Electronic Supplementary Material (ESI) for ChemComm.

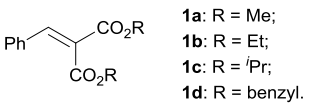

**Supporting Information**

## 1. General remarks

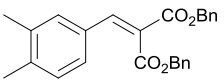
Reactions were carried out using commercial available reagents in over-dried apparatus. $CH_2ClCH_2Cl$ and $CHCl_2CHCl_2$ were dried over powdered $CaH_2$ and distilled under nitrogen just before use. Optical rotation was measured with a Perkin-Elmer model 241 polarimeter. Specific rotations are reported as follows: $[\alpha]_D^T$ (*c*: g/100 mL, in $CH_2Cl_2$, unless otherwise noted, $\lambda$ = 589 nm). The unit is deg•cm$^3$•g$^{-1}$•dm$^{-1}$. All ee values were determined by high-performance liquid chromatography (HPLC) and supercritical fluid chromatography (SFC) on systems of an Agilent 1100 or 1200 series with chiral stationary phases (Chiralpak IA, Chiralpak IC, Chiralpak IE) from Chiral Technologies Inc. The enantiomers were identified and confirmed by comparing their HPLC or SFC retention times with those of authentic racemates. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on an Agilent 400 MHz spectrometer. The chemical shifts were given in ppm relative to the residual peak of the non-deuterated solvent ($CDCl_3$ 7.26 ppm). $^1$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (in Hz), integration. $^{13}C\{^1H\}$ NMR data was collected at 100 MHz with complete proton decoupling ($CDCl_3$ 77.0 ppm). $^{19}$F NMR: chemical shifts $\delta$ are given relative to $CFCl_3$ (external reference, $\delta$ $^{19}F(CFCl_3)$ = 0). IR spectra were recorded on Pierkin Elmer 100 FT/IR spectrometer, and the wave numbers of the absorption peaks are given in cm$^{-1}$. Mass spectra (MS) were acquired on a Finnigan SSQ 7000 spectrometer [electron spray ionization (ESI), 70 eV]. High resolution mass spectra (HRMS) analyses were recorded on a Thermo Scientific LTQ Orbitrap XL with positive ion mode. Reactions were monitored by thin layer chromatography (TLC) from Merck. Column chromatography was performed using silica gel 60 (63–200 μm) from Merck.

## 2. Preparation of alkylidene malonates, *N*-allenamides and *N,N'*-dioxides

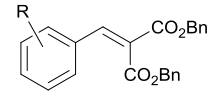
Alkylidene malonates **1a-1z** were prepared according to the literature.[1]

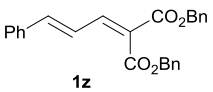


**1a**: R = Me;
**1b**: R = Et;
**1c**: R = $^i$Pr;
**1d**: R = benzyl.



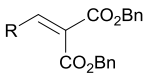
**1n**



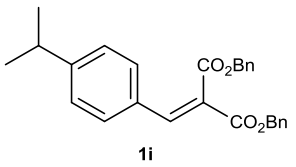


**1z**

**1e**: R = 4-F;
**1f**: R = 4-Cl;
**1g**: R = 4-Br;
**1h**: R = 4-Me;
**1i**: R = 4-$^i$Pr;
**1j**: R = 4-Ph;
**1k**: R = 3-Cl;
**1l**: R = 3-Br;
**1m**: R = 3-Me;
**1o**: R = 2-Cl;
**1p**: R = 2-Me.

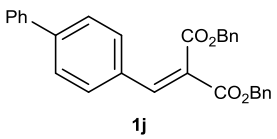


**1q**: R = 2-naphthyl;
**1r**: R = 2-thienyl;
**1s**: R = 2-benzothienyl;
**1t**: R = 2-furanyl;
**1u**: R = 2-benzofuranyl;
**1v**: R = $^i$Pr;
**1w**: R = cyclohexyl;
**1x**: R = $^i$Bu;
**1z**: R = $^n$Bu.



**1i**

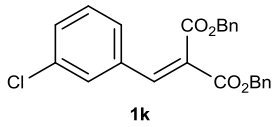
**Dibenzyl 2-(4-isopropylbenzyidene)malonate 1i** White solid; m.p. 54-57 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.76 (s, 1H), 7.36 – 7.21 (m, 12H), 7.12 – 7.09 (m, 2H), 5.28 (s, 2H), 5.26 (s, 2H), 2.96 – 2.80 (m, 1H), 1.21 (d, *J* = 7.2 Hz, 6H). **$^{13}C\{1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 166.5, 164.0, 152.0, 143.2, 135.5, 134.8, 130.1, 129.7, 128.8, 128.5, 128.4, 128.3, 128.2, 127.9, 126.9, 124.4, 67.4, 67.0, 34.0, 23.6. **IR (KBr)**: 2363, 1730, 1615, 1259, 1207, 1058, 746, 692. **HRMS** (ESI-FT) calcud for $C_{27}H_{26}O_4Na^+$ [M+Na$^+$] = 437.1723, Found 437.1723.



**1j**

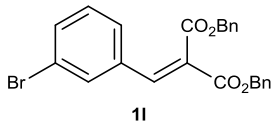
**Dibenzyl 2-[(1,1'-biphenyl)-4-ylmethylene] malonate 1j** White solid; m.p. 86-87 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.80 (s, 1H), 7.57 – 7.54 (m, 2H), 7.48 – 7.37 (m, 8H), 7.38 – 7.34 (m, 5H), 7.30 – 7.28 (s, 4H), 5.31 (s, 2H), 5.27 (s, 2H). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 166.4, 163.8, 143.3, 142.7, 139.8, 135.5, 134.8, 131.4, 130.1, 128.9, 128.53, 128.50, 128.4, 128.2, 127.98, 127.95, 127.3, 127.0, 125.2, 67.5, 67.1. **IR**

**(KBr)**: 2361, 1724, 1621, 1261, 1215, 1190, 1061, 757, 691. **HRMS** (ESI-FT) calcd for $C_{30}H_{24}O_4Na^+$ [M+Na$^+$] = 471.1567, Found 471.1566.



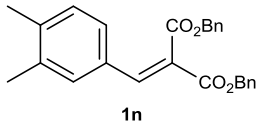
**1k**

**Dibenzyl 2-(3-chlorobenzylidene)malonate 1k** White solid; m.p. 58-61 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.38 – 7.36 (m, 1H), 7.35 – 7.33 (m, 5H), 7.30 – 7.23 (m, 6H), 7.21 – 7.16 (m, 1H), 7.15 – 7.10 (m, 1H), 5.26 (d, *J* = 1.6 Hz, 4H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 165.7, 163.3, 141.3, 135.2, 134.6, 134.5, 134.3, 130.4, 129.9, 129.2, 128.7, 128.5, 128.4, 128.3, 128.0, 127.2, 127.0, 67.6, 67.3. **IR (KBr)**: 2361, 1732, 1630, 1260, 1202, 1067, 735, 691. **HRMS** (ESI-FT) calcd for $C_{24}H_{19}{}^{34.9689}ClO_4Na^+$ [M+Na$^+$] = 429.0864, Found 429.0867. $C_{24}H_{19}{}^{36.9659}ClO_4Na^+$ [M+Na$^+$] = 431.0835, Found 431.0837.



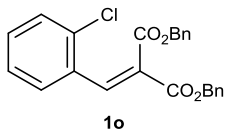
**1l**

**Dibenzyl 2-(3-bromobenzylidene)malonate 1l** White solid; m.p. 64-67 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.55 – 7.54 (m, 1H), 7.47 – 7.45 (m, 1H), 7.36 – 7.32 (m, 5H), 7.30 – 7.22 (m, 6H), 7.10 – 7.06 (m, 1H), 5.26 (s, 4H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 165.7, 163.4, 141.3, 135.2, 134.7, 134.6, 133.3, 132.2, 130.2, 128.7, 128.6, 128.5, 128.3, 128.0, 127.6, 127.1, 122.8, 67.7, 67.3. **IR (KBr)**: 2631, 1724, 1683, 1257, 1193, 1061, 752, 693. **HRMS** (ESI-FT) calcd for $C_{24}H_{19}{}^{78.9183}BrO_4Na^+$ [M+Na$^+$] = 473.0359, Found 473.0341. $C_{24}H_{19}{}^{80.9163}BrO_4Na^+$ [M+Na$^+$] = 475.0338, Found 475.0341.



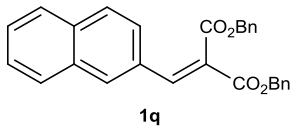
**1n**

**Dibenzyl 2-(3,4-dimethylbenzylidene)malonate 1n** White solid; m.p. 64-66 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.34 – 7.29 (m, 5H), 7.28 – 7.27 (m, 5H), 7.15 – 7.14 (m, 1H), 7.11 – 7.08 (m, 1H), 7.01 – 6.98 (m, 1H), 5.28 (s, 2H), 5.25 (s, 2H), 2.21 (s, 3H), 2.14 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 166.6, 164.0, 143.3, 140.0, 137.0, 135.0, 134.9, 130.9, 130.1, 130.0, 128.53, 128.45, 128.4, 128.31, 128.26, 128.2, 128.1, 127.9, 127.0, 124.2, 67.3, 66.9, 19.7, 19.6. **IR (KBr)**: 2631, 1722, 1627, 1265, 1207, 1066, 752, 700. **HRMS** (ESI-FT) calcd for $C_{26}H_{24}O_4Na^+$ [M+Na$^+$] = 423.1567, Found 423.1566.



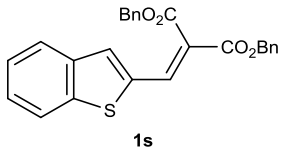
**1o**

**Dibenzyl 2-(2-chlorobenzylidene)malonate 1o** White solid; m.p. 62-65 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.39 – 7.33 (m, 6H), 7.29 – 7.22 (m, 5H), 7.20 – 7.16 (m, 2H), 7.02 – 6.97 (m, 1H), 5.29 (s, 2H), 5.19 (s, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 165.4, 163.3, 140.2, 135.3, 134.7, 134.6, 131.6, 131.2, 129.7, 129.2, 128.6, 128.5, 128.4, 128.34, 128.26, 128.1, 128.0, 126.8, 67.4, 67.3. **IR (KBr)**: 2631, 1728, 1629, 1248, 1209, 1065, 752, 696. **HRMS** (ESI-FT) calcd for $C_{24}H_{19}{}^{35}ClO_4Na^+$ [M+Na$^+$] = 429.0864, Found 429.0866. $C_{24}H_{19}{}^{37}ClO_4Na^+$ [M+Na$^+$] = 431.0835, Found 431.0835.



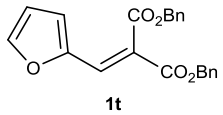
**1q**

**Dibenzyl 2-(naphthalen-2-ylmethylene)malonate 1q** White solid; m.p. 69-73 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.87 – 7.86 (m, 1H), 7.78 – 7.75 (m, 1H), 7.71 – 7.68 (m, 1H), 7.67 – 7.64 (m, 1H), 7.54 – 7.19 (m, 13H), 5.30 (d, *J* = 7.5 Hz, 4H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 166.4, 163.9, 143.2, 135.5, 134.8, 134.0, 132.9, 131.1, 130.1, 128.74, 128.71, 128.54, 128.48, 128.4, 128.2, 128.0, 127.7, 127.6, 126.6, 125.5, 125.1, 67.5, 67.2. **IR (KBr)**: 2360, 1730, 1620, 1242, 1205, 1172, 1062, 740, 697. **HRMS** (ESI-FT) calcd for $C_{28}H_{22}O_4Na^+$ [M+Na$^+$] = 445.1410, Found 445.1409.



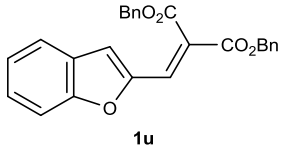
**1s**

**Dibenzyl 2-(benzo[*b*]thiophen-2-ylmethylene)malonate 1s** White solid; m.p. 97-102 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.72 – 7.67 (m, 2H), 7.47 – 7.46 (m, 1H), 7.39 – 7.35 (m, 2H), 7.34 – 7.25 (m, 10H), 5.40 (s, 2H), 5.24 (s, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 165.7, 163.6, 141.9, 138.4, 135.9, 135.6, 135.3, 134.8, 132.1, 128.7, 128.5, 128.4, 128.3, 128.2, 127.9, 126.6, 124.8, 124.7, 123.8, 122.2, 67.8, 67.1. **IR (KBr)**: 1718, 1618, 1238, 1202, 1141, 1063, 750, 698. **HRMS** (ESI-FT) calcd for $C_{26}H_{20}O_4SNa^+$ [M+$Na^+$] = 451.0975, Found 451.0975.



**1t**

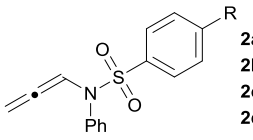
**Dibenzyl 2-(furan-2-ylmethylene)malonate 1t** White solid; m.p. 97-100 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.38 – 7.35 (m, 2H), 7.34 – 7.28 (m, 8H), 7.26 – 7.25 (m, 1H), 6.67 – 6.65 (m, 1H), 6.39 – 6.37 (m, 1H), 5.34 (s, 2H), 5.23 (s, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 165.8, 163.8, 148.7, 146.2, 135.4, 135.2, 128.7, 128.4, 128.3, 128.2, 128.1, 127.8, 121.1, 118.3, 112.5, 67.2, 66.9. **IR (KBr)**: 2361, 1724, 1687, 1631, 1261, 1209, 1053, 748, 696. **HRMS** (ESI-FT) calcd for $C_{22}H_{18}O_5Na^+$ [M+$Na^+$] = 385.1046, Found 385.1046.



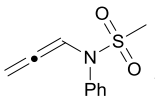
**1u**

**Dibenzyl 2-(benzofuran-2-ylmethylene)malonate 1u** White solid; m.p. 114-117 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.55 – 7.52 (m, 1H), 7.41 – 7.37 (m, 2H), 7.36 – 7.32 (m, 5H), 7.32 – 7.27 (m, 4H), 7.26 – 7.19 (m, 2H), 7.00 – 6.99 (m, 1H), 5.42 (s, 2H), 5.27 (s, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 165.7, 163.6, 156.0, 150.0, 135.3, 135.2, 128.54, 128.51, 128.30, 128.26, 128.0, 127.7, 127.2, 124.0, 123.5, 122.1, 114.4, 111.5, 67.6, 67.3. **IR (KBr)**: 2365, 1732, 1695, 1629, 1238, 1219, 1058, 758, 700. **HRMS** (ESI-FT) calcd for $C_{26}H_{20}O_5Na^+$ [M+$Na^+$] = 435.1203, Found 435.1203.

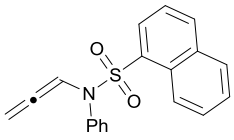
*N*-allenamides **2a-g** were prepared according to the literature.[2]



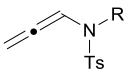
**2a**: R = Me;
**2b**: R = H;
**2c**: R = MeO;
**2d**: R = $^t$Bu.



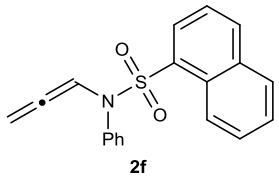
**2e**



**2f**



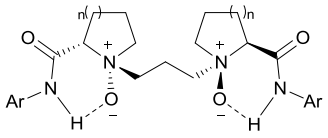
**2g**: R = 4-Me$C_6H_4$;
**2h**: R = benzyl.



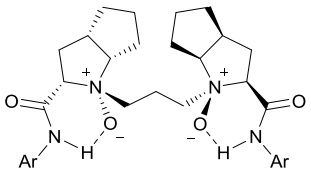
**2f**

***N*-Phenyl-*N*-(propa-1,2-dien-1-yl)naphthalene-1-sulfonamide 2f** White solid; m.p. 103-106 ºC. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.55 – 8.52 (m, 1H), 8.07 – 8.01 (m, 2H), 7.91 – 7.88 (m, 1H), 7.58 – 7.51 (m, 2H), 7.42 – 7.38 (m, 1H), 7.31 – 7.27 (m, 1H), 7.24 – 7.13 (m, 3H), 6.96 – 6.93 (m, 2H), 4.97 (d, *J* = 6.4 Hz, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 200.8, 136.7, 134.7, 134.1, 133.6, 130.9, 129.7, 128.8, 128.63, 128.61, 128.5, 128.1, 126.8, 125.0, 124.0, 102.4, 87.5. **IR (KBr)**: 2359, 1728, 1492, 1440, 1353, 1262, 1165, 1084, 898, 700, 574. **HRMS** (ESI-FT) calcd for $C_{19}H_{15}NO_2SNa^+$ [M+$Na^+$] = 344.0716, Found 344.0715.

Chiral *N,N'*-dioxides were prepared accoding to the literature.[3]

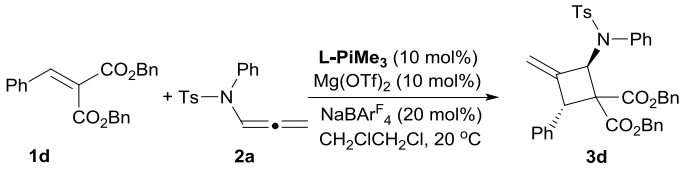


**L-PrPr$_2$**: Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$, n = 1
**L-PiPr$_2$**: Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$, n = 2
**L-PiEt$_2$**: Ar = 2,6-Et$_2$C$_6$H$_3$, n = 2
**L-PiEt$_2$Me**: Ar = 2,6-Et$_2$-4-MeC$_6$H$_2$, n = 2
**L-PiMe$_2$**: Ar = 2,6-Me$_2$C$_6$H$_3$, n = 2
**L-PiMe$_3$**: Ar = 2,4,6-Me$_3$C$_6$H$_2$, n = 2
**L-PiMe$_2$$^t$Bu**: Ar = 2,6-Me$_2$-4-$^t$BuC$_6$H$_2$, n = 2
**L-PiPh**: Ar = phenyl, n = 2
**L-PiCy**: Ar = cyclohexyl, n = 2
**L-PiBn**: Ar = benzyl, n = 2



**L-RaPr$_2$**: Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$

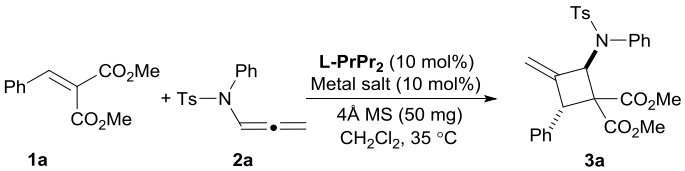
## 3. General procedure for the catalytic asymmetric [2+2] cycloaddition




A dry reaction tube was charged with **L-PiMe$_3$** (0.01 mmol, 5.6 mg), Mg(OTf)$_2$ (0.01 mmol, 3.2 mg), alkylidene malonate **1d** (0.10 mmol, 39.2 mg) and NaBAr$^F_4$ (0.02 mmol, 17.6 mg). Under $N_2$ atmosphere, $CH_2ClCH_2Cl$ (1.0 mL) was added. The mixture was stirred at 35 ºC for 15 min and then cooled to 20 ºC. Then *N*-allenamide **2a** (0.20 mmol, 57.0 mg) were added under stirring and the reaction mixture continued stirring at 20 ºC for 48 h. The product was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). The major isomer of the product **3d** was obtained in 99% yield (65.5 mg). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel Chiralcel **IE** (90% ee).

## 4. Optimization of the reaction conditions

### (a) Screening of metal salts[a]

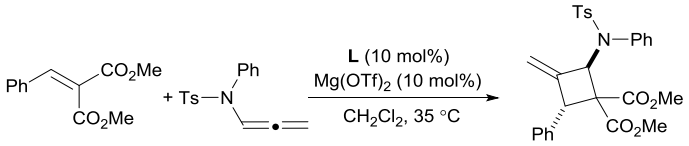



| Entry | Metal salt | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|
| 1 | Sc(OTf)$_3$ | 3 | race |
| 2 | Fe(OTf)$_3$ | < 2 | 5 |
| 3 | Fe(OTf)$_2$ | N.R.[f] | -- |
| 4 | Ni(OTf)$_2$ | < 2 | 60 |
| 5 | Zn(OTf)$_2$ | < 2 | 38 |
| 6 | Y(OTf)$_3$ | 60 | race |

| | | | |
|---|---|---|---|
| 7 | $La(OTf)_3$ | 18 | 4 |
| 8 | $Yb(OTf)_3$ | 70 | race |
| 9 | $Mg(OTf)_2$ | 3 | 46 |
| 10[d] | $Mg(OTf)_2$ | 12 | 46 |
| 11[e] | $Mg(OTf)_2$ | 18 | 46 |
| 12 | $Mg(NTf_2)_2$ | 40 | 5 |
| 13 | $Mg(ClO_4)_2$ | 15 | 41 |

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), **L-PrPr$_2$**-Metal salt (1:1, 10 mol%) and 4Å MS (50.0 mg) in $CH_2Cl_2$ (1.0 mL) at 35 ºC under $N_2$ for 24 h. Dr values (> 95:5) were determined by $^1$H NMR of the crude mixture. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Without 4Å MS. [e] 48 h. [f] N.R. = no reaction.

## (b) Screening of ligands[a]

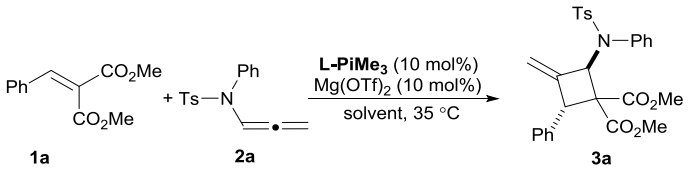



**1a** **2a** **3a**

| Entry | Ligand | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|
| 1 | **L-PrPr$_2$** | 18 | 46 |
| 2 | **L-RaPr$_2$** | 53 | 23 |
| 3 | **L-PiPr$_2$** | 29 | 47 |
| 4 | **L-PiPr$_3$** | 11 | 8 |
| 5 | **L-PiEt$_2$** | 56 | 67 |
| 6 | **L-PiEt$_2$Me** | 55 | 71 |
| 7 | **L-PiMe$_2$** | 59 | 69 |
| 8 | **L-PiMe$_3$** | 65 | 75 |
| 9 | **L-PiPh** | 53 | 9 |
| 10 | **L-PiCy** | 11 | 5 |
| 11 | **L-PiBn** | 31 | race |
| 12[d] | **L-PiMe$_3$** | N.R.[e] | -- |

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **L**-$Mg(OTf)_2$ (1:1, 10 mol%) in $CH_2Cl_2$ (1.0 mL) at 35 ºC under $N_2$ for 48 h. Dr values (> 95:5) were determined by $^1$H NMR of the crude mixture. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Carried out with $Mg(ClO_4)_2$ instead of $Mg(OTf)_2$. [e] N.R. = no reaction.

### (c) Screening of solvents[a]

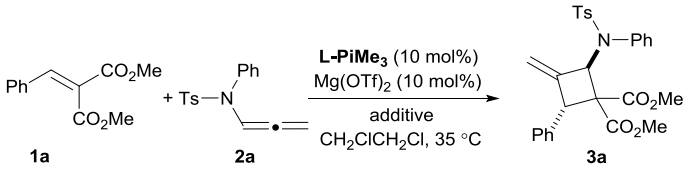



**1a** **2a** **3a**

| Entry | Solvent | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|
| 1 | THF | N.R.[d] | -- |
| 2 | Toluene | N.R.[d] | -- |
| 3 | EtOAc | N.R.[d] | -- |
| 4 | MeCN | < 2 | 69 |
| 5 | $Et_2O$ | 22 | 75 |
| 6 | $CH_2Cl_2$ | 65 | 75 |
| 7 | $CH_2ClCH_2Cl$ | 63 | 77 |
| 8 | $CHCl_3$ | 15 | 81 |
| 9 | $CHCl_2CHCl_2$ | 9 | 65 |

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **L-PiMe$_3$**-Mg(OTf)$_2$ (1:1, 10 mol%) in solvent (1.0 mL) at 35 ºC under $N_2$ for 48 h. Dr values (> 95:5) were determined by $^1$H NMR of the crude mixture. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] N.R. = no reaction.

### (d) Screen of additives[a]

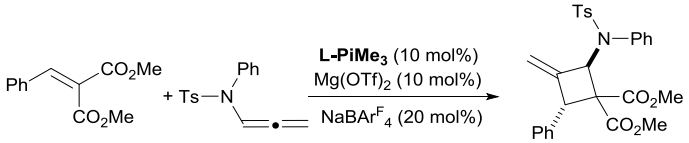



**1a** **2a** **3a**

| Entry | Additive | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|
| 1 | 4Å MS (20 mg) | N.R.[e] | -- |
| 2 | $NaBAr^F{}_4$ (20 mol%) | 80 | 79 |
| 3 | $LiNTf_2$ (20 mol%) | 82 | 75 |
| 4 | $H_2O$ (5 μL) | < 2 | 77 |
| 5[d] | 4Å MS (50 mg) | N.R.[e] | -- |

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), **L-PiMe$_3$**-Mg(OTf)$_2$ (1:1, 10 mol%) and additive in $CH_2ClCH_2Cl$ (1.0 mL) at 35 ºC under $N_2$ for 48 h. Dr values (> 95:5) were determined by $^1$H NMR of the crude mixture. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Carried out with $Mg(ClO_4)_2$ instead of Mg(OTf)$_2$. [e] N.R. = no reaction.

### (e) Screen of temperature[a]

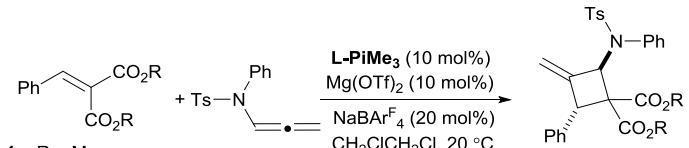



**1a** **2a** **3a**

| Entry | T (ºC) | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|
| 1 | 35 | 80 | 79 |
| 2 | 20 | 80 | 85 |
| 3 | 10 | 58 | 88 |
| 4 | 0 | 18 | 90 |
| 5 | –5 | 14 | 91 |
| 6 | –10 | 9 | 92 |
| 7 | –20 | 3 | 93 |

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), **L-PiMe$_3$**-Mg(OTf)$_2$ (1:1, 10 mol%) and NaBAr$^F{}_4$ (20 mol%) in $CH_2ClCH_2Cl$ (1.0 mL) under $N_2$ for 48 h. Dr values (> 95:5) were determined by $^1$H NMR of the crude mixture. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

### (f) Screen of the alkylidene malonate substrates[a]




**1a**: R = Me
**1d**: R = Bn

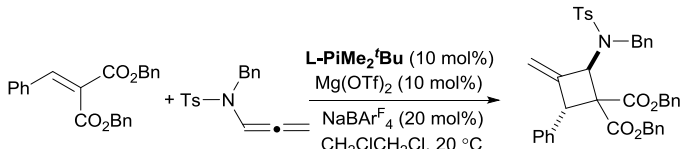
**2a**

**3a**: R = Me
**3d**: R = Bn

| Entry | Substrates | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|
| 1 | **1a** | 80 | 85 |
| 2 | **1d** | 86 | 90 |
| 3[d] | **1d** | 99 | 90 |

[a] Unless otherwise noted, all reactions were carried out with **1** (0.10 mmol), **2a** (0.10 mmol), **L-PiMe$_3$**-Mg(OTf)$_2$ (1:1, 10 mol%) and NaBAr$^F{}_4$ (20 mol%) in $CH_2ClCH_2Cl$ (1.0 mL) at 20 ºC under $N_2$ for 48 h. Dr values (> 95:5) were determined by $^1$H NMR of the crude mixture. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] 0.20 mmol of **2a** was used.

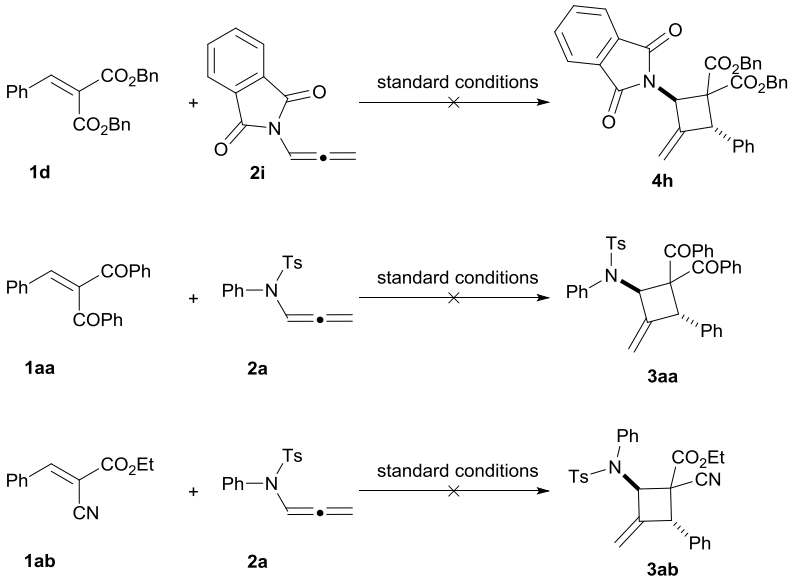
### (g) Failed examples




**1d** **2h**

**4g**
10% yield, 49% ee.

The reaction was carried out with **1d** (0.10 mmol), **2h** (0.20 mmol), **L-PiMe$_2$$^t$Bu**-Mg(OTf)$_2$ (1:1, 10 mol%) and NaBAr$^F{}_4$ (20 mol%) in $CH_2ClCH_2Cl$ (1.0 mL) at 20 ºC under $N_2$ for 48 h. Dr values (> 95:5) were determined by $^1$H NMR of the crude mixture.



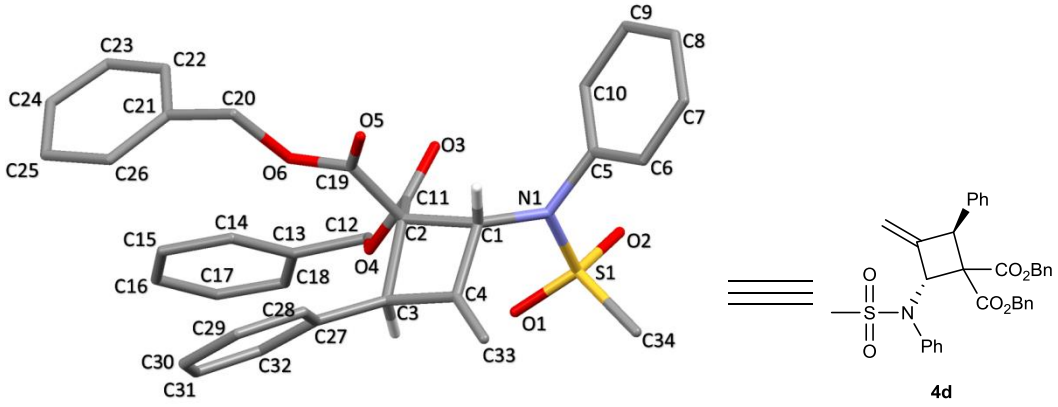

The reaction was carried out with **1** (0.10 mmol), **2** (0.20 mmol), **L-PiMe$_3$**-Mg(OTf)$_2$ (1:1, 10 mol%) and NaBAr$^F{}_4$ (20 mol%) in $CH_2ClCH_2Cl$ (1.0 mL) at 20 ºC under $N_2$ for 48 h.

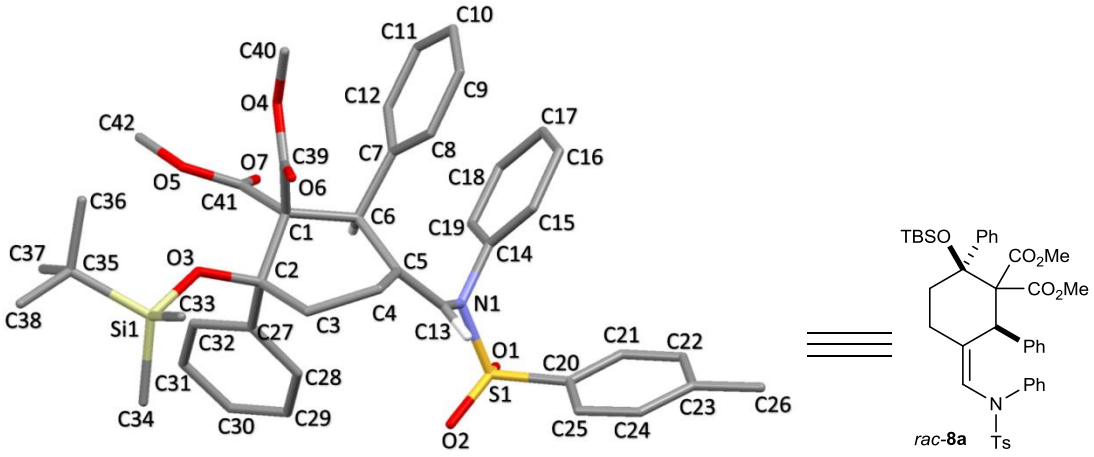
## 5. The X-ray data for 4d and *rac*-8a

Crystals of compound **4d** suitable for the X-ray crystal structure analysis were recrystallized from the mixture solution of petroleum ether and dimethylchloride (3/1, v/v) at room temperature.

Unfortunately, we didn't get the single crystal of enantioenriched compound **8a**. To determine the relative configuration of the product **8a**, we cultured the single crystals of compound *rac*-**8a** from the mixture solution of tetrahydrofuran and isopropanol (6/1, v/v) at room temperature.

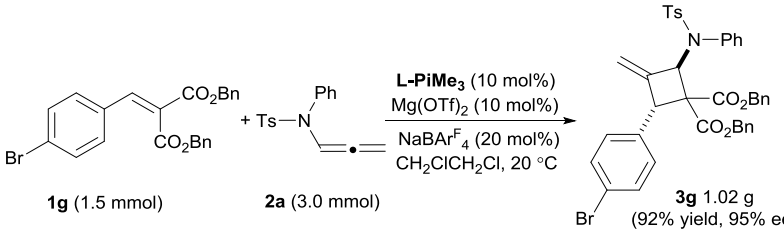
CCDC-1831461 (**4d**) and CCDC-1848226 (*rac*-**8a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif.





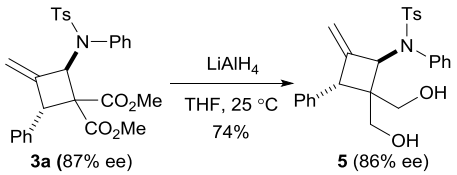

## 6. Experimental procedure for the scale-up reaction and transformations of the products

a) Scale-up version of the reaction

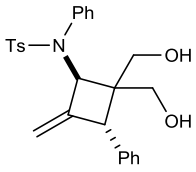



A dry round-bottom flask was charged with **L-PiMe$_3$** (0.15 mmol, 84.0 mg), Mg(OTf)$_2$ (0.15 mmol, 48.0 mg), alkylidene malonate **1g** (1.50 mmol 676.0 mg) and NaBAr$^F_4$ (0.30 mmol, 264.0 mg). Under $N_2$ atmosphere, $CH_2ClCH_2Cl$ (15.0 mL) was added. The mixture was stirred at 35 ºC for 30 min and then cooled to 20 ºC. Then *N*-allenamide **2a** (3.0 mmol, 855.0 mg) was added under stirring and the mixture continued stirring at 20 ºC for 72 h. The product was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8/1). The product **3g** was obtained in 92% yield (1016.0 mg). The enantiomeric excess (ee) of the product **3g** was determined by HPLC with Daicel Chiralcel **IE** (95% ee).

b) Reduction of the product **3a** by $LiAlH_4$

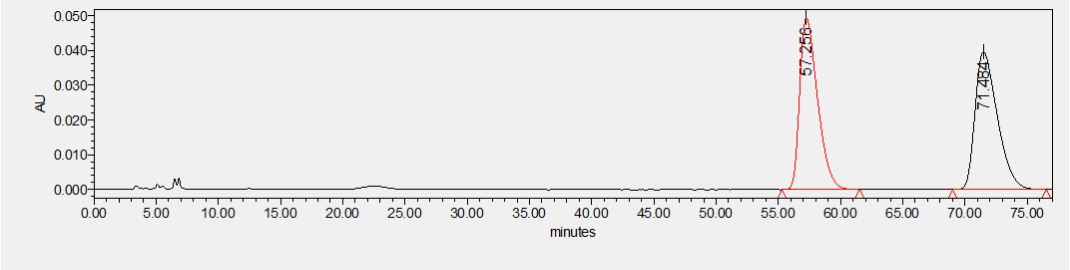



A dry tube was charged with compound **3a** (0.10 mmol, 50.5 mg) and $LiAlH_4$ (0.20 mmol, 7.6 mg). THF (1.0 mL) was added and the resulting reaction mixture was stirred at 25 ºC. After 2 h, the reaction was quenched by water (2.0 mL) and the aqueous phase was extracted by ethyl acetate (3 x 2.0 mL). The organic layer was dried by $Na_2SO_4$ and filtered. The solvent was removed under reduced pressure. The product was purified by column chromatograghy (petroleum ether/ethyl acetate = 1.5/1). The product **5** was obtained in 74% yield (33.2 mg). The enantiomeric excess (ee) was determined by HPLC with Daicel Chiralcel **IE** (86% ee).

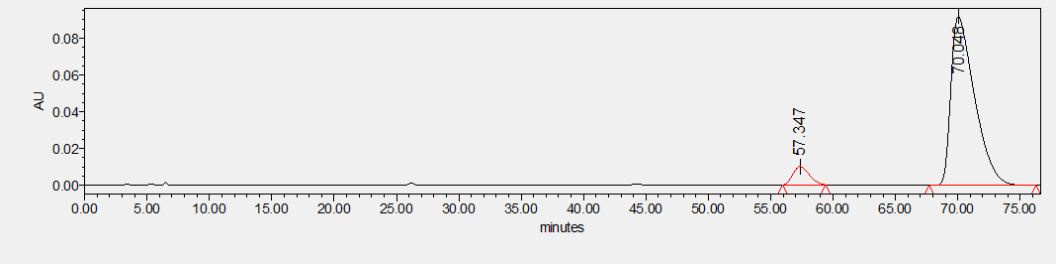



**5**

***N*-[2,2-Bis(hydroxymethyl)-4-methylene-3-phenylcyclobutyl]-4-methyl-*N*-phenylbenzenesulfonamide 5** The compound **5** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 1.5/1) to afford a colorless oil in 74% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 70.05 min, $t_r$ (minor) = 57.35 min, ee = 86%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{17.7}$ = +104.1 (*c* = 0.59 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.34 – 7.26 (m, 7H), 7.24 – 7.15 (m, 5H), 5.08 – 5.07 (m, 2H), 4.84 (s, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 3.88 (d, *J* = 11.2 Hz, 1H), 3.75 – 3.73 (m, 2H), 3.56 (d, *J* = 12.0 Hz, 1H), 3.34 (s, 1H), 2.46 – 2.40 (m, 4H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 144.7, 144.1, 137.8, 136.3, 135.3, 132.1, 129.6, 128.8, 128.7, 128.5, 128.2, 128.1, 127.2, 115.7, 66.1, 65.7, 64.5, 52.1, 51.8, 21.6. **IR (film)**: 3459, 1597, 1342, 1159, 898, 702, 577. **HRMS** (ESI-FT) calcd for $C_{26}H_{27}NO_4SNa$ ([M+Na$^+$]) = 472.1553, Found 472.1555.

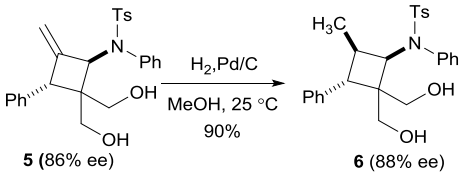



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 57.256 | 4930612 | 50.02 |
| 2 | 71.484 | 4926424 | 49.98 |



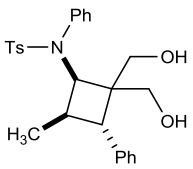

| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 57.347 | 909032 | 6.99 |
| 2 | 70.048 | 12102577 | 93.01 |

c) Reduction of the product **5** by Pd/C




**5** (86% ee) **6** (88% ee)

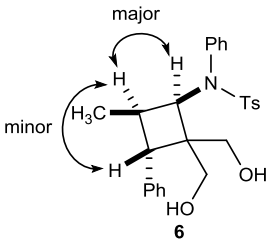
A dry tube was charged with product **5** (0.10 mmol, 45.0 mg) and Pd/C (10%, 9.0 mg). MeOH (1.0 mL) was added and the resulting mixture was stirred at 25 ºC under $H_2$ atmosphere (1.0 atm, $H_2$ balloon). After 12 h, the reaction mixture was filtered. The solvent was removed under reduced pressure. The product was purified by column chromatograghy (petroleum ether/ethyl acetate = 1.5/1). The product **6** was obtained in 90% yield (40.5 mg). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel Chiralcel **IA** (88% ee).



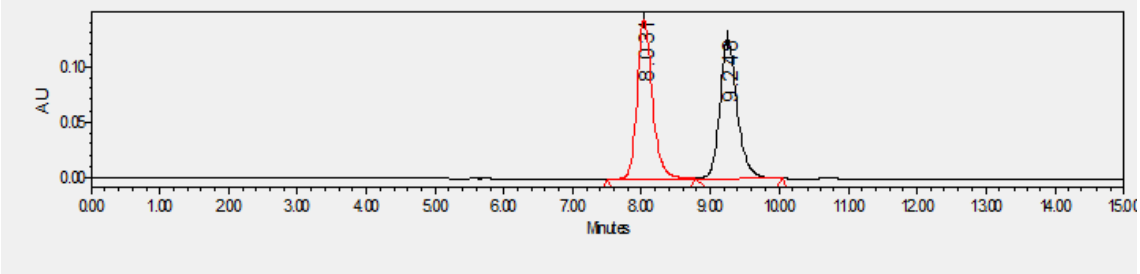

**6**

***N*-[2,2-Bis(hydroxymethyl)-4methyl-3-phenylcyclobutyl]-4-*N*-phenylbenzenesulfonamide 6** The compound **6** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 1.5/1) to afford a colorless oil in 90% yield. **Major diastereomer:** **HPLC** (Daicel Chiralcel **IA**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 9.23 min, $t_r$ (minor) = 8.04 min, ee = 88%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{22.4}$ = +69.3 (*c* = 1.03 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 13H), 6.92 – 6.91 (m, 1H), 4.41 (d, *J*=9.2, 1H), 4.24 (d, *J*=11.6, 1H), 4.12 – 4.02 (m, 1H), 3.90 – 3,85 (m, 1H), 3.51 – 3.46 (m, 1H), 3.25 – 3.23 (m, 1H), 2.90 – 2.74 (m, 2H), 2.43 (s, 3H), 1.87 – 1.83 (m, 1H), 0.81 (d, *J*=7.2, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 144.2, 140.1, 139.6, 132.0, 129.2, 128.8, 128.71, 128.67, 128.4, 128.2, 126.8, 67.5, 66.7, 58.9, 51.2, 49.0, 37.4, 21.6, 18.6. **IR (film)**: 3445, 1597, 1348, 1163, 702, 663, 592, 555. **HRMS** (ESI-FT) calcd for $C_{26}H_{29}NO_4SNa$ ([M+Na$^+$]) = 474.1710, Found 474.1711.

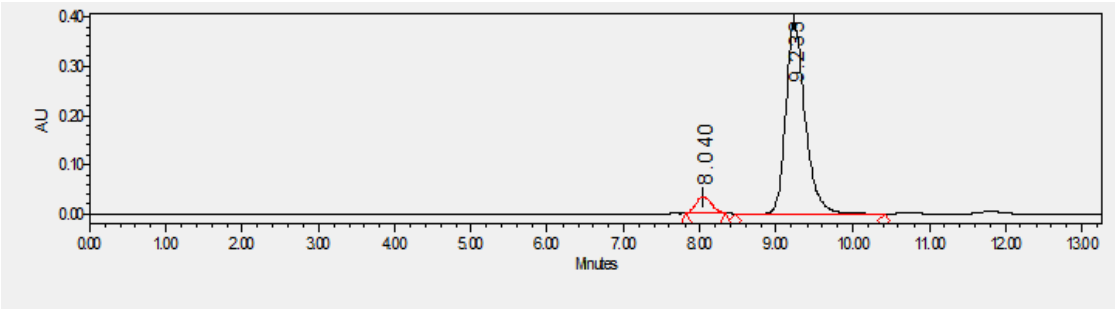
Relative configuration of **6** was determined by COSYGPSW and NOESYPHSW NMR spectra:




**6**

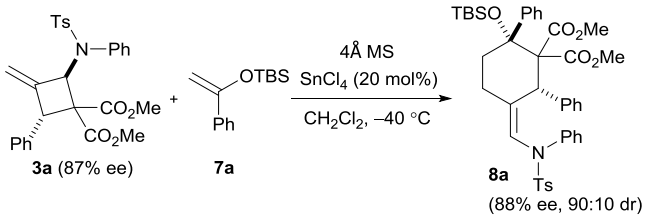



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 8.031 | 2182068 | 50.06 |
| 2 | 9.248 | 2176728 | 49.94 |

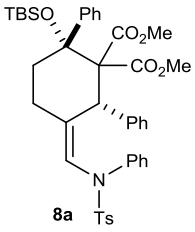



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 8.040 | 446781 | 6.05 |
| 2 | 9.233 | 6932017 | 93.95 |

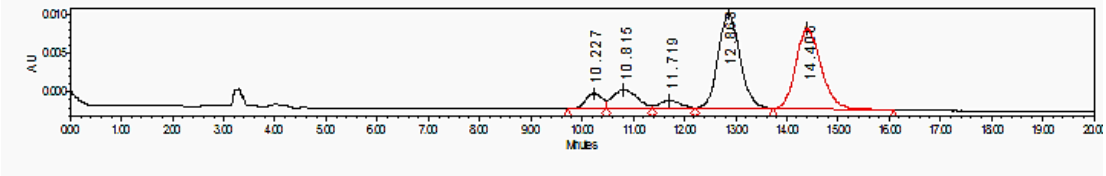
d) Formal [4+2] reaction of product **3a** and *tert*-butyldimethyl [(1-phenylvinyl)oxy] silane



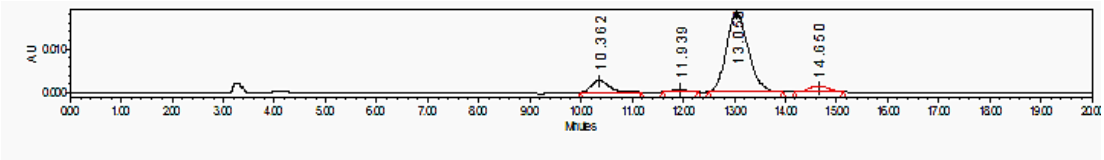

A dry reaction was tube charged with compound **3a** (0.10 mmol, 50.5 mg), *tert*-butyldimethyl [(1-phenylvinyl)oxy] silane (**7a**) (0.30 mmol, 70.2 mg) and 4Å MS (10 mg). $CH_2Cl_2$ (1.0 mL) was added at -40 ºC under $N_2$. A solution of $SnCl_4$ (0.20 mol/L in $CH_2Cl_2$, 20 mol%, 10.0 μL) was added dropwise and the reaction was stirred for 2 h at -40 ºC. The reaction was then quenched by adding $Et_3N$ (0.1 mL) and the solvent was removed under reduced pressure. The product was purified by column chromagraphy (petroleum ether/ethyl acetate = 8/1). The product **8a** was obtained in 44% yield (33.2 mg). The enantiomeric excess (ee) was determined by HPLC with Daicel Chiralcel **IC** (88% ee).



