Supplementary Information

One-Pot Synthesis of Carbazoles via Tandem C-C Cross-Coupling and Reductive Amination

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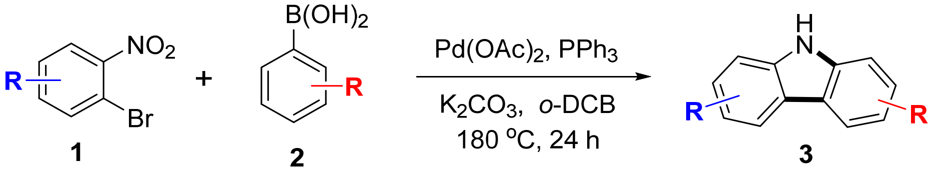
General Information

All reactions were run under an atmosphere of air under anhydrous conditions unless otherwise indicated. Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), dimethylformamide (DMF) and toluene (PhMe) were obtained from Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Pressure tubes (13 x 100 mm, PYREXPLUS, and 350 mL flask, purchased from Chem Glass) were dried in oven for overnight and cooled under a stream of nitrogen prior to use. All commercial reagents were used directly without further purification.

The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F_{254}), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into a *p*-anisaldehyde solution (5.6 mL of *p*-anisaldehyde, 2.3 mL actic acid and 3.0 mL of concentrated sulfuric acid in 200 mL of ethanol) or a $KMnO_4$ solution (3 g of $KMnO_4$, 20 g of K_2CO_3, and 5 mL of 5% NaOH solution in 300 mL of water). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using hexanes-EtOAc (v/v) or hexanes-acetone (v/v). The solvents were simple distilled unless otherwise noted.

Infrared spectra were recorded on a Varian 2000 FT-IR. High-resolution mass spectra (EI) were obtained on a Jeol JMS 700 HRMS at the Korea Basic Science Center (KBSI), Daegu, Korea. Low-resolution mass spectra (EI) were obtained on a Varian 450-GC/Varian 220-MS and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion ($[M+H]^+$ or $[M+Na]^+$). Nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded with a Bruker (300 MHz) spectrometer. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz. The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc.

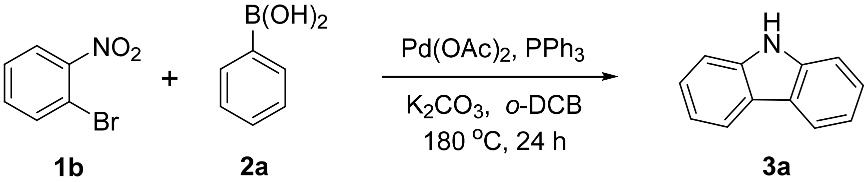
General Procedure for Carbazole Synthesis



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added *o*-bromonitrobenzene **1** (0.5 mmol, 100 mol%), aryl boronic acid **2** (0.65 mmol, 130 mol%), Pd(OAc) (0.01 mmol, 2 mol%), PPh_3 (1.25 mmol, 250 mol %), K_2CO_3 (1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to *o*-bromonitrobenzene **1**. The mixture was heated at 180 ^{o}C (oil bath temperature) for 24-48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) under the conditions noted to furnish the corresponding product.

Detailed Procedure and Spectral Data for Compounds

9*H*-carbazole (3a)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), phenylboronic acid **2a** (82 mg, 0.65 mmol, 130 mol%), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 ^{o}C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3a** as a white solid (72 mg, 86% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[1]

TLC (SiO_2): $R_f = 0.34$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO): δ 11.33 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 3H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.21 – 7.16 (m, 3H).

^{13}C NMR (75 MHz, DMSO): δ 139.79, 125.54, 122.48, 120.18, 118.53, 110.98.

FTIR (neat): υ 3379, 2946, 1450, 1033 cm^{-1}.

LRMS *m/z* (EI): 166.8 (M^{+}-1), 139.0, 83.4, 62.8.

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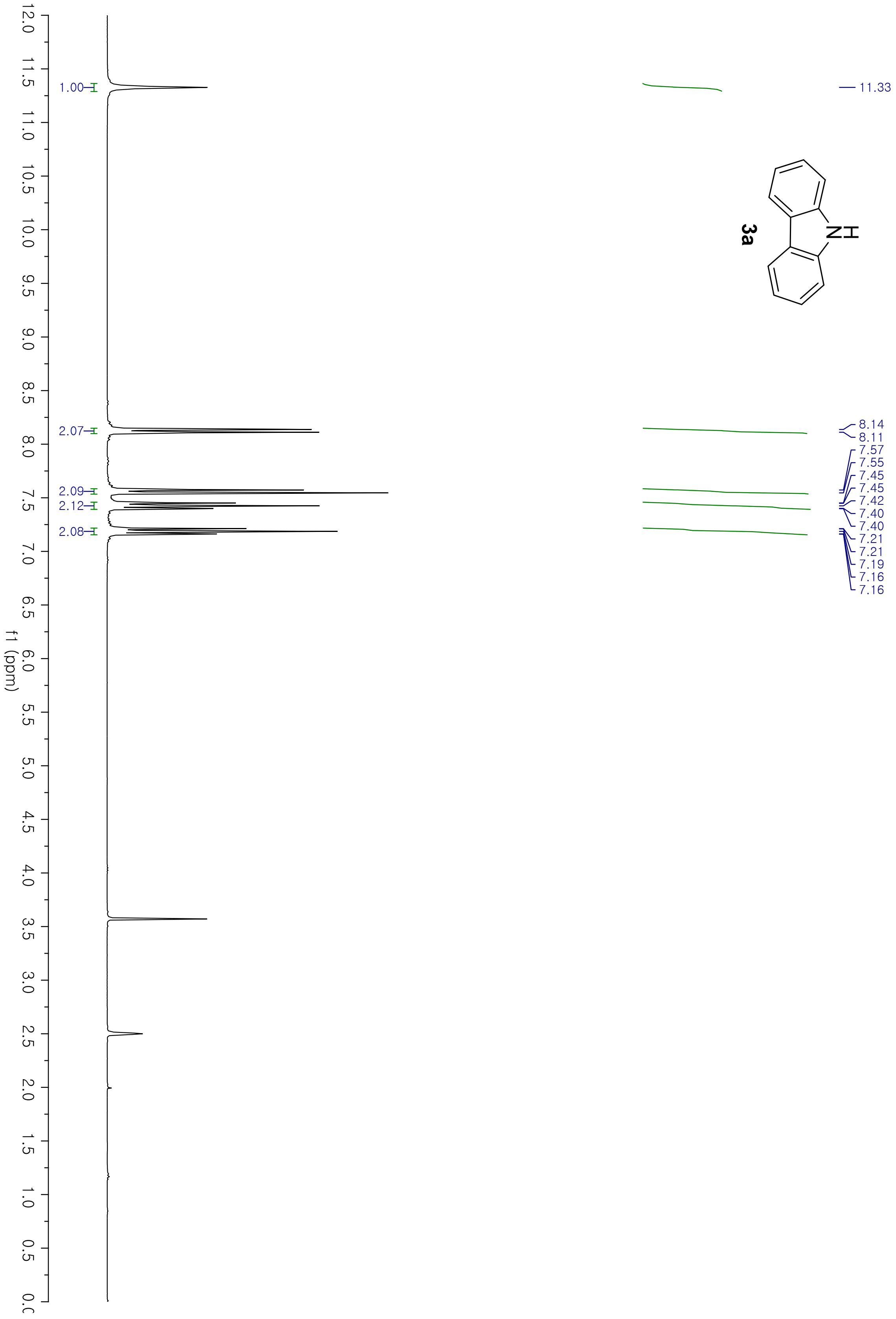
[1] C. Suzuki, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2015, **17**, 1597-1600.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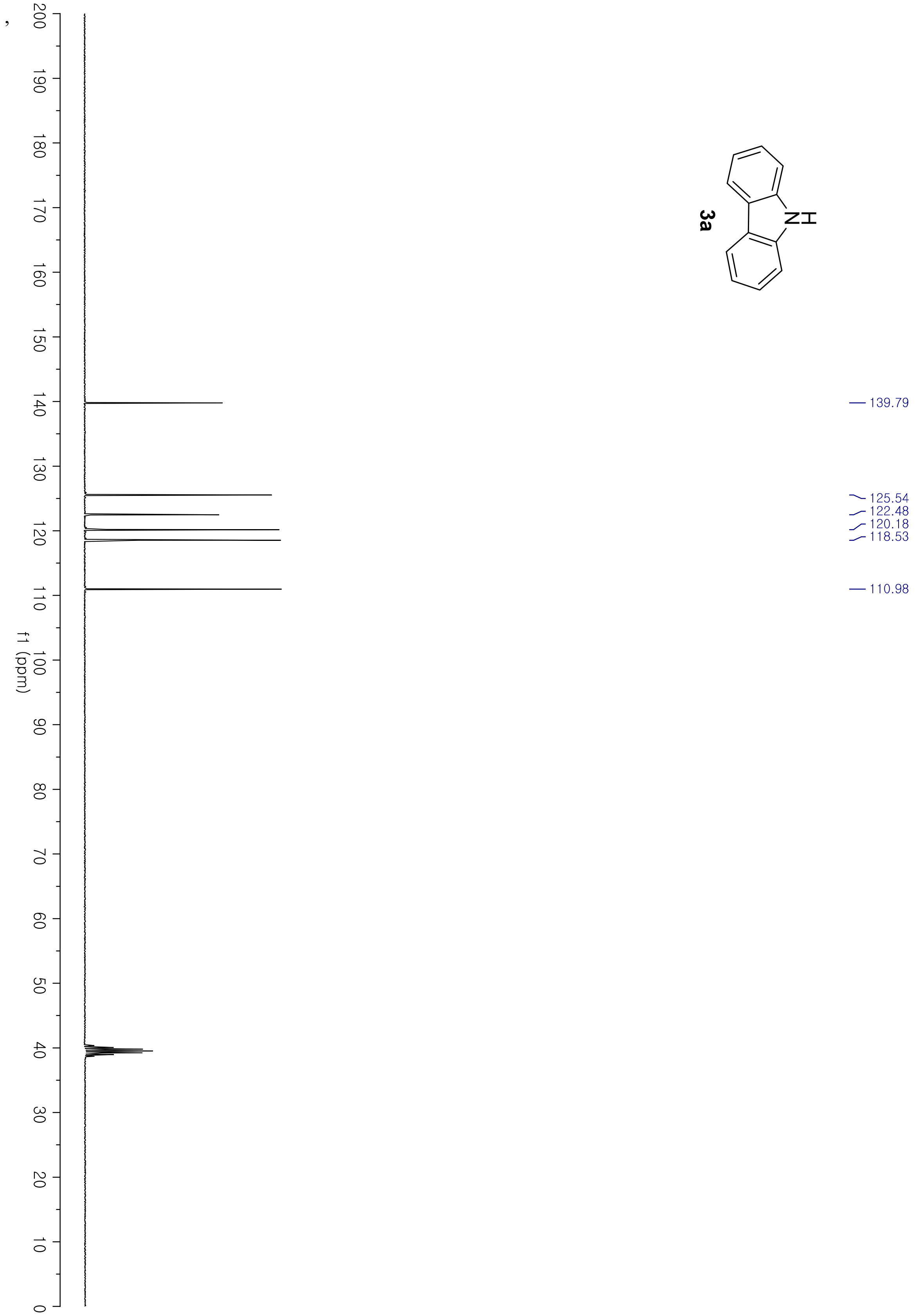
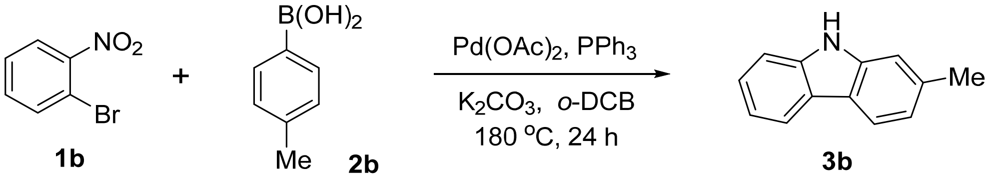
N
H
11.33
8.14
8.11
7.57
7.55
7.45
7.45
7.42
7.40
7.40
7.21
7.21
7.19
7.16
7.16
1.00
2.07
2.09
2.12
2.08
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3a
139.79
125.54
122.48
120.18
118.53
110.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-Methyl-9*H*-carbazole (3b)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), *p*-Tolyboronic acid **2b** (88 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3b** as a white solid (76 mg, 84% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[2]

TLC (SiO_2): $R_f = 0.32$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.24 – 7.18 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 2.53 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.09, 139.59, 136.15, 125.41, 123.58, 121.19, 121.12, 120.14, 120.13, 119.46, 110.86, 110.60, 22.21.

FTIR (neat) υ 3394, 2920, 1652, 1530, 1365 cm^{-1}.

LRMS *m*/*z* (EI): 179.8 (M$^+$-1), 151.8, 76.8, 62.8.

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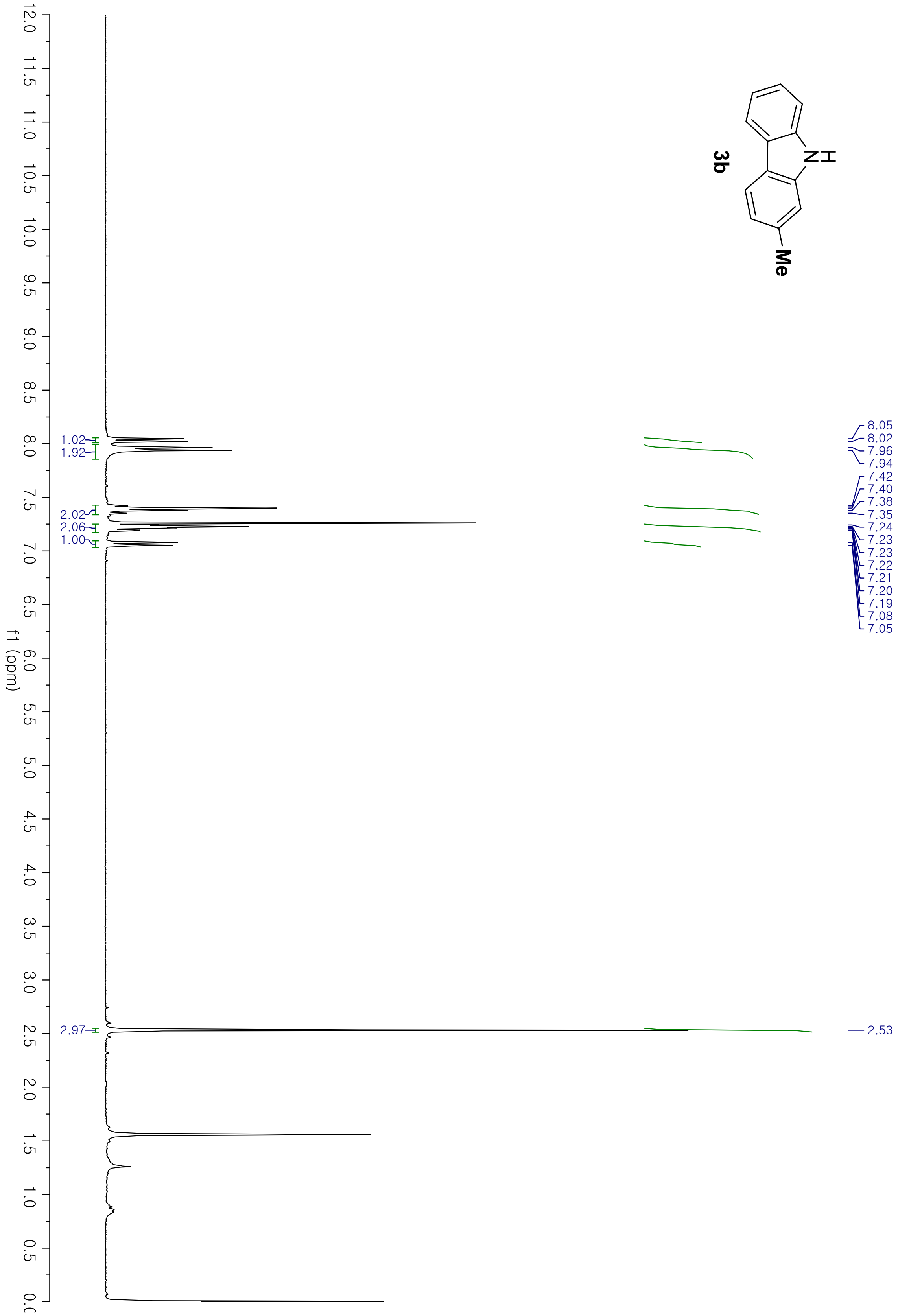
(2) B. Alcaide, P. Almendros, J. M. Alonso, M. T. Quirós and P. Gadziński, *Adv. Synth. Catal.*, 2011, **353**, 1871-1876.



3b
N
H
Me
8.05
8.02
7.96
7.94
7.42
7.40
7.38
7.35
7.24
7.23
7.23
7.22
7.21
7.20
7.19
7.08
7.05
2.53
1.02
1.92
2.02
2.06
1.00
2.97
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
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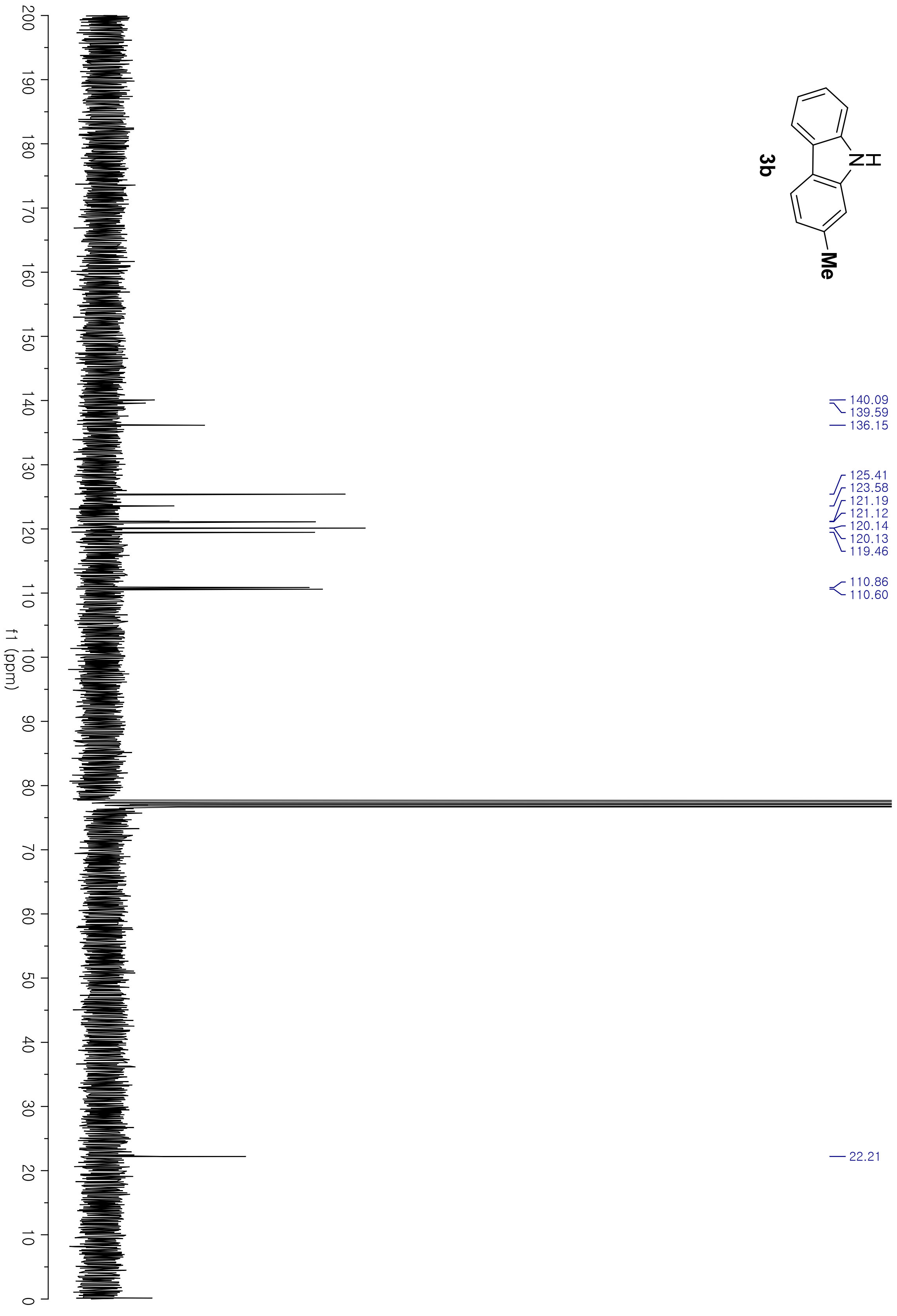
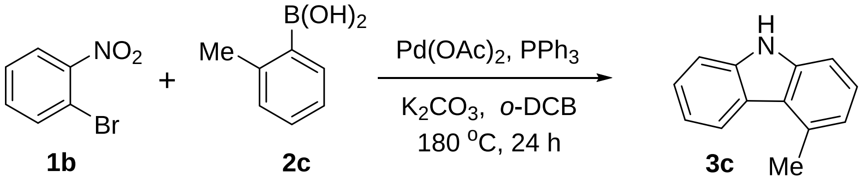
0.0
f1 (ppm)


3b
Me
H
N
140.09
139.59
136.15
125.41
123.58
121.19
121.12
120.14
120.13
119.46
110.86
110.60
22.21
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

4-Methyl-9*H*-carbazole (3c)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), *o*-Tolyboronic acid **2c** (88 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3c** as a white solid (79 mg, 87% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[3]

TLC (SiO_2): $R_f = 0.33$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, J = 7.9 Hz, 1H), 8.09 (br s, 1H), 7.50 – 7.39 (m, 2H), 7.37 – 7.31 (m, 1H), 7.32 – 7.26 (m, 2H), 7.02 (dd, J = 7.3, 0.8 Hz, 1H), 2.89 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 139.54, 139.51, 133.49, 125.77, 125.29, 123.93, 122.68, 121.90, 120.99, 119.44, 110.49, 108.26, 20.92.

FTIR (neat) υ 3396, 3200, 2924, 1653, 1521, 1267, 1048 cm^{-1}.

LRMS *m*/*z* (EI): 181.3 (M$^+$), 182.3, 180.4, 177.5, 155.3, 125.8, 93.7.

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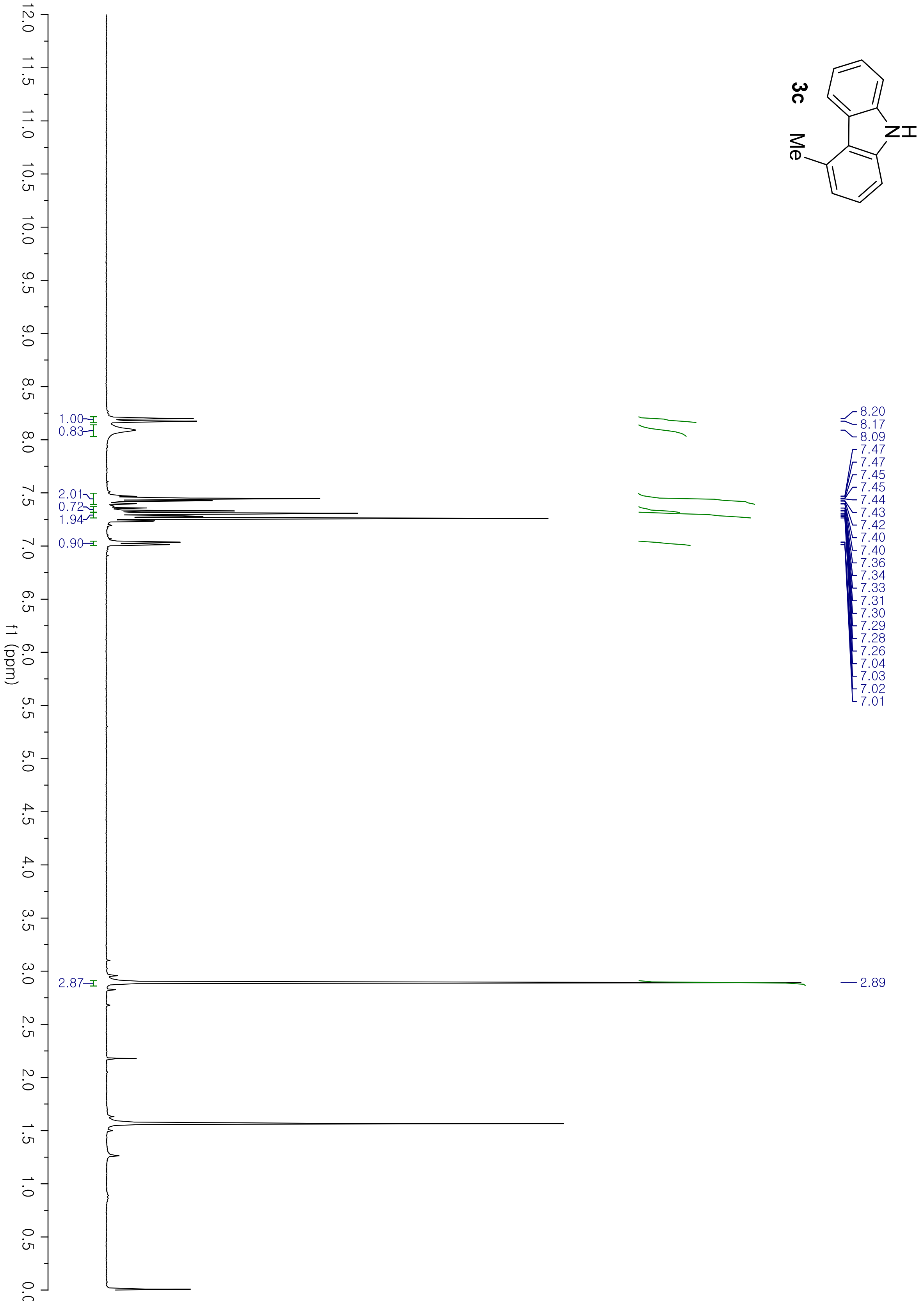
[3] B. J. Stokes, B. Jovanović, H. Dong, K. J. Richert, R. D. Riell and T. G. Driver, *J. Org. Chem.*, 2009, **74**, 3225-3228.


3c
Me
NH
8.20
8.17
8.09
7.47
7.47
7.45
7.45
7.44
7.43
7.42
7.40
7.40
7.36
7.34
7.33
7.31
7.30
7.29
7.28
7.26
7.04
7.03
7.02
7.01
2.89
1.00
0.83
2.01
0.72
1.94
0.90
2.87
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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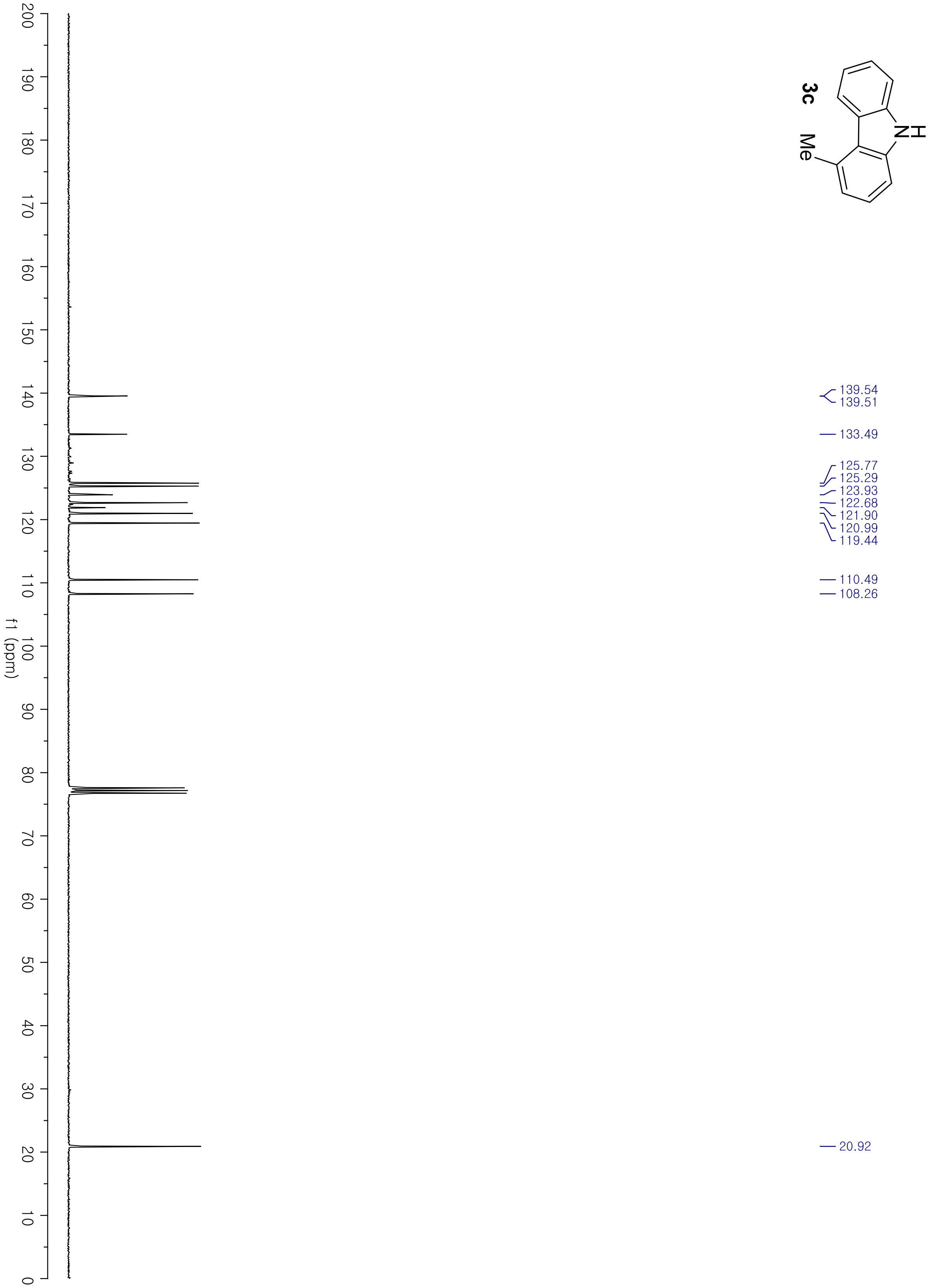
0.0


3c
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N
H
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139.51
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125.77
125.29
123.93
122.68
121.90
120.99
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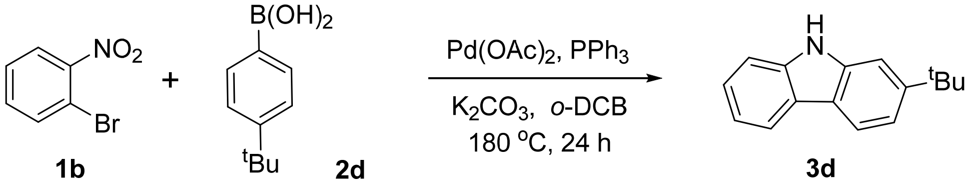
110.49
108.26
20.92
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-(Tert-butyl)-9*H*-carbazole (3d)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), (4-(tert-butyl)phenyl)boronic acid **2d** (116 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 ^{o}C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3d** as a white solid (94 mg, 84% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[\4]

TLC (SiO_2): $R_f = 0.35$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 7.0 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.94 (s, 1H), 7.44 (d, J = 1.6 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.32 (dd, J = 8.3, 1.4 Hz, 1H), 7.25 – 7.20 (m, 1H), 1.44 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.72, 139.89, 139.82, 125.40, 123.49, 121.03, 120.21, 119.90, 119.41, 117.65, 110.57, 107.25, 35.25, 31.90.

FTIR (neat) υ 3194, 2916, 1650, 1525, 1267 cm^{-1}.

LRMS *m*/*z* (EI): 222.7 (M^{+}-1), 207.8, 180.0, 167.0, 89.9.

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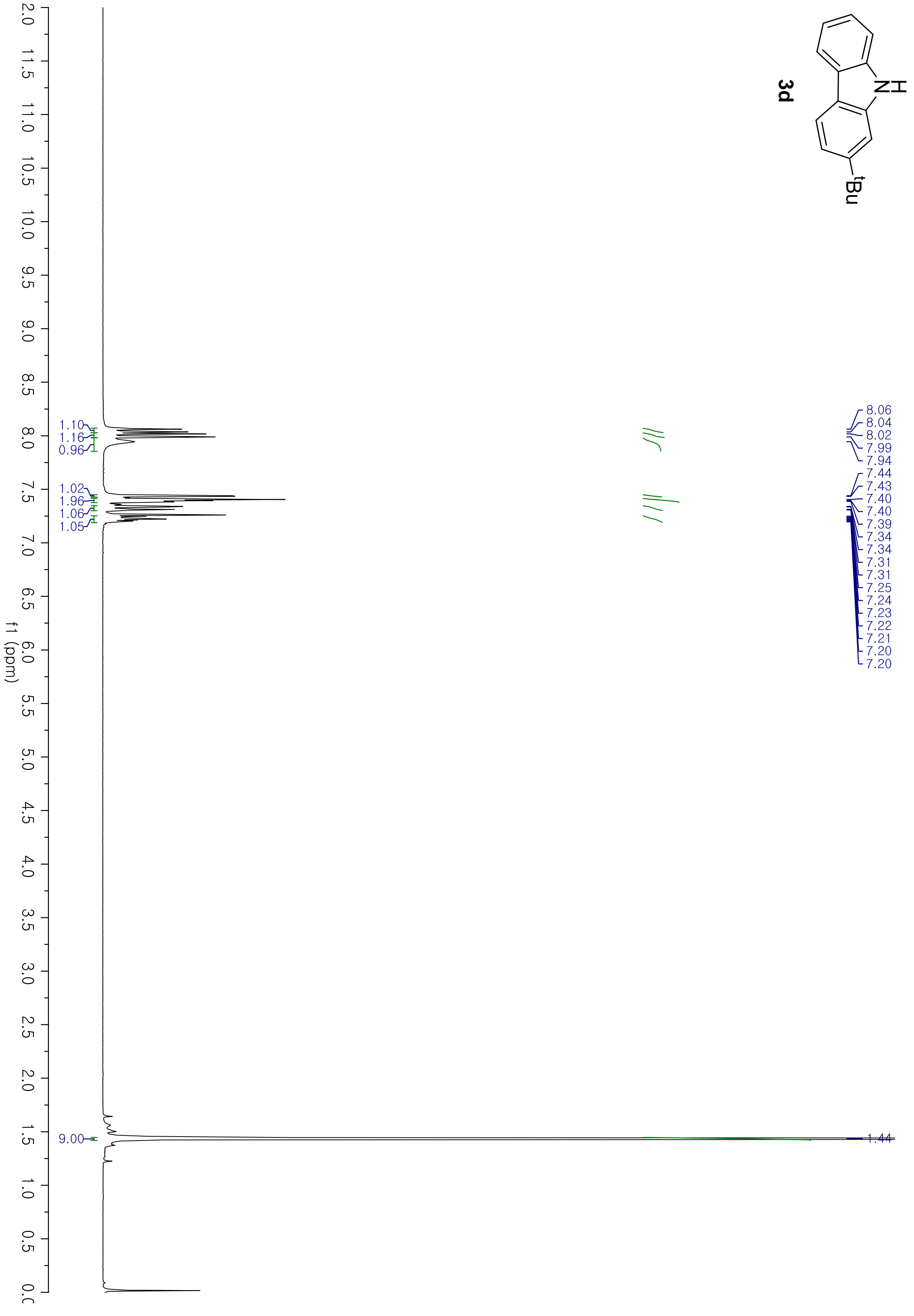
(4) A. W. Freeman, M. Urvoy and M. E. Criswell, *J. Org. Chem.*, 2005, **70**, 5014-5019.



8.06
8.04
8.02
7.99
7.94
7.44
7.43
7.40
7.40
7.39
7.34
7.34
7.31
7.31
7.25
7.24
7.23
7.22
7.21
7.20
7.20
1.44
1.10
1.16
0.96
1.02
1.96
1.06
1.05
9.00
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
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6.5
6.0
5.5
5.0
4.5
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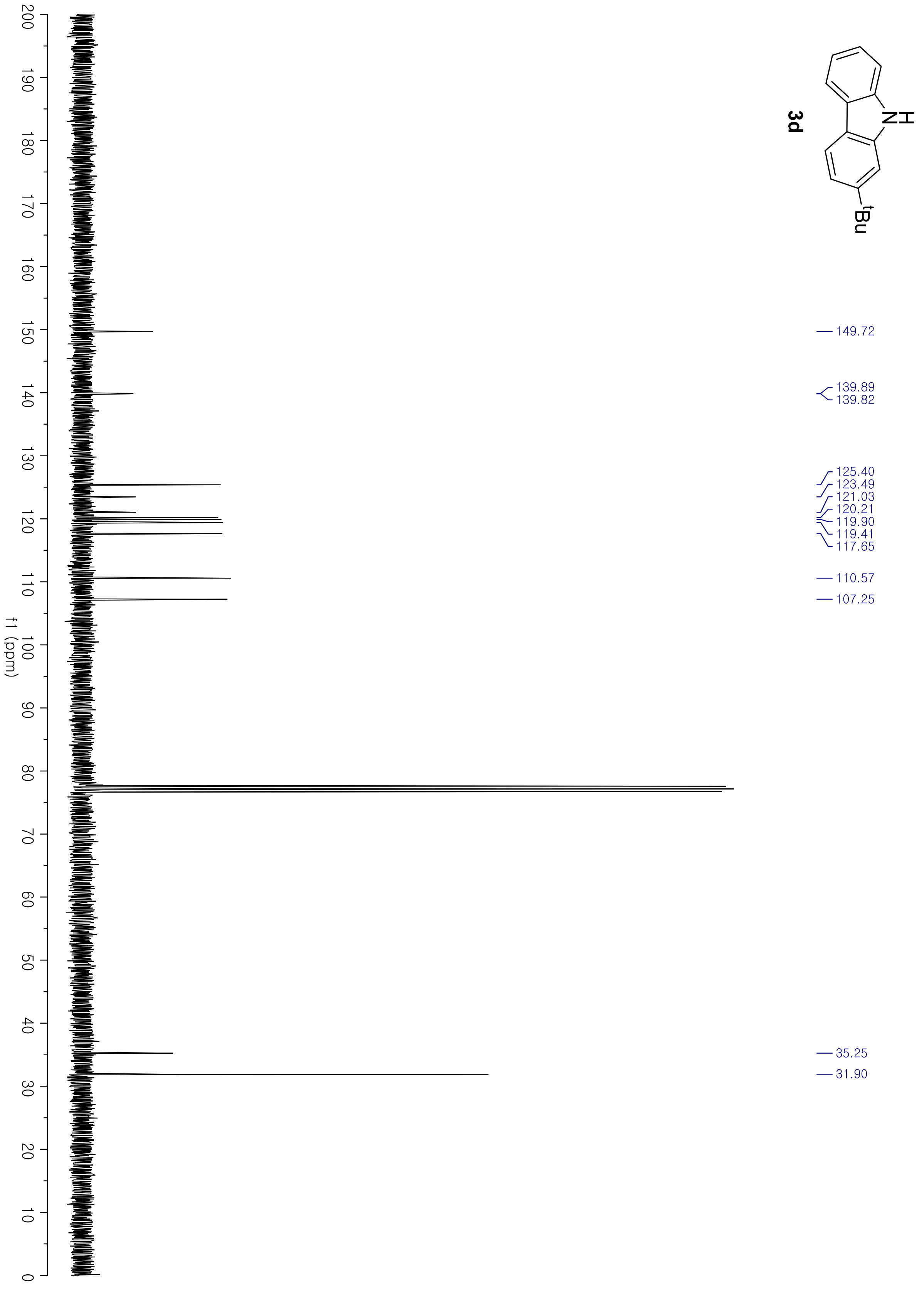
1.0
0.5
0.0
H
N
tBu

3d


3d
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H
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149.72
139.89
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123.49
121.03
120.21
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110.57
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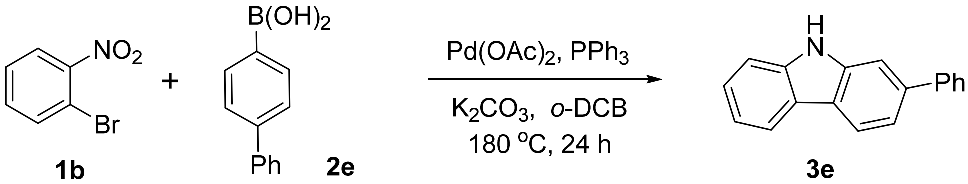
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-Phenyl-9*H*-carbazole (3e)

From reaction of 1-bromo-2-nitrobenzene ***1b*** *with [1,1'-biphenyl]-4-ylboronic acid* ***2e***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), [1,1'-biphenyl]-4-ylboronic acid **2e** (129 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 ^{o}C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3e** as a white solid (110 mg, 90% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[2, 5]

TLC (SiO_2): $R_f = 0.37$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, Acetone-d6) δ 10.50 (s, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.57 – 7.32 (m, 6H), 7.21 (td, *J* = 8.2, 4.3 Hz, 1H).

^{13}C NMR (75 MHz, DMSO): δ 141.26, 140.43, 140.35, 137.88, 128.99, 127.12, 127.06, 125.70, 122.23, 121.88, 120.68, 120.32, 118.76, 117.89, 111.06, 108.93.

FTIR (neat) υ 3377, 3268, 1692, 1528, 1367, 1227 cm^{-1}.

LRMS *m*/*z* (EI): 242.8 (M^{+}-1), 120.3, 76.7, 50.9.

