Supporting Information for

Rhodium-Catalyzed *ortho*-Cyanation of Symmetrical Azobenzenes with *N*-Cyano-*N*-phenyl-*p*-toluenesulfonamide

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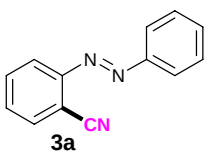
1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker spectrometer using $CDCl_3$ as the solvent, and all chemical shifts are given as δ value with $(CH_3)_4Si$ as the internal standard. Coupling constants (*J*) are reported in Hertz (Hz). The peaks are indicated according to following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. HRMS were measured on a TOF mass analyzer. C, H, and N analyses were performed on an elemental analyzer. Melting points are uncorrected.

2. Typical Procedure for Rhodium-Catalyzed *ortho*-Cyanation of Symmetrical Azobenzenes with NCTS.

A 20 mL reaction tube was charged with azobenzene **1** (0.15 mmol), NCTS **2** (81.6 mg, 2 equiv), $[Cp^*RhCl_2]_2$ (4.6 mg, 5 mol %), $AgNTf_2$ (29.1 mg, 50 mol %), NaOAc (12.3 mg, 1 equiv) and DCE (1 mL). The reaction mixture was stirred at 130 °C for 24 h and monitored by TLC. After the reaction completed, the solvent was removed and the residue was further purified by preparative thin layer chromatography (silica gel, ethyl acetate / petroleum ether = 1:5), affording the cyanated product **3.**

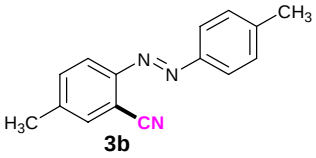
3. Characterization Data of Products 3a-q



3a

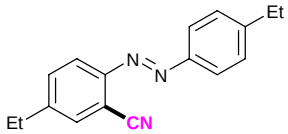
2-Cyanoazobenzene (3a). Yellow solid(23.3 mg, 75%), mp 57−59°C (lit,[1] 58.6-59.7°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.03 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.58-7.54 (m, 4H). ^{13}C NMR (100MHz,

$CDCl_3$): δ 153.2, 152.3, 133.6, 133.4, 132.5, 130.9, 129.3, 123.7, 117.1, 116.9, 113.2. Anal. Calcd for $C_{13}H_9N_3$: C, 75.35; H, 4.38; N, 20.28. Found: C, 75.42; H, 4.31; N, 20.35.



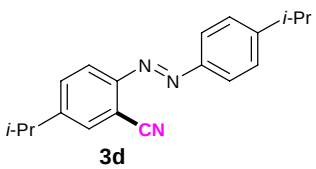
3b

2-Cyano-4,4'-dimethylazobenzene (3b). Yellow solid (25.7 mg, 73%), mp 84−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 0.8 Hz, 1H), 7.48 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 150.5, 143.0, 141.5, 134.2, 133.7, 129.9, 123.6, 117.1, 116.9, 113.0, 21.6, 21.2. HRMS (ESI) m/z: Calcd for $C_{15}H_{13}N_3Na$ $[M+Na]^+$ 258.1002, Found 258.1006. Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.62; H, 5.49; N, 17.91.



3c

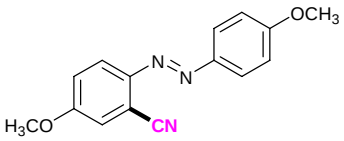
2-Cyano-4,4'-diethylazobenzene (3c). Yellow solid(23.9 mg, 61%), mp 47−49 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.49 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 2.74 (dq, *J* = 7.6, 3.6 Hz, 4H), 1.29 (dt, *J* = 7.6, 1.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 150.7, 149.3, 147.6, 133.1, 132.6, 128.7, 123.7, 117.3, 116.9, 113.0, 28.9, 28.5, 15.4, 15.1. HRMS (ESI) m/z: Calcd for $C_{17}H_{17}N_3Na$ $[M+Na]^+$ 286.1315, Found 286.1312. Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.47; H, 6.58; N, 16.05.



3d

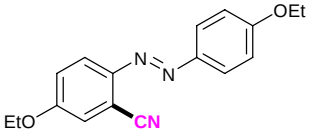
2-Cyano-4,4'-di-iso-propylazobenzene (3d). Yellow solid (29.2 mg, 67%), mp 57−59 °C; ^{1}H NMR (400 MHz, $CDCl_3$):

δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 1.6 Hz, 1H), 7.52 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 3.02-2.97 (m, 2H), 1.30 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 152.2, 151.7, 150.8, 131.8, 131.4, 127.3, 123.7, 117.3, 117.1, 113.0, 34.3, 33.9, 23.8, 23.6. HRMS (ESI) m/z: Calcd for $C_{19}H_{21}N_3Na$ $[M+Na]^+$ 314.1628, Found 314.1630.



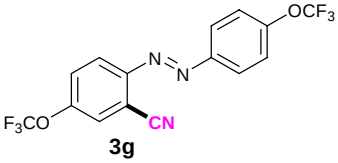
3e

2-Cyano-4,4'-dimethoxyazobenzene (3e). Yellow solid (19.8 mg, 72%), mp 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.25 (d, *J* = 2.8 Hz, 1H), 7.18 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.01 (d, *J* = 9.2 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 160.9, 147.8, 146.8, 129.9, 125.4, 120.2, 118.4, 117.0, 116.9, 114.4, 56.0, 55.7. HRMS (ESI) m/z: Calcd for $C_{15}H_{13}N_3NaO_2$ $[M+Na]^+$ 290.0900, found 290.0903.



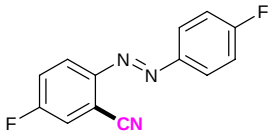
3f

2-Cyano-4,4'-diethoxyazobenzene (3f). Yellow solid (32.3 mg, 73%), mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 7.16 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.99 (dd, *J* = 7.2, 2.0 Hz, 2H), 4.11 (qd, *J* = 6.8, 4.8 Hz, 4H), 1.46 (td, *J* = 6.8, 1.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 160.3, 147.7, 146.7, 125.4, 120.6, 118.4, 117.3, 117.1, 114.8, 114.3, 64.3, 63.9, 14.8, 14.6. HRMS (ESI) m/z: Calcd for $C_{17}H1_7N_3NaO_2$ $[M+Na]^+$ 318.1213, Found 318.1217. Anal. Calcd for $C_{17}H_{17}N_3O_2$: C, 69.14; H, 5.80; N, 14.23. Found: C, 69.23; H, 5.73; N, 14.15.



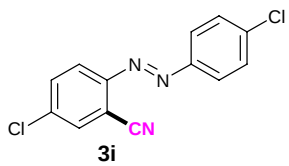
3g

2-Cyano-4,4'-ditrifluoromethoxyazobenzene (3g). Yellow oil (21.9 mg, 39%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.55 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 151.0, 150.5, 150.1, 125.9, 125.5, 125.2, 121.6, 121.5, 121.3, 119.0, 115.3, 114.9. HRMS (ESI) m/z: Calcd for $C_{15}H_7F_6N_3NaO_2$ $[M+Na]^+$ 398.0335, Found 398.0333.



3h

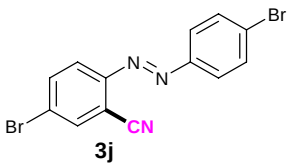
2-Cyano-4,4'-difluoroazobenzene (3h). Yellow solid (20.0 mg, 55%), mp 117−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 9.2, 1.2 Hz, 2H), 7.94 (dd, *J* = 9.2, 1.2 Hz, 1H), 7.54 (dd, *J* = 7.6, 2.8 Hz, 1H), 7.43-7.38 (m, 1H), 7.23 (t, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 164.5, 164.1, 161.9, 149.7 (d, J_{C-F} = 3.9 Hz), 148.7 (d, J_{C-F} = 2.9 Hz), 125.9 (d, J_{C-F} = 9.2 Hz), 121.2 (d, J_{C-F} = 22.7 Hz), 120.1 (d, J_{C-F} = 25.6 Hz), 119.2 (d, J_{C-F} = 9.0 Hz), 116.4 (d, J_{C-F} = 22.9 Hz), 115.6 (d, J_{C-F} = 2.8 Hz), 114.9 (d, J_{C-F} = 9.8 Hz). HRMS (ESI) m/z: Calcd for $C_{13}H_7F_2N_3Na$ $[M+Na]^+$ 266.0500, Found 266.0504.



3i

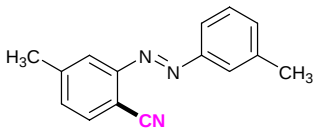
2-Cyano-4,4'-dichloroazobenzene (3i). Yellow solid (27.6 mg, 67%), mp 117−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.66 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.51 (dd, *J* = 6.8, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 150.5, 139.0, 137.3, 133.8, 133.2, 129.7, 125.0,

118.3, 115.5, 114.7. HRMS (ESI) m/z: Calcd for $C_{13}H_7Cl_2N_3Na$: $[M+Na]^+$ 297.9909, Found 297.9911. Anal. Calcd for $C_{13}H_7Cl_2N_3$: C, 56.55; H, 2.56; N, 15.22. Found: C, 56.64; H, 2.48; N, 15.28.



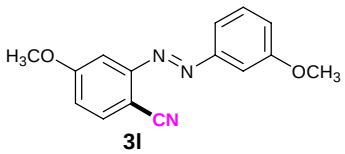
3j

2-Cyano-4,4'-dibromoazobenzene (3j). Yellow solid (20.2 mg, 37%), mp 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.90 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.70 (s, 1H), 7.68 (dd, *J* = 6.8, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 150.8, 136.8, 136.1, 132.7, 127.7, 125.3, 125.2, 118.4, 115.3, 114.9. HRMS (ESI) m/z: Calcd for $C_{13}H_7Br_2N_3Na$ $[M+Na]^+$ 387.8884, Found 387.8885.



3k

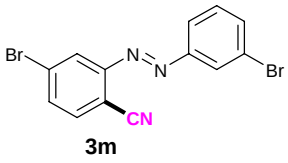
2-Cyano-5,5'-dimethylazobenzene (3k). Yellow solid (29.9 mg, 85%), mp 64−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 6.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 2.48 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 152.4, 144.6, 139.2, 133.4, 133.2, 131.6, 129.1, 123.8, 121.3, 117.5, 117.2, 110.1, 21.9, 21.4. HRMS (ESI) m/z: Calcd for $C_{15}H_{13}N_3Na$ $[M+Na]^+$ 258.1002, Found 258.1001.



3l

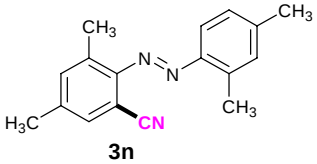
2-Cyano-5,5'-dimethoxyazobenzene (3l). Yellow solid (15.8 mg, 60%), mp 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 2.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 2.8 Hz, 1H), 7.12-7.06 (m, 2H), 3.94 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2,

163.4, 160.4, 154.9, 153.4, 134.6, 129.9, 119.5, 118.3, 118.2, 117.2, 106.1, 100.8, 60.4, 55.5. HRMS (ESI) m/z: Calcd for $C_{15}H_{13}N_3NaO_2$ $[M+Na]^+$ 290.0900, Found 290.0904. Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.51; H, 4.82; N, 15.66.



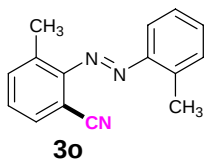
3m

2-Cyano-5,5'-dibromoazobenzene (3m). Yellow solid (21.8 mg, 40%), mp 153−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (t, *J* = 1.6 Hz, 1H), 8.03 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 1.2 Hz, 2H), 7.69 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 152.8, 135.7, 134.6, 134.3, 130.7, 128.6, 126.3, 123.4, 123.2, 120.7, 116.0, 112.3. HRMS (ESI) m/z: Calcd for $C_{13}H_7Br_2N_3Na$ $[M+Na]^+$ 387.8884, Found 387.8887. Anal. Calcd for $C_{13}H_7Br_2N_3$: C, 42.78; H, 1.93; N, 11.51. Found: C, 42.85; H, 1.85; N, 11.42.



3n

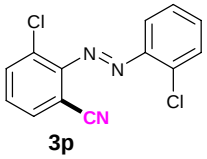
2-Cyano-4,6,4',6'-tetramethylazobenzene (3n). Yellow solid (16.2 mg, 41%), mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 7.32 (s, 1H), 7.18 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 2.78 (s, 3H), 2.60 (s, 3H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 148.9, 142.8, 140.3, 139.6, 136.6, 136.3, 133.2, 132.2, 127.2, 118.9, 115.5, 102.8, 21.5, 20.9, 18.5, 18.1. HRMS (ESI) m/z: Calcd for $C_{17}H_{17}N_3Na$ $[M+Na]^+$ 286.1315, Found 286.1310.



3o

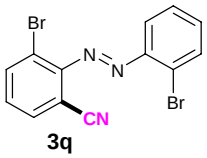
2-Cyano-6,6'-dimethylazobenzene (3o). Yellow solid (16.9 mg, 48%), mp 54−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* =

8.0 Hz, 1H), 7.63 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43-7.36 (m, 3H), 7.26 (d, *J* = 6.8 Hz, 1H), 2.83 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 150.7, 140.4, 136.6, 135.6, 132.8, 132.4, 131.7, 129.3, 126.4, 118.5, 115.6, 102.8, 18.5, 18.1. HRMS (ESI) m/z: Calcd for $C_{15}H_{13}N_3Na$ $[M+Na]^+$ 258.1002, Found 258.1005. Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.58; N, 17.86. Found: C, 76.64; H, 5.48; N, 17.95.



3p

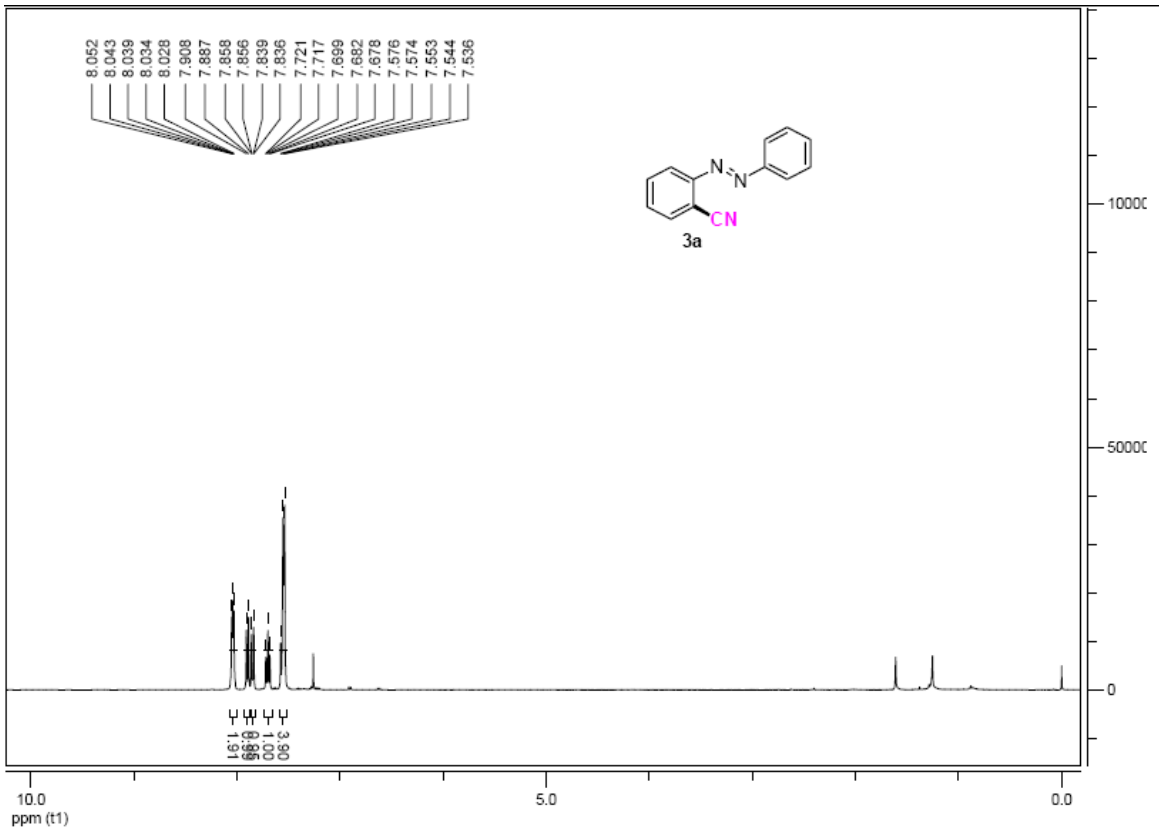
2-Cyano-6,6'-dichloroazobenzene (3p). Yellow solid (13.2 mg, 32%), mp 103−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.77 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.50 (td, *J* = 8.0, 1.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.38 (td, *J* = 8.4, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 148.6, 137.5, 134.9, 133.8, 133.4, 133.1, 131.2, 130.4, 127.4, 117.9, 116.4, 104.5. HRMS (ESI) m/z: Calcd for $C_{13}H_7Cl_2N_3Na$: $[M+Na]^+$ 297.9909, Found 297.9909.



