Photocatalyzed Oxidative Dehydrogenation of Hydrazobenzenes to Azobenzenes

Haiping Lv,[a,§] Ronibala Devi Laishram,[a,§] Jiayan Li,[a] Yongyun Zhou,[a,*] Dandan Xu,[a] Sagar More,[a] Yuze Dai,[a] Baomin Fan[a,b*]

[a]YMU-HKBU Joint Laboratory of Traditional Natural Medicine, Yunnan Minzu University, Kunming, 650500, China

[b]Key Laboratory of Chemistry in Ethnic Medicinal Resources, Yunnan Minzu University, Kunming, 650500, China.

Fax: (+86)-871-65946330; E-mail addresses: zhouyongyundf@163.com (Yongyun Zhou), FanBM@ynni.edu.cn (Baomin Fan)

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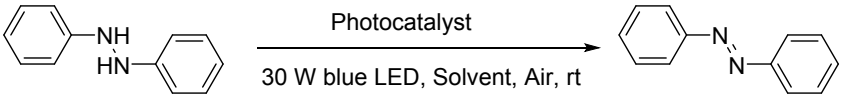
1. General Information

All commercially available reagents were obtained from commercial suppliers and used without further purification. All catalytic experiments were carried out using standard techniques. Chromatography was carried out over silica gel (Innochem 200–300 mesh) and TLC was performed using silica gel 60 F254 (Merck) plates. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker NMR spectrometer in $CDCl_3$ using TMS as an internal reference with chemical shift values reported in ppm. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The blue LED [30.0 W, λ_{max} = 450 nm] was used as a visible light source. Steady-state fluorescence measurements were performed with Cary Eclipse Fluorescence Spectrophotometer NO. G9800A of Agilent technologies. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique. The diphenyl hydrazine derivatives (except for commercially available **1a**) were prepared by modified literature procedures. [1, 2]

2. Procedure for the oxidative hydrogenation of hydrazobenzenes

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (2 ml) followed by the addition of 1,2-Diphenyl hydrazine **1a** (0.3 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **2a** (54.4 mg, 99%).

3. Optimization of the reaction conditions



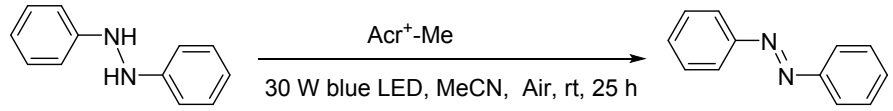
1a **2a**

Table S1 Optimization of the reaction conditions

Entry	photosensitizer	Time (h)	Yield (%)[a, b]
1	Mes-Acr$^+$-Me (10-mehyl-9-mesitylacridinium)	22	87
2	DCB (1,4-dicyanobenzene)	72	46
3	FLN (fluorenone)	72	66
4	AQ （anthraquinone）	72	81
5	TPT$^+$ (triphenylpyrylium)	56	92
6	Acr$^+$-Me (10-mehylacridinium)	25	99
7	Ph-Acr$^+$-Me (10-mehyl-9-phenylacridinium)	27	93
8	Mes-Acr$^+$-TriMe (9-Mesityl-2,7,10-trimethylacridinium)	24	94
9	AcrF$^+$ (acriflavin)	26	90
10	[FL] (fluorescein)	72	59
11	[EY] (eosin y)	38	88
12	[RB] (rose bengal)	23	95
13	MB$^+$ (methylene blue)	52	95
14	V_{B2} (Riboflavin)	72	55
15	$[Ru(bpy)_3]Cl_2$	42	83
16	$Ir(ppy)_3$	48	69
17	DCE	67	93
18	Toluene	48	97
19	THF	30	96
20	1,4-dioxane	32	92
21	EtOH	48	93
22	Acetone	72	88
23	Acr$^+$-Me (3%)	28	98
24	Acr$^+$-Me (1%)	52	98
25	Acr$^+$-Me (0.1%)	120	97
26[c]	Acr$^+$-Me	72	9
27	/	72	Trace
28[d]	Acr$^+$-Me (10-mehylacridinium)	5	98%
29[e]	Acr$^+$-Me (10-mehylacridinium)	72	NR

[a] Reaction conditions: Reaction were conducted with **1a** (0.3 mmol), photosensitizer (5 mol %) in 2.0 mL of dry solvent (0.15 M) at room temperature in the open air under 30 W LED irradiated, unless otherwise noted. NR= no reaction. [b] Isolated yield. [c] No blue LED. [d] Reaction under O_2. [e] Reaction under Ar.

4. The gram scale reaction



1a
6 mmol (1.105 g)

2a
1.061g (97%)

To a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (40 ml) 1,2-Diphenyl hydrazine **1a** (6 mmol, 1.103 g) was added. The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **2a** in 97% yield (1.061 g).

5. UV-Visible absorption spectra of reactants and product

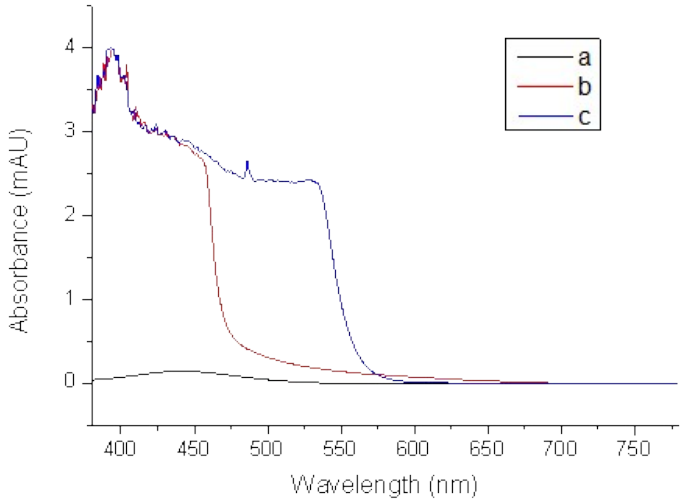


Figure S1 UV-Visible absorption spectra of reactants and product: (a) absorption spectra of 1,2-Diphenyl hydrazine (**1a**, 0.3 mml) in MeCN (2.0 ml). (b) absorption spectra of 1,2-Diphenyl hydrazine (**1a**, 0.3 mml) and 10-methylacridinium perchlorate(0.015 mmol) in MeCN (2.0 ml). (c) absorption spectra of diphenyldiazene(1a, 0.3 mml) in MeCN (2.0 ml).

6. Fluorescence quenching experiments

Emission intensities were recorded using a Cary Eclipse Fluorescence Spectrophotometer NO. G9800A of Agilent technologies. The photocatalyst 10-methylacridinium perchlorate (5.0 µM in MeCN) and quencher **1a** (diphenyldiazene) was added into a srewtop 1.0 cm quartz cuvette in increasing concentrations of (20, 40, 60, 80 100 µM in MeCN). Each sample was irradiated at 380 nm and the emission spectrum was recorded. Plots of intensity of emission (490 nm) vs concentration of quencher are shown according to the SternVolmer equation.[3,4]

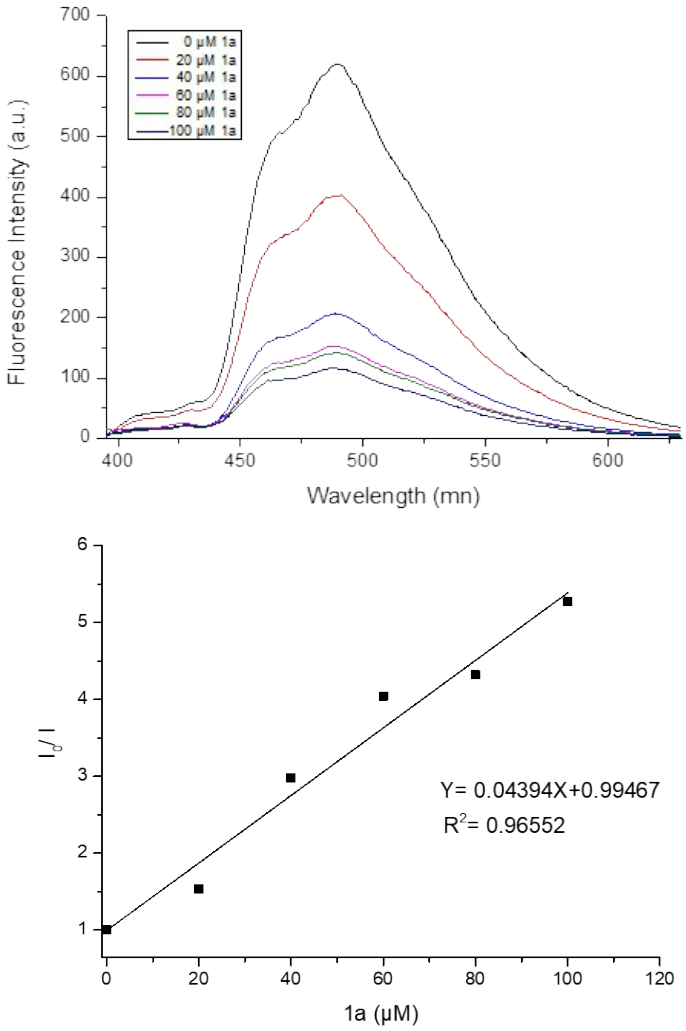
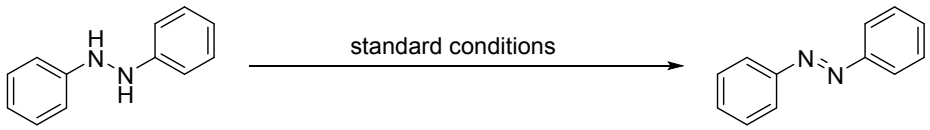


Figure S2. Luminescence quenching study

7. Control experiment

7.1. Light/Dark experiments



1a 2a

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (2 ml) followed by the addition of 1,2-Diphenyl hydrazine **1a** (0.3 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature. Six hours later, the light was turned off. The reaction mixture was taken and concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **2a**. After another 6 hours, the light was turned on and the reaction mixture was taken again and purified to give the desired product **2a**. The procedure was repeated four times and generated the profile of the reaction under the light off/on over time.

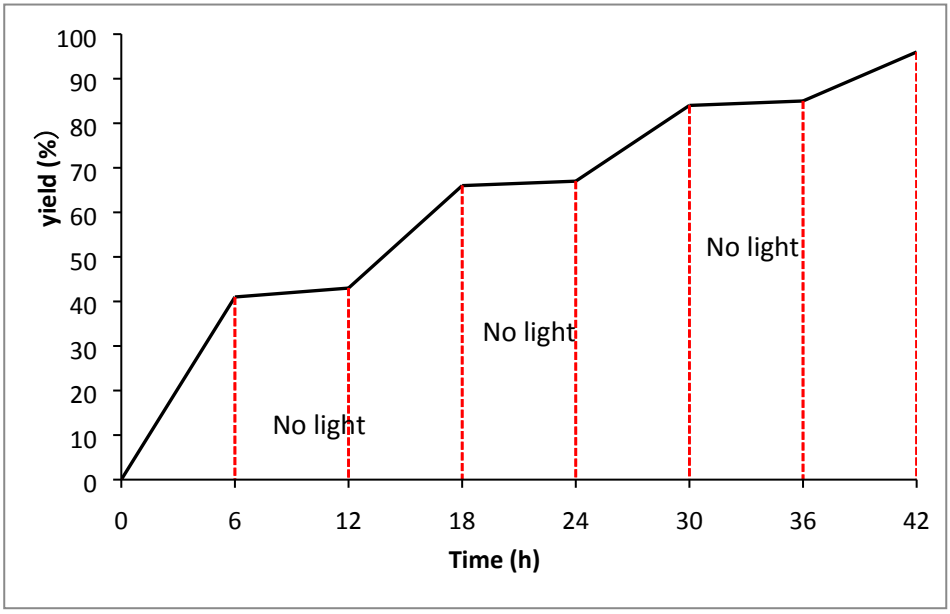
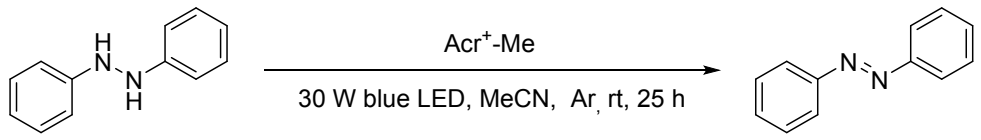


Figure S3. On/Off LED irradiation experiment for the synthesis of **2a**

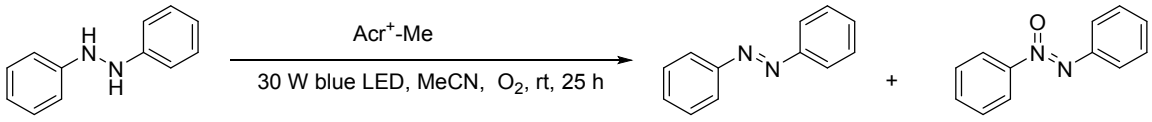
7.2. The model reaction was carried under Ar



1a 2a (Trace)

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (2 ml) followed by the addition of 1,2-Diphenyl hydrazine **1a** (0.3 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. The solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent, only a trace amount of the desired product **2a** was detected.

