

Supporting Information

Electrochemical Dehydrogenation of Hydrazins to Azo Compounds

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General information

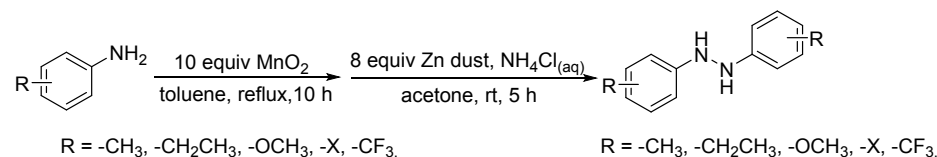
Unless otherwise noted, all the chemicals were purchased commercially, and used without further purification. Ethanol (EtOH, H₂O ≤ 0.3%) was purchased from Chengdu cologne chemical Co., Ltd. Analytical thin layer chromatography (TLC) plates and the silica gel (300-400 mesh) for column chromatography were purchased from Qingdao Haiyang Chemical and Special Silica Gel Co., Ltd.

Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectroscopy were performed on Bruker Advance III-400 spectrometers (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR). The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ¹H), CDCl₃ (δ 7.26 ppm for ¹H NMR and δ 77.3 ppm for ¹³C). Multiplicities were given as: s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplets). The number of protons (*n*) for a given resonance was indicated by *n*H.

Electrolysis reactions were conducted using a Model QJ3003T (32 V) power supply purchased from Qiujiang Instruments (Shenzhen) Co., Ltd. Cyclic voltammetry (CV) analysis was performed on Ingsens 1030 electrochemical workstation (Ingsens Instruments (Guangzhou) Co., Ltd., China), using a platinum electrode (d = 2 mm) as working electrode, a Pt wire as counter electrode and saturated calomel electrode (SCE) as a reference electrode. Cyclic voltammograms were recorded at 0.1V/s scan rate.

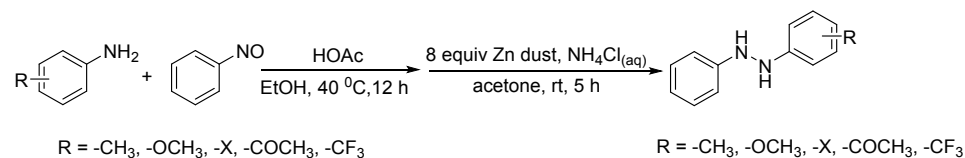
General method for the synthesis of starting materials

General method A



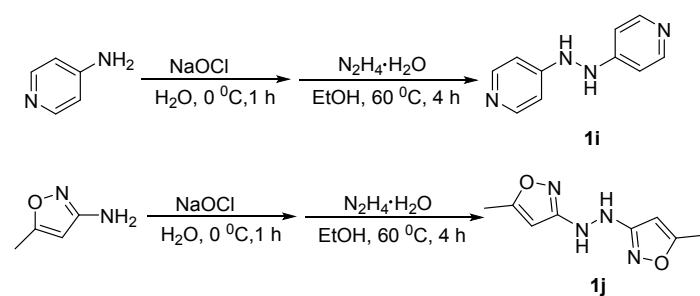
Symmetric hydrazo compounds were prepared according to the cited literatures.^{1,2}

General method B



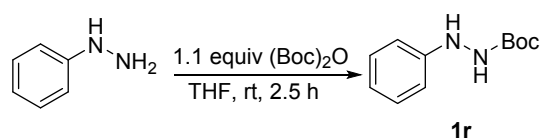
Unsymmetric hydrazo compounds were prepared according to the cited literatures.^{1,2}

General method C



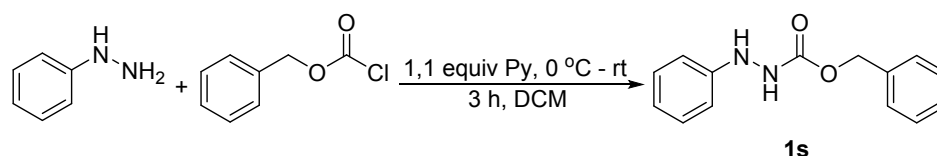
Heterocyclic hydrazo compounds were prepared according to the cited literatures.^{1,2}

General method D



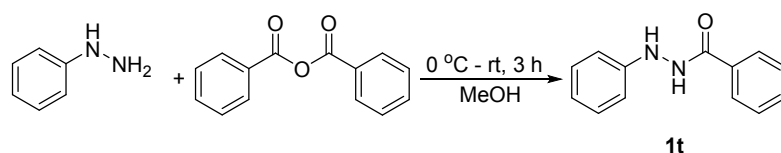
1-Boc-2-phenylhydrazine **1r** was prepared according to the reported literature procedure.³

General method E



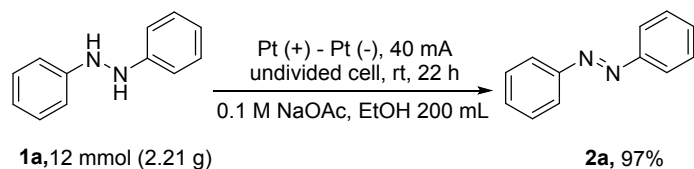
Benzyl 2-Phenylazocarboxylate **1s** was prepared according to the reported literature procedure.⁴

General method F

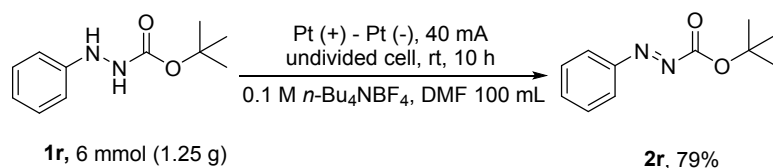


*N*²-Phenylbenzohydrazide **1t** was prepared according to the reported literature procedure.⁵

Scale-up experimental procedure for the synthesis of azo compounds



Procedure for **2a**. To a round-bottomed flask (250 mL) was added **1a** (12 mmol), EtOH (200 mL) and NaOAc (0.1 M). The reaction flask was equipped with Pt foils as anode (2.0 × 3.0 cm²) and cathode (2.0 × 3.0 cm²). The solution was electrolyzed under a constant current (40 mA) for 22 h at ambient temperature. After electrolysis, the mixture was concentrated in *vacuo*. To the residue was added 100 mL water and the resulting mixture was then extracted with ethyl acetate (3 × 100 mL), The combined organic layer was washed with brine (80 mL) and dried over MgSO₄, filtered and concentrated. The resulting mixture was purified by silica gel column chromatography to afford **2a** in the yield of 97%.



Procedure for **2r**. To a round-bottomed flask (150 mL) was added **1r** (6 mmol), DMF (100 mL) and *n*-Bu₄NBF₄ (0.1 M). The reaction flask was equipped with Pt foils as anode (2.0 × 3.0 cm²) and cathode (2.0 × 3.0 cm²). The

solution was electrolyzed under a constant current (40 mA) for 10 h at ambient temperature. After electrolysis, the mixture was added 200 mL water and the resulting mixture was then extracted with ethyl acetate (3×100 mL). The combined organic layer was washed with brine (80 mL) and dried over MgSO_4 , filtered and concentrated. The resulting mixture was purified by silica gel column chromatography to afford **2R** in the yield of 79%.

