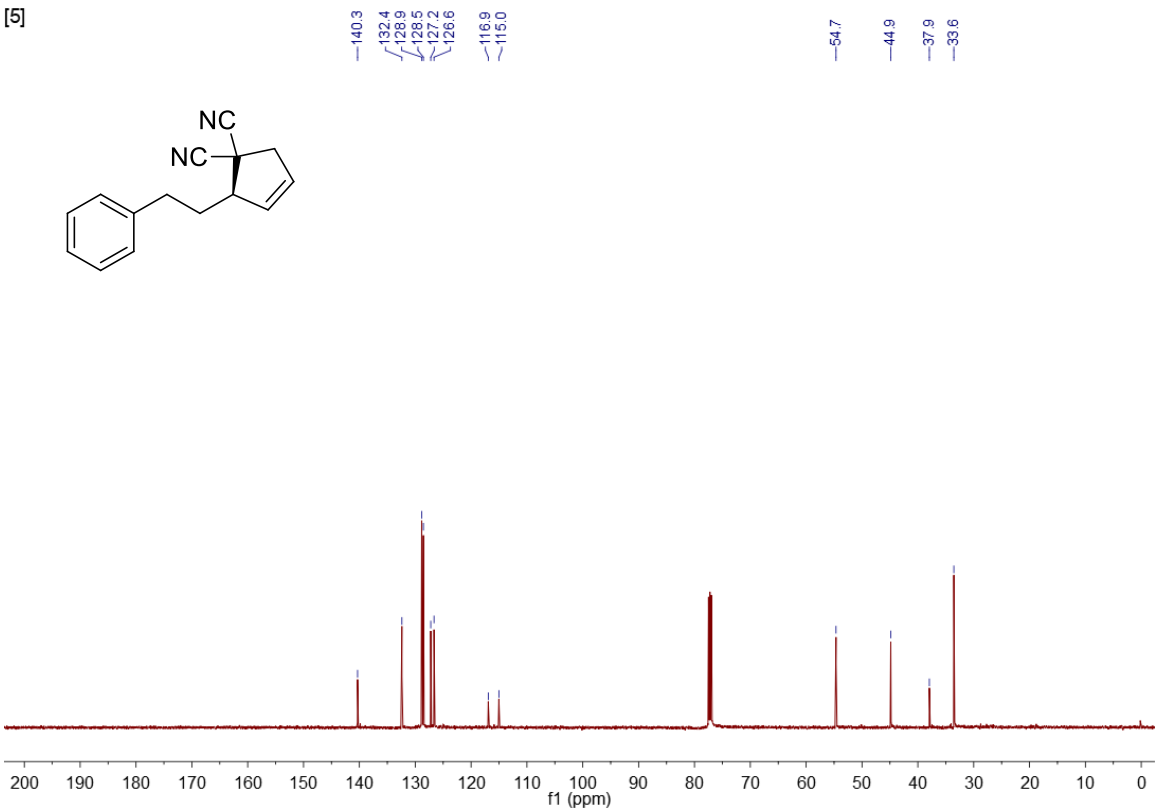
400 MHz, $CDCl_3$

[5]



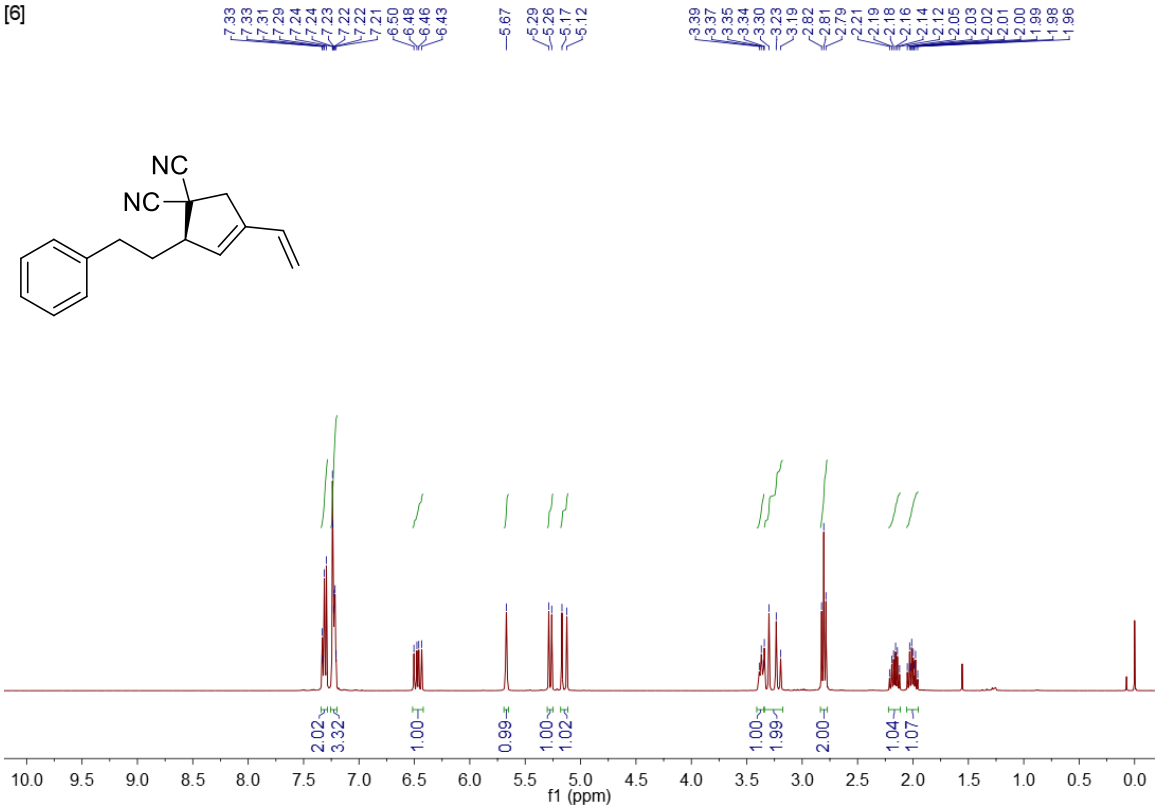
126 MHz, $CDCl_3$

[5]



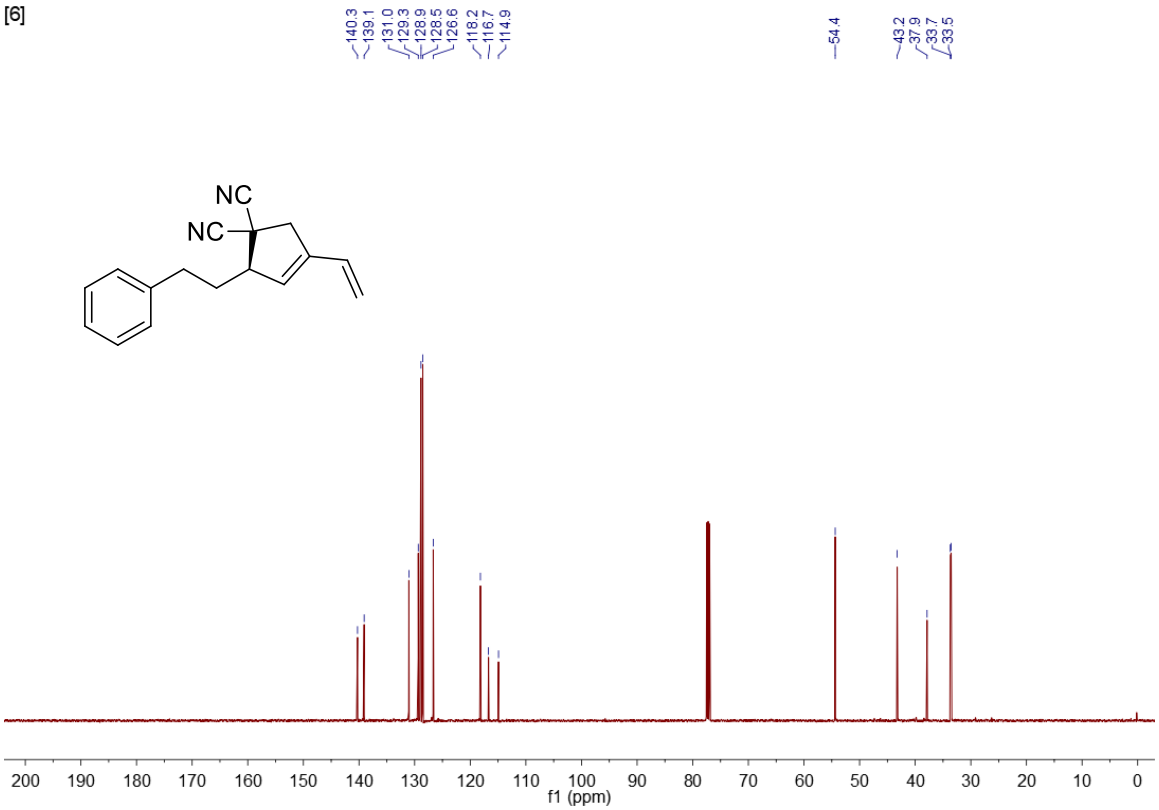
400 MHz, $CDCl_3$

[6]



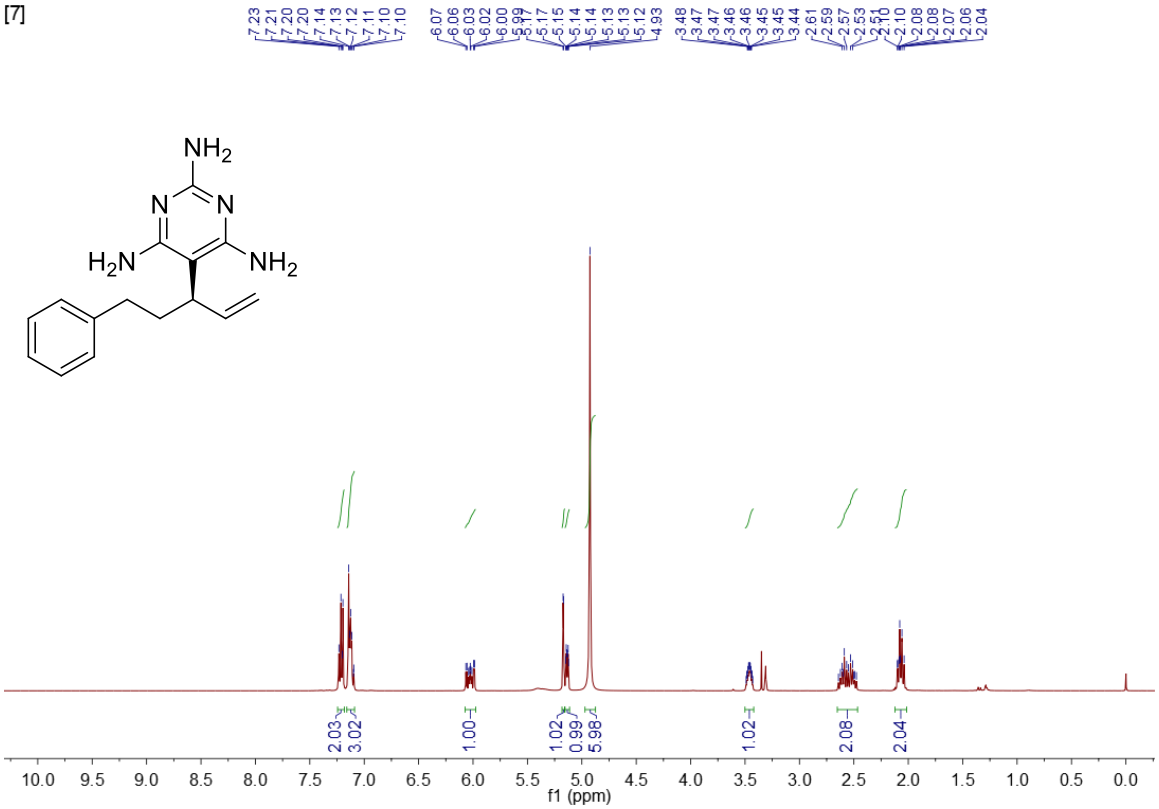
126 MHz, $CDCl_3$

[6]



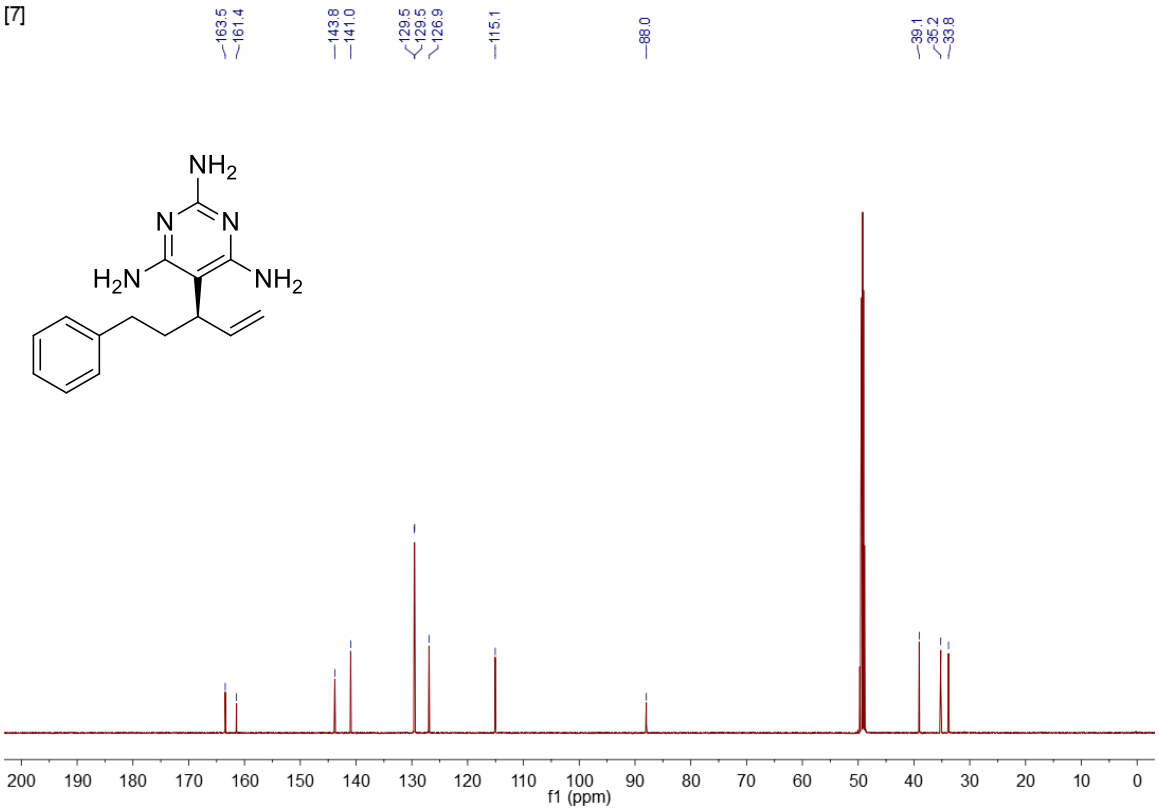
400 MHz, CD_3OD

[7]

