SUPPORTING INFORMATION

Iron-Catalyzed Direct Arylation Through an Aryl Radical Transfer Pathway

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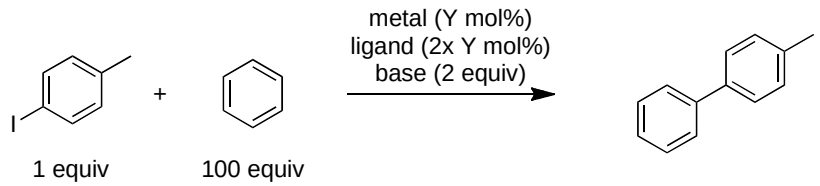
General Considerations: All reactions were run under an inert atmosphere (argon) with flame-dried glassware using standard techniques for manipulating air-sensitive compounds. Anhydrous solvents were obtained by filtration through drying columns (benzene) or by distillation over sodium and calcium hydride (*p*-xylene, pyridine).

Flash column chromatography was performed using 230-400 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) and/or aqueous potassium permanganate.

Nuclear magnetic resonance spectra were recorded either on 300 MHz or 400 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ = 7.27 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (77.36 ppm) as the internal standard. Preparative High Performance Liquid Chromatography was performed using reverse phase elution on a system equipped with simultaneous diode array UV detection. Data are reported as follows: (column type, eluent, flow rate: retention time (t_r)). Low resolution mass spectra were performed either on a GC/MS Agilent 6890 Series GC system equipped with an Agilent 5973 Network-G2578A Standard Turbo EI MSD and/or on an Agilent 1100 Series LC/MSD system equipped with an APCI mass detector with simultaneous diode array UV detection.

Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary.

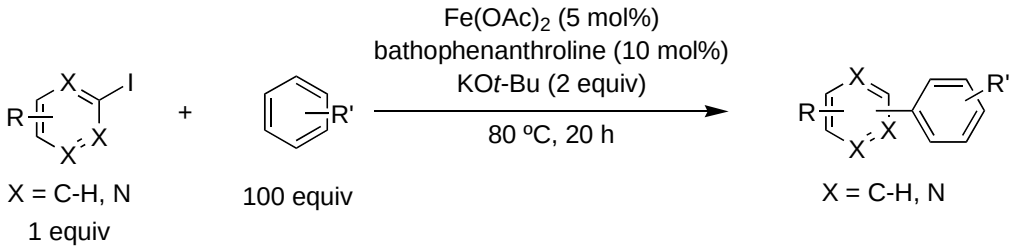
Table S-1. Selected optimization for the direct arylation of 4-iodotoluene with benzene.



entry	metal	ligand	catalyst loading (mol%)	base	temp. (°C)	yield (%)[a]
1	Fe(phthalocyanine)	none	8	KO*t*-Bu	125	37
2	$Fe(acac)_3$	bathophenanthroline	8	KO*t*-Bu	125	68
3	$FeCl_3$	bathophenanthroline	8	KO*t*-Bu	125	21
4	$Fe(OAc)_2$	bathophenanthroline	8	KO*t*-Bu	125	70
5	$Fe(OAc)_2$	1,10-phenanthroline	8	KO*t*-Bu	125	59
6	$Fe(OAc)_2$	bi-pyridine	8	KO*t*-Bu	125	35
7	$Fe(OAc)_2$	TMEDA	8	KO*t*-Bu	125	35
8	$Fe(OAc)_2$	DavePHOS	8	KO*t*-Bu	125	32
9	$Fe(OAc)_2$	P(*t*-Bu)$_3$	8	KO*t*-Bu	125	20
10	$Fe(OAc)_2$	No Ligand	8	KO*t*-Bu	125	22
11	$Fe(OAc)_2$	bathophenanthroline	8	No Base	125	2
12	$Fe(OAc)_2$	bathophenanthroline	8	NaOMe	125	12
13	$Fe(OAc)_2$	bathophenanthroline	8	KHMDS	125	75
14	$Fe(OAc)_2$	bathophenanthroline	0.5	KO*t*-Bu	125	76
15	$Fe(OAc)_2$	bathophenanthroline	5	KO*t*-Bu	125	87
16	$Fe(OAc)_2$	bathophenanthroline	5	KO*t*-Bu	80	91
17	No metal	No ligand	n/a	KO*t*-Bu	80	0
18	No metal	bathophenanthroline	10	KO*t*-Bu	80	0
19	$Fe(OAc)_2$	bathophenanthroline	5	KO*t*-Bu	60	69
20	$Fe(OAc)_2$	bathophenanthroline	5	KO*t*-Bu	40	45

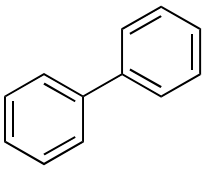
[a] Yields were measured by GC/MS using 1,3,5-trimethylbenzene as an internal standard.

Experimental Procedures and Characterization Data

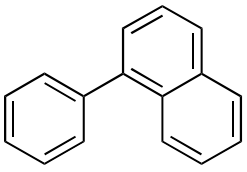


General procedure for the synthesis of biaryl products (3a-o, 5a-d).
In a drybox under argon atmosphere, to a flame dried microwave vial equipped with a stir bar, was added the $Fe(OAc)_2$ (0.025 mmol, 5 mol%), bathophenanthroline (0.05 mmol, 10 mol%), and crushed dry KO*t*-Bu (1.0 mmol, 2 equiv). The vial was then sealed with a septum. To a separate flame dried vial was added the aryl iodide (0.5 mmol, 1 equiv). The vial was subsequently sealed with a septum and purged with argon. The iodide was diluted in the corresponding dried arene (12.5 mmol, 25 equiv) and added to the reaction vessel via syringe. The vial and syringe were then rinsed with the arene (3 x 12.5 mmol, 25 equiv), bringing the total amount of arene added to 100 equiv. The reaction was stirred vigorously at room temperature for 20 min and then at 80 ºC for 20 h. Following cooling, 2 mL of CH_2Cl_2/hexanes (1:1) was added, and the solution was filtered though a silica pad. The pad was then rinsed with 15 mL of CH_2Cl_2/hexanes (1:1). The combined solution was concentrated and the crude mixture was purified via column chromatography to afford the biphenyl products **3** / **5**.

Compound details
All the products are known compounds and the CAS numbers are provided.



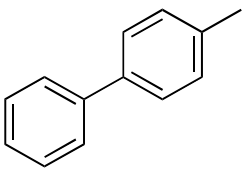
Biphenyl[1,2] (3a) [92-52-4]
The title compound **3a** was prepared according to the general procedure described above using iodobenzene **1a** with benzene, and purified by column chromatography (100% hexanes) as a white solid (75 mg, 89%). R_f = 0.37 (100% hexanes). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.50 (m, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.43-7.34 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 128.7, 126.9, 126.7; LRMS Calcd for $C_{12}H_{10}$ M^+: 154.08. Found: 154.