Cyclic voltammograms

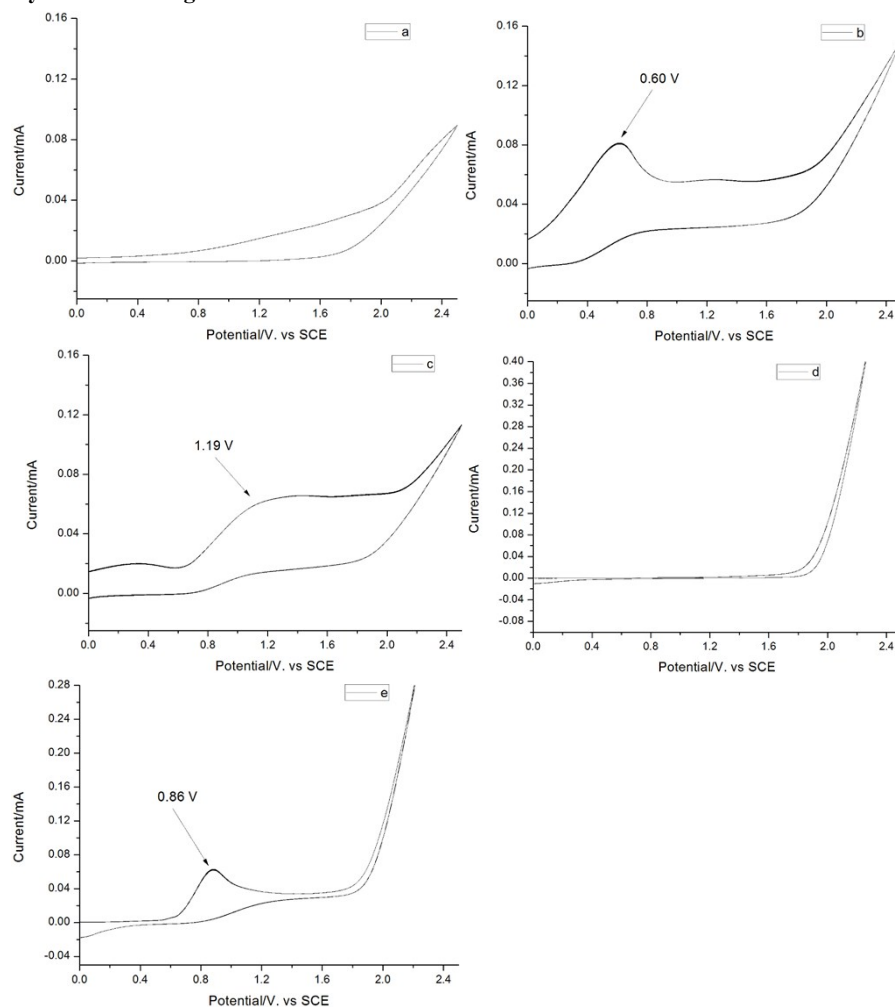


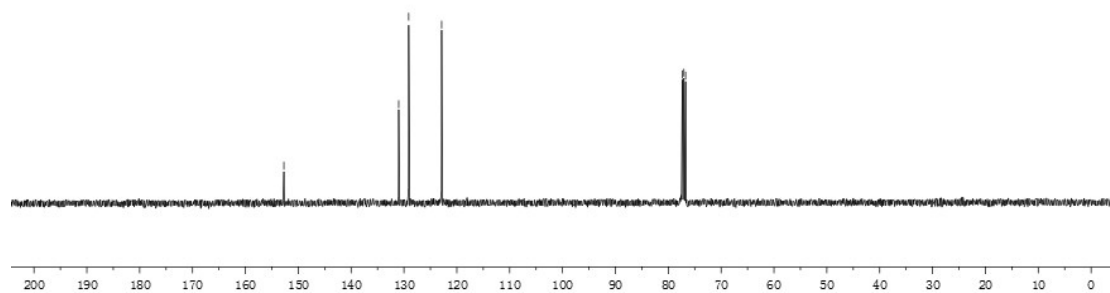
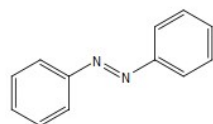
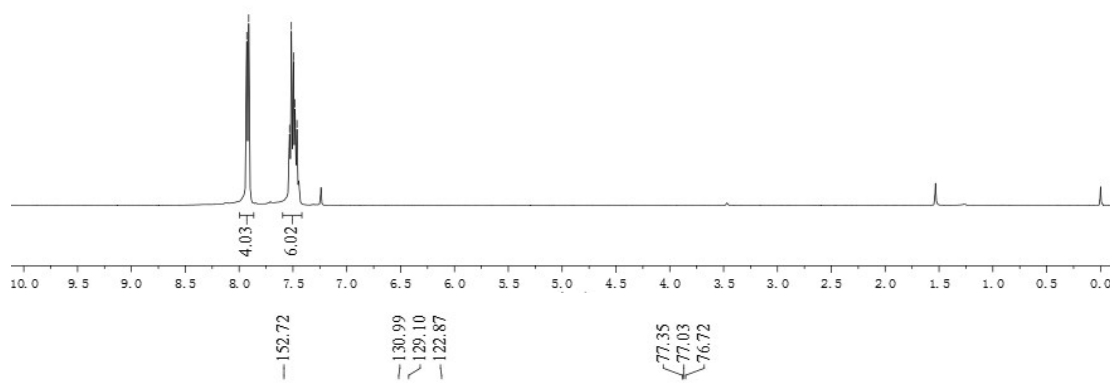
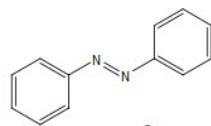
Figure S1. Cyclic voltammogram of 0.1 M NaOAc solution in EtOH at room temperature: a) none, b) **1a** (0.01 M), c) **1j** (0.01 M). Cyclic voltammogram of 0.1 M $n\text{-Bu}_4\text{NBF}_4$ solution in DMF at room temperature: d) none, e) **1r** (0.01 M). The voltammogram was obtained with Pt wire as auxiliary electrode and a saturate calomel electrode (SCE) as a reference electrode. The scan rate was 0.1 V/s on a platinum disk electrode ($d = 2$ mm).

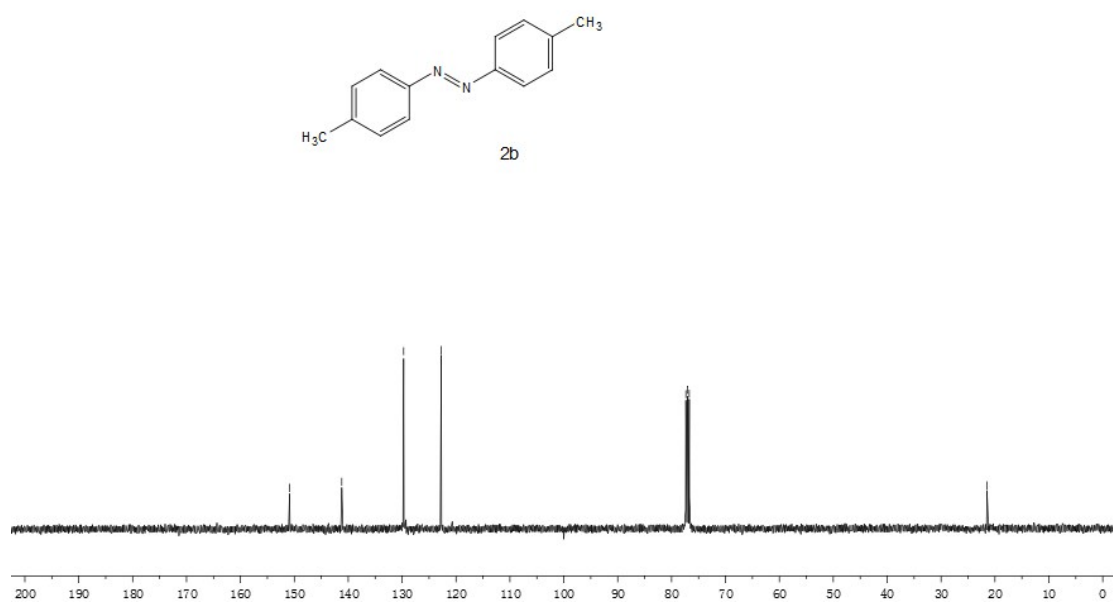
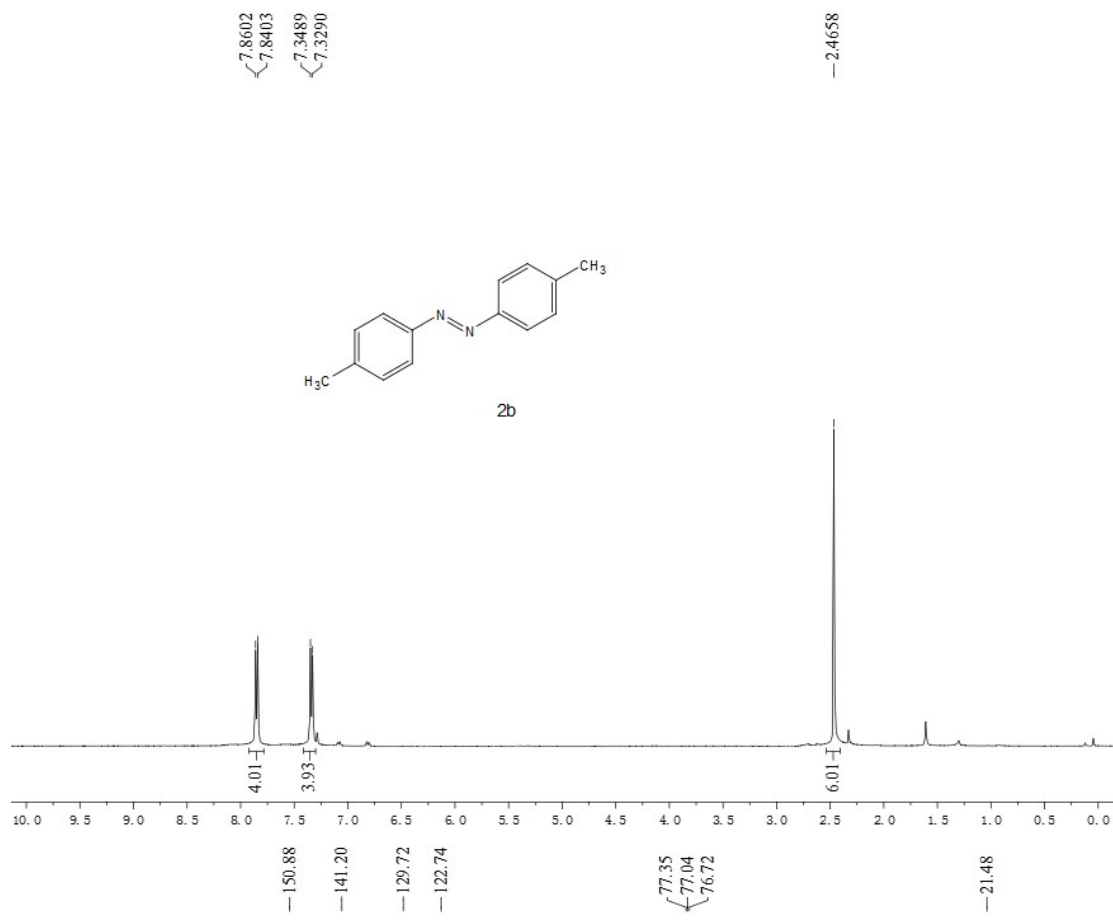
References

1. L. Wang, A. Ishida, Y. Hashidoko, M. Hashimoto, *Angew. Chem. Int. Ed.* 2017, **56**, 870.
2. A. M. Gilbert, A. Failli, J. Shumsky, Y. Yang, A. Severin, G. Singh, W. Hu, D. Keeney, P. J. Petersen, A. H. Katz, *J. Med. Chem.* 2006, **49**, 6027.
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Copies of NMR Spectra of Products

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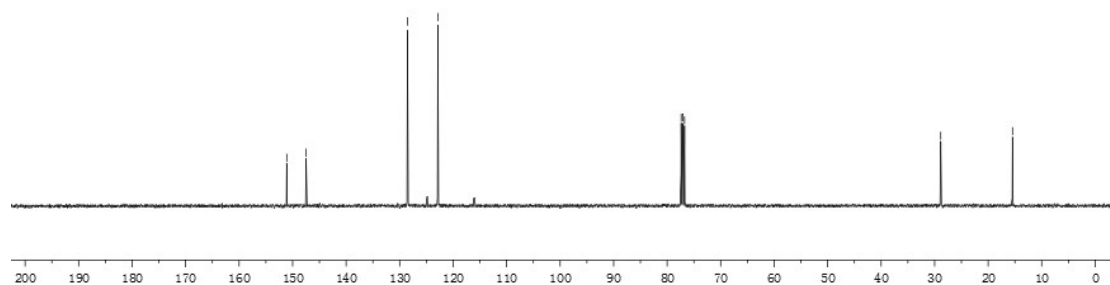
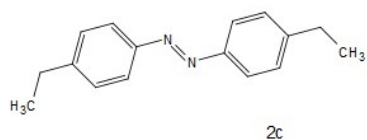
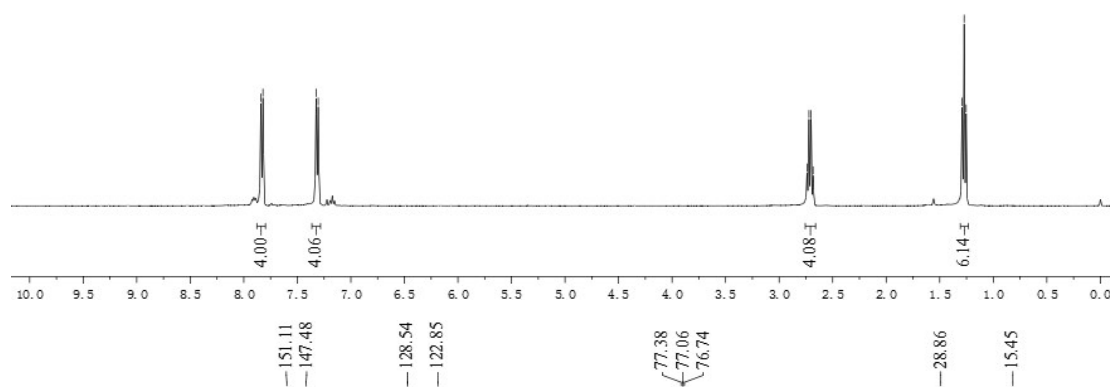
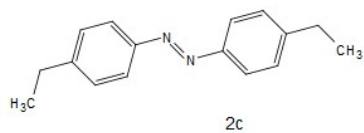