3q

2-Cyano-6,6'-dibromoazobenzene (3q). Yellow solid (16.4 mg, 30%), mp 112−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.84-7.78 (m, 2H), 7.76 (d, *J* = 1.2 Hz, 1H), 7.44-7.40 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 149.5, 138.0, 134.4, 134.1, 133.9, 130.5, 128.1, 127.8, 122.5, 118.3, 116.3, 104.3. HRMS (ESI) m/z: Calcd for $C_{13}H_7Br_2N_3Na$ $[M+Na]^+$ 387.8884, Found 387.8882. Anal. Calcd for $C_{13}H_7N_3Br_2$: C, 42.78; H, 1.93; N, 11.51. Found: C, 42.81; H, 1.88; N, 11.60.

4. Spectral Copies of ^{1}H and ^{13}C NMR of Products 3a-q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8.034
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7.908
7.887
7.858
7.856
7.839
7.836
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7.717
7.699
7.682
7.678
7.576
7.574
7.553
7.544
7.536
N
N
CN
3a
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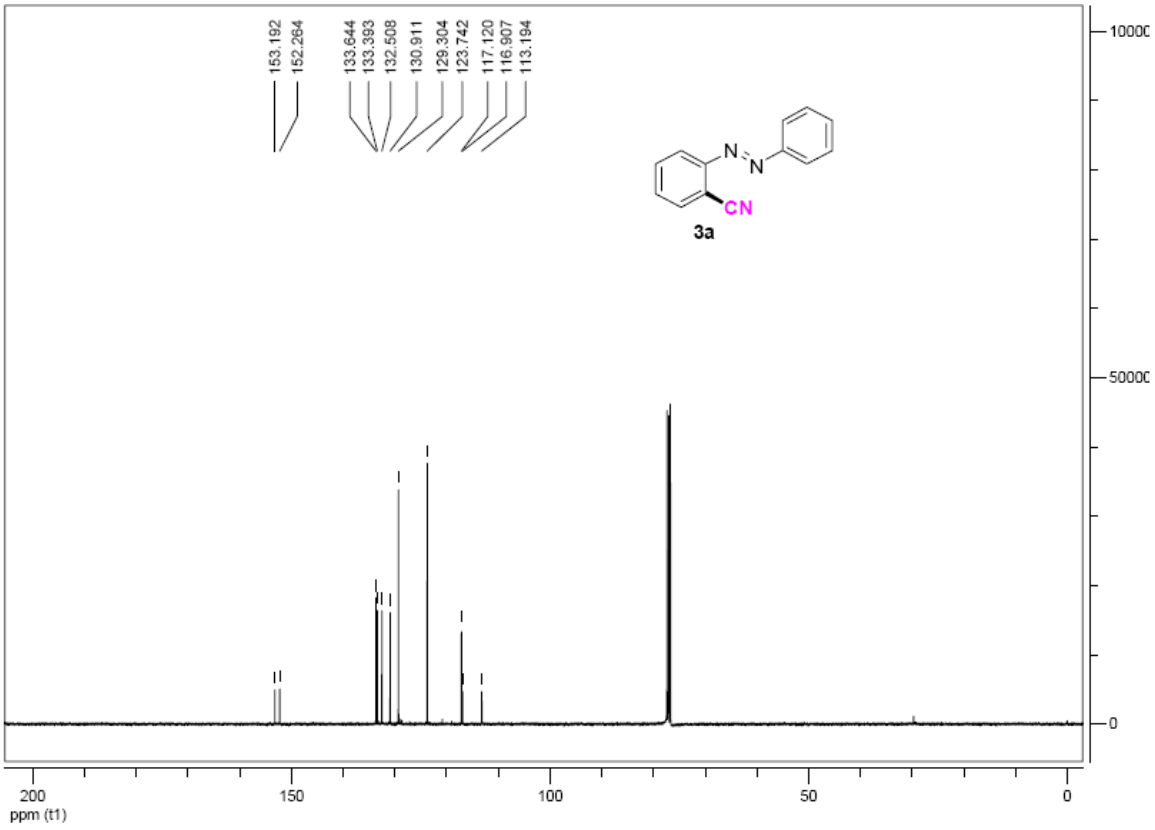
0
10.0
ppm (t1)
5.0
0.0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152.264
133.644
133.393
132.508
130.911
129.304
123.742
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116.907
113.194
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N
CN
3a
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0
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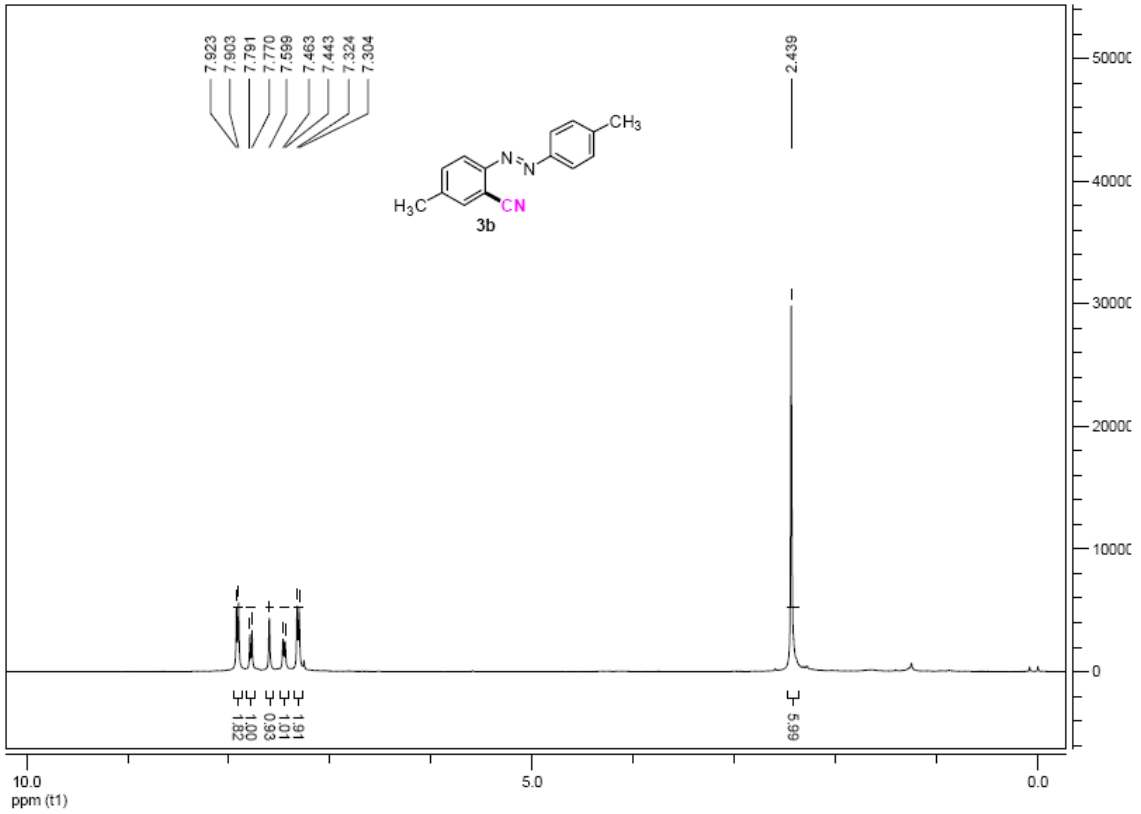
50
0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7.903
7.791
7.770
7.599
7.463
7.443
7.324
7.304
2.439
3b
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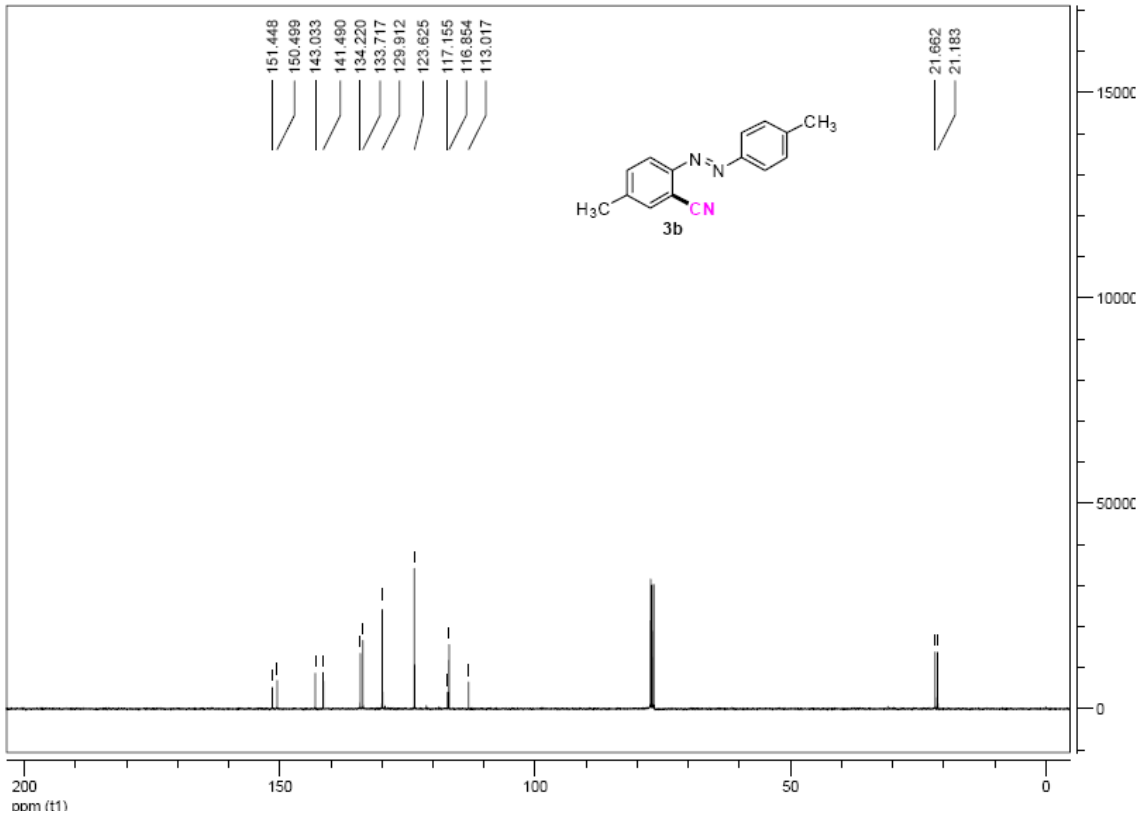
1.00
0.93
1.01
1.91
6.99
10.0
ppm (t1)
5.0
0.0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150.499
143.033
141.490
134.220
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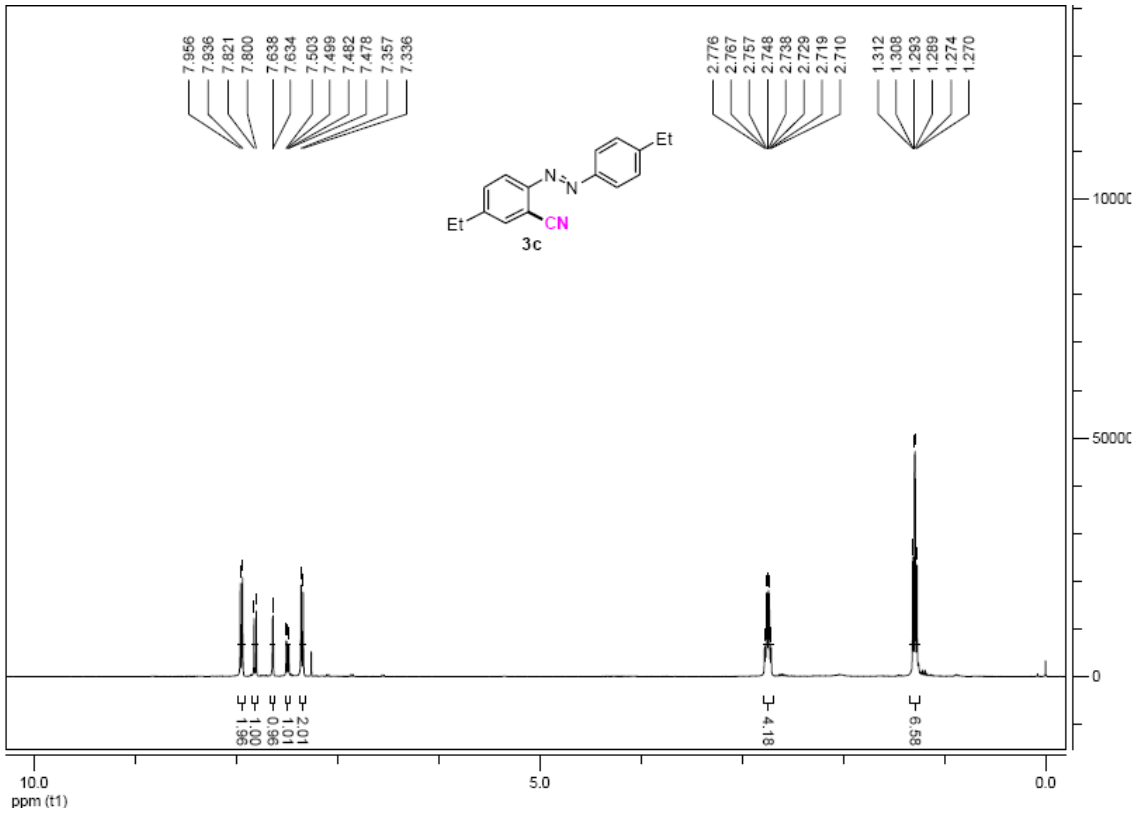
123.625
117.155
