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Salicylic Acids as Readily Available Starting Materials for the Synthesis of meta-Substituted Biaryls

Supporting Information

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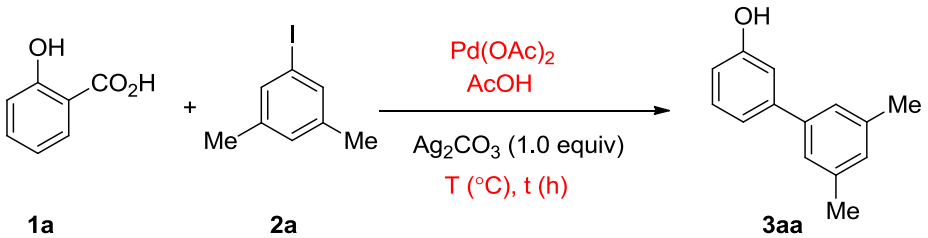
General experimental information

All chemicals used in this work were purchased from commercial sources and used without further purification, except 5-iodo-1-tosyl-1*H*-indole and 4-acetamido-2-hydroxybenzoic acid that were prepared following literature procedures.[1] Analytical thin-layer chromatography was performed on pre-coated Merk silica gel F_{254} plates and visualized under a UV light. Melting points were obtained using a Bibby Stuart Scientific apparatus and are uncorrected. IR spectra were recorded using a Bruker Tensor 37 FTIR machine and are quoted in cm^{-1}. ^{1}H NMR spectra, recorded at 400 MHz, are referenced to the residual solvent peak at 7.26 ppm ($CDCl_3$) and 2.05 ppm (acetone-d_6). ^{13}C NMR spectra, recorded at 101 MHz, are referenced to the residual solvent peak at 77.0 ppm ($CDCl_3$) and 29.8 ppm (acetone-d_6).

Optimization tables

Table 1. Systematic screening of reaction conditions.[a]



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

Entries	T (°C)	t (h)	AcOH (equiv)	$Pd(OAc)_2$ (mol%)	Yield of 3a (%)
1	130	16	3.5	2	35
2	130	16	7.0	2	42
3	130	16	10.5	2	44
4	110	16	3.5	2	32
5	120	16	3.5	2	35
6	140	16	7.0	2	50
7	130	16	7.0	2	42
8	130	16	3.5	5	36
9	130	16	3.5	1	45
10[b]	130	16	3.5	2	0
11[c]	130	16	3.5	2	33
12	130	60	3.5	2	63
13	130	60	3.5	1	45

[a] Unless otherwise noted, all reactions were carried out using 1.0 equiv of **1a**, 3.0 equiv of **2a** and 1.0 equiv of silver carbonate, yields were determined by ^{1}H NMR analysis using mesitylene as an internal standard.

[b] 200 µL of DMSO were also added.

[c] 5.0 equiv of water were also added.

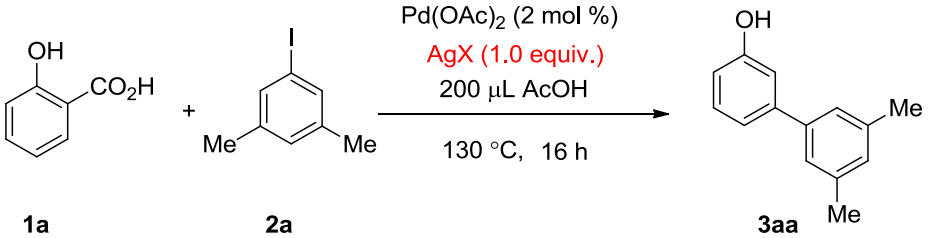
Table 2. Palladium catalysts screening.[a]

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

Entries	Cat. (2 mol%)	Yield of 3a (%)
14	$Pd(OAc)_2$	42
15	$Pd(TFA)_2$	42
16	$Pd(CAN)_2Cl_2$	46
17	PEPPSI-IPr	57
18	PEPPSI-IPent	61
19	$Pd_2(dba)_3$[b]	51
20	$Pd(P^tBu)_2$	0
21	$Pd(OAc)_2$[c]	45
22	$Pd(OAc)_2$[d]	38
23	$Pd(PPh_3)_4$	46

[a] Unless otherwise noted, all reactions were carried out using 1.0 equiv of **1a**, 3.0 equiv of **2a**, 1.0 equiv of silver carbonate and 200 µL (7.0 equiv) of acetic acid for 16 h at the temperature of 130 °C, yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.
[b] 1 mol% of $Pd_2(dba)_3$ was used .
[c] 2 mol% of IMesCl were also added.
[d] 2 mol% of IPrCl were also added.

Table 3. Silver salts screening.[a]

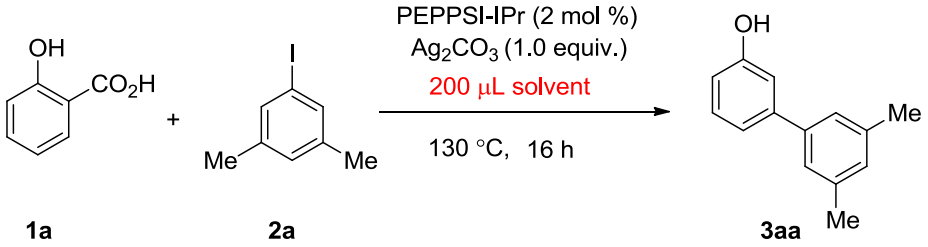


1a **2a** **3aa**

Entries	AgX (1.0 equiv)	Yield of 3a (%)
24	Ag_2CO_3	42
25	Ag_2O[b]	38
26	AgOAc	41
27	$AgNO_2$	0

[a] Unless otherwise noted, all reactions were carried out using 1.0 equiv of **1a**, 3.0 equiv of **2a**, 2 mol% of $Pd(OAc)_2$, 200 µL (7.0 equiv) of acetic acid, ran for 16 h at 130 °C, yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.
[b] 0.5 equiv of silver oxide were used in the reaction.

Table 4. Solvent screening.[a]

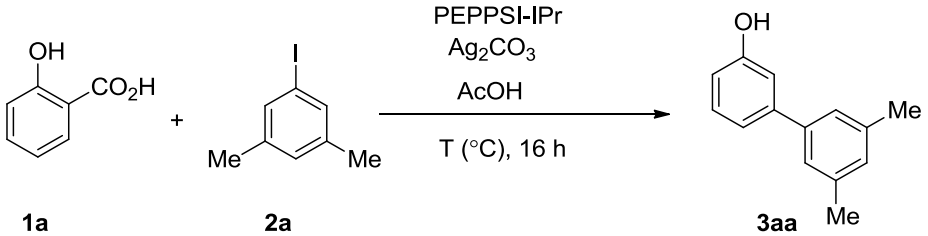


1a **2a** **3aa**

Entries	Solvent (200 µL)	Yield of 3a (%)
28	Acetic acid	56
29	TFA	54
30	Pivalic acid	28

[a] Unless otherwise noted, all reactions were carried out using 1.0 equiv of **1a**, 3.0 equiv of **2a**, 2 mol% of PEPPSI-IPr and 1.0 equiv of silver carbonate, ran for 16 h at the temperature of 130 °C, yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table 5. Optimization of the formal meta-arylation using PEPPSI-IPr



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

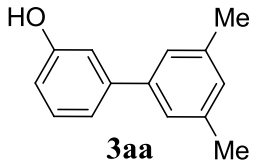
Entries	T (ºC)	Ag_2CO_3 (equiv)	AcOH (equiv)	PEPPSI-IPr (mol%)	Yield of 3a (%)
31	130	1.0	7.0	2	57
32	130	1.0	7.0	1	51
33	130	1.0	7.0	3	57
34	130	1.0	7.0	4	56
35	120	1.0	7.0	2	48
36	140	1.0	7.0	2	66
37	150	1.0	7.0	2	70
38	160	1.0	7.0	2	68
39	180	1.0	7.0	2	49
40	150	1.2	7.0	2	64
41	150	0.5	14.0	2	83
42[b]	150	0.5	14.0	2	92
43[c]	150	0.5	14.0	2	90

[a] Unless otherwise noted, all reactions were carried out using 1.0 equiv of **1a**, 3.0 equiv of **2a**, 2 mol% of PEPPSI-IPr, ran for 16 h, yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

[b] 0.5 equiv of K_2CO_3 were used in the reaction.

[c] 0.5 equiv of Cs_2CO_3 were used in the reaction.

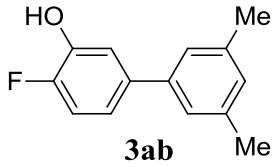
3',5'-Dimethyl-[1,1'-biphenyl]-3-ol



3aa

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 3',5'-dimethyl-[1,1'-biphenyl]-3-ol (**3aa**) as a light orange oil (80.0 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.9 Hz, 1H), 7.20 (s, 2H), 7.17-7.15 (m, 1H), 7.07-7.05 (m, 1H), 7.01 (s, 1H), 6.80 (ddd, *J* = 8.0, 2.6, 0.9 Hz, 1H), 4.76 (s, 1H), 2.38 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.7, 143.3, 140.8, 138.3, 129.9, 129.1, 125.1, 119.9, 114.1, 114.0, 21.4 ppm. These data are consistent with those previously reported.[2]

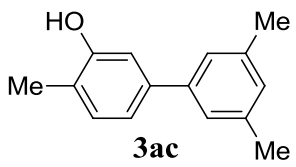
4-Fluoro-3',5'-dimethyl-[1,1'-biphenyl]-3-ol



3ab

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), 3-fluoro-2-hydroxybenzoic acid (78.1 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (1.0 mL) was heated at 160 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 4-fluoro-3',5'-dimethyl-[1,1'-biphenyl]-3-ol (**3ab**) as a light orange oil (81.1 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.15 (s, 2H), 7.14-7.09 (m, 1H), 7.06-7.04 (m, 1H), 6.99 (s, 1H), 5.17 (s, 1H), 2.37 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.6 (d, *J* = 237.4 Hz), 143.5 (d, *J* = 14.6 Hz), 140.1, 138.7 (d, *J* = 3.6 Hz), 138.3, 129.1, 125.0, 119.5 (d, *J* = 6.4 Hz), 116.0 (d, *J* = 1.8 Hz), 115.5 (d, *J* = 18.3 Hz), 21.4 ppm. These data are consistent with those previously reported.[2]

3',4,5'-Trimethyl-[1,1'-biphenyl]-3-ol

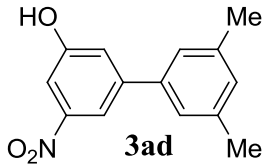


3ac

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), 2-hydroxy-3-methylbenzoic acid (76.1 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (1.0 mL) was heated at 160 ºC for 16 h. After this time, the reaction mixture was filtered

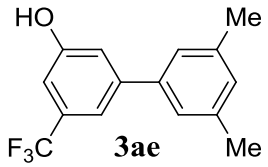
through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 3',4,5'-trimethyl-[1,1'-biphenyl]-3-ol (**3ac**) as an orange oil (75.3 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18-7.16 (m, 3H), 7.08 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.01-7.00 (m, 1H), 6.98 (s, 1H), 4.69 (s, 1H), 2.37 (s, 6H), 2.29 (s, 3 H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.9, 140.8, 140.8, 138.2, 131.2, 128.8, 124.9, 122.5, 119.6, 113.7, 21.4, 15.4 ppm. These data are consistent with those previously reported.[2]

3',5'-Dimethyl-5-nitro-[1,1'-biphenyl]-3-ol



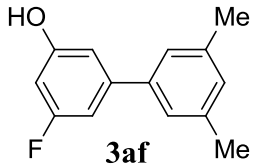
A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), 2-hydroxy-4-nitrobenzoic acid (91.6 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 75:25) to afford 3',5'-dimethyl-5-nitro-[1,1'-biphenyl]-3-ol (**3ad**) as a yellow solid (63.2 mg, 52%). **m. p.** 147-148 ºC. **IR**: 3424, 3092, 1591, 1343, 745 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 2.0, 1.6 Hz, 1H), 7.64 (app. t, *J* = 2.2 Hz, 1H), 7.38 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.21 (s, 2H), 7.07(s, 1H), 5.36 (s, 1H), 2.40 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 149.5, 144.5, 138.8, 138.4, 130.3, 125.0, 120.3, 114.8, 108.9, 21.4 ppm. **HRMS**: calcd for $C_{14}H_{13}NO_3$, 243.0895 (M^+); found, 243.0890.

3',5'-Dimethyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-ol



A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), 2-hydroxy-4-(trifluoromethyl) benzoic acid (103.1 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 3',5'-dimethyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-ol (**3ae**) as a brownish red oil (89.0 mg, 67%). **IR**: 3350, 2918, 1599, 1120, 699 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.39 (m, 1H), 7.21-7.20 (m, 1H), 7.18 (s, 2H), 7.04 (s, 2H), 5.08 (s, 1H), 2.39 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 144.2, 139.4, 138.6, 132.3 (q, *J* = 32.3 Hz), 129.8, 125.0, 123.9(q, *J* = 272.4 Hz), 117.4, 116.6 (q, *J* = 3.9 Hz), 110.9 (q, *J* = 3.8 Hz), 21.3 ppm. **HRMS**: calcd for $C_{15}H_{13}F_3O$, 266.0918 (M^+); found, 266.0913.

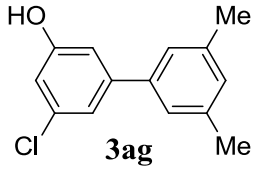
5-Fluoro-3',5'-dimethyl-[1,1'-biphenyl]-3-ol



3af

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), 4-fluoro-2-hydroxybenzoic acid (78.1 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 5-fluoro-3',5'-dimethyl-[1,1'-biphenyl]-3-ol (**3af**) as a brownish orange solid (73.1 mg, 68%). **m. p**. 95-96 ºC. IR: 3375, 2917, 1620, 1126, 840 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.15 (m, 2H), 7.02-7.01 (m, 1H), 6.87 (ddd, *J* = 9.8, 2.3, 1.5 Hz, 1H), 6.83-6.82 (m, 1H), 6.54 (dt, *J* = 9.8, 2.3 Hz, 1H), 4.90 (s, 1H), 2.37 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8 (d, *J* = 244.9 Hz), 156.8 (d, *J* = 12.0 Hz), 144.6 (d, *J* = 9.8 Hz), 139.7 (d, *J* = 2.6 Hz), 138.4, 129.7, 124.9, 109.9 (d, *J* = 2.7 Hz), 106.7 (d, *J* = 22.3 Hz), 101.8 (d, *J* = 24.9 Hz), 21.36 ppm. **HRMS**: calcd for $C_{14}H_{13}FO$, 216.0959 (M^+); found, 216.0945.

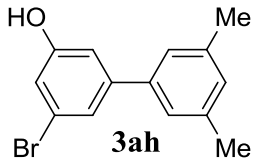
5-Chloro-3',5'-dimethyl-[1,1'-biphenyl]-3-ol



3ag

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), 4-chloro-2-hydroxybenzoic acid (86.3 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 160 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 5-chloro-3',5'-dimethyl-[1,1'-biphenyl]-3-ol (**3ag**) as a light orange solid (73.3 mg, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15-7.14 (m, 3H), 7.02 (s, 1H), 6.93-6.92 (m, 1H), 6.82-6.81 (m, 1H), 4.84 (s, 1H), 2.37 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 144.4, 139.5, 138.4, 135.1, 129.7, 124.9, 120.1, 114.4, 112.6, 21.3 ppm. **HRMS**: calcd for $C_{14}H_{13}ClO$, 232.0655 (M^+); found, 232.0649. These data are consistent with those previously reported.[2]

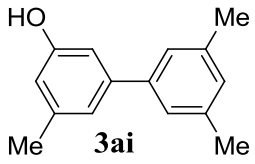
5-Bromo-3',5'-dimethyl-[1,1'-biphenyl]-3-ol



3ah

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), 4-bromo-2-hydroxybenzoic acid (108.5 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 5-bromo-3',5'-dimethyl-[1,1'-biphenyl]-3-ol (**3ah**) as a light yellow solid (92.5 mg, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (app. t, *J* = 1.6 Hz, 1H), 7.15 (s, 2H), 7.02 (s, 1H), 6.97 (app. p, *J* = 2.3 Hz, 2H), 4.83 (s, 1H), 2.37 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 144.7, 139.4, 138.4, 129.7, 125.0, 123.0 (CH+C), 117.3, 113.1, 21.4 ppm. These data are consistent with those previously reported.[2]

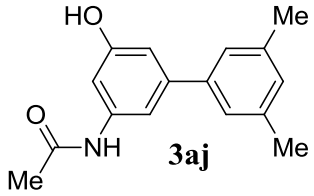
3',5,5'-Trimethyl-[1,1'-biphenyl]-3-ol



3ai

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), 2-hydroxy-4-methylbenzoic acid (76.1 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 3',5,5'-trimethyl-[1,1'-biphenyl]-3-ol (**3ai**) as a light orange solid (75.2 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 6.99-6.97 (m, 2H), 6.85-6.84 (m, 1H), 6.63 (s, 1H), 4.66 (s, 1H), 2.37 (s, 6H), 2.36 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.7, 143.1, 140.9, 139.9, 138.2, 129.0, 125.0, 120.8, 114.8, 111.3, 21.44, 21.37 ppm. These data are consistent with those previously reported.[2]

***N*-(5-hydroxy-3',5'-dimethyl-[1,1'-biphenyl]-3-yl)acetamide**

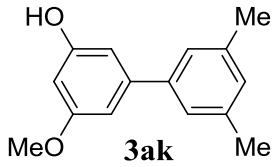


3aj

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), 4-acetamido-2-hydroxybenzoic acid (97.6 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 m). The filtrate was evaporated to dryness. The crude product was purified by long column chromatography (hexanes:EtOAc 50:50) to afford *N*-(5-hydroxy-3',5'-dimethyl-[1,1'-biphenyl]-3-yl)acetamido (**3aj**) as a light brown solid (52 mg, 41%). **m. p**. 238-240 ºC. **IR**: 3355, 3098, 1746, 1626, 1656, 1592, 1552, 1268, 695 cm^{-1}. **^{1}H NMR** (400 MHz, acetone-d_6) δ 9.09 (s, 1H), 8.35 (s, 1H), 7.37 (s, 1H), 7.28 (s, 1H), 7.17 (s, 2H), 6.98 (s, 1H), 6.79-6.78 (m, 1H), 2.33

(s, 6H), 2.09 (s, 3H) ppm. **^{13}C NMR** (101 MHz, acetone-d_6) δ 168.9, 158.9, 143.7, 141.9, 141.9, 138.9, 129.8, 125.5, 109.9, 109.7, 106.1, 24.4, 21.4 ppm. **HRMS**: calcd for $C_{16}H_{17}NO_2$, 255.1259 (M^+); found, 255.1254.