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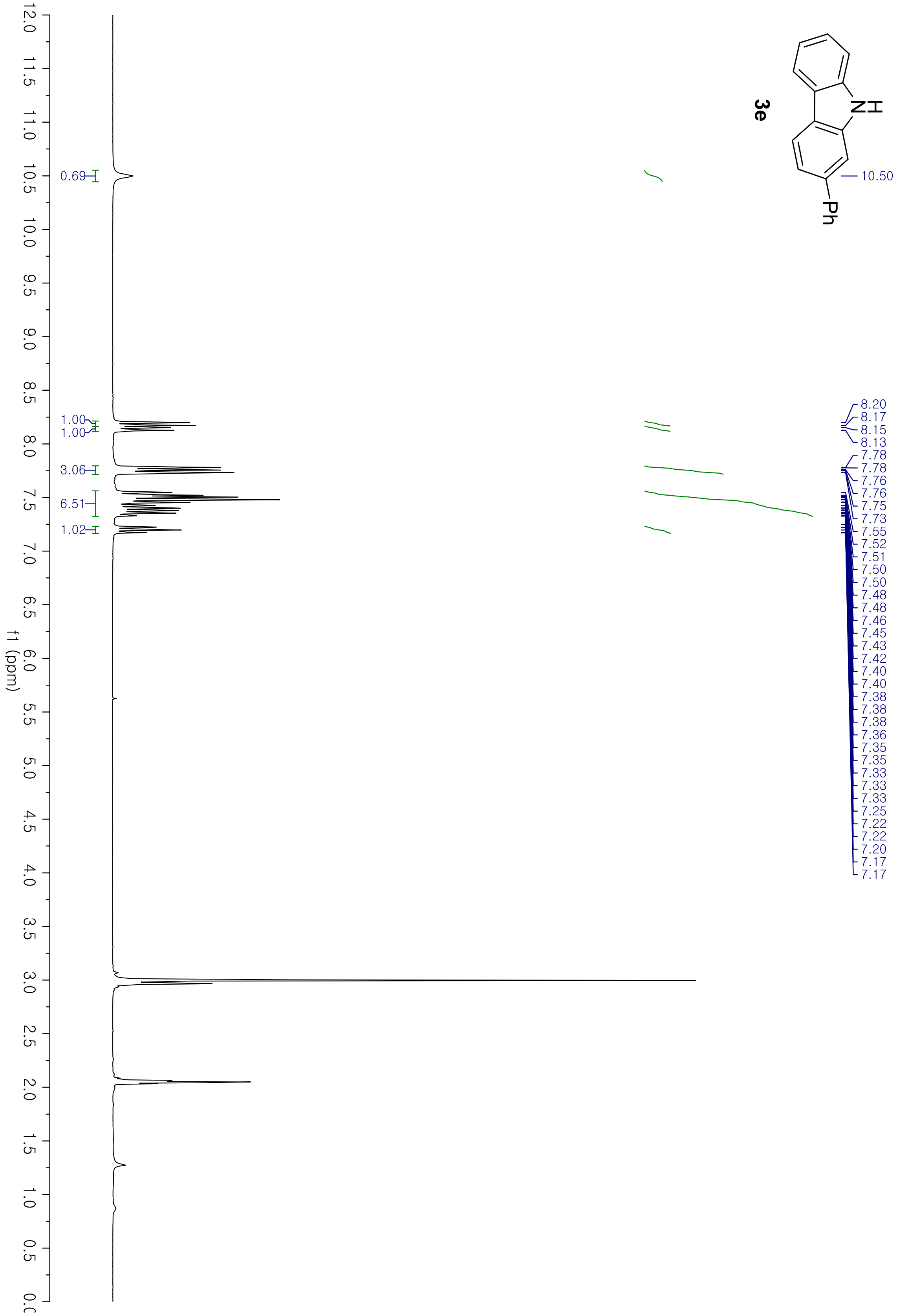
(2) B. Alcaide, P. Almendros, J. M. Alonso, M. T. Quirós and P. Gadziński, *Adv. Synth. Catal.*, 2011, **353**, 1871-1876.

(5) K. Takamatsu, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2014, **16**, 2892-2895.


3e
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NH
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8.20
8.17
8.15
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7.76
7.76
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7.55
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7.36
7.35
7.35
7.33
7.33
7.33
7.25
7.22
7.22
7.20
7.17
7.17
0.69
1.00
1.00
3.06
6.51
1.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
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6.5
6.0
5.5
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2.5
2.0
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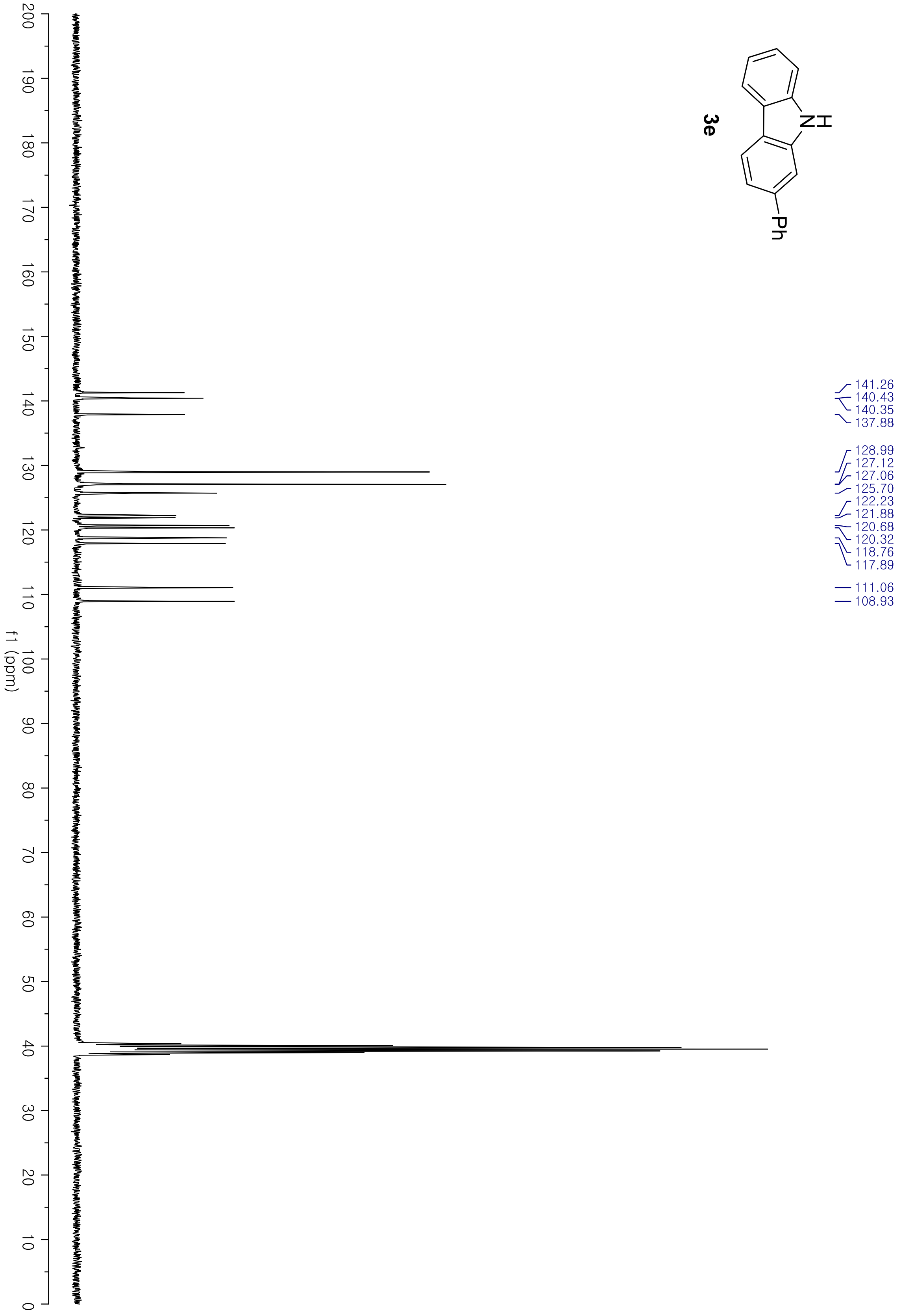
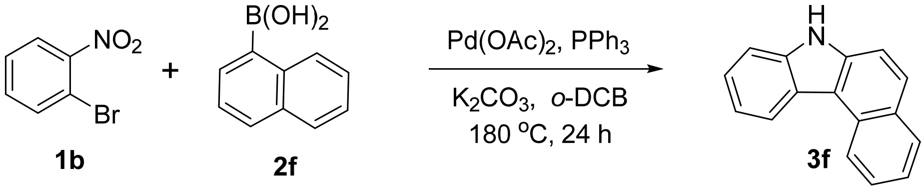
1.0
0.5
0.0
f1 (ppm)


3e
NH
Ph
141.26
140.43
140.35
137.88
128.99
127.12
127.06
125.70
122.23
121.88
120.68
120.32
118.76
117.89
111.06
108.93
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

7*H*-Benzo[c]carbazole (3f)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), naphthalen-1-ylboronic acid **2f** (122 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 ^{o}C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3f** as a white solid (91 mg, 84% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[6]

TLC (SiO_2): $R_f = 0.40$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.3 Hz, 1H), 8.58 (d, *J* = 7.8 Hz, 1H), 8.44 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.36 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.52, 137.16, 130.03, 129.32, 127.55, 127.01, 124.46, 124.09, 123.38, 123.13, 122.16, 120.36, 115.54, 112.71, 111.25.

FTIR (neat) υ 3396, 2920, 1876, 1465, 1267, 1120 cm^{-1}.

LRMS *m*/*z* (EI): 217.7 (M^{+}+1), 216.8, 188.8, 108.2, 95.3.

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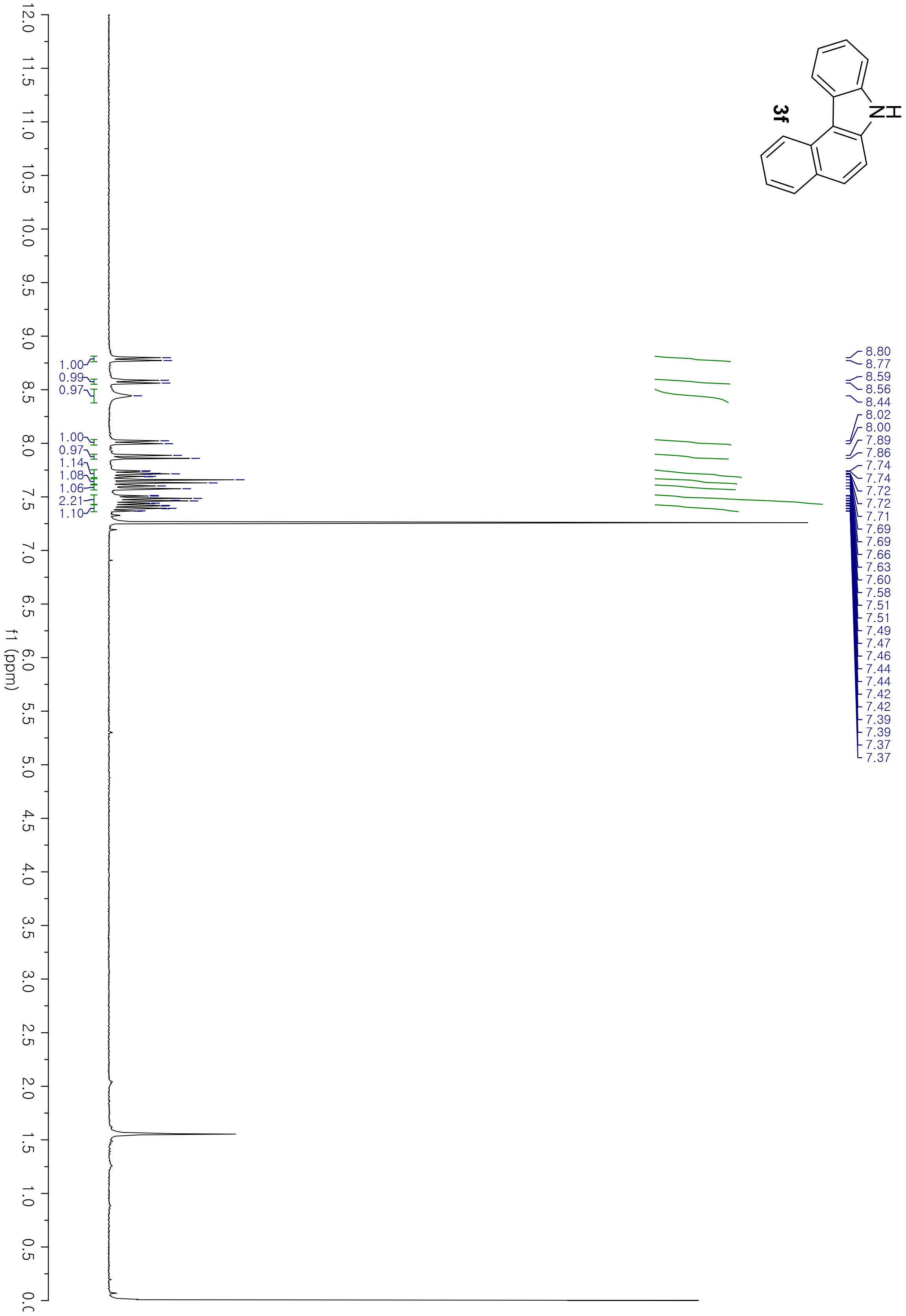
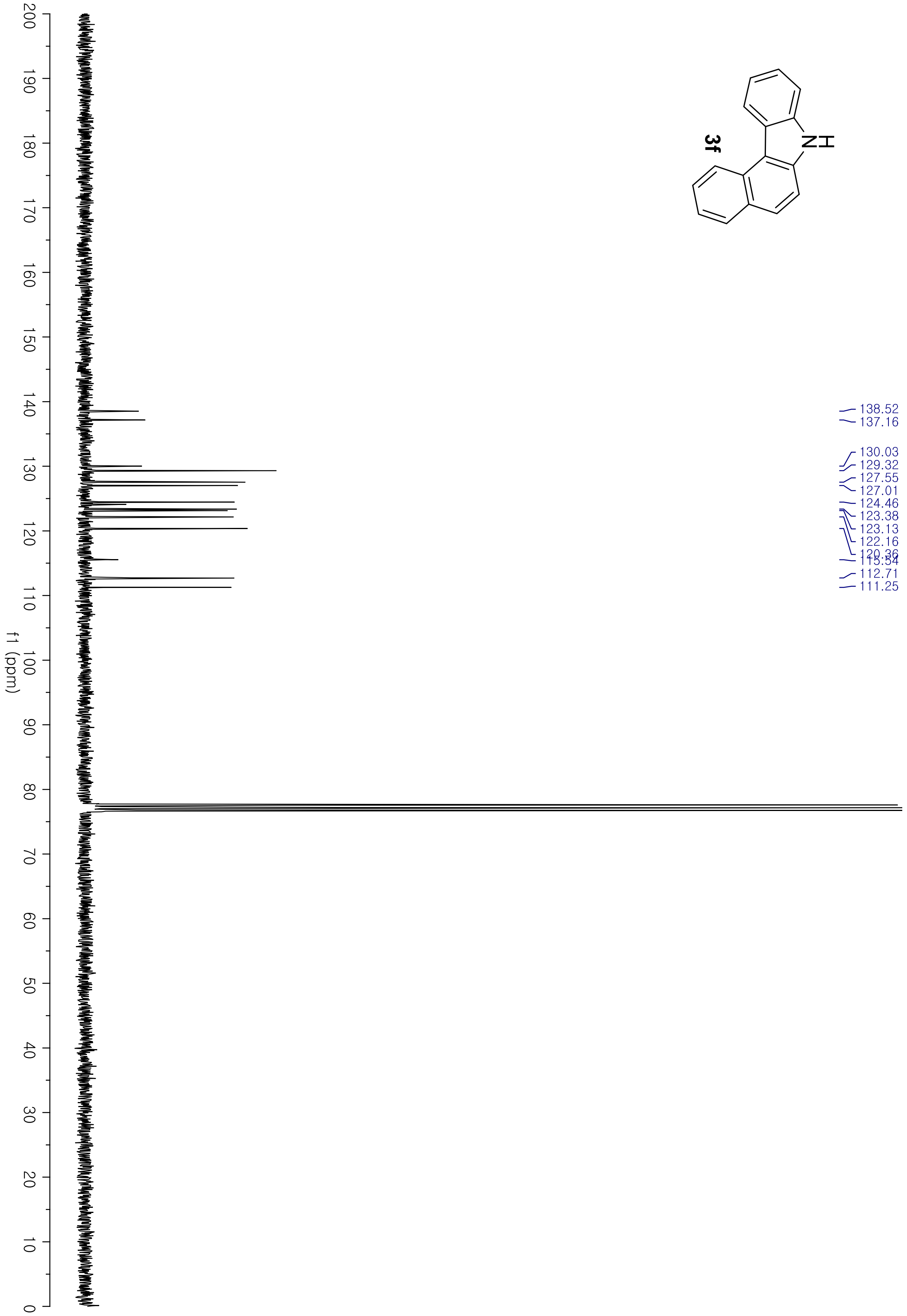
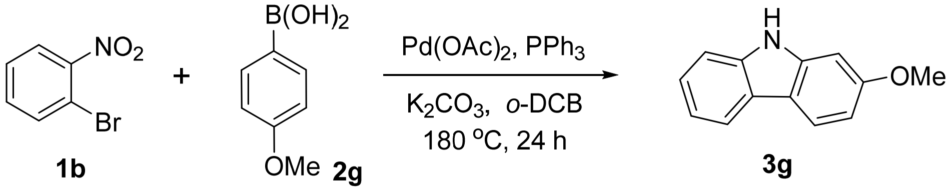
[6] C. Wang, W. Zhang, S. Lu, J. Wu and Z. Shi, *Chem. Commun.*, 2008, 5176-5178.


3f
NH
8.80
8.77
8.59
8.56
8.44
8.02
8.00
7.89
7.86
7.74
7.74
7.72
7.72
7.71
7.69
7.69
7.66
7.63
7.60
7.58
7.51
7.51
7.49
7.47
7.46
7.44
7.44
7.42
7.42
7.39
7.39
7.37
7.37
1.00
0.99
0.97
1.00
0.97
1.14
1.08
1.06
2.21
1.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3f
NH
138.52
137.16
130.03
129.32
127.55
127.01
124.46
123.38
123.13
122.16
120.36
115.54
112.71
111.25
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

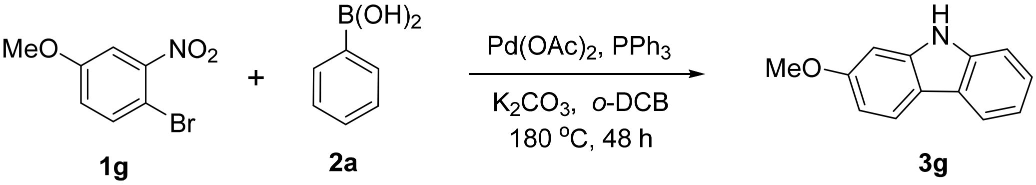
2-Methoxy-9*H*-carbazole (3g)

From reaction of 1-bromo-2-nitrobenzene ***1b*** *with (4-methoxyphenyl)boronic acid* ***2g***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), (4-methoxyphenyl)boronic acid **2g** (99 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3g** as a white solid (76 mg, 77% yield). ^1H and ^{13}C NMR data were consistent with literature values.[7]

From reaction of 1-bromo-4-methoxy-2-nitrobenzene ***1g*** *with phenylboronic acid* ***2a***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-4-methoxy-2-nitrobenzene **1g** (120 mg, 0.5 mmol, 100 mol%), phenylboronic acid **2a** (94 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-4-methoxy-2-nitrobenzene **1g**). The mixture was heated at 180 °C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give 3g as a white solid (72 mg, 73% yield).

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(7) T. Watanabe, S. Oishi, N. Fujii and H. Ohno, *J. Org. Chem.*, 2009, **74**, 4720-4726.

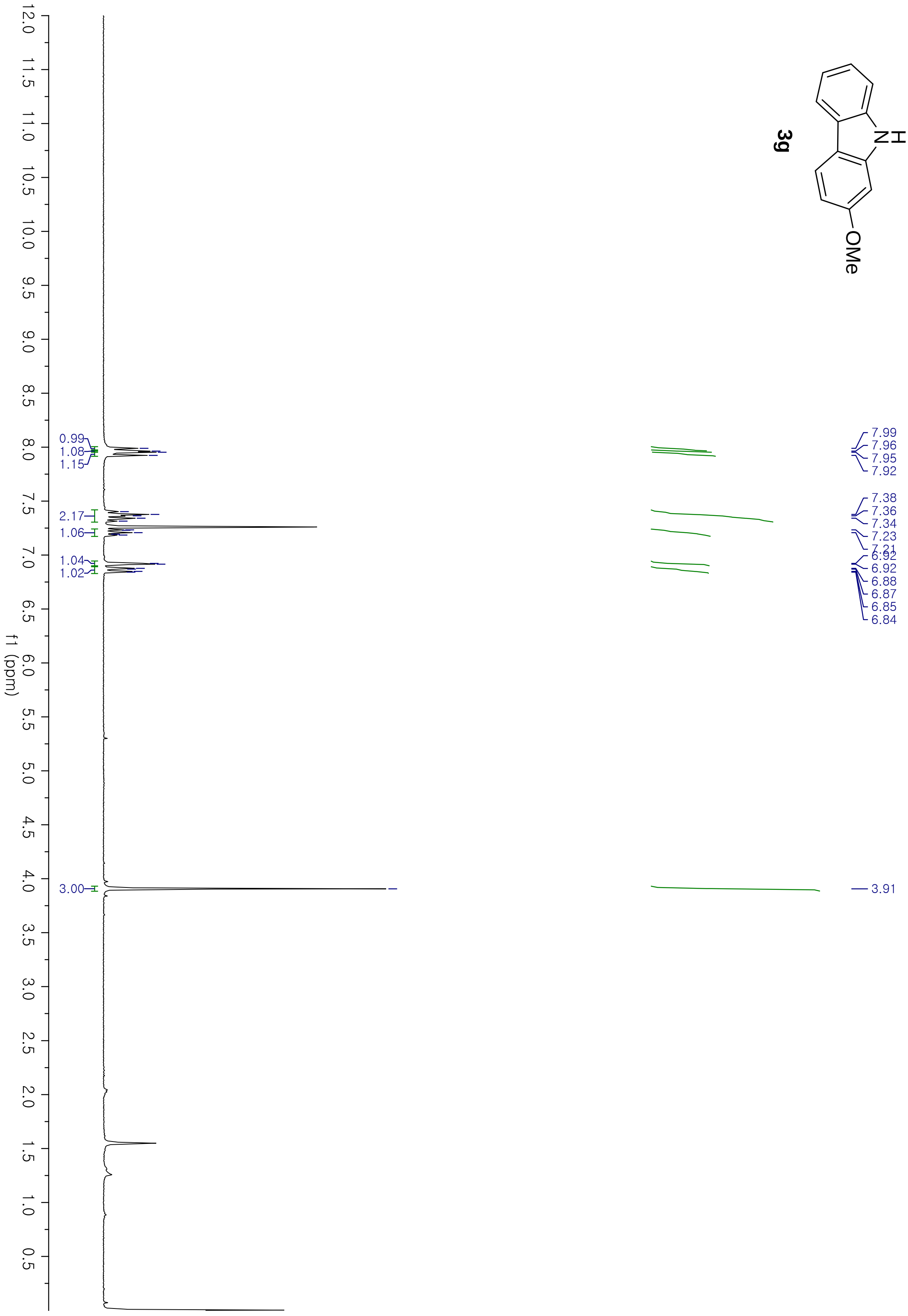
TLC (SiO_2): R_f = 0.26 (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.96 (d, *J* = 3.4 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.41 – 7.31 (m, 1H), 7.24 – 7.18 (m, 1H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.91 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.21, 140.93, 139.63, 124.69, 123.67, 121.19, 119.70, 119.63, 117.39, 110.44, 108.29, 94.83, 55.77.

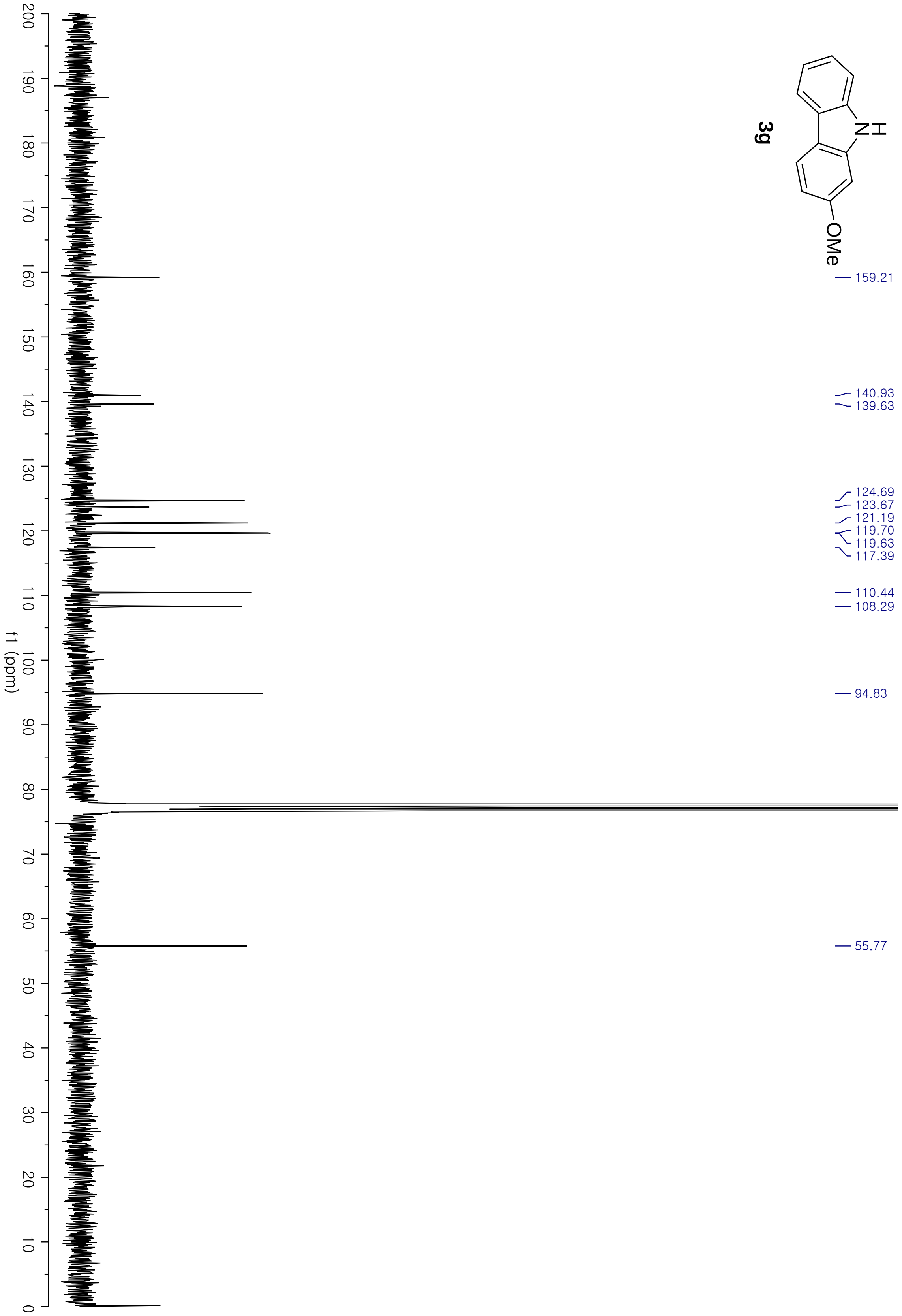
FTIR (neat) υ 3395, 1336, 1200, 1030 cm^{-1}.

LRMS *m*/*z* (EI): 197.7 (M^++1), 196.7, 181.8, 153.8, 127.8.

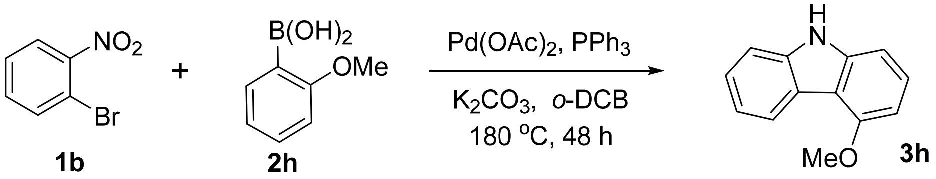


OMe
N
H
7.99
7.96
7.95
7.92
7.38
7.36
7.34
7.23
7.21
6.92
6.92
6.88
6.87
6.85
6.84
3.91
0.99
1.08
1.15
2.17
1.06
1.04
1.02
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

3g


3g
OMe
H
N
159.21
140.93
139.63
124.69
123.67
121.19
119.70
119.63
117.39
110.44
108.29
94.83
55.77
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4-Methoxy-9*H*-carbazole (3h)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), (2-methoxyphenyl)boronic acid **2h** (99 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1**). The mixture was heated at 180 ^{o}C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3h** as a white solid (66 mg, 67% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[8]

TLC (SiO_2): $R_f = 0.26$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.8 Hz, 1H), 8.02 (s, 1H), 7.43 – 7.38 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.09 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.32, 140.92, 138.72, 126.77, 125.01, 123.12, 122.67, 119.70, 112.60, 110.07, 103.62, 100.42, 55.51.

FTIR (neat) υ 3386, 2938, 1405, 1248, 1184, 1045 cm^{-1}.

LRMS *m/z* (EI): 197.8 (M^{+}+1), 196.7, 181.9, 153.9, 128.0.

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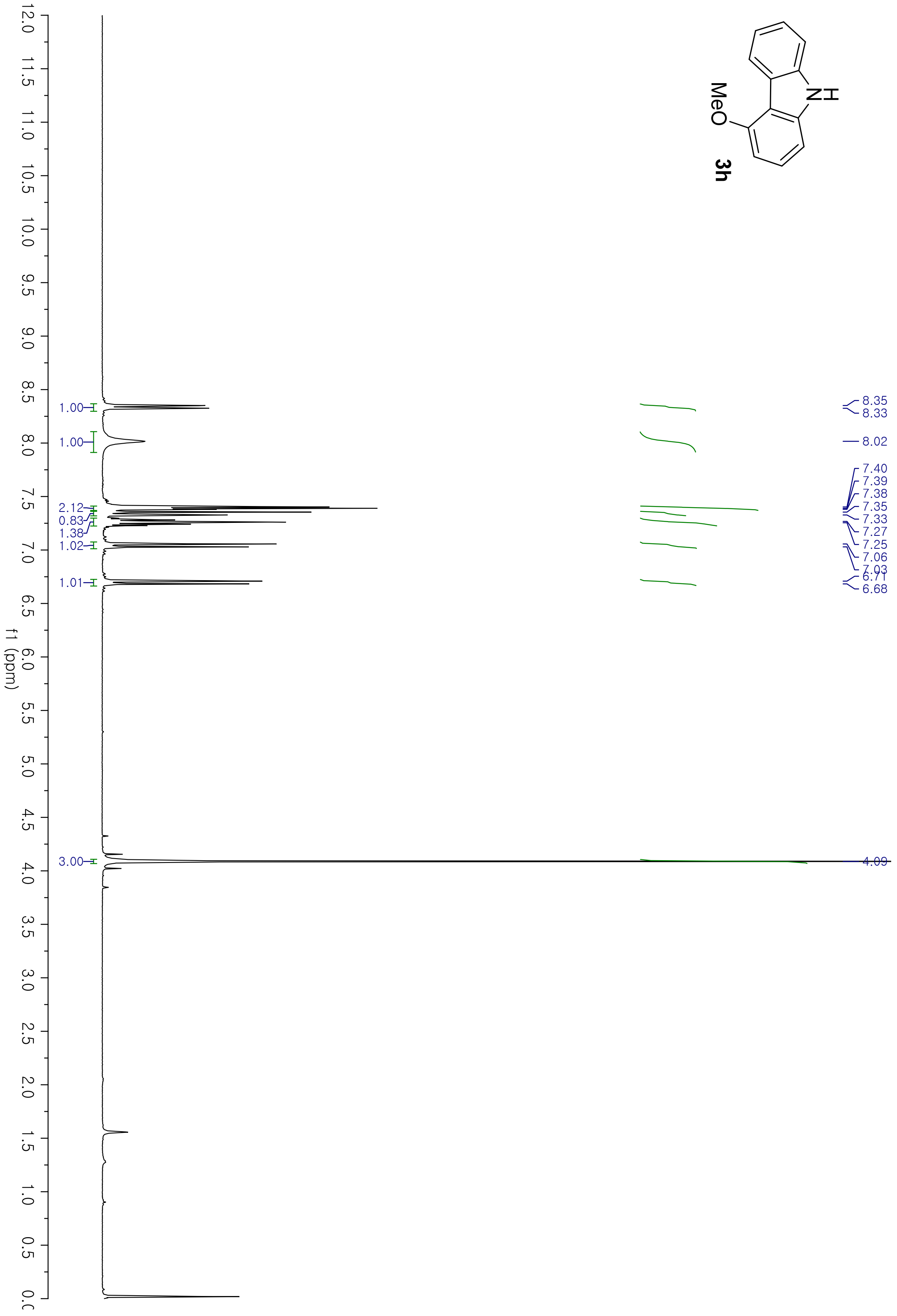
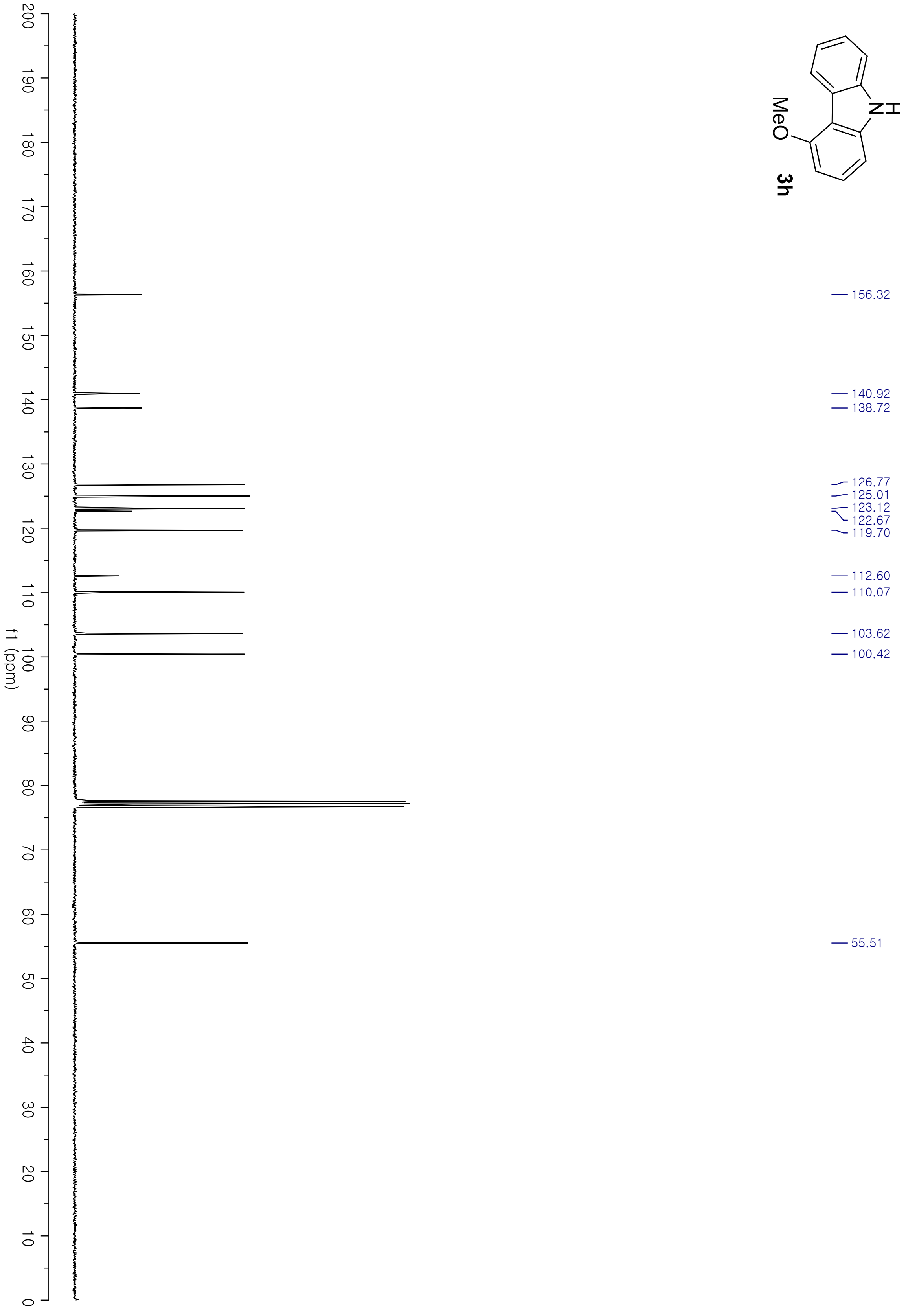
[8] S. Chakrabarty, I. Chatterjee, L. Tebben and A. Studer, *Angew. Chem. Int. Ed.*, 2013, **52**, 2968-2971.

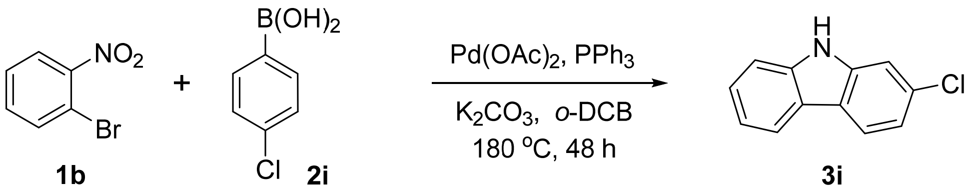

3h
MeO
H
N
8.35
8.33
8.02
7.40
7.39
7.38
7.35
7.33
7.27
7.25
7.06
7.03
6.71
6.68
4.09
1.00
1.00
2.12
0.83
1.38
1.02
1.01
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



MeO
N
H
3h
156.32
140.92
138.72
126.77
125.01
123.12
122.67
119.70
112.60
110.07
103.62
100.42
55.51
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

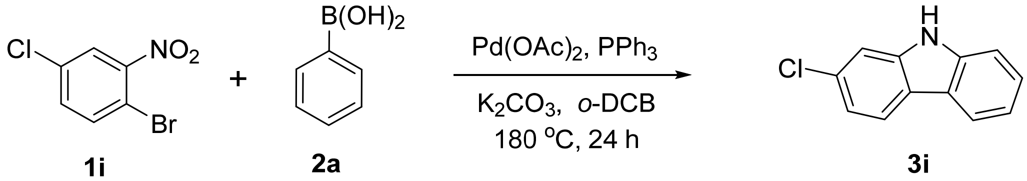
2-Chloro-9*H*-carbazole (3i)

From reaction of 1-bromo-2-nitrobenzene ***1b*** *with (4-chlorophenyl)boronic acid* ***2i***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), (4-chlorophenyl)boronic acid **2i** (102 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3i** as a white solid (71 mg, 70% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[1]

From reaction of 1-bromo-4-chloro-2-nitrobenzene ***1i*** *with phenylboronic acid* ***2a***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-4-chloro-2-nitrobenzene **1i** (113 mg, 0.5 mmol, 100 mol%), phenylboronic acid **2a** (94 mg, 0.65 mmol, 130 mol%), Pd(OAc) (5.6 mg, 0.025 mmol, 5 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-4-chloro-2-nitrobenzene **1i**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3i** as a white solid (68 mg, 67% yield).

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(1) C. Suzuki, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2015, **17**, 1597-1600.

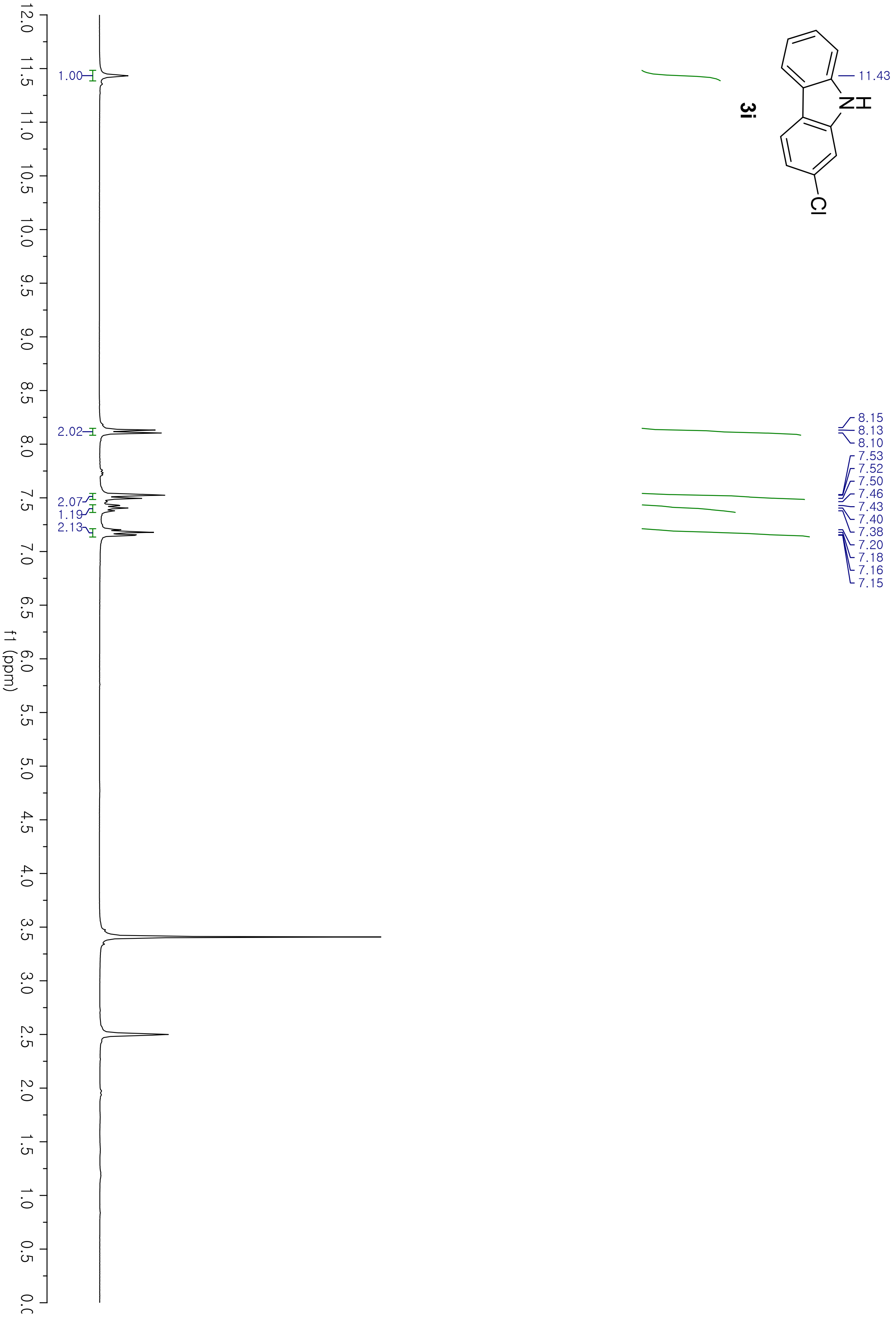
TLC (SiO_2): R_f = 0.38 (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 11.43 (s, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.14 (m, 2H).

