Cu-Catalyzed Cross-Coupling of Nitroarenes with Aryl Boronic Acids to Construct Diarylamines

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Supporting Information

Contents:

General. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 500 MHz or 300 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High-resolution mass spectra were obtained by peak matching. Melting points are reported uncorrected. Infrared spectroscopy was obtained using a diamond attenuated total reflectance (ATR) accessory. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. HPLC analysis was conducted on an Agilent 1100 instrument equipped with a binary pump and diode array detector. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on 60Å (40 – 60 μm) mesh silica gel (SiO_2). Medium pressure liquid chromatography (MPLC) was performed to force flow the indicated solvent system down columns that had been packed with 60Å (40 – 60 μm) mesh silica gel (SiO_2). All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Acetonitrile, methanol, Toluene, THF, Et_2O, and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs.[1] Metal salts were stored in a nitrogen atmosphere dry box.

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

I. Cu-Catalyzed Formation of Diarylamines

A. Screening of Reductive Cross-coupling Conditions

In a 10 mL Schlenk tube under nitrogen, methyl 4-nitrobenzoate, 4-methoxyphenylboronic acid, catalyst and ligands were suspended in 1 mL of solvent. To the resulting mixture was added the silane reductant and the Schlenk tube was sealed. The reaction mixture was heated. After 30 h, the reaction mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo*, and the residue was analyzed using ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

Table s1. Optimization of Cu-catalyzed reductive cross-coupling reaction conditions to form diarylamines.

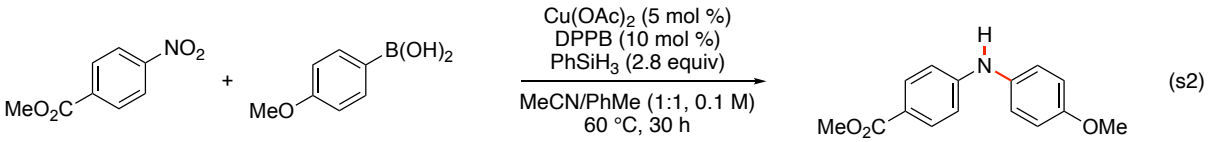
Entry[a]	$ArNO_2$ (equiv)	$ArB(OH)_2$ (equiv)	catalyst	mol %	ligand	mol %	silane	equiv	additive	mol %	solvent (0.1 M)	T (°C)	%, Yield **3a**[a]	%, Yield aniline[a]
1	1.0	1.0	$Pd(OAc)_2$	10	Cy_2PhP	20	$PhSiH_3$	3.0	none	...	PhMe	100	0	86
2	1.0	1.0	$Ni(acac)_2$	10	Cy_2PhP	20	$PhSiH_3$	3.0	none	...	PhMe	100	n.r.	n.r.
3	1.0	1.0	$Fe(OAc)_2$	10	Cy_2PhP	20	$PhSiH_3$	3.0	none	...	PhMe	100	dec.	dec.
4	1.0	1.0	$Cu(OAc)_2$	10	Cy_2PhP	20	$PhSiH_3$	3.0	none	...	PhMe	100	21	40
5	1.0	1.0	$Cu(OAc)_2$	10	DPPB	10	$PhSiH_3$	3.0	none	...	PhMe	100	39	42
6	1.0	1.0	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	PhMe	100	35	21
7	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	PhMe	100	65	32
8	1.0	2.0	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	PhMe	100	33	42
9	1.5	1.0	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	PhMe	100	42	54
10	2.0	1.0	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	PhMe	100	45	69
11	1.5	1.0	CuCl	10	DPPB	20	$PhSiH_3$	3.0	none	...	PhMe	100	25	0
12	1.5	1.0	CuOTf•PhMe	10	DPPB	20	$PhSiH_3$	3.0	none	...	PhMe	100	n.r.	0
13	1.5	1.0	Cu_2O	10	DPPB	20	$PhSiH_3$	3.0	none	...	PhMe	100	0	60
14	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	xylenes	100	55	35
15	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	DMF	100	10	10
16	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	DME	100	23	74
17	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	1,4-dioxane	100	56	40
18	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	DCE	100	52	42

Entry[a]	$ArNO_2$ (equiv)	$ArB(OH)_2$ (equiv)	catalyst	mol %	ligand	mol %	silane	equiv	additive	mol %	solvent (0.1 M)	T (°C)	%, Yield **3a**	%, Yield aniline
19	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	EtOH	100	n.r.	n.r
20	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	MeCN	100	52	28
21	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	AcOH	10	MeCN	100	46	33
22	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	K_2CO_3	10	MeCN	100	0	45
23	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	KO*t*-Bu	10	MeCN	100	24	50
24	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	CsF	10	MeCN	100	39	28
25	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	MgO	10	MeCN	100	44	32
26	1.0	1.5	$Cu(OAc)_2$	10	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	100	42	48
27	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	100	55	26
28	1.0	1.5	$Cu(OAc)_2$	2	DPPB	4	$PhSiH_3$	3.0	none	...	MeCN	100	50	31
29	1.0	1.5	$Cu(OAc)_2$	1	DPPB	2	$PhSiH_3$	3.0	none	...	MeCN	100	31	47
30	1.0	1.5	$CuCl_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	100	35	50
31	1.0	1.5	$CuCl_2$	5	DPPB	10	$PhSiH_3$	3.0	$AgClO_4$	10	MeCN	100	0	64
32	1.0	1.5	$CuCl_2$	5	DPPB	10	$PhSiH_3$	3.0	$AgSbF_6$	10	MeCN	100	0	80
34	1.0	1.5	$Cu(acac)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	100	50	21
34	1.0	1.5	$Cu(tfacac)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	100	45	28
35	1.0	1.5	$CuSO_4$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	100	36	34
36	1.0	1.5	$Cu(TFA)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	100	55	25
37	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	80	61	24
38	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	60	63	33
39	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	40	21	8
40	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN	RT	n.r.	n.r.
41	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	MeCN/PhMe (9:1)	60	55	25
42	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	MeCN/PhMe (4:1)	60	70	20
43	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	MeCN/PhMe (1:1)	60	76	18
44	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	MeCN/xylenes (1:1)	60	55	26
45	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	MeCN/$PhCF_3$ (1:1)	60	65	24
46	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	MeCN/iPrOAc (1:1)	60	61	25
47	1.0	1.5	$Cu(OAc)_2$	10	DPPB	20	$PhSiH_3$	3.0	none	...	MeCN/DCE (1:1)	60	67	29
48	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN/DMF (1:1)	60	60	19
49	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN/$PhCF_3$ (1:1)	60	65	24
50	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN/PhMe (1:1)[b]	60	60	24

Entry[a]	$ArNO_2$ (equiv)	$ArB(OH)_2$ (equiv)	catalyst	mol %	ligand	mol %	silane	equiv	additive	mol %	solvent (0.1 M)	T (°C)	%, Yield **3a**	%, Yield aniline
51	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.0	none	...	MeCN/PhMe (1:1)[c]	60	60	24
52	1.0	1.5	$Cu(OAc)_2$	5	DPPP	10	$PhSiH_3$	3.0	none	...	MeCN/PhMe (1:1)	60	55	27
53	1.0	1.5	$Cu(OAc)_2$	5	Davephos	10	$PhSiH_3$	3.0	none	...	MeCN/PhMe (1:1)	60	31	50
54	1.0	1.5	$Cu(OAc)_2$	5	DPEPhos	20	$PhSiH_3$	3.0	none	...	MeCN/PhMe (1:1)	60	31	26
55	1.0	1.5	$Cu(OAc)_2$	5	BINAP	10	$PhSiH_3$	3.0	none	...	MeCN/PhMe (1:1)	60	33	37
56	1.0	1.5	$Cu(OAc)_2$	5	Ph_3P	20	$PhSiH_3$	3.0	none	...	MeCN/PhMe (1:1)	60	0	89
57	1.0	1.5	$Cu(OAc)_2$	5	1,10-phen	10	$PhSiH_3$	3.0	none	...	MeCN/PhMe (1:1)	60	0	90
58	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	Me_2ClSiH	4.0	none	...	MeCN/PhMe (1:1)	60	n.r.	n.r.
59	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	iPr_3SiH	4.0	none	...	MeCN/PhMe (1:1)	60	n.r.	n.r.
60	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$(MeO)_2MeSiH$	4.0	none	...	MeCN/PhMe (1:1)	60	27	48
61	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$BnMe_2SiH$	4.0	none	...	MeCN/PhMe (1:1)	60	n.r.	n.r.
62	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	PHMS	4.0	none	...	MeCN/PhMe (1:1)	60	27	48
63	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.2	none	...	MeCN/PhMe (1:1)	60	70	18
64	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.4	none	...	MeCN/PhMe (1:1)	60	62	21
65	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	3.6	none	...	MeCN/PhMe (1:1)	60	28	58
66	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	2.8	none	...	MeCN/PhMe (1:1)	60	83	16
67	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	2.6	none	...	MeCN/PhMe (1:1)	60	83	20
68	1.0	1.5	$Cu(OAc)_2$	5	DPPB	10	$PhSiH_3$	2.4	none	...	MeCN/PhMe (1:1)	60	55	17

[a] As determined using ^1H NMR spectroscopy with CH_2Br_2 as the internal standard. [b] 0.2 M solution. [c] 0.05 M solution.

B. Optimized Conditions



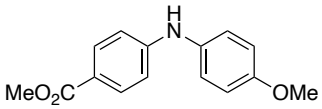
(s2)

3a

To a 10 mL Schlenk tube under nitrogen was added 0.10 mmol of nitroarene and 0.15 mmol of arylboronic acid. A solution of $Cu(OAc)_2$ (5 mol %) and 1,4-bis(diphenylphosphino)butane (dppb) (10 mol %) in 0.5 mL of MeCN were then added. The resulting mixture was diluted with 0.5 mL of toluene, and 0.0303 g of phenyl silane (2.8 equiv) was added in one portion before the Schlenk tube was sealed under nitrogen. The reaction mixture was heated to 60 °C. After 30 h, analysis of the reaction mixture using thin layer chromatography indicated that the reaction was complete. The mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo*, and the residue was purified using MPLC to afford diarylamine **3a**.

C. Characterization Data

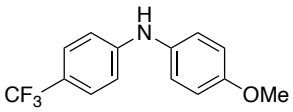
1. Scope and limitations with regards to the nitroarene



3a

Methyl 4-((4-methoxyphenyl)amino)benzoate 3a.[2] The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0228 g of 4-methoxyphenylboronic acid and 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb) in 0.50 mL of MeCN. Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3a** as a white solid (0.0214 g, 83%). The spectral data of **1a** matched that reported by Organ and co-workers:[2] mp = 83–84 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.87 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 5.92 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.1 (C), 156.6 (C), 149.8 (C), 133.3 (C), 131.5 (CH), 124.5 (CH), 120.0 (C), 114.8 (CH), 113.2 (CH), 55.6 (CH_3), 51.6 (CH_3); IR (thin film): 3384, 2954, 2801, 1690, 1595, 1520, 1448, 1411, 1346, 1248, 1236, 798, 763, 690 cm^{-1}.

1 mmol scale reaction to afford methyl 4-((4-methoxyphenyl)amino)benzoate 3a. The optimized method was followed by adding 0.181 g of methyl 4-nitrobenzoate, 0.228 g of 4-methoxyphenylboronic acid and 0.009 g $Cu(OAc)_2$ and 0.043 g of 1,4-bis(diphenylphosphino)butane (dppb) in 5.00 mL of MeCN. Then 5.00 mL of toluene and 0.303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3a** as a white solid (0.209 g, 81%).

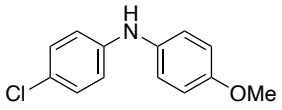


3b

4-Methoxy-*N*-(4-(trifluoromethyl)phenyl)aniline 3b.[3] The optimized method was followed by adding 0.0191 g of 4-nitrobenzotrifluoride, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3b** as a dark brown foam (0.0224 g,

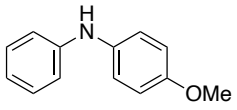
2. Pompeo, M.; Farmer, J.L.; Froese, R. D. J.; Organ, M.G. *Angew. Chem. Int. Ed.* **2014**, *53*, 3223.

84%). The spectral data of **3b** matched that reported by Nocera and co-workers:[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.72 (s, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.5 (C), 148.6 (C), 133.7 (C), 126.7 (q, J_{CF} = 3.7 Hz, CH), 124.7 (q, J_{CF} = 270.3 Hz, C), 124.3 (CH), 120.6 (q, J_{CF} = 32.8 Hz, C), 114.8 (CH), 113.7 (CH), 55.7 (CH_3); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –61.2; IR (thin film): 3415, 2936, 2837, 1670, 1563, 1454, 1377, 1150, 797 cm^{-1}.



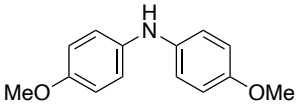
3c

***N*-(4-Methoxyphenyl)-4-chloroaniline 3c.**[4] The optimized method was followed by adding 0.0158 g of 4-chloro-1-nitrobenzene, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3c** as a pale yellow foam (0.0199 g, 85%). The spectral data of **3c** matched that reported by Fort and co-workers:[4] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.22 (t, *J* = 7.5 Hz, 2H), 7.08 (s, 2H), 6.92 – 6.83 (m, 5H), 5.50 (s, 1H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.6 (C), 151.8 (C), 135.2 (CH), 129.2 (C), 124.0 (CH), 122.6 (CH), 116.7 (CH), 114.8 (C), 55.6 (CH_3); IR (thin film): 3379, 3010, 2954, 2838, 1562, 1521, 1499, 1387, 783, 695 cm^{-1}.



3d

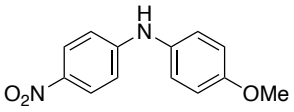
4-Methoxy-*N*-phenylaniline 3d.[5] The optimized method was followed by adding 0.0123 g of nitrobenzene, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3d** as a pale yellow solid (0.0132 g, 66%). The spectral data of **dc** matched that reported by Lavigne and Cesar and co-workers:[5] mp = 104–106 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.15 (d, *J* = 10.0 Hz, 2H), 7.05 (s, 2H), 6.87 (d, *J* = 10.0 Hz, 2H), 6.81 (s, 2H), 5.49 (s, 1H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.3 (C), 145.2 (C), 129.3 (CH), 122.2 (CH), 119.6 (CH), 115.7 (CH), 114.7 (CH), 55.6 (CH_3) only signals visible; IR (thin film): 3387, 3013, 2960, 2841, 1561, 1507, 1498, 1443, 1307, 1252, 1236, 750, 693 cm^{-1}.



3e

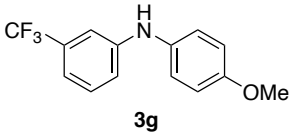
***N*-(4-Methoxyphenyl)-4-methoxylaniline 3e.** The optimized method was followed by adding 0.0153 g of 4-nitroanisole, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043g 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. The cross-coupling product was not observed and 4-nitroanisole starting material was recovered.

3. Sun, R.; Qin, Y.; Nocera, D.G. *Angew. Chem. Int. Ed.* **2020**, *59*, 9527.
4. Desmarets, C.; Schneider, R.; Fort, Y. *J. Org. Chem.* **2002,** *67,* 3029.
5. Zhang, Y.; Cesar V.; Storch, G.; Lugan N.; Lavigne, G. *Angew. Chem. Int. Ed.* **2014**, *53*, 6482.



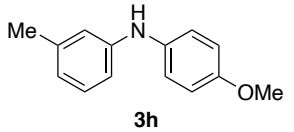
3f

***N*-(4-Methoxyphenyl)-4-nitrolaniline 3f.**[6] The optimized method was followed by adding 0.0168 g of 1,4-dinitrobenzene, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3f** as a brown solid (0.0144 g, 59%). The spectral data of **3f** matched that reported by Buchwald and co-workers:[6] mp = 137–140 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.09 (d, *J* = 9.3 Hz, 2H), 7.16 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 9.3 Hz, 2H), 6.77 (d, *J* = 9.3 Hz, 2H), 6.10 (s, 1H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.5 (C), 151.8 (C), 139.1 (C), 132.0 (C), 126.4 (CH), 125.5 (CH), 115.0 (CH), 112.6 (CH), 55.6 (CH_3); IR (thin film): 3326, 3199, 3124, 2953, 2835, 1592, 1511, 1482, 1444, 1293, 1230, 762, 749, 697 cm^{-1}.



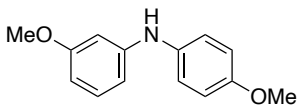
3g

***N*-(4-Methoxyphenyl)-3-trifluoromethylaniline 3g.**[4] The optimized method was followed by adding 0.0191 g of 3-(trifluoromethyl)nitrobenzene, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3g** as a white solid (0.0238 g, 89%). The spectral data of **3g** matched that reported by Lavigne and Cesar and co-workers:[4] mp = 56–58 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.9 Hz, 1H), 7.13 – 7.05 (m, 3H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.62 (s, 1H), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.2 (C), 146.0 (C), 134.3 (C), 131.6 (q, J_{CF} = 31.7 Hz, C), 129.8 (CH), 124.2 (q, J_{CF} = 272.5 Hz, C), 123.5 (CH), 117.9 (CH), 115.6 (q, J_{CF} = 3.8 Hz, C), 114.9 (CH), 111.3 (q, J_{CF} = 3.8 Hz, CH), 55.5 (CH_3); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –62.8; IR (thin film): 3421, 2944, 2812, 1673, 1559, 1421, 1375, 1141, 772 cm^{-1}.



3h

***N*-(4-Methoxyphenyl)-3-methylaniline 3h.**[5] The optimized method was followed by adding 0.0137 g of 3-nitrotoluene, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added.Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3h** as a yellow oil (0.0156 g, 73%). The spectral data of **3h** matched that reported by Fort and co-workers:[5] ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.13 – 7.05 (m, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 6.6 Hz, 1H), 3.81 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$ 125 MHz) δ 155.3 (C), 145.2 (C), 139.2 (C), 129.2 (CH), 124.4 (C), 122.3 (CH), 120.6 (CH), 116.4 (CH), 114.7 (CH), 112.9 (CH), 55.6 (CH_3), 21.6 (CH_3); IR (thin film): 3406, 2956, 2817, 1665, 1523, 1436, 1354, 1014, 912, 772 cm^{-1}.

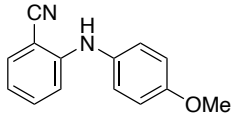


3i

***N*-(4-Methoxyphenyl)-3-methoxyaniline 3i.**[7] The optimized method was followed by adding 0.0153 g of 4-nitroanisole, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-

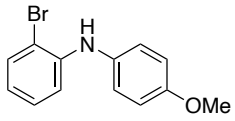
6. Wolfe, J.P.; Tomori, H.; Sadighi, J.P.; Yin J.; Buchwald, S.L. *J. Org. Chem.* **2000,** *65,* 1158.

bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3i** as a white foam (0.0195 g, 85%). The spectral data of **3i** matched that reported by Hartwig and co-workers:[7] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21 – 7.04 (m, 3H), 6.86 (d, J = 8.8 Hz, 2H), 6.58 – 6.42 (m, 2H), 6.40 (d, J = 7.8 Hz, 1H), 5.62 (s, 1H), 3.80 (s, 3H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.8 (C), 155.5 (C), 146.7 (C), 135.4 (C), 130.1 (CH), 122.8 (CH), 114.7 (CH), 108.4 (CH), 104.8 (CH), 101.4 (CH), 55.6 (CH_3), 55.2 (CH_3); IR (thin film): 3380, 2924, 2071, 1634, 1414, 1379, 952 cm^{-1}.



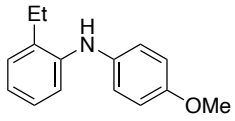
3j

2-[(4-Methoxyphenyl)amino]benzonitrile 3j.[8] The optimized method was followed by adding 0.0148 g of 2-nitrobenzonitrile, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3j** as a white solid (0.0186 g, 83%). The spectral data of **3j** matched that reported by Zeng and co-workers:[8] mp = 118–120 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.46 (d, J = 5.0 Hz, 1H), 7.31 (t, J = 5.0 Hz, 1H), 7.15 (d, J = 5.0 Hz, 2H), 6.93-6.89 (m, 3H), 6.75 (t, J = 5.0 Hz, 1H), 6.18 (s, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.3 (C), 149.0 (C), 134.0 (CH), 132.9 (CH), 132.3 (C), 125.7 (CH), 118.1 (CH), 117.8 (C), 114.9 (CH), 112.9 (CH), 96.9 (CN), 55.6 (CH_3); IR (thin film): 3392, 2921, 2852, 2241, 1317, 1290, 1203, 966 cm^{-1}.



3k

***N*-(4-Methoxyphenyl)-2-bromoaniline 3k.** The optimized method was followed by adding 0.0202 g of 2-bromo-1-nitrobenzene, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3k** as a yellow oil (0.0248 g, 89%). The spectral data of **3l** matched that reported by Martin, Rossi and co-workers:[9] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (d, J = 10.0 Hz, 1H), 7.14 – 7.08(m, 3H), 6.95 – 6.89 (m, 3H), 6.65 (t, J = 5.0 Hz, 1H), 5.94 (s, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.4 (C), 143.3 (C), 134.2 (C), 132.8 (CH), 128.2 (CH), 124.7 (CH), 119.6 (CH), 114.8 (CH), 114.0 (CH), 110.6 (C), 55.6 (CH_3); IR (thin film): 3401, 3061, 2925, 2878, 1603, 1422, 1250, 947 cm^{-1}.

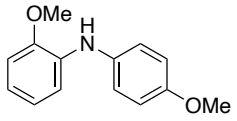


3l

***N*-(4-Methoxyphenyl)-2-ethylaniline 3l.**[10] The optimized method was followed by adding 0.0151 g of 2-ethyl-1-nitrobenzene, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3l** as a yellow oil (0.0186 g, 82%). The spectral data of **3l** matched that reported by Schmidt and co-workers:[9] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.19 (d, J = 5.0 Hz, 1H), 7.09 (t, J

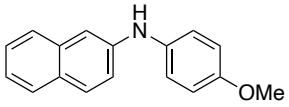
7. Shen, Q.; Ogata, T.; Hartwig, J.F. *J. Am. Chem. Soc.* **2008**, *130,* 6586.
8. Rao, B.; Zeng, X. *Org. Lett.* **2014**, *16*, 314.
9. Budén, M. E.; Vaillard, V. A.; Martin, S. E.; Rossi, R. A. *J. Org. Chem.* **2009**, *74*, 4490.
10. Samblanet, D.C.; Schmidt, J.A.R. *J. Organomet. Chem.* **2012**, *720*, 7.

= 5.0 Hz, 1H), 7.04 – 6.99 (m, 3H), 6.90 – 6.85 (m, 3H), 3.80 (s, 3H), 2.62 (q, *J* = 5.0 Hz, 2H), 1.29 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.0 (C), 142.7 (C), 136.8 (C), 131.6 (C), 128.7 (CH), 126.7 (CH), 121.8 (CH), 120.5 (CH), 116.3 (CH), 114.7 (C), 55.6 (CH_3), 24.2 (CH_2), 13.5 (CH_3); IR (thin film): 3422, 3038, 2961, 2928, 2833, 1595, 1500, 1294, 1243, 1033, 824, 747 cm^{-1}.