1-Phenylnaphthalene[3, 4, 5] [605-02-7] (3b)
The title compound **3b** was prepared according to the general procedure described above using 1-iodonapthalene **1b** with benzene, and purified by

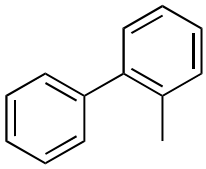
[1] Lafrance, M.; Fagnou, K. *J. Am. Chem. Soc*. **2006**, *128*, 16496.
[2] Proch, S.; Kempe, R. *Angew. Chem. Int. Ed.* **2007**, *46*, 3135; *Angew. Chem.* **2007**, *119*, 3196.
[3] Kuriyama, M.; Shimazawa, R.; Shirai, R. *Tetrahedron* **2007**, *63*, 9393.
[4] Stevens, P. D.; Fan, J.; Gardimalla, H. M. R.; Yen, M.; Gao, Y. *Org. Lett.* **2005**, *7*, 2085.
[5] Spivey, A. C.; Tseng, C.-C.; Hannah, J. P.; Gripton, C. J. G.; de Fraine, P.; Parr, N. J.; Scicinski, J. J. *Chem. Commun.* **2007**, 2926.

preparative HPLC (ZORBAX Eclipse XDB-C18, 50:50 MeOH:H_2O over 20 min at 20 mL/min, go to 90:10 MeOH:H_2O over 4 min at 30 mL/min *rt* = 26.50 min) as a colourless oil (61.7 mg, 60%). R_f = 0.31 (100% hexanes). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, *J* = 6.3 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.60-7.54 (m, 6H), 7.53-7.45 (m, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 141.2, 134.7, 132.5, 131.0, 129.2, 128.6, 128.1, 127.8, 127.0, 126.7, 126.3; LRMS Calcd for $C_{16}H_{12}$ M^+: 204.08. Found: 204.



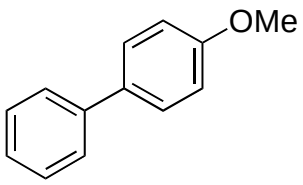
4-Methylbiphenyl[3, 4, 6, 7] [644-08-6] (3c)

The title compound **3c** was prepared according to the general procedure described above using 4-iodotoluene **1c** with benzene, and purified by column chromatography (100% hexanes) as a white solid (75.3 mg, 86%). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. R_f = 0.45 (100% hexanes). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.7 Hz, 2H), 7.59 (d, *J* = 8.3 Hz 2H), 7.51 (t, *J* = 7.9, 2H), 7.43-7.36 (m, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 138.7, 137.3, 129.8, 129.1, 127.3, 21.3; LRMS Calcd for $C_{13}H_{12}$ M^+: 168.09. Found: 168.



2-Methylbiphenyl[3, 4, 6] [643-58-3] (3d)

The title compound **3d** was prepared according to the general procedure described above using 2-iodotoluene **1e** with benzene, and purified by preparative HPLC (ZORBAX Eclipse XDB-C18, 50:50 MeOH: H_2O over 20 min at 20 mL/min, go to 90:10 MeOH:H_2O over 4 min at 30 mL/min *rt* = 25.60 min) as a colorless oil (69.8 mg, 80%). R_f = 0.41 (100% hexanes). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.7 Hz, 2H), 7.39-7.30 (m, 3H), 7.22-7.27 (m, 4H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.32, 142.26, 135.7, 130.7, 130.1, 129.6, 128.5, 127.6, 127.2, 126.1, 20.1; LRMS Calcd for $C_{13}H_{12}$ M^+: 168.09. Found: 168.



4-Methoxybiphenyl[3, 4, 6, 7] [613-37-6] (3e)

The title compound **3e** was prepared according to the general procedure described above using 4-iodoanisole **1f** with benzene, and purified by column chromatography (100% hexanes) as a white solid (89.2 mg, 93%). R_f = 0.14 (100% hexanes). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.6 Hz, 4H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 141.2, 134.1, 129.1, 128.5, 127.1, 127.0, 114.5, 55.7; LRMS Calcd for $C_{13}H_{12}O$ M^+: 184.09. Found: 184.

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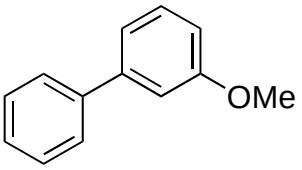
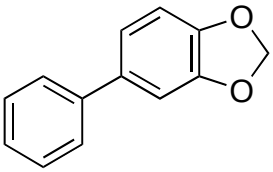
[6] Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2005**, *7*, 2229.

[7] Zhang, L.; Wu, J. *J. Am. Chem. Soc.* **2008**, *130*, 12250.



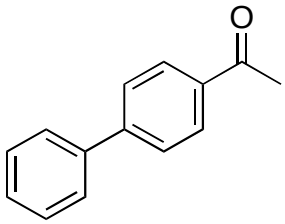
3-Methoxybiphenyl[1, 6] (3f) [2113-56-6]

The title compound **3f** was prepared according to the general procedure described above using 3-iodoanisole **3f** with benzene, and purified by column chromatography (100% hexanes) as a colorless oil (83.8 mg, 88%). R_f = 0.14 (100% hexanes). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.9 Hz, 2H), 7.40 (m, 2H), 7.25-7.15 (m, 2H), 6.94 (dd, J = 8.2, 2.5 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 143.1, 141.4, 130.0, 129.0, 127.7, 127.5, 120.0, 113.2, 113.8, 55.6; LRMS Calcd for $C_{13}H_{12}O$ M^+: 184.09. Found: 184.



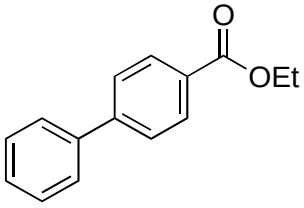
1-Phenyl-3,4-methylenedioxybenzene[8] [33954-03-9] (3g)

The title compound **3g** was prepared according to the general procedure described above using 1-iodo-3,4-methylenedioxybenzene **1h** with benzene, and purified by column chromatography (9:1 hexanes:Et_2O) as a cream colored solid (74.8 mg, 72%). R_f = 0.15 (100% hexanes). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 2H),7.44 (t, J = 7.7 Hz, 2H), 7.38-7.31 (m, 1H), 7.10 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 7.7 Hz, 1H), 6.02 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 148.0, 141.8, 136.5, 129.7, 127.79, 127.76, 121.5, 109.5, 108.6, 102.0; LRMS Calcd for $C_{13}H_{10}O_2$ M^+: 198.07. Found: 198.



