Supporting information

α-Diimine-mediated C-H functionalization of arenes for aryl-aryl cross-coupling reactions

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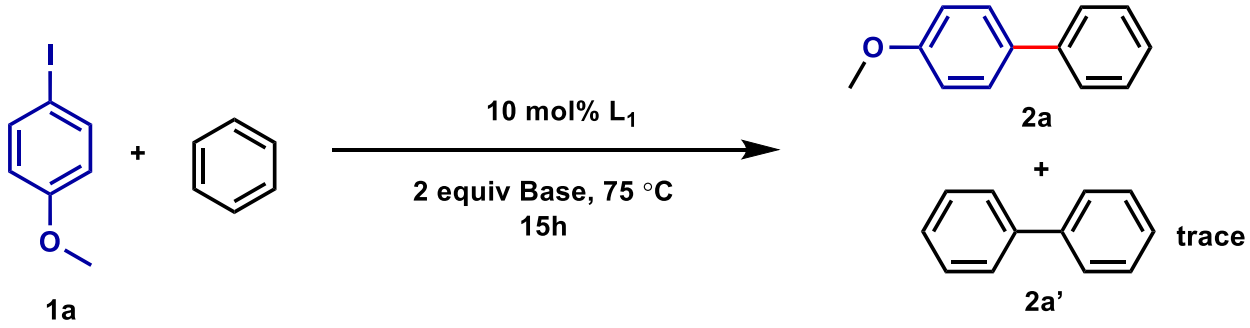
Contents

1. General Consideration

All reagents were purchased from commercial vendors and were used without further purification unless otherwise noted. Ar-BIAN (**L_1-L_8**) were synthesized according to the reported procedure.[1] All preparations of samples were performed under an inert atmosphere (Argon) using Schlenk and glovebox techniques unless otherwise noted. ^{1}H and ^{13}C NMR were recorded on an Agilent MR-DD2 400 MHz NMR spectrometer at 300K. ^{1}H NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 7.26 ppm and CD_3OD, δ 3.31 ppm), and ^{13}C NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 77.16 ppm and CD_3OD, δ 49.15 ppm). Data for ^{1}H NMR are recorded as follows: the chemical shifts are reported in (δ, ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet), and coupling constants in Hz as absolute values. GC−MS data were acquired using Thermo Scientific ISQ Single Quadrupole system. ICP-MS analysis was performed on an Agilent 7500ce while X-ray crystallography was recorded on an XtaLab Synergy by Rigaku Oxford Diffraction.

2. Table S1: Reaction condition screenings and base optimizations



Entry	Base	Conversion (%)[a]
1	KO*t*Bu	>99%
2	NaO*t*Bu	<1%
3	$Mg(OtBu)_2$	<1%
4	$Be(OtBu)_2$	<1%
5	K_2CO_3	<1%
6	$NaHBEt_3$	<1%
7	NaH	<1%

[a]Conversion determined by GC-MS

3. General procedure for C_{Ar}-C_{Ar} formation

An oven dried 20 mL scintillation vial was charged with ^{dm}BIAN (19.4 mg, 0.05 mmol), anhydrous benzene (2 mL), and a stir bar. A bright orange homogenous solution was obtained. Aryl halide (1.0 mmol) and KO*t*Bu (168.3 mg, 1.5 mmol) were then added to the reaction mixture. The scintillation vial was sealed and then placed on a preheated oil bath at 75 ^{o}C for 15 hrs. The reaction was quenched by exposing the reaction mixture to air, then the solvent was then reduced under *vacuo*. The crude products were purified by flash column chromatography using hexanes/ ethyl acetate mixture (95/5) as eluent to afford the desired products.

4. Spectral data for products

4-Methoxybiphenyl (2a)[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.44 (m, 4H), 7.40-7.35 (t, J = 7.6, 2H), 7.32-7.19 (m, 3H) 2.34 (s, 3H); 13C NMR (100 MHz, $CDCl_3$): δ = 159.3, 141.0, 133.9, 132.2, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5.

2-methylbiphenyl (2b)[2]
^{1}H NMR (400 MHz, CD_3OD) δ 7.43-7.20 (m, 9H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 143.4, 143.2, 136.2, 131.2, 130.6, 130.1, 129.1, 128.3, 127.8, 126.8, 20.6.

3-Methylbiphenyl (2c)[2]
^{1}H NMR (400 MHz, CD_3OD) δ 7.58-7.54 (m, 2H), 7.43-7.27 (m, 6H), 7.15 (d, J = 7.5, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 142.6, 142.4.2, 139.4, 129.7, 129.7, 128.9, 128.6, 128.2, 127.9, 125.1, 21.6.

4-Methylbiphenyl (2d)[3]
^{1}H NMR (400 MHz, CD_3OD): δ = 7.57-7.44 (m, 4H), 7.40-7.35 (t, J = 7.6, 2H), 7.32-7.19 (m, 3H) 2.34 (s, 3H); 13C NMR (100 MHz, CD_3OD): δ = 142.3, 139.5, 138.0, 130.4, 129.8, 127.9, 127.7, 127.7, 21.1.

3,5-Dimethylbiphenyl (2e)[2]
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59-7.57 (m, 2H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 1H), 7.22 (s, 2H), 7.01 (s, 1H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 141.4, 138.4, 129.0, 128.7, 127.3, 127.2, 125.3, 21.6.

2-phenylpyridine (2f)[4]
^{1}H NMR (400 MHz, CD_3OD) δ 8.56 (d, 1H, J = 3.68 Hz), 7.88 (d, 2H, J = 5.8 Hz), 7.83 (dt, 1H, J = 1.2, 6.1 Hz), 7.80-7.74 (m, 1H), 7.46-7.42 (m, 1H), 7.41-7.37 (m, 1H), 7.31 (dt, 1H, J = 1.1, 4.8 Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 158.6, 150.1, 140.2, 138.8, 130.1, 129.7, 127.9, 123.7, 122.4.

3-phenylpyridine (2g)[4]
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86-8.85 (m, 1H), 8.59 (dd, J = 4.8, 1.2 Hz, 1H), 7.87 (dt, J = 8.0, 1.86 Hz, 1H), 7.60-7.56 (m, 2H), 7.51-7.45 (m, 2H), 7.43-7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 148.3, 137.8, 134.4, 129.1, 128.1, 127.2, 126.7, 123.6.

4-phenylpyridine (2h)[4]
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.7 (d, J = 5.08 Hz, 2H), 7.64-7.66 (m, 2H), 7.43-7.52 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.5, 138.3, 129.2, 129.2, 127.1, 121.8.

[1,1'-Biphenyl]-4-carbonitrile (2i)[3]
^{1}H NMR (400 MHz, CD_3OD) δ 7.72-7.66 (m, 4H), 7.56 (d, J = 7.3 Hz, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 146.7, 139.9, 133.7, 130.1, 128.7, 128.0, 127.9, 119.8, 111.3.

4-aminobiphenyl (2j)[3]
^{1}H NMR (400 MHz, CD_3OD): δ 7.49 (d, J = 7.52, 2H), 7.44-7.36 (m, 4H), 7.29-7.23 (m, 1H), 6.8 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ 146.8, 141.2, 131.1, 130.9, 128.3, 127.2, 125.7, 115.5.

1-Phenyladamantane (2k)[5]
^{1}H NMR (400 MHz, CD_3OD): δ 7.35 -7.31 (m, 2H), 7.26 (t, J = 15.1, 2H), 7.15 (t, J = 7.2, 1H), 2.05 - 2.10 (m, 3H), 1.87 - 1.89 (m, 6H), 1.78 - 1.81 (m, 6H); ^{13}C NMR (100 MHz, CD_3OD,): δ 151.0, 127.7, 125.1, 124.3, 49.4, 43.0, 36.5, 29.0.

1-Phenyldecane (2l)[6]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.59-7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 128.5, 128.3, 125.6, 36.1, 33.9, 31.7, 29.8, 29.7, 29.7, 29.6, 29.5, 22.6, 14.1.

2-Phenylthiophene (2m)[4]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 2H), 7.48 – 7.40 (m, 2H), 7.40 – 7.31 (m, 3H), 7.11 – 7.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 134.6, 129.7, 129.0, 127.6, 125.7, 124.1, 123.2.

