Supporting Information

Single-atom dispersed Co-N-C catalyst: structure identification and performance for hydrogenative coupling of nitroarenes

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1. **Characterization of the Co-N-C catalyst.**

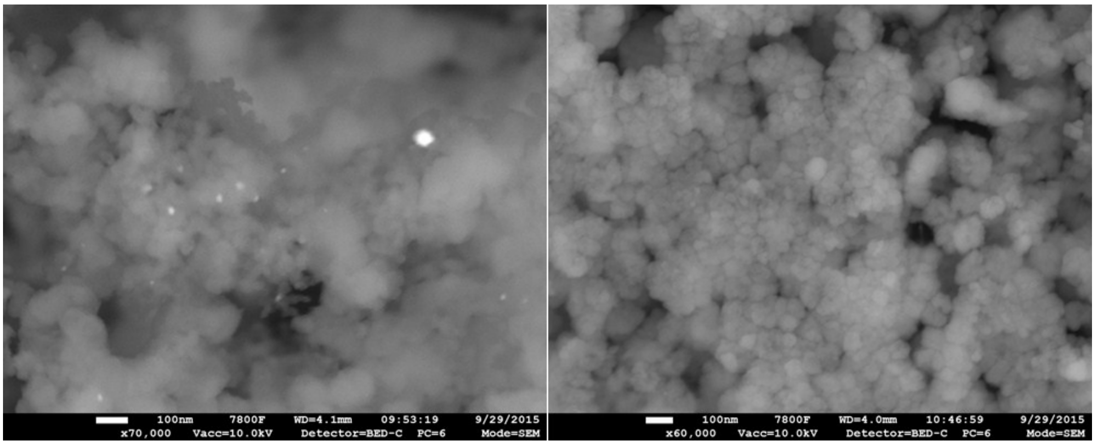


Figure S1. Representative SEM images of Co-N-C/Carbon (left) and Co-N-C/MgO (right) catalysts under back-scattering electron detector mode. The bright spots in the left image are big Co particles due to aggregation; in contrast, they are absent in the right image, indicating MgO support effectively limited the aggregation of cobalt particles.

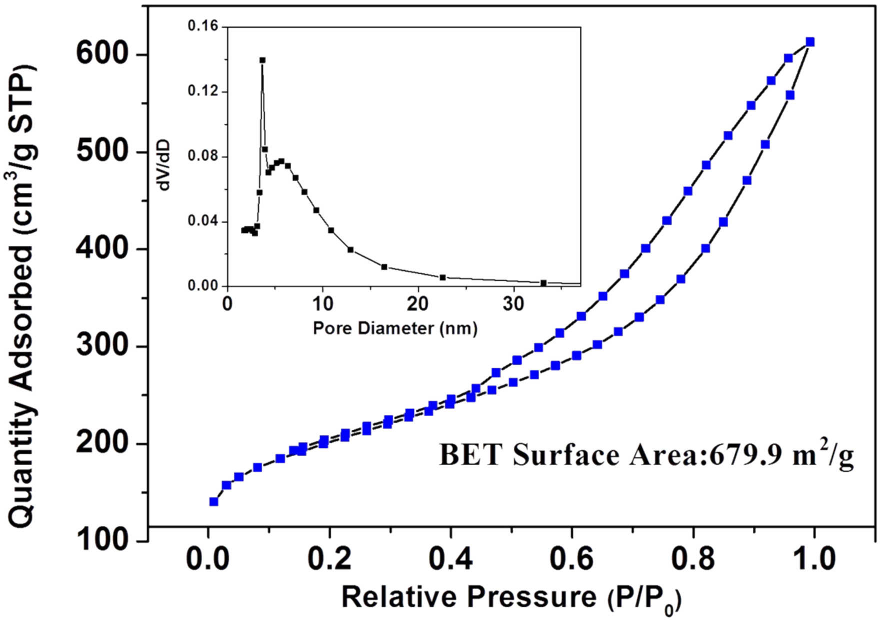


Figure S2. N_2 adsorption-desorption isotherms of Co-N-C catalyst. Inset is the mesopore size distribution.

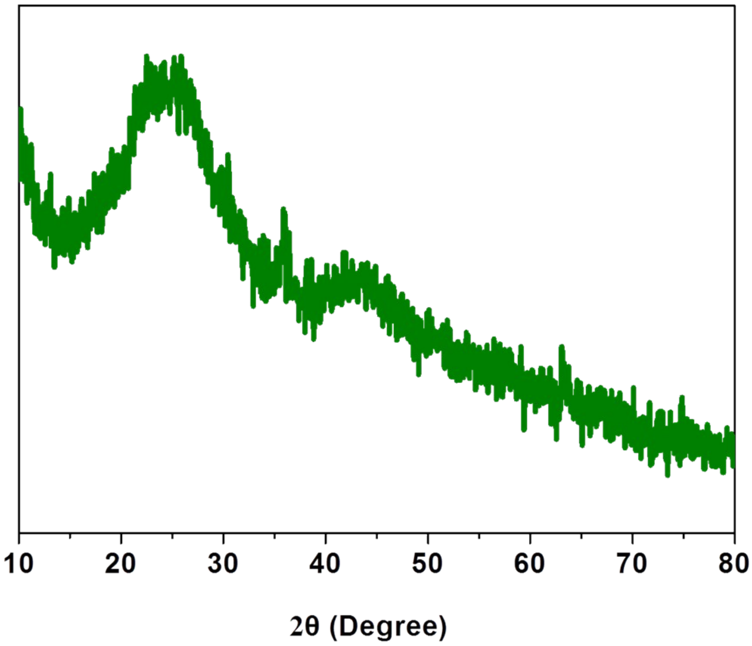


Figure S3. XRD pattern of the Co-N-C catalyst. The broad peaks located at 23^{o} and 43^{o} could be ascribed to the (002) and (004) planes of carbon matrix. No diffraction patterns of Co/CoO_x can be observed.

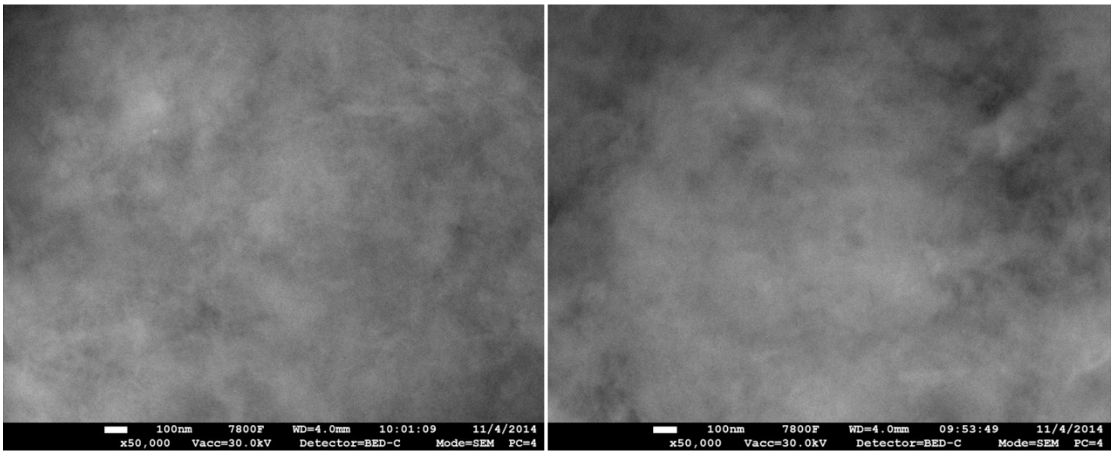


Figure S4. SEM images of Co-N-C catalyst under back-scattering electron detector mode.

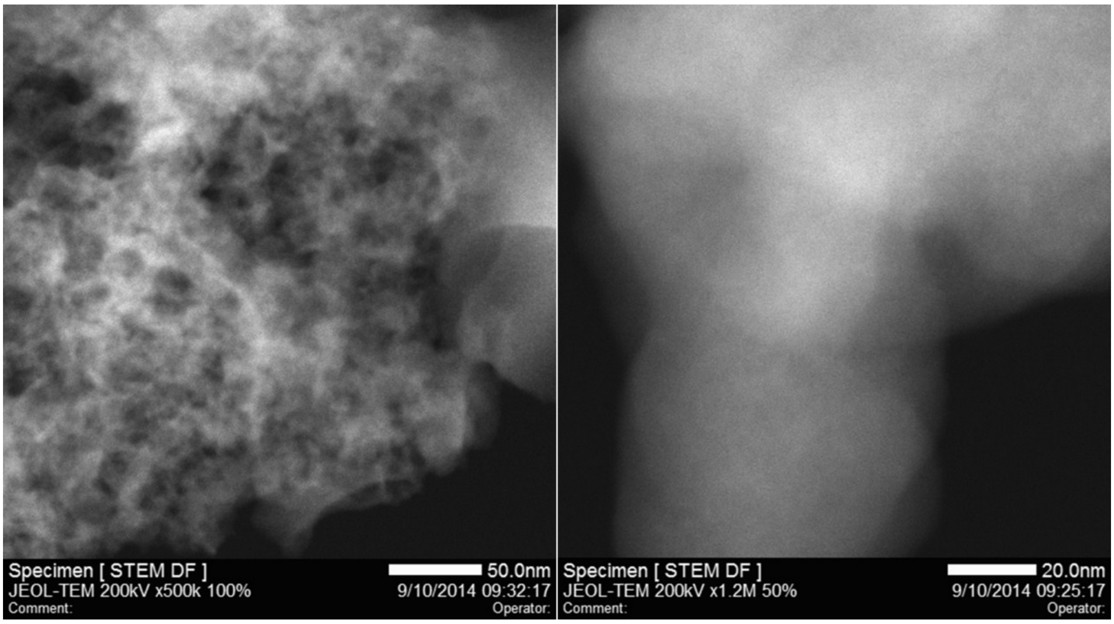


Figure S5. STEM images of Co-N-C catalyst

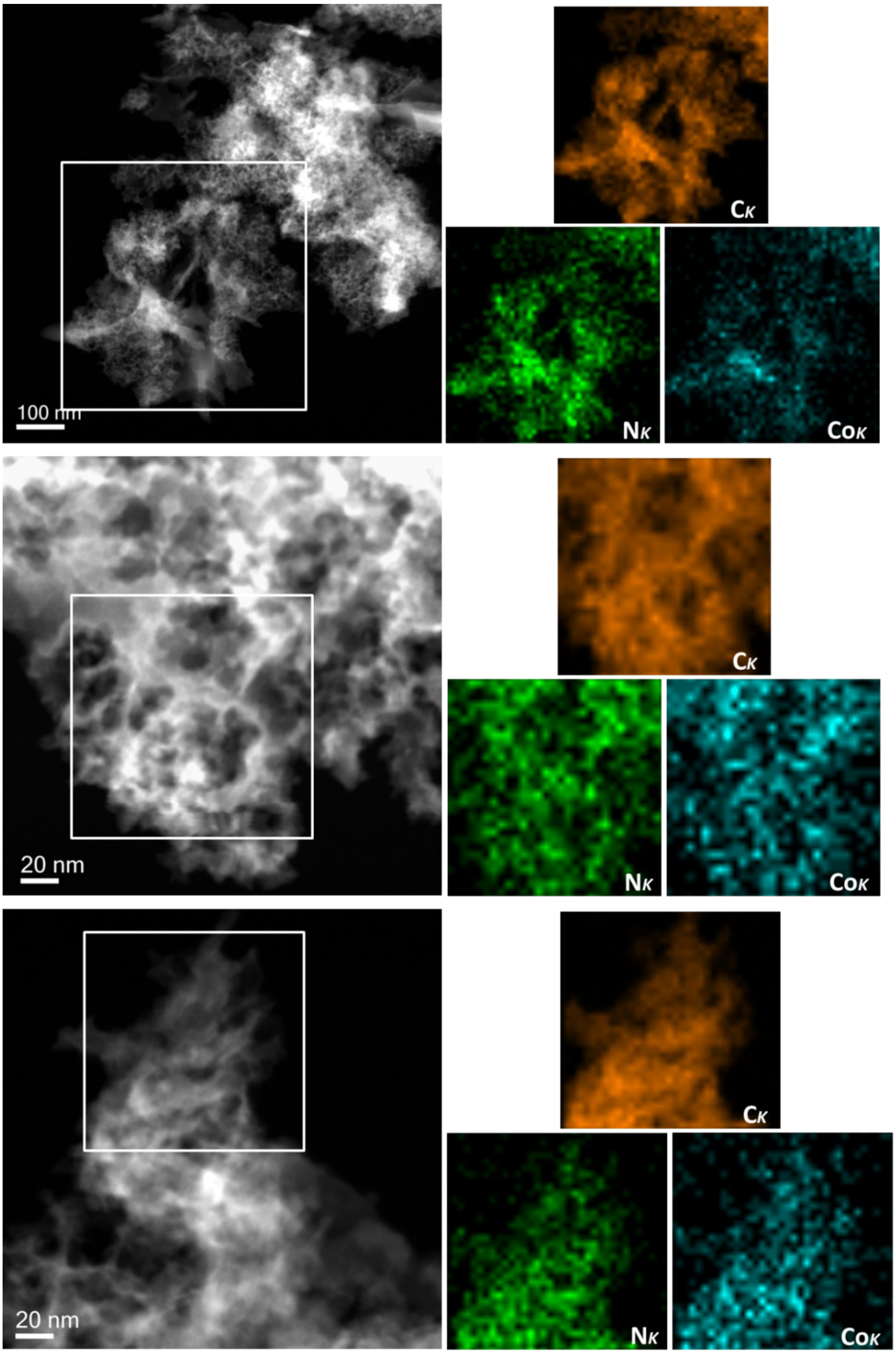


Figure S6. Elemental mapping of Co-N-C catalyst in different regions.

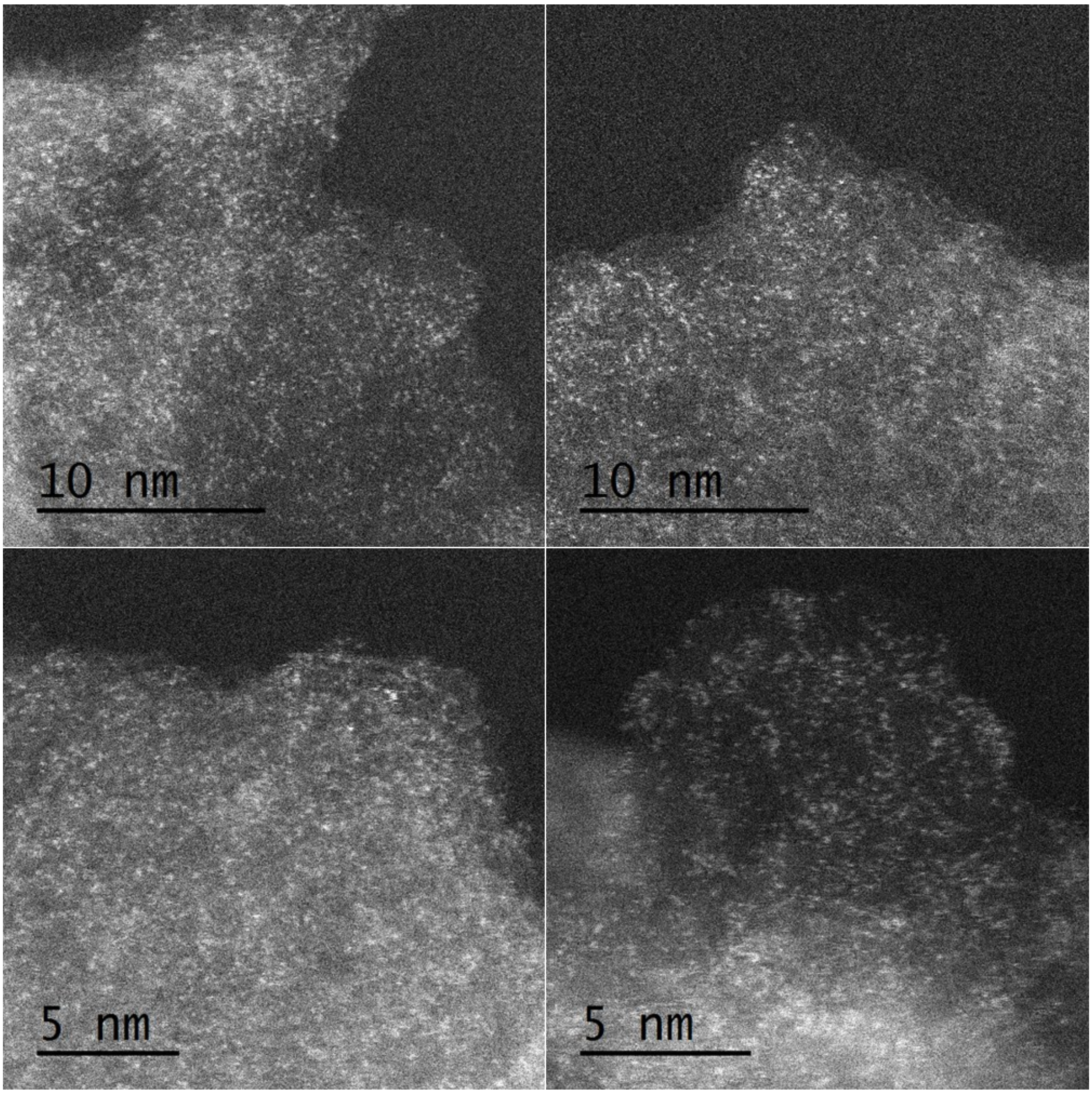


Figure S7. Subångström-resolution HAADF-STEM images of different regions of Co-N-C catalyst. The white dots in images are Co single atoms.