4-Acetyl-biphenyl[9] [92-91-1] (3h)

The title compound **3h** was prepared according to the general procedure described above using 4'-iodoacetophenone **1i** with benzene, and purified by column chromatography (100% hexanes to 80:20 hexanes/Et_2O) as a cream colored solid (64.5 mg, 69%). R_f = 0.32 (4:1 hexanes/Et_2O). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.51-7.40 (m, 3H), 2.65 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9, 146.3, 140.3, 136.2, 129.3, 129.2, 128.5, 127.6, 127.5, 27.0; LRMS Calcd for $C_{14}H_{12}O$ M^+: 196.07. Found: 196.

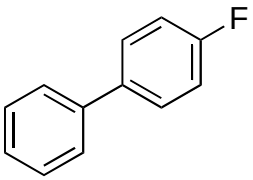


Ethyl 4-phenylbenzoate[10, 11, 12] [6301-56-0] (3i)

The title compound **3i** was prepared according to the general procedure described above using ethyl 4-iodobenzoate **1j** with benzene, and purified by column chromatography (9:1 hexanes/Et_2O) as yellow solid (47.6 mg, 40%). R_f = 0.34 (9:1 hexanes/Et_2O). The observed characterization data (^{1}H) was consistent with that previously reported in the literature. ^{1}H NMR

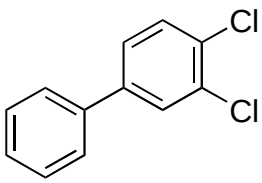
[8] So, C. M.; Lee, Lau, H. W.; C. P.; Kwong, F. Y. *Org. Lett.* **2009**, *11*, 371.
[9] Hajipour, A. R.; Mallakpour, S. E.; Baltork, I. M.; Adibi, H. *Syn. Commun.*, **2001**, *31*, 1625.
[10] Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2005**, *7*, 2229.
[11] Zhang, L.; Wu, J. *J. Am. Chem. Soc.* **2008**, *130*, 12250.
[12] Inamoto, K.; Kuroda, J.; Hiroya, K.; Noda, Y.; Watanabe, M.; Sakamoto, T. *Organometallics* **2006**, *25*, 3095.

(400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.3 Hz, 2H), 7.72-7.60 (m, 4H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.5 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.6 Hz 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 146.1, 140.5, 130.4, 129.5, 129.2, 128.4, 127.6, 127.3, 61.3, 14.7; LRMS Calcd for $C_{15}H_{14}O_2$ M^+: 226.1. Found: 226.



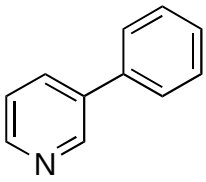
4-Fluorobiphenyl[13] [324-74-3] (3j)

The title compound **3j** was prepared according to the general procedure described above using 1-fluoro-4-iodobenzene **1k** with benzene, and purified by column chromatography (100% hexanes) as a white solid (81.8 mg, 86%). R_f = 0.42 (100% hexanes). The observed characterization data (^1H) was consistent with that previously reported in the literature. ^1H NMR (300 MHz, $CDCl_3$) δ 7.63-7.56 (m, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.40 (m, 1H), 7.18 (t, J = 8.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 161.1, 140.6, 137.7, 137.6, 129.1 (t, J = 8.0 Hz), 127.4 (d, J = 18.8 Hz), 115.9 (d, J = 22.2 Hz).



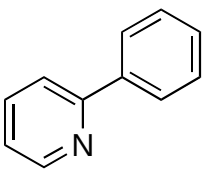
3,4-Dichlorobiphenyl [2974-92-7] (3k)

The title compound **3k** was prepared according to the general procedure described above using 3,4-dichloroiodobenzene **1l** with benzene, and purified by column chromatography (100% Hexanes), (59.6 mg, 53%). R_f = 0.53 (100% hexanes). The observed characterization data (^1H) was consistent with that previously reported in the literature. ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.60-7.38 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 139.1, 133.2, 131.7, 131.0, 129.32, 129.27, 128.4, 127.3, 126.7; LRMS Calcd for $C_{12}H_8Cl_2$ M^+: 223.1. Found: 223.



3-Phenylpyridine[3, 6, 14] [1008-88-4] (3l)

The title compound **3l** was prepared according to the general procedure described above using 3-iodopyridine **1m** with benzene, and purified by column chromatography (4:1 DCM/Et_2O) as yellow oil (68.8 mg, 85%). R_f = 0.20 (9:1 DCM/Et_2O). The observed characterization data (^1H) was consistent with that previously reported in the literature. ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.60 (s, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.51-7.45 (m, 2H), 7.44-7.33 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 148.7, 138.1, 136.9, 134.7, 129.4, 128.4, 127.5, 123.9; LRMS Calcd for $C_{11}H_9N$ M^+: 155.07. Found: 155.

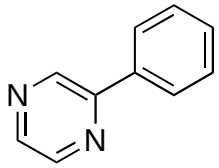


2-Phenylpyridine[10, 14] [1008-89-5] (3m)

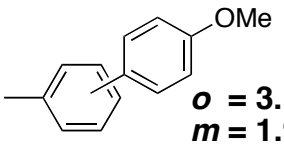
The title compound **3m** was prepared according to the general procedure described above using 2-iodopyridine **1n** with benzene, and purified by column chromatography (80:20 DCM/Et_2O) as colorless oil (75.4 mg, 85%). R_f = 0.50 (9:1 DCM/Et_2O). The observed characterization data (^1H) was consistent with that previously reported in the literature. ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (td, J = 4.9, 1.5 Hz 1H), 8.02 (dd, J = 7.2, 1.5 Hz 2H), 7.78-7.72 (m, 2H), 7.49-7.43 (m, 3H), 7.26-7.20 (m, 1H). ^{13}C NMR (75

[13] Lemo, J.; Heuze, K.; Astruc, D. *Org. Lett.*, **2005**, *7*, 2253.
[14] Núñez, A.; Sánchez, A.; Burgos, C.; A-Builla, J. *Tetrahedron* **2004**, *60*, 6217

MHz, $CDCl_3$) δ 158.3, 150.6, 140.3, 137.6, 129.9, 129.7, 127.8, 123.0, 121.5; LRMS Calcd for $C_{11}H_9N$ M^+: 155.07. Found: 155.