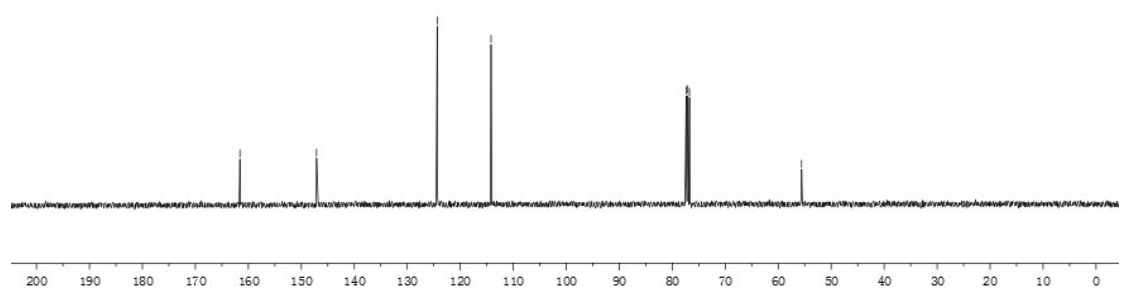
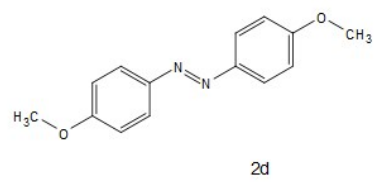
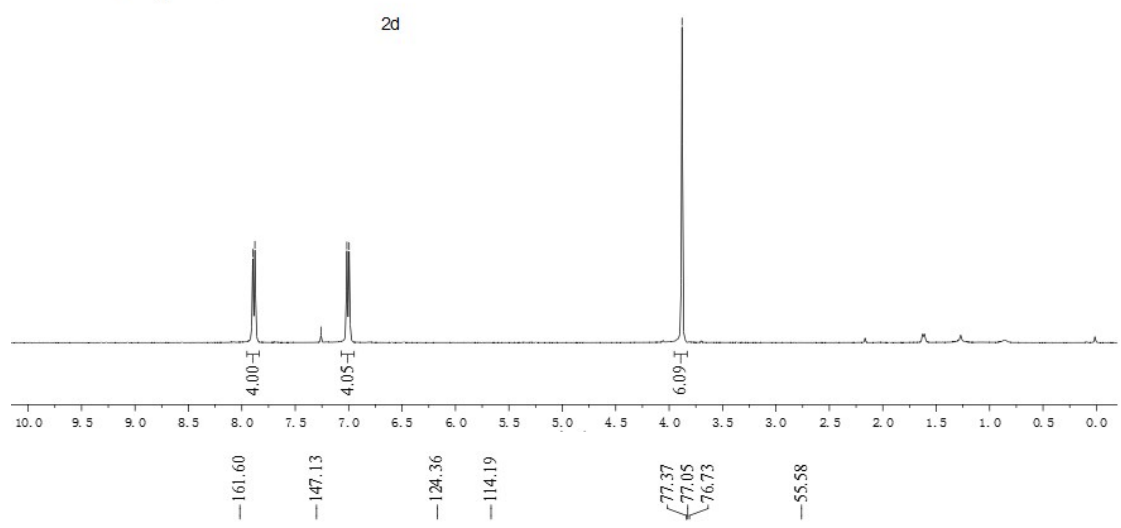
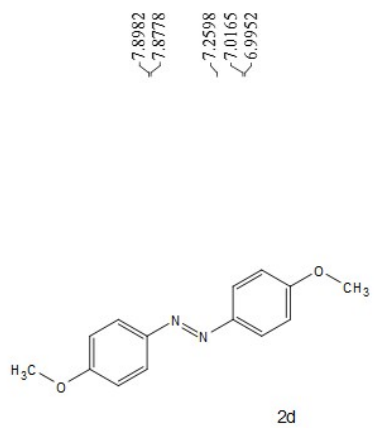


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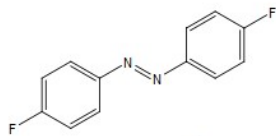
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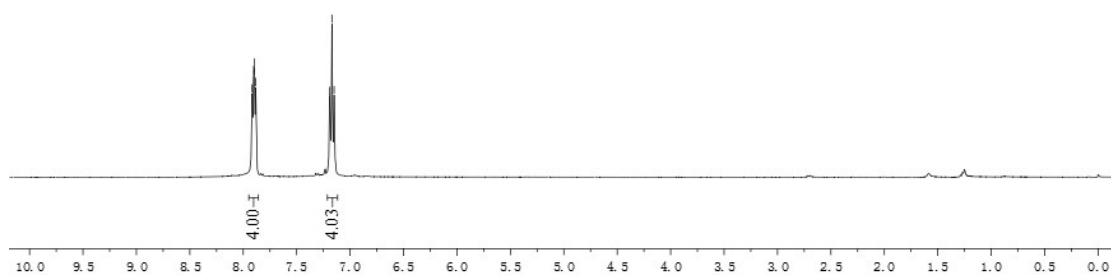