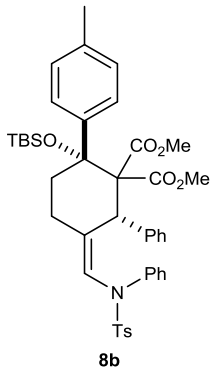

**Dimethyl (*Z*)-2-[(*tert*-butylaimethylsilyl)oxy]-5-{[(4-methyl-*N*-phenylphenyl)sulfonamido]methylene}-2,6-diphenylcyclohexane-1,1-dicarboxylate 8a** The compound **8a** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1) to afford a colorless oil in 44% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IC**, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 13.05 min, $t_r$ (minor) = 14.65 min, ee = 88%. dr = 90:10 (by $^1$H NMR). $[\alpha]_D^{17.7}$ = +23.8 (*c* = 0.92 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.23 (m, 2H), 7.10 – 7.07 (m, 3H), 7.02 – 6.96 (m, 5H), 6.89 – 6.85 (m, 2H), 6.84 – 6.79 (m, 5H), 6.54 – 6.52 (m, 2H), 6.07 (s, 1H), 4.49 (s, 1H), 3.49 – 3.38 (m, 1H), 3.22 (s, 3H), 2.80 – 2.71 (m, 4H), 2.52 – 2.42 (m, 2H), 2.25 – 2.20 (m, 3H), 0.77 (s, 9H), -0.00 (s, 3H), -0.39 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$): δ 169.7, 169.0, 145.6, 143.5, 140.2, 139.8, 139.5, 134.0, 129.1, 128.2, 127.96, 127.3, 127.2, 127.0, 126.7, 126.2, 121.6, 79.9, 71.4, 51.9, 51.2, 44.5, 37.9, 29.9, 25.9, 21.5, 18.8, -1.6, -2.6. **IR (film)**: 1724, 1487, 1448, 1359, 1256, 1169, 1086, 833, 698, 575. **HRMS** (ESI-FT) calcd for $C_{42}H_{49}NO_7SSiNa$ ([M+Na$^+$]) = 762.2891, Found 762.2891.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 10.227 | 42814 | 4.96 |
| 2 | 10.815 | 79271 | 9.17 |
| 3 | 11.719 | 28663 | 3.32 |
| 4 | 12.863 | 359856 | 41.65 |
| 5 | 14.406 | 353437 | 40.91 |

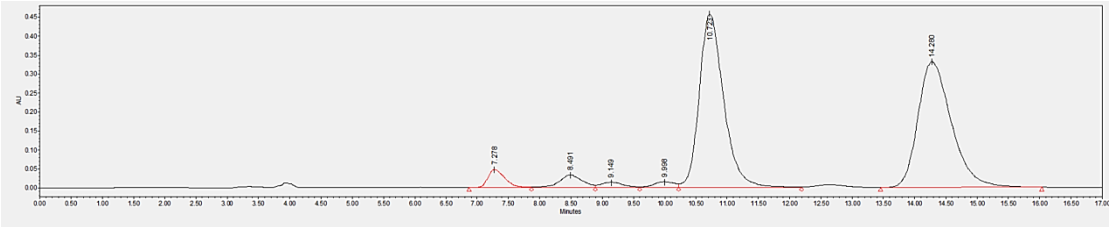



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 10.362 | 69086 | 10.54 |
| 2 | 11.939 | 15307 | 2.33 |
| 3 | 13.050 | 537300 | 81.95 |
| 4 | 14.650 | 33948 | 5.18 |

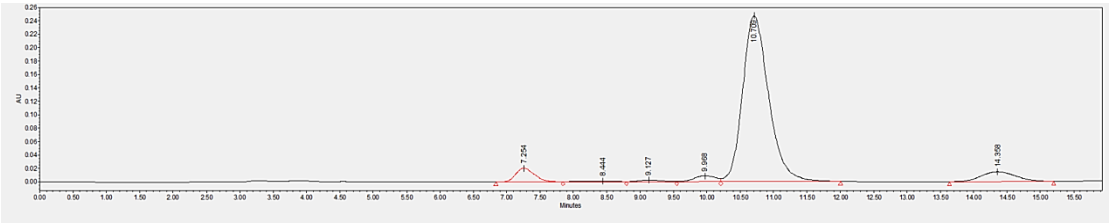


**8b**

**Dimethyl 2-[(*tert*-butyldimethylsilyloxy)]-5-{[(4-methyl-*N*-phenylphenyl)sulfonamido]methylene}-6-phenyl-2-(*p*-tolyl)cyclohexane-1,1-dicarboxylate 8b** The compound **8b** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1) to afford a colorless oil in 36% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IC**, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_r$ (major-major) = 10.709 min, $t_r$ (major-minor) = 14.358 min, ee = 87%. dr = 94:6 (by $^1$H NMR). $[\alpha]_D^{26.4}$ = +38.7 (*c* = 0.30 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33 – 7.28 (m, 10H), 7.24 – 7.20 (m, 2H), 7.15 – 7.03 (m, 6H), 5.49 (s, 1H), 4.94 (s, 1H), 3.46 (s, 3H), 3.39 (s, 3H), 2.99 – 2.86 (m, 1H), 2.74 – 2.65 (m, 1H), 2.41 – 2.29 (m, 7H), 2.03 – 1.87 (m, 1H), 1.01 (s, 9H), 0.00 (s, 3H), -0.36 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 168.8, 168.3, 143.3, 141.8, 140.5, 140.4, 137.8, 137.0, 134.3, 129.1, 128.7, 127.8, 127.7, 127.6, 127.6, 126.8, 126.3, 126.3, 123.8, 80.2, 71.4, 51.43, 51.35, 50.9, 34.2, 26.2, 23.9, 21.5, 21.0, 19.1, -1.5, -2.4. **IR (film)**:1731, 1486, 1459, 1359, 1248, 1167, 1059, 834, 704, 585. **HRMS (ESI-FT)** calcd for $C_{43}H_{51}NO_7SSiNa$ ([M+Na$^+$]) = 776.3048, Found 776.3041.

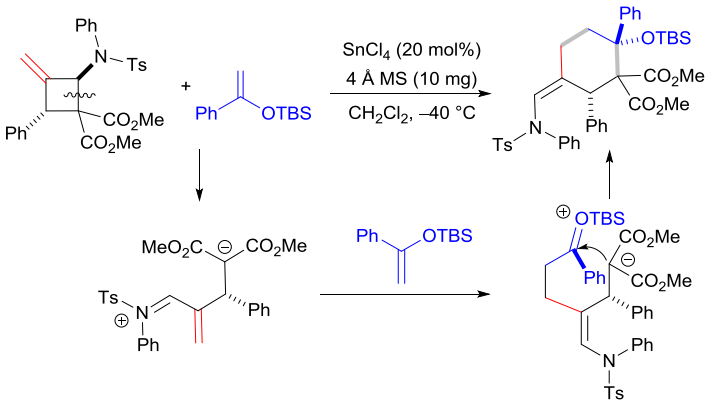



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 7.278 | 889357 | 3.27 |
| 2 | 8.491 | 852360 | 3.13 |
| 3 | 9.149 | 345186 | 1.27 |
| 4 | 9.998 | 346058 | 1.27 |
| 5 | 10.723 | 12445795 | 45.73 |
| 6 | 14.280 | 12335056 | 45.33 |



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 7.254 | 400741 | 5.06 |
| 2 | 8.444 | 42210 | 0.53 |
| 3 | 9.127 | 58378 | 0.74 |
| 4 | 9.968 | 190524 | 2.40 |
| 5 | 10.709 | 6705390 | 84.63 |
| 6 | 14.358 | 525783 | 6.64 |

Proposed mechanism of the formal [4+2] reaction:



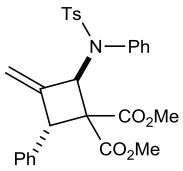

## 7. References


[1] (a) C.-K. Sha and R.-S. Lee, *Tetrahedron*, 1995, **51**, 193; (b) H. Mukherjee and C. A. Martinez, *ACS Catal.*, 2011, **1**, 1010; (c) O. A. Ivanova, E. M. Budynina, A. O. Chagarovskiy, A. E. Kaplum, I. V. Trushkov and M. Y. Melnikov, *Adv. Synth. Catal.*, 2011, **353**, 1125; d) F. Nanteuil and J. Waser, *Angew Chem., Int. Ed.*, 2013, **52**, 9009; (e) M. Skvorcova, L. Grigotjeve and A. Jirgensons, *Org. Lett.*, 2015, **17**, 2902; (f) W. W. Luo, X. Yuan, L. L. Lin, P. F. Zhou, X. H. Liu and X. M. Feng, *Chem. Sci.*, 2016, **7**, 4736.

[2] S. Suárez-Pantiga, C. Hernández-Díaz, M. Piedrafita, E. Rubio and J. González, *Adv. Synth. Catal.*, 2012, **354**, 1651.

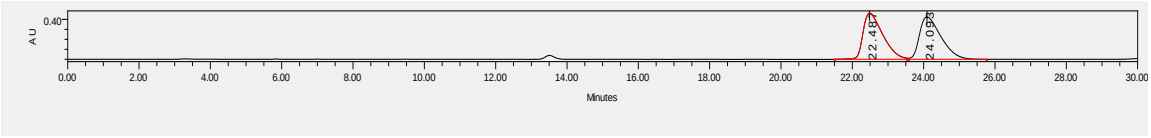
[3] Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett*, 2005, 2445.

## 8. The analytical and spectral characterization data of the products




**3a**

**Dimethyl 2-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-4-phenylcyclobutane-1,1-dicarboxylate 3a** The compound **3a** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 99% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 24.61 min, $t_r$ (minor) = 23.12 min, ee = 87%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{26.8}$ = +46.7 (*c* = 0.92 in $CH_2Cl_2$, ). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.36 – 7.25 (m, 5H), 7.23 – 7.22 (m, 5H), 7.16 – 7.13 (m, 2H), 6.13 – 6.12 (m, 1H), 5.20 (s, 1H), 5.09 (s, 1H), 4.87 – 4.85 (m, 1H), 3.85 (s, 3H), 3.12 (s, 3H), 2.42 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 168.3, 168.0, 145.5, 143.5, 137.9, 137.4, 136.1, 131.525 129.3, 128.7, 128.6, 128.4, 128.1, 127.8, 127.6, 114.6, 65.3, 64.8, 53.4, 52.9, 52.3, 21.5. **IR (film)**: 1732, 1493, 1440, 1271, 1163, 1088, 700, 573. **HRMS** (ESI-FT) calcd for $C_{28}H_{27}NO_6SNa$ ([M+Na$^+$]) = 528.1451, Found 528.1447.




| | Retention Time | Area | % Area |
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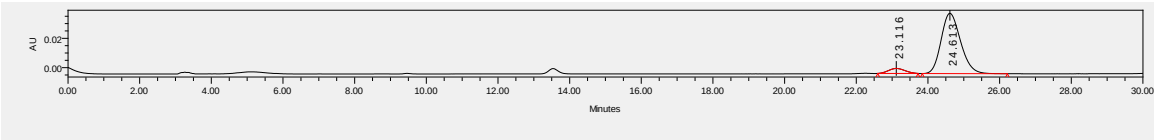
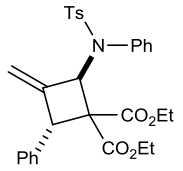
| 2 | 24.093 | 17815572 | 49.96 |

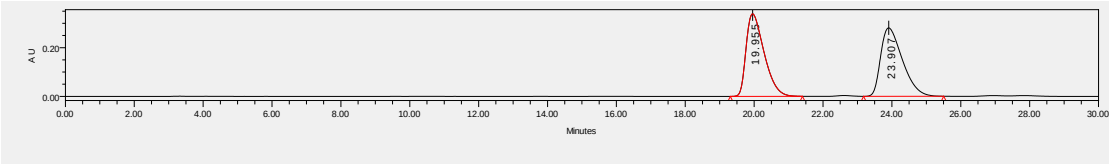



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 23.116 | 107723 | 6.51 |
| 2 | 24.613 | 1547340 | 93.49 |

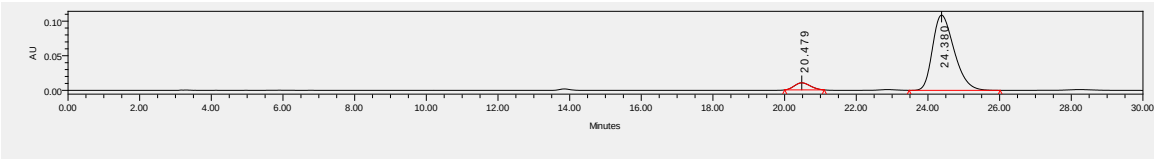



**3b**

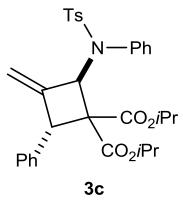
**Diethyl 2-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-4-phenylcyclobutane-1,1-dicarboxylate 3b** The compound **3b** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 95% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 24.38 min, $t_r$ (minor) = 20.48 min, ee = 87%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{28.0}$ = +42.9 (*c* = 0.84 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.34 – 7.15 (m, 12H), 6.15 – 6.12 (m, 1H), 5.19 – 5,18 (m, 1H), 5.08 – 5.07 (m, 1H), 4.87 – 4.83 (m, 1H), 4.41 – 4.32 (m, 1H), 4.29 – 4.02 (m, 1H), 3.77 – 3.68 (m, 1H), 3.57 – 3.48 (m, 1H), 2.42 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.68 (t, *J* = 7.2 Hz, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.8, 167.7, 145.7, 143.4, 137.9, 137.5, 136.2, 131.5, 129.2, 128.62, 128.57, 128.5, 128.0, 127.8, 127.5, 114.4, 65.2, 64.5, 61.9, 61.4, 53.1, 21.5, 13.8, 13.3. **IR (film)**: 1728, 1493, 1452, 1265, 1163, 1089, 898, 702, 574. **HRMS** (ESI-FT) calcd for $C_{30}H_{31}NO_6SNa$ ([M+Na$^+$]) = 556.1764, Found 556.1763.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 19.955 | 12288063 | 49.99 |
| 2 | 23.907 | 12293277 | 50.01 |

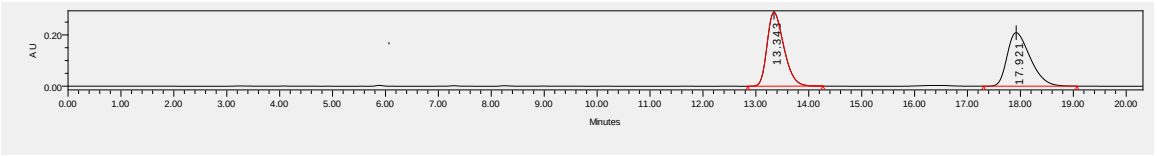



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 20.479 | 315852 | 6.51 |
| 2 | 24.380 | 4539412 | 93.49 |




**3c**

**Diisopropyl 2-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-4-phenylcyclobutane-1,1-dicarboxylate 3c** The compound **3c** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1) to afford a colorless oil in 31% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 17.93 min, $t_r$ (minor) = 13.42 min, ee = 67%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{25.9}$ = +30.7 (*c* = 0.29 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.30 – 7.14 (m, 12H), 6.07 – 6.06 (m, 1H), 5.23 – 5.15 (m, 2H), 5.01 (s, 1H), 4.82 – 4.80 (m, 1H), 4.59 – 4.51 (m, 1H), 2.42 (s, 3H), 1.48 (d, *J* = 6.4 Hz, 3H), 1.29 (d, *J* = 6.0 Hz, 3H), 1.01 (d, *J* = 6.0 Hz, 3H), 0.34 (d, *J* = 6.0 Hz, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.39, 167.36, 145.6, 143.4, 138.1, 137.6, 136.2, 131.6, 129.2, 128.9, 128.6, 128.5, 128.1, 127.8, 127.4, 114.3, 69.9, 69.3, 65.5, 64.5, 53.3, 21.7, 21.6, 21.4, 20.4. **IR (film)**: 1727, 1494, 1458, 1273, 1165, 1101, 903, 700, 572. **HRMS** (ESI-FT) calcd for $C_{32}H_{35}NO_6SNa$ ([M+Na$^+$]) = 584.2077, Found 584.2073.




| | Retention Time | Area | % Area |
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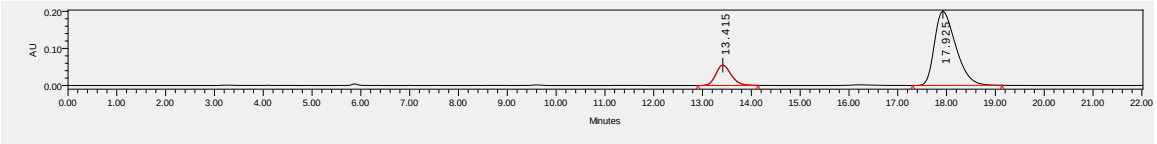
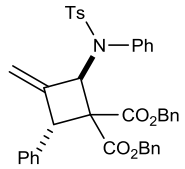
| 2 | 17.921 | 6299110 | 49.87 |

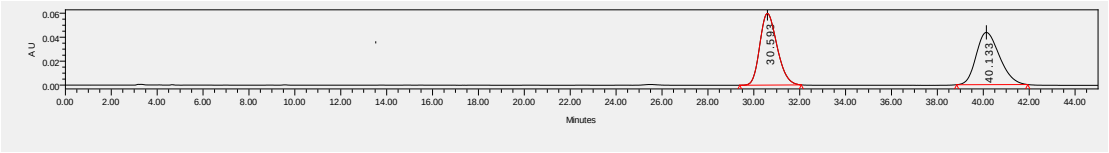



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 13.415 | 1191033 | 16.44 |
| 2 | 17.925 | 6054217 | 83.56 |




**3d**

**Dibenzyl 2-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-4-phenylcyclobutane-1,1-dicarboxylate 3d** The compound **3d** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 99% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 40.34 min, $t_r$ (minor) = 30.79 min, ee = 90%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.9}$ = +31.5 (*c* = 1.08 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.32 – 7.21 (m, 12H), 7.20 – 7.16 (m, 5H), 7.15 – 7.10 (m, 3H), 6.76 – 6.73 (m, 2H), 6.16 – 6.14 (m, 1H), 5.32 (d, *J* = 12.0 Hz, 1H), 5.20 (s, 1H), 5.14 – 5.07 (m, 2H), 4.95 – 4.93 (m, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.24 (d, *J* = 12.0 Hz, 1H), 2.40 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.5, 145.7, 143.5, 138.1, 137.4, 136.1, 135.1, 134.6, 131.5, 129.2, 128.64, 128.62, 128.56, 128.39, 128.35, 128.2, 128.1, 127.9, 127.8, 127.6, 114.4, 67.8, 67.3, 65.6, 64.8, 53.4, 21.5. **IR (film)**: 1730, 1494, 1452, 1265, 1163, 1086, 900, 700, 574. **HRMS** (ESI-FT) calcd for $C_{40}H_{35}NO_6SNa$ ([M+Na$^+$]) = 680.2077, Found 680.2073.




| | Retention Time | Area | % Area |
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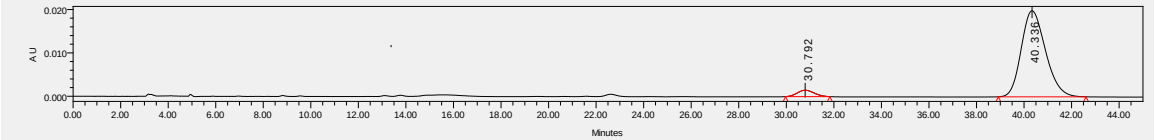
| 2 | 40.133 | 3069453 | 49.56 |

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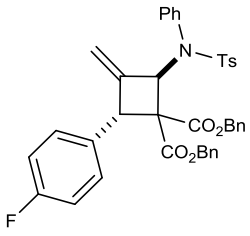
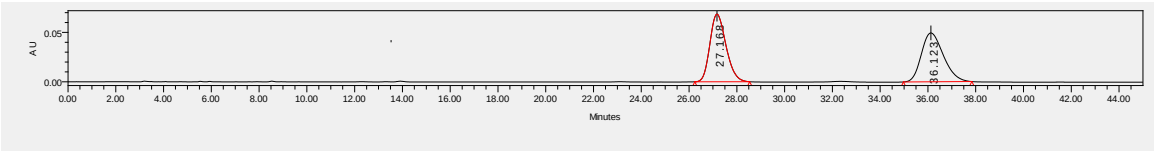
| 2 | 40.336 | 1404609 | 95.06 |

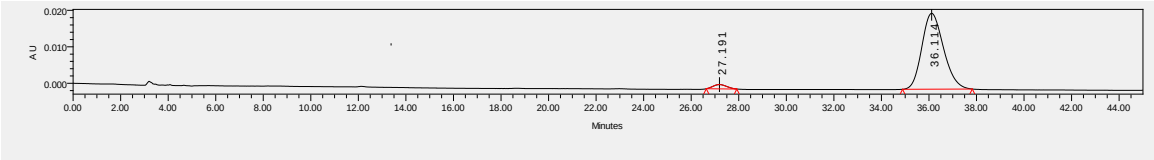



**3e**

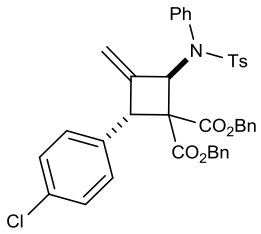
**Dibenzyl 4-(4-flourophenyl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3e** The compound **3e** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 94% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 36.11 min, $t_r$ (minor) = 27.19 min, ee = 93%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.1}$ = +33.2 (*c* = 0.86 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.34 – 7.27 (m, 6H), 7.26 – 7.21 (m, 4H), 7.20 – 7.09 (m, 7H), 6.82 – 6.76 (m, 4H), 6.11 – 6.09 (m, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 5.18 – 5.10 (m, 3H), 4.92 – 4.90 (m, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 12.4 Hz, 1H), 2.40 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.52, 167.49, 162.1 (d, *J* = 247.2 Hz), 145.8, 143.5, 138.1, 137.3, 135.1, 134.4, 131.7, 131.7, 131.4, 130.2 (d, *J* = 8.1 Hz), 129.2, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.8, 115.0 (d, *J* = 21.3 Hz), 114.5, 67.8, 67.4, 65.6, 64.8, 52.6, 21.5. **$^{19}$F{$^1$H} NMR** (376 MHz, $CDCl_3$) δ -114.30. **IR (film)**: 1728, 1502, 1452, 1265, 1163, 1086, 899, 700, 570. **HRMS** (ESI-FT) calcd for $C_{40}H_{34}FNO_6SNa$ ([M+Na$^+$]) = 698.1983, Found 698.1977.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 27.168 | 3197931 | 50.29 |
| 2 | 36.123 | 3161242 | 49.71 |

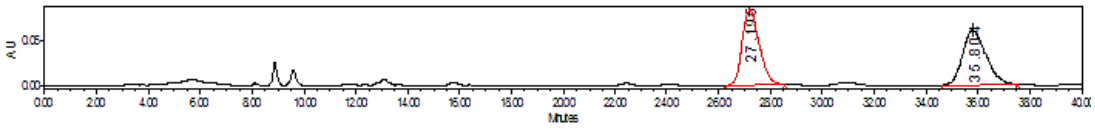



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 27.191 | 46396 | 3.41 |
| 2 | 36.114 | 1315262 | 96.59 |

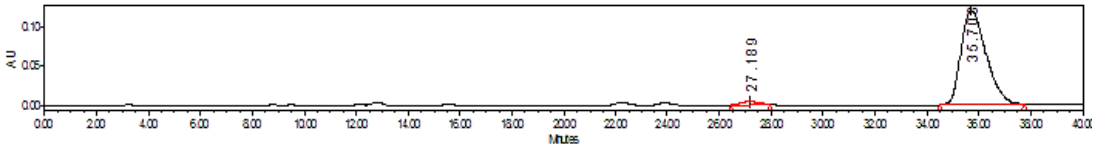



**3f**

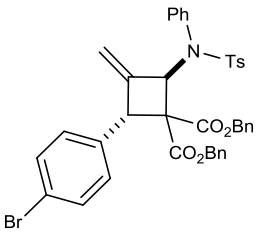
**Dibenzyl 4-(4-chlorophenyl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3f** The compound **3f** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 99% yield. **Major diastereomer:** **HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_r$ (major) = 35.80 min, $t_r$ (minor) = 27.20 min, ee = 95%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{20.2}$ = +26.8 (*c* = 1.25 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.59 – 7.56 (m, 2H), 7.33 – 7.29 (m, 5H), 7.28 – 7.16 (m, 8H), 7.14 – 6.99 (m, 6H), 6.77 – 6.74 (m, 2H), 6.11 – 6.08 (m, 1H), 5.35 (d, *J* = 12.4 Hz, 1H), 5.19 – 5.07 (m, 3H), 4.92 – 4.88 (m, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 2.40 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 167.5, 167.4, 145.4, 143.5, 138.1, 137.3, 135.1, 134.5, 134.3, 133.4, 131.4, 130.0, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 128.23, 128.15, 127.8, 114.6, 67.8, 67.5, 65.7, 64.7, 52.6, 21.5. **IR (film)**: 1730, 1490, 1454, 1267, 1163, 1088, 901, 700, 583. **HRMS** (ESI-FT) calcd for $C_{40}H_{34}{}^{34.9689}ClNO_6SNa$ ([M+Na$^+$]) = 714.1688, Found 714.1688, **HRMS** (ESI-FT) calcd for $C_{40}H_{34}{}^{36.9659}ClNO_6SNa$ ([M+Na$^+$]) = 716.1658, Found 716.1661.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 27.195 | 3875256 | 50.32 |
| 2 | 35.804 | 3826466 | 49.68 |

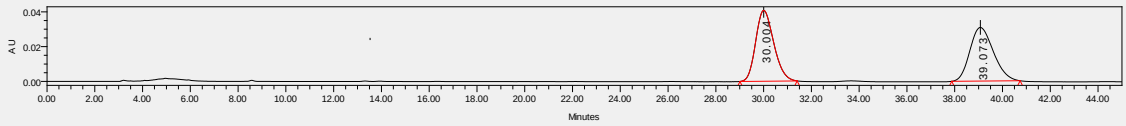



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 27.189 | 215402 | 2.57 |
| 2 | 35.708 | 8153144 | 97.43 |

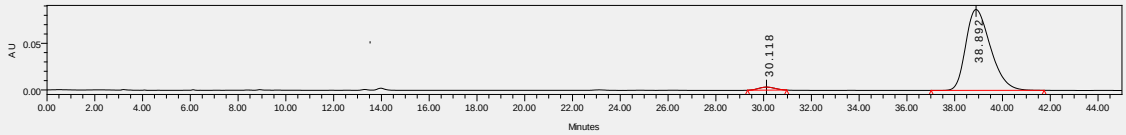



**3g**

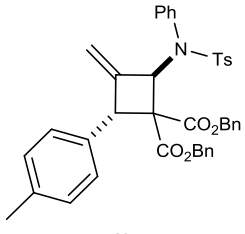
**Dibenzyl 4-(4-bromophenyl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3g** The compound **3g** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 99% yield. **Major diastereomer:** **HPLC** (Chiralcel **IE**, hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 38.89 min, $t_r$ (minor) = 30.12 min, ee = 95%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{26.9}$ = +27.4 (c = 0.85 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.33 – 7.29 (m, 5H), 7.27 – 7.17 (m, 10H), 7.11 – 7.03 (m, 4H), 6.76 – 6.74 (m, 2H), 6.10 – 6.08 (m, 1H), 5.35 (d, *J* = 12.4 Hz, 1H), 5.16 – 5.09 (m, 3H), 4.89 – 4.87 (m, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 2.41 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.5, 167.4, 145.3, 143.5, 138.1, 137.4, 135.1, 135.0, 134.3, 131.4, 131.3, 130.3, 129.3, 128.7, 128.63, 128.56, 128.4, 128.29, 128.25, 128.21, 128.18, 127.9, 121.7, 114.6, 67.9, 67.6, 65.8, 64.6, 52.7, 21.6. **IR (film)**: 1730, 1487, 1454, 1267, 1163, 1088, 899, 700, 570. **HRMS** (ESI-FT) calcd for $C_{40}H_{35}{}^{78.9183}BrNO_6S$ ([M+H$^+$]) = 736.1363, Found 736.1355, **HRMS** (ESI-FT) calcd for $C_{40}H_{35}{}^{80.9163}BrNO_6S$ ([M+H$^+$]) = 738.1343, Found 738.1339.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 30.004 | 2134134 | 50.30 |
| 2 | 39.073 | 2108383 | 49.70 |



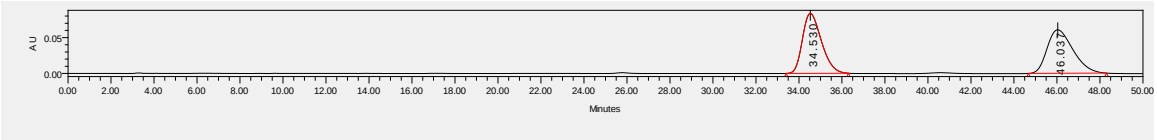

| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 30.118 | 155592 | 2.44 |
| 2 | 38.892 | 6226320 | 97.56 |




**3h**

**Dibenzyl 2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylene-4-(*p*-tolyl)cyclobutane-1,1-dicarboxylate 3h** The compound **3h** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 93% yield. **Major diastereomer:** **HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 45.96 min, $t_r$ (minor) = 34.55 min, ee

= 93%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.9}$ = +26.1 (*c* = 1.02 in $CH_2Cl_2$, λ = 254 nm). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.32 – 7.20 (m, 11H), 7.18 – 7.06 (m, 6H), 6.98 – 6.95 (m, 2H), 6.75 – 6.72 (m, 2H), 6.15 – 6.13 (m, 1H), 5.32 (d, *J* = 12.4 Hz, 1H), 5.18 – 5.17 (m, 1H), 5.13 – 5.01 (m, 2H), 4.93 – 4.83 (m, 1H), 4.63 (d, *J* = 12.4 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 2.41 (s, 3H), 2.25 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.7, 167.6, 146.0, 143.4, 138.0, 137.4, 137.2, 135.2, 134.6, 133.0, 131.5, 129.2, 128.9, 128.63, 128.55, 128.5, 128.39, 128.36, 128.1, 128.0, 127.88, 127.86, 114.2, 67.7, 67.3, 65.5, 64.8, 53.2, 21.6, 21.1. **IR (film)**: 1730, 1498, 1452, 1265, 1163, 901, 700, 571. **HRMS** (ESI-FT) calcd for $C_{41}H_{37}NO_6SNa$ ([M+Na$^+$]) = 694.2234, Found 694.2231.




| | Retention Time | Area | % Area |
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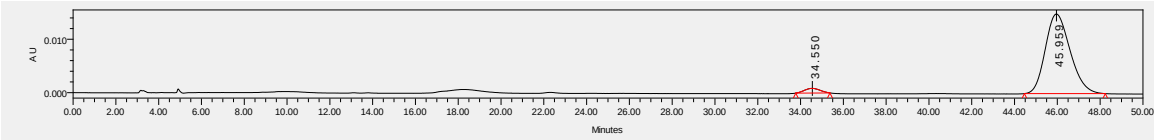
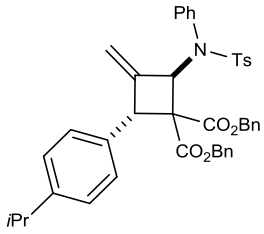
| 1 | 34.530 | 5120999 | 50.31 |
| 2 | 46.037 | 5058243 | 49.69 |

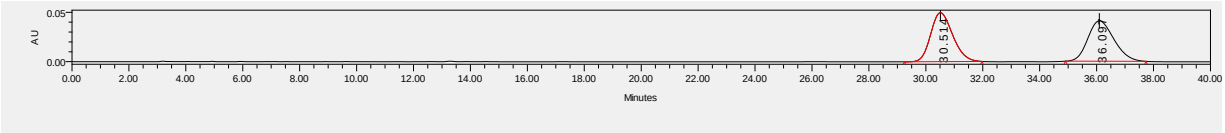



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 34.550 | 43730 | 3.52 |
| 2 | 45.959 | 1198707 | 96.48 |

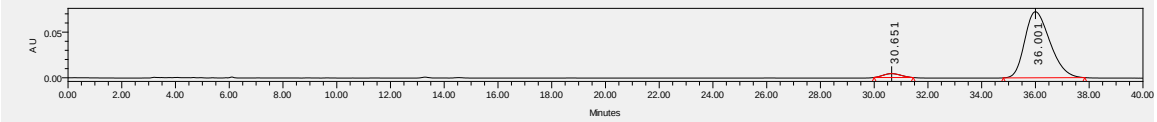



**3i**

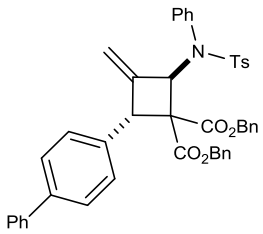
**Dibenzyl 4-(4-isopropylphenyl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3i** The compound **3i** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 92% yield. **Major diastereomer:** **HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 36.00 min, $t_r$ (minor) = 30.65 min, ee = 92%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.8}$ = +19.2 (*c* = 0.79 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.31 – 7.20 (m, 11H), 7.18 – 7.10 (m, 6H), 7.08 – 7.05 (m, 2H), 6.75 – 6.72 (m, 2H), 6.16 – 6.13 (m, 1H), 5.30 (d, *J* = 12.0 Hz, 1H), 5.20 – 5,19 (m, 1H), 5.13 – 5.06 (m, 2H), 4.91 – 4.87 (m, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.17 (d, *J* = 12.4 Hz, 1H), 2.86 – 2.78 (m, 1H), 2.41 (s, 3H), 1.18 – 1.15 (m, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.7, 167.5, 148.3, 145.9, 143.4, 138.0, 137.4, 135.2, 134.6, 133.5, 131.5, 129.3, 128.62, 128.56, 128.4, 128.13, 128.07, 127.94, 127.91, 127.87, 126.2, 114.3, 67.7, 67.4, 65.5, 64.9, 53.3, 33.7, 24.0, 23.9, 21.5. **IR (film)**: 1730, 1498, 1454, 1265, 1163, 1088, 901, 698, 573. **HRMS** (ESI-FT) calcd for $C_{43}H_{41}NO_6SNa$ ([M+Na$^+$]) = 722.2547, Found 722.2538.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 30.514 | 2661853 | 50.54 |
| 2 | 36.097 | 2605276 | 49.46 |

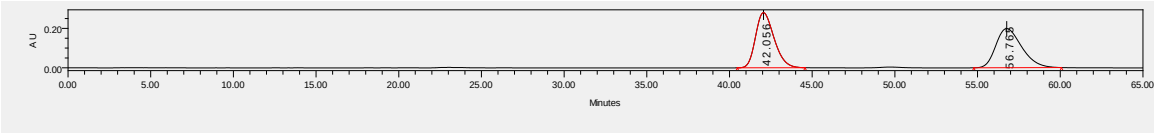



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 30.651 | 193285 | 3.94 |
| 2 | 36.001 | 4713944 | 96.06 |

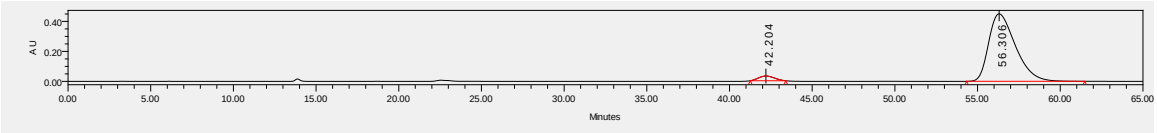



**3j**

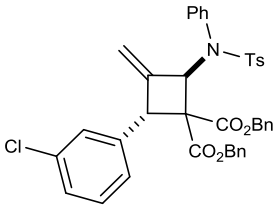
**Dibenzyl 4-[(1,1'-biphenyl)-4-yl]-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3j** The compound **3j** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 98% yield. **Major diastereomer:** **HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_r$ (major) = 56.31 min, $t_r$ (minor) = 42.24 min, ee = 92%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.8}$ = +23.3 (*c* = 0.81 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.62 – 7.59 (m, 2H), 7.52 – 7.50 (m, 2H), 7.42 – 7.38 (m, 4H), 7.34 – 7.17 (m, 14H), 7.15 – 7.12 (m, 2H), 7.09 – 7.04 (m, 2H), 6.73 – 6.70 (m, 2H), 6.19 – 6.17 (m, 1H), 5.35 (d, *J* = 12.4 Hz, 1H), 5.23 (s, 1H), 5.17 – 5.08 (m, 2H), 4.98 – 4.96 (m, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 12.4 Hz, 1H), 2.41 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 167.6, 167.5, 145.7, 143.5, 140.5, 140.4, 138.1, 137.4, 135.2, 134.5, 131.5, 129.3, 129.1, 128.70, 128.67, 128.6, 128.44, 128.39, 128.1, 128.0, 127.9, 127.3, 126.9, 126.8, 121.7, 114.5, 67.8, 67.5, 65.6, 64.9, 53.2, 21.5. **IR (film)**: 1728, 1489, 1452, 1265, 1163, 1086, 901, 698, 576. **HRMS** (ESI-FT) calcd for $C_{46}H_{39}NO_6SNa$ ([M+Na$^+$]) = 756.2390, Found 756.2391.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 42.056 | 21803457 | 50.28 |
| 2 | 56.765 | 21560564 | 49.72 |

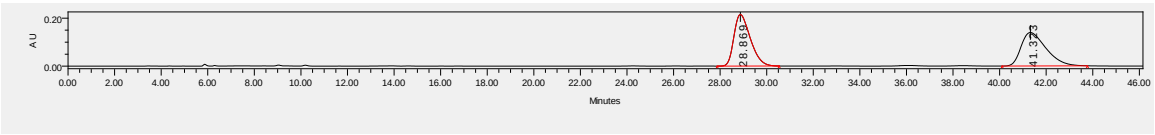



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 42.204 | 2089826 | 3.97 |
| 2 | 56.306 | 50575139 | 96.03 |

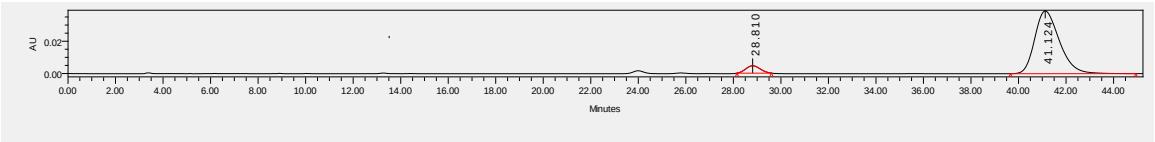



**3k**

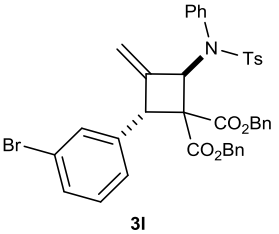
**Dibenzyl 4-(3-chlorophenyl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3k** The compound **3k** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 99% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 41.12 min, $t_r$ (minor) = 28.81 min, ee = 87%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.6}$ = +37.88 (*c* = 0.79 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.32 – 7.26 (m, 6H), 7.25 – 7.15 (m, 8H), 7.13 – 6.96 (m, 5H), 6.91 – 6.74 (m, 2H), 6.11 – 6.09 (m, 1H), 5.33 (d, *J* = 12.4 Hz, 1H), 5.23 – 5.18 (m, 1H), 5.16 – 5.12 (m, 2H), 4.92 – 4.90 (m, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.39 (d, *J* = 12.4 Hz, 1H), 2.40 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.4, 167.3, 145.0, 143.5, 138.12, 138.07, 137.3, 135.0, 134.3, 134.0, 131.4, 129.4, 129.3, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 126.6, 114.8, 67.89, 67.5, 65.7, 64.6, 52.8, 21.5. **IR (film)**: 1730, 1489, 1454, 1267, 1163, 1085, 902, 698, 579. **HRMS** (ESI-FT) calcd for $C_{40}H_{34}^{34.9689}ClNO_6SNa$ ([M+Na$^+$]) = 714.1688, Found 714.1697, **HRMS** (ESI-FT) calcd for $C_{40}H_{34}^{36.9659}ClNO_6SNa$ ([M+Na$^+$]) = 716.1658, Found 716.1662.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 28.869 | 10501086 | 50.42 |
| 2 | 41.323 | 10326713 | 49.58 |

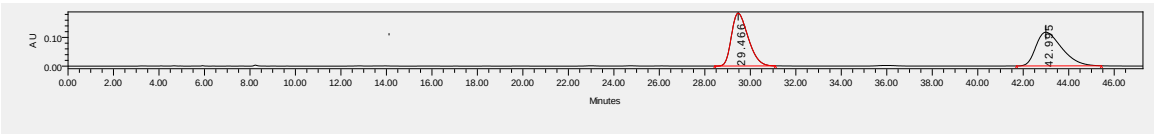



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 28.810 | 191470 | 6.40 |
| 2 | 41.124 | 2799711 | 93.60 |

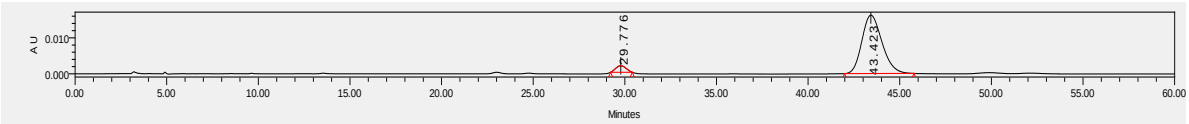



**3l**

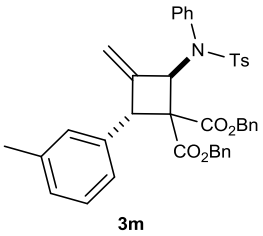
**Dibenzyl 4-(3-bromophenyl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3l** The compound **3l** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 99% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 43.42 min, $t_r$ (minor) = 29.78 min, ee = 89%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{26.9}$ = +27.4 (*c* = 0.85 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.37 – 7.36 (m, 1H), 7.32 – 7.16 (m, 14H), 7.15 – 7.09 (m, 3H), 7.01 – 6.97 (m, 1H), 6.80 – 6.77 (m, 2H), 6.10 – 6.09 (m, 1H), 5.32 (d, *J* = 12.0 Hz, 1H), 5.23 – 5.07 (m, 3H), 4.90 – 4.89 (m, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 2.40 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.34, 167.28, 145.0, 143.5, 138.4, 138.1, 137.3, 135.0, 134.3, 131.7, 131.4, 130.8, 129.7, 129.3, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.1, 122.3, 114.8, 67.9, 67.5, 65.7, 64.7, 52.7, 21.5. **IR (film)**: 1730, 1487, 1454, 1267, 1163, 1085, 900, 698, 577. **HRMS** (ESI-FT) calcd for $C_{40}H_{35}^{78.9183}BrNO_6S$ ([M+H$^+$]) = 736.1363, Found 736.1355, **HRMS** (ESI-FT) calcd for $C_{40}H_{35}^{80.9163}BrNO_6S$ ([M+H$^+$]) = 738.1343, Found 738.1339.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 29.466 | 9377298 | 50.38 |
| 2 | 42.995 | 9235499 | 49.62 |

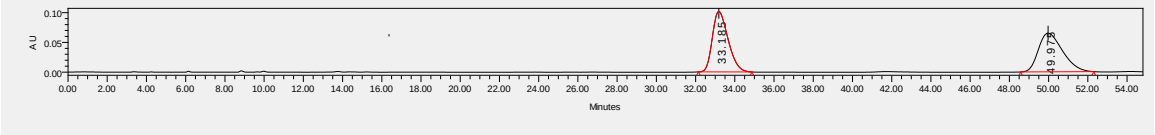



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 29.776 | 71410 | 5.47 |
| 2 | 43.423 | 1233910 | 94.53 |