116.854
113.017
21.662
21.183
3b
200
150
100
50
0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7.821
7.800
7.638
7.634
7.503
7.499
7.482
7.478
7.357
7.336
2.776
2.767
2.757
2.748
2.738
2.729
2.719
2.710
1.312
1.308
1.293
1.289
1.274
1.270
Et
N
N
Et
CN
3c
10000
50000
0
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1.01
2.01
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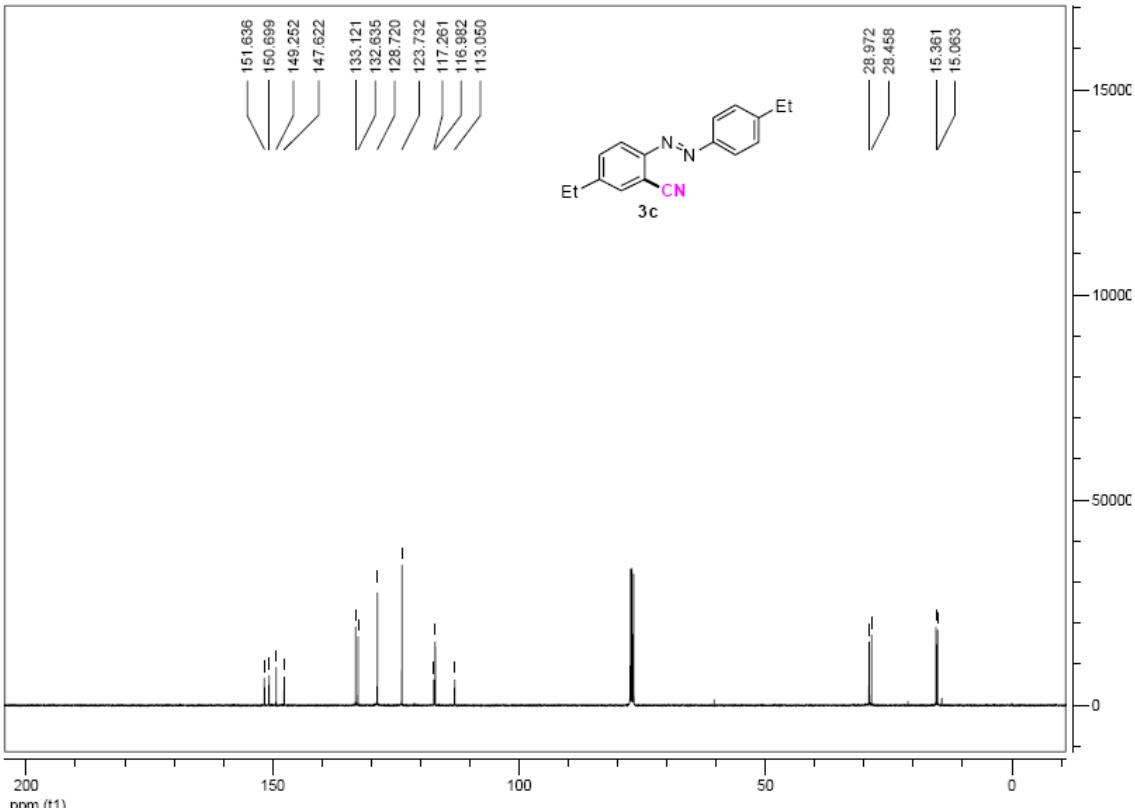
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149.252
147.622
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123.732
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116.982
113.050
28.972
28.458
15.361
15.063
Et
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N
Et
CN
3c
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ppm (t1)
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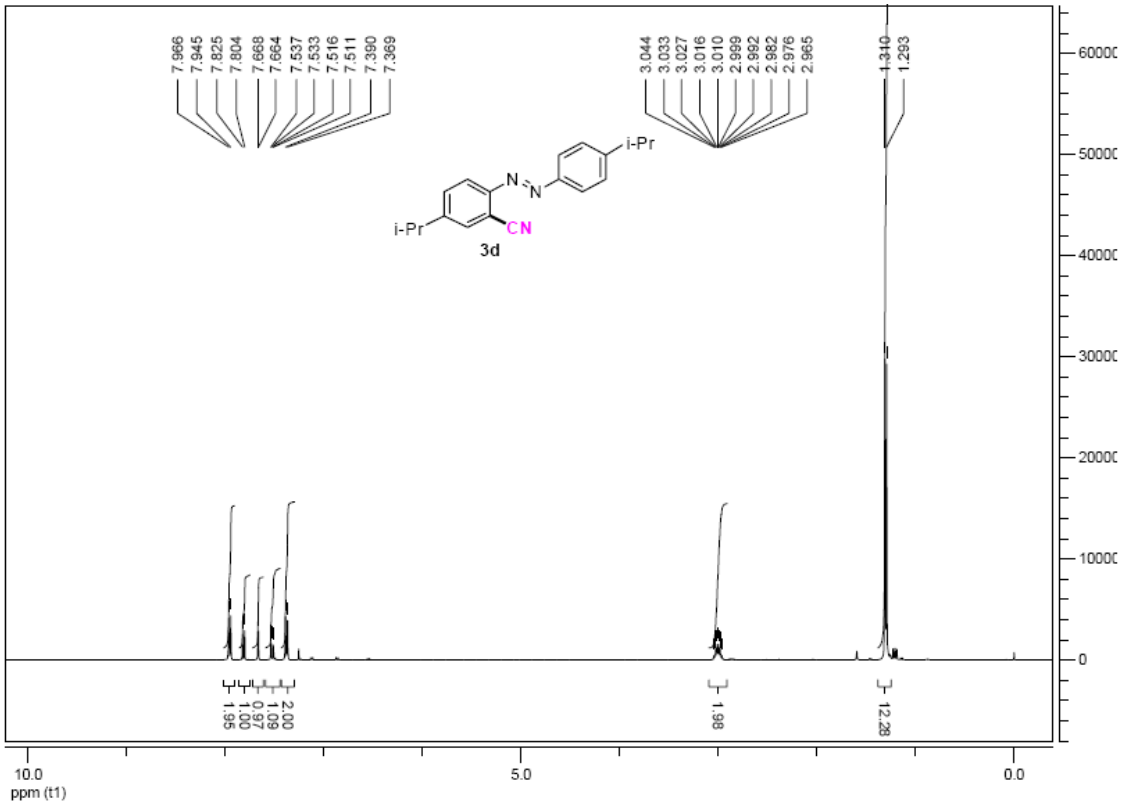
100
50
0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7.825
7.804
7.668
7.664
7.537
7.533
7.516
7.511
7.390
7.369
3.044
3.033
3.027
3.016
3.010
2.999
2.992
2.982
2.976
2.965
1.310
1.293
i-Pr
i-Pr
CN
3d
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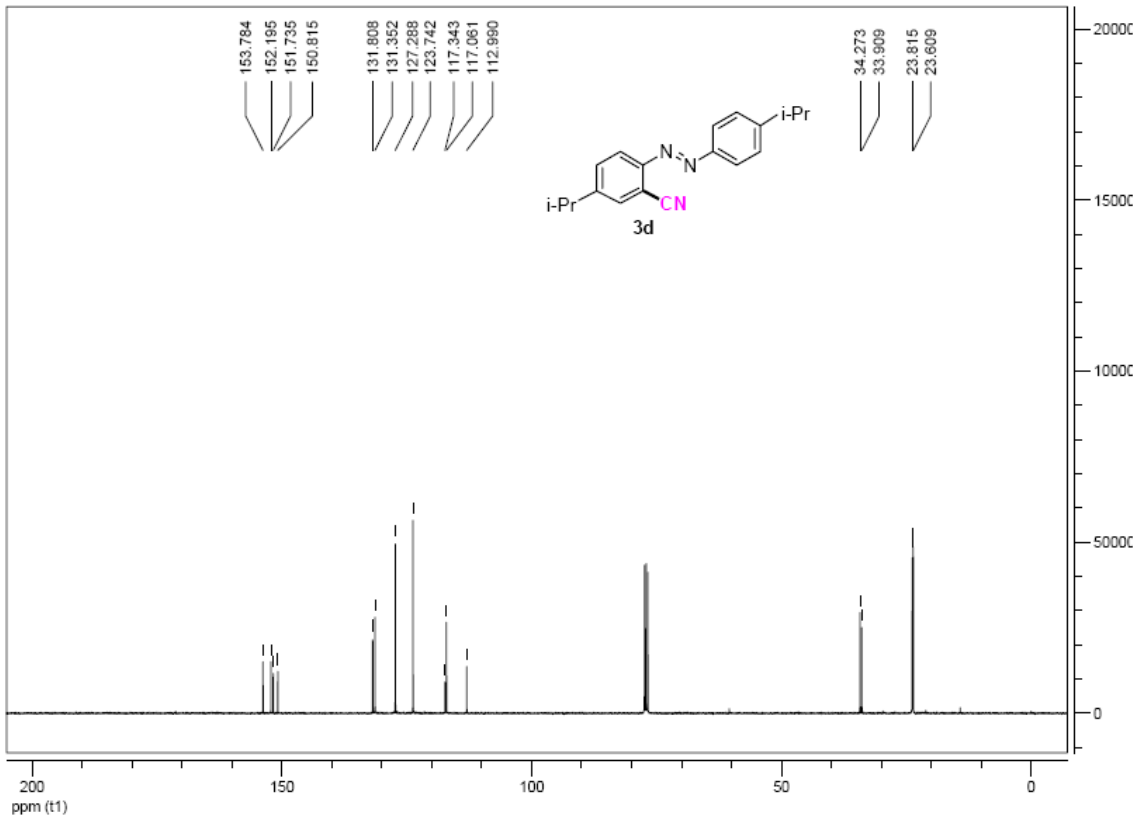
1.00
0.97
1.09
2.00
1.98
12.28
10.0
ppm (t1)
5.0
0.0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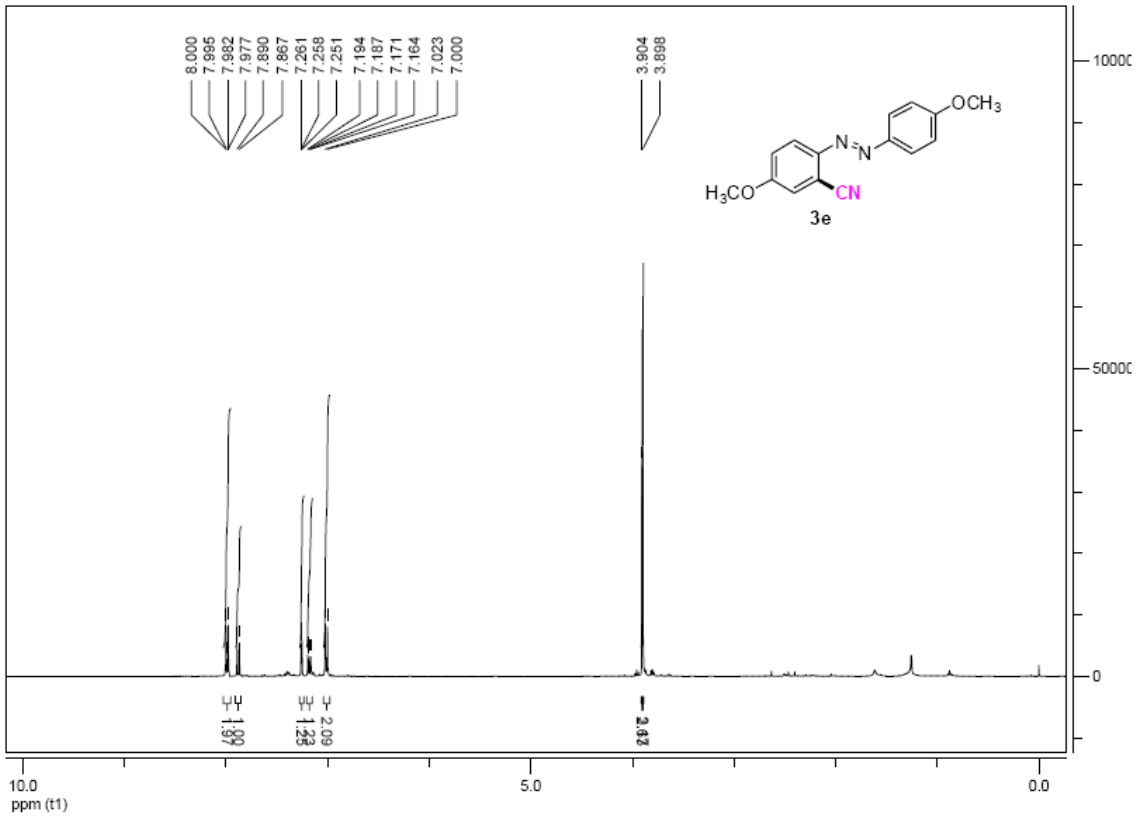
151.735
150.815
131.808
131.352
127.288
123.742
117.343
117.061
112.990
34.273
33.909
23.815
23.609
i-Pr
i-Pr
CN
3d
200
ppm (t1)
150
100
50
0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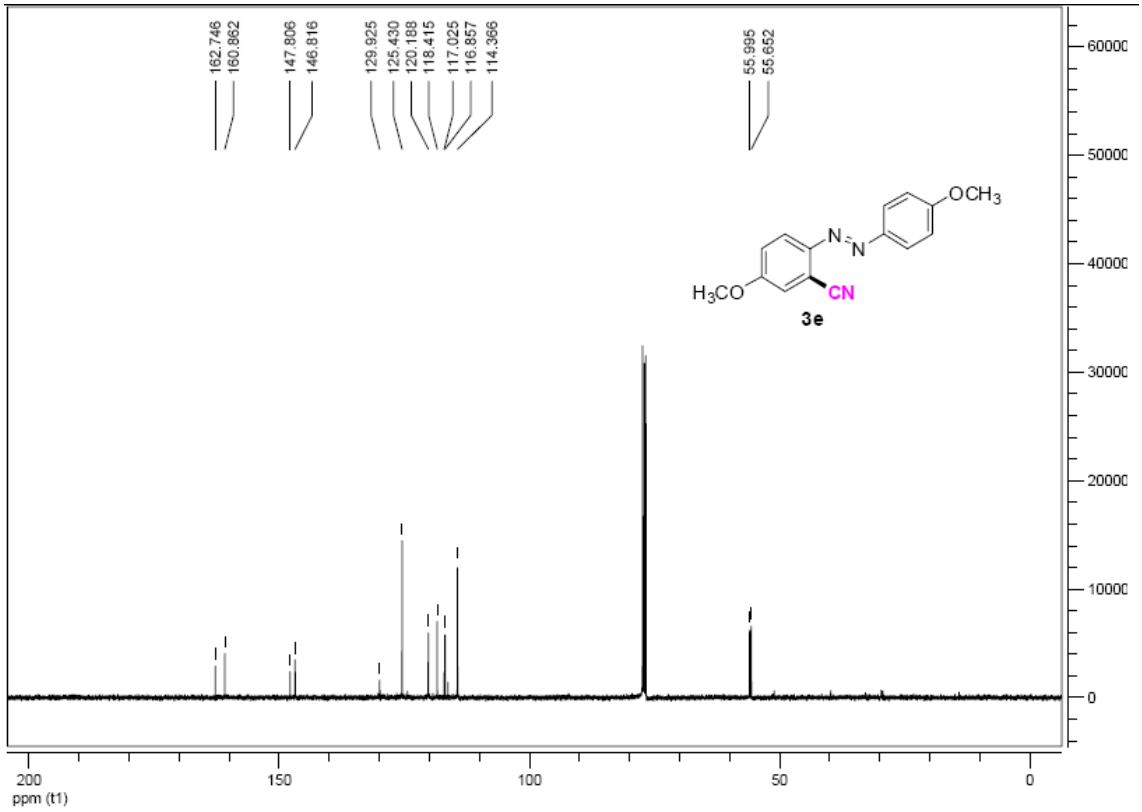
7.995
7.982
7.977
7.890
7.867
7.261
7.258
7.251
7.194
7.187
7.171
7.164
7.023
7.000
3.904
3.898
OCH3
N
N
H3CO
CN
3e
10000
5000
0
1.00
1.23
2.09
3.12
10.0
ppm (t1)
5.0
0.0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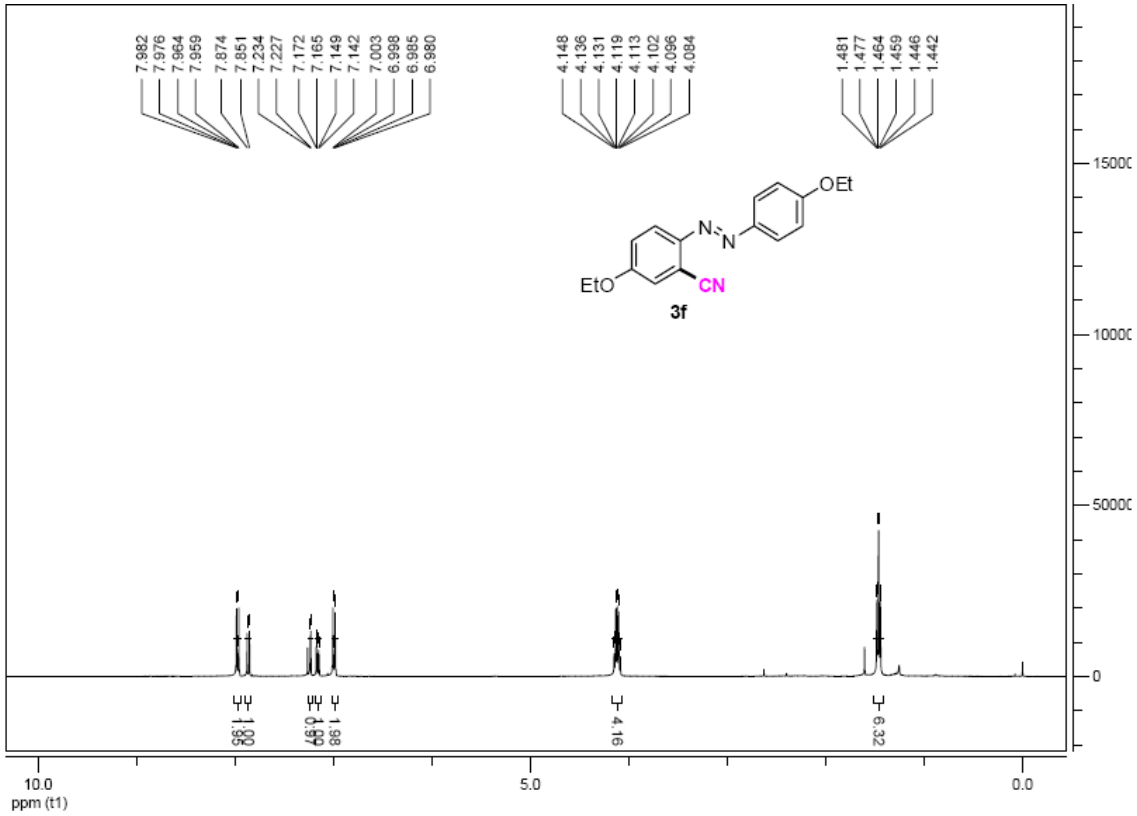
