# Supporting Information

## Palladium(I)-Iodide Catalyzed Deoxygenative Heck Reaction of Vinyl Triflates: A Formate-Mediated Cross-Electrophile Reductive Coupling with *cine*-Substitution

Yu-Hsiang Chang, Weijia Shen,[§] Jonathan Z. Shezaf,[§] Eliezer Ortiz, and Michael J. Krische*
Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States
EMAIL: mkrische@cm.utexas.edu*

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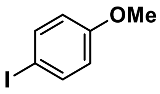
## I. General Information

All reactions were run under an atmosphere of argon, unless otherwise indicated. Resealable pressure tubes (13x100 mm) were purchased from Fischer Scientific (catalog number 14–959–35C) and were flame dried followed by cooling in a desiccator or under a stream of argon prior to use. All commercial reagents, which includes $Pd(OAc)_2$, $Bu_4NI$, $NaO_2CH$, $Na_2CO_3$, aryl iodides **1a-1j**, and anhydrous solvents were used as received from vendors without further purification. The palladium complex $[Pd_2I_6][NBu_4]_2$ was prepared in accord with the literature procedure.[1] Purification of reaction products was carried out by flash column chromatography using 40-63 μm silica gel. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynamic Absorbents F254).

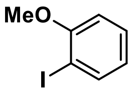
## II. Spectroscopy, Spectrometry, and Data Collection

Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were isolated on a Karatos MS9 and are reported as m/z (relative intensity). Electron spray ionization (ESI) was used unless otherwise indicated. Accurate masses are reported for the molecular ion (M+, M+H, M+Na), or a suitable fragment ion. Proton nuclear magnetic resonance ($^1H$ NMR) spectra were recorded with a Varian INOVA (400, 500 MHz) spectrometer equipped with a Bruker AVANCE III cryoprobe. Data reported as multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Integration and coupling constants were reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance ($^{13}C$ NMR) spectra were recorded with a Varian INOVA (100, 125 MHz) spectrometer and were routinely run with broadband decoupling. Decoupled Proton Phosphorus-31 nuclear magnetic resonance ($^{31}P\{1H\}$ NMR) spectra were recorded with a Varian INOVA (202 MHz) spectrometer. Deuterium nuclear magnetic resonance ($^2H$ NMR) spectra were recorded in $CHCl_3$ solution with a Varian Gemini 500 (92 MHz) spectrometer (relaxation delay 2.00s).

## III. Known Aryl Iodides (1a-1j)



**1a**
**commercial**



**1b**
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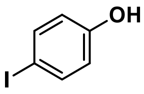
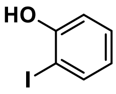
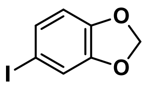


**1c**
**commercial**



**1d**
**commercial**



**1e**
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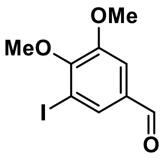
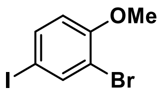
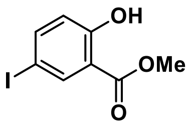


**1f**
**commercial**



**1g**
**commercial**



**1h**
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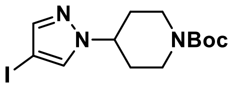

**1i**
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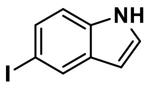
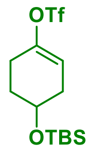
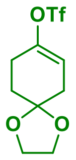


**1j**
**commercial**

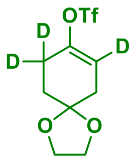
## IV. Known Vinyl Triflates (2a-2f, *deuterio*-2b)



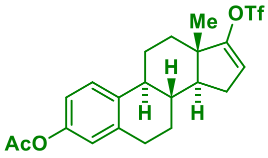
**2a**
**Ref. 2**



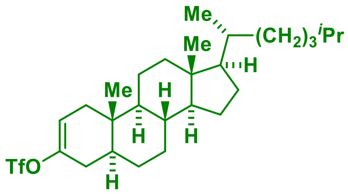
**2b**
**Ref. 3**



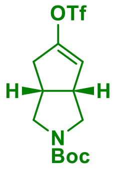
*deuterio*-**2b**
**Ref. 3**



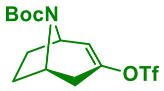
**2c**
**Ref. 4**



**2d**
**Ref. 5**

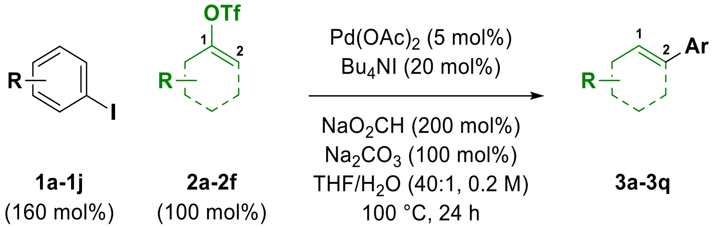


**2e**
**Ref. 6**



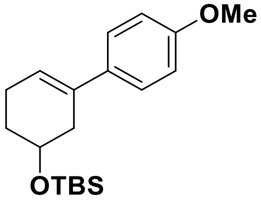
**2f**
**Ref. 7**

## V. Products 3a-3q



**General Procedure:** An oven-dried pressure tube equipped with a magnetic stir bar was charged with aryl iodide **1a-1j** (0.32 mmol, 160 mol%), vinyl triflate **2a-2f** (0.2 mmol, 100 mol%), $Pd(OAc)_2$ (0.01 mmol, 5 mol%), $Bu_4NI$ (0.04 mmol, 20 mol%), $NaO_2CH$ (0.40 mmol, 200 mol%), and $Na_2CO_3$ (0.20 mmol, 100 mol%), under an argon atmosphere. The pressure tube was evacuated and backfilled with argon, followed by the addition of water (25 µL, 1.4 mmol, 700 mol%) and anhydrous THF (1.0 mL, 0.2 M). The tube was sealed with a PTFE lined cap and the reaction vessel was placed in a 100 °C oil bath and stirred for 24 hours. After reaching ambient temperature, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography ($SiO_2$) under the noted conditions to furnish products **3a**-**3q**. Regioisomeric ratios were determined by $^1$H NMR of a purified mixture of regioisomers.

**_tert_-butyl((4'-methoxy-2,3,4,5-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)dimethylsilane (3a)**



Following the general procedure, aryl iodide **1a** (74.9 mg, 0.32 mmol) and vinyl triflate **2a** (72.0 mg, 0.2 mmol) were subjected to standard reaction conditions (100 °C, 24 h). Upon flash column chromatography ($SiO_2$: 1:99 EtOAc:hexanes) the title compound **3a** was isolated as a clear oil in 88% yield (56.0 mg, 0.18 mmol, 14:1 rr).

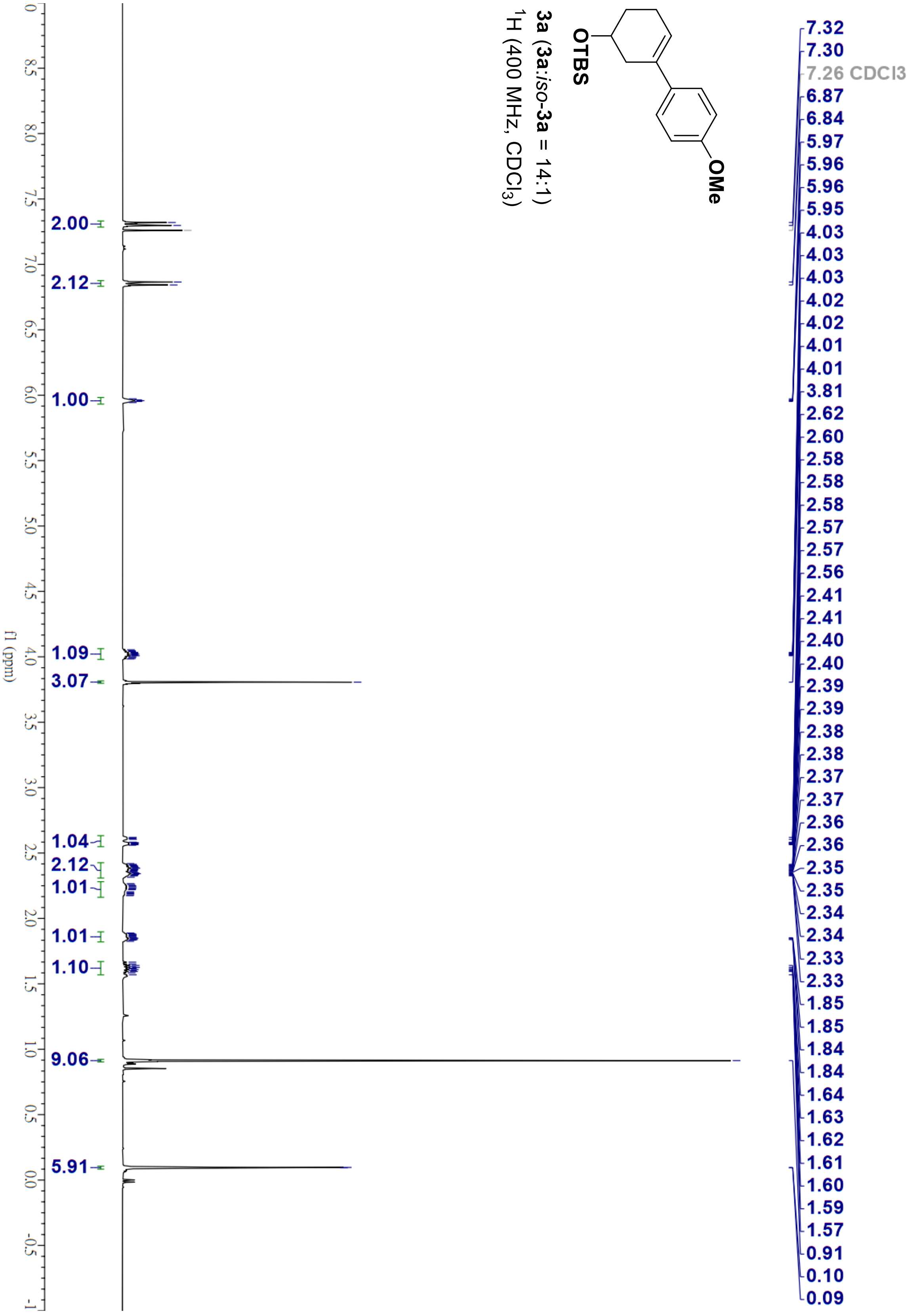
**TLC** ($SiO_2$): $R_f$ = 0.6 (1:5 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.31 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 5.96 (t, J = 2.4 Hz, 1H), 4.02 (dddd, J = 10.1, 8.4, 5.2, 3.3 Hz, 1H), 3.81 (s, 3H), 2.64 – 2.54 (m, 1H), 2.44 – 2.29 (m, 2H), 2.29 – 2.15 (m, 1H), 1.91 – 1.80 (m, 1H), 1.69 – 1.56 (m, 1H), 0.91 (s, 9H), 0.09 (d, J = 1.2 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 158.7, 134.7, 134.2, 126.2, 122.3, 113.7, 68.7, 55.4, 37.6, 31.5, 26.1, 24.8, 18.4, -4.4, -4.4.

**HRMS** (ESI) m/z: [M+Na$^+$] calcd. for $C_{19}H_{30}O_2Si$: 341.1907; found = 341.1916.

**FTIR** (neat): 2952, 2929, 2856, 1609, 1512, 1249, 1092, 830, 774 cm$^{-1}$.

OMe
OTBS
3a (3a:iso-3a = 14:1)
1H (400 MHz, CDCl3)
7.32
7.30
7.26 CDCl3
6.87
6.84
5.97
5.96
5.96
5.95
4.03
4.03
4.03
4.02
4.02
4.01
4.01
3.81
2.62
2.60
2.58
2.58
2.58
2.57
2.57
2.56
2.41
2.41
2.40
2.40
2.39
2.39
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2.38
2.37
2.37
2.36
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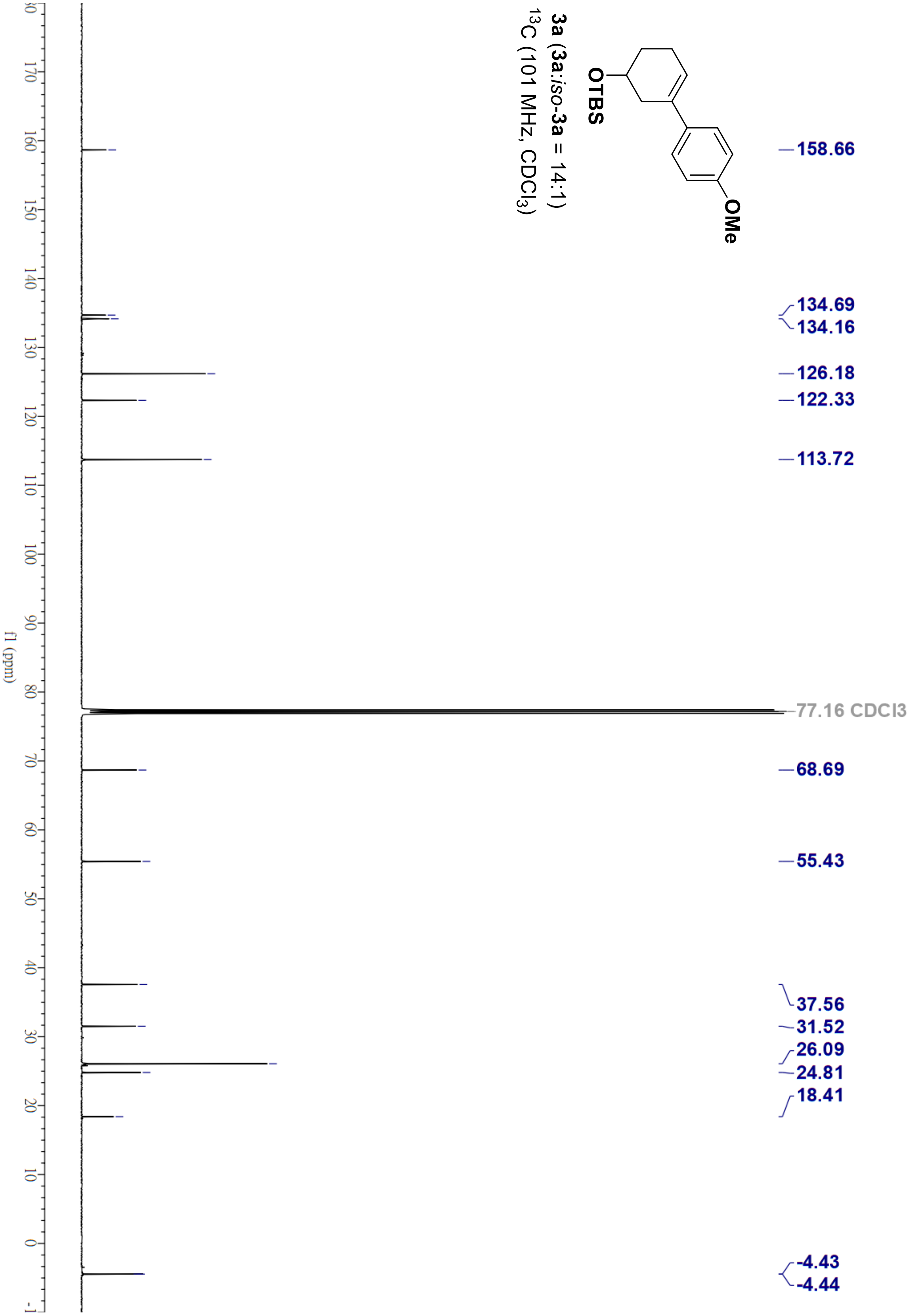
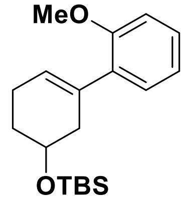
2.35
2.35
2.34
2.34
2.33
2.33
1.85
1.85
1.84
1.84
1.64
1.63
1.62
1.61
1.60
1.59
1.57
0.91
0.10
0.09
2.00
2.12
1.00
1.09
3.07
1.04
2.12
1.01
1.01
1.10
9.06
5.91
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



**3a** (**3a**:*iso*-**3a** = 14:1)

$^{13}$C (101 MHz, $CDCl_3$)

**tert-butyl((2'-methoxy-2,3,4,5-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)dimethylsilane (3b)**



Following the general procedure, aryl iodide **1b** (74.9 mg, 0.32 mmol) and vinyl triflate **2a** (72.0 mg, 0.2 mmol) were subjected to modified reaction conditions (10 mol% $Pd(OAc)_2$, 100 °C, 24 h). Upon flash column chromatography ($SiO_2$: 10:90 $CH_2Cl_2$:hexanes) the title compound **3b** was isolated as a clear oil in 61% yield (38.9 mg, 0.12 mmol, >20:1 rr).

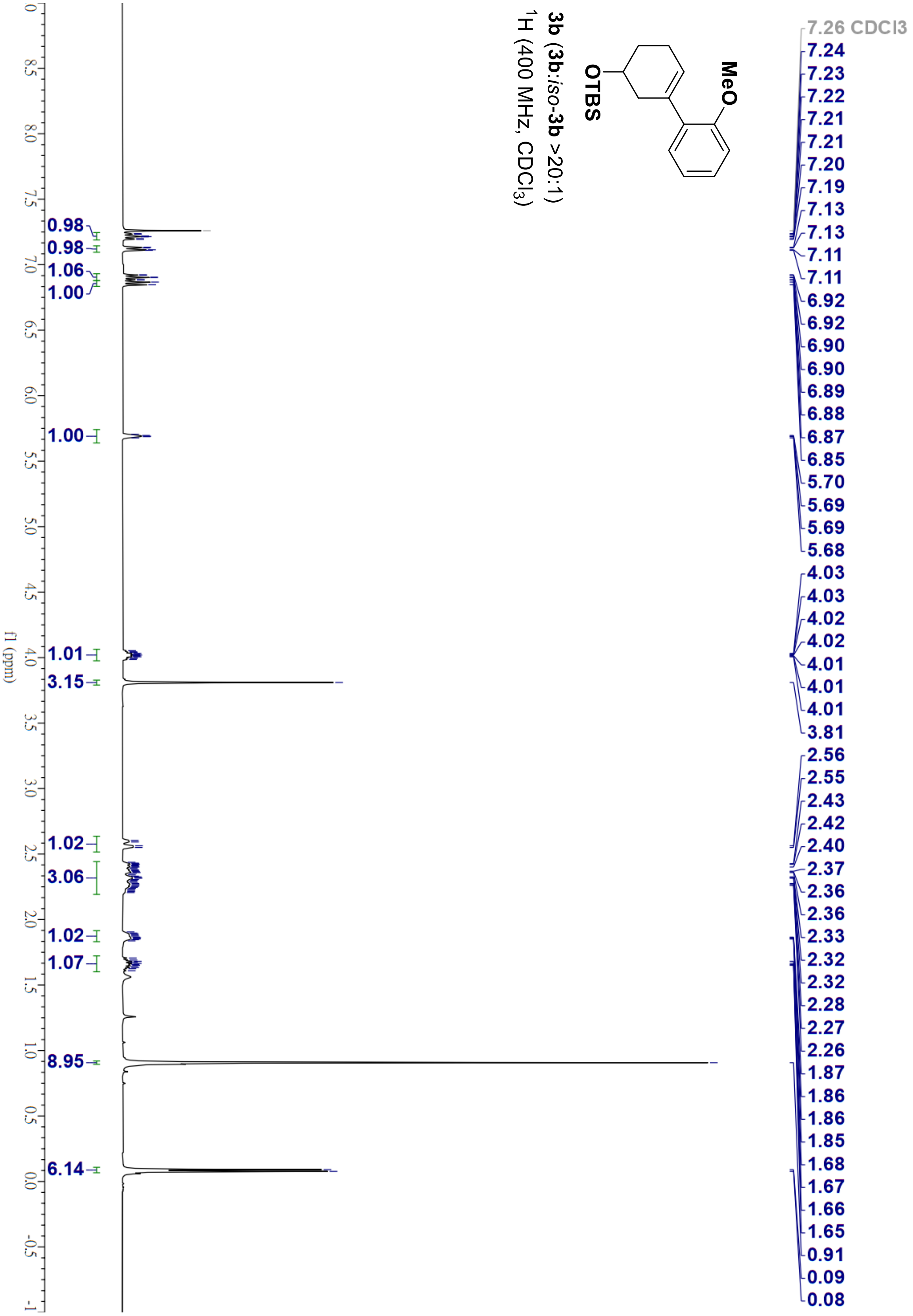
**TLC** ($SiO_2$): $R_f$ = 0.6 (1:5 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.22 (td, J = 7.7, 1.8 Hz, 1H), 7.12 (dd, J = 7.5, 1.8 Hz, 1H), 6.90 (td, J = 7.4, 1.1 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 5.69 (dd, J = 4.7, 2.4 Hz, 1H), 4.02 (dddd, J = 10.1, 8.3, 5.1, 3.3 Hz, 1H), 3.81 (s, 3H), 2.58 (dd, J = 16.7, 5.0 Hz, 1H), 2.44 – 2.19 (m, 3H), 1.92 – 1.83 (m, 1H), 1.66 (dtd, J = 12.4, 10.0, 6.3 Hz, 1H), 0.91 (s, 9H), 0.08 (d, J = 5.2 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 156.8, 135.5, 133.1, 129.7, 128.1, 125.5, 120.7, 110.9, 68.6, 55.5, 38.7, 31.5, 26.1, 24.9, 18.4, -4.5.

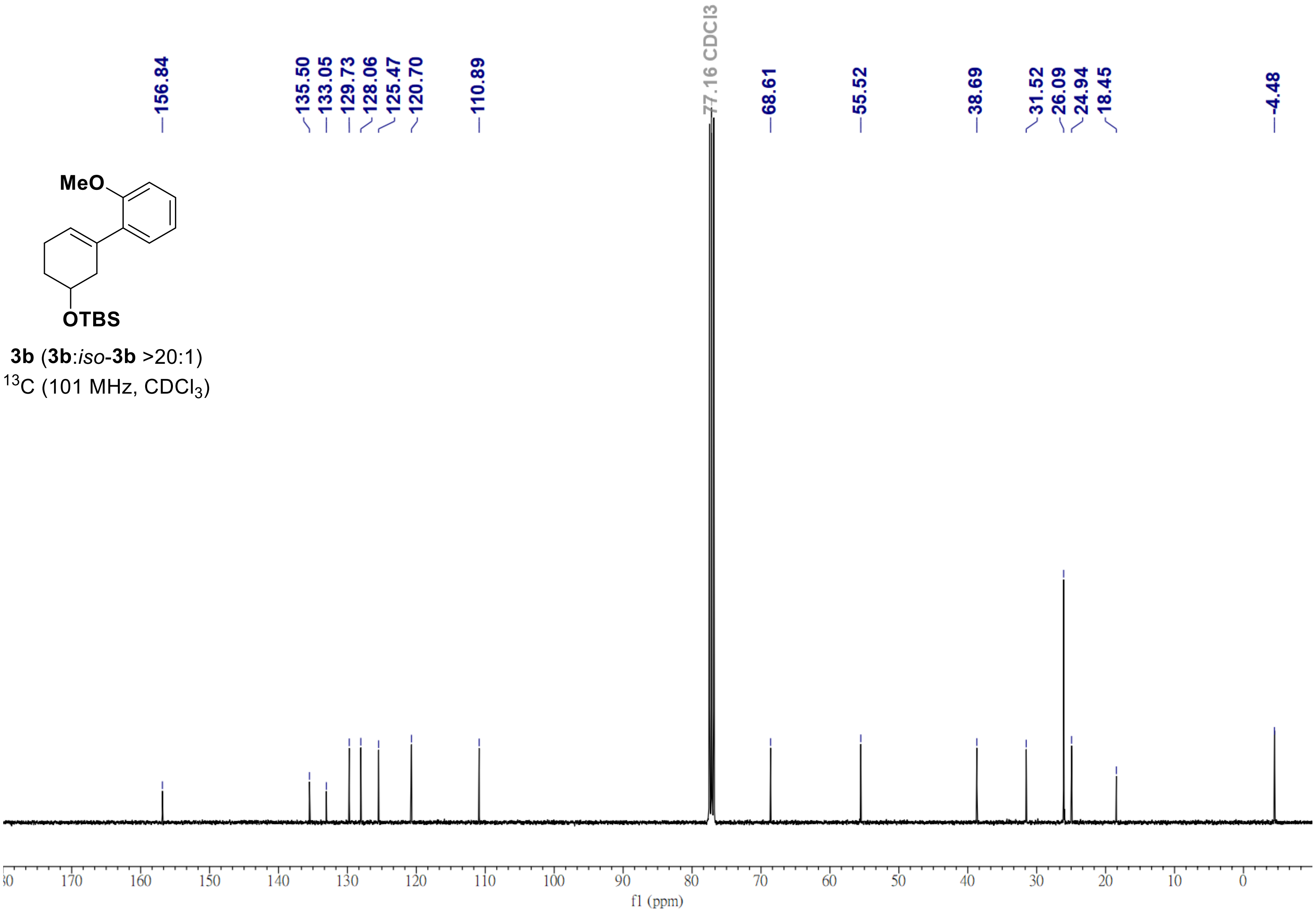
**HRMS** (ESI) m/z: [M+Na$^+$] calcd. for $C_{19}H_{30}O_2Si$: 341.1907; found = 341.1911.

**FTIR** (neat): 2927, 2855, 1487, 1462, 1247, 1091, 833, 773, 749 cm$^{-1}$.



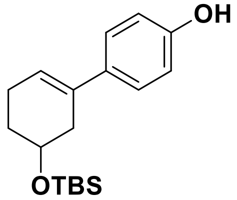
**3b** (**3b**:*iso*-**3b** >20:1)

$^1$H (400 MHz, $CDCl_3$)



**3b** (**3b**:*iso*-**3b** >20:1)
$^{13}$C (101 MHz, CDCl$_3$)

**3'-((*tert*-butyldimethylsilyl)oxy)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-ol (3c)**



Following the general procedure, aryl iodide **1c** (70.4 mg, 0.32 mmol) and vinyl triflate **2a** (72.0 mg, 0.2 mmol) were subjected to modified reaction conditions (10 mol% $Pd(OAc)_2$, 100 °C, 24 h). Upon flash column chromatography ($SiO_2$: 10:90 EtOAc:hexanes) the title compound **3c** was isolated as a clear wax in 59% yield (35.8 mg, 0.12 mmol, 20:1 rr).