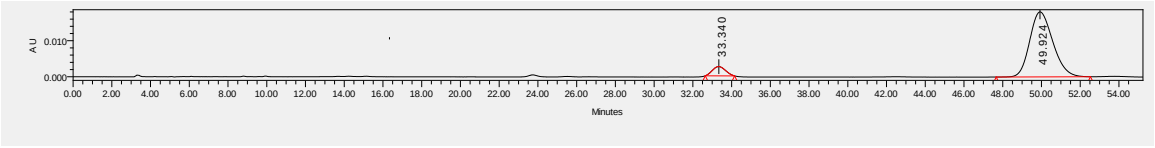



**3m**

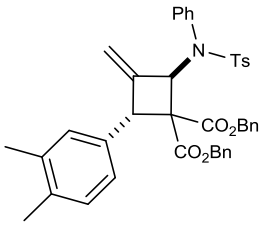
**Dibenzyl 2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylene-4-(*m*-tolyl)cyclobutane-1,1-dicarboxylate 3m** The compound **3m** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 70% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_r$ (major) = 49.92 min, $t_r$ (minor) = 33.34 min, ee = 85%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.7}$ = +30.4 (*c* = 0.74 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.61 – 7.58 (m, 2H), 7.34 – 7.20 (m, 11H), 7.17 – 7.11 (m, 4H), 7.09 – 6.96 (m, 4H), 6.74 – 6.71 (m, 2H), 6.16 – 6.15 (m, 1H), 5.31 (d, *J* = 12.0 Hz, 1H), 5.20 – 5.19 (m, 1H), 5.14 – 5.10 (m, 2H), 4.90 – 4.88 (m, 1H), 4.64 (d, *J* = 12.4 Hz, 1H), 4.27 (d, *J* = 12.4 Hz, 1H), 2.40 (s, 3H), 2.19 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 167.6, 167.5, 145.7, 143.4, 138.0, 137.7, 137.4, 136.0, 135.2, 134.6, 131.46, 129.6, 129.2, 128.6, 128.5, 128.4, 128.3, 128.12, 128.08, 128.0, 127.88, 127.85, 127.8, 125.3, 114.4, 67.7, 67.3, 65.5, 64.8, 53.4, 21.5, 21.2. **IR (film)**: 1730, 1489, 1452, 1265, 1163, 1084, 901, 698, 577. **HRMS** (ESI-FT) calcd for $C_{41}H_{37}NO_6SNa$ ([M+Na$^+$]) = 694.2234, Found 694.2228.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 33.185 | 5667291 | 50.45 |
| 2 | 49.975 | 5566192 | 49.55 |

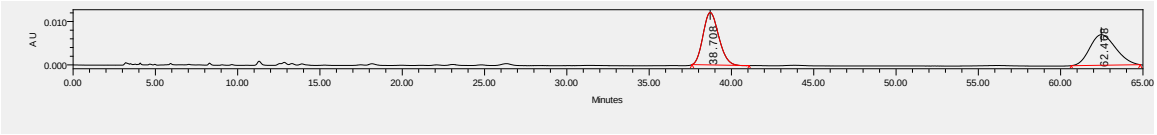



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 33.340 | 120502 | 7.46 |
| 2 | 49.924 | 1494006 | 92.54 |

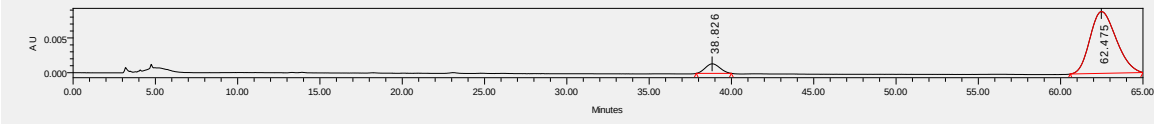



**3n**

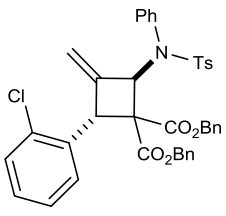
**Dibenzyl 4-(3,4-dimethylphenyl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3n** The compound **3n** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 91% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 62.48 min, $t_r$ (minor) = 38.83 min, ee = 84%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{26.8}$ = +26.6 (*c* = 0.71 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.31 – 7.23 (m, 8H), 7.23 – 7.19 (m, 3H), 7.16 – 7.11 (m, 4H), 6.94 – 6.92 (m, 3H), 6.71 – 6.68 (m, 2H), 6.16 – 6.14 (m, 1H), 5.31 (d, *J* = 12.0 Hz, 1H), 5.17 – 5.16 (m, 1H), 5.13 – 5.05 (m, 2H), 4.85 – 4.83 (m, 1H), 4.60 (d, *J* = 12.4 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 2.40 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.5, 146.0, 143.4, 138.0, 137.4, 136.3, 135.8, 135.2, 134.6, 133.4, 131.5, 130.2, 129.4, 129.2, 128.61, 128.55, 128.37, 128.35, 128.1, 128.0, 127.88, 127.86, 127.8, 125.6, 114.2, 67.6, 67.3, 65.4, 64.8, 53.3, 21.5, 19.5, 19.4. **IR (film)**: 1730, 1494, 1452, 1265, 1163, 1086, 903, 700, 577. **HRMS** (ESI-FT) calcd for $C_{42}H_{39}NO_6SNa$ ([M+Na$^+$]) = 708.2390, Found 708.2385.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 38.708 | 801819 | 51.07 |
| 2 | 62.468 | 768222 | 48.93 |



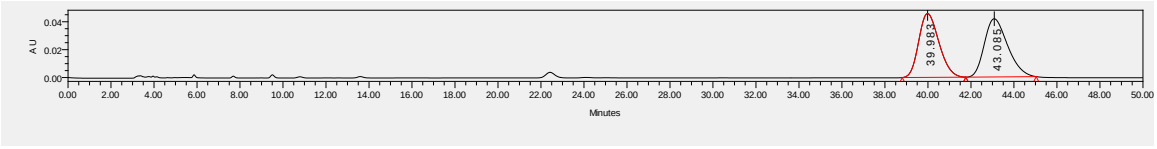

| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 38.826 | 84188 | 7.89 |
| 2 | 62.475 | 982490 | 92.11 |



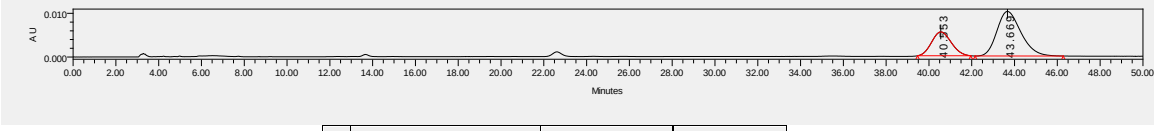

**3o**

**Dibenzyl 4-(2-chlorophenyl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3o** The compound **3o** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 52% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 43.67 min, $t_r$ (minor) = 40.55 min, ee =

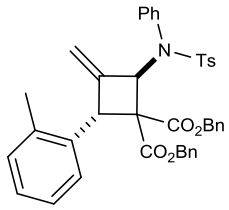
39%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.0}$ = +22.0 (*c* = 0.55 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.32 – 7.15 (m, 17H), 7.11 – 7.04 (m, 2H), 6.87 – 6.84 (d, *J* = 7.2 Hz, 2H), 6.35 – 6.33 (m, 1H), 5.47 (d, *J* = 3.1 Hz, 1H), 5.22 (d, *J* = 12.4 Hz, 1H), 5.12 – 5.10 (m, 2H), 5.01 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.4 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 2.40 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.5, 166.7, 146.3, 143.5, 137.8, 137.2, 135.5, 135.1, 134.7, 134.5, 131.5, 129.3, 129.0, 128.8, 128.6, 128.27, 128.25, 128.2, 128.00, 127.98, 127.9, 126.4, 114.8, 67.6, 67.3, 64.7, 64.4, 48.9, 21.5. **IR (film)**: 1730, 1492, 1452, 1265, 1163, 1088, 905, 700, 576. **HRMS** (ESI-FT) calcd for $C_{40}H_{35}^{34.9689}ClNO_6S$ ([M+H$^+$]) = 692.1868, Found 692.1860, **HRMS** (ESI-FT) calcd for $C_{40}H_{35}^{36.9659}ClNO_6S$ ([M+H$^+$]) = 694.1839, Found 694.1841.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 39.983 | 2987345 | 48.78 |
| 2 | 43.085 | 3136795 | 51.22 |

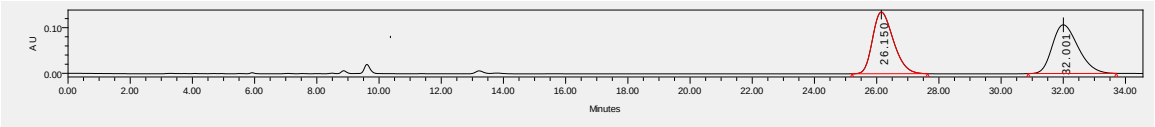



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 40.553 | 348047 | 30.40 |
| 2 | 43.669 | 797029 | 69.60 |

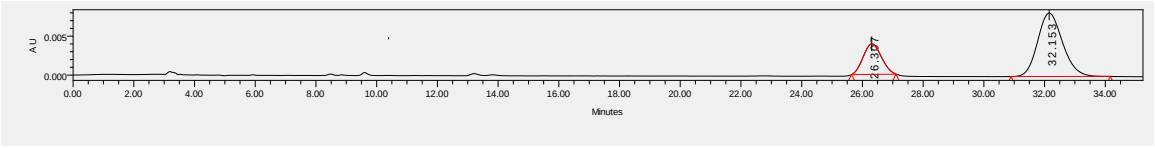



**3p**

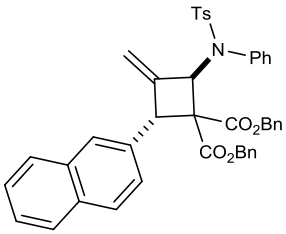
**Dibenzyl 2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylene-4-(*o*-tolyl)cyclobutane-1,1-dicarboxylate 3p** The compound **3p** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 32% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 32.15 min, $t_r$ (minor) = 26.31 min, ee = 48%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.1}$ = +29.7 (*c* = 0.39 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.33 – 7.15 (m, 17H), 7.10 – 7.03 (m, 2H), 7.01 – 6.98 (m, 1H), 6.78 – 6.75 (m, 2H), 6.26 – 6.24 (m, 1H), 5.31 (d, *J* = 12.0 Hz, 1H), 5.19 – 5.17 (m, 1H), 5.13 (s, 1H), 5.09 (s, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.14 (d, *J* = 12.0 Hz, 1H), 2.41 (s, 3H), 2.18 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.52, 167.50, 147.0, 143.5, 138.44, 138.38, 137.5, 135.2, 135.0, 134.5, 131.3, 130.1, 129.3, 128.7, 128.5, 128.43, 128.37, 128.2, 128.12, 128.10, 128.0, 127.9, 127.5, 127.4, 125.6, 114.2, 67.8, 67.4, 65.3, 64.9, 49.1, 21.6, 19.9. **IR (film)**: 1730, 1498, 1454, 1261, 1161, 1086, 900, 698, 579. **HRMS** (ESI-FT) calcd for $C_{41}H_{37}NO_6SNa$ ([M+Na$^+$]) = 694.2234, Found 694.2229.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 26.150 | 6291551 | 50.44 |
| 2 | 32.001 | 6180993 | 49.56 |

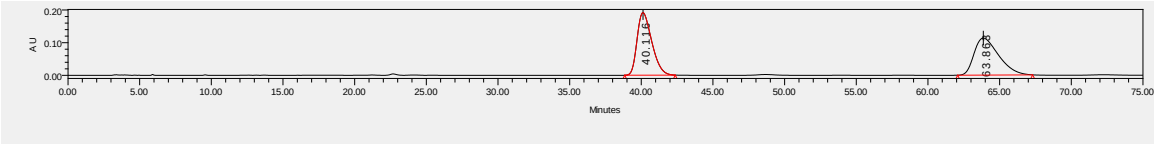



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 26.307 | 163664 | 26.00 |
| 2 | 32.153 | 465794 | 74.00 |

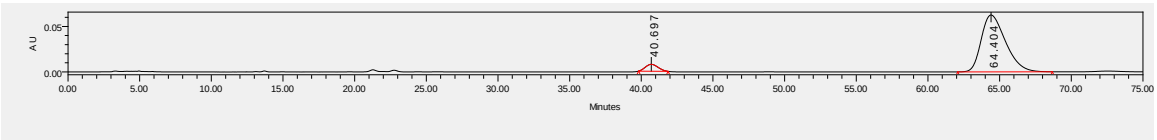



**3q**

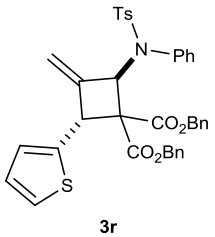
**Dibenzyl 2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylene-4-(naphthalene-2-yl)cyclobutane-1,1-dicarboxylate 3q** The compound **3q** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 99% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 64.40 min, $t_r$ (minor) = 40.70 min, ee = 88%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{26.9}$ = +33.7 (*c* = 1.21 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 1H), 7.69 – 7.66 (m, 2H), 7.63 – 7.59 (m, 3H), 7.45 – 7.41 (m, 2H), 7.32 – 7.21 (m, 11H), 7.17 – 7.14 (m, 2H), 7.07 – 7.02 (m, 1H), 6.89 – 6.84 (m, 2H), 6.43 – 6.40 (m, 2H), 6.23 – 6.21 (m, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 5.26 (s, 1H), 5.14 – 5.09 (m, 3H), 4.48 (d, *J* = 12.4 Hz, 1H), 4.20 (d, *J* = 12.0 Hz, 1H), 2.41 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.5, 145.7, 143.5, 138.1, 137.4, 135.2, 134.2, 133.5, 133.1, 132.8, 131.5, 129.3, 128.7, 128.6, 128.5, 128.4, 128.2, 127.93, 127.89, 127.88, 127.85, 127.80, 127.78, 127.6, 127.5, 126.6, 125.92, 125.88, 114.6, 67.8, 67.4, 65.7, 64.9, 53.5, 21.6. **IR (film)**: 1730, 1494, 1452, 1265, 1163, 1088, 903, 698, 571. **HRMS** (ESI-FT) calcd for $C_{44}H_{37}NO_6SNa$ ([M+Na$^+$]) = 730.2234, Found 730.2231.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 40.116 | 13621155 | 50.36 |
| 2 | 63.863 | 13424231 | 49.64 |



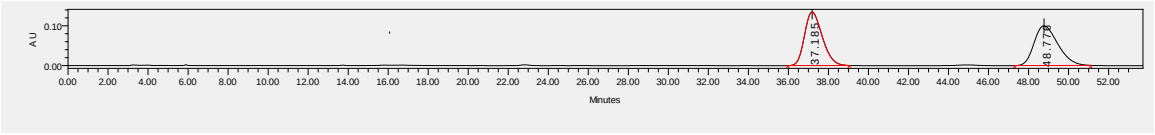

| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 40.697 | 465006 | 5.95 |
| 2 | 64.404 | 7356124 | 94.05 |



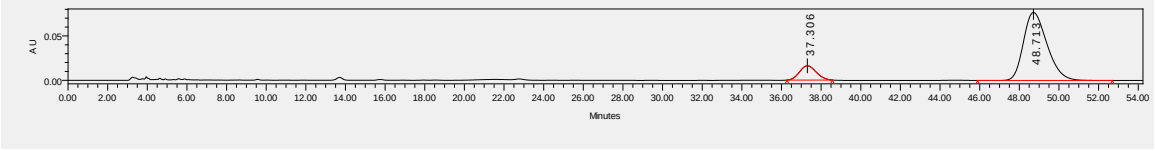

**3r**

**Dibenzyl 2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylene-4-(thiophen-2-yl)cyclobutane-1,1-dicarboxylate 3r** The compound **3r** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 86% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 48.71 min, $t_r$ (minor) = 37.31 min, ee = 74%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.9}$ = +32.5 (*c* = 1.00 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.32 – 7.23 (m, 8H), 7.22 – 7.15 (m, 5H), 7.10 – 7.05 (m, 3H),

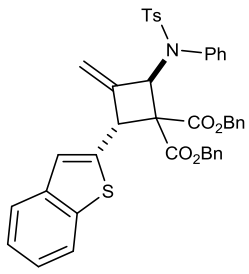
6.89 – 6.86 (m, 3H), 6.84 – 6.81 (m, 1H), 6.13 – 6.10 (m, 1H), 5.35 – 5.30 (m, 2H), 5.14 (d, *J* = 12.4 Hz, 1H), 5.12 – 5.09 (m, 2H), 4.78 (d, *J* = 12.4 Hz, 1H), 4.46 (d, *J* = 12.4 Hz, 1H), 2.39 (s, 3H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 167.3, 167.2, 146.2, 143.5, 138.5, 137.8, 137.2, 135.0, 134.6, 131.5, 129.2, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 126.7, 126.5, 125.0, 114.6, 67.8, 67.5, 65.4, 65.2, 48.6, 21.5. **IR (film)**: 1730, 1493, 1454, 1267, 1163, 1086, 906, 700, 571. **HRMS** (ESI-FT) calcd for $C_{38}H_{33}NO_6S_2Na$ ([M+Na$^+$]) = 686.1642, Found 686.1640.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 37.185 | 8276671 | 50.18 |
| 2 | 48.776 | 8218548 | 49.82 |

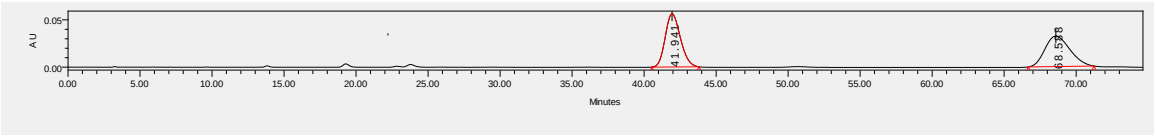



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 37.306 | 940553 | 12.95 |
| 2 | 48.713 | 6321473 | 87.05 |

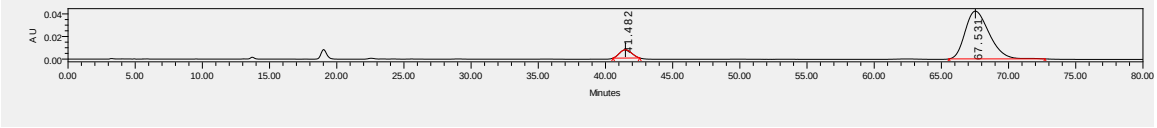



**3s**

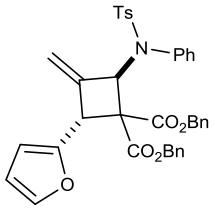
**Dibenzyl 4-(benzo[*b*]thiophen-2-yl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido ]-3-methylenecyclobutane-1,1-dicarboxylate 3s** The compound **3s** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 98% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 67.53 min, $t_r$ (minor) = 41.48 min, ee = 84%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.8}$ = +36.2 (*c* = 1.21 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 1H), 7.60 – 7.57 (m, 3H), 7.34 – 7.26 (m, 8H), 7.25 – 7.19 (m, 4H), 7.11 – 7.05 (m, 4H), 6.94 – 6.90 (m, 2H), 6.60 – 6.57 (m, 2H), 6.17– 6.15 (m, 1H), 5.43 – 5.31 (m, 2H), 5.18 – 5.14 (m, 3H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 2.40 (s, 3H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 167.4, 167.1, 145.6, 143.6, 139.6, 139.5, 139.4, 137.9, 137.2, 135.1, 134.2, 131.5, 129.3, 128.73, 128.67, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 124.1, 123.4, 123.3, 122.1, 115.0, 67.9, 67.8, 65.7, 65.0, 49.0, 21.5. **IR (film)**: 1730, 1492, 1454, 1267, 1163, 1086, 907, 702, 577. **HRMS** (ESI-FT) calcd for $C_{42}H_{35}NO_6S_2Na$ ([M+Na$^+$]) = 736.1798, Found 736.1793.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 41.941 | 4115480 | 51.52 |
| 2 | 68.588 | 3873359 | 48.48 |

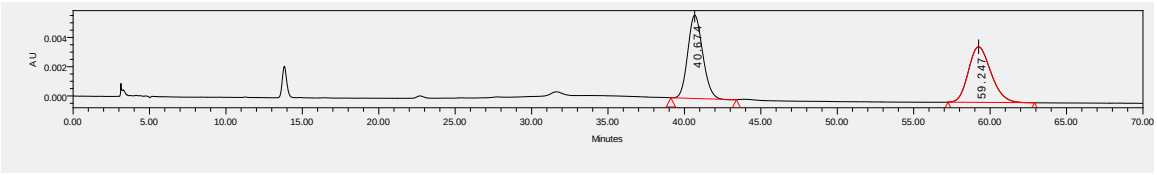



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 41.482 | 455786 | 7.98 |
| 2 | 67.531 | 5255377 | 92.02 |

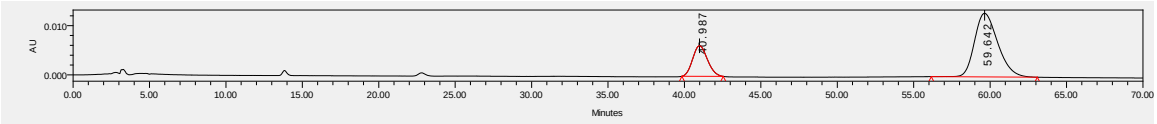



**3t**

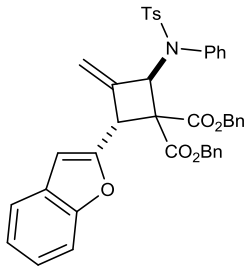
**Dibenzyl 4-(furan-2-yl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3t** The compound **3t** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 58% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 59.64 min, $t_r$ (minor) = 40.99 min, ee = 51%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{19.5}$ = +56.6 (*c* = 0.53 in $CH_2Cl_2$, D = 405 nm). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.33 – 7.24 (m, 8H), 7.23 – 7.19 (m, 5H), 7.17 – 7.16 (m, 1H), 7.09 – 7.06 (m, 2H), 6.99 – 6.95 (m, 2H), 6.19 – 6.14 (m, 3H), 5.30 (d, *J* = 12.4 Hz, 1H), 5.23 – 5.22 (m, 1H), 5.08 (d, *J* = 12.4 Hz, 1H), 5.04 – 5.03 (m, 1H), 4.92 – 4.85 (m, 2H), 4.61 (d, *J* = 12.4 Hz, 1H), 2.41 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.5, 167.0, 150.6, 144.4, 143.5, 142.4, 137.8, 137.2, 135.1, 134.8, 131.6, 129.6, 129.3, 128.7, 128.4, 128.3, 128.11, 128.05, 128.0, 127.9, 127.2, 121.7, 114.4, 110.2, 108.4, 67.8, 67.7, 65.4, 63.9, 46.8, 21.6. **IR (film)**: 1732, 1495, 1454, 1265, 1163, 1086, 908, 698, 581. **HRMS** (ESI-FT) calcd for $C_{38}H_{33}NO_7SNa$ ([M+Na$^+$]) = 670.1870, Found 670.1866.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 40.674 | 386887 | 49.83 |
| 2 | 59.247 | 389542 | 50.17 |



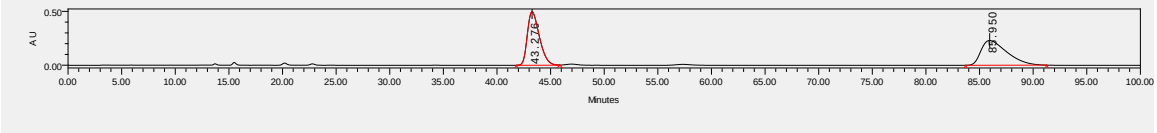

| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 40.987 | 417285 | 23.41 |
| 2 | 59.642 | 1365134 | 76.59 |



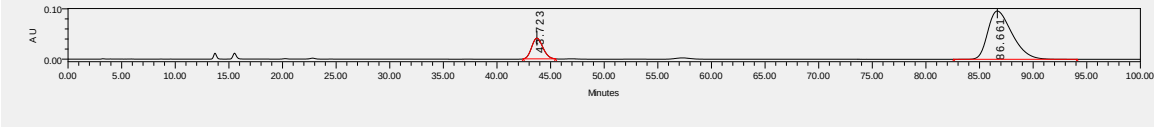

**3u**

**Dibenzyl 4-(benzofuran-2-yl)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3u** The compound **3u** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 92% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 86.66 min, $t_r$ (minor) = 43.72 min, ee = 67%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.9}$ = +20.8 (*c* = 1.18 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.44 – 7.41 (m, 1H), 7.32 – 7.24 (m,

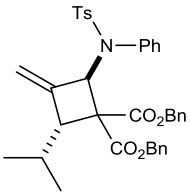
8H), 7.23 – 7.14 (m, 5H), 7.14 – 7.09 (m, 3H), 7.00 – 6.95 (m, 2H), 6.61 – 6.58 (m, 2H), 6.54 – 6.53 (m, 1H), 6.25 – 6.24 (m, 1H), 5.34 (d, *J* = 12.0 Hz, 1H), 5.29 – 5.28 (m, 1H), 5.14 – 5.08 (m, 2H), 5.07 – 5.02 (m, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 2.39 (s, 3H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 167.4, 166.7, 154.9, 153.5, 143.7, 143.6, 137.8, 137.1, 135.0, 134.1, 131.4, 129.2, 128.67, 128.65, 128.34, 128.30, 128.1, 128.02, 127.96, 127.93, 127.91, 127.8, 124.1, 122.7, 120.8, 114.8, 111.1, 105.4, 67.9, 67.8, 65.7, 63.7, 46.9, 21.5. **IR (film)**: 1734, 1492, 1456, 1263, 1163, 1085, 907, 700, 571. **HRMS** (ESI-FT) calcd for $C_{42}H_{35}NO_7SNa$ ([M+$Na^+$]) = 720.2026, Found 720.2022.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 43.276 | 38698940 | 50.22 |
| 2 | 85.950 | 38365570 | 49.78 |

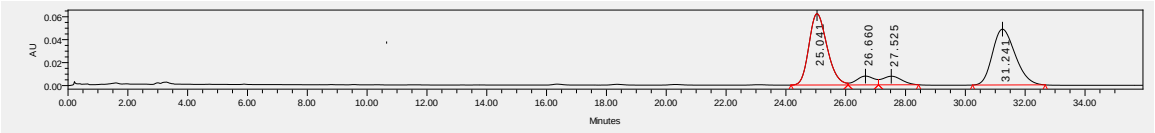



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 43.723 | 2991401 | 16.56 |
| 2 | 86.661 | 15075809 | 83.44 |

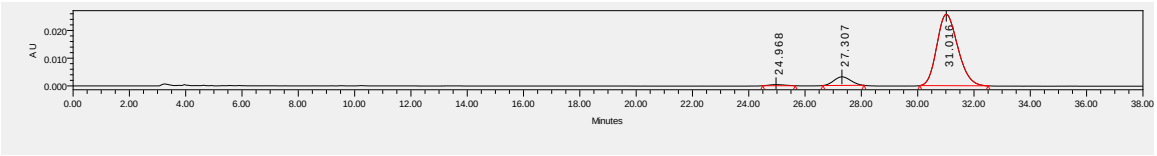



**3v**

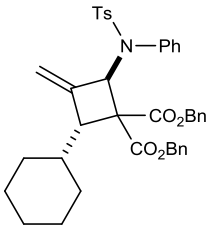
**Dibenzyl 4-isopropyl-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3v** The compound **3v** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1) to afford a yellow oil in 95% yield. **Major diastereomer:** **HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major-major) = 31.02 min, $t_r$ (major-minor) = 24.97 min, ee = 96%. dr = 89/11 (by $^1$H NMR). $[\alpha]_D^{18.8}$ = –29.0 (*c* = 1.17 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.33 – 7.24 (m, 10H), 7.21 – 7.16 (m, 5H), 7.05 – 7.02 (m, 2H), 5.84 – 5.83 (m, 1H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.15 – 5.11 (m, 2H), 5.09 – 5.01 (m, 2H), 4.81 – 4.80 (m, 1H), 3.40 – 3.37 (m, 1H), , 2.39 (s, 3H), 1.72 – 1.63 (m, 1H), , 0.83 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.4 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 169.2, 168.2, 146.7, 143.3, 137.9, 137.5, 135.4, 134.80, 129.1, 128.49, 128.45, 128.4, 128.34, 128.30, 128.1, 127.8, 111.8, 67.6, 65.8, 61.7, 54.8, 28.4, 21.6, 21.5, 19.8. **IR (film)**: 1728, 1492, 1456, 1263, 1167, 1084, 903, 700, 571. **HRMS** (ESI-FT) calcd for $C_{37}H_{37}NO_6SNa$ ([M+$Na^+$]) = 646.2234, Found 646.2234.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 25.041 | 2613277 | 44.72 |
| 2 | 26.660 | 317413 | 5.43 |
| 3 | 27.525 | 338531 | 5.79 |
| 4 | 31.241 | 2574487 | 44.06 |

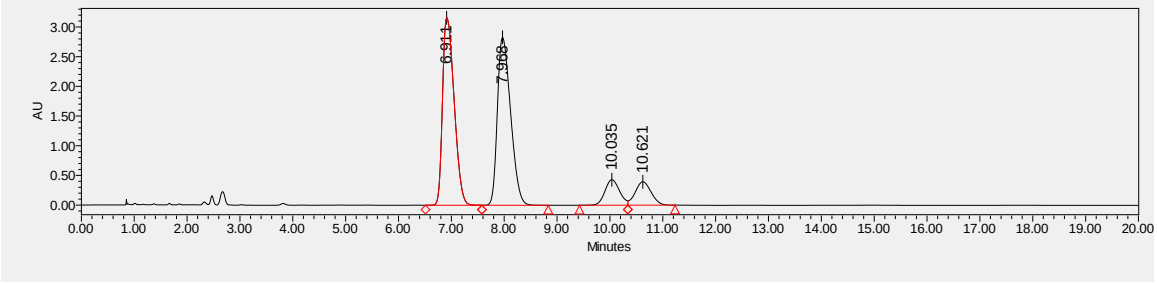



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 24.968 | 15589 | 1.06 |
| 2 | 27.307 | 127969 | 8.68 |
| 3 | 31.016 | 1330046 | 90.26 |

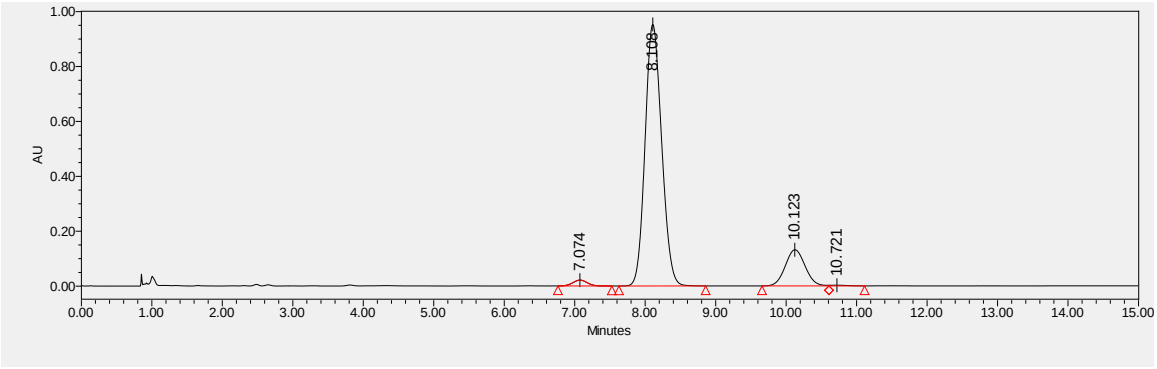



**3w**

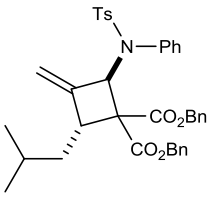
**Dibenzyl 4-cylohexyl-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3w** The compound **3w** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1) to afford a yellow oil in 83% yield. **Major diastereomer: SFC** (SFC Daicel Chiralcel **IC-3**, $CO_2$/MeOH = 80/20, flow rate 1.5 mL/min, λ = 210.4 nm), $t_r$ (major-major) = 8.11 min, $t_r$ (major-minor) = 7.07 min, ee = 96%. dr = 85/15 (by $^1$H NMR). $[\alpha]_D^{18.8}$ = –31.8 (*c* = 0.94 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.36 – 7.24 (m, 10H), 7.23 – 7.17 (m, 5H), 7.06 – 7.03 (m, 2H), 5.85 – 5.83 (m, 1H), 5.24 (d, *J* = 12.4 Hz, 1H), 5.18 – 5.10 (m, 2H), 5.03 – 4.98 (m, 2H), 4.81 – 4.76 (m, 1H), 3.40 – 3.36 (m, 1H), 2.40 (s, 3H), 1.67 – 1.48 (m, 5H), 1.38 – 1.30 (m, 1H), 1.05 – 0.82 (m, 5H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 169.3, 168.3, 146.7, 143.3, 137.9, 137.6, 135.35, 134.9, 131.6, 129.15, 128.7, 128.5, 128.42, 128.36, 128.06, 127.8, 111.8, 67.6, 67.5, 65.8, 61.59, 53.6, 38.0, 31.8, 29.8, 26.0, 25.81, 25.75, 21.5. **IR (film)**: 1728, 1493, 1452, 1265, 1163, 1084, 901, 700, 574. **HRMS** (ESI-FT) calcd for $C_{40}H_{41}NO_6SNa$ ([M+Na$^+$]) = 686.2547, Found 686.2549.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 6.911 | 48232040 | 42.33 |
| 2 | 7.968 | 49216299 | 43.20 |
| 3 | 10.035 | 8252414 | 7.24 |
| 4 | 10.621 | 8229213 | 7.22 |

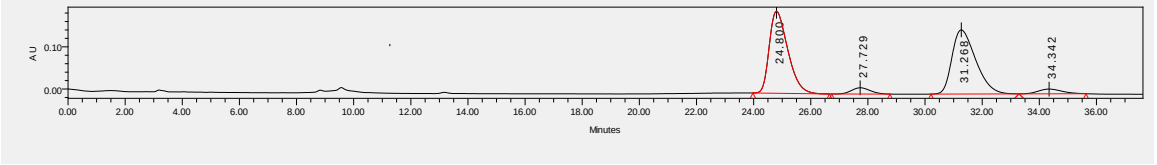



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 7.074 | 303092 | 1.64 |
| 2 | 8.108 | 15559409 | 84.21 |
| 3 | 10.123 | 2573100 | 13.93 |
| 4 | 10.721 | 40934 | 0.22 |

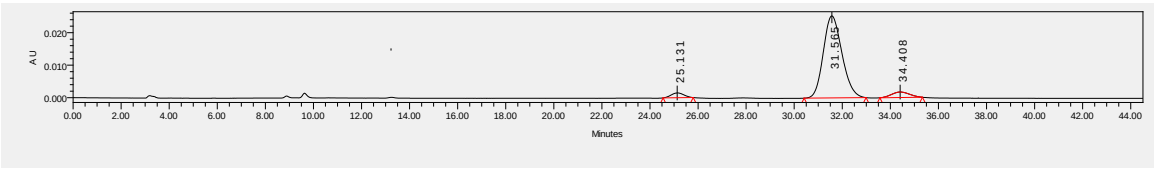



**3x**

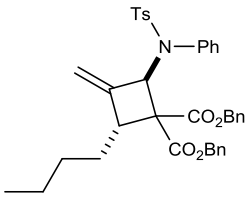
**Dibenzyl 4-isobutyl-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclobutane-1,1-dicarboxylate 3x** The compound **3x** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1) to afford a yellow oil in 86% yield. **Major diastereomer:** **HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_r$ (major-major) = 31.57 min, $t_r$ (major-minor) = 25.13 min, ee = 92%. dr = 92/8 (by $^1$H NMR). $[\alpha]_D^{19.0}$ = –29.4 (*c* = 1.06 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.55 – 7.52 (m, 2H), 7.33 – 7.28 (m, 5H), 7.27 – 7.23 (m, 4H), 7.21 – 7.16 (m, 6H), 7.05 – 7.02 (m, 2H), 5.94 – 5.93 (m, 1H), 5.29 – 5.24 (m, 1H), 5.16 – 5.12 (m, 1H), 5.07 – 5.02 (m, 3H), 4.82 – 4.79 (m, 1H), 3.60 – 3.52 (m, 1H) , 2.38 (s, 3H), 1.54 – 1.46 (m, 1H), 1.17 – 1.04 (m, 2H), 0.72 (d, *J* = 6.4 Hz, 3H), 0.66 (d, *J* = 6.4 Hz, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 168.6, 168.0, 148.3, 143.3, 137.6, 137.3, 135.2, 134.9, 131.6, 129.2, 128.5, 128.42, 128.41, 128.32, 128.29, 128.1, 127.8, 111.0, 67.5, 67.4, 65.4, 62.1, 46.2, 38.8, 25.3, 22.5, 22.1, 21.5. **IR (film)**: 1730, 1493, 1456, 1267, 1167, 1086, 903, 700, 571. **HRMS** (ESI-FT) calcd for $C_{38}H_{39}NO_6SNa$ ([M+Na$^+$]) = 660.2390, Found 660.2390.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 24.800 | 8742645 | 46.45 |
| 2 | 27.729 | 677220 | 3.60 |
| 3 | 31.268 | 8748772 | 46.48 |
| 4 | 34.342 | 653227 | 3.47 |

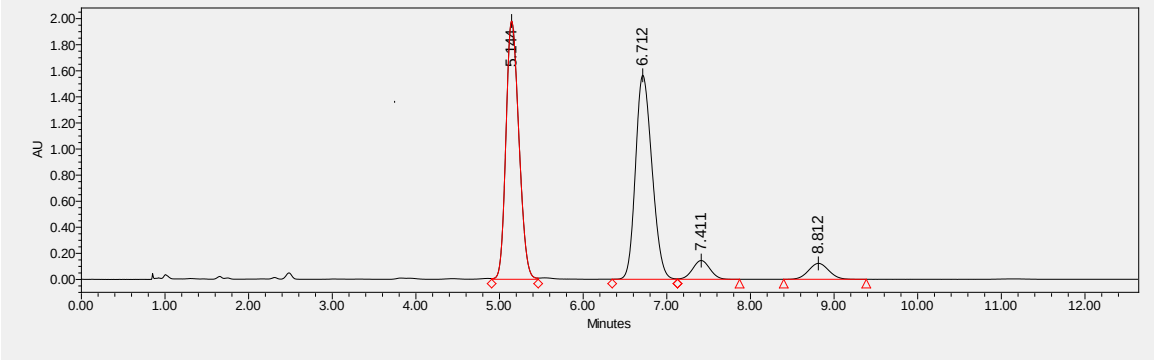



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 25.131 | 54686 | 3.64 |
| 2 | 31.565 | 1358996 | 90.50 |
| 3 | 34.408 | 87988 | 5.86 |

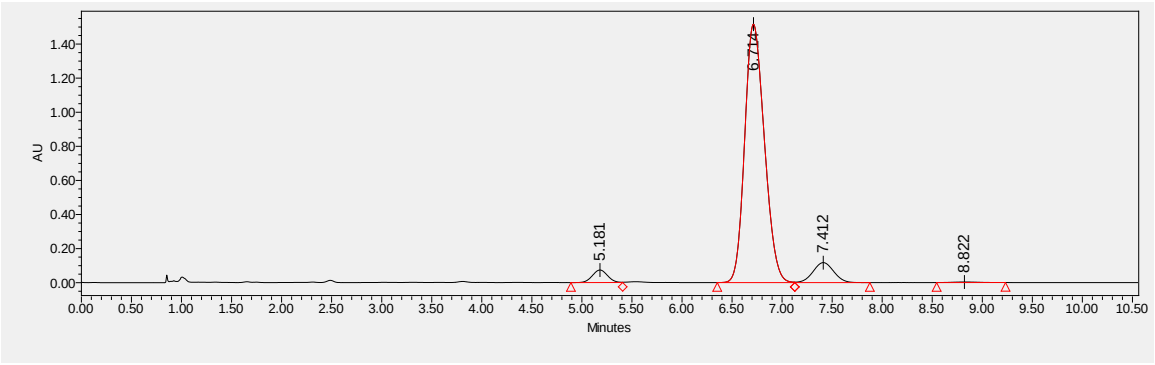



**3y**

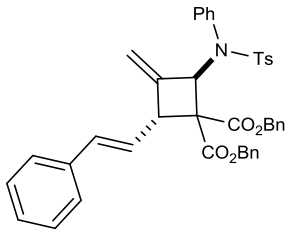
**Dibenzyl 4-butyl-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylenecyclbutane-1,1-dicarboxylate 3y** The compound **3y** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1) to afford a yellow oil in 57% yield. **Major diastereomer: SFC** (SFC Daicel Chiralcel **IC-3**, $CO_2$/MeOH = 80/20, flow rate 1.5 mL/min, λ = 210.4 nm), $t_r$ (major-major) = 6.71 min, $t_r$ (major-minor) = 5.18 min, ee = 93%. dr = 92/8 (by $^1$H NMR). $[\alpha]_D^{19.1}$ = –34.4 (*c* = 0.71 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.36 – 7.24 (m, 10H), 7.22 – 7.17 (m, 5H), 7.05 – 7.02 (m, 2H), 6.00 – 5.95 (m, 1H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.16 (d, *J* = 12.4 Hz, 1H), 5.12 – 4.98 (m, 3H), 4.80 (s, 1H), 3.45 – 3.43 (m, 1H), 2.39 (s, 3H), 1.26 – 1.02 (m, 6H), 0.71 (t, *J* = 7.2 Hz, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 168.59, 167.96, 148.15, 143.33, 137.60, 137.30, 135.26, 134.93, 131.64, 129.16, 128.46, 128.43, 128.41, 128.34, 128.30, 128.07, 127.80, 111.12, 67.48, 67.40, 65.31, 62.02, 48.20, 29.46, 29.28, 22.50, 21.50, 21.49, 13.77. **IR (film)**: 1729, 1493, 1456, 1265, 1165, 1083, 899, 700, 570. **HRMS** (ESI-FT) calcd for $C_{38}H_{39}NO_6SNa$ ([M+Na$^+$]) = 660.2390, Found 66.2386.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 5.144 | 21284762 | 45.41 |
| 2 | 6.712 | 21432845 | 45.73 |
| 3 | 7.411 | 2086089 | 4.45 |
| 4 | 8.812 | 2064218 | 4.40 |

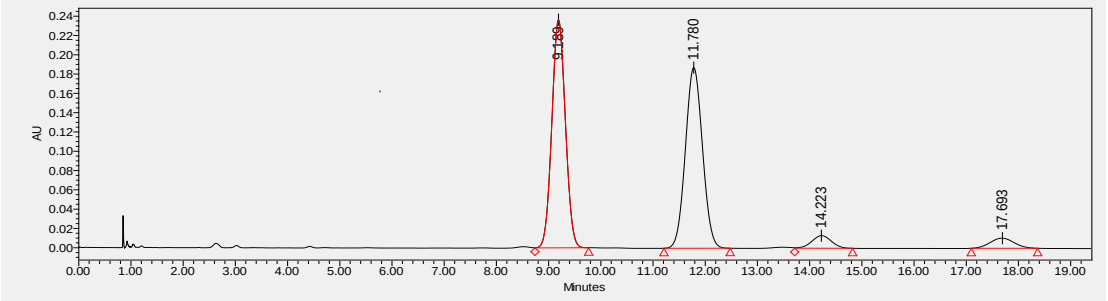



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 5.181 | 777781 | 3.35 |
| 2 | 6.714 | 20721563 | 89.14 |
| 3 | 7.412 | 1686334 | 7.25 |
| 4 | 8.822 | 60415 | 0.26 |

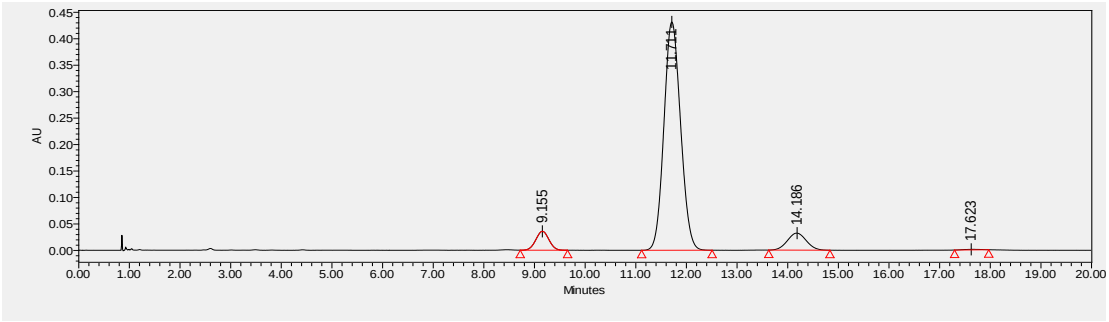



**3z**

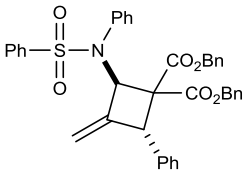
**Dibenzyl (*E*)-2-[(4-methyl-*N*-phenylphenyl)sulfonamido]-3-methylene-4-styrylcyclobutane-1,1-dicarboxylate 3z** The compound **3z** was purified by silica gel chromatography (petroleum ether /ethyl acetate = 6/1) to afford a yellow oil in 49% yield. **Major diastereomer: SFC** (SFC Daicel Chiralcel **IC-3**, $CO_2$/MeOH = 80/20, flow rate 1.5 mL/min, λ = 254 nm), $t_r$ (major-major) = 9.16 min, $t_r$ (major-minor) = 11.71 min, ee = 88%. dr = 92/8 (by $^1$H NMR). $[\alpha]_D^{19.5}$ = – 38.1 (*c* = 0.67 in $CH_2Cl_2$, D = 405 nm). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.33 – 7.27 (m, 6H), 7.25 – 7.12 (m, 11H), 7.09 – 7.01 (m, 5H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.13 – 6.04 (m, 1H), 5.89 – 5.82 (m, 1H), 5.32 (d, *J* = 12.4 Hz, 1H), 5.16 – 5.12 (m, 1H), 5.11 – 5.03 (m, 2H), 4.99 – 4.86 (m, 2H), 4.37 – 4.33 (m, 1H), 2.40 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 168.1, 167.4, 146.2, 143.5, 137.8, 137.2, 136.4, 135.2, 134.8, 134.5, 131.5, 129.2, 128.6, 128.4, 128.4, 128.3, 128.2, 128.12, 128.08, 127.9, 127.8, 127.6, 126.3, 124.2, 113.7, 67.7, 67.5, 65.2, 63.2, 50.8, 21.5. **IR (film)**: 1730, 1493, 1452, 1265, 1163, 1084, 904, 698, 570. **HRMS** (ESI-FT) calcd for $C_{42}H_{37}NO_6SNa$ ([M+Na$^+$]) = 706.2234, Found 706.2234.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 9.189 | 4252758 | 46.28 |
| 2 | 11.780 | 4261774 | 46.38 |
| 3 | 14.223 | 341050 | 3.71 |
| 4 | 17.693 | 333688 | 3.63 |