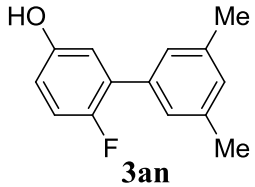
5-Methoxy-3',5'-dimethyl-[1,1'-biphenyl]-3-ol



3ak

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), 2-hydroxy-4-methoxybenzoic acid (84.1 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by long column chromatography (hexanes:EtOAc 50:50) to afford 5-methoxy-3',5'-dimethyl-[1,1'-biphenyl]-3-ol (**3ak**) as a brownish orange oil (25.0 mg, 22%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (s, 2H), 7.00 (s, 1H), 6.71-6.70 (m, 1H), 6.65-6.64 (m, 1H), 6.39 (app. t, *J* = 2.3 Hz, 1H), 4.83 (s, 1H), 3.84 (s, 3H), 2.37 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1, 156.8, 144.1, 140.8, 138.2, 129.3, 125.0, 106.9, 105.7, 100.3, 55.4, 21.4 ppm. These data are consistent with those previously reported.[2]

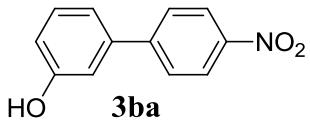
6-Fluoro-3',5'-dimethyl-[1,1'-biphenyl]-3-ol



3an

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), 5-fluoro-2-hydroxybenzoic acid (78.1 mg, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 6-fluoro-3',5'-dimethyl-[1,1'-biphenyl]-3-ol (**3an**) as an orange solid (58.0 mg, 53%). **m. p**. 53-54 ºC. **IR**: 3352, 2916, 1420, 1204, 765 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (s, 2H), 7.03-6.98 (m, 2H), 6.89-6.86 (m, 1H), 6.76-6.72 (m, 1H), 4.70 (s, 1H), 2.37 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.4 (d, *J* = 239.9 Hz), 151.6 (d, *J* = 2.3 Hz), 138.1, 135.6 (d, *J* = 1.4 Hz), 130.3 (d, *J* = 15.5 Hz), 129.7, 126.9 (d, *J* = 2.9 Hz), 117.1 (d, *J* = 3.5 Hz), 116.9 (d, *J* = 25.1 Hz), 115.1 (d, *J* = 8.1 Hz), 21.5 ppm. **HRMS**: calcd for $C_{14}H_{13}FO$, 216.0950 (M^+); found, 216.0945.

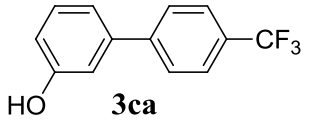
4'-Nitro-[1,1'-biphenyl]-3-ol



3ba

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol) and 1-iodo-4-nitrobenzene (374.0 mg, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 75:25) to afford 4'-nitro-[1,1'-biphenyl]-3-ol (**3ba**) as a yellow solid (64.5 mg, 60%). **^{1}H NMR** (400 MHz, acetone-d_6) δ 8.61 (s, 1H), 8.36-8.32 (m, 2H), 7.94-7.91 (m, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.27-7.23 (m, 2H), 6.98 (ddd, *J* = 8.1, 2.4, 0.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, acetone-d_6) δ 159.0, 148.3, 148.1, 141.0, 131.2, 128.7, 124.8, 119.5, 116.8, 115.0 ppm. These data are consistent with those previously reported.[2]

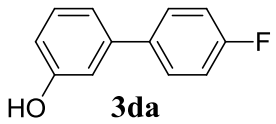
4'-(Trifluoromethyl)-[1,1'-biphenyl]-3-ol



3ca

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 4-iodobenzotrifluoride (220 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 4'-(trifluoromethyl)-[1,1'-biphenyl]-3-ol (**3ca**) as a pale yellow solid (79.5 mg, 67%). **m. p**. 73-75 ºC. **IR**: 3261, 1573, 1322, 840 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.68 (m, 4H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.21 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.11-7.10 (m, 1H), 6.91 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 4.91 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 144.2, 141.6, 130.3, 129.6 (q, *J* = 32.5 Hz), 124.3 (q, *J* = 272.0 Hz), 127.4, 125.7 (q, *J* = 3.8 Hz), 119.9, 115.1, 114.3 ppm. **HRMS**: calcd for $C_{13}H_9F_3O$, 238.0605 (M^+); found, 238.0600.

4'-Fluoro-[1,1'-biphenyl]-3-ol

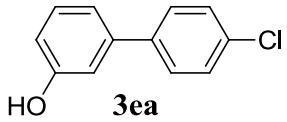


3da

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 1-fluoro-4-iodobenzene (173 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 4'-fluoro-[1,1'-biphenyl]-3-ol (**3da**) as an off white solid (64.9 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 2H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.15-7.09 (m, 3H), 7.02-7.01 (m, 1H), 6.82 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 4.83 (bs, 1H)

ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.6 Hz), 155.9, 142.1, 136.9 (d, *J* = 3.2 Hz), 130.1, 128.7, 128.6, 119.7, 115.6 (d, *J* = 21.4 Hz), 114.1 (d, *J* = 18.4 Hz) ppm. These data are consistent with those previously reported.[2]

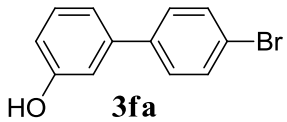
4'-Chloro-[1,1'-biphenyl]-3-ol



3ea

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 1-chloro-4-iodobenzene (358 mg, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 4'-chloro-[1,1'-biphenyl]-3-ol (**3ea**) as a light orange solid (69.5 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.41-7.38 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.13 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.03-7.02 (m, 1H), 6.83 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 4.85 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 141.8, 139.2, 133.6, 130.1, 128.9, 128.4, 119.6, 114.5, 114.0 ppm. These data are consistent with those previously reported.[2]

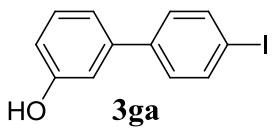
4'-Bromo-[1,1'-biphenyl]-3-ol



3fa

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 1-bromo-4-iodobenzene (424 mg, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 4'-bromo-[1,1'-biphenyl]-3-ol (**3fa**) as a light orange solid (74.7 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58-7.54 (m, 2H), 7.45-7.42 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.13 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.03-7.02 (m, 1H), 6.83 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 4.79 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 141.9, 139.8, 132.0, 130.3, 128.8, 121.9, 119.7, 114.7, 114.1 ppm. These data are consistent with those previously reported.[2]

4'-Iodo-[1,1'-biphenyl]-3-ol

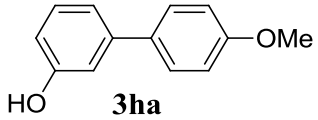


3ga

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 1,4-diiodobenzene (495 mg, 1.5 mmol) in acetic acid (500

µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 4'-iodo-[1,1'-biphenyl]-3-ol (**3ga**) as an orange solid (59.2 mg, 40%). **m. p.** 123-126 ºC. **IR:** 3335, 1593, 1445, 1388, 1194, 1002, 878, 823, 780, 688 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.33-7.29 (m, 3H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.02-7.01 (m, 1H), 6.83 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.84 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9, 141.9, 140.2, 137.9, 130.2, 129.0, 119.6, 114.6, 113.8, 93.3 ppm. **HRMS**: calcd for $C_{12}H_{10}IO$, 296.9698 ($M+H^+$); found, 296.9771.

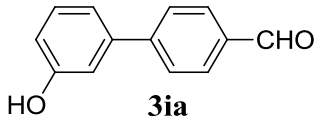
4'-Methoxy-[1,1'-biphenyl]-3-ol



3ha

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (35.0 mg, 0.25 mmol), salicylic acid (69.1 mg, 0.50 mmol), 1-iodo-4-methoxybenzene (39.1 mg, 0.167 mmol) in acetic acid (500 µL) was heated at 130 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 4'-methoxy-[1,1'-biphenyl]-3-ol (**3ha**) as an off white solid (27.7 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.13 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.03-7.02 (m, 1H), 6.99-6.95 (m, 2H), 6.78 (ddd, *J* = 8.0, 2.5, 0.9 Hz, 1H), 4.78 (s, 1H), 3.85 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 155.8, 142.6, 133.3, 129.9, 128.1, 119.4, 114.2, 113.7, 113.6, 55.4 ppm. These data are consistent with those previously reported.[2]

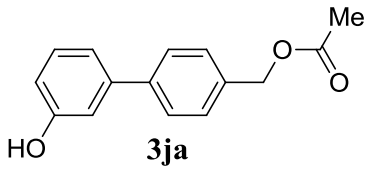
3'-Hydroxy-[1,1'-biphenyl]-4-carbaldehyde



3ia

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (35.0 mg, 0.25 mmol), salicylic acid (69.1 mg, 0.50 mmol), 4-iodobenzaldehyde (38.7 mg, 0.167 mmol) in acetic acid (500 µL) was heated at 130 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 80:20) to afford 3'-hydroxy-[1,1'-biphenyl]-4-carbaldehyde (**3ia**) as a white solid (28.2 mg, 85%). **^{1}H NMR** (400 MHz, acetone-d_6) δ 10.09 (s, 1H), 8.56 (s, 1H), 8.01-7.99 (m, 2H), 7.86-7.84 (m, 2H), 7.34 (app. t, *J* = 7.7 Hz, 1H), 7.23-7.19 (m, 2H), 6.94-6.91 (m, 1H) ppm. **^{13}C NMR** (101 MHz, acetone-d_6) δ 192.5, 158.9, 147.6, 142.0, 136.6, 131.1, 130.9, 128.4, 119.4, 116.4, 115.0 ppm. These data are consistent with those previously reported.[2]

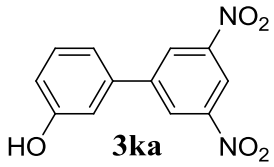
(3'-Hydroxy-[1,1'-biphenyl]-4-yl)mEtOAc



3ja

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (35.0 mg, 0.25 mmol), salicylic acid (69.1 mg, 0.50 mmol), 4-iodobenzyl alcohol (39.1 mg, 0.167 mmol) in acetic acid (500 µL) was heated at 130 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 75:25) to afford 3'-hydroxy-[1,1'-biphenyl]-4-carbaldehyde (**3ja**) as an off white solid (32.3 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H), 7.43-7.41 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.16-7.14 (m, 1H), 7.07-7.06 (m, 1H), 6.83 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 5.26 (s, 1H), 5.15 (s, 2H), 2.13 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 156.0, 142.4, 140.9, 135.1, 130.0, 128.8, 127.3, 119.7, 114.4, 114.1, 66.1, 21.1 ppm. These data are consistent with those previously reported.[2]

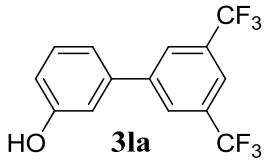
3',5'-Dinitro-[1,1'-biphenyl]-3-ol



3ka

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 1-Iodo-3,5-dinitrobenzene (441 mg, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 50:50) to afford 3',5'-dinitro-[1,1'-biphenyl]-3-ol (**3ka**) as a yellow solid (82.1 mg, 63%). **m. p**. 208-210 ºC. **IR**: 3440, 3076, 1522, 1336, 727 cm^{-1}. **^{1}H NMR** (400 MHz, acetone-d_6) δ 8.93 (t, *J* = 2.1 Hz, 1H), 8.84 (d, *J* = 2.1 Hz, 2H), 8.70 (s, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.38 (ddd, *J* = 7.7, 1.7, 1.1 Hz, 1H), 7.34 (t, *J* = 2.0 Hz, 1H), 7.04 (ddd, *J* = 8.0, 2.4, 1.1 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, acetone-d_6) δ 159.2, 150.0, 145.2, 138.9, 131.6, 127.6, 119.4, 117.8, 117.5, 115.0 ppm. HRMS: calcd for $C_{12}H_8N_2O_5$, 260.0433 (M^+); found, 260.0428.

3',5'-Bis(trifluoromethyl)-[1,1'-biphenyl]-3-ol

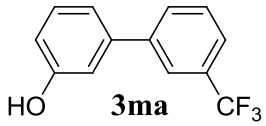


3la

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 1-Iodo-3,5-bis(trifluoromethyl)benzene (266 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The

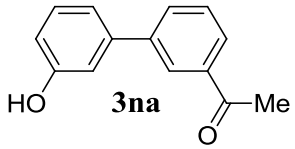
crude product was purified by column chromatography (hexanes:EtOAc 85:15) to afford 3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-3-ol (**3la**) as a white solid (97.0 mg, 63%). **m. p**. 93-94 ºC. **IR**: 3296, 1378, 701 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.86 (s, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.18 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.08 (t, *J* = 2.4 Hz, 1H), 6.92 (ddd, *J* = 8.1, 2.5, 0.8 Hz, 1H), 4.96 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 142.8, 140.0, 132.1 (q, *J* = 33.2 Hz), 130.6, 127.2 (d, *J* = 2.7 Hz), 123.4 (q, *J* = 272.7 Hz), 121.1 (dt, *J* = 7.8, 3.8 Hz), 119.8, 115.8, 114.2 ppm. **HRMS**: calcd for $C_{14}H_8F_6O$, 306.0479 (M^+); found, 306.0474.

3'-(Trifluoromethyl)-[1,1'-biphenyl]-3-ol



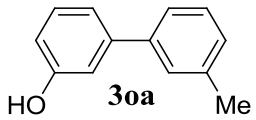
A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 3-iodobenzotrifluoride (216 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 3'-(trifluoromethyl)-[1,1'-biphenyl]-3-ol (**3ma**) as an off white solid (80.9 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.75-7.73 (m, 1H), 7.62-7.53 (m, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.17 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.08-7.07 (m, 1H), 6.87 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 4.85 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 141.5, 131.2 (q, *J* = 32.2 Hz), 130.4, 130.4, 130.3, 129.2, 124.2 (q, *J* = 272.4 Hz), 124.2 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 3.8 Hz), 119.8, 115.0, 114.2 ppm. These data are consistent with those previously reported.[2]

1-(3'-Hydroxy-[1,1'-biphenyl]-3-yl)ethanone



A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (35.0 mg, 0.25 mmol), salicylic acid (69.1 mg, 0.50 mmol), 3′-iodoacetophenone (41.0 mg, 0.167 mmol) in acetic acid (500 µL) was heated at 130 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 80:20) to afford1-(3'-hydroxy-[1,1'-biphenyl]-3-yl)ethanone (**3na**) as a light orange oil (27.3 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (app. t, *J* = 1.6 Hz, 1H), 7.93 (ddd, *J* = 7.7, 1.7, 1.2 Hz, 1H), 7.77 (ddd, *J* = 7.7, 1.9, 1.1 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.18 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.12-7.11 (m, 1H), 6.88 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 5.34 (s, 1H), 2.66 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.5, 156.2, 141.9, 141.3, 137.6, 131.8, 130.2, 129.1, 127.5, 126.9, 119.7, 114.8, 114.2, 26.8 ppm. These data are consistent with those previously reported.[2]

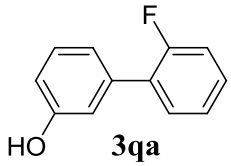
3'-Methyl-[1,1'-biphenyl]-3-ol



3oa

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (35 mg, 0.25 mmol), salicylic acid (69.1 mg, 0.50 mmol), 3-Iodotoluene (193 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 3'-methyl-[1,1'-biphenyl]-3-ol (**3oa**) as an orange oil (50.6 mg, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 4H), 7.18-7.16 (m, 2H), 7.07-7.06 (m, 1H), 6.82 (ddd, *J* = 8.0, 2.6, 0.9 Hz, 1H), 4.84 (s, 1H), 2.42 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.8, 143.2, 140.7, 138.4, 129.9, 128.7, 128.3, 127.9, 124.2, 119.8, 114.1, 114.1, 21.5 ppm. These data are consistent with those previously reported.[2]

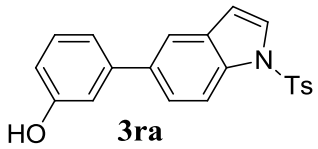
2'-Fluoro-[1,1'-biphenyl]-3-ol



3qa

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 2-fluoroiodobenzene (175 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 2'-fluoro-[1,1'-biphenyl]-3-ol (**3qa**) as a light brown solid (23.0 mg, 24%). **m. p**. 99-101 ºC. **IR**: 3222, 2926, 1571, 1584, 1180, 759 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34-7.29 (m, 2H), 7.22-7.12 (m, 3H), 7.05-7.03 (m, 1H), 6.85 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 4.78 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 248.0 Hz), 155.5, 137.4, 130.7 (d, *J* = 3.4 Hz), 129.7, 129.1 (d, *J* = 8.3 Hz), 128.6 (d, *J* = 13.3 Hz), 124.3 (d, *J* = 3.7 Hz), 121.6 (d, *J* = 2.8 Hz), 116.2 (d, *J* = 17.6 Hz), 116.0 (d, *J* = 2.0 Hz), 114.7 ppm. **HRMS**: calcd for $C_{12}H_9FO$, 188.0637 (M^+); found, 188.0632.

3-(1-Tosyl-1*H*-indol-5-yl)phenol

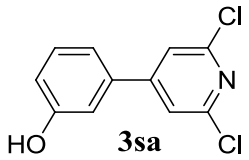


3ra

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 5-iodo-1-tosyl-1H-indole (596 mg, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 70:30) to afford 3-(1-tosyl-1*H*-indol-5-yl)phenol (**3ra**) as a brown solid (54.5 mg, 30%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 1H), 7.81-

7.78 (m, 2H), 7.70-7.69 (m, 1H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.51 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.24-7.22 (m, 2H), 7.16-7.14 (m, 1H), 7.07-7.05 (m, 1H), 6.80 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 6.69 (dd, *J* = 3.7, 0.7 Hz, 1H), 4.91 (s, 1H), 2.34 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9, 145.1, 143.1, 136.3, 135.3, 134.3, 131.3, 130.0, 130.0, 127.0, 126.9, 124.1, 120.0, 119.8, 114.3, 114.0, 113.7, 109.3, 21.6 ppm. These data are consistent with those previously reported.[2]

3-(2,6-Dichloropyridin-4-yl)phenol

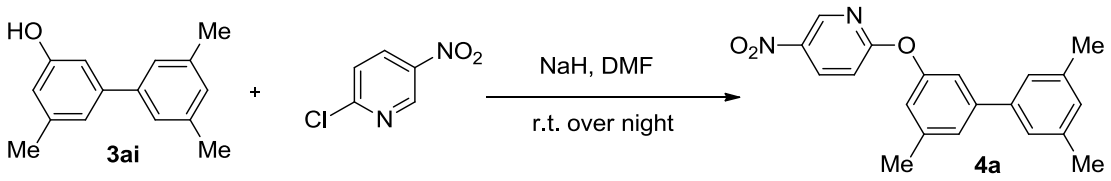


3sa

A mixture of PEPPSI-IPr (6.8 mg, 0.010 mmol), Ag_2CO_3 (69.0 mg, 0.25 mmol), K_2CO_3 (25.0 mg, 0.18 mmol), salicylic acid (69.1 mg, 0.50 mmol), 2,6-dichloro-4-iodopyridine (409 µL, 1.5 mmol) in acetic acid (500 µL) was heated at 150 ºC for 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 85:15) to afford 3-(2,6-dichloropyridin-4-yl)phenol (**3sa**) as a pale yellow solid (84.0 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (s, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.17-7.15 (m, 1H), 7.06-7.05 (m, 1H), 6.95 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H) 5.01 (bs, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 153.7, 151.1, 137.4, 130.7, 120.9, 119.5, 117.3, 114.1 ppm. These data are consistent with those previously reported.[2]

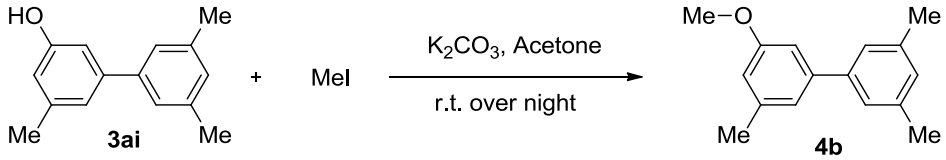
Derivatization of product 3ai

Procedure to prepare 2-((3',5'-dimethyl-[1,1'-biphenyl]-3-yl)methyl)-5-nitropyridine (4a).[3]



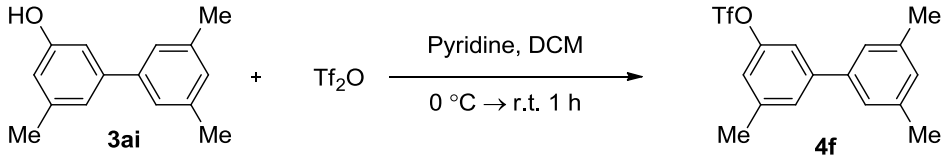
NaH (11 mg, 0.275 mmol, 60% in mineral oil) was slowly added to a solution of biaryl **3ai** (53.1 mg, 0.25 mmol) in DMF (0.5 mL), at 0 °C. After stirring for 30 min, 2-chloro-5-nitro-pyridine (40.0 mg, 0.25 mmol) was added, and the resulting mixture was stirred at room temperature for 16 h. After that time, the crude mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL), the filtrate was evaporated to dryness, and the crude product was purified by column chromatography (hexanes:EtOAc 85:15) to afford 2-((3',5'-dimethyl-[1,1'-biphenyl]-3-yl)methyl)-5-nitropyridine (**4a**) as a pale brownish solid (81.0 mg, 97%). **m. p**. 93-95 ºC. **IR**: 2916, 1569, 1347, 1300, 1259, 842, 684 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.07 (d, *J* = 2.8 Hz, 1H), 8.47 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.33 (s, 1H), 7.19 (s, 2H), 7.16 (s, 1H), 7.04 (d, *J* = 9.1 Hz, 1H), 7.00 (s, 1H), 6.94 (s, 1H), 2.45 (s, 3H), 2.37 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 153.1, 145.2, 143.4, 140.4, 140.3, 140.2, 138.4, 134.9, 129.4, 125.7, 125.1, 120.5, 117.3, 111.2, 21.6, 21.4 ppm. **HRMS**: calcd for $C_{20}H_{19}N_2O_3$, 335.1317 ($M+H^+$); found, 335.1390.