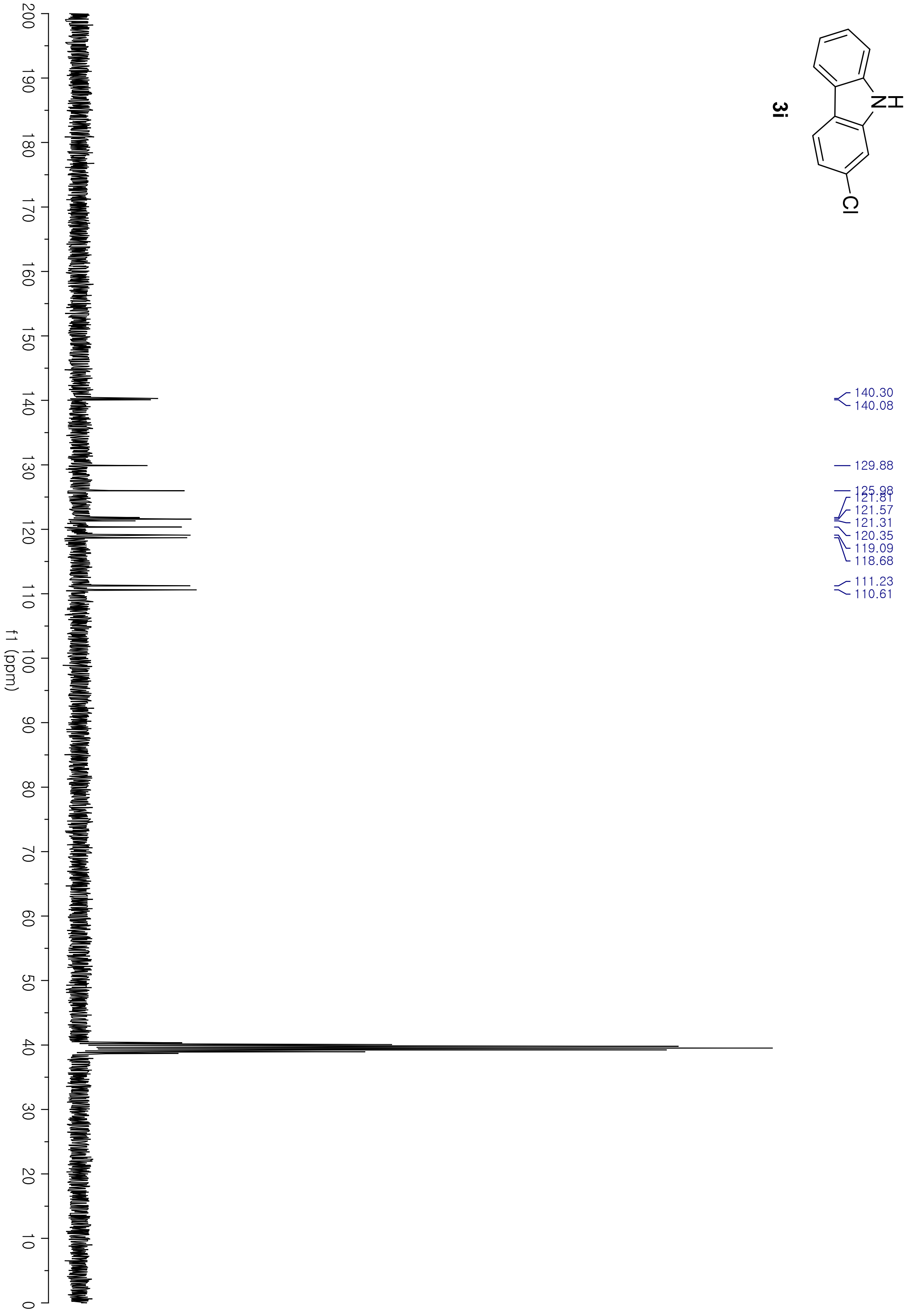
^{13}C NMR (75 MHz, DMSO) δ 140.30, 140.08, 129.88, 125.98, 121.81, 121.57, 121.31, 120.35, 119.09, 118.68, 111.23, 110.61.

FTIR (neat) υ 3393, 3128, 1636, 1406, 1321, 1178, 754 cm^{-1}.

LRMS *m*/*z* (EI): 200.7 (M^+-1), 165.7, 138.8, 100.3.

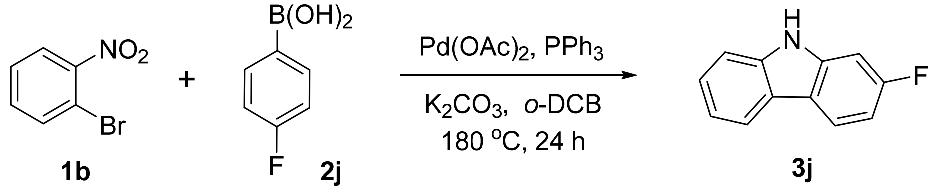

11.43
8.15
8.13
8.10
7.53
7.52
7.50
7.46
7.43
7.40
7.38
7.20
7.18
7.16
7.15
1.00
2.02
2.07
1.19
2.13
Cl
NH
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

3i


3i
NH
Cl
140.30
140.08
129.88
125.98
121.81
121.57
121.31
120.35
119.09
118.68
111.23
110.61
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

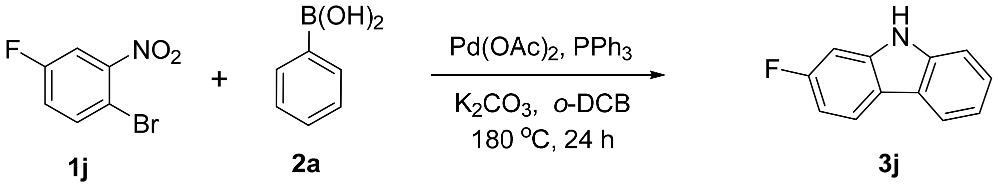
2-Fluoro-9*H*-carbazole (3j)

*From reaction of 1-bromo-2-nitrobenzene **1b** with (4-fluorophenyl)boronic acid **2j***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), (4-fluorophenyl)boronic acid **2j** (94 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3j** as a white solid (75 mg, 81% yield). ^1H and ^{13}C NMR data were consistent with literature values.[4]

*From reaction of 1-bromo-4-fluoro-2-nitrobenzene **1j** with phenylboronic acid **2a***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-4-fluoro-2-nitrobenzene **1j** (110 mg, 0.5 mmol, 100 mol%), phenylboronic acid **2a** (94 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-4-fluoro-2-nitrobenzene **1j**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3j** as a white solid (70 mg, 76% yield).

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(4) A. W. Freeman, M. Urvoy and M. E. Criswell, *J. Org. Chem.*, 2005, **70**, 5014-5019.

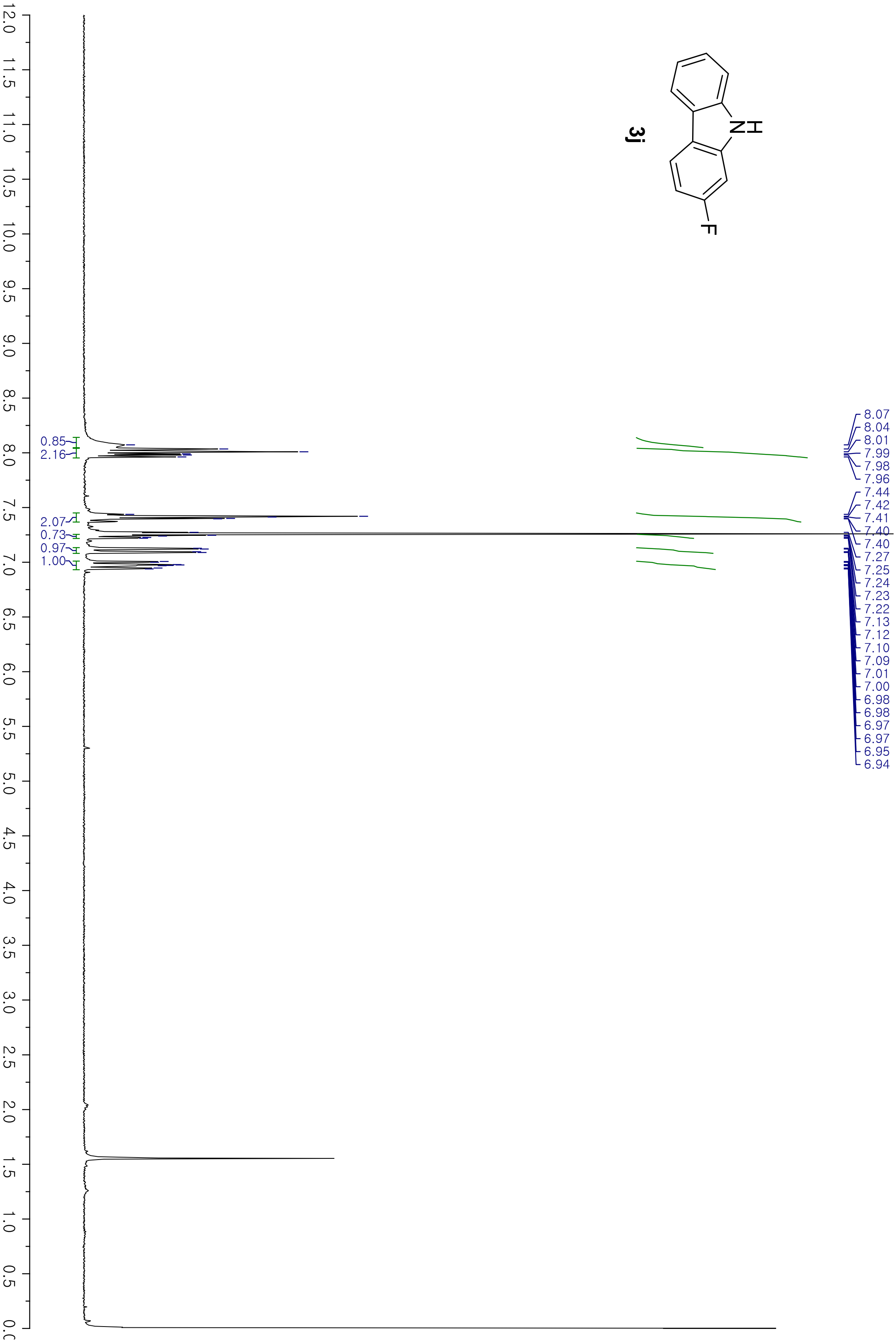
TLC (SiO_2): $R_f = 0.43$ (acetone:hexanes, 1:5).

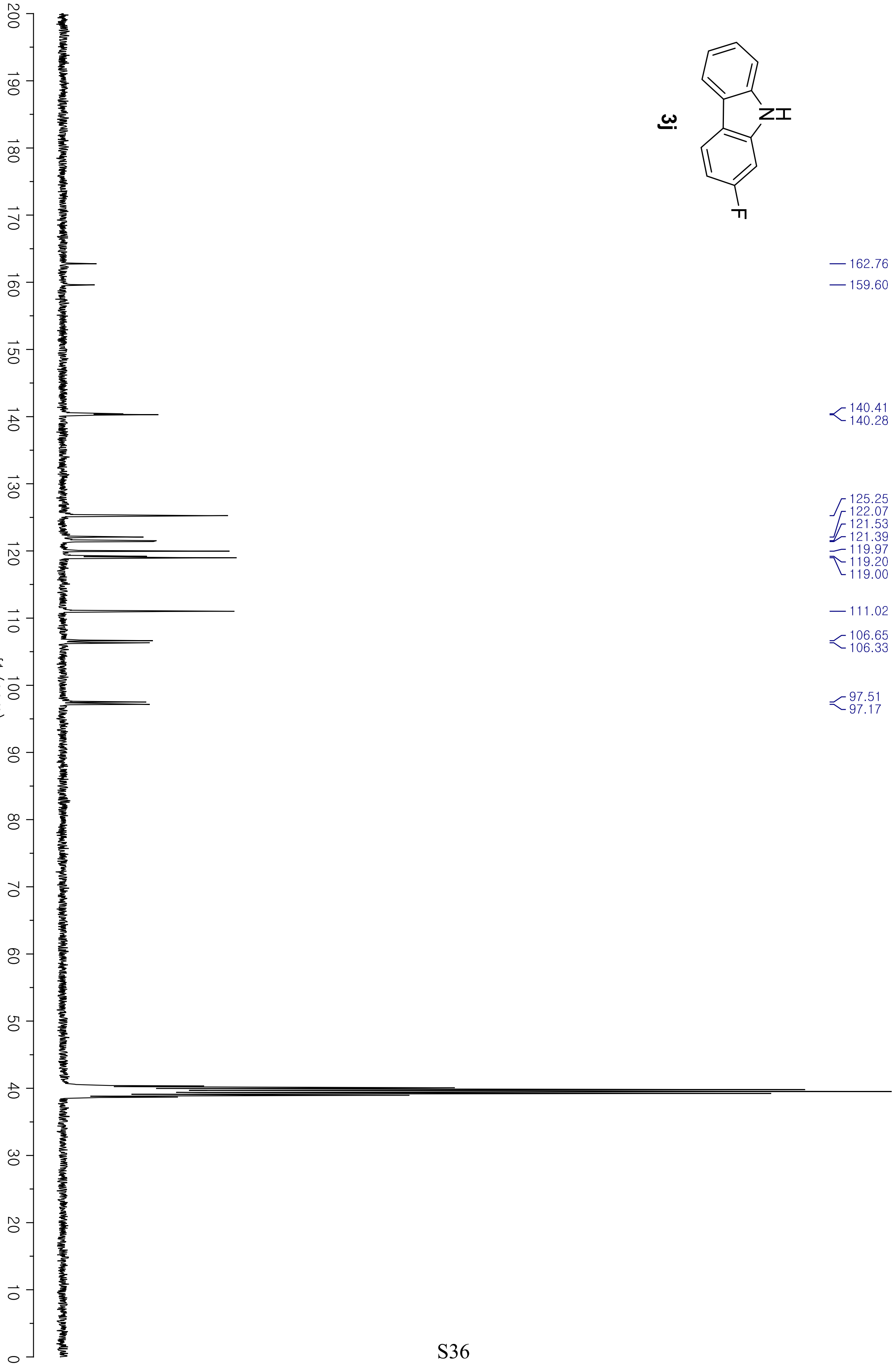
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.03 – 7.97 (m, 2H), 7.44 – 7.39 (m, 2H), 7.26 – 7.21 (m, 1H), 7.11 (dd, *J* = 9.6, 2.2 Hz, 1H), 7.02 – 6.93 (m, 1H).

^{13}C NMR (75 MHz, DMSO) δ 161.18 (d, J = 238.6 Hz), 140.41, 140.28, 125.25, 122.07, 121.46 (d, J = 10.6 Hz), 119.97, 119.20, 119.00, 111.02, 106.49 (d, J = 24.1 Hz), 97.34 (d, J = 26.1 Hz).

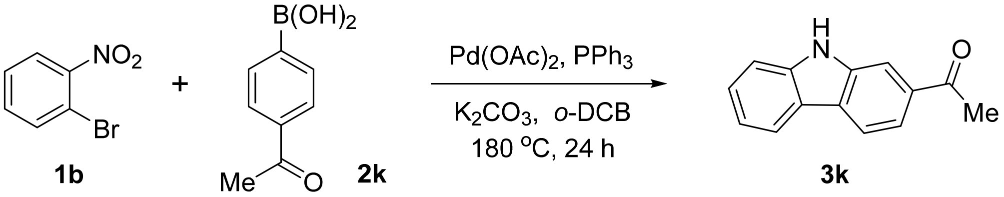
FTIR (neat) υ 3411, 2919, 1362, 1263 cm^{-1}.

LRMS *m*/*z* (EI): 186.2 (M^++1), 185.2, 184.3, 157.3, 92.8.


3j
F
N
H
8.07
8.04
8.01
7.99
7.98
7.96
7.44
7.42
7.41
7.40
7.40
7.27
7.25
7.24
7.23
7.22
7.13
7.12
7.10
7.09
7.01
7.00
6.98
6.98
6.97
6.97
6.95
6.94
0.85
2.16
2.07
0.73
0.97
1.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3j
H
N
F
162.76
159.60
140.41
140.28
125.25
122.07
121.53
121.39
119.97
119.20
119.00
111.02
106.65
106.33
97.51
97.17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1-(*9H*-Carbazole-2-yl)ethan-1-one (3k)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), (4-acetylphenyl)boronic acid **2k** (107 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 7% acetone in hexanes as eluant to give **3k** as a white solid (41 mg, 43% yield). ^1H and ^{13}C NMR data were consistent with literature values.[9]

TLC (SiO_2): $R_f = 0.28$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 11.56 (s, 1H), 8.22 (t, *J* = 8.3 Hz, 2H), 8.08 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 2.68 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 197.86, 141.29, 139.15, 134.10, 127.03, 126.13, 121.59, 121.15, 120.06, 119.12, 118.66, 111.39, 111.35, 26.98.

FTIR (neat) υ 3332, 1738, 1366, 1216, 889, 779 cm^{-1}.

LRMS *m/z* (EI) : 210.2 (M^++1), 209.3, 194.3, 166.3, 139.3.

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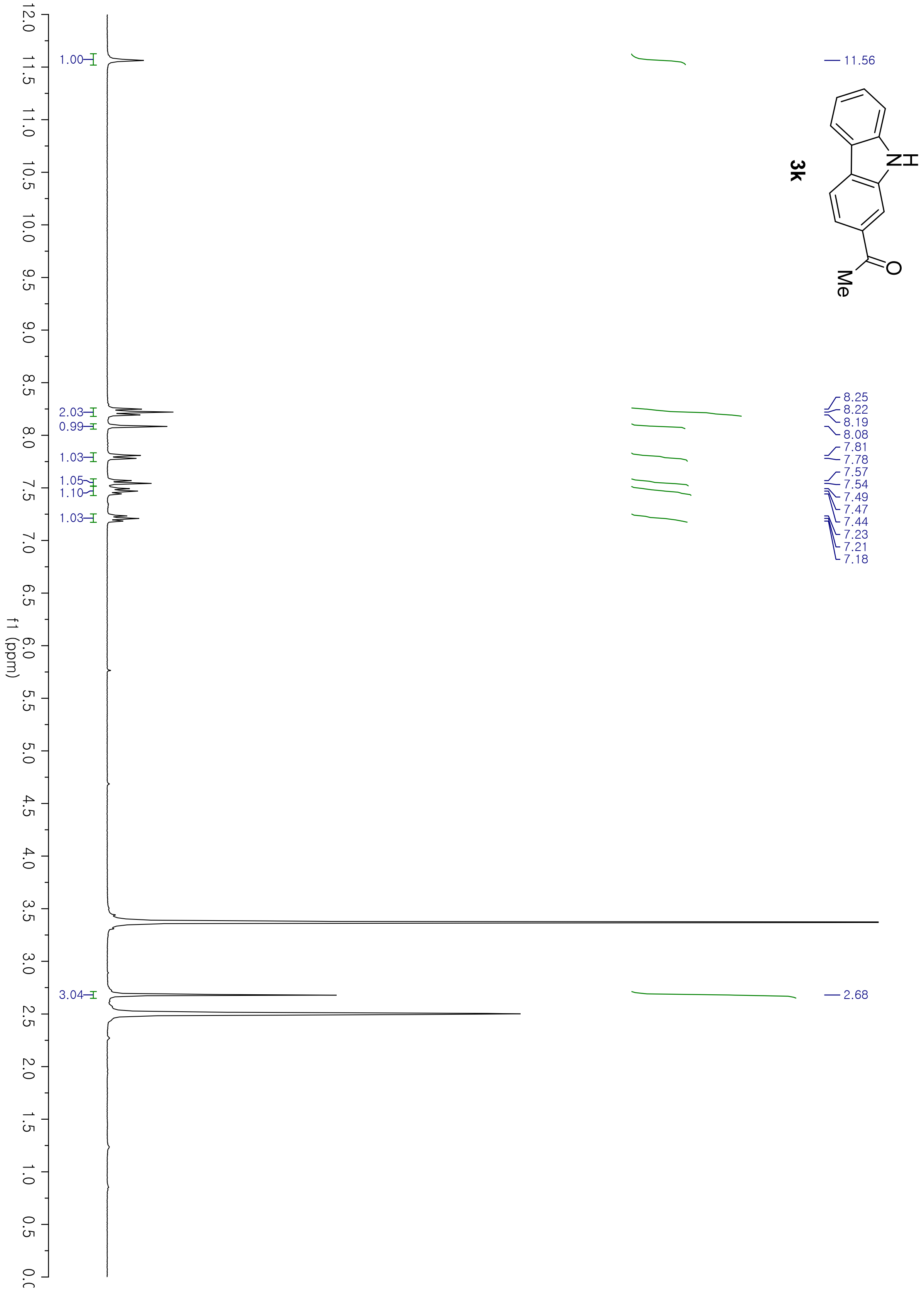
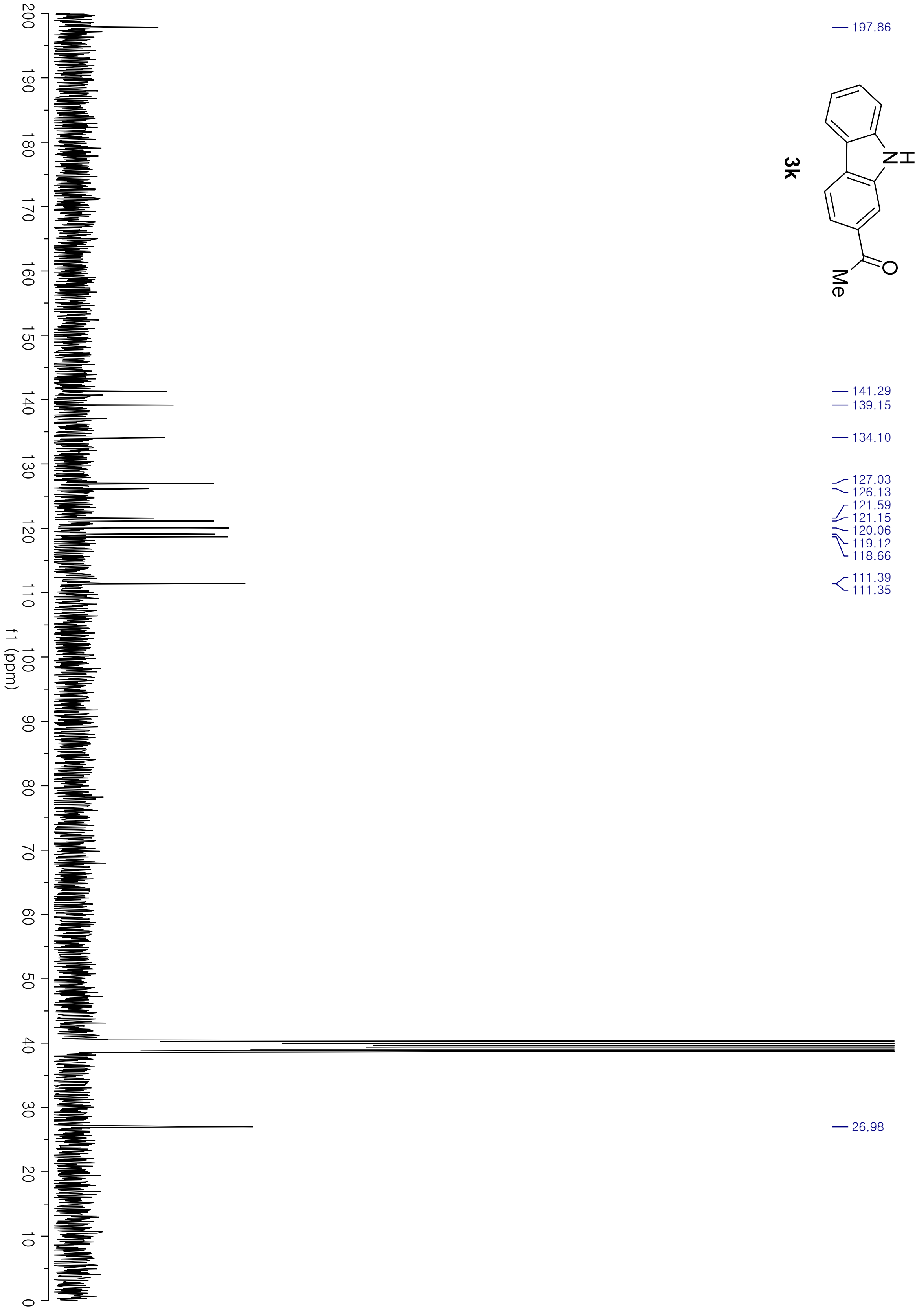
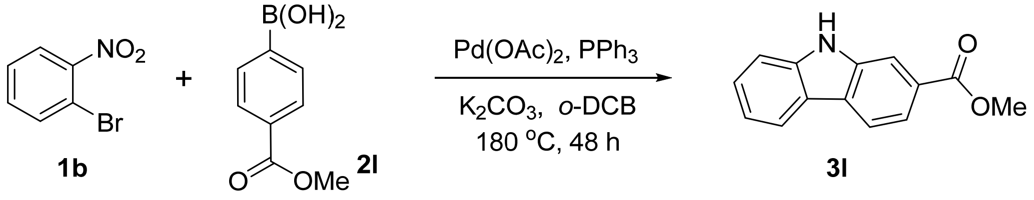
[9] T. M. Gogsig, J. Kleimark, S. O. N. Lill, S. Korsager, A. T. Lindhardt, P.-O. Norrby and T. Skrydstrup, *J. Am. Chem. Soc.*, 2012, **134**, 443-452.


3k
NH
O
Me
11.56
8.25
8.22
8.19
8.08
7.81
7.78
7.57
7.54
7.49
7.47
7.44
7.23
7.21
7.18
2.68
1.00
2.03
0.99
1.03
1.05
1.10
1.03
3.04
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3k
Me
O
N
H
197.86
141.29
139.15
134.10
127.03
126.13
121.59
121.15
120.06
119.12
118.66
111.39
111.35
26.98
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Methyl-9*H*-carbazole-2-carboxylate (3l)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), (4-(methoxycarbonyl)phenyl)boronic acid **2l** (94 mg, 0.65 mmol, 130 mol%), Pd(OAc) (5.6 mg, 0.025 mmol, 5 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 7% acetone in hexanes as eluant to give **3l** as a white solid (69 mg, 61% yield). ^1H and ^{13}C NMR data were consistent with literature values.[1]

TLC (SiO_2): $R_f = 0.33$ (acetone:hexanes, 1:5).

^1H NMR (300 MHz, DMSO) δ 11.58 (s, 1H), 8.21 (t, *J* = 8.8 Hz, 2H), 8.12 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 166.95, 141.10, 139.05, 127.06, 126.30, 126.20, 121.60, 121.10, 120.14, 119.25, 119.16, 112.35, 111.42, 52.05.

FTIR (neat) : υ 3337, 2937, 1738, 1365, 1216, 888 cm^{-1}.

LRMS *m*/*z* (EI): 226.2 (M^++1), 225.2, 194.2, 166.2, 139.2, 97.2, 83.2, 69.7.

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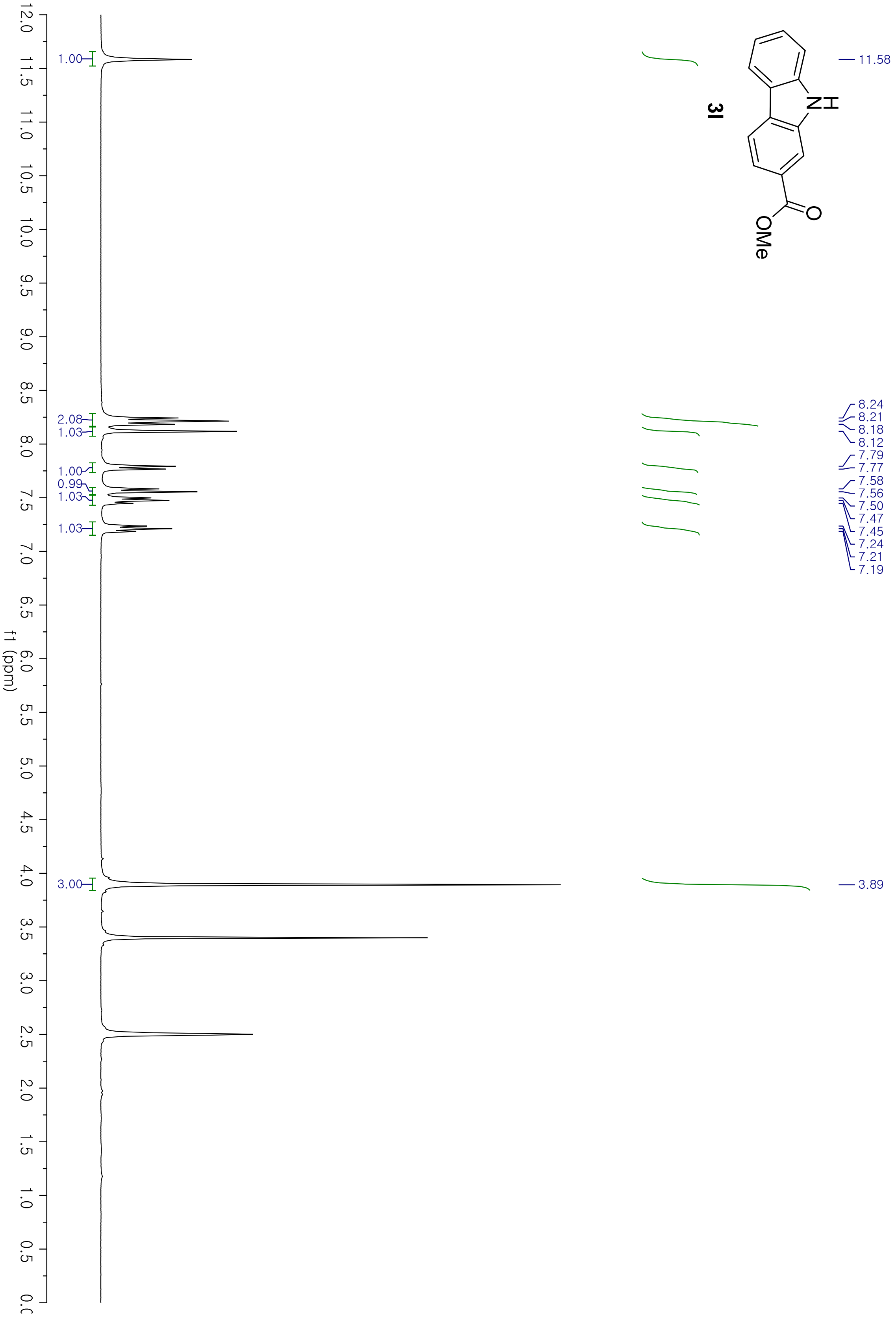
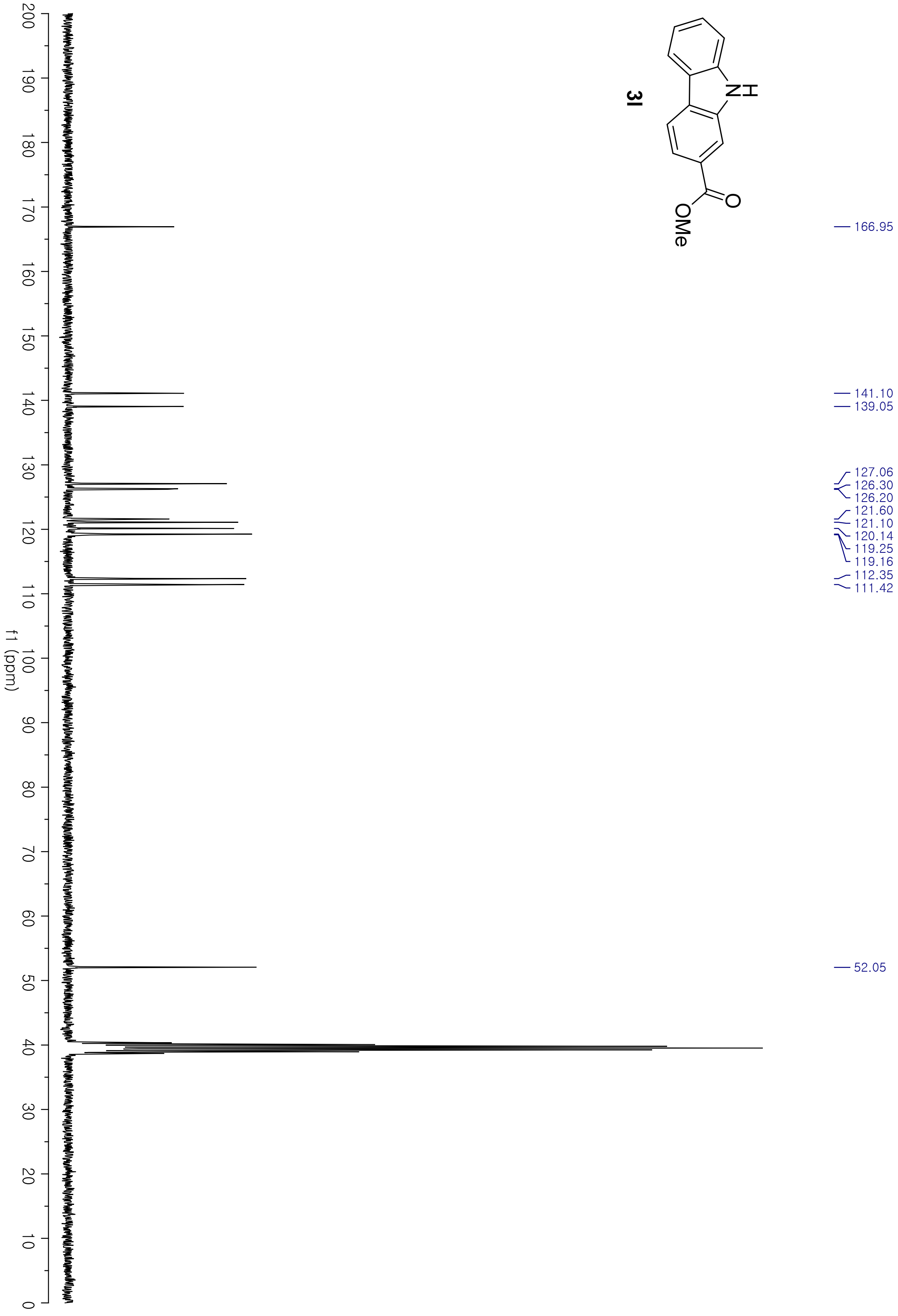
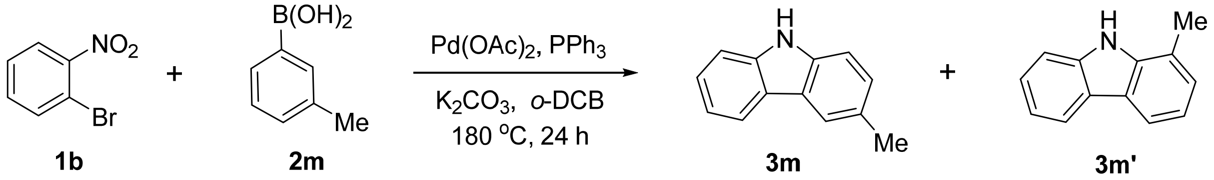
(1) C. Suzuki, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2015, **17**, 1597-1600.


3l
N
H
O
OMe
11.58
8.24
8.21
8.18
8.12
7.79
7.77
7.58
7.56
7.50
7.47
7.45
7.24
7.21
7.19
3.89
1.00
2.08
1.03
1.00
0.99
1.03
1.03
3.00
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


3l
OMe
O
N
H
166.95
141.10
139.05
127.06
126.30
126.20
121.60
121.10
120.14
119.25
119.16
112.35
111.42
52.05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3-Methyl-*9H*-carbazole (3m) and 1-Methyl-*9H*-carbazole (3m')

*From reaction of 1-bromo-2-nitrobenzene **1b** with m-tolylboronic acid **2m***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), *m*-tolylboronic acid **2m** (90 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.001 mmol, 5 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give inseparable mixture of **3m** and **3m'** as a white solid (80 mg, 88% yield, **3m:3m'**=1:1.2 (determined by ^{1}H NMR and GC-Mass spectrometer)). ^{1}H and ^{13}C NMR data were consistent with literature values.[1,10]

3-Methyl-*9H*-carbazole (3m)

TLC (SiO_2): $R_f = 0.44$ (Acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 11.10 (s, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.89 (s, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 139.98, 137.96, 127.08, 126.82, 125.29, 122.54, 122.22, 120.02, 119.90, 118.23, 110.85, 110.63, 21.10.

FTIR (neat) : υ 3442, 1701, 1371, 1207 cm^{-1}.

LRMS *m/z* (EI): 182.2 (M$^+$+1), 181.2, 180.3, 152.3, 90.2, 77.2, 63.2, 51.1.

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(1) C. Suzuki, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2015, **17**, 1597-1600.
(10) S. Chakrabarty, I. Chatterjee, L. Tebben and A. Studer, *Angew. Chem. Int. Ed.*, 2013, **52**, 2968-2971.

1-Methyl-*9H*-carbazole (3m')

TLC (SiO_2): $R_f = 0.44$ (Acetone:hexanes, 1:5).

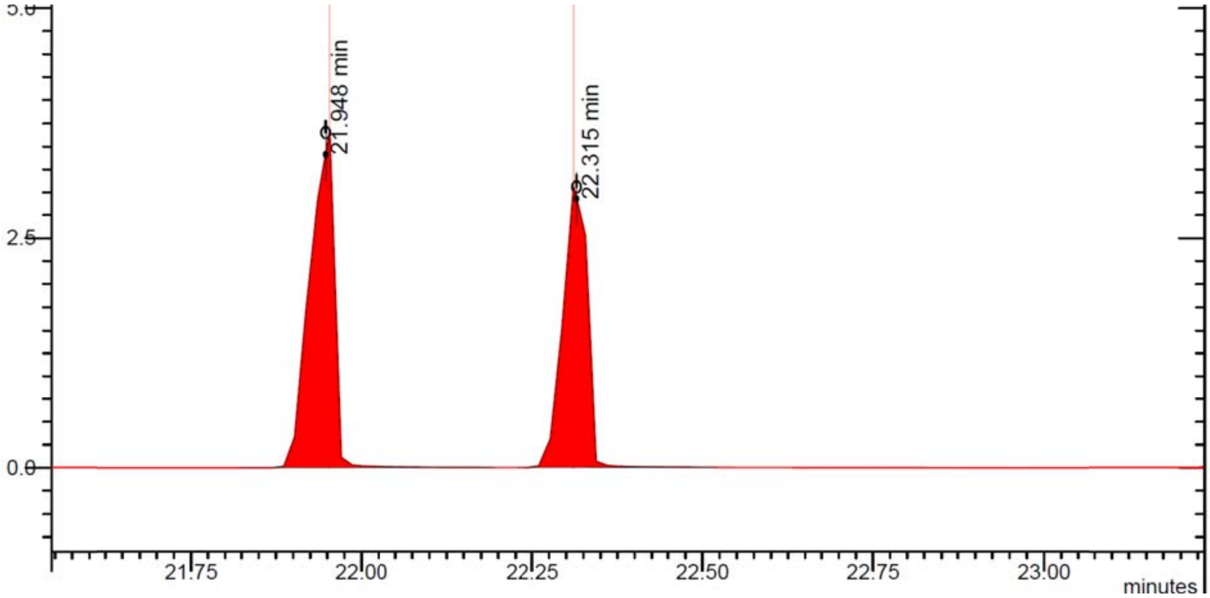
^{1}H NMR (300 MHz, DMSO) δ 11.16 (s, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.20 – 7.10 (m, 2H), 7.10 – 7.02 (m, 1H), 2.55 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 139.79, 139.04, 125.94, 125.29, 122.79, 121.95, 120.17, 120.05, 118.62, 118.46, 117.60, 111.03, 17.00.

FTIR (neat) : υ 3442, 1701, 1371, 1207 cm^{-1}.

LRMS *m/z* (EI): 181.2 (M^+), 180.2, 152.3, 135.2, 77.2, 63.2, 51.1

GC: (Varian 450-GC, SPB™-680 (30 m x 0.25 mm x 0.25 μm), T_0 : 60 °C (hold 4 min), T_1 : Ramp, 250 °C at 10 °C/min, Carrier: He (1.0 mL/min), Total time 60 min), $t_{3m'}$ = 21.95 min, t_{3m} = 22.32 min, Ratio (**3m:3m'** = 1:1.2).



