Supporting Information

Divergent Protosilylation and Protoborylation of Polar Enynes

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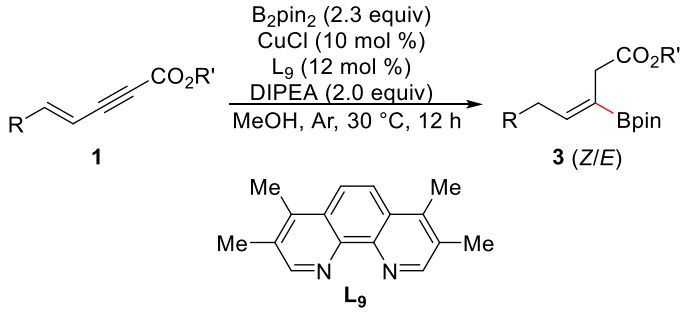
Table of Contents

1. General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR and ^{11}B-NMR spectra were recorded at 25 ºC on a Bruker Advance 400M NMR spectrometer ($CDCl_3$). Chemical shifts for ^{1}H NMR spectra are reported as δ in parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of $CHCl_3$ residual peak (δ 7.26 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and *etc*. Coupling constants are reported as *J* value in Hz. ^{13}C NMR spectra are reported as δ in parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of chloroform-*d* (δ 77.16 triplet). High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system. The enynoates **1a-1t** were prepared following the reported procedures [1] and spectra data for new compounds **1p**, **1t** and **1s** are recorded herein.

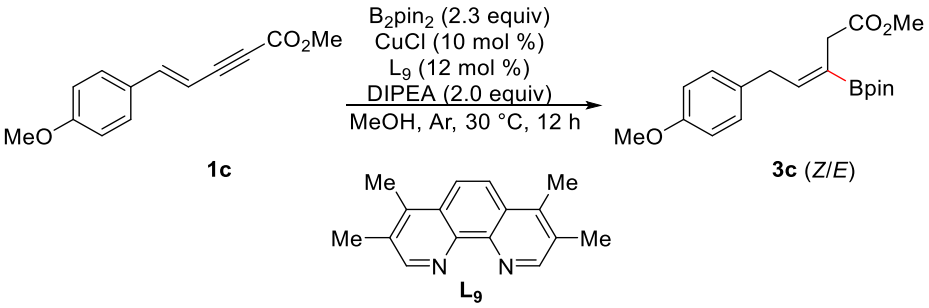
2. Experimental Procedures

General Procedure A:



Under argon atmosphere, an oven-dried 10 mL Schlenck tube was charged with a stirring bar, CuCl (2.0 mg, 0.02 mmol, 10 mol %), 3,4,7,8-tetramethyl-1,10-phenanthroline (5.7 mg, 0.024 mmol, 12 mol %) and MeOH (1 mL, 0.2 M). After stirring for 10 min, B_2pin_2 (116.8 mg, 0.46 mmol, 2.3 equiv), substrate **1** (0.2 mmol, 1.0 equiv) and N,N-diisopropylethylamine (51.7 mg, 0.4 mmol, 2.0 equiv) were added in sequence. Then the reaction mixture was kept at 30 ℃ for 12 h. Dichloromethane was added and the precipitate was removed by filtration. The resultant solution was concentrated and the crude product was purified by column chromatography.

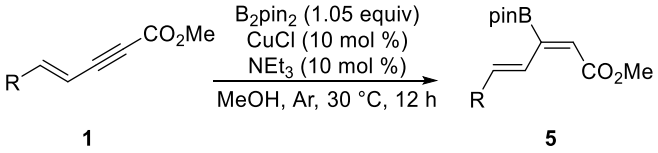
*1 mmol scale experiment for the preparation of **3c***:



Under argon atmosphere, an oven-dried 35 mL Schlenck tube was charged with a stirring bar, CuCl

(9.9 mg, 0.10 mmol, 10 mol %), 3,4,7,8-tetramethyl-1,10-phenanthroline (28.4 mg, 0.12 mmol, 12 mol %) and MeOH (5 mL, 0.2 M). After stirring for 10 min, B_2pin_2 (584.0 mg, 2.3 mmol, 2.3 equiv), substrate **1c** (216.2 mg, 1.0 mmol, 1.0 equiv) and *N,N*-diisopropylethylamine (258.4 mg, 2.0 mmol, 2.0 equiv) were added in sequence. Then the reaction mixture was kept at 30 ℃ for 12 h. Dichloromethane was added and the precipitate was removed by filtration. The resultant solution was concentrated and the crude product was purified by column chromatography (petroleum ether/ethyl acetate from 100:0 to 90:10) to give **3c** (289.4 mg, 83% yield, 93:7 *Z*/*E*) as a light yellow oil.

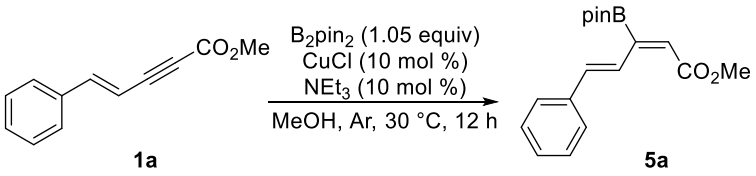
General Procedure B:



1 **5**

An oven-dried 10 mL Schlenck tube was charged with a stirring bar, CuCl (2.0 mg, 0.02 mmol, 10 mol %), B_2pin_2 (53.3 mg, 0.21 mmol, 1.05 equiv) and substrate **1** (0.2 mmol, 1.0 equiv). Under argon atmosphere, triethylamine (10 mol%) in MeOH (1 mL, 0.2 M) were added via syringe. K_3PO_4 (4.2 mg, 10 mol %) was used as base instead of triethylamine for δ-alkyl substituted dienoates. Then the reaction mixture was kept at 30 ℃ for 12 h. Dichloromethane was added and the precipitate was removed by filtration. The resultant solution was concentrated and the crude product was purified by column chromatography.

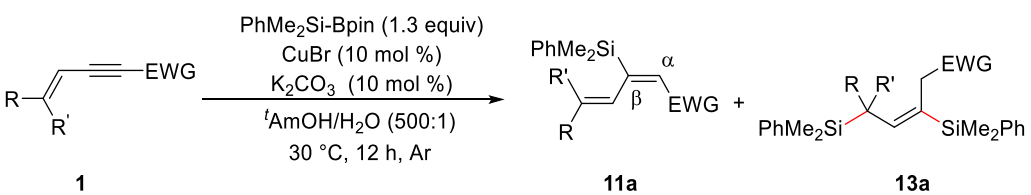
5 mmol scale experiment for the preparation of ***5a***:



1a **5a**

An oven-dried 50 mL 50 mL round-bottom flask was charged with a stirring bar, CuCl (49.5 mg, 0.5 mmol, 10 mol %), B_2pin_2 (1.334 g, 5.25 mmol, 1.05 equiv) and substrate **1a** (931 mg, 5 mmol, 1.0 equiv). Under argon atmosphere, triethylamine (50.6 mg, 10 mol%) in MeOH (25 mL, 0.2 M) were added via syringe. Then the reaction mixture was kept at 30 ℃ for 12 h. Dichloromethane was added and the precipitate was removed by filtration. The resultant solution was concentrated and the crude product was purified by column chromatography (dichloromethane) to give **5a** (1.109 g, 71% yield) as a colorless oil.

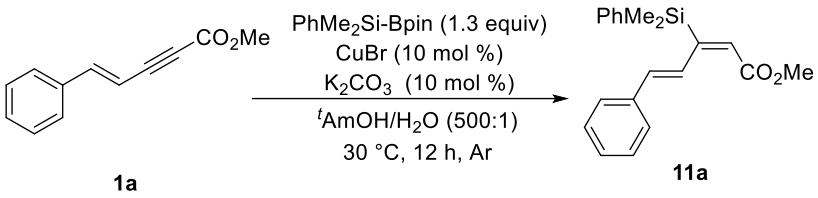
General Procedure C:



1 **11a** **13a**

An oven-dried 10 mL Schlenck tube was charged with a stirring bar, CuBr (2.9 mg, 0.02 mmol, 10 mol %), K_2CO_3 (2.8 mg, 0.02 mmol, 10 mol %) and substrate **1** (0.2 mmol). Under Ar atmosphere, ^{t}AmOH/H_2O (1 mL, 500:1, 0.2 M) and $PhMe_2Si$-Bpin (68.2 mg, 0.26 mmol, 1.3 equiv) were added in sequence via syringe. Then the reaction mixture was kept at 30 ℃. Another batch of water was added after 1h as indicated if necessary. After another 11 h, dichloromethane was added and the precipitate was removed by filtration. The resultant solution was concentrated and the crude product was purified by preparative thin-layer chromatography (PTLC) or column chromatography.

*3 mmol scale experiment for the preparation of **11a***:

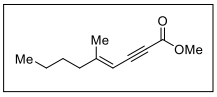


An oven-dried 50 mL round-bottom flask was charged with a stirring bar, CuBr (43.0 mg, 0.3 mmol, 10 mol %), K_2CO_3 (41.5 mg, 0.3 mmol, 10 mol %) and substrate **1a** (558.6 mg, 3.0 mmol). Under Ar atmosphere, ^{t}AmOH/H_2O (15 mL, 500:1, 0.2 M) and $PhMe_2Si$-Bpin (1.023 g, 3.9 mmol, 1.3 equiv) were added in sequence via syringe. Then the reaction mixture was kept at 30 ℃. Another batch of water (30 μL) was added after 1h if the reaction system didn't turn black. After another 11 h, dichloromethane was added and the precipitate was removed by filtration. The resultant solution was concentrated and the crude product was purified by column chromatography to give **11a** in (907.5 mg, 93% yield, β:α = 96:4) as a colorless oil.

3. Characterization Data and Spectra of Substrates and Products

3.1 Spectra of New Starting Materials

methyl (*E*)-5-methylnon-4-en-2-ynoate (1p)



Prepared according to reported procedure[1] using corresponding TMS-protected alkyne (1.65 g, 8.5 mmol). The product **1p** was isolated in 62% yield (0.95 g) by column chromatography as light yellow oil.

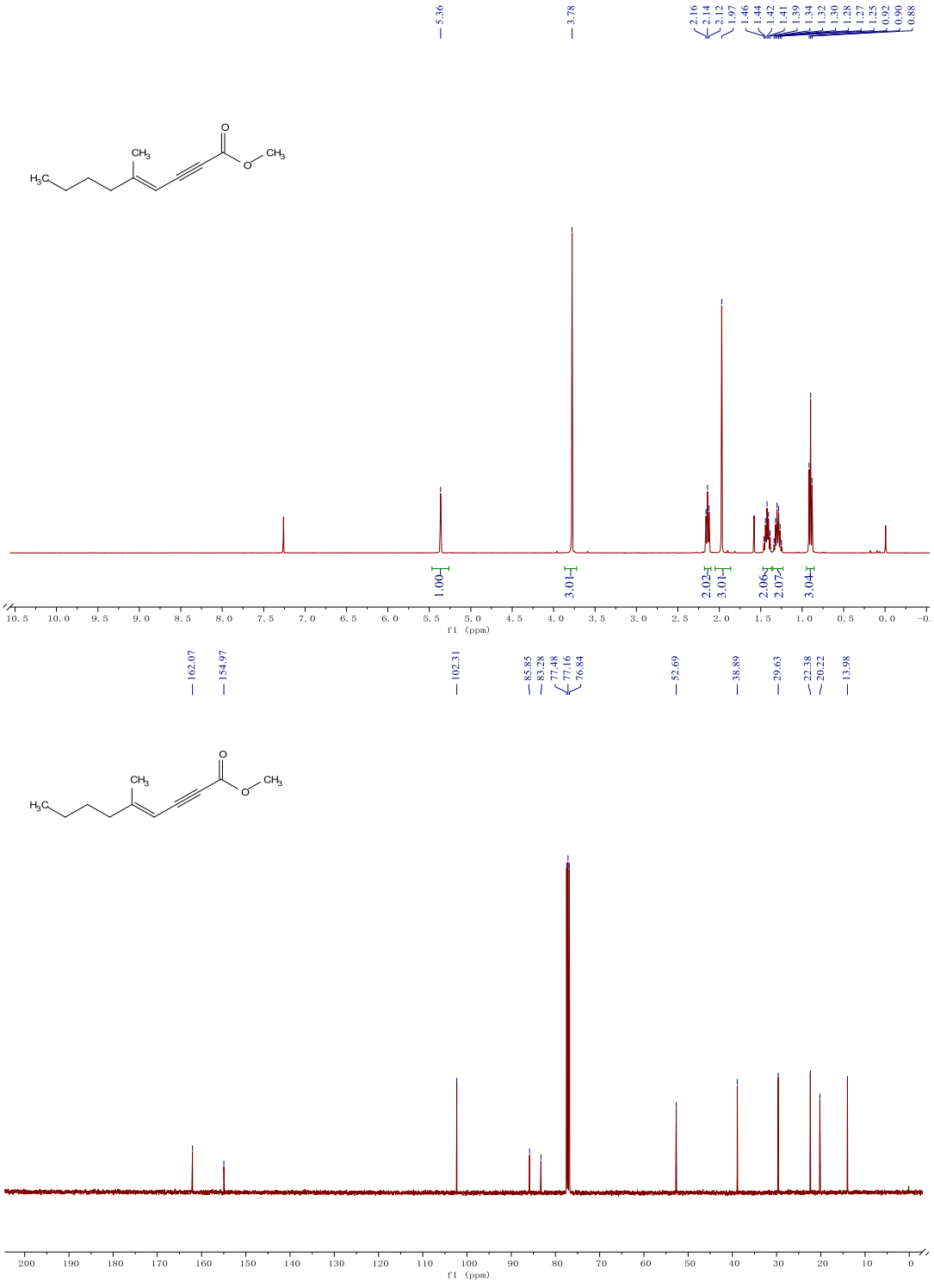
Eluent: petroleum ether/ethyl acetate (100:0 – 100:5).

R_f: 0.37 (petroleum ether/ethyl acetate = 20:1).

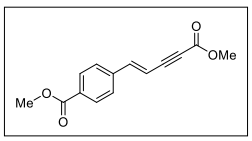
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 3.78 (s, 3H), 2.14 (t, *J* = 7.6 Hz, 2H), 1.97 (s, 3H), 1.42 (m, 2H), 1.36 – 1.23 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.07, 154.97, 102.31, 85.85, 83.28, 52.69, 38.89, 29.63, 22.38, 20.22, 13.98.

HRMS (ESI**)** (m/z): Calcd for $C_{11}H_{17}O_2^+$ $[M+H]^+$: 181.1229, found: 181.1231.



methyl (*E*)-4-(5-methoxy-5-oxopent-1-en-3-yn-1-yl)benzoate (1f)



Prepared according to reported procedure[1] using corresponding TMS-protected alkyne (1.06 g, 4.12 mmol). The product **1f** was isolated in 79% yield (0.80 g) by column chromatography as white solid.

Eluent: petroleum ether/ethyl acetate (85:15).

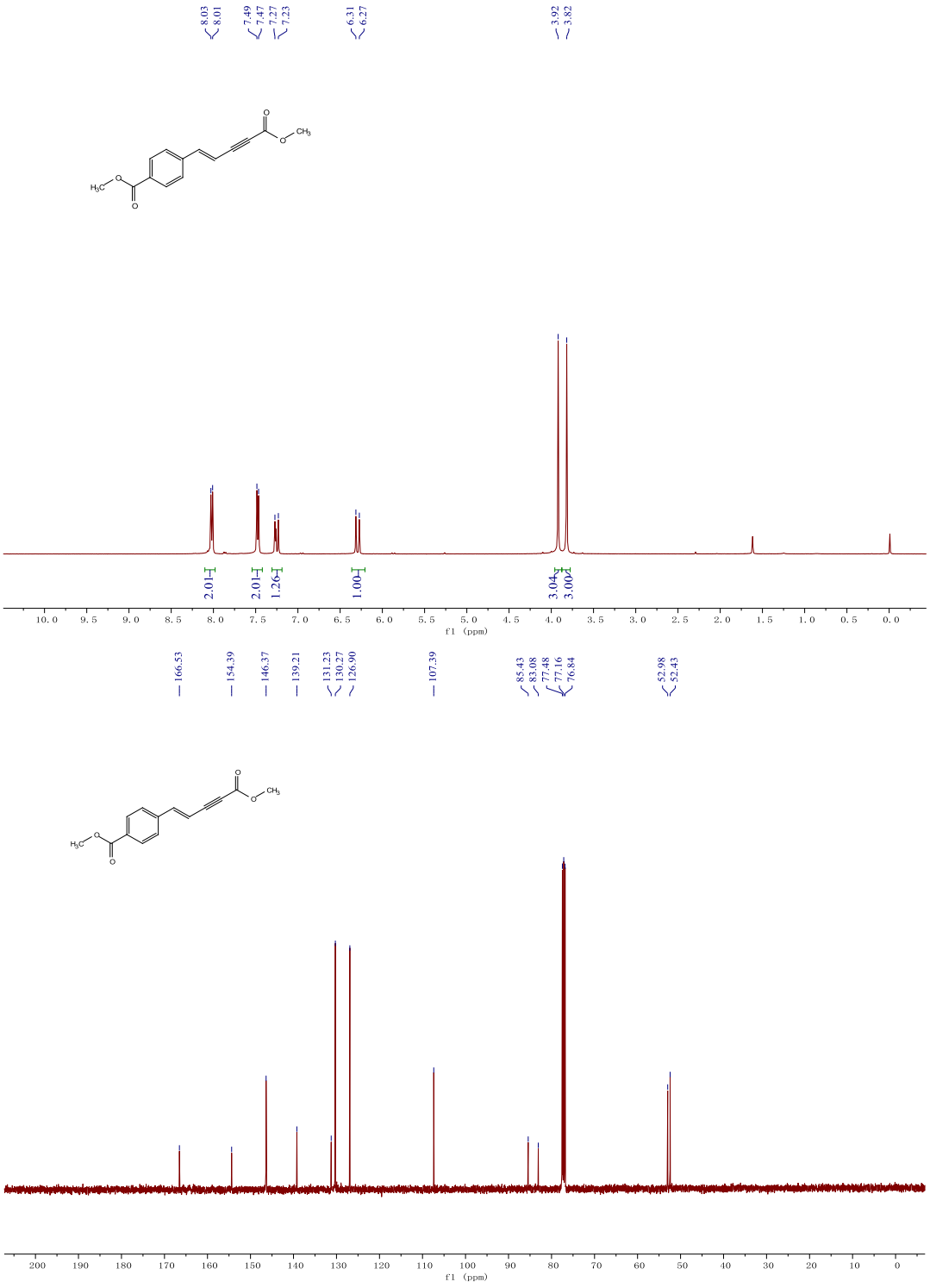
R_f: 0.26 (petroleum ether/ethyl acetate = 85:15).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 16.3 Hz,

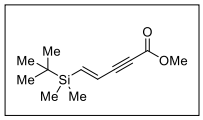
1H), 6.29 (d, J = 16.3 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.53, 154.39, 146.37, 139.21, 131.23, 130.27, 126.90, 107.39, 85.43, 83.08, 52.98, 52.43.

HRMS (ESI) (m/z): Calcd for $C_{14}H_{13}O_4^+$ $[M+H]^+$: 245.0814, found: 245.0811.



methyl (*E*)-5-(tert-butyldimethylsilyl)pent-4-en-2-ynoate (1t)



Prepared according to reported procedure[1a, 2] using corresponding terminal alkyne (1.00g, 6.0 mmol). The product **1t** was isolated in 38% yield (0.51 g) by column chromatography as yellow oil.

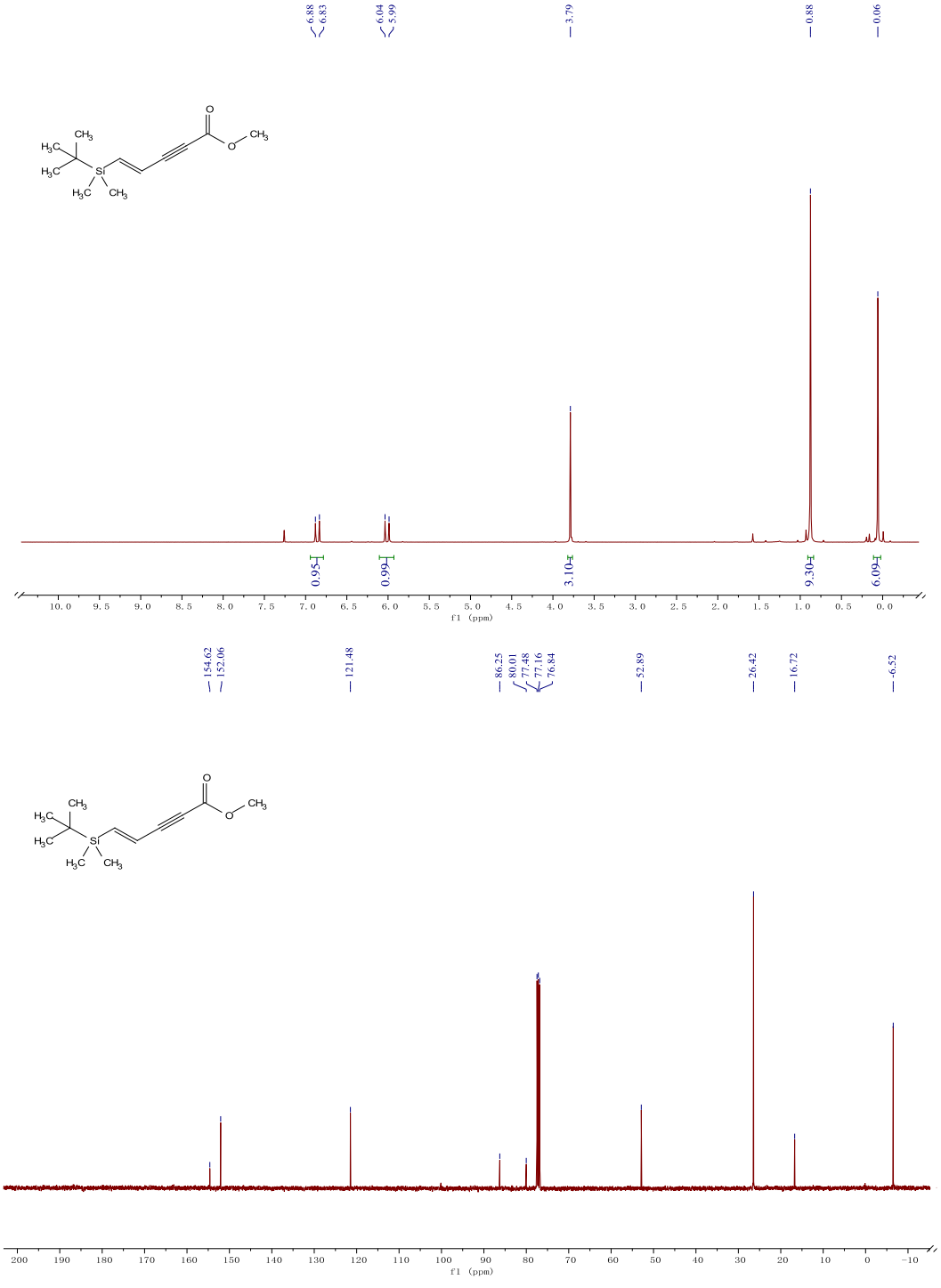
Eluent: petroleum ether/ethyl acetate (100:0 – 100:2).

R_f: 0.50 (petroleum ether/ethyl acetate = 20:1).

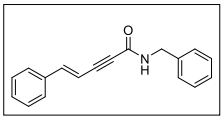
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 19.4 Hz, 1H), 6.01 (d, *J* = 19.5 Hz, 1H), 3.79 (s, 3H), 0.88 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.62, 152.06, 121.48, 86.25, 80.01, 52.89, 26.42, 16.72, -6.52.

HRMS (ESI) (m/z): Calcd for $C_{12}H_{21}O_2Si^+$ $[M+H]^+$: 225.1311, found: 225.1311.



(*E*)-N-benzyl-5-phenylpent-4-en-2-ynamide (1s)



Prepared according to reported procedure[3] using **1a** (0.372 g, 2.0 mmol, 1.0 equiv) and benzylamine (0.257 g, 2.4 mmol, 1.2 equiv) as substrates. The product **1s** was isolated in 62% yield (0.323 g) by column chromatography as pale solid.

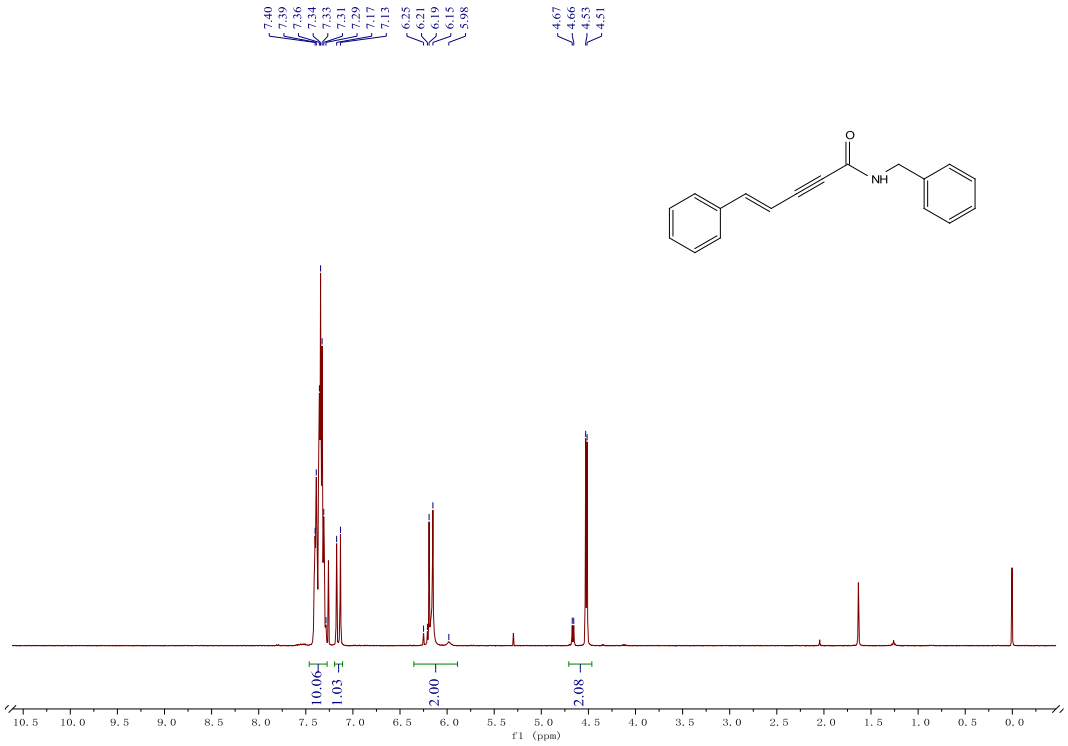
Eluent: petroleum ether/ethyl acetate (90:10 - 80:20).

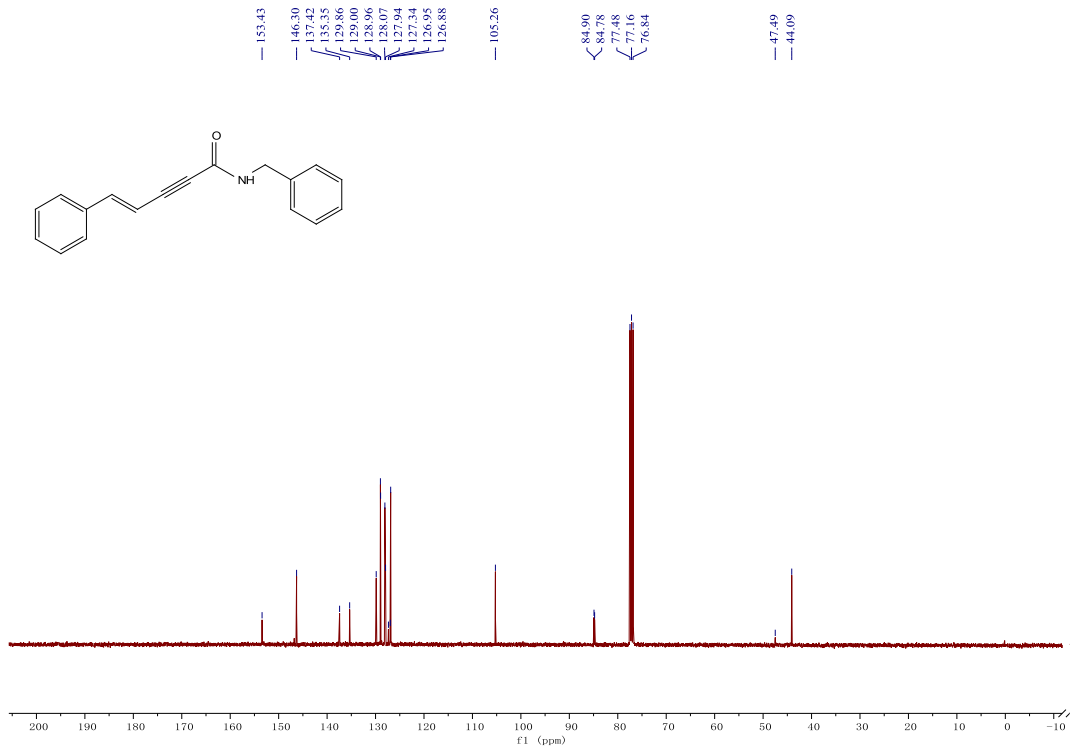
R_f: 0.15 (petroleum ether/ethyl acetate = 85:15).

^{1}H NMR (400 MHz, $CDCl_3$) (C-N cis/trans) δ 7.47 – 7.27 (m, 10H), 7.15 (d, *J* = 16.3 Hz, 1H), 6.29 – 5.92 (m, 2H), 4.66 (d, *J* = 6.5 Hz, 0.21H) and 4.52 (d, *J* = 5.9 Hz, 1.86H).

^{13}C NMR (101 MHz, $CDCl_3$) (C-N cis/trans) δ 153.43, 146.30, 137.42, 135.35, 129.86, 129.00, 128.96, 128.07, 127.94, 127.34, 126.95, 126.88, 105.26, 84.90, 84.78, 47.49, 44.09.

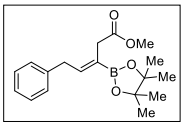
HRMS (ESI) (m/z): Calcd for $C_{18}H_{16}NO^+$, $[M+H]^+$: 262.1232, found: 262.1232.





3.2 Spectra of Vinylboronates

methyl (*Z*)-5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3a)



Prepared according to General Procedure A from **1a** (37.2 mg, 0.20 mmol). The product **3a** was isolated in 75% yield (47.4 mg) by flash column chromatography as white solid.

Stereoselectivity: 95:5 (*Z*/*E*, GC, crude).

Eluent: petroleum ether/ethyl acetate = 20:1 to 10:1.

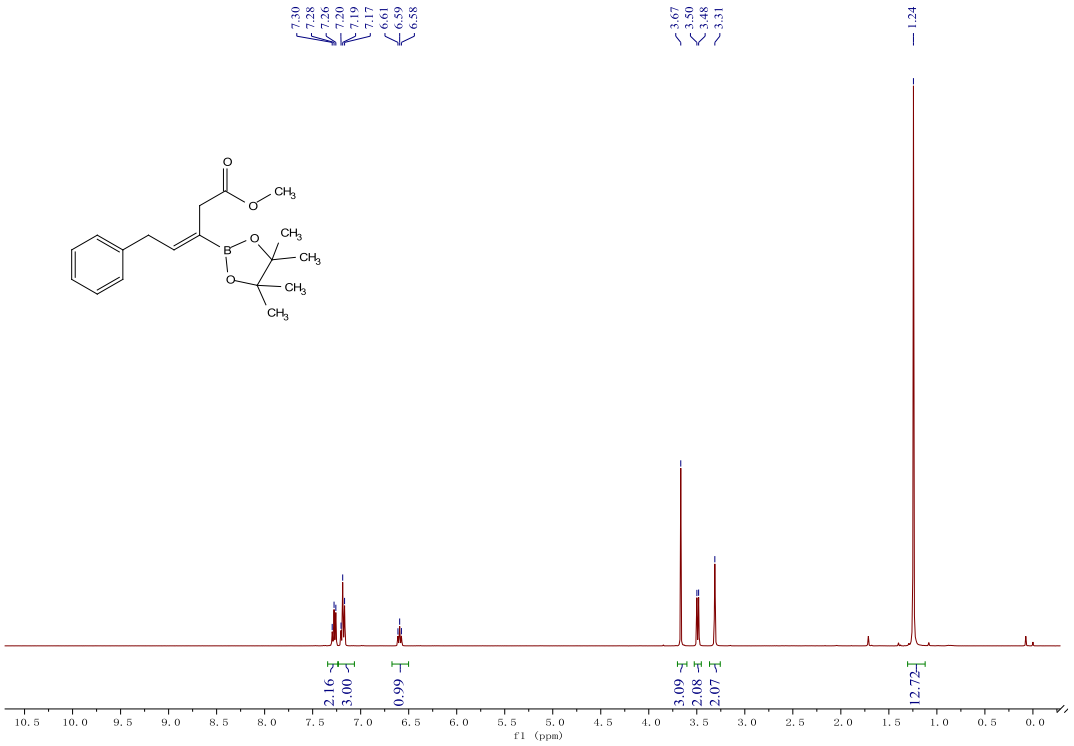
R_f: 0.15 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 3H), 6.59 (t, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 3.49 (d, *J* = 7.2 Hz, 2H), 3.31 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69, 146.41, 139.69, 128.78, 128.61, 126.22, 83.65, 51.82, 35.28, 33.97, 24.81.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.80.

HRMS (ESI) (m/z): Calcd for $C_{18}H_{25}O_4{}^{11}BNa$ $[M+Na]^+$: 339.1744, found: 339.1747.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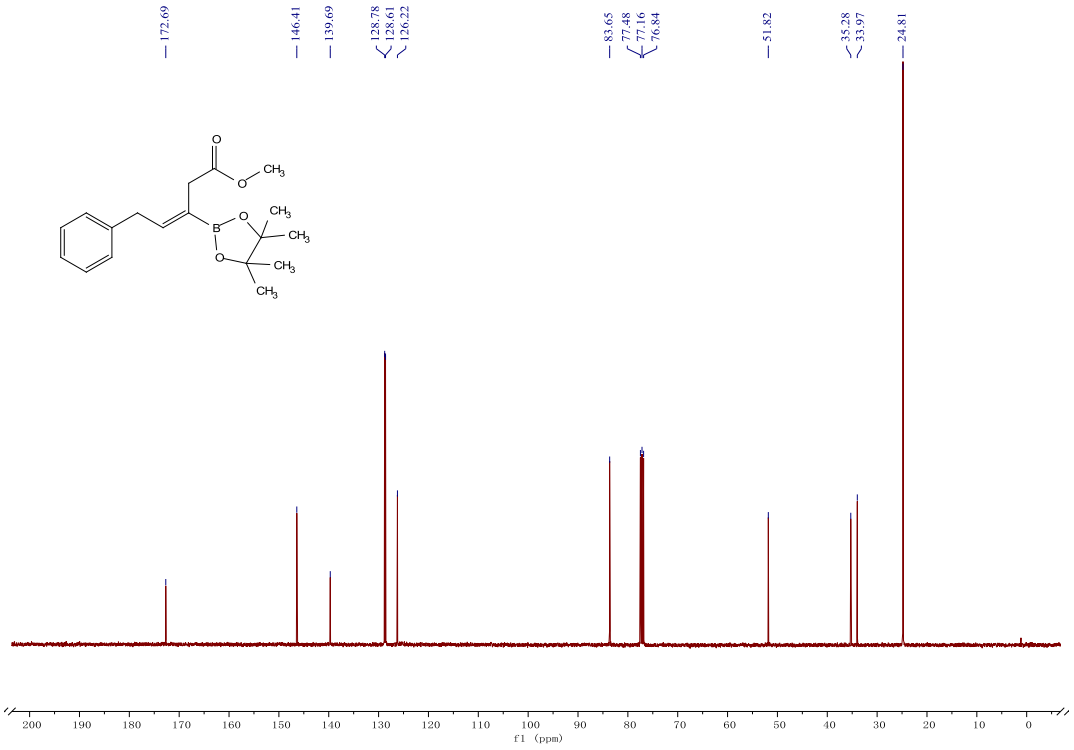
7.28
7.26
7.20
7.19
7.17
6.61
6.59
6.58
3.67
3.50
3.48
3.31
1.24
O
O
CH3
B
O
O
CH3
CH3
CH3
CH3
2.16
3.00
0.99
3.09
2.08
2.07
12.72
f1 (ppm)


172.69
146.41
139.69
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128.61
126.22
83.65
77.48
77.16
76.84
51.82
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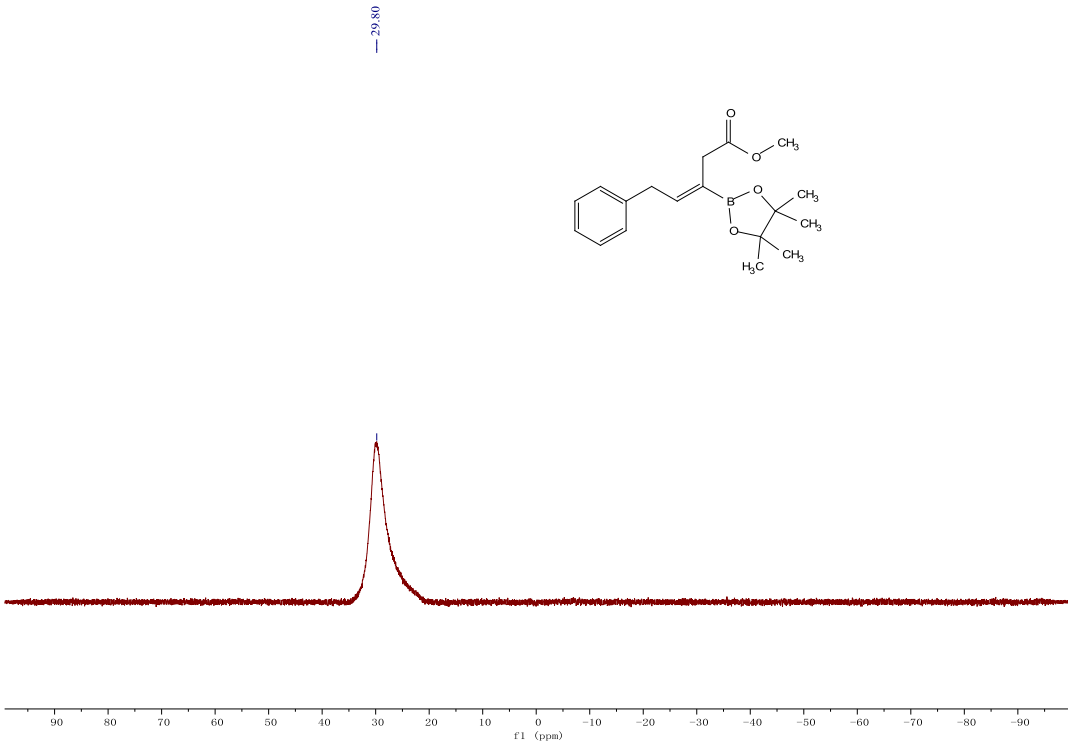
O
CH3
B
O
O
CH3
CH3
CH3
CH3
f1 (ppm)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O
CH3
B
O
O
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CH3
H3C
CH3
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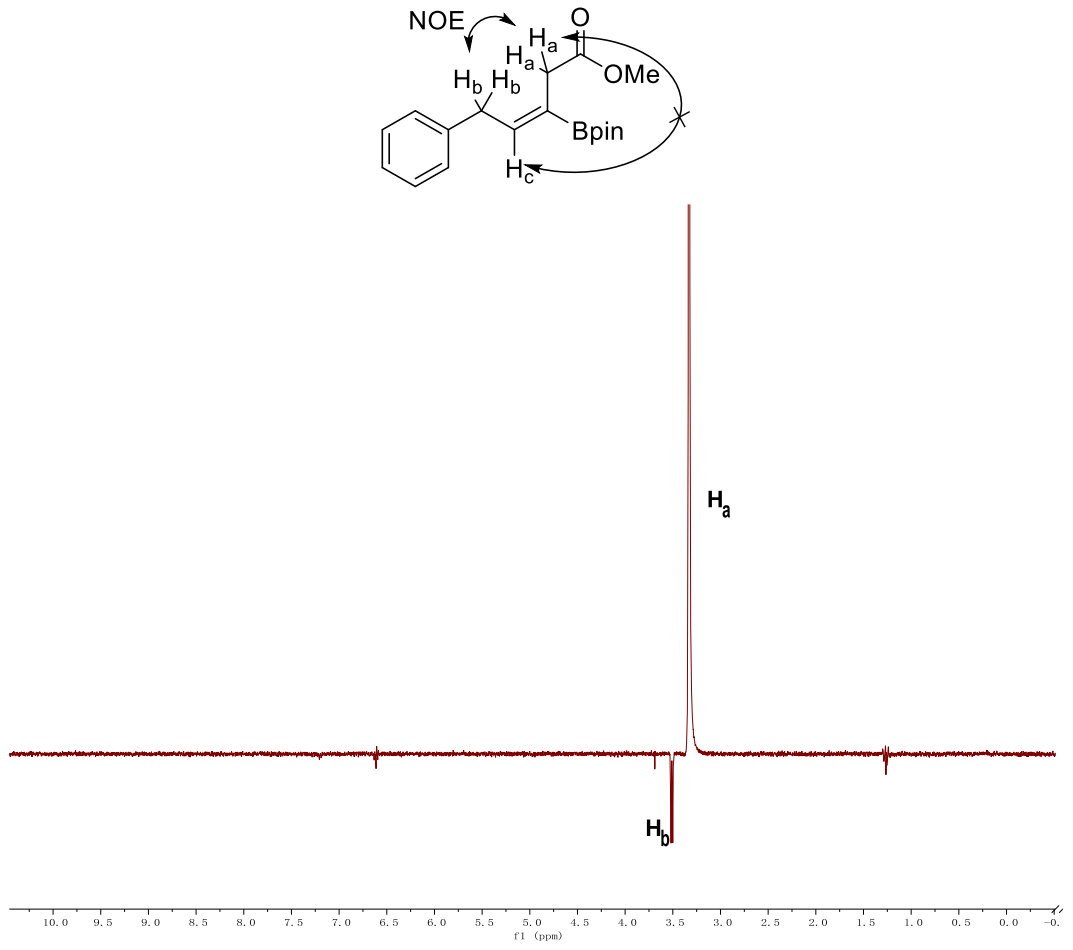
f1 (ppm)


NOE
O
Ha
Ha
OMe
Hb Hb
Bpin
Hc
Ha
Hb
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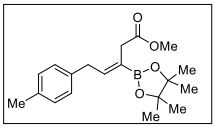
f1 (ppm)

methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(p-tolyl)pent-3-enoate (3b)



Prepared according to General Procedure A from **1b** (40.0 mg, 0.20 mmol). The product **3b** was isolated in 73% yield (48.0 mg) by flash column chromatography as light yellow oil.

Stereoselectivity: 92:8 (*Z*/*E*, GC, crude).

Eluent: dichloromethane.

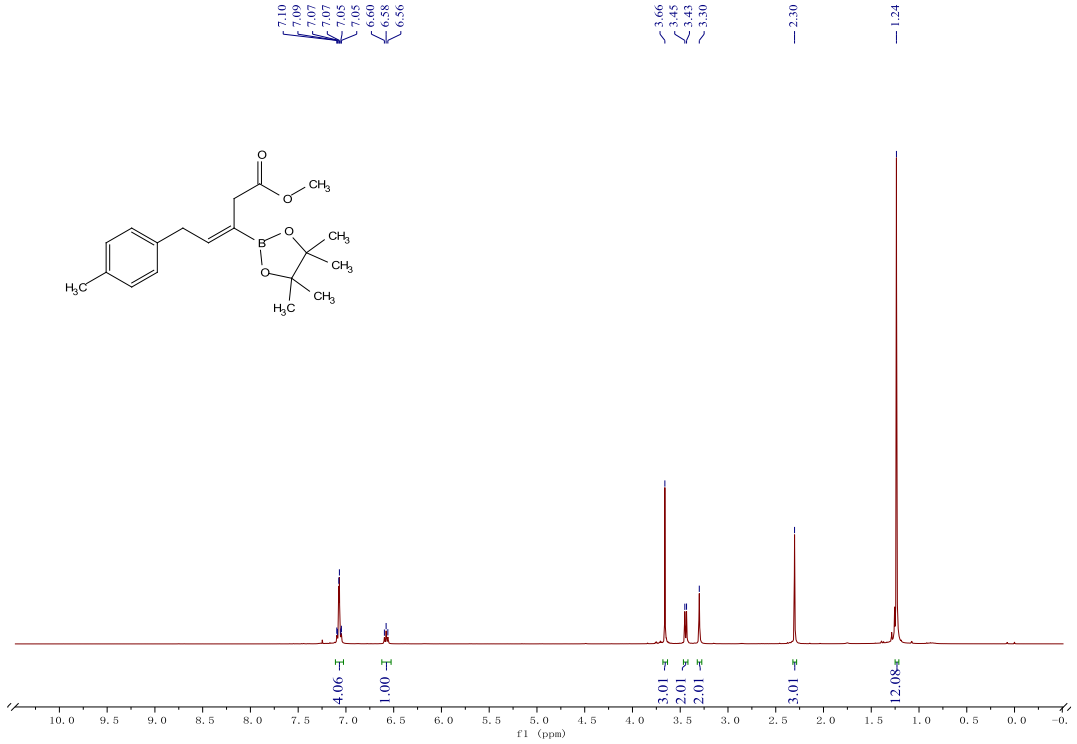
R_f: 0.09 (petroleum ether/ethyl acetate = 40:1).