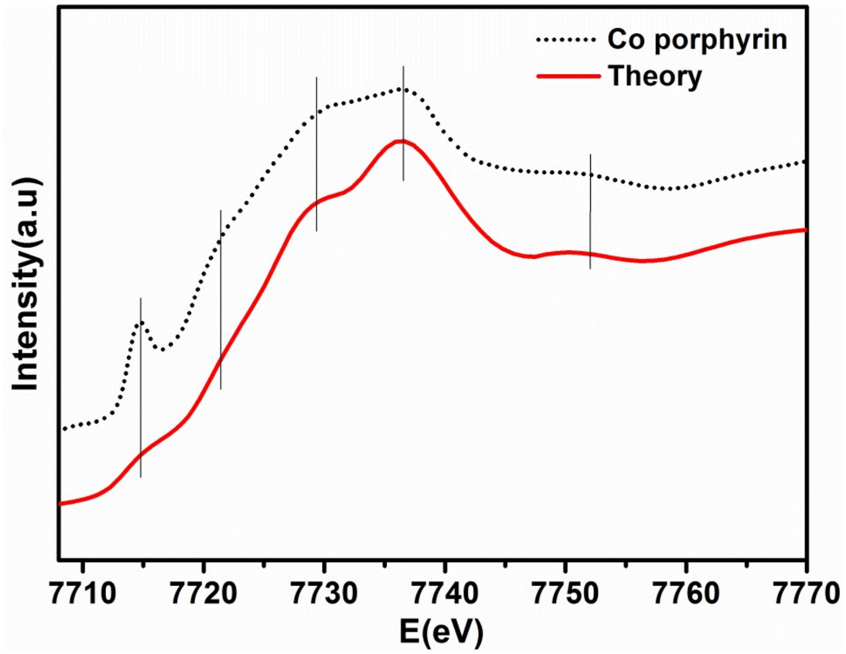
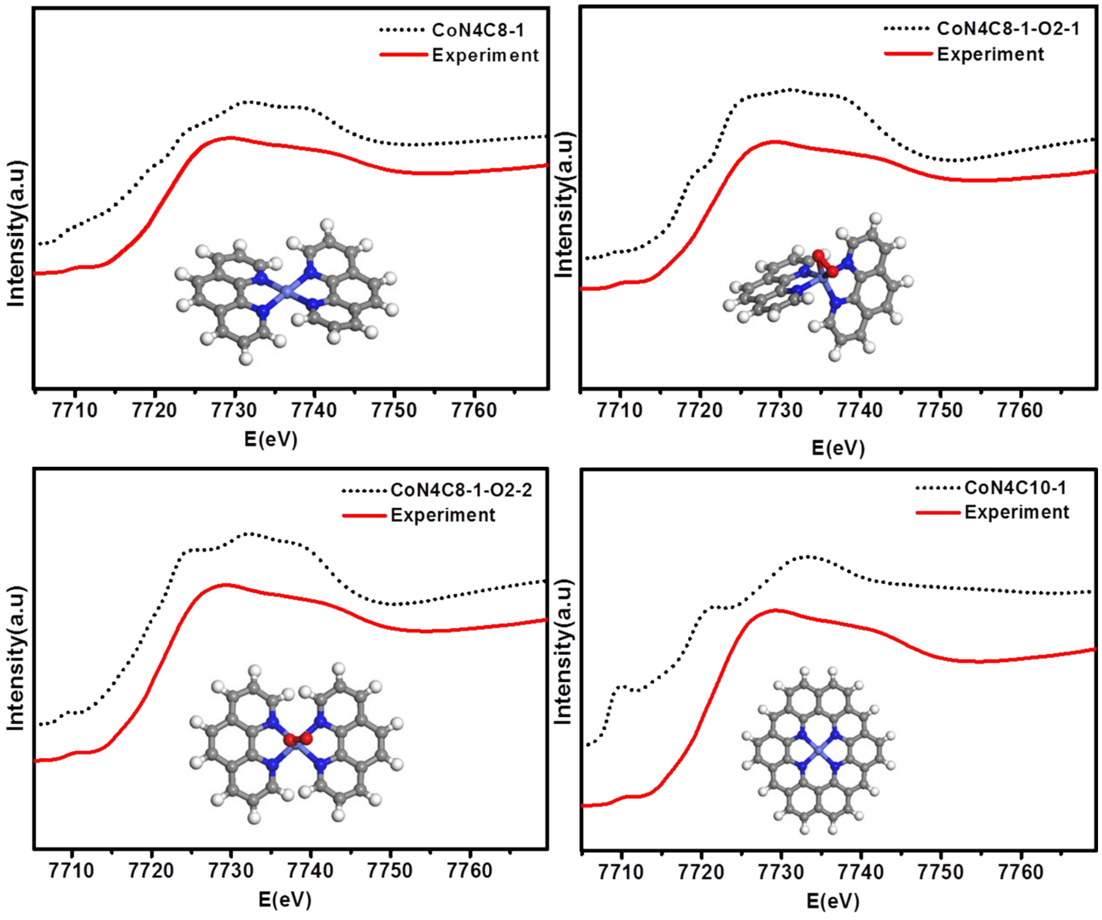
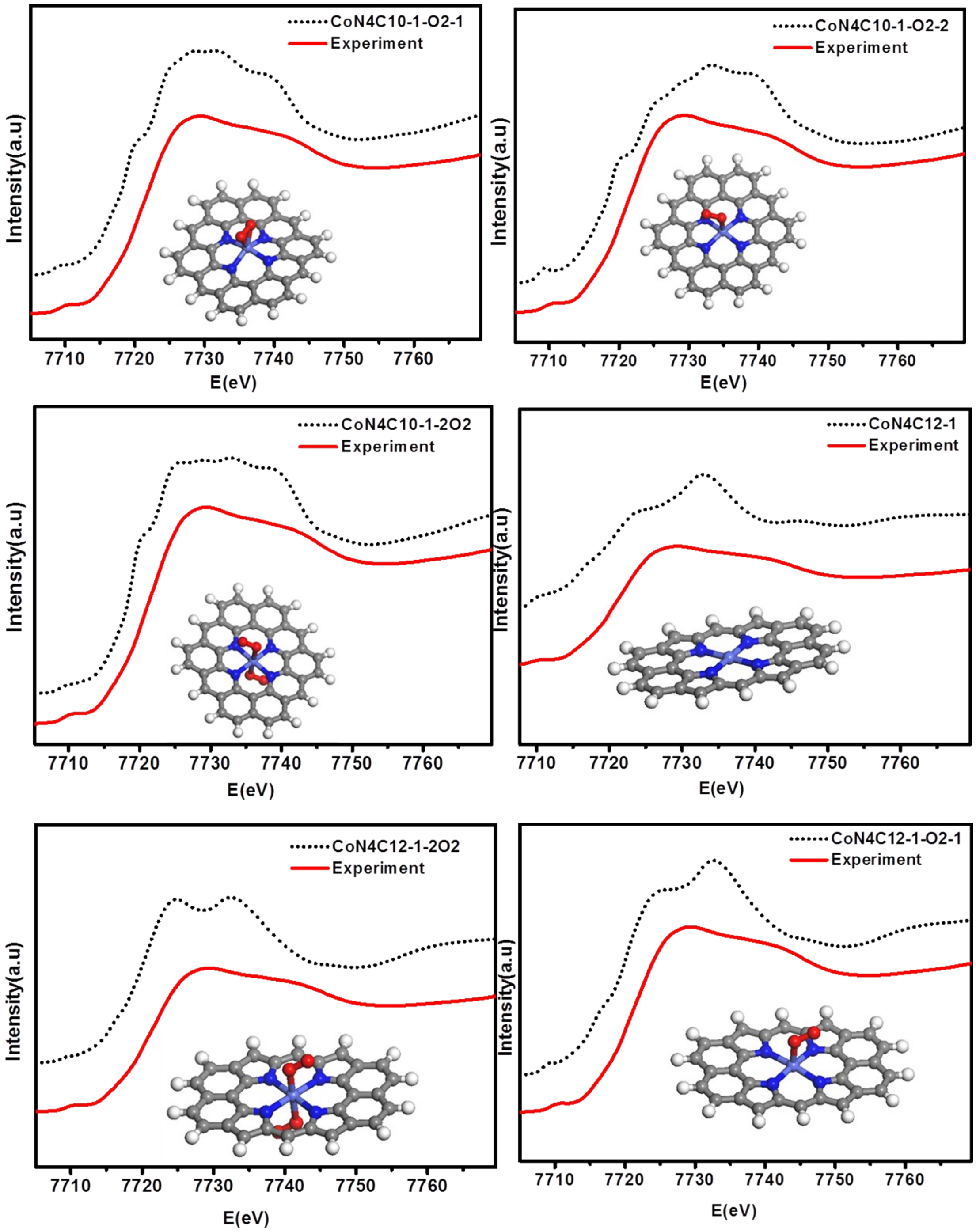
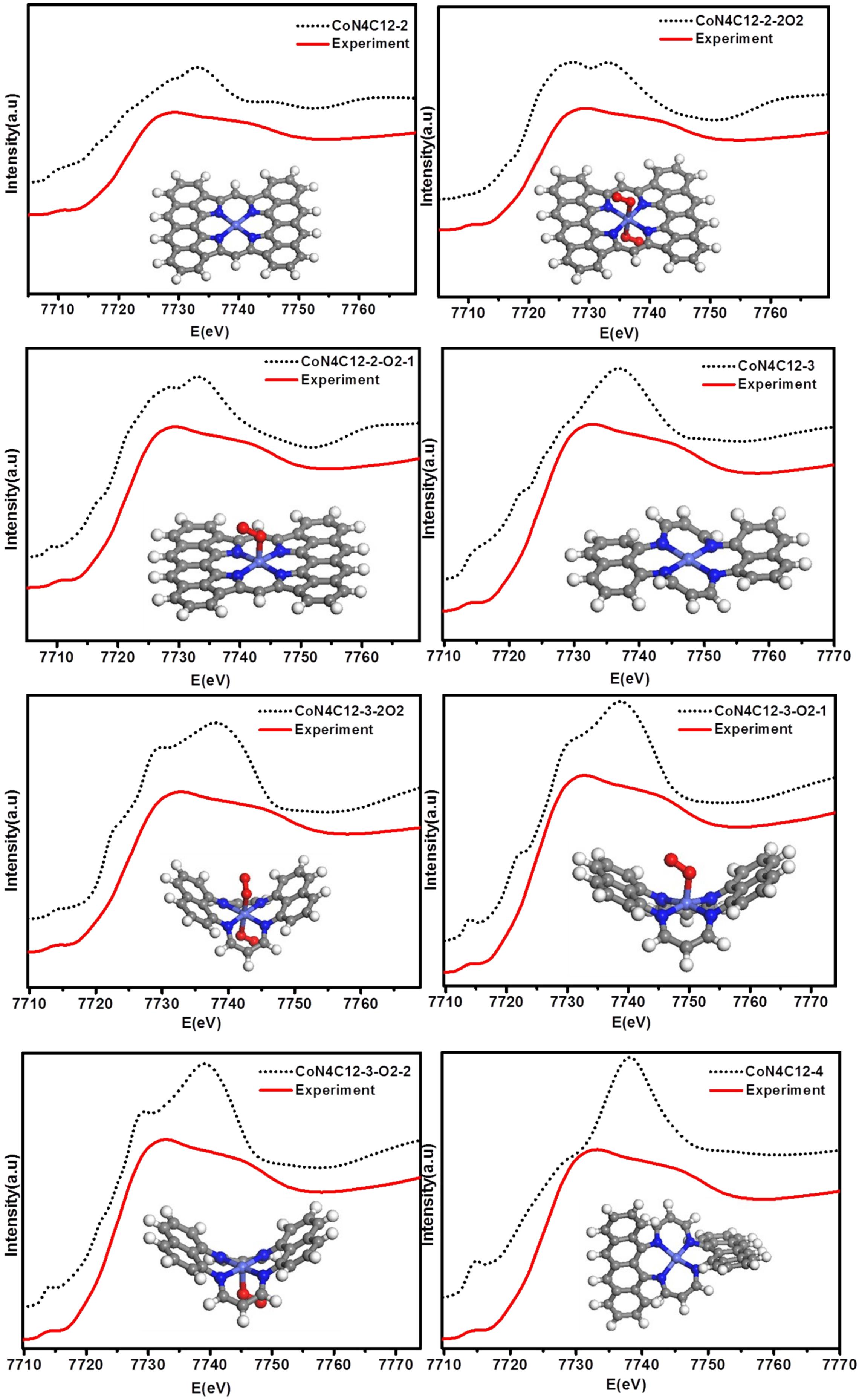


Figure S8. Comparison between the XANES experimental spectrum of Co porphyrin at Co K edge (solid red lines) and the theoretical spectra calculated with the depicted structures (black dashed lines).




CoN4C10-1-O2-1
Experiment
Intensity(a.u)
E(eV)
7710
7720
7730
7740
7750
7760
CoN4C10-1-O2-2
Experiment
Intensity(a.u)
E(eV)
CoN4C10-1-2O2
Experiment
Intensity(a.u)
E(eV)
CoN4C12-1
Experiment
Intensity(a.u)
E(eV)
CoN4C12-1-2O2
Experiment
Intensity(a.u)
E(eV)
CoN4C12-1-O2-1
Experiment
Intensity(a.u)
E(eV)
N