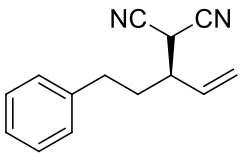


126 MHz, CD_3OD

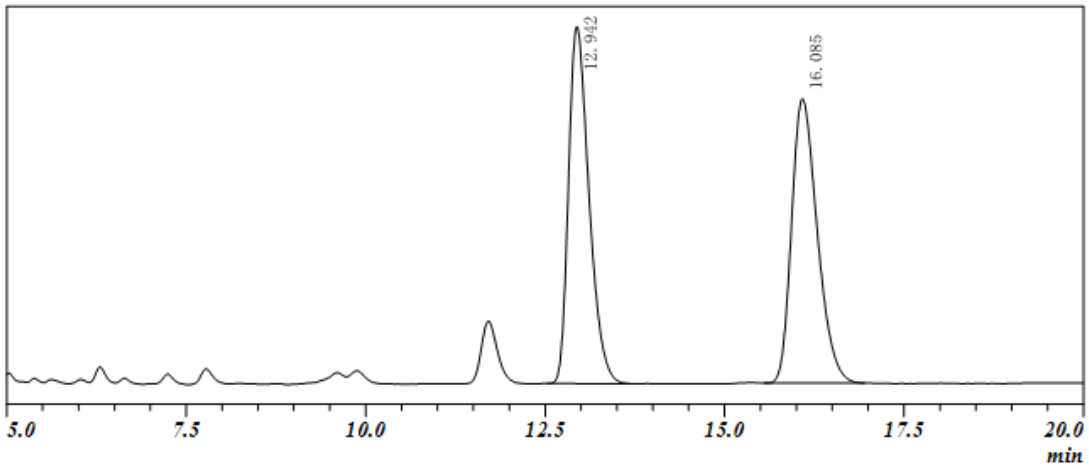
[7]



15. HPLC spectra of new compounds:



[3aa]

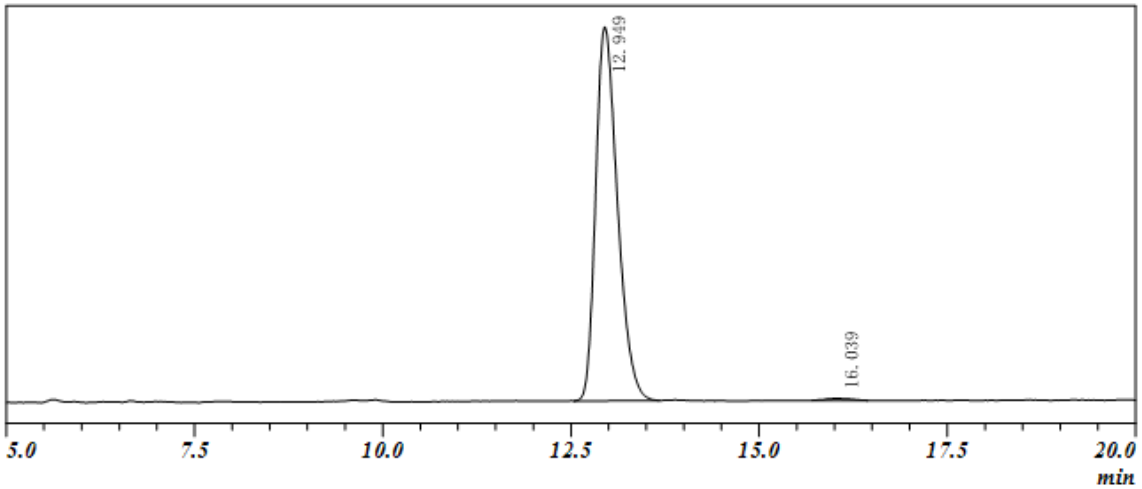


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	Retention time	Area	Area%	Height	Height%
1	12.942	445638	50.013	22428	55.669
2	16.085	445410	49.987	17860	44.331
总计		891047	100.000	40289	100.000

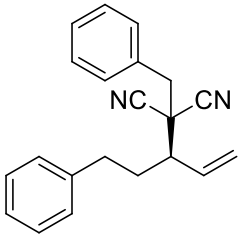


PEAK TABLE

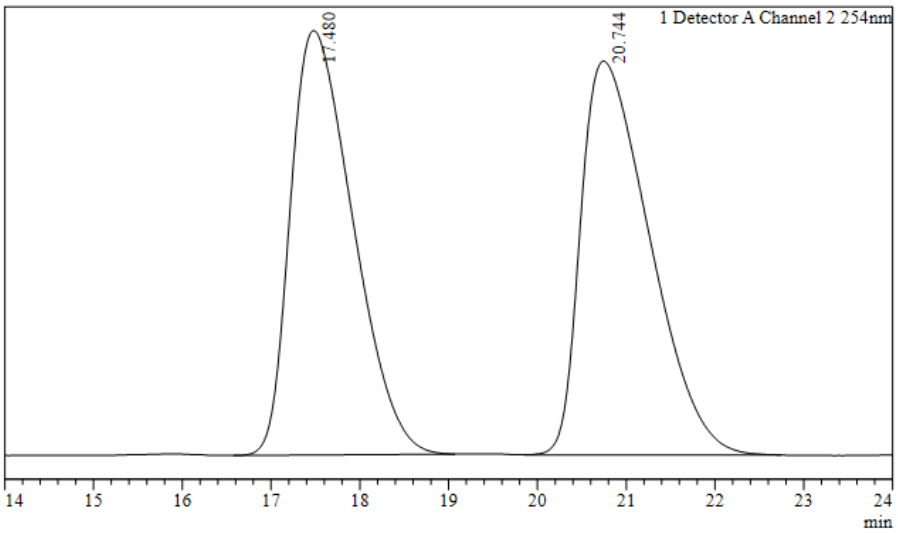
<峰表>

检测器A Ch1 254nm

Peak NO.	Retention time	Area	Area%	Height	Height%
1	12.949	372283	99.406	18484	99.485
2	16.039	2226	0.594	96	0.515
总计		374509	100.000	18579	100.000



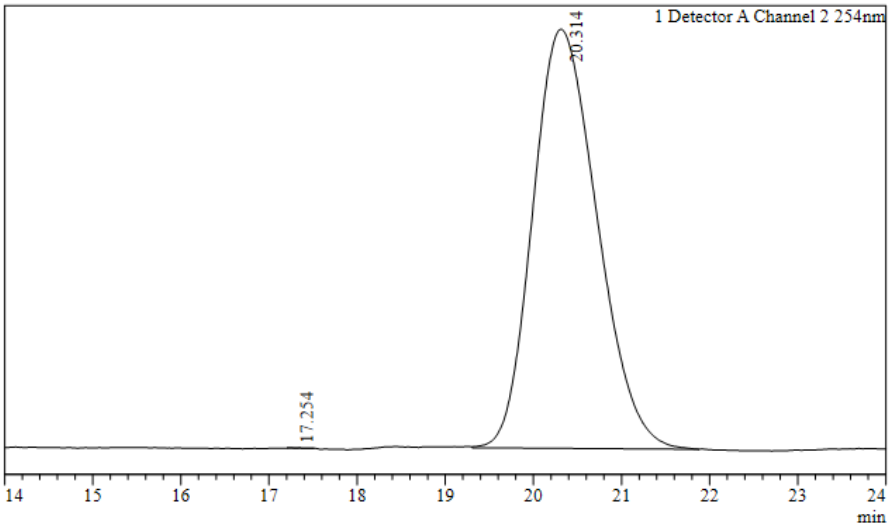
[3ab]



Peak Table

Detector A Channel 2 254nm

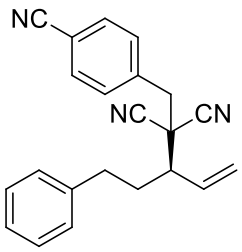
Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.480	2565596	49.413	52344	51.876
2	20.744	2626524	50.587	48559	48.124
Total		5192120	100.000	100903	100.000



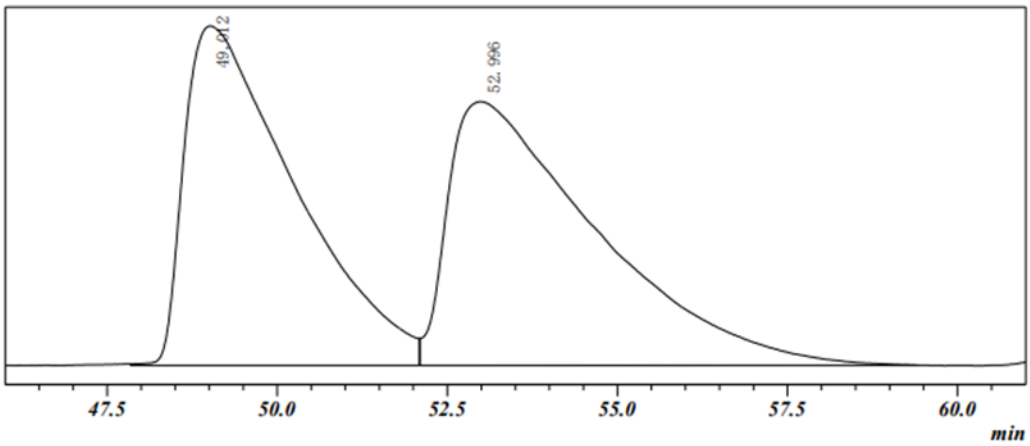
Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.254	8	0.001	2	0.016
2	20.314	704197	99.999	13856	99.984
Total		704206	100.000	13858	100.000



[3ac]

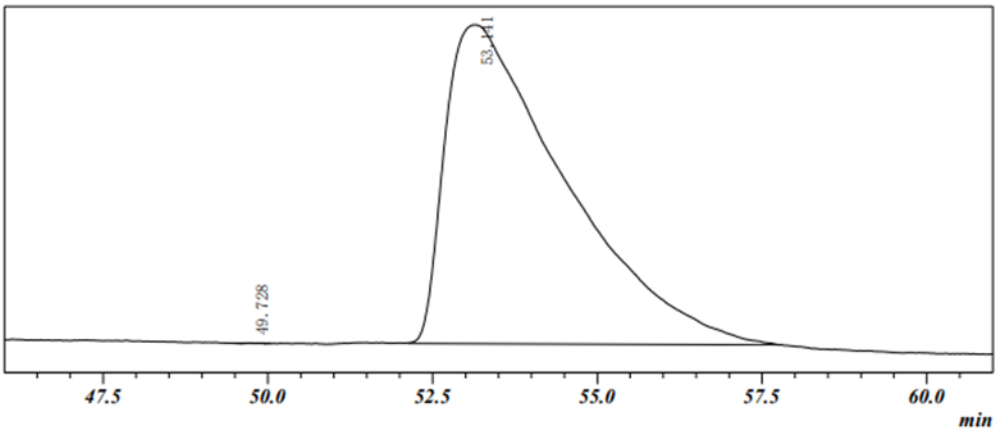


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	Retention time	Area	Area%	Height	Height%
1	49.012	2396442	48.859	21214	56.272
2	52.996	2508391	51.141	16485	43.728
总计		4904832	100.000	37699	100.000

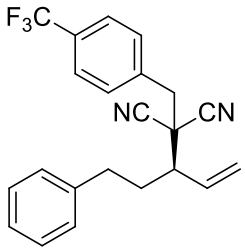


PEAK TABLE

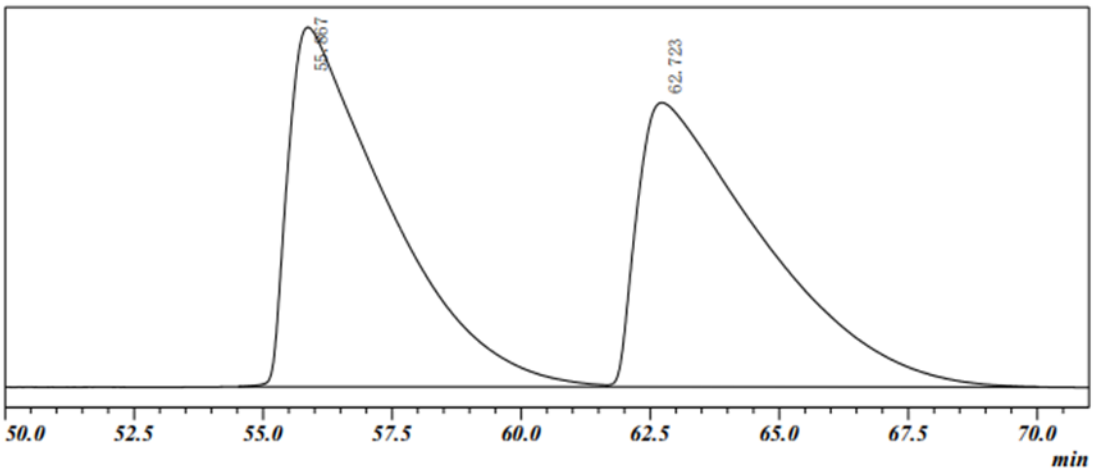
<峰表>

检测器A Ch1 254nm

Peak NO.	Retention time	Area	Area%	Height	Height%
1	49.728	16	0.001	14	0.133
2	53.141	1368344	99.999	10787	99.867
总计		1368360	100.000	10801	100.000



[**3ad**]