	Retention Time	Area	% of Total	Signal/Noise	Scan Description
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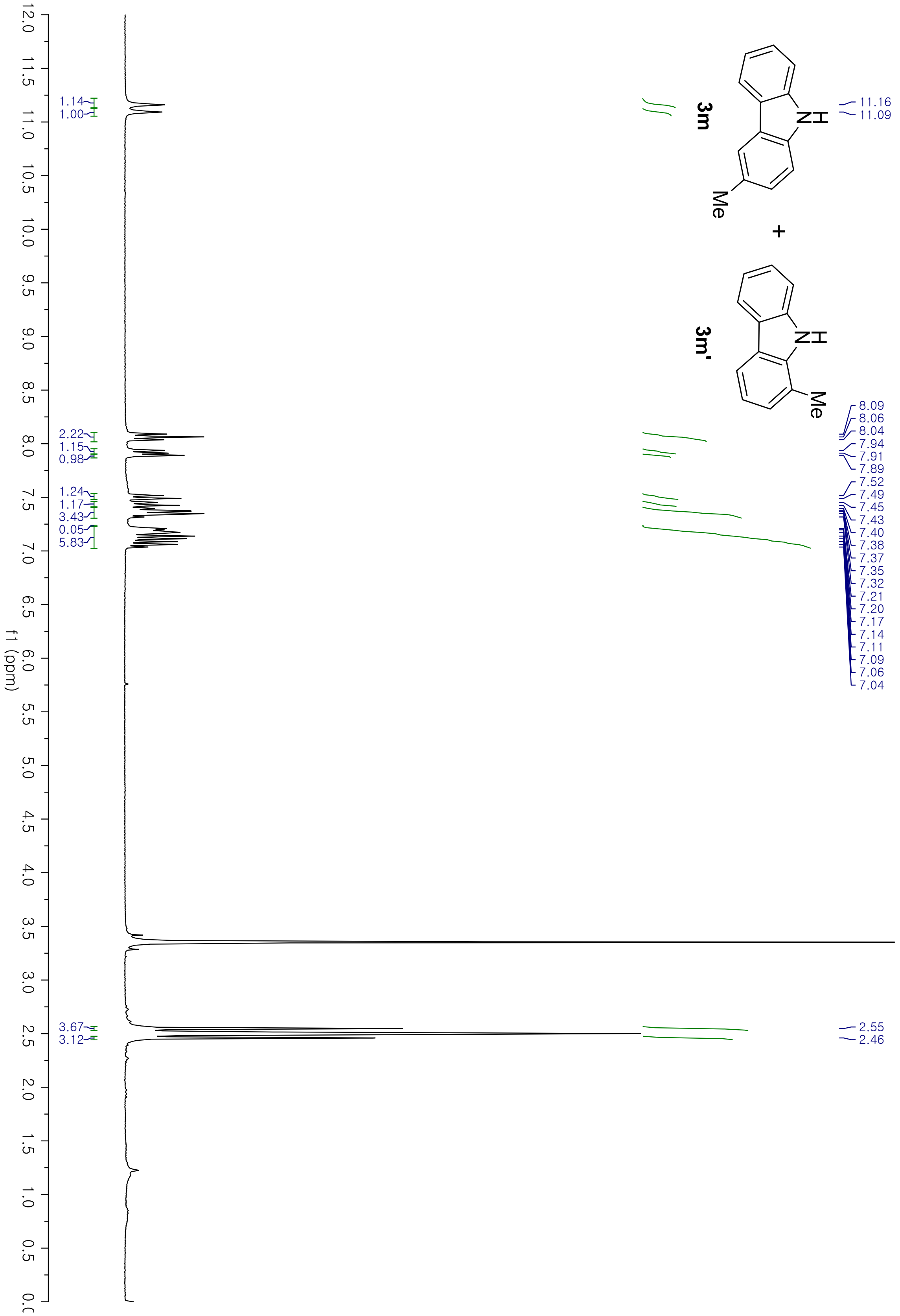
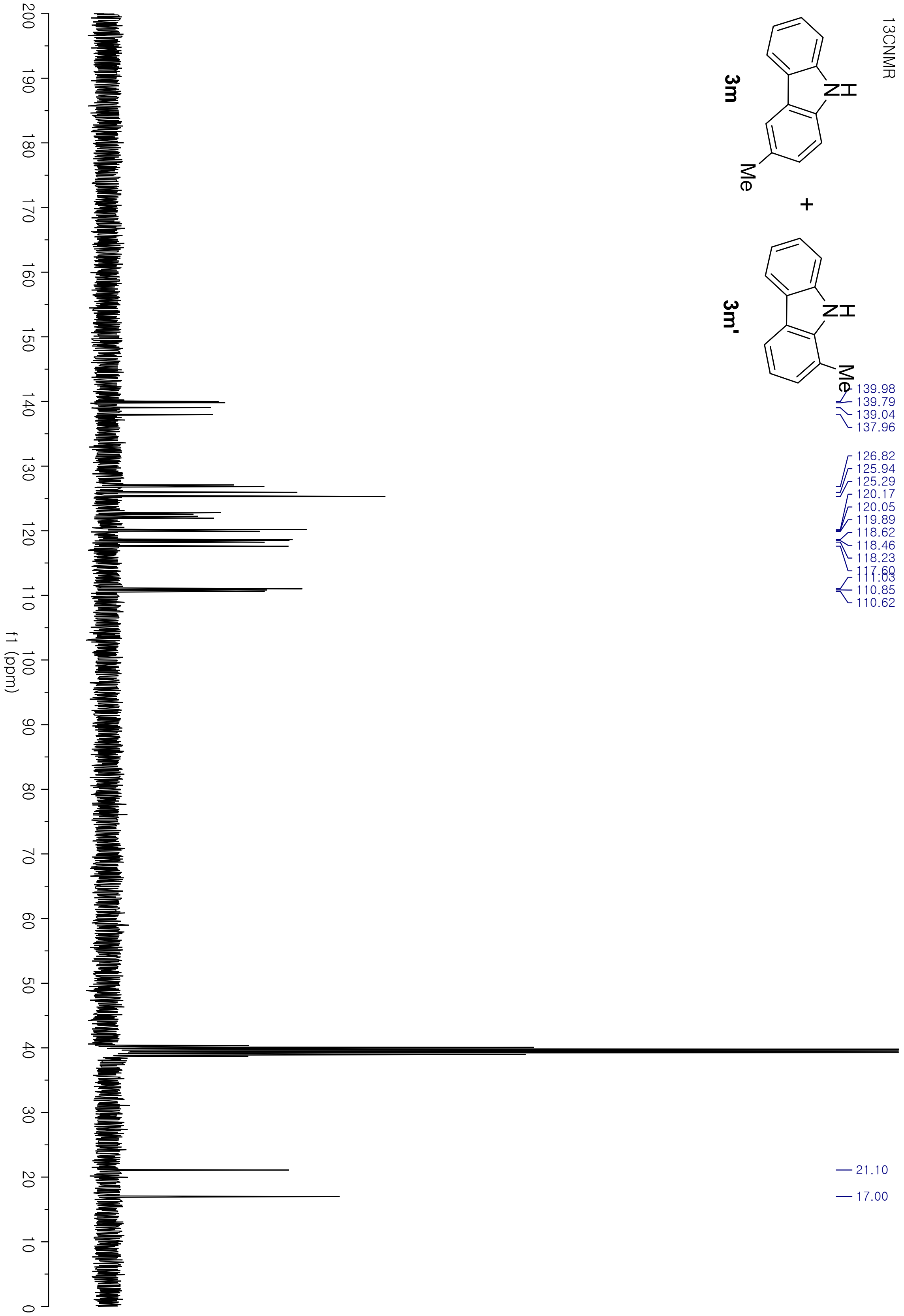
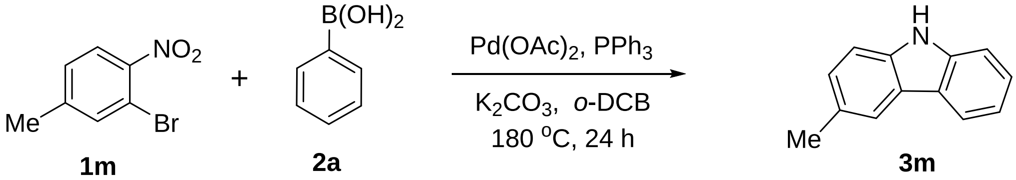
2.	22.315	7.512e+6	45.668	17526	Merged

3m
3m'
Me
Me
N
H
+
11.16
11.09
8.09
8.06
8.04
7.94
7.91
7.89
7.52
7.49
7.45
7.43
7.40
7.38
7.37
7.35
7.32
7.21
7.20
7.17
7.14
7.11
7.09
7.06
7.04
2.55
2.46
1.14
1.00
2.22
1.15
0.98
1.24
1.17
3.43
0.05
5.83
3.67
3.12
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


13CNMR
3m
3m'
+
Me
N
H
139.98
139.79
139.04
137.96
126.82
125.94
125.29
120.17
120.05
119.89
118.62
118.46
118.23
117.60
111.03
110.85
110.62
21.10
17.00
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3-Methyl-9*H*-carbazole (3m)

*From reaction of 2-bromo-4-methyl-1-nitrobenzene **1m** with phenylboronic acid **2a***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 2-bromo-4-methyl-1-nitrobenzene **1m** (100 mg, 0.5 mmol, 100 mol%), phenylboronic acid **2a** (94 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 2-bromo-4-methyl-1-nitrobenzene **1m**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3m** as a brown solid (70 mg, 77% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[1]

TLC (SiO_2): $R_f = 0.44$ (Acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 11.10 (s, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.89 (s, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 139.98, 137.96, 127.08, 126.82, 125.29, 122.54, 122.22, 120.02, 119.90, 118.23, 110.85, 110.63, 21.10.

FTIR (neat) : υ 3442, 1701, 1371, 1207 cm^{-1}.

LRMS *m*/*z* (EI): 182.2 (M$^+$+1), 181.2, 180.3, 152.3, 90.2, 77.2, 63.2, 51.1.

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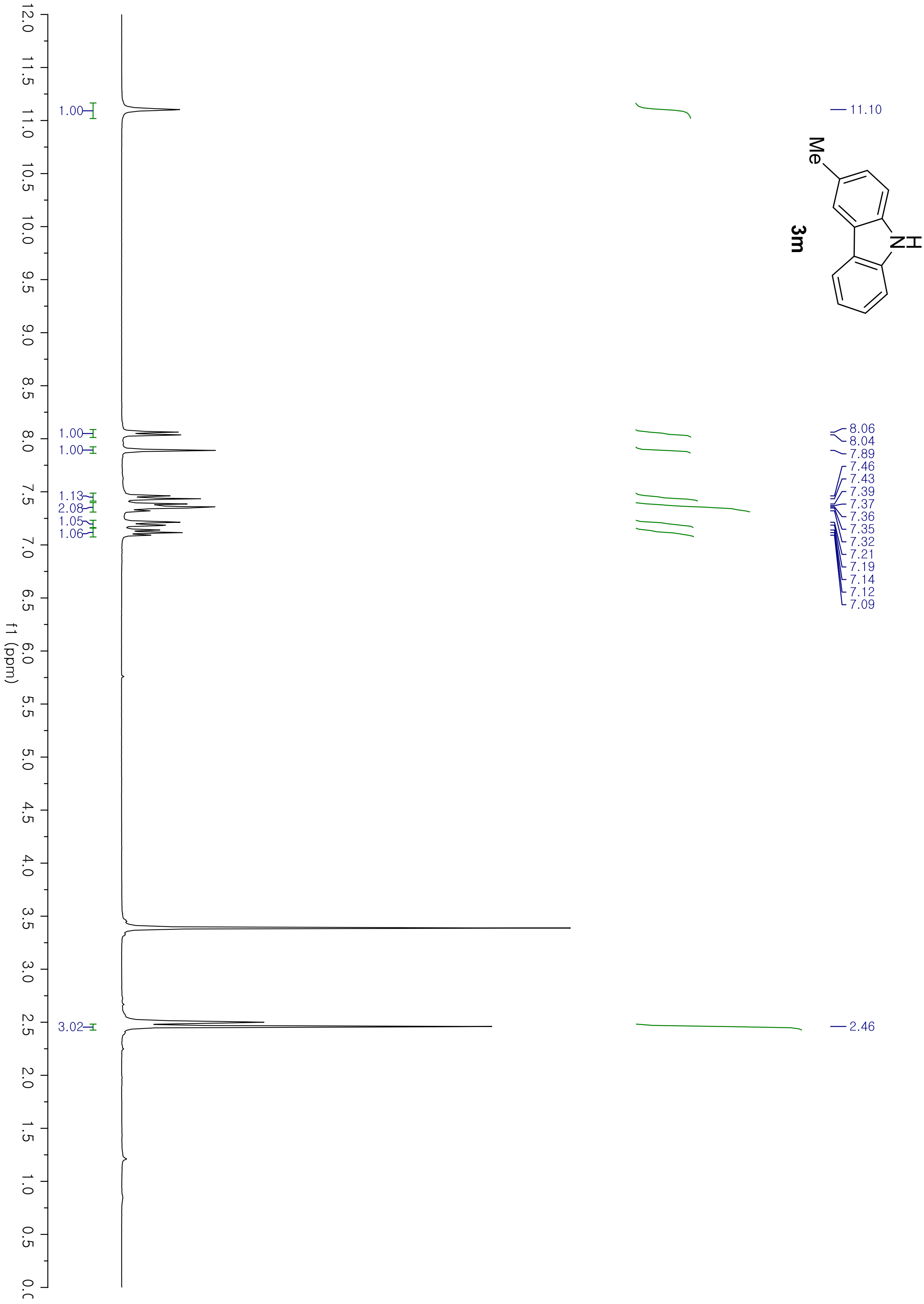
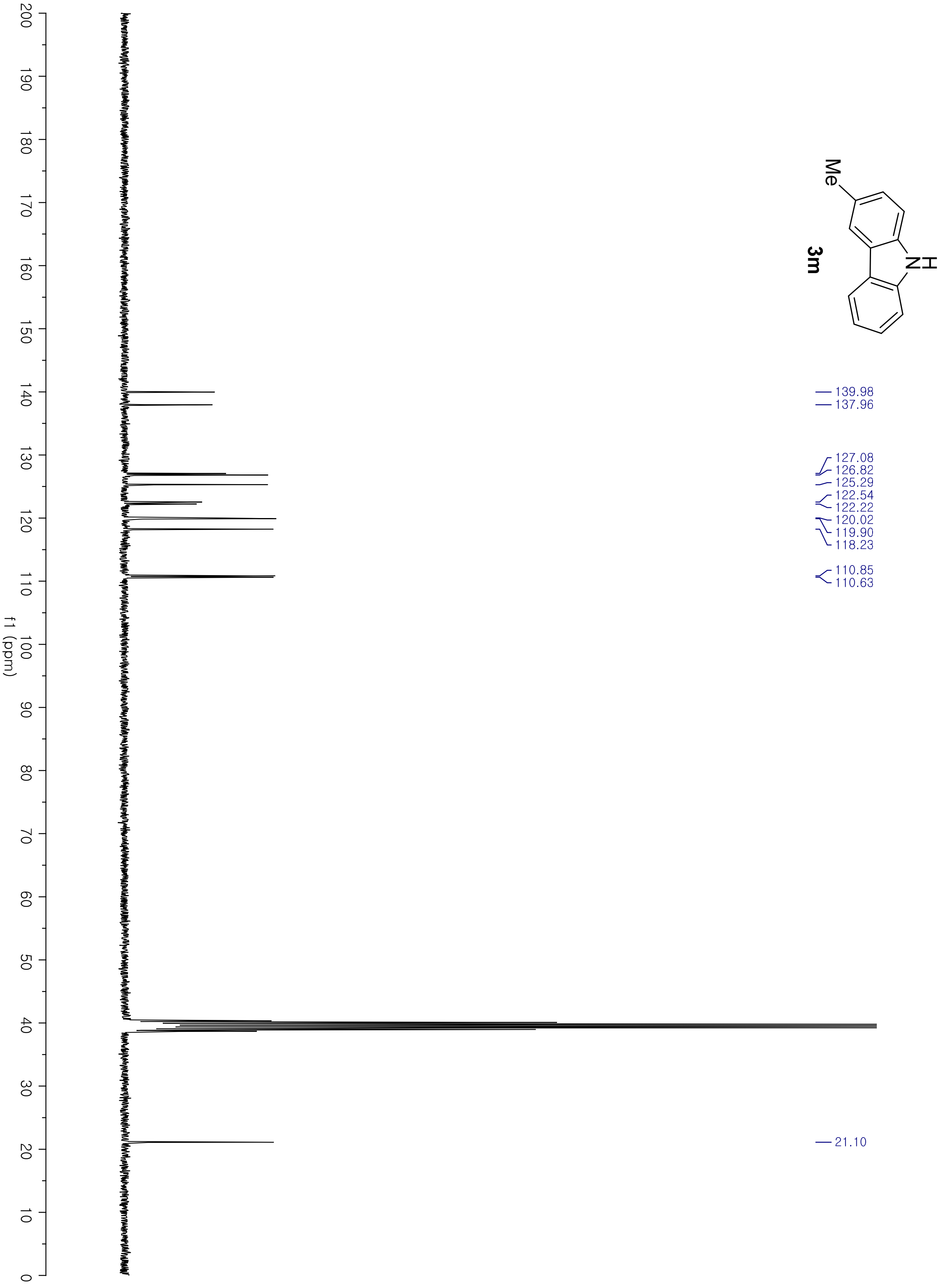
(1) C. Suzuki, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2015, **17**, 1597-1600.



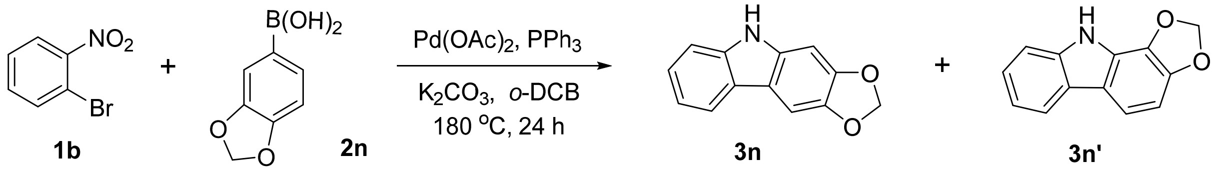
3m
Me
H
N
11.10
8.06
8.04
7.89
7.46
7.43
7.39
7.37
7.36
7.35
7.32
7.21
7.19
7.14
7.12
7.09
2.46
1.00
1.00
1.00
1.13
2.08
1.05
1.06
3.02
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Me
N
H
— 139.98
— 137.96
127.08
126.82
125.29
122.54
122.22
120.02
119.90
118.23
110.85
110.63
— 21.10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3m

5*H*-[1,3]dioxolo[4,5-*b*]carbazole (3n) and 5*H*-[1,3]dioxolo[4,5-*a*]carbazole (3n')

*From reaction of 1-bromo-2-nitrobenzene **1b** with benzo[d][1,3]dioxol-5-ylboronic acid **2n***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), benzo[d][1,3]dioxol-5-ylboronic acid **2n** (108 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.001 mmol, 5 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give mixture of **3n** and **3n'** as a white solid (90 mg, 87% yield, **3n:3n'**=5.9:1 (determined by ^{1}H NMR and GC-Mass spectrometer)). ^{1}H and ^{13}C NMR data were consistent with literature values.[11]

5*H*-[1,3]dioxolo[4,5-*b*]carbazole (3n)

TLC (SiO_2): $R_f = 0.42$ (Acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 11.08 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.62 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.03 (s, 2H).

^{13}C NMR (75 MHz, DMSO) δ 146.72, 141.52, 139.56, 135.14, 123.76, 122.83, 119.26, 118.20, 115.40, 110.79, 100.69, 99.36, 92.16.

FTIR (neat) υ 3397, 1710, 1266, 1043, 936, 748 cm^{-1}.

LRMS *m*/*z* (EI): 212.0 (M^++1), 211.2.

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[11] S. Chakraborty, G. Chattopadhyay and C. Saha, *J. Heterocycl. Chem.*, 2013, **50**, 91-98.

5*H*-[1,3]dioxolo[4,5-*a*]carbazole (3n')

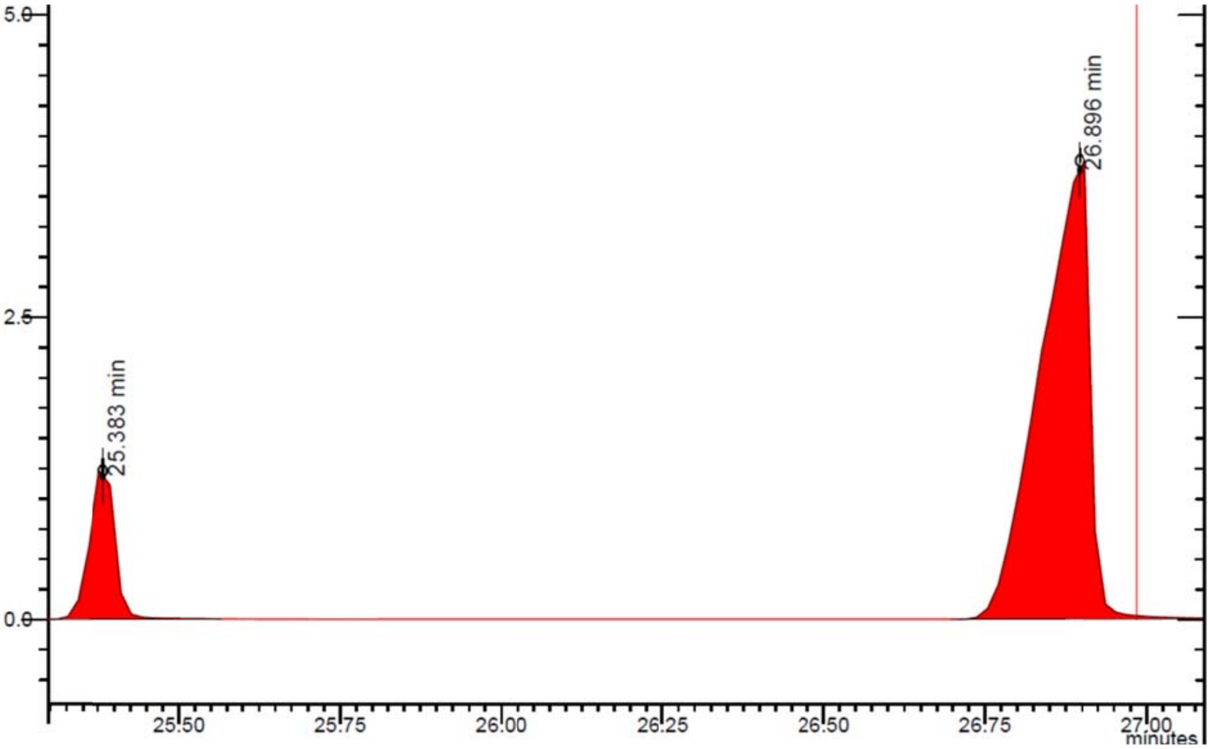
TLC (SiO_2): R_f = 0.42 (Acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 11.35 (s, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 15.0 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.16 – 7.06 (m, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.13 (s, 2H).

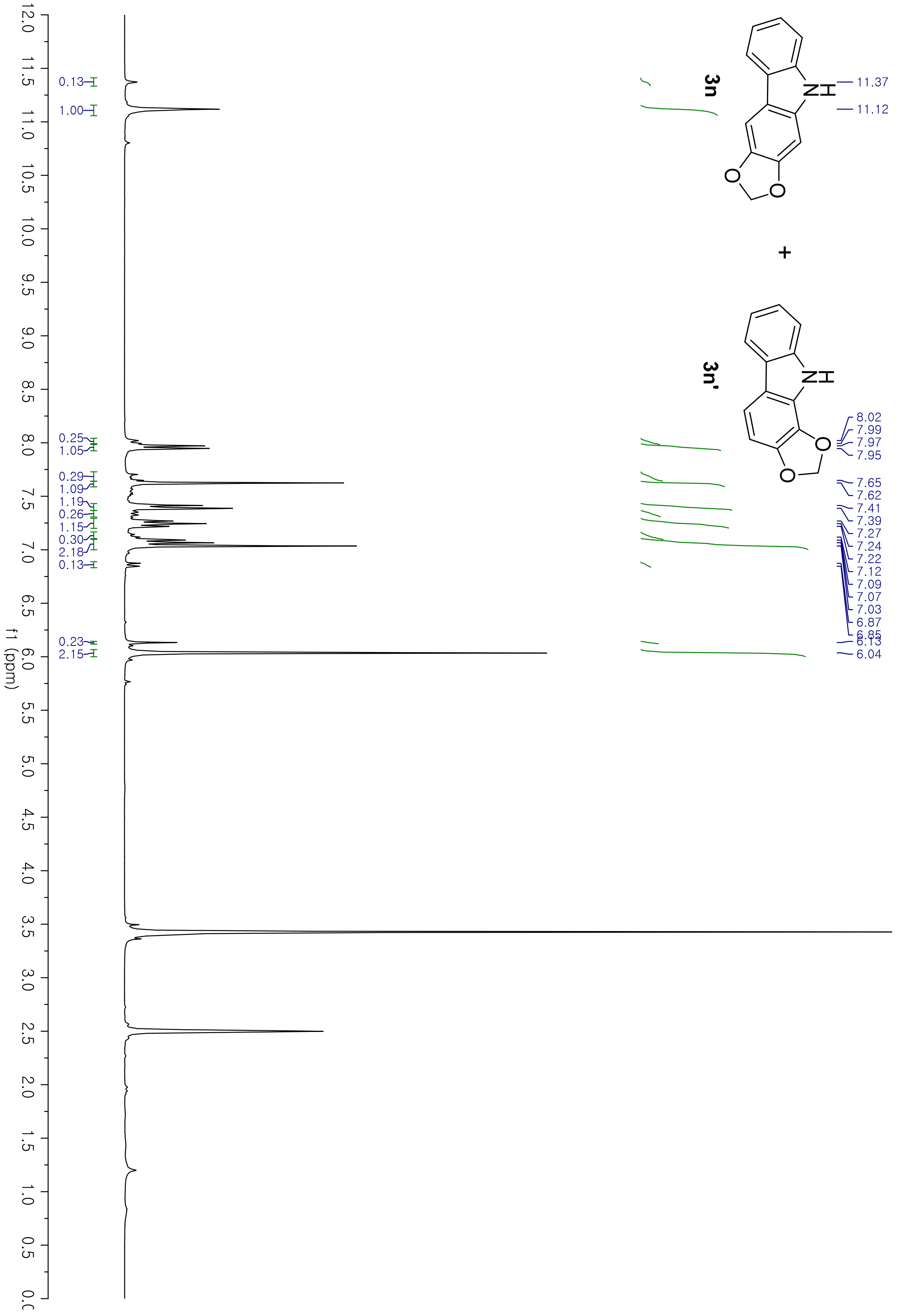
FTIR (neat) υ 3397, 1710, 1266, 1043, 936, 748 cm^{-1}.

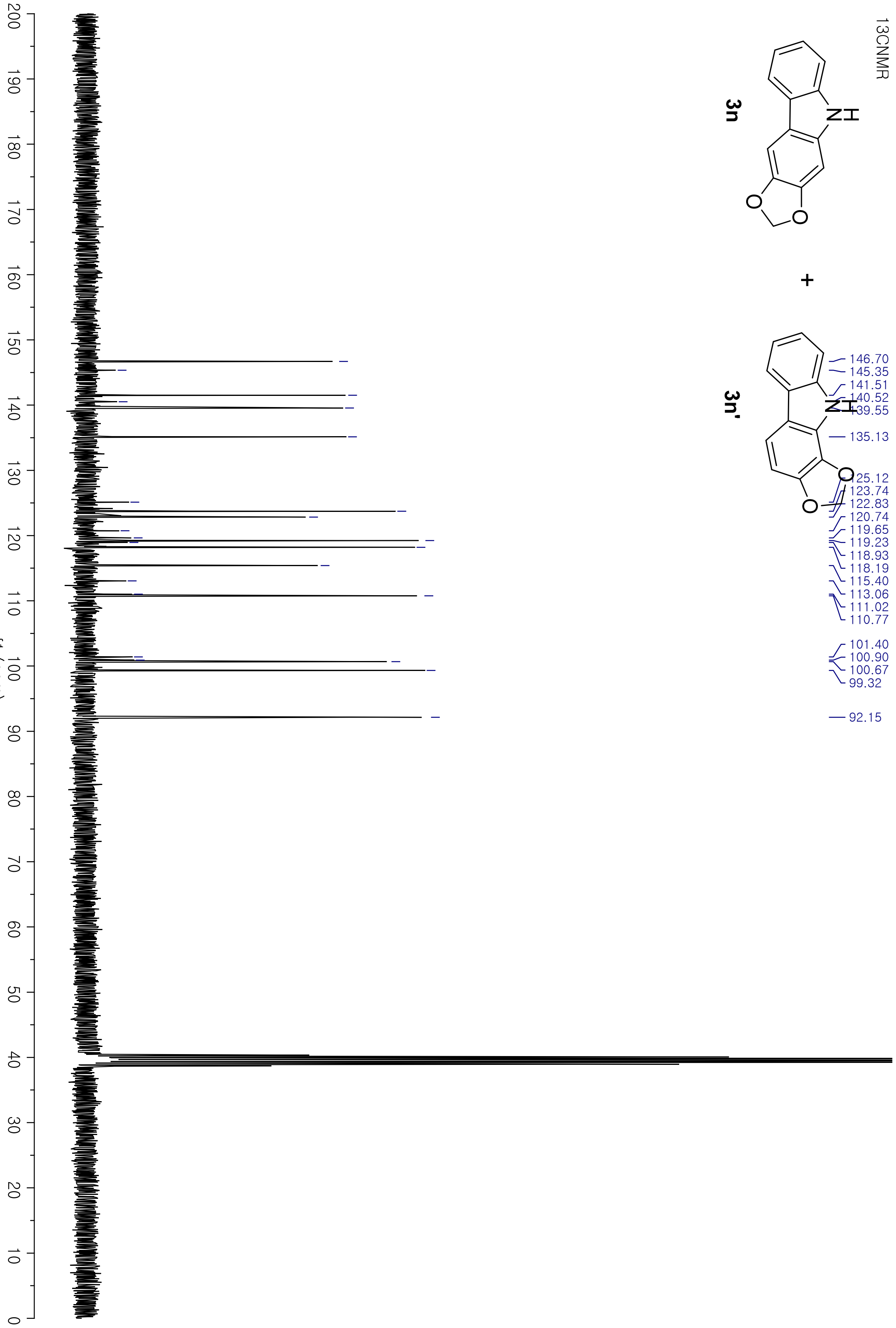
LRMS *m*/*z* (EI): 211.9 (M^++1), 211.1, 154.2.

GC: (Varian 450-GC, SPB^{TM}-680 (30 m x 0.25 mm x 0.25 μm), T_0 : 60 °C (hold 4 min), T_1 : Ramp, 250 °C at 10 °C/min, Carrier: He (1.0 mL/min), Total time 60 min), $t_{\mathbf{3n'}}$ = 25.38 min, $t_{\mathbf{3n}}$ = 26.90 min, Ratio (**3n:3n'** = 5.9:1).



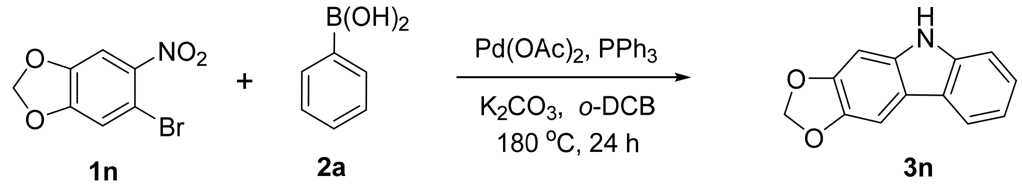
	Retention Time	Area	% of Total	Signal/Noise	Scan Description
1.	25.383	3.432e+6	14.564	11908	Merged
2.	26.896	2.013e+7	85.436	32671	Merged


3n
+
3n'
NH
O
11.37
11.12
8.02
7.99
7.97
7.95
7.65
7.62
7.41
7.39
7.27
7.24
7.22
7.12
7.09
7.07
7.03
6.87
6.85
6.13
6.04
0.13
1.00
0.25
1.05
0.29
1.09
1.19
0.26
1.15
0.30
2.18
0.13
0.23
2.15
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


13CNMR
3n
+
3n'
146.70
145.35
141.51
140.52
139.55
135.13
125.12
123.74
122.83
120.74
119.65
119.23
118.93
118.19
115.40
113.06
111.02
110.77
101.40
100.90
100.67
99.32
92.15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5*H*-[1,3]dioxolo[4,5-*b*]carbazole (3n)

*From reaction of 5-bromo-6-nitrobenzo[d][1,3]dioxole **1n** with phenylboronic acid **2a***



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 5-bromo-6-nitrobenzo[d][1,3]dioxole **1n** (100 mg, 0.5 mmol, 100 mol%), phenylboronic acid **2a** (94 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 5-bromo-6-nitrobenzo[d][1,3]dioxole **1n**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3n** as a white solid (80 mg, 76% yield). ^1H and ^{13}C NMR data were consistent with literature values.[11]

TLC (SiO_2): $R_f = 0.42$ (Acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 11.08 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.62 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.03 (s, 2H).

^{13}C NMR (75 MHz, DMSO) δ 146.72, 141.52, 139.56, 135.14, 123.76, 122.83, 119.26, 118.20, 115.40, 110.79, 100.69, 99.36, 92.16.

FTIR (neat) υ 3390, 1715, 1324, 1049, 982, 739 cm^{-1}.

LRMS *m*/*z* (EI): 212.0 (M^++1), 211.1

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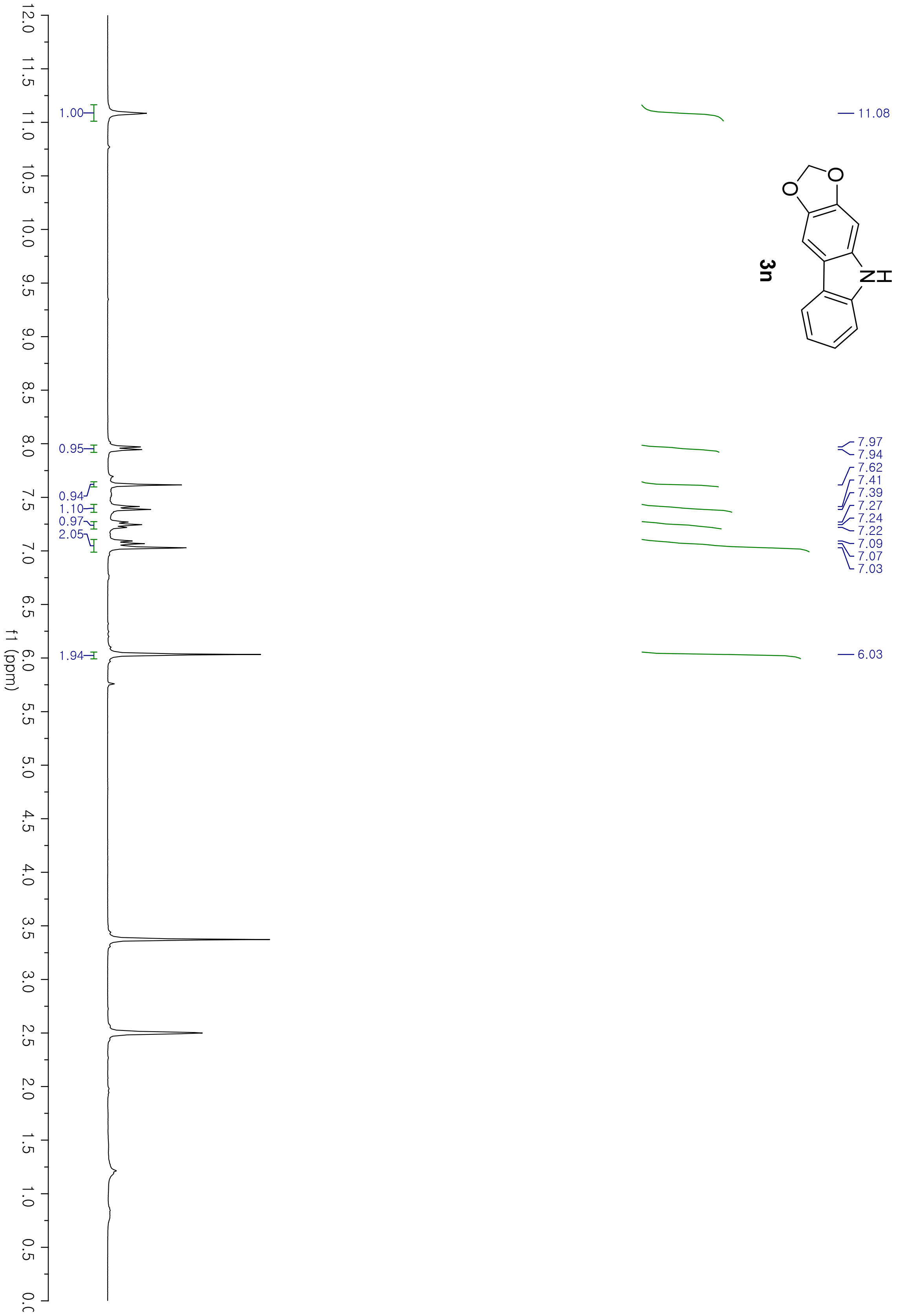
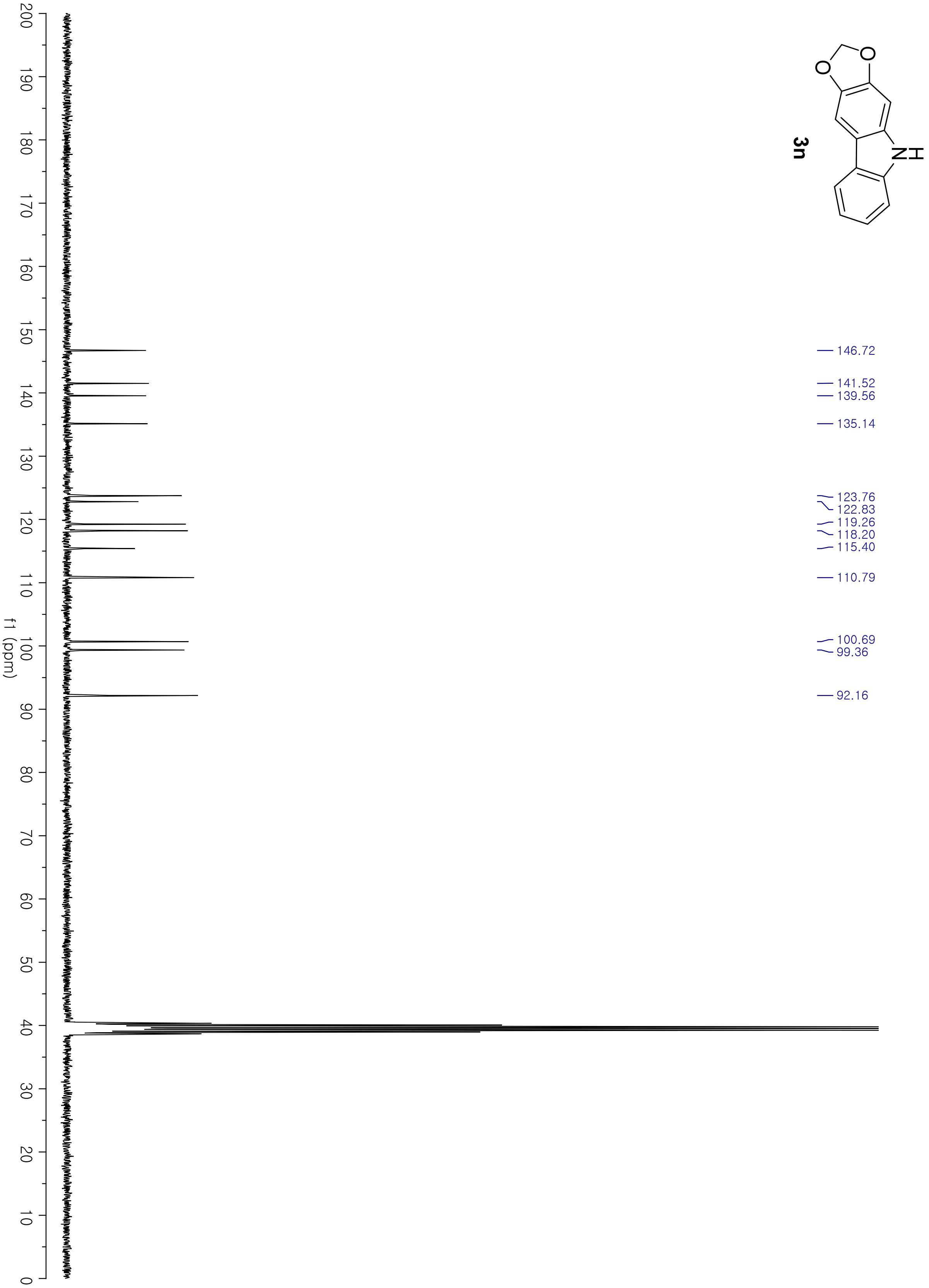
[11] S. Chakraborty, G. Chattopadhyay and C. Saha, *J. Heterocycl. Chem.*, 2013, **50**, 91-98.

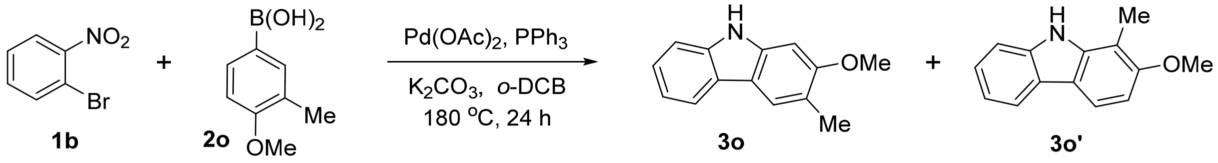

3n
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.00
0.95
0.94
1.10
0.97
2.05
1.94
11.08
7.97
7.94
7.62
7.41
7.39
7.27
7.24
7.22
7.09
7.07
7.03
6.03
O
O
N
H



3n

146.72
141.52
139.56
135.14
123.76
122.83
119.26
118.20
115.40
110.79
100.69
99.36
92.16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
N
H

3-Methoxy-2-methyl-*9H*carbazole (3o) and 1-Methoxy-2-methyl-*9H*carbazole (3o’)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-2-nitrobenzene **1b** (100 mg, 0.5 mmol, 100 mol%), (4-methoxy-3-methylphenyl)boronic acid **2o** (108 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-2-nitrobenzene **1b**). The mixture was heated at 180 °C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3o** as yellow solid (54mg, 51% yield) and **3o’** as yellow solid (29mg, 27% yield). ^1H and ^{13}C NMR data were consistent with literature values.[12, 13]

3-Methoxy-2-methyl-*9H*carbazole (3o)

TLC (SiO_2): $R_f = 0.27$ (acetone:hexanes, 1:5).

^1H NMR (300 MHz, Acetone) δ 10.10 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.81 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.13 – 7.08 (m, 1H), 7.02 (s, 1H), 3.90 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (75 MHz, Acetone) δ 158.18, 140.73, 140.68, 124.60, 124.12, 121.94, 119.79, 119.42, 118.89, 116.68, 111.28, 93.30, 55.67, 16.92.

FTIR (neat) : υ 3313, 3069, 1783, 1689, 1404, 1270, 1169 cm^{-1}.

LRMS *m*/*z* (EI): 212.2(M^++1), 211.3, 196.6, 195.7, 167.5.

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(12) R. Hesse, K. K. Gruner, O. Kataeva, A. W. Schmidt and H.-J. Knölker, *Chem.-Eur. J.*, 2013, **19**, 14098-14111.

(13) S. Kureel, R. Kapil and S. Popli, *Journal of the Chemical Society D: Chemical Communications*, 1969, 1120-1121.

1-Methoxy-2-methyl-*9H*carbazole (3o')

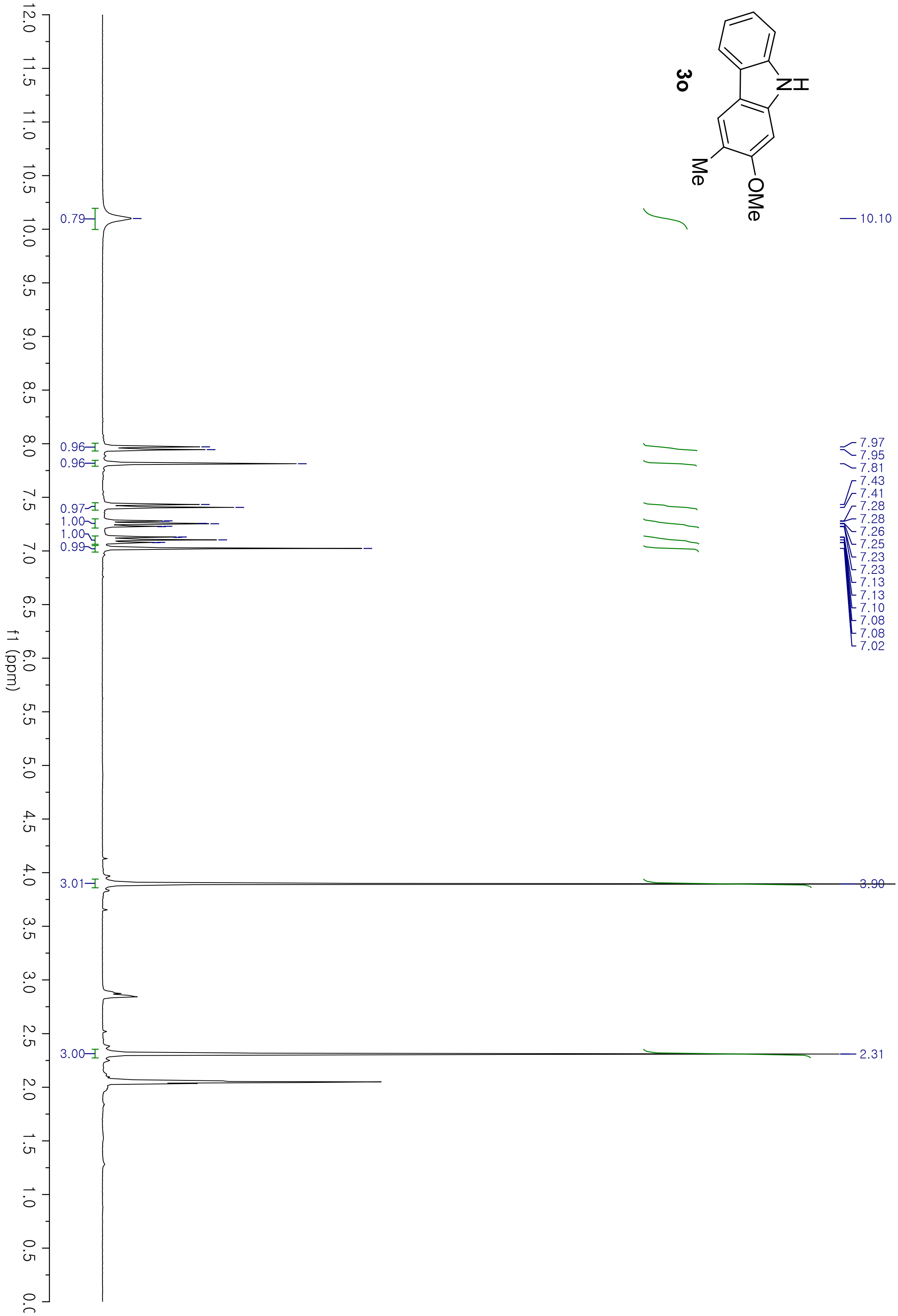
'**TLC (SiO_2)**: R_f = 0.28 (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, Acetone) δ 10.16 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.19 – 7.10 (m, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, Acetone) δ 156.86, 141.66, 141.42, 125.16, 124.60, 120.13, 119.56, 118.53, 118.01, 111.33, 107.65, 104.63, 56.46, 10.15.