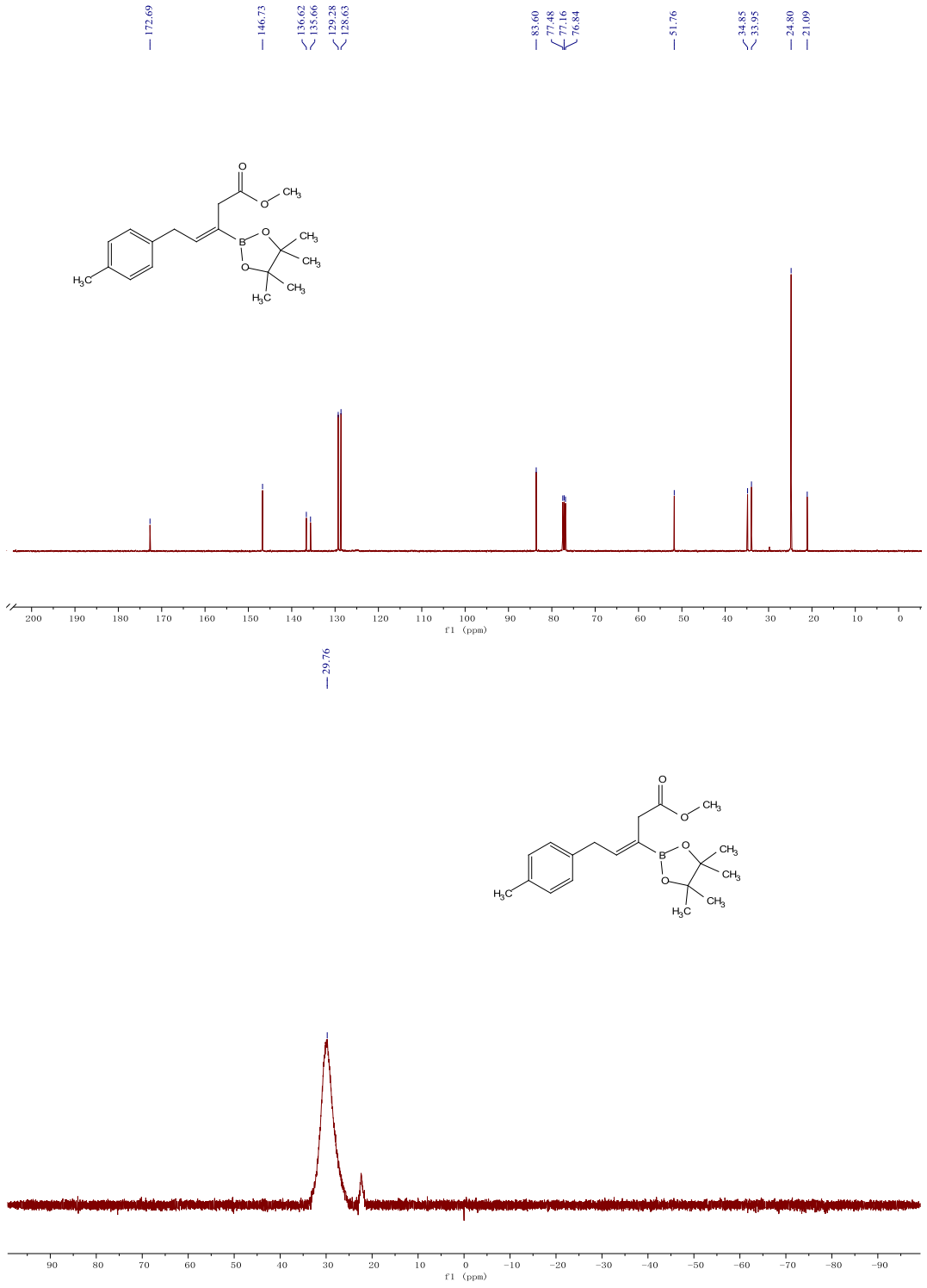
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.03 (m, 4H), 6.58 (t, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 3.44 (d, *J* = 7.2 Hz, 2H), 3.30 (s, 2H), 2.30 (s, 3H), 1.24 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69, 146.73, 136.62, 135.66, 129.28, 128.63, 83.60, 51.76, 34.85, 33.95, 24.80, 21.09.

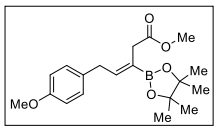
^{11}B NMR (128 MHz, $CDCl_3$) δ 29.76.

HRMS (ESI) (m/z): Calcd for $C_{19}H_{27}O_4{}^{11}BNa$ $[M+Na]^+$: 353.1900, found: 353.1907.





methyl (*Z*)-5-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3c)



Prepared according to General Procedure A from **1c** (43.2 mg, 0.20 mmol). The product **3c** was isolated in 80% yield (55.4 mg) by flash column chromatography as light yellow oil.

Stereoselectivity: 96:4 (Z/E, GC, crude).

Eluent: Dichloromethane.

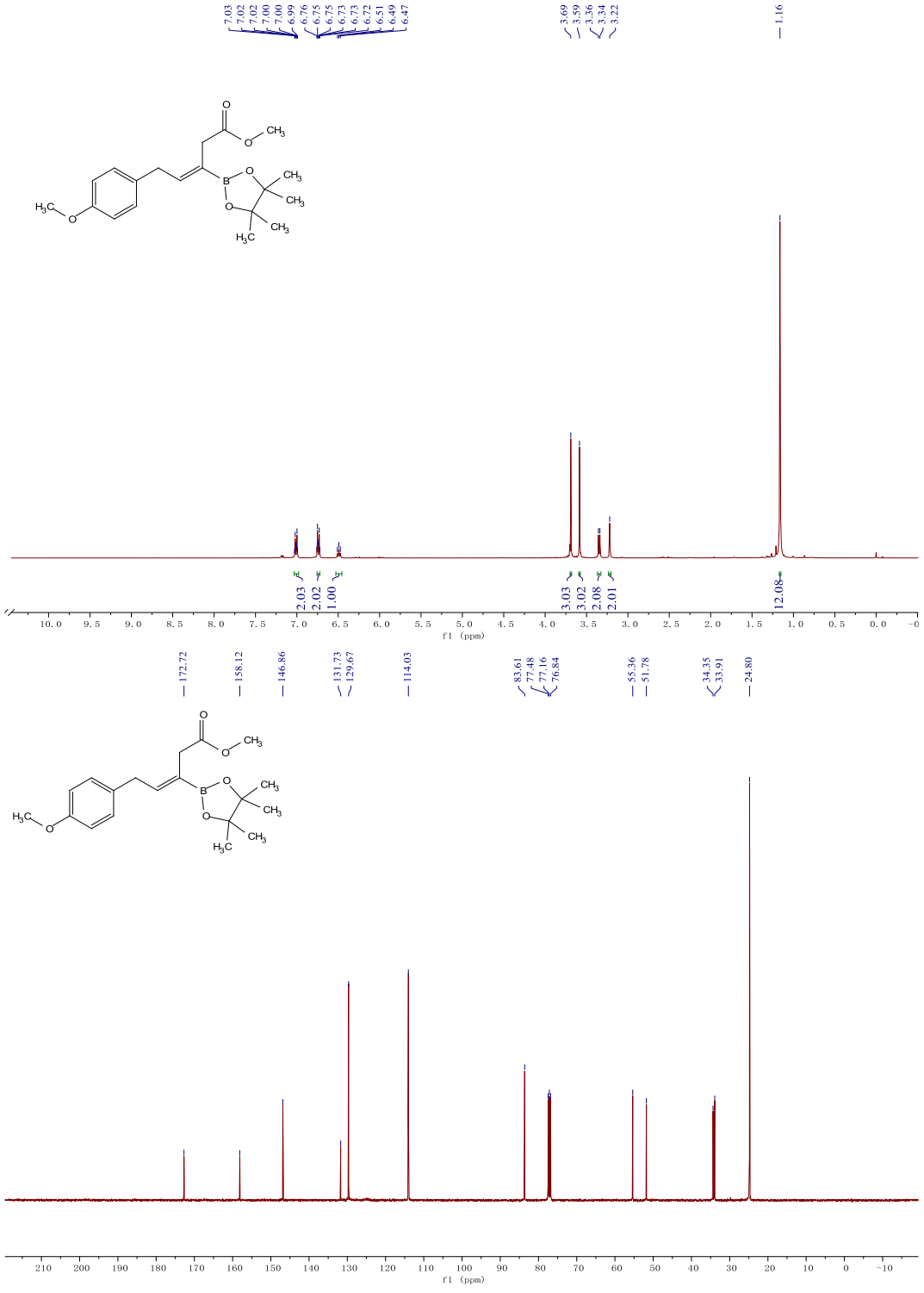
R_f: 0.13 (petroleum ether/ethyl acetate = 20:1)

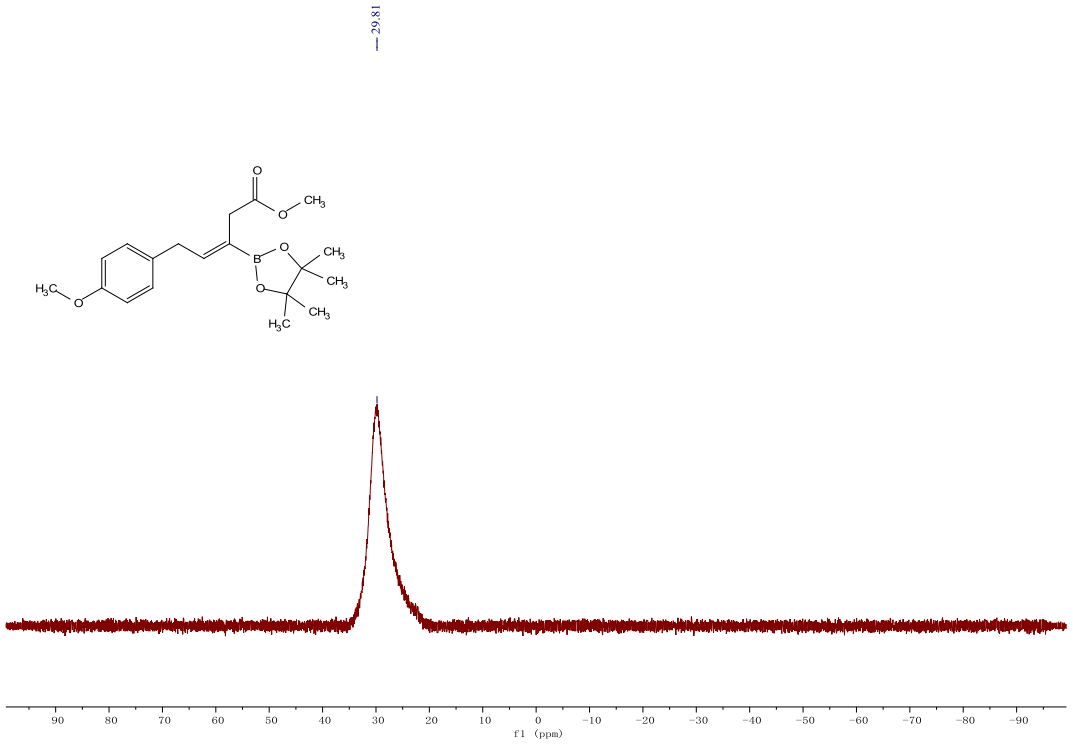
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.98 (m, 2H), 6.76 – 6.72 (m, 2H), 6.49 (t, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 3.59 (s, 3H), 3.35 (d, *J* = 7.2 Hz, 2H), 3.22 (s, 2H), 1.16 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.72, 158.12, 146.86, 131.73, 129.67, 114.03, 83.61, 55.36, 51.78, 34.35, 33.91, 24.80.

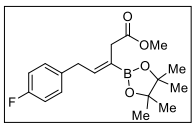
^{11}B NMR (128 MHz, $CDCl_3$) δ 29.81.

HRMS (ESI) (m/z): Calcd for $C_{19}H_{27}O_5{}^{11}BNa$ $[M+Na]^+$: 369.1849, found: 369.1851.





methyl (*Z*)-5-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3d)



Prepared according to General Procedure A from **1d** (40.8 mg, 0.20 mmol). The product **3d** was isolated in 69% yield (46.4 mg) by flash column chromatography as light yellow oil.

Stereoselectivity: 98:2 (*Z*/*E*, GC, crude).

Eluent: Dichloromethane.

R_f: 0.31 (petroleum ether/ethyl acetate = 15:1)

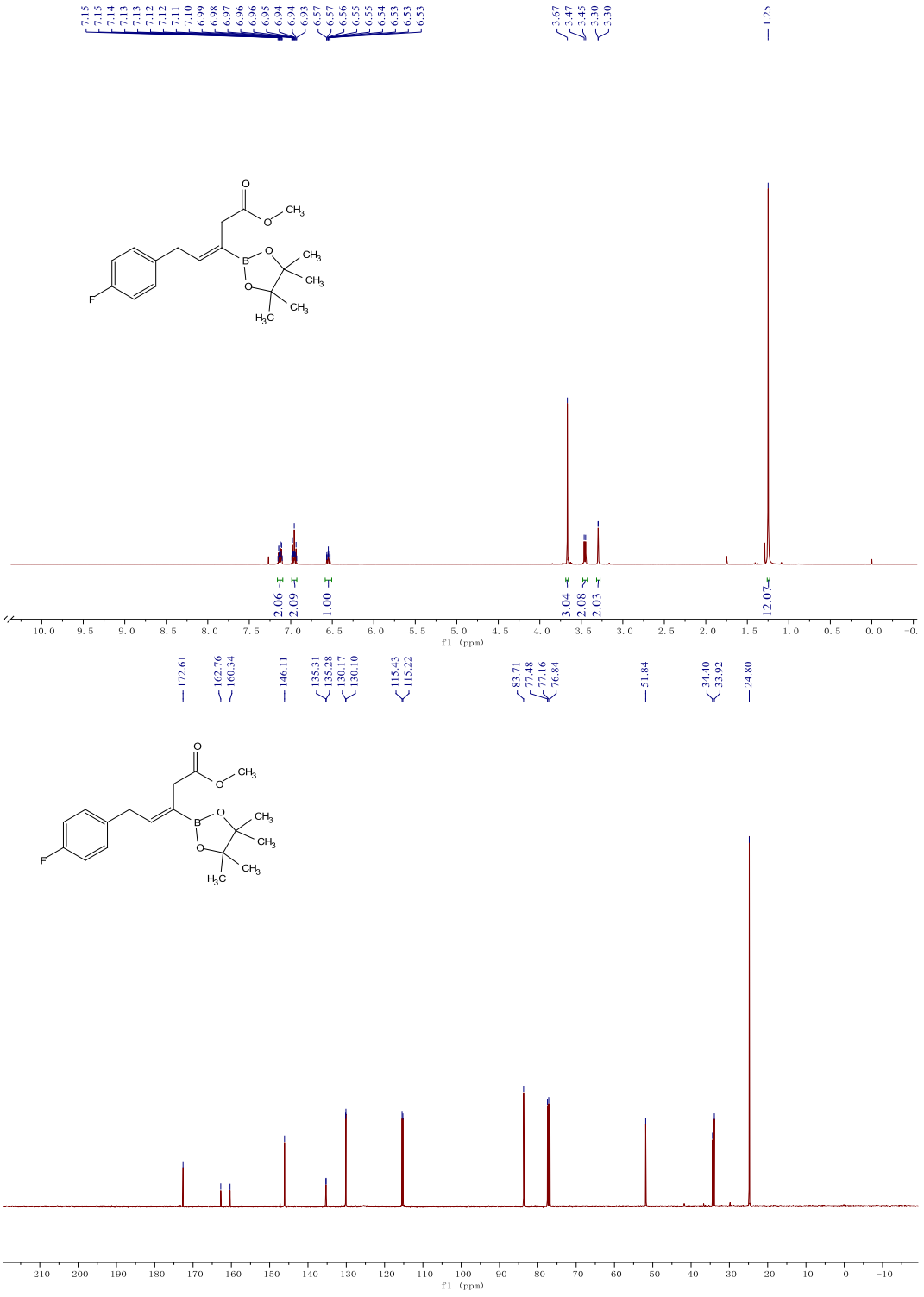
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 2H), 6.99 – 6.92 (m, 2H), 6.55 (tt, *J* = 7.2, 1.0 Hz, 1H), 3.67 (s, 3H), 3.46 (d, *J* = 7.2 Hz, 2H), 3.30 (d, *J* = 0.6 Hz, 2H), 1.25 (s, 12H).

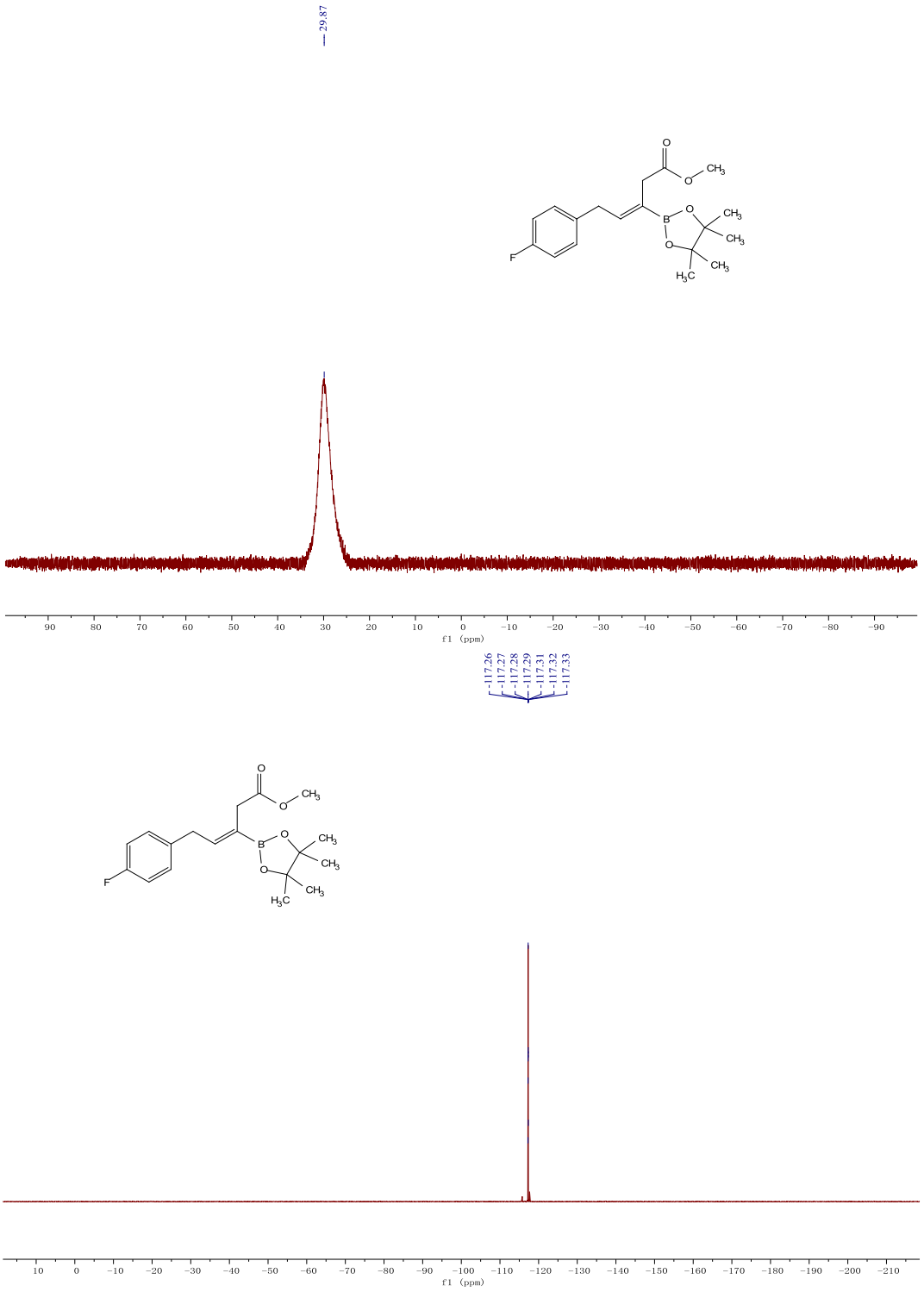
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.61, 161.55 (d, *J* = 243.8 Hz), 146.11, 135.29 (d, *J* = 3.2 Hz), 130.14 (d, *J* = 7.9 Hz), 115.33 (d, *J* = 21.2 Hz), 83.71, 51.84, 34.40, 33.92, 24.80.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.87.

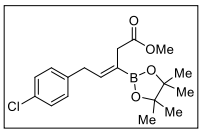
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.24 – -117.35 (m).

HRMS (ESI) (m/z): Calcd for $C_{18}H_{24}O_4{}^{11}BFNa$ $[M+Na]^+$: 357.1649, found: 357.1660.


7.15
7.15
7.14
7.13
7.13
7.12
7.12
7.11
7.10
6.99
6.98
6.97
6.96
6.96
6.95
6.94
6.94
6.93
6.57
6.57
6.56
6.55
6.55
6.54
6.53
6.53
6.53
3.67
3.47
3.45
3.30
3.30
1.25
O
O
CH3
B
O
CH3
CH3
O
CH3
H3C
F
2.06
2.09
1.00
3.04
2.08
2.03
12.07
f1 (ppm)
172.61
162.76
160.34
146.11
135.31
135.28
130.17
130.10
115.43
115.22
83.71
77.48
77.16
76.84
51.84
34.40
33.92
24.80
f1 (ppm)



methyl (*Z*)-5-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3e)



Prepared according to General Procedure A from **1e** (44.1 mg, 0.20 mmol). The product **3e** was isolated in 67% yield (47.1 mg) by flash column chromatography as light yellow oil.

Stereoselectivity: 96:4 (*Z*/*E*, GC, crude).

Eluent: dichloromethane.

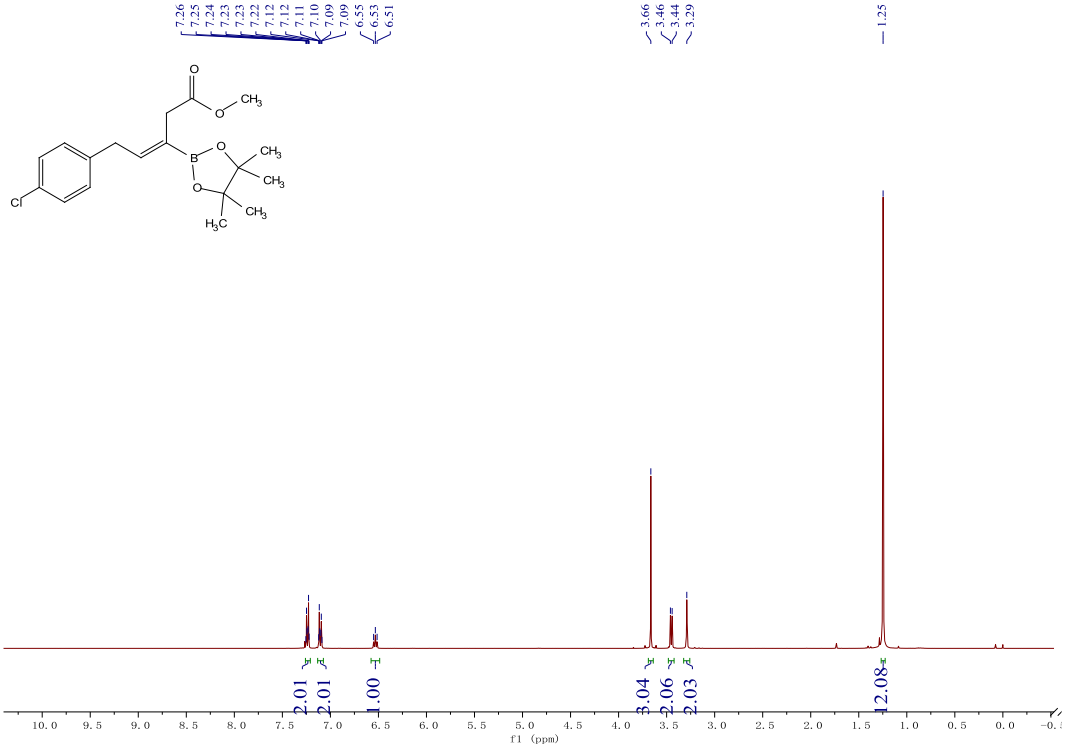
R_f: 0.24 (petroleum ether/ethyl acetate = 15:1)

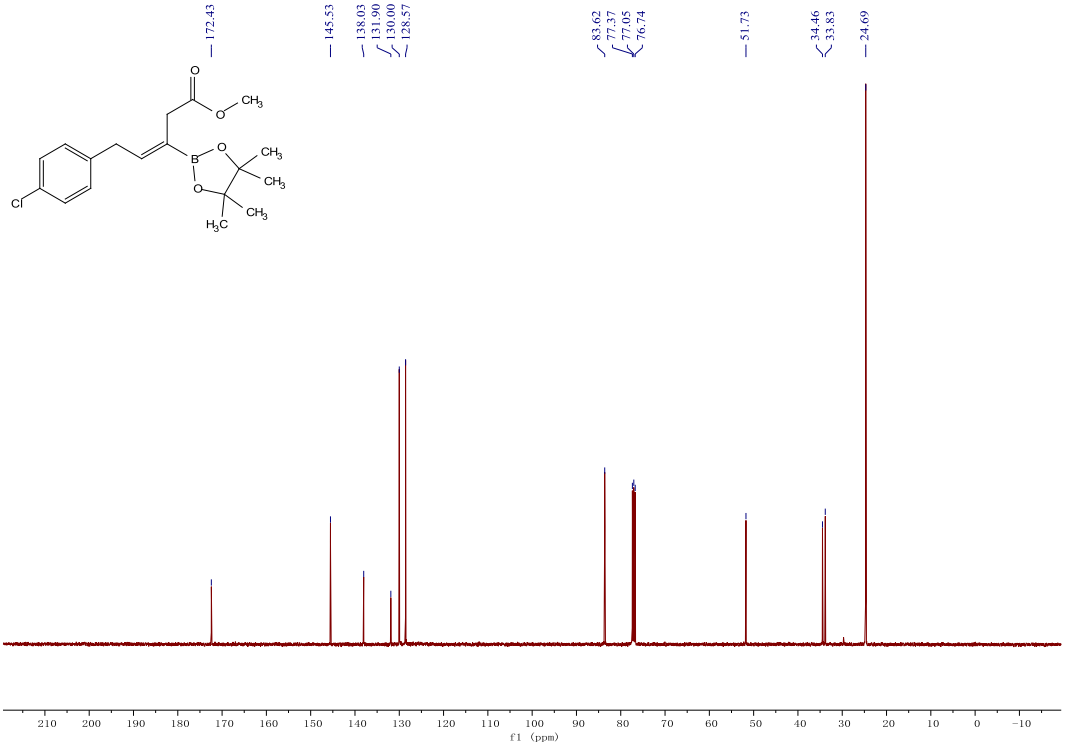
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.13 – 7.08 (m, 2H), 6.53 (t, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 3.45 (d, *J* = 7.2 Hz, 2H), 3.29 (s, 2H), 1.25 (s, 12H).

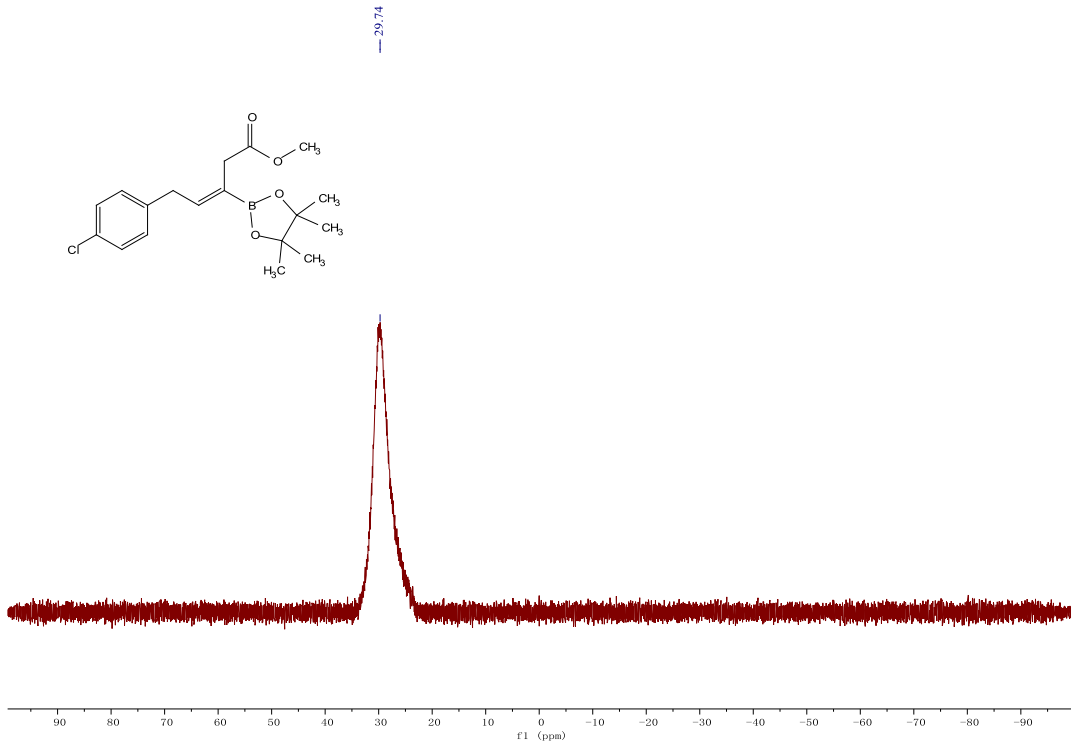
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.43, 145.53, 138.03, 131.90, 130.00, 128.57, 83.62, 51.73, 34.46, 33.83, 24.69.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.74.

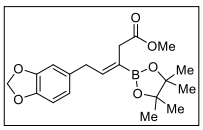
HRMS (ESI) (m/z): Calcd for $C_{18}H_{24}O_4{}^{11}BClNa$ $[M+Na]^+$:373.1354, found: 373.1361.







methyl (*Z*)-5-(benzo[d][1,3]dioxol-5-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3g)



Prepared according to General Procedure A from **1g** (46.0 mg, 0.20 mmol). The product **3g** was isolated in 75% yield (54.3 mg) by flash column chromatography as light yellow solid.

Stereoselectivity: 95:5 (*Z*/*E*, NMR, crude).

Eluent: Dichloromethane.

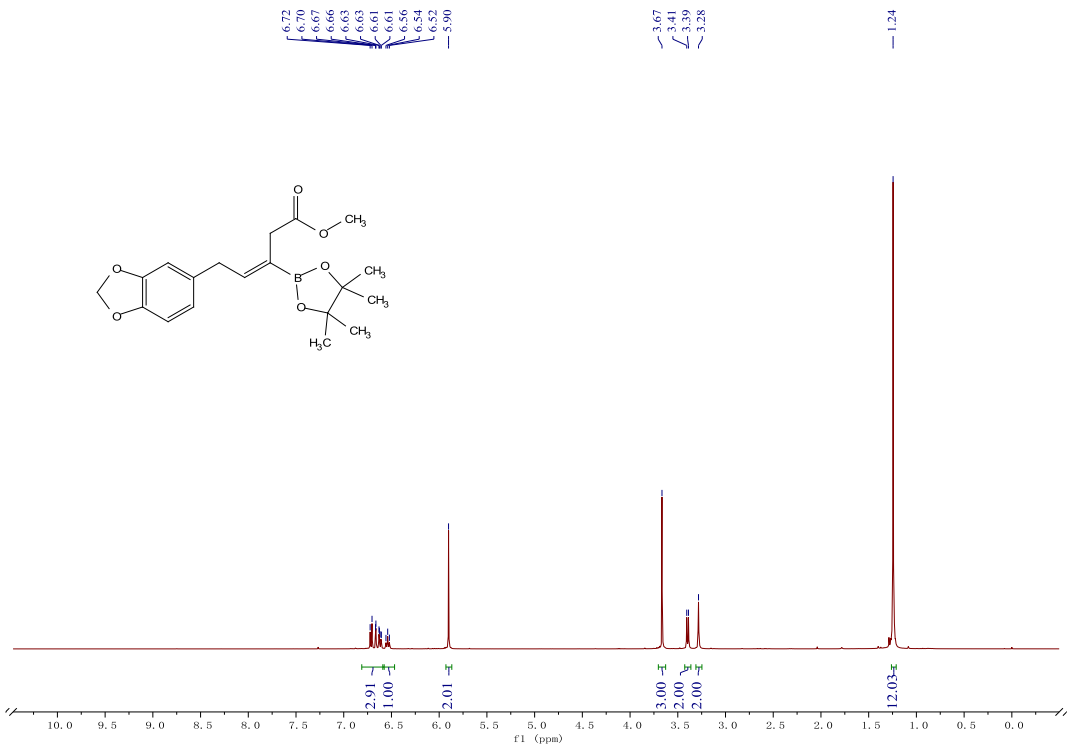
R_f: 0.14 (petroleum ether/ethyl acetate = 15:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 – 6.59 (m, 3H), 6.54 (t, *J* = 7.2 Hz, 1H), 5.90 (s, 2H), 3.67 (s, 3H), 3.40 (d, *J* = 7.2 Hz, 2H), 3.28 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.51, 147.69, 146.39, 145.89, 133.34, 121.41, 109.16, 108.22, 100.80, 83.55, 51.68, 34.80, 33.80, 24.70.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.76.

HRMS (ESI) (m/z): Calcd for $C_{19}H_{25}O_6{}^{11}BNa^+$ $[M+Na]^+$:383.1642, found: 383.1642.


6.72
6.70
6.67
6.66
6.63
6.61
6.61
6.56
6.54
6.52
5.90
3.67
3.41
3.39
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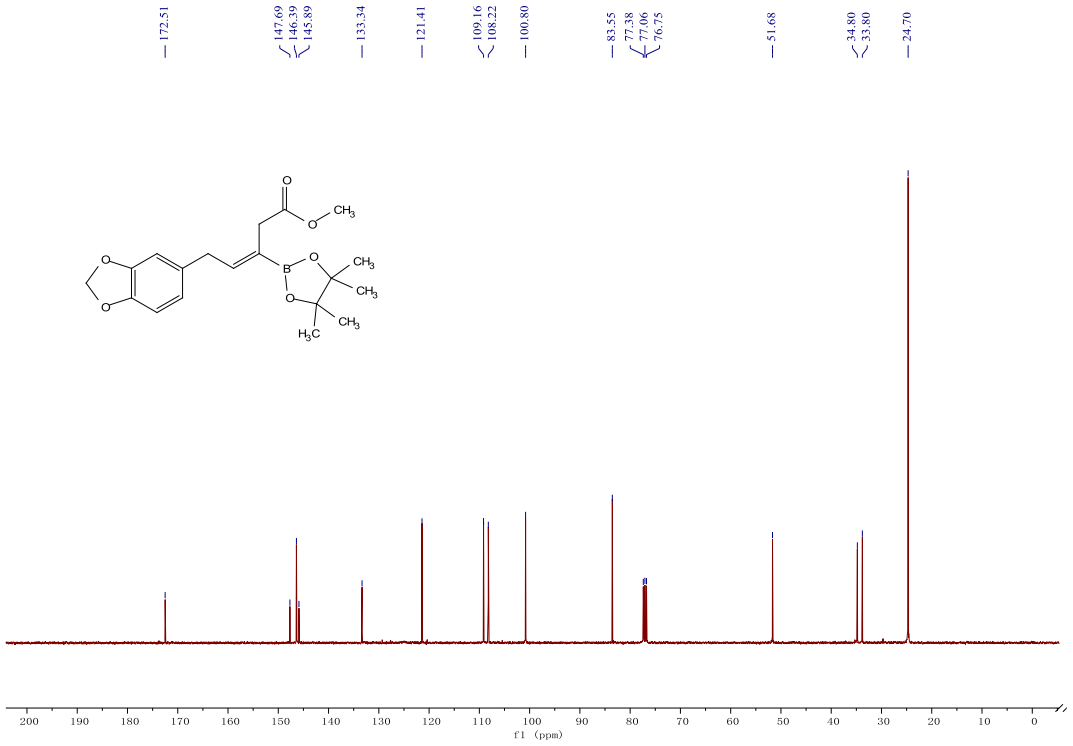
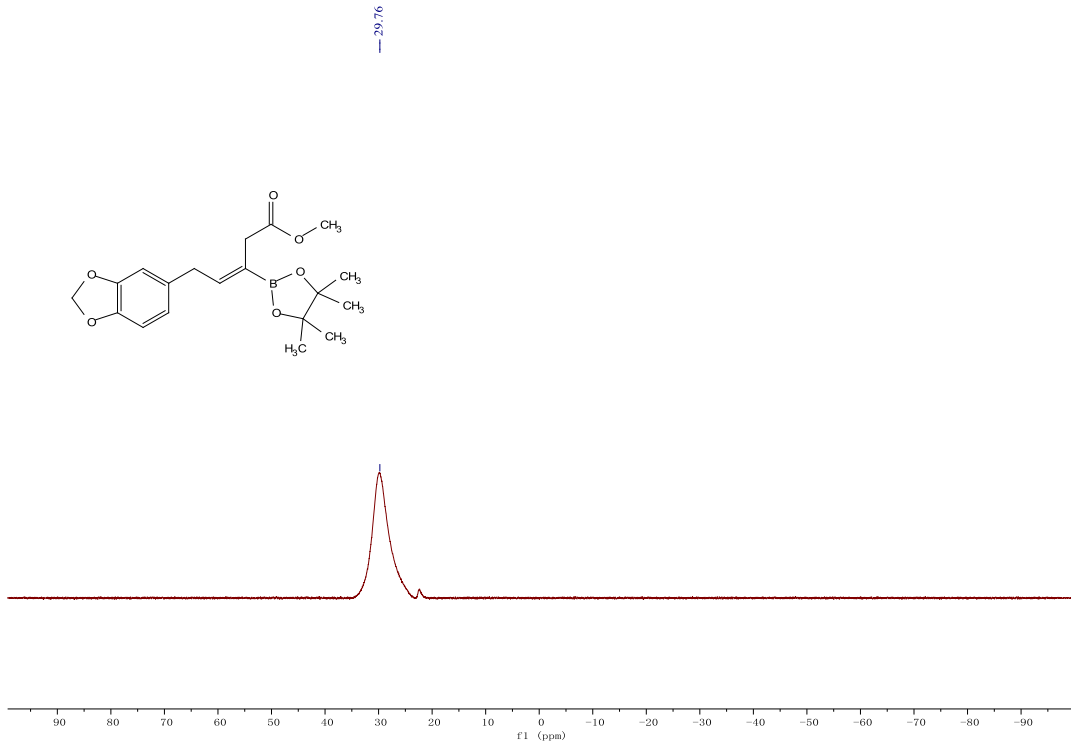
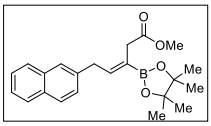
1.24
2.91
1.00
2.01
3.00
2.00
2.00
12.03
f1 (ppm)


172.51
147.69
146.39
145.89
133.34
121.41
109.16
108.22
100.80
83.55
77.38
77.06
76.75
51.68
34.80
33.80
24.70
f1 (ppm)



methyl (*Z*)-5-(naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3h)



Prepared according to General Procedure A from **1h** (47.3 mg, 0.20 mmol). The product **3h** was isolated in 40% yield (28.7 mg) by flash column chromatography as light yellow solid.

Stereoselectivity: 95:5 (*Z*/*E*, GC, crude).

Eluent: dichloromethane.

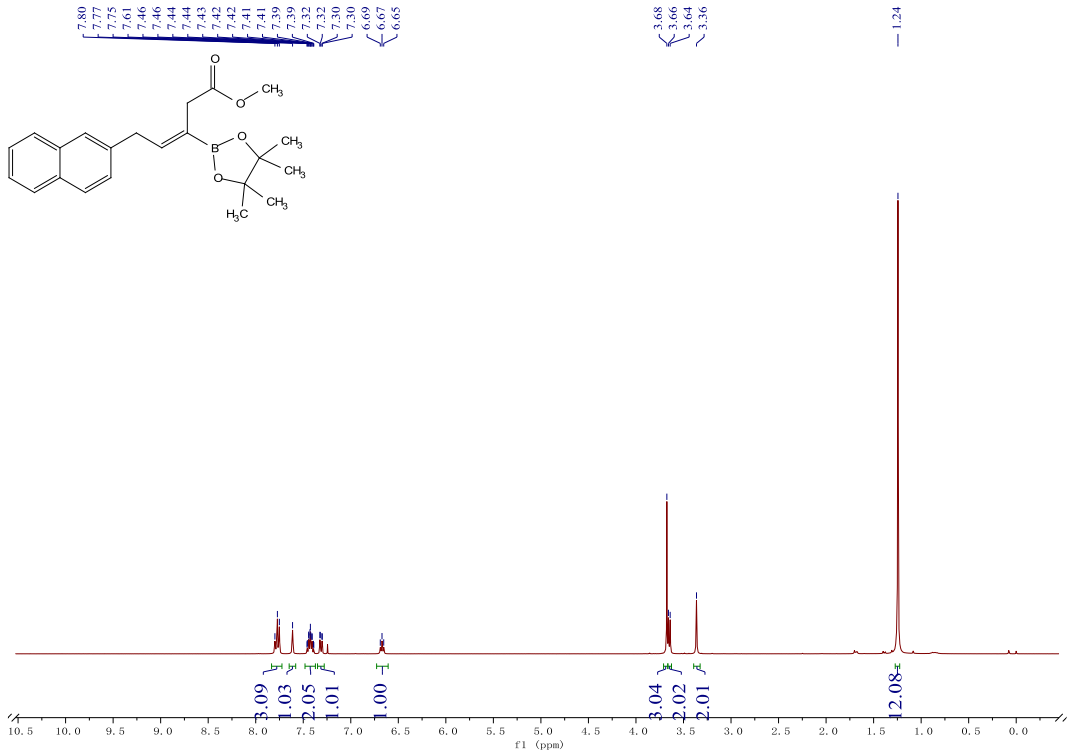
R_f: 0.15 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 3H), 7.61 (s, 1H), 7.47 – 7.38 (m, 2H), 7.31 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.67 (t, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 3.65 (d, *J* = 7.2 Hz, 2H), 3.36 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.70, 146.22, 137.18, 133.73, 132.19, 128.21, 127.71, 127.59, 127.51, 126.86, 126.07, 125.42, 83.69, 51.86, 35.45, 34.06, 24.81.

^{11}B NMR (128 MHz, $CDCl_3$) δ 28.83.

HRMS (ESI) (m/z): Calcd for $C_{22}H_{27}O_4{}^{11}BNa^+$ $[M+Na]^+$: 389.1900 found: 389.1898.


7.80
7.77
7.75
7.61
7.46
7.46
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.39
7.39
7.32
7.32
7.30
7.30
6.69
6.67
6.65
3.68
3.66
3.64
3.36
1.24
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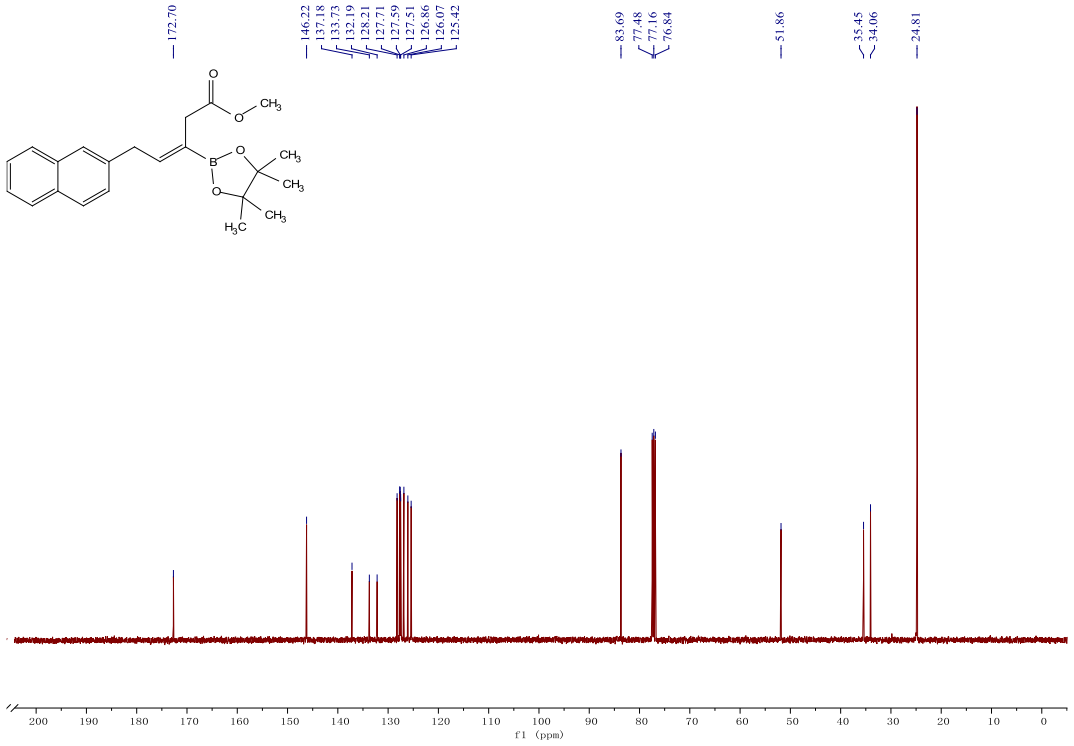
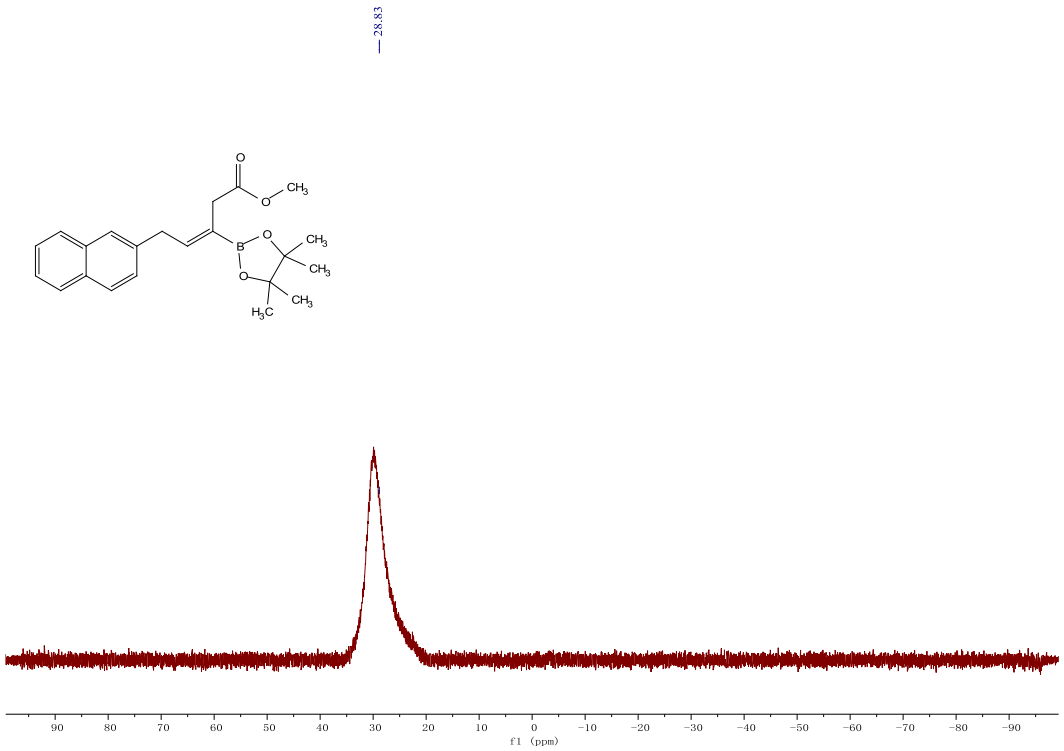
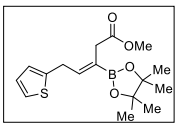
1.01
1.00
3.04
2.02
2.01
12.08
f1 (ppm)


172.70
146.22
137.18
133.73
132.19
128.21
127.71
127.59
127.51
126.86
126.07
125.42
83.69
77.48
77.16
76.84
51.86
35.45
34.06
24.81
f1 (ppm)



methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(thiophen-2-yl)pent-3-enoate (3i)



Prepared according to General Procedure A from **1i** (38.4 mg, 0.20 mmol). The product **3i** was isolated in 63% yield (40.9 mg) by flash column chromatography as light yellow solid.