7.3. The model reaction was carried under O_2

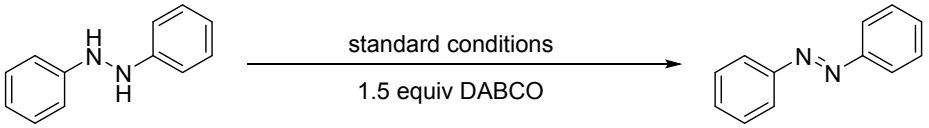


1a 2a (98%)

In an oven-dried reaction tube with a magnetic stirring bar to a solution of 10-methylacridinium perchlorate (5 mol%), MeCN (2 ml) was added 1,2-Diphenyl hydrazine **1a** (0.3 mmol), The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 5 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **2a** (53.7 mg, 98%).

8. Mechanistic Investigation

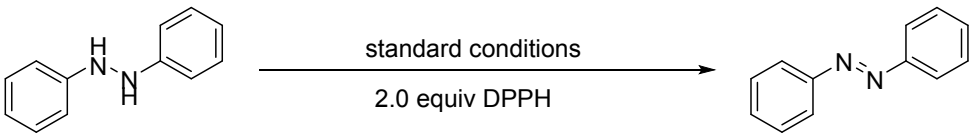
8.1 Singlet oxygen quenching experimental



1a 2a(97 %)

In an oven-dried reaction tube containing a magnetic stirring bar a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (2 ml) was charged followed by the addition of 1,2-Diphenyl hydrazine **1a** (0.3 mmol) and DABCO (0.45 mmol, 1.5 equiv). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **2a** (53.1 mg, 97%).

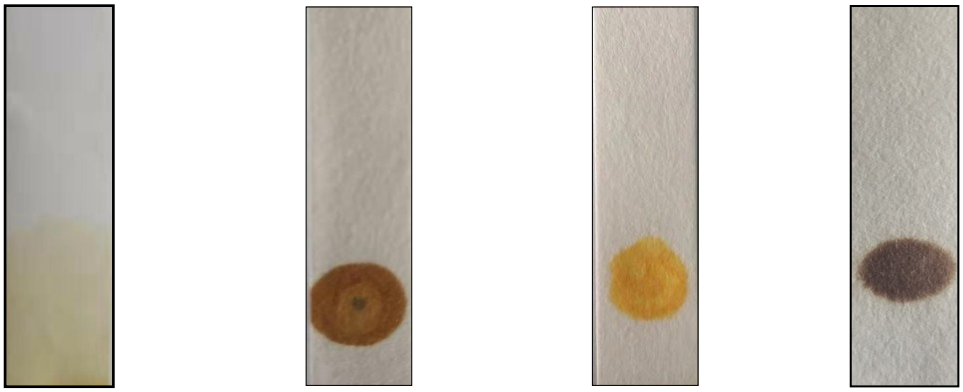
8.2 $O_2^{\cdot-}$ Radical Quenching Experiment



1a 2a (Trace)

In an oven-dried reaction tube with a magnetic stirring bar a solution of 10-methylacridinium perchlorate (5 mol%), MeCN (2 ml), 1,2-Diphenyl hydrazine **1a** (0.3 mmol) was added DPPH (0.6 mmol, 2 equiv). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give only a trace amount of product **2a**.

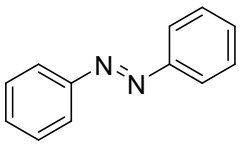
8.3 Test for hydrogen peroxide production



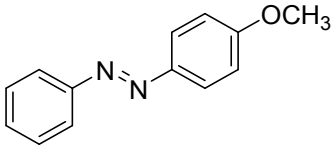
(a)	(b)	(c)	(d)
Addition of reaction mixture at 0 h to (a)	Addition of reaction mixture at 25 h to (a)	Addition of product (b)	Addition of H_2O_2

Figure S4. Test for production of hydrogen peroxide. (a) Reaction mixture of 0.30 mmol of **1a** and 5 mol% of 10-methylacridinium perchlorate in 2.0 ml MeCN under Standard condition. (b) Reaction mixture of 0.30 mmol of diphenyldiazene **2a** in 2.0 ml MeCN.

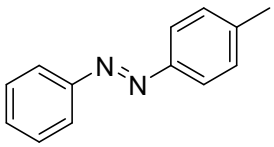
9. Characterization data for the products



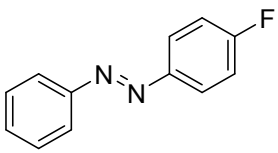
1,2-diphenyldiazene (**2a**): Orange solid; m.p. 66-68 ℃; 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.93 (m, 4H), 7.56–7.52 (m, 4H), 7.51–7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 131.1, 129.2, 123.0; HRMS(EI$^+$): m/z calcd for $C_{12}H_{10}N_2$ [M]$^+$: 182.0844. Found 182.0849.



1-(4-methoxyphenyl)-2-phenyldiazene (**2b**) : Red solid; m.p. 52-54 ℃; 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.89 (m, 4H), 7.54–7.43 (m, 3H), 7.03 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 152.9, 147.1, 130.5, 129.2, 124.9, 122.7, 114.3, 55.7; HRMS(EI$^+$): m/z calcd for $C_{13}H_{12}N_2O$[M]$^+$: 212.0950. Found 212.0945.

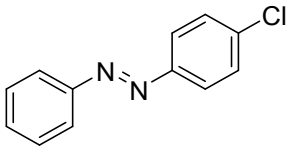


1-phenyl-2-(*p*-tolyl)diazene (**2c**): Orange solid; m.p. 65-67 ℃; 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.55–7.51 (m, 2H), 7.49–7.46 (m, 1H), 7.33 (d, J = 8.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 150.7, 141.5, 130.7, 129.7, 129.0, 122.8, 122.7, 21.5; HRMS(EI$^+$): m/z calcd for $C_{13}H_{12}N_2$ [M]$^+$:196.1000. Found 196.0997.

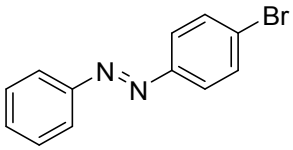


1-(4-fluorophenyl)-2-phenyldiazene (**2d**) : Yellow solid; m.p. 76-78 ℃; 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.91 (m, 4H), 7.55–7.47 (m, 3H), 7.24–7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5(d, $^1J_{CF}$ = 250.6 Hz), 152.6, 149.3(d, $^4J_{CF}$ = 2.9

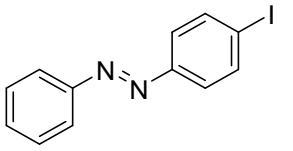
Hz), 131.2, 129.3, 125.0 (d, $^3J_{CF}$ = 8.9 Hz), 123.0, 116.3 (d, $^2J_{CF}$ = 22.7 Hz); HRMS (EI^+): m/z calcd for $C_{12}H_9N_2F$ $[M]^+$: 200.0750. Found 200.0754.



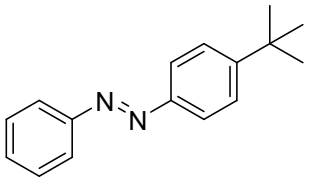
1-(4-chlorophenyl)-2-phenyldiazene (**2e**): Yellow solid; m.p. 81-83 ℃; 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.91 (m, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.56–7.48 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 151.1, 137.0, 131.4, 129.5, 129.3, 124.3, 123.1; HRMS(EI^+): m/z calcd for $C_{12}H_9N_2Cl$ $[M]^+$: 216.0454. Found 216.0452.



1-(4-bromophenyl)-2-phenyldiazene (**2f**) : Orange solid; m.p. 90-92 ℃; 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.91 (m, 2H), 7.81 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.55–7.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 151.4, 132.5, 131.5, 129.3, 125.5, 124.5, 123.1; HRMS(EI^+): m/z calcd for $C_{12}H_9N_2Br$ $[M]^+$: 259.9949. Found 259.9945.

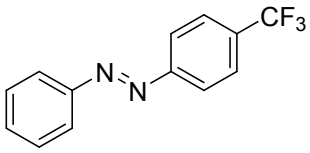


1-(4-iodophenyl)-2-phenyldiazene (**2g**): Orange solid; m.p. 91-93 ℃; 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.91 (m, 2H), 7.88–7.86 (m, 2H), 7.67–7.65 (m, 2H), 7.55-7.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 152.0, 138.5, 131.5, 129.3, 124.6, 123.1, 97.8; HRMS(EI^+): m/z calcd for $C_{12}H_9N_2I$ $[M]^+$: 307.9810. Found 307.9805.

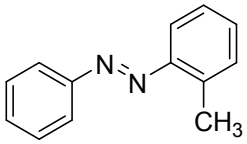


1-(4-(*tert*-butyl)phenyl)-2-phenyldiazene (**2h**): Orange solid; m.p. 51-53 ℃; 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H), 7.91–7.89 (m, 2H), 7.58–7.46 (m, 5H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 152.9, 150.7, 130.8, 129.2,

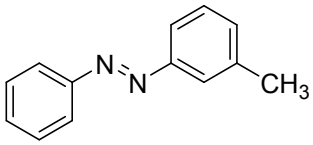
126.2, 122.9, 122.7, 35.2, 31.4; HRMS(EI$^+$): m/z calcd for $C_{16}H_{18}N_2$ [M]$^+$: 238.1470. Found 238.1467.



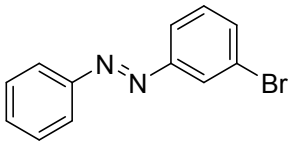
1-phenyl-2-(4-(trifluoromethyl)phenyl)diazene (**2i**): Orange solid; m.p. 81-83 ℃; 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–8.00 (m, 2H), 7.97–7.95 (m, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.58–7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 152.4, 132.2 (q, $^2J_{CF}$ = 32.2 Hz), 131.8, 129.2, 126.3 (q, $^3J_{CF}$ = 3.7 Hz), 123.9 (q, $^1J_{CF}$ = 270.6 Hz), 123.2，123.0; HRMS(EI$^+$): m/z calcd for $C_{13}H_9N_2F_3$ [M]$^+$: 250.0718. Found 250.0715.



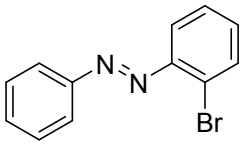
1-phenyl-2-(*o*-tolyl)diazene (**2j**): Red oil; 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.95 (m, 2H) , 7.68 (d, J = 7.8 Hz, 1H), 7.57–7.47 (m, 3H), 7.42–7.28 (m, 3H) , 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 150.9, 138.3, 131.4, 131.1, 130.9, 129.2, 126.6, 123.1, 115.6, 17.7; HRMS(EI$^+$): m/z calcd for $C_{13}H_{12}N_2$ [M]$^+$: 196.1000. Found 196.0999.



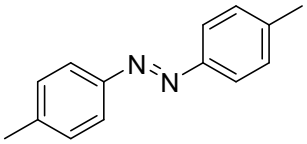
1-phenyl-2-(*m*-tolyl)diazene (**2k**): Red oil; 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H) , 7.76–7.74 (m, 2H), 7.55–7.46 (m, 3H), 7.42 (t, J = 8.3 Hz, 1H) , 7.32–7.30 (m, 1H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 152.8, 139.1, 131.9, 131.0, 129.2, 129.0, 123.0, 122.9, 120.7, 21.5; HRMS(EI$^+$): m/z calcd for $C_{13}H_{12}N_2$ [M]$^+$: 196.1000. Found 196.0995.



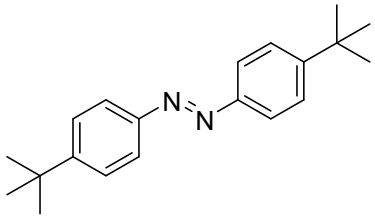
1-(3-bromophenyl)-2-phenyldiazene (**2l**): Orange solid; m.p. 62-64 ℃; 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–8.07 (m, 1H), 7.95–7.88 (m, 3H), 7.62–7.48 (m, 4H), 7.41 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 152.4, 133.7, 131.7, 130.6, 129.3, 124.7, 123.3, 123.2, 123.2; HRMS(EI$^+$): m/z calcd for $C_{12}H_9N_2Br$ [M]$^+$: 259.9949. Found 259.9946.