FTIR (neat) : υ 3313, 3069, 1783, 1689, 1404, 1270, 1169 cm^{-1}.

LRMS *m/z* (EI): 212.3 (M^++1), 211.4, 196.6, 195.7, 167.7.


3o
N
H
OMe
Me
10.10
7.97
7.95
7.81
7.43
7.41
7.28
7.28
7.26
7.25
7.23
7.23
7.13
7.13
7.10
7.08
7.08
7.02
3.90
2.31
0.79
0.96
0.96
0.97
1.00
1.00
0.99
3.01
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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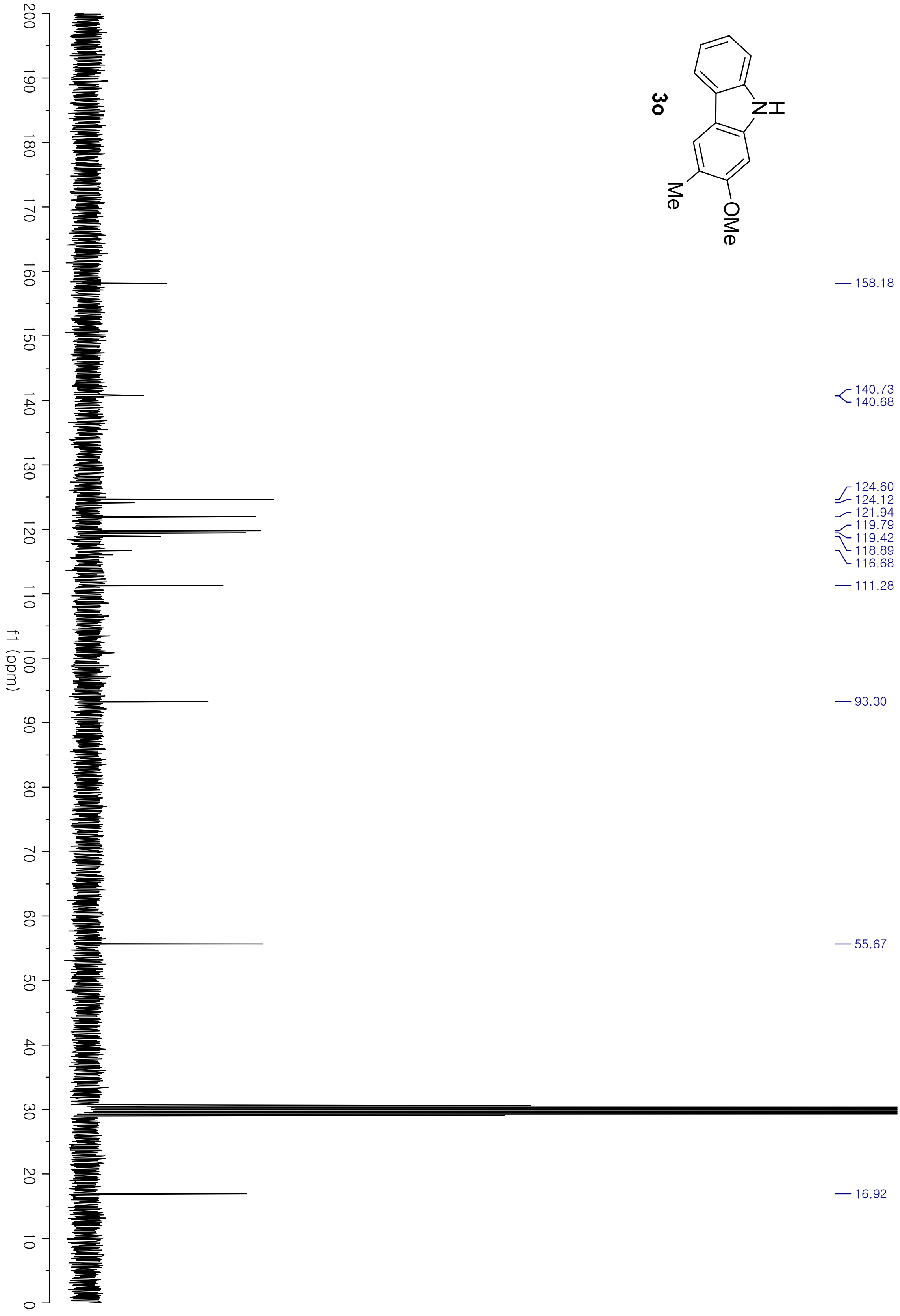
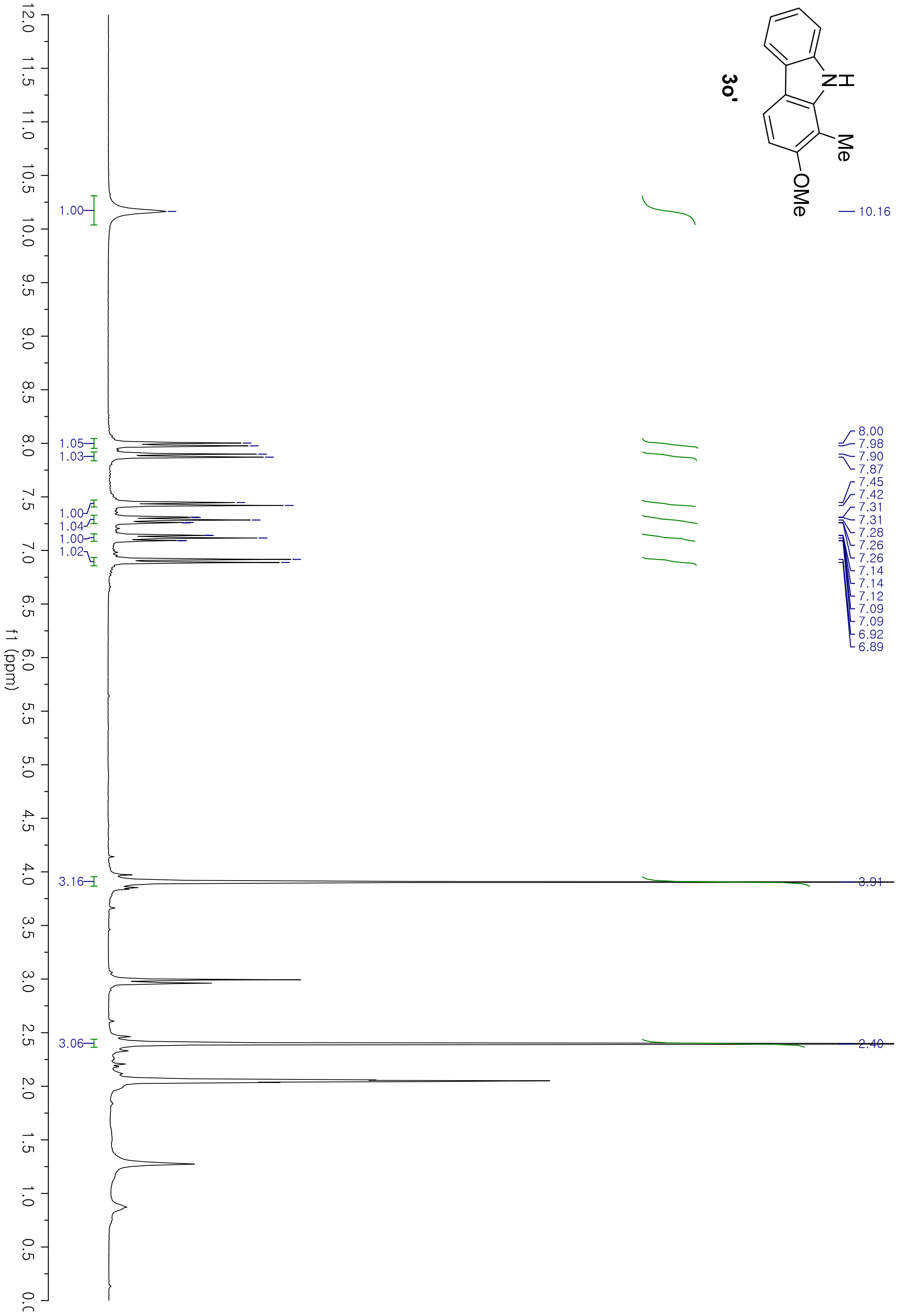
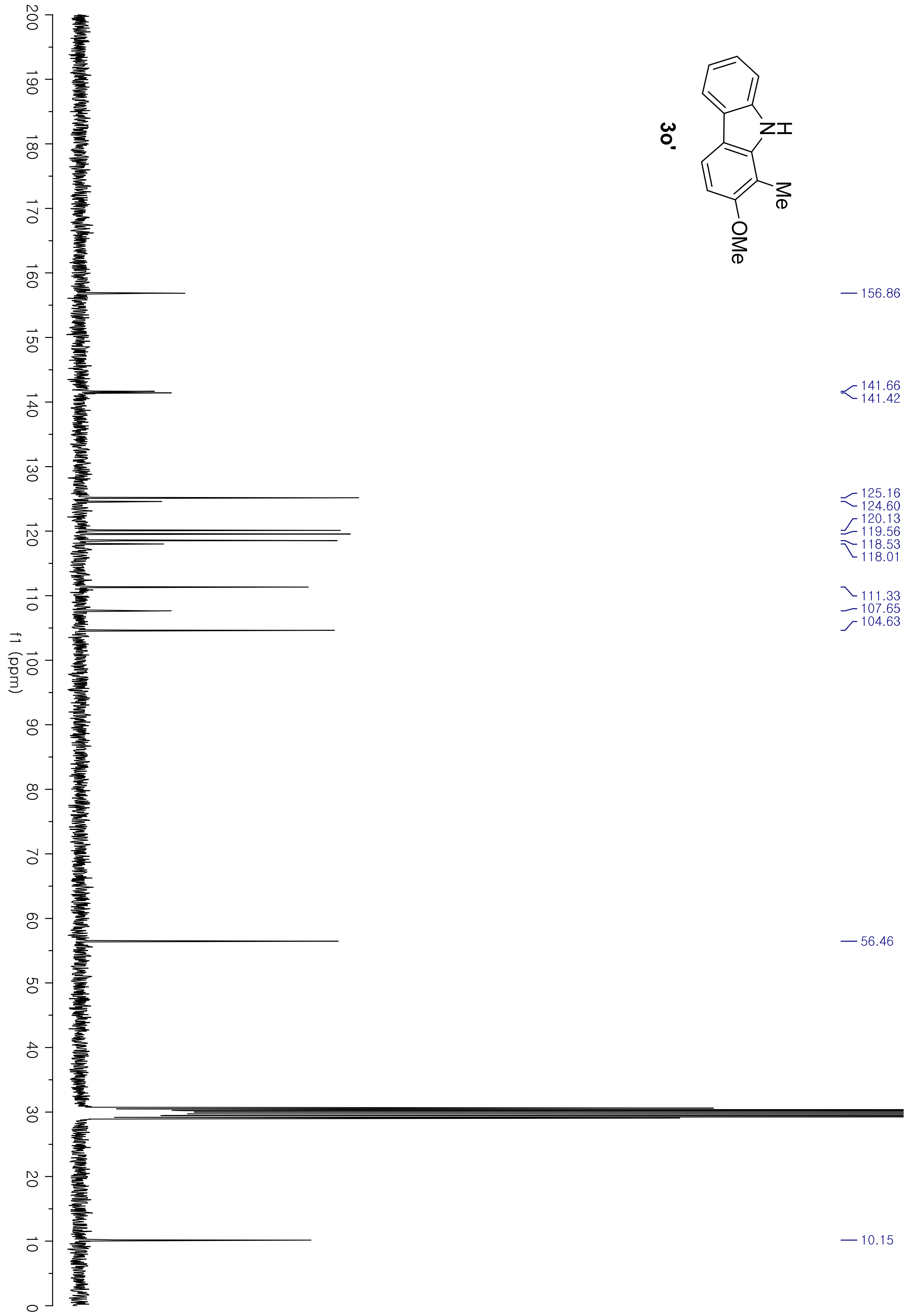
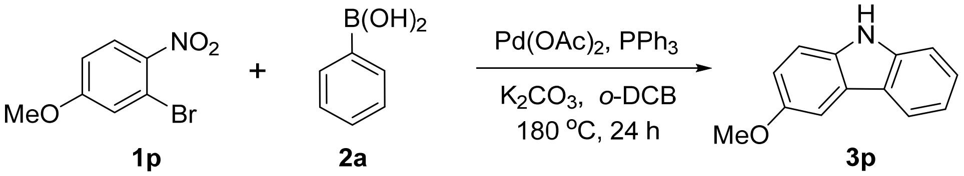
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3o
Me
OMe
N
H
158.18
140.73
140.68
124.60
124.12
121.94
119.79
119.42
118.89
116.68
111.28
93.30
55.67
16.92
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3o'
H
N
Me
OMe
10.16
8.00
7.98
7.90
7.87
7.45
7.42
7.31
7.31
7.28
7.26
7.26
7.14
7.14
7.12
7.09
7.09
6.92
6.89
3.91
2.40
1.00
1.05
1.03
1.00
1.04
1.00
1.02
3.16
3.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3o'
H
N
Me
OMe
156.86
141.66
141.42
125.16
124.60
120.13
119.56
118.53
118.01
111.33
107.65
104.63
56.46
10.15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3-Methoxy-9*H*-carbazole (3p)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 2-bromo-4-methoxy-1-nitrobenzene **1p** (116 mg, 0.5 mmol, 100 mol%), phenylboronic acid **2a** (80 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 2-bromo-4-methoxy-1-nitrobenzene **1p**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3p** as a brown solid (59 mg, 60% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[1]

TLC (SiO_2): $R_f = 0.32$ (acetones:hexanes, 1:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, $J = 7.8$ Hz, 1H), 7.85 (s, 1H), 7.54 (d, $J = 2.4$ Hz, 1H), 7.44 – 7.30 (m, 2H), 7.28 – 7.12 (m, 2H), 7.05 (dd, $J = 8.7, 2.4$ Hz, 1H), 3.91 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.88, 140.32, 134.42, 125.89, 123.76, 123.34, 120.34, 119.10, 115.16, 111.46, 110.88, 103.13, 56.14.

FTIR (neat) υ 3405, 1788, 1685, 1400, 1260, 1031 cm^{-1}.

LRMS *m*/*z* (EI): 198.3 (M^++1), 197.4, 182.7, 181.7, 154.3, 101.5.

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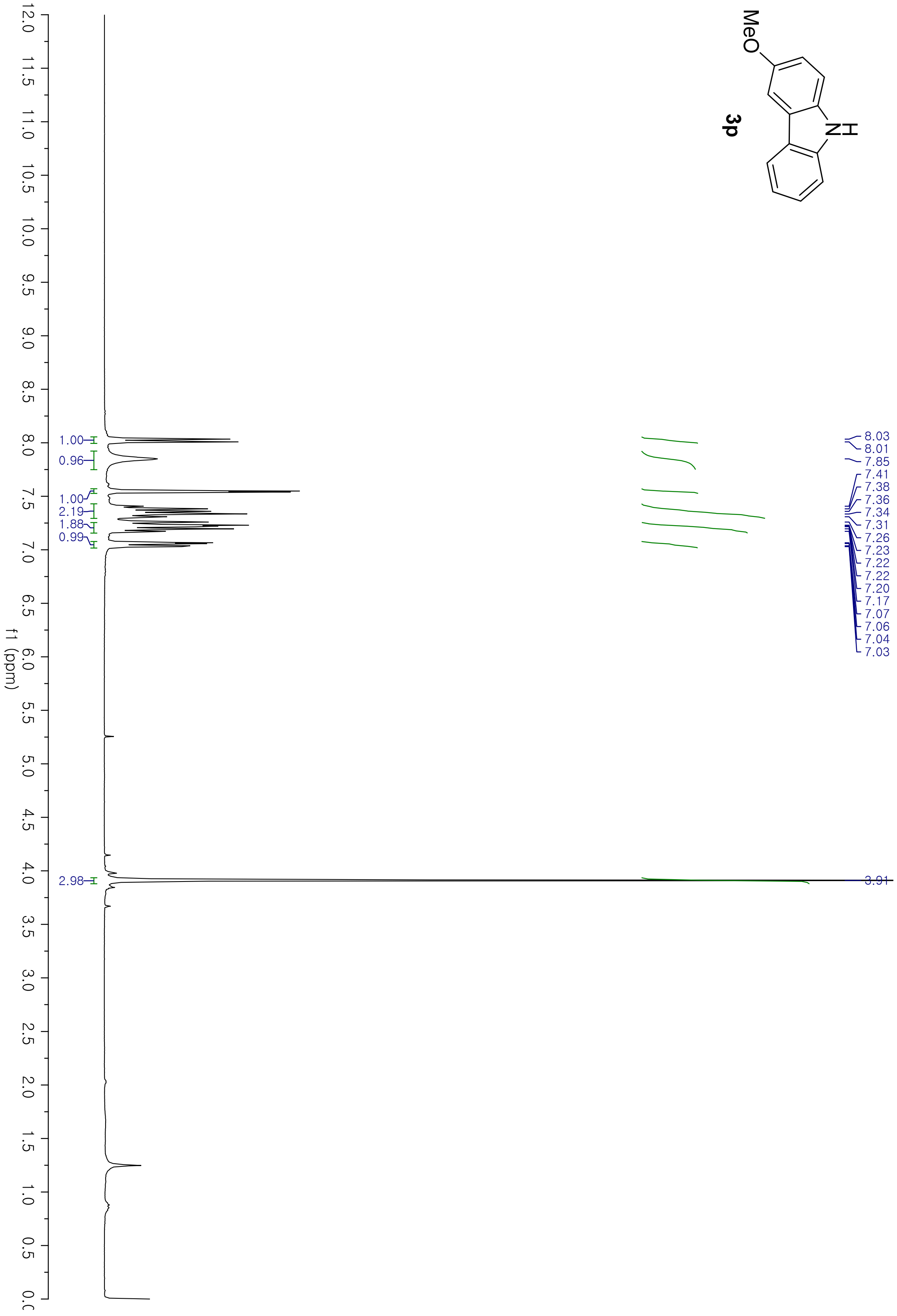
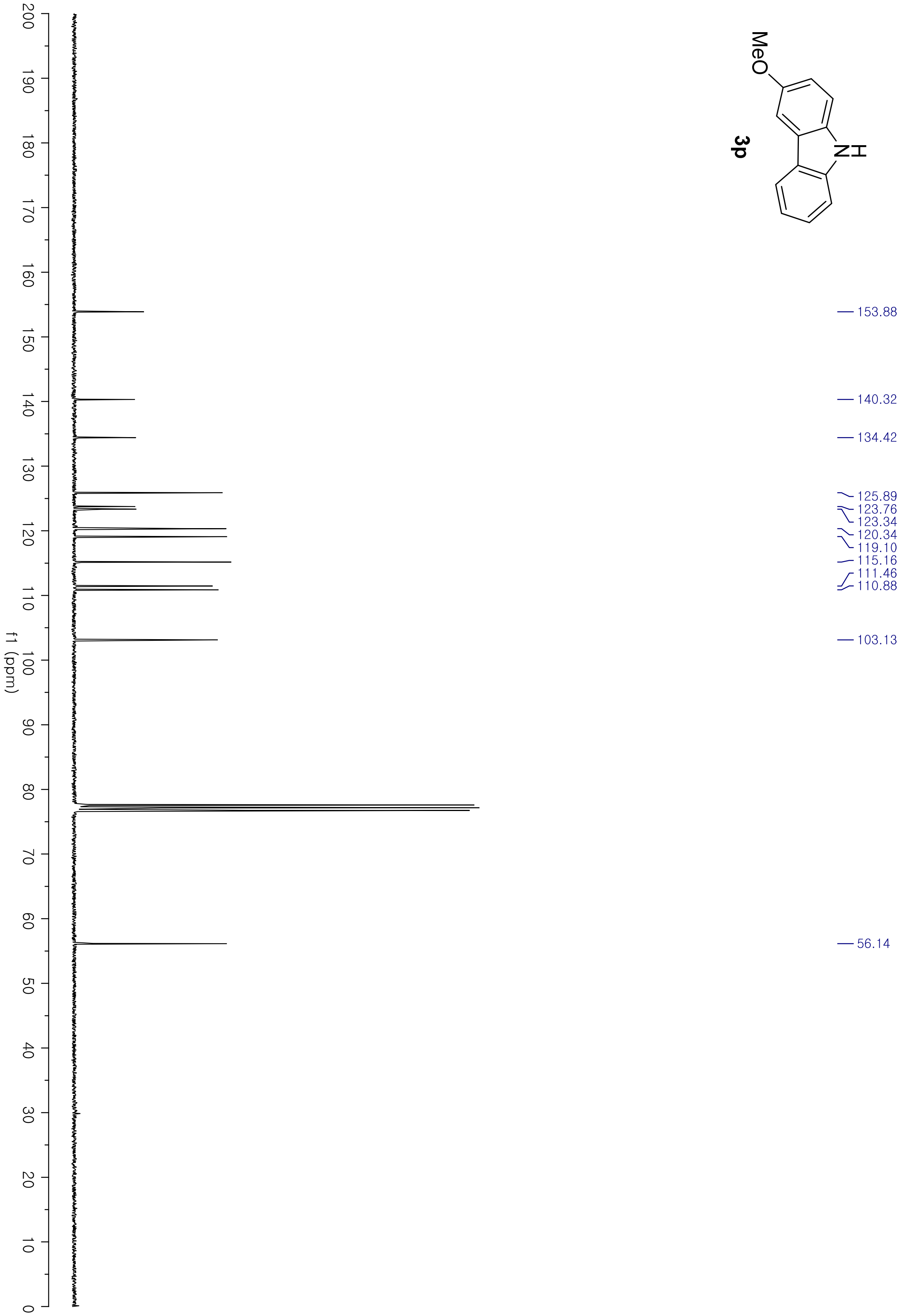
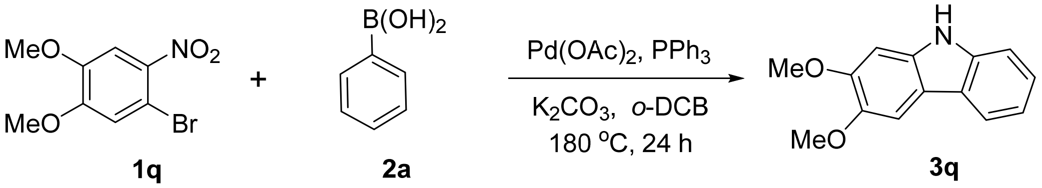
[1] C. Suzuki, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2015, **17**, 1597-1600.


MeO
N
H
8.03
8.01
7.85
7.41
7.38
7.36
7.34
7.31
7.26
7.23
7.22
7.22
7.20
7.17
7.07
7.06
7.04
7.03
3.91
1.00
0.96
1.00
2.19
1.88
0.99
2.98
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3p


MeO
NH
3p
153.88
140.32
134.42
125.89
123.76
123.34
120.34
119.10
115.16
111.46
110.88
103.13
56.14
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

2,3-Dimethoxy-*9H*-carbazole (3q)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-4,5-dimethoxy-2-nitrobenzene **1q** (131mg, 0.5 mmol, 100 mol%), phenylboronic acid **2a** (80 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-4,5-dimethoxy-2-nitrobenzene **1q**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 7% acetone in hexanes as eluant to give 3q as a white solid (70 mg, 62% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[14]

TLC (SiO_2): $R_f = 0.28$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 10.98 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.66 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.04 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (75 MHz, $DMSO_3$) δ 149.18, 143.71, 139.56, 134.63, 123.67, 123.00, 119.26, 118.12, 114.30, 110.72, 103.33, 94.62, 56.21, 55.63.

FTIR (neat) υ 3337, 2917, 1402, 1186, 1090 cm^{-1}.

LRMS *m/z* (EI): 228.2 (M^++1), 227.5, 212.7, 211.7, 184.5.

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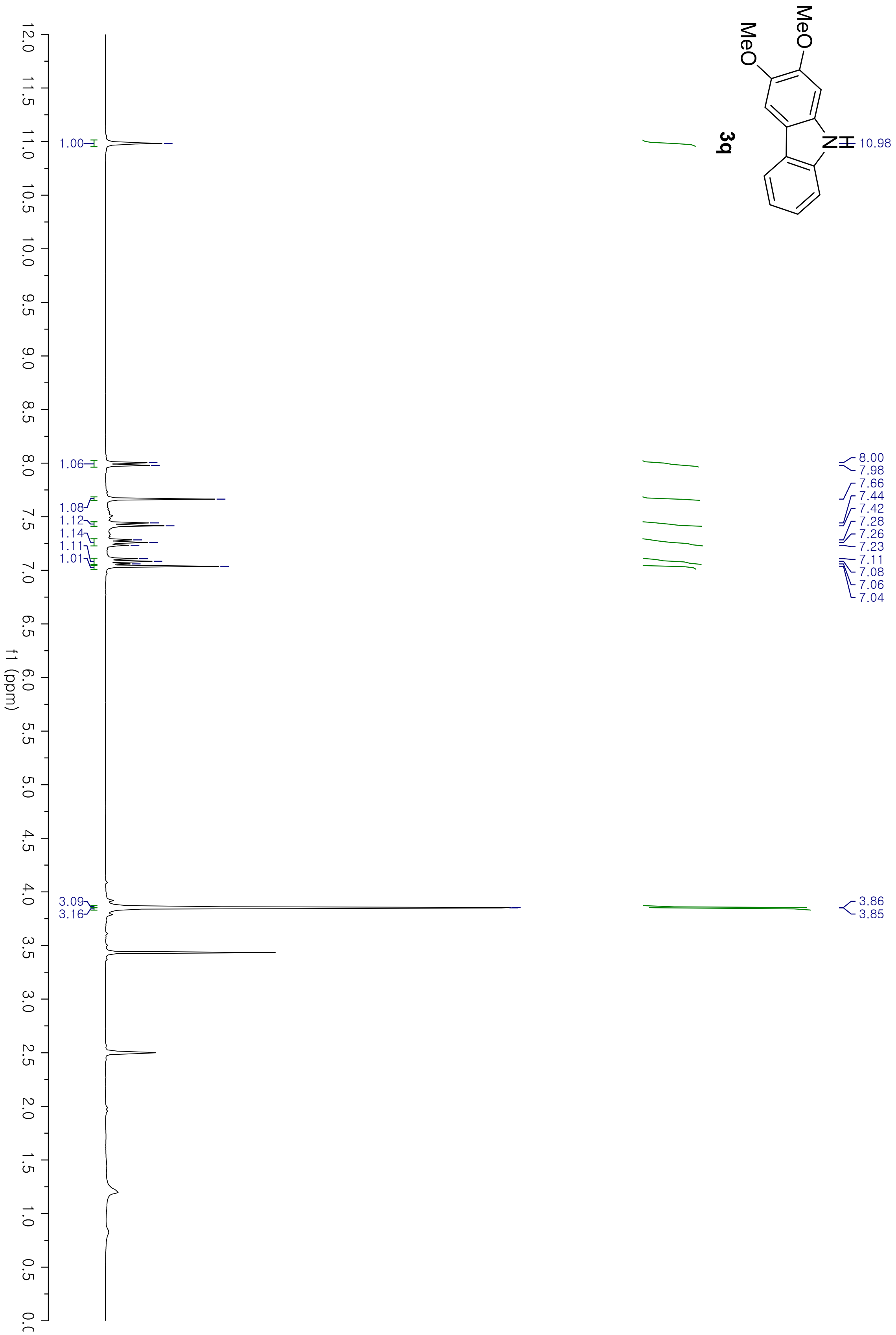
[14] B. Liegault, D. Lee, M. P. Huestis, D. R. Stuart and K. Fagnou, *J. Org. Chem.*, 2008, **73**, 5022-5028.


MeO
MeO
NH
3q
10.98
8.00
7.98
7.66
7.44
7.42
7.28
7.26
7.23
7.11
7.08
7.06
7.04
3.86
3.85
1.00
1.06
1.08
1.12
1.14
1.11
1.01
3.09
3.16
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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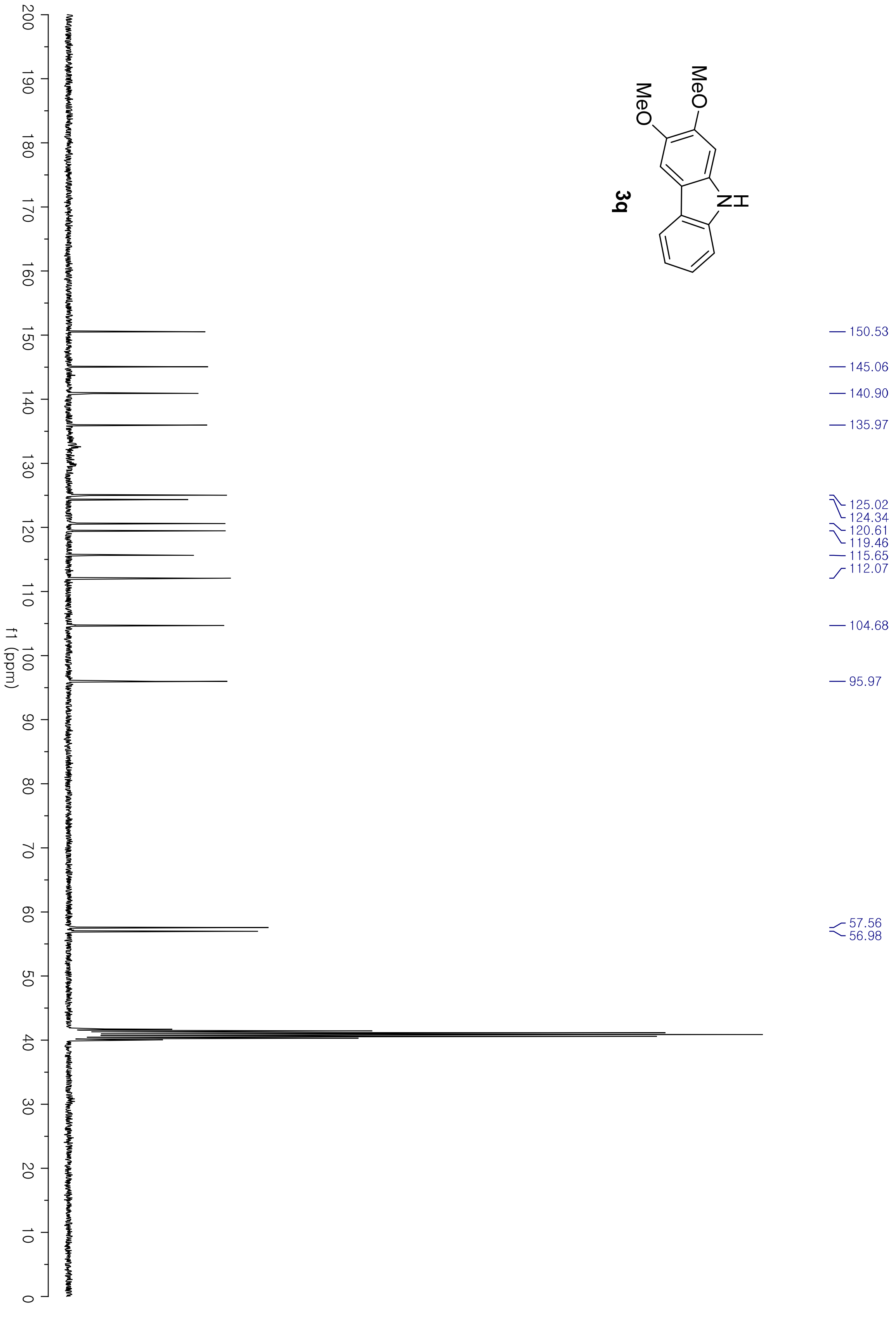
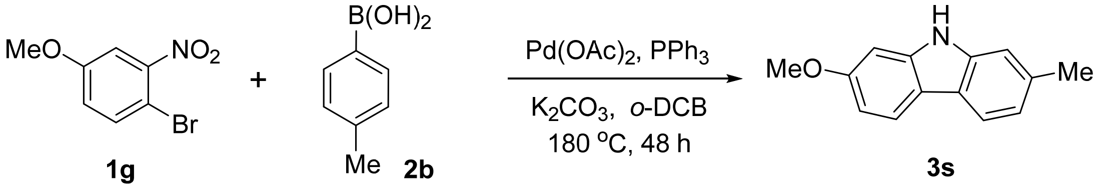
1.0
0.5
0.0
f1 (ppm)


MeO
MeO
N
H
3q
150.53
145.06
140.90
135.97
125.02
124.34
120.61
119.46
115.65
112.07
104.68
95.97
57.56
56.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-Methoxy-7-methyl-*9H*-carbazole (3s)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-4-methoxy-2-nitrobenzene **1g** (120 mg, 0.5 mmol, 100 mol%), *p*-tolylboronic acid **2b** (88 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-4-methoxy-2-nitrobenzene **1g**). The mixture was heated at 180 ^{o}C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3s** as a white solid (75 mg, 71% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[15]

TLC (SiO_2): $R_f = 0.31$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 10.98 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.21 (s, 1H), 6.96 – 6.88 (m, 2H), 6.73 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (75 MHz DMSO) δ 158.14, 141.07, 140.22, 133.50, 120.54, 120.44, 120.03, 119.02, 116.32, 110.73, 107.42, 94.53, 55.25, 21.65.

FTIR (neat) υ 3394, 1726, 1366, 1219, 1091 cm^{-1}.

LRMS *m/z* (EI): 212.5 (M^{+}+1), 211.6, 196.6, 195.7, 168.5.

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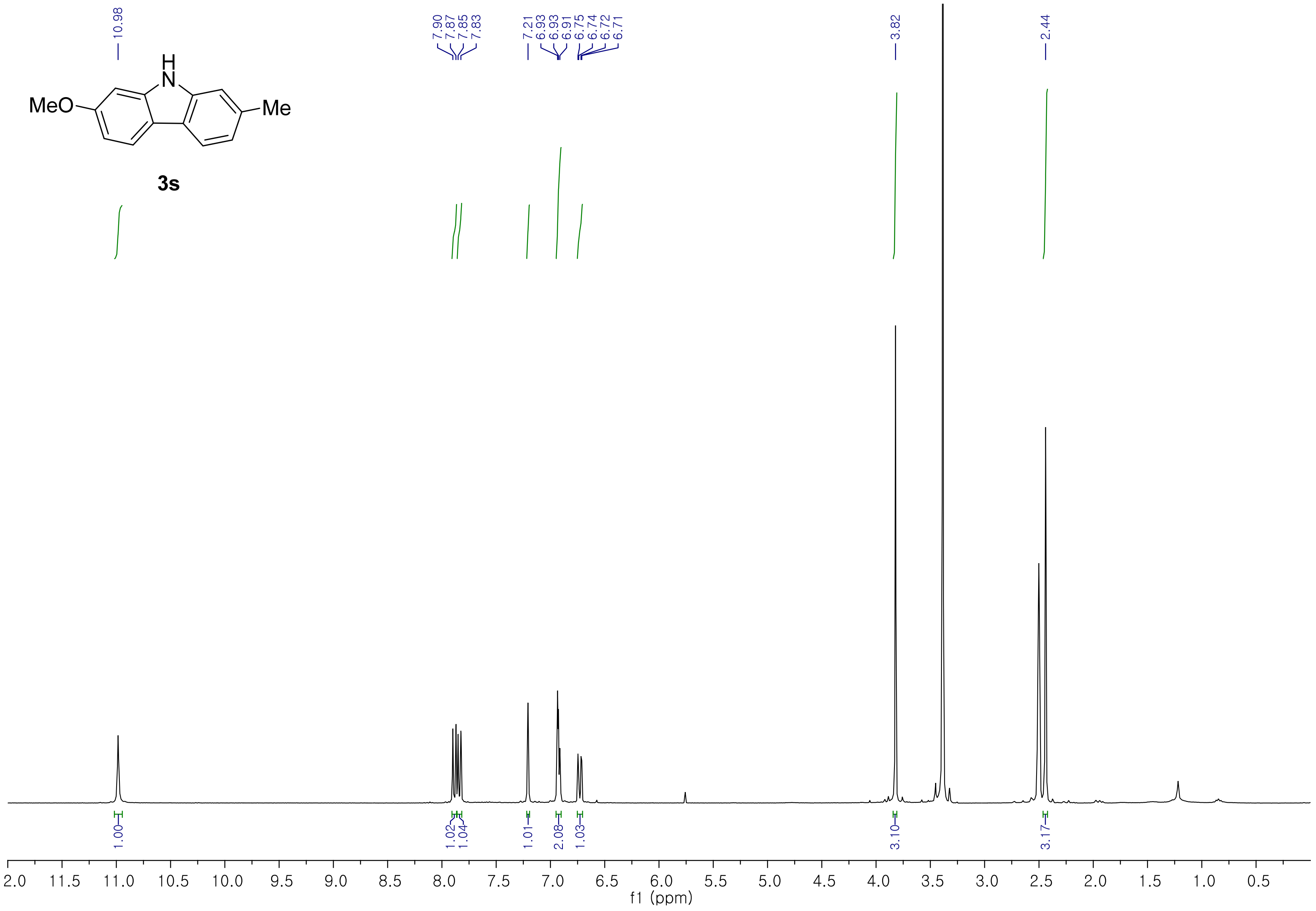
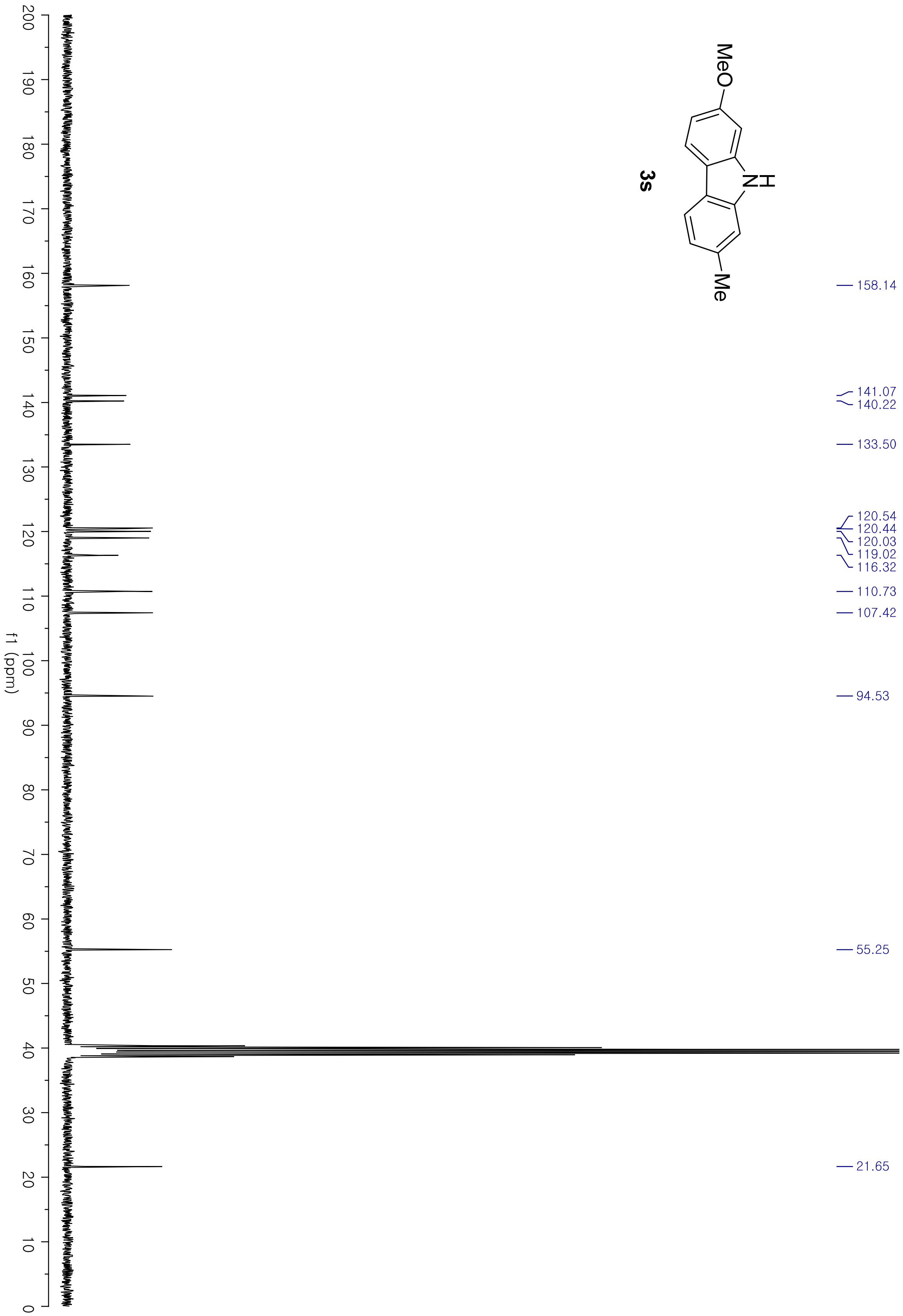
[15] C. Schuster, C. Boerger, K. K. Julich-Gruner, R. Hesse, A. Jaeger, G. Kaufmann, A. W. Schmidt and H.-J. Knoelker, *Eur. J. Org. Chem.*, 2014, 4741-4752.



3s

MeO
H
N
Me
10.98
7.90
7.87
7.85
7.83
7.21
6.93
6.93
6.91
6.75
6.74
6.72
6.71
3.82
2.44
1.00
1.02
1.04
1.01
2.08
1.03
3.10
3.17
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


3s
MeO
H
N
Me
158.14
141.07
140.22
133.50
120.54
120.44
120.03
119.02
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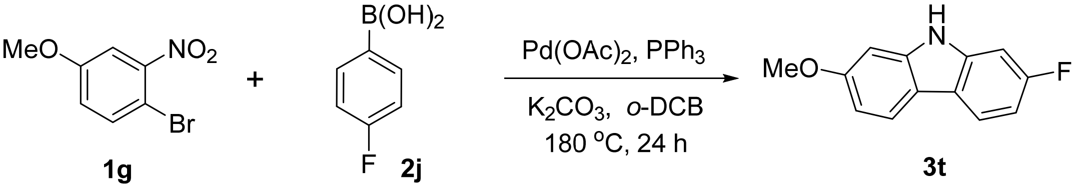
107.42
94.53
55.25
21.65
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-Fluoro-7-methoxy-*9H*-carbazole (3t)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-4-methoxy-2-nitrobenzene **1g** (120 mg, 0.5 mmol, 100 mol%), (4-fluorophenyl)boronic acid **2j** (91 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-4-methoxy-2-nitrobenzene **1g**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3t** as a white solid (71 mg, 66% yield).

TLC (SiO_2): $R_f = 0.37$ (acetone:hexanes, 1:5).