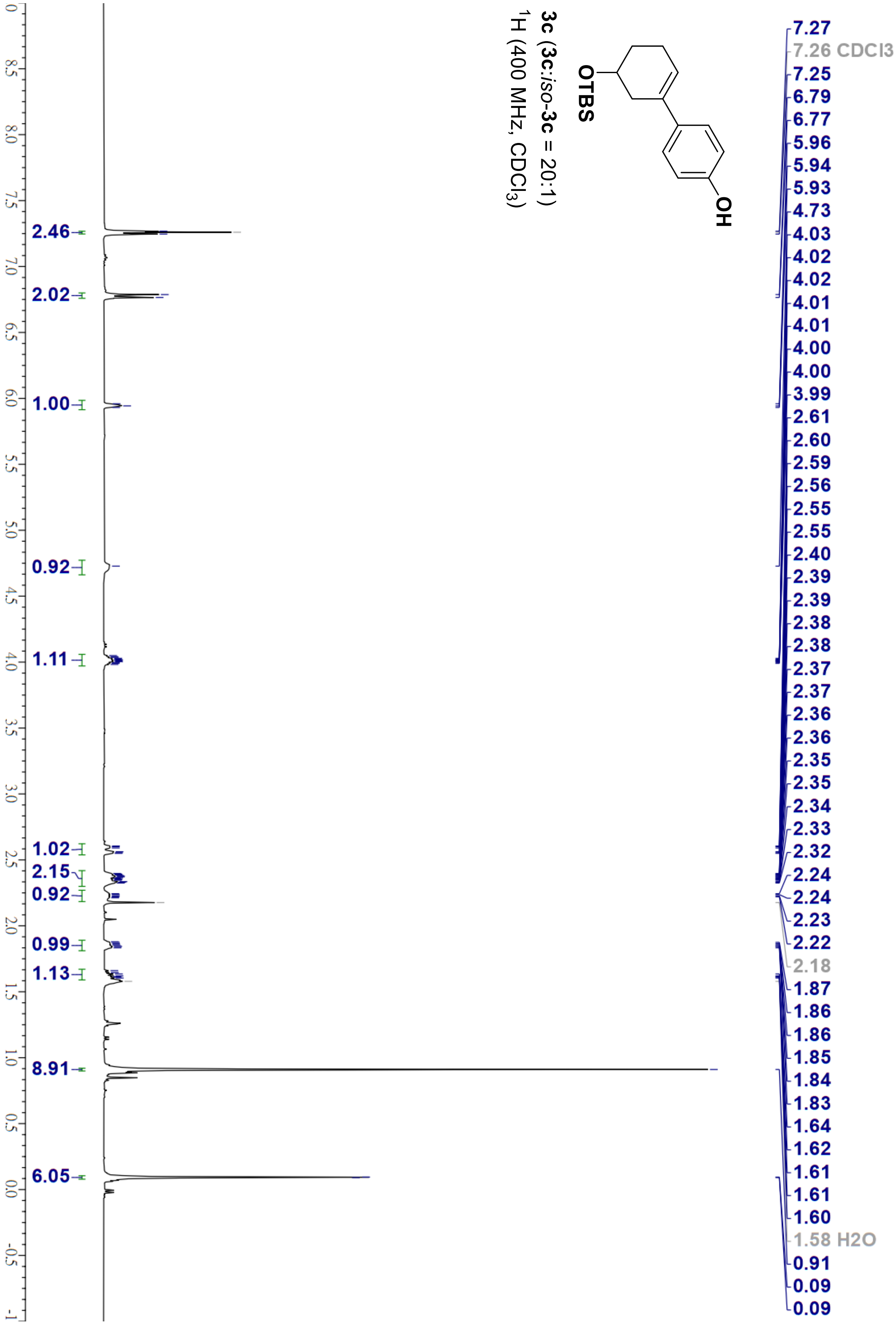
**TLC** ($SiO_2$): $R_f$ = 0.3 (1:4 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.26 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.7 Hz, 2H), 5.98 – 5.91 (m, 1H), 4.73 (s, 1H), 4.05 – 3.97 (m, 1H), 2.61 – 2.53 (m, 1H), 2.43 – 2.27 (m, 2H), 2.27 – 2.19 (m, 1H), 1.91 – 1.80 (m, 1H), 1.66 – 1.59 (m, 1H), 0.91 (s, 9H), 0.09 (d, J = 1.4 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 154.6, 134.9, 134.1, 126.4, 122.4, 115.2, 68.7, 37.6, 31.5, 26.1, 24.8, 18.4, -4.4.

**HRMS** (ESI) m/z: [M-H$^-$] calcd. for $C_{18}H_{28}O_2Si$: 303.1786; found = 303.1786.

**FTIR** (neat): 3346, 2928, 2856, 1513, 1462, 1252, 1092, 834, 775 cm$^{-1}$.

OTBS
OH
3c (3c:iso-3c = 20:1)
$^1$H (400 MHz, CDCl$_3$)
7.27
7.26 CDCl3
7.25
6.79
6.77
5.96
5.94
5.93
4.73
4.03
4.02
4.02
4.01
4.01
4.00
4.00
3.99
2.61
2.60
2.59
2.56
2.55
2.55
2.40
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2.39
2.38
2.38
2.37
2.37
2.36
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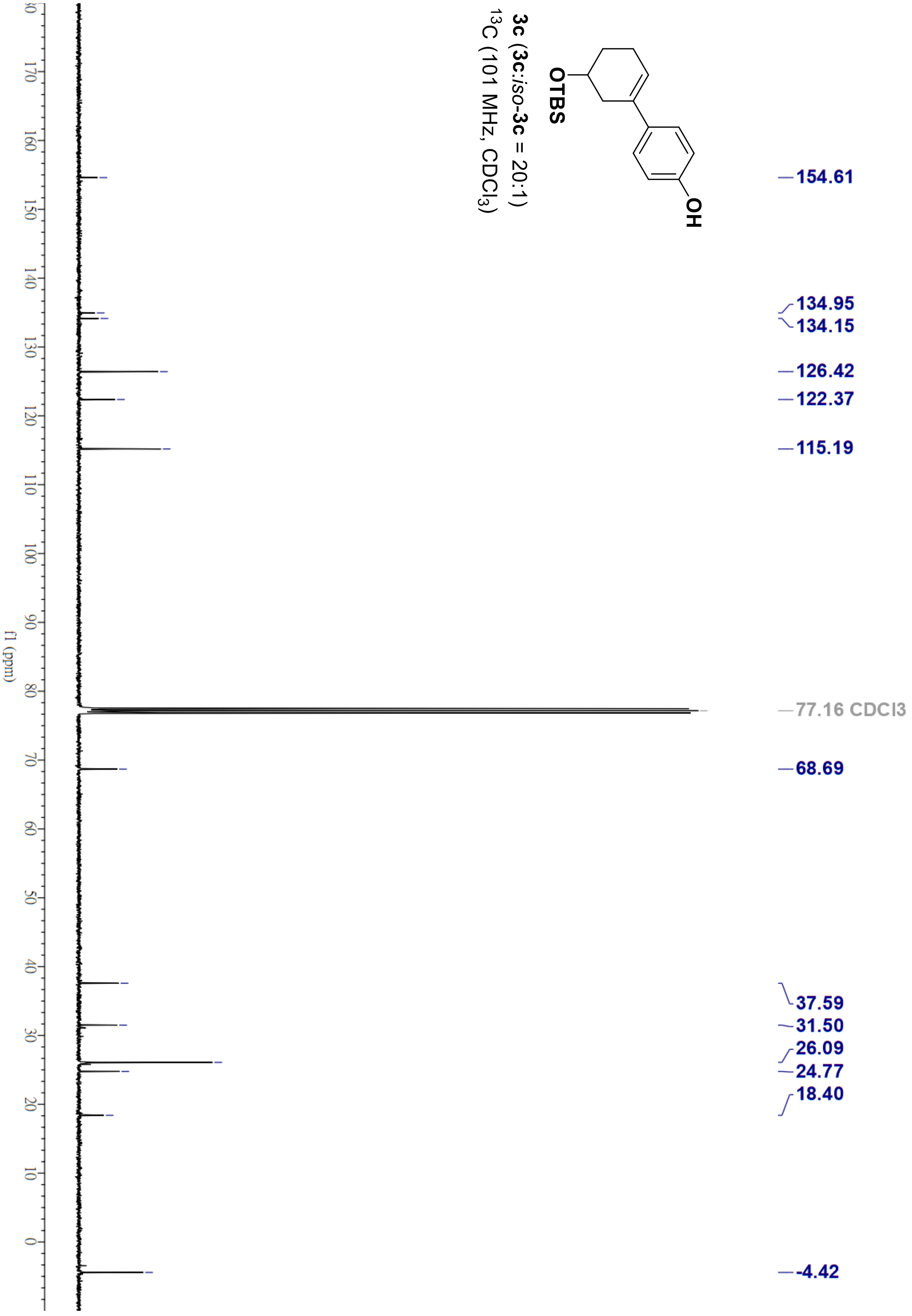
2.34
2.33
2.32
2.24
2.24
2.23
2.22
2.18
1.87
1.86
1.86
1.85
1.84
1.83
1.64
1.62
1.61
1.61
1.60
1.58 H2O
0.91
0.09
0.09
2.46
2.02
1.00
0.92
1.11
1.02
2.15
0.92
0.99
1.13
8.91
6.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

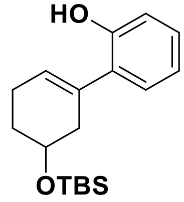
f



**3c** (**3c**:*iso*-**3c** = 20:1)

$^{13}$C (101 MHz, CDCl$_3$)

### 3'-((*tert*-butyldimethylsilyl)oxy)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-ol (3d)



Following the general procedure, aryl iodide **1d** (70.4 mg, 0.32 mmol) and vinyl triflate **2a** (72.0 mg, 0.2 mmol) were subjected to modified reaction conditions (105 °C, 24 h). Upon flash column chromatography ($SiO_2$: 1:99 EtOAc:hexanes) the title compound **3d** was isolated as a clear oil in 58% yield (35.3 mg, 0.12 mmol, >20:1 rr).

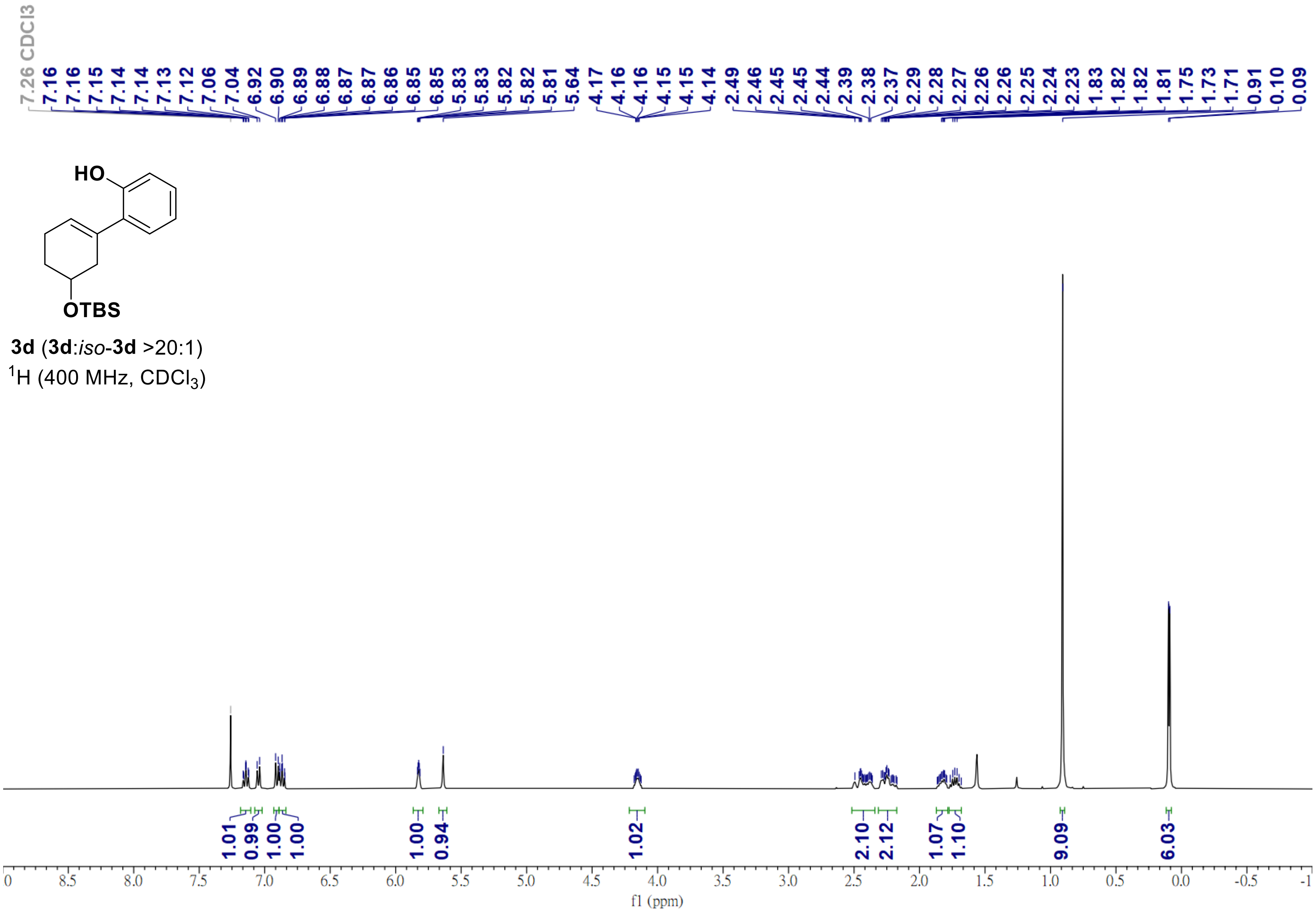
**TLC** ($SiO_2$): $R_f$ = 0.5 (1:4 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.14 (ddd, J = 8.9, 7.7, 1.7 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 6.91 – 6.82 (m, 1H), 5.82 (dt, J = 3.8, 1.8 Hz, 1H), 5.64 (s, 1H), 4.15 (tq, J = 8.8, 2.9 Hz, 1H), 2.52 – 2.34 (m, 2H), 2.32 – 2.15 (m, 2H), 1.83 (tdd, J = 9.5, 6.4, 2.9 Hz, 1H), 1.72 (dq, J = 12.9, 7.2 Hz, 1H), 0.91 (s, 9H), 0.09 (d, J = 3.9 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 152.5, 132.1, 129.7, 128.4, 128.1, 128.0, 120.2, 115.4, 67.2, 39.2, 30.1, 26.0, 23.4, 18.3, -4.5, -4.6.

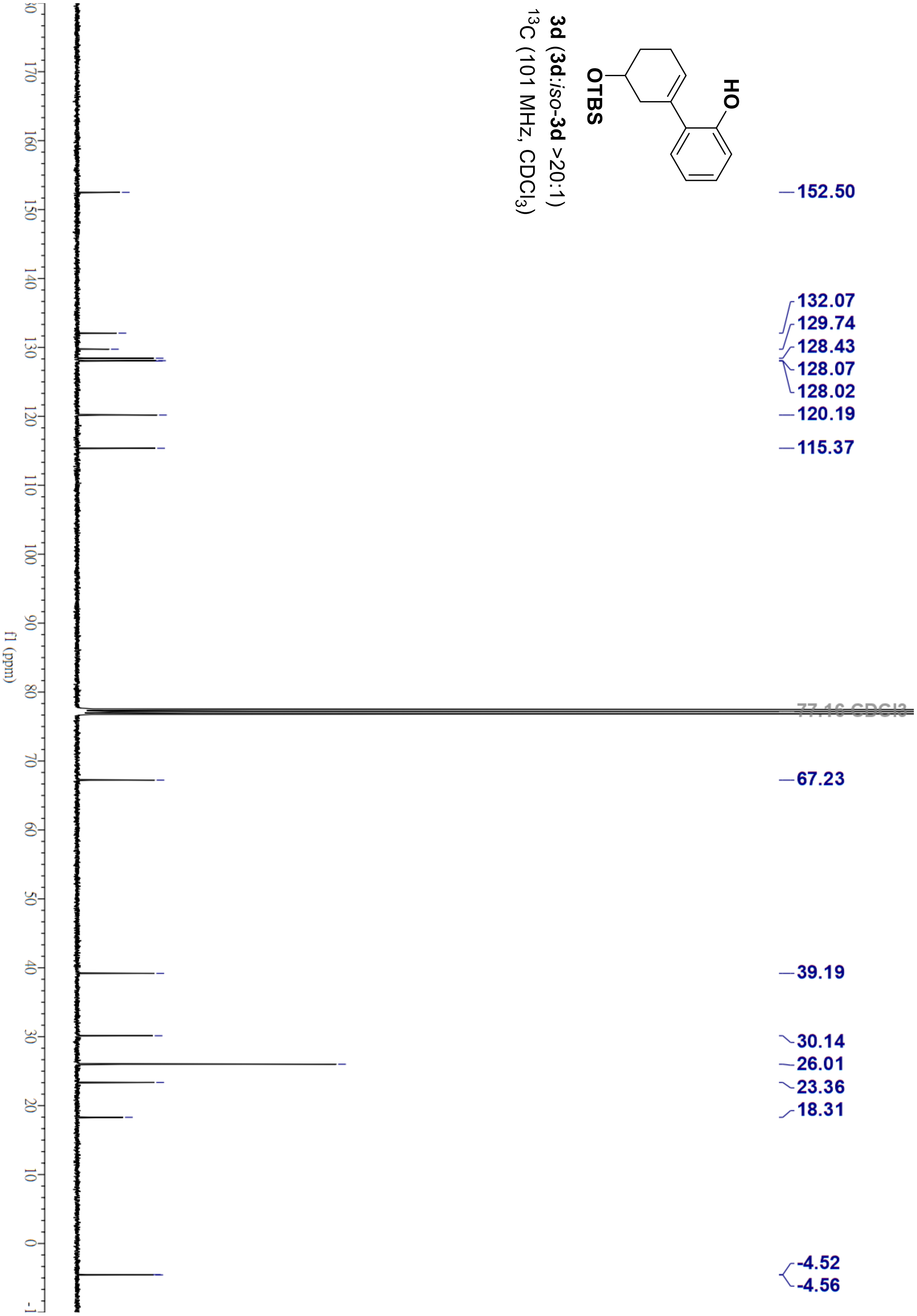
**HRMS** (ESI) m/z: [M+Na$^+$] calcd. for $C_{18}H_{28}O_2Si$: 327.1751; found = 327.1756.

**FTIR** (neat): 3504, 2927, 2855, 1486, 1360, 1252, 1090, 833, 750 cm$^{-1}$.



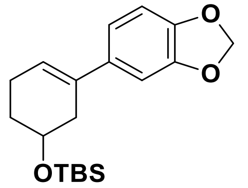
**3d** (**3d**:*iso*-**3d** >20:1)

$^1$H (400 MHz, CDCl$_3$)


**3d** (**3d**:*iso*-**3d** >20:1)

$^{13}$C (101 MHz, CDCl$_3$)

**((3-(benzo[d][1,3]dioxol-5-yl)cyclohex-3-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (3e)**



Following the general procedure, aryl iodide **1e** (79.3 mg, 0.32 mmol) and vinyl triflate **2a** (72.0 mg, 0.2 mmol) were subjected to standard reaction conditions (100 °C, 24 h). Upon flash column chromatography ($SiO_2$: 10:90 $CH_2Cl_2$:hexanes) the title compound **3e** was isolated as a clear oil in 67% yield (44.3 mg, 0.13 mmol, 8:1 rr).

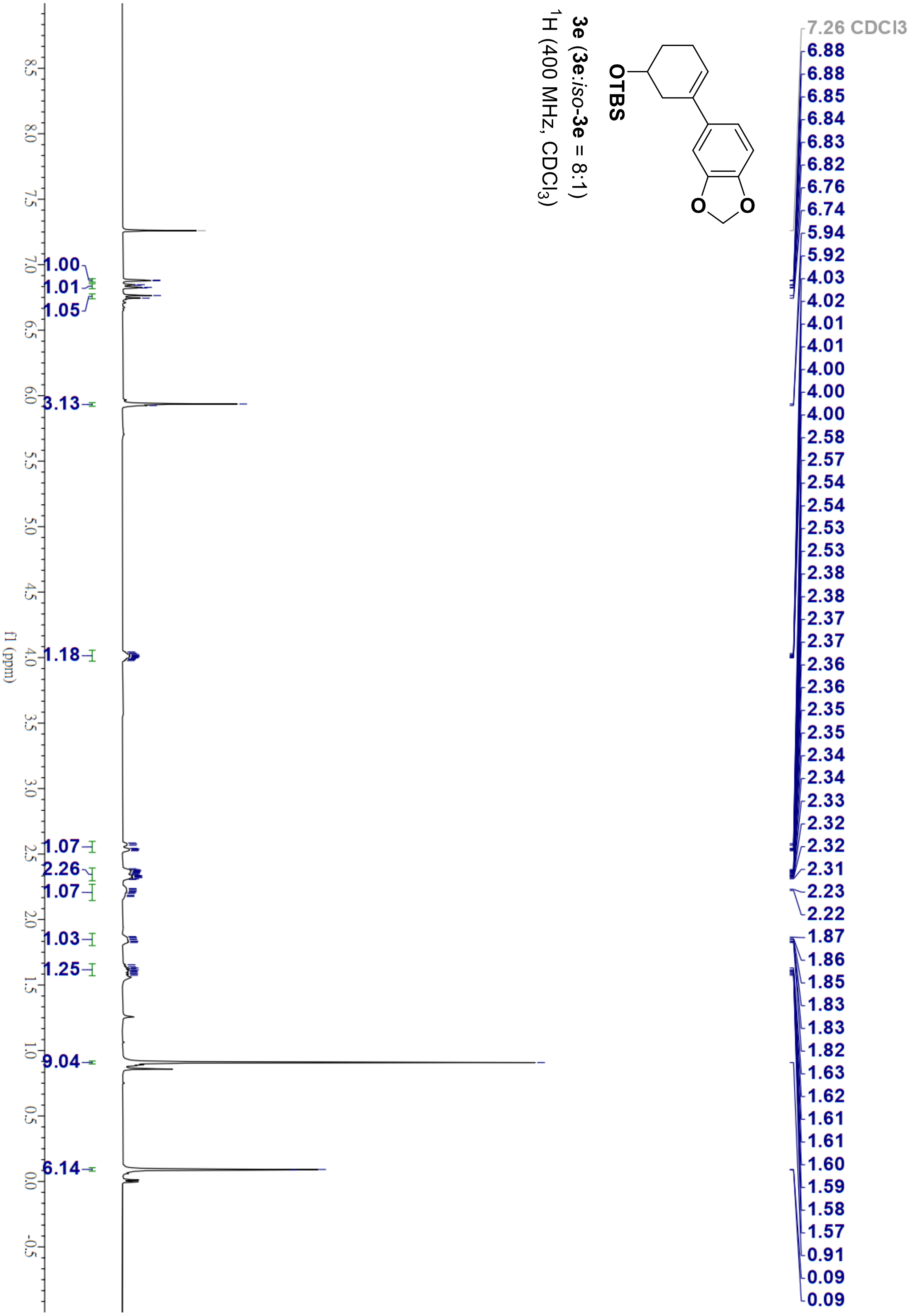
**TLC** ($SiO_2$): $R_f = 0.6$ (1:5 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 6.88 (d, J = 1.8 Hz, 1H), 6.83 (dd, J = 8.1, 1.9 Hz, 1H), 6.75 (d, J = 8.1 Hz, 1H), 5.96 – 5.90 (m, 3H), 4.07 – 3.95 (m, 1H), 2.61 – 2.50 (m, 1H), 2.41 – 2.28 (m, 2H), 2.26 – 2.15 (m, 1H), 1.89 – 1.80 (m, 1H), 1.66 – 1.55 (m, 1H), 0.91 (s, 9H), 0.09 (d, J = 1.4 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 147.8, 146.5, 136.7, 134.4, 123.0, 118.5, 108.1, 105.9, 101.0, 68.5, 37.8, 31.4, 26.1, 24.7, 18.4, -4.4.

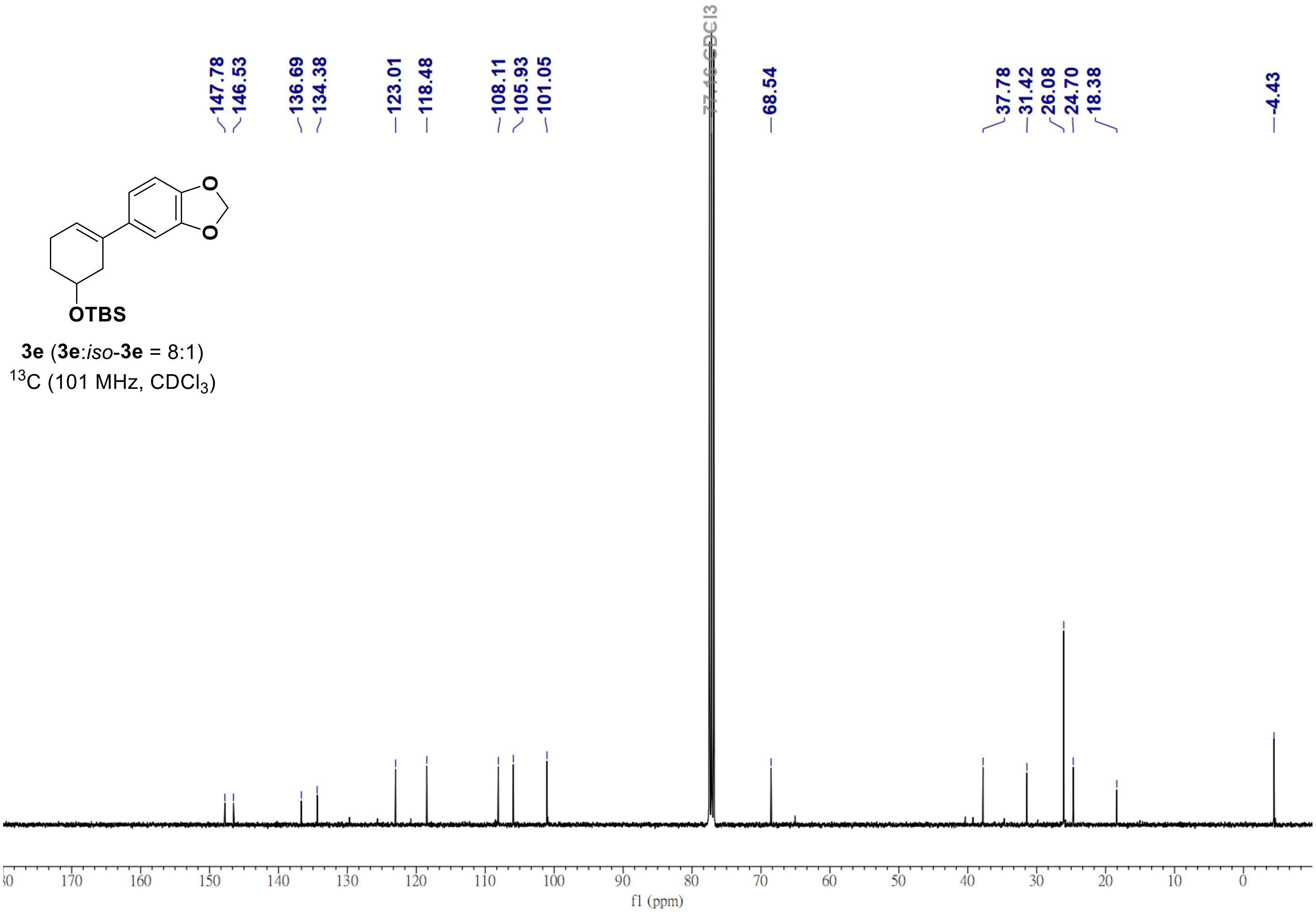
**HRMS** (ESI) m/z: [M+H$^+$] calcd. for $C_{19}H_{28}O_3Si$: 333.1880; found = 333.1890.

**FTIR** (neat): 2927, 2855, 1504, 1486, 1246, 1087, 1040, 834, 773 cm$^{-1}$.



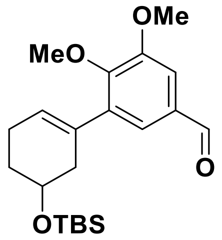
**3e** (**3e**:*iso*-**3e** = 8:1)

$^1$H (400 MHz, CDCl$_3$)



**3e** (**3e**:*iso*-**3e** = 8:1)
$^{13}$C (101 MHz, $CDCl_3$)

### 3'-((*tert*-butyldimethylsilyl)oxy)-5,6-dimethoxy-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-3-carbaldehyde (3f)



Following the general procedure, aryl iodide **1f** (116.8 mg, 0.4 mmol) and vinyl triflate **2a** (72.0 mg, 0.2 mmol) were subjected to modified reaction conditions (105 °C, 24 h). Upon flash column chromatography ($SiO_2$: 15:85 EtOAc:hexanes) the title compound **3f** was isolated as a red oil in 67% yield (50.4 mg, 0.13 mmol, >20:1 rr).