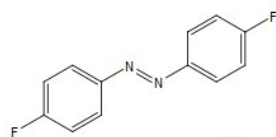
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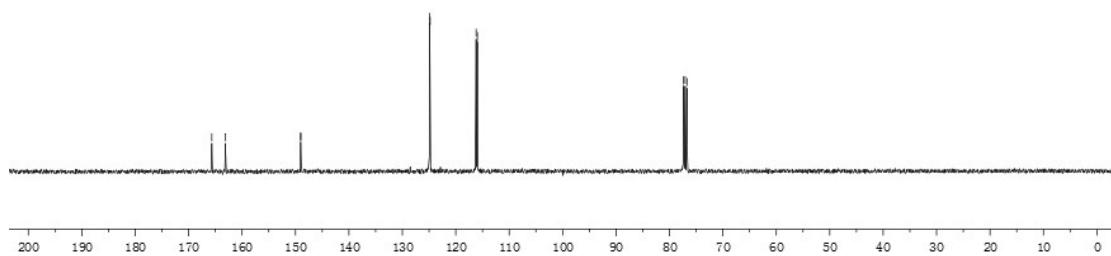
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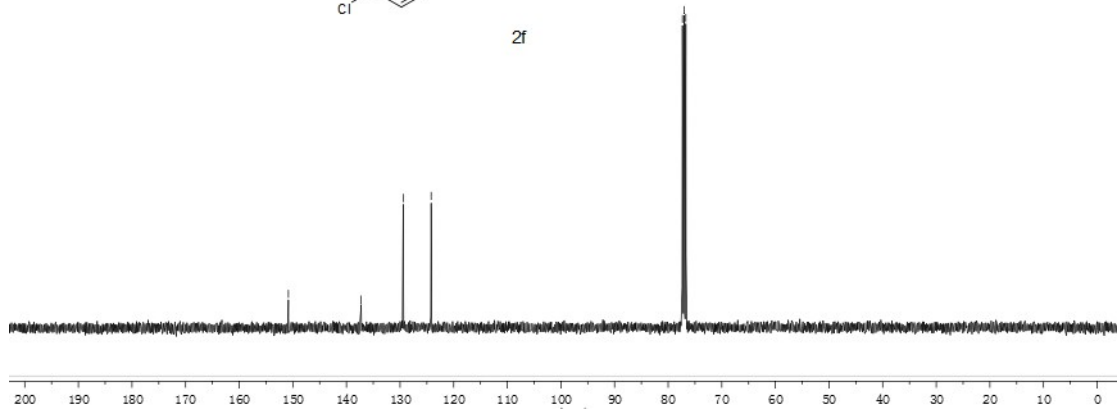
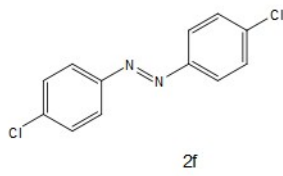
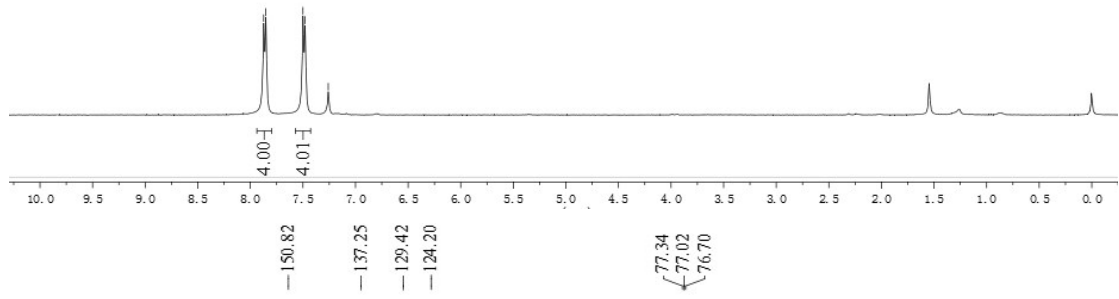
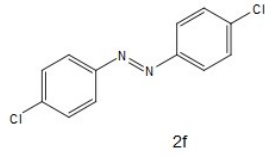
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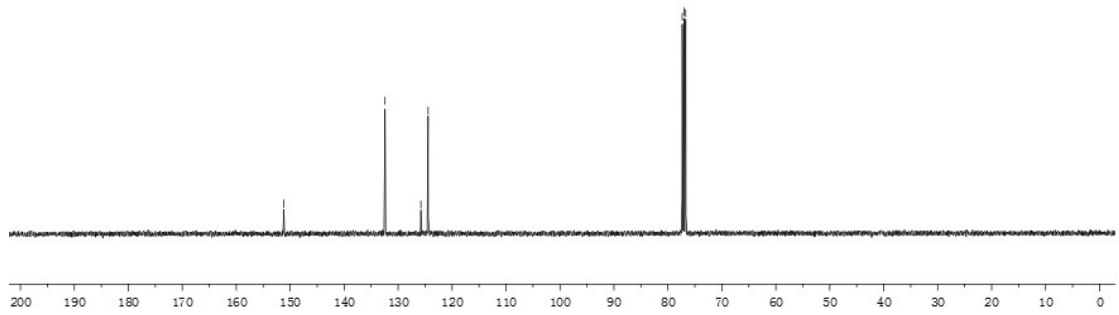
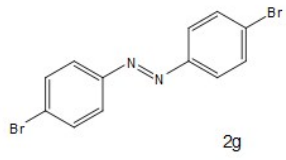
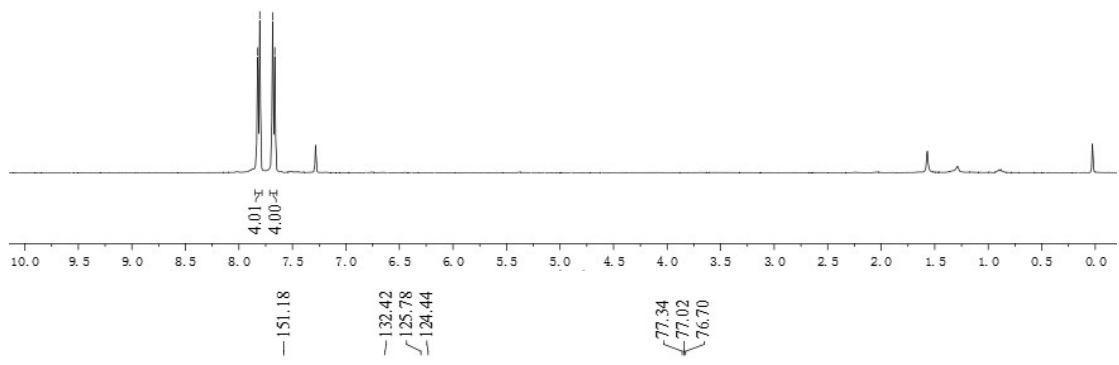
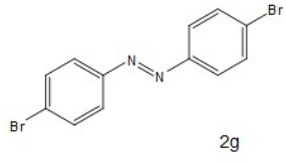
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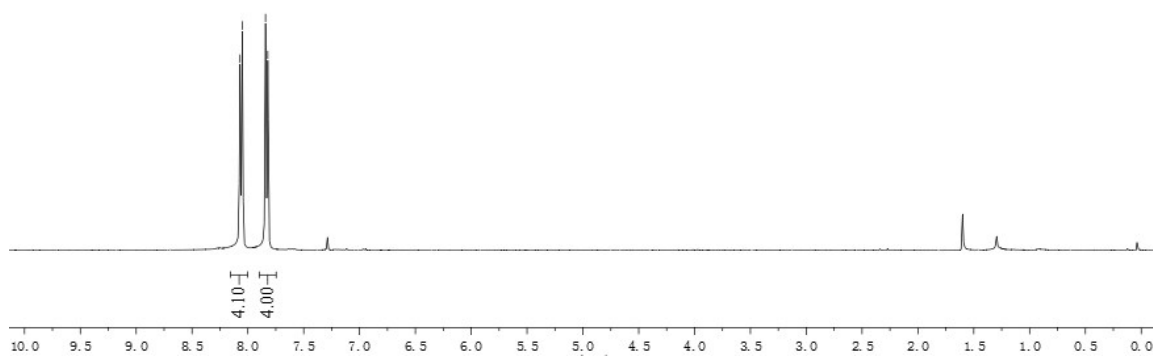
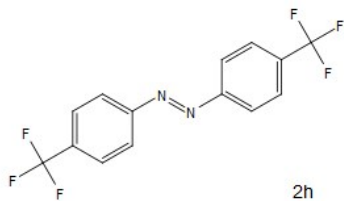
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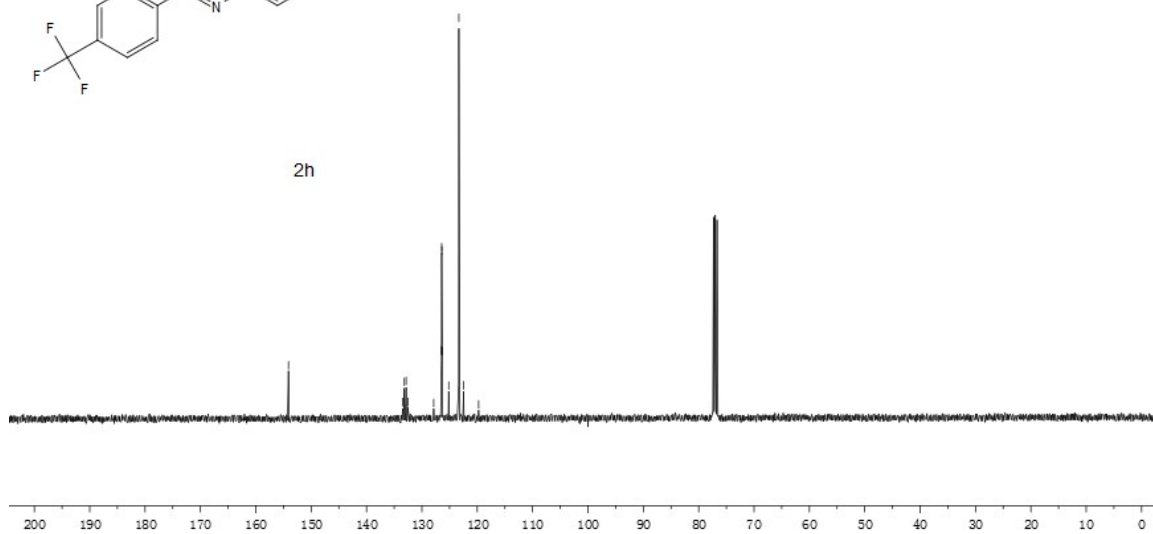
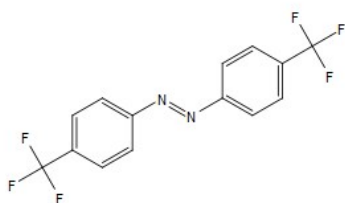
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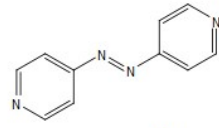


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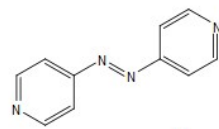
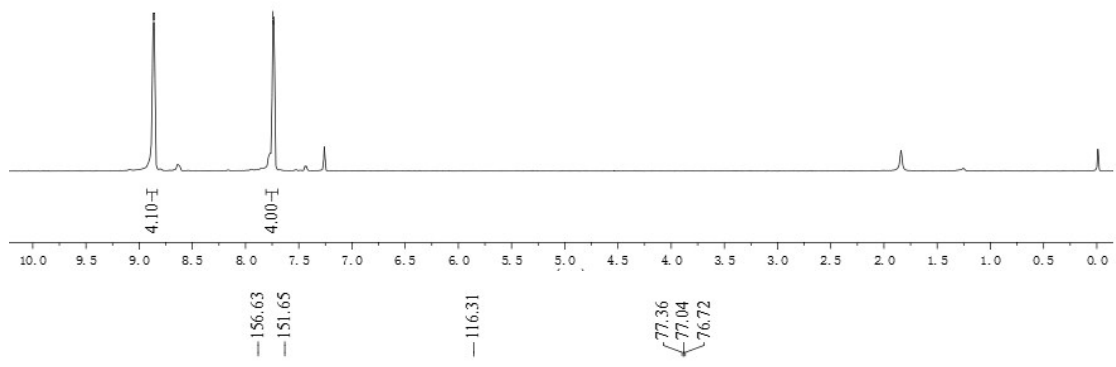


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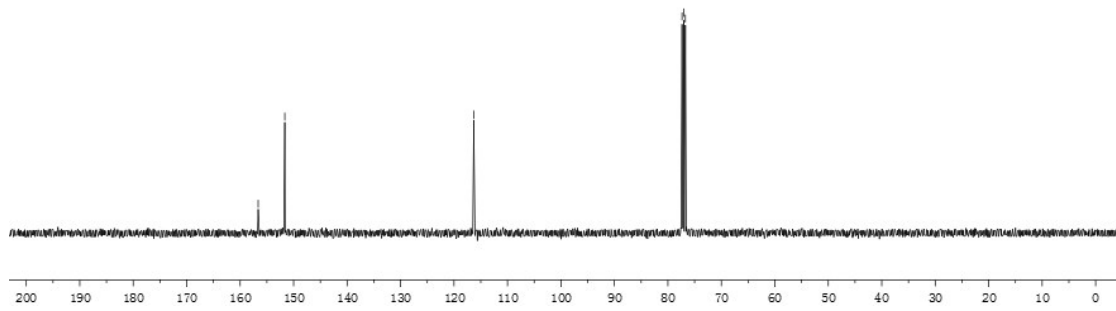
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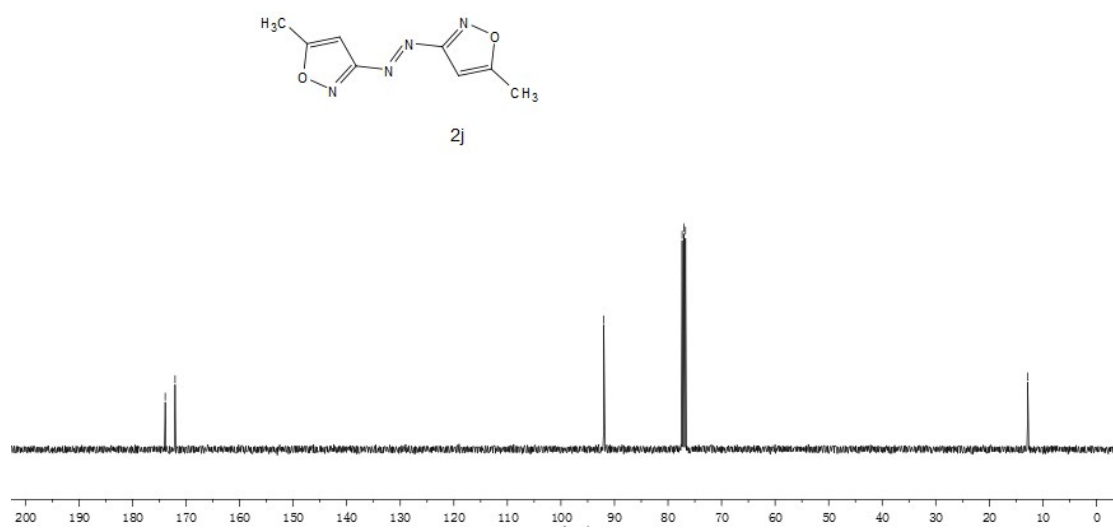
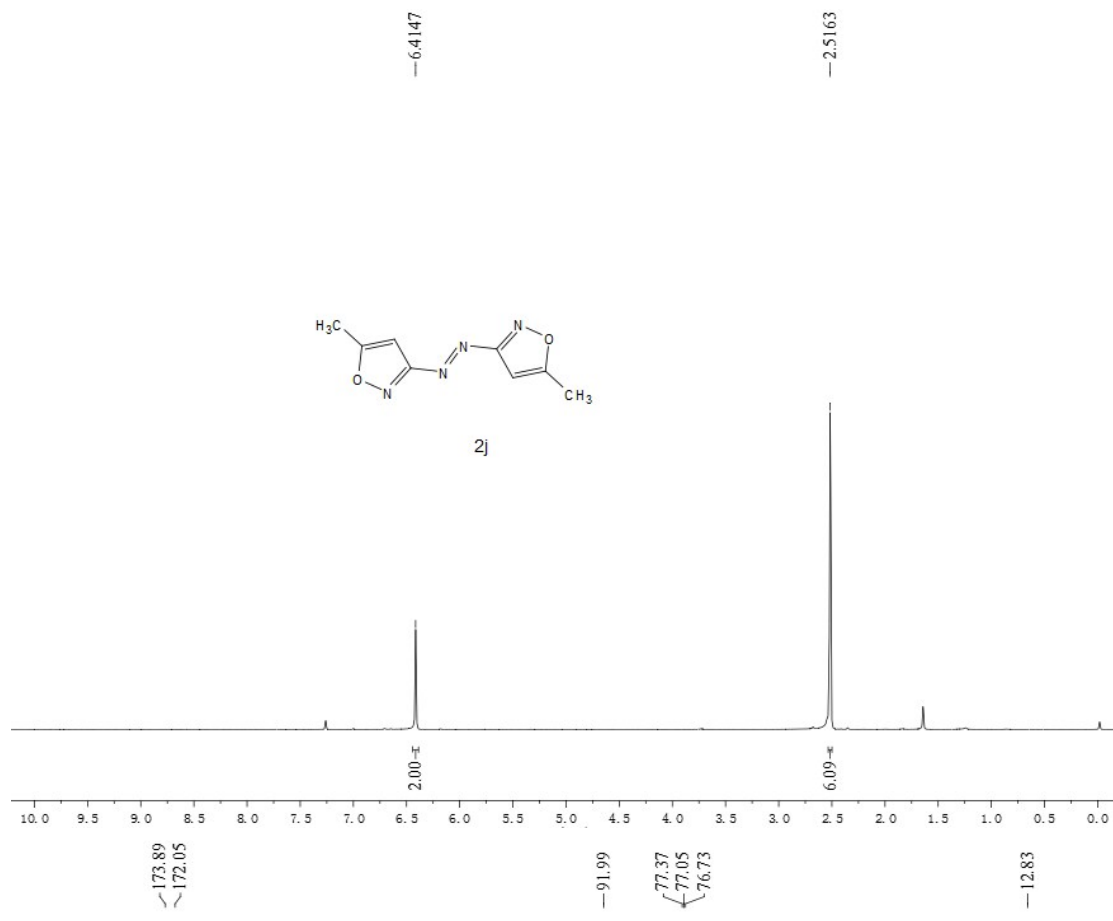