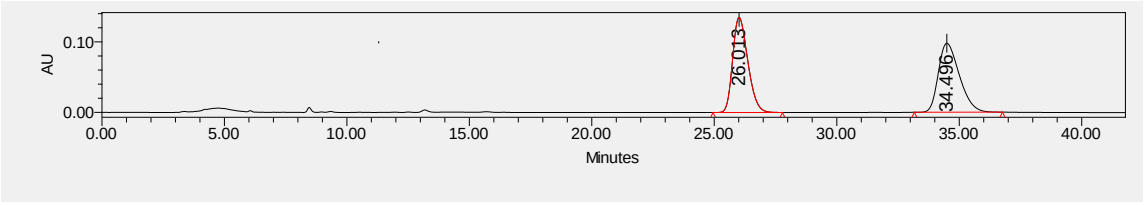



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 9.155 | 645636 | 5.69 |
| 2 | 11.711 | 9844323 | 86.72 |
| 3 | 14.186 | 837555 | 7.38 |
| 4 | 17.623 | 24011 | 0.21 |

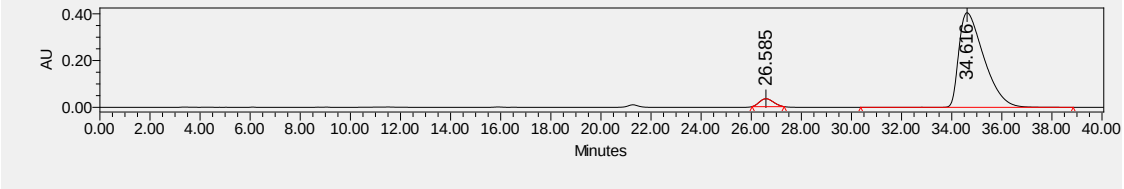



**4a**

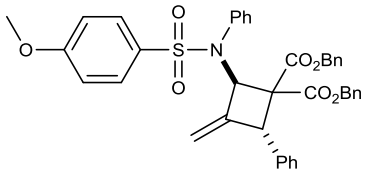
**Dibenzyl 3-methylene-4-phenyl-2-(*N*-phenylphenylsulfoamido)cyclobutane-1, 1-dicarboxylate 4a** The compound **4a** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 95% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 34.62 min, $t_r$ (minor) = 26.59 min, ee = 90%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{26.3}$ = +34.1 (*c* = 1.01 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.57 – 7.53 (m, 1H), 7.45 – 7.40 (m, 2H), 7.32 – 7.12 (m, 18H), 6.76 – 6.73 (m, 2H), 6.17 – 6.15 (m, 1H), 5.31 (d, *J* = 12.0 Hz, 1H), 5.21 – 5.20 (m, 1H), 5.13 – 5.09 (m, 2H), 4.95 – 4.92 (m, 1H), 4.66 (d, *J* = 12.4 Hz, 1H), 4.24 (d, *J* = 12.4 Hz, 1H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.5, 145.6, 140.3, 137.9, 136.0, 135.1, 134.6, 132.7, 131.5, 128.71, 128.66, 128.6, 128.44, 128.39, 128.19, 128.15, 128.0, 127.8, 127.7, 114.5, 67.8, 67.4, 65.6, 64.8, 53.4. **IR (film)**: 1728, 1498, 1452, 1265, 1163, 1085, 899, 696, 588. **HRMS** (ESI-FT) calcd for $C_{39}H_{33}NO_6SNa$ ([M+Na$^+$]) = 666.1921, Found 666.1915.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 26.013 | 5800750 | 49.90 |
| 2 | 34.496 | 5823035 | 50.10 |

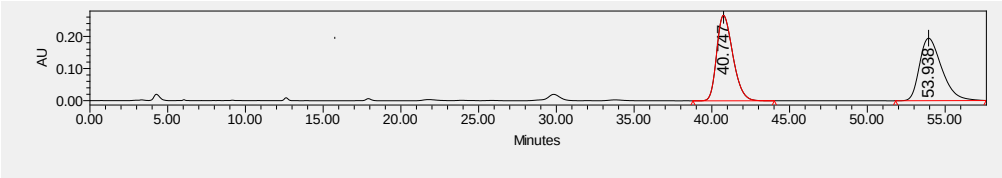



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 26.585 | 1296211 | 4.41 |
| 2 | 34.616 | 28097463 | 95.59 |

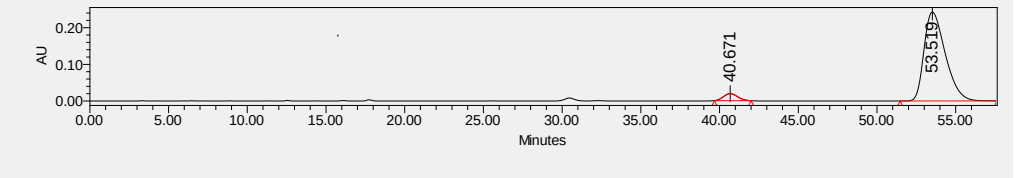



**4b**

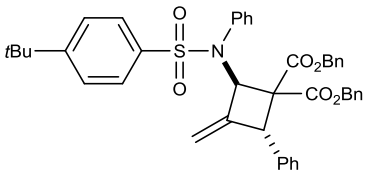
**Dibenzyl 2-[(4-methoxy-*N*-phenylphenyl)sulfonamido]-3-methylene-4-phenylcyclobutane-1,1-dicarboxylate 4b** The compound **4b** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a colorless oil in 99% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 53.52 min, $t_r$ (minor) = 40.67 min, ee = 90%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{26.6}$ = +32.4 (*c* = 0.75 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.32 – 7.11 (m, 18H), 6.89 – 6.85 (m, 2H), 6.76 – 6.73 (m, 2H), 6.14 – 6.12 (m, 1H), 5.32 (d, *J* = 12.4 Hz, 1H), 5.21 (s, 1H), 5.17 – 5.09 (m, 2H), 4.96 – 4.95 (m, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 3.84 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.5, 162.9, 145.8, 138.2, 136.1 135.1, 134.6, 132.0, 131.5, 130.0, 128.7, 128.6, 128.5, 128.39, 128.36, 128.2, 128.1, 127.9, 127.6, 114.4, 113.7, 67.8, 67.3, 65.5, 64.8, 55.5, 53.4. **IR (film)**: 1730, 1494, 1456, 1261, 1159, 1088, 900, 698, 574. **HRMS** (ESI-FT) calcd for $C_{40}H_{35}NO_7SNa$ ([M+Na$^+$]) = 696.2026, Found 696.2020.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 40.747 | 19144692 | 49.88 |
| 2 | 53.938 | 19239290 | 50.12 |

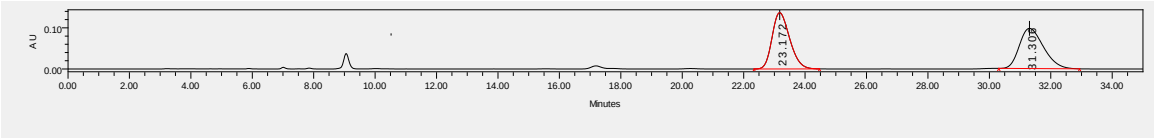



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 40.671 | 1191243 | 4.97 |
| 2 | 53.519 | 22768689 | 95.03 |

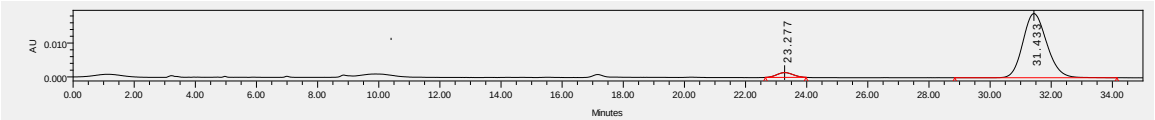



**4c**

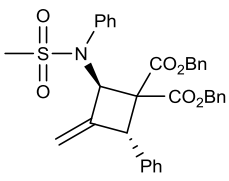
**Dibenzyl 2-{[4-(*tert*-butyl)-*N*-phenylphenyl]sulfonamido}-3-methylene-4-phenylcyclobutane-1,1-dicarboxylate 4c** The compound **4c** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 99% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 31.43 min, $t_r$ (minor) = 23.28 min, ee = 90%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{26.8}$ = +27.5 (*c* = 0.75 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 2H), 7.44 – 7.41 (m, 2H), 7.33 – 7.20 (m, 12H), 7.18 – 7.13 (m, 6H), 6.75 – 6.73 (m, 2H), 6.15 – 6.13 (m, 1H), 5.32 (d, *J* = 12.0 Hz, 1H), 5.19 – 5.18 (m, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 5.05 – 5.04 (m, 1H), 4.95 – 4.93 (m, 1H), 4.65 (d, *J* = 12.4 Hz, 1H), 4.24 (d, *J* = 12.4 Hz, 1H), 1.33 (s, 9H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.5, 156.6, 145.7, 138.1, 137.3, 136.1, 135.2, 134.6, 131.4, 128.63, 128.62, 128.40, 128.36, 128.2, 128.1, 127.9, 127.7, 125.6, 114.3, 67.7, 67.3, 65.5, 64.8, 53.4, 35.1, 31.1. **IR (film)**: 1730, 1492, 1456, 1265, 1165, 1082, 901, 698, 580. **HRMS** (ESI-FT) calcd for $C_{43}H_{41}NO_6SNa$ ([M+Na$^+$]) = 722.2547, Found 722.2538.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 23.172 | 5434524 | 50.55 |
| 2 | 31.306 | 5315703 | 49.45 |

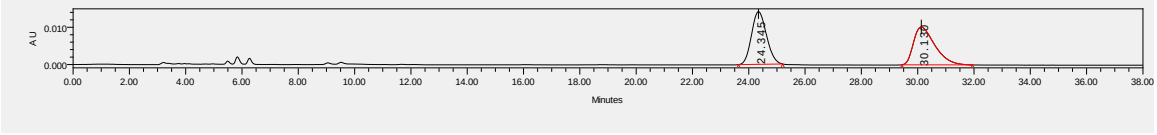



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 23.277 | 52037 | 4.81 |
| 2 | 31.433 | 1030911 | 95.19 |

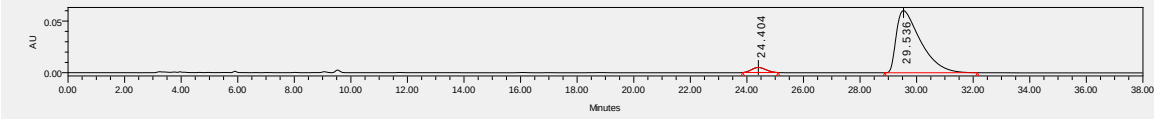



**4d**

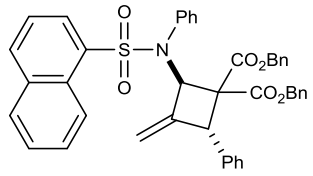
**Dibenzyl (2*R*,4*R*)-3-methylene-4-phenyl-2-(*N*-phenylmethylsulfoamido)cyclobutane-1,1-dicarboxylate 4d** The compound **4c** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a colorless oil in 85% yield. **Major diastereomer:** **HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 29.54 min, $t_r$ (minor) = 24.40 min, ee = 91%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{27.9}$ = +33.9 (*c* = 0.77 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 5H), 7.28 – 7.15 (m, 13H), 6.82 – 6.79 (m, 2H), 5.97 – 5.95 (m, 1H), 5.62 (s, 1H), 5.35 (s, 1H), 5.20 (q, *J* = 12.0, 126.4 Hz, 2H), 5.13 – 5.11 (m, 1H), 4.67 (d, *J* = 12.4 Hz, 1H), 4.26 (d, *J* = 12.0 Hz, 1H), 2.99 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.78, 167.76, 146.8, 139.4, 136.2, 135.0, 134.6, 130.0, 129.3, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 113.4, 67.9, 67.5, 66.2, 64.7, 53.3, 41.1. **IR (film)**: 1728, 1493, 1454, 1363, 1157, 1083, 905, 698. **HRMS** (ESI-FT) calcd for $C_{34}H_{31}NO_6SNa$ ([M+Na$^+$]) = 604.1764, Found 604.1759.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 24.345 | 521943 | 49.54 |
| 2 | 30.130 | 531711 | 50.46 |

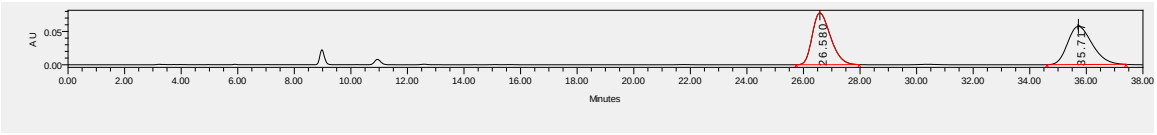



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 24.404 | 170811 | 4.54 |
| 2 | 29.536 | 3593317 | 95.46 |

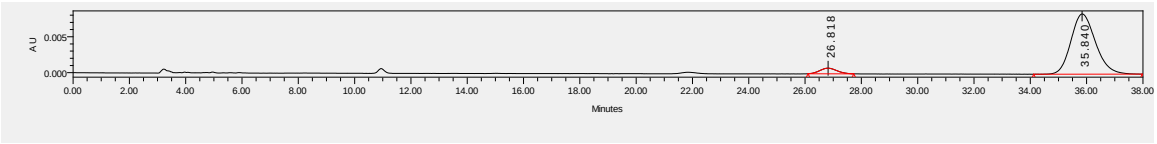


4e

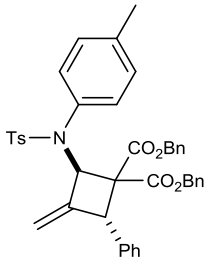
**Dibenzyl 3-methylene-4-phenyl-2-(*N*-phenylnaphthalene-1-sulfonaimdo)cyclobutane-1,1-dicarboxylate 4e** The compound **4e** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 98% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 35.84 min, $t_r$ (minor) = 26.82 min, ee = 88%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{25.9}$ = +40.5 (*c* = 0.97 in $CH_2Cl_2$, D = 405 nm). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.58 – 8.55 (m, 1H), 8.11 – 8.08 (m, 1H), 8.03 – 8.00 (m, 1H), 7.92 – 7.90 (m, 1H), 7.59 – 7.51 (m, 2H), 7.40 – 7.35 (m, 2H), 7.26 – 7.11 (m, 15H), 7.01 – 6.98 (m, 2H), 6.72 – 6.69 (m, 2H), 6.56 – 6.55 (m, 1H), 5.29 (d, *J* = 12.0 Hz, 1H), 5.12 (s, 1H), 5.05 (s, 1H), 4.96 (d, *J* = 12.0 Hz, 1H), 4.76 – 4.74 (m, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.26 (d, *J* = 12.4 Hz, 1H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.5, 167.4, 145.4, 136.3, 135.9, 135.1, 134.6, 134.4, 134.0, 132.3, 131.1, 128.8, 128.7, 128.6, 128.3, 128.24, 128.19, 128.15, 128.1, 128.03, 127.95, 127.9, 127.7, 126.8, 125.5, 124.0, 114.8, 67.6, 67.4, 64.7, 64.4, 53.6. **IR (film)**: 1728, 1497, 1452, 1265, 1161, 1080, 901, 696, 590. **HRMS** (ESI-FT) calcd for $C_{43}H_{35}NO_6SNa$ ([M+Na$^+$]) = 716.2077, Found 716.2073.




| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 26.580 | 3487724 | 50.14 |
| 2 | 35.717 | 3467911 | 49.86 |

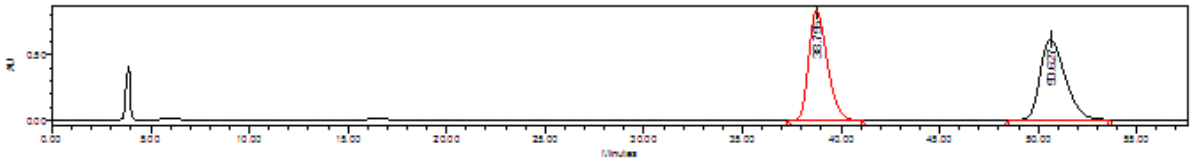



| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 26.818 | 32598 | 6.04 |
| 2 | 35.840 | 507075 | 93.96 |



4f

**Dibenzy 2-{[4-methyl-*N*-(*p*-tolyl)phenyl]sulfonamido}-3-methylene-4-phenylcyclobutane-1,1-dicarboxylate 4f** The compound **4f** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford a colorless oil in 99% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm), $t_r$ (major) = 50.83 min, $t_r$ (minor) = 39.55 min, ee = 91%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{20.7}$ = +15.6 (*c* = 1.37 in $CH_2Cl_2$). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.29 – 7.14 (m, 15H), 7.05 – 7.02 (m, 2H), 6.99 – 6.96 (m, 2H), 6.76 – 6.73 (m, 2H), 6.16 – 6.15 (m, 1H), 5.33 (d, *J* = 12.0 Hz, 1H), 5.19 (s, 1H), 5.13 – 5.09 (m, 2H), 4.90 – 4.89 (m, 1H), 4.66 (d, *J* = 12.4 Hz, 1H), 4.24 (d, *J* = 12.4 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.5, 145.6, 143.4, 138.6, 137.4, 136.1, 135.1, 135.0, 134.6, 131.4, 129.3, 129.2, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 114.4, 67.7, 67.3, 65.4, 64.8, 53.4, 21.5, 21.1. **IR (film)**: 1730, 1503, 1452, 1267, 1163, 1086, 905, 702. **HRMS** (ESI-FT) calcd for $C_{41}H_{37}NO_6SNa$ ([M+Na$^+$]) = 694.2234, Found 694.2238.



| | Retention Time | Area | % Area |
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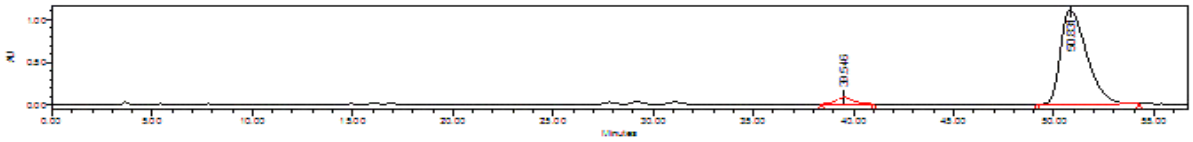
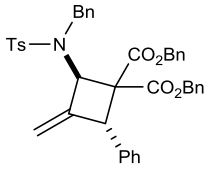
| 2 | 50.527 | 54741841 | 49.98 |

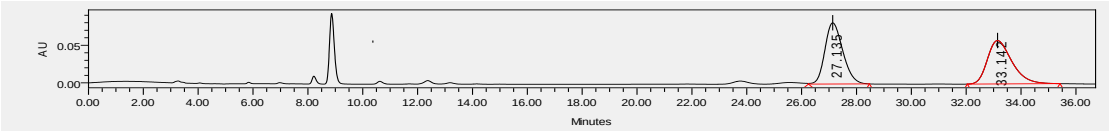


| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 39.546 | 4705125 | 4.50 |
| 2 | 50.831 | 99959212 | 95.50 |



**4g**

**Dibenzy 2-[(*N*-benzyl-4-methylphenyl)sulfoamido]-3-methylene-4-phenylcyclobutane-1,1-dicarboxylate 4g** The compound **4g** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1) to afford a colorless oil in 10% yield. **Major diastereomer: HPLC** (Daicel Chiralcel **IE**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_r$ (major) = 26.63 min, $t_r$ (minor) = 32.54 min, ee = 49%. dr > 95/5 (by $^1$H NMR). $[\alpha]_D^{29.9}$ = –50.0 (*c* = 0.07 in $CH_2Cl_2$, D = 405 nm). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 2H), 7.30 – 7.25 (m, 7H), 7.22 – 7.18 (m, 11H), 7.16 – 7.14 (m, 2H), 6.80 – 6.77 (m, 2H), 5.85 – 5.78 (m, 1H), 5.31 – 5.24 (m, 2H), 5.15 – 5.12 (m, 1H), 4.96 (d, *J* = 12.4 Hz, 1H), 4.92 – 4.88 (m, 1H), 4.65 – 4.58 (m, 2H), 4.33 (d, *J* = 15.6 Hz, 1H), 4.22 (d, *J* = 12.4 Hz, 1H), 2.39 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 168.1, 167.6, 145.3, 143.2, 138.3, 136.7, 136.5, 135.3, 134.6, 129.3, 128.7, 128.51, 128.46, 128.4, 128.34, 128.29, 128.26, 128.21, 128.16, 128.13, 128.10, 128.00, 127.97, 127.5, 127.4, 113.9, 67.9, 67.3, 67.1, 64.3, 63.4, 52.8, 21.5. **HRMS** (ESI-FT) calcd for $C_{41}H_{37}NO_6SNa$ ([M+Na$^+$]) = 694.2234, Found 694.2227.



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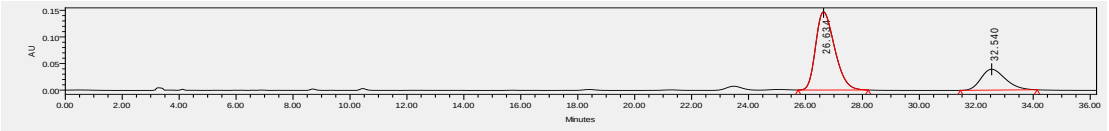
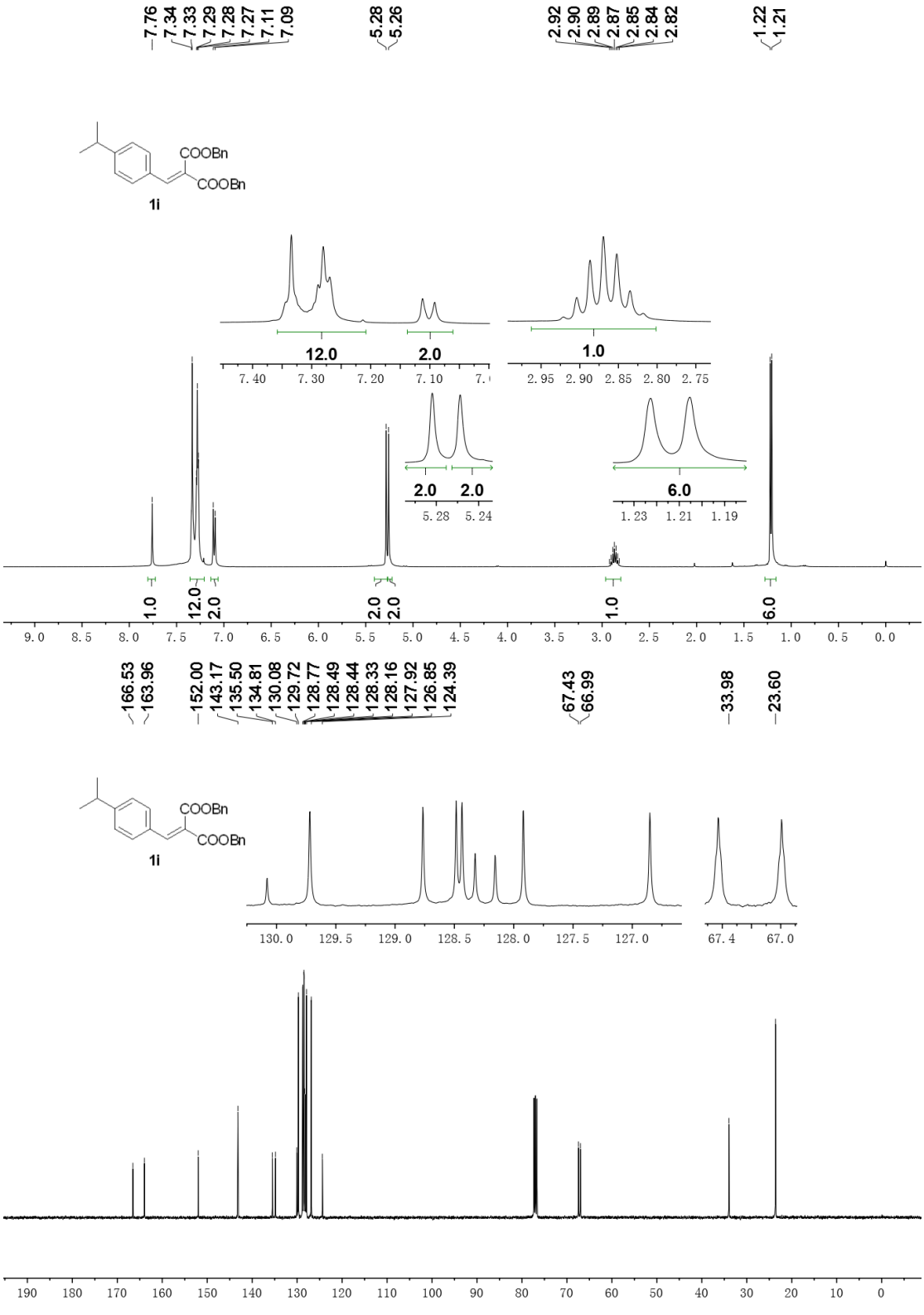


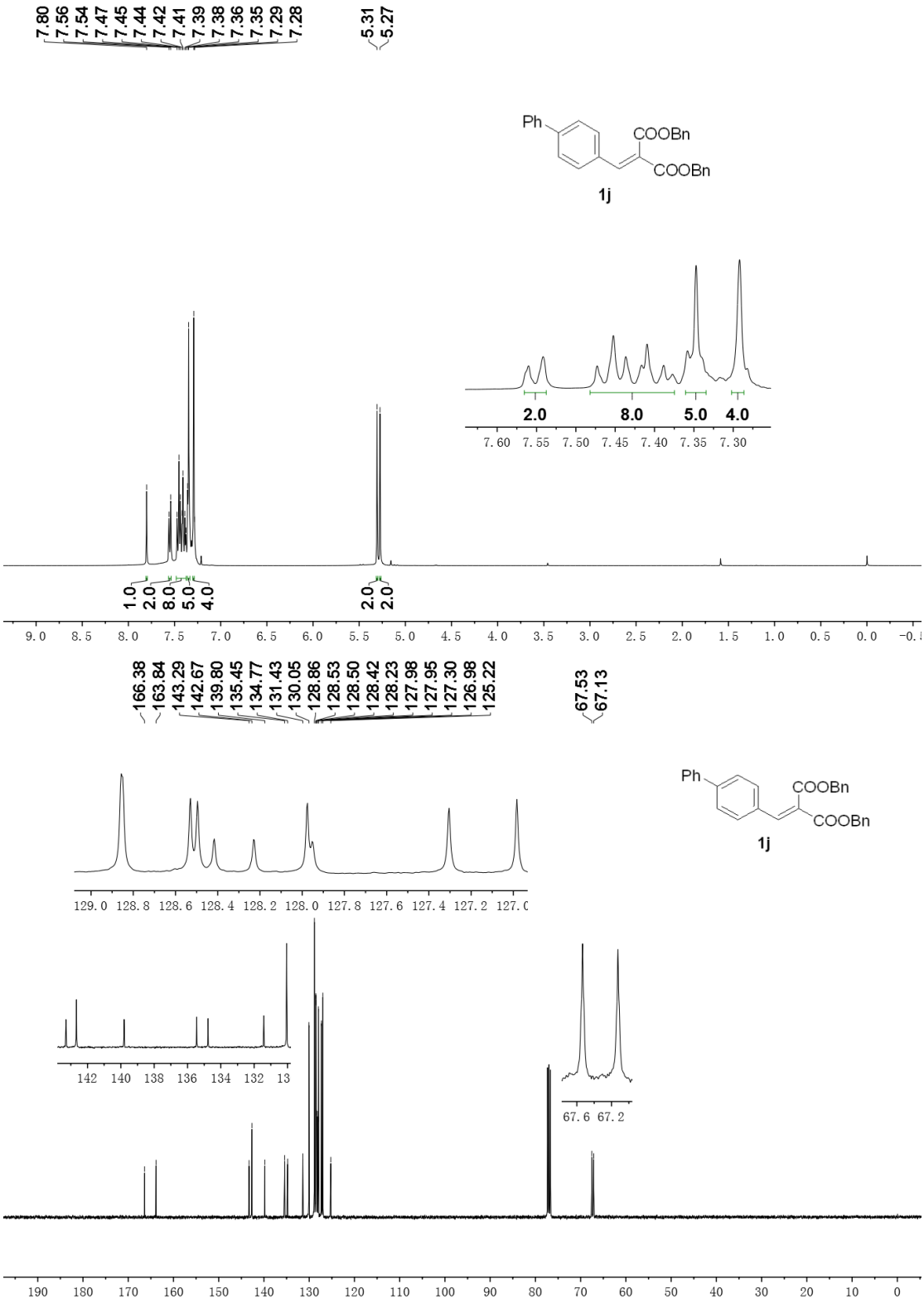
| | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 26.634 | 6794579 | 74.36 |
| 2 | 32.540 | 2342302 | 25.64 |

## 9. Copies of NMR spectra

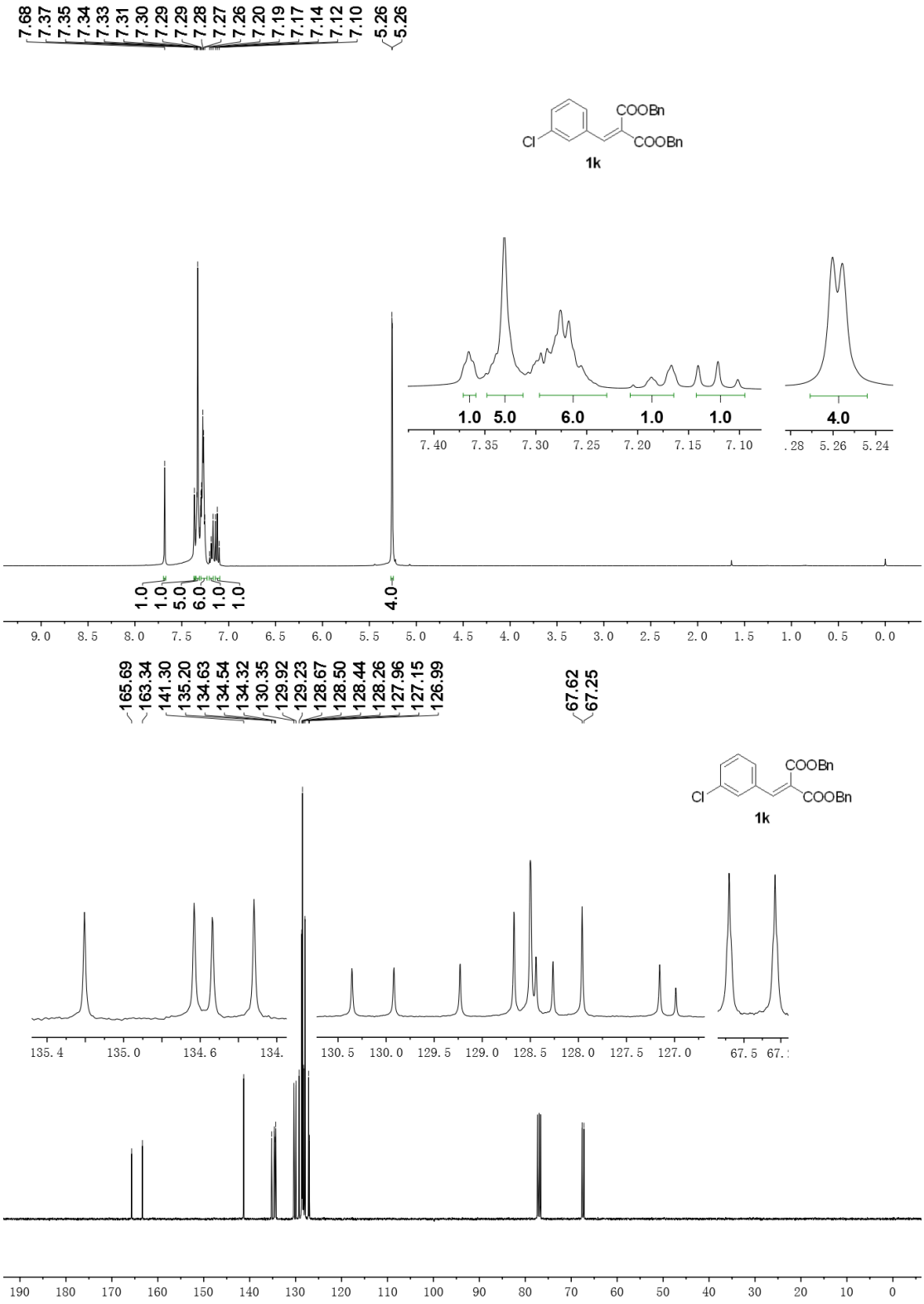
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1i**



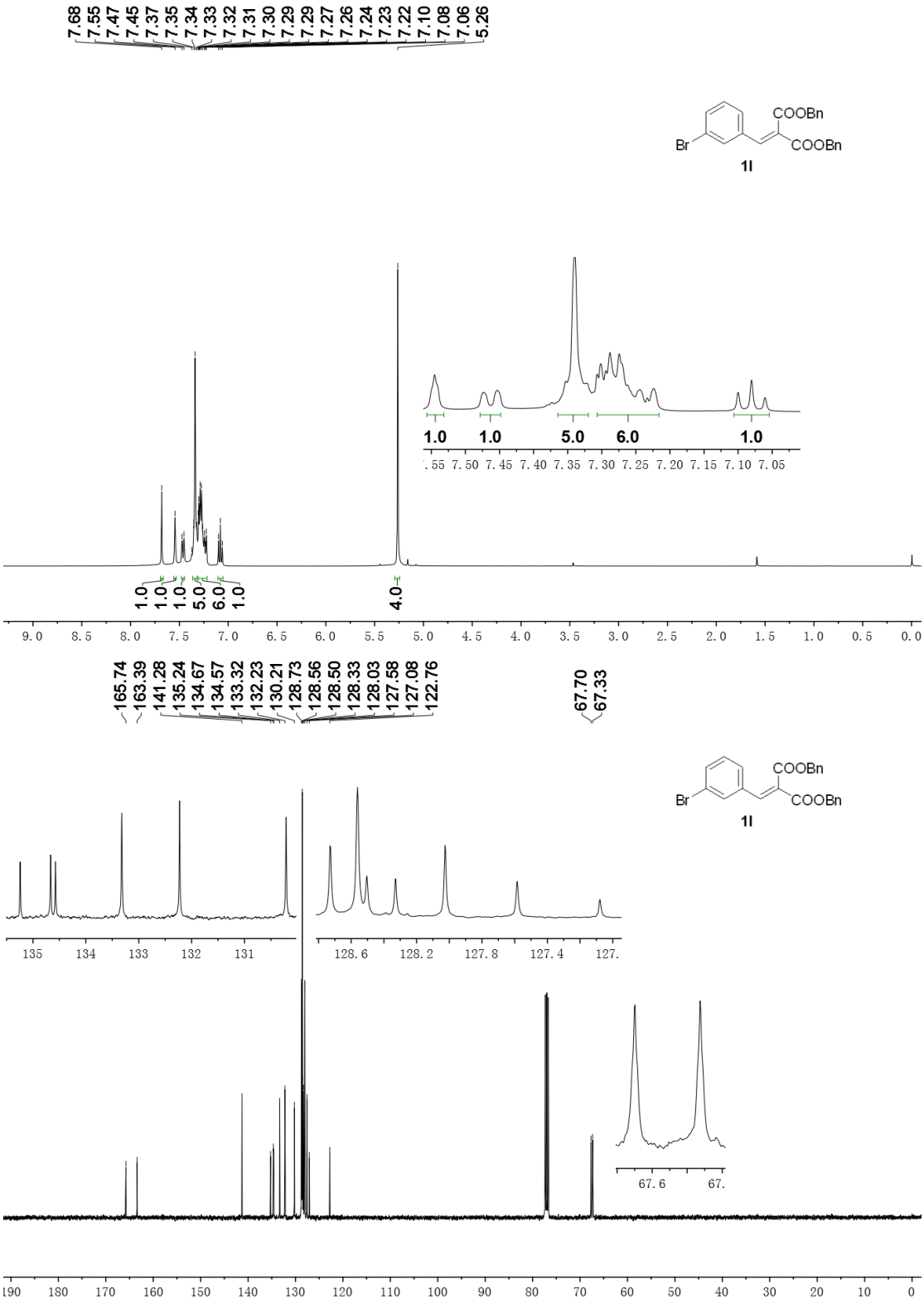
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1j**



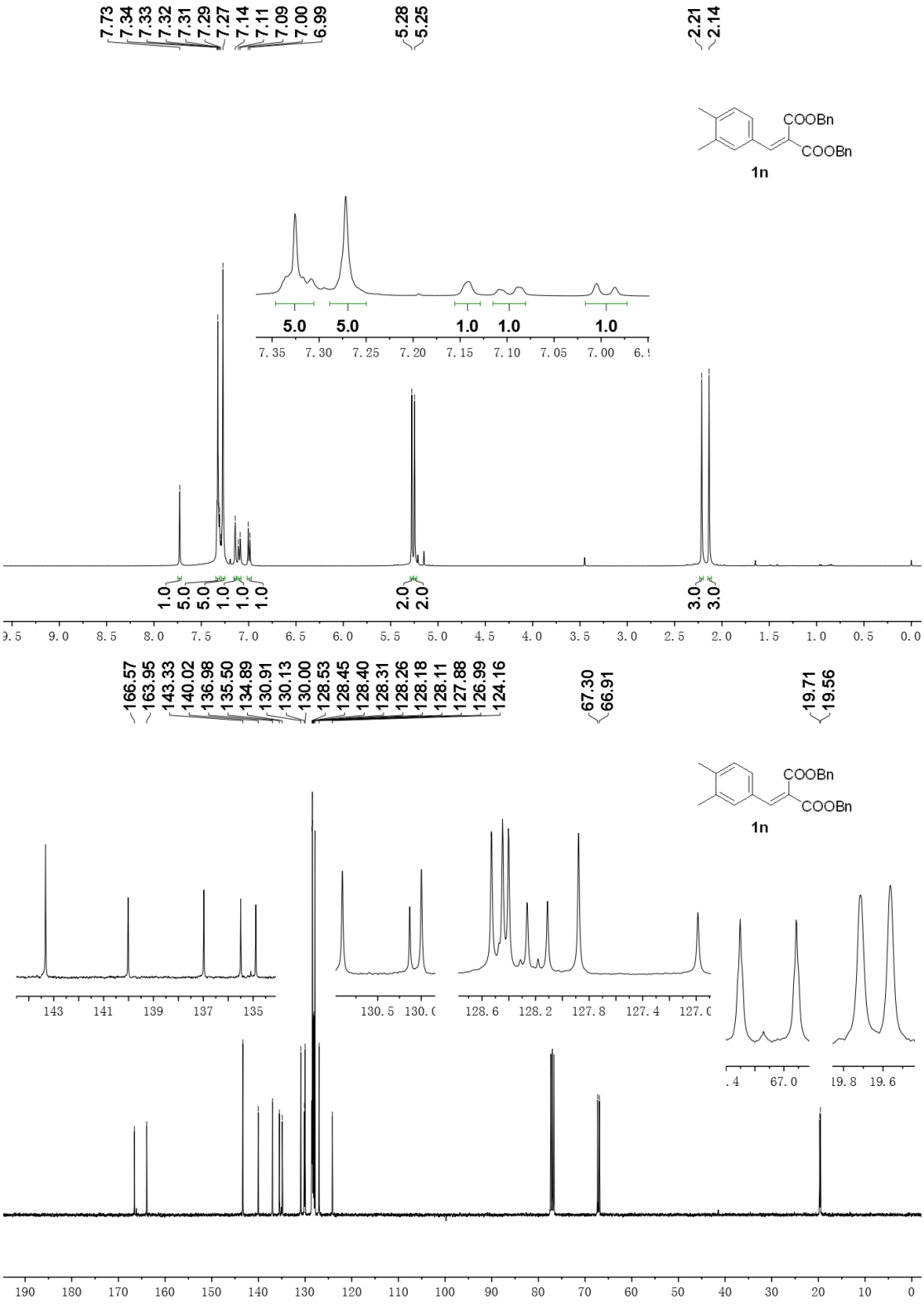
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1k**



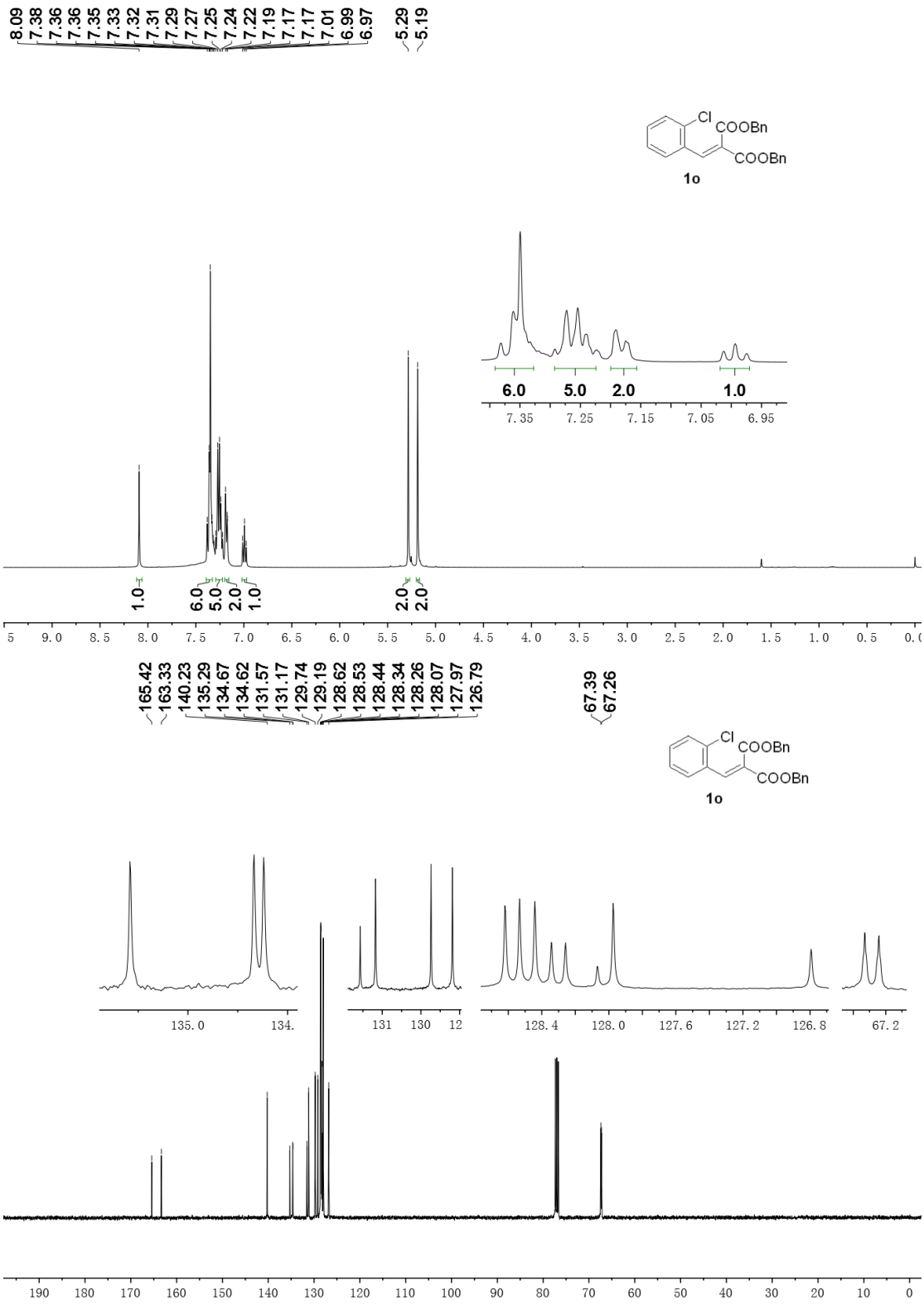
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1l**



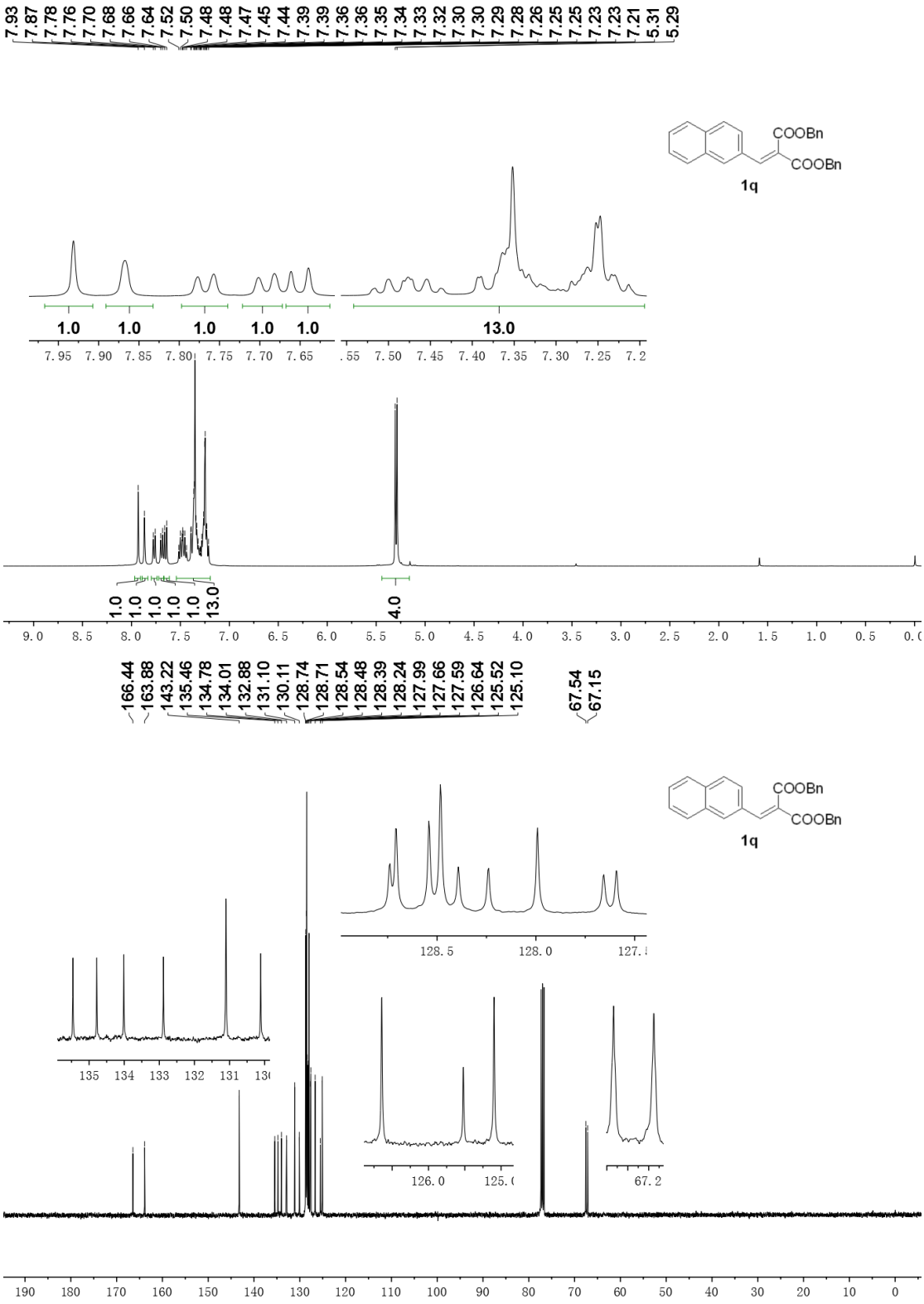
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1n**