CoN4C12-2
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
E(eV)
CoN4C12-2-2O2
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
E(eV)
CoN4C12-2-O2-1
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
E(eV)
CoN4C12-3
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
7770
E(eV)
CoN4C12-3-2O2
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
E(eV)
CoN4C12-3-O2-1
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
7770
E(eV)
CoN4C12-3-O2-2
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
7770
E(eV)
CoN4C12-4
Experiment
Intensity(a.u)
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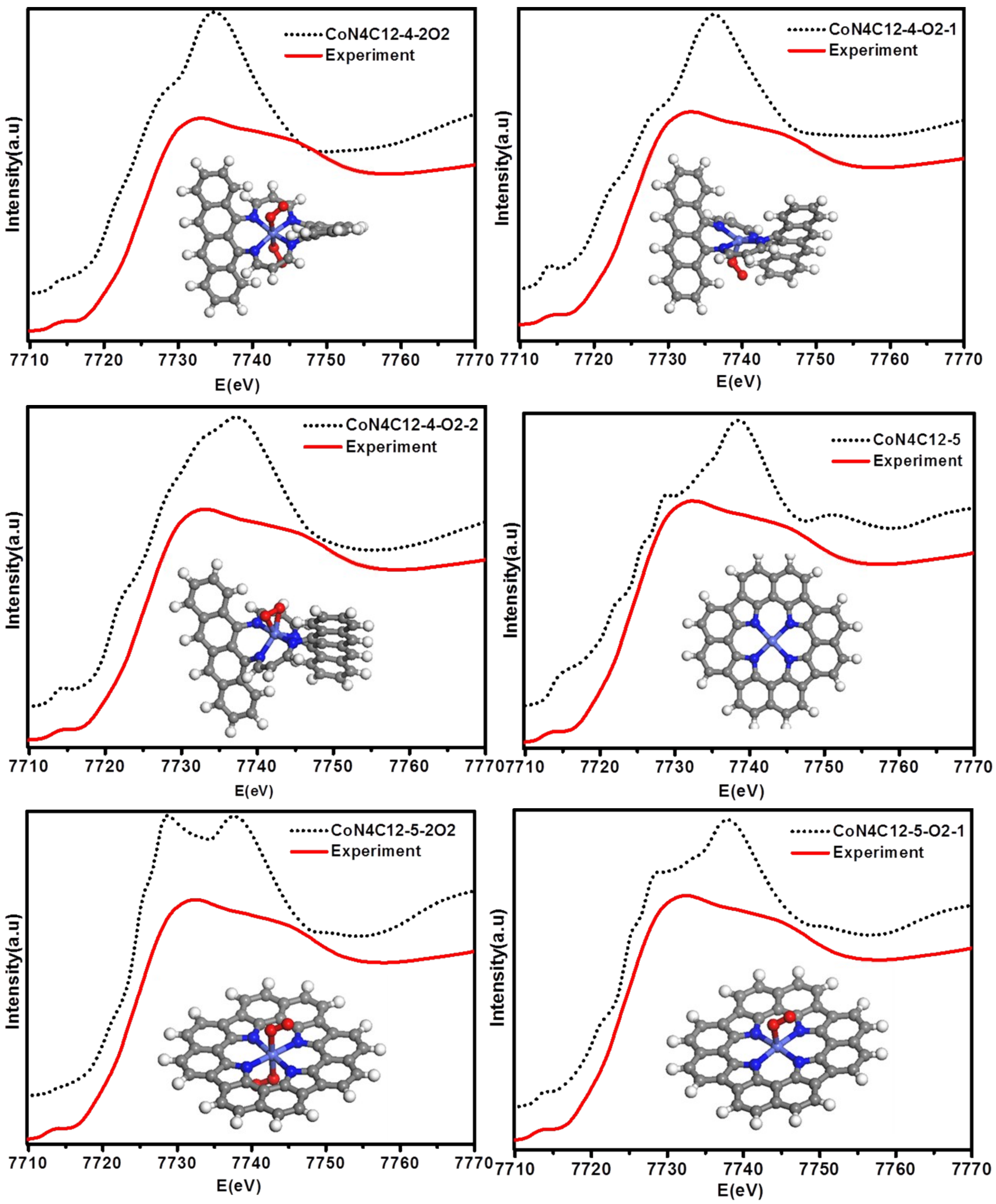
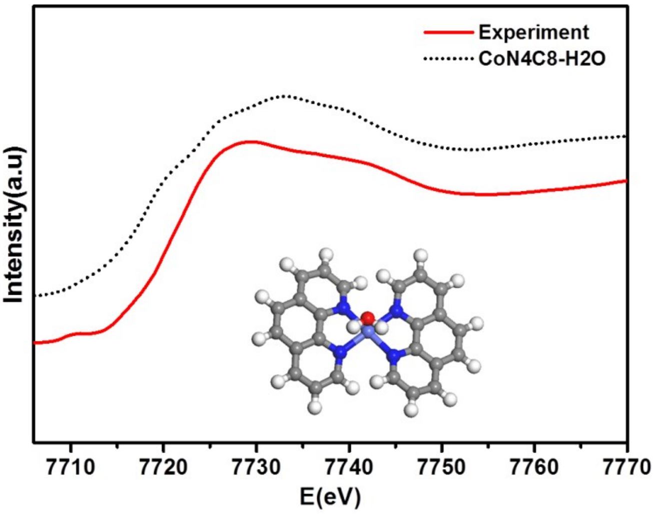
7740
7750
7760
7770
E(eV)


CoN4C12-4-2O2
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
7770
E(eV)
CoN4C12-4-O2-1
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
7770
E(eV)
CoN4C12-4-O2-2
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
7770
E(eV)
CoN4C12-5
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
7770
E(eV)
CoN4C12-5-2O2
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
7770
E(eV)
CoN4C12-5-O2-1
Experiment
Intensity(a.u)
7710
7720
7730
7740
7750
7760
7770
E(eV)



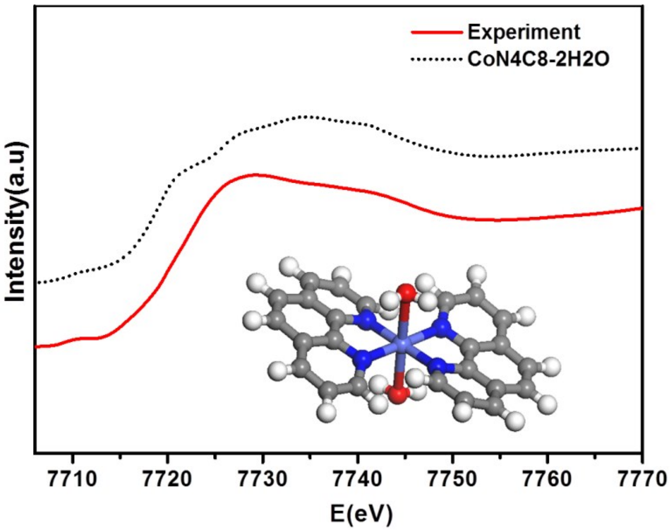


Figure S9. Comparison between the XANES experimental spectrum of Co-N-C at Co K edge (solid red lines) and the theoretical spectra calculated with the depicted structures (black dashed lines). In these calculations, the total scattering potentials including a fully relaxed core-hole were obtained iteratively, by successive calculations of the potential until self-consistency was reached. Based on this scattering potential, the final states of the excited photoelectron were then calculated. The Hedin-Lundqvist model of exchange potential with a 2 eV shift and additional broadening of 0.8 eV was used to give a closest match between the simulated and experimental spectra.

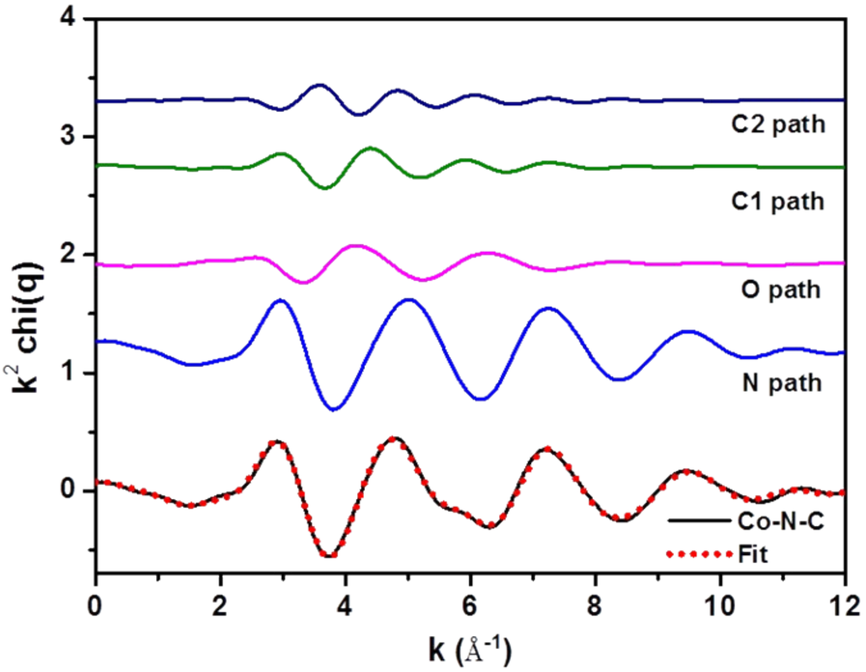


Figure S10. The contribution of every path including Co-N (blue line), Co-O (pink line) and Co-C (green and navy blue lines) in q-space for Co-N-C sample.

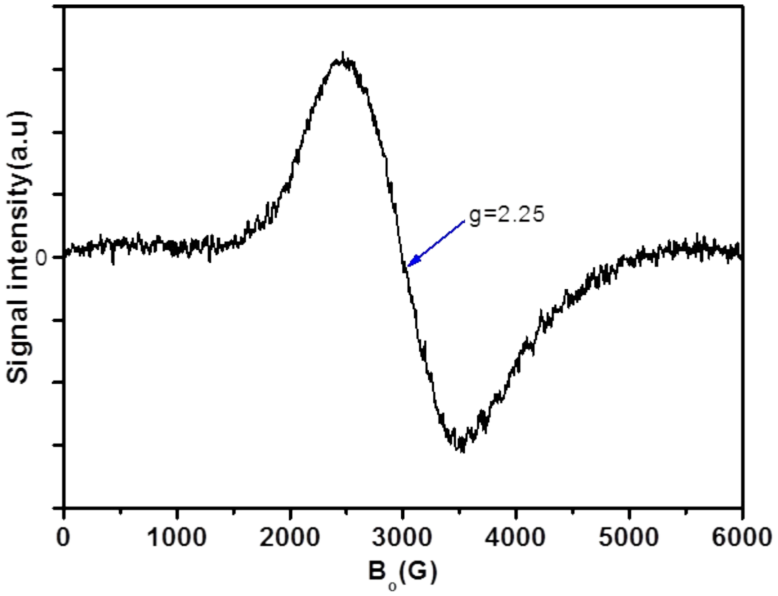


Figure S11. EPR spectra obtained at room temperature on the Co-N-C catalyst. A EPR signal with a Lorentzian shape and a g factor = 2.25 can be assigned to Co^{2+}.

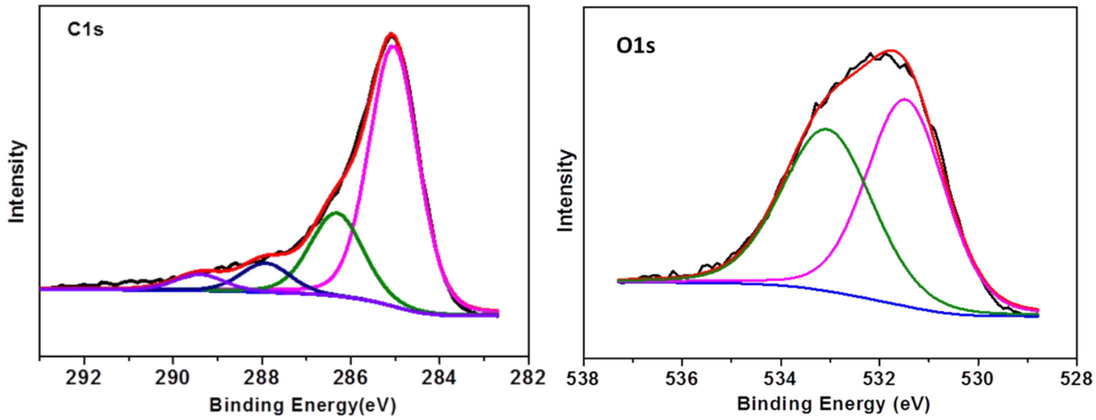


Figure S12. The C1s and O1s spectra of the Co-N-C catalyst. For the C1s spectrum, the four peaks with binding energies at 285, 286.4, 287.9 and 289.4 eV can be assigned to the graphitic C, C-O, C=O and C-OOH, respectively. For the O1s spectrum, the two peaks are ascribed to ketonic C=O groups (531.5 eV) and C−O groups (533.1 eV), respectively.

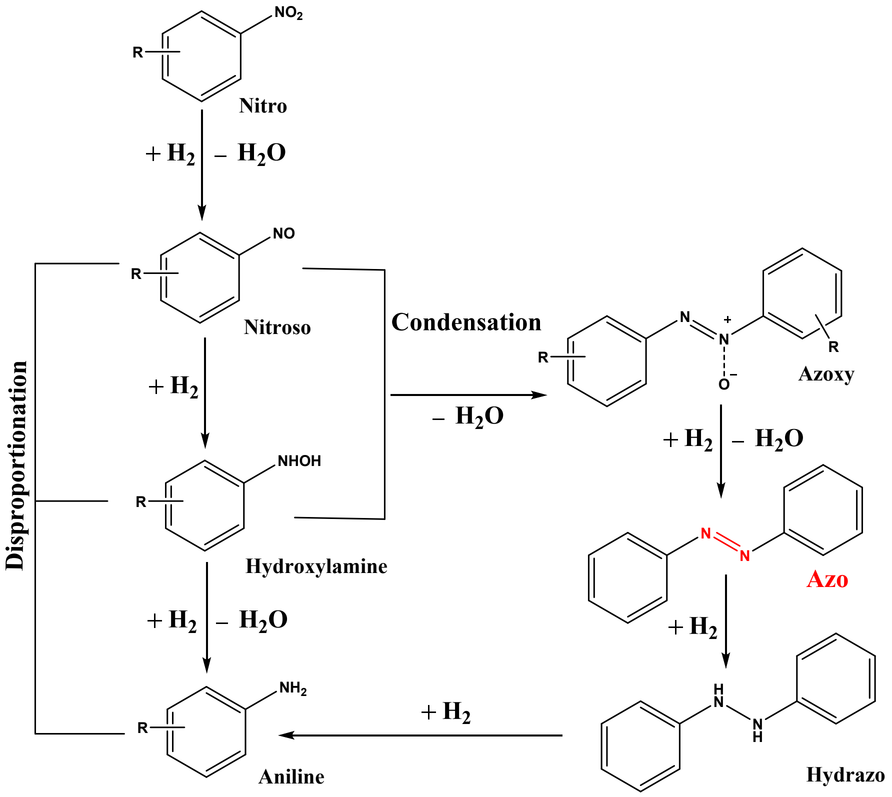


Figure S13. Proposed pathways for the reduction of nitroarenes on Co-N-C catalyst.

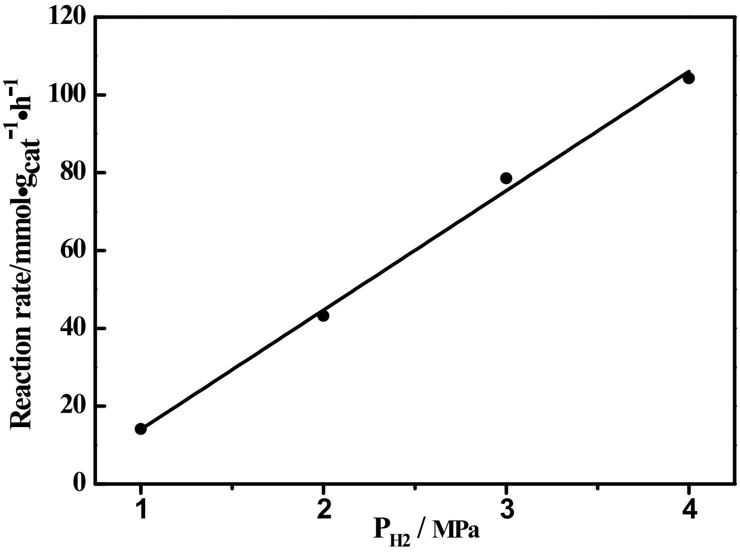


Figure S14. Dependency of the reaction rate on the pressure of H_2.

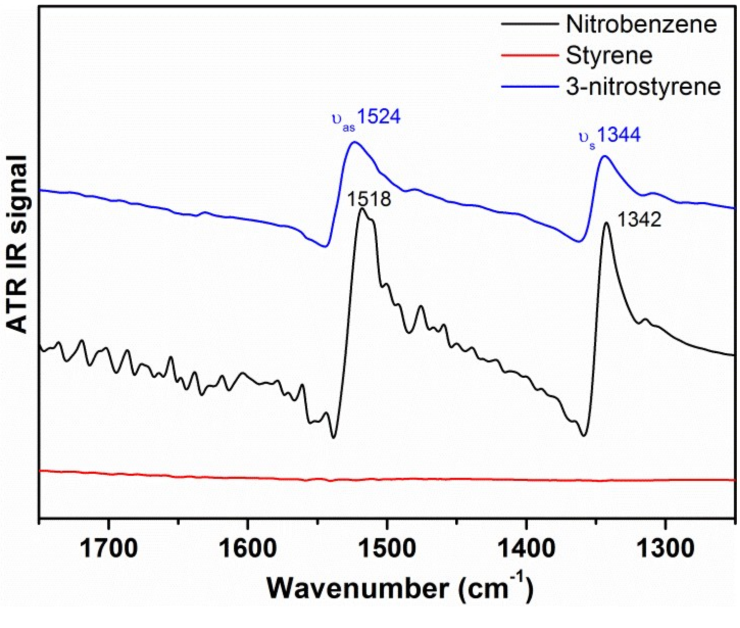


Figure S15. ATR-IR spectra of nitrobenzene, styrene and 3-nitrostyrene adsorbed on the Co-N-C catalyst at 25 ^{o}C.