4-Fluorobiphenyl (4a)[3]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 4H), 7.438 (t, 2H, J = 15 Hz), 7.37-7.32 (m, 1H), 7.13 (t, 2H, J = 17 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, J = 245.1 Hz), 140.2, 137.3 (d, J = 3.3 Hz), 128.8, 128.7 (d, J = 7.9 Hz), 127.2, 127.0, 115.6 (d, J = 21.4).

4-Chlorobiphenyl (4b)[3]
^{1} H NMR (400 MHz, $CDCl_3$): δ 7.62−7.49 (m, 4H), 7.48−7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 139.8, 133.5, 129.0, 128.5, 127.7, 127.1.

4-Iodobiphenyl (4c)[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.75 (m, 2H), 7.58-7.53 (m, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.30-7.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 140.2, 138.0, 129.2, 129.0, 127.8, 127.0, 93.2.

***p*-Terphenyl (5)**[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.63 (m, 8H), 7.50-7.43 (m, 4H), 7.39-7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 140.3, 129.0, 127.7, 127.5, 127.2.

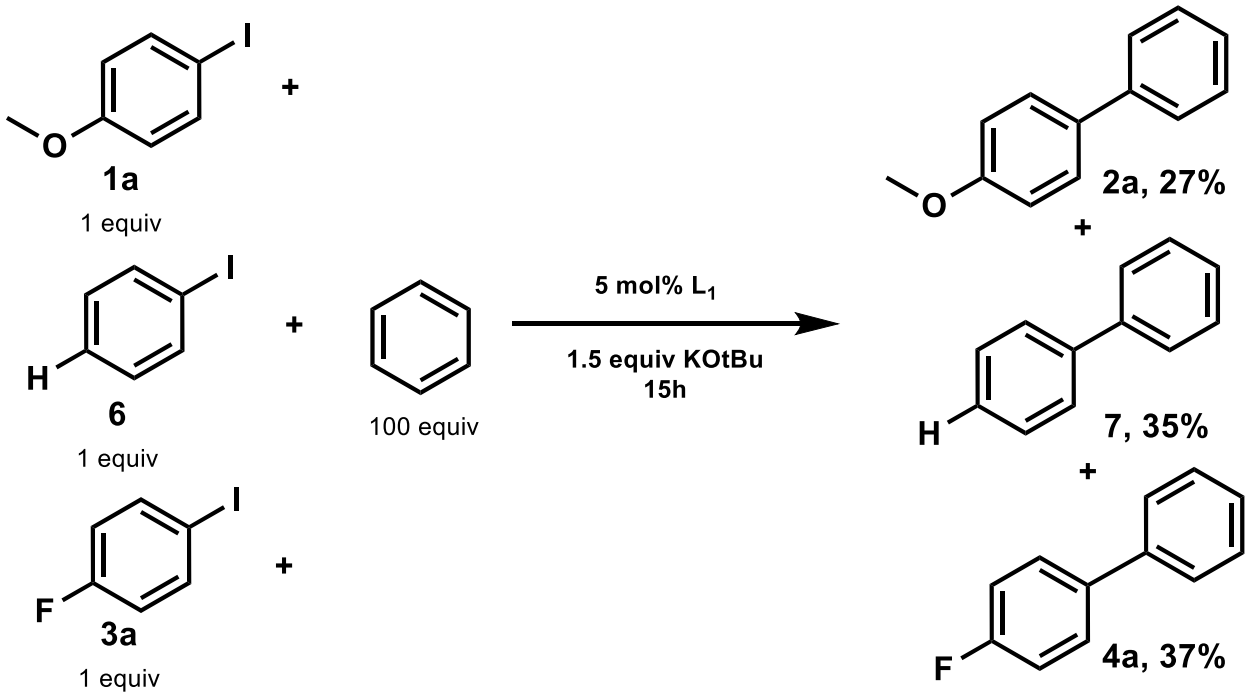
1-(4-methylphenyl)-naphthalene (9a)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (t, J = 8.2 Hz, 2H), 7.85 (d, J = 8.2 Hz, 1H), 7.54-7.37 (m, 6H), 7.31 (d, J = 7.6 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 137.9, 137.1, 133.9, 131.8, 130.1, 129.1, 128.4, 127.6, 127.0, 126.2, 126.1, 125.8, 125.6, 21.4.

1-(4-methoxyphenyl)-naphthalene (9b)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.83 (m, 3H), 7.55-7.41 (m, 6H), 7.05 (d, J = 6.6 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 140.0, 133.9, 133.2, 131.9, 131.2, 128.4, 127.5, 127.0, 1276.2, 126.1, 125.8, 125.5, 113.9, 55.5.

5. Qualitative competition study



Scheme S1: Based on GC-MS analysis.

6. ICP-MS analysis on the contents (in ppm) of transition metals (Zn, Ru, Rh, and Pd) in ^{dm}BIAN

A Curve Data		Values in ppg (ng/mL)	Liquid	Digestion	66 -> 66 Zn [He]	101 -> 101 Ru [He]	103 -> 103 Rh [He]	105 -> 105 Pd [He]
Data File	Sample Name	Comment	Dilution	Factors	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]
RA.d	Rinse	Kotono Babaguchi/Michael Findlater PI - UC Merced	1	NA	0.39243	-0.00007	0.00000	-0.00027
CB1.d	Center Blank 1	9/30/22 He Mode, ppb, 4% (conc.) HCl/1% (conc.) HNO3; Zn, Pd, Ru, and Rh	1	NA	-0.03031	-0.00012	0.00002	0.00002
CB2.d	Center Blank 2	Microwave Digested Sample (0.8mL HCl + 0.2mL HNO3, FV = 20.0mL with MQ	1	NA	-0.02541	-0.00006	0.00001	-0.00012
CB3.d	Center Blank 3	IS: Sc, In, Ce, Tm, and Bi @ 750ppb, Inorg Vent	1	NA	-0.75296	0.00011	-0.00002	0.00047
A1A.d	Standard Blank 1		1	NA	0.43492	0.00010	0.00003	0.00002
A1B.d	Standard Blank 2		1	NA	-0.04654	-0.00006	0.00000	-0.00006
A2A.d	0.01	CMS-2 and Zn - Inorg. Vent.	1	NA	1.97276	0.01054	0.00974	0.01030
A3A.d	0.05		1	NA	6.04783	0.05508	0.05123	0.05229
A4A.d	0.1		1	NA	10.78899	0.10120	0.10132	0.09943
A5A.d	0.5		1	NA	50.42593	0.50804	0.49784	0.50084
A6A.d	1		1	NA	99.96588	1.02392	1.00017	0.99648
A7A.d	5		1	NA	495.72575	4.98411	4.98980	5.00432
A8A.d	10		1	NA	964.73445	10.12556	9.98888	10.04959
RB.d	Rinse		1	NA	-0.29725	0.00017	0.00004	0.00156
RC.d	Rinse		1	NA	-0.39783	0.00000	0.00008	0.00114
RD.d	Rinse		1	NA	-0.43040	-0.00012	0.00003	0.00044
ME3ICV1.d	ME3andICV	Independent Source: 1ppb ME3 - SPEX; 100ppb ICV - Inorg. Vent.	1	NA	93.70174	0.99677	0.98704	0.98217
%Recovery					93.70	99.68	98.70	98.22
RE.d	Rinse		1	NA	-0.33264	-0.00006	0.00018	0.00009
Q1A.d	Q1A	0.1ppb CMS-2 and 10ppb Zn - Inorg. Vent.	1	NA	10.37983	0.09895	0.09699	0.10104
%Recovery					103.80	98.95	96.99	101.04
Q1B.d	Q1B	0.5ppb CMS-2 and 50ppb Zn - Inorg. Vent.	1	NA	49.01677	0.49586	0.48667	0.49751
%Recovery					98.03	99.17	97.33	99.50
Q1C.d	Q1C	1ppb CMS-2 and 100ppb Zn - Inorg. Vent.	1	NA	97.08056	0.97585	0.99052	0.98633
%Recovery					97.08	97.59	99.05	98.63
R1.d	Rinse		1	NA	-0.52869	0.00005	0.00008	-0.00005
MB.d	MB	Method Blank, 100uL MQW, FV = 20.0mL	1	1.3333	3.51674	-0.00007	0.00003	-0.00014
1.d	1	15.87mg 2,6-Me BIAN, FV = 20.0mL	10	1.2602	0.62163	0.00021	0.00002	0.35626
1B.d	1	15.87mg 2,6-Me BIAN, FV = 20.0mL	1	1.2602	13.34098	0.00219	0.00014	3.60232
LCS1.d	LCS1	LCS1, 100uL 100ppb CMS-2 and 10ppm Zn - Inorg. Vent., FV = 20.0mL	1	1.3333	55.23404	0.49601	0.49107	0.49508
%Recovery					110.47	99.20	98.21	99.02
LCS2.d	LCS2	LCS2, 100uL 1ppm CMS-2 and 100ppm Zn - Inorg. Vent., FV = 20.0mL	1	1.3333	526.09162	4.85007	4.84994	4.89385
%Recovery					105.22	97.00	97.00	97.88
Q2A.d	Q2A	0.1ppb CMS-2 and 10ppb Zn - Inorg. Vent.	1	NA	10.15146	0.09804	0.09711	0.09931
%Recovery					101.51	98.04	97.11	99.31
Q2B.d	Q2B	0.5ppb CMS-2 and 50ppb Zn - Inorg. Vent.	1	NA	48.72947	0.48531	0.48320	0.48211
%Recovery					97.46	97.06	96.64	96.42
Q2C.d	Q2C	1ppb CMS-2 and 100ppb Zn - Inorg. Vent.	1	NA	99.14757	0.99685	1.00492	0.98913
%Recovery					99.15	99.69	100.49	98.91
R2.d	Rinse		1	NA	-0.65610	-0.00006	0.00000	0.00019

