Diastereodivergent Synthesis of Cyclopropananes *via* On-Water Annulation of Diazo Compounds with Electron-Deficient Alkenes

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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 °C 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

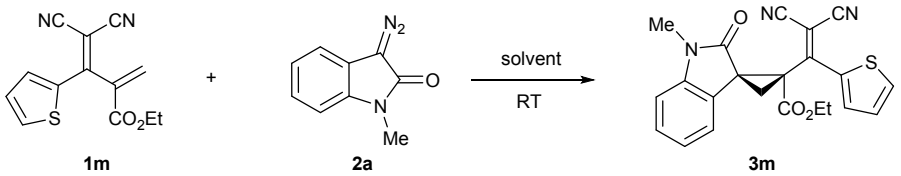
- Commercial reagents and solvents were were purchased from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin and Energy Chemical and used as received with the following exceptions: THF, Et_2O and toluene were purified by refluxing over Na-benzophenone under positive argon pressure followed by distillation.[1] The allylidenemalononitriles **1**[2], 3-diazooxindole **2**[3], alkenes **6** and **9**[4]**,** diazoacetate **7a** and **7b**[5] 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

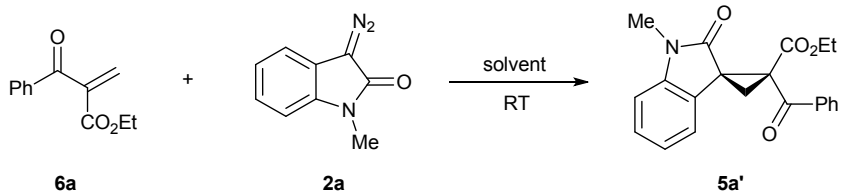
Table S1. Optimization of the cyclopropanation of alkene **1m** and 3-diazooxindole **2a**[a]



Entry	Solvent	Time (h)	D. r.[b]	Yield (%)[c]
1	MeCN	15	3:1	79
2	DCM	12	2:1	81
3	THF	15	2:1	92
4	toluene	24	2:1	89
5	EtOH	10	2:1	85
6	H_2O	5	2:1	98

[a] Reactions were performed with 0.15 mmol of **1m** and 0.1 mmol of **2a**, in 1 mL solvent at room temperature. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yields of the two diastereoisomers.

Table S2. Optimization of the cyclopropanation of alkene **6a** and 3-diazooxindole **2a**[a]

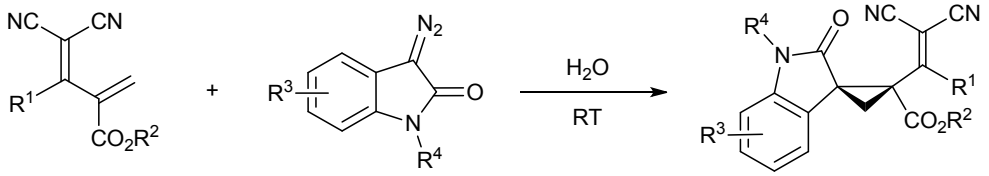


Entry	Solvent	Time (h)	D. r.[b]	Yield (%)[c]
1	MeCN	15	2:1	71
2	DCM	12	3:1	75
3	$CHCl_3$	36	4:1	75
4	THF	15	4:1	82
5	toluene	24	**5:1**	86
6	H_2O	5	3:1	**99**

[a] Reactions were performed with 0.15 mmol of **6a** and 0.1 mmol of **2a**, in 1 mL solvent at room temperature. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yields of the two diastereoisomers.

3. General Procedure for the Preparation of Cyclopropanes 3

*General procedure for the synthesis of cyclopropanes **3***

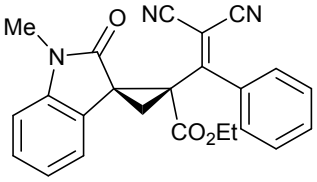


A glass tube was charged with diene **1** (0.15 mmol) and 3-diazooxindole **2** (0.10 mmol) in water (1 mL). Unless otherwise noted, the mixture was stirred at room temperature for 1 hour. Then the mixture was extracted with ethyl acetate (10 mL × 2), and the organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 3/1) to afford the corresponding cyclopropane **3a**–**3aa** in 62%–99% yields.

*Gram-scale synthesis of cyclopropane **3a***

A 50 mL flask was charged with diene **1a** (1.89 g, 7.5 mmol) and 3-diazooxindole **2a** (0.87 g, 5.0 mmol) in water (30 mL). The mixture was stirred at room temperature. After 5 hours, the mixture was extracted with ethyl acetate (50 mL × 3). 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 cyclopropane **3a** (1.69 g) in 85% yield.

ethyl-2-(2,2-dicyano-1-phenylvinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3a



Prepared according to the general procedure to afford **3a** (39.3 mg, m. p. = 166 – 172 °C) in 99% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

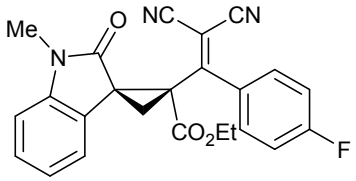
NMR and HRMS data for the product **3a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 (d, *J* = 7.2 Hz, 2H), 7.57 – 7.50 (m, 3H), 7.40 – 7.33 (m, 2H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 4.43 – 4.25 (m, 2H), 3.32 (s, 3H), 2.75 (d, *J* = 5.4 Hz, 1H), 1.69 (d, *J* = 6.0 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.6, 170.2, 165.0, 144.7, 135.4, 132.0, 129.2, 129.0, 128.4, 123.7, 122.6, 122.5, 113.0, 112.2, 108.8, 90.6, 63.7, 45.5, 44.0, 26.8, 25.7, 14.0.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{24}H_{19}N_3O_3Na^+$: 420.1319, found: 420.1320.

ethyl-2-(2,2-dicyano-1-(4-fluorophenyl)vinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3b



Prepared according to the general procedure to afford **3b** (37.8 mg, m. p. = 175 – 182 °C) in 91% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

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

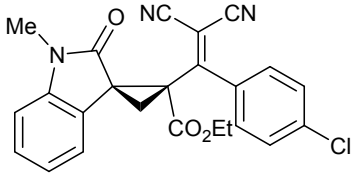
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.62 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 16.8 Hz, 2H), 7.22 (t, *J* = 8.4 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 4.43 – 4.24 (m, 2H), 3.31 (s, 3H), 2.75 (d, *J* = 6.0 Hz, 1H), 1.66 (d, *J* = 5.4 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.5, 169.1, 164.9, 164.7 (d, J_{C-F} = 252.9 Hz), 144.7, 131.5 (d, J_{C-F} = 3.0 Hz), 130.9 (d, J_{C-F} = 8.6 Hz), 129.3, 123.6, 116.5 (d, J_{C-F} = 23.1 Hz), 116.5, 116.4, 113.0, 112.1, 108.8, 90.6, 63.8, 45.4, 44.2, 26.8, 25.7, 14.1.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -105.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}FN_3O_3Na^+$: 438.1224, found: 438.1227.

ethyl-2-(1-(4-chlorophenyl)-2,2-dicyanovinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3c



Prepared according to the general procedure to afford **3c** (36.7 mg, m. p. = 168 – 171 °C) in 85% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

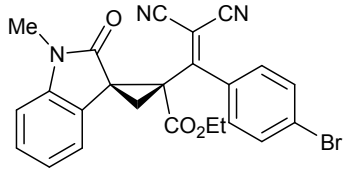
NMR and HRMS data for the product **3c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.54 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 4.43 – 4.24 (m, 2H), 3.31 (s, 3H), 2.74 (d, *J* = 5.4 Hz, 1H), 1.66 (d, *J* = 6.0 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.5, 169.1, 164.8, 144.7, 138.4, 133.7, 129.8, 129.4, 129.3, 123.5, 122.7, 122.6, 112.8, 112.0, 108.9, 90.9, 63.9, 45.2, 44.2, 26.8, 25.7, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}{}^{35}ClN_3O_3Na^+$: 454.0929, found: 454.0925; calculated for $C_{24}H_{18}{}^{37}ClN_3O_3Na^+$: 456.0899, found: 456.0903.

ethyl-2-(1-(4-bromophenyl)-2,2-dicyanovinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3d



Prepared according to the general procedure to afford **3d** (43.8 mg, m. p. = 173 – 175 °C) in 92% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

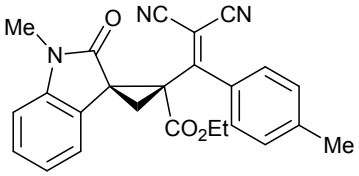
NMR and HRMS data for the product **3d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.66 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 4.44 – 4.22 (m, 2H), 3.31 (s, 3H), 2.74 (d, *J* = 5.4 Hz, 1H), 1.66 (d, *J* = 6.0 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.5, 169.2, 164.8, 144.7, 134.2, 132.4, 129.9, 129.3, 126.9, 123.5, 122.7, 122.6, 112.8, 112.0, 108.8, 90.9, 63.9, 45.2, 44.3, 26.8, 25.7, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}{}^{79}BrN_3O_3Na^+$: 498.0424, found: 498.0426; calculated for $C_{24}H_{18}{}^{81}BrN_3O_3Na^+$: 500.0403, found: 500.0399.

ethyl-2-(2,2-dicyano-1-(p-tolyl)vinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3e



Prepared according to the general procedure to afford **3e** (39.9 mg, m. p. = 172 – 175 °C) in 97% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

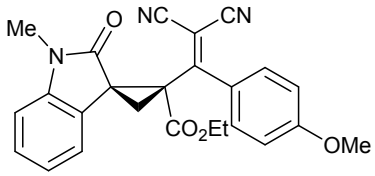
NMR and HRMS data for the product **3e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.51 (d, *J* = 7.8 Hz, 2H), 7.39 – 7.29 (m, 4H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 4.42 – 4.23 (m, 2H), 3.31 (s, 3H), 2.75 (d, *J* = 5.4 Hz, 1H), 2.43 (s, 3H), 1.69 (d, *J* = 5.4 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.6, 170.1, 165.1, 144.7, 143.0, 132.6, 129.7, 129.2, 128.5, 123.8, 122.6, 122.4, 113.3, 112.4, 108.7, 89.5, 63.7, 45.5, 43.8, 26.8, 25.8, 21.6, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}N_3O_3Na^+$: 434.1475, found: 434.1472.

ethyl-2-(2,2-dicyano-1-(4-methoxyphenyl)vinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3f



Prepared according to the general procedure to afford **3f** (38.0 mg, m. p. = 132 – 135 °C) in 89% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

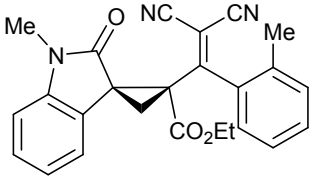
NMR and HRMS data for the product **3f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.62 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.29 (m, 2H), 7.07 – 6.99 (m, 3H), 6.93 (d, *J* = 7.8 Hz, 1H), 4.41 – 4.22 (m, 2H), 3.88 (s, 3H), 3.30 (s, 3H), 2.77 (d, *J* = 5.4 Hz, 1H), 1.72 (d, *J* = 5.4 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.6, 169.2, 165.2, 162.8, 144.7, 130.8, 129.1, 127.6, 123.8, 122.5, 122.4, 114.4, 113.8, 112.7, 108.7, 87.8, 63.6, 55.6, 45.4, 43.7, 26.7, 25.9, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}N_3O_4Na^+$: 450.1424, found: 450.1427.

ethyl-2-(2,2-dicyano-1-(o-tolyl)vinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3g



Prepared according to the general procedure to afford a mixture of diastereoisomers (34.9 mg, 85% yield, yellow solid, m. p. = 169 – 175 °C), which cannot be separated by column chromatography. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis.

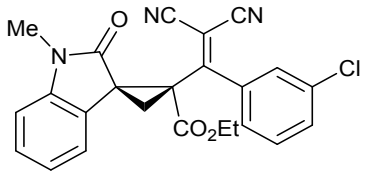
NMR and HRMS data for the product **3g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.78 (d, *J* = 7.2 Hz, 1H), 7.43 – 7.33 (m, 3H), 7.29 – 7.20 (m, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 4.47 – 4.18 (m, 2H), 3.34 (s, 3H), 2.67 (d, *J* = 5.4 Hz, 1H), 2.27 (s, 3H), 1.76 (d, *J* = 5.4 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.1, 171.4, 164.6, 144.6, 135.4, 134.5, 131.1, 131.02, 131.00, 129.3, 126.4, 123.6, 122.5, 122.4, 112.3, 111.8, 108.8, 94.7, 63.6, 45.9, 44.3, 26.8, 23.9, 20.1, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}N_3O_3Na^+$: 434.1475, found: 434.1476.

ethyl-2-(1-(3-chlorophenyl)-2,2-dicyanovinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3h



Prepared according to the general procedure to afford **3h** (39.7 mg, m. p. = 176 – 180 °C) in 92% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

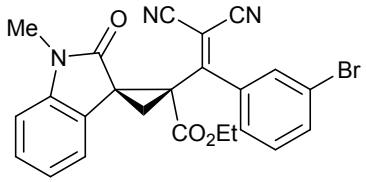
NMR and HRMS data for the product **3h**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 – 7.44 (m, 4H), 7.39 – 7.34 (m, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 4.47 – 4.24 (m, 2H), 3.32 (s, 3H), 2.75 (d, *J* = 5.4 Hz, 1H), 1.68 (d, *J* = 5.4 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.5, 168.9, 164.6, 144.7, 137.0, 135.1, 131.8, 130.4, 129.3, 127.9, 126.6, 123.5, 122.8, 122.6, 112.4, 111.8, 108.8, 91.9, 63.9, 45.2, 44.3, 26.8, 25.6, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}{}^{35}ClN_3O_3Na^+$: 454.0929, found: 454.0924; calculated for $C_{24}H_{18}{}^{37}ClN_3O_3Na^+$: 456.0899, found: 456.0906.

ethyl-2-(1-(3-bromophenyl)-2,2-dicyanovinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3i



Prepared according to the general procedure to afford **3i** (39.5 mg, m. p. = 182 – 187 °C) in 83% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

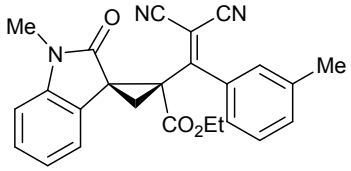
NMR and HRMS data for the product **3i**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.71 – 7.63 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 4.47 – 4.24 (m, 2H), 3.32 (s, 3H), 2.75 (d, *J* = 6.0 Hz, 1H), 1.69 (d, *J* = 5.4 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.5, 168.7, 164.6, 144.7, 137.3, 134.8, 130.7, 130.6, 129.3, 127.1, 123.5, 123.0, 122.8, 122.6, 112.4, 111.8, 108.8, 92.0, 63.9, 45.2, 44.3, 26.8, 25.6, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}{}^{79}BrN_3O_3Na^+$: 498.0424, found: 498.0429; calculated for $C_{24}H_{18}{}^{81}BrN_3O_3Na^+$: 500.0403, found: 500.0407.

ethyl-2-(2,2-dicyano-1-(m-tolyl)vinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3j



Prepared according to the general procedure to afford **3j** (40.3 mg, m. p. = 177 – 179 °C) in 98% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

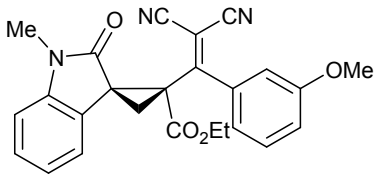
NMR and HRMS data for the product **3j**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.42 – 7.38 (m, 2H), 7.38 – 7.33 (m, 4H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 4.43 – 4.25 (m, 2H), 3.32 (s, 3H), 2.75 (d, *J* = 5.4 Hz, 1H), 2.44 (s, 3H), 1.70 (d, *J* = 5.4 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.6, 170.3, 165.0, 144.7, 138.9, 135.4, 132.8, 129.2, 128.9, 128.7, 125.5, 123.8, 122.6, 122.5, 113.1, 112.3, 108.7, 90.4, 63.7, 45.5, 43.9, 26.8, 25.7, 21.4, 14.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}N_3O_3Na^+$: 434.1475, found: 434.1476.

ethyl-2-(2,2-dicyano-1-(3-methoxyphenyl)vinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3k



Prepared according to the general procedure to afford **3k** (42.3 mg, m. p. = 163 – 168 °C) in 99% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

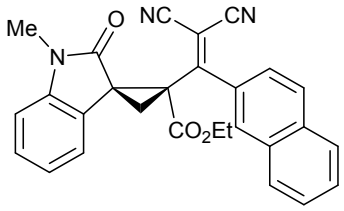
NMR and HRMS data for the product **3k**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.42 (t, *J* = 8.4 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.18 – 7.12 (m, 2H), 7.09 – 7.03 (m, 2H), 6.94 (d, *J* = 7.8 Hz, 1H), 4.43 – 4.22 (m, 2H), 3.88 (s, 3H), 3.32 (s, 3H), 2.75 (d, *J* = 5.4 Hz, 1H), 1.73 (d, *J* = 5.4 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.6, 170.0, 164.9, 159.7, 144.7, 136.6, 130.2, 129.2, 123.7, 122.6, 122.5, 120.5, 117.9, 113.6, 113.0, 112.2, 108.7, 90.8, 63.7, 55.6, 45.5, 43.9, 26.8, 25.7, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}N_3O_4Na^+$: 450.1424, found: 450.1426.

ethyl-2-(2,2-dicyano-1-(naphthalen-2-yl)vinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3l



Prepared according to the general procedure to afford **3l** (42.5 mg, m. p. = 193 – 194 °C) in 95% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

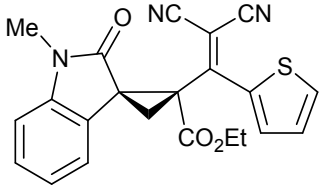
NMR and HRMS data for the product **3l**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 4.52 – 4.25 (m, 2H), 3.34 (s, 3H), 2.79 (d, *J* = 5.4 Hz, 1H), 1.71 (d, *J* = 6.0 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.6, 170.1, 165.1, 144.7, 134.6, 132.7, 132.5, 129.8, 129.3, 129.2, 129.0, 128.6, 127.8, 127.2, 124.0, 123.7, 122.6, 122.5, 113.2, 112.4, 108.8, 90.5, 63.8, 45.6, 44.0, 26.8, 25.8, 14.1.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{28}H_{21}N_3O_3Na^+$: 470.1475, found: 470.1477.

ethyl-2-(2,2-dicyano-1-(thiophen-2-yl)vinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3m



Prepared according to the general procedure except the reaction time for 5 hours. A mixture of diastereoisomers (39.5 mg, 98% yield, yellow solid, m. p. = 128 – 133 °C) were obtained, which cannot be separated by column chromatography. The diastereomeric ratio was determined to be 2:1 by crude ^{1}H NMR analysis.

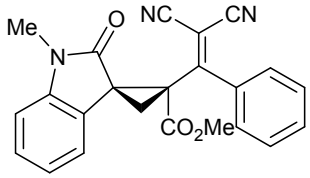
NMR and HRMS data for the product **3m**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.99 (d, *J* = 4.8 Hz, 1H), 7.78 (d, *J* = 4.2 Hz, 1H), 7.52 (t, *J* = 6.6 Hz, 1H), 7.41 – 7.30 (m, 1H), 7.24 (t, *J* = 4.8 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.40 – 4.13 (m, 2H), 3.30 (s, 3H), 2.93 (d, *J* = 4.8 Hz, 1H), 2.14 (d, *J* = 5.4 Hz, 1H), 1.19 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.6, 164.9, 159.2, 144.8, 137.8, 134.4, 134.2, 129.2, 128.8, 122.7, 122.5, 122.4, 114.0, 112.7, 108.8, 85.1, 63.7, 45.5, 42.3, 27.0, 26.8, 14.0.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{22}H_{17}N_3O_3SNa^+$: 426.0883, found: 426.0880.

methyl-2-(2,2-dicyano-1-phenylvinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3n



Prepared according to the general procedure to afford **3n** (35.2 mg, m. p. = 174 – 178 °C) in 92% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

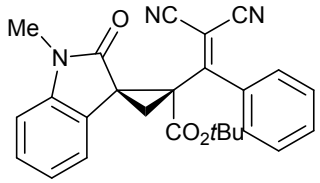
NMR and HRMS data for the product **3n**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.38 – 7.31 (m, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 3H), 3.32 (s, 3H), 2.76 (d, *J* = 5.4 Hz, 1H), 1.70 (d, *J* = 5.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.5, 170.0, 165.7, 144.7, 135.3, 132.0, 129.3, 129.0, 128.4, 123.7, 122.6, 113.0, 112.1, 108.8, 90.7, 54.3, 45.3, 44.1, 26.8, 26.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{23}H_{17}N_3O_3Na^+$: 406.1162, found: 406.1164.

tert-butyl-2-(2,2-dicyano-1-phenylvinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3o



Prepared according to the general procedure to afford **3o** (38.3 mg, m. p. = 178 – 180 °C) in 90% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

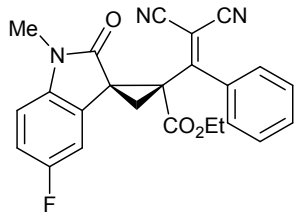
NMR and HRMS data for the product **3o**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 – 7.57 (m, 2H), 7.56 – 7.51 (m, 3H), 7.37 – 7.33 (m, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 3.32 (s, 3H), 2.69 (d, *J* = 5.4 Hz, 1H), 1.61 (d, *J* = 6.0 Hz, 1H), 1.46 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.7, 170.8, 163.4, 144.7, 135.7, 131.9, 129.12, 129.06, 128.2, 123.8, 122.7, 122.2, 113.1, 112.4, 108.7, 90.4, 85.3, 46.5, 43.5, 27.8, 26.8, 25.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{26}H_{23}N_3O_3Na^+$: 449.1632, found: 448.1630.

ethyl-2-(2,2-dicyano-1-phenylvinyl)-5'-fluoro-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3p



Prepared according to the general procedure except the reaction time for 24 hours, to afford **3p** (31.1 mg, m. p. = 131 – 135 °C) in 75% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

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

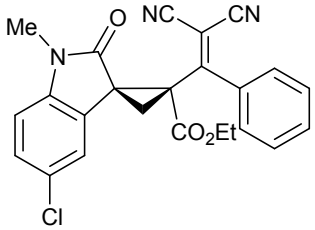
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.63 – 7.48 (m, 5H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.07 (t, *J* = 9.0 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.50 – 4.27 (m, 2H), 3.30 (s, 3H), 2.74 (d, *J* = 5.4 Hz, 1H), 1.72 (d, *J* = 5.4 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.3, 170.1, 164.8, 159.0 (d, $J_{C\text{-}F}$ = 238.4 Hz), 140.7, 135.2, 132.1, 129.0, 128.3, 125.2 (d, $J_{C\text{-}F}$ = 8.6 Hz), 115.4 (d, $J_{C\text{-}F}$ = 23.0 Hz), 112.8, 112.2, 111.3 (d, $J_{C\text{-}F}$ = 25.8 Hz), 109.1 (d, $J_{C\text{-}F}$ = 7.2 Hz), 90.6, 64.0, 45.6, 44.0, 26.9, 26.1, 14.0.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -119.8.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}FN_3O_3Na^+$: 438.1224, found: 438.1223.

ethyl-5'-chloro-2-(2,2-dicyano-1-phenylvinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3q



Prepared according to the general procedure except the reaction time for 36 hours, to afford **3q** (29.4 mg, m. p. = 169 – 175 °C) in 68% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

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

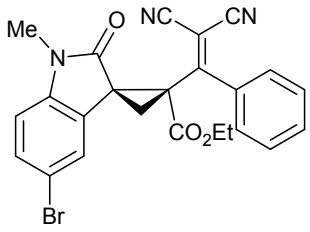
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.61 – 7.50 (m, 5H), 7.38 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.49 – 4.26 (m, 2H), 3.30 (s, 3H), 2.74 (d, *J* = 5.4 Hz, 1H), 1.71

(d, J = 5.4 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.2, 169.9, 164.8, 143.3, 135.2, 132.1, 129.1, 128.3, 128.1, 125.4, 123.4, 112.8, 112.2, 109.6, 90.7, 64.1, 45.7, 43.7, 26.9, 26.0, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}{}^{35}ClN_3O_3Na^+$: 454.0929, found: 454.0935; calculated for $C_{24}H_{18}{}^{37}ClN_3O_3Na^+$: 456.0899, found: 456.0910.

ethyl-5'-bromo-2-(2,2-dicyano-1-phenylvinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3r



Prepared according to the general procedure except the reaction time for 36 hours, to afford **3r** (29.5 mg, m. p. = 171 – 176 °C) in 62% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

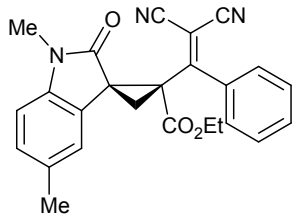
NMR and HRMS data for the product **3r**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.62 – 7.46 (m, 7H), 6.82 (d, J = 9.0 Hz, 1H), 4.51 – 4.25 (m, 2H), 3.30 (s, 3H), 2.74 (d, J = 5.4 Hz, 1H), 1.71 (d, J = 6.6 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.1, 169.9, 164.8, 143.7, 135.2, 132.1, 132.0, 129.1, 128.3, 126.0, 125.7, 115.3, 112.8, 112.2, 110.1, 90.7, 64.1, 45.7, 43.5, 26.9, 26.0, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}{}^{79}BrN_3O_3Na^+$: 498.0424, found: 498.0426; calculated for $C_{24}H_{18}{}^{81}BrN_3O_3Na^+$: 500.0403, found: 500.0431.

ethyl-2-(2,2-dicyano-1-phenylvinyl)-1',5'-dimethyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3s



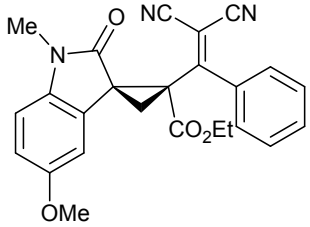
Prepared according to the general procedure to afford **3s** (40.7 mg, m. p. = 150 – 153 °C) in 99% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

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

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 (d, J = 6.6 Hz, 2H), 7.57 – 7.49 (m, 3H), 7.18 – 7.11 (m, 2H), 6.83 (d, J = 7.8 Hz, 1H), 4.44 – 4.25 (m, 2H), 3.29 (s, 3H), 2.71 (d, J = 5.4 Hz,

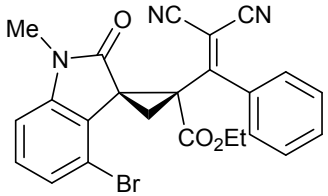
1H), 2.34 (s, 3H), 1.66 (d, *J* = 5.4 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.5, 170.4, 165.0, 142.4, 135.4, 132.0, 131.9, 129.5, 129.0, 128.4, 123.7, 123.3, 113.0, 112.2, 108.5, 90.6, 63.7, 45.4, 44.1, 26.8, 25.7, 21.2, 14.0.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}N_3O_3Na^+$: 434.1475, found: 434.1478.

ethyl-2-(2,2-dicyano-1-phenylvinyl)-5'-methoxy-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3t



Prepared according to the general procedure to afford **3t** (42.3 mg, m. p. = 124 – 126 °C) in 99% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **3t**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.59 (d, *J* = 6.6 Hz, 2H), 7.57 – 7.47 (m, 3H), 7.02 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.43 – 4.26 (m, 2H), 3.79 (s, 3H), 3.29 (s, 3H), 2.71 (d, *J* = 5.4 Hz, 1H), 1.68 (d, *J* = 6.0 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.2, 170.4, 164.9, 155.8, 138.2, 135.4, 131.9, 129.0, 128.3, 125.0, 113.5, 113.0, 112.2, 110.3, 109.0, 90.6, 63.8, 55.8, 45.4, 44.2, 26.8, 25.9, 14.0.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}N_3O_4Na^+$: 450.1424, found: 450.1427.

ethyl-4'-bromo-2-(2,2-dicyano-1-phenylvinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3u

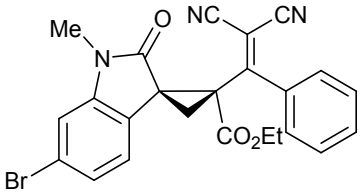


Prepared according to the general procedure except the reaction time for 24 hours, to afford **3u** (36.2 mg, m. p. = 146 – 151 °C) in 76% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **3u**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.97 (d, *J* = 6.0 Hz, 2H), 7.59 – 7.50 (m, 3H), 7.23 – 7.16 (m, 2H), 6.91 (d, *J* = 6.6 Hz, 1H), 4.41 – 4.21 (m, 2H), 3.37 (d, *J* = 6.6 Hz, 1H), 3.30 (s, 3H), 1.59 (d, *J* = 6.0 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.2, 171.1, 165.9, 146.7, 135.3, 132.1, 130.0, 129.5, 128.8, 127.1, 122.4, 117.9, 113.1, 111.7, 108.2, 88.4, 63.8, 44.9, 43.6, 26.9, 21.5, 13.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}{}^{79}BrN_3O_3Na^+$: 498.0424, found: 498.0420; calculated for $C_{24}H_{18}{}^{81}BrN_3O_3Na^+$: 500.0403, found: 500.0411.

ethyl-6'-bromo-2-(2,2-dicyano-1-phenylvinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3v



Prepared according to the general procedure except the reaction time for 36 hours, to afford **3v** (45.7 mg, m. p. = 179 – 185 °C) in 96% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

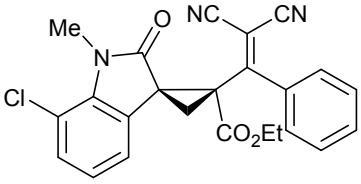
NMR and HRMS data for the product **3v**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.61 – 7.49 (m, 5H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.08 (s, 1H), 4.44 – 4.24 (m, 2H), 3.29 (s, 3H), 2.74 (d, *J* = 6.0 Hz, 1H), 1.69 (d, *J* = 5.4 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.4, 169.9, 164.8, 145.9, 135.2, 132.0, 129.0, 128.3, 125.3, 124.1, 123.1, 122.6, 112.8, 112.3, 112.2, 90.7, 63.9, 45.6, 43.7, 26.9, 25.9, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}{}^{79}BrN_3O_3Na^+$: 498.0424, found: 498.0428; calculated for $C_{24}H_{18}{}^{81}BrN_3O_3Na^+$: 500.0403, found: 500.0409.

ethyl-7'-chloro-2-(2,2-dicyano-1-phenylvinyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3w



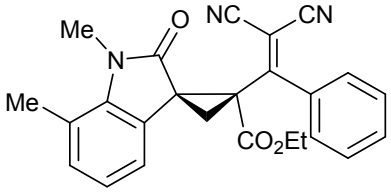
Prepared according to the general procedure except the reaction time for 36 hours, to afford **3w** (36.3 mg, m. p. = 190 – 192 °C) in 84% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

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

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.59 (d, *J* = 6.0 Hz, 2H), 7.57 – 7.50 (m, 3H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 8.4 Hz, 1H), 4.43 – 4.23 (m, 2H), 3.69 (s, 3H), 2.73 (d, *J* = 6.0 Hz, 1H), 1.70 (d, *J* = 5.4 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H).

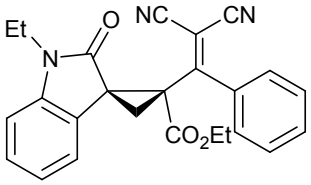
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.0, 169.7, 164.7, 140.6, 135.3, 132.1, 131.6, 129.1, 128.4, 126.5, 123.1, 120.9, 116.3, 112.9, 112.2, 90.7, 63.9, 46.3, 43.4, 30.4, 26.1, 14.0.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{18}{}^{35}ClN_3O_3Na^+$: 454.0929, found: 454.0931; calculated for $C_{24}H_{18}{}^{37}ClN_3O_3Na^+$: 456.0899, found: 456.0908.

ethyl-2-(2,2-dicyano-1-phenylvinyl)-1',7'-dimethyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3x



Prepared according to the general procedure to afford **3x** (37.0 mg, m. p. = 184 – 187 °C) in 90% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **3x**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 (d, *J* = 7.2 Hz, 2H), 7.56 – 7.48 (m, 3H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 4.42 – 4.21 (m, 2H), 3.59 (s, 3H), 2.69 (d, *J* = 6.6 Hz, 1H), 2.60 (s, 3H), 1.66 (d, *J* = 6.0 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.4, 170.2, 164.9, 142.6, 135.5, 133.1, 131.9, 129.0, 128.4, 124.3, 122.3, 120.5, 120.1, 113.1, 112.2, 90.5, 63.7, 46.0, 43.6, 30.3, 25.7, 19.2, 14.0.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}N_3O_3Na^+$: 434.1475, found: 434.1478.

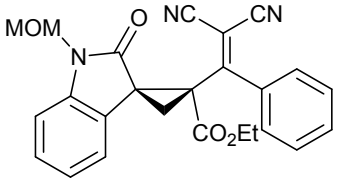
ethyl-2-(2,2-dicyano-1-phenylvinyl)-1'-ethyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3y



Prepared according to the general procedure to afford **3y** (38.2 mg, m. p. = 142 – 145 °C) in 93% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **3y**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 (d, *J* = 6.6 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.39 – 7.30 (m, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 1H), 4.44 – 4.26 (m, 2H), 3.96 – 3.75 (m, 2H), 2.74 (d, *J* = 5.4 Hz, 1H), 1.67 (d, *J* = 5.4 Hz, 1H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).

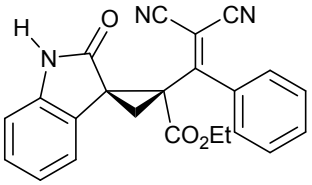
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.2, 170.4, 165.0, 143.8, 135.4, 131.9, 129.1, 129.0, 128.4, 124.0, 122.9, 122.3, 113.0, 112.3, 108.8, 90.5, 63.7, 45.4, 44.1, 35.5, 26.1, 14.1, 12.4.
HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calculated for $C_{25}H_{21}N_3O_3Na^+$: 434.1475, found: 434.1483.

ethyl-2-(2,2-dicyano-1-phenylvinyl)-1'-(methoxymethyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3z



Prepared according to the general procedure to afford **3z** (38.0 mg, m. p. = 118 – 121 °C) in 89% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **3z**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 (d, *J* = 6.0 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.39 – 7.30 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 5.25 (d, *J* = 11.4 Hz, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 4.44 – 4.22 (m, 2H), 3.40 (s, 3H), 2.78 (d, *J* = 6.6 Hz, 1H), 1.71 (d, *J* = 5.4 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.6, 170.1, 164.8, 143.2, 135.3, 132.1, 129.4, 129.1, 128.4, 123.4, 123.1, 122.7, 112.9, 112.4, 110.3, 90.6, 72.5, 63.9, 56.8, 45.9, 44.0, 26.5, 14.1.
HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calculated for $C_{25}H_{21}N_3O_4Na^+$: 450.1424, found: 450.1428.

ethyl-2-(2,2-dicyano-1-phenylvinyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 3aa

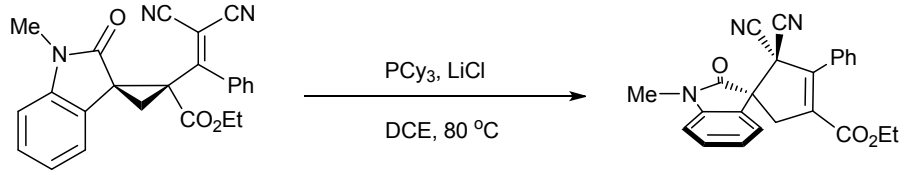


Prepared according to the general procedure to afford **3aa** (33.3 mg, m. p. = 176 – 180 °C) in 87% yield as yellow solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **3aa**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.95 (s, 1H), 7.60 – 7.49 (m, 5H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 4.51 – 4.20 (m, 2H), 2.76 (d, *J* = 5.4 Hz, 1H), 1.69 (d, *J* = 6.0 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.9, 170.1, 164.9, 141.6, 135.3, 132.0, 129.2, 129.0, 128.4, 124.3, 123.2, 122.6, 112.9, 112.3, 110.3, 90.7, 63.8, 45.6, 44.2, 26.3, 14.1.

HRMS (ESI-TOF) m/z: **[M + Na]**$^{+}$ calculated for $C_{23}H_{17}N_3O_3Na^{+}$: 406.1162, found: 406.1166.

4. Synthetic Transformation of Cyclopropane 3a

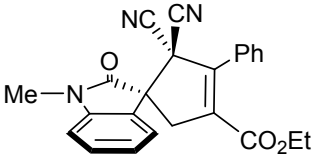
4.1 Procedure for the vinylcyclopropane-cyclopentene rearrangement



3a **4**

A glass tube was charged with vinylcyclopropane **3a** (39.7 mg, 0.1 mmol), PCy_3 (28.0 mg, 0.1 mmol), LiCl (12.7 mg, 0.3 mmol) in DCE (1 mL) under argon atmosphere. The mixture was stirred at 80 °C for 8 hours, and then cooled to room temperature. The mixture was then directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 5/1) to provide the cyclopentene **4** (26.6 mg, 67% yield) as brown semisolid, which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*.

ethyl-2,2-dicyano-1'-methyl-2'-oxo-3-phenylspiro[cyclopentane-1,3'-indolin]-3-ene-4-carboxylate 4



Purification of the crude product *via* column chromatography delivered **4** (26.6 mg) in 67% yield as brown semisolid.

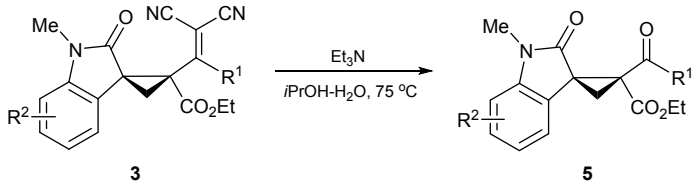
NMR and HRMS data for the product **4**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.67 (d, *J* = 7.2 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.49 – 7.45 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 4.09 (q, *J* = 6.6 Hz, 2H), 3.45 (d, *J* = 16.8 Hz, 1H), 3.34 (d, *J* = 17.4 Hz, 1H), 3.30 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 173.2, 162.5, 143.6, 143.1, 135.9, 131.1, 130.8, 130.0, 128.5, 128.4, 124.6, 124.5, 123.7, 111.6, 111.0, 109.2, 61.4, 57.8, 53.7, 41.3, 26.8, 13.6.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{24}H_{19}N_3O_3Na^+$: 420.1319, found: 420.1318.

*4.2 General procedure for the hydrolysis of product **3***

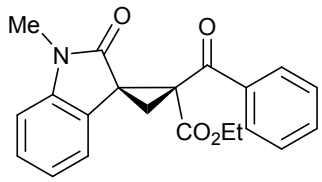


3 **5**

A glass tube was charged with cyclopropane **3** (0.1 mmol), triethylamine (30.4 mg, 0.3

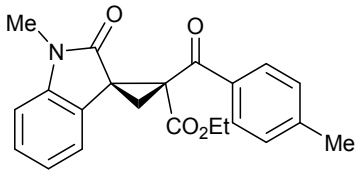
mmol) in *i*-PrOH/H_2O (2 mL, 3:1 (*v*/*v*)). The mixture was stirred at 75 °C for 12 hour. Then the mixture was added with water (5 mL) and extracted with ethyl acetate (5 mL × 2). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 5/1) to provide the *cis*-cyclopropane **5a-5d**, in 62%-43% yields as solid or semisolid, which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*.

ethyl-2-benzoyl-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5a



Prepared according to the general procedure to afford **5a** (21.6 mg) in 62% yield as colorless semisolid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **5a**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.81 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.18 – 4.04 (m, 2H), 3.09 (s, 3H), 2.72 (d, *J* = 4.8 Hz, 1H), 2.50 (d, *J* = 5.4 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.4, 172.3, 166.5, 144.7, 136.2, 133.1, 128.7, 128.5, 128.3, 124.4, 123.4, 122.3, 108.3, 62.4, 47.8, 38.8, 26.5, 24.6, 13.8.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{21}H_{19}NO_4Na^+$: 372.1206, found: 372.1205.

ethyl-1'-methyl-2-(4-methylbenzoyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5b



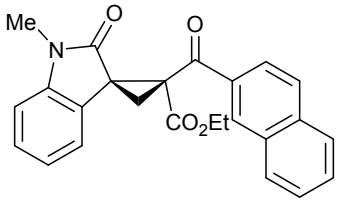
Prepared according to the general procedure to afford **5b** (17.4 mg) in 48% yield as colorless semisolid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **5b**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.15 – 4.03 (m, 2H), 3.11 (s, 3H), 2.71 (d, *J* = 4.8 Hz, 1H), 2.48 (d, *J* = 4.8 Hz, 1H), 2.38 (s,

3H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.0, 172.4, 166.6, 144.8, 144.0, 133.8, 129.0, 128.8, 128.5, 124.5, 123.3, 122.3, 108.2, 62.4, 48.0, 38.7, 26.6, 24.7, 21.7, 13.9.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{22}H_{21}NO_4Na^+$: 386.1363, found: 386.1360.

ethyl-2-(2-naphthoyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5c



Prepared according to the general procedure to afford **5c** (17.2 mg, m. p. = 146 – 150 °C) in 43% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

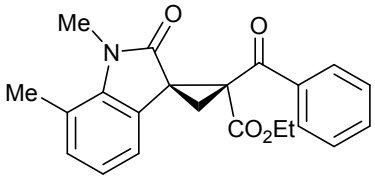
NMR and HRMS data for the product **5c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.30 (s, 1H), 7.91 – 7.80 (m, 5H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 4.17 – 4.06 (m, 2H), 3.01 (s, 3H), 2.80 (d, *J* = 4.8 Hz, 1H), 2.57 (d, *J* = 4.8 Hz, 1H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.5, 172.4, 166.5, 144.8, 135.6, 133.7, 132.3, 130.5, 129.6, 128.6, 128.5, 128.1, 127.7, 126.6, 124.4, 124.3, 123.4, 122.4, 108.3, 62.5, 48.0, 39.0, 26.5, 24.6, 13.9.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}NO_4Na^+$: 422.1363, found: 422.1370.

ethyl-2-benzoyl-1',7'-dimethyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5d



Prepared according to the general procedure to afford **5d** (18.9 mg) in 52% yield as pure yellow semisolid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

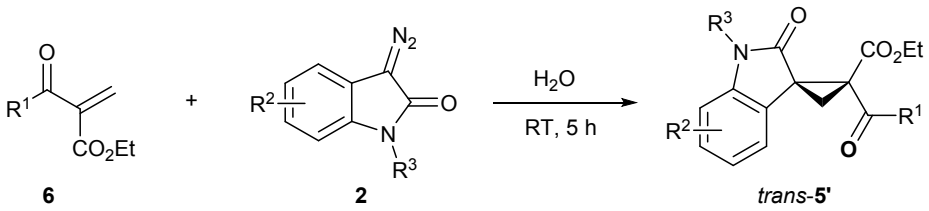
NMR and HRMS data for the product **5d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.47 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 4.15 – 4.02 (m, 2H), 3.37 (s, 3H), 2.70 (d, *J* = 4.8 Hz, 1H), 2.61 (s, 3H), 2.48 (d, *J* = 4.8 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.5, 173.3, 166.2, 142.6, 136.3, 133.1, 132.4, 128.8, 128.3, 125.0, 122.1, 120.8, 120.0, 62.4, 48.4, 38.4, 30.1, 24.8, 19.2, 13.9.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{22}H_{21}NO_4Na^+$: 386.1363, found: 386.1366.

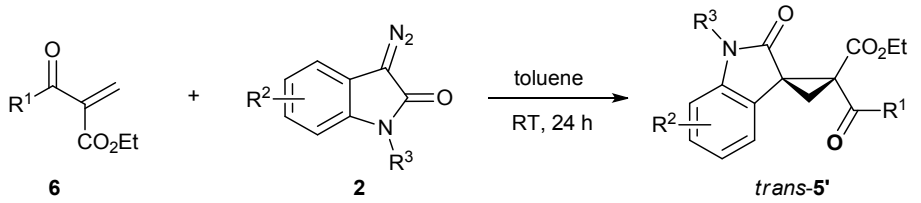
5. General Procedure for the Preparation of Cyclopropanes 5'

*Proceduer A: the "on water" cyclopropanation of 3-diazooxindoles **2** with alkenes **6***



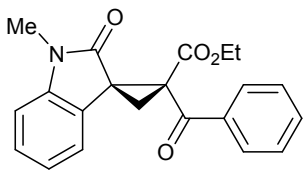
A glass tube was charged with alkene **6** (0.15 mmol) and 3-diazooxindole **2** (0.10 mmol) in water (1 mL). Unless otherwise noted, the mixture was stirred at room temperature for 5 hours. Then the mixture was extracted with ethyl acetate (10 mL × 2), and the organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 3/1) to afford the corresponding cyclopropane **5a'–5l'** in 83–99% yields.

*Proceduer B: the cyclopropanation of 3-diazooxindoles **2** with alkenes **6** in toluene*



A glass tube was charged with alkenes **6** (0.15 mmol) and 3-diazooxindole **2** (0.10 mmol) in toluene (1 mL). Unless otherwise noted, the mixture was stirred at room temperature for 24 hours. Unless otherwise noted, when the reaction was completed (by TLC), the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to 3/1) to afford the corresponding cyclopropane **5a'–5l'** in 71–89% yields.

ethyl-2-benzoyl-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5a'



Prepared according to the general procedure A to afford the diastereoisomers (34.6 mg) in 99% yield as white solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (30.0 mg) in 86% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.

The desired major isomer **5a'** was isolated by column chromatography as white solid (m. p. = 153 – 158 °C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

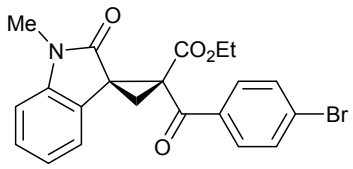
NMR and HRMS data for the product **5a'**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 6.6 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.81 (t, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 7.2 Hz, 1H), 4.21 – 4.12 (m, 2H), 3.33 (s, 3H), 2.67 (d, *J* = 5.4 Hz, 1H), 2.41 (d, *J* = 5.4 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.7, 172.7, 165.2, 144.0, 135.5, 133.8, 130.1, 128.18, 128.16, 125.1, 122.2, 121.3, 108.4, 62.4, 50.0, 36.7, 26.8, 23.7, 13.8.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{21}H_{19}NO_4Na^+$: 372.1206, found: 372.1210.

ethyl-2-(4-bromobenzoyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5b'



Prepared according to the general procedure A to afford the diastereoisomers (39.8 mg) in 93% yield as white solid. The diastereomeric ratio was determined to be 4:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (35.1 mg) in 82% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.

The desired major isomer **5b'** was isolated by column chromatography as white solid (m. p. = 179 – 181 °C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

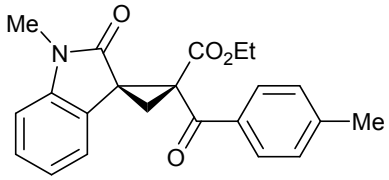
NMR and HRMS data for the product **5b'**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.67 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.80 (t, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.2 Hz, 1H), 4.24 – 4.11 (m, 2H), 3.34 (s, 3H), 2.64 (d, *J* = 5.4 Hz, 1H), 2.42 (d, *J* = 5.4 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.0, 172.3, 164.9, 143.8, 134.1, 131.6, 131.4, 129.1, 128.4, 124.7, 122.3, 121.0, 108.5, 62.5, 49.9, 36.7, 26.9, 23.2, 13.8.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{21}H_{18}{}^{79}BrNO_4Na^+$: 450.0311, found: 450.0312; calculated for $C_{21}H_{18}{}^{81}BrNO_4Na^+$: 452.0291, found: 452.0296.

ethyl-1'-methyl-2-(4-methylbenzoyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5c'



Prepared according to the general procedure A to afford the diastereoisomers (34.5 mg) in 95% yield as white solid. The diastereomeric ratio was determined to be 4:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (29.0 mg) in 80% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.

The desired major isomer **5c'** was isolated by column chromatography as white solid (m. p. = 141 – 144 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

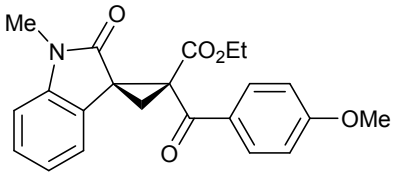
NMR and HRMS data for the product **5c'**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.77 (d, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 9.0 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 4.24 – 4.11 (m, 2H), 3.33 (s, 3H), 2.65 (d, *J* = 4.8 Hz, 1H), 2.38 (d, *J* = 4.8 Hz, 1H), 2.34 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.0, 172.6, 165.2, 144.8, 143.9, 132.8, 130.3, 128.9, 128.1, 125.2, 122.1, 121.3, 108.3, 62.3, 49.9, 36.5, 26.8, 23.9, 21.7, 13.9.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{22}H_{21}NO_4Na^+$: 386.1363, found: 386.1371.

ethyl-2-(4-methoxybenzoyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5d'



Prepared according to the general procedure A to afford the diastereoisomers (37.1 mg) in 98% yield as white solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (33.4 mg) in 88% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.

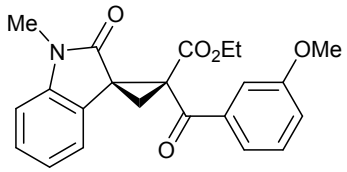
The desired major isomer **5d'** was isolated by column chromatography as white solid (m. p. = 128 – 132 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

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

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.88 (d, *J* = 9.0 Hz, 2H), 7.20 (t, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.82 – 6.76 (m, 3H), 6.49 (d, *J* = 7.8 Hz, 1H), 4.24 – 4.14 (m, 2H), 3.80 (s,

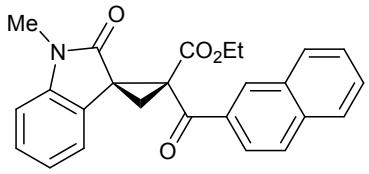
3H), 3.33 (s, 3H), 2.64 (d, *J* = 5.4 Hz, 1H), 2.36 (d, *J* = 5.4 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 188.6, 172.7, 165.3, 164.0, 143.8, 132.7, 128.2, 128.0, 125.3, 122.1, 121.3, 113.4, 108.3, 62.3, 55.4, 49.8, 36.3, 26.8, 24.0, 13.9.
HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calculated for $C_{22}H_{21}NO_5Na^+$: 402.1312, found: 402.1315.

ethyl-2-(3-methoxybenzoyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5e'



Prepared according to the general procedure A to afford the diastereoisomers (33.7 mg) in 89% yield as white solid. The diastereomeric ratio was determined to be 4:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (32.2 mg) in 85% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.
The desired major isomer **5e'** was isolated by column chromatography as white solid (m. p. = 148 – 151 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.
NMR and HRMS data for the product **5e'**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.48 (d, *J* = 7.2 Hz, 1H), 7.38 (s, 1H), 7.25 – 7.20 (m, 2H), 7.04 (dd, *J* = 7.8 Hz, 2.4 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 6.6 Hz, 1H), 4.22 – 4.14 (m, 2H), 3.76 (s, 3H), 3.32 (s, 3H), 2.68 (d, *J* = 5.4 Hz, 1H), 2.39 (d, *J* = 5.4 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.2, 172.5, 165.0, 159.3, 143.9, 136.6, 129.2, 128.2, 125.2, 122.9, 122.2, 121.4, 120.8, 113.6, 108.3, 62.4, 55.2, 50.0, 36.6, 26.8, 23.9, 13.9.
HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calculated for $C_{22}H_{21}NO_5Na^+$: 402.1312, found: 402.1316.

ethyl-2-(2-naphthoyl)-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5f'



Prepared according to the general procedure A to afford the diastereoisomers (38.3 mg) in 96% yield as white solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (31.1 mg) in 78% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude

^{1}H NMR analysis.

The desired major isomer **5f'** was isolated by column chromatography as white solid (m. p. = 165 – 169 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

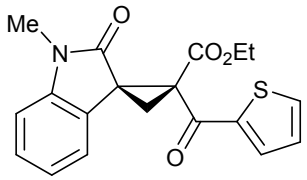
NMR and HRMS data for the product **5f'**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.46 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 8.4 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.78 (t, *J* = 7.8 Hz, 1H), 6.53 (d, *J* = 6.6 Hz, 1H), 4.22 – 4.12 (m, 2H), 3.37 (s, 3H), 2.75 (d, *J* = 5.4 Hz, 1H), 2.46 (d, *J* = 5.4 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.3, 172.6, 165.2, 143.9, 135.7, 132.7, 132.0, 129.9, 128.9, 128.2, 128.0, 127.7, 126.7, 125.1, 125.0, 122.2, 121.4, 108.3, 62.4, 50.1, 36.7, 26.9, 23.9, 13.9.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{21}NO_4Na^+$: 422.1363, found: 422.1359.

ethyl-1'-methyl-2'-oxo-2-(thiophene-2-carbonyl)spiro[cyclopropane-1,3'-indoline]-2-carboxylate 5g'



Prepared according to the general procedure A to afford the diastereoisomers (34.8 mg) in 98% yield as white solid. The diastereomeric ratio was determined to be 2:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (25.2 mg) in 71% yield as white solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis. A mixture of diastereoisomers (m. p. = 128 – 132 ^{o}C) cannot be separated by column chromatography.