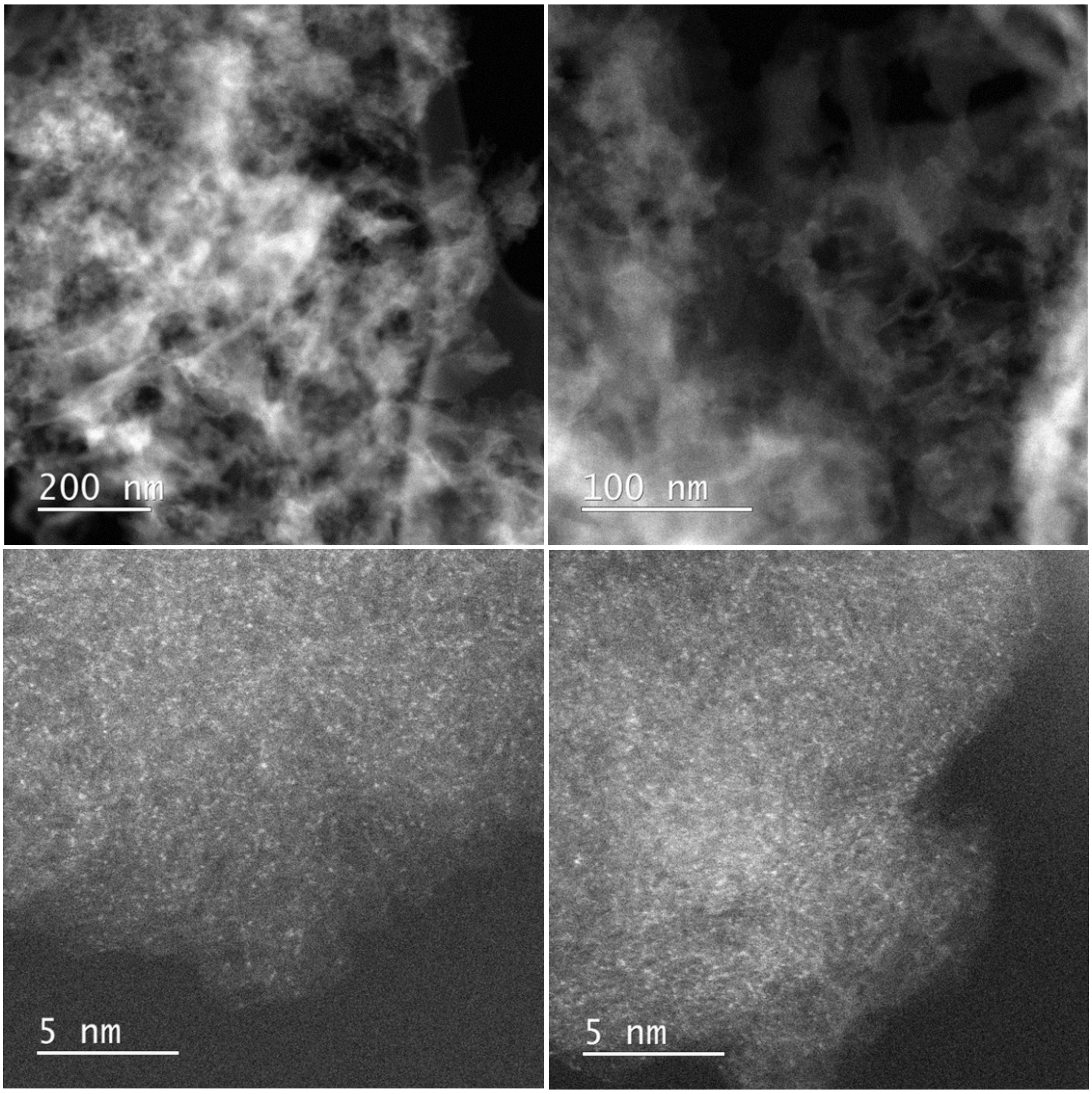


Figure S16. HAADF-STEM images of Co-N-C catalyst after reuse.

Table S1. E_0 value (the first inflection point) of the Co-N-C sample. CoPc = Cobalt phthalocyanine complex, CoPTT = Co porphyrin complex.

Sample	Co foil	Co-N-C -500	Co-N-C -700	Co-N-C -900	$Co(phen)_2 (OAc)_2$	CoPc	CoPTT	Co_3O_4
E_0(eV)	7709	7719.2	7719.4	7709.2	7720.3	7714.8	7712.7	7727

Table S2. The optimized bond parameters of some selected models of Co-N-C, with the corresponding geometric structures.

	CoN_4C_8-1	CoN_4C_8-1-$2O_2$	CoN_4C_{10}-1	CoN_4C_{10}-1-$2O_2$

CoN1 / Å	1.925	1.972	1.894	1.908
CoN2 / Å	1.927	1.972	1.894	1.908
CoN3 / Å	1.927	1.972	1.894	1.908
CoN4 / Å	1.925	1.972	1.894	1.908
N1-Co-N2 /°	82.977	82.481	87.380	87.476
N3-Co-N4 /°	82.950	82.482	87.380	87.471
N1-Co-N4 /°	96.732	97.549	92.618	92.530
N2-Co-N3 /°	97.343	97.488	92.617	92.525
Co-O1 / Å		2.000		2.024
Co-O2 / Å		2.000		2.023
Co-C1 / Å	~2.76	~2.78	~2.74	~2.70
Co-C2 / Å	~3.02	~3.04	~2.96	~2.96

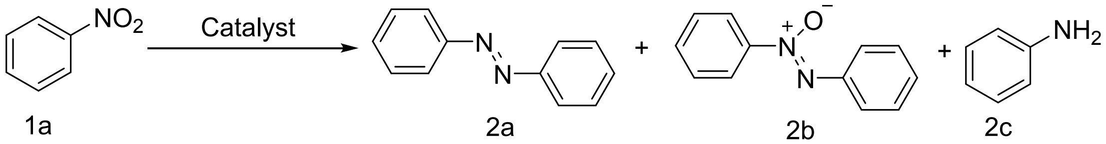
	CoN_4C_{12}-3	CoN_4C_{12}-3-$2O_2$	CoN_4C_{12}-4	CoN_4C_{12}-4-$2O_2$
CoN1 / Å	1.990	1.954	1.899	1.991
CoN2 / Å	1.981	1.946	1.915	1.999
CoN3 / Å	1.990	1.950	1.900	1.984
CoN4 / Å	1.982	1.956	1.915	1.992
N1-Co-N2 /°	87.008	88.172	92.193	88.829
N3-Co-N4 /°	87.037	88.397	92.088	88.741
N1-Co-N4 /°	92.990	91.634	94.907	93.722
N2-Co-N3 /°	92.965	91.547	94.842	93.667
Co-O1 / Å		1.972		1.991
Co-O2 / Å		2.058		2.035

Table S3. Surface composition of Co-N-C catalyst determined by XPS.

Entry	Elements	Atomic (%)
1	C 1s	79.26
2	N 1s	8.66
3	O 1s	11.36
4	Co 2p	0.66
5	Mg 1s	0.06

2. Optimization of the reaction conditions, and control experiment results

Table S4. Optimization of the reaction conditions.



Entry	Solvent	T(°C)	P(MPa)	Base	Conv.(%)	Yield(%)		
						2a	2b	2c
1	Toluene	80	3	NaOH	47	0	33	7
2	THF	80	3	NaOH	100	7	89	0
3	Ethanol	80	3	NaOH	83	0	39	14
4	TBA	80	2	NaOH	100	17	82	0
5	TBA	80	1	NaOH	46	0	46	0
6	TBA	60	3	NaOH	58	0	58	0
7	TBA	40	3	NaOH	30	0	28	0
8	TBA	80	3	Na_2CO_3	14	0	0	5
9	TBA	80	3	$NaHCO_3$	15	0	0	10
10	TBA	80	3	NaOH	100	99	0	0

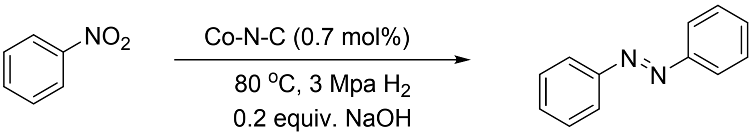
Reaction conditions：3.6 wt% Co-N-C catalyst (0.7 mol%Co), 1.0 mmol nitrobenzene，Base 0.2 mmol, H_2，2 mL solvent，1.5 h. Yield were Determined by GC, using 100 μl Dodecane as an internal standard. TBA=tert butyl alcohol.

Table S5. Hydrogenation of nitrobenzene and styrene over Co-N-C based catalysts.

Feed (mmol)		TOF (h^{-1})	
nitrobenzene	styrene	nitrobenzene	styrene
1	0	271	-
0	1	-	0
0.5	0.5	268	0

Reation conditions：3.6 wt% Co-N-C catalyst (0.7 mol%Co), substrate，NaOH 0.2 mmol, 3 MPa H_2，80℃，20 min, 2 mL TBA solvent, TBA=tert butyl alcohol.

Table S6. Recovery and reuse of Co-N-C based catalyst.



Recycle	1st	2nd	3rd	4th	5th
Reaction time (h)	1.5	2	2.5	3	3.5
Conversion (%)	100	100	100	100	100
Yield (%)	99	94	99	100	98

3. Characterization of the obtained products

All chemicals (Analytical Grade) were used as received without further purification. The aerobic oxidative coupling reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F_{254} plates and visualized under UV (254 nm).

Gas chromatography (GC) analysis was performed on an Agilent 7890B system equipped with a 5% phenyl methyl siloxane capillary column (30 m × 320 μm × 0.25 μm). The GC yield was obtained from the calibration curve using dodecane as an internal standard.

^{1}H NMR spectra were recorded on commercial instruments (500 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). ^{13}C NMR spectra were collected on commercial instruments (125 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). The structures of the known compounds were confirmed by comparison with commercially available compounds or data published in literature.

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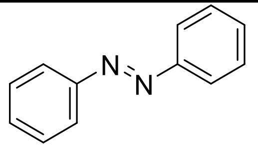
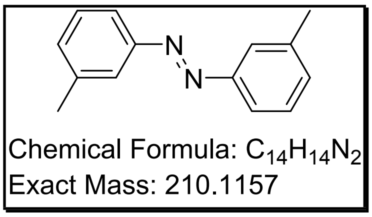


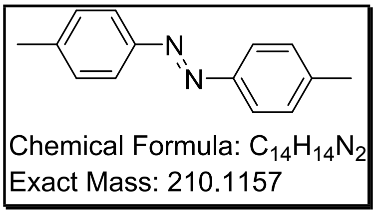
Chemical Formula: $C_{12}H_{10}N_2$
Exact Mass: 182.0844

Azobenzene (1a): This reaction was carried out according to general procedure with nitrobenzene(102 μL, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow red solid (97% yield). ^{1}H NMR (500 MHz, CDC$_{13}$) δ 7.95 – 7.90 (m, J = 7.3 Hz, 4H), 7.54 – 7.46 (m, 6H).^{13}C NMR (126 MHz, CDC$_{13}$) δ 152.67, 130.92, 129.03, 122.81.



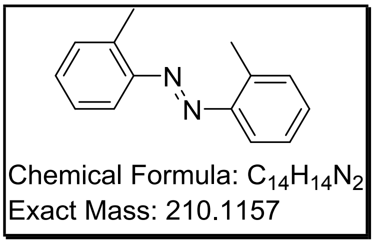
Chemical Formula: $C_{14}H_{14}N_2$
Exact Mass: 210.1157

3,3’-Dimethylazobenzene(2a): This reaction was carried out according to general procedure with 3-nitrotoluene (119 µL, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow red solid (94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 6.5 Hz, 4H), 7.67 – 7.63 (m, 2H), 7.53 (d, J = 7.5 Hz, 2H), 2.70 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.81, 138.94, 131.68, 128.88, 122.89, 120.46, 21.36.



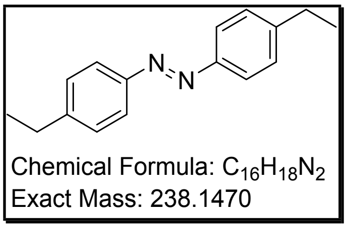
Chemical Formula: $C_{14}H_{14}N_2$
Exact Mass: 210.1157

4,4’-Dimethylazobenzene(3a): This reaction was carried out according to general procedure with 4-nitrotoluene (137.1 mg, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow solid (88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.3 Hz, 4H), 7.54 (d, J = 8.1 Hz, 4H), 2.66 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.83, 141.17, 129.68, 122.71, 21.45.



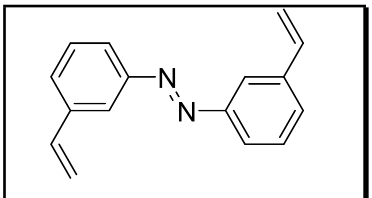
Chemical Formula: $C_{14}H_{14}N_2$
Exact Mass: 210.1157

2,2’-Dimethylazobenzene(4a): This reaction was carried out according to general procedure with 2-nitrotoluene (118 µL, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a red solid (63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.9 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.28 – 7.24 (m, 2H), 2.74 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.11, 137.93, 131.21, 130.61, 126.31, 115.84, 17.54.



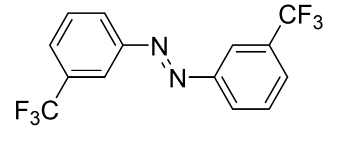
Chemical Formula: $C_{16}H_{18}N_2$
Exact Mass: 238.1470

2,2’-Dimethylazobenzene(5a): This reaction was carried out according to general procedure with 4-nitroethylbenzene (135 μL, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow solid (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 4H), 7.33 (d, J = 7.4 Hz, 4H), 2.72 (q, J = 7.5 Hz, 4H), 1.29 (ddd, J = 7.6, 4.3, 1.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.46, 151.10, 147.45, 128.51, 122.83, 28.84, 15.41.



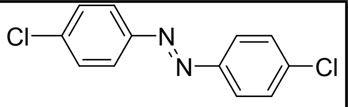
Chemical Formula: $C_{16}H_{14}N_2$
Exact Mass: 234.1157

1,2-Bis(3-vinylphenyl)diazene (6a): This reaction was carried out according to general procedure with 3-nitrostyrene (145 μL, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow solid (99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, J = 1.7 Hz, 2H), 7.74 (dt, J = 7.6, 1.6 Hz, 2H), 7.46 – 7.35 (m, 4H), 6.73 (dd, J = 17.6, 10.9 Hz, 2H), 5.82 – 5.77 (m, 2H), 5.27 (d, J = 10.9 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.94, 138.71, 136.24, 129.23, 128.78, 122.17, 120.62, 115.05.



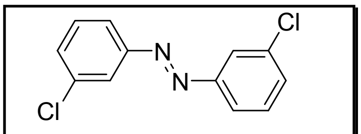
Chemical Formula: $C_{14}H_8F_6N_2$
Exact Mass: 318.0592

1,2-Bis(3-(trifluoromethyl)phenyl)diazene(7a): This reaction was carried out according to general procedure with 3-nitrobenzotrifluoride (137 μL, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a red solid (85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 2H), 8.14 (d, J = 7.9 Hz, 2H), 7.78 (d, J = 7.7 Hz, 2H), 7.68 (t, J = 7.8 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 152.18, 131.99, 131.72, 129.79, 127.84 (d, J = 3.6 Hz, 1H), 126.45, 124.80, 122.64, 119.72 (q, J = 3.7 Hz, 1H).



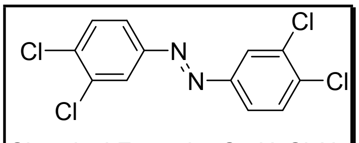
Chemical Formula: $C_{12}H_8Cl_2N_2$
Exact Mass: 250.0065

1,2-Bis(4-chlorophenyl)diazene (8a): This reaction was carried out according to general procedure with 4-chloronitrobenzene (158 mg, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow solid (97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 4H), 7.49 (d, J = 7.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.79, 137.20, 129.36, 124.15.



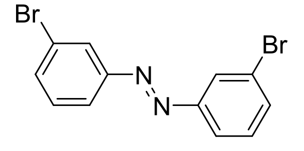
Chemical Formula: $C_{12}H_8Cl_2N_2$
Exact Mass: 250.0065

1,2-Bis(3-chlorophenyl)diazene (9a): This reaction was carried out according to general procedure with 3-chloronitrobenzene (158 mg, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow solid (98% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.83 (d, J = 4.0 Hz, 2H), 7.46 (d, J = 3.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.11, 135.22, 131.16, 130.15, 122.55, 121.89.



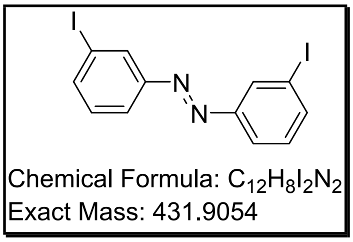
Chemical Formula: $C_{12}H_6Cl_4N_2$
Exact Mass: 317.9285

1,2-Bis(3,4-dichlorophenyl)diazene(10a): This reaction was carried out according to general procedure with 3,4-dichloronitrobenzene (202.1 mg, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow solid (99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.02, 135.68, 133.66, 130.99, 124.05, 123.01.