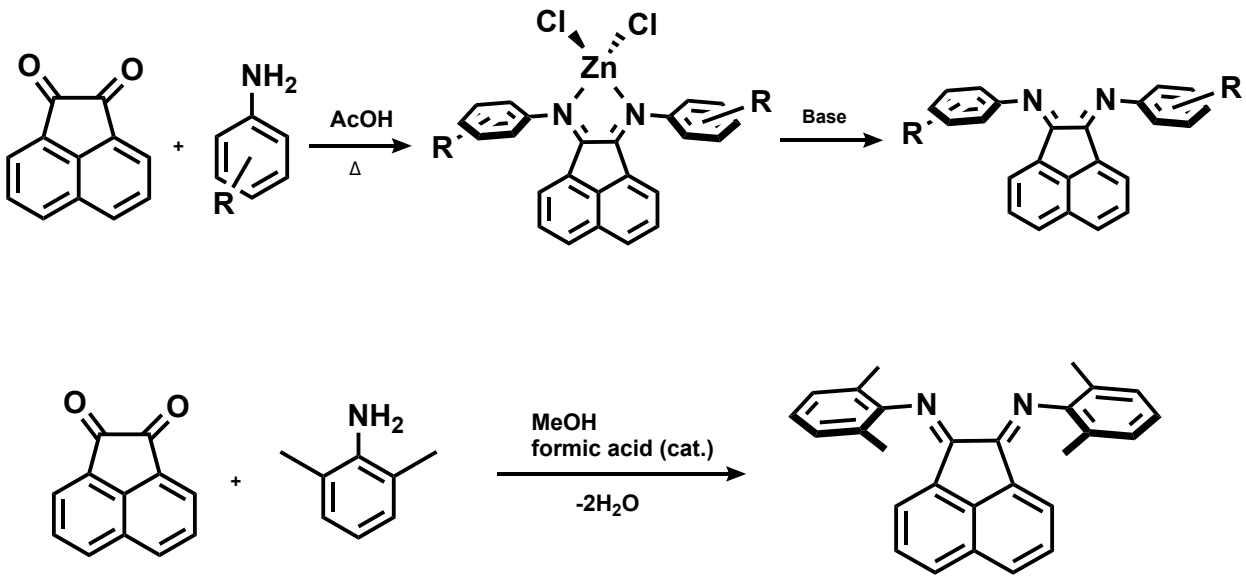
A Curve Detection Limits											
Tune Mode	Scan Type	Q1	Q2	Name	ISTD	R	a	b (blank)	DL	BEC	Units
He	MS/MS	66	66	Zn	45 -> 45 Sc [He]	0.999916	0.010211	0.019555	0.101689	1.915138	ppb
He	MS/MS	101	101	Ru	115 -> 115 In [He	0.999972	0.0053	6.35E-07	0.000289	0.00012	ppb
He	MS/MS	103	103	Rh	115 -> 115 In [He	1	0.030066	9.50E-07	8.96E-05	3.16E-05	ppb
He	MS/MS	105	105	Pd	115 -> 115 In [He	0.999998	0.006249	3.41E-06	0.001086	0.000545	ppb

Zn Residue results:

Residue results were calculated by multiplying the raw result by the liquid dilution and then by the subsequent multiplication by the digestion factor.

There was 2.55(3453) ppm Zn impurity in catalysis from synthesis. There were nearly no Ru, Rh, and Pd detected under ICP-MS analysis.

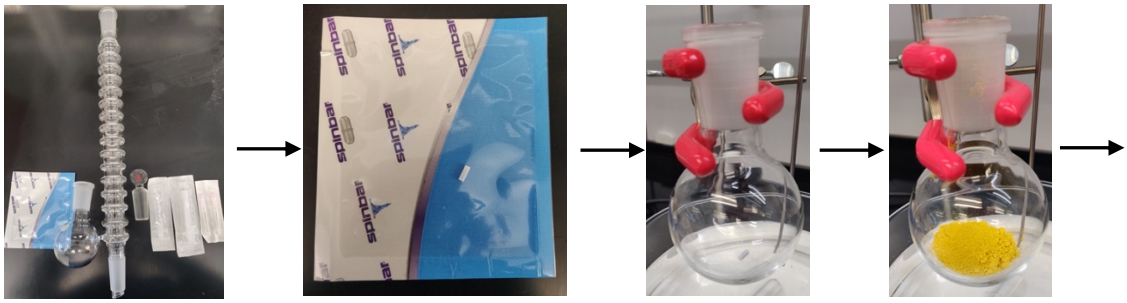
7. General procedure for Ar-BIAN additives



Scheme S2. Synthetic strategies of Ar-BIAN compounds with Zn[1] and adapted current method without any metals

Adapted procedure without metal[8]:

MeOH (60 ml) was added to a flask charged with acenaphthenequinone (2.00 g, 10.98 mmol) to give a yellow suspension. 2,6-Dimethylaniline (2.974 ml, 24.15 mmol) was syringed in whilst stirring and approximately 0.5 ml of formic acid (cat.) was added. The suspension started to darken to orange and then to red at which point the solid entered into solution and was stirred overnight (16 hours). The solvent was removed under reduced pressure and the residue subjected to dynamic vacuum (10^{-3}mbar) for six hours. The residue was washed with −78 °C hexane and the product extracted with room temperature hexane and reduced to minimum volume. Three crops were cooled in pentane to −35 °C, which deposited yellow/orange crystals that turned red under vacuum (2.692g, 6.92 mmol) in 63% yield, from all three crops. The starting materials were purchased from Sigma-Aldrich and used as received. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 3.8 Hz, 3H), 7.16 (m, 4H), 7.09 (d, J = 7.3 Hz, 2H), 6.71 (d, J = 7.1 Hz, 2H), 2.14 (s, 12H).