147.806
146.816
129.925
125.430
120.188
118.415
117.025
116.857
114.366
55.995
55.652
OCH3
N
N
H3CO
CN
3e
60000
50000
40000
30000
20000
10000
0
200
ppm (t1)
150
100
50
0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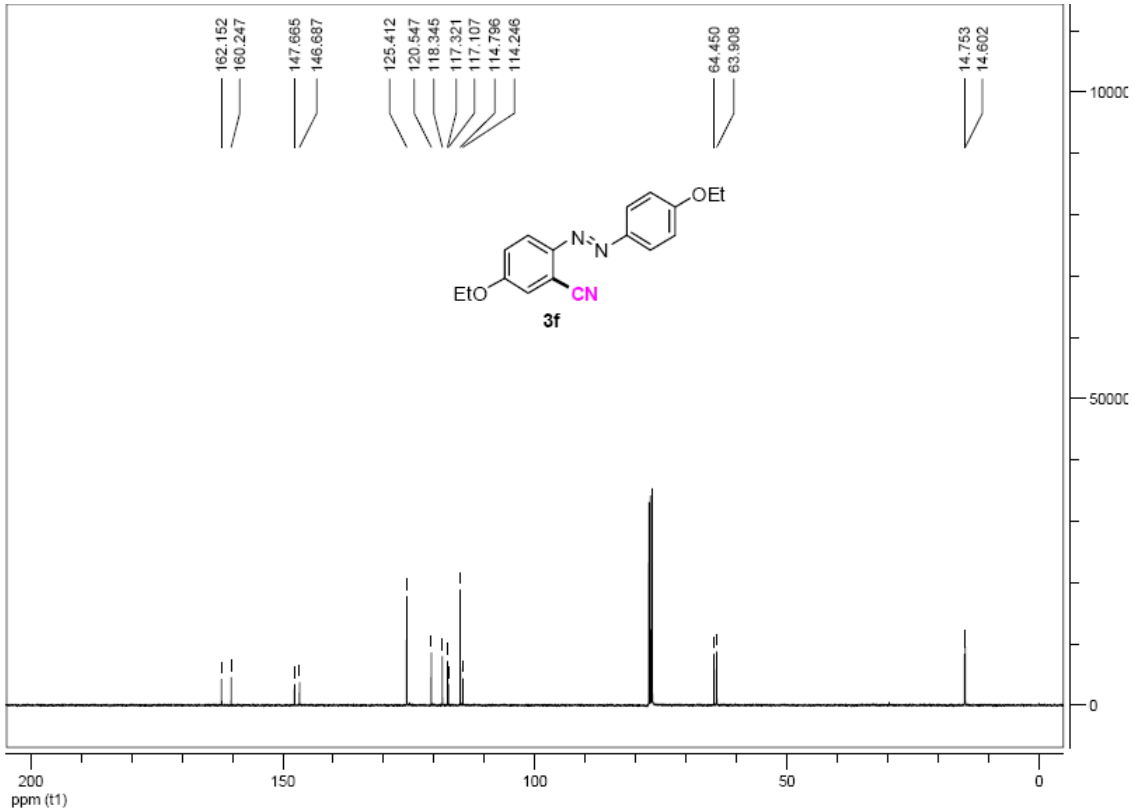
7.976
7.964
7.959
7.874
7.851
7.234
7.227
7.172
7.165
7.149
7.142
7.003
6.998
6.985
6.980
4.148
4.136
4.131
4.119
4.113
4.102
4.096
4.084
1.481
1.477
1.464
1.459
1.446
1.442
OEt
N
N
EtO
CN
3f
1.98
2.09
1.98
4.16
6.32
10.0
5.0
0.0
ppm (t1)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147.665
146.687
125.412
120.547
118.345
117.321
117.107
114.796
114.246
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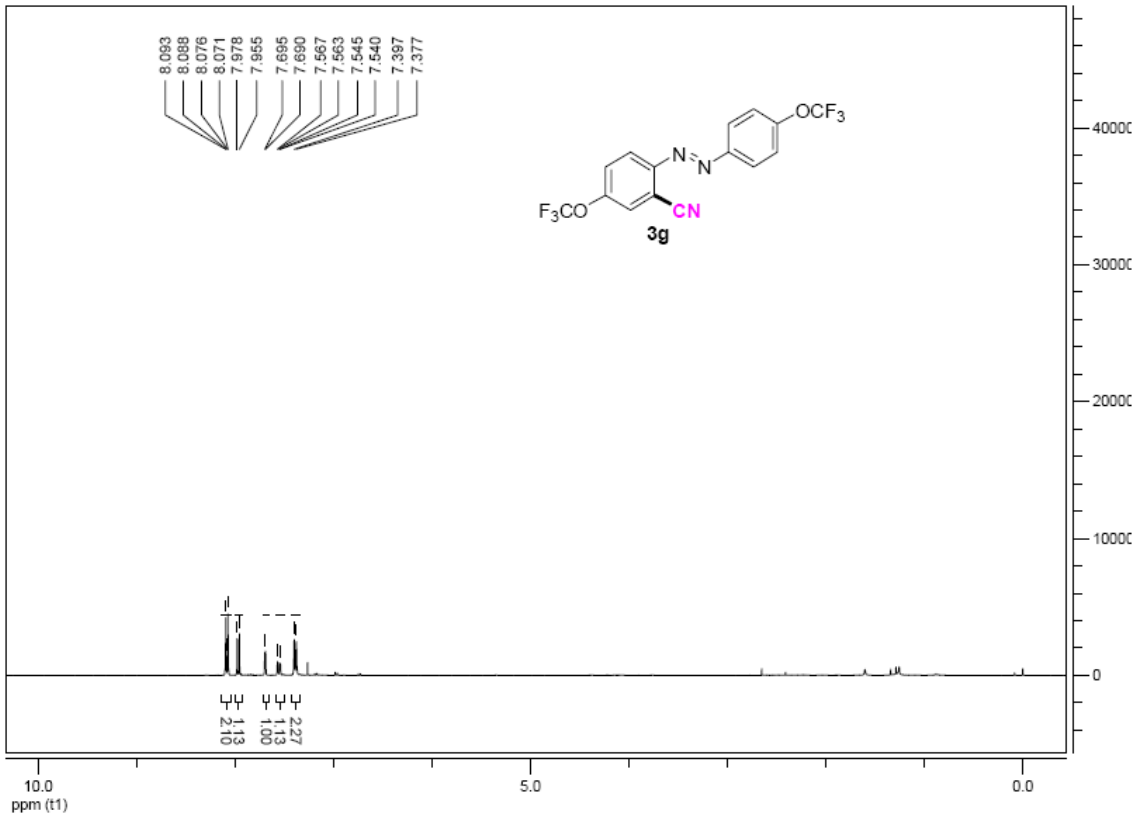
63.908
14.753
14.602
OEt
N
N
EtO
CN
3f
200
150
100
50
0
ppm (t1)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8.088
8.076
8.071
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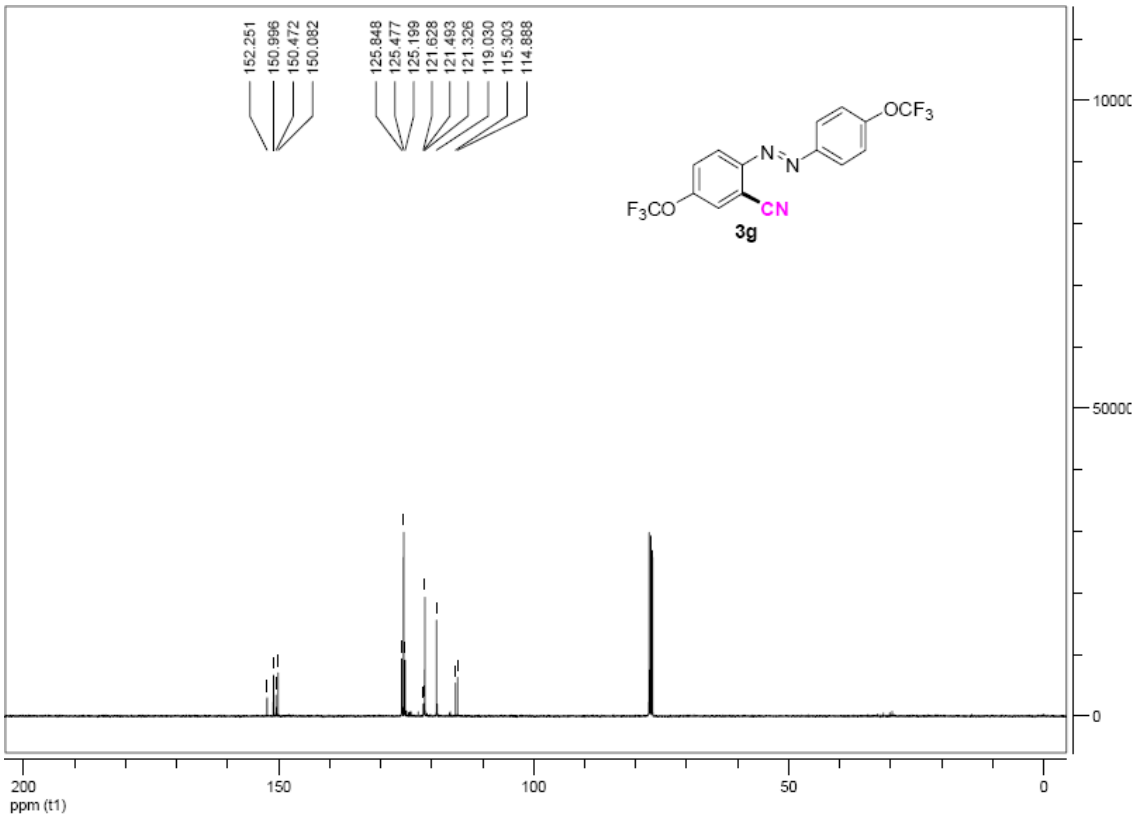
7.955
7.695
7.690
7.567
7.563
7.545
7.540
7.397
7.377
OCF3
N
N
F3CO
CN
3g
2.10
1.13
1.00
1.13
2.27
10.0
ppm (t1)
5.0
0.0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150.472
150.082
125.848
125.477
125.199
121.628
121.493
121.326
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115.303
114.888
OCF3
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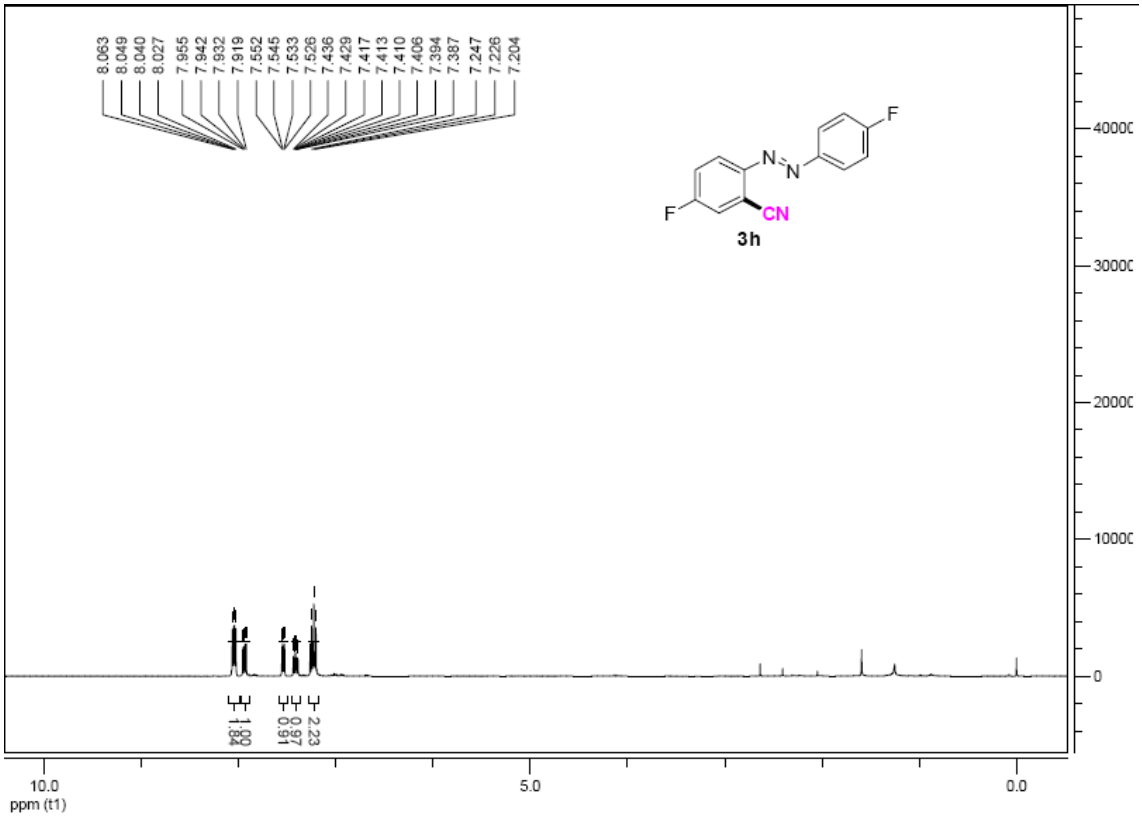
N
F3CO
CN
3g
200
ppm (t1)
150
100
50
0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8.040
8.027
7.955
7.942
7.932
7.919
7.552
7.545
7.533
7.526
7.436
7.429
7.417
7.413
7.410
7.406
7.394
7.387
7.247
7.226
7.204
F
N
N
F
CN
3h
4000
3000
2000
1000
0
1.84
1.00
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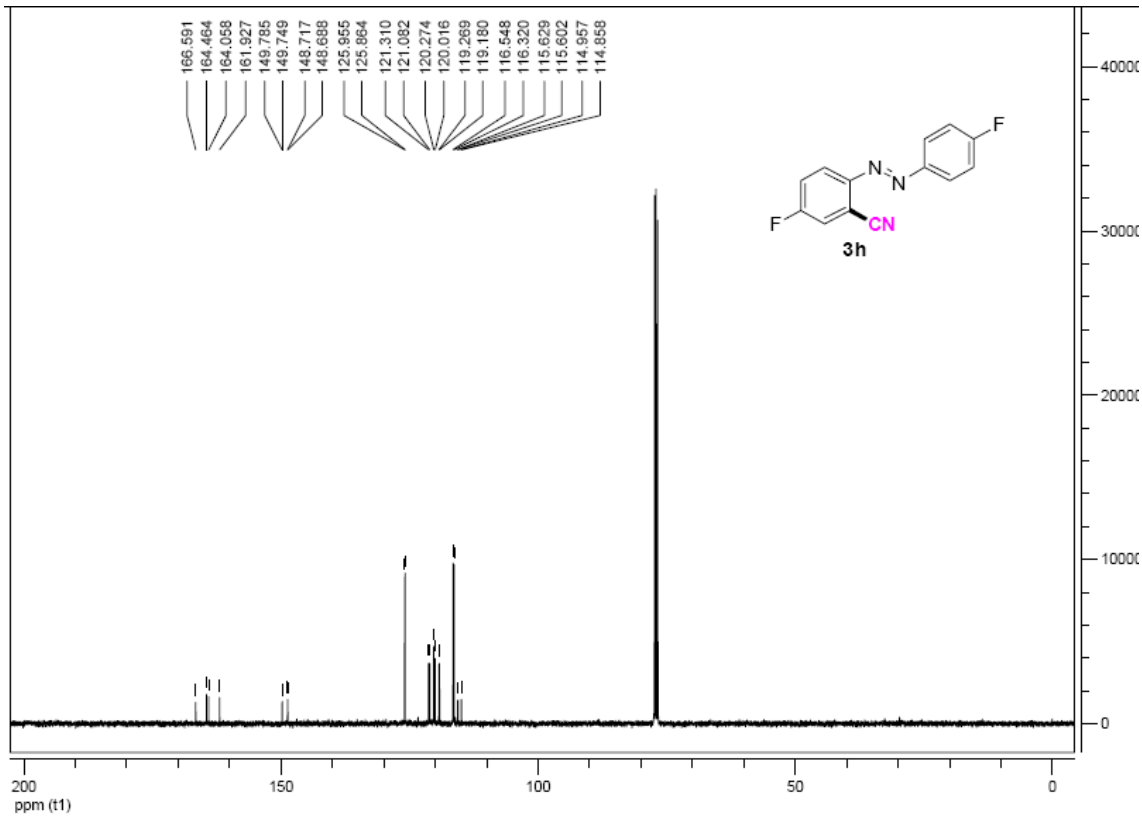
2.23
10.0
5.0
0.0
ppm (t1)