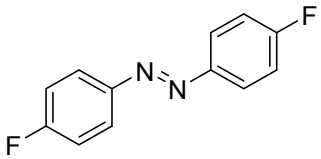
1-(2-bromophenyl)-2-phenyldiazene (**2m**): Red oil; 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.98 (m, 2H), 7.77–7.75 (m, 1H), 7.70–7.67 (m, 1H), 7.58–7.48 (m, 3H), 7.42–7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 149.8, 133.9, 132.0, 131.7, 129.3, 128.1, 125.9, 123.6, 117.9; HRMS(EI$^+$): m/z calcd for $C_{12}H_9N_2Br$ [M]$^+$: 259.9949. Found 259.9943.



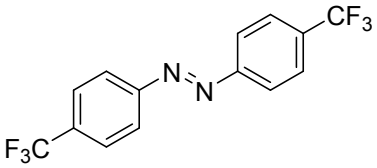
1,2-di-*p*-tolyldiazene (**2n**): Orange solid; m.p. 140-142 ℃; 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 4H), 7.33 (d, J = 8.4 Hz, 4H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 141.3, 129.8, 122.9, 21.6; HRMS(EI$^+$): m/z calcd for $C_{14}H_{14}N_2$ [M]$^+$: 210.1157. Found 210.1161.



1,2-*bis*(4-(*tert*-butyl)phenyl)diazene (**2o**): Orange solid; m.p. 182-184 ℃; 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 4H), 7.54 (d, J = 8.4 Hz, 4H), 1.38 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 150.9, 126.1, 122.6, 35.1, 31.4; HRMS(EI$^+$): m/z calcd for $C_{20}H_{26}N_2$ [M]$^+$: 294.2096. Found 294.2095.



1,2-*bis*(4-fluorophenyl)diazene (**2p**): Red solid; m.p. 93-95 ℃; 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 5.2Hz, J = 8.4Hz, 4H), 7.20 (t, J = 8.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (d, $^{1}J_{CF}$ = 251.4 Hz), 149.1 (d, $^{4}J_{CF}$ = 2.3 Hz), 125.0 (d, $^{3}J_{CF}$ = 9.1 Hz), 116.2 (d, $^{1}J_{CF}$ = 23.0 Hz); HRMS(EI^{+}): m/z calcd for $C_{12}H_8N_2F_2$ $[M]^{+}$: 218.0656. Found 218.0651.



1,2-*bis*(4-(trifluoromethyl)phenyl)diazene (**2q**): Red solid; m.p. 110-112 ℃; 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 4H), 7.80 (d, J = 8.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 133.1 (q, $^{2}J_{CF}$ = 32.4 Hz), 126.6 (q, $^{3}J_{CF}$ = 3.8 Hz), 123.9 (q, $^{1}J_{CF}$ = 270.6 Hz), 123.5; HRMS(EI^{+}): m/z calcd for $C_{14}H_8N_2F_6$ $[M]^{+}$: 318.0592. Found 318.0584.

10. References

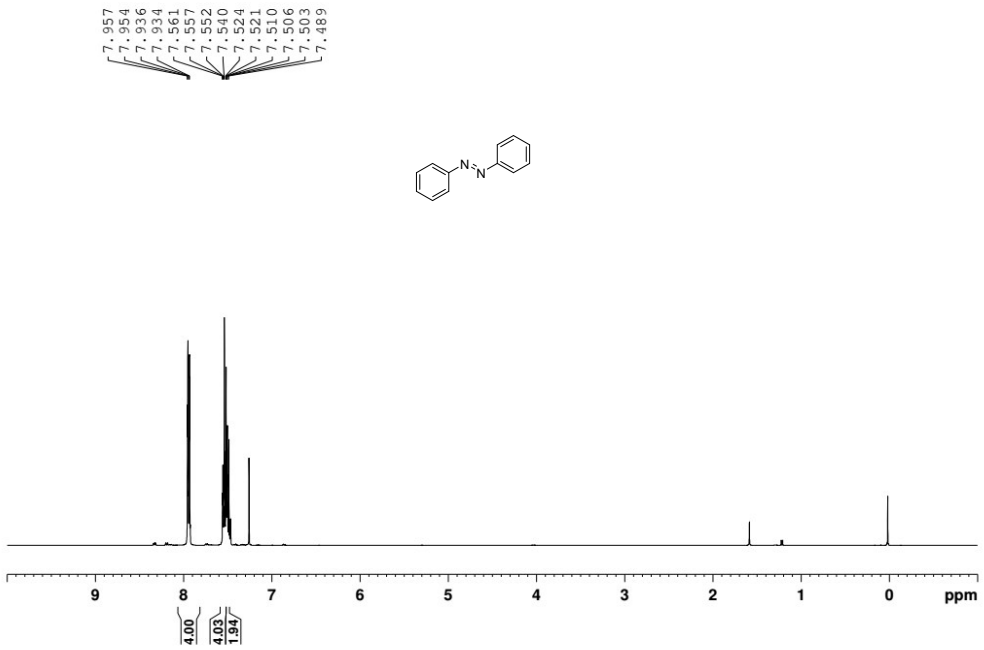
[1] A. M. Gilbert, A. Failli, J. Shumsky, Y.-J. Yang, A. Severin, G. Singh, W. Hu, D. Keeney, P. J. Petersen, A.H. Katz. *J. Med. Chem.,* 2006, **49**, 6027-6036.

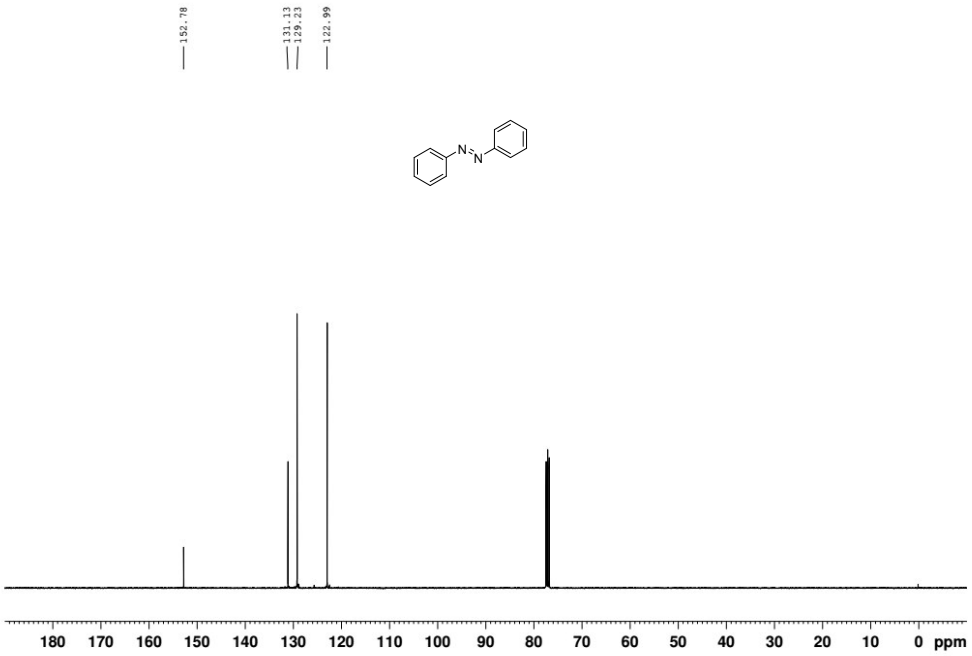
[2] L. Wang, A. Ishida, Y. Hashidoko, M. Hashimoto. *Angew. Chem. Int. Ed.,* 2017, **56**, 870-873.

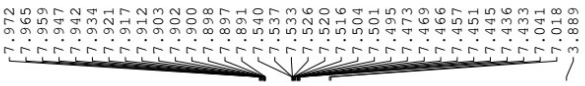
[3] H.-Y. Wang, Y.-Q. Man, K.-Y. Wang, X.-Y. Wan, L. Tong, N. Lia, B.Tang, *Chem. Commun.*, 2018, **54**, 10989-10992.

[4] G.-Q. Xu, J.-T. Xu, Z.-T. Feng, H. Liang, Z.-Y. Wang, Y. Qin, P.-F. Xu, *Angew. Chem. Int. Ed.*, 2018, **57**, 5110-5114.

