Synthetic Approach to Skeletally Diverse Nitrogen Heterocycles from Dicyano-2-methylenebut-3-enoates

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supplementary information

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1. General Information

General Procedures

- All reactions were performed in oven-dried or flame-dried reaction vessels, modified Schlenk flasks, or round-bottom flasks. The flasks were fitted with Teflon screw caps and reactions were conducted under an atmosphere of argon if needed. Gas-tight syringes with stainless steel needles were used to transfer air- and moisture-sensitive liquids. All moisture and/or air sensitive solid compounds were manipulated inside normal desiccators. Flash column chromatography was performed using silica gel (40–63 μm, 230–400 mesh).
- Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates (Merck) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and I_2.
- Organic solutions were concentrated at 30-50 ℃ on rotary evaporators at ~10 torr followed by drying on vacuum pump at ~1 torr. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Materials

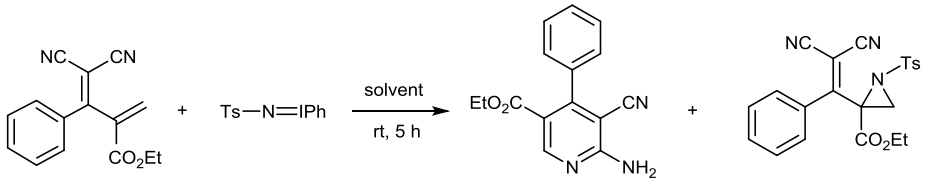
- Commercial reagents and solvents were were purchased from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin and Energy Chemical and used as received with the following exceptions: THF, Et_2O and toluene were purified by refluxing over Na-benzophenone under positive argon pressure followed by distillation.[1] The allylidenemalononitriles **1**[2], carbamate **2**[3] and iminoiodinane **9a**[4] were prepared according to literature procedure.

Instrumentation

- Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with JEOL-600M. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant(s) (Hz), integration].
- Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with JEOL 150 MHz spectrometers. Carbon chemical shifts are reported in parts per million (δ scale), and are referenced using the carbon resonances of the solvent (δ 77.0 ($CHCl_3$)). Data are reported as follows: chemical shift [multiplicity (if not singlet), assignment (C_q = fully substituted carbon)].
- High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2 using an electrospray (ESI) ionization source.
- Melting points were recorded on WRX-X-4A melting point apparatus.

2. Further Optimization Studies

Table S1. Solvent screening of the [5+1] cyclization [a]



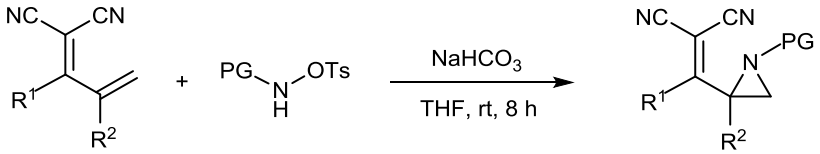
1a **9a** **10a** **3r**

Entry	Solvent	**10a**:**3r**[b]	Yield (%)[c]
1	MeCN	2:1	52
2	DCM	1.7:1	59
3	$CHCl_3$	2:1	45
4	toluene	2:1	62
5	THF	3:1	36
6	**H_2O**	**>20:1**	**91**

[a] Reactions were performed with 0.12 mmol of **1a** and 0.1 mmol of **10a**, in 1 mL solvent at room temperature for 5 hours. [b] Determined by ^1H NMR analysis of the crude reaction mixture. [c] Isolated yields of **10a**.

3. General Procedure for the Preparation of Vinylaziridine 3

*3.1 General procedure for the synthesis of vinylaziridine **3***

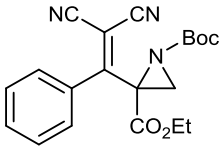


A glass tube was charged with diene **1** (0.12 mmol), carbamate **2** (0.10 mmol) and $NaHCO_3$ (10.1 mg, 0.12 mmol) in THF (1 mL). The mixture was stirred at room temperature for 8 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/dichloromethane = 3/1 to 1/1) to afford the corresponding vinylaziridine **3a**–**3r** in 75%–99% yields.

*3.2 Procedure for the gram-scale synthesis of vinylaziridine **3a***

A 50 mL flask was charged with diene **1a** (1.06 g, 4.20 mmol) carbamate **2a** (1.00 g, 3.50 mmol) and $NaHCO_3$ (0.35 g, 4.20 mmol) in THF (20 mL). The mixture was stirred at room temperature for 8 hours, and then the solvent was concentrated. The residue was added with water (20 mL) and extracted with ethyl acetate (20 mL × 2). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/dichloromethane = 3/1 to 1/1) to afford the corresponding vinylaziridine **3a** (1.20 g) in 94% yield.

1-(tert-butyl) 2-ethyl 2-(2,2-dicyano-1-phenylvinyl)aziridine-1,2-dicarboxylate 3a



Prepared according to the general procedure to afford **3a** (36.3 mg, m. p. = 92 – 96 ^{o}C) in 99% yield as white solid.

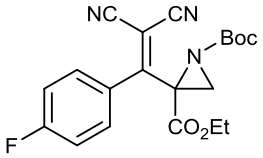
NMR and HRMS data for the product **3a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.74 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 4.40 – 4.29 (m, 2H), 3.41 (d, *J* = 1.2 Hz, 1H), 2.65 (d, *J* = 1.2 Hz, 1H), 1.45 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.9, 165.0, 156.8, 132.82, 132.77, 129.2, 128.7, 112.4, 111.5, 87.9, 83.3, 63.8, 47.5, 41.3, 27.8, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{21}N_3O_4Na^{+}$: 390.1424, found: 390.1424.

1-(tert-butyl) 2-ethyl 2-(2,2-dicyano-1-(4-fluorophenyl)vinyl)aziridine-1,2-dicarboxylate 3b



Prepared according to the general procedure to afford **3b** (38.1 mg, m. p. = 90 – 93 ^{o}C) in 99% yield as pure yellow solid.

NMR and HRMS data for the product **3b**:

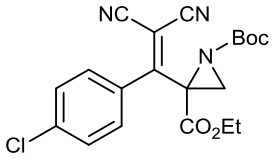
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.19 (t, *J* = 9.0 Hz, 2H), 4.41 – 4.29 (m, 2H), 3.42 (d, *J* = 1.8 Hz, 1H), 2.64 (d, *J* = 1.2 Hz, 1H), 1.45 (s, 9H), 1.32 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.6, 165.2 (d, J_{C-F} = 255.6 Hz), 164.9, 156.8, 131.9 (d, J_{C-F} = 8.6 Hz), 128.8 (d, J_{C-F} = 2.9 Hz), 116.2 (d, J_{C-F} = 21.6 Hz), 112.3, 111.4, 87.6, 83.4, 63.9, 47.4, 41.4, 27.8, 14.0.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -104.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{20}FN_3O_4Na^{+}$: 408.1330, found: 408.1331.

1-(tert-butyl) 2-ethyl 2-(1-(4-chlorophenyl)-2,2-dicyanovinyl)aziridine-1,2-dicarboxylate 3c



Prepared according to the general procedure to afford **3c** (31.4 mg, m. p. = 100 – 102 ^{o}C) in 78% yield as pure yellow solid.

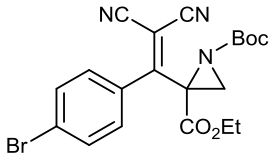
NMR and HRMS data for the product **3c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 4.40 – 4.30 (m, 2H), 3.42 (d, *J* = 1.8 Hz, 1H), 2.64 (d, *J* = 1.2 Hz, 1H), 1.45 (s, 9H), 1.32 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.6, 164.8, 156.8, 139.4, 131.1, 130.6, 129.2, 112.1, 111.3, 88.1, 83.5, 64.0, 47.3, 41.4, 27.8, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{20}{}^{35}ClN_3O_4Na^{+}$: 424.1035, found: 424.1036; calculated for $C_{20}H_{20}{}^{37}ClN_3O_4Na^{+}$: 426.1005, found: 426.1001.

1-(tert-butyl) 2-ethyl 2-(1-(4-bromophenyl)-2,2-dicyanovinyl)aziridine-1,2-dicarboxylate 3d



Prepared according to the general procedure to afford **3d** (36.6 mg, m. p. = 94 – 96 ^{o}C) in 82% yield as pure yellow solid.

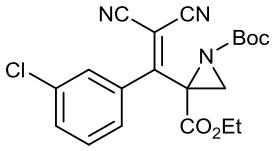
NMR and HRMS data for the product **3d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.69 – 7.60 (m, 4H), 4.40 – 4.30 (m, 2H), 3.42 (d, *J* = 1.2 Hz, 1H), 2.64 (d, *J* = 1.2 Hz, 1H), 1.45 (s, 9H), 1.32 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.8, 164.8, 156.8, 132.2, 131.5, 130.7, 128.0, 112.1, 111.3, 88.1, 83.5, 64.0, 47.3, 41.5, 27.8, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{20}{}^{79}BrN_3O_4Na^{+}$: 468.0529, found: 468.0520; calculated for $C_{20}H_{20}{}^{81}BrN_3O_4Na^{+}$: 470.0509, found: 470.0511.

1-(tert-butyl) 2-ethyl 2-(1-(3-chlorophenyl)-2,2-dicyanovinyl)aziridine-1,2-dicarboxylate 3e



Prepared according to the general procedure to afford **3e** (39.8 mg, m. p. = 75 – 77 ^{o}C) in 99% yield as yellow solid.

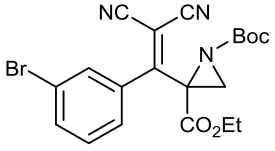
NMR and HRMS data for the product **3e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.73 – 7.70 (m, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 8.4 Hz, 1H), 4.42 – 4.30 (m, 2H), 3.42 (d, *J* = 1.2 Hz, 1H), 2.65 (d, *J* = 1.8 Hz, 1H), 1.45 (s, 9H), 1.33 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.6, 164.7, 156.7, 134.9, 134.3, 132.6, 130.0, 129.0, 127.2, 111.8, 111.0, 89.3, 83.6, 64.0, 47.3, 41.2, 27.8, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{20}{}^{35}ClN_3O_4Na^{+}$: 424.1035, found: 424.1029; calculated for $C_{20}H_{20}{}^{37}ClN_3O_4Na^{+}$: 426.1005, found: 426.0998.

1-(tert-butyl) 2-ethyl 2-(1-(3-bromophenyl)-2,2-dicyanovinyl)aziridine-1,2-dicarboxylate 3f



Prepared according to the general procedure to afford **3f** (38.4 mg, m. p. = 110 – 113 ^{o}C) in

86% yield as pure pink solid.

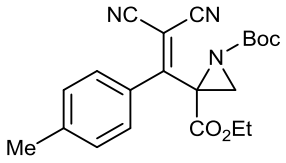
NMR and HRMS data for the product **3f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.89 – 7.82 (m, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 6.6 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 1H), 4.42 – 4.30 (m, 2H), 3.42 (d, *J* = 1.2 Hz, 1H), 2.64 (d, *J* = 1.8 Hz, 1H), 1.45 (s, 9H), 1.33 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.5, 164.7, 156.7, 135.5, 134.6, 131.7, 130.2, 127.7, 122.8, 111.7, 111.0, 89.3, 83.6, 64.0, 47.3, 41.2, 27.8, 14.0.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{20}H_{20}{}^{79}BrN_3O_4Na^+$: 468.0529, found: 468.0528; calculated for $C_{20}H_{20}{}^{81}BrN_3O_4Na^+$: 470.0509, found: 470.0506.

1-(tert-butyl) 2-ethyl 2-(2,2-dicyano-1-(p-tolyl)vinyl)aziridine-1,2-dicarboxylate 3g



Prepared according to the general procedure to afford **3g** (36.2 mg, m. p. = 89 – 94 °C) in 95% yield as yellow solid.

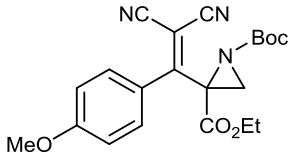
NMR and HRMS data for the product **3g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 4.42 – 4.28 (m, 2H), 3.41 (s, 1H), 2.62 (s, 1H), 2.43 (s, 3H), 1.46 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.7, 165.1, 156.9, 144.1, 130.0, 129.5, 129.4, 112.8, 111.7, 86.5, 83.2, 63.8, 47.5, 41.3, 27.8, 21.7, 14.0.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{21}H_{23}N_3O_4Na^+$: 404.1581, found: 404.1584.

1-(tert-butyl)2-ethyl 2-(2,2-dicyano-1-(4-methoxyphenyl)vinyl)aziridine-1,2-dicarboxylate 3h



Prepared according to the general procedure to afford **3h** (31.4 mg, m. p. = 136 – 141 °C) in 79% yield as pure yellow solid.

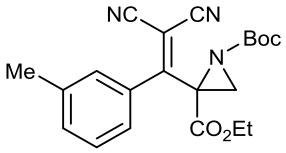
NMR and HRMS data for the product **3h**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 6.6 Hz, 2H), 6.99 (d, *J* = 6.6 Hz, 2H), 4.40 – 4.30 (m, 2H), 3.88 (s, 3H), 3.41 (d, *J* = 1.2 Hz, 1H), 2.60 (d, *J* = 1.2 Hz, 1H), 1.47 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.7, 165.2, 163.6, 157.1, 131.9, 125.0, 114.3, 113.3, 112.1, 84.3, 83.3, 63.7, 55.6, 47.5, 41.5, 27.9, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calculated for $C_{21}H_{23}N_3O_5Na^+$: 420.1530, found: 420.1526.

1-(tert-butyl) 2-ethyl 2-(2,2-dicyano-1-(m-tolyl)vinyl)aziridine-1,2-dicarboxylate 3i



Prepared according to the general procedure to afford **3i** (31.2 mg, m. p. = 96 – 102 ^{o}C) in 82% yield as pure yellow solid.

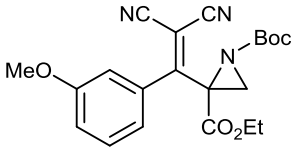
NMR and HRMS data for the product **3i**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 – 7.50 (m, 2H), 7.44 – 7.34 (m, 2H), 4.41 – 4.30 (m, 2H), 3.41 (d, *J* = 2.4 Hz, 1H), 2.62 (d, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 1.45 (s, 9H), 1.32 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.2, 165.0, 156.9, 138,7, 133.6, 132.8, 129.5, 128.7, 126.4, 112.5, 111.6, 87.6, 83.2, 63.8, 47.5, 41.3, 27.8, 21.4, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calculated for $C_{21}H_{23}N_3O_4Na^+$: 404.1581, found: 404.1579.

1-(tert-butyl)2-ethyl 2-(2,2-dicyano-1-(3-methoxyphenyl)vinyl)aziridine-1,2-dicarboxylate 3j



Prepared according to the general procedure to afford **3j** (32.6 mg, m. p. = 63 – 68 ^{o}C) in 82% yield as yellow solid.

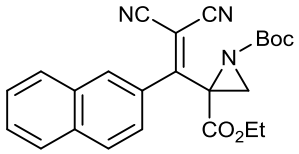
NMR and HRMS data for the product **3j**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.40 (t, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.30 (s, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 4.40 – 4.29 (m, 2H), 3.85 (s, 3H), 3.41 (d, *J* = 1.2 Hz, 1H), 2.64 (d, *J* = 1.8 Hz, 1H), 1.45 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.7, 165.0, 159.5, 156.9, 133.8, 129.8, 121.5, 119.0, 114.2, 112.4, 111.5, 87.8, 83.3, 63.8, 55.5, 47.4, 41.4, 27.8, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calculated for $C_{21}H_{23}N_3O_5Na^+$: 420.1530, found: 420.1532.

1-(tert-butyl) 2-ethyl 2-(2,2-dicyano-1-(naphthalen-2-yl)vinyl)aziridine-1,2-dicarboxylate 3k



Prepared according to the general procedure to afford **3k** (41.3 mg) in 99% yield as yellow semisolid.

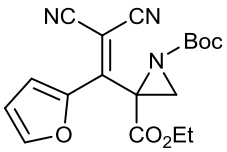
NMR and HRMS data for the product **3k**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.32 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 10.8 Hz, 1H), 7.63 (t, *J* = 6.6 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 4.44 – 4.32 (m, 2H), 3.46 (d, *J* = 1.2 Hz, 1H), 2.69 (d, *J* = 1.2 Hz, 1H), 1.46 (s, 9H), 1.33 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.9, 165.1, 157.0, 135.0, 132.3, 130.8, 130.2, 129.4, 129.0, 128.6, 127.8, 127.2, 124.9, 112.7, 111.7, 87.5, 83.3, 63.9, 47.6, 41.4, 27.9, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{23}N_3O_4Na^+$: 440.1581, found: 440.1586.

1-(tert-butyl) 2-ethyl 2-(2,2-dicyano-1-(furan-2-yl)vinyl)aziridine-1,2-dicarboxylate 3l



Prepared according to the general procedure to afford **3l** (35.0 mg) in 98% yield as yellow semisolid.

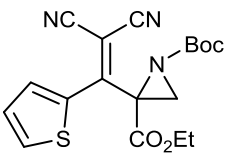
NMR and HRMS data for the product **3l**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 – 8.00 (m, 1H), 7.85 – 7.75 (m, 1H), 6.70 (d, *J* = 3.6 Hz, 1H), 4.42 – 4.19 (m, 2H), 3.31 (s, 1H), 2.65 (s, 1H), 1.52 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.9, 157.3, 150.8, 148.9, 148.4, 124.5, 114.5, 112.9, 112.6, 83.7, 81.9, 63.8, 45.0, 40.4, 27.9, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{18}H_{19}N_3O_5Na^+$: 380.1217, found: 380.1215.

1-(tert-butyl) 2-ethyl 2-(2,2-dicyano-1-(thiophen-2-yl)vinyl)aziridine-1,2-dicarboxylate 3m



Prepared according to the general procedure to afford **3m** (34.7 mg, m. p. = 166 – 172 ^{o}C) in 93% yield as yellow semisolid.

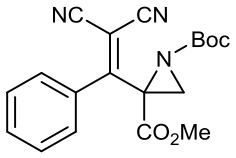
NMR and HRMS data for the product **3m**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.52 – 8.32 (m, 1H), 7.81 (d, *J* = 4.8 Hz, 1H), 7.24 (t, *J* = 4.8 Hz, 1H), 4.35 – 4.20 (m, 2H), 3.37 (s, 1H), 2.68 (s, 1H), 1.50 (s, 9H), 1.24 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.9, 157.1, 151.0, 136.9, 135.6, 135.4, 128.8, 113.5, 112.2, 83.6, 81.3, 63.7, 47.4, 41.3, 27.8, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{18}H_{19}N_3O_4SNa^{+}$: 306.0988, found: 396.0989.

1-(tert-butyl) 2-methyl 2-(2,2-dicyano-1-phenylvinyl)aziridine-1,2-dicarboxylate 3n



Prepared according to the general procedure to afford **3n** (34.2 mg, m. p. = 117 – 121 ^{o}C) in 97% yield as white solid.

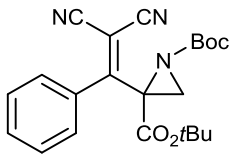
NMR and HRMS data for the product **3n**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.74 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 3.43 (d, *J* = 1.2 Hz, 1H), 2.66 (d, *J* = 1.2 Hz, 1H), 1.45 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.7, 165.6, 156.8, 132.9, 132.7, 129.2, 128.8, 112.3, 111.5, 88.0, 83.4, 54.2, 47.4, 41.4, 27.8.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{19}H_{19}N_3O_4Na^{+}$: 376.1268, found: 376.1262.

di-tert-butyl 2-(2,2-dicyano-1-phenylvinyl)aziridine-1,2-dicarboxylate 3o



Prepared according to the general procedure to afford **3o** (33.6 mg, m. p. = 112 – 115 ^{o}C) in 85% yield as white solid.

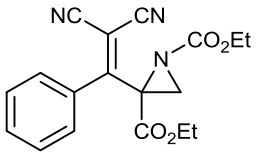
NMR and HRMS data for the product **3o**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.73 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 3.34 (d, *J* = 1.2 Hz, 1H), 2.59 (d, *J* = 1.2 Hz, 1H), 1.49 (s, 9H), 1.45 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.7, 163.6, 157.1, 133.1, 132.7, 129.1, 128.7, 112.5, 111.6, 87.4, 85.7, 83.1, 48.2, 41.1, 27.8, 27.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{22}H_{25}N_3O_4Na^+$: 418.1737, found: 418.1740.

diethyl 2-(2,2-dicyano-1-phenylvinyl)aziridine-1,2-dicarboxylate 3p



Prepared according to the general procedure to afford **3p** (27.1 mg) in 80% yield as pure yellow semisolid.

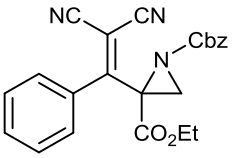
NMR and HRMS data for the product **3p**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.75 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 2H), 4.41 – 4.28 (m, 2H), 4.26 – 4.12 (m, 2H), 3.44 (d, *J* = 1.2 Hz, 1H), 2.71 (d, *J* = 1.2 Hz, 1H), 1.31 (t, *J* = 6.6 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.5, 164.9, 158.4, 132.9, 132.7, 129.1, 128.8, 112.3, 111.5, 88.1, 64.0, 63.5, 47.4, 41.4, 14.2, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{18}H_{17}N_3O_4Na^+$: 362.1111, found: 362.1110.

1-benzyl 2-ethyl 2-(2,2-dicyano-1-phenylvinyl)aziridine-1,2-dicarboxylate 3q



Prepared according to the general procedure to afford **3q** (39.7 mg) in 99% yield as yellow semisolid.

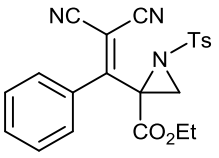
NMR and HRMS data for the product **3q**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.70 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 6.6 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 5.18 (d, *J* = 12.0 Hz, 1H), 5.10 (d, *J* = 12.6 Hz, 1H), 4.31 – 4.18 (m, 2H), 3.48 (d, *J* = 1.2 Hz, 1H), 2.74 (d, *J* = 1.2 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.4, 164.8, 158.3, 134.7, 132.8, 132.6, 129.1, 128.8, 128.64, 128.57, 128.4, 112.2, 111.4, 88.2, 69.1, 64.0, 47.5, 41.3, 13.9.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{23}H_{19}N_3O_4Na^+$: 424.1268, found: 424.1264.

ethyl 2-(2,2-dicyano-1-phenylvinyl)-1-tosylaziridine-2-carboxylate 3r



Prepared according to the general procedure to afford **3r** (31.6 mg, m. p. = 138 – 143 ^{o}C) in 75% yield as white solid.

NMR and HRMS data for the product **3r**:

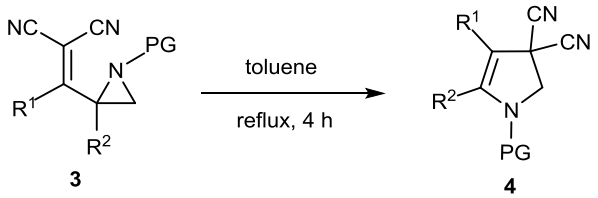
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.67 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.55 – 7.47 (m, 4H), 7.20 (d, *J* = 7.8 Hz, 2H), 4.51 – 4.39 (m, 2H), 3.97 (s, 1H), 2.74 (s, 1H), 2.38 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.1, 163.9, 144.9, 136.3, 133.0, 132.5, 129.6, 129.0, 128.9, 127.6, 111.9, 111.1, 88.4, 64.4, 52.2, 42.7, 21.6, 13.8.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{22}H_{19}N_3O_4SNa^{+}$: 444.0988, found: 444.0988.

4. General Procedure for the Preparation of 2-Pyrrolines 4

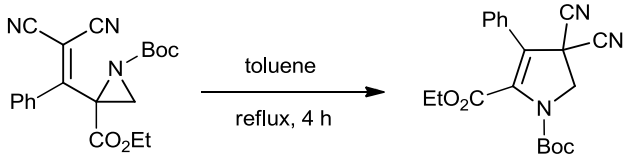
4.1 General procedure for the pyrroline rearrangement



3 **4**

A glass tube was charged with vinylaziridine **3** (0.10 mmol) in toluene (1 mL). The mixture was stirred at 110 ^{o}C for 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 10/1) to afford the corresponding 2,3-dihydropyrroles **4a**–**4p** in 75%–95% yields.

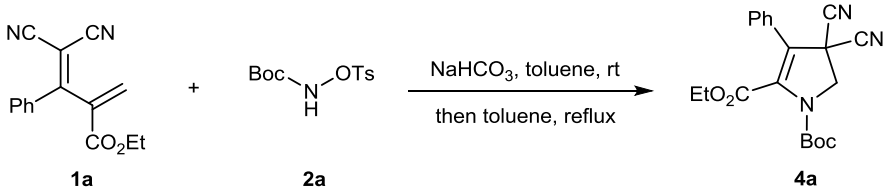
*4.2 Gram-scale synthesis of 2-pyrroline **4a** from vinylaziridine **3a***



3a **4a**

A 50 mL flask was charged with vinylaziridine **3a** (1.20 g, 3.27 mmol) in the toluene (20 mL). The mixture was stirred at 110 ^{o}C for 4 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 10/1) to afford the corresponding 2,3-dihydropyrroles **4a** (1.03 g) in 86% yield.

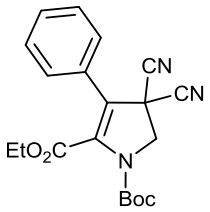
*4.3 One-pot synthesis of 2-pyrroline **4a** from diene **1a***



1a **2a** **4a**

A glass tube was charged with diene **1a** (30.3 mg, 0.12 mmol), carbamate **2a** (28.7 mg, 0.10 mmol) and $NaHCO_3$ (10.1 mg, 0.12 mmol) in toluene (1 mL). The mixture was stirred at room temperature for 8 hours. Then the mixture was added with toluene (1 mL) and washed with brine (3 mL × 2). The organic layer was dried over anhydrous Na_2SO_4 and refluxed at 110 ^{o}C for another 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 10/1) to afford the corresponding pyrroline **4a** (19.8 mg) in 54% overall yield.

1-(tert-butyl) 2-ethyl 4,4-dicyano-3-phenyl-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4a



Prepared according to the general procedure to afford **4a** (34.9 mg, m. p. = 142 – 144 ^{o}C) in 95% yield as white solid.

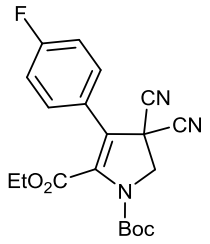
NMR and HRMS data for the product **4a**:

^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.53 – 7.39 (m, 5H), 4.60 (s, 2H), 4.23 (q, *J* = 6.6 Hz, 2H), 1.50 (s, 9H), 1.14 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$) δ (ppm): 160.6, 149.5, 136.3, 129.8, 129.0, 128.0, 127.8, 113.1, 84.3, 62.6, 56.9, 40.0, 28.0, 13.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{20}H_{21}N_3O_4Na^+$: 390.1424, found: 390.1424.

1-(tert-butyl)2-ethyl4,4-dicyano-3-(4-fluorophenyl)-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4b



Prepared according to the general procedure to afford **4b** (28.9 mg, m. p. = 115 – 119 ^{o}C) in 75% yield as pure yellow solid.

NMR and HRMS data for the product **4b**:

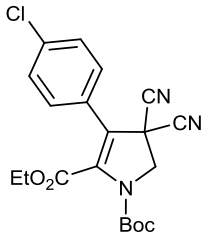
^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.45 (d, *J* = 4.8 Hz, 1H), 7.44 (d, *J* = 5.4 Hz, 1H), 7.13 (t, *J* = 9.0 Hz, 2H), 4.59 (s, 2H), 4.22 (q, *J* = 6.6 Hz, 2H), 1.50 (s, 9H), 1.15 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$) δ (ppm): 163.4 (d, J_{C-F} = 248.6 Hz), 160.4, 149.4, 136.8, 131.5, 130.2 (d, J_{C-F} = 8.7 Hz), 123.9 (d, J_{C-F} = 2.9 Hz), 116.3 (d, J_{C-F} = 21.5 Hz), 112.9, 84.4, 62.6, 56.7, 40.1, 27.9, 13.6.

^{19}F NMR (564 MHz, CDCl$_3$) δ (ppm): -109.8.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{20}H_{20}FN_3O_4Na^+$: 408.1330, found: 408.1327.

1-(tert-butyl)2-ethyl3-(4-chlorophenyl)-4,4-dicyano-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4c



Prepared according to the general procedure to afford **4c** (31.0 mg, m. p. = 123 – 128 ^{o}C) in 77% yield as pure yellow solid.

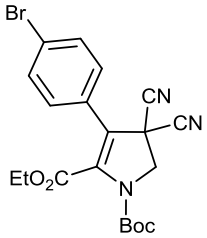
NMR and HRMS data for the product **4c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.41 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 4.59 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.50 (s, 9H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.3, 149.3, 136.9, 136.0, 130.1, 129.4, 129.2, 126.4, 112.9, 84.5, 62.7, 56.8, 39.9, 28.0, 13.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{20}{}^{35}ClN_3O_4Na^{+}$: 424.1035, found: 424.1031; calculated for $C_{20}H_{20}{}^{37}ClN_3O_4Na^{+}$: 426.1005, found: 426.1001.

1-(tert-butyl)2-ethyl3-(4-bromophenyl)-4,4-dicyano-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4d



Prepared according to the general procedure to afford **4d** (34.8 mg, m. p. = 128 – 131 ^{o}C) in 78% yield as pure yellow solid.

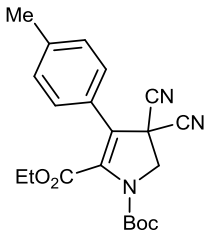
NMR and HRMS data for the product **4d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.56 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.59 (s, 2H), 4.24 (q, *J* = 7.8 Hz, 2H), 1.50 (s, 9H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.3, 149.3, 137.0, 132.4, 129.4, 129.2, 126.9, 124.2, 112.9, 84.6, 62.8, 56.8, 39.8, 28.0, 13.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{20}{}^{79}BrN_3O_4Na^{+}$: 468.0529, found: 468.0526; calculated for $C_{20}H_{20}{}^{81}BrN_3O_4Na^{+}$: 470.0509, found: 470.0501.

1-(tert-butyl) 2-ethyl 4,4-dicyano-3-(p-tolyl)-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4e



Prepared according to the general procedure to afford **4e** (33.1 mg, m. p. = 118 – 121 ^{o}C) in 87% yield as white solid.

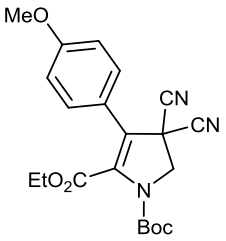
NMR and HRMS data for the product **4e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.33 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 4.58 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.49 (s, 9H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.7, 149.5, 140.0, 130.0, 129.7, 128.9, 127.6, 125.0, 113.2, 84.2, 62.5, 56.8, 40.0, 28.0, 21.4, 13.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{21}H_{23}N_3O_4Na^{+}$: 404.1581, found: 404.1582.

1-(tert-butyl)2-ethyl4,4-dicyano-3-(4-methoxyphenyl)-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4f



Prepared according to the general procedure to afford **4f** (36.9 mg, m. p. = 100 – 103 ^{o}C) in 93% yield as white solid.

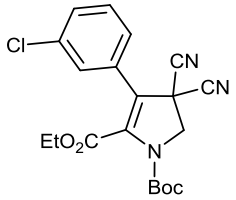
NMR and HRMS data for the product **4f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.38 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.57 (s, 2H), 4.23 (q, *J* = 7.8 Hz, 2H), 3.83 (s, 3H), 1.49 (s, 9H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.8, 160.6, 149.6, 135.3, 129.3, 120.0, 114.5, 113.2, 84.2, 62.5, 56.7, 55.3, 40.1, 28.0, 13.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{21}H_{23}N_3O_5Na^{+}$: 420.1530, found: 420.1533.

1-(tert-butyl)2-ethyl3-(3-chlorophenyl)-4,4-dicyano-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4g



Prepared according to the general procedure to afford **4g** (35.8 mg, m. p. = 118 – 122 ^{o}C) in 89% yield as pure yellow solid.

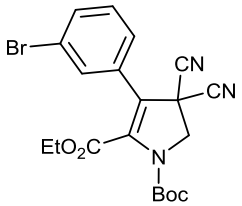
NMR and HRMS data for the product **4g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.44 – 7.35 (m, 4H), 4.59 (s, 2H), 4.26 (q, *J* = 6.6 Hz, 2H), 1.50 (s, 9H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.2, 149.3, 137.4, 135.0, 130.4, 129.9, 129.8, 128.7, 128.0, 125.8, 112.9, 84.6, 62.8, 56.9, 39.7, 28.0, 13.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{20}{}^{35}ClN_3O_4Na^{+}$: 424.1035, found: 424.1041; calculated for $C_{20}H_{20}{}^{37}ClN_3O_4Na^{+}$: 426.1005, found: 426.1012.

1-(tert-butyl)2-ethyl3-(3-bromophenyl)-4,4-dicyano-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4h



Prepared according to the general procedure to afford **4h** (34.8 mg, m. p. = 120 – 122 ^{o}C) in 78% yield as pure yellow solid.

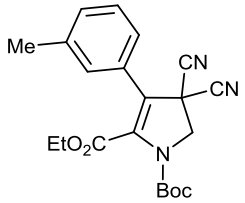
NMR and HRMS data for the product **4h**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.59 – 7.52 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 4.59 (s, 2H), 4.27 (q, *J* = 7.8 Hz, 2H), 1.50 (s, 9H), 1.20 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.2, 149.3, 137.4, 132.8, 130.8, 130.6, 130.0, 126.2, 123.0, 112.8, 84.6, 62.8, 56.9, 39.7, 27.9, 13.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{20}{}^{79}BrN_3O_4Na^{+}$: 468.0529, found: 468.0529; calculated for $C_{20}H_{20}{}^{81}BrN_3O_4Na^{+}$: 470.0509, found: 470.0507.

1-(tert-butyl) 2-ethyl 4,4-dicyano-3-(m-tolyl)-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4i



Prepared according to the general procedure to afford **4i** (32.0 mg, m. p. = 108 – 112 ^{o}C) in 84% yield as yellow solid.

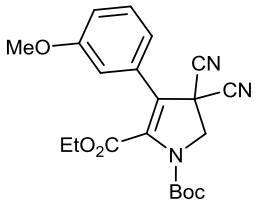
NMR and HRMS data for the product **4i**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.30 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.19 (m, 3H), 4.59 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.50 (s, 9H), 1.15 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.6, 149.5, 138.8, 136.0, 130.6, 128.9, 128.2, 127.9, 124.8, 113.1, 84.2, 62.5, 56.9, 39.9, 27.9, 21.4, 13.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{21}H_{23}N_3O_4Na^{+}$: 404.1581, found: 404.1584.

1-(tert-butyl)2-ethyl4,4-dicyano-3-(3-methoxyphenyl)-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4j



Prepared according to the general procedure to afford **4j** (34.9 mg) in 88% yield as yellow semisolid.

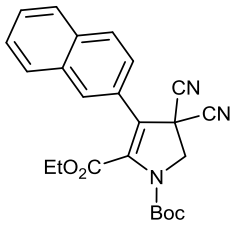
NMR and HRMS data for the product **4j**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.33 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.99 – 6.92 (m, 2H), 4.59 (s, 2H), 4.24 (q, *J* = 6.6 Hz, 2H), 3.81 (s, 3H), 1.50 (s, 9H), 1.17 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.6, 159.8, 149.5, 136.4, 130.2, 129.2, 120.0, 115.5, 113.1, 84.3, 62.6, 56.9, 55.3, 39.9, 28.0, 13.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{21}H_{23}N_3O_5Na^{+}$: 420.1530, found: 420.1530.

1-(tert-butyl)2-ethyl4,4-dicyano-3-(naphthalen-2-yl)-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4k



Prepared according to the general procedure to afford **4k** (34.2 mg) in 82% yield as yellow semisolid.

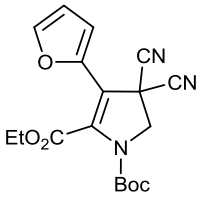
NMR and HRMS data for the product **4k**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.94 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 5.4 Hz, 1H), 7.85 (d, *J* = 4.8 Hz, 1H), 7.54 (t, *J* = 4.2 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 1H), 4.65 (s, 2H), 4.24 (q, *J* = 6.6 Hz, 2H), 1.52 (s, 9H), 1.12 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.7, 149.5, 136.5, 133.4, 133.0, 129.0, 128.3, 127.7, 127.6, 127.3, 127.0, 125.4, 124.4, 113.2, 84.4, 62.6, 57.0, 40.0, 28.0, 13.6.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{24}H_{23}N_3O_4Na^+$: 440.1581, found: 440.1581.

1-(tert-butyl) 2-ethyl 4,4-dicyano-3-(furan-2-yl)-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4l



Prepared according to the general procedure to afford **4l** (32.5 mg) in 91% yield as yellow semisolid.

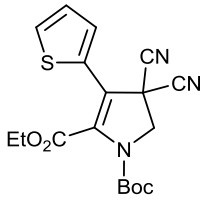
NMR and HRMS data for the product **4l**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.47 (d, *J* = 1.8 Hz, 1H), 6.66 (d, *J* = 3.6 Hz, 1H), 6.50 (dd, *J* = 3.0, 1.8 Hz, 1H), 4.56 (s, 2H), 4.41 (q, *J* = 6.6 Hz, 2H), 1.50 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.3, 149.2, 143.8, 143.1, 133.1, 112.9, 112.0, 110.1, 84.5, 62.8, 56.5, 37.1, 28.0, 13.9.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{18}H_{19}N_3O_5Na^+$: 380.1217, found: 380.1218 .

1-(tert-butyl)2-ethyl4,4-dicyano-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4m



Prepared according to the general procedure to afford **4m** (32.1 mg) in 86% yield as yellow semisolid.

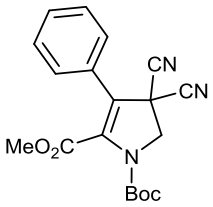
NMR and HRMS data for the product **4m**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.39 (d, *J* = 4.8 Hz, 1H), 7.34 (d, *J* = 4.2 Hz, 1H), 7.11 – 7.07 (m, 1H), 4.57 (s, 2H), 4.36 (q, *J* = 6.6 Hz, 2H), 1.50 (s, 9H), 1.31 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.4, 149.2, 135.1, 128.9, 128.8, 127.9, 127.7, 127.6, 113.0, 84.5, 63.0, 56.4, 39.7, 28.0, 13.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{18}H_{19}N_3O_4SNa^+$: 396.0988, found: 396.0992.

1-(tert-butyl) 2-methyl 4,4-dicyano-3-phenyl-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4n



Prepared according to the general procedure to afford **4n** (32.8 mg, m. p. = 110 – 114 ^{o}C) in 93% yield as white solid.

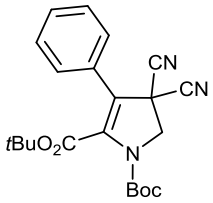
NMR and HRMS data for the product **4n**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.49 – 7.38 (m, 5H), 4.60 (s, 2H), 3.79 (s, 3H), 1.50 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 161.2, 149.5, 135.8, 129.8, 129.2, 127.9, 127.4, 113.0, 84.4, 56.9, 53.2, 28.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{19}H_{19}N_3O_4Na^+$: 376.1268, found: 376.1271.

di-tert-butyl 4,4-dicyano-3-phenyl-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4o



Prepared according to the general procedure to afford **4o** (35.6 mg, m. p. = 126 – 129 ^{o}C) in 90% yield as white solid.

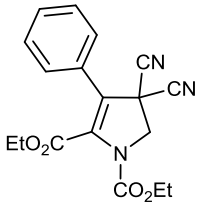
NMR and HRMS data for the product **4o**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.48 – 7.44 (m, 2H), 7.44 – 7.39 (m, 3H), 4.56 (s, 2H), 1.51 (s, 9H), 1.34 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 158.9, 149.5, 137.8, 129.6, 128.9, 128.4, 128.3, 113.2, 84.5, 83.9, 57.0, 40.3, 28.1, 27.6.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{22}H_{25}N_3O_4Na^+$: 418.1737, found: 418.1740.

diethyl 4,4-dicyano-3-phenyl-4,5-dihydro-1H-pyrrole-1,2-dicarboxylate 4p



Prepared according to the general procedure to afford **4p** (27.8 mg) in 82% yield as pure yelllow semisolid.

NMR and HRMS data for the product **4p**:

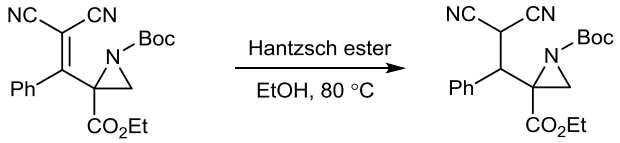
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.49 – 7.39 (m, 5H), 4.65 (s, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.8 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.5, 150.7, 135.9, 129.9, 129.2, 129.1, 127.7, 112.9, 63.7, 62.8, 56.7, 40.1, 14.3, 13.6.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{18}H_{17}N_3O_4Na^+$: 362.1111, found: 362.1113.

5. Synthetic Transformation of Vinylaziridine 3 and 2-Pyrrolines 4

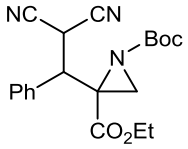
*5.1 Reduction of C-C doulbe bond on vinylaziridine **3a***



3a **5**

A glass tube was charged with vinylaziridine **3a** (39.7 mg, 0.1 mmol) and Hantzsch ester (30.4 mg, 0.12 mmol) in EtOH (1 mL). The mixture was stirred at 80 ^{o}C for 8 hours and then cooled to room temperature. After that the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to 10/1) to provide **5** (28.4 mg, 77% yield) as colorless oil, which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*.

1-(tert-butyl) 2-ethyl 2-(2,2-dicyano-1-phenylethyl)aziridine-1,2-dicarboxylate 5



Purification of the crude product *via* column chromatography delivered **5** (28.4 mg) in 77% yield as colorless oil. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

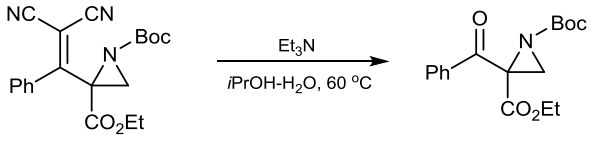
NMR and HRMS data for the product **5**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.41 – 7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 4.59 (d, *J* = 8.4 Hz, 1H), 4.37 – 4.29 (m, 1H), 4.24 – 4.16 (m, 1H), 4.22 (d, *J* = 7.8 Hz, 1H), 2.79 (s, 1H), 2.06 (s, 1H), 1.47 (s, 9H), 1.31 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.5, 157.7, 132.8, 129.5, 129.3, 128.4, 111.9, 111.7, 83.1, 63.1, 45.4, 45.0, 37.4, 27.9, 26.3, 13.9.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{20}H_{23}N_3O_4Na^{+}$: 392.1581, found: 392.1582.

*5.2 Hydrolysis of vinylaziridine **3a***

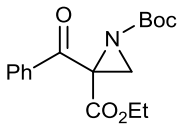


3a **6**

A glass tube was charged with vinylaziridine **3a** (39.7 mg, 0.1 mmol), triethylamine (30.4

mg, 0.3 mmol) in *i*-PrOH/H_2O (2 mL, 3:1 (*v*/*v*)). The mixture was stirred at 60 ^oC for 12 hour. Then the mixture was added with water (5 mL) and extracted with ethyl acetate (5 mL × 2). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 5/1) to provide the product **6** (27.4 mg, 86% yield) as colorless oil, which was dried under vacuum and further analyzed by ^1H NMR, ^{13}C NMR, HRMS, *etc*.

1-(tert-butyl) 2-ethyl 2-benzoylaziridine-1,2-dicarboxylate 6



Purification of the crude product *via* column chromatography delivered **6** (27.4 mg) in 86% yield as colorless oil.

NMR and HRMS data for the product **4**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.25 (d, *J* = 9.0 Hz, 2H), 7.60 (t, *J* = 9.0 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 4.31 – 4.22 (m, 1H), 4.19 – 4.11 (m, 1H), 2.95 (s, 1H), 2.71 (s, 1H), 1.53 (s, 9H), 1.12 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.8, 166.6, 158.0, 134.7, 133.8, 129.6, 128.4, 82.9, 62.8, 48.6, 36.5, 27.9, 13.9.

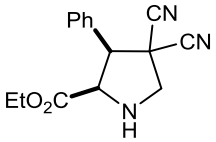
HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{17}H_{21}NO_5Na^+$: 342.1312, found: 342.1318.

5.3 Reduction of the enamine moiety on pyrroline ***4a***

4a **7**

A glass tube was charged with 2-pyrroline **4a** (36.7 mg, 0.1 mmol), BF_3 OEt_2 (71.0 mg, 0.5 mmol) and Et_3SiH (58.2 mg, 0.5 mmol) in DCM (1 mL). The mixture was stirred at room temperature for 4 hours. Then the mixture was added with water (5 mL) and extracted with ethyl acetate (5 mL × 2). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 3/1) to provide the product **7** (17.2 mg, 64% yield) as colorless oil, which was dried under vacuum and further analyzed by ^1H NMR, ^{13}C NMR, HRMS, *etc*.

ethyl 4,4-dicyano-3-phenylpyrrolidine-2-carboxylate 7



Purification of the crude product *via* column chromatography delivered **7** (17.2 mg) in 64% yield as colorless oil. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis, and the relative configuration of the adjacent stereocenters was determined as *cis* by NOEDS analysis.

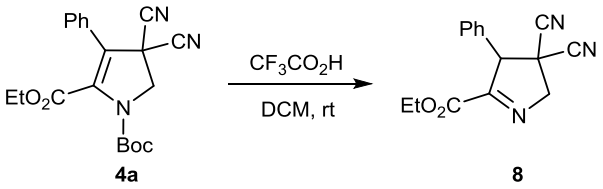
NMR and HRMS data for the product **7**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.42 – 7.36 (m, 3H), 7.33 – 7.28 (m, 2H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H), 4.00 (d, *J* = 12.6 Hz, 1H), 3.94 – 3.80 (m, 2H), 3.75 (d, *J* = 11.4 Hz, 1H), 3.04 (s, 1H), 0.82 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.7, 132.5, 129.5, 129.0, 128.8, 115.2, 113.1, 64.2, 61.7, 58.2, 57.3, 41.6, 13.5.

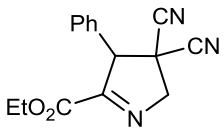
HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{15}H_{15}N_3O_2Na^+$: 292.1056, found: 292.1063.

*5.4 Deprotection of pyrroline **4a***



A glass tube was charged with 2-pyrroline **4a** (36.7 mg, 0.1 mmol) and CF_3CO_2H (57 mg, 0.50 mmol) in DCM (1 mL). The mixture was stirred at room temperature for 1 hour. Then the mixture was added with saturated $NaHCO_3$ (5 mL) and extracted with ethyl acetate (5 mL × 2). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 3/1) to provide the product **8** (21.1 mg, 79% yield) as pure yellow oil, which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*.

ethyl 3,3-dicyano-4-phenyl-3,4-dihydro-2H-pyrrole-5-carboxylate 8



Purification of the crude product *via* column chromatography delivered **8** (21.1 mg) in 79% yield as pure yellow oil.

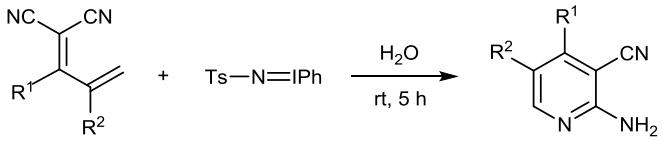
NMR and HRMS data for the product **8**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.51 – 7.40 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 2H), 5.08 (s, 1H), 5.01 (d, *J* = 18.0 Hz, 1H), 4.80 (d, *J* = 17.4 Hz, 1H), 4.33 – 4.20 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.3, 159.7, 130.7, 130.2, 129.9, 127.9, 115.1, 111.9, 70.7, 65.2, 63.0, 39.8, 13.8.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{15}H_{13}N_3O_2Na^+$: 290.0900, found: 290.0902.

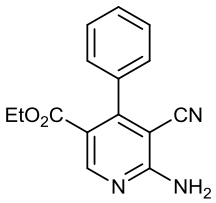
6. General Procedure for the Preparation of 2-Aminopyridine 10



1 **9a** **10**

A glass tube was charged with alkene **1** (0.12 mmol) and iminoiodinane **9a** (37.3 mg, 0.10 mmol) in water (1 mL). The mixture was stirred at room temperature for 5 hours. Then the mixture was extracted with ethyl acetate (10 mL × 2), and the organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 3/1) to afford the corresponding 2-aminopyridine **10a**–**10k** in 64%–92% yields.

ethyl 6-amino-5-cyano-4-phenylnicotinate 10a



Prepared according to the general procedure to afford **10a** (24.3 mg, m. p. = 158 – 163 °C) in 91% yield as yellow solid.

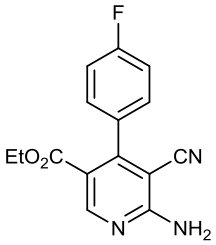
NMR and HRMS data for the product **10a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.83 (s, 1H), 7.50 – 7.43 (m, 3H), 7.31 – 7.26 (m, 2H), 5.65 (s, 2H), 4.05 (q, *J* = 7.8 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.9, 160.8, 156.6, 155.3, 136.2, 129.2, 128.3, 127.6, 117.0, 115.4, 92.6, 61.0, 13.6.

HRMS (ESI-TOF) m/z: **$[M + H]^+$** calculated for $C_{15}H_{13}N_3O_2Na^+$: 268.1081, found: 268.1079.

ethyl 6-amino-5-cyano-4-(4-fluorophenyl)nicotinate 10b



Prepared according to the general procedure to afford **10b** (20.8 mg, m. p. = 157 – 161 °C) in 73% yield as yellow solid.

NMR and HRMS data for the product **10b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.84 (s, 1H), 7.31 – 7.26 (m, 2H), 7.17 (t, *J* = 9.0 Hz,

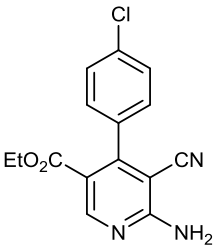
2H), 5.67 (s, 2H), 4.08 (q, *J* = 7.8 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.7, 163.2 (d, J_{C-F} = 247.1 Hz), 160.9, 155.6, 155.5, 132.1 (d, J_{C-F} = 2.9 Hz), 129.7 (d, J_{C-F} = 8.6 Hz), 116.8, 115.5 (d, J_{C-F} = 21.6 Hz), 115.3, 92.7, 61.1, 13.7.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -111.5.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{15}H_{12}FN_3O_2Na^+$: 308.0806, found: 308.0803.

ethyl 6-amino-4-(4-chlorophenyl)-5-cyanonicotinate 10c



Prepared according to the general procedure to afford **10c** (26.3 mg, m. p. = 172 – 177 °C) in 87% yield as yellow solid.

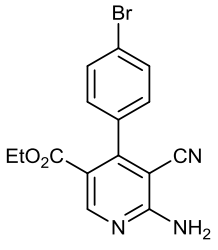
NMR and HRMS data for the product **10c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.85 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.66 (s, 2H), 4.09 (q, *J* = 6.6 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.5, 160.8, 155.6, 155.5, 135.4, 134.6, 129.1, 128.6, 116.6, 115.2, 92.5, 61.1, 13.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{15}H_{12}{}^{35}ClN_3O_2Na^+$: 324.0510, found: 324.0517; calculated for $C_{15}H_{12}{}^{37}ClN_3O_2Na^+$: 326.0481, found: 326.0475.

ethyl 6-amino-4-(4-bromophenyl)-5-cyanonicotinate 10d



Prepared according to the general procedure to afford **10d** (26.0 mg, m. p. = 185 – 189 °C) in 75% yield as yellow solid.

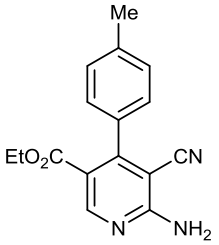
NMR and HRMS data for the product **10d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.85 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.64 (s, 2H), 4.09 (q, *J* = 7.8 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.5, 160.8, 155.6, 155.5, 135.0, 131.5, 129.2, 123.6, 116.4, 115.1, 92.3, 61.2, 13.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{15}H_{12}{}^{79}BrN_3O_2Na^+$: 368.0005, found: 368.0007; calculated for $C_{15}H_{12}{}^{81}BrN_3O_2Na^+$: 369.9985, found: 369.9991.

ethyl 6-amino-5-cyano-4-(p-tolyl)nicotinate 10e



Prepared according to the general procedure to afford **10e** (25.9 mg, m. p. = 189 – 193 ^{o}C) in 92% yield as yellow solid.

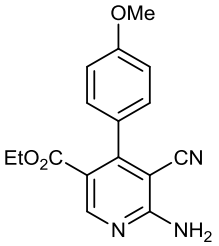
NMR and HRMS data for the product **10e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.80 (s, 1H), 7.27 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.60 (s, 2H), 4.08 (q, *J* = 7.8 Hz, 2H), 2.42 (s, 3H), 1.04 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.9, 160.8, 156.8, 155.1, 139.3, 133.1, 129.0, 127.6, 117.1, 115.6, 92.7, 61.0, 21.4, 13.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{16}H_{15}N_3O_2Na^+$: 304.1056, found: 304.1058.

ethyl 6-amino-5-cyano-4-(4-methoxyphenyl)nicotinate 10f



Prepared according to the general procedure to afford **10f** (25.5 mg, m. p. = 137 – 140 ^{o}C) in 86% yield as pure yellow solid.

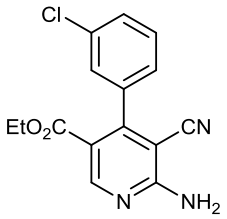
NMR and HRMS data for the product **10f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.78 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 5.59 (s, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.06 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 165.1, 160.9, 160.4, 156.3, 155.1, 129.3, 128.1, 117.3, 115.7, 113.7, 92.6, 61.0, 55.3, 13.8.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{16}H_{15}N_3O_3Na^+$: 320.1006, found: 320.1011.

ethyl 6-amino-4-(3-chlorophenyl)-5-cyanonicotinate 10g



Prepared according to the general procedure to afford **10g** (26.6 mg, m. p. = 165 – 167 ^{o}C) in 88% yield as yellow solid.

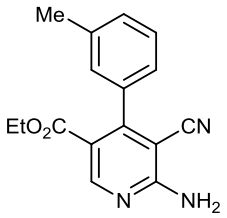
NMR and HRMS data for the product **10g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.86 (s, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 5.76 (s, 2H), 4.08 (q, *J* = 6.6 Hz, 2H), 1.03 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.4, 160.9, 155.6, 155.0, 137.9, 134.2, 129.6, 129.2, 127.8, 125.8, 116.5, 115.0, 92.4, 61.1, 13.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{15}H_{12}{}^{35}ClN_3O_2Na^{+}$: 324.0510, found: 324.0508; calculated for $C_{15}H_{12}{}^{37}ClN_3O_2Na^{+}$: 326.0481, found: 326.0480.

ethyl 6-amino-5-cyano-4-(m-tolyl)nicotinate 10h



Prepared according to the general procedure to afford **10h** (19.1 mg, m. p. = 137 – 142 ^{o}C) in 68% yield as yellow solid.

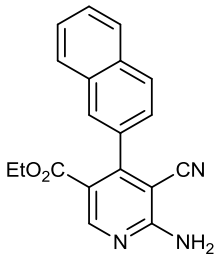
NMR and HRMS data for the product **10h**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.81 (s, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 4.8 Hz, 1H), 7.07 (d, *J* = 6.6 Hz, 2H), 5.60 (s, 2H), 4.06 (q, *J* = 6.6 Hz, 2H), 2.40 (s, 3H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 165.0, 160.8, 156.8, 155.1, 137.9, 136.1, 129.9, 128.18, 128.16, 124.7, 117.1, 115.4, 92.6, 60.9, 21.4, 13.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{16}H_{15}N_3O_2Na^{+}$: 304.1056, found: 304.1053.

ethyl 6-amino-5-cyano-4-(naphthalen-2-yl)nicotinate 10i



Prepared according to the general procedure to afford **10i** (23.1 mg, m. p. = 176 – 180 ^{o}C) in 73% yield as yellow solid.

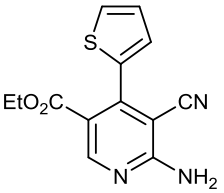
NMR and HRMS data for the product **10i**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.87 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 9.6 Hz, 2H), 7.79 (s, 1H), 7.62 – 7.48 (m, 2H), 7.36 (d, *J* = 6.6 Hz, 1H), 5.66 (s, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 0.87 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.9, 160.9, 156.6, 155.3, 133.6, 133.3, 132.7, 128.4, 127.94, 127.85, 127.1, 127.0, 126.6, 125.3, 117.1, 115.5, 92.8, 61.0, 13.6.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{19}H_{15}N_3O_2Na^+$: 340.1056, found: 340.1058.

ethyl 6-amino-5-cyano-4-(thiophen-2-yl)nicotinate 10j



Prepared according to the general procedure to afford **10j** (17.5 mg, m. p. = 138 – 142 ^{o}C) in 64% yield as yellow solid.