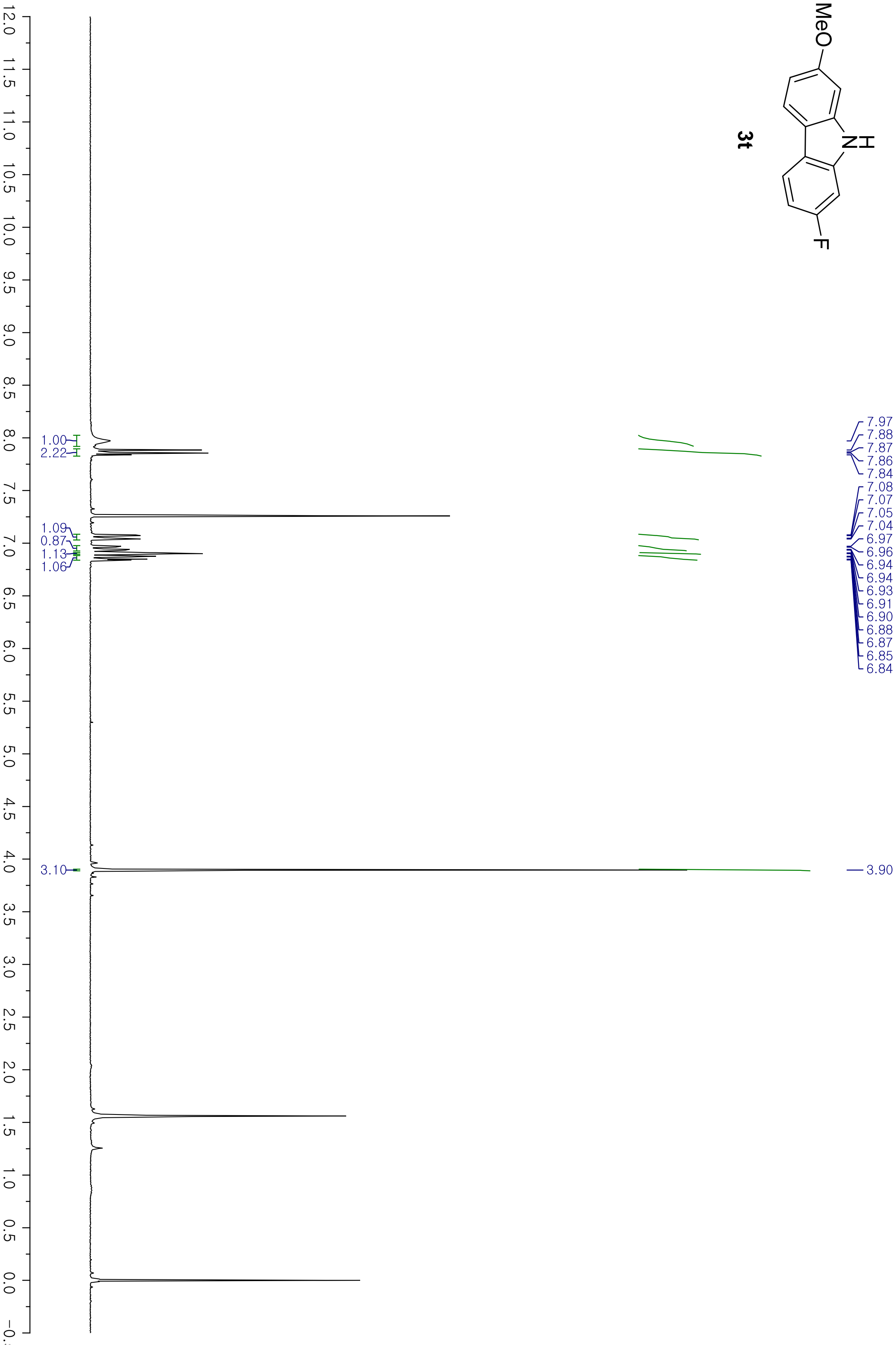
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (br s, 1H), 7.87 (d, J = 8.5 Hz, 1H),, 7.85 (d, *J* = 8.3 Hz, 1H), 7.06 (dd, *J* = 9.5, 2.3 Hz, 1H), 6.98 – 6.93 (m, 1H), 6.90 (d, *J* = 2.2 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.90 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.87, 141.31, 120.78, 120.38, 120.25, 116.91, 108.55, 107.82, 107.50, 97.63, 97.27, 95.02, 55.78.

FTIR (neat) υ 3192, 2843, 1539, 1406, 1155 cm^{-1}.

LRMS *m/z* (EI): 216.5 (M^++1), 215.5, 200.6, 199.7, 172.5, 171.5

HRMS *m/z* (EI): calcd. For $C_{13}H_{10}FNO$ (M^+) 215.0747, found 215.0746



3t

MeO
N
H
F
7.97
7.88
7.87
7.86
7.84
7.08
7.07
7.05
7.04
6.97
6.96
6.94
6.94
6.93
6.91
6.90
6.88
6.87
6.85
6.84
3.90
1.00
2.22
1.09
0.87
1.13
1.06
3.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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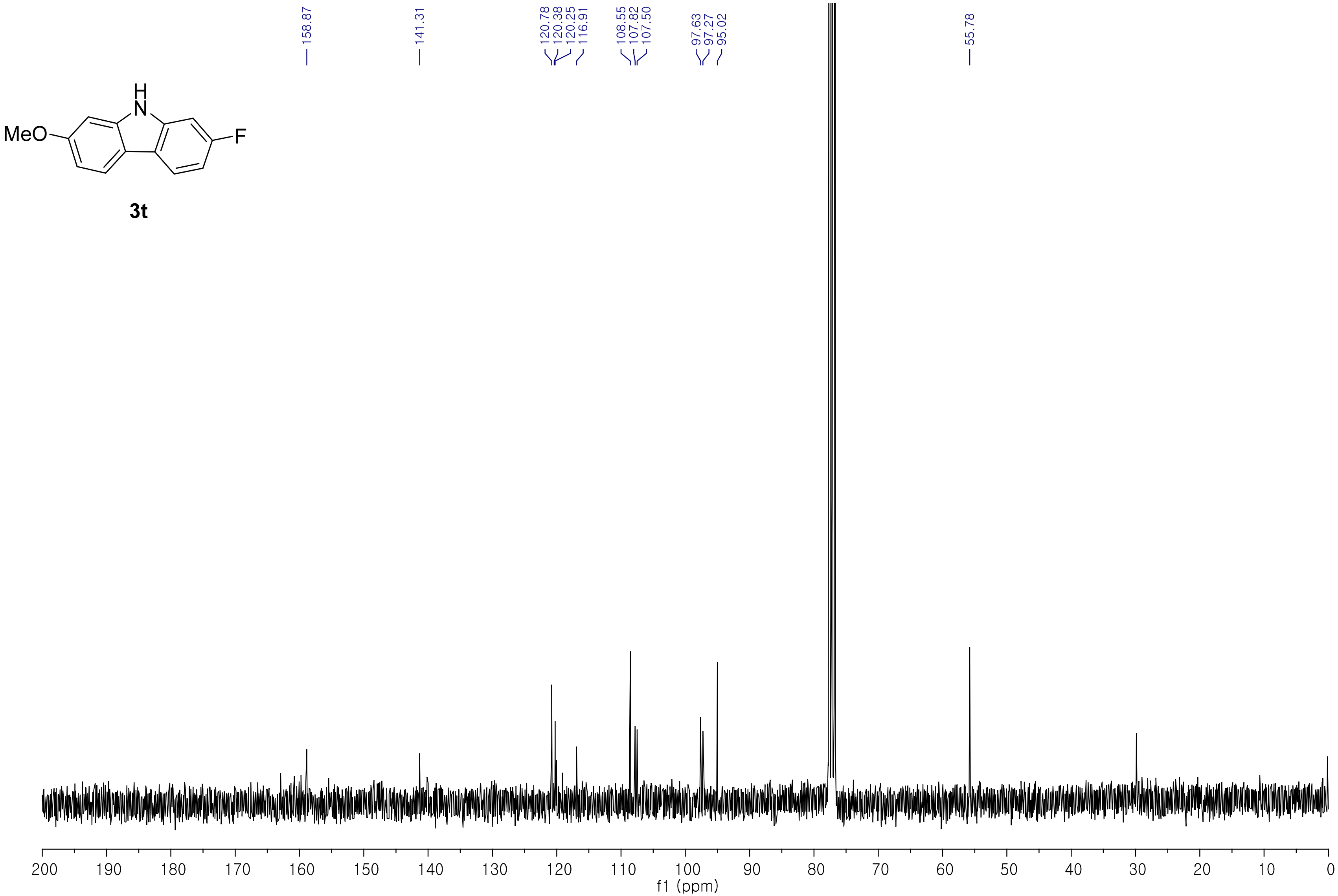
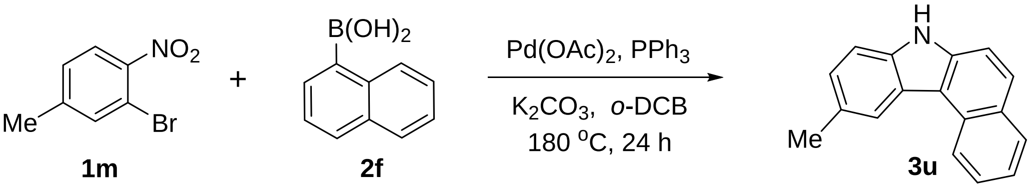
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


MeO
H
N
F
3t
158.87
141.31
120.78
120.38
120.25
116.91
108.55
107.82
107.50
97.63
97.27
95.02
55.78
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

10-Methyl-7*H*-benzo[c]carbazole (3u)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 2-bromo-4-methyl-1-nitrobenzene **1m** (108 mg, 0.5 mmol, 100 mol%), naphthalen-1-ylboronic acid **2f** (112 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 2-bromo-4-methyl-1-nitrobenzene **1m**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3u** as a white solid (81 mg , 70% yield). ^1H and ^{13}C NMR data were consistent with literature values.[16]

TLC (SiO_2): $R_f = 0.34$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, J = 8.3 Hz, 1H), 8.37 (s, 1H), 8.31 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.29 (d, J = 8.4 Hz, 1H), 2.64 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 137.41, 136.78, 130.09, 129.60, 129.27, 127.27, 126.90, 125.87, 124.27, 123.39, 122.98, 122.06, 115.22, 112.79, 110.88, 21.96.

FTIR (neat) υ 3470, 2897, 1696, 1542, 1267, 1152 cm^{-1}.

LRMS *m*/*z* (EI): 232.7 (M^++1), 231.2, 230.2, 228.8, 197.2, 118.8.

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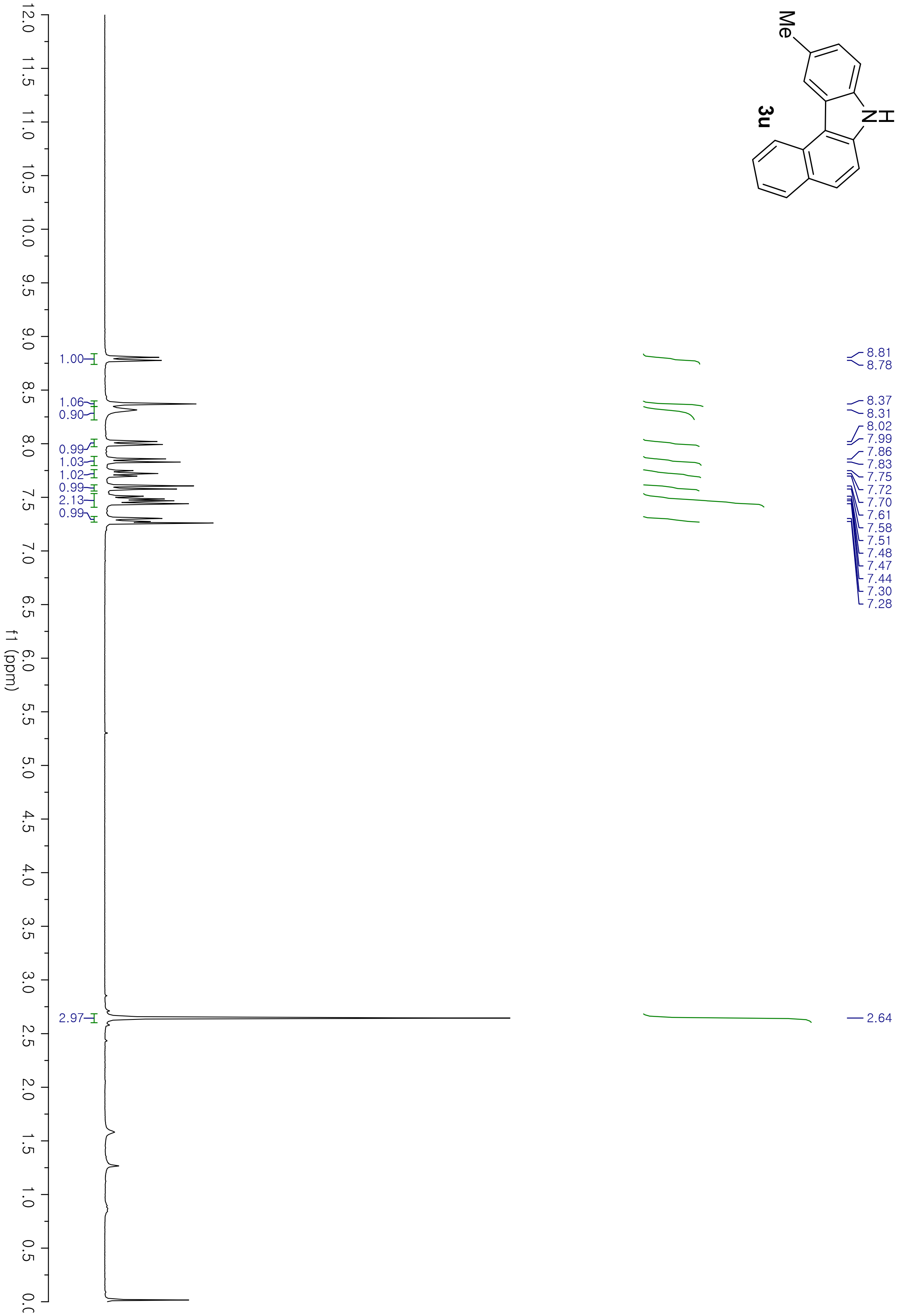
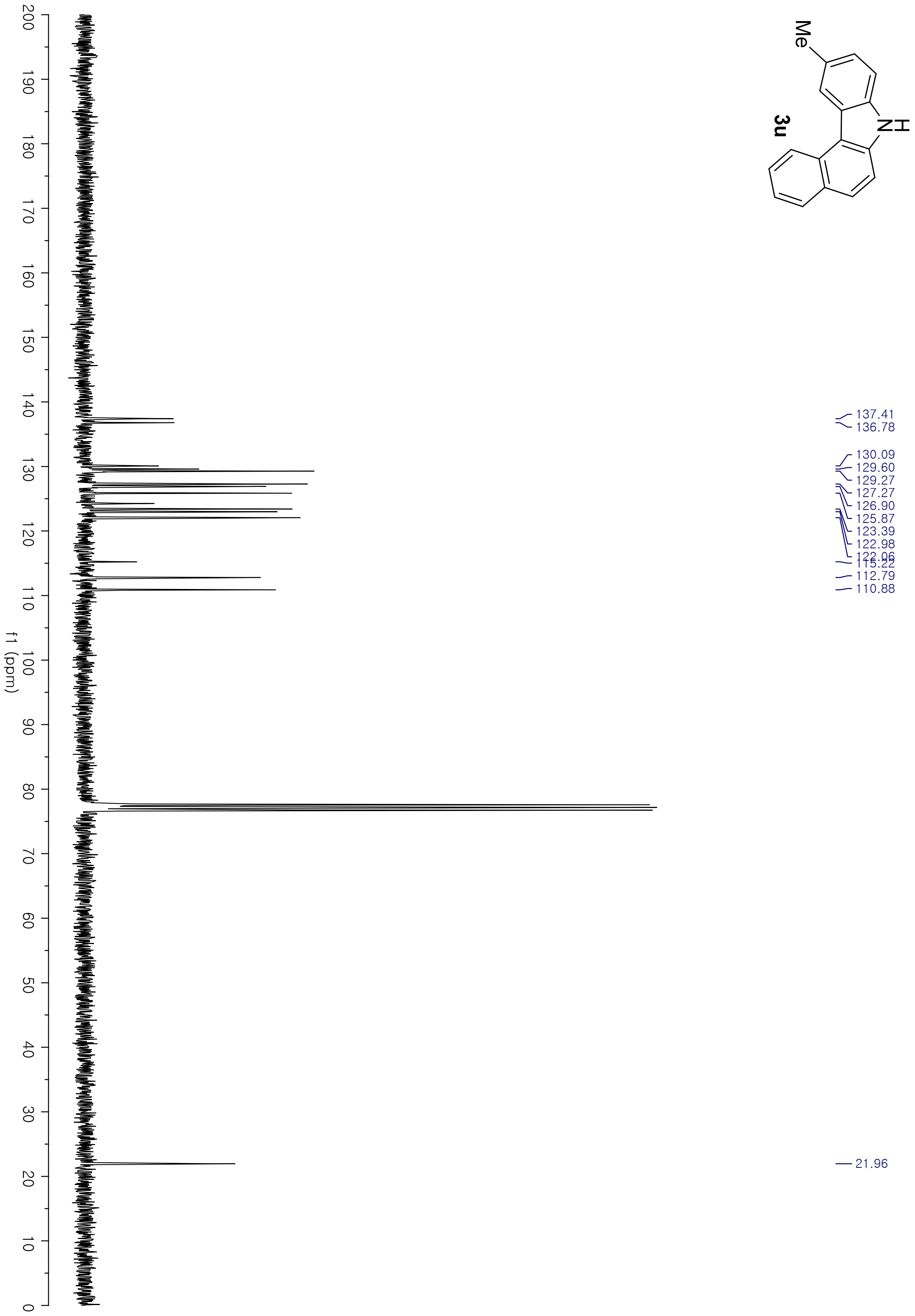
(16) B.-Y. Lim, M.-K. Choi and C.-G. Cho, *Tetrahedron Lett.*, 2011, **52**, 6015-6017.



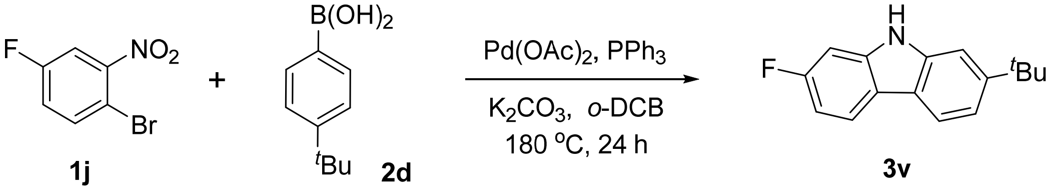
Me
NH
3u
8.81
8.78
8.37
8.31
8.02
7.99
7.86
7.83
7.75
7.72
7.70
7.61
7.58
7.51
7.48
7.47
7.44
7.30
7.28
2.64
1.00
1.06
0.90
0.99
1.03
1.02
0.99
2.13
0.99
2.97
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3u

Me
N
H
137.41
136.78
130.09
129.60
129.27
127.27
126.90
125.87
123.39
122.98
122.06
115.22
112.79
110.88
21.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-(Tert-butyl)-7-fluoro-*9H*-carbazole (3v)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 1-bromo-4-fluoro-2-nitrobenzene **1j** (110 mg, 0.5 mmol, 100 mol%), (4-(tert-butyl)phenyl)boronic acid **2d** (116 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 1-bromo-4-fluoro-2-nitrobenzene **1j**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3v** as a yellow solid (64 mg, 53% yield).

TLC (SiO_2): $R_f = 0.36$ (acetone:hexanes, 1:5).

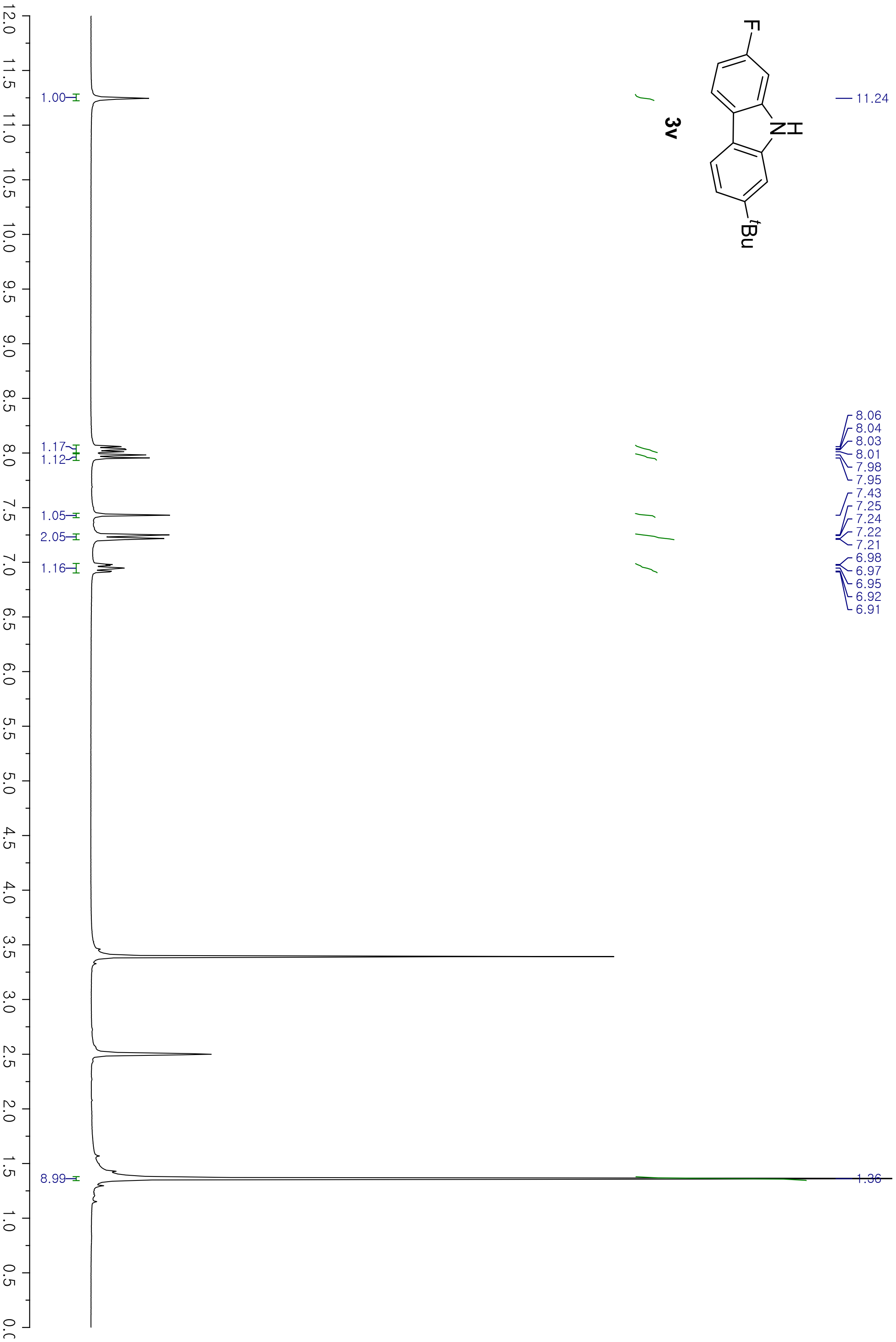
^{1}H NMR (300 MHz, DMSO) δ 11.24 (s, 1H), 8.04 (dd, *J* = 8.5, 5.7 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.43 (s, 1H), 7.23 (dd, *J* = 10.3, 2.1 Hz, 2H), 6.99 – 6.91 (m, 1H), 1.36 (s, 9H).

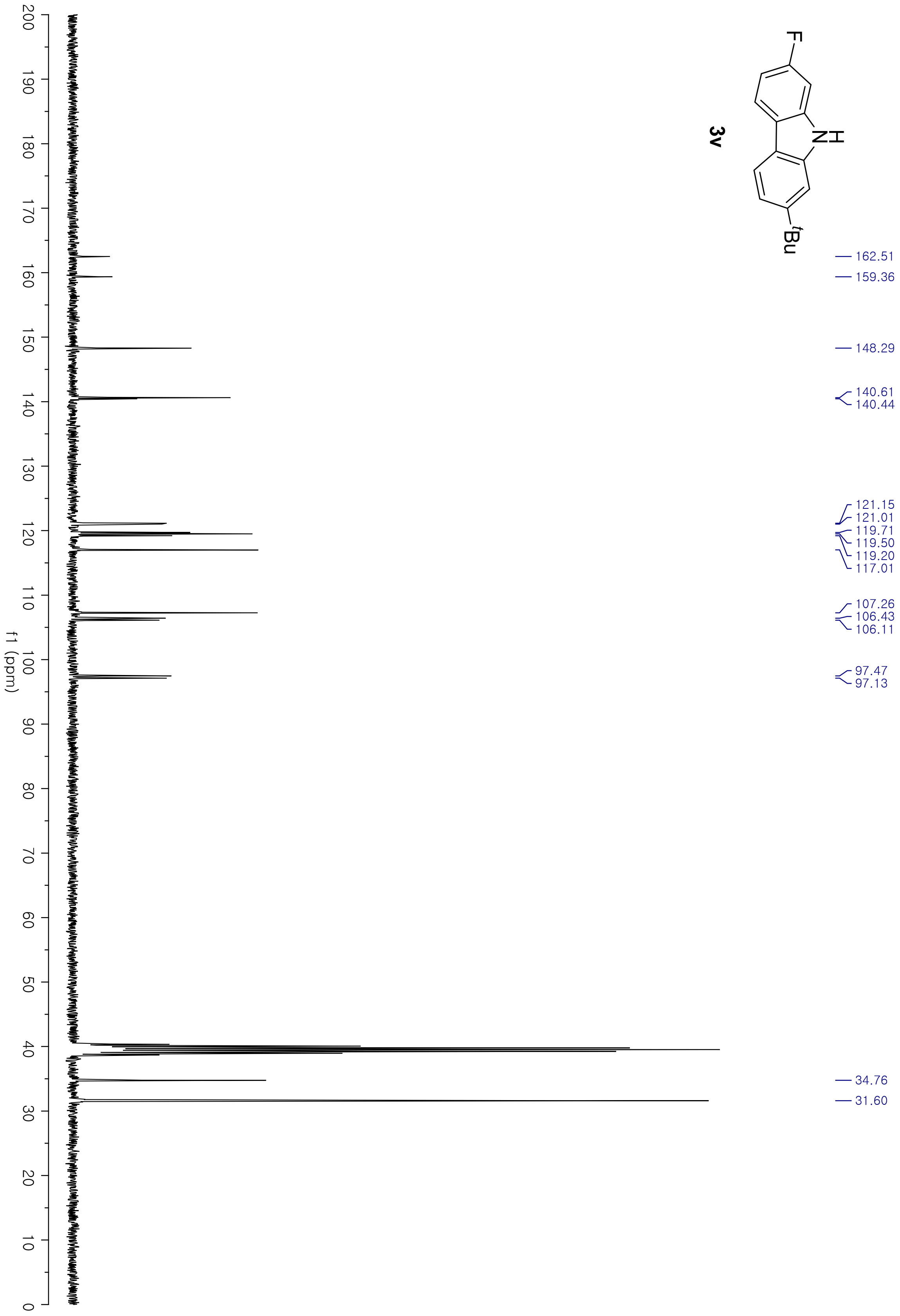
^{13}C NMR (75 MHz, DMSO) δ 160.94 (d, *J* = 237.8 Hz), 148.29, 140.61, 140.44, 121.08 (d, *J* = 10.5 Hz), 119.71, 119.50, 119.20, 117.01, 107.26, 106.27 (d, *J* = 24.1 Hz), 97.30 (d, *J* = 26.0 Hz), 34.76, 31.60.

FTIR (neat) υ 3475, 3187, 1741, 1598, 1266 cm^{-1}.

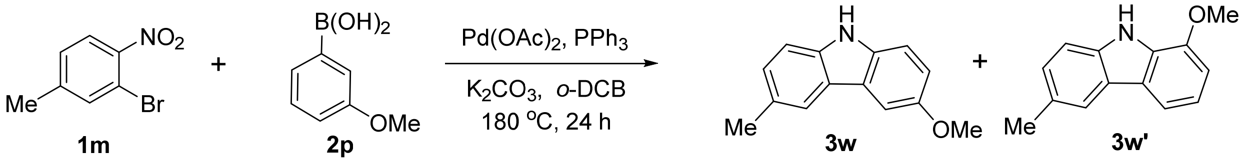
LRMS *m*/*z* (EI): 242.1 (M^++1), 241.1, 227.4, 226.5, 198.2.

HRMS *m*/*z* (EI): calcd. For $C_{16}H_{16}FN$ (M^+) 241.1268, found 241.1267.


F
NH
tBu
3v
11.24
8.06
8.04
8.03
8.01
7.98
7.95
7.43
7.25
7.24
7.22
7.21
6.98
6.97
6.95
6.92
6.91
1.36
1.00
1.17
1.12
1.05
2.05
1.16
8.99
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3v
F
H
N
tBu
162.51
159.36
148.29
140.61
140.44
121.15
121.01
119.71
119.50
119.20
117.01
107.26
106.43
106.11
97.47
97.13
34.76
31.60
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Glycozoline (3w) and Glycozolicine (3w')



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 2-bromo-4-methyl-1-nitrobenzene **1m** (108 mg, 0.5 mmol, 100 mol%), (3-methoxyphenyl)boronic acid **2p** (100 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 2-bromo-4-methyl-1-nitrobenzene **1m**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3w** as a green solid (37 mg, 35% yield) and **3w'** as a yellow solid (41 mg, 39% yield). ^1H and ^{13}C NMR data were consistent with literature values.[15,17]

Glycozoline(3w)

TLC (SiO_2): $R_f = 0.32$ (acetone:hexanes, 1:6).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.77 (s, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.06 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.94 (s, 3H), 2.54 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.87, 138.69, 134.89, 128.45, 127.32, 123.76, 123.64, 120.25, 115.01, 111.41, 110.56, 103.23, 56.19, 21.54.

FTIR (neat) υ 3410, 2894, 1706, 1492, 1266, 1131 cm^{-1}.

LRMS *m*/*z* (EI): 212.1 (M^{+}+1), 211.2, 197.2, 196.3, 168.2, 167.2.

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(15) T. Pirali, F. Zhang, A. H. Miller, J. L. Head, D. McAusland and M. F. Greaney, *Angew. Chem. Int. Ed.*, 2012, **51**, 1006-1009.

(17) C. Schuster, C. Boerger, K. K. Julich-Gruner, R. Hesse, A. Jaeger, G. Kaufmann, A. W. Schmidt and H.-J. Knoelker, *Eur. J. Org. Chem.*, 2014, 4741-4752.

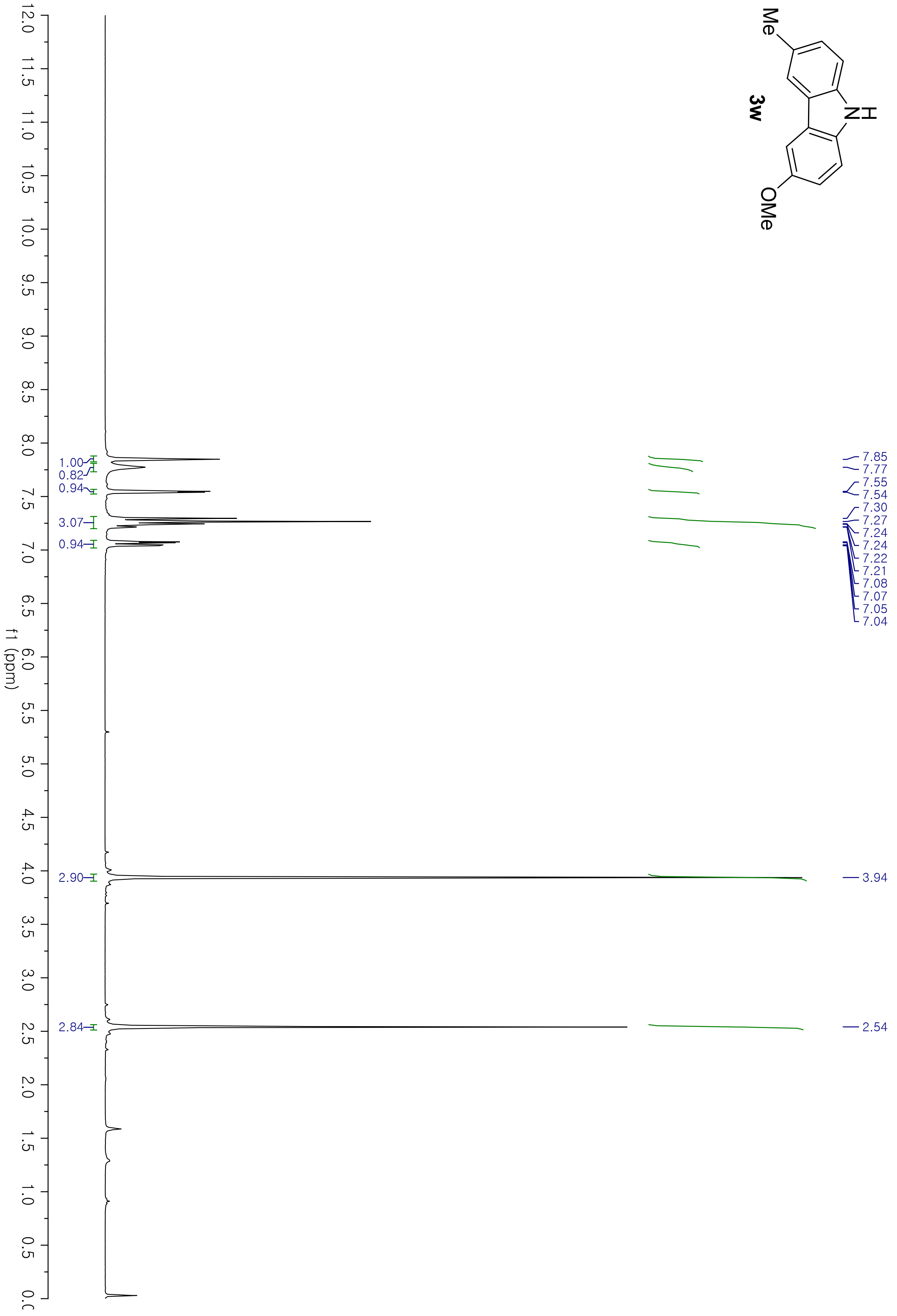
Glycozolicine (3w')

TLC (SiO_2): R_f = 0.35 (acetone:hexanes, 1:6).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.87 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.00 (s, 3H), 2.54 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 145.79, 137.57, 130.24, 128.76, 127.19, 124.32, 123.96, 120.54, 119.61, 112.94, 110.71, 105.87, 55.59, 21.56.

FTIR (neat) υ 3410, 2894, 1706, 1492, 1266, 1131 cm^{-1}.

LRMS *m*/*z* (EI): 212.2 (M^++1), 211.3, 197.2, 196.3, 169.1, 168.2, 142.1.


Me
NH
OMe
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7.77
7.55
7.54
7.30
7.27
7.24
7.24
7.22
7.21
7.08
7.07
7.05
7.04
3.94
2.54
1.00
0.82
0.94
3.07
0.94
2.90
2.84
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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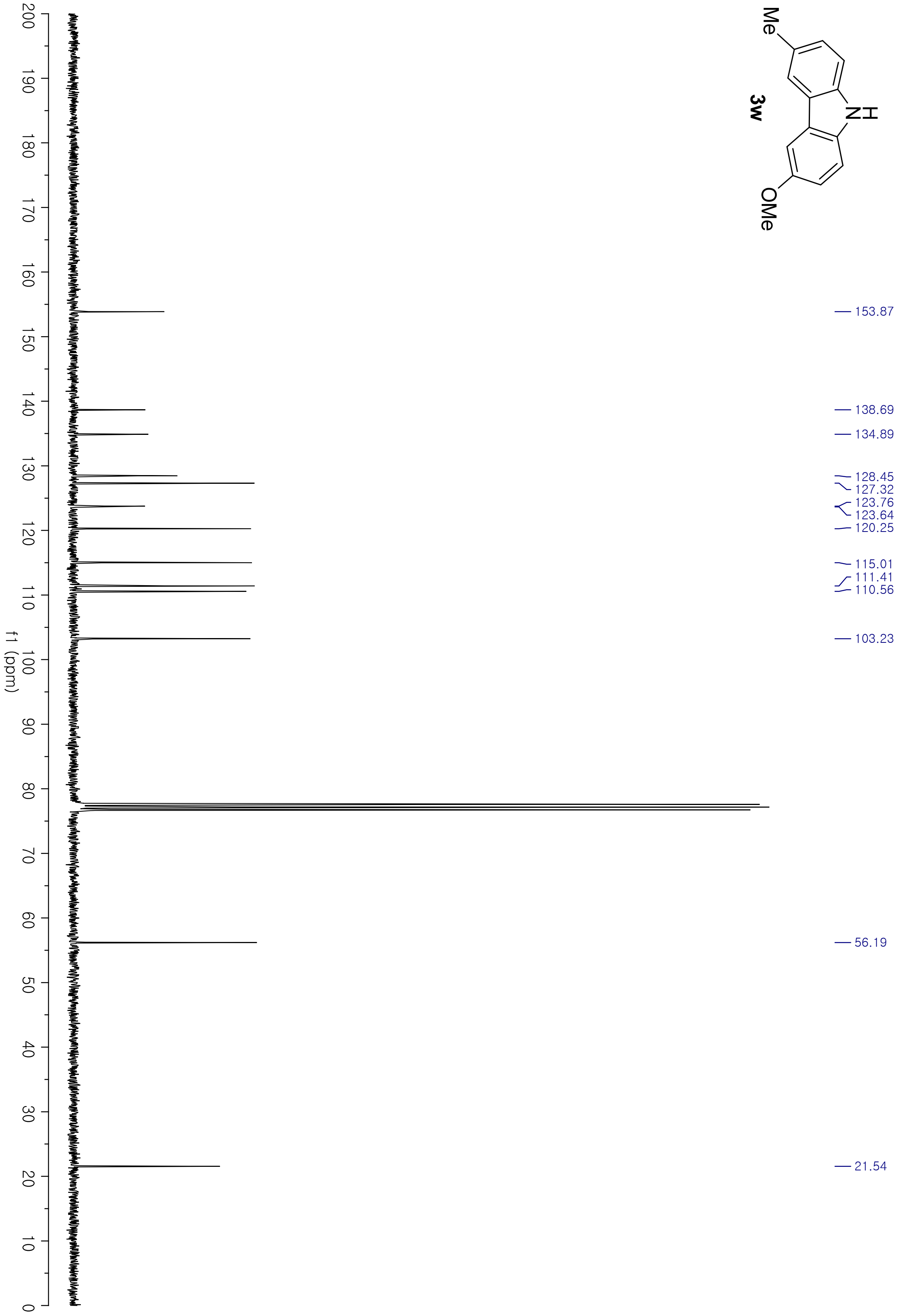
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3w


3w
Me
OMe
H
N
153.87
138.69
134.89
128.45
127.32
123.76
123.64
120.25
115.01
111.41
110.56
103.23
56.19
21.54
f1 (ppm)
200
190
180
170
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150
140
130
120
110
100
90
80
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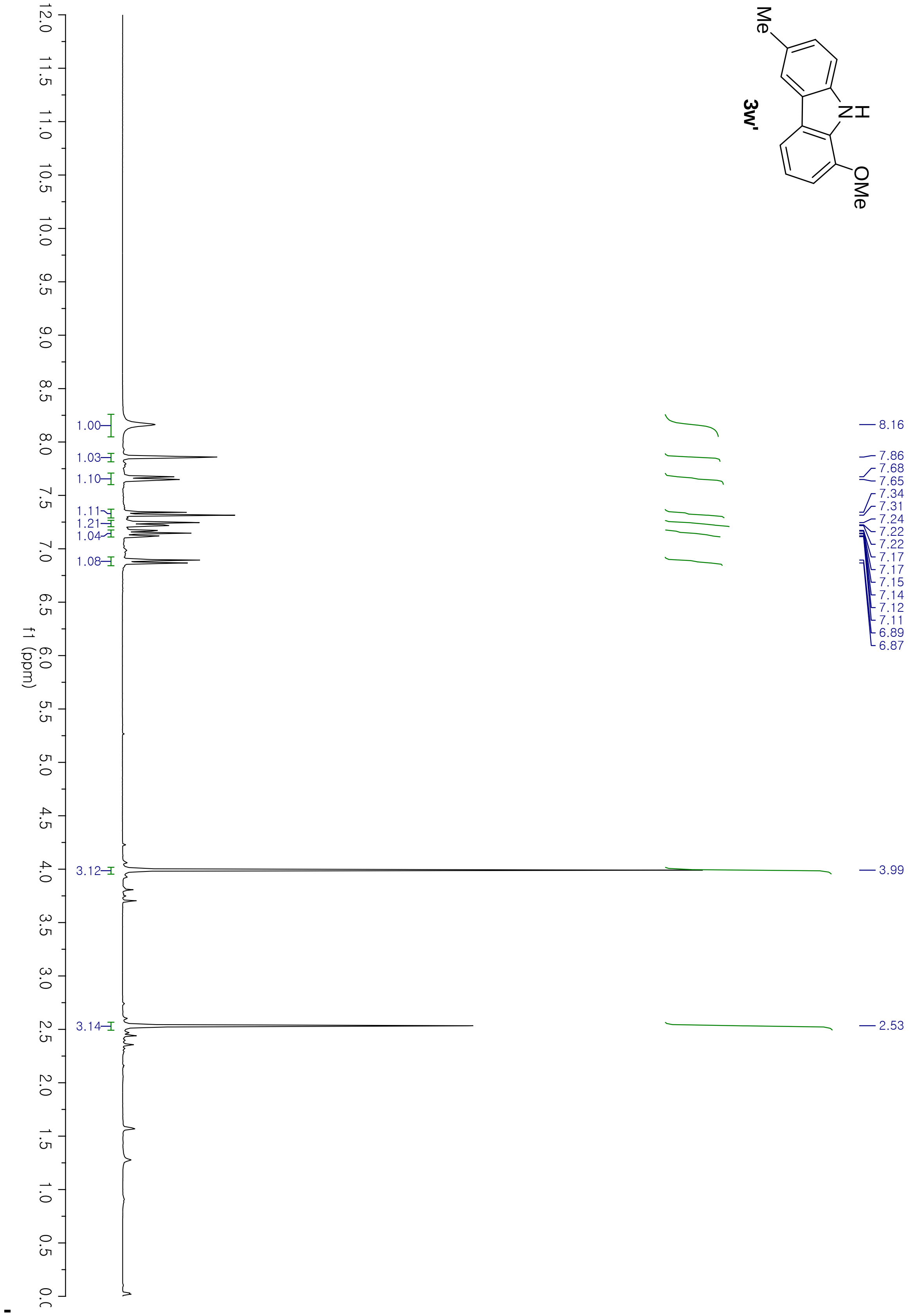
50
40
30
20
10
0



3w'
Me
N
H
OMe
8.16
7.86
7.68
7.65
7.34
7.31
7.24
7.22
7.22
7.17
7.17
7.15
7.14
7.12
7.11
6.89
6.87
3.99
2.53
1.00
1.03
1.10
1.11
1.21
1.04
1.08
3.12
3.14
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11.5
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6.5
6.0
5.5
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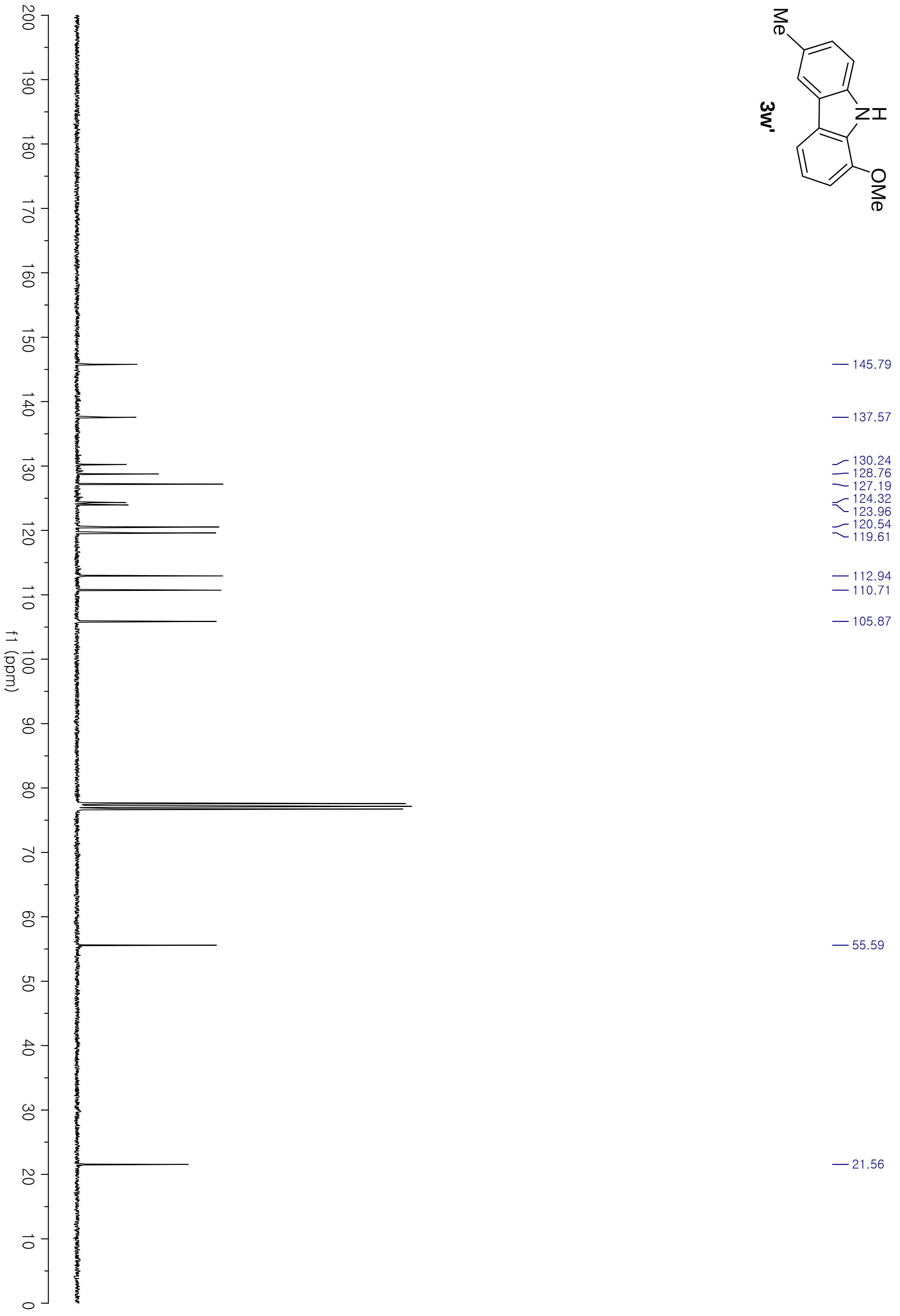
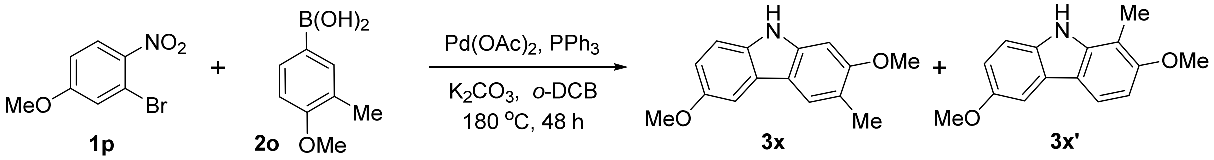
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3w'
Me
H
N
OMe
145.79
137.57
130.24
128.76
127.19
124.32
123.96
120.54
119.61
112.94
110.71
105.87
55.59
21.56
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Glycozolidine (3x) and 2,6-Dimethoxy-1-methyl-*9H*-carbazole (3x')



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 2-bromo-4-methoxy-1-nitrobenzene **1p** (116 mg, 0.5 mmol, 100 mol%), (4-methoxy-3-methylphenyl)boronic acid **2o** (110 mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 2-bromo-4-methoxy-1-nitrobenzene **1p**). The mixture was heated at 180 °C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3x** as a white solid (56mg, 46% yield) and **3x'** as a white solid (27mg, 22% yield). ^{1}H and ^{13}C NMR data were consistent with literature values.[15]

Glycozolidine (3x)

TLC (SiO_2): $R_f = 0.25$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.56 (s, 1H), 7.46 (d, J = 2.2 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 6.96 (dd, J = 8.6, 2.3 Hz, 1H), 6.63 (s, 1H), 3.92 (s, 3H), 3.83 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.50, 153.90, 140.10, 134.23, 123.96, 121.47, 118.98, 116.17, 113.10, 111.10, 102.53, 92.53, 56.14, 55.52, 16.87.