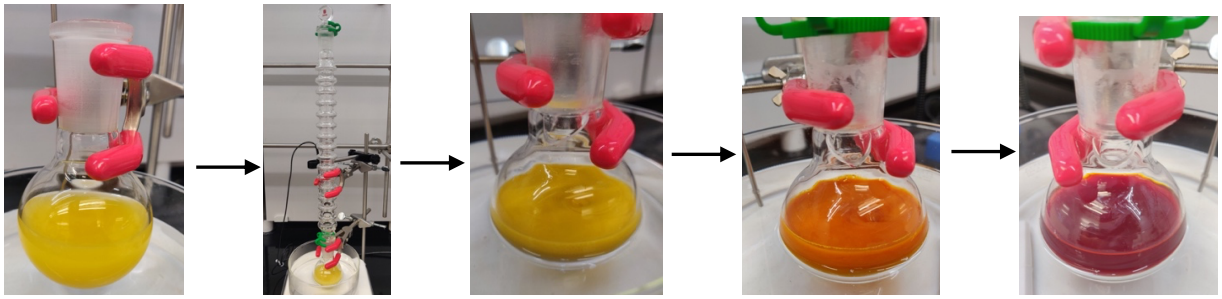


1. All glassware and equipment

2. New stir bar

3. Inserted stir bar in a clean flask

4. Added acenaphthenequinone



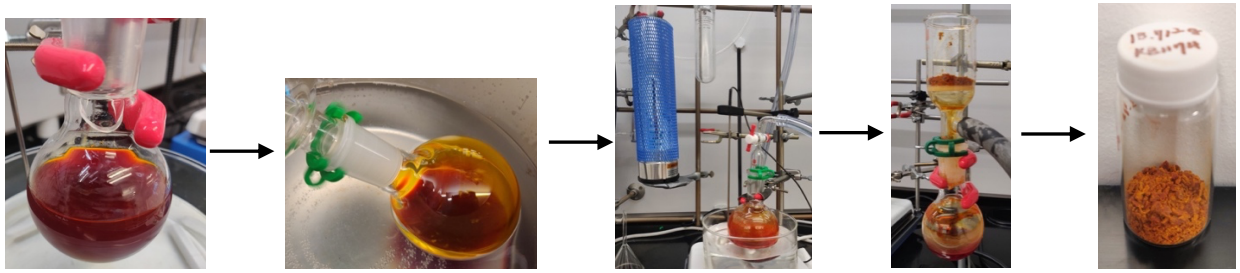
5. Added methanol

4. Set up

7. Yellow suspension as it began to reflux

8. Orange suspension after adding acetic acid

3. Red suspension after adding 2,6-dimethylaniline



10. After overnight reflux

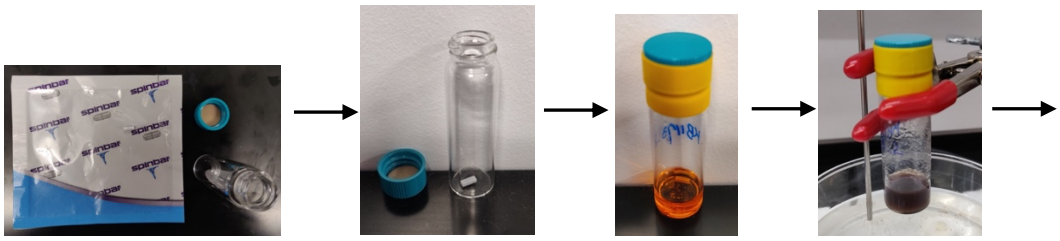
9. The solvent was removed.

8. The residue was dried over dynamic vaccum.

7. The product was filtered.

6. Product

Figure S1. Synthesis procedure for $\mathbf{L_1}$ without zinc

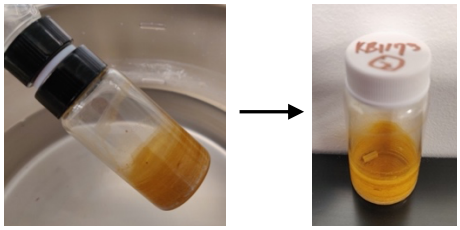


2. All glassware and equipment

1. New stir bar inserted in a new vial

3. Reaction mixture

4. Reaction mixture after heat



6. The resulting solution was concentrated.

5. Catalytic product

Figure S2. Catalytic reaction using the $\mathbf{L_1}$ prepared according to zinc-free protocol (see: Figure S1)

8. Mechanistic experiment

8.1 KIE experiment

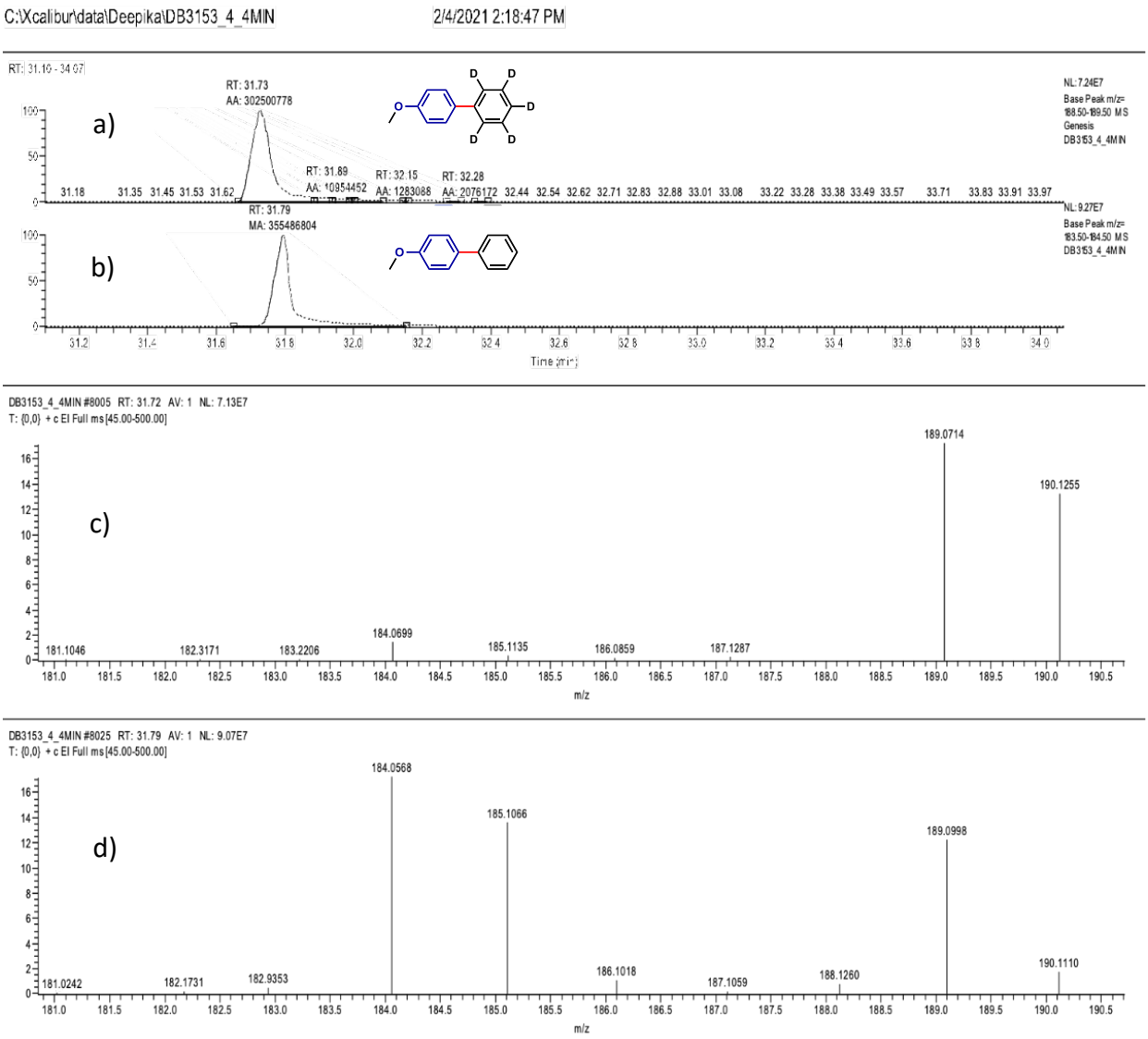


Figure S3. GC-MS analysis for KIE experiment. a) The GC analysis obtained the retention time of methoxylbiphenyl-d_5 to be 31.72 min while b) the peak for product showed 31.79 min. The predicted m/z value is 189 for methoxybiphenyl-d_5 and 184 for the product. Both of structures were confirmed by the MS spectra of c) and d), and those areas of peaks from GC were used to calculate the KIE accordingly.

