Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

n-Bu_4NI/TBHP-catalyzed direct amination of allylic and benzylic C(sp^3)−H with anilines under metal-free conditions

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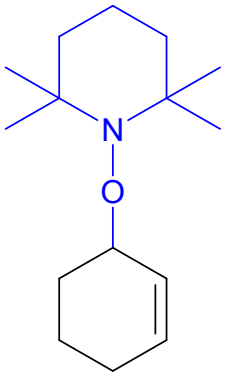
1. General considerations

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz and 100 MHz respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). The chemicals and solvents were purchased from commercial suppliers either from Aldrich, USA or Shanghai Chemical Company, China. Products were purified by flash chromatography on 100–200 mesh silica gels, SiO_2.

2. Procedures for Catalytic C-H Amination Reactions

The Schlenk tube equipped with a stir bar was charged with 4-aminobenzonitrile (0.50 mmol), TBAI (0.10 mmol), cyclohexene (2.0 mL) and TBHP (1.5 mmol) was added by syringe. The reaction mixture was stirred at 90 °C for 10 h. The organic phase was concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography on silica gel with ethyl acetate-petroleum ether (100:1→9:1) to provide the corresponding product.

3. LC-HRMS of TEMPO with allylic radical generated from cyclohexene under the standard reaction conditions

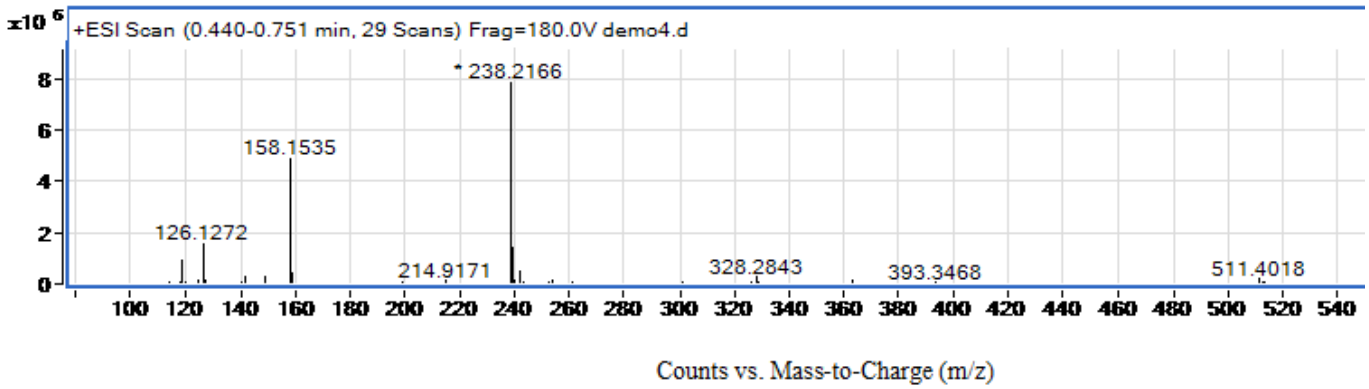


Chemical Formula: $C_{15}H_{27}NO$

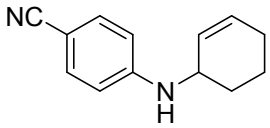
$[M+H] = C_{15}H_{28}NO$
Exact Mass: 238.2171
Molecular Weight: 238.3889
m/z: 238.2171 (100.0%), 239.2204 (16.2%), 240.2238 (1.2%)
Elemental Analysis: C, 75.57; H, 11.84; N, 5.88; O, 6.71

Calculated: [M+H] = 238.2171

Found: [M+H] = 238.2166

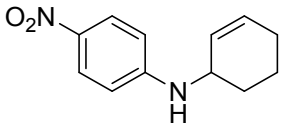


4. Characterization data for the products



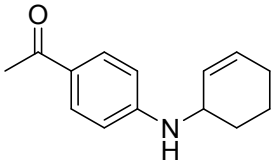
4-(Cyclohex-2-en-1-ylamino)benzonitrile (3a)[1]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.38 (m, 2H), 6.58–6.55 (m, 2H), 5.93–5.89 (m, 1H), 5.71–5.67 (m, 1H), 4.30–4.28 (m, 1H), 4.02–4.01 (m, 1H), 2.06–2.04 (m, 2H), 1.93–1.87 (m, 1H), 1.73–1.70 (m, 1H), 1.69–1.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.37, 133.75, 131.34, 127.04, 120.59, 112.44, 98.19, 47.40, 28.50, 24.96, 19.41.



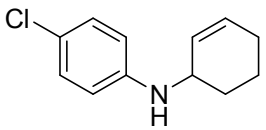
***N*-(Cyclohex-2-en-1-yl)-4-nitroaniline (3b)**[2]

Yellow soild. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08–8.05 (m, 2H), 6.54–6.53 (m, 2H), 5.93 (s, 1H), 5.69 (s, 1H), 4.59 (s, 1H), 4.07 (s, 1H), 2.06 (s, 2H), 1.93 (s, 1H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.42, 152.40, 131.74, 126.62, 126.53, 111.29, 47.73, 28.53, 24.91, 19.36.



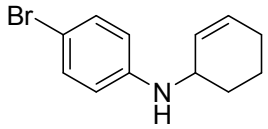
1-(4-(Cyclohex-2-en-1-ylamino)phenyl)ethanone (3c)[1]

Yellow soild. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J = 8.60 Hz, 2H), 6.57 (d, J = 8.60 Hz, 2H), 5.92–5.89 (m, 1H), 5.73–5.71 (m, 1H), 4.29–4.28 (s, 1H), 4.07 (s, 1H), 2.50 (s, 3H), 2.05 (s, 2H), 1.95–1.90 (m, 1H), 1.73–1.64 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.19, 151.18, 131.06, 130.89, 127.42, 126.48, 111.67, 47.46, 28.69, 25.95, 25.00, 19.47.



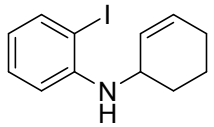
4-Chloro-*N*-(cyclohex-2-en-1-yl)aniline (3d)[1]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (d, *J* = 8.72 Hz, 2H), 6.55 (d, *J* = 8.68 Hz, 2H), 5.88–5.86 (m, 1H), 5.75–5.72 (m, 1H), 3.95 (s, 1H), 3.65 (s, 1H), 2.05 (s, 2H) , 1.93–1.87 (m, 1H), 1.73–1.59 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.76, 130.44, 129.10, 128.14, 121.60, 114.29, 48.08, 28.76, 25.11, 19.61.



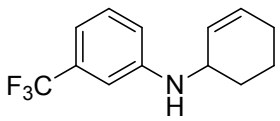
4-Bromo-*N*-(cyclohex-2-en-1-yl)aniline (3e)[1]

Yellow soild. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, *J* = 8.72 Hz, 2H), 6.50 (d, *J* = 8.72 Hz, 2H), 5.88–5.86 (m, 1H), 5.74–5.72 (m, 1H), 3.94 (s, 1H), 3.67 (s, 1H), 2.05 (s, 2H), 1.92–1.89 (m, 1H), 1.71–1.70 (m, 1H), 1.68–1.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.17, 131.97, 130.50, 128.06, 114.77, 108.54, 47.96, 28.70, 25.11, 19.59.



***N*-(cyclohex-2-en-1-yl)-2-iodoaniline (3f)**

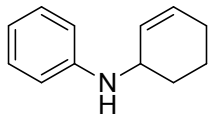
Colorless oil. IR (film, cm^{-1}): 3392 (ν_{N-H}), 740 ($\nu_{C=C-H}$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69–7.67 (m, 1H), 7.23–7.19 (m, 1H), 6.65–6.63 (m, 1H), 6.46–6.42 (m, 1H), 5.93–5.90 (m, 1H), 5.80–5.77 (m, 1H), 4.19 (s, 1H) 4.04 (s, 1H), 2.14–2.02 (m, 2H), 1.95–1.87 (m, 1H), 1.78–1.65 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.36, 139.26, 130.71, 129.35, 127.89, 118.37, 111.12, 85.90, 48.27, 28.64, 25.14, 19.54. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{12}H_{15}IN$: 300.0249, Found: 300.0246.



2-(3,4-Dimethylphenyl)-1-methyl-1*H*-indole (3g)[3]

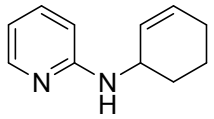
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.23 (m, 1H), 6.93–6.91 (m, 1H), 6.82 (s, 1H), 6.76–6.74 (m, 1H), 5.91–5.89 (m, 1H), 5.76–5.73 (m, 1H), 4.02 (s, 1H), 3.86 (s, 1H), 2.06 (s, 2H), 1.96–1.91 (m, 1H), 1.78–1.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.24, 131.52 (q, *J* = 31.47 Hz), 130.61,

129.55, 127.71, 124.25 (q, J = 270.69 Hz), 115.94, 113.30 (q, J = 3.95 Hz), 109.09 (q, J= 3.91 Hz), 47.66, 28.58, 24.96, 19.43.



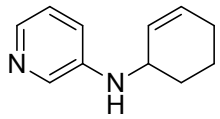
***N*-(Cyclohex-2-en-1-yl)aniline (3h)**[1]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21–7.17 (m, 2H), 6.72–6.68 (m, 1H), 6.65–6.63 (m, 2H), 5.88–5.86 (m, 1H), 5.78–5.76 (m, 1H), 4.01 (s, 1H), 3.65 (s, 1H), 2.05 (s, 2H), 1.96–1.90 (m, 1H), 1.74–1.65 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.20, 130.11, 129.31, 128.60, 117.15, 113.25, 47.89, 28.92, 25.17, 19.67.



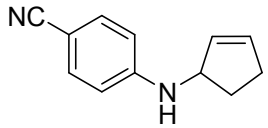
***N*-(Cyclohex-2-en-1-yl)pyridin-2-amine (3i)**[1]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08–8.07 (m, 1H), 7.42–7.38 (m, 1H), 6.56–6.53 (m, 1H), 6.40–6.38 (m, 1H), 5.88–5.86 (m, 1H), 5.75–5.72 (m, 1H), 4.52 (s, 1H), 4.32 (s, 1H), 2.04–1.94 (m, 3H), 1.73–1.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.83, 148.07, 137.24, 130.22, 128.28, 112.52, 107.00, 46.37, 29.14, 24.93, 19.60.



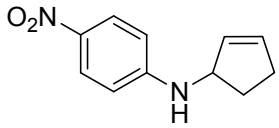
***N*-(Cyclohex-2-en-1-yl)pyridin-3-amine (3j)**[4]

Yellow soild. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03–8.02 (m, 1H), 7.94–7.93 (m, 1H), 7.09–7.06 (m, 1H), 6.90–6.88 (m, 1H), 5.90–5.88 (m, 1H), 5.74–5.72 (m, 1H), 3.99 (s, 1H), 3.70 (s, 1H), 2.05 (s, 2H), 1.95–1.89 (m, 1H), 1.77–1.59 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.17, 138.51, 136.47, 130.80, 127.77, 123.73, 118.87, 47.66, 28.66, 25.05, 19.50.



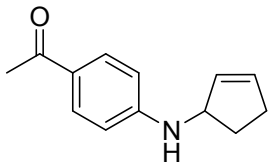
4-(Cyclopent-2-en-1-ylamino)benzonitrile (3k)

Yellow oil. IR (film, cm^{-1}): 3567 (ν_{N-H}), 2211 ($\nu_{C\equiv N}$), 741 ($\nu_{C=C-H}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 8.32 Hz, 2H), 6.57 (d, *J* = 8.36 Hz, 2H), 6.03 (s, 1H), 5.80–5.79 (m, 1H), 4.55 (s, 1H), 4.33 (s, 1H) , 2.53–2.45 (m, 1H) , 2.39–2.30 (m, 2H) 1.71–1.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.64, 135.35, 133.59, 130.38, 120.51, 112.43, 98.12, 58.71, 31.10, 30.90. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{12}H_{13}N_2$: 185.1079, Found: 185.1084.



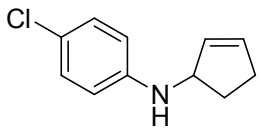
***N*-(Cyclopent-2-en-1-yl)-4-nitroaniline (3l)**[5]

Yellow soild. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 9.00 Hz, 2H), 6.54 (d, *J* = 9.04 Hz, 2H), 6.06–6.05 (m, 1H), 5.80–5.79 (m, 1H), 4.65 (s, 1H), 4.62–4.61 (m, 1H), 2.55–2.47 (m, 1H), 2.43–2.34 (m, 2H), 1.73–1.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.66, 137.56, 135.77, 130.00, 126.36, 111.27, 58.97, 31.13, 30.93.



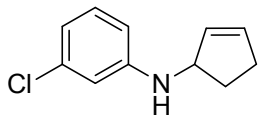
1-(4-(Cyclopent-2-en-1-ylamino)phenyl)ethanone (3m)

Yellow soild. m.p. 86–87 °C. IR (KBr, cm^{-1}): 3654 (ν_{N-H}), 1646 ($\nu_{C=O}$), 733 ($\nu_{C=C-H}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.56 Hz, 2H), 6.58 (d, *J* = 8.56 Hz, 2H), 6.03–6.02 (m, 1H), 5.82–5.81 (m, 1H), 4.61 (s, 1H), 4.30 (s, 1H), 2.50 (s, 4H), 2.39–2.36 (m, 2H) 1.71–1.64 (m, 1H); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 196.18, 151.46, 135.06, 130.73, 126.38, 111.66, 58.79, 31.09, 31.05, 25.86. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{13}H_{15}NO$:202.1232 Found: 202.1227.



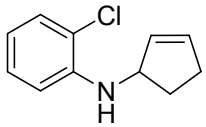
4-Chloro-*N*-(cyclopent-2-en-1-yl)aniline (3n)

Yellow oil. IR (film, cm^{-1}): 3420 (ν_{N-H}), 736 ($\nu_{C=C-H}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.12 (d, *J* = 8.60 Hz, 2H), 6.56 (d, *J* = 8.60 Hz, 2H), 6.00–5.99 (m, 1H), 5.83–5.82 (m, 1H), 4.51 (s, 1H), 3.69 (s, 1H) , 2.52–2.45 (m, 1H), 2.40–2.29 (m, 2H), 1.70–1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.12, 134.41, 131.36, 128.96, 121.62, 114.24, 59.45, 31.04, 30.95. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{11}H_{13}ClN$: 194.0737, Found: 194.0737.



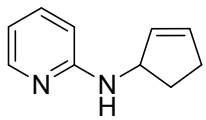
3-Chloro-*N*-(cyclopent-2-en-1-yl)aniline (3o)

Yellow oil. IR (film, cm^{-1}): 3411 (ν_{N-H}), 726 ($\nu_{C=C-H}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.10–7.06 (m, 1H), 6.68–6.66 (m, 1H), 6.62 (s, 1H), 6.51–6.49 (m, 1H), 6.02–6.01 (m, 1H), 5.84–5.83 (m, 1H), 4.53–4.52 (m, 1H), 3.76 (s, 1H), 2.54–2.46 (m, 1H), 2.41–2.33 (m, 2H), 1.69–1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.71, 134.90, 134.54, 131.25, 130.09, 116.86, 112.68, 111.49, 59.20 31.07, 31.03. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{11}H_{13}ClN$: 194.0737, Found: 194.0730.



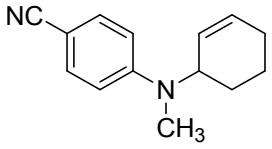
2-Chloro-*N*-(cyclopent-2-en-1-yl)aniline (3p)

Yellow oil. IR (film, cm^{-1}): 3420 (ν_{N-H}), 740 ($\nu_{C=C-H}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30–7.28 (m, 1H), 7.20–7.16 (m, 1H), 6.79–6.77 (m, 1H), 6.68–6.64 (m, 1H), 6.05 (s, 1H), 5.90 (s, 1H), 4.61 (s, 1H), 4.34 (s, 1H), 2.59–2.51 (m, 1H), 2.44–2.40 (m, 2H) 1.76–1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.43, 134.66, 131.22, 129.12, 127.67, 119.09, 116.88, 111.78, 59.11, 31.18, 31.14. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{11}H_{13}ClN$: 194.0737, Found: 194.0735.



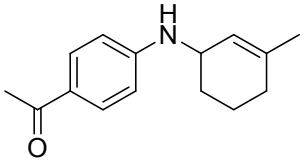
***N*-(Cyclopent-2-en-1-yl)pyridin-2-amine (3q)**

Yellow soild. m.p. 79–80 °C. IR (KBr, cm^{-1}): 3247 (ν_{N-H}), 735 ($\nu_{C=C-H}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 4.56 Hz, 1H), 7.42–7.38 (m, 2H), 6.57–6.53 (m, 1H), 6.41–6.39 (m, 1H), 5.97–5.96 (m, 1H), 5.82–5.81 (m, 1H), 4.80 (s, 1H) , 4.63 (s, 1H) , 2.50–2.45 (m, 1H), 2.41–2.30 (m, 2H), 1.68–1.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.23, 148.15, 137.24, 134.13, 131.62, 112.57, 106.78, 57.75, 31.39, 31.00. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{10}H_{13}N_2$: 161.1079, Found: 161.1076.



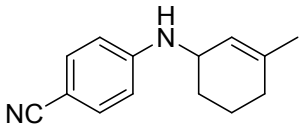
4-(Cyclohex-2-en-1-yl(methyl)amino)benzonitrile (3r)[1]

Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 8.64 Hz, 2H), 6.71 (d, *J* = 8.64 Hz, 2H), 5.99–5.97 (m, 1H), 5.58–5.55 (m, 1H), 4.48 (s, 1H), 2.85 (s, 3H), 2.07 (s, 2H), 1.91–1.82 (m, 2H), 1.73–1.55 (m, 2H); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 151.94, 133.35, 131.64, 128.12, 120.60, 111.62, 97.03, 54.39, 32.44, 25.74, 24.58, 21.09.



1-(4-((3-Methylcyclohex-2-en-1-yl)amino)phenyl)ethanone (3s)

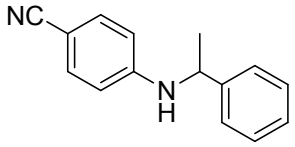
Yellow soild. m.p. 101−102 °C. IR (KBr, cm^{-1}): 3363 (ν_{N-H}), 1645 ($\nu_{C=O}$), 730 ($\nu_{C=C-H}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.52 Hz, 2H), 6.56 (d, *J* = 8.52 Hz, 2H), 5.45 (s, 1H), 4.28 (d, *J* = 6.60 Hz, 1H), 4.04 (s, 1H), 2.49 (s, 3H), 2.08–1.62 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.02, 151.21, 138.69, 130.77, 126.21, 121.60, 111.52, 47.79, 29.86, 28.24, 25.79, 23.56, 19.55. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{20}NO$: 230.1545, Found: 230.1539.



4-((3-Methylcyclohex-2-en-1-yl)amino)benzonitrile (3t)

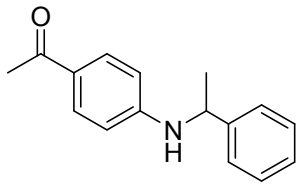
Yellow oil. IR (film, cm^{-1}): 3358 (ν_{N-H}), 2208 ($\nu_{C\equiv N}$), 731 ($\nu_{C=C-H}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 8.68 Hz, 2H), 6.55 (d, *J* = 8.64 Hz, 2H), 5.42 (s, 1H), 4.27 (d, *J* = 7.32 Hz, 1H), 3.98 (s, 1H), 2.08–

1.54 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.37, 138.99, 133.59, 121.23, 120.49, 112.30, 97.90, 47.76, 29.82, 28.06, 23.56, 19.49. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{14}H_{17}N_2$: 212.1392, Found: 212.1396.



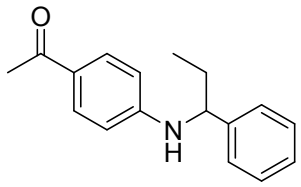
4-((1-Phenylethyl)amino)benzonitrile (4a)[6]

Yellow soild. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.24 (m, 7H), 6.46 (d, *J* = 7.60 Hz, 2H), 4.68 (s, 1H), 4.52 (q, *J* = 6.40 Hz, 2H), 1.53 (d, *J* = 6.40 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.18, 143.52, 133.44, 128.78, 127.26, 125.52, 120.22, 112.81, 98.83, 52.99, 24.53.



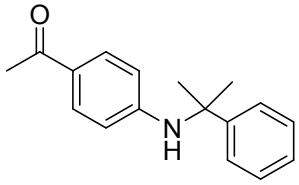
1-(4-((1-Phenylethyl)amino)phenyl)ethanone (4b)[6]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 7.64 Hz, 2H), 7.34–7.24 (m, 5H), 6.48 (d, *J* = 7.68 Hz, 2H), 4.59–4.58 (m, 2H), 2.45 (s, 3H), 1.56 (d, *J* = 5.68 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.27, 151.09, 144.03, 130.61, 128.81, 127.22, 126.85, 125.68, 112.13, 53.06, 25.91, 24.63.



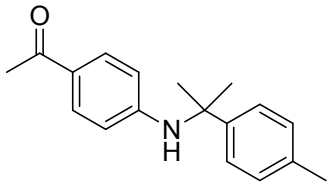
1-(4-((1-Phenylpropyl)amino)phenyl)ethanone (4c)

Yellow soild. m.p. 83–84 °C. IR (KBr, cm^{-1}): 3309 (ν_{N-H}), 1650 ($\nu_{C=O}$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 8.40 Hz, 2H), 7.36–7.30 (m, 4H), 7.27–7.25 (m, 1H), 6.50 (d, *J*= 8.40 Hz, 2H), 4.62 (s, 1H), 4.34–4.31 (m, 1H), 2.45 (s, 3H), 1.92–1.83 (m, 2H), 0.99 (t, *J* = 7.36 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.11, 151.26, 142.61, 130.50, 128.56, 127.13, 126.22, 112.00, 59.18, 31.25, 25.78, 10.59. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{17}H_{20}NO$: 254.1545, Found: 254.1542.



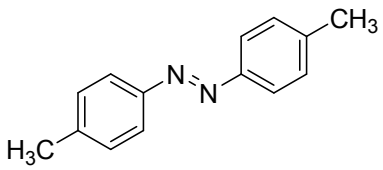
1-(4-((2-Phenylpropan-2-yl)amino)phenyl)ethanone (**4d**)

Yellow soild. m.p. 73–74 °C. IR (KBr, cm^{-1}): 3359 (ν_{N-H}), 1654 ($\nu_{C=O}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 8.04 Hz, 2H), 7.47–7.45 (m, 2H), 7.37–7.33 (m, 2H), 7.27–7.26 (m, 1H), 6.31 (d, *J* = 8.08 Hz, 2H), 4.72 (s, 1H), 2.43 (s, 3H), 1.70 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.18, 150.14, 146.12, 130.04, 128.63, 126.59, 126.33, 125.22, 113.71, 56.02, 30.46, 25.75. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{17}H_{20}NO$: 254.1545, Found: 254.1543.



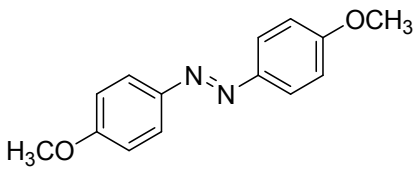
1-(4-((2-(*p*-Tolyl)propan-2-yl)amino)phenyl)ethanon (**4e**)

Yellow oil. IR (film, cm^{-1}): 3341 (ν_{N-H}), 1653 ($\nu_{C=O}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 8.04 Hz, 2H), 7.35–7.33 (m, 2H), 7.17–7.15 (m, 2H), 6.33 (d, *J* = 8.00 Hz, 2H), 4.79 (s, 1H), 2.43 (s, 3H), 2.35 (s, 3H), 1.68 (s, 6H), 0.99 (t, *J* = 7.36 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.19, 150.34, 143.20, 136.14, 130.07, 129.35, 126.24, 125.19, 113.74, 55.86, 30.52, 25.77, 20.85. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{18}H_{22}NO$: 268.1701, Found: 268.1696.