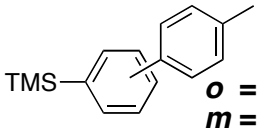


2-Phenylpyrazine [29460-97-7] (3n)
The title compound **3n** was prepared according to the general procedure described above using iodopyrazine **1o** with benzene, and purified by column chromatography (4:1 DCM/Et_2O) as a cream solid (59.0 mg, 79%). R_f = 0.34 (9:1 DCM/Et_2O). The observed characterization data (^1H) was consistent with that previously reported in the literature. ^1H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.65 (s, 1H), 8.52 (s, 1H), 8.04-8.01 (m, 2H), 7.56-7.45 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 144.5, 143.3, 142.6, 136.7, 130.3, 129.4, 127.3; LRMS Calcd for $C_{10}H_8N_2$ M^+: 156.07. Found: 156 (M+).



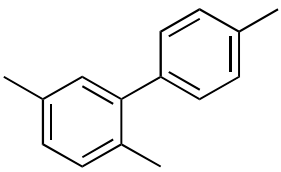
o **= 3.1**
m **= 1.9**
p **= 1.0**

Mixture of 4'-methoxy-2-methylbiphenyl, 4'-methoxy-3-methylbiphenyl, 4'-methoxy-2-methylbiphenyl The title compound **5a** was prepared according to the general procedure described above using 4-iodotoluene with toluene, and purified by column chromatography (5% ethyl ether/hexanes) as colorless oil (49.5 mg, 50%). R_f = 0.40 (5% ethyl ether/hexanes). HRMS Calcd for $C_{14}H_{14}O$ M^+: 198.10392. Found: 198.10394 (M+).



o **= 1.0**
m **= 1.4**
p **= 2.0**

Mixture of Trimethyl(4'-methylbiphenyl-4-yl)silane, Trimethyl(4'-methylbiphenyl-3-yl)silane, Trimethyl(4'-methylbiphenyl-2-yl)silane The title compound **5b** was prepared according to the general procedure described above using 4-iodotoluene **1c** with phenyltrimethylsilane, and purified by column chromatography (100% hexanes) as colorless oil (26.3 mg, 28%). R_f = 0.20 (100% hexanes). Trimethyl(4'-methylbiphenyl-4-yl)silane: trimethyl(4'-methylbiphenyl-3-yl)silane: trimethyl(4'-methylbiphenyl-2-yl)silane = 2.0: 1.4: 1.0, The ratio of the regioisomers was determined by 1H NMR.[15,16] HRMS Calcd for $C_{14}H_{14}O$ M^+: 240.13288. Found: 240.13299 (M+).



2,4',5-Trimethyl biphenyl[17] [2482-05-6] (5c)
The title compound **5c** was prepared according to the general procedure described above using 4-iodotoluene **1c** with *p*-xylene, and purified by column chromatography (100% hexanes) as colorless oil (76.3 mg, 81%). R_f = 0.48 (100% hexanes). The observed characterization data (^1H) was consistent with that previously reported in the literature. ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 4H), 7.18, (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H), 2.37 (s, 3H), 2.26 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 139.5, 136.6, 135.5, 132.6, 131.0, 130.6, 129.1, 128.1, 127.8, 126.7 21.5, 21.3, 20.4; LRMS Calcd for $C_{15}H_{16}$ M^+: 196.13. Found: 196 (M+).

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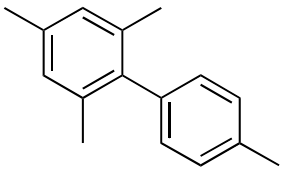
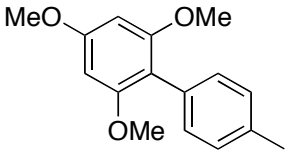
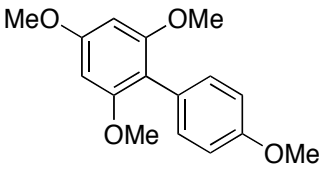
[15] Kaufmann, D. *Chem. Ber.* **1987**, *120*, 901. (*o*- and *p*- compounds)
[16] Ogawa. S.; Tajiri. Y.; Furukawa. N. Bull. Chem. Soc. Jnp. **1991**, *64*, 3182. (*m*- compound)
[17] Warner, K. F.; Bachrach, A.; Rehman, A.-u; Schnatter, W. F. K.; Mitra, A.; Shimanskas, C. *J. Chem. Research (S)*, **1998**, 814.



2,4,4',6-tetramethylbiphenyl The title compound **5d** was prepared according to the general procedure described above using 4-iodotoluene **1c** with mesitylene, and purified by column chromatography (100% pentane) as colorless oil (64.0 mg, 63%). R_f = 0.24 (100% pentane). The observed characterization data (^{1}H) was consistent with that previously reported in the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.7 Hz, 2H), 7.04, (d, J = 7.7 Hz, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 2.02 (s, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 138.3, 136.8, 136.5, 136.3, 129.5, 129.4, 128.4, 21.6, 21.4, 20.1; LRMS Calcd for $C_{16}H_{18}$ M^+: 210.14. Found: 210 (M+).



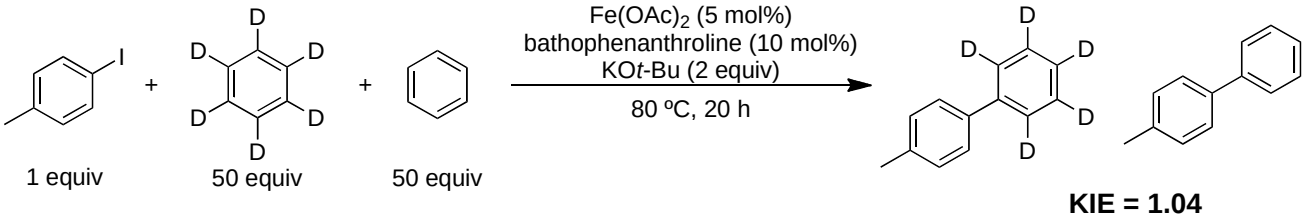
2,4,6-trimethoxy-4'-methylbiphenyl The title compound **5e** was prepared according to the general procedure described above using 4-iodotoluene **1c** with 1,3,5-trimethoxybenzene, and purified by column chromatography (10% ethyl ether/hexanes) as colorless oil (34.0 mg, 54%). R_f = 0.38 (10% ethyl ether/hexanes). The observed characterization data (^{1}H) was consistent with that previously reported in the literature.[19] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 4H), 6.24, (s, 2H), 3.88 (s, 3H), 3.74 (s, 6H), 2.39 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 158.7, 136.4, 131.35, 131.29, 112.7, 91.2, 56.2, 55.7, 21.7.; LRMS Calcd for $C_{16}H_{18}O_3$ M^+: 258.13. Found: 258 (M+).