Procedure to prepare 3-methoxy-3',5,5'-trimethyl-1,1'-biphenyl (4b).[4]



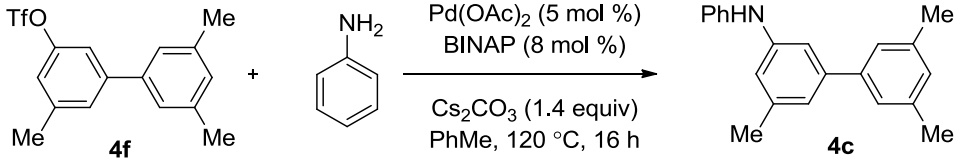
K_2CO_3 (32 mg, 0.23 mmol) was added to a solution of biaryl **3ai** (21.2 mg, 0.10 mmol) in acetone (0.5 mL). After stirring for 1 min, MeI (14 µL, 0.23 mmol) was added and the resulting mixture was stirred at room temperature for 16 h. After that time, the mixture was filtered through a small plug of silica with EtOAc (4 × 5 mL), the filtrate was evaporated to dryness, and the crude product was purified by column chromatography (hexanes) to afford 3-methoxy-3',5,5'-trimethyl-1,1'-biphenyl (**4b**) as a colorless oil (21.7 mg, 96%). **IR**: 2918, 1590, 1461, 1262, 1152, 1064, 836, 694 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 7.00 (s, 2H), 6.93 (s, 1H), 6.72 (s, 1H), 3.86 (s, 3H), 2.40 (s, 3H), 2.39 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 142.9, 141.3, 139.6, 138.2, 129.0, 125.1, 120.7, 113.5, 109.9, 55.3, 21.7, 21.4 ppm. **HRMS**: calcd for $C_{16}H_{19}O$, 227.1358 ($M+H^+$); found, 227.1430.

Procedure to prepare 3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate (4f).[5]



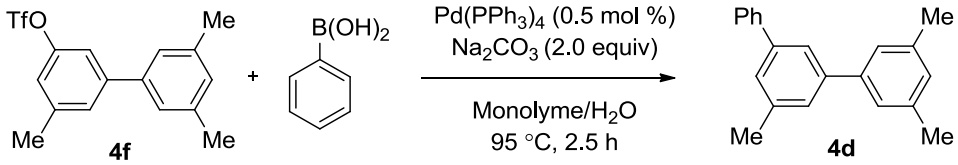
A solution of trifluoromethanesulfonic anhydride (245 µL, 1.44 mmol) in DCM (0.6 mL) was added dropwise to a solution of pyridine (195 µL, 2.4 mmol) and **3ai** (254 mg, 1.2 mmol) in anhydrous DCM into an ice bath. After complete addition, the mixture was warmed to room temperature and allowed to stir for 1 h. The mixture was then filtered through a small plug of silica with EtOAc (4 × 5 mL), the filtrate was evaporated to dryness, the crude product was purified by column chromatography (hexanes) to afford 3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate (**4f**) as a colorless oil (397 mg, 96%). **IR**: 2924, 1584, 1422, 1206, 1141, 959, 828, 691, 609 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.26 (s, 1H), 7.16 (s, 2H), 7.05 (s, 2H), 2.46 (s, 3H), 2.39 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 143.9, 140.9, 139.3, 138.6, 129.8, 127.9, 125.1, 120.1, 118.8 (d, J = 320.7 Hz), 117.0, 21.5, 21.4 ppm. **HRMS**: calcd for $C_{16}H_{16}F_3NO_3S$, 362.1038 ($M+NH_4^+$); found, 362.1032.

Procedure to prepare 3',5,5'-trimethyl-N-phenyl-[1,1'-biphenyl]-3-amine (4c).[6]



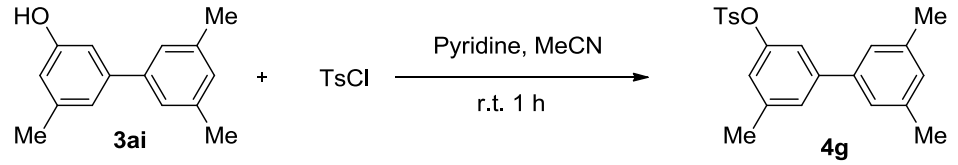
A flame-dried vial was charged with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), BINAP (5.0 mg, 0.008 mmol), Cs_2CO_3 (45.6 mg, 1.4 equiv) and **4f** (34.4 mg, 0.1 mmol) in PhMe (0.1 M). Aniline (11 µL, 0.12 mmol) was added at room temperature under an argon atmosphere. The reaction mixture was allowed to stir at 120 °C for 16 h. The mixture was then filtered through a small plug of silica with EtOAc (4 × 5 mL), the filtrate was evaporated to dryness, the crude product was purified by column chromatography (hexanes:EtOAc 85:15) to afford 3',5,5'-trimethyl-*N*-phenyl-[1,1'-biphenyl]-3-amine **(4c)** as a brown oil (27.6 mg, 96%). **IR**: 3394, 2916, 1586, 1494, 1348, 1235, 1030, 837, 741, 691 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.18 (s, 2H), 7.12-7.10 (m, 3H), 6.99-6.98 (m, 2H), 6.96-6.92 (m, 1H), 6.88 (s, 1H), 5.72 (s, 1H), 2.37 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 143.3, 142.7, 141.3, 139.5, 138.2, 129.4, 128.9, 125.1, 121.1, 120.9, 117.9, 117.4, 114.0, 21.6, 21.4 ppm. **HRMS**: calcd for $C_{21}H_{22}N$, 288.1674 ($M+H^+$); found, 288.1747.

Procedure to prepare 3,5,5''-trimethyl-1,1':3',1''-terphenyl (4d).[7]



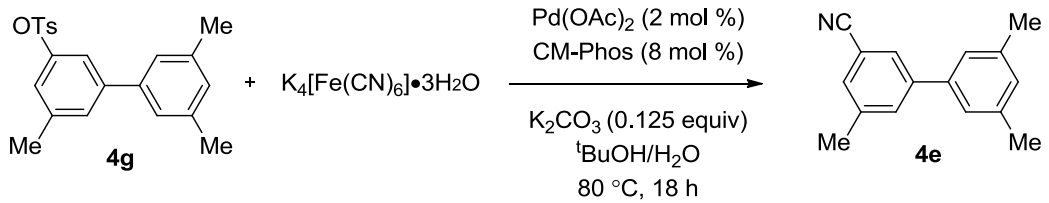
A solution of Na_2CO_3 (21.2 mg, 0.2 mmol) in degased H_2O (1.0 mL) was added to a mixture of $Pd(PPh_3)_4$ (0.6 mg, 0.0005 mmol), **4f** (34.4 mg, 0.1 mmol) and phenylboronic acid (13.7 mg, 0.112 mmol) in degased monolyme (1.0 mL), under an argon atmosphere. The reaction mixture was stirred at 95 °C for 2.5 h. The mixture was then filtered through a small plug of silica with EtOAc (4 × 5 mL), the filtrate was evaporated to dryness, the crude product was purified by column chromatography (hexanes) to afford 3,5,5''-trimethyl-1,1':3',1''-terphenyl (**4d**) as a colourless oil (26.3 mg, 97%). **IR**: 3030, 2917, 1560, 1459, 1032, 844, 761, 697 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.59 (s, 1H), 7.47-7.43 (m, 2H), 7.38-7.33 (m, 3H), 7.26-7.25 (m, 2H), 7.01 (s, 1H), 2.48 (s, 3H), 2.39 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 141.7, 141.5, 141.4, 138.7, 138.3, 129.0, 128.8, 127.3, 127.3, 127.0, 126.9, 125.2, 123.5, 21.6, 21.5 ppm. **HRMS**: calcd for $C_{21}H_{21}$, 273.1565 ($M+H^+$); found, 273.1638.

Procedure to prepare 3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl 4-methylbenzenesulfonate (4g).



Et_3N (31 µL, 0.22 mmol) was slowly added to a solution of **3ai** (42.4 mg, 0.2 mmol) and *p*-toluenesulfonyl chloride (41.9 mg, 0.22 mmol) in MeCN (1 mL). The reaction mixture was allowed to stir at room temperature for 1 h. The mixture was then filtered through a small plug of silica with EtOAc (4 × 5 mL), the filtrate was evaporated to dryness, and the crude product was purified by column chromatography (hexanes) to afford 3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl 4-methylbenzenesulfonate (**4g**) as a colourless oil (69.5 mg, 95%). **IR**: 1598, 1358, 1189, 1178, 965, 862, 847, 790, 671 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25 (s, 1H), 7.00 (s, 2H), 6.98 (s, 1H), 6.87 (s, 1H), 6.84 (s, 1H), 2.47 (s, 3H), 2.35 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 145.2, 142.8, 140.0, 139.8, 138.3, 132.7, 129.7, 129.4, 128.7, 126.6, 125.0, 121.6, 118.0, 21.7, 21.40, 21.35 ppm. **HRMS**: calcd for $C_{22}H_{26}NO_3S$, 384.1628 ($M+NH_4^+$); found, 384.1628.

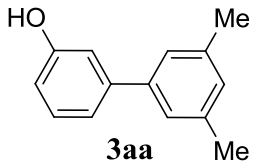
Procedure to prepare 3',5,5'-trimethyl-[1,1'-biphenyl]-3-carbonitrile (4e).[8]



Et_3N (0.1 µL) was added to a mixture of $Pd(OAc)_2$ (0.45 mg, 0.002 mmol) and CM-Phos (3.2 mg, 0.008 mmol) in degased anhydrous DCM (0.5 mL), under an argon atmosphere. The resulting mixture was very gently heated with a heat gun with constant stirring for 5 min. The solvent was then removed under vacuum. **4g** (34.4 mg, 0.1 mmol), K_2CO_3 (1.7 mg, 0.0125 mmol) and $K_4[Fe(CN)_6]\cdot H_2O$ (21.1 mg, 0.05 mmol) were charged successively to the tube, and degased ^tBuOH (0.25 mL) and H_2O (0.25 mL) were added as solvent. The reaction mixture was allowed to stir at 80 °C for 18 h. The mixture was then filtered through a small plug of silica with EtOAc (4 × 5 mL), the filtrate was evaporated to dryness, the crude product was purified by column chromatography (hexanes:EtOAc 85:15) to afford 3',5,5'-trimethyl-[1,1'-biphenyl]-3-carbonitrile (**4e**) as an offwhite solid (21.0 mg, 95%). **m. p**. 68-70 °C. **IR**: 2919, 2227, 1598, 1453, 1376, 840, 685 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.52 (s, 1H), 7.34 (s, 1H), 7.08 (s, 2H), 6.97 (s, 1H), 2.37 (s, 3H), 2.31 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 139.5, 139.1, 138.7, 132.4, 130.9, 129.9, 128.0, 125.0, 119.1, 112.6, 21.4, 21.3 ppm. **HRMS**: calcd for $C_{16}H_{16}N$, 222.1204 ($M+H^+$); found, 222.1277.

Silver free arylation of salicylic acids

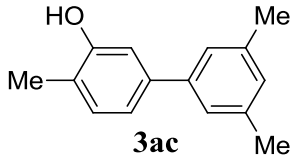
3',5'-Dimethyl-[1,1'-biphenyl]-3-ol



3aa

A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), salicylic acid (69.1 mg, 0.50 mmol), Me_4NCl (68.5 mg, 0.63 mmol), KOAc (98.0 mg, 1.0 mmol), 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) and acetic acid (43 µL, 0.75 mmol) was heated at 120 ºC for 24 h. The mixture was cooled down to room temperature, then extra Me_4NCl (44.0 mg, 0.4 mmol) and KOAc (39.0 mg, 0.4 mmol) were added into the mixture and heated at 120 ºC for extra 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 3',5'-dimethyl-[1,1'-biphenyl]-3-ol (**3aa**) as a light orange oil (59.5 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.9 Hz, 1H), 7.20 (s, 2H), 7.17-7.15 (m, 1H), 7.07-7.05 (m, 1H), 7.01 (s, 1H), 6.80 (ddd, *J* = 8.0, 2.6, 0.9 Hz, 1H), 4.76 (s, 1H), 2.38 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.7, 143.3, 140.8, 138.3, 129.9, 129.1, 125.1, 119.9, 114.1, 114.0, 21.4 ppm. These data are consistent with those previously reported.[2]

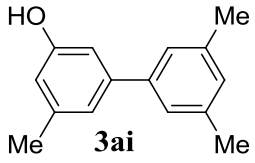
3',4,5'-Trimethyl-[1,1'-biphenyl]-3-ol



3ac

A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), 2-hydroxy-3-methylbenzoic acid (76.1 mg, 0.50 mmol), Me_4NCl (68.5 mg, 0.63 mmol), KOAc (98.0 mg, 1.0 mmol), 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) and acetic acid (43 µL, 0.75 mmol) was heated at 120 ºC for 24 h. The mixture was cooled down to room temperature, then extra Me_4NCl (44.0 mg, 0.4 mmol) and KOAc (39.0 mg, 0.4 mmol) were added into the mixture and heated at 120 ºC for extra 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 3',4,5'-trimethyl-[1,1'-biphenyl]-3-ol (**3ac**) as an orange oil (59.0 mg, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18-7.16 (m, 3H), 7.08 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.01-7.00 (m, 1H), 6.98 (s, 1H), 4.69 (s, 1H), 2.37 (s, 6H), 2.29 (s, 3 H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.9, 140.8, 140.8, 138.2, 131.2, 128.8, 124.9, 122.5, 119.6, 113.7, 21.4, 15.4 ppm. These data are consistent with those previously reported.[2]

3',5,5'-Trimethyl-[1,1'-biphenyl]-3-ol



3ai

A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), 2-hydroxy-4-methylbenzoic acid (76.1 mg, 0.50 mmol), Me_4NCl (68.5 mg, 0.63 mmol), KOAc (98.0 mg, 1.0 mmol), 1-iodo-3,5-dimethylbenzene (218 µL, 1.5 mmol) and acetic acid (43 µL, 0.75 mmol) was heated at 120 ºC for 24 h. The mixture was cooled down to room temperature, then extra Me_4NCl (44.0 mg, 0.4 mmol) and KOAc (39.0 mg, 0.4 mmol) were added into the mixture and heated at 120 ºC for extra 16 h. After this time, the reaction mixture was filtered through a plug of Celite® with EtOAc (4 × 5 mL). The filtrate was evaporated to dryness. The crude product was purified by column chromatography (hexanes:EtOAc 90:10) to afford 3',5,5'-trimethyl-[1,1'-biphenyl]-3-ol (**3ai**) as a light orange solid (74.1 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 6.99-6.97 (m, 2H), 6.85-6.84 (m, 1H), 6.63 (s, 1H), 4.66 (s, 1H), 2.37 (s, 6H), 2.36 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.7, 143.1, 140.9, 139.9, 138.2, 129.0, 125.0, 120.8, 114.8, 111.3, 21.44, 21.37 ppm. These data are consistent with those previously reported.[2]