166.591
164.464
164.058
161.927
149.785
149.749
148.717
148.688
125.955
125.864
121.310
121.082
120.274
120.016
119.269
119.180
116.548
116.320
115.629
115.602
114.957
114.858
F
N
N
F
CN
3h
4000
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2000
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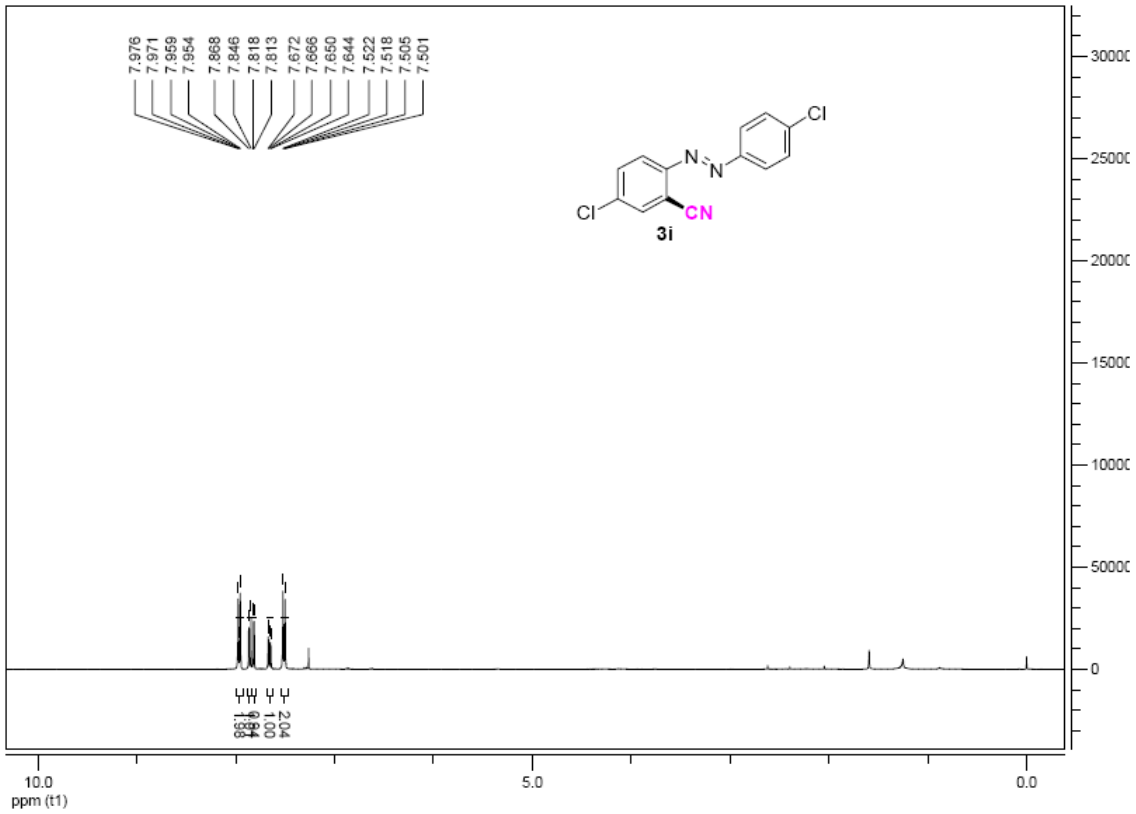
0
200
150
100
50
0
ppm (t1)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7.971
7.959
7.954
7.868
7.846
7.818
7.813
7.672
7.666
7.650
7.644
7.522
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7.501
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N
Cl
CN
3i
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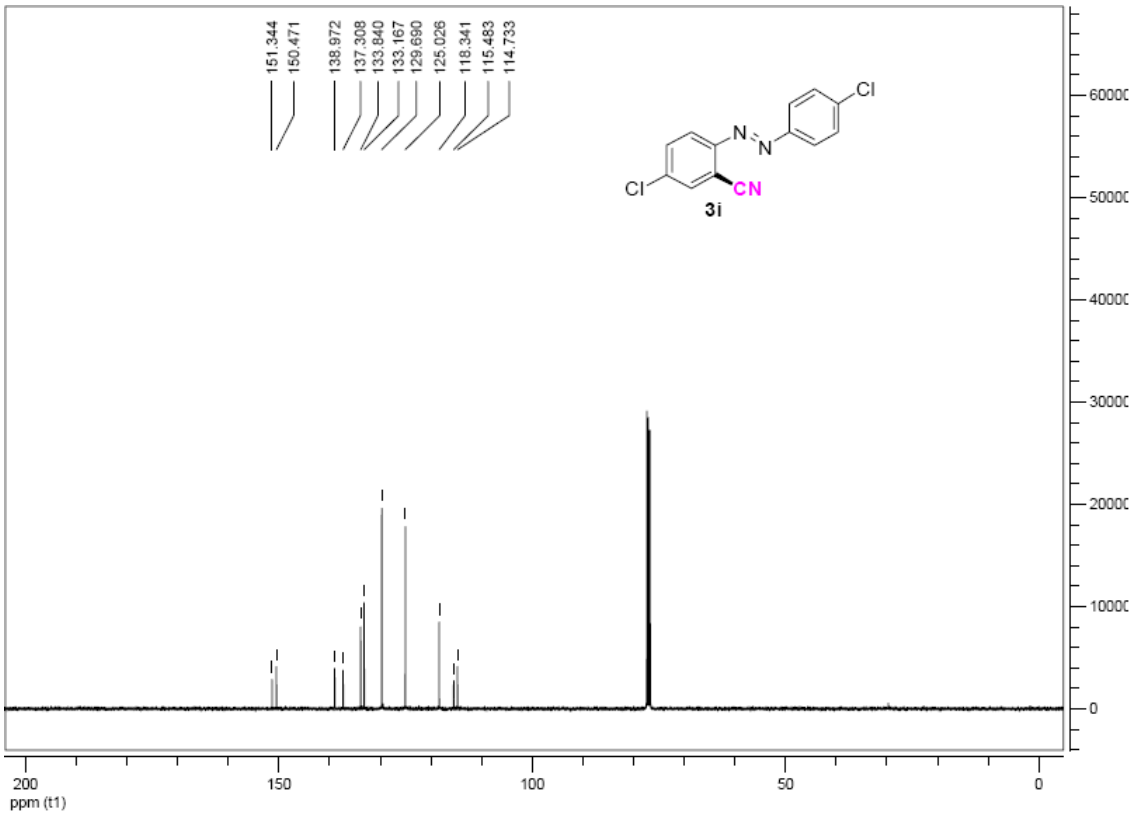
0.0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129.690
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114.733
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N
Cl
CN
3i
200
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100
50
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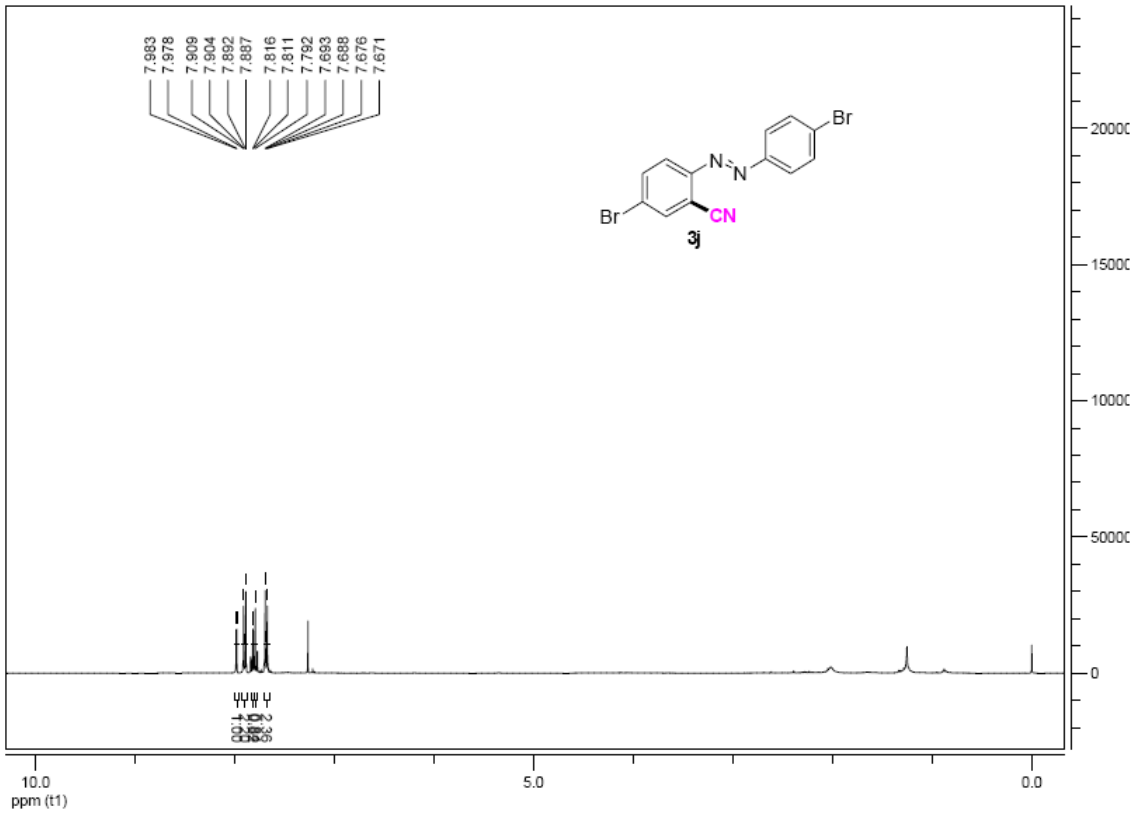
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7.811
7.792
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7.671
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CN
3j
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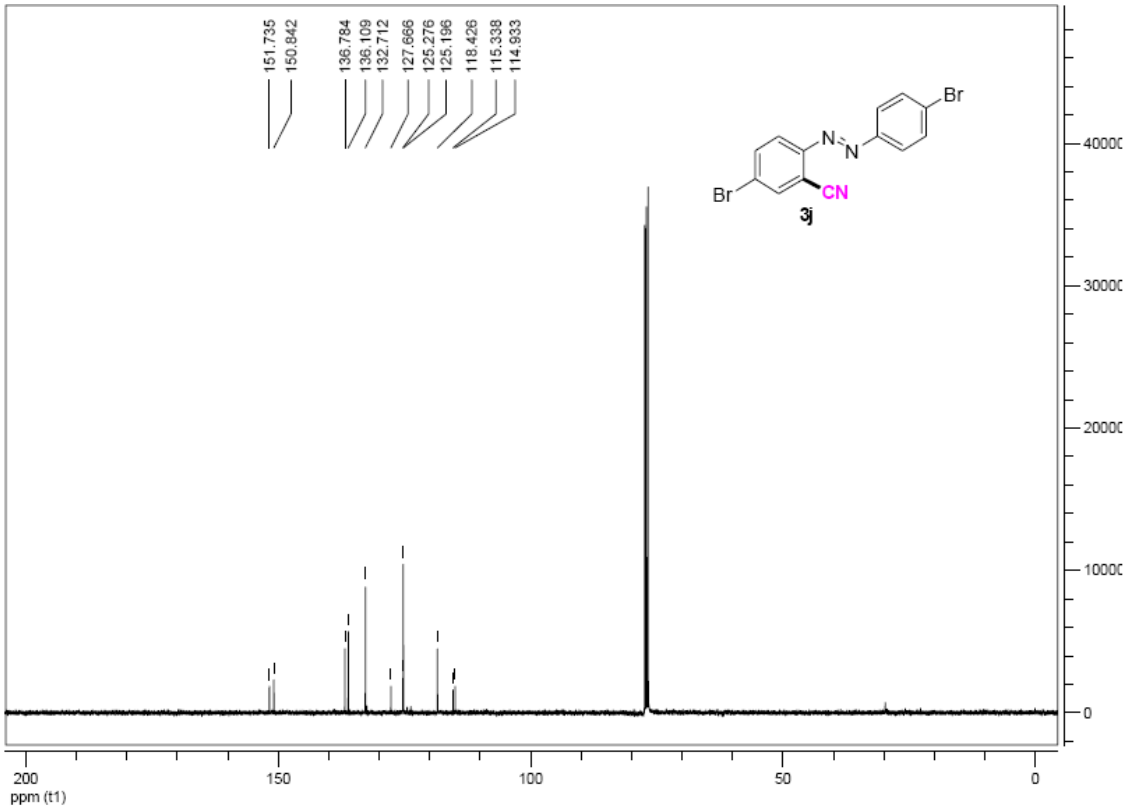
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118.426
115.338
114.933
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N
Br
CN
3j
200
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150
100
50