(*E*)-1,2-Bis(4-methyphenyl)diazene[7]

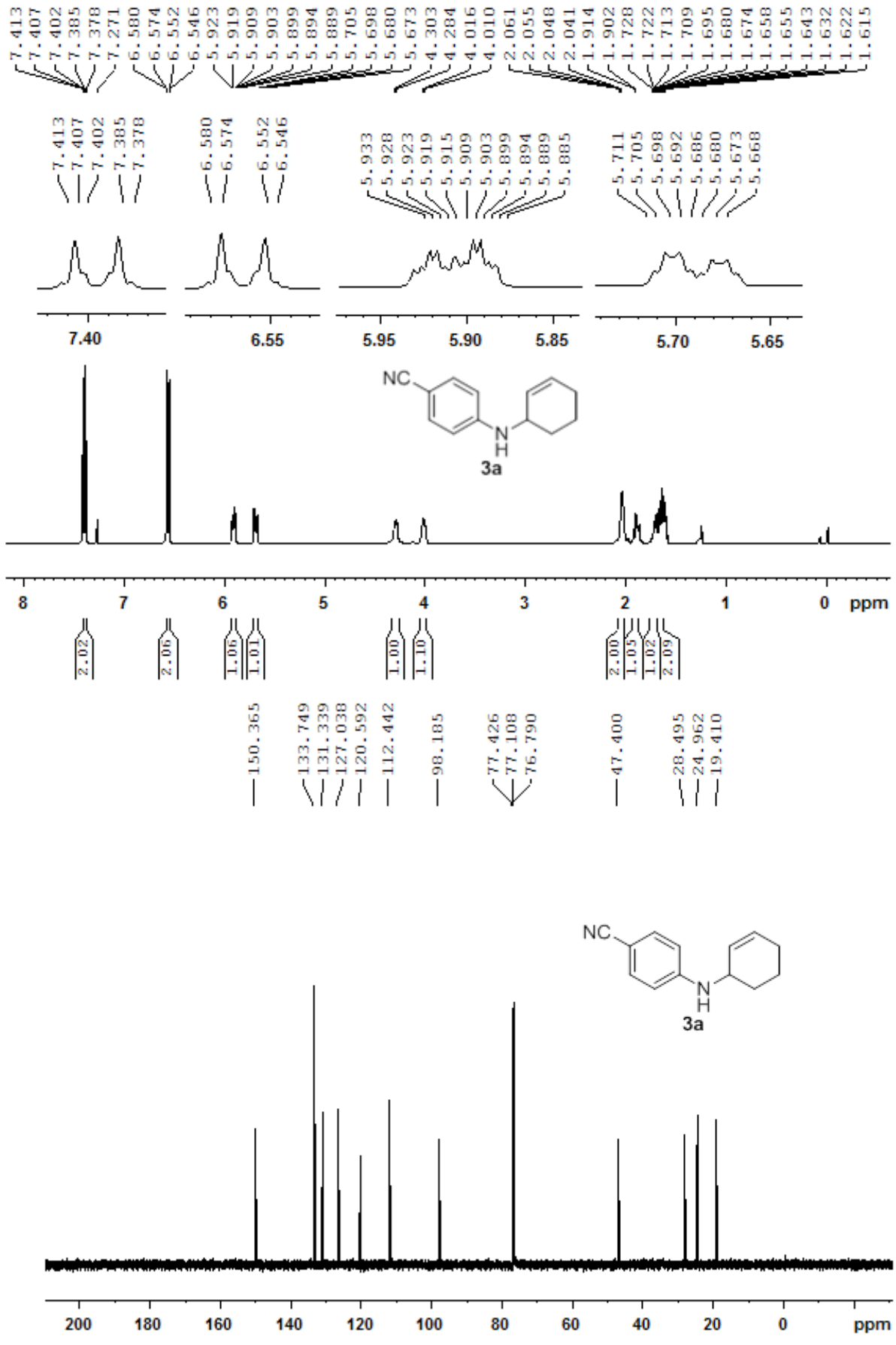
Yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 8.0 Hz, 4H), 7.33 (d, *J* = 8.0 Hz, 4H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.76, 141.07, 129.60, 122.63, 21.36.

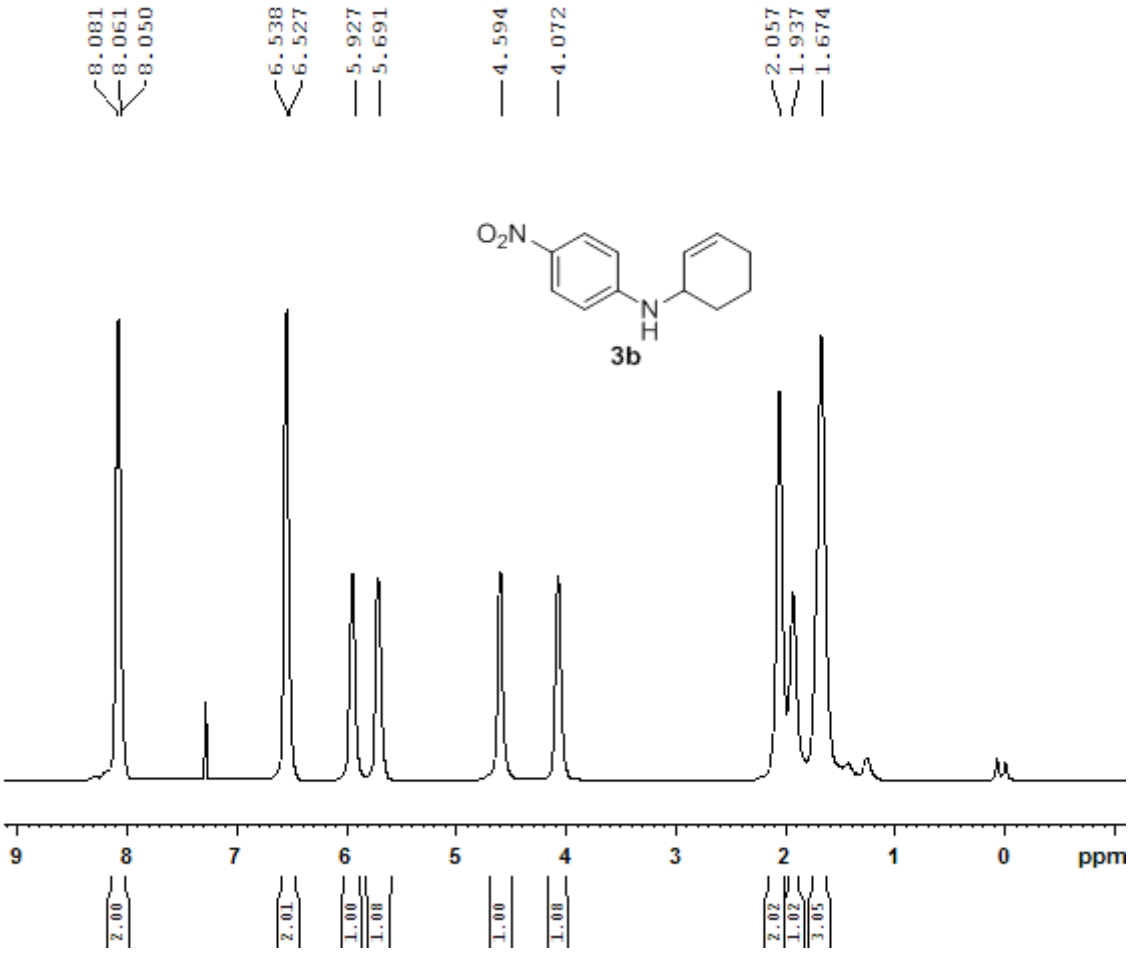


(*E*)-1,2-Bis(4-methoxyphenyl)diazene[7]

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.8 Hz, 4H), 7.02 (d, *J* = 8.8 Hz, 4H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.46, 147.00, 124.22, 114.05, 55.43.