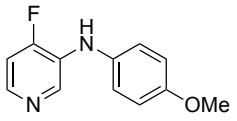
3m

***N*-(4-Methoxyphenyl)-2-methoxyaniline 3m.**[11] The optimized method was followed by adding 0.0151 g of 2-ethyl-1-nitrobenzene, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3m** as a yellow oil (0.0165 g, 72%). The spectral data of **3m** matched that reported by Ichitsuka, Koumura, Kobayashi and co-workers:[11] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.13 (d, *J* = 10.0 Hz, 2H), 7.04 (d, *J* = 5.0 Hz, 1H), 6.88 – 6.76 (m, 5H), 5.98 (br s, 1H) 3.90 (s, 3H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.3 (C), 147.4 (C), 135.4 (C), 135.0 (C), 122.8 (CH), 121.0 (CH), 118.6 (C), 114.6 (CH), 112.6 (CH), 110.2 (CH), 55.6 (CH_3), only signals visible; IR (thin film): 3371, 2932, 1631, 1582, 1418, 1336, 929 cm^{-1}.



3n

Methyl 4-(naphthalen-2-ylamino)benzoate 3n.[17] The optimized method was followed by adding 0.0173 g of 2-nitronaphthalene, 0.0228 g of 4-methoxyphennylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3n** as a yellow oil (0.0266 g, 96%). The spectral data of **3n** matched that reported by Deng, Huang and co-workers:[12] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00 (dd, J = 5.0, 5.0 Hz, 2H), 7.60 (d, J = 10.0 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.28 – 7.11 (m, 6H), 6.93 – 6.91 (m, 2H), 5.66 (s, 1H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.2 (C), 149.0 (C), 134.2 (C), 128.6 (CH), 126.2 (CH), 126.0 (C), 125.4 (CH), 121.8 (CH), 121.1 (CH), 120.9 (CH), 114.8 (CH), 111.7 (CH), 55.6 (CH_3), only signals visible; IR (thin film): 3461, 3358, 3037, 2944, 2339, 1673, 1665, 1521, 1466, 1256, 1030, 837, 742 cm^{-1}.



3o

4-Fluoro-*N*-(4-methoxyphenyl)pyridine-3-amine 3o.[13] The optimized method was followed by adding 0.0142 g of 4-fluoro-3-nitropyridine, 0.0228 g of 4-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **3o** as a white solid (0.0164 g, 75%). The spectral data of **3o** matched that reported by Clark and co-workers:[11] mp = 122–126 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (s, 1H), 7.34 (m, 1H), 7.02 (d, *J* = 5 Hz, 2H), 6.87 (d, *J* = 5 Hz, 2H), 6.79 – 6.77 (m, 1H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.7 (C), 155.8 (C), 139.7 (C), 135.2 (C), 134.8 (d, *J* = 14.8 Hz, CH), 128.5 (d, *J* = 7.4 Hz, CH), 121.9 (CH), 115.0 (CH), 109.4 (d, *J* = 39.3 Hz, CH), 55.6 (CH_3). IR (thin film): 3253, 3177, 3052, 2911, 2865, 1508, 1336, 1259, 1033 cm^{-1}.

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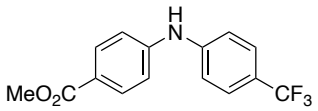
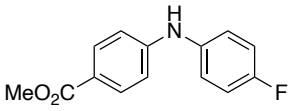
11. Ichitsuka, T.; Takahashi, I.; Koumura, N.; Sato, K.; Kobayashi, S. *Angew. Chem. Int. Ed.* **2020**, *59*, 15891.
12. Wang, Z.; Li, C.; Huang, H.; Deng, G-J. *J. Org. Chem.* **2020**, *85*, 9415.
13. Wilson, R. J.; Rosenberg, A. J.; Kaminsky, L.; Clark, D. A. *J. Org. Chem.* **2014**, *79*, 2203.

2. Scope and limitations with regards to the boronic acid



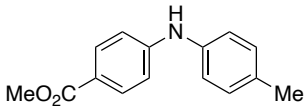
12a

Methyl 4-[4-(trifluoromethyl)anilino]benzoate 12a. The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0285 g of 4-trifluoromethylphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **12a** as a white foam (0.0266 g, 90%). The spectral data of **12a** matched that reported by Winkler, Penning and co-workers:[14] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.97 (d, J = 5.0 Hz, 2H), 7.55 (d, J = 5.0 Hz, 2H), 7.19 (d, J = 5.0 Hz, 2H), 7.10 (d, J = 5.0 Hz, 2H), 6.18 (s, 1H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.7 (C), 146.1 (C), 144.5 (C), 131.5 (CH), 126.8 (q, J = 3.6 Hz, CH), 124.6 (q, J = 270.6 Hz, C), 123.9 (C), 123.0 (C), 117.9 (CH), 116.4 (CH), 51.9 (CH_3); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –61.8; IR (thin film) cm^{-1}; 3403, 2955, 2844, 1685, 1401, 1314, 1225, 764 cm^{-1}



12b

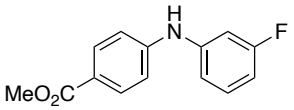
Methyl 4-[(4-fluorophenyl)amino]benzoate 12b.[12] The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0210 g of 4-fluorophenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **12b** as a pale yellow viscous oil (0.0238 g, 97%). The spectral data of **12b** matched that reported by Xue and co-workers:[15] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (d, J = 8.4 Hz, 2H), 7.16 – 7.13 (m, 2H), 7.04 (t, J = 8.4 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.91 (s, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.3 (C), 159.5 (d, J_{CF} = 241.3 Hz, C), 149.1 (C), 137.0 (d, J_{CF} = 2.8 Hz, CH), 131.9 (CH), 123.7 (d, J_{CF} = 8.1 Hz, CH), 121.1 (C), 116.6 (d, J_{CF} = 22.5 Hz, CH), 114.2 (CH), 52.1 (CH_3); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –118.7; IR (thin film): 3401, 1687, 1579, 1461, 1413, 1245, 752 cm^{-1}.



12c

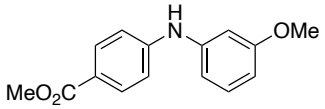
Methyl 4-(tolylamino)benzoate 12c.[13] The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0204 g of 4-tolylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **4c** as a white solid (0.0217 g, 90%). The spectral data of **12c** matched that reported by Ma and co-workers:[16] mp = 105–106 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94 – 7.84 (m, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.11 – 7.02 (m, 2H), 6.96 – 6.86 (m, 2H), 6.01 (s, 1H), 3.87 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.1 (C), 148.9 (C), 138.1 (C), 133.2 (C), 131.5 (CH), 130.1 (CH), 121.4 (CH), 120.5 (C), 114.0 (CH), 51.7 (CH_3), 20.9 (CH_3); IR (thin film): 3396, 1676, 1553, 1477, 1405, 1062, 771 cm^{-1}.

14. Adeniji, A.O.; Twenter, B.M.; Byrns, M.C.; Jin, Y.; Chen, M.; Winkler, J.D.; Penning, T.M. *J. Med. Chem.* **2012**, *55*, 2311.
15. Li, G.; Yang, L.; Liu, J-J.; Zhang, W.; Cao, R.; Wang, C.; Zhang, Z.; Xiao, J.; Xue, D. *Angew. Chem. Int. Ed.* **2021**, *60*, 5230.
16. Zhang, H.; Cai, Q.; Ma, D. *J. Org. Chem*. **2005**, *70*, 5164.



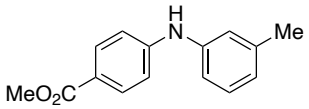
12d

Methyl 4-(3-fluorophenylamino)benzoate 12d.[17] The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0210 g of 3-fluorophenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **12d** as a white solid (0.0216 g, 88%). Diarylamine **12d** was previously reported by Griffioen *et al.*:[14] mp = 39–40 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00 – 7.90 (m, 2H), 7.30 – 7.26 (m, 1H), 7.05 – 6.99 (m, 2H), 6.93 – 6.84 (m, 2H), 6.73 (ddd, J = 10.1, 7.9, 2.7 Hz, 1H), 6.07 (s, 1H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.8 (C), 163.6 (d, J = 245.5 Hz, C), 146.9 (C), 142.9 (d, J = 9.3 Hz, C), 131.5 (CH), 130.7 (d, J = 9.7 Hz, CH), 122.2 (C), 115.6 (CH), 115.0 (CH), 109.3 (d, J = 21.3 Hz, CH), 106.4 (d, J = 24.5 Hz, CH), 51.8 (CH_3); IR (thin film): 3364, 3041, 2959, 2841, 1610, 1501,1232, 837, 764 cm^{-1}.



12e

Methyl 4-(3-methoxyphenylamino)benzoate 12e.[15] The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0228 g of 3-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **12e** as a pale yellow oil (0.0237 g, 92%). The spectral data of **12e** matched that reported by Winkler, Penning and co-workers:[18] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92 (d, J = 8.8 Hz, 2H), 7.24 (t, J = 8.1 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 7.9 Hz, 1H), 6.73 (t, J = 2.2 Hz, 1H), 6.61 (dd, J = 8.2, 2.4 Hz, 1H), 6.14 (s, 1H), 3.88 (s, 3H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.0 (C), 160.7 (C), 147.9 (C), 142.3 (C), 131.5 (CH), 130.3 (CH), 121.2 (C), 115.0 (CH), 112.6 (CH), 108.3 (CH), 106.0 (CH), 55.3 (CH_3), 51.8 (CH_3); IR (thin film): 3361, 2945, 2813, 1689, 1517, 1440, 1409, 1352, 1248, 789, 689 cm^{-1}.



12f

Methyl 4-(3-tolylamino)benzoate 12f.[15] The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0204 g of 3-methylphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **12f** as a yellow oil (0.0212 g, 88%). The spectral data of **12f** matched that reported by Winkler, Penning and co-workers:[15] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.91 (d, J = 8.8 Hz, 2H), 7.24 – 7.21 (m, 1H), 7.00 – 6.96 (m, 4H), 6.89 (d, J = 7.5 Hz, 1H), 6.00 (s, 1H), 3.87 (s, 3H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.0 (C), 148.2 (C), 140.8 (C), 139.5 (C), 131.5 (CH), 129.4 (CH), 124.0 (CH), 121.2 (CH), 117.6 (CH), 114.6 (CH), 51.8 (CH_3), 21.6 (CH_3), only signals visible; IR (thin film): 3412, 1691, 1565, 1523, 1481, 1416, 1059, 794 cm^{-1}.

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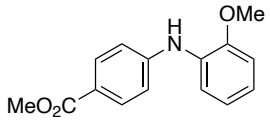
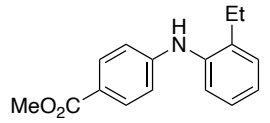
17. Griffioen, G.; Van Dooren, T.; Rojas de la Parra, V.; Allasia, S.; Marchand, A.; Kilonda, A.; Chaltin, P. Preparation of indolylethylbenzamide derivatives as inhibitors of TAU for the treatment of neurodegenerative diseases. WO2012080221 A1, 06/21/2012.

18. Adeniji, A.O.; Twenter, B.M.; Byrns, M.C.; Jin, Y.; Chen, M.; Winkler, J.D.; Penning, T.M. *J. Med. Chem.* **2012**, *55*, 2311.



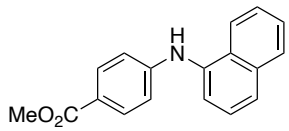
12g

Methyl 4-((2-methoxyphenyl)amino)benzoate 12g.[16] The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0228 g of 2-methoxyphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **12g** as a light yellow oil (0.0219 g, 85%). The spectral data of **12g** matched that reported by Organ and co-workers:[19] ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.96 – 7.90 (m, 2H), 7.40 (dd, J = 7.6, 1.8 Hz, 1H), 7.10 – 7.05 (m, 2H), 7.02 – 6.90 (m, 3H), 6.37 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ167.0 (C), 149.5 (C), 147.6 (C), 131.4 (CH), 130.5 (C), 122.2 (CH), 121.2 (C), 120.8 (CH), 117.7 (CH), 115.2 (CH), 110.9 (CH), 55.6 (CH_3), 51.7 (CH_3); IR (thin film): cm^{-1}. 3324, 2950, 1682, 1447, 1398, 1084, 844 cm^{-1}



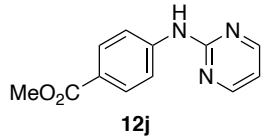
12h

Methyl 4-((2-ethylphenyl)amino)benzoate 12h. The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0228 g of 2-ethylphenylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Visualization of the reaction progress using thin layer chromatography revealed that no reaction had occurred. The only visible species were methyl 4-nitrobenzoate and 2-ethylphenylboronic acid. The cross-coupling product was not observed.



12i

Methyl 4-(naphthalen-1-ylamino)benzoate 12i.[17] The optimized method was followed by adding 0.0181 g of methyl 4-nitrobenzoate, 0.0258 g of 1-naphthylboronic acid and 0.50 mL of MeCN solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb). Then 0.50 mL of toluene and 0.0303 g of phenylsilane were sequentially added. Purification by MPLC (3:97 – 20:80 EtOAc:hexanes) afforded **12i** as a yellow oil (0.0230 g, 83%). The spectral data of **12i** matched that reported by Deng, Huang and co-workers:[17] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, J = 5.0 Hz, 2H), 7.90 (d, J = 5.0 Hz, 3H), 7.72 (s, 1H), 7.58 – 7.46 (m, 4H), 6.84 (d, J = 5.0 Hz, 1H), 6.22 (s, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.0 (C), 147.9 (C), 138.5 (C), 134.3 (C), 131.6 (CH), 130.1 (C), 129.4 (CH), 127.7 (CH), 126.9 (CH), 126.7 (CH), 124.6 (CH), 121.5 (C), 121.3 (CH), 115.6 (CH), 115.0 (CH), 51.8 (CH_3); IR (thin film): 3467, 3385, 3042, 2933, 1677, 1623, 1586, 1496, 1464, 1330, 1180, 857, 738 cm^{-1}.



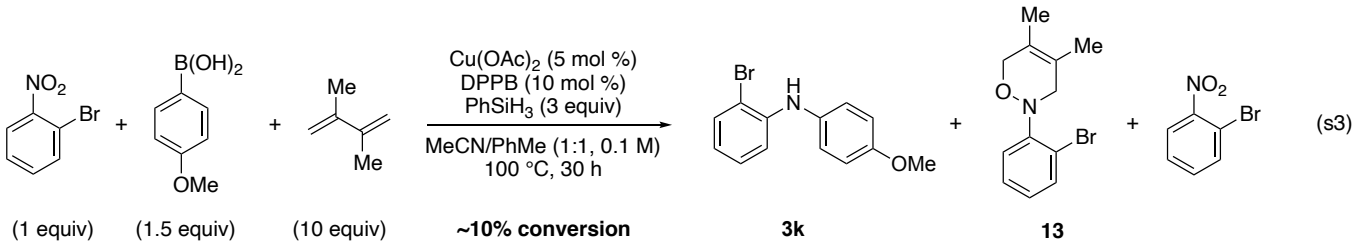
12j

Methyl 4-(pyrimidine-2-ylamino)benzoate 12j.[17] The optimized method was followed by adding 0.0362 g of methyl 4-nitrobenzoate, 0.0372 g of pyrimidin-2-yl-boronic acid and 1.00 mL of MeCN solution of 0.0018 g $Cu(OAc)_2$ and 0.0086

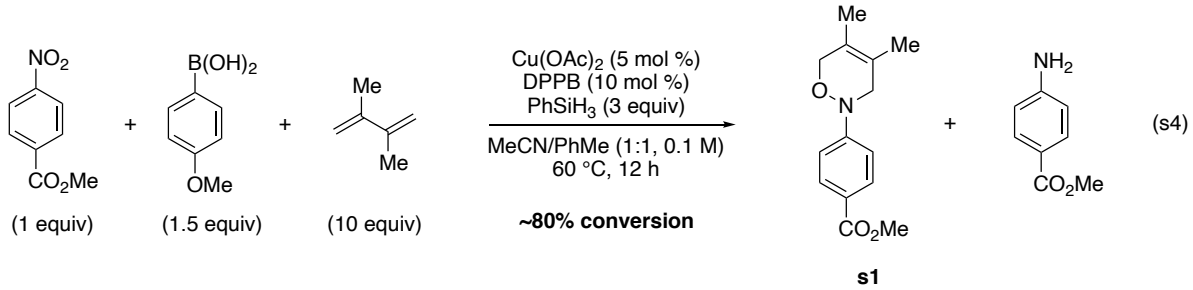
19. Pompeo, M.; Farmer, J. L.; Froese, R. D. J.; Organ, M. G. *Angew. Chem. Int. Ed.* **2014**, *53*, 3223.

g of 1,4-bis(diphenylphosphino)butane (dppb). Then 1.00 mL of toluene and 0.0606 g of phenylsilane were sequentially added. Purification by MPLC (20:80 – 50:50 EtOAc:hexanes) afforded **12j** as a yellow solid (0.0270 g, 59%). The spectral data of **12j** matched that reported by Deng, Huang and co-workers:[17] mp = 149–150 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.37 (d, J = 4.8 Hz, 2H), 7.78 (s, 1H), 7.48 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.64 (t, J = 4.8 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.8 (C), 158.1 (CH), 155.8 (CH), 132.4 (C), 122.4 (C), 114.3 (CH), 111.9 (CH), 55.6 (CH_3); IR (thin film): 3345, 2960, 2830, 1679,1650, 1525, 1263, 764 cm^{-1}.

III. Mechanistic Experiments



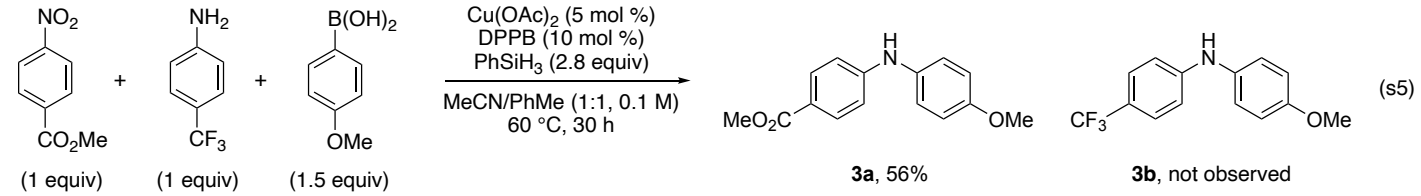
A 10 mL Schlenk tube was charged with 0.0606 g of 2-bromonitrobenzene and 0.0684 g of 4-methoxyphenylboronic acid under nitrogen. To this mixture was added a solution of 0.0027 g of $Cu(OAc)_2$ and 0.0129 g of 1,4-bis(diphenylphosphino)butane (dppb) in 1.5 mL of MeCN was then added. The mixture was diluted with 0.5 mL of toluene, and 0.0909 g of phenyl silane and 0.33 mL of 2,3-dimethyl-1,3-butadiene were sequentially added. The resulting reaction mixture was heated to 100 °C. After 30 hours, the mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo* and was purified by MPLC (hexanes) to remove the phenyl silane oligomeric by-product and the aryl boronic acid to obtain a 90:7:3 mixture of 2-bromonitrobenzene, diarylamine **3k** and oxazine **13**. Oxazine **13** was previously reported by Shigeki.[20] Visible peaks for oxazine **13**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.38 (s, 2H), 3.61 (s, 2H), 1.25 (s, 3H).



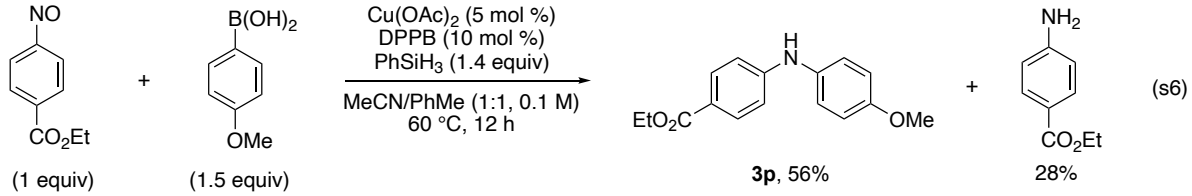
A 10 mL Schlenk tube was charged with 0.0181 g of methyl 4-nitrobenzoate and 0.0228 g of 4-methoxyphenylboronic acid under nitrogen. To this mixture was added a solution of 0.0009 g of $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb) in 0.5 mL of MeCN was then added. The mixture was diluted with 0.5 mL of toluene, and 0.0303 g of phenyl silane and 0.11 mL of 2,3-dimethyl-1,3-butadiene were sequentially added. The resulting reaction mixture was heated to 60 °C. After 12 hours, the mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo,* and analysis of the residue using ^{1}H NMR spectroscopy with CH_2Br_2 as the internal standard revealed that the reaction had gone to ~80% conversion. The coupling product was not observed, but aniline and oxazine **s1** were both present. Several peaks were also observed in the ^{1}H NMR spectrum in between 3.6 and 4.0 ppm. Oxazine **s1** was previously reported by Ragaini and co-workers.[21] While we were not able to purify the oxazine

20. Shigeki, K. *J. Chem. Soc. Jpn.* **1956**, *59*, 951.
21. El-Atawy, M. A.; Formenti, D.; Ferretti, F.; Ragaini, F. *ChemCatChem* **2018**, *10*, 4707.

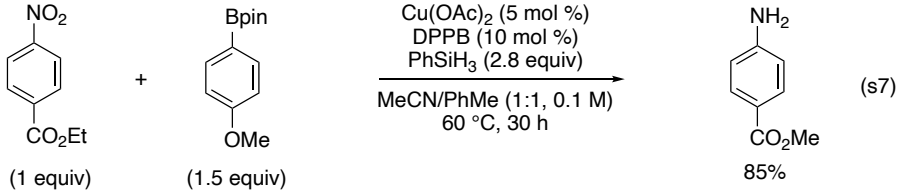
from the reaction mixture, its peaks at 4.35 and 3.76 ppm matched that in the 2018 Ragaini *ChemCatChem* paper. Visible peaks for oxazine **s1**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.35 (s, 2H), 3.76 (s, 2H).



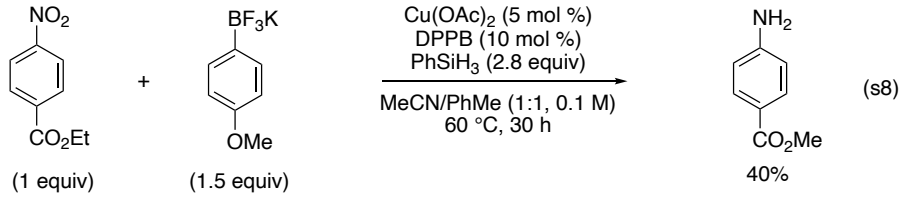
A 10 mL Schlenk was charged with 0.0090 g of methyl 4-nitrobenzoate, 0.0081 g of 4-trifluoromethylaniline and 0.0228 g of 4-methoxyphenylboronic acid. To this mixture was added 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb) in 0.5 mL of MeCN. The mixture was diluted with 0.5 mL of toluene, and 0.0303 g of phenyl silane was added. The reaction mixture was heated to 60 °C. After 30 hours, the mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo,* and analysis of the residue using ^{1}H NMR spectroscopy with CH_2Br_2 as the internal standard revealed formation of diarylamine **3a** as the only product.



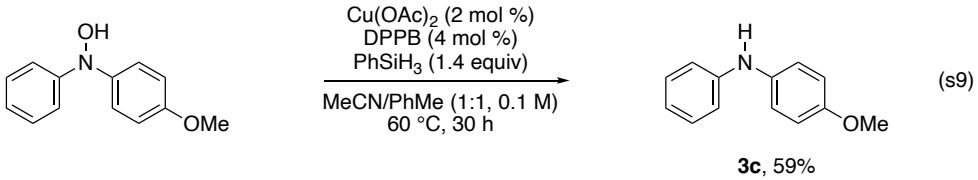
A 10 mL Schlenk tube was charged with 0.0179 g of ethyl 4-nitrosobenzoate and 0.0228 g of 4-methoxyphenylboronic acid under nitrogen. To this mixture was added a solution of 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb) in 0.5 mL of MeCN. The mixture was diluted with 0.5 mL of toluene and 0.0151 g of phenyl silane was added. The resulting reaction mixture was heated to 60 °C. After 12 hours, the reaction mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo,* and analysis of the residue using ^{1}H NMR spectroscopy with CH_2Br_2 as the internal standard revealed the formation of the diarylamine **3p** in 56% and ethyl 4-aminobenzoate in 28%.