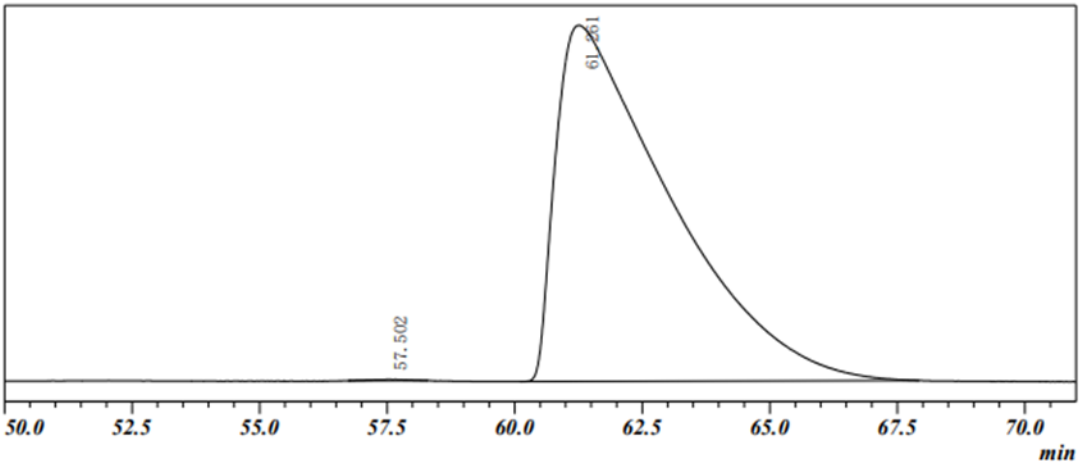


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*55.867*	*5838927*	*50.055*	*43380*	*55.836*
2	*62.723*	*5826080*	*49.945*	*34311*	*44.164*
总计		*11665007*	*100.000*	*77692*	*100.000*

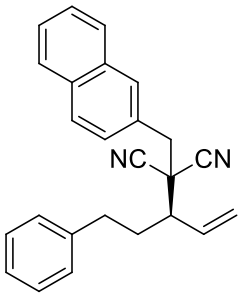


PEAK TABLE

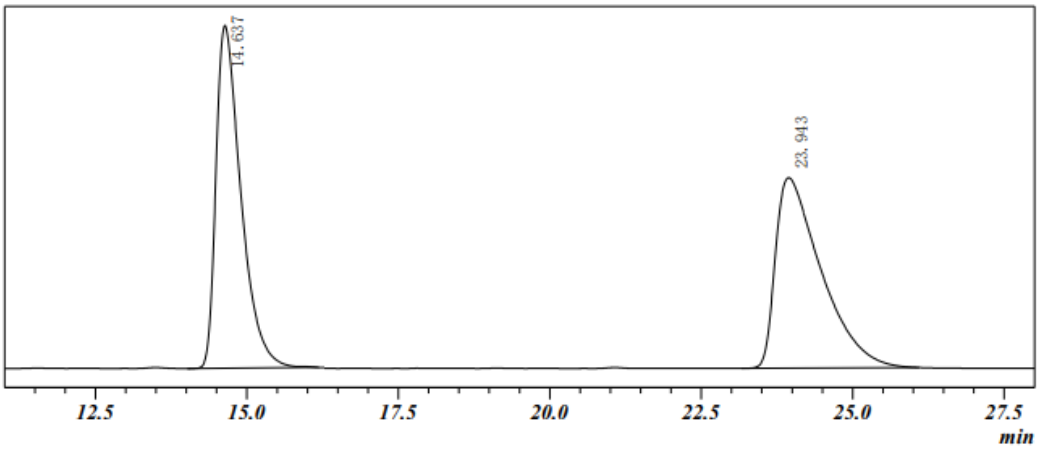
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*57.502*	*5098*	*0.103*	*103*	*0.325*
2	*61.261*	*4951409*	*99.897*	*31776*	*99.675*
总计		*4956507*	*100.000*	*31880*	*100.000*



[**3ae**]

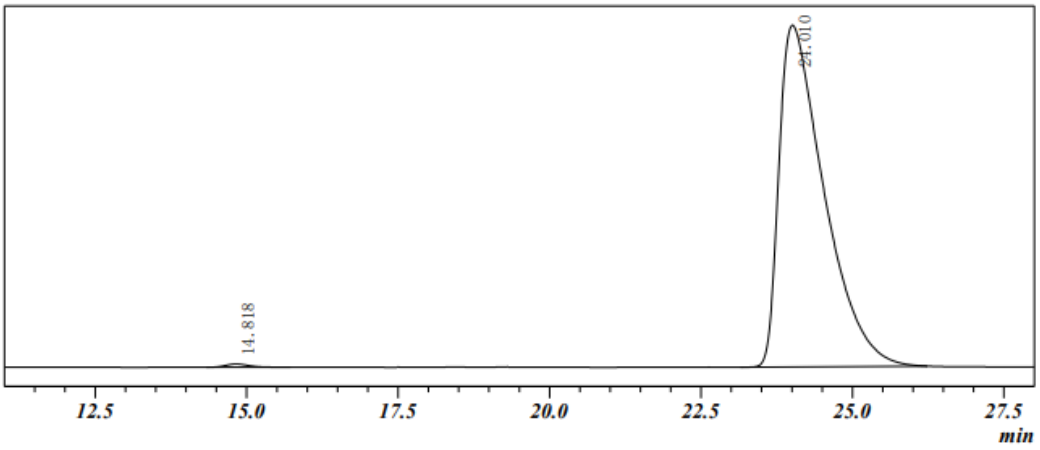


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*14.637*	*7714101*	*49.580*	*269138*	*64.280*
2	*23.943*	*7844726*	*50.420*	*149557*	*35.720*
总计		*15558827*	*100.000*	*418695*	*100.000*

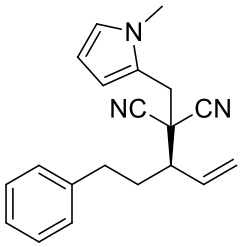


PEAK TABLE

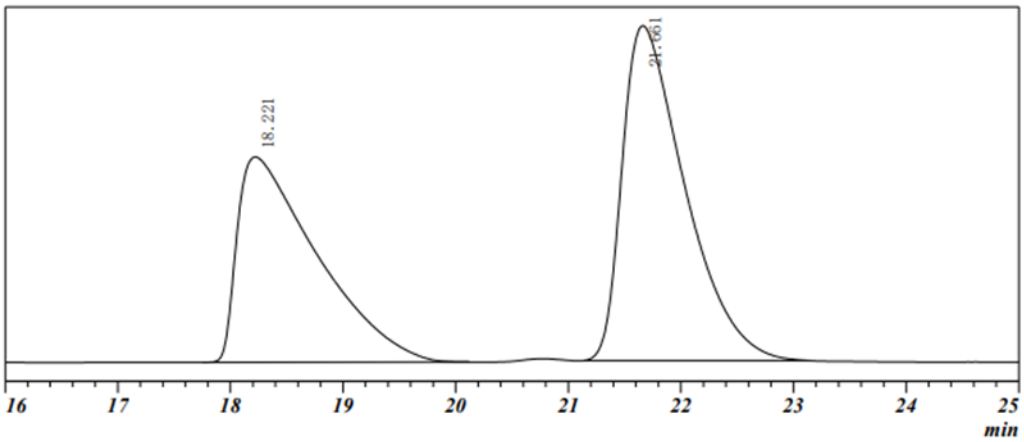
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*14.818*	*32896*	*0.494*	*1214*	*0.939*
2	*24.010*	*6620326*	*99.506*	*128047*	*99.061*
总计		*6653222*	*100.000*	*129261*	*100.000*



[**3af**]

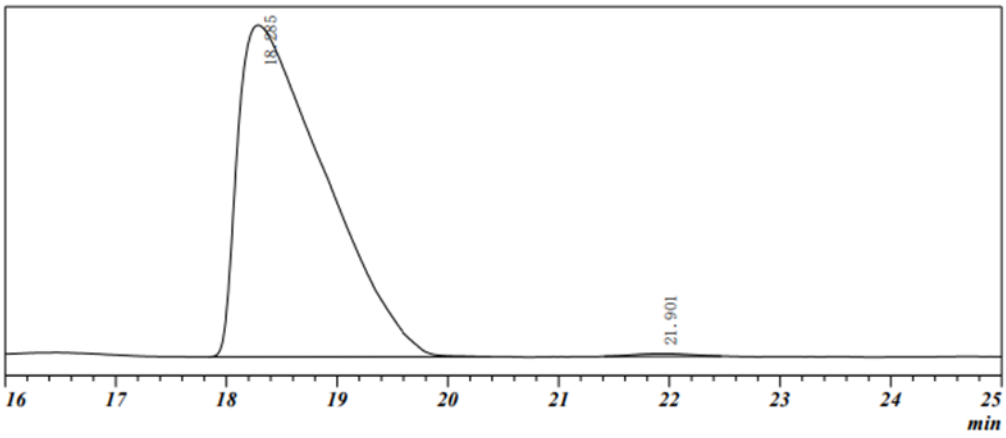


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*18.221*	*1914980*	*43.783*	*38940*	*38.009*
2	*21.661*	*2458813*	*56.217*	*63509*	*61.991*
总计		*4373793*	*100.000*	*102449*	*100.000*

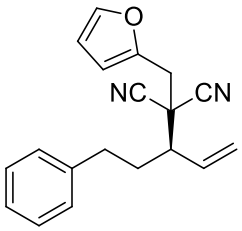


PEAK TABLE

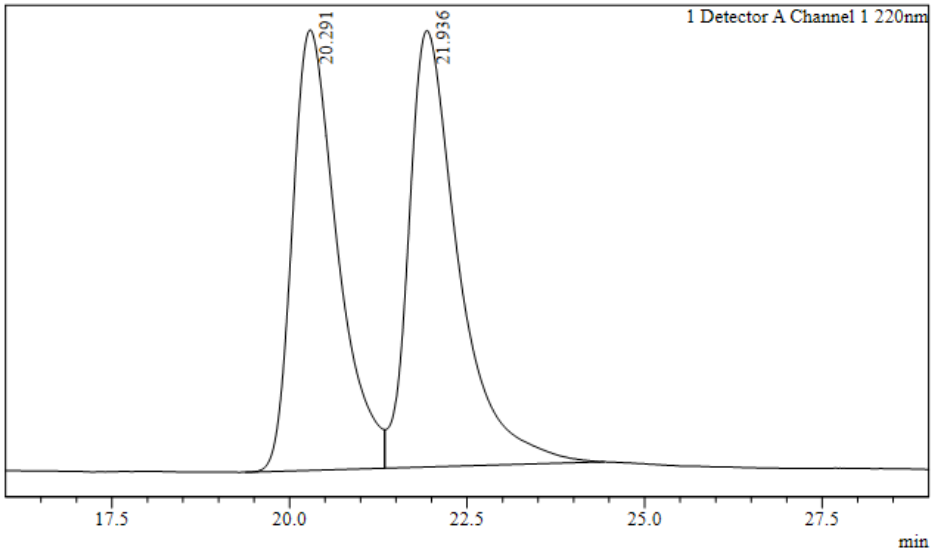
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*18.285*	*2118634*	*99.512*	*37319*	*99.202*
2	*21.901*	*10393*	*0.488*	*300*	*0.798*
总计		*2129027*	*100.000*	*37619*	*100.000*



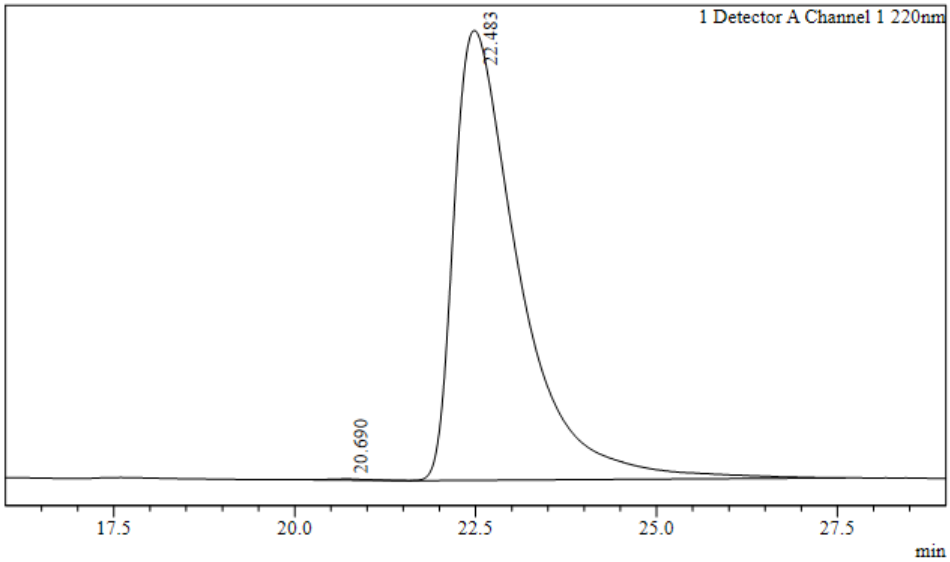
[3ag]



Peak Table

Detector A Channel 1 220nm

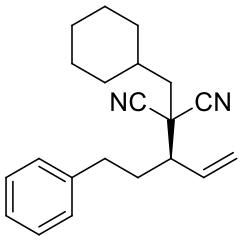
Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	20.291	1649204	37352	47.693	47.693	
2	21.936	1808721	37013	52.307	52.307	
Total		3457925	74365	100.000		