Stereoselectivity: 95:5 (*Z*/*E*, NMR, crude).

Eluent: dichloromethane.

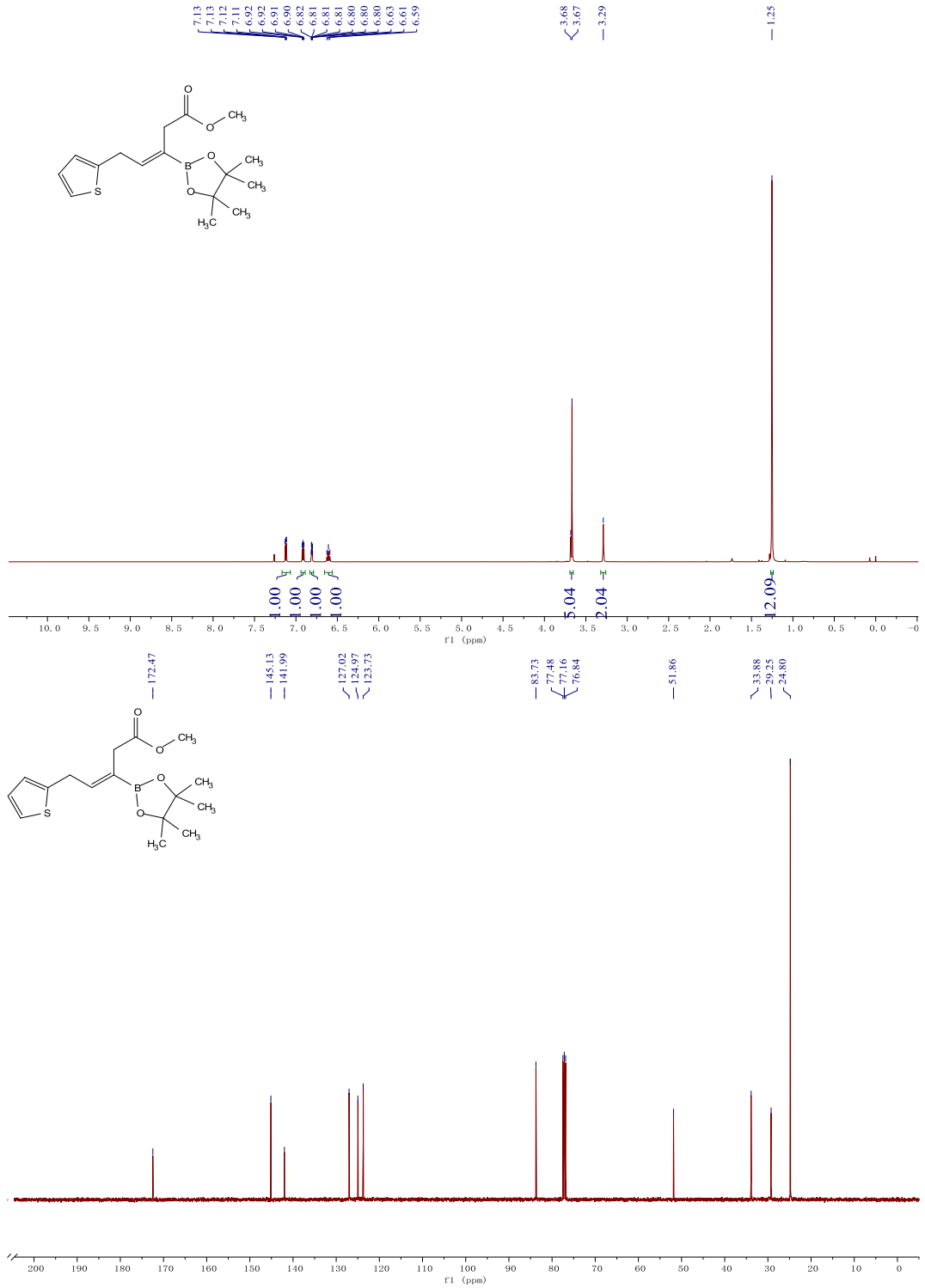
R_f: 0.15 (petroleum ether/ethyl acetate = 15:1)

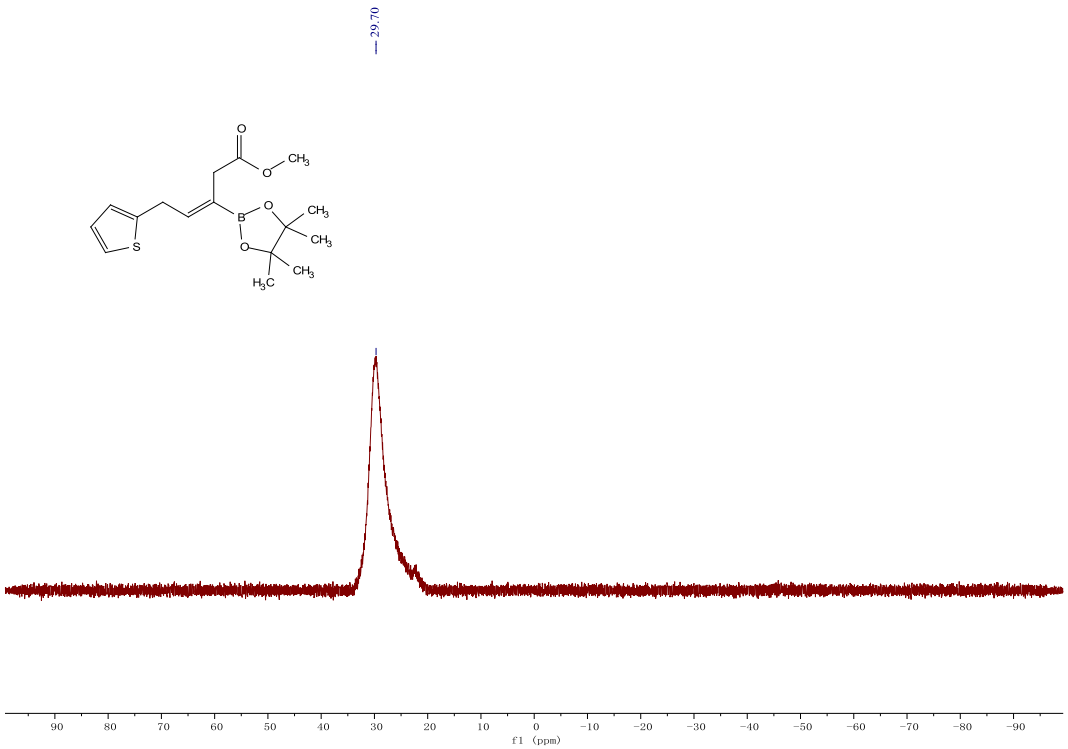
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.83 – 6.79 (m, 1H), 6.61 (tt, *J* = 7.2, 1.2 Hz, 1H), 3.69 – 3.65 (m, 5H), 3.29 (s, 2H), 1.25 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.47, 145.13, 141.99, 127.02, 124.97, 123.73, 83.73, 51.86, 33.88, 29.25, 24.80.

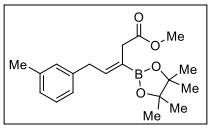
^{11}B NMR (128 MHz, $CDCl_3$) δ 29.70.

HRMS (ESI) (m/z): Calcd for $C_{16}H_{23}O_4{}^{11}BSNa$ $[M+Na]^+$: 345.1308, found: 345.1304.


7.13
7.13
7.12
7.11
6.92
6.92
6.91
6.90
6.82
6.81
6.81
6.81
6.80
6.80
6.80
6.63
6.61
6.59
3.68
3.67
3.29
1.25
1.00
1.00
1.00
1.00
5.04
2.04
12.09
f1 (ppm)
172.47
145.13
141.99
127.02
124.97
123.73
83.73
77.48
77.16
76.84
51.86
33.88
29.25
24.80
f1 (ppm)



methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(m-tolyl)pent-3-enoate (3u)



Prepared according to General Procedure A from **1u** (40.0 mg, 0.20 mmol). The product **3u** was isolated in 68% yield (45.2 mg) by flash column chromatography as colorless oil.

Stereoselectivity: 94:6 (*Z*/*E*, GC, crude).

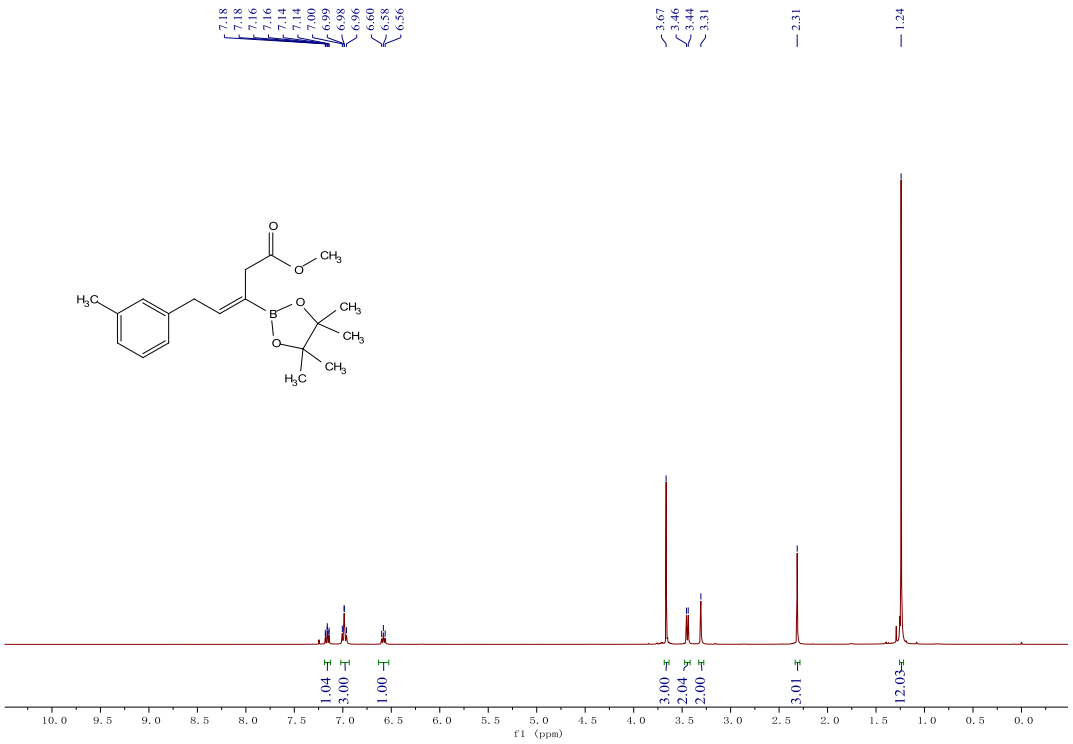
Eluent: dichloromethane.

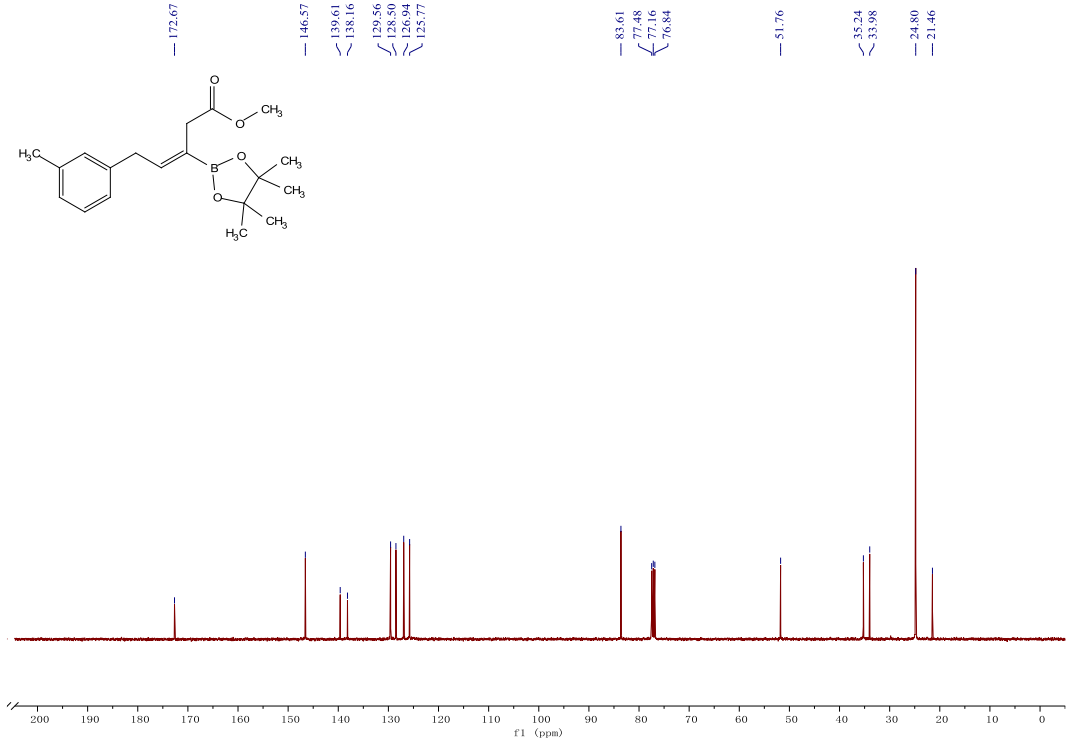
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 1H), 7.02 – 6.94 (m, 3H), 6.58 (t, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 3.45 (d, *J* = 7.2 Hz, 2H), 3.31 (s, 2H), 2.31 (s, 3H), 1.24 (s, 12H).

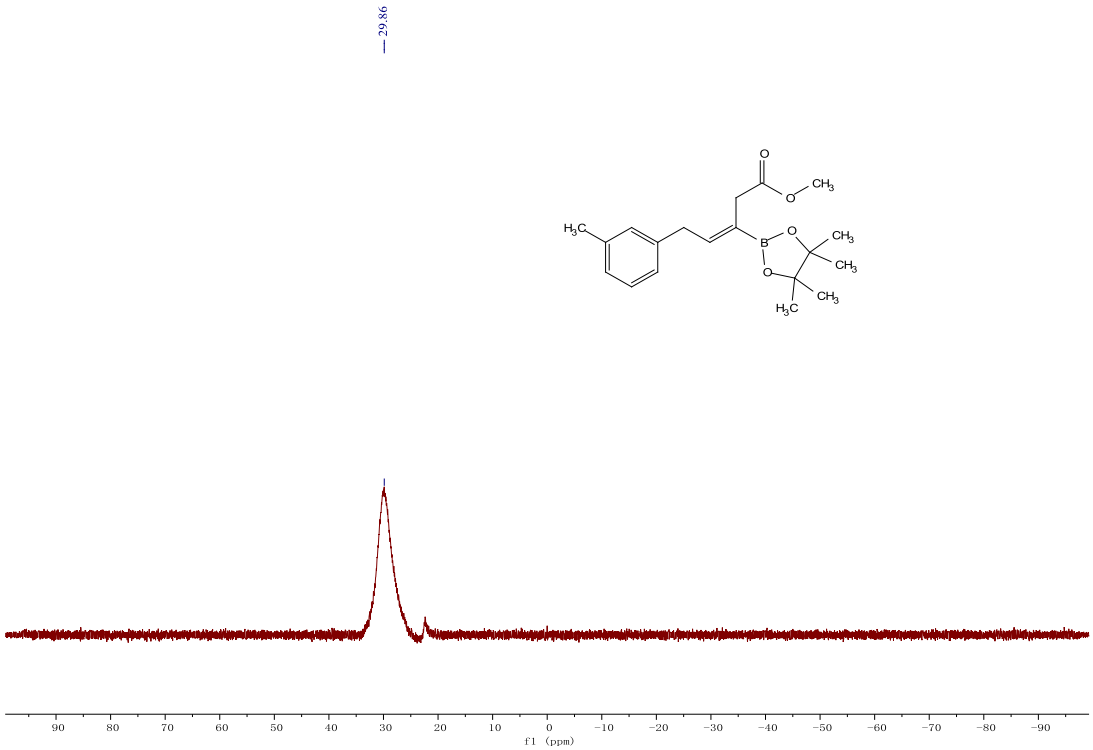
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.67, 146.57, 139.61, 138.16, 129.56, 128.50, 126.94, 125.77, 83.61, 51.76, 35.24, 33.98, 24.80, 21.46.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.86.

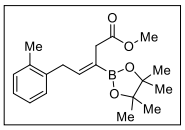
HRMS (ESI) (m/z): Calcd for $C_{19}H_{27}O_4{}^{11}BNa^+$ $[M+Na]^+$: 353.1900, found: 353.1904.


7.18
7.18
7.16
7.16
7.14
7.14
7.00
6.99
6.98
6.96
6.60
6.58
6.56
3.67
3.46
3.44
3.31
2.31
1.24
O
O
CH3
H3C
B
O
CH3
CH3
O
CH3
H3C
1.04
3.00
1.00
3.00
2.04
2.00
3.01
12.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.67
146.57
139.61
138.16
129.56
128.50
126.94
125.77
83.61
77.48
77.16
76.84
51.76
35.24
33.98
24.80
21.46
O
O
CH3
H3C
B
O
CH3
CH3
O
CH3
H3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(o-tolyl)pent-3-enoate (3v)



Prepared according to General Procedure A from **1v** (40.0 mg, 0.20 mmol). The product **3v** was isolated in 79% yield (52.5 mg) by flash column chromatography as colorless oil.

Stereoselectivity: 97:3 (*Z*/*E*, NMR, crude).

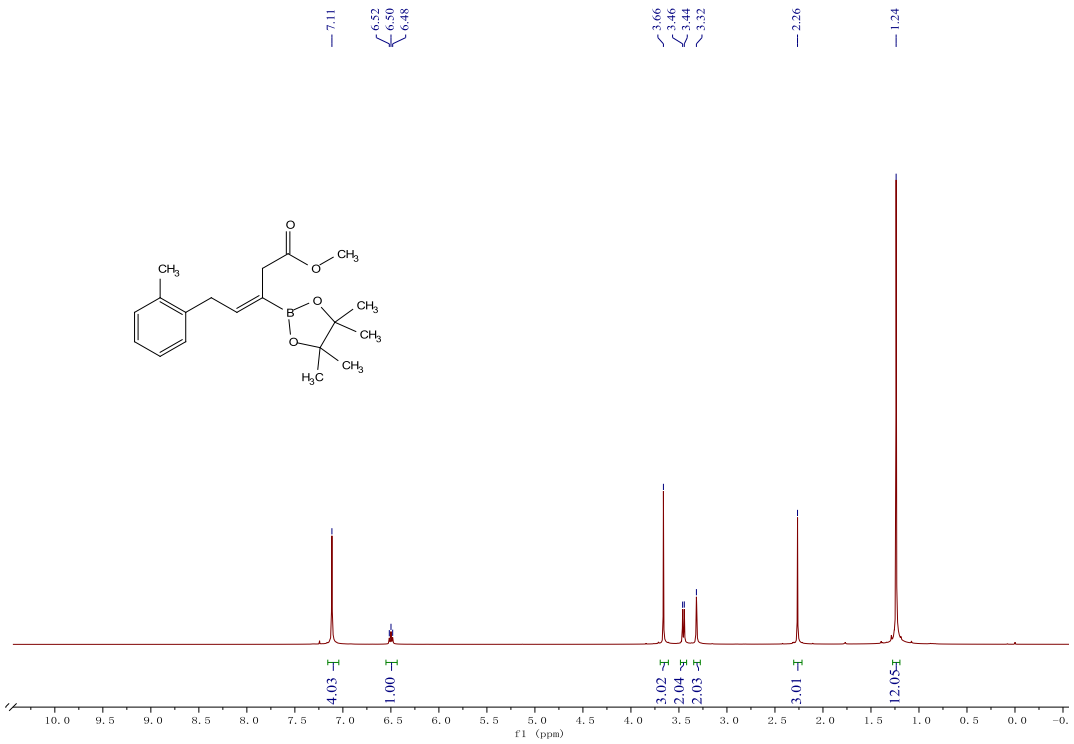
Eluent: dichloromethane.

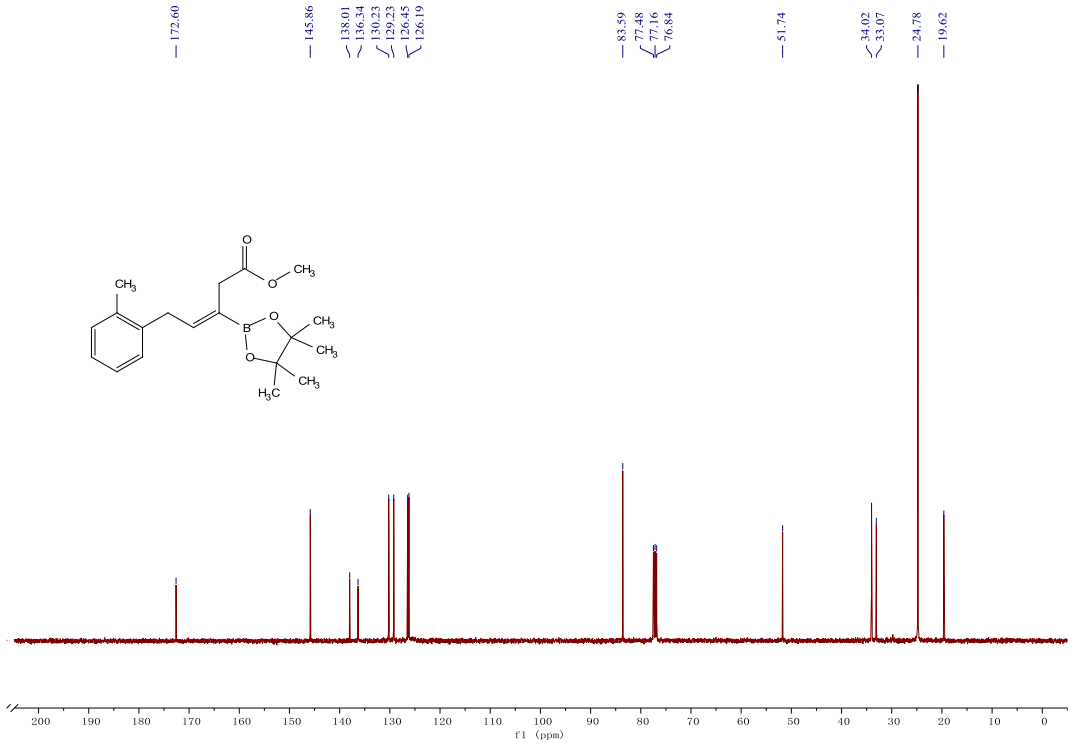
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 4H), 6.50 (t, *J* = 7.0 Hz, 1H), 3.66 (s, 3H), 3.45 (d, *J* = 7.0 Hz, 2H), 3.32 (s, 2H), 2.26 (s, 3H), 1.24 (s, 12H).

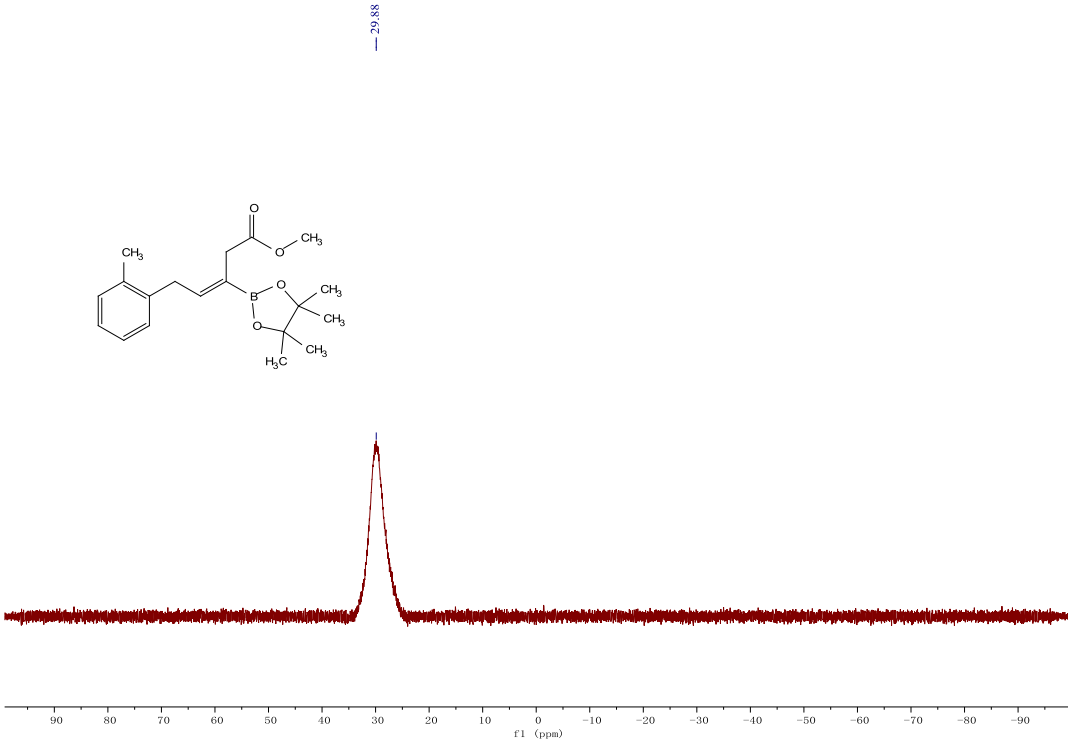
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.60, 145.86, 138.01, 136.34, 130.23, 129.23, 126.45, 126.19, 83.59, 51.74, 34.02, 33.07, 24.78, 19.62.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.88.

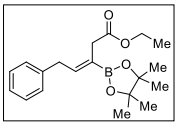
HRMS (ESI) (m/z): Calcd for $C_{19}H_{27}O_4{}^{11}BNa^+$ $[M+Na]^+$: 353.1900, found: 353.1902.


7.11
6.52
6.50
6.48
3.66
3.46
3.44
3.32
2.26
1.24
4.03
1.00
3.02
2.04
2.03
3.01
12.05
f1 (ppm)


172.60
145.86
138.01
136.34
130.23
129.23
126.45
126.19
83.59
77.48
77.16
76.84
51.74
34.02
33.07
24.78
19.62
f1 (ppm)



ethyl (Z)-5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate (3w)



Prepared according to General Procedure A from **1w** (40.0 mg, 0.20 mmol). The product **3w** was isolated in 72% yield (46.1 mg) by flash column chromatography as light yellow solid.

Stereoselectivity: 92:8 (*Z*/*E*, GC, crude).

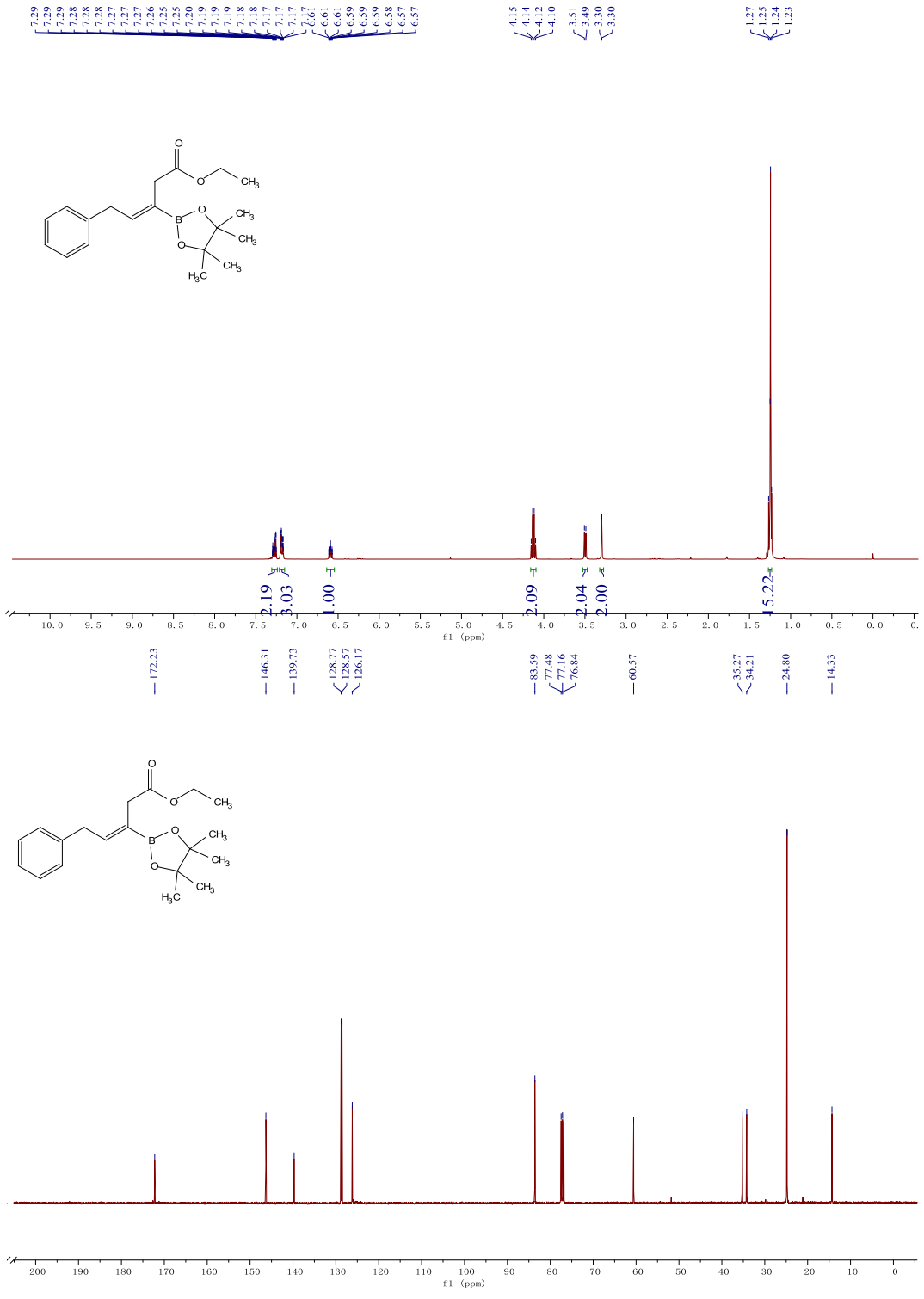
Eluent: Dichloromethane.

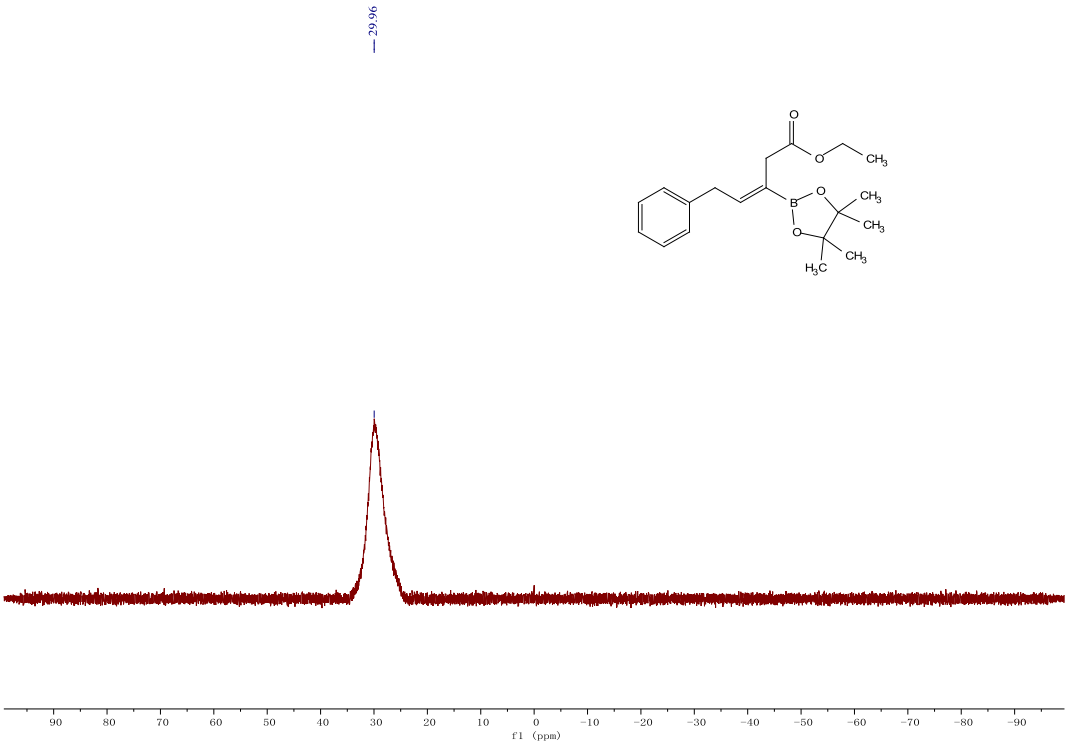
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.16 (m, 3H), 6.59 (tt, *J* = 7.2, 1.1 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.50 (d, *J* = 7.2 Hz, 2H), 3.30 (d, *J* = 0.8 Hz, 2H), 1.24 (t, *J* = 3.6 Hz, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.23, 146.31, 139.73, 128.77, 128.57, 126.17, 83.59, 60.57, 35.27, 34.21, 24.80, 14.33.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.96.

HRMS (ESI) (m/z): Calcd for $C_{19}H_{27}O_4{}^{11}BNa$ $[M+Na]^+$: 353.1900, found: 353.1906.

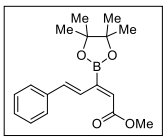

7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.20 7.19 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.17 7.17 6.61 6.61 6.61 6.59 6.59 6.59 6.58 6.57 6.57
4.15 4.14 4.12 4.10
3.51 3.49 3.30 3.30
1.27 1.25 1.24 1.23
O
O
CH3
B
O
CH3
CH3
O
CH3
H3C
2.19 3.03 1.00 2.09 2.04 2.00 15.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
172.23
146.31
139.73
128.77
128.57
126.17
83.59
77.48
77.16
76.84
60.57
35.27
34.21
24.80
14.33
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3.3 Spectra of Boryldienoates

methyl (2*Z*,4*E*)-5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-2,4-dienoate (5a)

Prepared according to General Procedure B from **1a** (37.2 mg, 0.20 mmol). The product **5a** was isolated in 79% yield (49.6 mg) by flash column chromatography as colorless oil.



Eluent: dichloromethane.

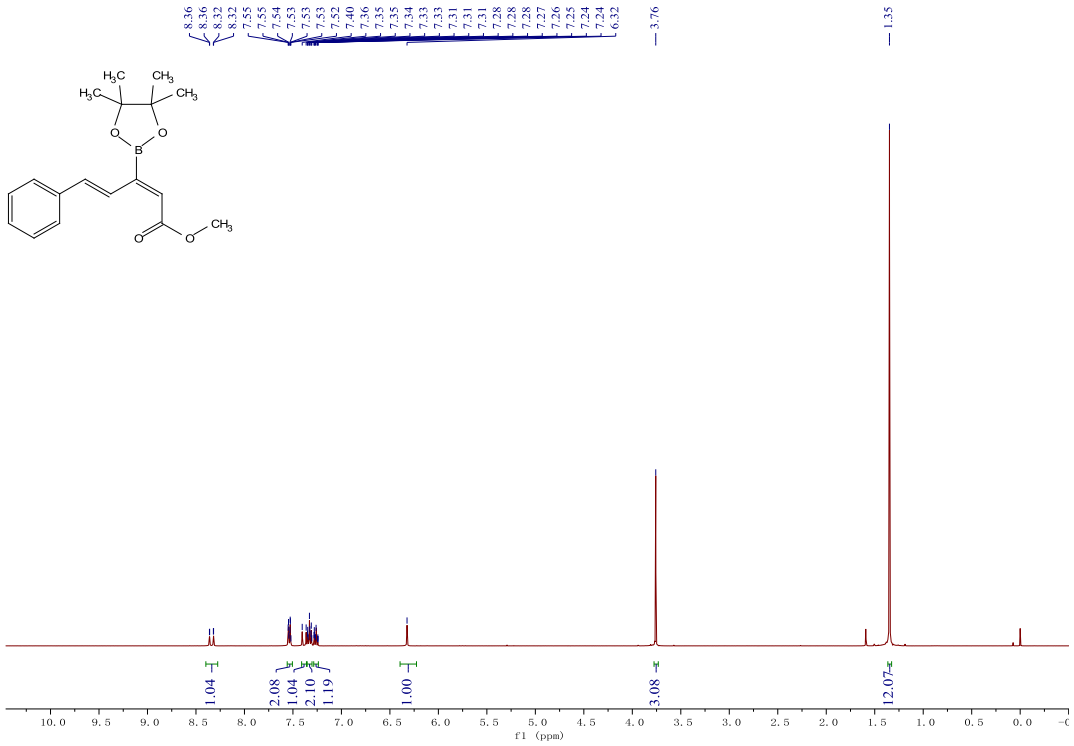
R_f: 0.32 (tailing, petroleum ether/ethyl acetate = 20:1)

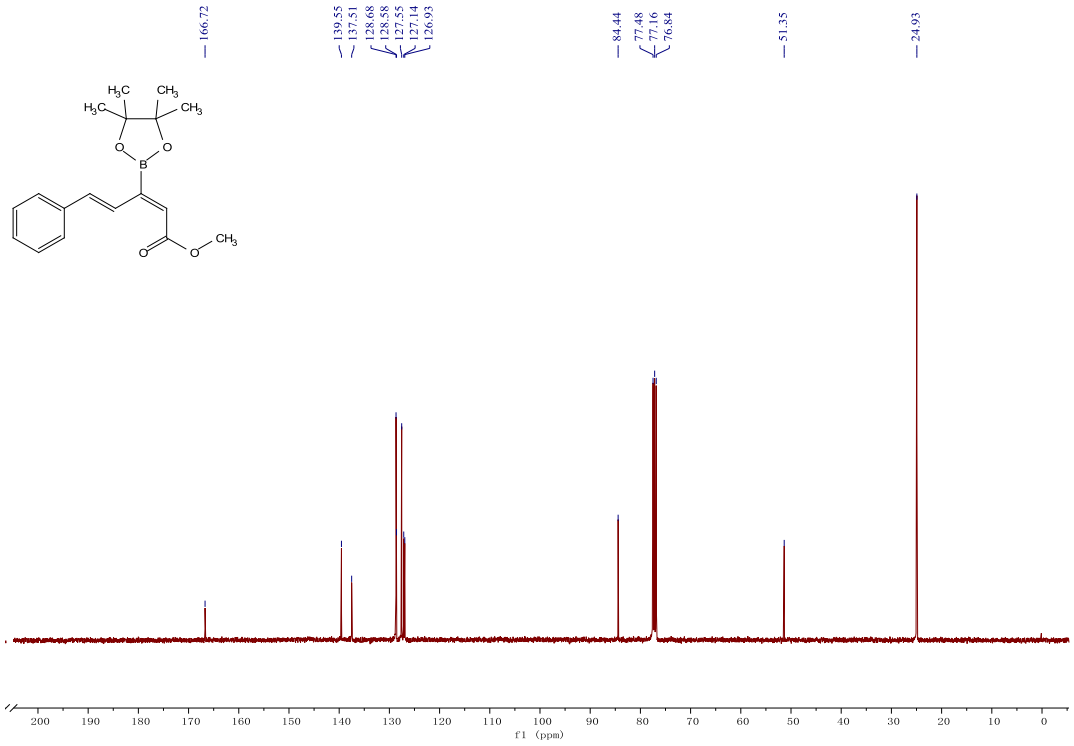
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 16.3, 0.7 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.38 (d, *J* = 16.3 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 6.32 (s, 1H), 3.76 (s, 3H), 1.35 (s, 12H).

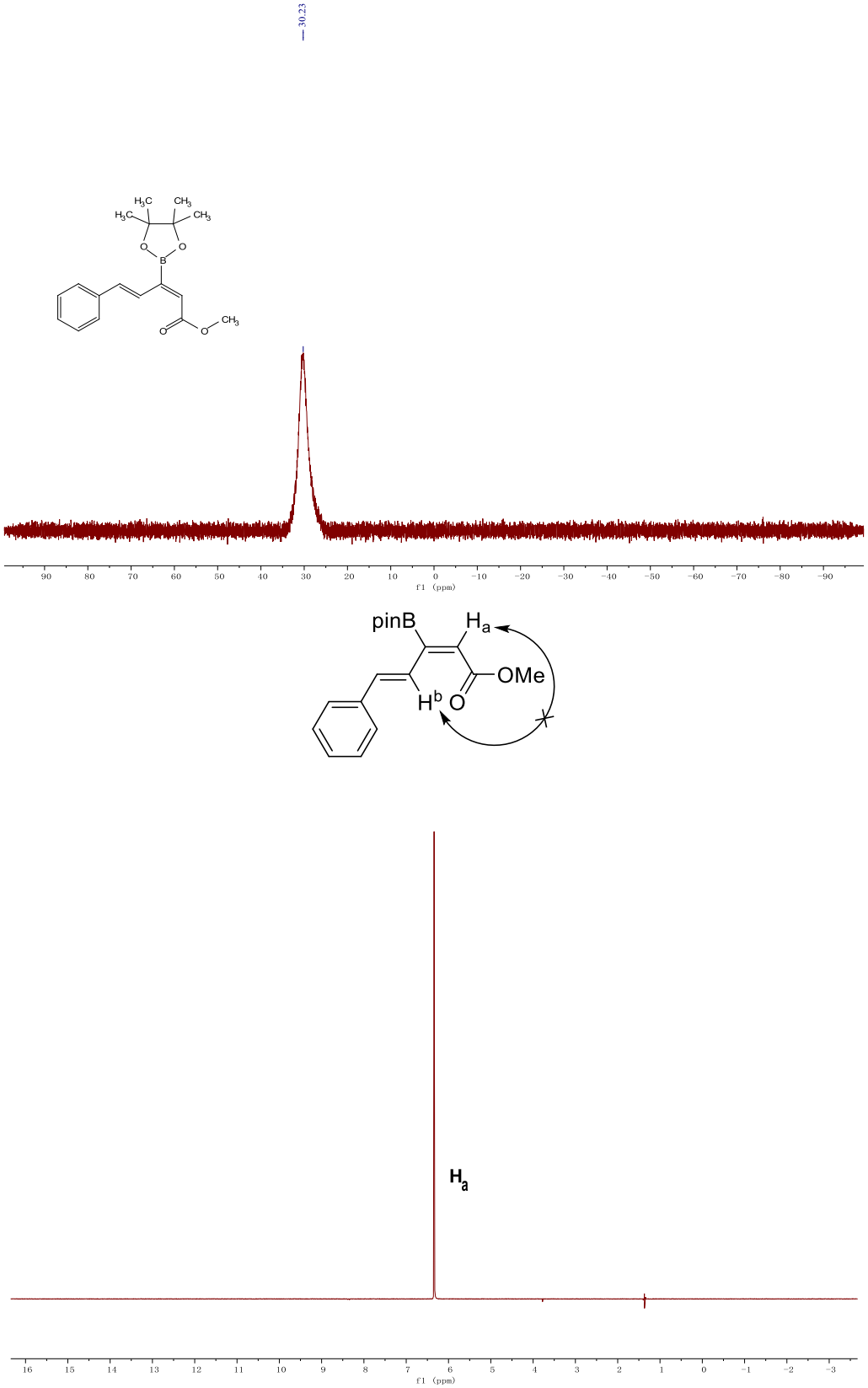
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 139.55, 137.51, 128.68, 128.58, 127.55, 127.14, 126.93, 84.44, 51.35, 24.93.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.23.