A 10 mL Schlenk tube was charged with 0.0181 g of methyl 4-nitrobenzoate and 0.0351 g of 4-methoxyphenylboronic acid pinacolate ester under nitrogen. To this mixture was added 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb) in 0.5 mL of MeCN. The mixture was diluted with 0.5 mL of toluene and 0.0303 g of phenyl silane was added. The reaction mixture was heated to 60 °C. After 30 hours, the reaction mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo,* and analysis of the residue using ^{1}H NMR spectroscopy with CH_2Br_2 as the internal standard revealed formation of methyl 4-aminobenzoate as the only product.

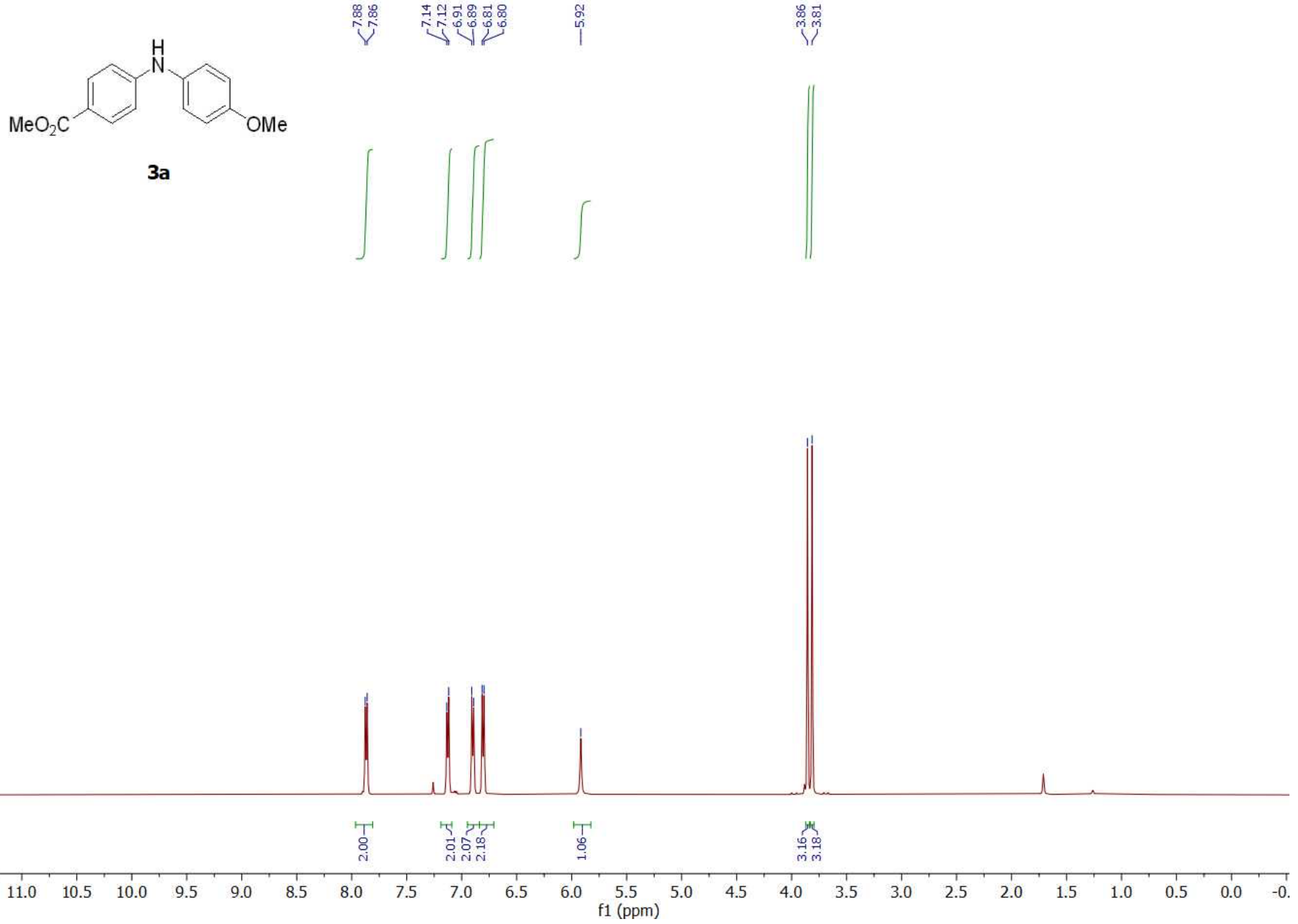


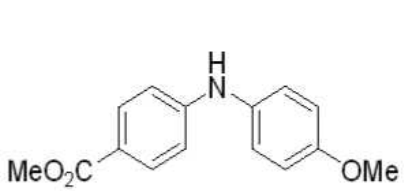
A 10 mL Schlenk tube was charged with 0.0181 g of methyl 4-nitrobenzoate and 0.0321 g of potassium 4-methoxyphenyltrifluoroborate under nitrogen. To this mixture was added 0.0009 g $Cu(OAc)_2$ and 0.0043 g of 1,4-bis(diphenylphosphino)butane (dppb) in 0.5 mL of MeCN. The mixture was diluted with 0.5 mL of toluene, and 0.0303 g of phenyl silane was added. The reaction mixture was heated to 60 °C. After 30 hours, the reaction mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo,* and analysis of the residue using ^1H NMR spectroscopy with CH_2Br_2 as the internal standard revealed formation of methyl 4-aminobenzoate as the only product.



To a 10 mL reaction tube under nitrogen, 0.0287 g of *N*-(4-methoxyphenyl)-*N*-phenylhydroxylamine and 0.5 mL of a solution of 0.0003 g $Cu(OAc)_2$ and 0.0016 g 1,4-bis(diphenylphosphino)butane in MeCN were added. The resulting mixture was diluted with 0.50 mL of toluene, and 0.0151 g of phenylsilane was added in one portion. The reaction tube was sealed and heated to 60 °C. After 12 h, the mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated *in vacuo.* Analysis of the resulting residue using ^1H NMR spectroscopy in $CDCl_3$ using CH_2Br_2 as the internal standard showed that diarylamine **3c** was formed in 59%. Repeating the reaction in the absence of $Cu(OAc)_2$ resulted in no reaction.

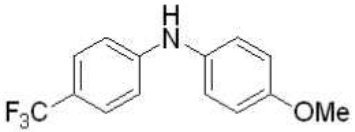
IV. Spectral Data


MeO2C
H
N
OMe
3a
7.88
7.86
7.14
7.12
6.91
6.89
6.81
6.80
5.92
3.86
3.81
2.00
2.01
2.07
2.18
1.06
3.16
3.18
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)


H
N
MeO2C
OMe

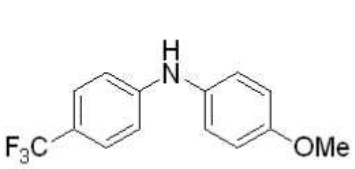
3a

167.10
156.59
149.83
133.42
131.54
124.47
120.07
114.80
113.24
55.56
51.64
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


H
N
F3C
OMe

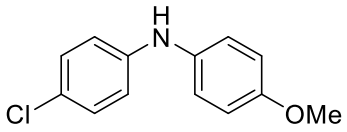
3b

7.42
7.41
7.13
7.11
6.91
6.90
6.86
6.85
5.72
3.82
2.00
1.91
2.01
2.10
0.88
3.07
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 -0.
f1 (ppm)


H
N
F3C
OMe

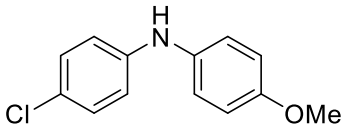
3c

156.52
148.61
141.81
133.69
126.69
126.66
124.31
120.62
114.83
113.76
113.05
96.38
55.56
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


H
N
Cl
OMe

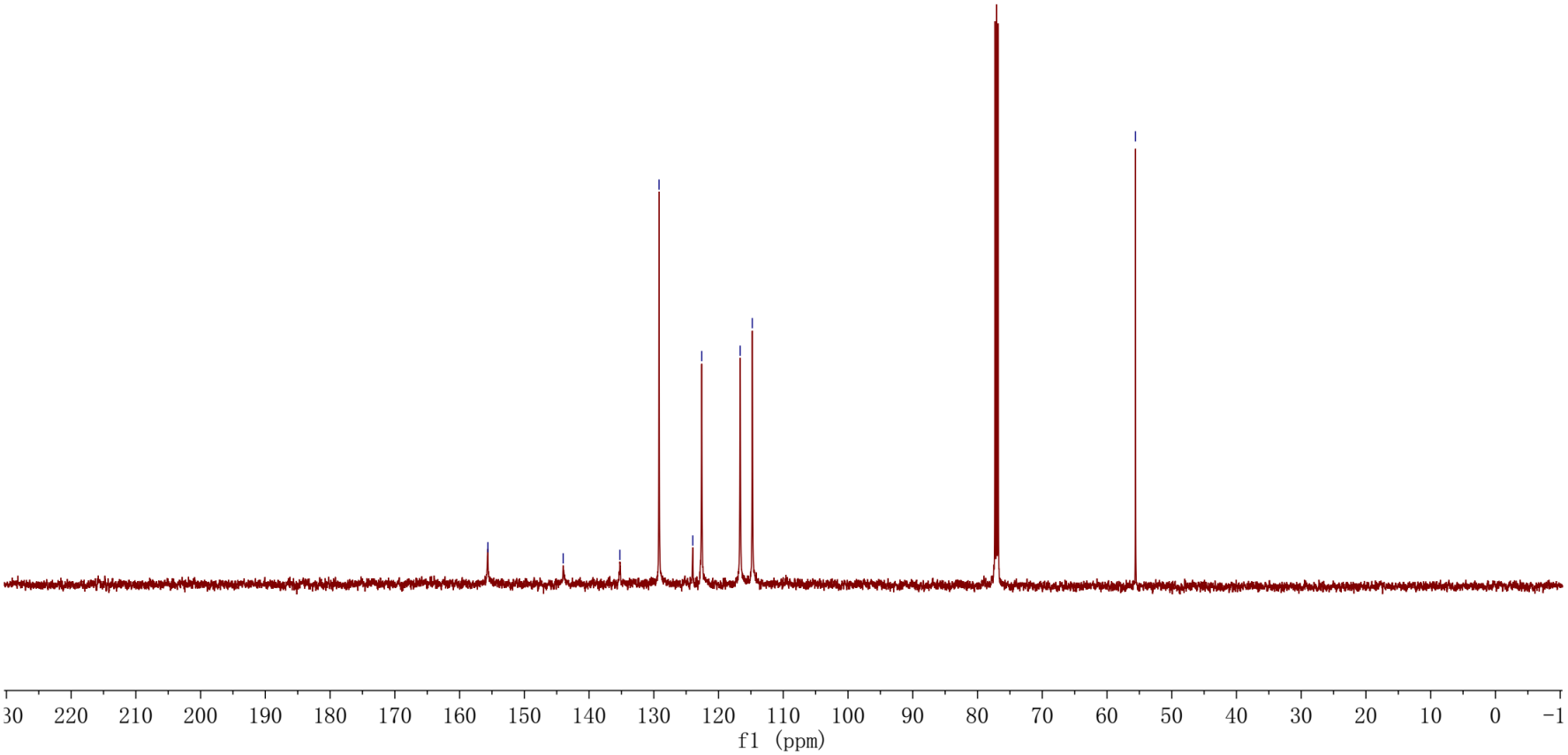
3c

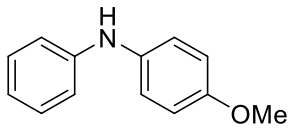
7.23
7.22
7.20
7.08
6.92
6.91
6.88
6.86
6.84
5.50
3.81
1.97
2.00
4.88
0.93
3.30
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3c

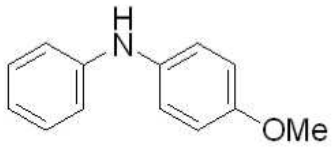
155.62
144.01
135.24
129.19
123.99
122.60
116.66
114.78
55.60




H
N
OMe

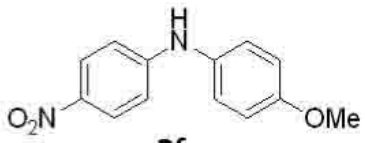
3d

7.16
7.14
7.05
6.88
6.86
6.81
5.49
3.80
1.92
1.53
2.29
1.46
1.07
3.00
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)


H
N
OMe

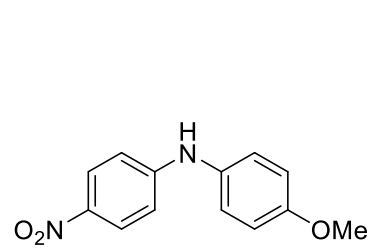
3d

155.31
145.19
129.32
122.23
119.58
115.66
114.69
55.60
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


O2N
OMe

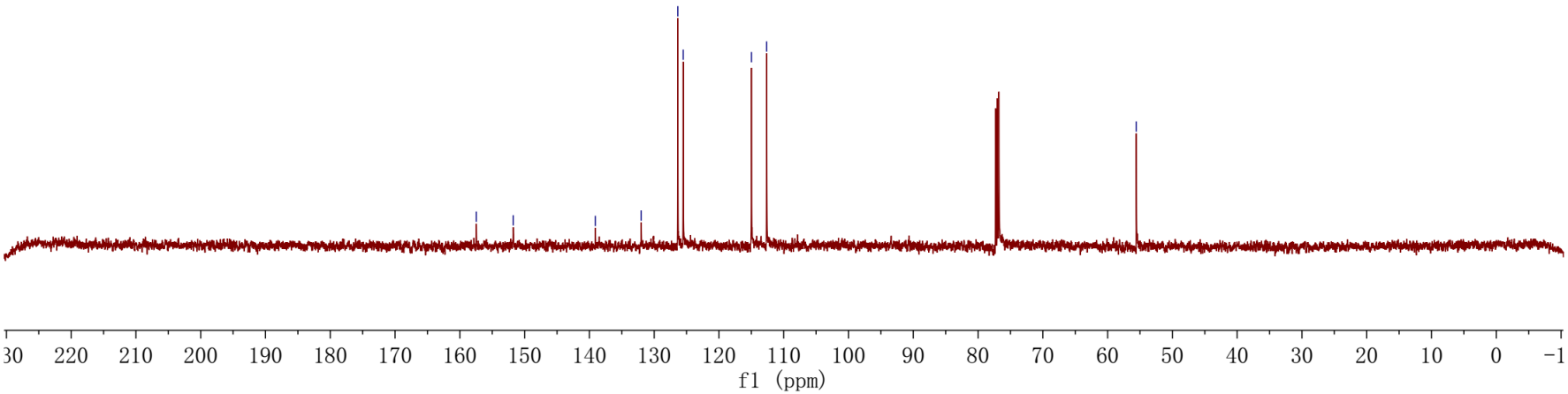
3f

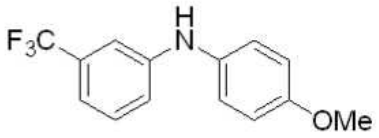
8.10
8.08
7.17
7.15
6.95
6.93
6.77
6.75
6.10
3.84
1.80
2.10
2.00
2.08
1.03
3.20
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3f

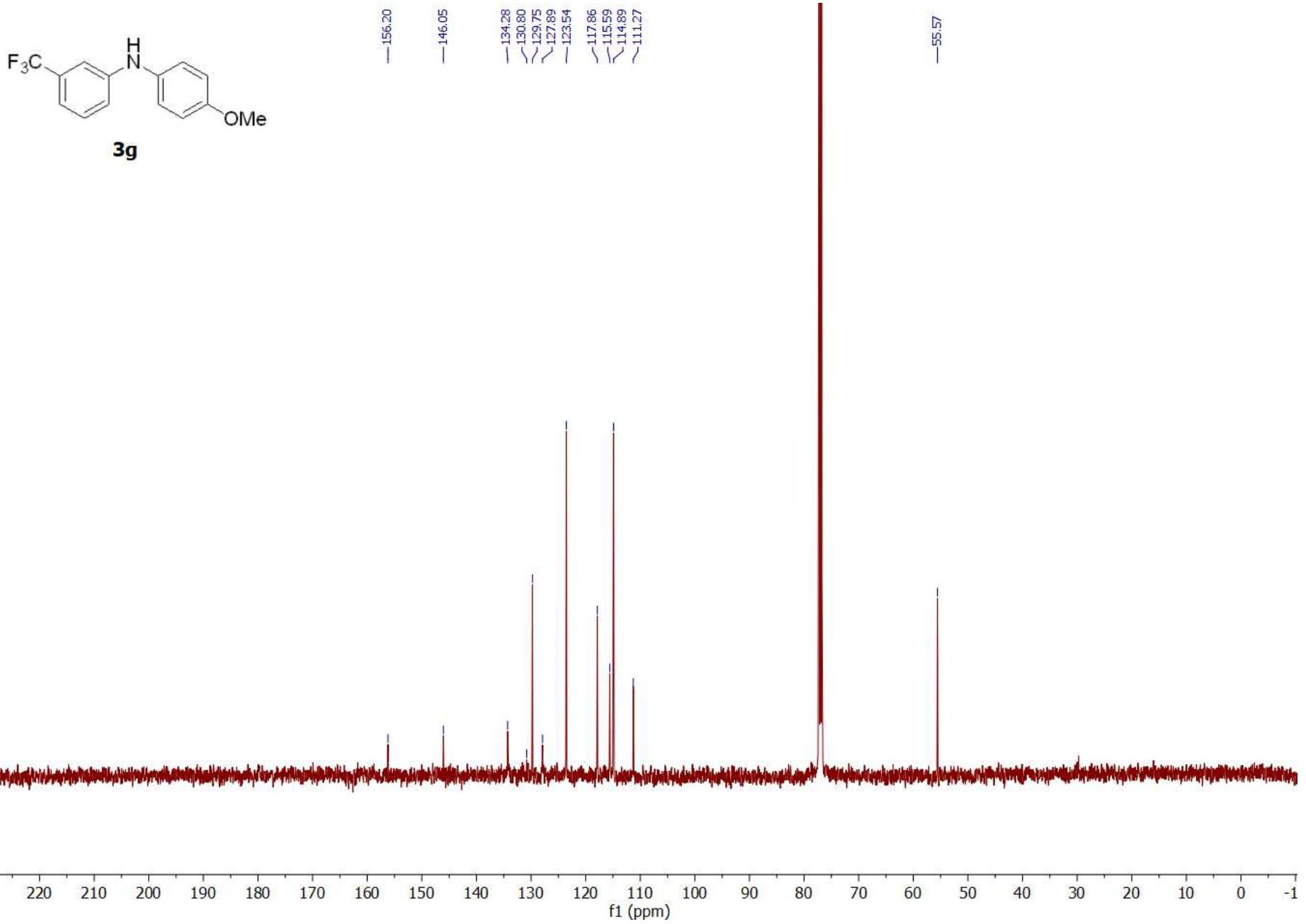
157.46
151.75
139.08
132.00
126.35
125.52
114.98
112.64
55.57

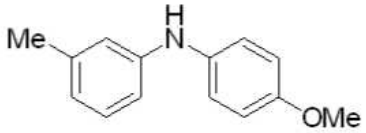



F3C
H
N
OMe

3g

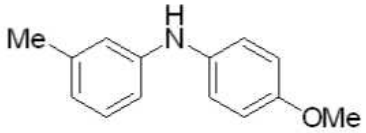
7.29
7.28
7.26
7.10
7.09
7.07
7.04
7.02
7.01
6.99
6.91
6.89
5.62
3.82
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F3C
H
N
OMe
3g
156.20
146.05
134.28
130.80
129.75
127.89
123.54
117.86
115.59
114.89
111.27
55.57
f1 (ppm)


Me
H
N
OMe

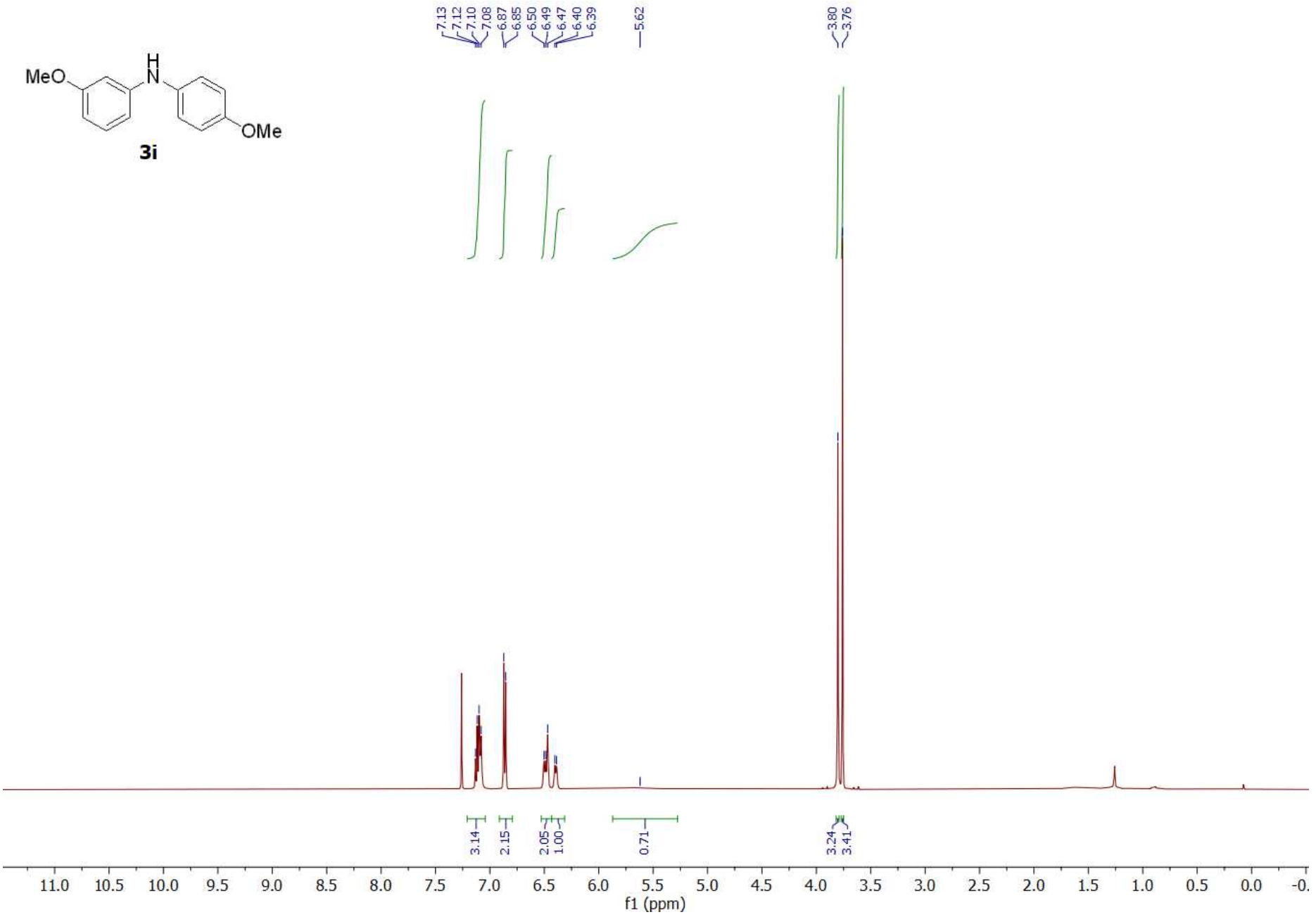
3h

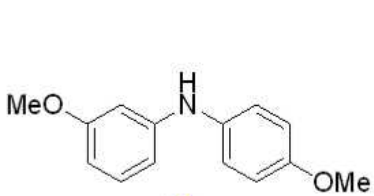
7.12
7.11
7.09
7.08
7.07
6.88
6.86
6.74
6.72
6.68
6.66
3.81
2.29
2.93
2.00
1.84
0.91
3.33
3.12
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Me
H
N
OMe