References

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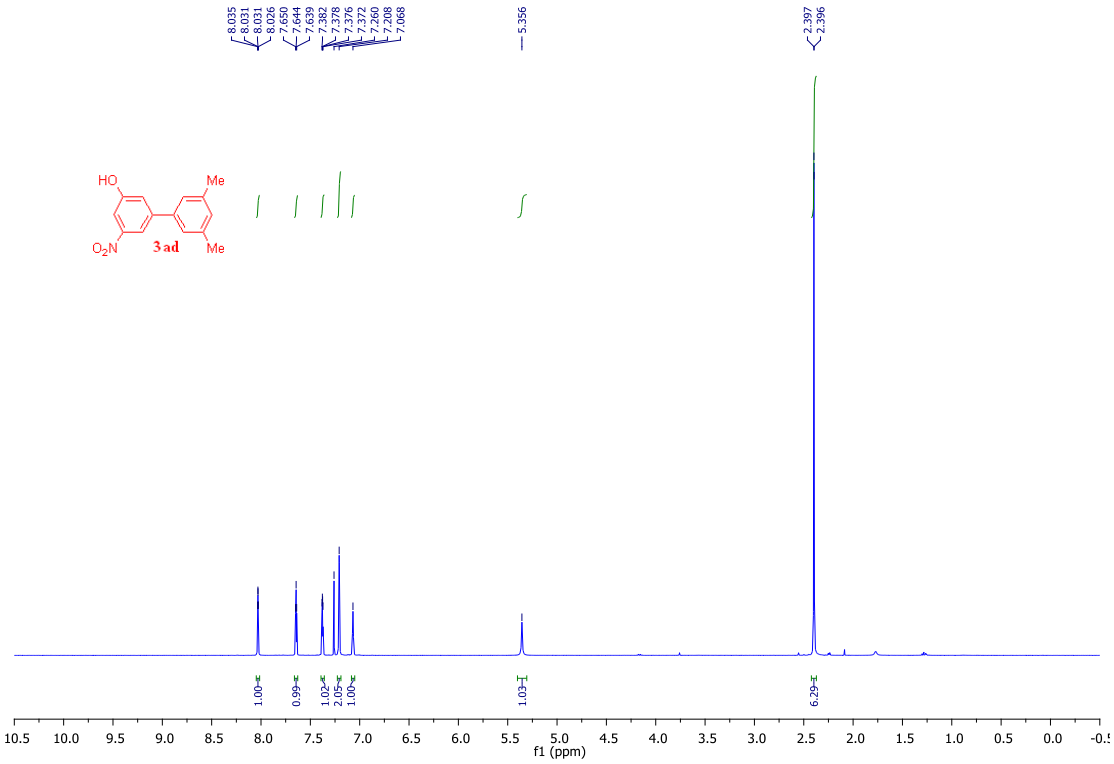
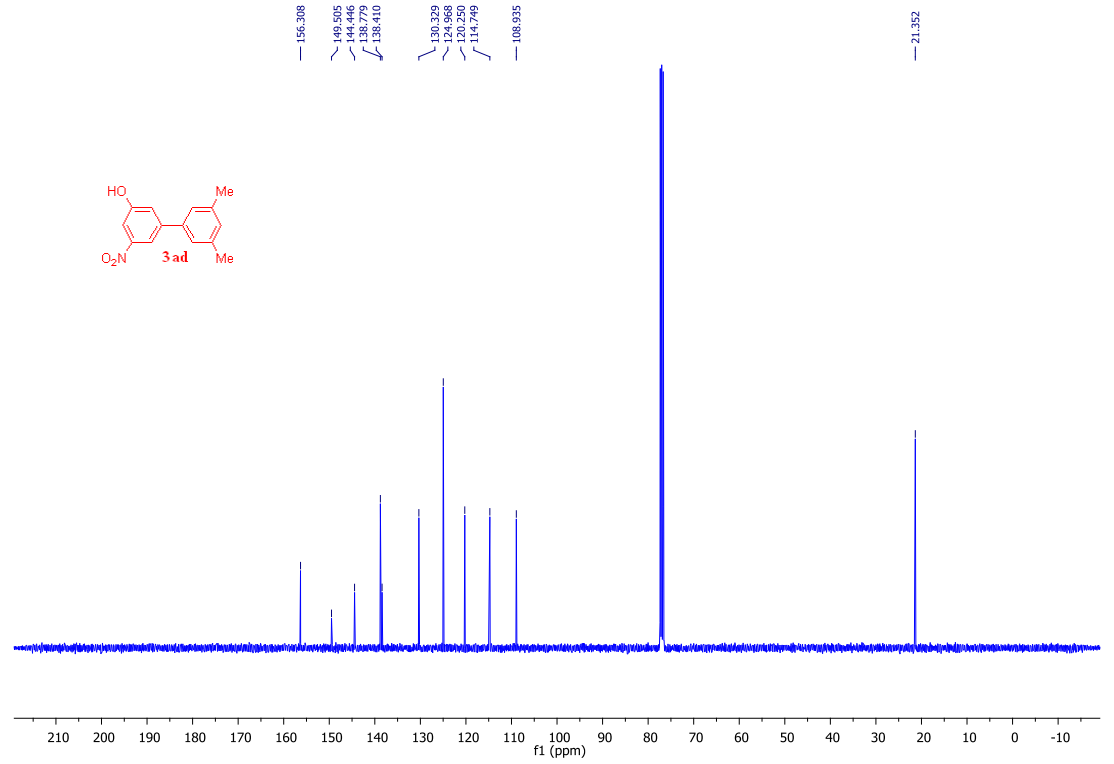
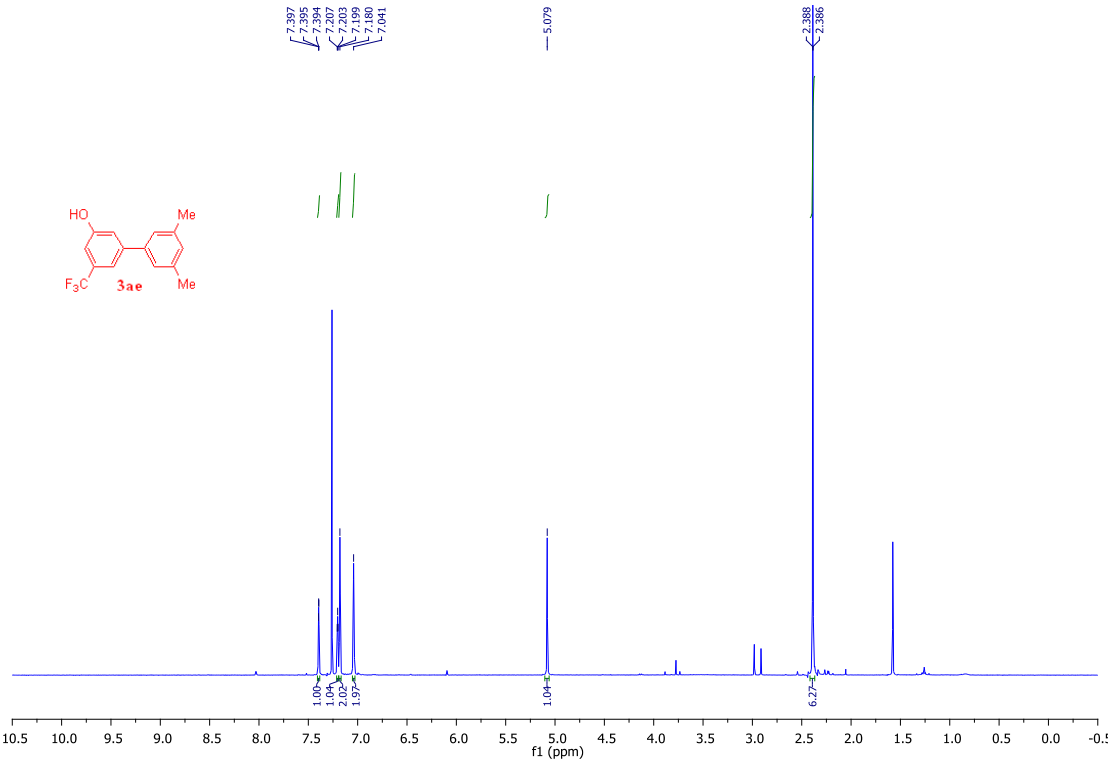
Spectroscopic data