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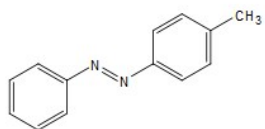
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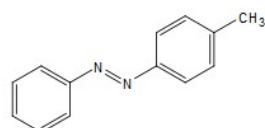
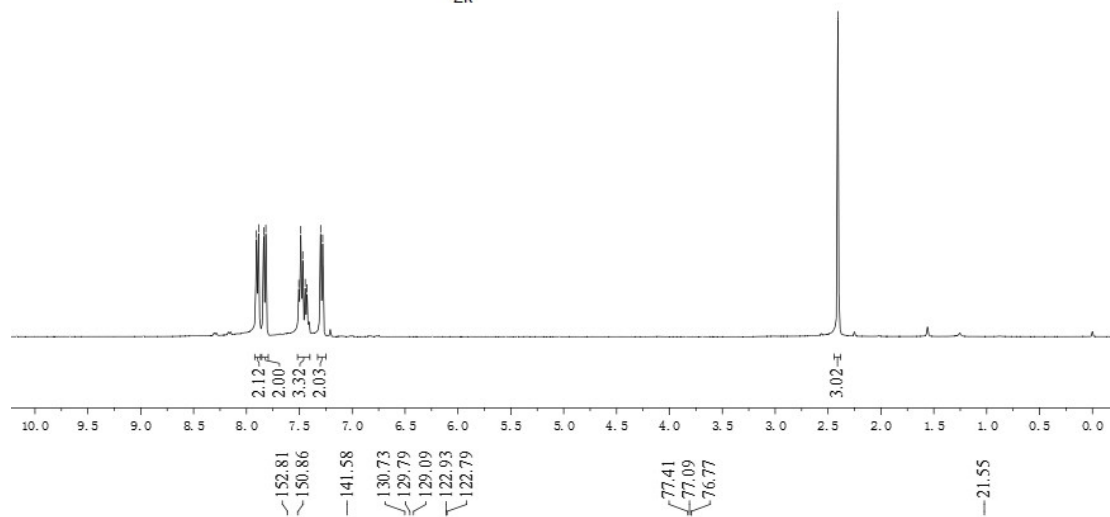


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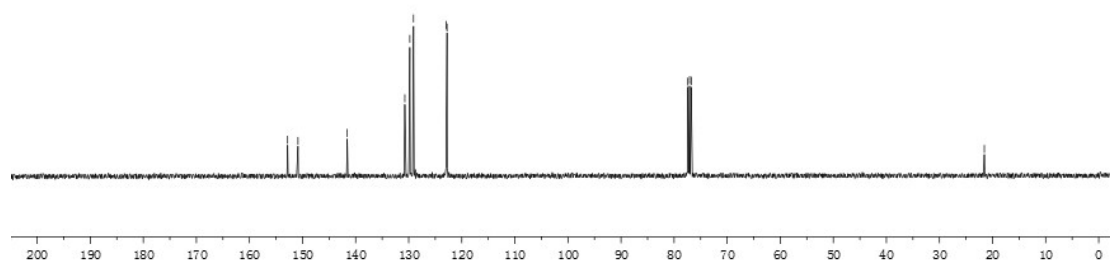
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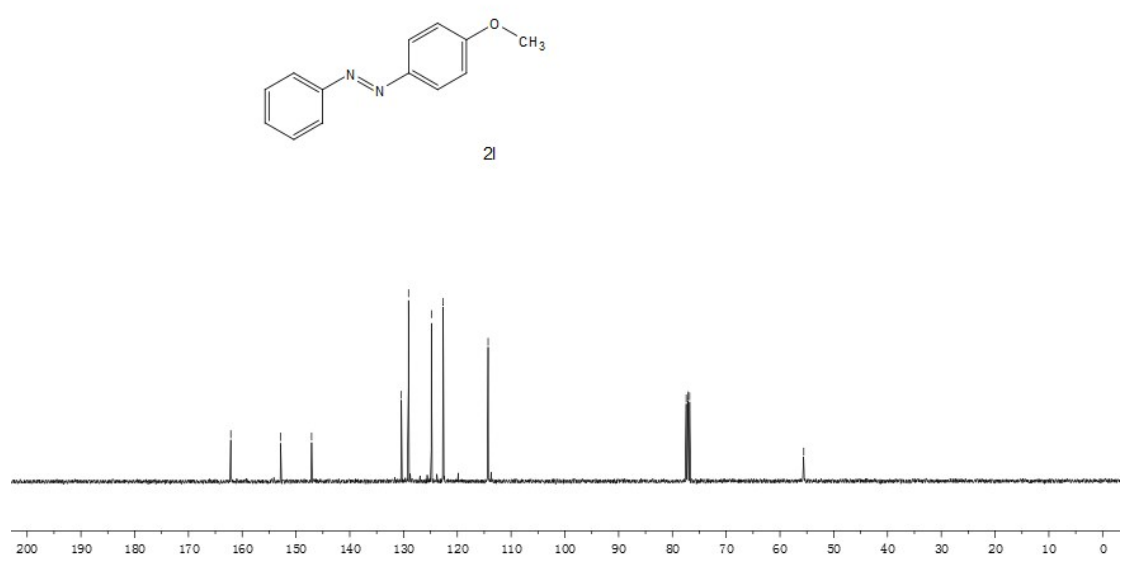
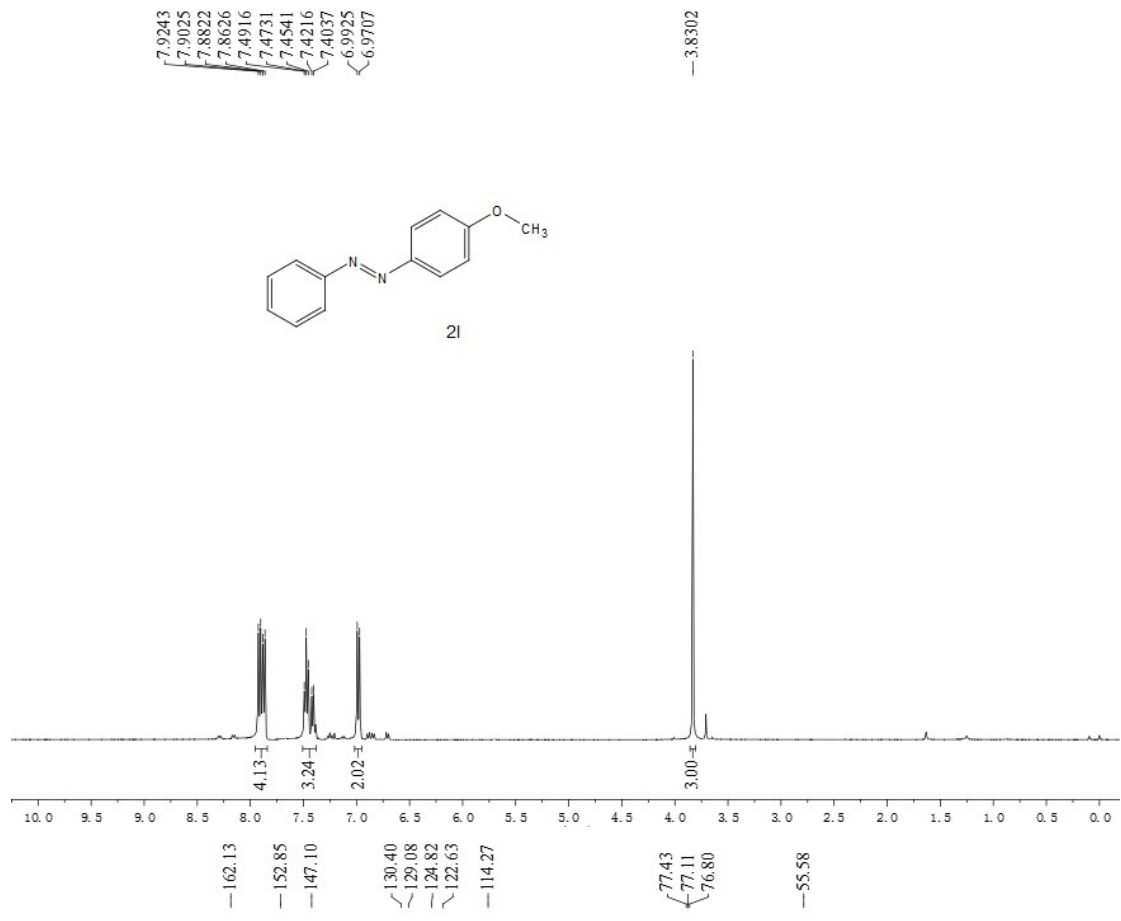