5. ^{1}H and ^{13}C spectra of the products

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8.050
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5.927
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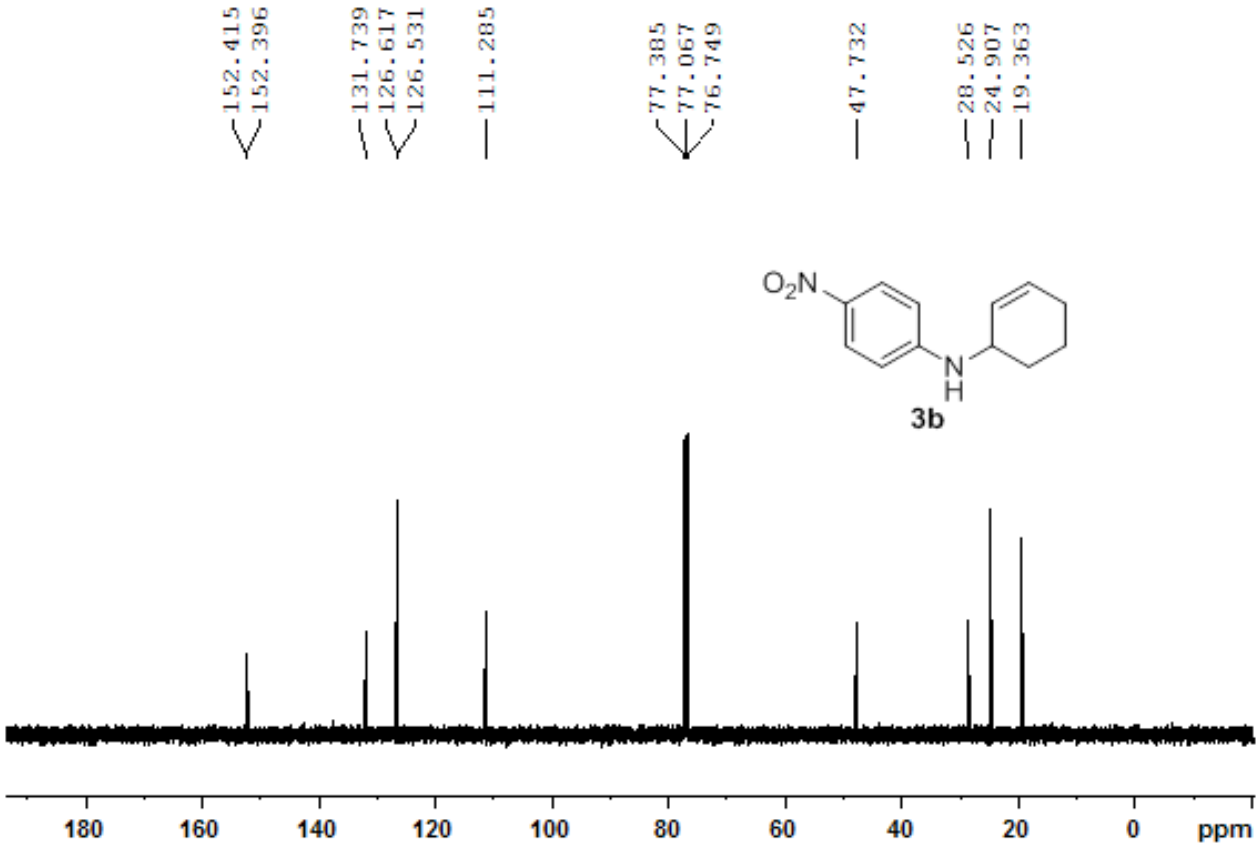
4.594
4.072
2.057
1.937
1.674
O2N
N
H
3b
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
1.00
1.08
1.00
1.08
2.02
1.02
3.05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N
H
3b
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140
120
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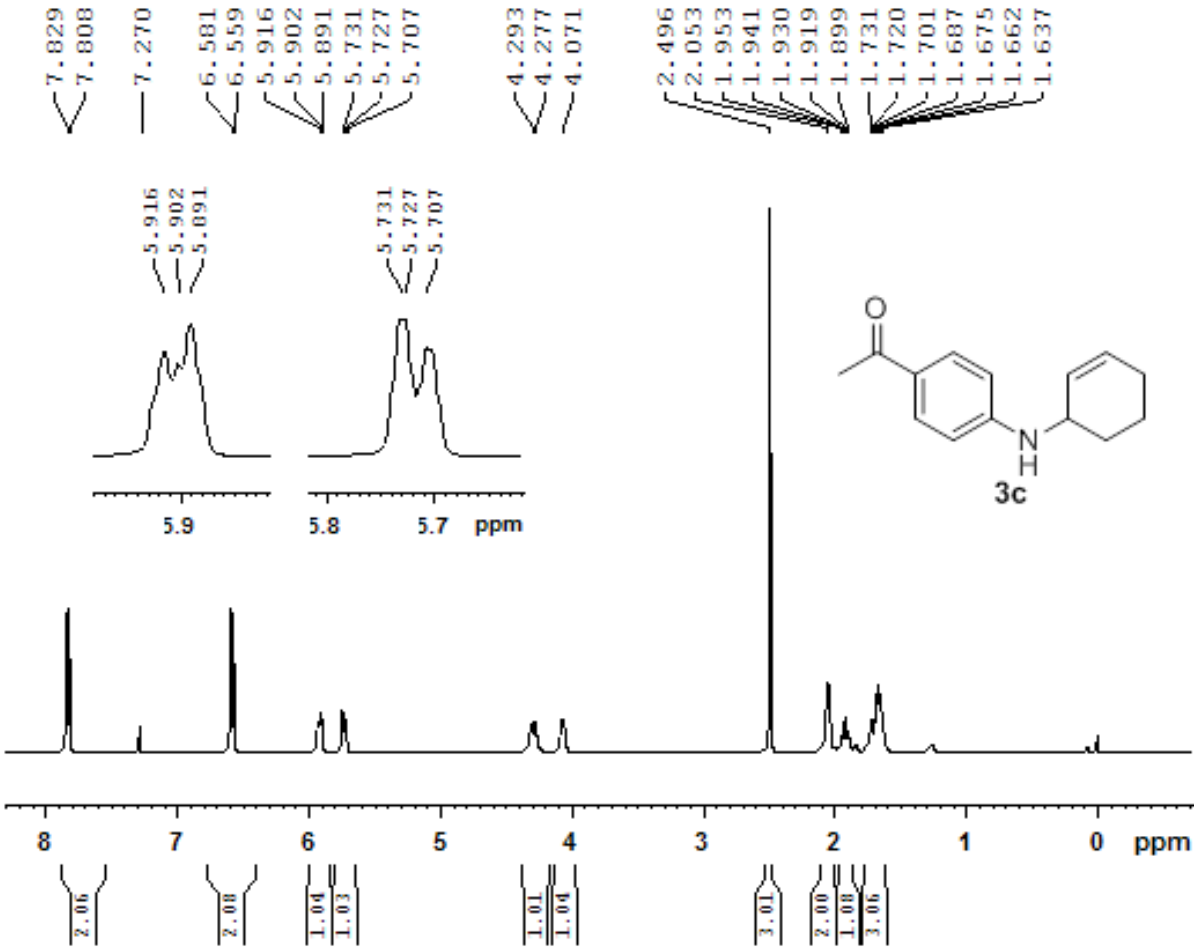
80
60
40
20
0
ppm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5.731
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4.293
4.277
4.071
2.496
2.053
1.953
1.941
1.930
1.919
1.899
1.731
1.720
1.701
1.687
1.675
1.662
1.637
5.916
5.902
5.891
5.731
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5.707
5.9
5.8
5.7
ppm
O
N
H
3c
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7
6
5
4
3
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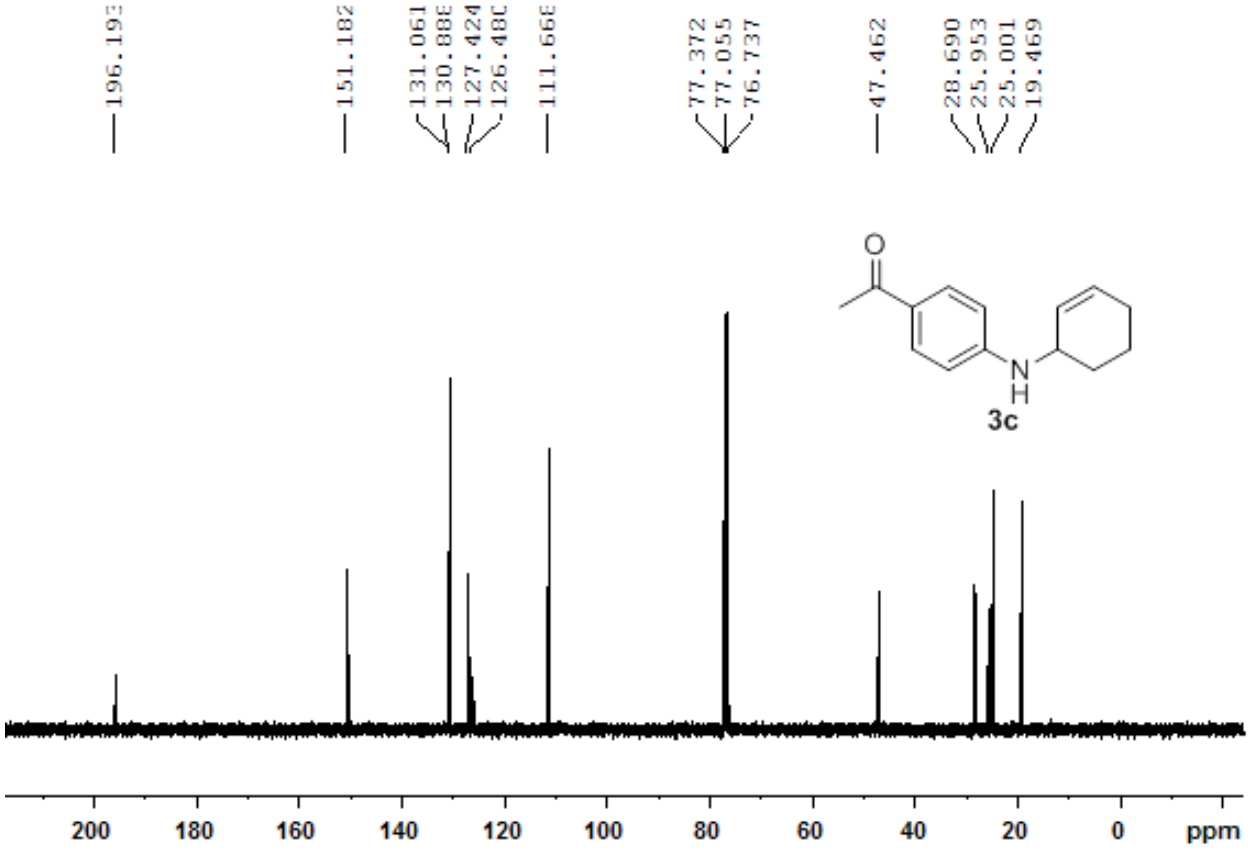
2.08
1.04
1.03
1.01
1.04
3.01
2.00
1.08
3.06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126.480
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76.737
47.462
28.690
25.953
25.001
19.469
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N
H
3c
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120
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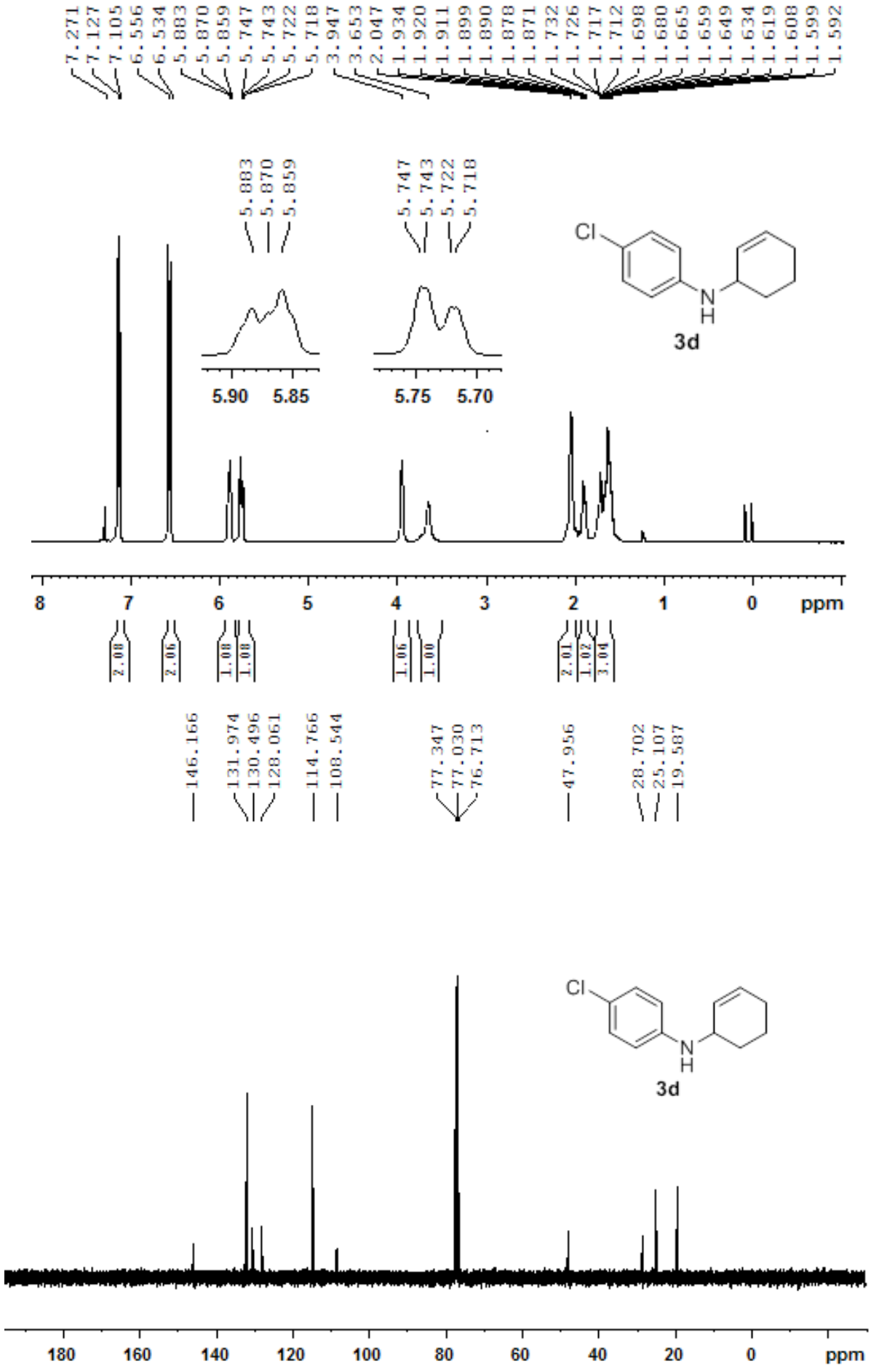
80
60
40
20
0
ppm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5.870
5.859
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5.743
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5.718
3.947
3.653
2.047
1.934
1.920
1.911
1.899
1.890
1.878
1.871
1.732
1.726
1.717
1.712
1.698
1.680
1.665
1.659
1.649
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1.619
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1.592
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5.747
5.743
5.722
5.718
5.90
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5.70
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ppm
2.08
2.06
1.08
1.08
1.06
1.00
2.01
1.02
3.04
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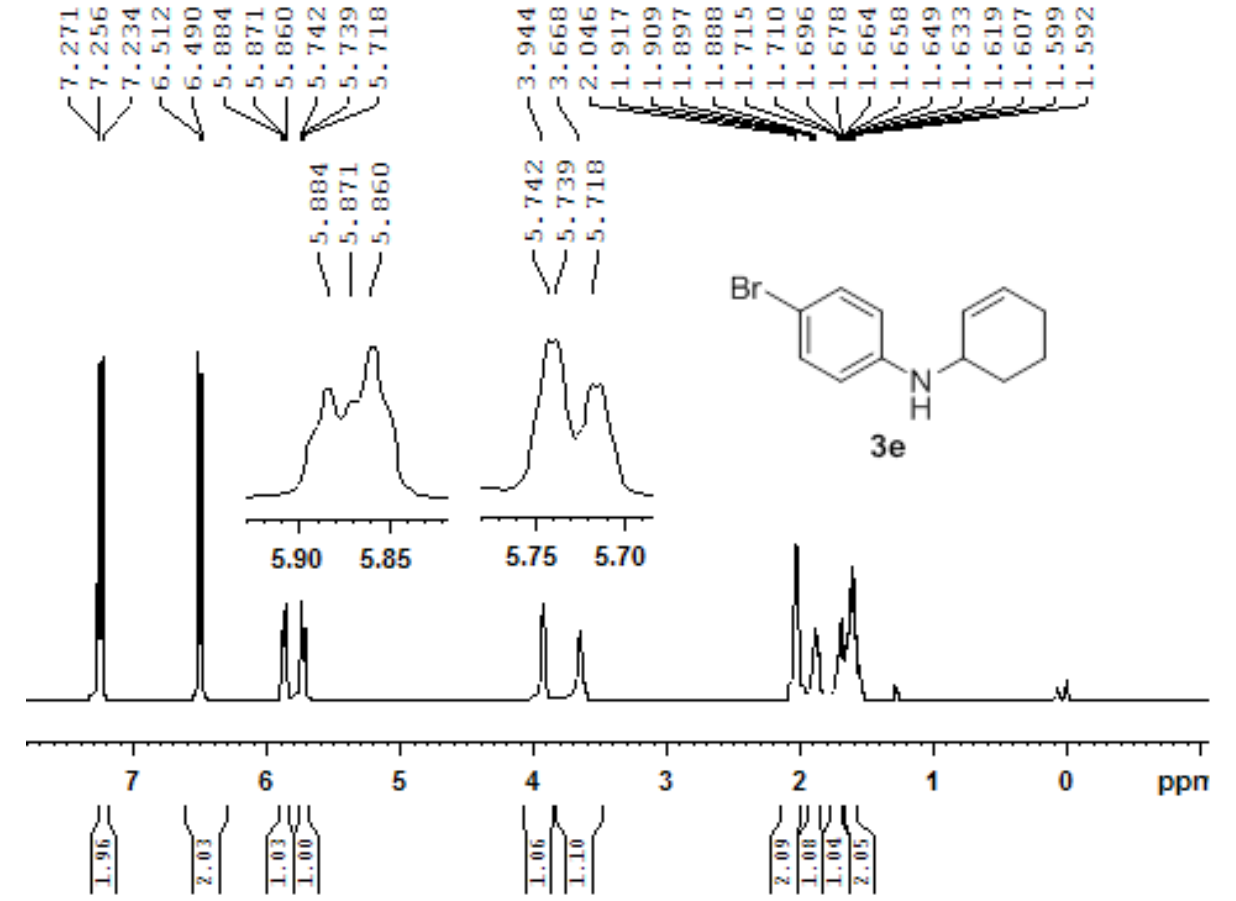
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3.668
2.046
1.917
1.909
1.897
1.888
1.715
1.710
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1.678
1.664
1.658
1.649
1.633
1.619
1.607
1.599
1.592
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H
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5.75
5.70
7
6
5
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3
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1.10
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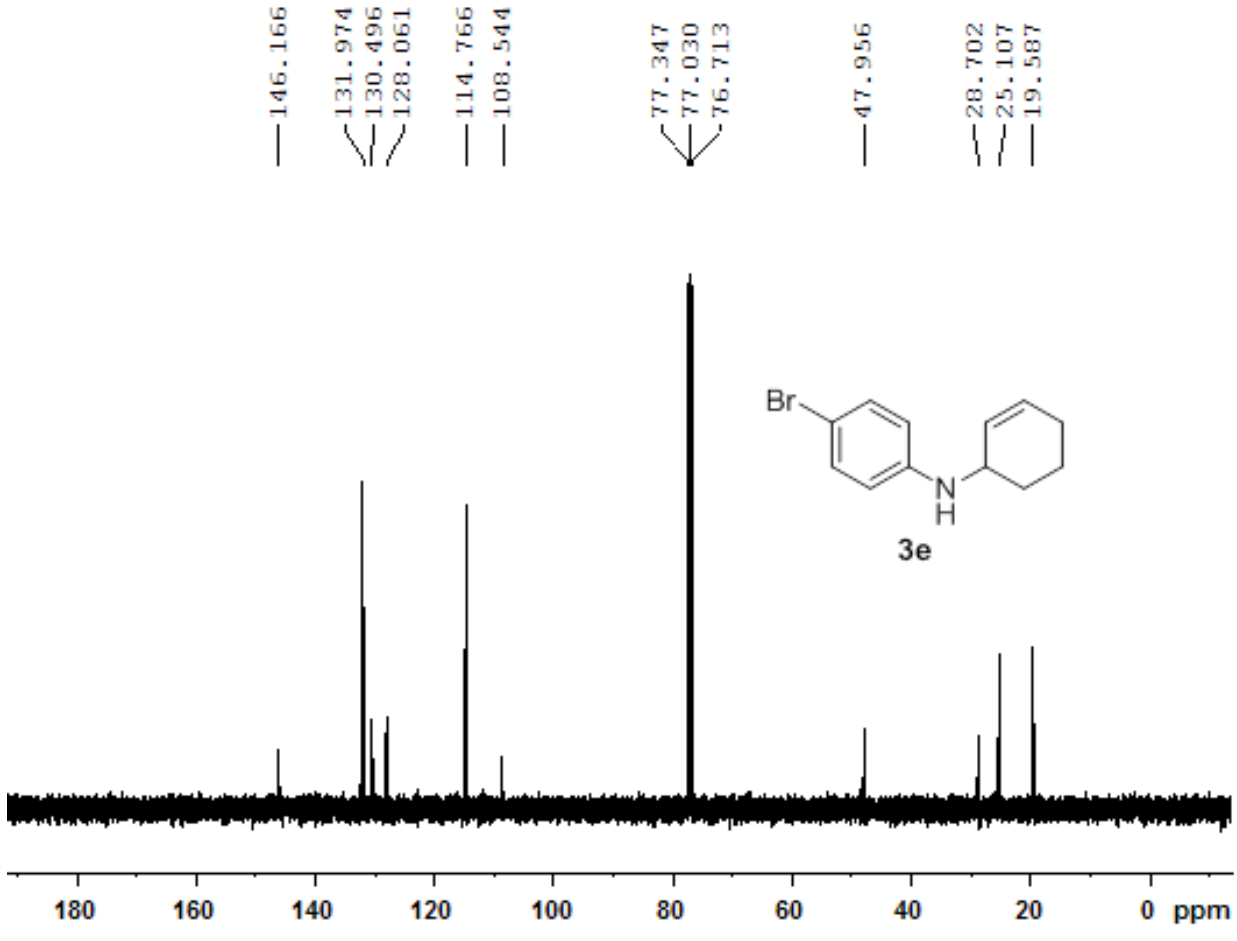
1.08
1.04
2.05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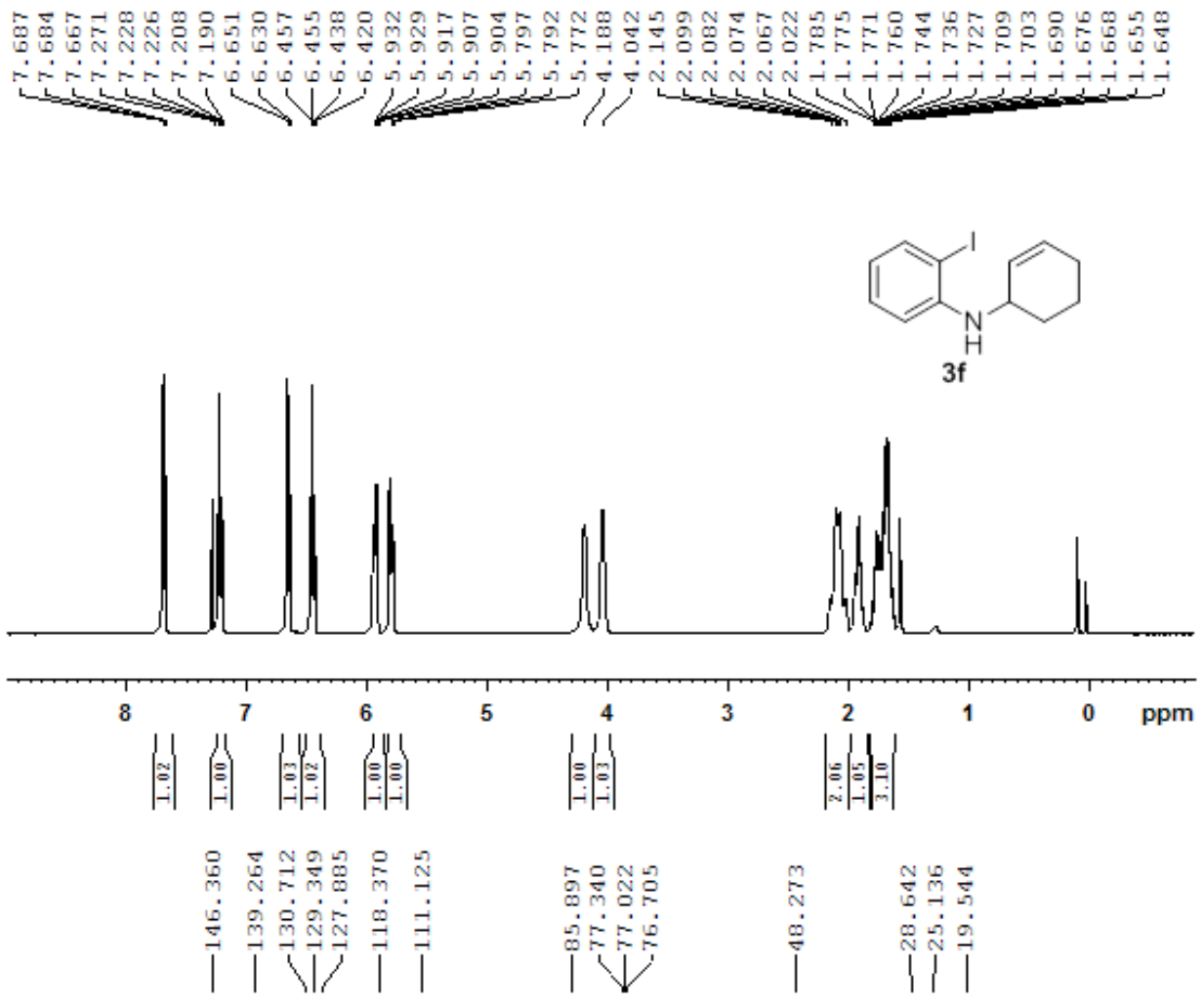
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7.271
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7.226
7.208
7.190
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6.630
6.457
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5.917
5.907
5.904
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5.792
5.772
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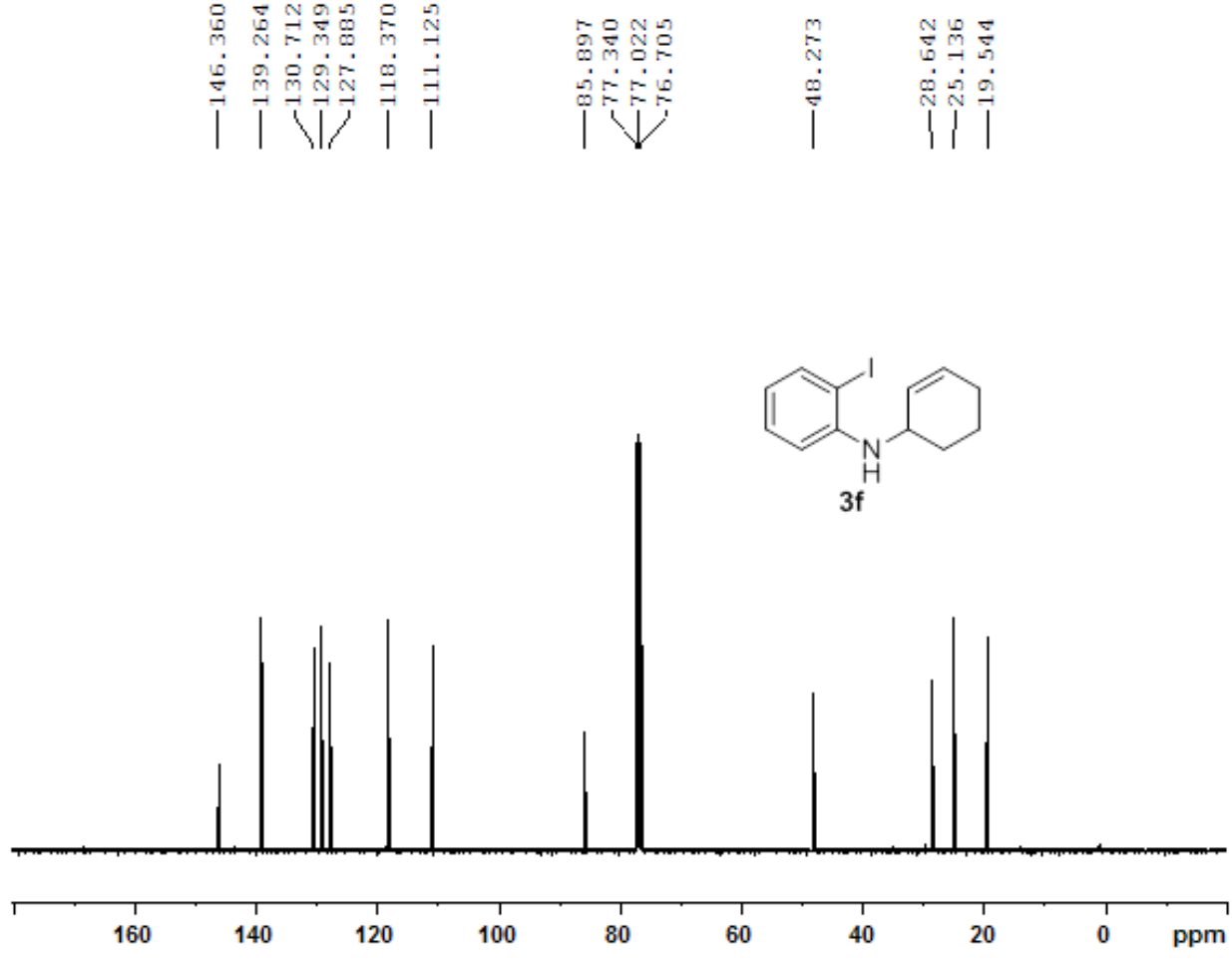
3.10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H
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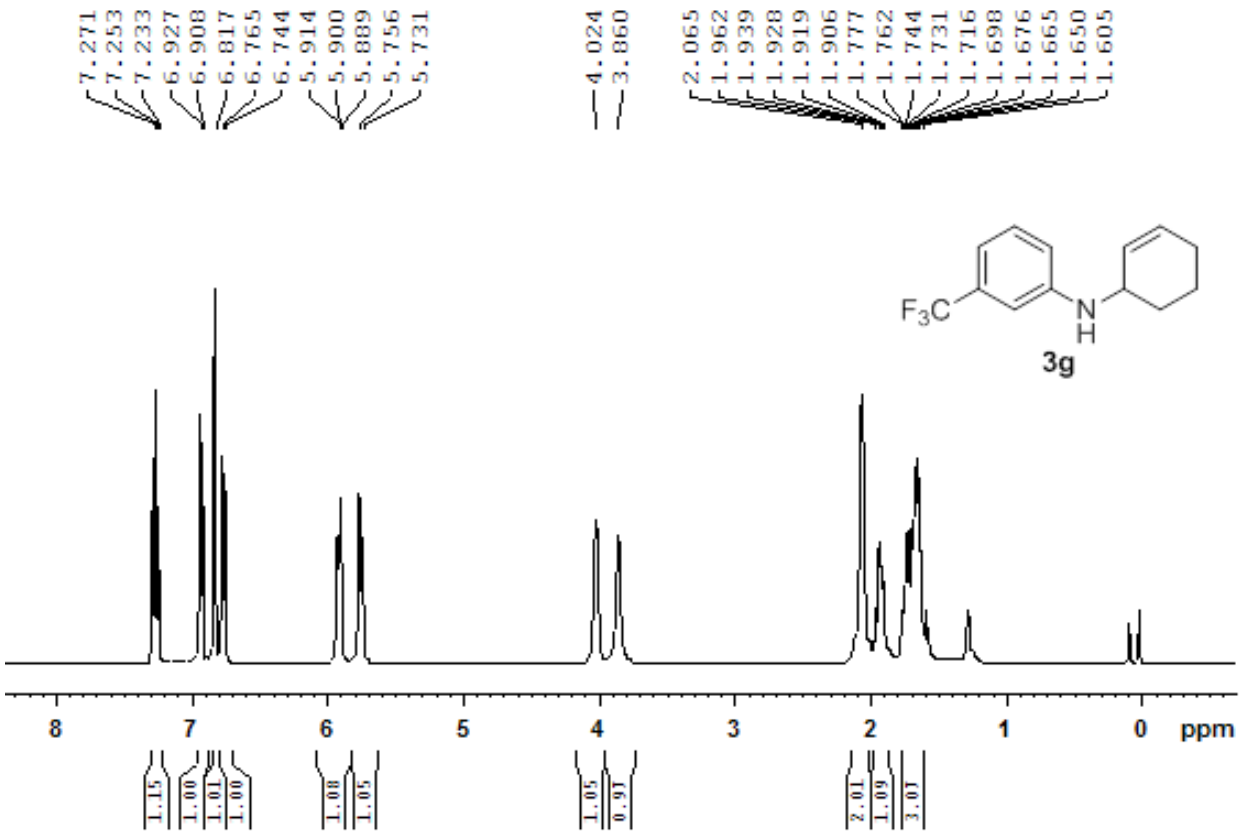
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5.731
4.024
3.860
2.065
1.962
1.939
1.928
1.919
1.906
1.777
1.762
1.744
1.731
1.716
1.698
1.676
1.665
1.650
1.605
F3C
N
H
3g
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7
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5
4
3
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1
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1.05
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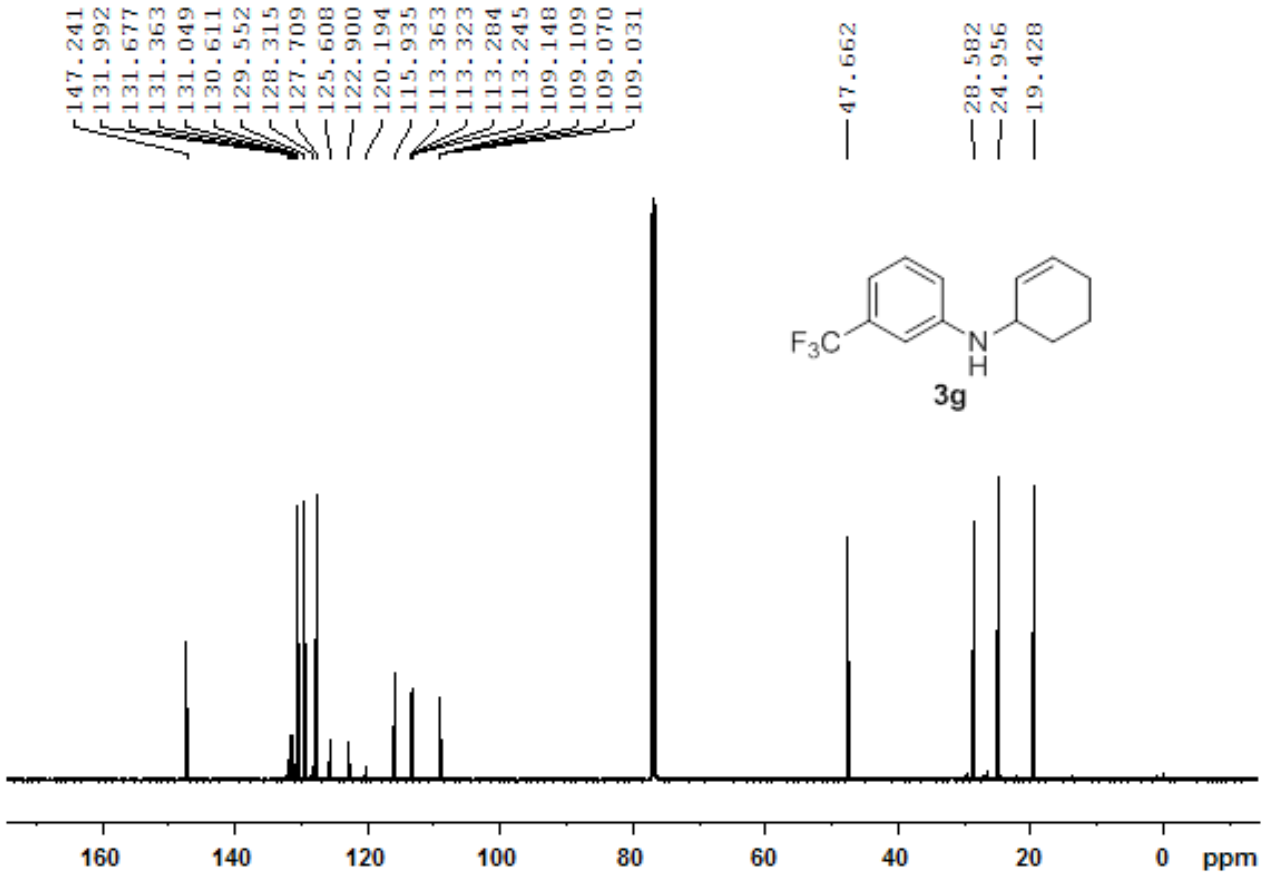
2.01
1.09
3.07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125.608