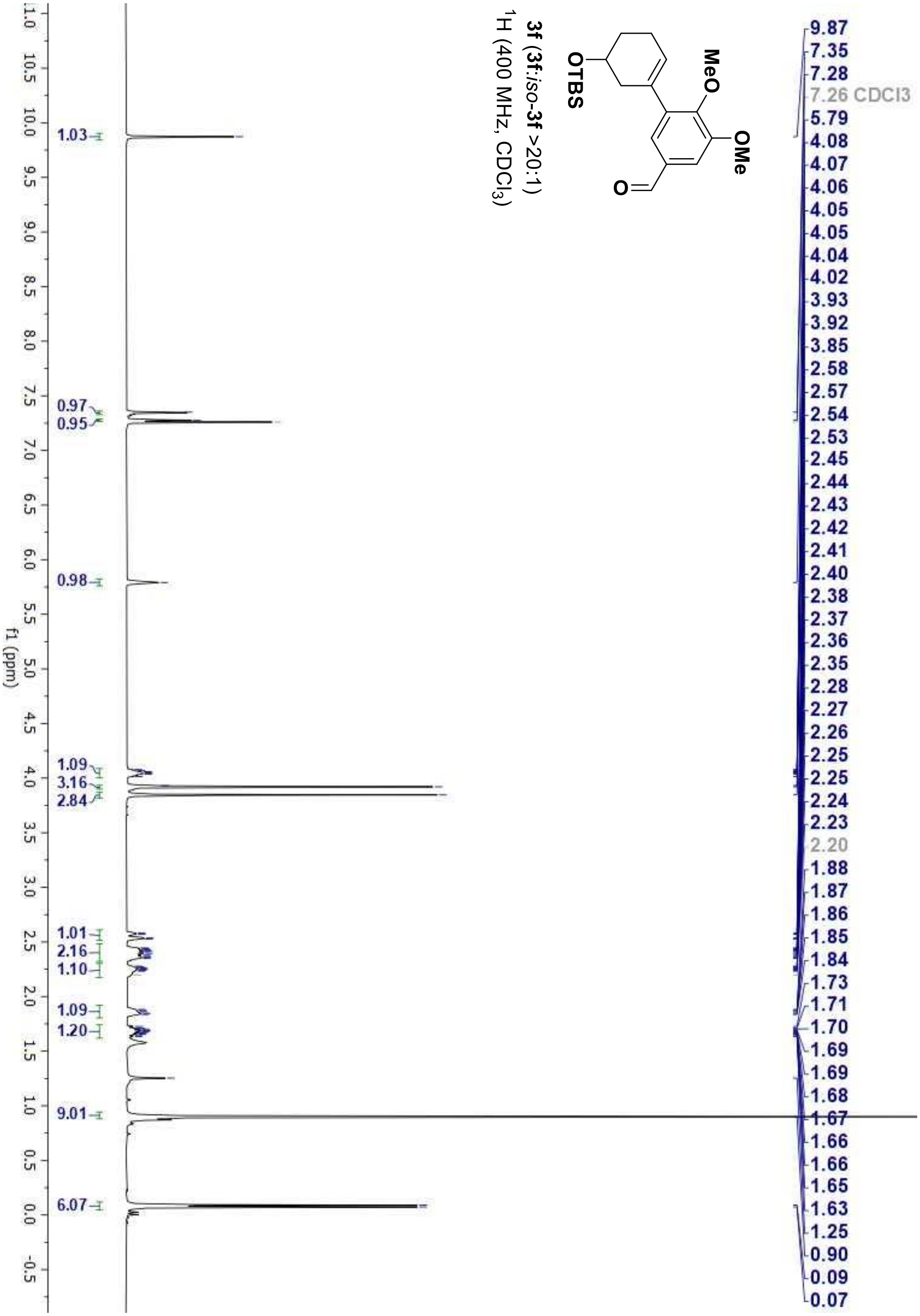
**TLC** ($SiO_2$): $R_f$ = 0.4 (1:2 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 9.87 (s, 1H), 7.35 (s, 1H), 7.28 (s, 1H), 5.79 (s, 1H), 4.09 – 4.00 (m, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 2.55 (dd, J = 17.0, 4.7 Hz, 1H), 2.48 – 2.32 (m, 2H), 2.30 – 2.17 (m, 1H), 1.92 – 1.80 (m, 1H), 1.74 – 1.62 (m, 1H), 0.90 (s, 9H), 0.08 (d, J = 6.6 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 191.5, 153.5, 152.2, 138.3, 133.7, 132.3, 127.1, 126.7, 109.2, 68.0, 61.0, 56.2, 38.6, 31.0, 26.0, 24.4, 18.4, -4.5.

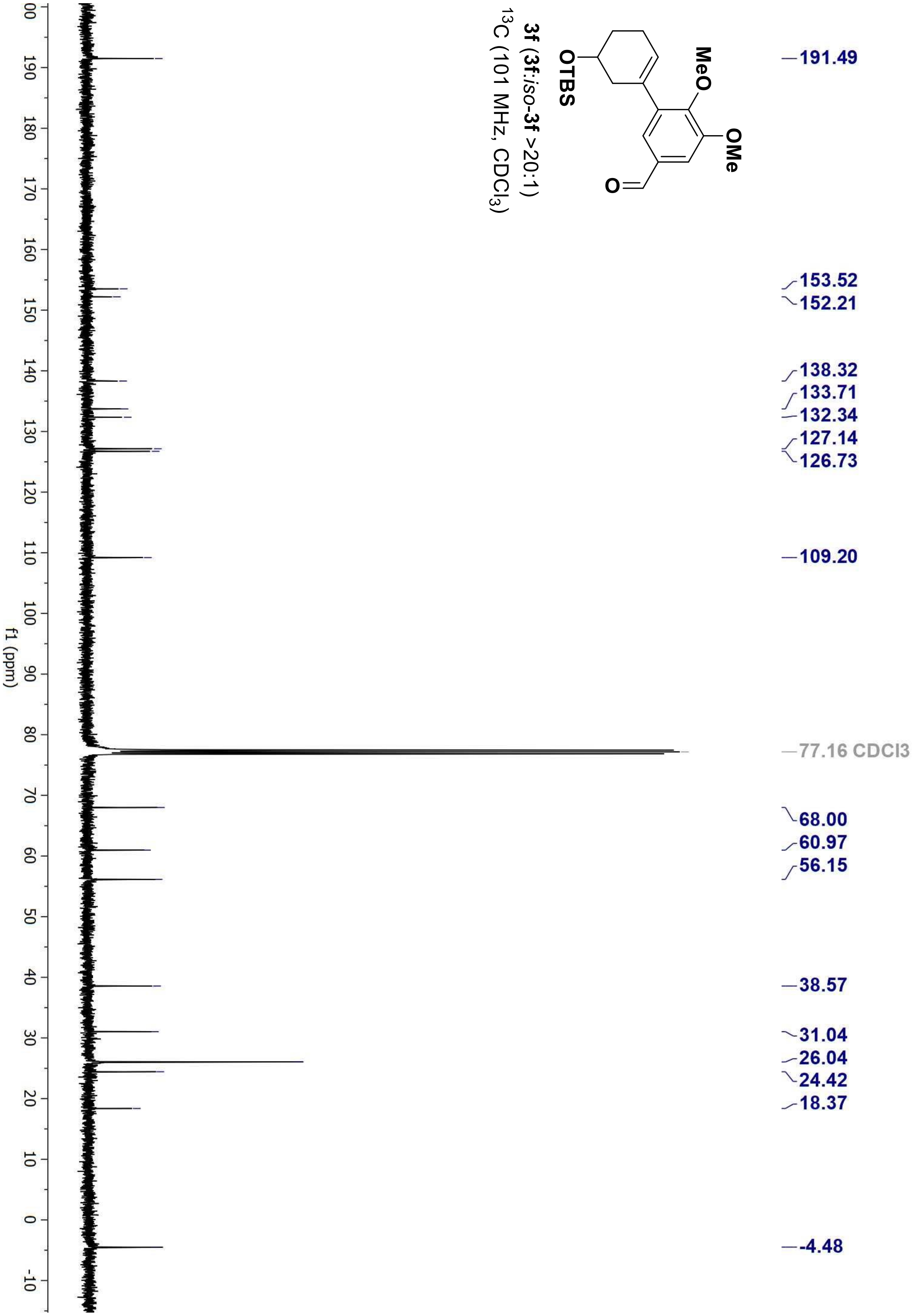
**HRMS** (ESI) m/z: [M+Na$^+$] calcd. for $C_{21}H_{32}O_4Si$: 399.1962; found = 399.1680.

**FTIR** (neat): 2928, 2855, 1694, 1578, 1462, 1249, 1088, 836, 775 cm$^{-1}$.



**3f** (**3f**:*iso*-**3f** >20:1)

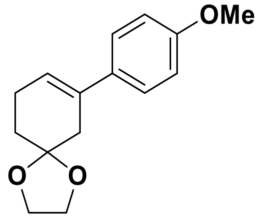
$^1$H (400 MHz, CDCl$_3$)



**3f** (**3f**:*iso*-**3f** >20:1)

$^{13}C$ (101 MHz, $CDCl_3$)

**7-(4-methoxyphenyl)-1,4-dioxaspiro[4.5]dec-7-ene (3g)**



Following the general procedure, aryl iodide **1a** (74.9 mg, 0.32 mmol) and vinyl triflate **2b** (57.6 mg, 0.2 mmol) were subjected to standard reaction conditions (100 °C, 24 h). Upon flash column chromatography ($SiO_2$: 2:98 EtOAc:hexanes) the title compound **3g** was isolated as a white solid in 69% yield (34.0 mg, 0.14 mmol, >20:1 rr).

**TLC** ($SiO_2$): $R_f$ = 0.3 (1:4 EtOAc:hexanes).

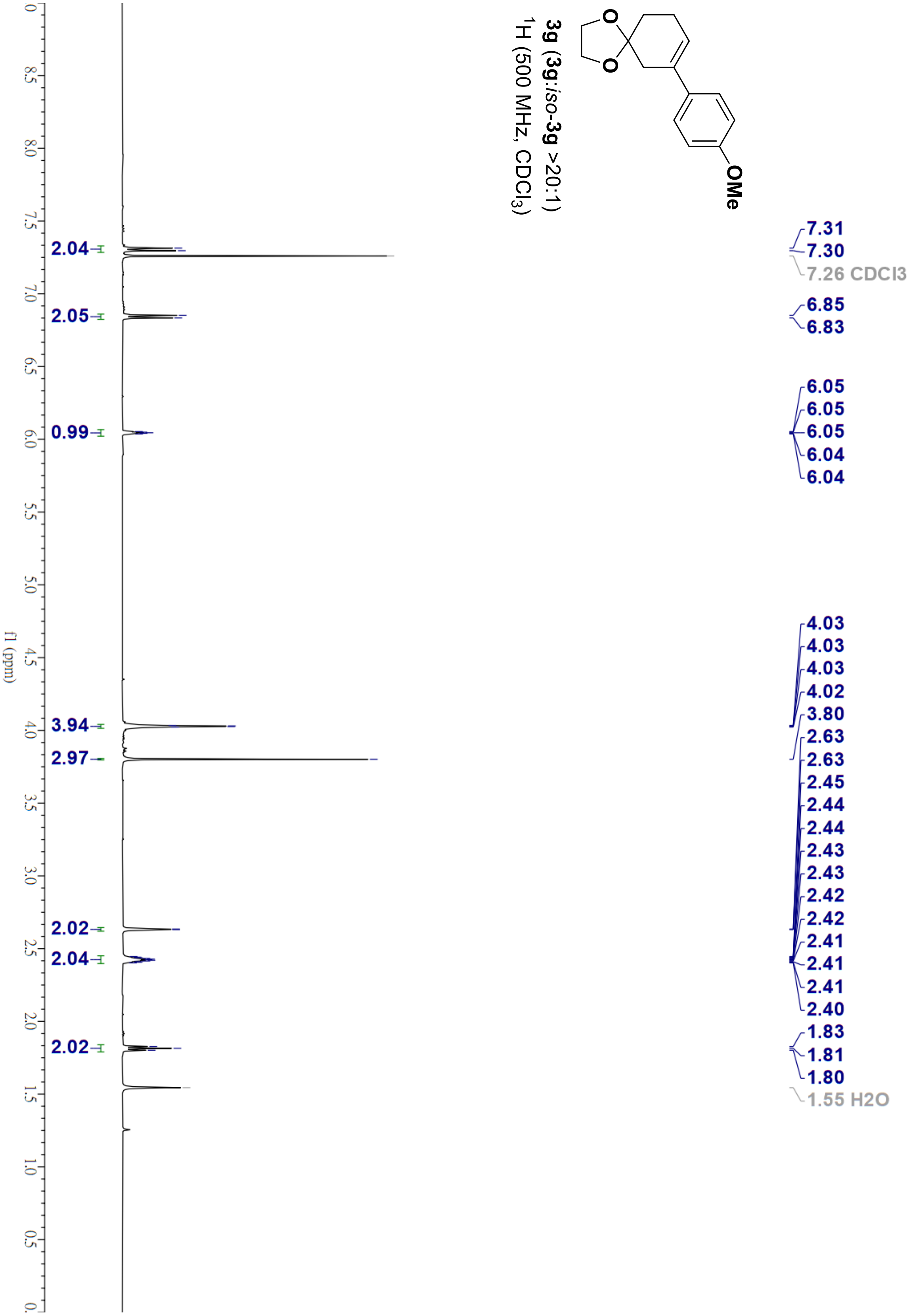
**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.31 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 6.05 (p, J = 2.1 Hz, 1H), 4.03 (q, J = 1.7 Hz, 4H), 3.80 (s, 3H), 2.63 (d, J = 2.0 Hz, 2H), 2.42 (dtt, J = 6.4, 4.1, 2.1 Hz, 2H), 1.81 (t, J = 6.5 Hz, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 158.8, 134.1, 134.0, 126.2, 121.8, 113.7, 108.7, 64.7, 55.4, 38.0, 30.8, 24.9.

**HRMS** (ESI) m/z: [M+H$^+$] calcd. for $C_{15}H_{18}O_3$: 247.1329; found = 247.1330.

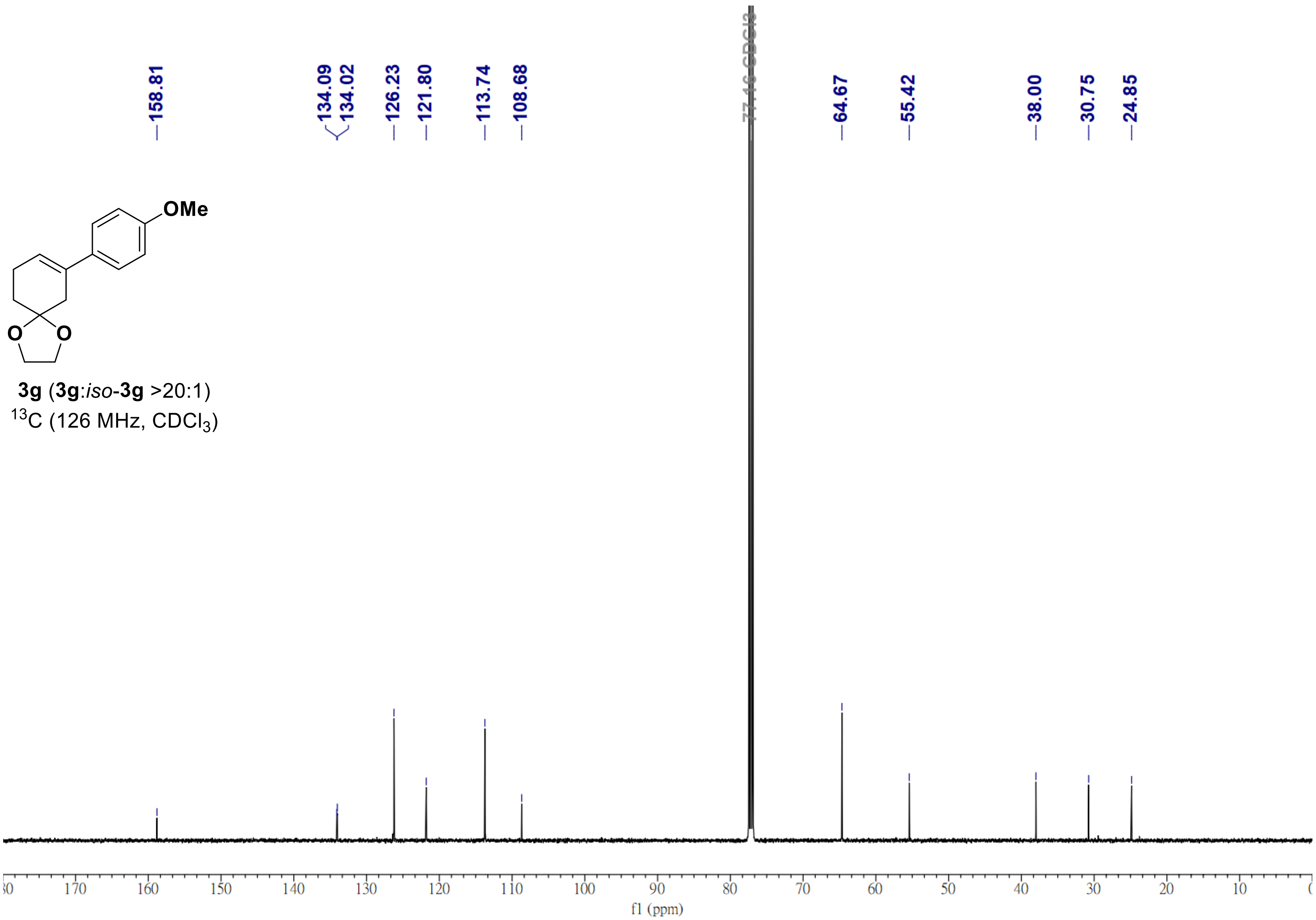
**FTIR** (neat): 2956, 2885, 1513, 1363, 1235, 1115, 1022, 824, 806 cm$^{-1}$.

**Melting Point:** 92-94 °C



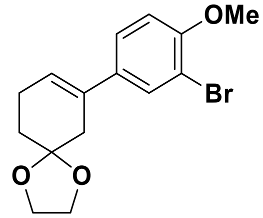
**3g** (**3g**:*iso*-**3g** >20:1)

$^1$H (500 MHz, $CDCl_3$)



**3g** (**3g**:*iso*-**3g** >20:1)
$^{13}$C (126 MHz, $CDCl_3$)

### 7-(3-bromo-4-methoxyphenyl)-1,4-dioxaspiro[4.5]dec-7-ene (3h)



Following the general procedure, aryl iodide **1g** (125.0 mg, 0.4 mmol) and vinyl triflate **2b** (57.6 mg, 0.2 mmol) were subjected to modified reaction conditions (10 mol% $Pd(OAc)_2$, 105 °C, 24 h). Upon flash column chromatography ($SiO_2$: 2:98 EtOAc:hexanes) the title compound **3h** was isolated as a clear wax in 59% yield (38.4 mg, 0.12 mmol, >20:1 rr).

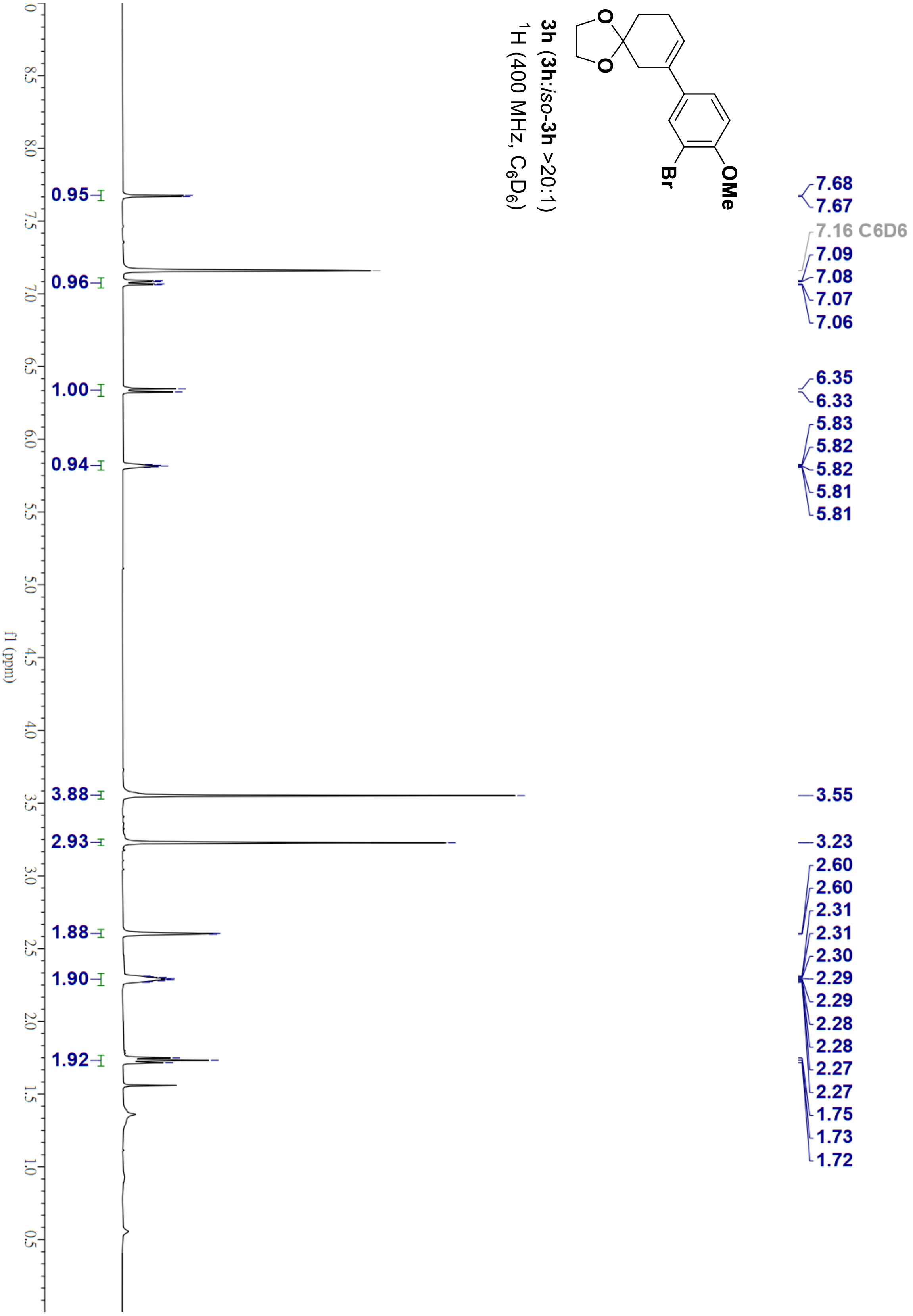
**TLC** ($SiO_2$): $R_f$ = 0.4 (1:2 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $C_6D_6$): $\delta$ 7.67 (d, J = 2.4 Hz, 1H), 7.08 (dd, J = 8.5, 2.3 Hz, 1H), 6.34 (d, J = 8.5 Hz, 1H), 5.82 (dt, J = 4.1, 2.1 Hz, 1H), 3.55 (s, 4H), 3.23 (s, 3H), 2.60 (s, 2H), 2.29 (dtd, J = 6.6, 4.2, 1.9 Hz, 2H), 1.73 (t, J = 6.5 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $C_6D_6$): $\delta$ 155.4, 136.0, 133.3, 130.7, 125.2, 123.3, 112.4, 111.8, 108.5, 64.5, 55.6, 38.3, 31.2, 25.1.

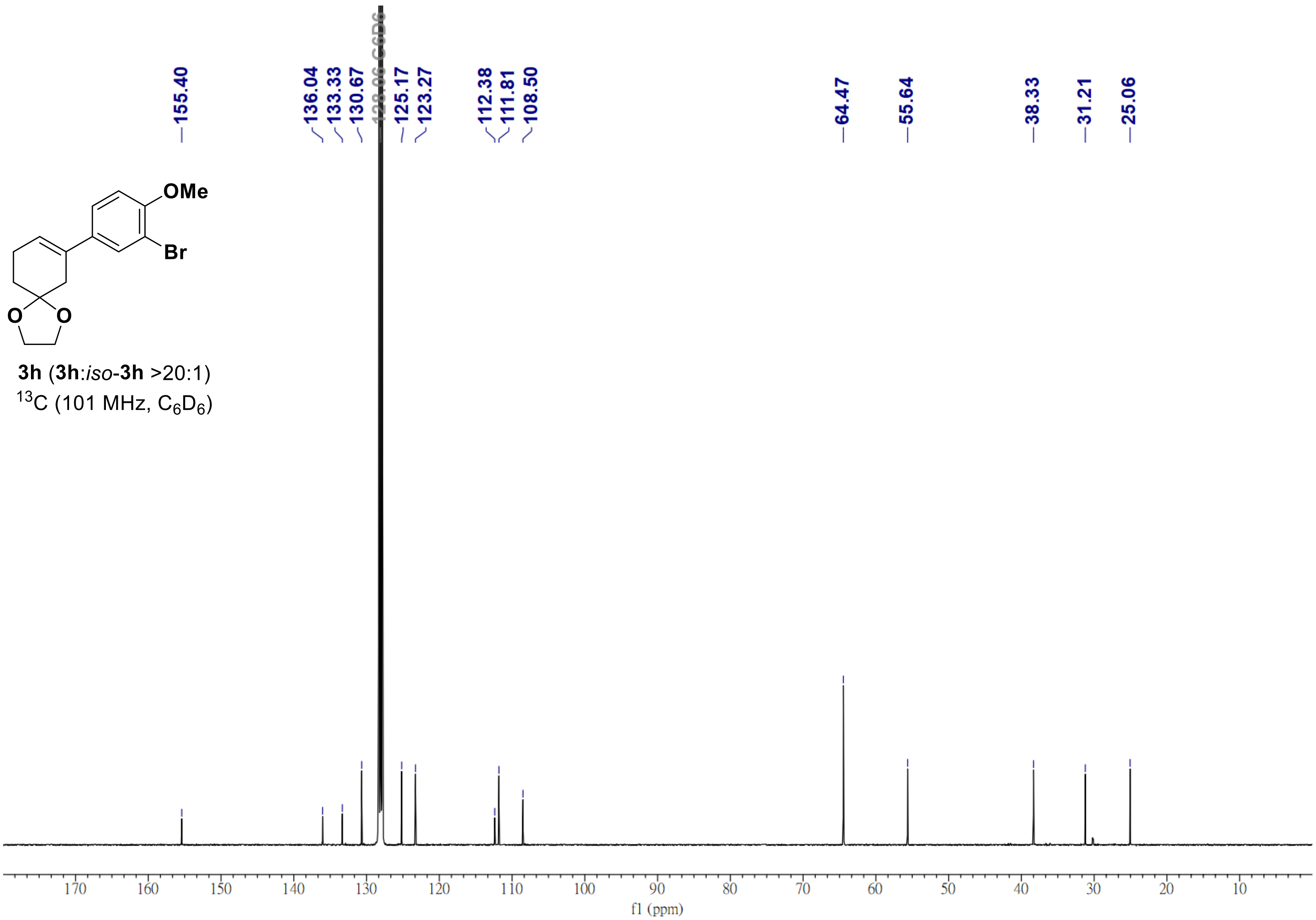
**HRMS** (ESI) m/z: [M+H$^+$] calcd. for $C_{15}H_{17}BrO_3$: 325.0434; found = 325.0437.

**FTIR** (neat): 2928, 2837, 1498, 1284, 1254, 1142, 1054, 1026, 806 cm$^{-1}$.



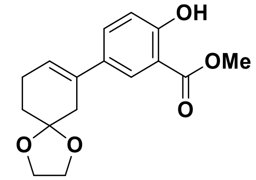
**3h** (**3h**:*iso*-**3h** >20:1)

$^1$H (400 MHz, $C_6D_6$)



**3h** (**3h**:*iso*-**3h** >20:1)
$^{13}$C (101 MHz, $C_6D_6$)

**Methyl 2-hydroxy-5-(1,4-dioxaspiro[4.5]dec-7-en-7-yl)benzoate (3i)**



Following the general procedure, aryl iodide **1h** (111.2 mg, 0.4 mmol) and vinyl triflate **2b** (58.2 mg, 0.2 mmol) were subjected to standard reaction conditions (100 °C, 24 h). Upon flash column chromatography ($SiO_2$: 3:97 EtOAc:hexanes) the title compound **3i** was isolated as a clear oil in 62% yield (36.0 mg, 0.12 mmol, 16:1 rr).