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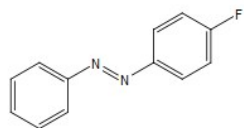


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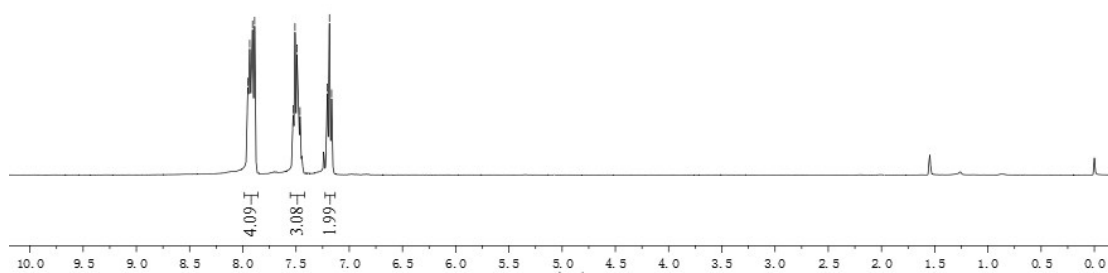




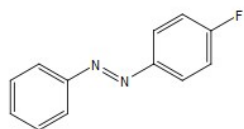
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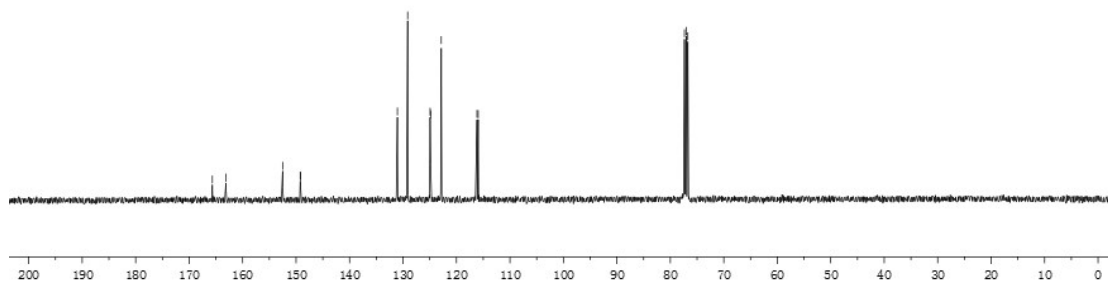
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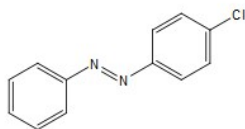
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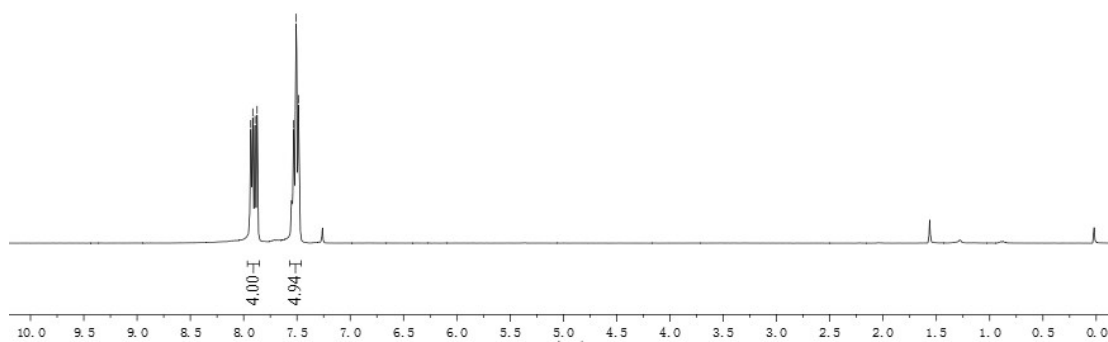
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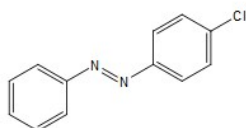
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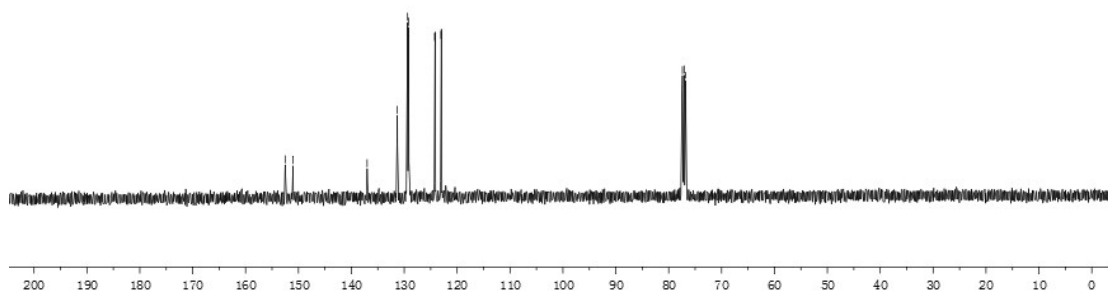
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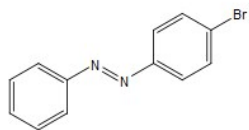
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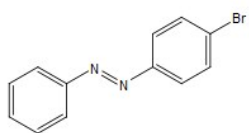
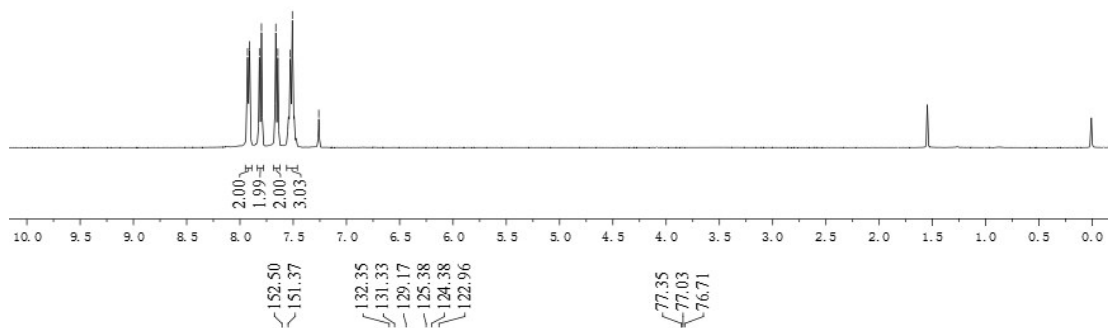
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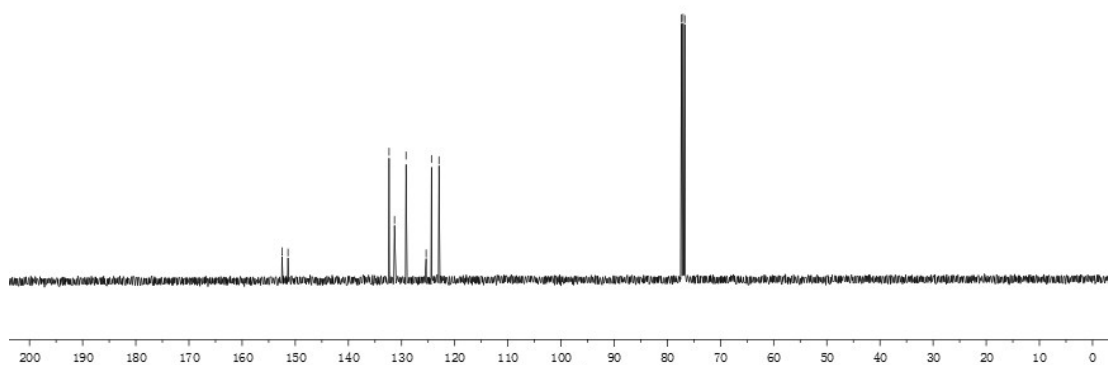
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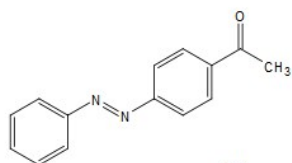


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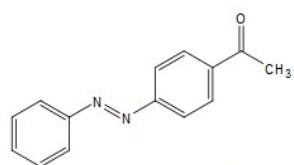
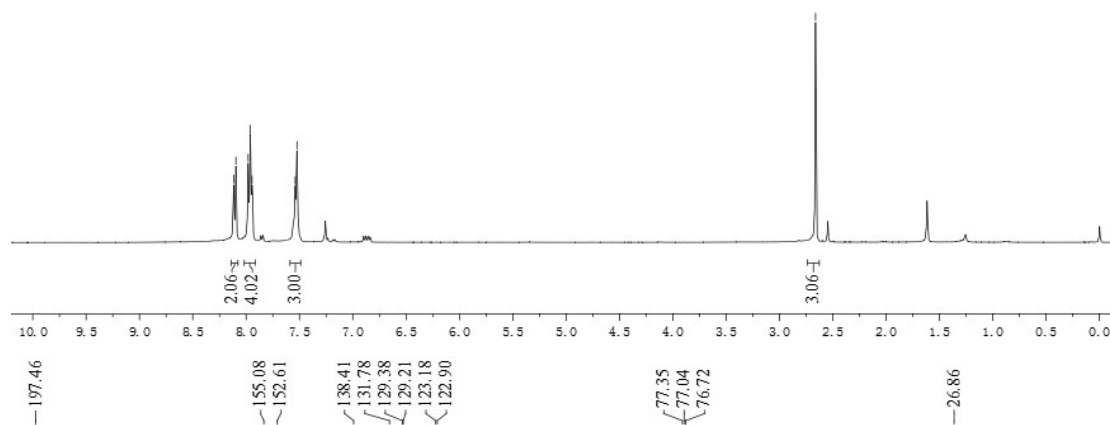