2,4,4',6-tetramethoxybiphenyl The title compound **5f** was prepared according to the general procedure described above using 4-iodoanisole with 1,3,5-trimethoxybenzene, and purified by column chromatography (10% ethyl ether/hexanes) as colorless oil (28.3 mg, 54%). R_f = 0.28 (10% ethyl ether/hexanes). The observed characterization data (^{1}H) was consistent with that previously reported in the literature.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.9 Hz, 2H), 7.26, (d, J = 8.9 Hz, 2H), 6.24 (s, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 3.74 (s, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 158.7, 132.5, 126.5, 113.6, 112.3, 91.2, 56.2, 55.7, 55.4. LRMS Calcd for $C_{16}H_{18}O_4$ M^+: 274.12. Found: 274 (M+).

[18] Limmert, M. E.; Roy, A. H; Hartwig, J. F. *J. Org. Chem.* **2005**, *70*, 9364.
[19] Ban, I.; Sudo, T.; Taniguchi, T.; Itami, K. *Org. Lett.* **2008**, *10*, 3607.
[20] Becht, J.-M.; Catala, C.; Le Drian, C.; Wagner, A. *Org. Lett.*, **2007**, *7*, 1781.

Kinetic Isotope Experiments[21]



KIE = 1.04

KIE study using benzene as the reagent. The reaction was performed with a modification of the general procedure using a 1:1 mixture of benzene and benzene-*d*6 (50 mmol each). The crude mixture was purified via column chromatography to afford the biphenyl product as per **3c**. The kinetic isotope was determined through integration of the proton at the C2 position of the benzene ring and the d1 of the ^{1}H NMR pulse sequence was set at 10 s to ensure maximum relaxation.[22] The protons of the C2 of the tolyl ring were chosen as calibration. The spectrum can be observed on page S19.

Radical Experiments

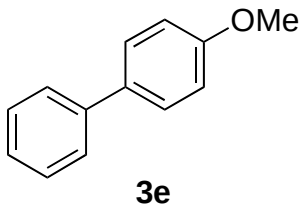
Investigation of radical scavenger effect. The experiment was performed as per the general procedure using 4-iodotoluene (1 mmol) and 2, 2, 6, 6-tetramethyl-1-piperridinyloxy (free radical, TEMPO, 1 mmol) or 2,6-Di-tert-butyl-α-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-p-tolyloxy (free radical, galvinoxyl, 1 mmol) and benzene (100 mmol). These reagents completely inhibited the reaction, and we therefore considered that there was radical species participated in the reaction.

Investigation of role the iron. The experiment was performed as per the general procedure using 4-iodotoluene (1 mmol) and AIBN (0.2 mmol) and benzene (100 mmol). The yield was affected by having AIBN in place of the iron-catalyst. We therefore considered that the iron in conjunction with the ligand are playing the important role of helping the radical initiation in the reaction as well as creating an adduct which cannot by itself auto-propagate or auto-terminate.

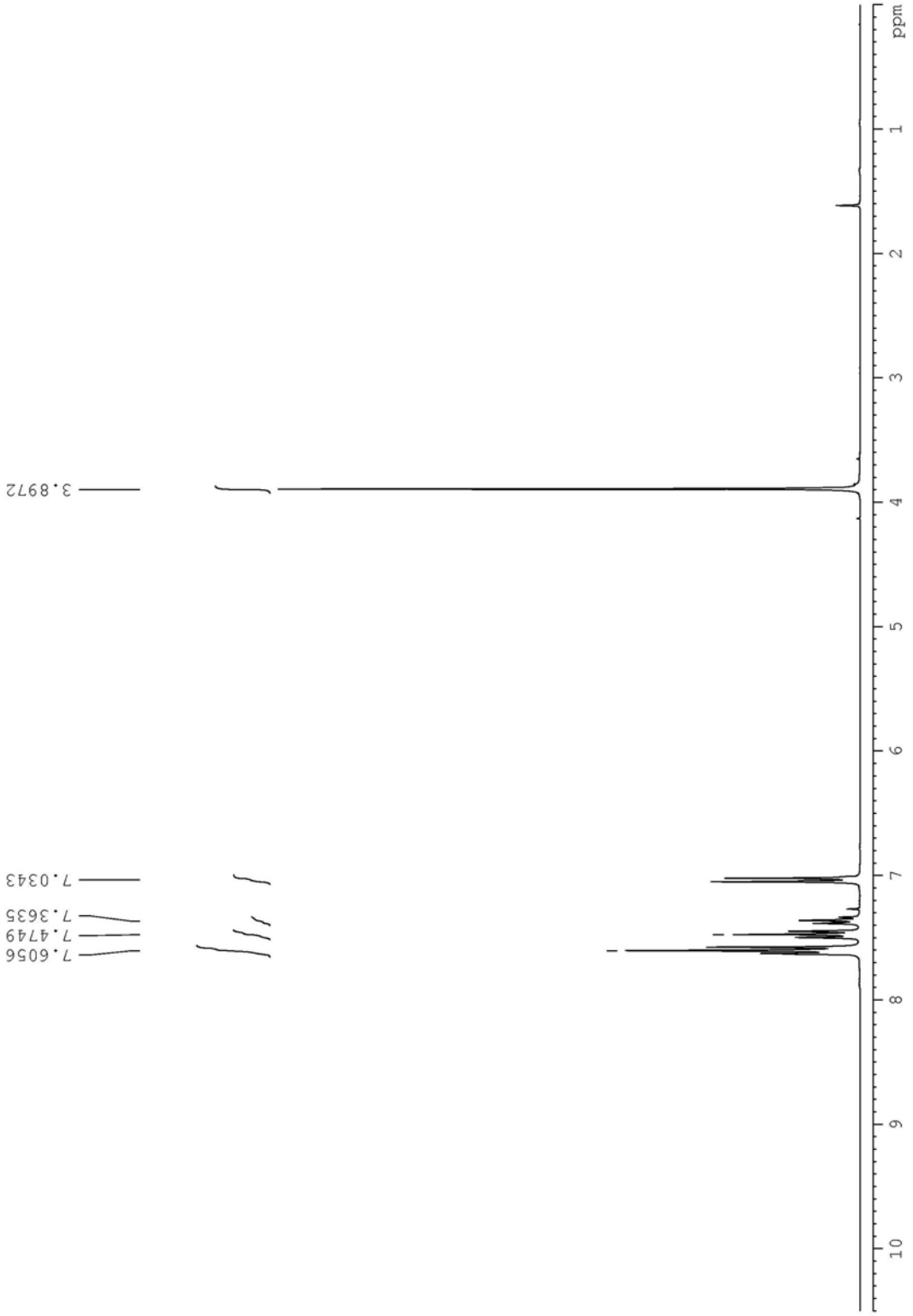
[21] For similar study see: Campeau, L. C.; Rousseaux, S.; Fagnou, K., *J. Am. Chem. Soc.* **2005,** *127*, 18020-18021.