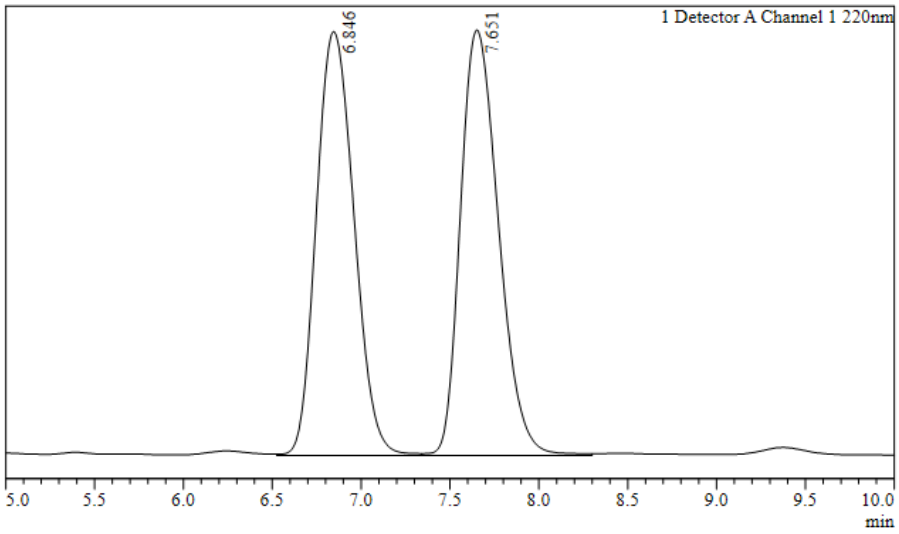
Peak Table

Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	20.690	6424	167	0.132	0.132	
2	22.483	4871944	77709	99.868	99.868	
Total		4878368	77875	100.000		



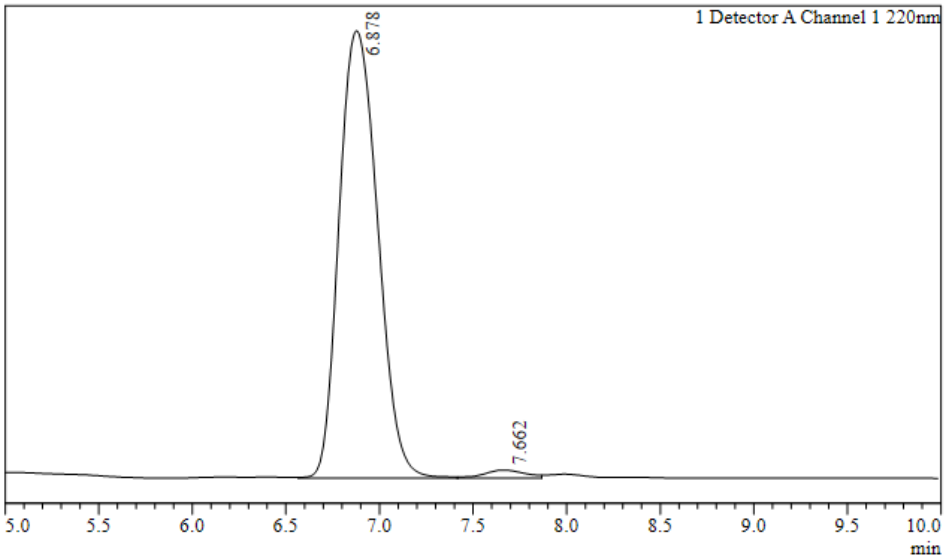
[3ah]



Peak Table

Detector A Channel 1 220nm

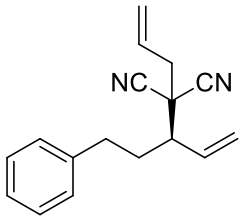
Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	6.846	1293880	87549	49.678	49.678	
2	7.651	1310653	87951	50.322	50.322	
Total		2604532	175500	100.000		



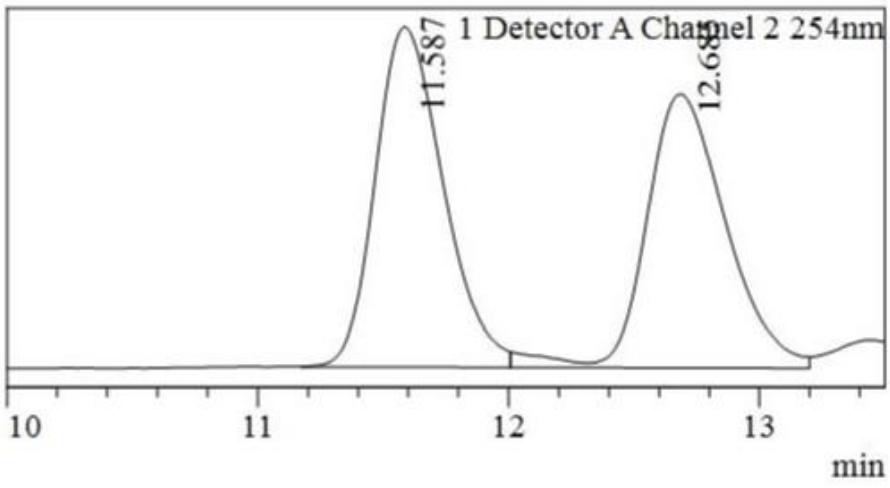
Peak Table

Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	6.878	3194491	222366	98.067	98.067	
2	7.662	62980	4035	1.933	1.933	
Total		3257471	226401	100.000		



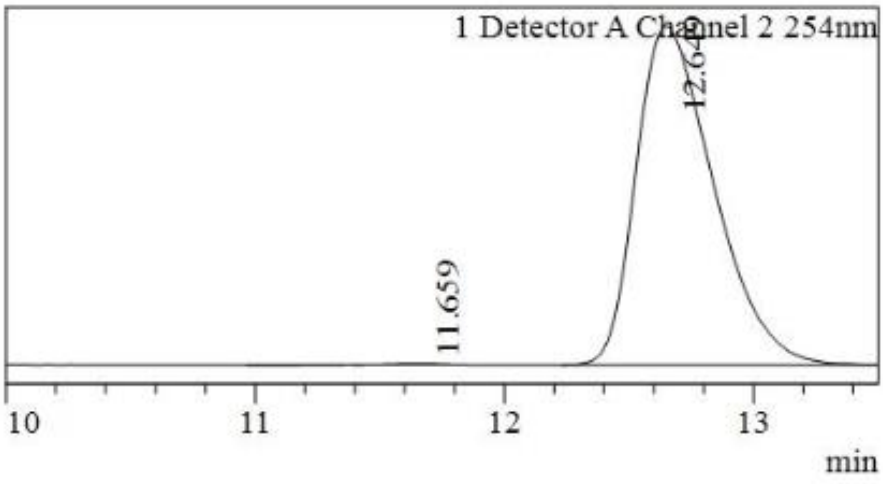
[3ai]



Peak Table

Detector A Channel 2 254nm

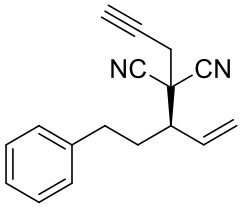
Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	11.587	136918	7246	51.456	51.456	
2	12.685	129171	5833	48.544	48.544	
Total		266089	13080	100.000		



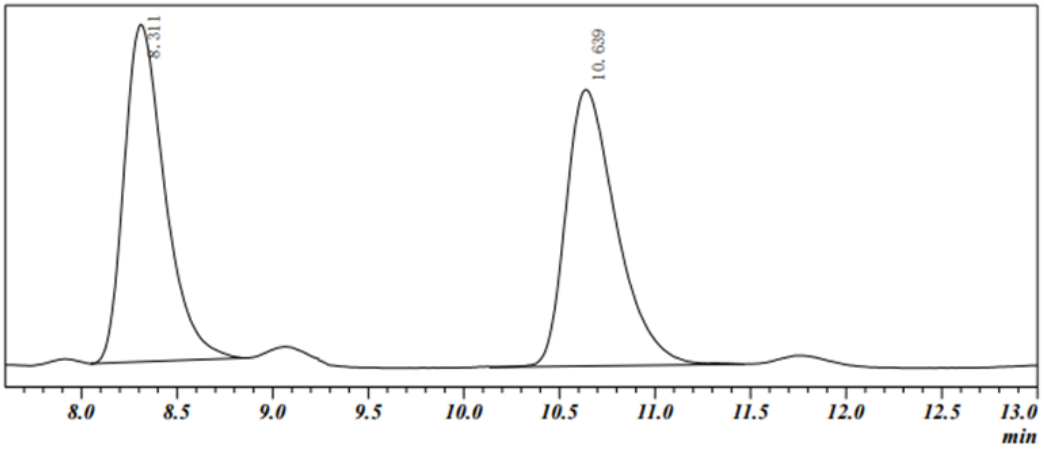
Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	11.659	255	32	0.117	0.117	
2	12.649	216522	9986	99.883	99.883	
Total		216777	10018	100.000		



[3aj]

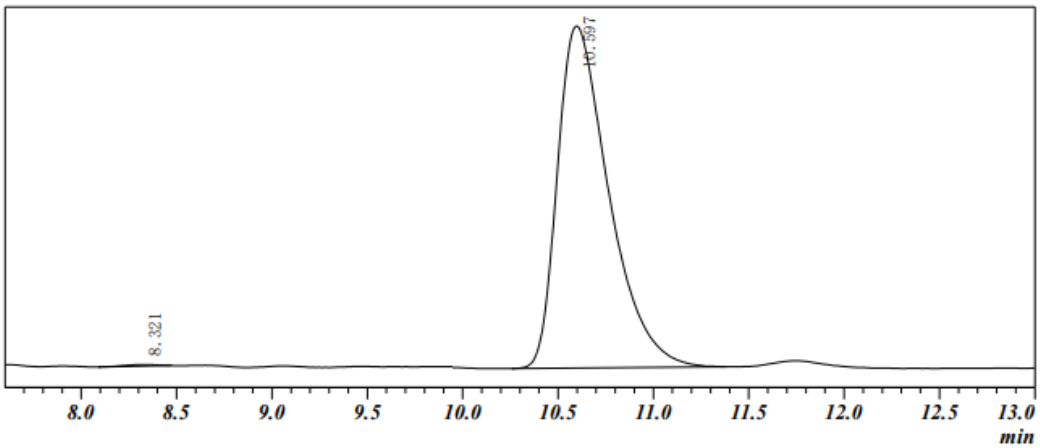


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	Retention time	Area	Area%	Height	Height%
1	8.311	204038	49.592	13778	54.983
2	10.639	207392	50.408	11281	45.017
总计		411429	100.000	25058	100.000

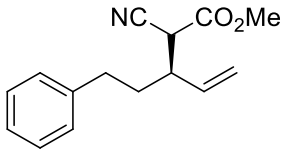


PEAK TABLE

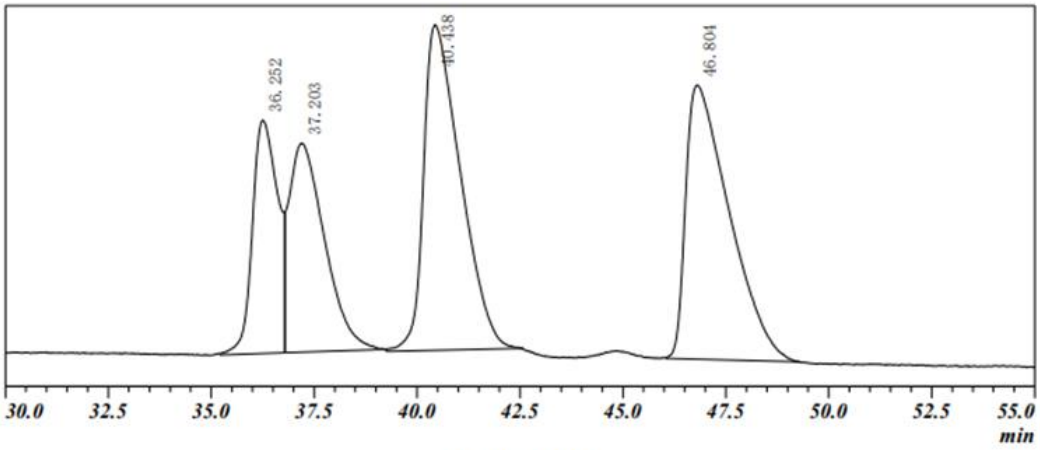
<峰表>

检测器A Ch1 254nm

Peak NO.	Retention time	Area	Area%	Height	Height%
1	8.321	1004	0.271	87	0.443
2	10.597	368719	99.729	19634	99.557
总计		369723	100.000	19721	100.000



[3ak]

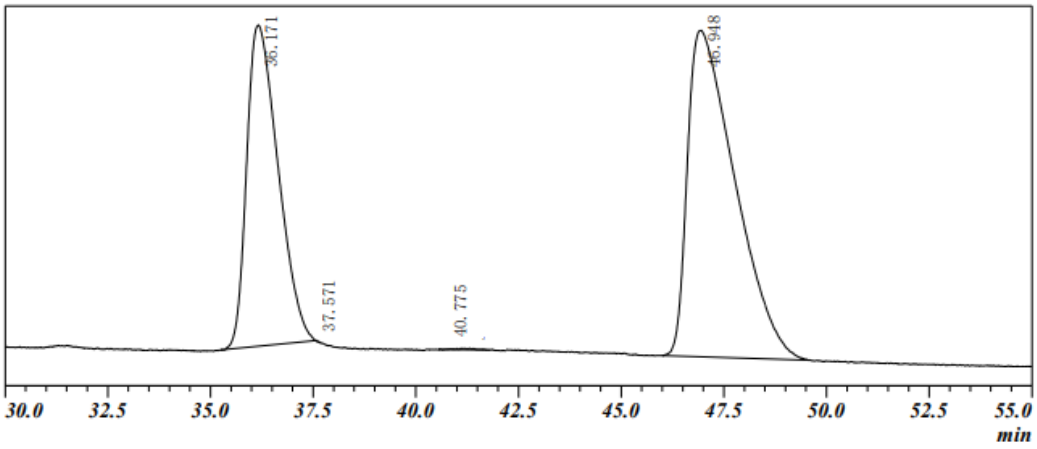


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*36.252*	*250839*	*16.021*	*5796*	*22.400*
2	*37.203*	*310104*	*19.806*	*5189*	*20.054*
3	*40.438*	*502717*	*32.108*	*8086*	*31.248*
4	*46.804*	*502063*	*32.066*	*6805*	*26.298*
总计		*1565723*	*100.000*	*25876*	*100.000*