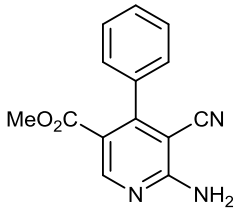
NMR and HRMS data for the product **10j**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.75 (s, 1H), 7.53 (d, *J* = 6.0 Hz, 1H), 7.20 (d, *J* = 3.0 Hz, 1H), 7.14 (dd, *J* = 4.8, 4.2 Hz, 1H), 5.62 (s, 2H), 4.13 (q, *J* = 7.8 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.9, 160.8, 154.9, 149.0, 135.4, 128.6, 128.2, 127.3, 118.1, 115.3, 93.1, 61.3, 13.7.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{13}H_{11}N_3O_2SNa^+$: 296.0464, found: 296.0460.

methyl 6-amino-5-cyano-4-phenylnicotinate 10k



Prepared according to the general procedure to afford **10k** (22.5 mg, m. p. = 175 – 179 ^{o}C) in 89% yield as pure yellow solid.

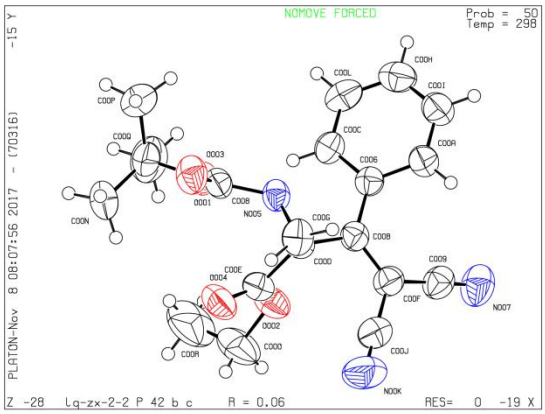
NMR and HRMS data for the product **10k**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.83 (s, 1H), 7.50 – 7.46 (m, 3H), 7.30 – 7.26 (m, 2H), 5.64 (s, 2H), 3.63 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 165.1, 160.9, 156.9, 155.3, 135.9, 129.3, 128.3, 127.6, 116.5, 115.3, 92.8, 52.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^{+}$** calculated for $C_{14}H_{11}N_3O_2Na^{+}$: 276.0743, found: 276.0745.

8. Crystal Data and Structure Refinement for the Representative Products 3a, 4a and 10a



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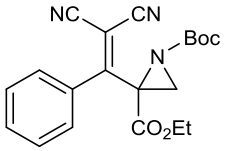
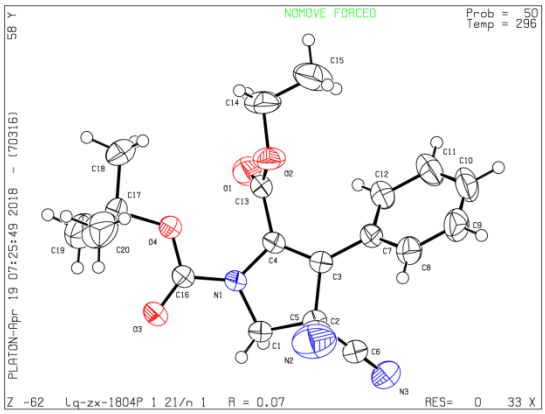


3a
CCDC 1905939

Identification code	**3a**
Empirical formula	$C_{20}H_{21}N_3O_4$
Formula weight	367.40
Temperature/K	297.8(2)
Crystal system	tetragonal
Space group	$P4_2bc$
a/Å	21.7832(3)
b/Å	21.7832(3)
c/Å	8.49552(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4031.20(13)
Z	8
ρ_{calc}g/cm^3	1.211
μ/mm^{-1}	0.704
F(000)	1552.0
Crystal size/mm^3	0.7 × 0.35 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.118 to 145.272
Index ranges	$-26 \le h \le 26$, $-26 \le k \le 26$, $-7 \le l \le 10$
Reflections collected	21310
Independent reflections	3049 [R_{int} = 0.0432, R_{sigma} = 0.0224]
Data/restraints/parameters	3049/1/248
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0634, wR_2 = 0.1510
Final R indexes [all data]	R_1 = 0.0659, wR_2 = 0.1561
Largest diff. peak/hole / e Å^{-3}	0.29/-0.41



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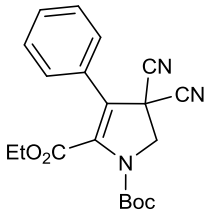
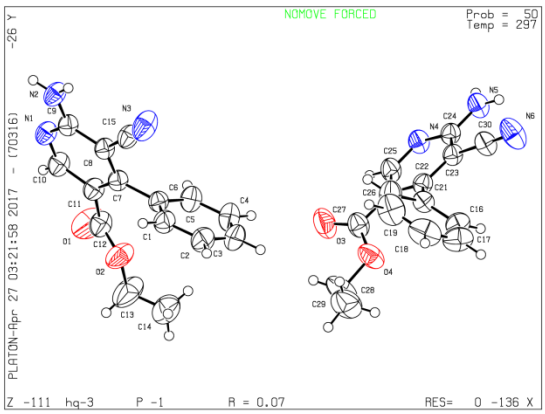


4a
CCDC 1905940

Identification code	**4a**
Empirical formula	$C_{20}H_{21}N_3O_4$
Formula weight	367.40
Temperature/K	295.91(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.8238(4)
b/Å	10.3557(3)
c/Å	17.8199(7)
α/°	90
β/°	96.908(3)
γ/°	90
Volume/Å^3	1982.89(12)
Z	4
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	0.715
F(000)	776.0
Crystal size/mm^3	0.7 × 0.6 × 0.4
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10 to 144.73
Index ranges	$-13 \le h \le 13$, $-8 \le k \le 12$, $-21 \le l \le 17$
Reflections collected	10517
Independent reflections	3854 [R_{int} = 0.0237, R_{sigma} = 0.0228]
Data/restraints/parameters	3854/0/248
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0671, wR_2 = 0.1697
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1800
Largest diff. peak/hole / e Å^{-3}	0.30/-0.41



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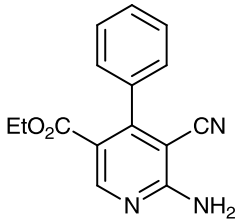


10a (dimer)
CCDC 1905941

Identification code	**10a**
Empirical formula	$C_{30}H_{26}N_6O_4$
Formula weight	534.57
Temperature/K	296.9(6)
Crystal system	triclinic
Space group	P-1
a/Å	6.9944(3)
b/Å	7.8586(4)
c/Å	26.1858(11)
α/°	85.696(4)
β/°	89.837(4)
γ/°	79.658(4)
Volume/Å^3	1411.88(11)
Z	2
ρ_{calc}g/cm^3	1.257
μ/mm^{-1}	0.704
F(000)	560.0
Crystal size/mm^3	0.65 × 0.5 × 0.4
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.164 to 144.908
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 8, -30 ≤ l ≤ 32
Reflections collected	15449
Independent reflections	5505 [R_{int} = 0.0409, R_{sigma} = 0.0344]
Data/restraints/parameters	5505/0/363
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0706, wR_2 = 0.1941
Final R indexes [all data]	R_1 = 0.0788, wR_2 = 0.2078
Largest diff. peak/hole / e Å^{-3}	0.29/-0.38

9. References and Notes

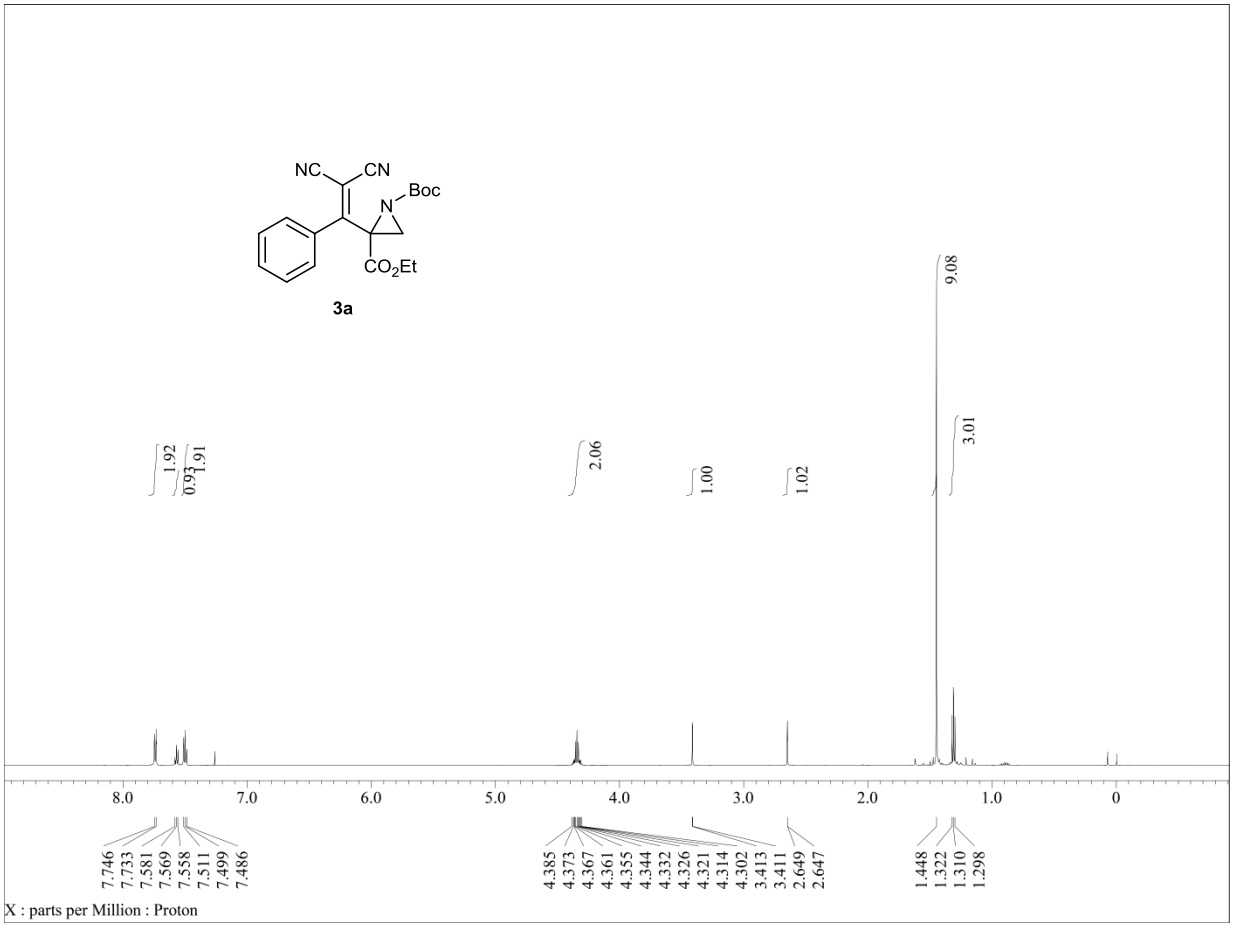
[1] (a) E. Krell, *Handbook of Laboratory Distillation*, Elseriver Publishing Company, Amsterdam-London-New York, 1963; (b) M. J. Rosengart, *The Technique of Distillation and Rectification in the Laboratory*, VEB Verlag Technik, Berlin, 1954; (c) F. Stage, *Angew. Chem.* 1947, **19**, 175.

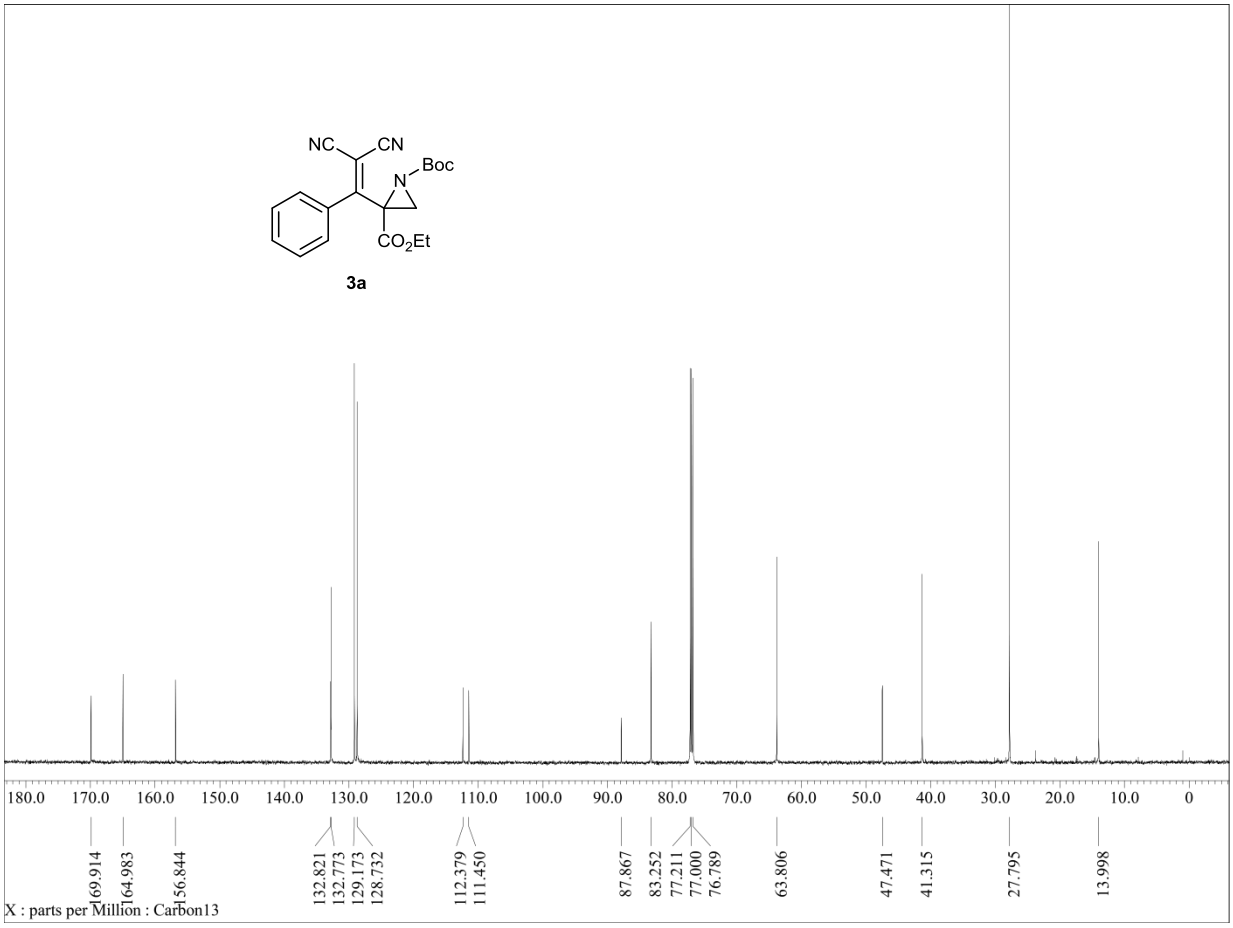
[2] X. Jiang, D. Fu, X. Shi, S. Wang, and R. Wang, *Chem. Commun.* 2011, **47**, 8289.

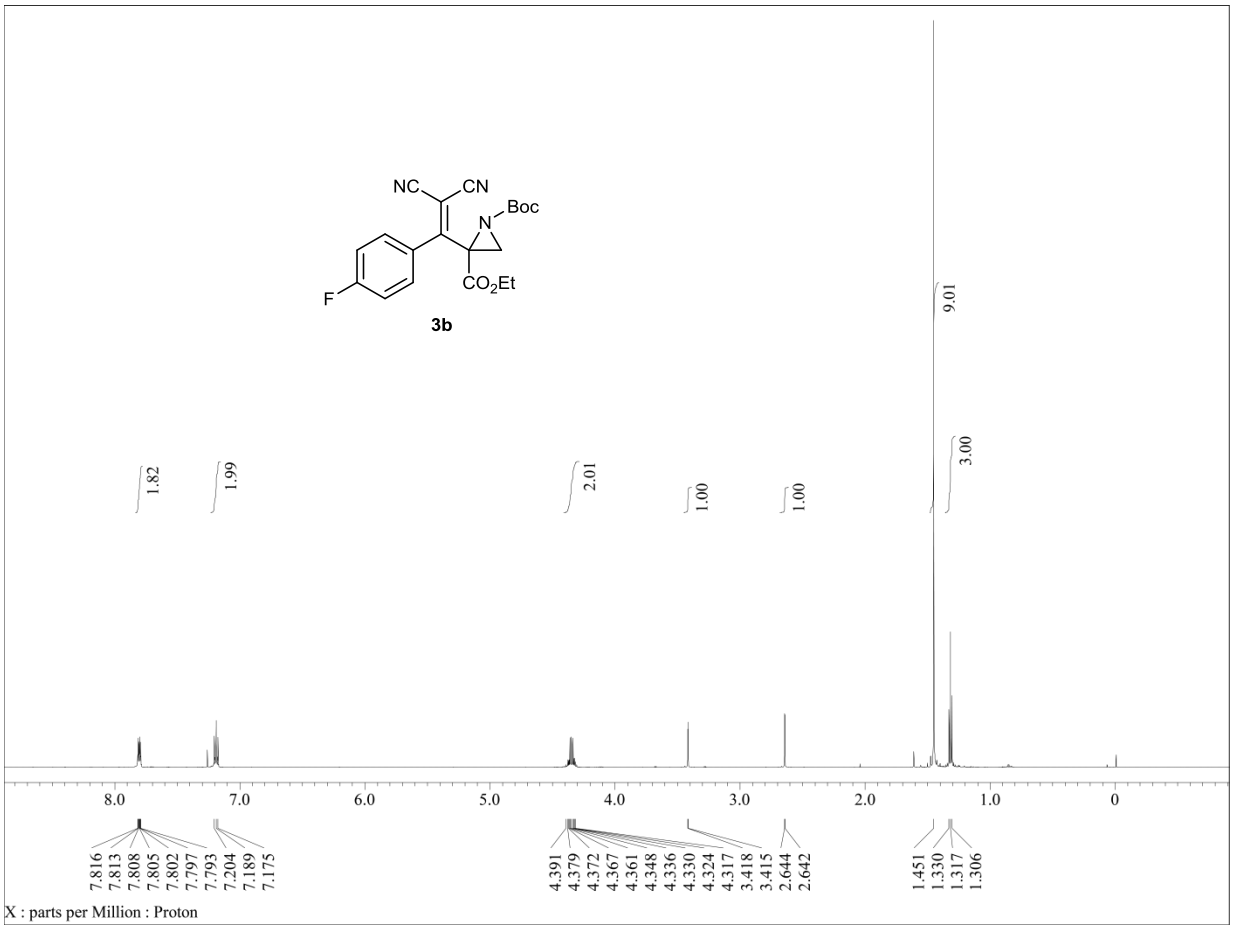
[3] (a) I. G. Molnár, E. Tanzer, C. Daniliuc, and R. Gilmour, *Chem. Eur. J*. 2014, **20**, 794; (b) Masruri, A. C. Willis, and M. D. McLeod, *J. Org. Chem.* 2012, **77**, 8480; (c) Ł. Albrecht, H. Jiang, G. Dickmeiss, B. Gschwend, S. G. Hansen and K. A. Jørgensen, *J. Am. Chem. Soc.* 2010, **132**, 9188.

[4] A. Yoshimura, K. R. Middleton, M. W. Luedtke, C. J. Zhu, and V. V. Zhdankin, *J. Org. Chem.* 2012, **77**, 2087.

10. NMR Spectra






NC
CN
Boc
N
CO2Et
F
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1.82
1.99
2.01
1.00
1.00
9.01
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.816
7.813
7.808
7.805
7.802
7.797
7.793
7.204
7.189
7.175
4.391
4.379
4.372
4.367
4.361
4.348
4.336
4.330
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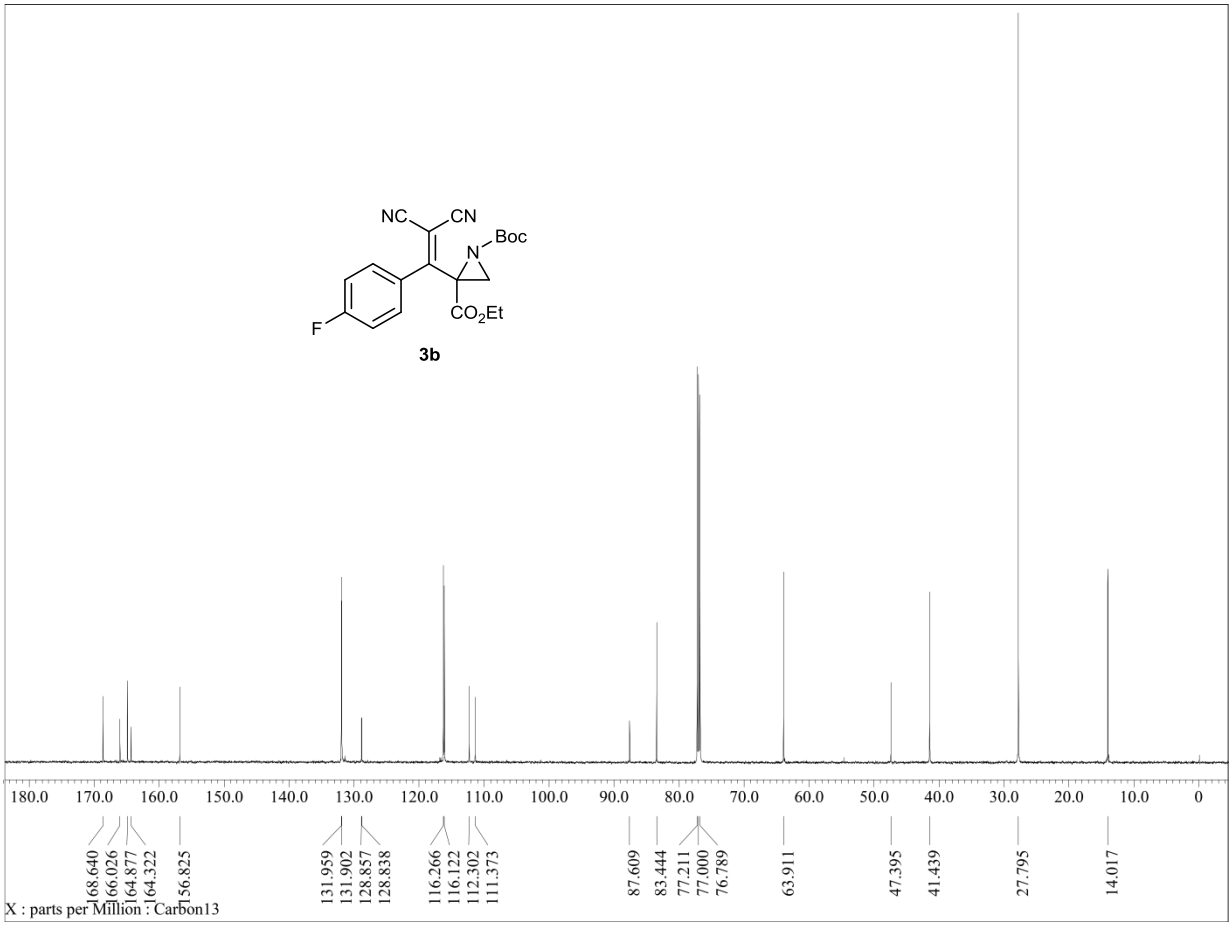
1.451
1.330
1.317
1.306
X : parts per Million : Proton