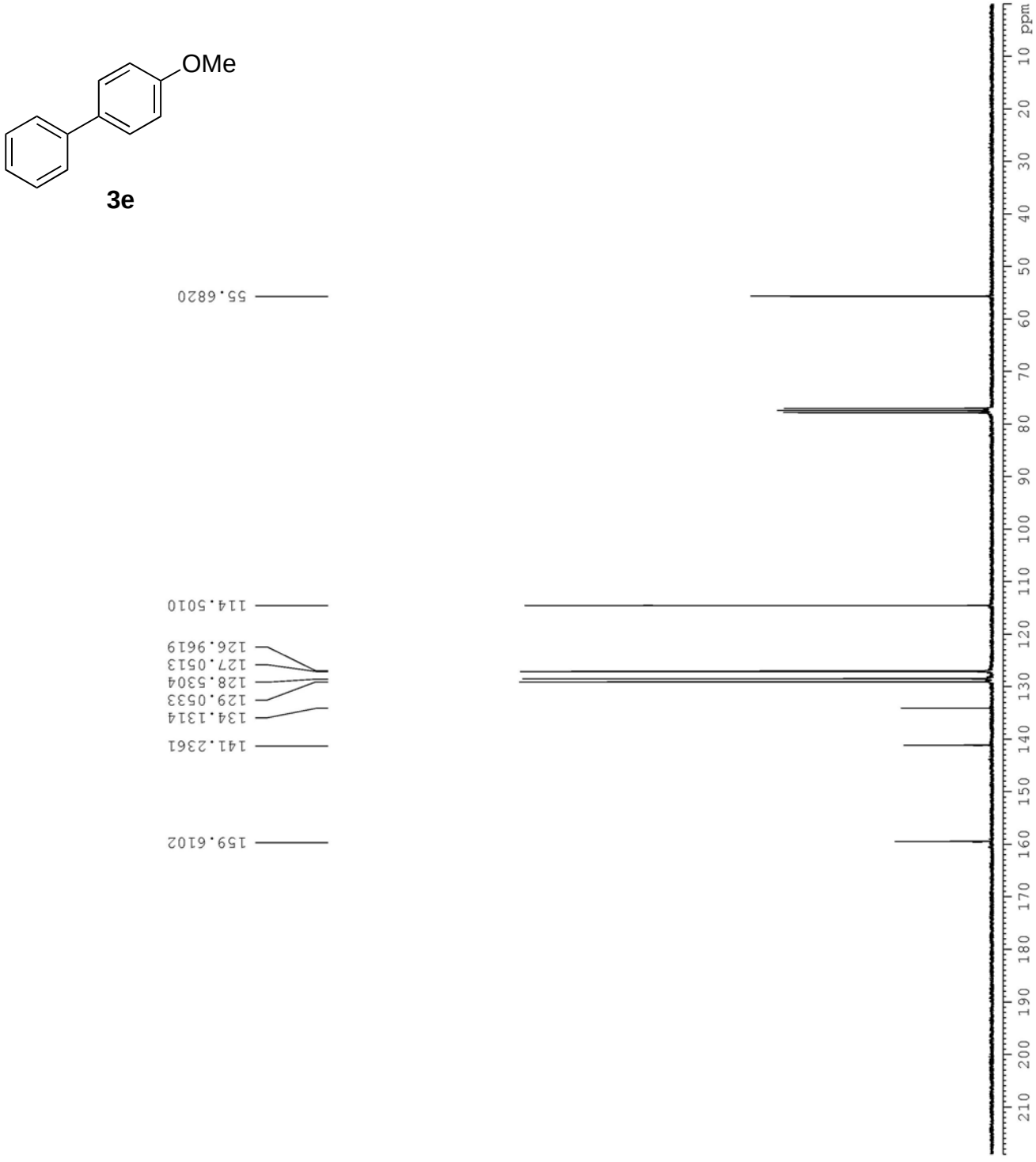
[22] KIE determined as follows: 1.02/0.98 = 1.04.

^{1}H and ^{13}C NMR spectra of selected compounds



3e




OMe
3e
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127.0513
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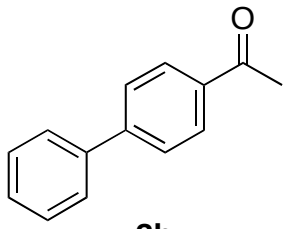
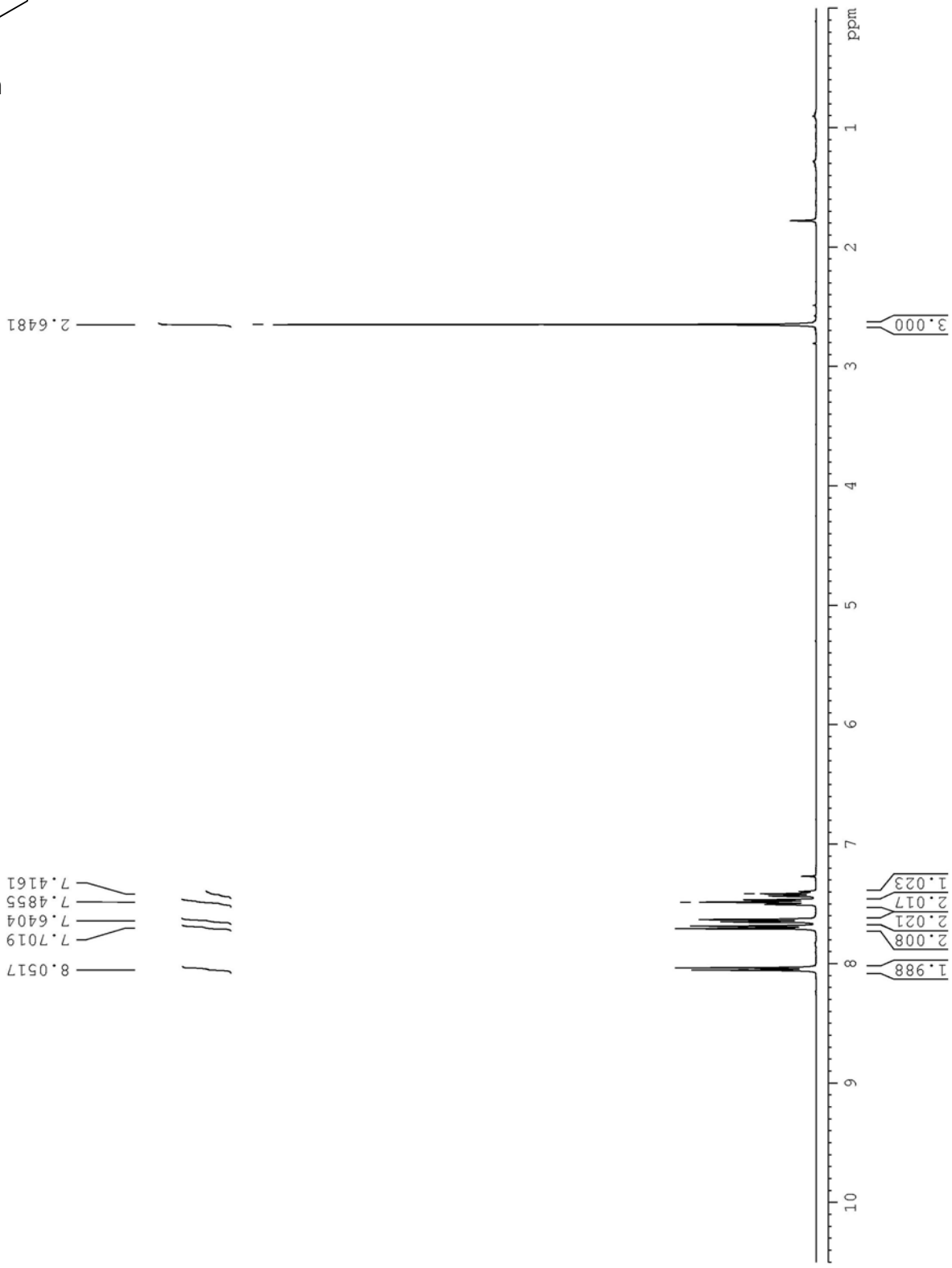
134.1314
141.2361
159.6102
ppm