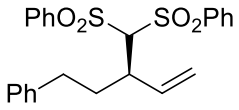


PEAK TABLE

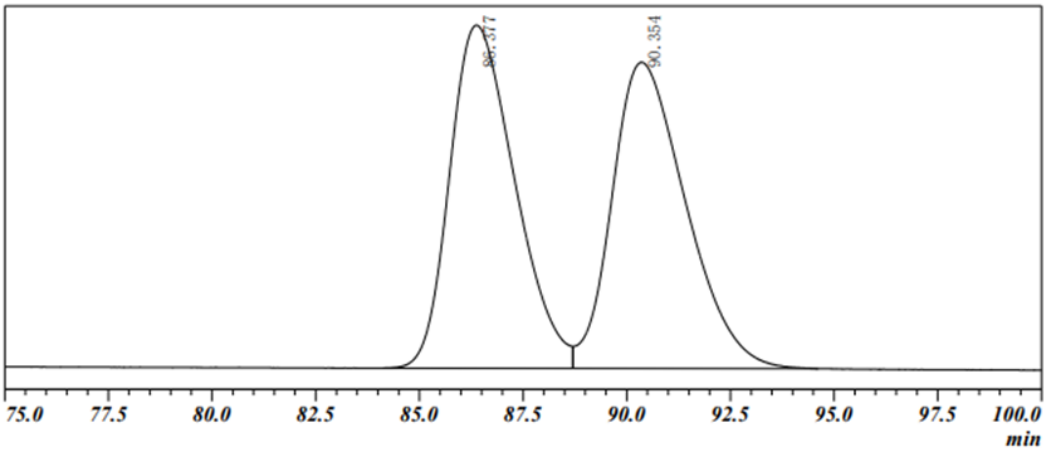
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*36.171*	*332437*	*39.364*	*6255*	*49.473*
2	*37.571*	*2*	*0.000*	*0*	*0.001*
3	*40.775*	*290*	*0.034*	*30*	*0.235*
4	*46.948*	*511795*	*60.602*	*6359*	*50.290*
总计		*844525*	*100.000*	*12644*	*100.000*



[**3al**]

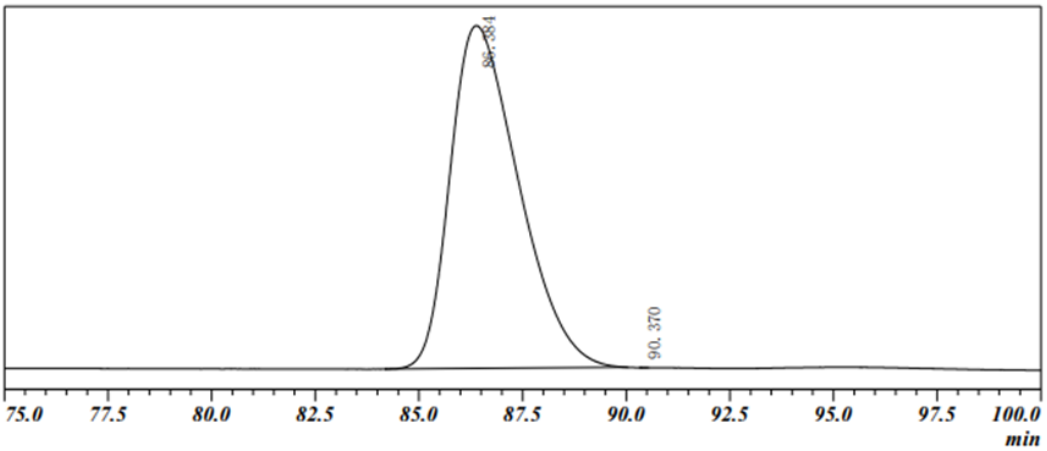


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*86.377*	*4326177*	*49.674*	*39624*	*52.843*
2	*90.354*	*4383030*	*50.326*	*35360*	*47.157*
总计		*8709206*	*100.000*	*74984*	*100.000*

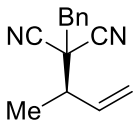


PEAK TABLE

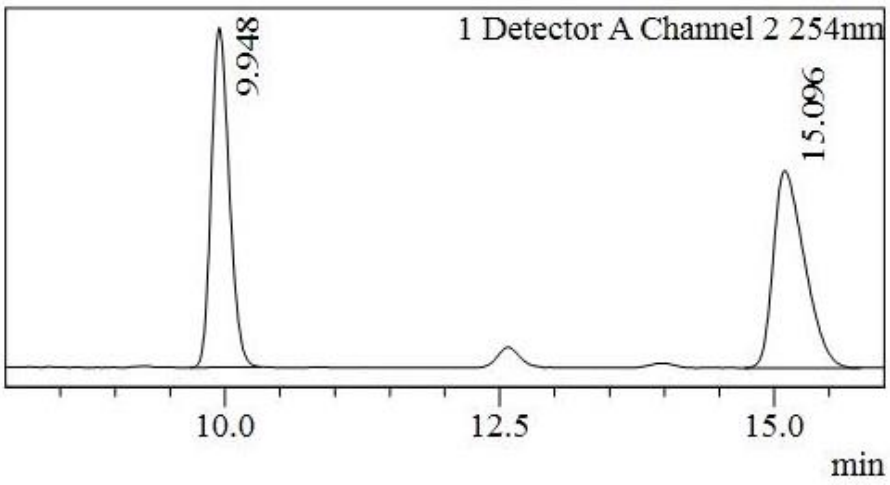
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*86.384*	*6273413*	*100.000*	*54546*	*99.988*
2	*90.370*	*17*	*0.000*	*7*	*0.012*
总计		*6273429*	*100.000*	*54552*	*100.000*



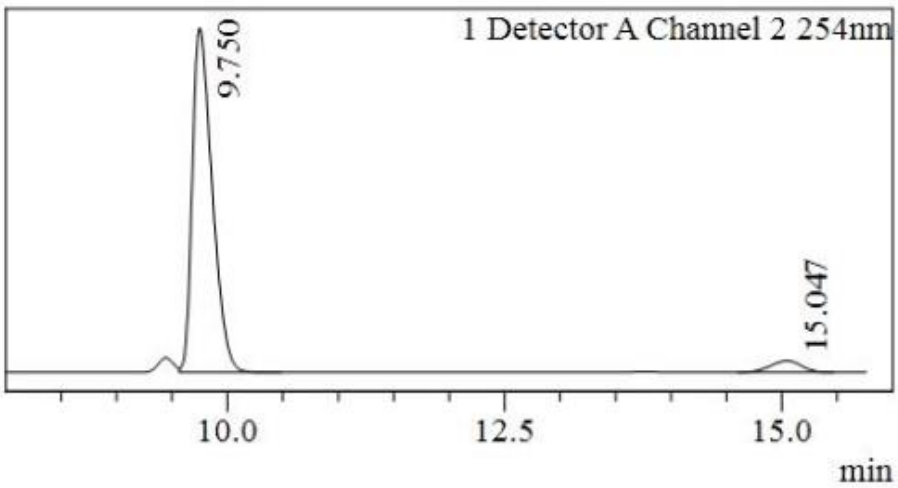
[**3bb**]



Peak Table

Detector A Channel 2 254nm

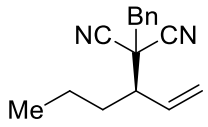
Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	9.948	98529	8677	49.661	49.661	
2	15.096	99874	5039	50.339	50.339	
Total		198403	13716	100.000		



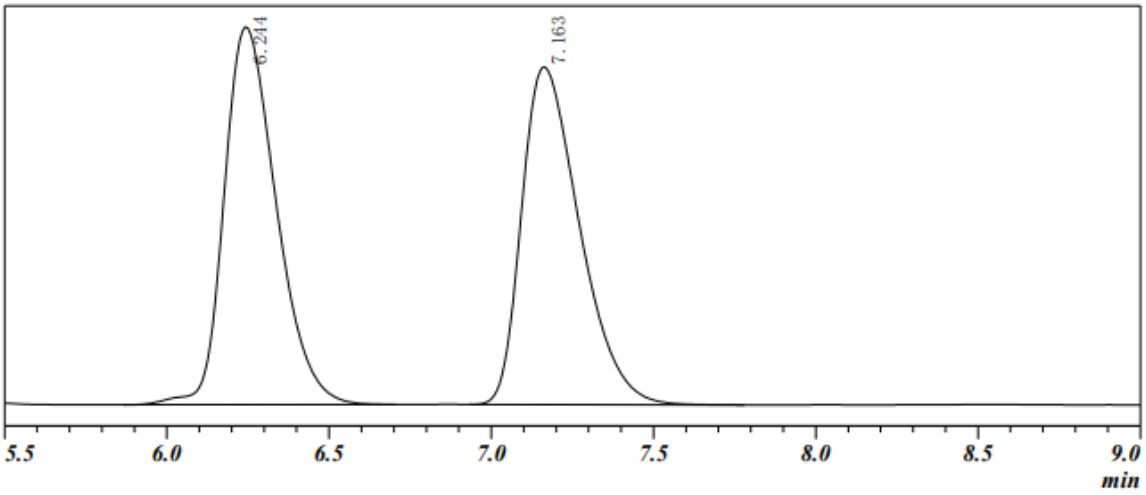
Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	9.750	423862	33937	94.974	94.974	
2	15.047	22428	1132	5.026	5.026	
Total		446290	35069	100.000		



[3cb]

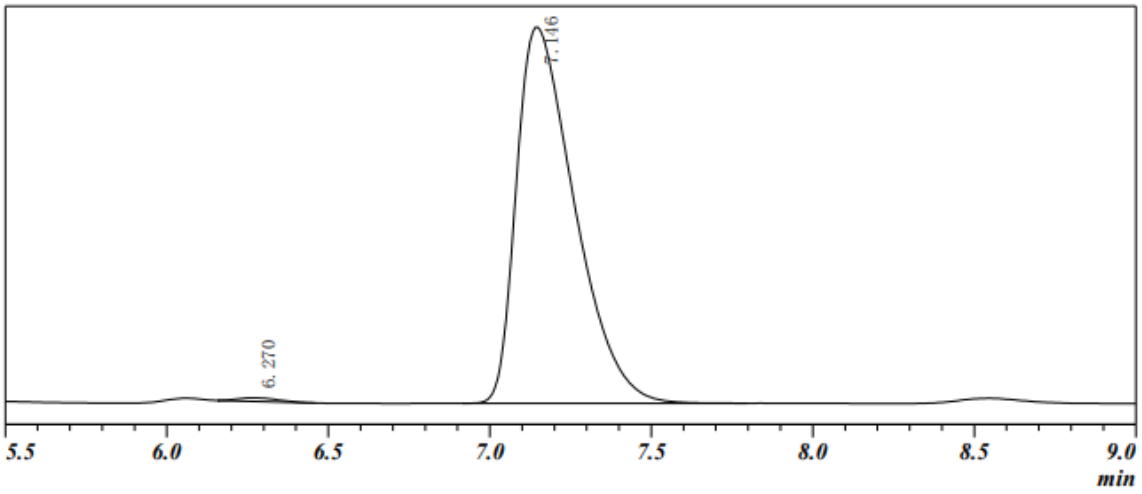


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*6.244*	*574136*	*50.238*	*51284*	*52.819*
2	*7.163*	*568696*	*49.762*	*45810*	*47.181*
总计		*1142832*	*100.000*	*97094*	*100.000*

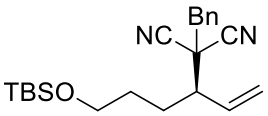


PEAK TABLE

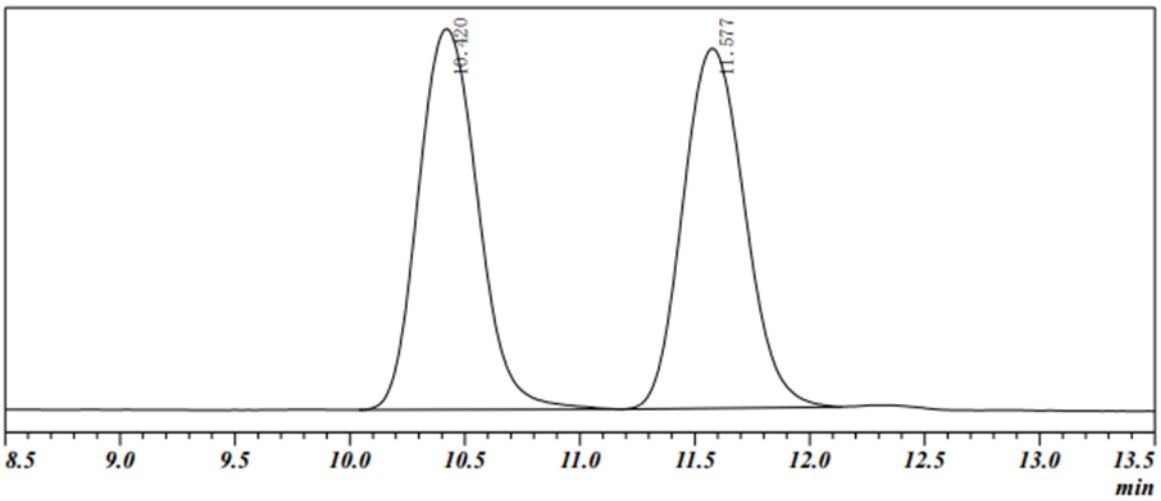
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*6.270*	*5628*	*0.618*	*679*	*0.932*
2	*7.146*	*904633*	*99.382*	*72211*	*99.068*
总计		*910261*	*100.000*	*72890*	*100.000*



[**3db**]