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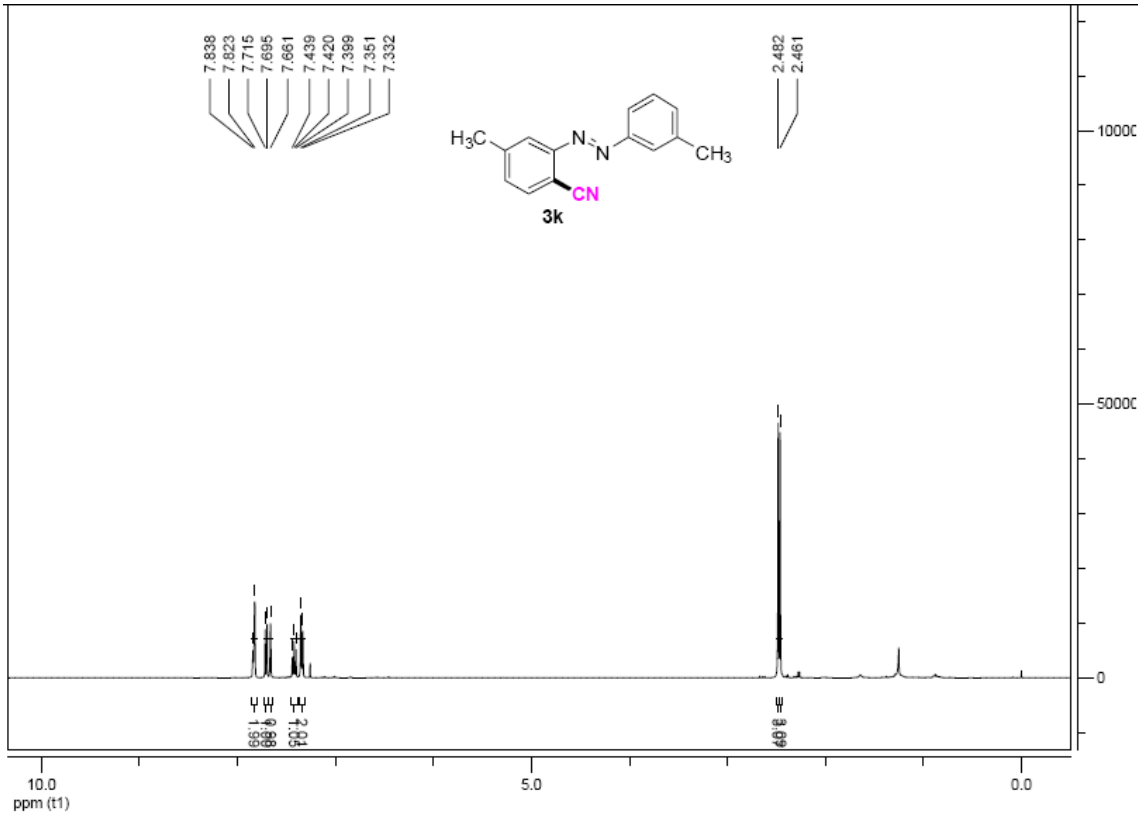
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7.715
7.695
7.661
7.439
7.420
7.399
7.351
7.332
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2.461
3k
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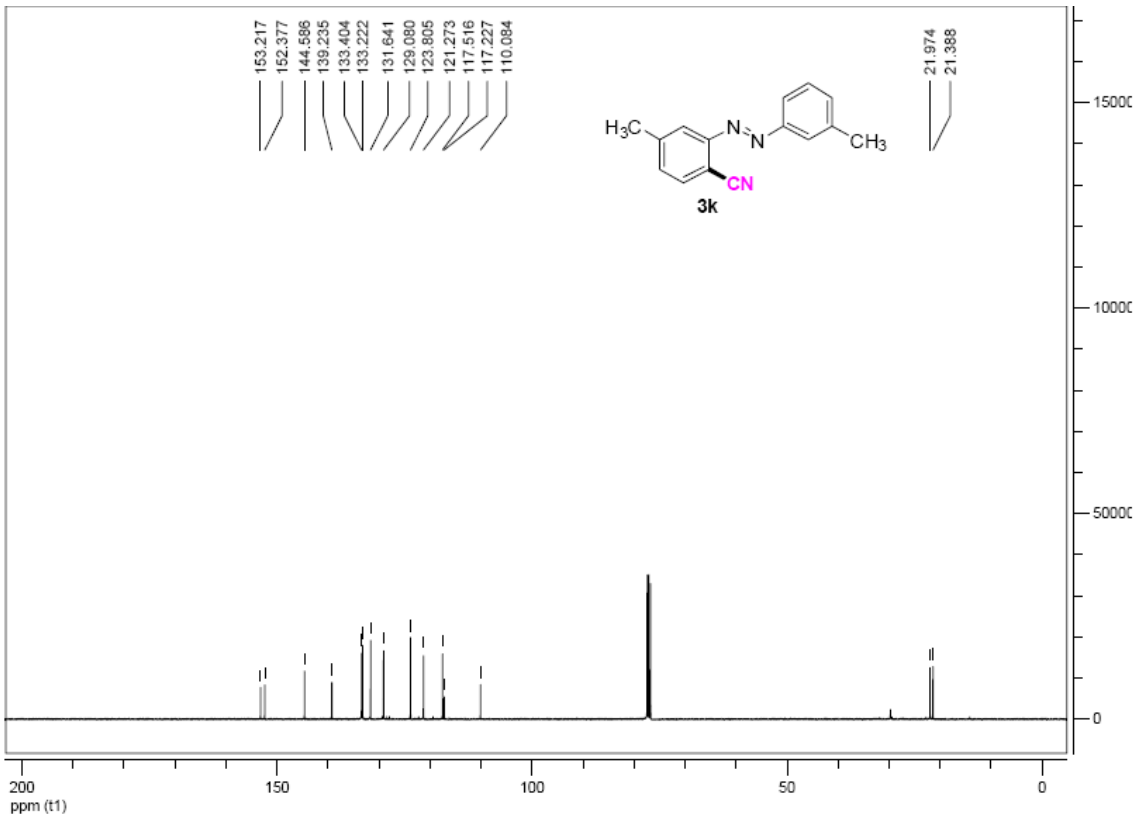
0
10.0
ppm (t1)
5.0
0.0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133.222
131.641
129.080
123.805
121.273
117.516
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21.388
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50
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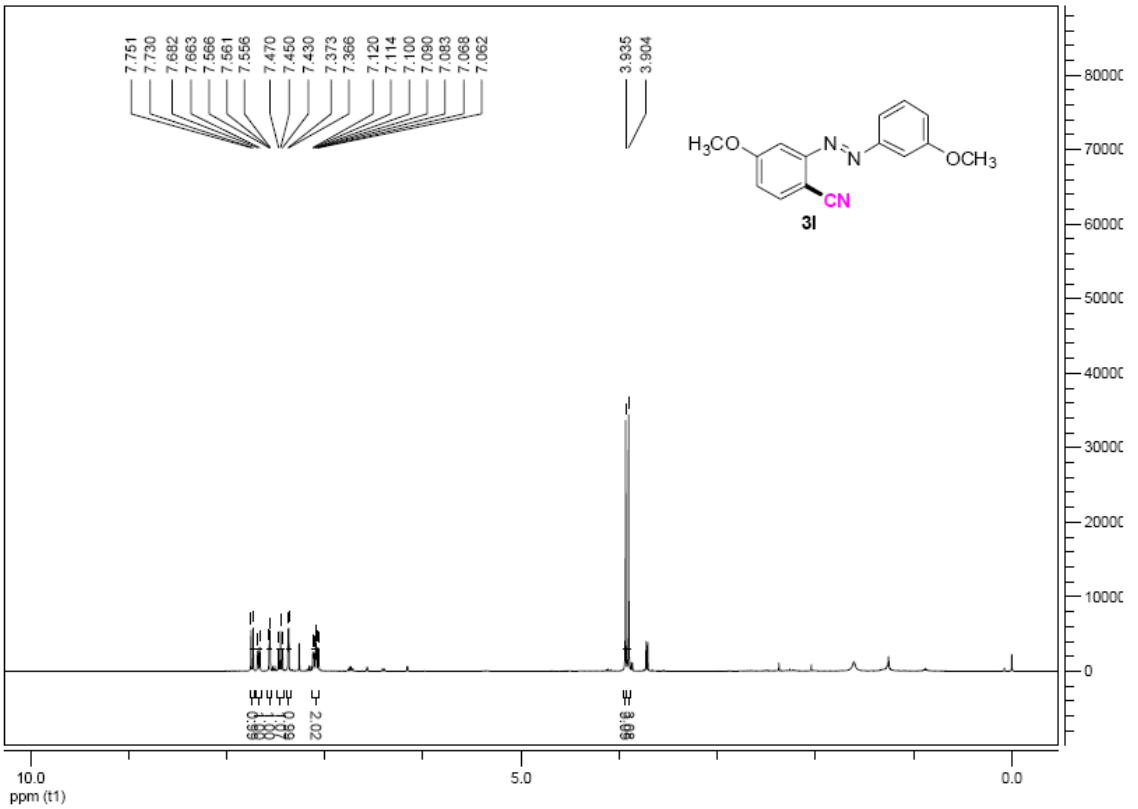
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7.470
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7.430
7.373
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7.114
7.100
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7.068
7.062
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3.904
H3CO
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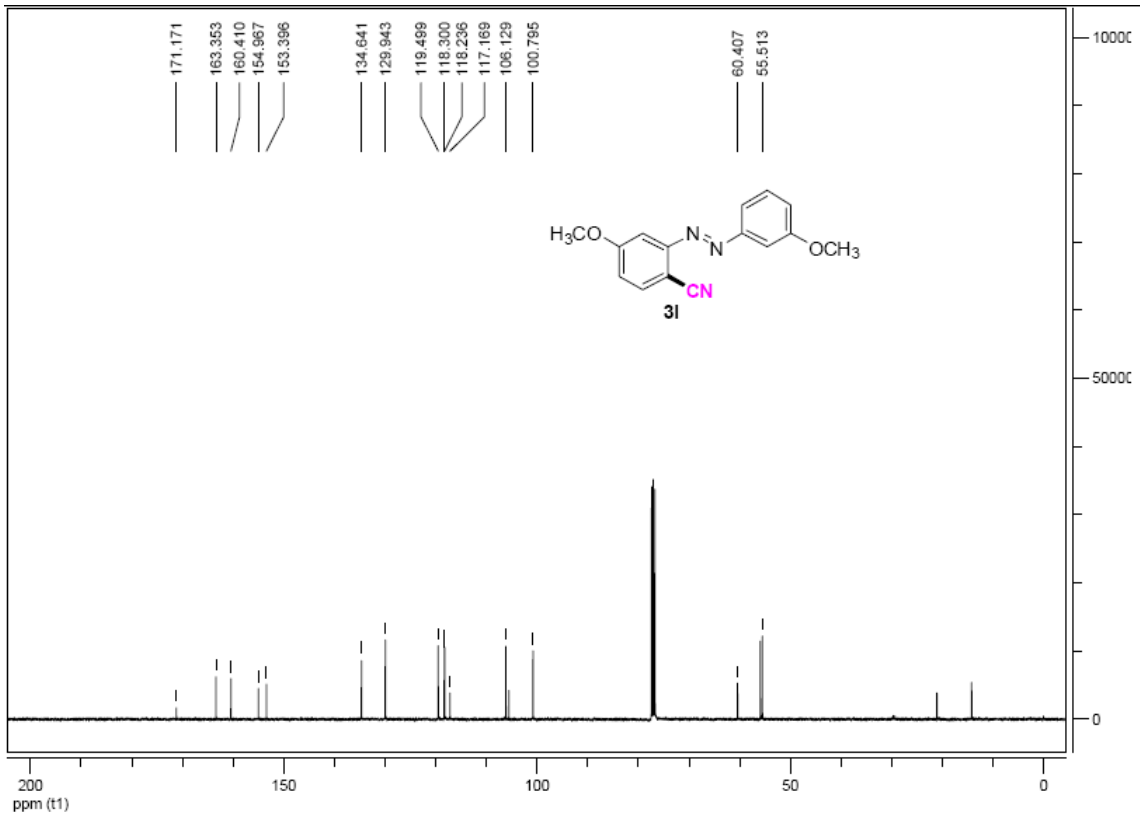
N
OCH3
CN
3l
10.0
ppm (t1)
5.0
0.0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154.967
153.396
134.641
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119.499
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118.236
117.169
106.129
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55.513
H3CO
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N
OCH3
CN
3l
200
ppm (t1)
150
100
50
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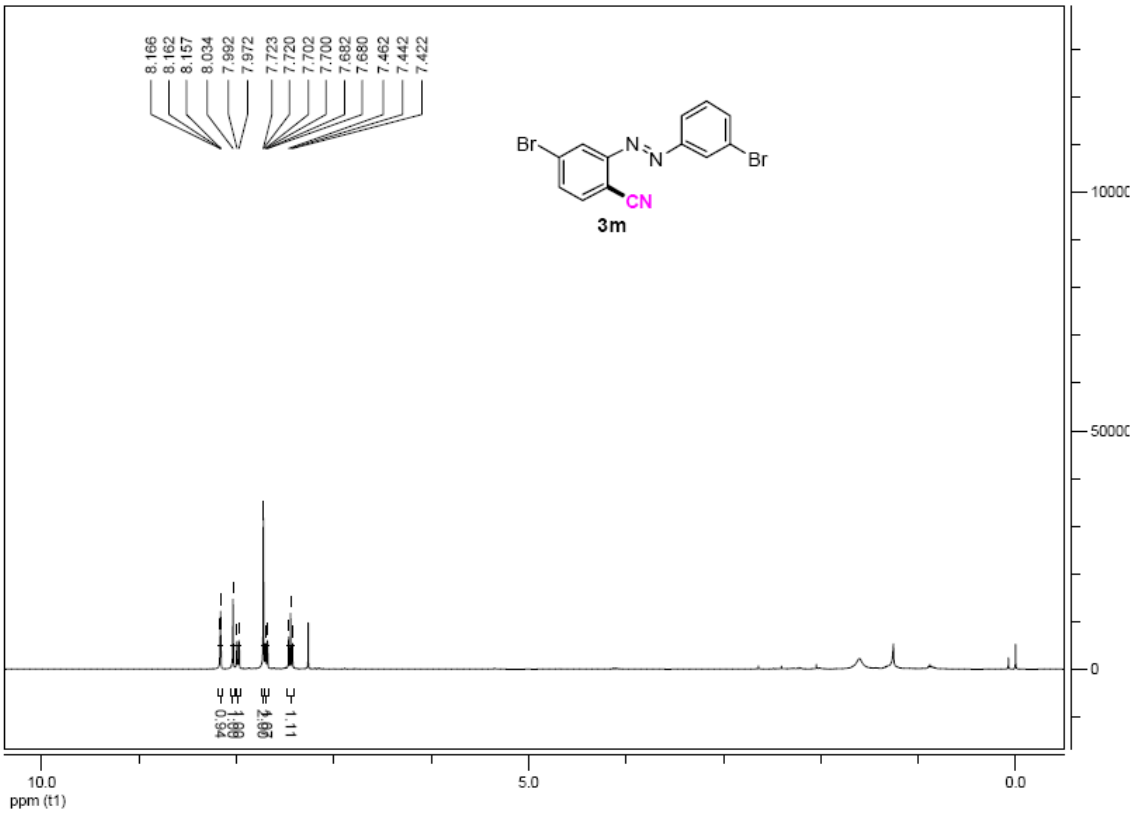
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7.972