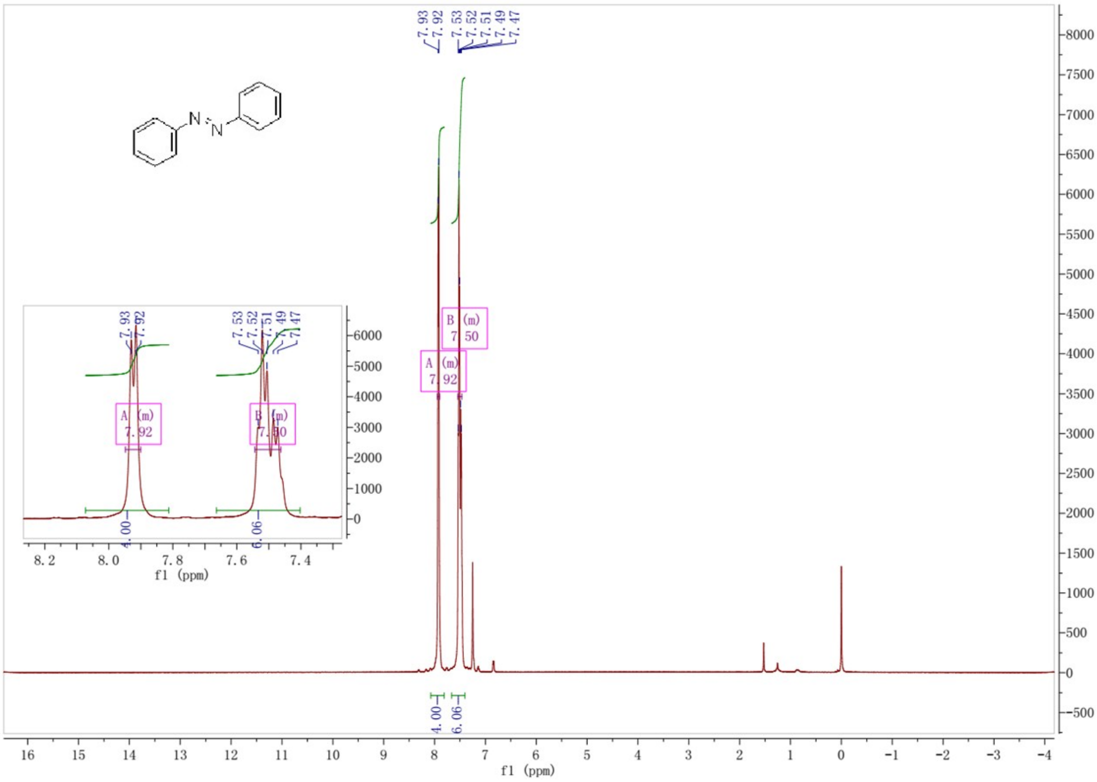
Chemical Formula: $C_{12}H_8Br_2N_2$
Exact Mass: 337.9054

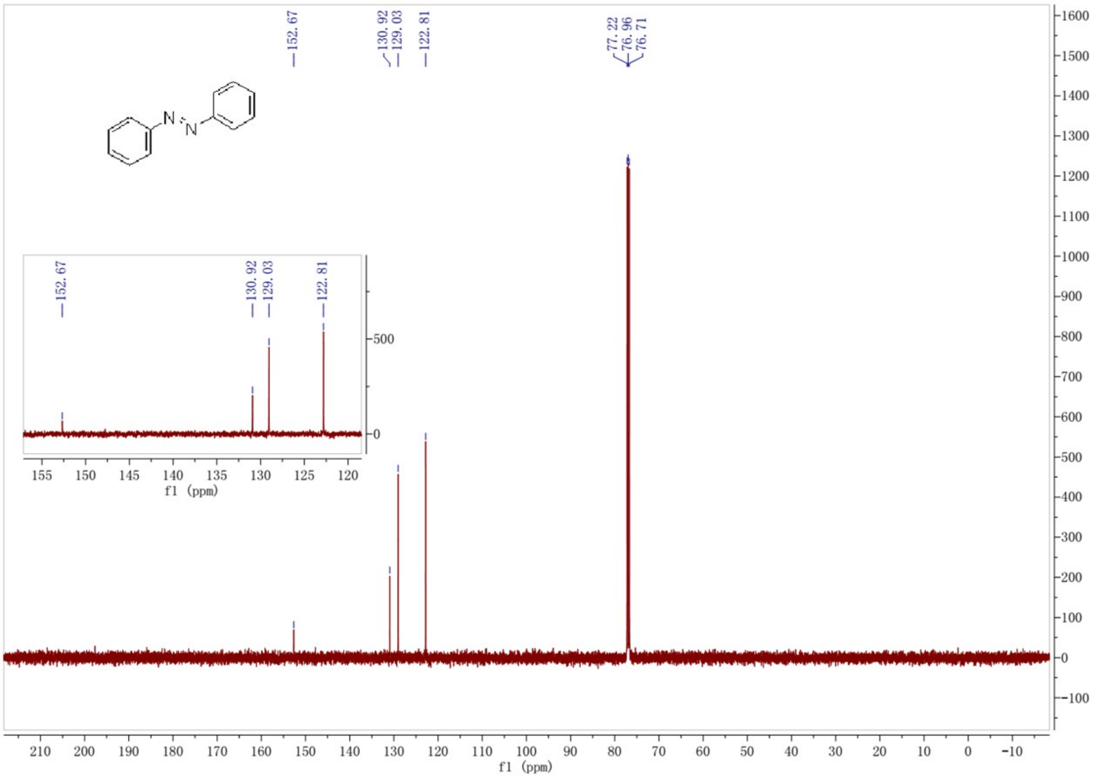
1,2-Bis(3-bromophenyl)diazene(11a): This reaction was carried out according to general procedure with 1-bromo-3-nitrobenzene (206.1 mg, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow solid (96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.19, 134.06, 130.44, 124.77, 123.15, 123.07.



1,2-Bis(3-iodophenyl)diazene(12a): This reaction was carried out according to general procedure with 3-iodonitrobenzene (249.1 mg, 1 mmol, 1 equiv). The crude reaction mixture was purified on silica gel (2% ethyl acetate/petroleum ether) to afford the product as a yellow solid (94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 2H), 7.90 (d, J = 7.8 Hz, 2H), 7.81 (d, J = 7.7 Hz, 2H), 7.31 – 7.26 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.06, 139.96, 130.77, 130.64, 123.63, 94.48.

4. Copy of ^{1}H NMR and ^{13}C NMR spectra for products

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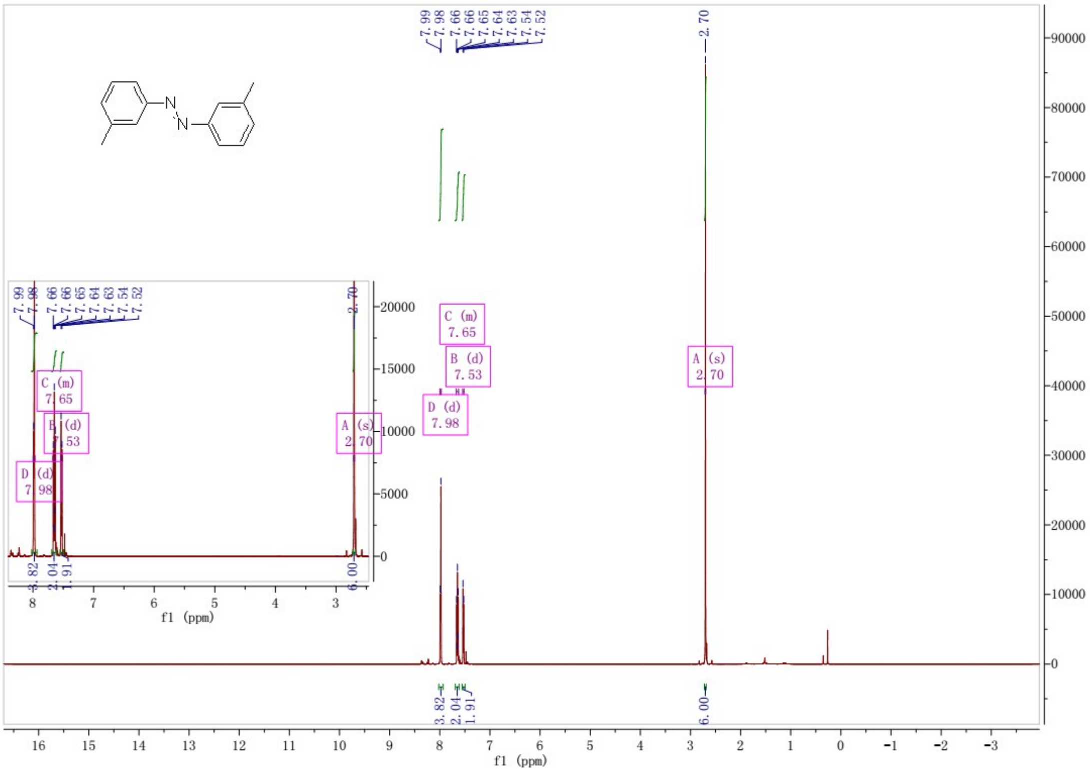
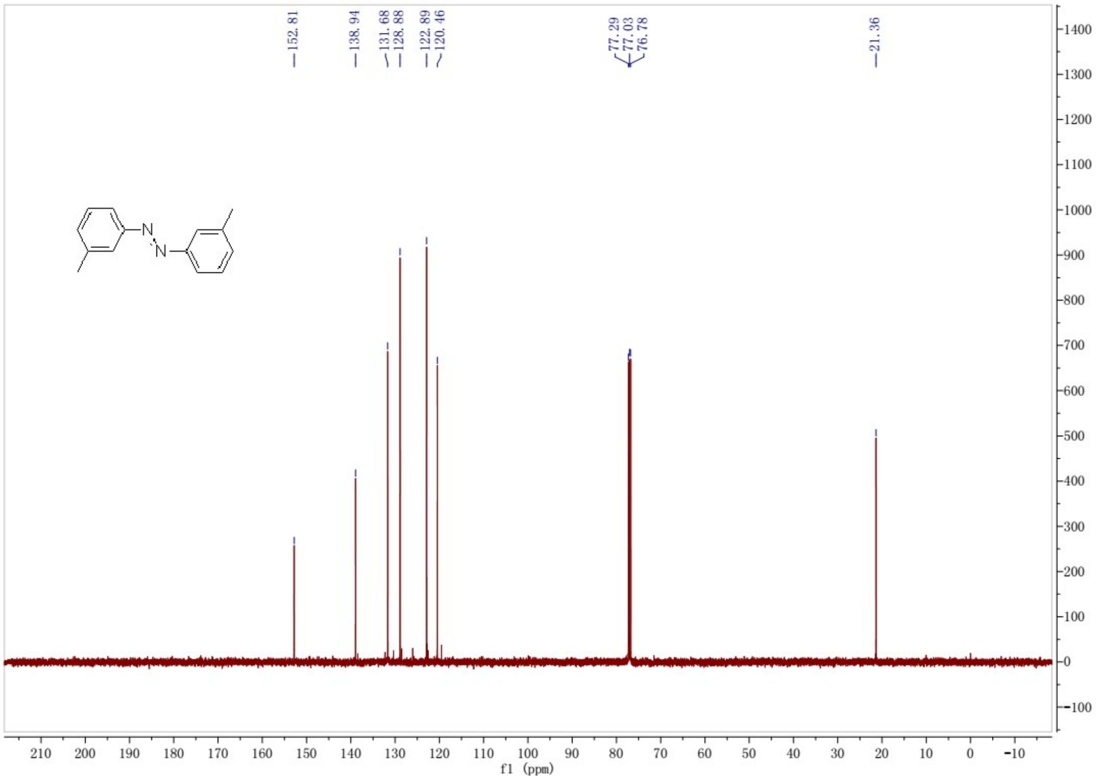
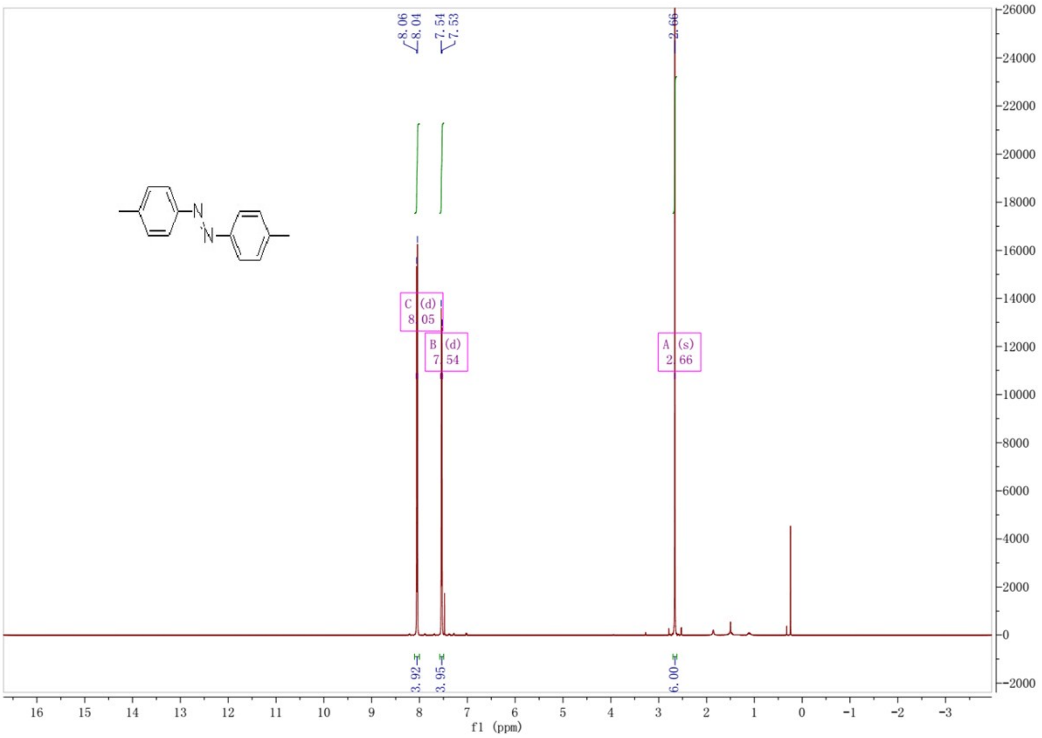
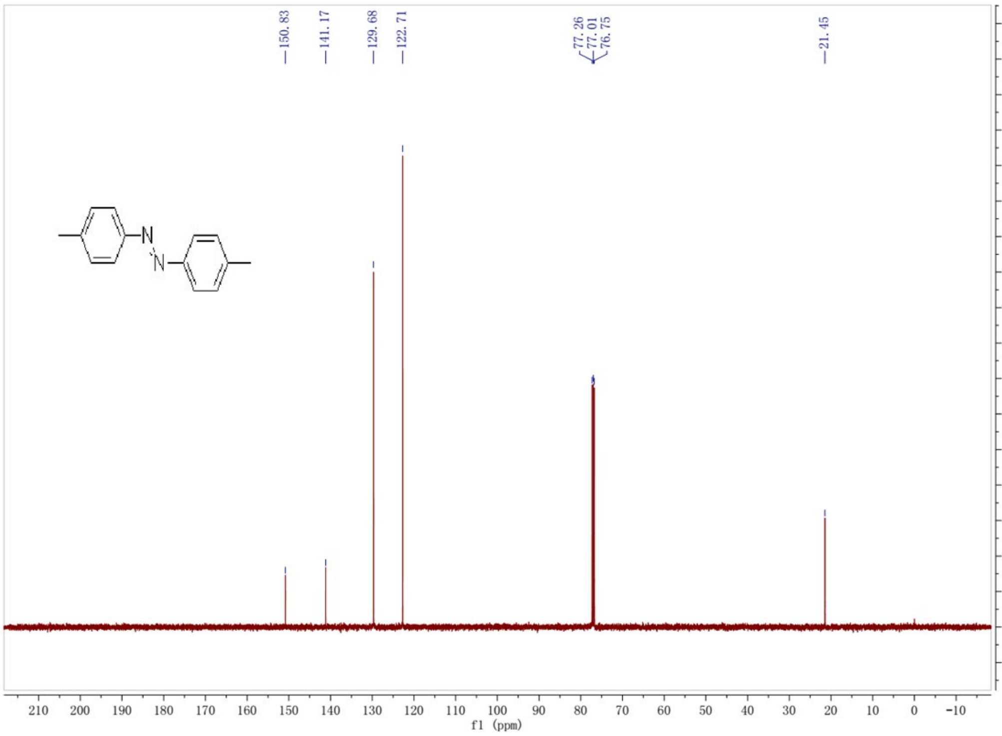
130.92
129.03
122.81
77.22
76.96
76.71
N
N
152.67
130.92
129.03
122.81
500
0
155 150 145 140 135 130 125 120
f1 (ppm)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.99
7.98
7.66
7.66
7.65
7.64
7.63
7.54
7.52
2.70
N
N
C (m)
7.65
B (d)
7.53
D (d)
7.98
A (s)
2.70
3.82
2.04
1.91
6.00
20000
15000
10000
5000
0
8 7 6 5 4 3
f1 (ppm)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