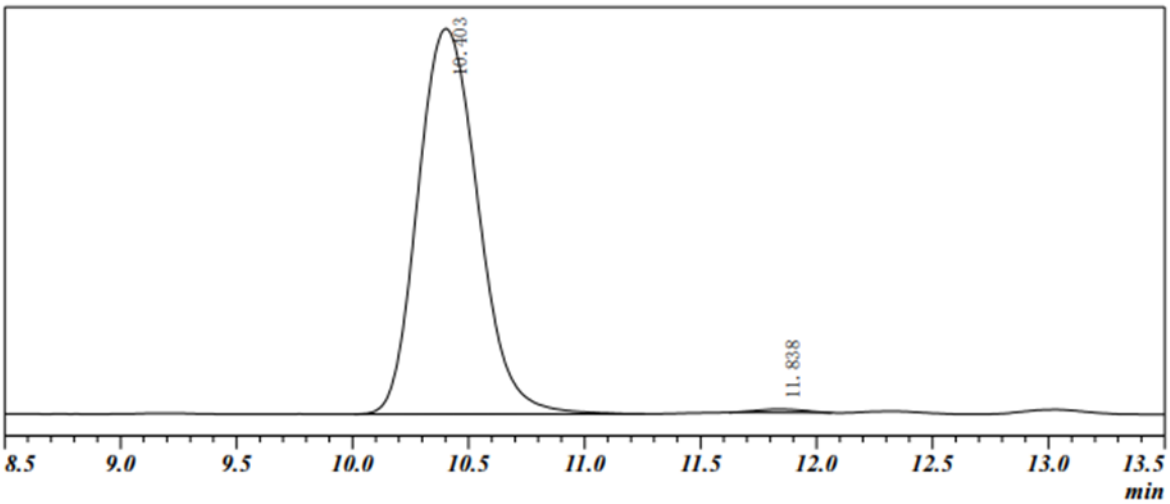


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*10.420*	*279693*	*50.465*	*15548*	*51.405*
2	*11.577*	*274537*	*49.535*	*14698*	*48.595*
总计		*554230*	*100.000*	*30245*	*100.000*

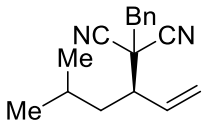


PEAK TABLE

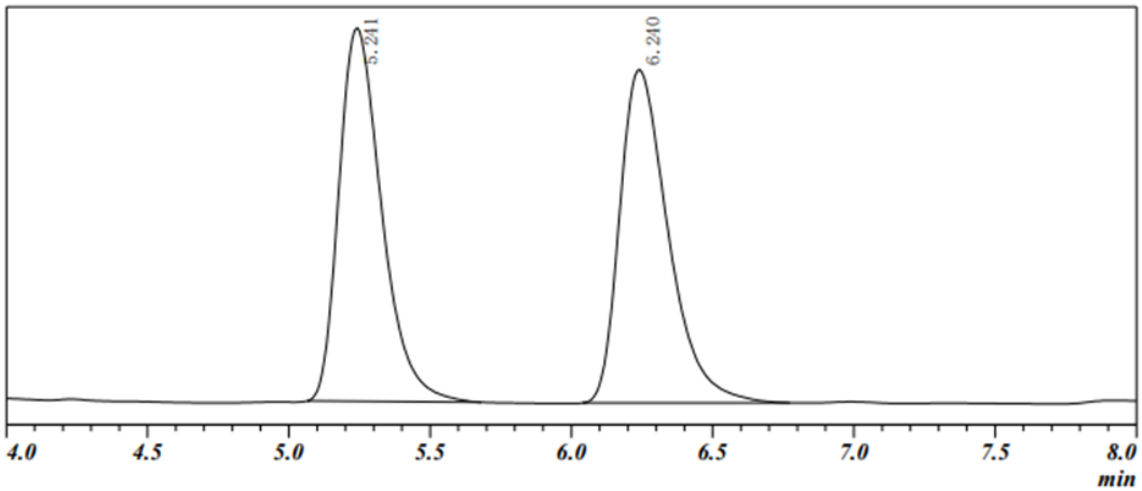
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*10.403*	*689112*	*99.323*	*38258*	*99.147*
2	*11.838*	*4700*	*0.677*	*329*	*0.853*
总计		*693812*	*100.000*	*38588*	*100.000*



[3eb]

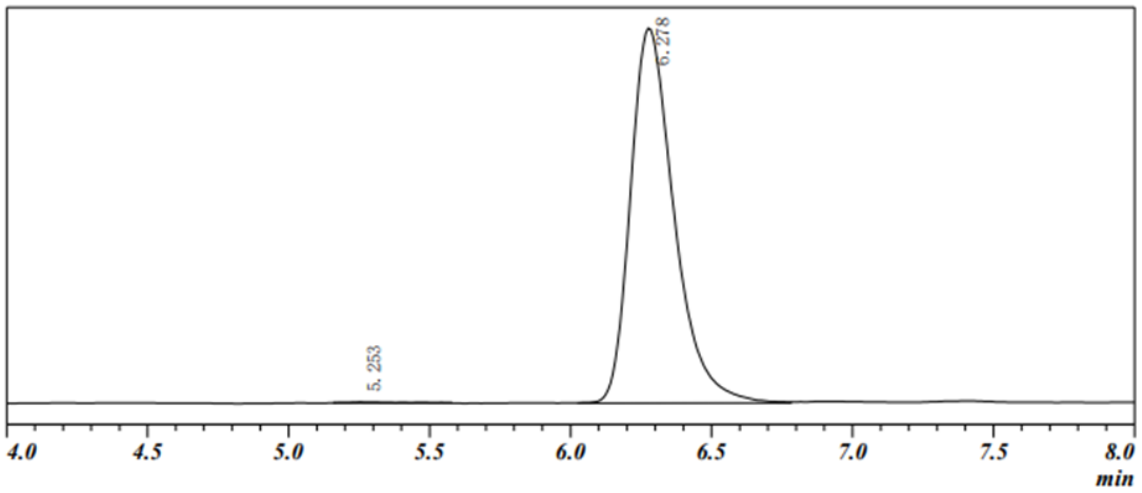


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*5.241*	*475890*	*49.659*	*45227*	*52.835*
2	*6.240*	*482431*	*50.341*	*40373*	*47.165*
总计		*958321*	*100.000*	*85601*	*100.000*

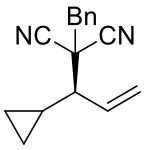


PEAK TABLE

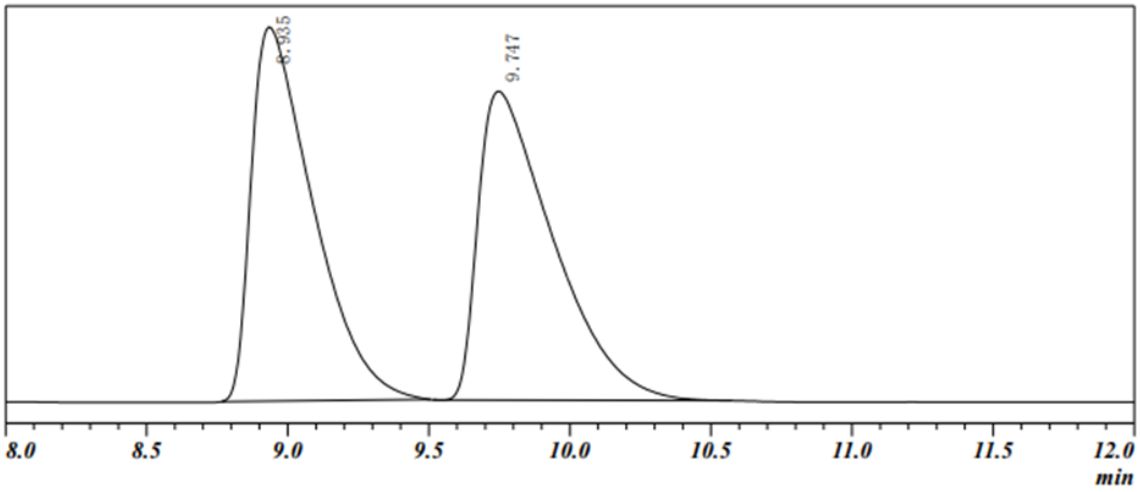
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*5.253*	*334*	*0.182*	*32*	*0.188*
2	*6.278*	*182937*	*99.818*	*16976*	*99.812*
总计		*183270*	*100.000*	*17008*	*100.000*



[**3fb**]

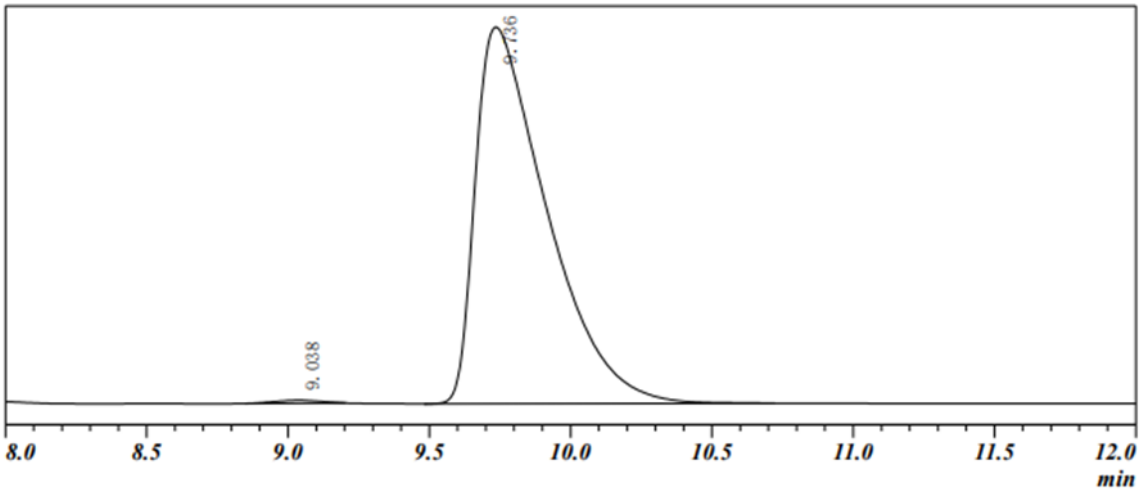


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	Retention time	Area	Area%	Height	Height%
1	8.935	1249131	49.978	82062	54.789
2	9.747	1250224	50.022	67717	45.211
总计		2499355	100.000	149779	100.000

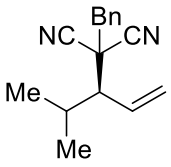


PEAK TABLE

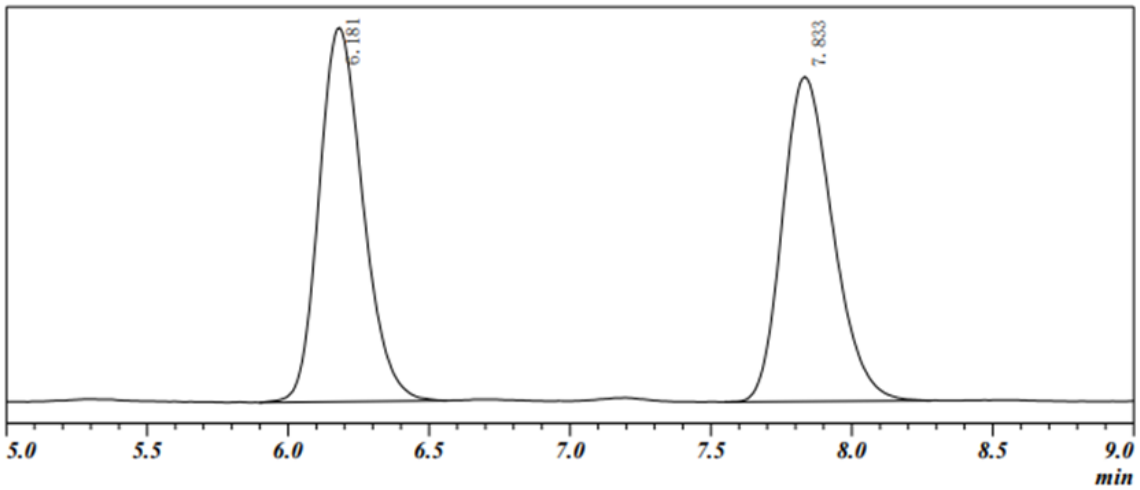
<峰表>

检测器A Ch1 254nm

Peak NO.	Retention time	Area	Area%	Height	Height%
1	9.038	5008	0.490	456	0.782
2	9.736	1017316	99.510	57887	99.218
总计		1022325	100.000	58343	100.000



[**3gb**]

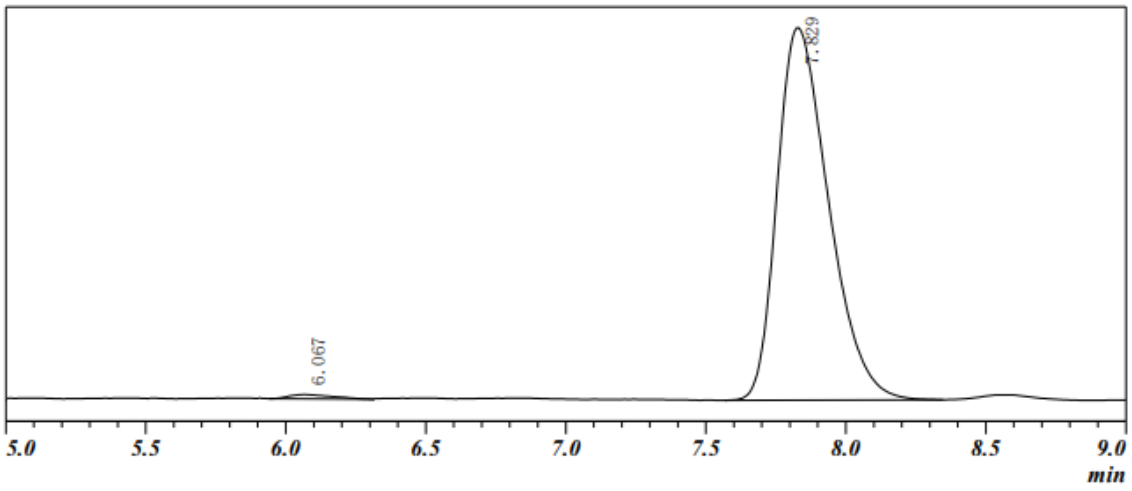


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*6.181*	*98978*	*50.066*	*9126*	*53.522*
2	*7.833*	*98717*	*49.934*	*7925*	*46.478*
总计		*197695*	*100.000*	*17051*	*100.000*