NC
CN
Boc
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CO2Et
F
3b
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160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.640
166.026
164.877
164.322
156.825
131.959
131.902
128.857
128.838
116.266
116.122
112.302
111.373
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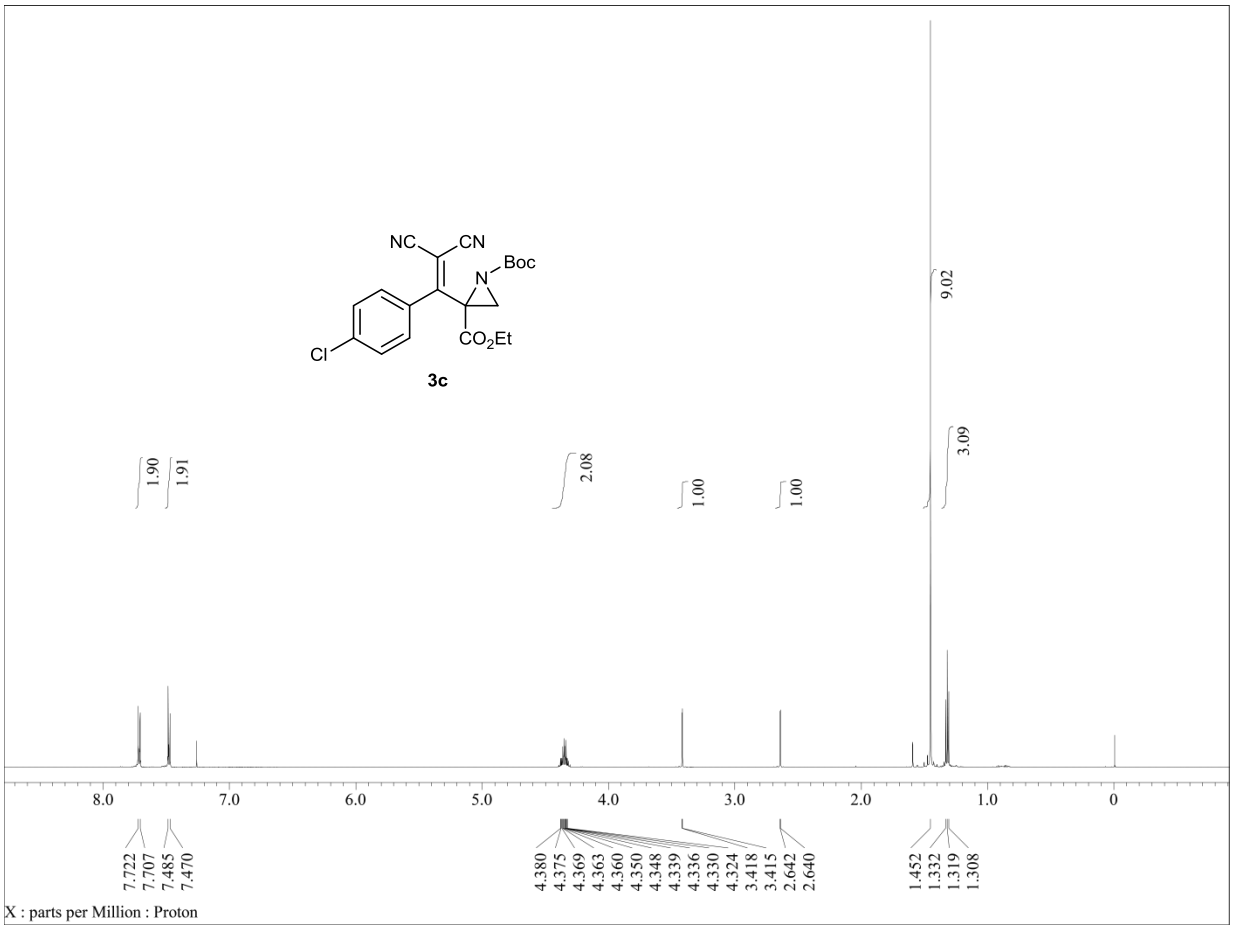
14.017
X : parts per Million : Carbon13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Cl
CO2Et
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2.08
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1.00
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
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7.722
7.707
7.485
7.470
4.380
4.375
4.369
4.363
4.360
4.350
4.348
4.339
4.336
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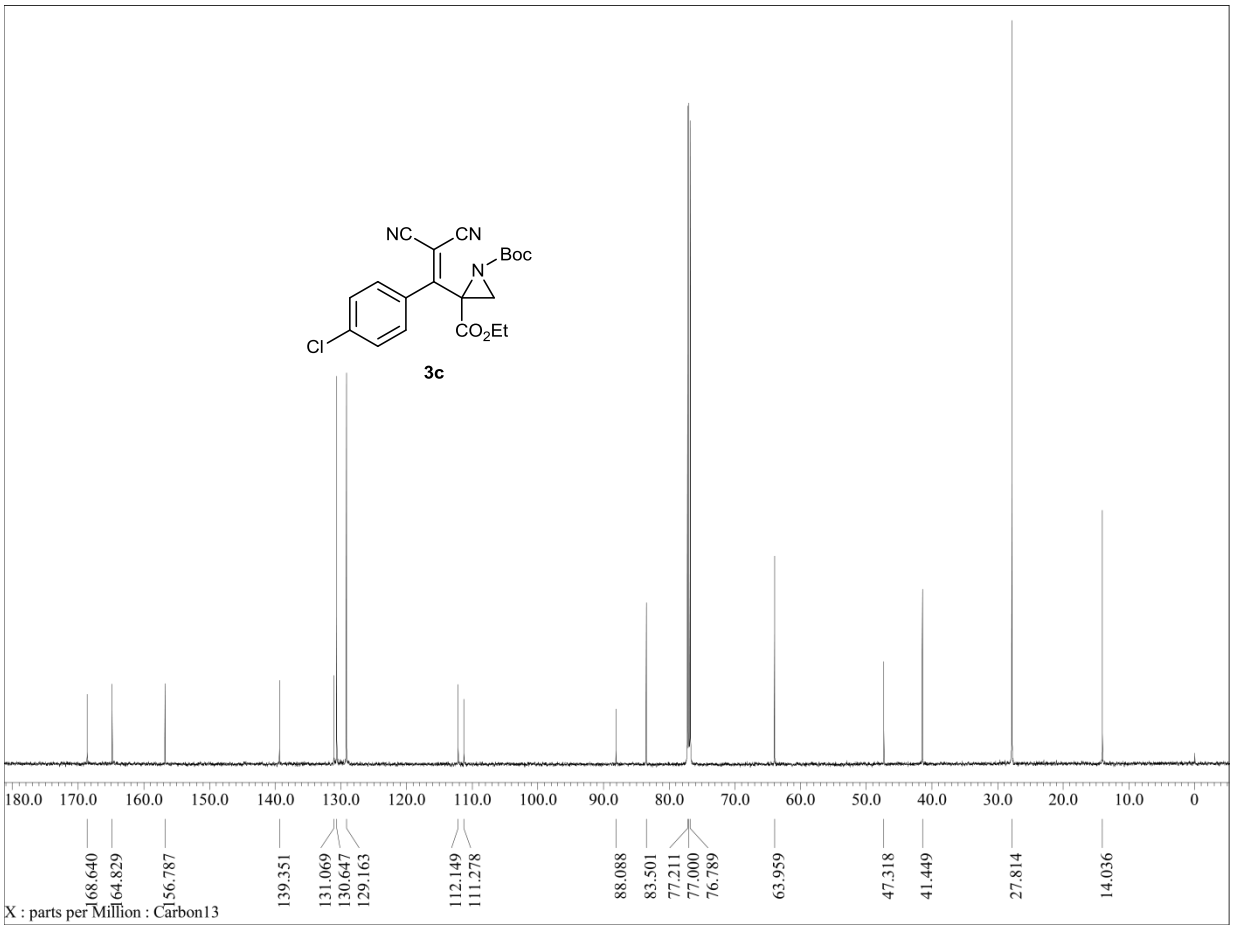
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Boc
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Cl
CO2Et
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70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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156.787
139.351
131.069
130.647
129.163
112.149
111.278
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14.036
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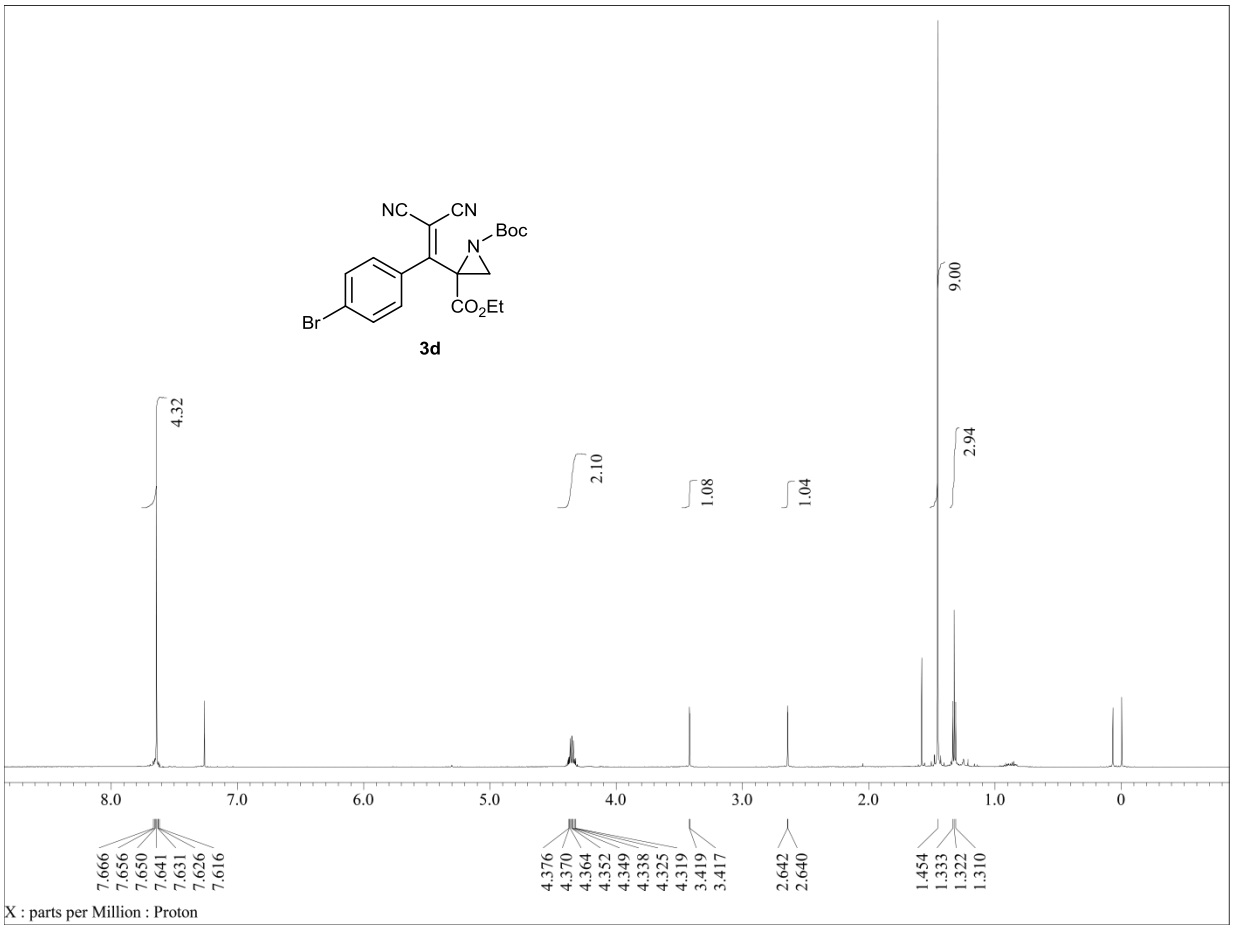
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.666
7.656
7.650
7.641
7.631
7.626
7.616
4.376
4.370
4.364
4.352
4.349
4.338
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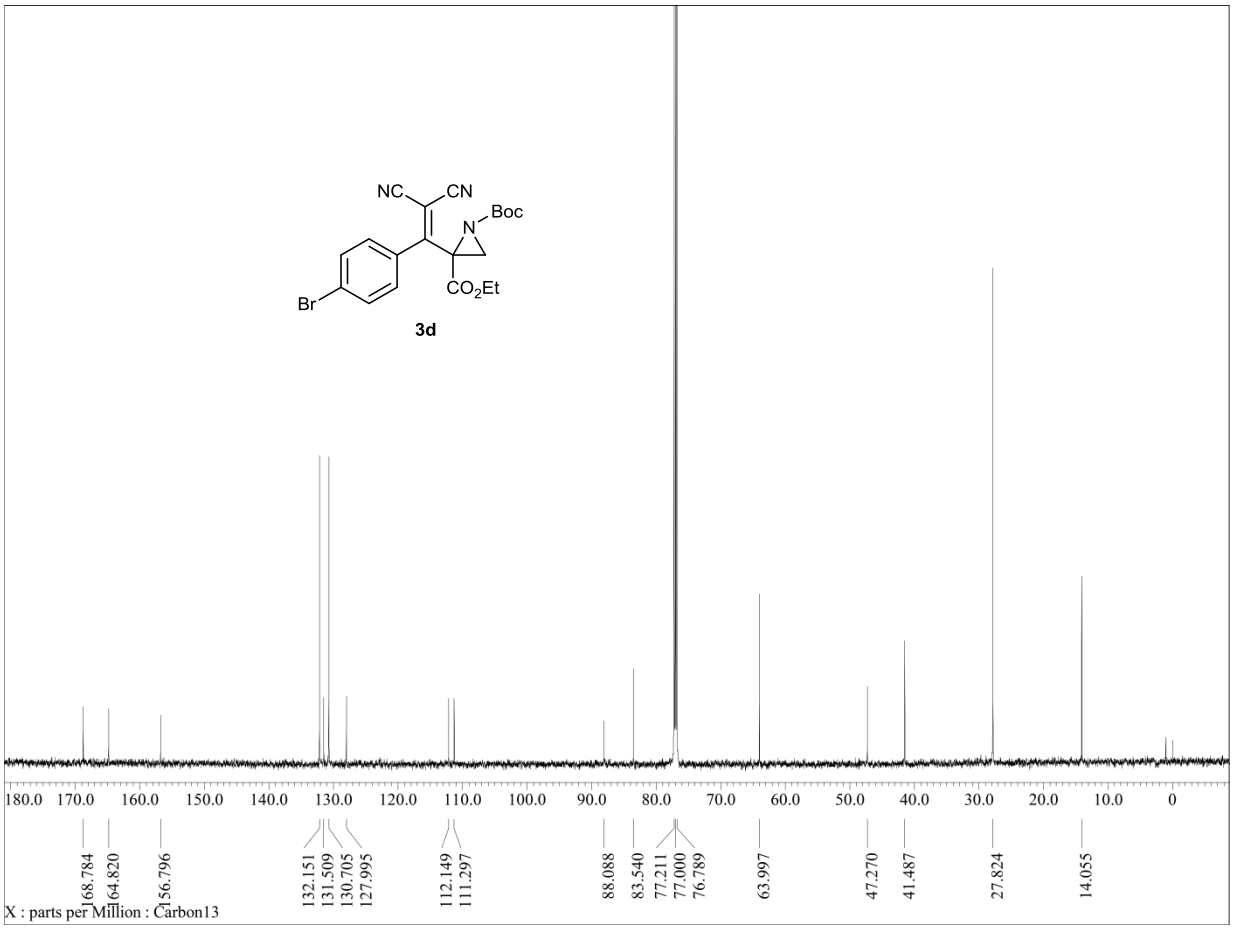
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Boc
N
Br
CO2Et
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150.0
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130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.784
164.820
156.796
132.151
131.509
130.705
127.995
112.149
111.297
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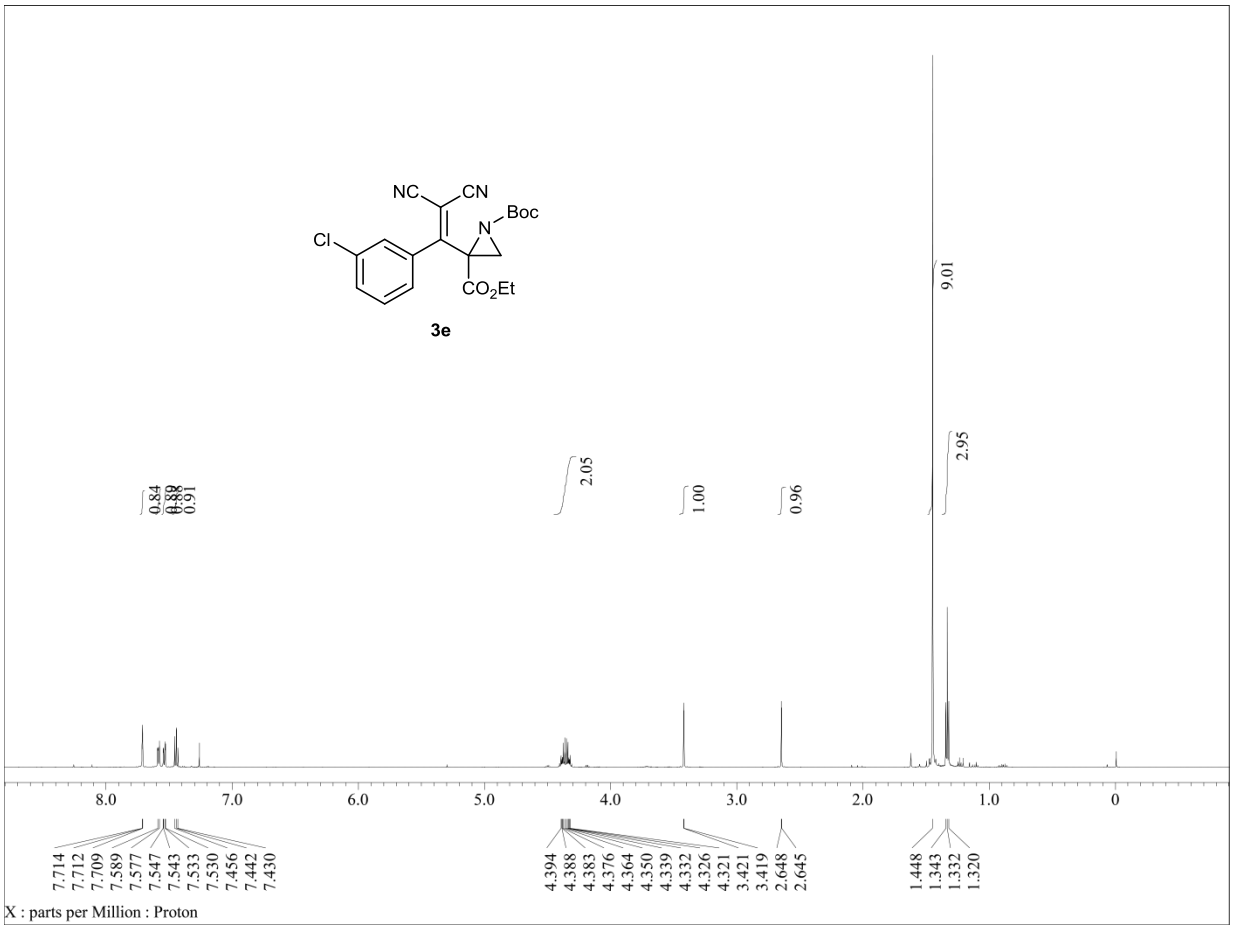
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Cl
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0.91
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.712
7.709
7.589
7.577
7.547
7.543
7.533
7.530
7.456
7.442
7.430
4.394
4.388
4.383
4.376
4.364
4.350
4.339
4.332
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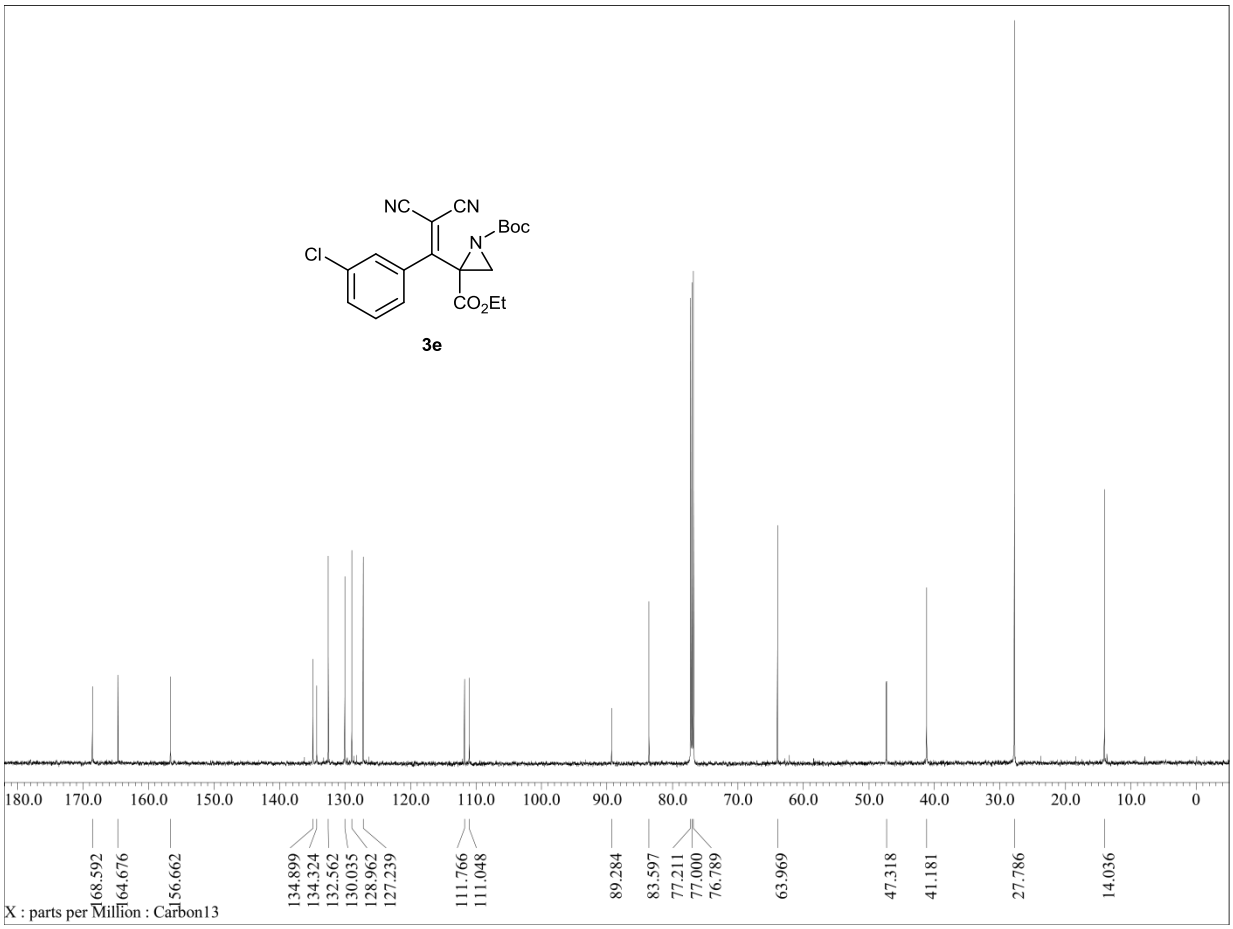
1.320
X : parts per Million : Proton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Boc
N
Cl
CO2Et
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130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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156.662
134.899
134.324
132.562
130.035
128.962
127.239
111.766
111.048
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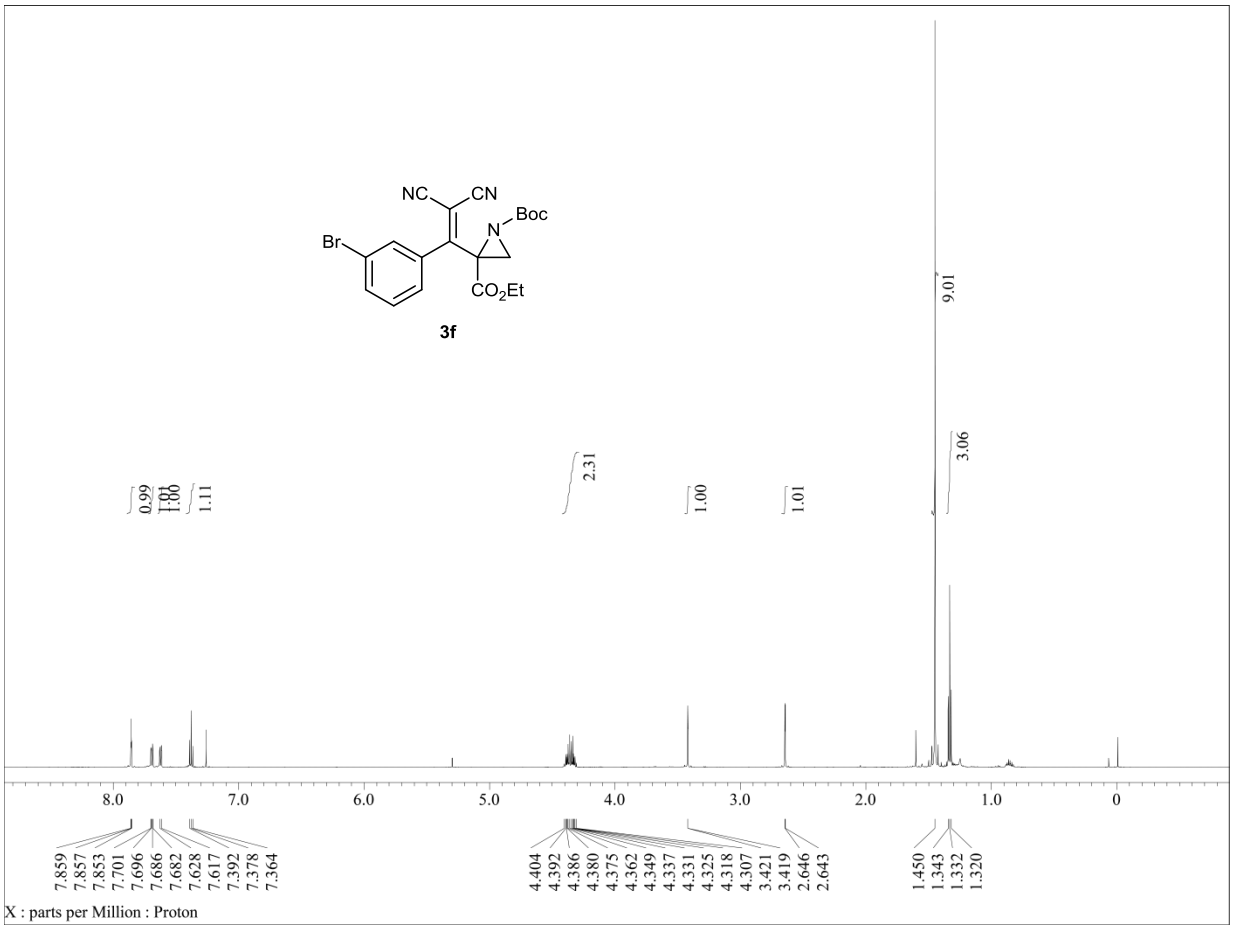
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N
Br
CO2Et
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1.00
1.01
0.99
1.00
1.11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.859
7.857
7.853
7.701
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7.686
7.682
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7.378
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4.392
4.386
4.380
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4.337
4.331
4.325
4.318
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3.419
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2.643
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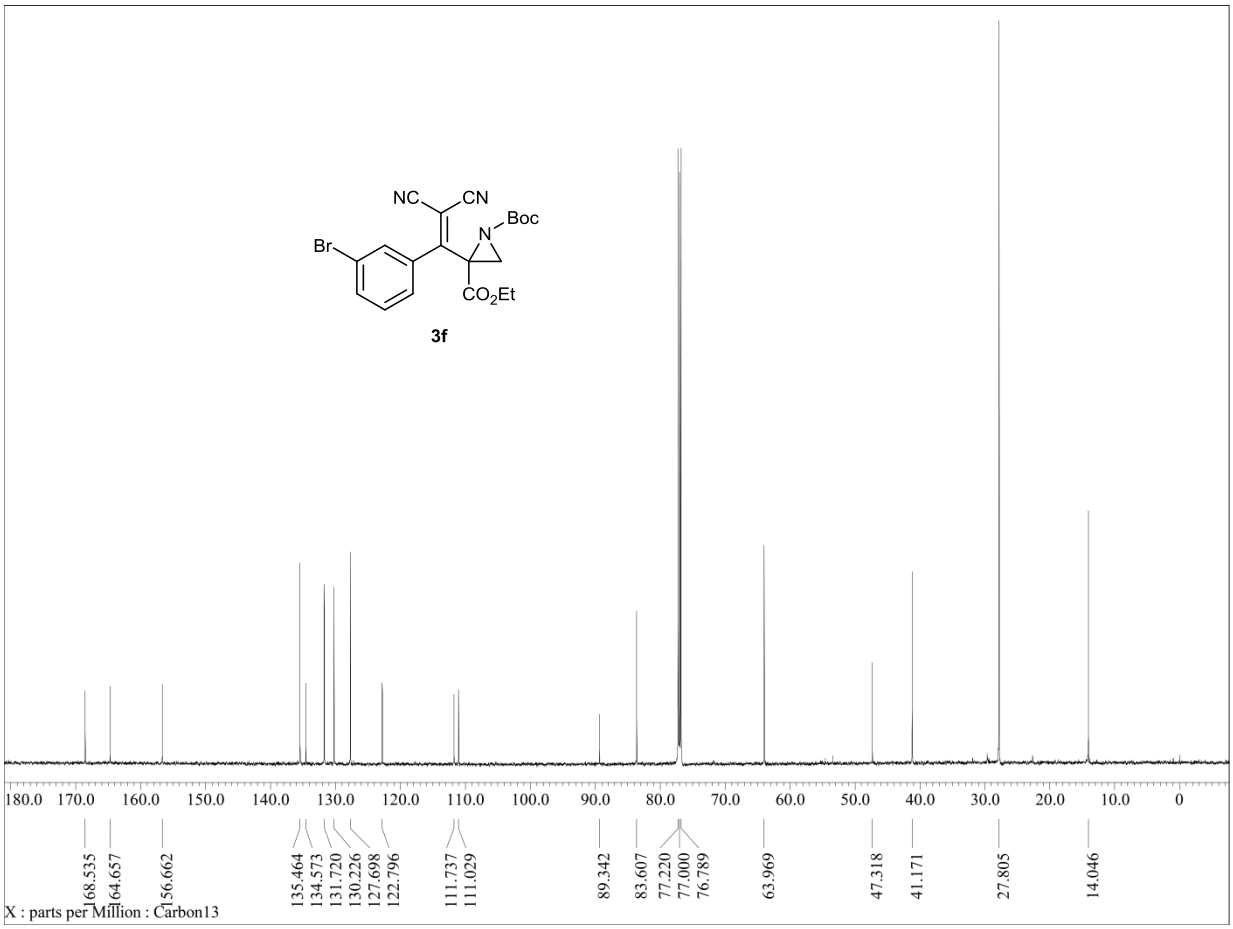
1.343
1.332
1.320
X : parts per Million : Proton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Boc
N
Br
CO2Et
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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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164.657
156.662
135.464
134.573
131.720
130.226
127.698
122.796
111.737
111.029
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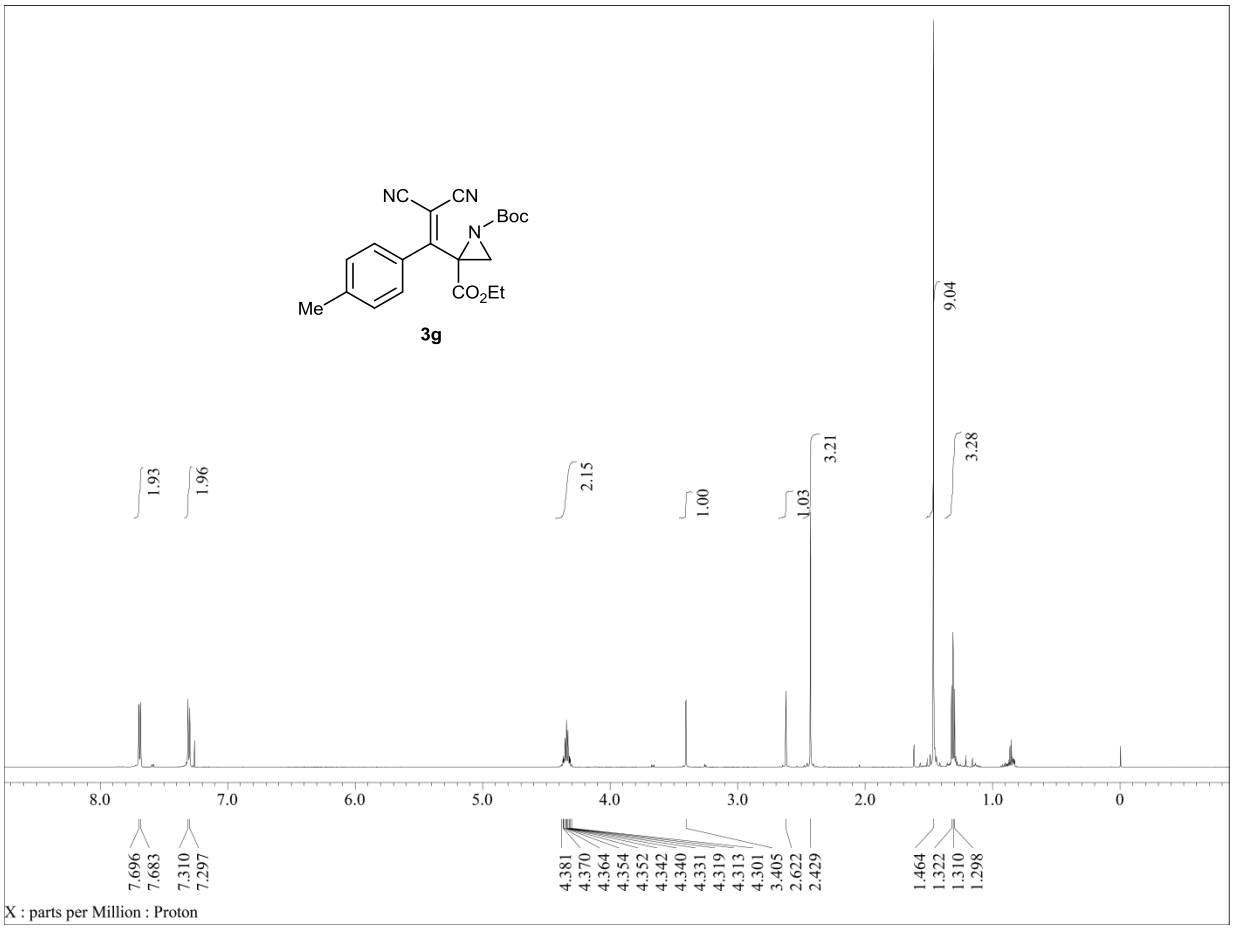
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Me
CO2Et
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1.03
3.21
9.04
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2.0
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4.342
4.340
4.331
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1.298
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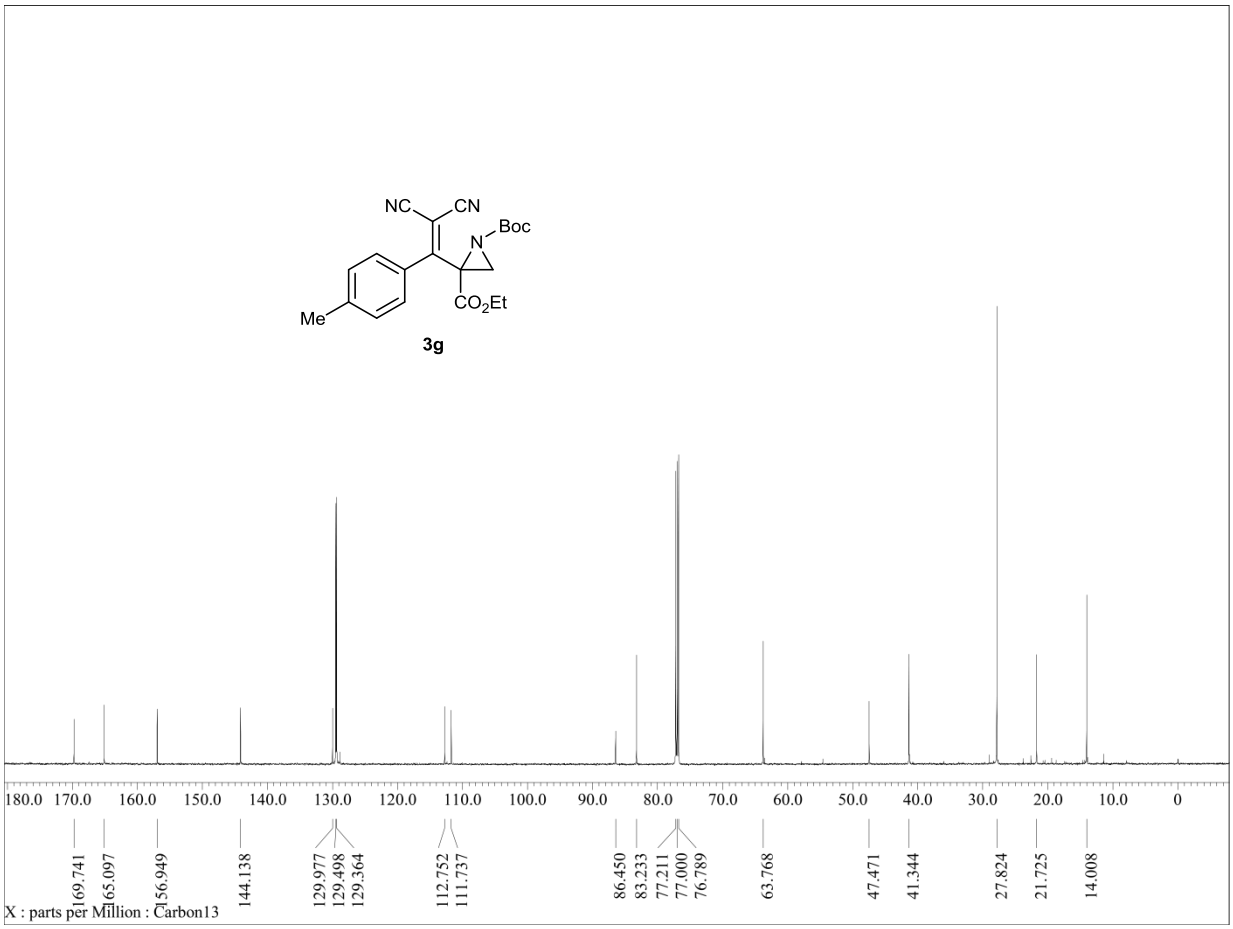
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Boc
N
Me
CO2Et
3g
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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.741
165.097
156.949
144.138
129.977
129.498
129.364
112.752
111.737
86.450
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76.789
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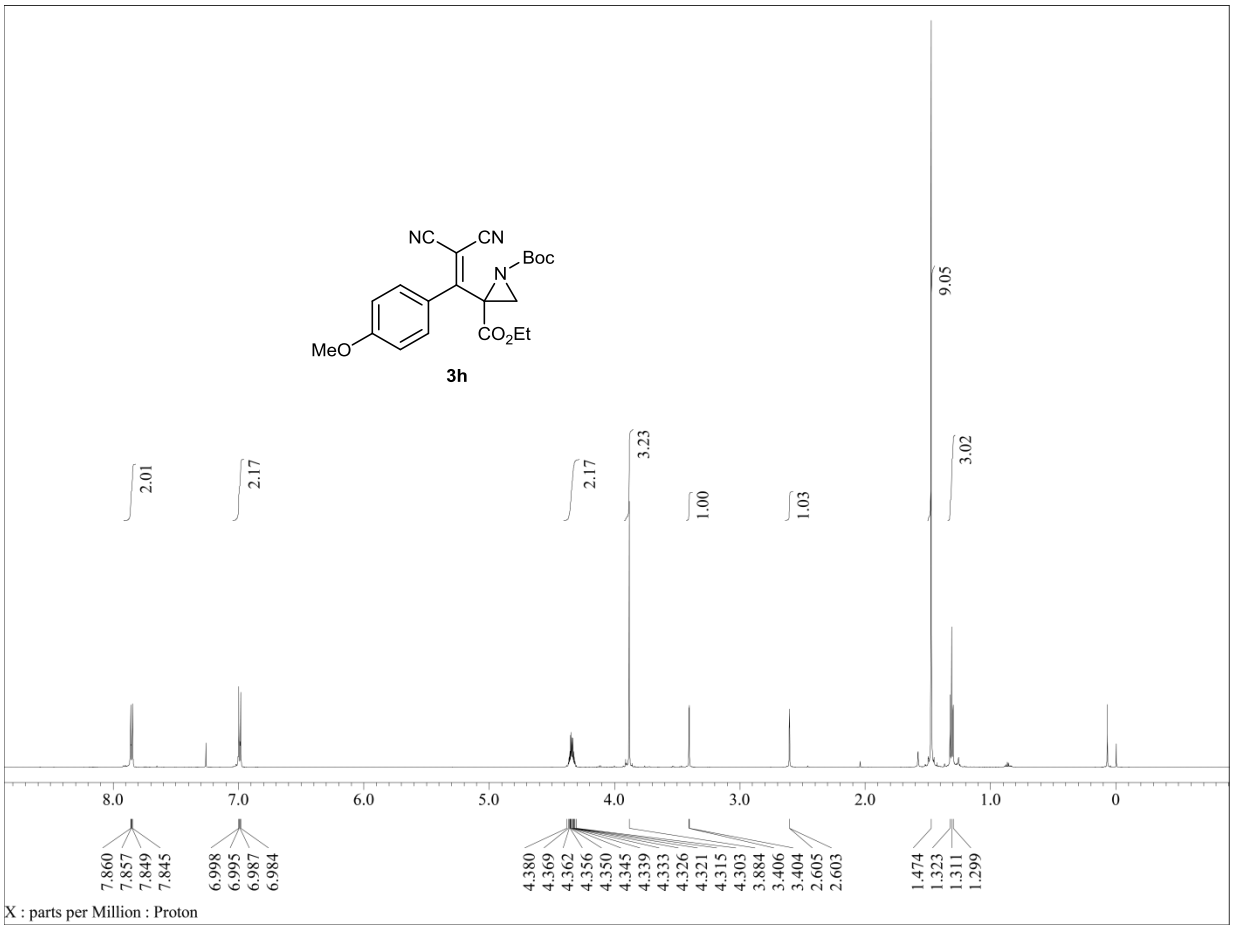
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Boc
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MeO
CO2Et
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1.00
1.03
9.05
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.860
7.857
7.849
7.845
6.998
6.995
6.987
6.984
4.380
4.369
4.362
4.356
4.350
4.345
4.339
4.333
4.326
4.321
4.315
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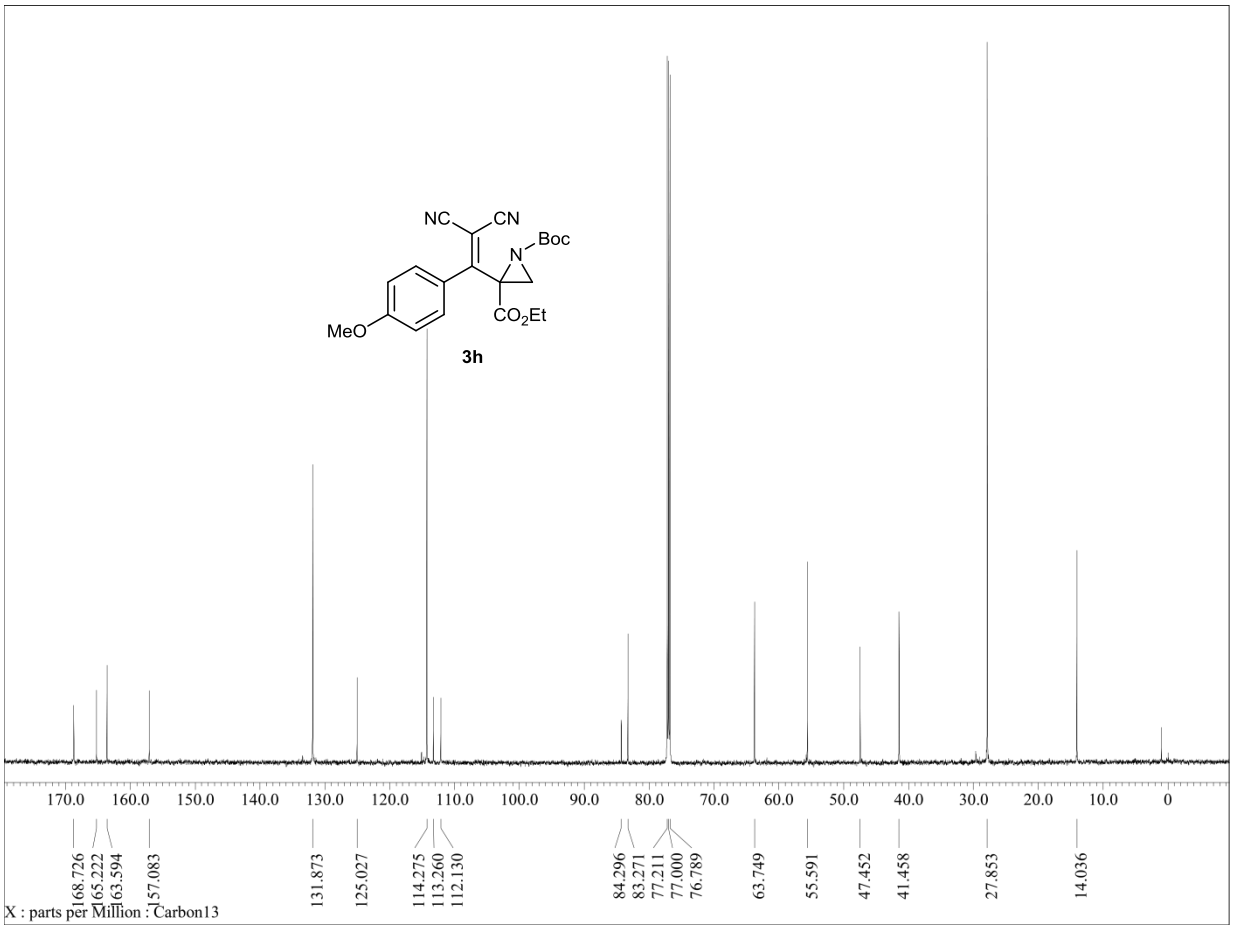
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Boc
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MeO
CO2Et
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130.0
120.0
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113.260
112.130
84.296
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76.789
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55.591
47.452
41.458
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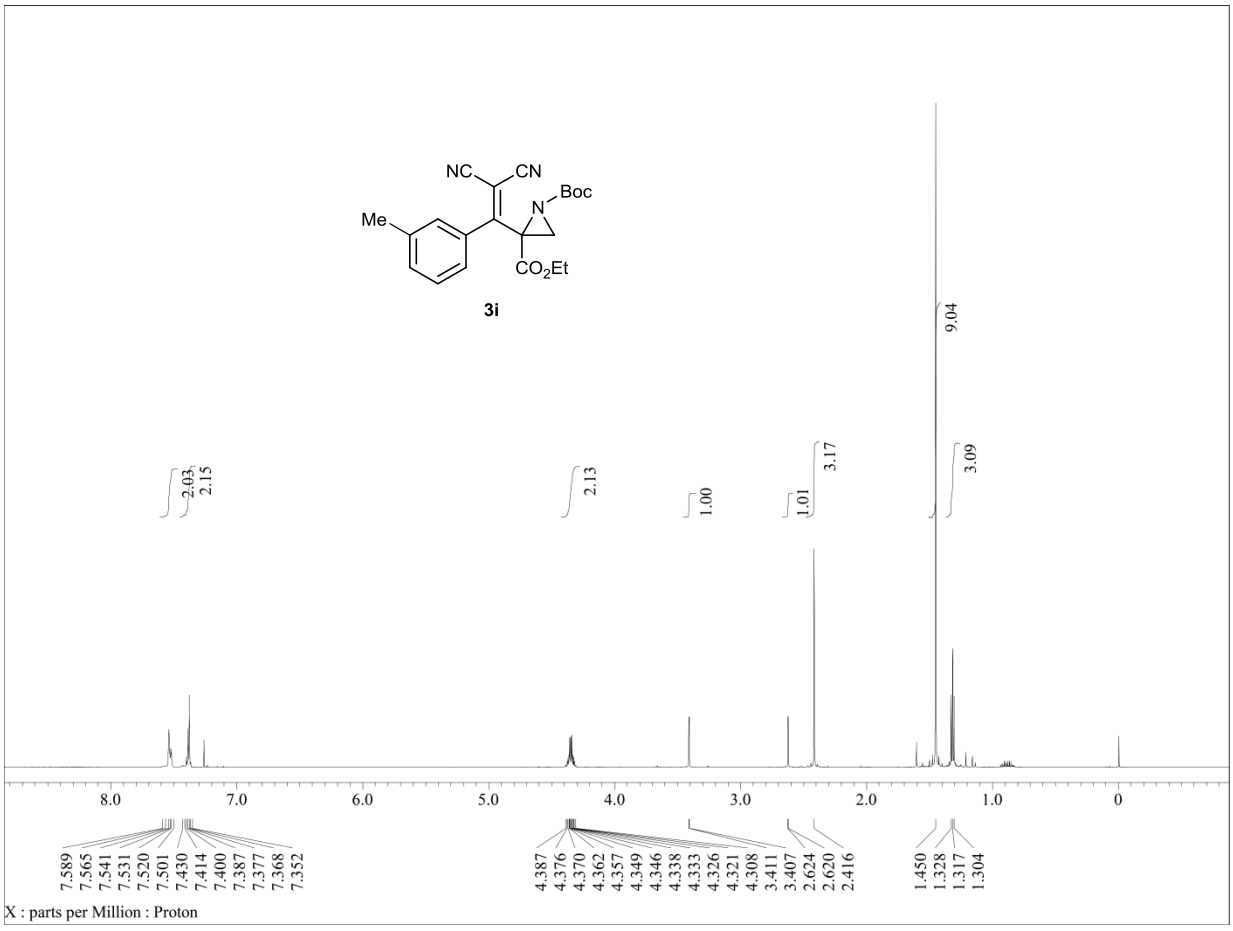
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Me
CO2Et
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3.09
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2.15
2.13
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1.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.589
7.565
7.541
7.531
7.520
7.501
7.430
7.414
7.400
7.387
7.377
7.368
7.352
4.387
4.376
4.370
4.362
4.357
4.349
4.346
4.338
4.333
4.326
4.321
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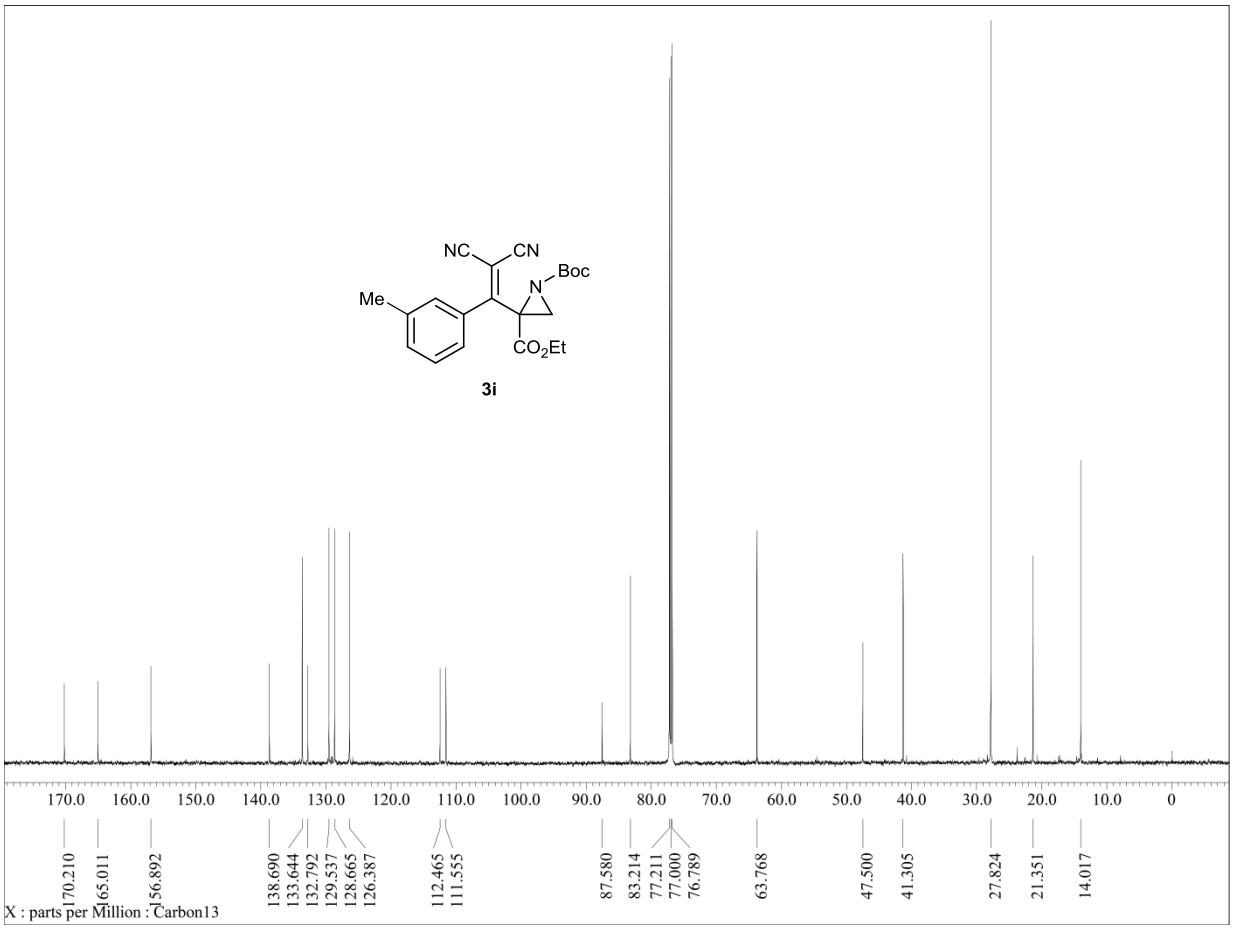
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N
Me
CO2Et
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120.0
110.0
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60.0
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30.0
20.0
10.0
0
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165.011
156.892
138.690
133.644
132.792
129.537
128.665
126.387
112.465
111.555
87.580
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76.789
63.768
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41.305
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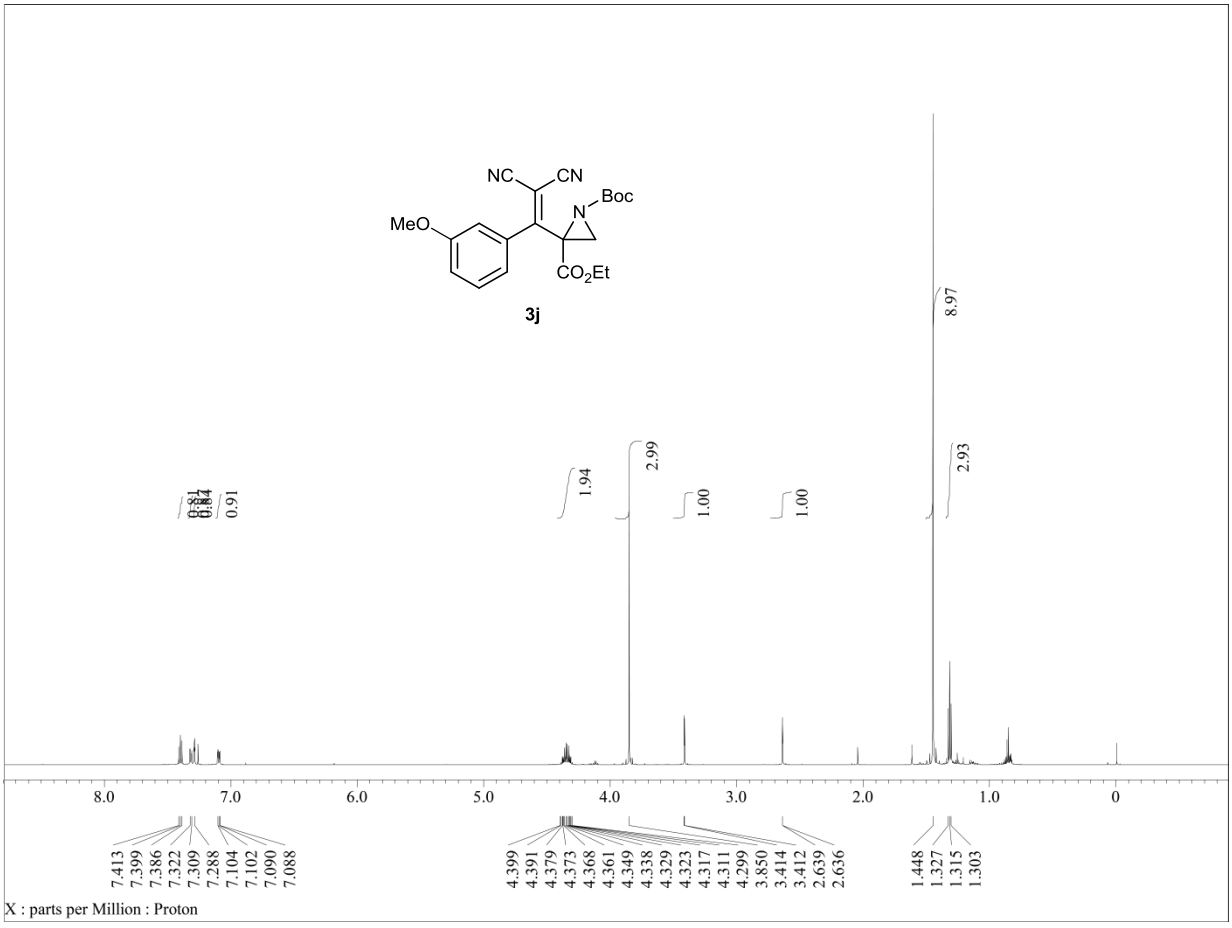
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MeO
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4.0
3.0
2.0
1.0
0
7.413
7.399
7.386
7.322
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7.102
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4.379
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4.349
4.338
4.329
4.323
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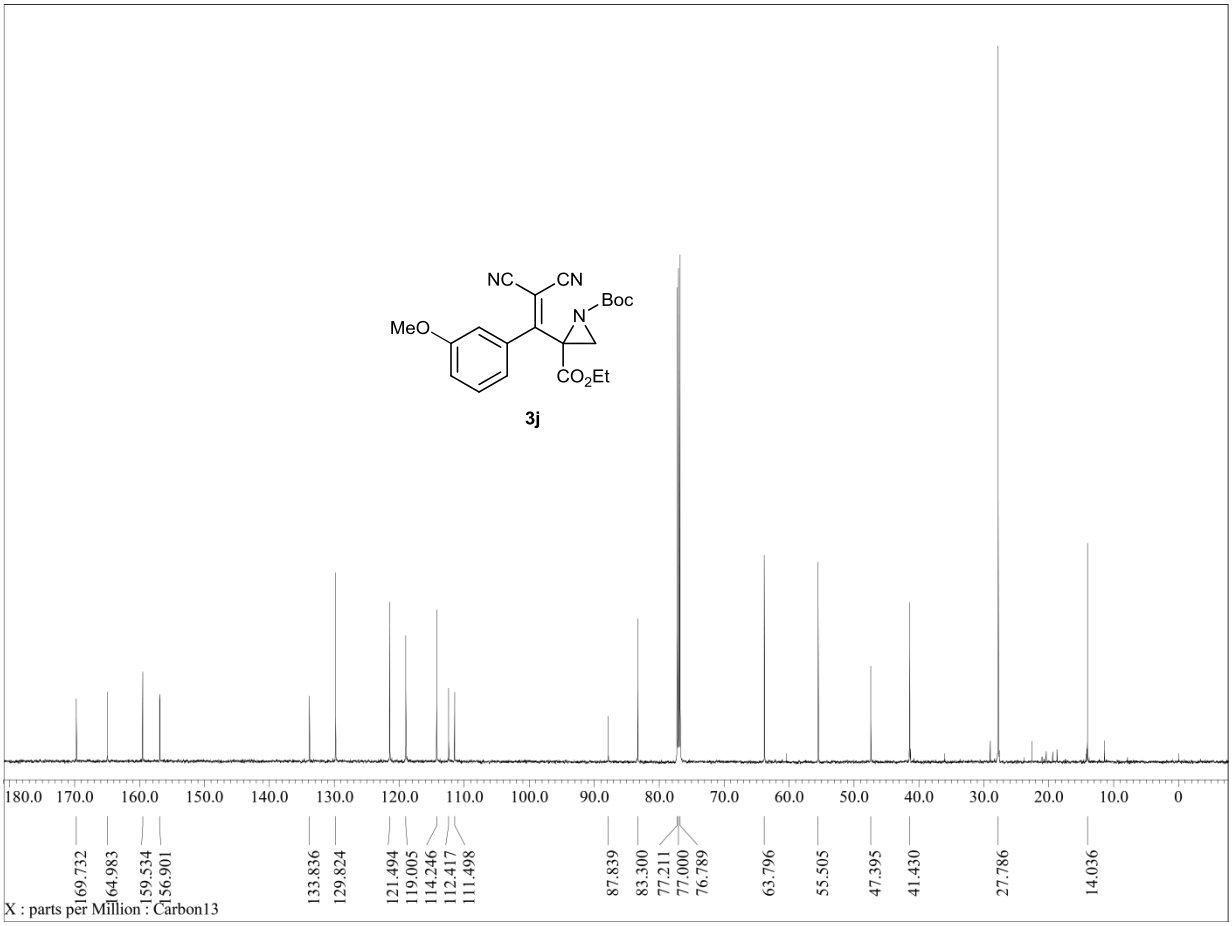
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MeO
CO2Et
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140.0
130.0
120.0
110.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.732
164.983
159.534
156.901
133.836
129.824
121.494
119.005
114.246
112.417
111.498
87.839
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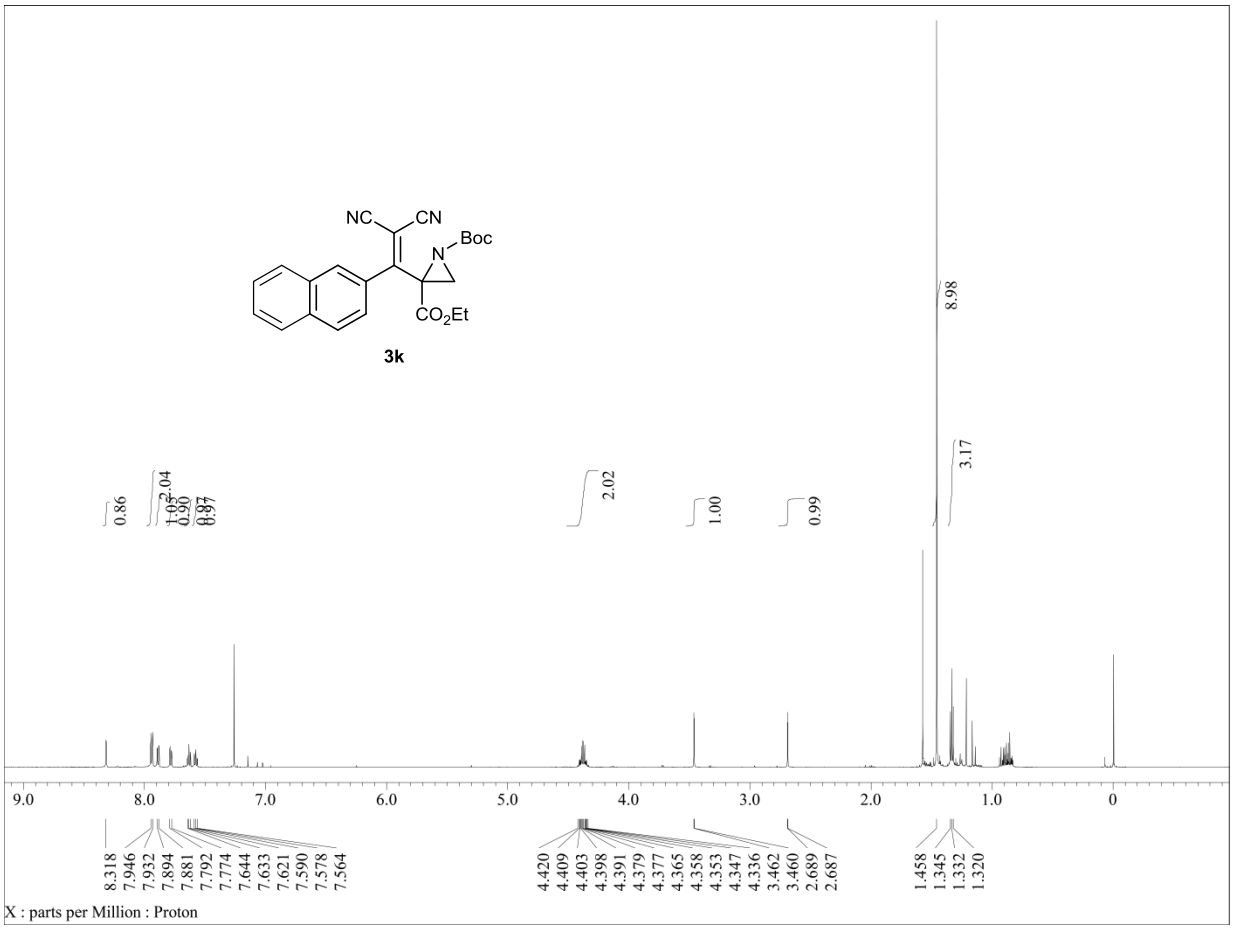
76.789
63.796
55.505
47.395
41.430
27.786
14.036
X : parts per Million : Carbon13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4.0
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2.0
1.0
0
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7.644
7.633
7.621
7.590
7.578
7.564
4.420
4.409
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4.398
4.391
4.379
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4.353
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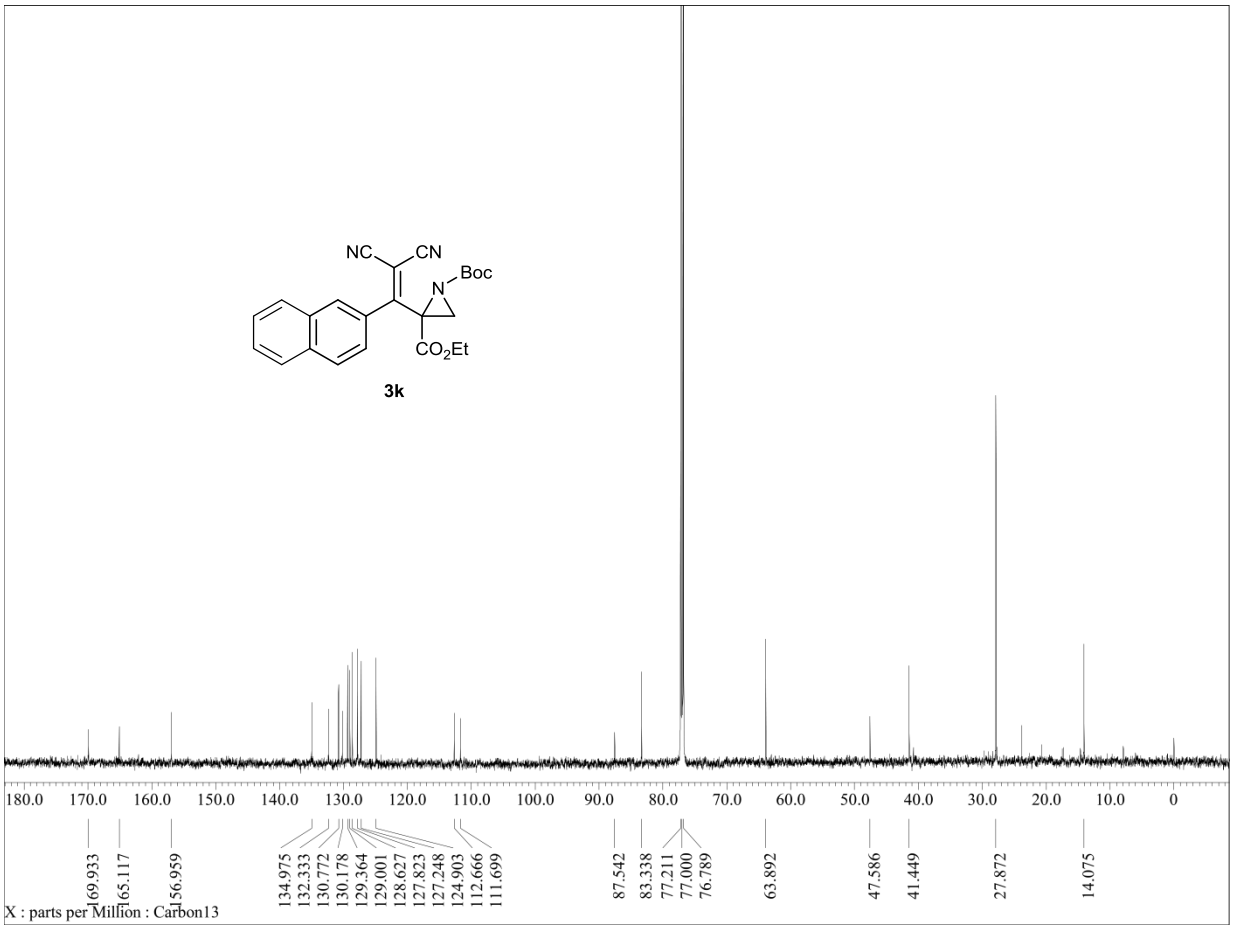
1.320
X : parts per Million : Proton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CO2Et
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70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.933
165.117
156.959
134.975
132.333
130.772
130.178
129.364
129.001
128.627
127.823
127.248
124.903
112.666
111.699
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76.789
63.892
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41.449
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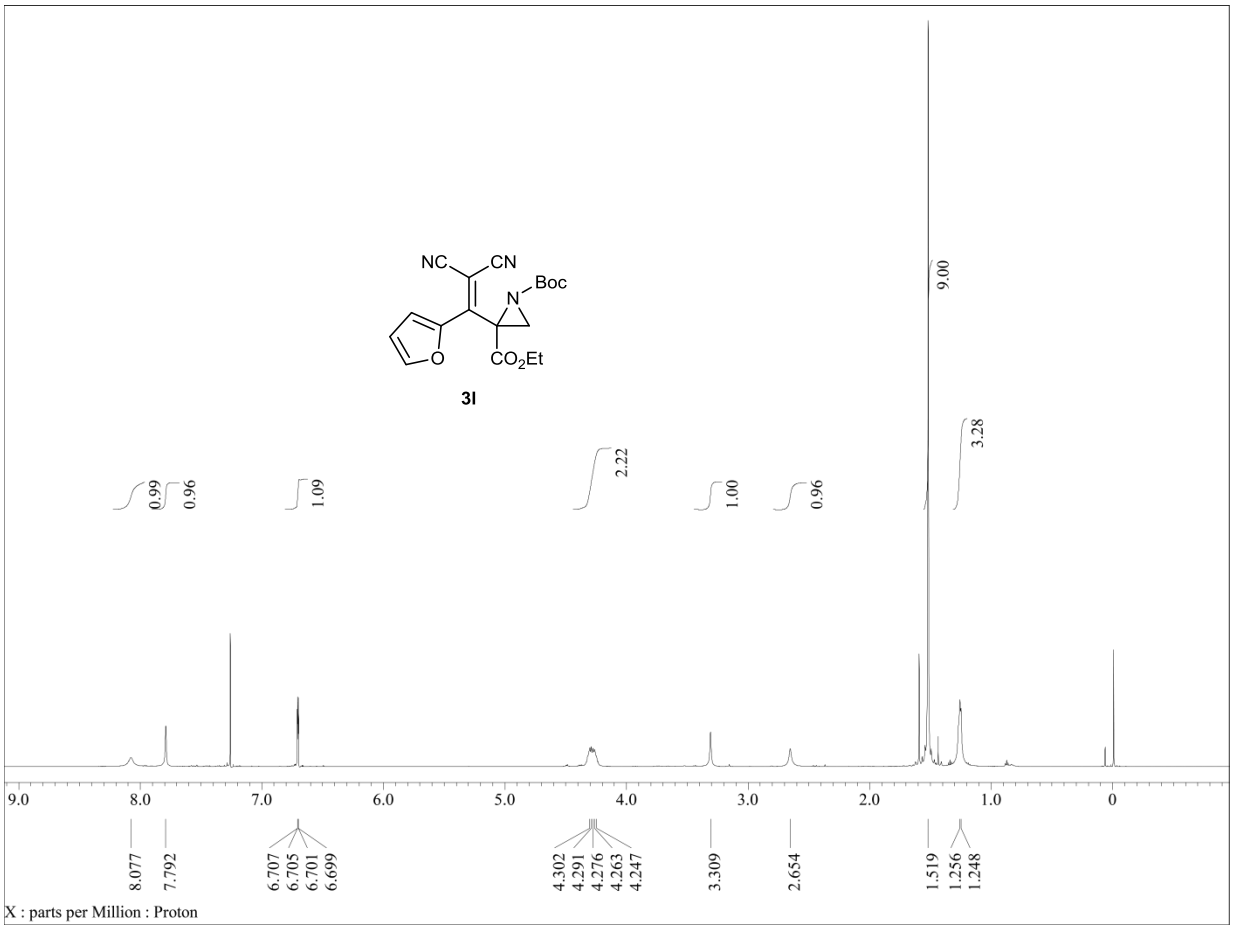
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Boc
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O
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0.96
9.00
3.28
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.077
7.792
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6.705
6.701
6.699
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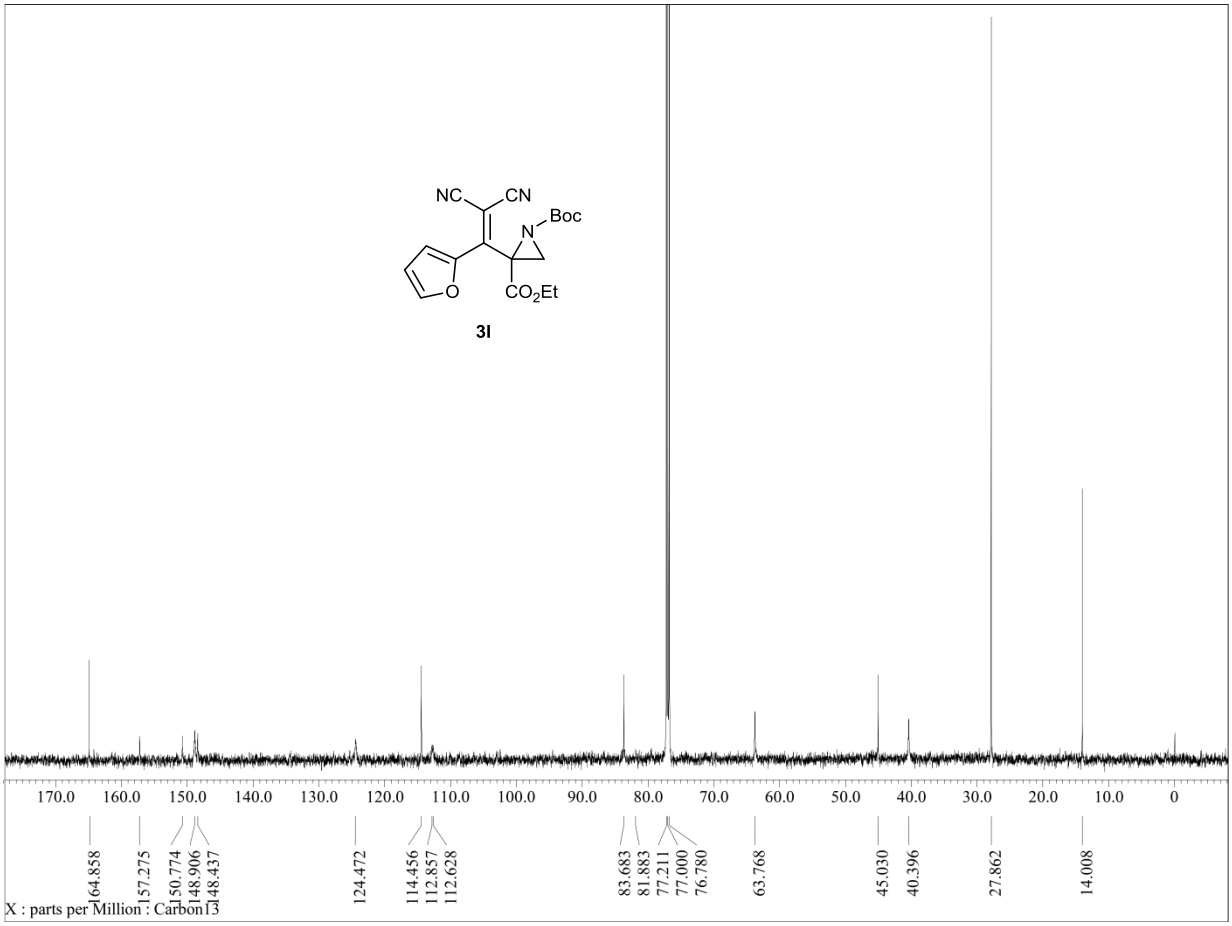
4.276
4.263
4.247
3.309
2.654
1.519
1.256
1.248
X : parts per Million : Proton