152.81
138.94
131.68
128.88
122.89
120.46
77.29
77.03
76.78
21.36
N
N
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.06
8.04
7.54
7.53
2.66
N
N
C (d)
8.05
B (d)
7.54
A (s)
2.66
3.92
3.95
6.00
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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129.68
122.71
77.26
77.01
76.75
21.45
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N
f1 (ppm)
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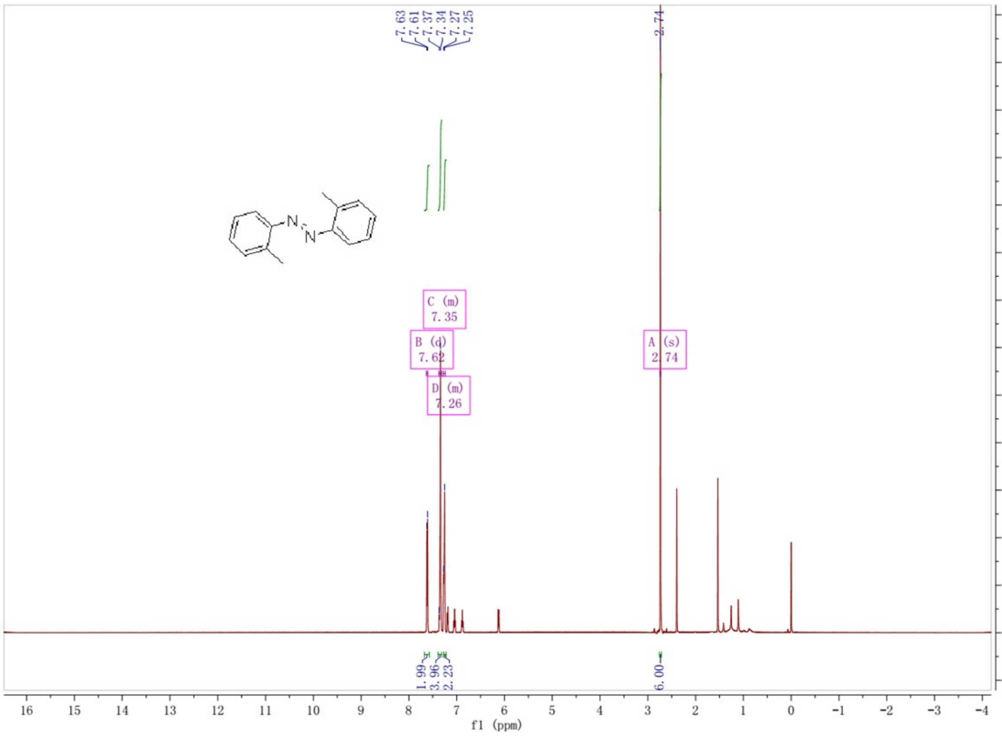
1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100


7.63
7.61
7.37
7.34
7.27
7.25
2.74
N
N
C (m)
7.35
B (d)
7.62
D (m)
7.26
A (s)
2.74
1.99
3.96
2.23
6.00
f1 (ppm)
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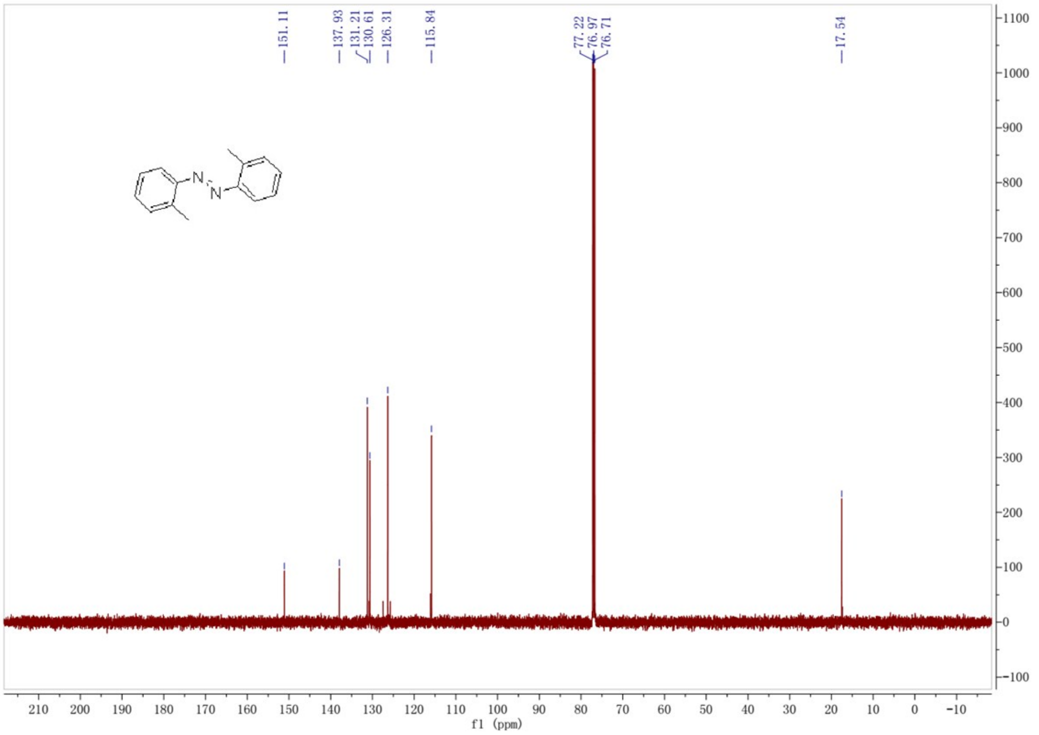
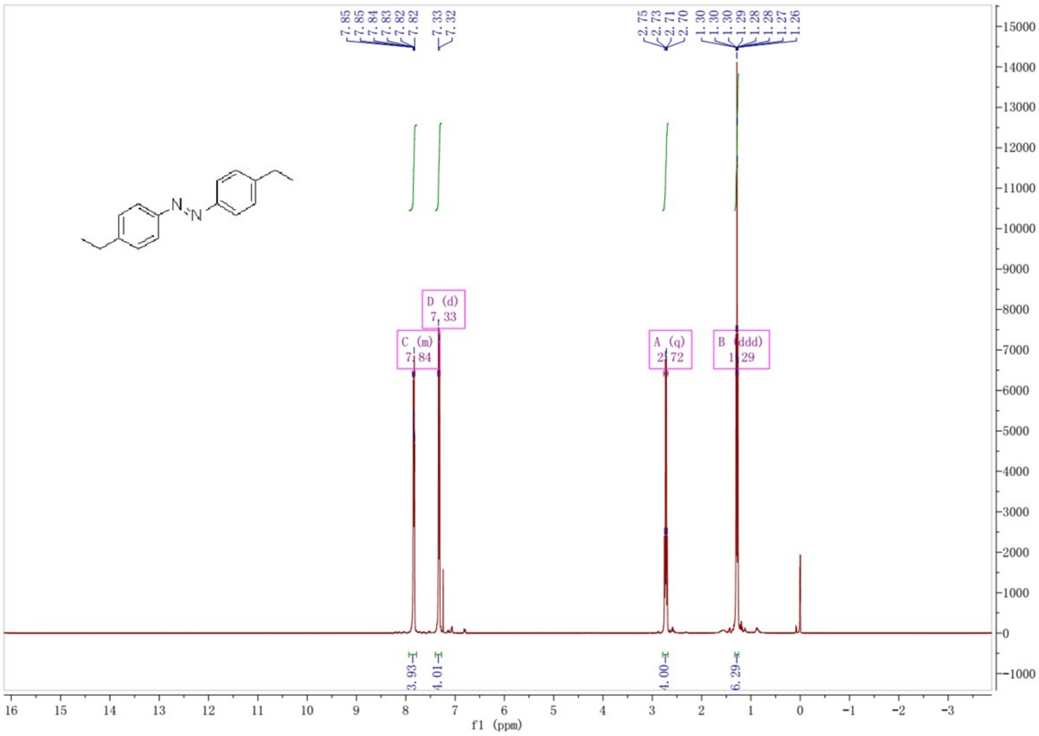
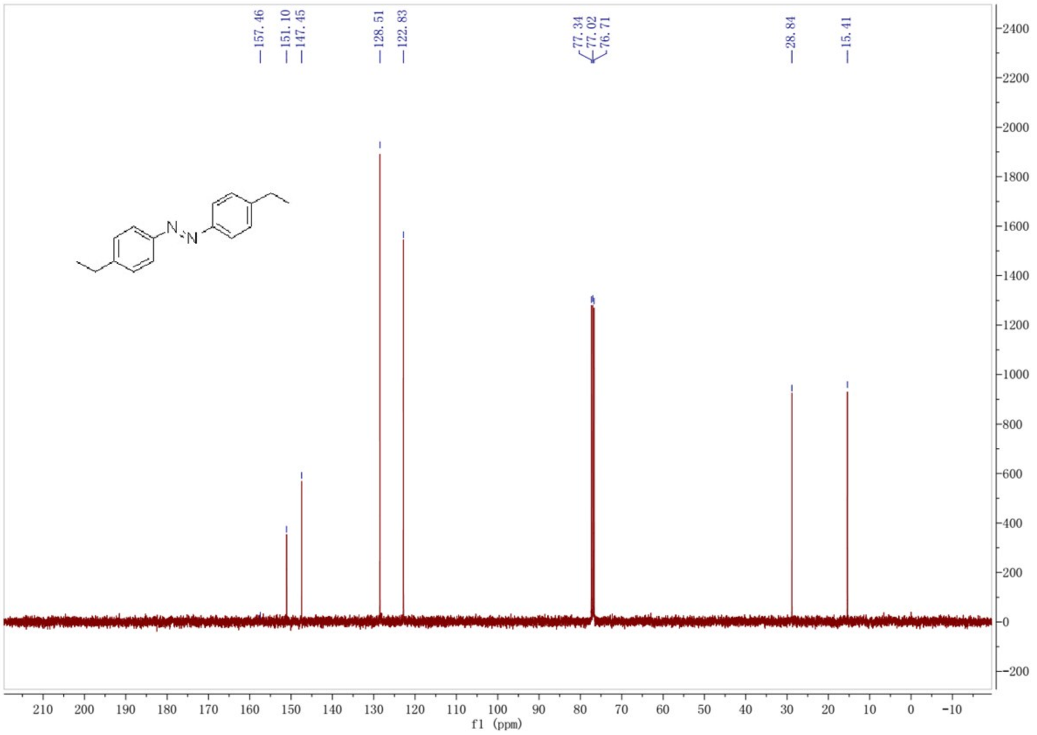
13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000



151.11
137.93
131.21
130.61
126.31
115.84
77.22
76.97
76.71
17.54
N
N
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



7.85
7.85
7.84
7.83
7.82
7.82
7.82
7.33
7.32
2.75
2.73
2.71
2.70
1.30
1.30
1.30
1.29
1.28
1.28
1.27
1.26
N
N
D (d)
7.33
C (m)
7.84
A (q)
2.72
B (ddd)
1.29
3.93
4.01
4.00
6.29
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