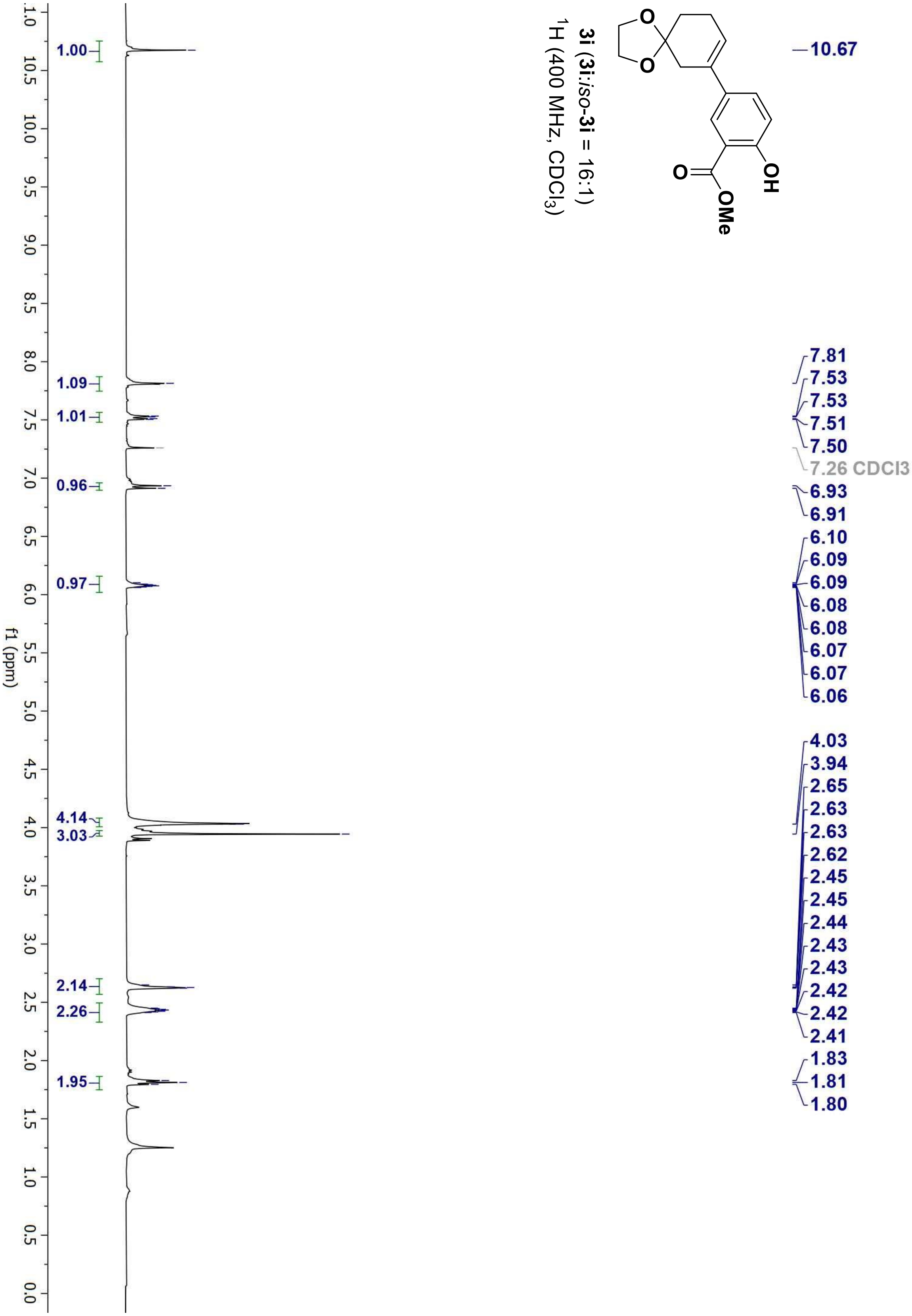
**TLC** ($SiO_2$): $R_f$ = 0.6 (1:2 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.67 (s, 1H), 7.81 (s, 1H), 7.52 (dd, J = 8.7, 2.5 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 6.08 (td, J = 4.0, 2.0 Hz, 1H), 4.03 (s, 4H), 3.94 (s, 3H), 2.70 – 2.57 (m, 2H), 2.43 (ddt, J = 6.6, 4.6, 2.0 Hz, 2H), 1.81 (t, J = 6.5 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 170.7, 160.8, 133.3, 132.7, 132.7, 126.1, 122.6, 117.6, 112.0, 108.5, 64.7, 52.4, 38.0, 30.6, 24.8.

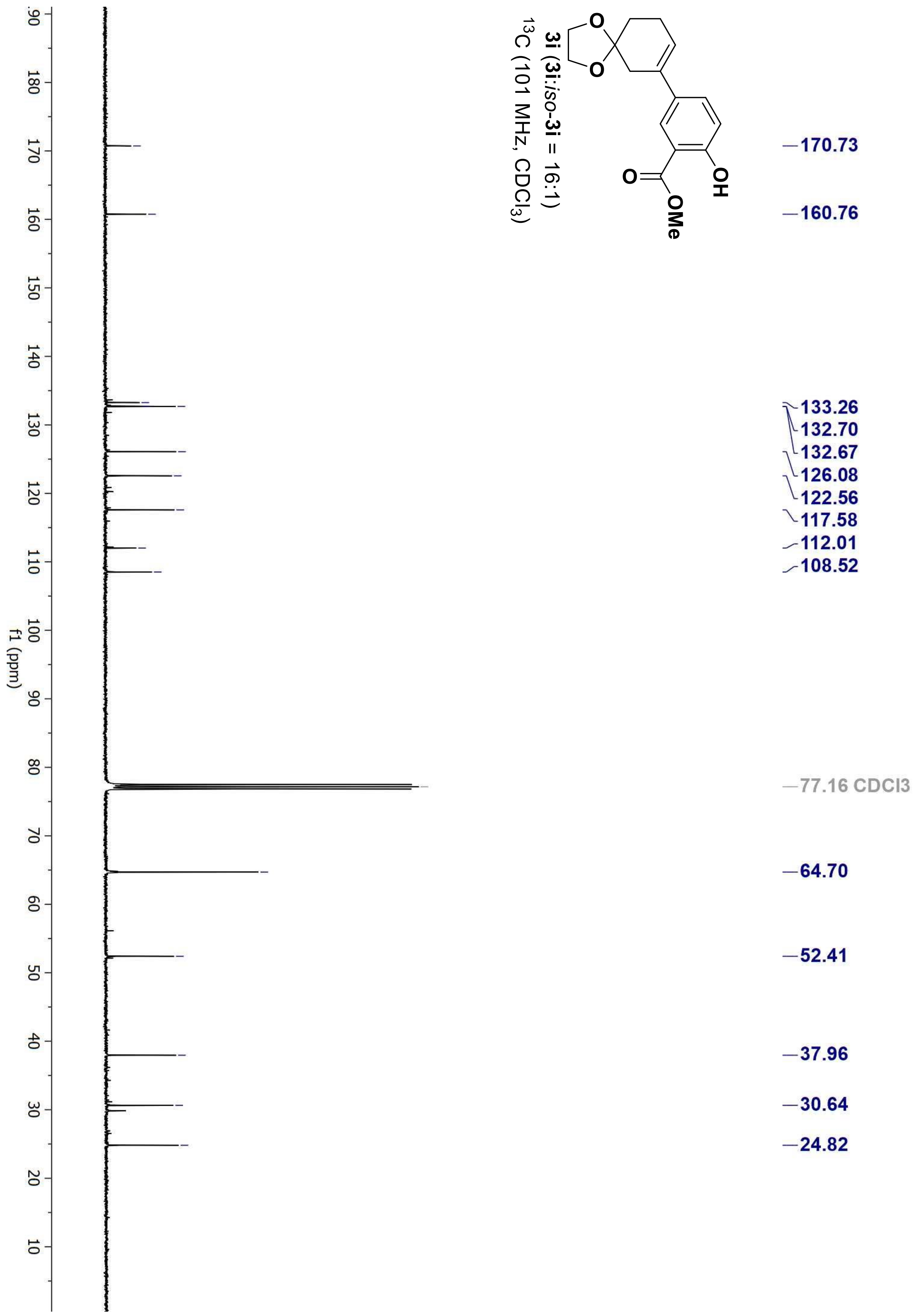
**HRMS** (ESI) m/z: [M+H$^+$] calcd. for $C_{16}H_{18}O_5$: 291.1227; found = 291.1237.

**FTIR** (neat): 3345, 2929, 2845, 1650, 1499, 1364, 1285, 1113, 808 cm$^{-1}$.

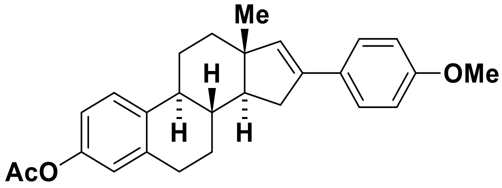


**3i** (**3i**:*iso*-**3i** = 16:1)

$^1$H (400 MHz, CDCl$_3$)


3i (3i:iso-3i = 16:1)
13C (101 MHz, CDCl3)
OH
O
OMe
O
O
170.73
160.76
133.26
132.70
132.67
126.08
122.56
117.58
112.01
108.52
77.16 CDCl3
64.70
52.41
37.96
30.64
24.82
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

**(8S,9S,13S,14S)-16-(4-methoxyphenyl)-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthren-3-yl acetate (3j)**



Following the general procedure, aryl iodide **1a** (74.9 mg, 0.32 mmol) and vinyl triflate **2c** (88.9 mg, 0.2 mmol) were subjected to standard reaction conditions (100 °C, 24 h). Upon flash column chromatography ($SiO_2$: 1:99 EtOAc:hexanes) the title compound **3j** was isolated as a white solid in 60% yield (48.3 mg, 0.12 mmol, >20:1 rr).

**TLC** ($SiO_2$): $R_f$ = 0.3 (1:4 EtOAc:hexanes).

**$^1$H NMR** (500 MHz, $C_6D_6$): $\delta$ 7.37 (d, J = 8.7 Hz, 2H), 7.19 – 7.17 (m, 1H), 7.01 (dd, J = 8.4, 2.6 Hz, 1H), 6.92 (d, J = 2.6 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 6.14 (d, J = 2.3 Hz, 1H), 3.35 (s, 3H), 2.78 – 2.62 (m, 2H), 2.44 (dd, J = 14.2, 6.7 Hz, 1H), 2.22 (ddd, J = 14.0, 11.6, 2.3 Hz, 1H), 2.18 – 2.09 (m, 2H), 1.85 – 1.80 (m, 4H), 1.74 (ddd, J = 12.7, 6.4, 2.7 Hz, 1H), 1.64 – 1.44 (m, 4H), 1.26 (tt, J = 11.9, 6.0 Hz, 1H), 0.85 (s, 3H).

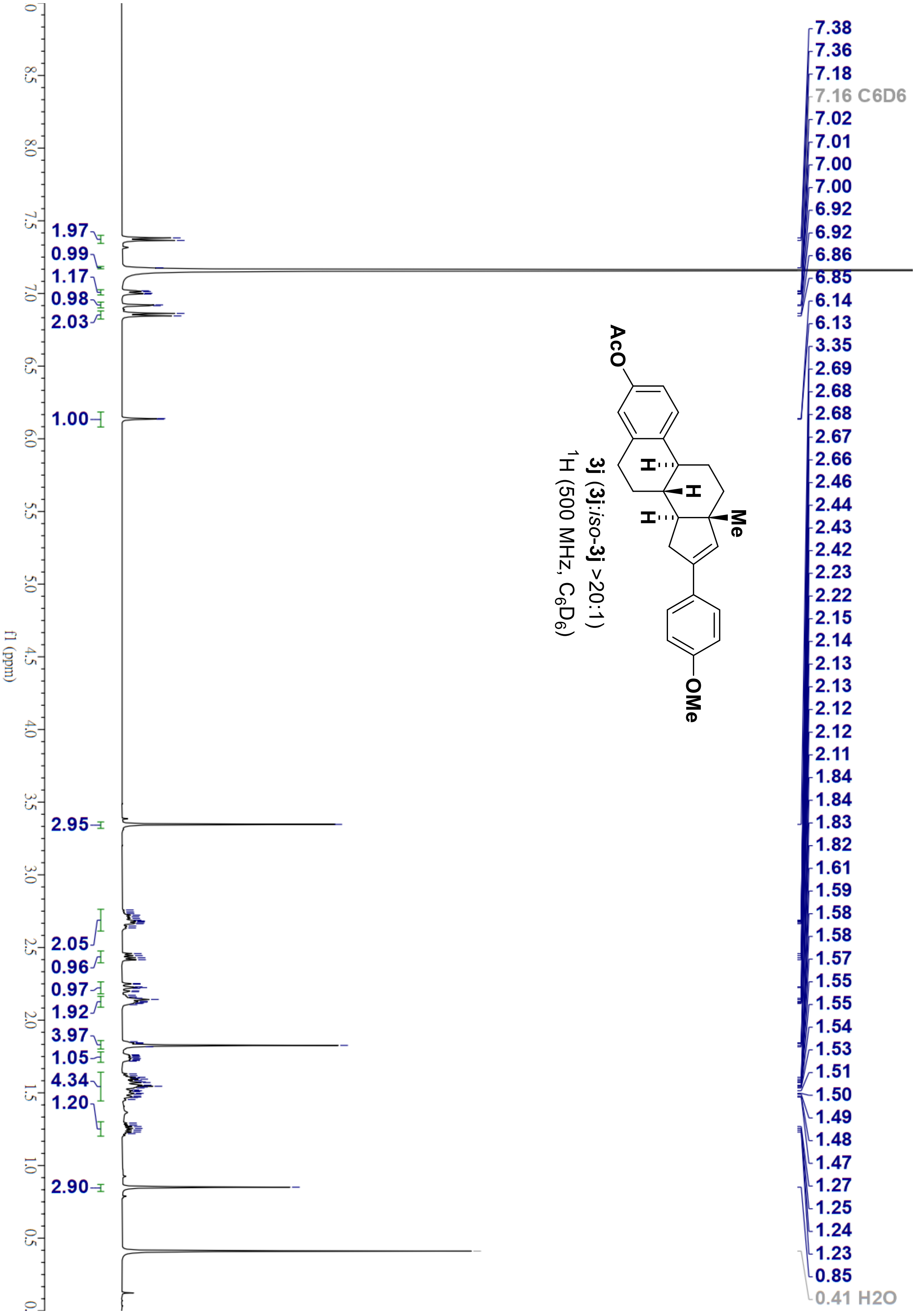
**$^{13}$C NMR** (126 MHz, $C_6D_6$): $\delta$ 168.8, 159.5, 149.4, 141.6, 138.3, 138.2, 136.0, 130.5, 127.0, 126.3, 122.1, 119.1, 114.1, 55.3, 54.8, 46.7, 45.0, 37.3, 36.5, 33.1, 29.7, 28.1, 26.7, 20.7, 17.4.

**HRMS** (ESI) m/z: [M+H$^+$] calcd. for $C_{27}H_{30}O_3$: 403.2268; found = 403.2263.

**FTIR** (neat): 2927, 2846, 1762, 1599, 1510, 1364, 1202, 1037, 809 cm$^{-1}$.

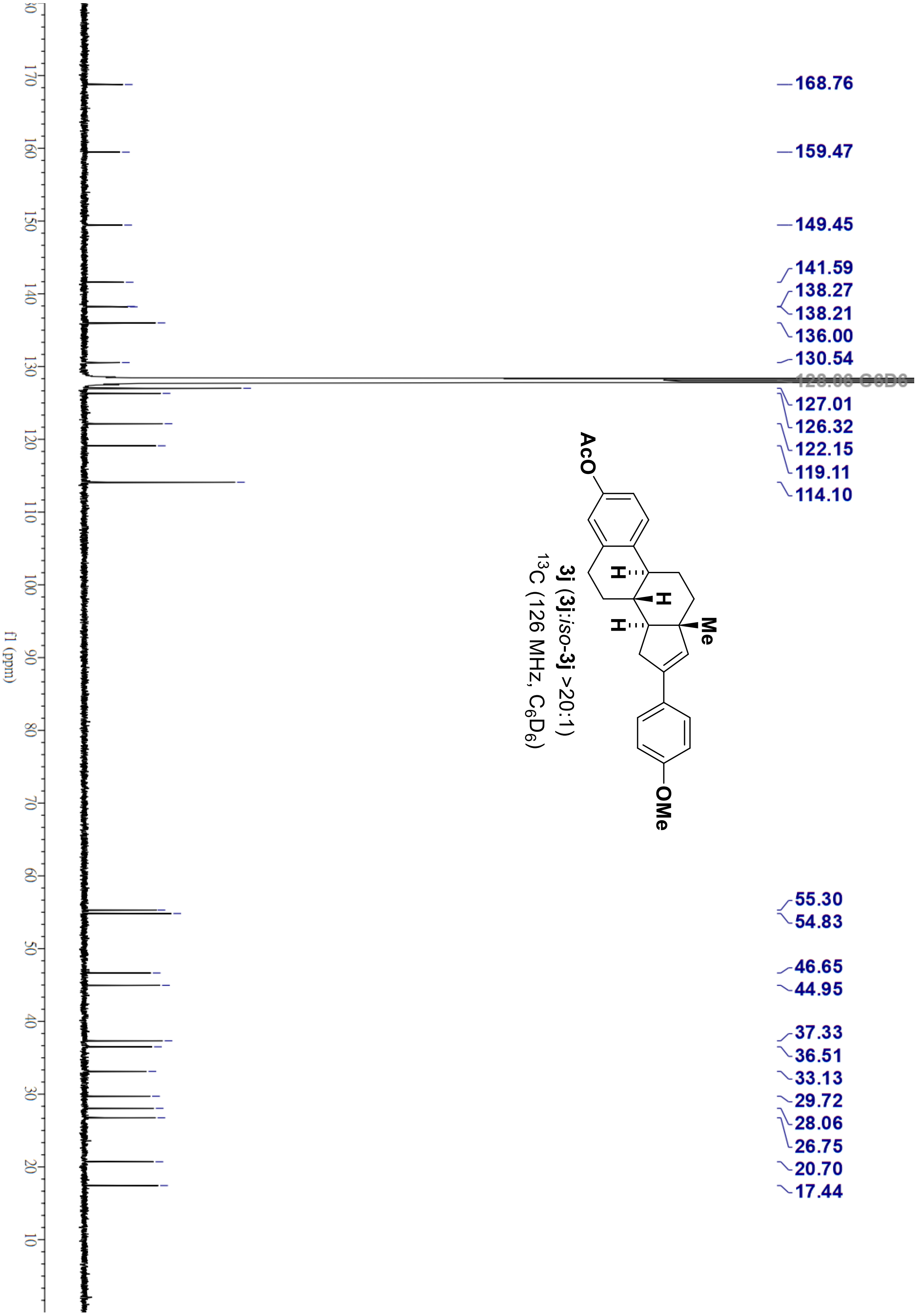
$[\alpha]\frac{D}{24}$ = 80.0 (c = 0.001, $CHCl_3$).

**Melting Point:** 164-166 °C



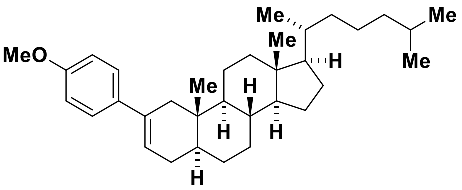
**3j** (**3j**:*iso*-**3j** >20:1)

$^1$H (500 MHz, $C_6D_6$)


**3j** (**3j**:*iso*-**3j** >20:1)

$^{13}C$ (126 MHz, $C_6D_6$)

**(8R,9S,10S,13R,14S,17R)-2-(4-methoxyphenyl)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[α]phenanthrene (3k)**



Following the general procedure, aryl iodide **1a** (74.9 mg, 0.32 mmol) and vinyl triflate **2d** (103.7 mg, 0.2 mmol) were subjected to modified reaction conditions (10 mol% $Pd(OAc)_2$, 105 °C, 48 h). Upon flash column chromatography ($SiO_2$: 2:98 EtOAc:hexanes) the title compound **3k** was isolated as a white solid in 60% yield (57.0 mg, 0.12 mmol, 20:1rr).

**TLC** ($SiO_2$): $R_f$ = 0.7 (1:9 EtOAc:hexanes).

**$^1$H NMR** (500 MHz, $C_6D_6$): δ 7.38 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.01 (dd, J = 5.2, 2.5 Hz, 1H), 3.36 (s, 3H), 2.43 (d, J = 16.5 Hz, 1H), 2.15 – 2.09 (m, 1H), 2.09 – 2.06 (m, 1H), 2.06 – 2.02 (m, 1H), 1.94 – 1.85 (m, 2H), 1.71 (dd, J = 12.9, 3.4 Hz, 1H), 1.65 – 1.60 (m, 1H), 1.57 (dd, J = 13.0, 6.0 Hz, 2H), 1.49 – 1.48 (m, 1H), 1.47 – 1.46 (m, 1H), 1.45 – 1.44 (m, 1H), 1.36 (dt, J = 7.7, 4.0 Hz, 3H), 1.32 (d, J = 3.7 Hz, 1H), 1.30 (d, J = 3.7 Hz, 1H), 1.27 (d, J = 3.3 Hz, 1H), 1.26 – 1.24 (m, 1H), 1.23 – 1.22 (m, 1H), 1.21 – 1.19 (m, 1H), 1.18 (d, J = 3.3 Hz, 1H), 1.16 (d, J = 2.5 Hz, 1H), 1.14 (d, J = 2.2 Hz, 1H), 1.13 – 1.11 (m, 1H), 1.11 – 1.08 (m, 1H), 1.05 (d, J = 6.5 Hz, 3H), 0.94 (dd, J = 6.6, 1.4 Hz, 6H), 0.86 (s, 3H), 0.72 (s, 3H), 0.41 (s, 2H).

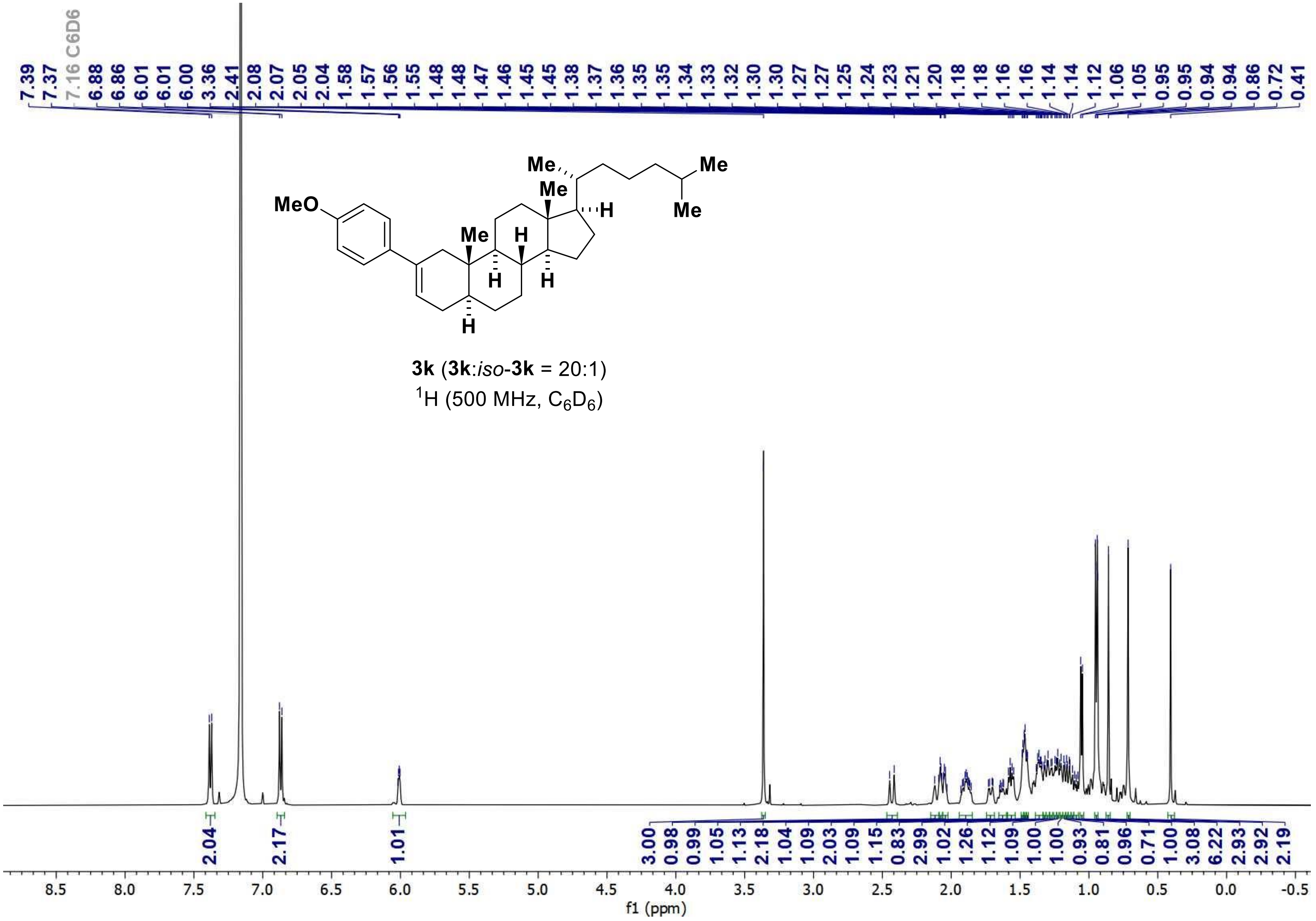
**$^{13}$C NMR** (126 MHz, $C_6D_6$): δ 159.3, 136.2, 135.6, 126.7, 121.8, 114.0, 56.8, 54.9, 54.5, 42.9, 42.8, 41.5, 40.5, 40.0, 36.7, 36.3, 36.0, 35.3, 32.2, 31.4, 30.2, 28.9, 28.7, 28.4, 24.6, 24.4, 23.1, 22.8, 21.4, 19.1, 12.3, 12.0.