8.2 Crystal of the catalytic additive intermediate, C18-Crown-6

Preparation of **C**18-Crown-6**:**
In a 20 mL reaction vial, **L_1**(1 mmol), KO*t*Bu (1.2 mmol) and 18-Crown-6 (1.2 mmol) were charged under an inert atmosphere of a glovebox. To the mixture was added 5 mL of diethyl ether and drops of 1,2-dimethoxyethane followed by stirring for 20 min. After that, the stir bar was removed from the reaction mixture and the solution was kept unperturbed at -30 °C. After 2 days, the solution afforded brown needle-shaped crystals.[3] ^{1}H NMR (400 MHz, THF-d_8): δ = 6.78 (d, J = 5.6 Hz, 4H), 6.642 (s, 4H), 6.47 (t, J = 5.74 Hz, 2H), 5.9986 (s, 2H), 3.43 (s, 24H), 2.20 (s, 12H)

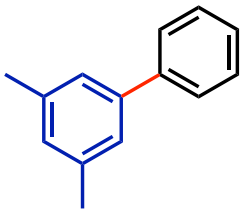
X Ray Crystallography: CCDC2309257 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

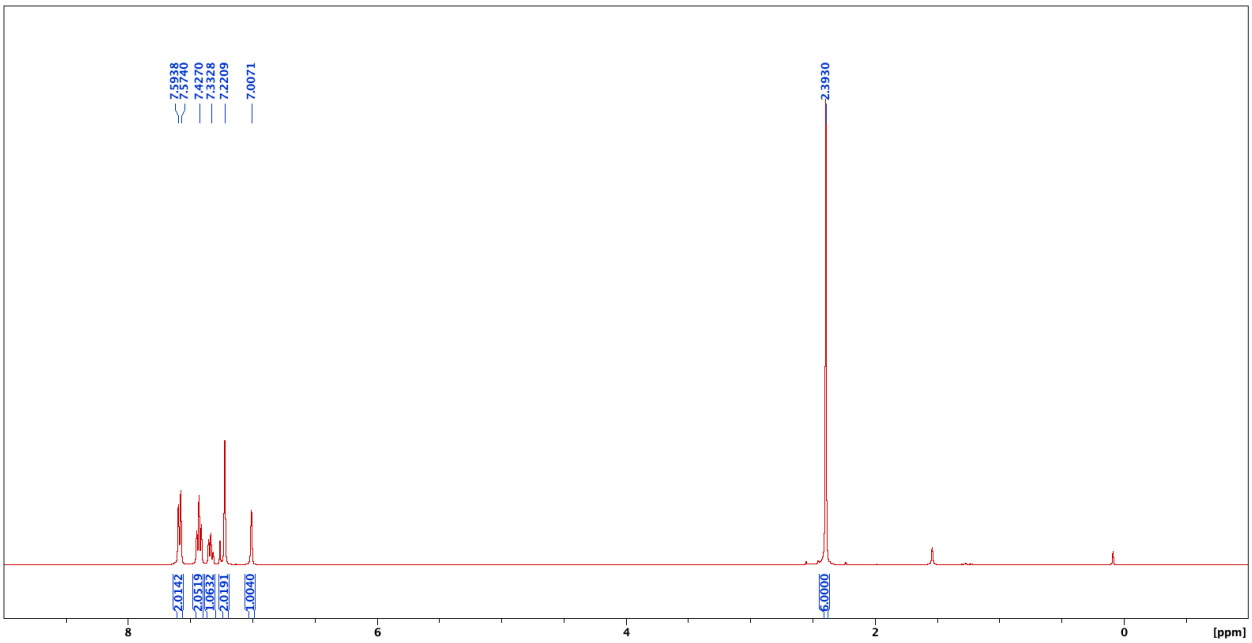
X-Ray crystallographic data and structure refinement:
Formula: C40 H48 K N2 O6
Bond precision: C-C = 0.0028 Å
Wavelength: = 1.54184
Crystal system: monoclinic
Space group: P 1 2_1/c 1
Color of crystal: Brown
Unit cell parameters: a = 16.87115(15) Å α = 90°
b = 14.15084(13) Å β = 90.5169(9)°
c = 17.71183(18) Å γ = 90°
Temperature of data collection: 173(K)
Values of Z and R: Z = 4
R(reflections) = 0.0478(8350), wR2(reflections) = 0.1278(8949)
Radiation type: Mo K/a
Radiation source: sealed X-ray tube
Radiation monochromator: graphite
Measurement device type: XtaLab Synergy by Rigaku Oxford Diffraction
Computing structure solution: OLEX
Computing structure refinement: SHELXL

8.3 Reaction with C18-Crown-6

An oven dried 20 mL scintillation vial was charged with **C18-Crown-6** (34.6 mg, 0.05 mmol), anhydrous benzene (2 mL), and a stir bar. A bright orange homogenous solution was obtained. Aryl halide (1 mmol) and KO*t*Bu (168.3 mg, 1.5 mmol) were then added to the reaction mixture. The scintillation vial was sealed and then placed on a preheated oil bath at 75 ^{o}C for 15 hrs. The reaction was quenched by exposing the reaction mixture to air, then the solvent was then reduced under *vacuo*. NMR yield reported employing hexamethylbenzene.

9. ^{1}H and ^{13}C NMR of isolated C-C formed products and ^{1}H of catalytically active species:





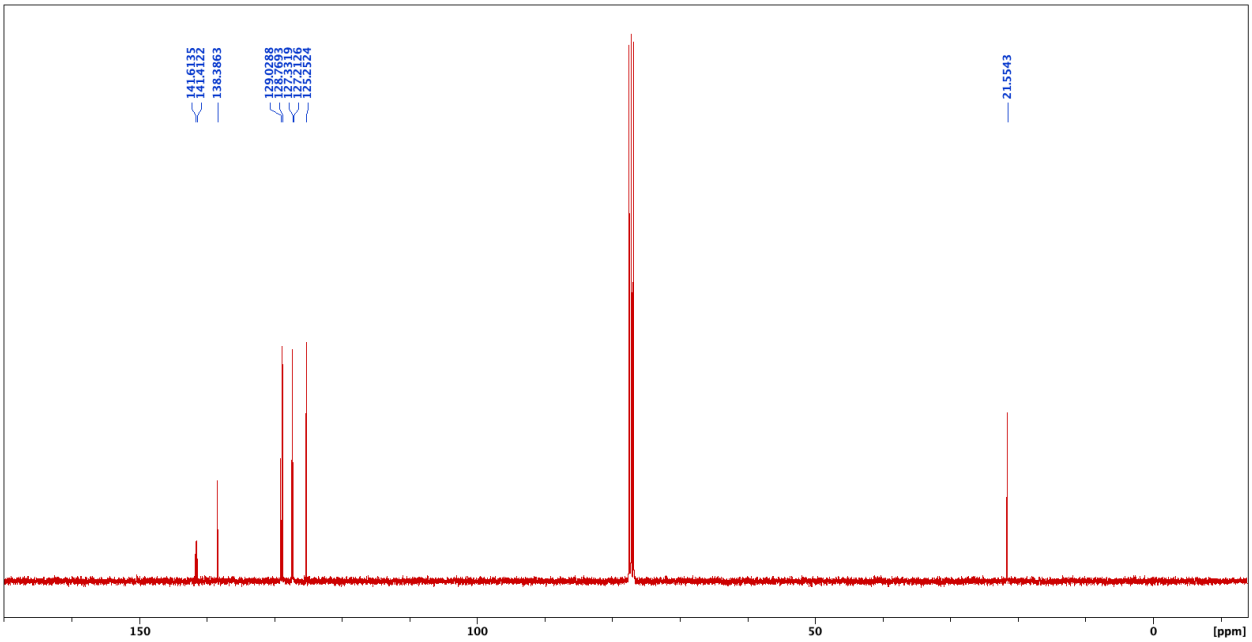


Figure S4. ^{1}H and ^{13}C of 3,5-Dimethylbiphenyl (**2e**)