3h

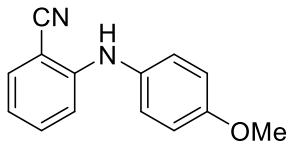
155.28
145.21
139.20
129.18
124.37
122.26
120.55
116.39
114.68
112.87
55.60
21.57
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


MeO
H
N
OMe
3i
7.13
7.12
7.10
7.08
6.87
6.85
6.50
6.49
6.47
6.40
6.39
5.62
3.80
3.76
3.14
2.15
2.05
1.00
0.71
3.24
3.41
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
H
N
OMe

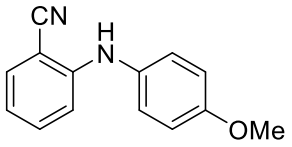
3i

160.79
155.53
146.68
135.36
130.08
122.77
114.68
108.40
104.81
101.39
55.59
55.18
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


CN
H
N
OMe

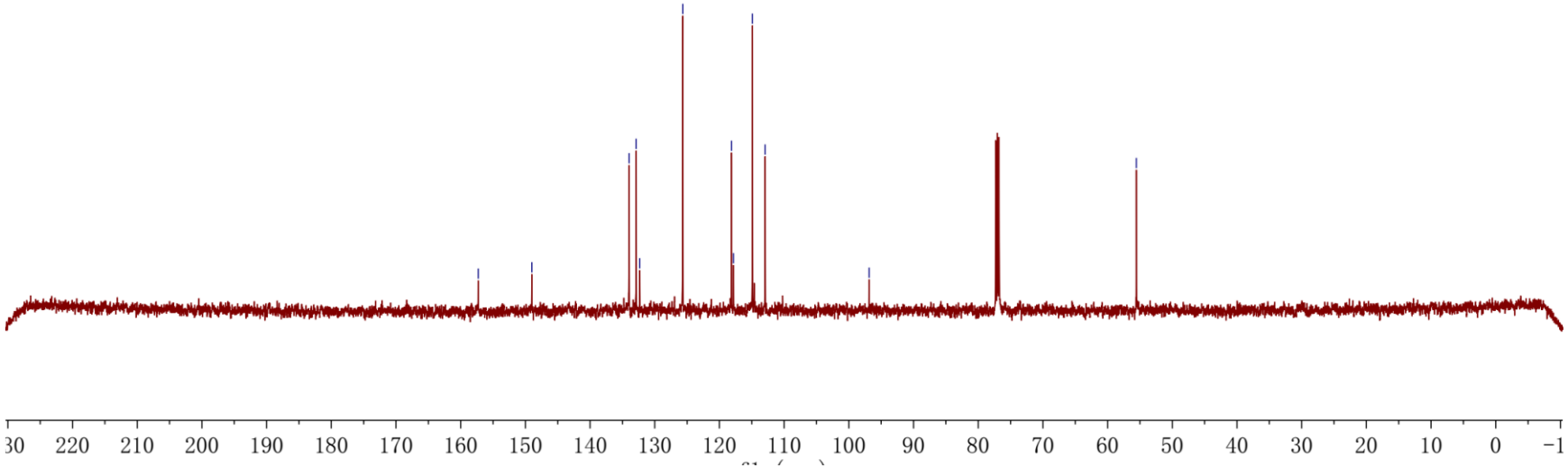
3j

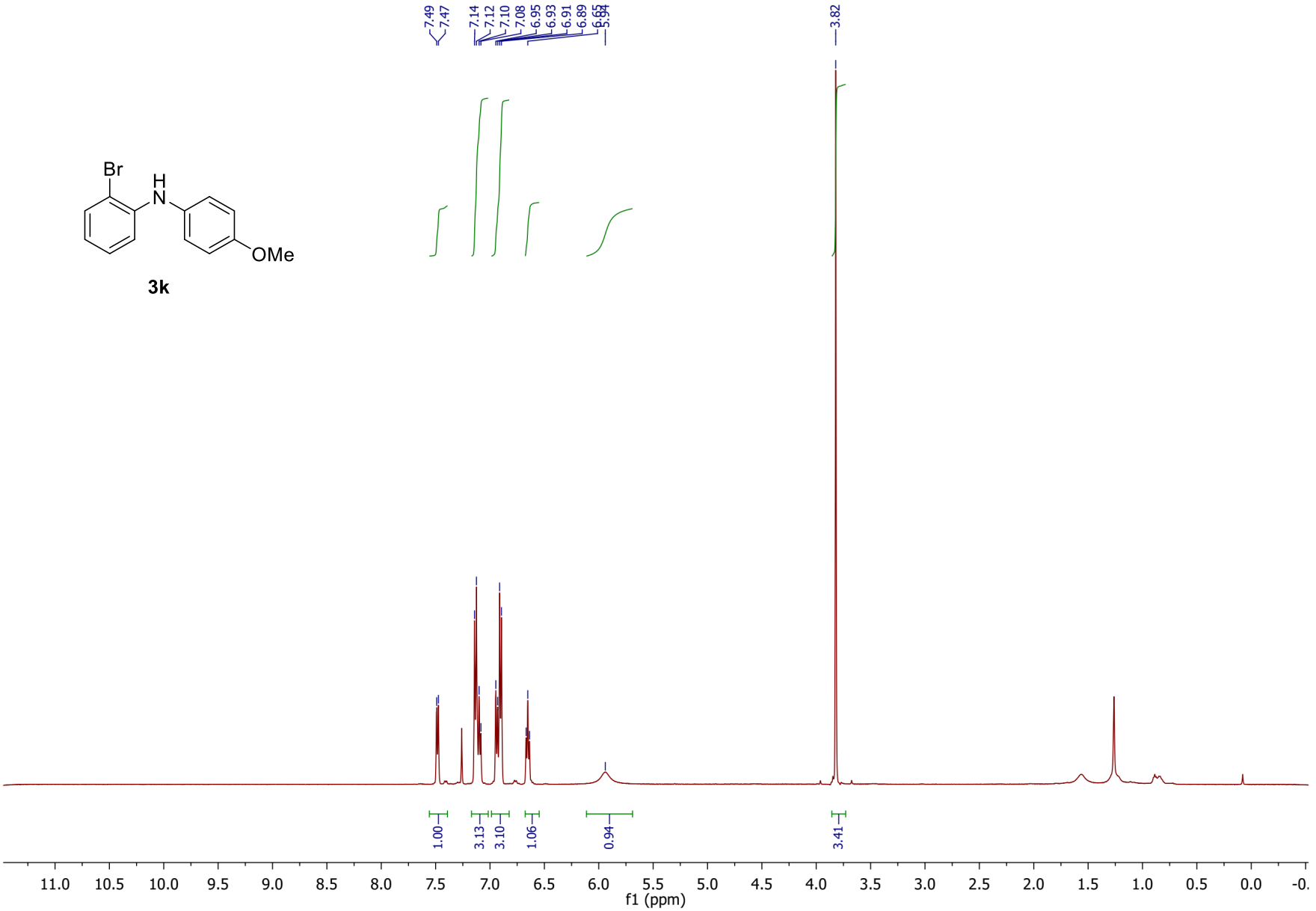
7.47
7.45
7.32
7.30
7.29
7.26
7.16
7.14
6.93
6.91
6.89
6.77
6.76
6.74
6.18
3.83
1.00
1.38
1.83
2.64
0.87
0.68
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

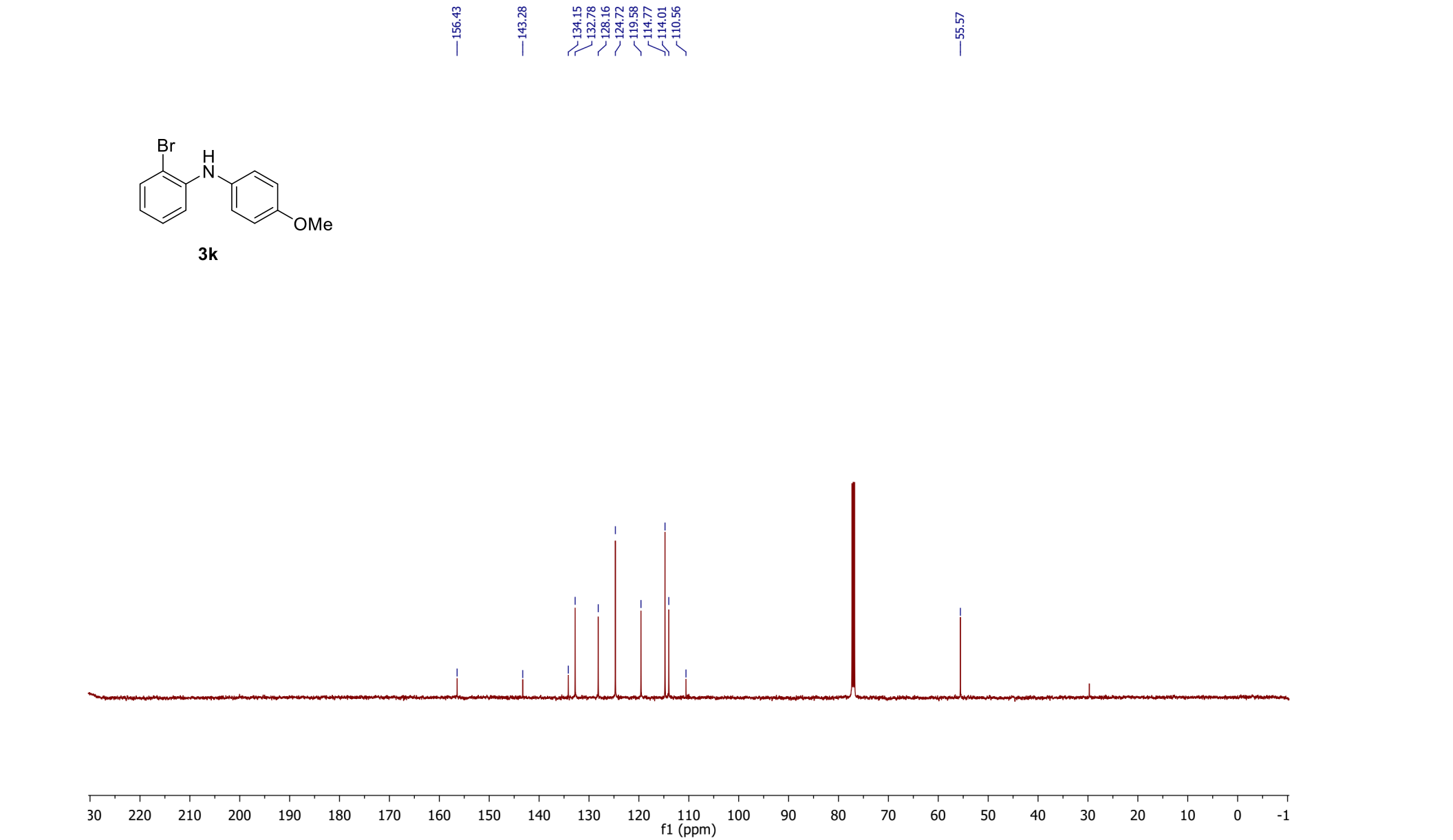


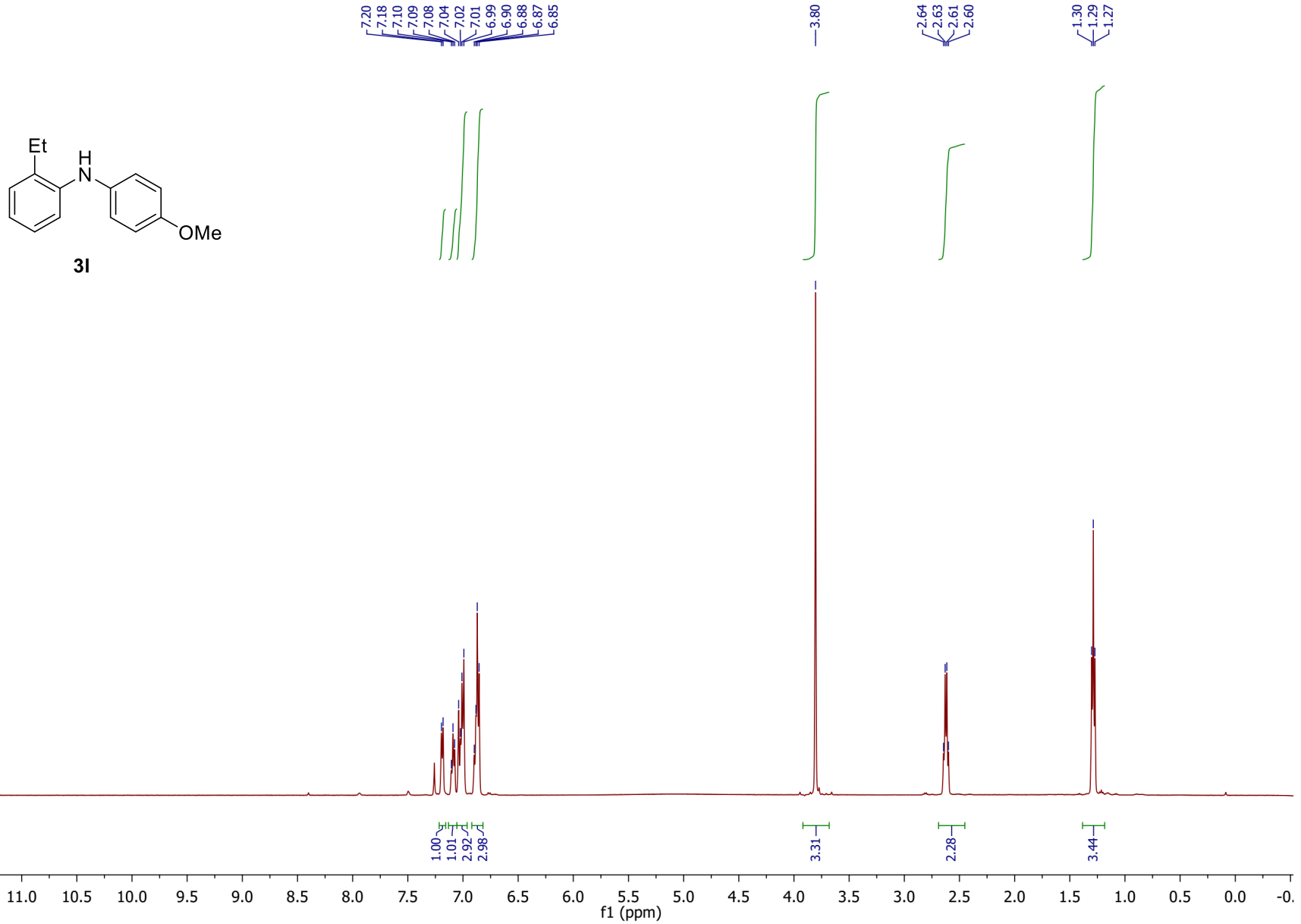
3j

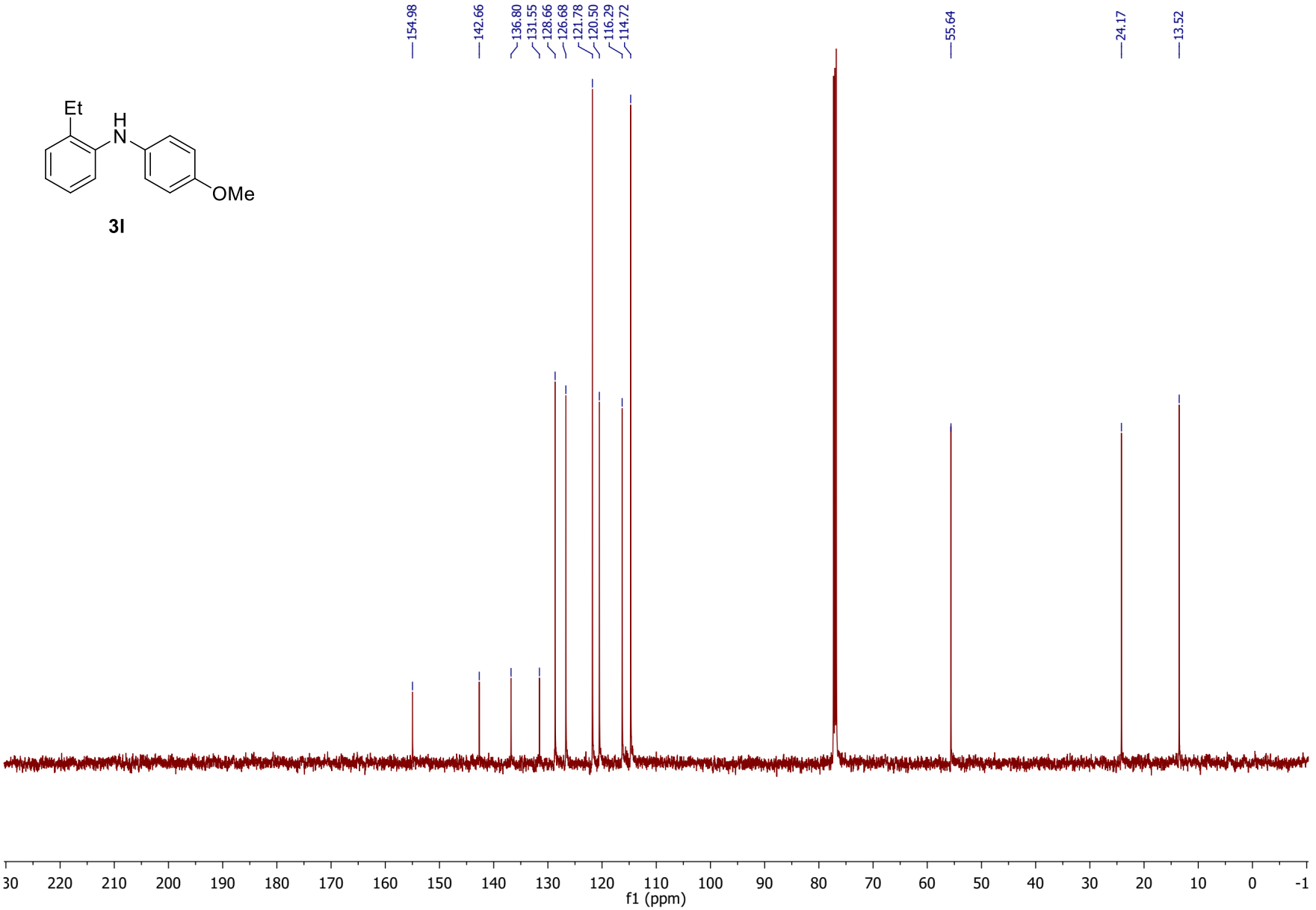
157.28
149.00
133.96
132.86
132.31
125.66
118.14
117.83
114.90
112.94
96.86
55.55

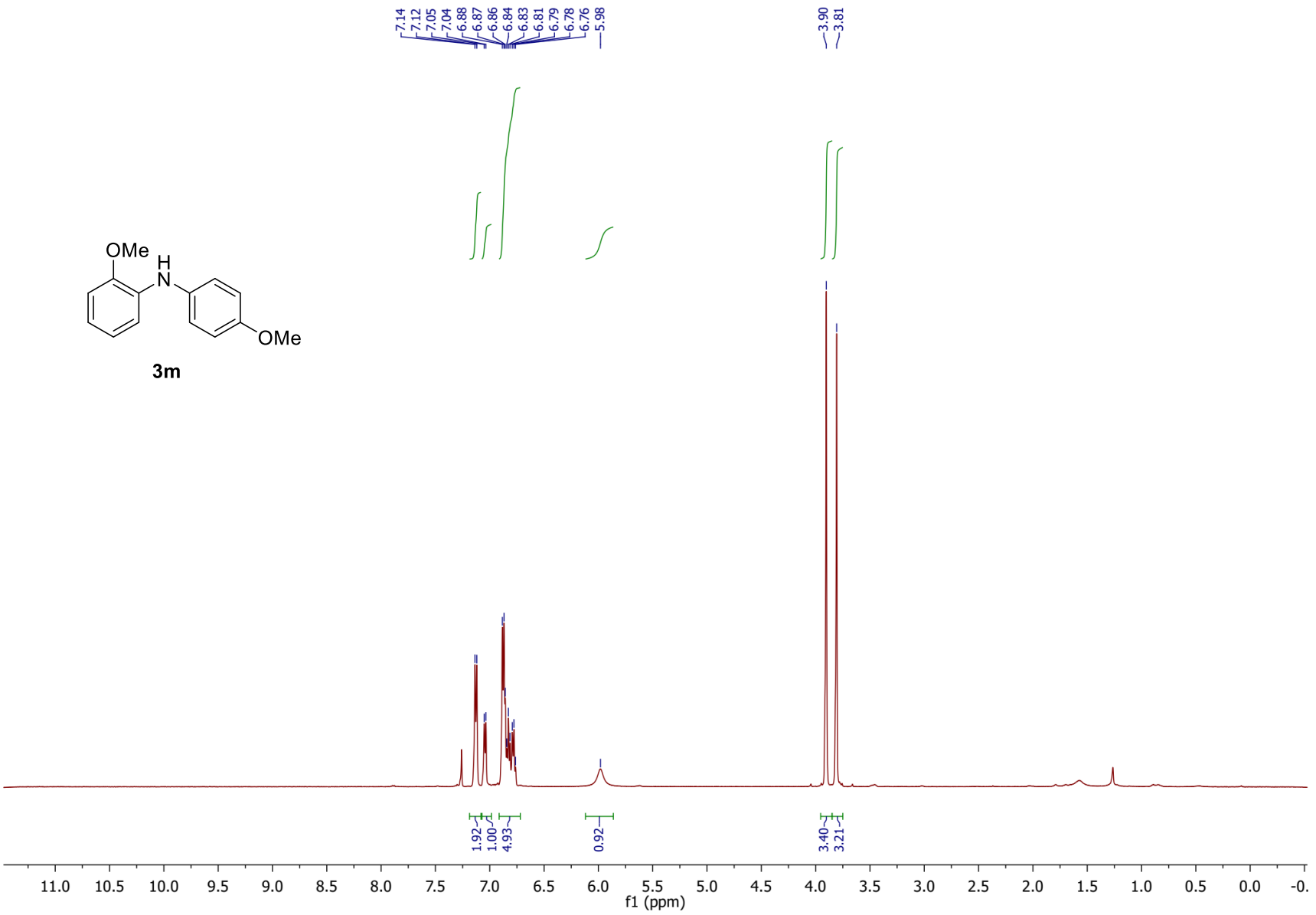



Br
H
N
OMe
3k
7.49
7.47
7.14
7.12
7.10
7.08
6.95
6.93
6.91
6.89
6.65
6.64
3.82
1.00
3.13
3.10
1.06
0.94
3.41
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

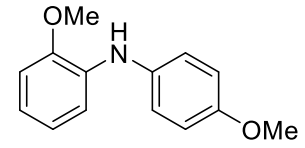

156.43
143.28
134.15
132.78
128.16
124.72
119.58
114.77
114.01
110.56
55.57
Br
H
N
OMe
3k
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.20
7.18
7.10
7.09
7.08
7.04
7.02
7.01
6.99
6.90
6.88
6.87
6.85
3.80
2.64
2.63
2.61
2.60
1.30
1.29
1.27
Et
H
N
OMe
3l
1.00
1.01
2.92
2.98
3.31
2.28
3.44
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)