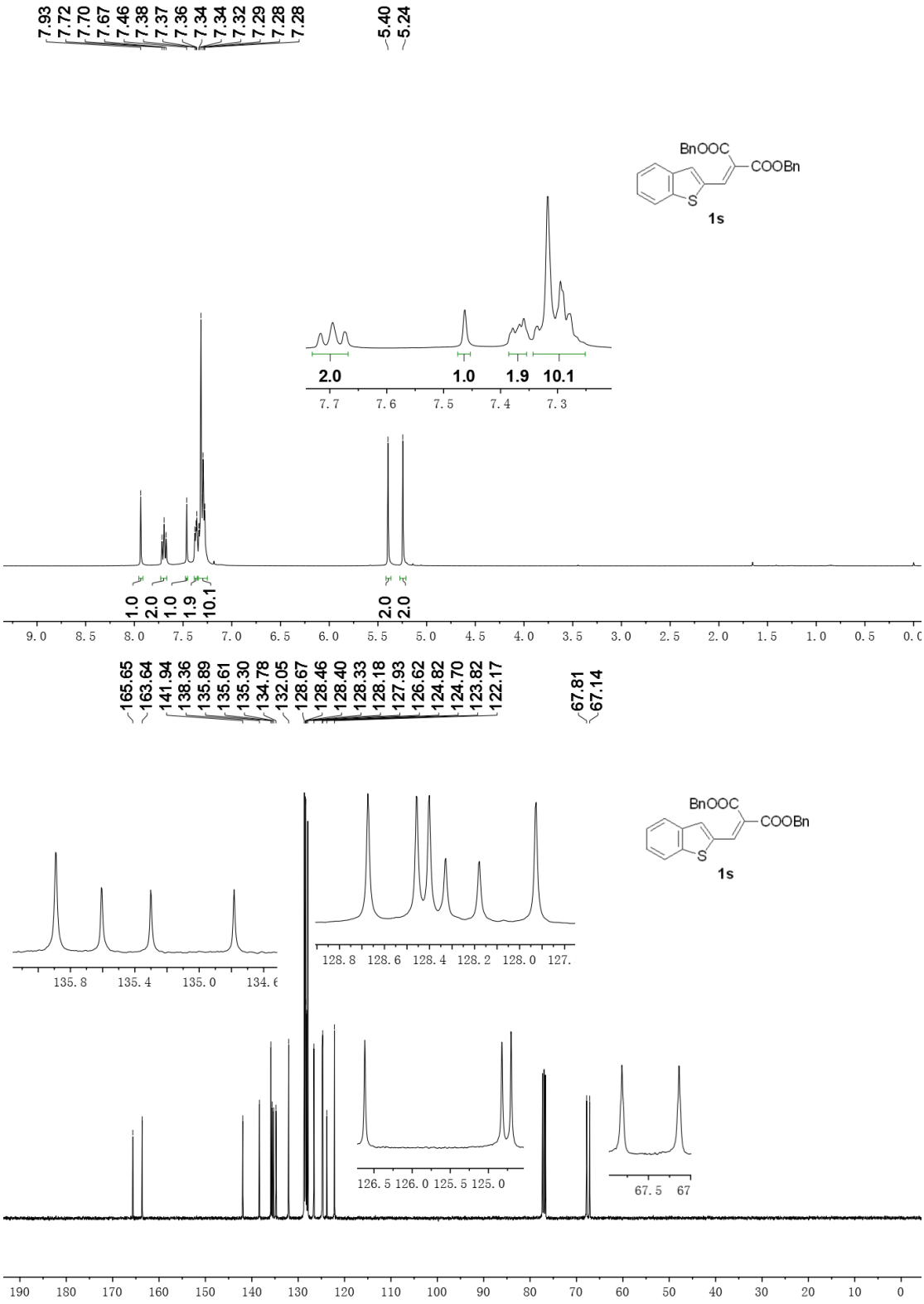
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1o**



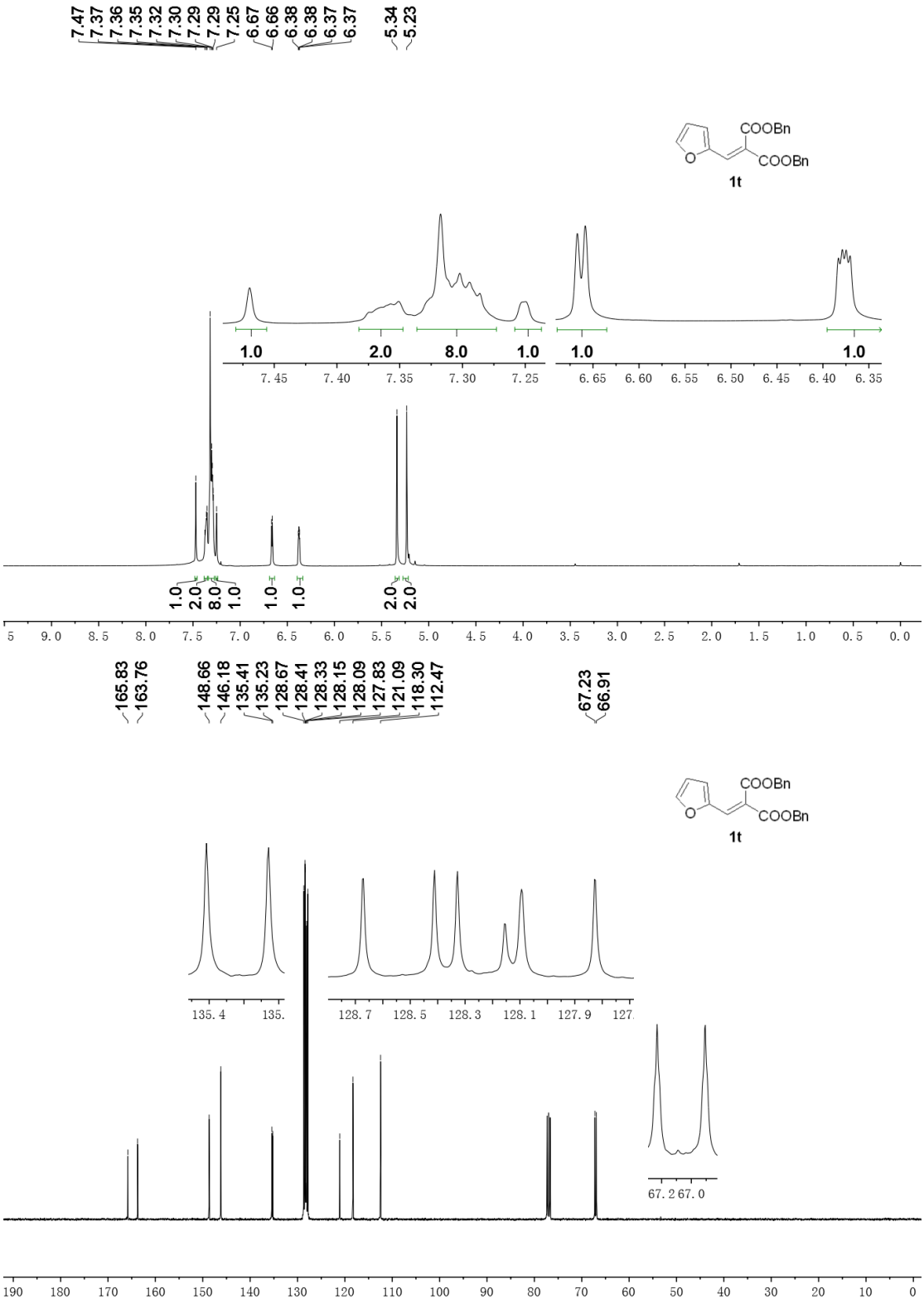
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1q**



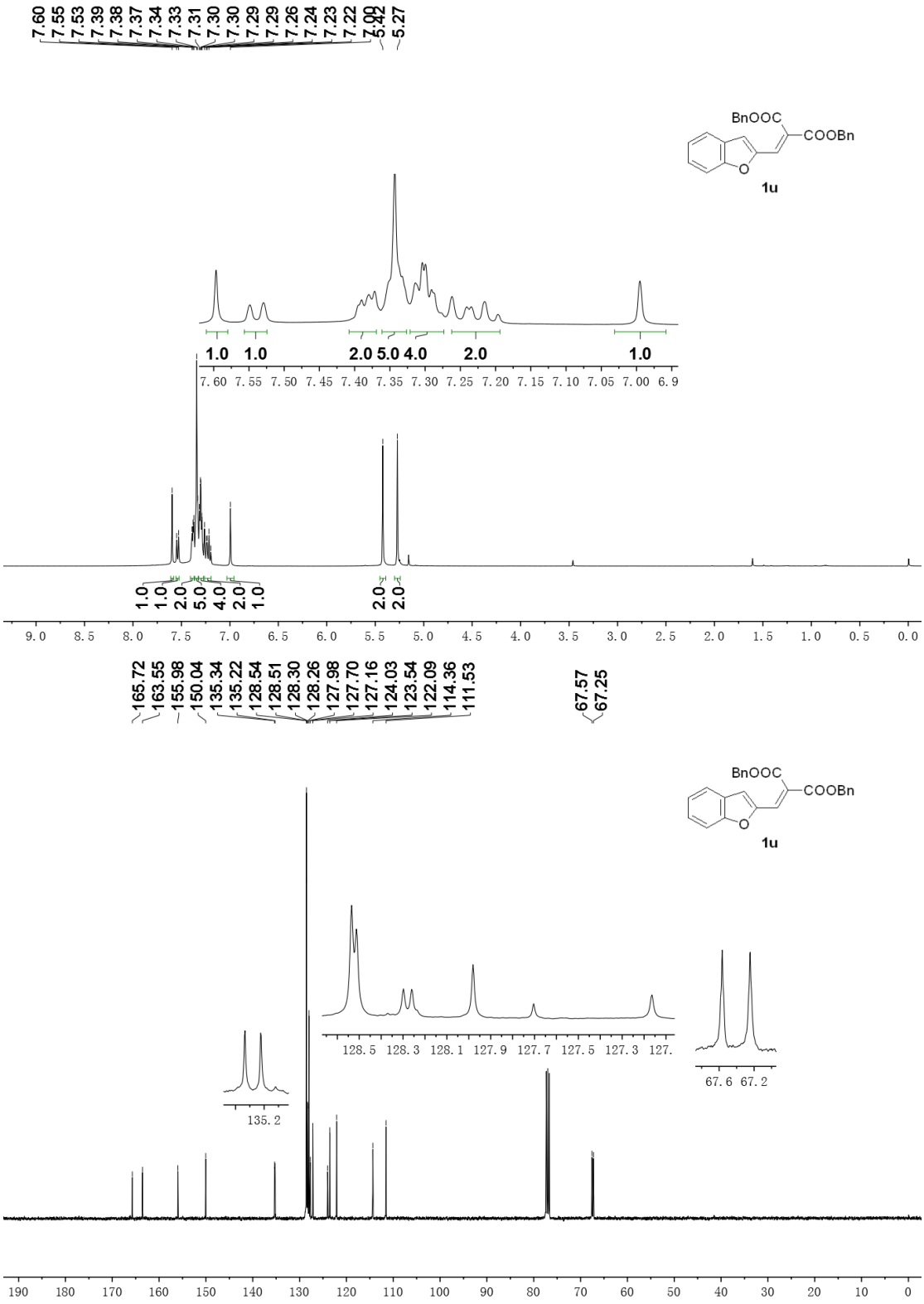
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1s**



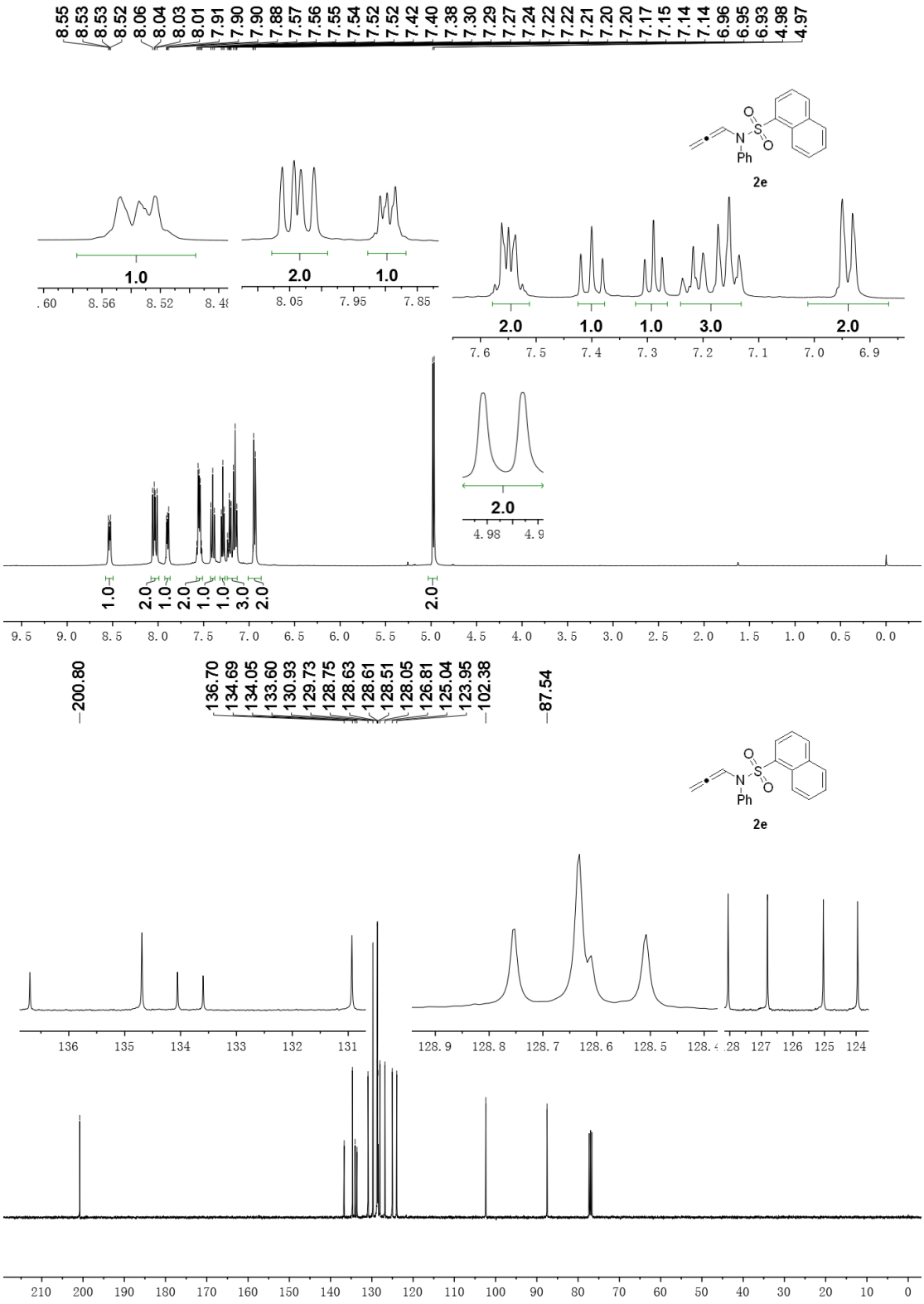
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1t**



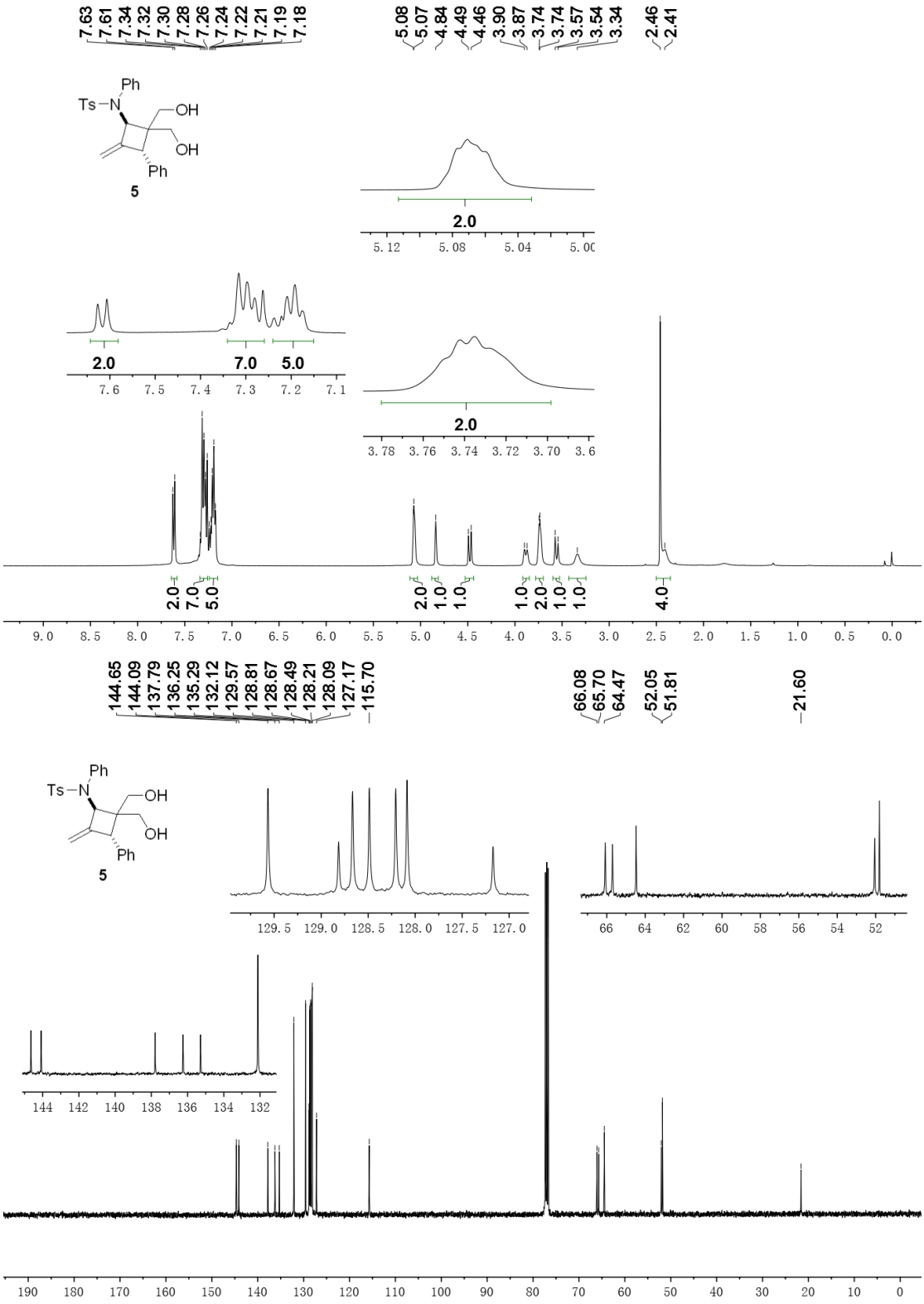
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **1u**



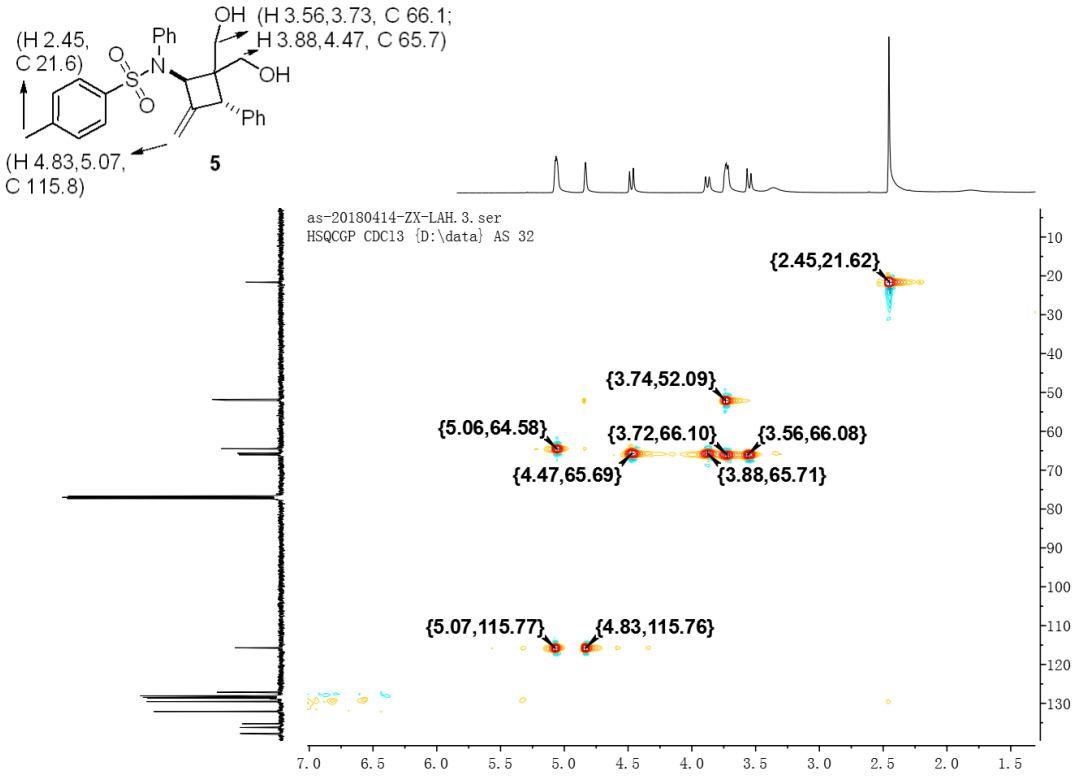
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **2e**

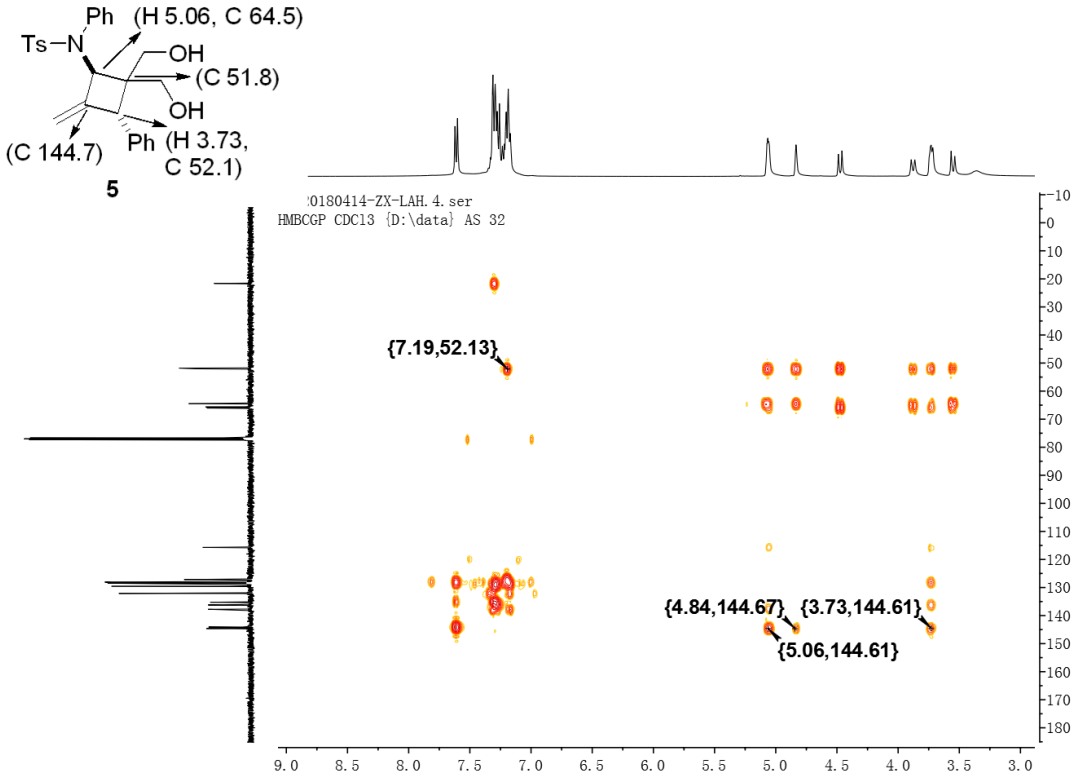


$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compounds **5**

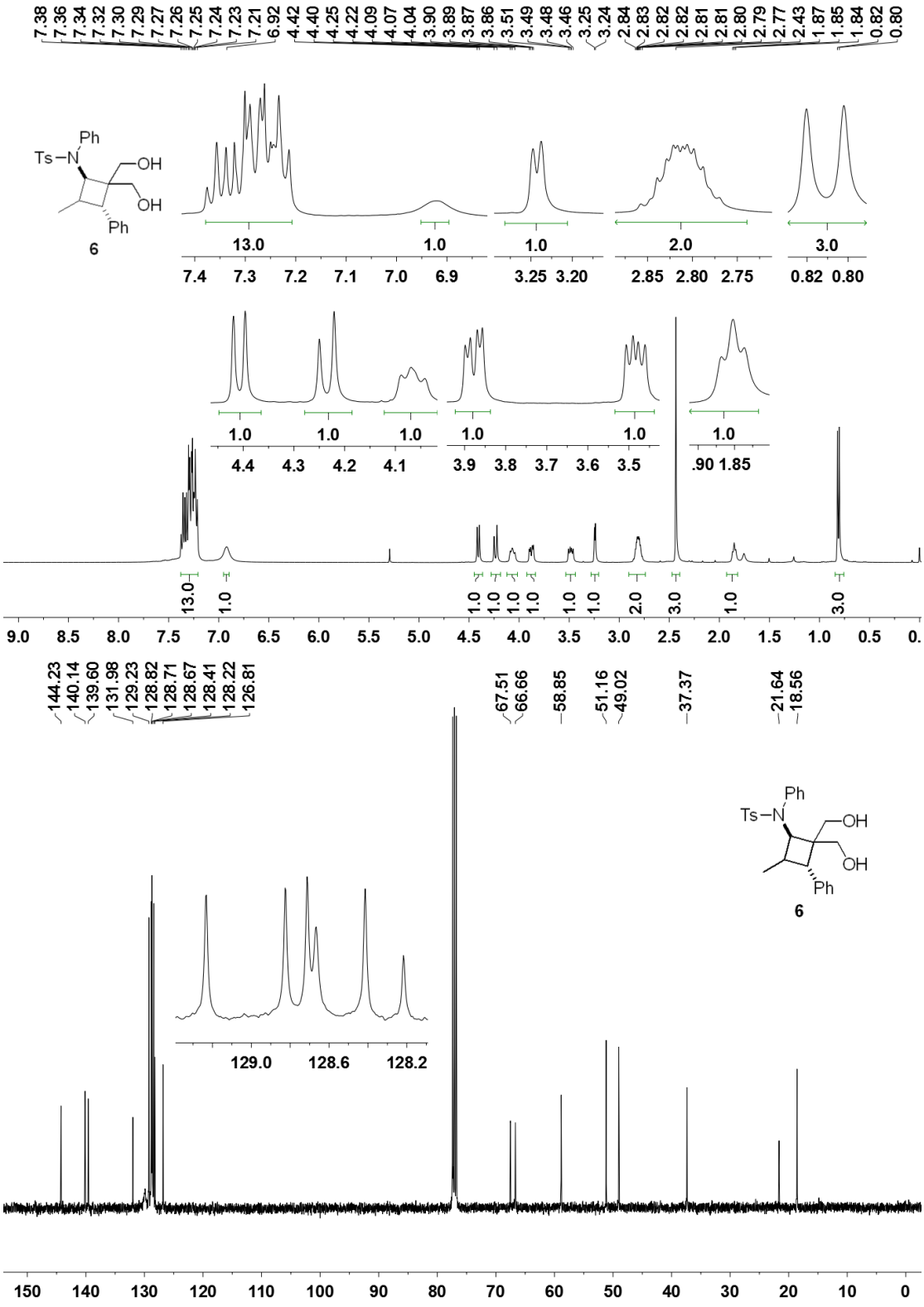


HSQGCP and HMBGCP NMR spectra of compounds **5**

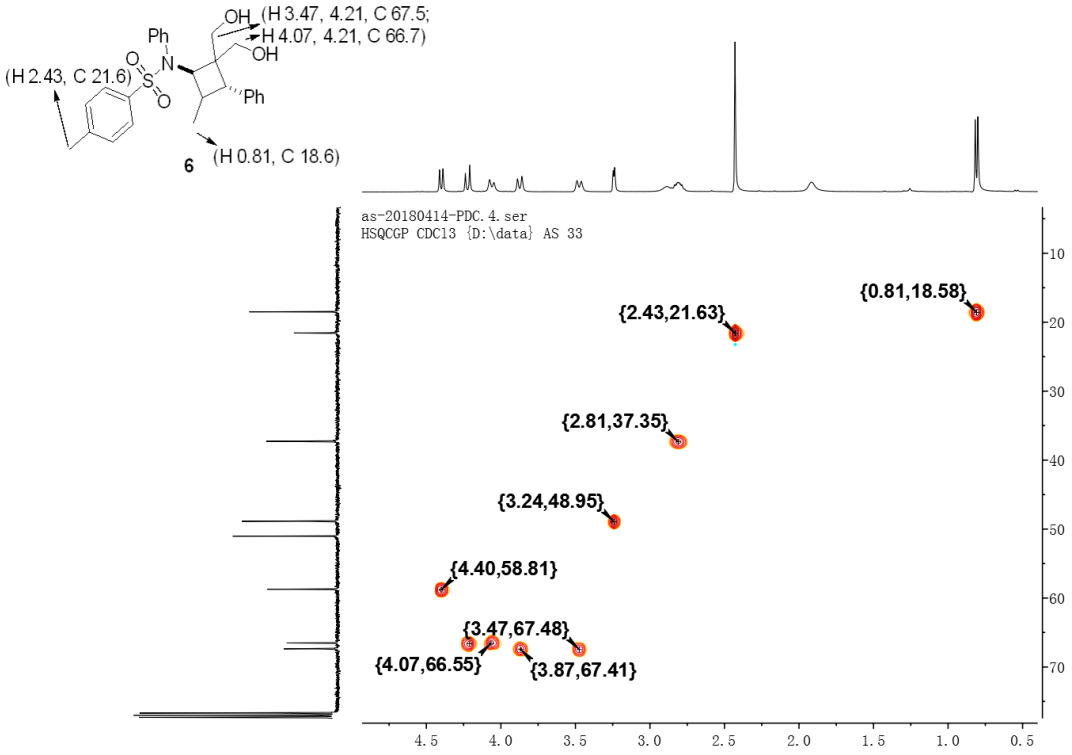


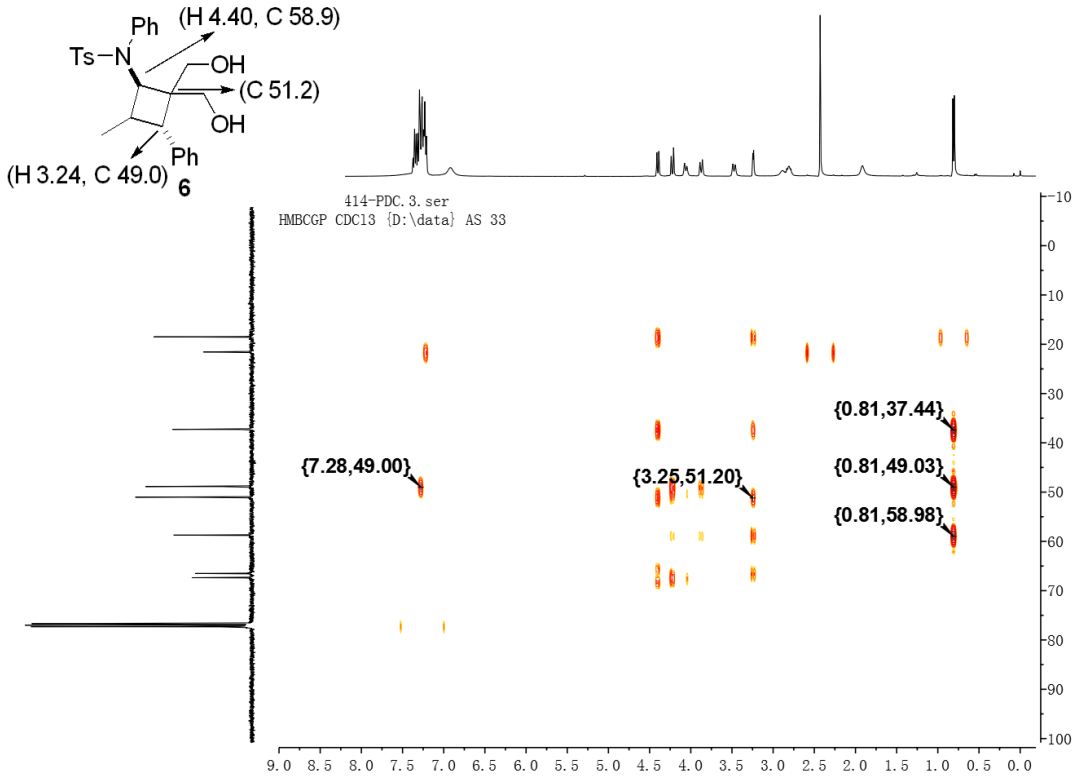



$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **6**

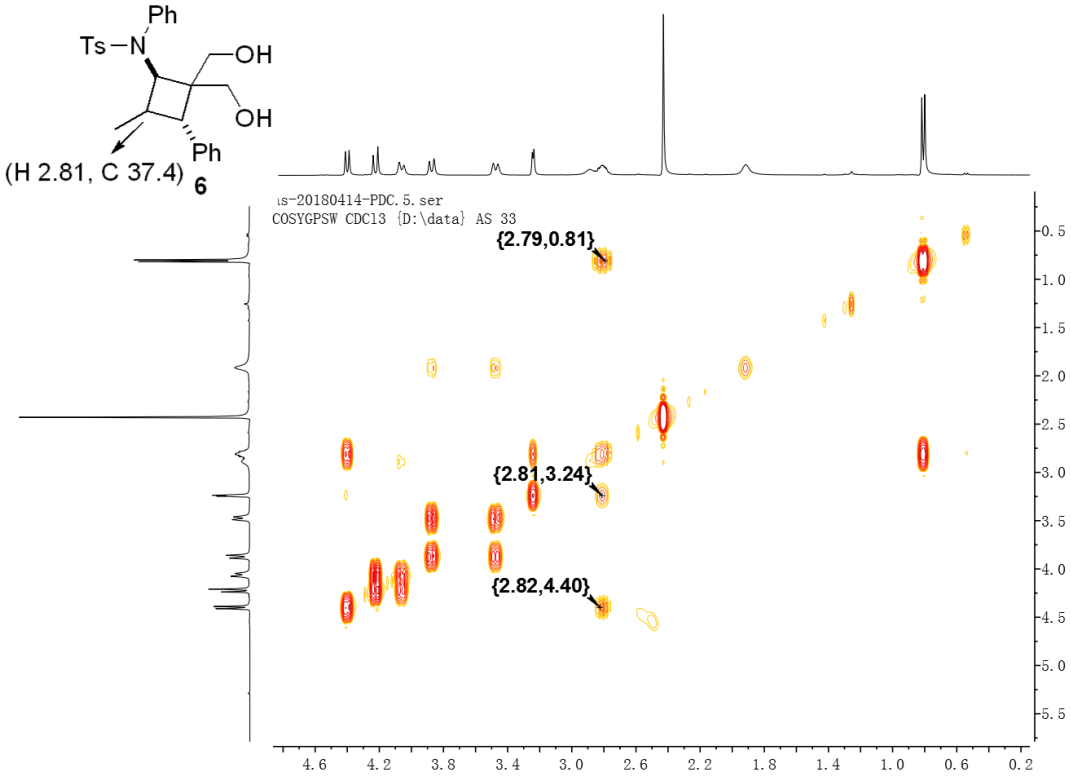


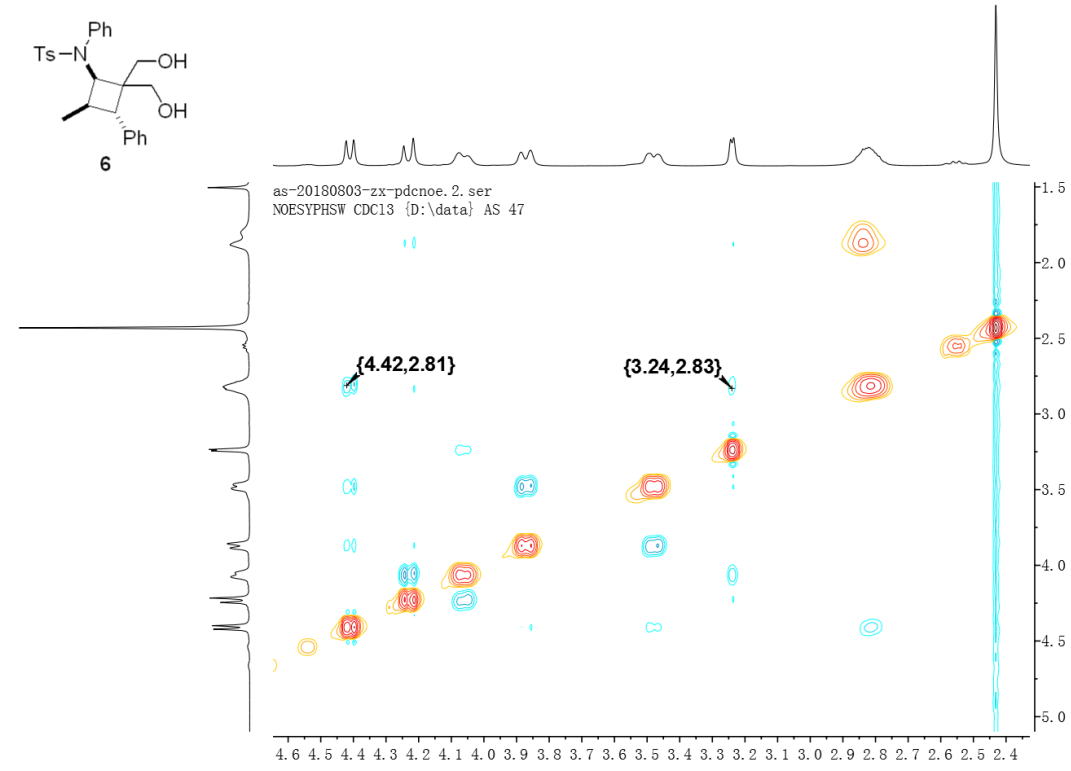
HSQCGP and HMBCGP NMR spectra of compound **6**



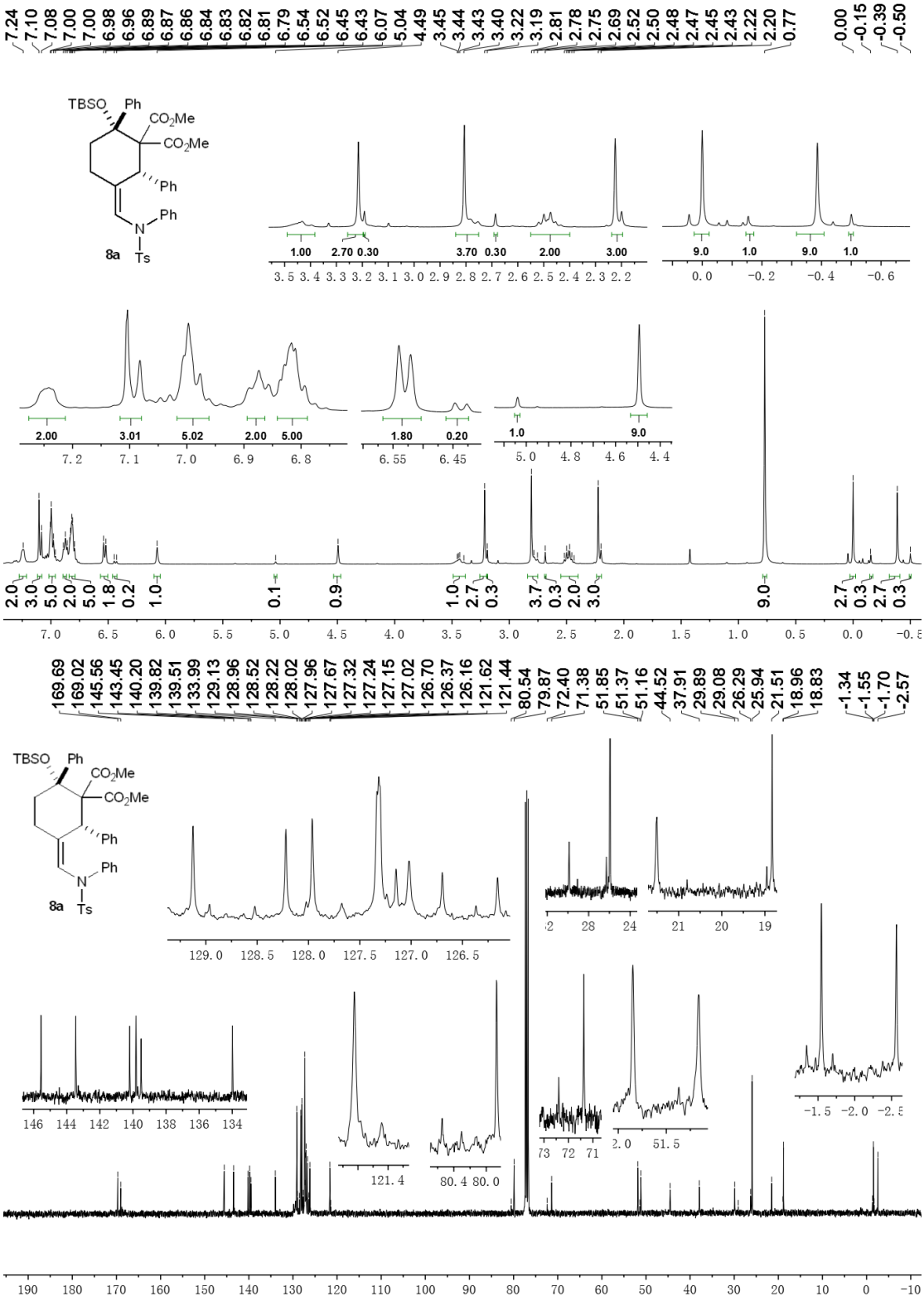



COSYGPSW and NOESYPHSW NMR spectra of compound **6**

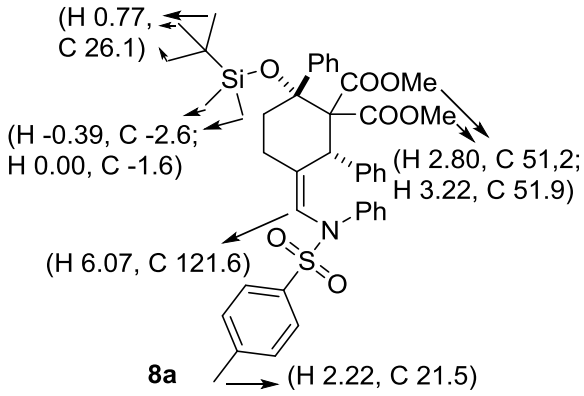


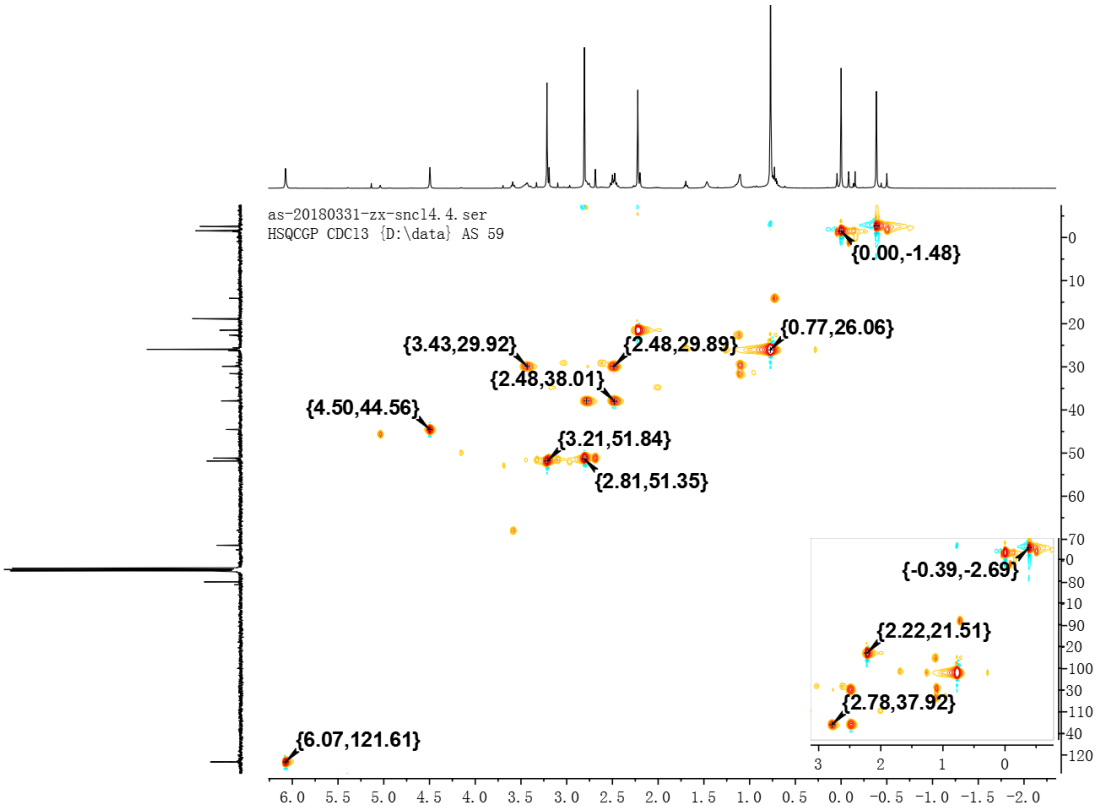



$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of two diastereomers of compounds **8a**