NC
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Boc
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O
CO2Et
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150.0
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130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.858
157.275
150.774
148.906
148.437
124.472
114.456
112.857
112.628
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76.780
63.768
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40.396
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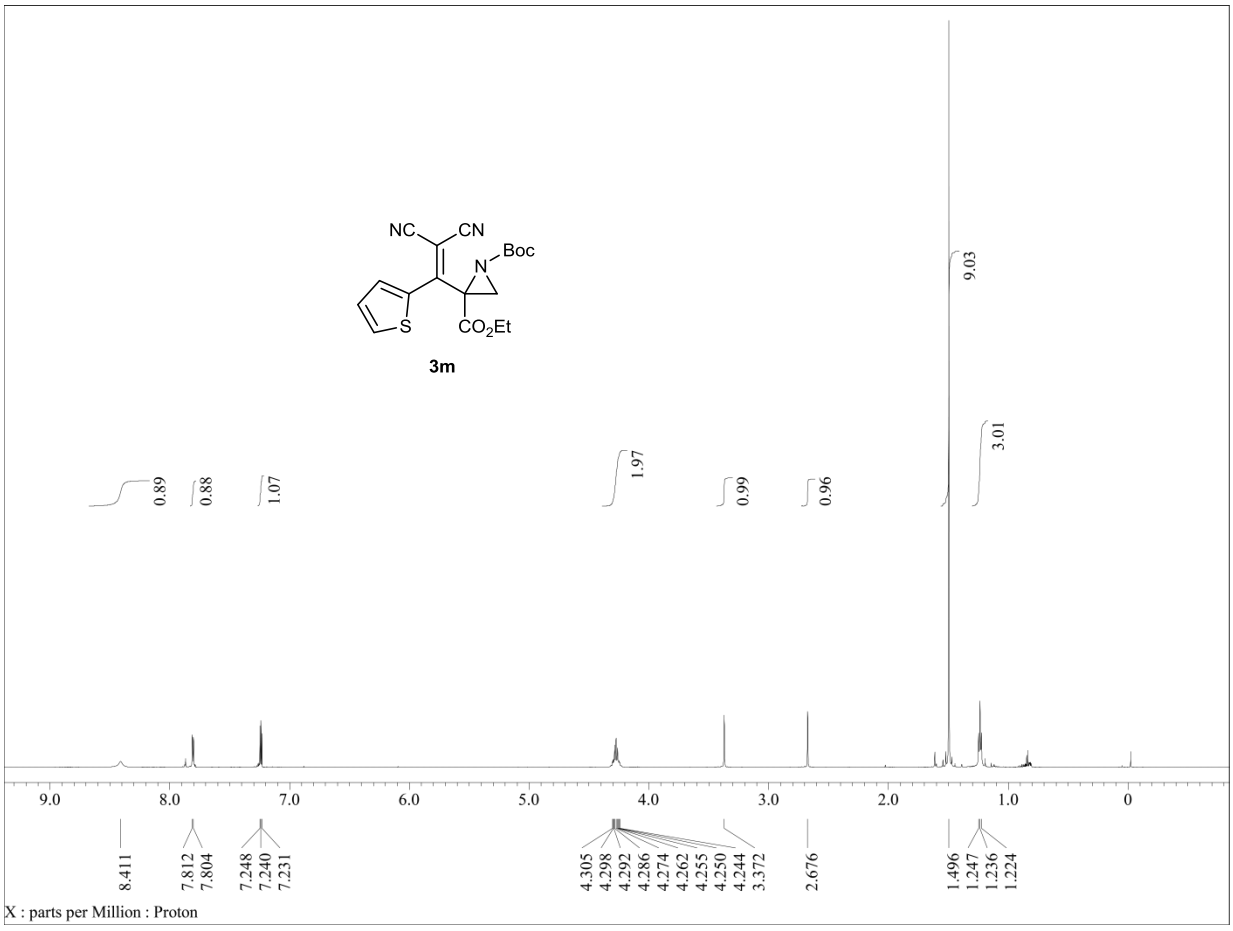
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0.96
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3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.411
7.812
7.804
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7.240
7.231
4.305
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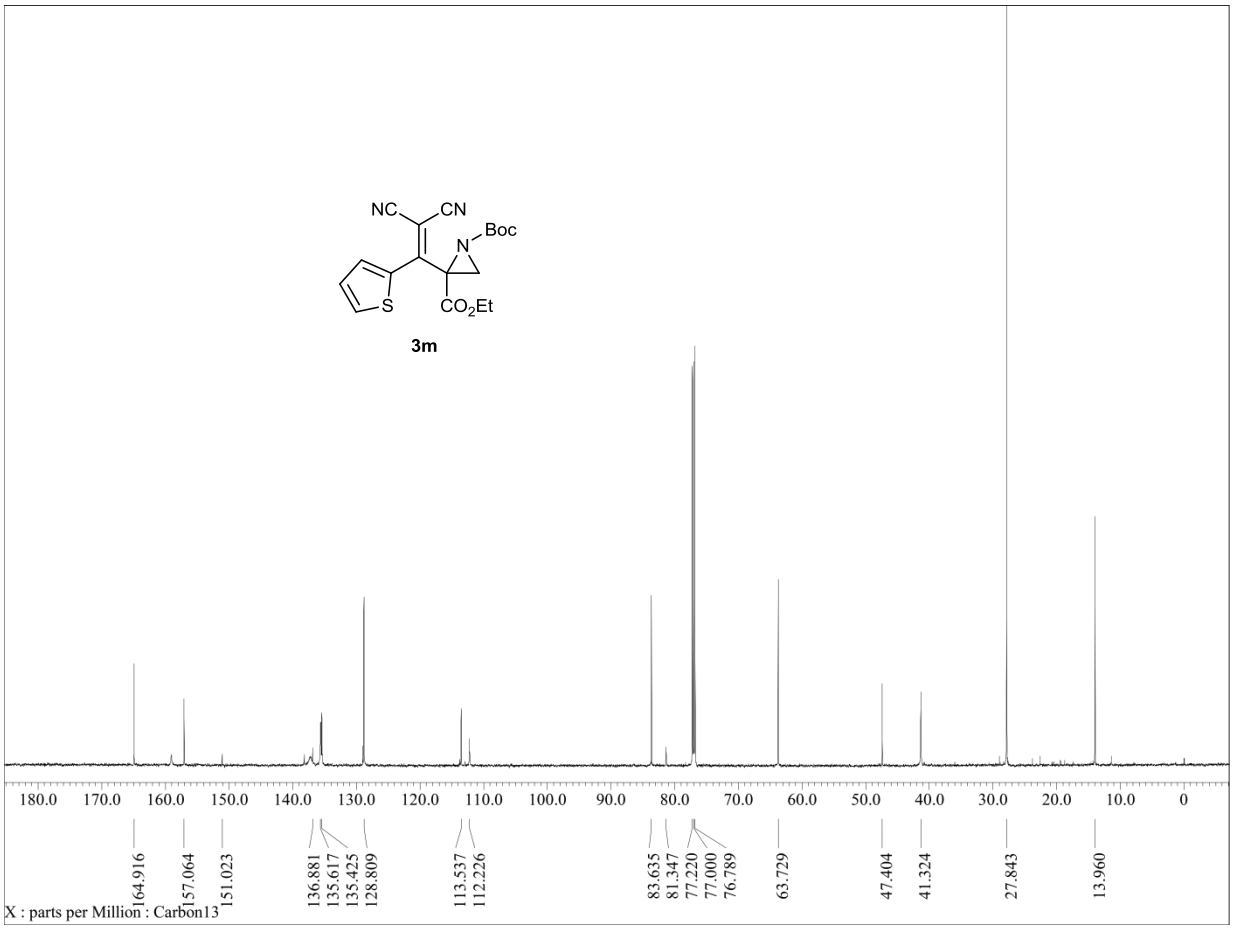
4.292
4.286
4.274
4.262
4.255
4.250
4.244
3.372
2.676
1.496
1.247
1.236
1.224
X : parts per Million : Proton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CN
Boc
N
S
CO2Et
3m
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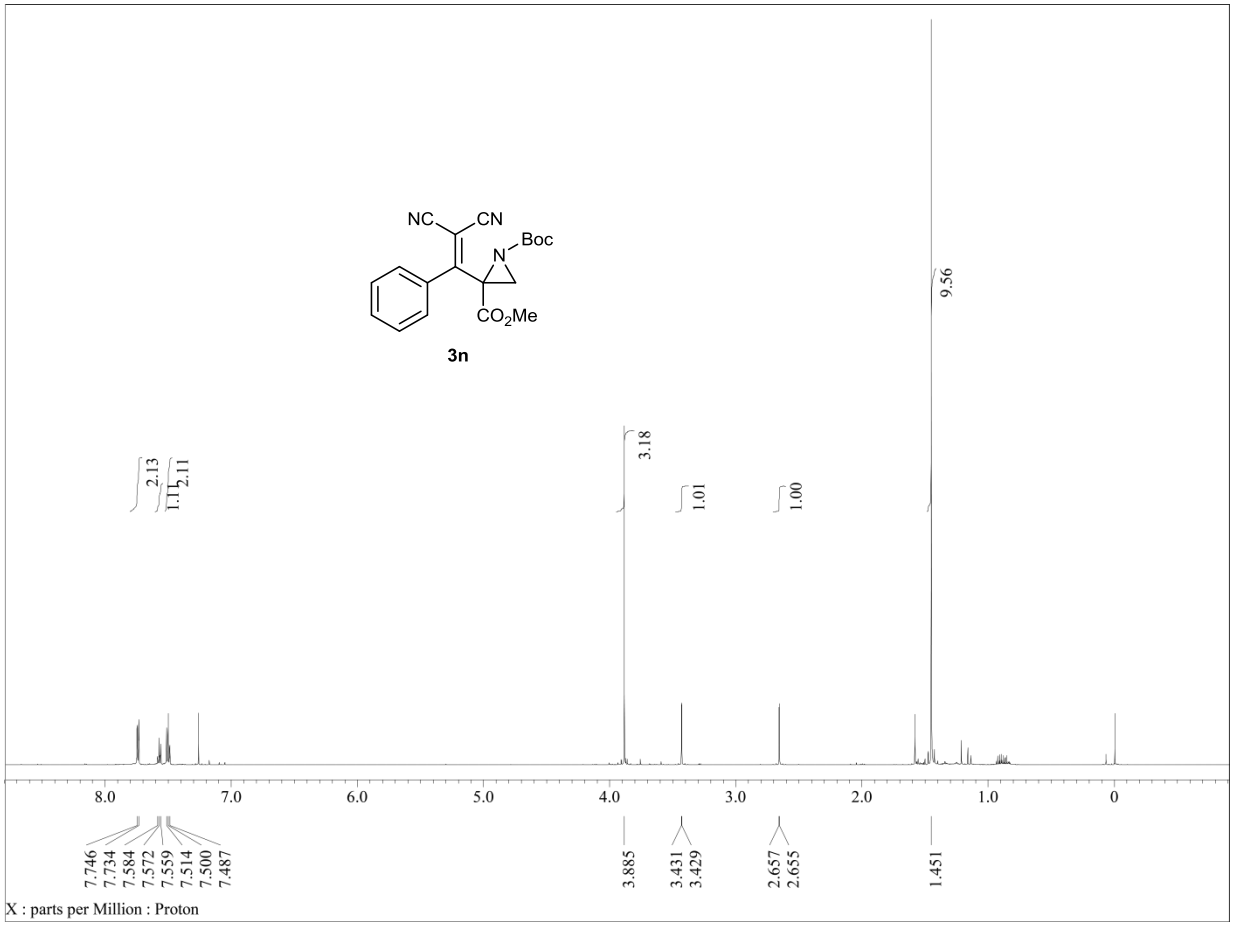
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.916
157.064
151.023
136.881
135.617
135.425
128.809
113.537
112.226
83.635
81.347
77.220
77.000
76.789
63.729
47.404
41.324
27.843
13.960
X : parts per Million : Carbon13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CN
Boc
N
CO2Me
3n
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3.18
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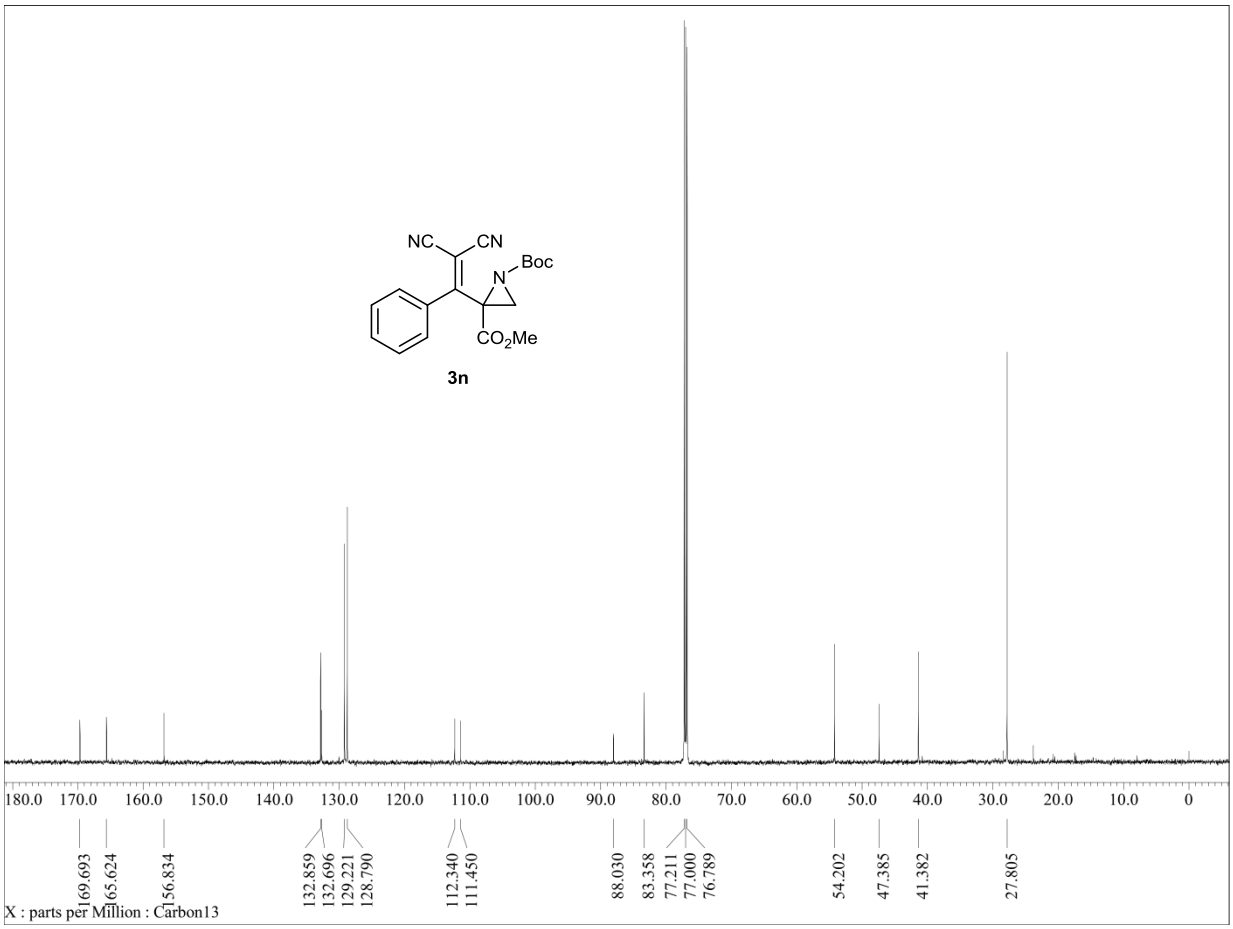
2.11
1.11
1.01
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.746
7.734
7.584
7.572
7.559
7.514
7.500
7.487
3.885
3.431
3.429
2.657
2.655
1.451
X : parts per Million : Proton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CN
Boc
N
CO2Me
3n
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160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.693
165.624
156.834
132.859
132.696
129.221
128.790
112.340
111.450
88.030
83.358
77.211
77.000
76.789
54.202
47.385
41.382
27.805
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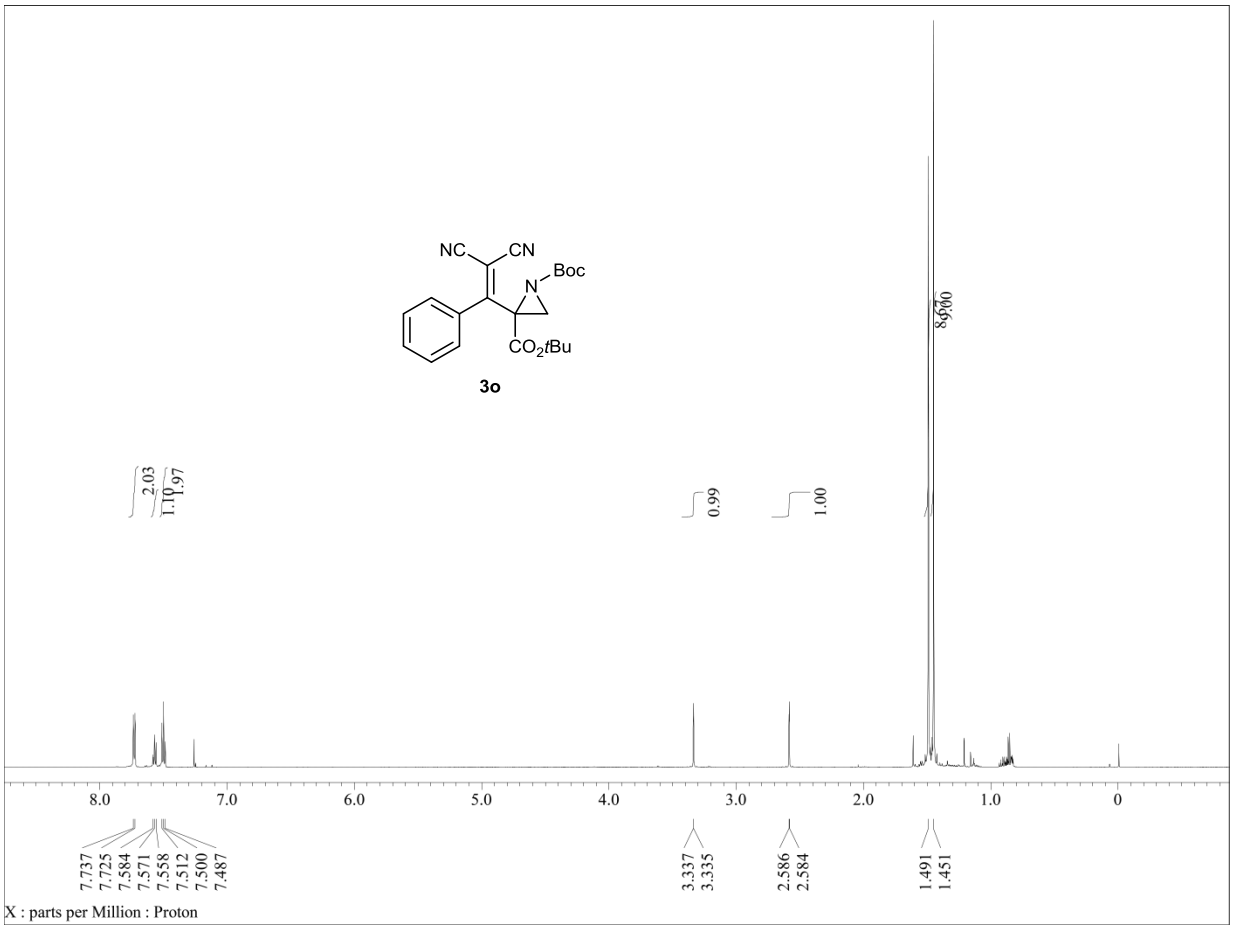
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CN
Boc
N
CO2tBu
3o
8.000
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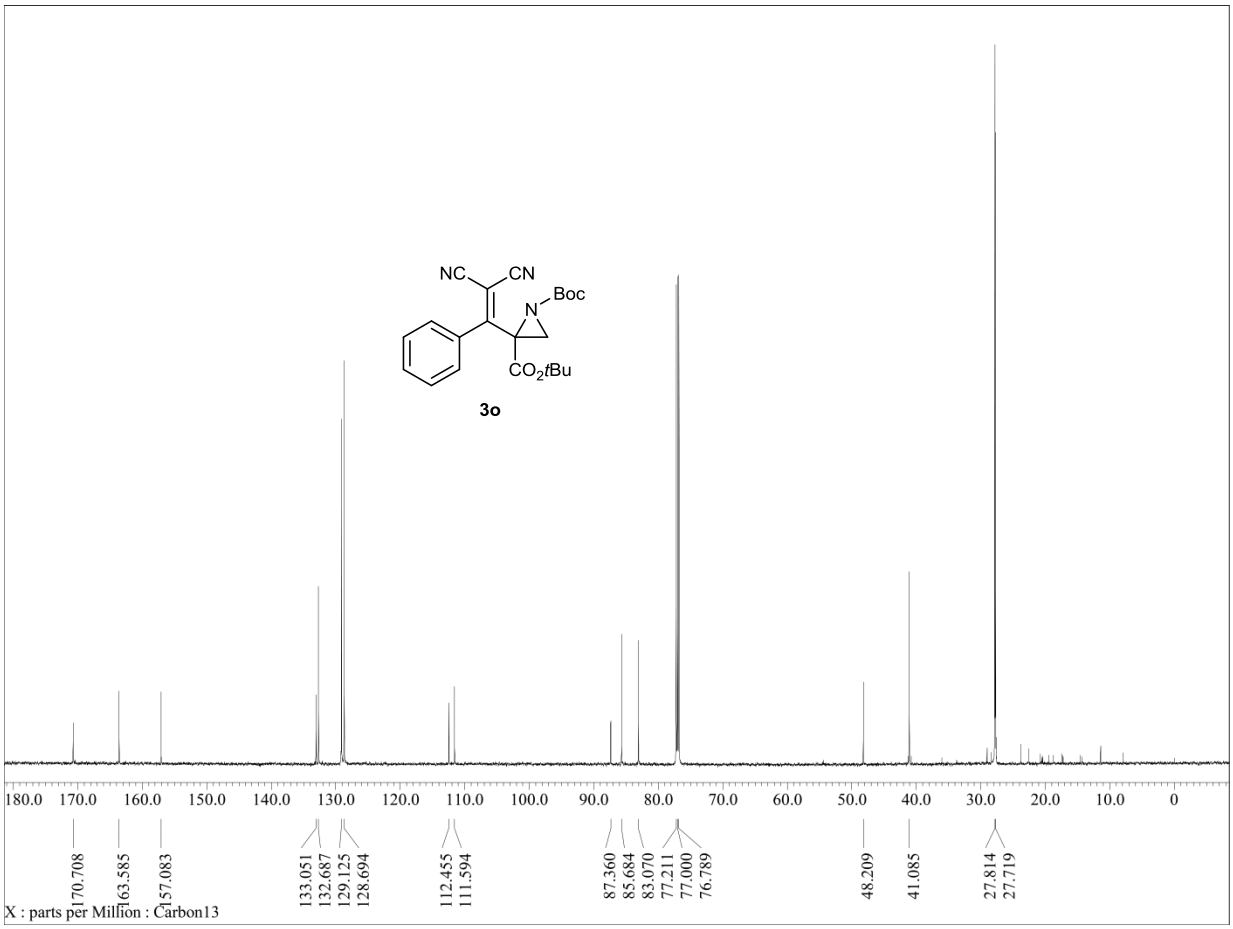
1.10
1.97
0.99
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.737
7.725
7.584
7.571
7.558
7.512
7.500
7.487
3.337
3.335
2.586
2.584
1.491
1.451
X : parts per Million : Proton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CN
Boc
N
CO2tBu
3o
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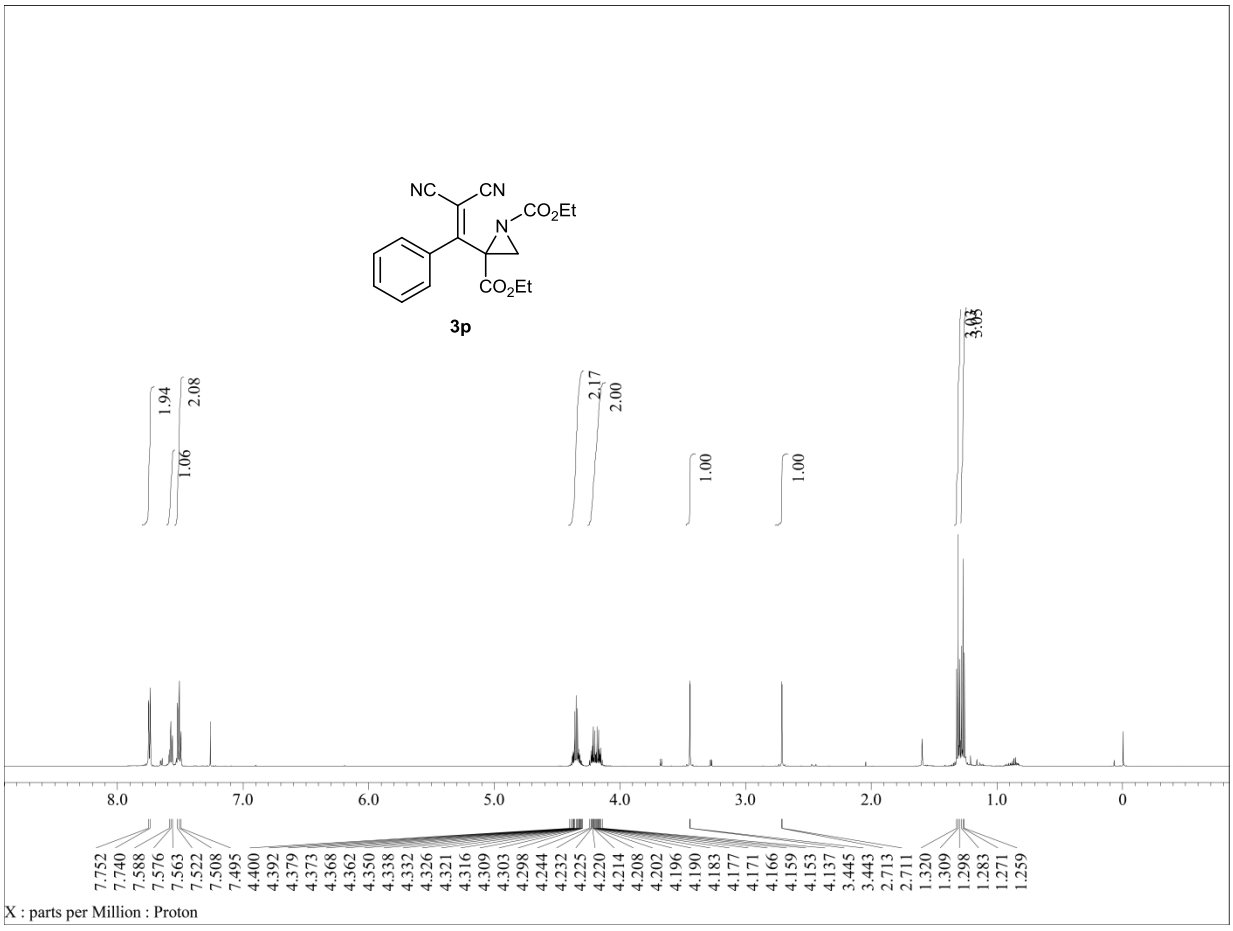
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.708
163.585
157.083
133.051
132.687
129.125
128.694
112.455
111.594
87.360
85.684
83.070
77.211
77.000
76.789
48.209
41.085
27.814
27.719
X : parts per Million : Carbon13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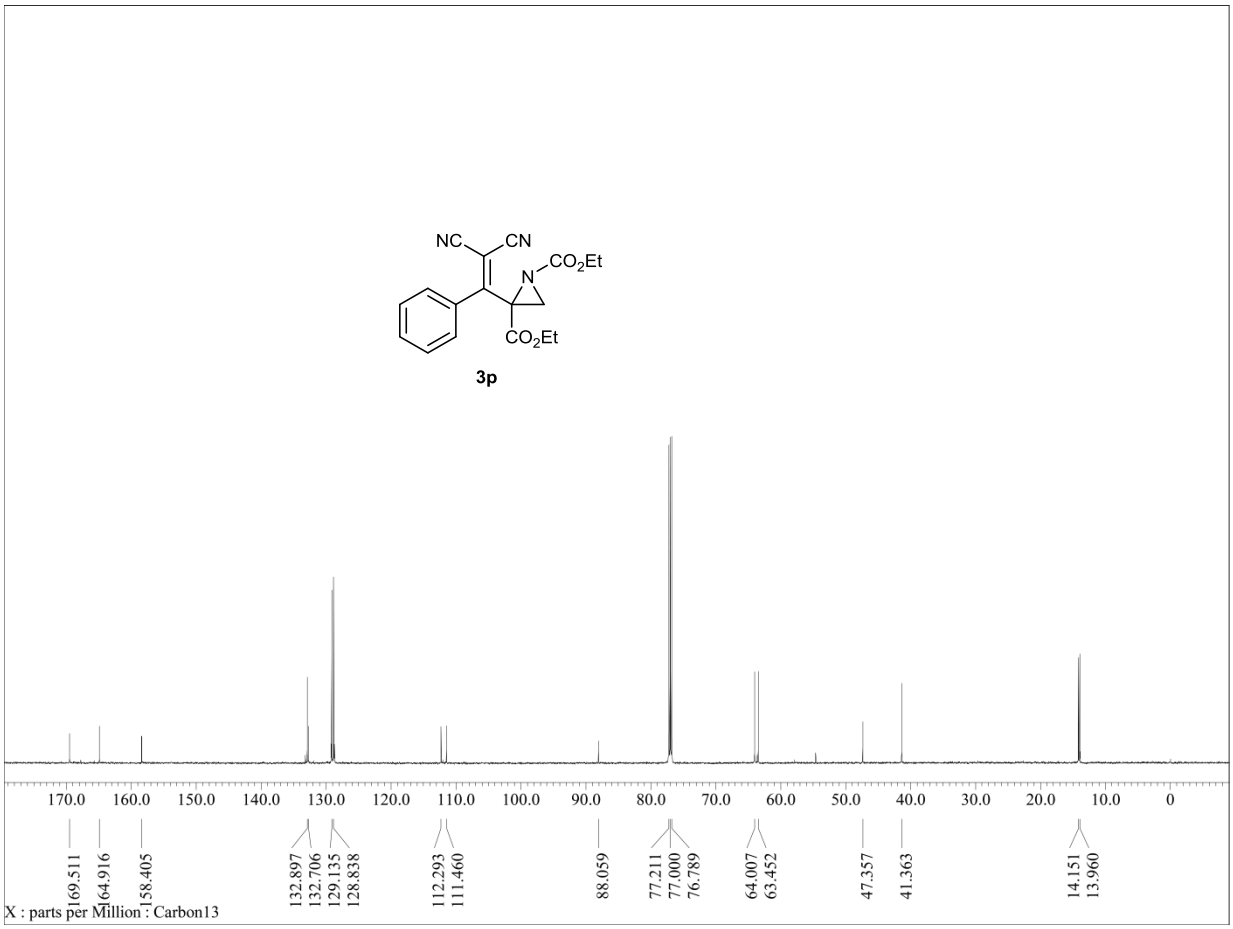
CN
CO2Et
N
CO2Et
3p
1.94
2.08
1.06
2.17
2.00
1.00
1.00
3.07
3.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.752
7.740
7.588
7.576
7.563
7.522
7.508
7.495
4.400
4.392
4.379
4.373
4.368
4.362
4.350
4.338
4.332
4.326
4.321
4.316
4.309
4.303
4.298
4.244
4.232
4.225
4.220
4.214
4.208
4.202
4.196
4.190
4.183
4.177
4.171
4.166
4.159
4.153
4.137
3.445
3.443
2.713
2.711
1.320
1.309
1.298
1.283
1.271
1.259
X : parts per Million : Proton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CN
CO2Et
N
CO2Et
3p
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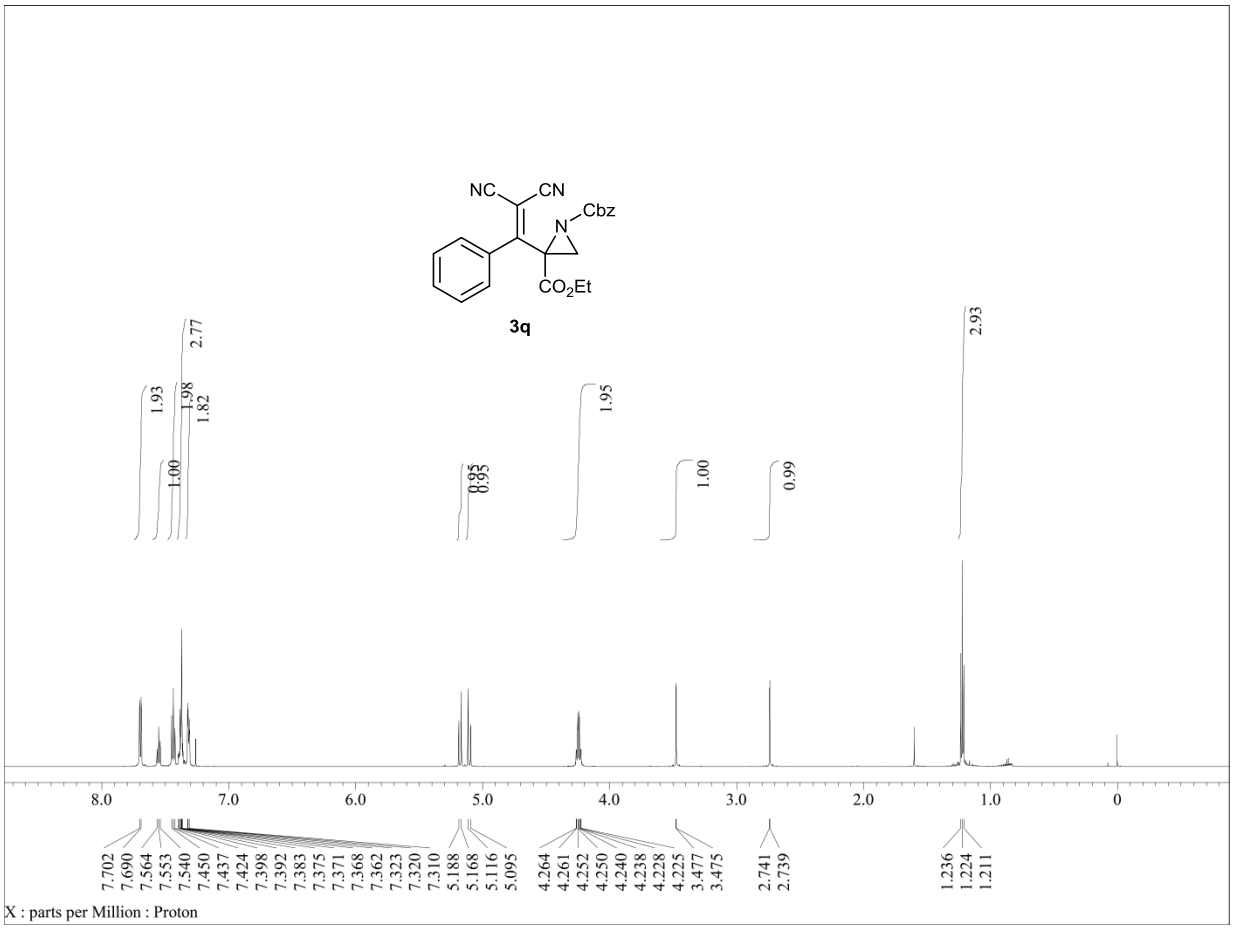
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.511
164.916
158.405
132.897
132.706
129.135
128.838
112.293
111.460
88.059
77.211
77.000
76.789
64.007
63.452
47.357
41.363
14.151
13.960
X : parts per Million : Carbon13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CN
Cbz
N
CO2Et
3q
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2.77
1.98
1.82
1.00
0.95
0.95
1.95
1.00
0.99
2.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.702
7.690
7.564
7.553
7.540
7.450
7.437
7.424
7.398
7.392
7.383
7.375
7.371
7.368
7.362
7.323
7.320
7.310
5.188
5.168
5.116
5.095
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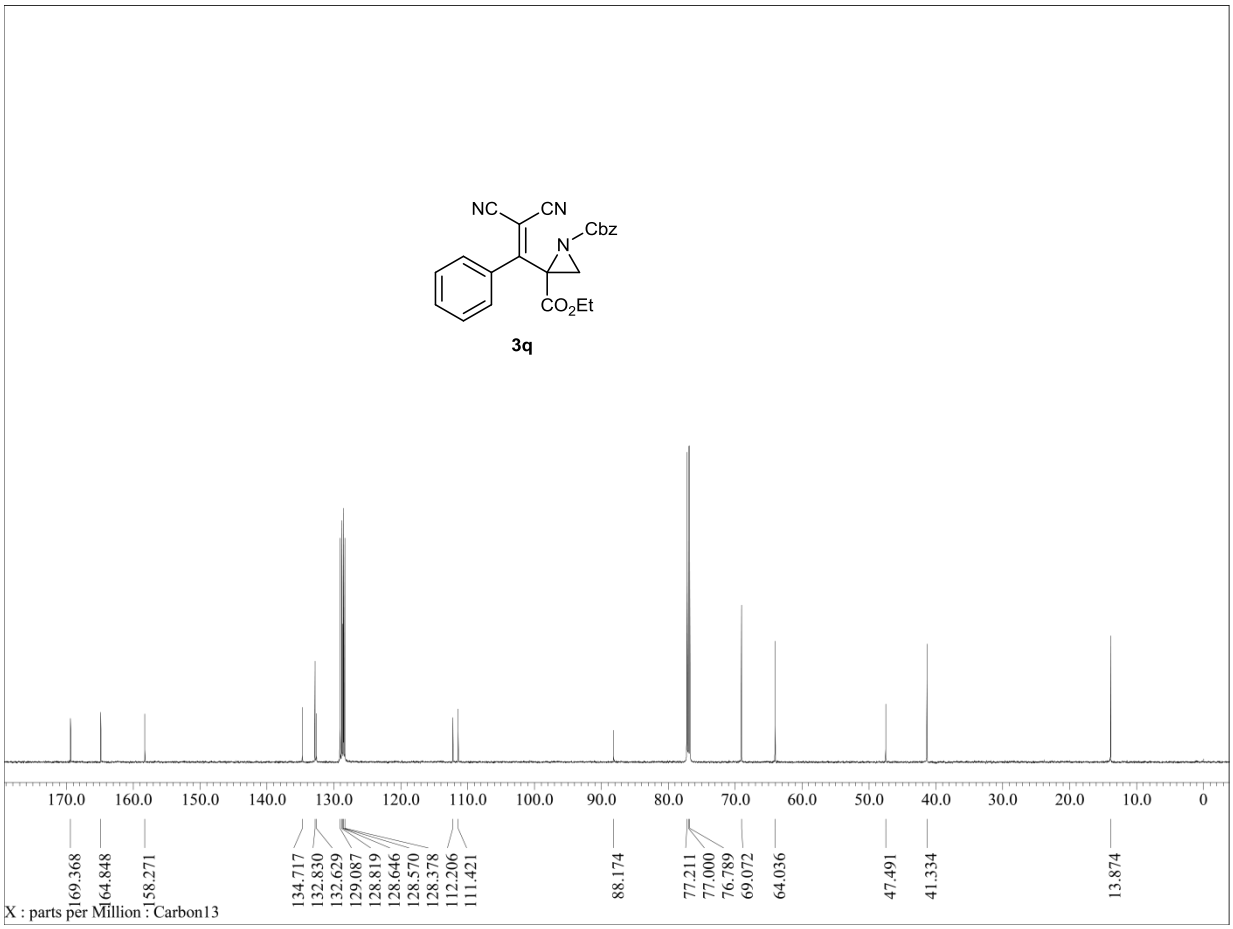
4.261
4.252
4.250
4.240
4.238
4.228
4.225
3.477
3.475
2.741
2.739
1.236
1.224
1.211
X : parts per Million : Proton


NC
CN
Cbz
N
CO2Et
3q
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.368
164.848
158.271
134.717
132.830
132.629
129.087
128.819
128.646
128.570
128.378
112.206
111.421
88.174
77.211
77.000
76.789
69.072
64.036
47.491
41.334
13.874
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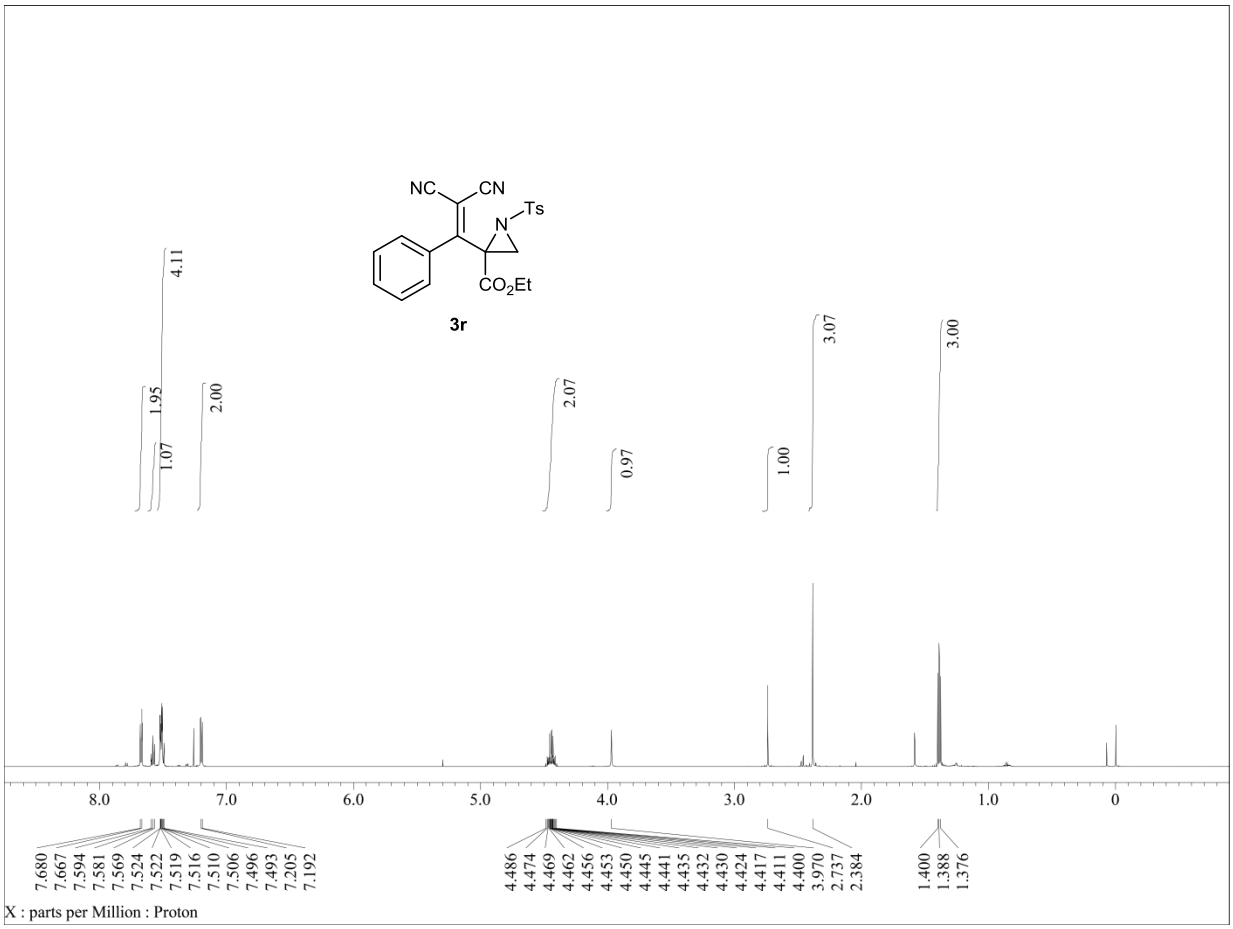
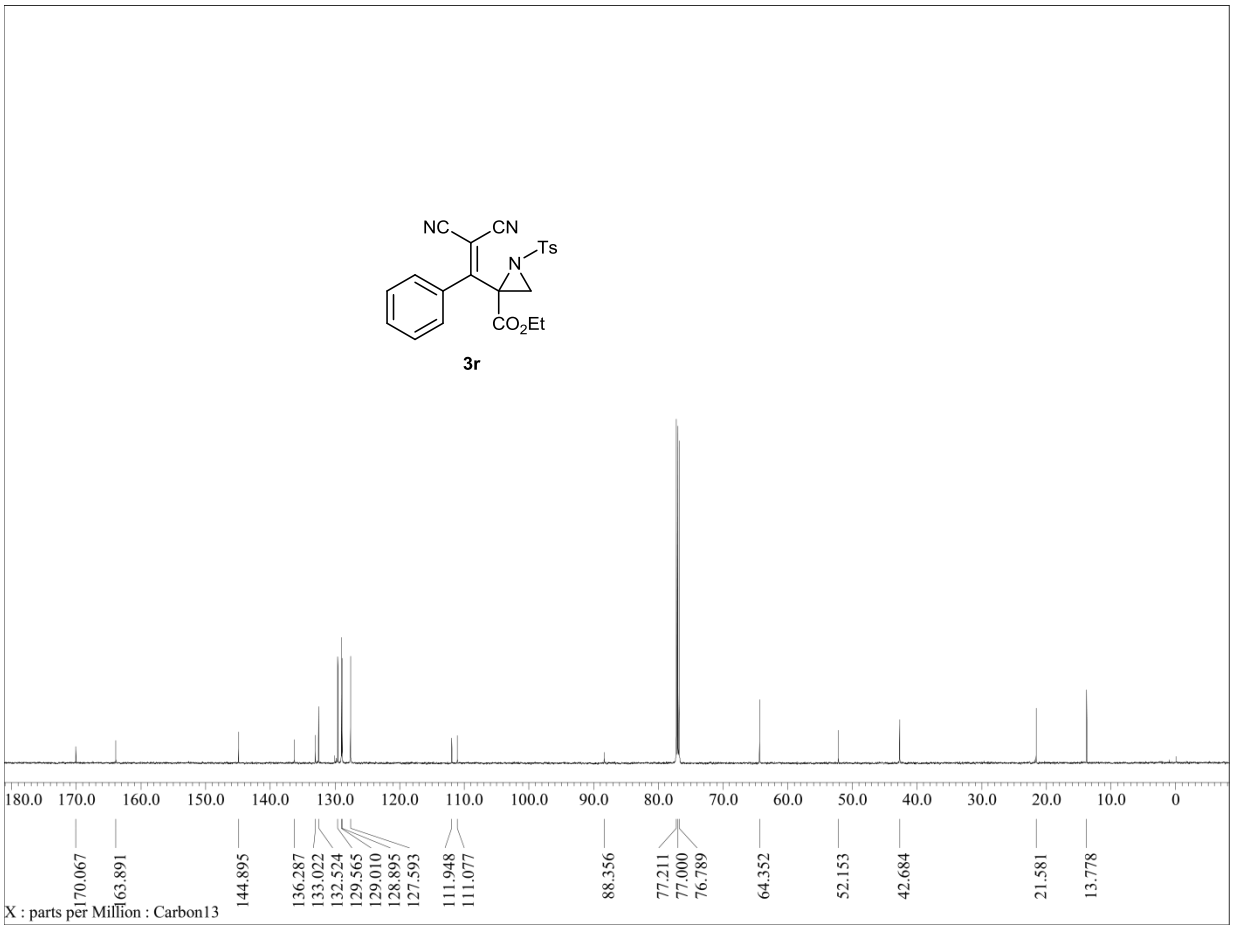

NC
CN
Ts
N
CO2Et
3r
4.11
1.95
1.07
2.00
2.07
0.97
1.00
3.07
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.680
7.667
7.594
7.581
7.569
7.524
7.522
7.519
7.516
7.510
7.506
7.496
7.493
7.205
7.192
4.486
4.474
4.469
4.462
4.456
4.453
4.450
4.445
4.441
4.435
4.432
4.430
4.424
4.417
4.411
4.400
3.970
2.737
2.384
1.400
1.388
1.376
X : parts per Million : Proton


NC
CN
Ts
N
CO2Et
3r
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170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.067
163.891
144.895
136.287
133.022
132.524
129.565
129.010
128.895
127.593
111.948
111.077
88.356
77.211
77.000
76.789
64.352
52.153
42.684
21.581
13.778
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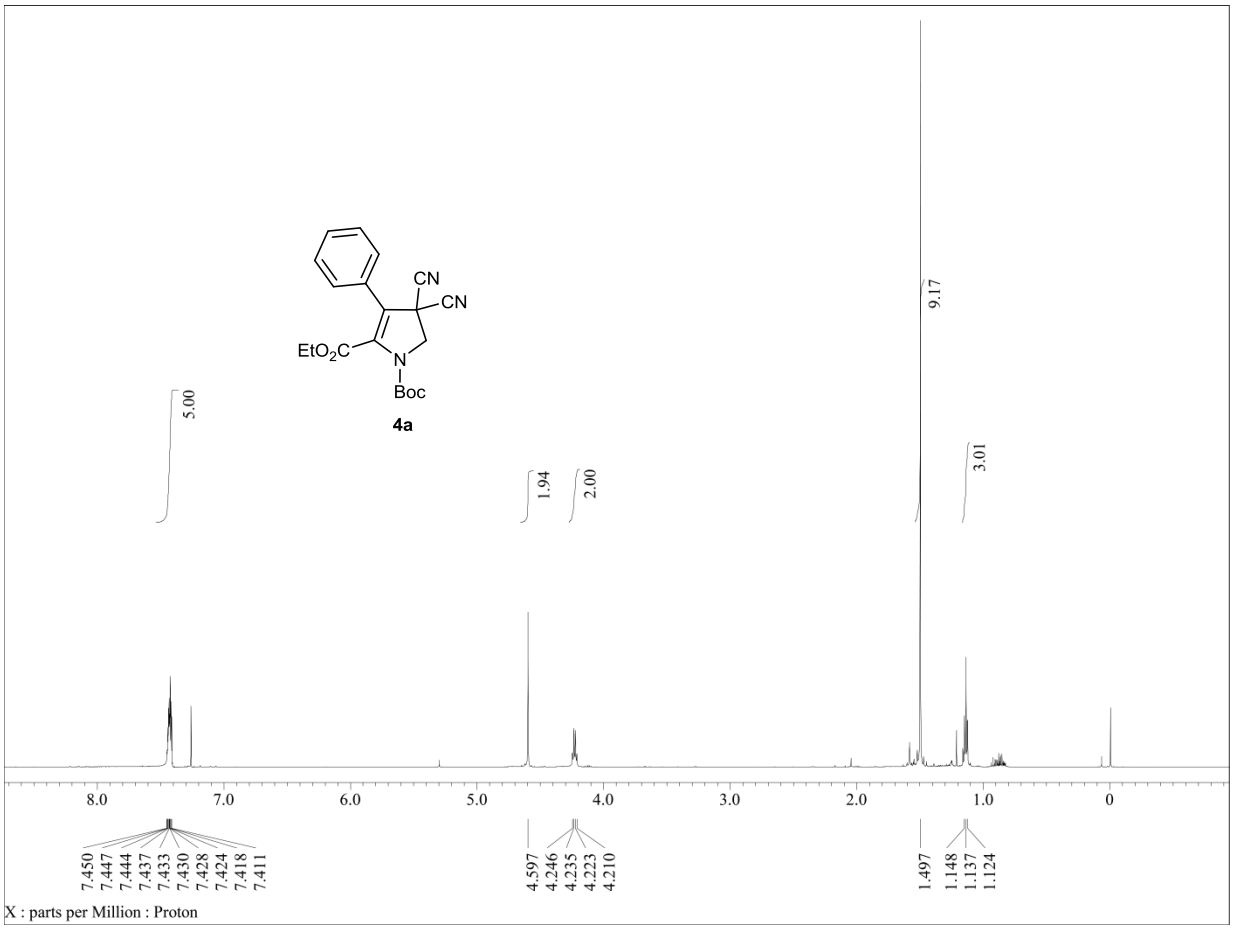
CN
CN
EtO2C
N
Boc
4a
5.00
1.94
2.00
9.17
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.450
7.447
7.444
7.437
7.433
7.430
7.428
7.424
7.418
7.411
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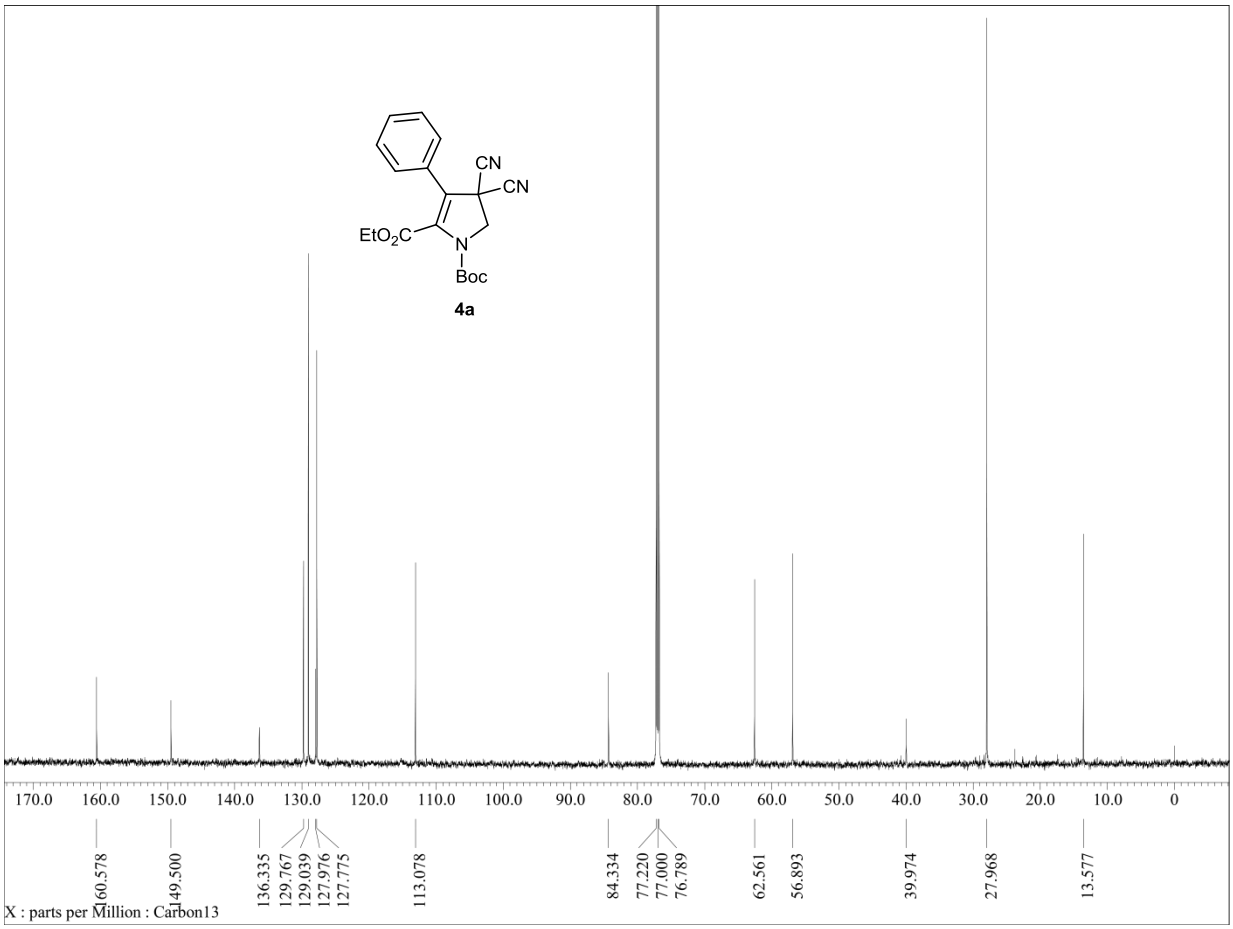
4.246
4.235
4.223
4.210
1.497
1.148
1.137
1.124
X : parts per Million : Proton


CN
CN
EtO2C
N
Boc
4a
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.578
149.500
136.335
129.767
129.039
127.976
127.775
113.078
84.334
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77.000
76.789
62.561
56.893
39.974
27.968
13.577
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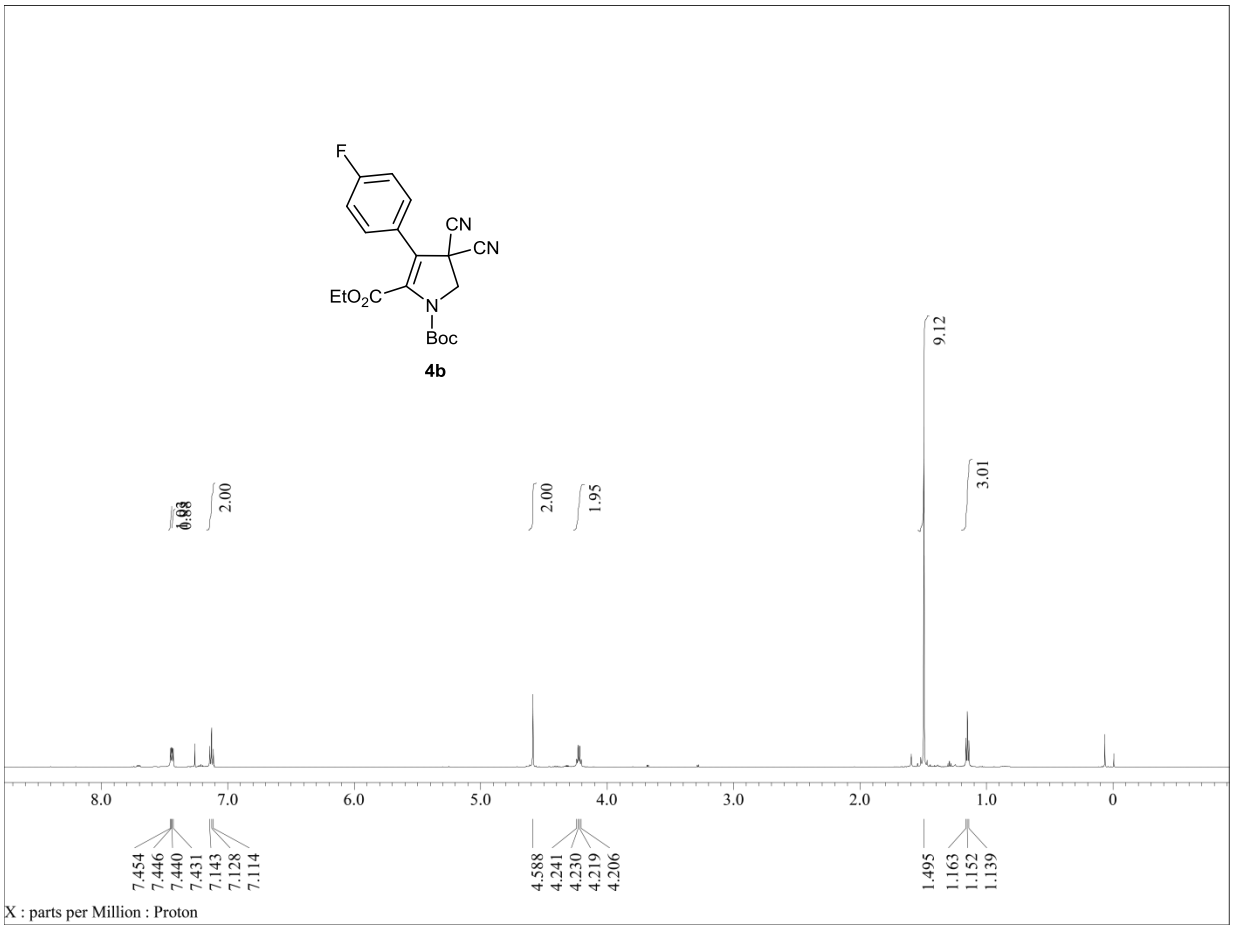
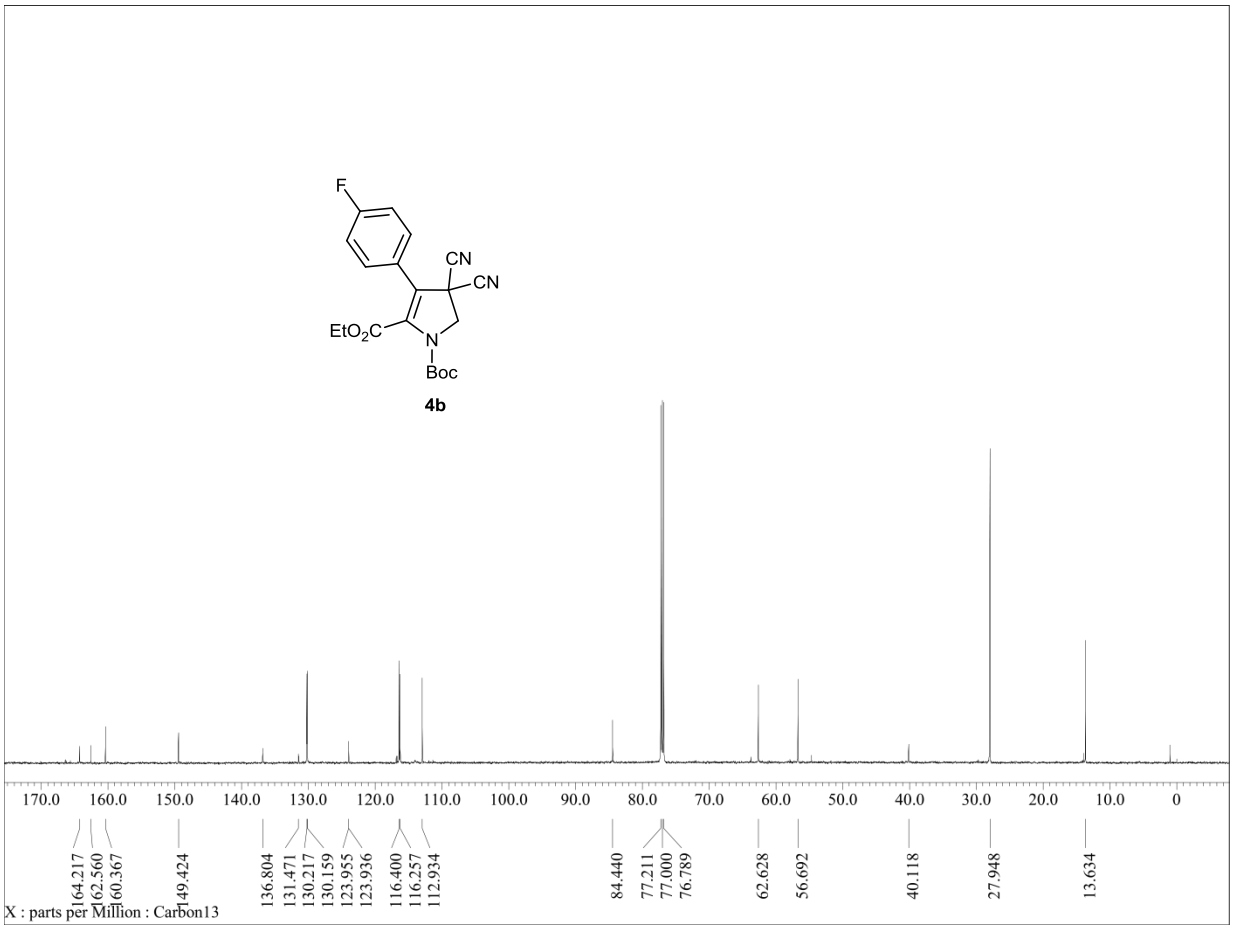

F
CN
CN
EtO2C
N
Boc
4b
9.12
3.01
2.00
2.00
1.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.454
7.446
7.440
7.431
7.143
7.128
7.114
4.588
4.241
4.230
4.219
4.206
1.495
1.163
1.152
1.139
X : parts per Million : Proton


F
CN
CN
EtO2C
N
Boc
4b
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.217
162.560
160.367
149.424
136.804
131.471
130.217
130.159
123.955
123.936
116.400
116.257
112.934
84.440
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77.000
76.789
62.628
56.692
40.118
27.948
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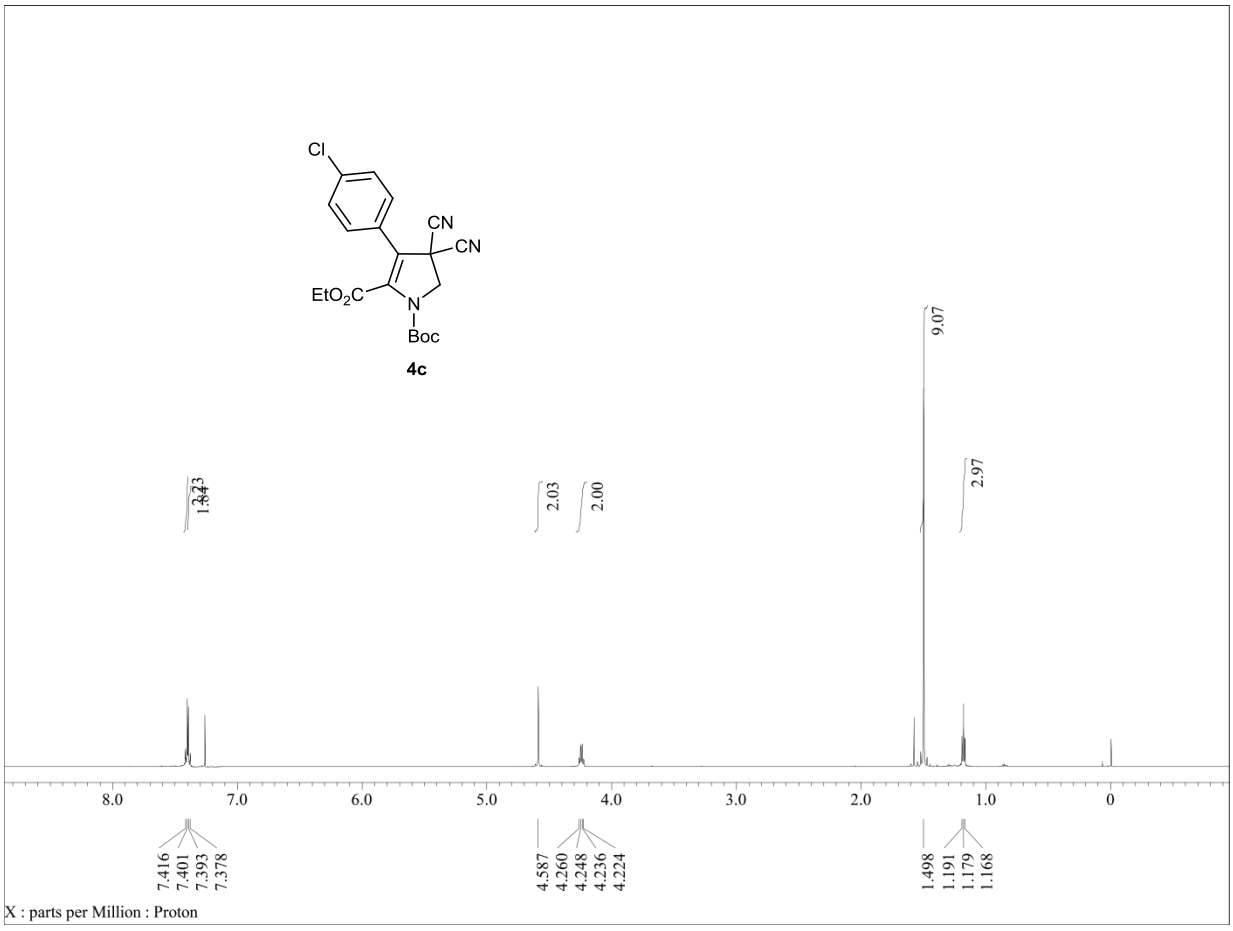
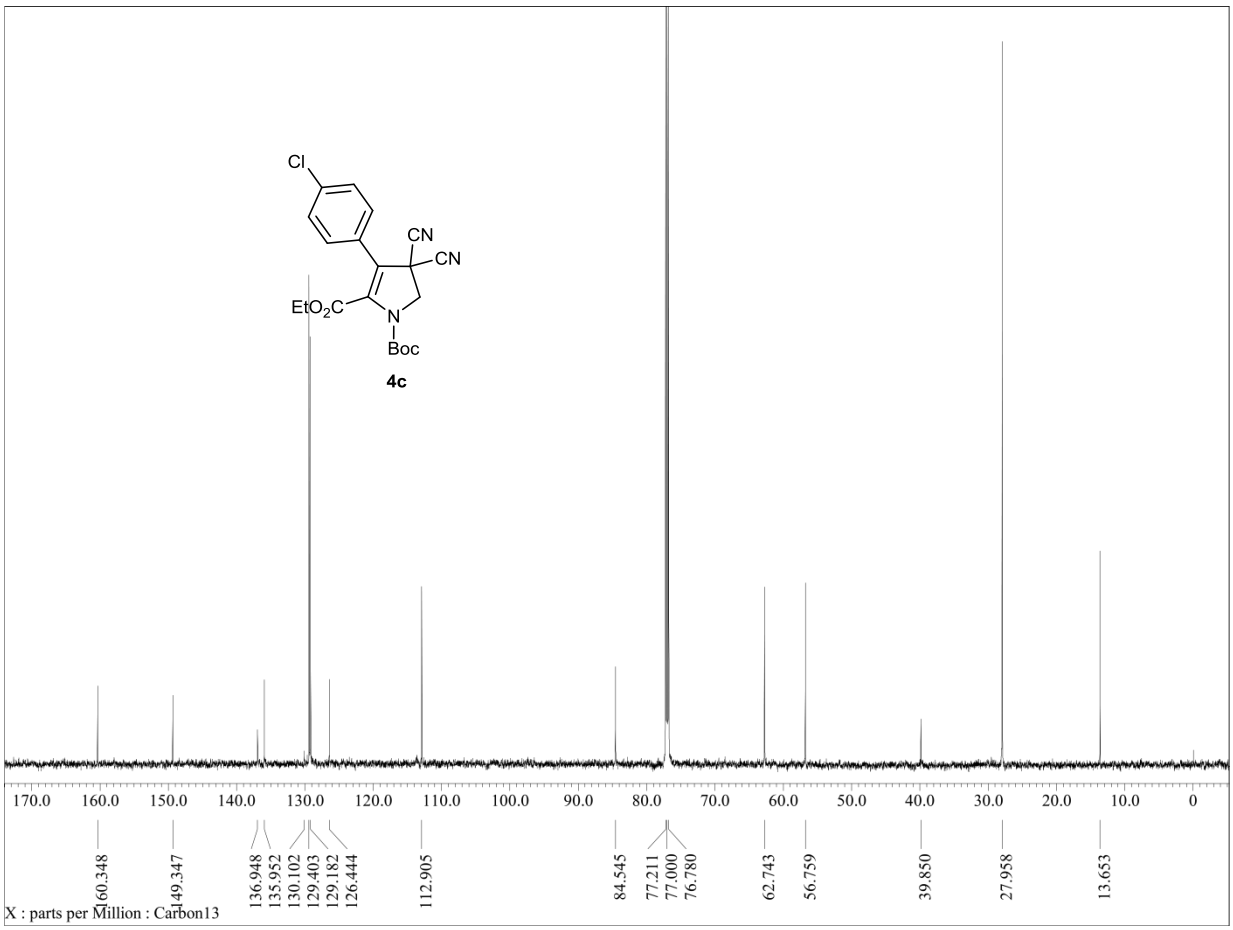
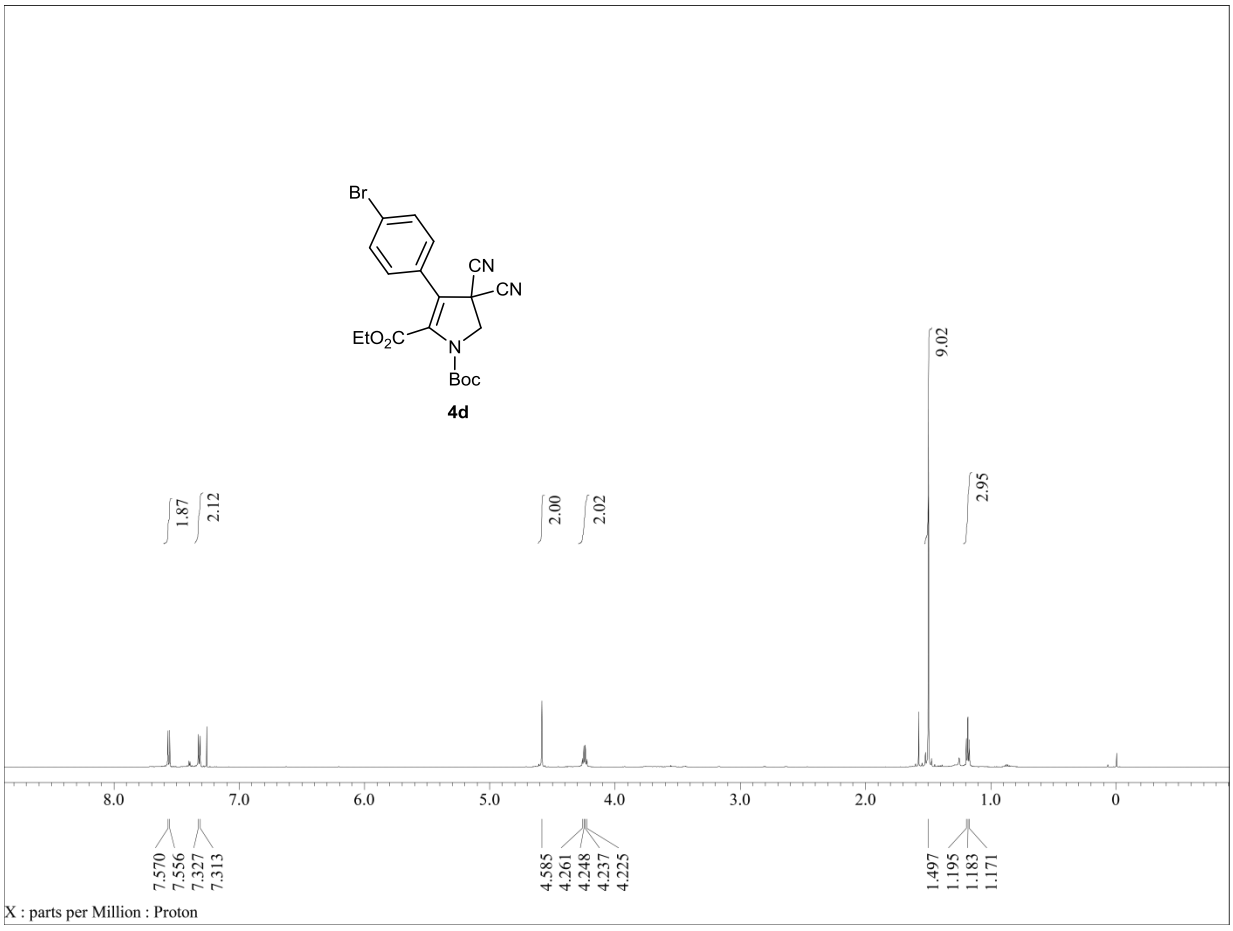