FTIR (neat) υ 3389, 3066, 1787, 1637, 1509, 1365, 1270 cm^{-1}.

LRMS *m*/*z* (EI): 242.3 (M^++1), 241.3, 227.2, 226.3, 198.2, 183.2, 154.1.

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[15] C. Schuster, C. Boerger, K. K. Julich-Gruner, R. Hesse, A. Jaeger, G. Kaufmann, A. W. Schmidt and H.-J. Knoelker, *Eur. J. Org. Chem.*, 2014, 4741-4752.

2,6-Dimethoxy-1-methyl-*9H*-carbazole (3x')

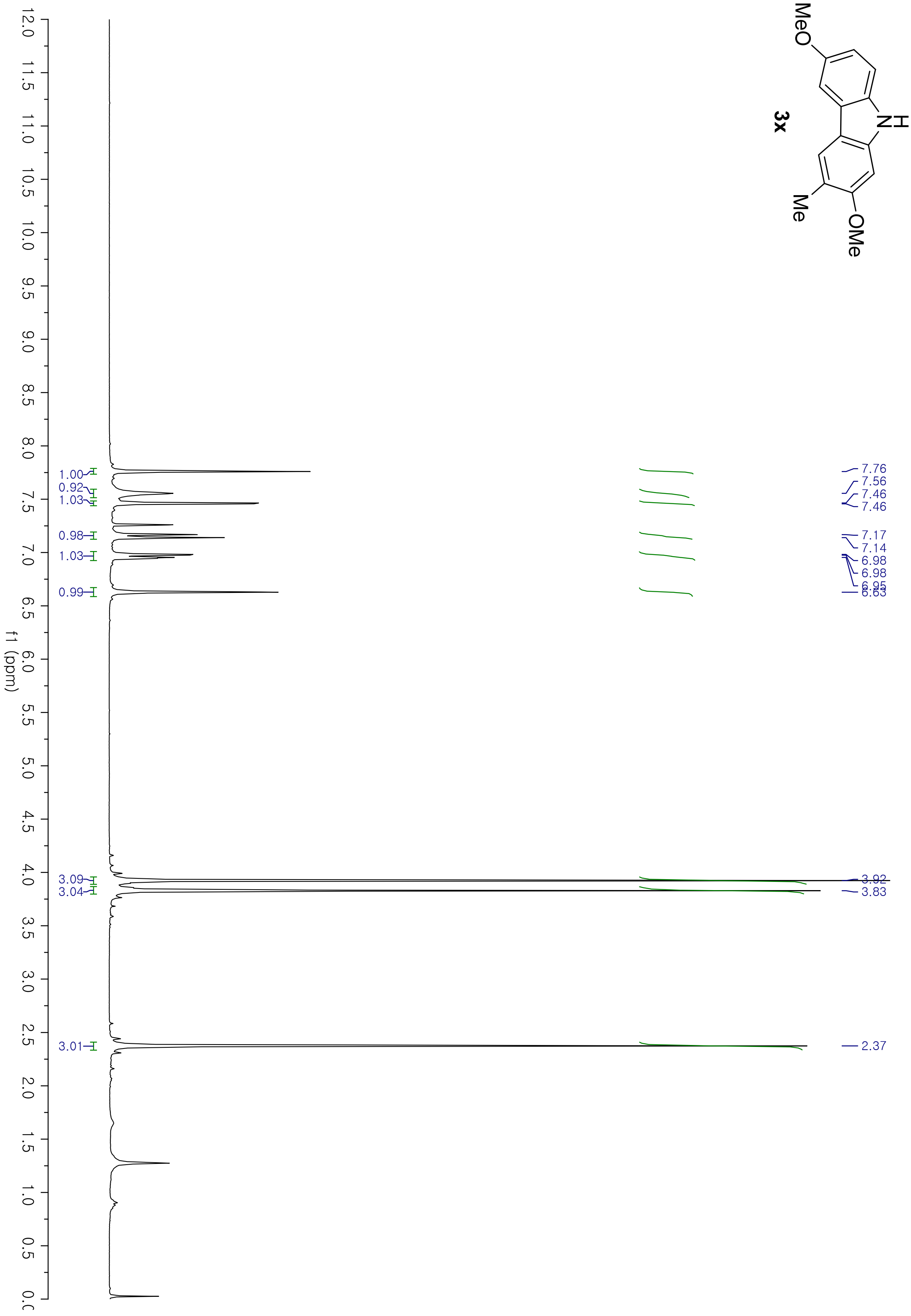
TLC (SiO_2): $R_f = 0.25$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, DMSO) δ 10.76 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 6.91 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 2.33 (s, 3H).

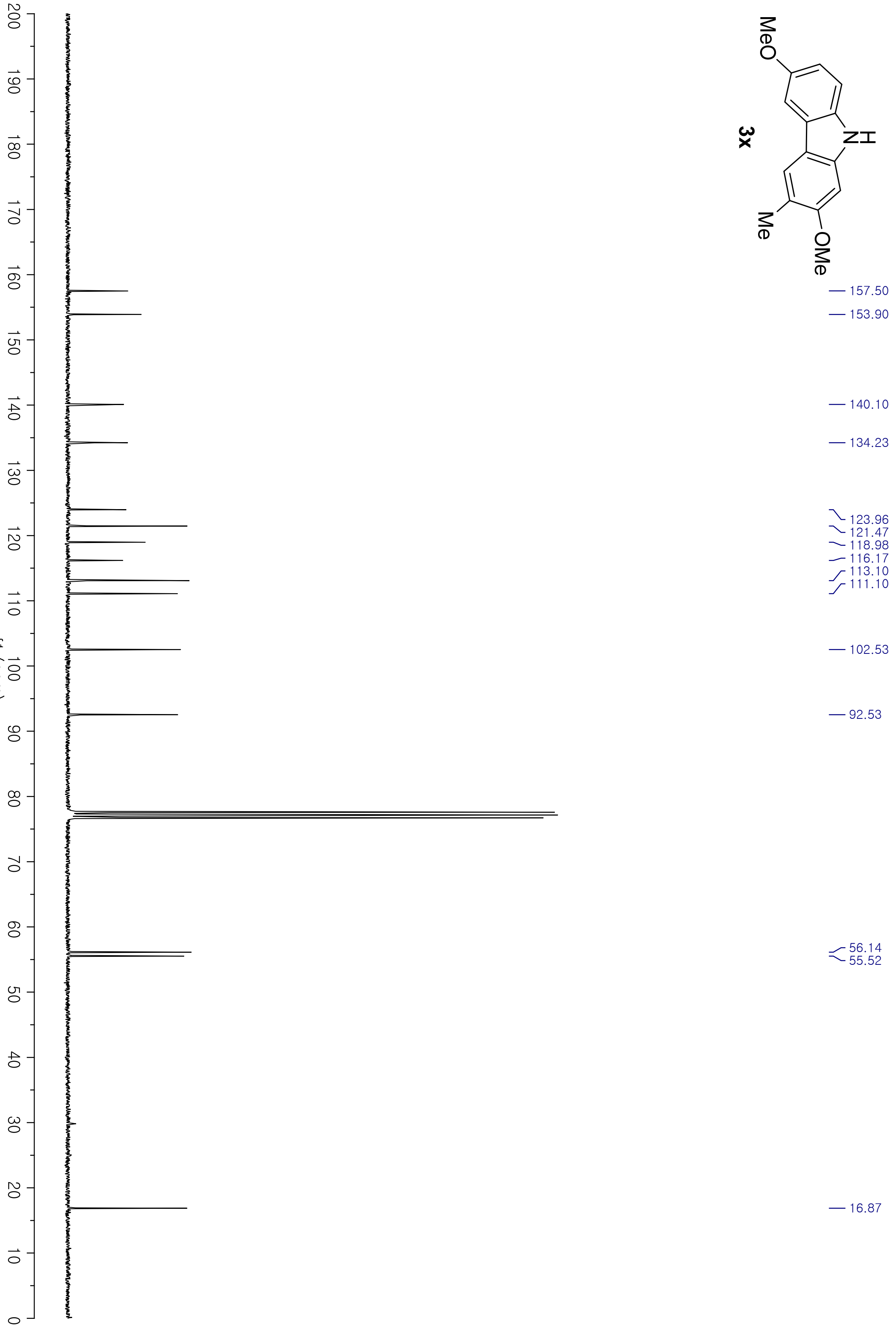
^{13}C NMR (75 MHz, DMSO). δ 155.44, 153.04, 141.29, 135.08, 123.59, 117.97, 116.79, 113.20, 111.23, 106.54, 103.49, 102.67, 56.08, 55.56, 10.24.

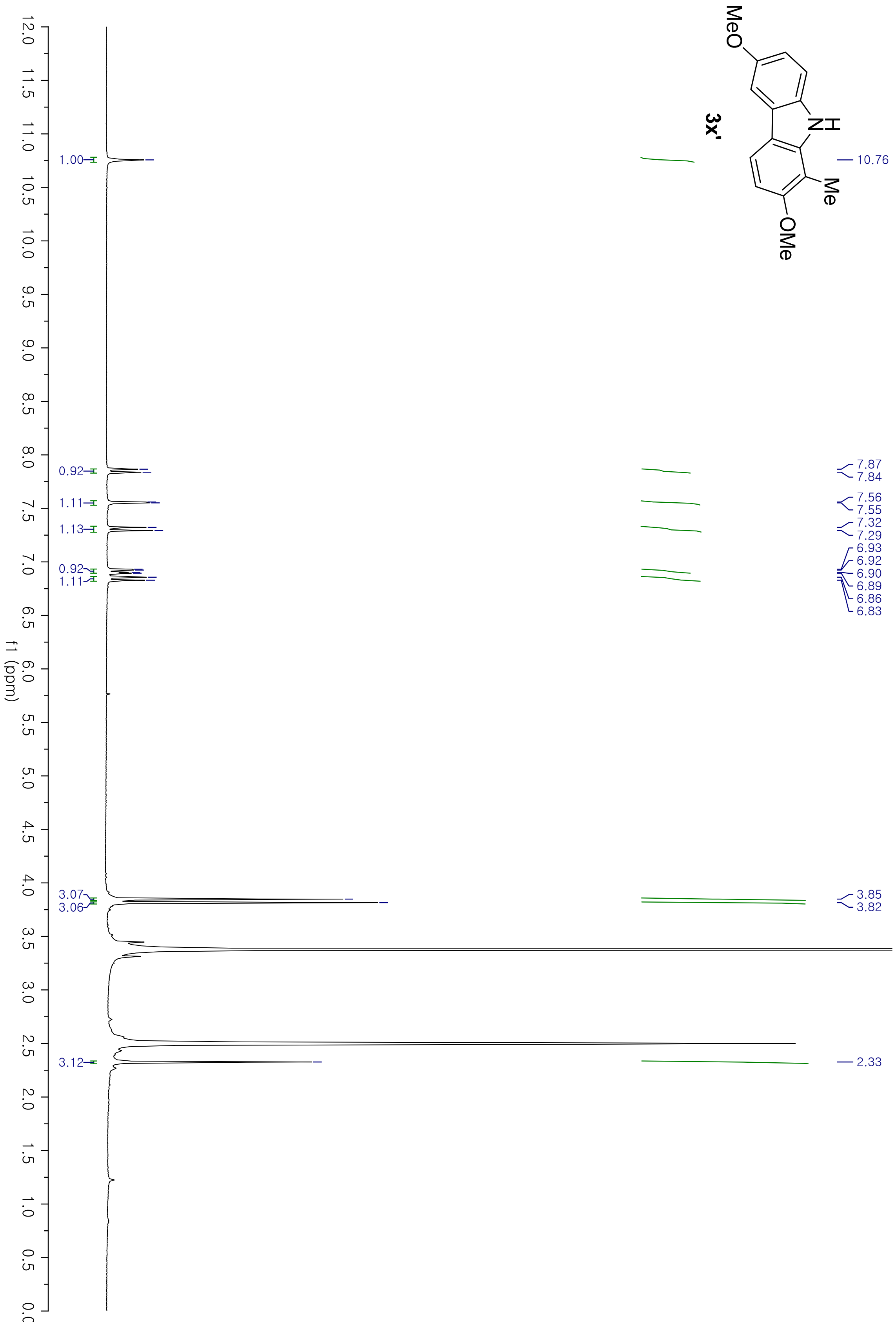
FTIR (neat) υ 3389, 3066, 1787, 1637, 1509, 1365, 1270 cm^{-1}.

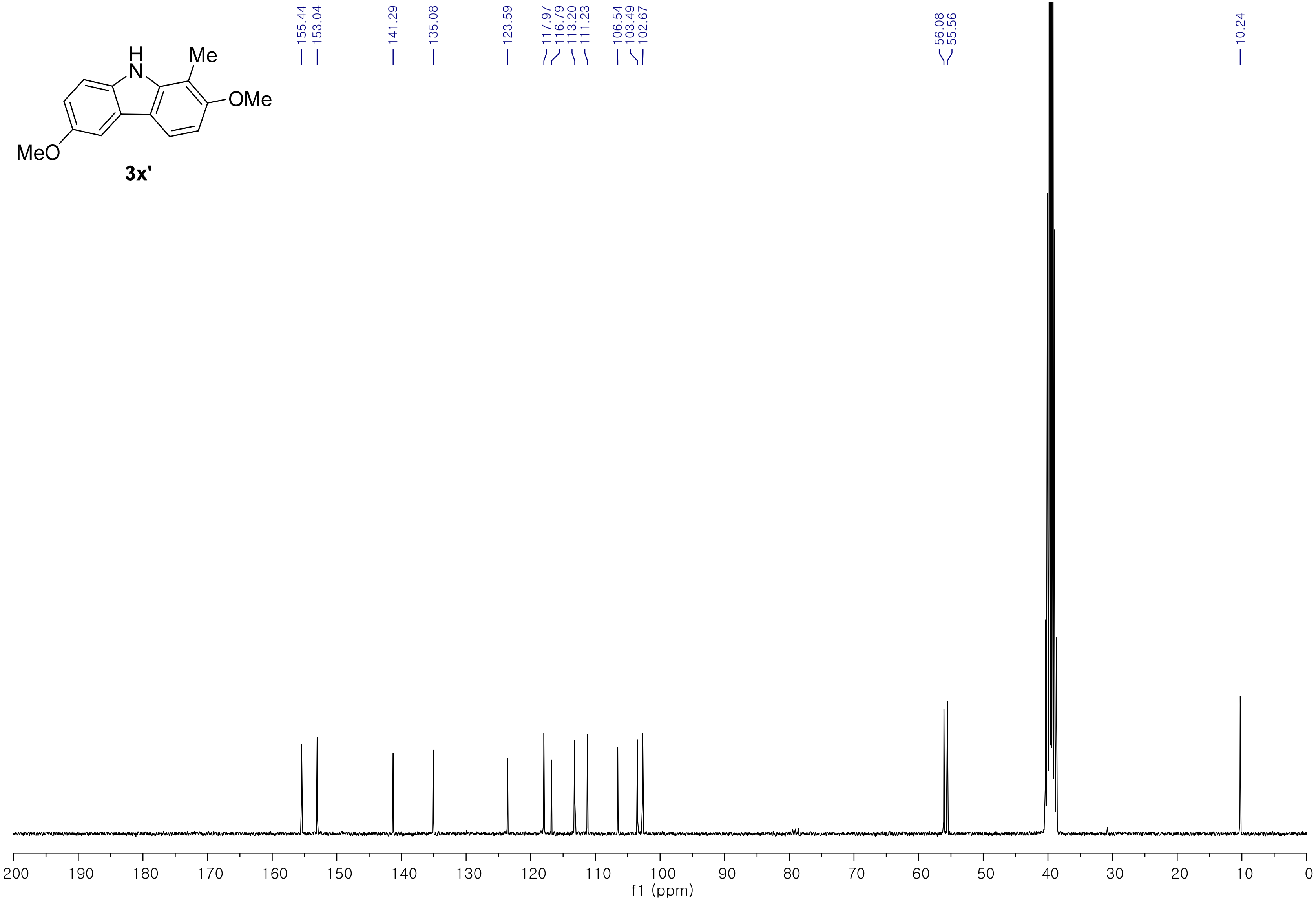
LRMS *m*/*z* (EI): 242.3 (M^++1), 241.3, 227.2, 226.3, 198.2, 197.2, 183.2, 154.1.


MeO
H
N
Me
OMe
7.76
7.56
7.46
7.46
7.17
7.14
6.98
6.98
6.95
6.63
3.92
3.83
2.37
1.00
0.92
1.03
0.98
1.03
0.99
3.09
3.04
3.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

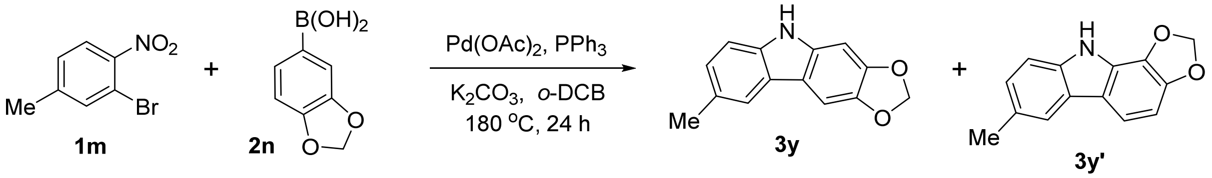
3x


MeO
N
H
3x
Me
OMe
157.50
153.90
140.10
134.23
123.96
121.47
118.98
116.17
113.10
111.10
102.53
92.53
56.14
55.52
16.87
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3x'
MeO
H
N
Me
OMe
10.76
7.87
7.84
7.56
7.55
7.32
7.29
6.93
6.92
6.90
6.89
6.86
6.83
3.85
3.82
2.33
1.00
0.92
1.11
1.13
0.92
1.11
3.07
3.06
3.12
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Me
OMe
MeO
H
N
3x'
155.44
153.04
141.29
135.08
123.59
117.97
116.79
113.20
111.23
106.54
103.49
102.67
56.08
55.56
10.24
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Calusenalene (3y) and 7-Methyl-10*H*-[1,3]dioxolo[4,5-*a*]carbazole (3y')



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added 2-bromo-4-methyl-1-nitrobenzene **1m** (108 mg, 0.5 mmol, 100 mol%), benzo[d][1,3]dioxol-5-ylboronic acid **2n** (110mg, 0.65 mmol, 130 mol%), Pd(OAc) (2.2 mg, 0.01 mmol, 2 mol%), PPh_3 (328 mg, 1.25 mmol, 250 mol %), K_2CO_3 (138 mg, 1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to 2-bromo-4-methyl-1-nitrobenzene **1m**). The mixture was heated at 180 °C (oil bath temperature) for 24 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give inseparable mixture of **3y** and **3y'** as a white solid (61 mg, 80% yield, **3y:3y'**=5.3:1 (determined by ^1H NMR and GC-Mass spectrometer)). Calusenalene **(3y)** can be separable by recrystallization from dichloromethane and hexanes. ^1H and ^{13}C NMR data were consistent with literature values.[18]

Calusenalene (3y)

TLC (SiO_2): R_f = 0.40 (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, Acetone) δ 10.09 (s, 1H), 7.76 (s, 1H), 7.50 (s, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.09 (dd, J = 8.2, 1.2 Hz, 1H), 6.98 (s, 1H), 6.00 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (75 MHz, Acetone) δ 147.94, 142.82, 139.11, 136.64, 128.26, 126.07, 124.45, 119.77, 116.76, 111.26, 101.66, 99.82, 92.85, 21.48.

FTIR (neat) : υ 3400, 3009, 1728, 1366, 1219, 1093, 533 cm^{-1}.

LRMS *m*/*z* (EI): 225.9 (M^++1), 225.2.

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[18] S. Rasheed, D. N. Rao, K. R. Reddy, S. Aravinda, R. A. Vishwakarma and P. Das, *RSC Adv.*, 2014, **4**, 4960-4969.

7-Methyl-10*H*-[1,3]dioxolo[4,5-*a*]carbazole (3y')

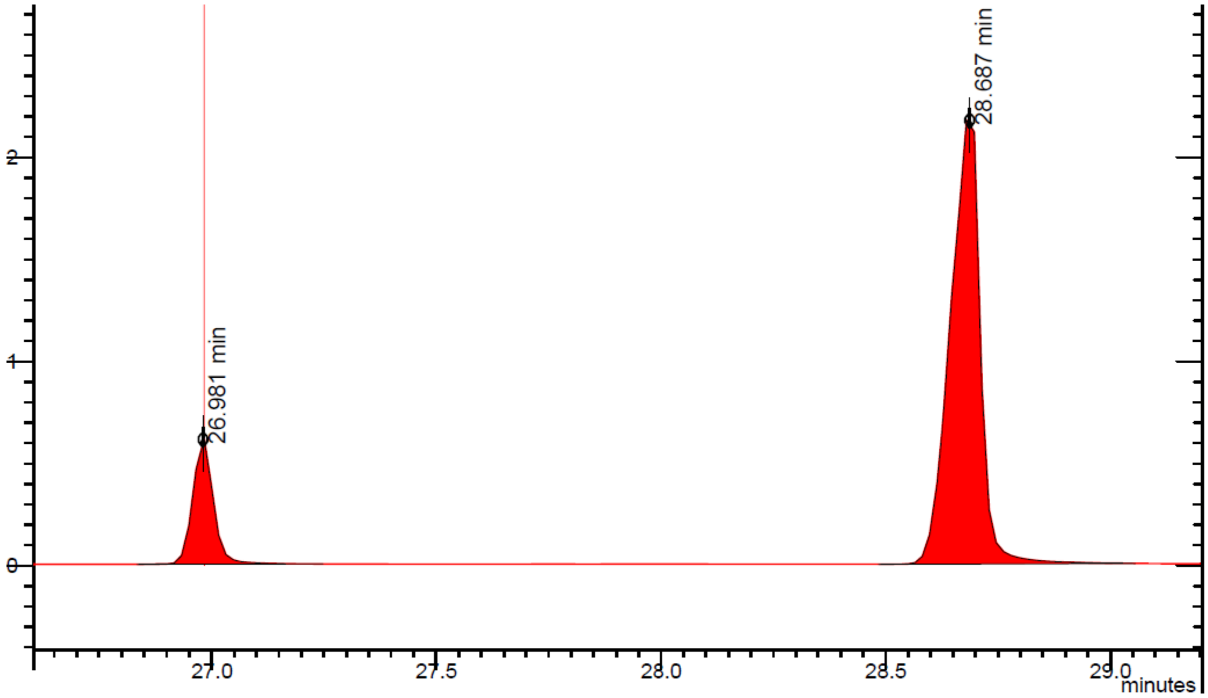
TLC (SiO_2): $R_f = 0.40$ (acetone:hexanes, 1:5).

^{1}H NMR (300 MHz, Acetone) δ 10.17 (s, 1H), 7.81 (s, J = 0.6 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.17 (dd, J = 8.2, 1.2 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.07 (s, 2H), 2.46 (s, 3H).

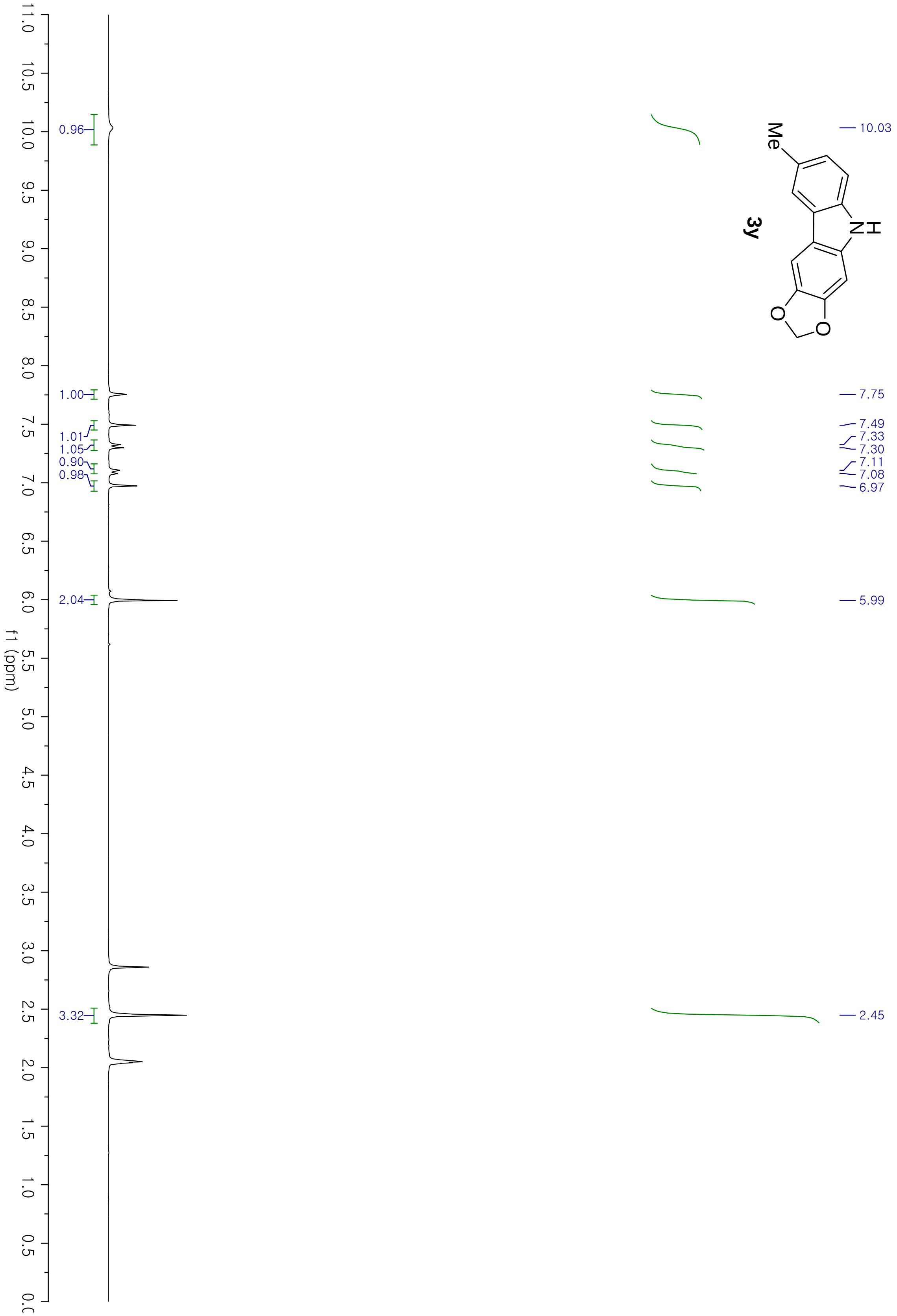
FTIR (neat) : υ 3400, 3009, 1728, 1366, 1219, 1093, 533 cm^{-1}.

LRMS *m*/*z* (EI): 225.9 (M^++1), 225.2.

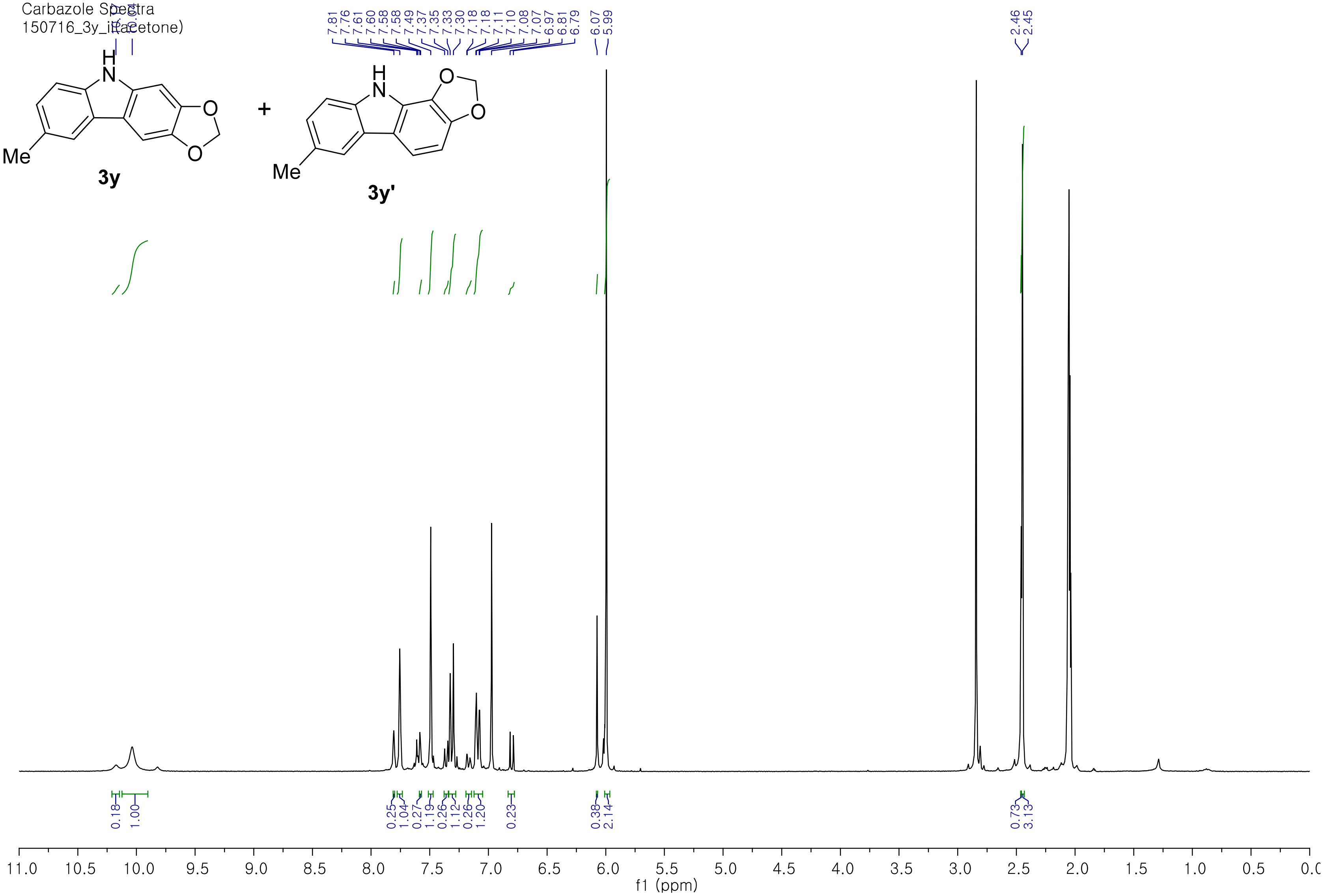
GC: (Varian 450-GC, SPB^{TM}-680 (30 m x 0.25 mm x 0.25 μm), T_0 : 60 ^{o}C (hold 4 min), T_1 : Ramp, 250 ^{o}C at 10 ^{o}C/min, Carrier: He (1.0 mL/min), Total time 60 min), $t_{\mathbf{3y'}}$ = 26.98 min, $t_{\mathbf{3y}}$ = 28.69 min, Ratio (**3y:3y'** = 5.3:1).

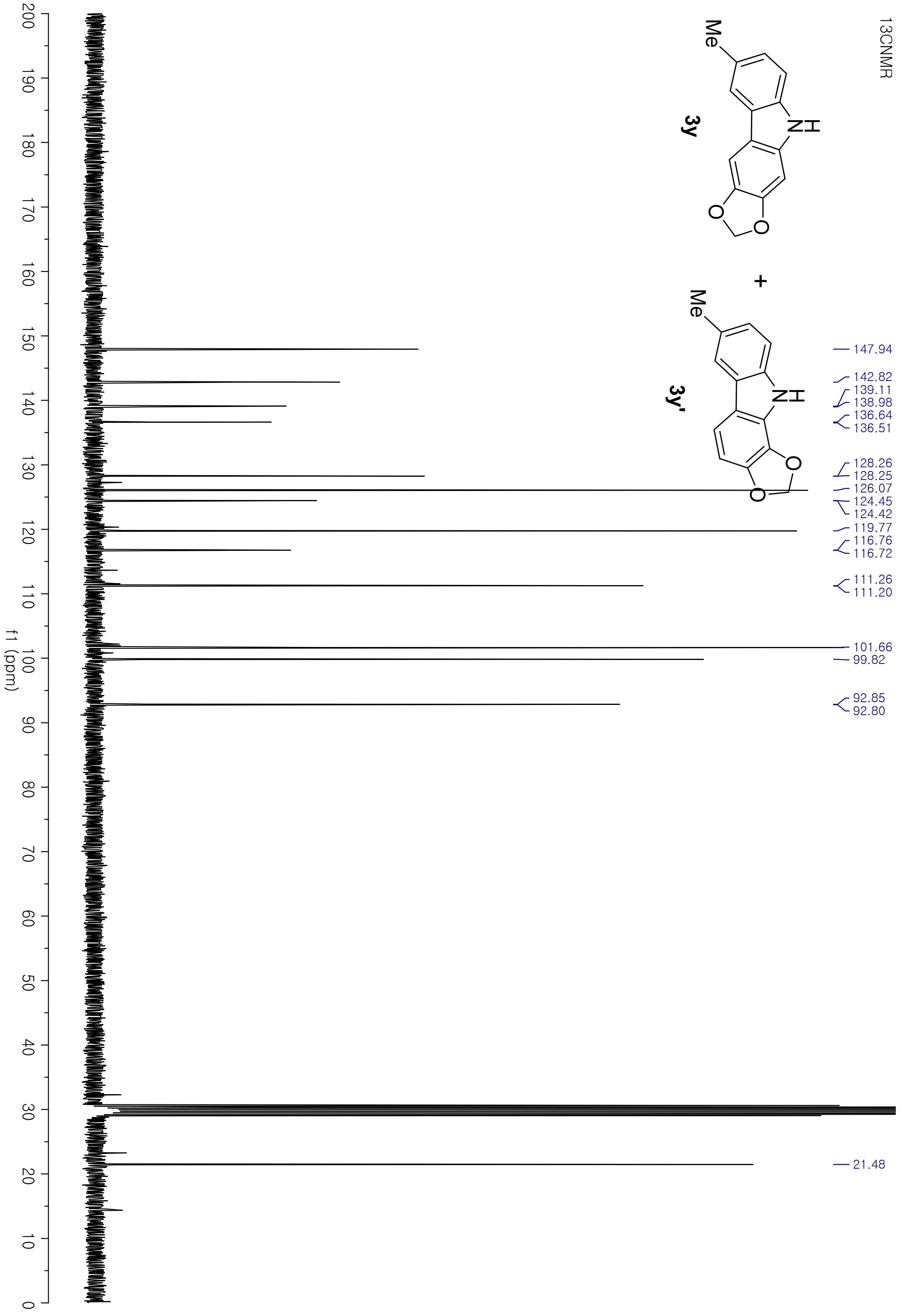


	Retention Time	Area	% of Total	Signal/Noise	Scan Description
2.	26.981	1.908e+6	15.823	1379	Merged
4.	28.687	1.011e+7	83.846	5406	Merged

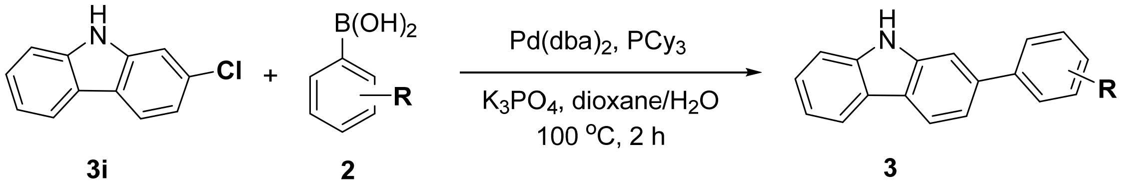

3y
Me
N
H
O
O
10.03
7.75
7.49
7.33
7.30
7.11
7.08
6.97
5.99
2.45
0.96
1.00
1.01
1.05
0.90
0.98
2.04
3.32
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

Carbazole Spectra
150716_3y_ii(acetone)



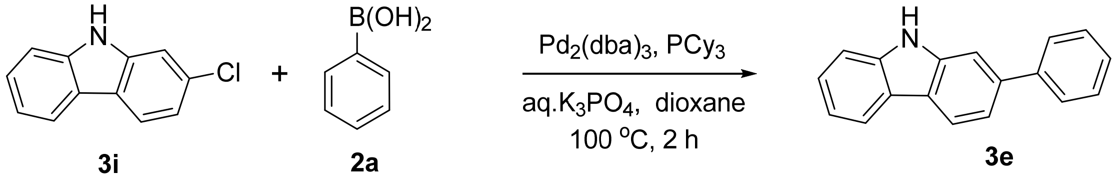

13CNMR
Me
NH
O
O
3y
+
Me
NH
O
O
3y'
147.94
142.82
139.11
138.98
136.64
136.51
128.26
128.25
126.07
124.45
124.42
119.77
116.76
116.72
111.26
111.20
101.66
99.82
92.85
92.80
21.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

General Procedure for Suzuki coupling of 3-chlorocarbazole (3i)



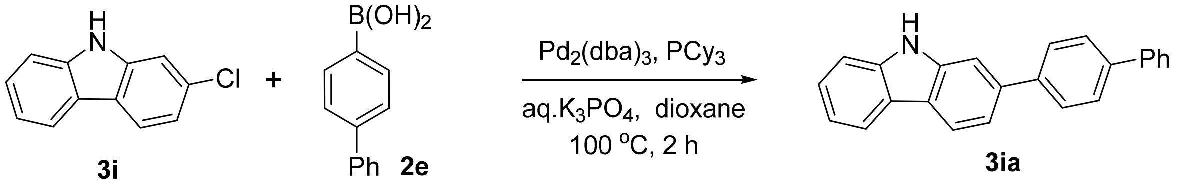
To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were 2-chloro-*9H*-carbazole **3i** (0.1 mmol, 100 mol%), aryl boronic acid **2** (0.15 mmol, 150 mol%), $Pd_2(dba)_3$ (0.01 mmol, 10 mol%), PCy_3 (0.25 mmol, 25 mol %), K_3PO_4 (1.27 M in water, 0.34 mmol) and dioxane (2 mL, 00.5 M concentration with respect to 2-chloro-*9H*-carbazole **3i**). The slurry was sealed and purged with Argon gas for 5 minutes. The mixture was heated at 100 ^oC (oil bath temperature) for 2 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture, treated with saturated sodium bicarbonate solution, and extracted with dichloromethane (3x). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated *in vacuo* and purified by flash column chromatography (SiO_2) and recrystallization from dichloromethane and hexanes under the conditions noted to furnish the corresponding product.