122.900
120.194
115.935
113.363
113.323
113.284
113.245
109.148
109.109
109.070
109.031
47.662
28.582
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19.428
F3C
N
H
3g
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120
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80
60
40
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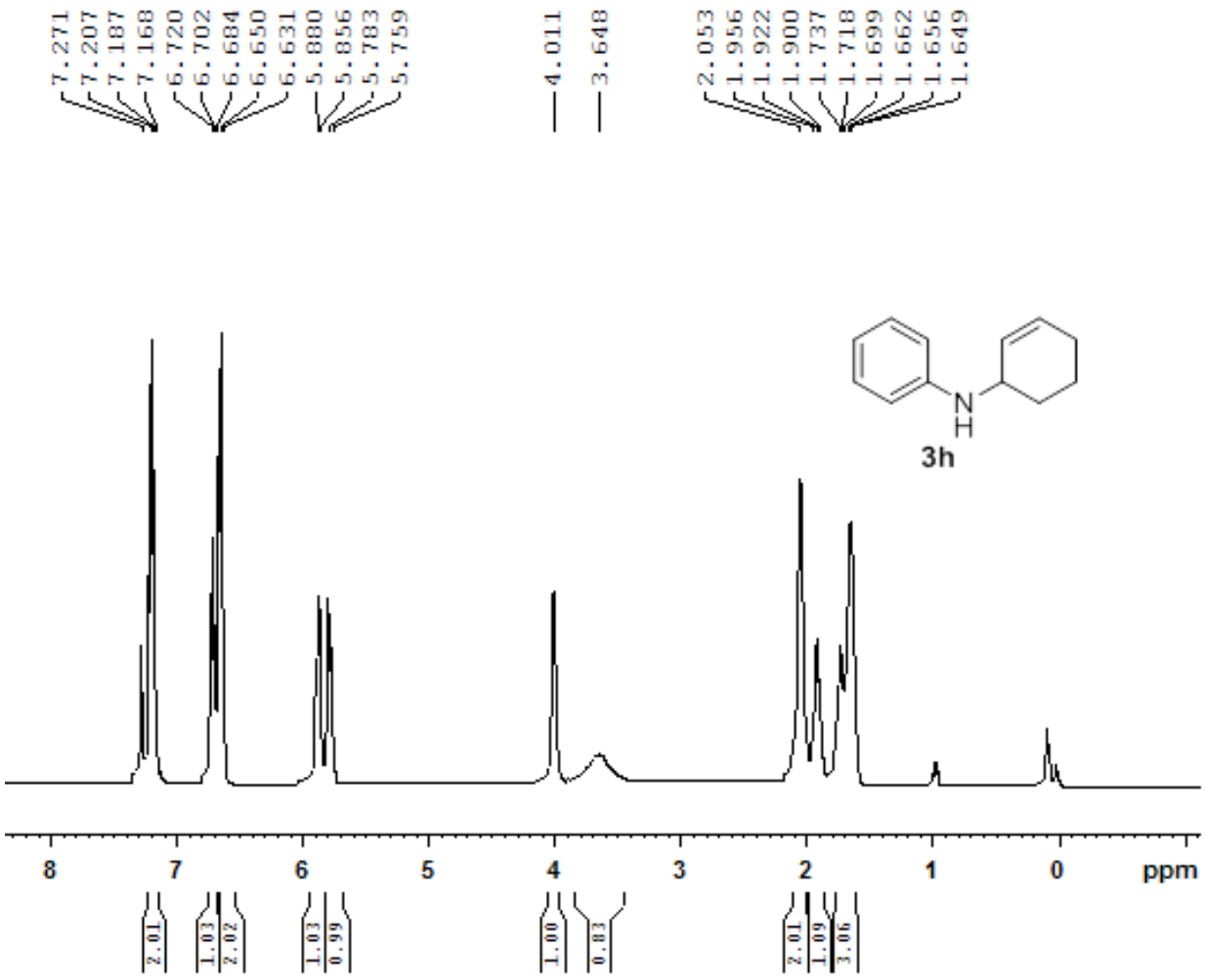
ppm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4.011
3.648
2.053
1.956
1.922
1.900
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1.718
1.699
1.662
1.656
1.649
3h
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7
6
5
4
3
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1.00
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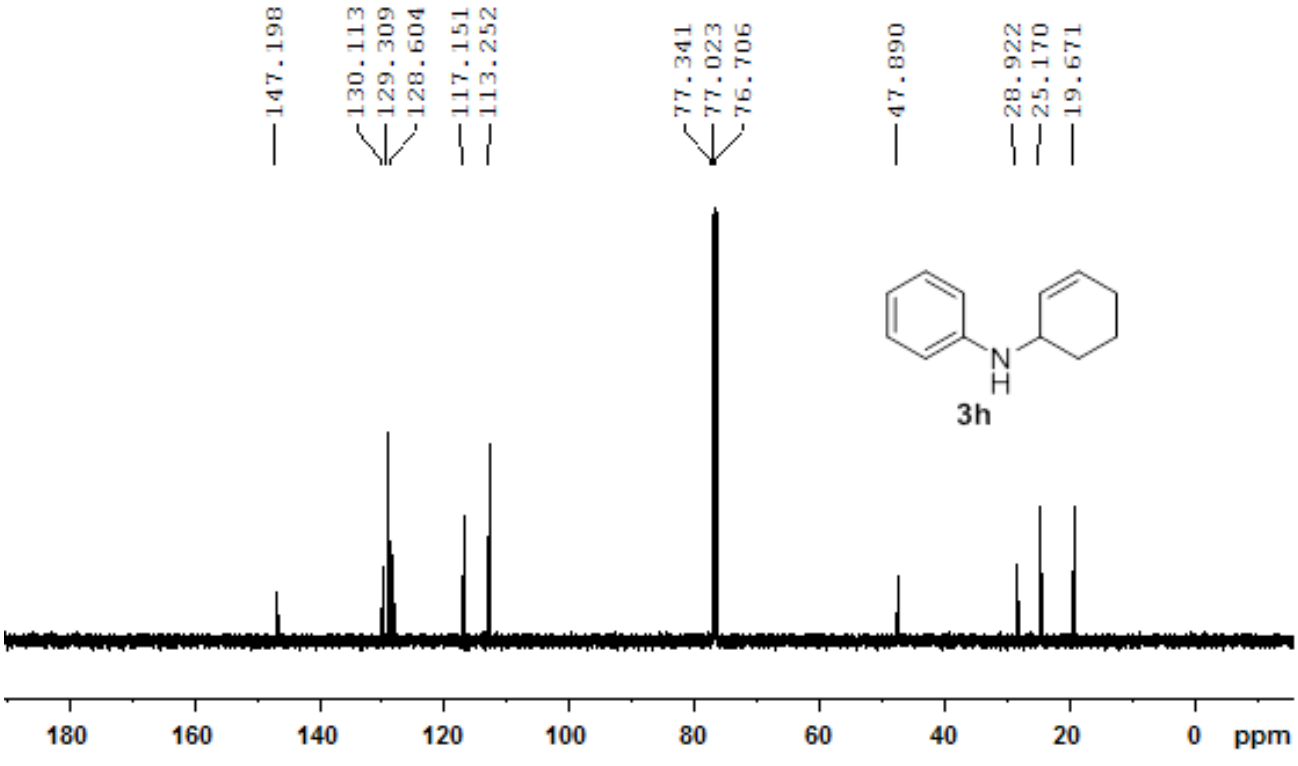
1.09
3.06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140
120
100
80
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40
20
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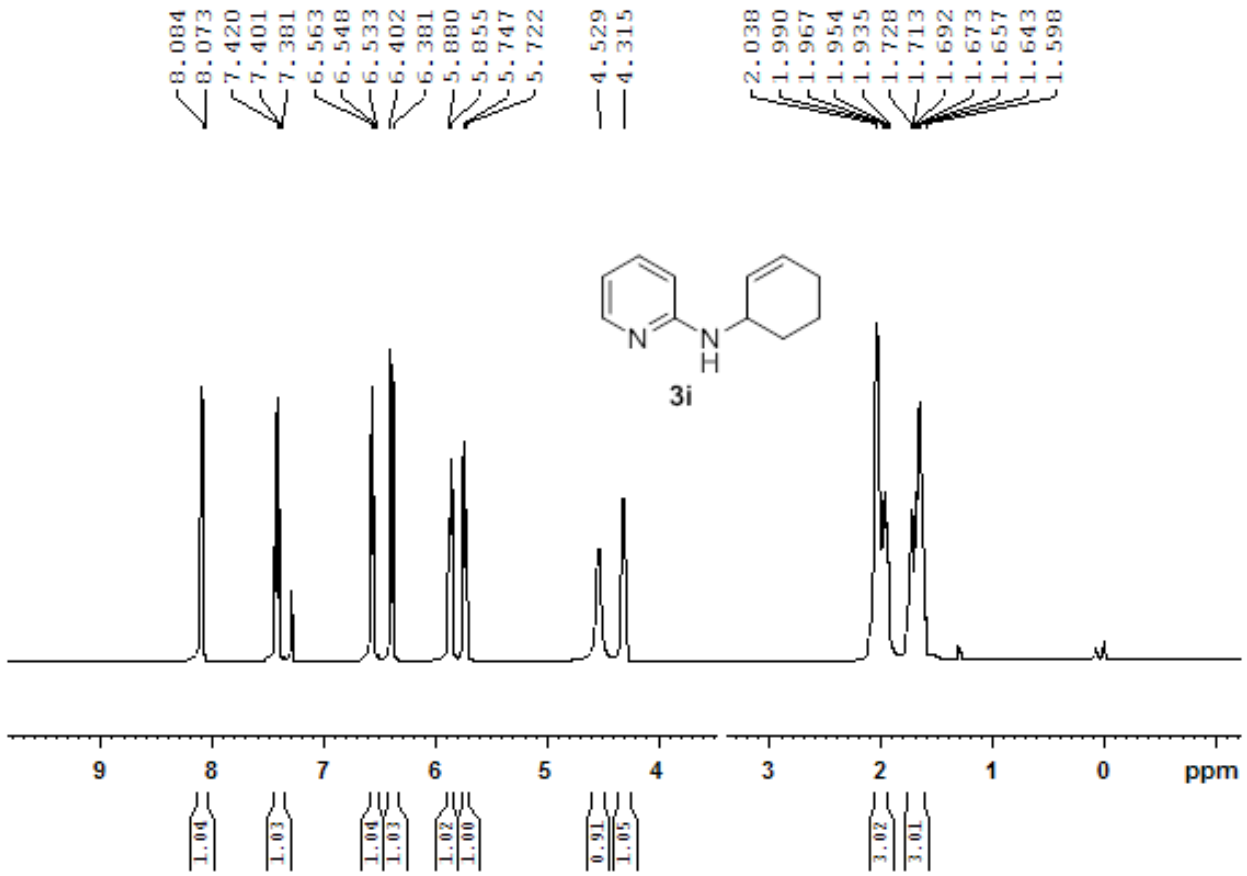
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4.315
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1.954
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1.713
1.692
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1.643
1.598
N
N
H
3i
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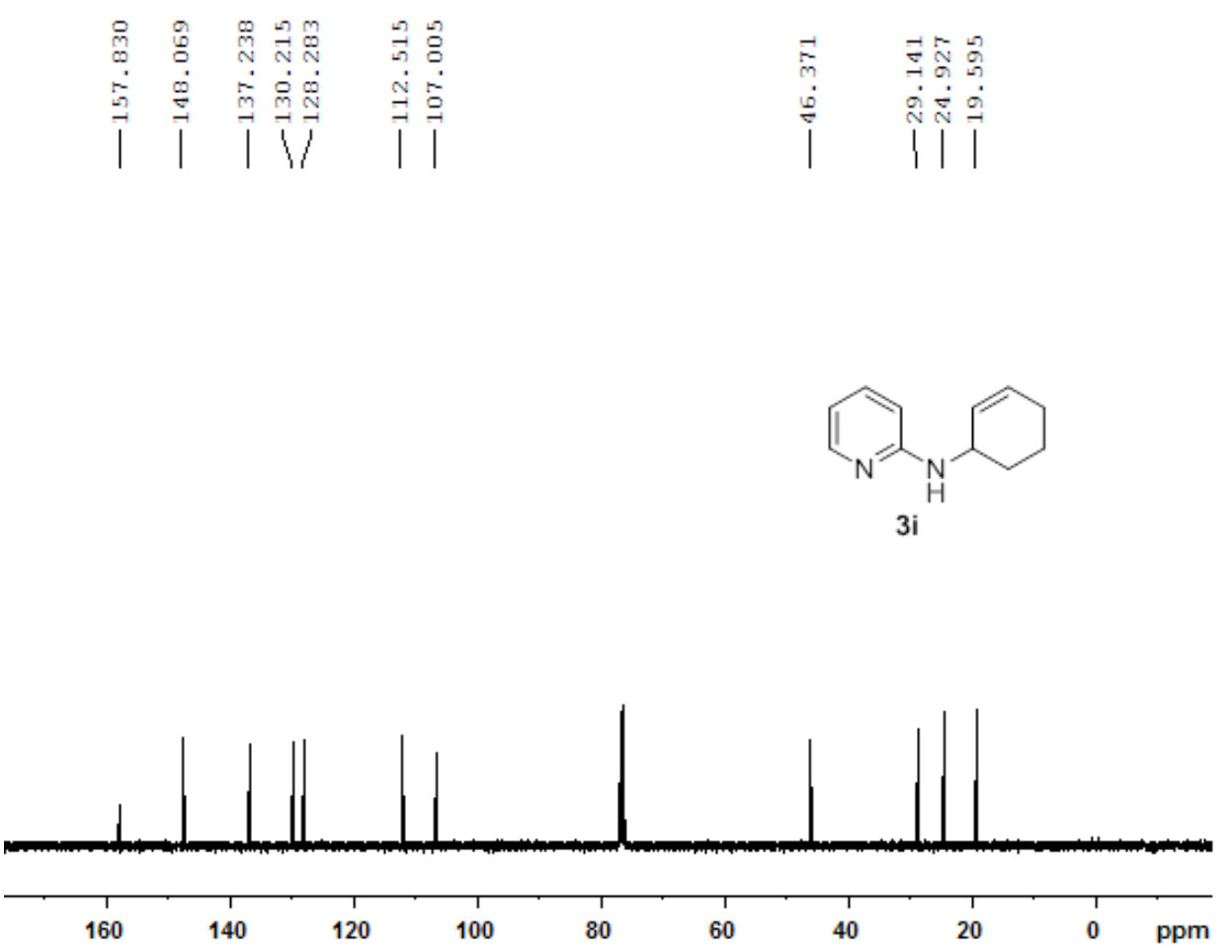
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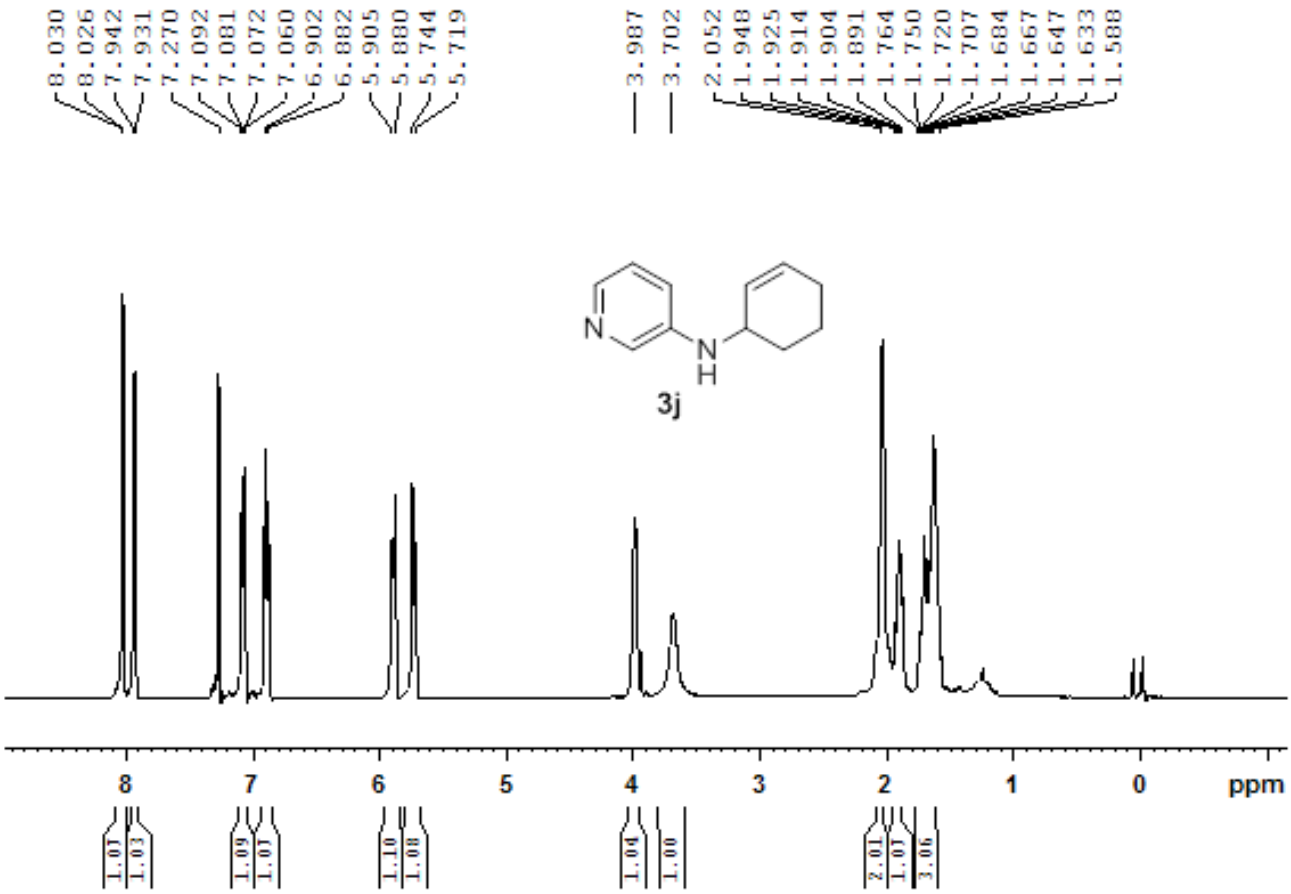
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5.880
5.744
5.719
3.987
3.702
2.052
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1.925
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1.764
1.750
1.720
1.707
1.684
1.667
1.647
1.633
1.588
3j
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7
6
5
4
3
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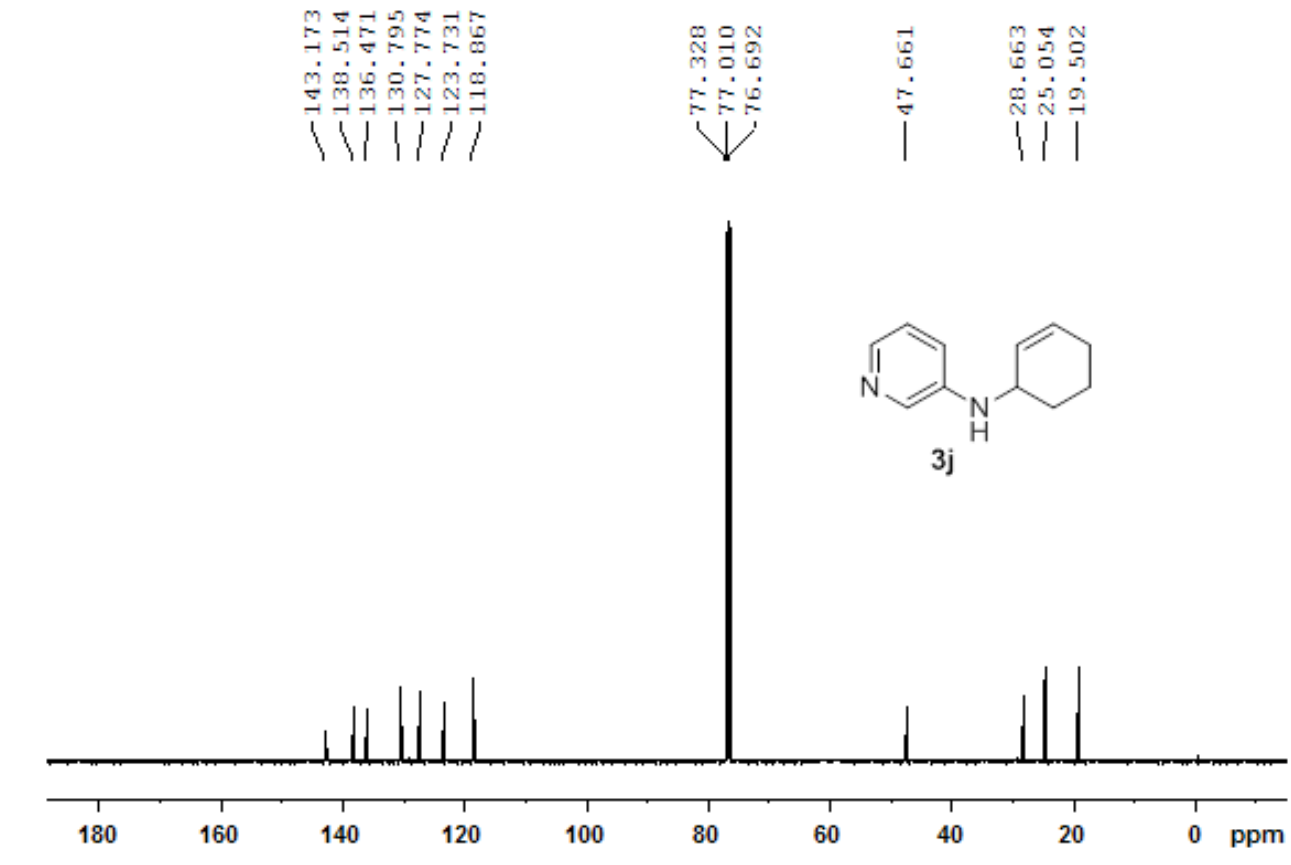
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77.010
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19.502
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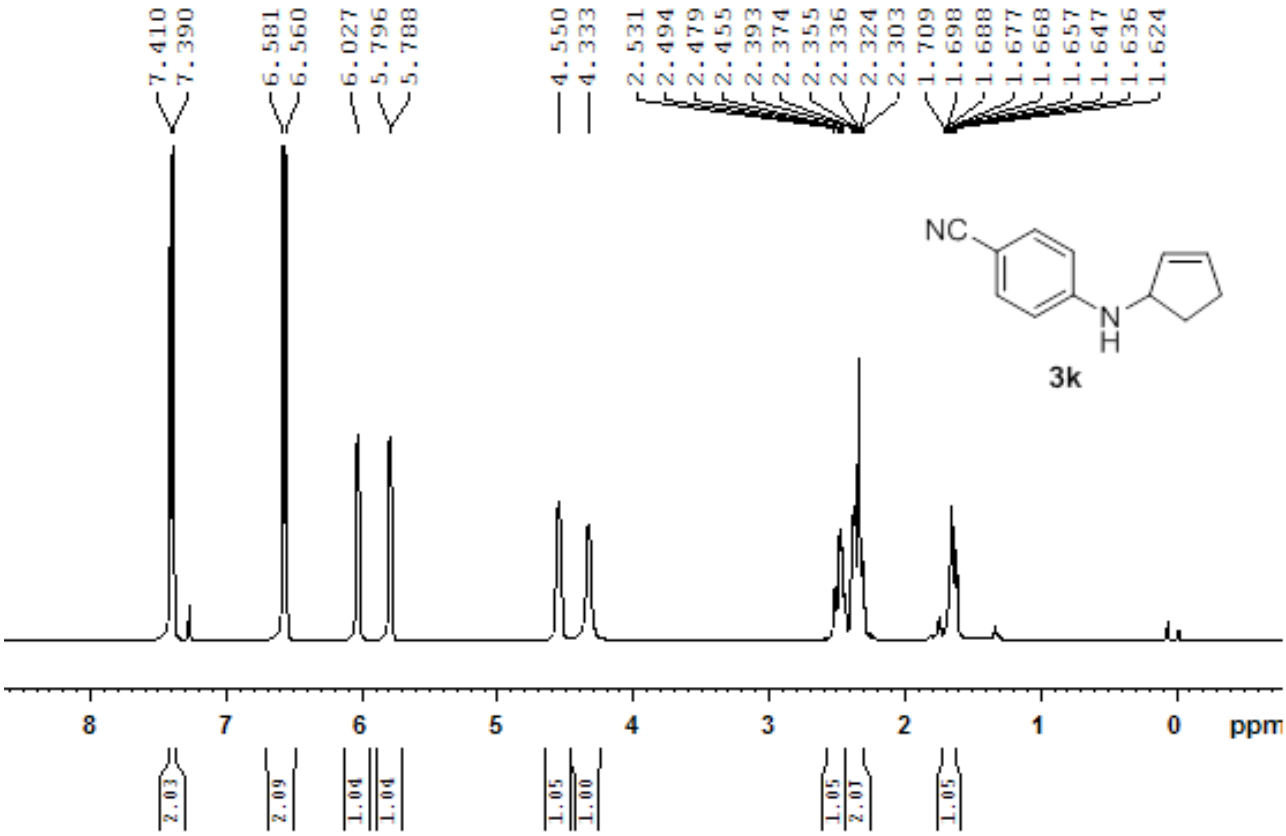
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2.479
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2.393
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2.355
2.336
2.324
2.303
1.709
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1.688
1.677
1.668
1.657
1.647
1.636
1.624
NC
N
H
3k
8
7
6
5
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1.05
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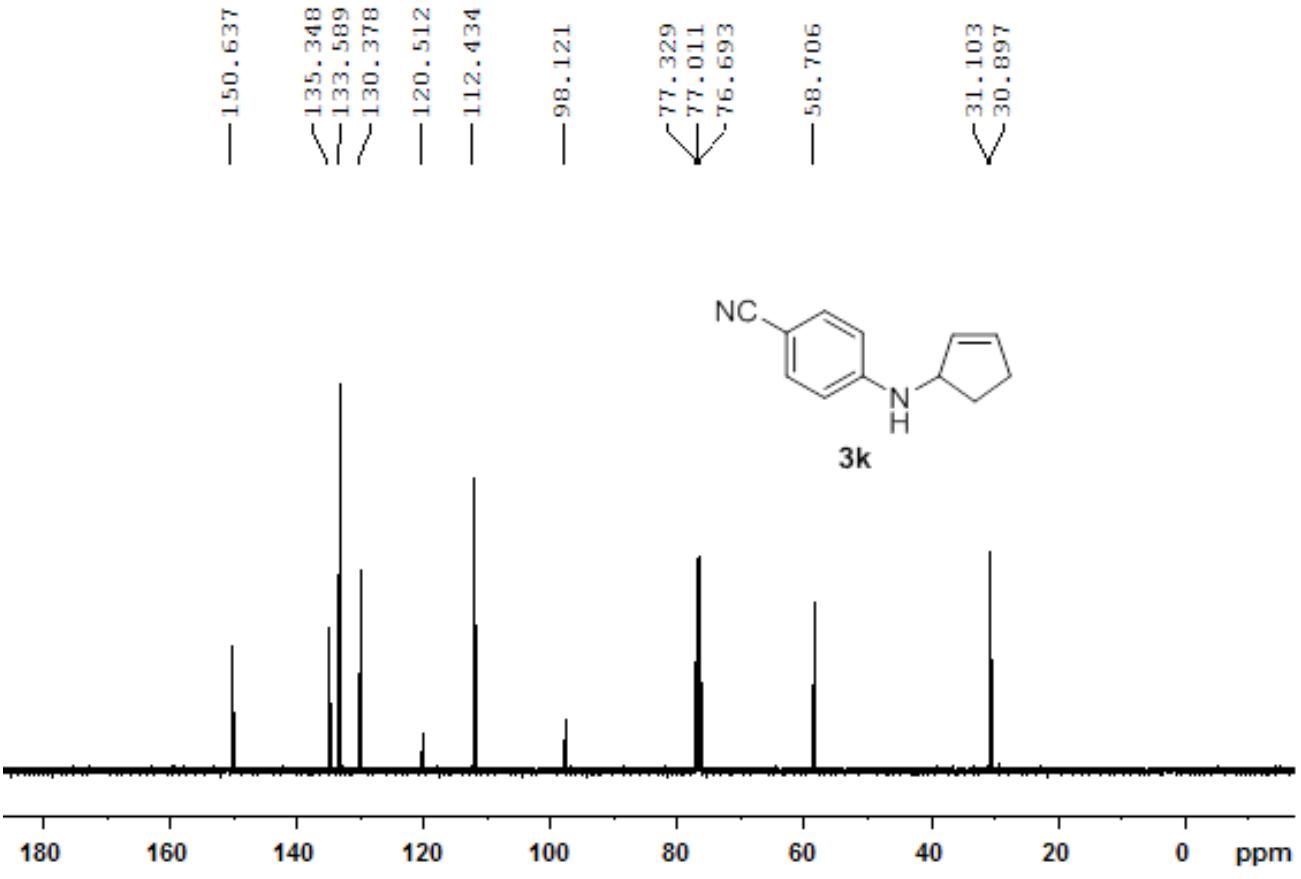
1.05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120
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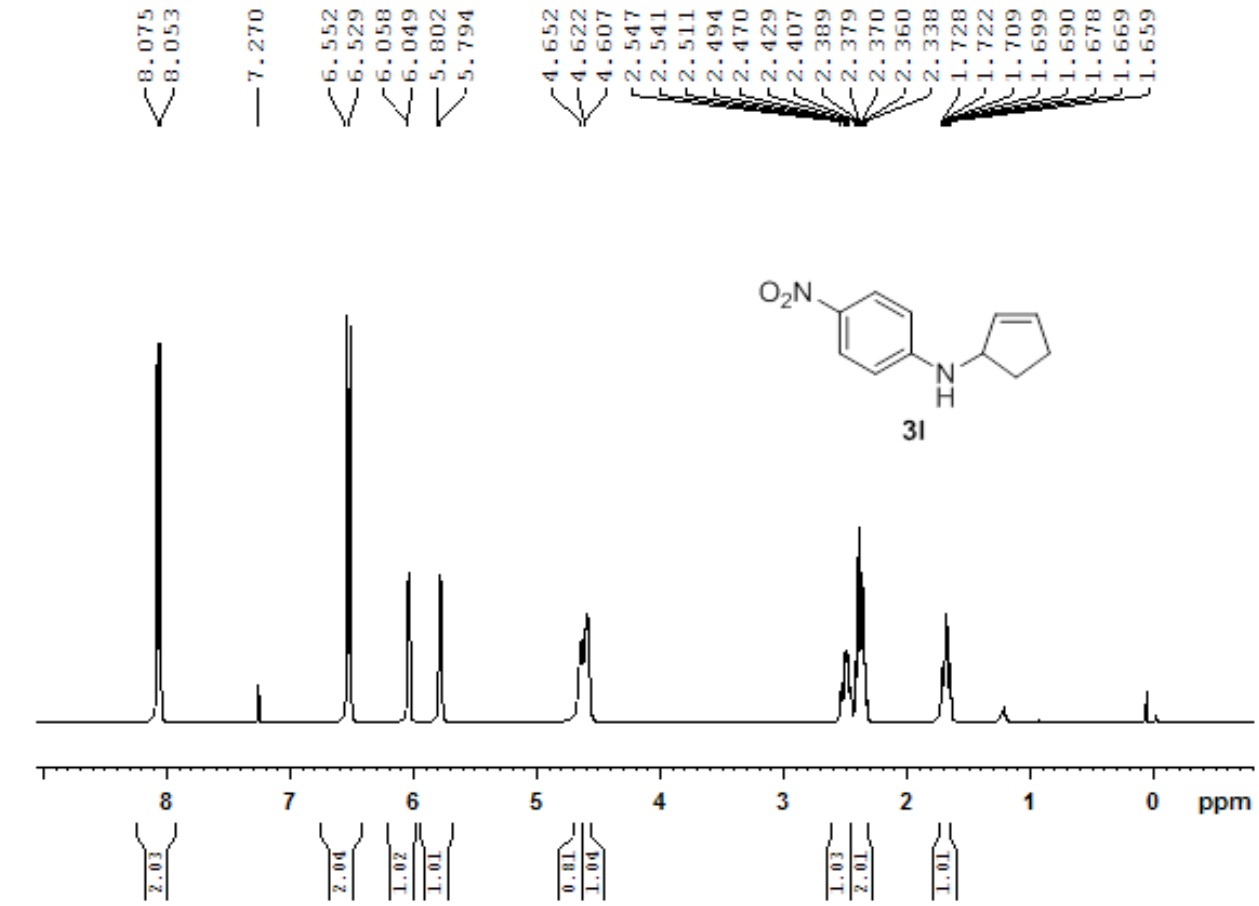
ppm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4.607
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2.541
2.511
2.494
2.470
2.429
2.407
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2.379
2.370
2.360
2.338
1.728
1.722
1.709
1.699
1.690
1.678
1.669
1.659
O2N
N
H
3l
8
7
6
5
4
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ppm
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2.04
1.02
1.01
0.81
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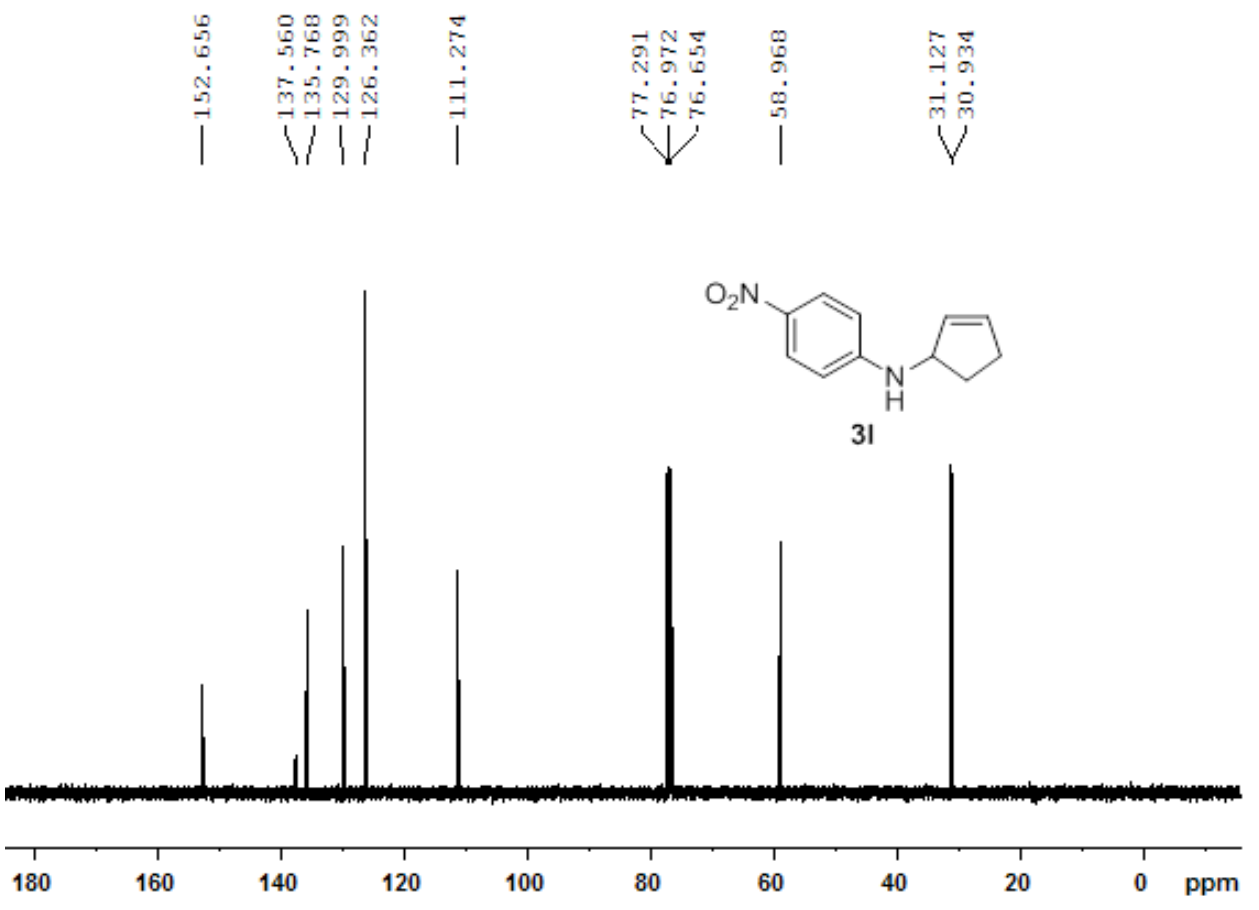
1.03
2.01
1.01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O2N
N
H
3l
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120
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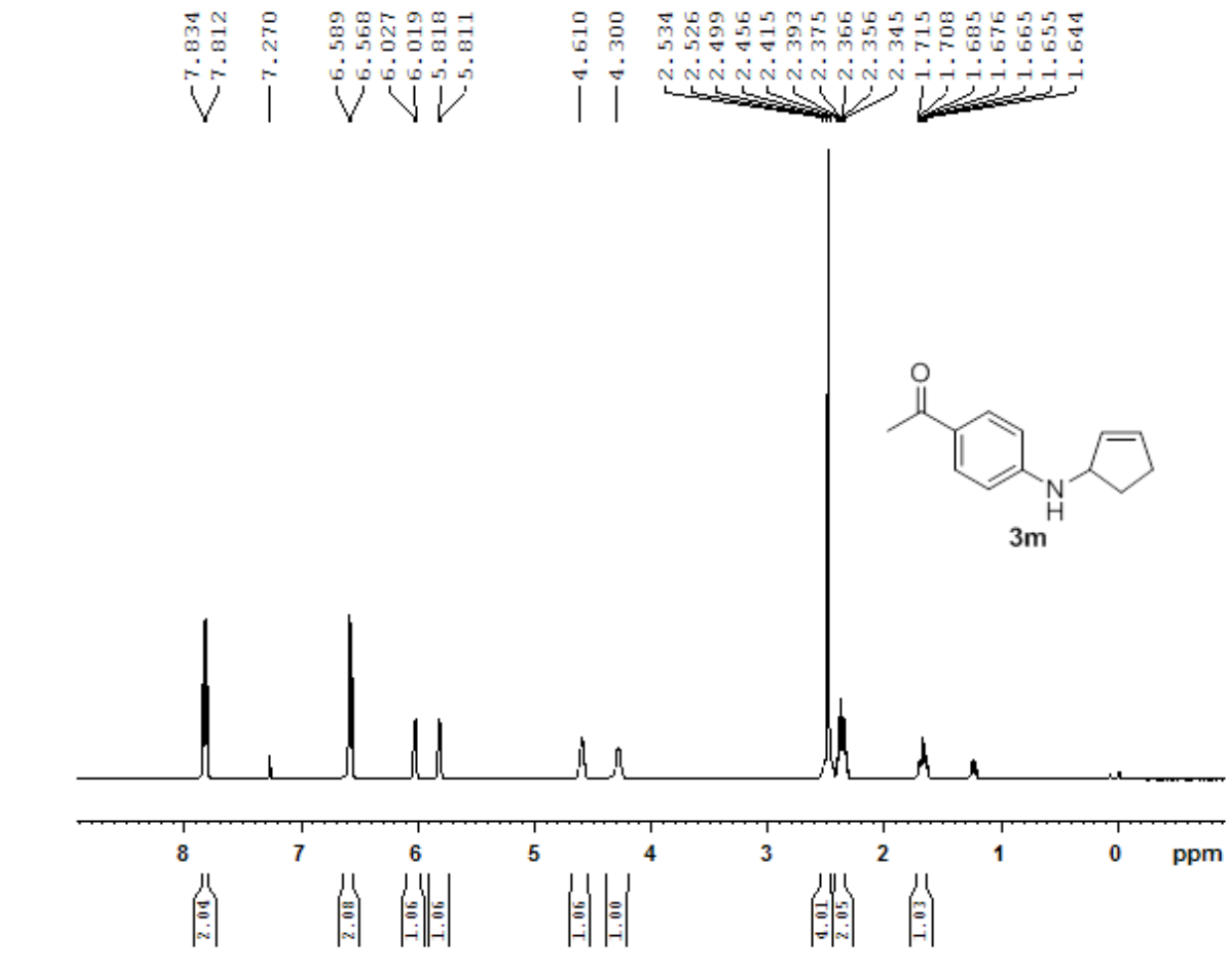
80
60
40
20
0
ppm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5.818
5.811
4.610
4.300
2.534
2.526
2.499
2.456
2.415
2.393
2.375
2.366
2.356
2.345
1.715
1.708
1.685
1.676
1.665
1.655
1.644
O
N
H
3m
8
7
6
5
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ppm
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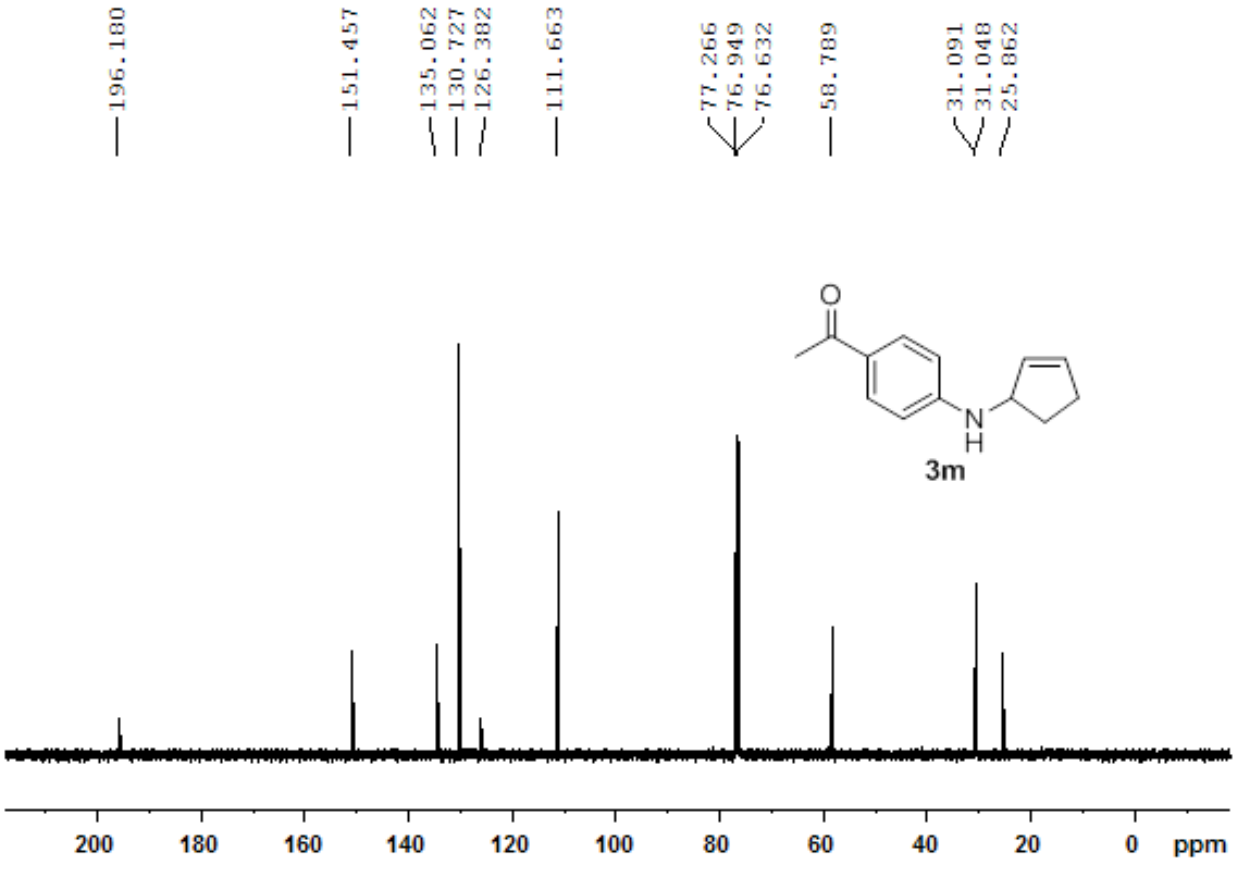
2.08
1.06
1.06
1.06
1.00
4.01
2.05
1.03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76.949
76.632
58.789
31.091
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O
N
H
3m