O

3h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4
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6
7
8
9
10
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1.988
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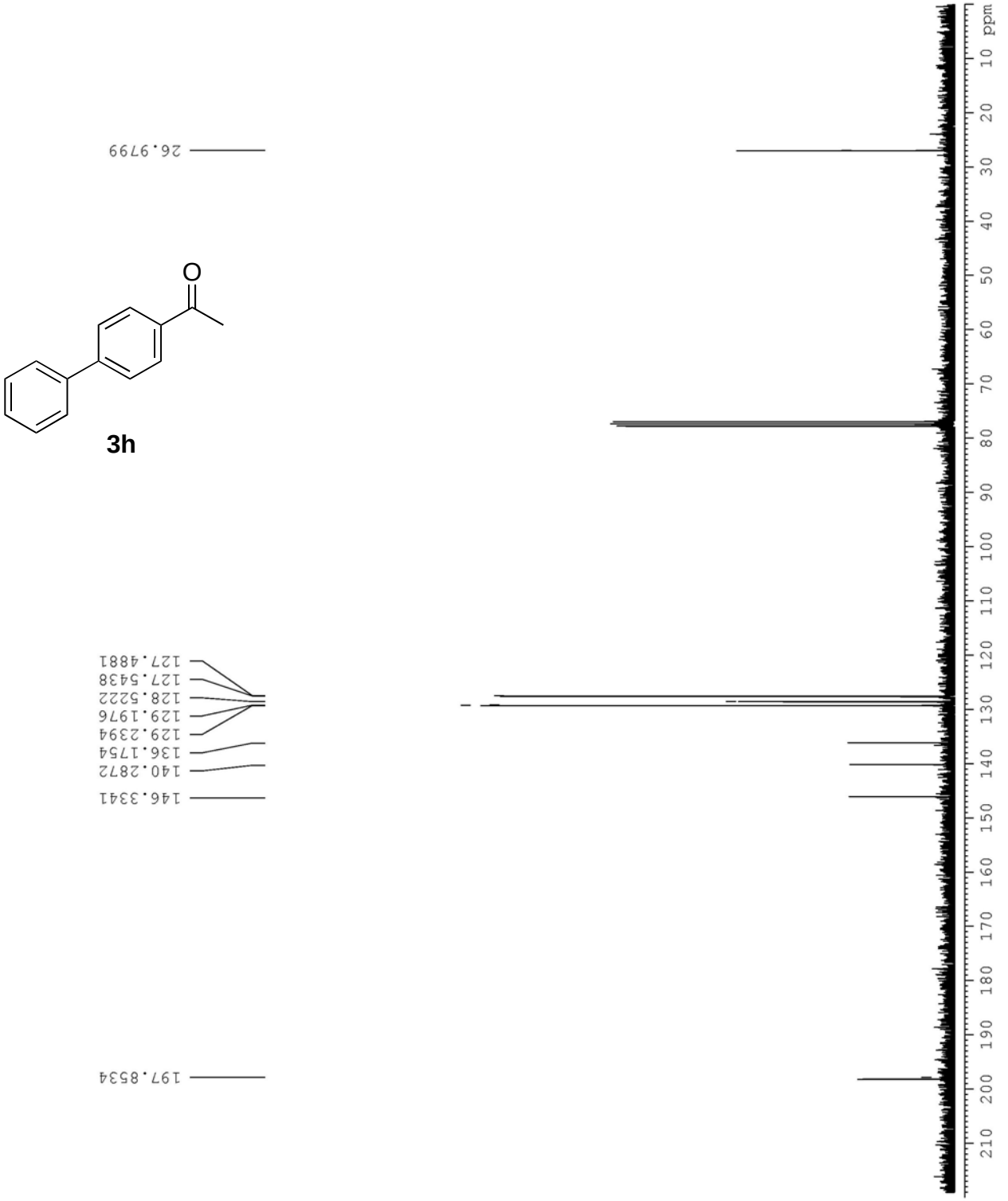
2.021
2.017
1.023