2-phenyl-9H-carbazole (3e)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were 2-chloro-*9H*-carbazole **3i** (20 mg, 0.1 mmol, 100 mol%), phenylboronic acid **2a** (18.3 mg, 0.15 mmol, 150 mol%), $Pd_2(dba)_3$ (9 mg, 0.01 mmol, 10 mol%), PCy_3 (7 mg, 0.25 mmol, 25 mol %), K_3PO_4 (1.27 M in water, 0.27 mL, 0.34 mmol) and dioxane (2 mL, 0.05 M concentration with respect to 2-chloro-*9H*-carbazole **3i**). The slurry was sealed and purged with Argon gas for 5 minutes. The mixture was heated at 100 °C (oil bath temperature) for 2 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture, treated with saturated sodium bicarbonate solution, and extracted with dichloromethane (3x). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% ethyl acetate in hexanes as eluant to give **3e** as a white solid (21.2 mg, 87% yield)

2-([1,1'-Biphenyl]-4-yl)-9*H*-carbazole (3ia)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were 2-chloro-9*H*-carbazole **3i** (20 mg, 0.1 mmol, 100 mol%), [1,1'-biphenyl]-4-ylboronic acid **2e** (30 mg, 0.15 mmol, 150 mol%), $Pd_2(dba)_3$ (9 mg, 0.01 mmol, 10 mol%), PCy_3 (7 mg, 0.25 mmol, 25 mol %), K_3PO_4 (1.27 M in water, 0.27 mL, 0.34 mmol) and dioxane (2 mL, 0.05 M concentration with respect to 2-chloro-9*H*-carbazole **3i**). The slurry was sealed and purged with Argon gas for 5 minutes. The mixture was heated at 100 °C (oil bath temperature) for 2 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture, treated with saturated sodium bicarbonate solution, and extracted with dichloromethane (3x). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated *in vacuo* and purified by recrystallization from dichloromethane and hexanes to give **3ia** as a white solid (23 mg, 72% yield).

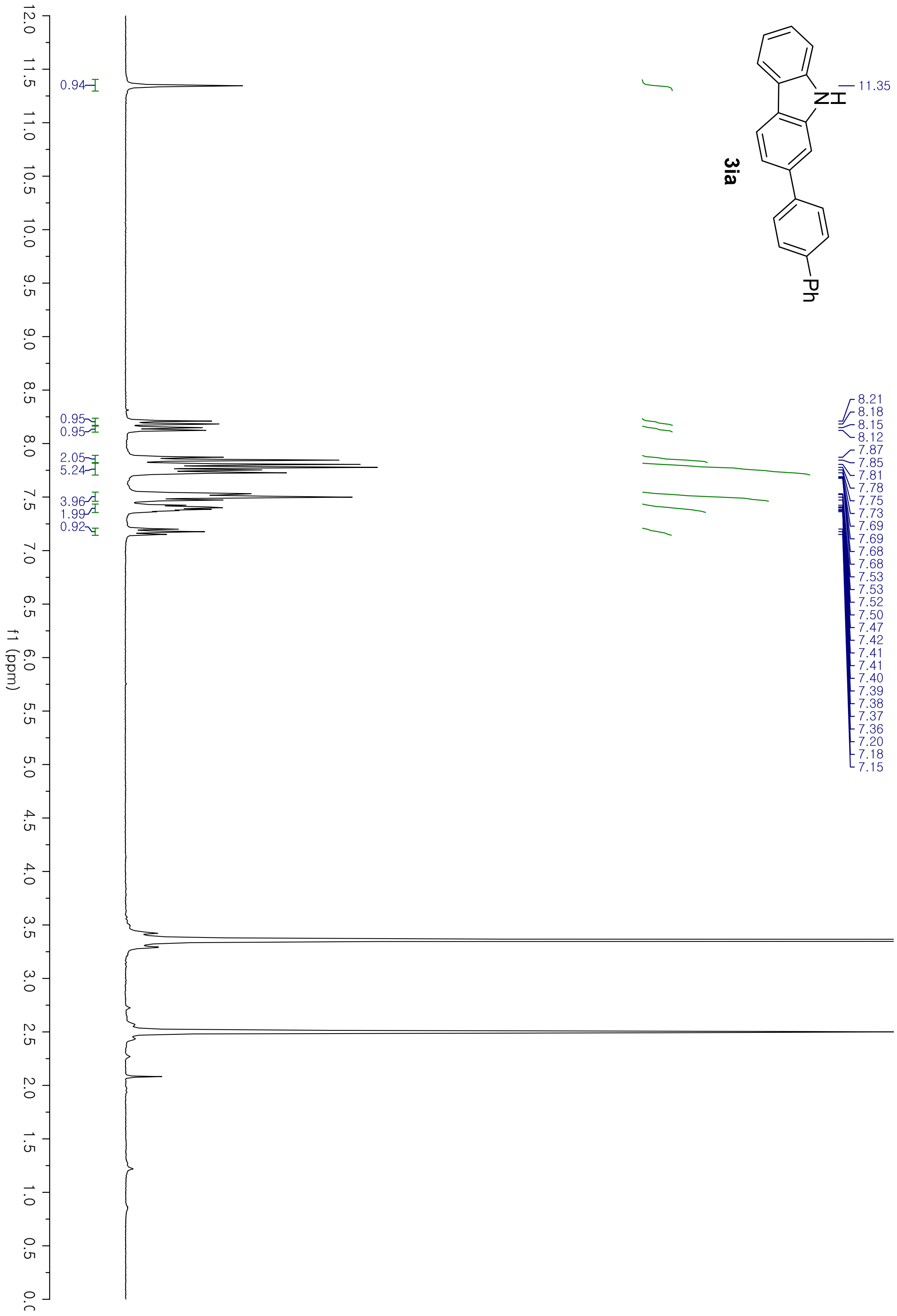
TLC (SiO_2): $R_f = 0.38$ (ethyl acetate:hexanes, 1:5)

^{1}H NMR (300 MHz, DMSO) 1H NMR (300 MHz, DMSO) δ 11.35 (s, 1H), 8.20 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.85 (s, 1H), 7.82 – 7.71 (m, 5H), 7.55 – 7.46 (m, 4H), 7.44 – 7.36 (m, 2H), 7.18 (t, J = 7.4 Hz, 1H).

^{13}C NMR (75 MHz, DMSO) δ 140.41, 140.33, 140.20, 139.70, 138.77, 137.20, 129.03, 127.50, 127.21, 126.56, 125.70, 122.19, 121.94, 120.70, 120.30, 118.74, 117.72, 111.03, 108.74.

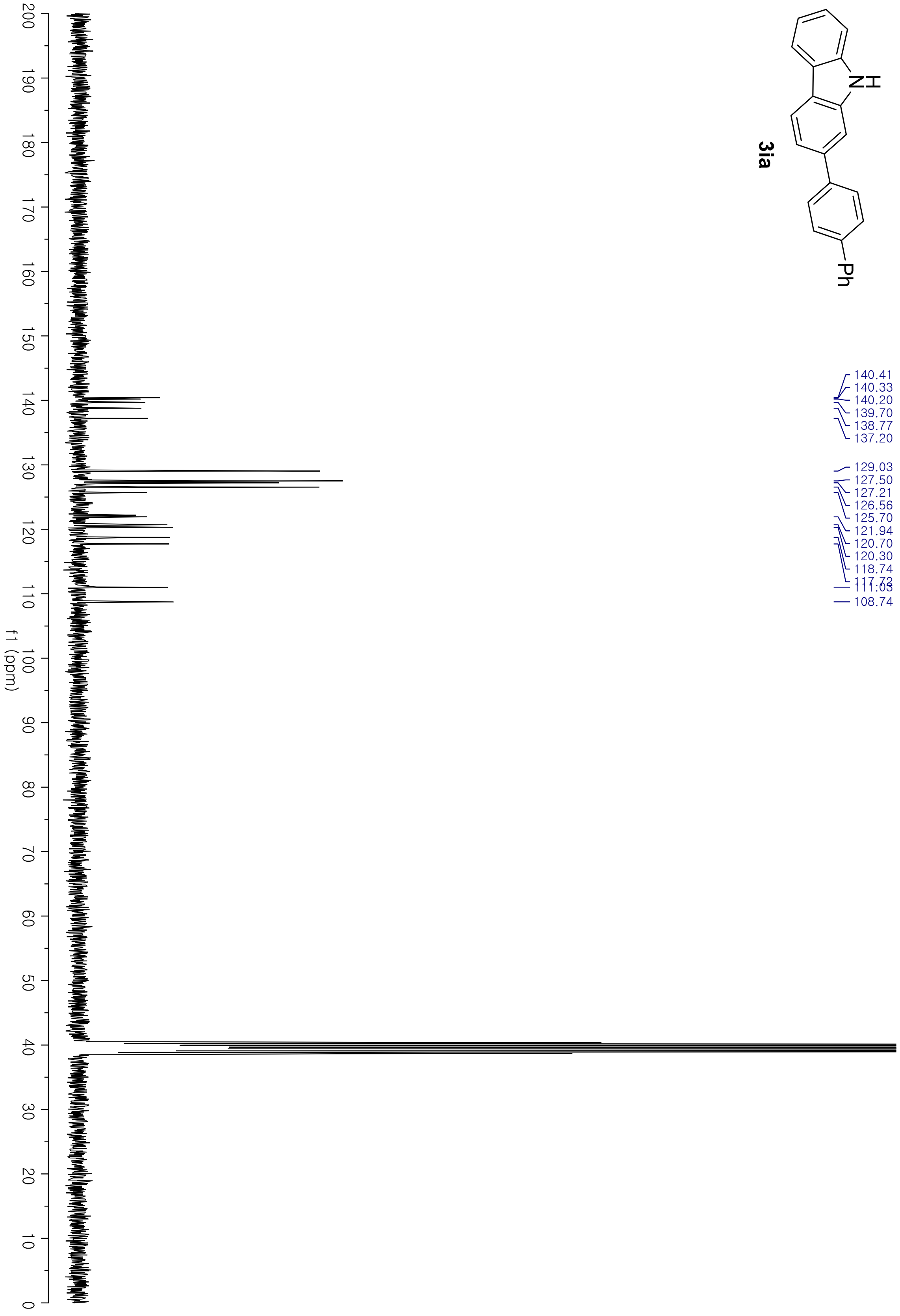
FTIR (neat) υ 3403, 3101, 1753, 1691, 1530, 1368, 1206, 763 cm^{-1}

HRMS *m*/*z* (EI): calcd. For $C_{24}H_{17}N$ (M^+) 319.1361, found 319.1360.

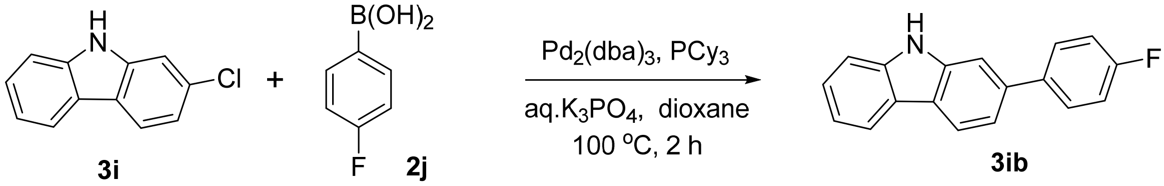


3ia

NH
Ph
11.35
8.21
8.18
8.15
8.12
7.87
7.85
7.81
7.78
7.75
7.73
7.69
7.69
7.68
7.68
7.53
7.53
7.52
7.50
7.47
7.42
7.41
7.41
7.40
7.39
7.38
7.37
7.36
7.20
7.18
7.15
0.94
0.95
0.95
2.05
5.24
3.96
1.99
0.92
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3ia
NH
Ph
140.41
140.33
140.20
139.70
138.77
137.20
129.03
127.50
127.21
126.56
125.70
121.94
120.70
120.30
118.74
117.72
111.03
108.74
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-(4-Fluorophenyl)-9*H*-carbazole (3ib)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were 2-chloro-9*H*-carbazole **3i** (20 mg, 0.1 mmol, 100 mol%), (4-fluorophenyl)boronic acid **2j** (21 mg, 0.15 mmol, 150 mol%), $Pd_2(dba)_3$ (9 mg, 0.01 mmol, 10 mol%), PCy_3 (7 mg, 0.25 mmol, 25 mol %), K_3PO_4 (1.27 M in water, 0.27 mL, 0.34 mmol) and dioxane (2 mL, 0.05 M concentration with respect to 2-chloro-9*H*-carbazole **3i**). The slurry was sealed and purged with Argon gas for 5 minutes. The mixture was heated at 100 °C (oil bath temperature) for 2 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture, treated with saturated sodium bicarbonate solution, and extracted with dichloromethane (3x). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated *in vacuo* and purified by flash column chromatography (SiO_2) using 5% ethyl acetate in hexanes as eluant to give **3ib** as a yellow solid (23 mg, 88% yield).

TLC (SiO_2): $R_f = 0.35$ (ethyl acetate:hexanes, 1:5)

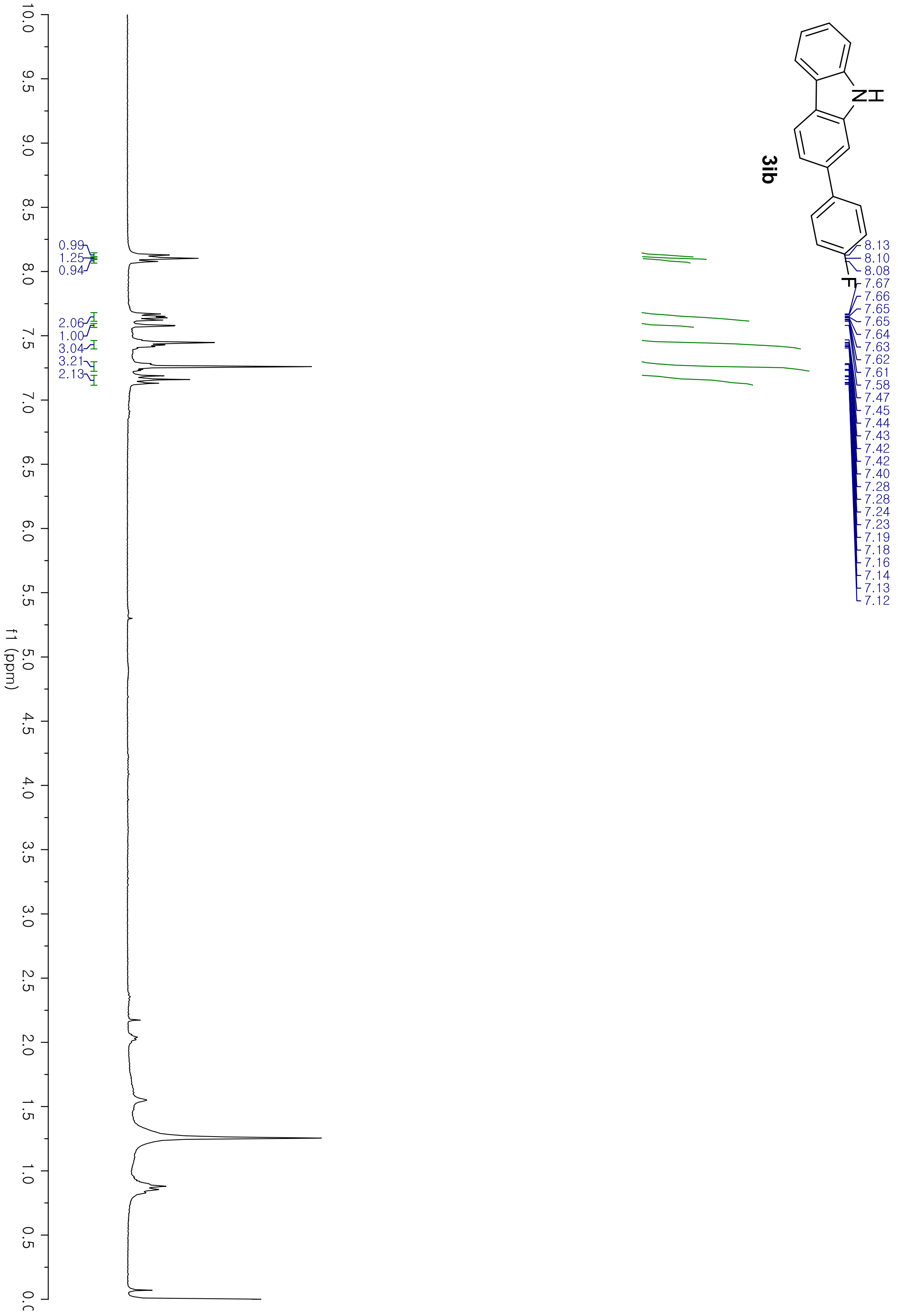
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 1H), 8.10 (s, 1H) 8.09 (d, J = 7.4 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.58 (s, 1H), 7.46 – 7.40 (m, 3H), 7.30 – 7.22 (m, 1H), 7.19 – 7.11 (m, 2H).

^{13}C NMR (75 MHz, Acetone) δ 163.17 (d, J = 243.9 Hz), 141.61, 141.56, 139.27 (d, J = 3.2 Hz), 138.56, 129.87 (d, J = 8.0 Hz), 126.59, 123.71, 123.33, 121.34, 121.00, 119.91, 119.11, 116.33 (d, J = 21.5 Hz), 111.80, 109.96.

FTIR (neat) υ 3400, 1650, 1367, 1223, 724 cm^{-1}

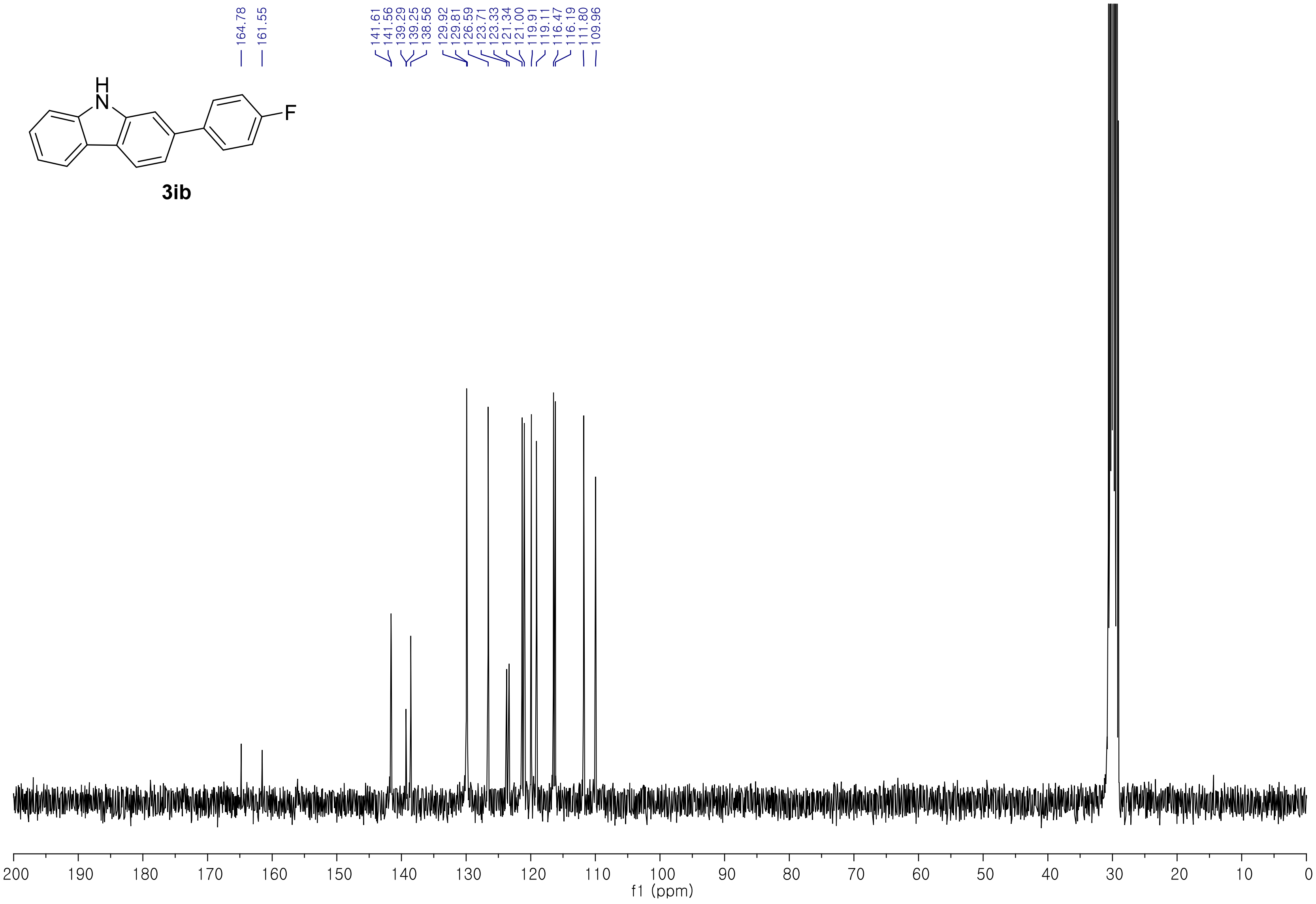
LRMS *m*/*z* (EI): 262.2 (M^++1), 262.2.

HRMS *m*/*z* (EI): calcd. For $C_{18}H_{12}FN$ (M^+) 261.0954, found 261.0953.

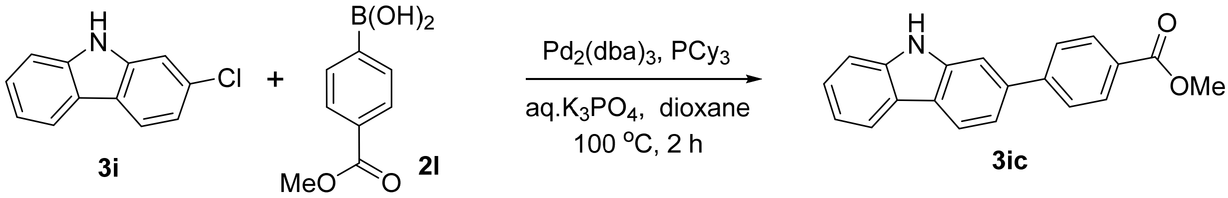


3ib

H
N
F
8.13
8.10
8.08
7.67
7.66
7.65
7.65
7.64
7.63
7.62
7.61
7.58
7.47
7.45
7.44
7.43
7.42
7.42
7.40
7.28
7.28
7.24
7.23
7.19
7.18
7.16
7.14
7.13
7.12
0.99
1.25
0.94
2.06
1.00
3.04
3.21
2.13
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)


3ib
N
H
F
164.78
161.55
141.61
141.56
139.29
139.25
138.56
129.92
129.81
126.59
123.71
123.33
121.34
121.00
119.91
119.11
116.47
116.19
111.80
109.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Methyl 4-(9*H*-carbazol-2-yl)benzoate (3ic)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were 2-chloro-*9H*-carbazole **3i** (20 mg, 0.1 mmol, 100 mol%), (4-(methoxycarbonyl)phenyl)boronic acid **2l** (27 mg, 0.15 mmol, 150 mol%), $Pd_2(dba)_3$ (9 mg, 0.01 mmol, 10 mol%), PCy_3 (7 mg, 0.25 mmol, 25 mol %), K_3PO_4 (1.27 M in water, 0.27 mL, 0.34 mmol) and dioxane (2 mL, 0.05 M concentration with respect to 2-chloro-*9H*-carbazole **3i**). The slurry was sealed and purged with Argon gas for 5 minutes. The mixture was heated at 100 °C (oil bath temperature) for 2 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture , treated with saturated sodium bicarbonate solution, and extracted with dichloromethane (3x). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated *in vacuo* and purified by recrystallization from dichloromethane and hexanes to give **3ic** as a white solid (21 mg, 70% yield).

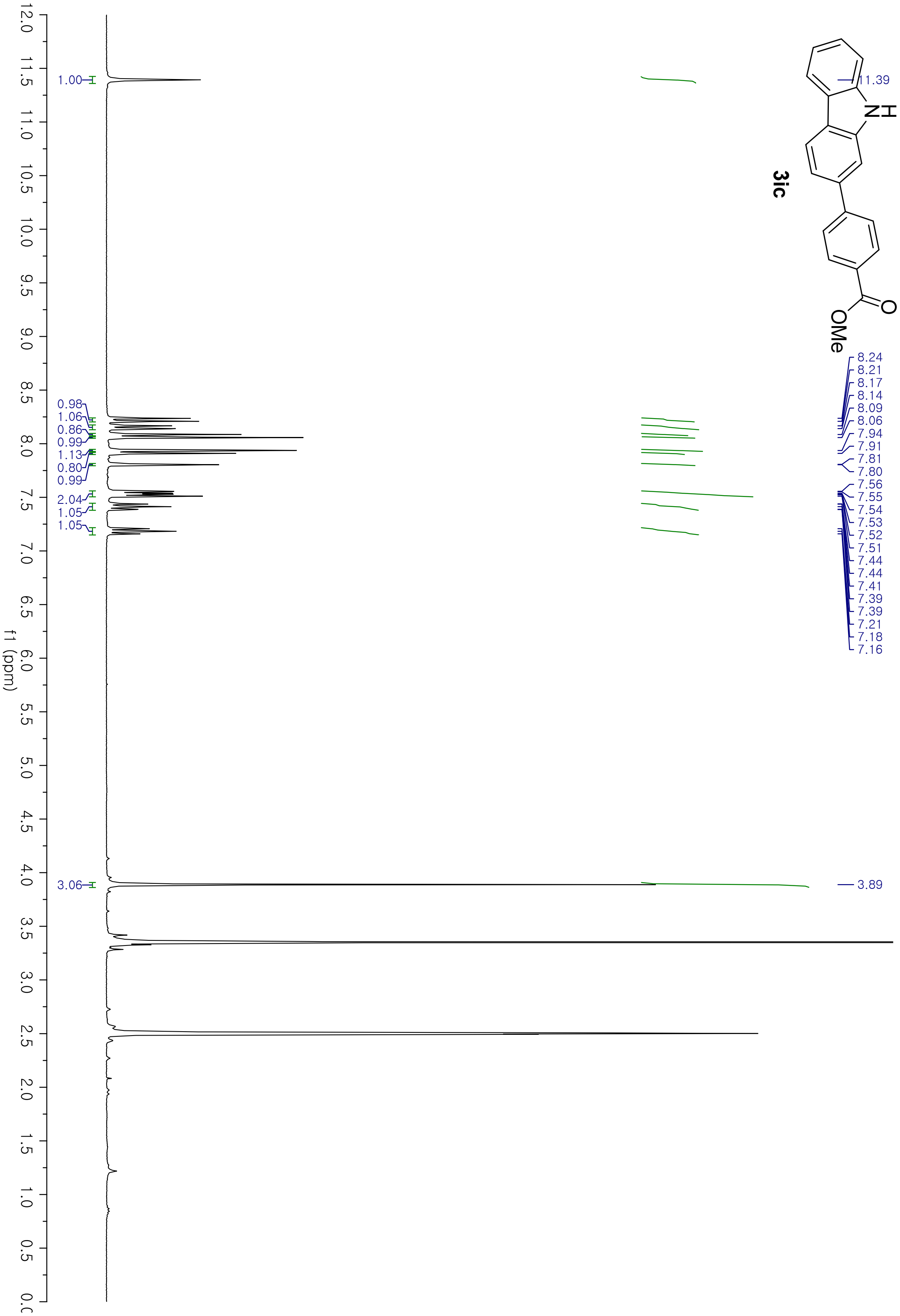
TLC (SiO_2): $R_f = 0.29$ (ethyl acetate:hexanes, 1:6)

^{1}H NMR (300 MHz, DMSO) δ 11.39 (s, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 7.7 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 1.3 Hz, 1H), 7.54 (dd, J = 8.2, 1.5 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.41 (td, J = 8.1, 0.9 Hz, 1H), 7.18 (td, J = 7.7, 0.5 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 166.18, 145.77, 140.47, 140.28, 136.26, 129.86, 128.01, 127.21, 125.98, 122.59, 122.03, 120.83, 120.47, 118.85, 117.91, 111.11, 109.26, 52.16.

FTIR (neat) υ 3388, 2139, 1719, 1363, 1218, 1095, 702 cm^{-1}.

HRMS *m*/*z* (EI): calcd. For $C_{20}H_{15}NO_2$ (M^+) 301.1103, found 301.1103.


3ic
NH
O
OMe
11.39
8.24
8.21
8.17
8.14
8.09
8.06
7.94
7.91
7.81
7.80
7.56
7.55
7.54
7.53
7.52
7.51
7.44
7.44
7.41
7.39
7.39
7.21
7.18
7.16
3.89
1.00
0.98
1.06
0.86
0.99
1.13
0.80
0.99
2.04
1.05
1.05
3.06
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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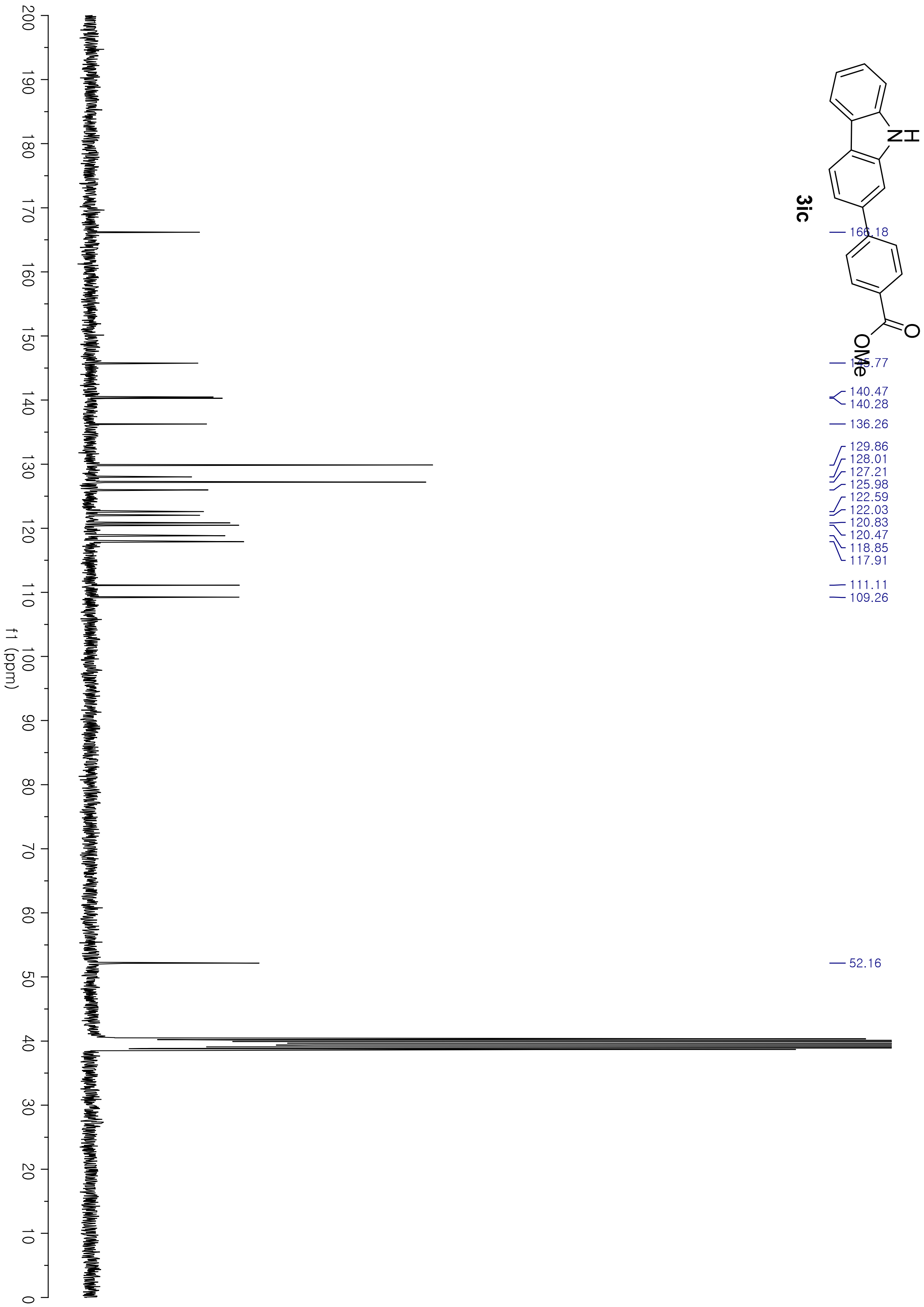
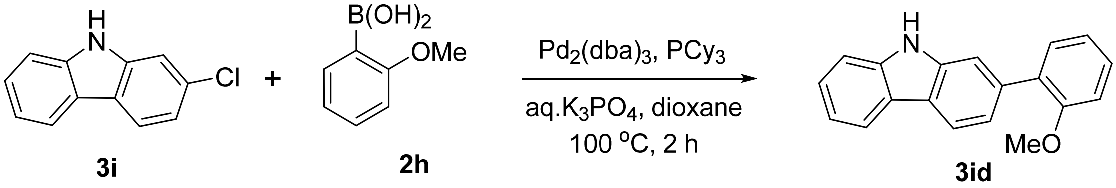


3ic

NH
O
OMe
166.18
145.77
140.47
140.28
136.26
129.86
128.01
127.21
125.98
122.59
122.03
120.83
120.47
118.85
117.91
111.11
109.26
52.16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-(2-Methoxyphenyl)-9H-carbazole (3id)



To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were 2-chloro-9*H*-carbazole **3i** (20 mg, 0.1 mmol, 100 mol%), (2-methoxyphenyl)boronic acid **2h** (23 mg, 0.15 mmol, 150 mol%), $Pd_2(dba)_3$ (9 mg, 0.01 mmol, 10 mol%), PCy_3 (7 mg, 0.25 mmol, 25 mol %), K_3PO_4 (1.27 M in water, 0.27 mL, 0.34 mmol) and dioxane (2 mL, 0.05 M concentration with respect to 2-chloro-9*H*-carbazole **3i**). The slurry was sealed and purged with Argon gas for 5 minutes. The mixture was heated at 100 °C (oil bath temperature) for 2 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture, treated with saturated sodium bicarbonate solution, and extracted with dichloromethane (3x). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated *in vacuo* and purified by recrystallization from dichloromethane and hexanes to give **3id** as a white solid (26 mg, 95% yield).

TLC (SiO_2): $R_f = 0.38$ (ethyl acetate:hexanes, 1:6)

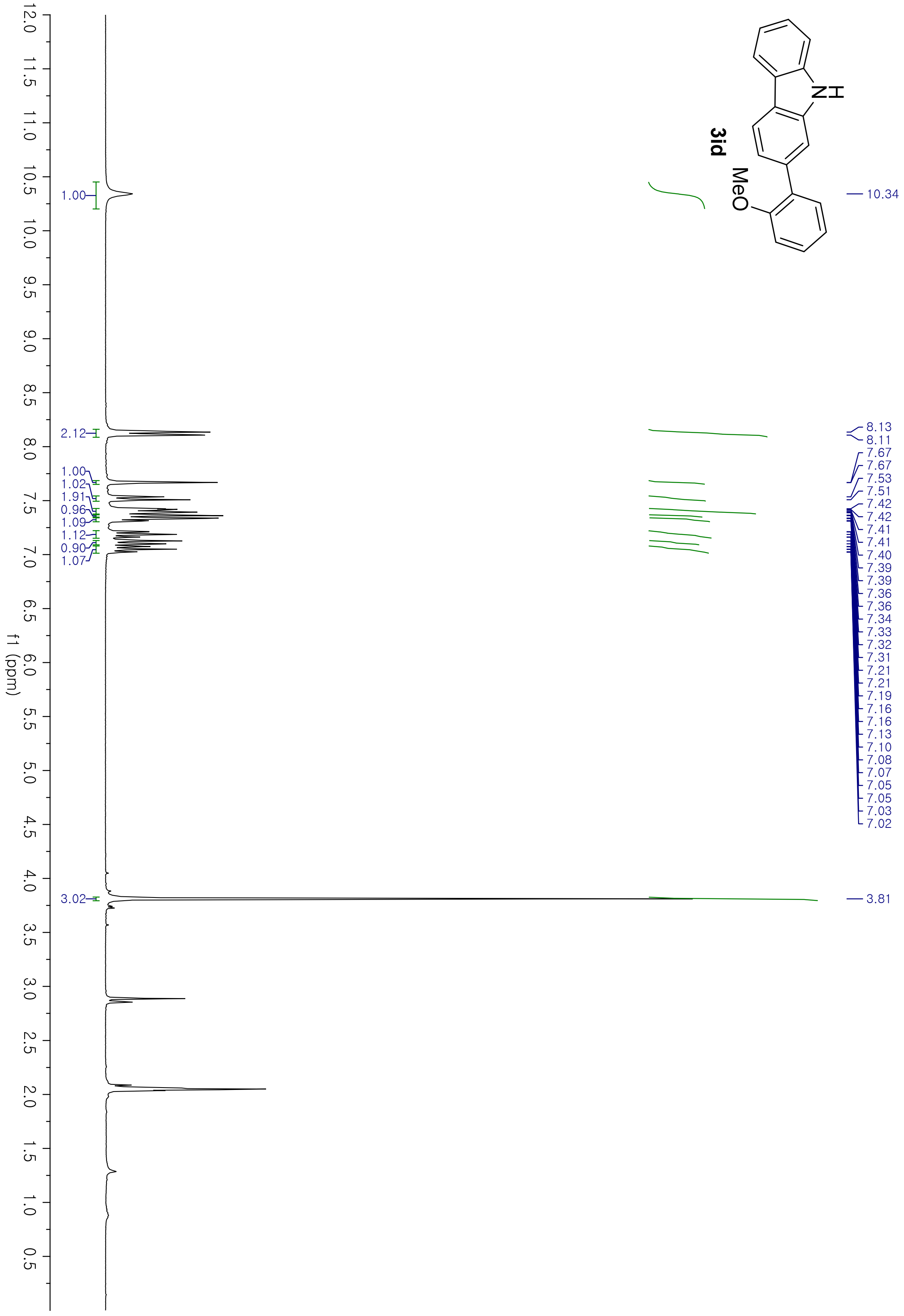
^{1}H NMR (300 MHz, Acetone) δ 10.34 (s, 1H), 8.12 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 0.6 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.22 – 7.16 (m, 1H), 7.11 (d, J = 8.0 Hz, 1H), 7.05 (td, J = 7.4, 0.9 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 156.58, 140.45, 140.02, 136.01, 131.16, 131.07, 129.05, 125.98, 122.63, 121.60, 121.27, 120.82, 120.53, 119.99, 119.10, 112.23, 112.02, 111.32, 55.90.

FTIR (neat) υ 3409, 3012, 1733, 1599, 1247, 1032, 866, 748 cm^{-1}

LRMS *m*/*z* (EI): 273.2 (M^+), 273.9, 258.3.

HRMS *m*/*z* (EI): calcd. $C_{19}H_{15}NO$ (M^+) 273.1155, found 273.1154.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8.11
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7.32
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7.19
7.16
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7.13
7.10
7.08
7.07
7.05
7.05
7.03
7.02
3.81
1.00
2.12
1.00
1.02
1.91
0.96
1.09
1.12
0.90
1.07
3.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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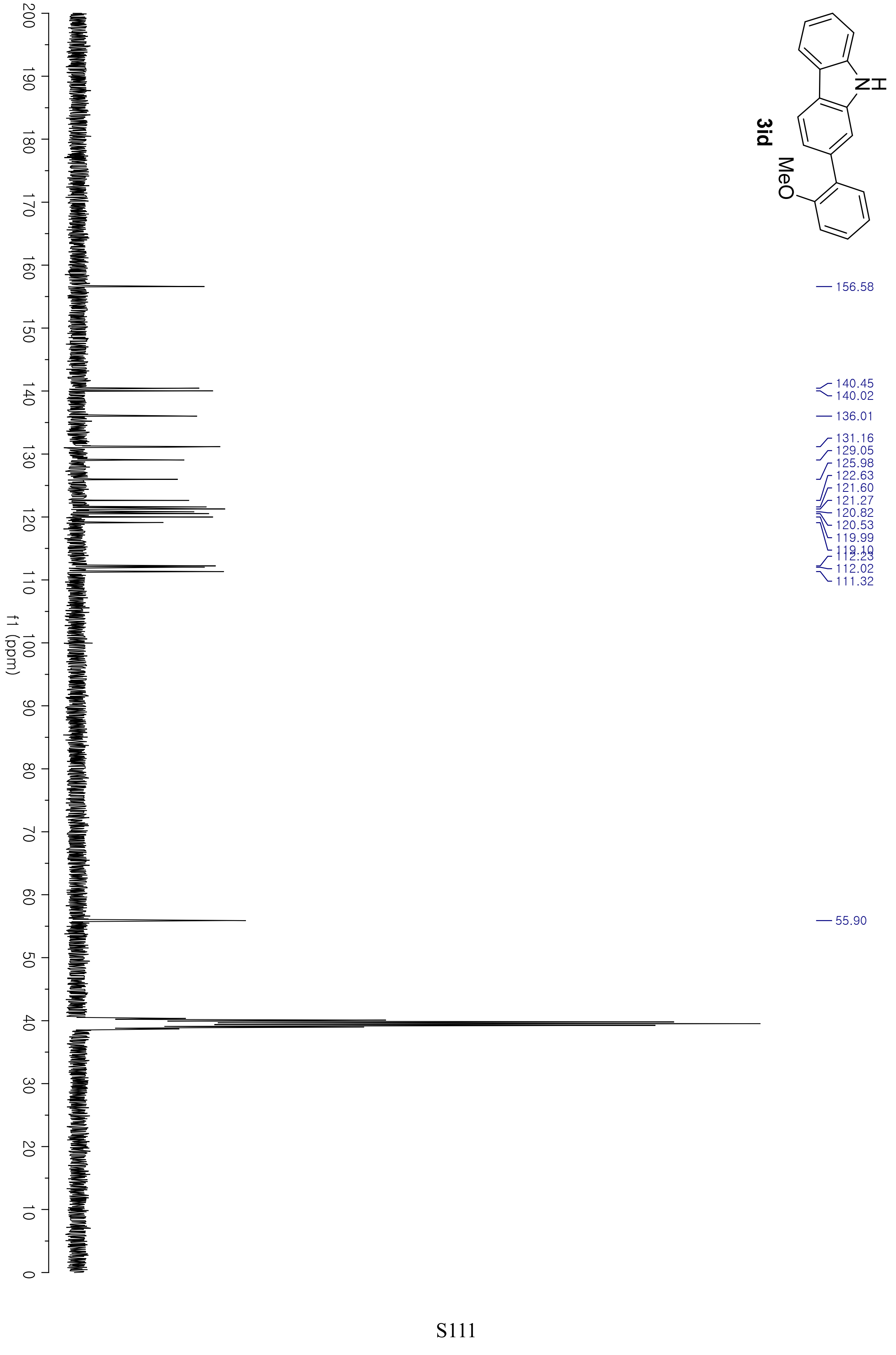
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

3id


3id
MeO
N
H
156.58
140.45
140.02
136.01
131.16
129.05
125.98
122.63
121.60
121.27
120.82
120.53
119.99
119.10
112.23
112.02
111.32
55.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)