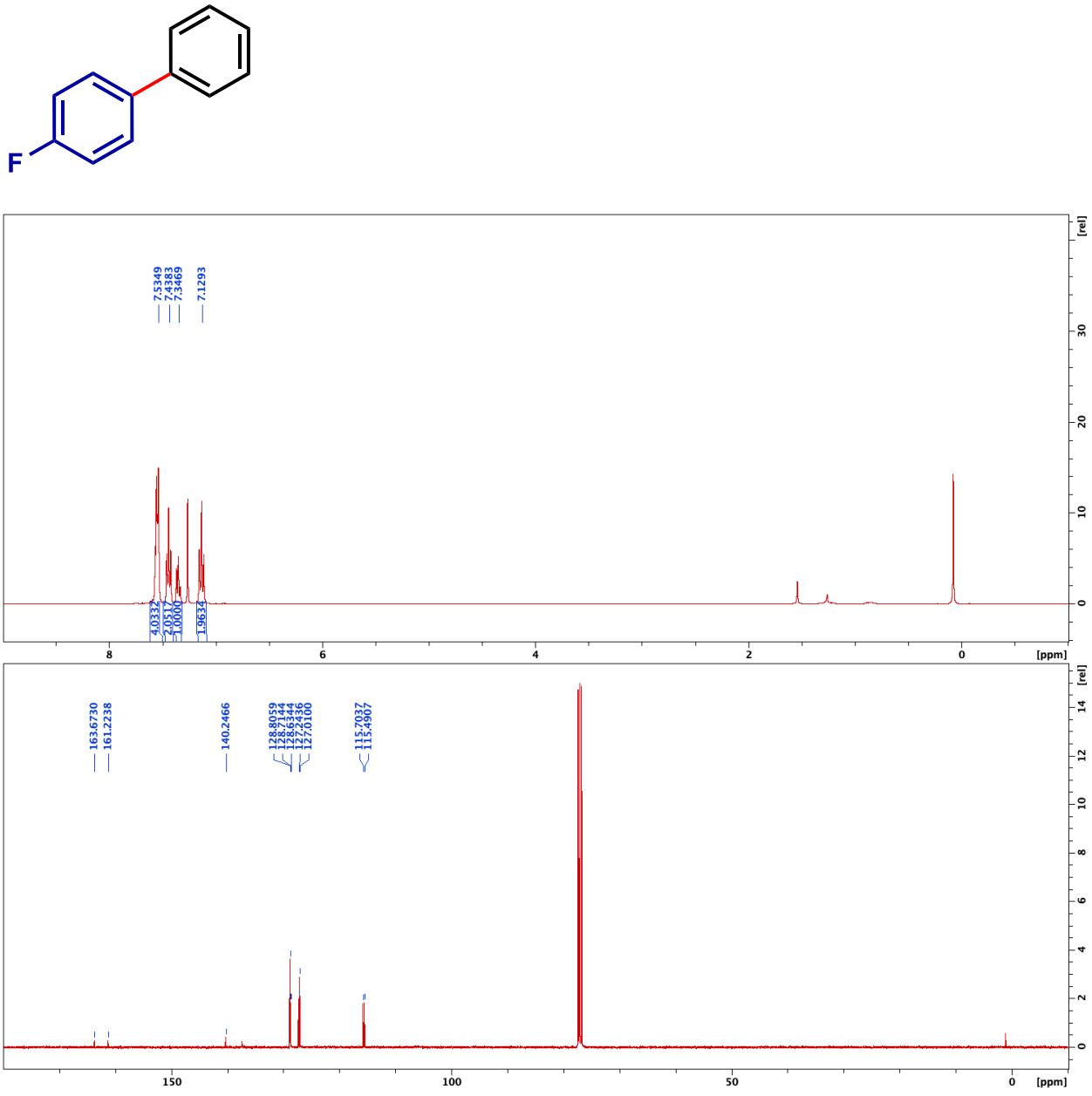


Figure S5. ^{1}H and ^{13}C of 4-Fluorobiphenyl (**4a**)

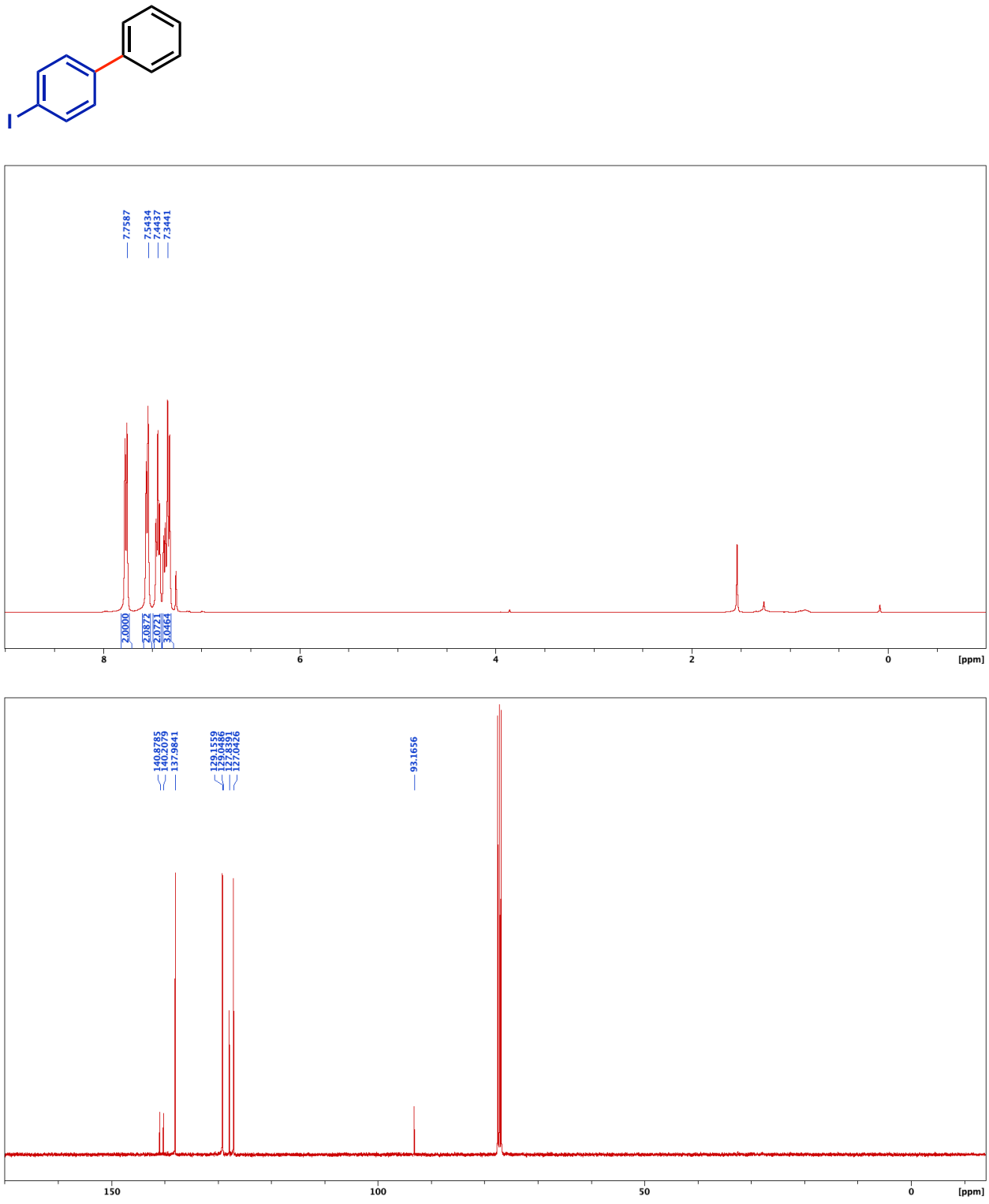


Figure S5. ^{1}H and ^{13}C of 4-Iodobiphenyl (**4c**)