O
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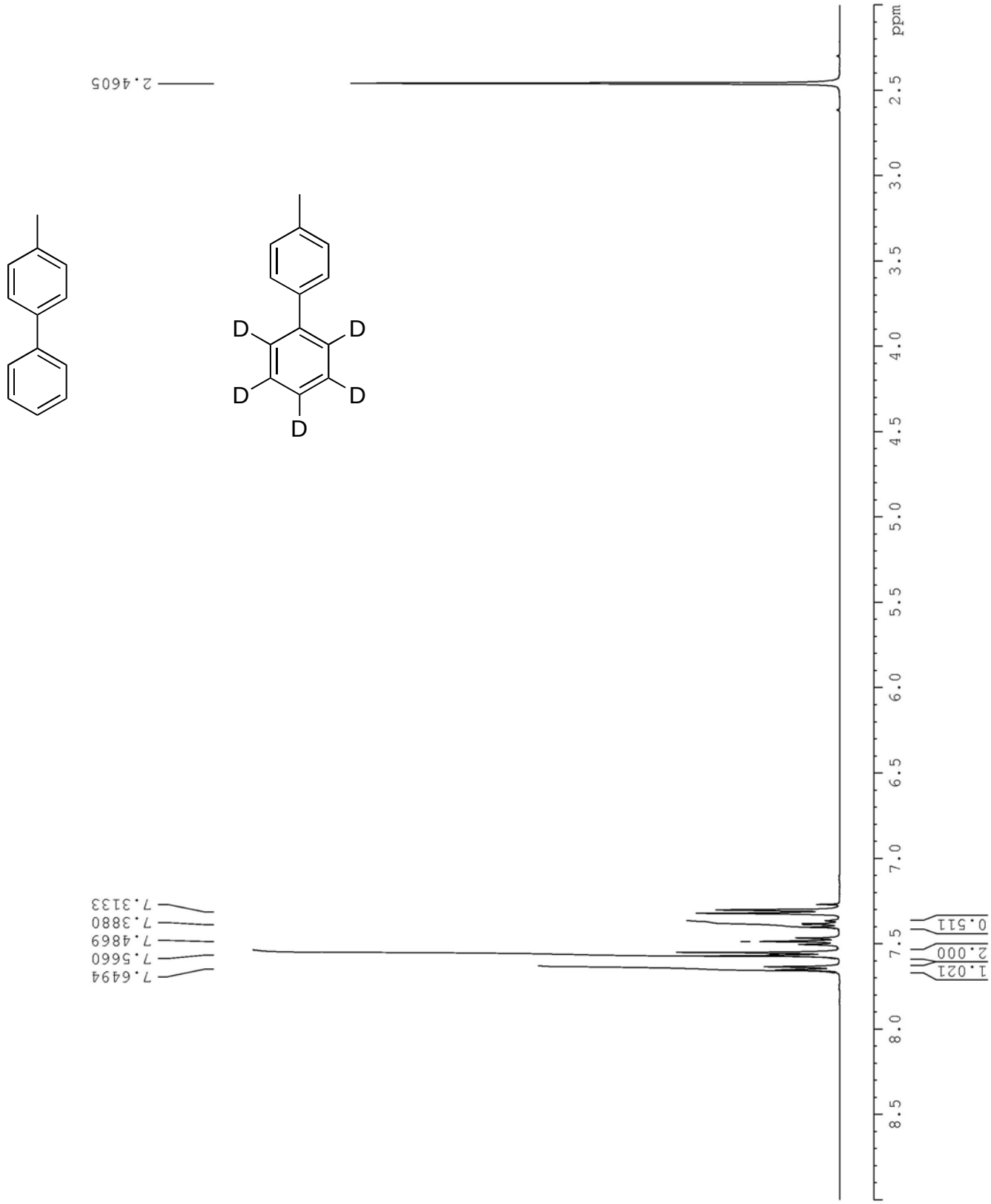
ppm

3h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ppm
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3.0
3.5
4.0
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5.0
5.5
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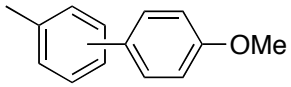
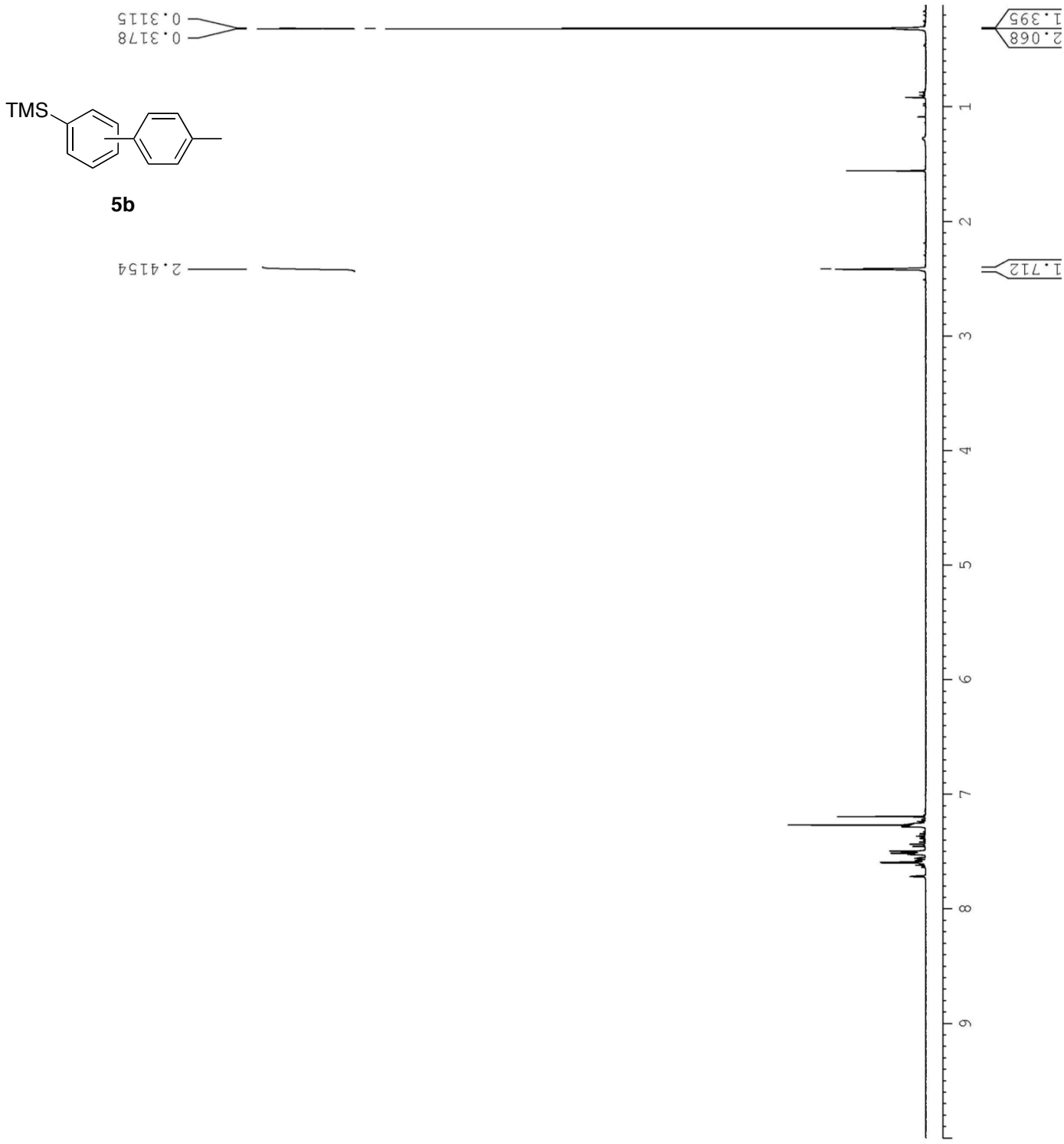
7.0
7.5
8.0
8.5
D
D
D
D
D



5a



5b