**HRMS** (ESI) m/z: [M+H$^+$] calcd. for $C_{34}H_{52}O$: 477.4091; found = 477.4086.

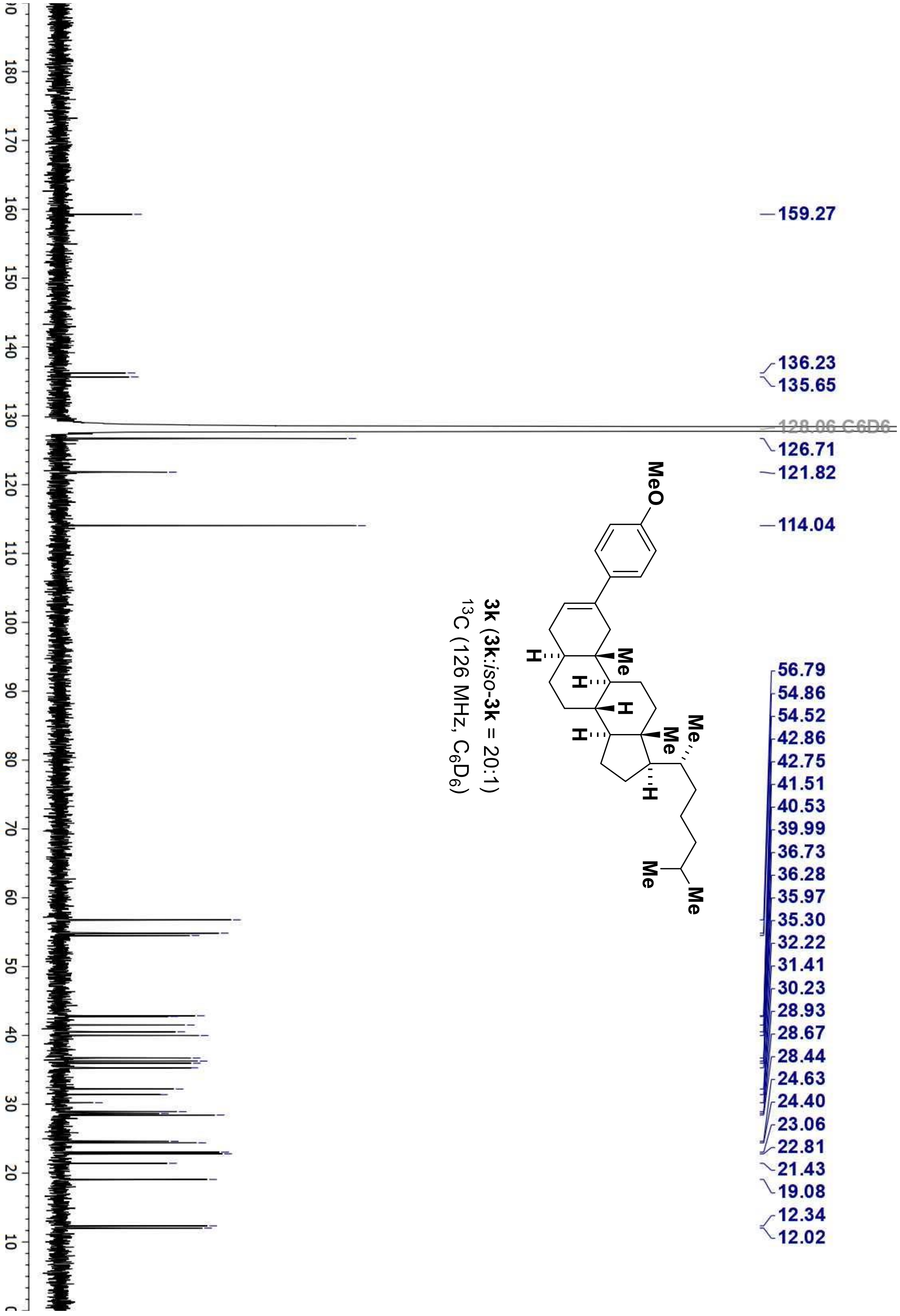
**FTIR** (neat): 2930, 2864, 1511, 1465, 1381, 1247, 1186, 1034, 802 cm$^{-1}$.

$[\alpha]\frac{D}{24}$ = 62.1 (c = 0.1, $CHCl_3$).

**Melting Point:** 116-118 °C

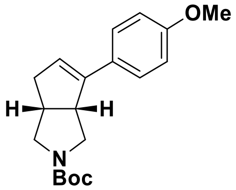


**3k** (**3k**:*iso*-**3k** = 20:1)
$^1$H (500 MHz, $C_6D_6$)



**3k** (**3k**:*iso*-**3k** = 20:1)
$^{13}C$ (126 MHz, $C_6D_6$)

### (±)-*tert*-butyl (3aR,6aR)-6-(4-methoxyphenyl)-3,3a,4,6a-tetrahydrocyclopenta[c]pyrrole-2(1H)-carboxylate (3l)



Following the general procedure, aryl iodide **1a** (74.9 mg, 0.32 mmol) and vinyl triflate **2e** (71.4 mg, 0.2 mmol) were subjected to standard reaction conditions (100 °C, 24 h). Upon flash column chromatography ($SiO_2$: 5:95 EtOAc:hexanes) the title compound **3l** was isolated as a clear oil in 69% yield (43.5 mg, 0.14 mmol, >20:1 rr).

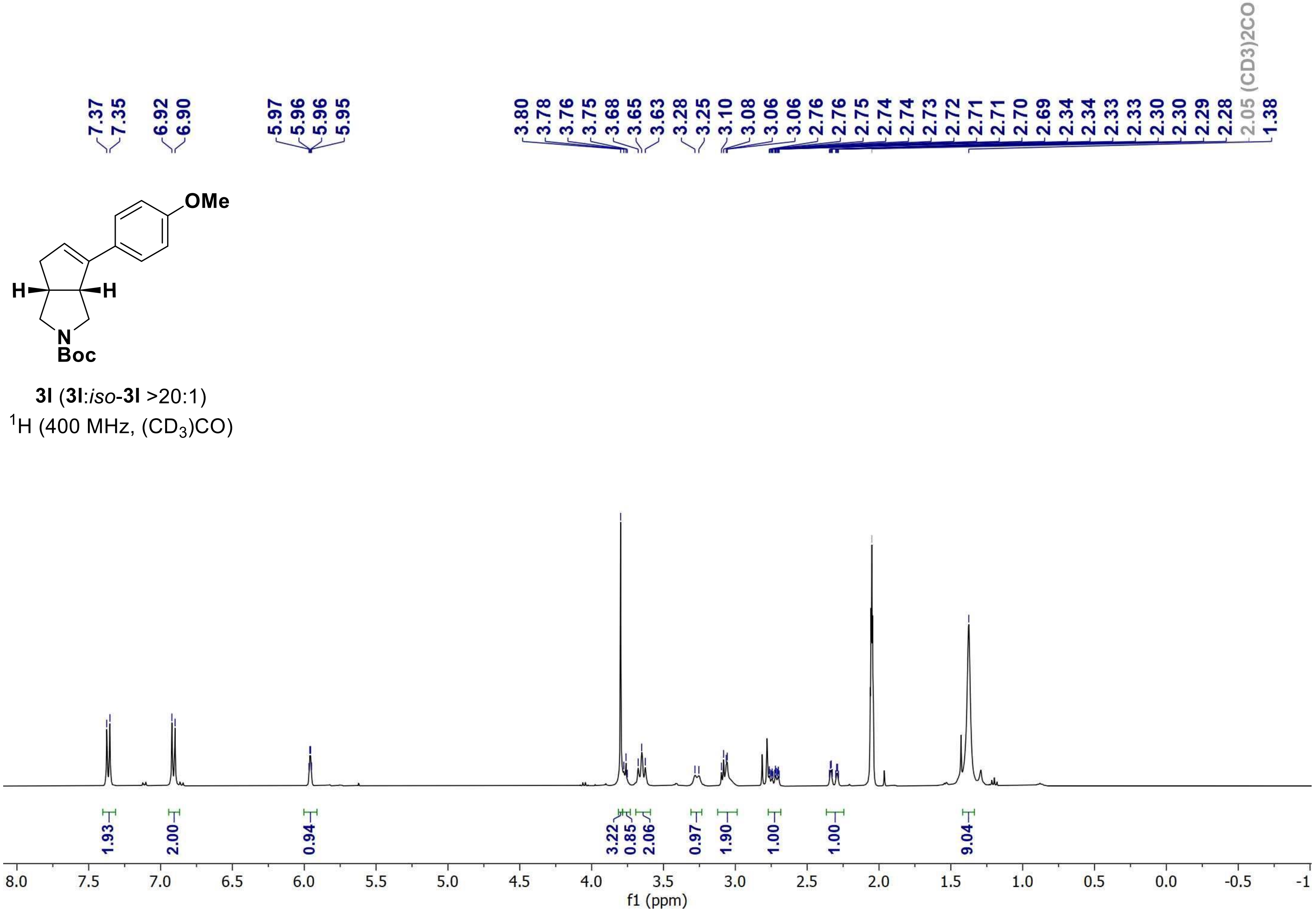
**TLC** ($SiO_2$): $R_f$ = 0.5 (1:3 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $(CD_3)_2CO$): $\delta$ 7.36 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 5.96 (q, J = 2.4 Hz, 1H), 3.80 (s, 3H), 3.77 (m, 1H), 3.65 (t, J = 9.9 Hz, 2H), 3.27 (d, J = 10.9 Hz, 1H), 3.07 (m, 2H), 2.77 – 2.68 (m, 1H), 2.31 (dq, J = 17.3, 2.6 Hz, 1H), 1.38 (s, 9H).

**$^{13}$C NMR** (101 MHz, $(CD_3)_2CO$): $\delta$ 160.2, 154.7, 144.9, 129.3, 128.3, 124.1, 114.9, 79.1, 55.7, 50.9, 39.0, 30.6, 30.4, 30.2, 30.0, 28.8.

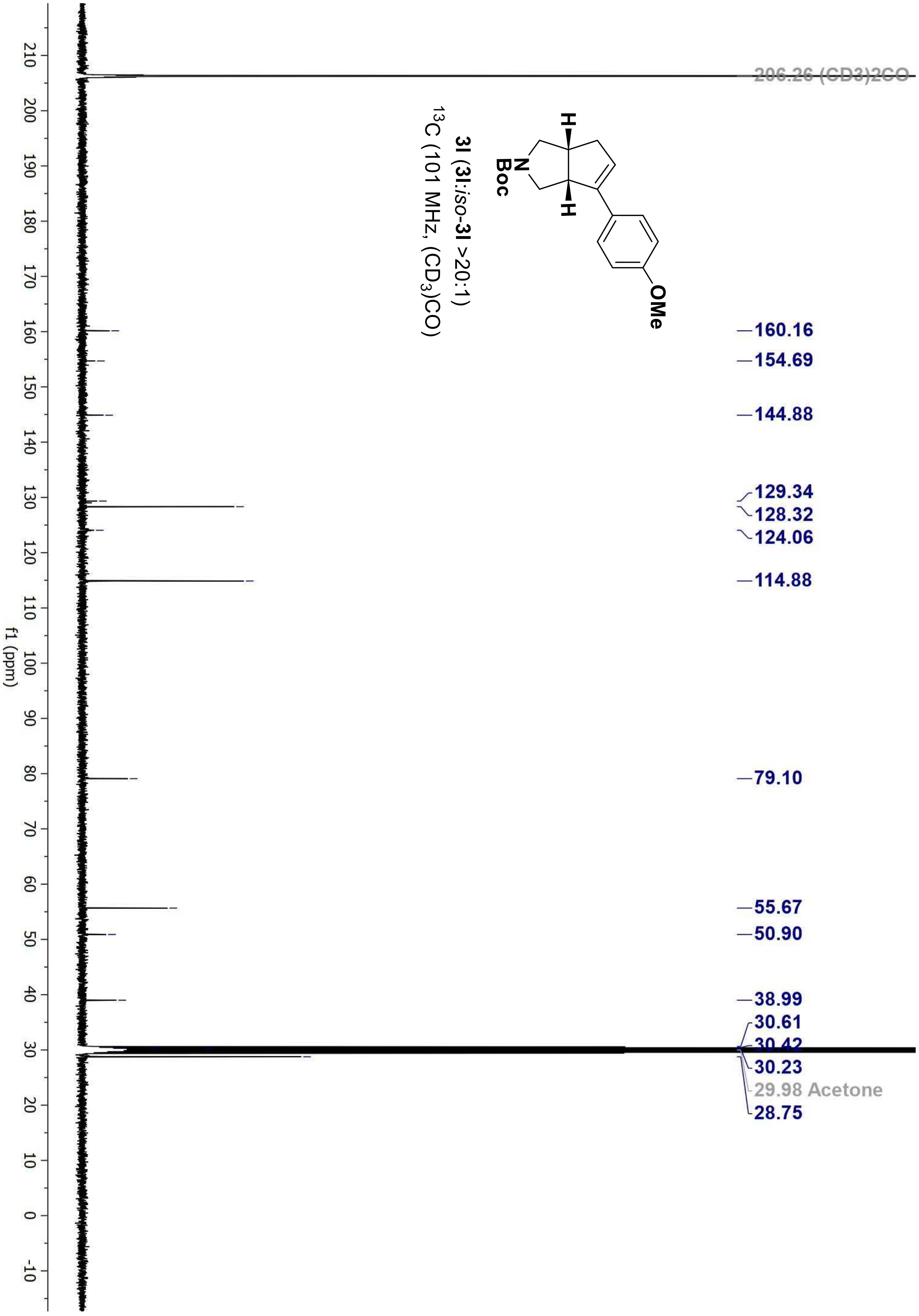
**HRMS** (ESI) m/z: [M+Na$^+$] calcd. for $C_{19}H_{25}NO_3$: 338.1727; found = 338.1735.

**FTIR** (neat): 2975, 2934, 1685, 1512, 1405, 1249, 1166, 909, 729 cm$^{-1}$.



**3l** (**3l**:*iso*-**3l** >20:1)

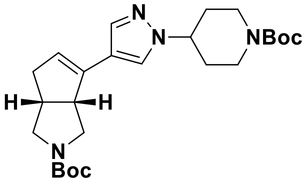
$^1$H (400 MHz, $(CD_3)CO$)



**3l** (**3l**:*iso*-**3l** >20:1)

$^{13}C$ (101 MHz, $(CD_3)CO$)

**(±)-*tert*-butyl (3aR,6aR)-6-(1-(1-(tert-butoxycarbonyl)piperidin-4-yl)-1H-pyrazol-4-yl)-3,3a,4,6a-tetrahydrocyclopenta[c]pyrrole-2(1H)-carboxylate (3m)**



Following the general procedure, aryl iodide **1i** (150.9 mg, 0.4 mmol) and vinyl triflate **2e** (71.4 mg, 0.2 mmol) were subjected to modified reaction conditions (105 °C, 24 h). Upon flash column chromatography ($SiO_2$: 20:80 EtOAc:hexanes) the title compound **3m** was isolated as a yellow wax in 75% yield (68.7 mg, 0.15 mmol, 14:1 rr).

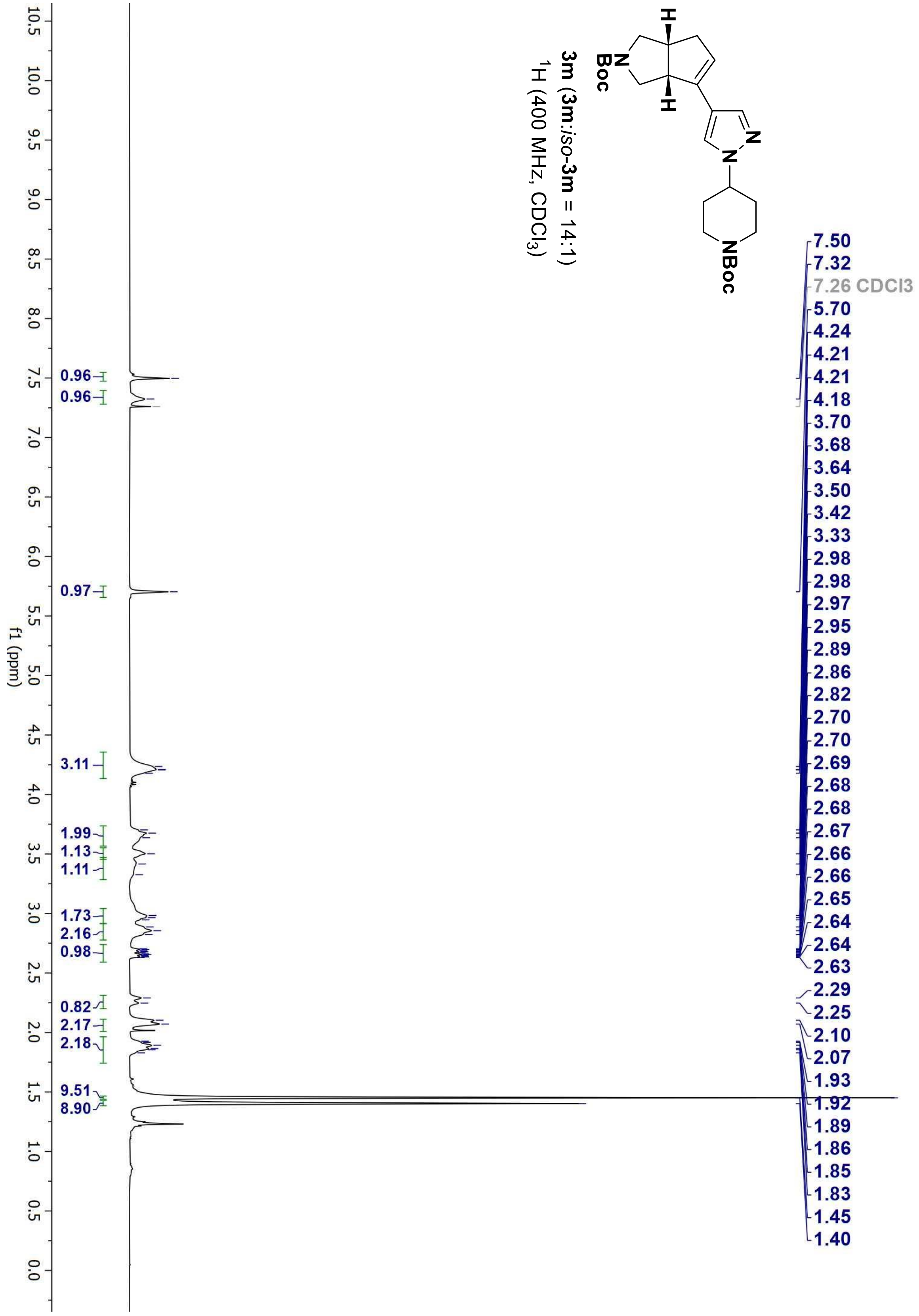
**TLC** ($SiO_2$): $R_f = 0.3$ (1:1 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.50 (s, 1H), 7.32 (s, 1H), 5.70 (s, 1H), 4.36 – 4.13 (m, 3H), 3.69 (m, 2H), 3.50 (m, 1H), 3.37 (m, 1H), 3.04 – 2.92 (m, 2H), 2.86 (t, J = 12.7 Hz, 2H), 2.67 (ddt, J = 17.1, 7.9, 2.2 Hz, 1H), 2.27 (d, J = 17.2 Hz, 1H), 2.09 (d, J = 12.8 Hz, 2H), 1.88 (td, J = 13.8, 7.1 Hz, 2H), 1.45 (s, 9H), 1.40 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 154.7, 154.5, 137.1, 135.6, 123.7, 122.5, 118.2, 80.1, 79.3, 77.5, 60.5, 59.5, 52.7, 49.7, 42.9, 38.2, 32.5, 29.9, 28.6.

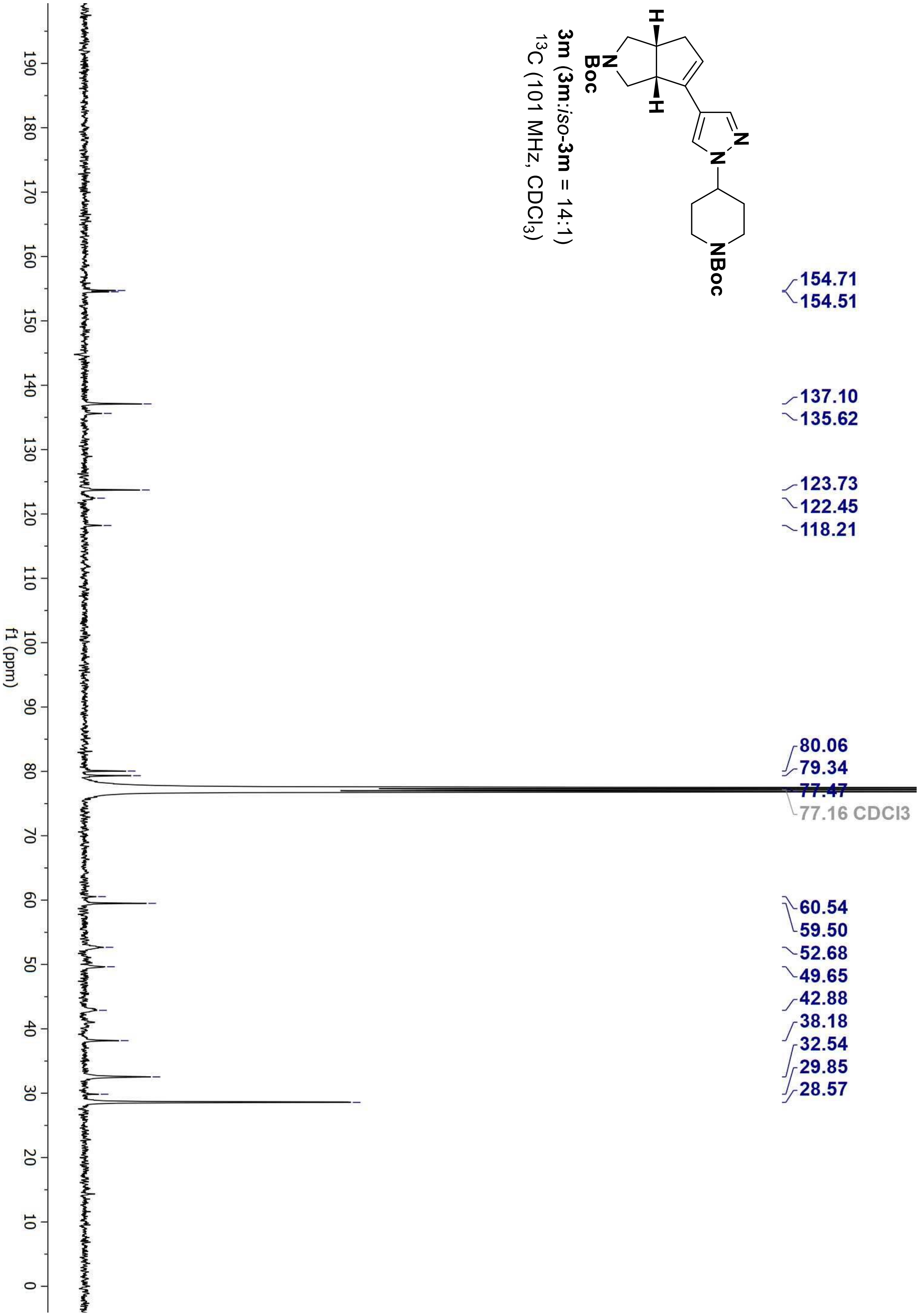
**HRMS** (ESI) m/z: [M+Na$^+$] calcd. for $C_{25}H_{38}N_4O_4$: 481.2785; found = 481.2796.

**FTIR** (neat): 2975, 2930, 1684, 1405, 1365, 1235, 1162, 1120, 729 cm$^{-1}$.



**3m** (**3m**:*iso*-**3m** = 14:1)

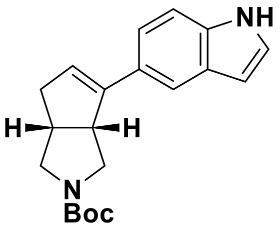
$^1$H (400 MHz, CDCl$_3$)



**3m** (**3m**:*iso*-**3m** = 14:1)

$^{13}C$ (101 MHz, $CDCl_3$)

**(±)-*tert*-butyl (3aR,6aR)-6-(1H-indol-5-yl)-3,3a,4,6a-tetrahydrocyclopenta[c]pyrrole-2(1H)-carboxylate (3n)**



Following the general procedure, aryl iodide **1j** (77.8 mg, 0.32 mmol) and vinyl triflate **2f** (71.4 mg, 0.2 mmol) were subjected to modified reaction conditions (10 mol% $Pd(OAc)_2$, 105 °C, 48 h). Upon flash column chromatography ($SiO_2$: 30:70 $Et_2O$:pentane) the title compound **3n** was isolated as a yellow waxy solid in 56% yield (36.3 mg, 0.11 mmol, >20:1 rr).

**TLC** ($SiO_2$): $R_f$ = 0.4 (2:1 $Et_2O$:pentane).

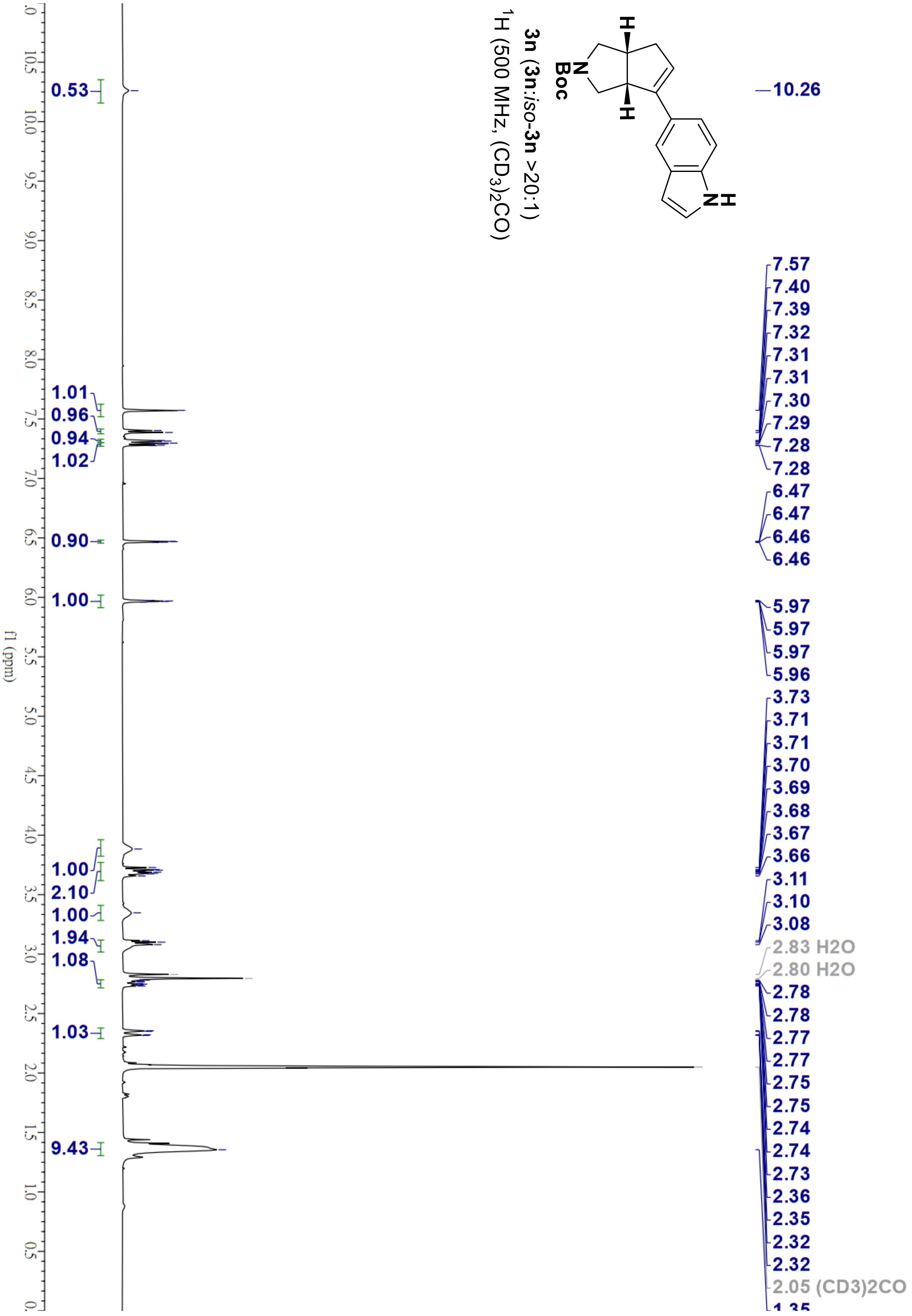
**$^1$H NMR** (500 MHz, $(CD_3)_2CO$): δ 10.26 (s, 1H), 7.57 (s, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.29 (dd, J = 8.5, 1.8 Hz, 1H), 6.47 (dd, J = 3.1, 1.0 Hz, 1H), 5.97 (q, J = 2.6 Hz, 1H), 3.88 (s, 1H), 3.69 (ddd, J = 15.9, 11.4, 8.7 Hz, 2H), 3.35 (s, 1H), 3.13 – 3.02 (m, 2H), 2.80 – 2.71 (m, 1H), 2.34 (dd, J = 17.2, 2.5 Hz, 1H), 1.35 (s, 9H).

**$^{13}$C NMR** (126 MHz, $(CD_3)_2CO$): δ 154.6, 146.5, 136.5, 129.2, 128.0, 126.0, 122.9, 121.1, 118.8, 112.2, 102.7, 78.9, 53.4, 51.0, 42.0, 41.1, 38.8, 28.6.