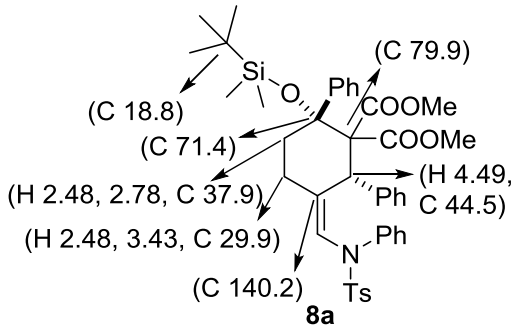


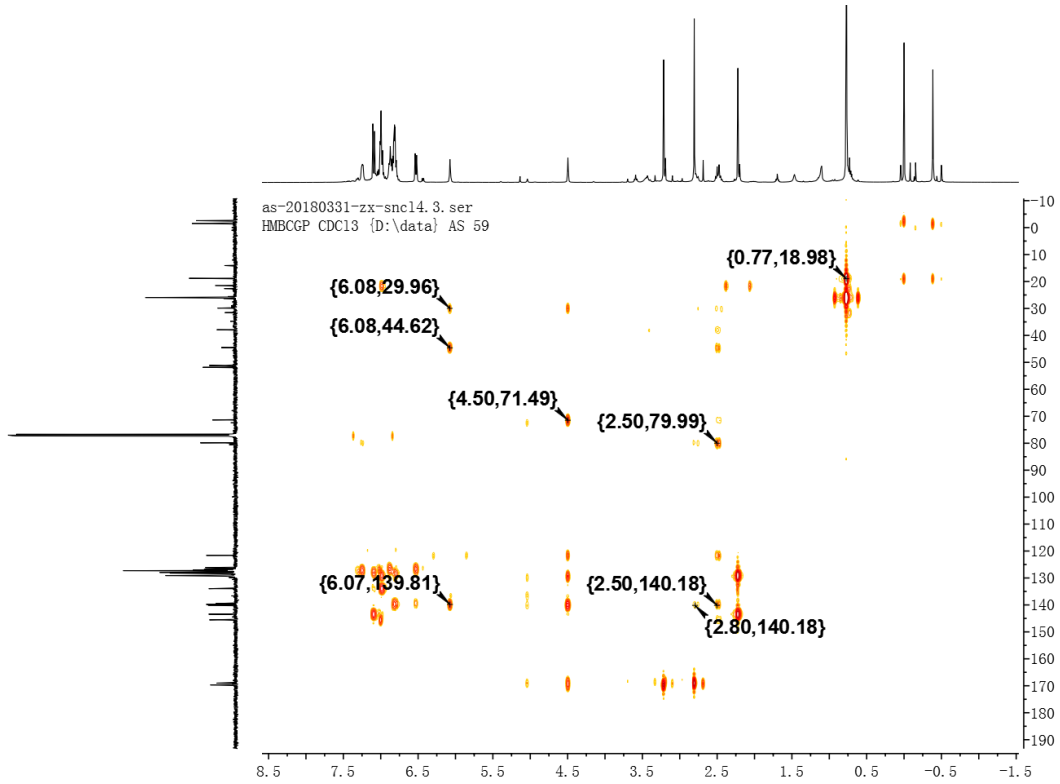
HSQCGP NMR spectra of compound **8a**



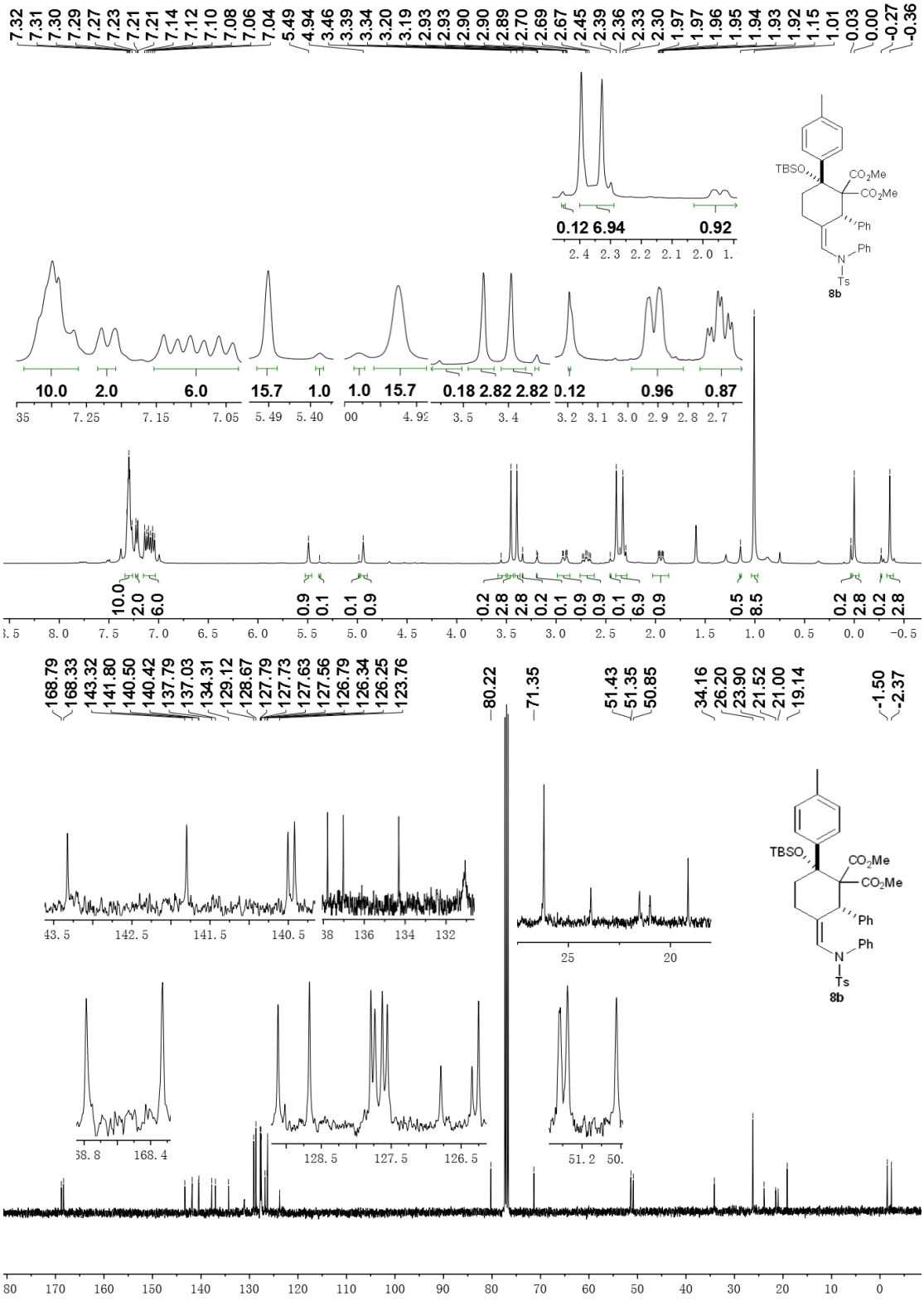



HMBCGP NMR spectra of compound **8a**

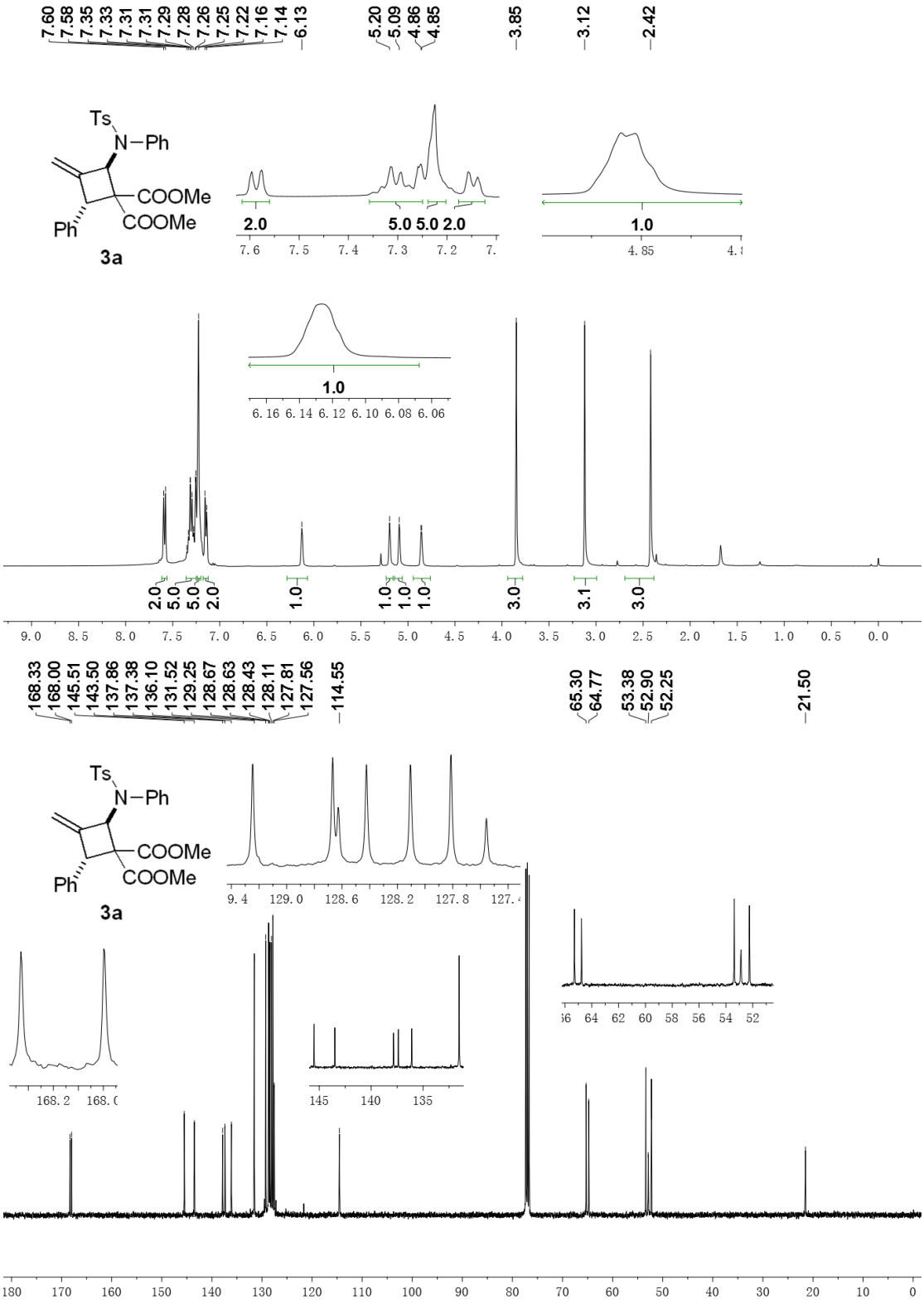


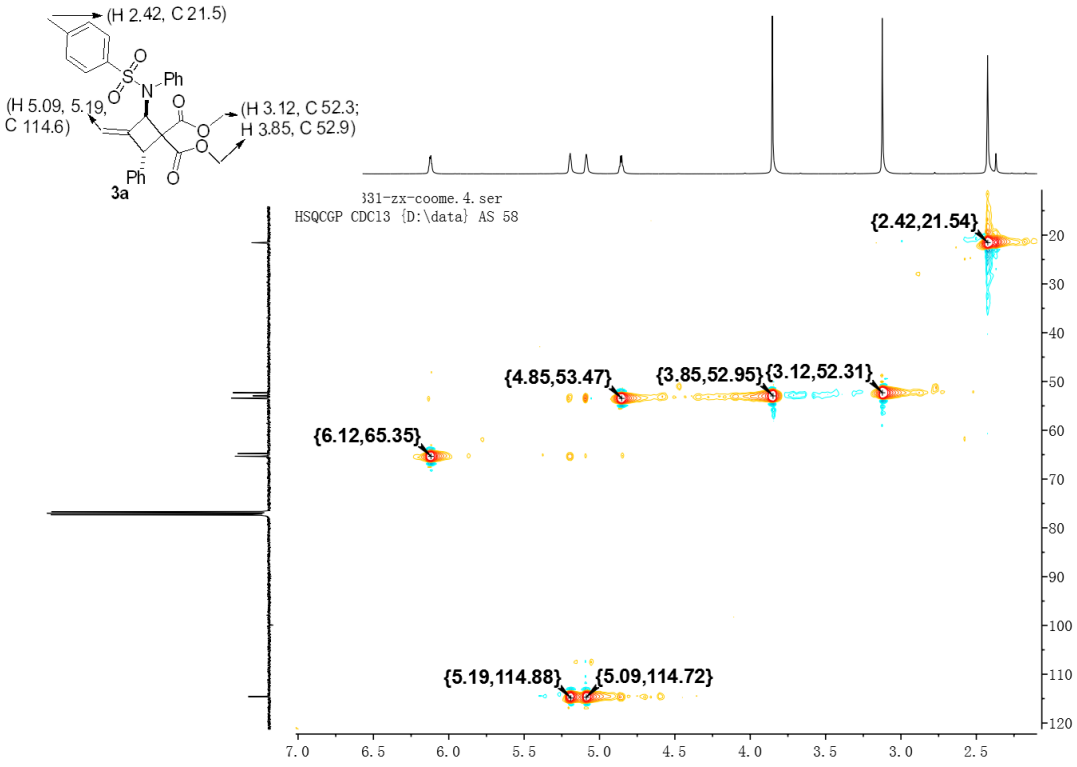
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of two diastereomers of compounds **8b**

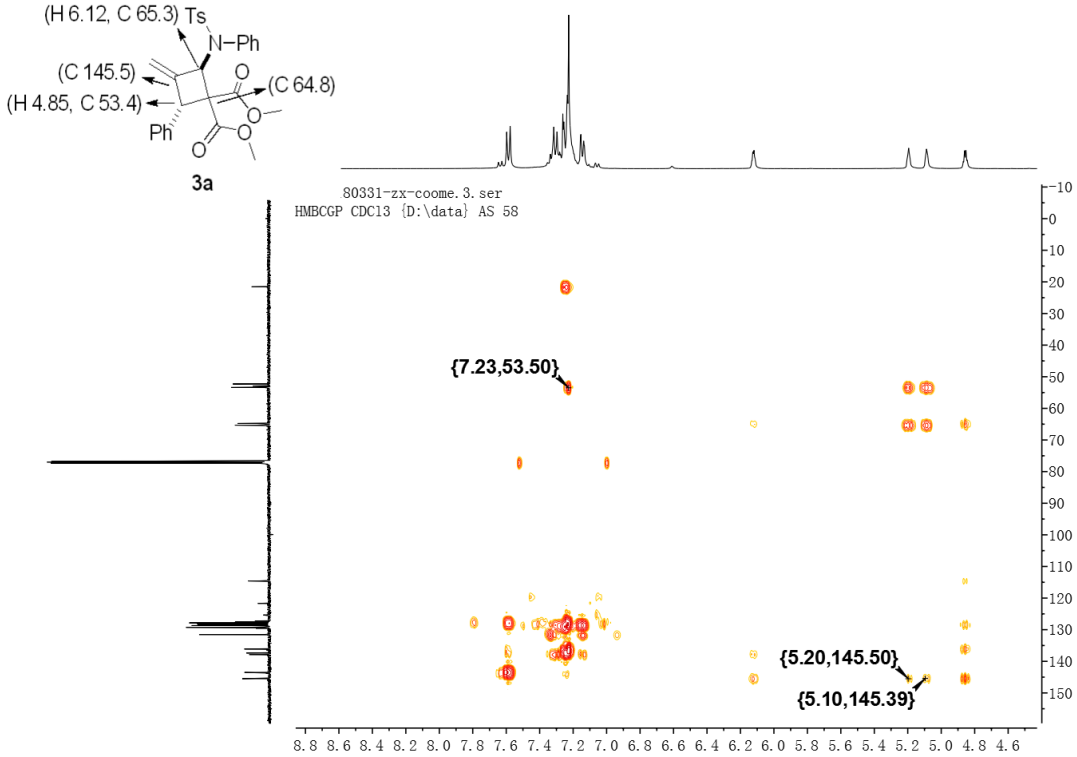


$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3a**

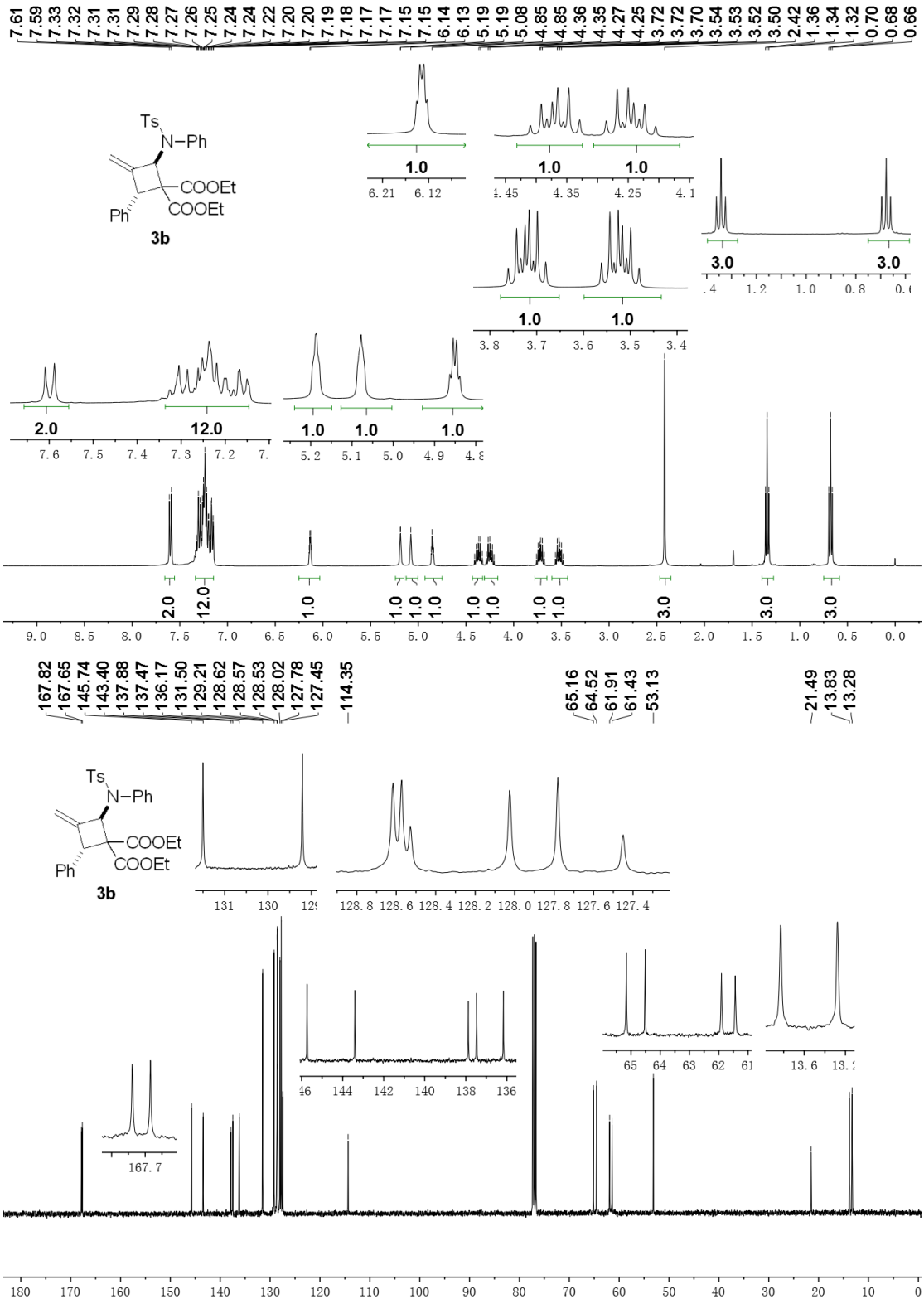


HSQCGP and HMBCGP NMR spectra of compound **3a**

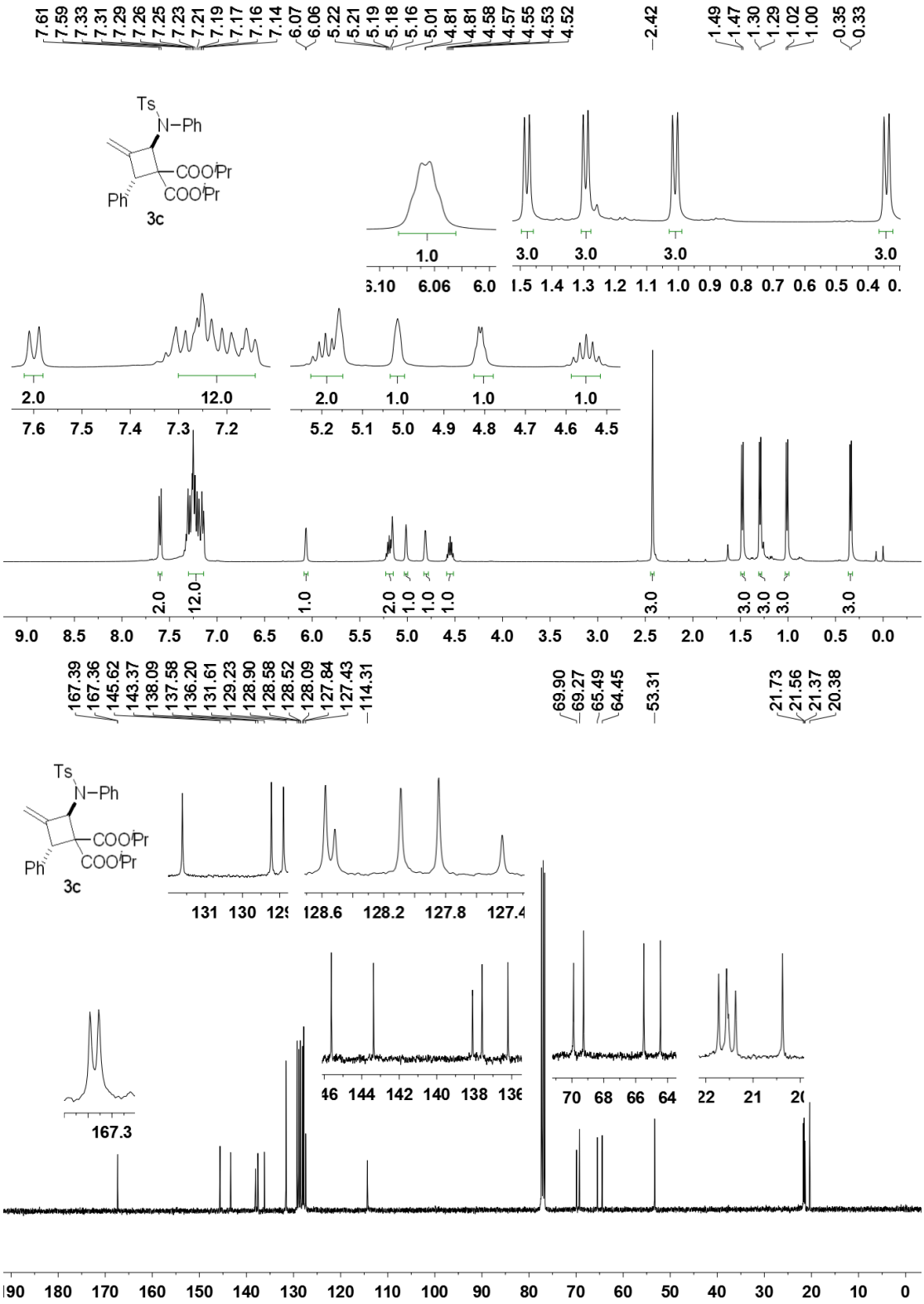


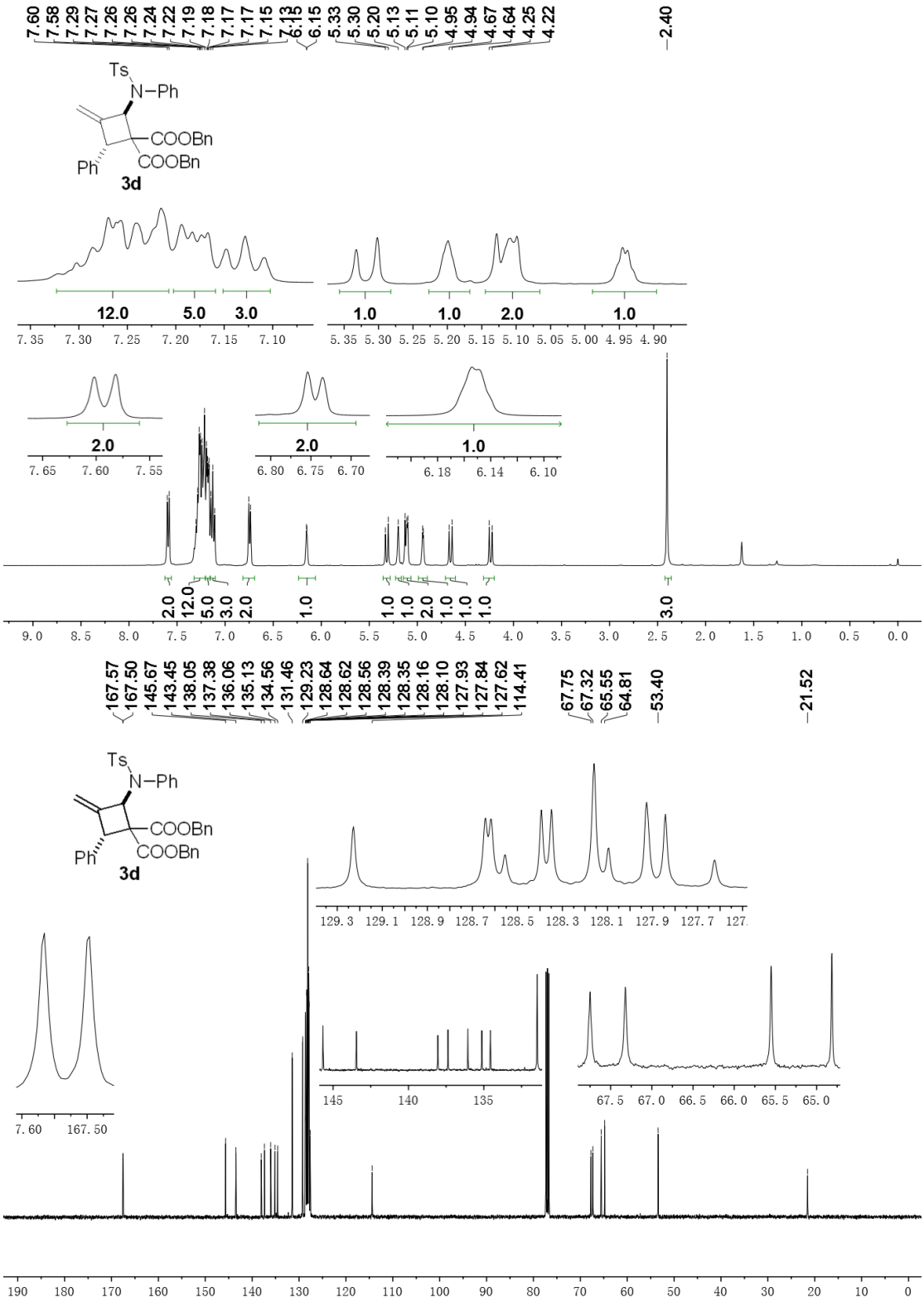
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3b**



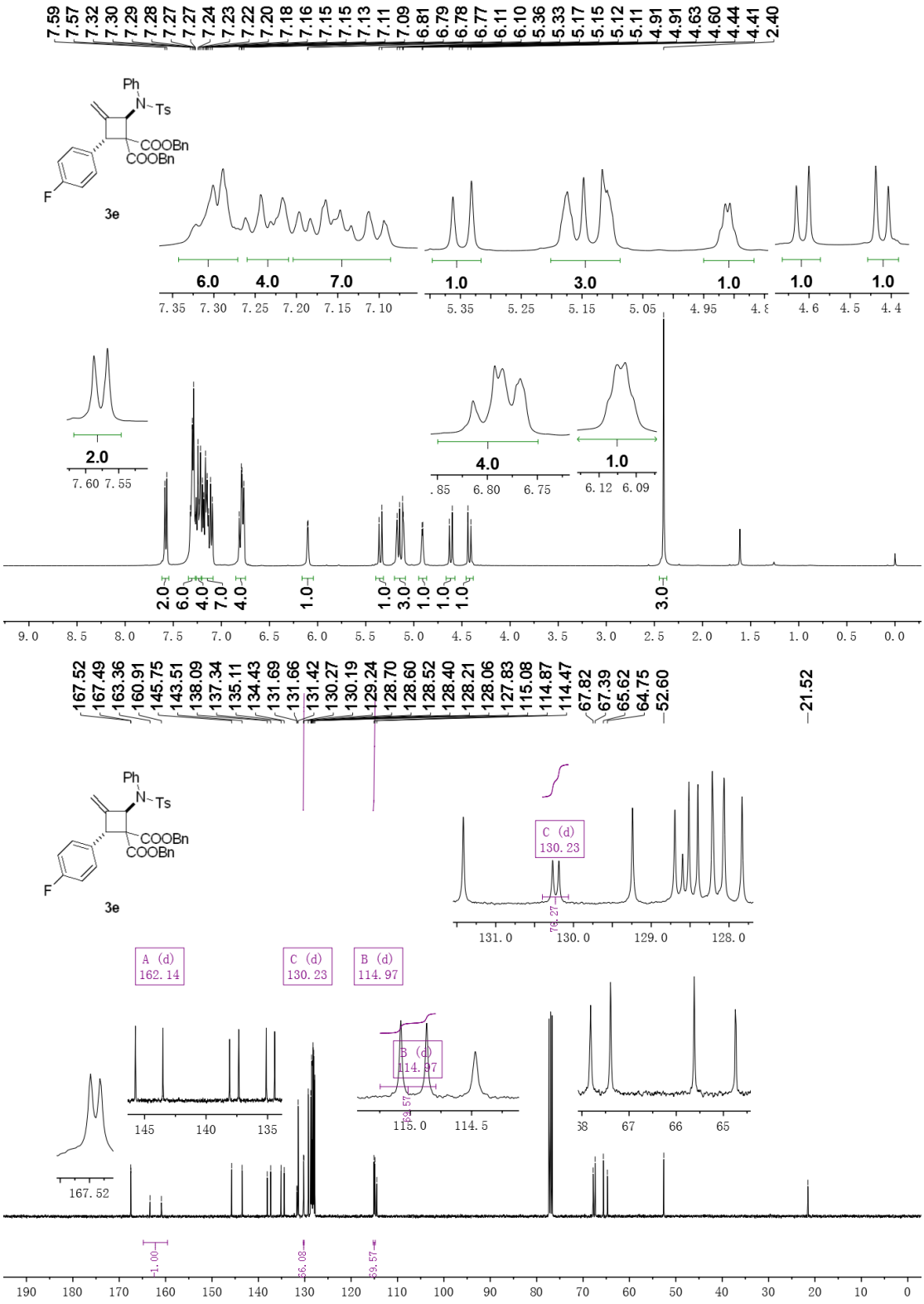
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3c**



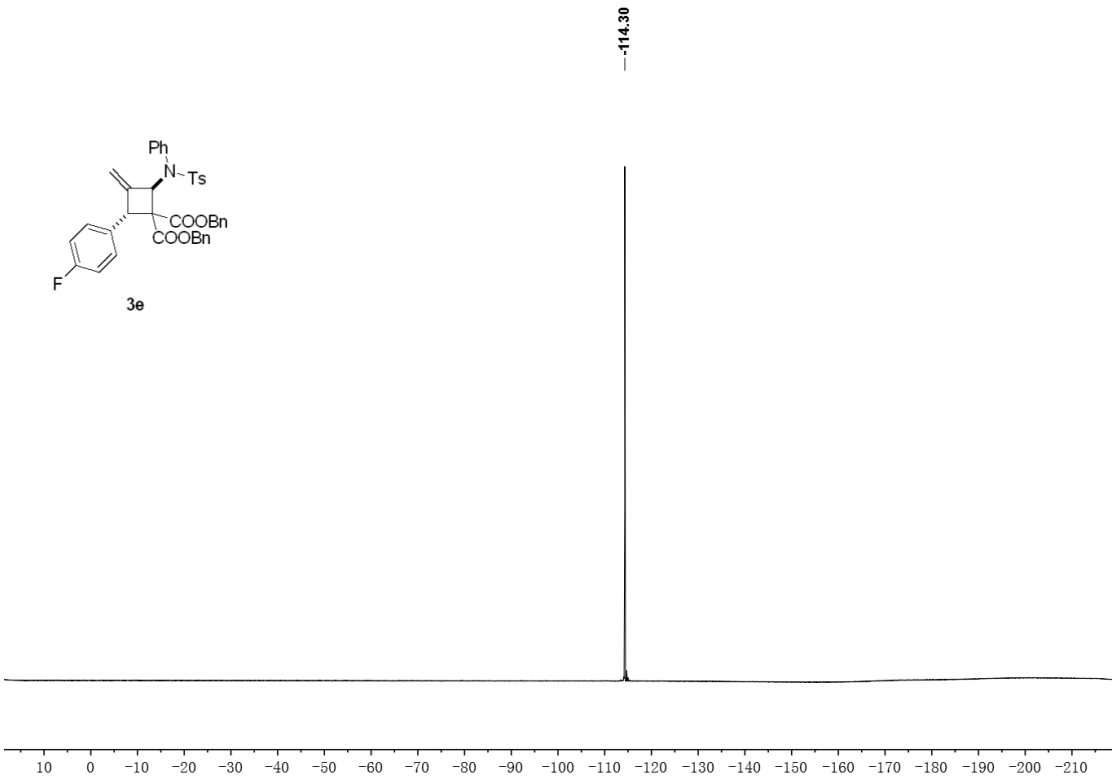
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3d**



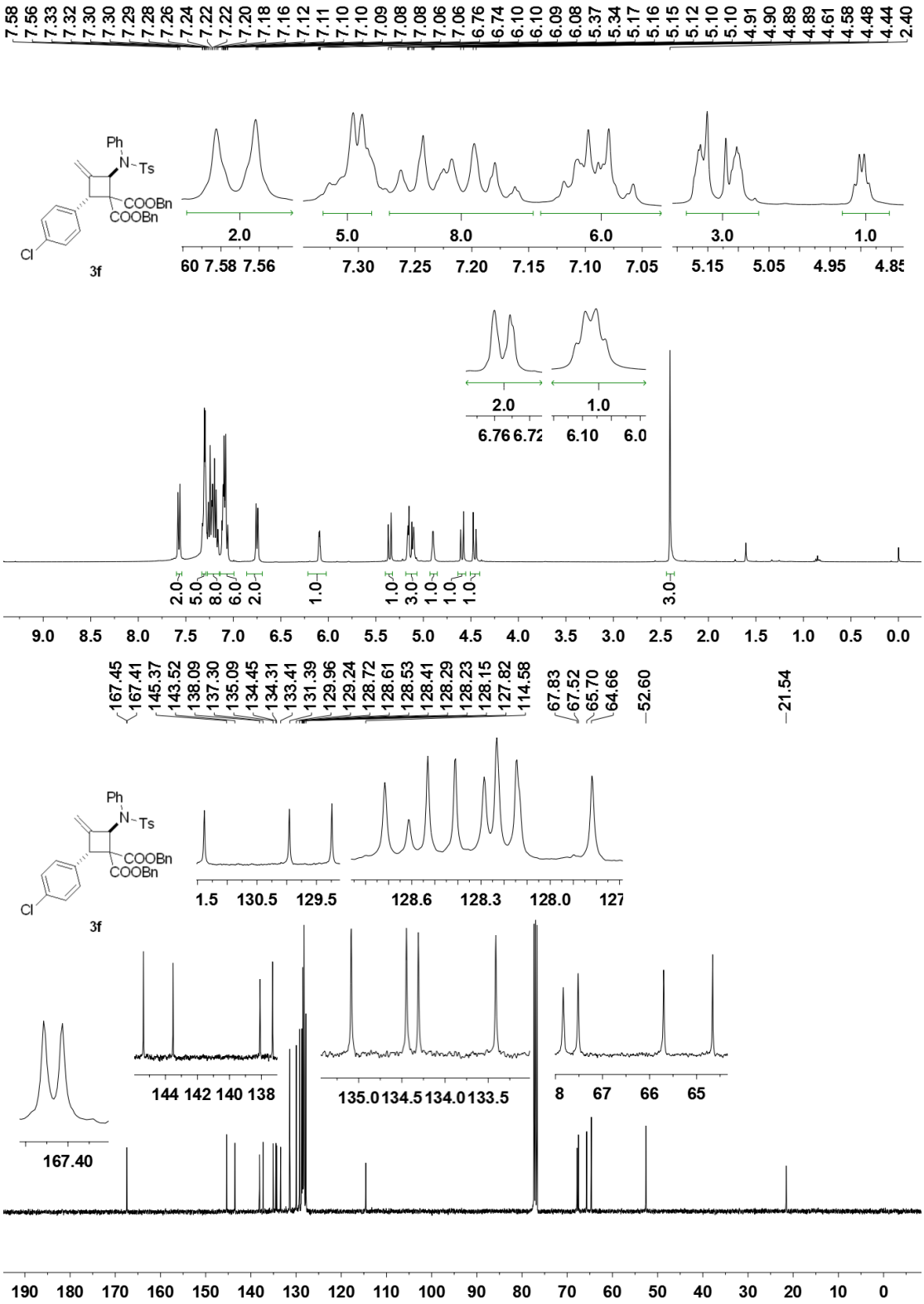
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3e**



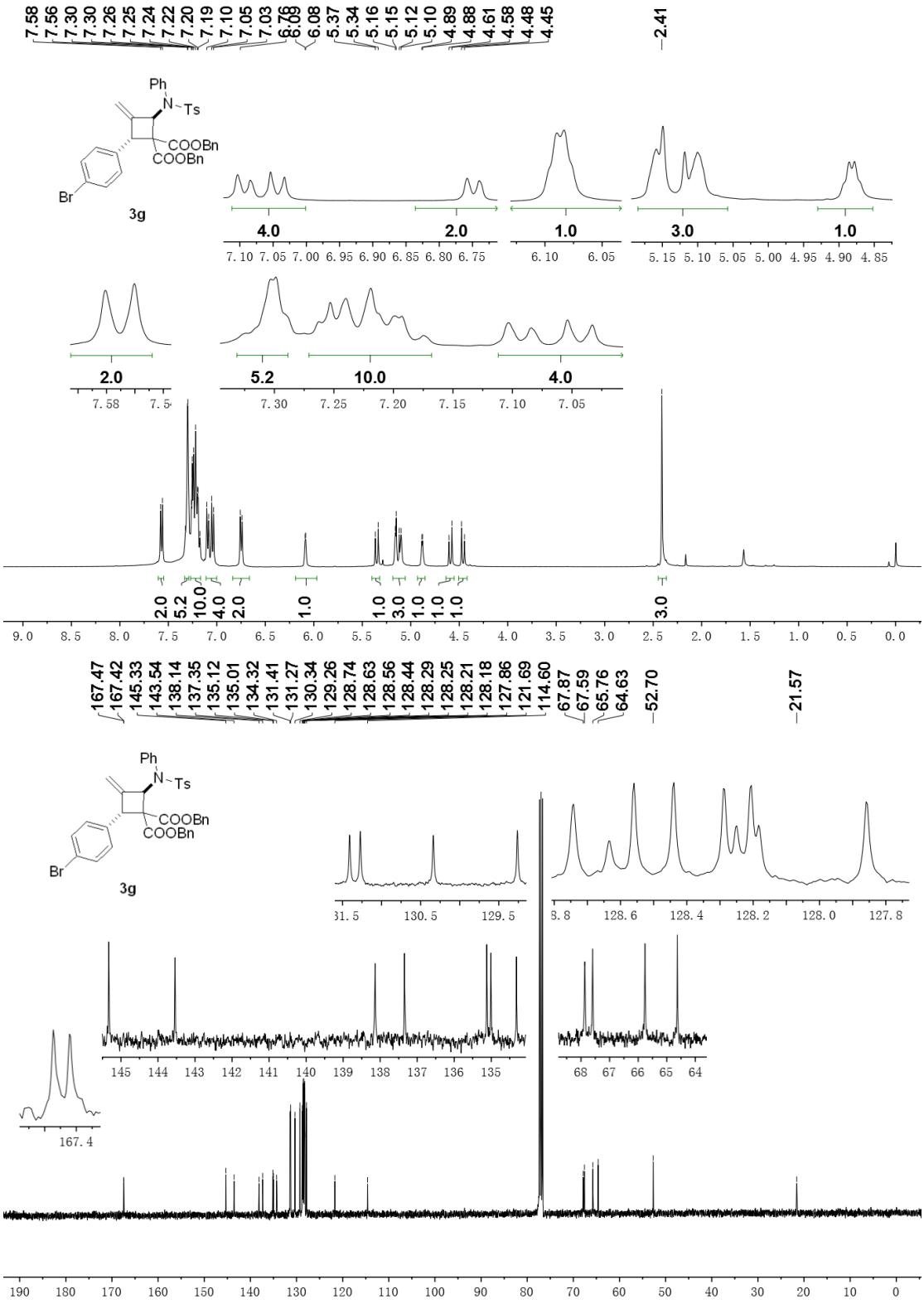
$^{19}$F NMR spectra of compound **3e**



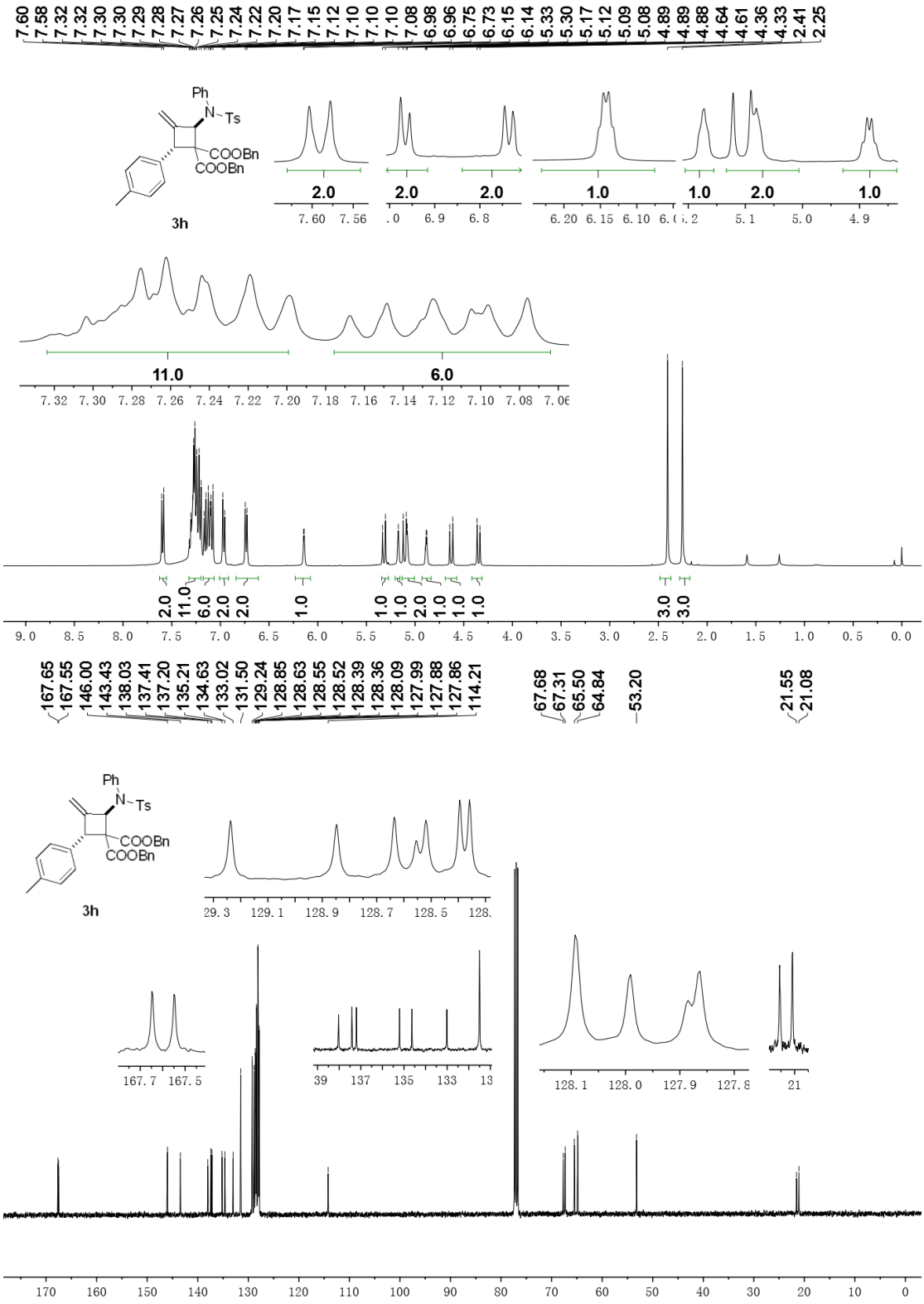
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3f**