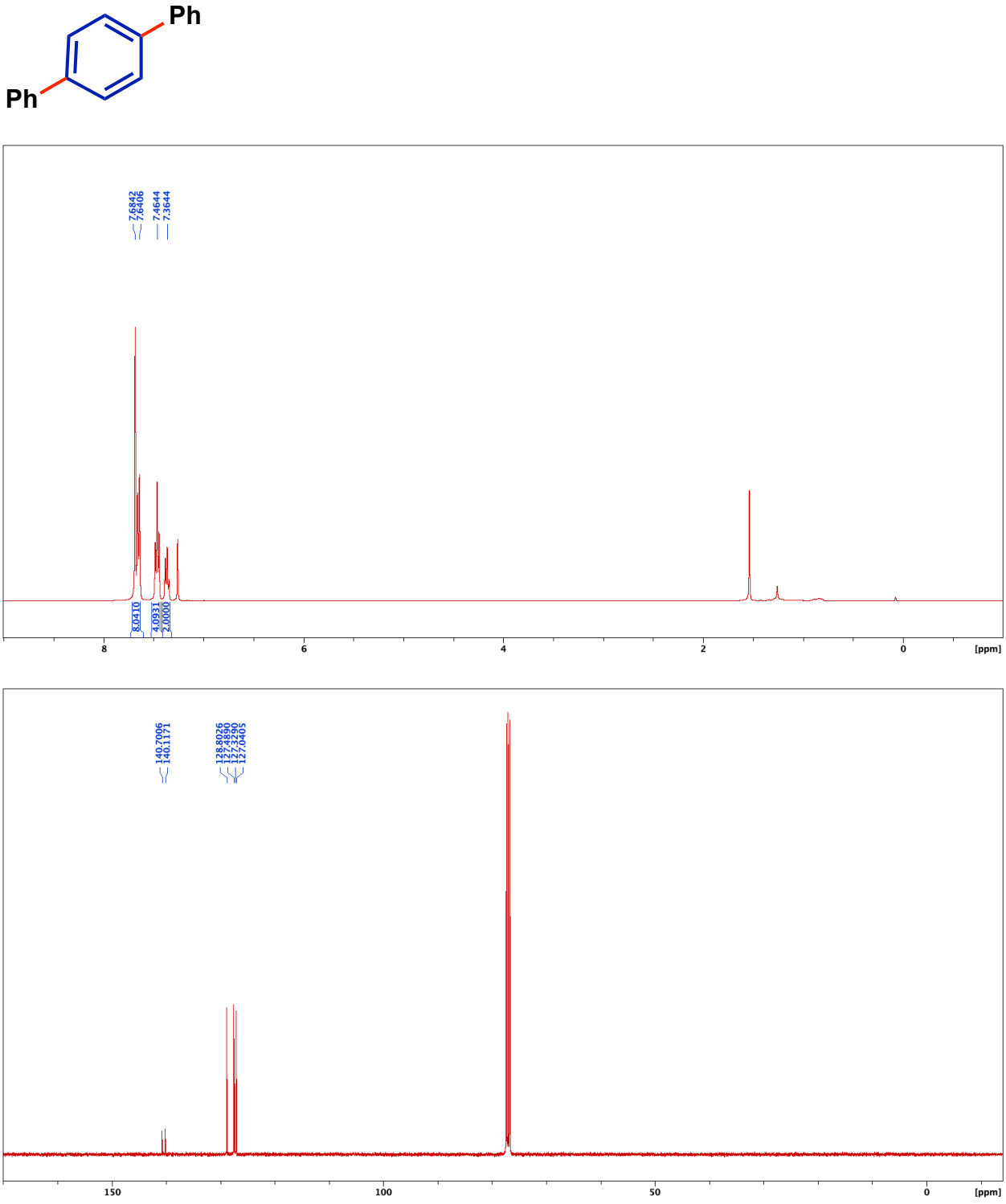


Figure S5. ^{1}H and ^{13}C of *p*-Terphenyl (**5**)

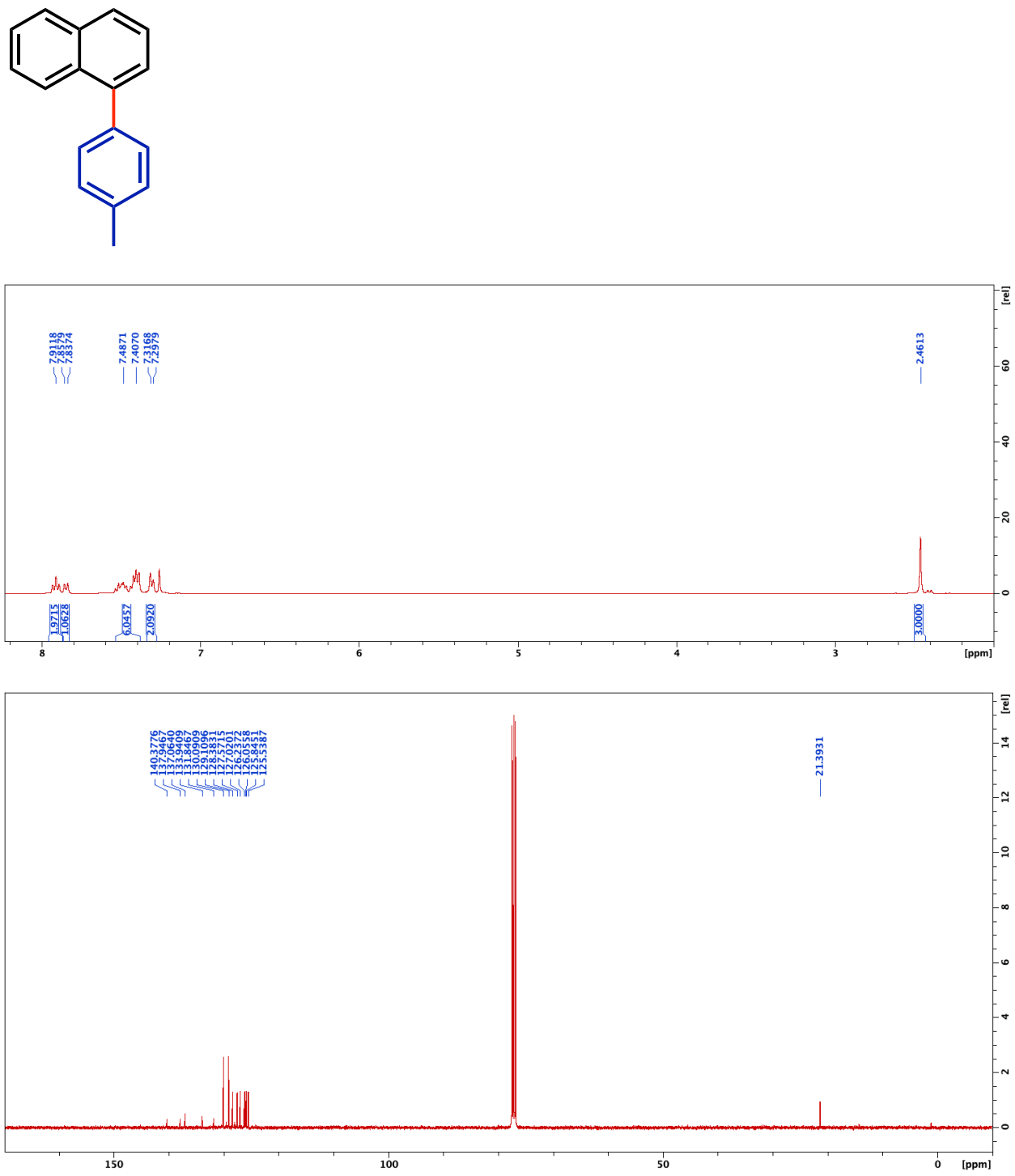


Figure S6. ^{1}H and ^{13}C of 1-(4-methylphenyl)-naphthalene (**9a**)

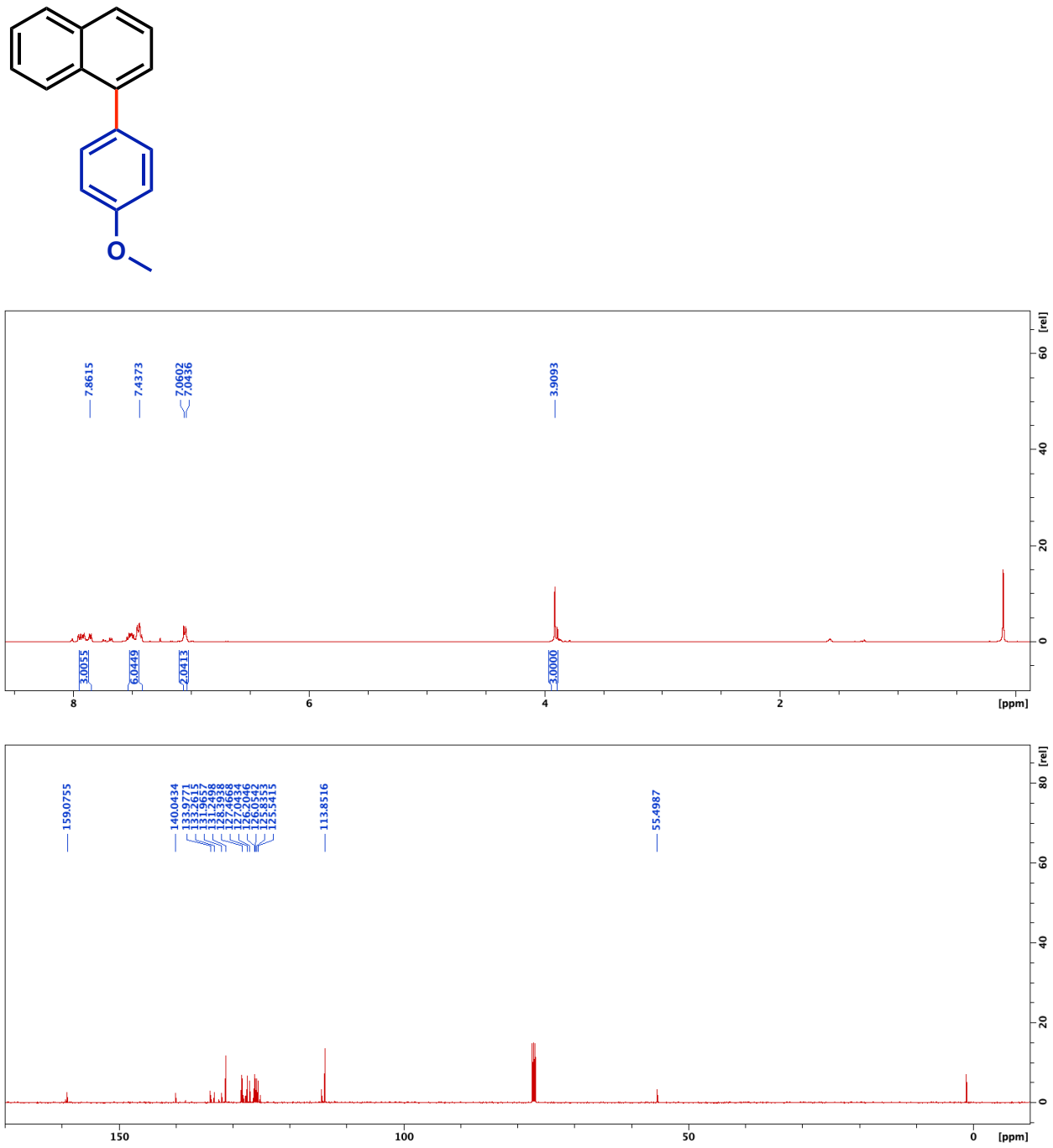
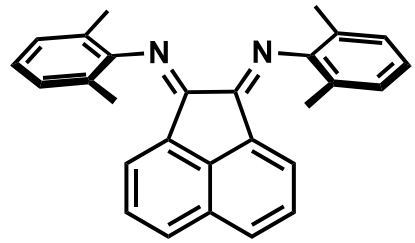