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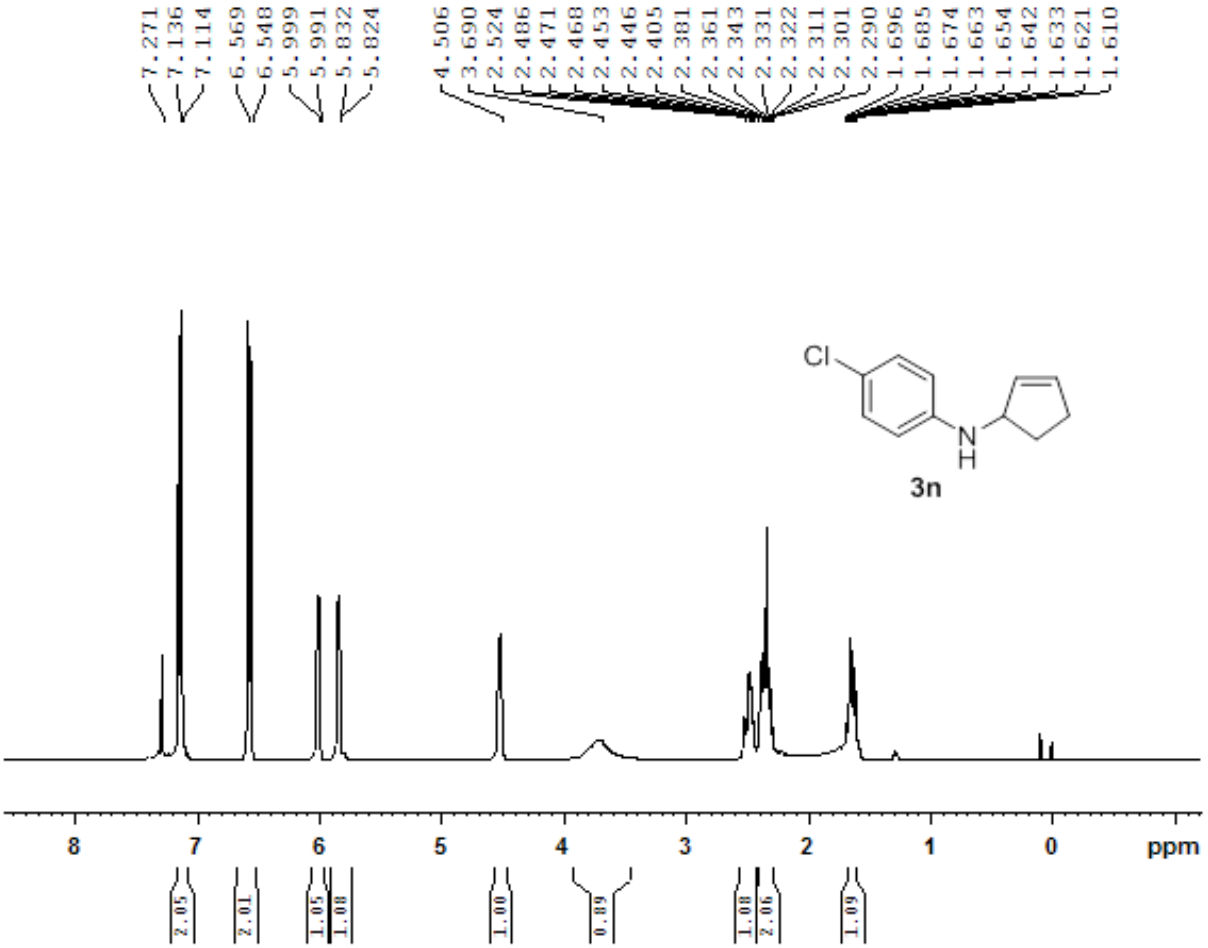
140
120
100
80
60
40
20
0
ppm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2.486
2.471
2.468
2.453
2.446
2.405
2.381
2.361
2.343
2.331
2.322
2.311
2.301
2.290
1.696
1.685
1.674
1.663
1.654
1.642
1.633
1.621
1.610
Cl
N
H
3n
8
7
6
5
4
3
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ppm
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2.01
1.05
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1.00
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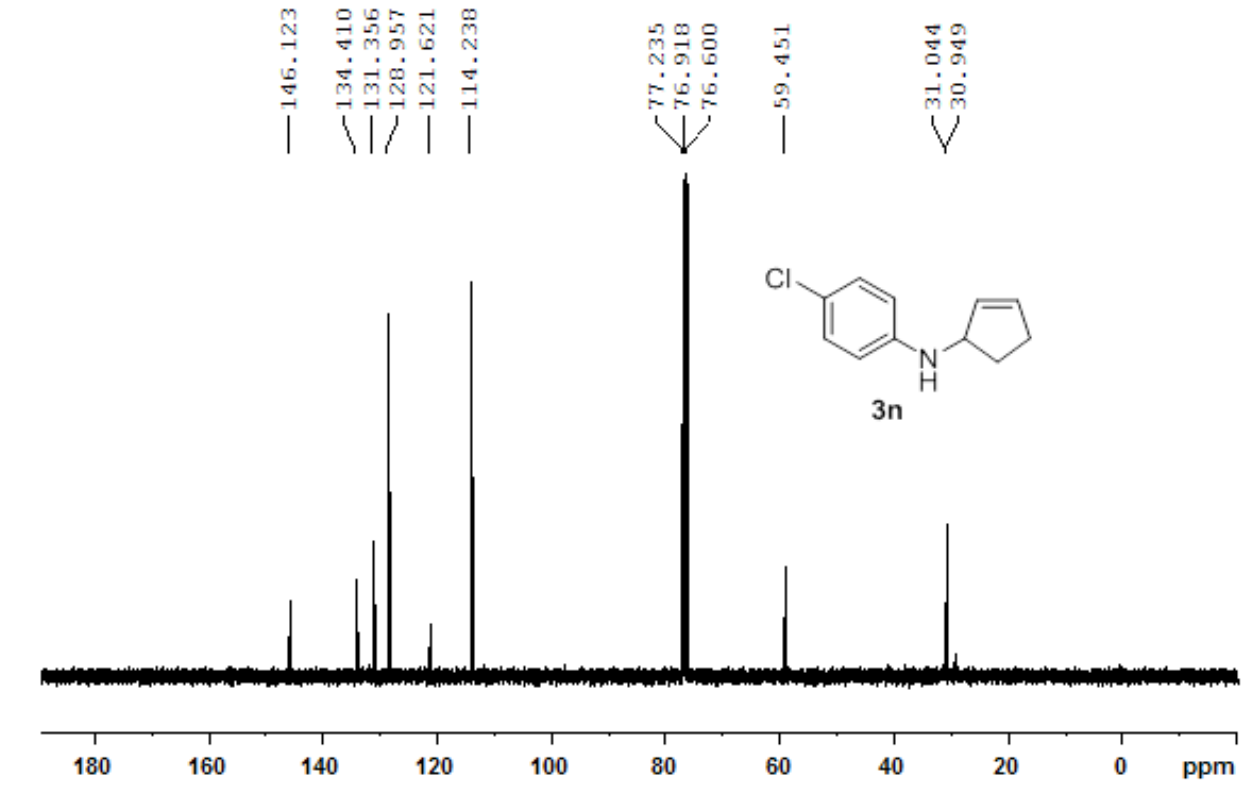
2.06
1.09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120
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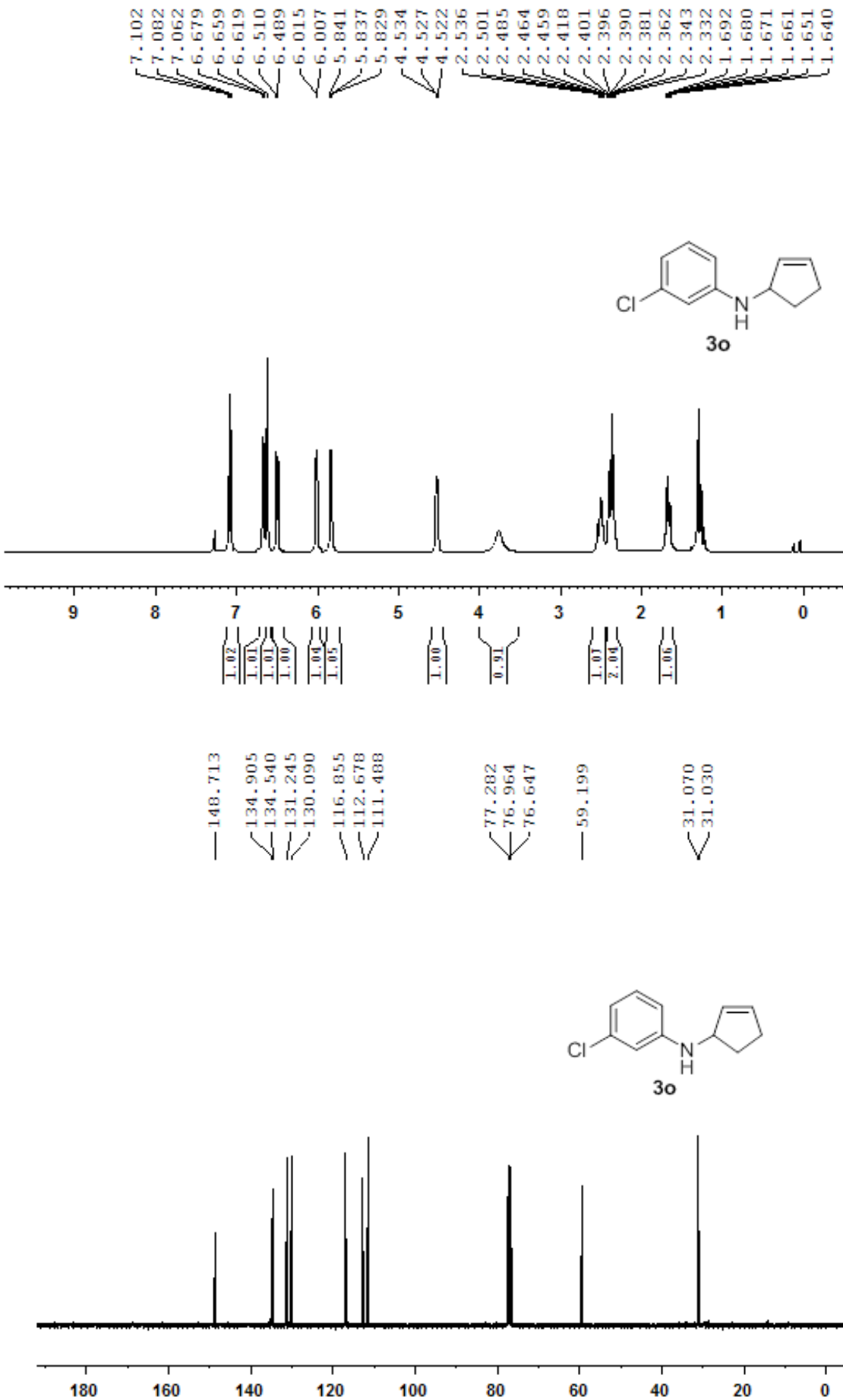
20
0
ppm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5.829
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4.527
4.522
2.536
2.501
2.485
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2.459
2.418
2.401
2.396
2.390
2.381
2.362
2.343
2.332
1.692
1.680
1.671
1.661
1.651
1.640
Cl
N
H
3o
9
8
7
6
5
4
3
2
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0
ppm
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1.01
1.01
1.00
1.04
1.05
1.00
0.91
1.07
2.04
1.06
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134.540
131.245
130.090
116.855
112.678
111.488
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76.964
76.647
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120
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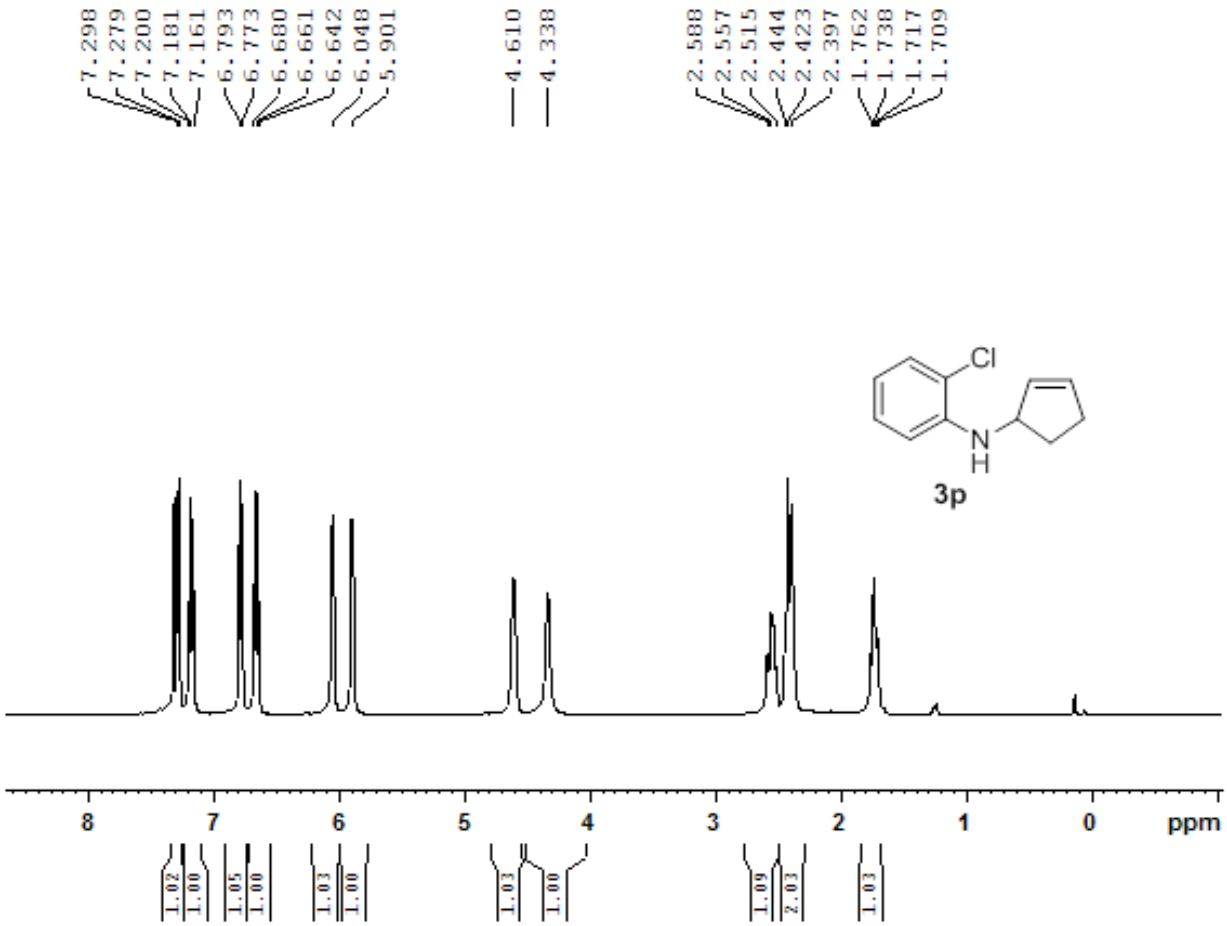
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6.680
6.661
6.642
6.048
5.901
4.610
4.338
2.588
2.557
2.515
2.444
2.423
2.397
1.762
1.738
1.717
1.709
Cl
N
H
3p
8
7
6
5
4
3
2
1
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ppm
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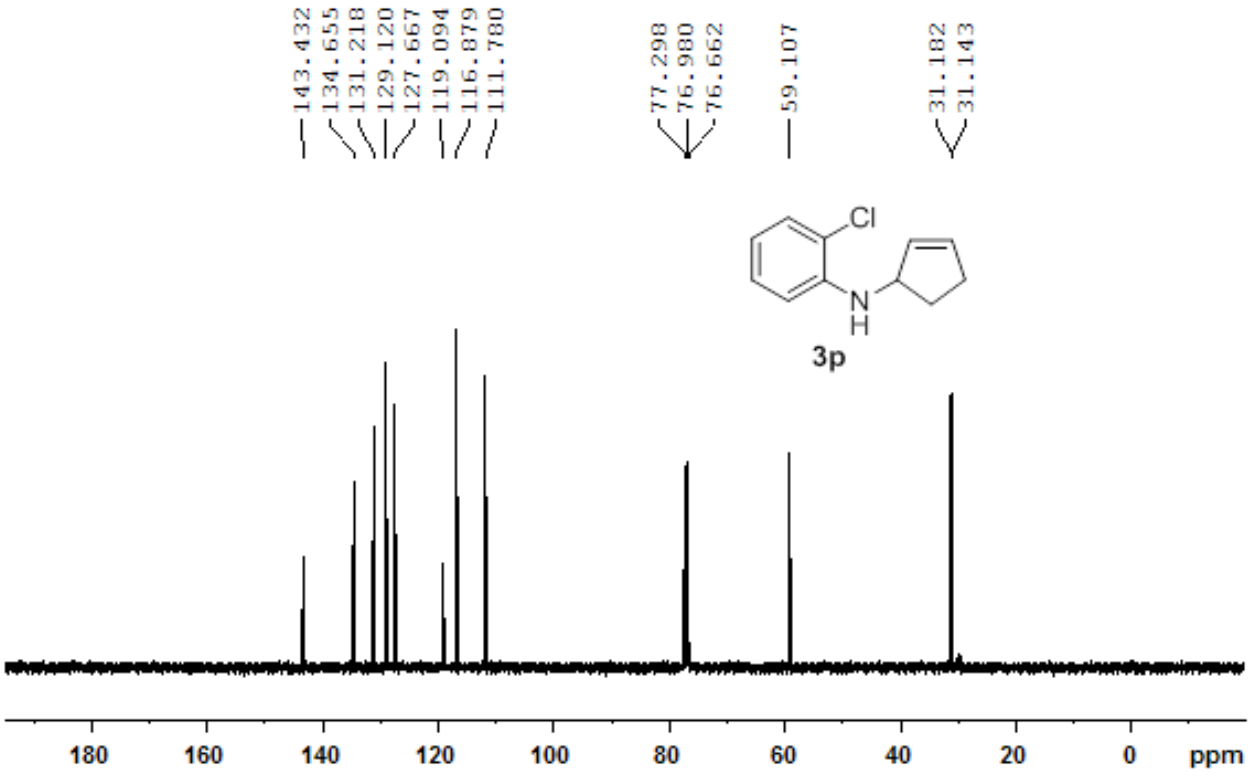
1.00
1.05
1.00
1.03
1.00
1.03
1.00
1.09
2.03
1.03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120
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60
40
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0
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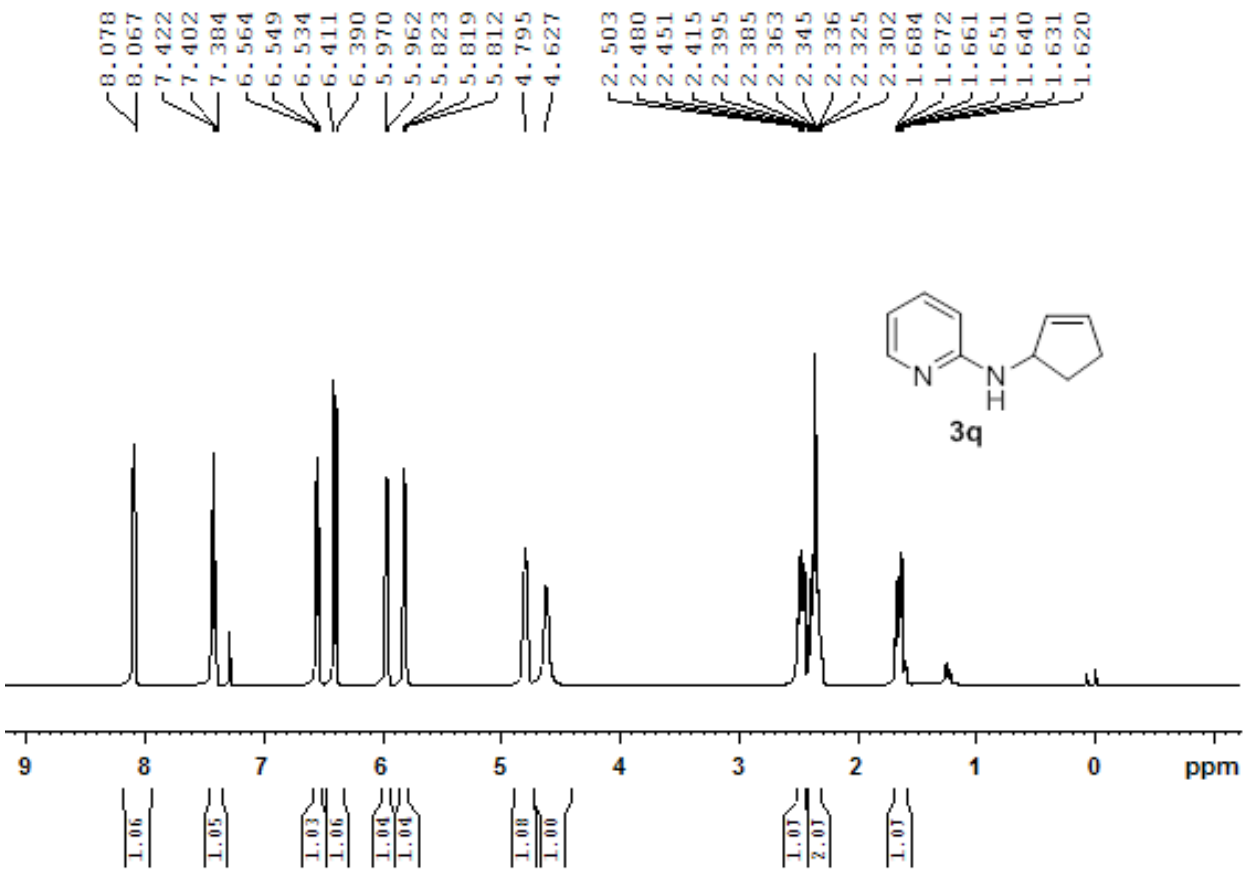
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5.819
5.812
4.795
4.627
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2.395
2.385
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2.345
2.336
2.325
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1.661
1.651
1.640
1.631
1.620
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N
H
3q
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4
3
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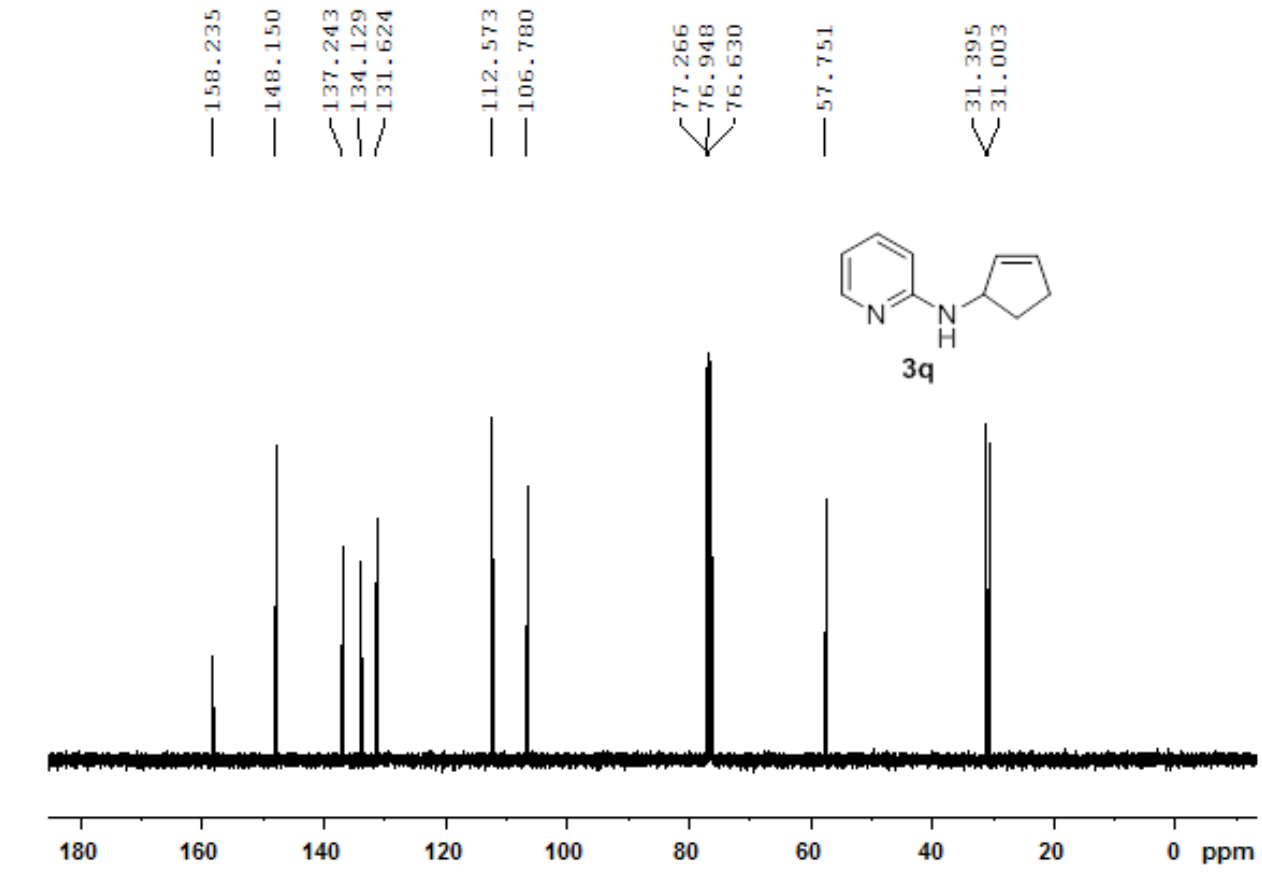
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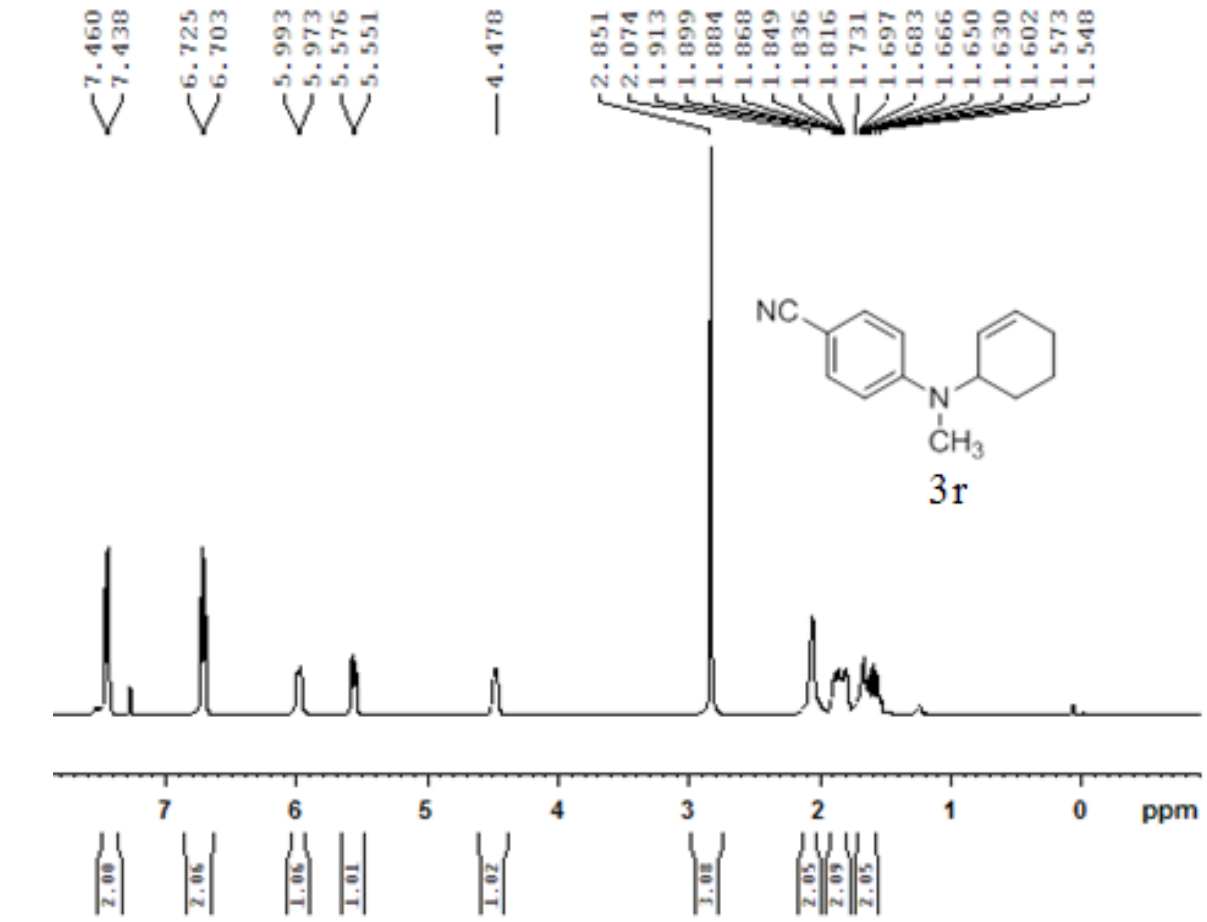
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1.884
1.868
1.849
1.836
1.816
1.731
1.697
1.683
1.666
1.650
1.630
1.602
1.573
1.548
NC
N
CH3
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1.02
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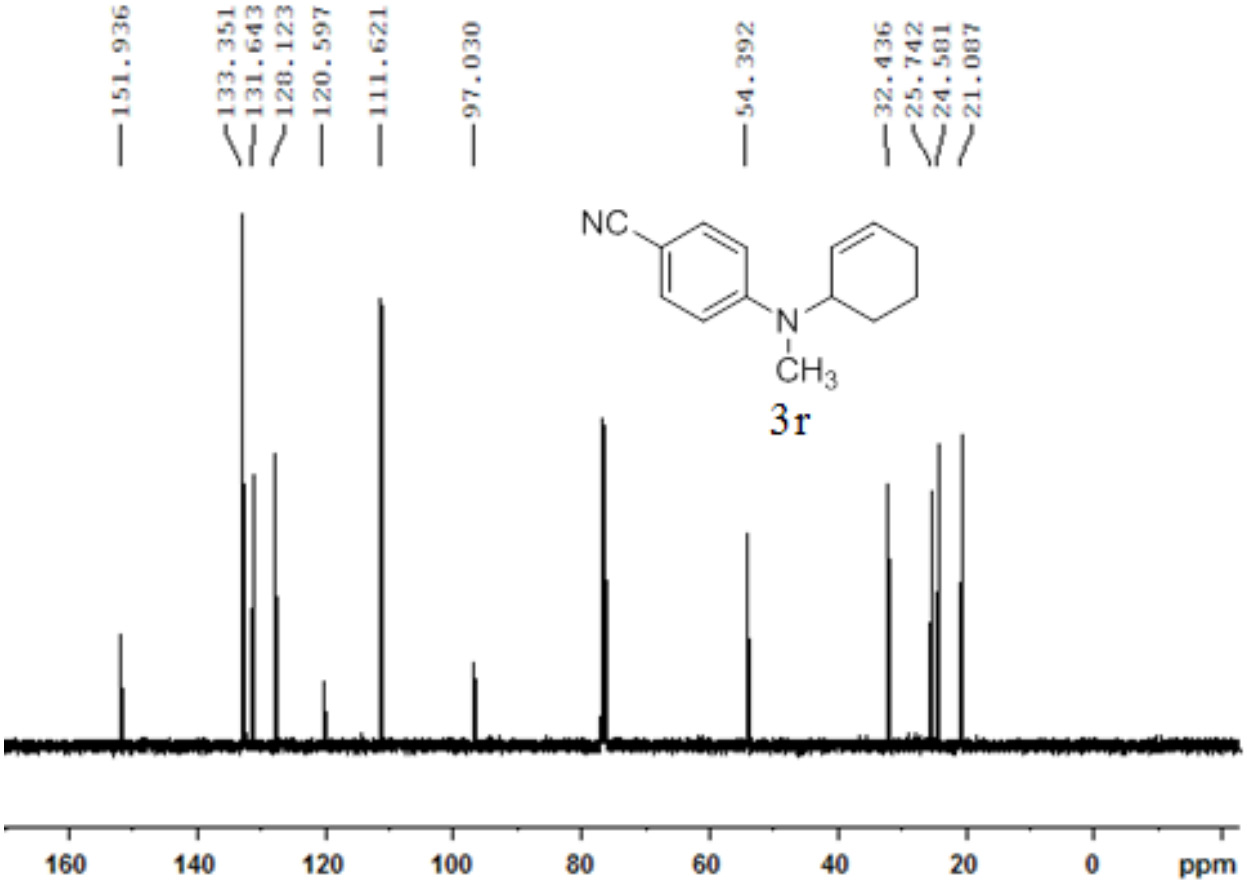
2.09
2.05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CH3
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120
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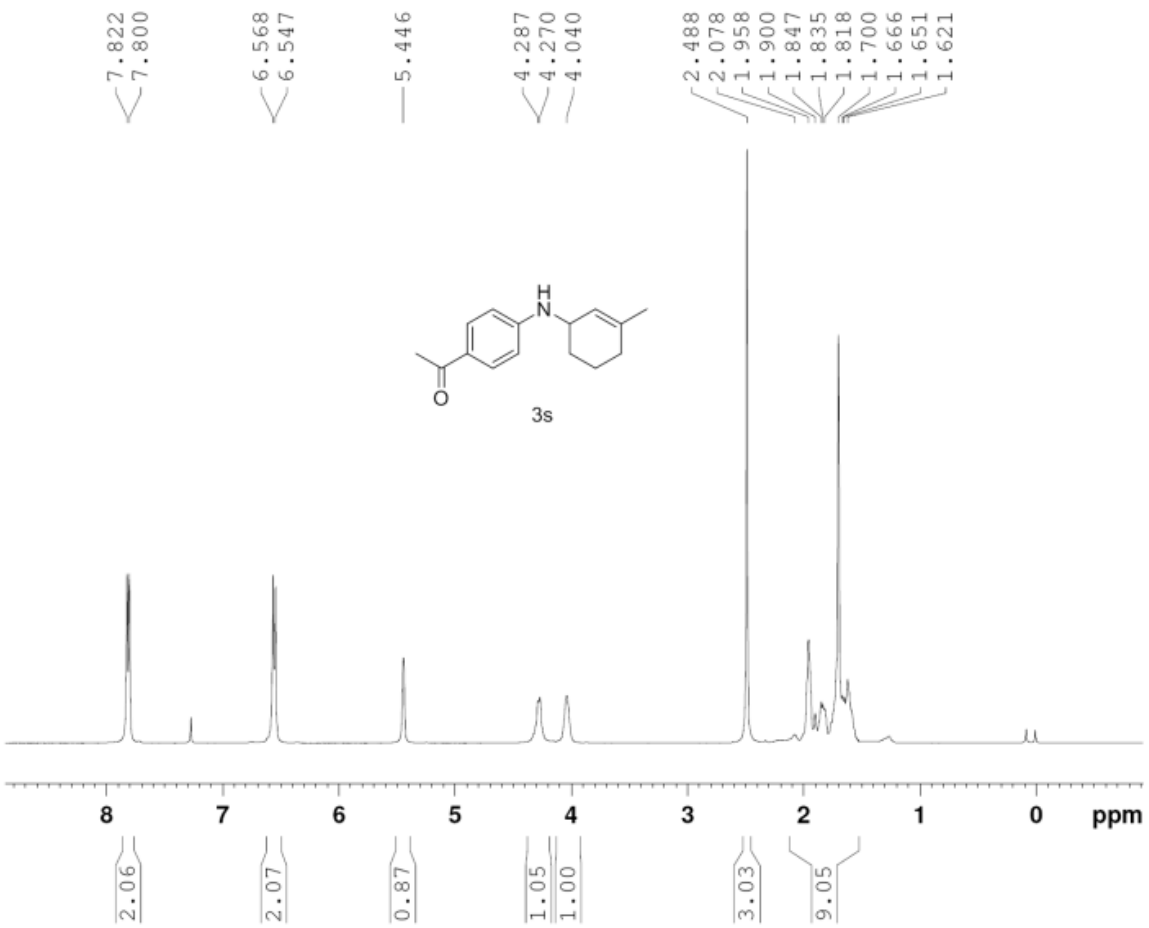
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1.835
1.818
1.700
1.666
1.651
1.621
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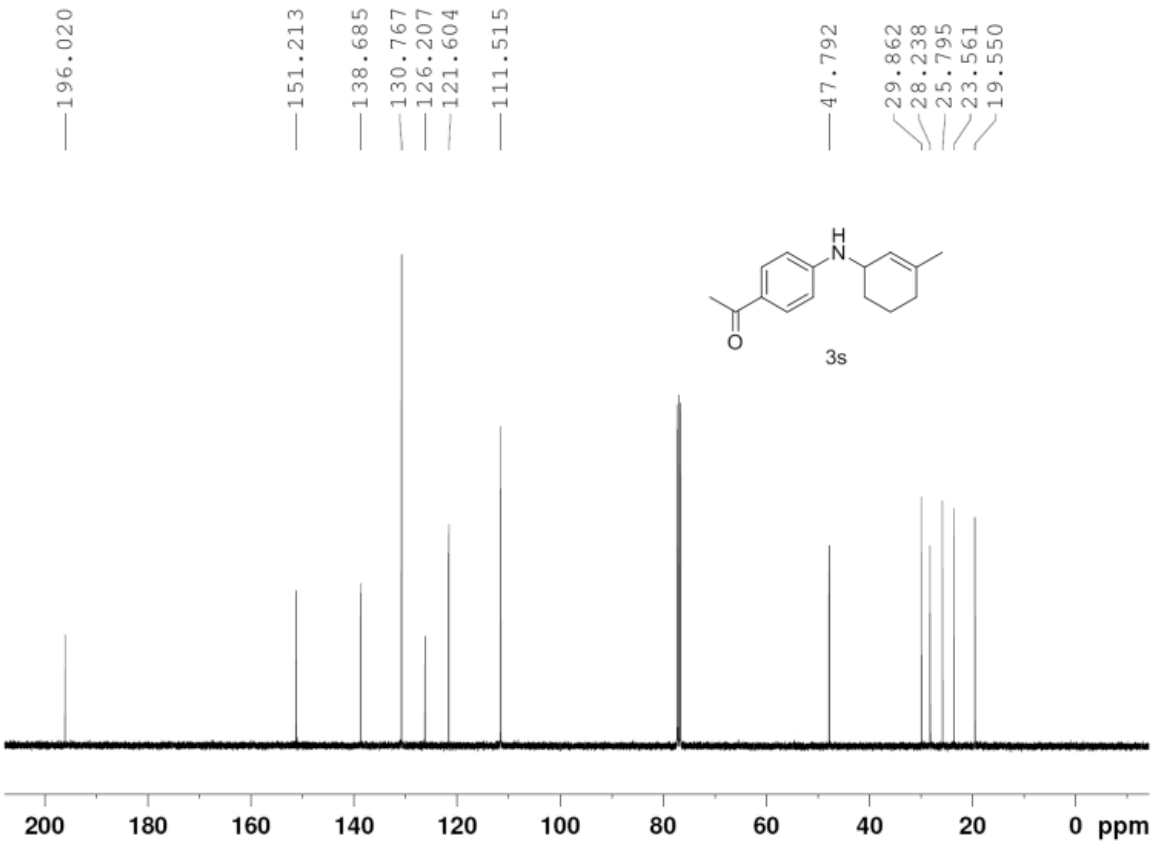
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120
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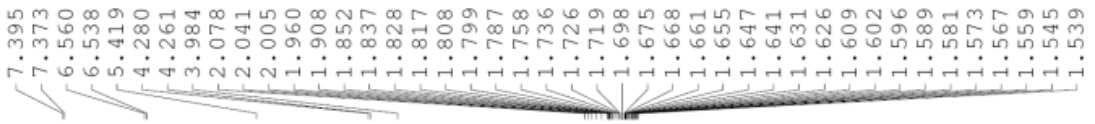
ppm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1.817
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1.719
1.698
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1.661
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1.647
1.641
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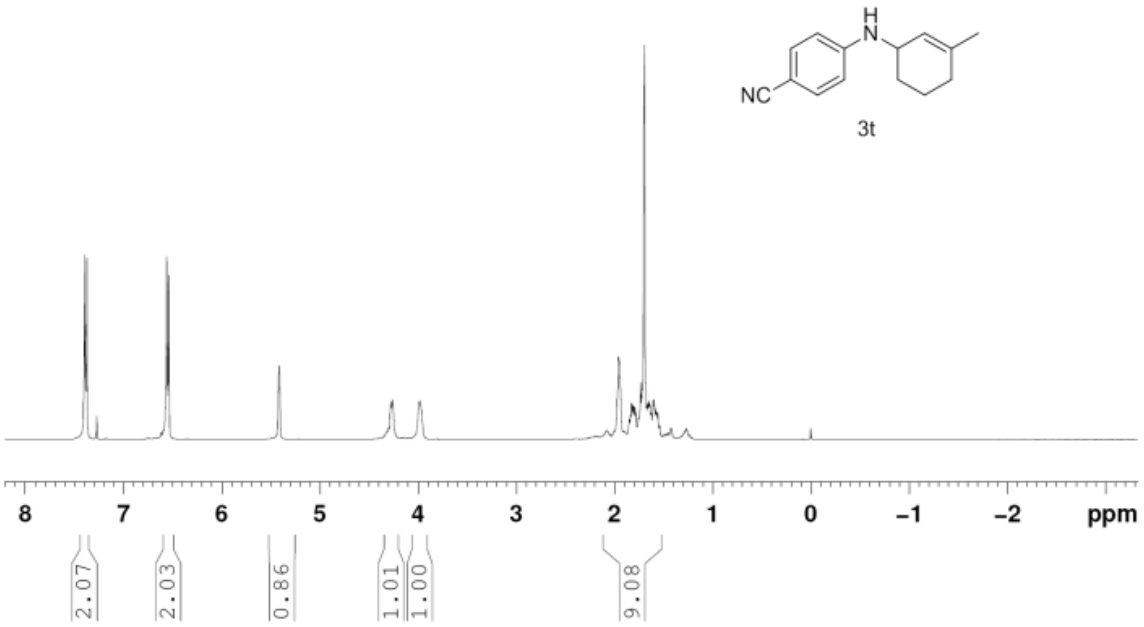
1.545
1.539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1.01
1.00
9.08