HRMS (ESI) (m/z): Calcd for $C_{18}H_{23}O_4{}^{11}BNa$ $[M+Na]^+$:337.1587, found: 337.1590.


8.36
8.36
8.32
8.32
7.55
7.55
7.54
7.53
7.53
7.53
7.52
7.40
7.36
7.35
7.35
7.34
7.33
7.33
7.31
7.31
7.31
7.28
7.28
7.28
7.27
7.26
7.25
7.24
7.24
6.32
3.76
1.35
1.04
2.08
1.04
2.10
1.19
1.00
3.08
12.07
f1 (ppm)


166.72
139.55
137.51
128.68
128.58
127.55
127.14
126.93
84.44
77.48
77.16
76.84
51.35
24.93
f1 (ppm)



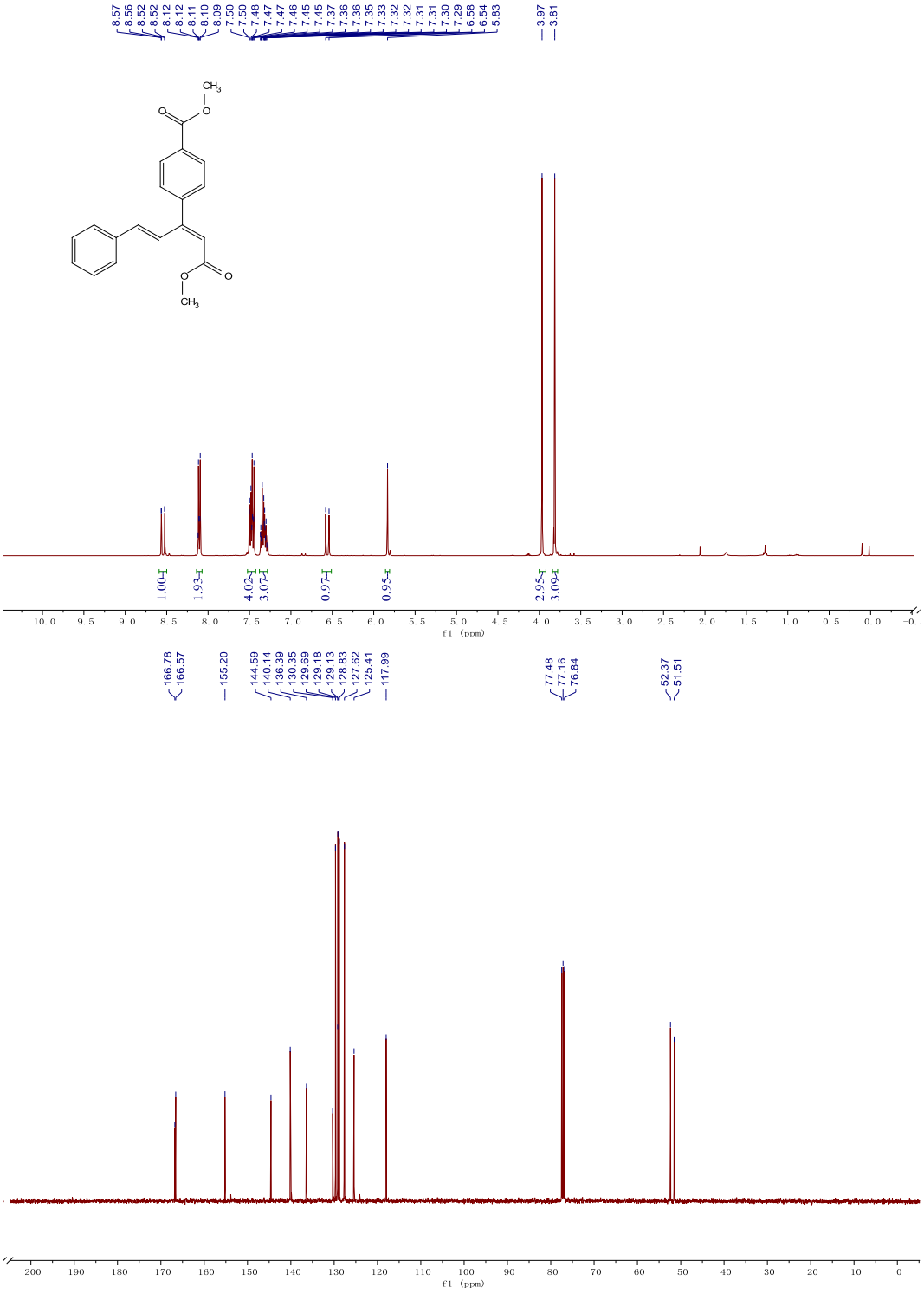
To further determine the Z/E of the newly formed double bond, the Suzuki-coupling reaction between **5a** and methyl 4-iodobenzoate was performed, according the procedure for preparation of **8a**. The product was obtained in 85% isolated yield and the configuration of the newly formed double bond was determined as *E*.

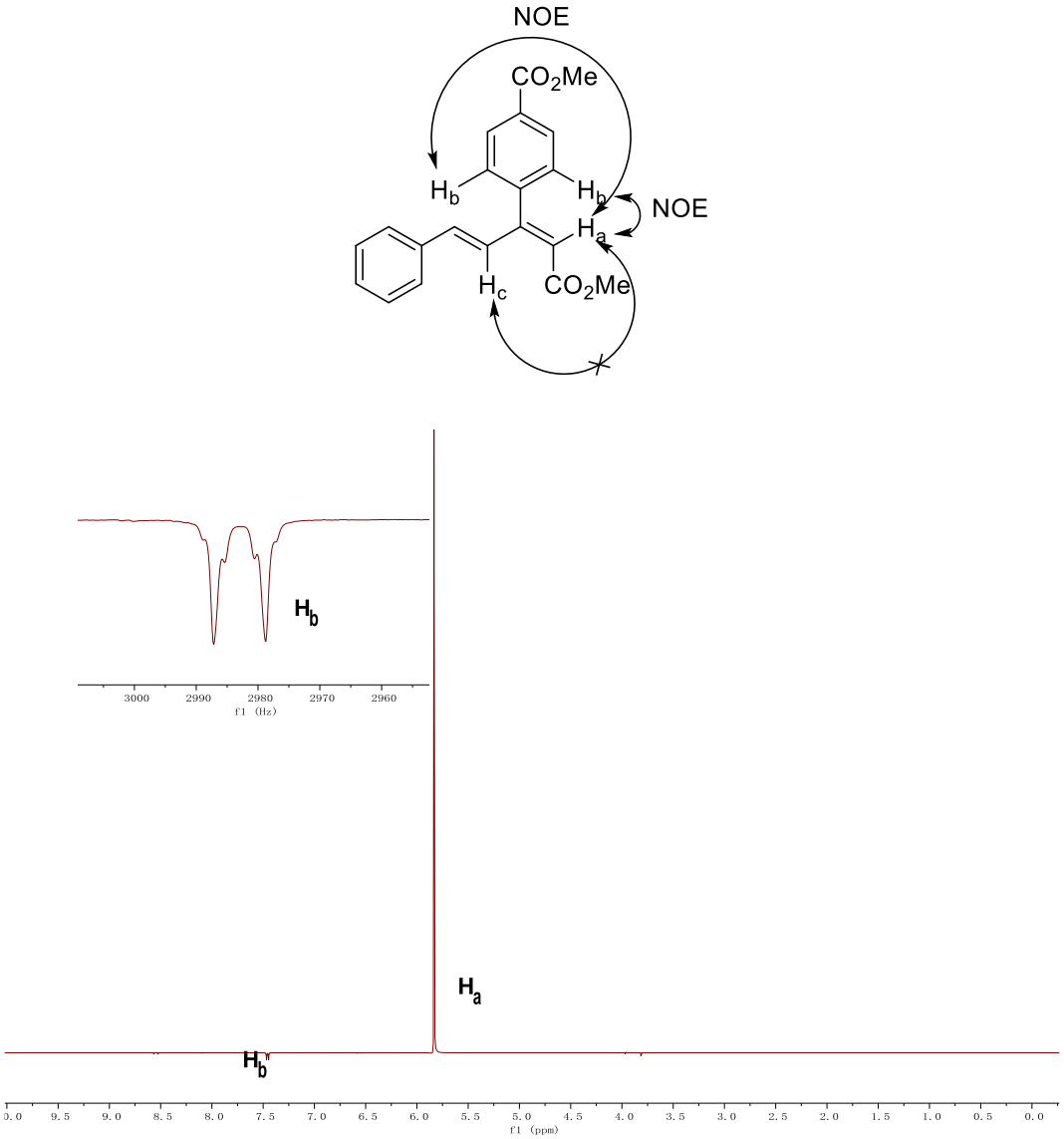
methyl 4-((1*E*,3*E*)-5-methoxy-5-oxo-1-phenylpenta-1,3-dien-3-yl)benzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 16.4, 0.7 Hz, 1H), 8.13 – 8.08 (m, 2H), 7.52 – 7.43 (m, 4H), 7.38 – 7.29 (m, 3H), 6.56 (d, *J* = 16.4 Hz, 1H), 5.83 (s, 1H), 3.97 (s, 3H), 3.81 (s, 3H).

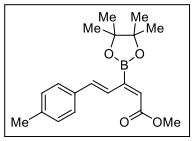
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.78, 166.57, 155.20, 144.59, 140.14, 136.39, 130.35, 129.69, 129.18, 129.13, 128.83, 127.62, 125.41, 117.99, 52.37, 51.51.

HRMS (ESI) (m/z): Calcd for $C_{20}H_{19}O_4$ $[M+H]^+$:323.1283, found: 323.1287.





methyl (2*Z*,4*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(*p*-tolyl)penta-2,4-dienoate (5b)



Prepared according to General Procedure B from **1b** (40.0 mg, 0.20 mmol). The product **5b** was isolated in 76% yield (49.8 mg) by flash column chromatography as colorless oil.

Eluent: dichloromethane.

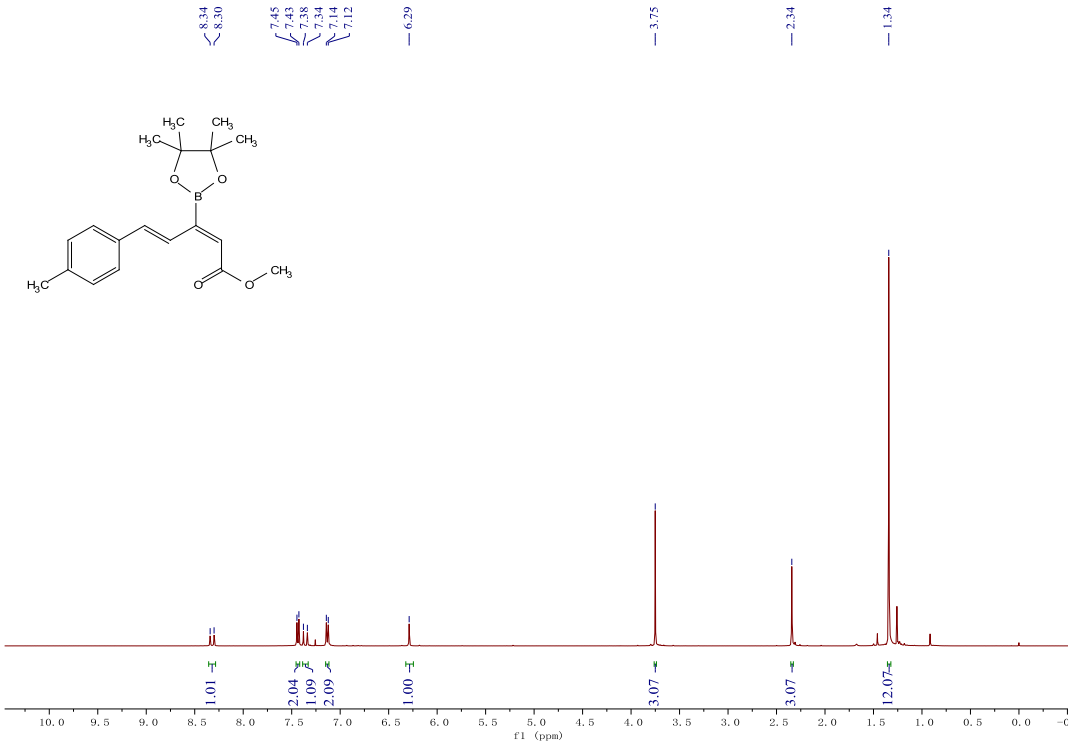
R_f: 0.45 (tailing, petroleum ether/ethyl acetate = 20:1)

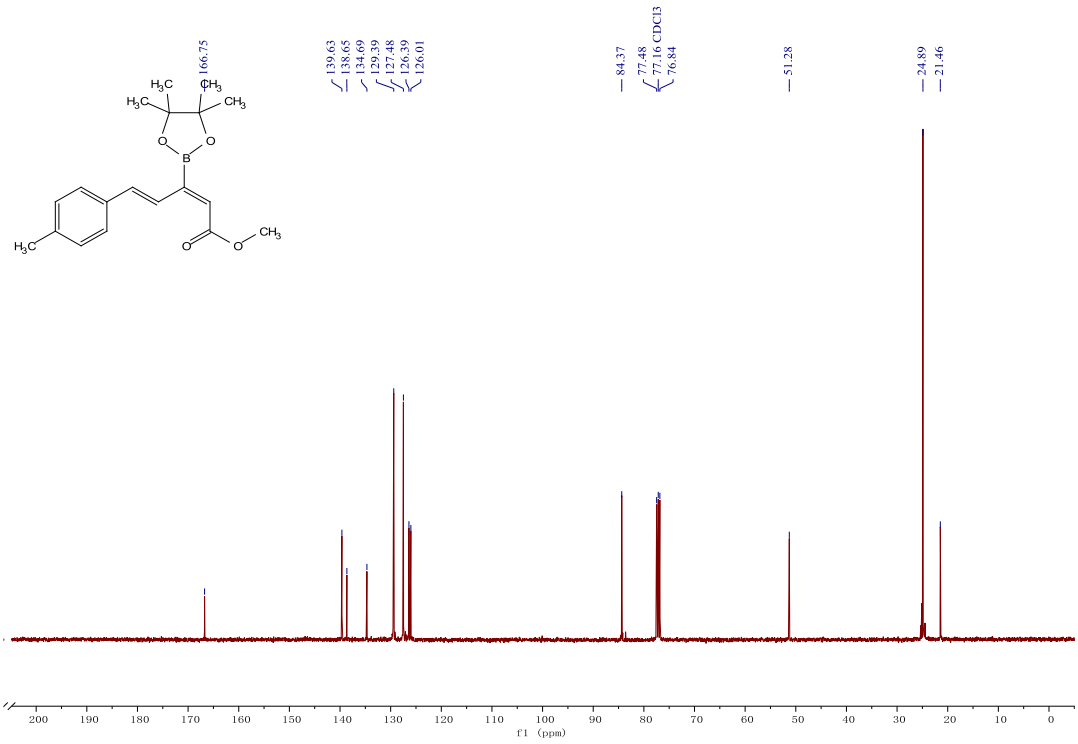
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 16.2 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 16.3 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.29 (s, 1H), 3.75 (s, 3H), 2.34 (s, 3H), 1.34 (s, 12H).

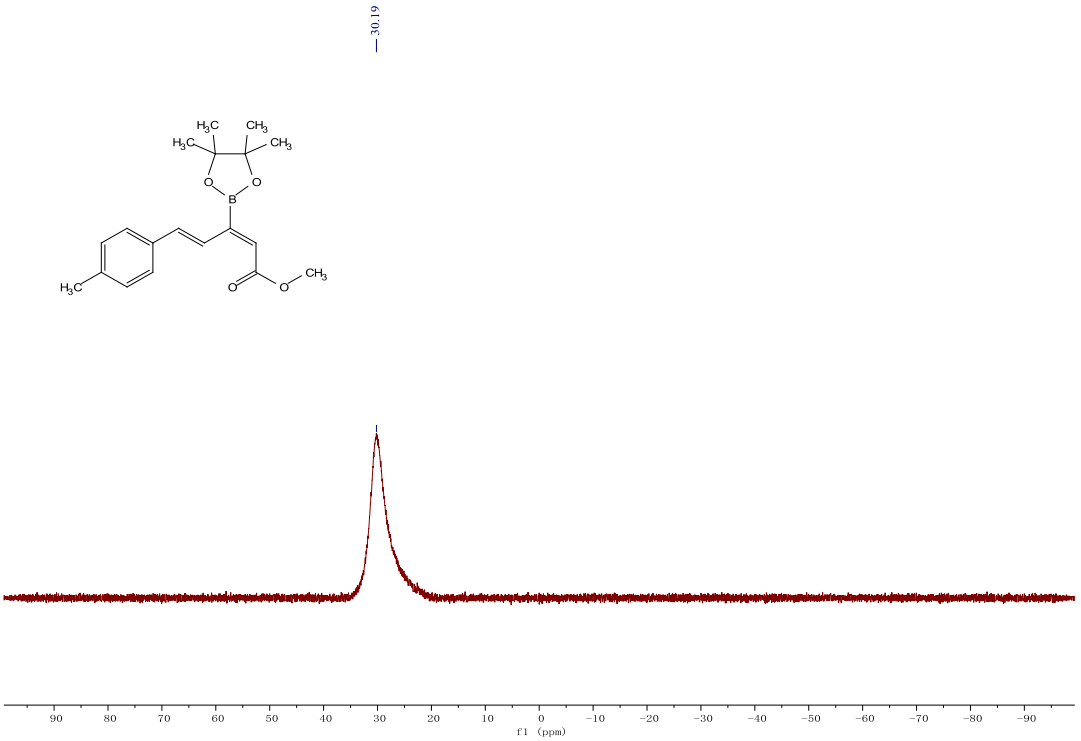
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.75, 139.63, 138.65, 134.69, 129.39, 127.48, 126.39, 126.01, 84.37, 51.28, 24.89, 21.46.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.19.

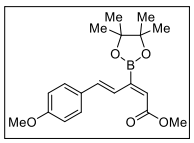
HRMS (ESI) (m/z): Calcd for $C_{19}H_{25}O_4{}^{11}BNa$ $[M+Na]^+$: 351.1744, found: 351.1742.


8.34
8.30
7.45
7.43
7.38
7.34
7.14
7.12
6.29
3.75
2.34
1.34
1.01
2.04
1.09
2.09
1.00
3.07
3.07
12.07
f1 (ppm)


166.75
139.63
138.65
134.69
129.39
127.48
126.39
126.01
84.37
77.48
77.16 CDCl3
76.84
51.28
24.89
21.46
f1 (ppm)



methyl (2*Z*,4*E*)-5-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-2,4-dienoate (5c)



Prepared according to General Procedure B from **1c** (43.2 mg, 0.20 mmol). The product **5c** was isolated in 50% yield (33.4 mg) by flash column chromatography as colorless oil.

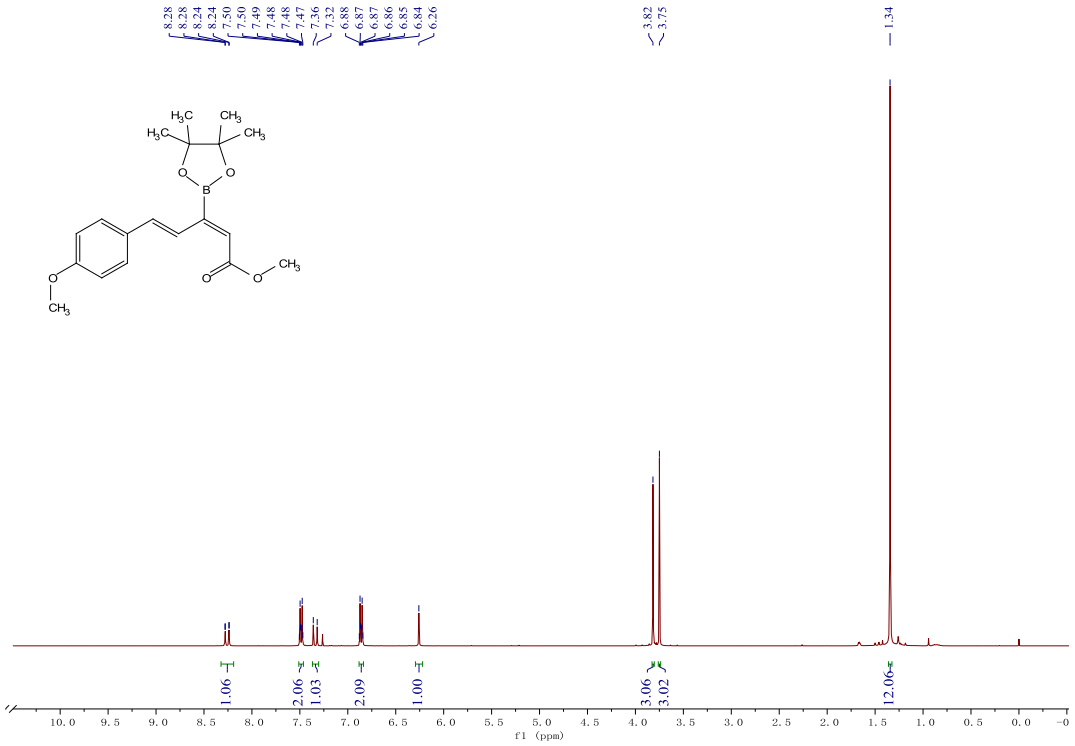
Eluent: dichloromethane.

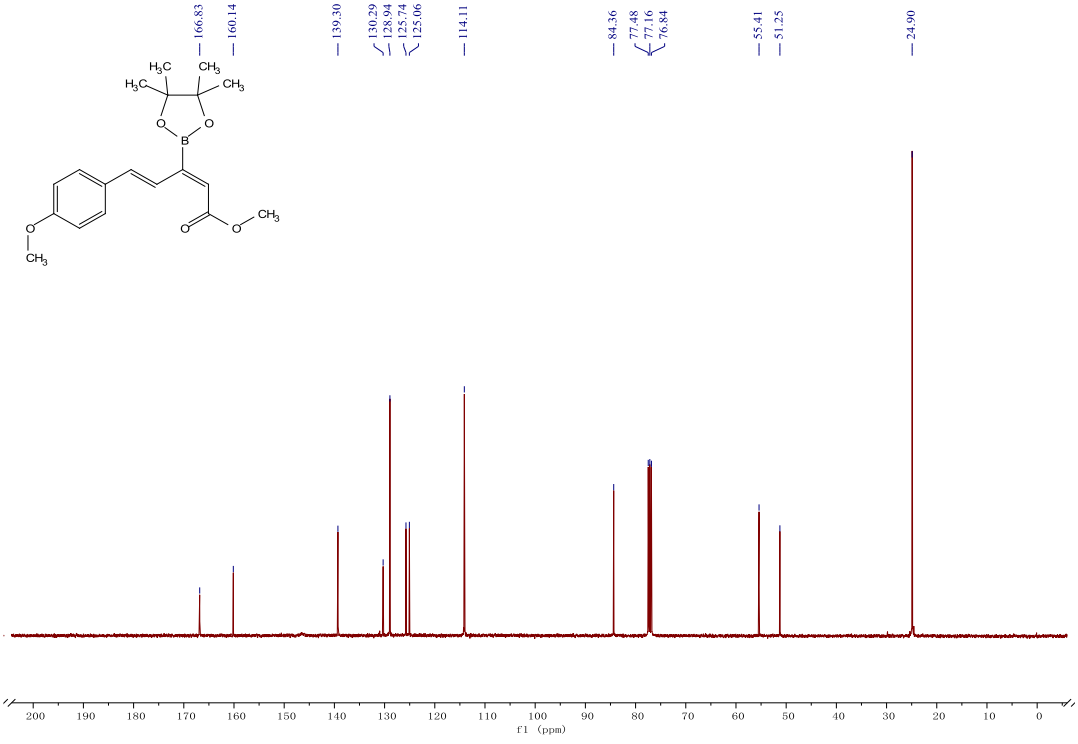
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 16.2, 0.7 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.34 (d, *J* = 16.2 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.26 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 1.34 (s, 12H).

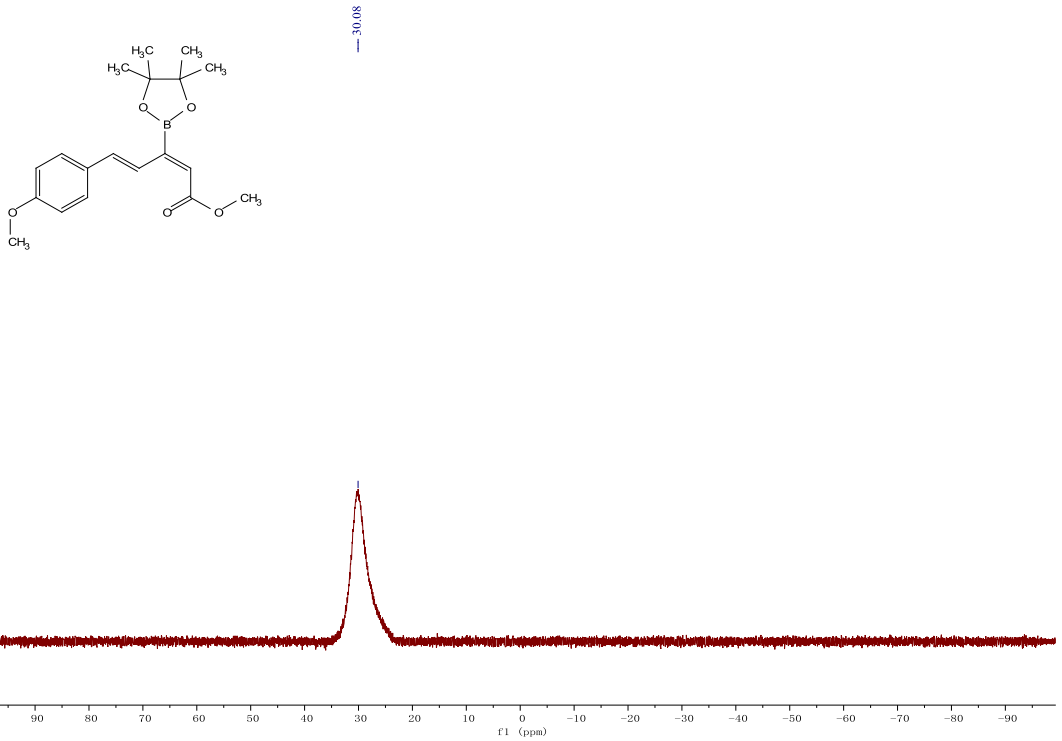
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.83, 160.14, 139.30, 130.29, 128.94, 125.74, 125.06, 114.12, 84.36, 55.41, 51.25, 24.90.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.08.

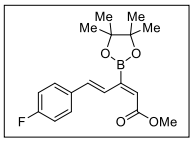
HRMS (ESI) (m/z): Calcd for $C_{19}H_{25}O_5{}^{11}BNa$ $[M+Na]^+$: 367.1693, found: 367.1695.


8.28
8.28
8.24
8.24
7.50
7.50
7.49
7.48
7.48
7.47
7.36
7.32
6.88
6.87
6.87
6.86
6.85
6.84
6.26
3.82
3.75
1.34
1.06
2.06
1.03
2.09
1.00
3.06
3.02
12.06
f1 (ppm)


166.83
160.14
139.30
130.29
128.94
125.74
125.06
114.11
84.36
77.48
77.16
76.84
55.41
51.25
24.90
f1 (ppm)



methyl (2*Z*,4*E*)-5-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-2,4-dienoate (5d)



Prepared according to General Procedure B from **1d** (40.8 mg, 0.20 mmol). The product **5d** was isolated in 80% yield (53.1 mg) by flash column chromatography as light yellow oil.

Eluent: dichloromethane.

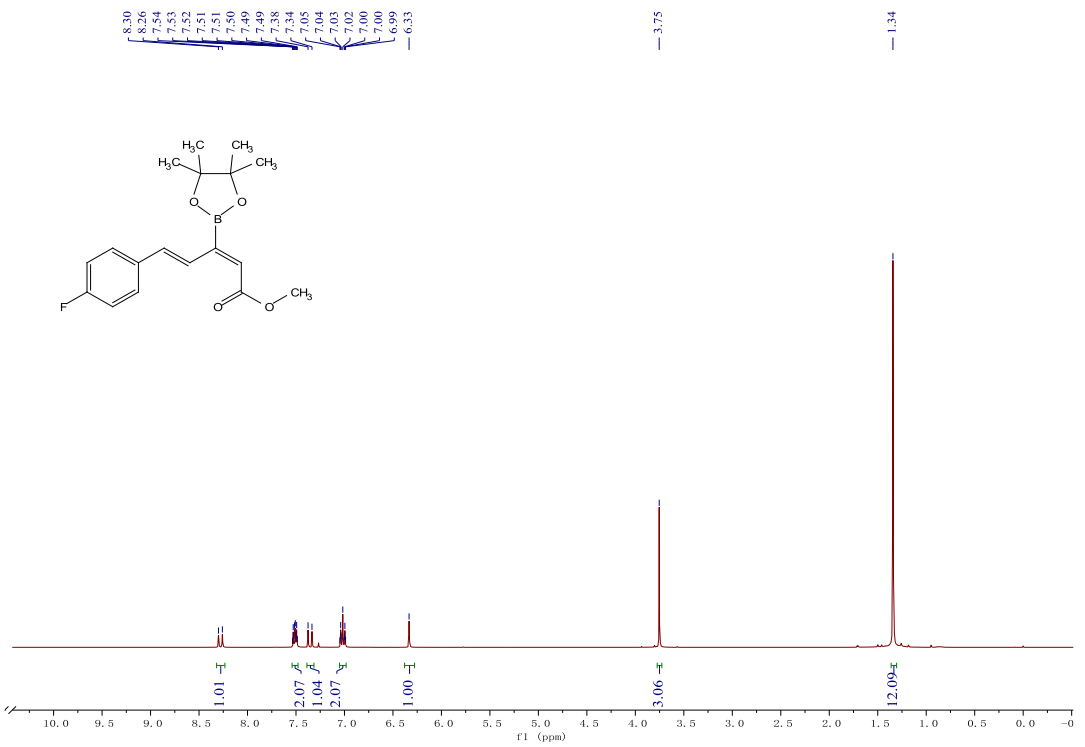
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 16.2 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.36 (d, *J* = 16.3 Hz, 1H), 7.07 – 6.96 (m, 2H), 6.33 (s, 1H), 3.75 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.67, 162.96 (d, *J* = 248.5 Hz), 138.14, 133.72, 133.69, 129.10 (d, *J* = 8.1 Hz), 127.22, 126.67 (d, *J* = 2.3 Hz), 115.64 (d, *J* = 21.7 Hz), 84.42, 51.32, 24.88.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.82.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.14.

HRMS (ESI) (m/z): Calcd for $C_{18}H_{22}O_4{}^{11}BFNa$ $[M+Na]^+$:355.1493, found: 355.1499.


8.30
8.26
7.54
7.53
7.52
7.51
7.51
7.50
7.49
7.49
7.38
7.34
7.05
7.04
7.03
7.02
7.00
7.00
6.99
6.33
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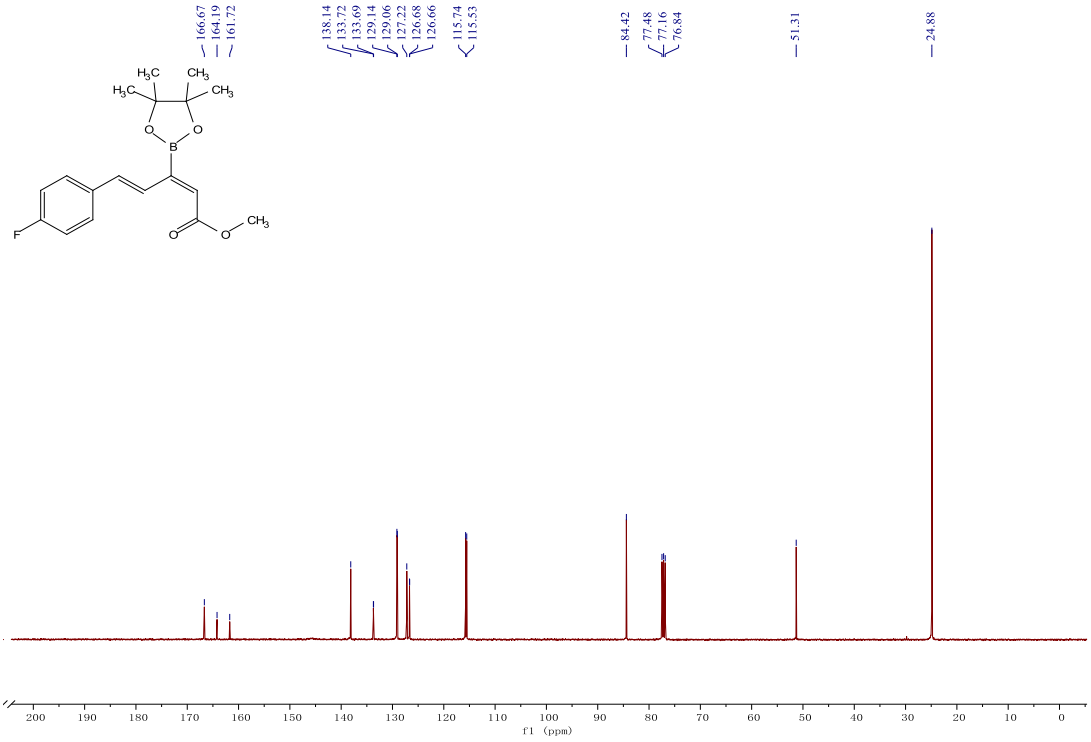
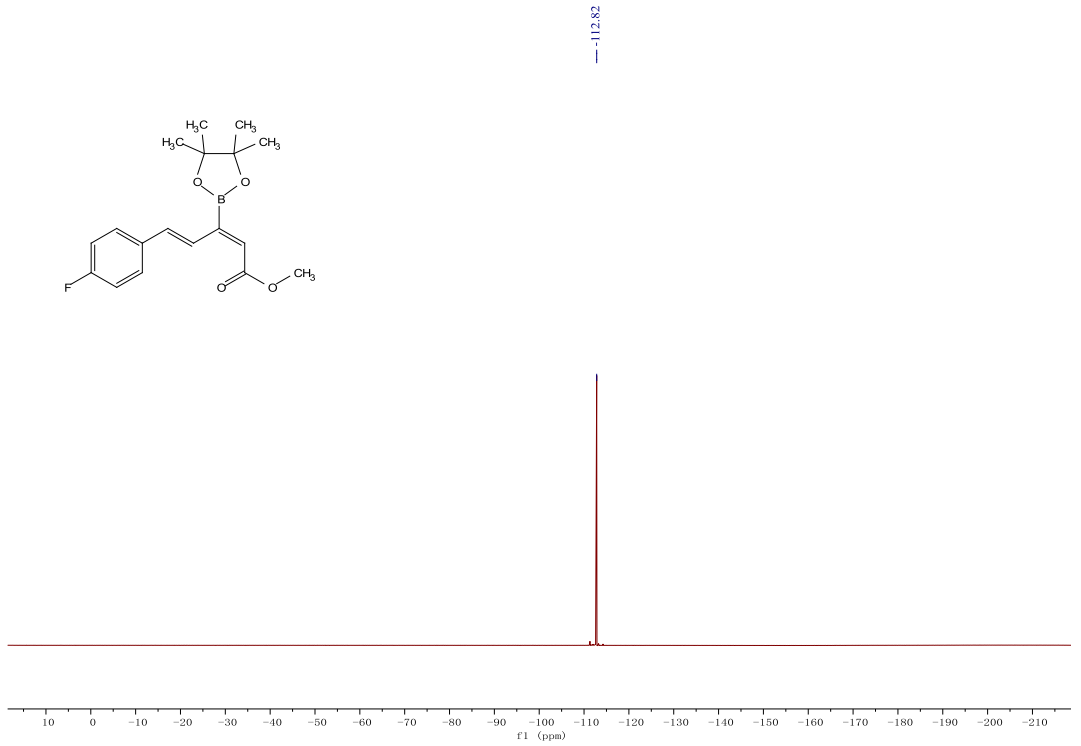
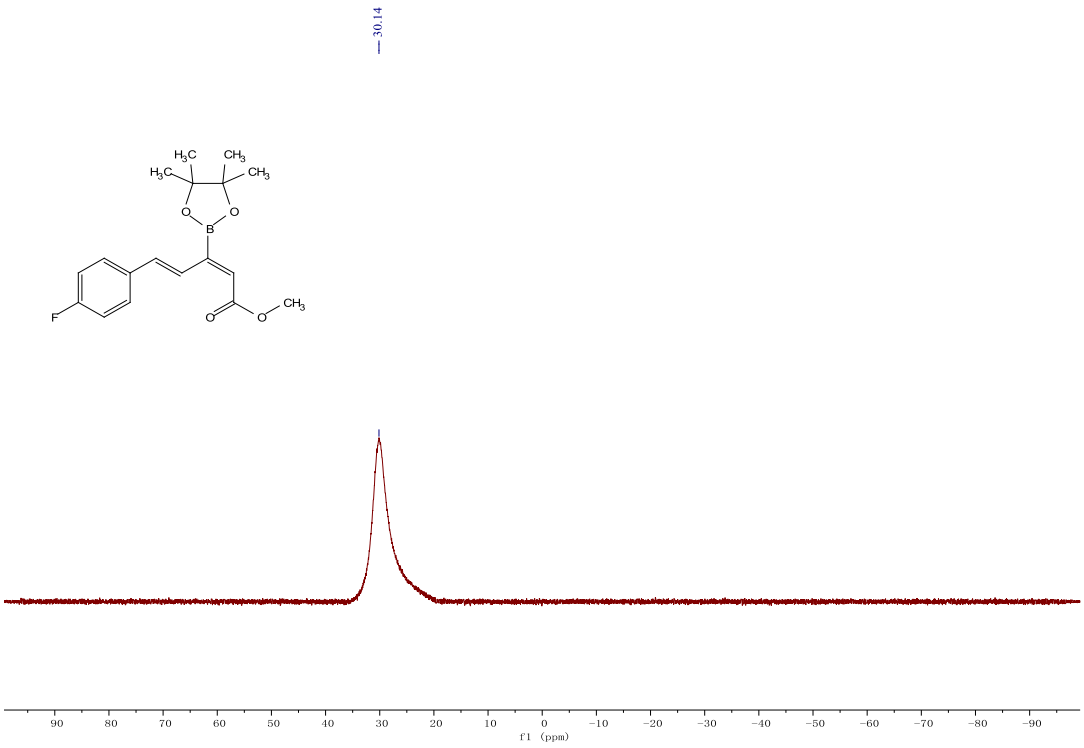
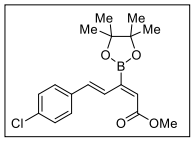
1.34
1.01
2.07
1.04
2.07
1.00
3.06
12.09
f1 (ppm)


166.67
164.19
161.72
138.14
133.72
133.69
129.14
129.06
127.22
126.68
126.66
115.74
115.53
84.42
77.48
77.16
76.84
51.31
24.88
f1 (ppm)





methyl (2*Z*,4*E*)-5-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-2,4-dienoate (5e)



Prepared according to General Procedure B from **1e** (44.1 mg, 0.20 mmol). The product **5e** was isolated in 83% yield (60.8 mg) by flash column chromatography as light yellow oil.

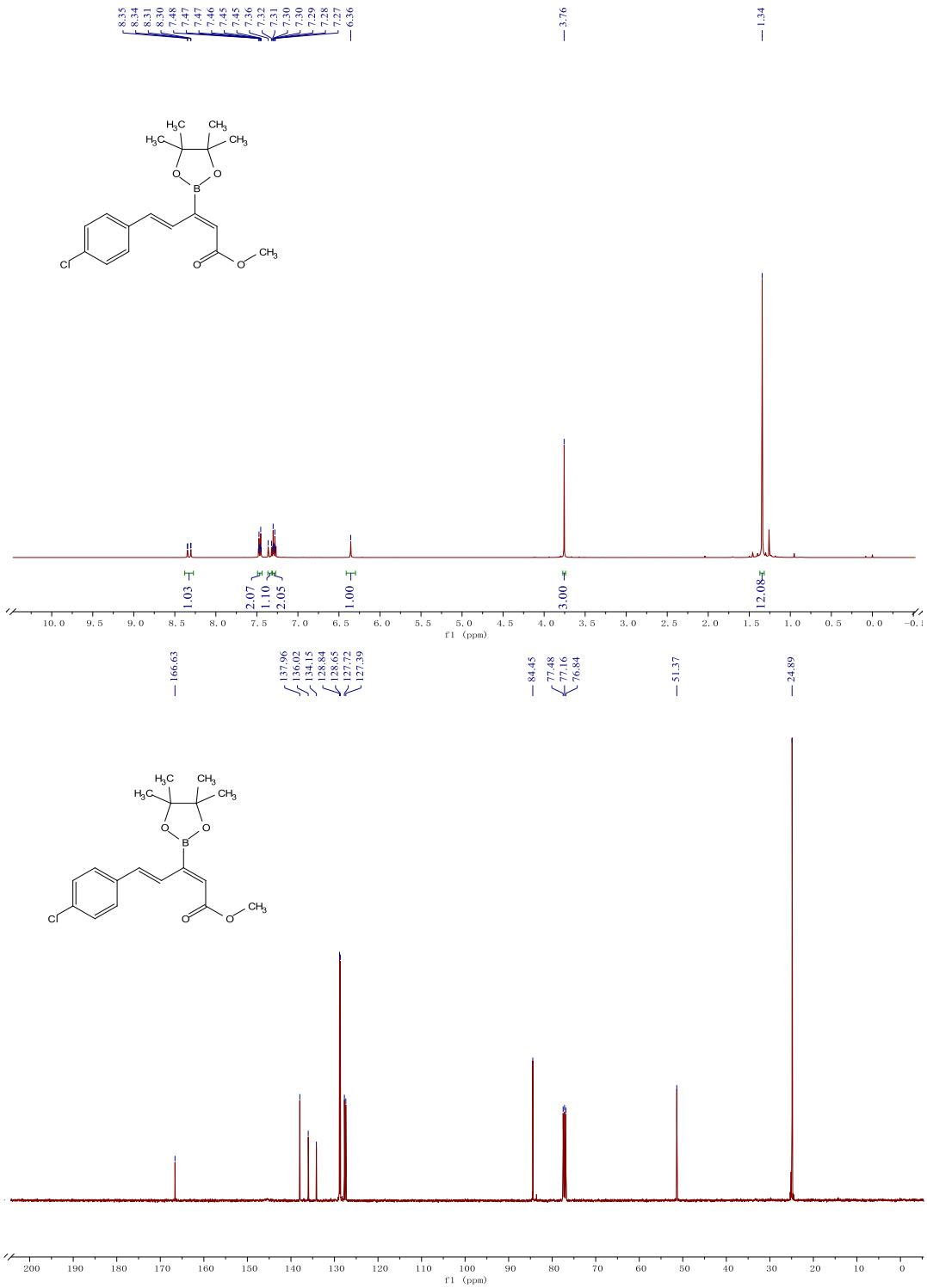
Eluent: dichloromethane.

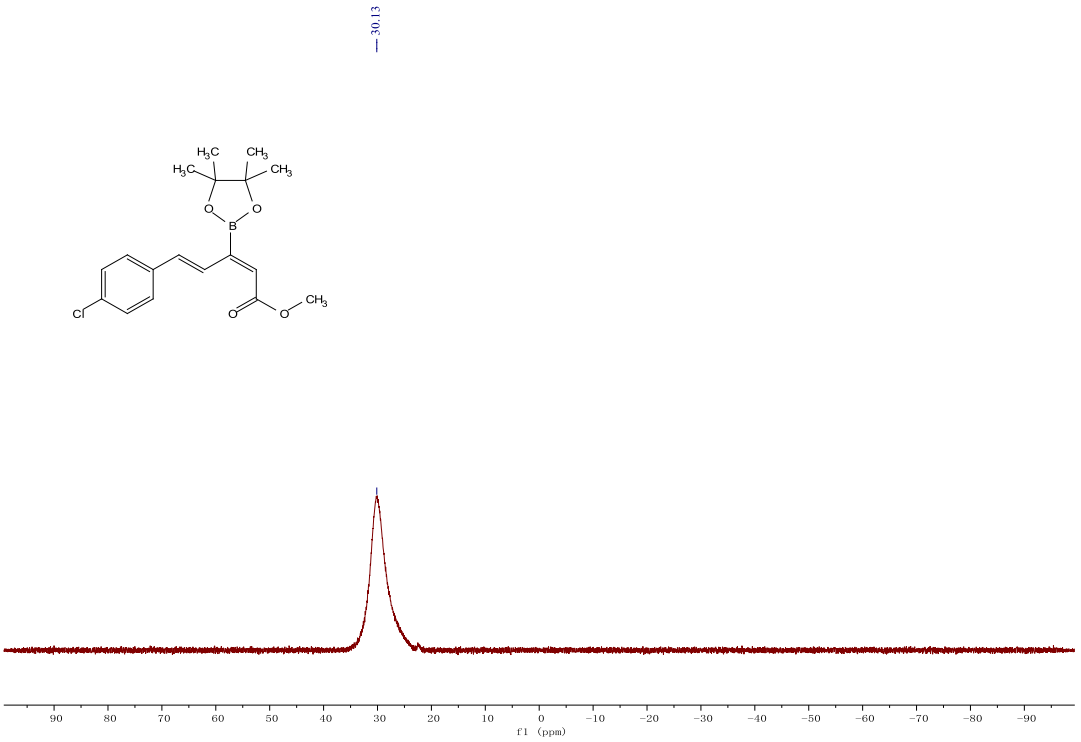
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 16.2, 0.9 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.34 (d, *J* = 16.3 Hz, 1H), 7.31 – 7.27 (m, 2H), 6.36 (s, 1H), 3.76 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.63, 137.96, 136.02, 134.15, 128.84, 128.65, 127.72, 127.39, 84.45, 51.37, 24.89.