**HRMS** (ESI) m/z: [M+Na$^+$] calcd. for $C_{20}H_{24}N_2O_2$: 347.1730; found = 347.1739.

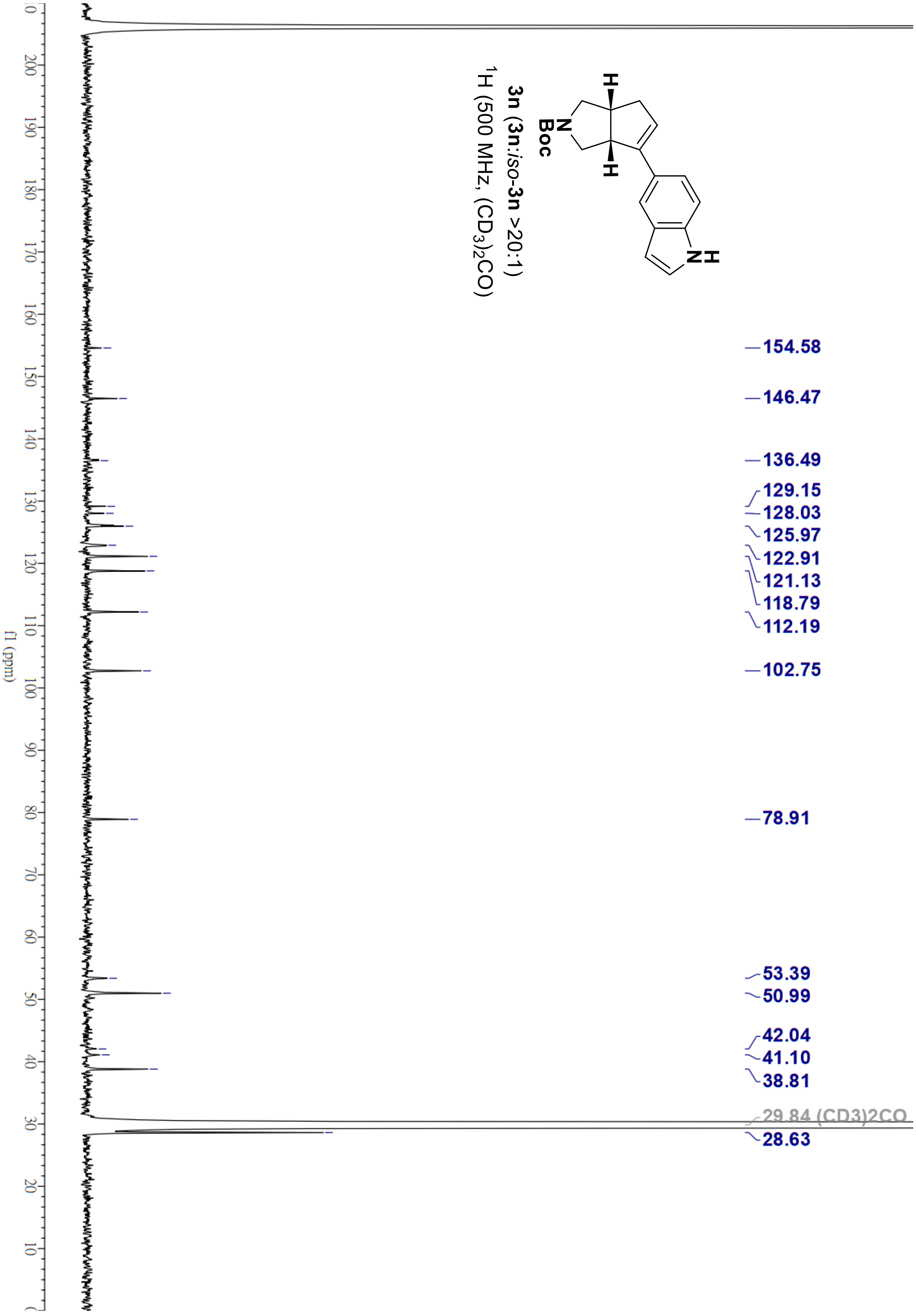
**FTIR** (neat): 3294, 2974, 2930, 1670, 1401, 1164, 1114, 877, 800 cm$^{-1}$.

**Melting Point:** 42-44 °C

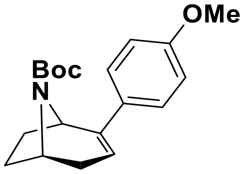


**3n (3n:*iso*-3n >20:1)**

$^1$H (500 MHz, $(CD_3)_2CO$)


3n (3n:*iso*-3n >20:1)
$^1$H (500 MHz, $(CD_3)_2CO$)
N
Boc
H
H
NH
154.58
146.47
136.49
129.15
128.03
125.97
122.91
121.13
118.79
112.19
102.75
78.91
53.39
50.99
42.04
41.10
38.81
29.84 (CD3)2CO
28.63
f1 (ppm)
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

**tert-butyl 2-(4-methoxyphenyl)-8-azabicyclo[3.2.1]oct-2-ene-8-carboxylate (3o)**



Following the general procedure, aryl iodide **1a** (74.9mg, 0.32 mmol) and vinyl triflate **2f** (71.4 mg, 0.2 mmol) were subjected to modified reaction conditions (105 °C, 24 h). Upon flash column chromatography ($SiO_2$: 2:98 EtOAc:hexanes) the title compound **3o** was isolated as a pale yellow oil in 60% yield (37.8 mg, 0.12 mmol, >20:1 rr).

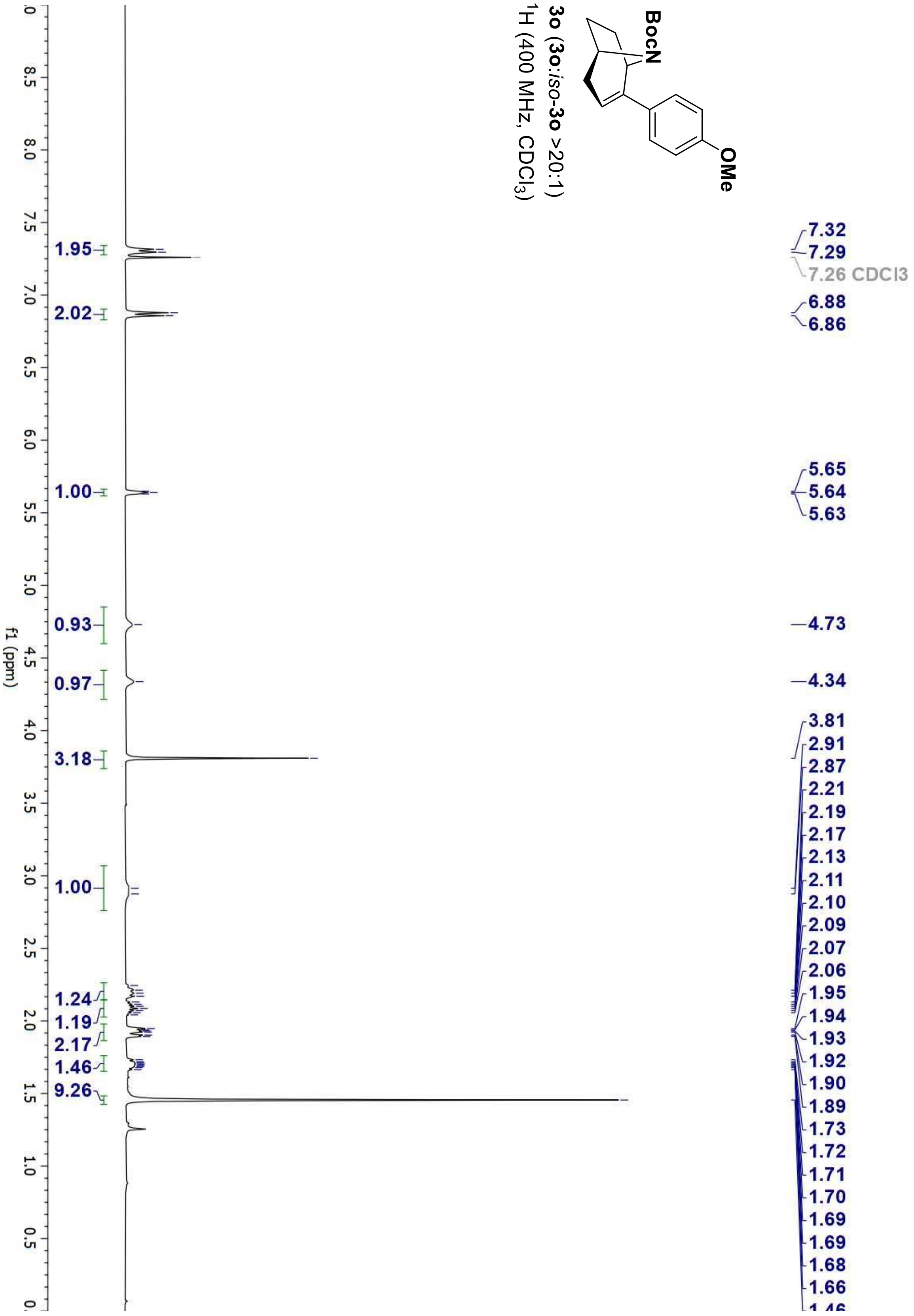
**TLC** ($SiO_2$) $R_f$ = 0.5 (1:9 EtOAc:hexanes).

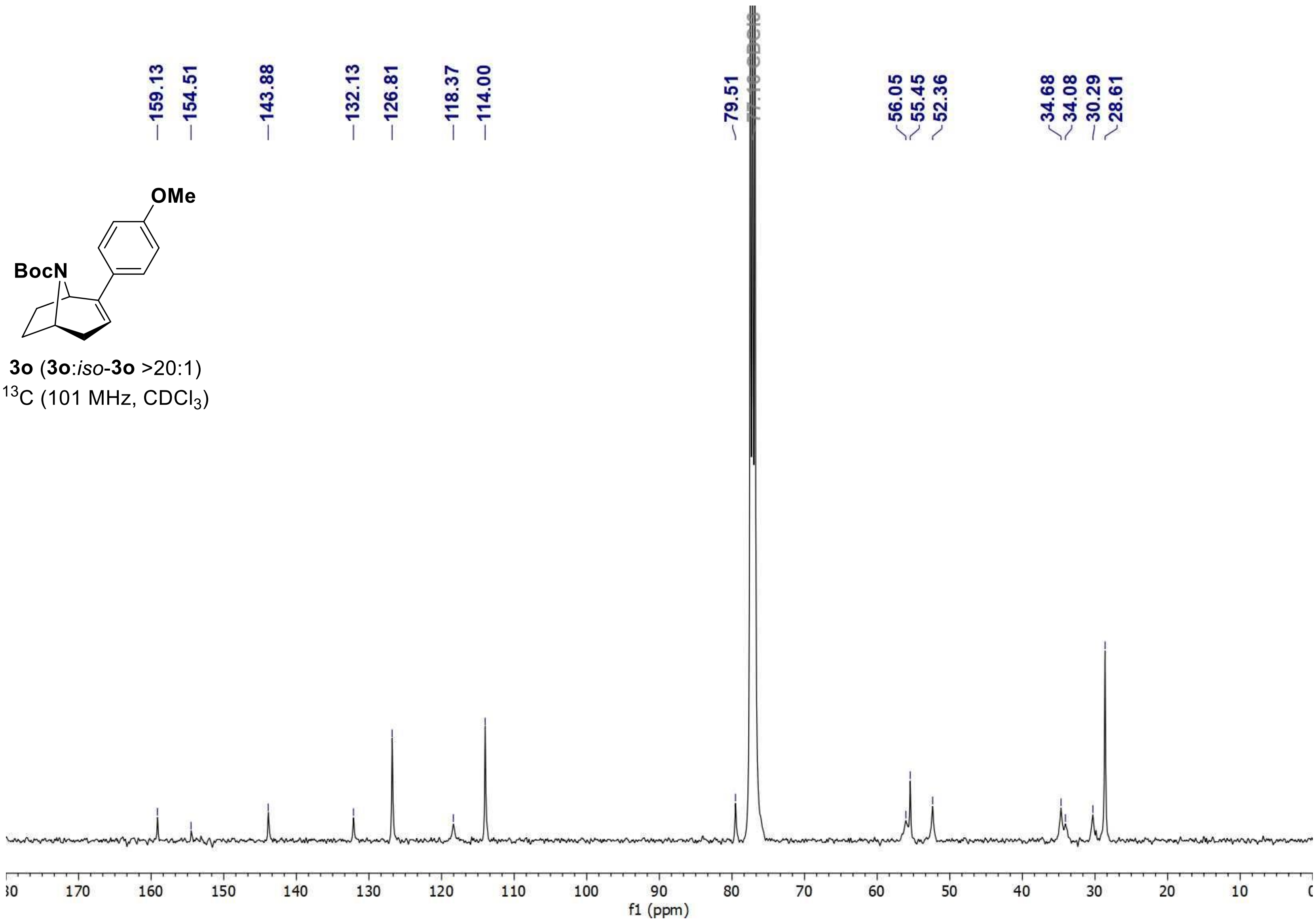
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.3 Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 5.64 (t, J = 3.7 Hz, 1H), 4.73 (s, 1H), 4.34 (s, 1H), 3.81 (s, 3H), 2.89 (d, J = 15.8 Hz, 1H), 2.30 – 2.14 (m, 1H), 2.09 (tt, J = 11.7, 6.2 Hz, 1H), 1.99 – 1.83 (m, 2H), 1.70 (ddd, J = 12.1, 9.0, 6.0 Hz, 1H), 1.46 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.1, 154.5, 143.9, 132.1, 126.8, 118.4, 114.0, 79.5, 56.1, 55.5, 52.4, 34.7, 34.1, 30.3, 28.6.

**HRMS** (ESI) m/z: [M+Na$^+$] calcd. for $C_{19}H_{25}NO_3$: 338.1727; found = 338.1735.

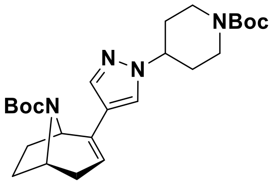
**FTIR** (neat): 2973, 2835, 1693, 1512, 1390, 1247, 1169, 1102, 1035 cm$^{-1}$.


BocN
OMe
**3o** (**3o**:*iso*-**3o** >20:1)
$^1$H (400 MHz, CDCl$_3$)
7.32
7.29
7.26 CDCl3
6.88
6.86
5.65
5.64
5.63
4.73
4.34
3.81
2.91
2.87
2.21
2.19
2.17
2.13
2.11
2.10
2.09
2.07
2.06
1.95
1.94
1.93
1.92
1.90
1.89
1.73
1.72
1.71
1.70
1.69
1.69
1.68
1.66
1.46
1.95
2.02
1.00
0.93
0.97
3.18
1.00
1.24
1.19
2.17
1.46
9.26
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)



**3o** (**3o**:*iso*-**3o** >20:1)
$^{13}$C (101 MHz, $CDCl_3$)

**_tert_-butyl 2-(1-(1-(_tert_-butoxycarbonyl)piperidin-4-yl)-1H-pyrazol-4-yl)-8-azabicyclo[3.2.1]oct-2-ene-8-carboxylate (3p)**



Following the general procedure, aryl iodide **1i** (150.9 mg, 0.4 mmol) and vinyl triflate **2f** (71.4 mg, 0.2 mmol) were subjected to modified reaction conditions (105 °C, 24 h). Upon flash column chromatography ($SiO_2$: 20:80 EtOAc:hexanes) the title compound **3p** was isolated as a clear oil in 67% yield (61.4 mg, 0.13 mmol, >20:1 rr).

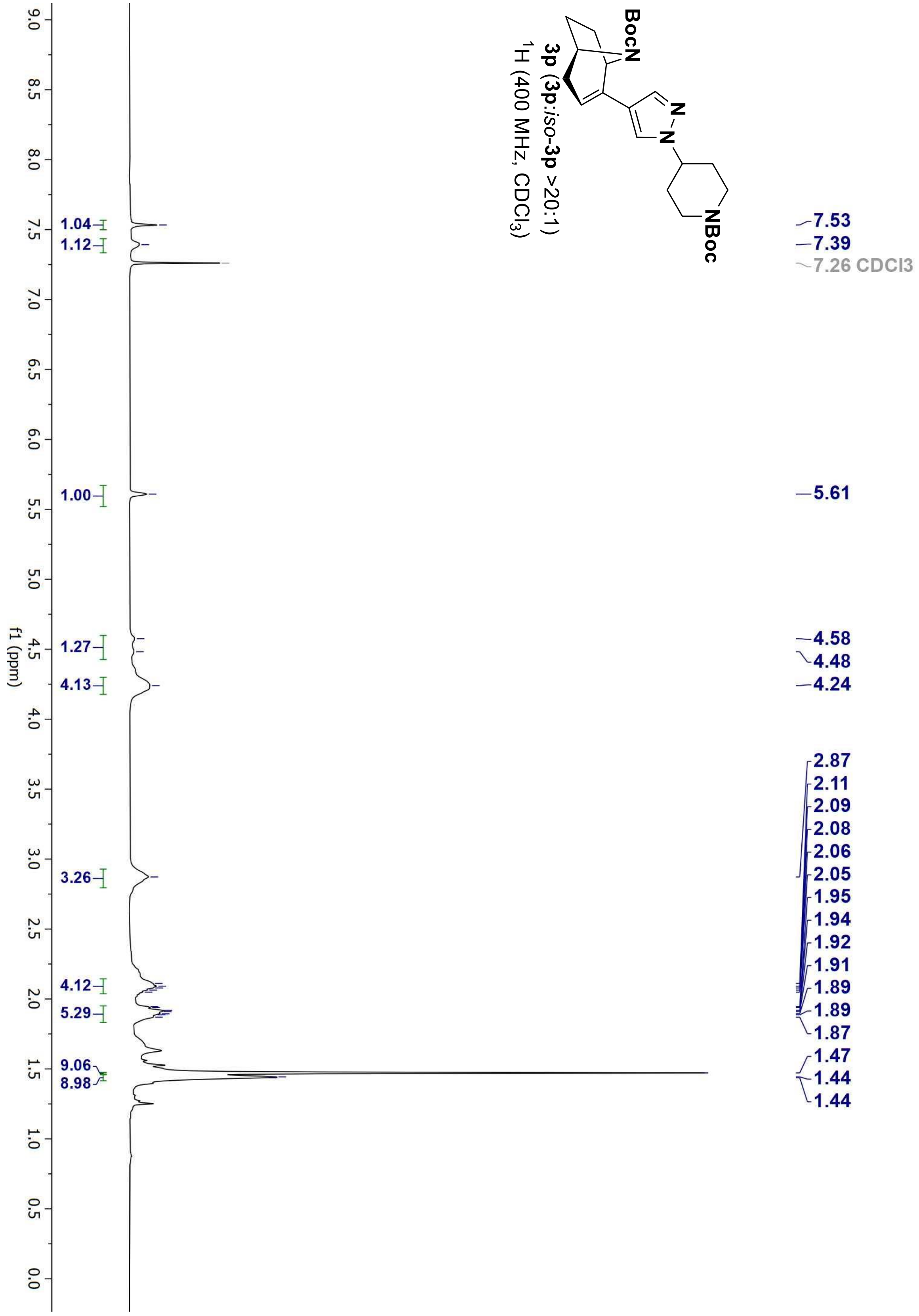
**TLC** ($SiO_2$): $R_f$ = 0.5 (1:3 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.53 (s, 1H), 7.39 (s, 1H), 5.61 (s, 1H), 4.53 (d, J = 37.3 Hz, 1H), 4.24 (s, 4H), 2.87 (s, 3H), 2.14 – 2.04 (m, 4H), 1.95 – 1.83 (m, 5H), 1.47 (s, 9H), 1.44 (s, 9H).

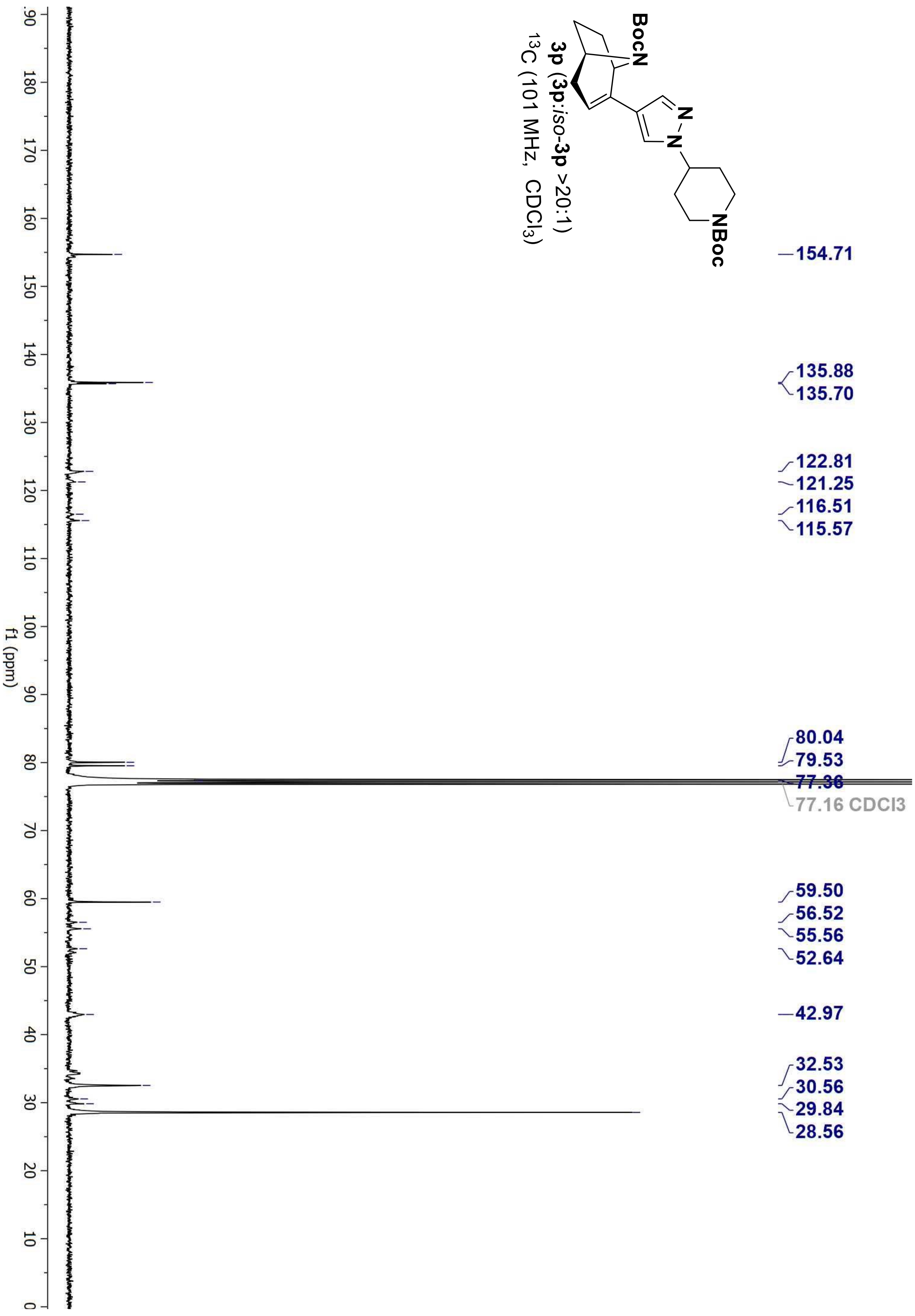
**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 154.7, 135.9, 135.7, 122.8, 121.3, 116.5, 115.6, 80.0, 79.5, 77.4, 59.5, 56.5, 55.6, 52.6, 43.0, 32.5, 30.6, 29.8, 28.6.

**HRMS** (ESI) m/z: [M+Na$^+$] calcd. for $C_{25}H_{38}N_4O_4$: 481.2785; found = 481.2806.

**FTIR** (neat): 2975, 2931, 1685, 1420, 1366, 1163, 977, 910, 728 cm$^{-1}$.


**3p** (**3p**:*iso*-**3p** >20:1)

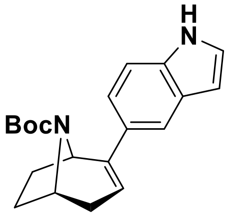
$^1$H (400 MHz, CDCl$_3$)



**3p** (**3p**:*iso*-**3p** >20:1)

$^{13}$C (101 MHz, CDCl$_3$)

**_tert_-butyl 2-(1H-indol-5-yl)-8-azabicyclo[3.2.1]oct-2-ene-8-carboxylate (3q)**



Following the general procedure, aryl iodide **1j** (77.8mg, 0.32 mmol) and vinyl triflate **2f** (71.4 mg, 0.2 mmol) were subjected to modified reaction condition (10 mol% $Pd(OAc)_2$, 105 °C, 24 h). Upon flash column chromatography ($SiO_2$: 6:94 EtOAc:hexanes) the title compound **3q** was isolated as a waxy solid in 50% yield (32.4 mg, 0.10 mmol, >20:1 rr).

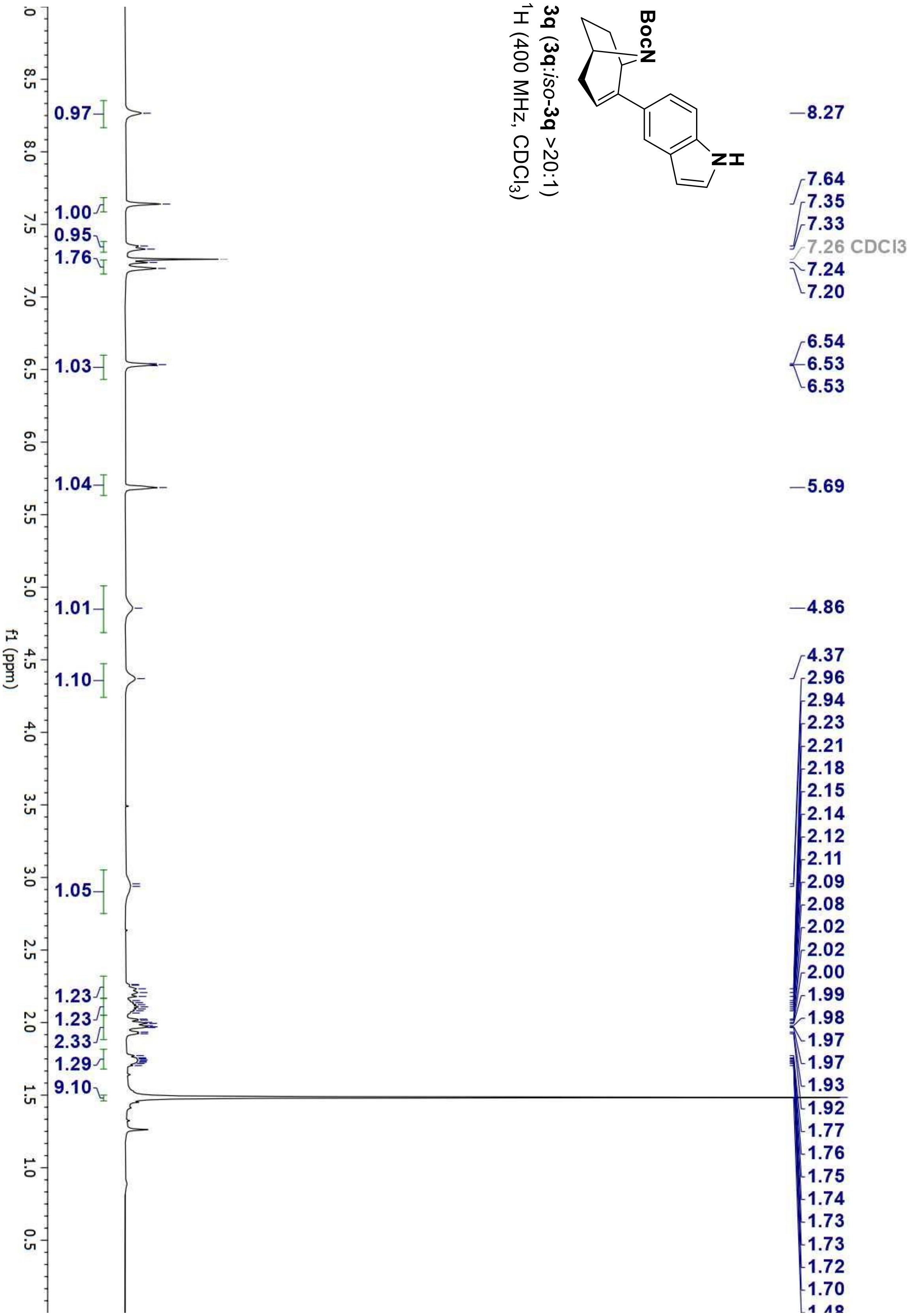
**TLC** ($SiO_2$) $R_f$ = 0.4 (1:4 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.64 (s, 1H), 7.34 (d, J = 8.6 Hz, 1H), 7.26 – 7.17 (m,2H), 6.53 (t, J = 2.7 Hz, 1H), 5.69 (s, 1H), 4.86 (s, 1H), 4.37 (s, 1H), 2.94 (s, 1H), 2.33 – 2.16 (m, 1H), 2.17 – 2.04 (m, 1H), 2.05 – 1.89 (m, 2H), 1.83 – 1.64 (m, 1H), 1.48 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.5, 145.3, 135.3, 131.6, 127.9, 124.7, 120.6, 118.33, 117.7, 110.9, 102.9, 79.4, 56.8, 52.2, 34.8, 33.8, 30.0, 28.5.