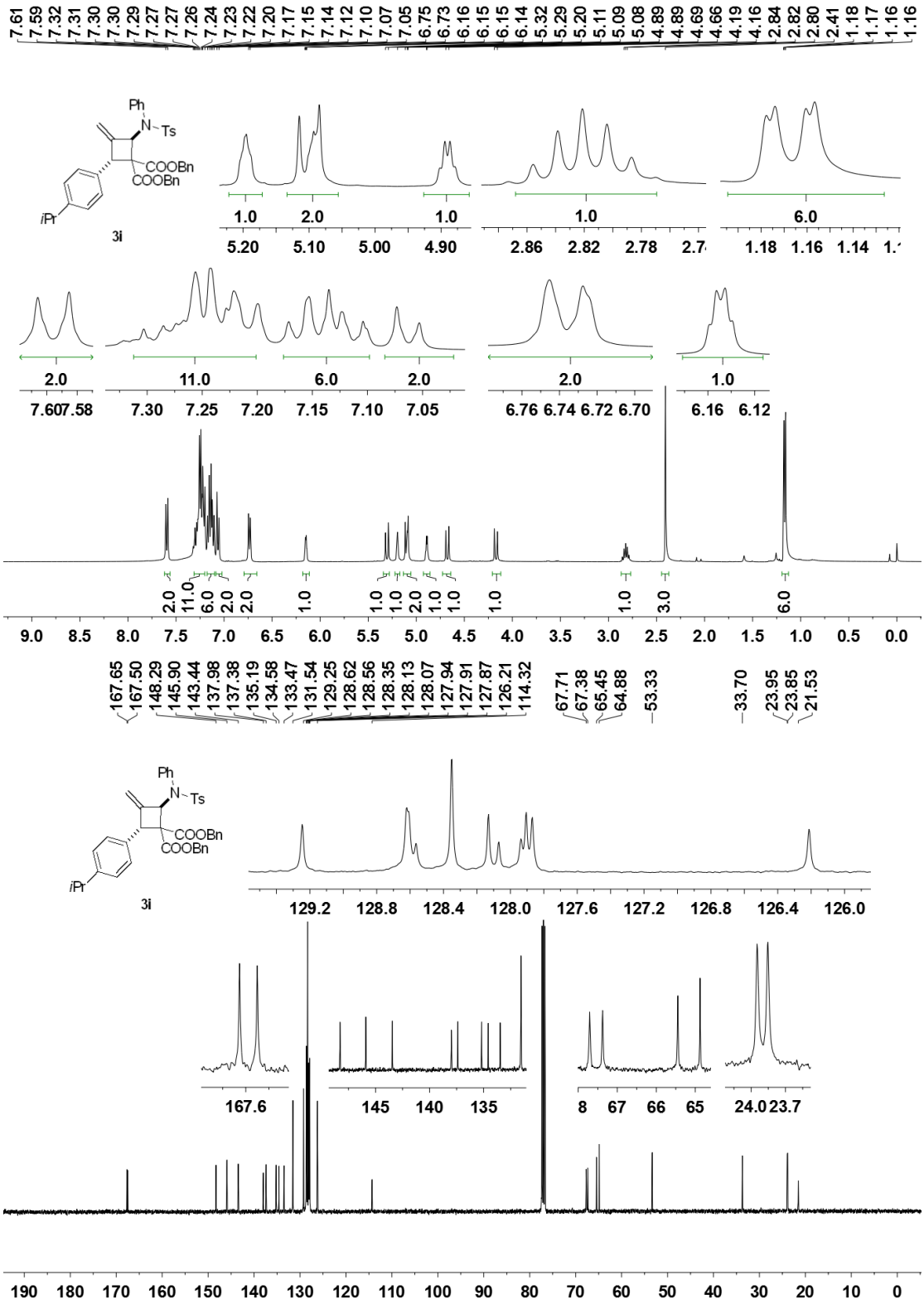
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3g**



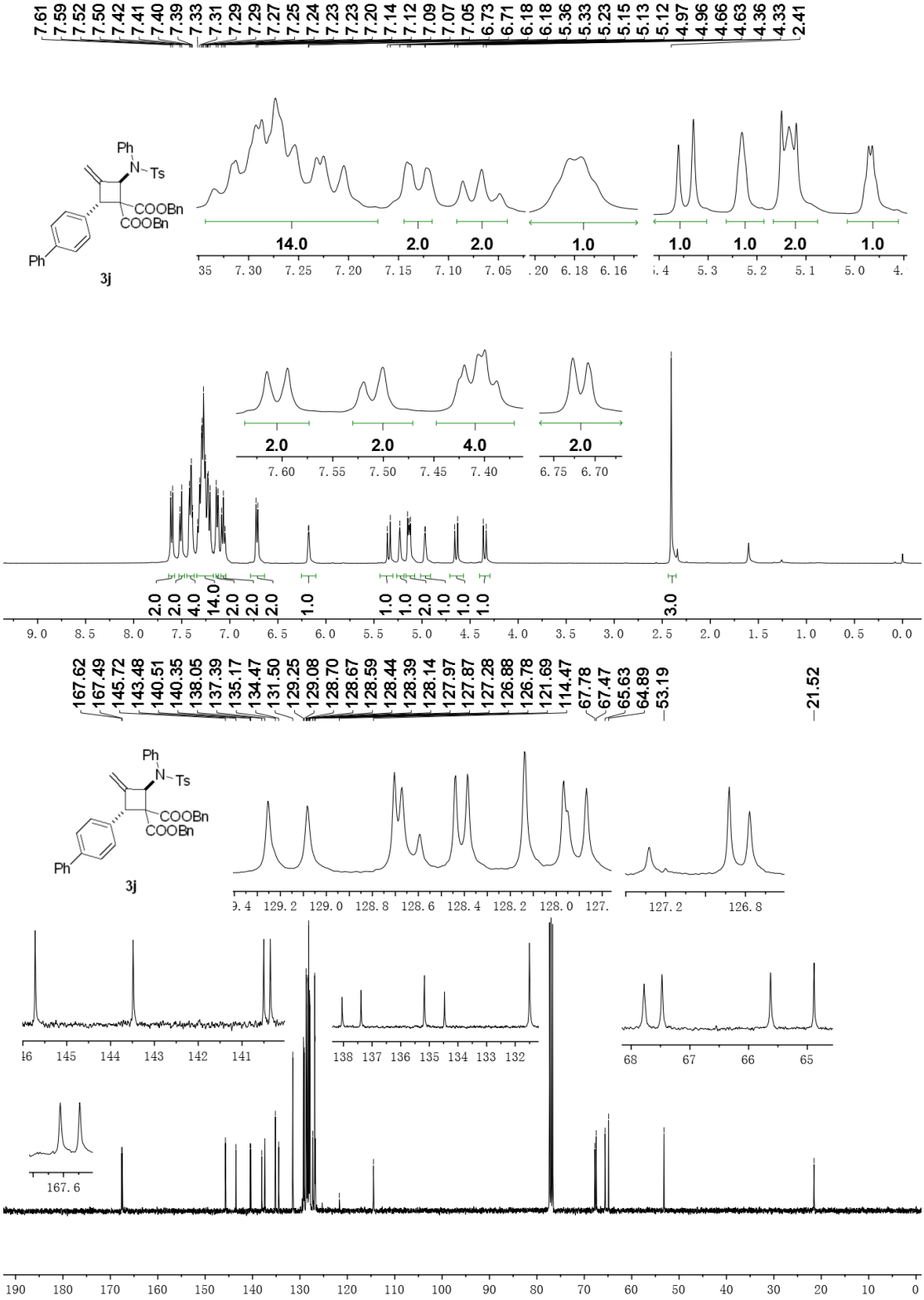
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3h**



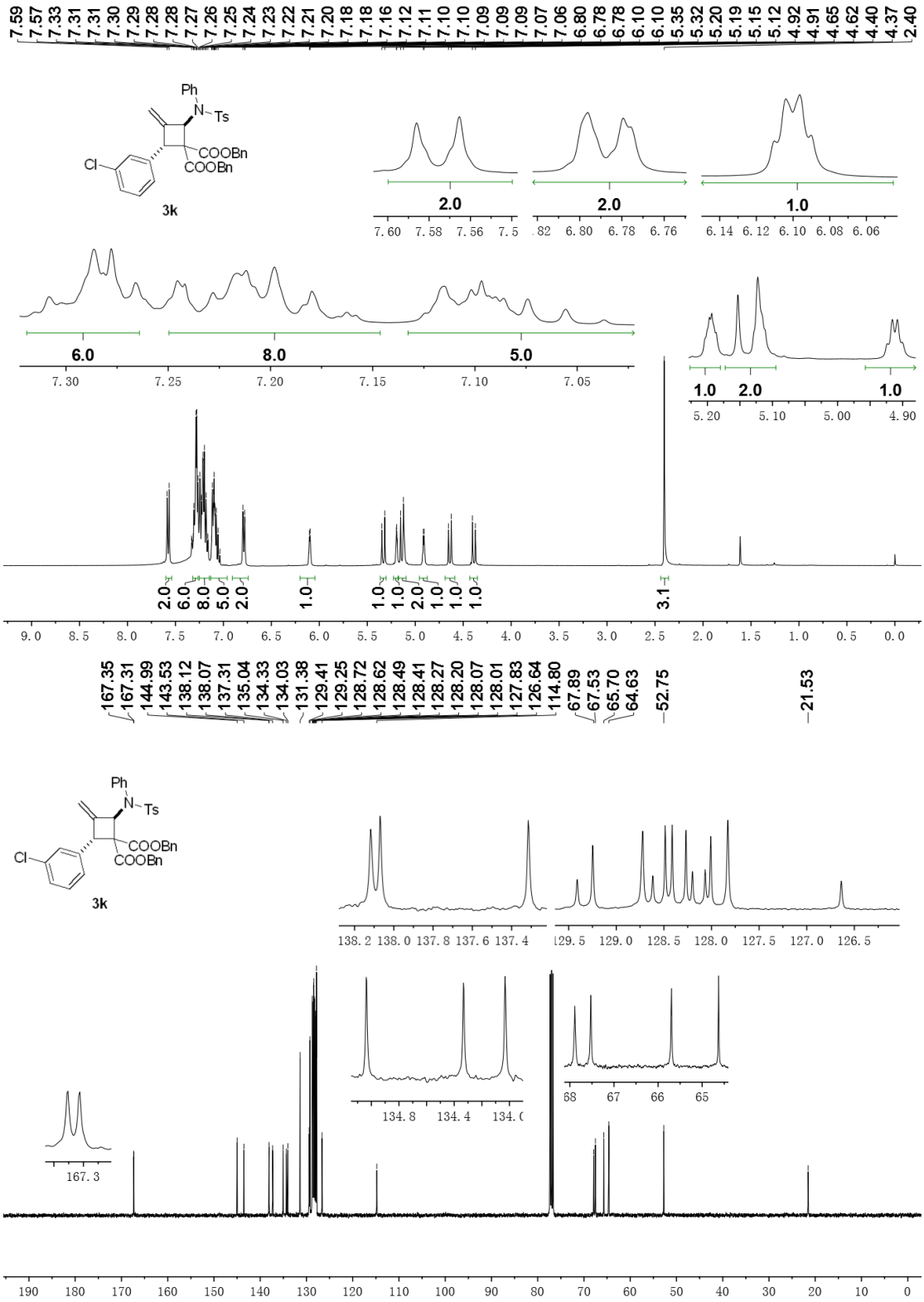
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3i**



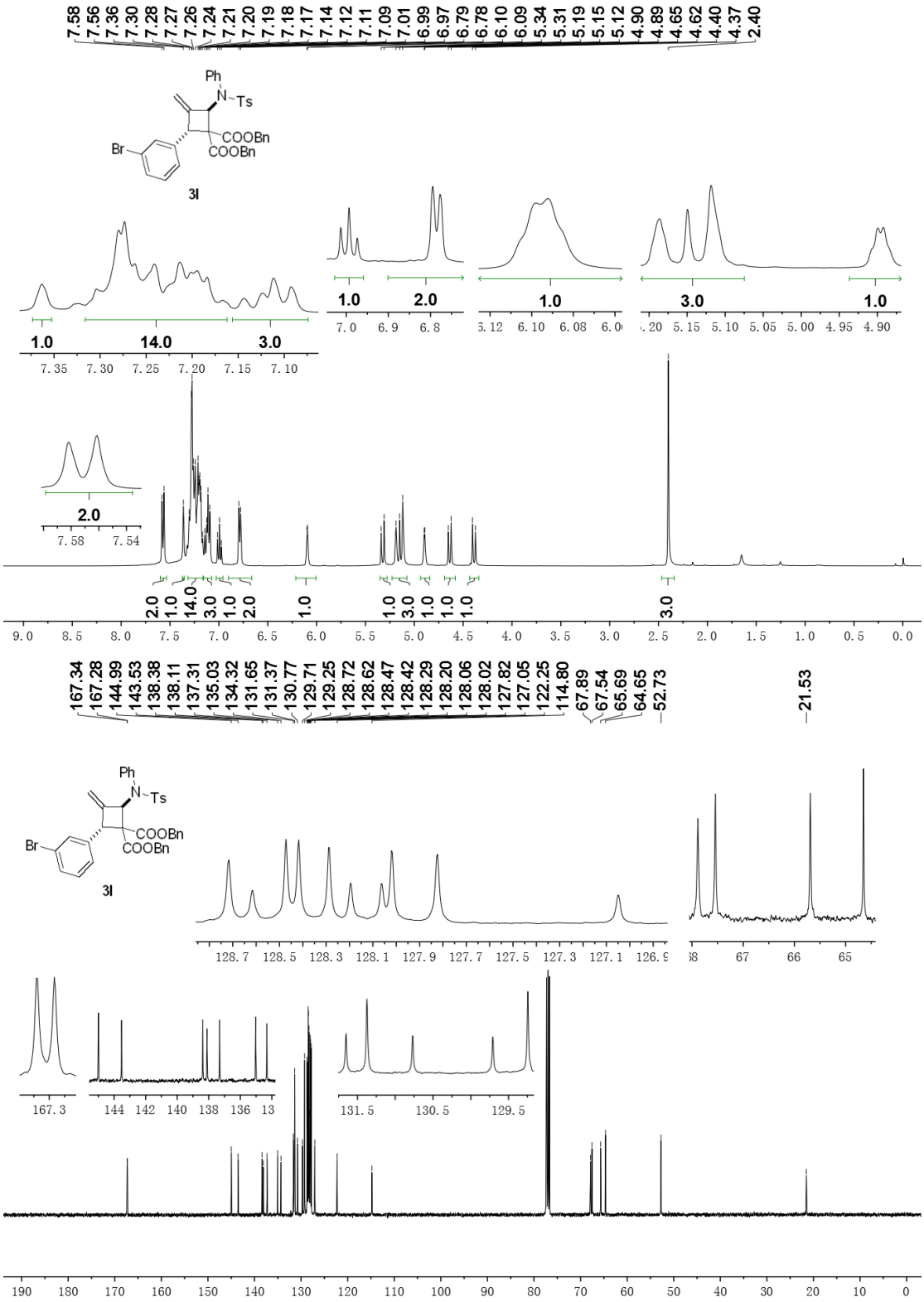
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3j**



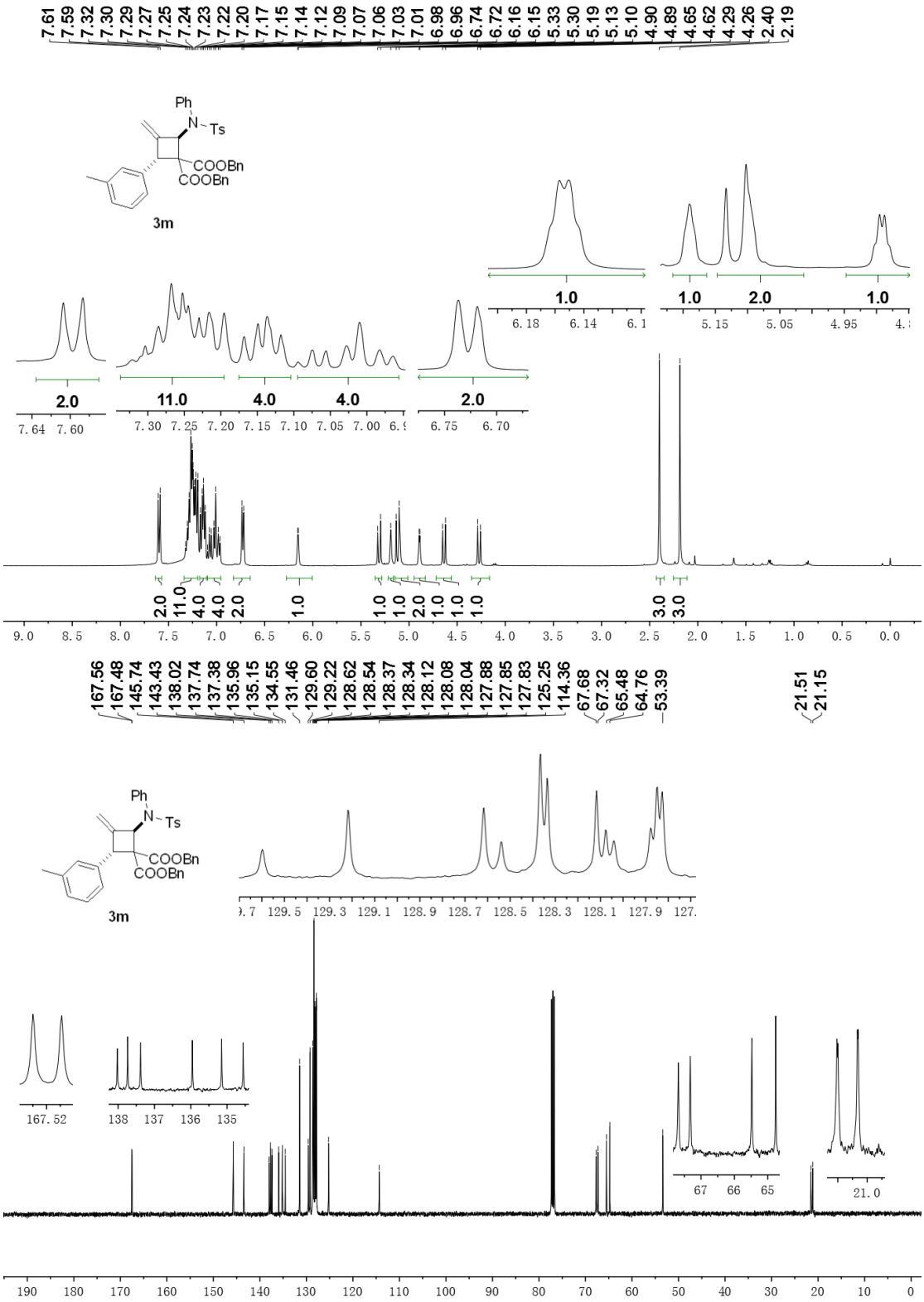
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3k**



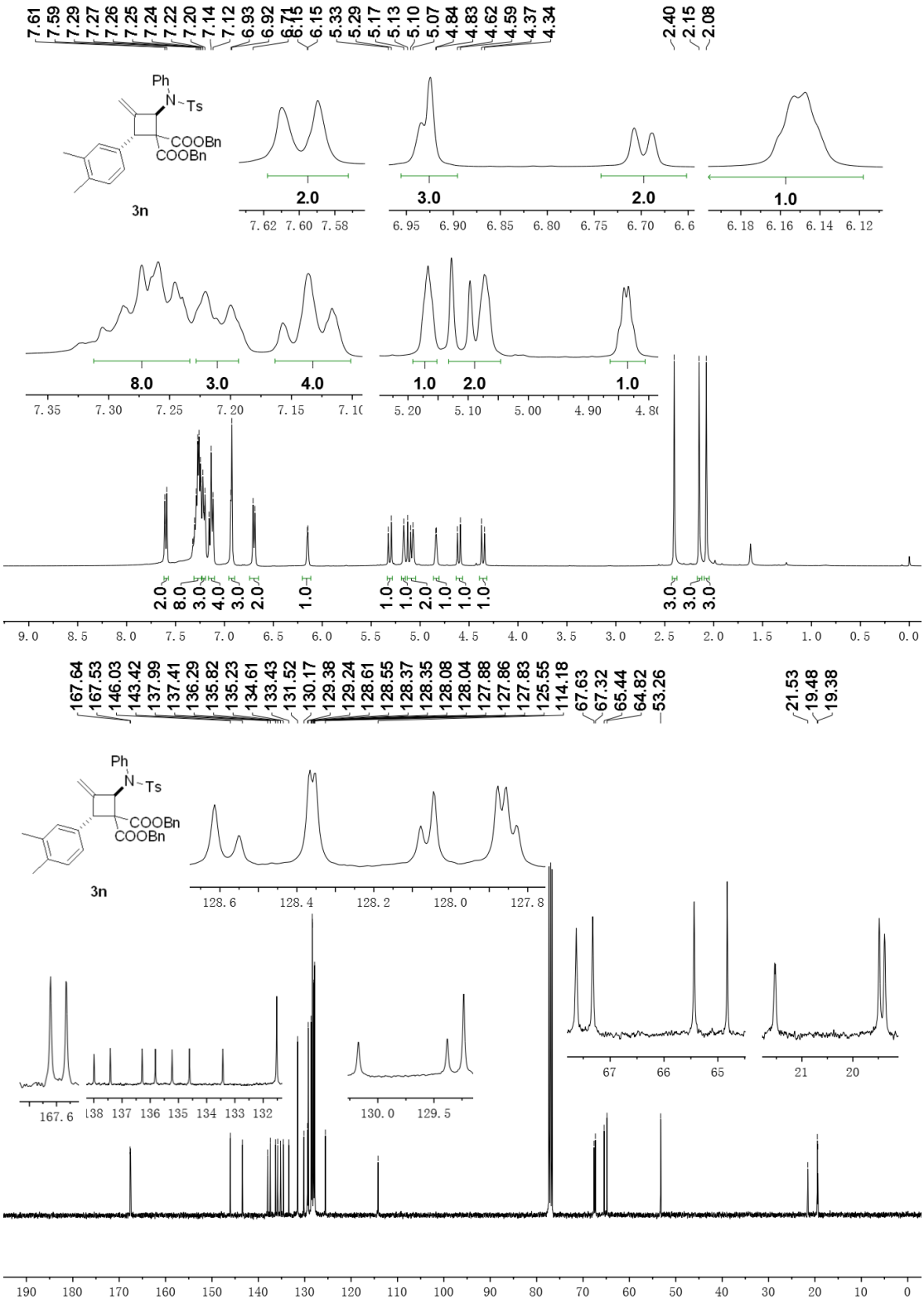
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3l**



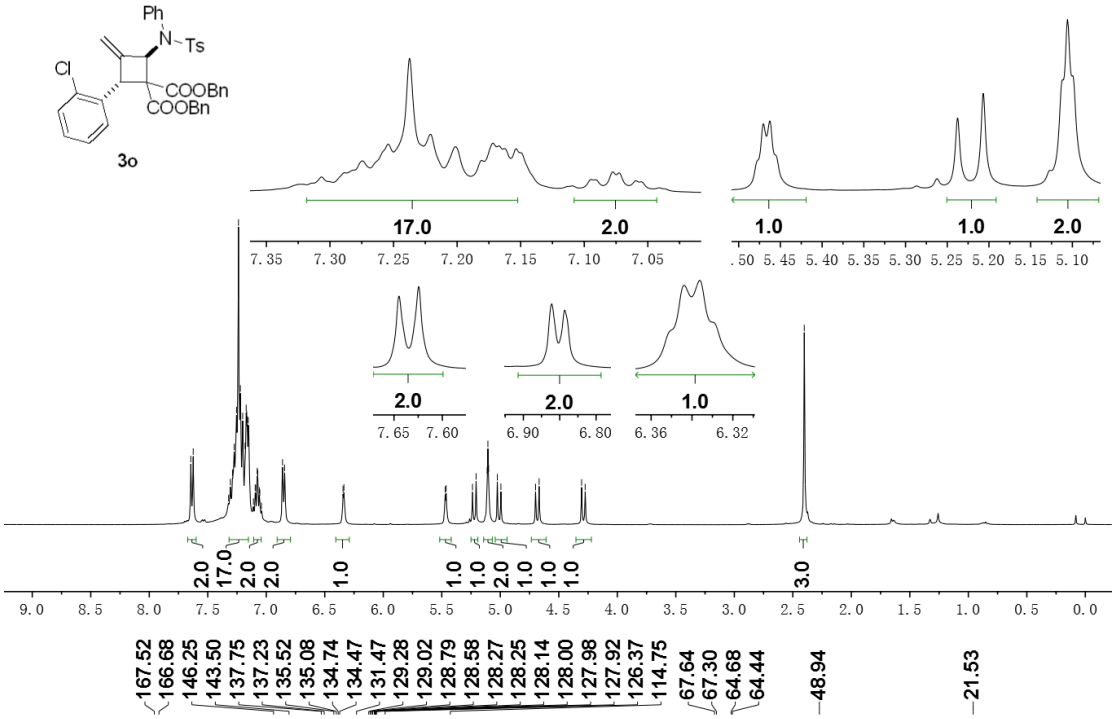
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3m**

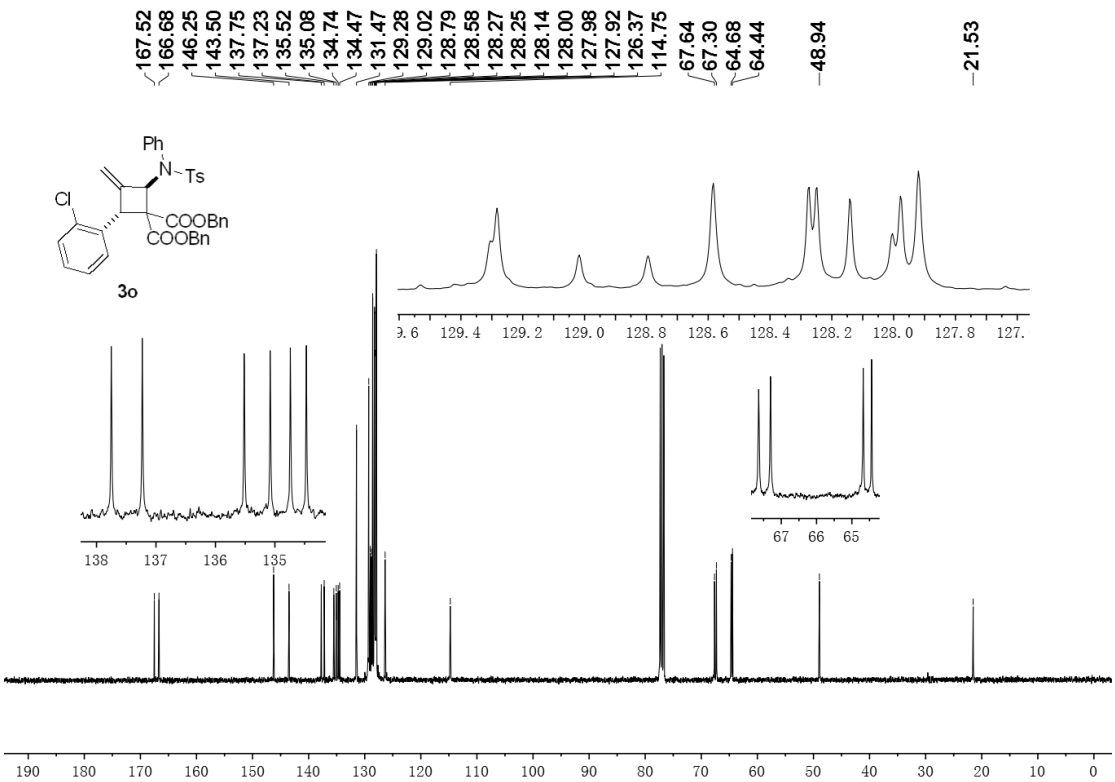


$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3n**

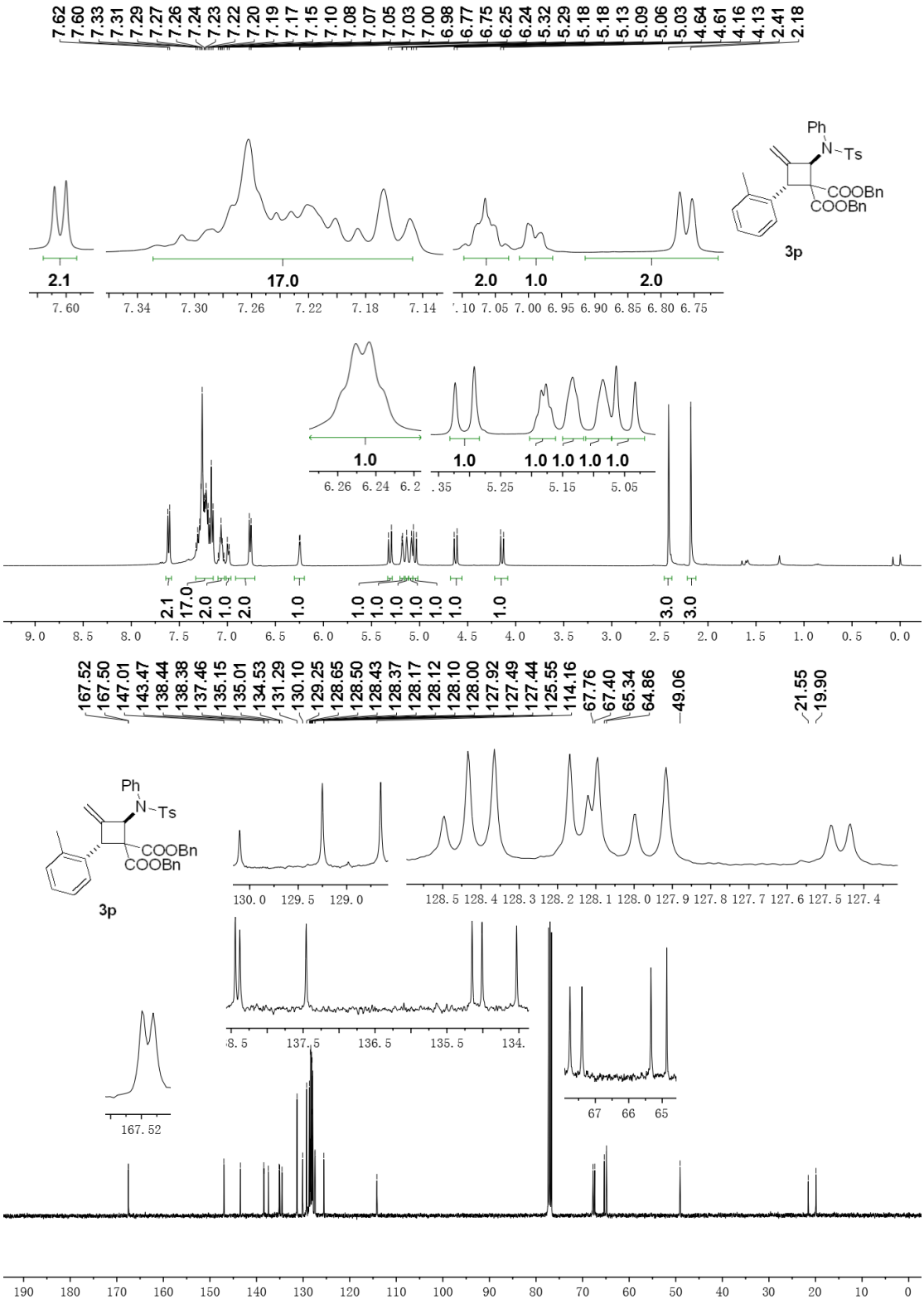


$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3o**

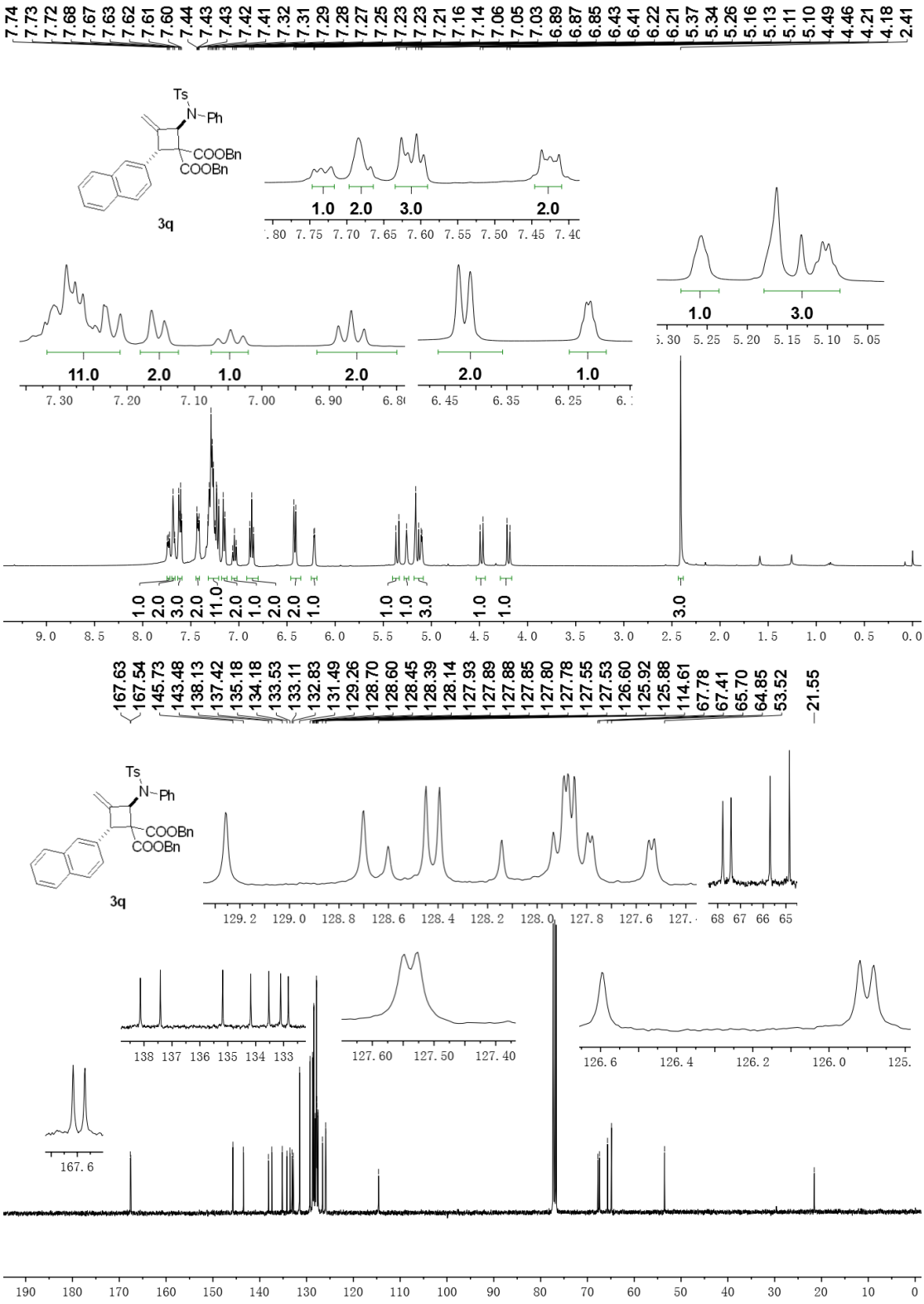



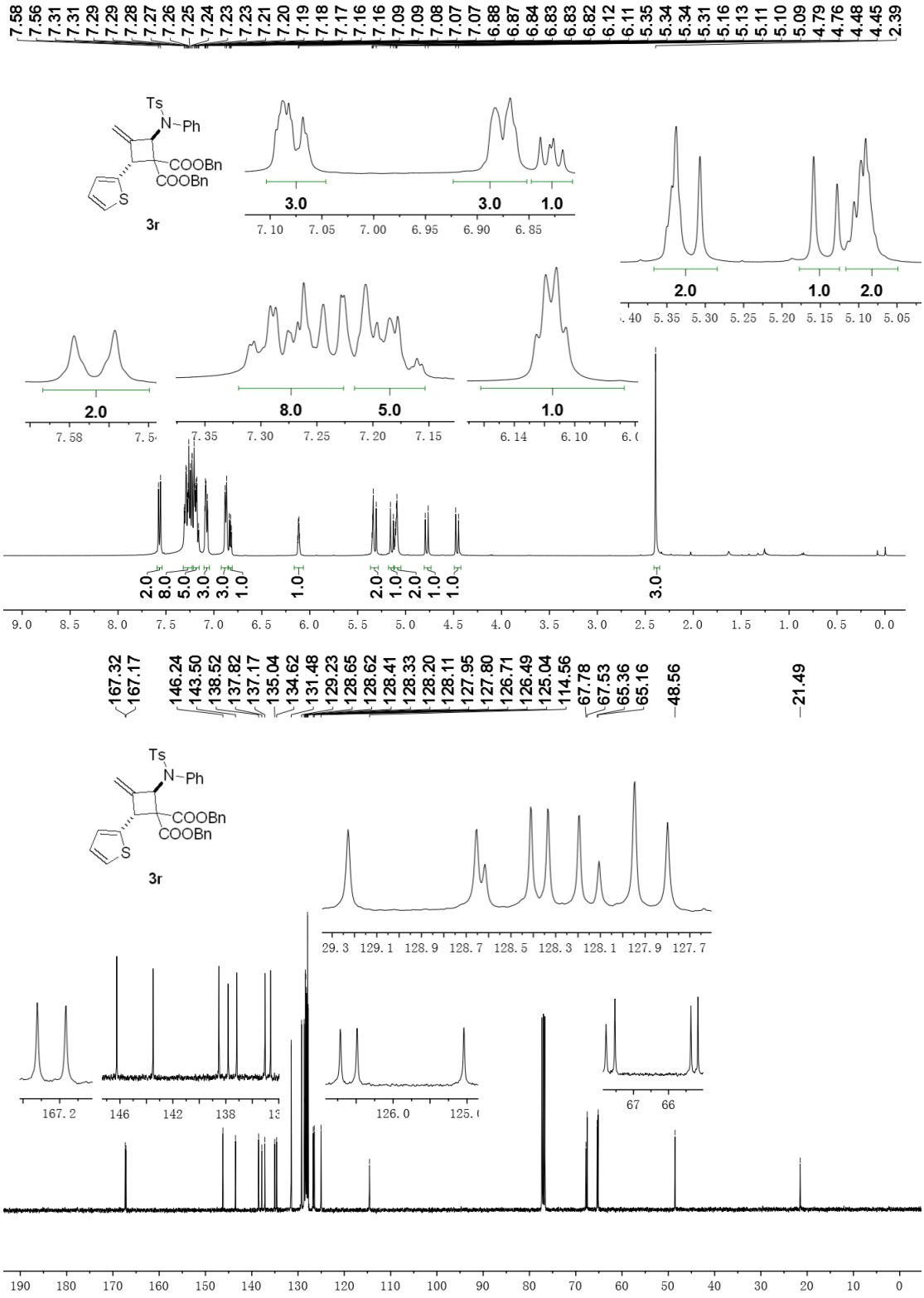
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3p**



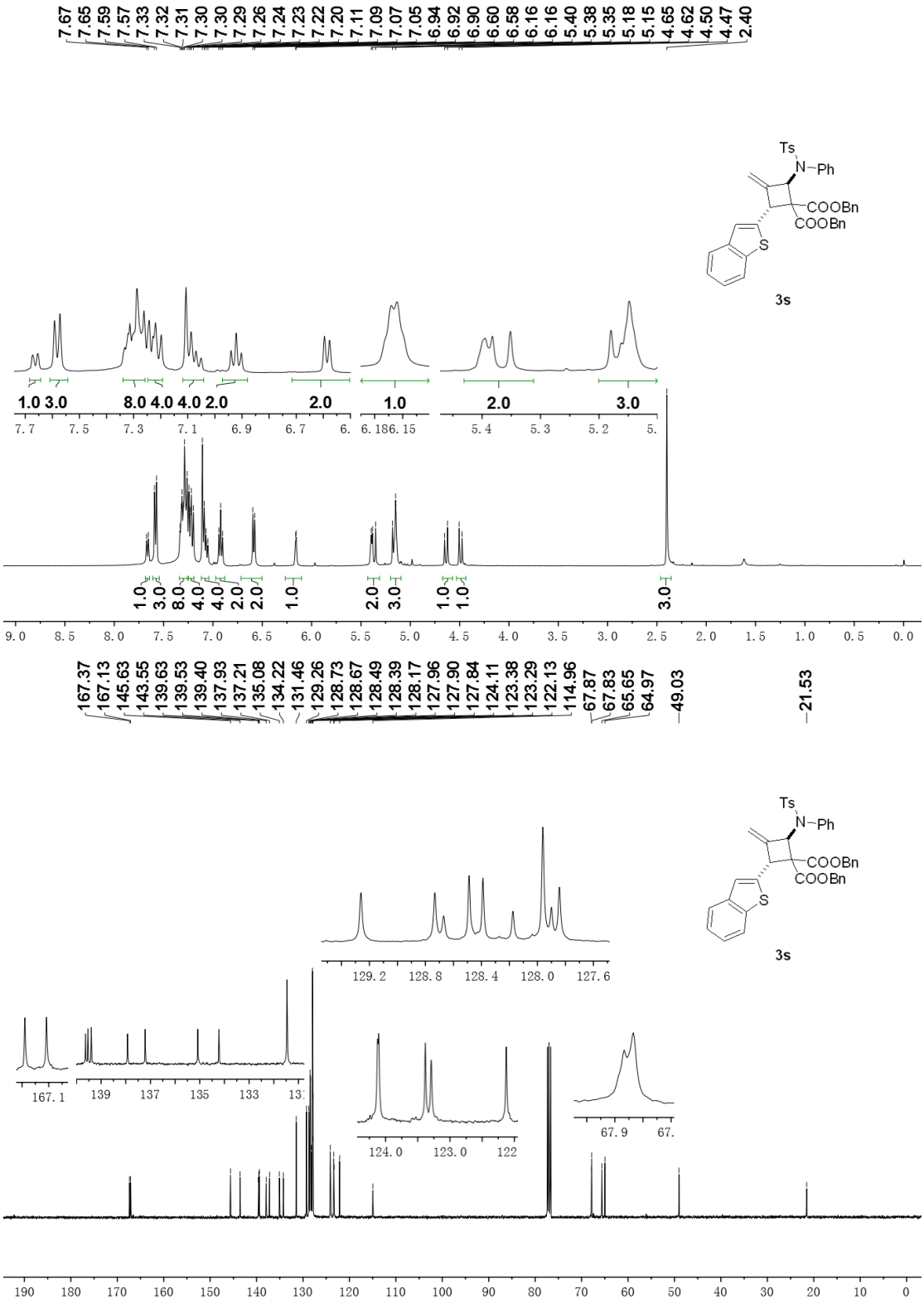
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3q**



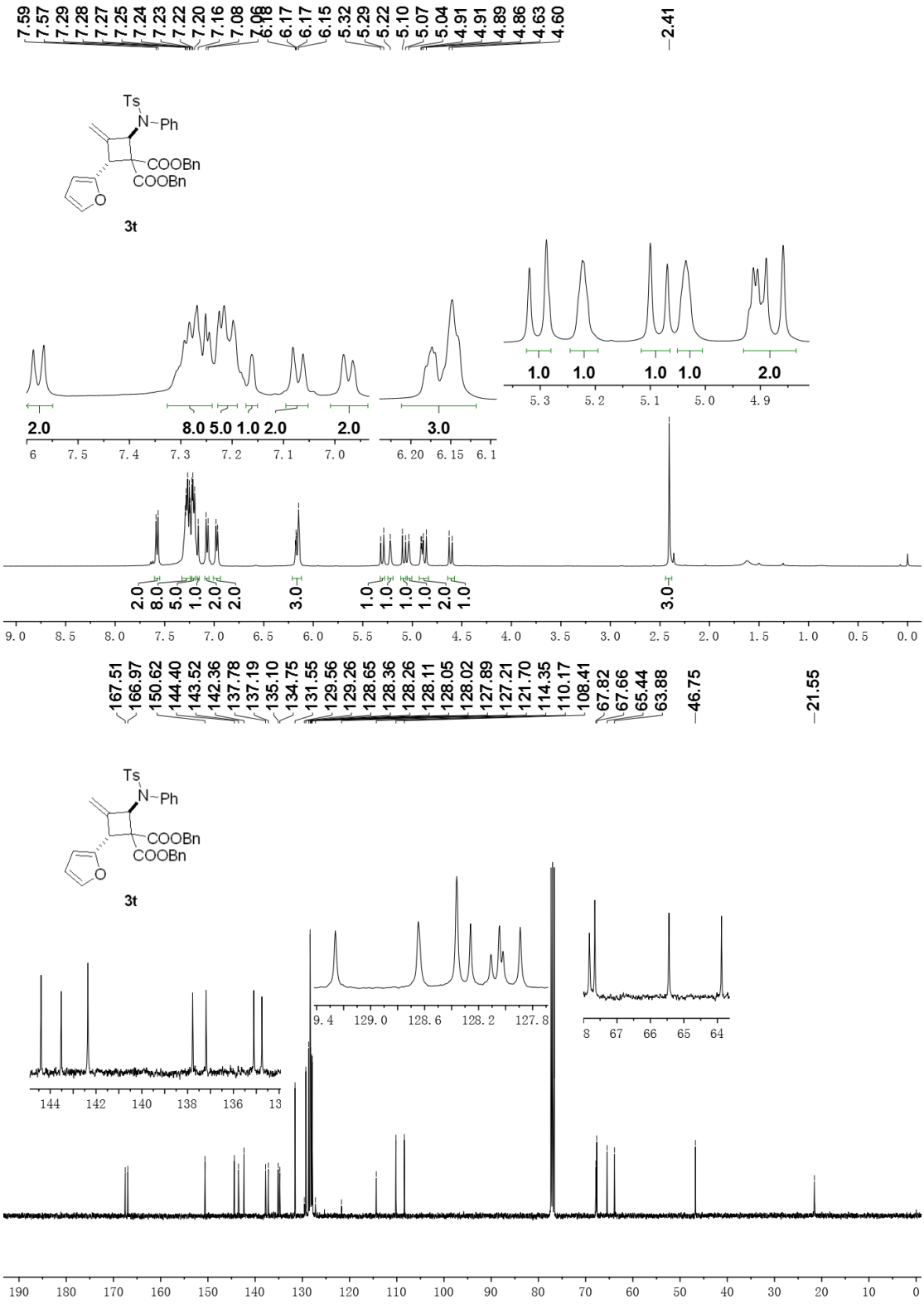
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3r**