11. NMR spectra of for the products



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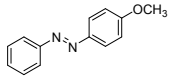
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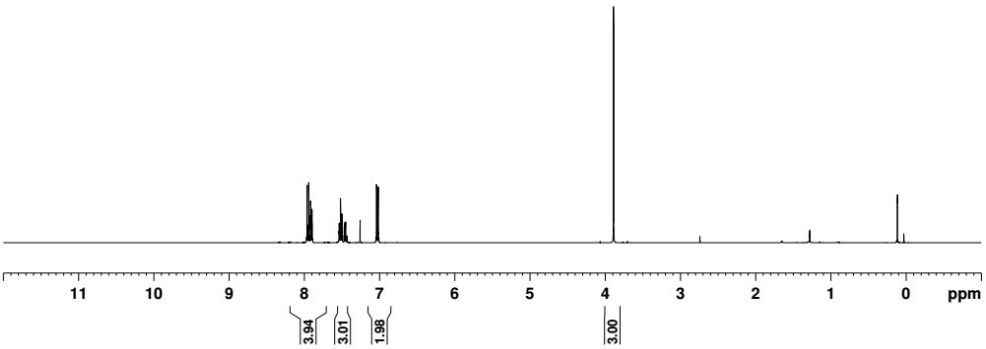
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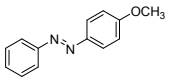
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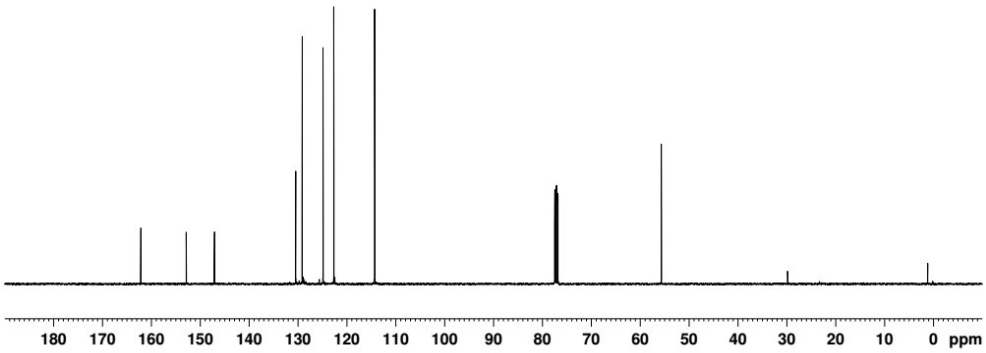
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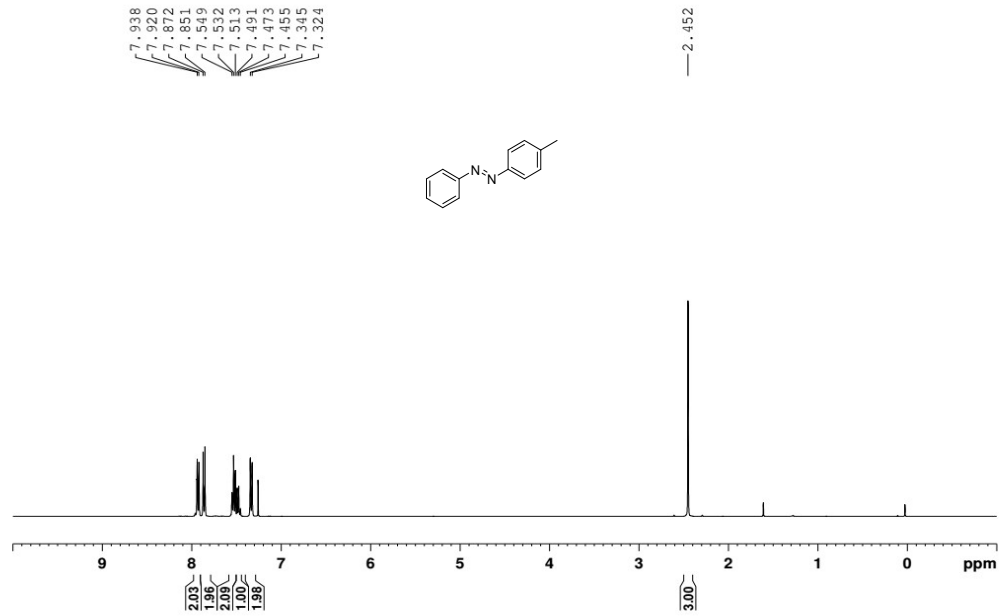
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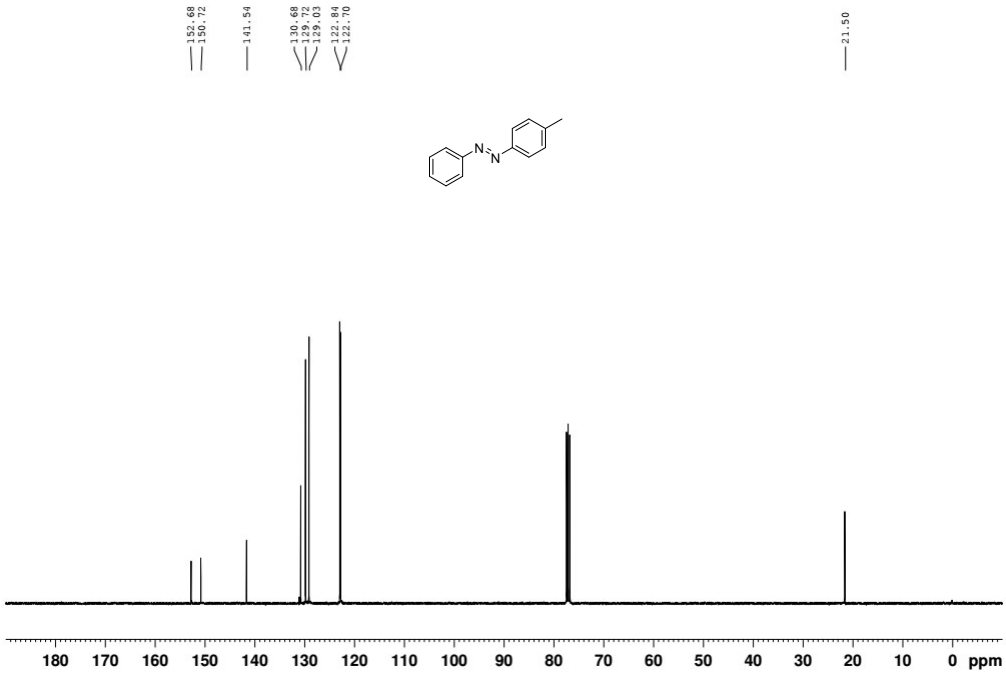
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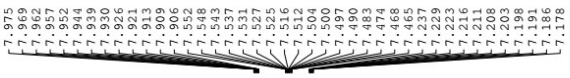
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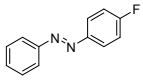
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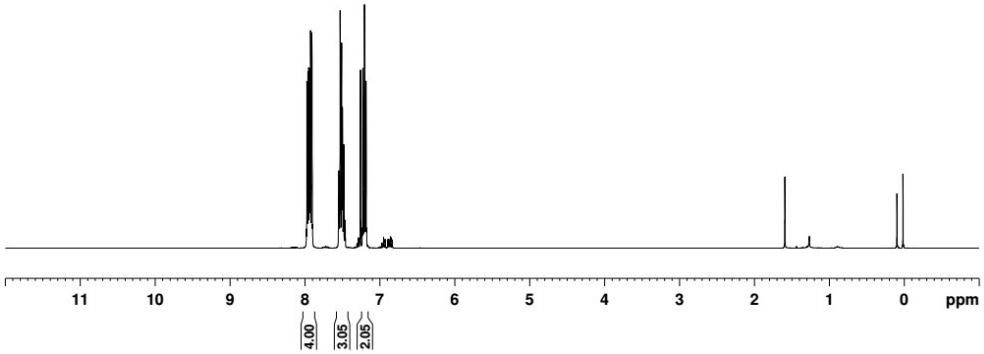
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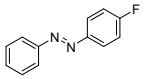
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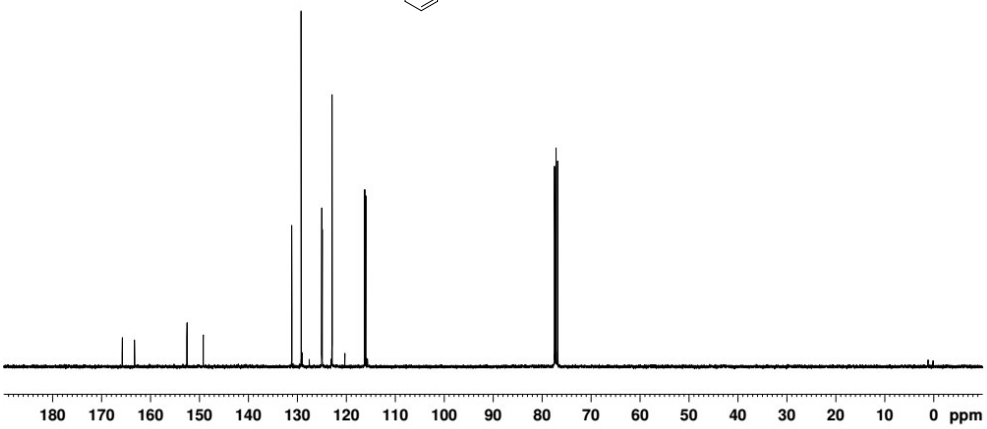
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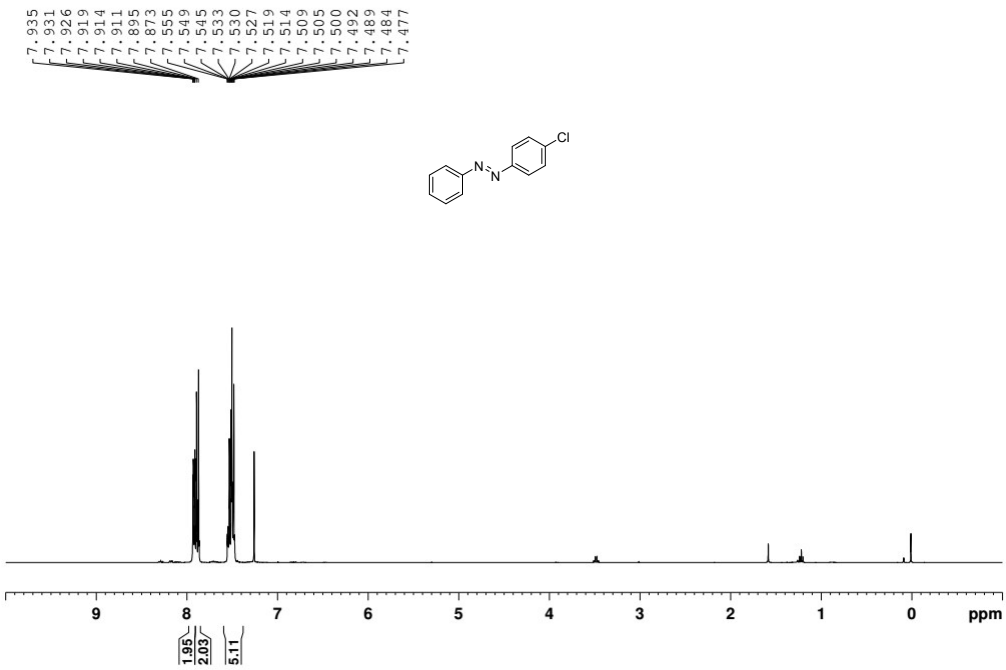
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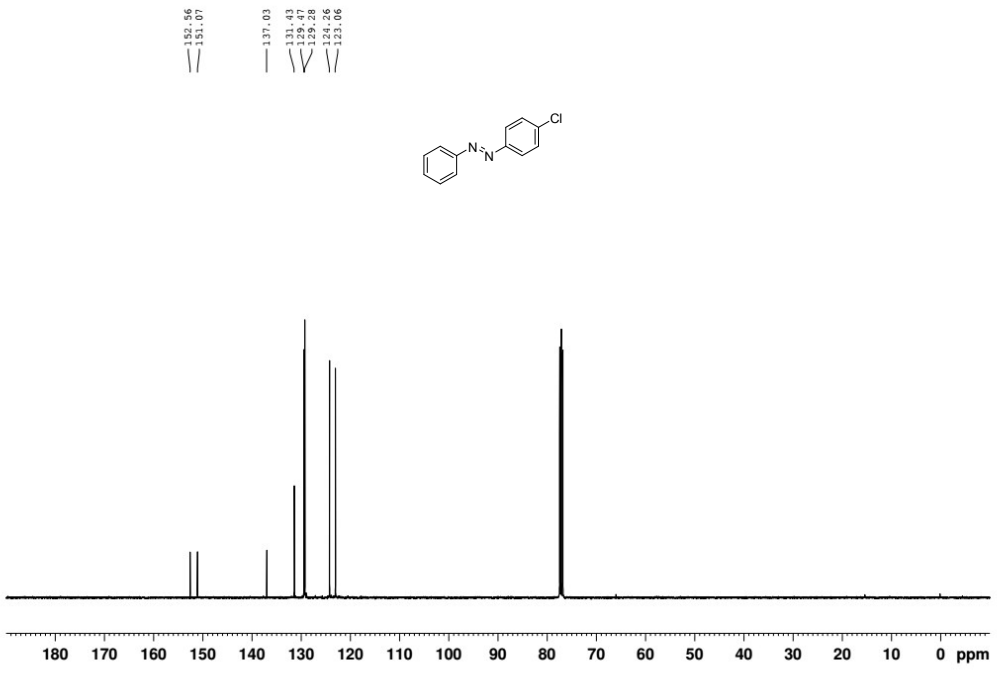
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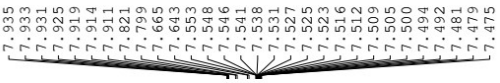
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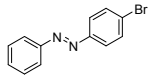
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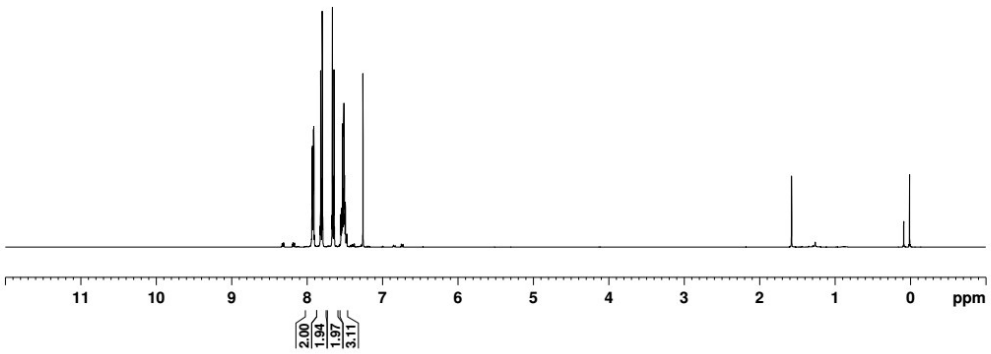
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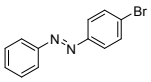
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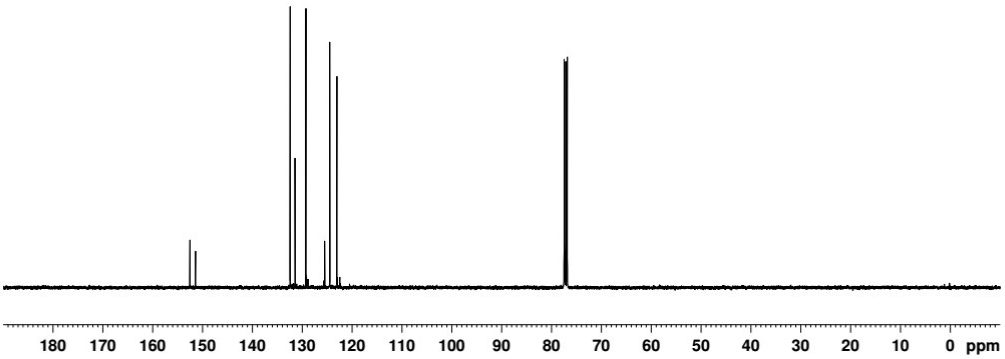