154.98
142.66
136.80
131.55
128.66
126.68
121.78
120.50
116.29
114.72
55.64
24.17
13.52
Et
H
N
OMe
3l
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

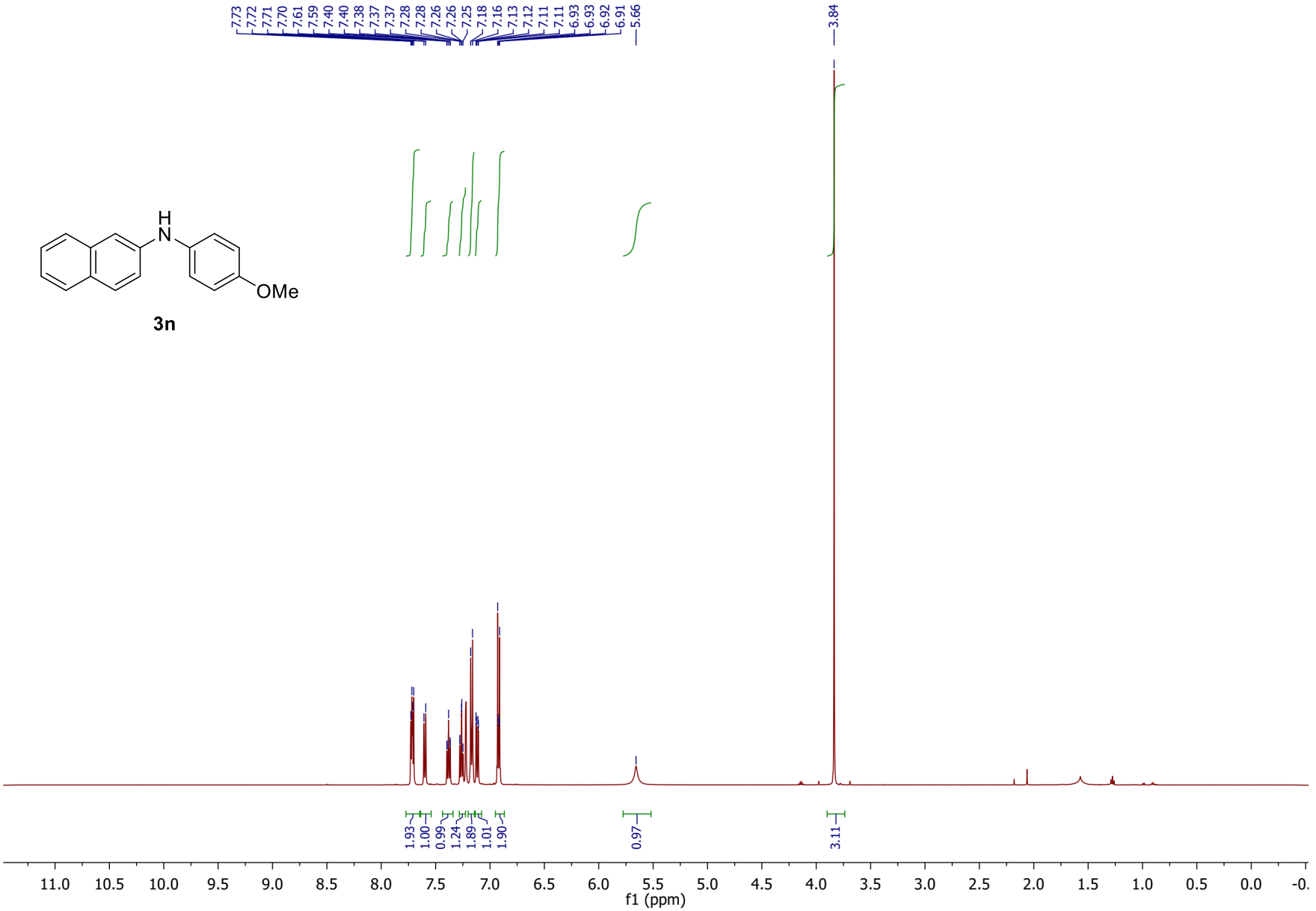

7.14
7.12
7.05
7.04
6.88
6.87
6.86
6.84
6.83
6.81
6.79
6.78
6.76
5.98
3.90
3.81
OMe
H
N
OMe
1.92
1.00
4.93
0.92
3.40
3.21
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

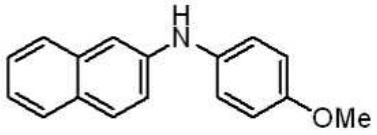
3m


OMe
H
N
OMe

3m

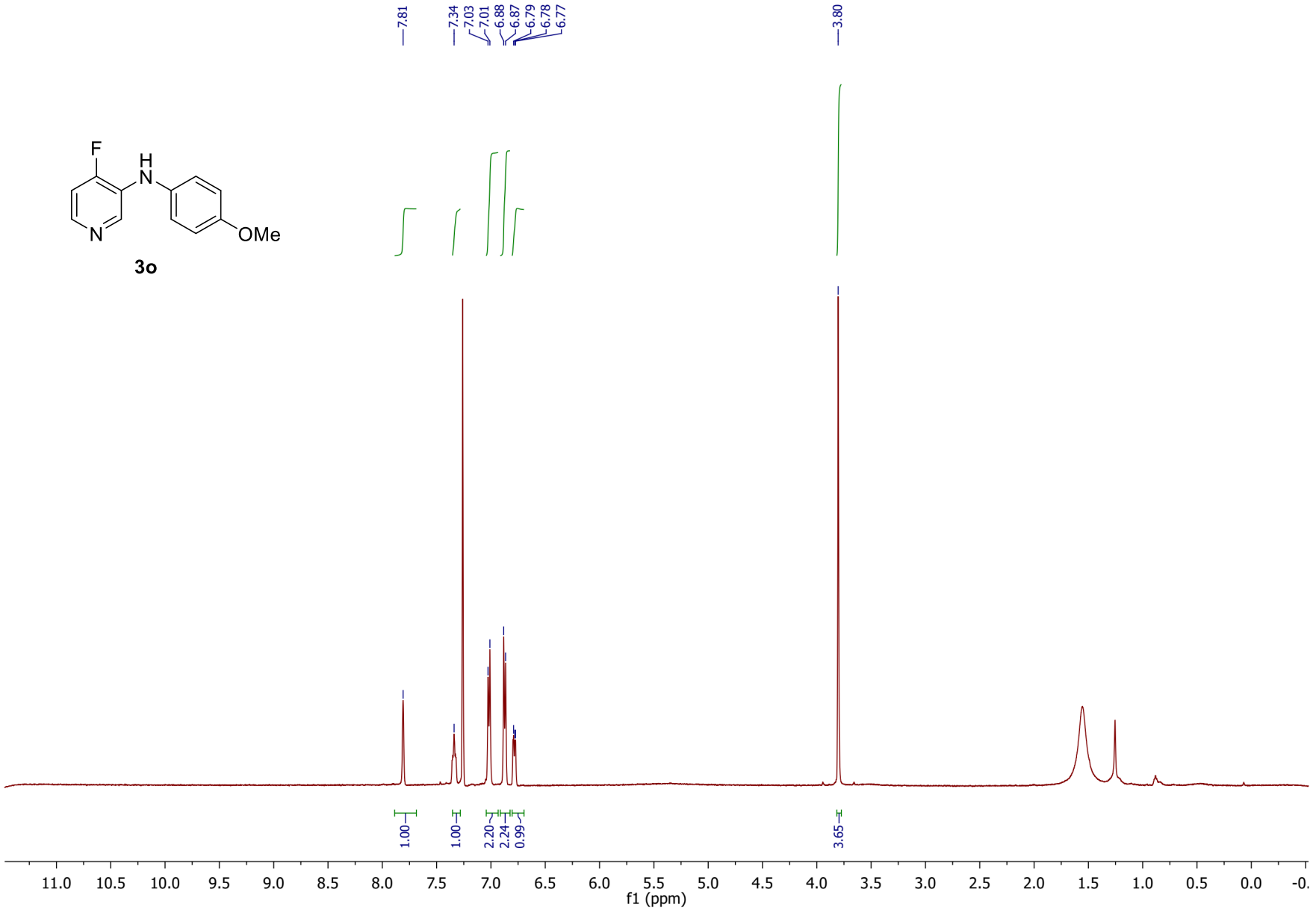
155.31
147.40
135.44
135.06
122.78
120.95
118.57
114.63
112.63
110.24
55.59
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

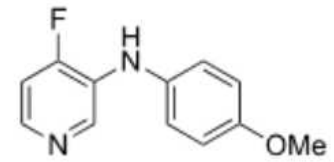

7.73
7.72
7.71
7.70
7.61
7.59
7.40
7.40
7.38
7.37
7.37
7.28
7.28
7.26
7.26
7.25
7.18
7.16
7.13
7.12
7.11
7.11
6.93
6.93
6.92
6.91
5.66
3.84
H
N
OMe
3n
1.93
1.00
0.99
1.24
1.89
1.01
1.90
0.97
3.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H
N
OMe

3n

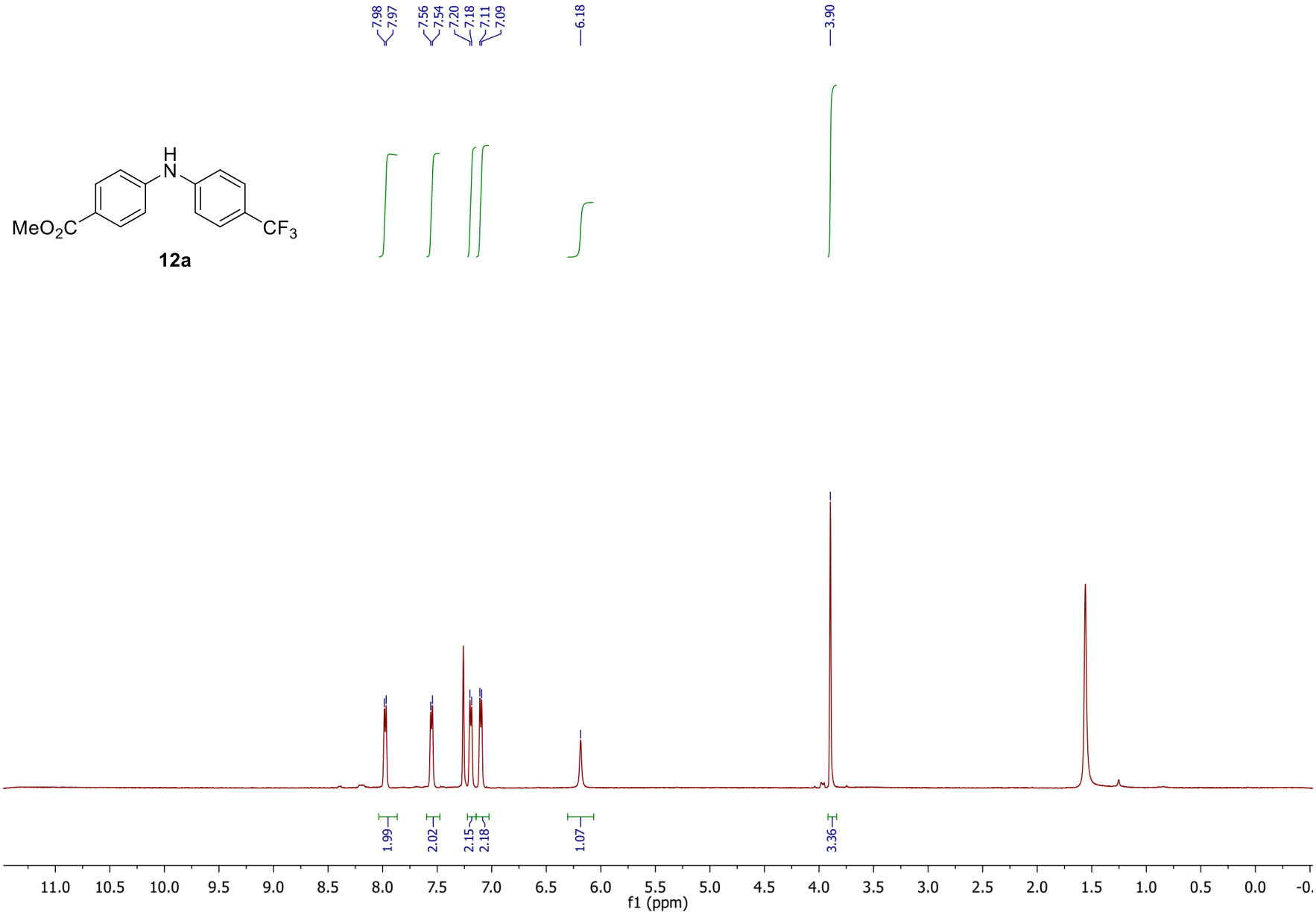
153.20
148.95
134.22
128.61
126.18
126.01
125.36
121.84
121.07
120.93
114.80
111.74
55.64
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

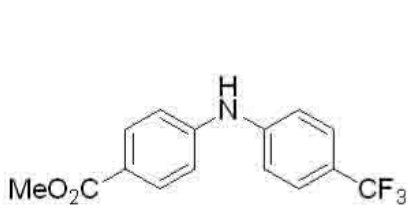

F
H
N
N
OMe
3o
7.81
7.34
7.03
7.01
6.88
6.87
6.79
6.78
6.77
3.80
1.00
1.00
2.20
2.24
0.99
3.65
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
H
N
N
OMe

3o

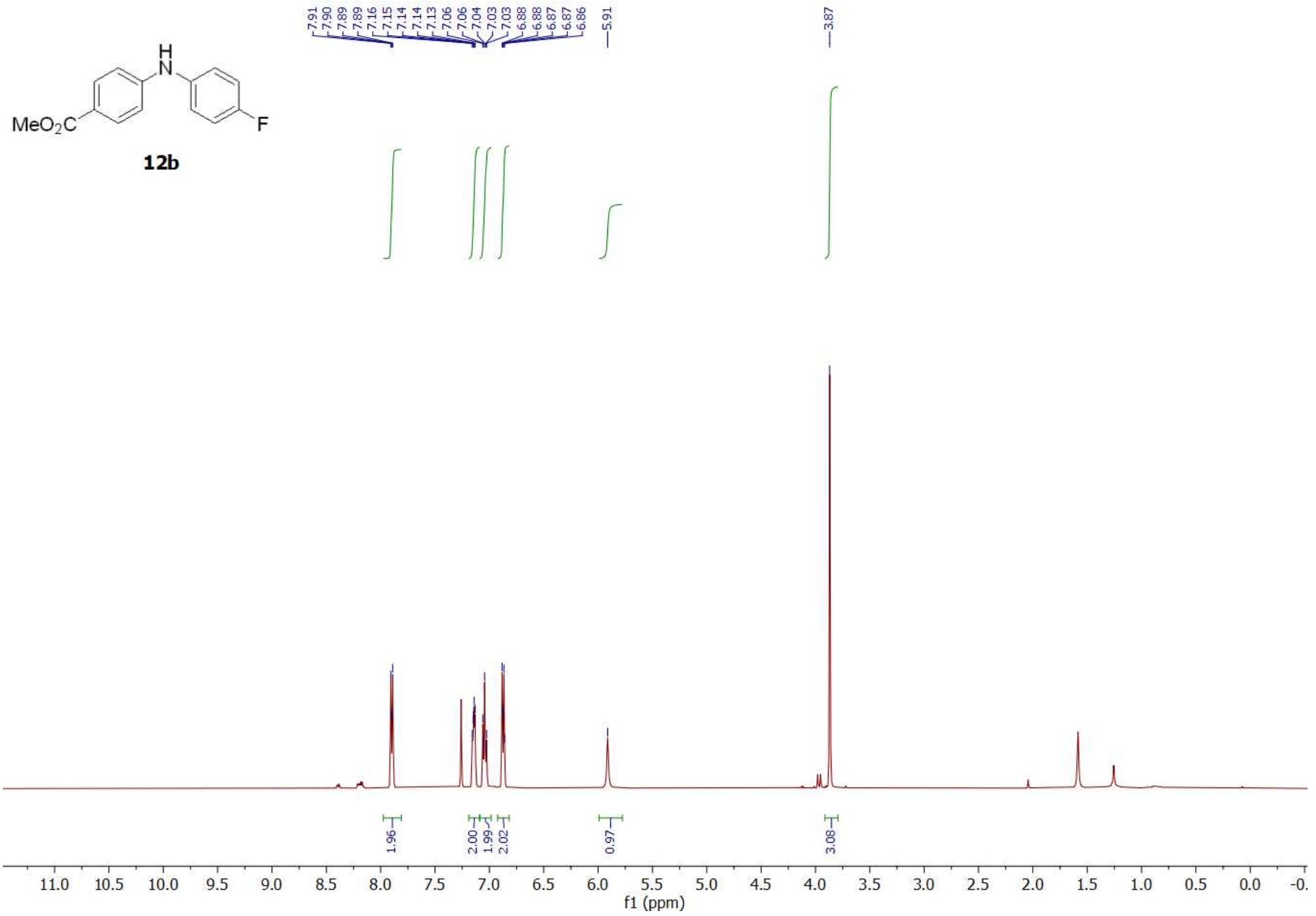
158.74
155.80
139.66
135.15
134.89
134.77
131.67
128.52
128.46
121.94
114.95
109.53
109.22
55.61
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

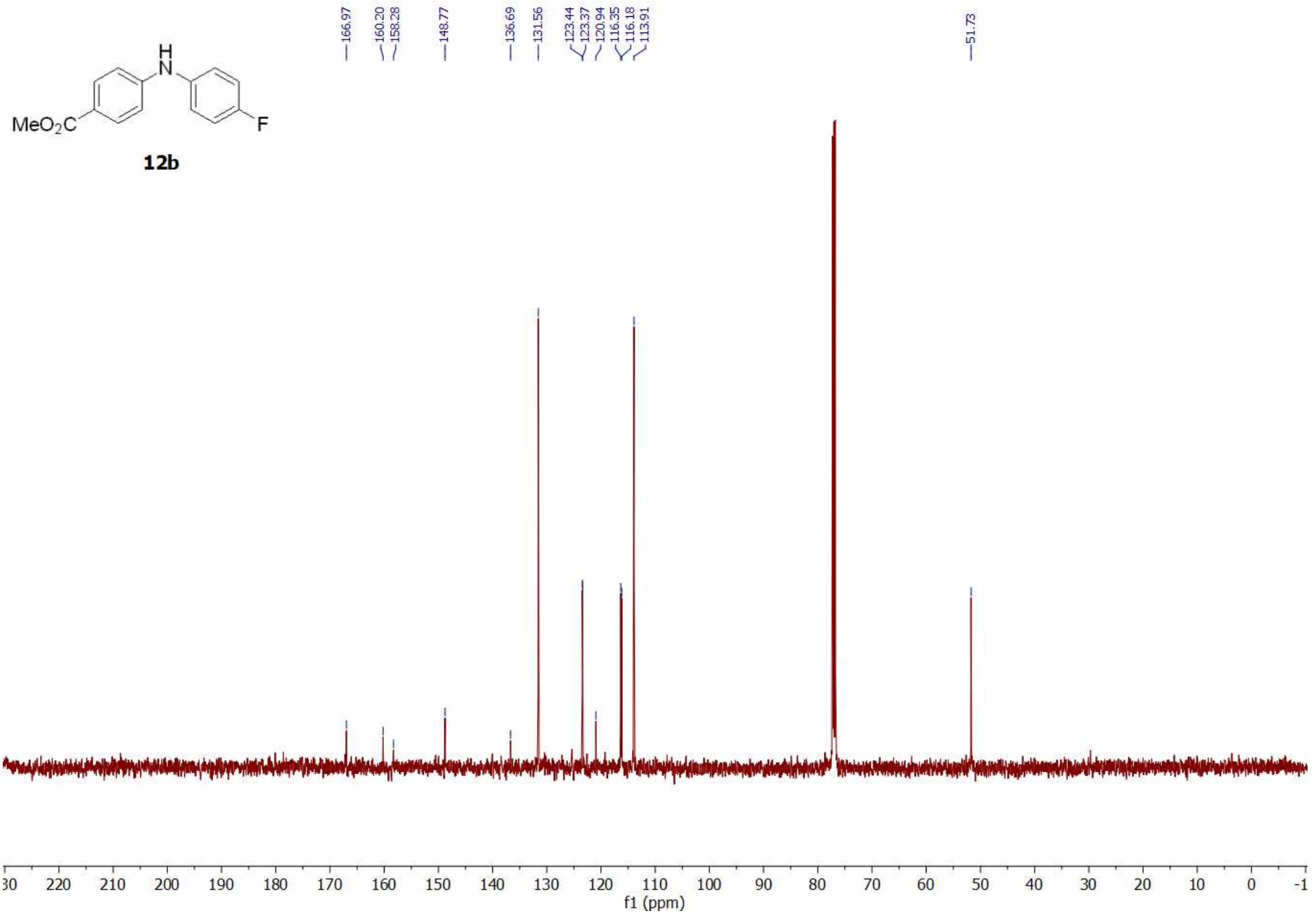

7.98
7.97
7.56
7.54
7.20
7.18
7.11
7.09
6.18
3.90
MeO2C
CF3
H
N
12a
1.99
2.02
2.15
2.18
1.07
3.36
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

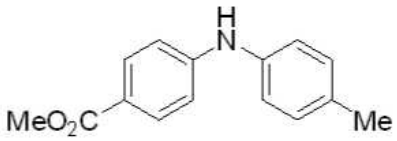

MeO2C
CF3
H
N

12a

166.73
146.11
144.54
131.53
129.14
126.83
123.92
122.99
121.79
117.90
116.45
51.91
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

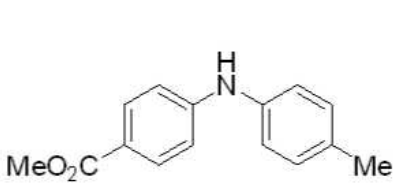

7.91
7.90
7.89
7.89
7.16
7.15
7.14
7.14
7.13
7.06
7.06
7.04
7.03
7.03
6.88
6.88
6.87
6.87
6.86
5.91
3.87
MeO2C
F
H
N
12b
1.96
2.00
1.99
2.02
0.97
3.08
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.97
160.20
158.28
148.77
136.69
131.56
123.44
123.37
120.94
116.35
116.18
113.91
51.73
MeO2C
H
N
F
12b
f1 (ppm)