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F3C
3ae
Me
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1.04
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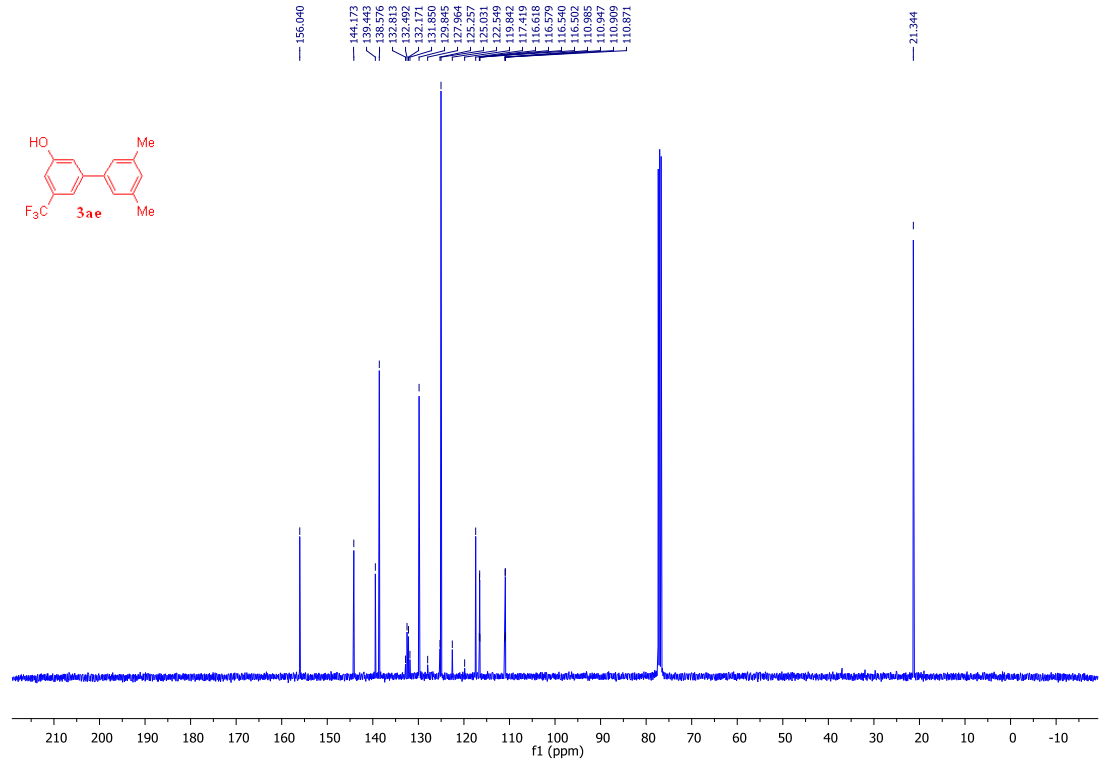
1.97
1.04
6.27
f1 (ppm)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116.618
116.579
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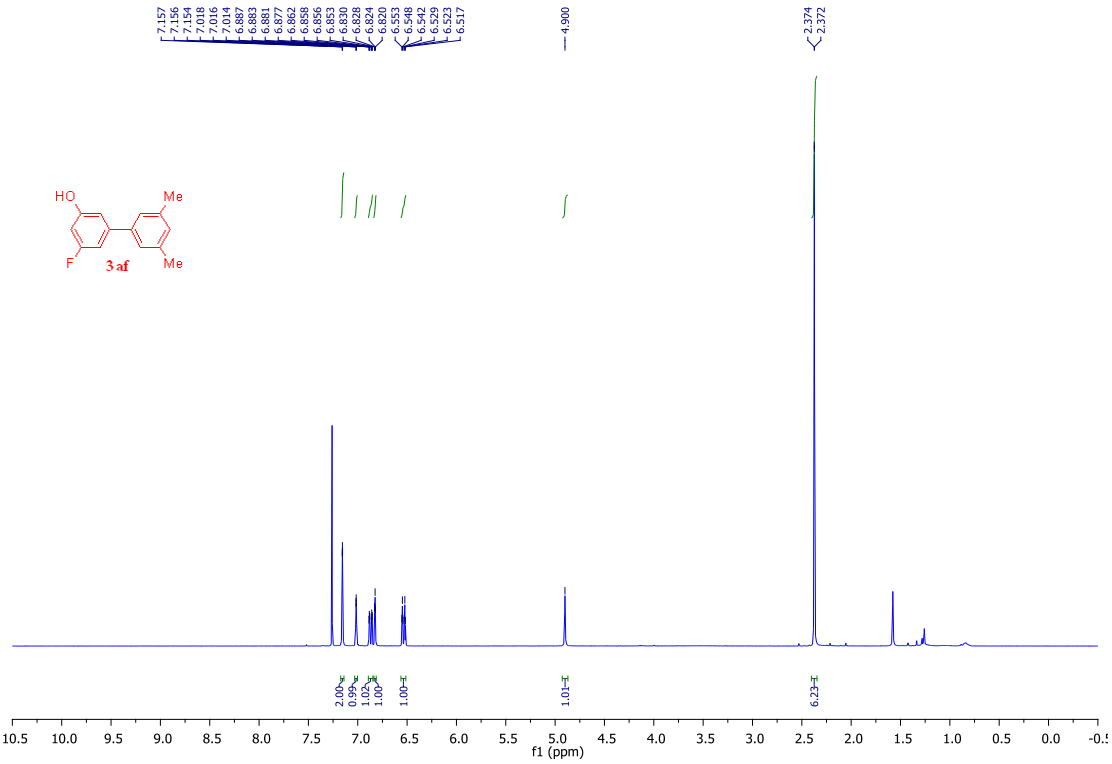
Me
F3C
3ae
Me
f1 (ppm)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6.830
6.828
6.824
6.820
6.553
6.548
6.542
6.529
6.523
6.517
4.900
2.374
2.372
HO
Me
F
Me
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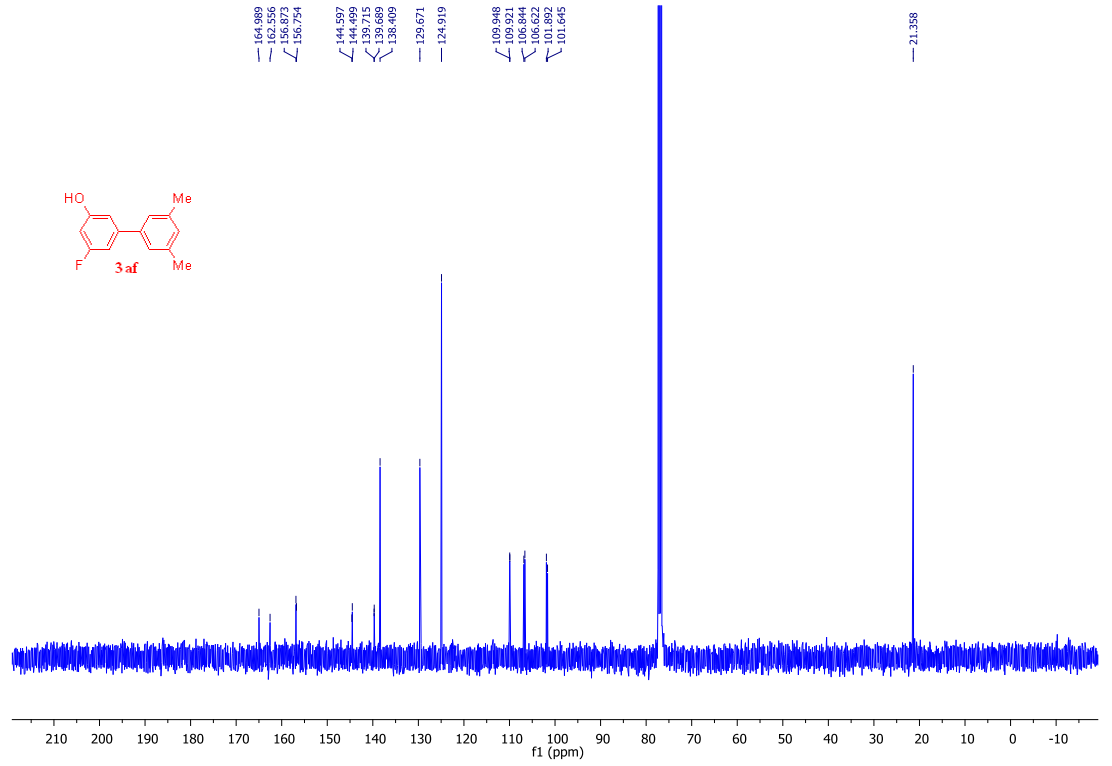
1.00
1.00
1.01
6.23
f1 (ppm)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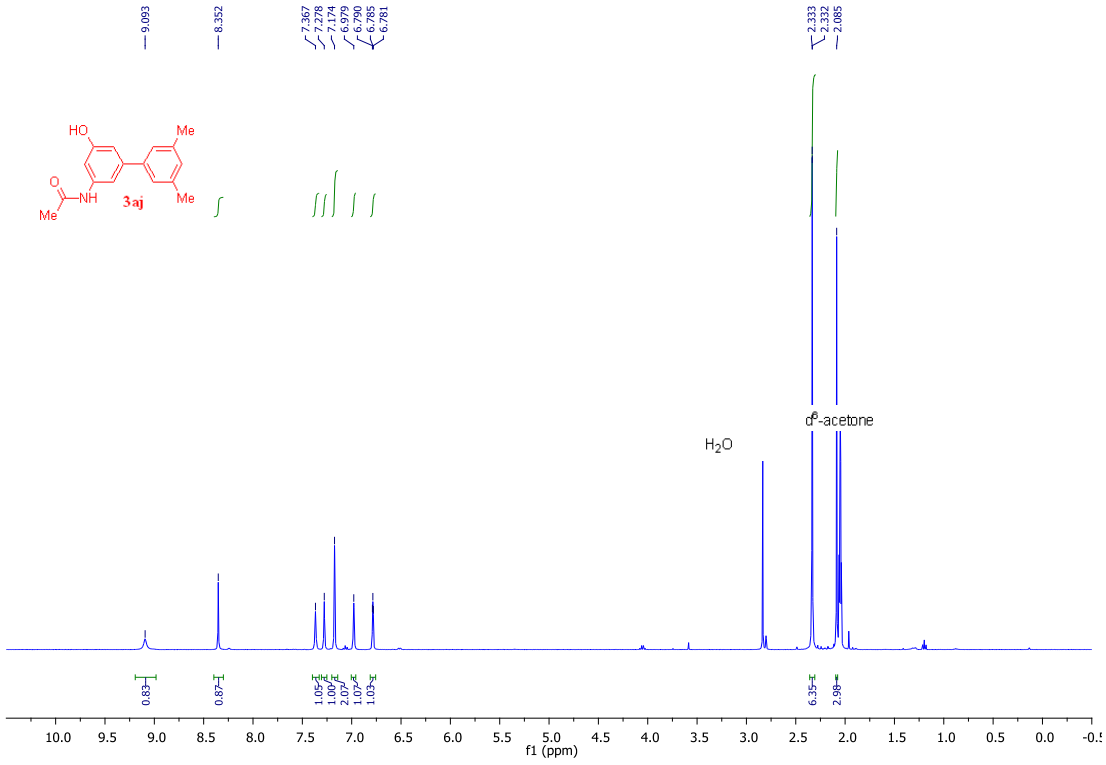
F
Me
3af
f1 (ppm)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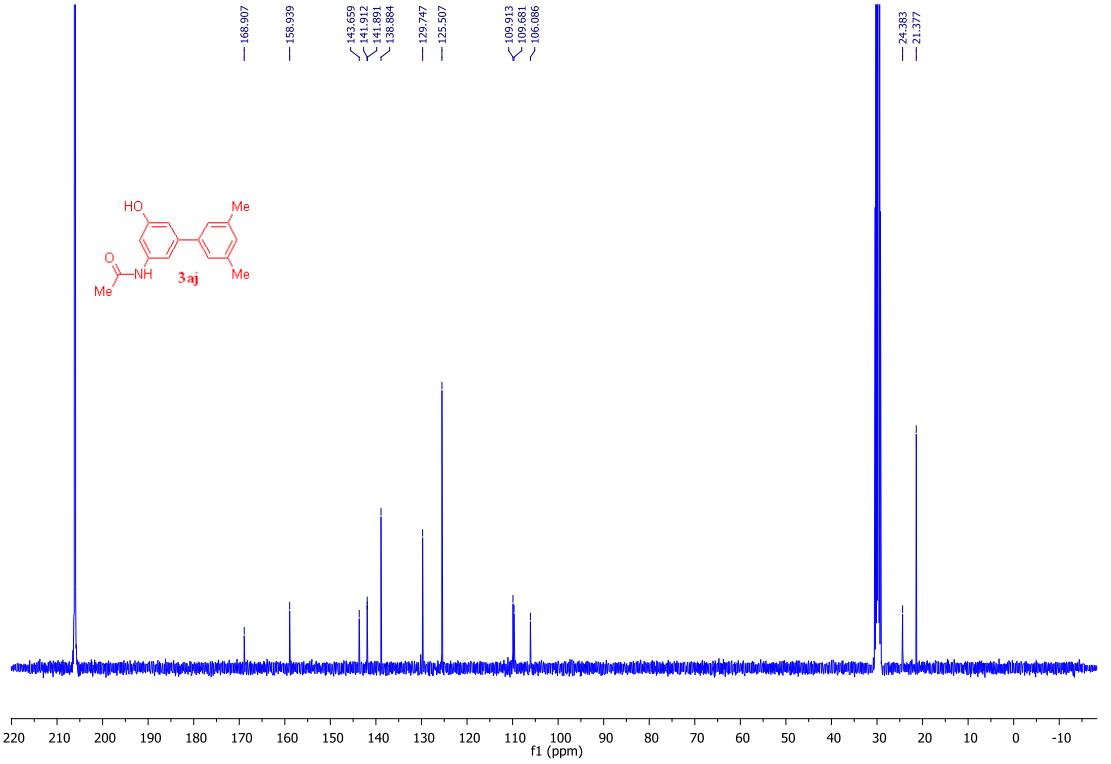
Me
O
NH
Me
Me
3aj
H2O
d6-acetone
0.83
0.87
1.05
1.00
2.07
1.03
6.35
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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O
NH
Me
Me
3aj
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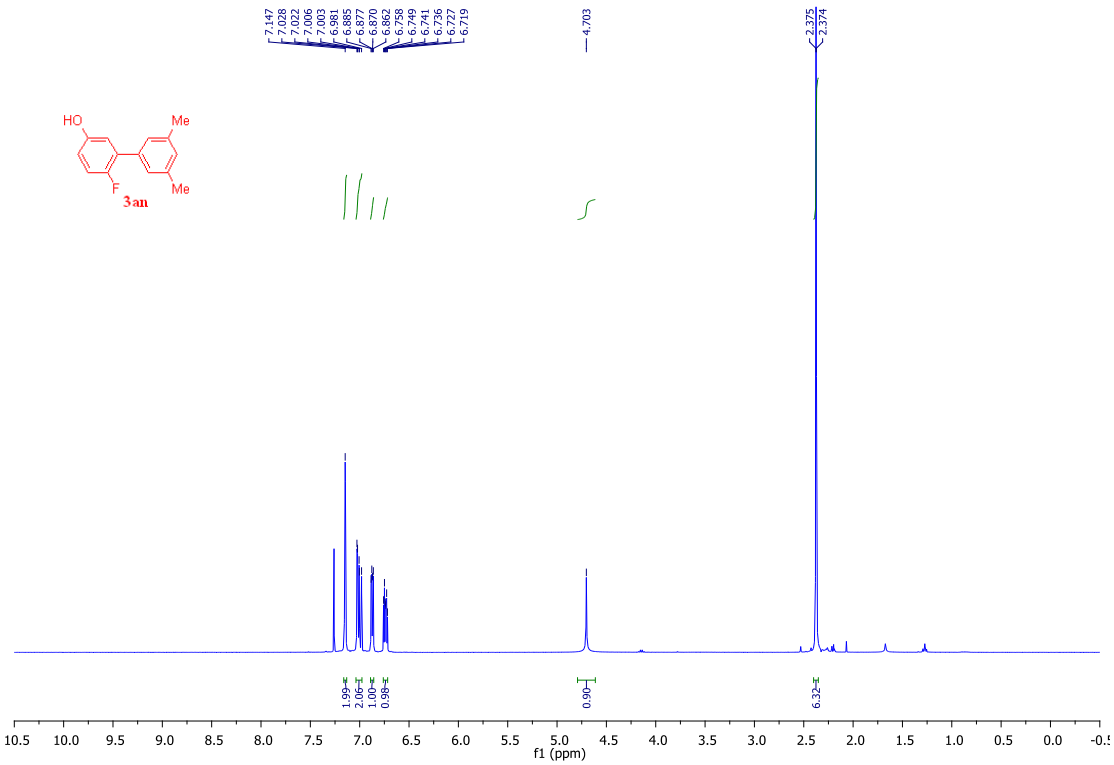
f1 (ppm)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4.703
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F
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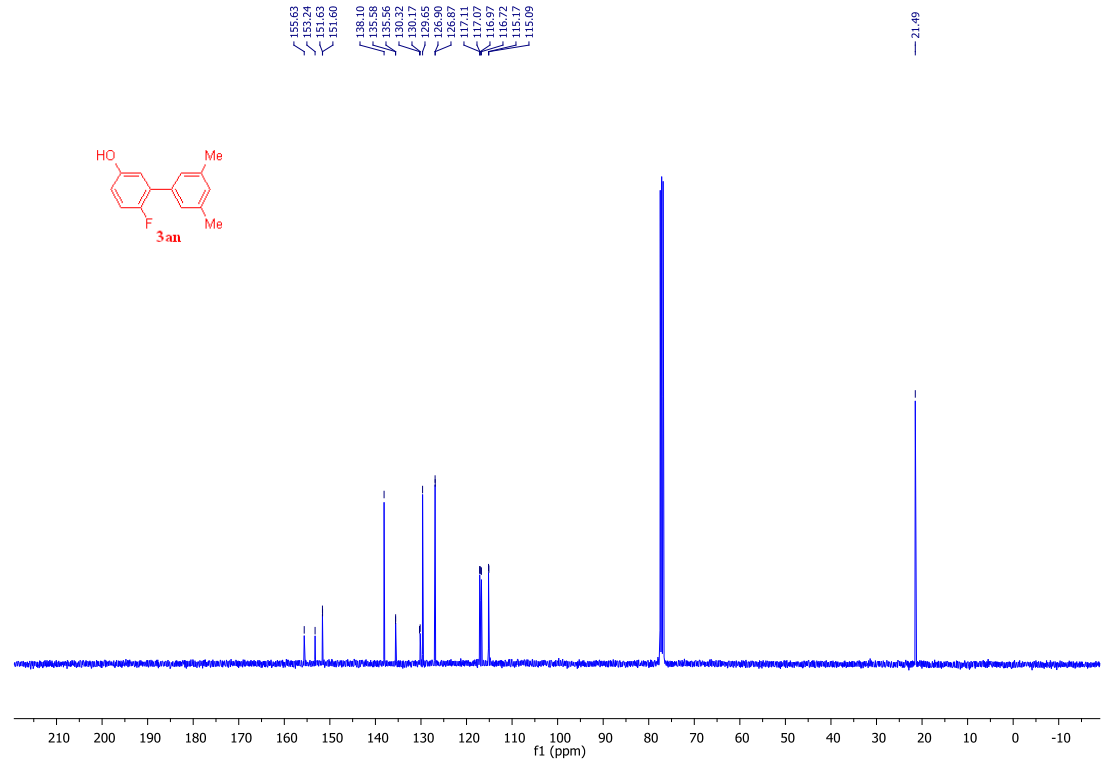
6.32
f1 (ppm)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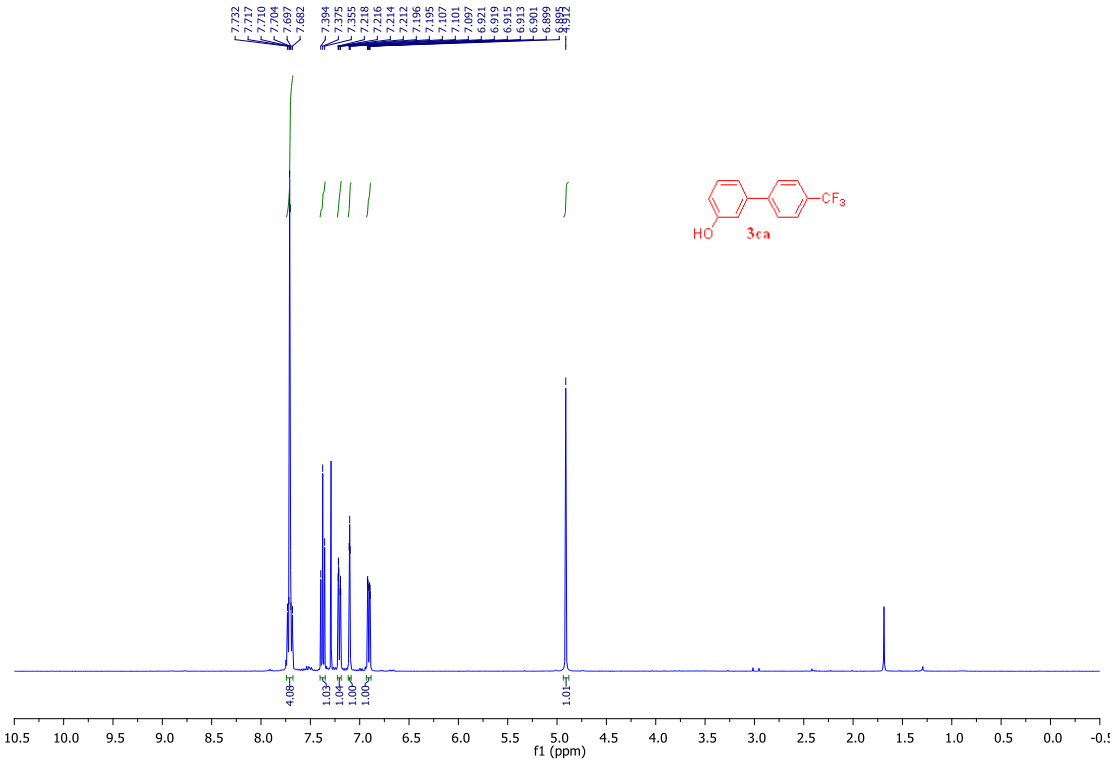
Me
F
Me
3an
f1 (ppm)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7.212
7.196
7.195
7.107
7.101
7.097
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6.919
6.915