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7.720
7.702
7.700
7.682
7.680
7.462
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Br
CN
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ppm (t1)
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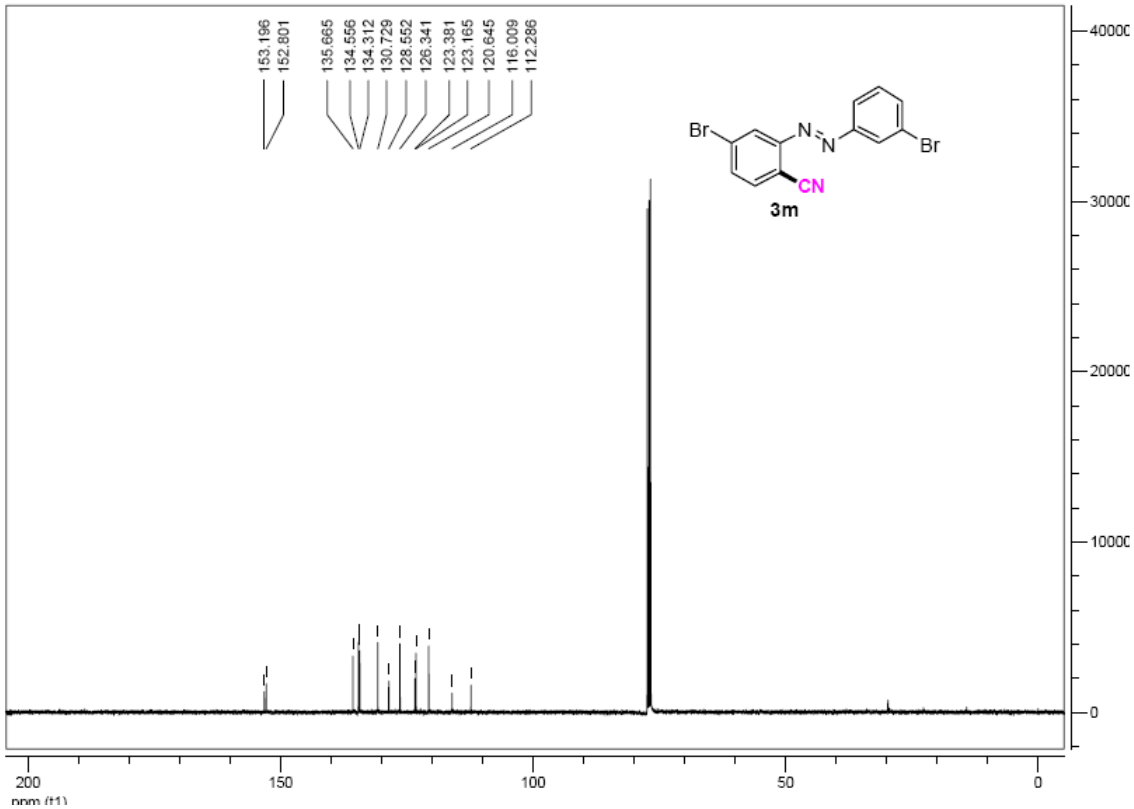
0.0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130.729
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123.165
120.645
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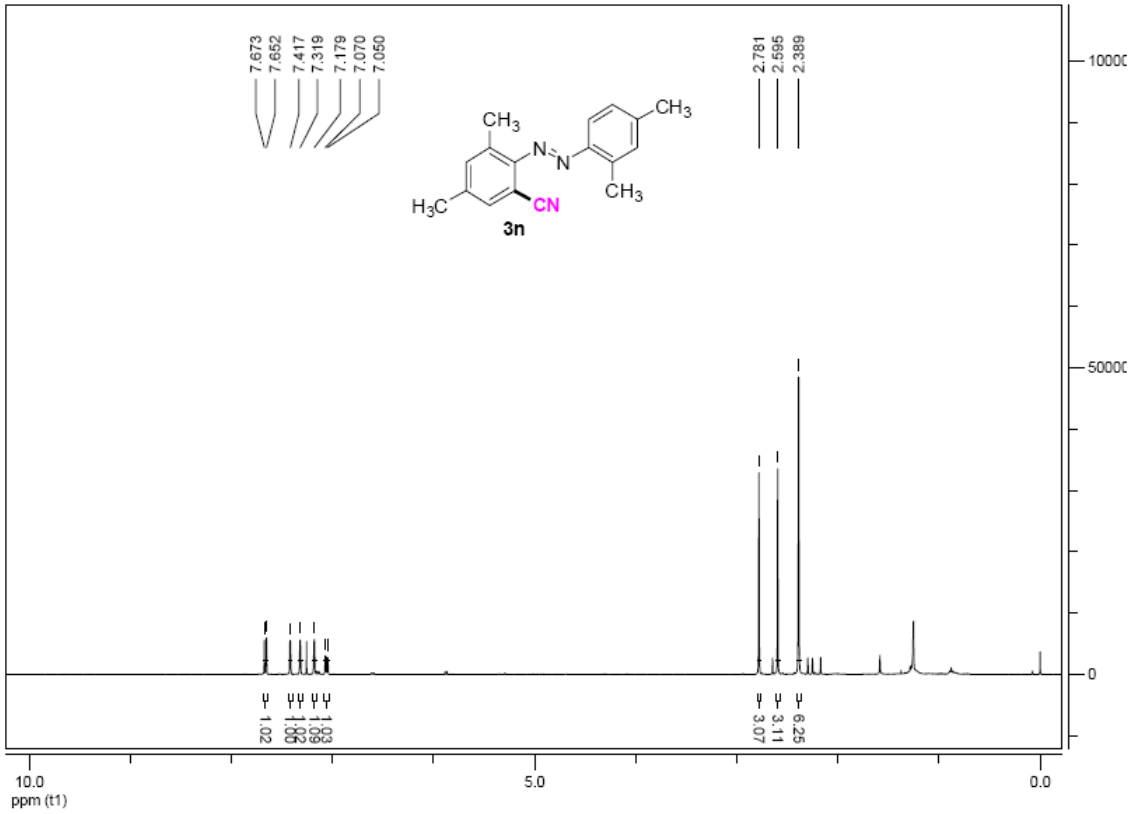
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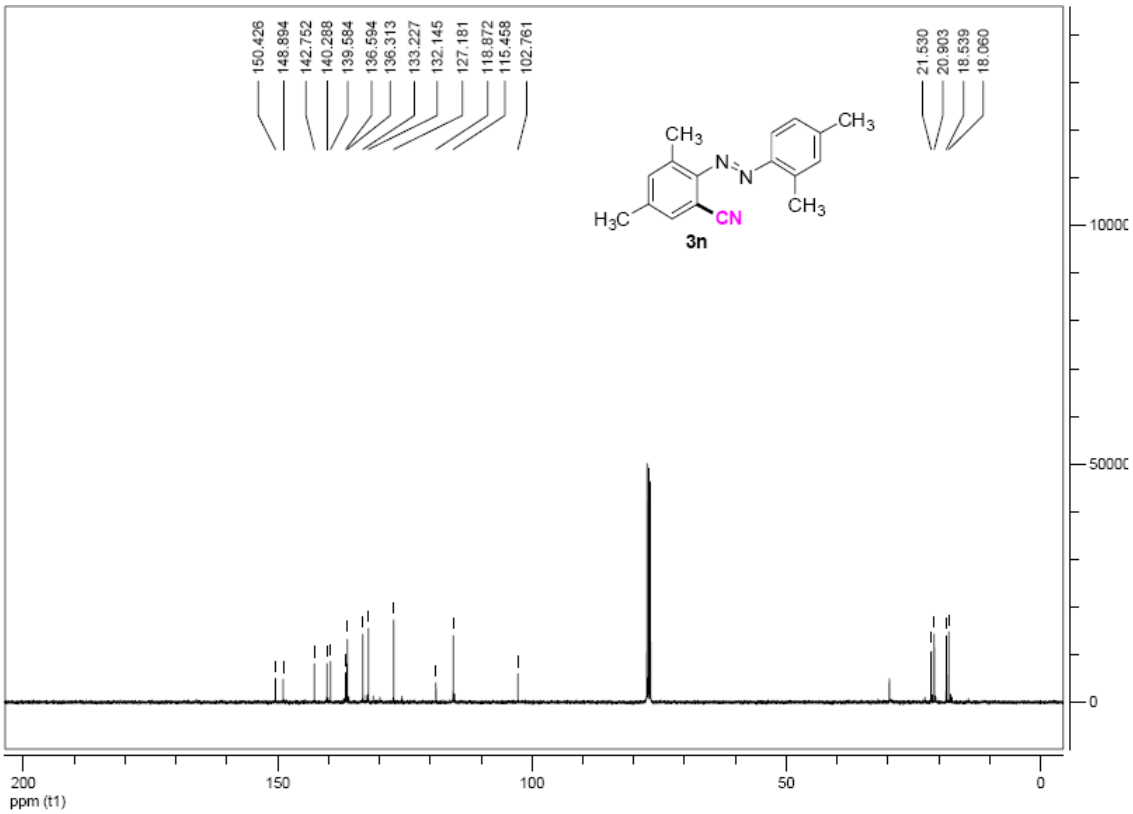
7.319
7.179
7.070
7.050
2.781
2.595
2.389
CH3
CH3
N=N
CH3
H3C
CN
3n
1.02
1.00
1.00
1.08
1.09
3.07
3.11
6.25
10000
5000
0
10.0
ppm (t1)
5.0
0.0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136.594
136.313
133.227
132.145
127.181
118.872
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102.761
21.530
20.903
18.539
18.060
CH3
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CH3
H3C
CN
3n
10000
5000
0
200
ppm (t1)
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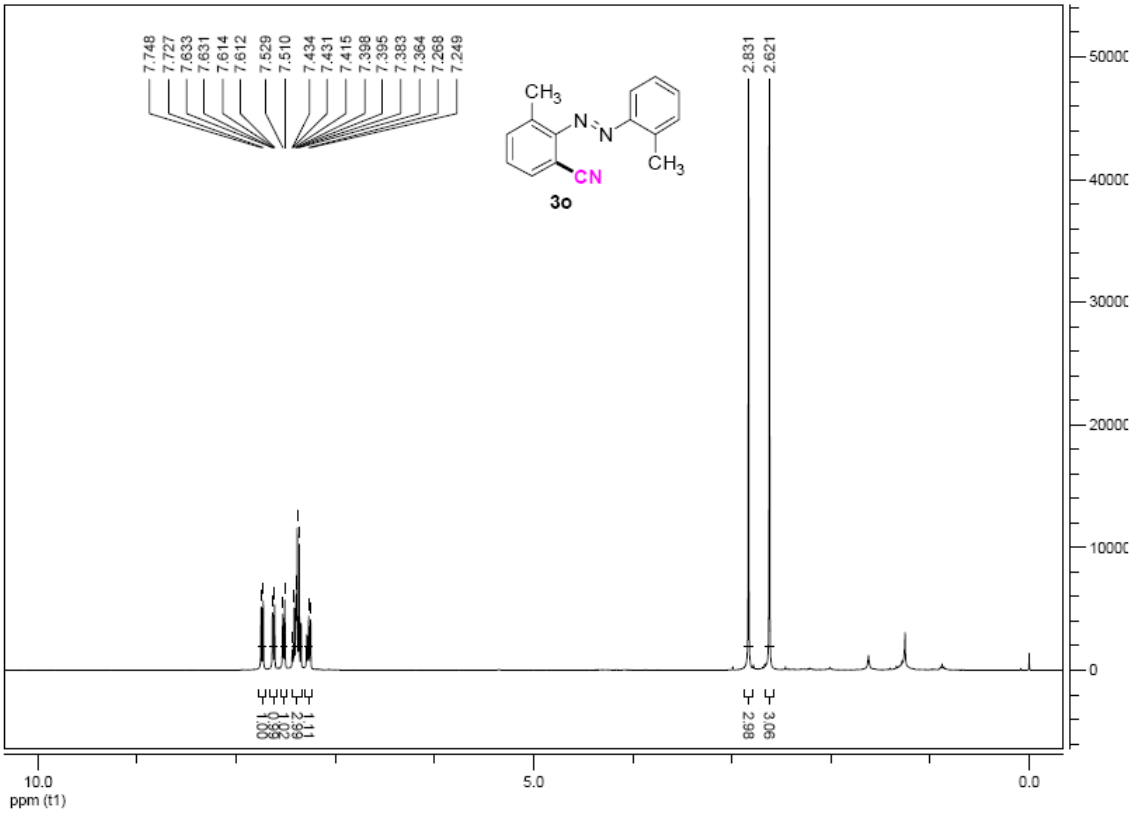
100
50
0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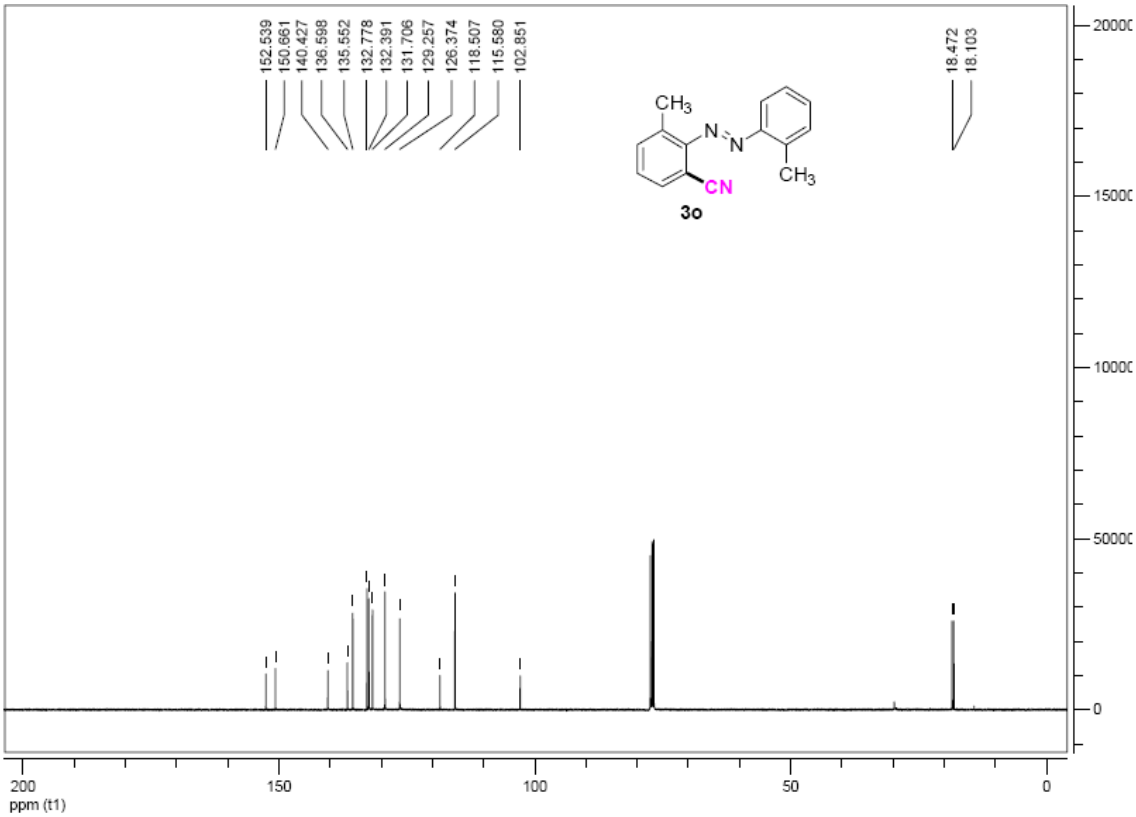
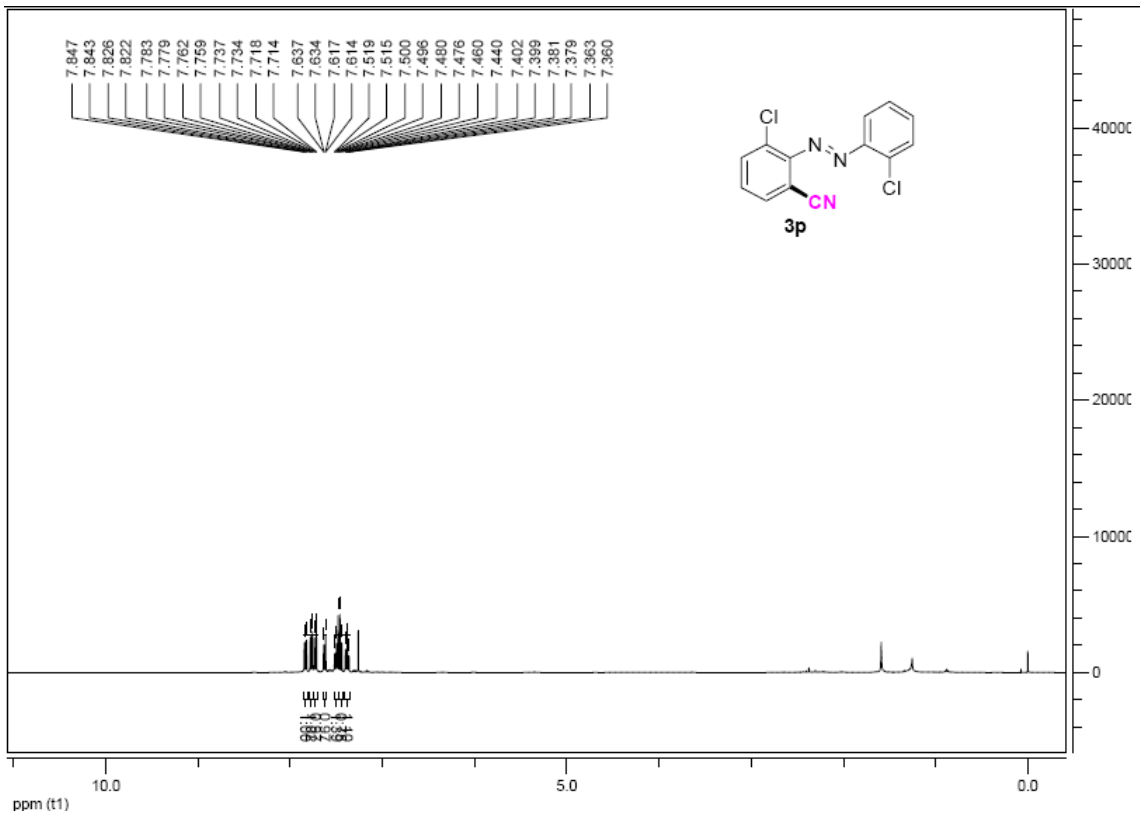
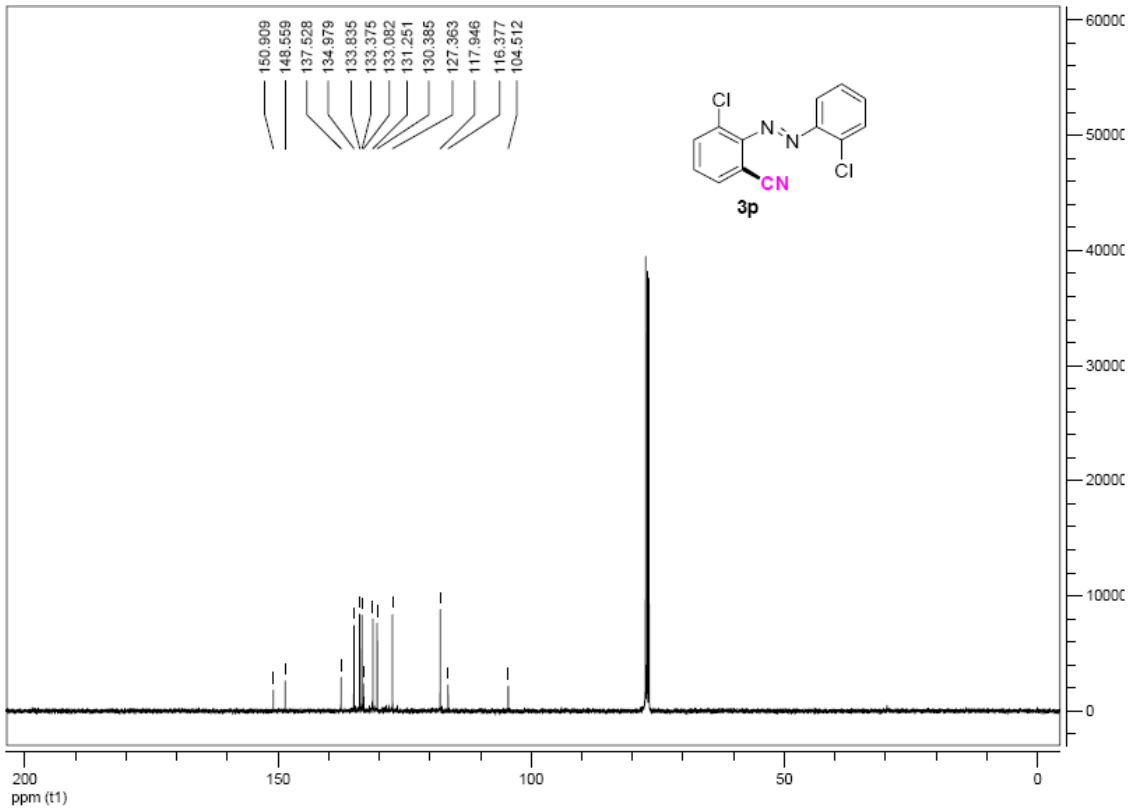
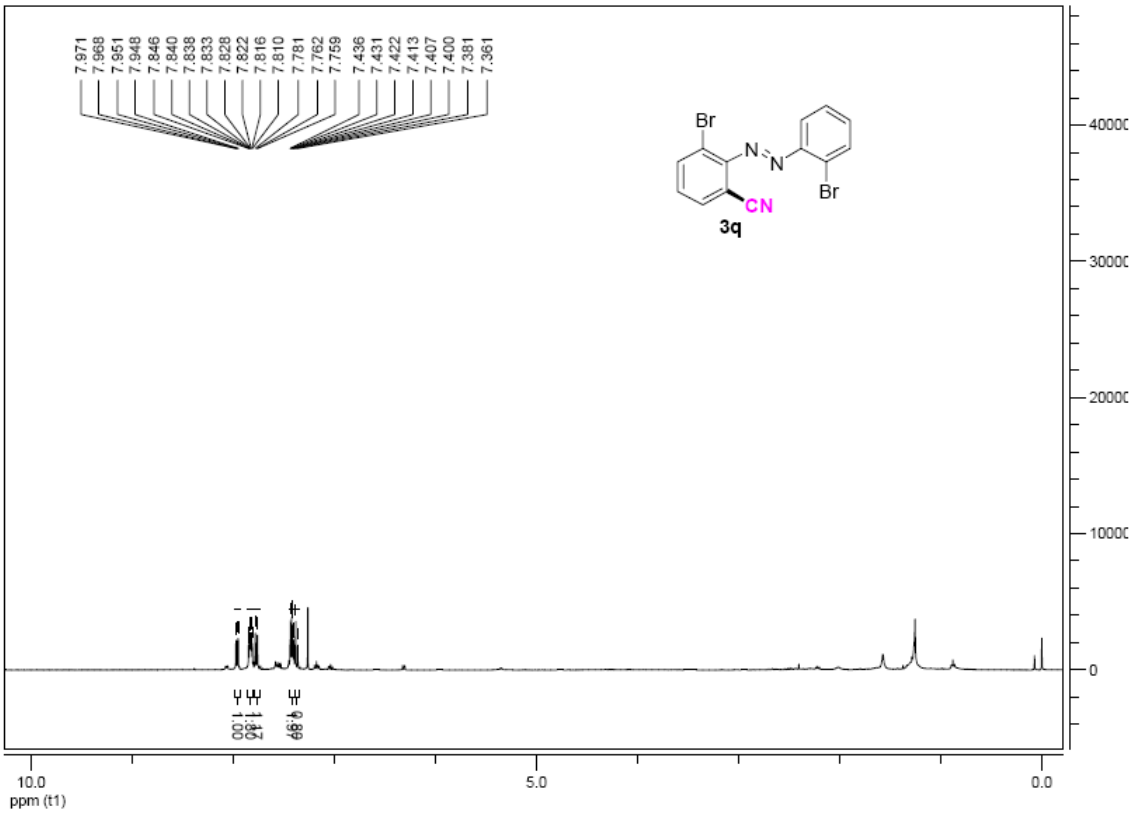
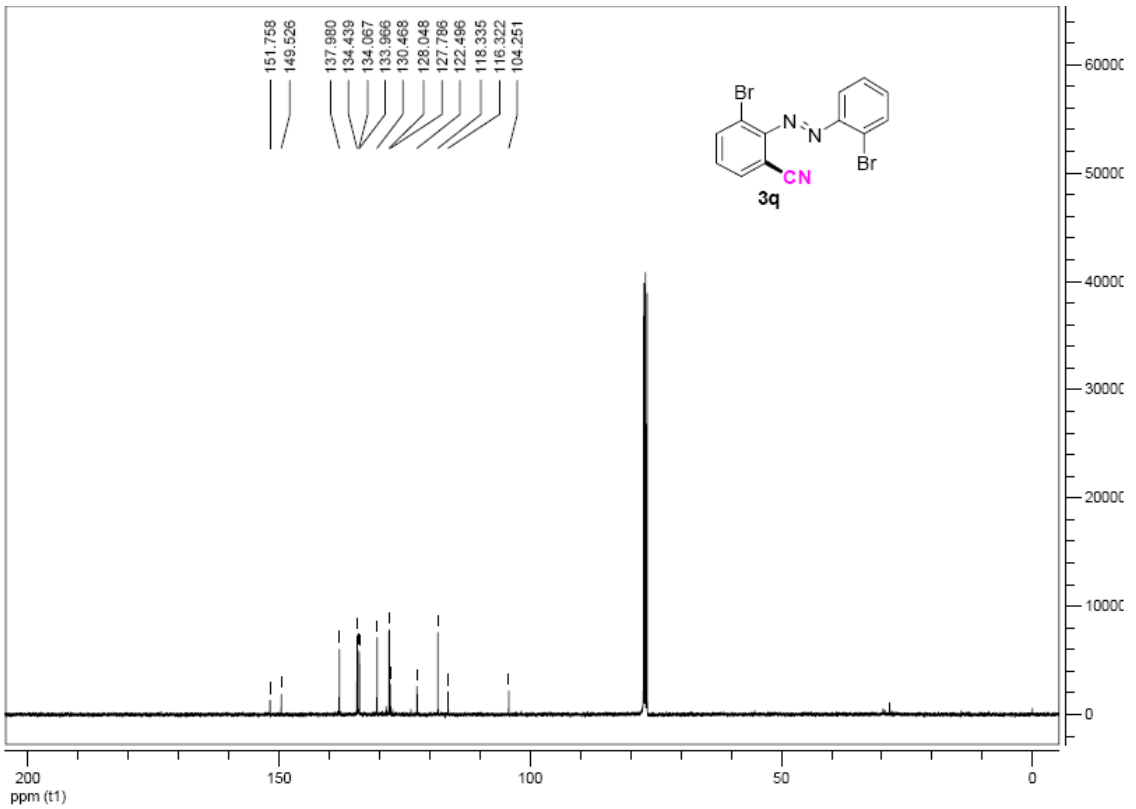
7.614
7.612
7.529
7.510
7.434
7.431
7.415
7.398
7.395
7.383
7.364
7.268
7.249
2.831
2.621
CH3
N
N
CH3
CN
3o
1.00
0.88
2.01
2.99
1.11
2.98
3.06
10.0
ppm (t1)
5.0
0.0