H
N
MeO2C
Me

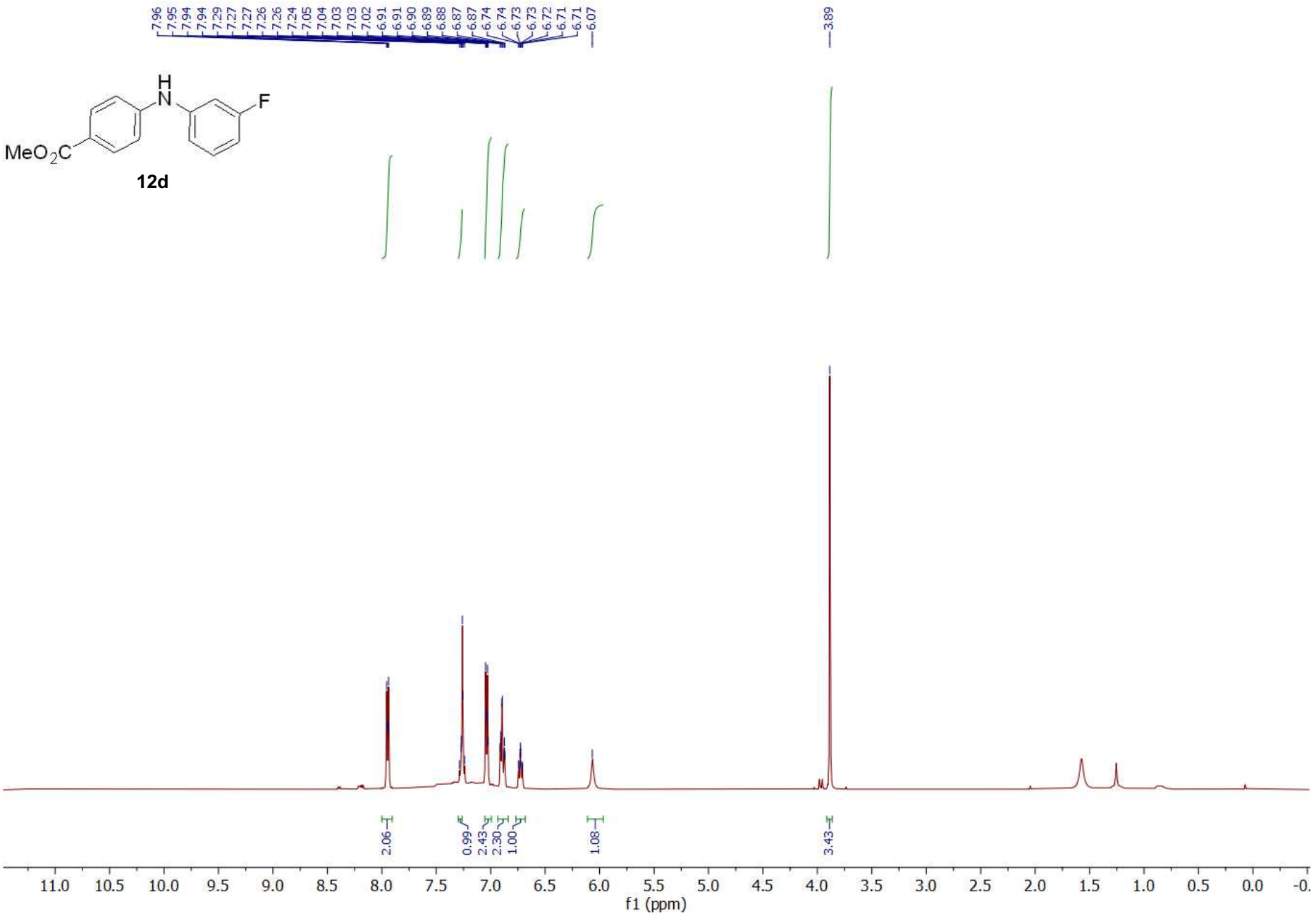
12c

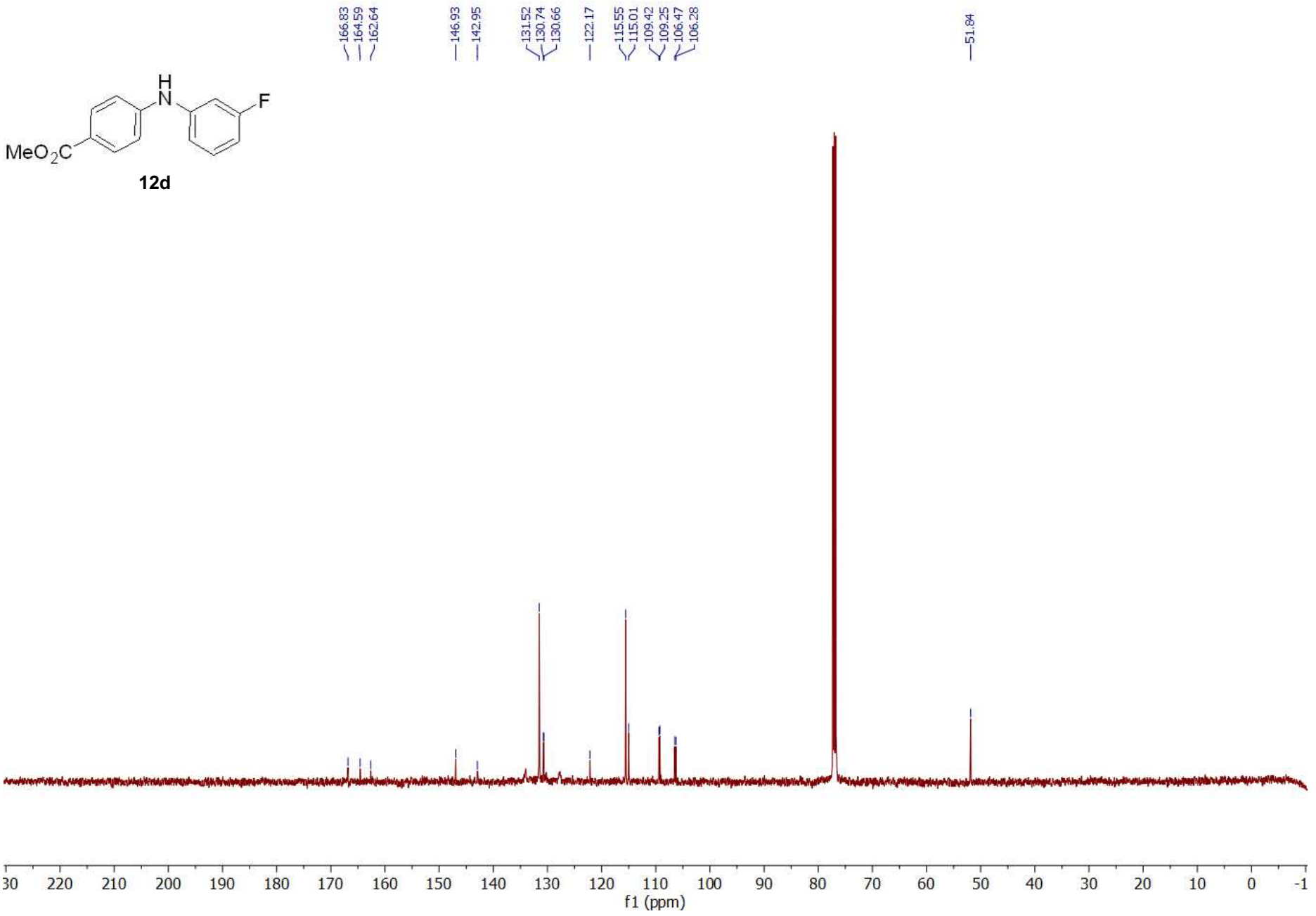
7.91
7.90
7.89
7.89
7.16
7.14
7.09
7.09
7.08
7.08
7.07
6.93
6.92
6.91
6.91
6.01
3.87
2.34
1.96
2.00
2.07
2.15
1.07
3.29
3.30
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

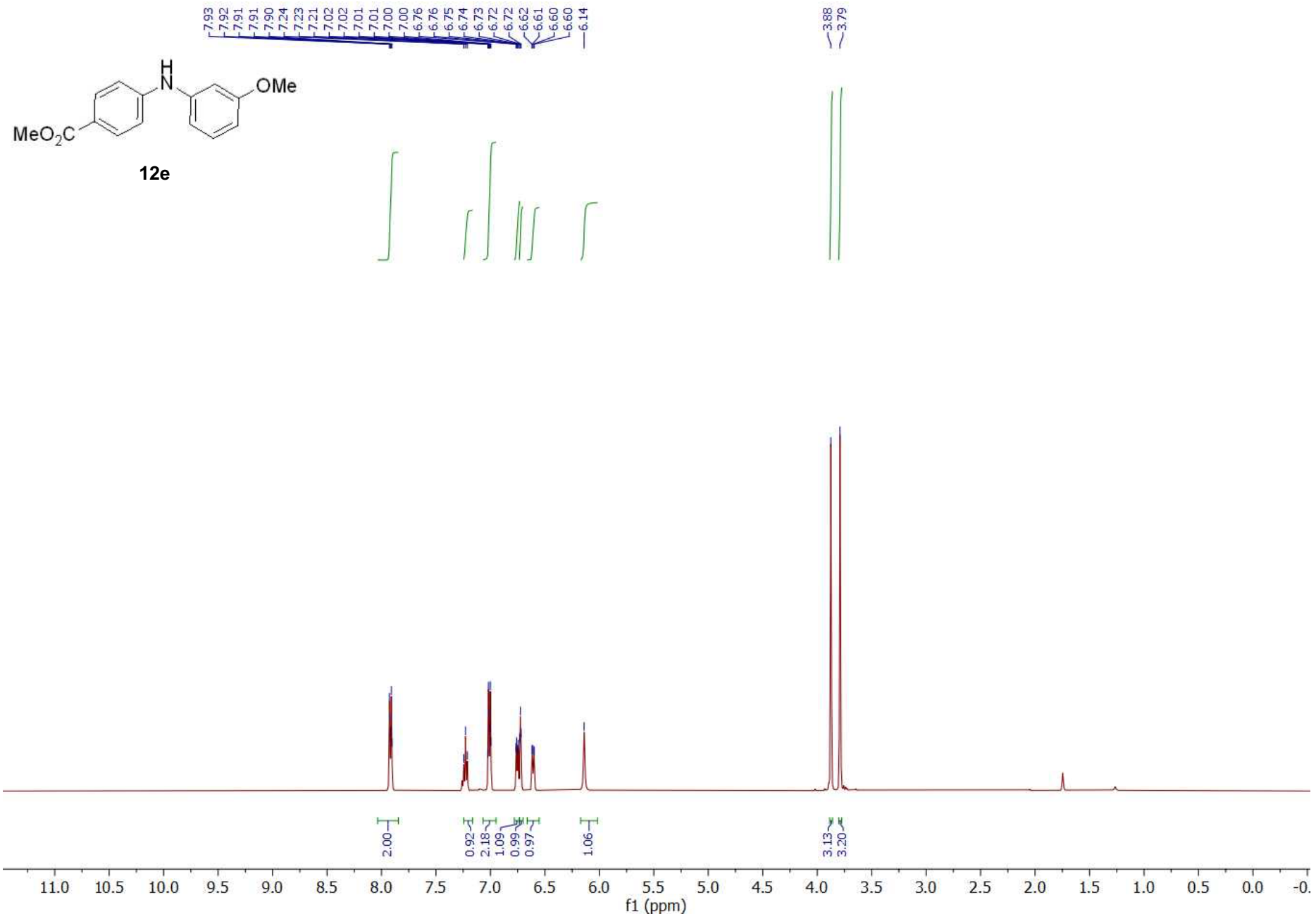

H
N
MeO2C
Me

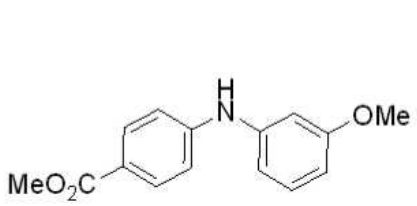
12c

167.09
148.86
138.08
133.18
131.51
130.06
121.39
120.50
113.98
51.70
20.85
f1 (ppm)


7.96
7.95
7.94
7.94
7.29
7.27
7.27
7.26
7.26
7.24
7.05
7.04
7.03
7.03
7.02
6.91
6.91
6.90
6.89
6.88
6.87
6.87
6.74
6.74
6.73
6.73
6.72
6.71
6.71
6.07
3.89
H
N
F
MeO2C
12d
2.06
0.99
2.43
2.30
1.00
1.08
3.43
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
-0.
f1 (ppm)

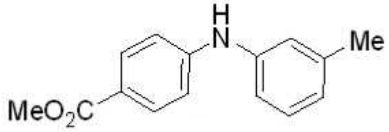

166.83
164.59
162.64
146.93
142.95
131.52
130.74
130.66
122.17
115.55
115.01
109.42
109.25
106.47
106.28
51.84
H
N
F
MeO2C
12d
f1 (ppm)


7.93
7.92
7.91
7.91
7.90
7.24
7.23
7.21
7.02
7.02
7.01
7.01
7.00
7.00
6.76
6.76
6.75
6.74
6.73
6.72
6.72
6.62
6.61
6.60
6.60
6.14
3.88
3.79
H
N
OMe
MeO2C
12e
2.00
0.92
2.18
1.09
0.99
0.97
1.06
3.13
3.20
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)


H
N
OMe
MeO2C

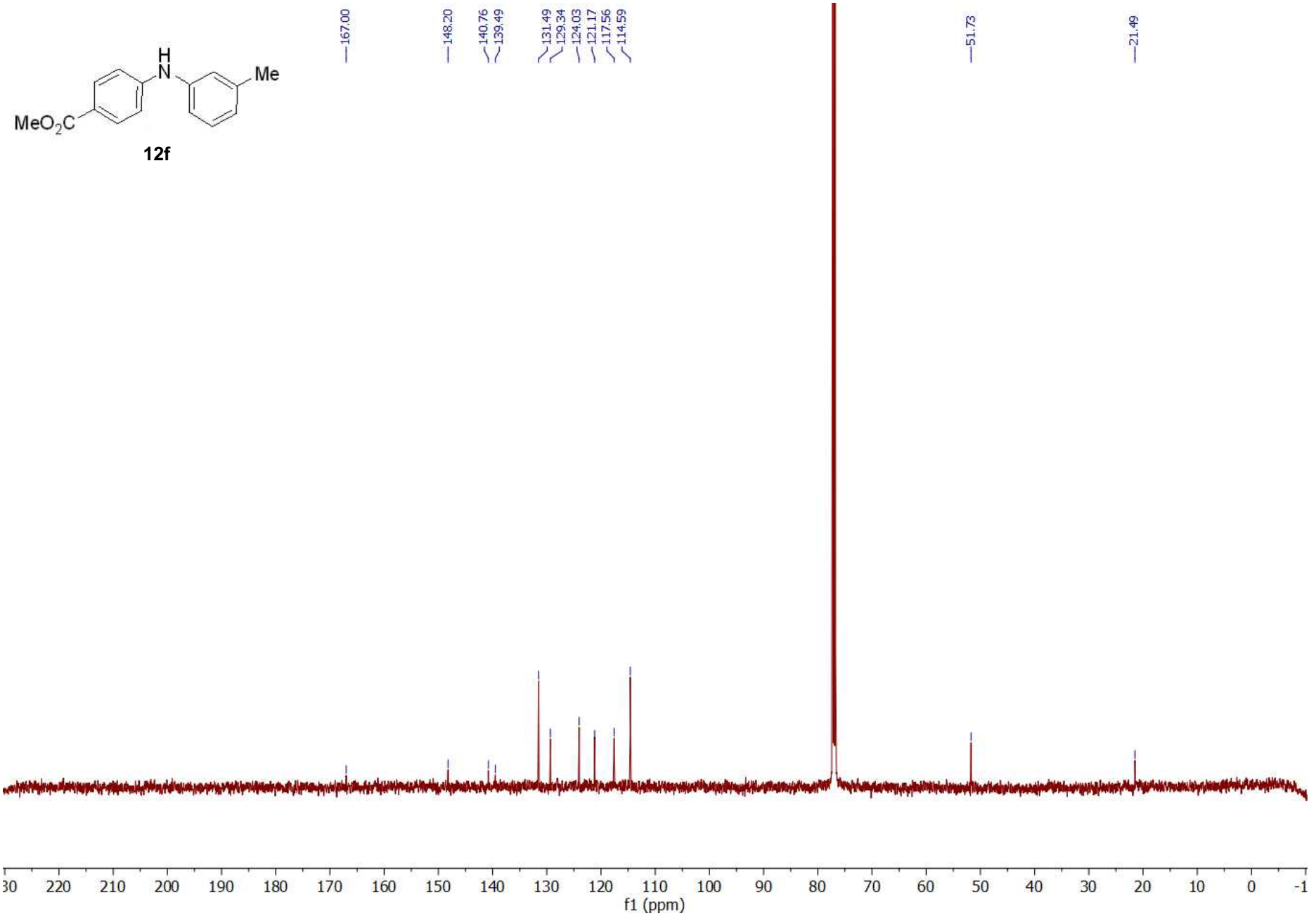
12e

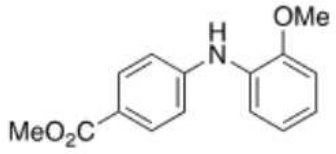
167.02
160.70
147.88
142.26
131.48
130.27
121.23
115.00
112.60
108.28
106.00
55.30
51.77
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


H
N
Me
MeO2C

12f

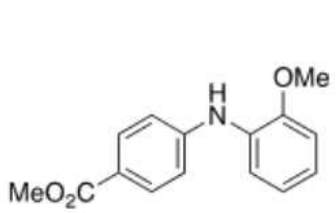
7.92
7.92
7.90
7.90
7.24
7.22
7.21
6.99
6.98
6.98
6.98
6.97
6.97
6.90
6.88
5.97
3.87
2.34
1.88
1.00
4.12
0.93
3.27
3.07
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


H
N
Me
MeO2C
12f
167.00
148.20
140.76
139.49
131.49
129.34
124.03
121.17
117.56
114.59
51.73
21.49
f1 (ppm)


H
N
OMe
MeO2C

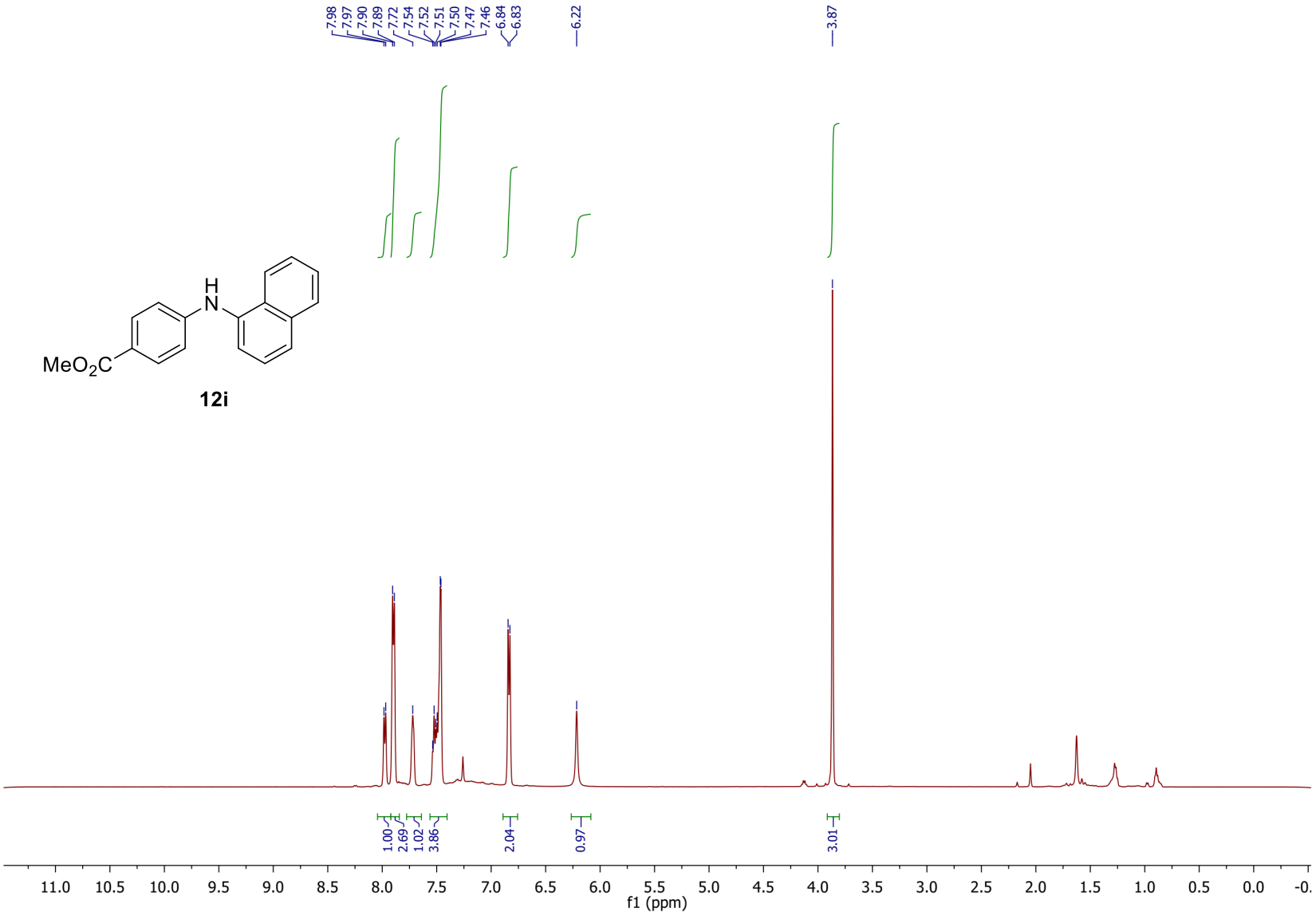
12g

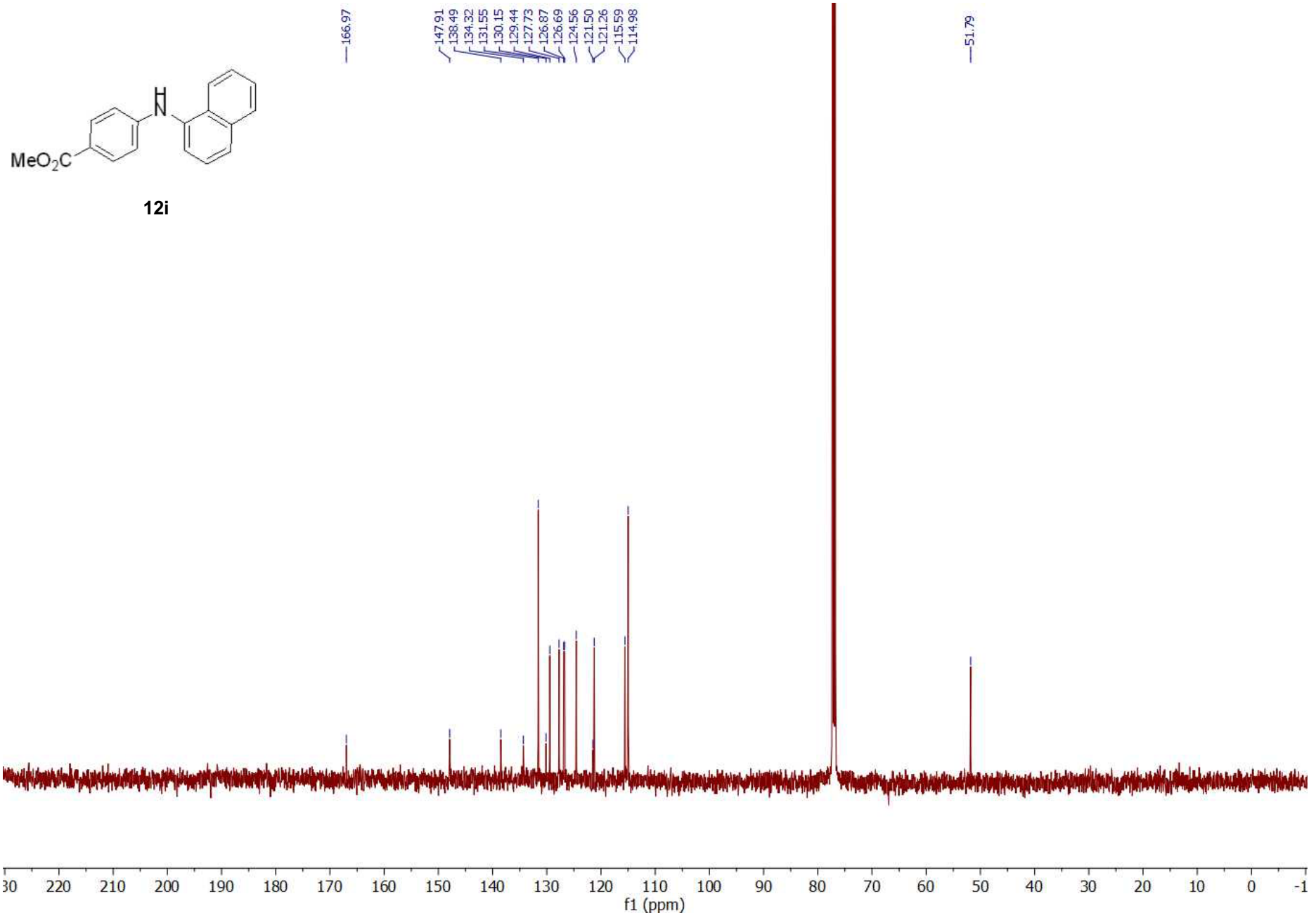
7.94
7.94
7.93
7.92
7.92
7.91
7.41
7.41
7.40
7.40
7.09
7.09
7.08
7.08
7.07
7.07
6.99
6.98
6.97
6.97
6.96
6.95
6.94
6.94
6.94
6.93
6.93
6.92
6.92
6.37
3.89
3.88
2.00
1.16
2.23
3.19
1.05
3.19
3.17
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