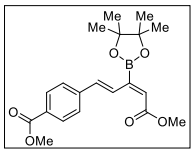
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.13.

HRMS (ESI) (m/z): Calcd for $C_{18}H_{22}O_4{}^{11}BClNa$ $[M+Na]^+$: 371.1197, found: 371.1199.





methyl 4-((1*E*,3*Z*)-5-methoxy-5-oxo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,3-dien-1-yl)benzoate (5f)



Prepared according to General Procedure B from **1f** (48.8 mg, 0.20 mmol). The product **5f** was isolated in 66% yield (49.3 mg) by flash column chromatography as light yellow solid.

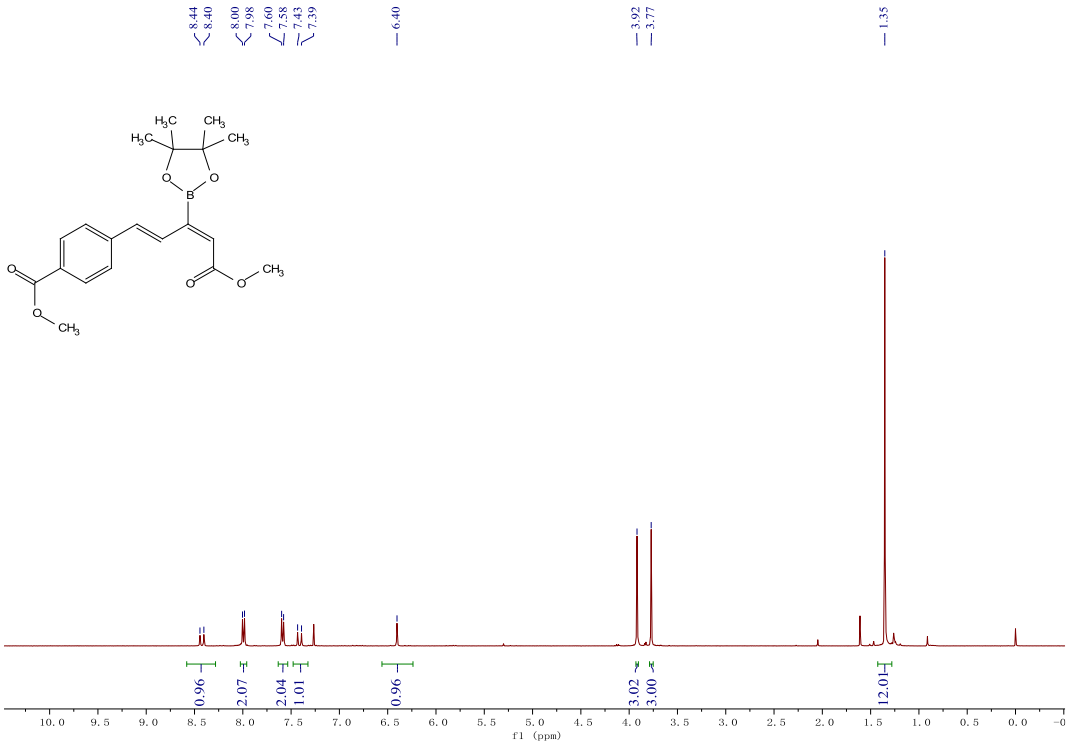
Eluent: Dichloromethane.

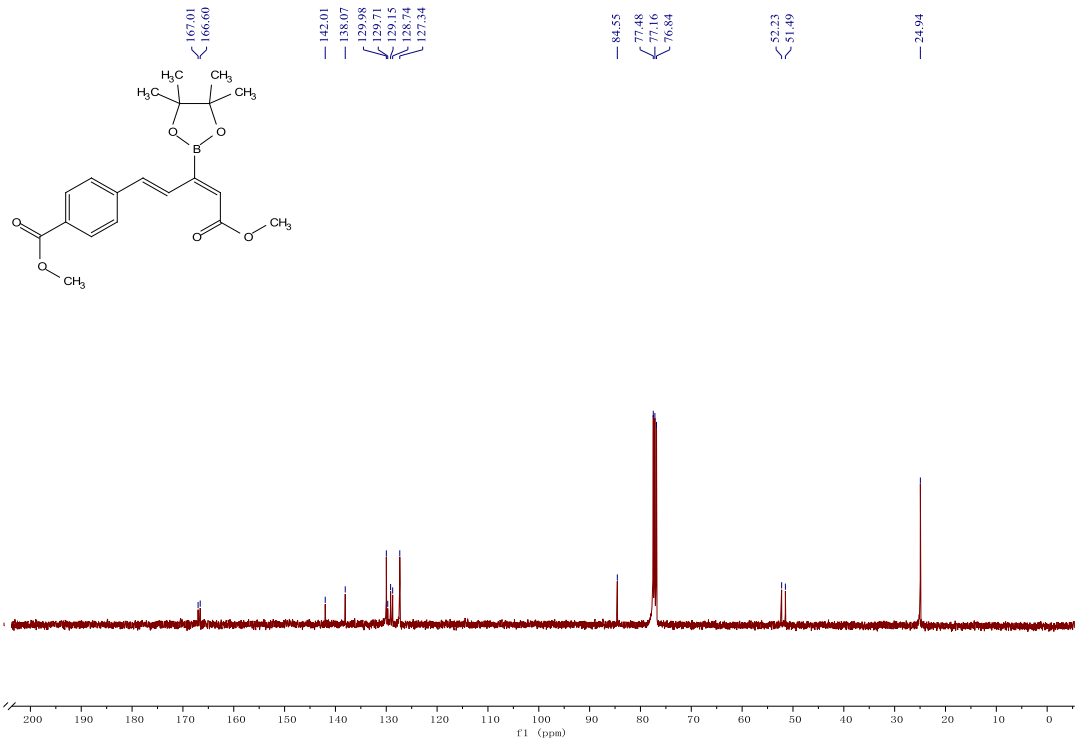
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 16.2 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 16.2 Hz, 1H), 6.40 (s, 1H), 3.92 (s, 3H), 3.77 (s, 3H), 1.35 (s, 12H).

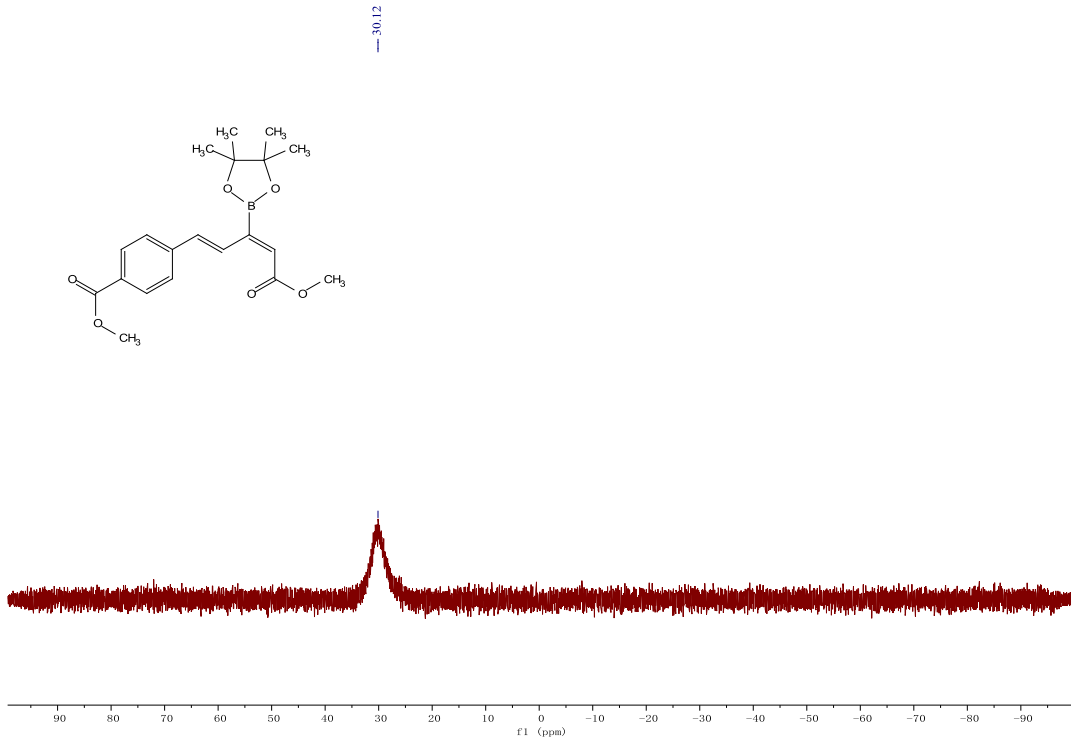
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.01, 166.60, 142.01, 138.07, 129.98, 129.71, 129.15, 128.74, 127.34, 84.55, 52.23, 51.49, 24.94.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.12.

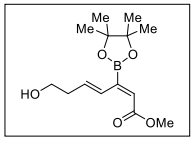
HRMS (ESI) (m/z): Calcd for $C_{20}H_{25}O_6{}^{11}BNa$ $[M+Na]^+$: 395.1642, found: 395.1638.


8.44
8.40
8.00
7.98
7.60
7.58
7.43
7.39
6.40
3.92
3.77
1.35
0.96
2.07
2.04
1.01
0.96
3.02
3.00
12.01
f1 (ppm)


167.01
166.60
142.01
138.07
129.98
129.71
129.15
128.74
127.34
84.55
77.48
77.16
76.84
52.23
51.49
24.94
f1 (ppm)



methyl (2*Z*,4*E*)-7-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-2,4-dienoate (5m)



Prepared according to General Procedure B from **1m** (44.1 mg, 0.20 mmol). K_3PO_4 (4.2 mg, 10 mol%) was used as base instead of NEt_3. The product **5m** was isolated in 74% yield (60.8 mg) by flash column chromatography as light yellow oil.

Eluent: dichloromethane.

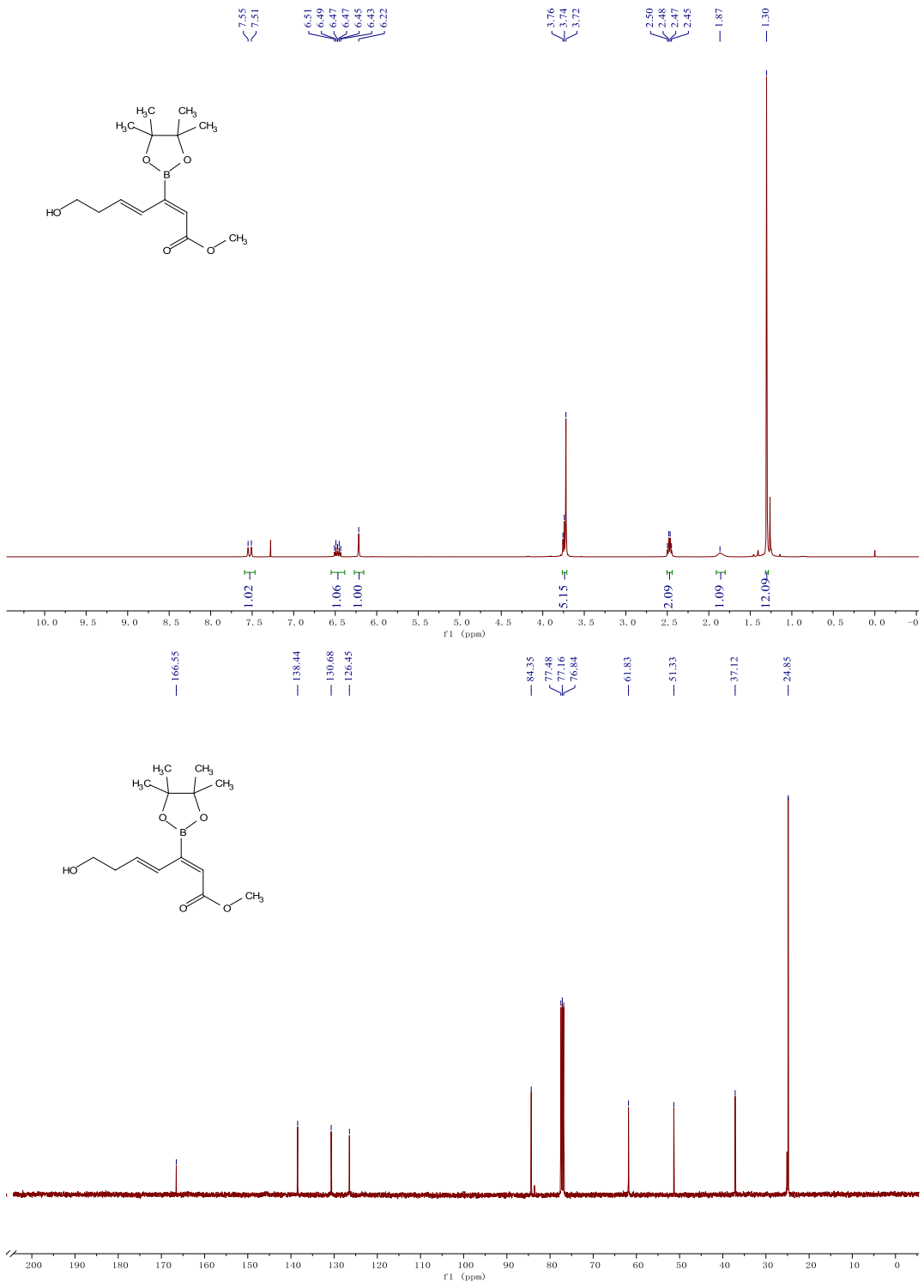
R_f: 0.52 (petroleum ether/ethyl acetate = 1:1)

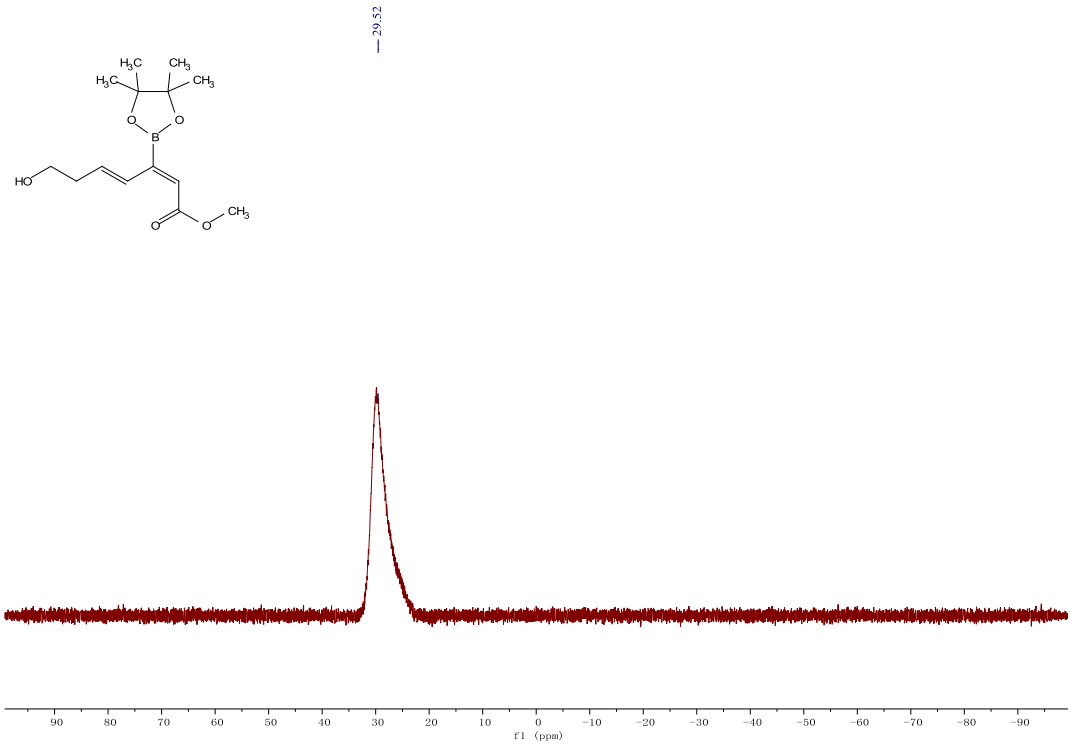
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 15.9 Hz, 1H), 6.47 (dt, *J* = 15.7, 7.1 Hz, 1H), 6.22 (s, 1H), 3.77 – 3.70 (m, 5H), 2.47 (m, 2H), 1.87 (s, 1H), 1.30 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.55, 138.44, 130.68, 126.45, 84.35, 61.83, 51.33, 37.12, 24.85.

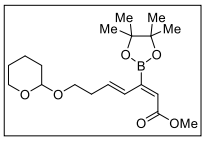
^{11}B NMR (128 MHz, $CDCl_3$) δ 29.52.

HRMS (ESI) (m/z): Calcd for $C_{14}H_{23}O_5{}^{11}BNa$ $[M+Na]^+$: 305.1536, found: 305.1538.


7.55
7.51
6.51
6.49
6.47
6.47
6.45
6.43
6.22
3.76
3.74
3.72
2.50
2.48
2.47
2.45
1.87
1.30
1.02
1.06
1.00
5.15
2.09
1.09
12.09
f1 (ppm)
166.55
138.44
130.68
126.45
84.35
77.48
77.16
76.84
61.83
51.33
37.12
24.85
f1 (ppm)



methyl (2*Z*,4*E*)-7-((tetrahydro-2H-pyran-2-yl)oxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-2,4-dienoate (5n)



Prepared according to General Procedure B from **1n** (47.6 mg, 0.20 mmol). K_3PO_4 (4.2 mg, 10 mol%) was used as base instead of NEt_3. The product **5n** was isolated in 65% yield (47.6 mg) by flash column chromatography as light yellow oil.

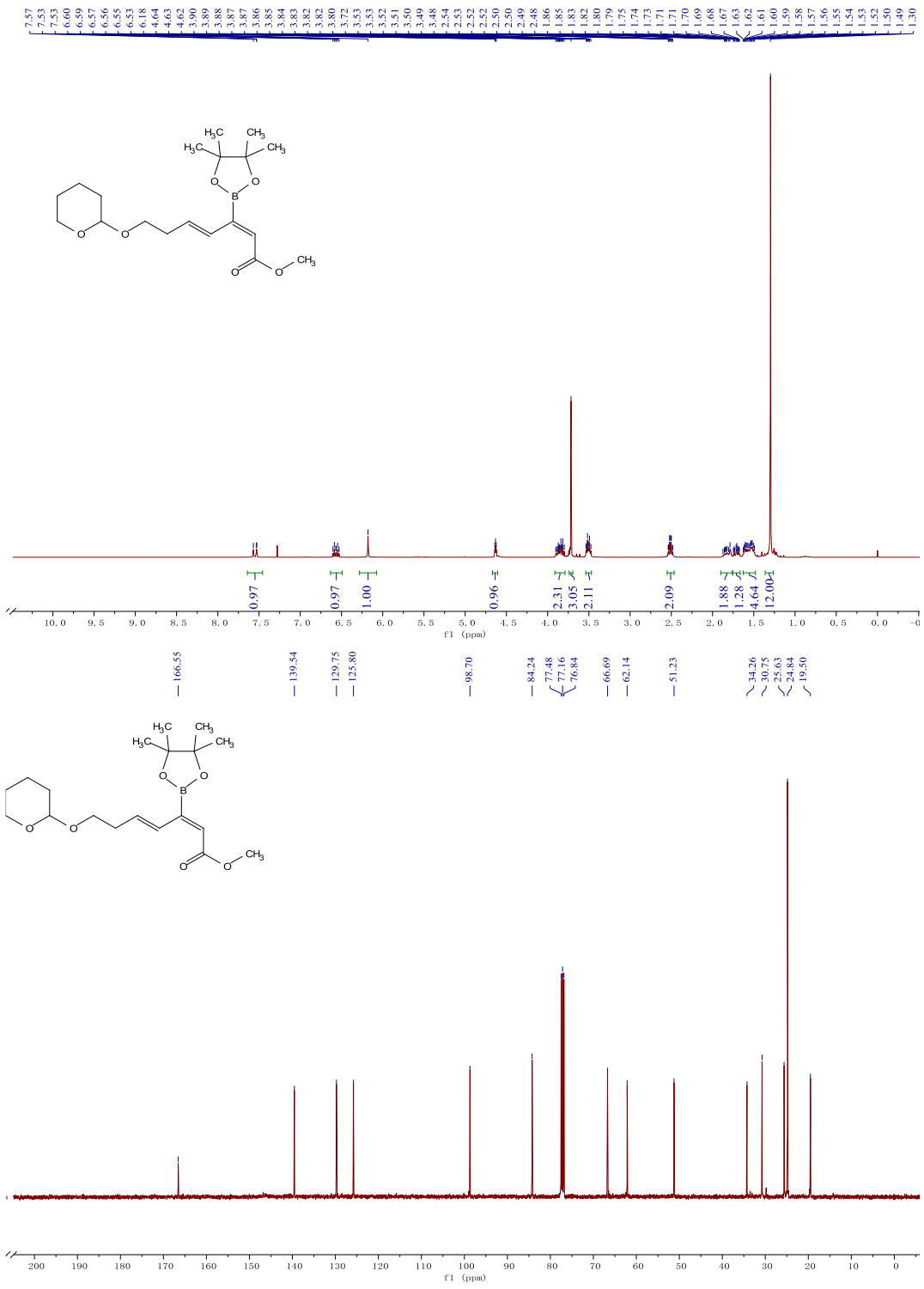
Eluent: dichloromethane.

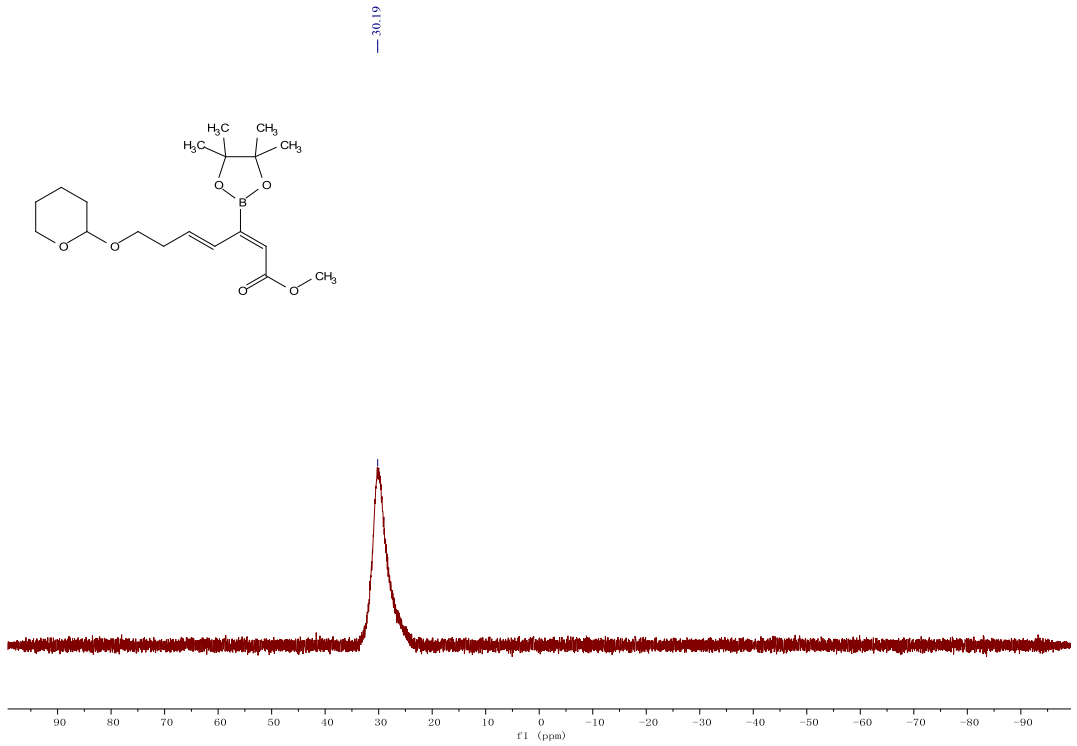
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.48 (m, 1H), 6.57 (dt, *J* = 15.8, 7.0 Hz, 1H), 6.18 (s, 1H), 4.65 – 4.61 (m, 1H), 3.90 – 3.79 (m, 2H), 3.72 (s, 3H), 3.54 – 3.47 (m, 2H), 2.51 (qd, *J* = 6.9, 0.9 Hz, 2H), 1.88 – 1.78 (m, 1H), 1.75 – 1.67 (m, 1H), 1.63 – 1.49 (m, 4H), 1.30 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.55, 139.54, 129.75, 125.80, 98.70, 84.24, 66.69, 62.14, 51.23, 34.26, 30.75, 25.63, 24.84, 19.50.

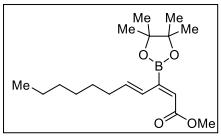
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.19.

HRMS (ESI) (m/z): Calcd for $C_{19}H_{31}O_6{}^{11}BNa$ $[M+Na]^+$: 389.2111, found: 389.2103.





methyl (2*Z*,4*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undeca-2,4-dienoate (5j)



Prepared according to General Procedure B from **1j** (38.9 mg, 0.20 mmol). K_3PO_4 (4.2 mg, 10 mol%) was used as base instead of NEt_3. The product **5j** was isolated in 69% yield (42.2 mg) by flash column chromatography as light yellow oil.

Eluent: dichloromethane.

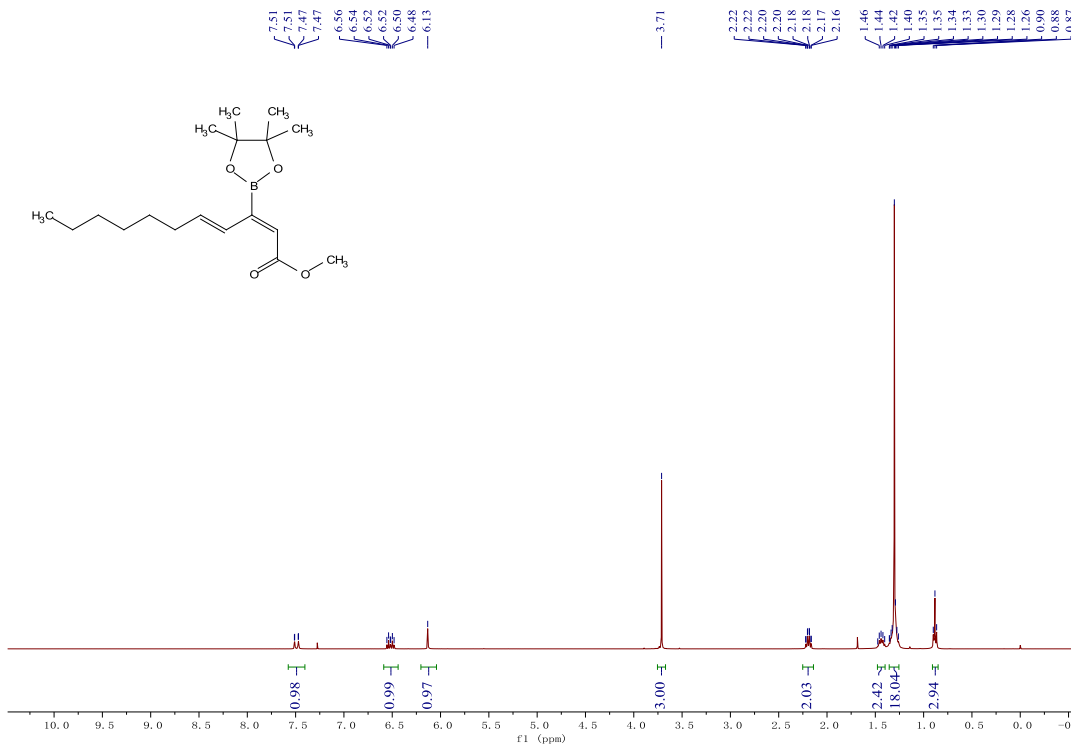
R_f: 0.38 (tailing, petroleum ether/ethyl acetate = 30:1)

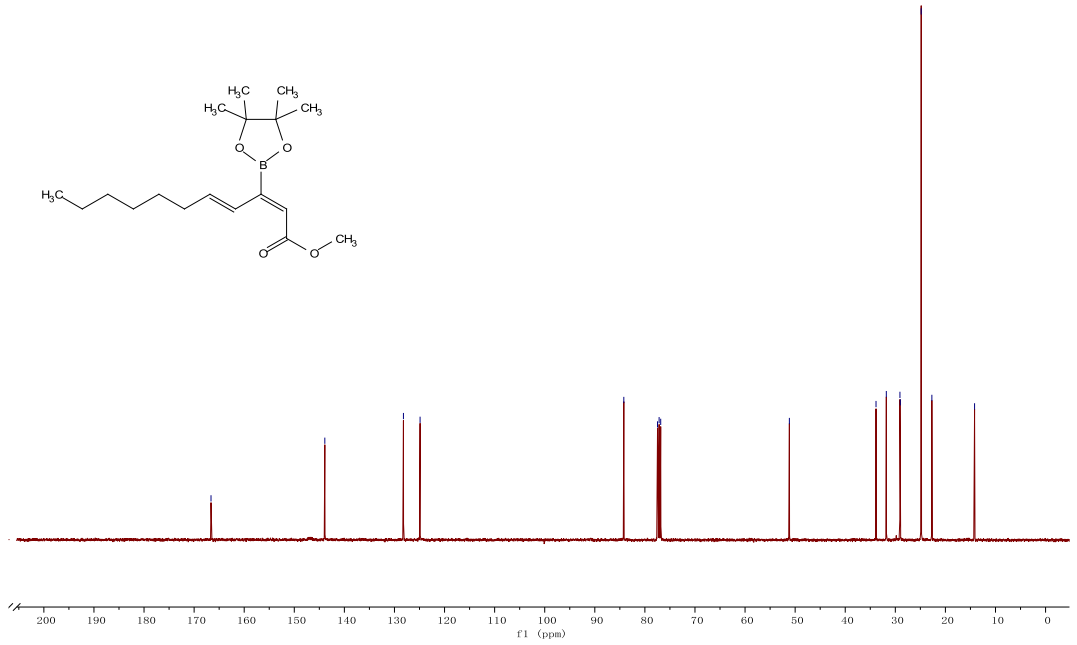
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 15.8, 1.0 Hz, 1H), 6.52 (dt, *J* = 15.7, 7.0 Hz, 1H), 6.13 (s, 1H), 3.71 (s, 3H), 2.19 (qd, *J* = 7.2, 1.0 Hz, 2H), 1.48 – 1.40 (m, 2H), 1.34 – 1.26 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H).

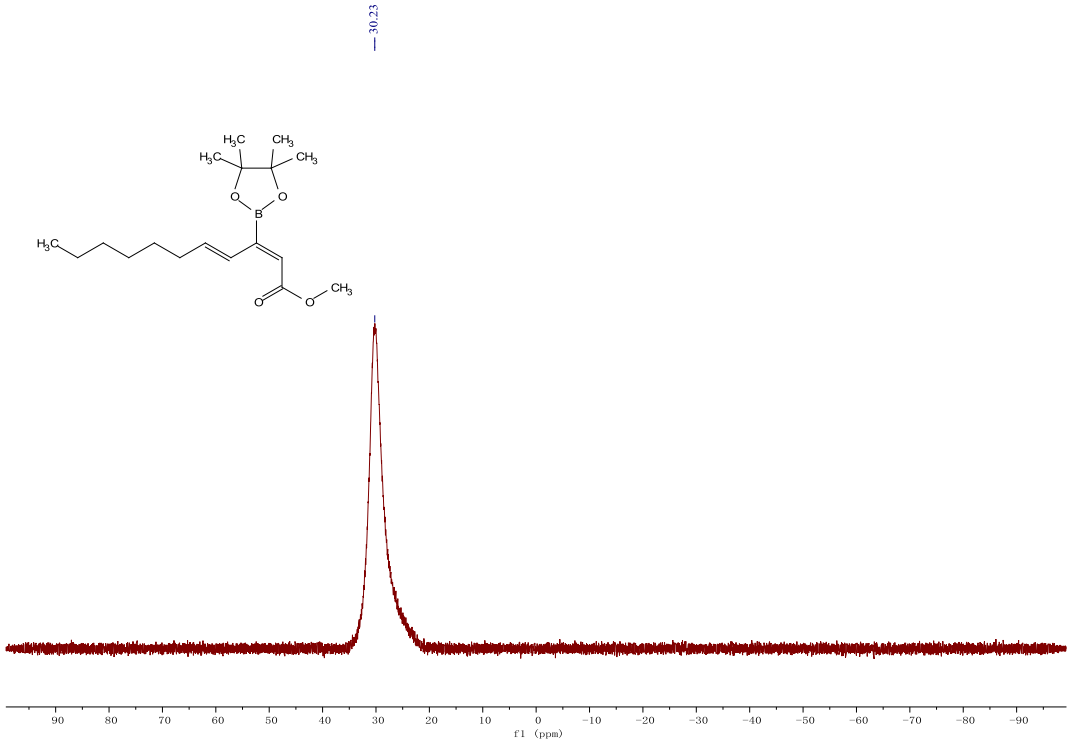
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.63, 143.90, 128.21, 124.89, 84.21, 51.15, 33.85, 31.80, 29.08, 29.00, 24.83, 22.70, 14.18.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.23.

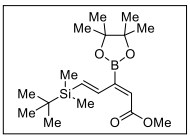
HRMS (ESI) (m/z): Calcd for $C_{18}H_{31}O_4{}^{11}BNa$ $[M+Na]^+$: 345.2213, found: 345.2220.


7.51
7.51
7.47
7.47
6.56
6.54
6.52
6.52
6.50
6.48
6.13
3.71
2.22
2.22
2.20
2.20
2.18
2.18
2.17
2.16
1.46
1.44
1.42
1.40
1.35
1.35
1.34
1.33
1.30
1.29
1.28
1.26
0.90
0.88
0.98
0.99
0.97
3.00
2.03
2.42
18.04
2.94
f1 (ppm)


166.63
143.90
128.21
124.89
84.21
77.48
77.16
76.84
51.15
33.85
31.80
29.08
29.00
24.83
22.70
14.18
f1 (ppm)



methyl (2*Z*,4*E*)-5-(*tert*-butyldimethylsilyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-2,4-dienoate (5t)



Prepared according to General Procedure B from **1t** (44.9 mg, 0.20 mmol). K_3PO_4 (4.2 mg, 10 mol%) was used as base instead of NEt_3. The product **5t** was isolated in 51% yield (35.8 mg) by flash column chromatography as light yellow oil.

Eluent: Dichloromethane.

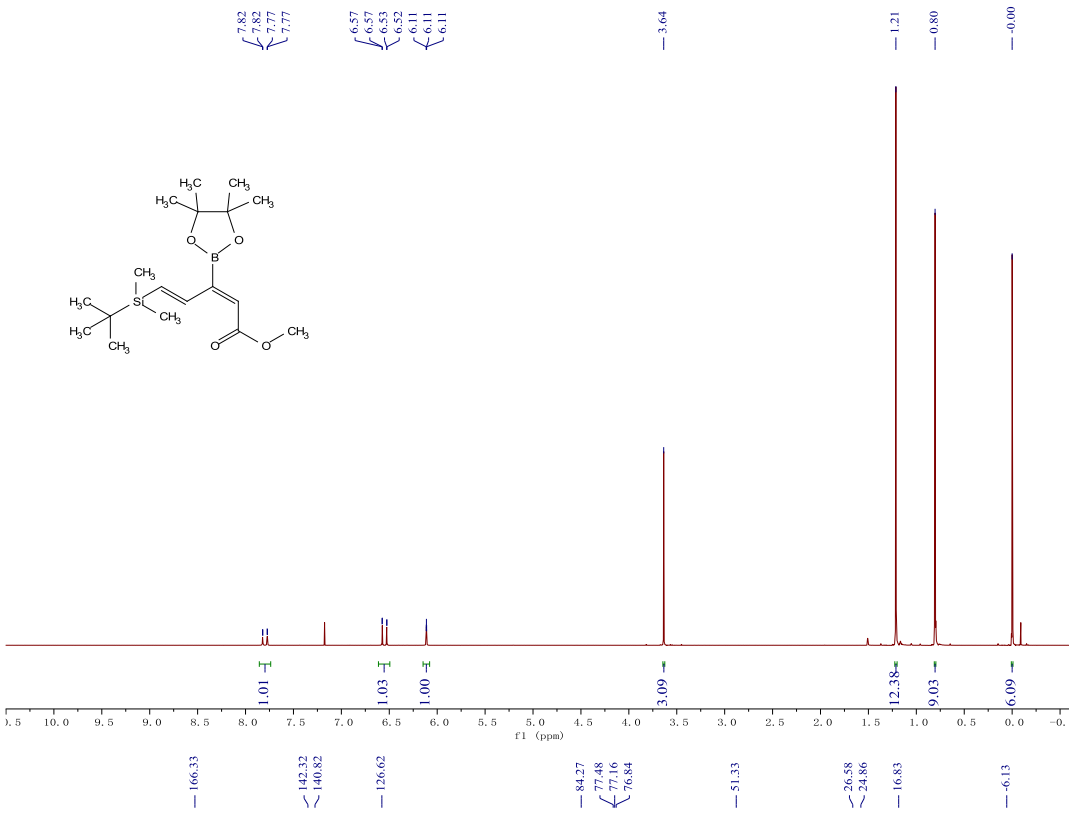
R_f: 0.38 (tailing, petroleum ether/ethyl acetate = 30:1)

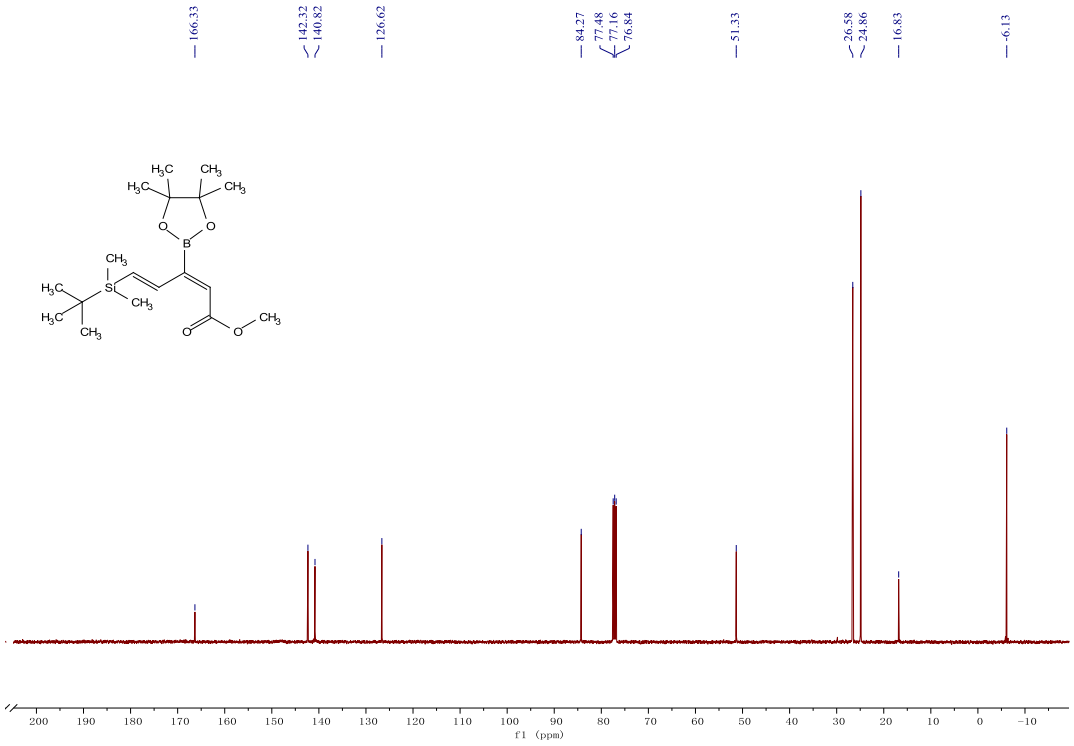
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 19.2, 1.0 Hz, 1H), 6.55 (dd, *J* = 19.2, 0.8 Hz, 1H), 6.11 (t, *J* = 0.8 Hz, 1H), 3.64 (s, 3H), 1.21 (s, 12H), 0.80 (s, 9H), -0.00 (s, 6H).

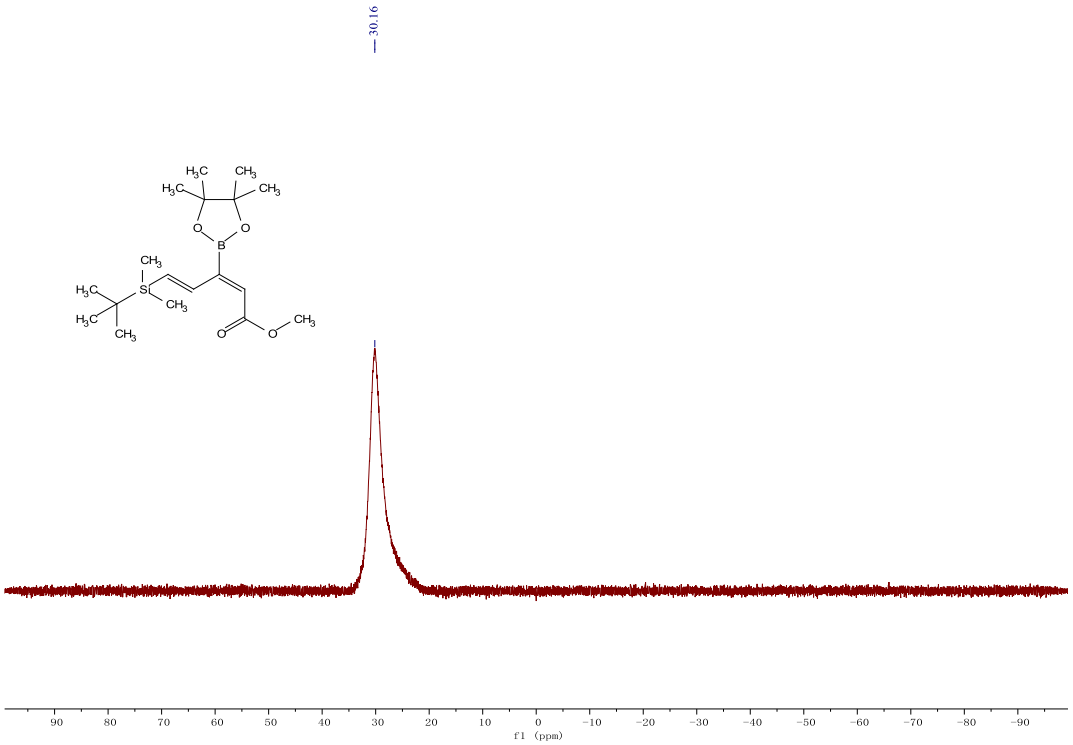
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.33, 142.32, 140.82, 126.62, 84.27, 51.33, 26.58, 24.86, 16.83, -6.13.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.16.

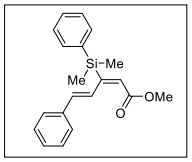
HRMS (ESI) (m/z): Calcd for $C_{18}H_{33}O_4{}^{11}BSiNa$ $[M+Na]^+$: 375.2139, found: 375.2146.


7.82
7.82
7.77
7.77
6.57
6.57
6.53
6.52
6.11
6.11
6.11
3.64
1.21
0.80
0.00
1.01
1.03
1.00
3.09
12.38
9.03
6.09
f1 (ppm)


166.33
142.32
140.82
126.62
84.27
77.48
77.16
76.84
51.33
26.58
24.86
16.83
-6.13
f1 (ppm)



3.4 Spectra of Silyldienoates



methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-5-phenylpenta-2,4-dienoate (11a)

Prepared according to General Procedure C from **1a** (37.2 mg, 0.20 mmol). The product **11a** was isolated in 87% yield (56.0 mg) by PTLC as colorless oil.

Regioselectivity: > 95:5 (β:α, crude ^{1}H NMR).

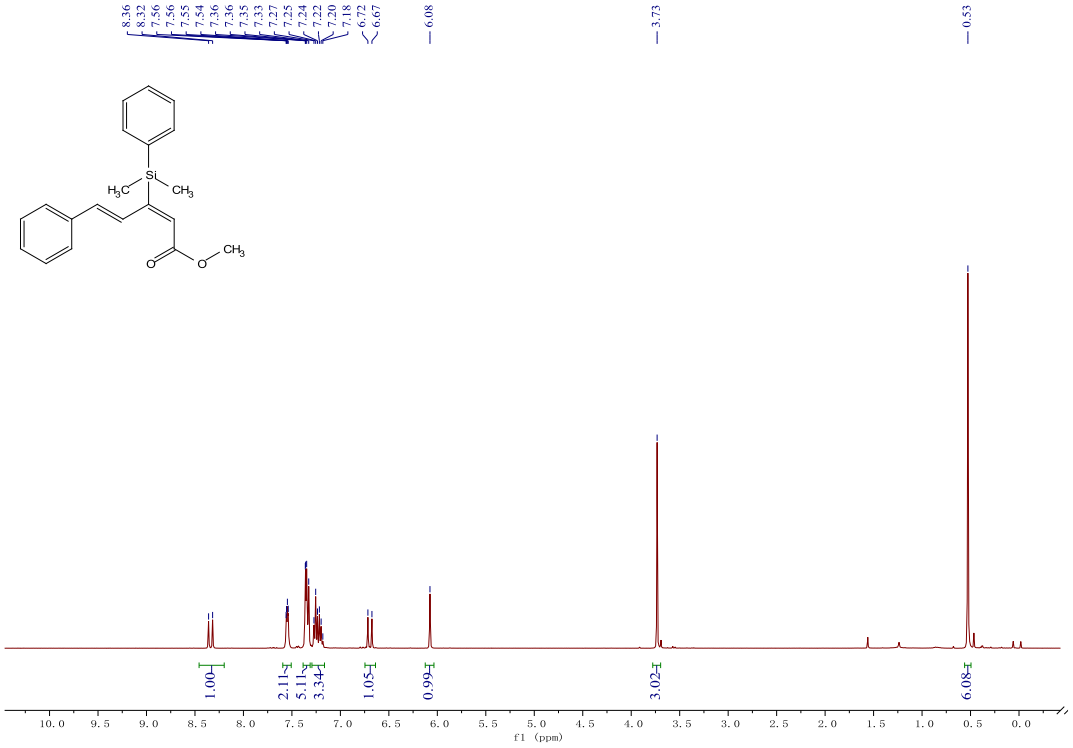
Eluent: petroleum ether/ethyl acetate (30:1).