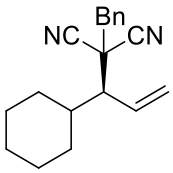


PEAK TABLE

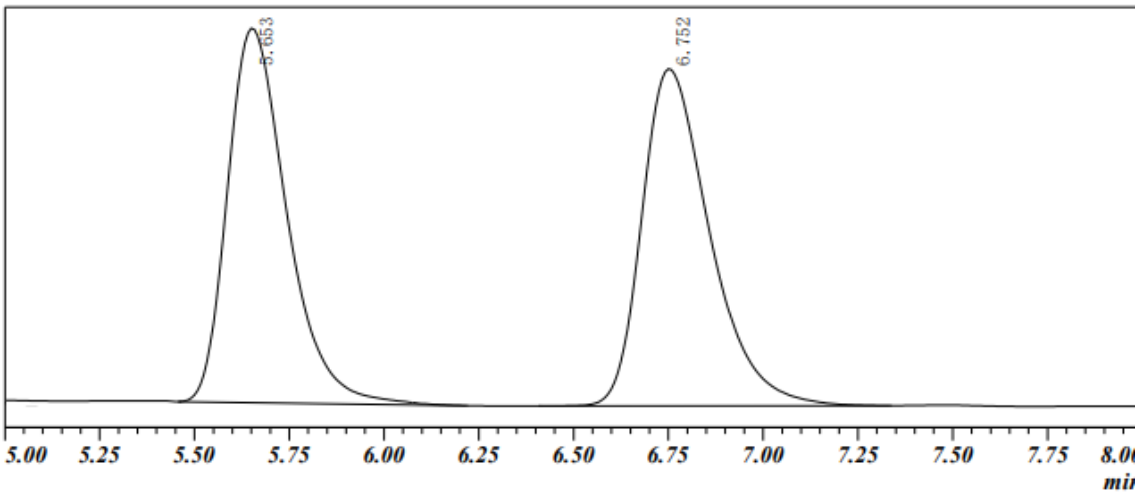
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*6.067*	*3004*	*0.983*	*278*	*1.159*
2	*7.829*	*302511*	*99.017*	*23664*	*98.841*
总计		*305514*	*100.000*	*23942*	*100.000*



[**3hb**]

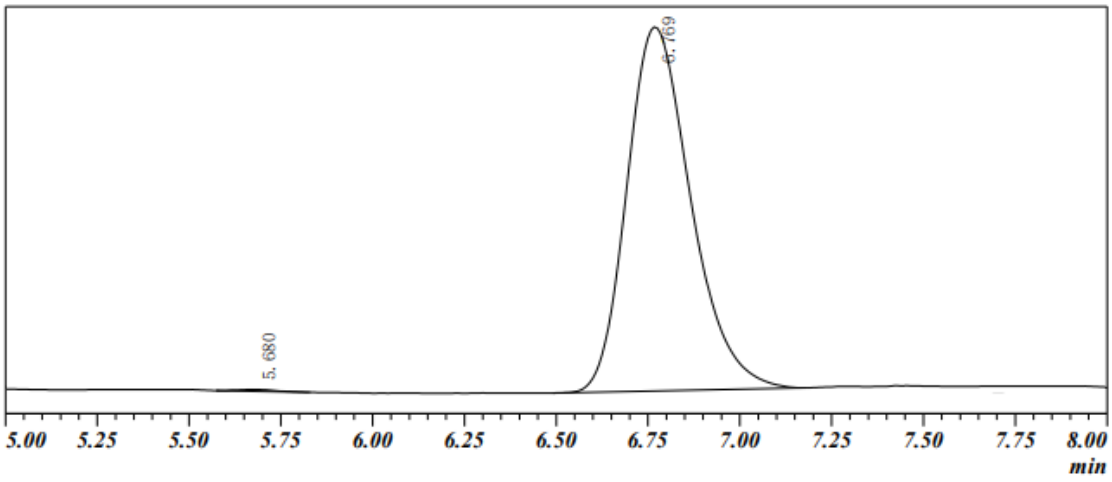


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*5.653*	*442411*	*49.206*	*40640*	*52.626*
2	*6.752*	*456690*	*50.794*	*36584*	*47.374*
总计		*899100*	*100.000*	*77224*	*100.000*

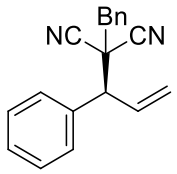


PEAK TABLE

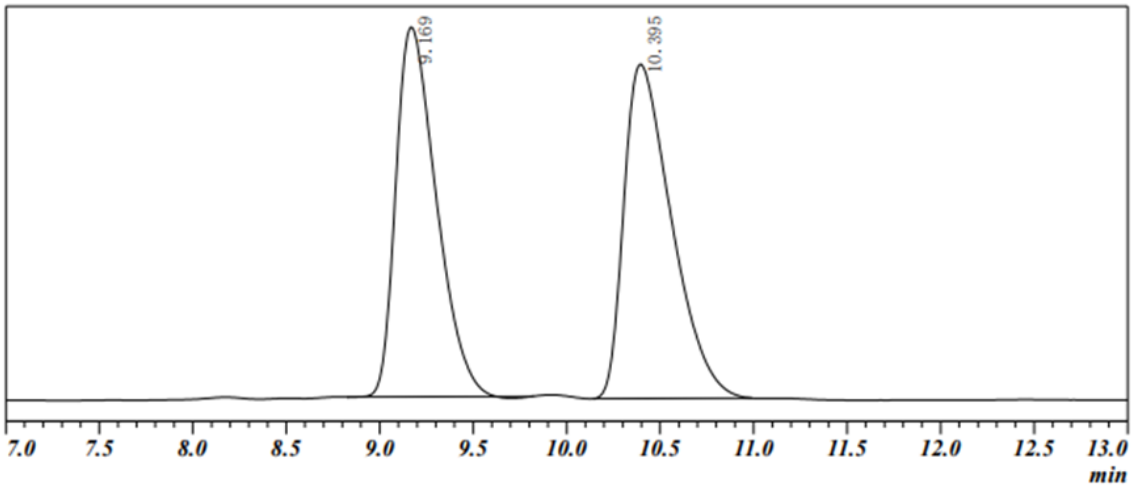
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*5.680*	*415*	*0.278*	*61*	*0.497*
2	*6.769*	*149005*	*99.722*	*12294*	*99.503*
总计		*149420*	*100.000*	*12355*	*100.000*



[**3ib**]

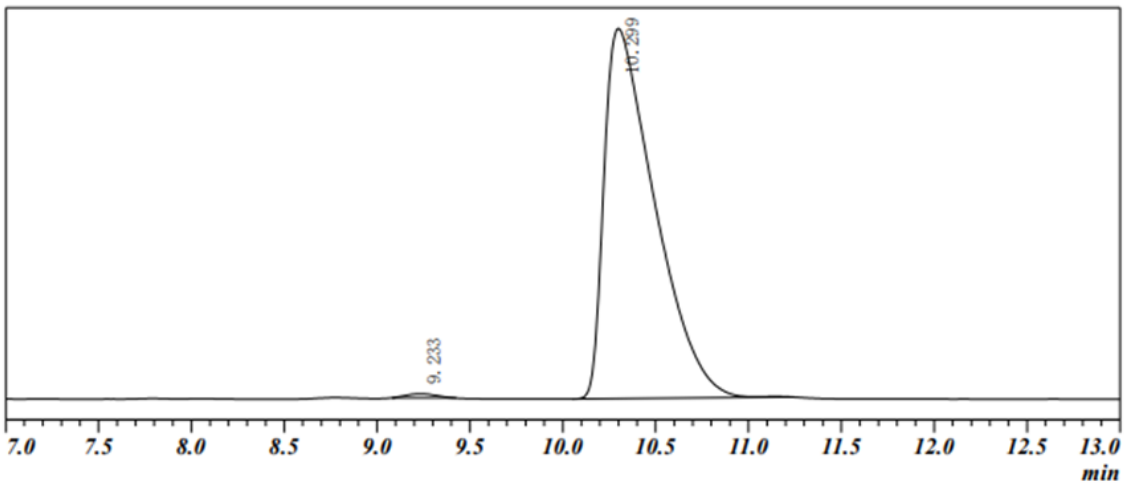


PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*9.169*	*1251278*	*48.382*	*83259*	*52.523*
2	*10.395*	*1334946*	*51.618*	*75259*	*47.477*
总计		*2586224*	*100.000*	*158518*	*100.000*

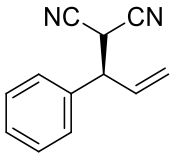


PEAK TABLE

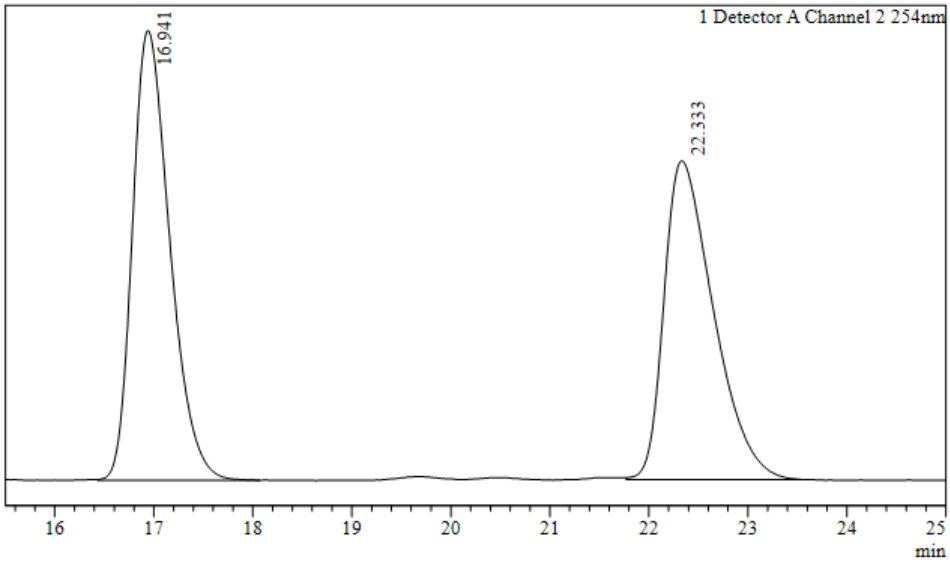
<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*9.233*	*17864*	*0.627*	*1628*	*1.079*
2	*10.299*	*2832343*	*99.373*	*149195*	*98.921*
总计		*2850207*	*100.000*	*150823*	*100.000*



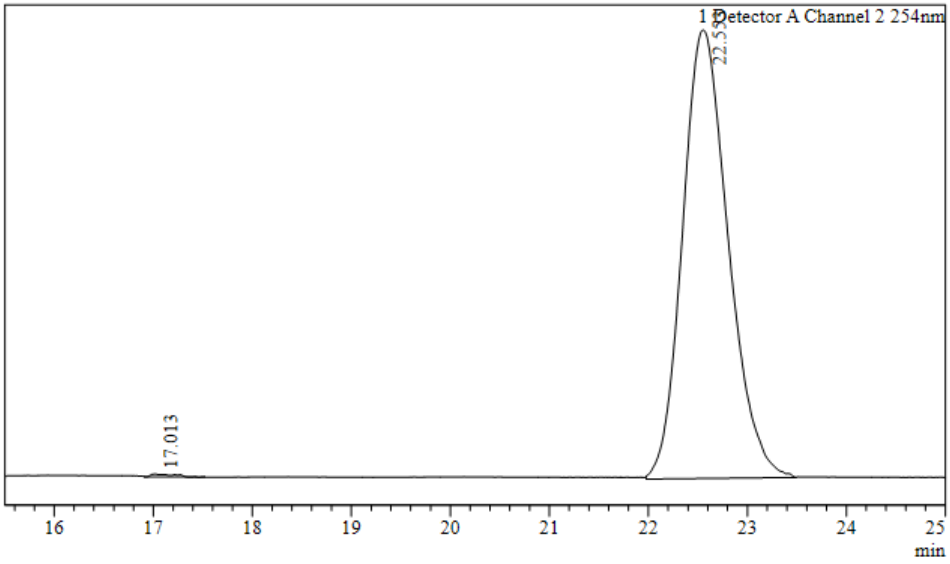
[**3ja**]



Peak Table

Detector A Channel 2 254nm

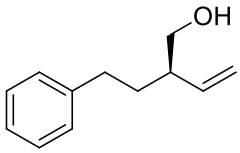
Peak#	Ret. Time	Area	Area%	Height	Height%
1	*16.941*	*457605*	*51.605*	*17411*	*58.517*
2	*22.333*	*429146*	*48.395*	*12343*	*41.483*
Total		*886751*	*100.000*	*29754*	*100.000*



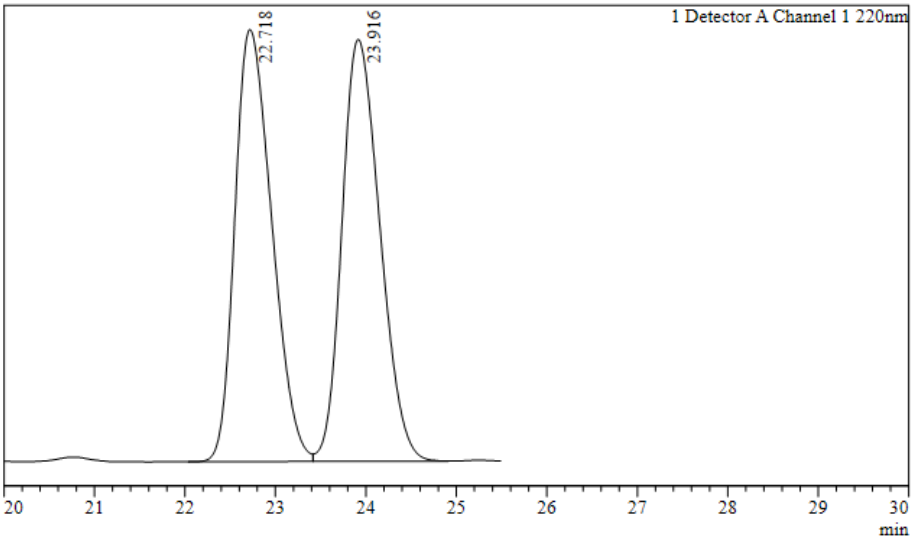
Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	*17.013*	*238*	*0.297*	*14*	*0.578*
2	*22.553*	*79817*	*99.703*	*2490*	*99.422*
Total		*80055*	*100.000*	*2504*	*100.000*