OMe
H
N
MeO2C

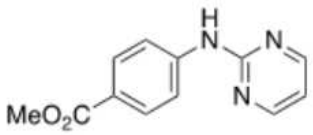
12g

167.02
149.51
147.58
131.41
130.51
122.21
121.23
120.77
117.73
115.21
110.89
55.64
51.73
f1 (ppm)


7.98
7.97
7.90
7.89
7.72
7.54
7.52
7.51
7.50
7.47
7.46
6.84
6.83
6.22
3.87
H
N
MeO2C
12i
1.00
2.69
1.02
3.86
2.04
0.97
3.01
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)

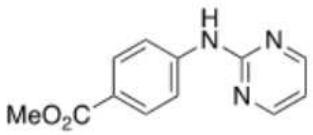

166.97
147.91
138.49
134.32
131.55
130.15
129.44
127.73
126.87
126.69
124.56
121.50
121.26
115.59
114.98
51.79
MeO2C
H
N
f1 (ppm)

12i


H
N
N
N
MeO2C

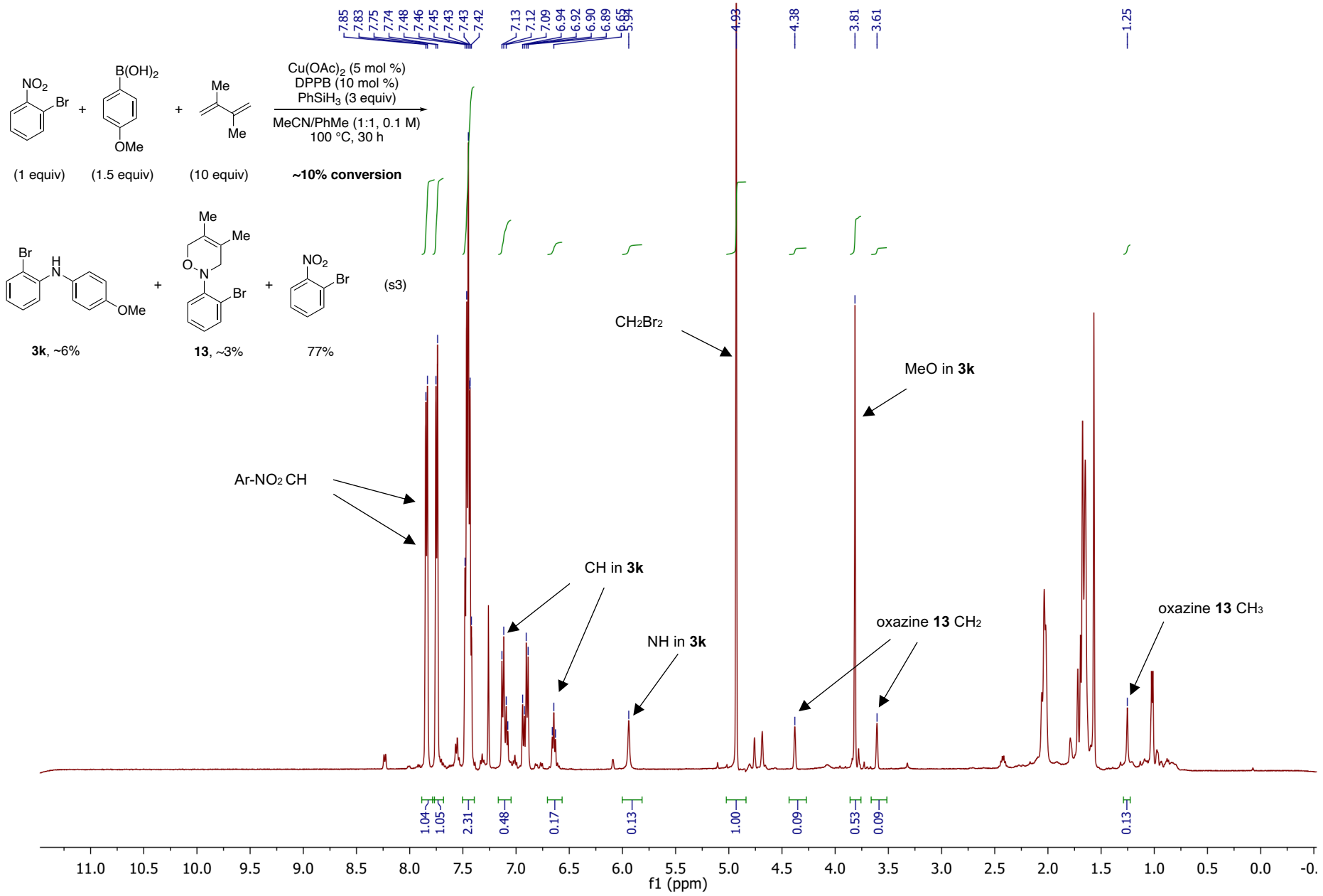
12j

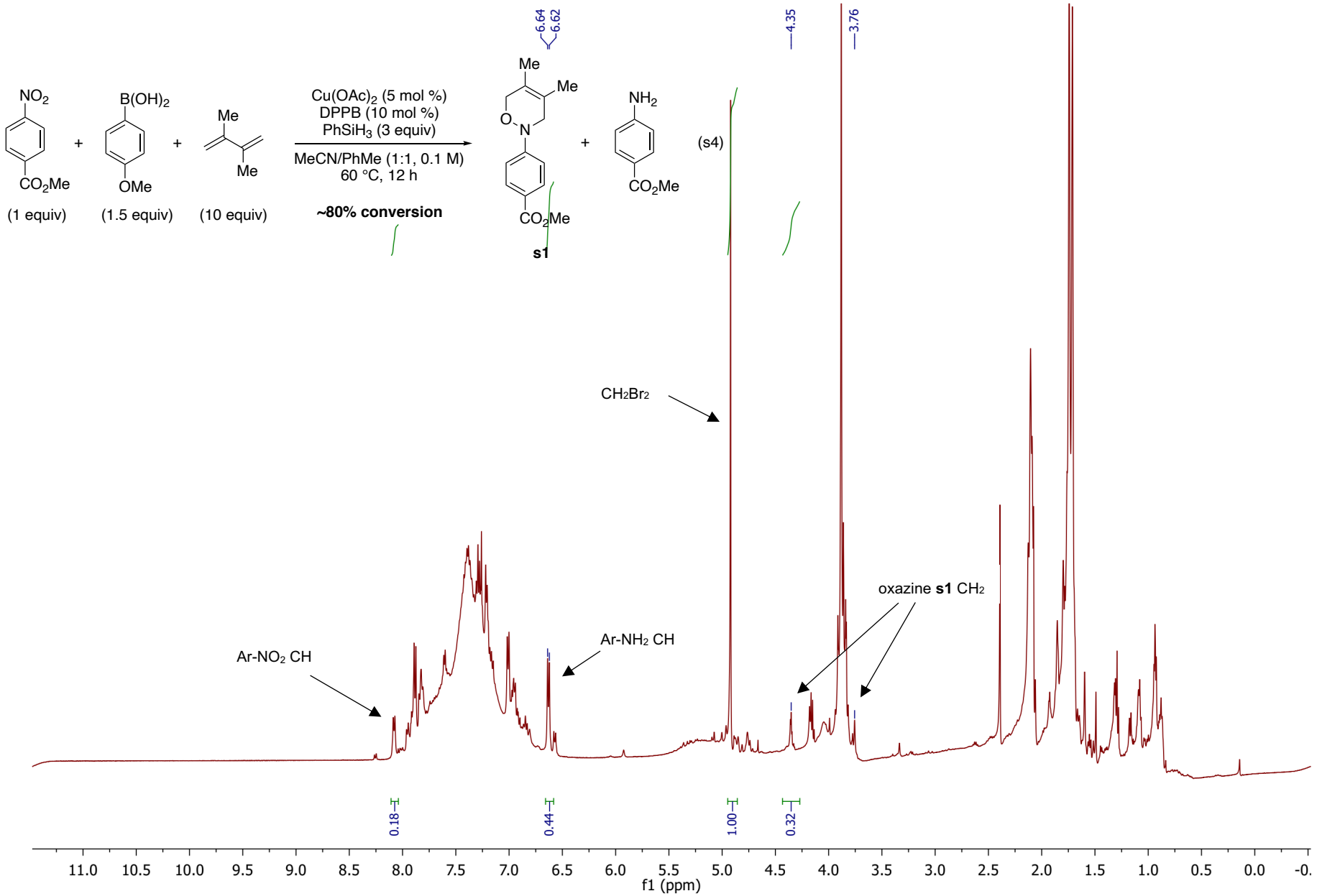
8.37
8.36
7.78
7.49
7.47
6.91
6.89
6.65
6.64
6.64
3.80
1.91
1.04
2.00
2.04
1.02
3.27
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

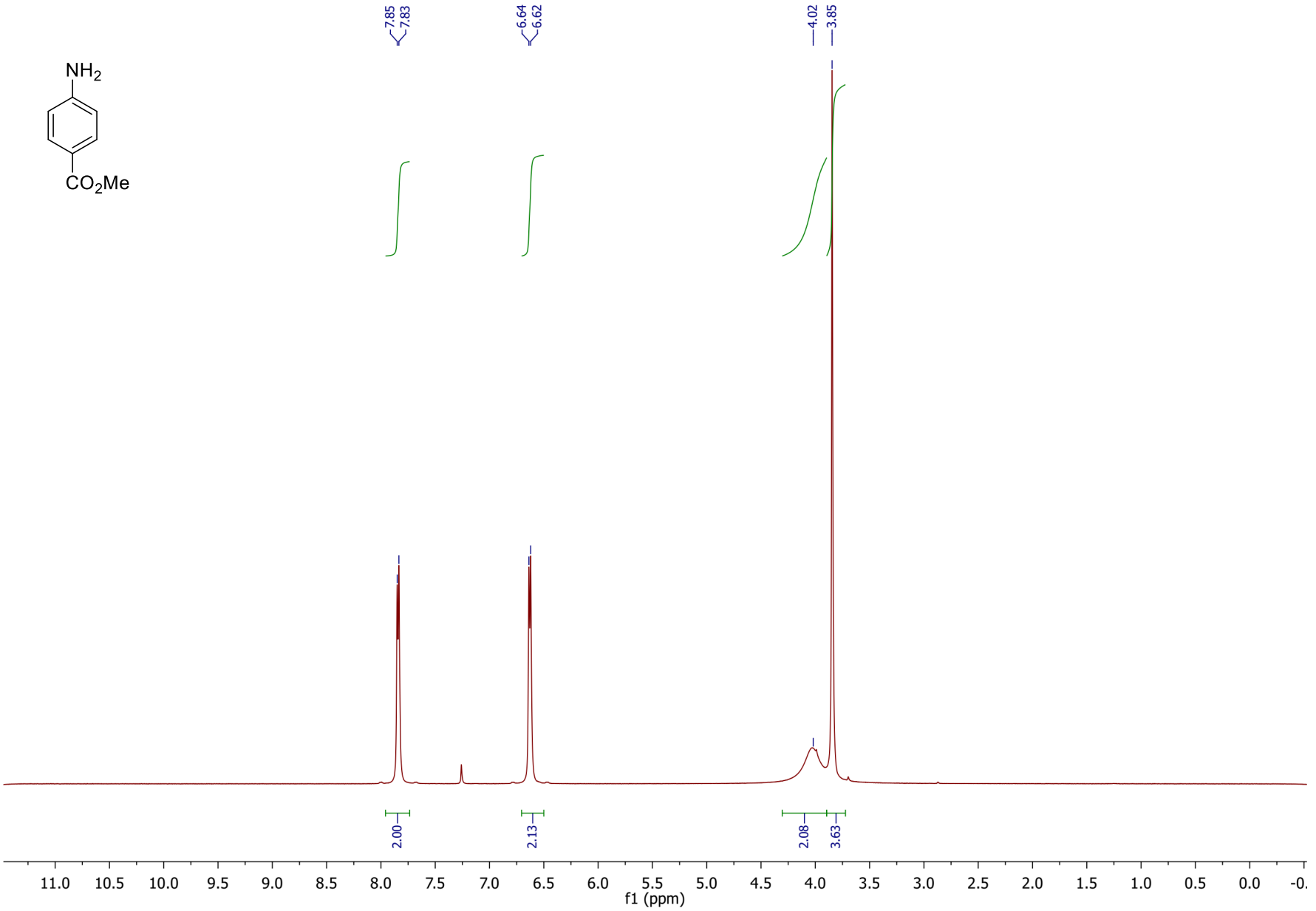

H
N
N
N
MeO2C

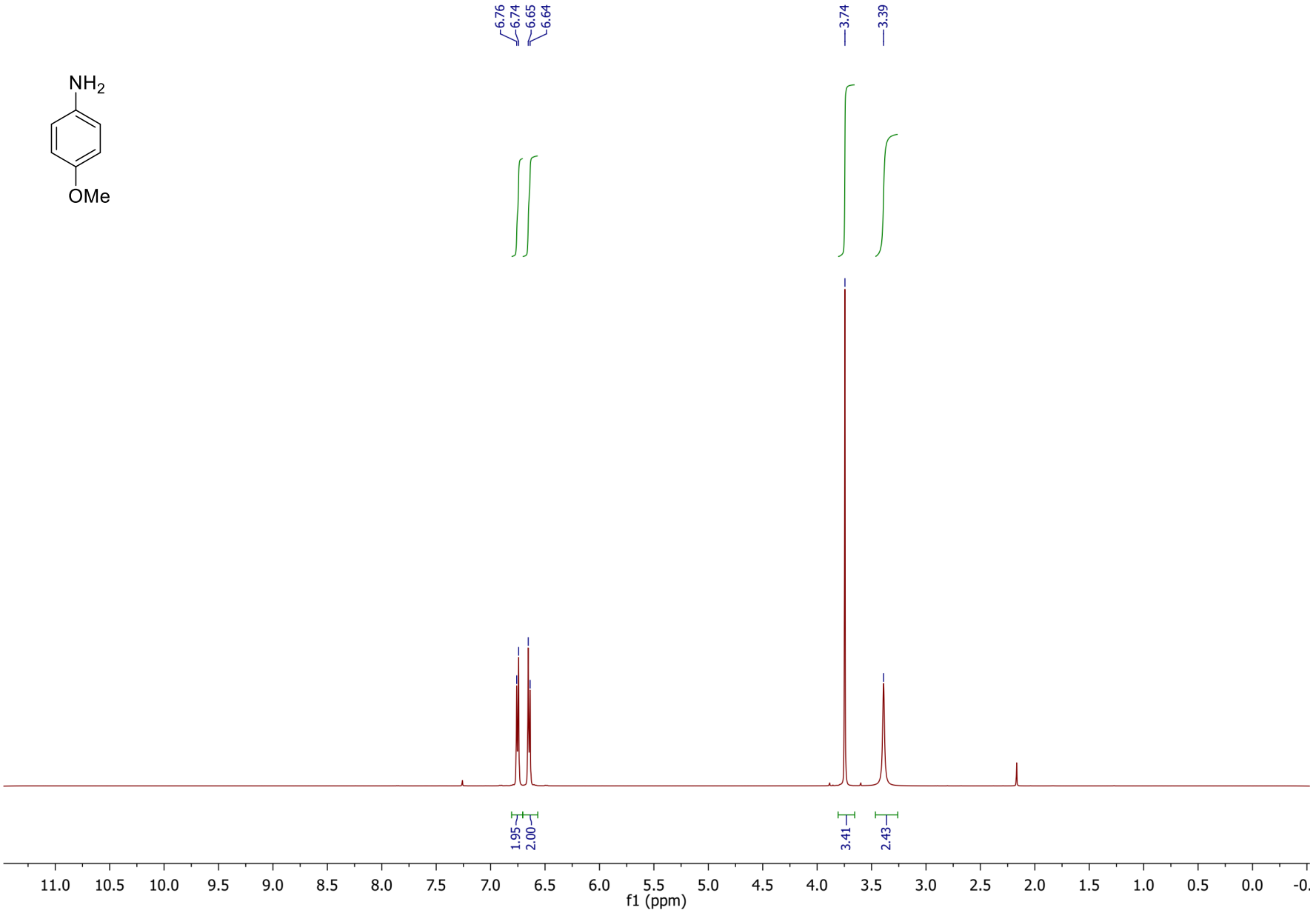
12j

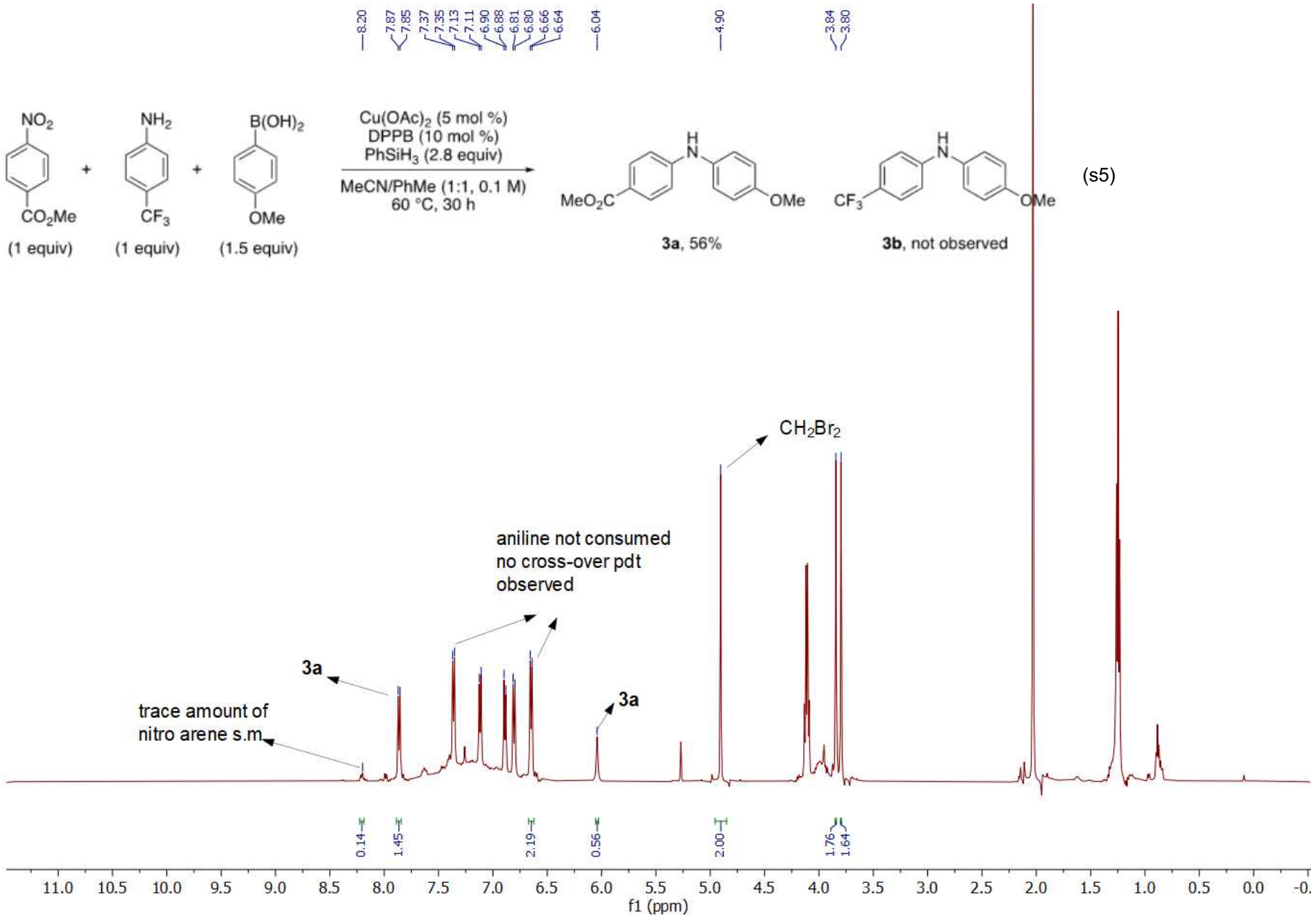
160.76
158.08
155.82
132.45
122.37
114.27
111.94
55.55
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

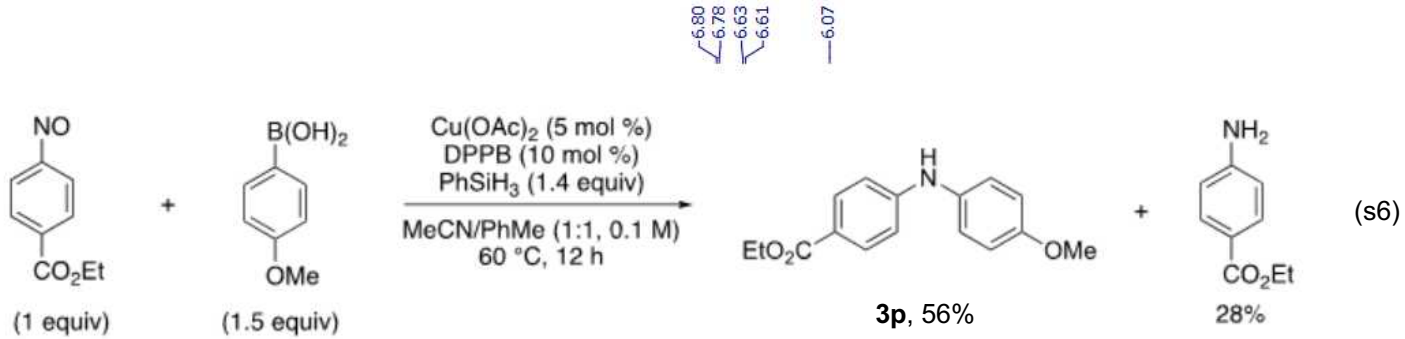

7.85
7.83
7.75
7.74
7.48
7.46
7.45
7.43
7.43
7.42
7.13
7.12
7.09
6.94
6.92
6.90
6.89
6.65
5.94
4.93
4.38
3.81
3.61
1.25
NO2
Br
B(OH)2
OMe
Me
Me
Cu(OAc)2 (5 mol %)
DPPB (10 mol %)
PhSiH3 (3 equiv)
MeCN/PhMe (1:1, 0.1 M)
100 °C, 30 h
(1 equiv)
(1.5 equiv)
(10 equiv)
~10% conversion
Br
H
N
OMe
3k, ~6%
Me
Me
O
N
Br
13, ~3%
NO2
Br
77%
(s3)
CH2Br2
MeO in 3k
Ar-NO2 CH
CH in 3k
NH in 3k
oxazine 13 CH2
oxazine 13 CH3
1.04
1.05
2.31
0.48
0.17
0.13
1.00
0.09
0.53
0.09
0.13
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
-0.
f1 (ppm)