152.539
150.861
140.427
136.598
135.552
132.778
132.391
131.706
129.257
126.374
118.507
115.580
102.851
18.472
18.103
CH3
N
N
CH3
CN
3o
200
ppm (t1)
150
100
50
0

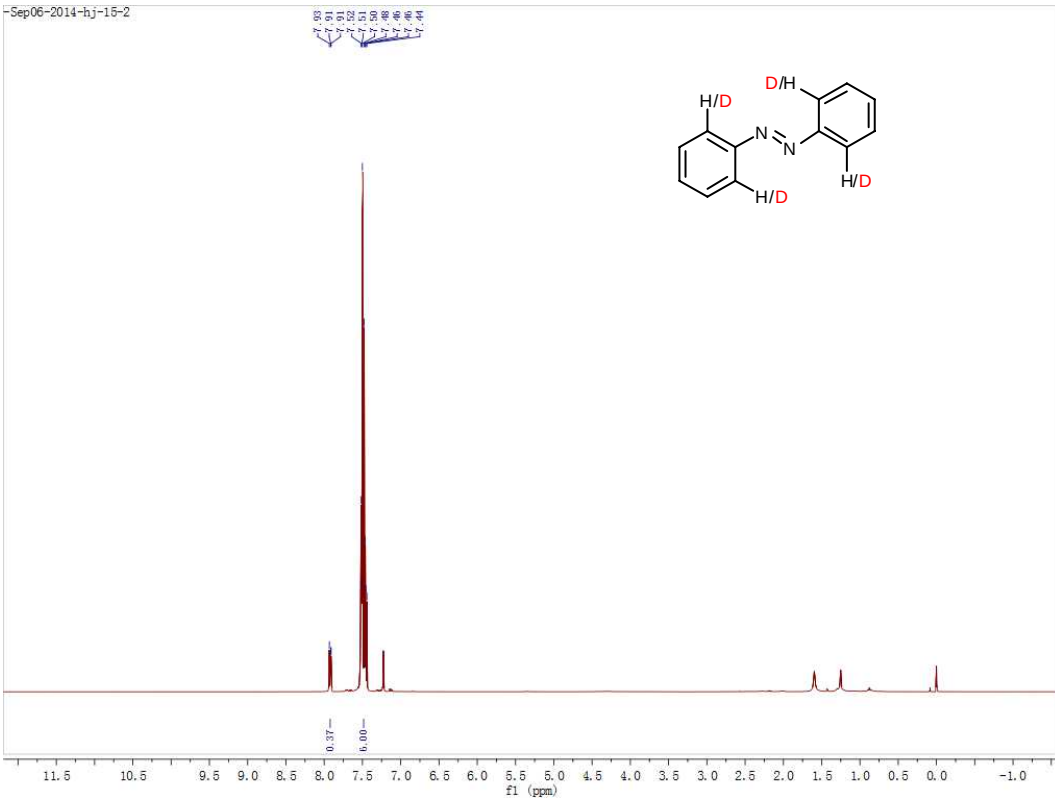

7.847
7.843
7.826
7.822
7.783
7.779
7.762
7.759
7.737
7.734
7.718
7.714
7.637
7.634
7.617
7.614
7.519
7.515
7.500
7.496
7.480
7.476
7.460
7.440
7.402
7.399
7.381
7.379
7.363
7.360
Cl
N
N
Cl
CN
3p
10.0
5.0
0.0
ppm (t1)


150.909
148.559
137.528
134.979
133.835
133.375
133.082
131.251
130.385
127.363
117.946
116.377
104.512
Cl
N
N
Cl
CN
3p
200
150
100
50
0
ppm (t1)


7.971
7.968
7.951
7.948
7.846
7.840
7.838
7.833
7.828
7.822
7.816
7.810
7.781
7.762
7.759
7.436
7.431
7.422
7.413
7.407
7.400
7.381
7.361
Br
N
N
Br
CN
3q
10.0
ppm (t1)
5.0
0.0


151.758
149.526
137.980
134.439
134.067
133.966
130.468
128.048
127.786
122.496
118.335
116.322
104.251
Br
N
N
Br
CN
3q
200
ppm (t1)
150
100
50
0

5. The ^{1}H NMR Spectrum of $[D]_n$-1a



^{1}H NMR(400MHz, $CDCl_3$) of $[D]_n$-1a : δ 7.93-7.91(m. 0.37 *ortho*-H), 7.52-7.44(m, 6H).

6. References

[1] L. D. Shirtcliff, J. Rivers and M. M. Haley, J. Org. Chem. 2006, **71**, 6619-6622.