157.46
151.10
147.45
128.51
122.83
77.34
77.02
76.71
28.84
15.41
N
N
2400
2200
2000
1800
1600
1400
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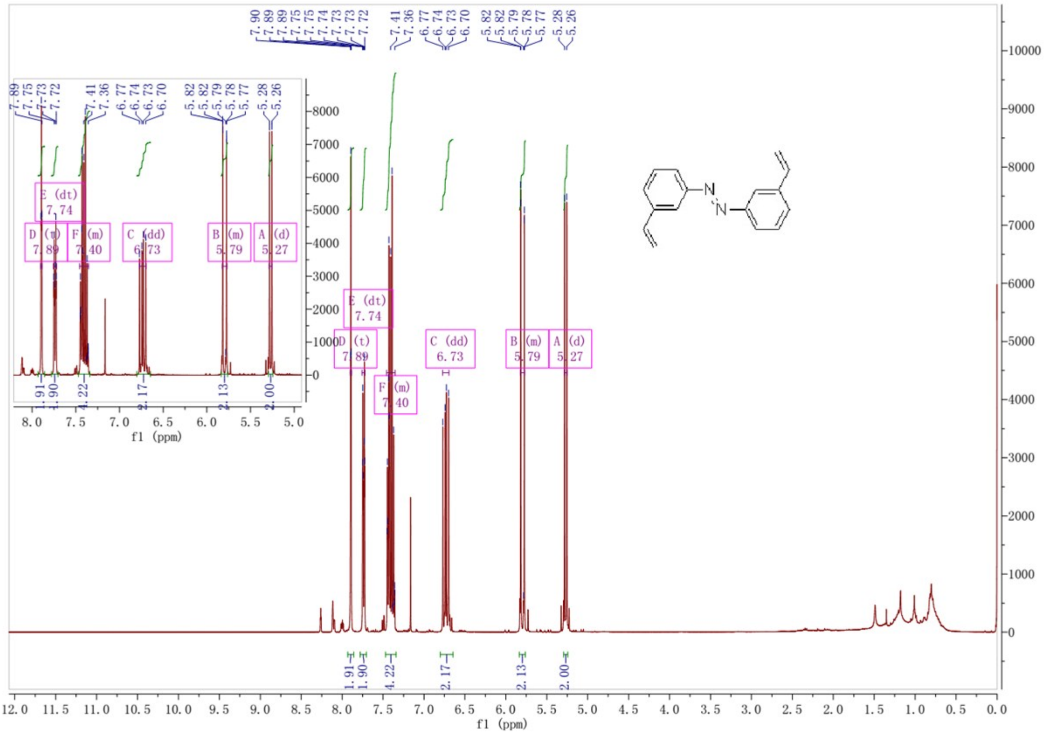
800
600
400
200
0
−200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.89
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7.75
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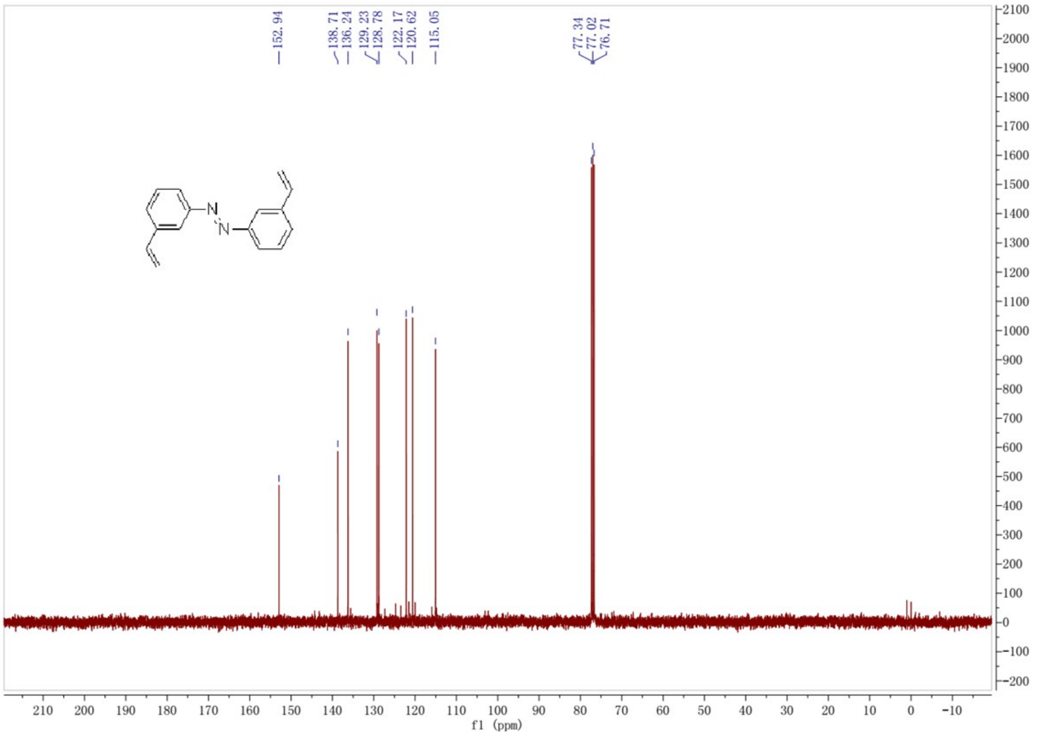
7.73
7.73
7.72
7.41
7.36
6.77
6.74
6.73
6.70
5.82
5.82
5.79
5.78
5.77
5.28
5.26
E (dt)
7.74
D (t)
7.89
F (m)
7.40
C (dd)
6.73
B (m)
5.79
A (d)
5.27
D (m)
7.89
1.91
1.90
4.22
2.17
2.13
2.00
N
N
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
8000
7000
6000
5000
4000
3000
2000
1000
0
8.0 7.5 7.0 6.5 6.0 5.5 5.0
f1 (ppm)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.23
128.78
122.17
120.62
115.05
77.34
77.02
76.71
N
N
f1 (ppm)
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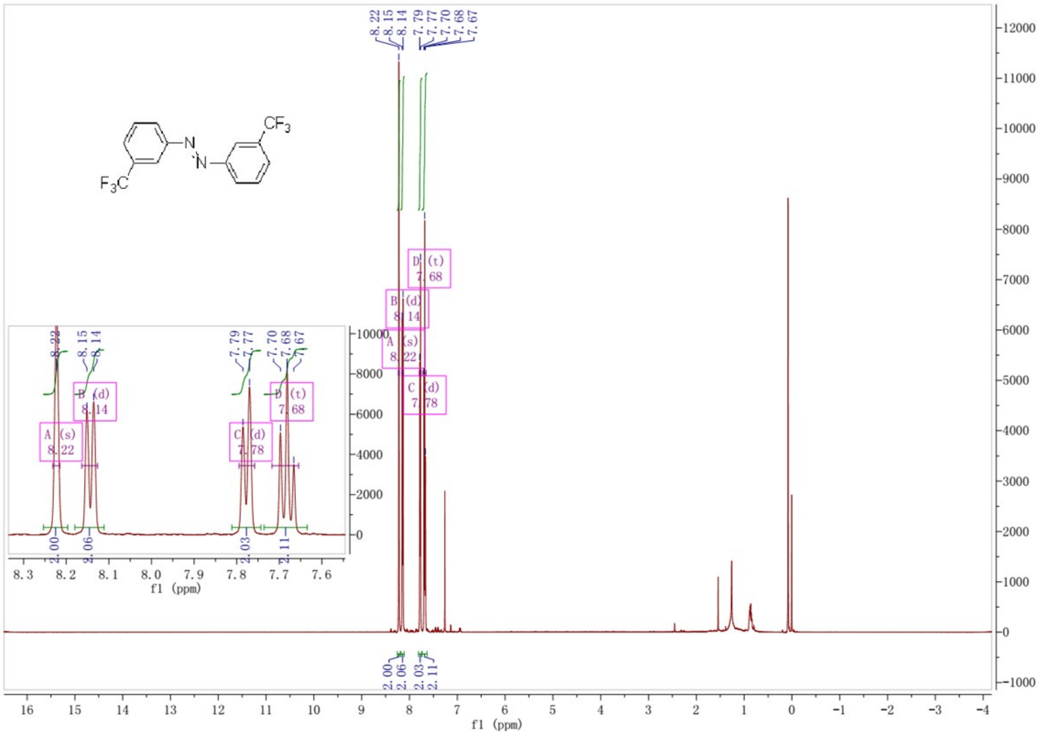
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8.15
8.14
7.79
7.77
7.70
7.68
7.67
CF3
F3C
N
N
A (s) 8.22
B (d) 8.14
C (d) 7.78
D (t) 7.68
2.00
2.06
2.03
2.11
f1 (ppm)
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6
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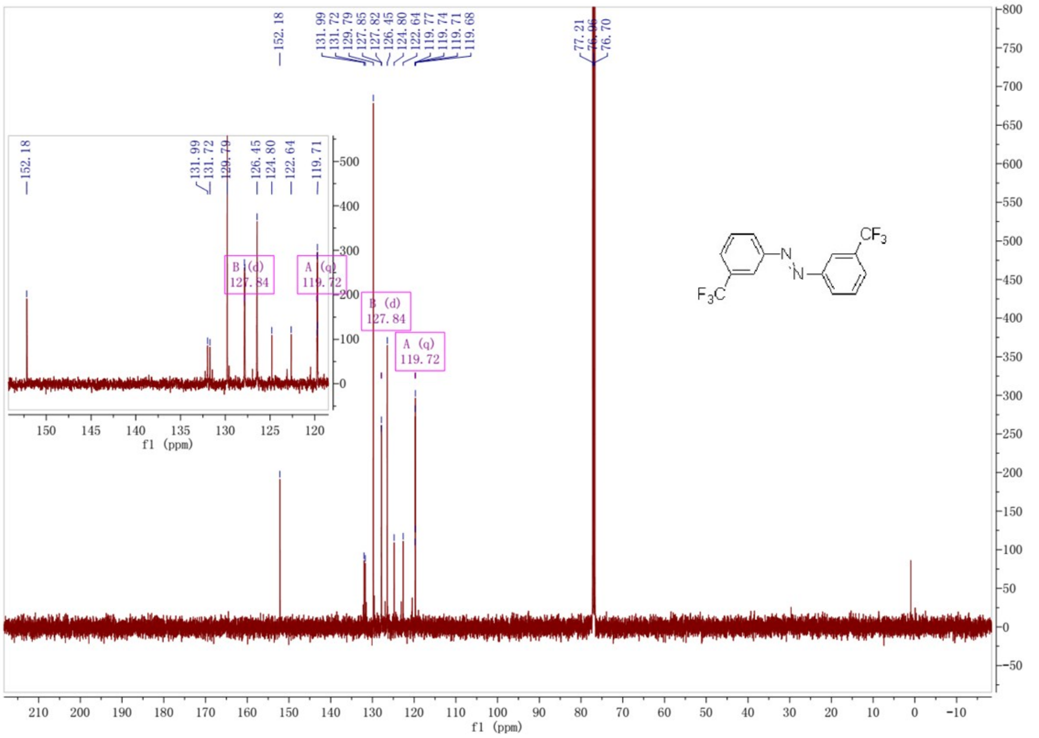
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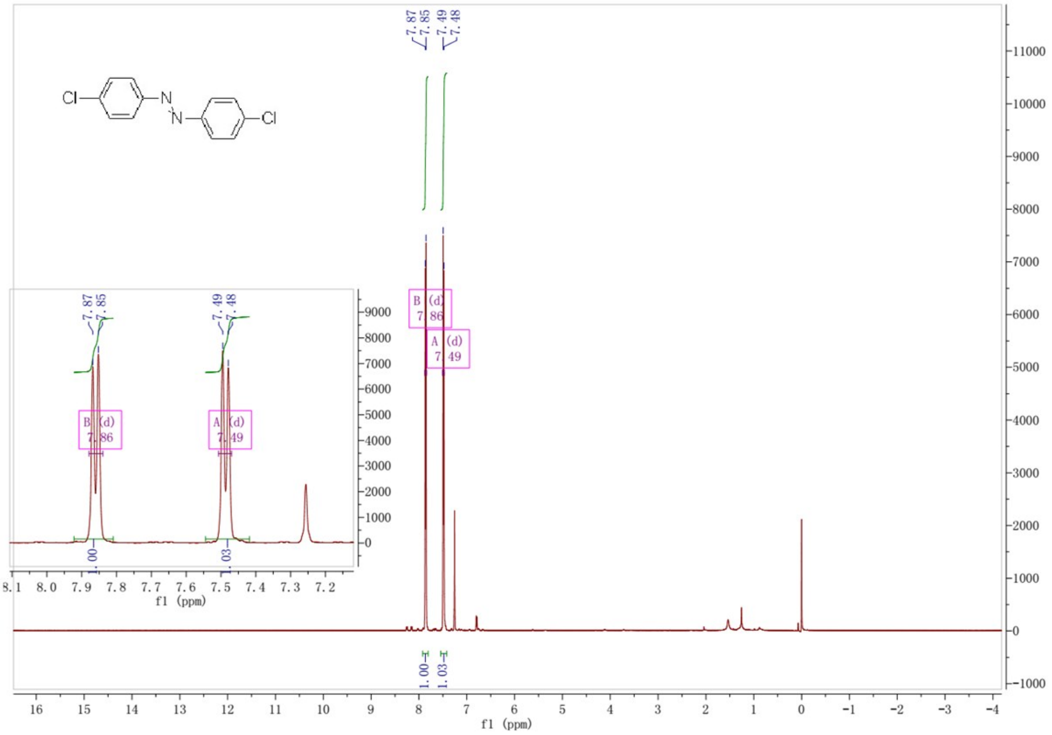
131.99
131.72
129.79
127.85
127.82
126.45
124.80
122.64
119.77
119.74
119.71
119.68
77.21
76.96
76.70
B (d)
127.84
A (q)
119.72
CF_3
F_3C
N
N
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50
150 145 140 135 130 125 120
500 400 300 200 100 0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7.85
7.49
7.48
B (d)
7.86
A (d)
7.49
1.00
1.03
Cl
Cl
N
N
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
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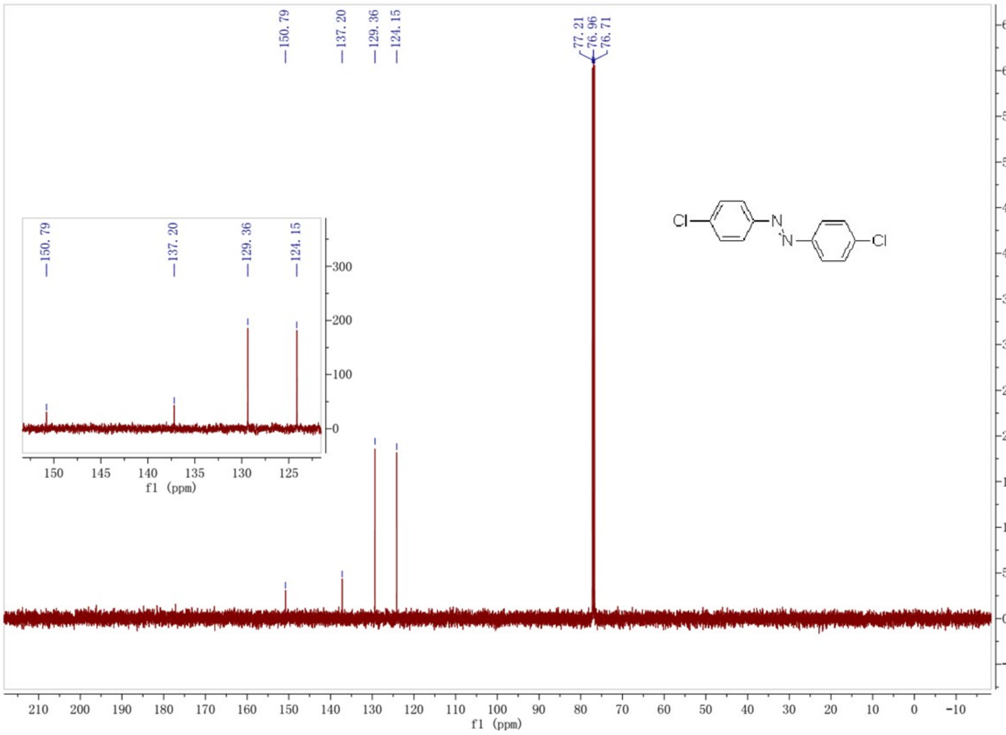
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77.21
76.96
76.71
Cl
N
N
Cl
f1 (ppm)
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550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
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90
80
70
60
50
40
30
20
10
0
-10
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200
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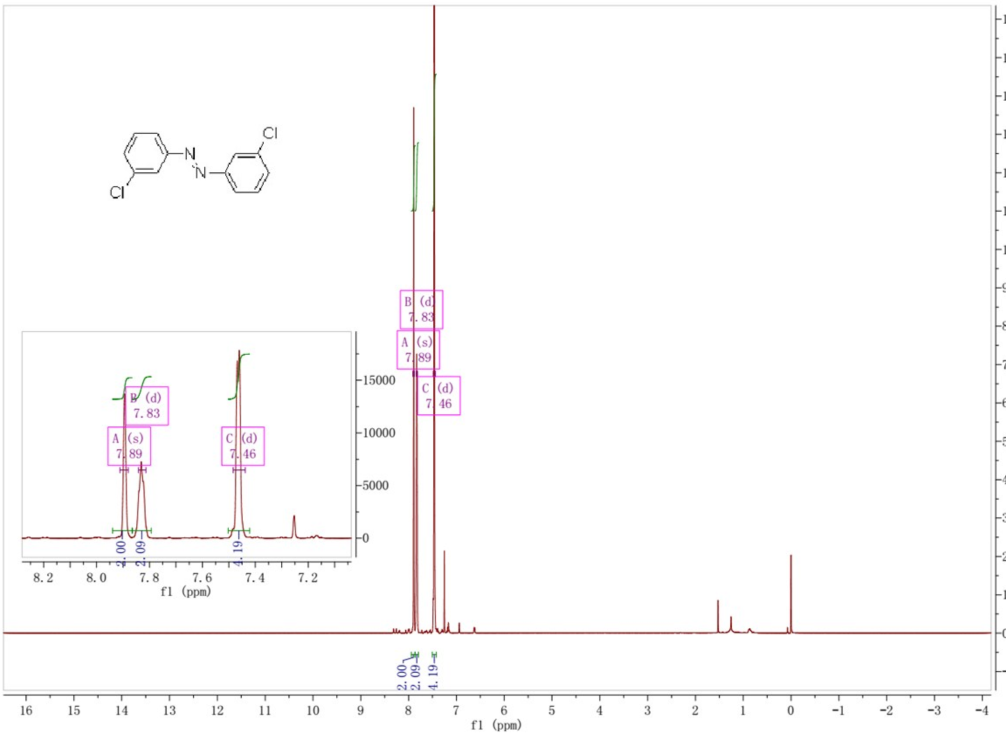
145
135
125