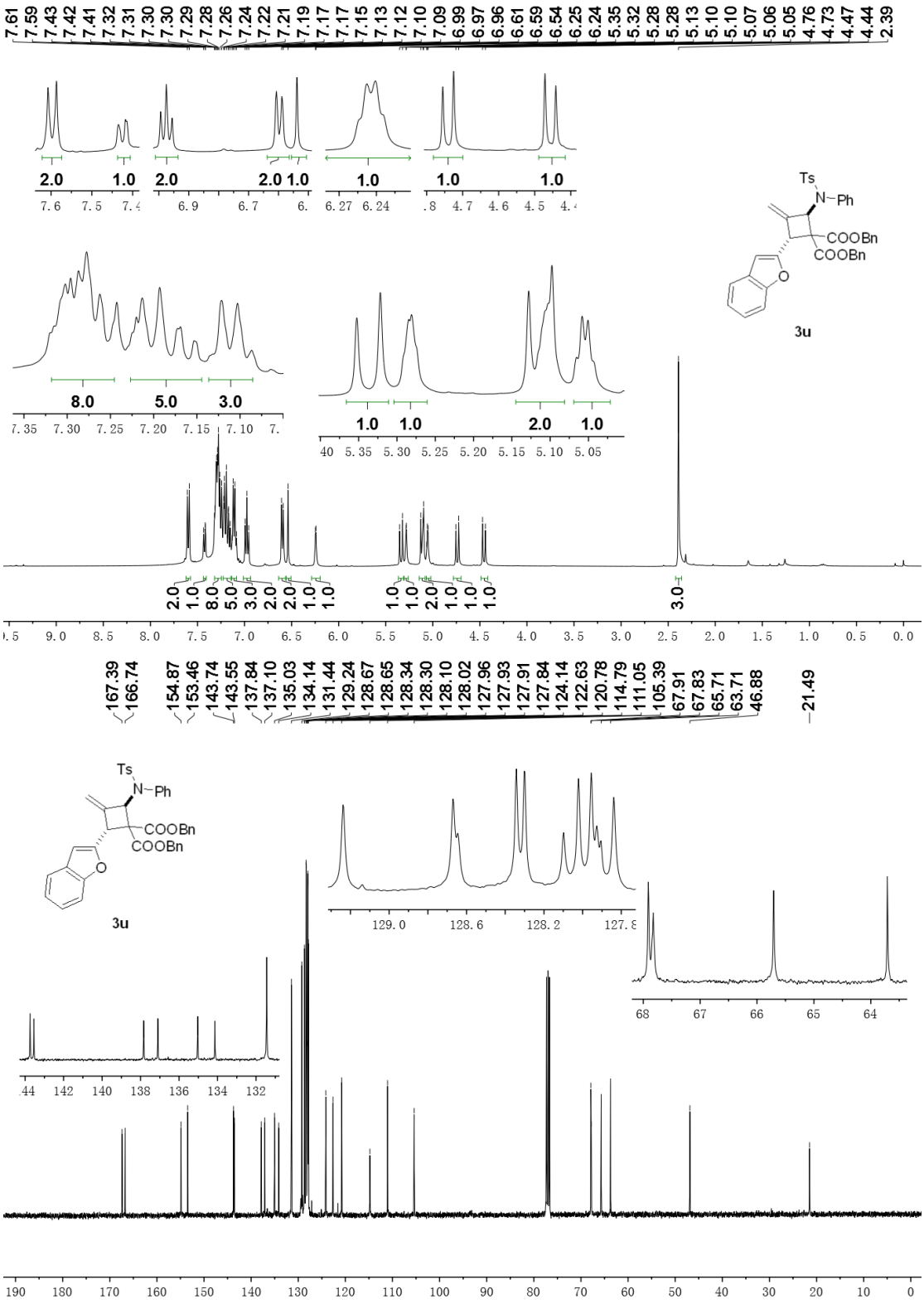
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3s**



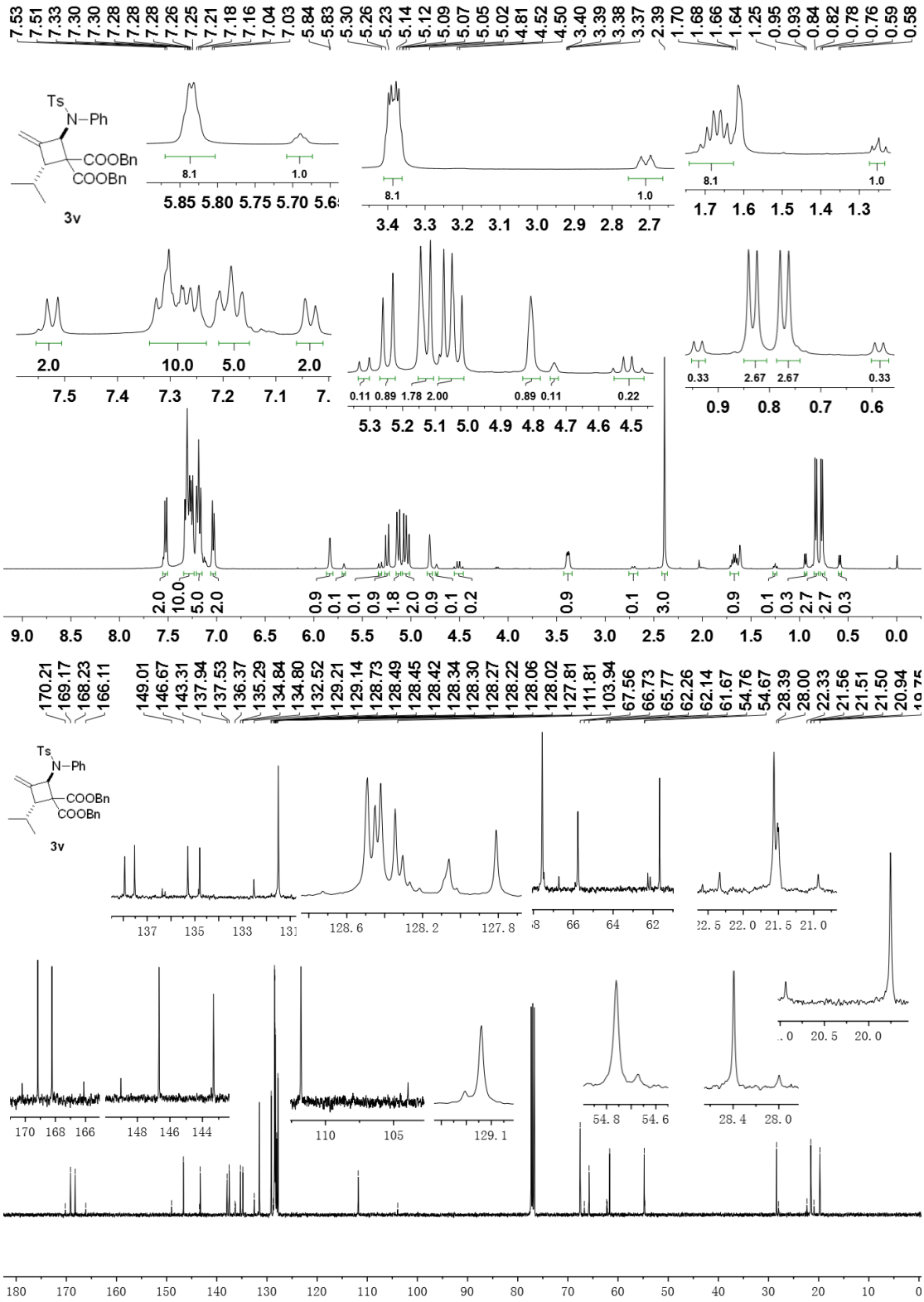
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3t**



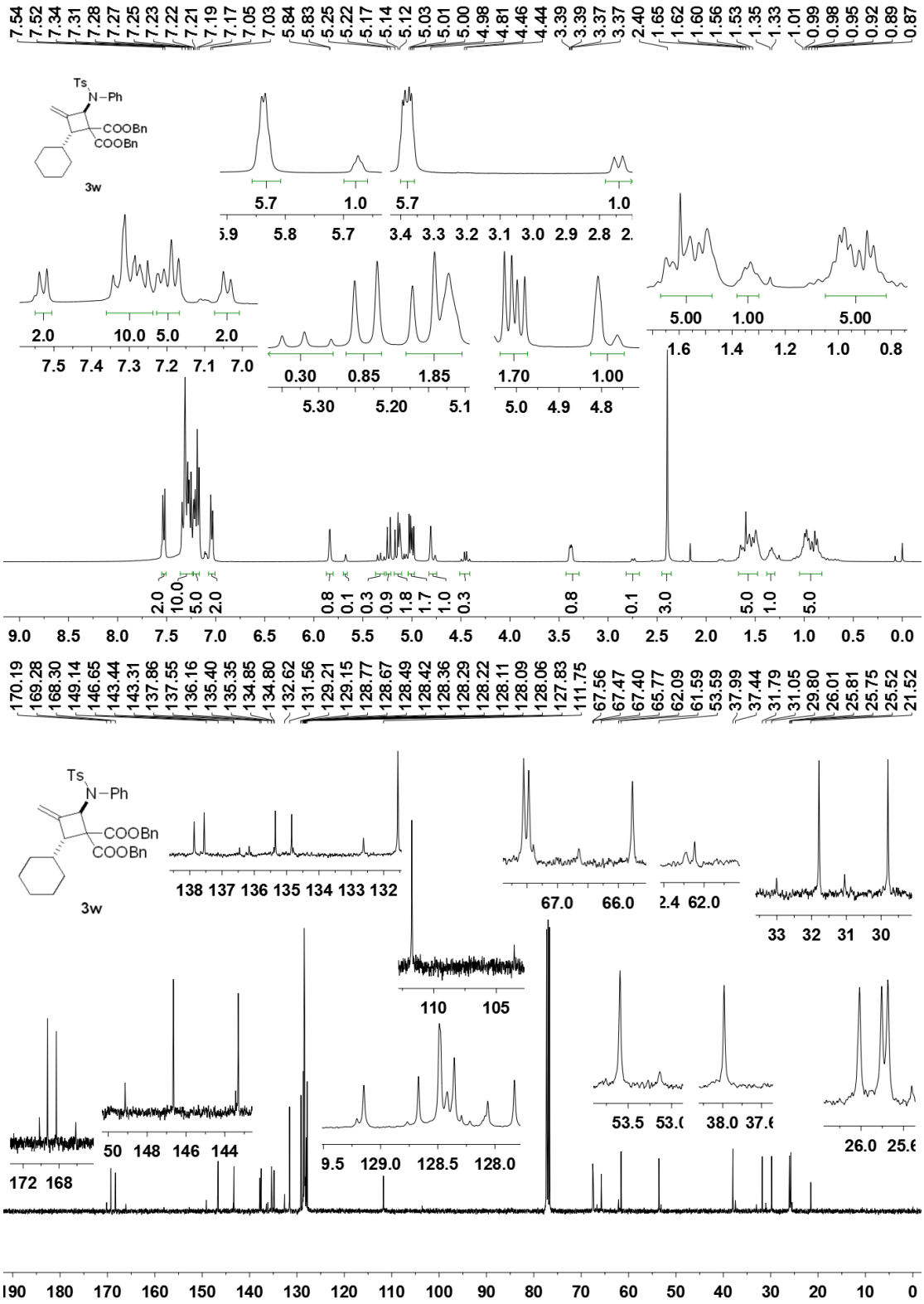
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **3u**



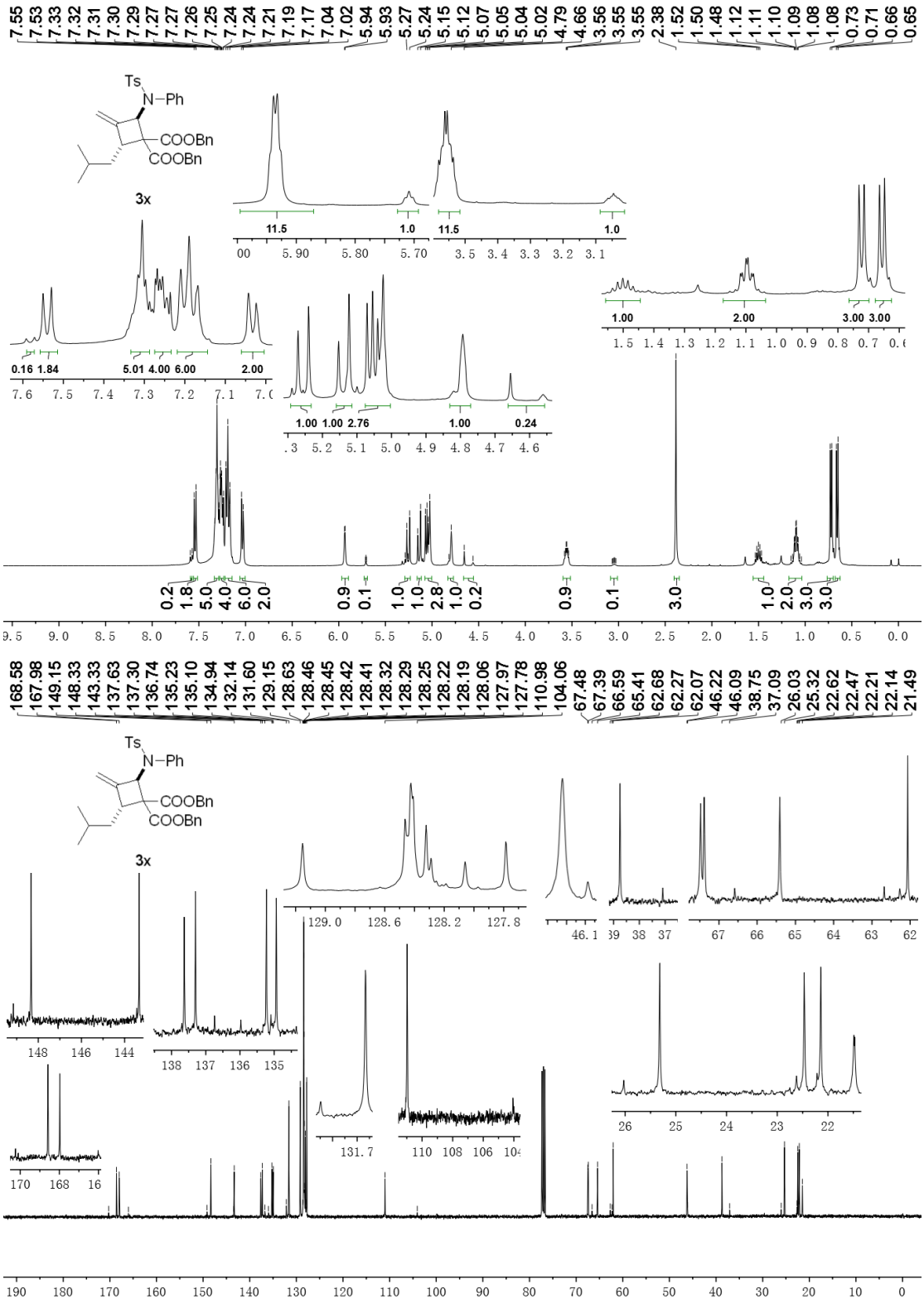
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of two diastereomers of compounds **3v**



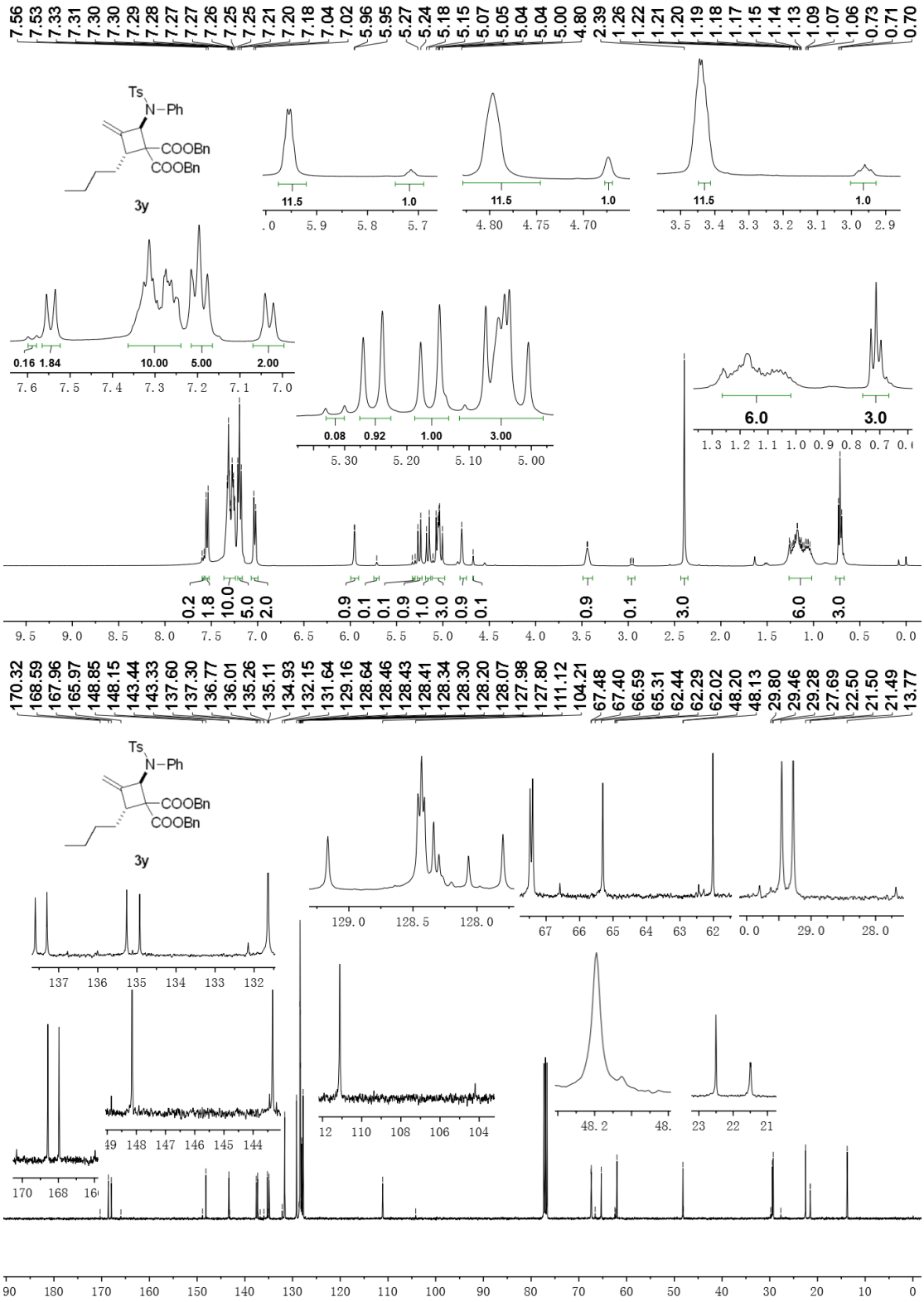
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of two diastereomers of compounds **3w**



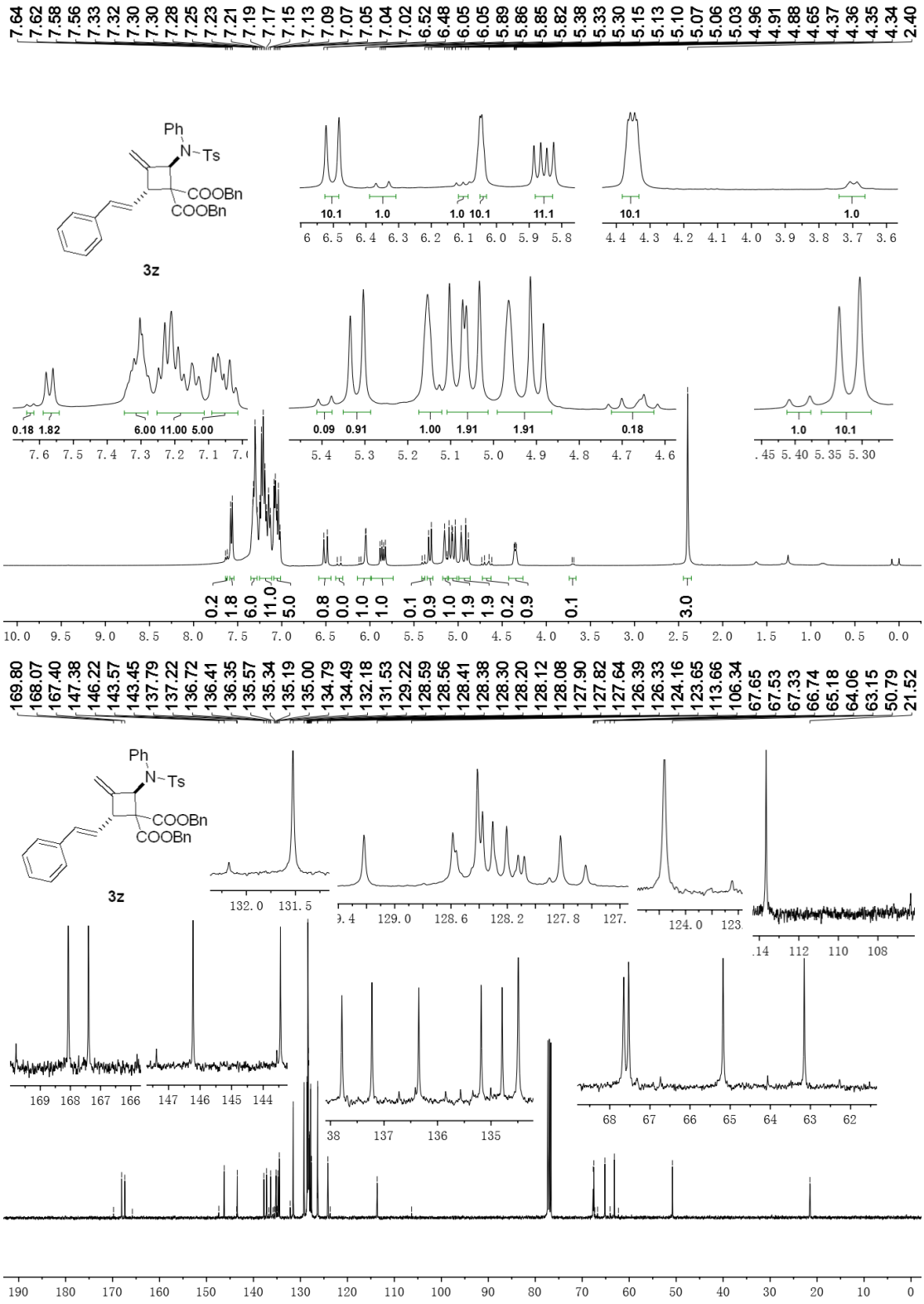
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of two diastereomers of compounds **3x**



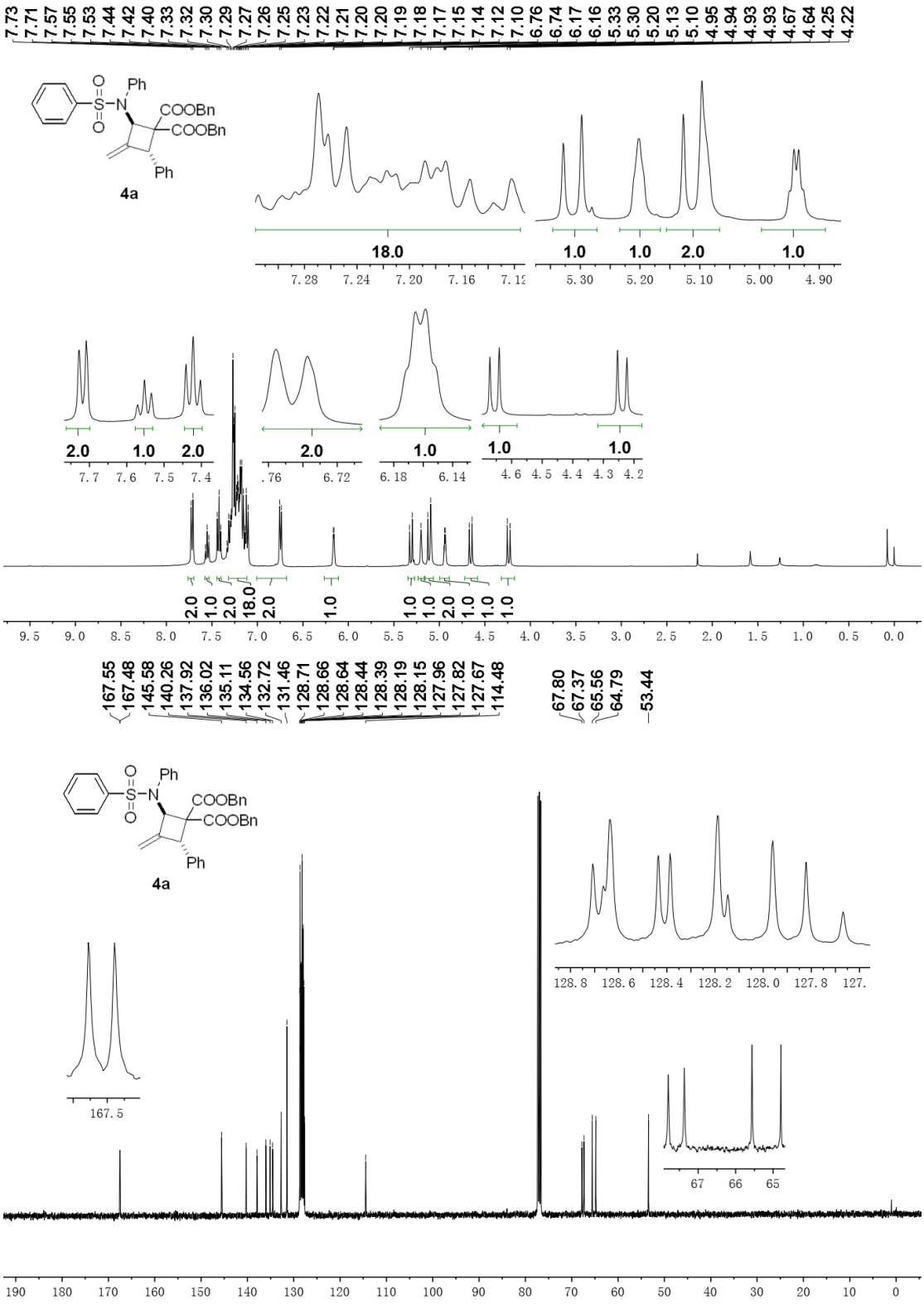
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of two diastereomers of compounds **3y**



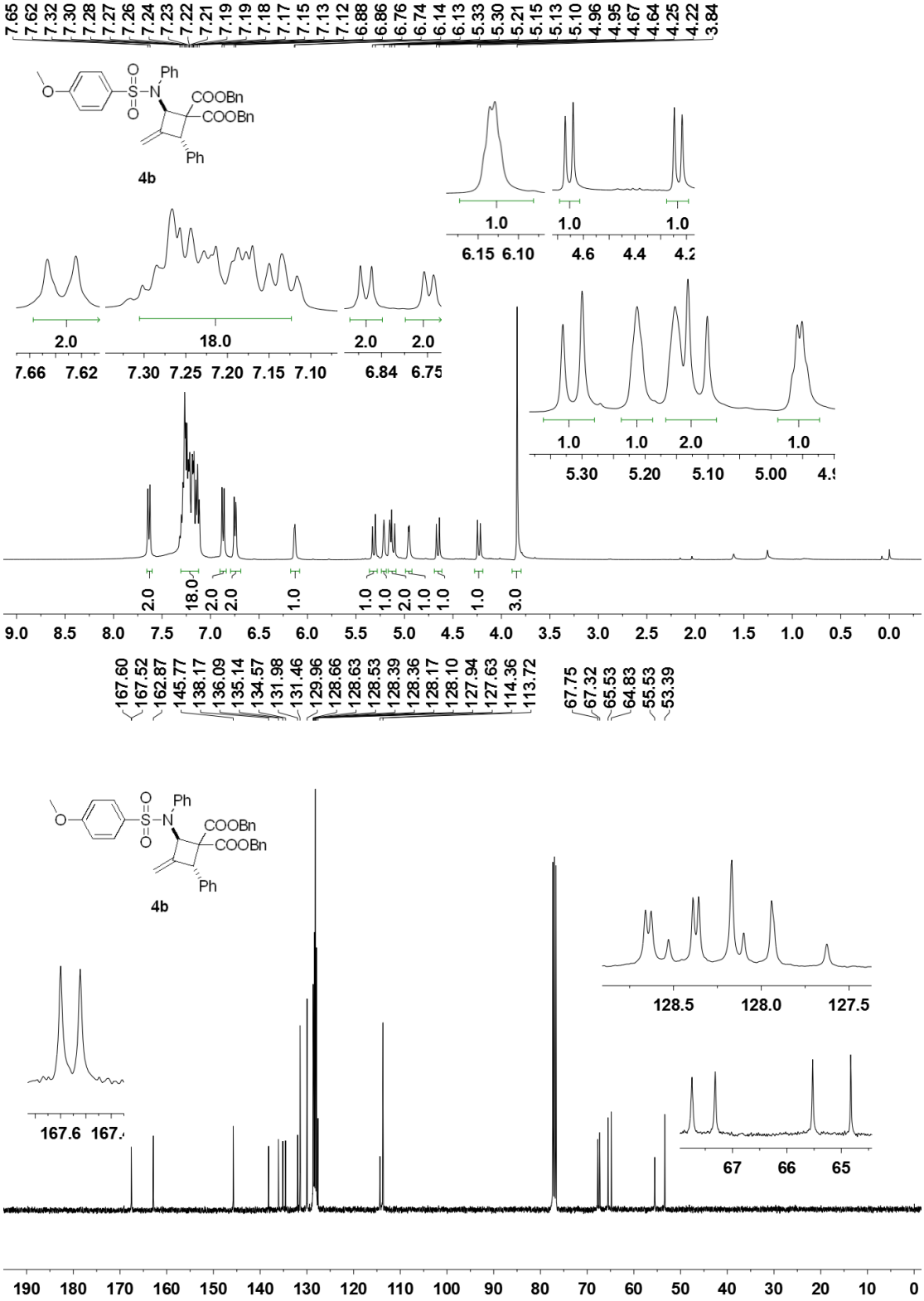
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of two diastereomers of compounds **3z**



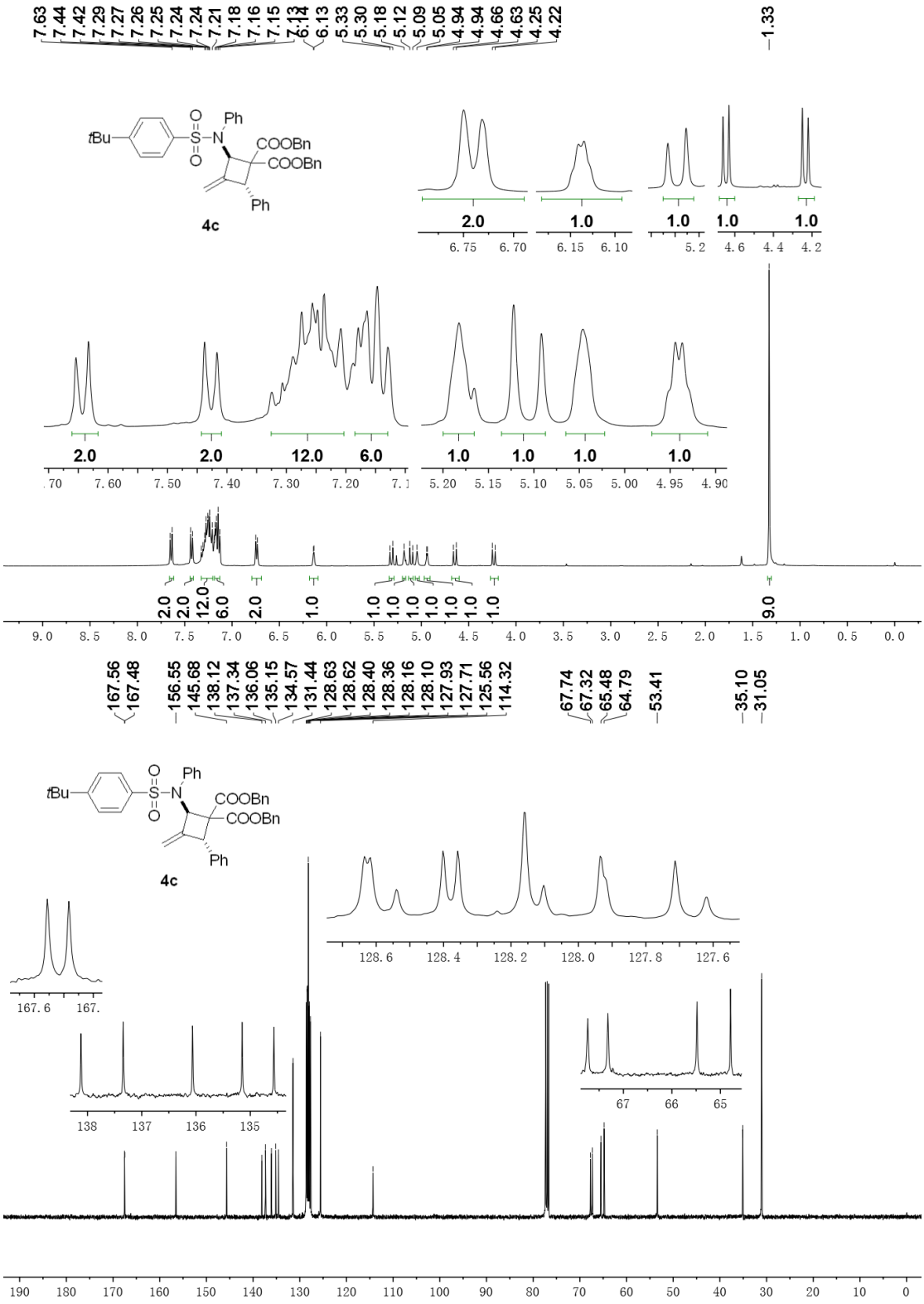
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **4a**



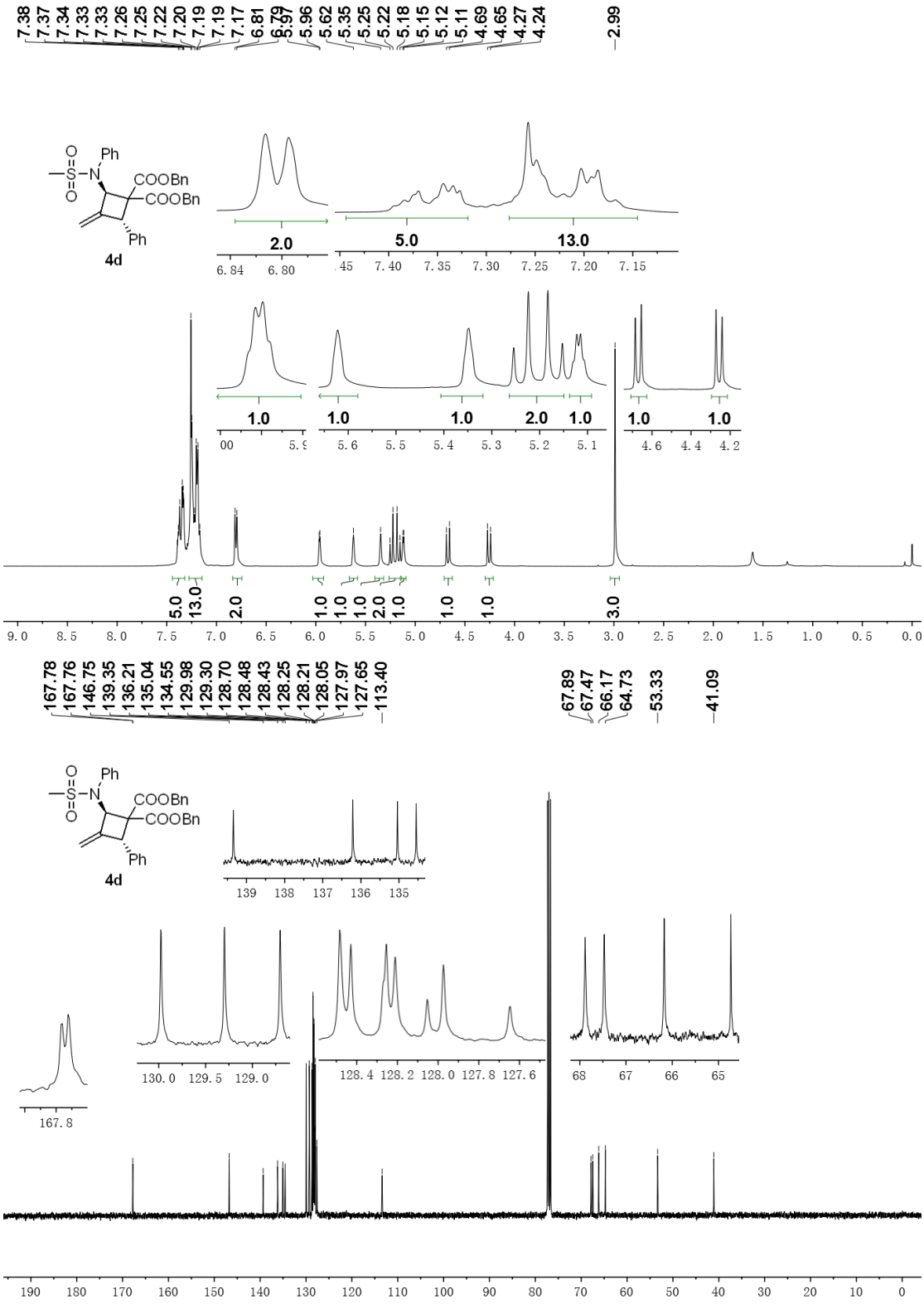
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **4b**



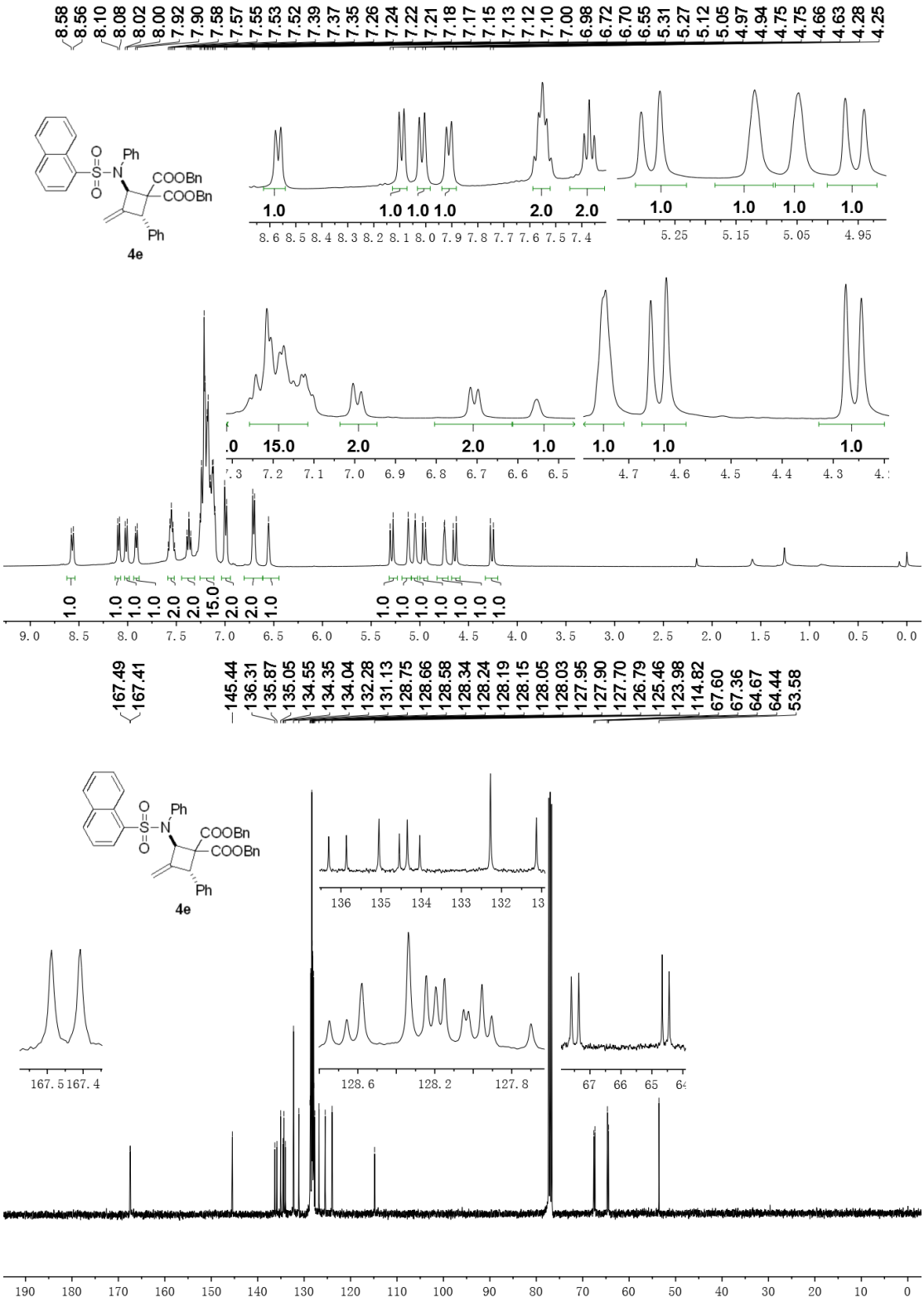
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **4c**



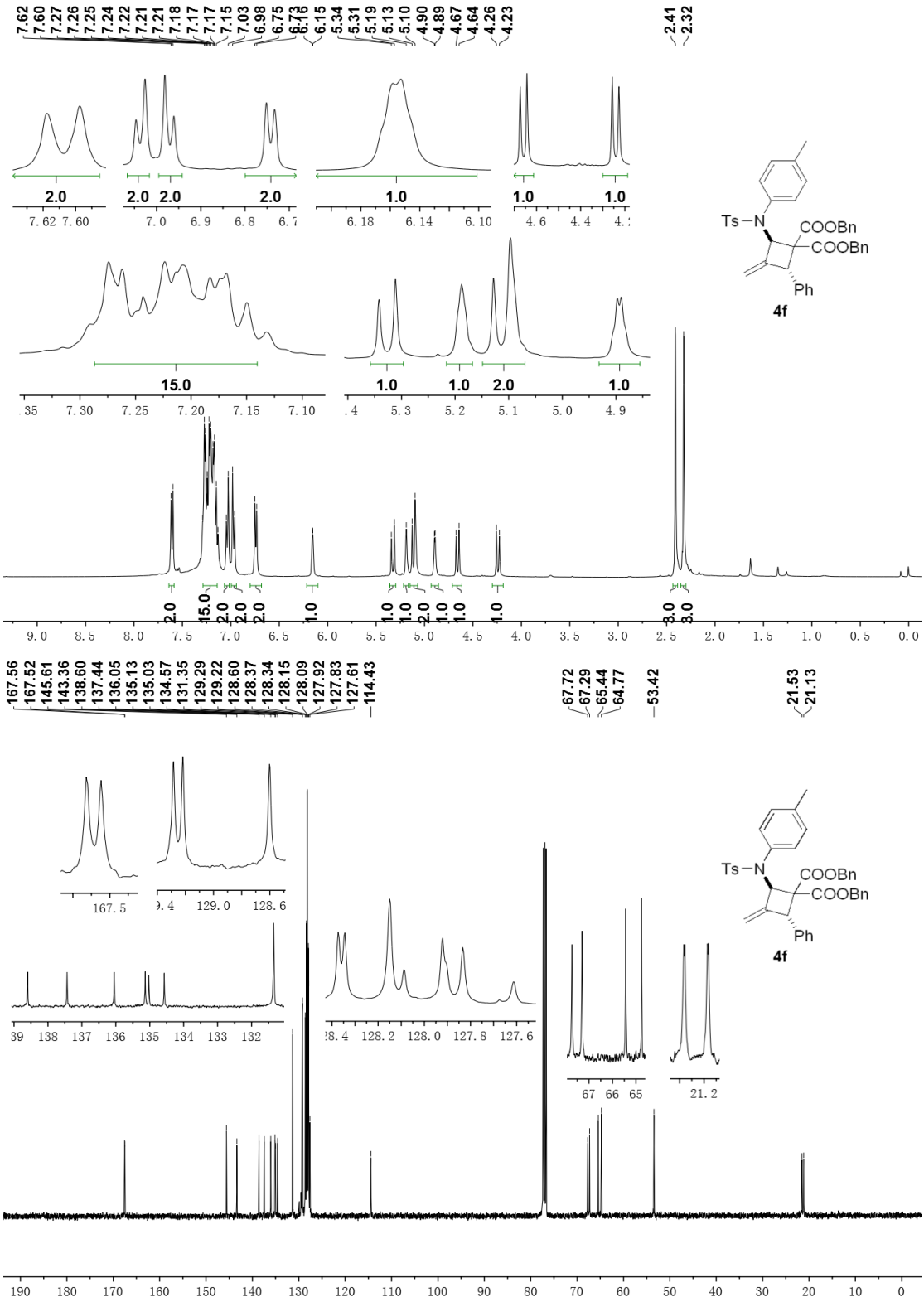
$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **4d**



$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **4e**



$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **4f**



$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra of compound **4g**