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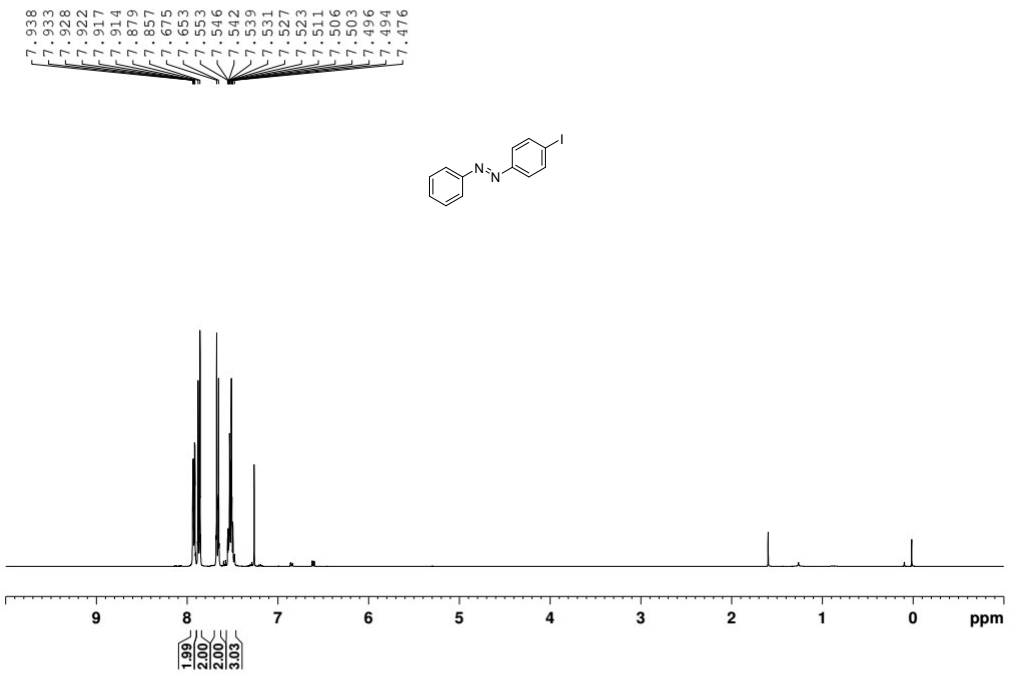
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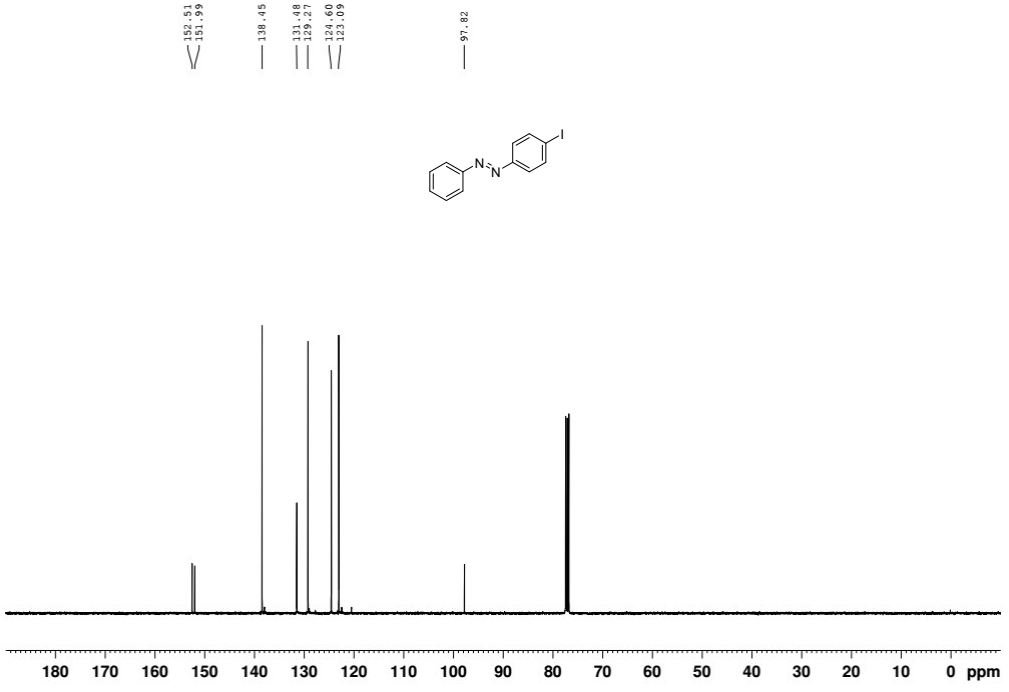
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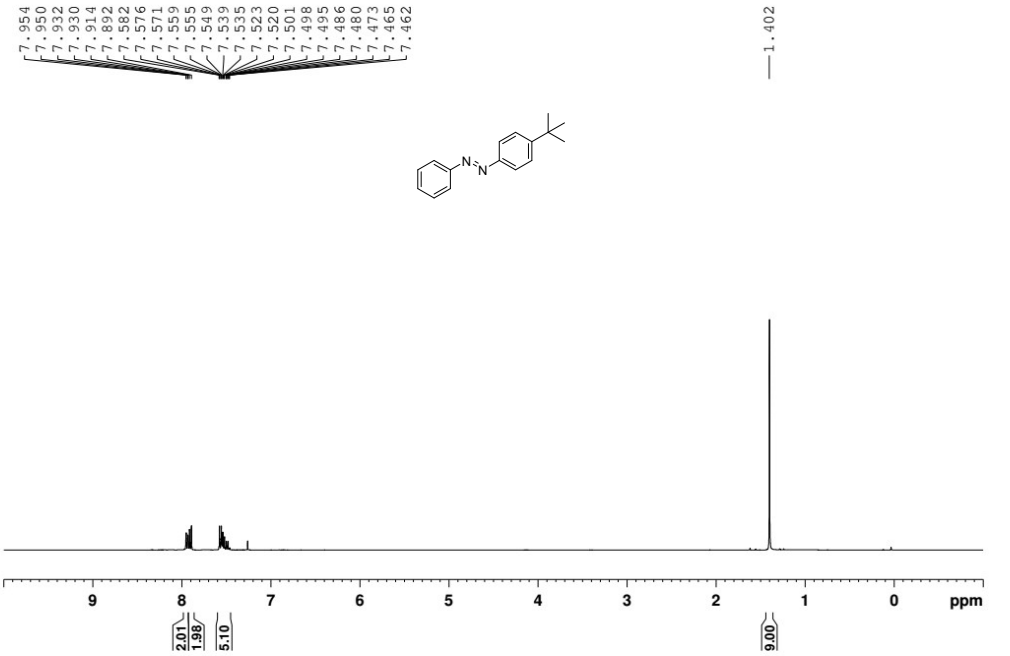
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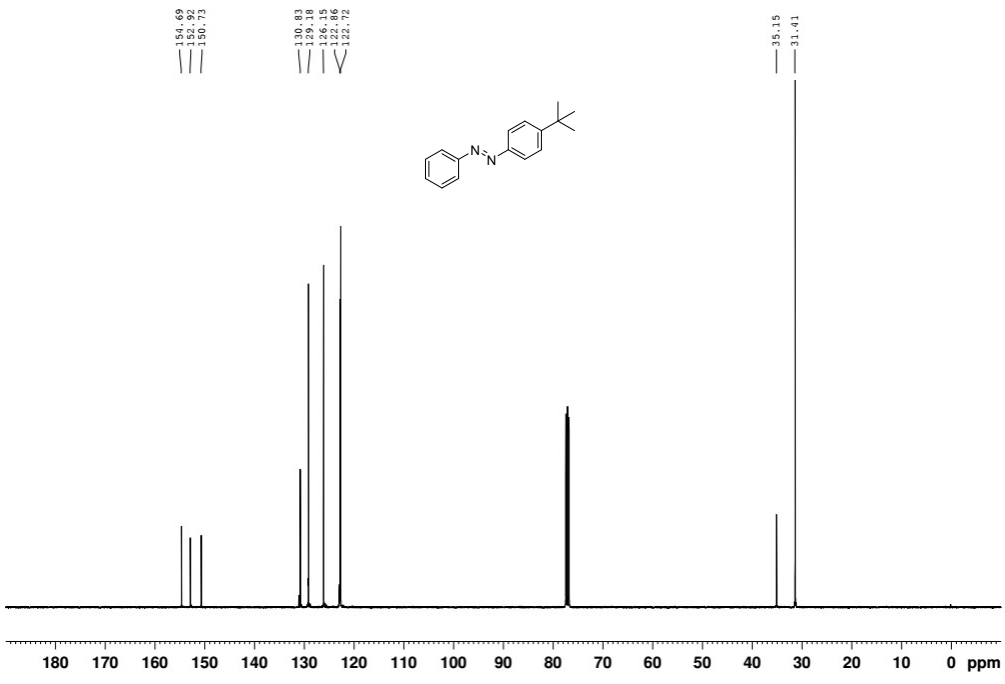
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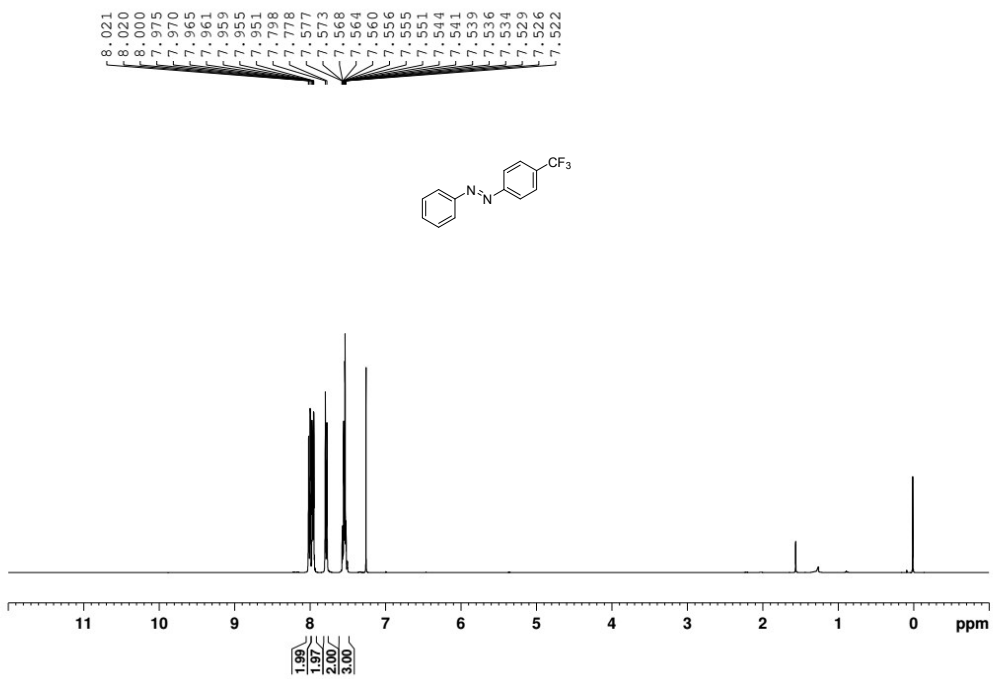
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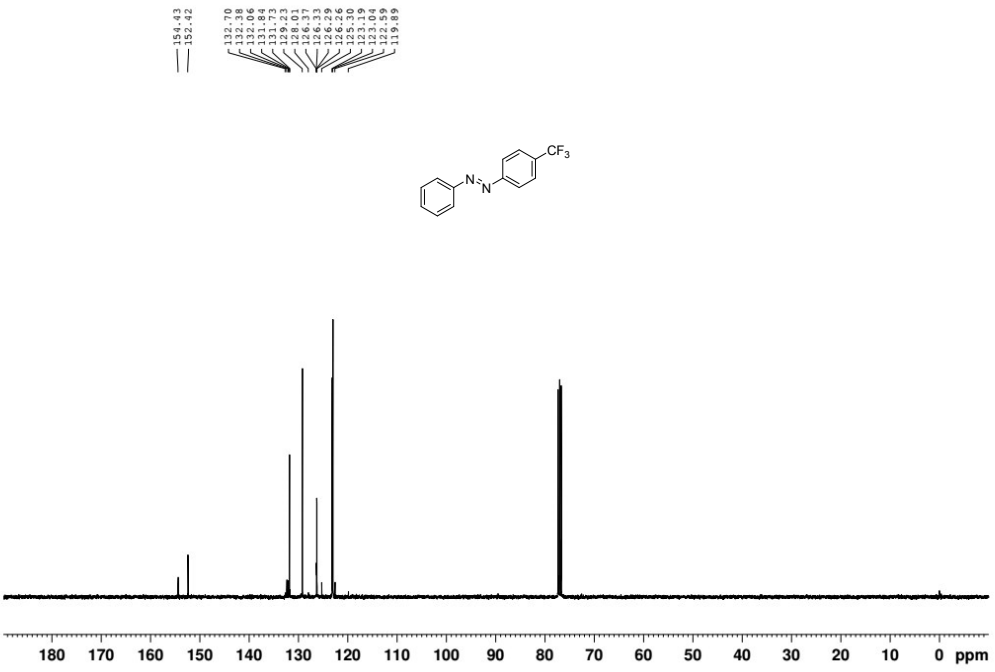
8.020
8.000
7.975
7.970
7.965
7.961
7.959
7.955
7.951
7.798
7.778
7.577
7.573
7.568
7.564
7.560
7.556
7.555
7.551
7.544
7.541
7.539
7.536
7.534
7.529
7.526
7.522
CF3
N
N
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.99
1.97
2.00
3.00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152.42
132.70
132.38
132.06
131.84
131.53
129.23
128.01
126.37
126.33
126.29
126.26
125.30
123.19
123.06
122.59
119.89
CF3
N
N
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140
130
120
110
100
90
80
70
60
50
40
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20
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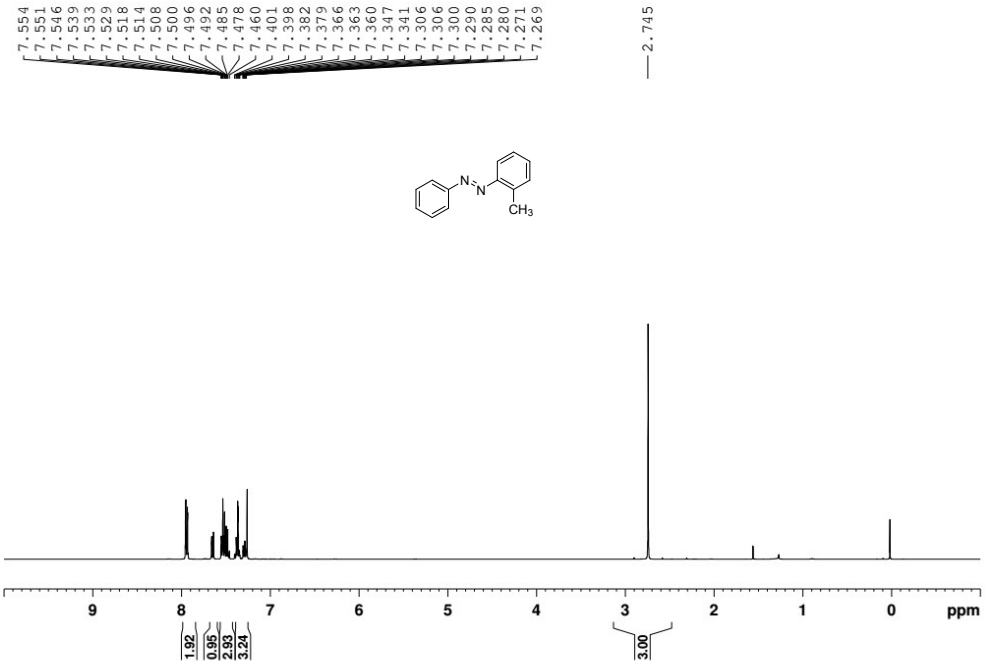
0
ppm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7.551
7.546
7.539
7.533
7.529
7.518
7.514
7.508
7.500
7.496
7.492
7.485
7.478
7.460
7.401
7.398
7.382
7.379
7.366
7.363
7.360
7.347
7.341
7.306
7.306
7.300
7.290
7.285
7.280
7.271
7.269
2.745
N
N
CH3
9
8
7
6
5
4
3
2
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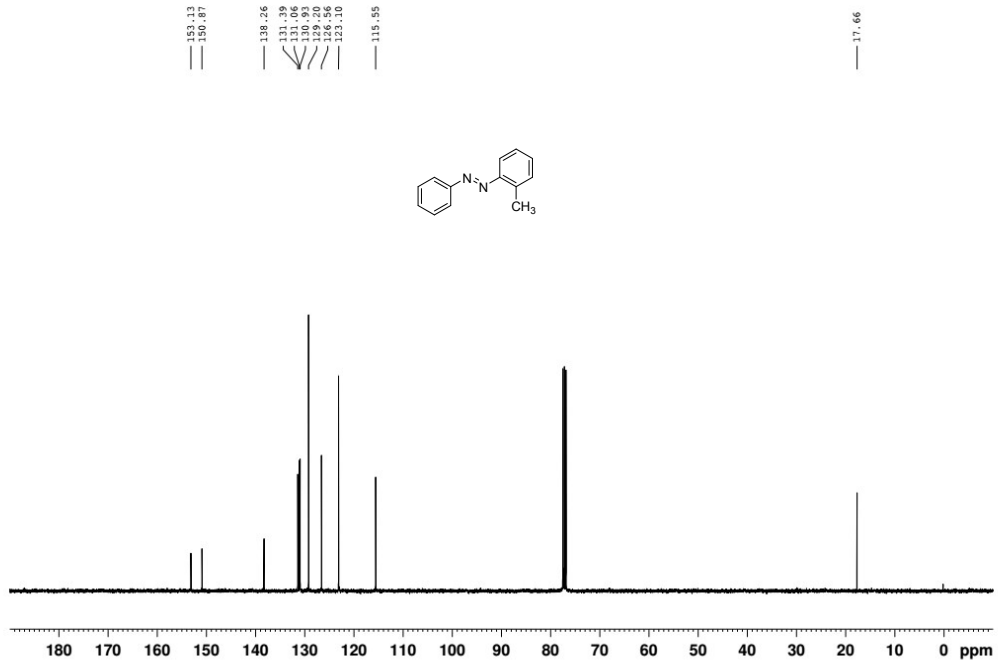
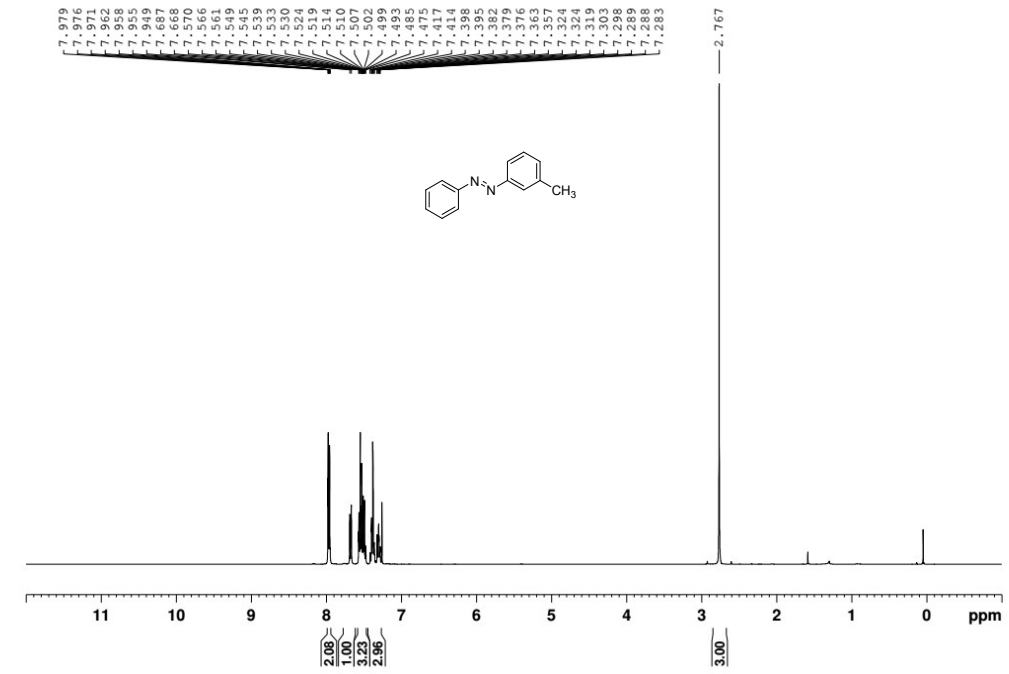
0
ppm
1.92
0.95
2.93
3.24
3.00