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6.901
6.899
6.895
6.892
4.912
CF3
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3ca
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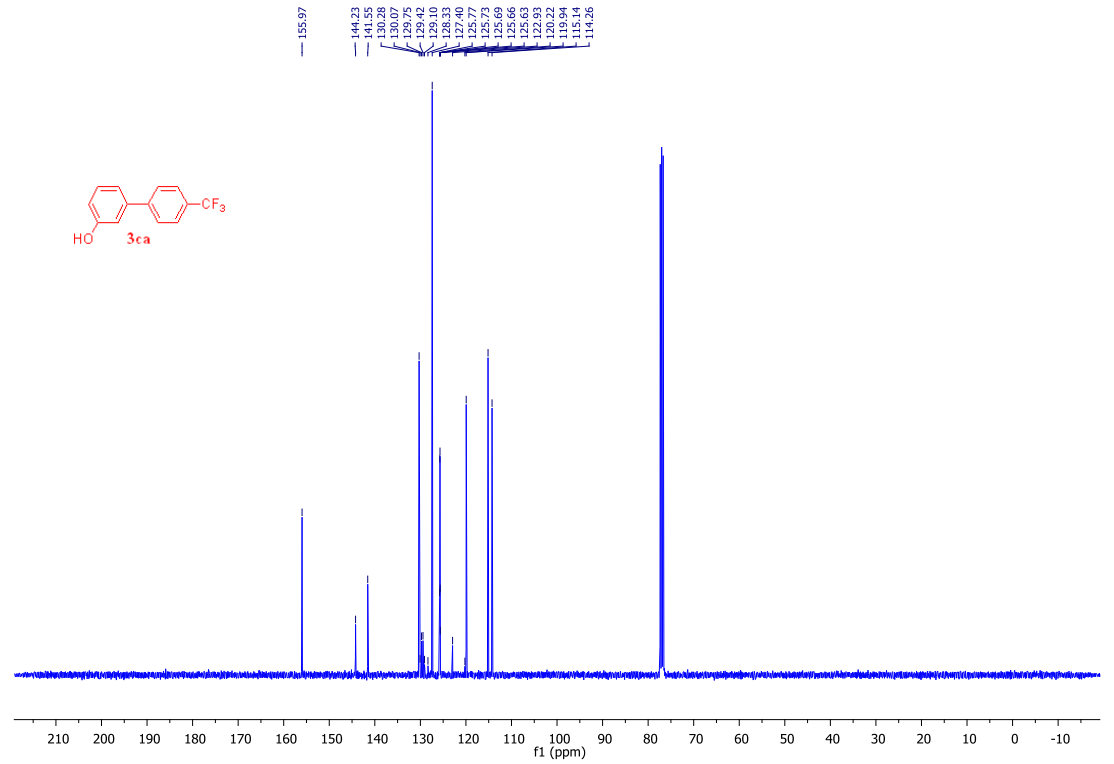
1.03
1.00
1.00
1.00
1.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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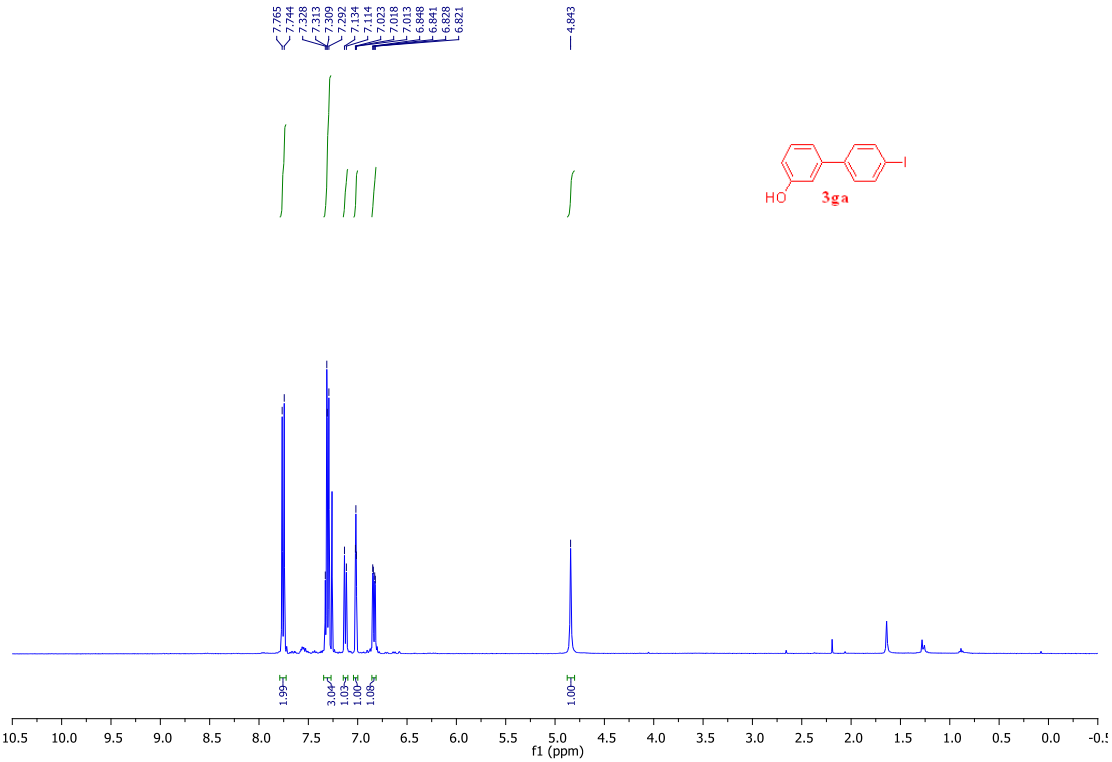
f1 (ppm)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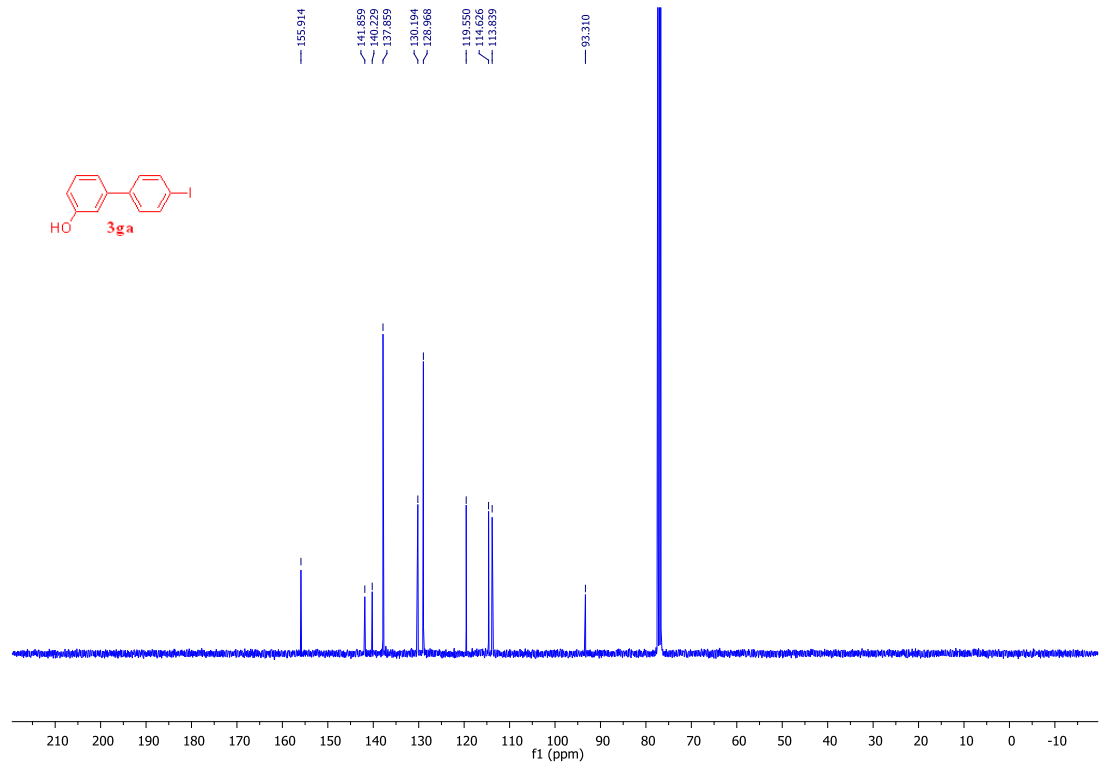
6.841
6.828
6.821
4.843
HO
3ga
1.99
3.04
1.03
1.00
1.08
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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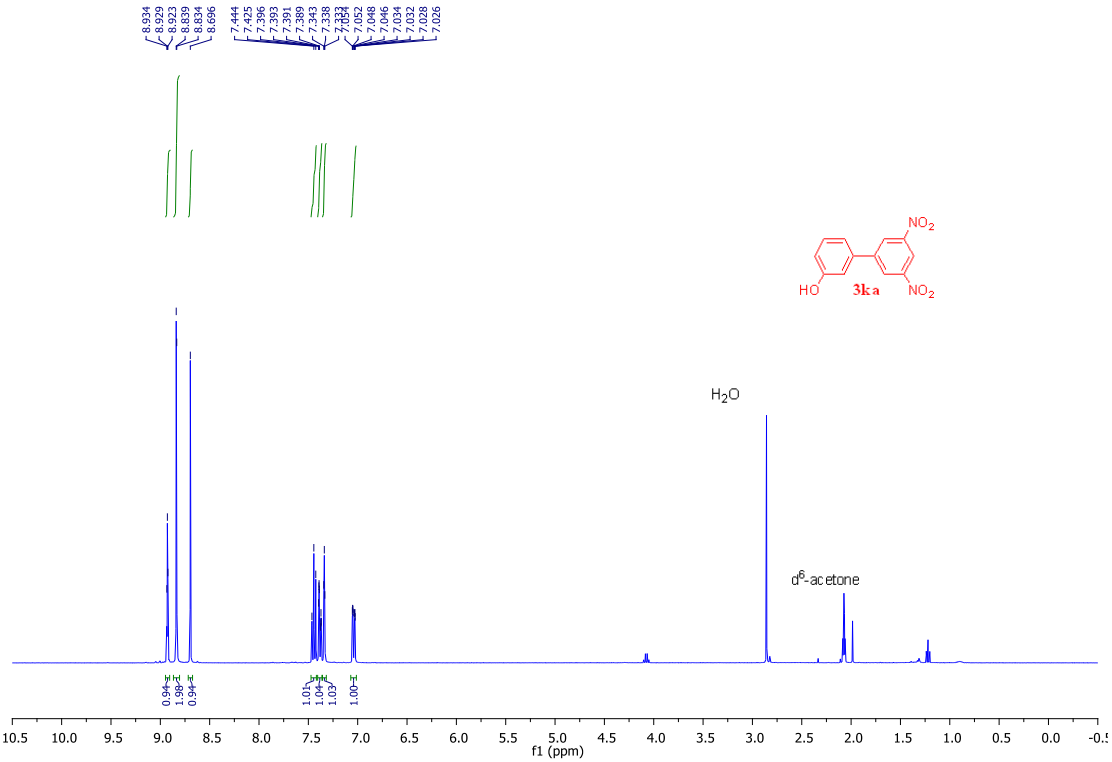
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7.046
7.034
7.032
7.028
7.026
NO2
HO
3ka
NO2
H2O
d6-acetone
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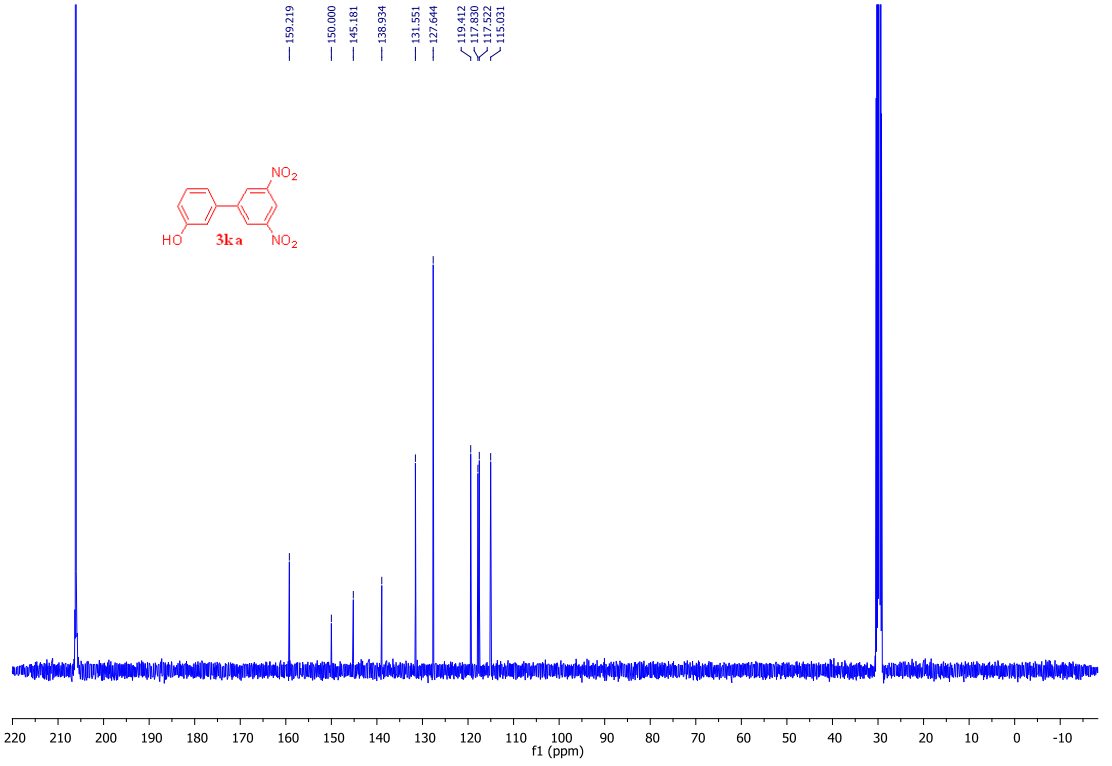
1.98
0.94
1.01
1.04
1.03
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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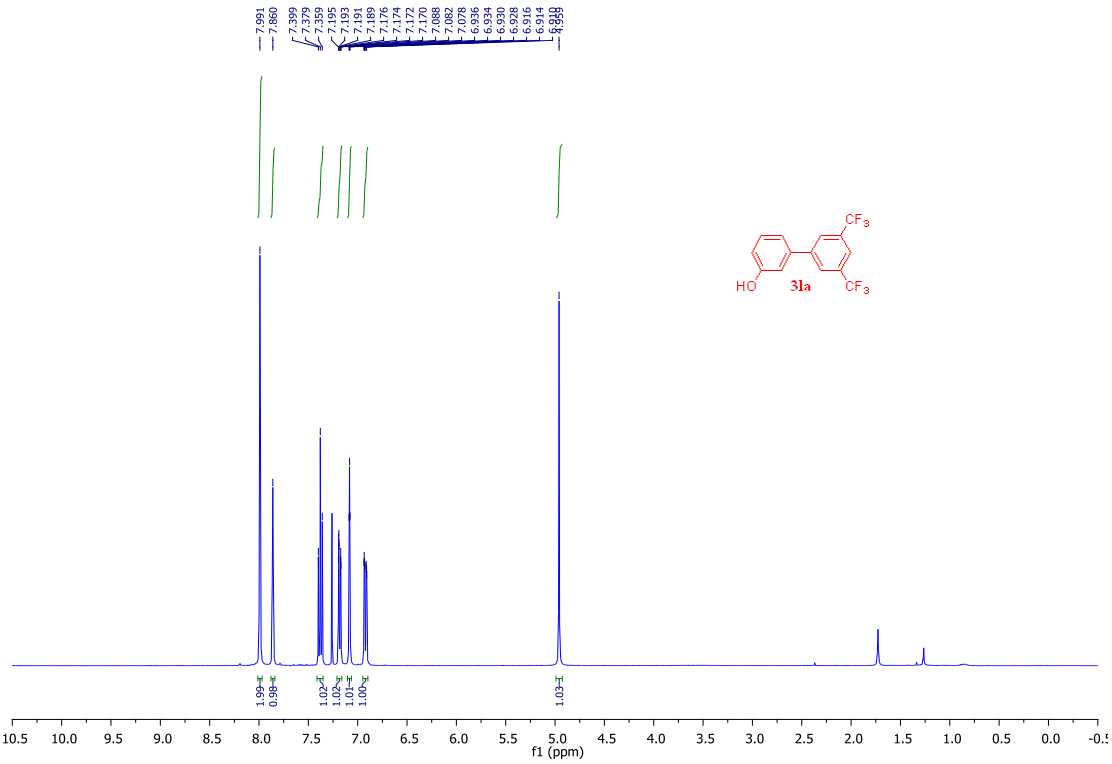
f1 (ppm)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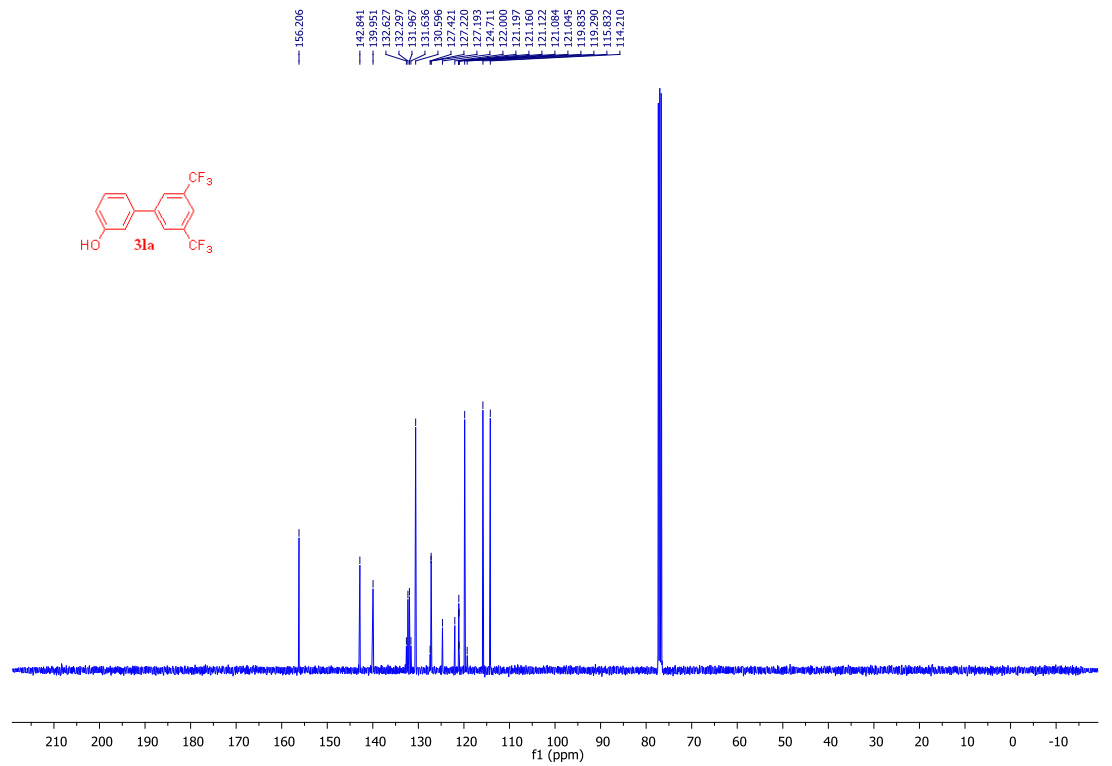
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CF3
HO
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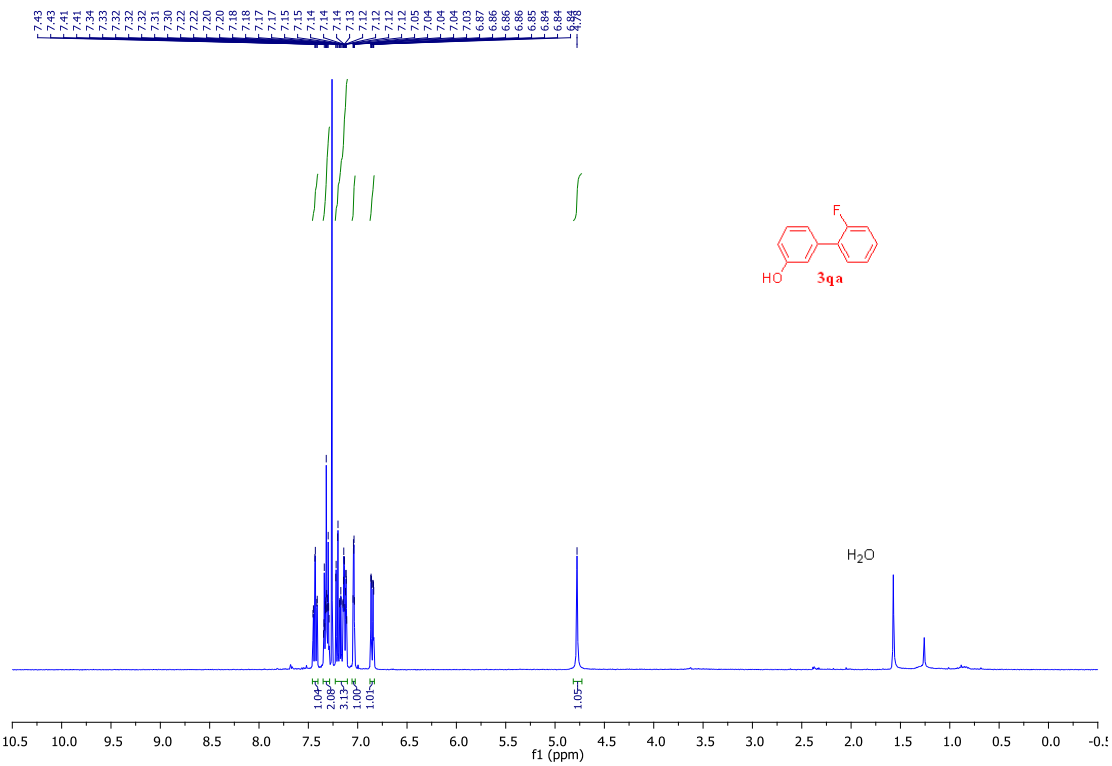
CF3
f1 (ppm)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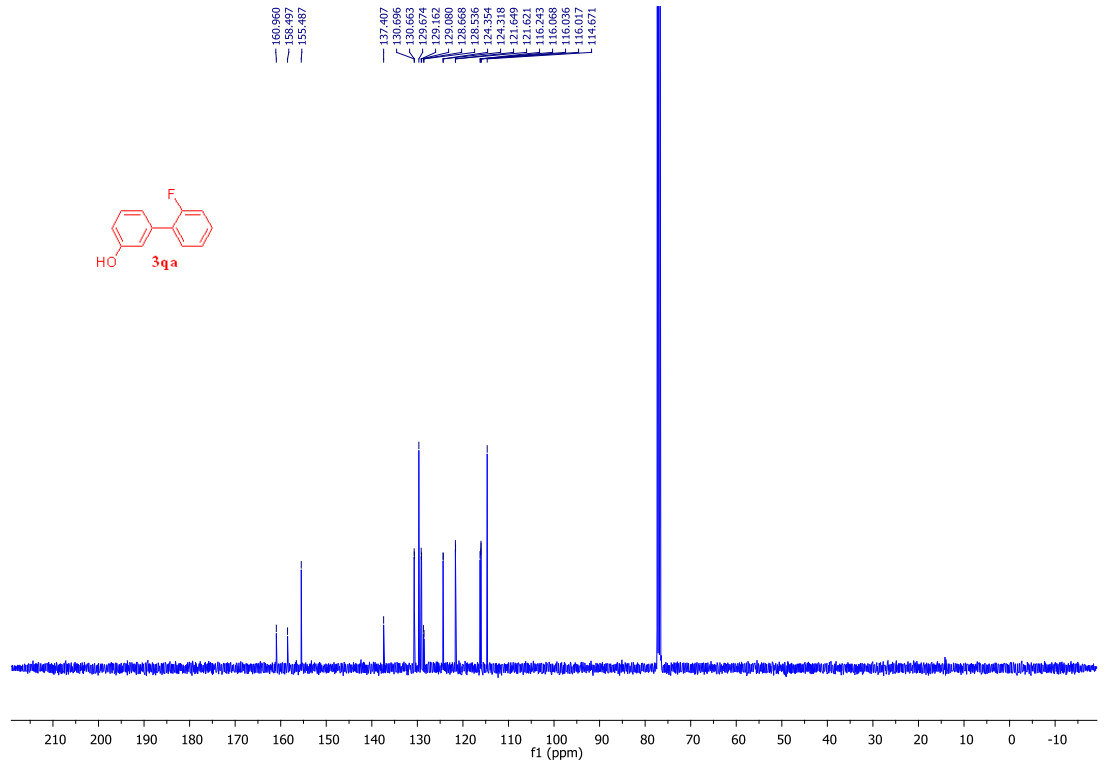
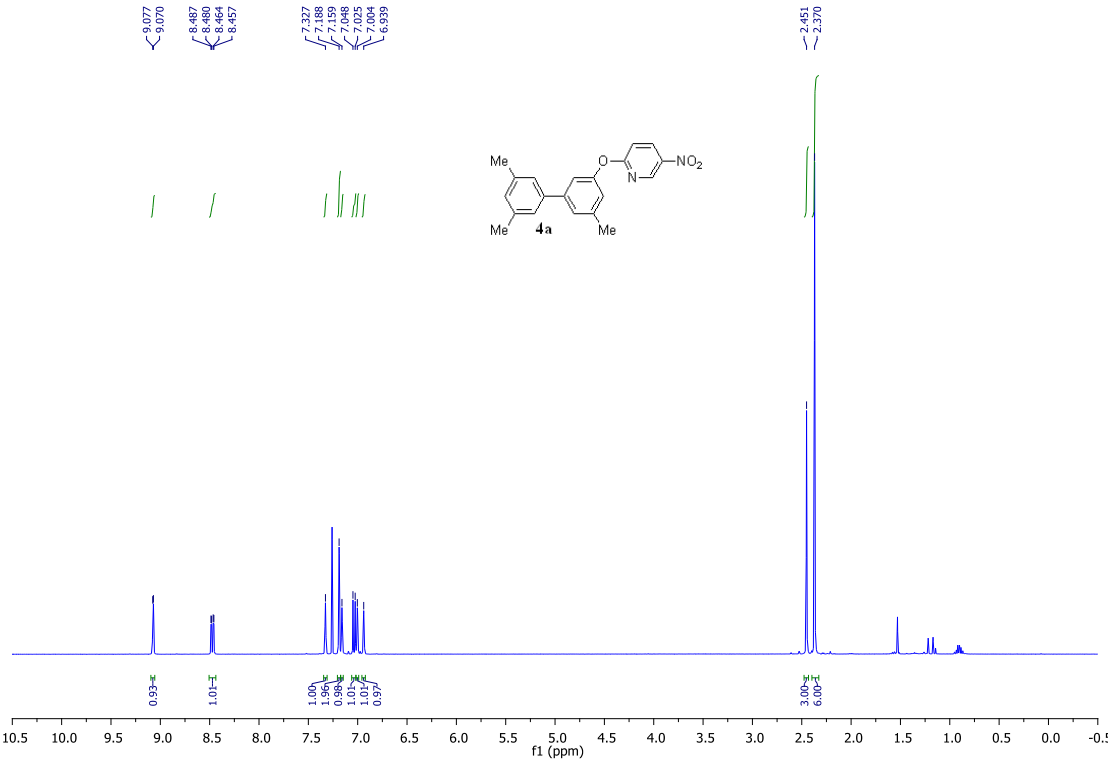
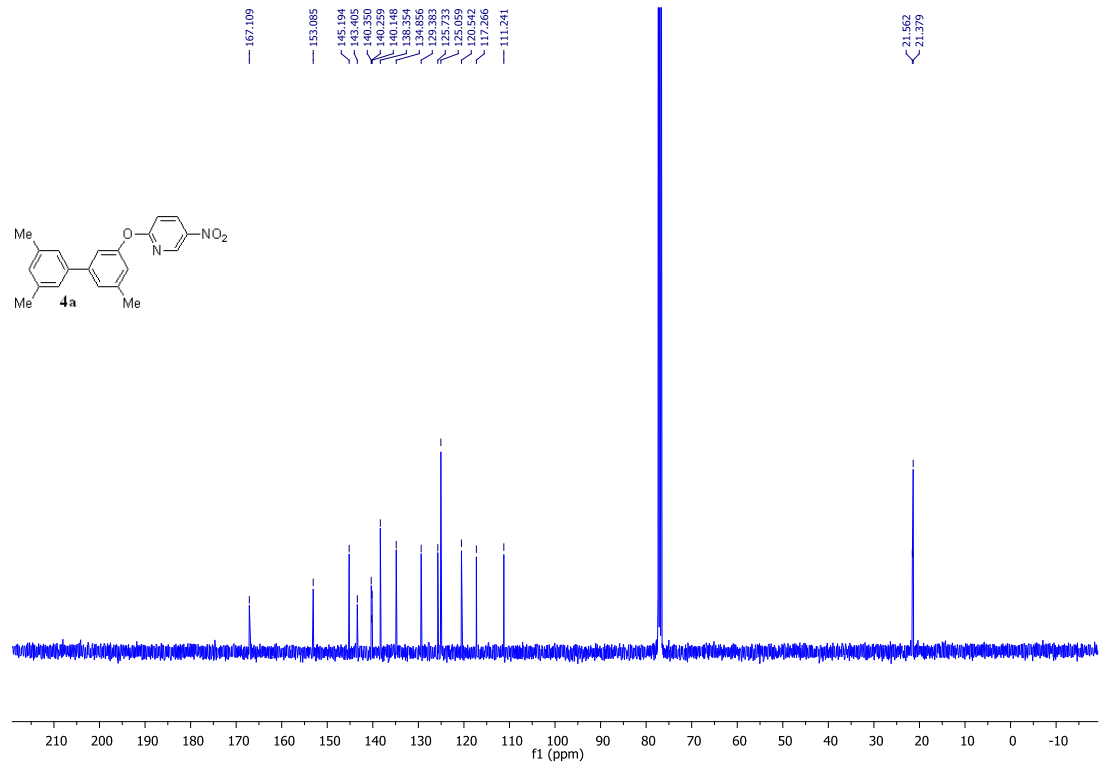
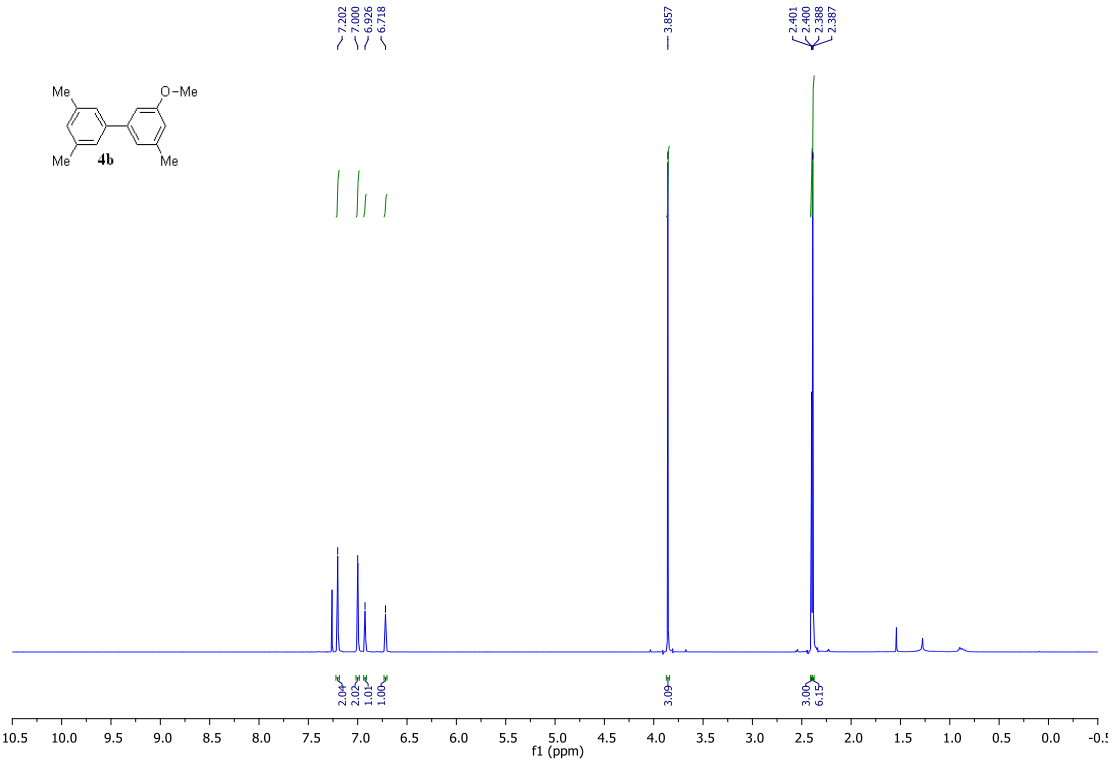
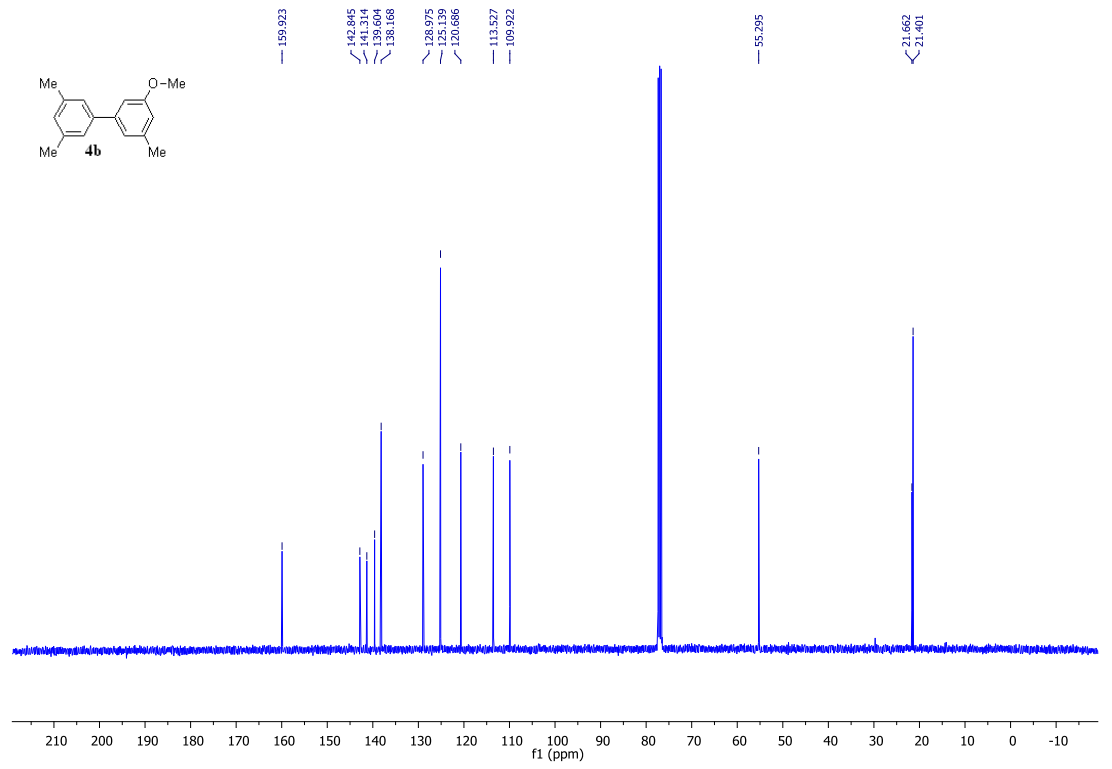
H2O
1.04
2.08
3.13
1.00
1.01
1.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