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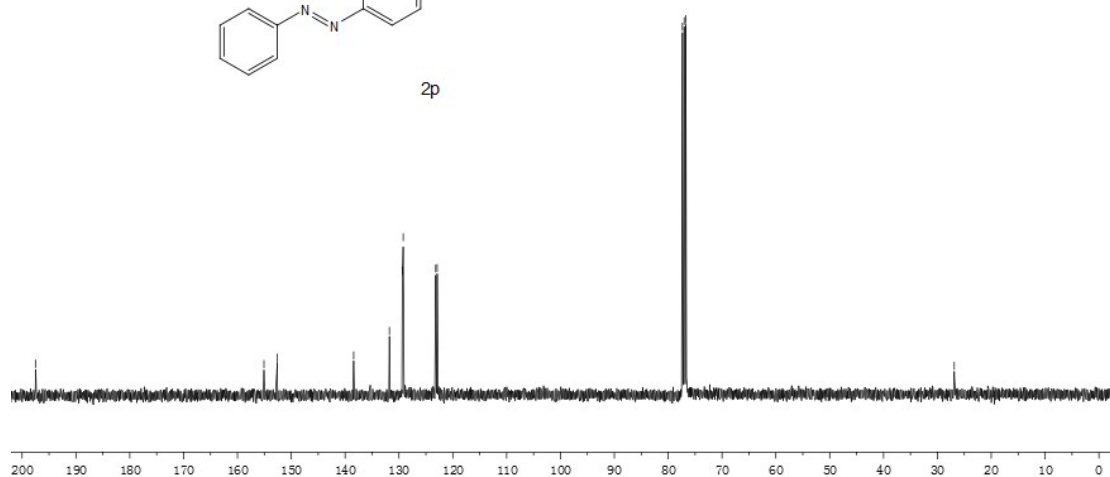
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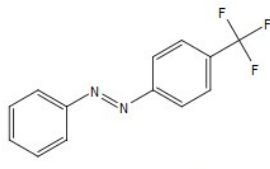
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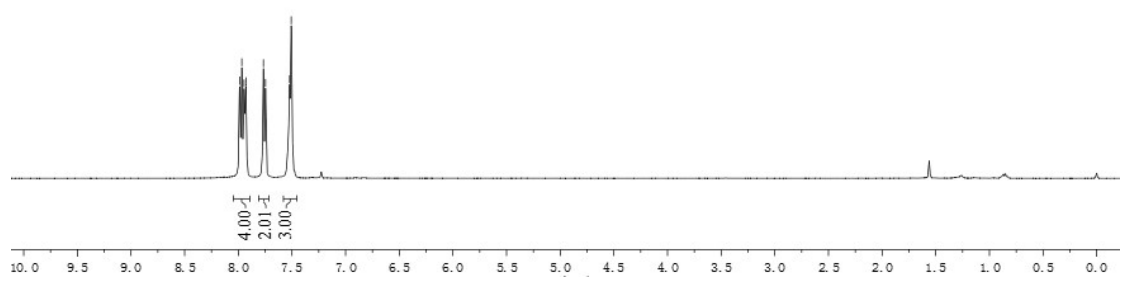
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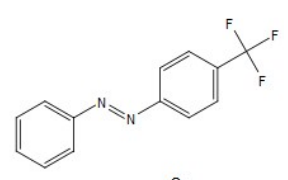
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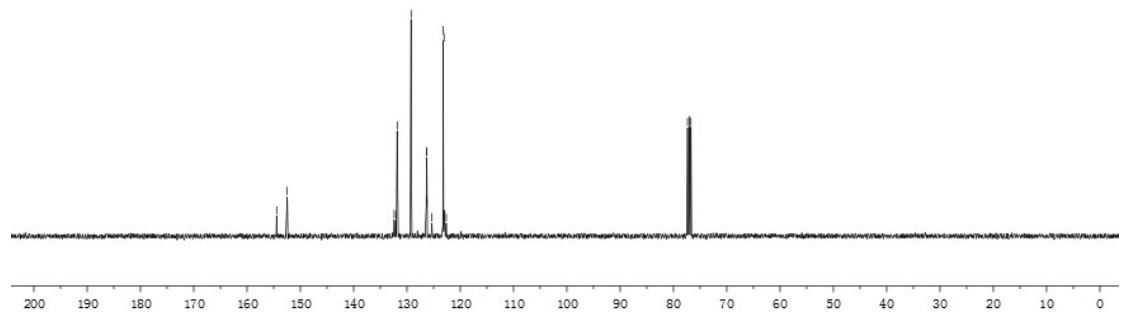
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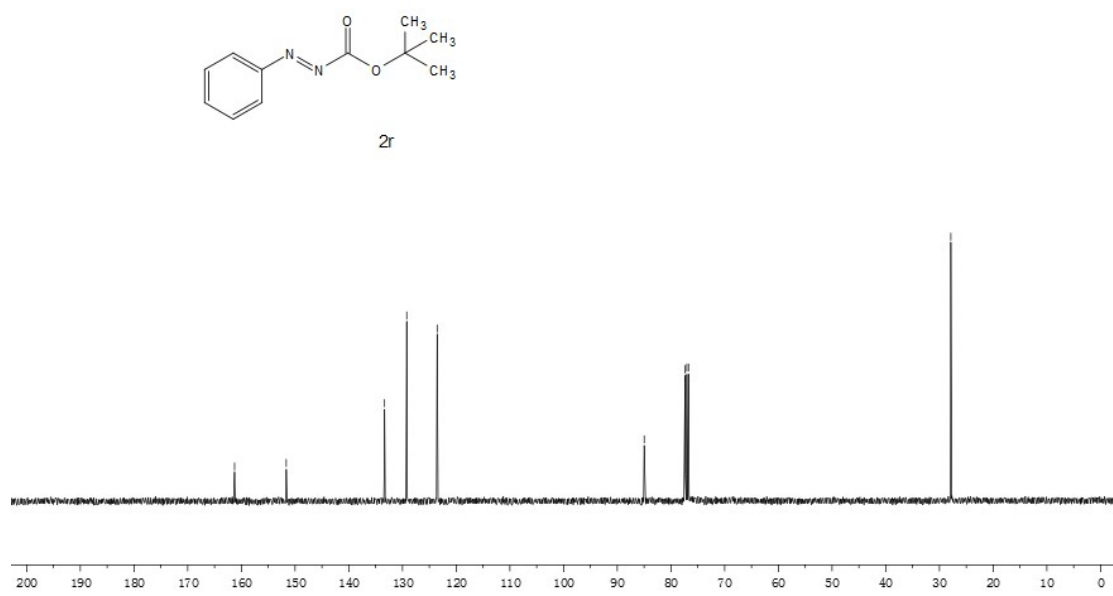
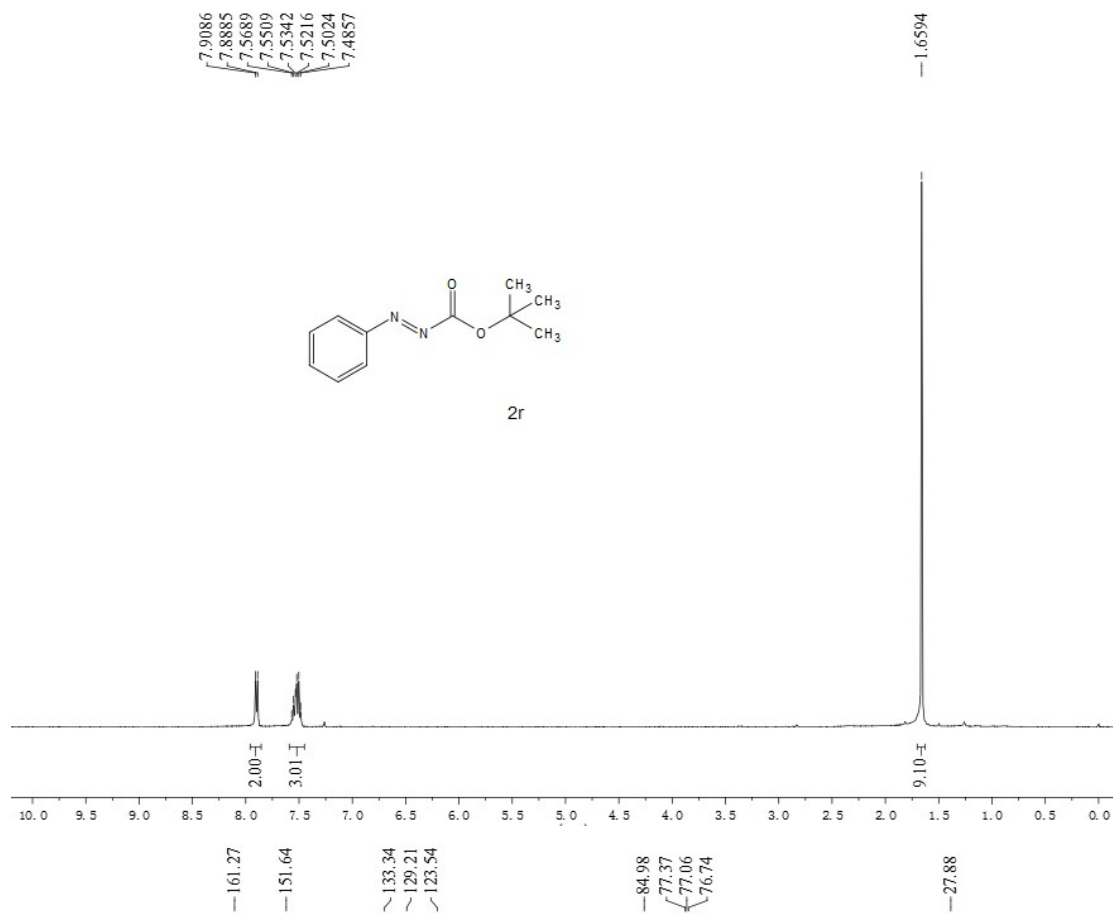


154.46
152.46
132.40
131.83
129.22
126.36
126.32
126.28
126.25
125.33
123.21
123.04
122.62
77.36
77.04
76.73

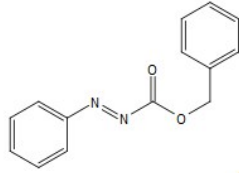


2q

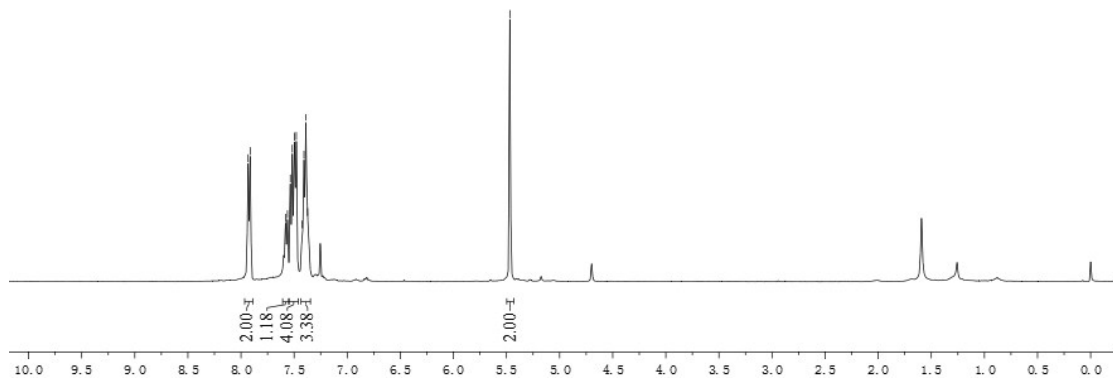




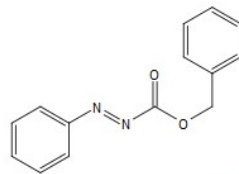
7.9327
7.9139
7.5808
7.5625
7.5353
7.5169
7.4969
7.4791
7.4232
7.4072
7.3893
7.3734
— 5.4687



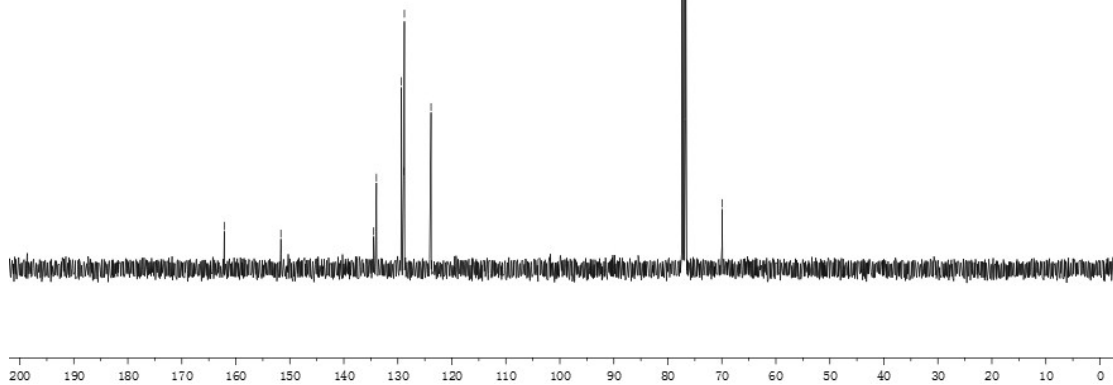
2s



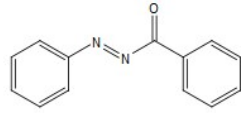
162.14
151.66
134.46
133.96
129.33
128.93
128.78
123.85
77.37
77.05
76.73
69.95



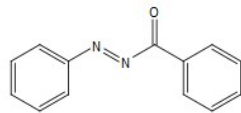
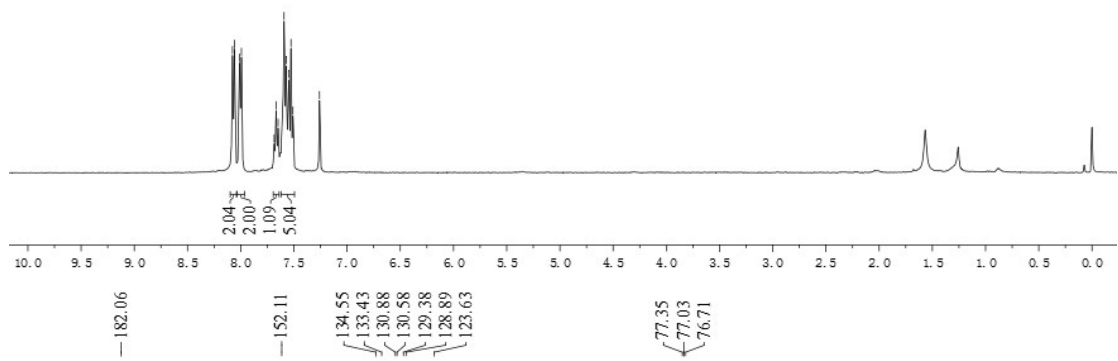
2s



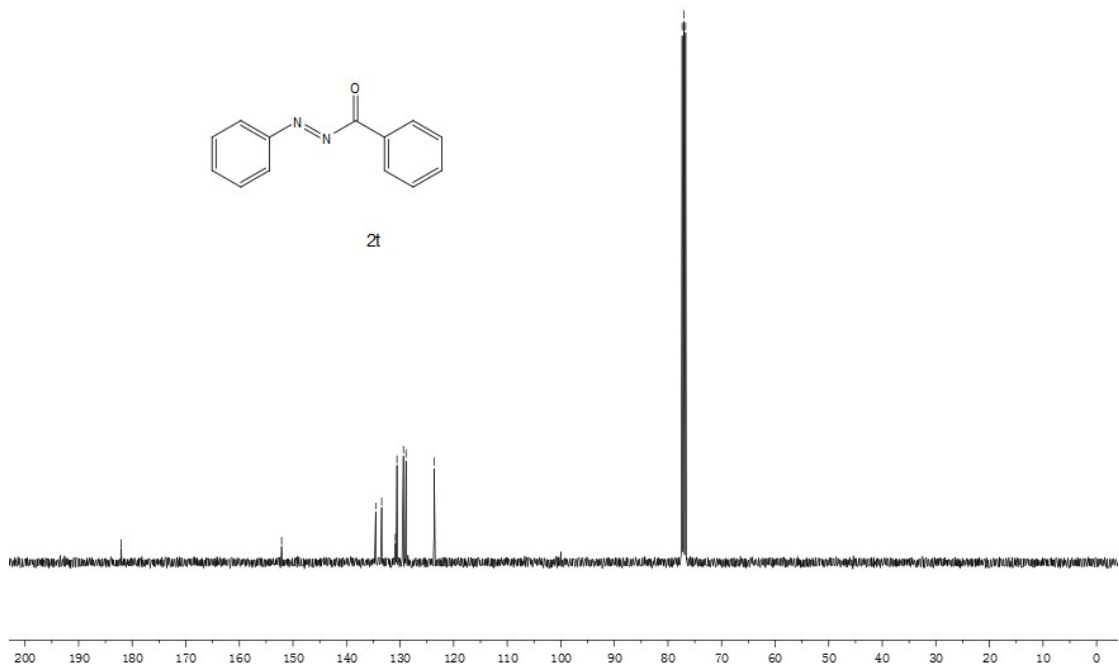
8.0770
8.0583
8.0107
7.9930
7.6852
7.6671
7.6485
7.5923
7.5730
7.5480
7.5276
7.5093
7.2593



2f

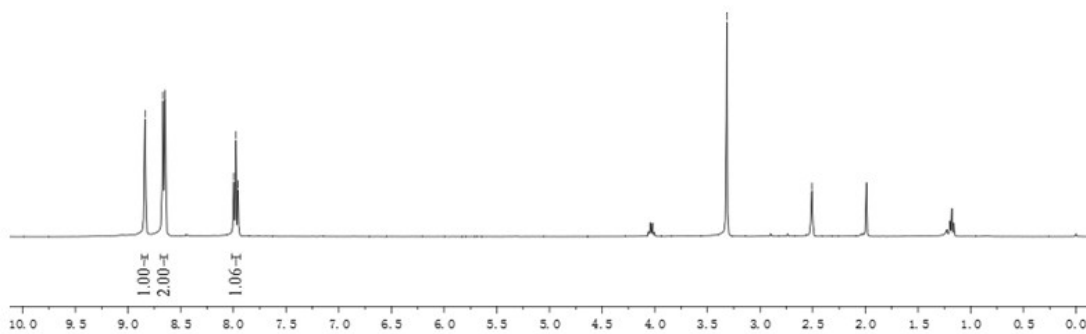
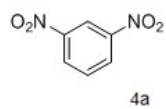


2f

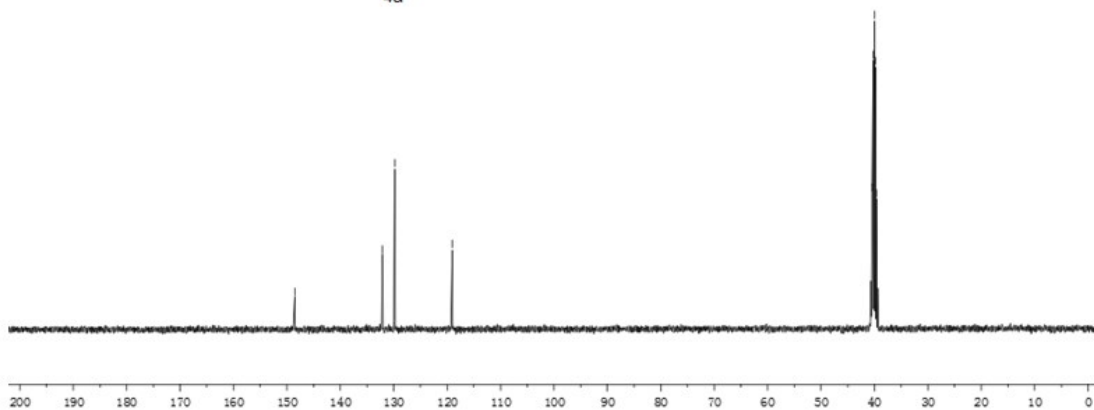
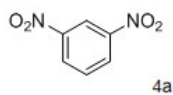


8.8391
8.6681
8.6477
7.9964
7.9759
7.9553

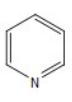
3.3157
2.5087



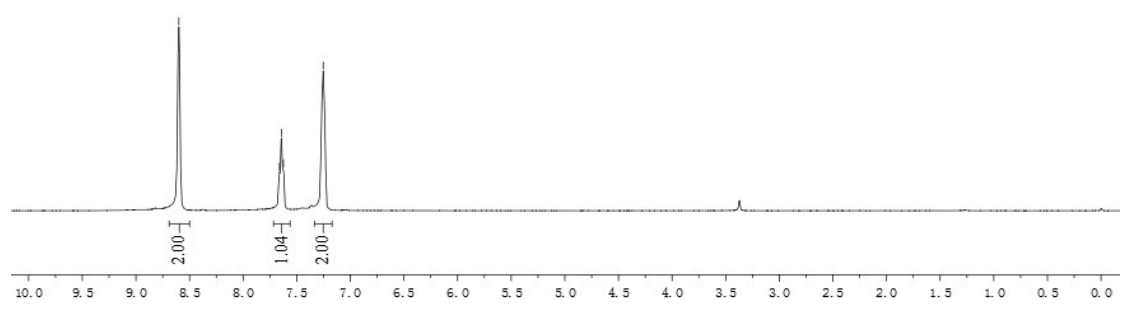
148.51
132.09
129.83
119.01
40.44
40.23
40.02
39.81
39.61



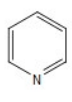
—8.5992
7.6608
7.6427
7.6245
7.2532



4b



—149.76
—135.84
—123.64
77.53
77.21
76.89



4b