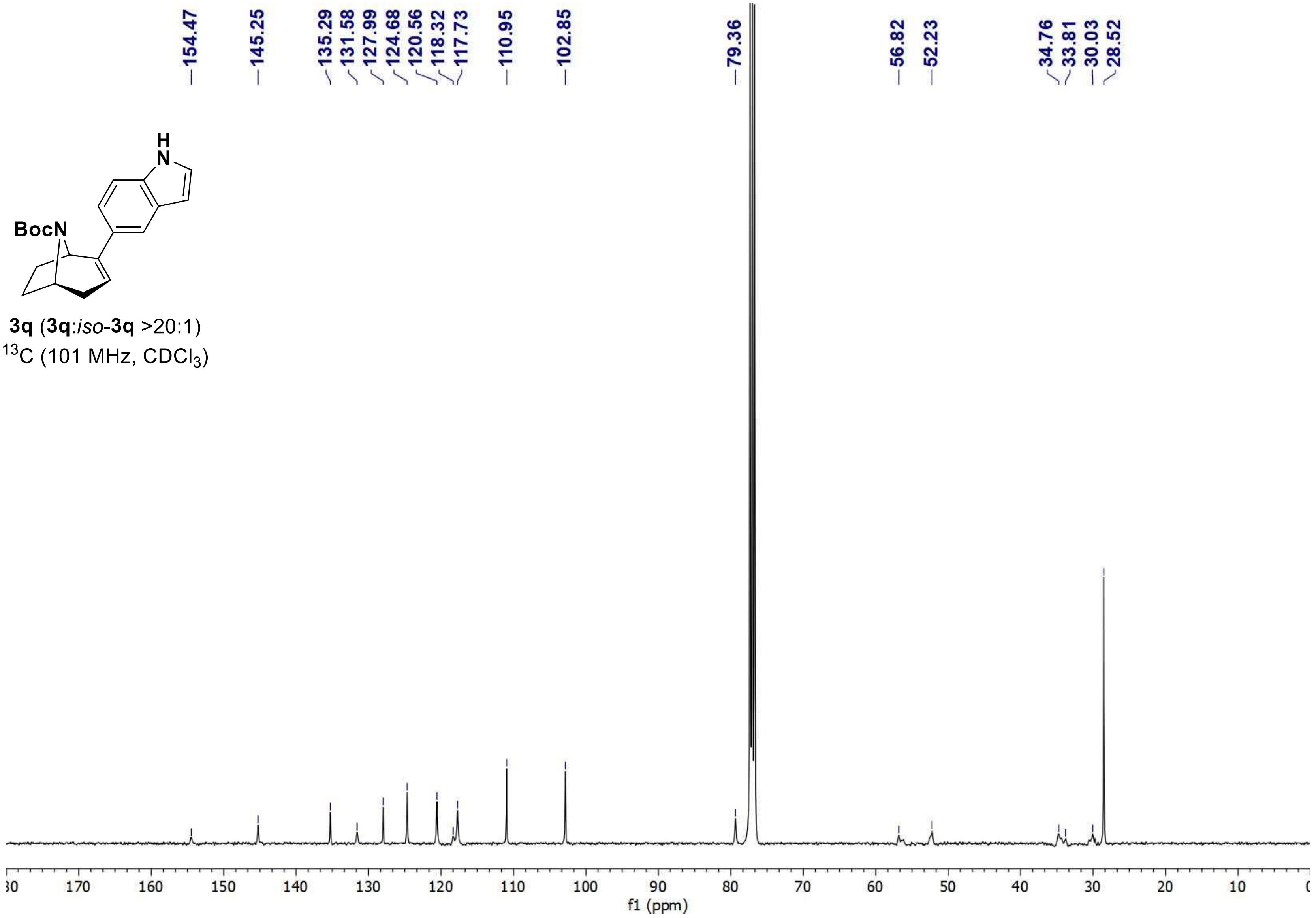
**HRMS** (ESI) m/z: [$M+Na^+$] calcd. for $C_{20}H_{24}N_2O_2$: 347.1730; found = 347.1736.

**FTIR** (neat): 3307, 2974, 1677, 1406, 1324, 1167, 1100, 984, 764 $cm^{-1}$.



**3q** (**3q**:*iso*-**3q** >20:1)

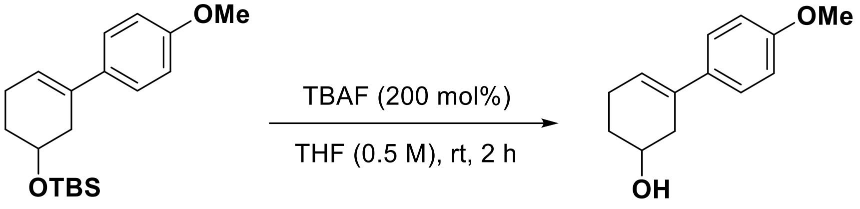
$^1$H (400 MHz, CDCl$_3$)



**3q** (**3q**:*iso*-**3q** >20:1)

$^{13}$C (101 MHz, $CDCl_3$)

## VI. Structure Determination: Desilylation of Product 3a



**3a**
(100 mol%)

*desilyl*-**3a**

To a solution of **3a** (90 mg; 0.28 mmol; 100 mol%) in THF (0.5 M, 0.6 mL) was added TBAF (1M solution in THF, 0.6 mL, 0.6 mmol, 200 mol%) dropwise at room temperature and stirred for 2 hours. To this solution was added a saturated solution of $NaHCO_3$ (5 mL). The mixture was diluted with $Et_2O$ (20 mL) and the organic layer was extracted. The organic layer was washed with brine (10 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The resulting residue was subjected to flash column chromatography ($SiO_2$: 5:95 EtOAc:hexanes) to afford the deprotected product in 85% yield (48.6 mg; 0.24 mmol) as a colorless solid.

**TLC** ($SiO_2$): $R_f = 0.5$ (1:4 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.31 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.01 (q, J = 2.6 Hz, 1H), 4.17 – 4.06 (m, 1H), 3.81 (s, 3H), 2.74 (dd, J = 16.9, 4.9 Hz, 1H), 2.45 – 2.33 (m, 2H), 2.28 (ddq, J = 12.2, 5.8, 3.1 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.68 (dtd, J = 12.3, 8.9, 6.1 Hz, 1H).

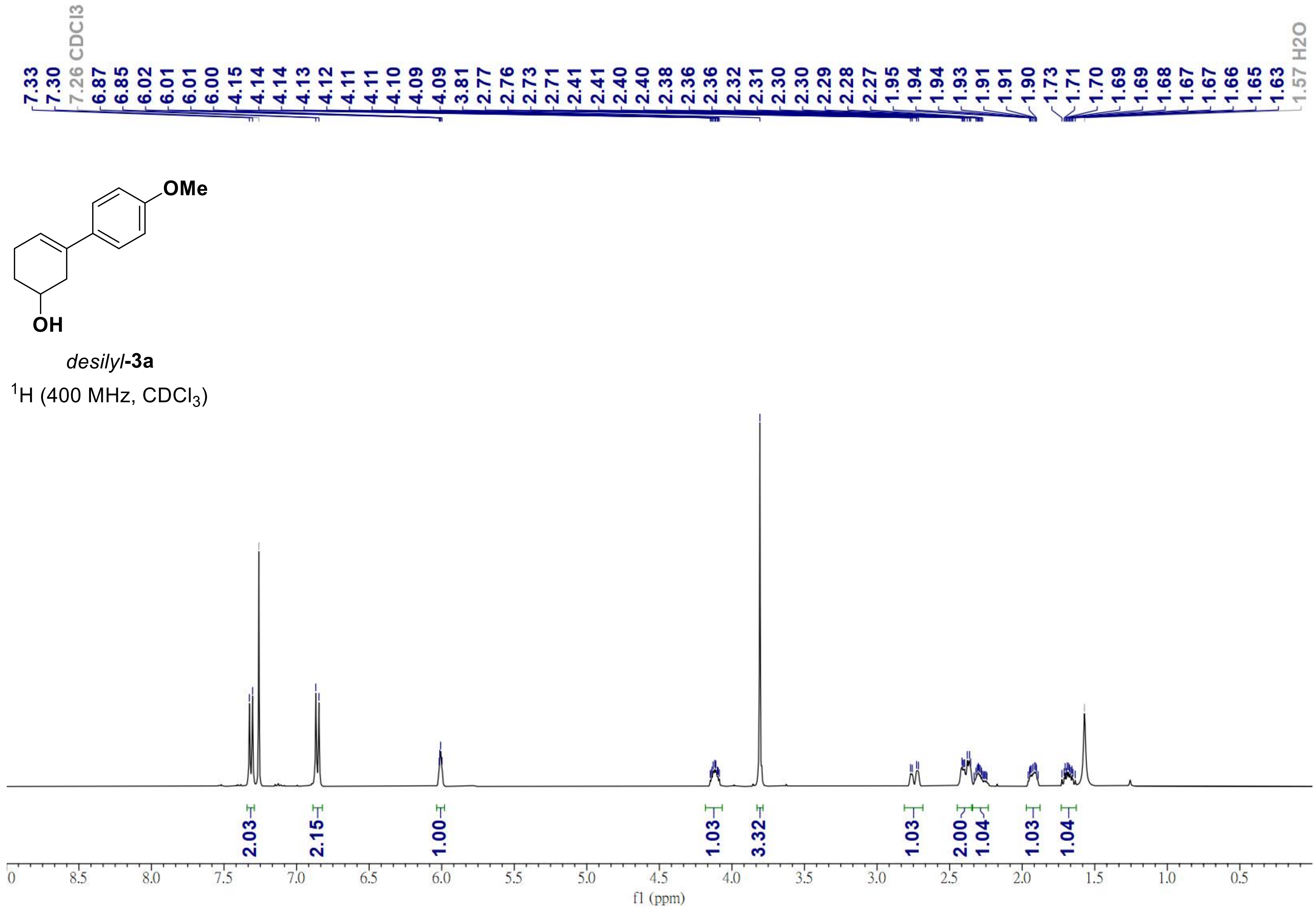
**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ 158.8, 134.4, 133.5, 126.2, 122.3, 113.8, 67.7, 55.4, 36.8, 30.6, 24.0.

**HRMS** (ESI) m/z: [M+H$^+$] calcd. for $C_{13}H_{16}O_2$: 205.1223; found = 205.1223.

**FTIR** (neat): 3359, 2921, 2839, 1511, 1280, 1237, 1181, 1025, 814 cm$^{-1}$.

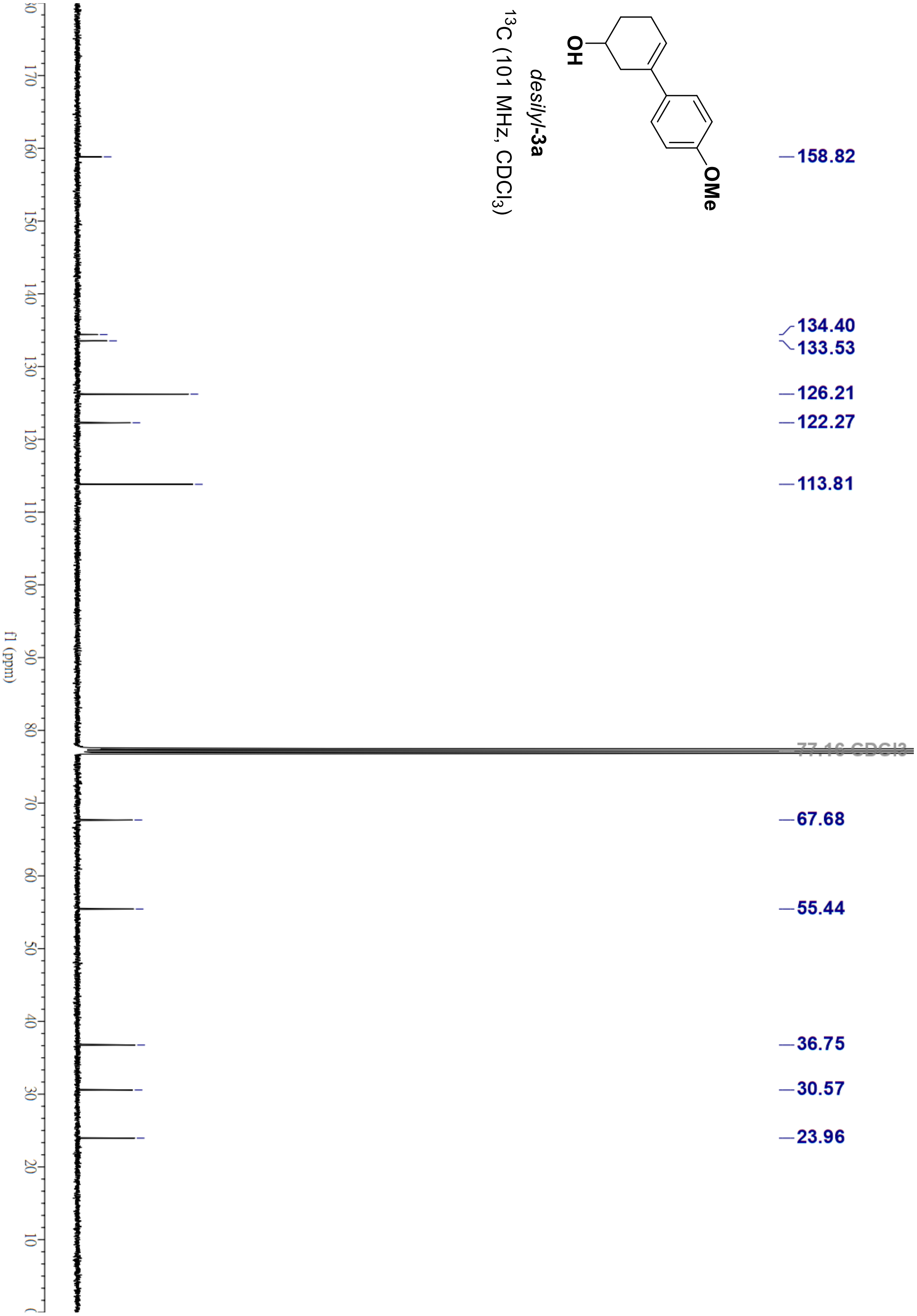
**Melting Point:** 89-91 °C

<< Spectral data for *desilyl*-**3a** was identical to that reported in the literature.[8] >>



*desilyl*-**3a**

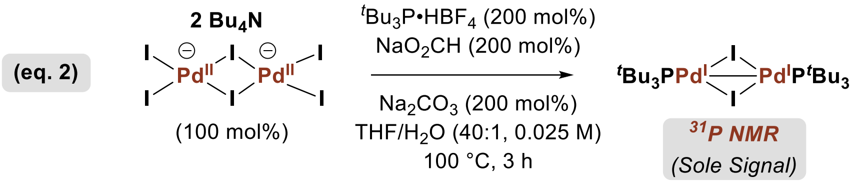
$^1$H (400 MHz, $CDCl_3$)



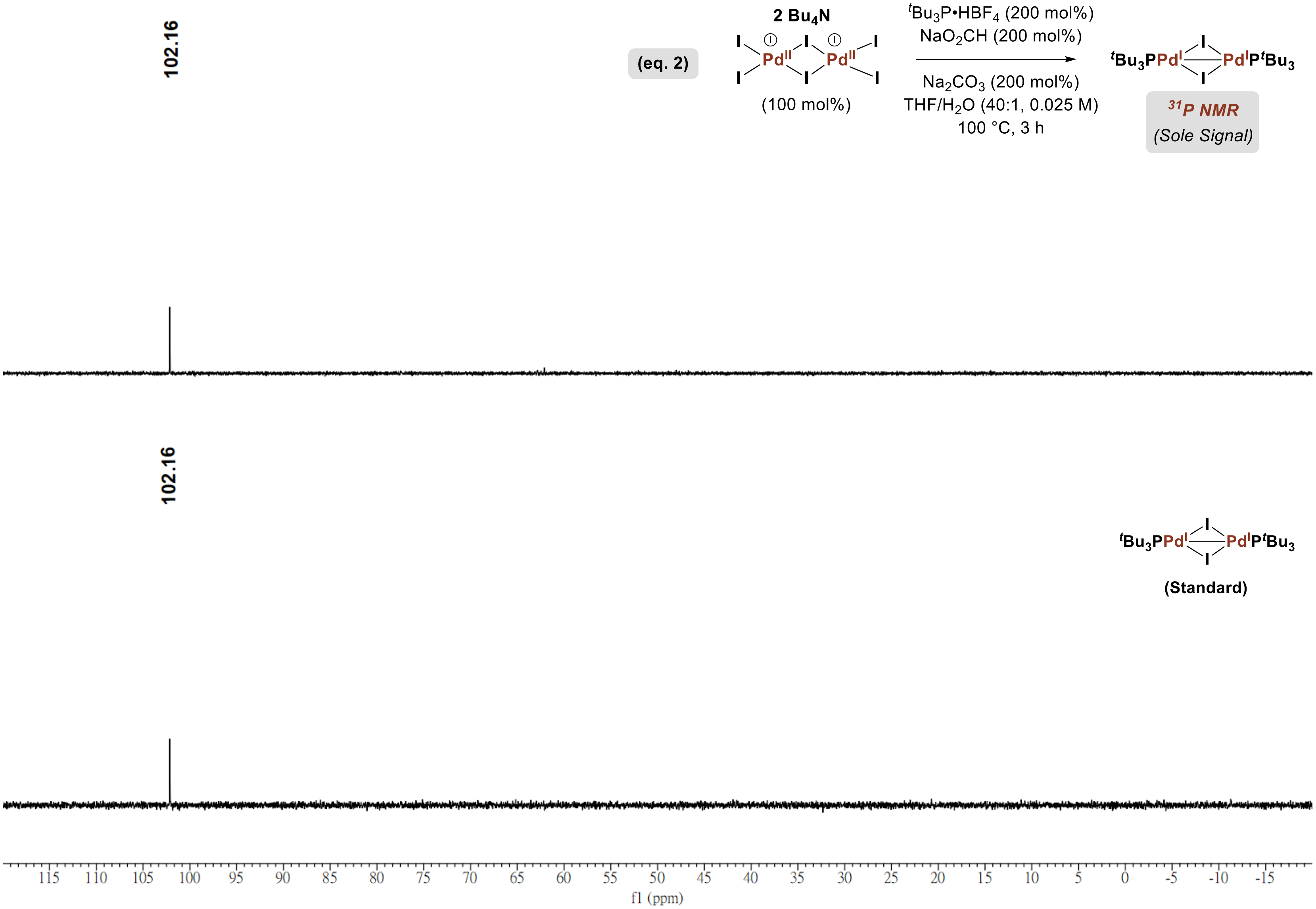
*desilyl*-**3a**

$^{13}$C (101 MHz, CDCl$_3$)

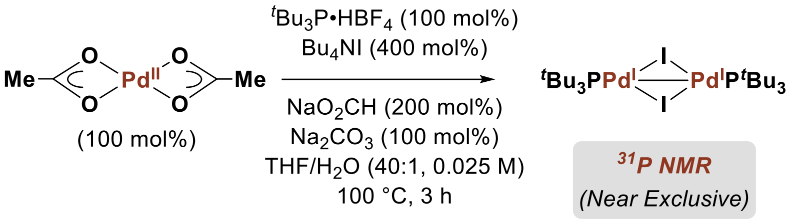
## VII. $^{31}$P NMR Experiments



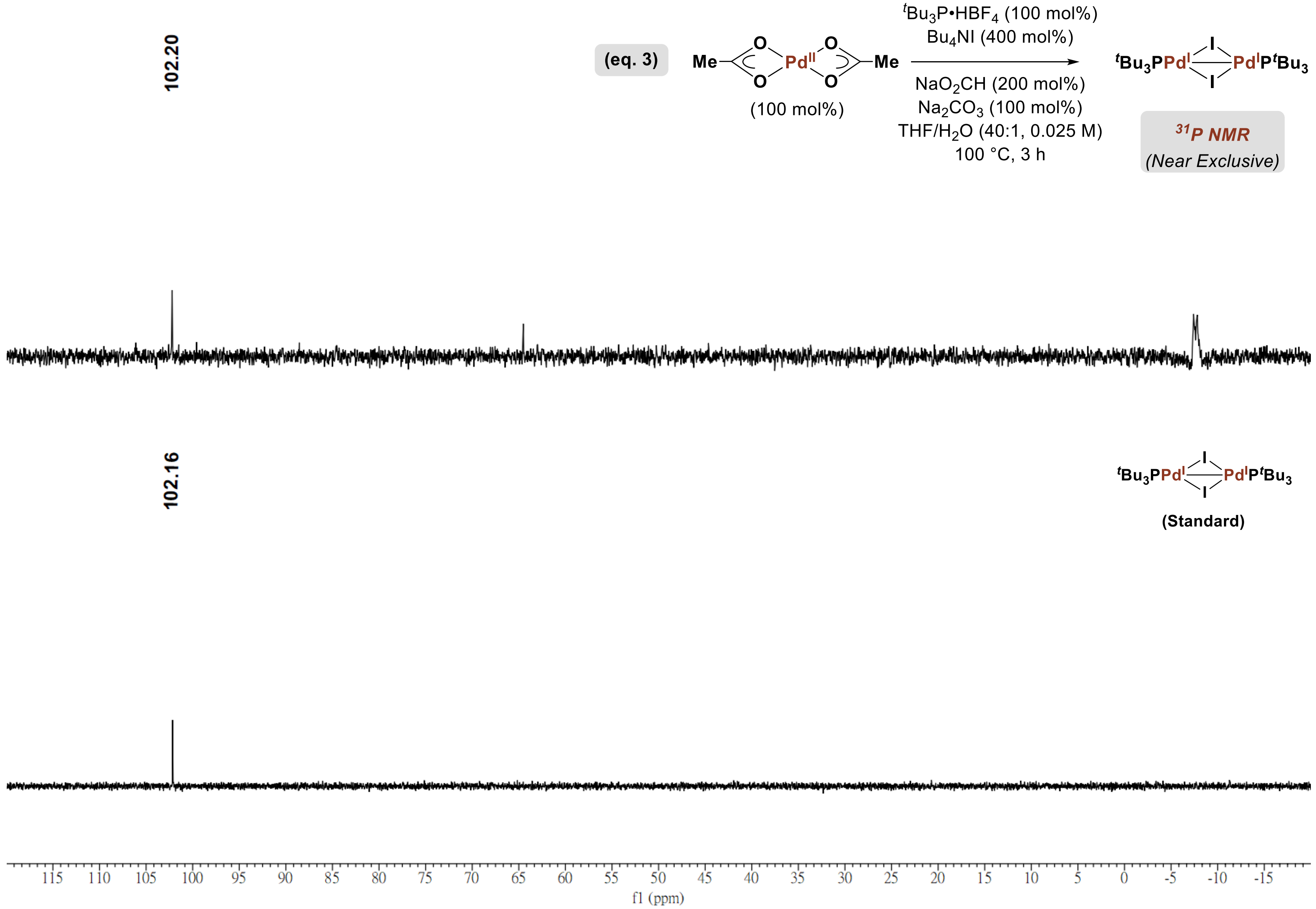
To a dried pressure tube equipped with a magnetic stir bar under an argon atmosphere charged with $[Pd_2I_6][NBu_4]_2$ (36.5 mg, 0.025 mmol), $^tBu_3P{\cdot}HBF_4$ (14.5 mg, 0.05 mmol), $NaO_2CH$ (3.4 mg, 0.05 mmol), and $Na_2CO_3$ (5.3 mg, 0.05 mmol) was added water (25 µL) and anhydrous THF (1.0 mL, 0.025 M). The tube was sealed with a PTFE lined cap and the reaction vessel was placed in a 100 °C oil bath and stirred for 3 hours. After reaching ambient temperature, the solvent was removed and $^{31}$P NMR was taken in $C_6D_6$.


102.16
(eq. 2)
2 Bu$_4$N
Pd$^{II}$
Pd$^{II}$
(100 mol%)
$^t$Bu$_3$P•HBF$_4$ (200 mol%)
NaO$_2$CH (200 mol%)
Na$_2$CO$_3$ (200 mol%)
THF/H$_2$O (40:1, 0.025 M)
100 °C, 3 h
$^t$Bu$_3$PPd$^I$ Pd$^I$P$^t$Bu$_3$
$^{31}$P NMR
(Sole Signal)
102.16
$^t$Bu$_3$PPd$^I$ Pd$^I$P$^t$Bu$_3$
(Standard)
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

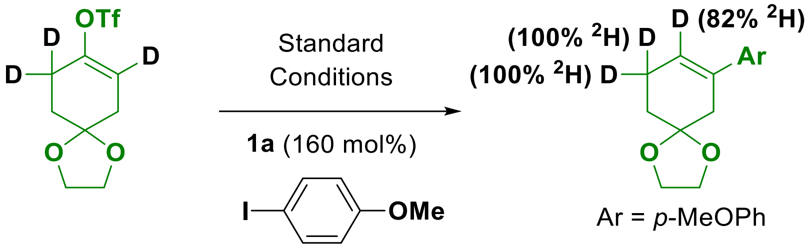
**(eq. 3)**



To a dried pressure tube equipped with a magnetic stir bar under an argon atmosphere charged with $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), ${}^tBu_3P{\cdot}HBF_4$ (7.3 mg, 0.025 mmol), $Bu_4NI$ (36.9 mg, 0.1 mmol), $NaO_2CH$ (3.4 mg, 0.05 mmol), and $Na_2CO_3$ (2.6 mg, 0.025 mmol) was added water (25 µL) and anhydrous THF (1.0 mL, 0.025 M). The tube was sealed with a PTFE lined cap and the reaction vessel was placed in a 100 °C oil bath and stirred for 3 hours. After reaching ambient temperature, the solvent was removed and ${}^{31}P$ NMR was taken in $C_6D_6$.