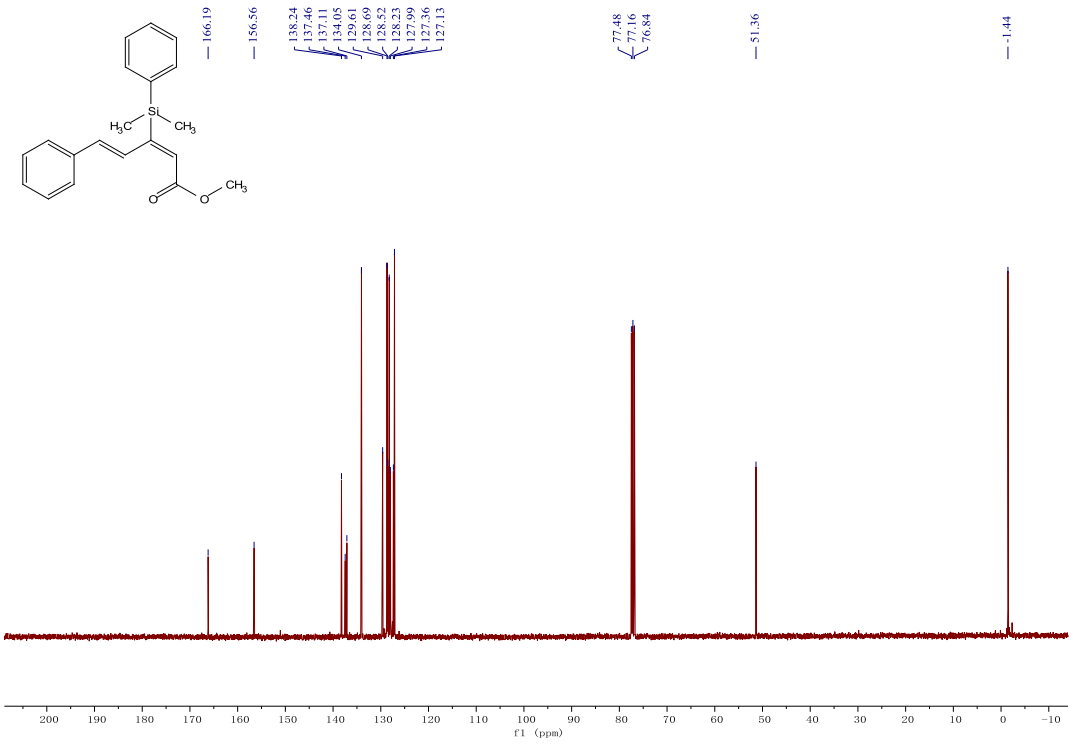
R_f: 0.18 (petroleum ether/ethyl acetate = 20:1).

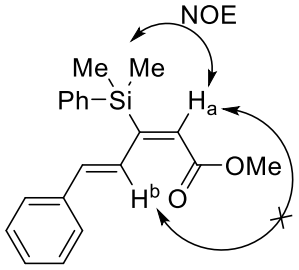
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 16.7 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.39 – 7.31 (m, 5H), 7.30 – 7.16 (m, 3H), 6.70 (d, *J* = 16.7 Hz, 1H), 6.08 (s, 1H), 3.73 (s, 3H), 0.53 (s, 6H).

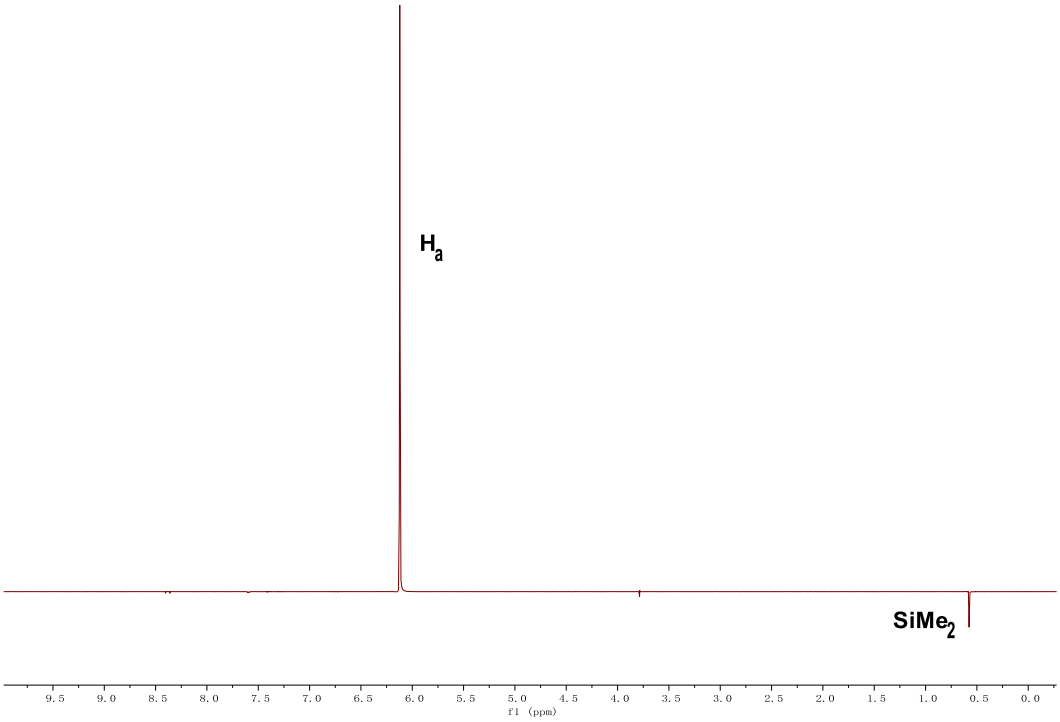
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.19, 156.56, 138.24, 137.46, 137.11, 134.05, 129.61, 128.69, 128.52, 128.23, 127.99, 127.36, 127.13, 51.36, -1.44.

HRMS (ESI) (m/z): Calcd for $C_{20}H_{22}O_2SiNa^+$ $[M+Na]^+$: 345.1287, found: 345.1288.

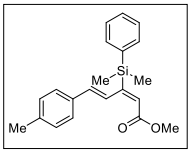

8.36
8.32
7.56
7.56
7.55
7.54
7.36
7.36
7.35
7.33
7.27
7.25
7.24
7.22
7.20
7.18
6.72
6.67
6.08
3.73
0.53
Si
H3C
CH3
O
O
CH3
1.00
2.11
5.11
3.34
1.05
0.99
3.02
6.08
f1 (ppm)


166.19
156.56
138.24
137.46
137.11
134.05
129.61
128.69
128.52
128.23
127.99
127.36
127.13
77.48
77.16
76.84
51.36
-1.44
Si
H3C
CH3
O
O
CH3
f1 (ppm)


NOE
Me
Me
Ph–Si
Ha
OMe
Hb
O



methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-5-(*p*-tolyl)penta-2,4-dienoate (11b)



Prepared according to General Procedure C from **1b** (40.0 mg, 0.20 mmol). The product **11b** was isolated in 89% yield (59.6 mg) by PTLC as colorless oil.

Regioselectivity: > 95:5 (β:α, crude ^{1}H NMR).

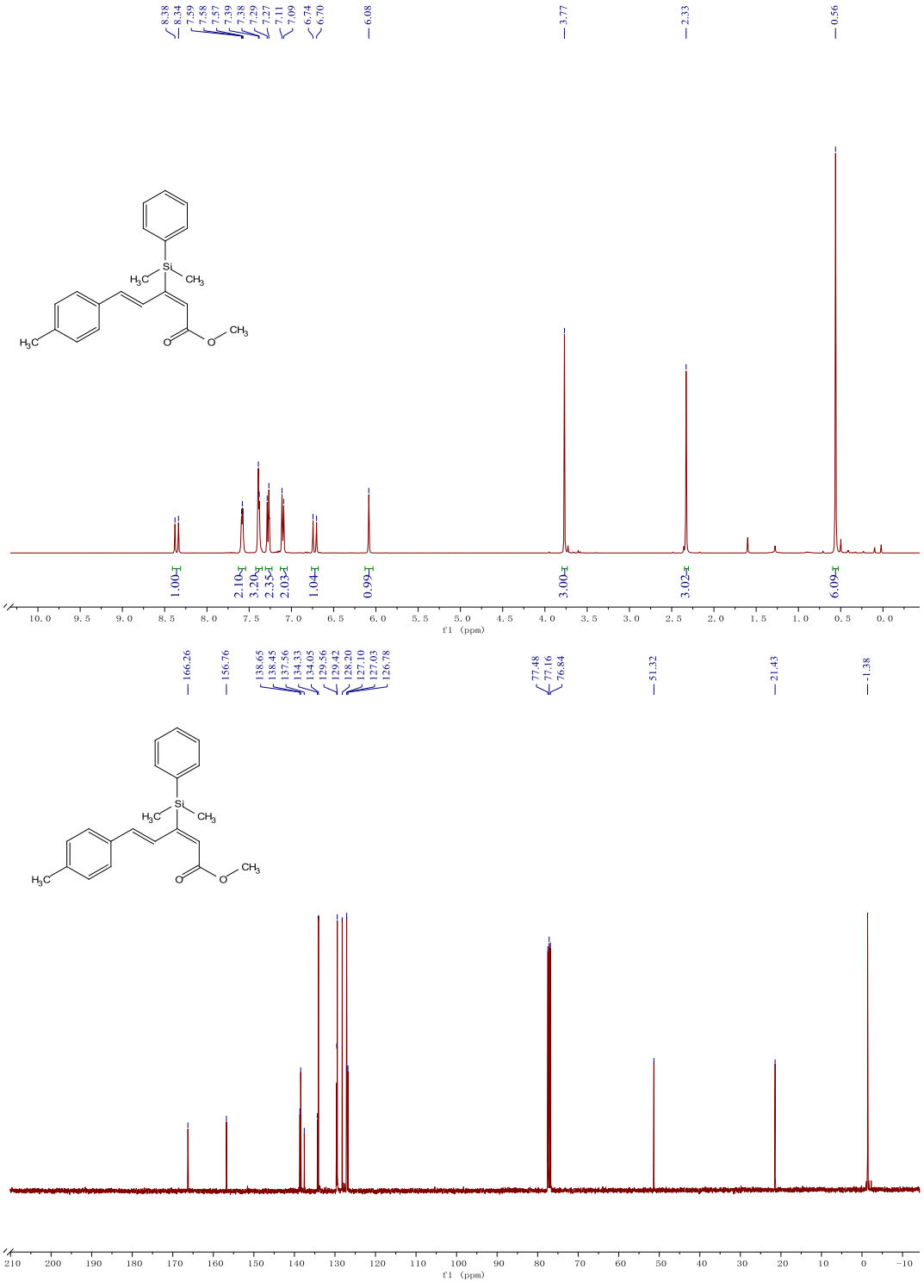
Eluent: petroleum ether/ethyl acetate (30:1).

R_f: 0.36 (petroleum ether/ethyl acetate = 30:1).

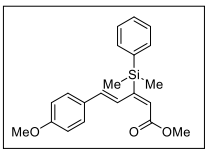
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 16.6 Hz, 1H), 7.64 – 7.49 (m, 2H), 7.43 – 7.32 (m, 3H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.72 (d, *J* = 16.7 Hz, 1H), 6.08 (s, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 0.56 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.26, 156.76, 138.65, 138.45, 137.56, 134.33, 134.05, 129.56, 129.42, 128.20, 127.10, 127.03, 126.78, 51.32, 21.43, -1.38.

HRMS (ESI) (m/z): Calcd for $C_{21}H_{24}O_2SiNa^+$ $[M+Na]^+$: 359.1443, found: 359.1443.



methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-5-(4-methoxyphenyl)penta-2,4-dienoate (11c)



Prepared according to General Procedure C from **1c** (43.2 mg, 0.20 mmol). The product **11c** was isolated in 96% yield (67.4 mg) by PTLC as colorless oil.

Regioselectivity: > 95:5 (β:α, crude ^{1}H NMR).

Eluent: petroleum ether/ethyl acetate (30:1).

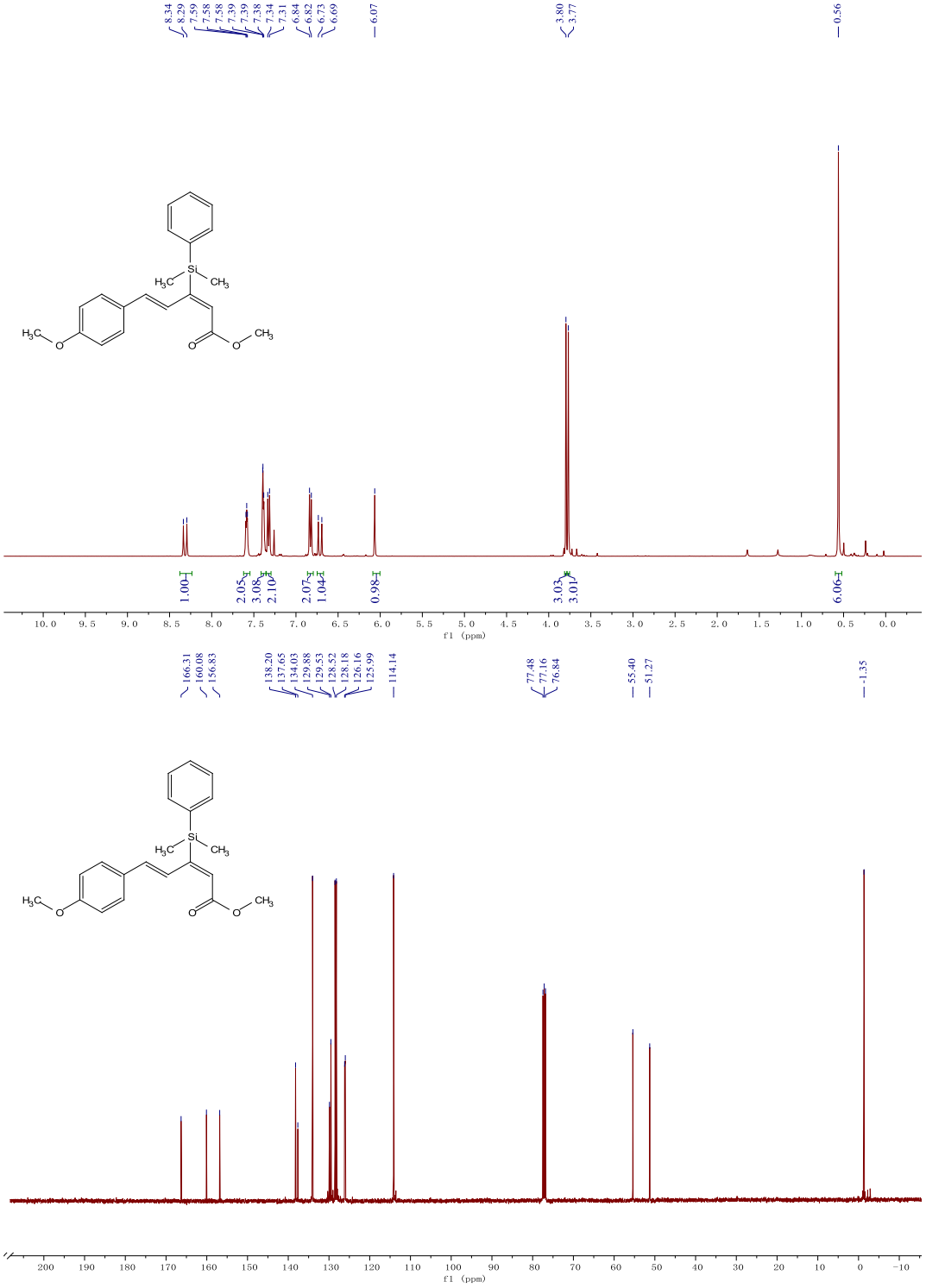
R_f: 0.22 (petroleum ether/ethyl acetate = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 16.6 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.42 – 7.35 (m, 3H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 16.6 Hz, 1H), 6.07 (s, 1H), 3.80 (s, 3H), 3.77

(s, 3H), 0.56 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.31, 160.08, 156.83, 138.20, 137.65, 134.03, 129.88, 129.53, 128.52, 128.18, 126.16, 125.99, 114.14, 55.40, 51.27, -1.35.

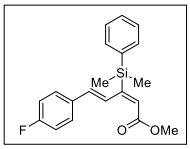
HRMS (ESI) (m/z): Calcd for $C_{21}H_{24}O_3SiNa^+$ $[M+Na]^+$: 375.1392, found: 375.1385.



methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-5-(4-fluorophenyl)penta-2,4-dienoate (11d)

Prepared according to General Procedure C from **1d** (40.8 mg, 0.20 mmol). The product **11d** was isolated in 86% yield (58.8 mg) by PTLC as colorless oil.

Regioselectivity: > 95:5 (β:α, crude ^{1}H NMR).



Eluent: petroleum ether/ethyl acetate (30:1).

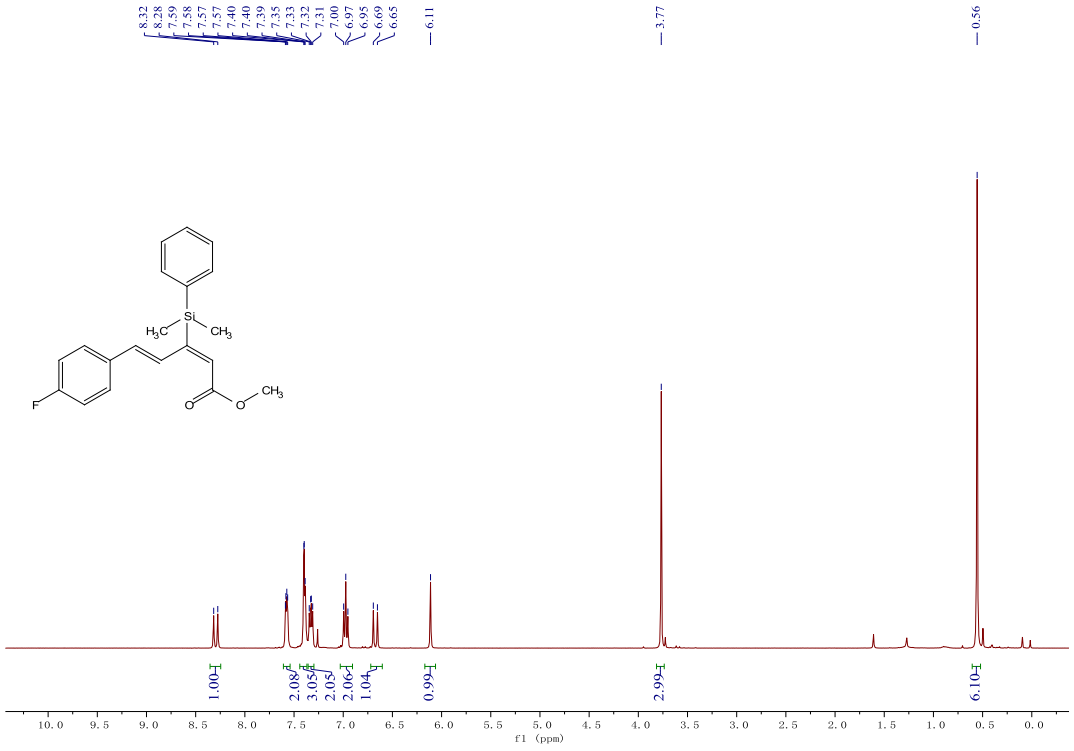
R_f: 0.38 (petroleum ether/ethyl acetate = 30:1).

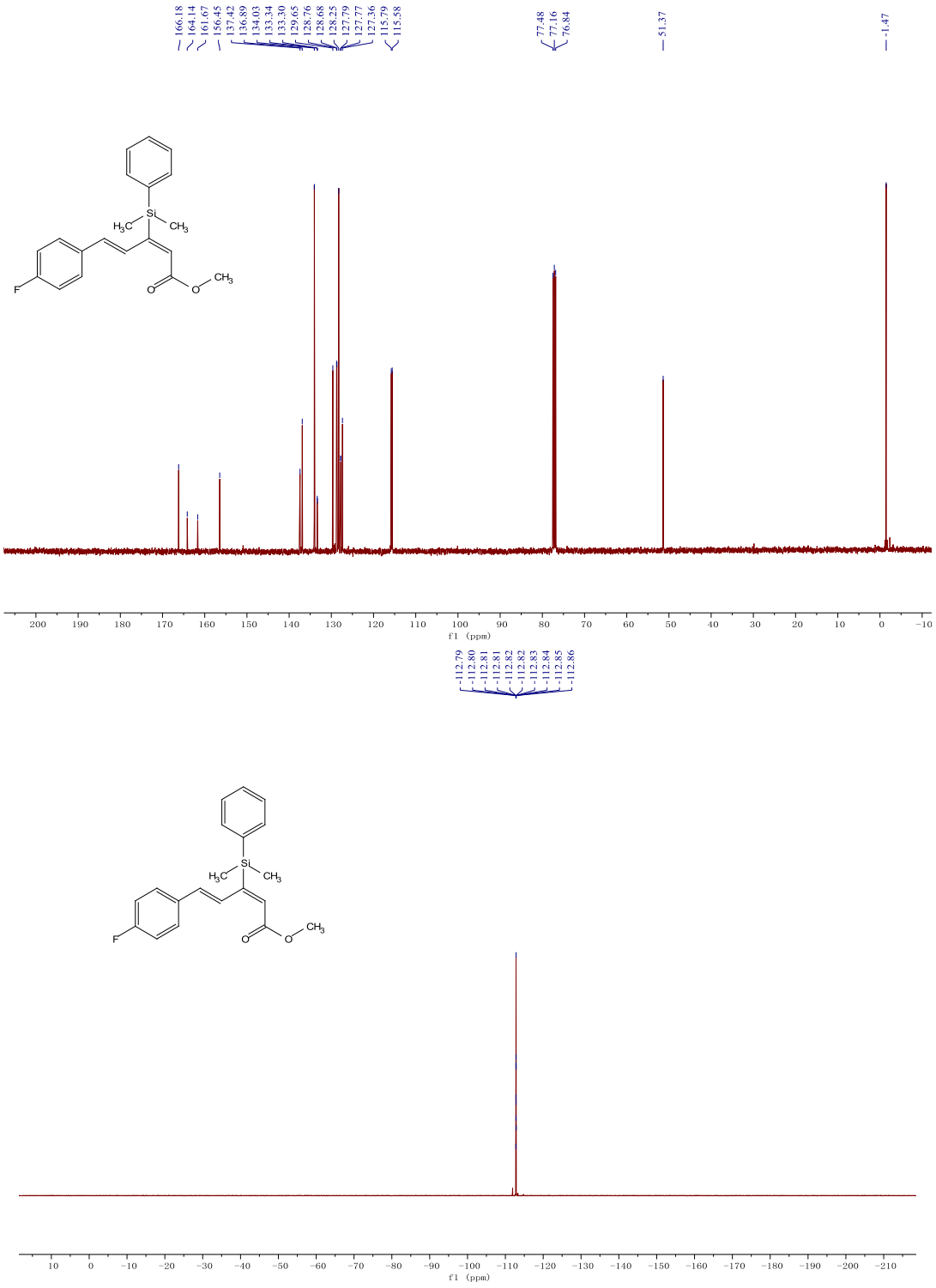
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 16.6 Hz, 1H), 7.58 (dd, *J* = 6.4, 2.6 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.33 (dd, *J* = 8.4, 5.6 Hz, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 16.7 Hz, 1H), 6.11 (s, 1H), 3.77 (s, 3H), 0.56 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 162.91 (d, *J* = 248.5 Hz) , 156.45, 137.42, 136.89, 134.03, 133.32 (d, *J* = 3.3 Hz), 129.65, 128.72 (d, *J* = 8.1 Hz), 128.25, 127.78 (d, *J* = 2.2 Hz), 127.36, 115.69 (d, *J* = 21.7 Hz), 51.37, -1.47.

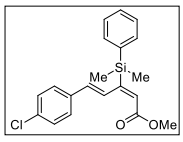
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.77 – -112.89 (m).

HRMS (ESI) (m/z): Calcd for $C_{20}H_{21}FO_2SiNa^+$ $[M+Na]^+$: 363.1193, found: 363.1192.





methyl (2*E*,4*E*)-5-(4-chlorophenyl)-3-(dimethyl(phenyl)silyl)penta-2,4-dienoate (11e)



Prepared according to General Procedure C from **1e** (44.1 mg, 0.20 mmol). H_2O (6 μL) was added after 1 h. The product **11e** was isolated in 83% yield (58.8 mg) by PTLC as colorless oil.

Regioselectivity: > 95:5 (β:α, crude ^{1}H NMR).

Eluent: petroleum ether/ethyl acetate (30:1).

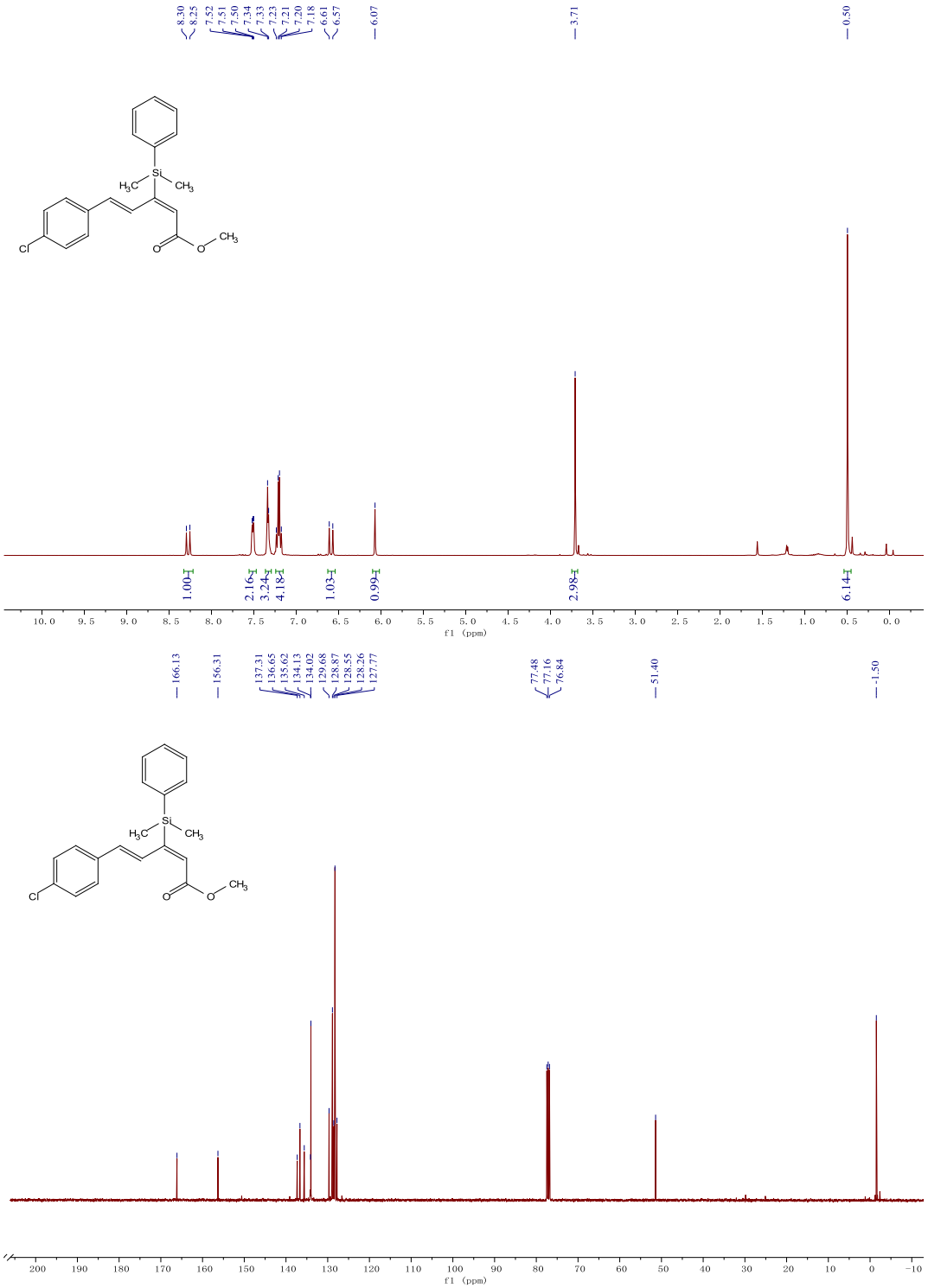
R_f: 0.33 (petroleum ether/ethyl acetate = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 16.6 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.38 – 7.29 (m, 3H), 7.24

– 7.16 (m, 4H), 6.59 (d, J = 16.6 Hz, 1H), 6.07 (s, 1H), 3.71 (s, 3H), 0.50 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.13, 156.31, 137.31, 136.65, 135.62, 134.13, 134.02, 129.68, 128.87, 128.55, 128.26, 127.77, 51.40, -1.50.

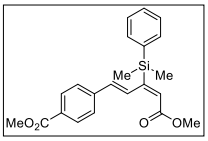
HRMS (ESI) (m/z): Calcd for $C_{20}H_{21}ClO_2SiNa^+$ $[M+Na]^+$: 379.0897, found: 379.0899.



methyl 4-((1*E*,3*E*)-3-(dimethyl(phenyl)silyl)-5-methoxy-5-oxopenta-1,3-dien-1-yl)benzoate (11f)

Prepared according to General Procedure C from **1f** (48.9 mg, 0.20 mmol). The product **11f** was isolated in 95% yield (72.6 mg) by PTLC as colorless oil.

Regioselectivity: 93:7 (β:α, crude ^{1}H NMR).



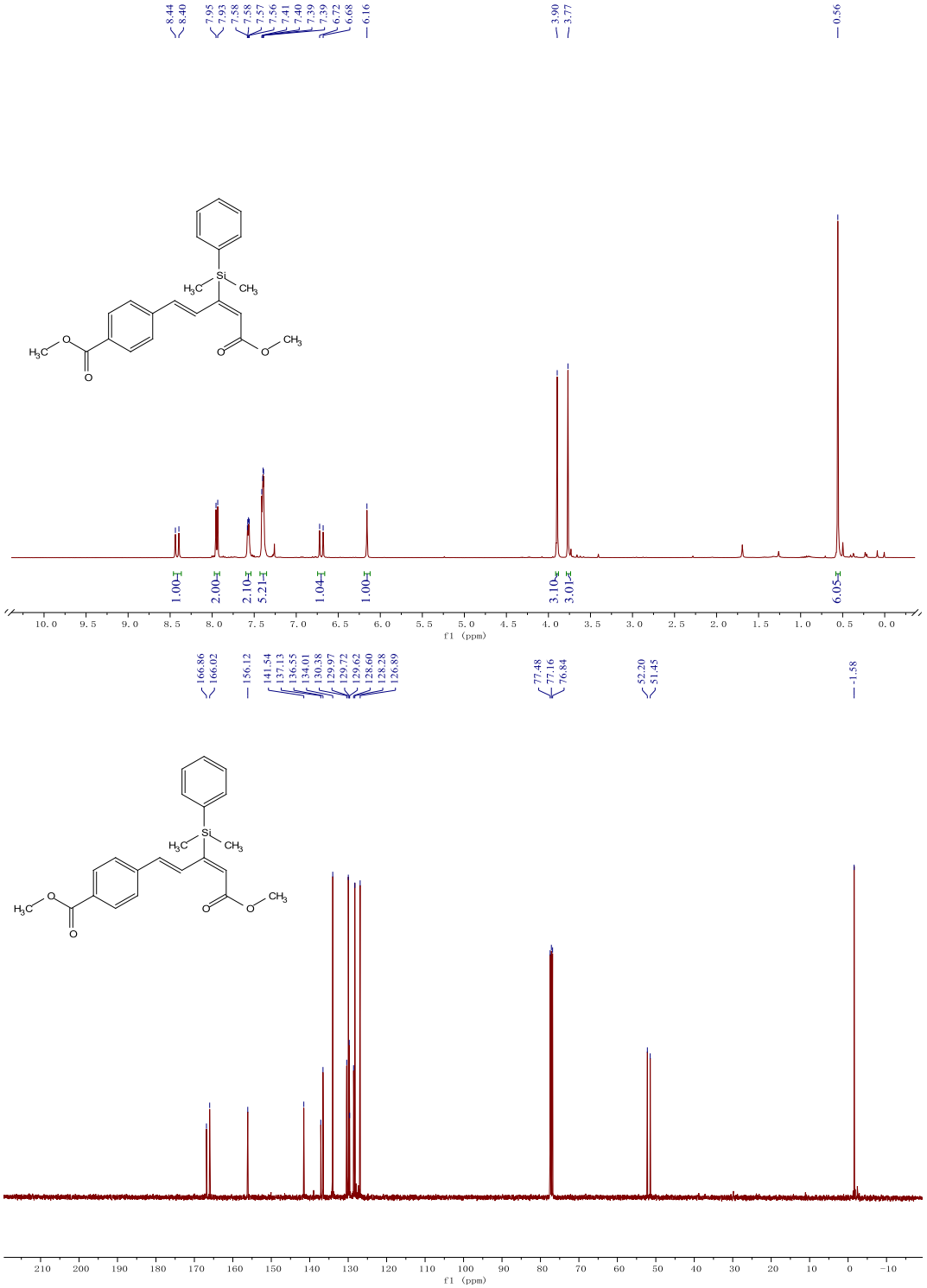
Eluent: petroleum ether/ethyl acetate (90:10).

R_f: 0.38 (petroleum ether/ethyl acetate = 90:10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 16.7 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.51 (m, 2H), 7.43 – 7.37 (m, 5H), 6.70 (d, *J* = 16.7 Hz, 1H), 6.16 (s, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 0.56 (s, 6H).

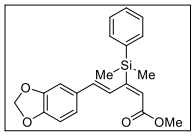
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.86, 166.02, 156.12, 141.54, 137.13, 136.55, 134.01, 130.38, 129.97, 129.72, 129.62, 128.60, 128.28, 126.89, 52.20, 51.45, -1.58.

HRMS (ESI) (m/z): Calcd for $C_{22}H_{24}O_4SiNa^+$ $[M+Na]^+$: 403.1342, found: 403.1336.



methyl (2*E*,4*E*)-5-(benzo[d][1,3]dioxol-5-yl)-3-(dimethyl(phenyl)silyl)penta-2,4-dienoate (11g)

Prepared according to General Procedure C from **1g** (46.0 mg, 0.20 mmol). H_2O (16 μL) was added after 1 h. The product **11g** was isolated in 95% yield (72.2 mg) by PTLC as yellow oil.



Regioselectivity: 97:3 (β:α, crude ^{1}H NMR).

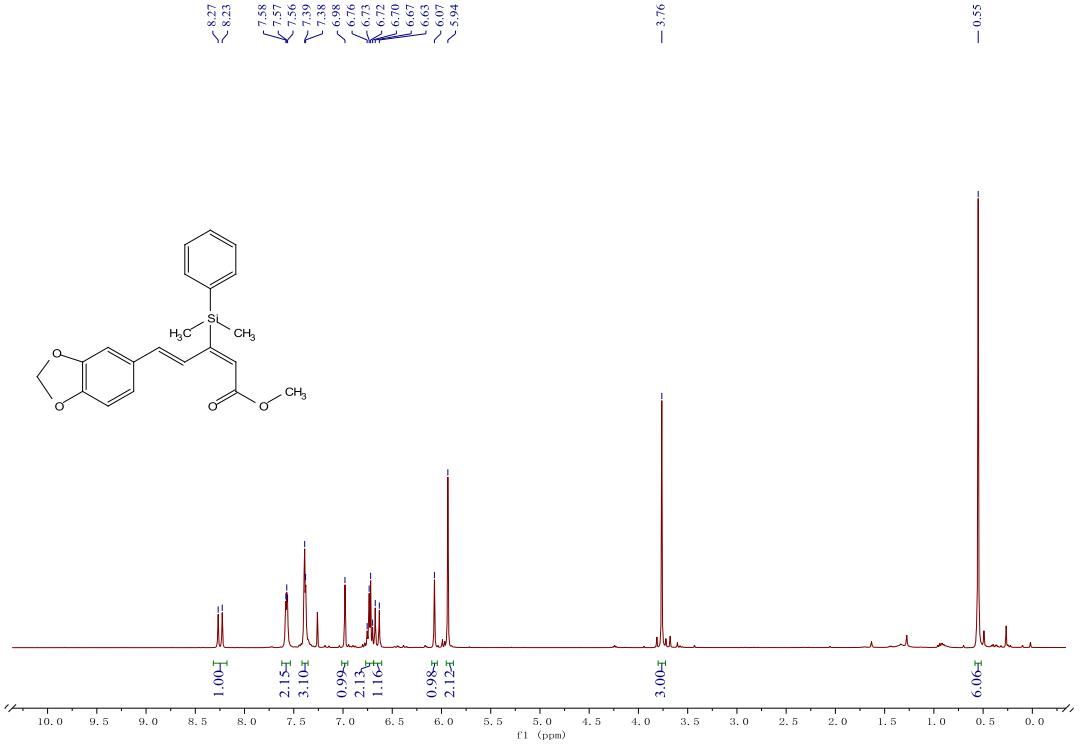
Eluent: petroleum ether/ethyl acetate (20:1).

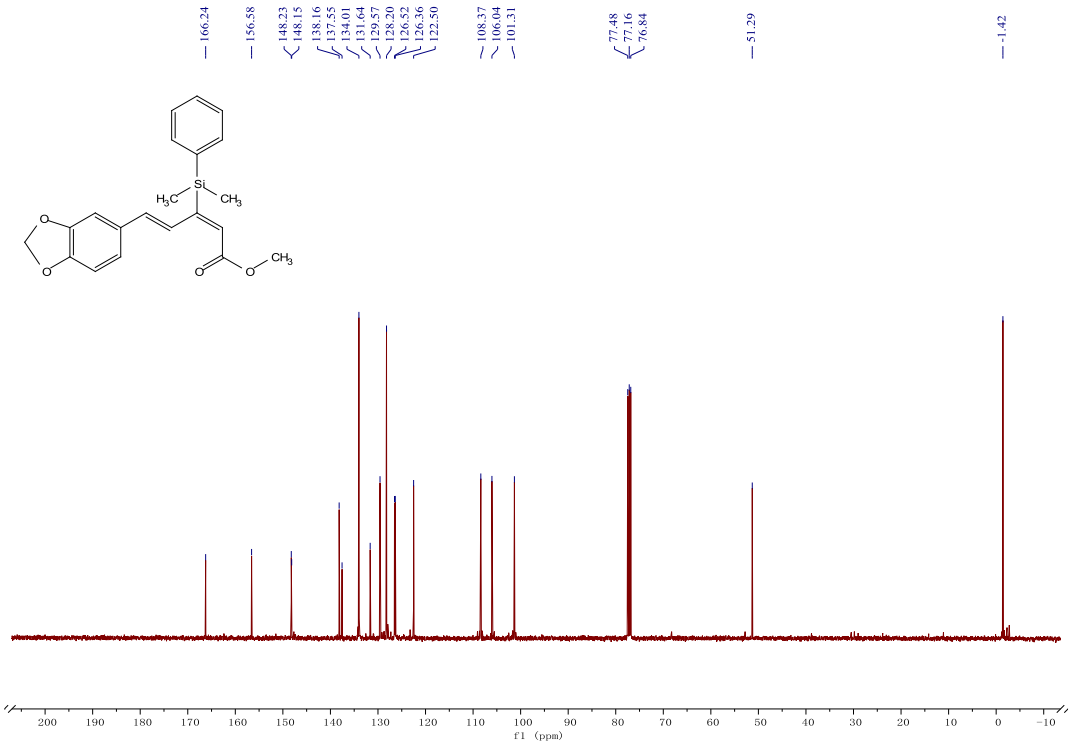
R_f: 0.22 (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 16.6 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.38 (d, *J* = 3.7 Hz, 3H), 6.98 (s, 1H), 6.73 (q, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 16.6 Hz, 1H), 6.07 (s, 1H), 5.94 (s, 2H), 3.76 (s, 3H), 0.55 (s, 6H).

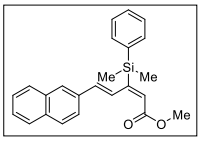
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.24, 156.58, 148.23, 148.15, 138.16, 137.55, 134.01, 131.64, 129.57, 128.20, 126.52, 126.36, 122.50, 108.37, 106.04, 101.31, 51.29, -1.42.

HRMS (ESI) (m/z): Calcd for $C_{21}H_{22}O_4SiNa^+$ $[M+Na]^+$: 389.1185, found: 389.1186.





methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-5-(naphthalen-2-yl)penta-2,4-dienoate (11h)



Prepared according to General Procedure C from **1h** (47.3 mg, 0.20 mmol). The product **11h** was isolated in 98% yield (72.2 mg) by PTLC as yellow oil.

Regioselectivity: 95:5 (β:α, crude ^{1}H NMR).

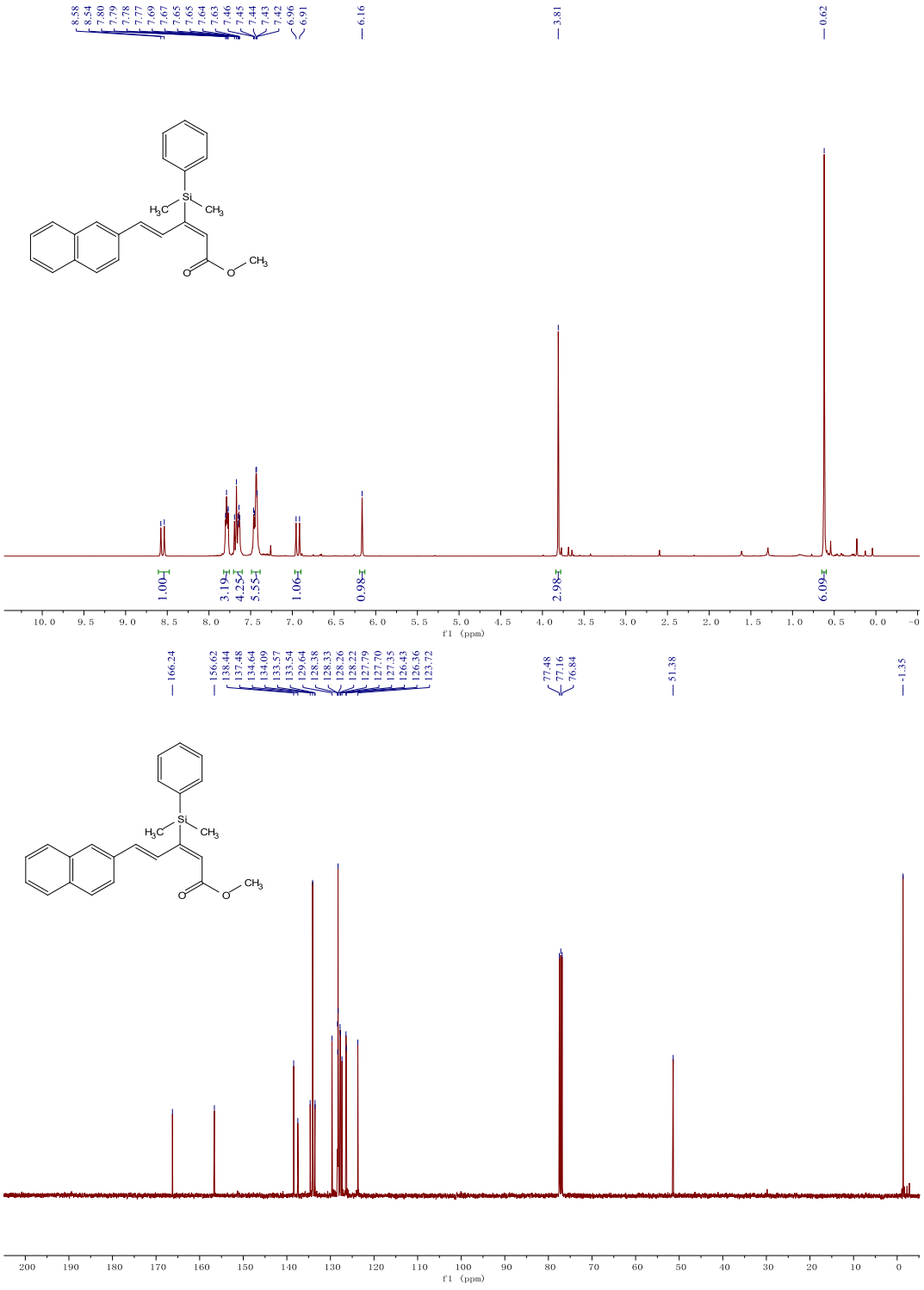
Eluent: petroleum ether/ethyl acetate (30:1).

R_f: 0.26 (petroleum ether/ethyl acetate = 30:1)

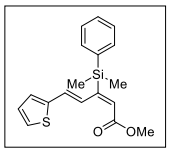
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 16.6 Hz, 1H), 7.78 (dd, *J* = 8.6, 4.4 Hz, 3H), 7.68 (d, *J* = 9.5 Hz, 2H), 7.64 (dd, *J* = 6.1, 2.7 Hz, 2H), 7.49 – 7.38 (m, 5H), 6.93 (d, *J* = 16.6 Hz, 1H), 6.16 (s, 1H), 3.81 (s, 3H), 0.62 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.24, 156.62, 138.44, 137.48, 134.64, 134.09, 133.57, 133.54, 129.64, 128.38, 128.33, 128.26, 128.22, 127.79, 127.70, 127.35, 126.43, 126.36, 123.72, 51.38, -1.35.