Cl
CN
CN
EtO2C
N
Boc
4c
9.07
2.97
2.03
2.00
1.23
1.44
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.416
7.401
7.393
7.378
4.587
4.260
4.248
4.236
4.224
1.498
1.191
1.179
1.168
X : parts per Million : Proton


Cl
CN
CN
EtO2C
N
Boc
4c
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.348
149.347
136.948
135.952
130.102
129.403
129.182
126.444
112.905
84.545
77.211
77.000
76.780
62.743
56.759
39.850
27.958
13.653
X : parts per Million : Carbon13


Br
CN
CN
EtO2C
N
Boc
4d
9.02
2.95
1.87
2.12
2.00
2.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.570
7.556
7.327
7.313
4.585
4.261
4.248
4.237
4.225
1.497
1.195
1.183
1.171
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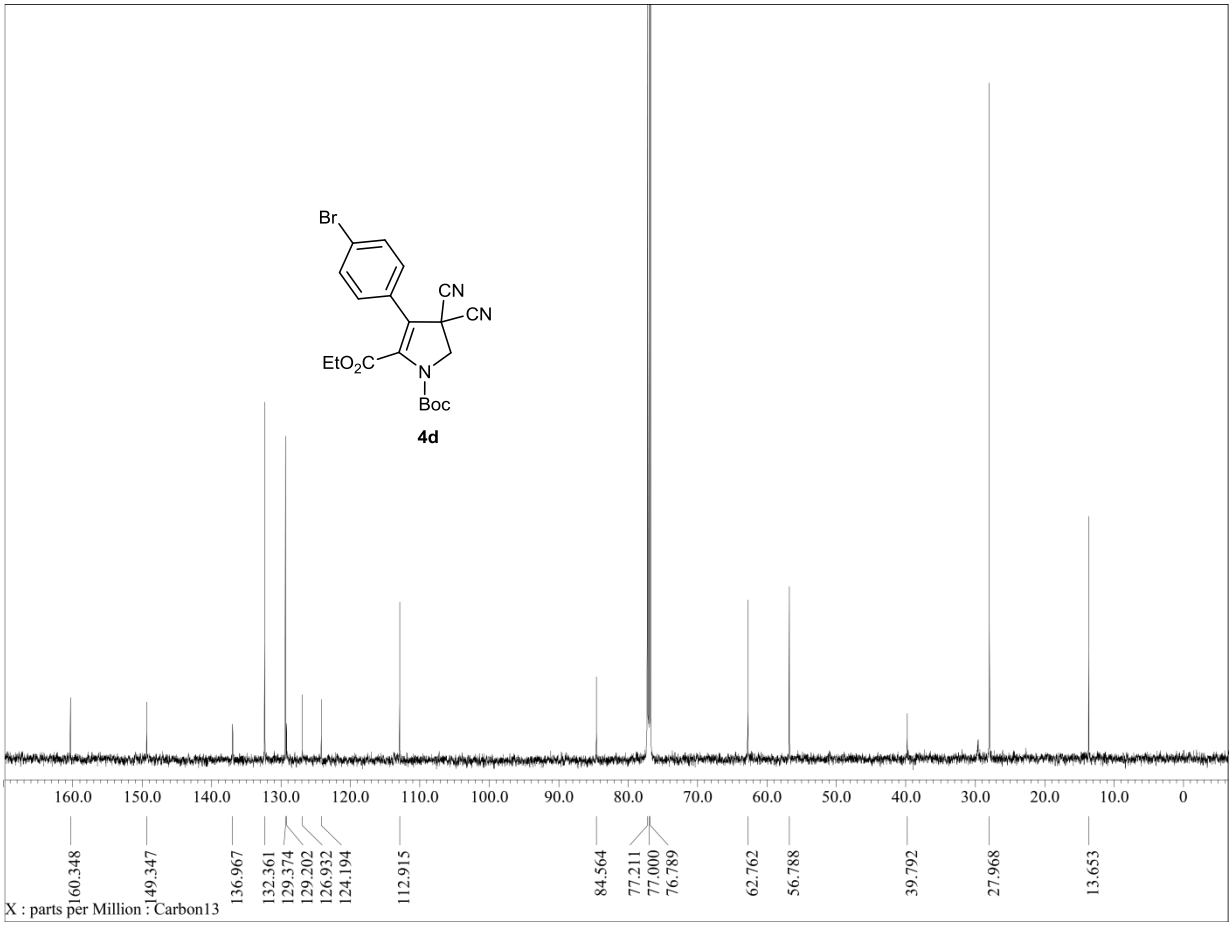
Br
CN
CN
EtO2C
N
Boc
4d
160.348
149.347
136.967
132.361
129.374
129.202
126.932
124.194
112.915
84.564
77.211
77.000
76.789
62.762
56.788
39.792
27.968
13.653
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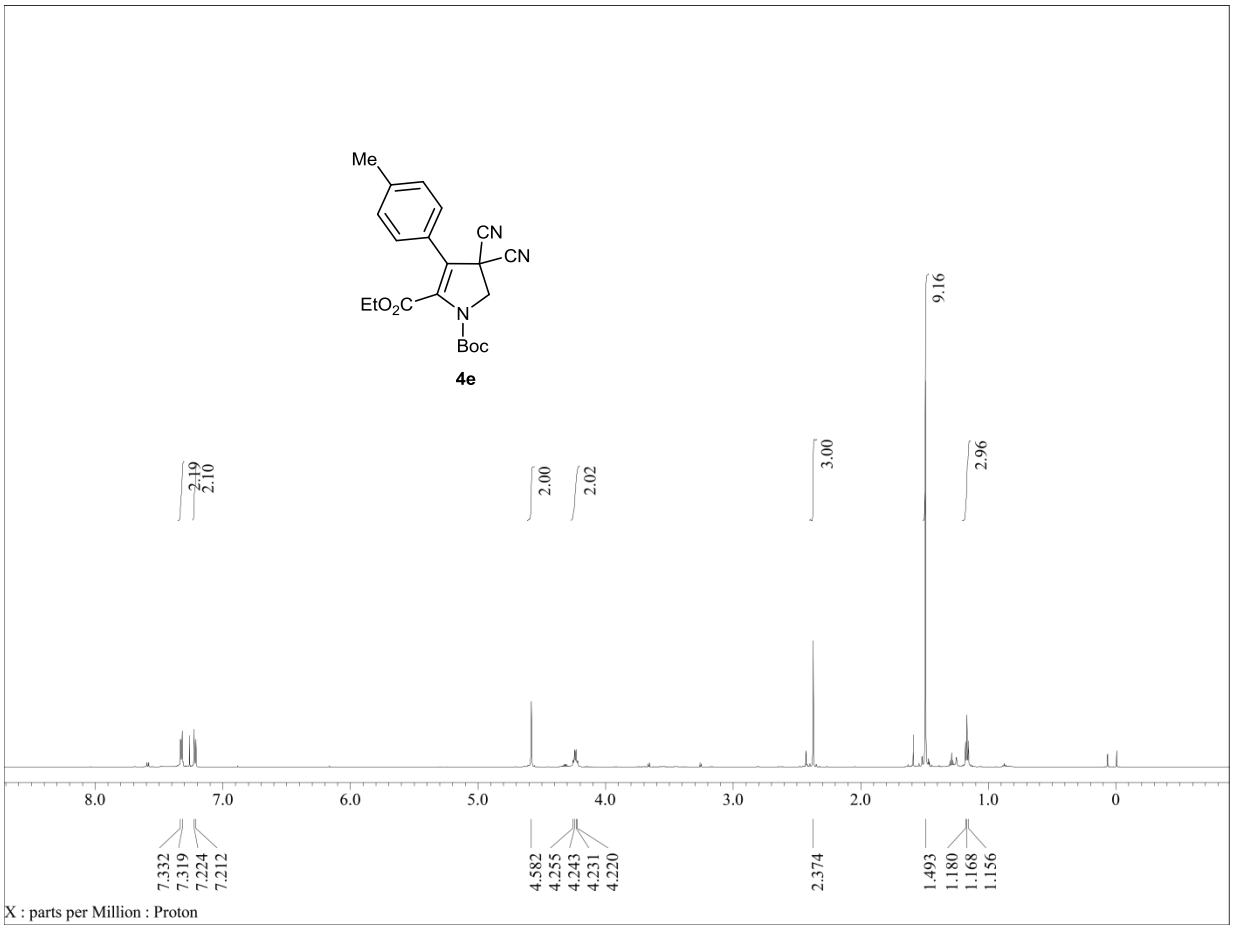
Me
CN
CN
EtO2C
N
Boc
4e
9.16
3.00
2.96
2.19
2.10
2.00
2.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.332
7.319
7.224
7.212
4.582
4.255
4.243
4.231
4.220
2.374
1.493
1.180
1.168
1.156
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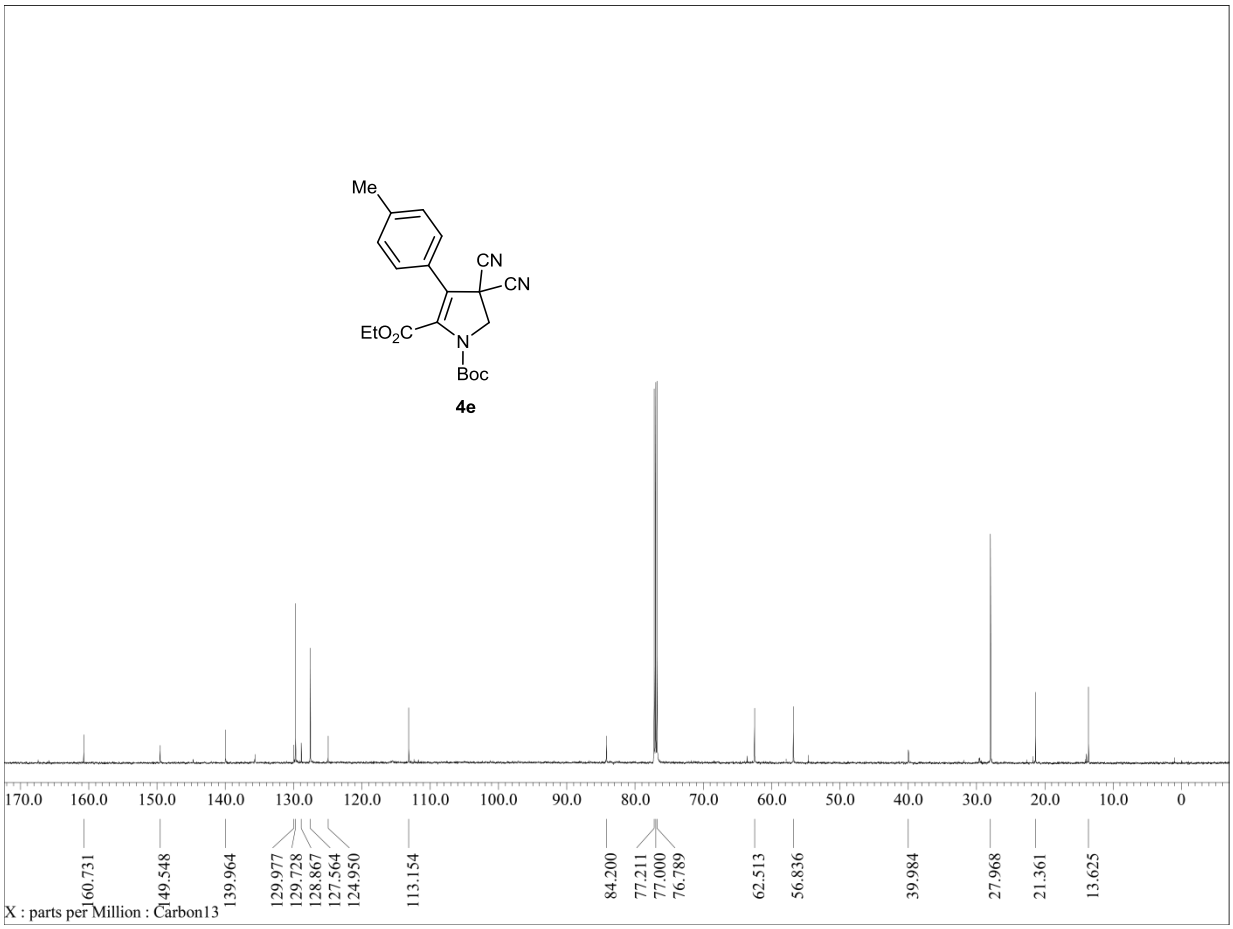
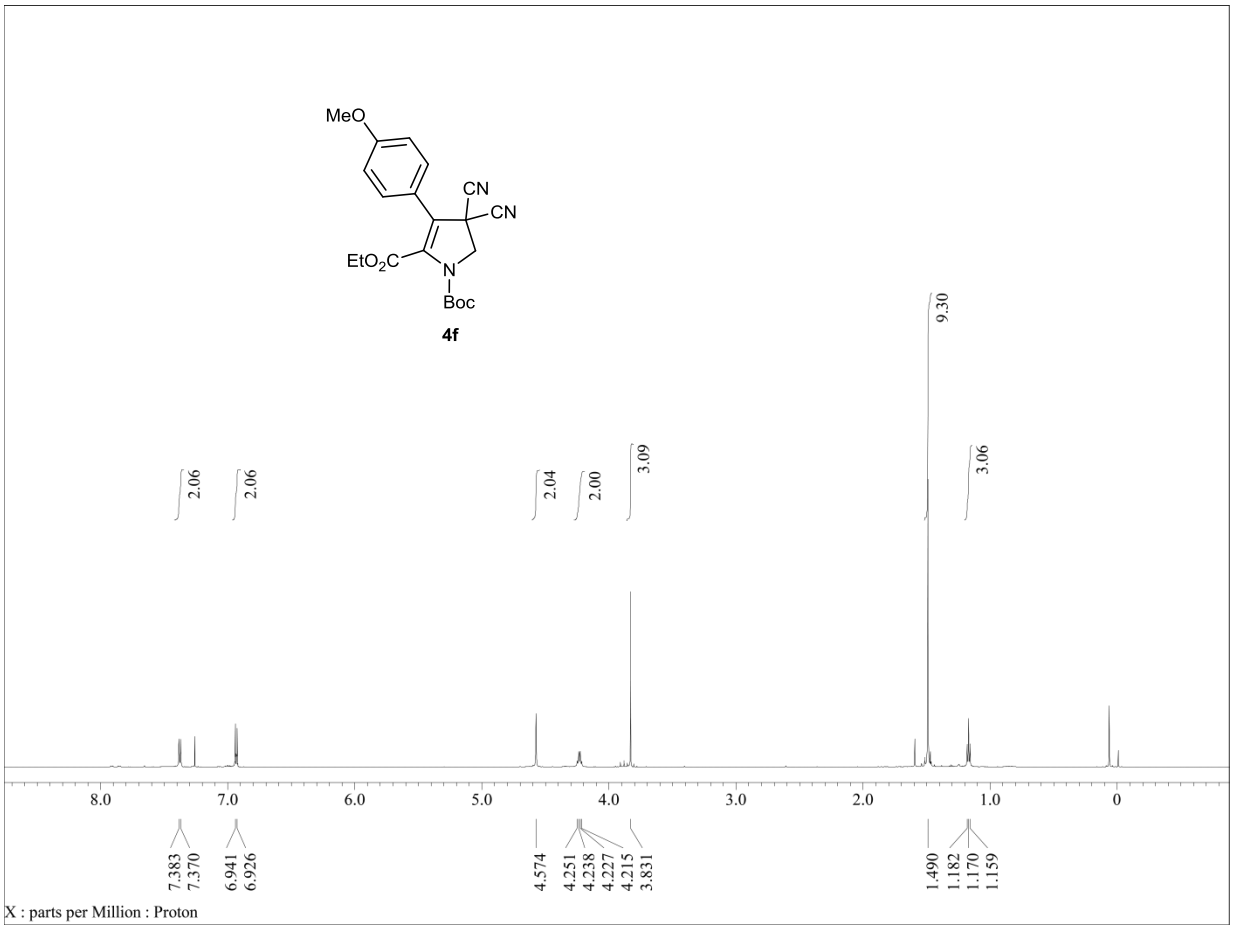
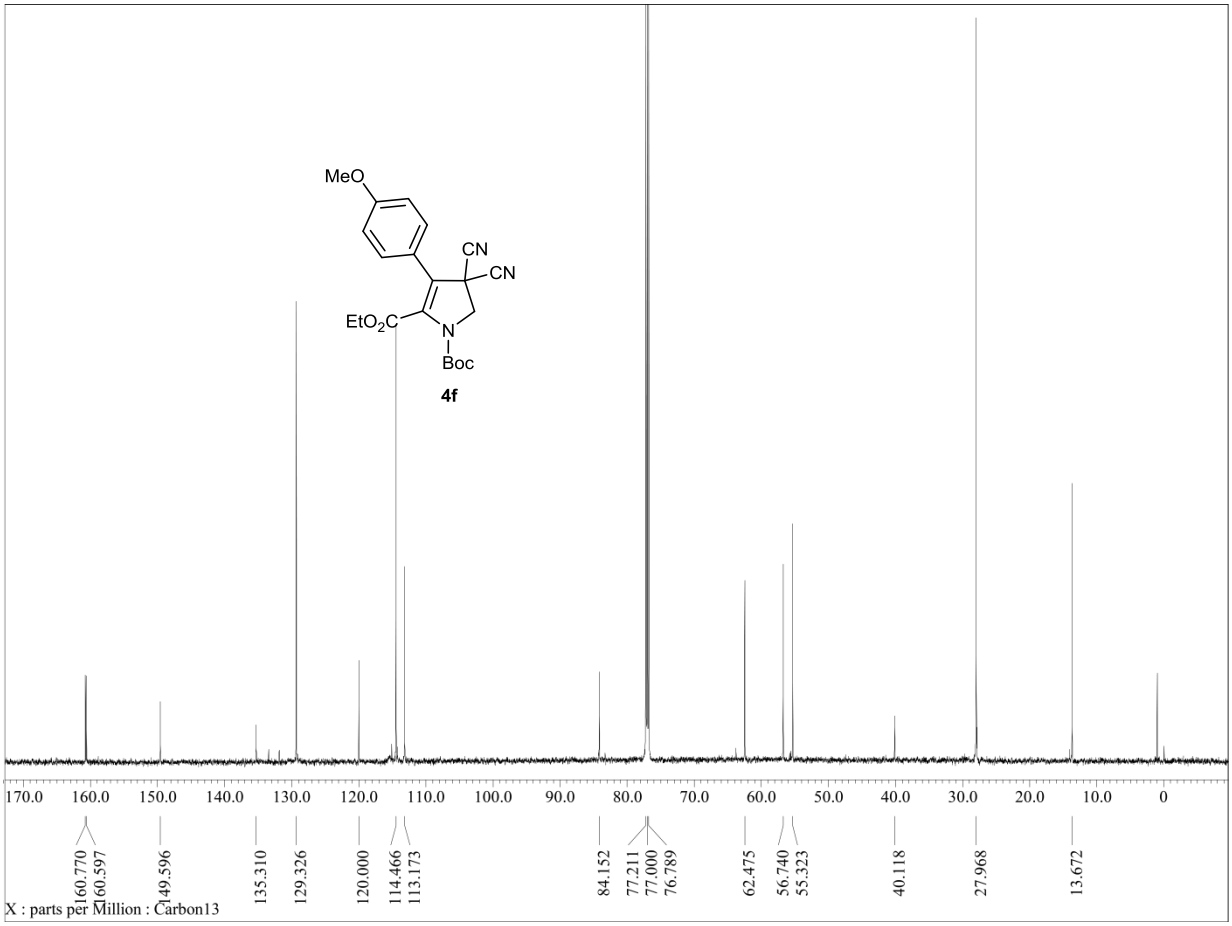
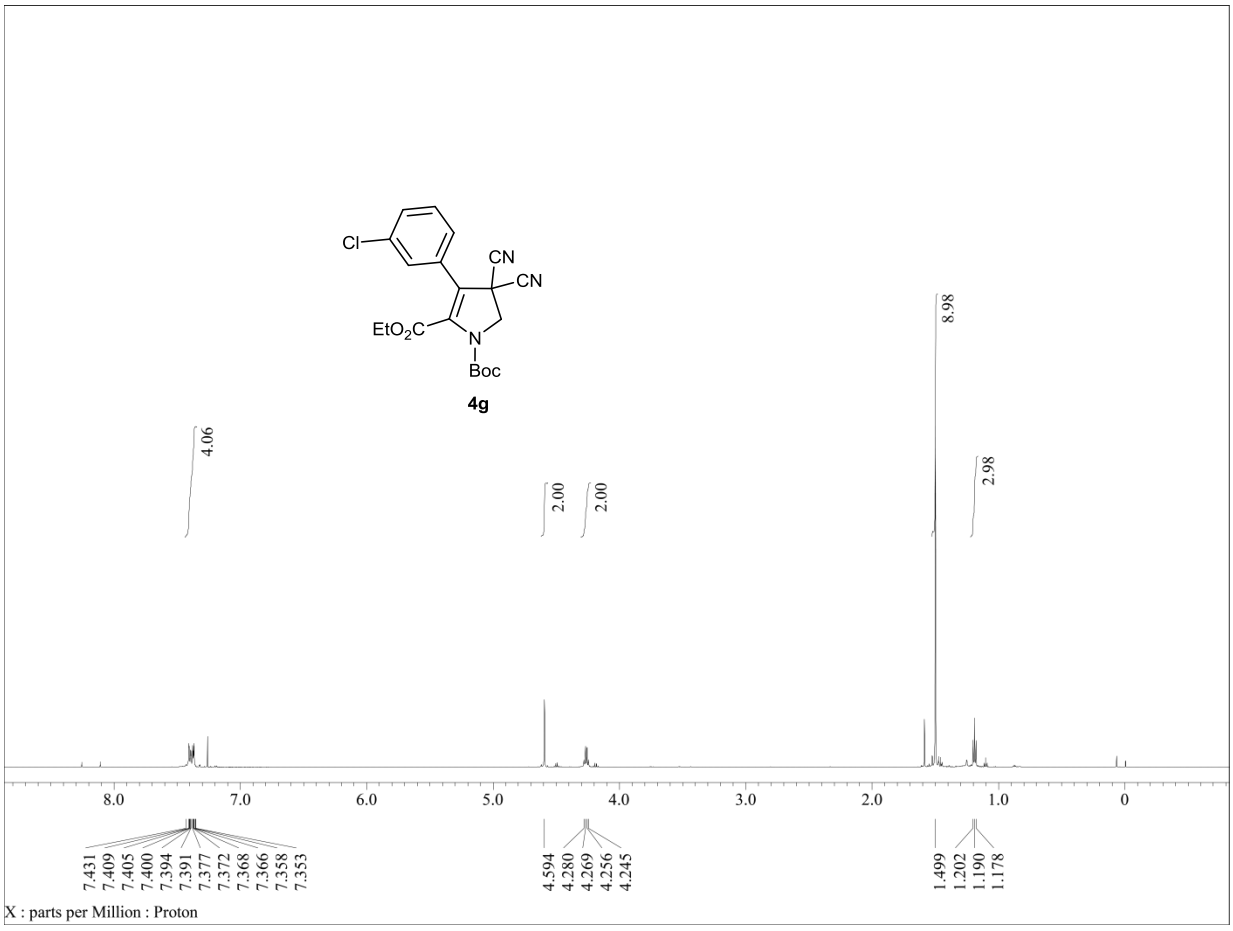
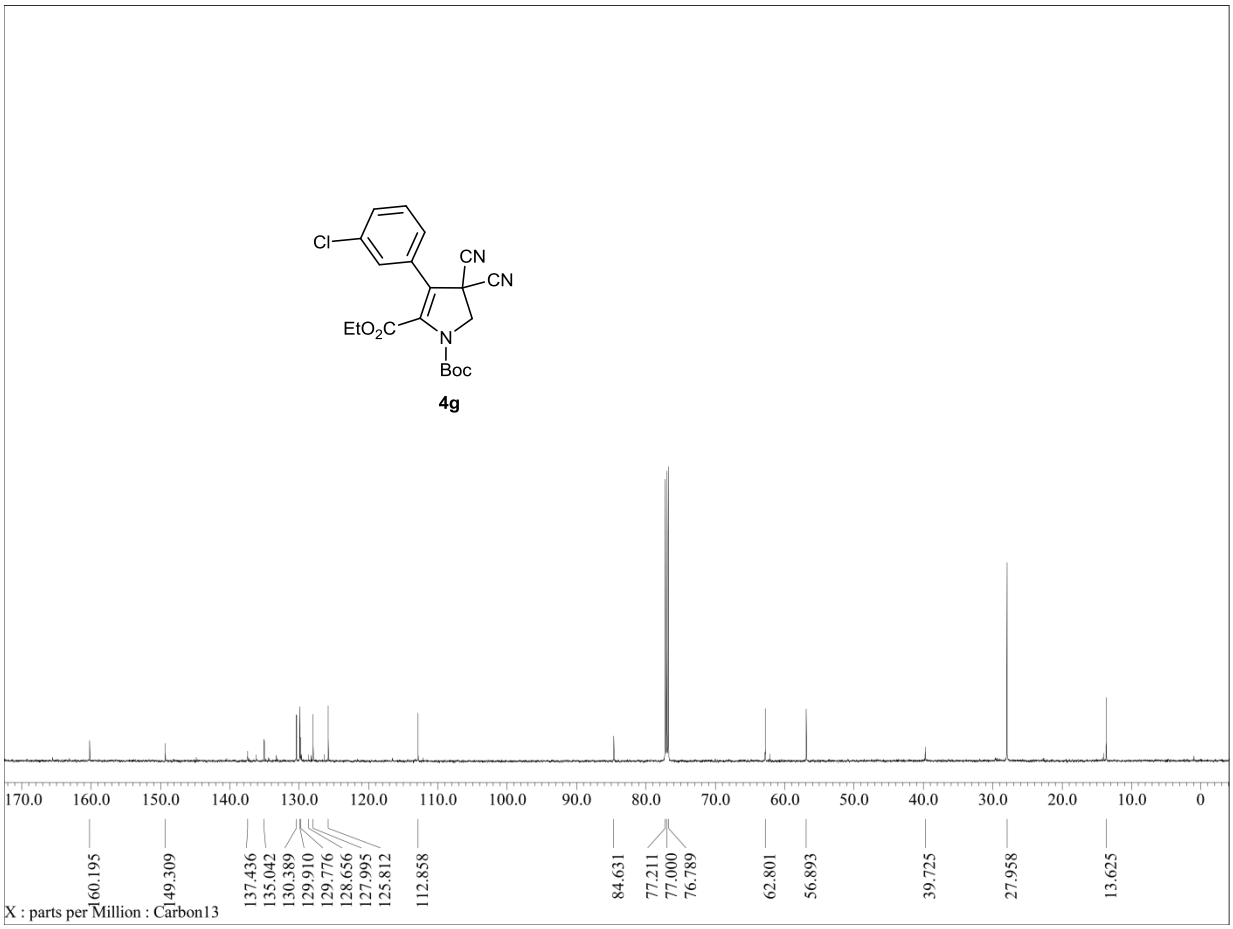
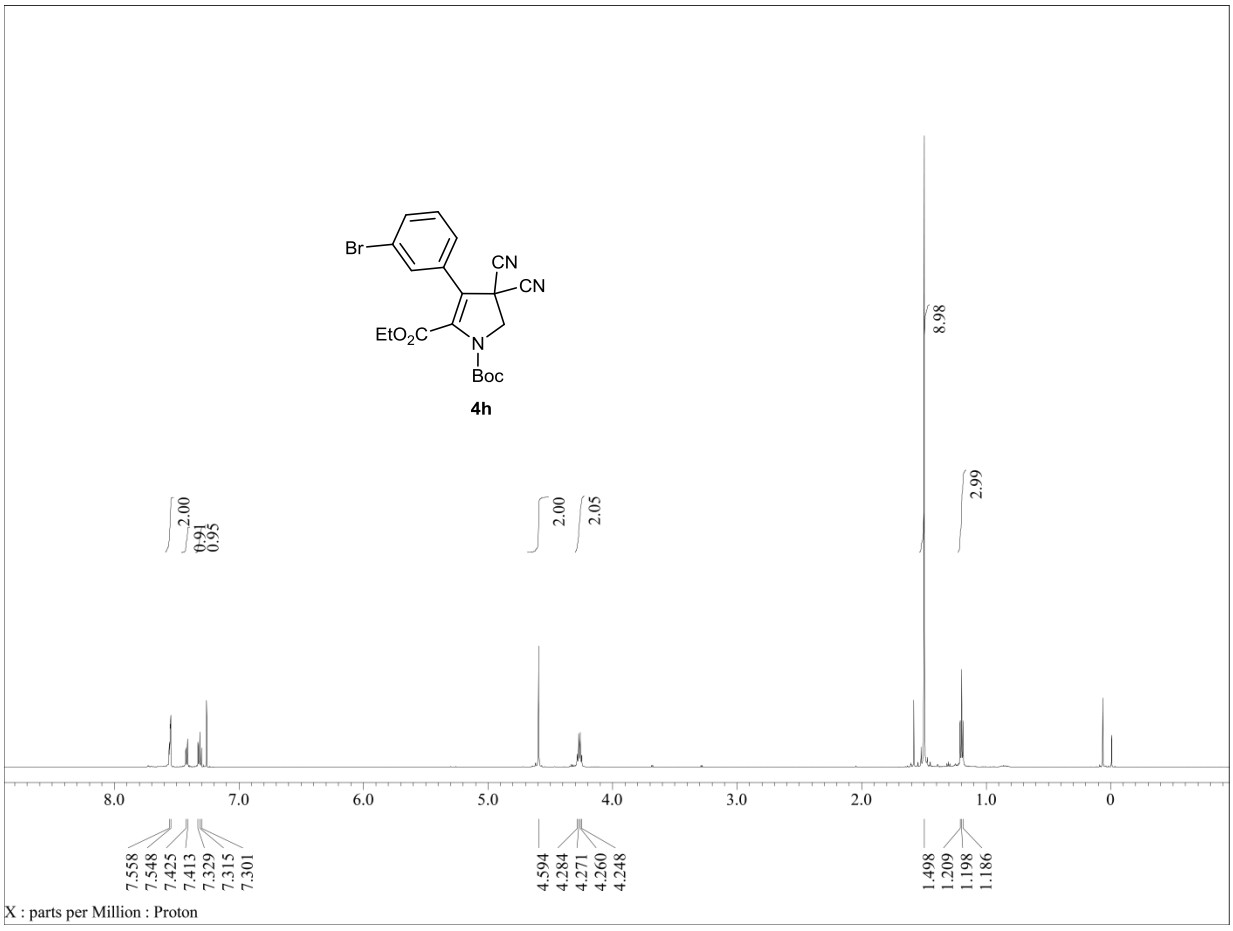

Me
CN
CN
EtO2C
N
Boc
4e
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.731
149.548
139.964
129.977
129.728
128.867
127.564
124.950
113.154
84.200
77.211
77.000
76.789
62.513
56.836
39.984
27.968
21.361
13.625
X : parts per Million : Carbon13

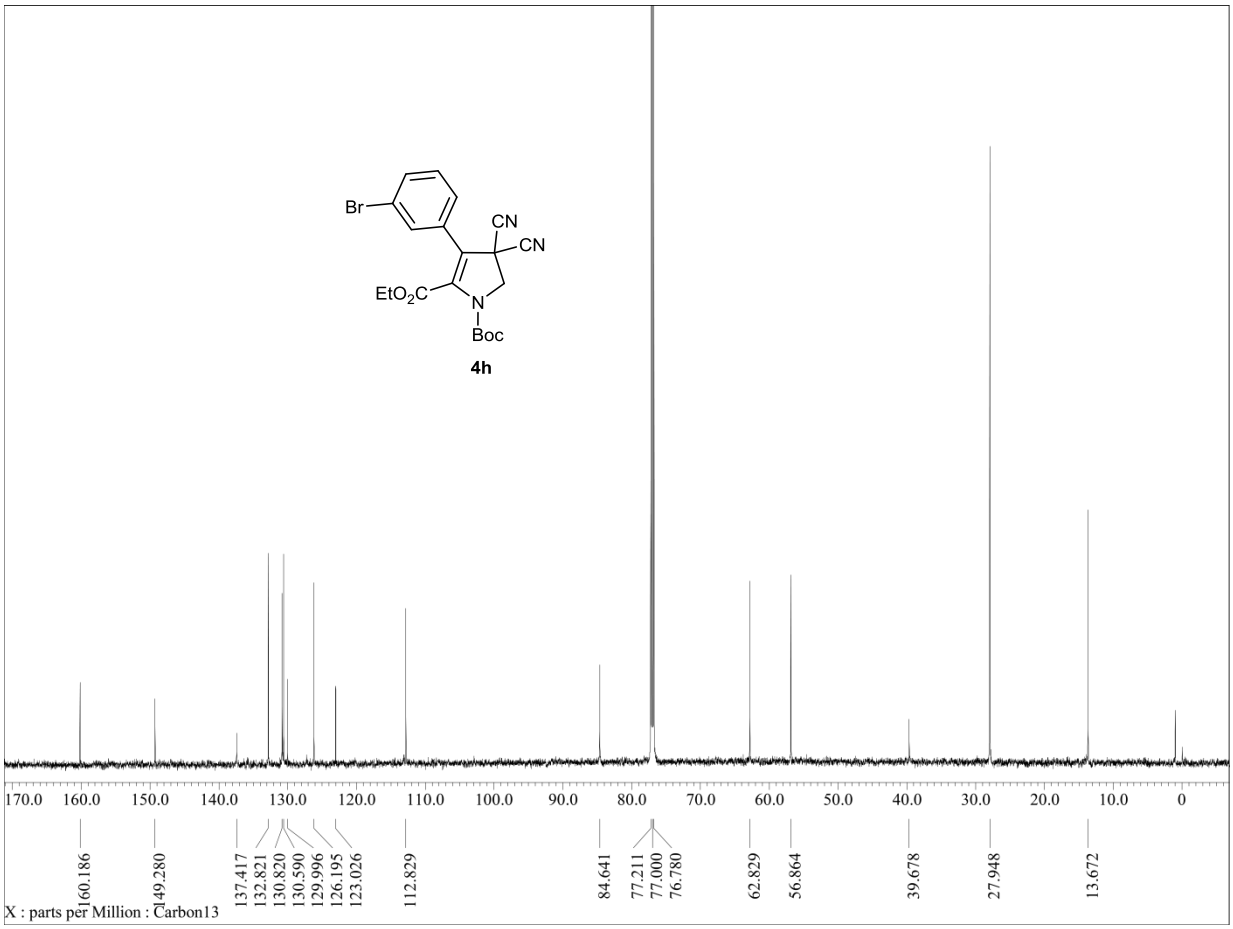

MeO
CN
CN
EtO2C
N
Boc
4f
2.06
2.06
2.04
2.00
3.09
9.30
3.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.383
7.370
6.941
6.926
4.574
4.251
4.238
4.227
4.215
3.831
1.490
1.182
1.170
1.159
X : parts per Million : Proton

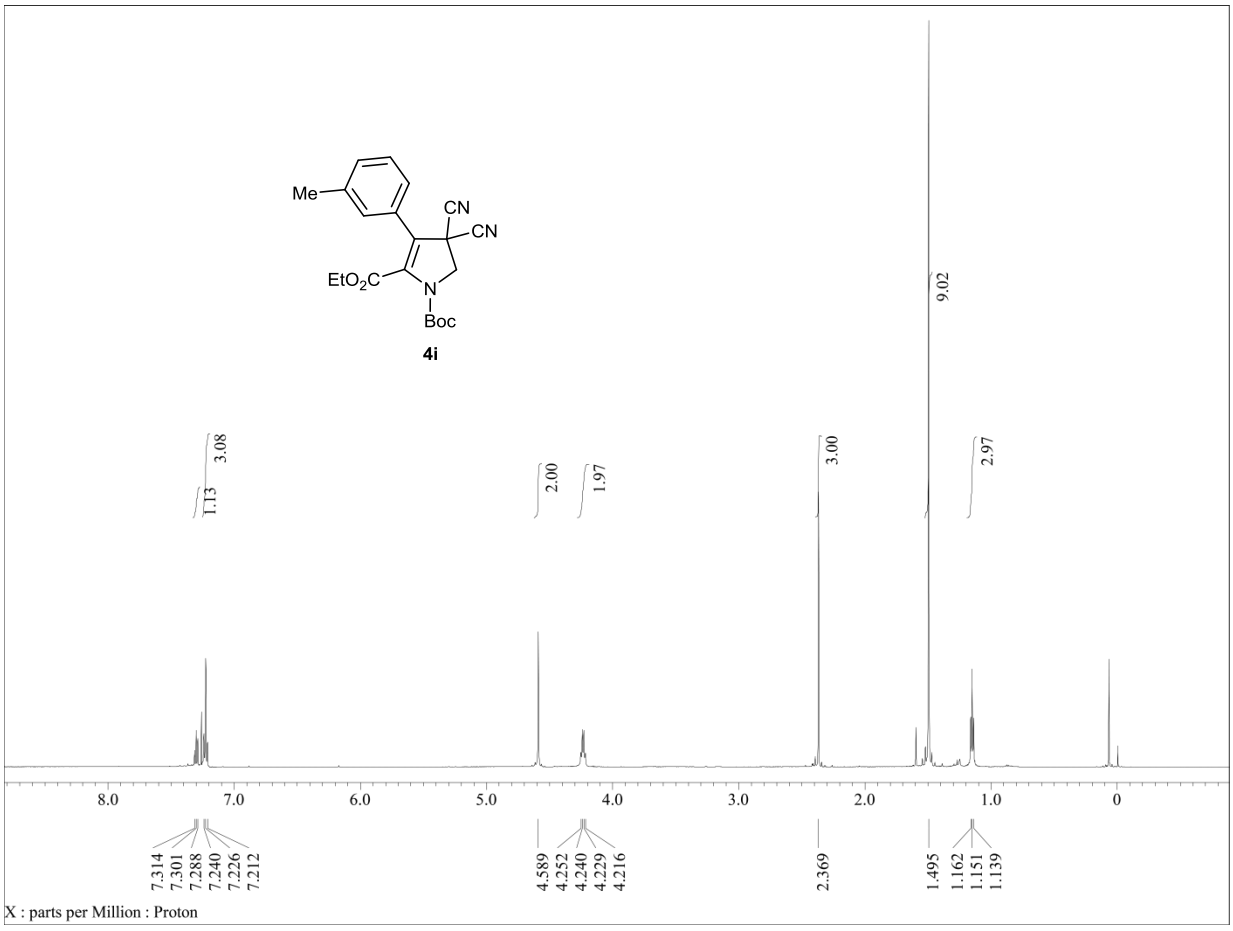

MeO
CN
CN
EtO2C
N
Boc
4f
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.770
160.597
149.596
135.310
129.326
120.000
114.466
113.173
84.152
77.211
77.000
76.789
62.475
56.740
55.323
40.118
27.968
13.672
X : parts per Million : Carbon13

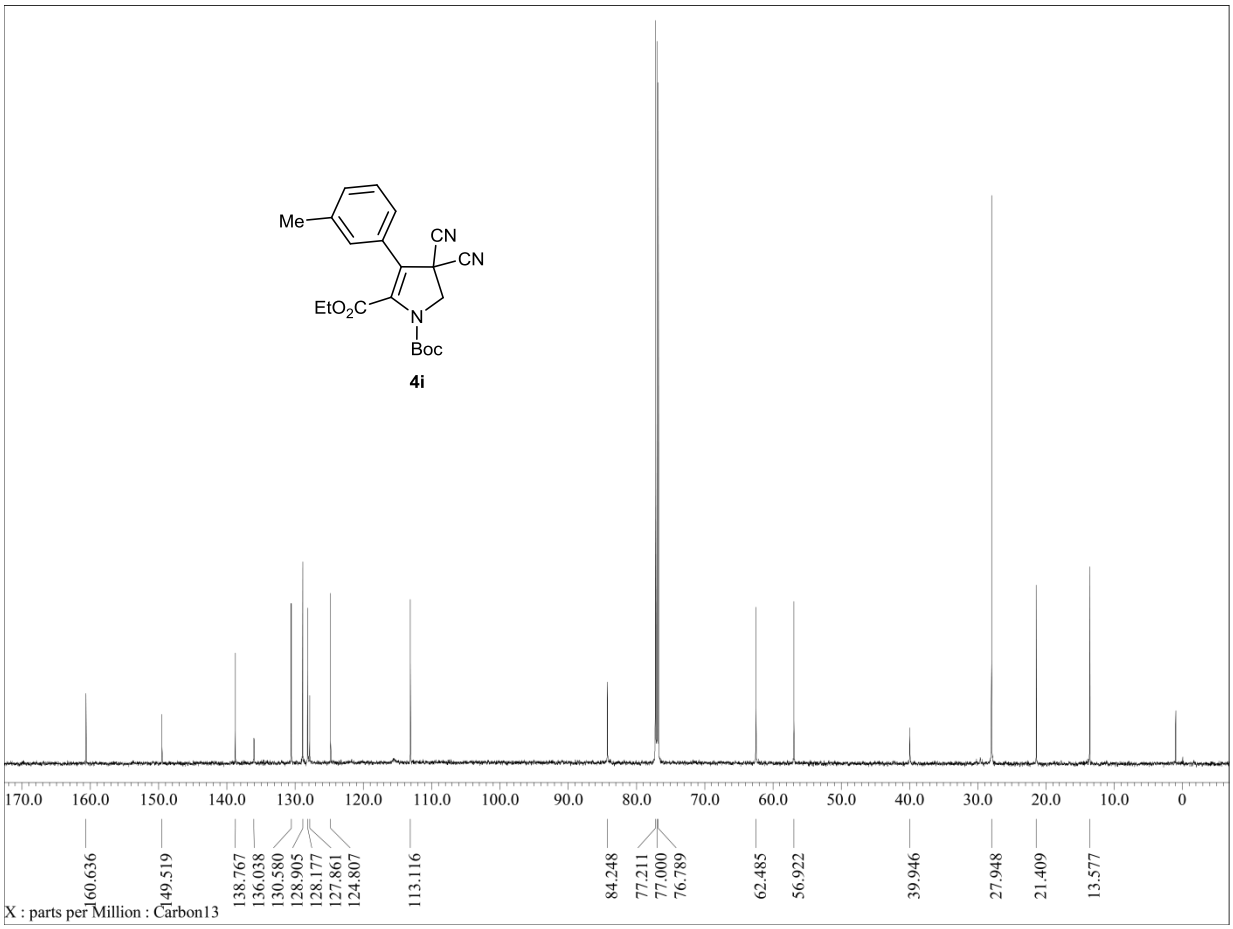

Cl
CN
CN
EtO2C
N
Boc
4g
4.06
2.00
2.00
8.98
2.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.431
7.409
7.405
7.400
7.394
7.391
7.377
7.372
7.368
7.366
7.358
7.353
4.594
4.280
4.269
4.256
4.245
1.499
1.202
1.190
1.178
X : parts per Million : Proton

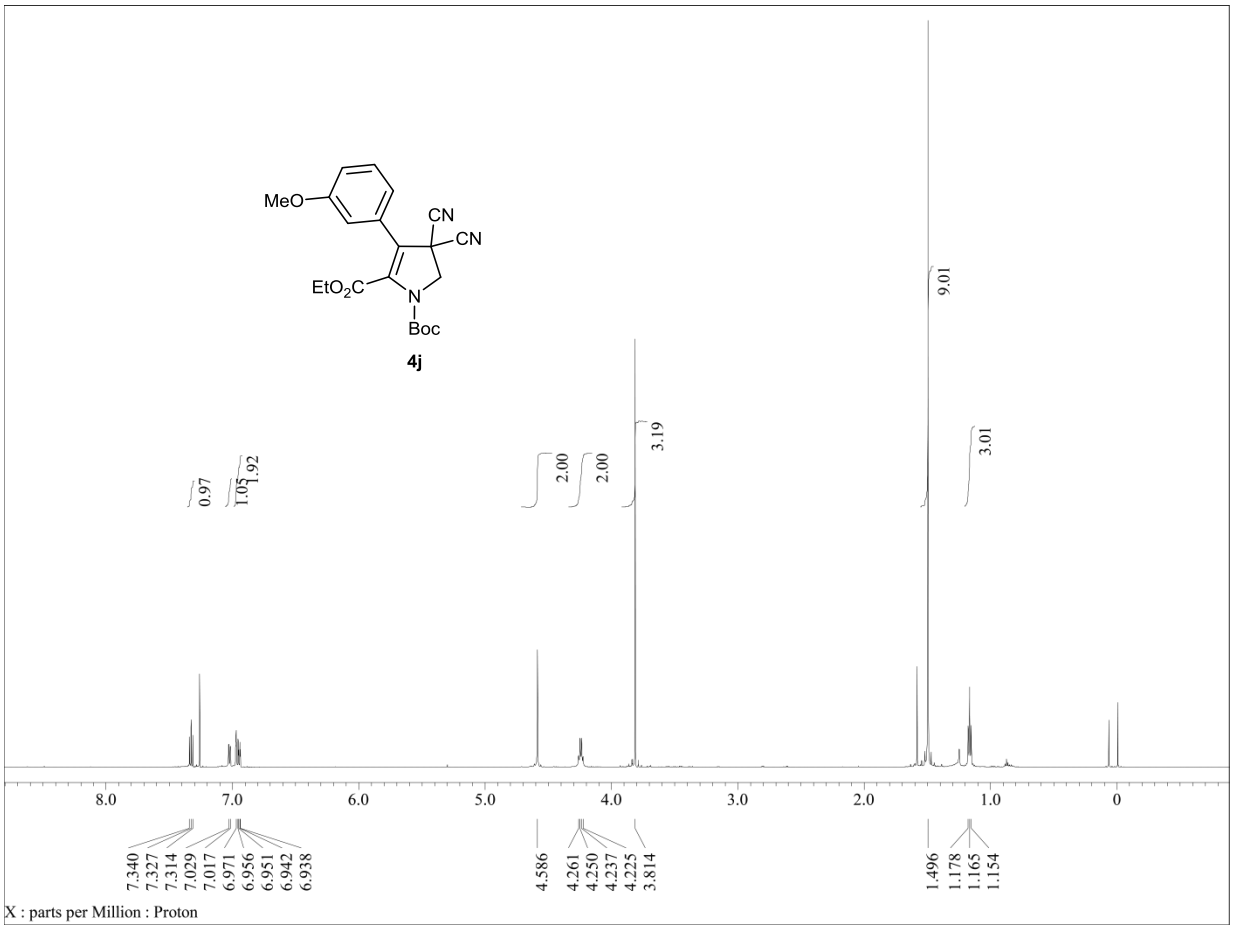

Cl
CN
CN
EtO2C
N
Boc
4g
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.195
149.309
137.436
135.042
130.389
129.910
129.776
128.656
127.995
125.812
112.858
84.631
77.211
77.000
76.789
62.801
56.893
39.725
27.958
13.625
X : parts per Million : Carbon13

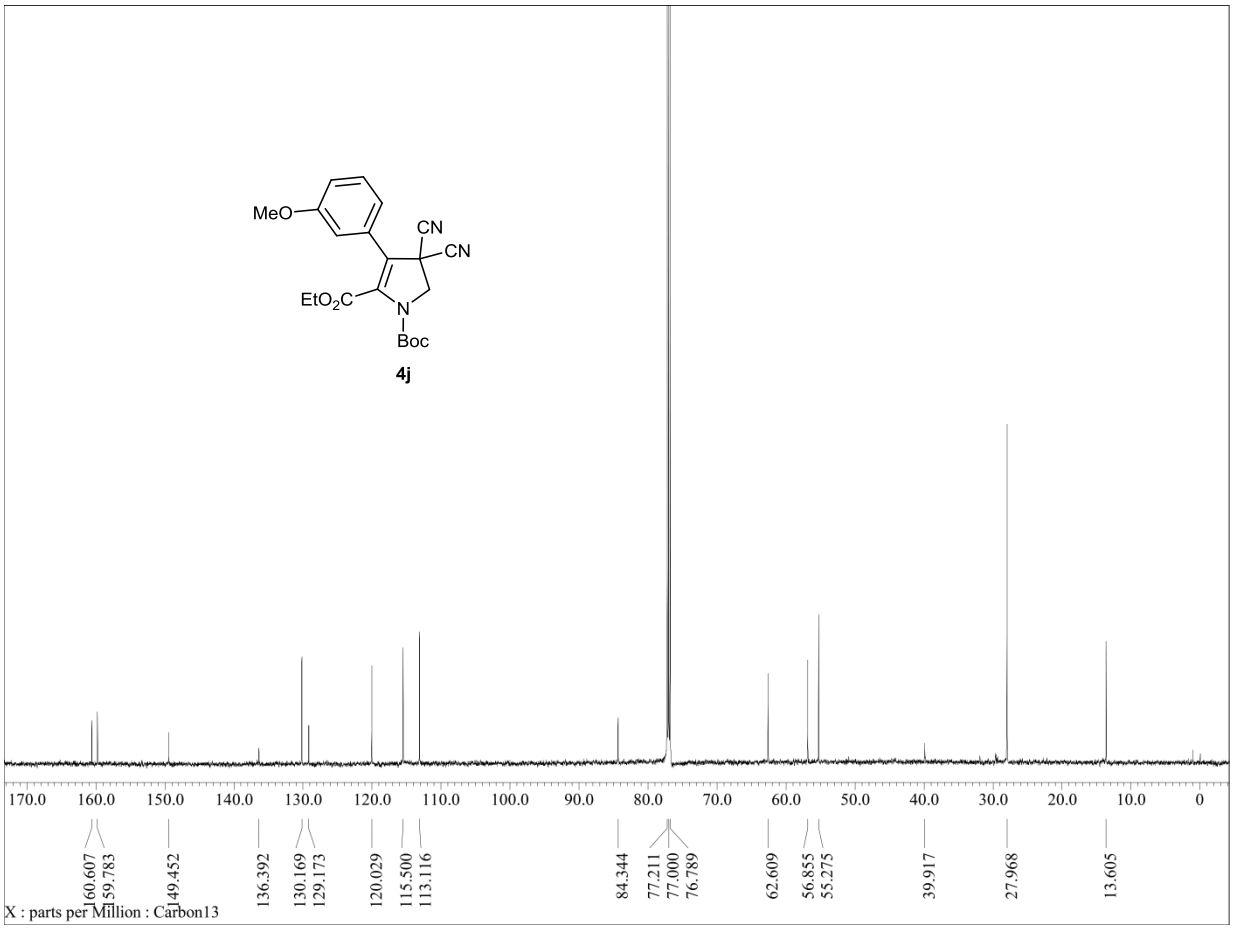

Br
CN
CN
EtO2C
N
Boc
4h
2.00
0.91
0.95
2.00
2.05
8.98
2.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.558
7.548
7.425
7.413
7.329
7.315
7.301
4.594
4.284
4.271
4.260
4.248
1.498
1.209
1.198
1.186
X : parts per Million : Proton

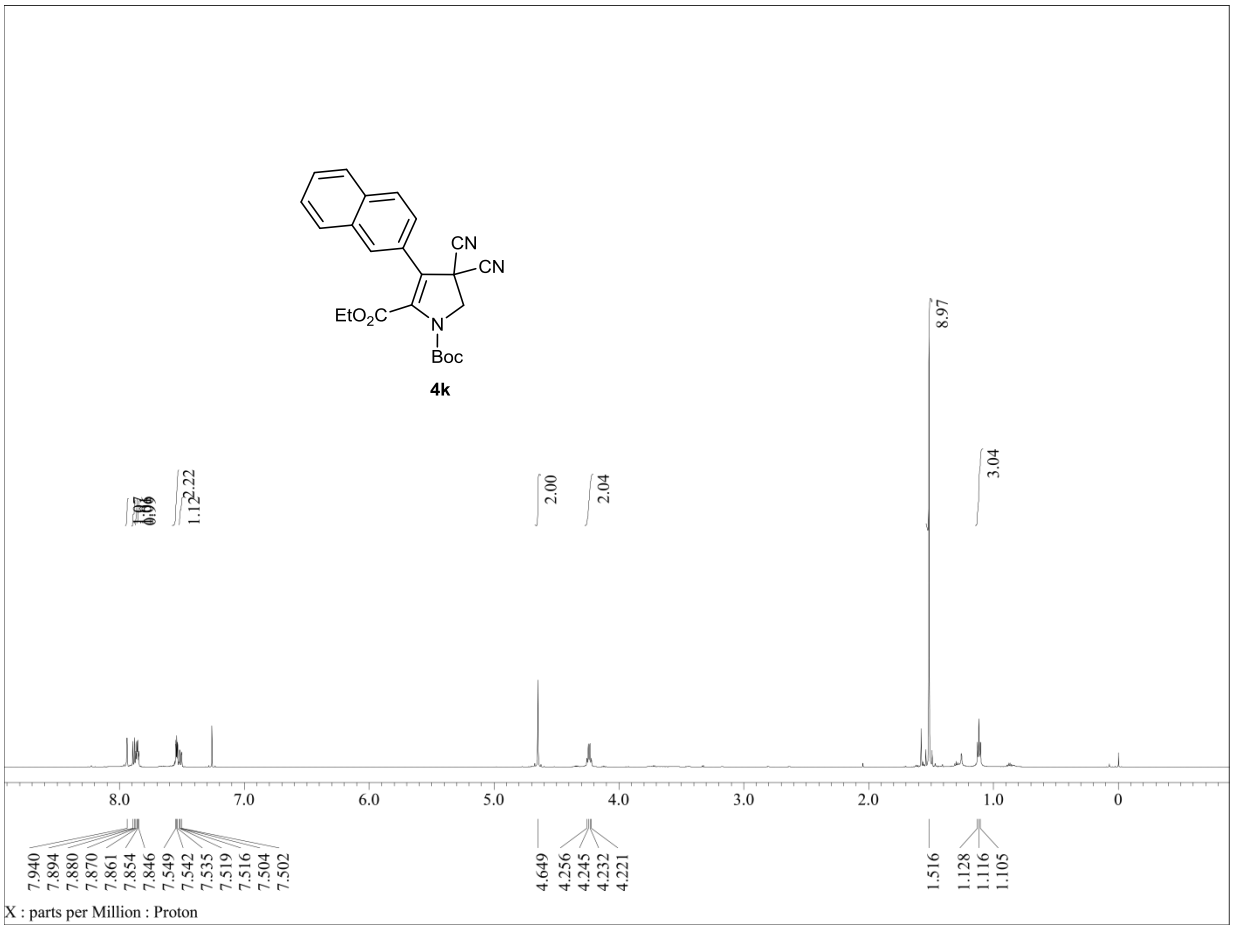

Br
CN
CN
EtO2C
N
Boc
4h
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.186
149.280
137.417
132.821
130.820
130.590
129.996
126.195
123.026
112.829
84.641
77.211
77.000
76.780
62.829
56.864
39.678
27.948
13.672
X : parts per Million : Carbon13