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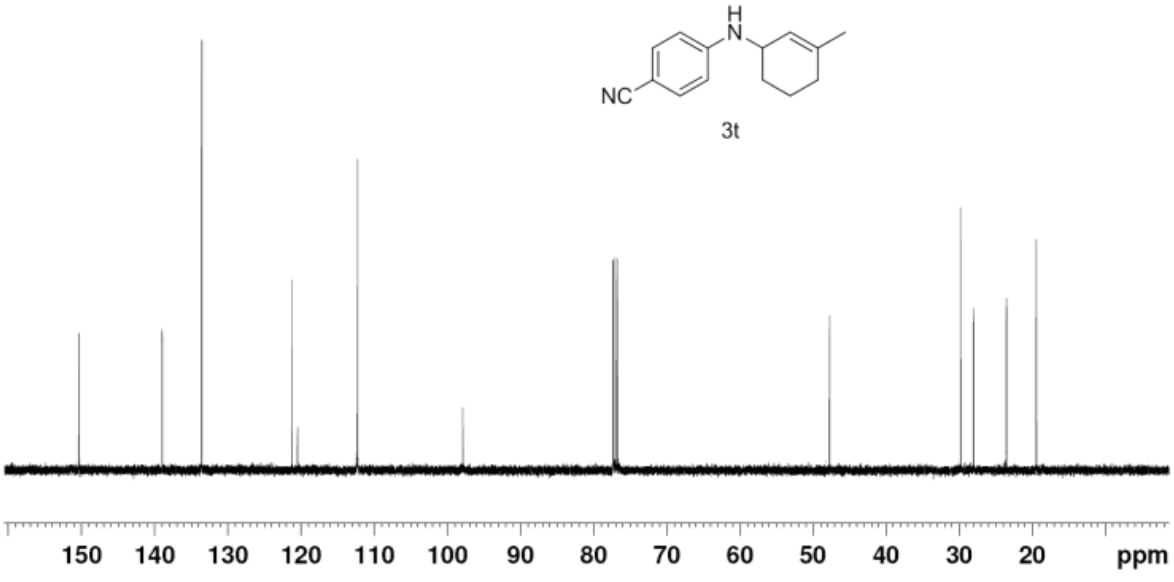
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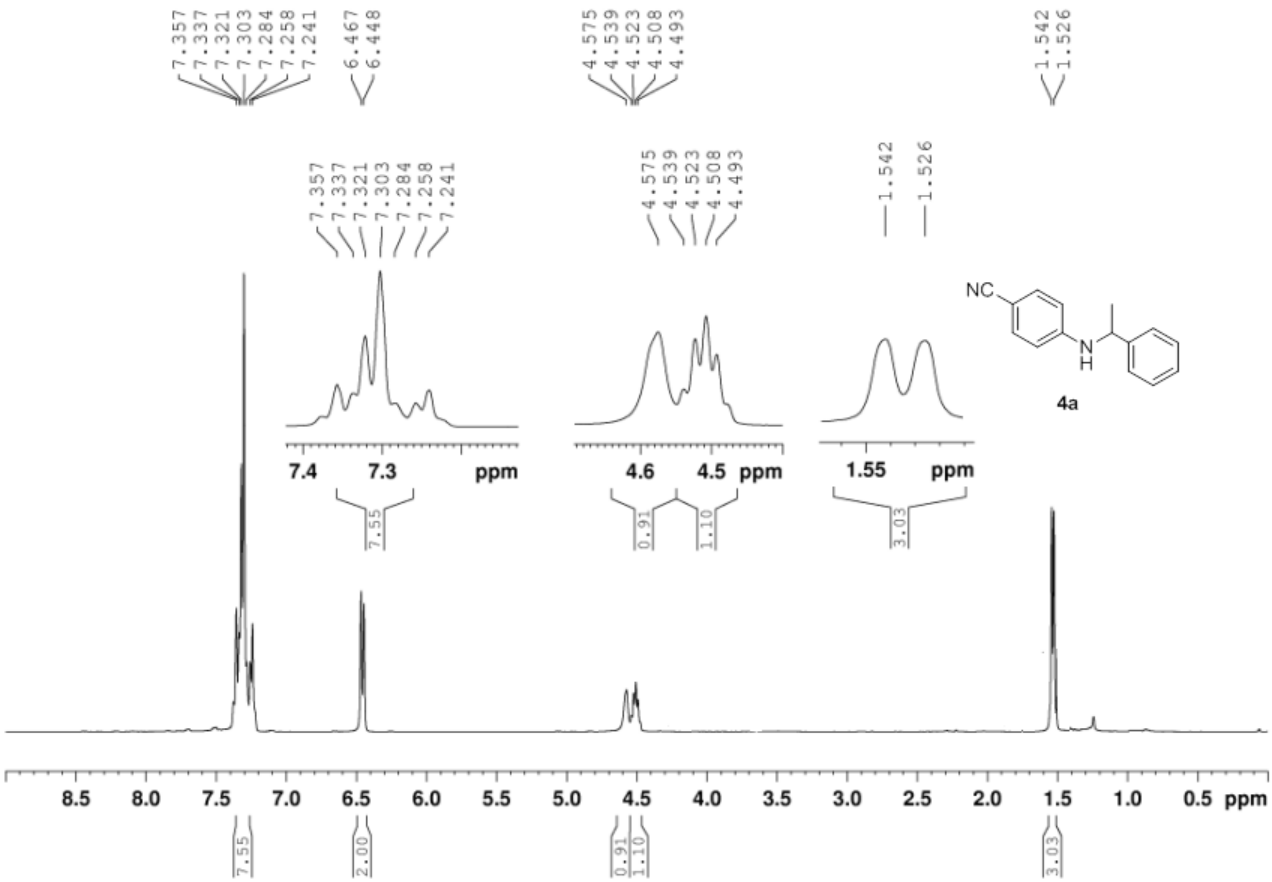
20
ppm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1.542
1.526
NC
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H
4a
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7.3
ppm
4.6
4.5
ppm
1.55
ppm
7.55
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1.10
3.03
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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1.0
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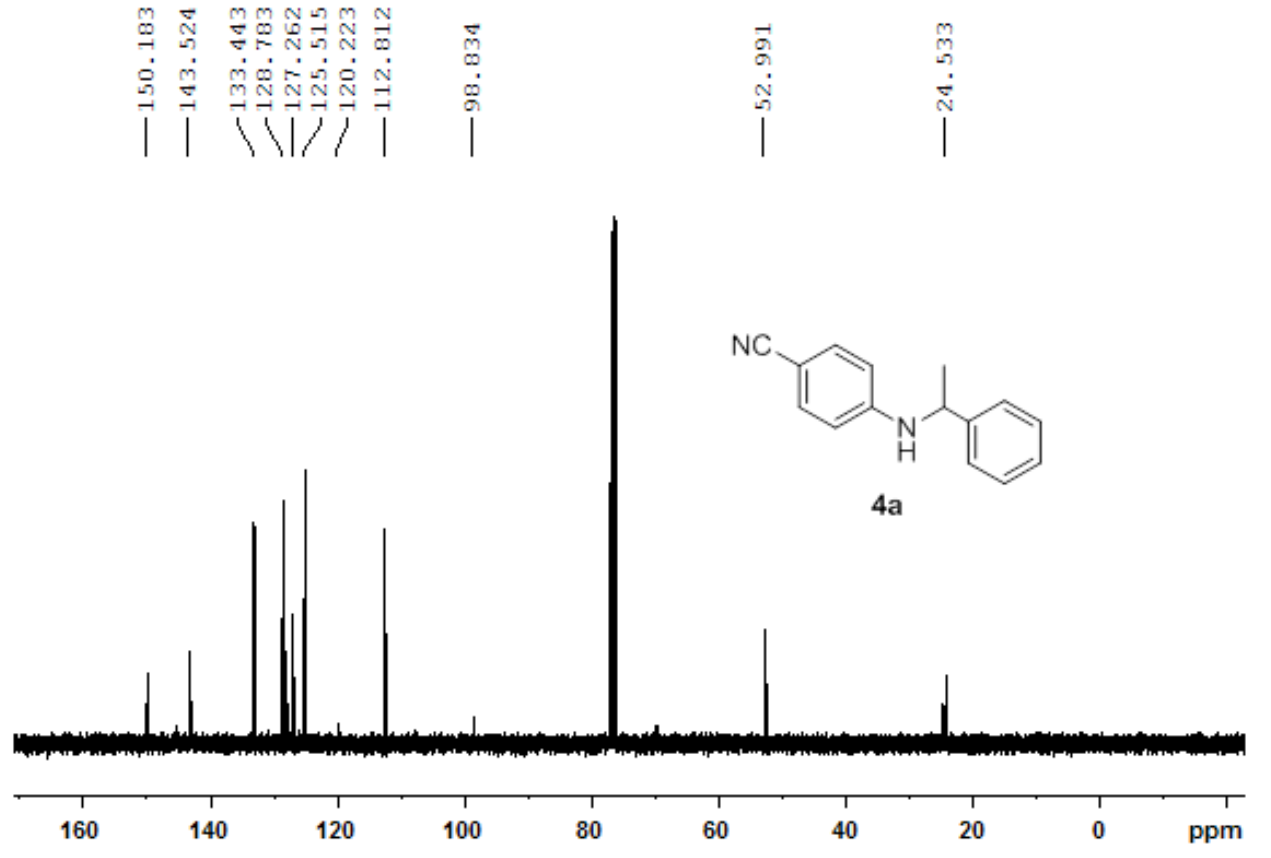
3.03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125.515
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NC
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120
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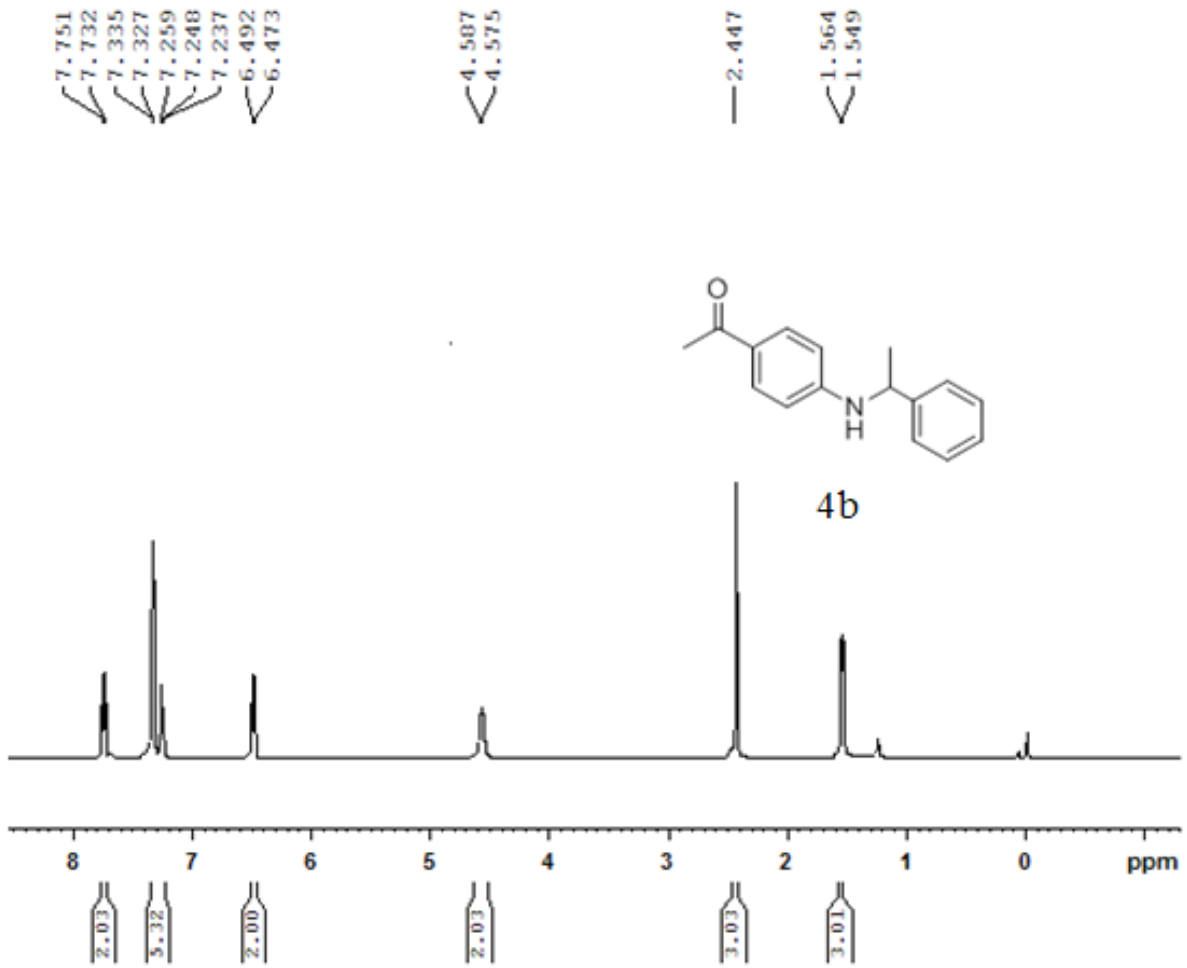
0
ppm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7.248
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6.492
6.473
4.587
4.575
2.447
1.564
1.549
4b
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7
6
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4
3
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0
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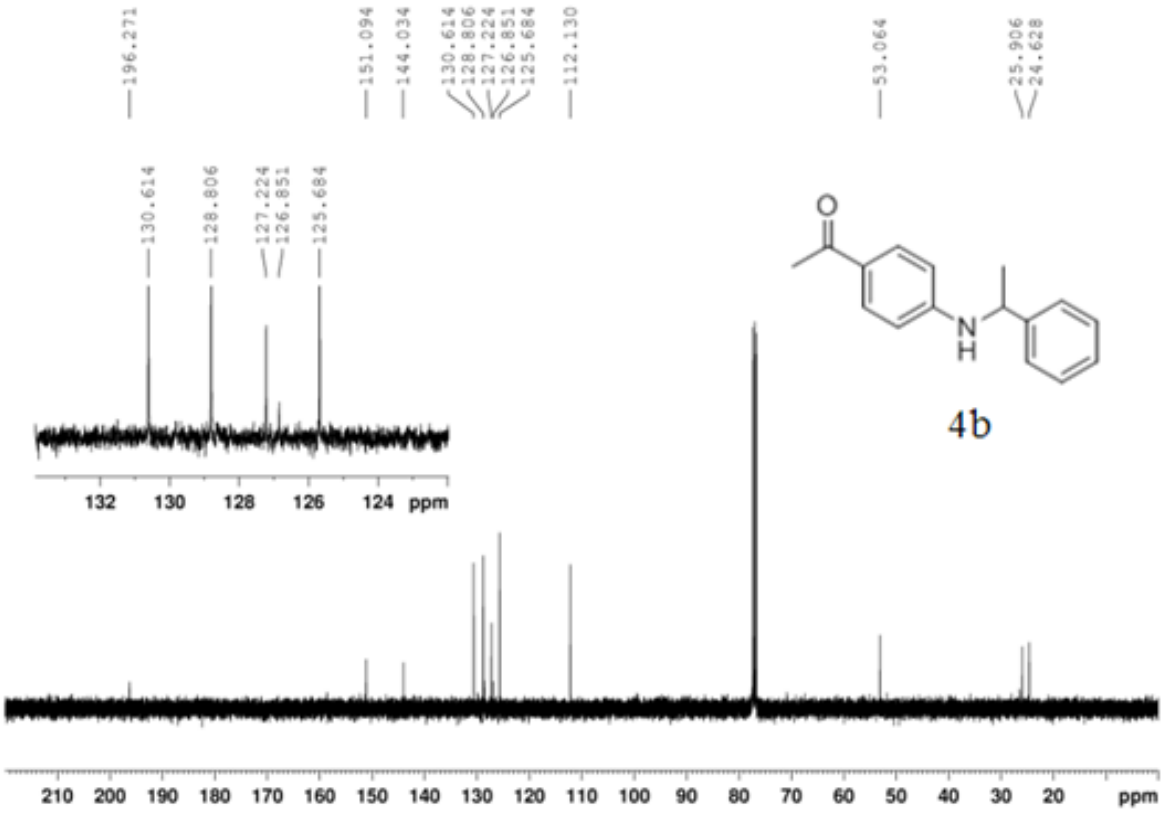
2.03
5.32
2.00
2.03
3.03
3.01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151.094
144.034
130.614
128.806
127.224
126.851
125.684
112.130
53.064
25.906
24.628
4b
132
130
128
126
124
ppm
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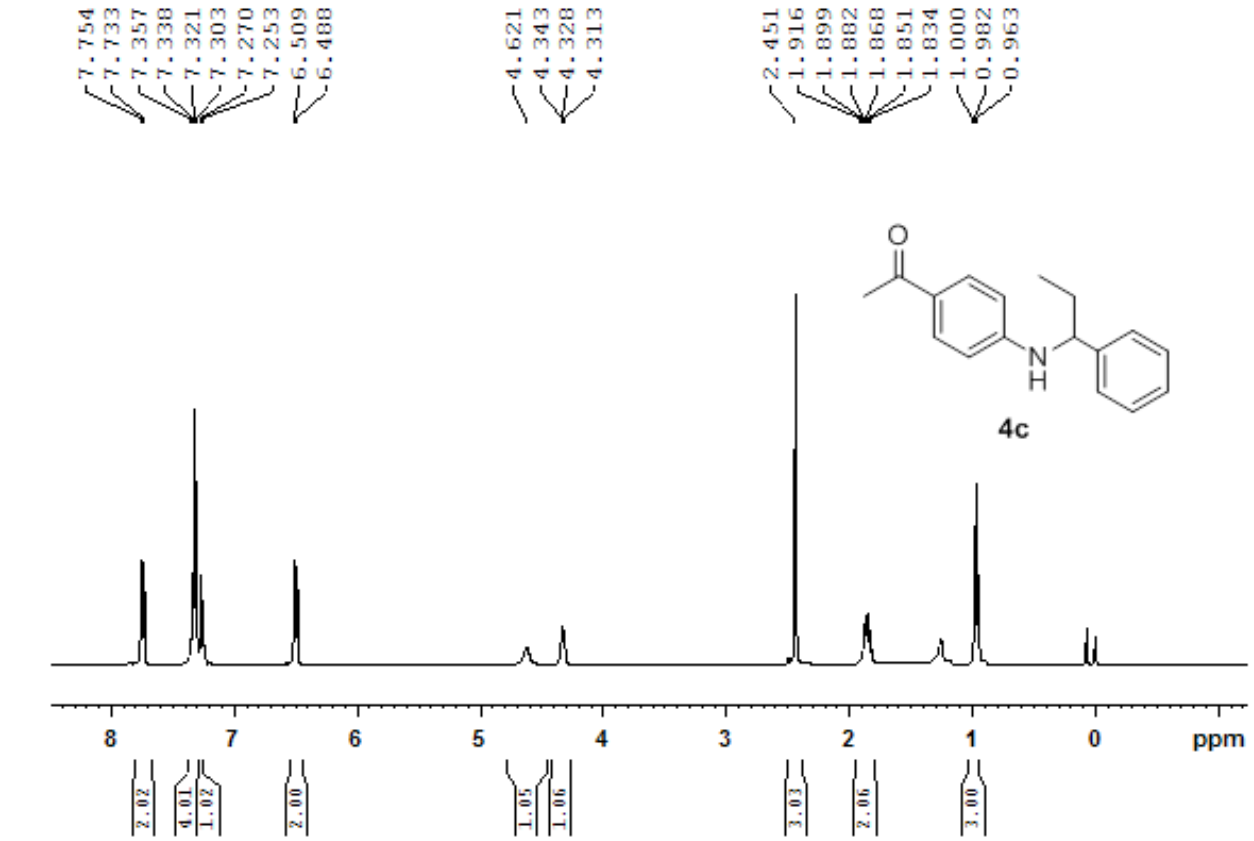
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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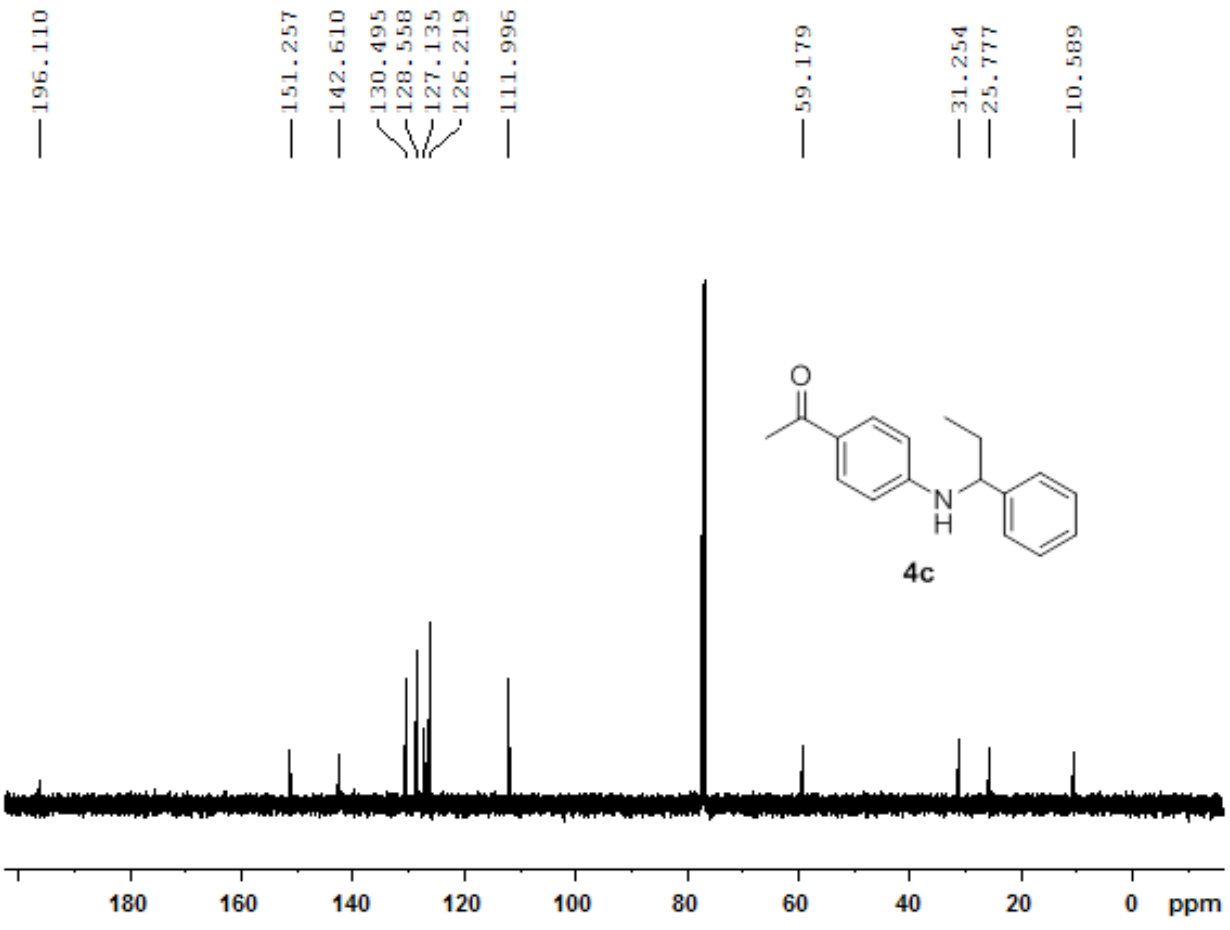
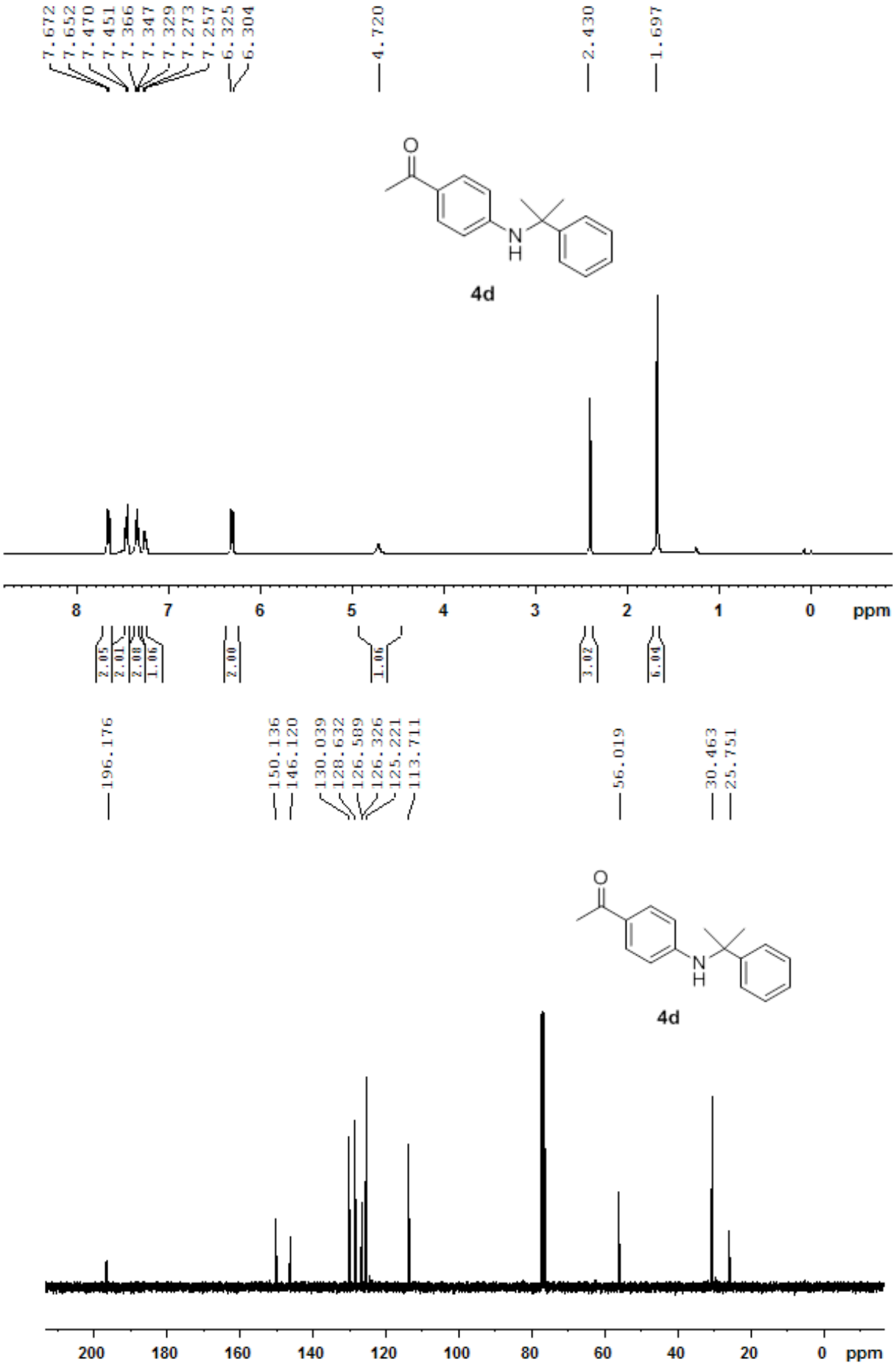
7.733
7.357
7.338
7.321
7.303
7.270
7.253
6.509
6.488
4.621
4.343
4.328
4.313
2.451
1.916
1.899
1.882
1.868
1.851
1.834
1.000
0.982
0.963
O
N
H
4c
8
7
6
5
4
3
2
1
0
ppm
2.02
4.01
1.02
2.00
1.05
1.06
3.03
2.06
3.00