HRMS (ESI) (m/z): Calcd for $C_{24}H_{24}O_2SiNa^+$ $[M+Na]^{+\cdot}$ 395.1443, found: 395.1440.



methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-5-(thiophen-2-yl)penta-2,4-dienoate (11i)



Prepared according to General Procedure C from **1i** (38.4 mg, 0.20 mmol). The product **11i** was isolated in 91% yield (59.6 mg) by PTLC as yellow oil.

Regioselectivity: > 95:5 (β:α, crude ^{1}H NMR).

Eluent: petroleum ether/ethyl acetate (20:1).

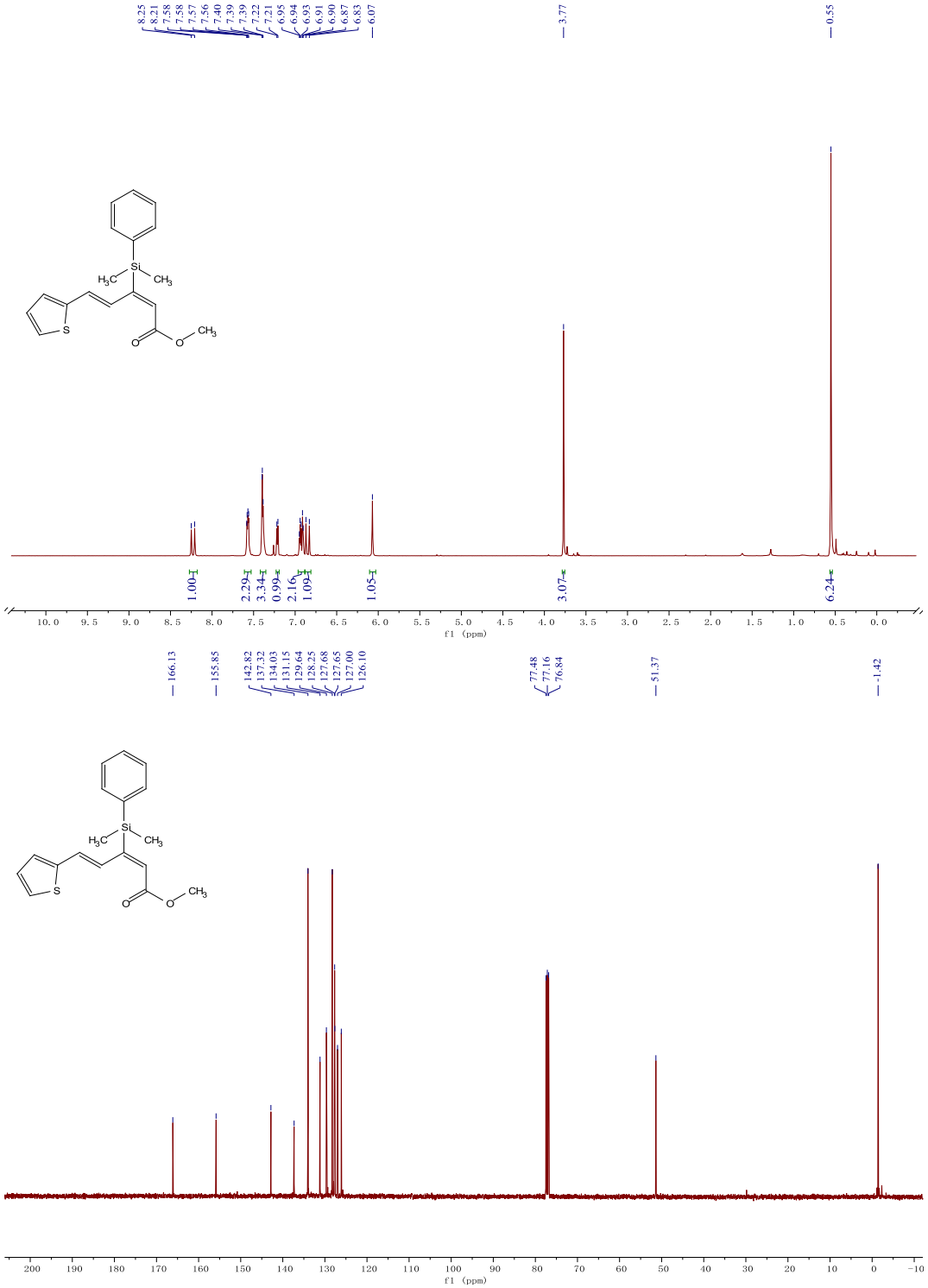
R_f: 0.29 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 16.4 Hz, 1H), 7.57 (dd, *J* = 6.5, 2.7 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.21 (d, *J* = 5.0 Hz, 1H), 6.97 – 6.89 (m, 2H), 6.85 (d, *J* = 16.4 Hz, 1H), 6.07 (s, 1H), 3.77 (s, 3H),

0.55 (s, 6H).

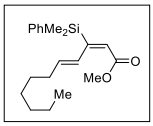
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.13, 155.85, 142.82, 137.32, 134.03, 131.15, 129.64, 128.25, 127.68, 127.65, 127.00, 126.10, 51.37, -1.42.

HRMS (ESI) (m/z): Calcd for $C_{18}H_{20}O_2SSiNa^+$ $[M+Na]^+$: 351.0851, found: 351.0849.



methyl (*2E*,*4E*)-3-(dimethyl(phenyl)silyl)undeca-2,4-dienoate (11j)

Prepared according to General Procedure C from **1j** (38.9 mg, 0.20 mmol). The product **11j** was isolated in 85% yield (62.3 mg) by PTLC as yellow oil.



Regioselectivity: 92:3:5 (β:α:**13j**, crude ^{1}H NMR).

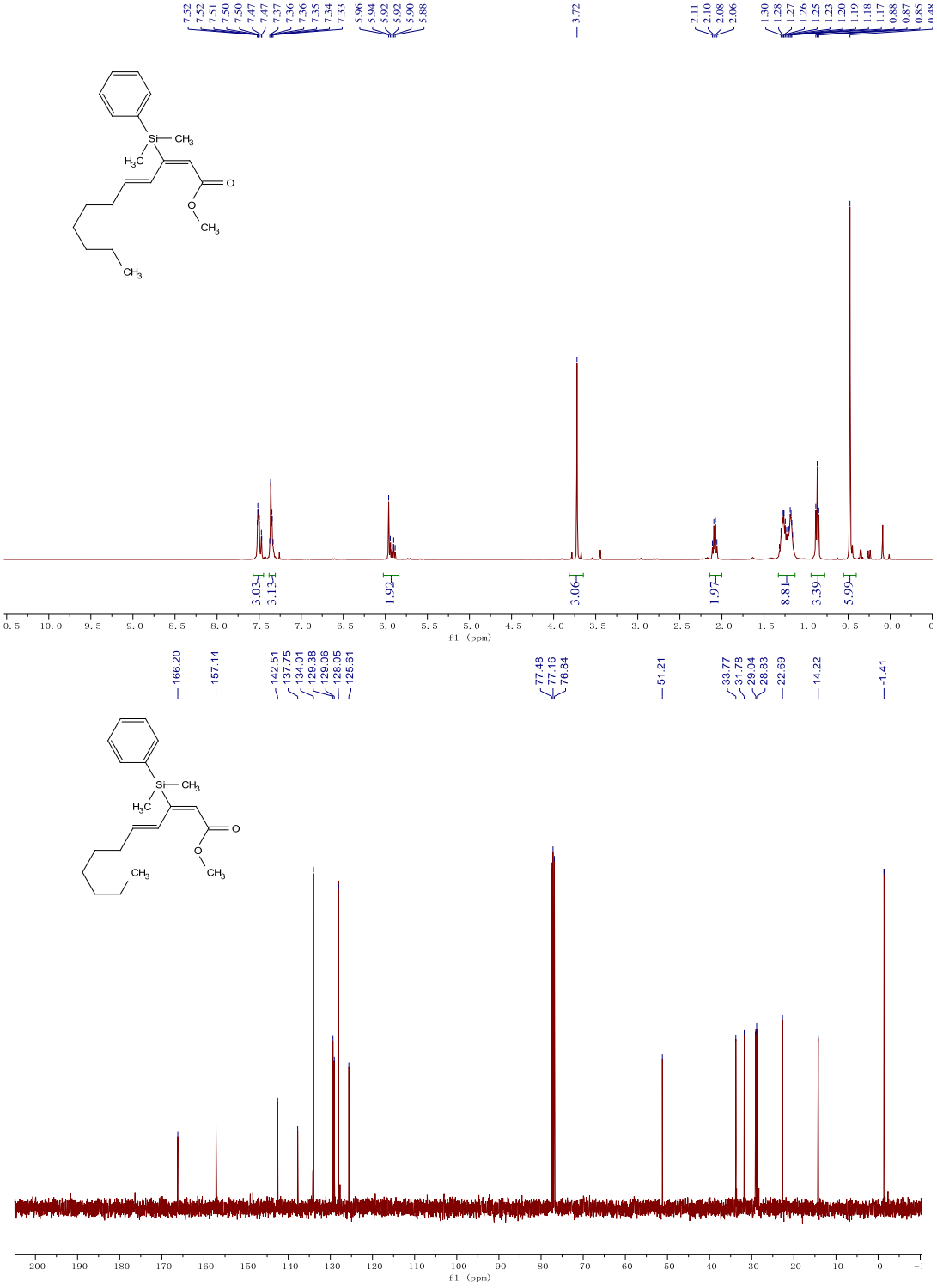
Eluent: petroleum ether/ethyl acetate (50:1).

R_f: 0.20 (petroleum ether/ethyl acetate = 50:1)

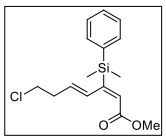
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.45 (m, 3H), 7.35 (dd, *J* = 5.8, 1.6 Hz, 3H), 6.00 – 5.86 (m, 2H), 3.72 (s, 3H), 2.09 (q, *J* = 7.2 Hz, 2H), 1.35 – 1.10 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.48 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.20, 157.14, 142.51, 137.75, 134.01, 129.38, 129.06, 128.05, 125.61, 51.21, 33.77, 31.78, 29.04, 28.83, 22.69, 14.22, -1.41.

HRMS (ESI) (m/z): Calcd for $C_{20}H_{30}O_2SiNa^+$ $[M+Na]^+$: 353.1913, found: 353.1906.



methyl (2*E*,4*E*)-7-chloro-3-(dimethyl(phenyl)silyl)hepta-2,4-dienoate (11k)



Prepared according to General Procedure C from **1k** (34.5 mg, 0.20 mmol). The product **11k** was isolated in 91% yield (59.7 mg) by PTLC as yellow oil.

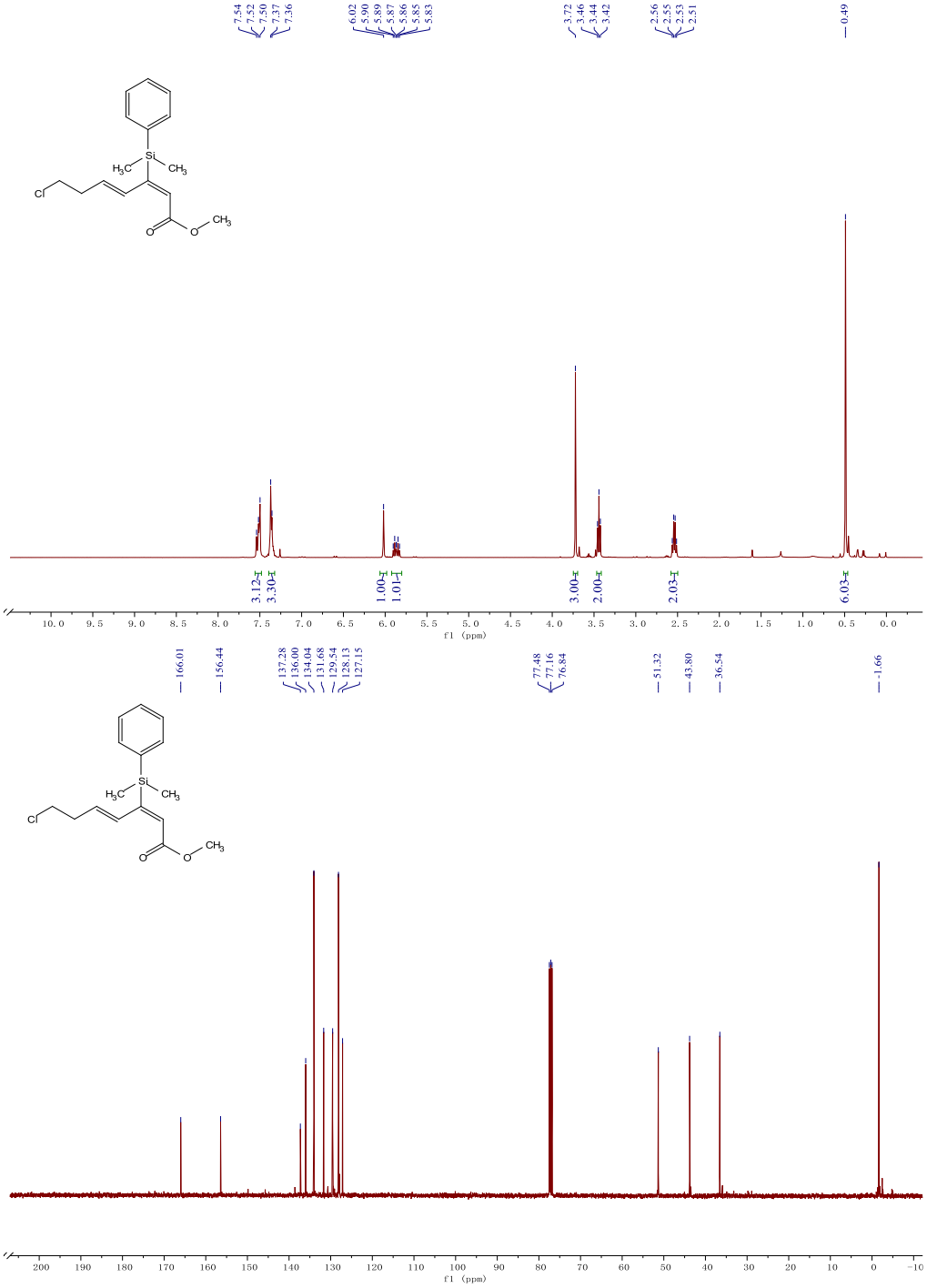
Regioselectivity: 92:4:4 (β:α:**13k**, crude ^{1}H NMR).

Eluent: petroleum ether/ethyl acetate (30:1). **R_f**: 0.32 (petroleum ether/ethyl acetate = 30:1)

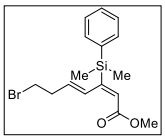
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 3H), 7.40 – 7.32 (m, 3H), 6.02 (s, 1H), 5.87 (dt, *J* = 16.0, 6.9 Hz, 1H), 3.72 (s, 3H), 3.44 (t, *J* = 6.8 Hz, 2H), 2.54 (q, *J* = 6.8 Hz, 2H), 0.49 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.01, 156.44, 137.28, 136.00, 134.04, 131.68, 129.54, 128.13, 127.15, 51.32, 43.80, 36.54, -1.66.

HRMS (ESI) (m/z): Calcd for $C_{16}H_{21}ClO_2SiNa^+$ [M+Na]$^+$: 331.0897, found: 331.0892.



methyl (2*E*,4*E*)-7-bromo-3-(dimethyl(phenyl)silyl)hepta-2,4-dienoate (11l)



Prepared according to General Procedure C from **1l** (43.4 mg, 0.20 mmol). The product **11l** was isolated in 89% yield (66.9 mg) by PTLC as yellow oil.

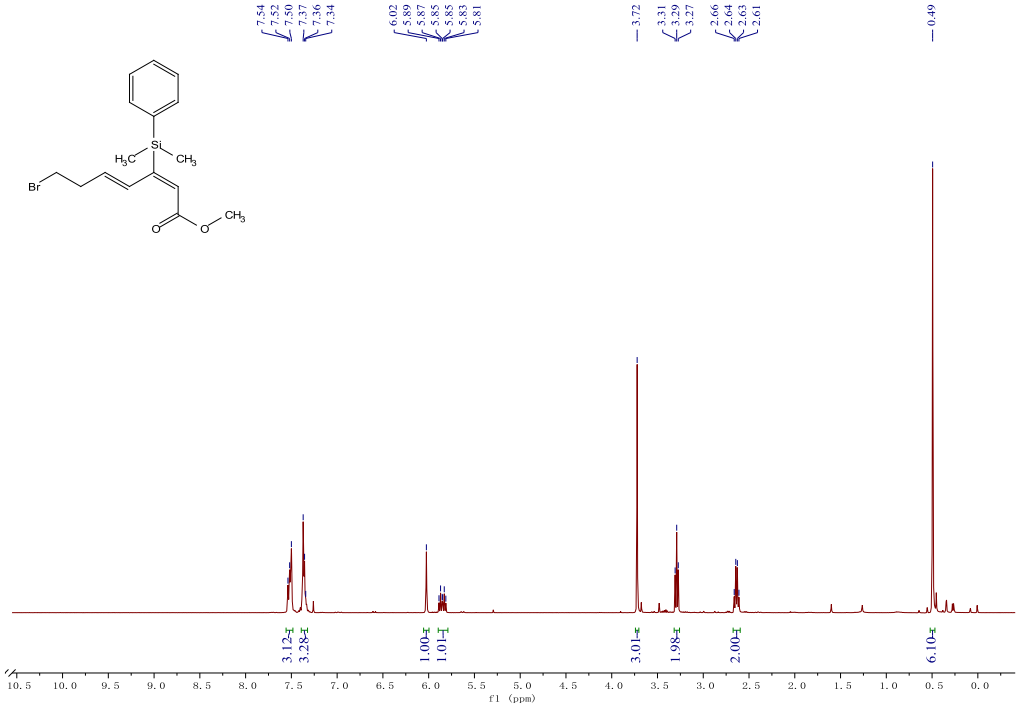
Regioselectivity: 92:4:4 (β:α:**13l**, crude ^{1}H NMR).

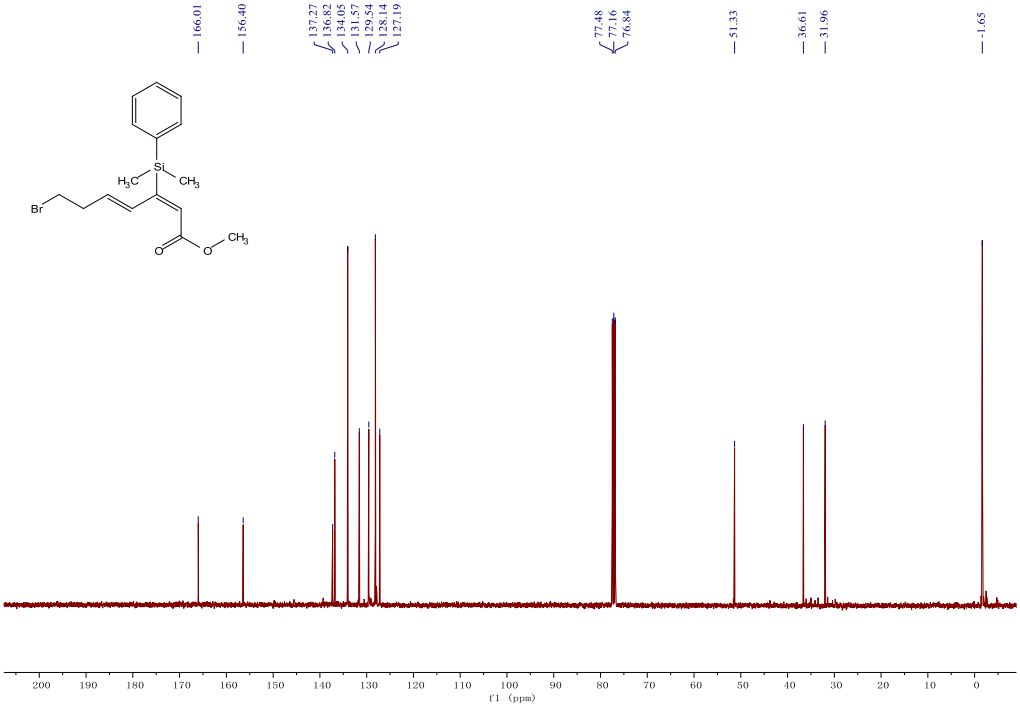
Eluent: petroleum ether/ethyl acetate (30:1). **R_f**: 0.32 (petroleum ether/ethyl acetate = 30:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 3H), 7.41 – 7.30 (m, 3H), 6.02 (s, 1H), 5.85 (dt, *J* = 16.0, 6.9 Hz, 1H), 3.72 (s, 3H), 3.29 (t, *J* = 6.9 Hz, 2H), 2.64 (q, *J* = 6.9 Hz, 2H), 0.49 (s, 6H).

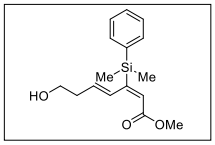
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.01, 156.40, 137.27, 136.82, 134.05, 131.57, 129.54, 128.14, 127.19, 51.33, 36.61, 31.96, -1.65.

HRMS (ESI) (m/z): Calcd for $C_{16}H_{21}{}^{79}BrO_2Na^+$ $[M+Na]^{+:}$ 375.0392, found: 375.0388.





methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-7-hydroxyhepta-2,4-dienoate (11m)



Prepared according to General Procedure C from **1m** (30.8 mg, 0.20 mmol). The product **11m** was isolated in 87% yield (50.5 mg) by PTLC as yellow oil.

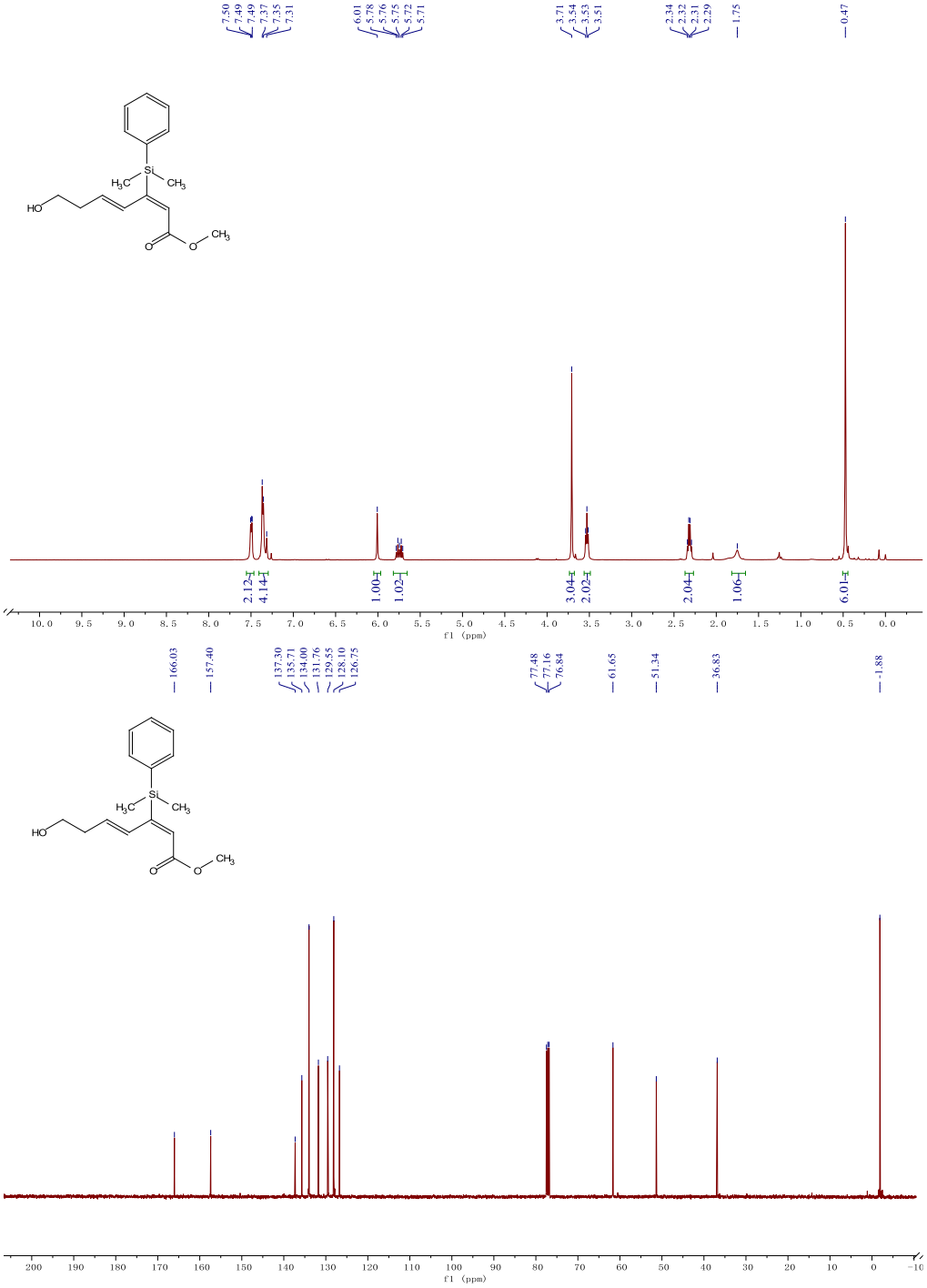
Regioselectivity: 98:2 (β:α, crude ^{1}H NMR).

Eluent: petroleum ether/ethyl acetate (4:1). **R_f**: 0.22 (petroleum ether/ethyl acetate = 4:1)

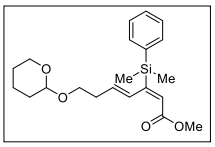
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 2H), 7.43 – 7.28 (m, 4H), 6.01 (s, 1H), 5.83 – 5.69 (m, 1H), 3.71 (s, 3H), 3.53 (t, *J* = 6.1 Hz, 2H), 2.32 (q, *J* = 6.4 Hz, 2H), 1.75 (s, 1H), 0.47 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.03, 157.40, 137.30, 135.71, 134.00, 131.76, 129.55, 128.10, 126.75, 61.65, 51.34, 36.83, -1.88.

HRMS(ESI) (m/z): Calcd for $C_{16}H_{22}O_3SiNa^+$ $[M+Na]^+$: 313.1236, found: 313.1240.



methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-7-((tetrahydro-2*H*-pyran-2-yl)oxy)hepta-2,4-dienoate (11n)



Prepared according to General Procedure C from **1n** (47.7 mg, 0.20 mmol). The product **11n** was isolated in 89% yield (70.3 mg) by PTLC as yellow oil.

Regioselectivity: 95:1:4 (β:α: **13n**, crude ^{1}H NMR).

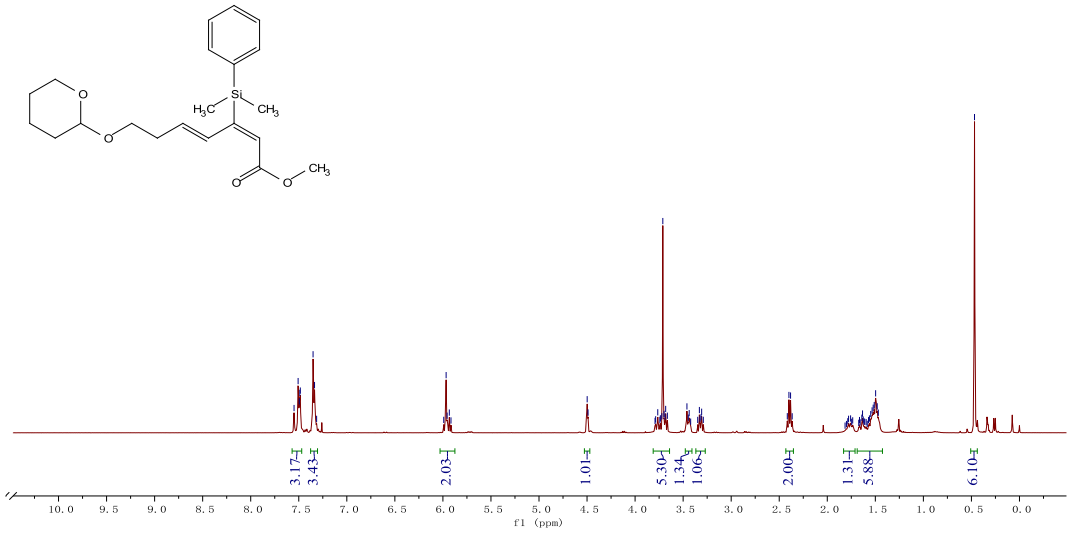
Eluent: petroleum ether/ethyl acetate (92:8).

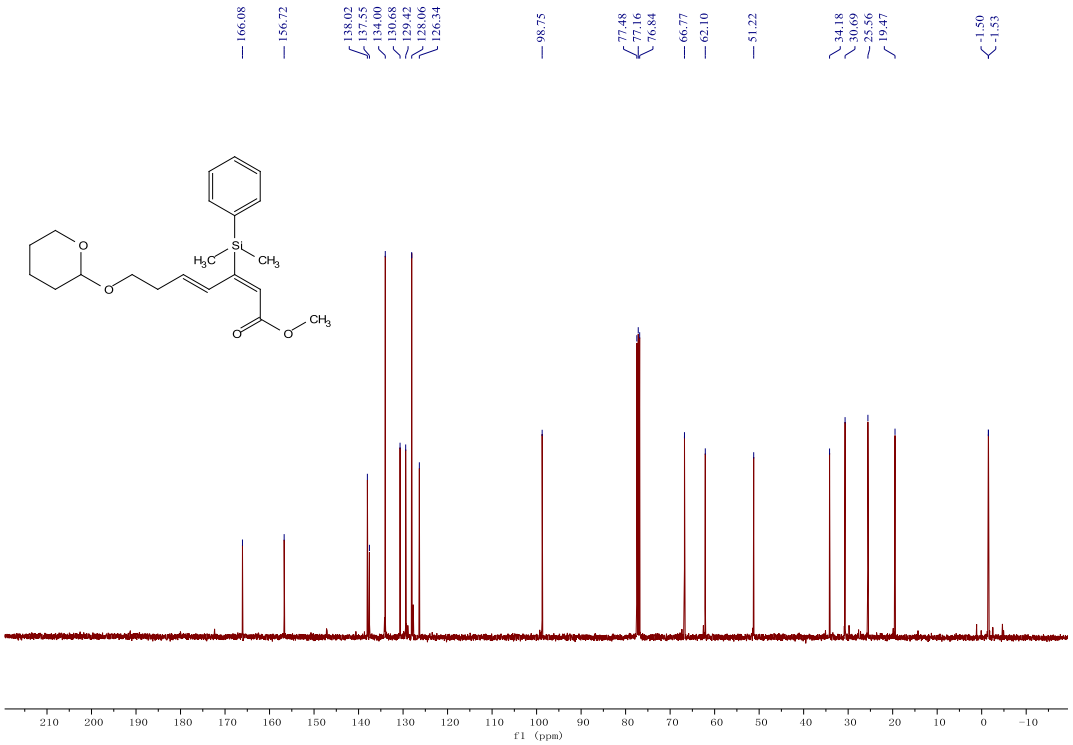
R$_f$: 0.34 (petroleum ether/ethyl acetate = 92:8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 3H), 7.38 – 7.30 (m, 3H), 6.01 – 5.89 (m, 2H), 4.49 (d, *J* = 3.5 Hz, 1H), 3.80 – 3.64 (m, 5H), 3.44 (dd, *J* = 9.6, 5.9 Hz, 1H), 3.32 (dt, *J* = 9.2, 6.9 Hz, 1H), 2.39 (q, *J* = 6.8 Hz, 2H), 1.84 – 1.71 (m, 1H), 1.69 – 1.40 (m, 5H), 0.47 (s, 6H).

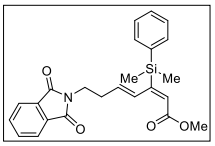
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.08, 156.72, 138.02, 137.55, 134.00, 130.68, 129.42, 128.06, 126.34, 98.75, 66.77, 62.10, 51.22, 34.18, 30.69, 25.56, 19.47, -1.50, -1.53.

HRMS (ESI) (m/z): Calcd for $C_{21}H_{30}O_4SiNa^+$ $[M+Na]^+$: 397.1811, found: 397.1812.





methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-7-(1,3-dioxoisoindolin-2-yl)hepta-2,4-dienoate (11o)



Prepared according to General Procedure C from **1o** (56.7 mg, 0.20 mmol). H_2O (6 μL) was added after 1 h. The product **11o** was isolated in 89% yield (79.1 mg) by PTLC as yellow oil.

Regioselectivity: 93:3:4 (β:α:**13o**, crude ^{1}H NMR).

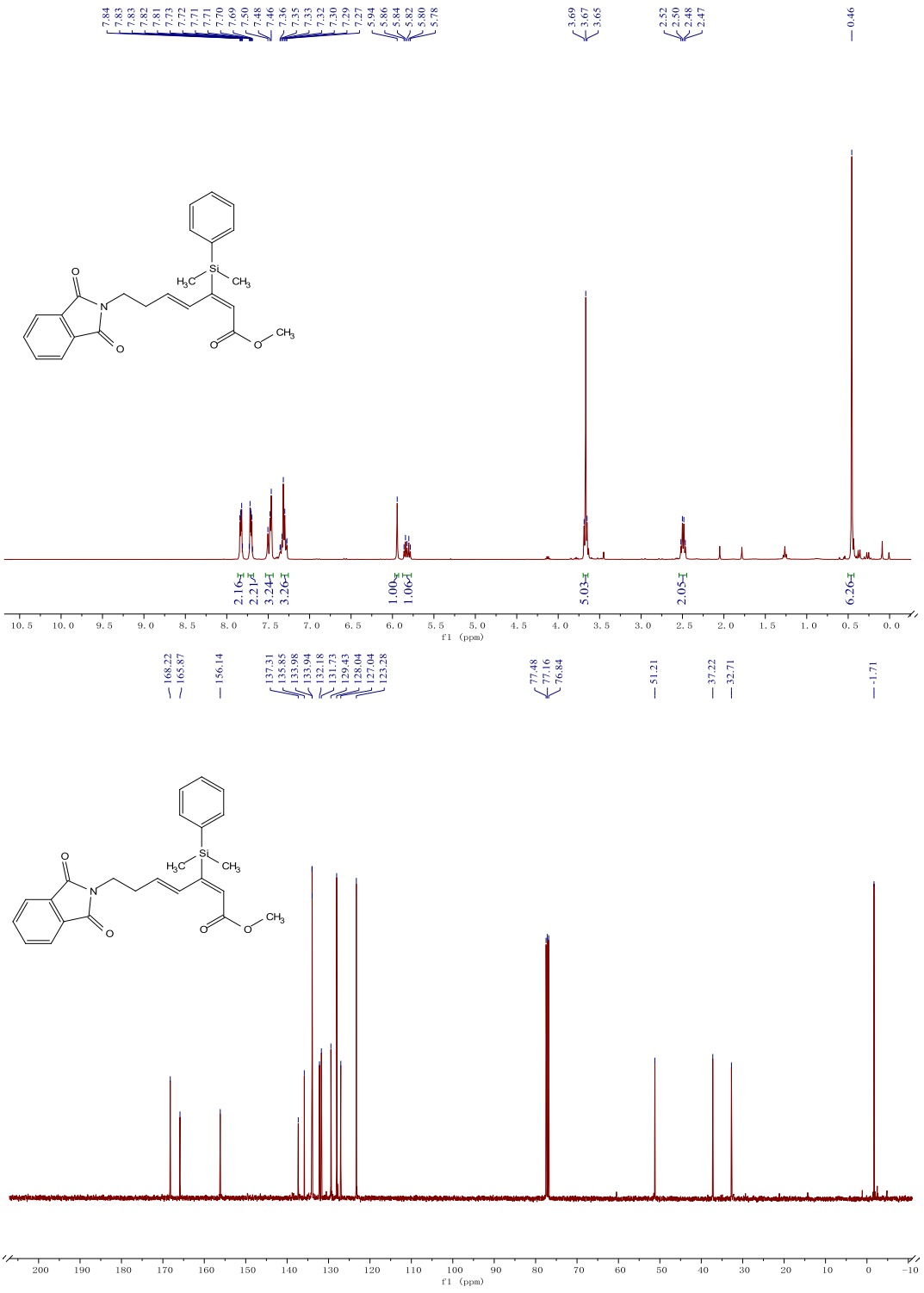
Eluent: petroleum ether/ethyl acetate (9:1).

R_f: 0.27 (petroleum ether/ethyl acetate = 9:1)

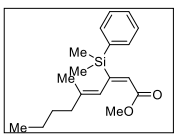
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.75 – 7.67 (m, 2H), 7.54 – 7.44 (m, 3H), 7.37 – 7.25 (m, 3H), 5.94 (s, 1H), 5.88 – 5.75 (m, 1H), 3.70 – 3.64 (m, 5H), 2.49 (q, *J* = 7.0 Hz, 2H), 0.46 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.22, 165.87, 156.14, 137.31, 135.85, 133.98, 133.94, 132.18, 131.73, 129.43, 128.04, 127.04, 123.28, 51.21, 37.22, 32.71, -1.71.

HRMS (ESI) (m/z): Calcd for $C_{24}H_{25}NO_4SiNa^+$ $[M+Na]^{+:}$ 442.1451, found: 442.1447.



methyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-5-methylnona-2,4-dienoate (11p)



Prepared according to General Procedure C from **1p** (36.1 mg, 0.20 mmol). The product **11p** was isolated in 72% yield (45.4 mg) by PTLC as colorless oil.

Eluent: petroleum ether/ethyl acetate (50:1).

Regioselectivity: > 95:5 (β:α, crude ^{1}H NMR).

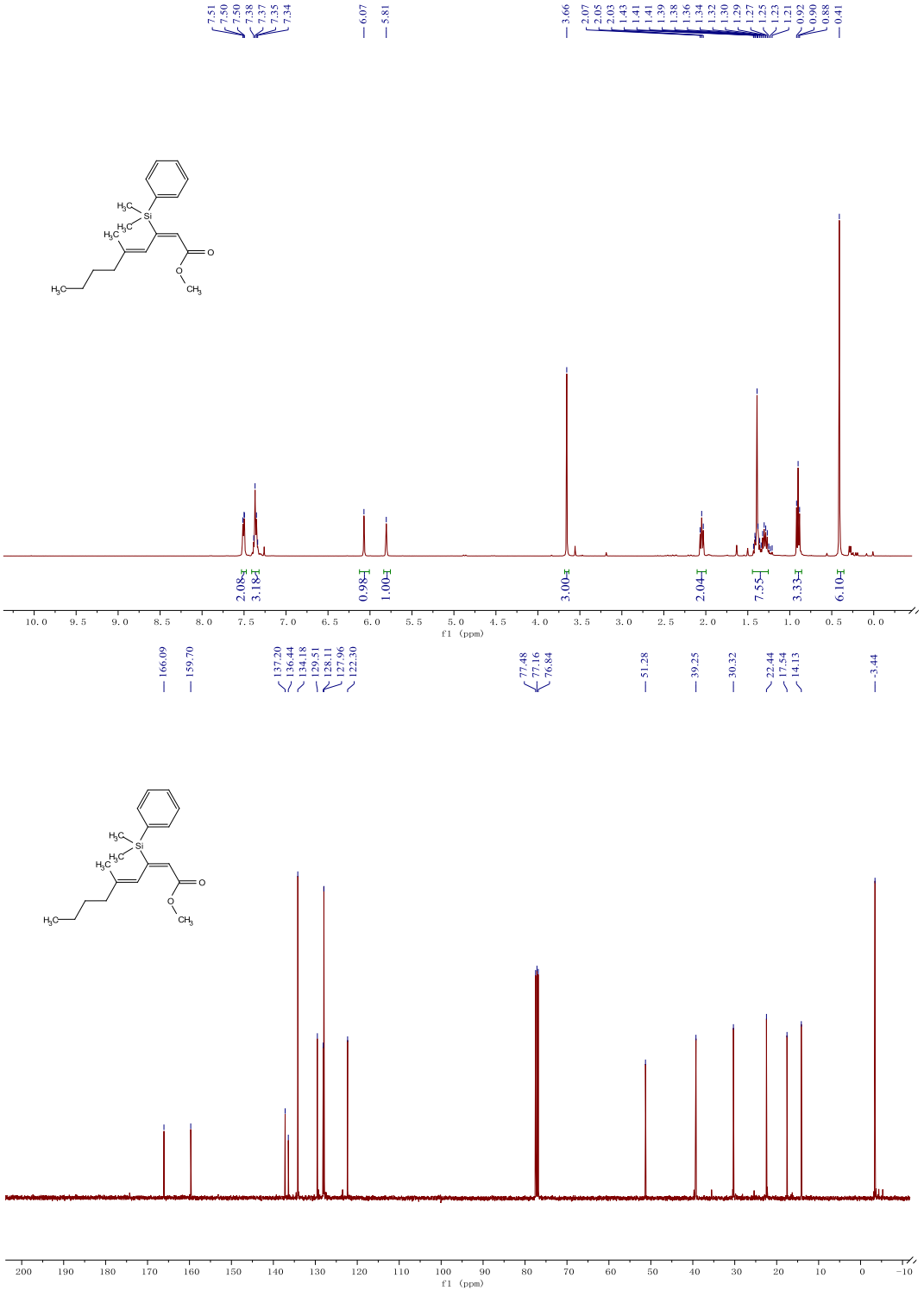
R_f: 0.18 (petroleum ether/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 2H), 7.41 – 7.29 (m, 3H), 6.07 (s, 1H), 5.81 (s, 1H), 3.66

(s, 3H), 2.05 (t, J = 7.4 Hz, 2H), 1.44 – 1.18 (m, 7H), 0.90 (t, J = 7.1 Hz, 3H), 0.41 (s, 6H).

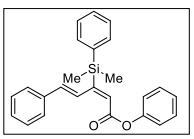
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.09, 159.70, 137.20, 136.44, 134.18, 129.51, 128.11, 127.96, 122.30, 51.28, 39.25, 30.32, 22.44, 17.54, 14.13, -3.44.

HRMS(ESI) (m/z): Calcd for $C_{19}H_{28}O_2SiNa^+$ $[M+Na]^+$: 339.1756, found: 339.1757.



phenyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-5-phenylpenta-2,4-dienoate (11q)

Prepared according to General Procedure C from **1q** (49.7 mg, 0.20 mmol). The product **11q** was isolated in 95% yield (73.4 mg) by PTLC as yellow oil.



Regioselectivity: > 95:5 (β:α, crude ^{1}H NMR).

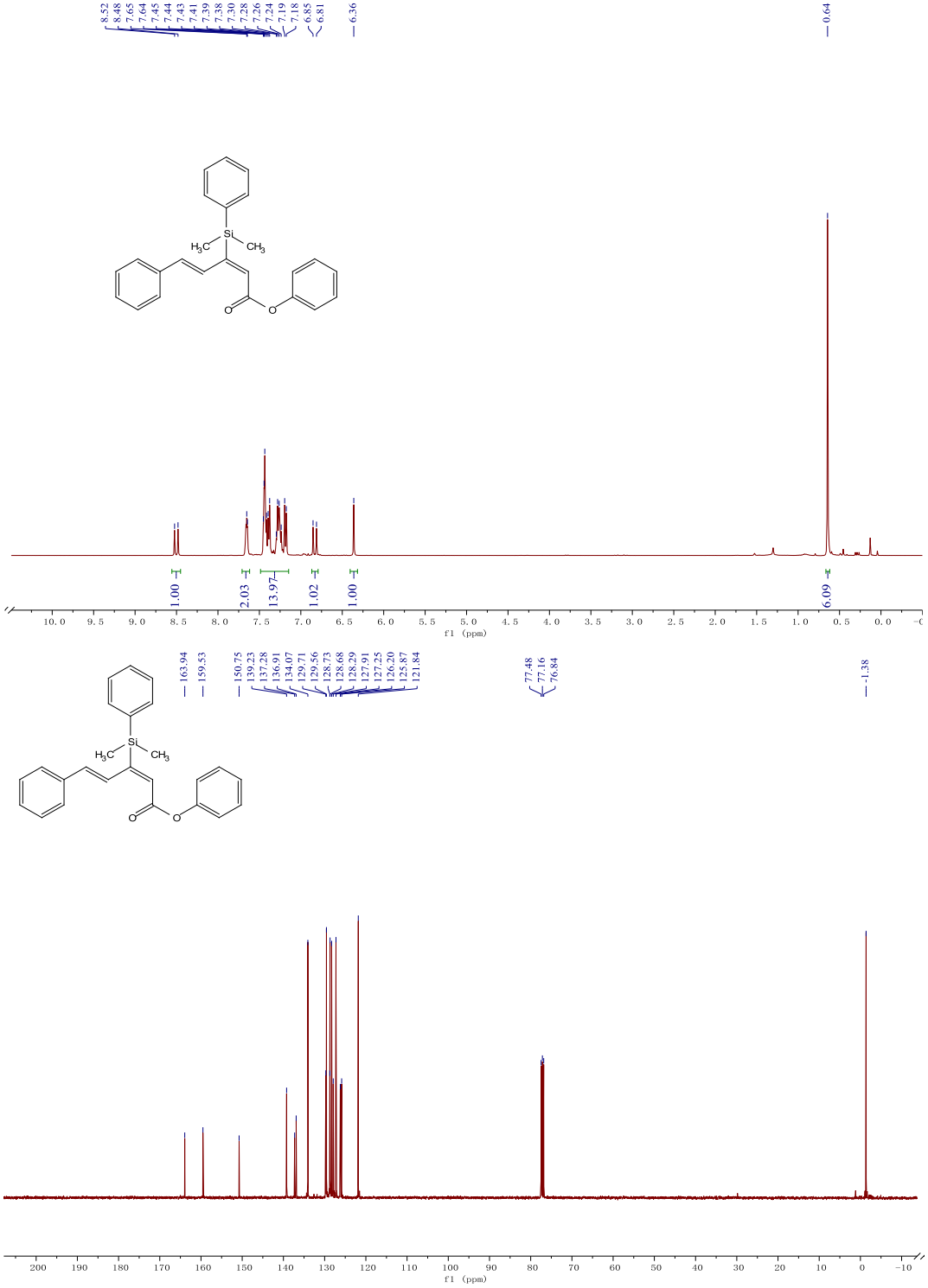
Eluent: petroleum ether/ethyl acetate (30:1).