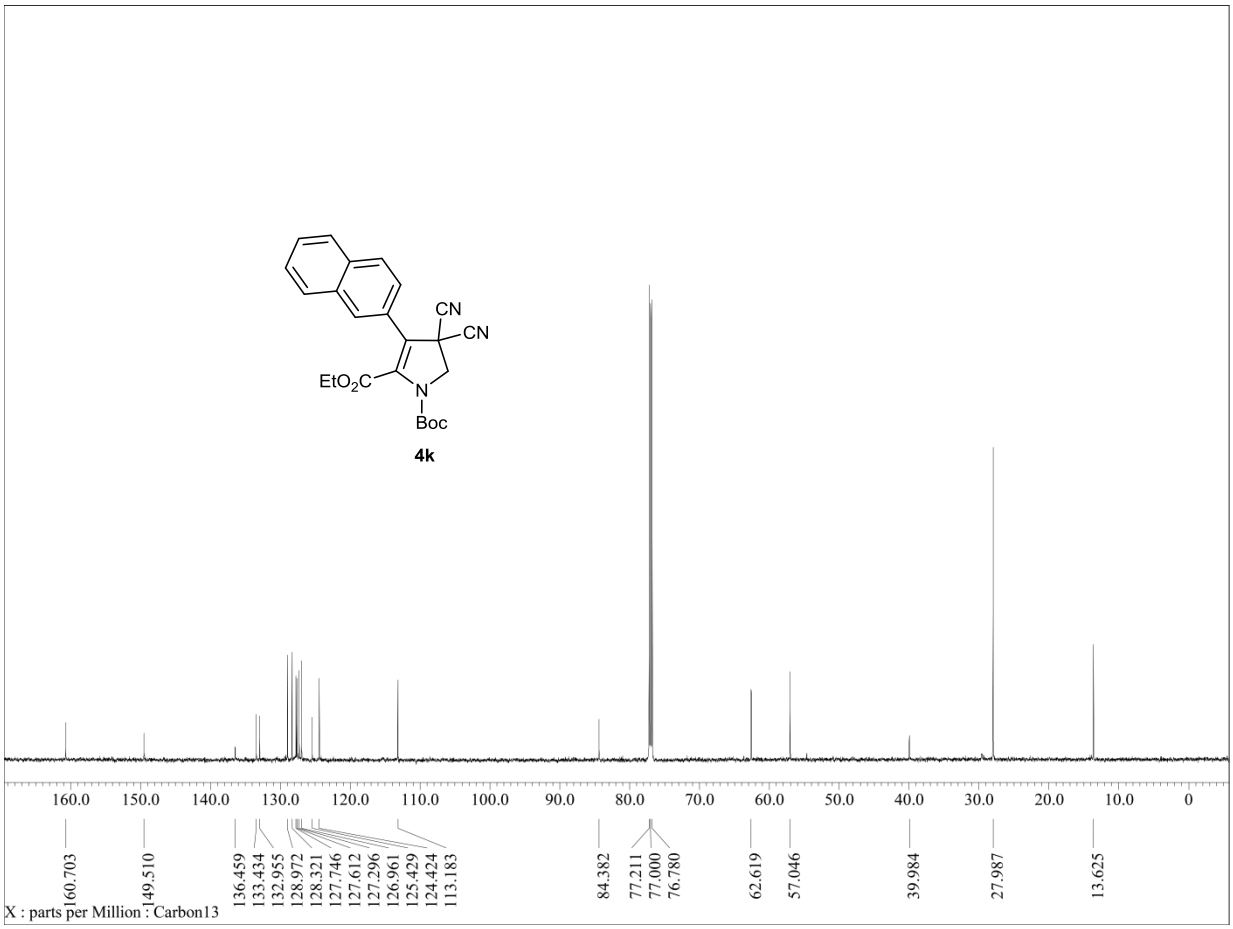

Me
CN
CN
EtO2C
N
Boc
4i
9.02
3.08
1.13
2.00
1.97
3.00
2.97
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.314
7.301
7.288
7.240
7.226
7.212
4.589
4.252
4.240
4.229
4.216
2.369
1.495
1.162
1.151
1.139
X : parts per Million : Proton

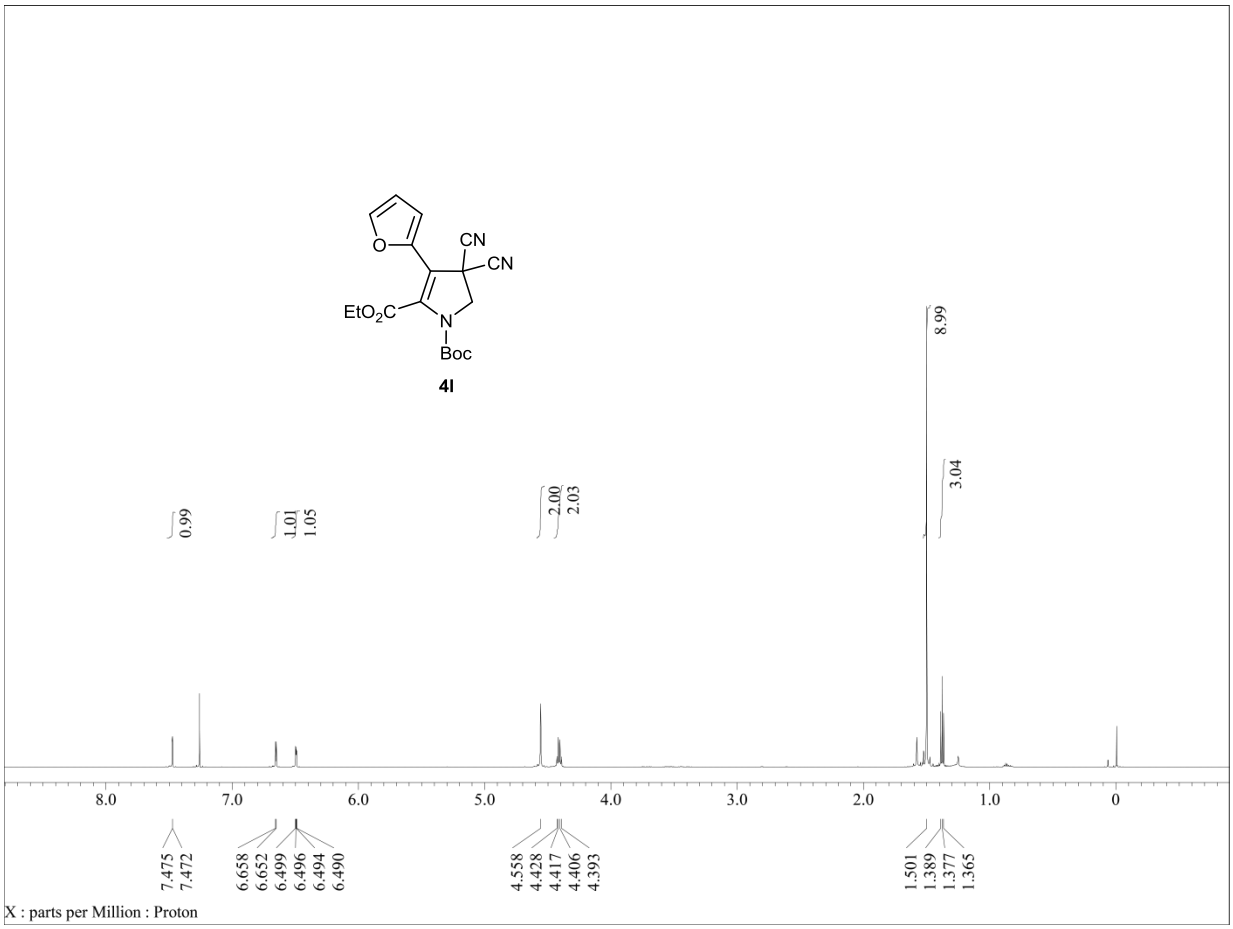

Me
CN
CN
EtO2C
N
Boc
4i
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.636
149.519
138.767
136.038
130.580
128.905
128.177
127.861
124.807
113.116
84.248
77.211
77.000
76.789
62.485
56.922
39.946
27.948
21.409
13.577
X : parts per Million : Carbon13

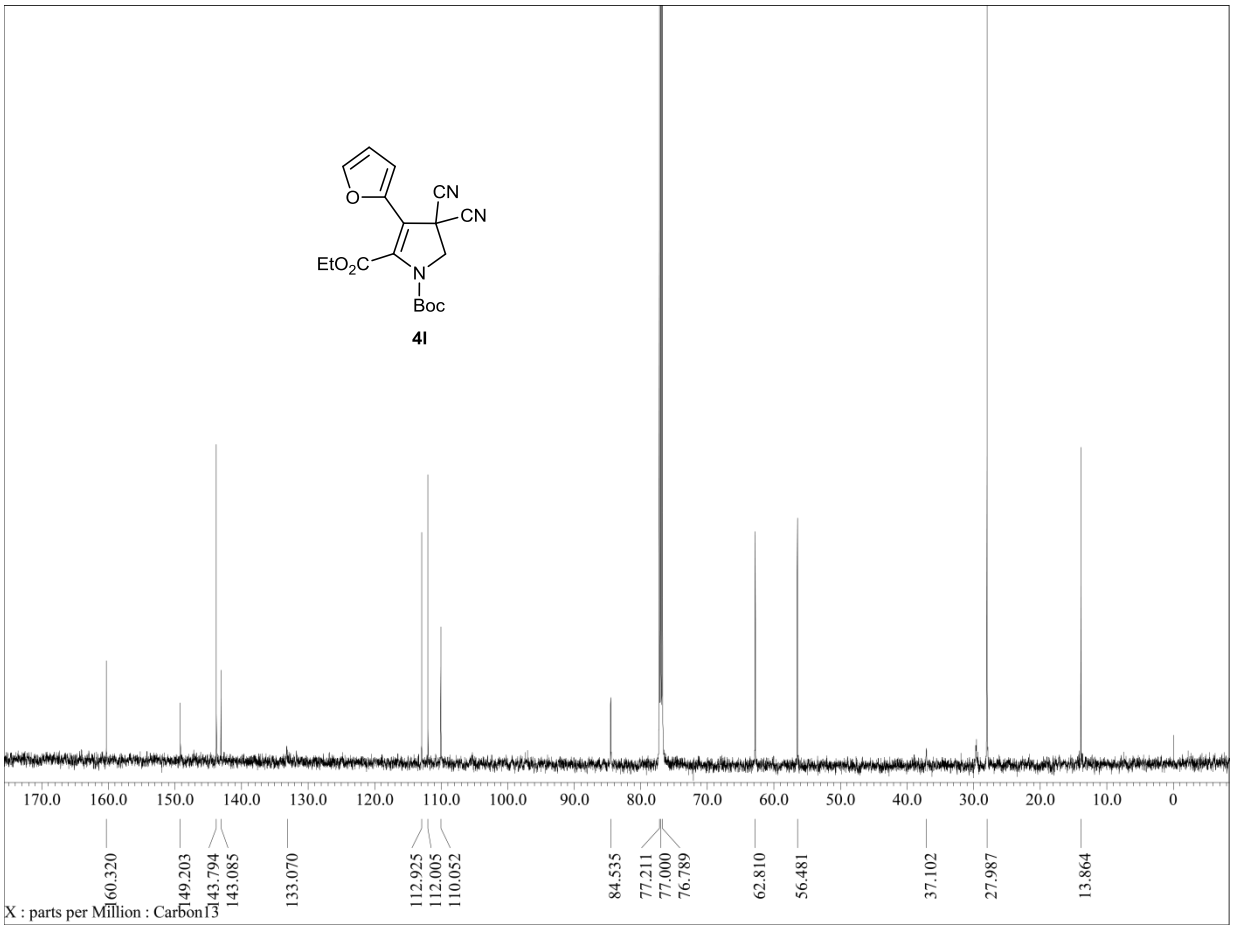

MeO
CN
CN
EtO2C
N
Boc
4j
0.97
1.05
1.92
2.00
2.00
3.19
9.01
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.340
7.327
7.314
7.029
7.017
6.971
6.956
6.951
6.942
6.938
4.586
4.261
4.250
4.237
4.225
3.814
1.496
1.178
1.165
1.154
X : parts per Million : Proton

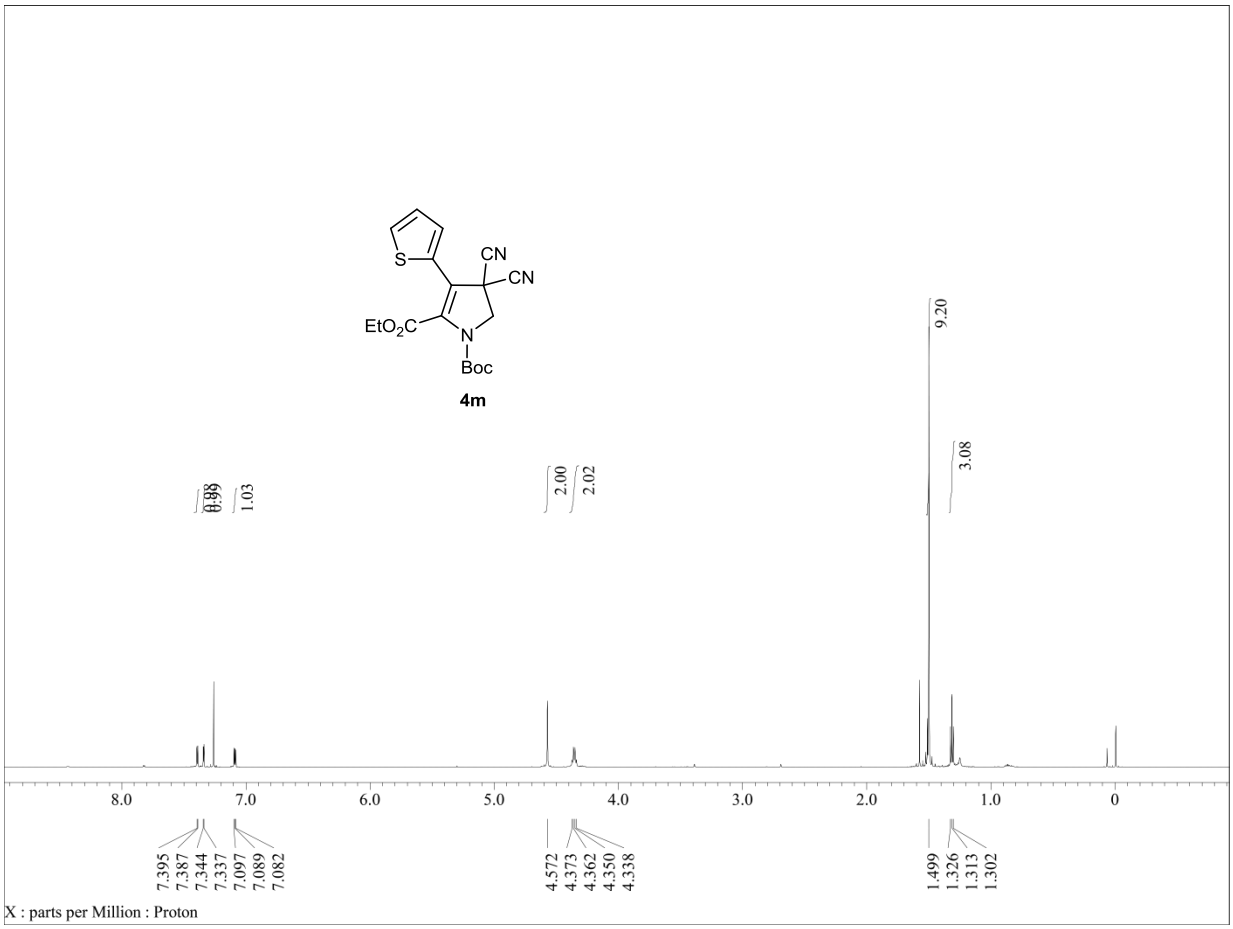

MeO
CN
CN
EtO2C
N
Boc
4j
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.607
159.783
149.452
136.392
130.169
129.173
120.029
115.500
113.116
84.344
77.211
77.000
76.789
62.609
56.855
55.275
39.917
27.968
13.605
X : parts per Million : Carbon13

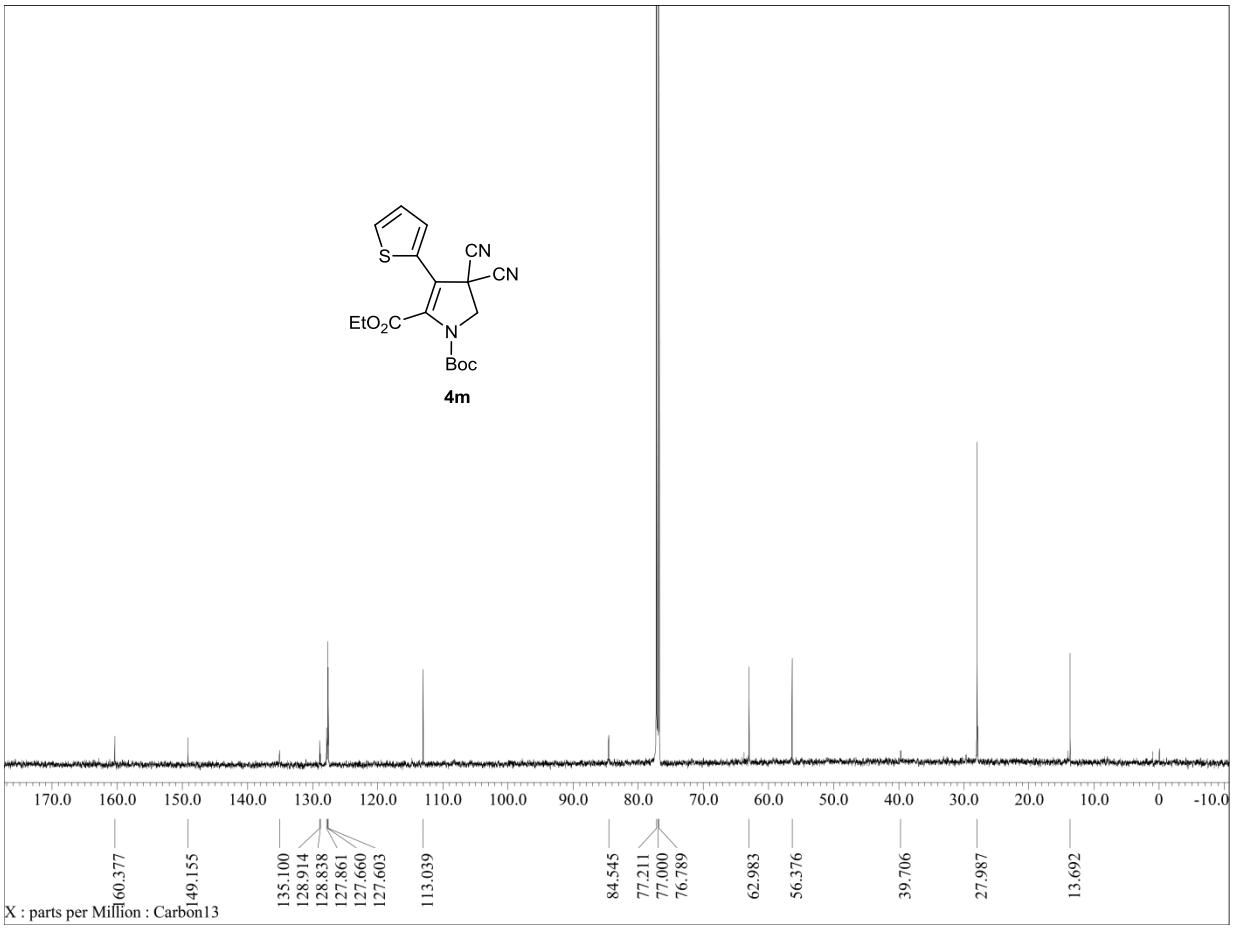

CN
CN
EtO2C
N
Boc
4k
8.97
3.04
2.22
2.00
2.04
1.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.940
7.894
7.880
7.870
7.861
7.854
7.846
7.549
7.542
7.535
7.519
7.516
7.504
7.502
4.649
4.256
4.245
4.232
4.221
1.516
1.128
1.116
1.105
X : parts per Million : Proton

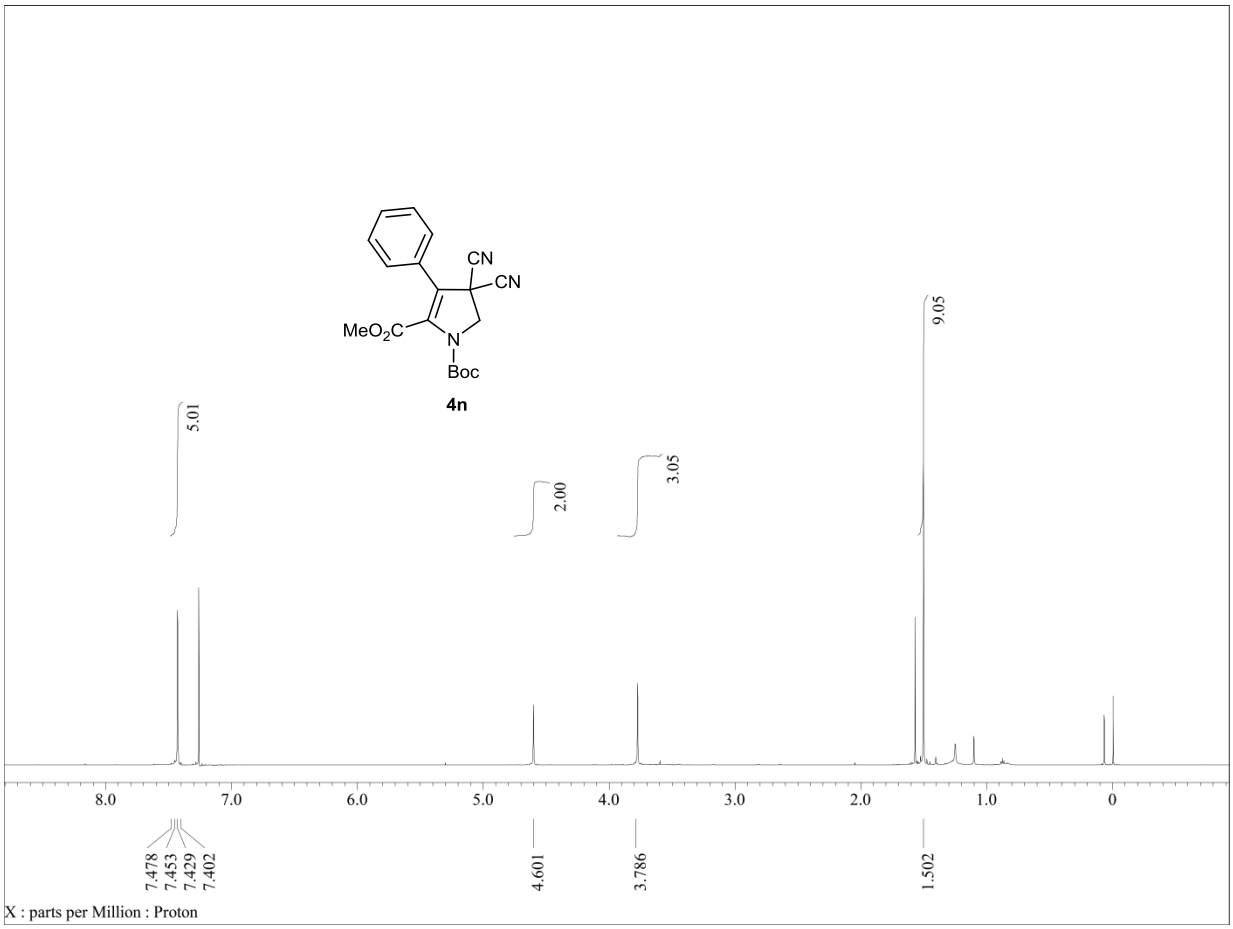

CN
CN
EtO2C
N
Boc
4k
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.703
149.510
136.459
133.434
132.955
128.972
128.321
127.746
127.612
127.296
126.961
125.429
124.424
113.183
84.382
77.211
77.000
76.780
62.619
57.046
39.984
27.987
13.625
X : parts per Million : Carbon13

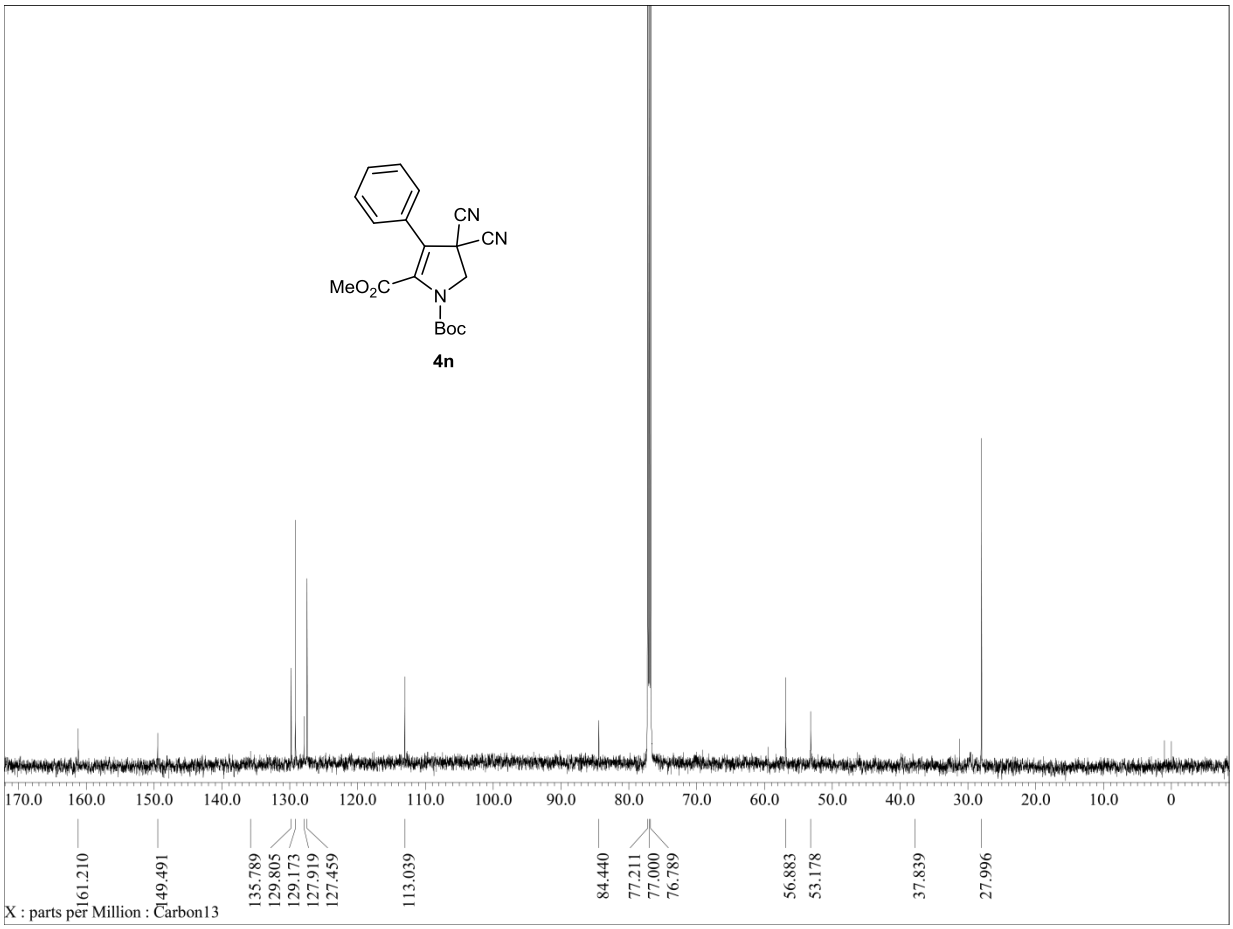

CN
CN
EtO2C
N
Boc
4l
8.99
3.04
2.00
2.03
1.01
1.05
0.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.475
7.472
6.658
6.652
6.499
6.496
6.494
6.490
4.558
4.428
4.417
4.406
4.393
1.501
1.389
1.377
1.365
X : parts per Million : Proton

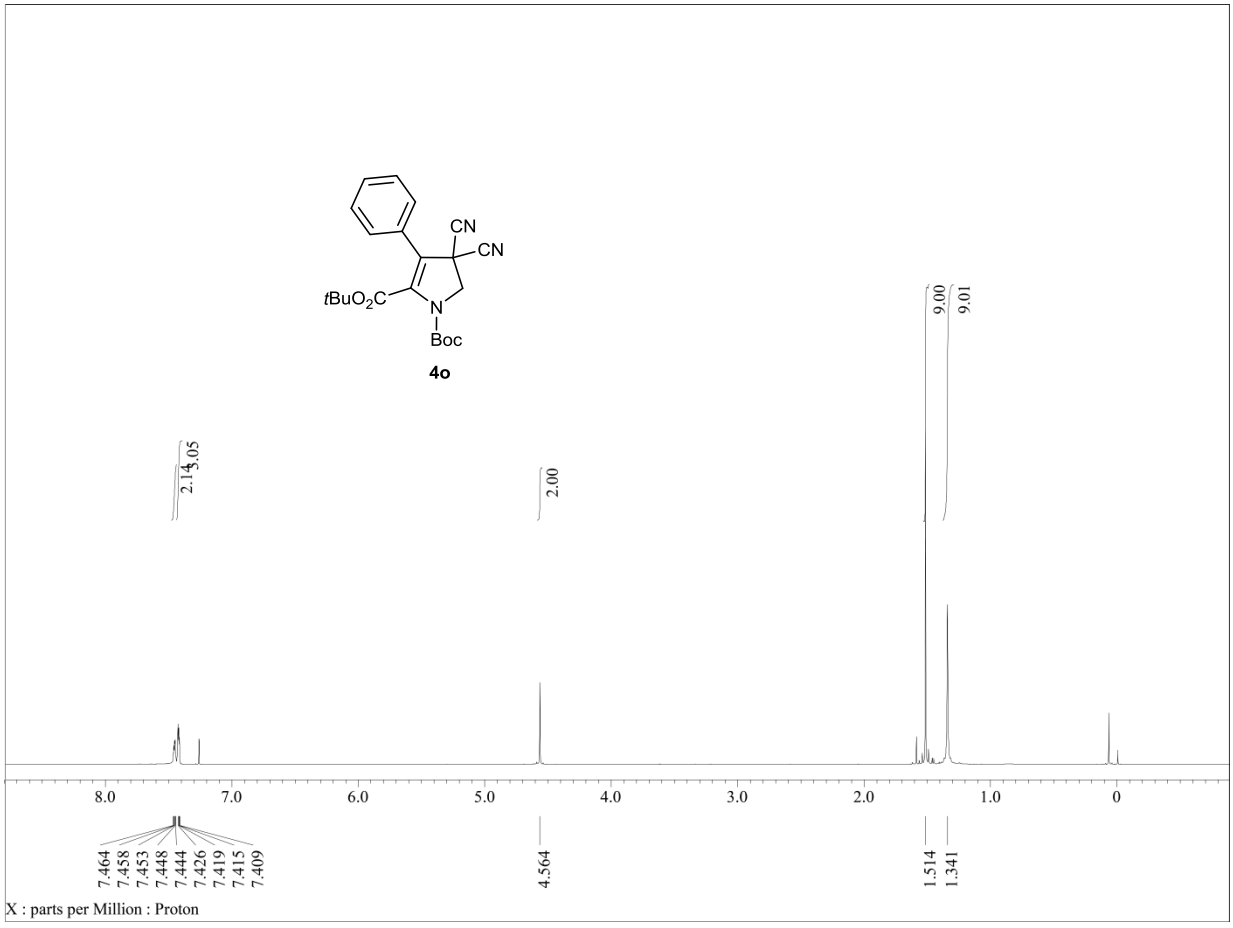

CN
CN
EtO2C
N
Boc
4l
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.320
149.203
143.794
143.085
133.070
112.925
112.005
110.052
84.535
77.211
77.000
76.789
62.810
56.481
37.102
27.987
13.864
X : parts per Million : Carbon13

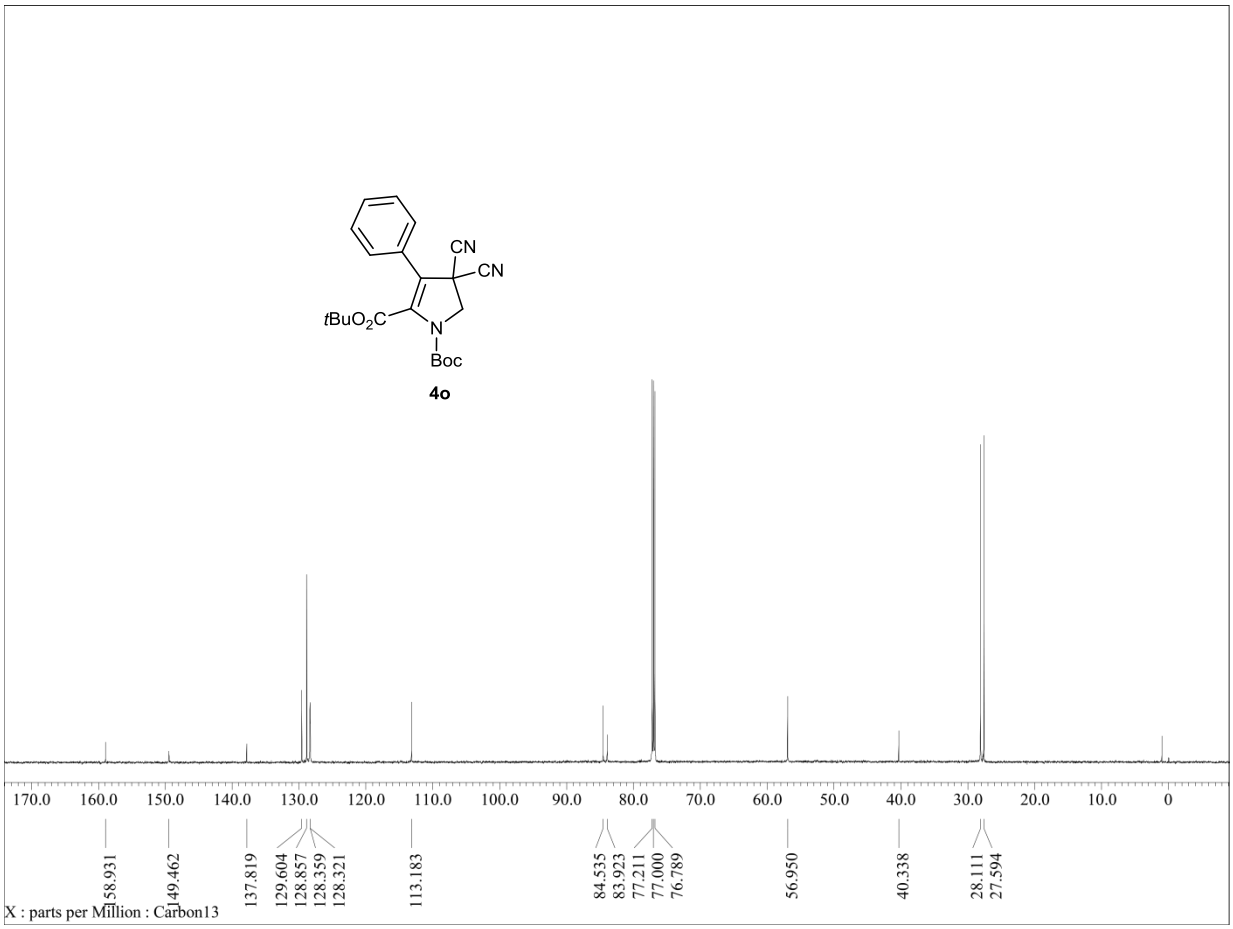

S
CN
CN
EtO2C
N
Boc
4m
9.20
3.08
2.00
2.02
1.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.395
7.387
7.344
7.337
7.097
7.089
7.082
4.572
4.373
4.362
4.350
4.338
1.499
1.326
1.313
1.302
X : parts per Million : Proton

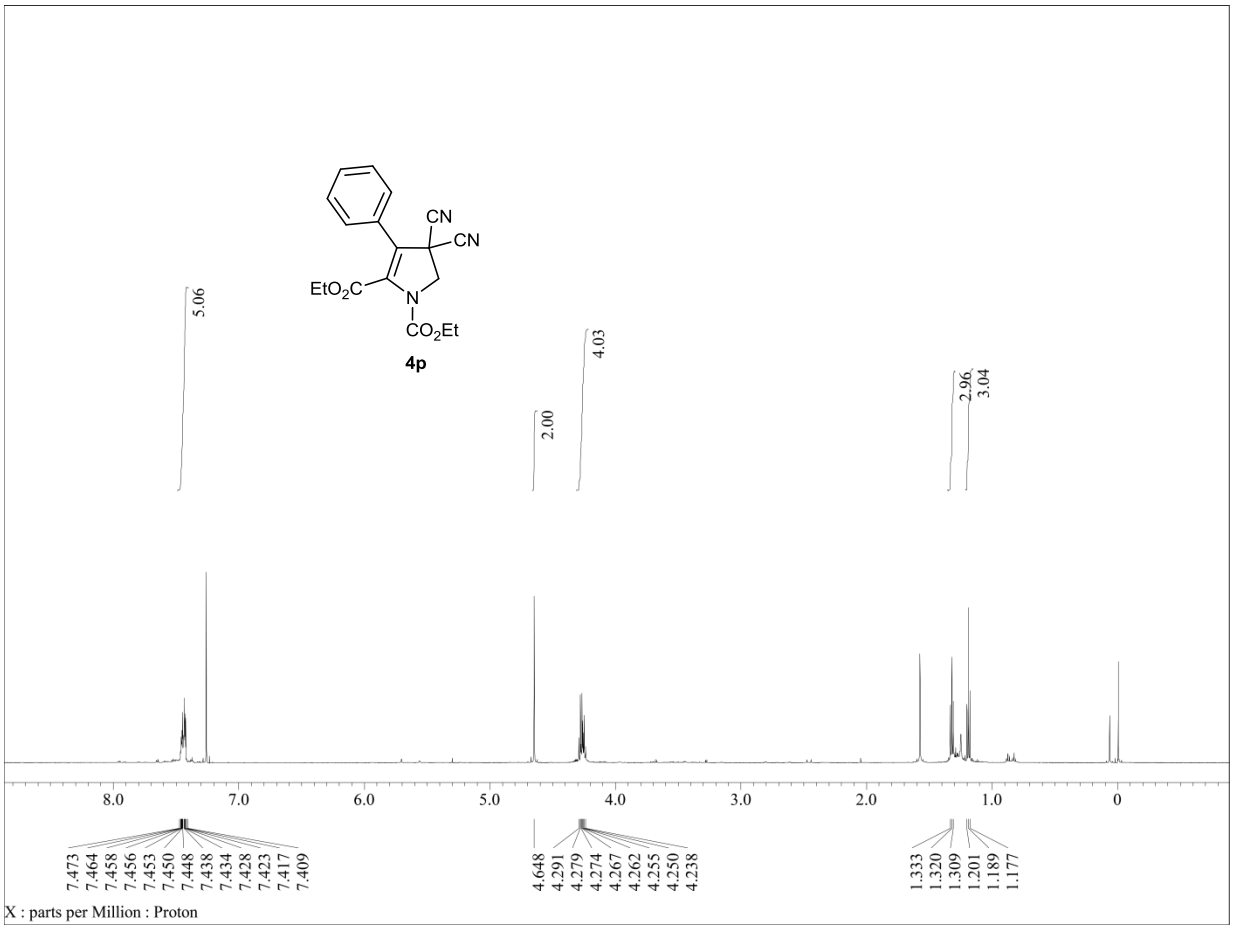

S
CN
CN
EtO2C
N
Boc
4m
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
160.377
149.155
135.100
128.914
128.838
127.861
127.660
127.603
113.039
84.545
77.211
77.000
76.789
62.983
56.376
39.706
27.987
13.692
X : parts per Million : Carbon13

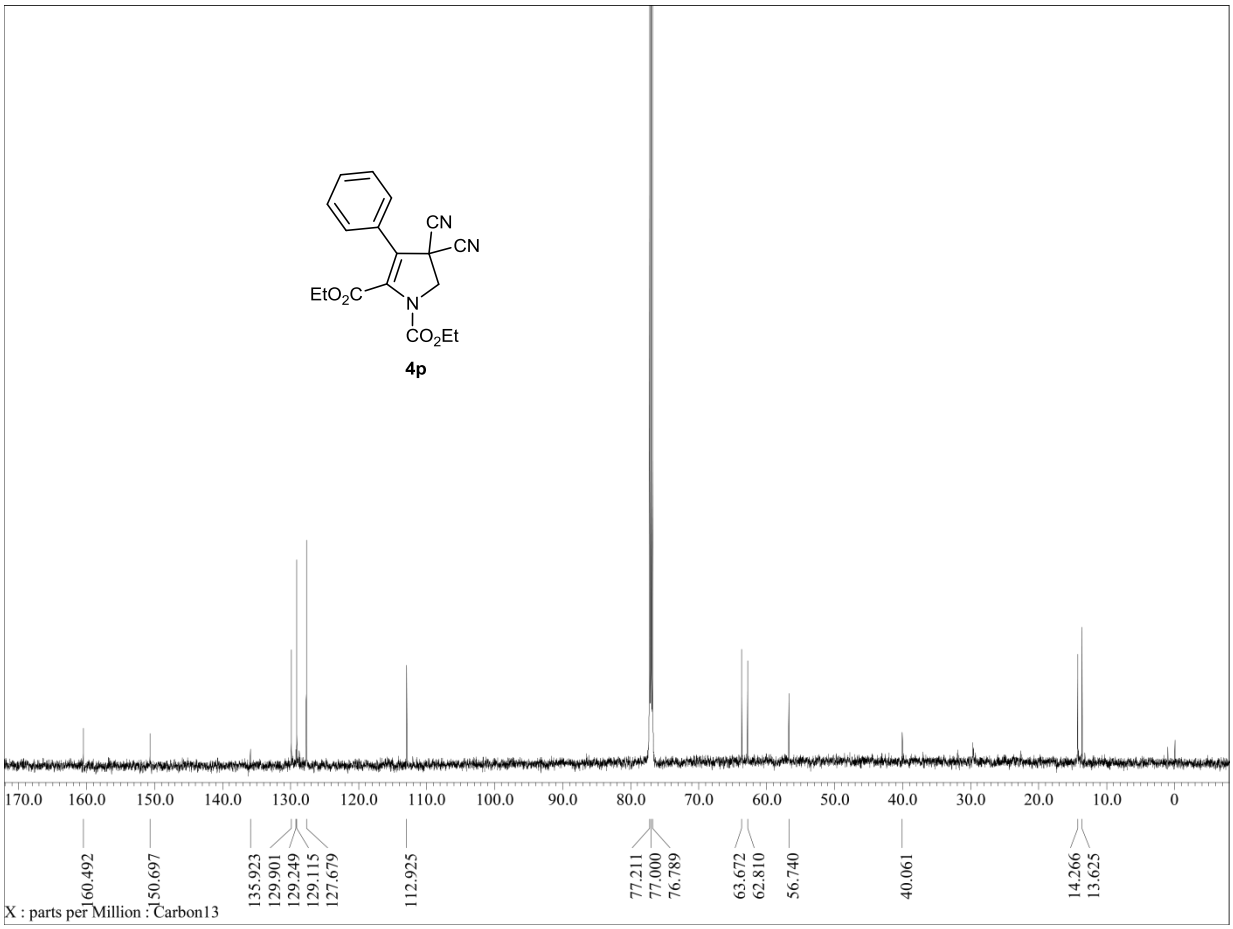

CN
CN
MeO2C
N
Boc
4n
5.01
2.00
3.05
9.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.478
7.453
7.429
7.402
4.601
3.786
1.502
X : parts per Million : Proton

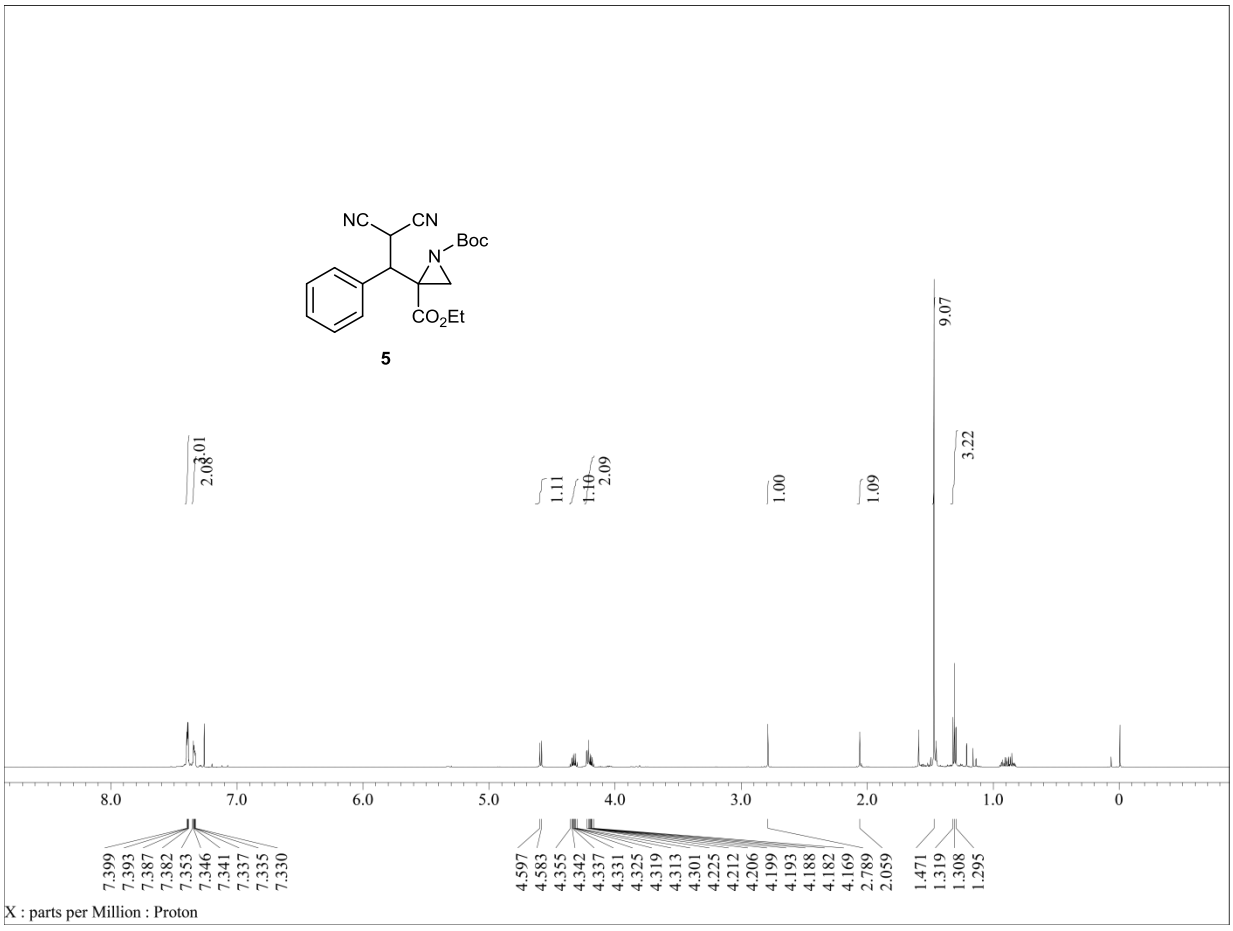

CN
CN
MeO2C
N
Boc
4n
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
161.210
149.491
135.789
129.805
129.173
127.919
127.459
113.039
84.440
77.211
77.000
76.789
56.883
53.178
37.839
27.996
X : parts per Million : Carbon13

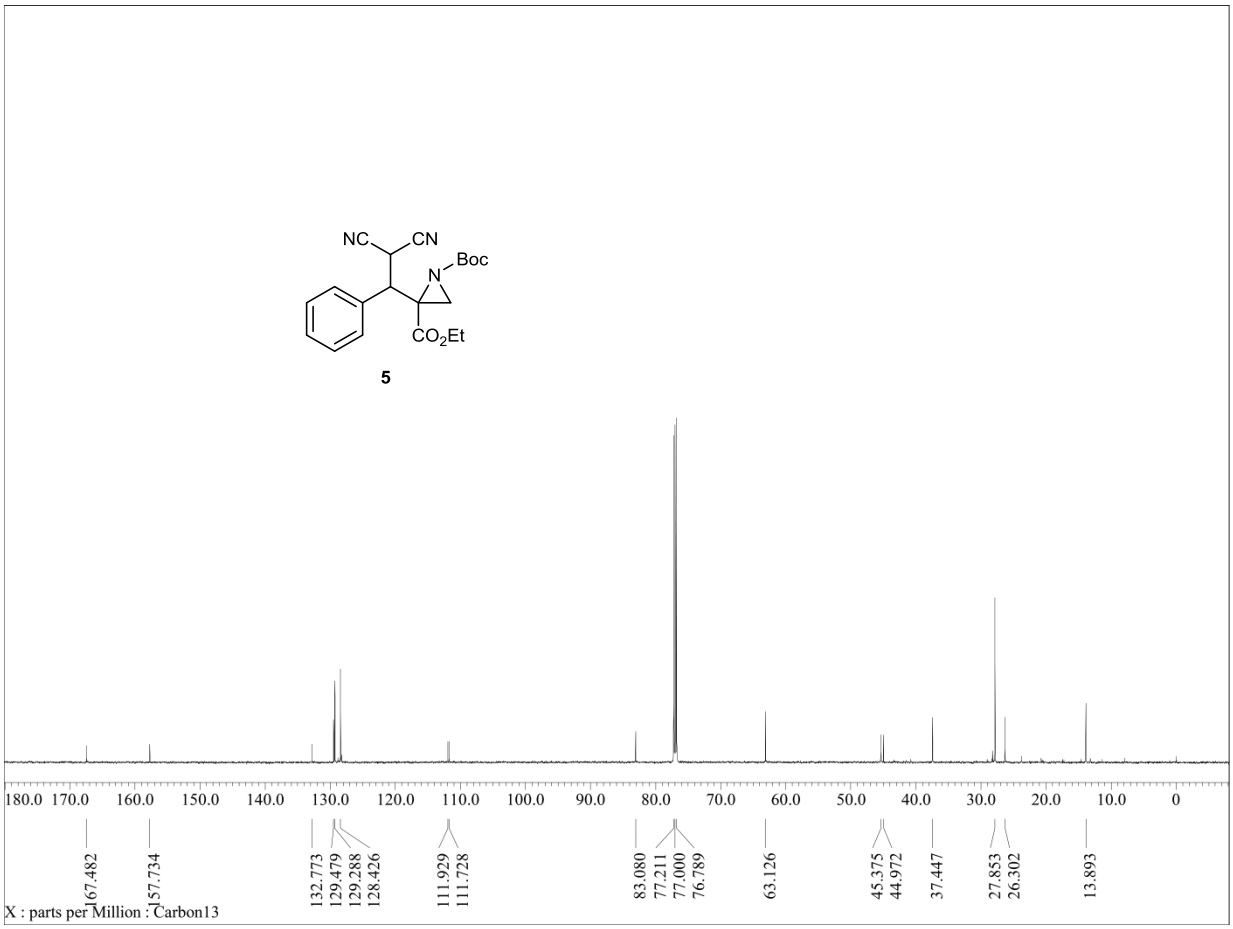

CN
CN
tBuO2C
N
Boc
4o
9.00
9.01
2.14
3.05
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.464
7.458
7.453
7.448
7.444
7.426
7.419
7.415
7.409
4.564
1.514
1.341
X : parts per Million : Proton

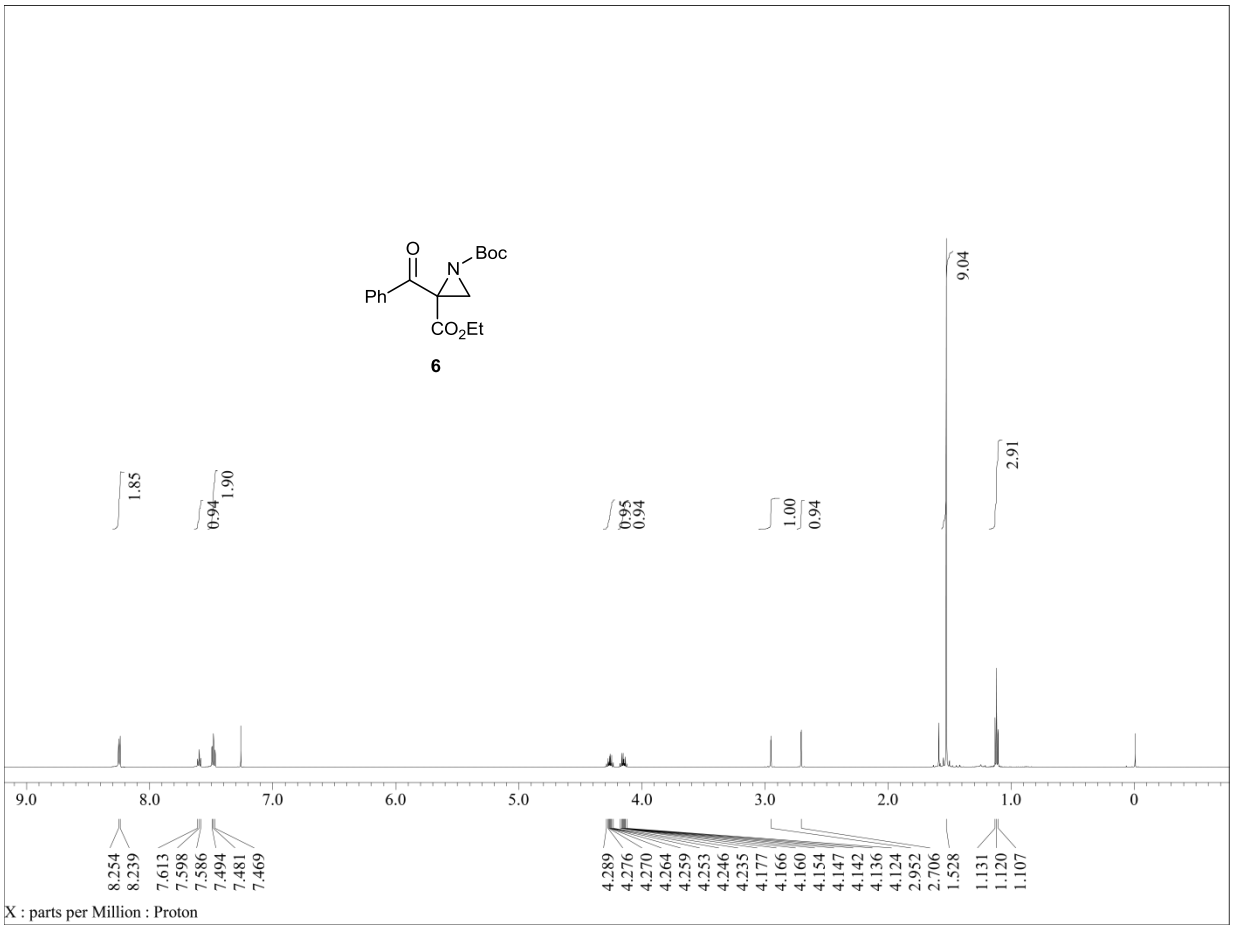

CN
CN
tBuO2C
N
Boc
4o
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.931
149.462
137.819
129.604
128.857
128.359
128.321
113.183
84.535
83.923
77.211
77.000
76.789
56.950
40.338
28.111
27.594
X : parts per Million : Carbon13