NO2
CO2Me
(1 equiv)
B(OH)2
OMe
(1.5 equiv)
Me
Me
(10 equiv)
Cu(OAc)2 (5 mol %)
DPPB (10 mol %)
PhSiH3 (3 equiv)
MeCN/PhMe (1:1, 0.1 M)
60 °C, 12 h
~80% conversion
Me
Me
O
N
CO2Me
s1
NH2
CO2Me
(s4)
6.64
6.62
4.35
3.76
CH2Br2
oxazine s1 CH2
Ar-NH2 CH
Ar-NO2 CH
0.18
0.44
1.00
0.32
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)

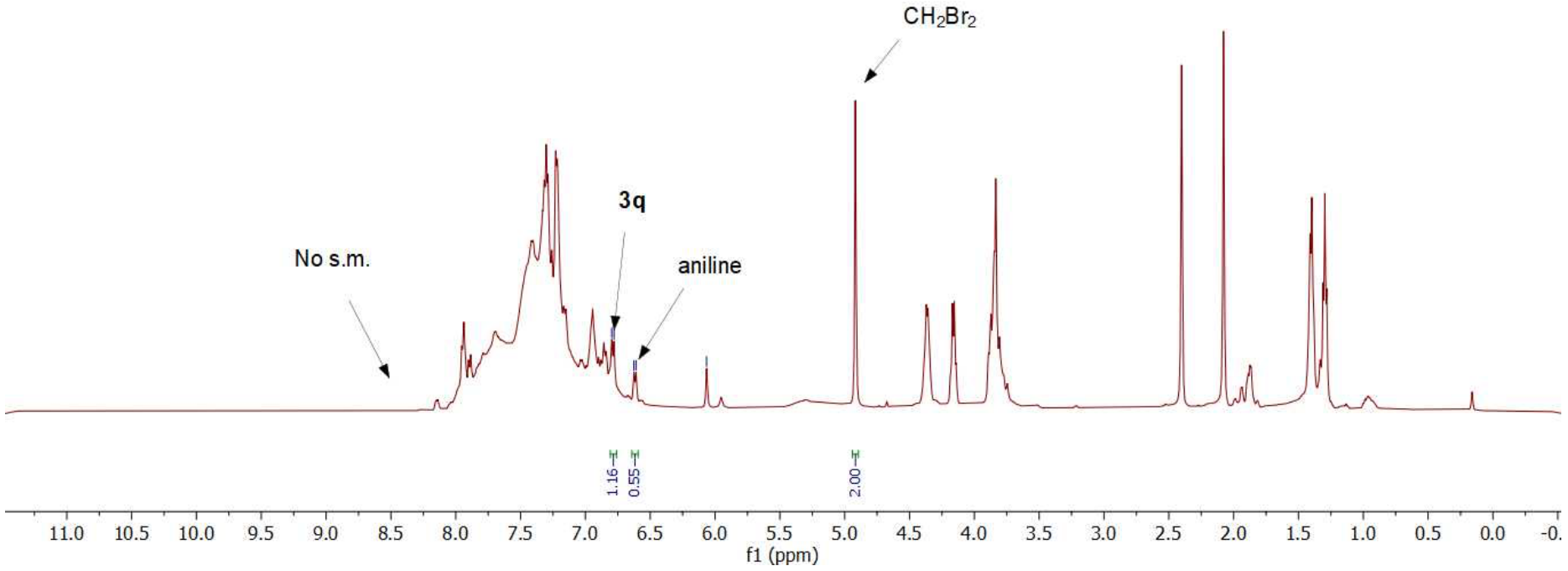

NH2
CO2Me
7.85
7.83
6.64
6.62
4.02
3.85
2.00
2.13
2.08
3.63
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

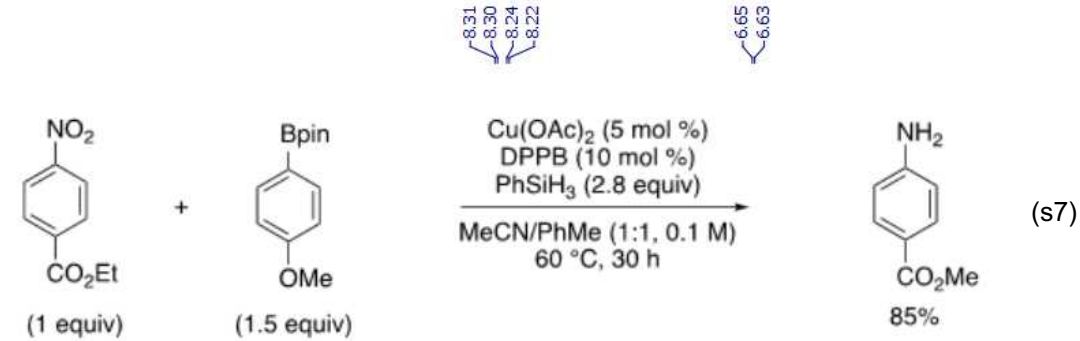

NH2
OMe
6.76
6.74
6.65
6.64
3.74
3.39
1.95
2.00
3.41
2.43
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


8.20
7.87
7.85
7.37
7.35
7.13
7.11
6.90
6.88
6.81
6.80
6.66
6.64
6.04
4.90
3.84
3.80
NO2
CO2Me
(1 equiv)
NH2
CF3
(1 equiv)
B(OH)2
OMe
(1.5 equiv)
Cu(OAc)2 (5 mol %)
DPPB (10 mol %)
PhSiH3 (2.8 equiv)
MeCN/PhMe (1:1, 0.1 M)
60 °C, 30 h
MeO2C
OMe
3a, 56%
CF3
OMe
3b, not observed
(s5)
CH2Br2
aniline not consumed
no cross-over pdt
observed
3a
3a
trace amount of
nitro arene s.m
0.14
1.45
2.19
0.56
2.00
1.76
1.64
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)

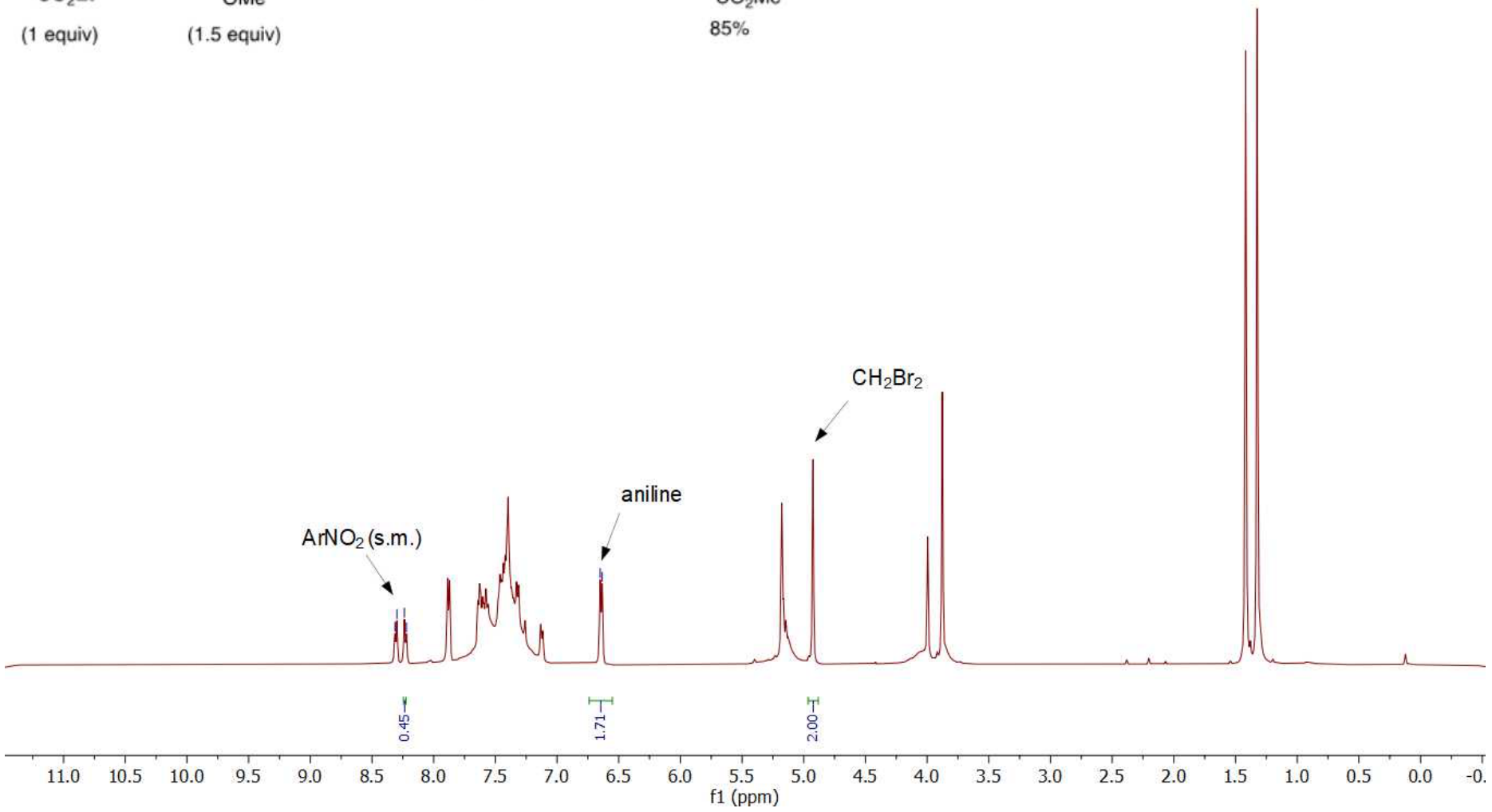

6.80
6.78
6.63
6.61
6.07
NO
CO2Et
(1 equiv)
+
B(OH)2
OMe
(1.5 equiv)
Cu(OAc)2 (5 mol %)
DPPB (10 mol %)
PhSiH3 (1.4 equiv)
MeCN/PhMe (1:1, 0.1 M)
60 °C, 12 h
H
N
EtO2C
OMe
3p, 56%
+
NH2
CO2Et
28%

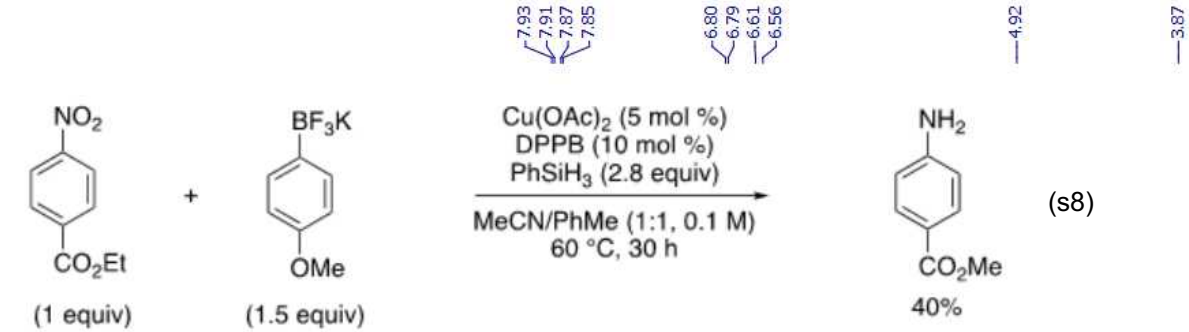
(s6)


CH2Br2
3q
No s.m.
aniline
1.16
0.55
2.00
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)

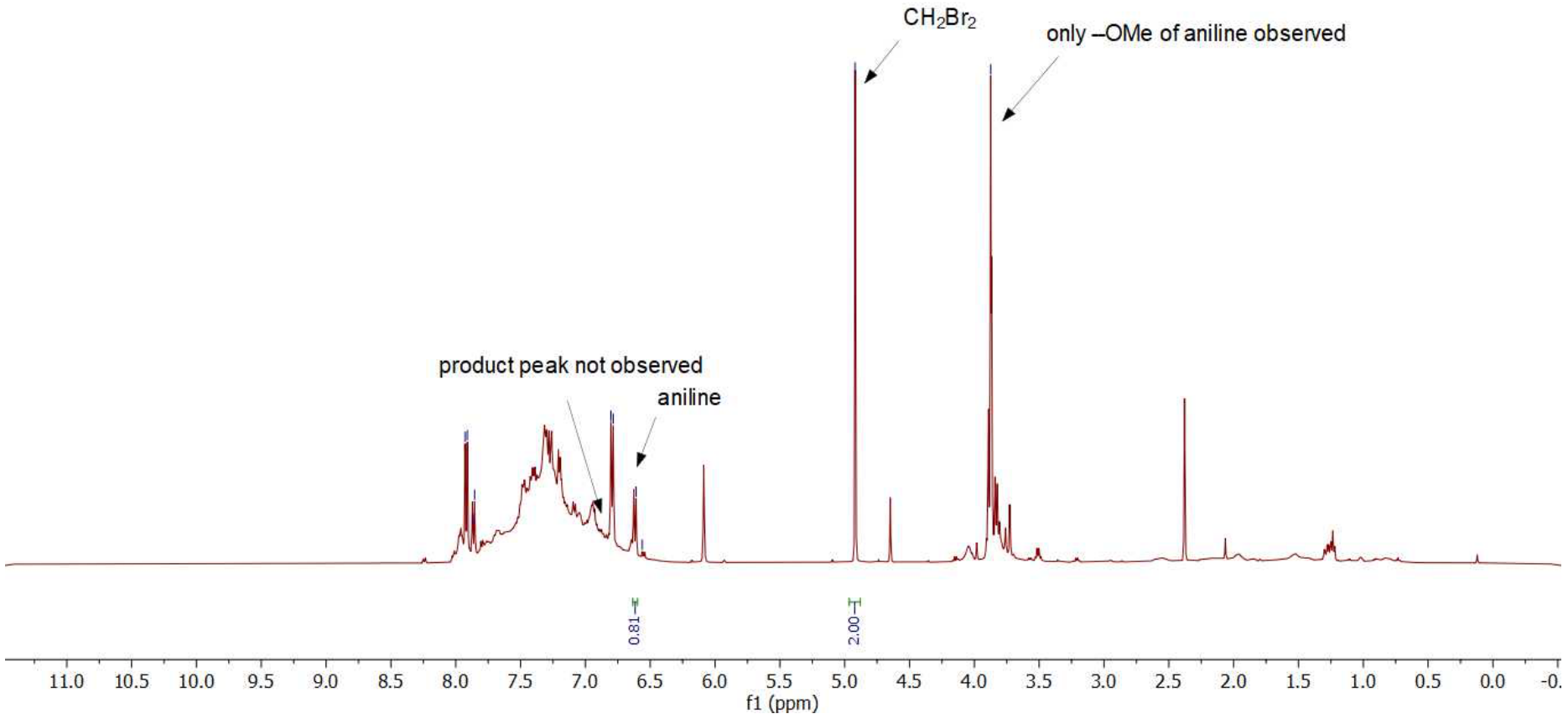

8.31
8.30
8.24
8.22
6.65
6.63
NO2
CO2Et
(1 equiv)
+
Bpin
OMe
(1.5 equiv)
Cu(OAc)2 (5 mol %)
DPPB (10 mol %)
PhSiH3 (2.8 equiv)
MeCN/PhMe (1:1, 0.1 M)
60 °C, 30 h
NH2
CO2Me
85%

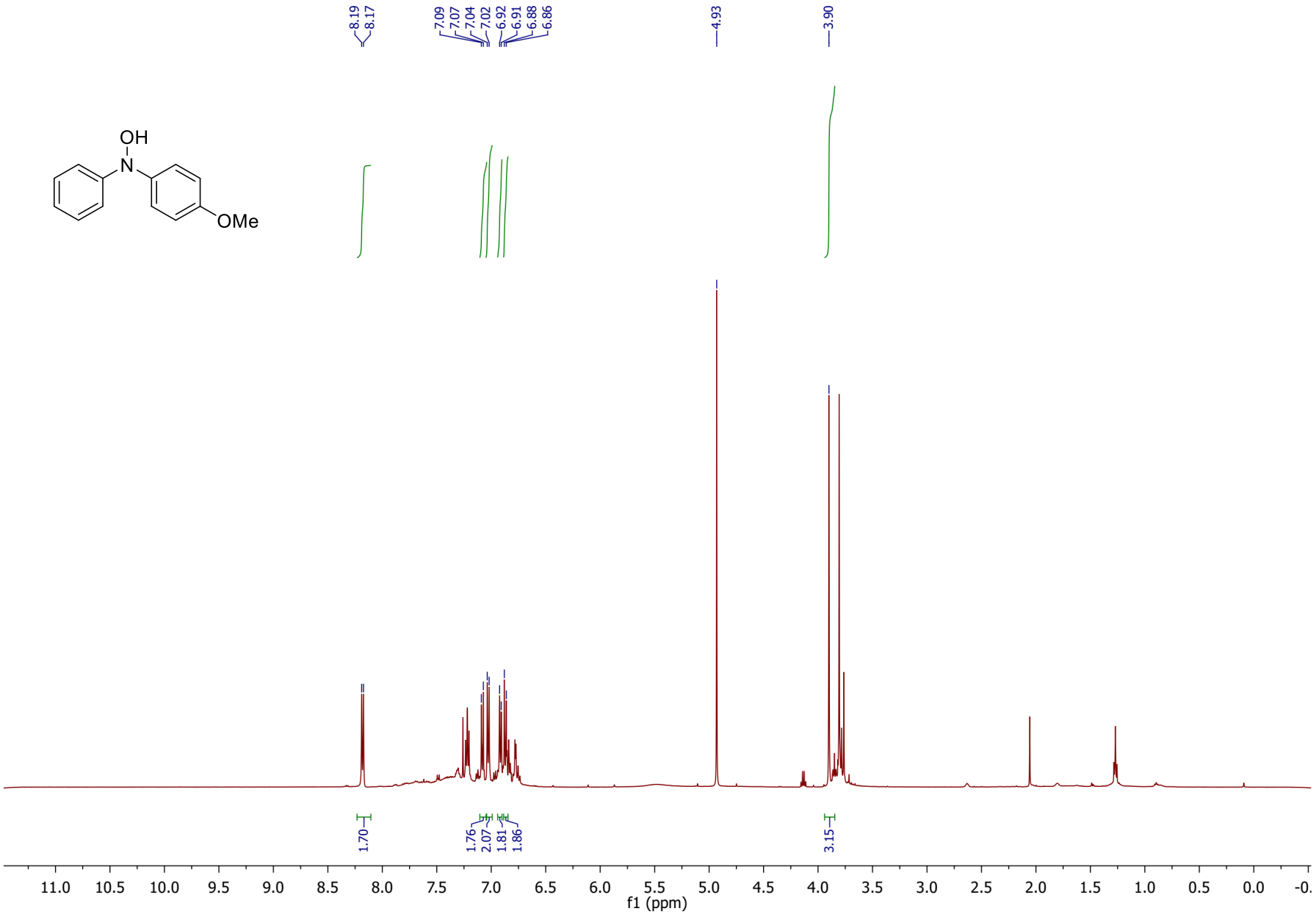
(s7)

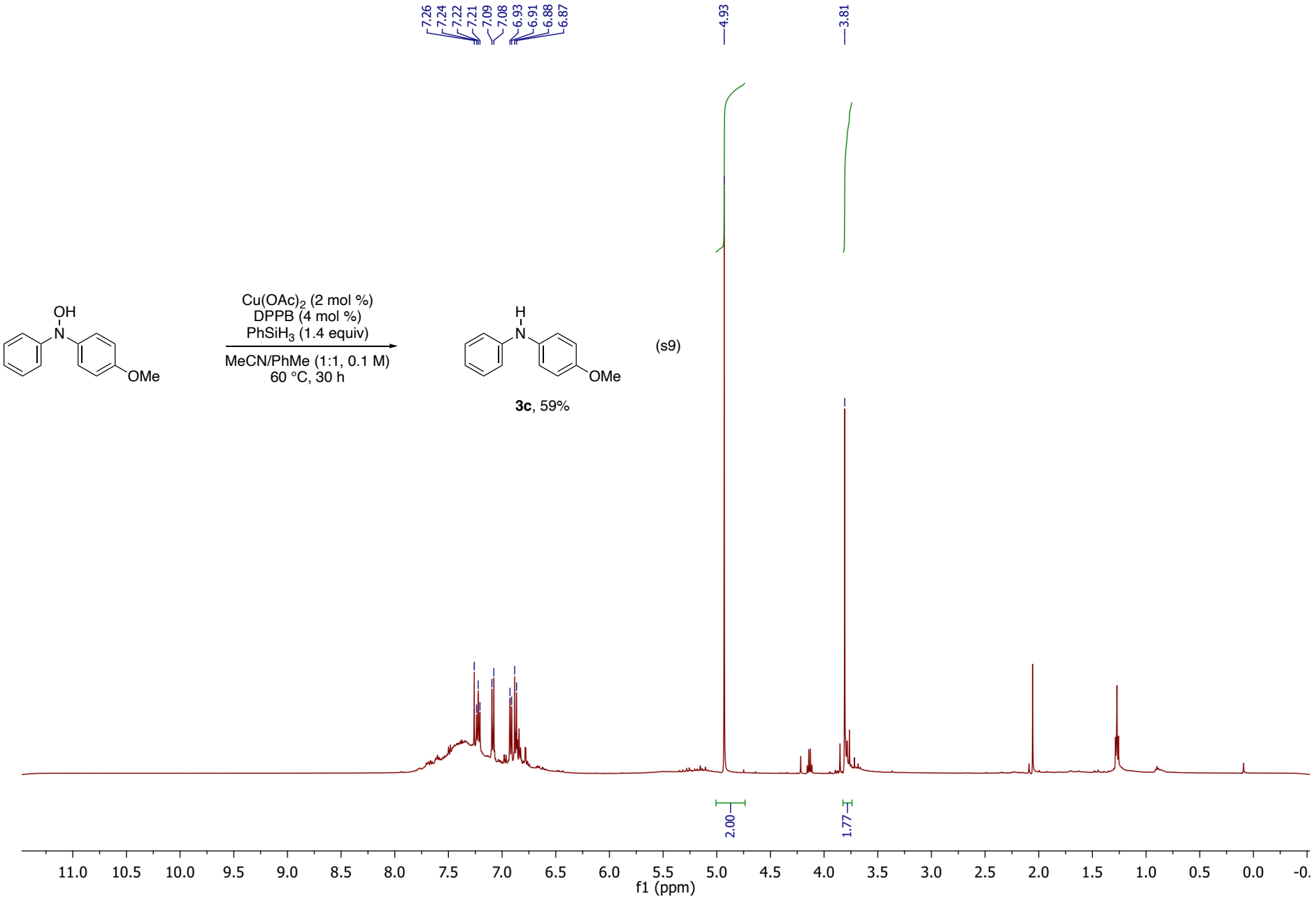

CH2Br2
aniline
ArNO2 (s.m.)
0.45
1.71
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.93
7.91
7.87
7.85
6.80
6.79
6.61
6.56
4.92
3.87
NO2
CO2Et
(1 equiv)
+
BF3K
OMe
(1.5 equiv)
Cu(OAc)2 (5 mol %)
DPPB (10 mol %)
PhSiH3 (2.8 equiv)
MeCN/PhMe (1:1, 0.1 M)
60 °C, 30 h
NH2
CO2Me
40%

(s8)


CH2Br2
only –OMe of aniline observed
product peak not observed
aniline
0.81
2.00
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)


8.19
8.17
7.09
7.07
7.04
7.02
6.92
6.91
6.88
6.86
4.93
3.90
OH
N
OMe
1.70
1.76
2.07
1.81
1.86
3.15
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)


7.26
7.24
7.22
7.21
7.09
7.08
6.93
6.91
6.88
6.87
4.93
3.81
OH
N
OMe
Cu(OAc)2 (2 mol %)
DPPB (4 mol %)
PhSiH3 (1.4 equiv)
MeCN/PhMe (1:1, 0.1 M)
60 °C, 30 h
H
N
OMe
3c, 59%
(s9)
2.00
1.77
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)