Figure S7. ^{1}H and ^{13}C of 1-(4-methoxyphenyl)-naphthalene (**9b**)



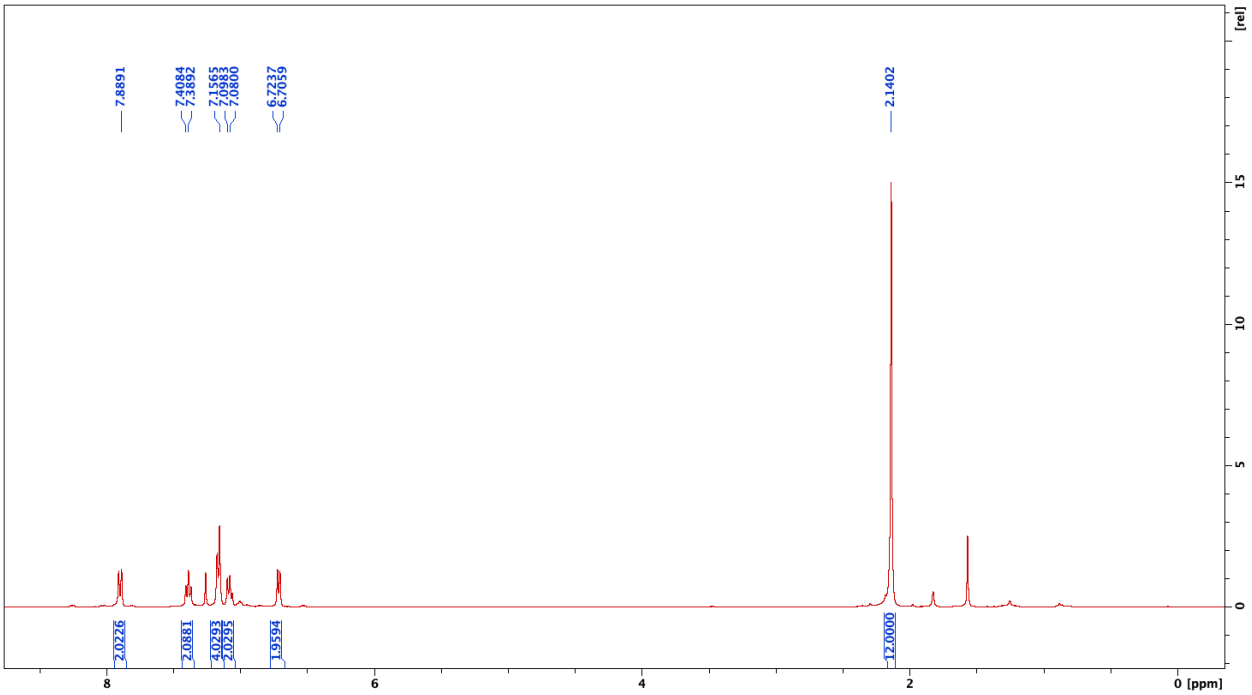
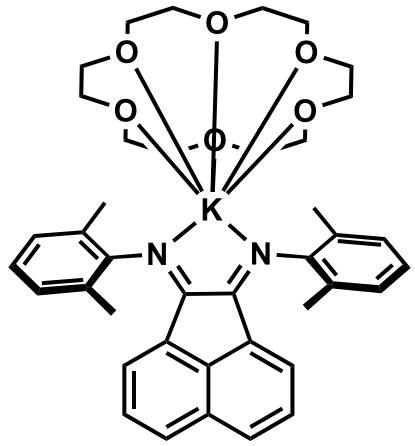


Figure S8. ^{1}H of $L_{1,}$ 2,6-dimethylBIAN.



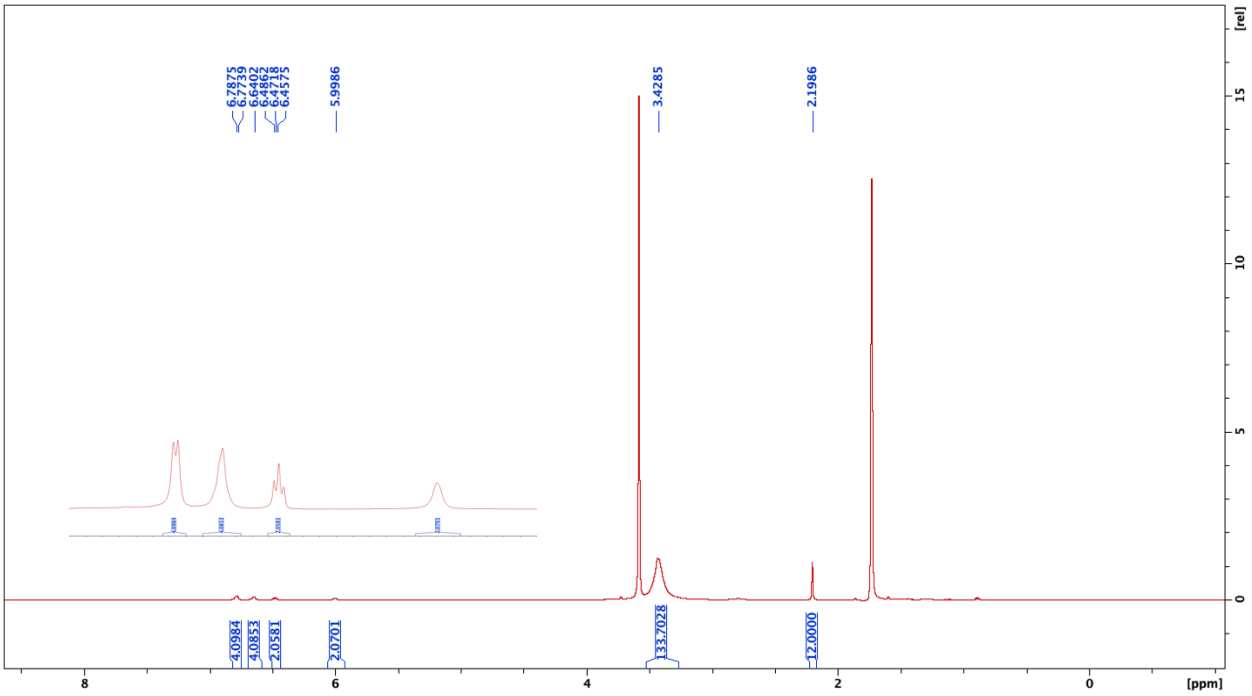


Figure S9. ^{1}H of **C**18-Crown-6

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