R_f: 0.39 (petroleum ether/ethyl acetate = 30:1)

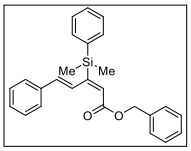
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 16.6 Hz, 1H), 7.65 (d, *J* = 3.4 Hz, 2H), 7.48 – 7.13 (m, 13H), 6.83 (d, *J* = 16.6 Hz, 1H), 6.36 (s, 1H), 0.64 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.94, 159.53, 150.75, 139.23, 137.28, 136.91, 134.07, 129.71, 129.56, 128.73, 128.68, 128.29, 127.91, 127.25, 126.20, 125.87, 121.84, -1.38.

HRMS (ESI) (m/z): Calcd for $C_{25}H_{24}O_2SiNa^+$ $[M+Na]^{+}$: 407.1443, found: 407.1438.



benzyl (2*E*,4*E*)-3-(dimethyl(phenyl)silyl)-5-phenylpenta-2,4-dienoate (11r)



Prepared according to General Procedure C from **1r** (52.5 mg, 0.20 mmol). The product **11r** was isolated in 96% yield (76.4 mg) by PTLC as yellow oil.

Regioselectivity: > 95:5 (β:α, crude ^{1}H NMR).

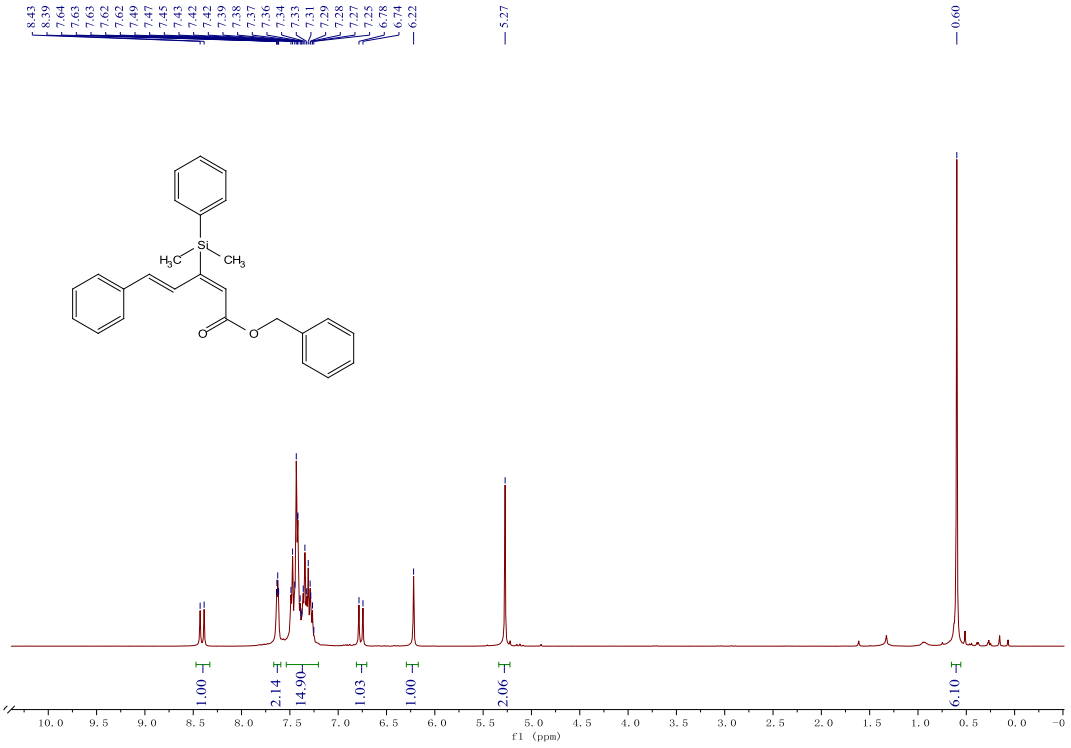
Eluent: petroleum ether/ethyl acetate (30:1).

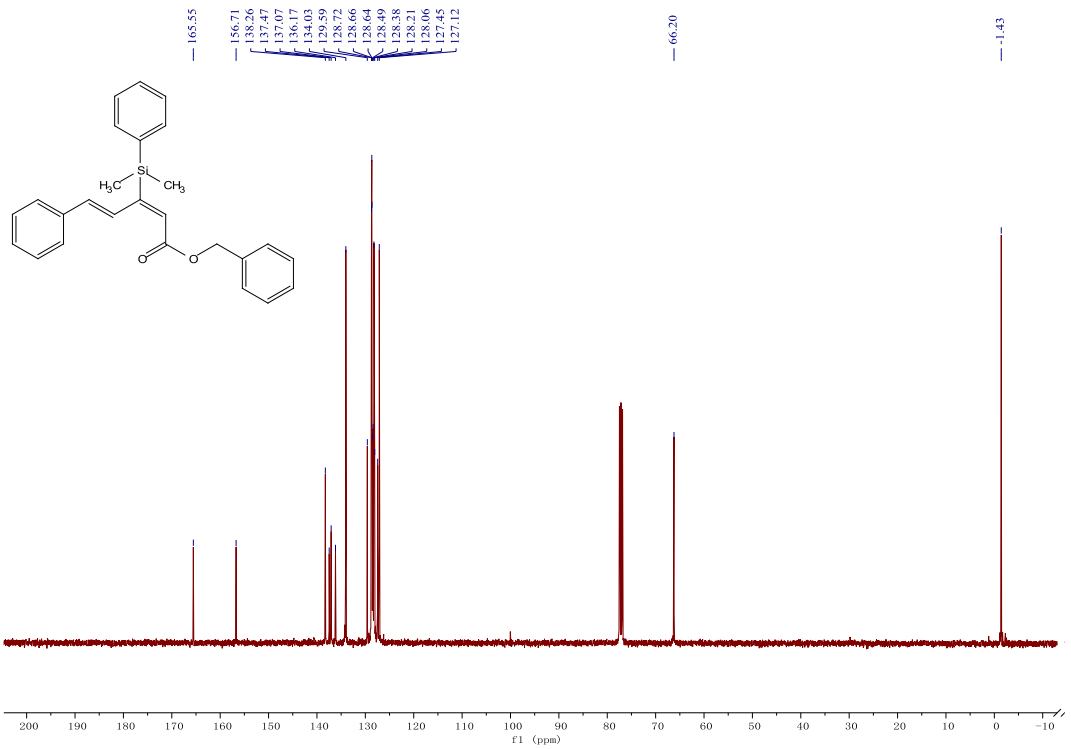
R_f: 0.36 (petroleum ether/ethyl acetate = 30:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 16.6 Hz, 1H), 7.70 – 7.56 (m, 3H), 7.55 – 7.17 (m, 13H), 6.76 (d, *J* = 16.7 Hz, 1H), 6.22 (s, 1H), 5.27 (s, 2H), 0.60 (s, 6H).

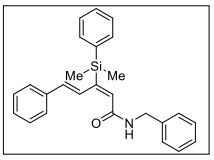
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.55, 156.71, 138.26, 137.47, 137.07, 136.17, 134.03, 129.59, 128.72, 128.66, 128.64, 128.49, 128.38, 128.21, 128.06, 127.45, 127.12, 66.20, -1.43.

HRMS (ESI) (m/z): Calcd for $C_{26}H_{26}O_2SiNa^+$ $[M+Na]^+$: 421.1600, found: 421.1601.





(2*E*,4*E*)-*N*-benzyl-3-(dimethyl(phenyl)silyl)-5-phenylpenta-2,4-dienamide (11s)



Prepared according to General Procedure C from **1s** (52.3 mg, 0.20 mmol). The product **11s** was isolated in 87% yield (69.3 mg) by PTLC as yellow oil.

Regioselectivity: 96:4 (β:α, crude ^{1}H NMR).

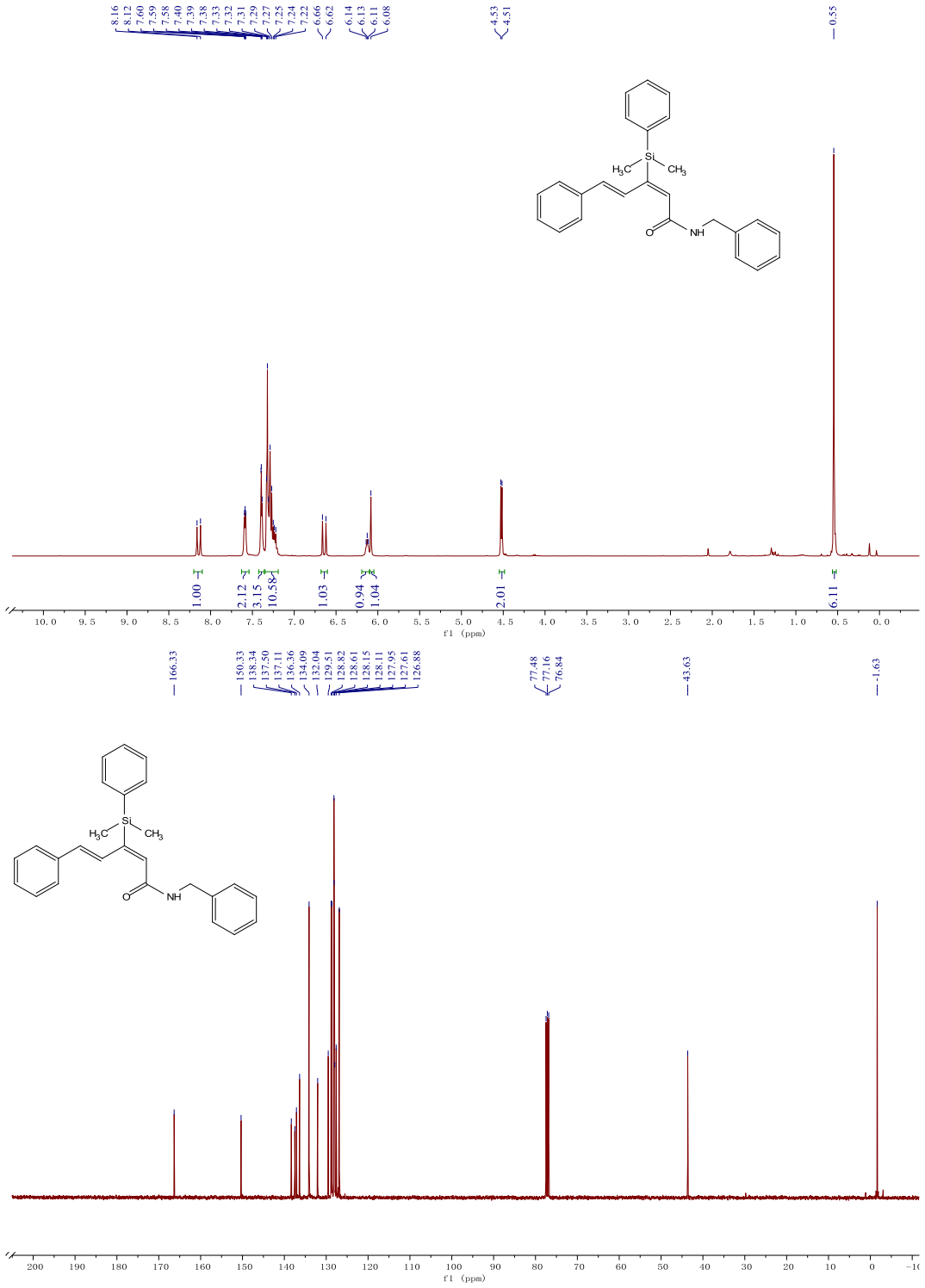
Eluent: petroleum ether/ethyl acetate (9:1).

R_f: 0.24 (petroleum ether/ethyl acetate = 9:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 16.7 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.46 – 7.35 (m, 3H), 7.35 – 7.15 (m, 10H), 6.64 (d, *J* = 16.7 Hz, 1H), 6.13 (t, *J* = 5.2 Hz, 1H), 6.08 (s, 1H), 4.52 (d, *J* = 5.8 Hz, 2H), 0.55 (s, 6H).

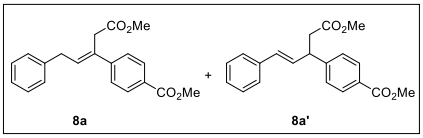
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.33, 150.33, 138.34, 137.50, 137.11, 136.36, 134.09, 132.04, 129.51, 128.82, 128.61, 128.15, 128.11, 127.95, 127.61, 126.88, 43.63, -1.63.

HRMS (ESI) (m/z): Calcd for $C_{26}H_{28}NOSi^+$ $[M+H]^+$: 398.1940, found: 398.1934.



3.5 Derivatizations of Products

methyl (*E*)-4-(5-methoxy-5-oxo-1-phenylpent-2-en-3-yl)benzoate (8a)



Following the procedure described by Burke *et al*,[4] under argon atmosphere, a mixture of **3a** (0.1 mmol), methyl 4-iodobenzoate (0.13 mmol, 34.1 mg), K_3PO_4 (0.3 mmol, 3.0 equiv, 63.7 mg) and Pd(dppf)Cl_2 (5 mol%, 3.7 mg) in DMSO (0.07 M, 1.4 mL) was stirred at 45 ºC for 12 h. Dichloromethane was added and the

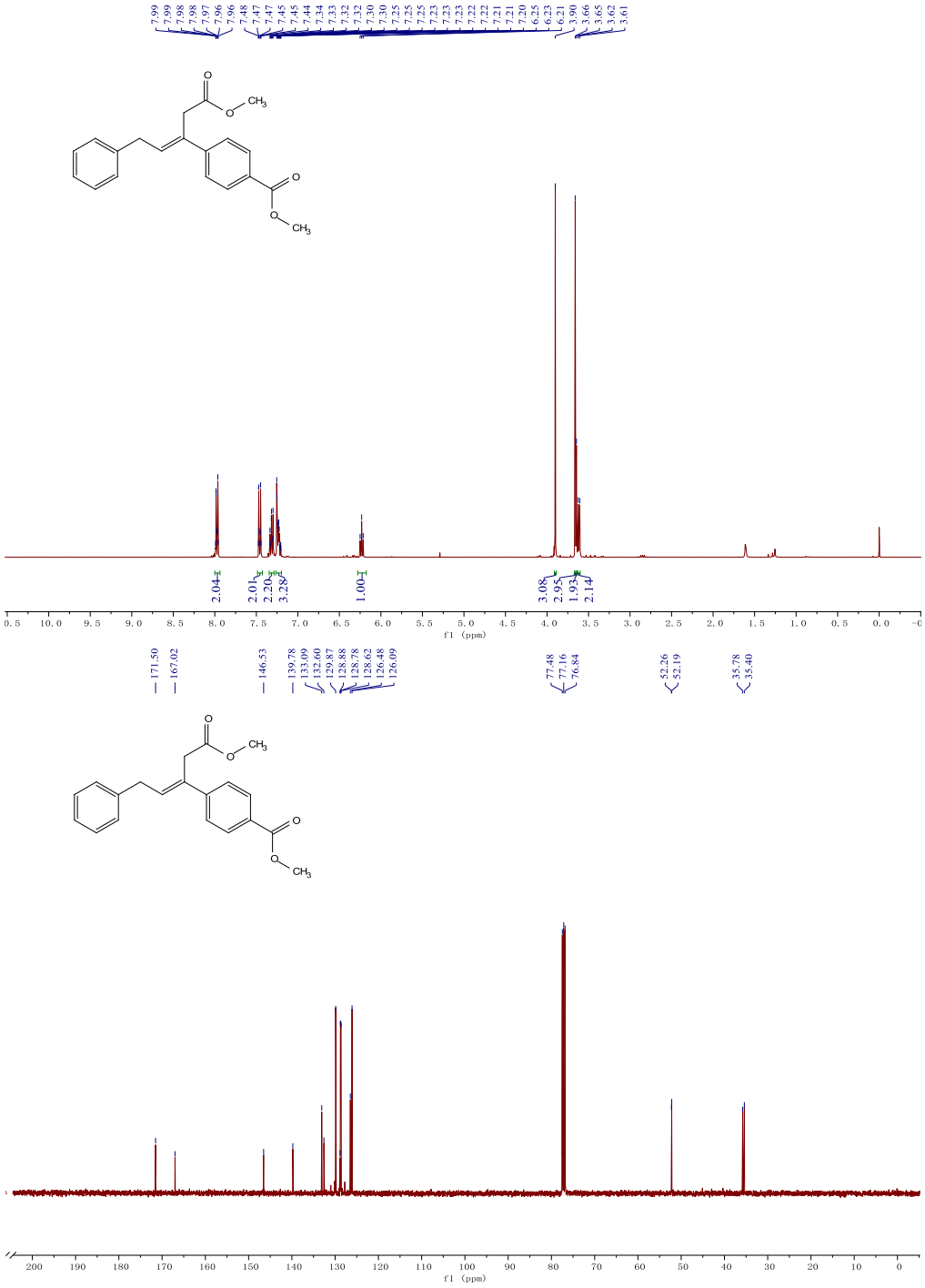
precipitate was removed by filtration. The resultant solution was concentrated and the mixture was extracted by ether. The combined organic phases were dried with Na_2SO_4 and concentrated and the residue was purified by column chromatography. **8a** was obtained in 85% yield with 5% of **8a′**.

Eluent: petroleum ether/ethyl acetate (100:0 - 90:10). **R_f**: 0.41 (petroleum ether/ethyl acetate = 9:1)

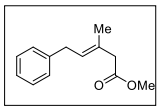
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.50 – 7.43 (m, 2H), 7.35 – 7.28 (m, 2H), 7.27 – 7.19 (m, 3H), 6.23 (t, *J* = 7.4 Hz, 1H), 3.90 (s, 3H), 3.66 (s, 3H), 3.65 (s, 2H), 3.62 (d, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.50, 167.02, 146.53, 139.78, 133.09, 132.60, 129.87, 128.88, 128.78, 128.62, 126.48, 126.09, 52.26, 52.19, 35.78, 35.40.

HRMS (ESI) (m/z): Calcd for $C_{20}H_{20}O_4Na^+$ [M+Na]$^+$: 347.1259, found: 347.1263.



methyl (*E*)-3-methyl-5-phenylpent-3-enoate (9a)

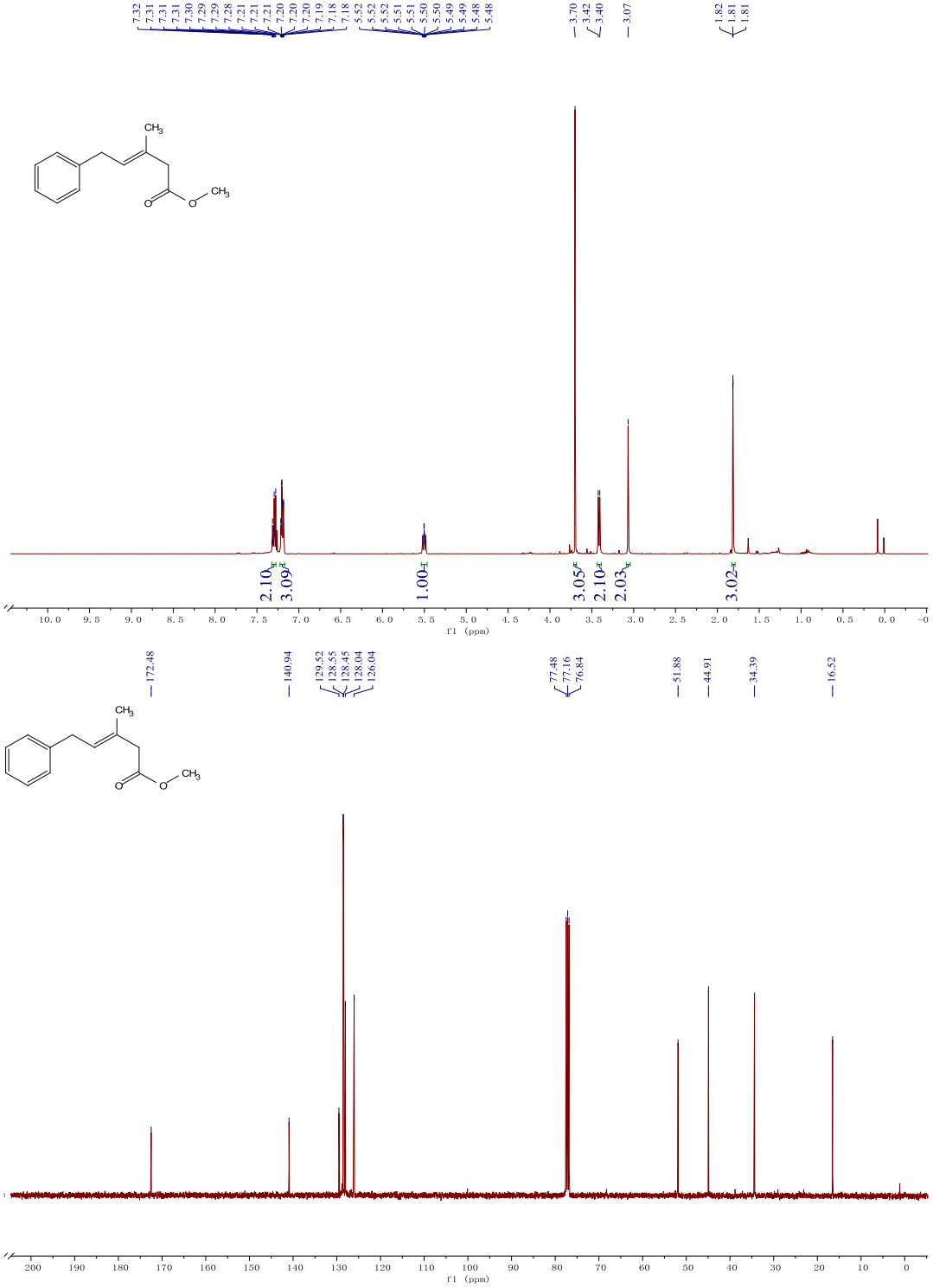


Following the procedure described by Negishi *et al* .[5] The product **9a** was isolated in 50% yield.

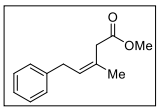
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 5.50 (qt, *J* = 7.4, 1.2 Hz, 1H), 3.70 (s, 3H), 3.41 (d, *J* = 7.3 Hz, 2H), 3.07 (s, 2H), 1.83 – 1.78 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.48, 140.94, 129.52, 128.55, 128.45, 128.04, 126.04, 51.88, 44.91, 34.39, 16.52.

HRMS (ESI) (m/z): Calcd for $C_{13}H_{16}O_2Na^+$ $[M+Na]^+$:227.1048, found: 227.1046.



methyl (*Z*)-3-methyl-5-phenylpent-3-enoate (10a)



Following the procedure described by Suzuki *et al*,[6] under argon atmosphere, a mixture of **3a** (0.2 mmol, 63.7 mg), $Pd(dba)_2$ (5 mol%, 5.8 mg), $P(o\text{-}tolyl)_3$ (10 mol%, 6.1 mg), MeI (0.8 mmol, 4.0 equiv, 113.6 mg) and K_2CO_3 (2.0 equiv, 55.3 mg) in DMF/H_2O (0.5 M, 9:1, 1.4 mL) was stirred at 60 ºC. After 16 h, another batch of MeI (0.4 mmol, 2 equiv, 56.8 mg) was added and the reaction was kept at the same temperature for 9 hours. The mixture was cooled to room temperature and extracted by ether. The combined organic phases were dried with Na_2SO_4 and concentrated and the residue was purified by column chromatography. **10a** was obtained in 44% (18.0 mg) yield.

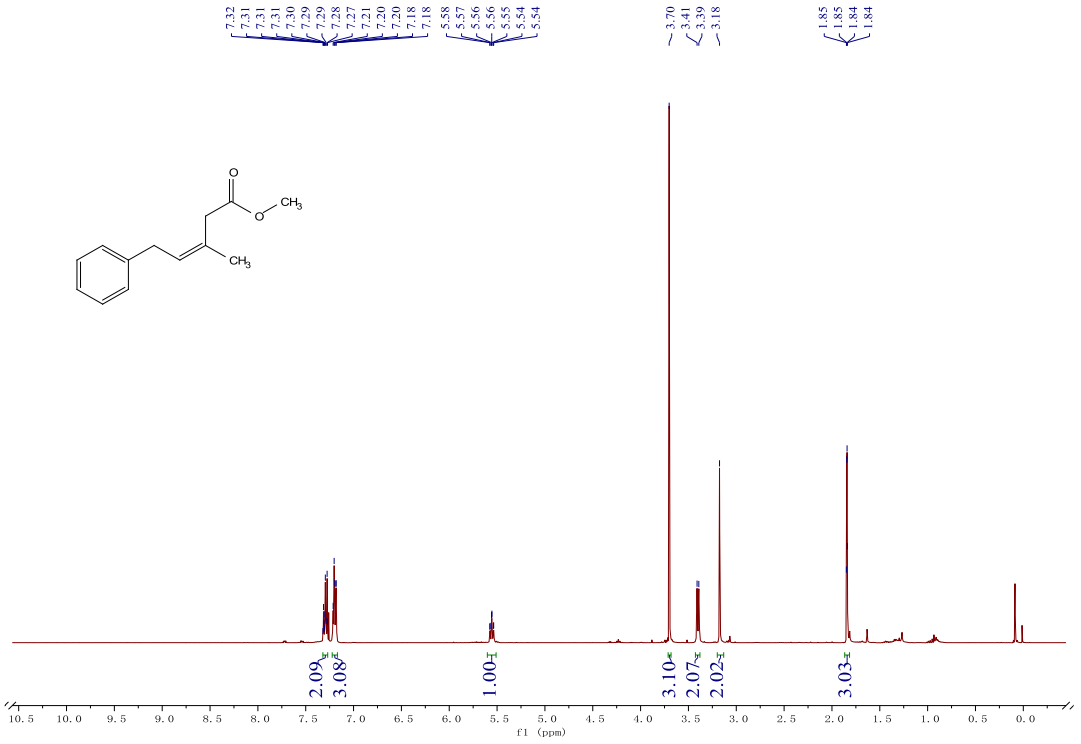
Eluent: petroleum ether/ethyl acetate (100:0 - 30:1).

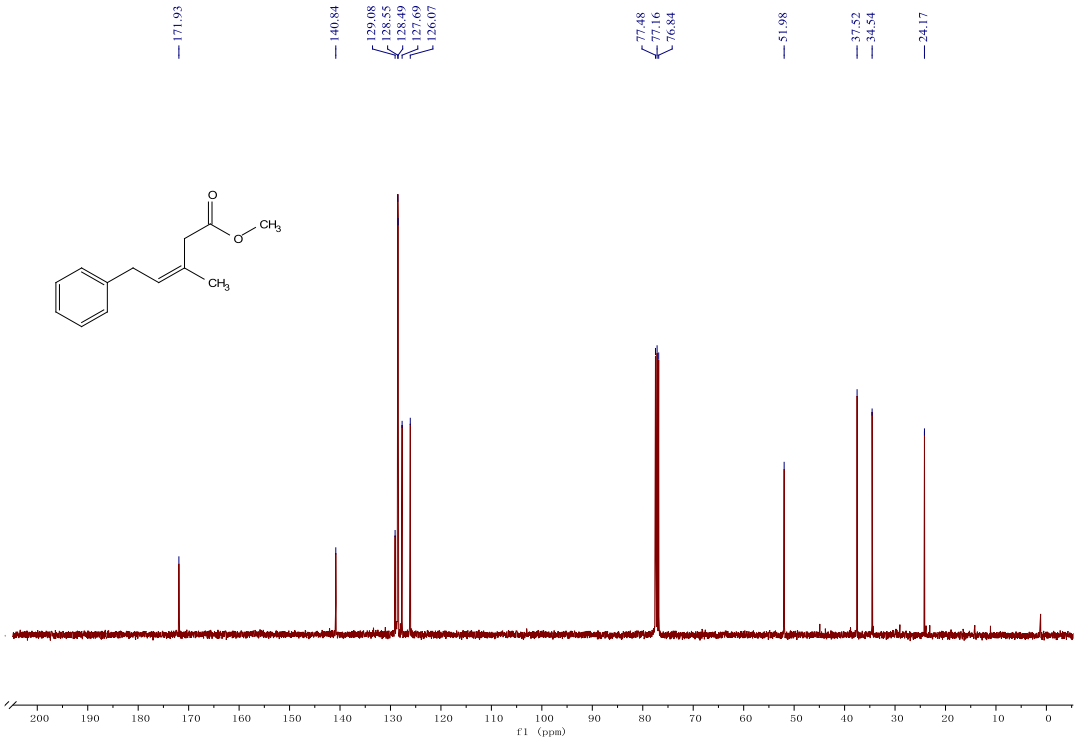
R_f: 0.42 (petroleum ether/ethyl acetate = 30:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 5.59 – 5.52 (m, 1H), 3.70 (s, 3H), 3.40 (d, J = 7.4 Hz, 2H), 3.18 (s, 2H), 1.84 (q, J = 1.2 Hz, 3H).

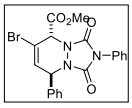
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.93, 140.84, 129.08, 128.55, 128.49, 127.69, 126.07, 51.98, 37.52, 34.54, 24.17.

HRMS (ESI) (m/z): Calcd for $C_{13}H_{16}O_2Na^+$ $[M+Na]^+$: 227.1048, found: 227.1043.





***anti*- methyl 6-bromo-1,3-dioxo-2,8-diphenyl-2,3,5,8-tetrahydro-1H-[1,2,4]triazolo[1,2-a] pyridazine-5-carboxylate (15a)**

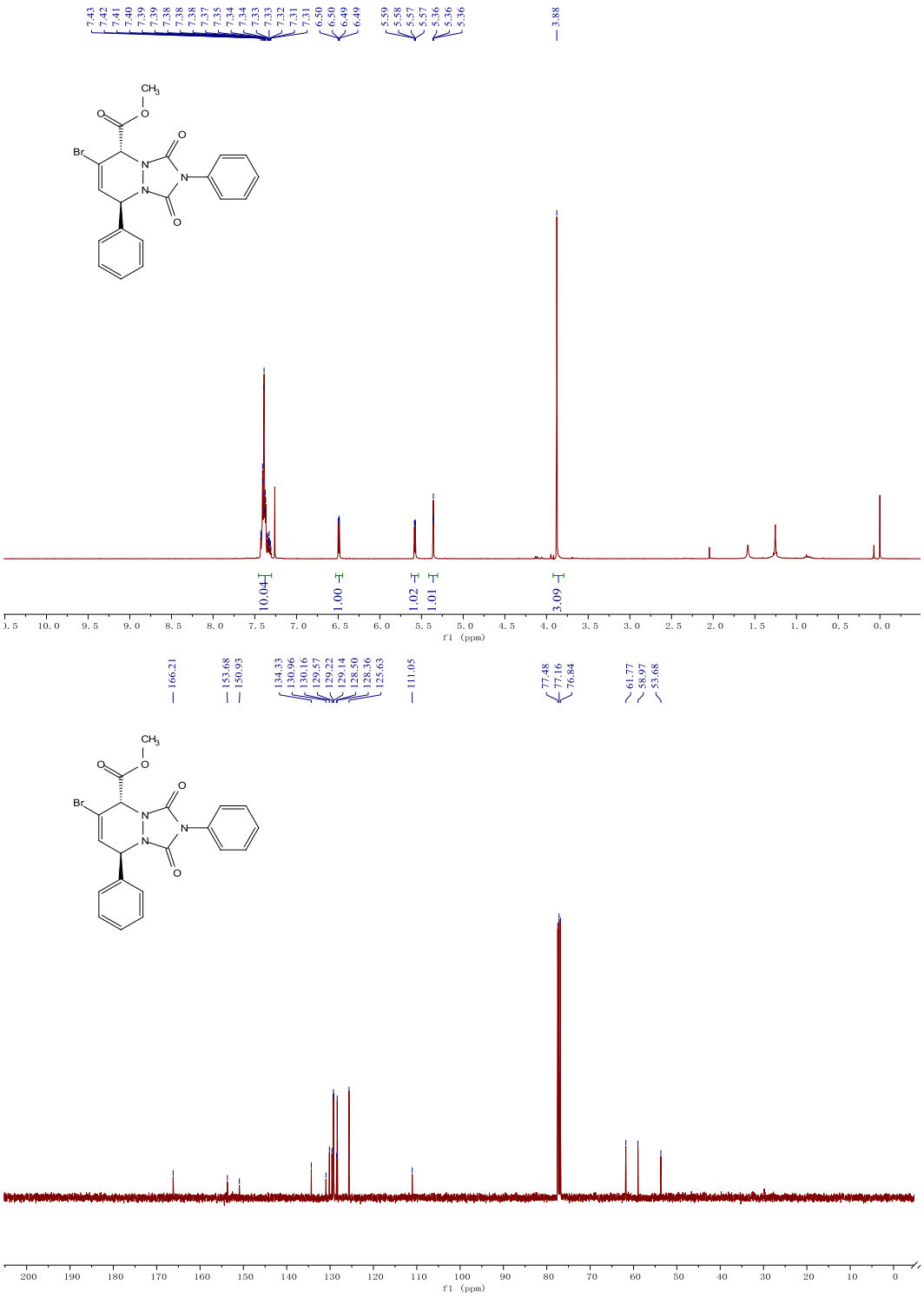


Following the procedure described by Stoodley and Hartwig *et al*,[7] diene **3a** (0.1 mmol, 31.4 mg), PTAD (0.11 mmol, 1.0 equiv, 19.3 mg) and benzene (0.1 M, 1 mL) were combined and the resulting solution was stirred at 30 ºC for 3 h. The solvent was removed under reduced pressure. Then $CuBr_2$ (2.0 equiv, 44.7 mg) and THF/H_2O (0.1 M, 1 mL, 1:1/v:v) was added and the mixture was stirred at 80 ºC for 18 h. The mixture was brought to room temperature and extracted with ethyl acetate and dried with Na_2SO_4. The residue was purified by column chromatography. **15a** was obtained in 51% (22.6 mg) yield. The stereochemistry of the product was determined by reported similar reactions.[7a, 8]

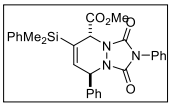
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 10H), 6.49 (dd, J = 4.6, 1.3 Hz, 1H), 5.58 (dd, J = 4.6, 0.9 Hz, 1H), 5.36 (t, J = 1.1 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.21, 153.68, 150.93, 134.33, 130.96, 130.16, 129.57, 129.22, 129.14, 128.50, 128.36, 125.63, 111.05, 61.77, 58.97, 53.68.

HRMS (ESI) (m/z): Calcd for $C_{20}H_{16}BrN_3O_4Na^+$ $[M+Na]^+$: 464.0222, found: 464.0227.



***anti*- methyl 6-(dimethyl(phenyl)silyl)-1,3-dioxo-2,8-diphenyl-2,3,5,8-tetrahydro-1H-[1,2,4]triazolo[1,2-a]pyridazine-5-carboxylate (16a)**

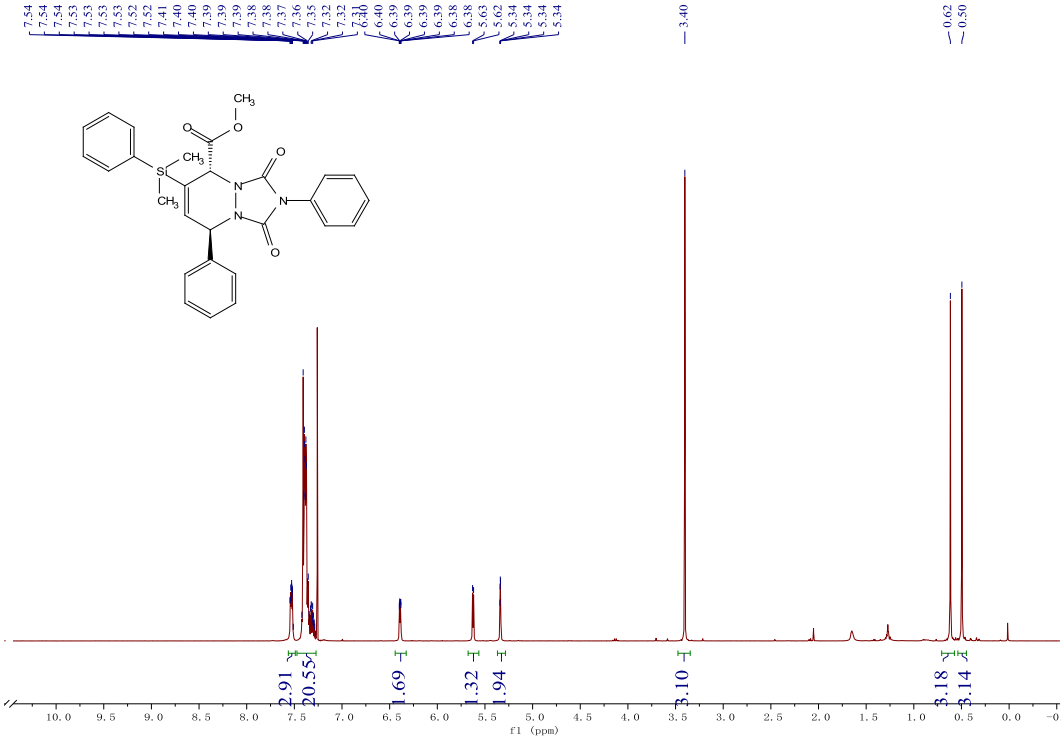


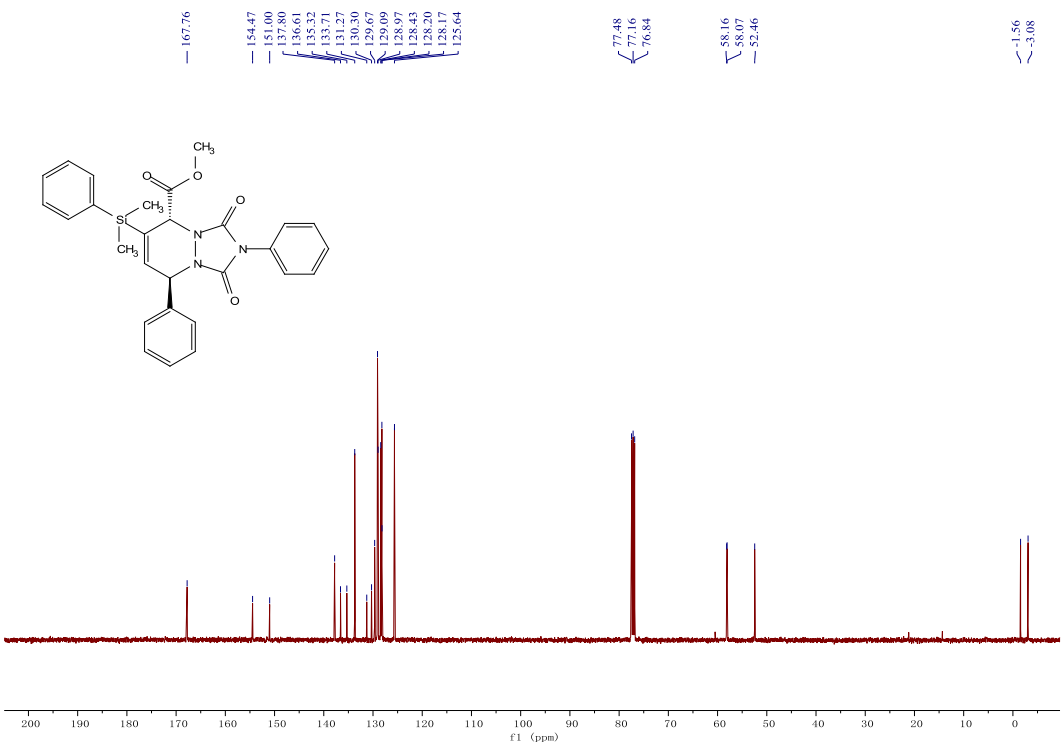
Following the procedure described by Stoodley *et al*,[7a] diene **11a** (0.1 mmol, 32.2 mg), PTAD (0.11 mmol, 1.0 equiv, 19.3 mg) and benzene (0.1 M, 1 mL) were combined and the resulting solution was stirred at 30 ºC for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography. **16a** was obtained in 74% (36.8 mg) yield with 93:7 dr The stereochemistry of the product was determined by reported similar reactions.[7a, 8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.44 – 7.27 (m, 13H), 6.39 (ddd, *J* = 4.3, 1.9, 0.5 Hz, 1H), 5.62 (d, *J* = 4.3 Hz, 1H), 5.34 (dd, *J* = 1.6, 0.9 Hz, 1H), 3.40 (s, 3H), 0.62 (s, 3H), 0.50 (s, 3H).

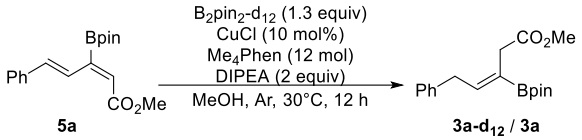
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.76, 154.47, 151.00, 137.80, 136.61, 135.32, 133.71, 131.27, 130.30, 129.67, 129.09, 128.97, 128.43, 128.20, 128.17, 125.64, 58.16, 58.07, 52.46, -1.56, -3.08.

HRMS (ESI) (m/z): Calcd for $C_{28}H_{28}N_3O_4Si^+$ $[M+H]^+$:498.1849, found: 498.1847.





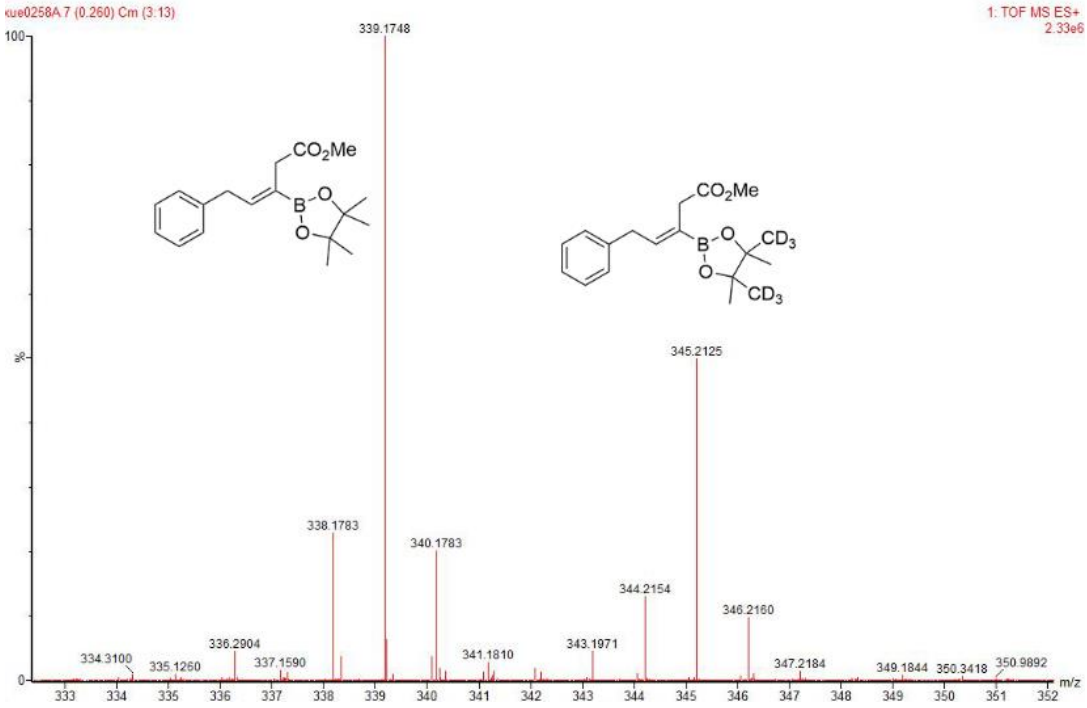
4. Mechanistic Study



Under argon atmosphere, an oven-dried 10 mL Schlenck tube was charged with a stirring bar, CuCl (2.0 mg, 0.02 mmol, 10 mol %), 3,4,7,8-tetramethyl-1,10-phenanthroline (5.7 mg, 0.024 mmol, 12 mol %) and MeOH (1 mL, 0.2 M). After stirring for 10 min, B_2pin_2-d_{12} [9] (66.0 mg, 0.46 mmol, 2.3 equiv), **5a** (62.8 mg, 0.2 mmol, 1.0 equiv) and N,N-diisopropylethylamine (51.7 mg, 0.4 mmol, 2.0 equiv) were added in sequence. Then the reaction mixture was kept at 30 ℃ for 12 h. Dichloromethane was added and the precipitate was removed by filtration. The resultant solution was concentrated and the crude product was purified by column chromatography using dichloromethane as eluent. **3a** and **3a**-d_6 were isolated in 60% yield as colorless oil and ESI indicates that the ratio of **3a**-d_6/**3a** = 1:2.

HRMS (ESI) (m/z): Calcd for $C_{18}H_{25}BO_4Na^+$ $[M+Na]^+$: 339.1744, found: 339.1748.

HRMS (ESI) (m/z): Calcd for $C_{18}H_{19}D_6BO_4Na^+$ $[M+Na]^+$: 345.2120, found: 345.2125.



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