153.13
150.87
138.26
131.39
131.06
130.93
129.20
126.56
123.10
115.55
17.66
N
N
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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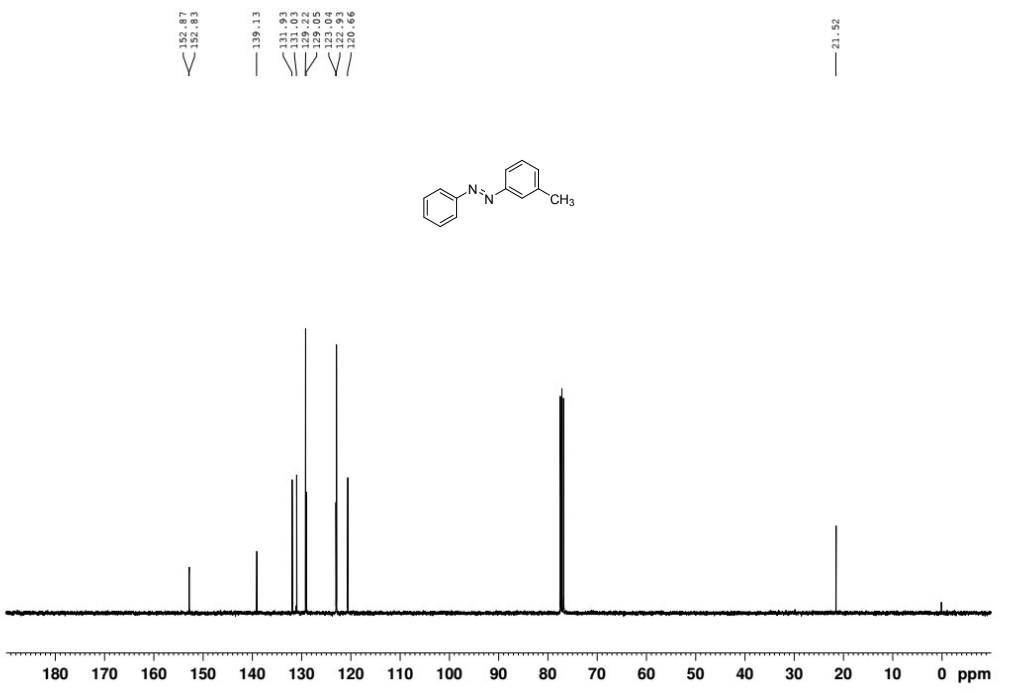
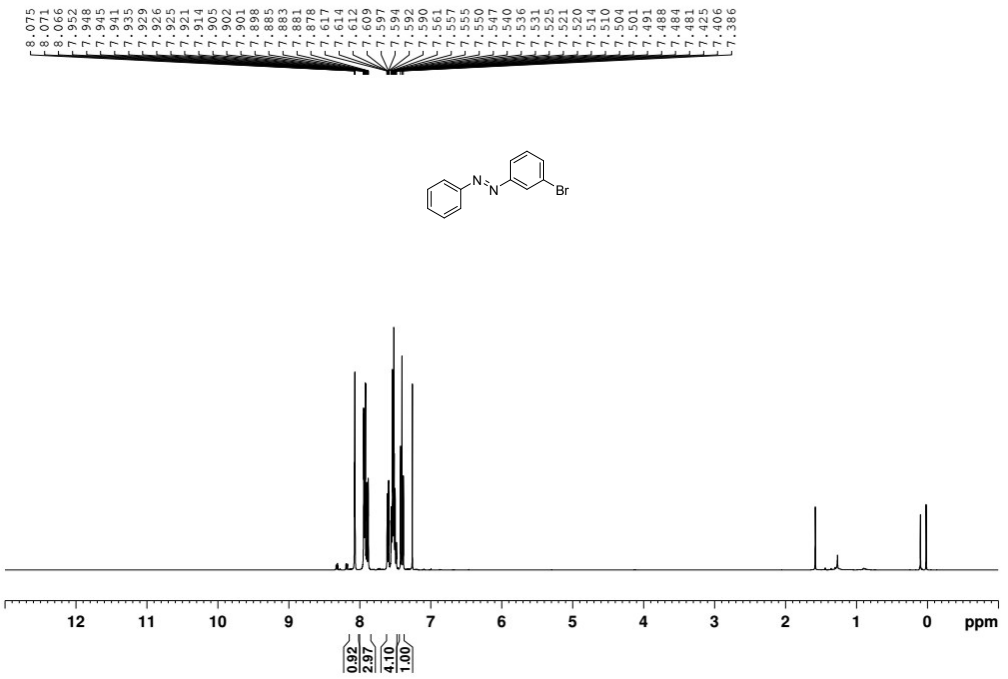
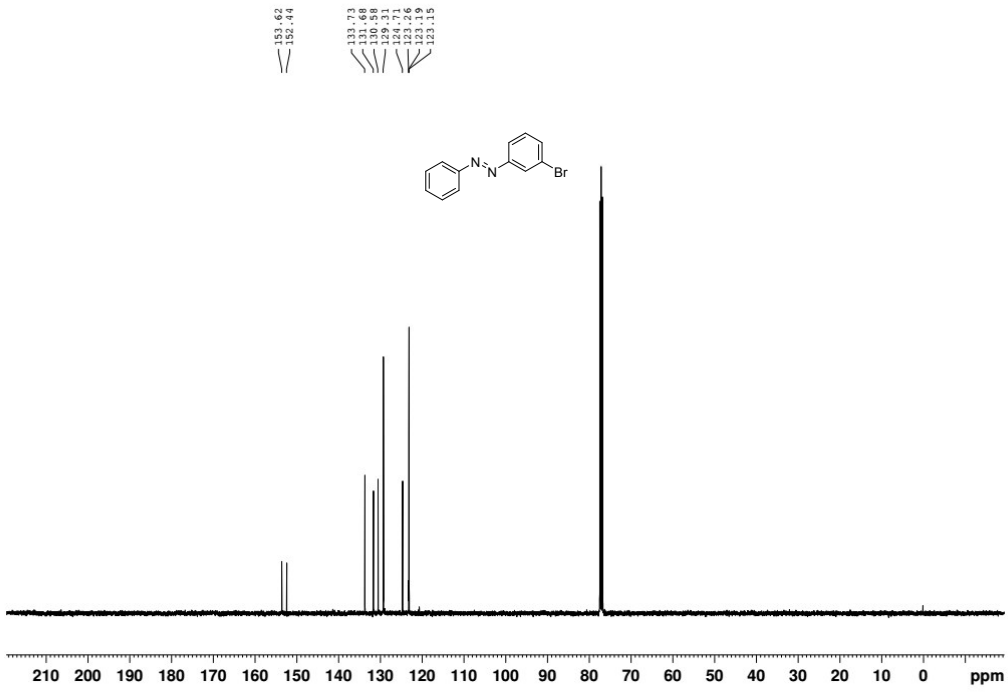
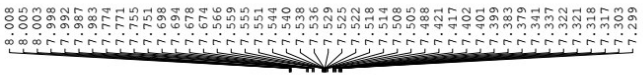
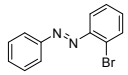
7.976
7.971
7.962
7.958
7.955
7.949
7.687
7.668
7.570
7.566
7.561
7.549
7.545
7.539
7.533
7.530
7.524
7.519
7.514
7.510
7.507
7.502
7.499
7.493
7.485
7.475
7.417
7.414
7.398
7.395
7.382
7.379
7.376
7.363
7.357
7.324
7.324
7.319
7.303
7.298
7.289
7.288
7.283
2.767
N
N
CH3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
1.00
3.23
2.96
3.00