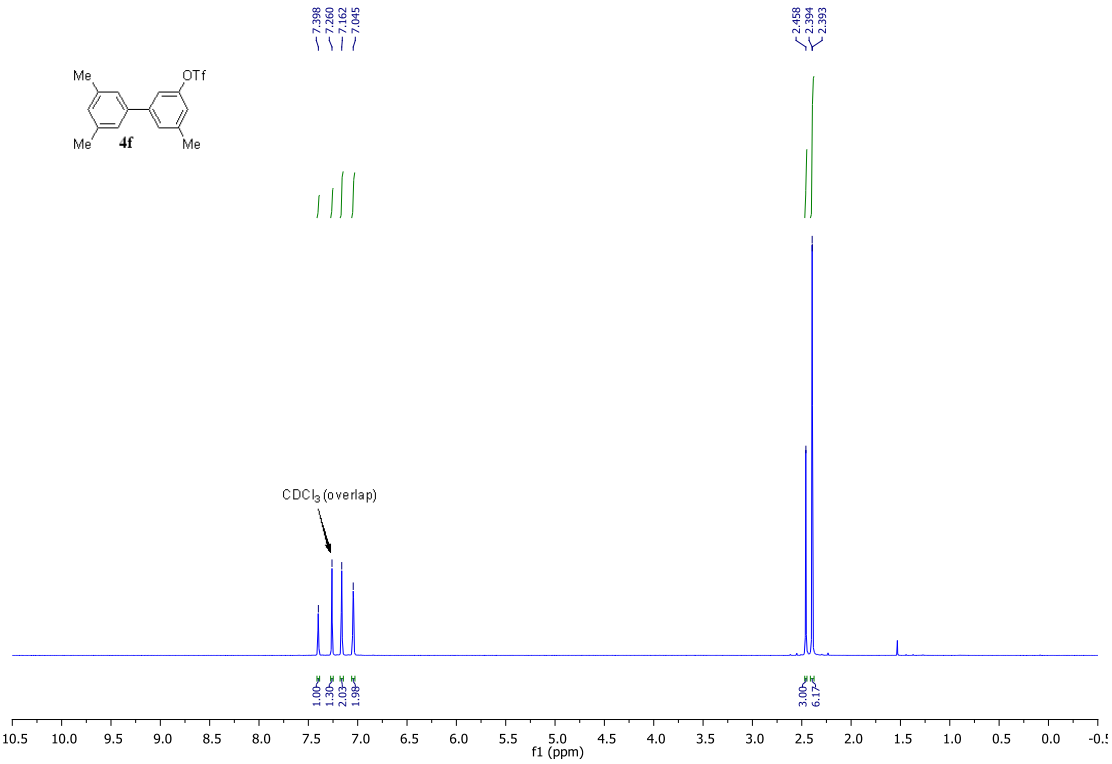

160.960
158.497
155.487
137.407
130.696
130.663
129.674
129.162
129.080
128.668
128.556
124.354
124.318
121.649
121.621
116.243
116.068
116.036
116.017
114.671
F
HO
3qa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

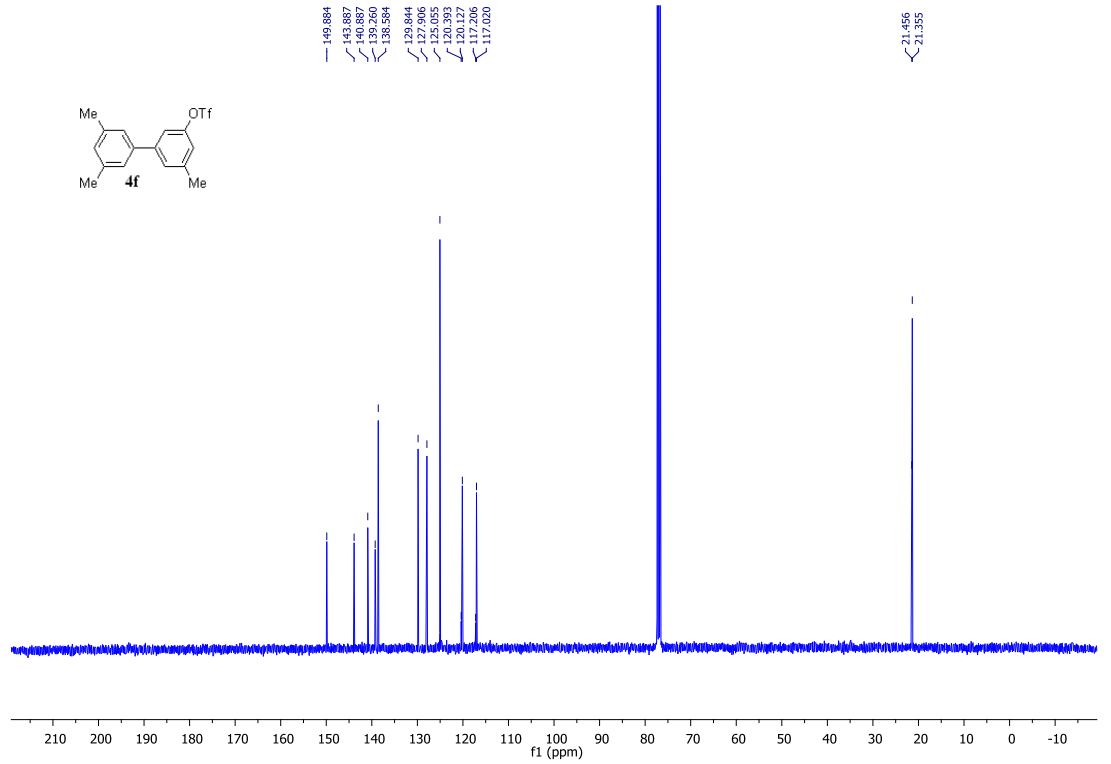

9.077
9.070
8.487
8.480
8.464
8.457
7.327
7.188
7.159
7.048
7.025
7.004
6.939
2.451
2.370
Me
O
N
NO2
Me
4a
Me
0.93
1.01
1.00
1.96
0.98
1.01
1.01
0.97
3.00
6.00
f1 (ppm)

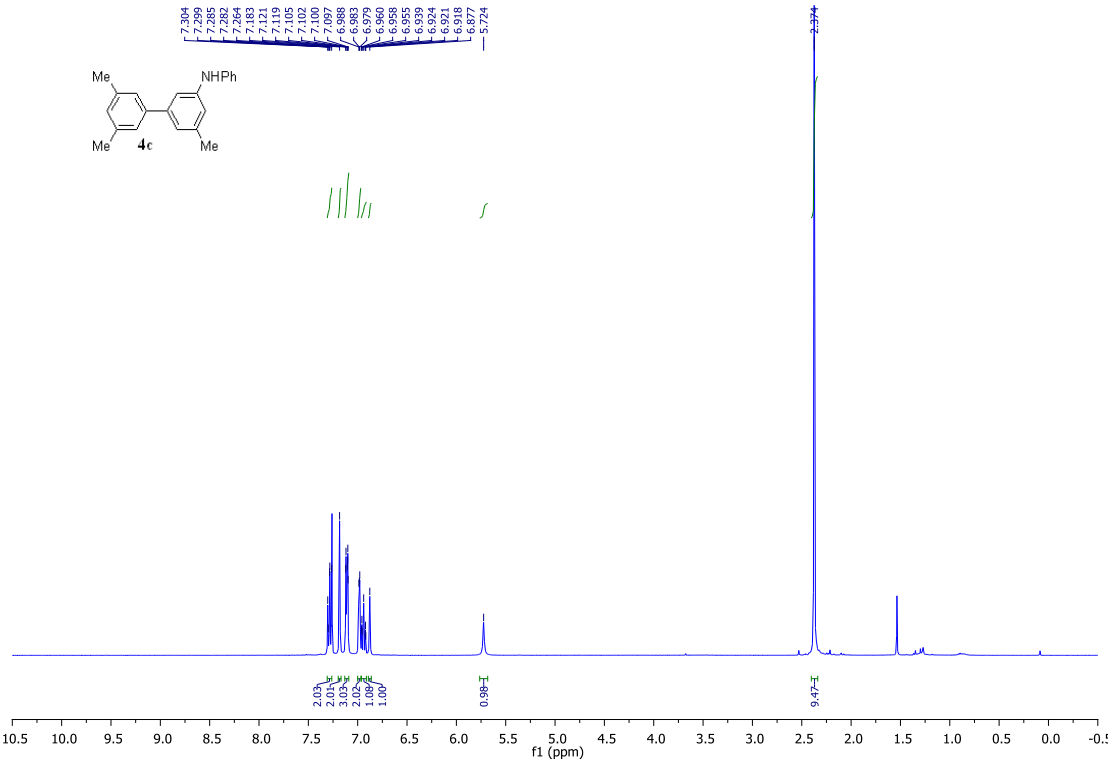

167.109
153.085
145.194
143.405
140.350
140.259
140.148
138.354
134.856
129.383
125.733
125.059
120.542
117.266
111.241
21.562
21.379
Me
O
N
NO2
Me
4a
Me
f1 (ppm)

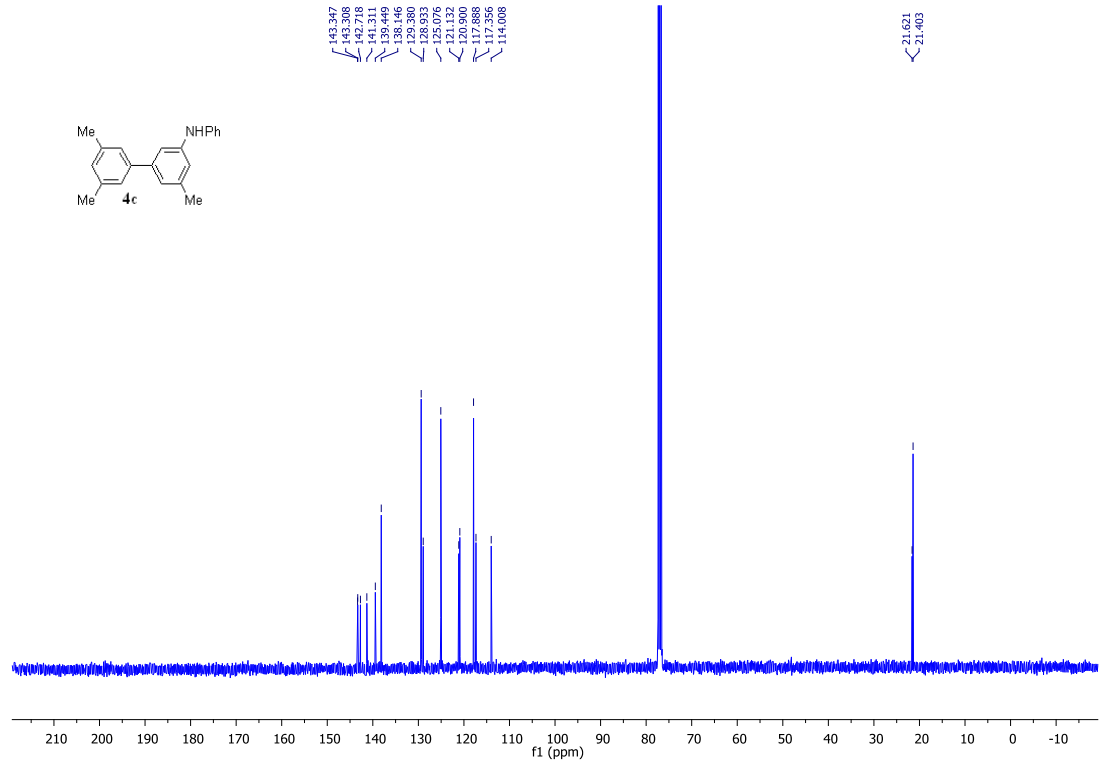

7.202
7.000
6.926
6.718
3.857
2.401
2.400
2.388
2.387
Me
O–Me
Me
Me
4b
2.04
2.02
1.01
1.00
3.09
3.00
6.15
f1 (ppm)