196.110
151.257
142.610
130.495
128.558
127.135
126.219
111.996
59.179
31.254
25.777
10.589
O
N
H
4c
180
160
140
120
100
80
60
40
20
0
ppm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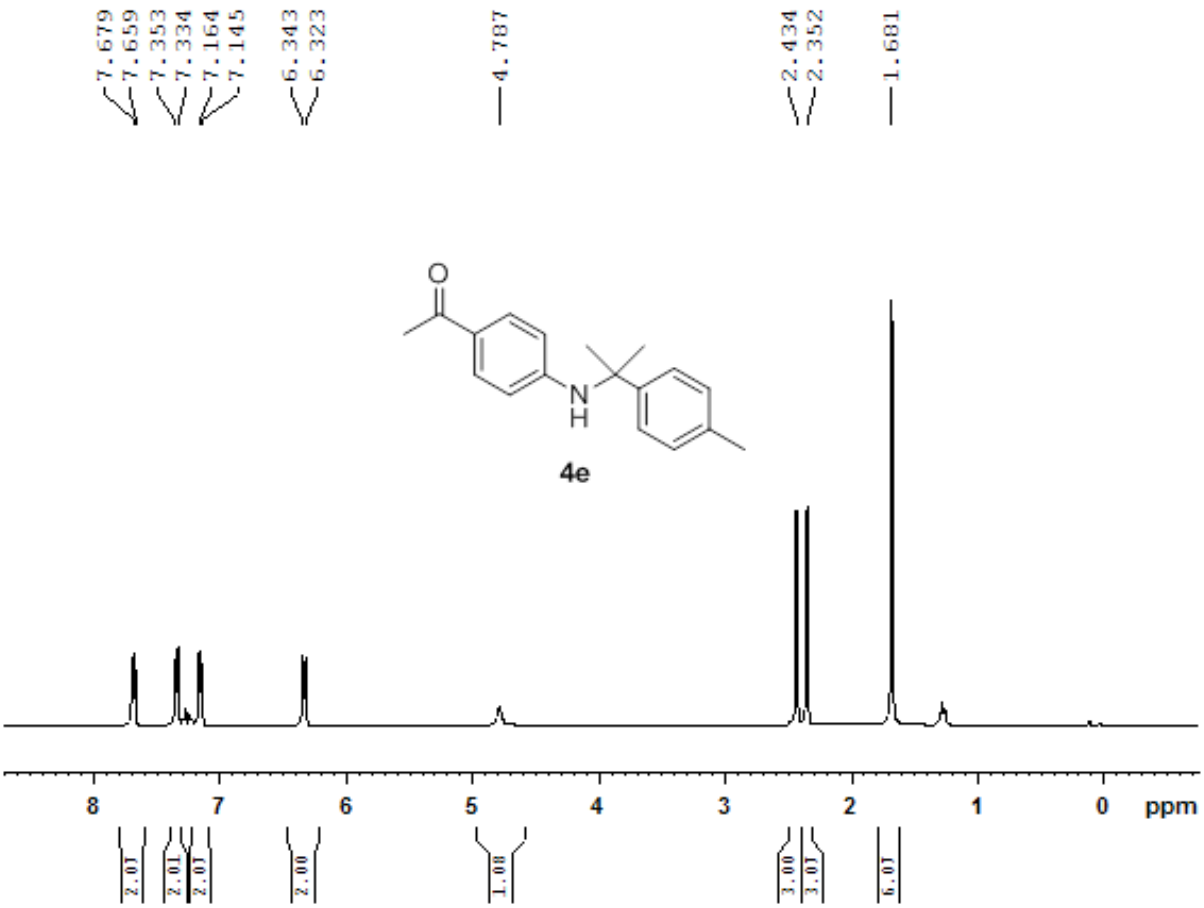
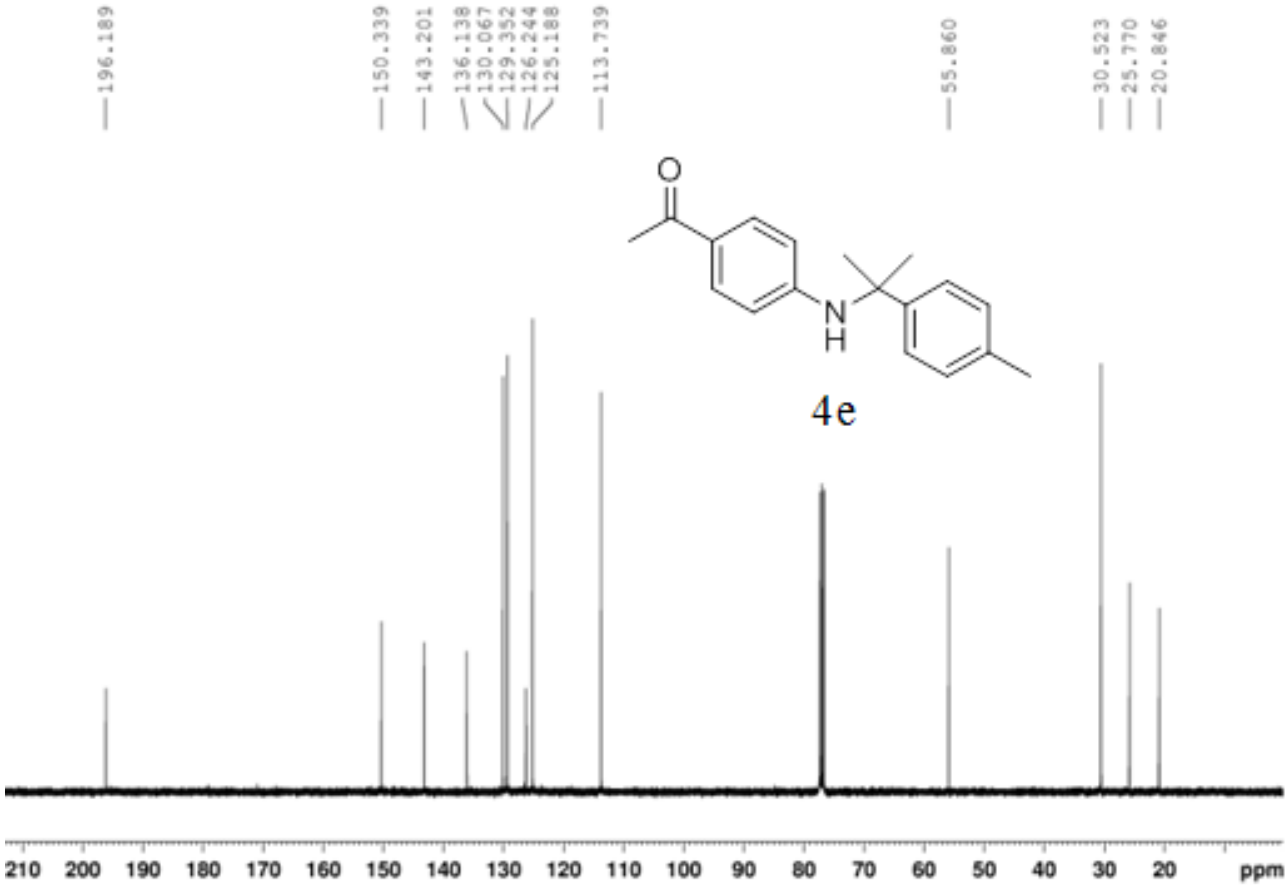
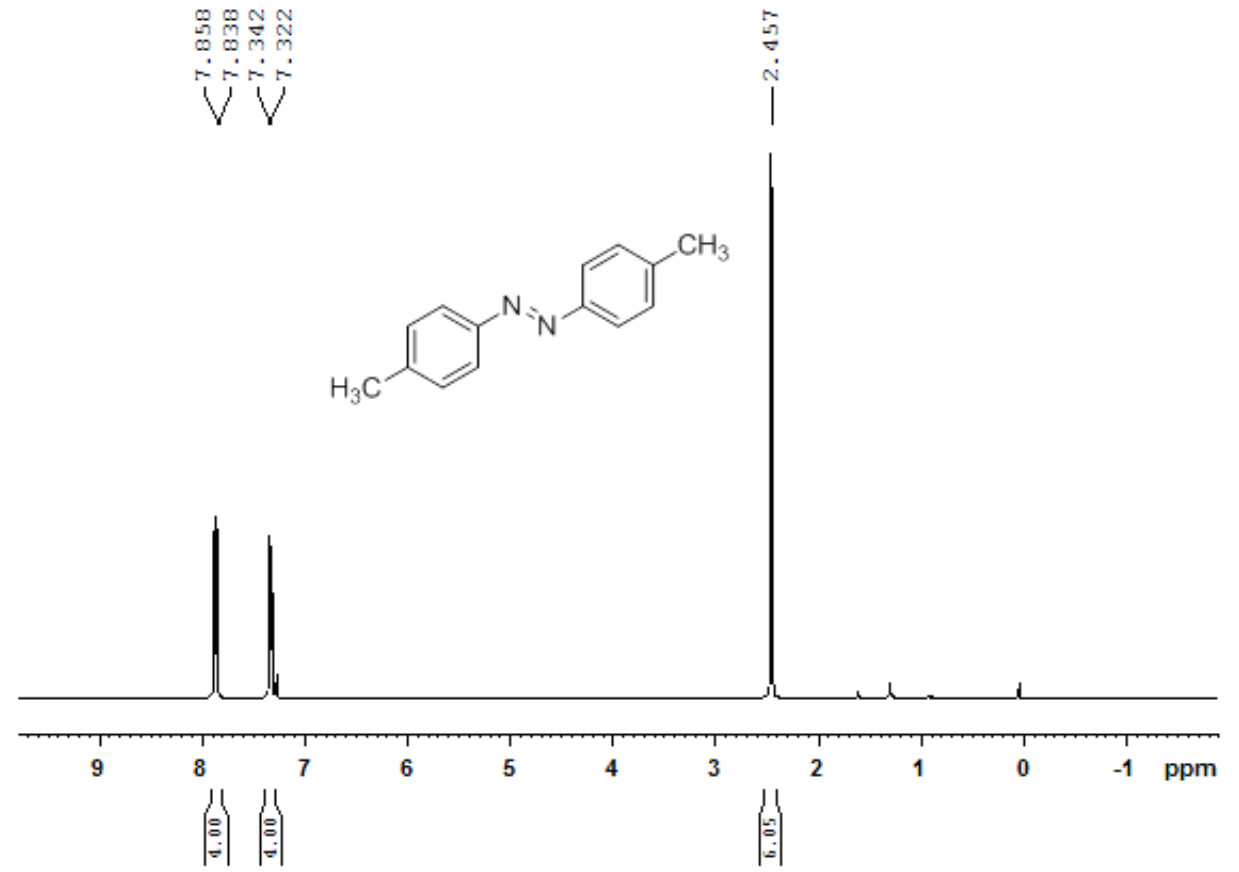
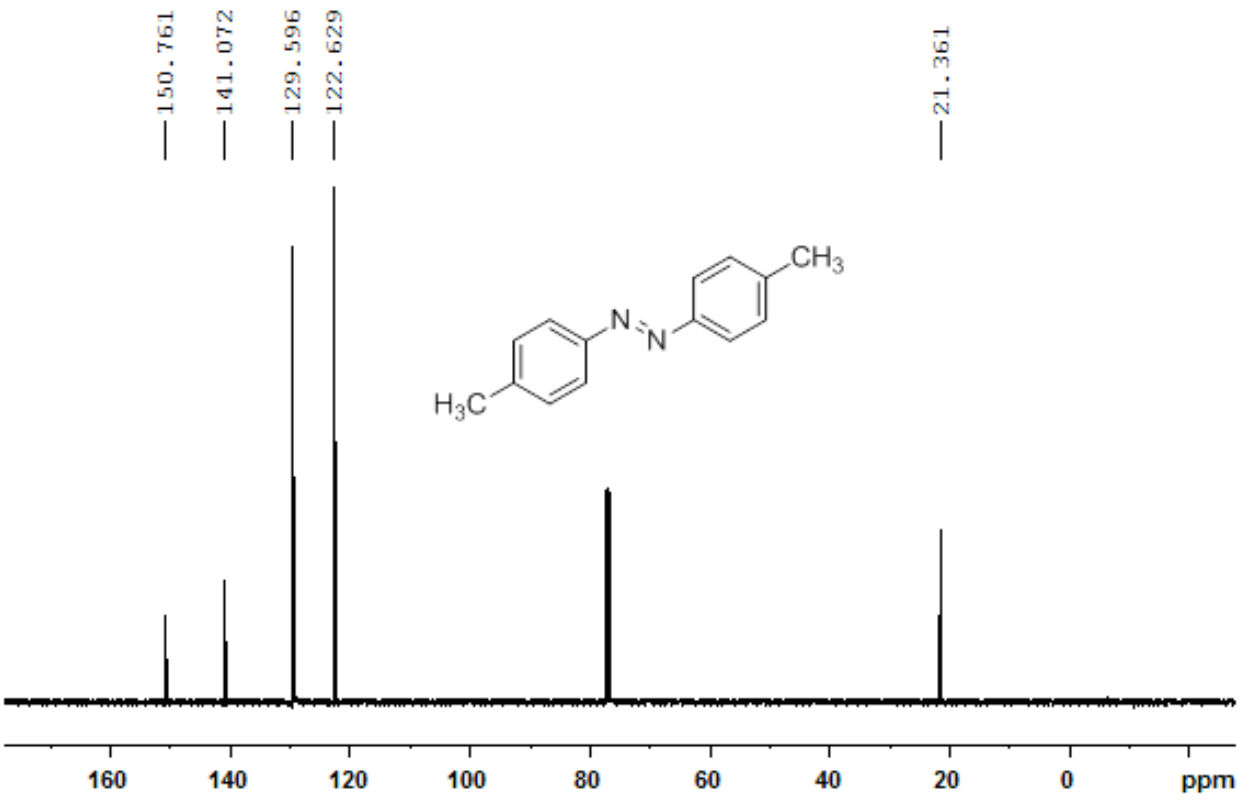
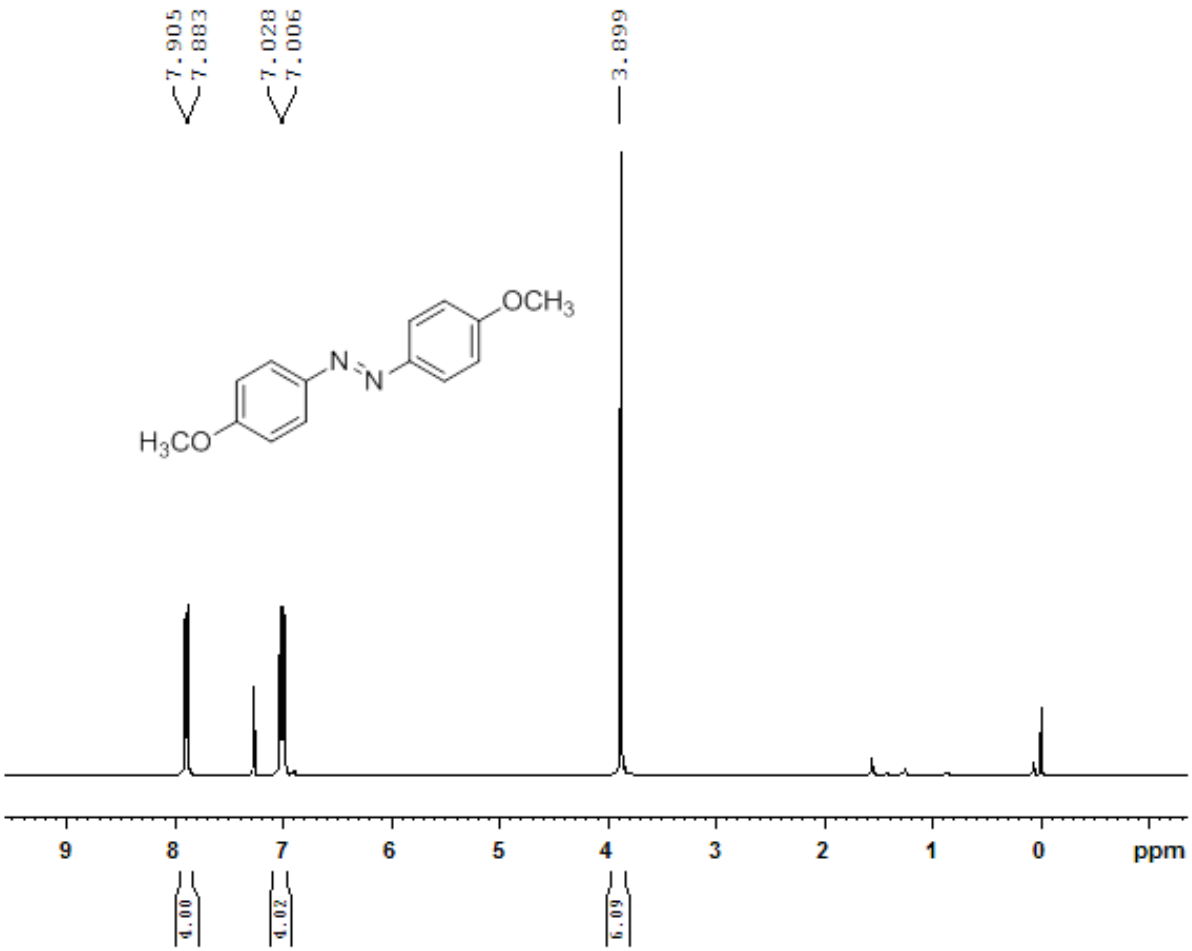
7.652
7.470
7.451
7.366
7.347
7.329
7.273
7.257
6.325
6.304
4.720
2.430
1.697
O
N
H
4d
8
7
6
5
4
3
2
1
0
ppm
2.05
2.01
2.08
1.06
2.00
1.06
3.02
6.04
196.176
150.136
146.120
130.039
128.632
126.589
126.326
125.221
113.711
56.019
30.463
25.751
O
N
H
4d
200
180
160
140
120
100
80
60
40
20
0
ppm