Cl
N
N
Cl
A (s)
7.89
B (d)
7.83
C (d)
7.46
2.00
2.09
4.19
f1 (ppm)
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15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
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-3
-4
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8.0
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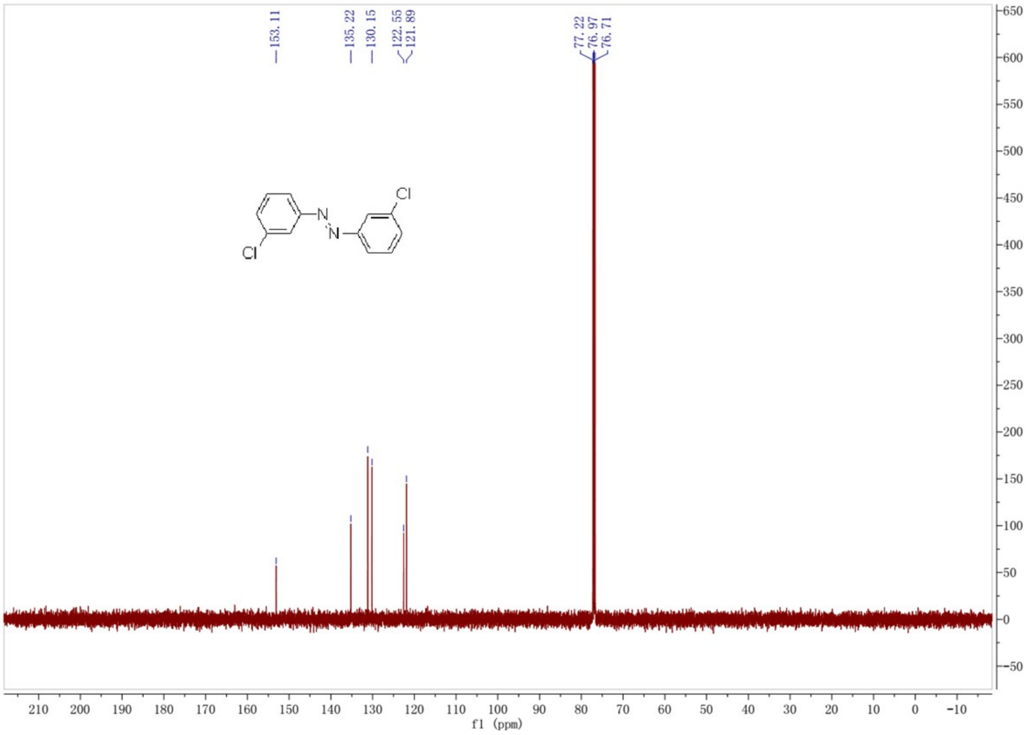
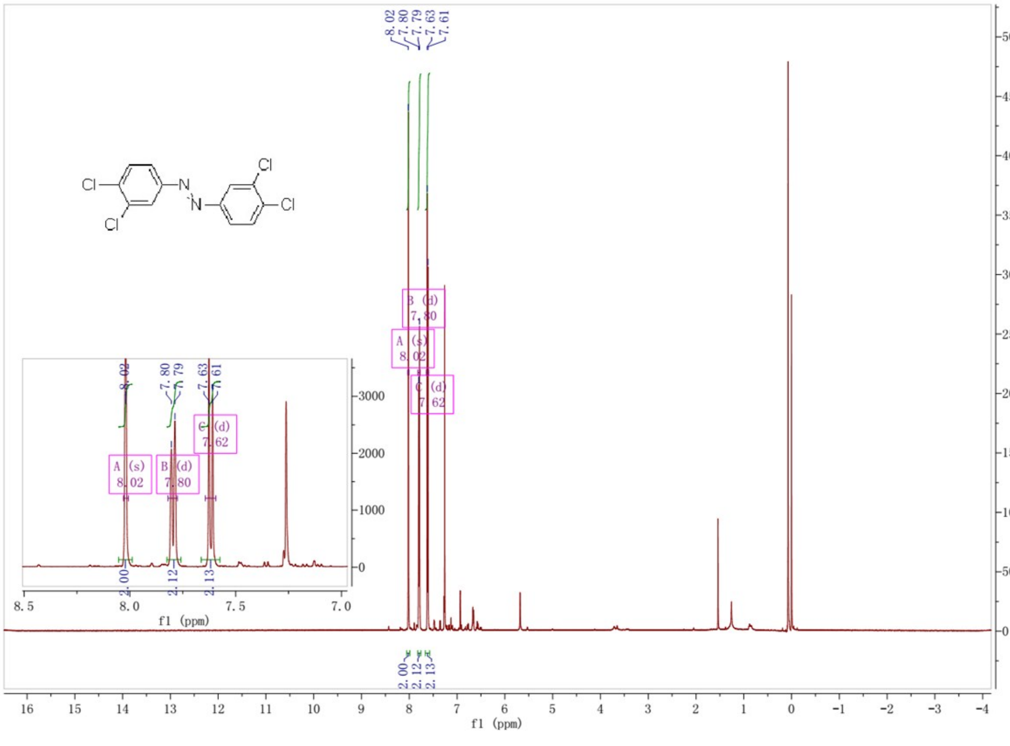
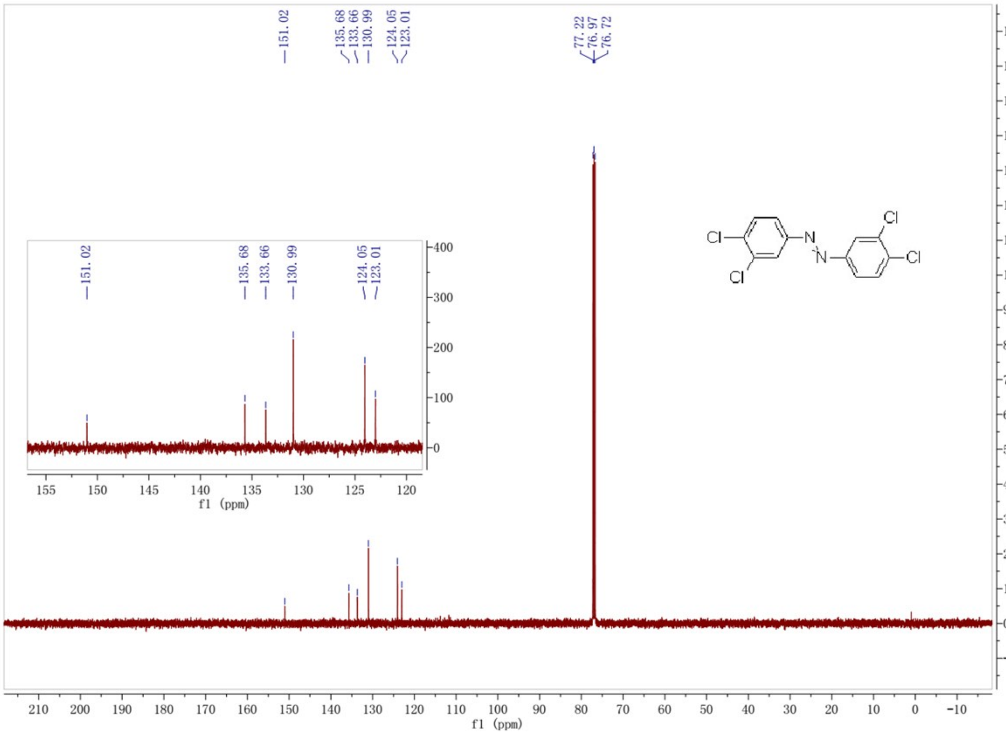
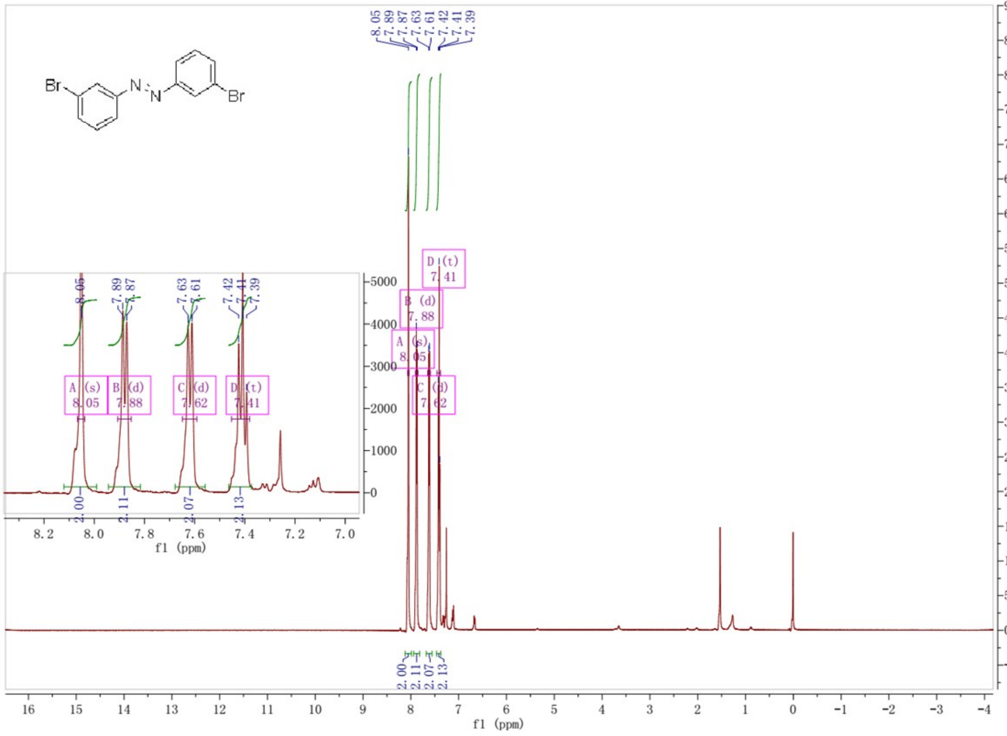
7.4
7.2


153.11
135.22
130.15
122.55
121.89
77.22
76.97
76.71
Cl
N
N
Cl
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

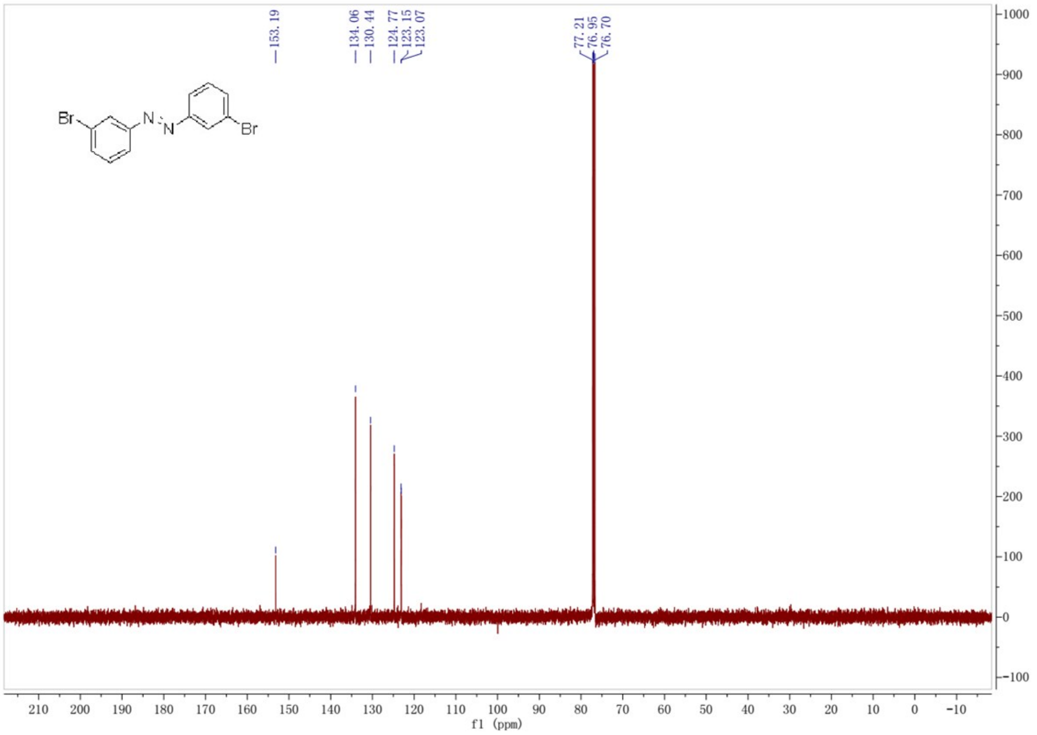

8.02
7.80
7.79
7.63
7.61
Cl
Cl
N
N
Cl
Cl
A (s)
8.02
B (d)
7.80
C (d)
7.62
2.00
2.12
2.13
8.5 8.0 7.5 7.0
f1 (ppm)
3000
2000
1500
1000
0
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

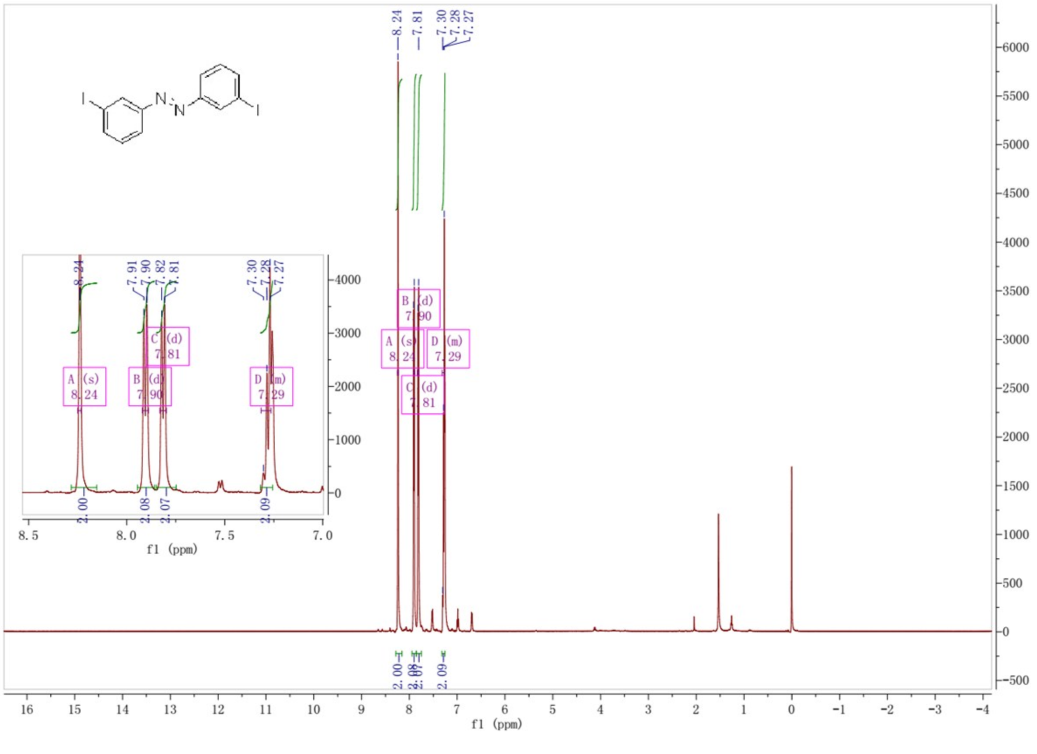


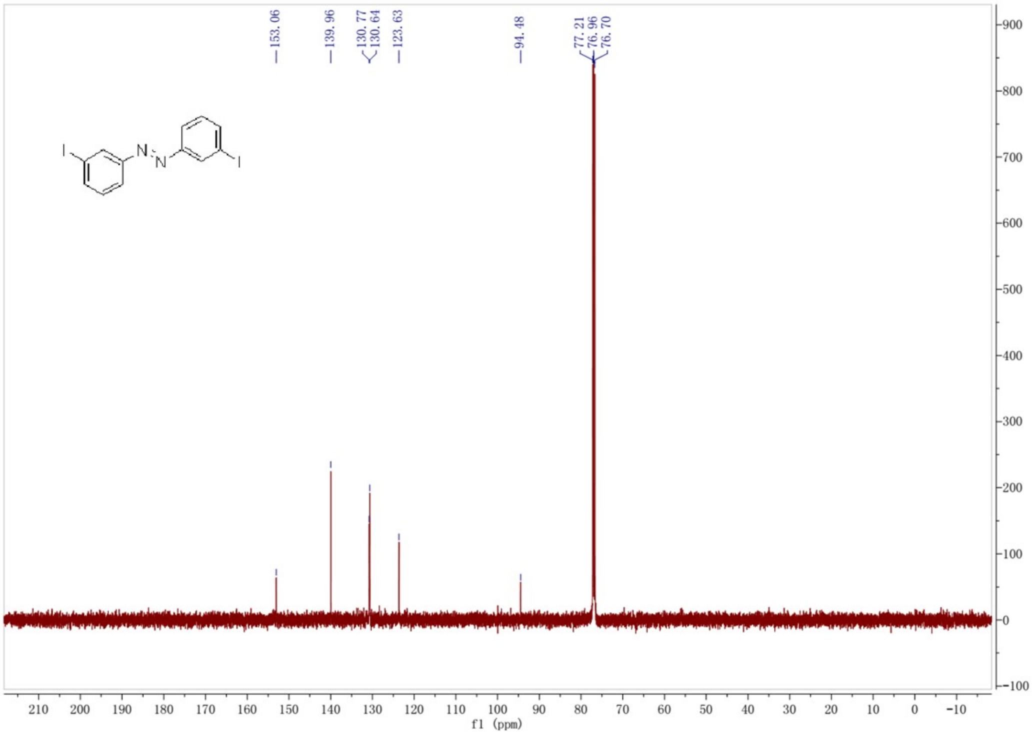
151.02
135.68
133.66
130.99
124.05
123.01
77.22
76.97
76.72
Cl
Cl
N
N
Cl
Cl
f1 (ppm)
f1 (ppm)



8.05
7.89
7.87
7.63
7.61
7.42
7.41
7.39
Br
N
N
Br
A (s) 8.05
B (d) 7.88
C (d) 7.62
D (t) 7.41
2.00
2.11
2.07
2.13
f1 (ppm)
f1 (ppm)


153.19
134.06
130.44
124.77
123.15
123.07
77.21
76.95
76.70
Br
N
N
Br
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
1000 900 800 700 600 500 400 300 200 100 0 -100


8.24
7.81
7.30
7.28
7.27
I
N
N
I
7.91
7.90
7.82
7.81
A (s) 8.24
B (d) 7.90
C (d) 7.81
D (m) 7.29
2.00
2.08
2.07
2.09
8.5 8.0 7.5 7.0
f1 (ppm)
4000 3000 2000 1000 0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500


153.06
139.96
130.77
130.64
123.63
94.48
77.21
76.96
76.70
I
N
N
I
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)