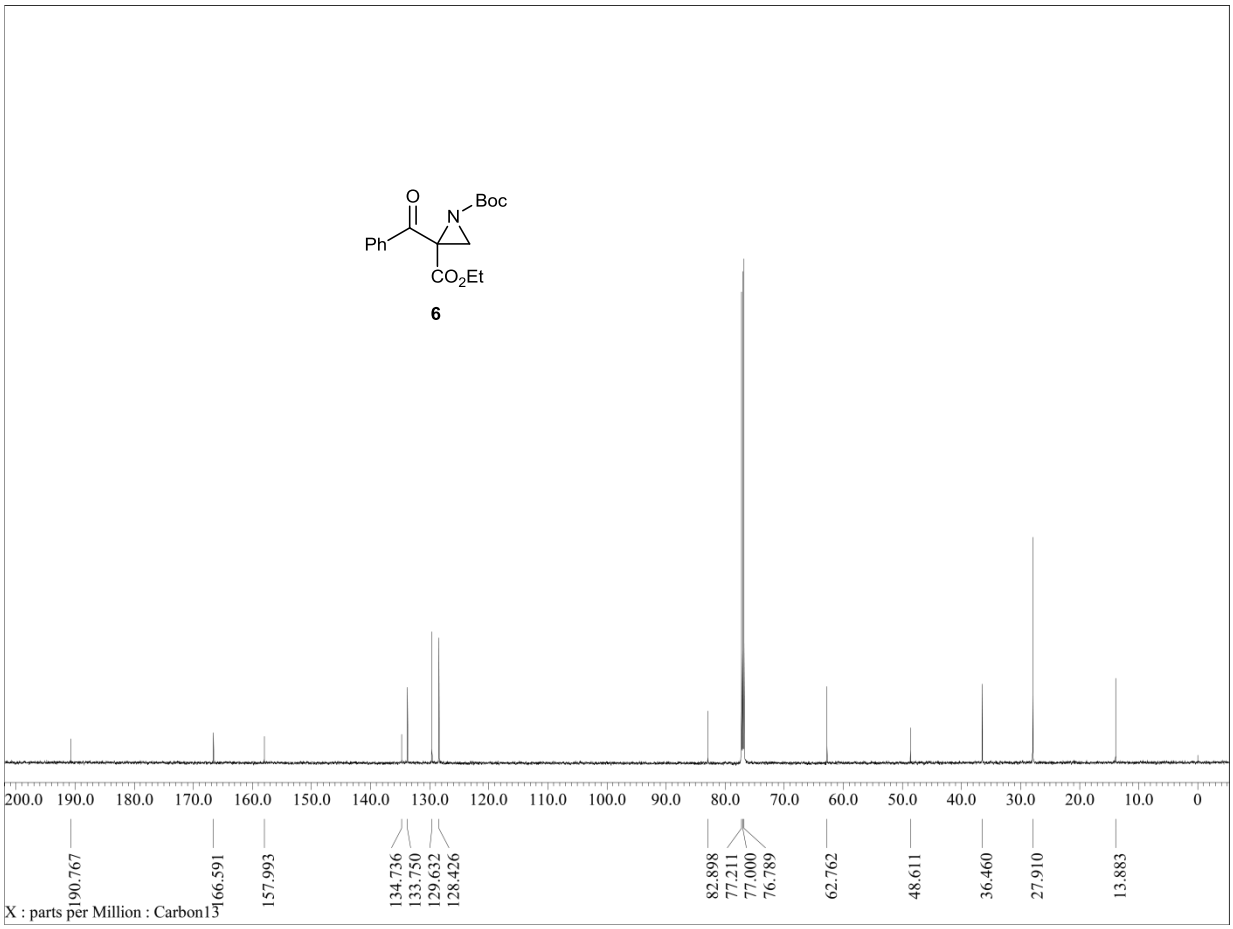

CN
CN
EtO2C
N
CO2Et
4p
5.06
2.00
4.03
2.96
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.473
7.464
7.458
7.456
7.453
7.450
7.448
7.438
7.434
7.428
7.423
7.417
7.409
4.648
4.291
4.279
4.274
4.267
4.262
4.255
4.250
4.238
1.333
1.320
1.309
1.201
1.189
1.177
X : parts per Million : Proton

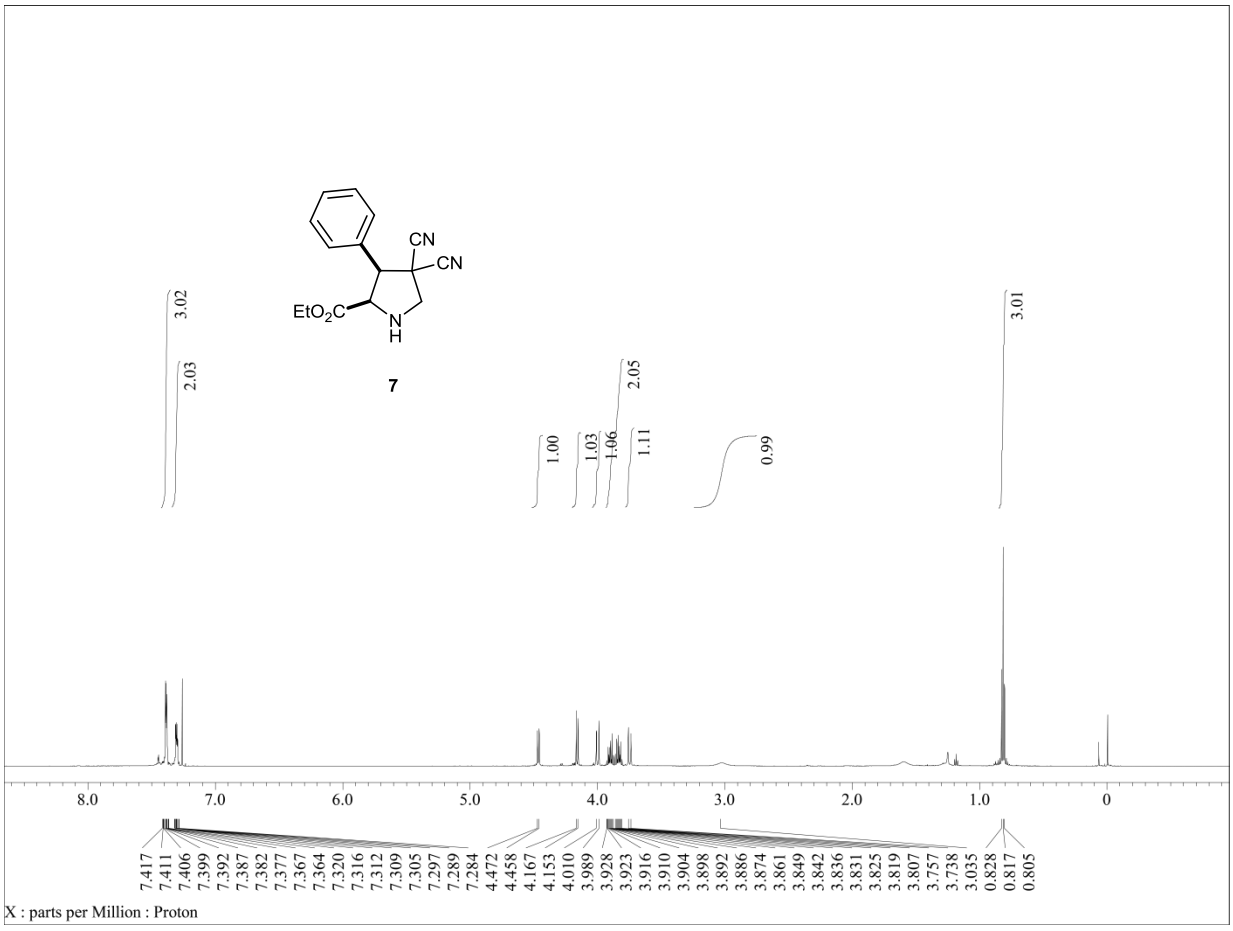

CN
CN
EtO2C
N
CO2Et
4p
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.492
150.697
135.923
129.901
129.249
129.115
127.679
112.925
77.211
77.000
76.789
63.672
62.810
56.740
40.061
14.266
13.625
X : parts per Million : Carbon13

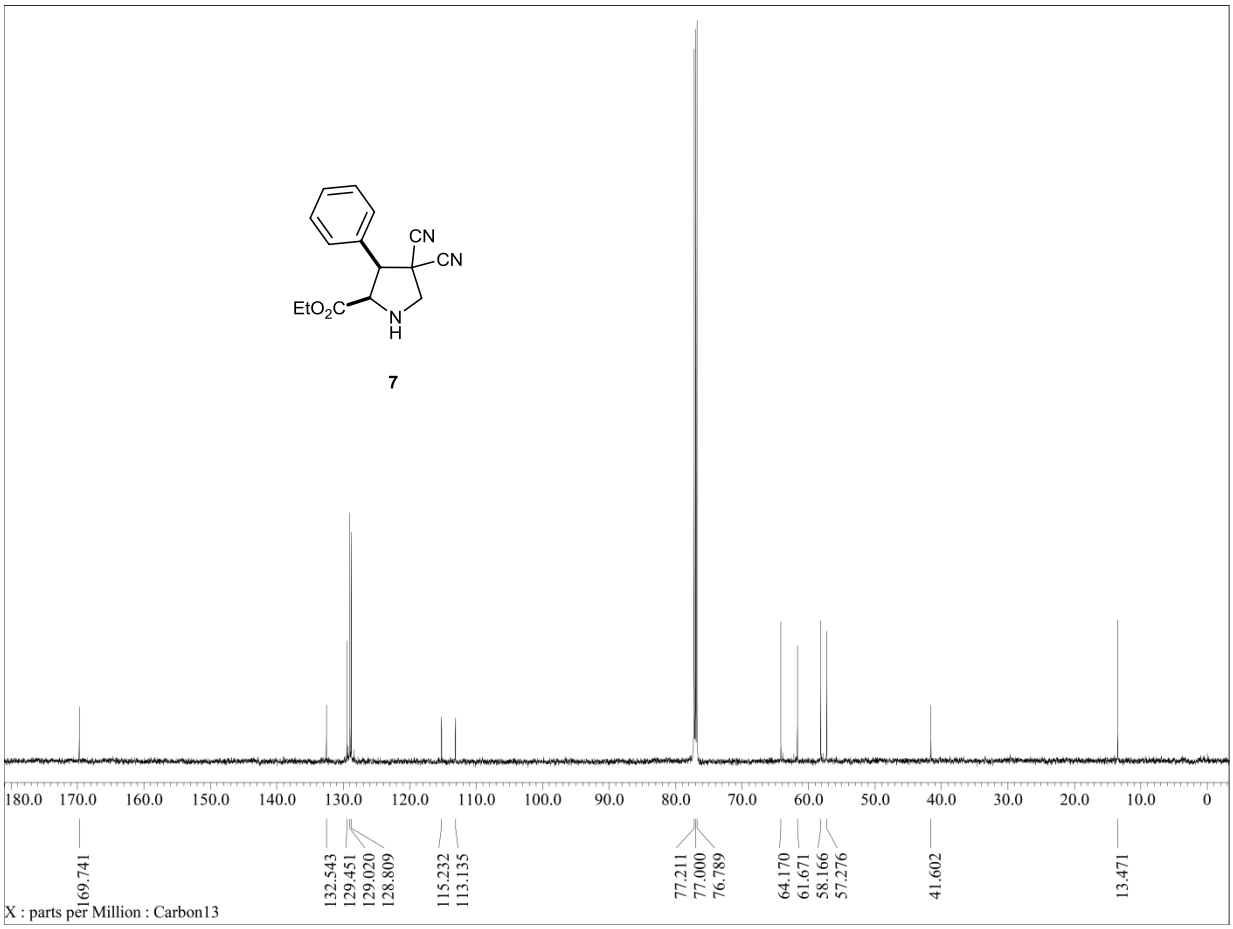

NC
CN
Boc
N
CO2Et
5
3.01
2.08
1.11
1.10
2.09
1.00
1.09
9.07
3.22
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.399
7.393
7.387
7.382
7.353
7.346
7.341
7.337
7.335
7.330
4.597
4.583
4.355
4.342
4.337
4.331
4.325
4.319
4.313
4.301
4.225
4.212
4.206
4.199
4.193
4.188
4.182
4.169
2.789
2.059
1.471
1.319
1.308
1.295
X : parts per Million : Proton

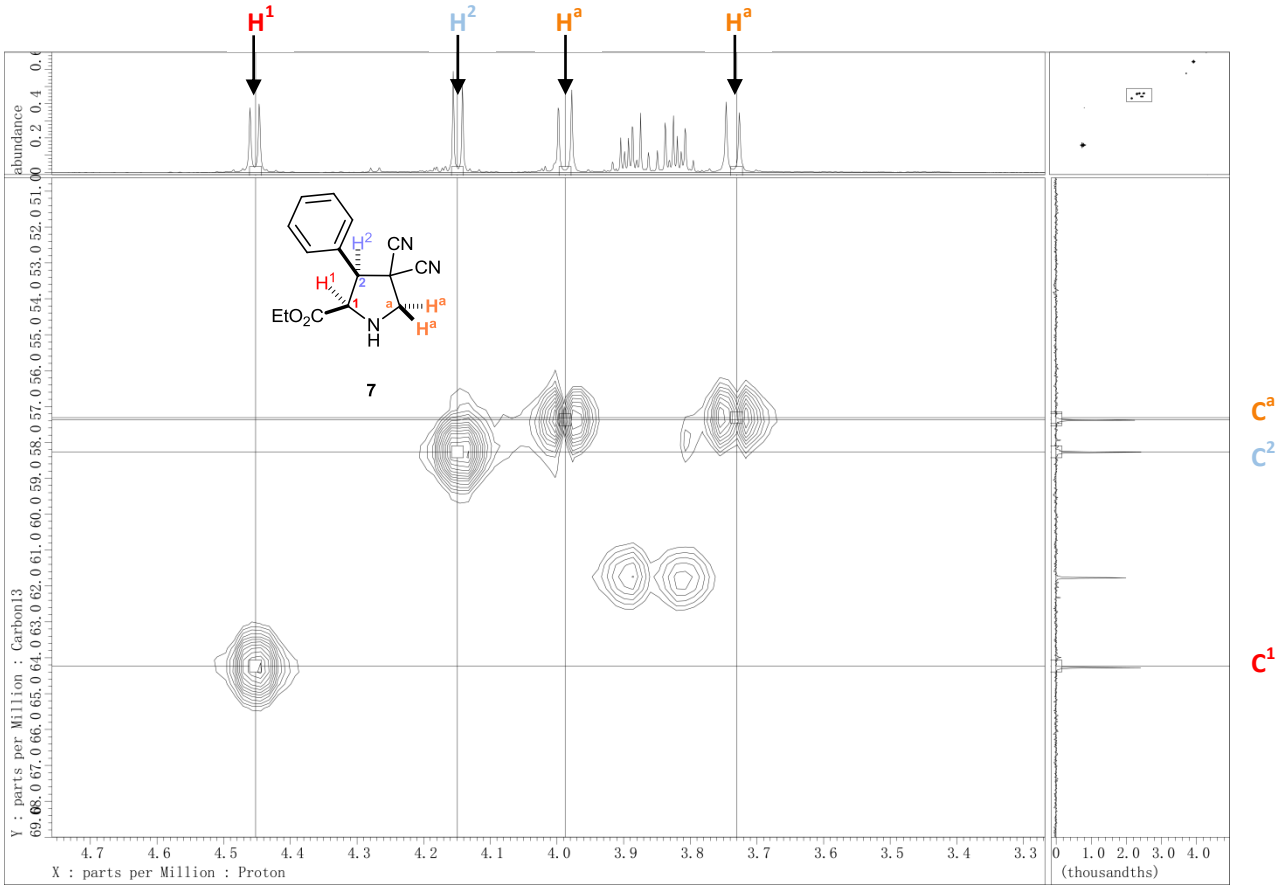

NC
CN
Boc
N
CO2Et
5
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.482
157.734
132.773
129.479
129.288
128.426
111.929
111.728
83.080
77.211
77.000
76.789
63.126
45.375
44.972
37.447
27.853
26.302
13.893
X : parts per Million : Carbon13

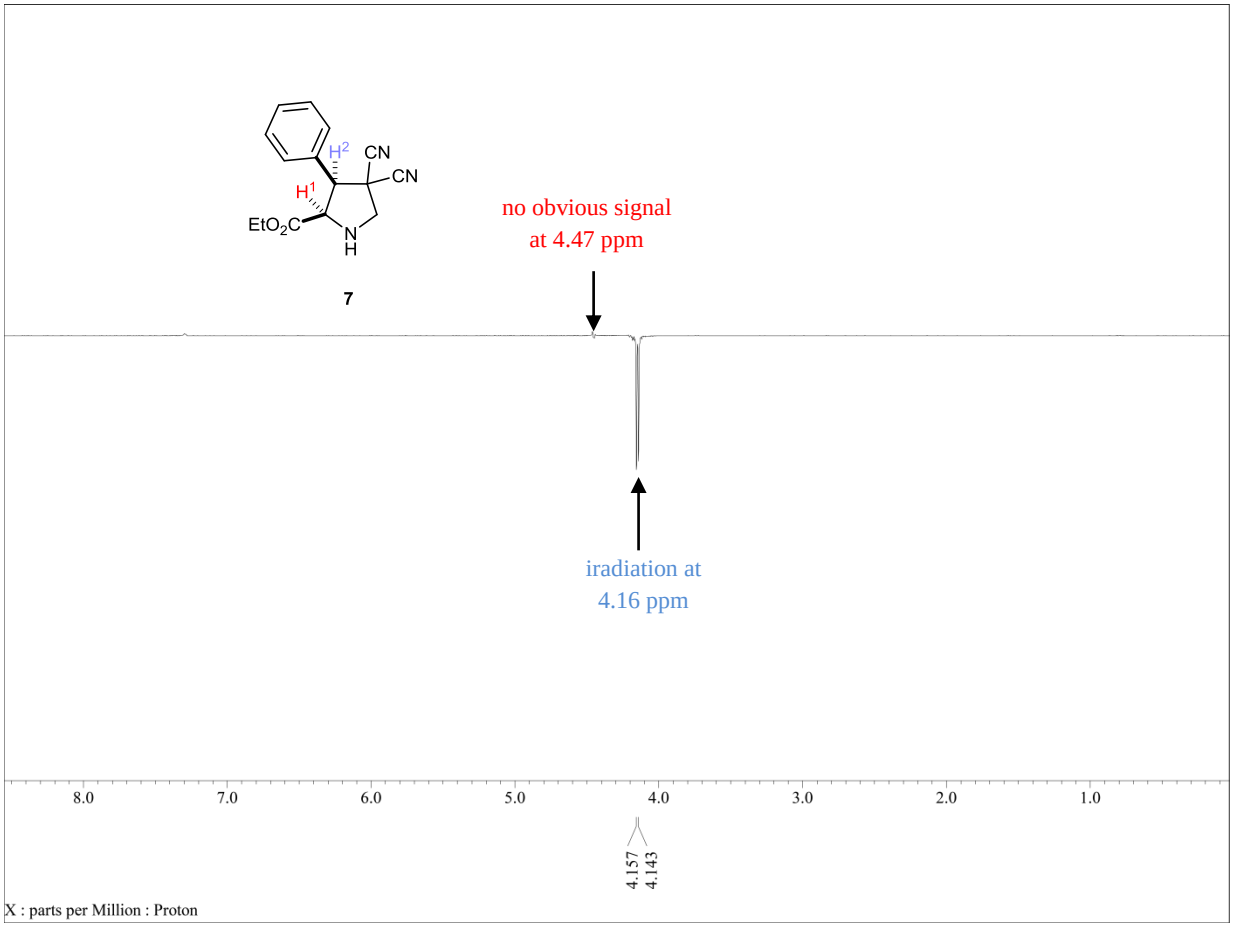

O
N
Boc
Ph
CO2Et
6
1.85
1.90
0.94
0.95
0.94
1.00
0.94
9.04
2.91
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.254
8.239
7.613
7.598
7.586
7.494
7.481
7.469
4.289
4.276
4.270
4.264
4.259
4.253
4.246
4.235
4.177
4.166
4.160
4.154
4.147
4.142
4.136
4.124
2.952
2.706
1.528
1.131
1.120
1.107
X : parts per Million : Proton

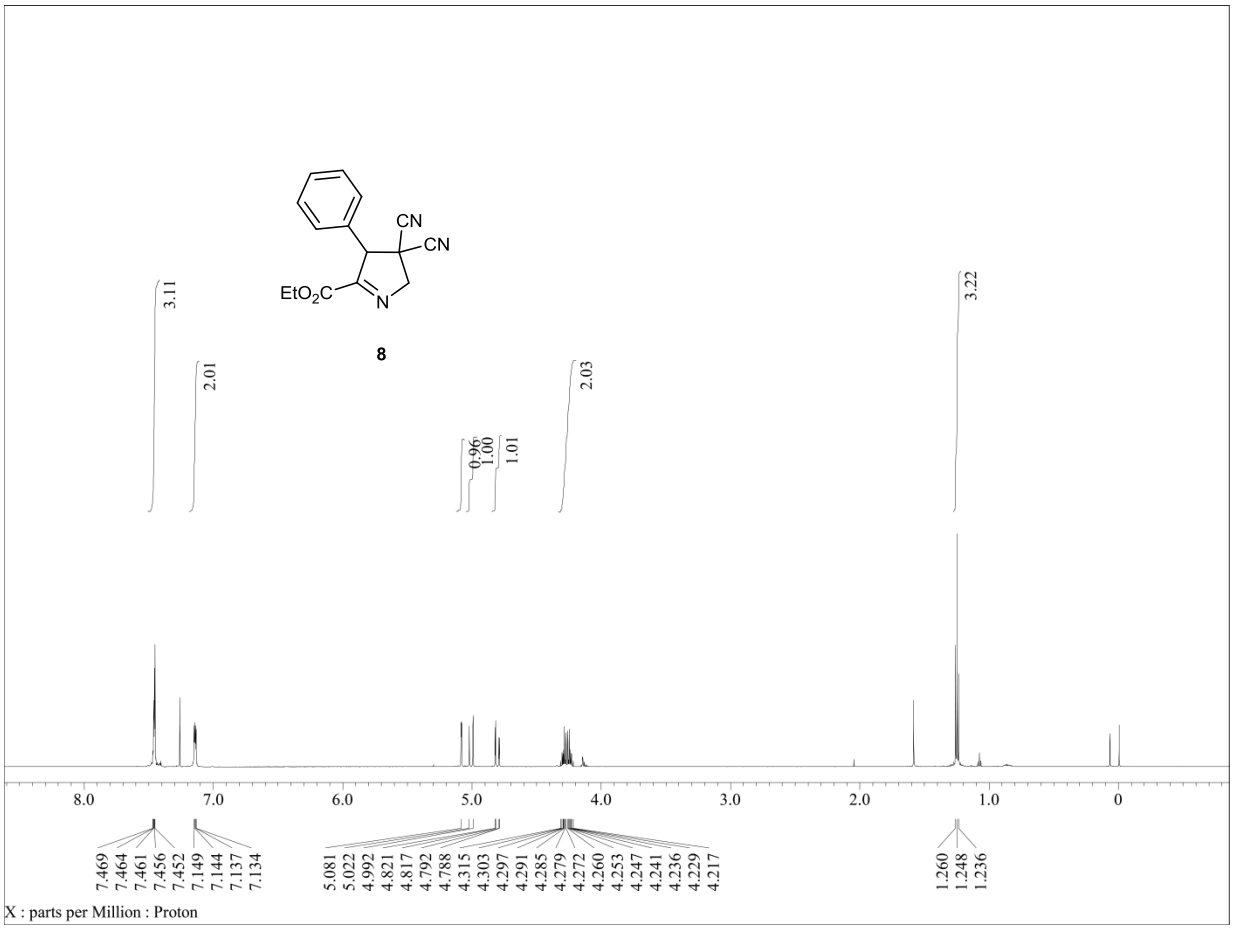

O
N
Boc
Ph
CO2Et
6
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.767
166.591
157.993
134.736
133.750
129.632
128.426
82.898
77.211
77.000
76.789
62.762
48.611
36.460
27.910
13.883
X : parts per Million : Carbon13

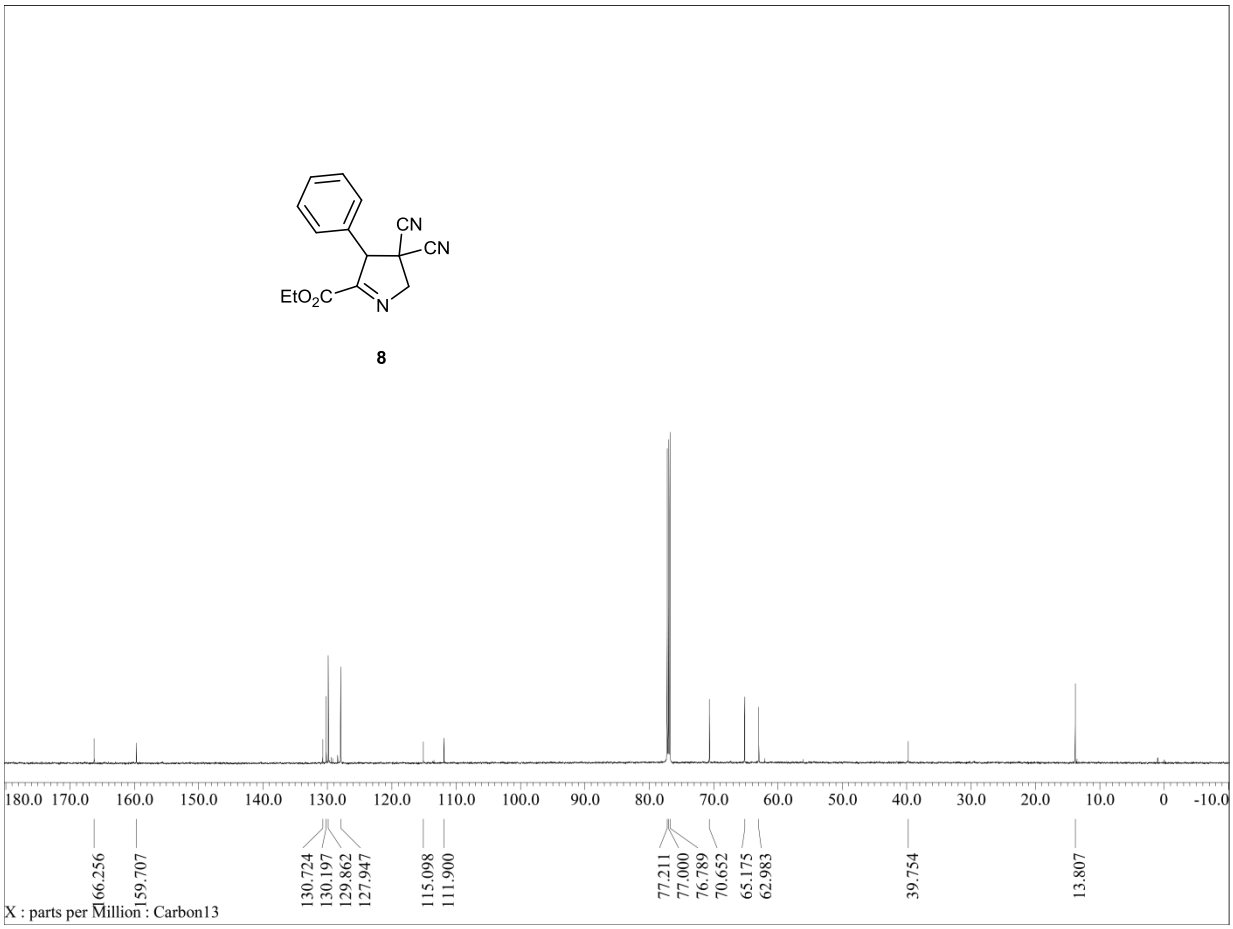

CN
CN
EtO2C
N
H
7
3.02
2.03
1.00
1.03
1.06
2.05
1.11
0.99
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.417
7.411
7.406
7.399
7.392
7.387
7.382
7.377
7.367
7.364
7.320
7.316
7.312
7.309
7.305
7.297
7.289
7.284
4.472
4.458
4.167
4.153
4.010
3.989
3.928
3.923
3.916
3.910
3.904
3.898
3.892
3.886
3.874
3.861
3.849
3.842
3.836
3.831
3.825
3.819
3.807
3.757
3.738
3.035
0.828
0.817
0.805
X : parts per Million : Proton

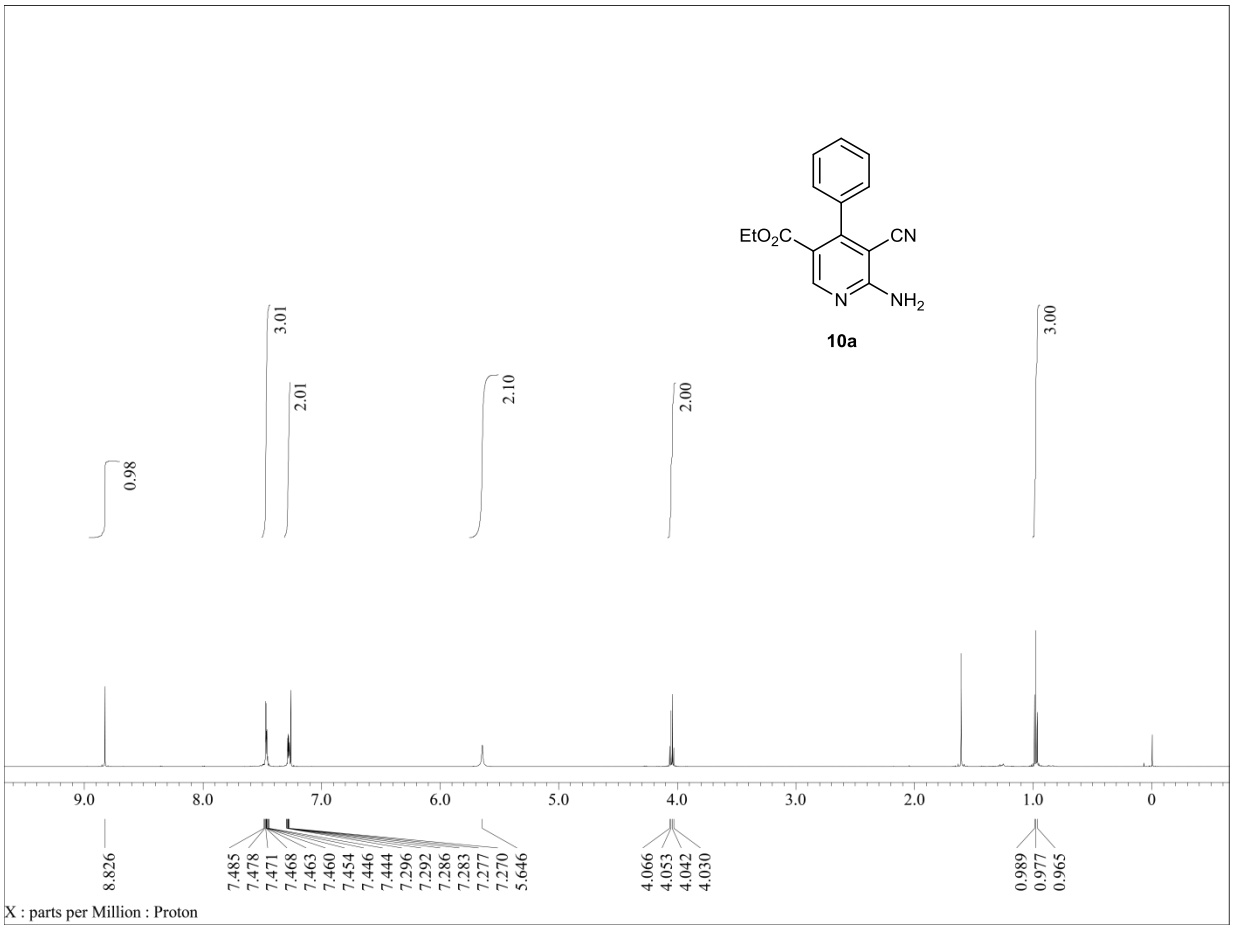

CN
CN
EtO2C
N
H
7
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.741
132.543
129.451
129.020
128.809
115.232
113.135
77.211
77.000
76.789
64.170
61.671
58.166
57.276
41.602
13.471
X : parts per Million : Carbon13

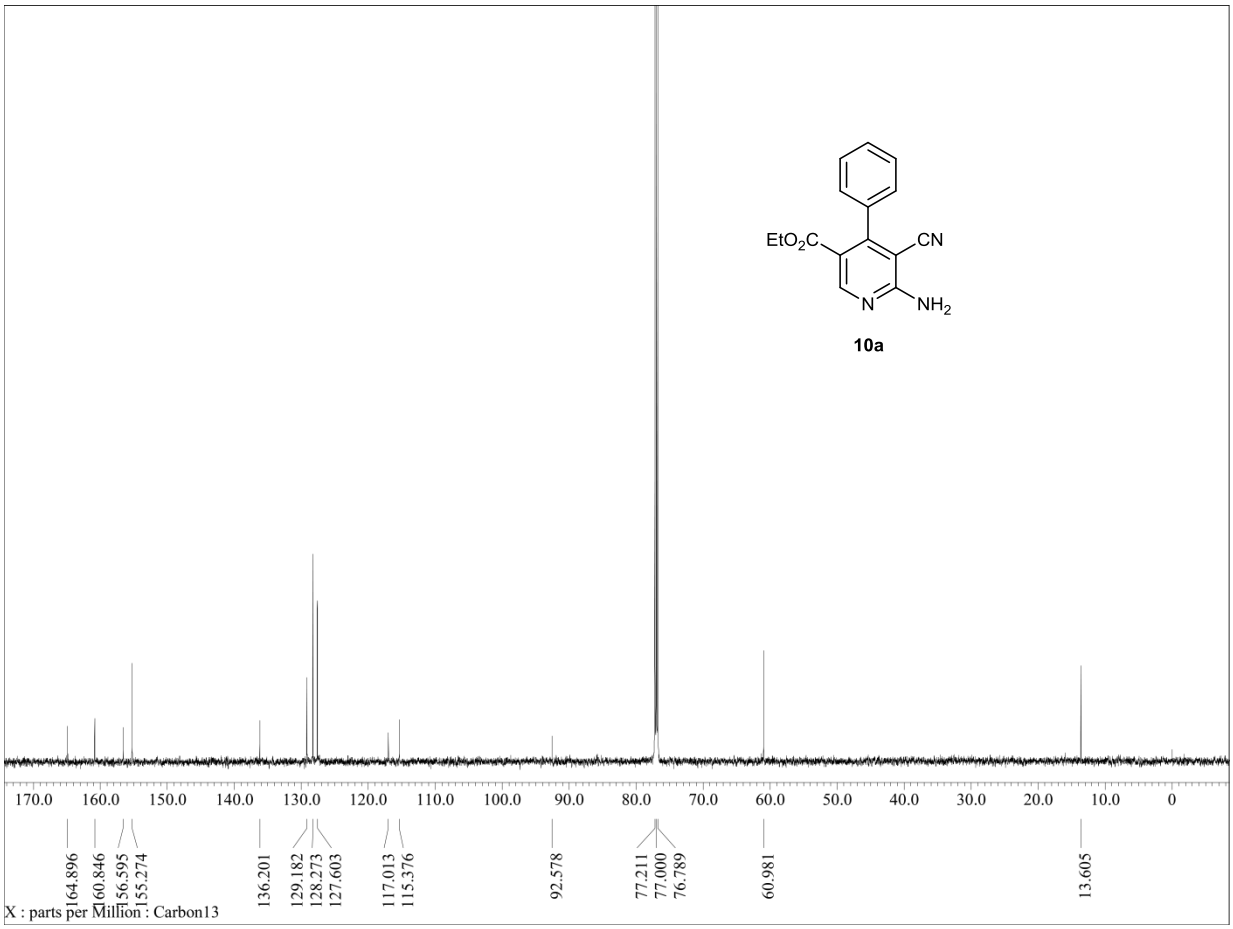

H1
H2
Ha
Ha
abundance
H2
CN
CN
H1
EtO2C
N
H
Ha
Ha
7
Ca
C2
C1
Y : parts per Million : Carbon13
X : parts per Million : Proton
(thousandths)

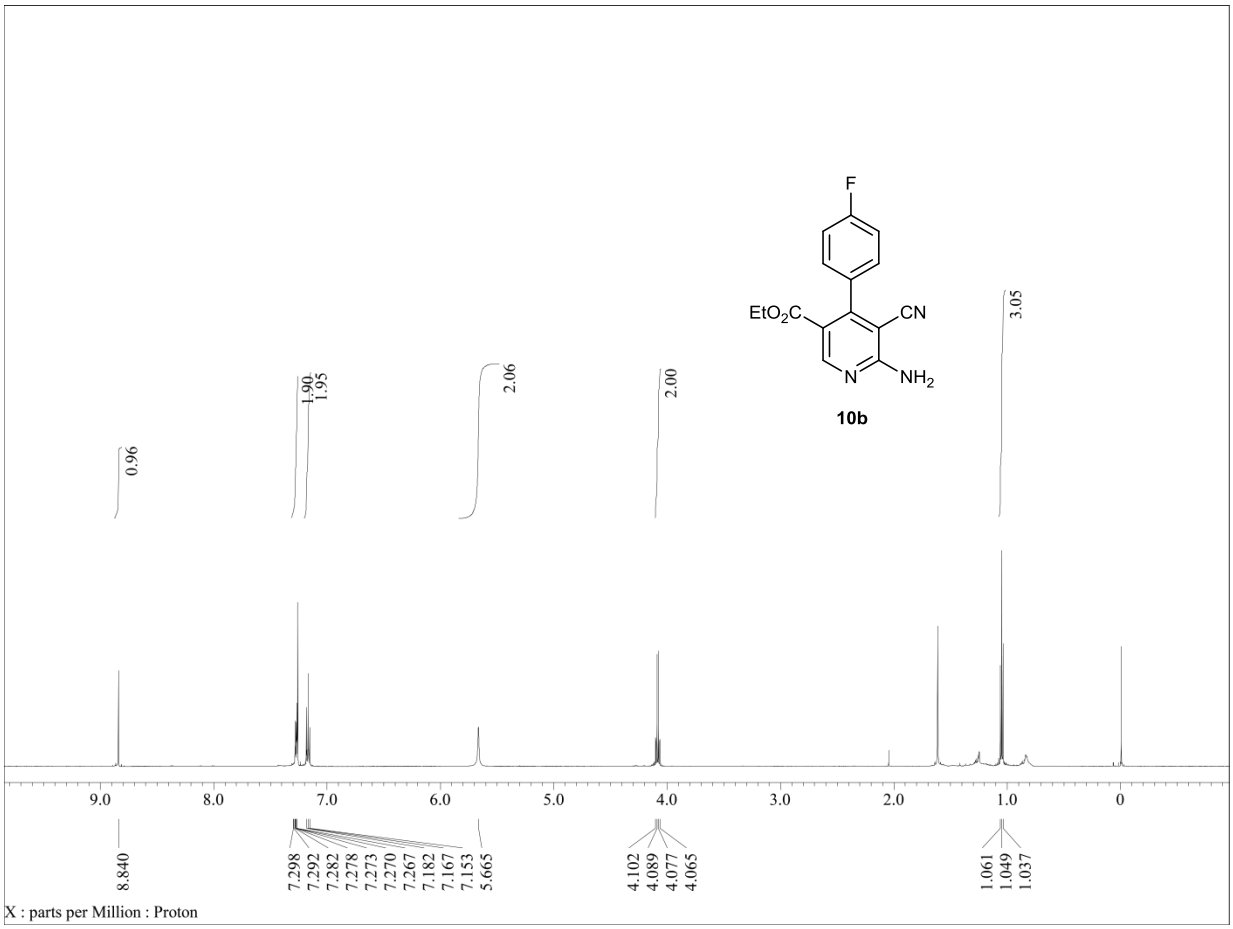

H2
CN
CN
H1
EtO2C
N
H
7
no obvious signal
at 4.47 ppm
iradiation at
4.16 ppm
4.157
4.143
X : parts per Million : Proton

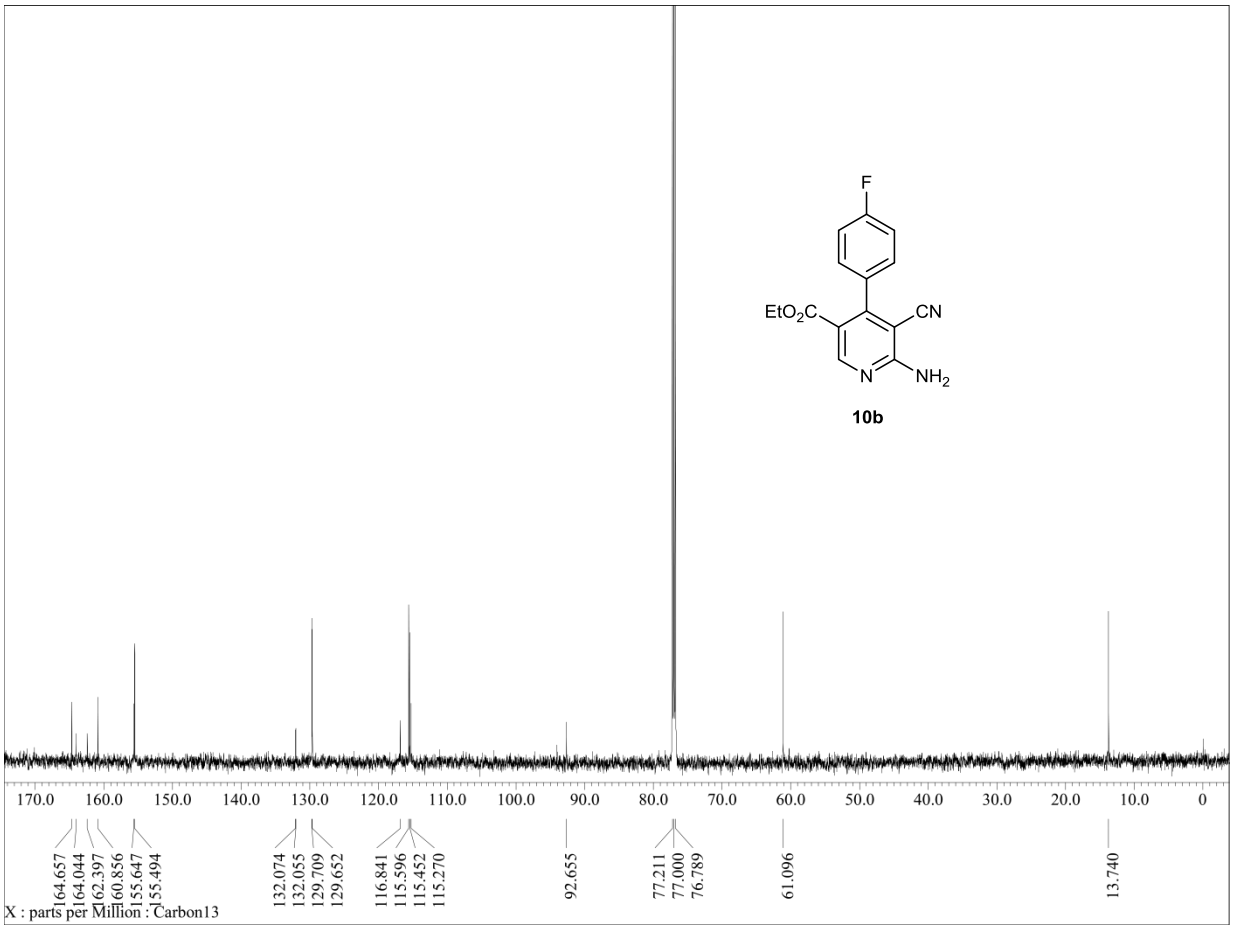

CN
CN
EtO2C
N
8
3.11
2.01
0.96
1.00
1.01
2.03
3.22
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.469
7.464
7.461
7.456
7.452
7.149
7.144
7.137
7.134
5.081
5.022
4.992
4.821
4.817
4.792
4.788
4.315
4.303
4.297
4.291
4.285
4.279
4.272
4.260
4.253
4.247
4.241
4.236
4.229
4.217
1.260
1.248
1.236
X : parts per Million : Proton

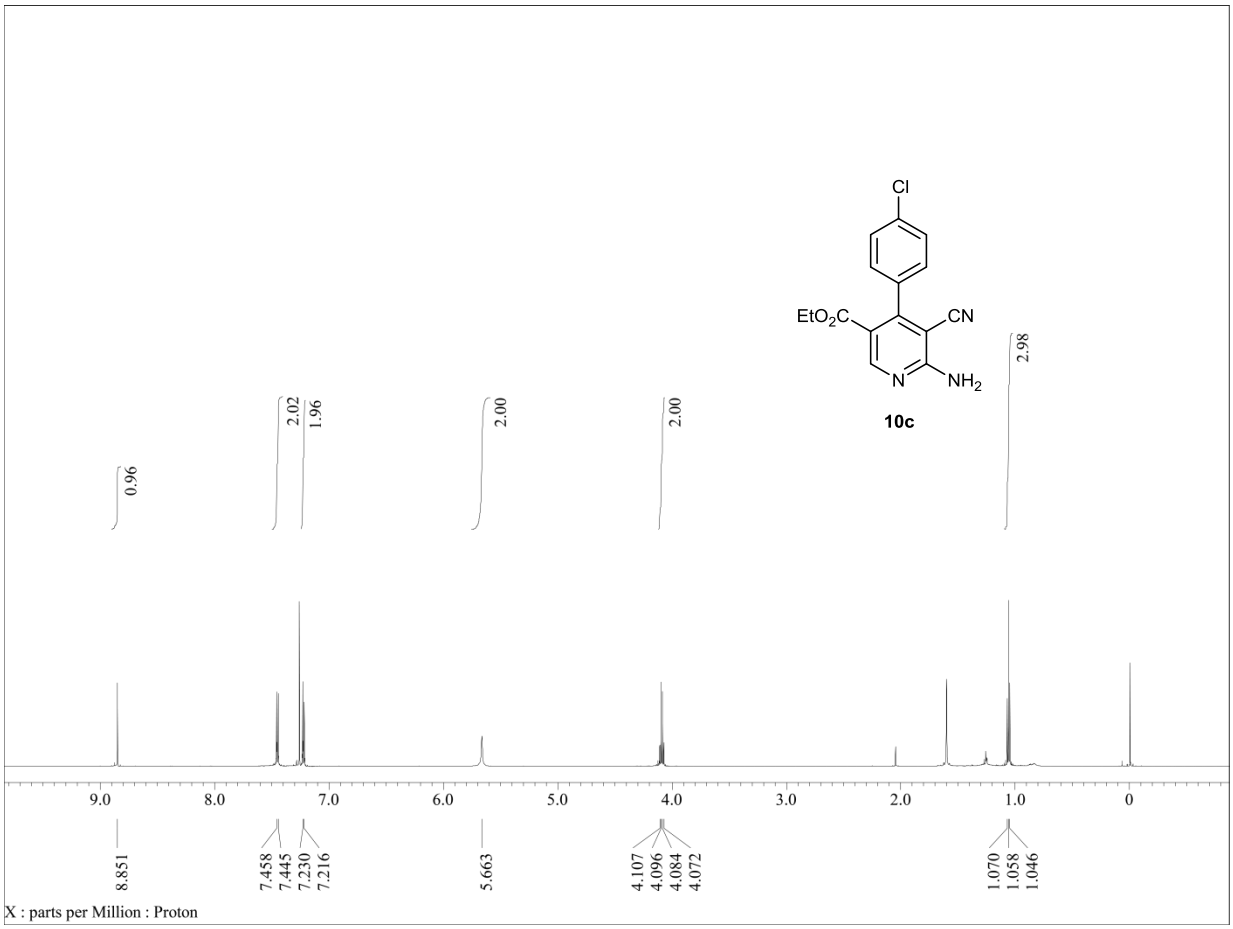

CN
CN
EtO2C
N
8
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
166.256
159.707
130.724
130.197
129.862
127.947
115.098
111.900
77.211
77.000
76.789
70.652
65.175
62.983
39.754
13.807
X : parts per Million : Carbon13

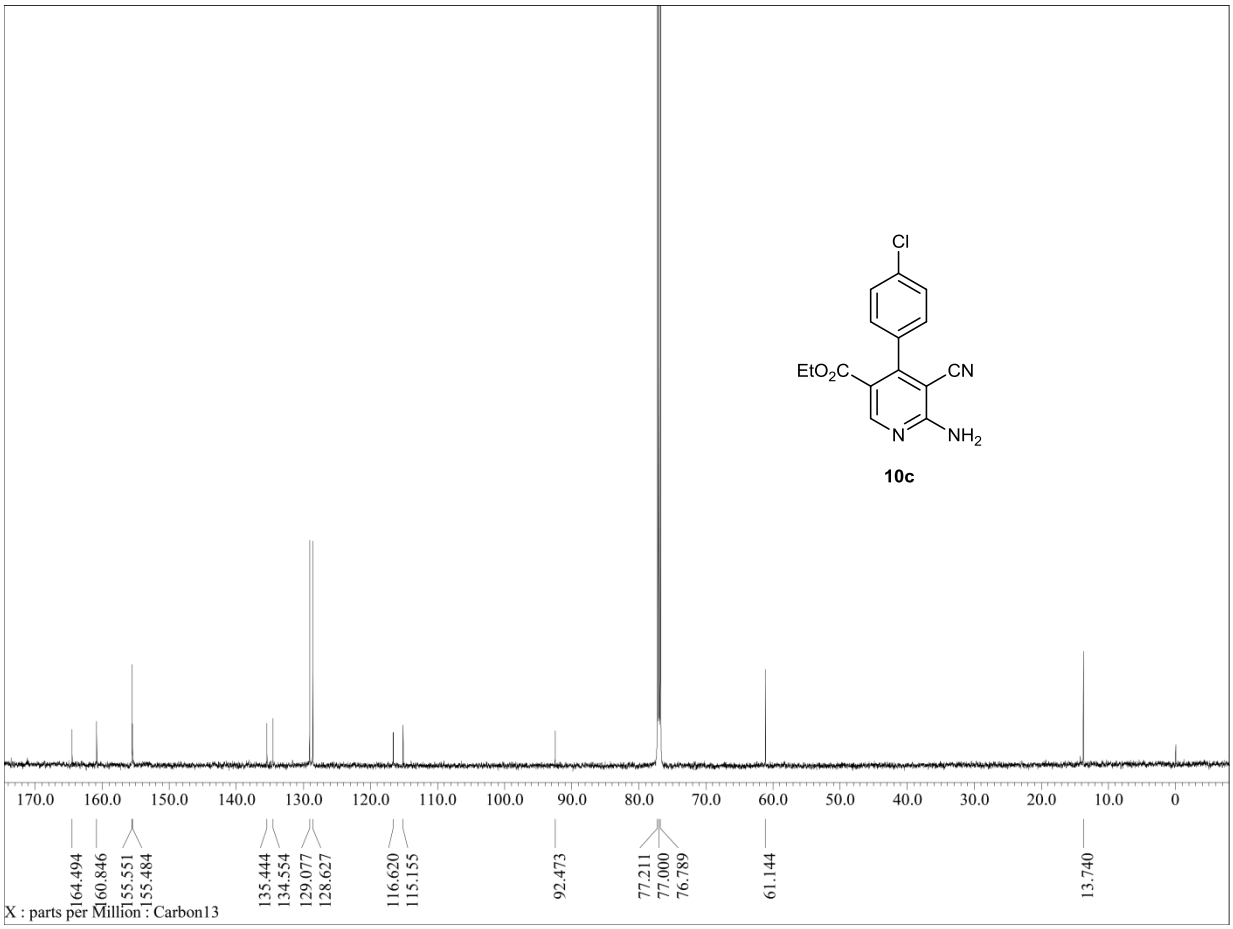

EtO2C
CN
N
NH2
10a
0.98
3.01
2.01
2.10
2.00
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.826
7.485
7.478
7.471
7.468
7.463
7.460
7.454
7.446
7.444
7.296
7.292
7.286
7.283
7.277
7.270
5.646
4.066
4.053
4.042
4.030
0.989
0.977
0.965
X : parts per Million : Proton

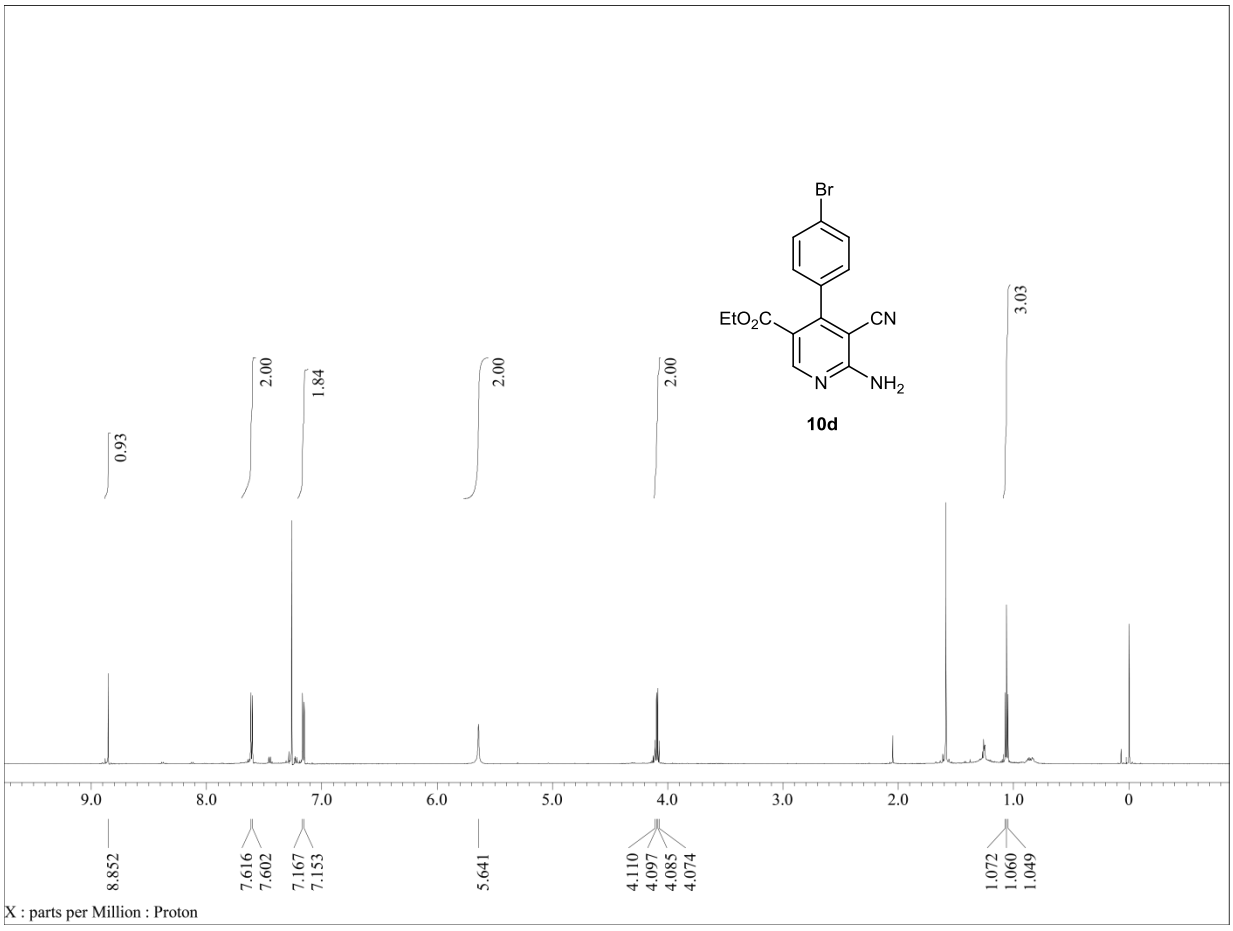

EtO2C
CN
N
NH2
10a
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.896
160.846
156.595
155.274
136.201
129.182
128.273
127.603
117.013
115.376
92.578
77.211
77.000
76.789
60.981
13.605
X : parts per Million : Carbon13

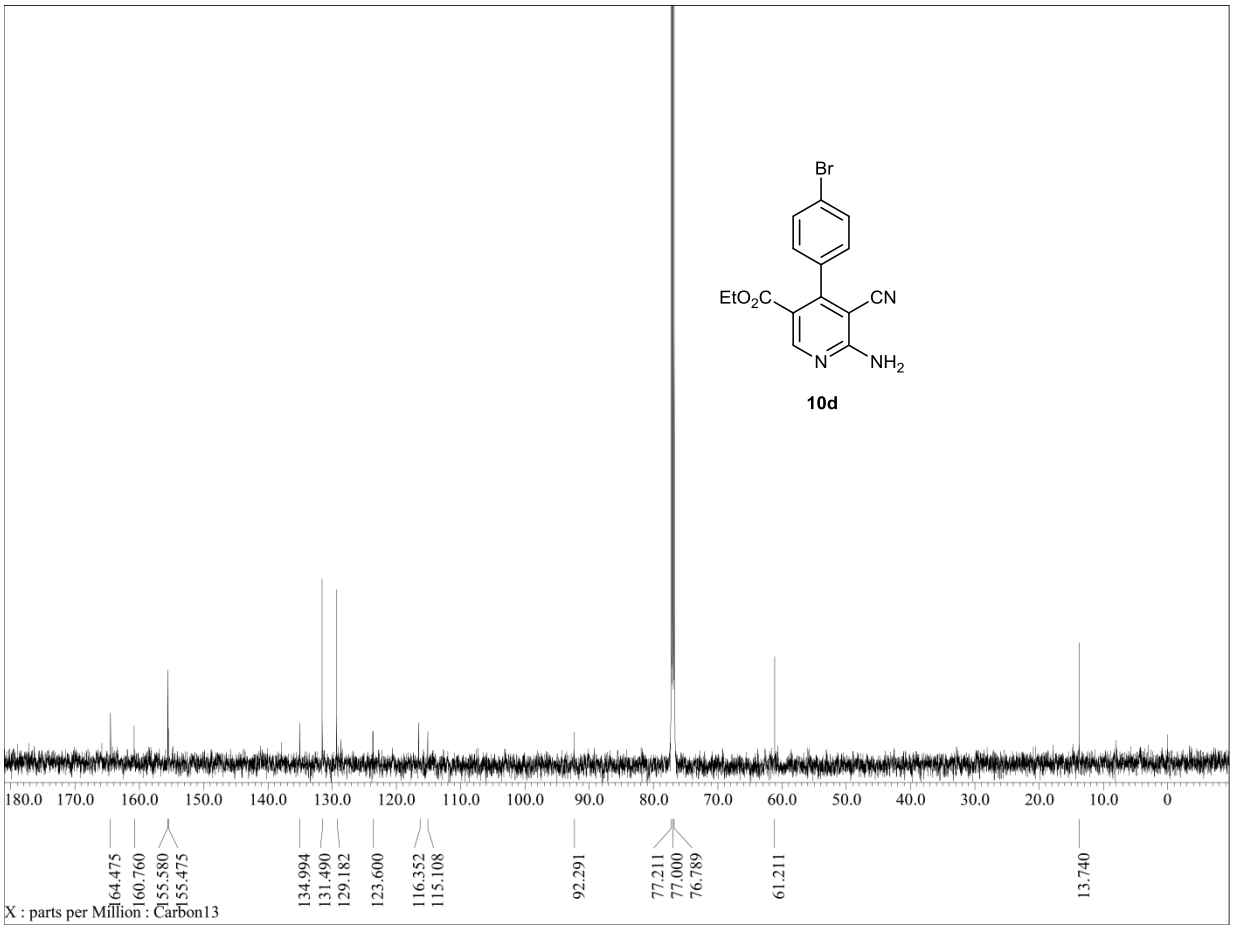

F
EtO2C
CN
N
NH2
10b
0.96
1.90
1.95
2.06
2.00
3.05
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.840
7.298
7.292
7.282
7.278
7.273
7.270
7.267
7.182
7.167
7.153
5.665
4.102
4.089
4.077
4.065
1.061
1.049
1.037
X : parts per Million : Proton