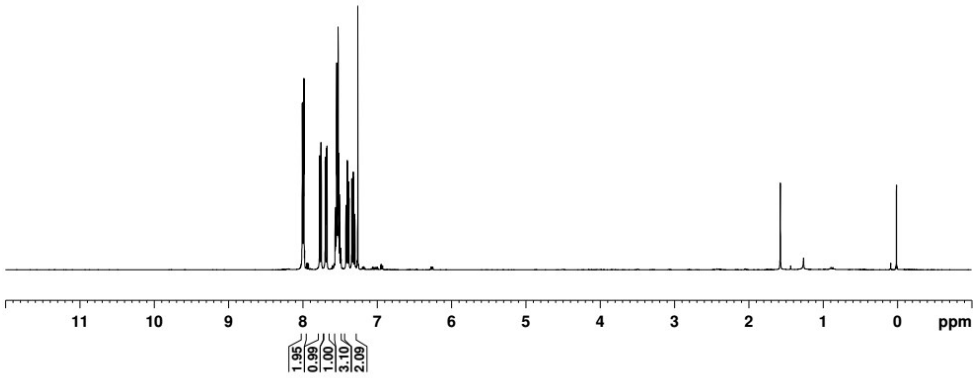

152.87
152.83
139.13
131.93
131.03
130.72
129.05
123.04
122.93
120.66
21.52
N
N
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.075
8.071
8.066
7.952
7.948
7.945
7.941
7.935
7.929
7.926
7.925
7.921
7.914
7.905
7.902
7.901
7.898
7.885
7.883
7.881
7.878
7.617
7.614
7.612
7.609
7.597
7.594
7.592
7.590
7.561
7.557
7.555
7.550
7.547
7.540
7.536
7.531
7.525
7.521
7.520
7.514
7.510
7.504
7.501
7.491
7.488
7.484
7.481
7.425
7.406
7.386
Br
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
2.97
4.10
1.00

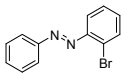

153.62
152.44
133.73
131.68
130.58
129.31
124.71
123.26
123.19
123.15
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

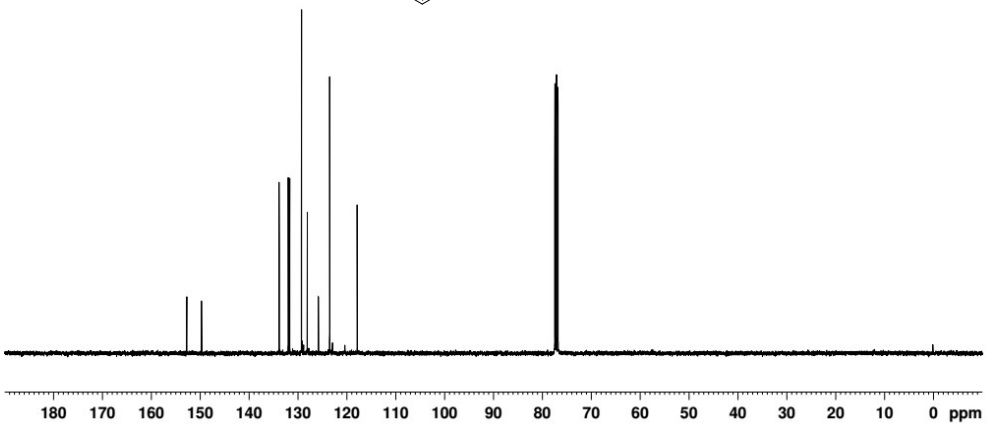

8.008
8.005
8.003
7.998
7.992
7.987
7.983
7.774
7.771
7.755
7.751
7.698
7.694
7.678
7.674
7.566
7.559
7.555
7.551
7.544
7.540
7.538
7.536
7.529
7.525
7.522
7.518
7.514
7.508
7.505
7.488
7.421
7.417
7.402
7.401
7.399
7.383
7.379
7.341
7.337
7.322
7.321
7.318
7.317
7.303
7.299