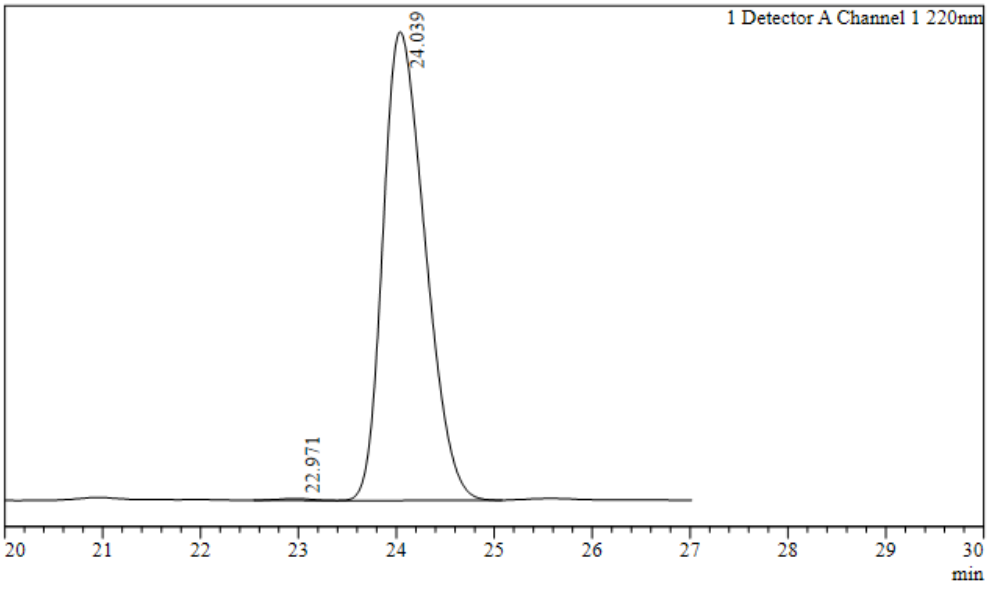
[**4**]



Peak Table

Detector A Channel 1 220nm

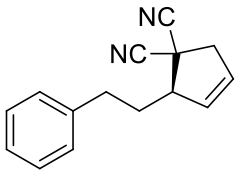
Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	22.718	2737301	96511	49.859	49.859	
2	23.916	2752797	94237	50.141	50.141	
Total		5490097	190748	100.000		



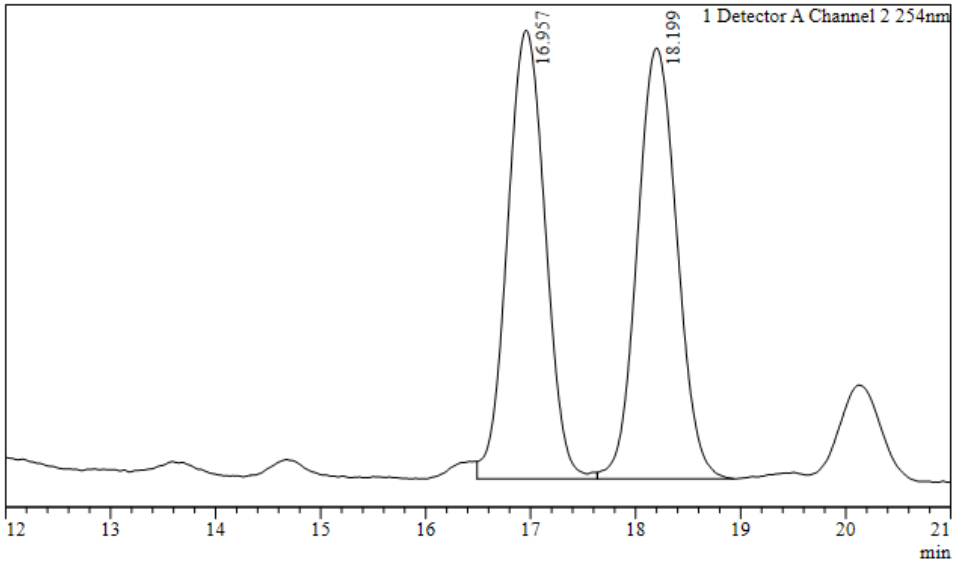
Peak Table

Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	22.971	9263	381	0.280	0.280	
2	24.039	3301121	110097	99.720	99.720	
Total		3310384	110477	100.000		



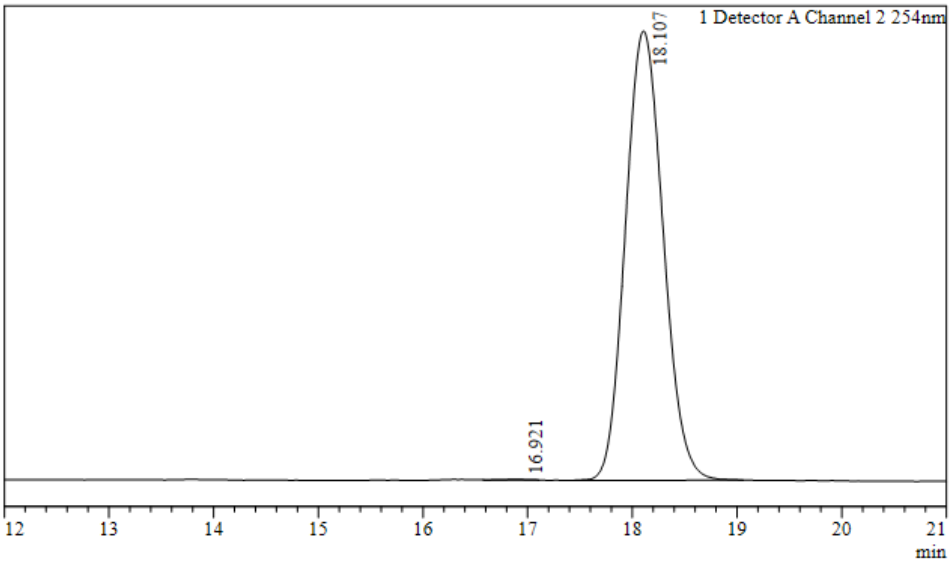
[**5**]



Peak Table

Detector A Channel 2 254nm

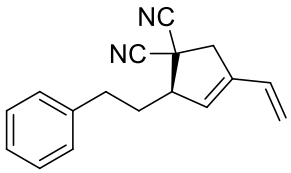
Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	16.957	118768	4752	49.759	49.759	
2	18.199	119920	4563	50.241	50.241	
Total		238689	9315	100.000		



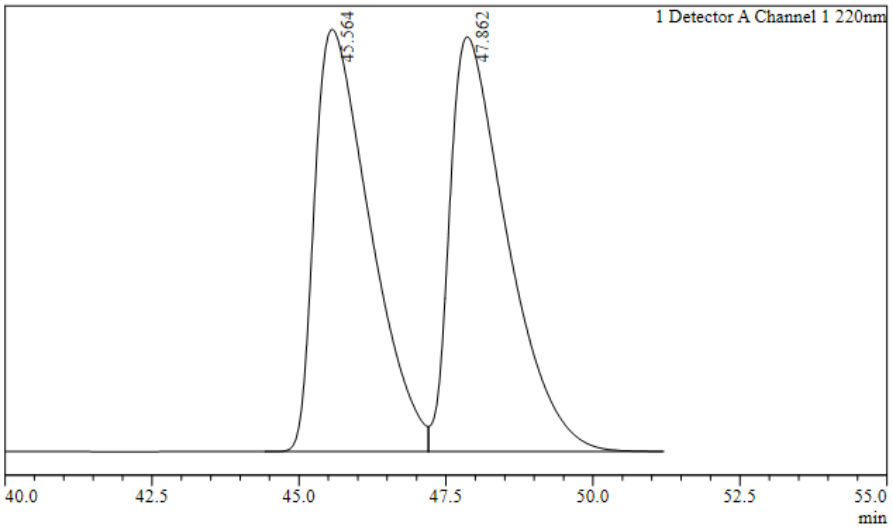
Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	16.921	773	48	0.104	0.104	
2	18.107	745205	29643	99.896	99.896	
Total		745978	29691	100.000		



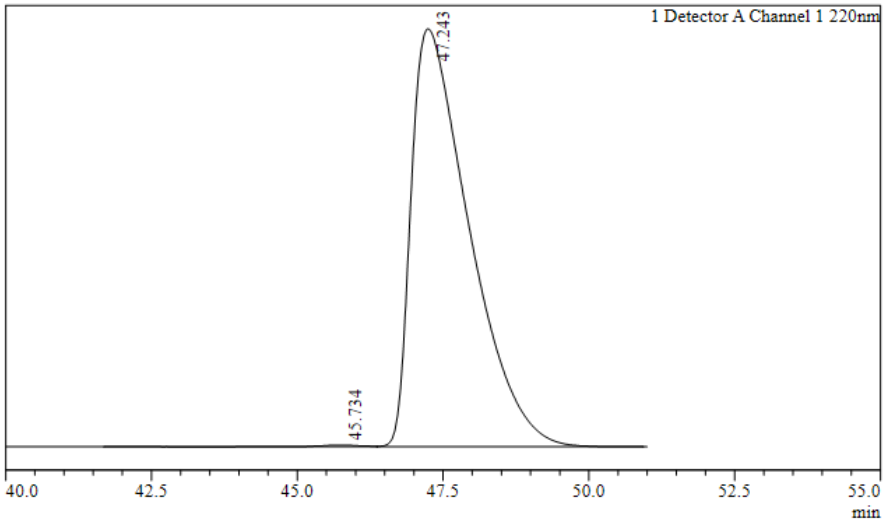
[**6**]



Peak Table

Detector A Channel 1 220nm

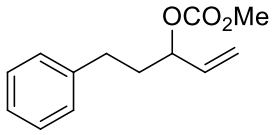
Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	45.564	27416406	417666	49.538	49.538	
2	47.862	27928078	410259	50.462	50.462	
Total		55344484	827924	100.000		



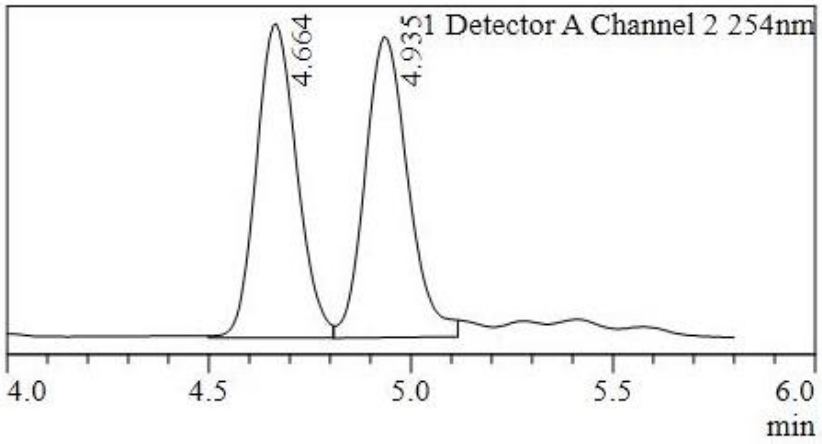
Peak Table

Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	45.734	61625	1687	0.181	0.181	
2	47.243	34049085	491251	99.819	99.819	
Total		34110710	492938	100.000		



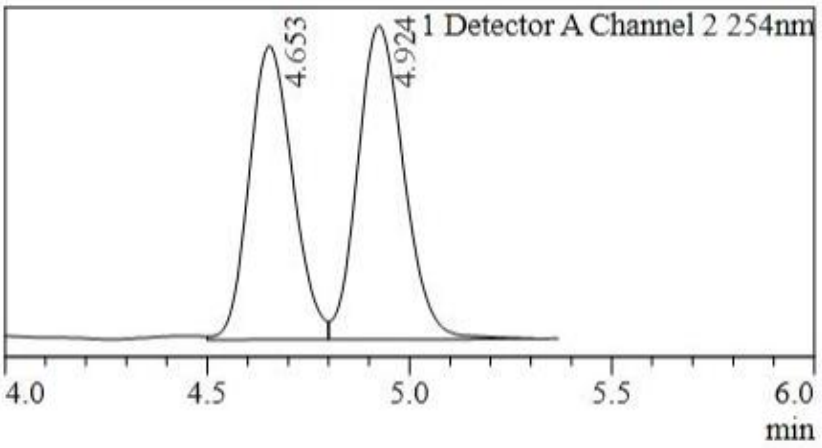
1a



Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	4.664	62394	8991	49.549	49.549	
2	4.935	63529	8603	50.451	50.451	
Total		125922	17595	100.000		



Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	4.653	452686	60356	46.951	46.951	
2	4.924	511472	64595	53.049	53.049	
Total		964159	124951	100.000		

16. References:

1. Ghorai, S.; Chirke, S. S.; Xu, W.-B.; Chen, J.-F.; Li, C. Cobalt-Catalyzed Regio- and Enantioselective Allylic Amination. *J. Am. Chem. Soc.* **2019**, *141*, 11430-11434.
2. Takizawa, K.; Sekino, T.; Sato, S.; Yoshino, T.; Kojima, M.; Matsunaga, S. Cobalt - Catalyzed Allylic Alkylation Enabled by Organophotoredox Catalysis. *Angew. Chem. Int. Ed.* **2019**, *58*, 9199-9203.
3. Tayyari, F.; Wood, D. E.; Fanwick, P. E.; Sammelson, R. E. Monosubstituted Malononitriles: Efficient One-Pot Reductive Alkylations of Malononitrile with Aromatic Aldehydes. *Synthesis*, **2008**, *2*, 279-285.
4. Ghorai, M. K.; Talukdar, R.; Tiwari, D. P. A Route to Highly Functionalized β-Enaminoesters via a Domino Ring-Opening Cyclization/Decarboxylative Tautomerization Sequence of Donor–Acceptor Cyclopropanes with Substituted Malononitriles. *Org. Lett.* **2014**, *16*, 2204-2207.
5. Grugel, C. P.; Breit, B. Rhodium - Catalyzed Asymmetric Allylation of Malononitriles as Masked Acyl Cyanide with Allenes: Efficient Access to β, γ - Unsaturated Carbonyls. C*hem. Eur. J.* **2018**, *24*, 15223-15226.
6. Stanley, L. M.; Bai, C.; Ueda, M.; Hartwig, J. F. Iridium-Catalyzed Kinetic Asymmetric Transformations of Racemic Allylic Benzoates. *J. Am. Chem. Soc.* **2010**, *132*, 8918-8920.