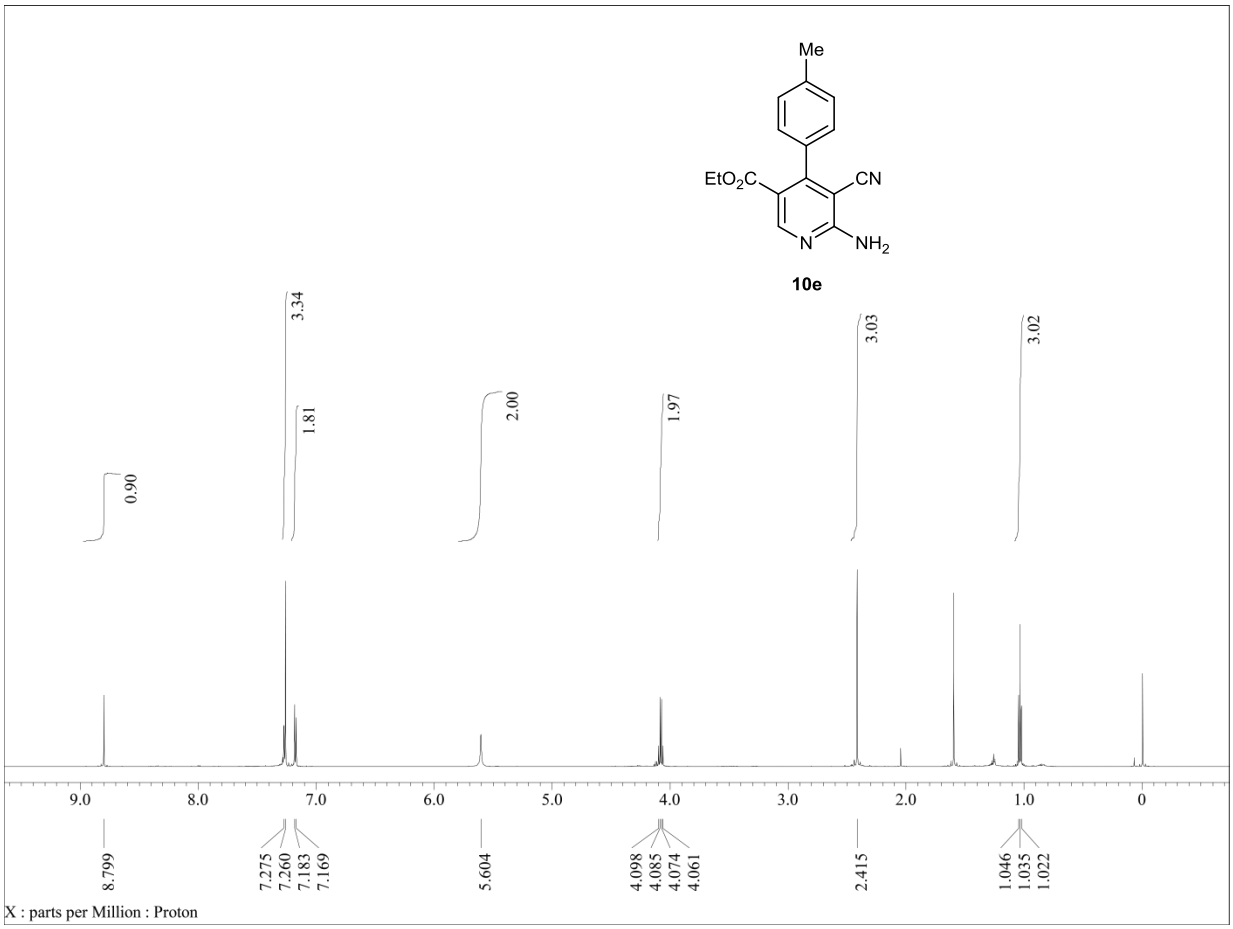

F
EtO2C
CN
N
NH2
10b
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.657
164.044
162.397
160.856
155.647
155.494
132.074
132.055
129.709
129.652
116.841
115.596
115.452
115.270
92.655
77.211
77.000
76.789
61.096
13.740
X : parts per Million : Carbon13

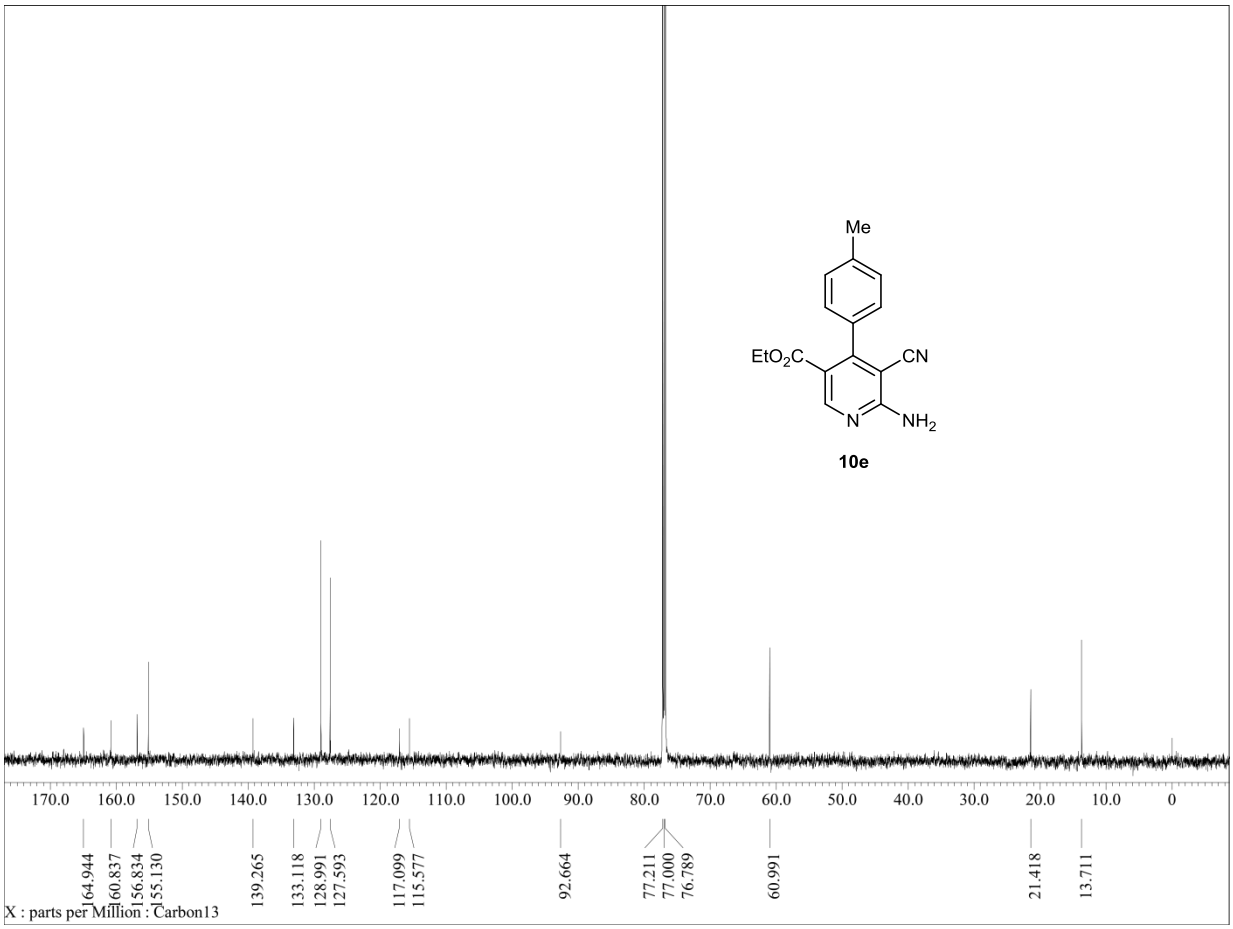

Cl
EtO2C
CN
N
NH2
10c
0.96
2.02
1.96
2.00
2.00
2.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.851
7.458
7.445
7.230
7.216
5.663
4.107
4.096
4.084
4.072
1.070
1.058
1.046
X : parts per Million : Proton

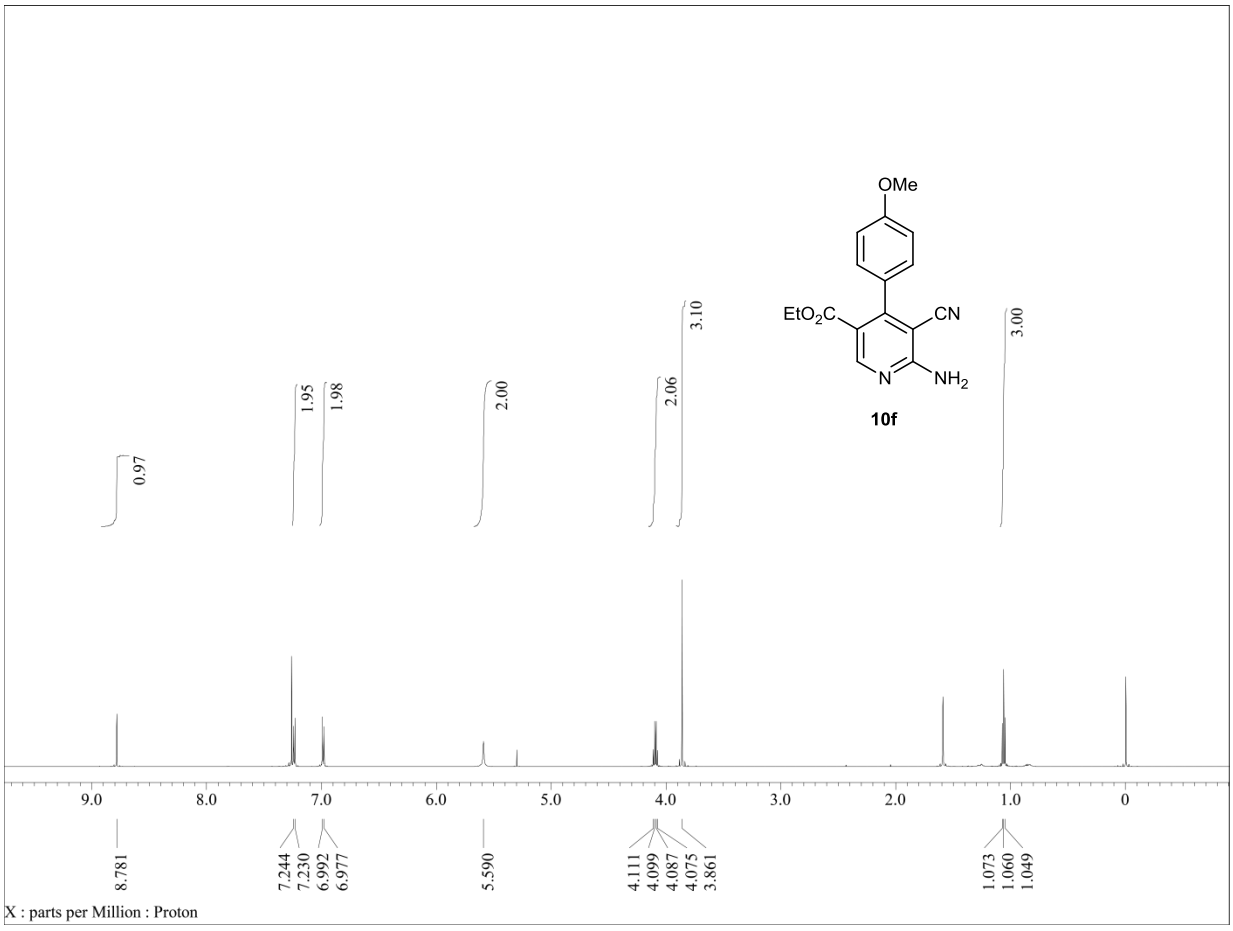

Cl
EtO2C
CN
N
NH2
10c
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.494
160.846
155.551
155.484
135.444
134.554
129.077
128.627
116.620
115.155
92.473
77.211
77.000
76.789
61.144
13.740
X : parts per Million : Carbon13

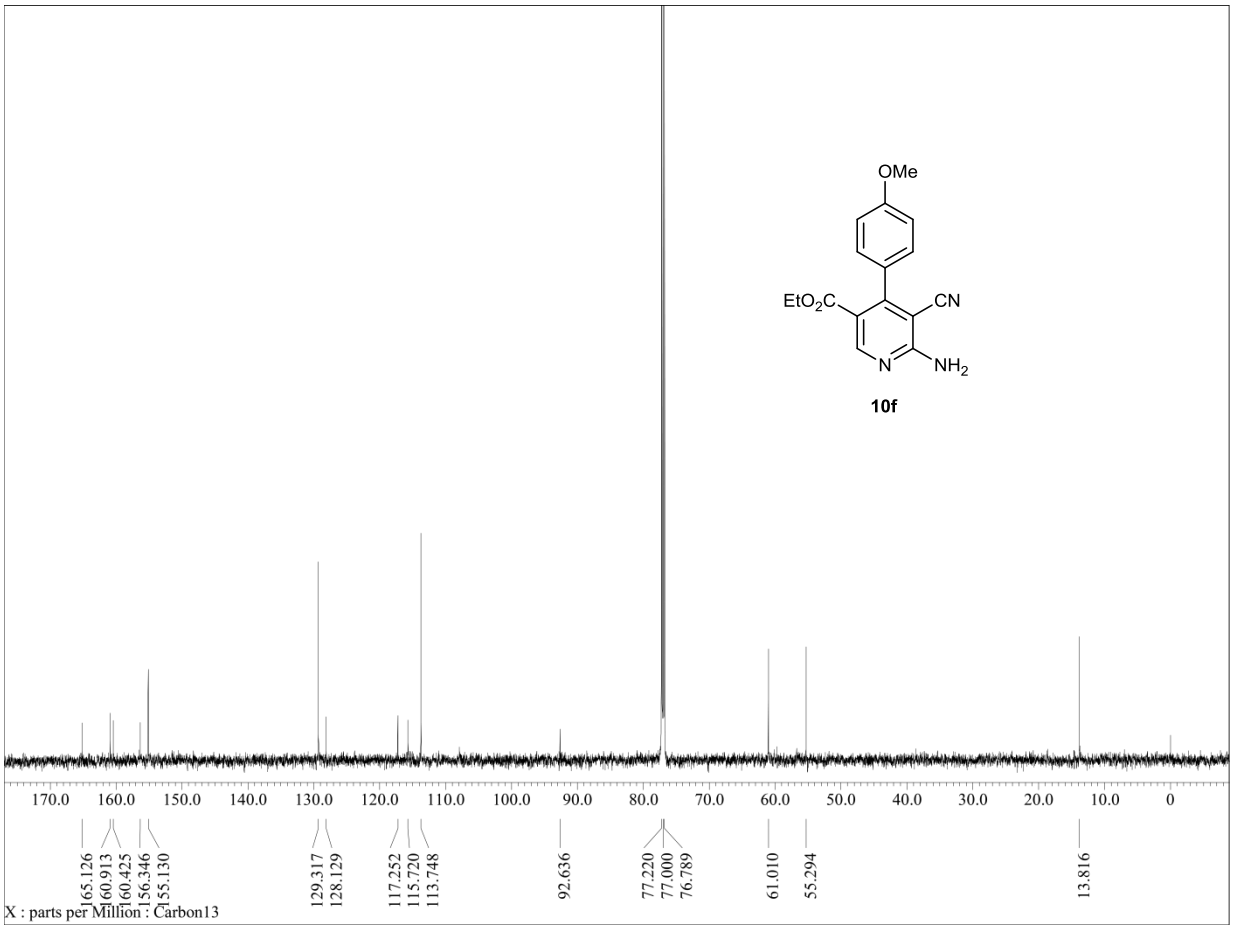

Br
EtO2C
CN
N
NH2
10d
0.93
2.00
1.84
2.00
2.00
3.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.852
7.616
7.602
7.167
7.153
5.641
4.110
4.097
4.085
4.074
1.072
1.060
1.049
X : parts per Million : Proton

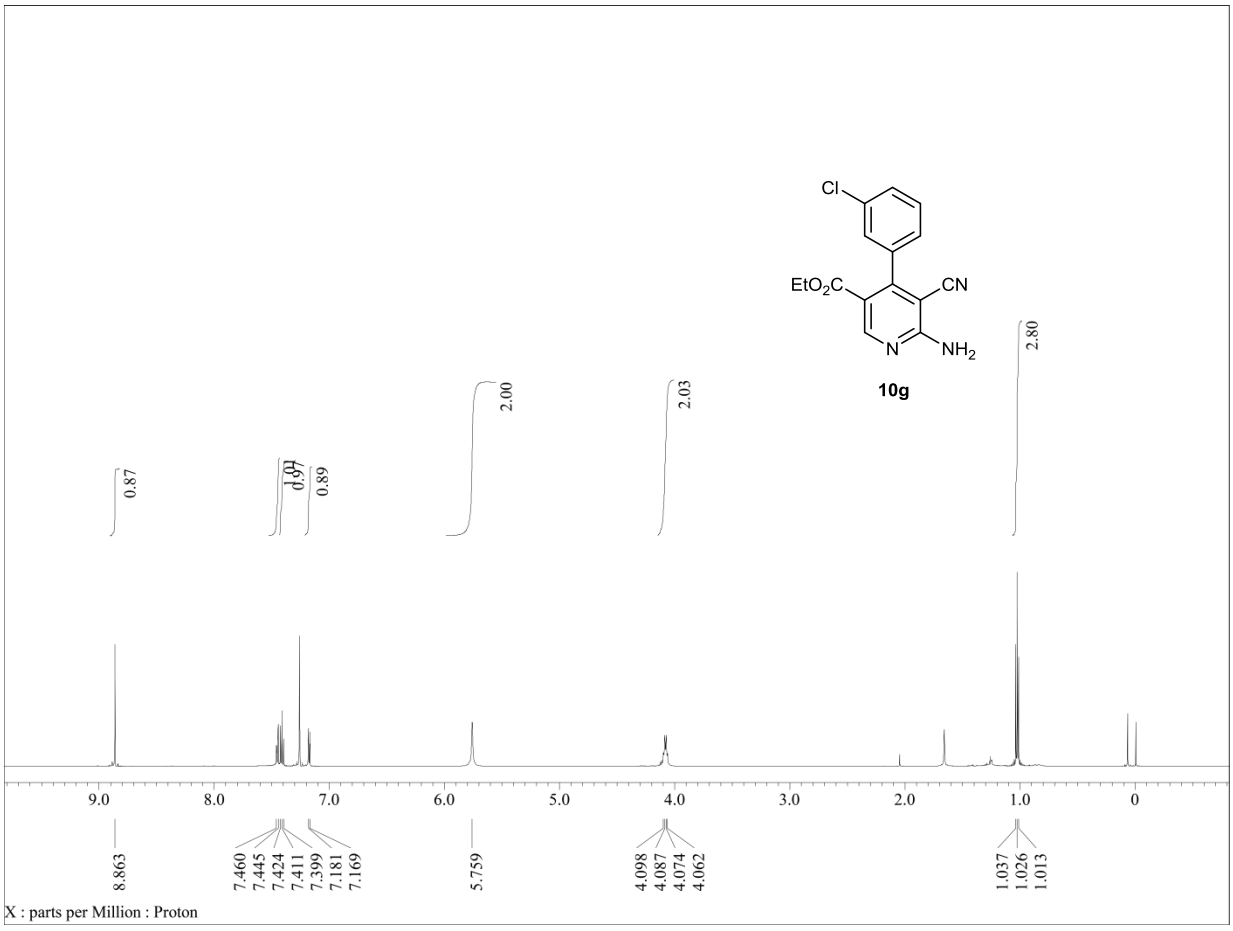

Br
EtO2C
CN
N
NH2
10d
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.475
160.760
155.580
155.475
134.994
131.490
129.182
123.600
116.352
115.108
92.291
77.211
77.000
76.789
61.211
13.740
X : parts per Million : Carbon13

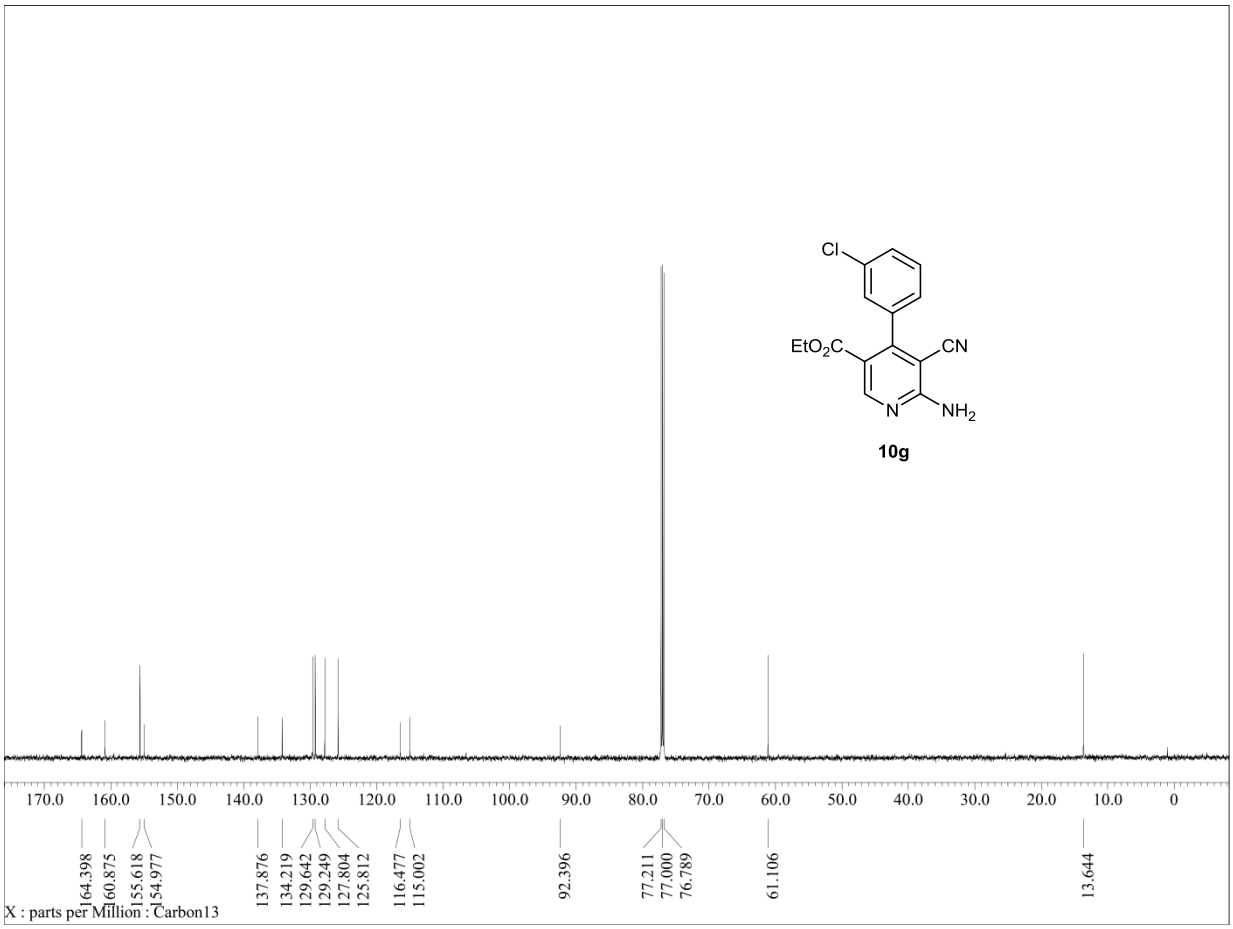

Me
EtO2C
CN
N
NH2
10e
3.34
1.81
2.00
1.97
3.03
3.02
0.90
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.799
7.275
7.260
7.183
7.169
5.604
4.098
4.085
4.074
4.061
2.415
1.046
1.035
1.022
X : parts per Million : Proton

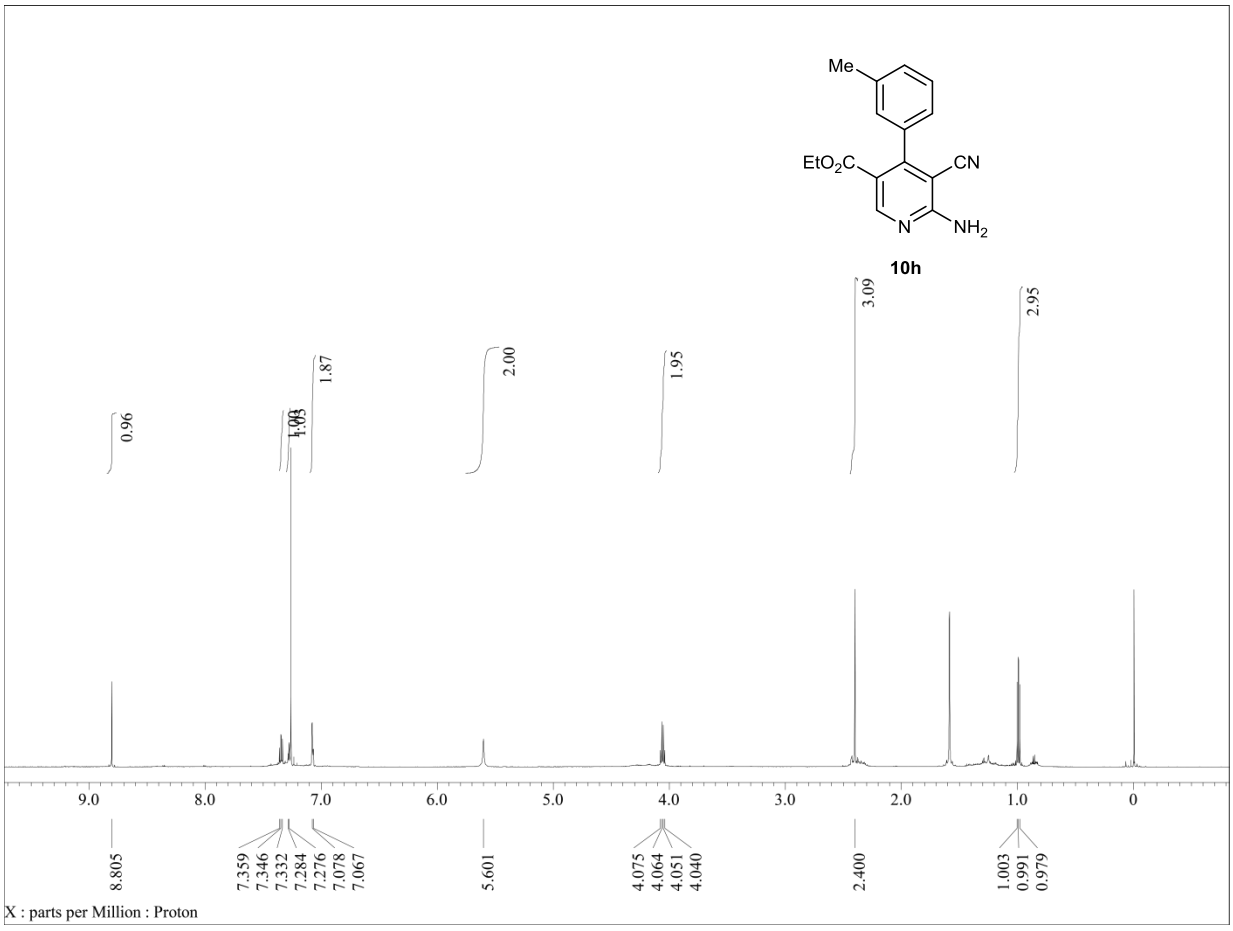

Me
EtO2C
CN
N
NH2
10e
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.944
160.837
156.834
155.130
139.265
133.118
128.991
127.593
117.099
115.577
92.664
77.211
77.000
76.789
60.991
21.418
13.711
X : parts per Million : Carbon13

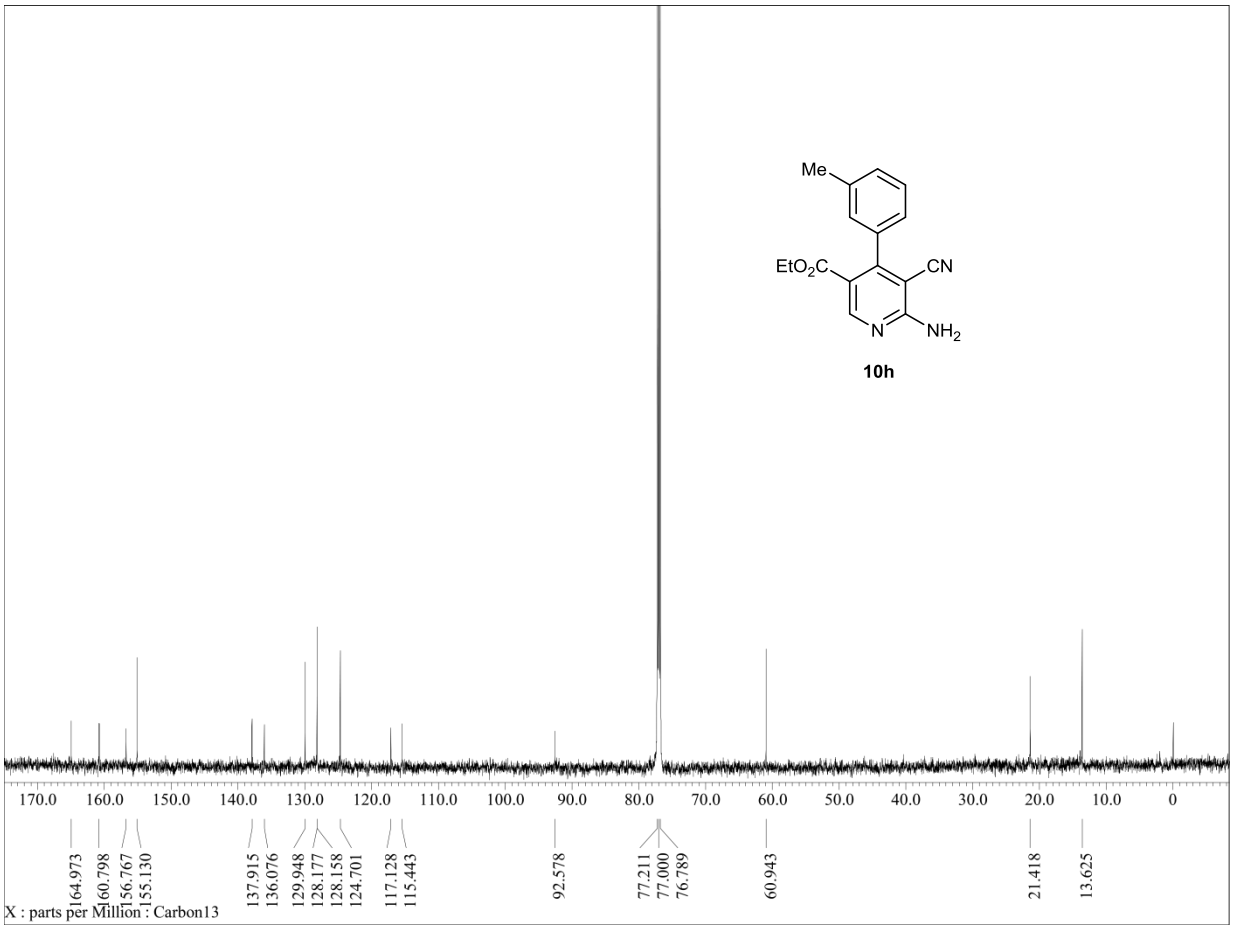

OMe
EtO2C
CN
N
NH2
10f
0.97
1.95
1.98
2.00
2.06
3.10
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.781
7.244
7.230
6.992
6.977
5.590
4.111
4.099
4.087
4.075
3.861
1.073
1.060
1.049
X : parts per Million : Proton

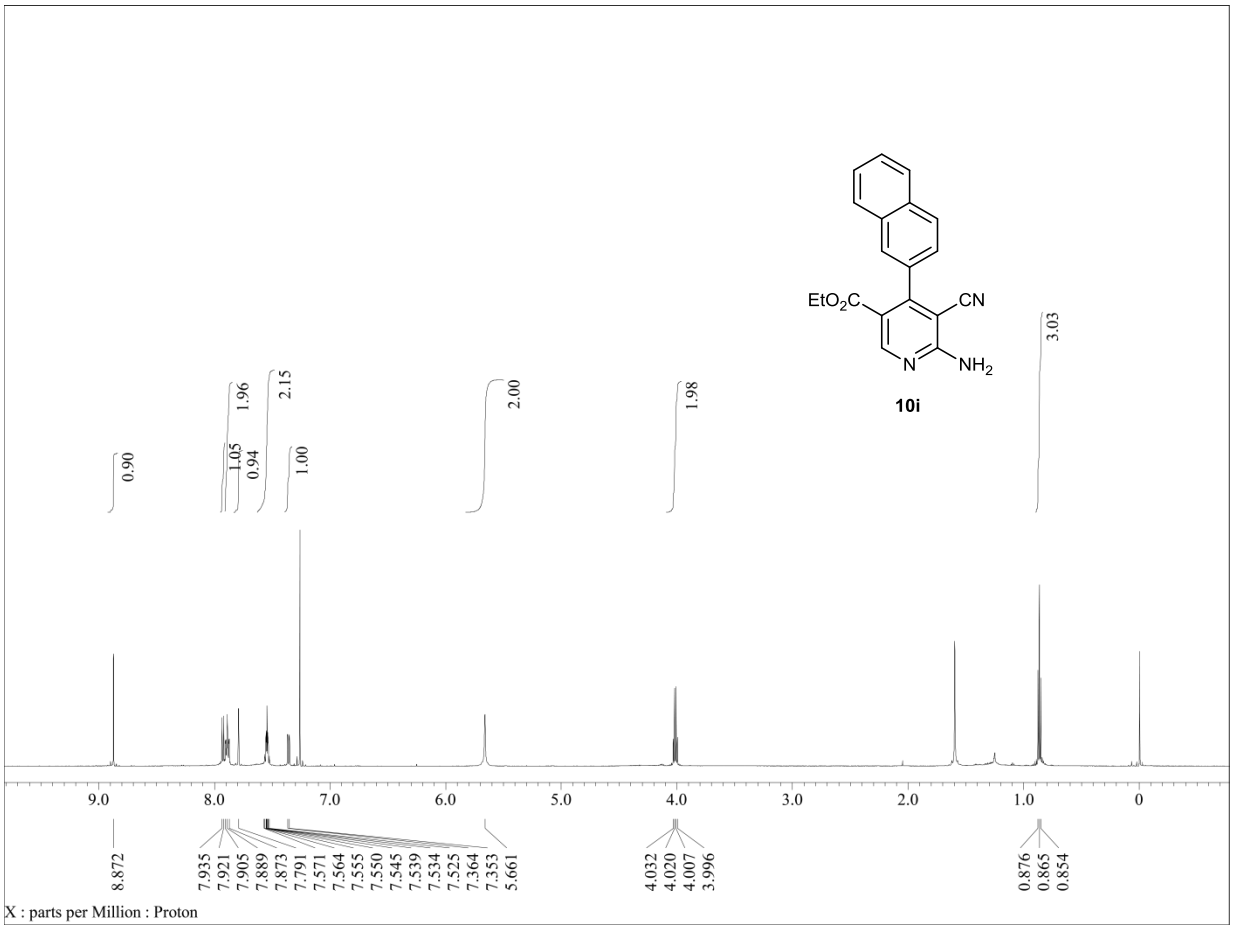

OMe
EtO2C
CN
N
NH2
10f
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
165.126
160.913
160.425
156.346
155.130
129.317
128.129
117.252
115.720
113.748
92.636
77.220
77.000
76.789
61.010
55.294
13.816
X : parts per Million : Carbon13

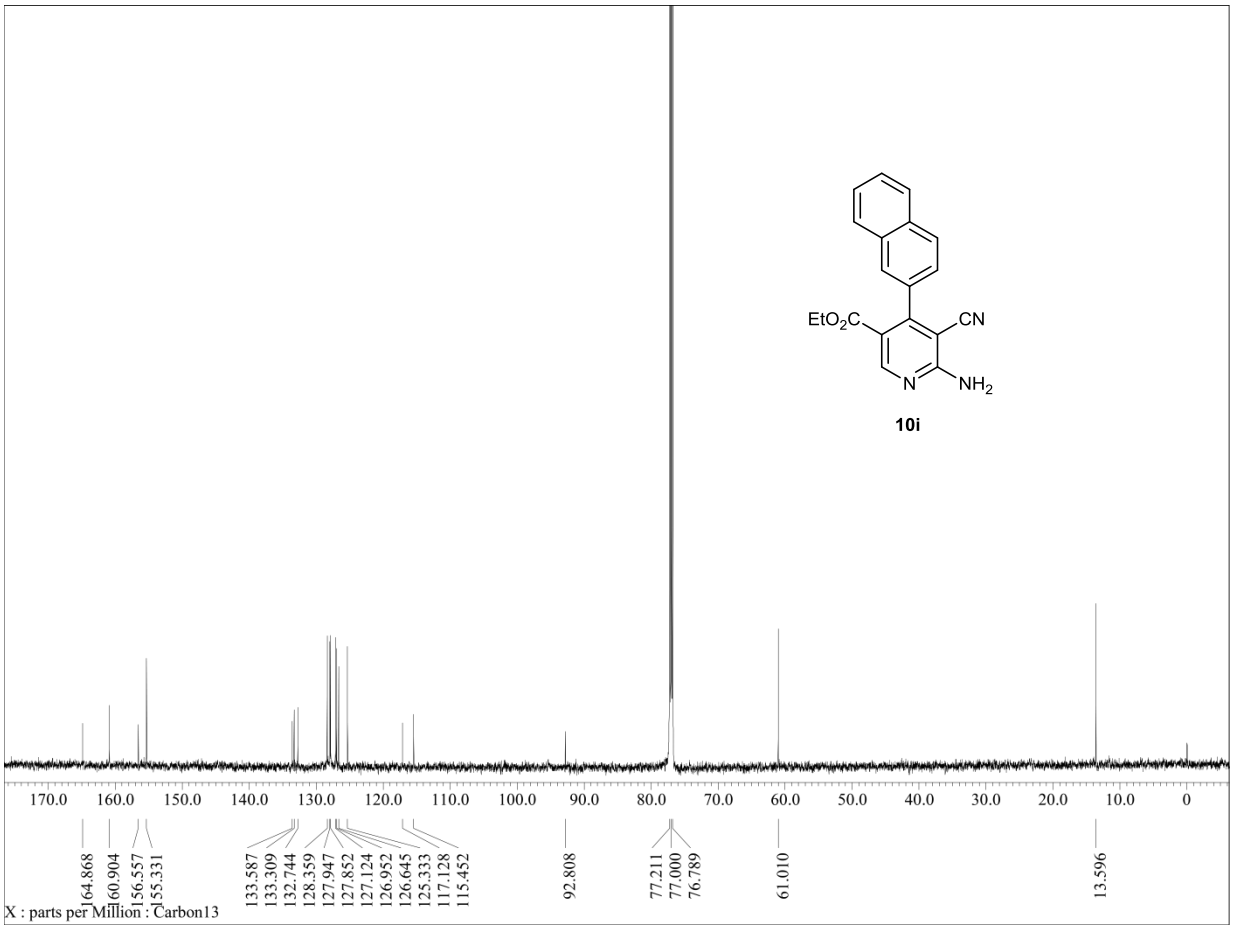

Cl
EtO2C
CN
N
NH2
10g
0.87
1.97
1.00
0.89
2.00
2.03
2.80
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.863
7.460
7.445
7.424
7.411
7.399
7.181
7.169
5.759
4.098
4.087
4.074
4.062
1.037
1.026
1.013
X : parts per Million : Proton

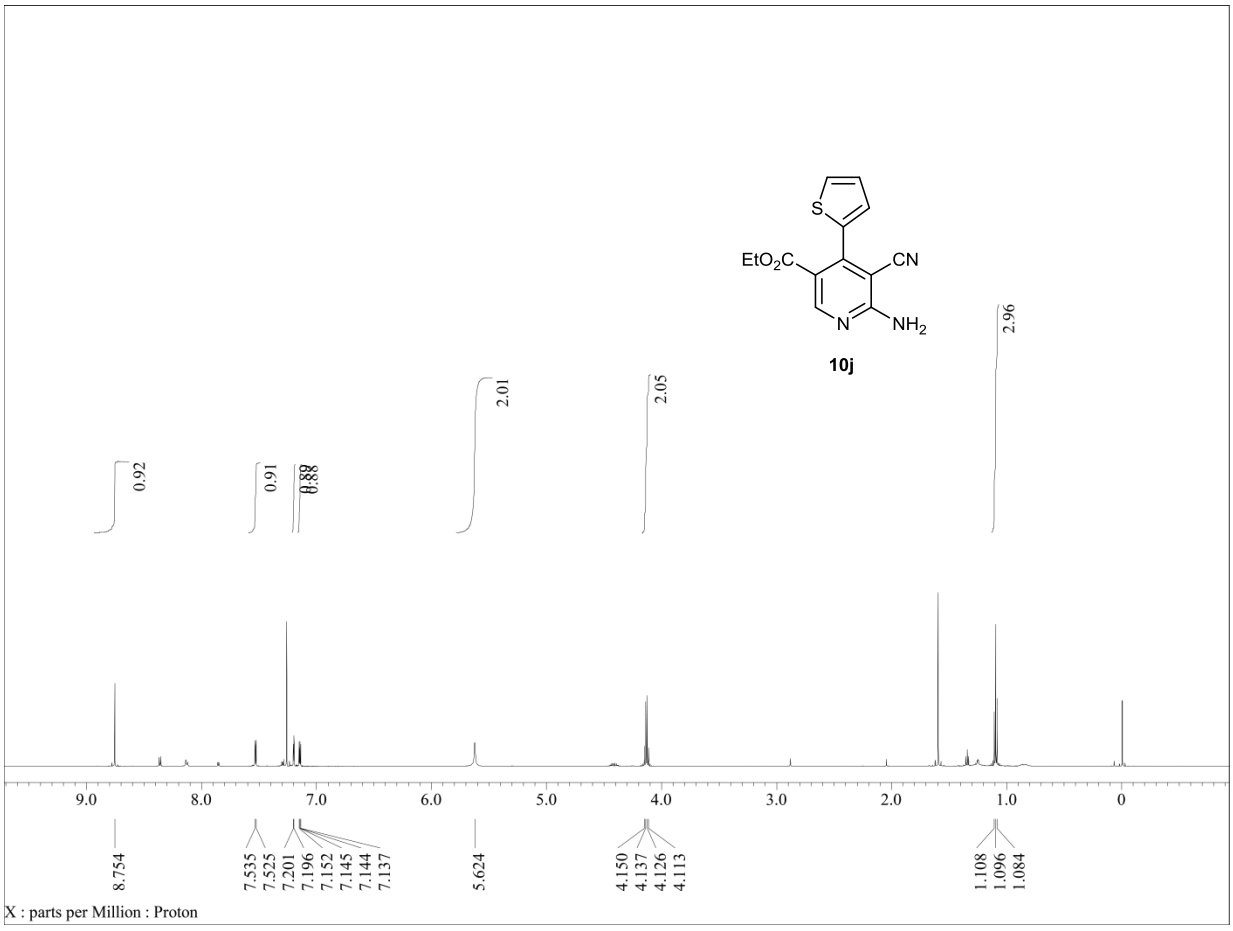

Cl
EtO2C
CN
N
NH2
10g
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.398
60.875
155.618
154.977
137.876
134.219
129.642
129.249
127.804
125.812
116.477
115.002
92.396
77.211
77.000
76.789
61.106
13.644
X : parts per Million : Carbon13

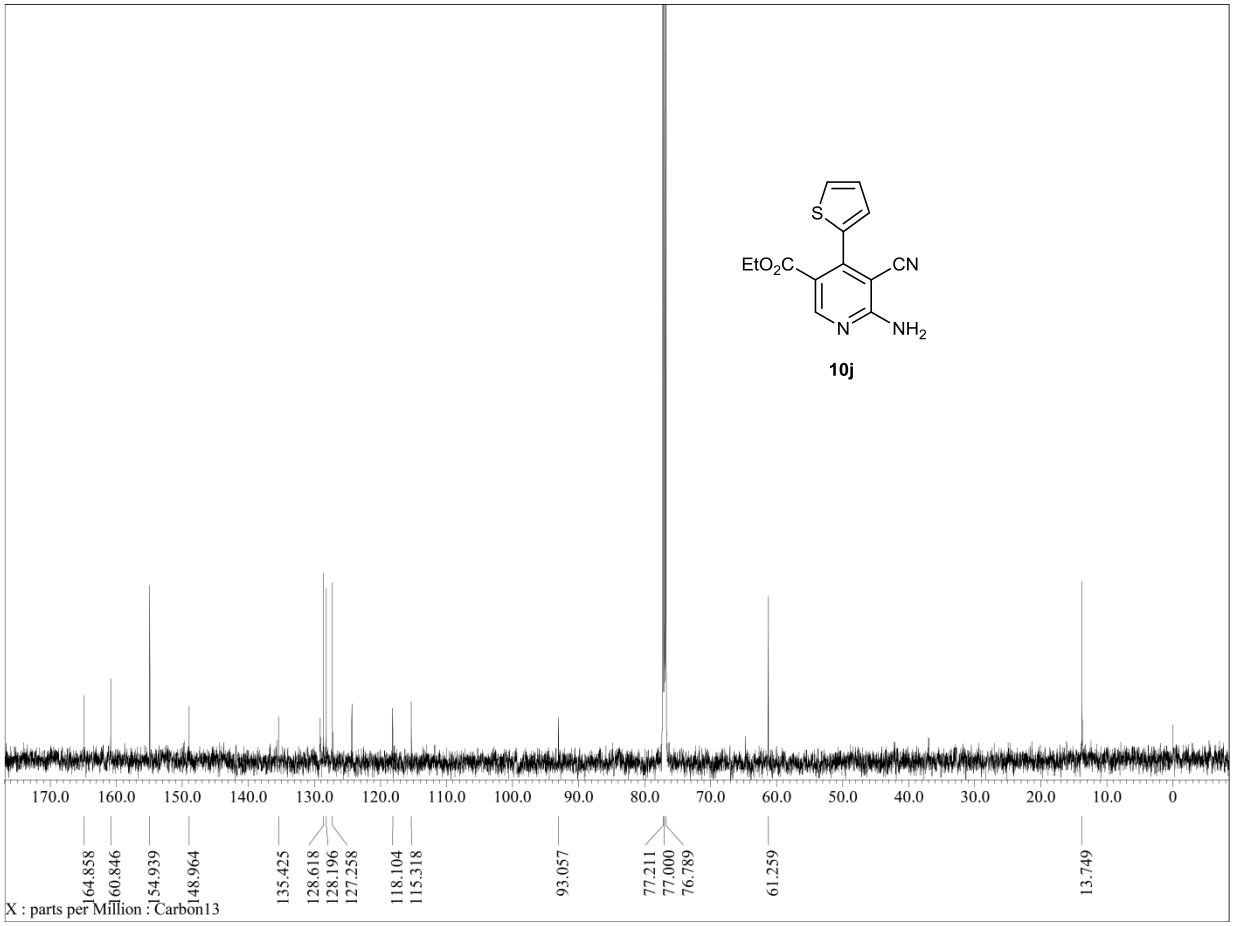

Me
EtO2C
CN
N
NH2
10h
0.96
1.87
2.00
1.95
3.09
2.95
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.805
7.359
7.346
7.332
7.284
7.276
7.078
7.067
5.601
4.075
4.064
4.051
4.040
2.400
1.003
0.991
0.979
X : parts per Million : Proton

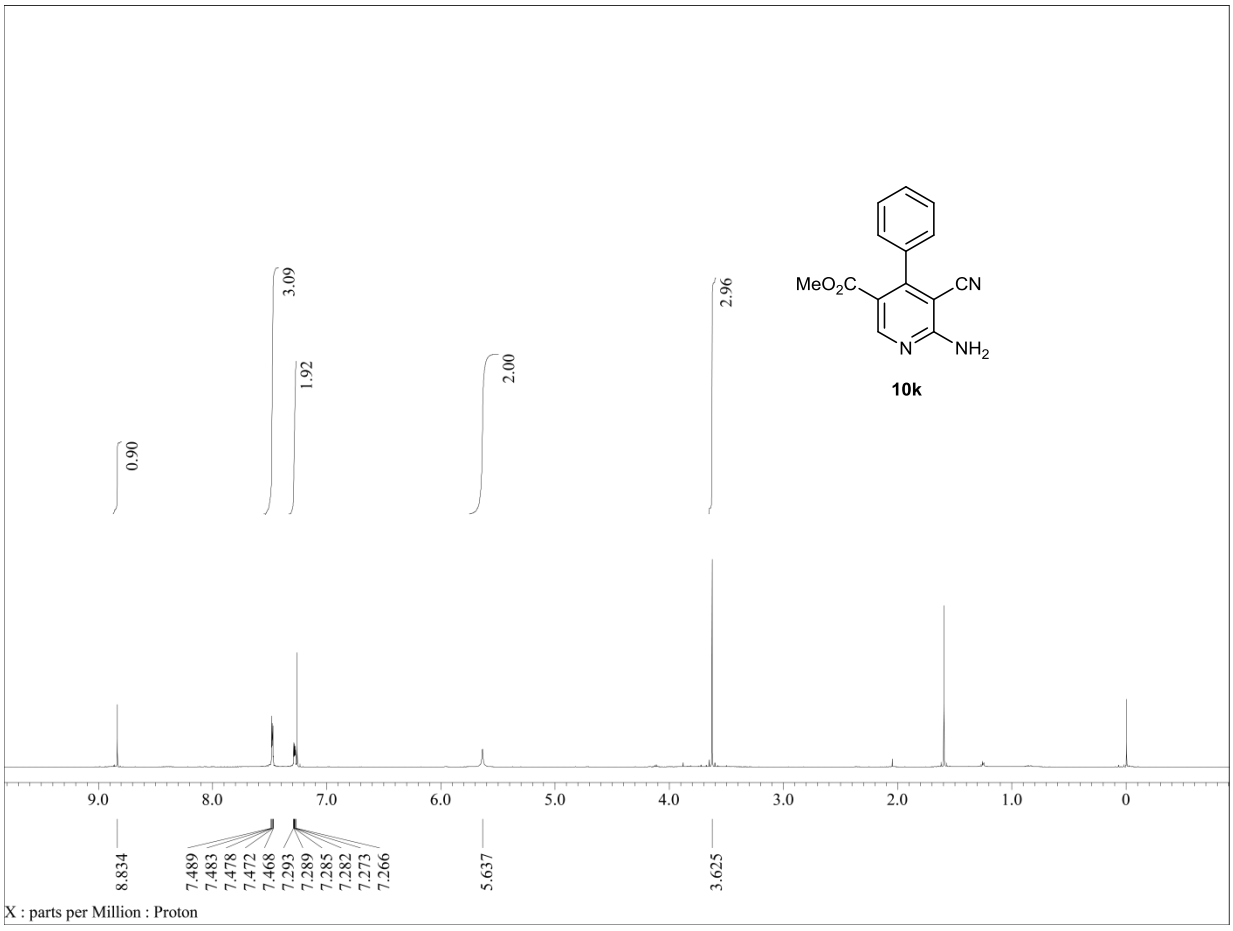

Me
EtO2C
CN
N
NH2
10h
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.973
160.798
156.767
155.130
137.915
136.076
129.948
128.177
128.158
124.701
117.128
115.443
92.578
77.211
77.000
76.789
60.943
21.418
13.625
X : parts per Million : Carbon13

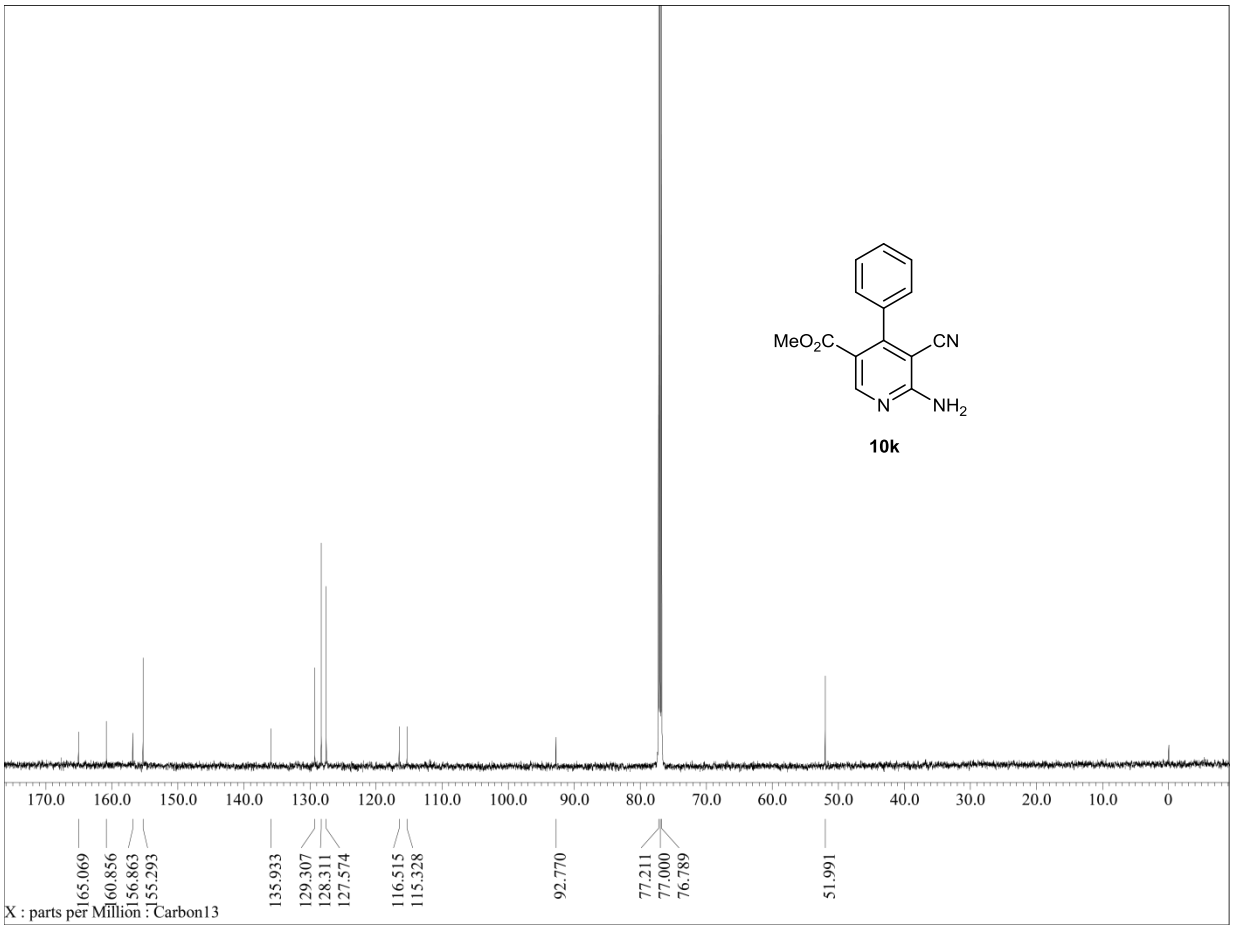

EtO2C
CN
N
NH2
10i
0.90
1.05
1.96
0.94
2.15
1.00
2.00
1.98
3.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.872
7.935
7.921
7.905
7.889
7.873
7.791
7.571
7.564
7.555
7.550
7.545
7.539
7.534
7.525
7.364
7.353
5.661
4.032
4.020
4.007
3.996
0.876
0.865
0.854
X : parts per Million : Proton


EtO2C
CN
N
NH2
10i
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.868
160.904
156.557
155.331
133.587
133.309
132.744
128.359
127.947
127.852
127.124
126.952
126.645
125.333
117.128
115.452
92.808
77.211
77.000
76.789
61.010
13.596
X : parts per Million : Carbon13


S
EtO2C
CN
N
NH2
10j
0.92
0.91
0.88
2.01
2.05
2.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.754
7.535
7.525
7.201
7.196
7.152
7.145
7.144
7.137
5.624
4.150
4.137
4.126
4.113
1.108
1.096
1.084
X : parts per Million : Proton


S
EtO2C
CN
N
NH2
10j
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.858
160.846
154.939
148.964
135.425
128.618
128.196
127.258
118.104
115.318
93.057
77.211
77.000
76.789
61.259
13.749
X : parts per Million : Carbon13


MeO2C
CN
N
NH2
10k
0.90
3.09
1.92
2.00
2.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.834
7.489
7.483
7.478
7.472
7.468
7.293
7.289
7.285
7.282
7.273
7.266
5.637
3.625
X : parts per Million : Proton


MeO2C
CN
N
NH2
10k
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
165.069
160.856
156.863
155.293
135.933
129.307
128.311
127.574
116.515
115.328
92.770
77.211
77.000
76.789
51.991
X : parts per Million : Carbon13