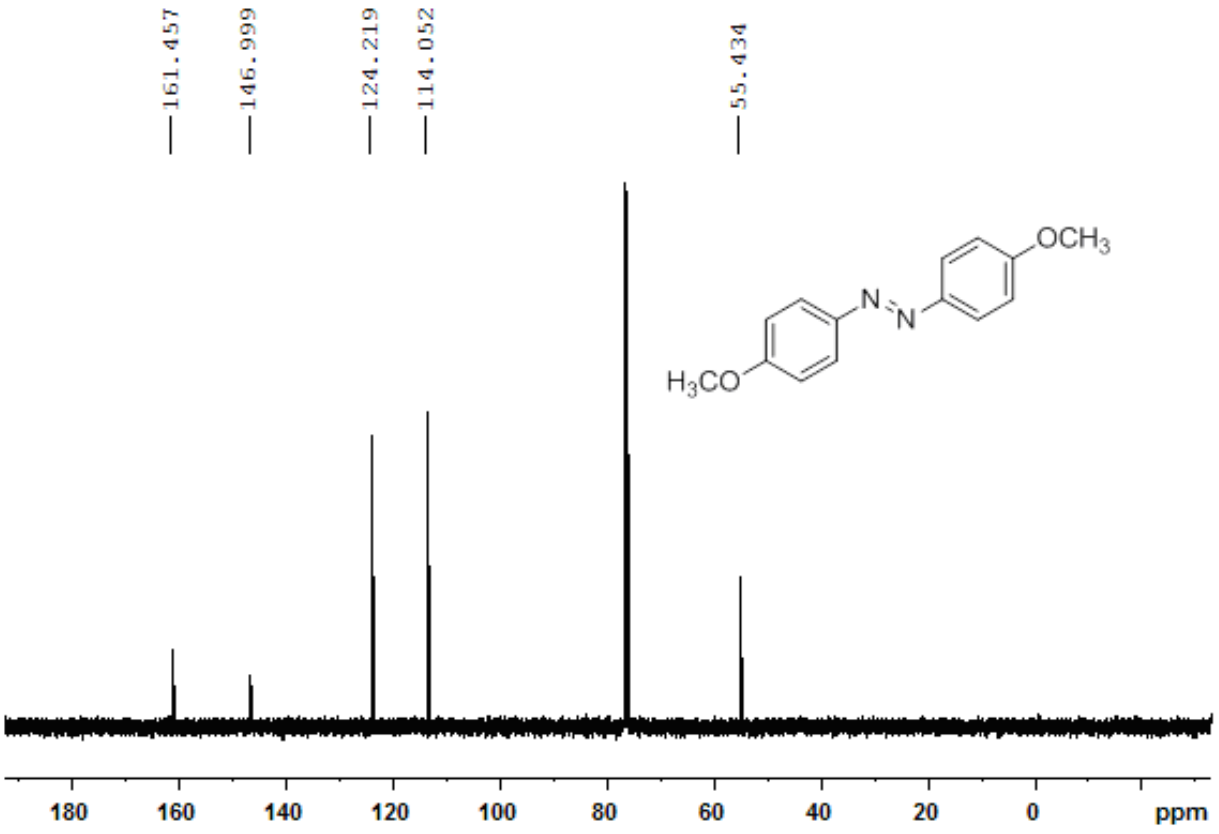

7.679
7.659
7.353
7.334
7.164
7.145
6.343
6.323
4.787
2.434
2.352
1.681
O
N
H
4e
8
7
6
5
4
3
2
1
0
ppm
2.03
2.01
2.03
2.00
1.08
3.00
3.03
6.03


196.189
150.339
143.201
136.138
130.067
129.352
126.244
125.188
113.739
55.860
30.523
25.770
20.846
O
N
H
4e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.858
7.838
7.342
7.322
2.457
CH3
N=N
H3C
9
8
7
6
5
4
3
2
1
0
-1
ppm
4.00
4.00
6.05


150.761
141.072
129.596
122.629
21.361
CH3
N=N
H3C
160
140
120
100
80
60
40
20
0
ppm


7.905
7.883
7.028
7.006
3.899
OCH3
N
N
H3CO
9
8
7
6
5
4
3
2
1
0
ppm
4.00
4.02
6.09


161.457
146.999
124.219
114.052
55.434
OCH3
N
N
H3CO
180
160
140
120
100
80
60
40
20
0
ppm

6. References

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