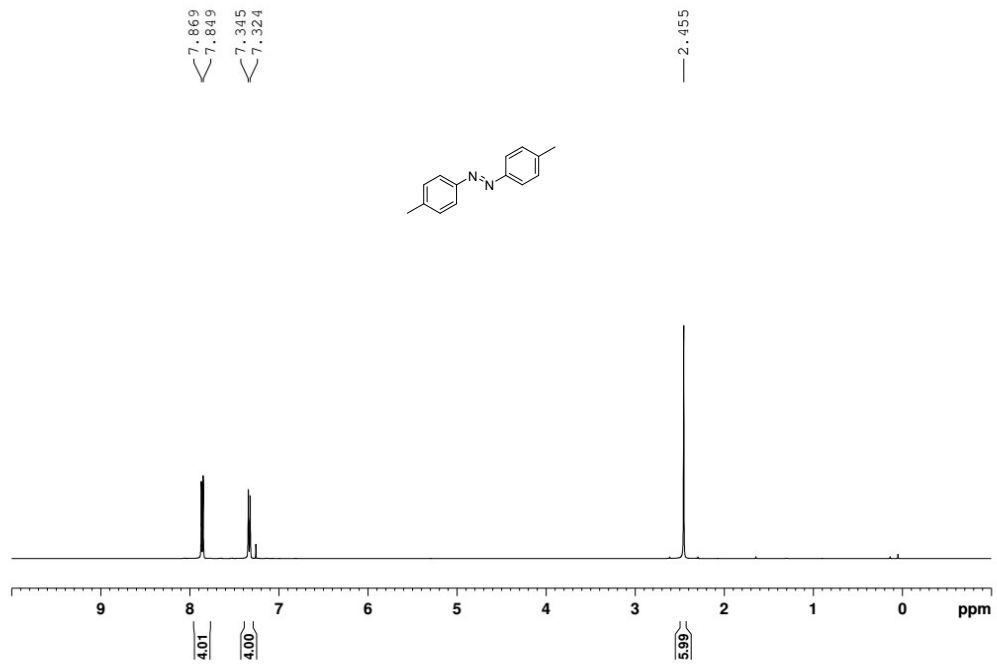

N
N
Br

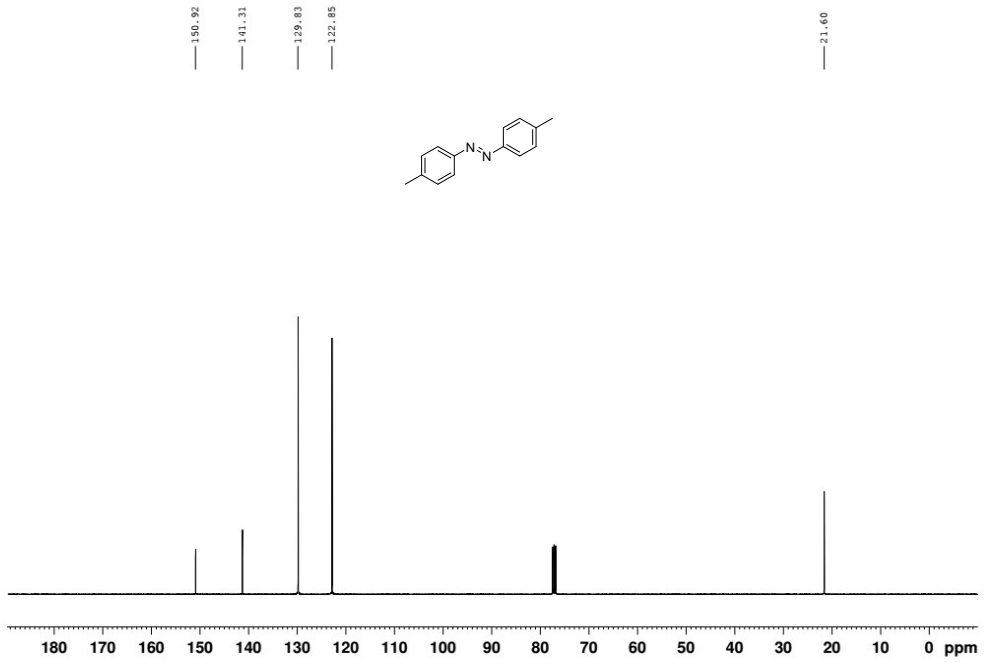

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.95
0.99
1.00
3.10
2.09

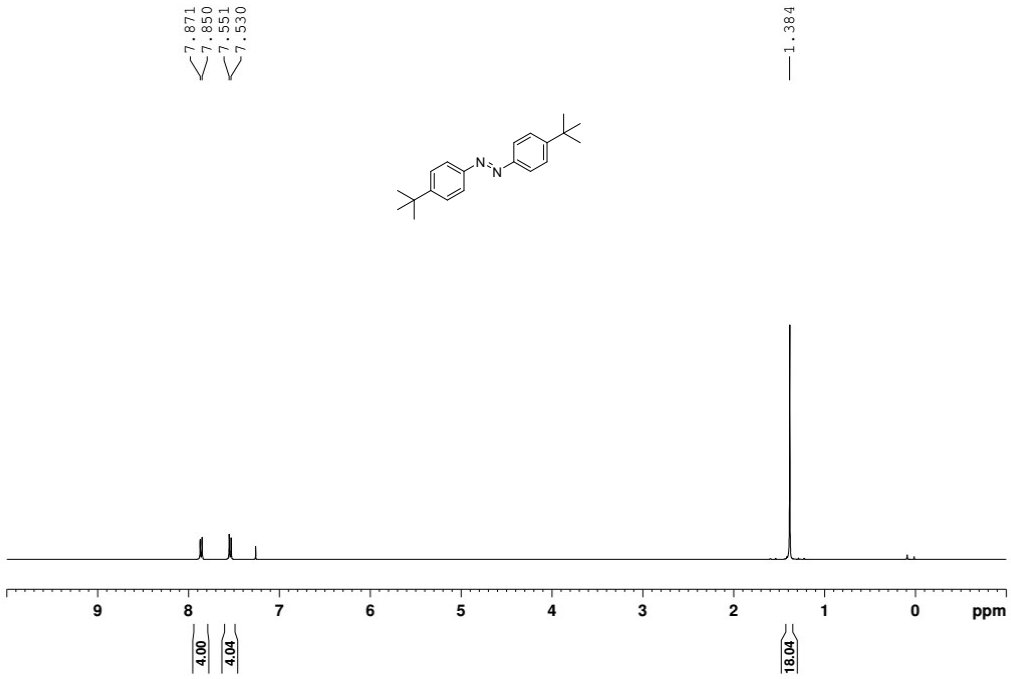

152.73
149.76
133.88
132.02
131.73
129.31
128.12
125.86
123.56
117.91

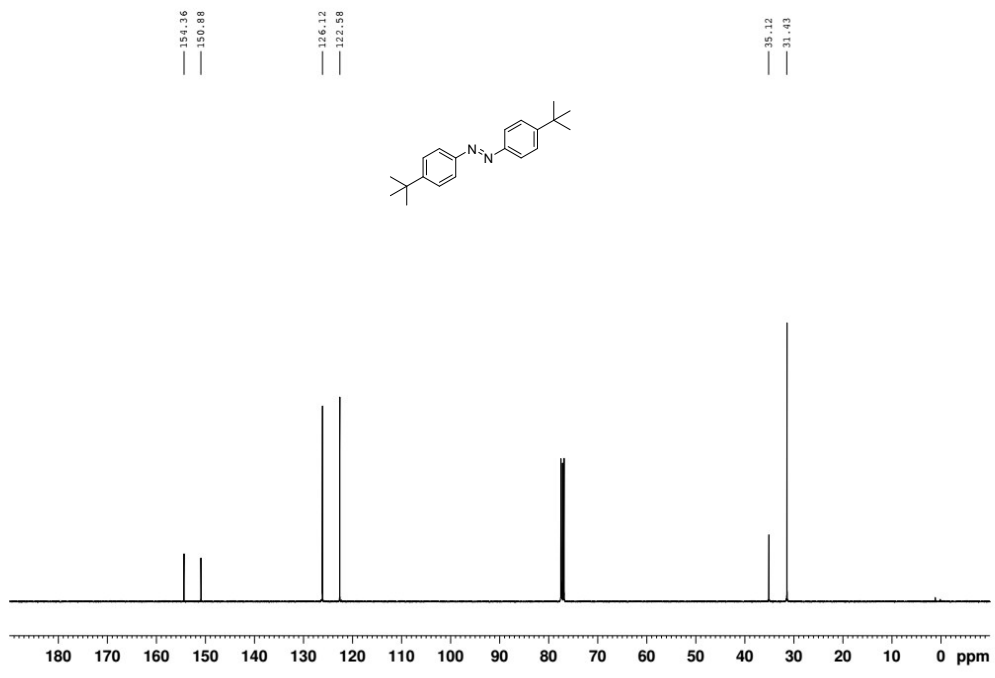

N
N
Br


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.869
7.849
7.345
7.324
2.455
9
8
7
6
5
4
3
2
1
0
ppm
4.01
4.00
5.99


150.92
141.31
129.83
122.85
21.60
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.871
7.850
7.551
7.530
1.384
9
8
7
6
5
4
3
2
1
0
ppm
4.00
4.04
18.04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150.88
126.12
122.58
35.12
31.43
180
170
160
150
140
130
120
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100
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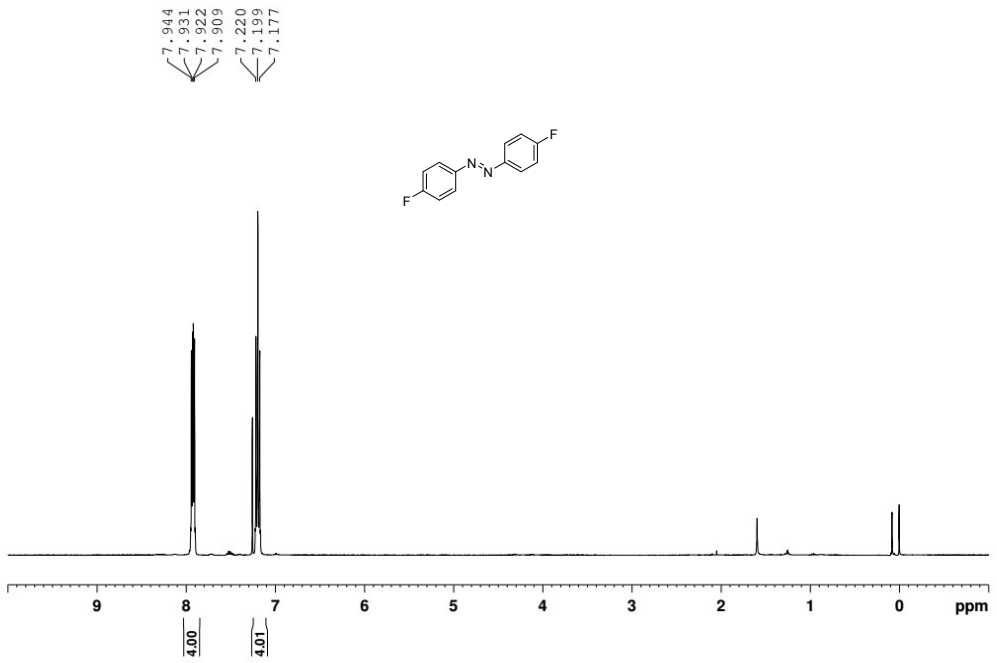
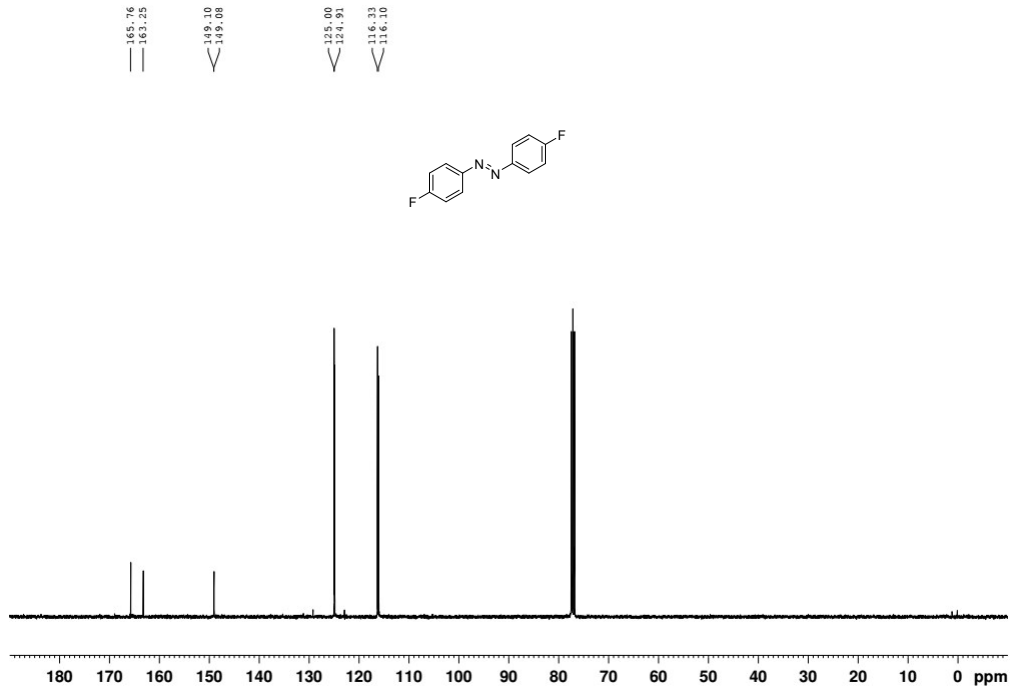
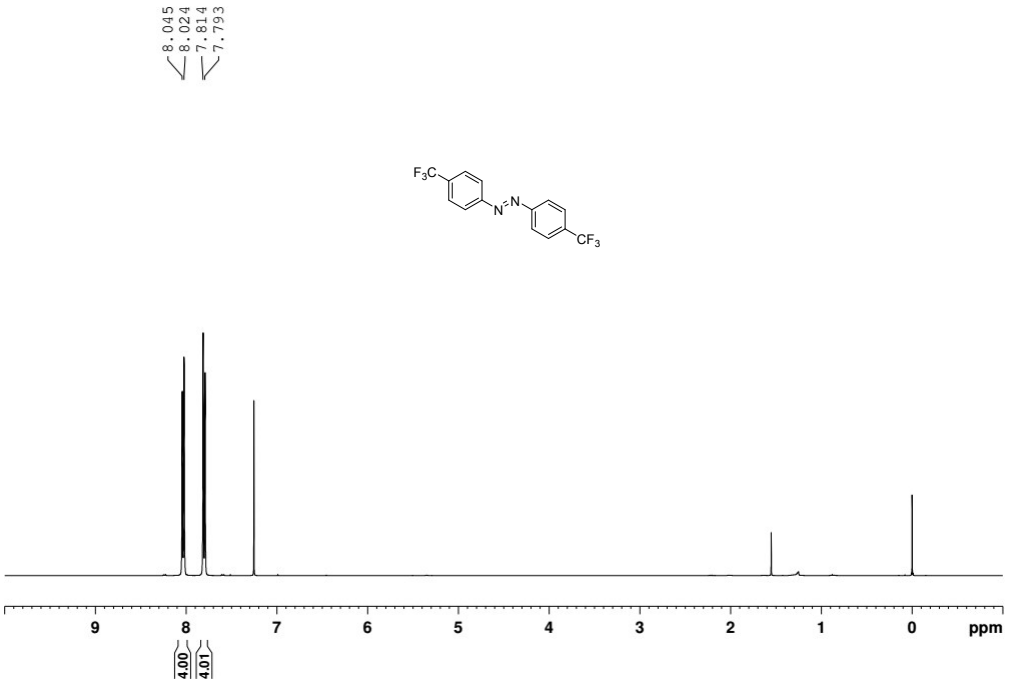
70
60
50
40
30
20
10
0
ppm


7.944
7.931
7.922
7.909
7.220
7.199
7.177
F
N
N
F
9
8
7
6
5
4
3
2
1
0
ppm
4.00
4.01


165.76
163.25
149.10
149.08
125.00
124.91
116.33
116.10
F
N
N
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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8.024
7.814
7.793
F3C
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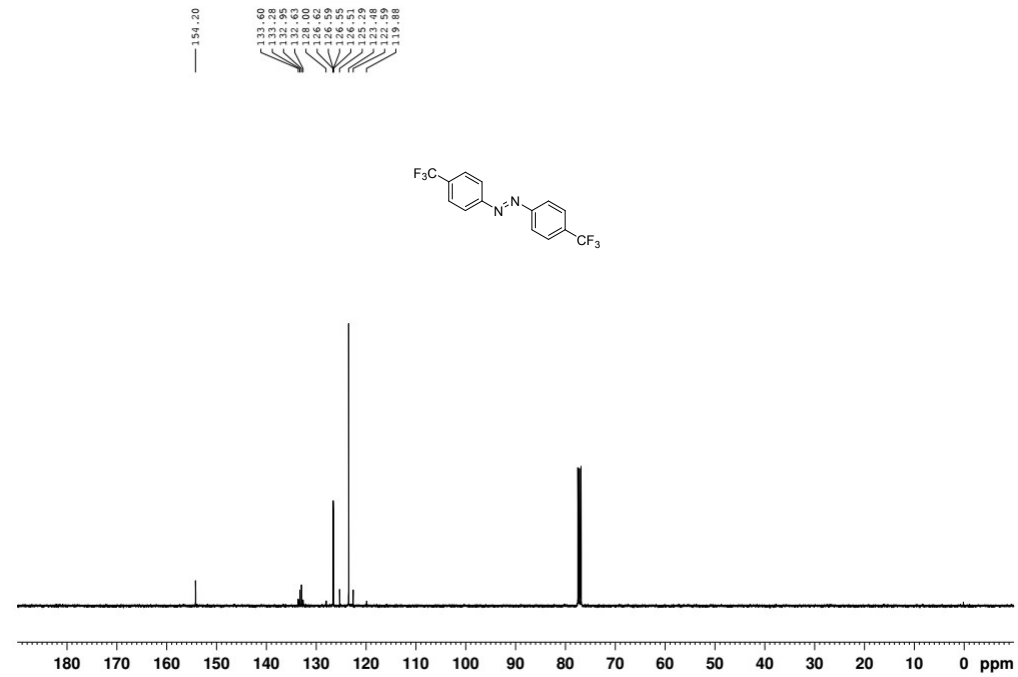
N
CF3
9
8
7
6
5
4
3
2
1
0
ppm
4.00
4.01


154.20
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133.28
132.95
132.63
128.00
126.62
126.59
126.55
126.51
125.29
123.48
122.59
119.88
F3C
N
N
CF3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm