Supporting Information

A Mild Copper-catalyzed Aerobic Oxidative Thiocyanation of Arylboronic Acids with TMSNCS

Nan Sun,[a,*] Liusheng Che,[a] Weimin Mo,[a] Baoxiang Hu,[a] Zhenlu Shen[a] and Xinquan Hu[a,b,*]

[a] College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310014, P. R. China

[b] Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China

E-mail: sunnan@zjut.edu.cn and xinquan@zjut.edu.cn

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General

All proton NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer in deuterium solvents with tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a NICOLET AVATAR 370 FT-IR instrument. GC analyses were performed on a Thermo TRACE GC Ultra instrument with FID detector using a HP-5 capillary column (30 m x 0.25 mm (i.d.), 0.25 μ). Flash column chromatography was performed on silica (200-300 mesh) with petroleum ether/ethyl acetate as eluent. Melting points (uncorrected) were determined on BUCHI M-565 apparatus. Acetonitrile was treated with CaH_2 and fresh distilled before use. 3 Å MS was dried at 400-450 ^{o}C for 5

h before use. Other solvents and reagents were directly used without further purification.

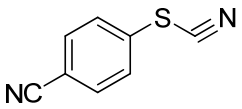
General procedure for the preparation of aryl thiocyanates

To 20 ml two-necked reaction flask was added with arylboronic acids (2.0 mmol), CuCl (0.2 mmol), TMEDA (0.2 mmol), K_2CO_3 (4.0 mmol), 3 Å MS (1.5 g) and CH_3CN (5 ml), followed by connecting an oxygen balloon. The suspension was stirred for 15 min at room temperature and then TMSNCS (1.0 mmol) and NaF (1.0mmol) was subsequently added. The mixture was stirred at room temperature for 12 h to complete the reaction. The resulting reaction mixture was filtrated to remove the insoluble catalyst and 3Å MS, and washed with CH_3CN. The combined filtrates were concentrated under reduced pressure. Finally, the residual was purified by flash column chromatography (petroleum ether/ethyl acetate) on silica gel to afford the desired aryl thiocyanates.

Characterization data for aryl thiocyanates 2l, 2m, 2p and 2q

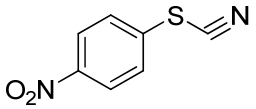
Note: For the Characterization data and NMR Spectra of aryl thiocyanates **2a-2k, 2n and 2o**, please see our previous report in "*Synlett* **2013**, *24*, 1443-1447" .

4-Cyanophenyl thiocyanate ***2l***



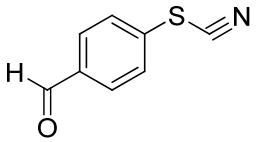
White solid, mp: 126.8 ^oC (lit.[1] mp: 127-128 ^oC); υ_{max}/cm^{-1} (KBr) 2163.8 and 2226.9; ^1H NMR (500 MHz; $CDCl_3$) δ = 7.62-7.75 (m, 4H); ^{13}C NMR (125 MHz; $CDCl_3$) δ = 108.1, 113.1, 117.4, 128.8, 133.3 and 133.5; GC-MS (EI) *m/z* 160 (M^+). CAS Reg. No. 122148-91-8.

4-nitrophenyl thiocyanate ***2m***



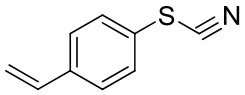
White solid, mp: 130 ^{o}C (lit.[1] mp: 128-129 ^{o}C); υ_{max}/cm^{-1} (KBr) 2164.0; ^{1}H NMR (500 MHz; $CDCl_3$) δ = 7.68-8.33 (m, 4H); ^{13}C NMR(125 MHz; $CDCl_3$) δ = 108.0, 125.1, 128.7, 133.3 and 148.0; GC-MS (EI) *m/z* 180 (M^+). CAS Reg. No. 2137-92-0.

4-Formylphenyl thiocyanate ***2p***



White solid, mp: 83.4 ^{o}C (lit.[2] mp: 82-83 ^{o}C); υ_{max}/cm^{-1} (KBr) 1699 and 2159; ^{1}H NMR (500 MHz; $CDCl_3$) δ = 7.67-7.97 (m, 4H), 10.04 (s, 1H); ^{13}C NMR (125 MHz; $CDCl_3$) δ = 108.6, 128.6, 130.9, 132.3, 136.4 and 190.4; GC-MS (EI) *m/z* 163 (M^+). CAS Reg. No. 89898-72-6.

4-Vinylphenyl thiocyanate ***2q***



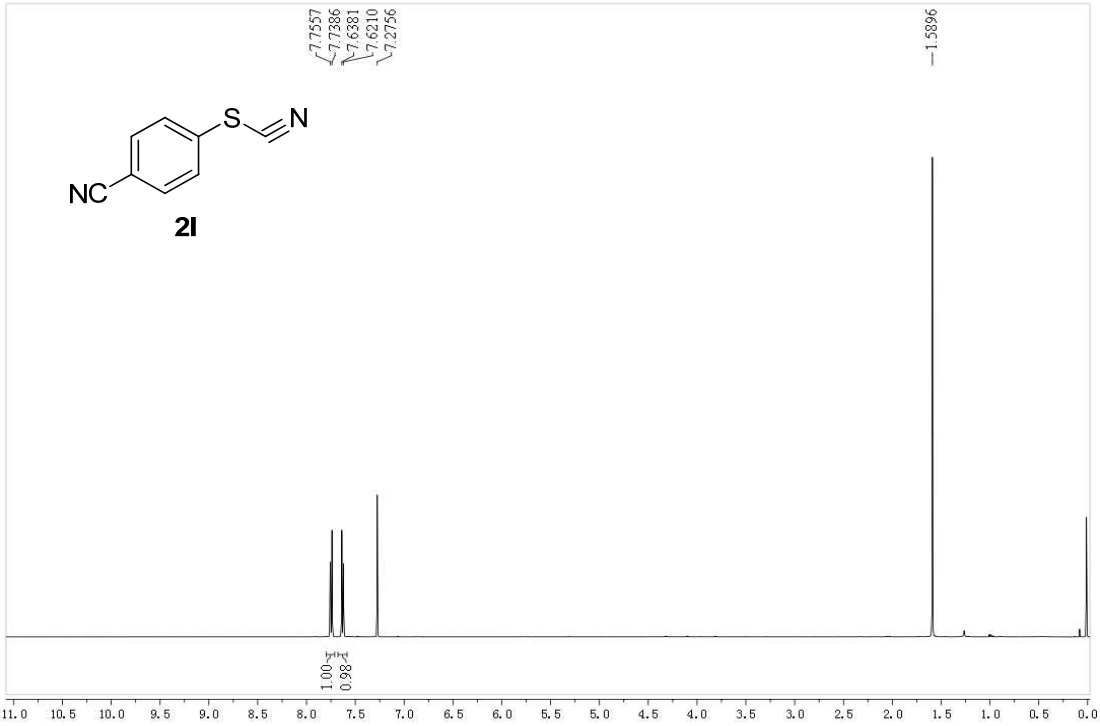
Colourless oil; υ_{max}/cm^{-1} (neat) 2156.6 and 1629.6; ^{1}H NMR (500 MHz; $CDCl_3$) δ = 5.37-5.84(m, 2H), 6.68-6.74(m, 1H), 7.46-7.51 (m, 4H); ^{13}C NMR(125 MHz; $CDCl_3$) δ = 110.5, 116.2, 123.0, 127.8, 130.3, 135.2 and 139.0; GC-MS (EI) *m/z* 161(M^+). CAS Reg. No. 187729-73-3.

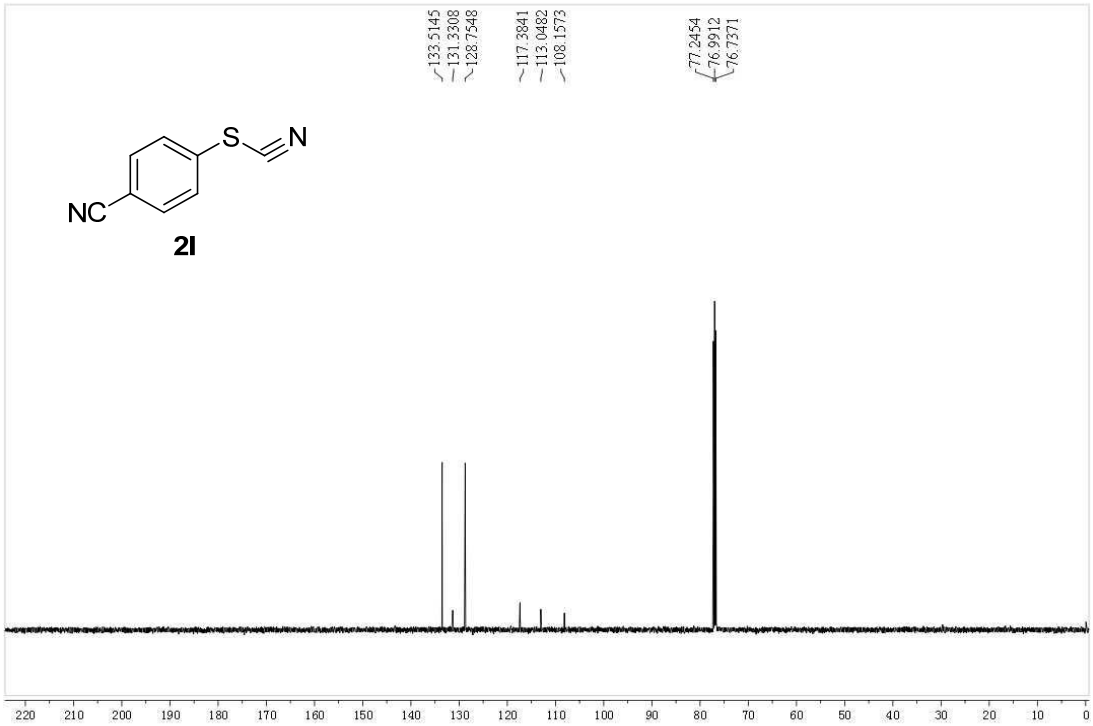
References

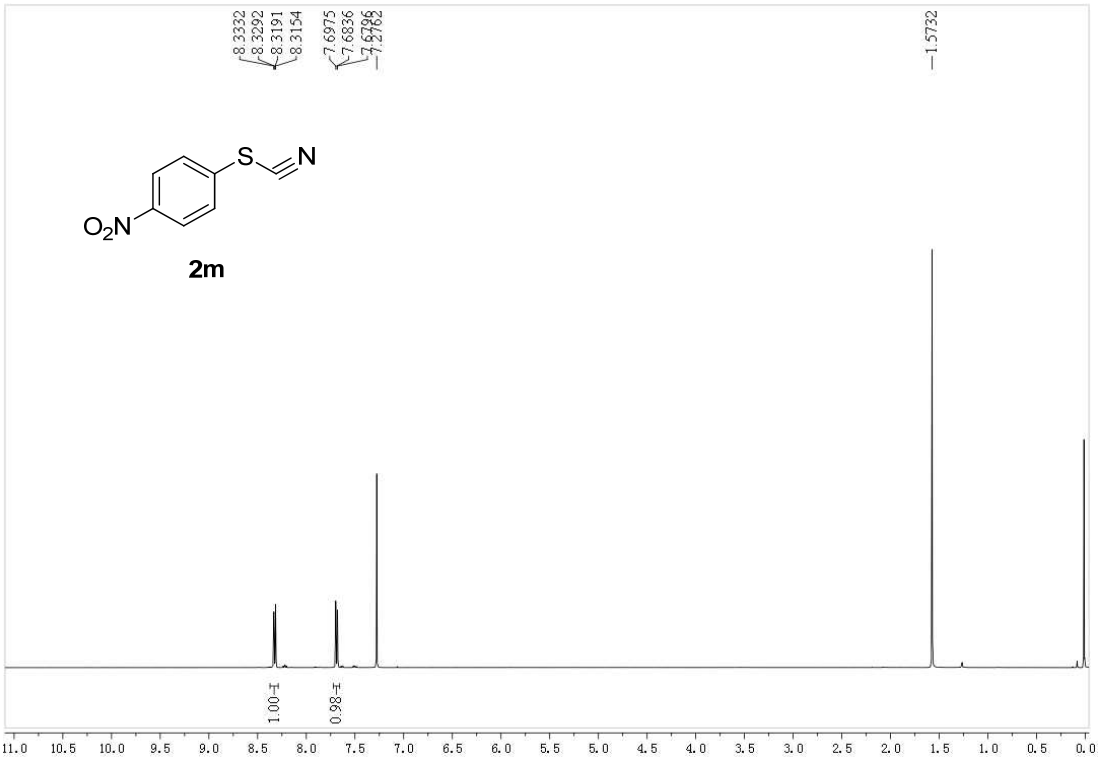
1. R. Riemeschneider, F. Wojahn and G. Orlick, *J. Am. Chem. Soc.* **1951**, *73*, 5905.

2. D. T. Gryko, C. Clausen and J. S. Lindsey, *J. Org. Chem.* **1999**, *64*, 8635.

Proton NMR and ^{13} C NMR Spectra for aryl thiocyanates 2l, 2m, 2p and 2q



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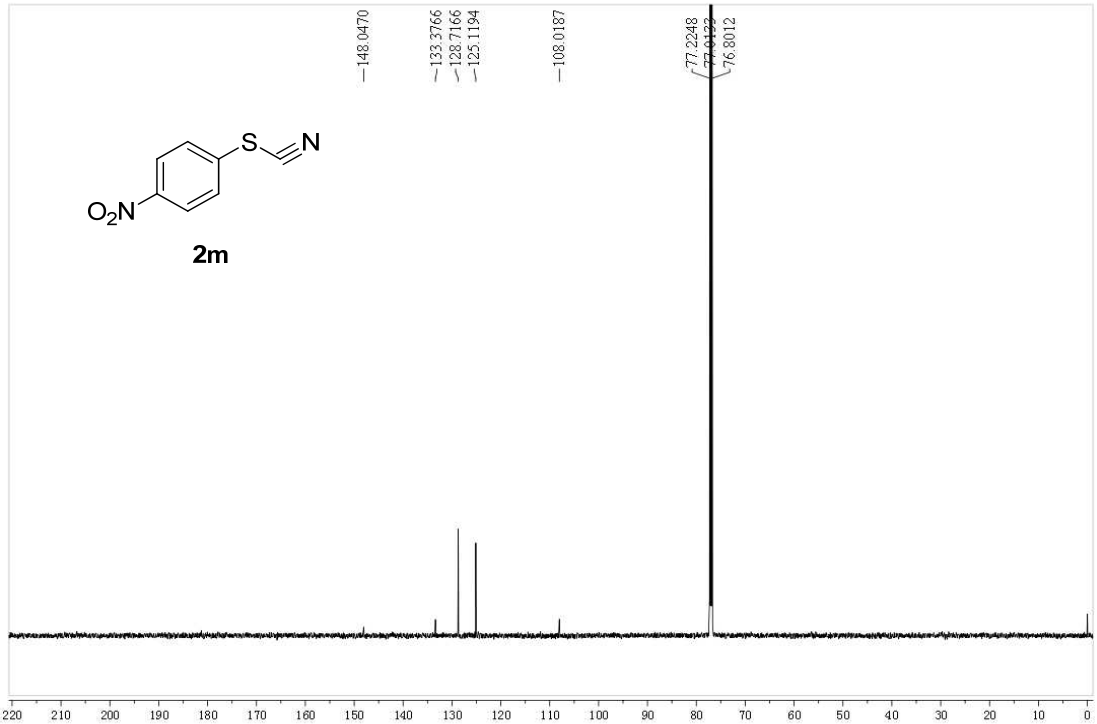
O2N
2m
1.00
0.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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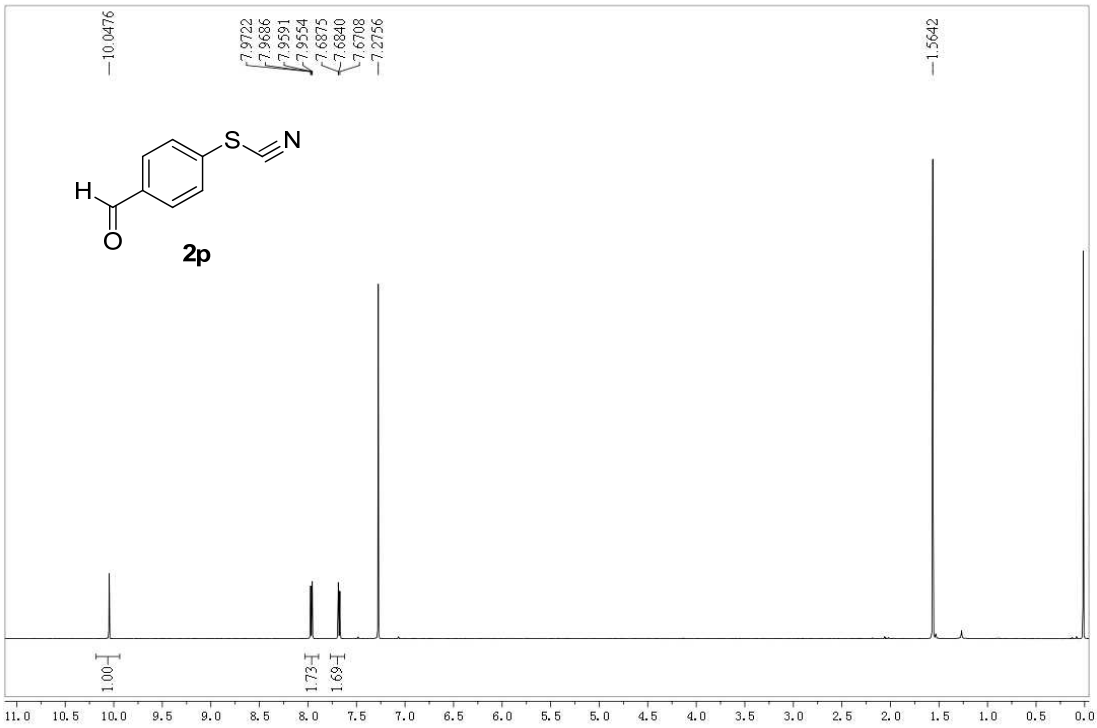
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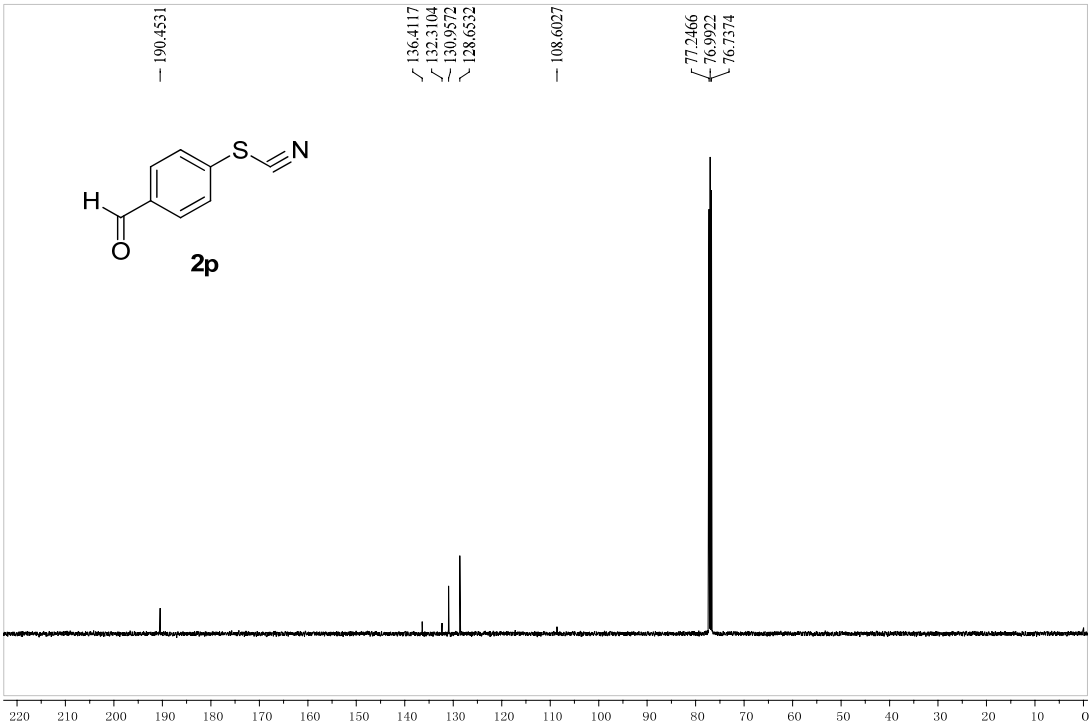
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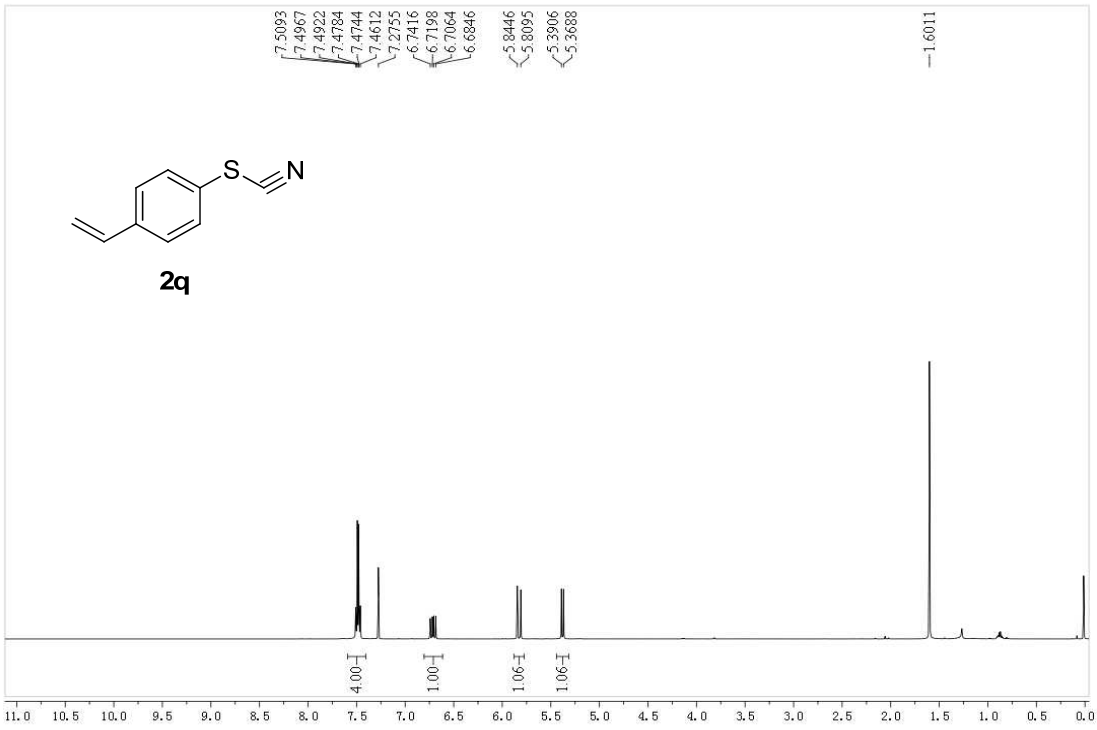
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5.3906
5.3688
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2q
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1.00
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1.06
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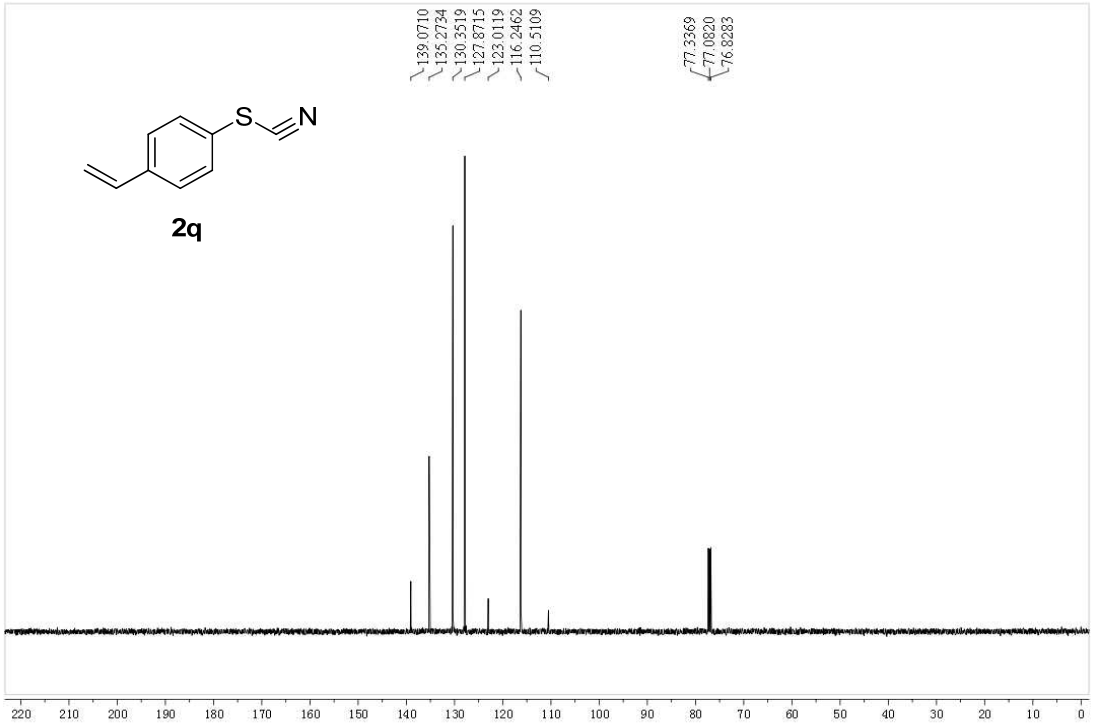
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