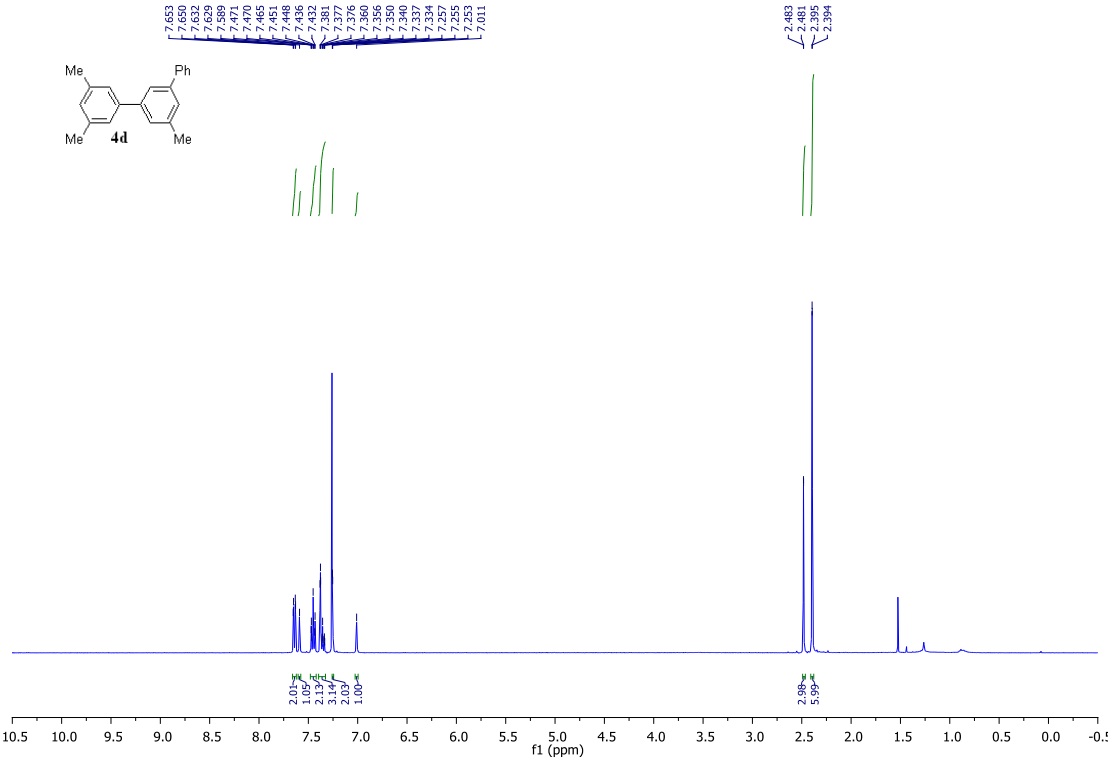

159.923
142.845
141.314
139.604
138.168
128.975
125.139
120.686
113.527
109.922
55.295
21.662
21.401
Me
O–Me
Me
Me
4b
f1 (ppm)

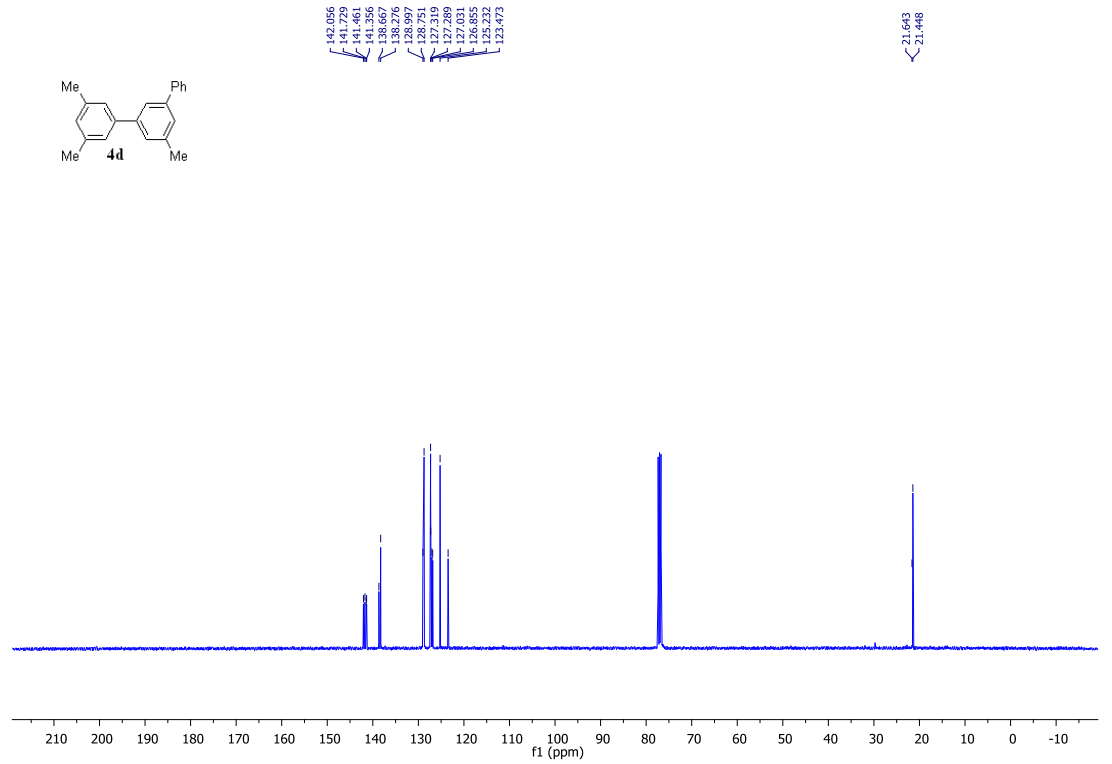

7.398
7.260
7.162
7.045
2.458
2.394
2.393
Me
OTf
Me
4f
Me
CDCl3 (overlap)
1.00
1.30
2.03
1.99
3.00
6.17
f1 (ppm)

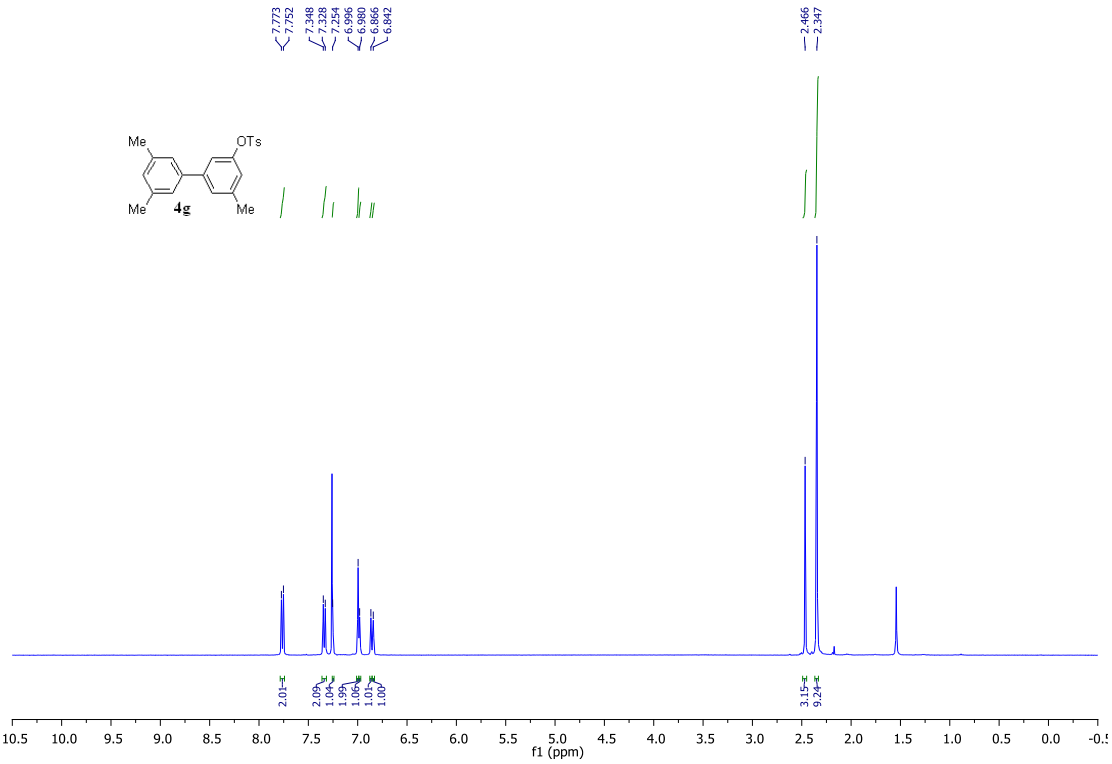

149.884
143.887
140.887
139.260
138.584
129.844
127.906
125.055
120.393
120.227
117.206
117.020
21.456
21.355
Me
OTf
Me
4f
Me
f1 (ppm)

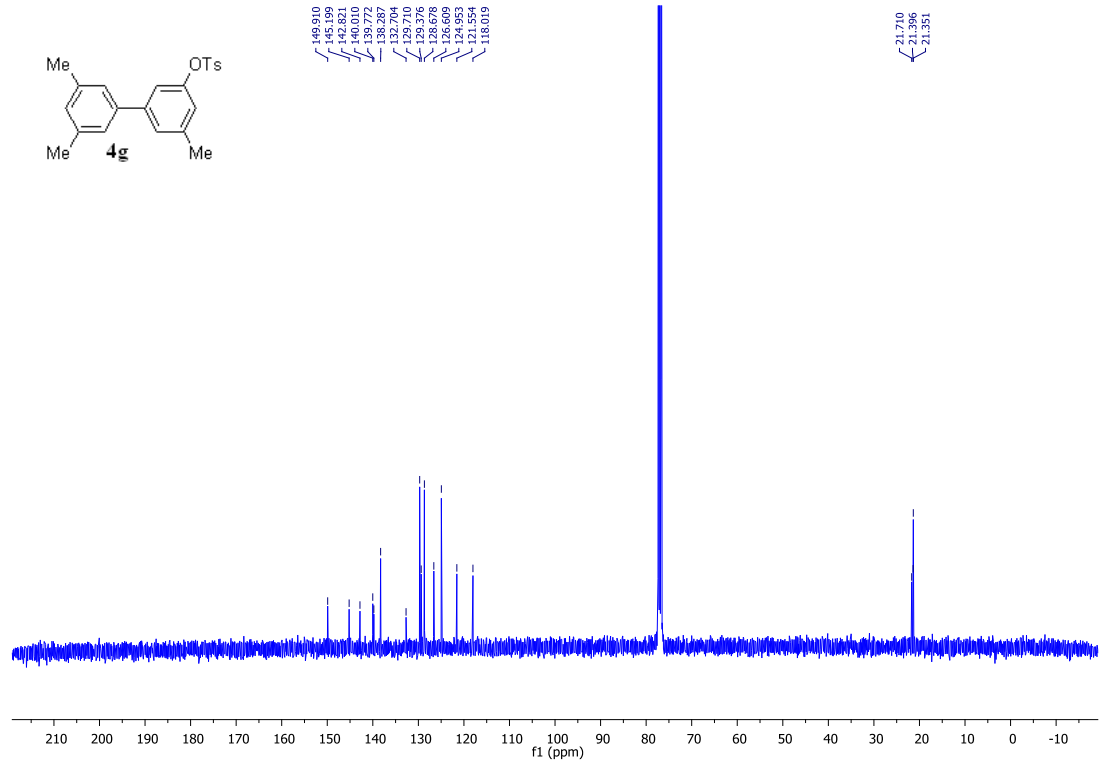

7.304
7.299
7.285
7.282
7.264
7.183
7.121
7.119
7.105
7.102
7.100
7.097
6.988
6.983
6.979
6.960
6.958
6.955
6.939
6.924
6.921
6.918
6.877
5.724
2.374
Me
NHPh
Me
4c
Me
2.03
2.01
3.03
2.02
1.09
1.00
0.98
9.47
f1 (ppm)

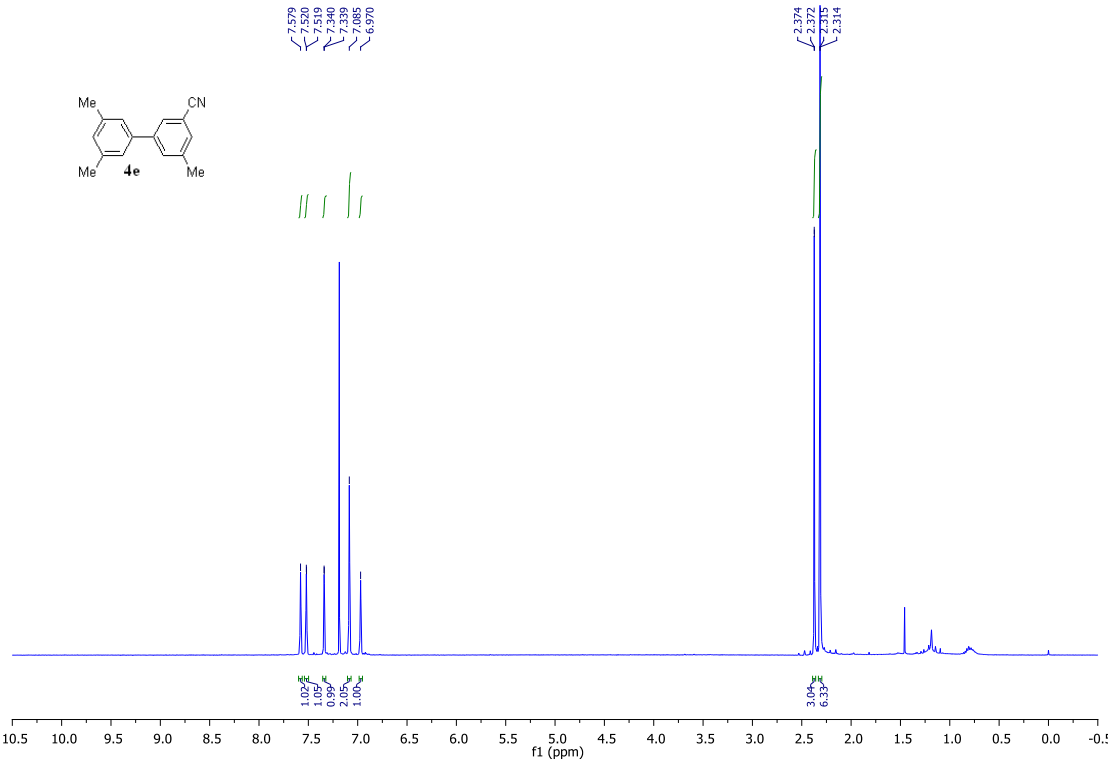

143.347
143.308
142.718
141.311
139.449
138.146
129.380
128.933
125.076
121.132
120.900
117.988
117.355
114.008
21.621
21.403
Me
NHPh
Me
4c
Me
f1 (ppm)

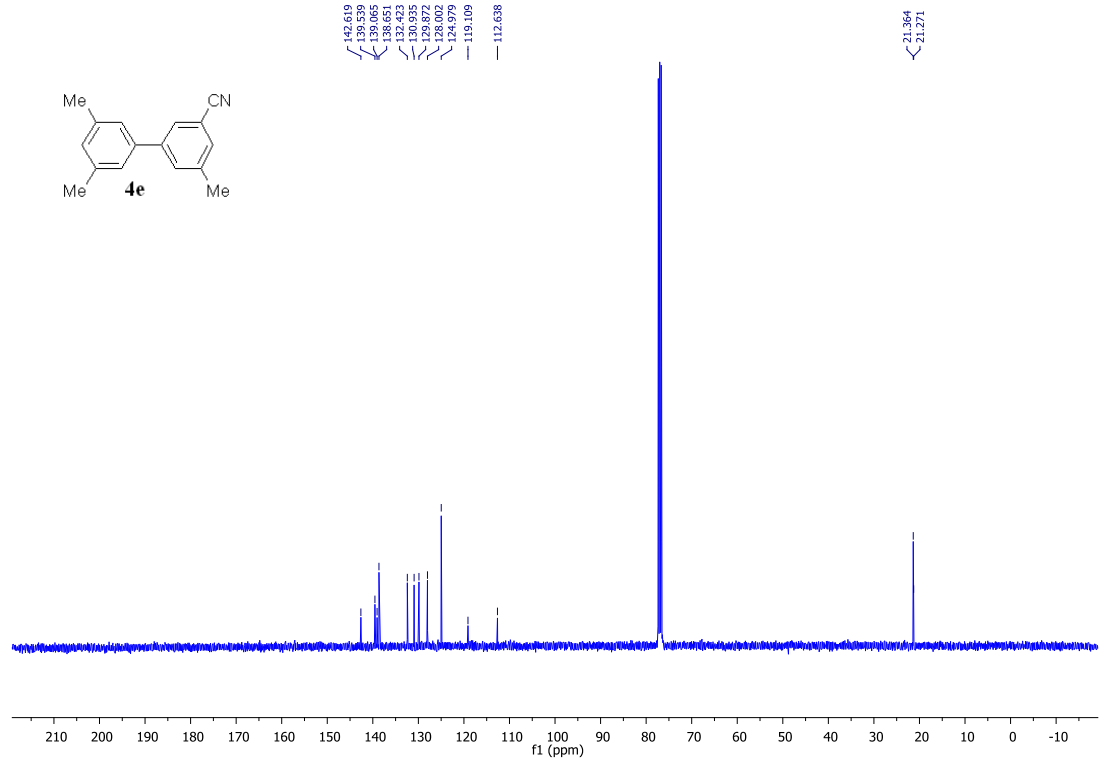

7.653
7.650
7.632
7.629
7.589
7.471
7.470
7.465
7.451
7.448
7.436
7.432
7.381
7.377
7.376
7.360
7.355
7.350
7.340
7.337
7.334
7.257
7.255
7.253
7.011
2.483
2.481
2.395
2.394
Me
Ph
Me
4d
Me
2.01
1.05
2.13
3.14
2.03
1.00
2.98
5.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.056
141.729
141.461
141.356
138.667
138.276
128.997
128.751
127.319
127.289
127.031
126.855
125.232
123.473
21.643
21.448
Me
Ph
Me
4d
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.773
7.752
7.348
7.328
7.324
6.996
6.980
6.866
6.842
2.466
2.347
Me
OTs
Me
4g
Me
2.01
2.09
1.04
1.99
1.06
1.01
1.00
3.15
9.24
f1 (ppm)


149.910
145.199
142.821
140.010
139.772
138.287
132.704
129.710
128.776
128.678
126.609
124.953
121.554
118.019
21.710
21.396
21.351
Me
OTs
Me
4g
Me
f1 (ppm)


7.579
7.520
7.519
7.340
7.339
7.085
6.970
2.374
2.372
2.315
2.314
Me
CN
Me
Me
4e
1.02
1.05
0.99
2.05
1.00
3.04
6.33
f1 (ppm)


142.619
139.539
139.065
138.651
132.423
130.935
129.872
128.002
124.979
119.109
112.638
21.364
21.271
Me
CN
Me
Me
4e
f1 (ppm)