102.20
(eq. 3)
Me
O
O
Pd^II
O
O
Me
(100 mol%)
ᵗBu₃P•HBF₄ (100 mol%)
Bu₄NI (400 mol%)
NaO₂CH (200 mol%)
Na₂CO₃ (100 mol%)
THF/H₂O (40:1, 0.025 M)
100 °C, 3 h
ᵗBu₃PPd^I
I
I
Pd^IPᵗBu₃
³¹P NMR
(Near Exclusive)
102.16
(Standard)
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

## VIII. Deuterium Labeling Study for *deuterio*-3g



*deuterio*-**2b**
(100 mol%)

*deuterio*-**3g**
65% Yield

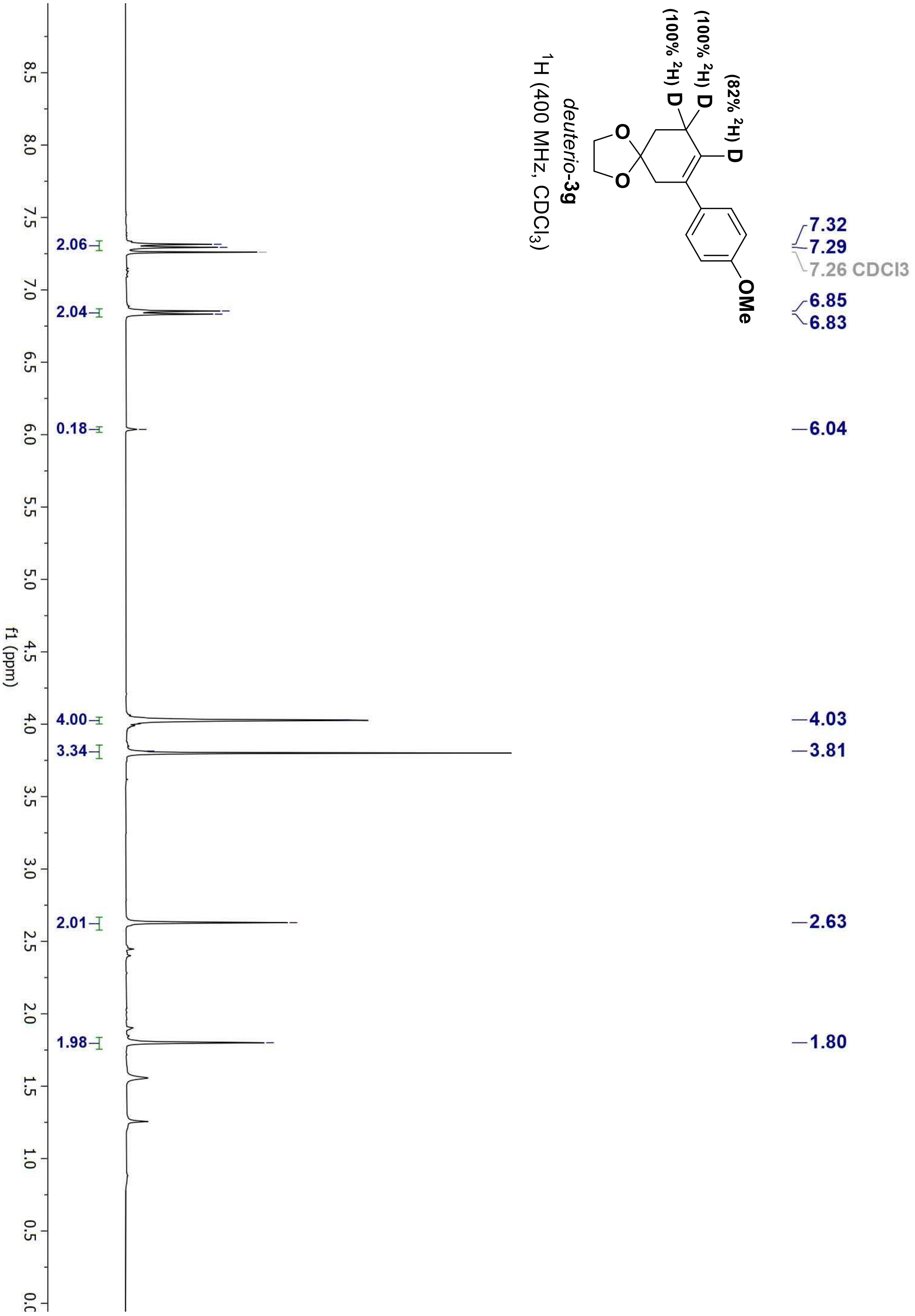
Following the general procedure, aryl iodide **1a** (74.9 mg, 0.32 mmol) and vinyl triflate *deuterio*-**2b** (58.2 mg, 0.2 mmol) were subjected to standard reaction conditions (100 °C, 24 h). Upon flash column chromatography ($SiO_2$: 1:99 EtOAc:hexanes) the title compound *deuterio*-**3g** was isolated as a clear oil in 65% yield (32.3 mg, 0.13 mmol, >20:1 rr).

**TLC** ($SiO_2$): $R_f$ = 0.6 (1:4 EtOAc:hexanes).

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.30 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.04 (s, 0.18H), 4.03 (s, 4H), 3.81 (s, 3H), 2.63 (s, 2H), 1.80 (s, 2H).

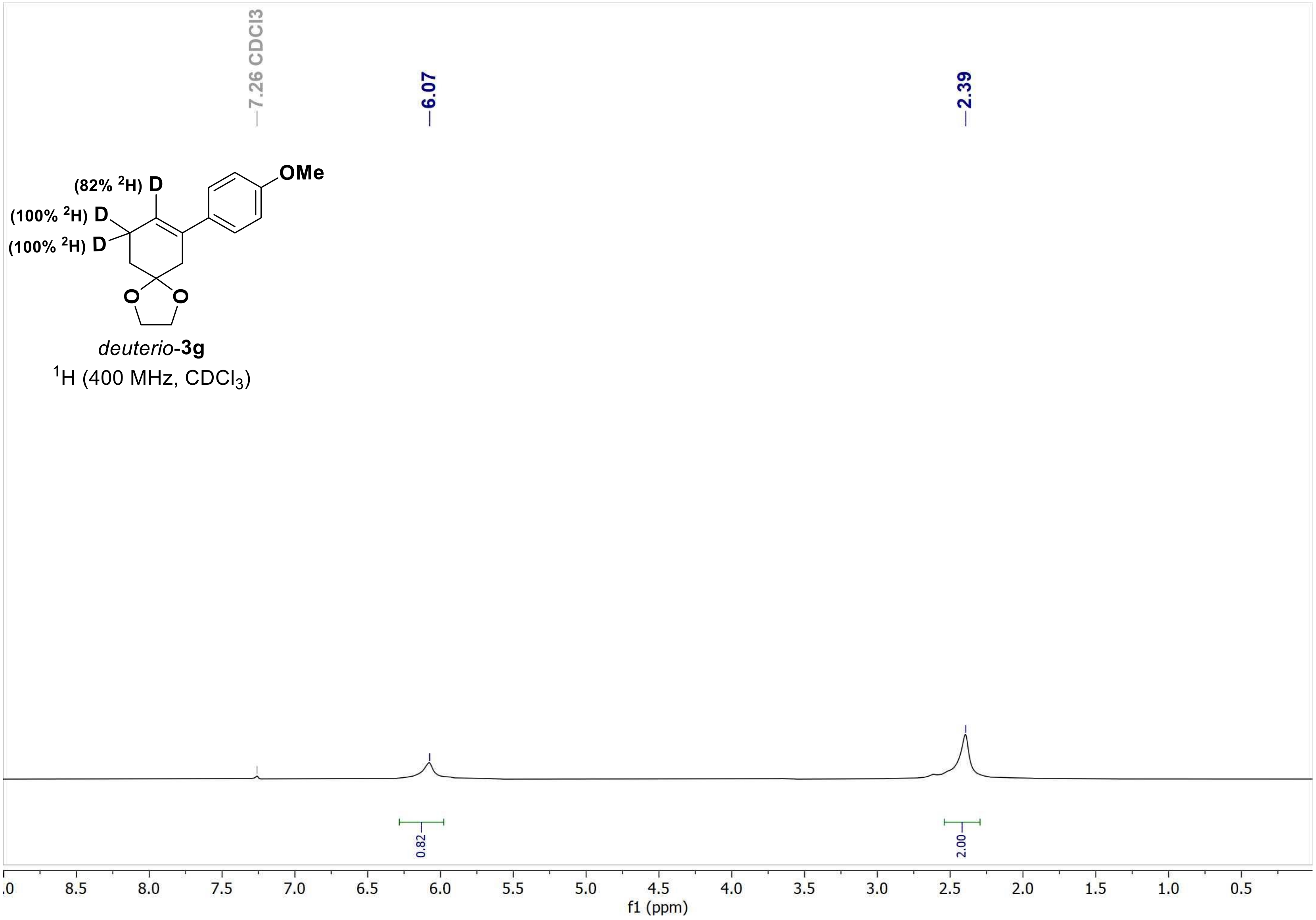
**$^2$H NMR** (92 MHz, $CHCl_3$): $\delta$ 6.07 (s, 0.82H), 2.39 (s, 2H).

**HRMS** (ESI) m/z: [M+H$^+$] calcd. for $C_{15}H_{16}D_2O_3$: 249.1454; found = 249.1448.
(ESI) m/z: [M+H$^+$] calcd. for $C_{15}H_{15}D_3O_3$: 250.1517; found = 250.1519.



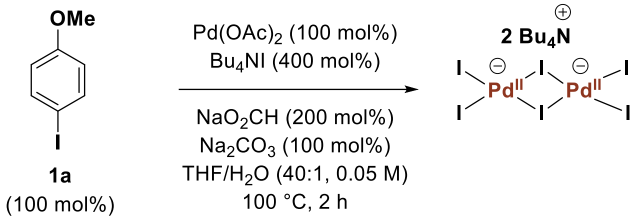
*deuterio*-**3g**

$^1$H (400 MHz, CDCl$_3$)

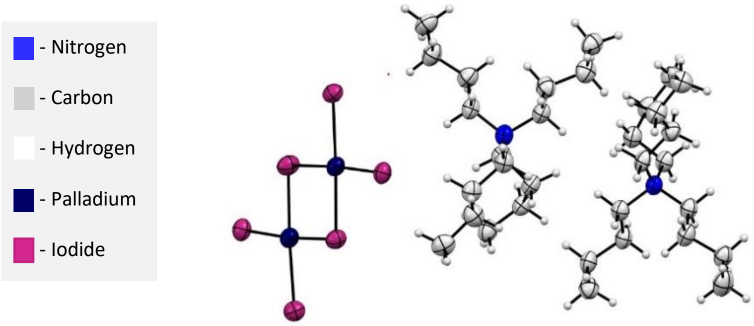

*deuterio*-**3g**

$^1$H (400 MHz, $CDCl_3$)

## IX. Single Crystal Diffraction Data for $[Pd_2I_6][NBu_4]_2$



**Experimental:** To a dried pressure tube equipped with a magnetic stir bar under an argon atmosphere charged with aryl iodide **1a** (23.4 mg, 0.1 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), $Bu_4NI$ (147.7 mg, 0.4 mmol), $NaO_2CH$ (13.6 mg, 0.2 mmol), and $Na_2CO_3$ (10.6 mg, 0.1 mmol) was added water (50 μL) and anhydrous THF (2.0 mL, 0.05 M). The tube was sealed with a PTFE lined cap and the reaction vessel was placed in a 100 °C oil bath and stirred for 2 hours. After reaching ambient temperature, the reaction mixture was filtered through Celite with the aid of THF.



Crystals grew as clusters of nicely formed orange plate-shaped crystals by slow diffusion of hexane into the liquor. A suitable crystal with dimensions 0.23 × 0.10 × 0.03 $mm^3$ was selected and mounted on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer. The crystal was kept at a steady $T$ = 119.99(10) K during data collection. The structure was solved with the ShelXT[9a] solution program using dual methods and by using Olex2 1.5-ac5-024[9b] as the graphical interface. The model was refined with ShelXL 2016/6[9c] using full matrix least squares minimization on $\boldsymbol{F^2}$.

**Crystal Data:** $C_{32}H_{72}I_6N_2Pd_2$, $M_r$ = 1459.11, monoclinic, $P2_1/c$ (No. 14), a = 14.51810(10) Å, b = 13.83070(10) Å, c = 23.8319(2) Å, $\beta$ = 101.7390(10)°, $\alpha$ = $\gamma$ = 90°, $V$ = 4685.25(6) Å$^3$, $T$ = 119.99(10) K, $Z$ = 4, $Z'$ = 1, $\mu$(Cu K$_\alpha$) = 37.383, 43270 reflections measured, 9550 unique ($R_{int}$ = 0.0807) which were used in all calculations. The final $wR_2$ was 0.1945 (all data) and $R_1$ was 0.0638 (I≥2 $\sigma$(I)).

| **Compound** | **yh-45_cu_autored** |
|---|---|
| Formula | $C_{32}H_{72}I_6N_2Pd_2$ |
| $D_{calc.}$/ g cm$^{-3}$ | 2.069 |
| $\mu$/mm$^{-1}$ | 37.383 |
| Formula Weight | 1459.11 |
| Colour | orange |
| Shape | plate-shaped |
| Size/mm$^3$ | 0.23×0.10×0.03 |
| $T$/K | 119.99(10) |
| Crystal System | monoclinic |
| Space Group | $P2_1/c$ |
| $a$/Å | 14.51810(10) |
| $b$/Å | 13.83070(10) |
| $c$/Å | 23.8319(2) |
| $\alpha$/° | 90 |
| $\beta$/° | 101.7390(10) |
| $\gamma$/° | 90 |
| V/Å$^3$ | 4685.25(6) |
| $Z$ | 4 |
| $Z'$ | 1 |
| Wavelength/Å | 1.54184 |
| Radiation type | Cu K$_\alpha$ |
| $\Theta_{min}$/° | 3.109 |
| $\Theta_{max}$/° | 76.639 |
| Measured Refl's. | 43270 |
| Indep't Refl's | 9550 |
| Refl's I≥2 $\sigma$(I) | 7849 |
| $R_{int}$ | 0.0807 |
| Parameters | 387 |
| Restraints | 0 |
| Largest Peak | 2.585 |
| Deepest Hole | -1.966 |
| GooF | 1.039 |
| $wR_2$ (all data) | 0.1945 |
| $wR_2$ | 0.1719 |
| $R_1$ (all data) | 0.0740 |
| $R_1$ | 0.0638 |

**Structure Quality Indicators:**

| | | | | |
|---|---|---|---|---|
| **Reflections:** | d min (CuKα)<br>2Θ=153.3° 0.79 | I/σ(I) 20.3 | Rint<br>m=4.67 8.07% | Full 135.4°<br>97% to 153.3° 99.8 |
| **Refinement:** | Shift 0.001 | Max Peak 2.6 | Min Peak -2.0 | GooF 1.039 |

An orange plate-shaped-shaped crystal crystalized from THF/hexane solution with dimensions 0.23 × 0.10 × 0.03 mm$^3$ was mounted. Data were collected using a XtaLAB Synergy, Single source at home/near, HyPix diffractometer operating at $T$ = 119.99(10) K.

Data were measured using $\omega$ scans with Cu $K_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023). The maximum resolution that was achieved was $\Theta$ = 76.639° (0.83 Å).

The unit cell was refined using CrysAlisPro 1.171.42.94a (Rigaku OD, 2023) on 24968 reflections, 58% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023). The final completeness is 99.80 % out to 76.639° in $\Theta$. A gaussian absorption correction was performed using CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Spherical absorption correction using equivalent radius and absorption coefficient. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient $\mu$ of this material is 37.383 mm$^{-1}$ at this wavelength ($\lambda$ = 1.54184Å) and the minimum and maximum transmissions are 0.013 and 0.373.

The structure was solved and the space group $P2_1/c$ (# 14) determined by the ShelXT[9a] structure solution program using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2016/6 of ShelXL 2016/6[9c]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

*_exptl_absorpt_process_details*: CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023) Numerical absorption correction based on gaussian integration overall multifaceted crystal model Spherical absorption correction using equivalent radius and absorption coefficient. Empirical absorption correction using spherical harmonics,implemented in SCALE3 ABSPACK scaling algorithm.

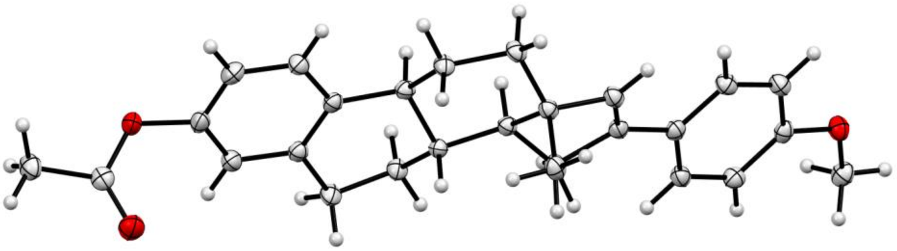
There is a single formula unit in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1. The moiety formula is I6 Pd2, 2(C16 H36 N).

## X. Single Crystal Diffraction Data for 3j

🟥 - Oxygen

▨ - Carbon

⬜ - Hydrogen

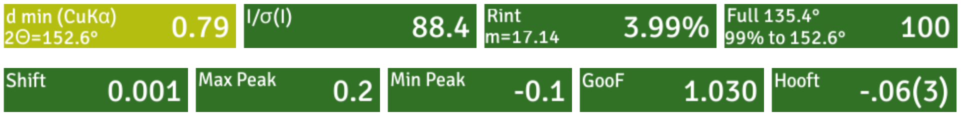


**Experimental:** Crystals grew as colorless needle-shaped crystals by slow evaporation from THF. A suitable crystal with dimensions 0.35 × 0.07 × 0.04 mm$^3$ was selected and mounted on a MITIGEN holder oil on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer. The crystal was kept at a steady $T$ = 100 K during data collection. The structure was solved with the ShelXT[9a] solution program using dual methods and by using Olex2 1.5[9b] as the graphical interface. The model was refined with ShelXL 2019/3[9c] using full matrix least squares minimization on $\boldsymbol{F^2}$.

**Crystal Data.** $C_{27}H_{30}O_3$, $M_r$ = 402.51, orthorhombic, $P2_12_12_1$ (No. 19), a = 6.03249(3) Å, b = 13.54875(6) Å, c = 26.16190(11) Å, $\alpha = \beta = \gamma = 90$, $V$ = 2138.282(16) Å$^3$, $T$ = 100 K, $Z$ = 4, $Z'$ = 1, $\mu$(Cu K$_\alpha$) = 0.628, 75150 reflections measured, 4402 unique ($R_{int}$ = 0.0399) which were used in all calculations. The final $wR_2$ was 0.0688 (all data) and $R_1$ was 0.0259 (I≥2 $\sigma$(I)).

| **Compound** | **YHC-08-71_new_auto** |
|---|---|
| Formula | $C_{27}H_{30}O_3$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.250 |
| $\mu$/mm$^{-1}$ | 0.628 |
| Formula Weight | 402.51 |
| Colour | colourless |
| Shape | needle-shaped |
| Size/mm$^3$ | 0.35×0.07×0.04 |
| $T$/K | 100 |
| Crystal System | orthorhombic |
| Flack Parameter | -0.07(4) |
| Hooft Parameter | -0.06(3) |
| Space Group | $P2_12_12_1$ |
| $a$/Å | 6.03249(3) |
| $b$/Å | 13.54875(6) |
| $c$/Å | 26.16190(11) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 90 |
| V/Å$^3$ | 2138.282(16) |
| $Z$ | 4 |
| $Z'$ | 1 |
| Wavelength/Å | 1.54184 |
| Radiation type | Cu K$_\alpha$ |
| $\Theta_{min}$/° | 3.379 |
| $\Theta_{max}$/° | 76.450 |
| Measured Refl's. | 75150 |
| Indep't Refl's | 4402 |
| Refl's I≥2 $\sigma$(I) | 4328 |
| $R_{\text{int}}$ | 0.0399 |
| Parameters | 275 |
| Restraints | 0 |
| Largest Peak | 0.202 |
| Deepest Hole | -0.142 |
| GooF | 1.030 |
| $wR_2$ (all data) | 0.0688 |
| $wR_2$ | 0.0684 |
| $R_1$ (all data) | 0.0263 |
| $R_1$ | 0.0259 |

### Structure Quality Indicators



| | | | | | |
|---|---|---|---|---|---|
| **Reflections:** | d min (CuKα) 2Θ=152.6° 0.79 | I/σ(I) 88.4 | Rint m=17.14 3.99% | Full 135.4° 99% to 152.6° 100 | |
| **Refinement:** | Shift 0.001 | Max Peak 0.2 | Min Peak -0.1 | GooF 1.030 | Hooft -.06(3) |

A colourless needle-shaped-shaped crystal with dimensions 0.35 × 0.07 × 0.04 mm$^3$ was mounted on a MITIGEN holder oil. Data were collected using a XtaLAB Synergy, Single source at home/near, HyPix diffractometer operating at $T$ = 100 K.

Data were measured using $\omega$ scans with Cu $K_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023). The maximum resolution that was achieved was $\Theta$ = 76.450° (0.79 Å).

The unit cell was refined using CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023) on 61204 reflections, 81% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023). The final completeness is 100.00 % out to 76.450° in $\Theta$. A multi-scan absorption correction was performed using CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient $\mu$ of this material is 0.628 mm$^{-1}$ at this wavelength ($\lambda$ = 1.54184Å) and the minimum and maximum transmissions are 0.352 and 1.000.

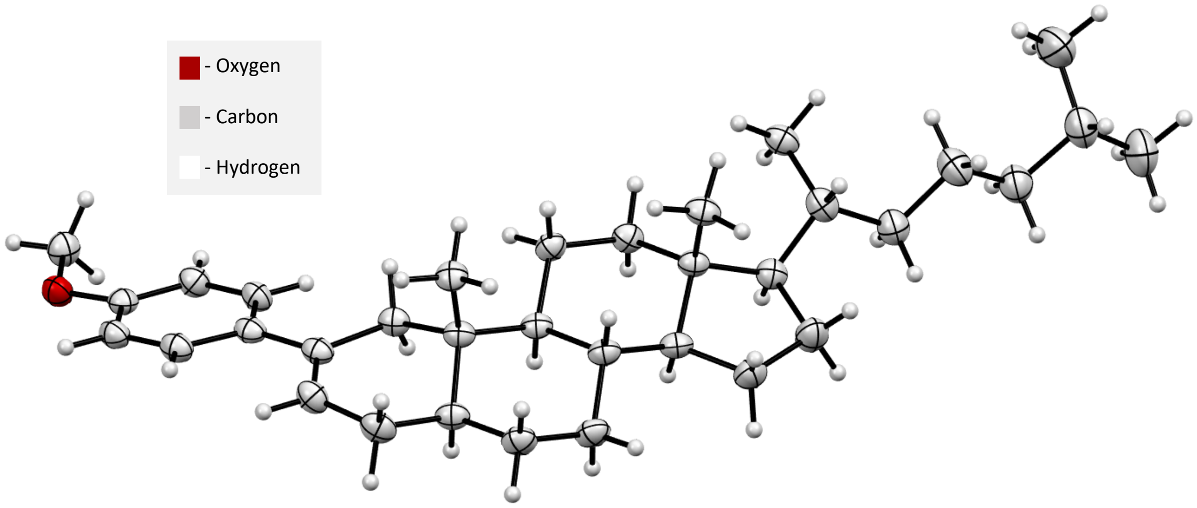
The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the ShelXT[9a] structure solution program using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F}^2$ using version 2019/3 of ShelXL 2019/3[9c]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_*exptl_absorpt_process_details*: CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023) using spherical harmonics,implemented in SCALE3 ABSPACK scaling algorithm.

There is a single formula unit in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1. The moiety formula is C27 H30 O3.

The Flack parameter was refined to -0.07(4). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.06(3). The chiral atoms in this structure are: C5(S), C6(S), C18(R), C20(S). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong, and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

## XI. Single Crystal Diffraction Data for 3k



**Experimental:** Crystals grew as colorless plate-shaped crystals by slow evaporation from hexanes and ether. A suitable crystal with dimensions 0.26 × 0.12 × 0.02 $mm^3$ was selected and mounted on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer. The crystal was kept at a steady T = 150.00(13) K during data collection. The structure was solved with the ShelXT 2014/5[9a] solution program using dual methods and by using Olex2 1.5-ac5-024[9b] as the graphical interface. The model was refined with ShelXL 2016/6[9c] using full matrix least squares minimization on $F^2$.

**Crystal Data:** $C_{34}H_{52}O$, $M_r$ = 476.75, monoclinic, $P2_1$ (No. 4), a = 6.06020(10) Å, b = 7.86450(10) Å, c = 30.3004(4) Å, $\beta$ = 92.3520(10)°, $\alpha = \gamma$ = 90°, $V$ = 1442.91(4) Å$^3$, $T$ = 150.00(13) K, $Z$ = 2, $Z'$ = 1, $\mu$(Cu K$_\alpha$) = 0.471, 18173 reflections measured, 5660 unique ($R_{int}$ = 0.0297) which were used in all calculations. The final $wR_2$ was 0.1332 (all data) and $R_1$ was 0.0458 (I≥2 $\sigma$(I)).

| **Compound** | **exp_1119_auto** |
|---|---|
| Formula | $C_{34}H_{52}O$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.097 |
| $\mu$/mm$^{-1}$ | 0.471 |
| Formula Weight | 476.75 |
| Colour | colourless |
| Shape | plate-shaped |
| Size/mm$^3$ | 0.26×0.12×0.02 |
| $T$/K | 150.00(13) |
| Crystal System | monoclinic |
| Flack Parameter | 0.02(13) |
| Space Group | $P2_1$ |
| $a$/Å | 6.06020(10) |
| $b$/Å | 7.86450(10) |
| $c$/Å | 30.3004(4) |
| $\alpha$/° | 90 |
| $\beta$/° | 92.3520(10) |
| $\gamma$/° | 90 |
| V/Å$^3$ | 1442.91(4) |
| $Z$ | 2 |
| $Z'$ | 1 |
| Wavelength/Å | 1.54184 |
| Radiation type | Cu K$_\alpha$ |
| $\Theta_{min}$/° | 2.919 |
| $\Theta_{max}$/° | 75.988 |
| Measured Refl's. | 18173 |
| Indep't Refl's | 5660 |
| Refl's I≥2 $\sigma$(I) | 5455 |
| $R_{\text{int}}$ | 0.0297 |
| Parameters | 322 |
| Restraints | 1 |
| Largest Peak | 0.321 |
| Deepest Hole | -0.174 |
| GooF | 1.074 |
| $wR_2$ (all data) | 0.1332 |
| $wR_2$ | 0.1326 |
| $R_1$ (all data) | 0.0468 |
| $R_1$ | 0.0458 |

**Structure Quality Indicators:**

**Reflections:**

| d min (CuKα) 2Θ=152.0° | I/σ(I) | Rint m=3.21 | Full 135.4° 98% to 152.0° |
|---|---|---|---|
| 0.79 | 37.2 | 2.97% | 99.9 |

**Refinement:**

| Shift | Max Peak | Min Peak | GooF | Hooft |
|---|---|---|---|---|
| 0.000 | 0.3 | -0.2 | 1.074 | .02(13) |

A colourless plate-shaped-shaped crystal with dimensions 0.26 × 0.12 × 0.02 mm$^3$ was mounted. Data were collected using a XtaLAB Synergy, Single source at home/near, HyPix diffractometer operating at $T$ = 150.00(13) K.

Data were measured using $\omega$ scans with Cu $K_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023). The maximum resolution that was achieved was $\Theta$ = 75.988$^\circ$ (0.83 Å). The unit cell was refined using CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023) on 12001 reflections, 66% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023). The final completeness is 99.90 % out to 75.988$^\circ$ in $\Theta$. A multi-scan absorption correction was performed using CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient $\mu$ of this material is 0.471 mm$^{-1}$ at this wavelength ($\lambda$ = 1.54184Å) and the minimum and maximum transmissions are 0.632 and 1.000.

The structure was solved and the space group $P2_1$ (# 4) determined by the ShelXT 2014/5[9a] structure solution program using using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F}^2$ using version 2016/6 of ShelXL 2016/6[9c]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

*_exptl_absorpt_process_details*: CrysAlisPro 1.171.42.94a (Rigaku Oxford Diffraction, 2023) using spherical harmonics,implemented in SCALE3 ABSPACK scaling algorithm.

There is a single formula unit in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1. The moiety formula is C34 H52 O.

The Flack parameter was refined to 0.02(13). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in None. The chiral atoms in this structure are: C1(R), C4(S), C5(R), C9(S), C10(S), C13(S), C14(S), C28(R). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

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