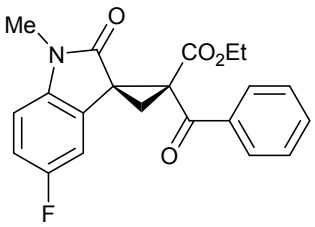
NMR and HRMS data for the product **5g'**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.77 (d, *J* = 4.2 Hz, 1H), 7.61 (d, *J* = 4.8 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 4.8 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.82 (t, *J* = 7.8 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 4.29 – 4.19 (m, 2H), 3.31 (s, 3H), 2.64 (d, *J* = 4.8 Hz, 1H), 2.38 (d, *J* = 6.0 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 182.4, 172.6, 165.0, 143.8, 142.2, 136.4, 135.5, 128.2, 128.1, 125.1, 122.1, 121.1, 108.3, 62.5, 50.3, 36.2, 26.8, 23.9, 13.9.

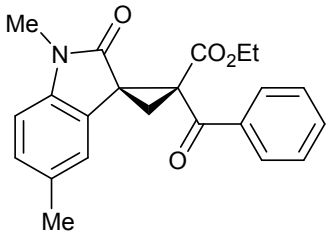
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{19}H_{17}NO_4SNa^+$: 378.0770, found: 378.0772.

ethyl-2-benzoyl-5'-fluoro-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5h'



Prepared according to the general procedure A except the reaction time for 24 hours, to afford the diastereoisomers (30.5 mg) in 83% yield as white solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B except the reaction time for 48 hours, to afford the diastereoisomers (27.9 mg) in 76% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.
The desired major isomer **5h'** was isolated by column chromatography as white solid (m. p. = 190 – 192 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.
NMR and HRMS data for the product **5h'**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.89 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 6.92 (t, *J* = 9.0 Hz, 1H), 6.81 (dd, *J* = 8.4, 4.2 Hz, 1H), 6.28 (dd, *J* = 8.4, 3.0 Hz, 1H), 4.22 – 4.12 (m, 2H), 3.31 (s, 3H), 2.69 (d, *J* = 5.4 Hz, 1H), 2.38 (d, *J* = 4.8 Hz, 1H), 1.18 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.1, 172.3, 164.9, 158.6 (d, J_{C-F} = 238.4 Hz), 139.9, 135.2, 133.9, 128.3, 126.8 (d, J_{C-F} = 8.7 Hz), 114.5 (d, J_{C-F} = 23.0 Hz), 109.8 (d, J_{C-F} = 25.8 Hz), 108.8 (d, J_{C-F} = 8.6 Hz), 62.5, 50.2, 36.7, 27.0, 24.3, 13.8.
^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -120.2.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{21}H_{18}FNO_4Na^+$: 390.1112, found: 390.1113.

ethyl-2-benzoyl-1',5'-dimethyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5i'



Prepared according to the general procedure A to afford the diastereoisomers (33.4 mg) in 92% yield as white solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (29.8 mg) in 82% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude

^{1}H NMR analysis.

The desired major isomer **5i'** was isolated by column chromatography as white solid (m. p. = 169 – 172 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

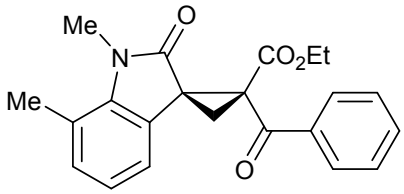
NMR and HRMS data for the product **5i'**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 6.6 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.30 (s, 1H), 4.23 – 4.10 (m, 2H), 3.31 (s, 3H), 2.64 (d, *J* = 4.8 Hz, 1H), 2.37 (d, *J* = 4.8 Hz, 1H), 2.11 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.7, 172.5, 165.1, 141.6, 135.5, 133.6, 131.7, 130.1, 128.5, 128.1, 125.1, 122.1, 108.1, 62.3, 49.9, 36.7, 26.9, 23.6, 21.0, 13.8.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{22}H_{21}NO_4Na^+$: 386.1363, found: 386.1365.

ethyl-2-benzoyl-1',7'-dimethyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5j'



Prepared according to the general procedure A to afford the diastereoisomers (33.8 mg) in 93% yield as white solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (31.6 mg) in 87% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.

The desired major isomer **5j'** was isolated by column chromatography as white solid (m. p. = 156 – 159 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

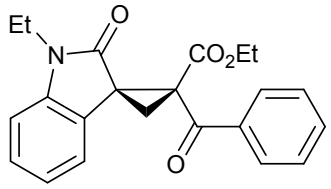
NMR and HRMS data for the product **5j'**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.67 (t, *J* = 7.8 Hz, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 4.23 – 4.11 (m, 2H), 3.61 (s, 3H), 2.66 (d, *J* = 4.8 Hz, 1H), 2.60 (s, 3H), 2.34 (d, *J* = 5.4 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.6, 173.3, 165.1, 141.7, 135.4, 133.7, 131.9, 130.1, 128.2, 125.6, 122.0, 120.0, 119.2, 62.4, 50.3, 36.4, 30.2, 24.1, 19.1, 13.8.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{22}H_{21}NO_4Na^+$: 386.1363, found: 386.1364.

ethyl-2-benzoyl-1'-ethyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5k'



Prepared according to the general procedure A to afford the diastereoisomers (35.9 mg) in 99% yield as white solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (32.3 mg) in 89% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.

The desired major isomer **5k'** was isolated by column chromatography as white solid (m. p. = 95 – 99 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

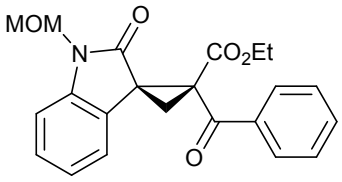
NMR and HRMS data for the product **5k'**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 7.2 Hz, 1H), 4.19 – 4.13 (m, 2H), 3.93 – 3.84 (m, 2H), 2.68 (d, *J* = 5.4 Hz, 1H), 2.40 (d, *J* = 6.0 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.7, 172.1, 165.1, 142.9, 135.4, 133.6, 130.1, 128.12, 128.08, 125.3, 121.9, 121.5, 108.4, 62.3, 50.1, 36.7, 35.3, 23.5, 13.8, 12.9.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{22}H_{21}NO_4Na^+$: 386.1363, found: 386.1367.

ethyl-2-benzoyl-1'-(methoxymethyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate 5l'



Prepared according to the general procedure A to afford the diastereoisomers (35.6 mg) in 94% yield as white solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H NMR analysis. Prepared according to the general procedure B to afford the diastereoisomers (29.2 mg) in 77% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.

The desired major isomer **5l'** was isolated by column chromatography as white solid (m. p. = 89 – 94 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

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

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 5.27 (d, *J* = 10.8 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 4.15 (q, *J* = 6.6

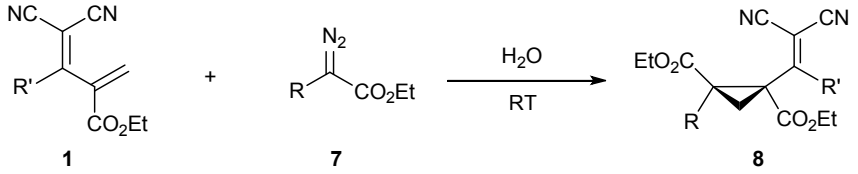
Hz, 2H), 3.41 (s, 3H), 2.70 (d, *J* = 5.4 Hz, 1H), 2.46 (d, *J* = 6.0 Hz, 1H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.3, 173.3, 165.0, 142.1, 135.3, 133.7, 130.0, 128.3, 128.1, 124.6, 122.7, 121.4, 109.8, 71.6, 62.4, 56.3, 50.5, 36.8, 23.7, 13.8.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{22}H_{21}NO_5Na^+$: 402.1312, found:402.1317 .

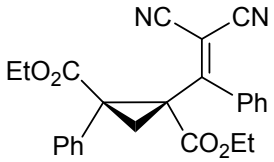
6. The On-Water Reacton with Other Kinds of Diazo Compounds and Alkenes

*6.1 General procedure for the cyclopropanation of alkene **1** and other diazo compounds 7*



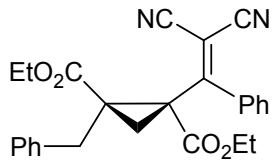
A glass tube was charged with diene **1** (0.15 mmol) and diazo compound **7** (0.10 mmol) in water (1 mL). The mixture was stirred at room temperature. After 5 to 12 hours the mixture was extracted with ethyl acetate (10 mL × 2). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to 6/1) to afford the corresponding vinylcyclopropane **8a**–**8e** in 37–85% yields.

diethyl-1-(2,2-dicyano-1-phenylvinyl)-2-phenylcyclopropane-1,2-dicarboxylate 8a



Prepared according to the general procedure to afford **8a** (24.7 mg) in 60% yield as colorless semisolid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **8a**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.40 (t, *J* = 7.2 Hz, 1H), 7.32 – 7.26 (m, 5H), 7.26 – 7.20 (m, 2H), 6.80 (d, *J* = 7.2 Hz, 2H), 4.45 – 4.30 (m, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.59 (d, *J* = 6.6 Hz, 1H), 1.99 – 1.87 (m, 1H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.9, 167.8, 167.6, 135.1, 131.6, 131.2, 129.1, 129.0, 128.6, 127.8, 112.6, 112.5, 91.9, 63.2, 62.1, 47.6, 40.9, 26.2, 14.0, 13.9.
HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{25}H_{22}N_2O_4Na^+$: 437.1472, found: 437.1475.

diethyl-1-benzyl-2-(2,2-dicyano-1-phenylvinyl)cyclopropane-1,2-dicarboxylate 8b



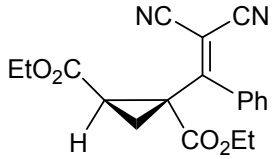
Prepared according to the general procedure to afford **8b** (36.4 mg) in 85% yield as colorless semisolid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.
NMR and HRMS data for the product **8b**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.56 – 7.49 (m, 3H), 7.49 – 7.44 (m, 2H), 7.28 – 7.16

(m, 5H), 4.50 – 4.31 (m, 2H), 4.03 – 3.75 (m, 2H), 3.65 (d, *J* = 14.4 Hz, 1H), 3.15 (d, *J* = 14.4 Hz, 1H), 2.40 – 2.26 (m, 1H), 2.06 – 1.80 (m, 1H), 1.38 (t, *J* = 7.8 Hz, 3H), 1.20 – 0.99 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 173.1, 169.4, 166.8, 138.4, 134.9, 132.0, 128.8, 128.7, 128.6, 128.3, 126.5, 112.9, 112.6, 89.6, 63.5, 62.2, 44.1, 41.7, 32.3, 27.1, 14.1, 13.8.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{26}H_{24}N_2O_4Na^+$: 451.1628, found: 451.1625.

diethyl-1-(2,2-dicyano-1-phenylvinyl)cyclopropane-1,2-dicarboxylate 8c



Prepared according to the general procedure to afford **8c** (19.6 mg) in 58% yield as colorless oil. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

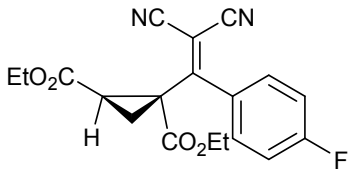
NMR and HRMS data for the product **8c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.74 – 7.69 (m, 2H), 7.60 – 7.55 (m, 1H), 7.54 – 7.50 (m, 2H), 4.40 – 4.24 (m, 2H), 4.24 – 4.10 (m, 2H), 2.49 (dd, *J* = 7.2, 5.4 Hz, 1H), 2.17 (dd, *J* = 9.6, 7.2 Hz, 1H), 1.52 (dd, *J* = 9.6, 5.4 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.6, 167.2, 167.1, 134.0, 132.9, 129.1, 129.0, 112.8, 111.9, 89.2, 63.1, 61.7, 36.6, 32.5, 22.6, 14.0, 14.0.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{19}H_{18}N_2O_4Na^+$: 361.1159, found: 361.1166.

diethyl-1-(2,2-dicyano-1-(4-fluorophenyl)vinyl)cyclopropane-1,2-dicarboxylate 8d



Prepared according to the general procedure to afford **8d** (17.1 mg) in 48% yield as pure yellow oil. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

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

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.76 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 2H), 4.35 – 4.24 (m, 2H), 4.24 – 4.14 (m, 2H), 2.51 (dd, *J* = 8.4, 6.0 Hz, 1H), 2.15 (dd, *J* = 9.0, 7.8 Hz, 1H), 1.55 (dd, *J* = 9.6, 5.4 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

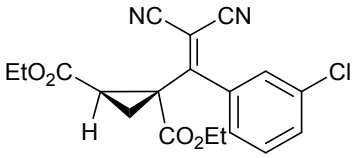
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm):

171.1, 167.1, 167.0, 165.1 (d, J_{C-F} = 255.6 Hz), 131.8 (d, J_{C-F} = 8.6 Hz), 130.1 (d, J_{C-F} = 2.9 Hz), 116.6 (d, J_{C-F} = 21.5 Hz), 112.8, 111.8, 88.9, 63.2, 61.8, 36.5, 32.4, 22.7, 14.04, 14.02.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -103.7.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{19}H_{17}FN_2O_4Na^+$: 379.1065, found: 379.1063.

diethyl-1-(1-(3-chlorophenyl)-2,2-dicyanovinyl)cyclopropane-1,2-dicarboxylate 8e



Prepared according to the general procedure to afford **8e** (13.8 mg) in 37% yield as yellow oil. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis.

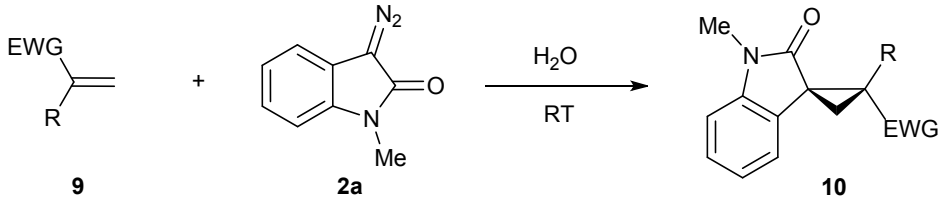
NMR and HRMS data for the product **8e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.70 (s, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 10.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 4.36 – 4.25 (m, 2H), 4.24 – 4.15 (m, 2H), 2.51 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.14 (dd, *J* = 10.2, 7.8 Hz, 1H), 1.56 (dd, *J* = 10.2, 6.0 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.9, 166.9, 166.8, 135.6, 135.5, 132.7, 130.4, 129.0, 127.0, 112.3, 111.5, 90.5, 63.2, 61.9, 36.4, 32.5, 22.7, 14.1, 14.0.

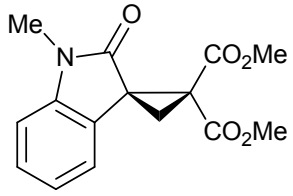
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{19}H_{17}{}^{35}ClN_2O_4Na^+$: 395.0769, found: 395.0772; calculated for $C_{19}H_{17}{}^{35}ClN_2O_4Na^+$: 397.0740, found: 397.0746.

6.2 General Procedure for the cyclopropanation of other alkene ***9*** *and 3-diazooxindole* ***2a***



A glass tube was charged with other alkenes **9** (0.15 mmol) and 3-diazooxindole **2a** (17.3 mg, 0.10 mmol) in water (1 mL). The mixture was stirred at room temperature. After 5 hours, the mixture was extracted with ethyl acetate (10 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 6/1) to afford the corresponding cyclopropane **10a-10c** in 96%-99% yields.

dimethyl-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,2-dicarboxylate 10a



Prepared according to the general procedure to afford **10a** (27.7 mg, m. p. = 149-150 °C) in 96% yield as white solid.

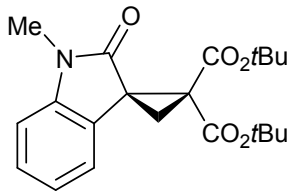
NMR and HRMS data for the product **10a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.34 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.25 (s, 3H), 2.48 (d, *J* = 4.8 Hz, 1H), 2.45 (d, *J* = 5.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.5, 166.0, 165.8, 144.7, 128.5, 124.3, 123.1, 122.3, 108.3, 53.3, 53.1, 45.3, 38.0, 26.7, 24.4.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{15}H_{15}NO_5Na^+$: 312.0842, found: 312.0852.

di-tert-butyl-1'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,2-dicarboxylate 10b



Prepared according to the general procedure to afford **10b** (36.9 mg, m. p. = 127-130 °C) in 99% yield as white solid.

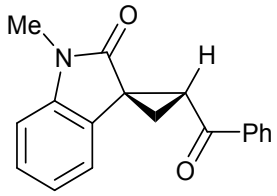
NMR and HRMS data for the product **10b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.36 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.26 (s, 3H), 2.38 (d, *J* = 4.8 Hz, 1H), 2.29 (d, *J* = 4.8 Hz, 1H), 1.46 (s, 9H), 1.40 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.8, 164.8, 164.30, 144.8, 128.0, 125.0, 123.2, 121.8, 107.9, 83.2, 81.9, 47.3, 37.5, 28.0, 27.8, 26.5, 24.0.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{21}H_{27}NO_5Na^+$: 369.1781, found: 396.1783.

2-benzoyl-1'-methylspiro[cyclopropane-1,3'-indolin]-2'-one 10c



Prepared according to the general procedure to afford the diastereoisomers (27.4 mg) in 99% yield as white solid. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H NMR analysis.

The desired major isomer **10c** was isolated by column chromatography as white solid (m. p. = 140–141 ^{o}C) for further ^{1}H NMR, ^{13}C NMR and HRMS analysis.

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

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.88 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 9.0 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.68 (t, *J* = 7.8 Hz, 1H), 3.33 (s, 3H), 2.55 (dd, *J* = 7.2, 4.2 Hz, 1H), 2.15 (dd, *J* = 8.4, 4.2 Hz, 1H).

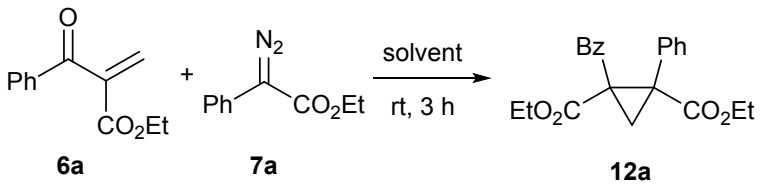
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 193.5, 174.9, 143.9, 137.2, 133.4, 128.6, 128.3, 127.6, 125.6, 122.4, 122.3, 108.0, 36.4, 36.0, 26.8, 20.5.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calculated for $C_{18}H_{15}NO_2Na^+$: 300.0995, found: 300.1002.

*6.3 The cyclopropanation of alkene **6a** and diazo compounds **7a***

As shown in Table S3, 2-benzoylacrylate **6a** could rapidly react with α-phenyl diazoacetate **7a** by using water as the solvent, to afford moderate yield and poor diastereoselectivity, while worse results were observed in the reaction using organic solvents.

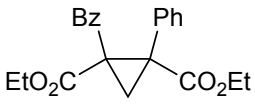
Table S3. Optimization of the cyclopropanation of alkene **6a** and diazo compounds **7a**[a]



Entry	Solvent	D. r.[b]	Yield (%)[c]
1	H_2O	1:1	48
2	MeCN	1:1	5
3	DCM	1:1	8
4	$CHCl_3$	1:1	12
5	THF	1:1	10
6	toluene	1:1	22

[a] Reactions were performed with 0.15 mmol of **6a** and 0.1 mmol of **7a**, in 1 mL solvent at room temperature for 3 hours. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yields of **12a**.

diethyl 1-benzoyl-2-phenylcyclopropane-1,2-dicarboxylate 12a



A glass tube was charged with other alkenes **6a** (0.15 mmol) and diazo compounds **7a** (0.10 mmol) in water (1 mL). The mixture was stirred at room temperature. After 3 hours, the mixture was extracted with ethyl acetate (10 mL × 2). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to 10/1) to afford the corresponding cyclopropane **12a** (17.6 mg) in 48% yields as colorless oil. The diastereomeric ratio was determined to be 1:1 by crude ^{1}H NMR analysis. The two diastereoisomers cannot be separated by column chromatography, so

the following spectra of NMR and HRMS were referred to the isomer mixture

NMR and HRMS data for the product **12a**:

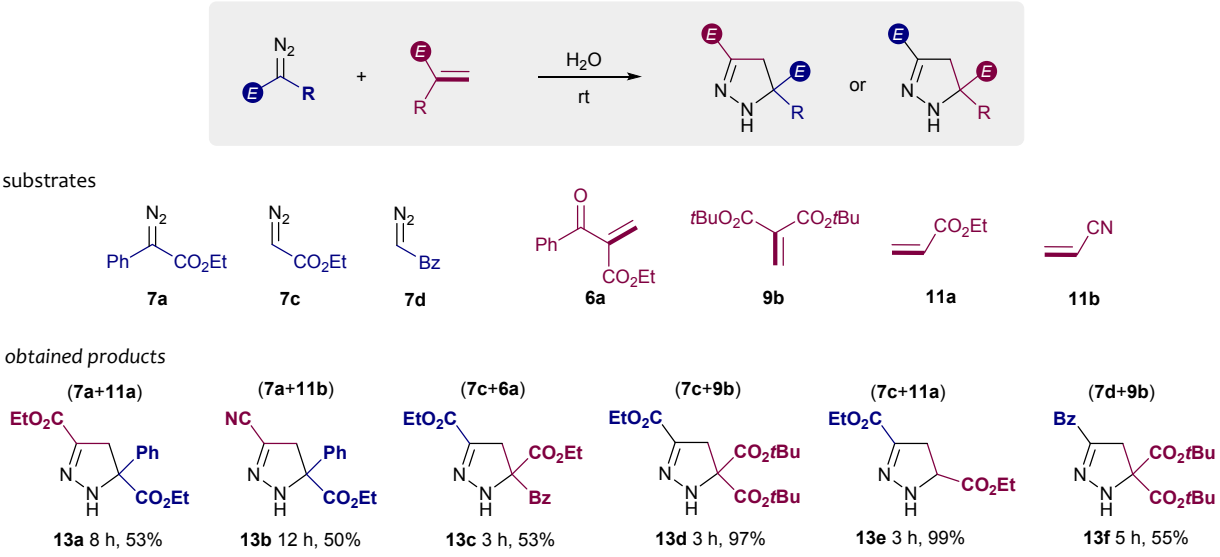
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.03 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.45 (m, 5H), 7.45 – 7.36 (m, 5H), 7.36 – 7.28 (m, 3H), 7.13 – 7.05 (m, 3H), 4.28 (q, *J* = 7.8 Hz, 2H), 4.17 – 4.05 (m, 2H), 4.05 – 3.90 (m, 2H), 3.90 – 3.74 (m, 2H), 2.70 (d, *J* = 4.8 Hz, 1H), 2.61 (d, *J* = 4.8 Hz, 1H), 2.55 (d, *J* = 4.8 Hz, 1H), 2.29 (d, *J* = 5.4 Hz, 1H), 1.34 (t, *J* = 7.8 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 6.6 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.5, 190.9, 169.7, 169.6, 168.9, 166.7, 137.1, 136.1, 134.6, 133.3, 133.0, 131.8, 130.5, 129.7, 129.0, 128.8, 128.6, 128.3, 128.1, 128.03, 128.00, 127.96, 62.04, 61.97, 61.9, 61.7, 46.1, 44.6, 43.8, 41.8, 23.3, 21.4, 14.0, 13.7, 13.60, 13.56.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{22}H_{22}O_5Na^+$: 389.1359, found: 389.1353.

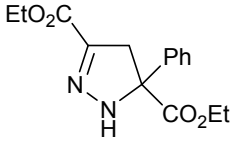
6.4 General procedure for the cyclization of other diazo compounds and other alkenes

However, under the standard conditions, the reactions involving reactants containing a *α*-H atom, such as alkenes (**11a** and **11b**) or diazo species (**7c** or **7d**), proceeded through a classic [3+2] pathway (for example, see: *Org. Biomol. Chem.* 2016, **14**, 8486–8492). In the previous synthesis, such reactions were always performed in the presence of catalysts or pushed by high temperature, so this transformation "on water" might be meaningful for green chemistry.



General Procedure: A glass tube was charged with other alkenes **6a**, **9b** or **11** (0.15 mmol) and diazo compounds **7** (0.10 mmol) in water (1 mL). The mixture was stirred at room temperature. After 3 to 12 hours, the mixture was extracted with ethyl acetate (10 mL × 2). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to 10/1) to afford the corresponding cyclopropane **13a-13f** in 50%-99% yields.

diethyl 5-phenyl-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate 13a



Prepared according to the general procedure to afford **13a** (15.4 mg) in 53% yield as colorless oil.

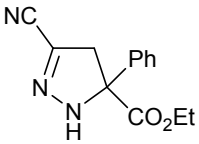
NMR and HRMS data for the product **13a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.41 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.24 (s, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.24 – 4.15 (m, 2H), 4.02 (d, *J* = 18.0 Hz, 1H), 3.10 (d, *J* = 16.8 Hz, 1H), 1.35 (t, *J* = 6.6 Hz, 3H), 1.23 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.4, 161.9, 142.7, 139.3, 128.8, 128.2, 125.5, 75.7, 62.6, 61.3, 42.3, 14.2, 13.9.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{15}H_{18}N_2O_4Na^+$: 313.1159, found: 313.1160.

ethyl 3-cyano-5-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate 13b



Prepared according to the general procedure to afford **13b** (12.2 mg) in 50% yield as colorless oil.

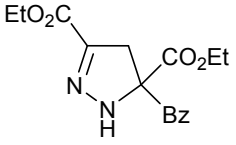
NMR and HRMS data for the product **13b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.42 – 7.32 (m, 6H), 4.29 – 4.20 (m, 2H), 3.95 (d, *J* = 17.4 Hz, 1H), 3.07 (d, *J* = 17.4 Hz, 1H), 1.26 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.5, 138.1, 129.1, 128.7, 125.3, 123.9, 113.7, 75.4, 63.0, 44.2, 13.9.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{13}H_{13}N_3O_2Na^+$: 266.0900, found: 266.0904.

diethyl 5-benzoyl-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate 13c



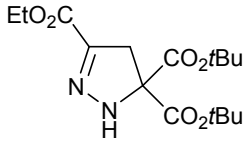
Prepared according to the general procedure to afford **13c** (16.9 mg) in 53% yield as colorless oil.

NMR and HRMS data for the product **13c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.88 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.49

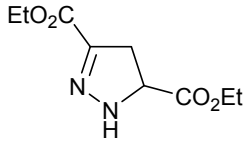
(t, *J* = 7.8 Hz, 2H), 7.39 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.21 (q, *J* = 7.8 Hz, 2H), 4.06 (d, *J* = 17.4 Hz, 1H), 3.51 (d, *J* = 18.0 Hz, 1H), 1.33 (t, *J* = 6.6 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.5, 168.7, 161.5, 143.4, 134.3, 131.7, 129.2, 129.0, 78.6, 63.1, 61.6, 39.4, 14.2, 13.7.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{16}H_{18}N_2O_5Na^+$: 341.1108, found: 341.1112.

3,3-di-tert-butyl 5-ethyl 2,4-dihydro-3H-pyrazole-3,3,5-tricarboxylate 13d



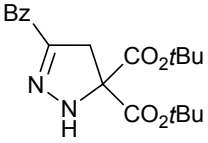
Prepared according to the general procedure to afford **13d** (33.2 mg) in 97% yield as colorless oil.
NMR and HRMS data for the product **13d**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 6.96 (s, 1H), 4.30 (q, *J* = 7.8 Hz, 2H), 3.48 (s, 2H), 1.47 (s, 18H), 1.34 (t, *J* = 7.8 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.1, 161.7, 142.7, 83.7, 76.2, 61.5, 38.4, 27.7, 14.2.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{16}H_{26}N_2O_6Na^+$: 365.1683, found: 365.1687.

diethyl 4,5-dihydro-1H-pyrazole-3,5-dicarboxylate 13e



Prepared according to the general procedure to afford **13e** (21.2 mg) in 99% yield as colorless oil.
NMR and HRMS data for the product **13e**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 6.70 (s, 1H), 4.44 (dd, *J* = 12.6, 5.4 Hz, 1H), 4.29 (q, *J* = 6.6 Hz, 2H), 4.21 (q, *J* = 6.6 Hz, 2H), 3.31 (dd, *J* = 17.4, 5.4 Hz, 1H), 3.17 (dd, *J* = 17.4, 12.0 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 6.6, Hz, 3H), .
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.5, 161.9, 142.9, 62.1, 61.3, 61.3, 34.7, 14.2, 14.1.
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_9H_{14}N_2O_4Na^+$: 237.0846, found: 237.0849.

di-tert-butyl 5-benzoyl-2,4-dihydro-3H-pyrazole-3,3-dicarboxylate 13f



Prepared according to the general procedure to afford **13f** (20.6 mg) in 55% yield as colorless oil.

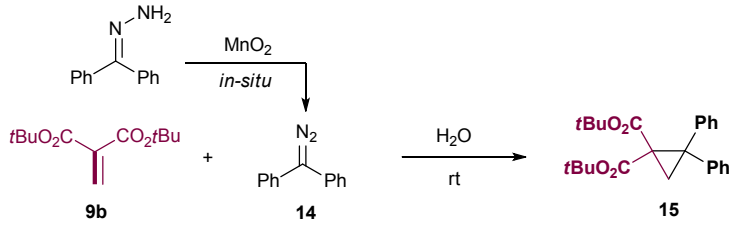
NMR and HRMS data for the product **13f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.12 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.17 (s, 1H), 3.64 (s, 2H), 1.49 (s, 18H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 187.2, 167.2, 149.9, 136.5, 132.7, 130.1, 128.1, 83.7, 75.5, 38.5, 27.8.

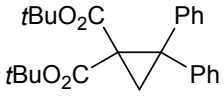
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{20}H_{26}N_2O_5Na^+$: 397.1734, found: 397.1736.

6.5 General procedure for the cyclopropanation of diphenyldiazomethane with alkenes



Benzophenone hydrazone (98.3 mg, 0.50 mmol), anhydrous $MgSO_4$ (43.8 mg), and 1.0 mL DCM was cooled to 0 °C. To this rapidly stirring mixture was added activated MnO_2 (152 mg, 0.70 mmol) in one portion. The reaction mixture was warmed to room temperature and kept stirring for 1 h, the solid was filtered off and washed with DCM. After removal of the solvent under reduced pressure quickly, 1.0 mL water and the alkene **9b** (22.8 mg, 0.10 mmol) was added. After another 16 h stirring, the mixture was extracted with ethyl acetate (10 mL × 2). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 to 30/1) to afford **15** (7.1 mg, m. p. = 132 – 135 °C) in 18% yield as white solid.

di-tert-butyl 2,2-diphenylcyclopropane-1,1-dicarboxylate 15



NMR and HRMS data for the product **15**:

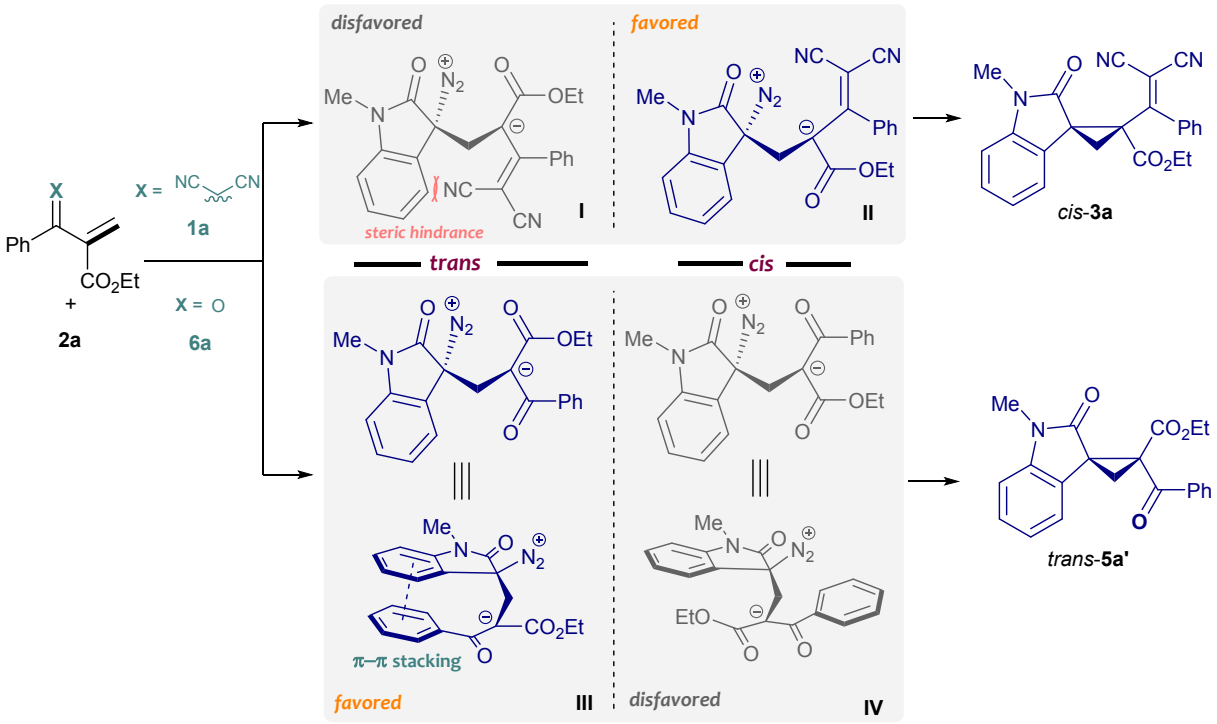
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.43 (d, *J* = 7.8 Hz, 4H), 7.24 (t, *J* = 7.8 Hz, 4H), 7.16 (t, *J* = 6.6 Hz, 2H), 2.33 (s, 2H), 1.21 (s, 18H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.4, 140.6, 129.3, 128.1, 126.9, 81.3, 45.8, 43.3, 27.6, 22.8.

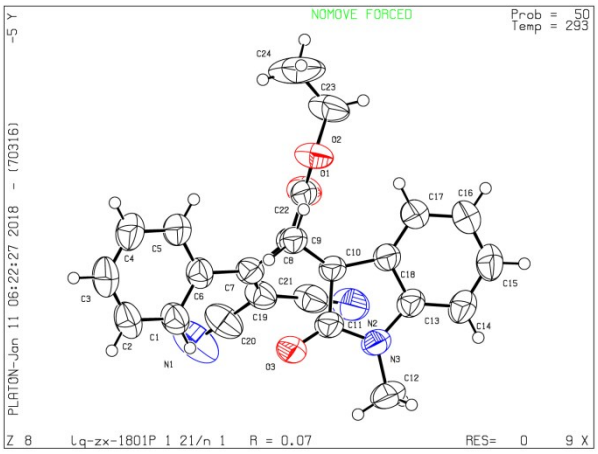
HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calculated for $C_{25}H_{30}O_4Na^+$: 417.2036, found: 417.2041.

7. Proposed Rationale for the Diastereoselectivity

As illustrated in the following scheme, the rationalization of the diastereoselectivity was reasonably proposed. Firstly, the nucleophilic addition of diazo substrate **2a** to the electron-deficient terminal alkenes **1a** or **6a** gives the similar betaine species. The key step is the subsequent intramolecular substitution reaction, which would determine the diastereoselectivity and give the products with *trans* or *cis* configuration (*cis*-**3a** and *trans*-**5a`** shown in the following cartoons). When X was malononitrile moiety (**1a**), the steric hindrance between the bulky malononitrile and phenyl group on the oxindole framework makes the transition state (TS) **I** disfavored and hinders the *trans*-selective reaction pathway, thereby delivering the corresponding product *cis*-**3a** through the less sterically hindered TS **II**. On the other hand, when X was changed to an oxygen atom (**6a**), the impact of the steric hindrance on the key intermediate is significantly reduced so that the steric effect could no longer determine the stereoselectivity; instead, a π-π stacking interaction between the two phenyl moieties might stabilize the corresponding intermediate **III**, favoring the *trans*-selective reaction pathway to give the observed *trans*-**5a`** as the major cyclopropane product.



8. Crystal Data and Structure Refinement for the Representative Product 3a and 5a'



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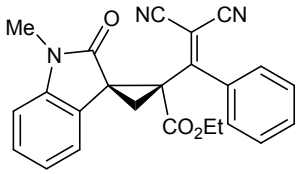
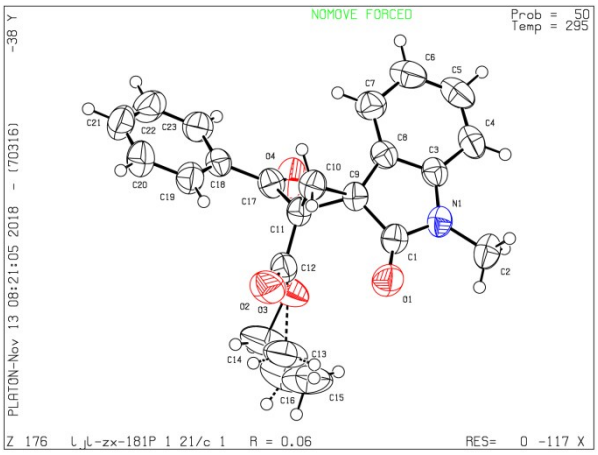


3a
CCDC 1882011

Identification code	**3a**
Empirical formula	$C_{24}H_{19}N_3O_3$
Formula weight	397.42
Temperature/K	293.06(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.6825(10)
b/Å	10.7919(5)
c/Å	14.7575(12)
α/°	90
β/°	108.476(8)
γ/°	90
Volume/Å^3	2066.8(3)
Z	4
ρ_{calc}g/cm^3	1.277
μ/mm^{-1}	0.697
F(000)	832.0
Crystal size/mm^3	0.6 × 0.5 × 0.4
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.35 to 145.394
Index ranges	$-16 \le h \le 14$, $-8 \le k \le 13$, $-17 \le l \le 18$
Reflections collected	11754
Independent reflections	4039 [R_{int} = 0.0456, R_{sigma} = 0.0296]
Data/restraints/parameters	4039/0/273
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0709, wR_2 = 0.1951
Final R indexes [all data]	R_1 = 0.0817, wR_2 = 0.2150
Largest diff. peak/hole / e Å^{-3}	0.27/-0.39



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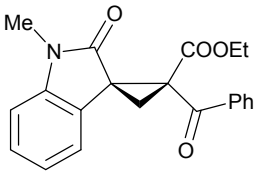


5a'
CCDC 1880418

Identification code	**5a'**
Empirical formula	$C_{21}H_{19}NO_4$
Formula weight	349.37
Temperature/K	295.3(4)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.5364(3)
b/Å	20.5621(11)
c/Å	11.4782(5)
α/°	90
β/°	94.877(4)
γ/°	90
Volume/Å^3	1772.25(14)
Z	4
ρ_{calc}g/cm^3	1.309
μ/mm^{-1}	0.742
F(000)	736.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.6 to 146.416
Index ranges	$-9 \le h \le 5$, $-25 \le k \le 24$, $-14 \le l \le 13$
Reflections collected	9024
Independent reflections	3393 [R_{int} = 0.0318, R_{sigma} = 0.0324]
Data/restraints/parameters	3393/0/258
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0568, wR_2 = 0.1572
Final R indexes [all data]	R_1 = 0.0739, wR_2 = 0.1776
Largest diff. peak/hole / e Å^{-3}	0.26/-0.19

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.

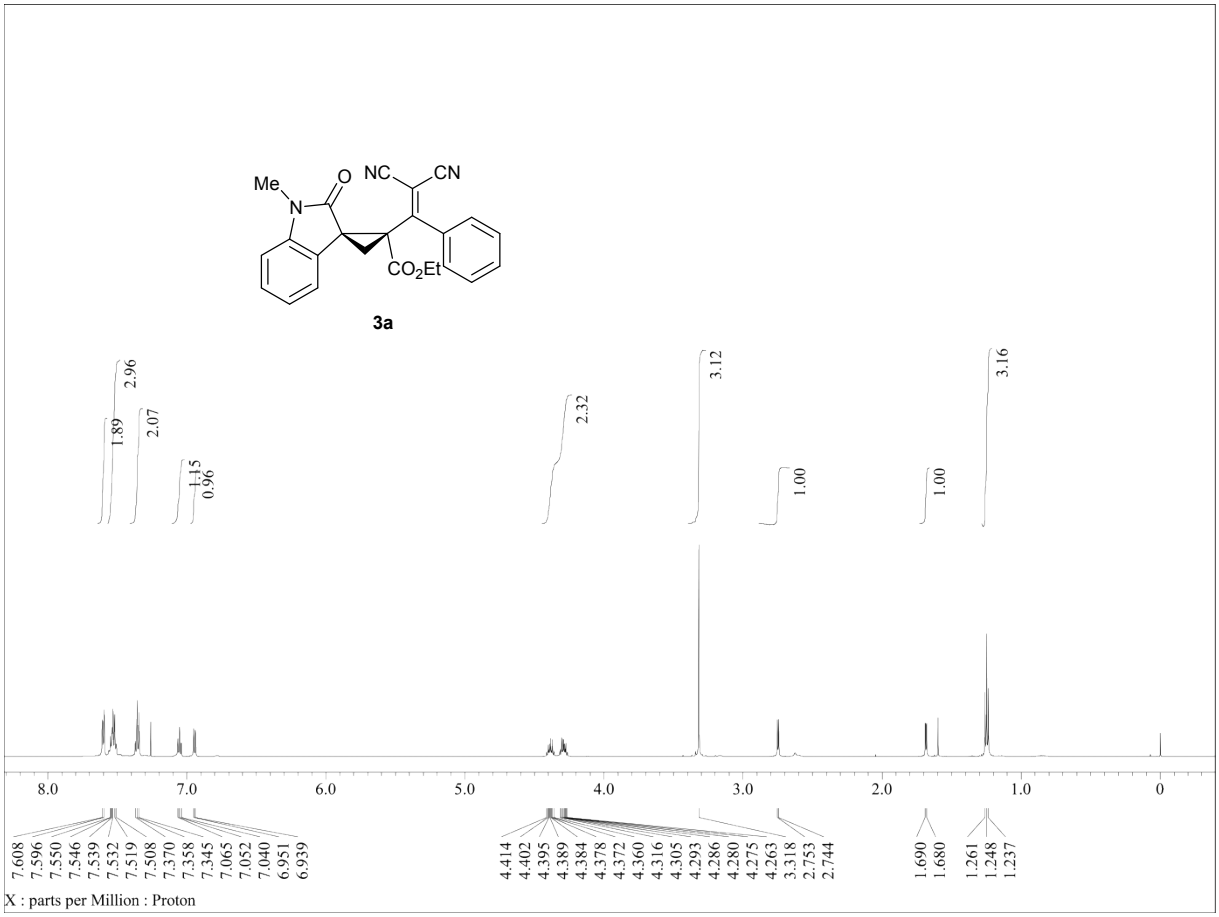
2 X. Jiang, D. Fu, X. Shi, S. Wang, R. Wang, *Chem. Commun.* 2011, **47**, 8289.

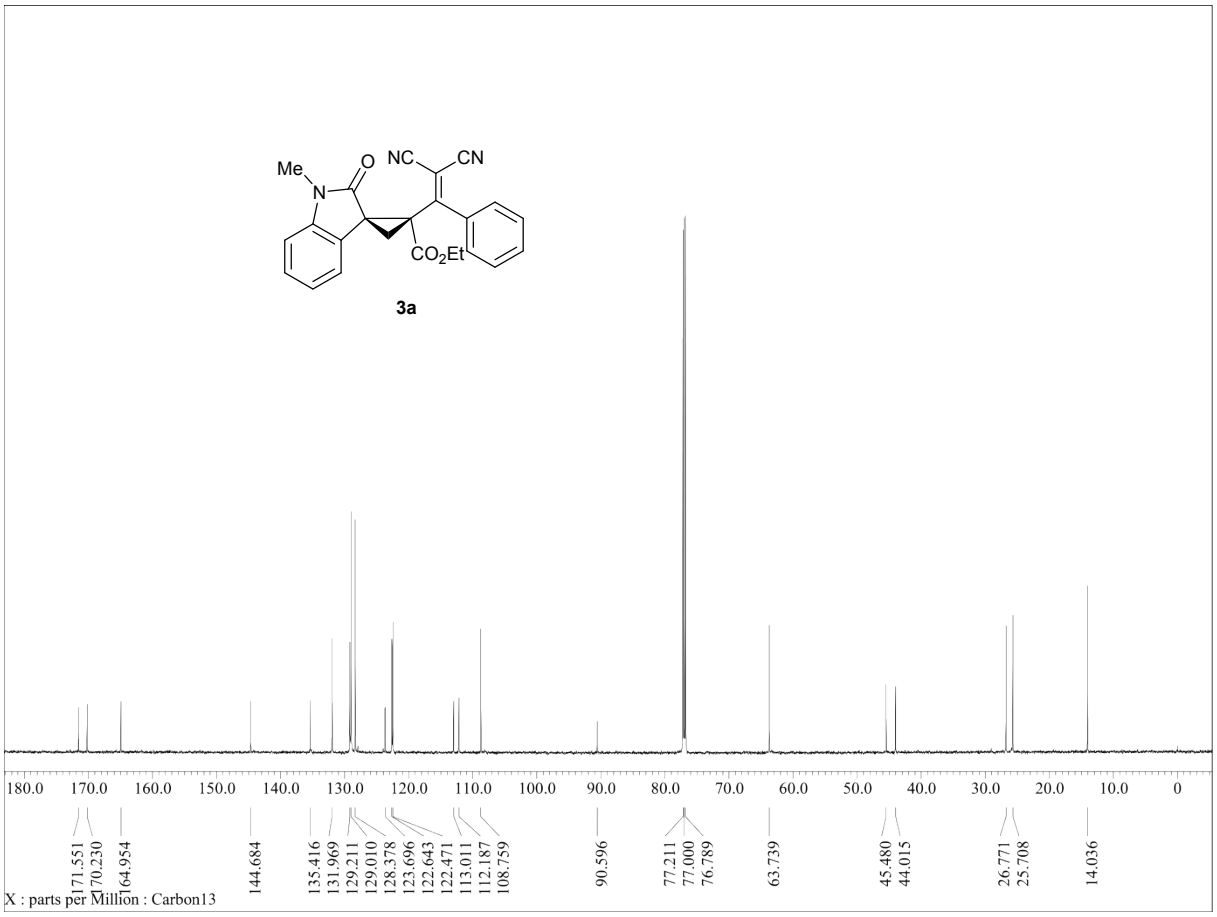
3 (a) H. Song, J. Yang, W. Chen and Y. Qin, *Org. Lett.* 2006, **8**, 6011; (b) C. Marti and E. M. Carreira, *J. Am. Chem. Soc.* 2005, **127**, 11505; (c) S. Muthusamy, C. Gunanathan and M. Nethaji, *J. Org. Chem.* 2004, **69**, 5631.

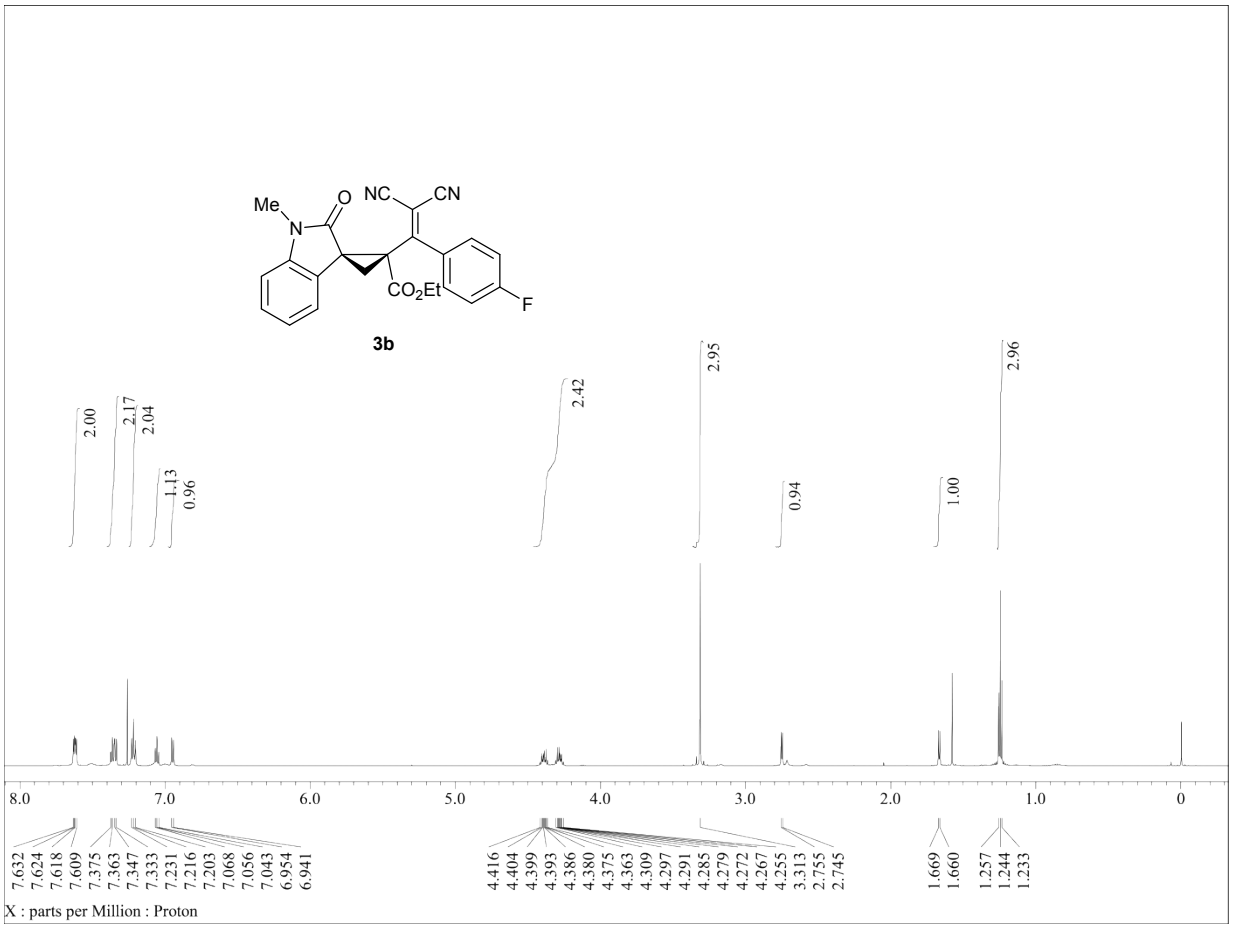
4 A. Bugarin, K. D. Jones and B. T. Connell, *Chem. Commun.* 2010, **46**, 1715.

5 (a) D. Bélanger, X. Tong, S. Soumaré, Y. L. Dory and Y. Zhao, *Chem. Eur. J.* 2009, **15**, 4428; (b) S.-F. Zhu, X.-G. Song, Y. Li, Y. Cai and Q.-L. Zhou, *J. Am. Chem. Soc.* 2010, **132**, 16374.

10. NMR Spectra



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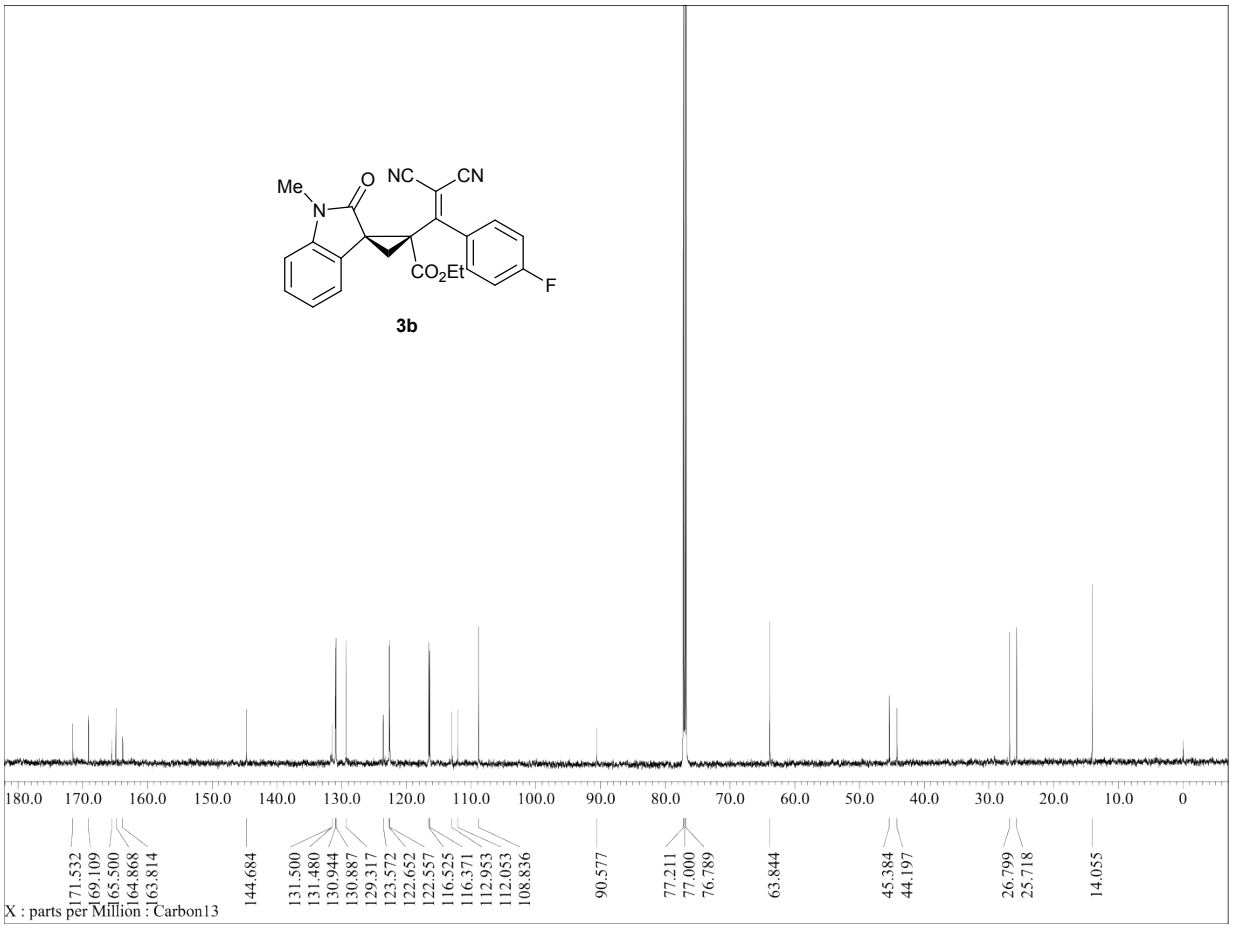
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116.371
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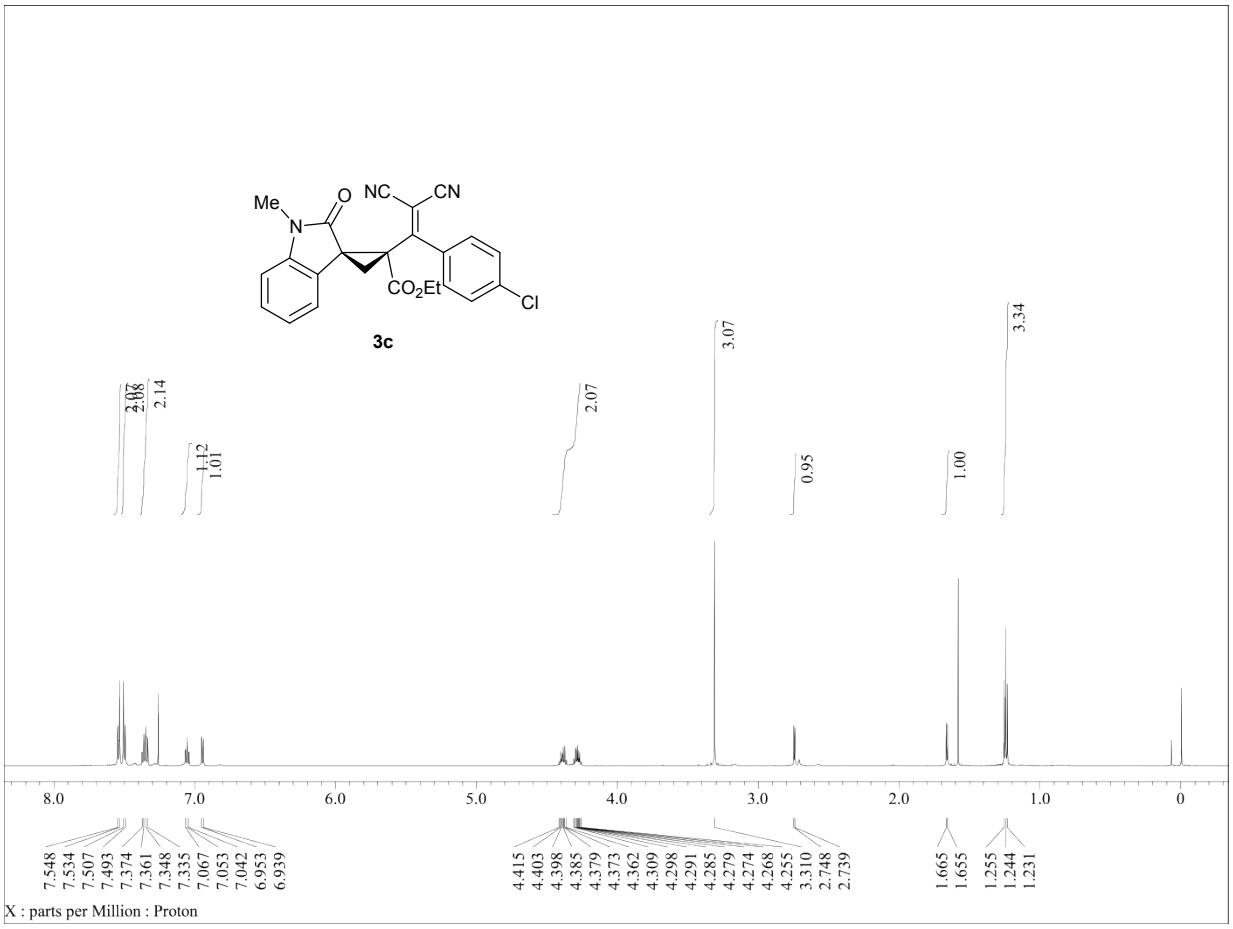
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7.0
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5.0
4.0
3.0
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1.0
0
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7.335
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6.953
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4.403
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4.291
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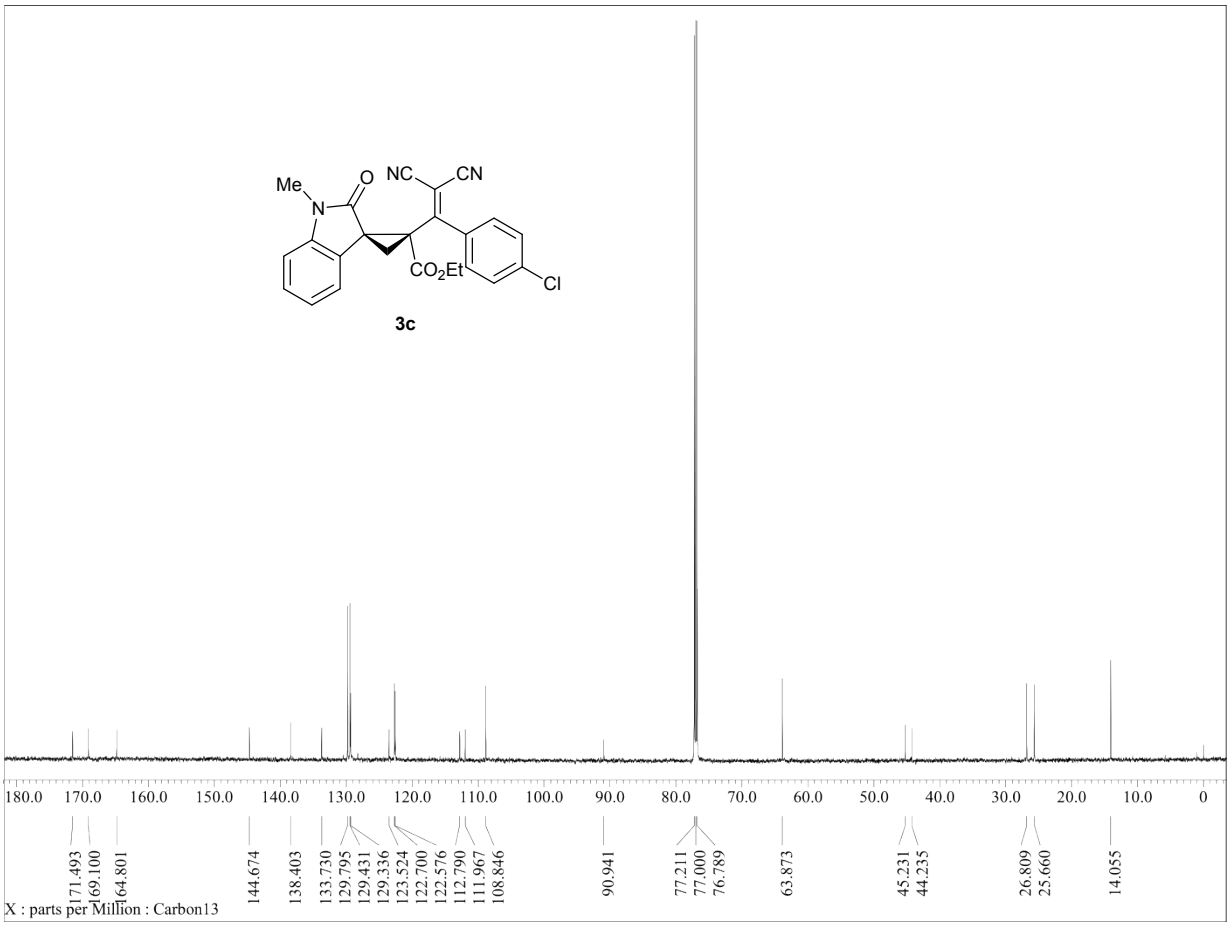
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129.431
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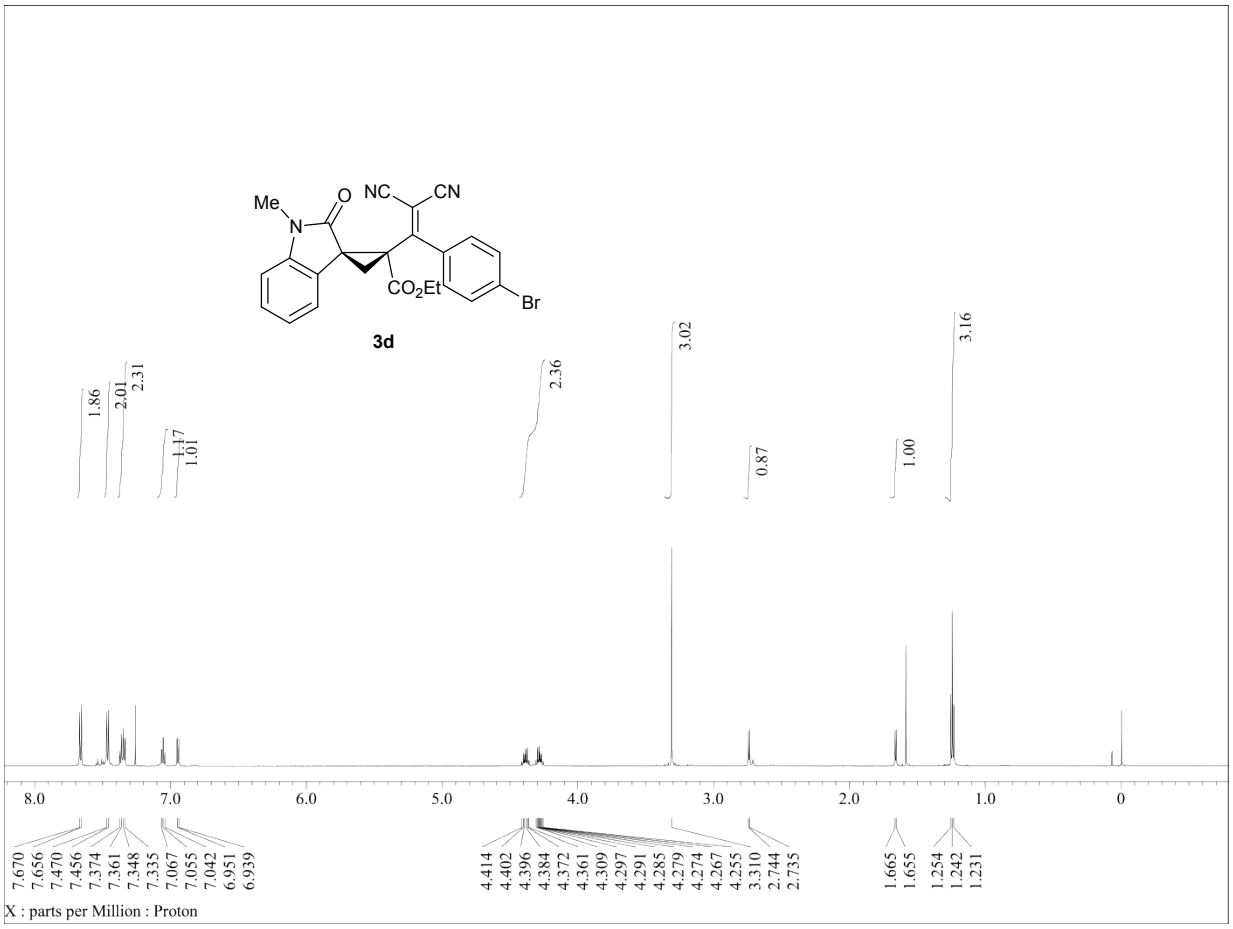
X : parts per Million : Carbon13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1.00
3.16
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.656
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4.402
4.396
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4.372
4.361
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4.297
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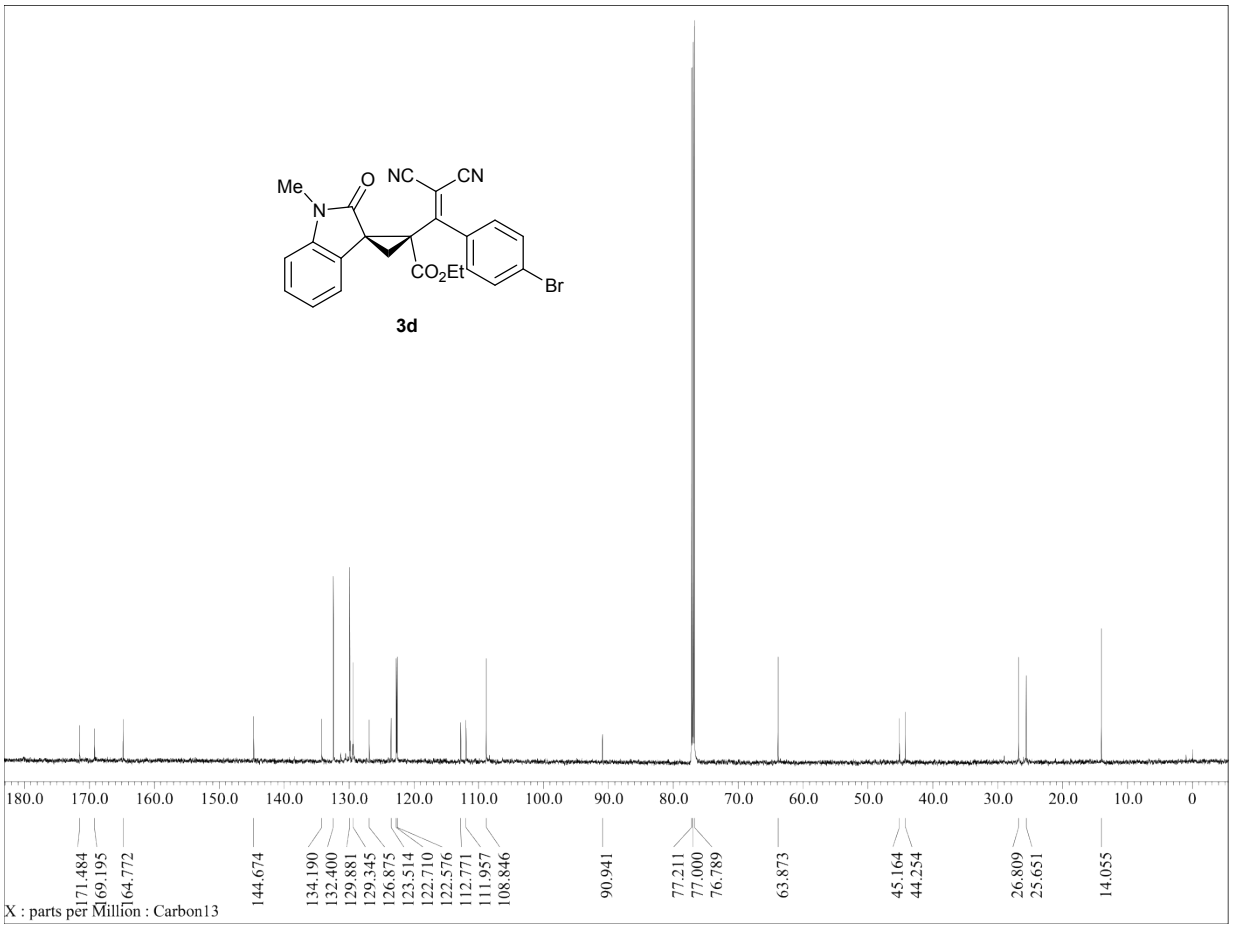
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110.0
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90.0
80.0
70.0
60.0
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30.0
20.0
10.0
0
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169.195
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134.190
132.400
129.881
129.345
126.875
123.514
122.710
122.576
112.771
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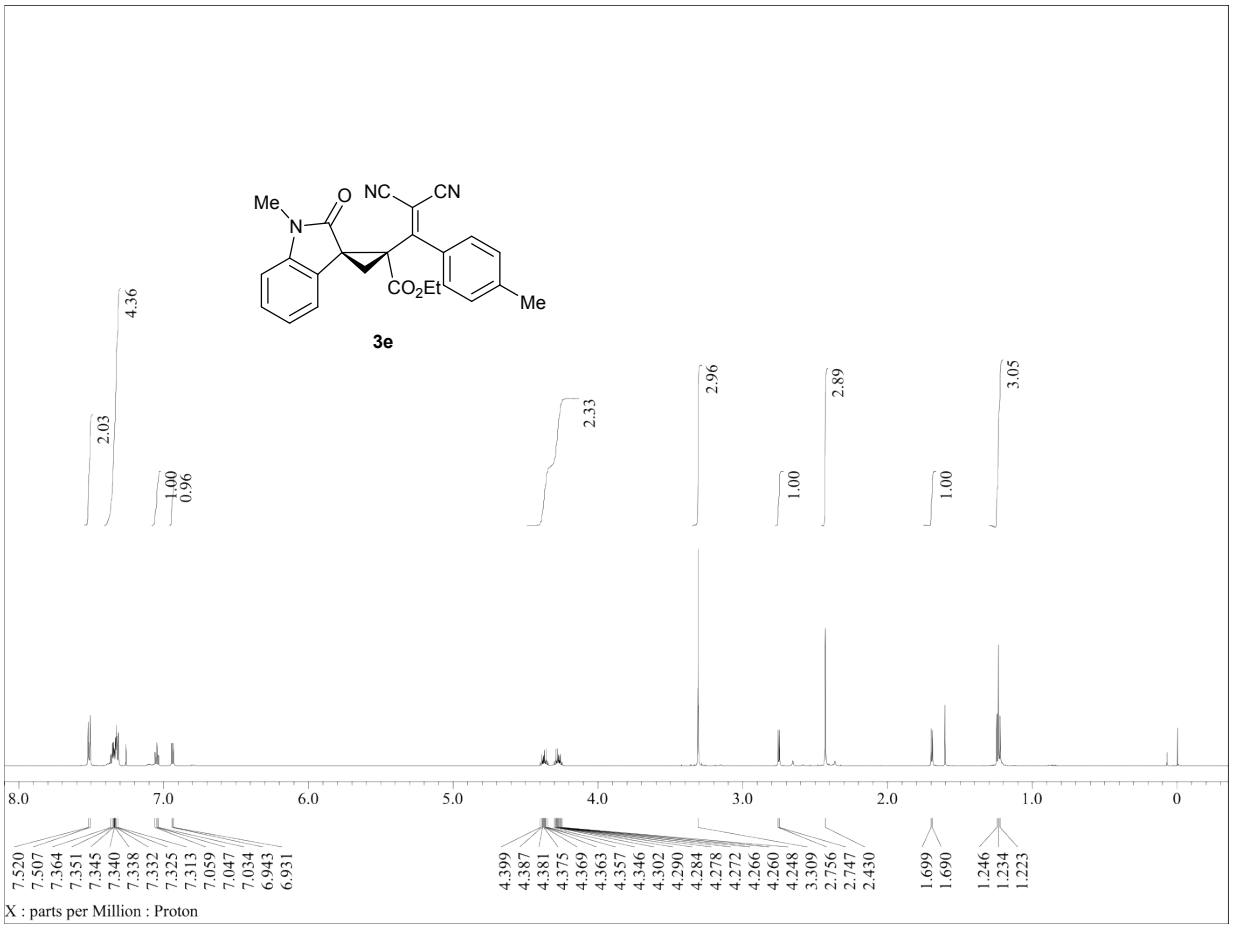
X : parts per Million : Carbon13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1.00
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.351
7.345
7.340
7.338
7.332
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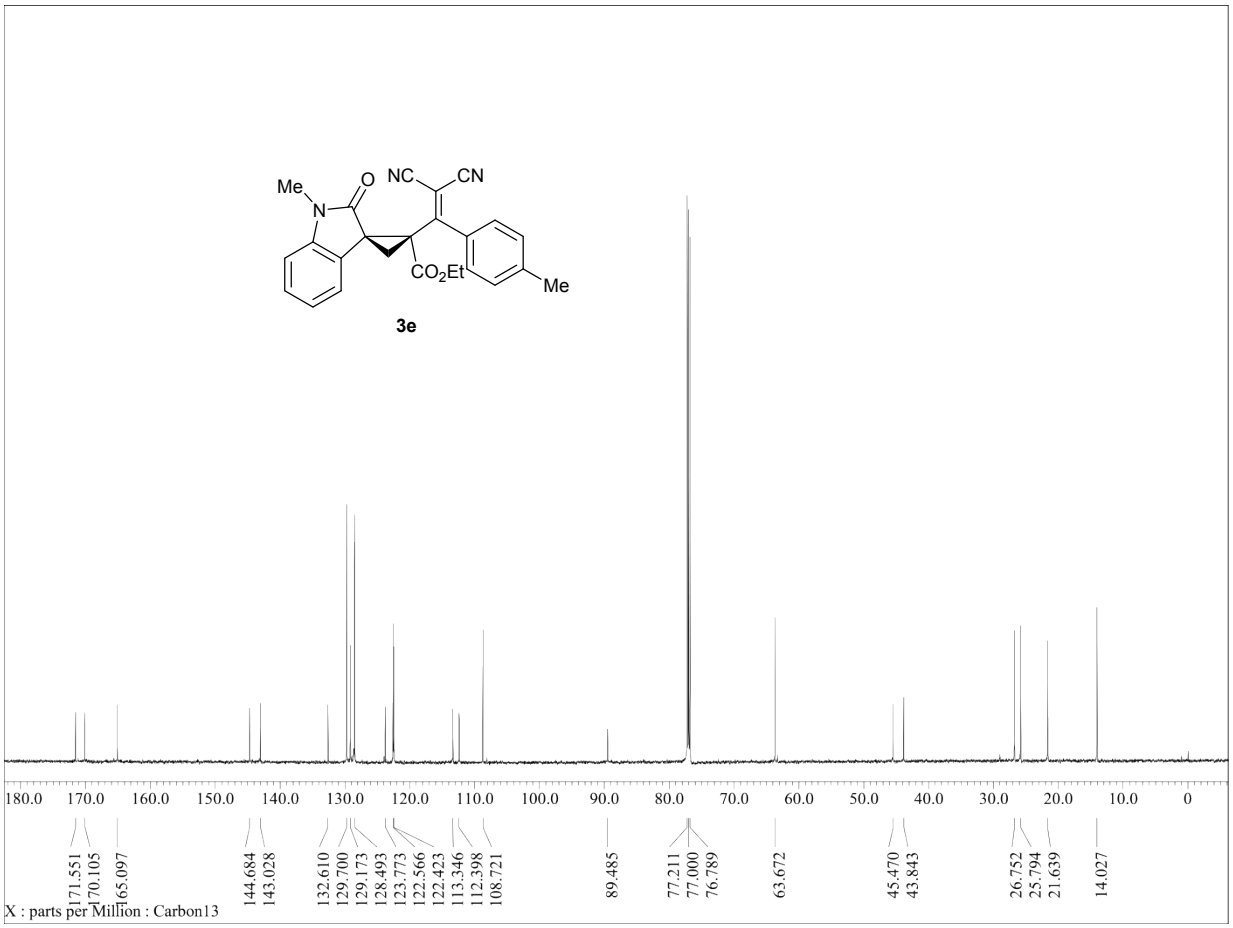
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180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.551
170.105
65.097
144.684
143.028
132.610
129.700
129.173
128.493
123.773
122.566
122.423
113.346
112.398
108.721
89.485
77.211
77.000
76.789
63.672
45.470
43.843
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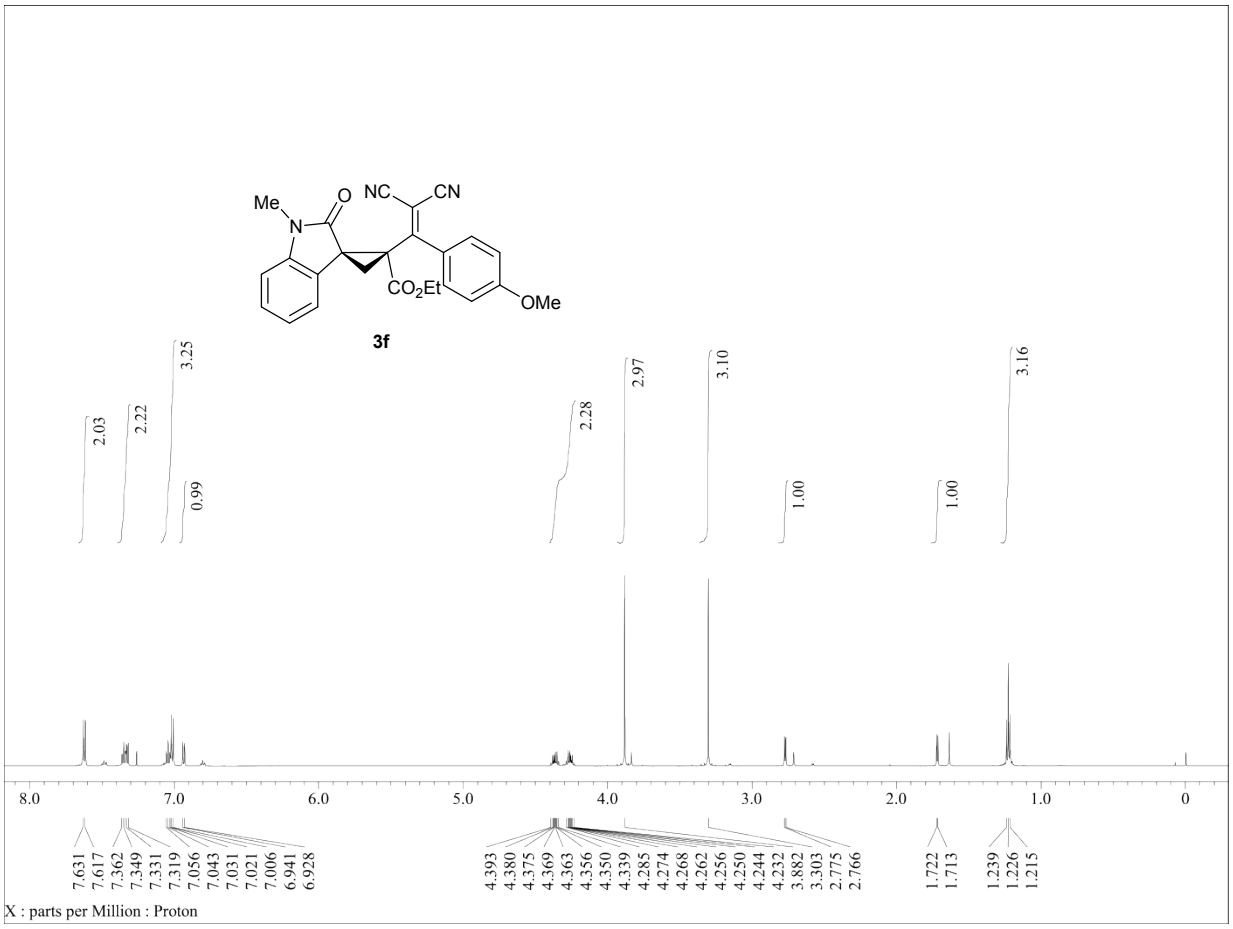
25.794
21.639
14.027
X : parts per Million : Carbon13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N
O
NC
CN
CO2Et
OMe
3f
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2.28
2.97
3.10
1.00
1.00
3.16
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.631
7.617
7.362
7.349
7.331
7.319
7.056
7.043
7.031
7.021
7.006
6.941
6.928
4.393
4.380
4.375
4.369
4.363
4.356
4.350
4.339
4.285
4.274
4.268
4.262
4.256
4.250
4.244
4.232
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1.722
1.713
1.239
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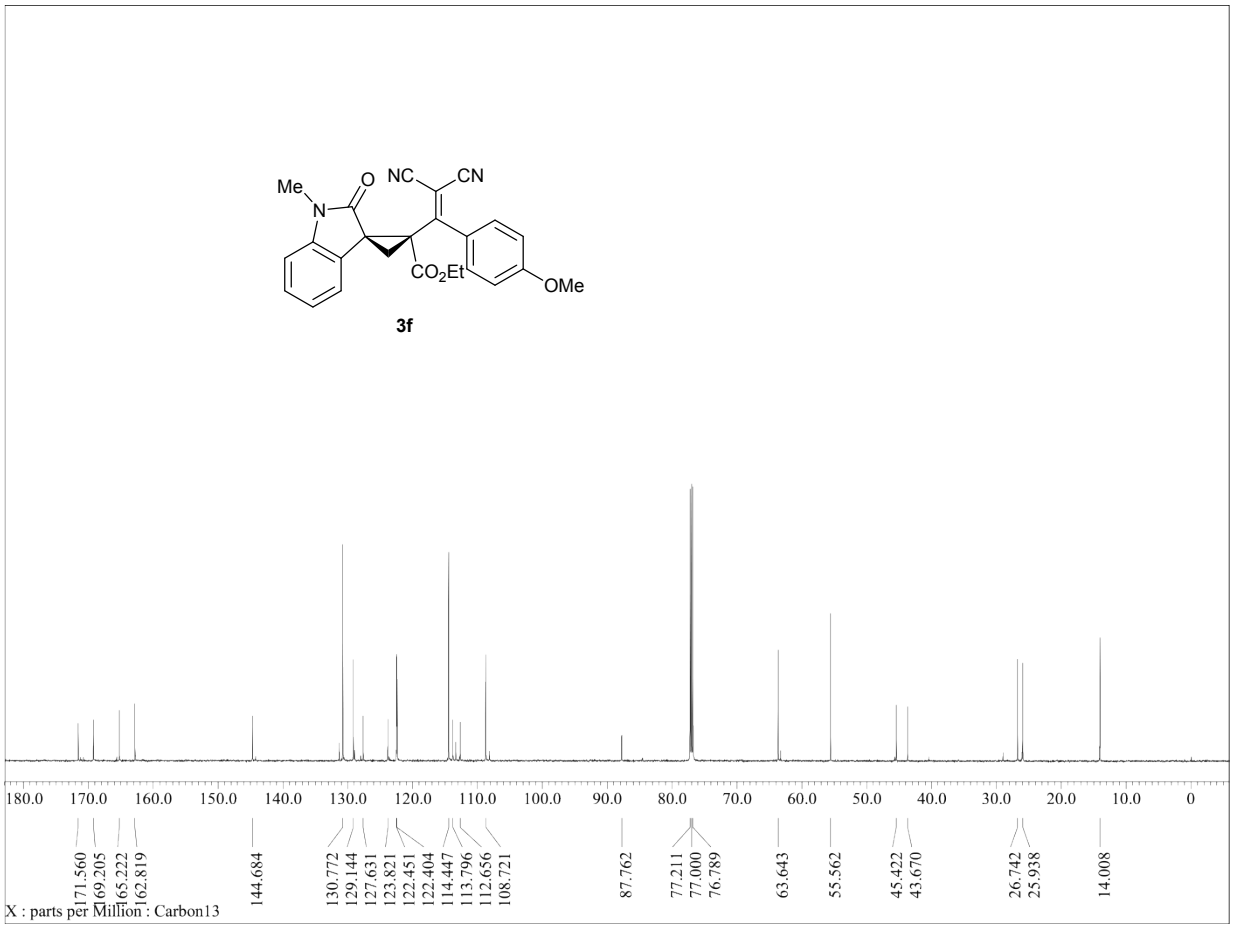
1.215
X : parts per Million : Proton


Me
N
O
NC
CN
CO2Et
OMe
3f
180.0
170.0
160.0
150.0
140.0
130.0
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110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.560
169.205
165.222
162.819
144.684
130.772
129.144
127.631
123.821
122.451
122.404
114.447
113.796
112.656
108.721
87.762
77.211
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63.643
55.562
45.422
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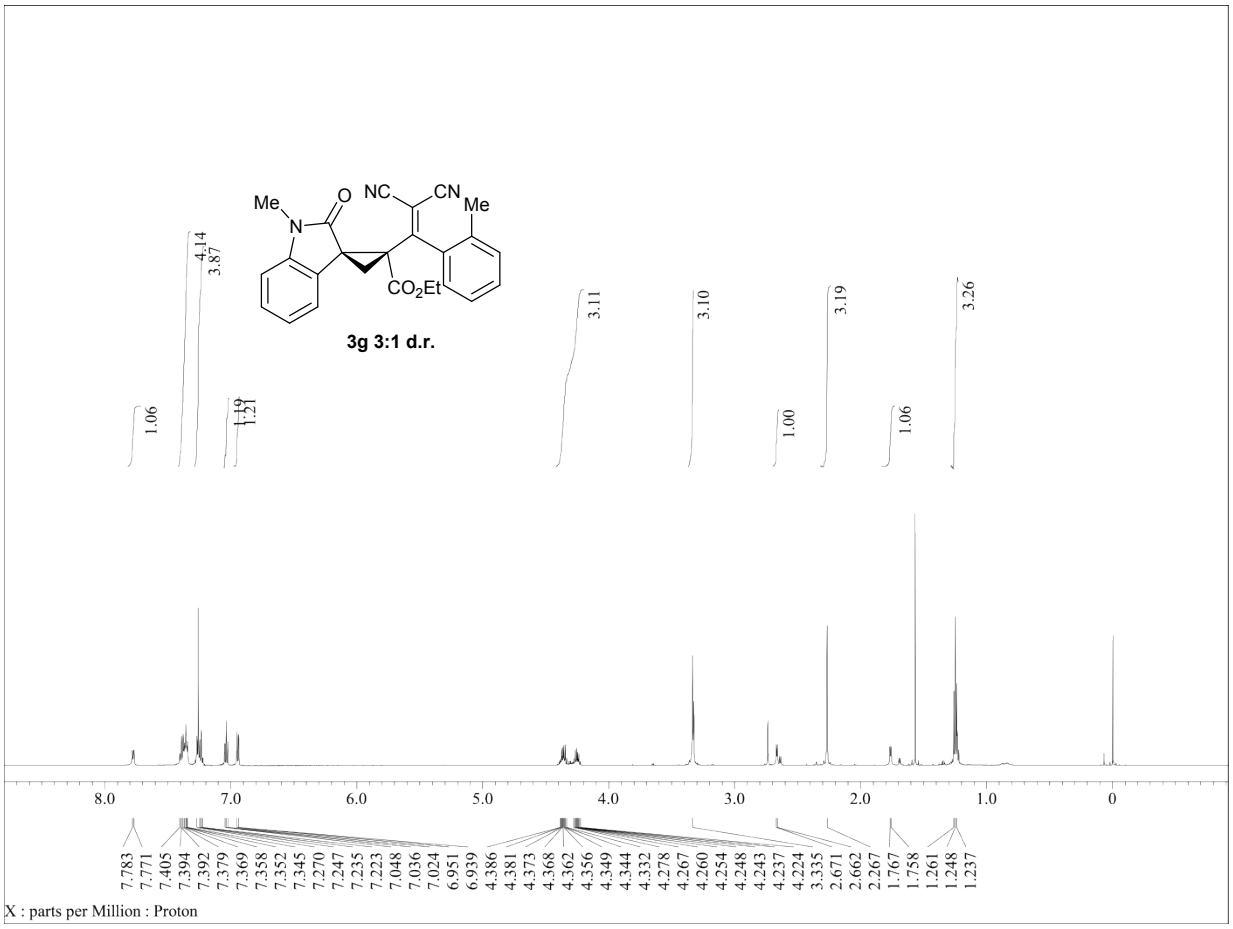
Me
O
NC
CN
Me
N
CO2Et
3g 3:1 d.r.
4.14
3.87
1.06
1.19
1.21
3.11
3.10
1.00
3.19
1.06
3.26
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.783
7.771
7.405
7.394
7.392
7.379
7.369
7.358
7.352
7.345
7.270
7.247
7.235
7.223
7.048
7.036
7.024
6.951
6.939
4.386
4.381
4.373
4.368
4.362
4.356
4.349
4.344
4.332
4.278
4.267
4.260
4.254
4.248
4.243
4.237
4.224
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2.662
2.267
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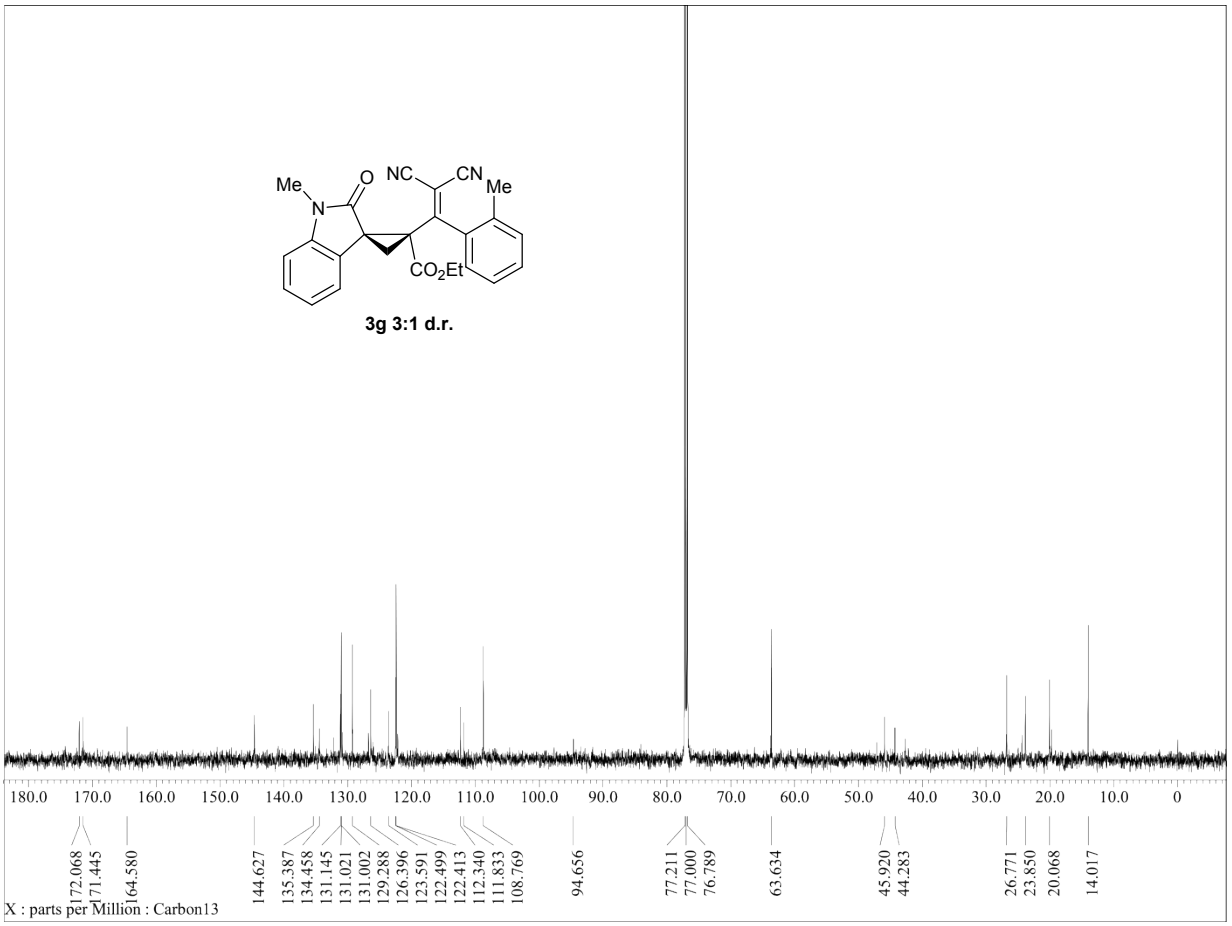
1.758
1.261
1.248
1.237
X : parts per Million : Proton


Me
O
NC
CN
Me
N
CO2Et
3g 3:1 d.r.
180.0
170.0
160.0
150.0
140.0
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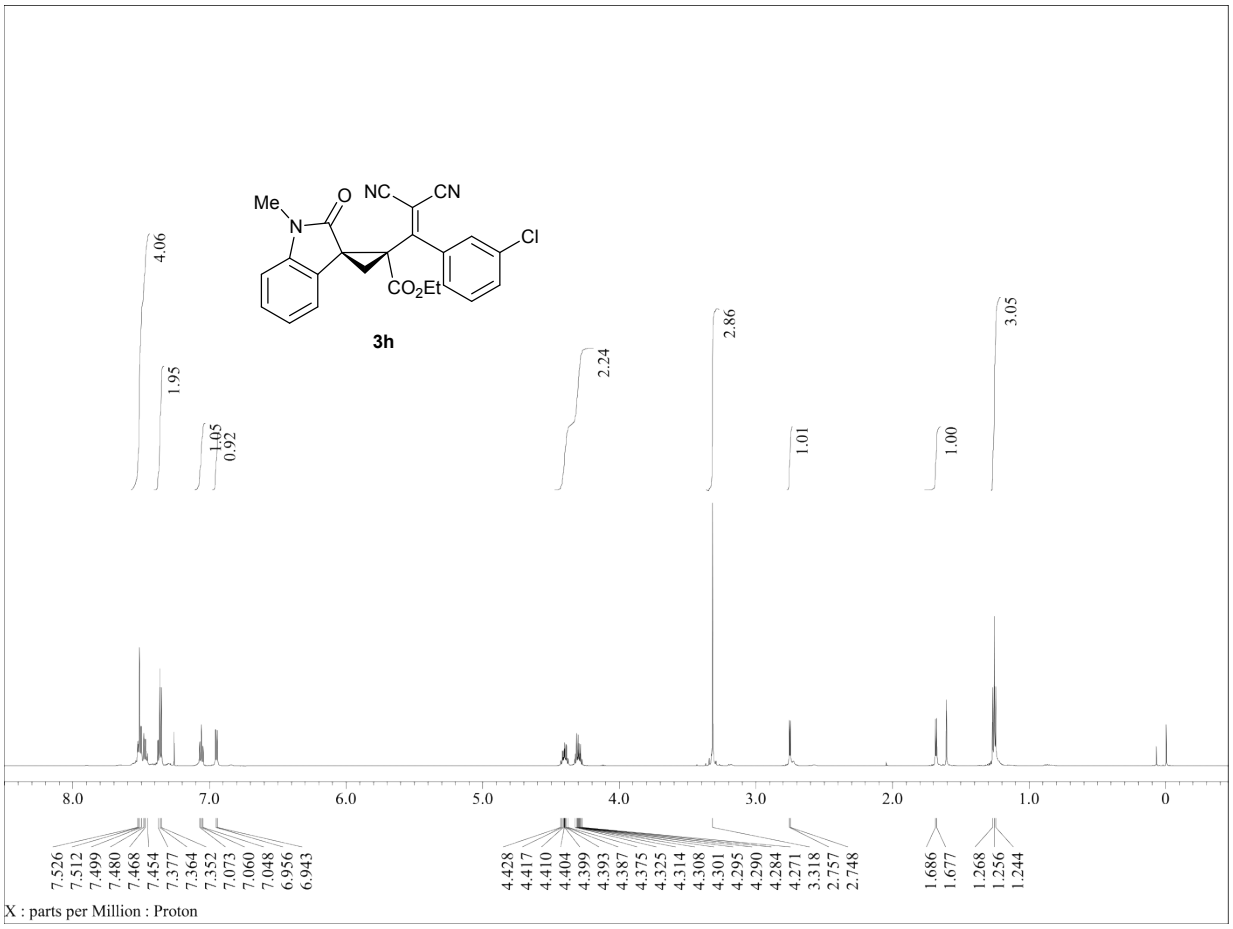
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.068
171.445
164.580
144.627
135.387
134.458
131.145
131.021
131.002
129.288
126.396
123.591
122.499
122.413
112.340
111.833
108.769
94.656
77.211
77.000
76.789
63.634
45.920
44.283
26.771
23.850
20.068
14.017
X : parts per Million : Carbon13


Me
N
O
NC
CN
Cl
CO2Et
3h
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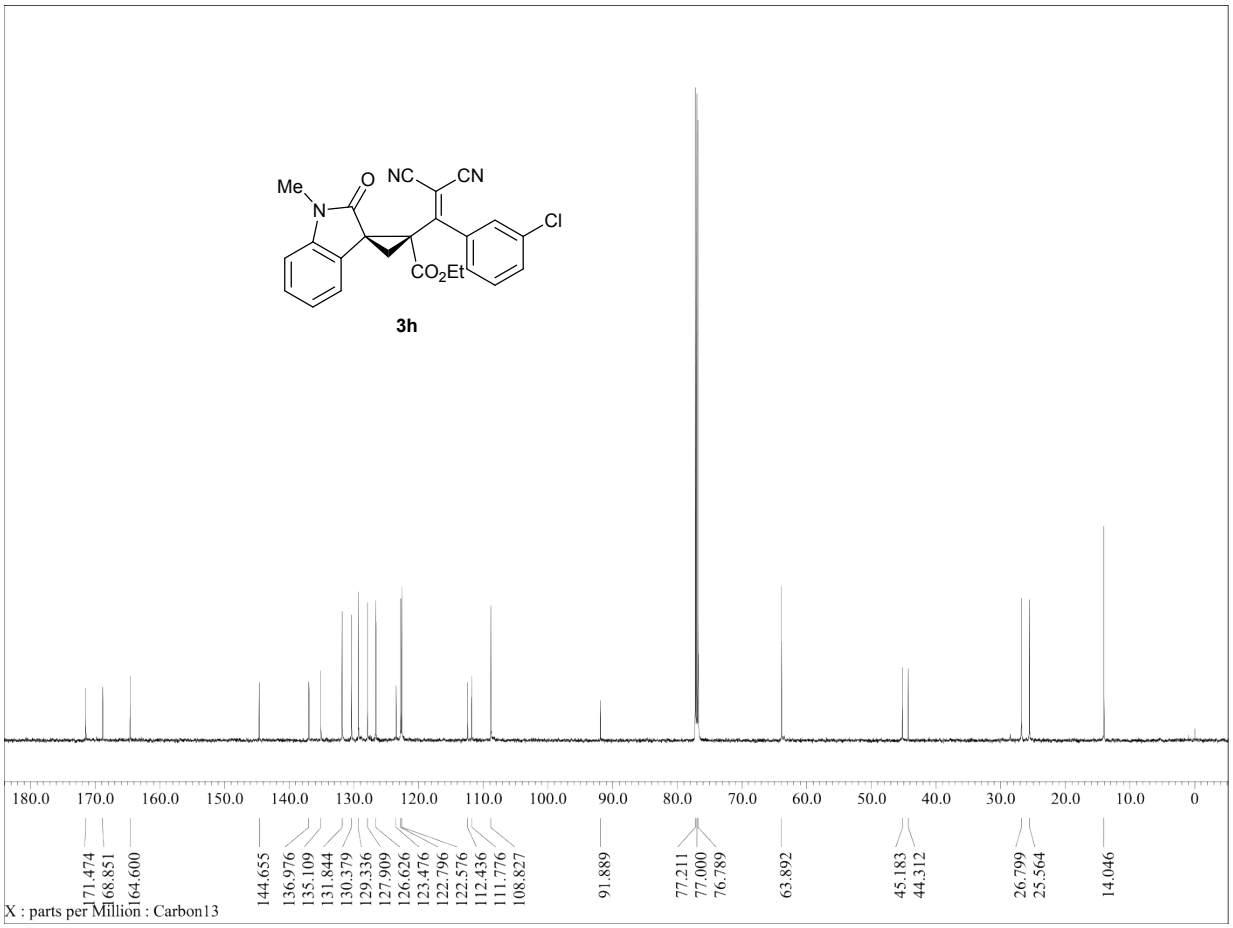
1.95
1.05
0.92
2.24
2.86
1.01
1.00
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.526
7.512
7.499
7.480
7.468
7.454
7.377
7.364
7.352
7.073
7.060
7.048
6.956
6.943
4.428
4.417
4.410
4.404
4.399
4.393
4.387
4.375
4.325
4.314
4.308
4.301
4.295
4.290
4.284
4.271
3.318
2.757
2.748
1.686
1.677
1.268
1.256
1.244
X : parts per Million : Proton


Me
N
O
NC
CN
Cl
CO2Et
3h
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
171.474
168.851
164.600
144.655
136.976
135.109
131.844
130.379
129.336
127.909
126.626
123.476
122.796
122.576
112.436
111.776
108.827
91.889
77.211
77.000
76.789
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14.046
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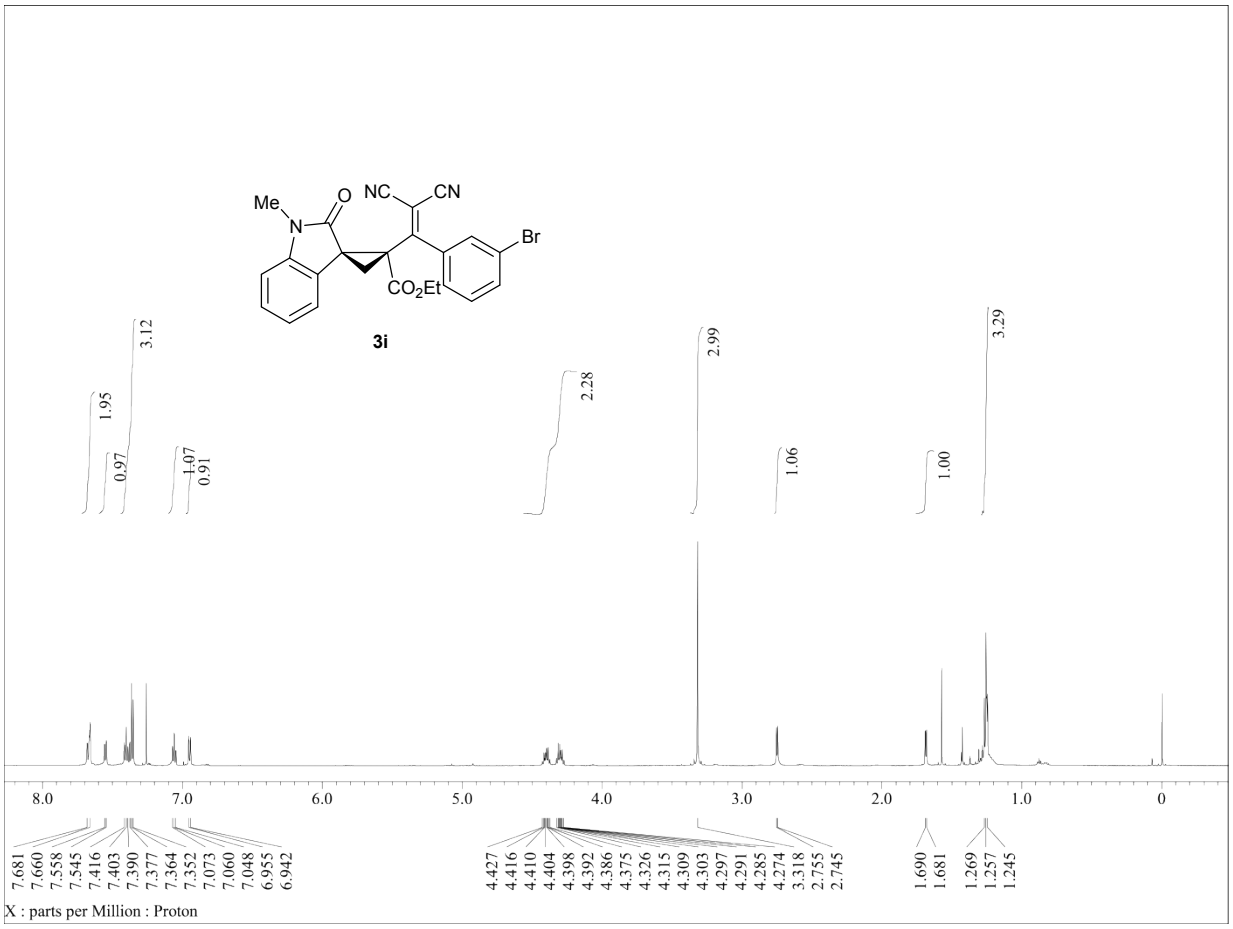
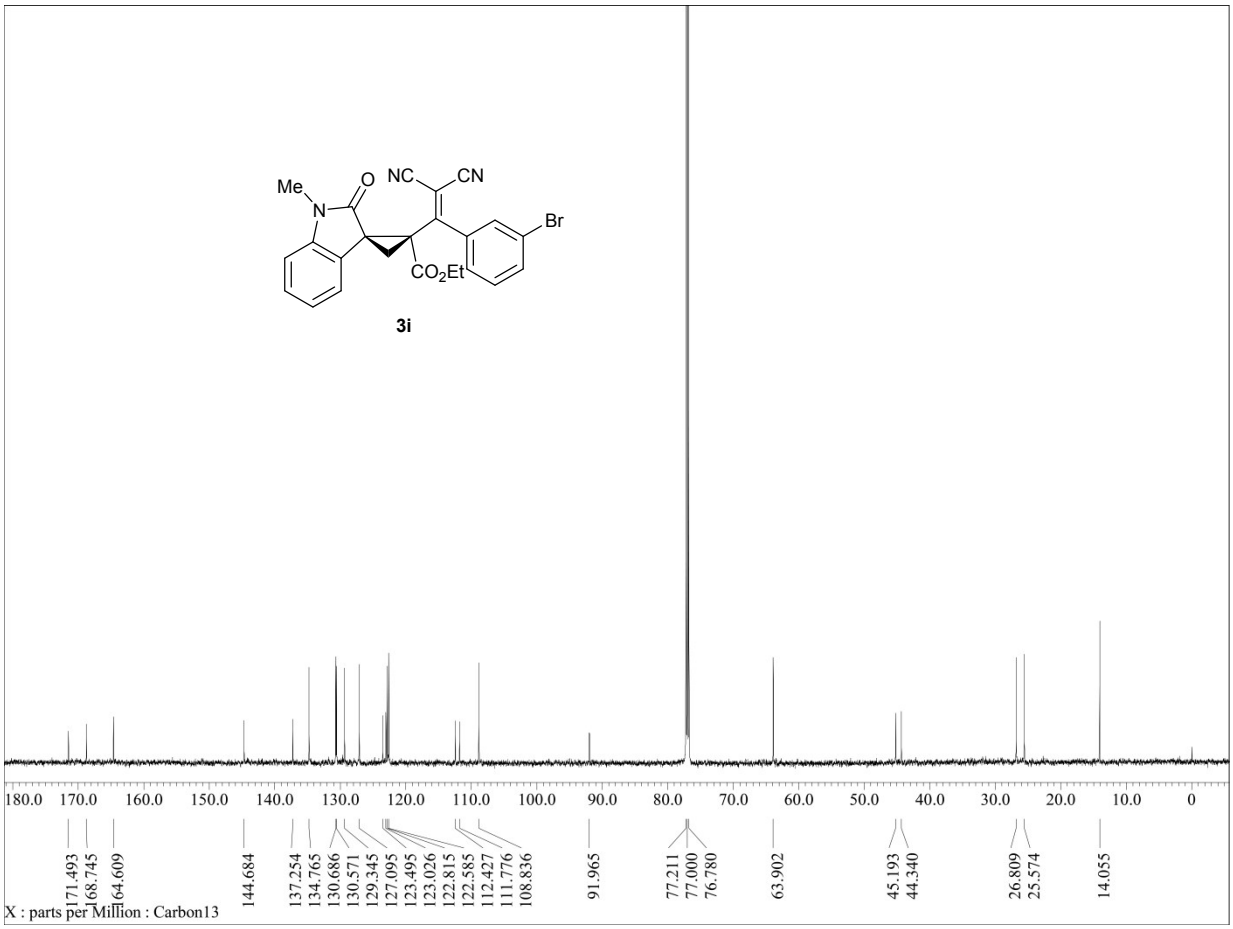
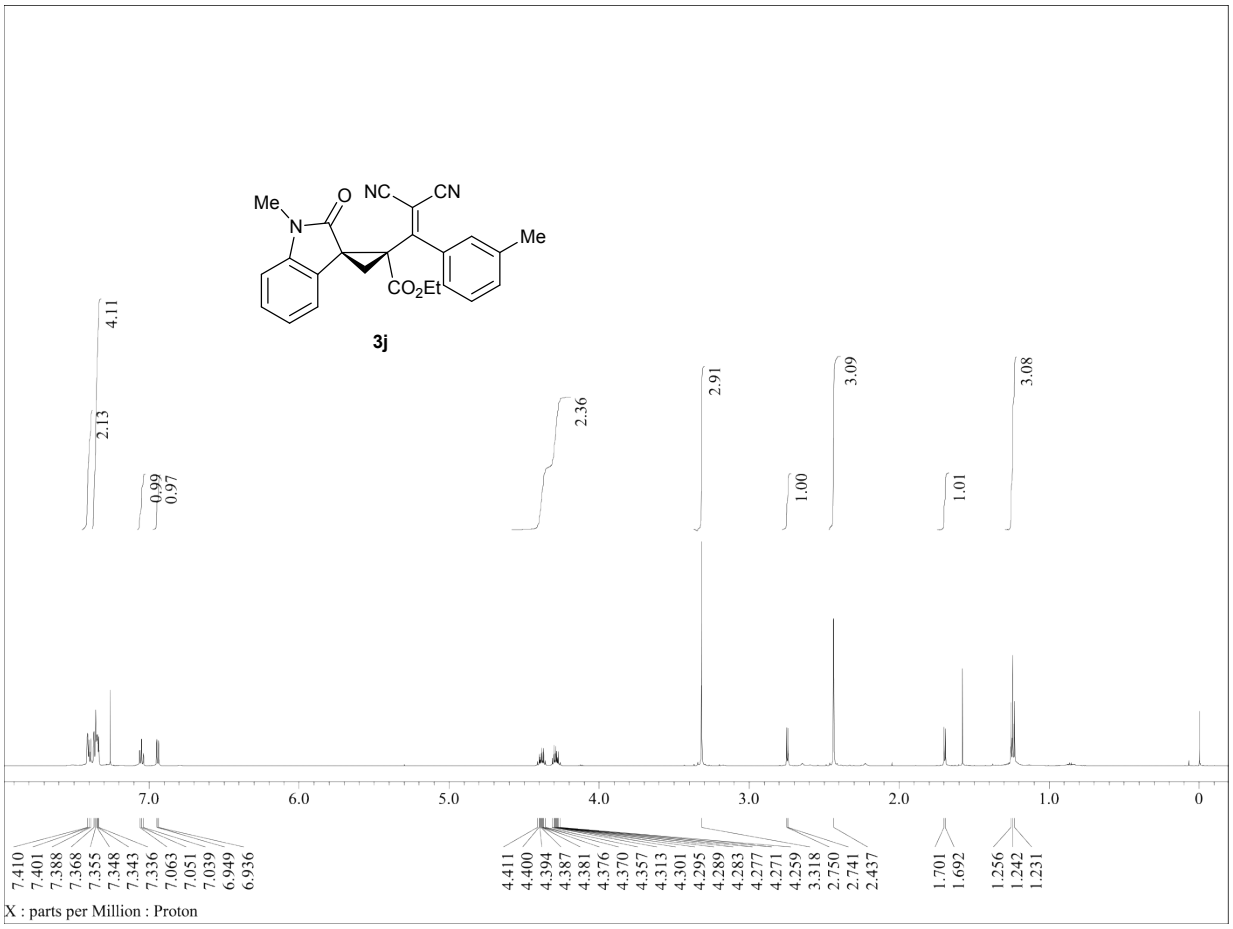
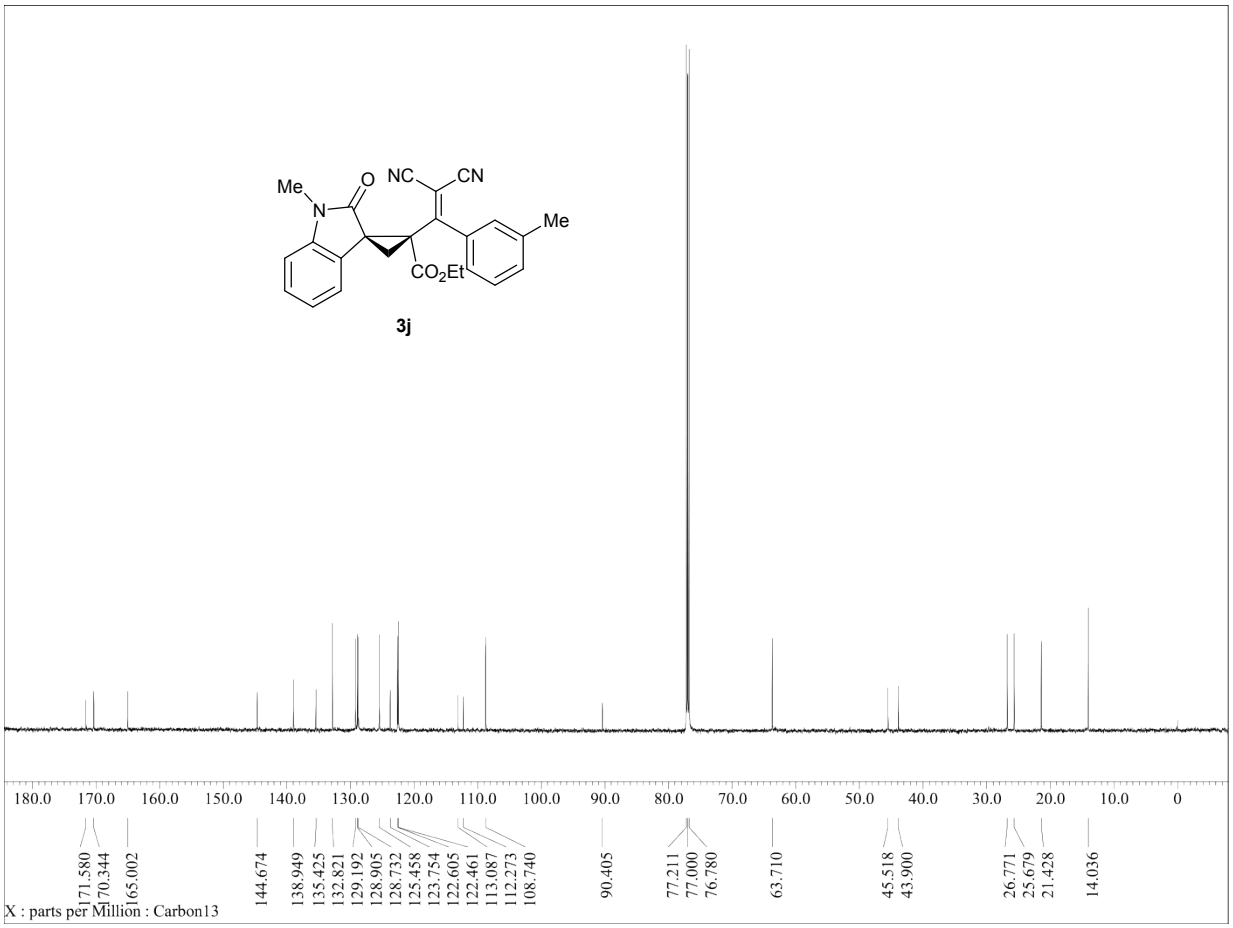
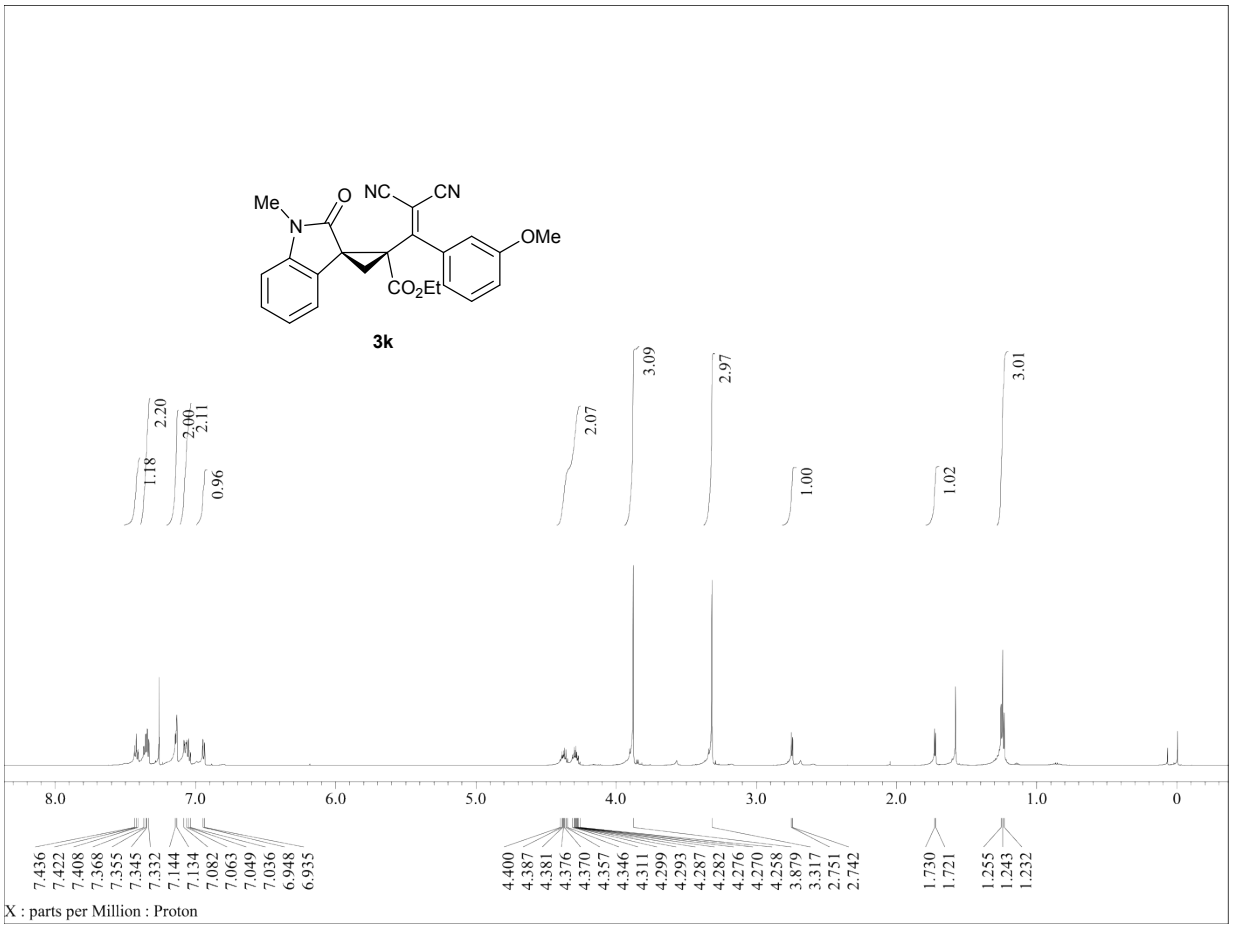

Me
N
O
NC
CN
Br
CO2Et
3i
1.95
0.97
3.12
1.07
0.91
2.28
2.99
1.06
1.00
3.29
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.681
7.660
7.558
7.545
7.416
7.403
7.390
7.377
7.364
7.352
7.073
7.060
7.048
6.955
6.942
4.427
4.416
4.410
4.404
4.398
4.392
4.386
4.375
4.326
4.315
4.309
4.303
4.297
4.291
4.285
4.274
3.318
2.755
2.745
1.690
1.681
1.269
1.257
1.245
X : parts per Million : Proton


Me
N
O
NC
CN
Br
CO2Et
3i
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
171.493
168.745
164.609
144.684
137.254
134.765
130.686
130.571
129.345
127.095
123.495
123.026
122.815
122.585
112.427
111.776
108.836
91.965
77.211
77.000
76.780
63.902
45.193
44.340
26.809
25.574
14.055
X : parts per Million : Carbon13


Me
N
O
NC
CN
Me
CO2Et
3j
4.11
2.13
0.99
0.97
2.36
2.91
1.00
3.09
1.01
3.08
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.410
7.401
7.388
7.368
7.355
7.348
7.343
7.336
7.063
7.051
7.039
6.949
6.936
4.411
4.400
4.394
4.387
4.381
4.376
4.370
4.357
4.313
4.301
4.295
4.289
4.283
4.277
4.271
4.259
3.318
2.750
2.741
2.437
1.701
1.692
1.256
1.242
1.231
X : parts per Million : Proton


Me
N
O
NC
CN
Me
CO2Et
3j
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
171.580
170.344
165.002
144.674
138.949
135.425
132.821
129.192
128.905
128.732
125.458
123.754
122.605
122.461
113.087
112.273
108.740
90.405
77.211
77.000
76.780
63.710
45.518
43.900
26.771
25.679
21.428
14.036
X : parts per Million : Carbon13


Me
N
O
NC
CN
OMe
CO2Et
3k
1.18
2.20
2.00
2.11
0.96
2.07
3.09
2.97
1.00
1.02
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.436
7.422
7.408
7.368
7.355
7.345
7.332
7.144
7.134
7.082
7.063
7.049
7.036
6.948
6.935
4.400
4.387
4.381
4.376
4.370
4.357
4.346
4.311
4.299
4.293
4.287
4.282
4.276
4.270
4.258
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2.742
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1.721
1.255
1.243
1.232
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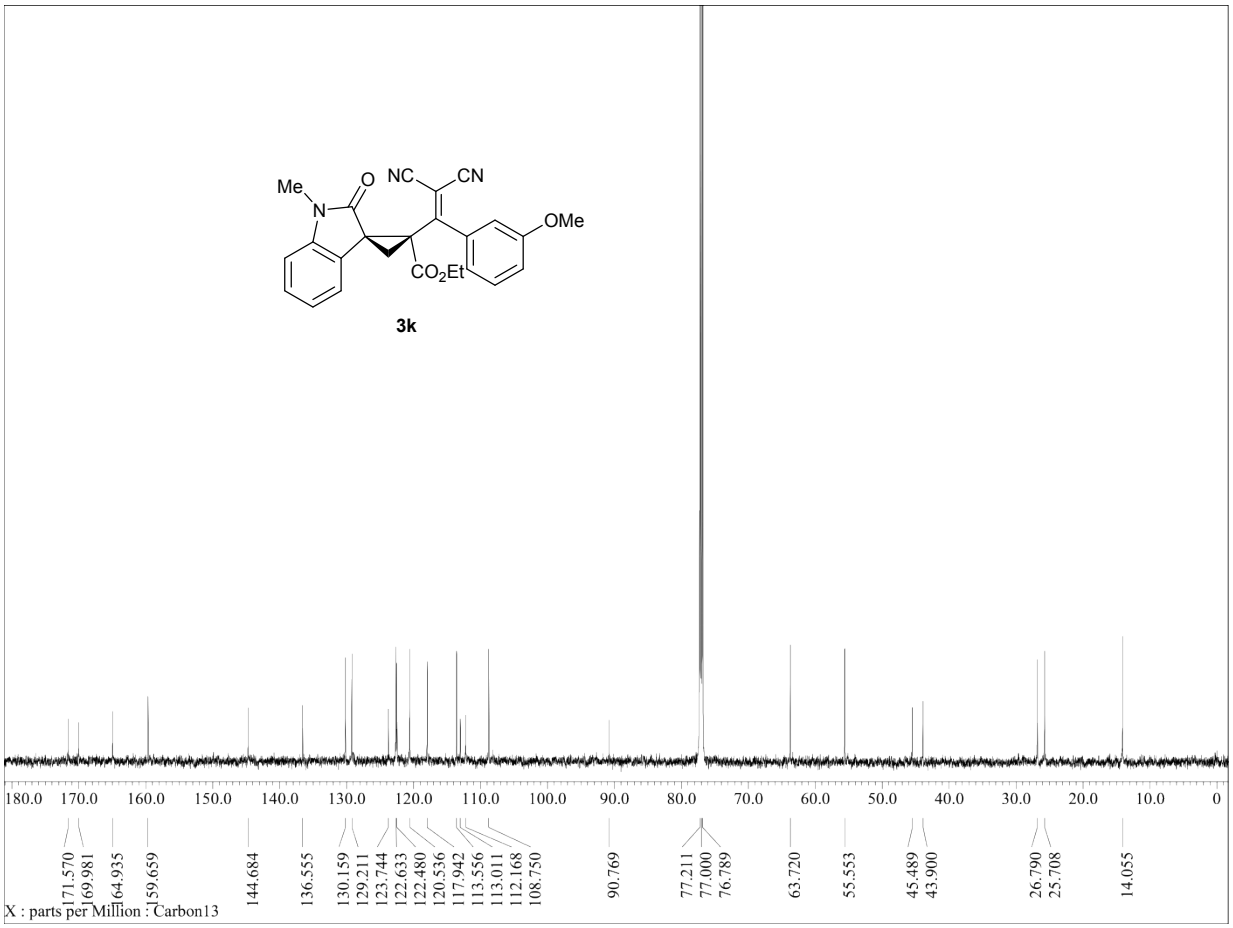
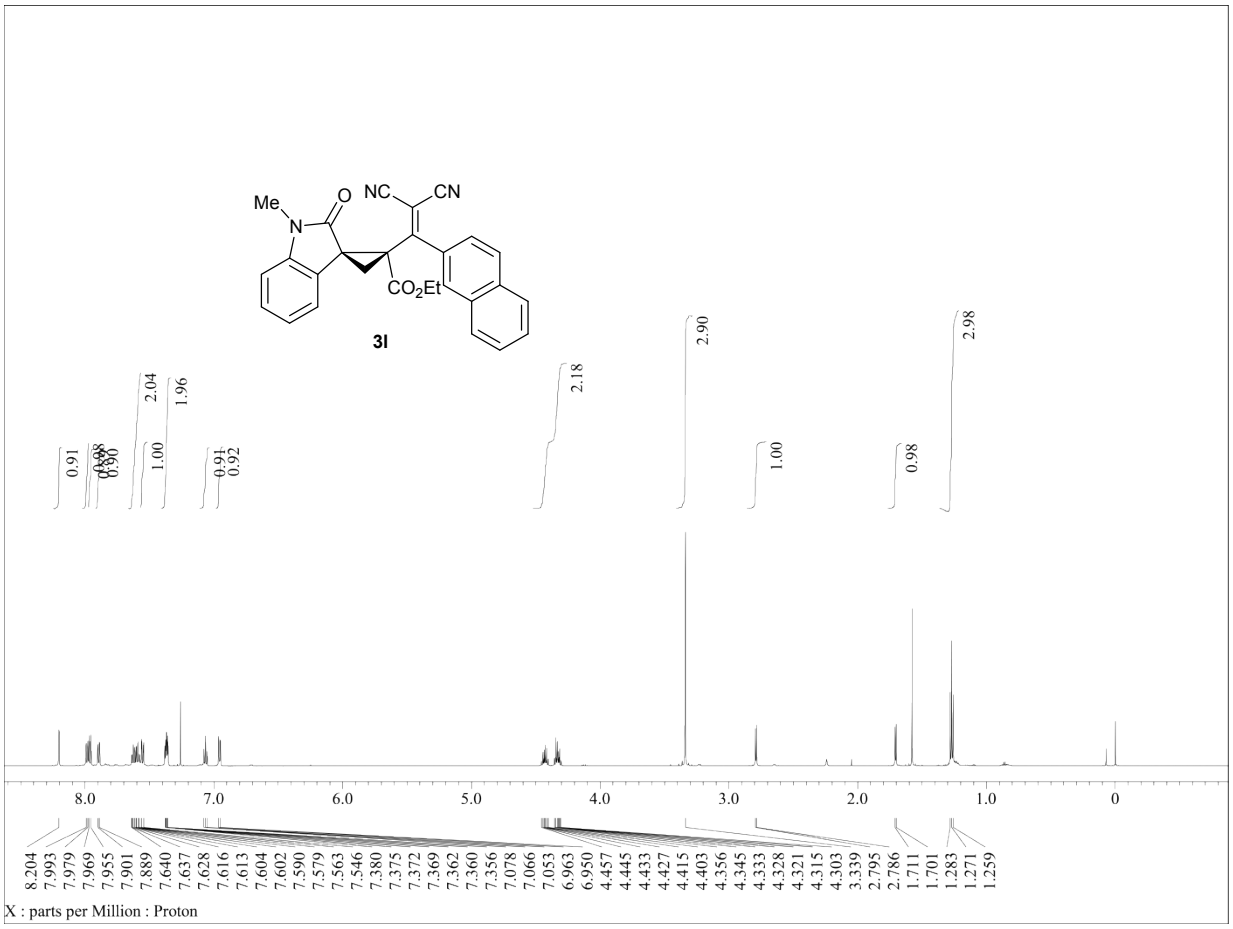

Me
N
O
NC
CN
OMe
CO2Et
3k
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.570
169.981
164.935
159.659
144.684
136.555
130.159
129.211
123.744
122.633
122.480
120.536
117.942
113.556
113.011
112.168
108.750
90.769
77.211
77.000
76.789
63.720
55.553
45.489
43.900
26.790
25.708
14.055
X : parts per Million : Carbon13


Me
N
O
NC
CN
CO2Et
3l
0.91
0.90
2.04
1.00
1.96
0.91
0.92
2.18
2.90
1.00
0.98
2.98
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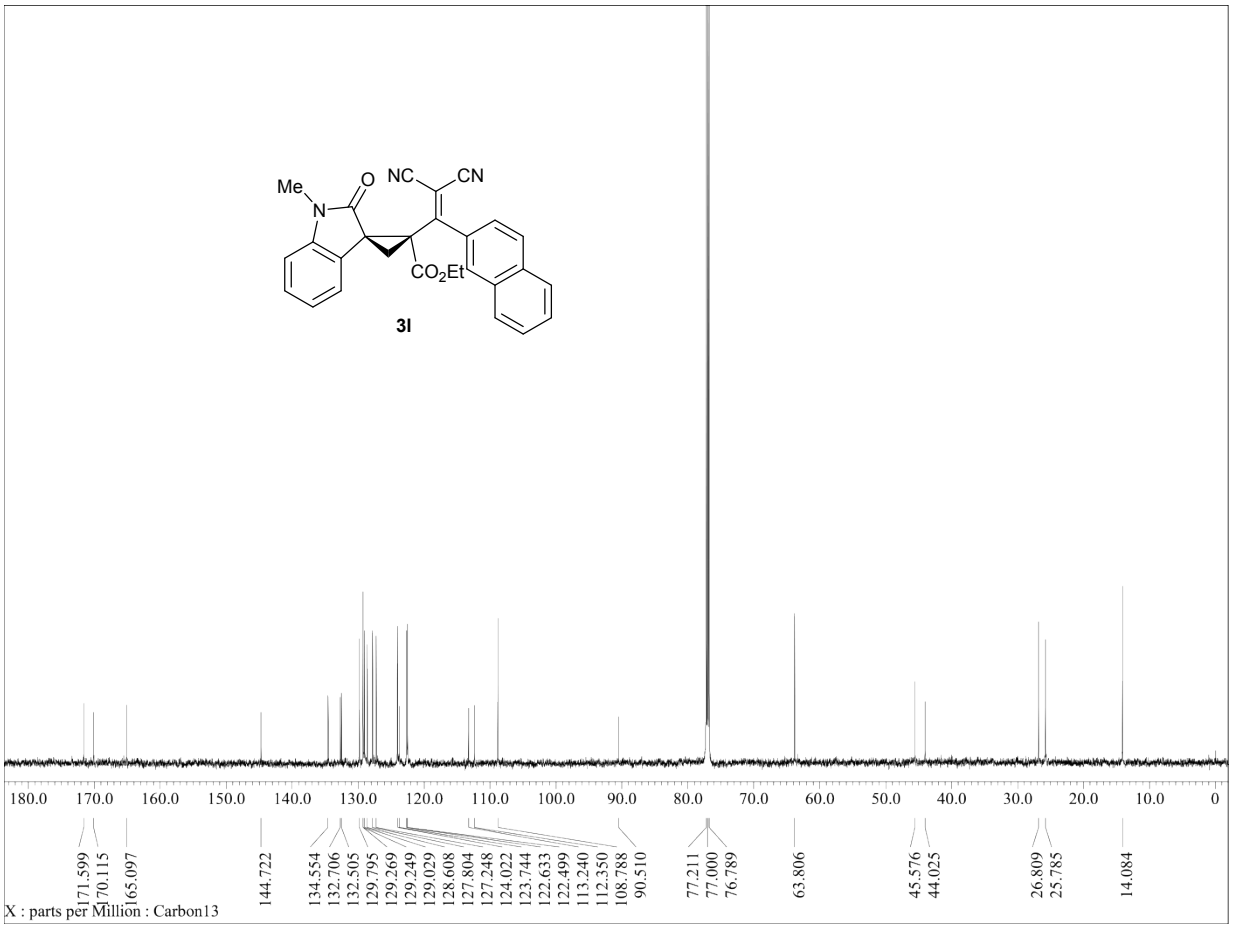
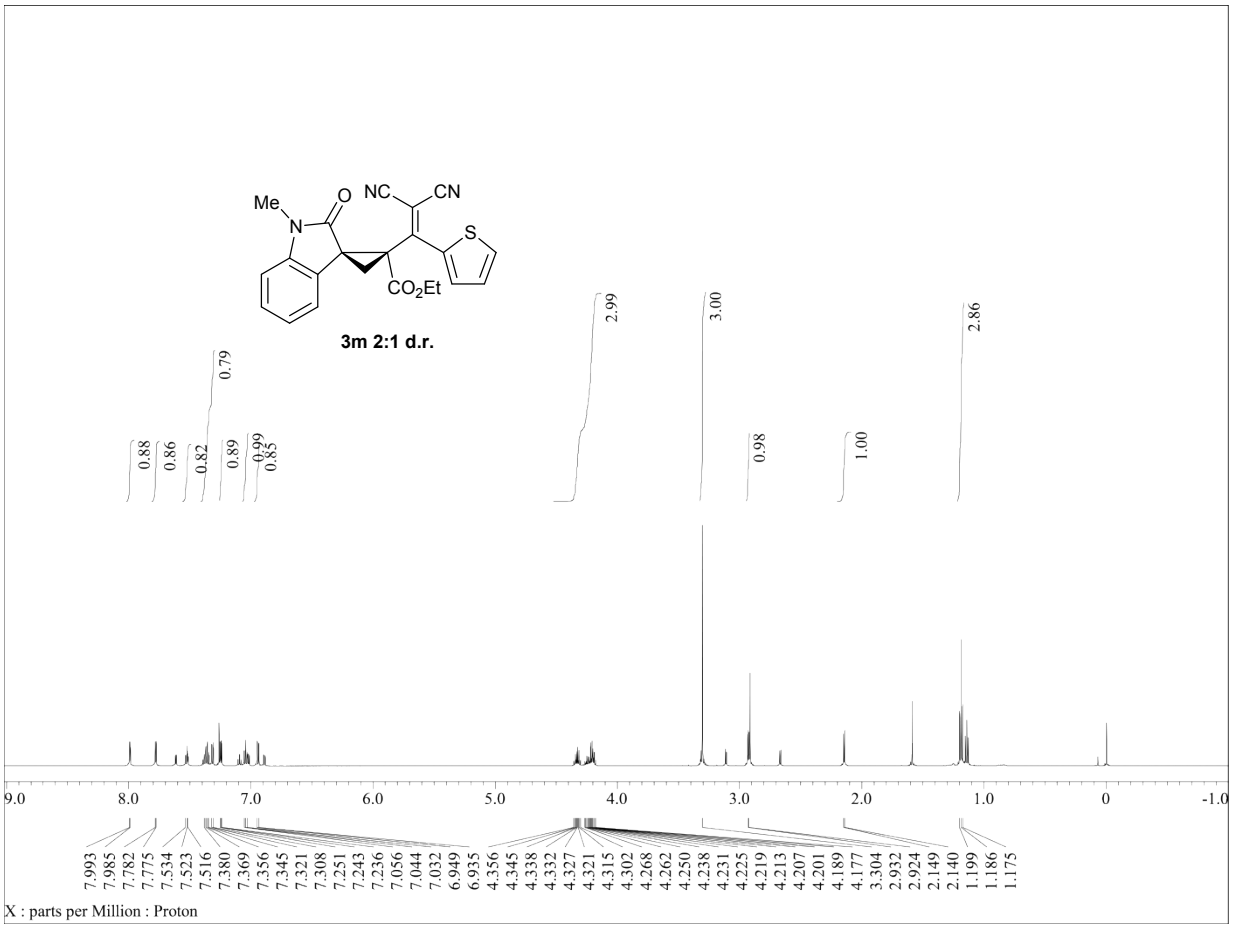
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


Me
N
O
NC
CN
CO2Et
3l
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
X : parts per Million : Carbon13


Me
N
O
NC
CN
S
CO2Et
3m 2:1 d.r.
0.88
0.86
0.82
0.79
0.89
0.99
0.85
2.99
3.00
0.98
1.00
2.86
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.993
7.985
7.782
7.775
7.534
7.523
7.516
7.380
7.369
7.356
7.345
7.321
7.308
7.251
7.243
7.236
7.056
7.044
7.032
6.949
6.935
4.356
4.345
4.338
4.332
4.327
4.321
4.315
4.302
4.268
4.262
4.250
4.238
4.231
4.225
4.219
4.213
4.207
4.201
4.189
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1.199
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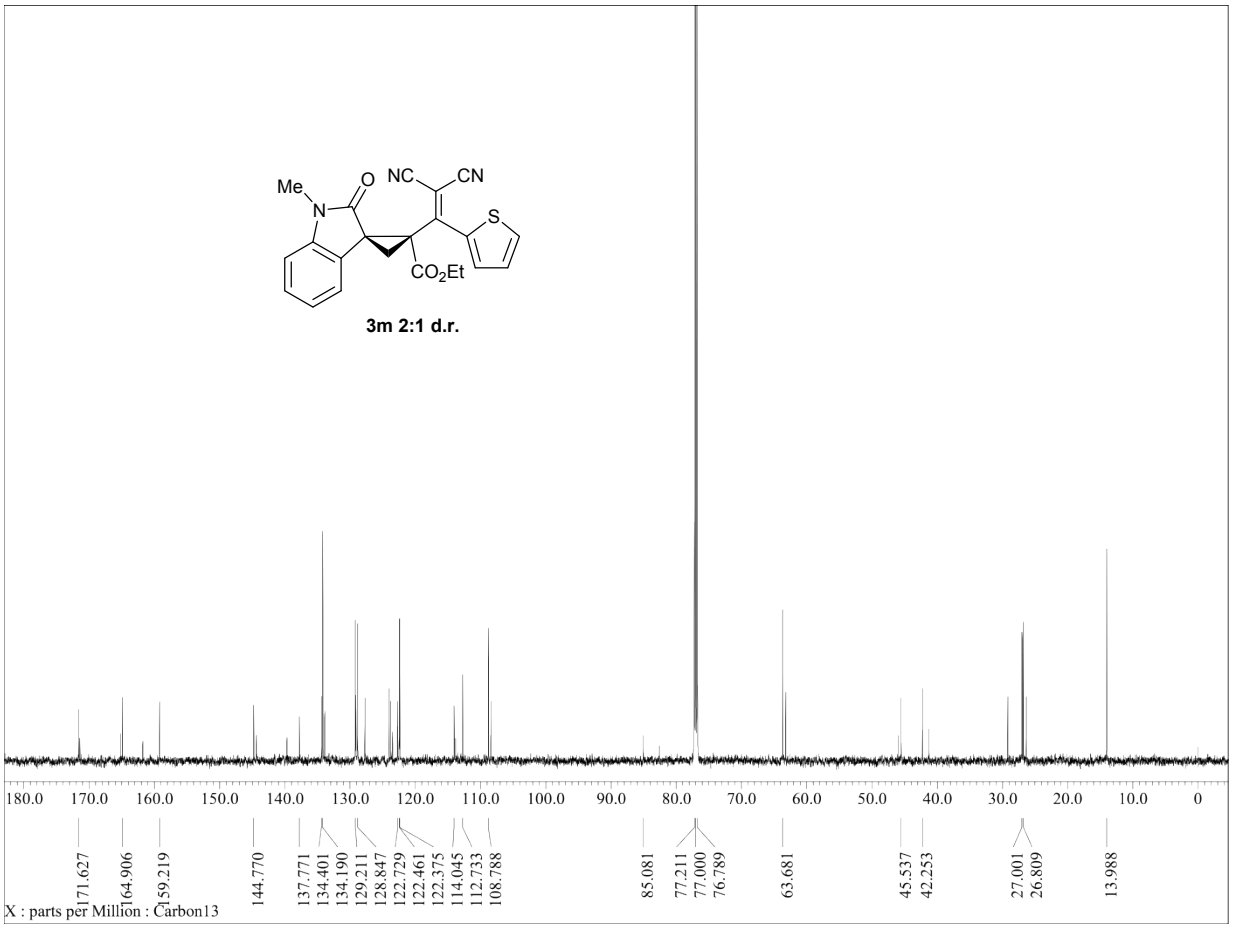
1.175
X : parts per Million : Proton


Me
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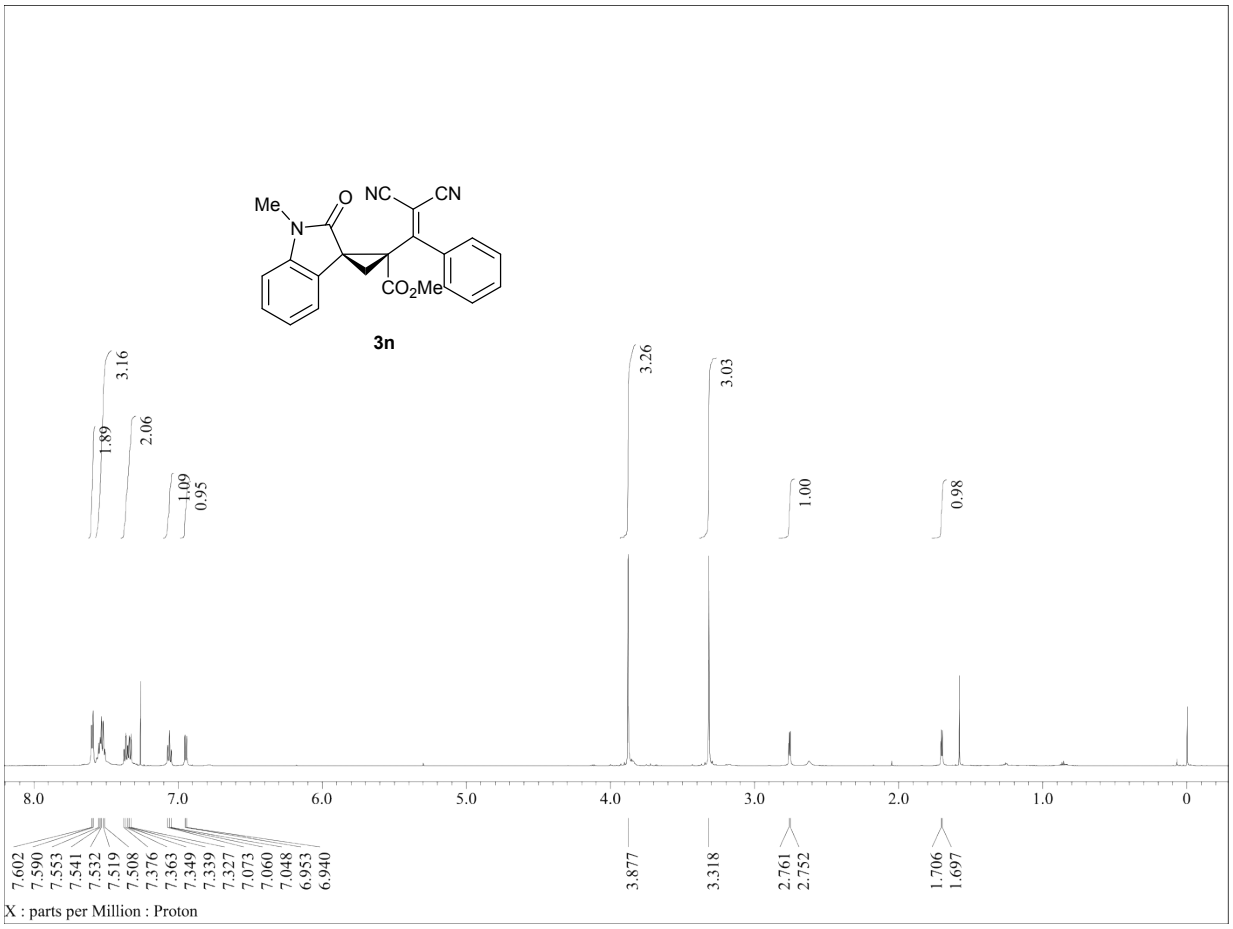
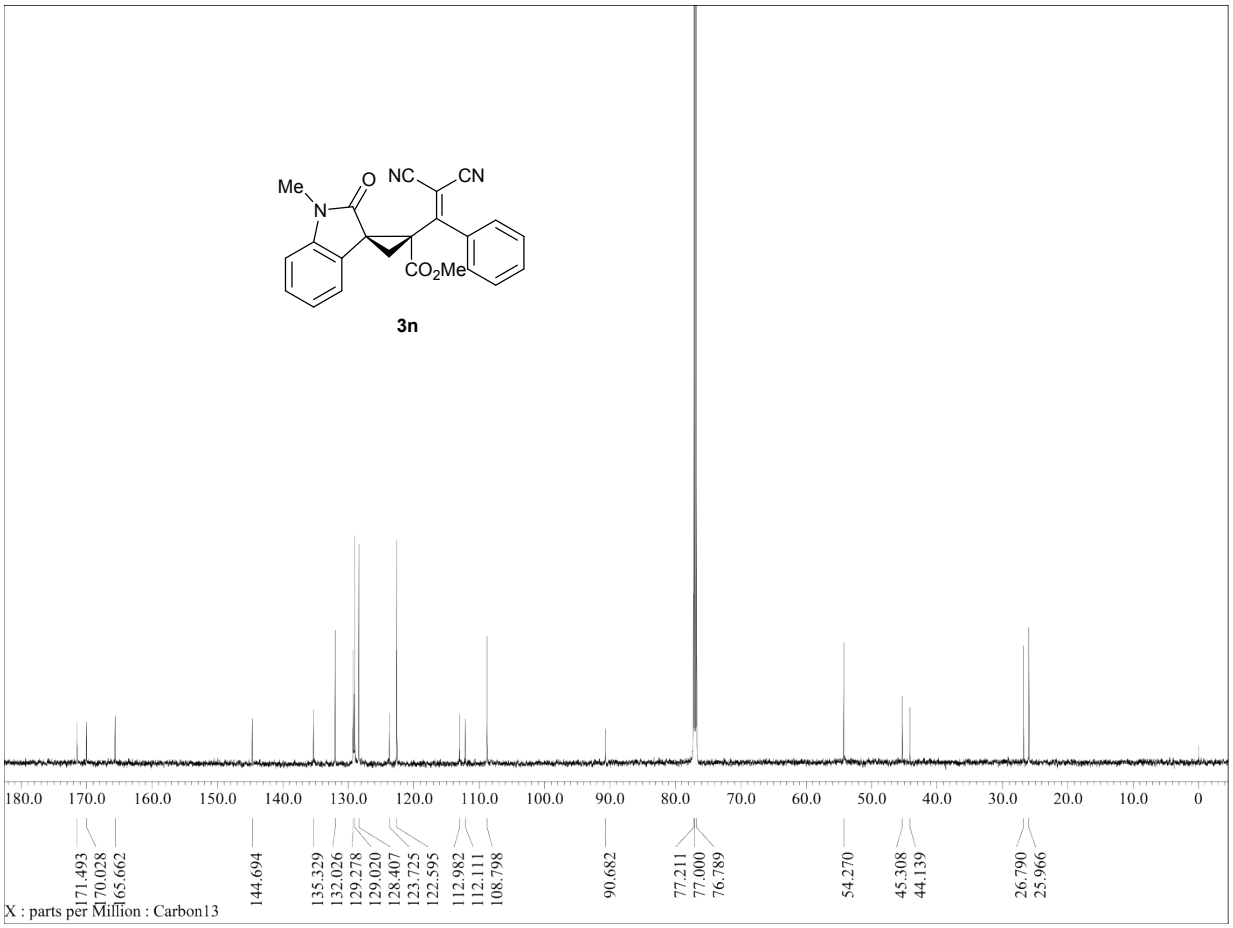
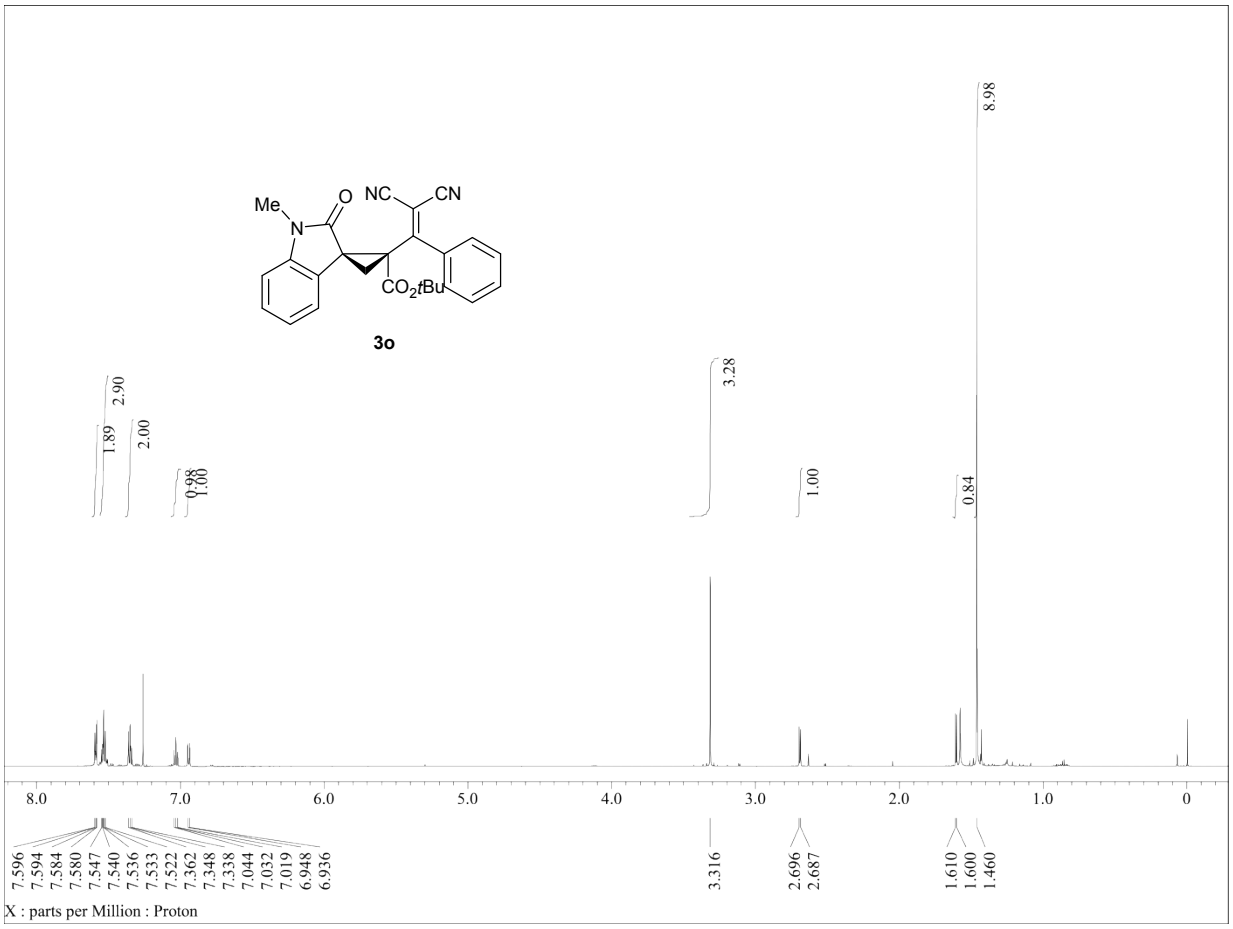
O
NC
CN
S
CO2Et
3m 2:1 d.r.
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.627
164.906
159.219
144.770
137.771
134.401
134.190
129.211
128.847
122.729
122.461
122.375
114.045
112.733
108.788
85.081
77.211
77.000
76.789
63.681
45.537
42.253
27.001
26.809
13.988
X : parts per Million : Carbon13


Me
N
O
NC
CN
CO2Me
3n
3.16
1.89
2.06
1.09
0.95
3.26
3.03
1.00
0.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.602
7.590
7.553
7.541
7.532
7.519
7.508
7.376
7.363
7.349
7.339
7.327
7.073
7.060
7.048
6.953
6.940
3.877
3.318
2.761
2.752
1.706
1.697
X : parts per Million : Proton


Me
N
O
NC
CN
CO2Me
3n
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
171.493
170.028
65.662
144.694
135.329
132.026
129.278
129.020
128.407
123.725
122.595
112.982
112.111
108.798
90.682
77.211
77.000
76.789
54.270
45.308
44.139
26.790
25.966
X : parts per Million : Carbon13


Me
N
O
NC
CN
CO2tBu
3o
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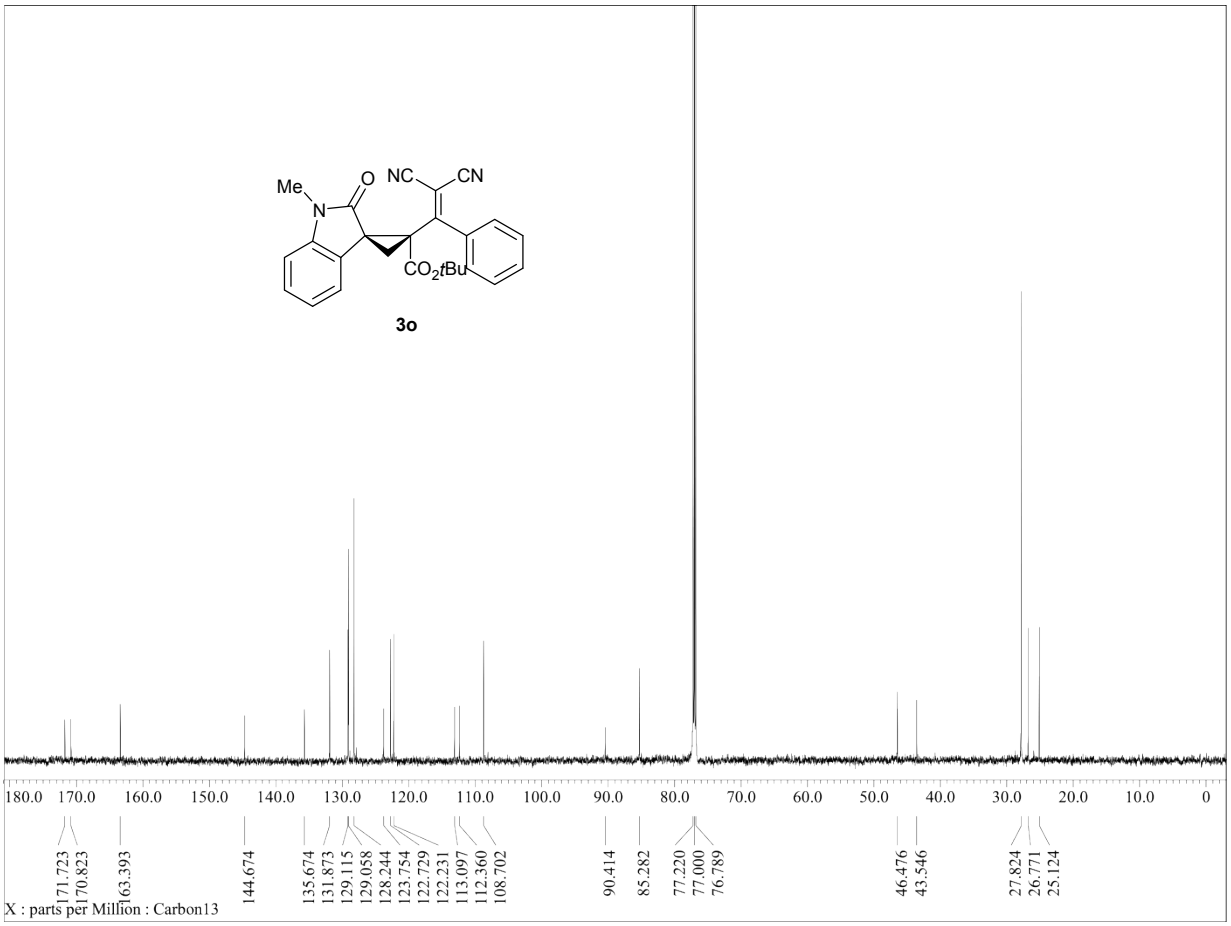
3.28
2.90
2.00
1.89
1.00
0.98
1.00
0.84
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.596
7.594
7.584
7.580
7.547
7.540
7.536
7.533
7.522
7.362
7.348
7.338
7.044
7.032
7.019
6.948
6.936
3.316
2.696
2.687
1.610
1.600
1.460
X : parts per Million : Proton


Me
N
O
NC
CN
CO2tBu
3o
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
171.723
170.823
163.393
144.674
135.674
131.873
129.115
129.058
128.244
123.754
122.729
122.231
113.097
112.360
108.702
90.414
85.282
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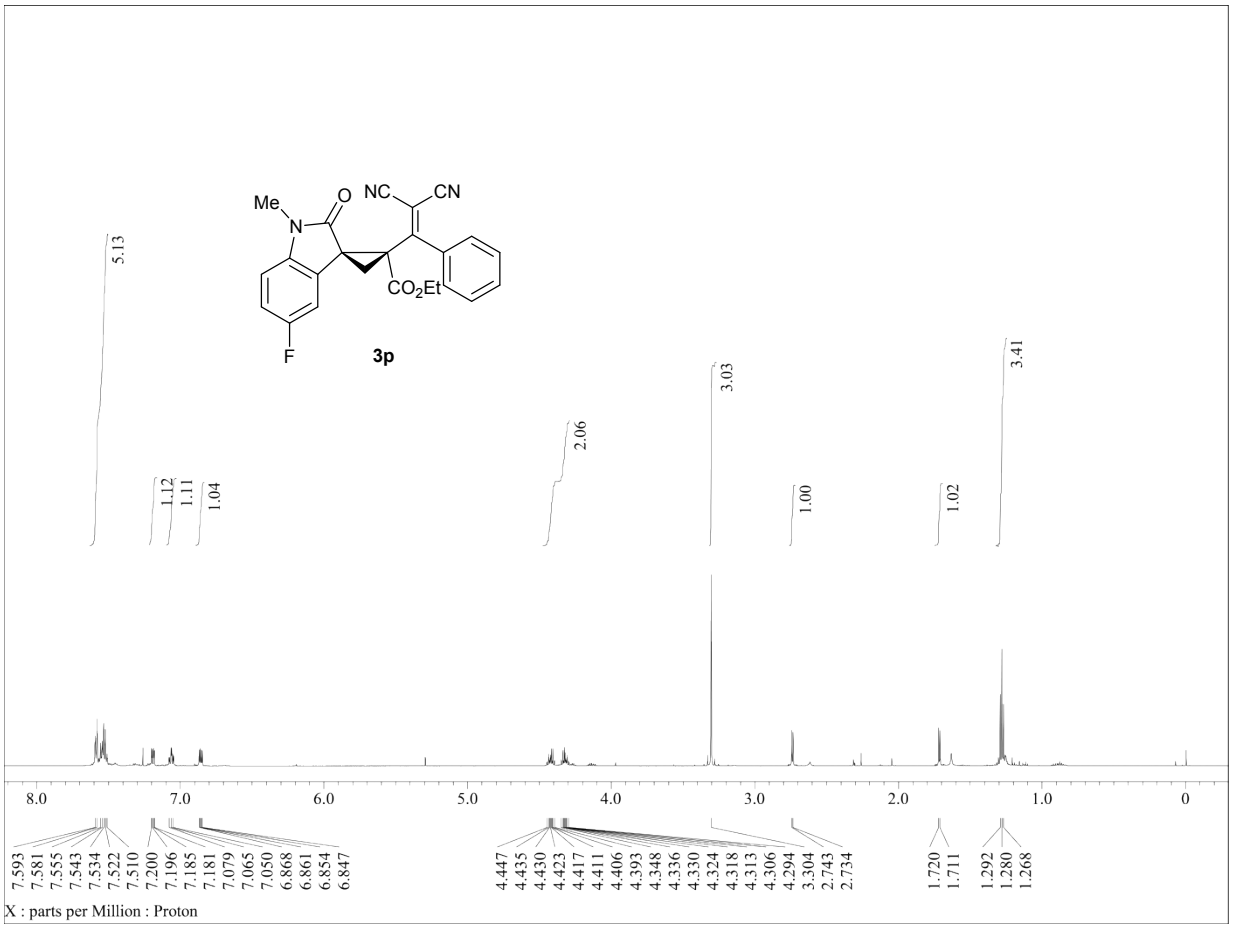
77.000
76.789
46.476
43.546
27.824
26.771
25.124
X : parts per Million : Carbon13


Me
N
O
NC
CN
CO2Et
F
3p
5.13
1.12
1.11
1.04
2.06
3.03
1.00
1.02
3.41
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.593
7.581
7.555
7.543
7.534
7.522
7.510
7.200
7.196
7.185
7.181
7.079
7.065
7.050
6.868
6.861
6.854
6.847
4.447
4.435
4.430
4.423
4.417
4.411
4.406
4.393
4.348
4.336
4.330
4.324
4.318
4.313
4.306
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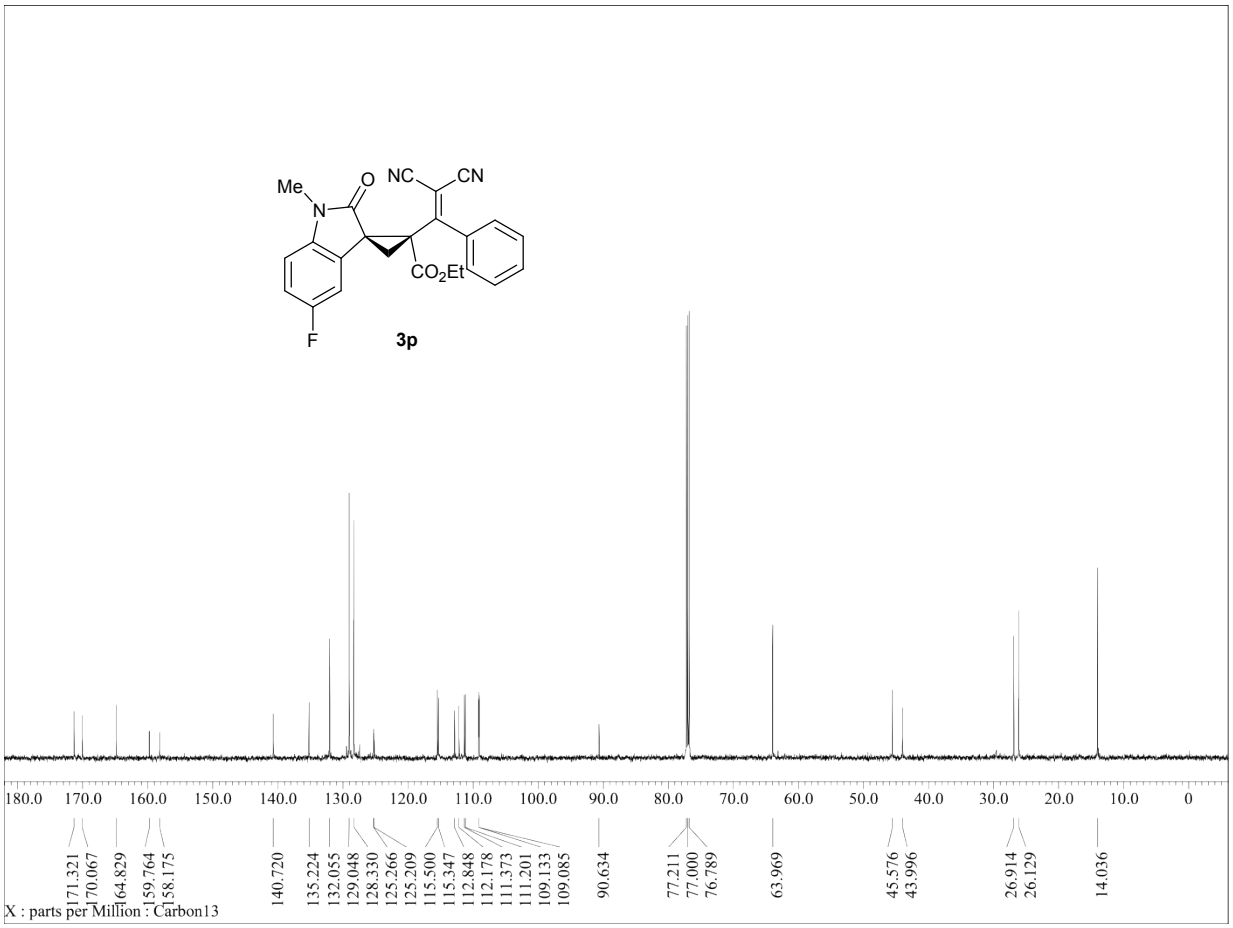
2.734
1.720
1.711
1.292
1.280
1.268
X : parts per Million : Proton


Me
N
O
NC
CN
CO2Et
F
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
171.321
170.067
64.829
59.764
58.175
140.720
135.224
132.055
129.048
128.330
125.266
125.209
115.500
115.347
112.848
112.178
111.373
111.201
109.133
109.085
90.634
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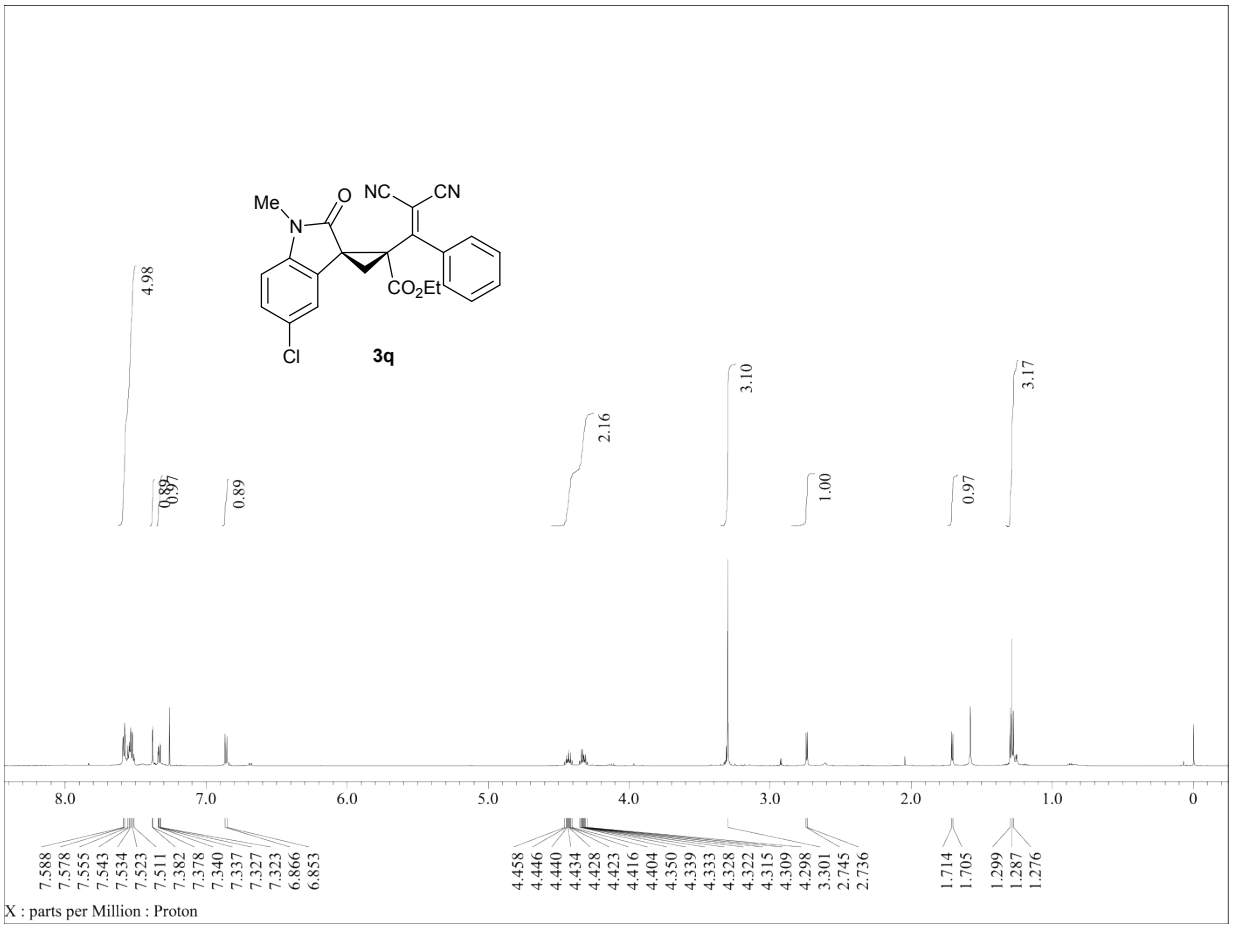
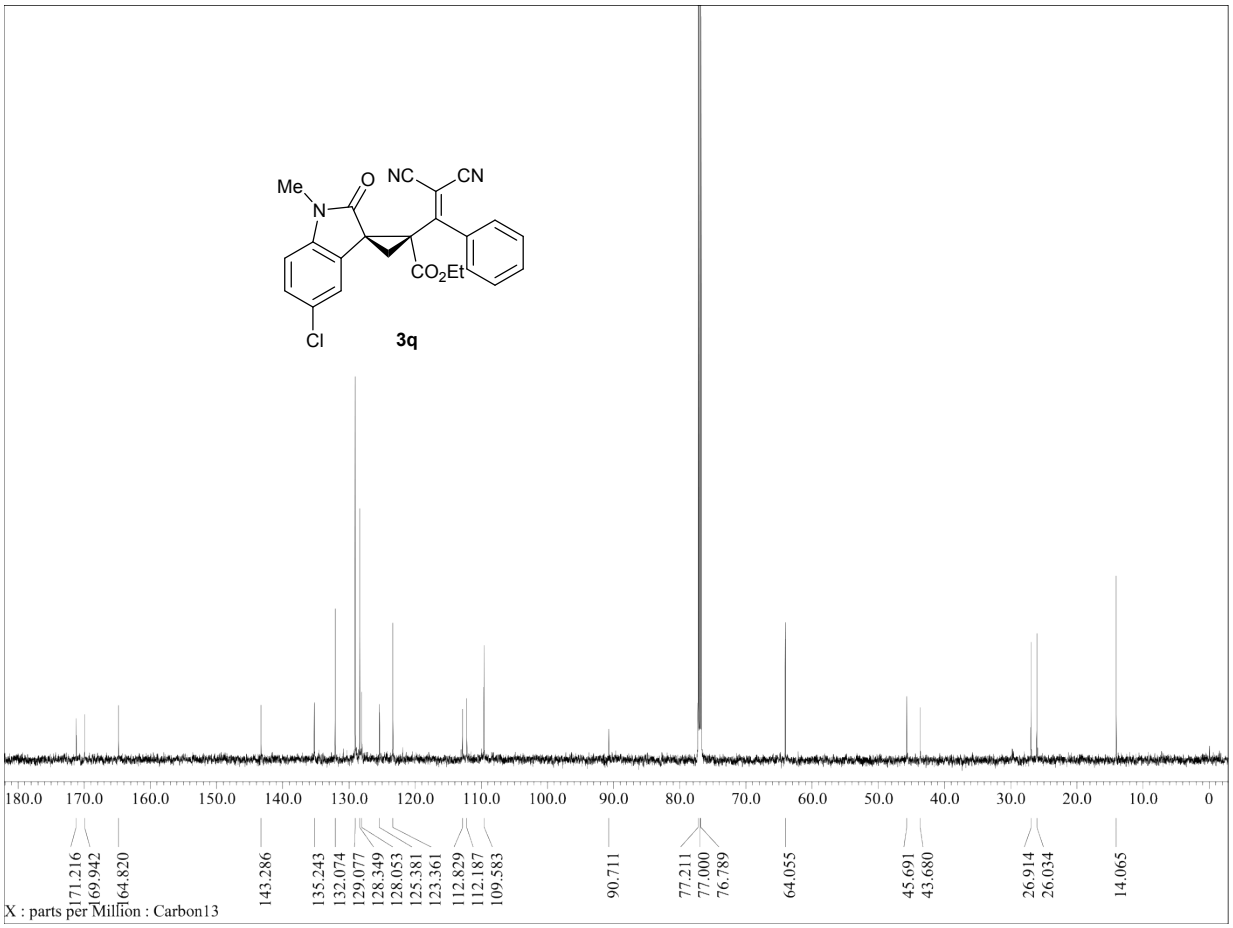
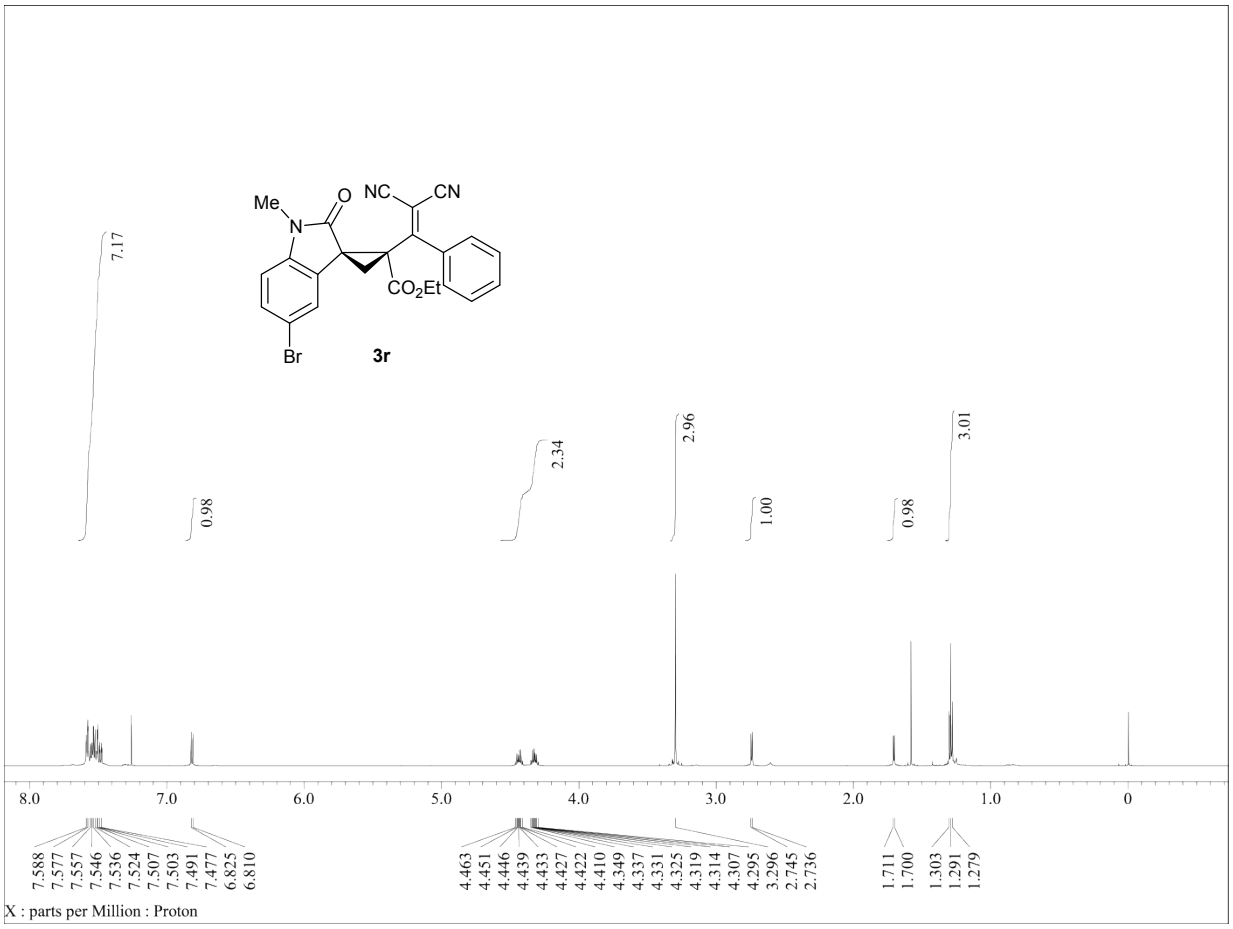
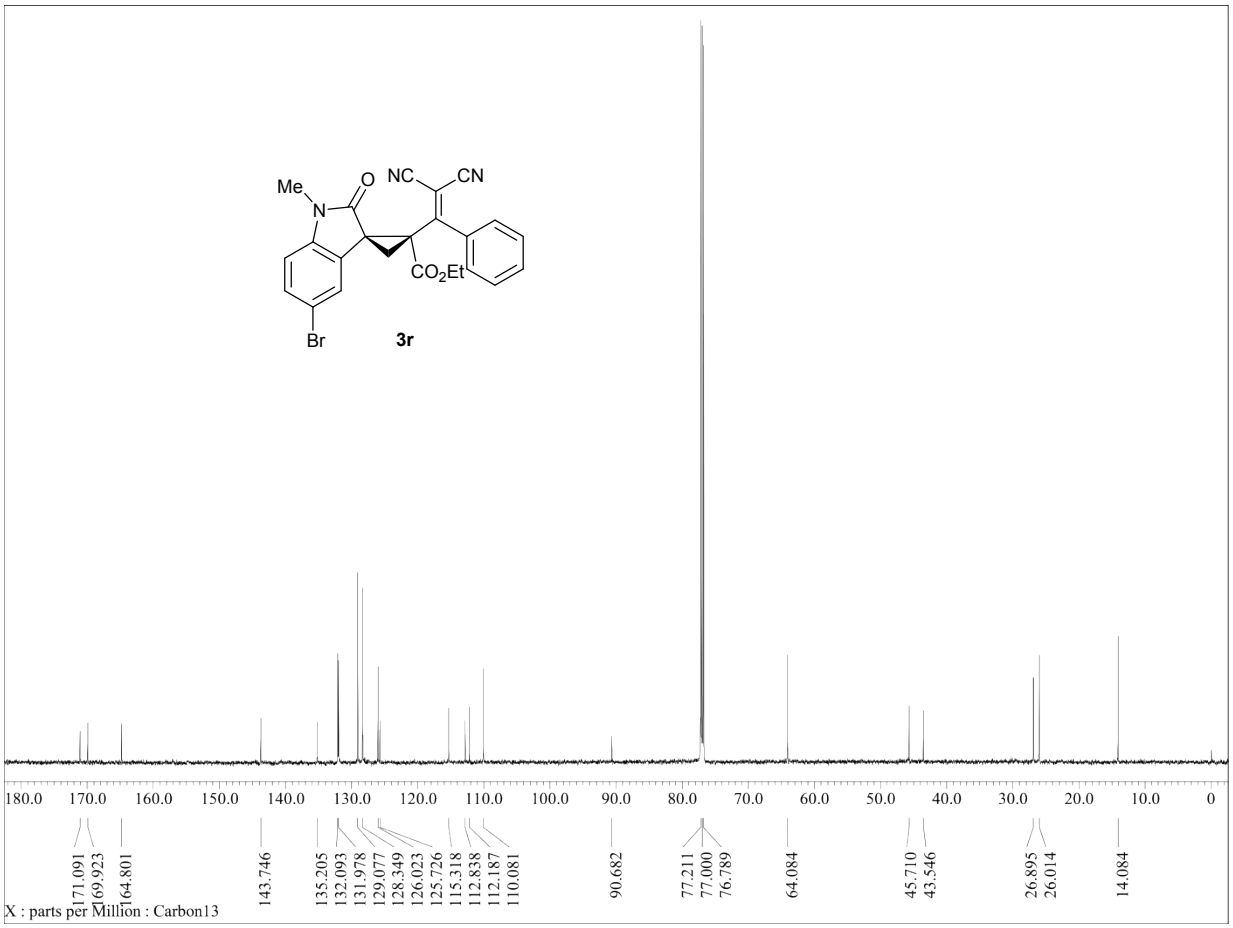
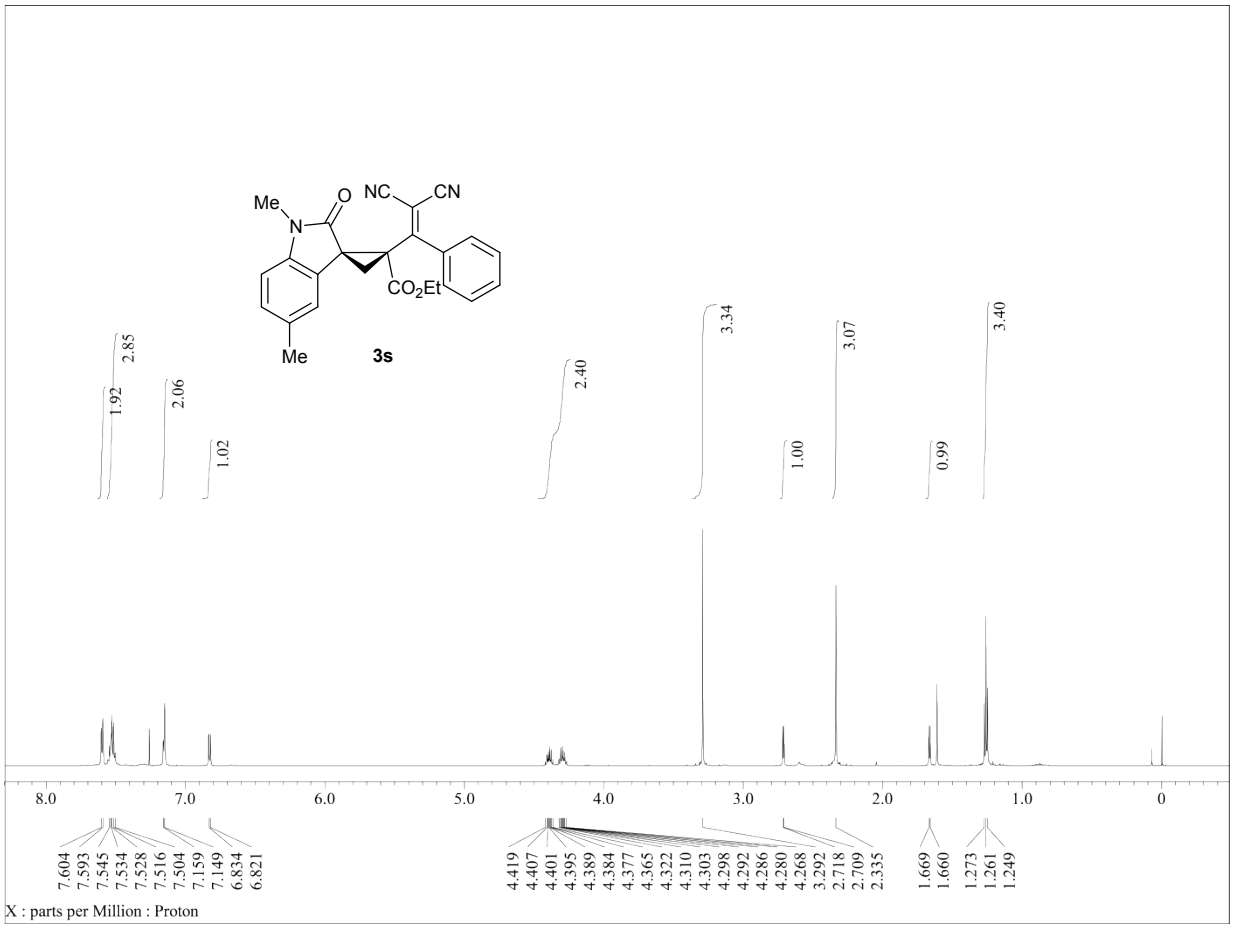
77.000
76.789
63.969
45.576
43.996
26.914
26.129
14.036
X : parts per Million : Carbon13


Me
N
O
NC
CN
CO2Et
Cl
3q
4.98
0.89
0.97
0.89
2.16
3.10
1.00
0.97
3.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.588
7.578
7.555
7.543
7.534
7.523
7.511
7.382
7.378
7.340
7.337
7.327
7.323
6.866
6.853
4.458
4.446
4.440
4.434
4.428
4.423
4.416
4.404
4.350
4.339
4.333
4.328
4.322
4.315
4.309
4.298
3.301
2.745
2.736
1.714
1.705
1.299
1.287
1.276
X : parts per Million : Proton


Me
N
O
NC
CN
CO2Et
Cl
3q
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
171.216
169.942
164.820
143.286
135.243
132.074
129.077
128.349
128.053
125.381
123.361
112.829
112.187
109.583
90.711
77.211
77.000
76.789
64.055
45.691
43.680
26.914
26.034
14.065
X : parts per Million : Carbon13


Me
N
O
NC
CN
CO2Et
Br
3r
7.17
0.98
2.34
2.96
1.00
0.98
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.588
7.577
7.557
7.546
7.536
7.524
7.507
7.503
7.491
7.477
6.825
6.810
4.463
4.451
4.446
4.439
4.433
4.427
4.422
4.410
4.349
4.337
4.331
4.325
4.319
4.314
4.307
4.295
3.296
2.745
2.736
1.711
1.700
1.303
1.291
1.279
X : parts per Million : Proton


Me
N
O
NC
CN
CO2Et
Br
3r
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
171.091
169.923
164.801
143.746
135.205
132.093
131.978
129.077
128.349
126.023
125.726
115.318
112.838
112.187
110.081
90.682
77.211
77.000
76.789
64.084
45.710
43.546
26.895
26.014
14.084
X : parts per Million : Carbon13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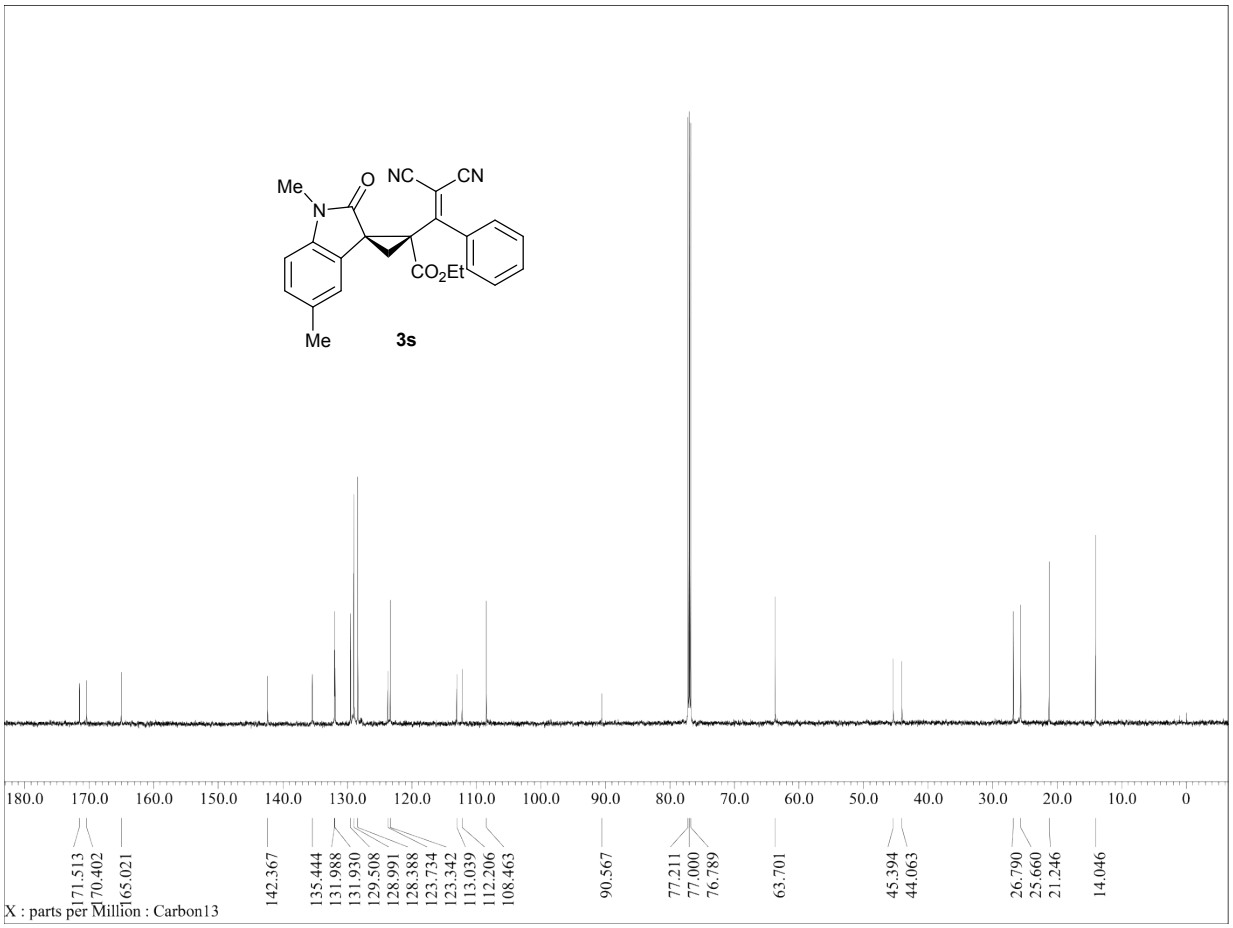
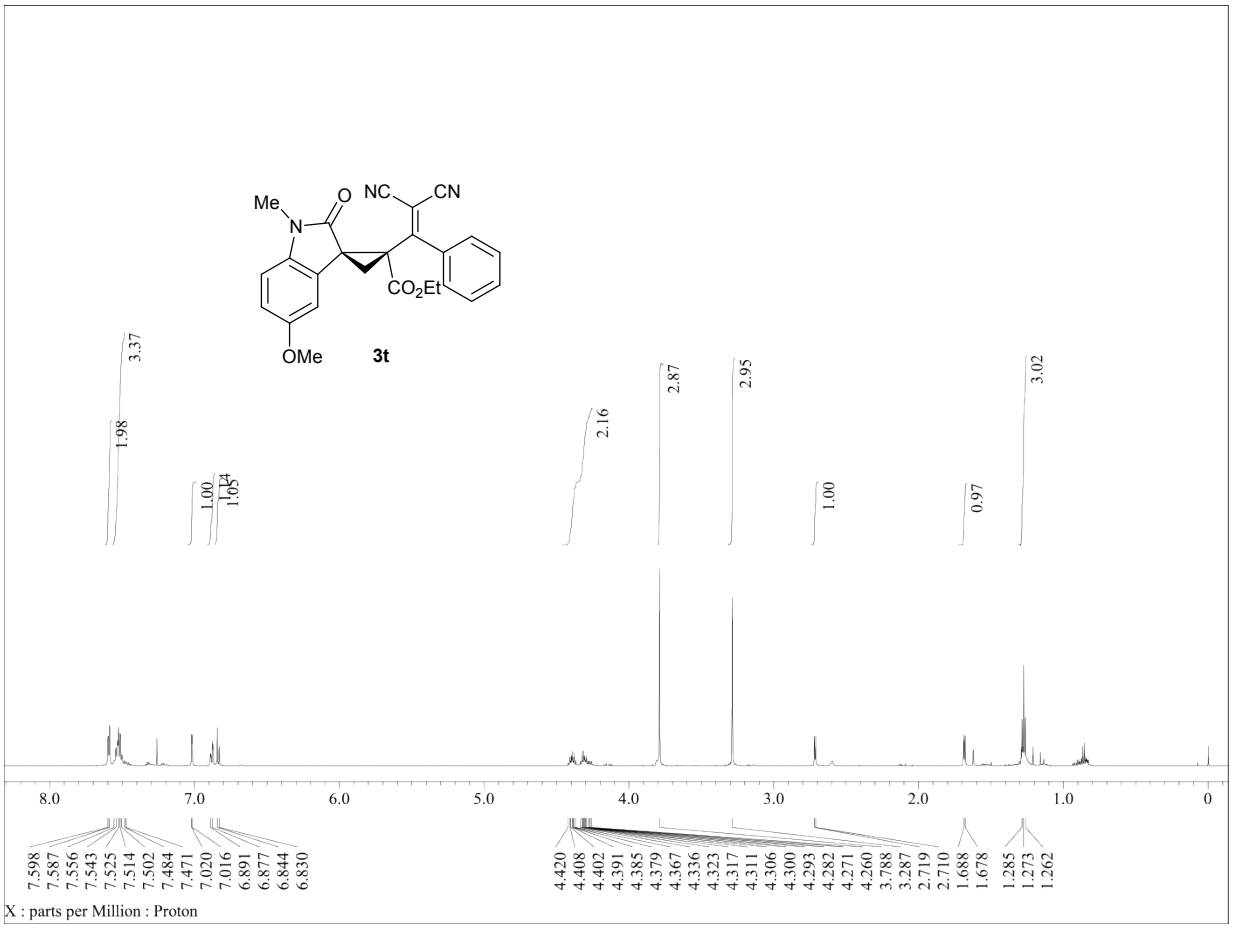
O
NC
CN
N
CO2Et
Me
3s
2.85
1.92
2.06
1.02
2.40
3.34
1.00
3.07
0.99
3.40
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.604
7.593
7.545
7.534
7.528
7.516
7.504
7.159
7.149
6.834
6.821
4.419
4.407
4.401
4.395
4.389
4.384
4.377
4.365
4.322
4.310
4.303
4.298
4.292
4.286
4.280
4.268
3.292
2.718
2.709
2.335
1.669
1.660
1.273
1.261
1.249
X : parts per Million : Proton


Me
O
NC
CN
N
CO2Et
Me
3s
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
171.513
170.402
165.021
142.367
135.444
131.988
131.930
129.508
128.991
128.388
123.734
123.342
113.039
112.206
108.463
90.567
77.211
77.000
76.789
63.701
45.394
44.063
26.790
25.660
21.246
14.046
X : parts per Million : Carbon13


Me
N
O
NC
CN
CO2Et
OMe
3t
3.37
1.98
1.00
1.04
1.05
2.16
2.87
2.95
1.00
0.97
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.598
7.587
7.556
7.543
7.525
7.514
7.502
7.484
7.471
7.020
7.016
6.891
6.877
6.844
6.830
4.420
4.408
4.402
4.391
4.385
4.379
4.367
4.336
4.323
4.317
4.311
4.306
4.300
4.293
4.282
4.271
4.260
3.788
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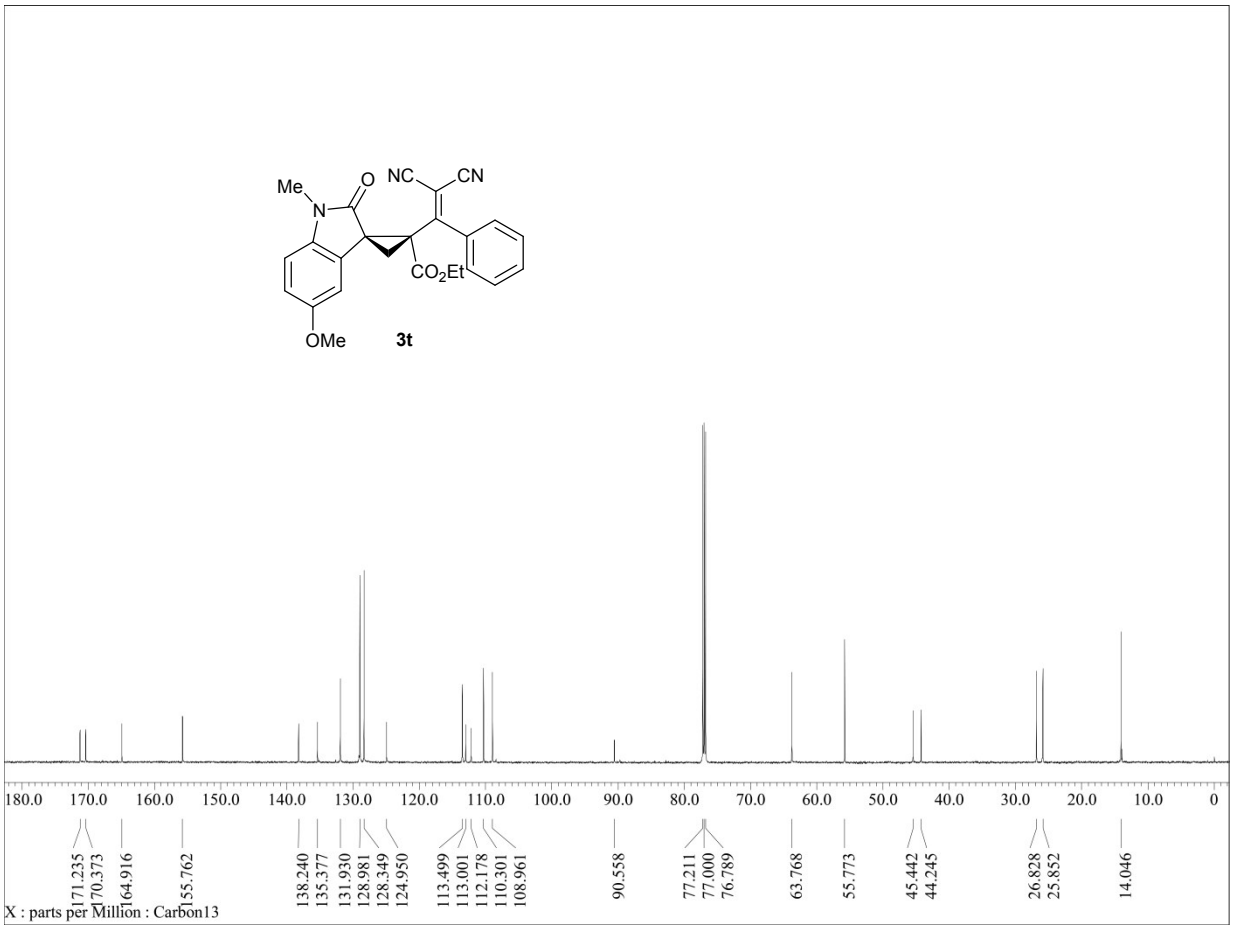
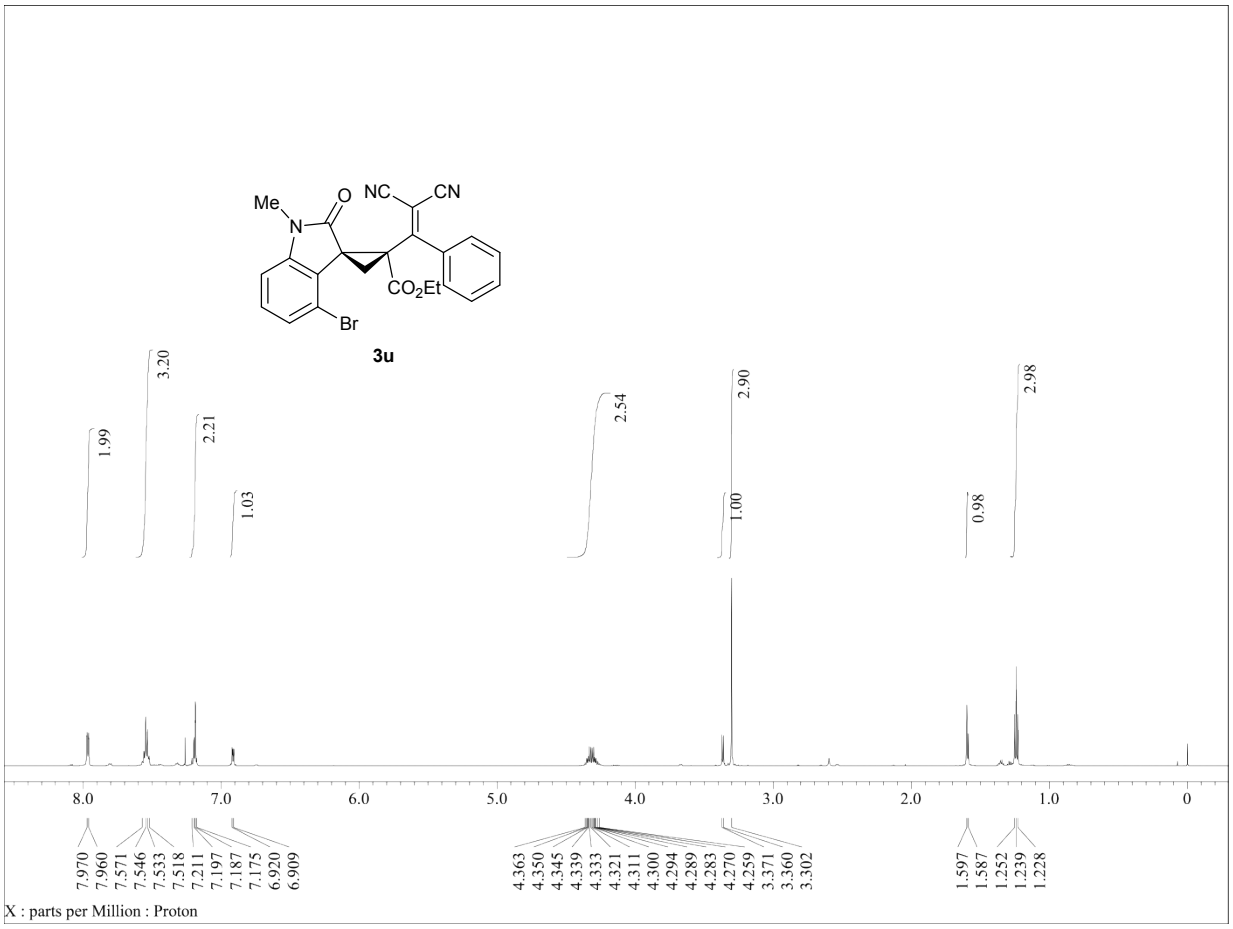
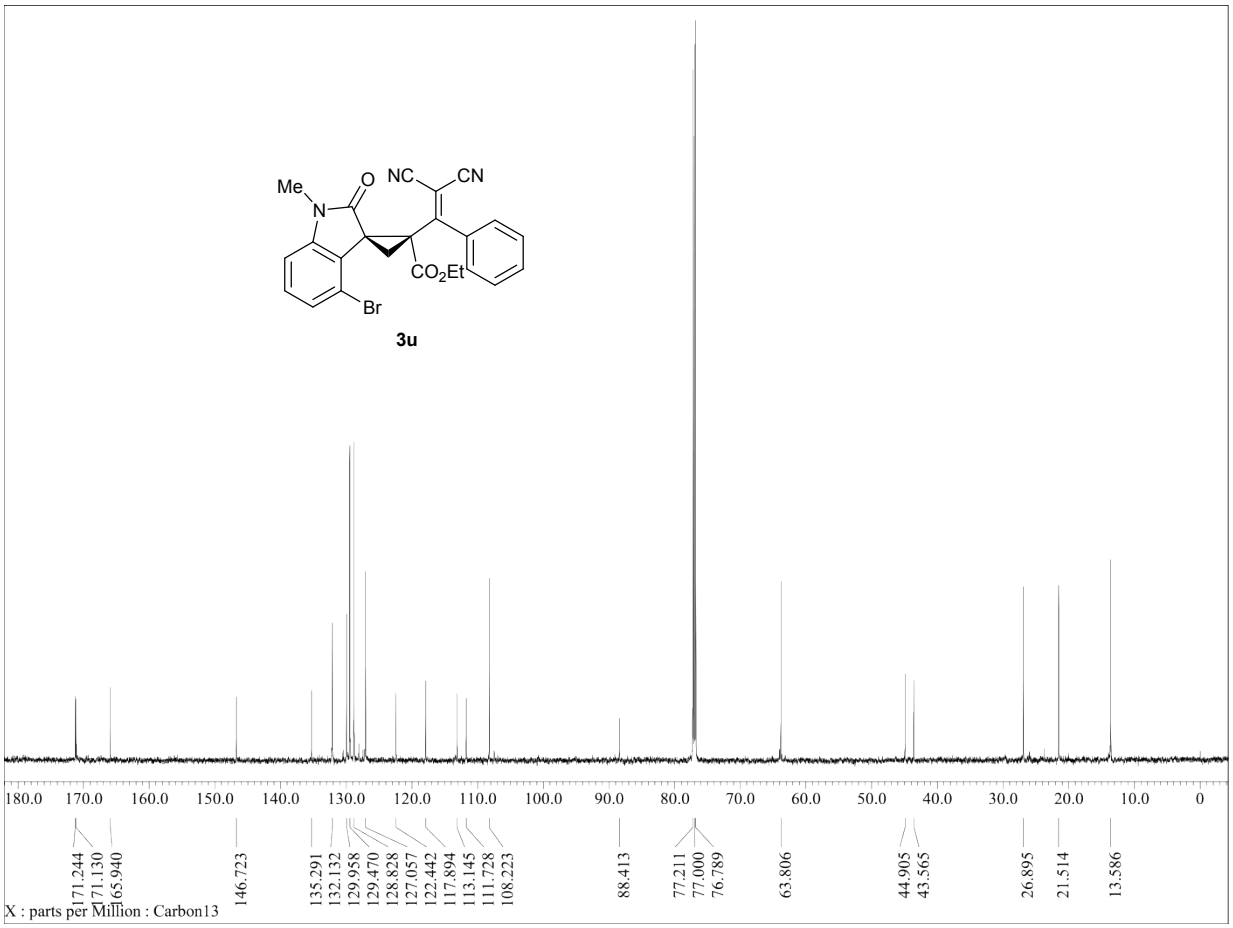
1.688
1.678
1.285
1.273
1.262
X : parts per Million : Proton


Me
N
O
NC
CN
CO2Et
OMe
3t
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
171.235
170.373
164.916
155.762
138.240
135.377
131.930
128.981
128.349
124.950
113.499
113.001
112.178
110.301
108.961
90.558
77.211
77.000
76.789
63.768
55.773
45.442
44.245
26.828
25.852
14.046
X : parts per Million : Carbon13


Me
N
O
NC
CN
CO2Et
Br
3u
1.99
3.20
2.21
1.03
2.54
2.90
1.00
0.98
2.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.970
7.960
7.571
7.546
7.533
7.518
7.211
7.197
7.187
7.175
6.920
6.909
4.363
4.350
4.345
4.339
4.333
4.321
4.311
4.300
4.294
4.289
4.283
4.270
4.259
3.371
3.360
3.302
1.597
1.587
1.252
1.239
1.228
X : parts per Million : Proton


Me
N
O
NC
CN
CO2Et
Br
3u
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
171.244
171.130
165.940
146.723
135.291
132.132
129.958
129.470
128.828
127.057
122.442
117.894
113.145
111.728
108.223
88.413
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77.000
76.789
63.806
44.905
43.565
26.895
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13.586
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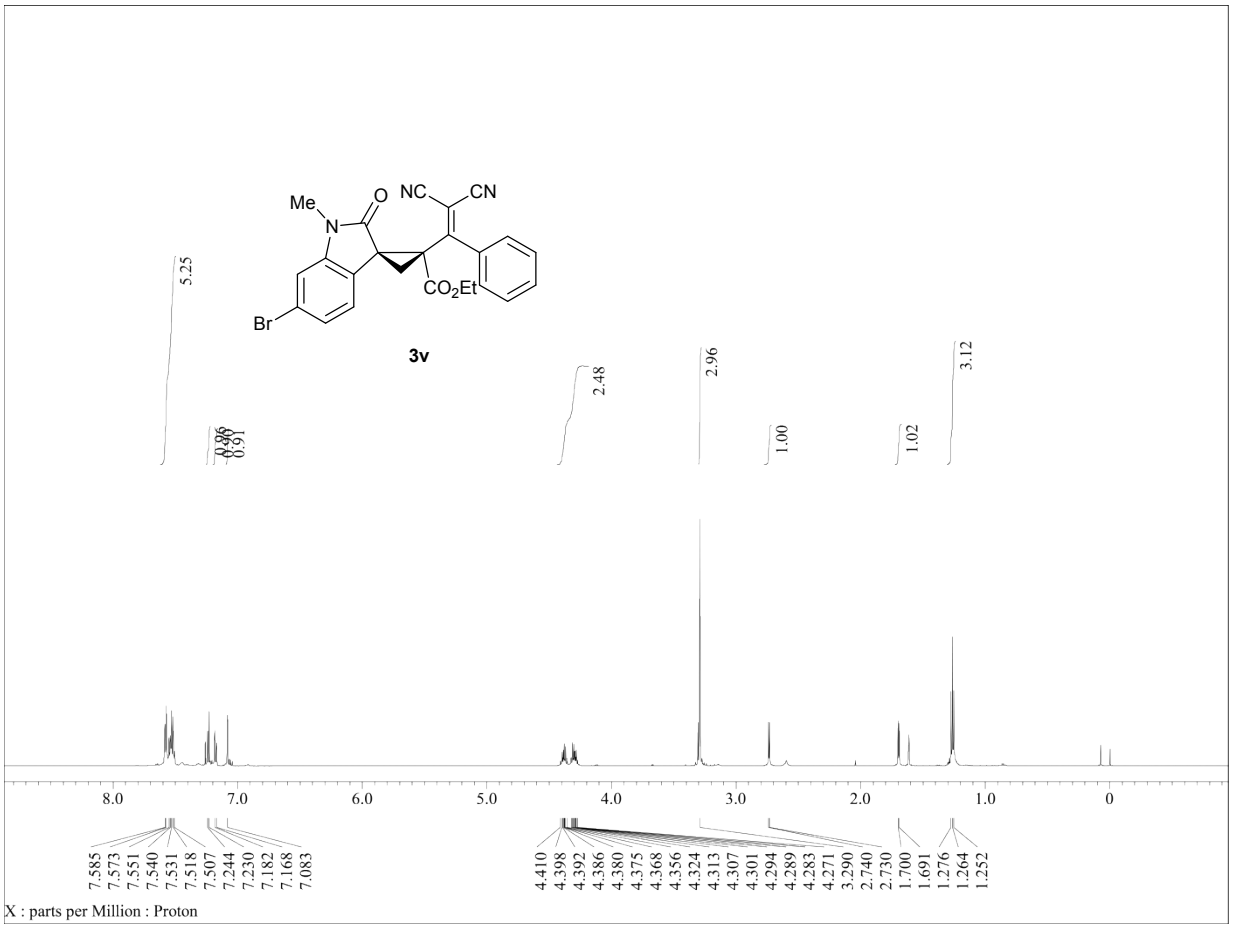
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O
NC
CN
CO2Et
Br
3v
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2.96
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1.02
3.12
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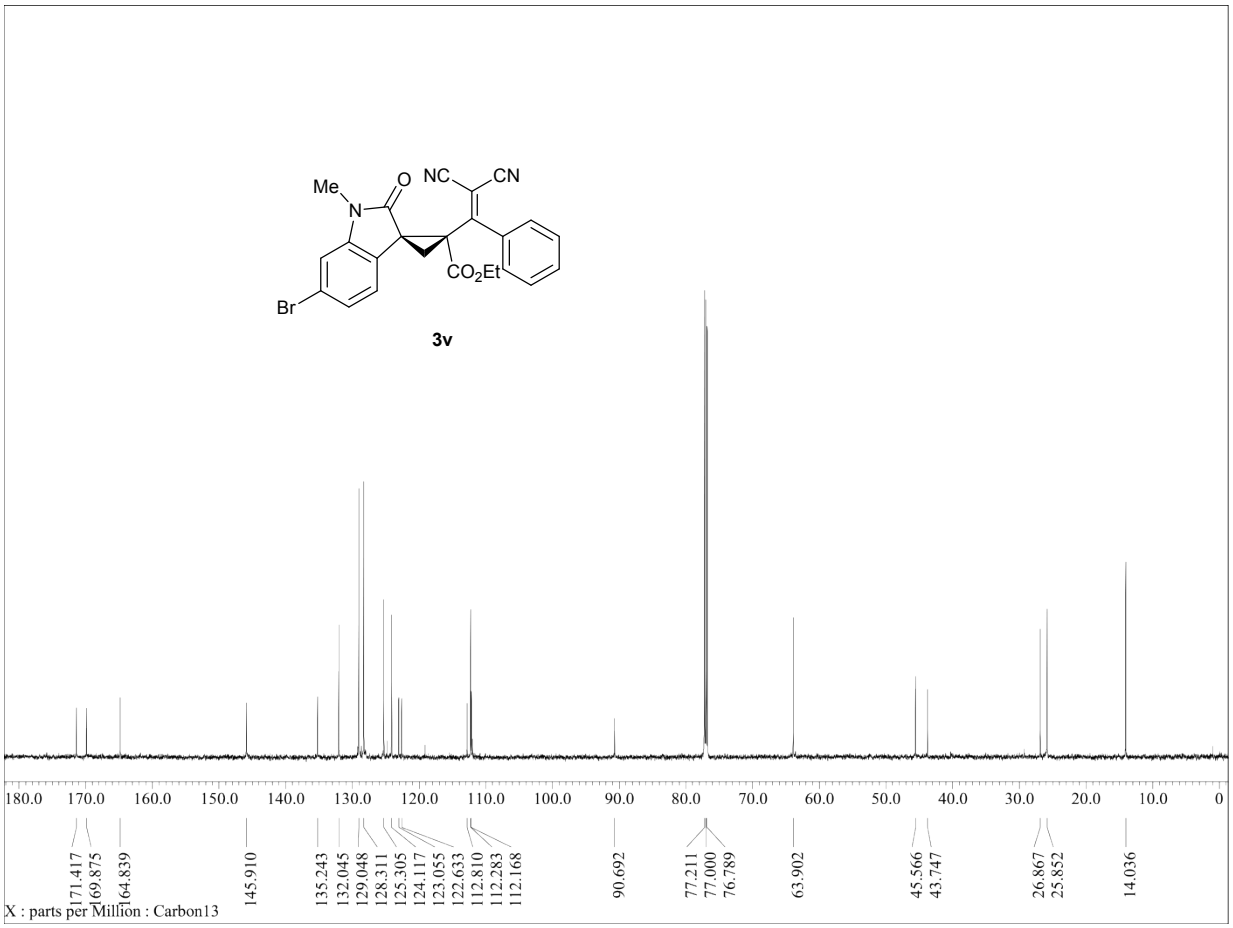
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.585
7.573
7.551
7.540
7.531
7.518
7.507
7.244
7.230
7.182
7.168
7.083
4.410
4.398
4.392
4.386
4.380
4.375
4.368
4.356
4.324
4.313
4.307
4.301
4.294
4.289
4.283
4.271
3.290
2.740
2.730
1.700
1.691
1.276
1.264
1.252
X : parts per Million : Proton


Me
N
O
NC
CN
CO2Et
Br
3v
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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
171.417
169.875
164.839
145.910
135.243
132.045
129.048
128.311
125.305
124.117
123.055
122.633
112.810
112.283
112.168
90.692
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76.789
63.902
45.566
43.747
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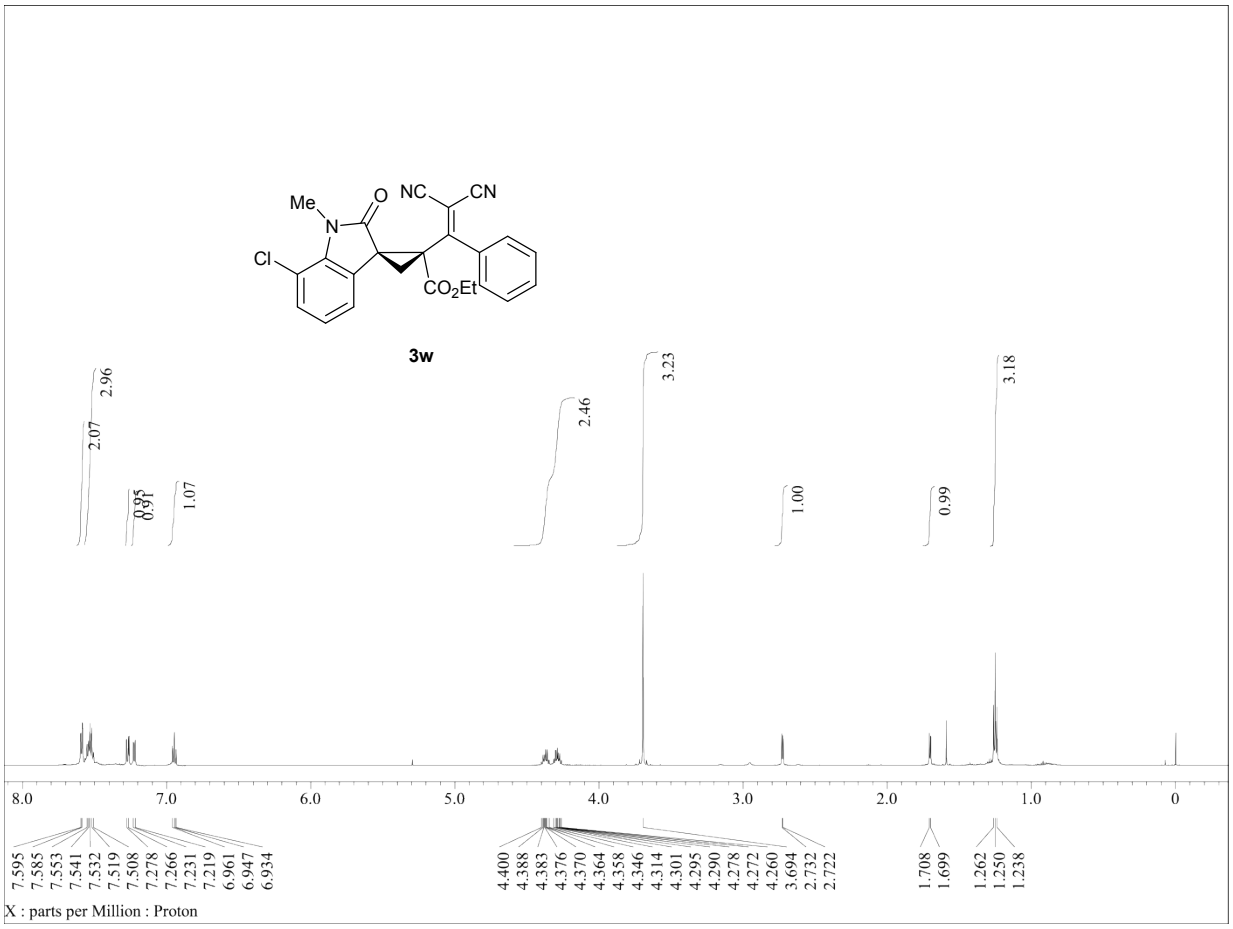
X : parts per Million : Carbon13


Me
N
O
NC
CN
Cl
CO2Et
3w
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2.07
0.95
0.91
1.07
2.46
3.23
1.00
0.99
3.18
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.595
7.585
7.553
7.541
7.532
7.519
7.508
7.278
7.266
7.231
7.219
6.961
6.947
6.934
4.400
4.388
4.383
4.376
4.370
4.364
4.358
4.346
4.314
4.301
4.295
4.290
4.278
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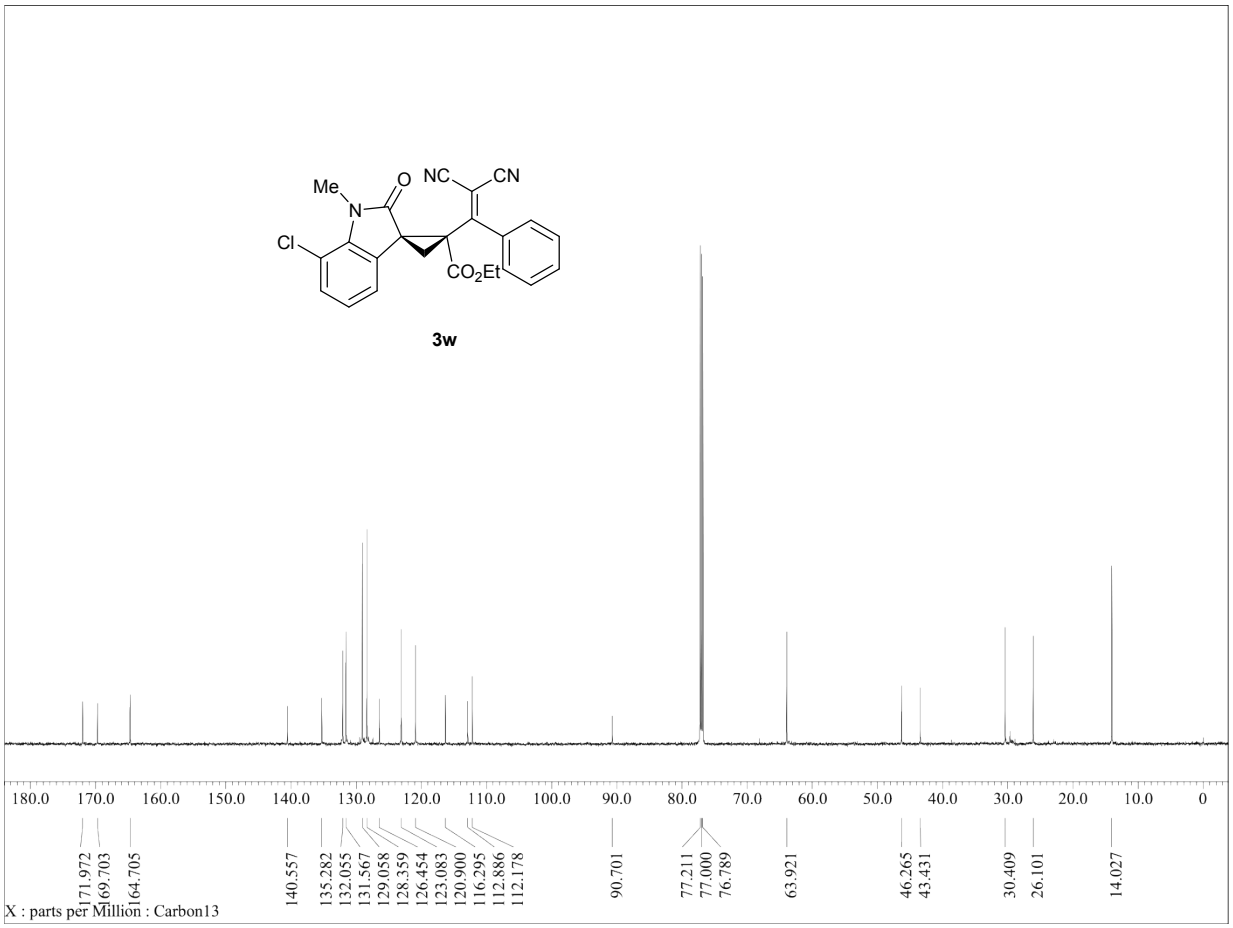
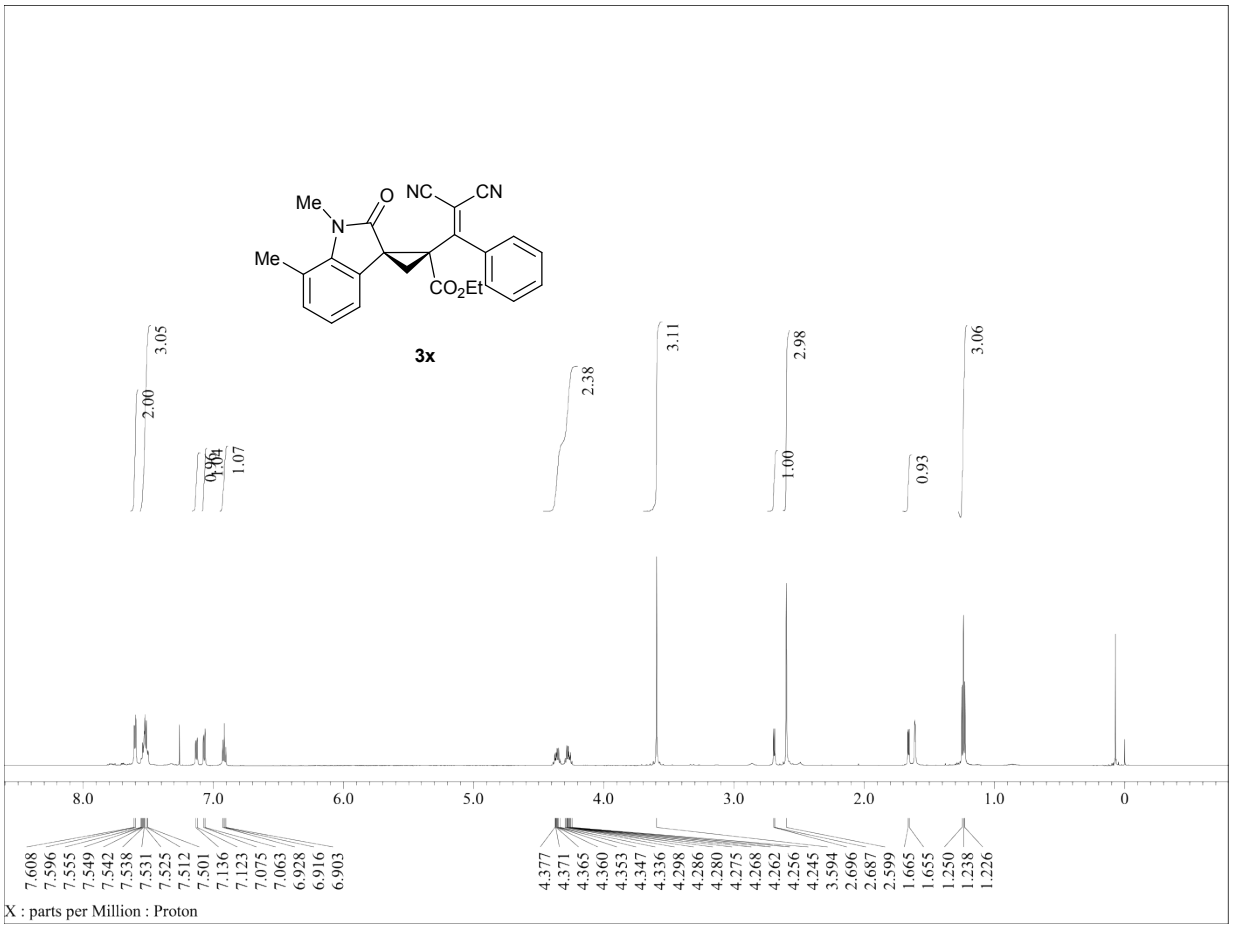
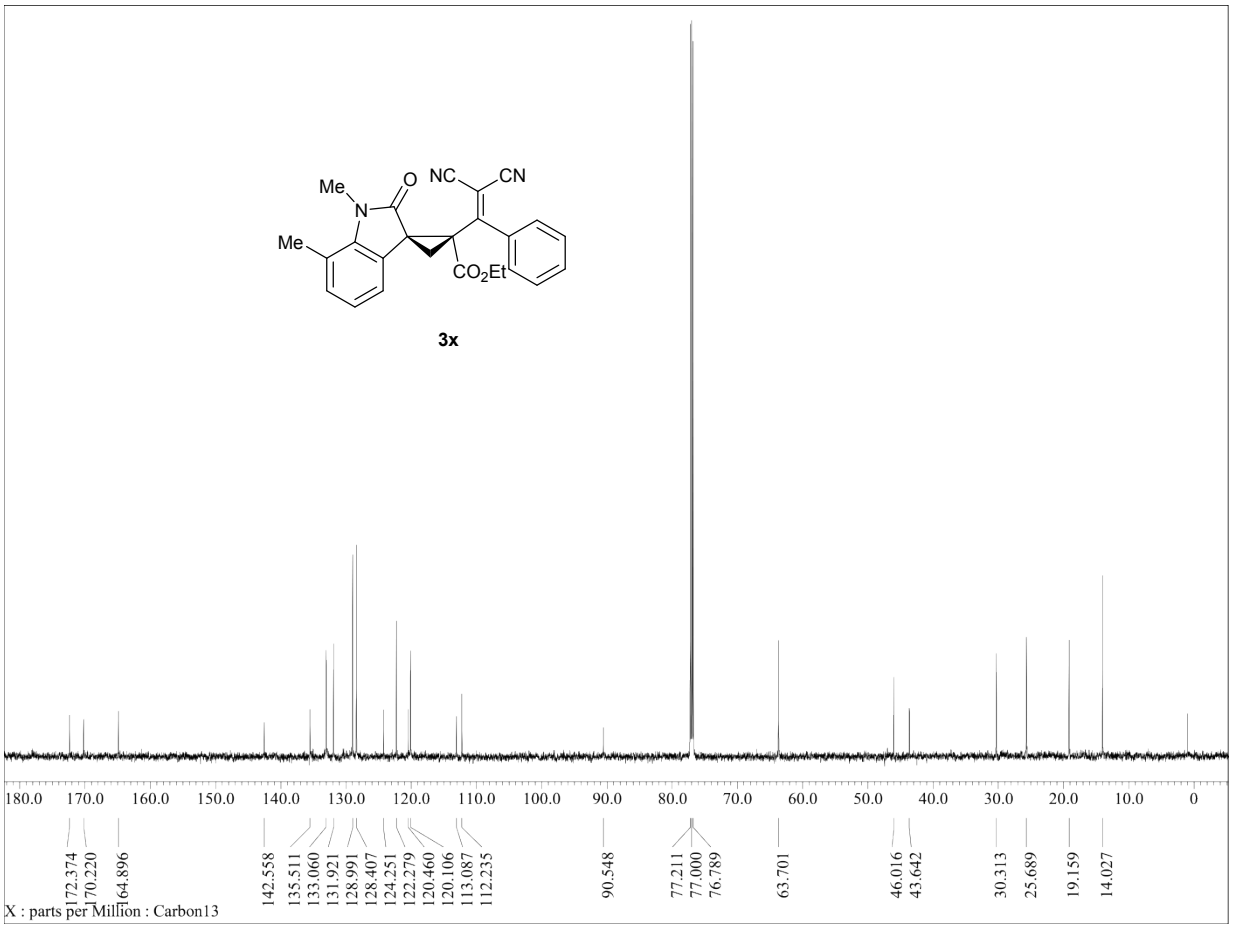
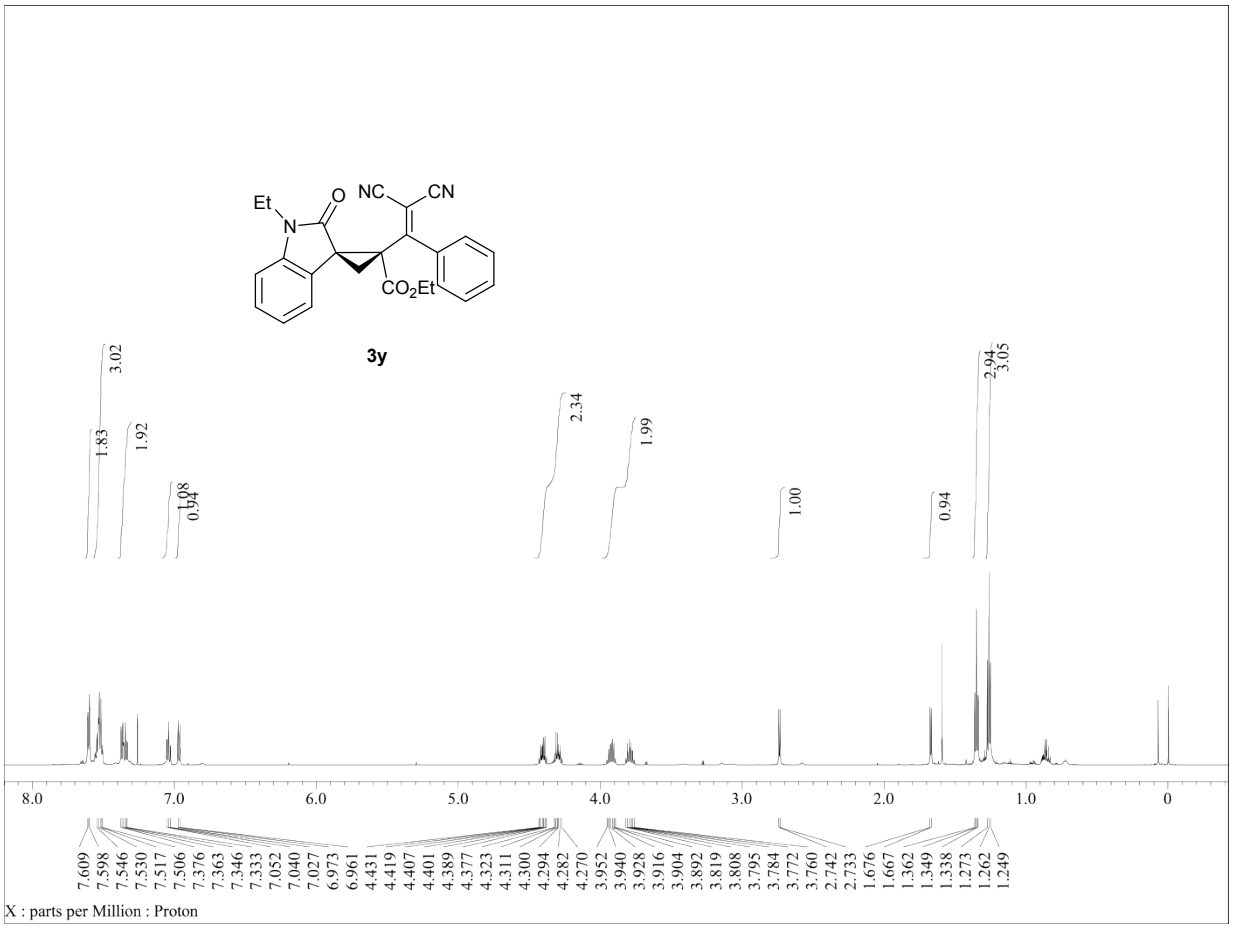
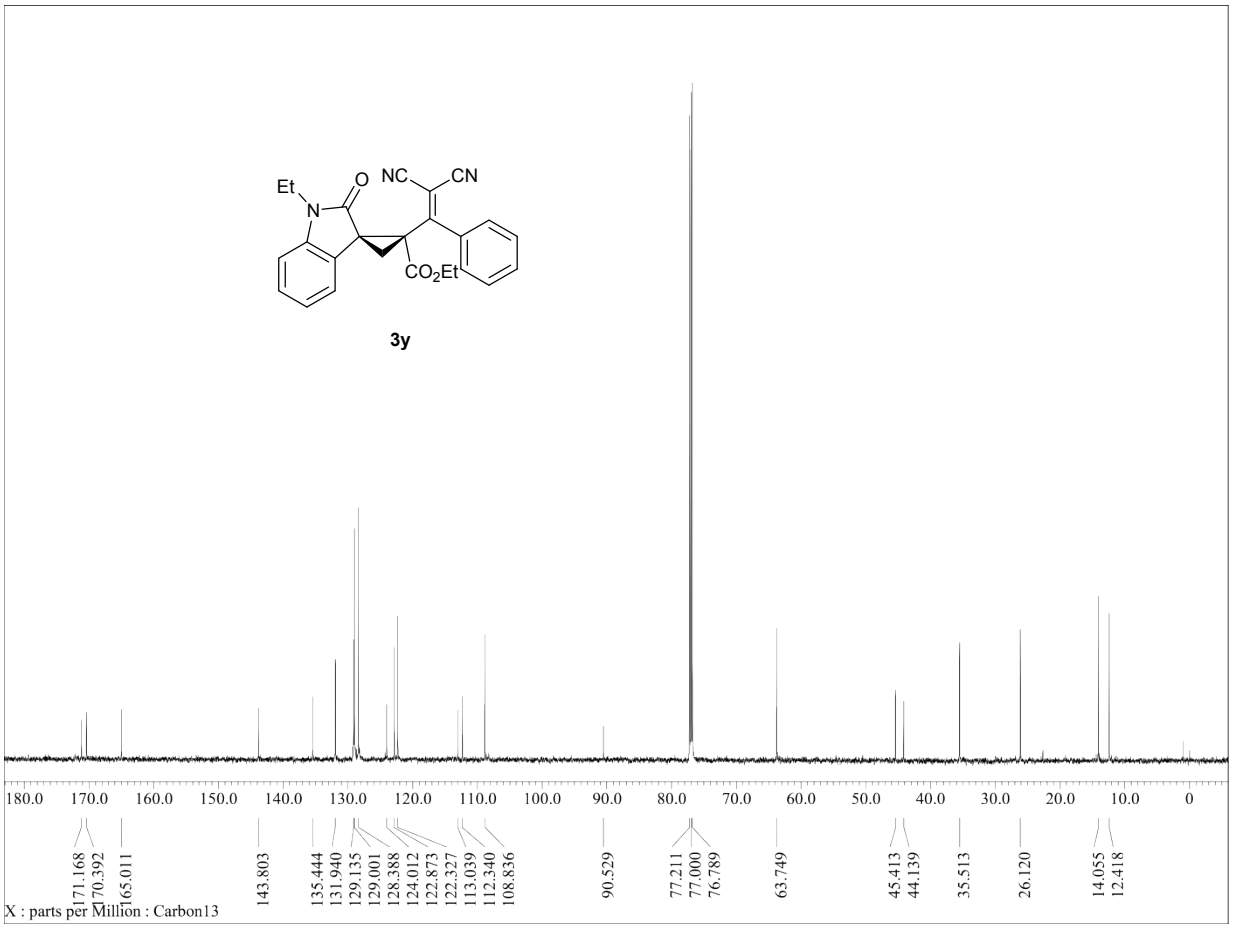
3.694
2.732
2.722
1.708
1.699
1.262
1.250
1.238
X : parts per Million : Proton


Me
N
O
NC
CN
Cl
CO2Et
3w
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
171.972
169.703
164.705
140.557
135.282
132.055
131.567
129.058
128.359
126.454
123.083
120.900
116.295
112.886
112.178
90.701
77.211
77.000
76.789
63.921
46.265
43.431
30.409
26.101
14.027
X : parts per Million : Carbon13


Me
N
O
NC
CN
Me
CO2Et
3x
3.05
2.00
0.96
1.04
1.07
2.38
3.11
2.98
1.00
0.93
3.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.608
7.596
7.555
7.549
7.542
7.538
7.531
7.525
7.512
7.501
7.136
7.123
7.075
7.063
6.928
6.916
6.903
4.377
4.371
4.365
4.360
4.353
4.347
4.336
4.298
4.286
4.280
4.275
4.268
4.262
4.256
4.245
3.594
2.696
2.687
2.599
1.665
1.655
1.250
1.238
1.226
X : parts per Million : Proton


Me
N
O
NC
CN
Me
CO2Et
3x
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
172.374
170.220
64.896
142.558
135.511
133.060
131.921
128.991
128.407
124.251
122.279
120.460
120.106
113.087
112.235
90.548
77.211
77.000
76.789
63.701
46.016
43.642
30.313
25.689
19.159
14.027
X : parts per Million : Carbon13


Et
N
O
NC
CN
CO2Et
3y
3.02
1.83
1.92
1.08
0.94
2.34
1.99
1.00
0.94
2.94
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.609
7.598
7.546
7.530
7.517
7.506
7.376
7.363
7.346
7.333
7.052
7.040
7.027
6.973
6.961
4.431
4.419
4.407
4.401
4.389
4.377
4.323
4.311
4.300
4.294
4.282
4.270
3.952
3.940
3.928
3.916
3.904
3.892
3.819
3.808
3.795
3.784
3.772
3.760
2.742
2.733
1.676
1.667
1.362
1.349
1.338
1.273
1.262
1.249
X : parts per Million : Proton


Et
N
O
NC
CN
CO2Et
3y
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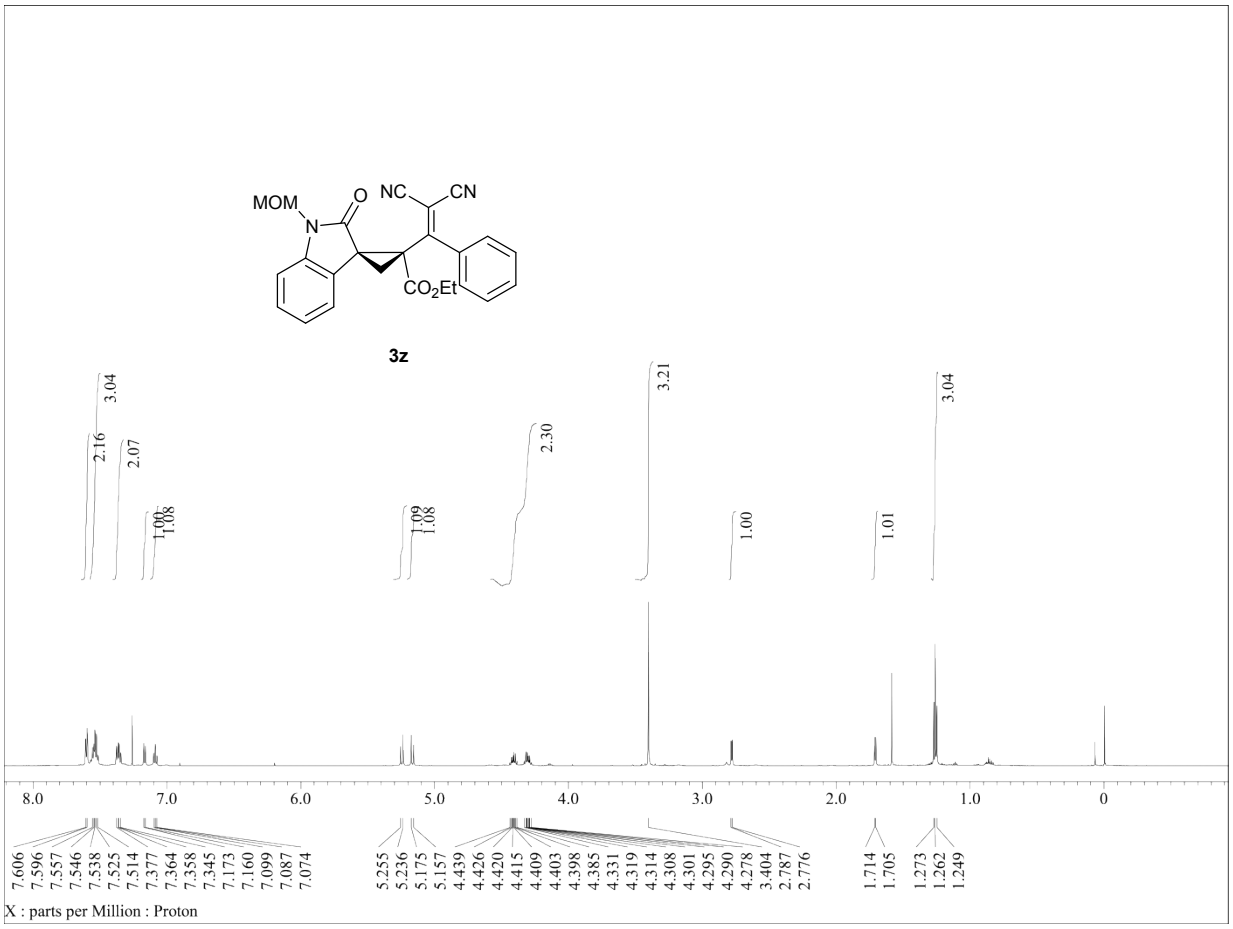
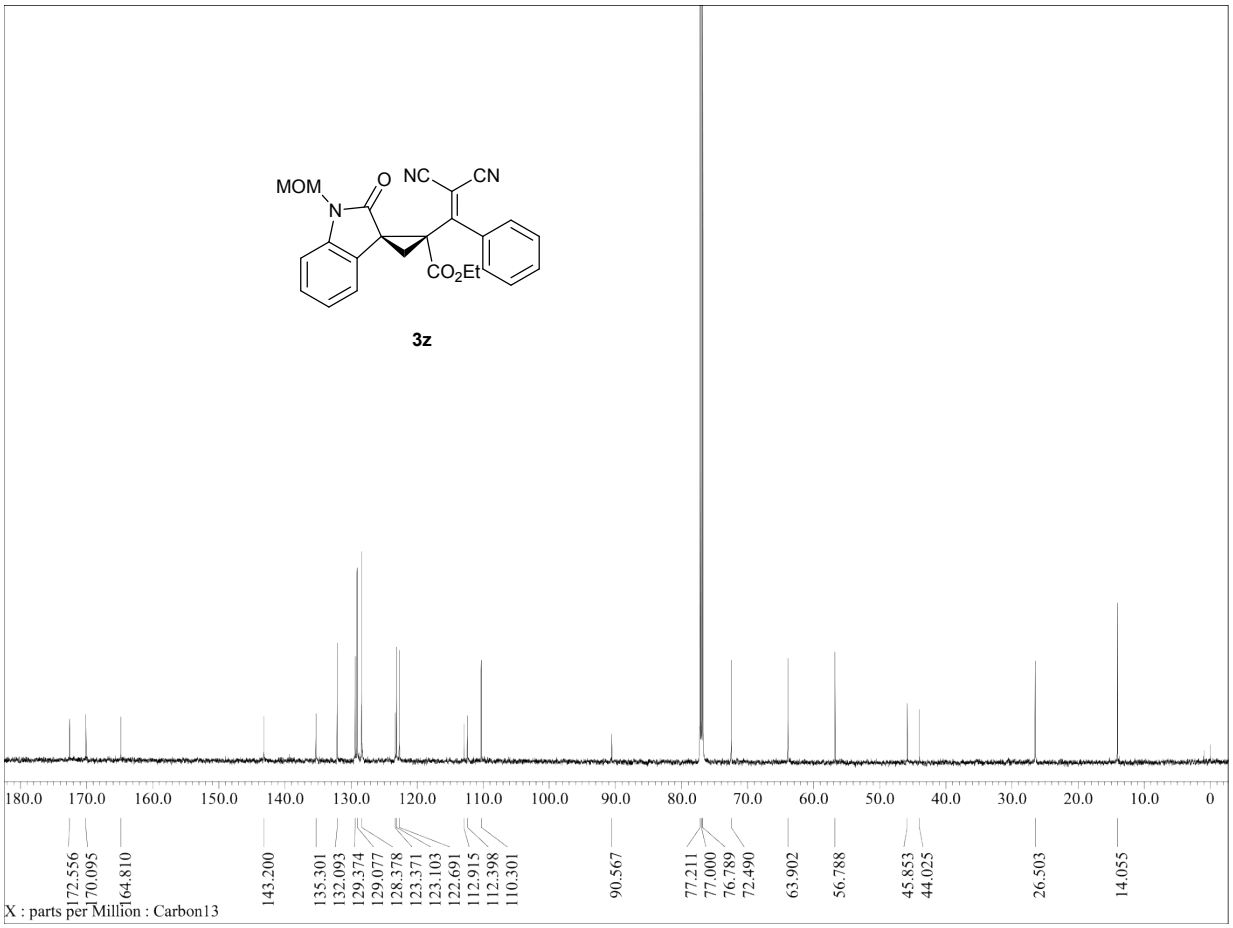
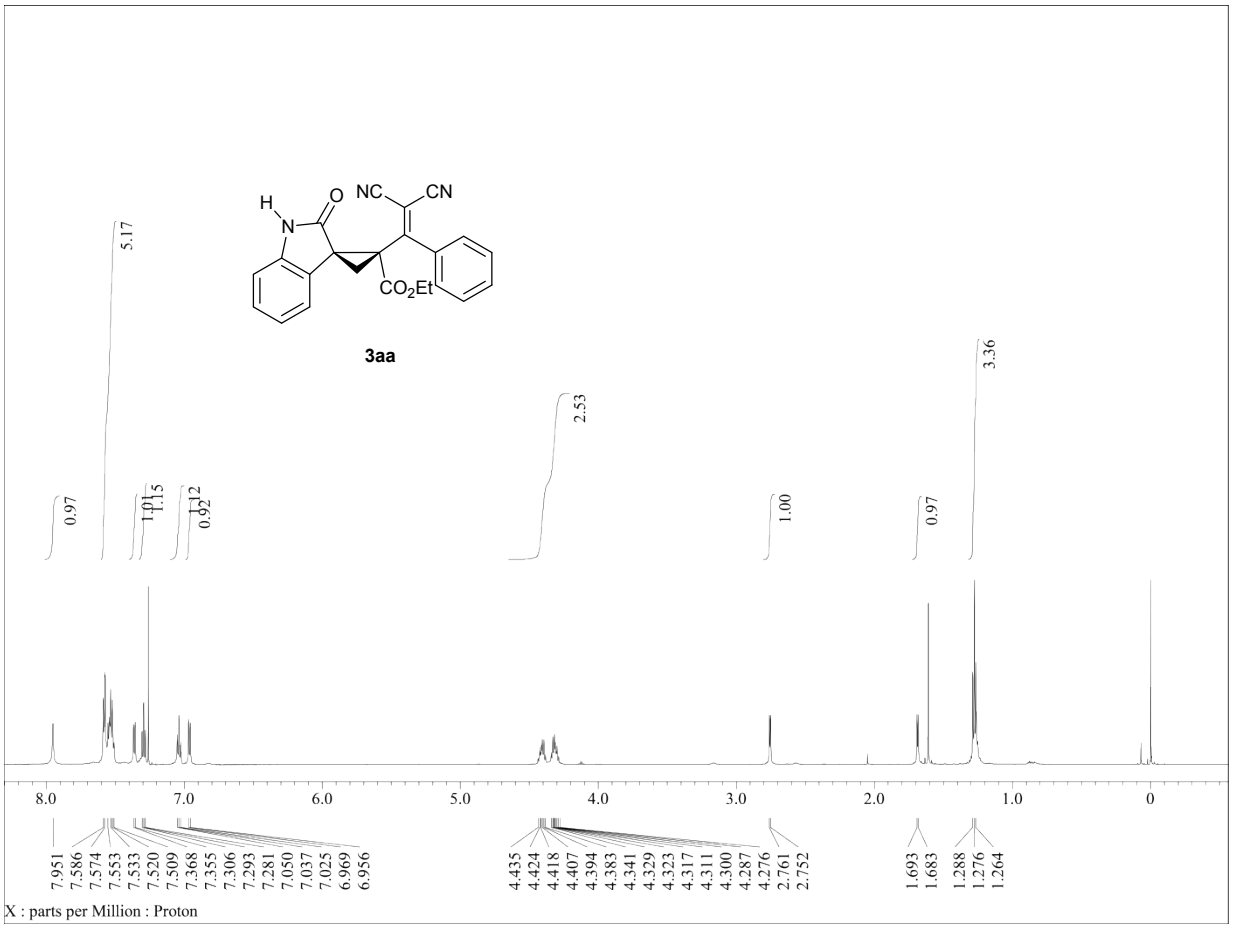
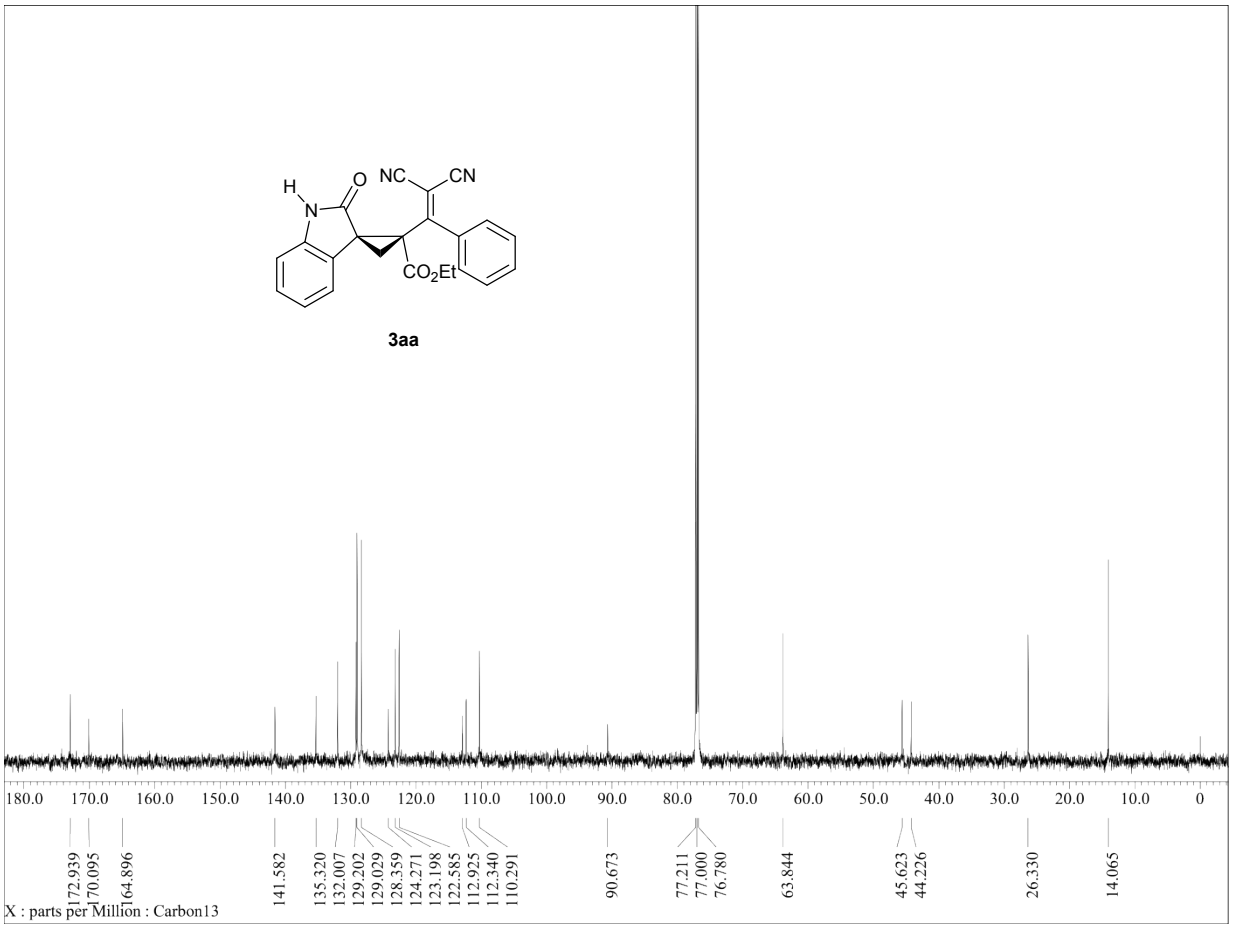
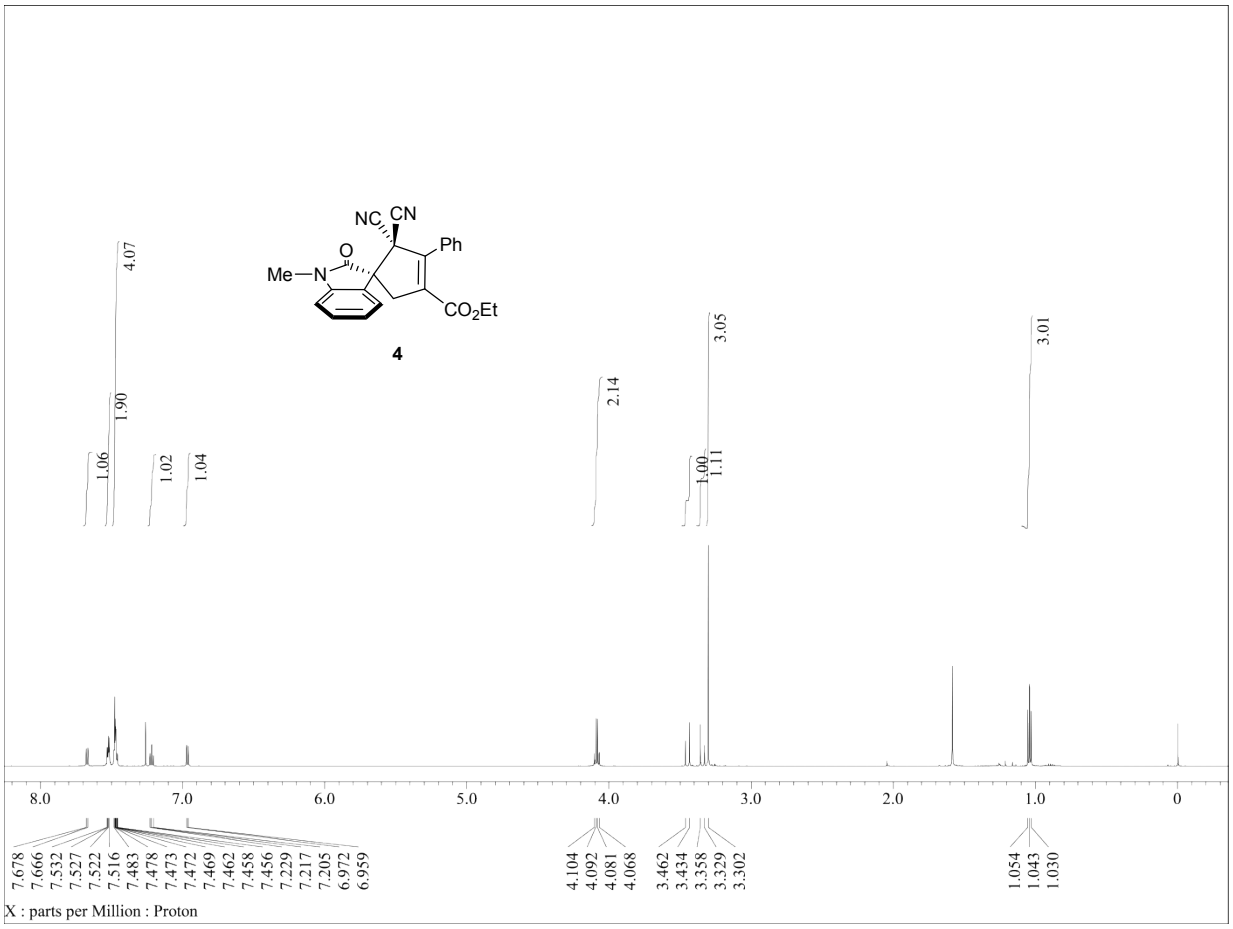
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.168
170.392
165.011
143.803
135.444
131.940
129.135
129.001
128.388
124.012
122.873
122.327
113.039
112.340
108.836
90.529
77.211
77.000
76.789
63.749
45.413
44.139
35.513
26.120
14.055
12.418
X : parts per Million : Carbon13

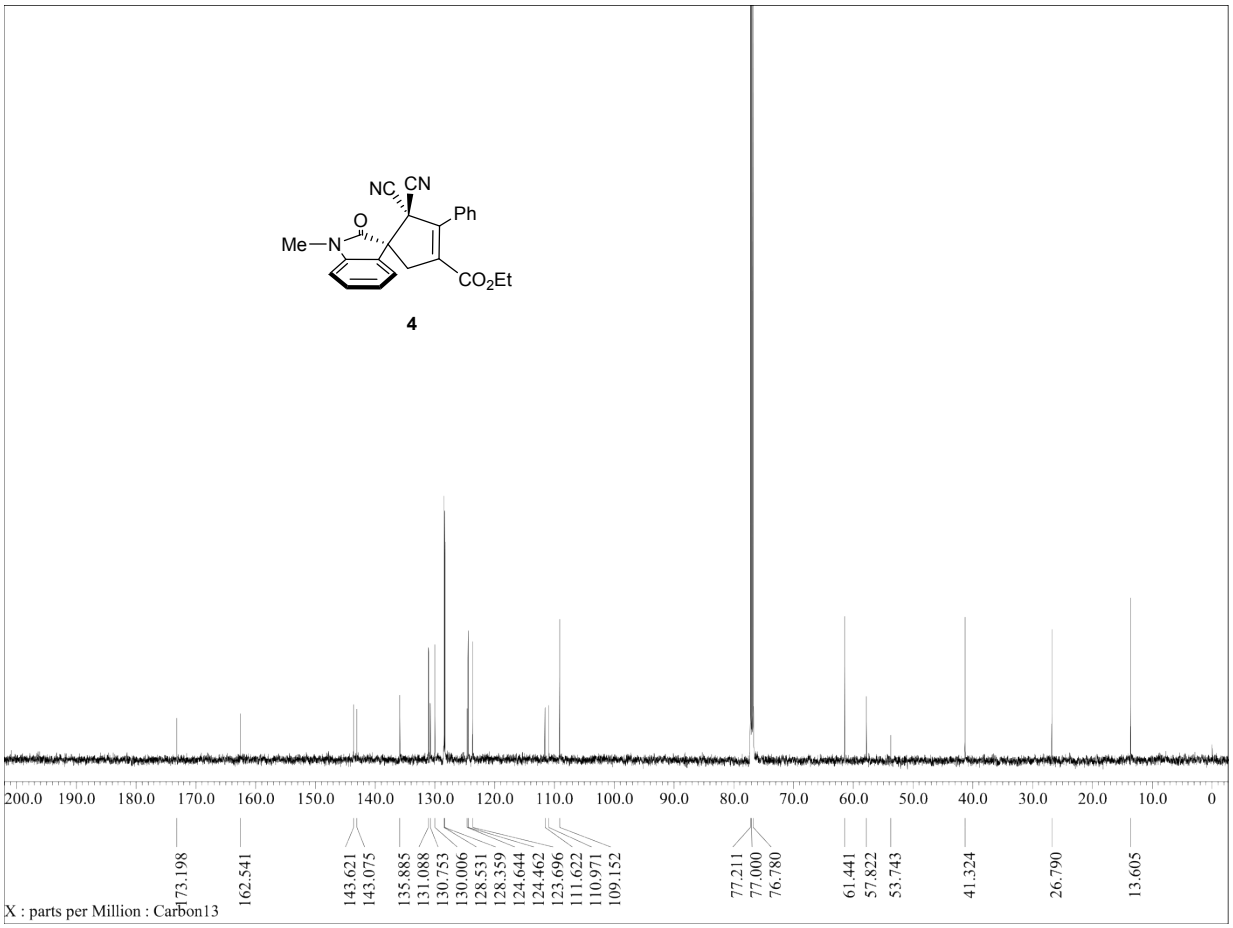

MOM
N
O
NC
CN
CO2Et
3z
3.04
2.16
2.07
1.00
1.08
1.09
1.08
2.30
3.21
1.00
1.01
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.606
7.596
7.557
7.546
7.538
7.525
7.514
7.377
7.364
7.358
7.345
7.173
7.160
7.099
7.087
7.074
5.255
5.236
5.175
5.157
4.439
4.426
4.420
4.415
4.409
4.403
4.398
4.385
4.331
4.319
4.314
4.308
4.301
4.295
4.290
4.278
3.404
2.787
2.776
1.714
1.705
1.273
1.262
1.249
X : parts per Million : Proton

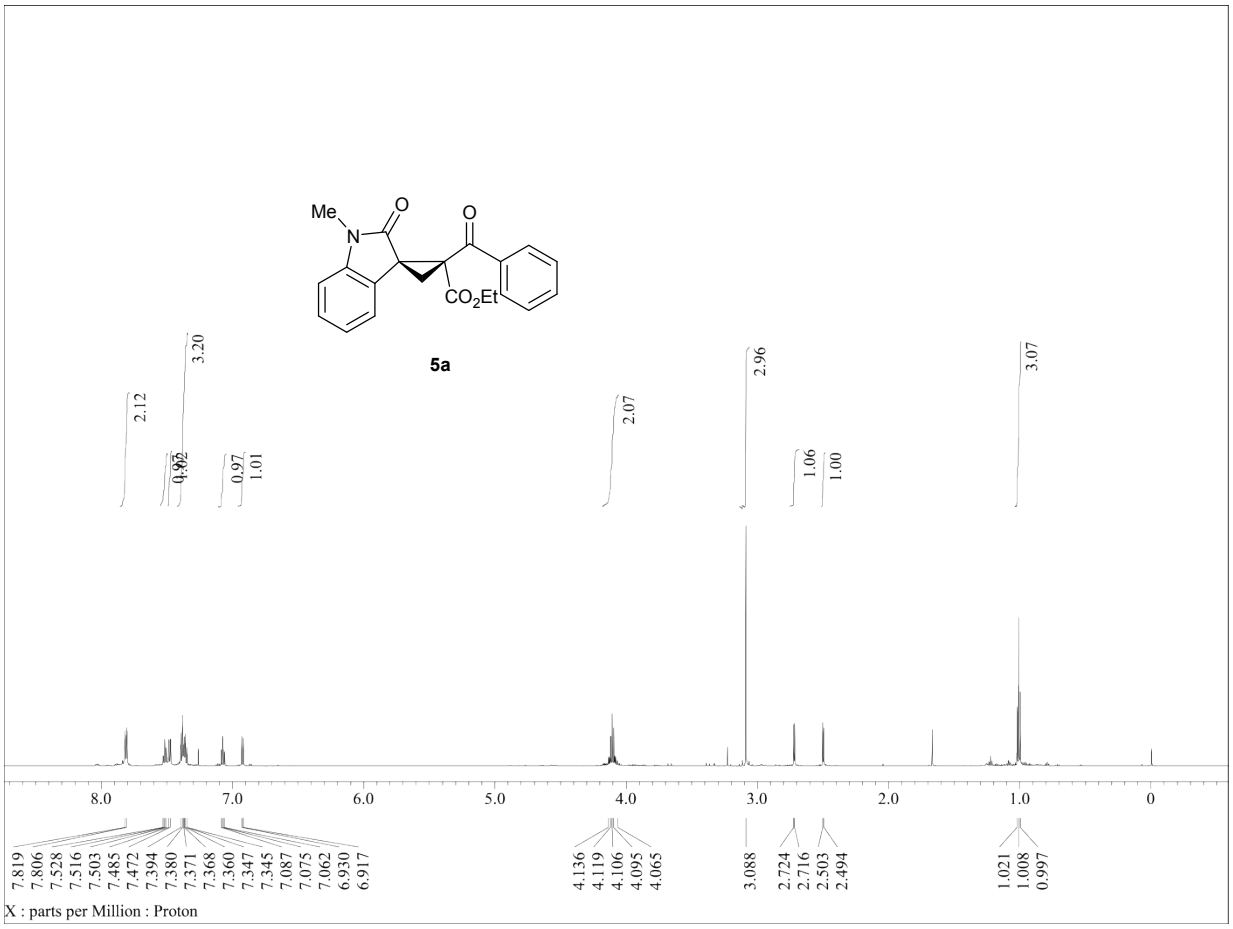

MOM
N
O
NC
CN
CO2Et
3z
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.556
170.095
64.810
143.200
135.301
132.093
129.374
129.077
128.378
123.371
123.103
122.691
112.915
112.398
110.301
90.567
77.211
77.000
76.789
72.490
63.902
56.788
45.853
44.025
26.503
14.055
X : parts per Million : Carbon13

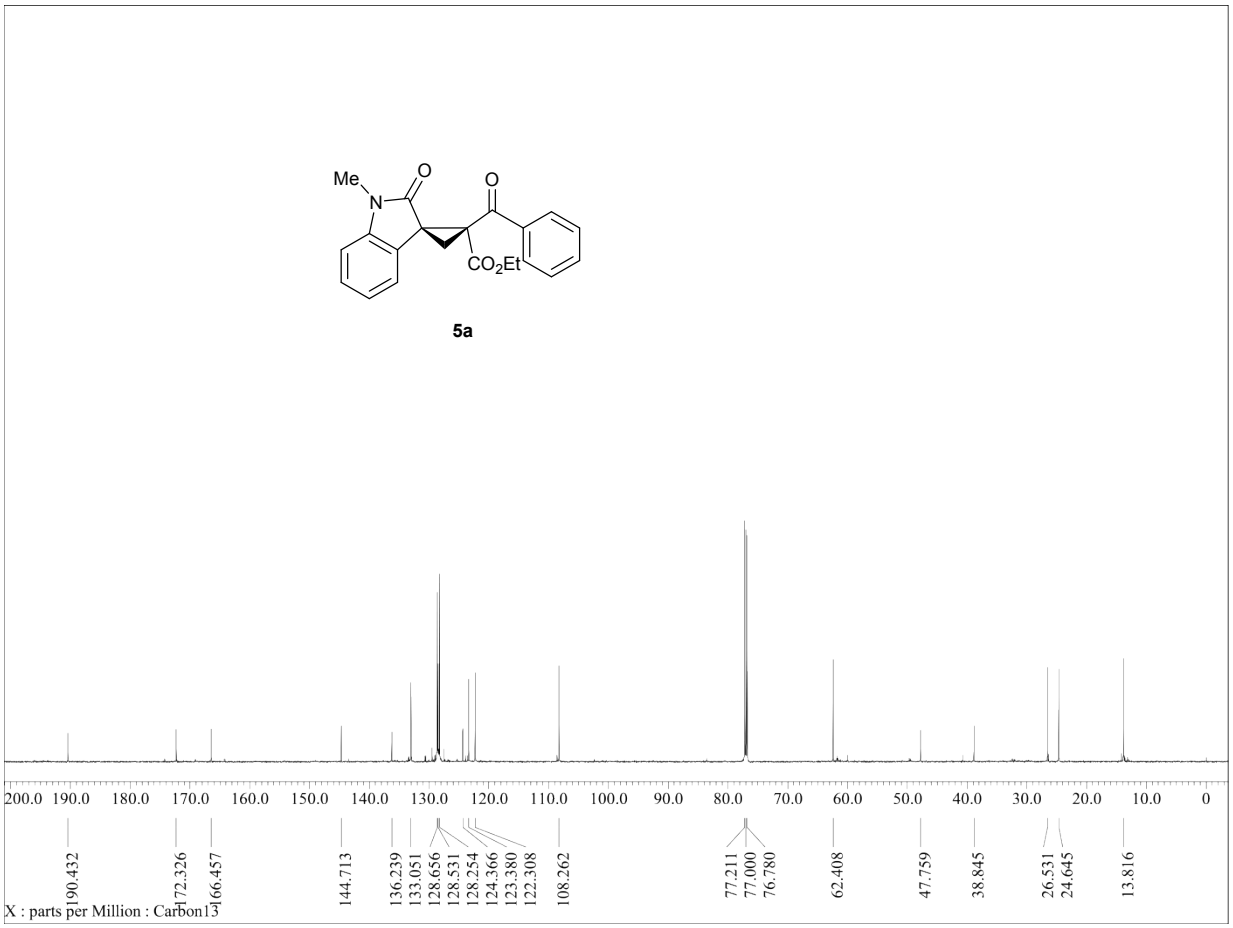

3aa
5.17
2.53
3.36
0.97
1.01
1.15
0.92
1.12
1.00
0.97
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.951
7.586
7.574
7.553
7.533
7.520
7.509
7.368
7.355
7.306
7.293
7.281
7.050
7.037
7.025
6.969
6.956
4.435
4.424
4.418
4.407
4.394
4.383
4.341
4.329
4.323
4.317
4.311
4.300
4.287
4.276
2.761
2.752
1.693
1.683
1.288
1.276
1.264
X : parts per Million : Proton

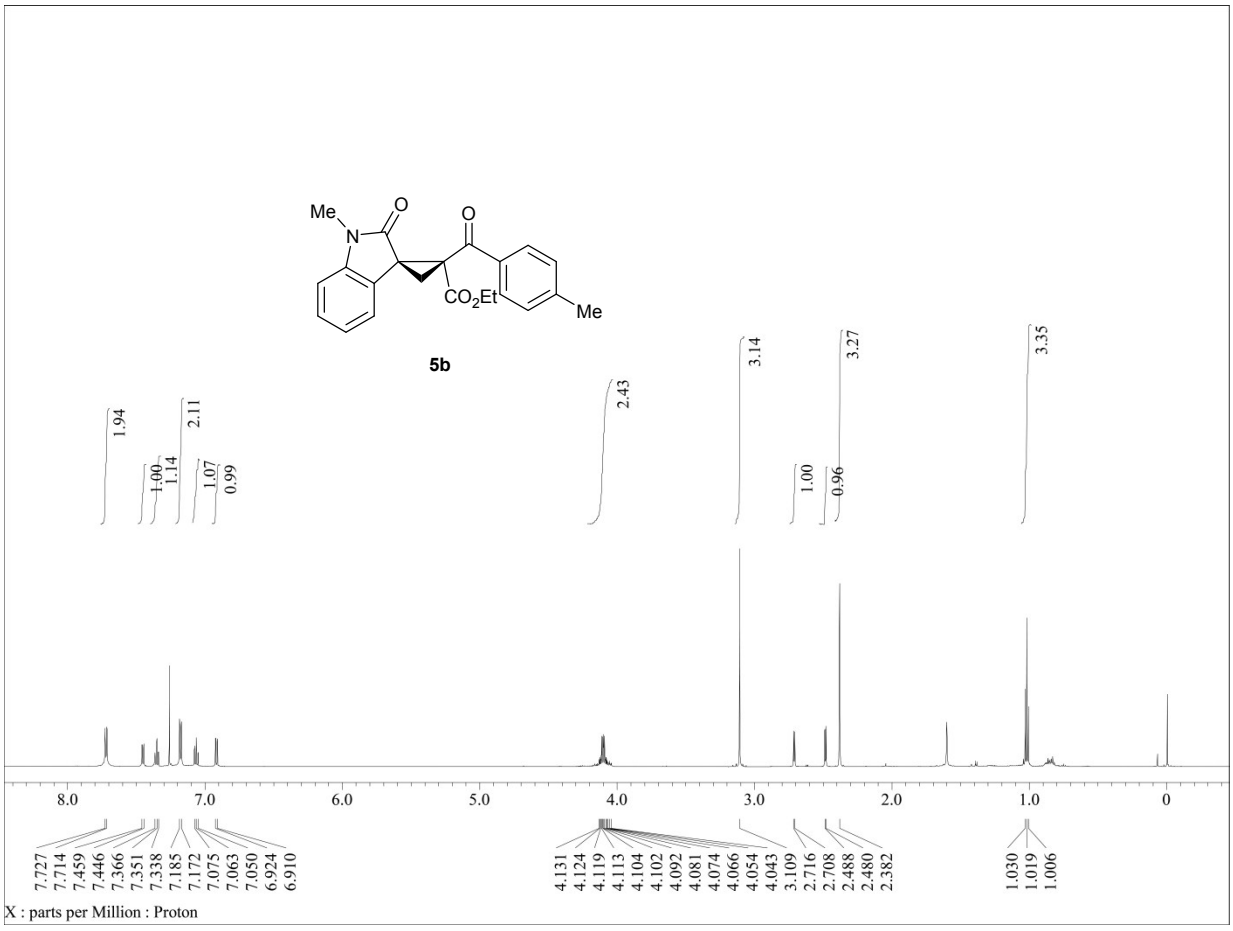

3aa
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.939
170.095
164.896
141.582
135.320
132.007
129.202
129.029
128.359
124.271
123.198
122.585
112.925
112.340
110.291
90.673
77.211
77.000
76.780
63.844
45.623
44.226
26.330
14.065
X : parts per Million : Carbon13

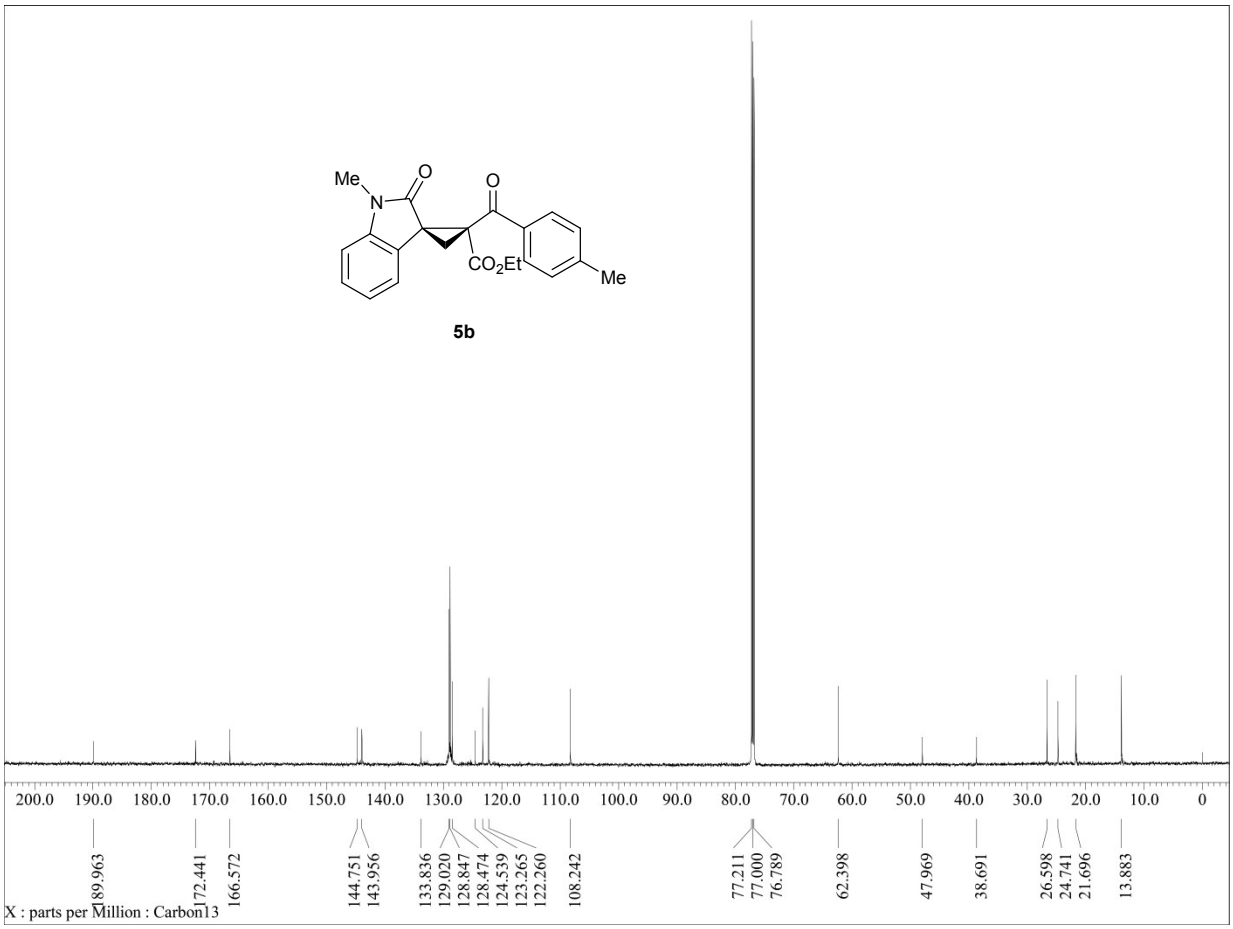

NC
CN
Ph
O
Me—N
CO2Et
4
4.07
1.90
1.06
1.02
1.04
2.14
3.05
1.00
1.11
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.678
7.666
7.532
7.527
7.522
7.516
7.483
7.478
7.473
7.472
7.469
7.462
7.458
7.456
7.229
7.217
7.205
6.972
6.959
4.104
4.092
4.081
4.068
3.462
3.434
3.358
3.329
3.302
1.054
1.043
1.030
X : parts per Million : Proton

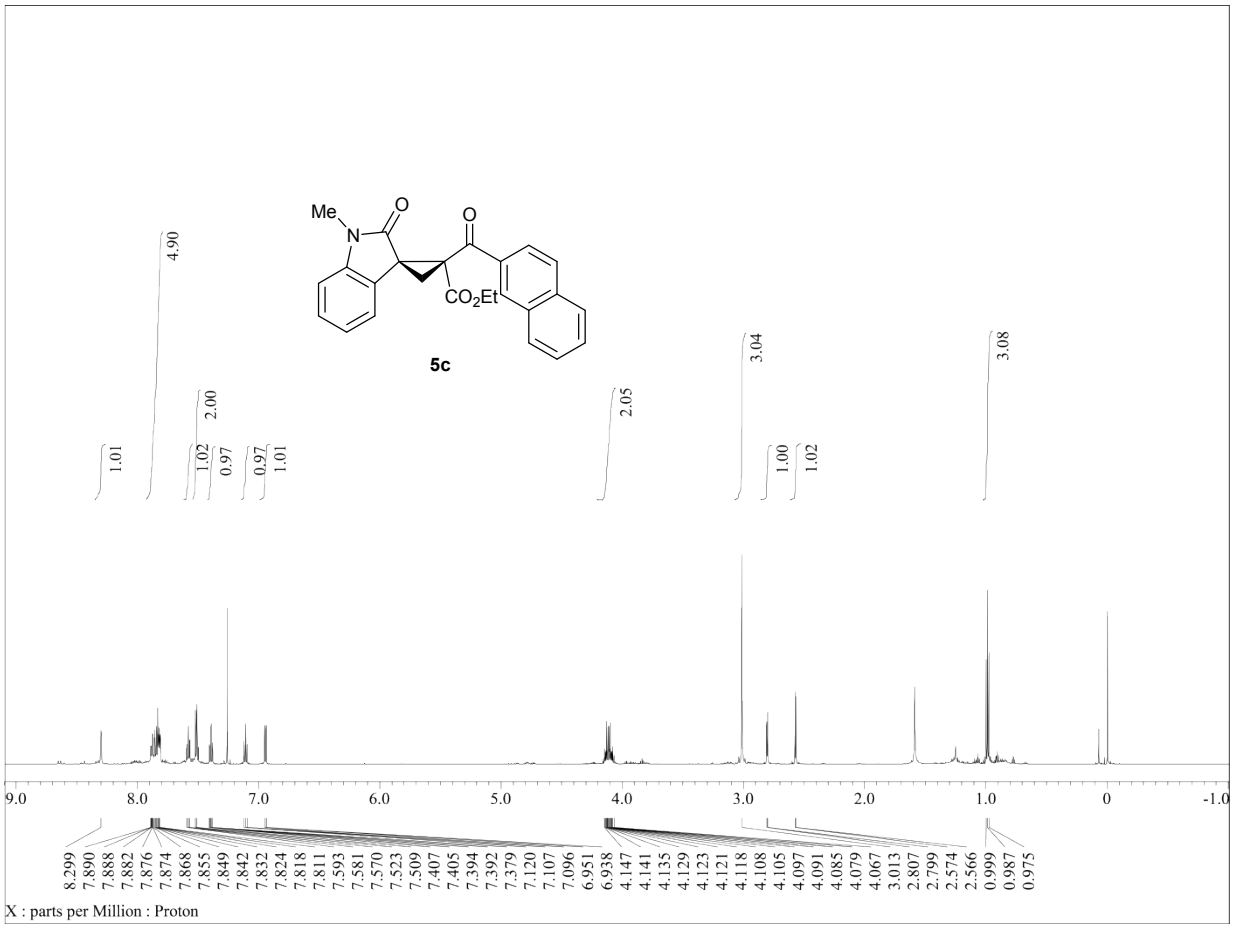

NC
CN
Ph
O
Me—N
CO2Et
4
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.198
162.541
143.621
143.075
135.885
131.088
130.753
130.006
128.531
128.359
124.644
124.462
123.696
111.622
110.971
109.152
77.211
77.000
76.780
61.441
57.822
53.743
41.324
26.790
13.605
X : parts per Million : Carbon13

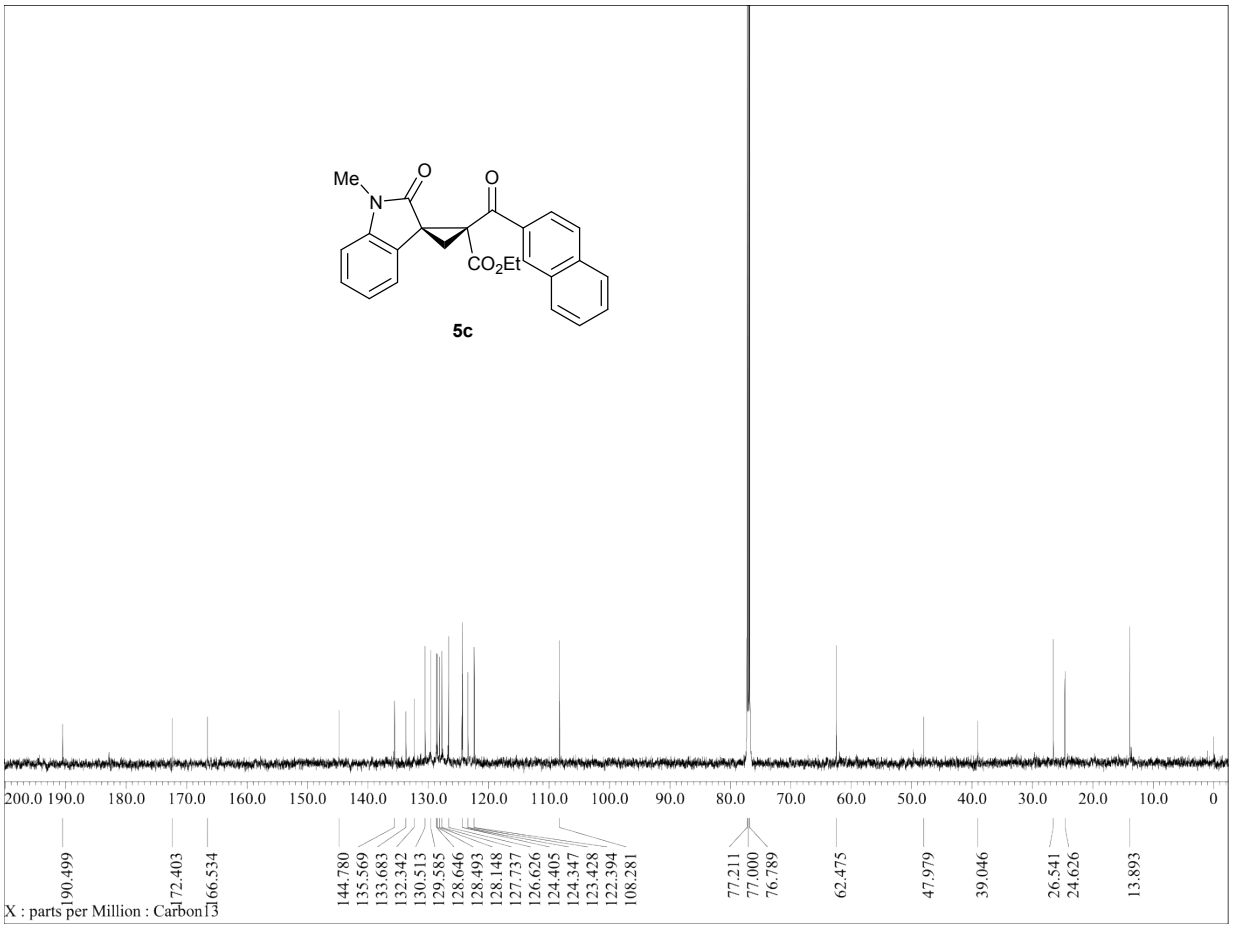

Me
N
O
O
O
CO2Et
5a
2.12
3.20
0.92
0.97
1.01
2.07
2.96
1.06
1.00
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.819
7.806
7.528
7.516
7.503
7.485
7.472
7.394
7.380
7.371
7.368
7.360
7.347
7.345
7.087
7.075
7.062
6.930
6.917
4.136
4.119
4.106
4.095
4.065
3.088
2.724
2.716
2.503
2.494
1.021
1.008
0.997
X : parts per Million : Proton

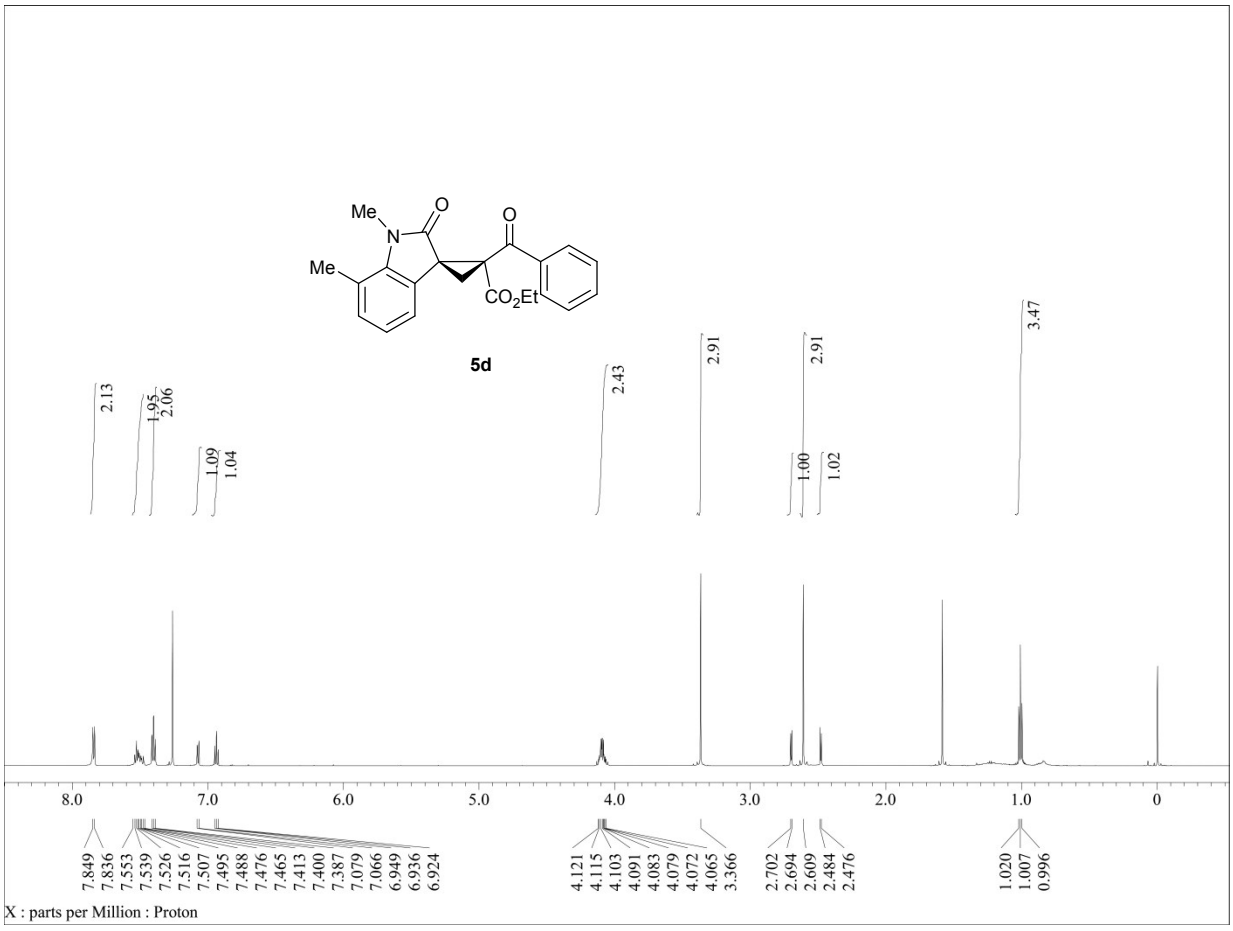

Me
N
O
O
O
CO2Et
5a
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.432
172.326
166.457
144.713
136.239
133.051
128.656
128.531
128.254
124.366
123.380
122.308
108.262
77.211
77.000
76.780
62.408
47.759
38.845
26.531
24.645
13.816
X : parts per Million : Carbon13

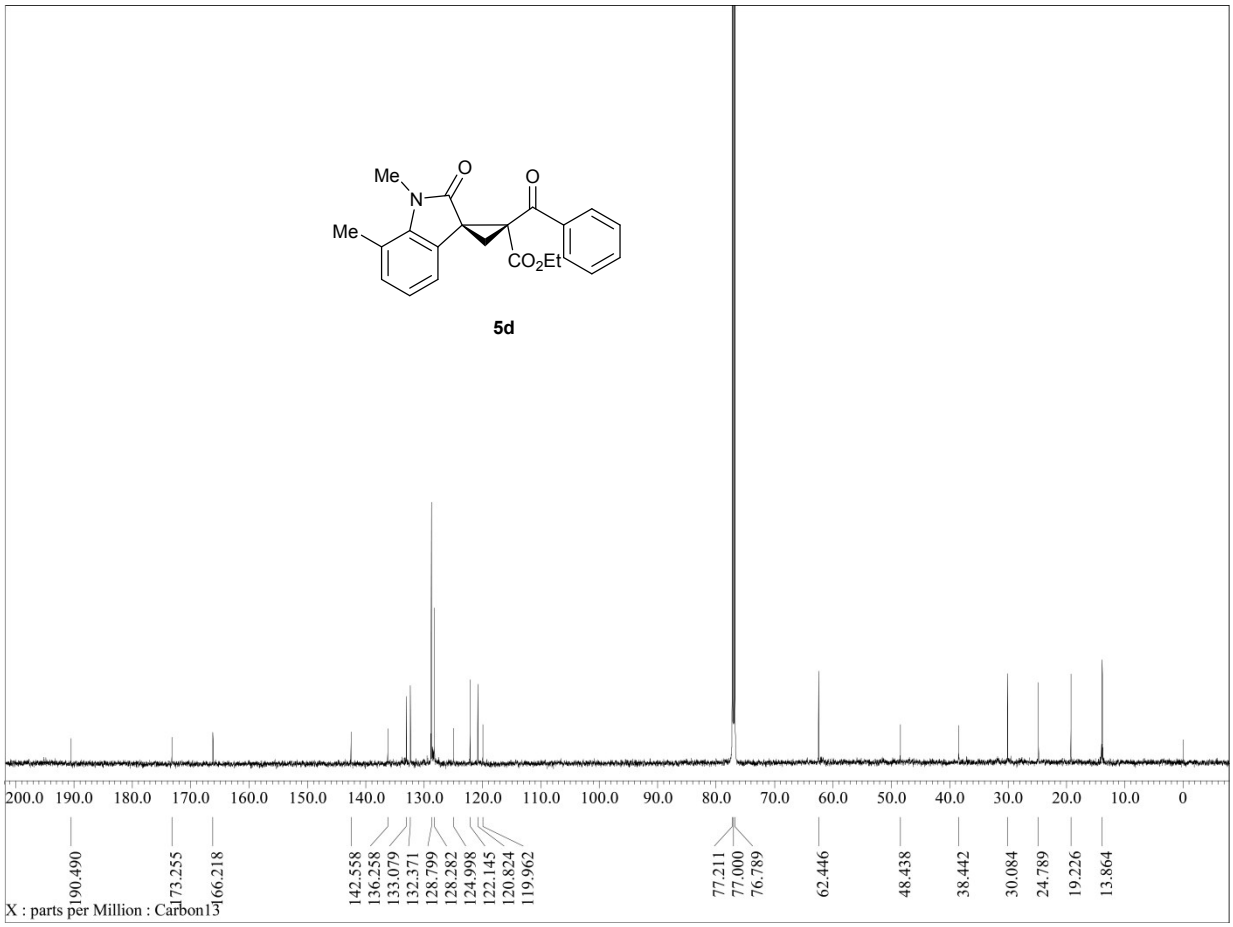

Me
N
O
O
CO2Et
Me
5b
1.94
1.00
1.14
2.11
1.07
0.99
2.43
3.14
1.00
0.96
3.27
3.35
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.727
7.714
7.459
7.446
7.366
7.351
7.338
7.185
7.172
7.075
7.063
7.050
6.924
6.910
4.131
4.124
4.119
4.113
4.104
4.102
4.092
4.081
4.074
4.066
4.054
4.043
3.109
2.716
2.708
2.488
2.480
2.382
1.030
1.019
1.006
X : parts per Million : Proton

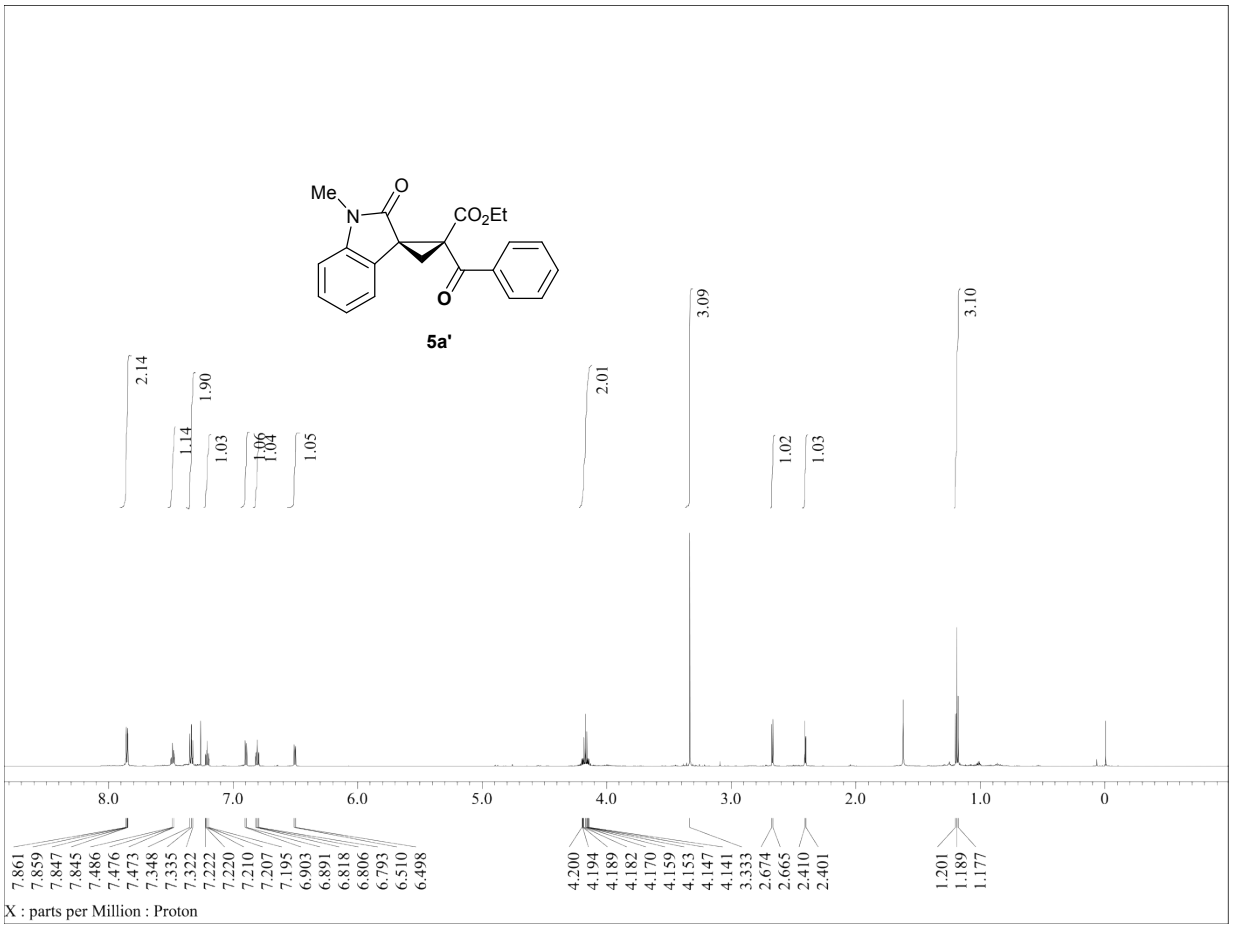

Me
N
O
O
CO2Et
Me
5b
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
89.963
172.441
166.572
144.751
143.956
133.836
129.020
128.847
128.474
124.539
123.265
122.260
108.242
77.211
77.000
76.789
62.398
47.969
38.691
26.598
24.741
21.696
13.883
X : parts per Million : Carbon13

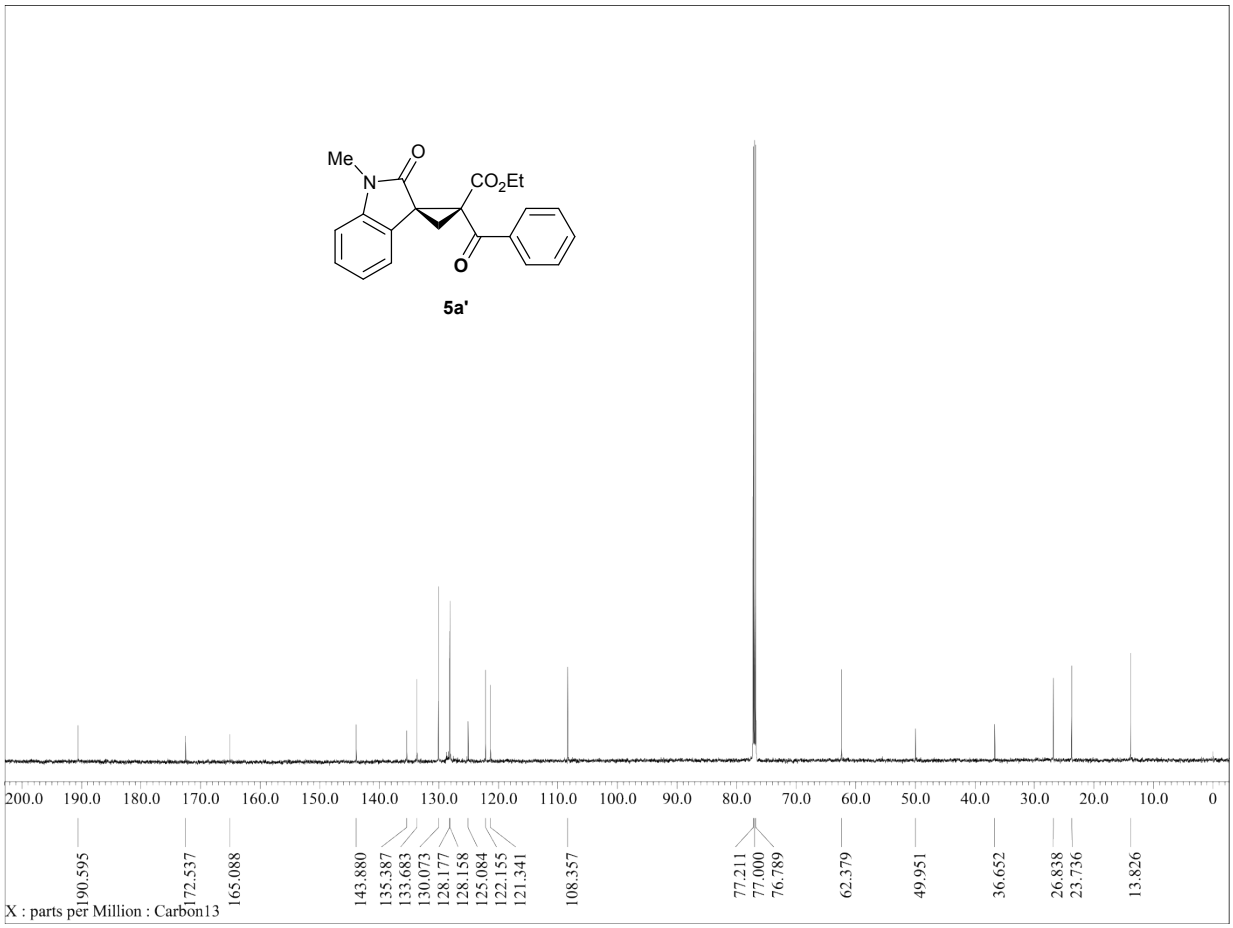

Me
N
O
O
CO2Et
5c
4.90
2.00
1.01
1.02
0.97
0.97
1.01
2.05
3.04
1.00
1.02
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
8.299
7.890
7.888
7.882
7.876
7.874
7.868
7.855
7.849
7.842
7.832
7.824
7.818
7.811
7.593
7.581
7.570
7.523
7.509
7.407
7.405
7.394
7.392
7.379
7.120
7.107
7.096
6.951
6.938
4.147
4.141
4.135
4.129
4.123
4.121
4.118
4.108
4.105
4.097
4.091
4.085
4.079
4.067
3.013
2.807
2.799
2.574
2.566
0.999
0.987
0.975
X : parts per Million : Proton

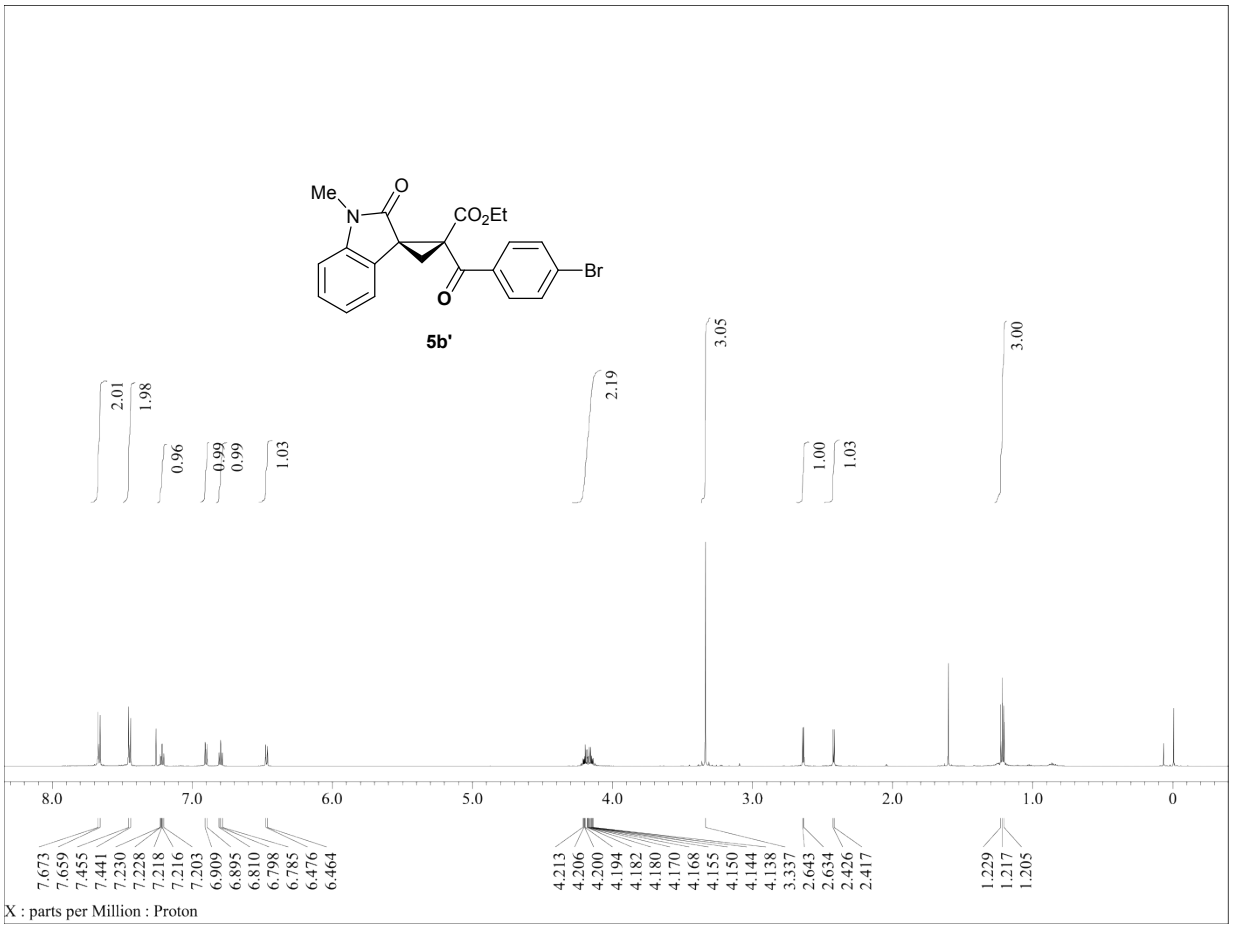

Me
N
O
O
CO2Et
5c
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.499
172.403
166.534
144.780
135.569
133.683
132.342
130.513
129.585
128.646
128.493
128.148
127.737
126.626
124.405
124.347
123.428
122.394
108.281
77.211
77.000
76.789
62.475
47.979
39.046
26.541
24.626
13.893
X : parts per Million : Carbon13

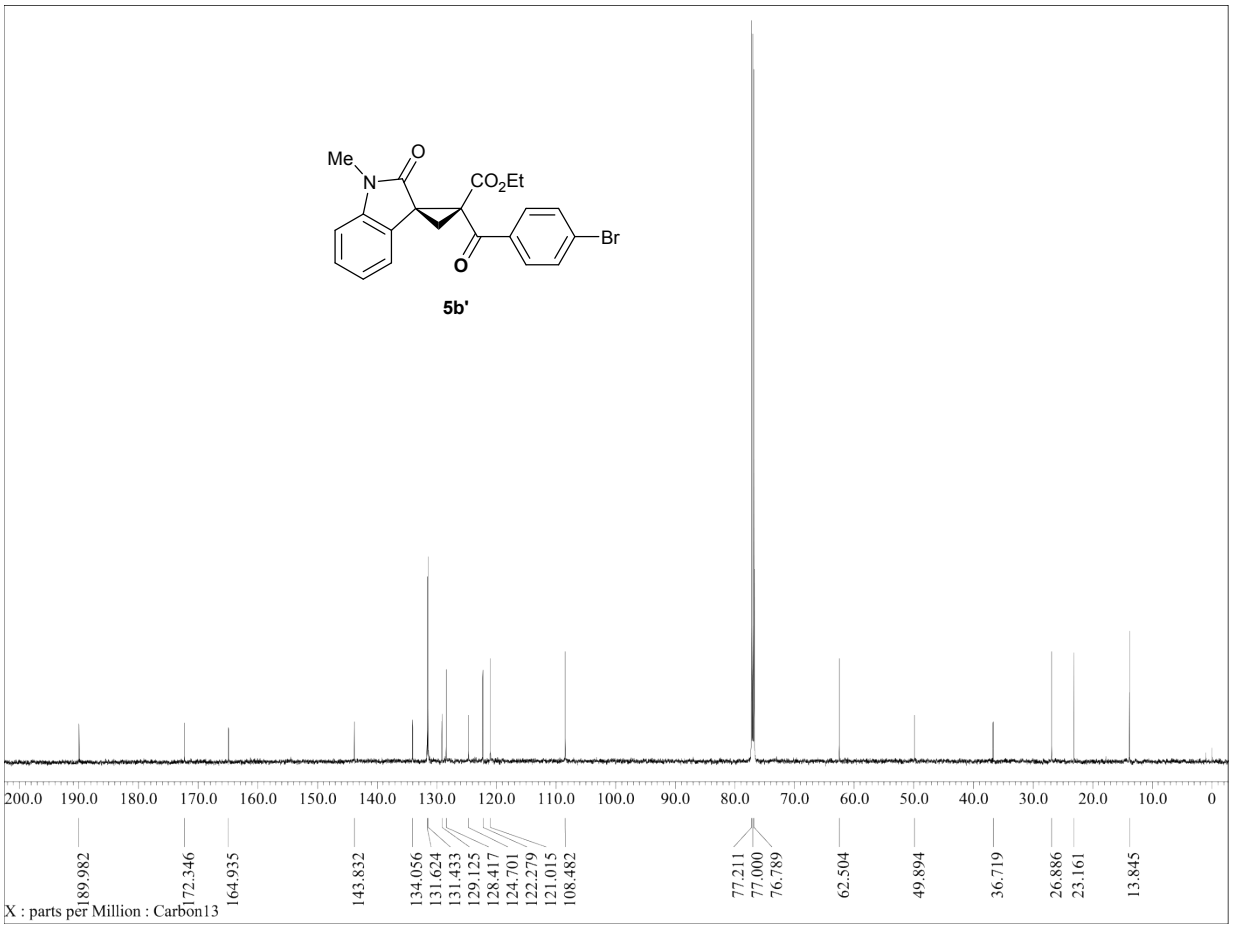

Me
N
O
O
Me
CO2Et
5d
2.13
1.95
2.06
1.09
1.04
2.43
2.91
2.91
1.00
1.02
3.47
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.849
7.836
7.553
7.539
7.526
7.516
7.507
7.495
7.488
7.476
7.465
7.413
7.400
7.387
7.079
7.066
6.949
6.936
6.924
4.121
4.115
4.103
4.091
4.083
4.079
4.072
4.065
3.366
2.702
2.694
2.609
2.484
2.476
1.020
1.007
0.996
X : parts per Million : Proton

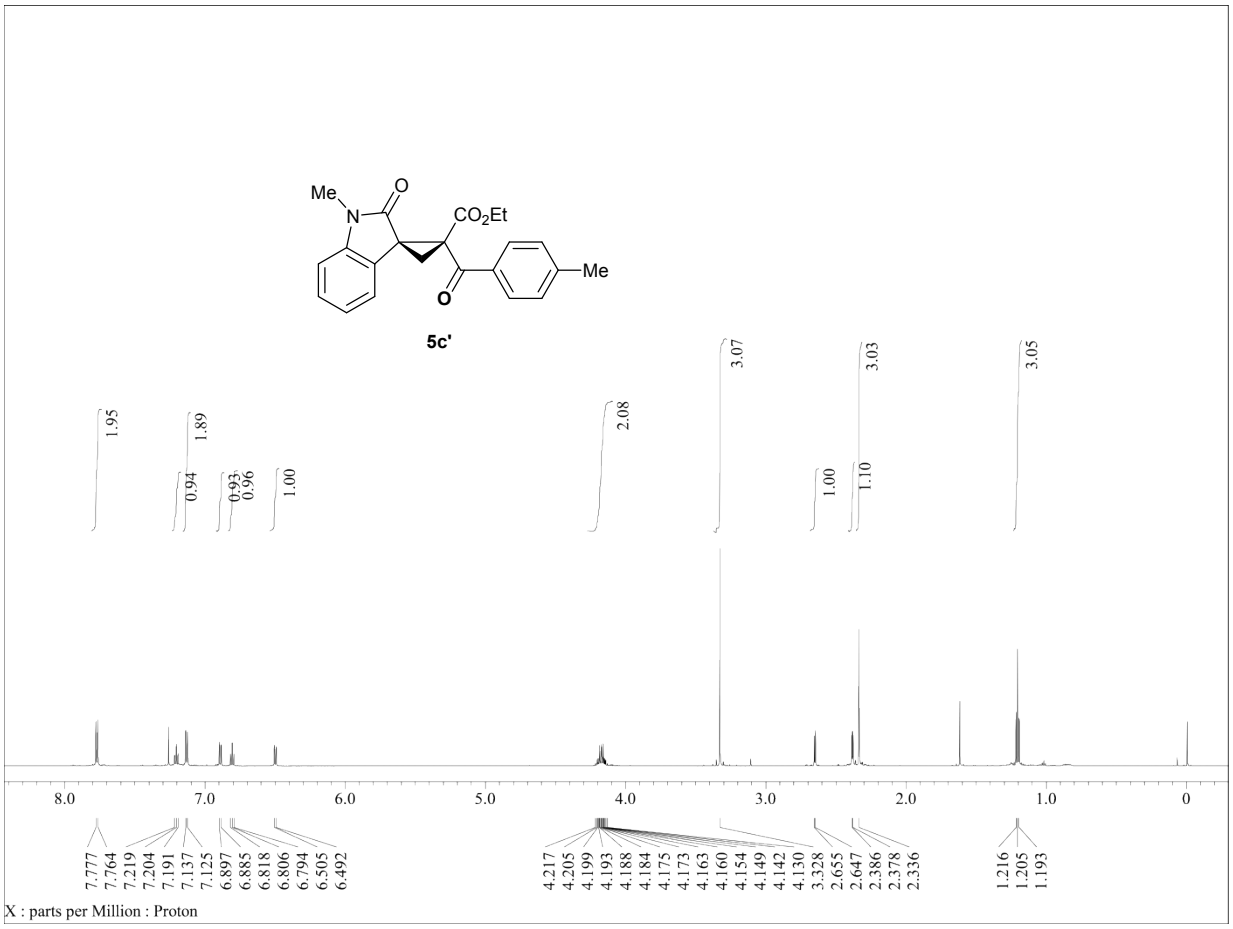

Me
N
O
O
Me
CO2Et
5d
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.490
173.255
166.218
142.558
136.258
133.079
132.371
128.799
128.282
124.998
122.145
120.824
119.962
77.211
77.000
76.789
62.446
48.438
38.442
30.084
24.789
19.226
13.864
X : parts per Million : Carbon13

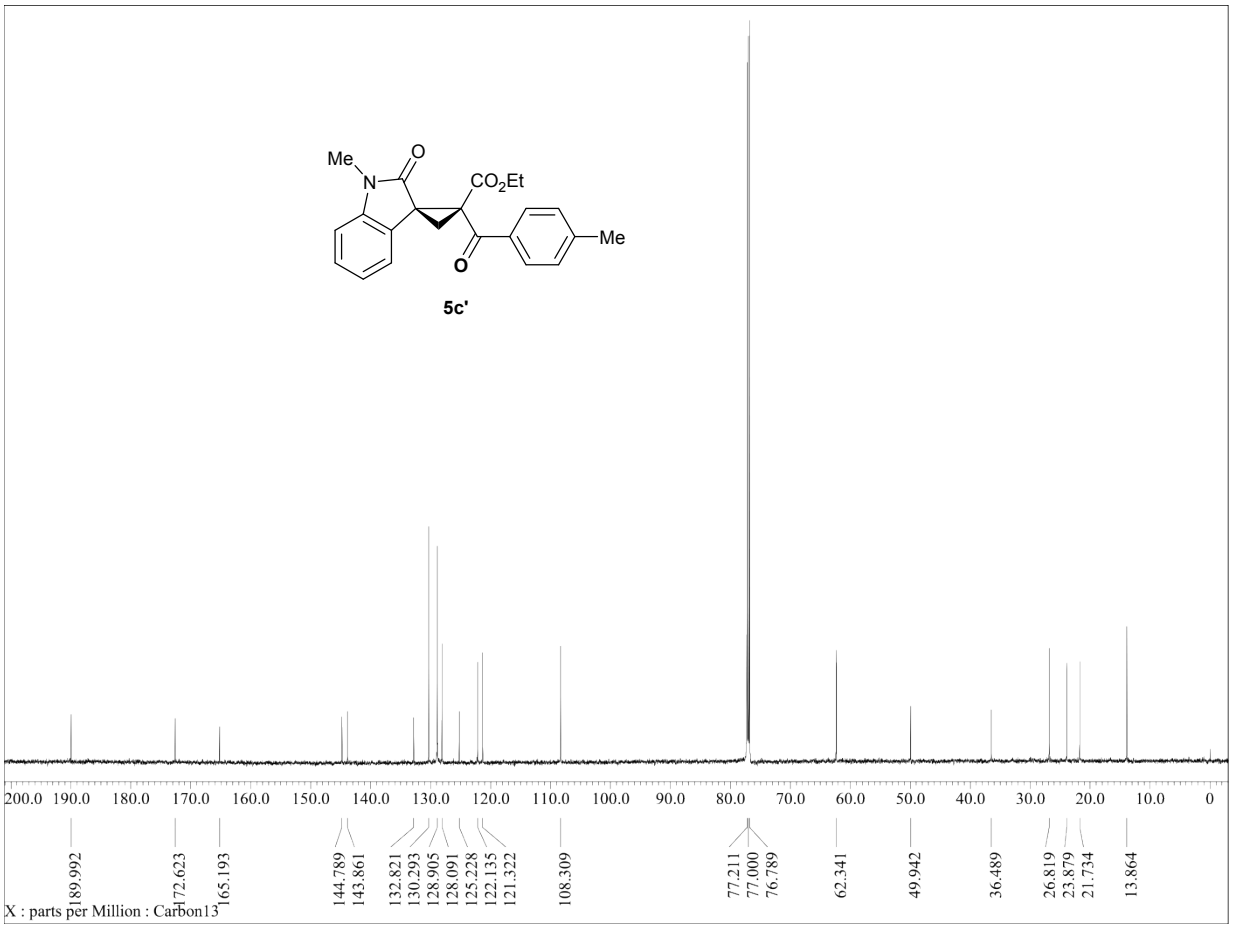

Me
N
O
CO2Et
O
5a'
2.14
1.90
1.14
1.03
1.06
1.04
1.05
2.01
3.09
1.02
1.03
3.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.861
7.859
7.847
7.845
7.486
7.476
7.473
7.348
7.335
7.322
7.222
7.220
7.210
7.207
7.195
6.903
6.891
6.818
6.806
6.793
6.510
6.498
4.200
4.194
4.189
4.182
4.170
4.159
4.153
4.147
4.141
3.333
2.674
2.665
2.410
2.401
1.201
1.189
1.177
X : parts per Million : Proton

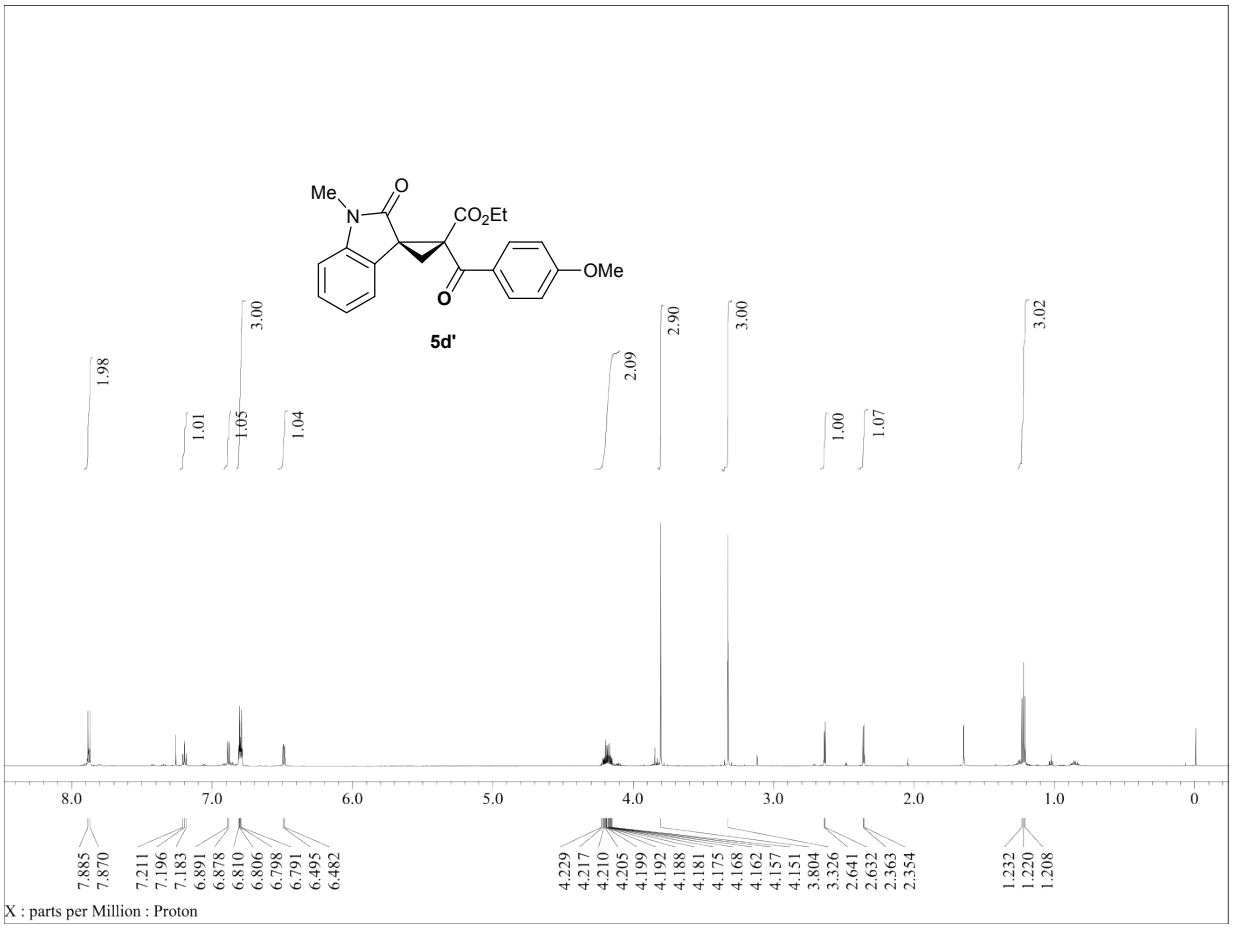

Me
N
O
CO2Et
O
5a'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.595
172.537
165.088
143.880
135.387
133.683
130.073
128.177
128.158
125.084
122.155
121.341
108.357
77.211
77.000
76.789
62.379
49.951
36.652
26.838
23.736
13.826
X : parts per Million : Carbon13

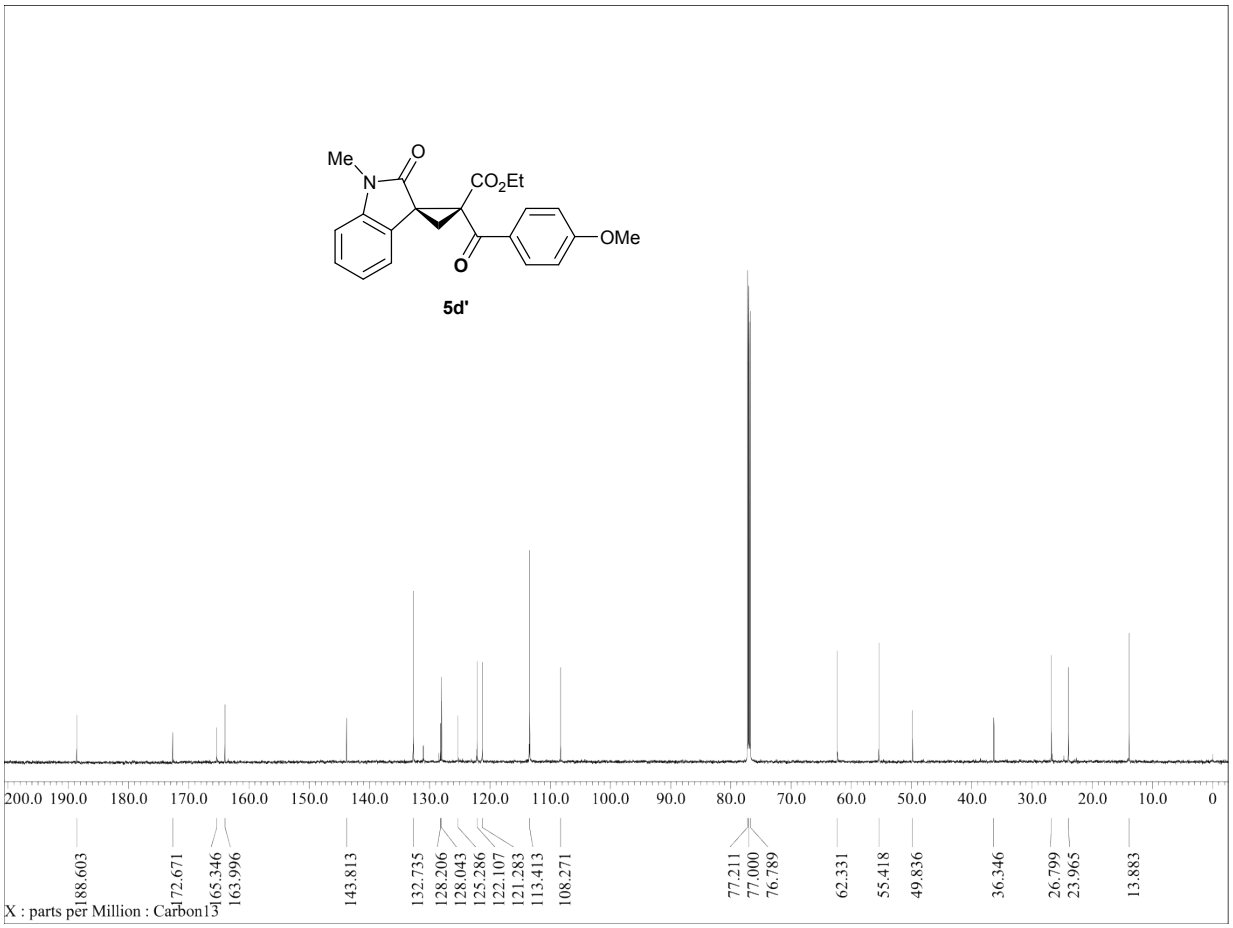

Me
N
O
CO2Et
Br
O
5b'
2.01
1.98
0.96
0.99
0.99
1.03
2.19
3.05
1.00
1.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.673
7.659
7.455
7.441
7.230
7.228
7.218
7.216
7.203
6.909
6.895
6.810
6.798
6.785
6.476
6.464
4.213
4.206
4.200
4.194
4.182
4.180
4.170
4.168
4.155
4.150
4.144
4.138
3.337
2.643
2.634
2.426
2.417
1.229
1.217
1.205
X : parts per Million : Proton

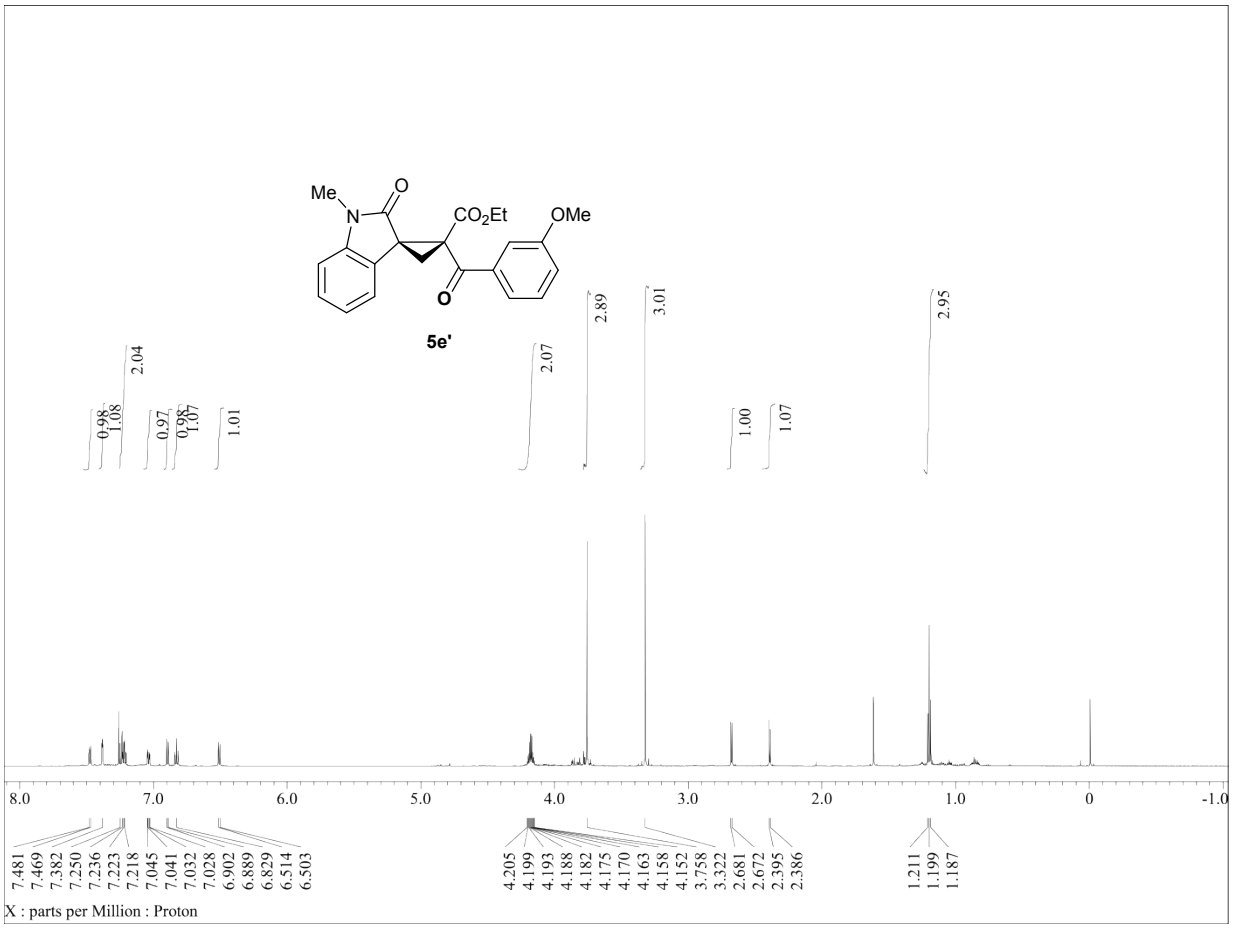

Me
N
O
CO2Et
Br
O
5b'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
189.982
172.346
164.935
143.832
134.056
131.624
131.433
129.125
128.417
124.701
122.279
121.015
108.482
77.211
77.000
76.789
62.504
49.894
36.719
26.886
23.161
13.845
X : parts per Million : Carbon13

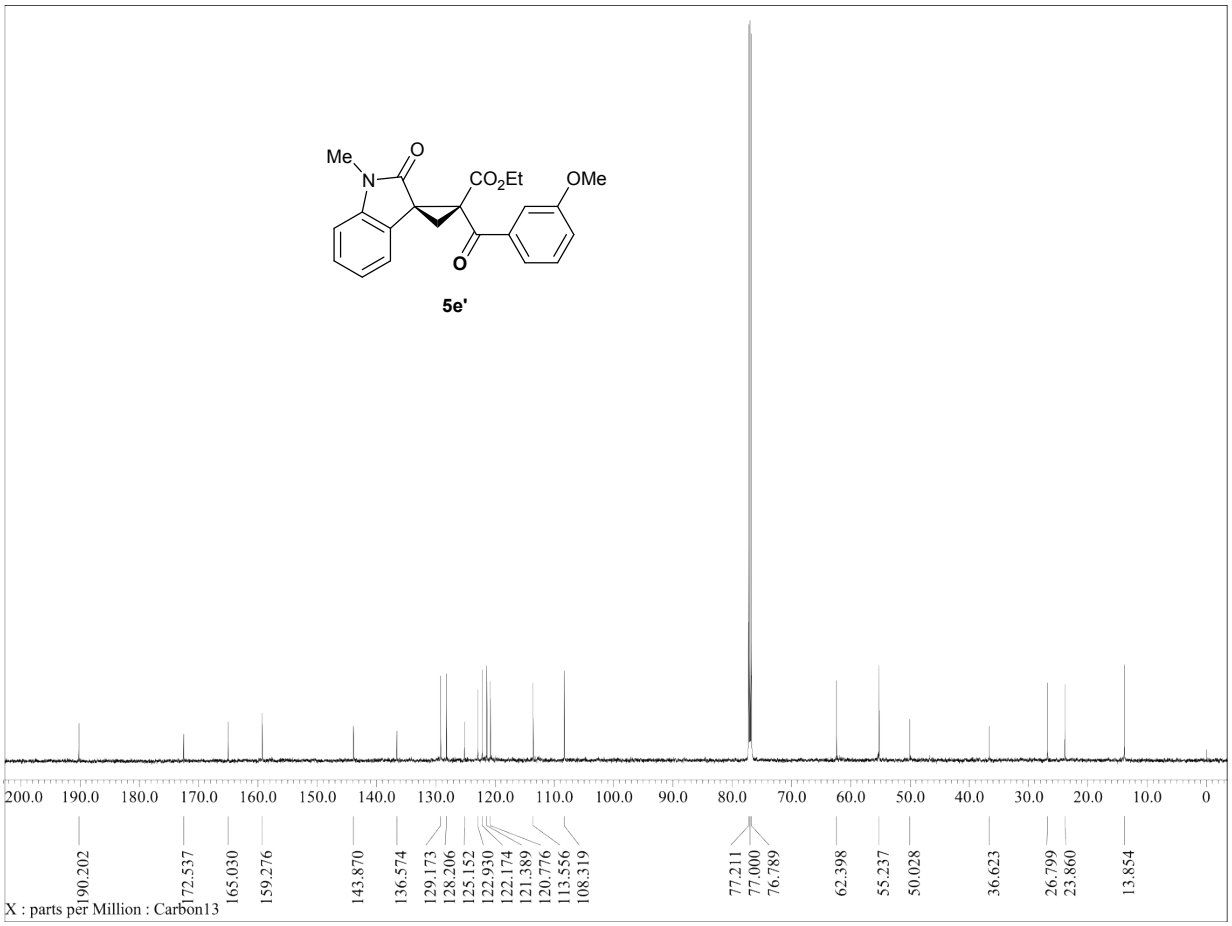

Me
N
O
CO2Et
Me
O
5c'
1.95
1.89
0.94
0.93
0.96
1.00
2.08
3.07
1.00
3.03
1.10
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.777
7.764
7.219
7.204
7.191
7.137
7.125
6.897
6.885
6.818
6.806
6.794
6.505
6.492
4.217
4.205
4.199
4.193
4.188
4.184
4.175
4.173
4.163
4.160
4.154
4.149
4.142
4.130
3.328
2.655
2.647
2.386
2.378
2.336
1.216
1.205
1.193
X : parts per Million : Proton

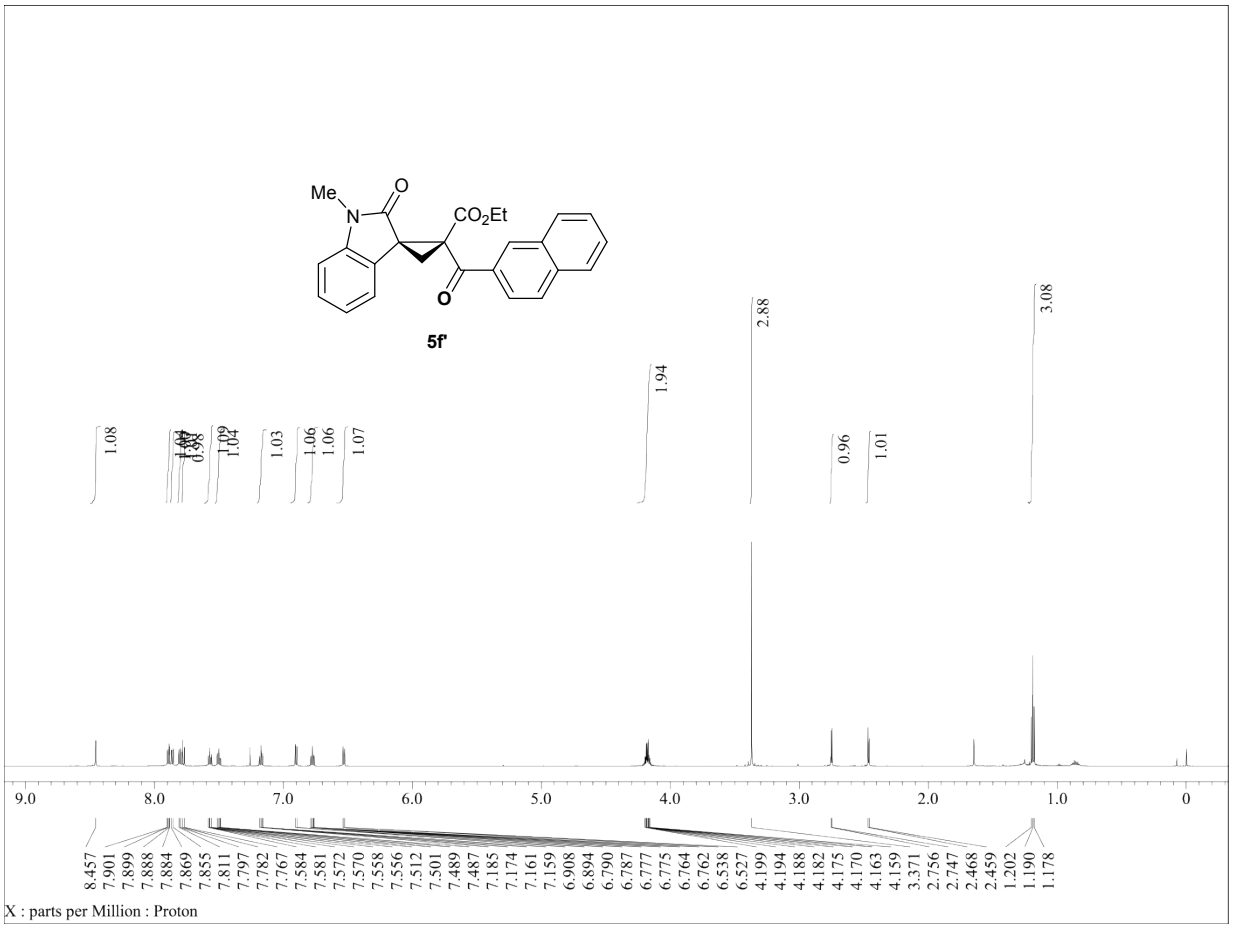

Me
N
O
CO2Et
Me
O
5c'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
189.992
172.623
165.193
144.789
143.861
132.821
130.293
128.905
128.091
125.228
122.135
121.322
108.309
77.211
77.000
76.789
62.341
49.942
36.489
26.819
23.879
21.734
13.864
X : parts per Million : Carbon13

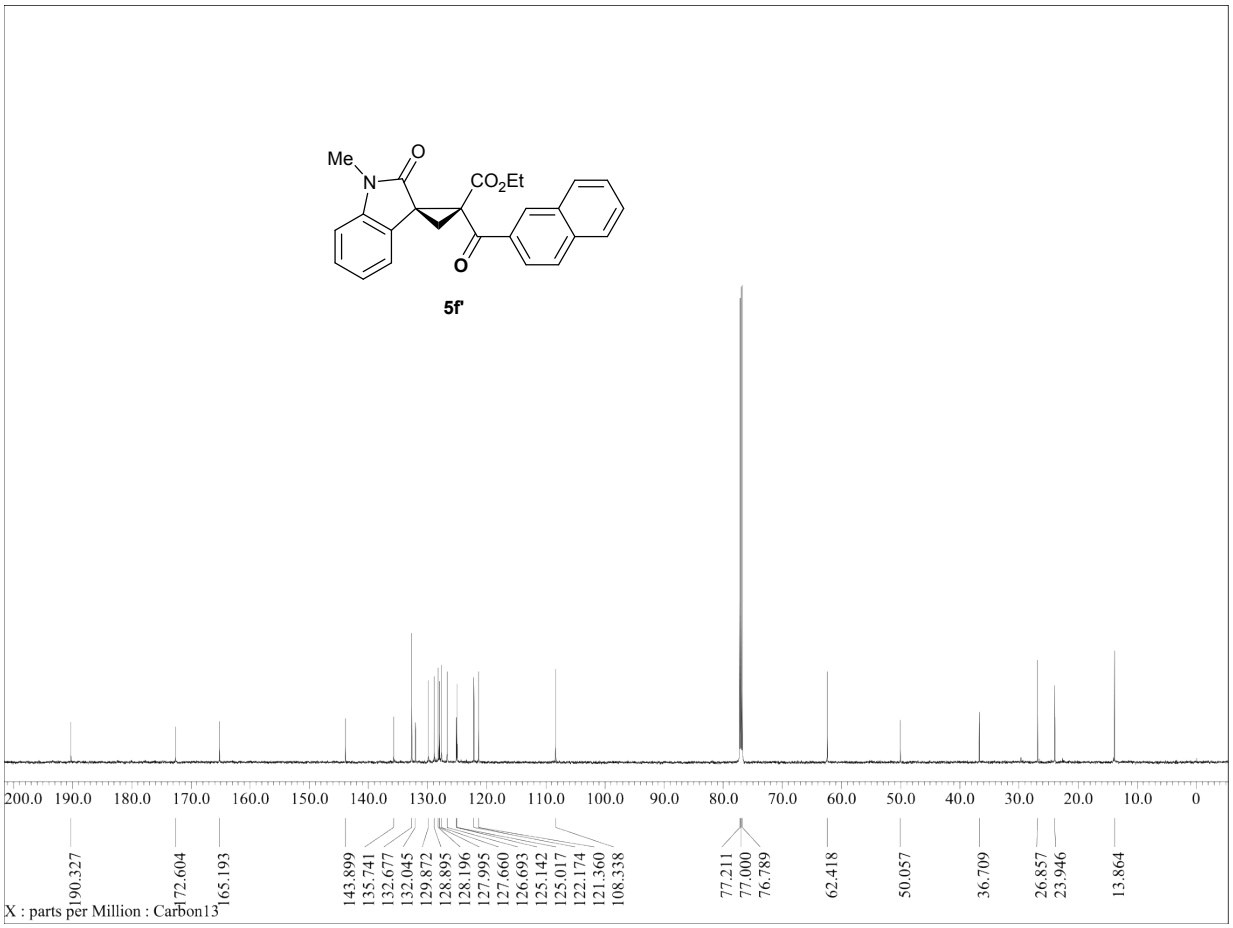

Me
N
O
CO2Et
OMe
O
5d'
1.98
1.01
1.05
3.00
1.04
2.09
2.90
3.00
1.00
1.07
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.885
7.870
7.211
7.196
7.183
6.891
6.878
6.810
6.806
6.798
6.791
6.495
6.482
4.229
4.217
4.210
4.205
4.199
4.192
4.188
4.181
4.175
4.168
4.162
4.157
4.151
3.804
3.326
2.641
2.632
2.363
2.354
1.232
1.220
1.208
X : parts per Million : Proton

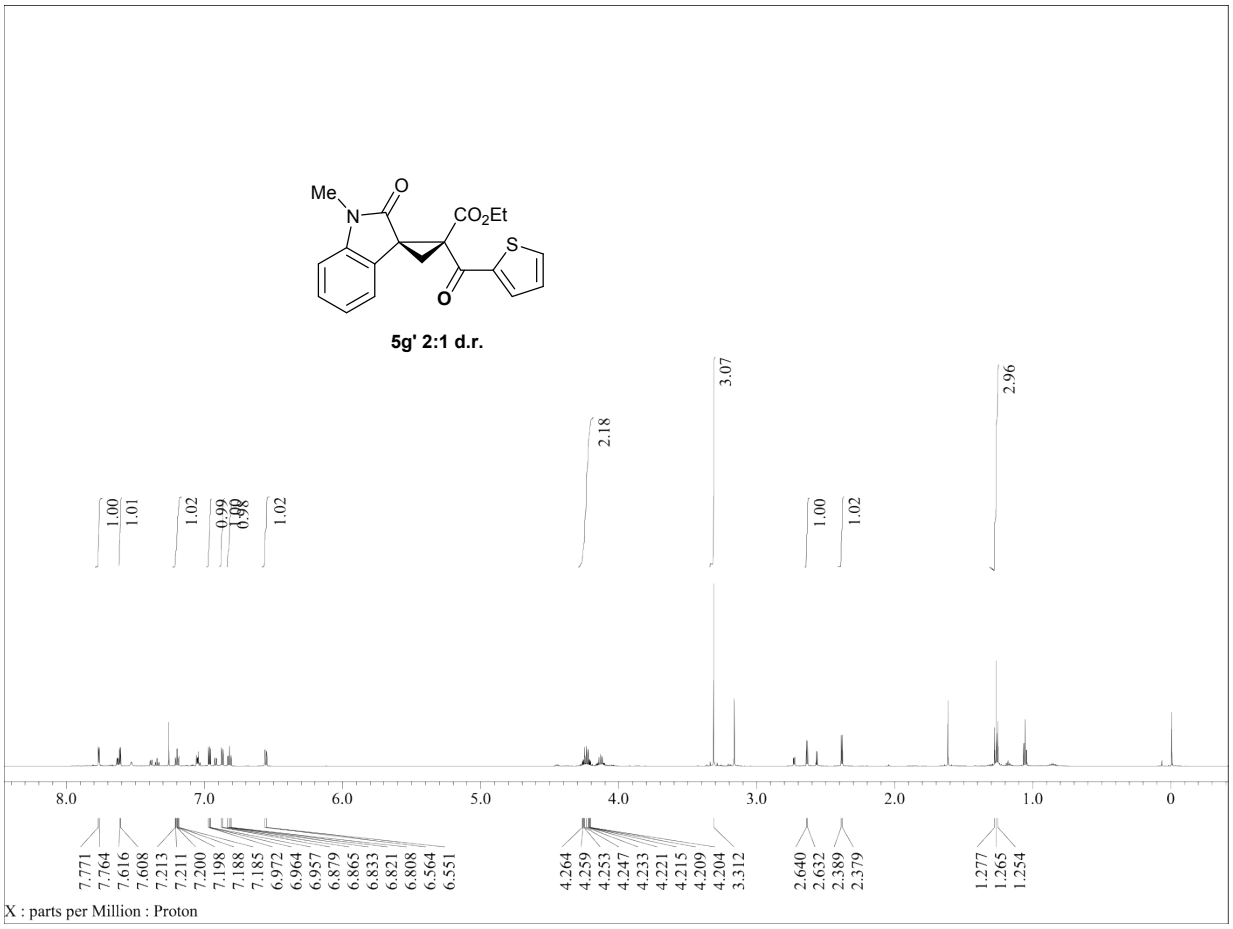

Me
N
O
CO2Et
OMe
O
5d'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
188.603
172.671
165.346
163.996
143.813
132.735
128.206
128.043
125.286
122.107
121.283
113.413
108.271
77.211
77.000
76.789
62.331
55.418
49.836
36.346
26.799
23.965
13.883
X : parts per Million : Carbon13

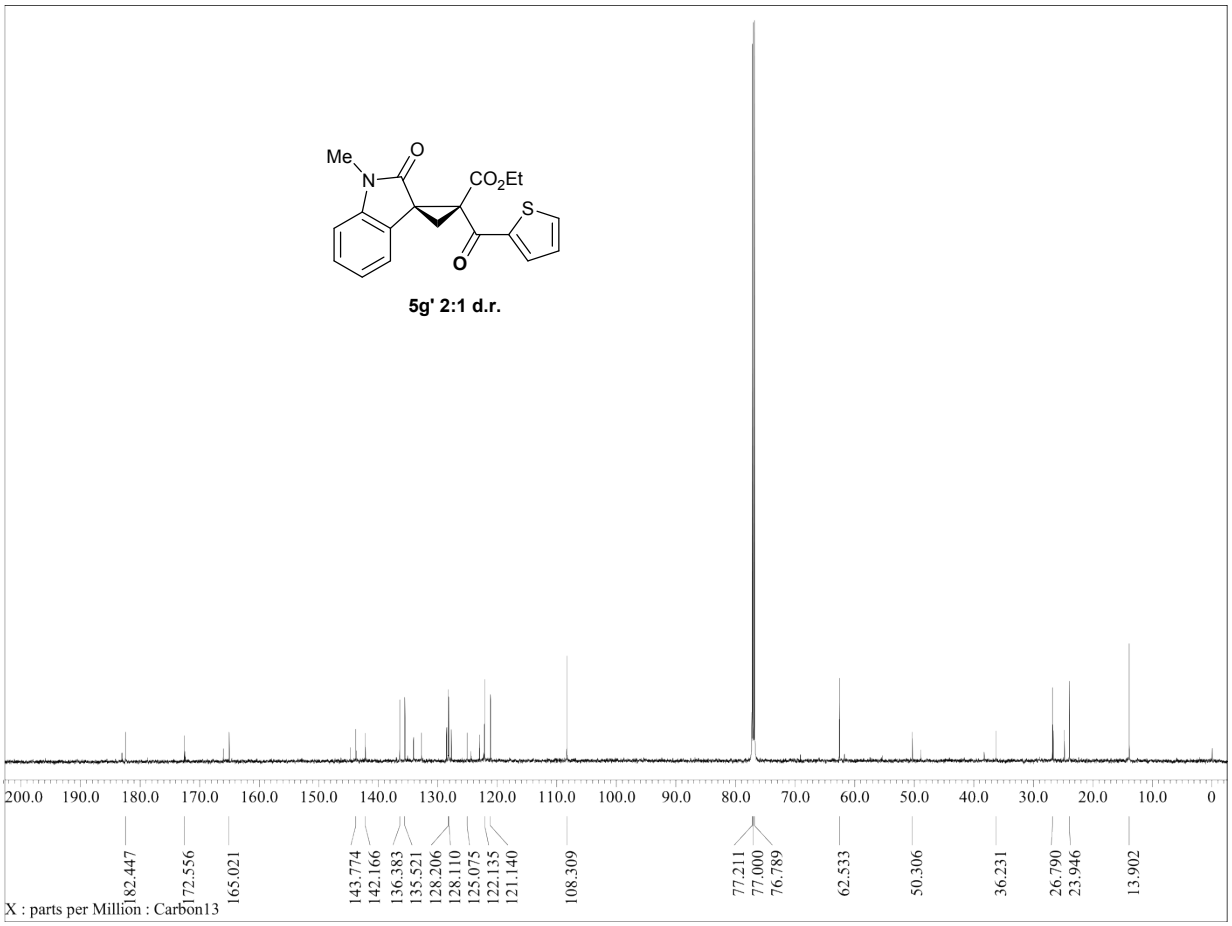

Me
N
O
CO2Et
OMe
O
5e'
0.98
1.08
2.04
0.97
0.98
1.07
1.01
2.07
2.89
3.01
1.00
1.07
2.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.481
7.469
7.382
7.250
7.236
7.223
7.218
7.045
7.041
7.032
7.028
6.902
6.889
6.829
6.514
6.503
4.205
4.199
4.193
4.188
4.182
4.175
4.170
4.163
4.158
4.152
3.758
3.322
2.681
2.672
2.395
2.386
1.211
1.199
1.187
X : parts per Million : Proton

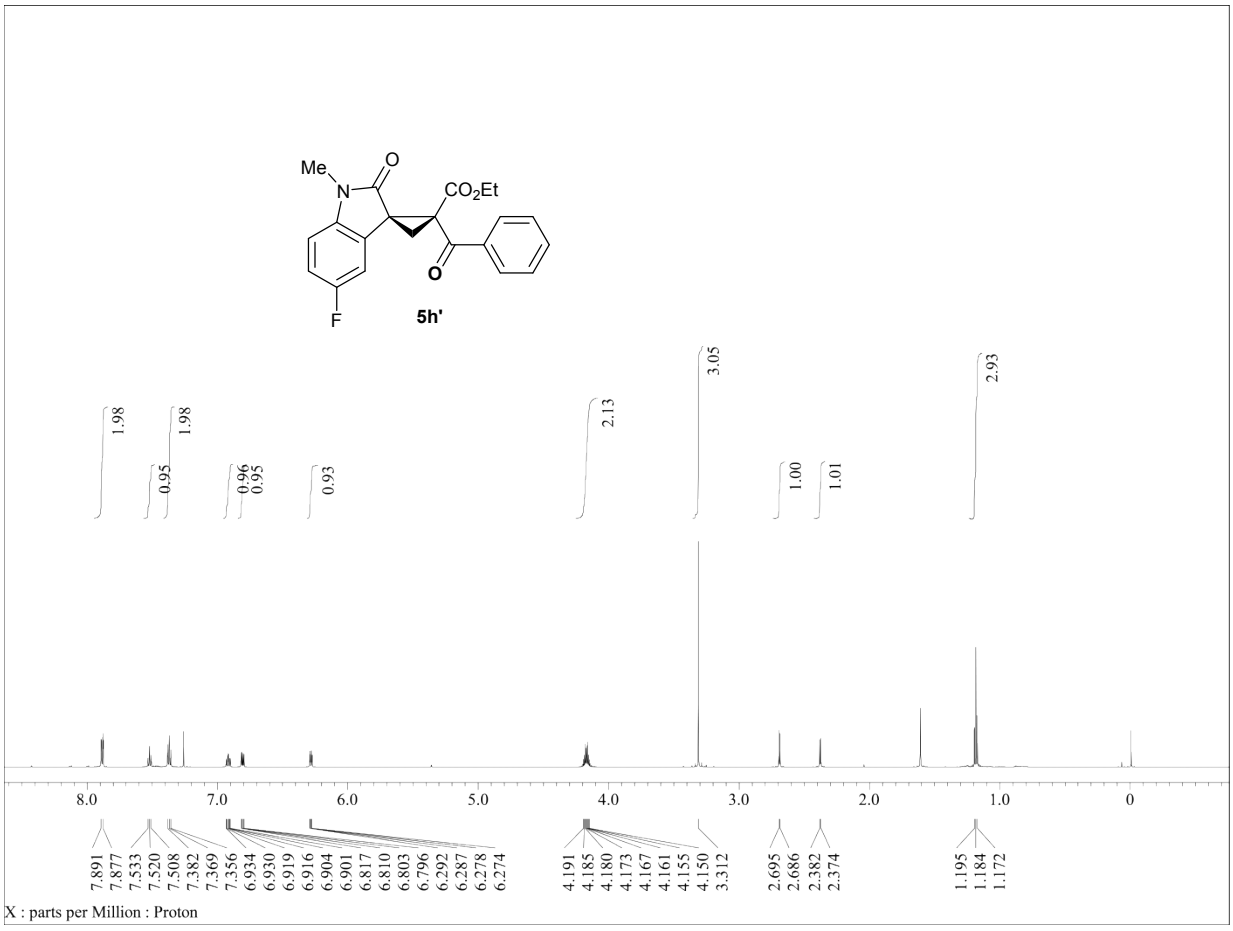

Me
N
O
CO2Et
OMe
O
5e'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.202
172.537
165.030
159.276
143.870
136.574
129.173
128.206
125.152
122.930
122.174
121.389
120.776
113.556
108.319
77.211
77.000
76.789
62.398
55.237
50.028
36.623
26.799
23.860
13.854
X : parts per Million : Carbon13

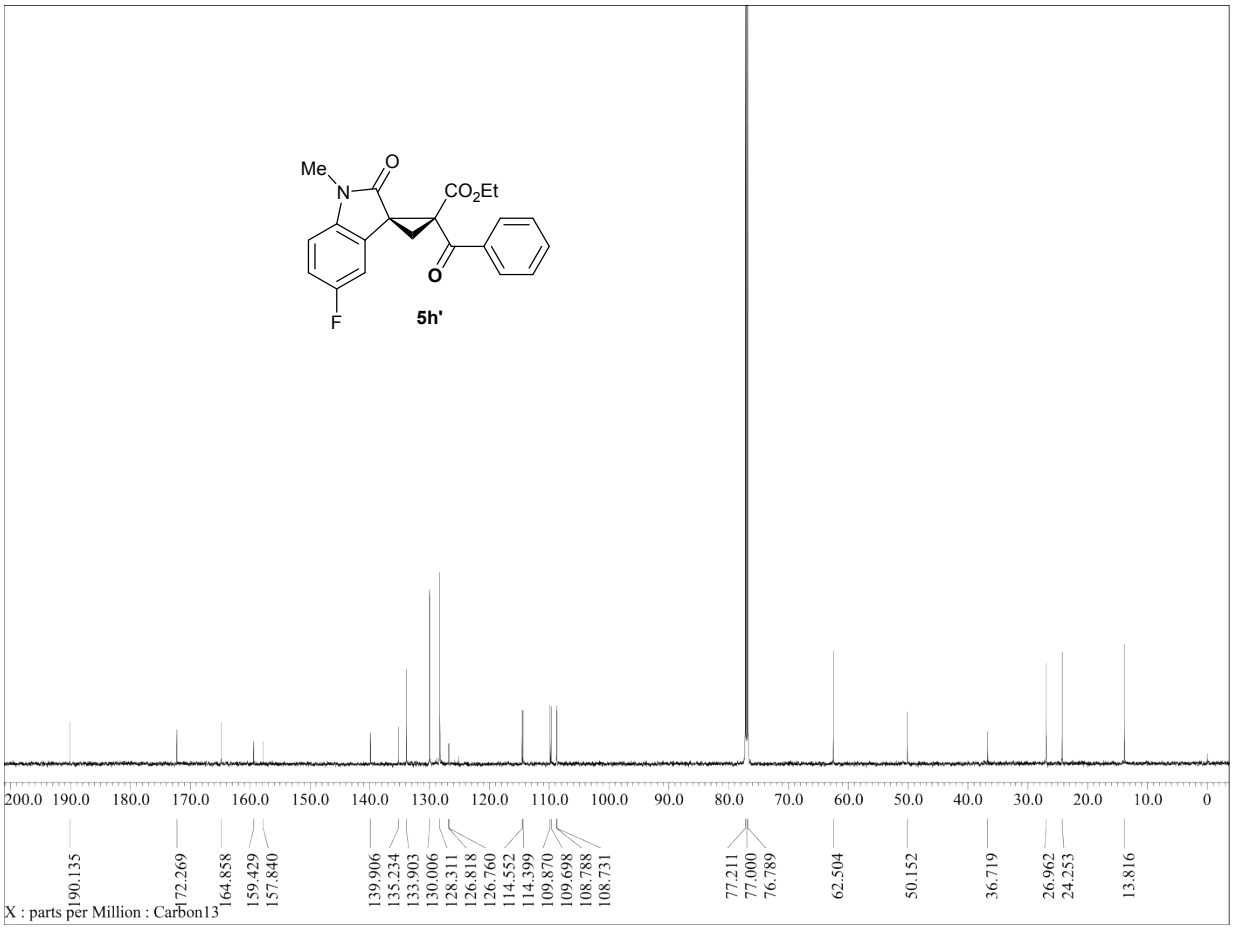

Me
N
O
CO2Et
O
5f'
1.08
1.03
1.06
1.06
1.07
1.94
2.88
0.96
1.01
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.457
7.901
7.899
7.888
7.884
7.869
7.855
7.811
7.797
7.782
7.767
7.584
7.581
7.572
7.570
7.558
7.556
7.512
7.501
7.489
7.487
7.185
7.174
7.161
7.159
6.908
6.894
6.790
6.787
6.777
6.775
6.764
6.762
6.538
6.527
4.199
4.194
4.188
4.182
4.175
4.170
4.163
4.159
3.371
2.756
2.747
2.468
2.459
1.202
1.190
1.178
X : parts per Million : Proton

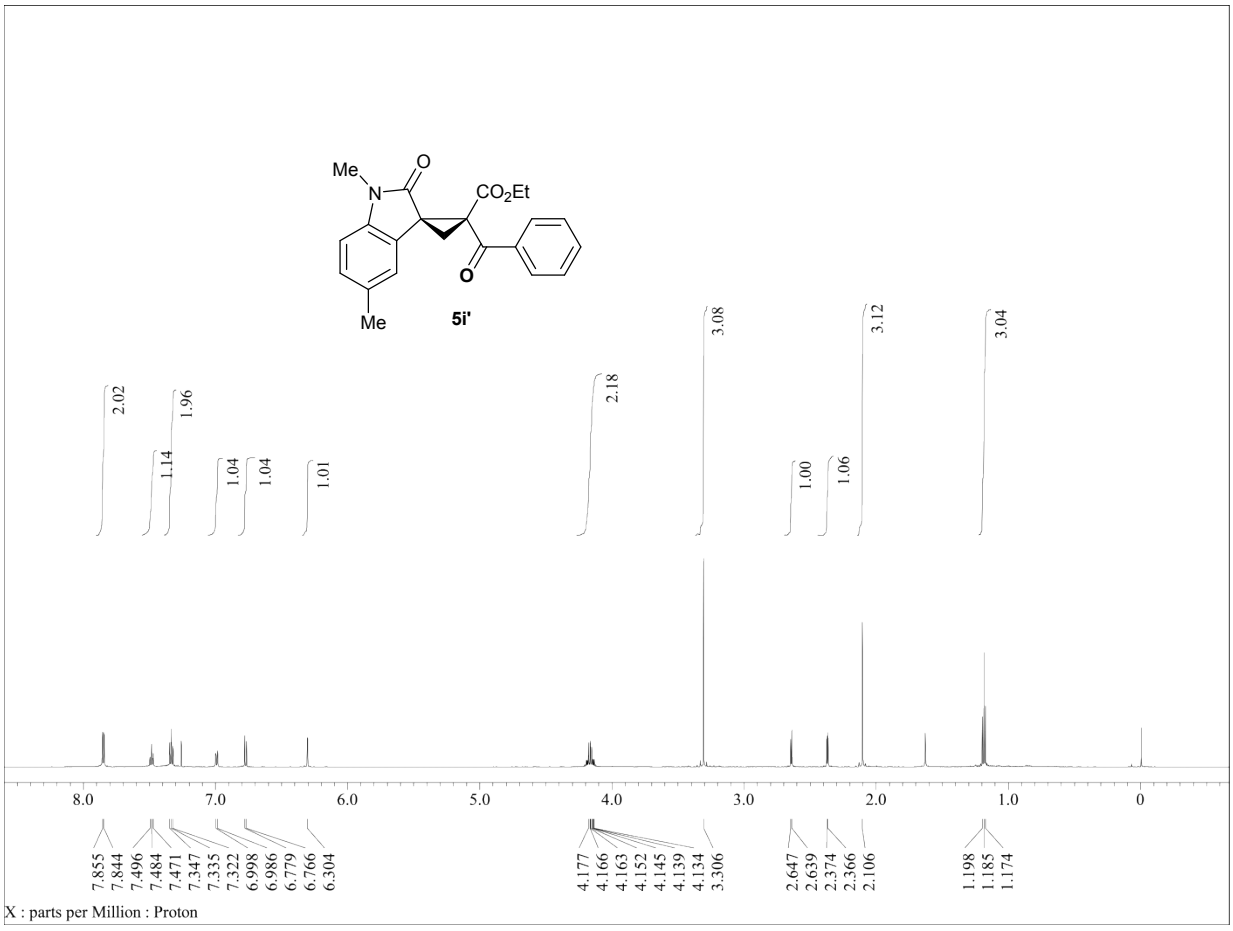

Me
N
O
CO2Et
O
5f'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.327
172.604
165.193
143.899
135.741
132.677
132.045
129.872
128.895
128.196
127.995
127.660
126.693
125.142
125.017
122.174
121.360
108.338
77.211
77.000
76.789
62.418
50.057
36.709
26.857
23.946
13.864
X : parts per Million : Carbon13

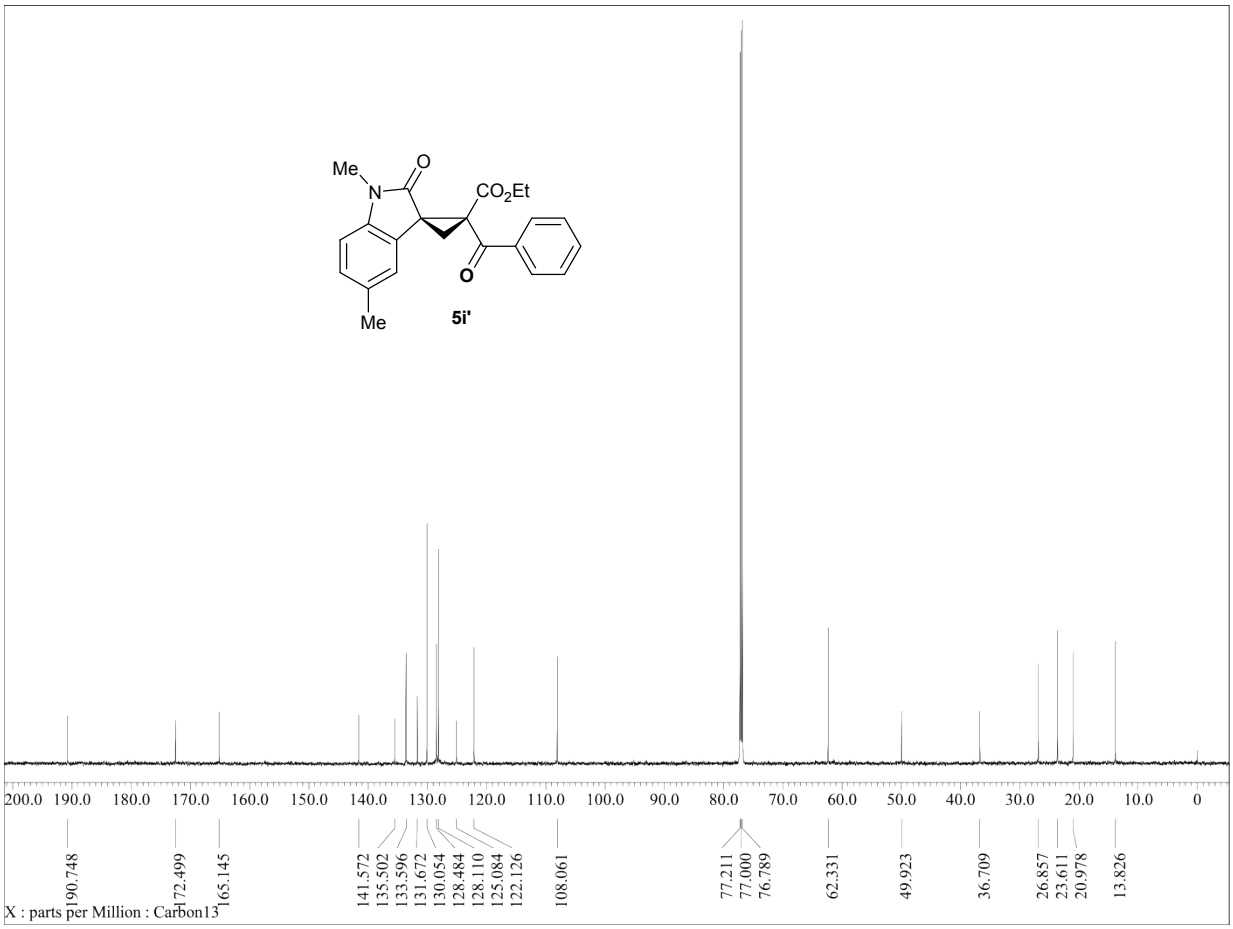

Me
N
O
CO2Et
S
O
5g' 2:1 d.r.
3.07
2.96
2.18
1.00
1.01
1.02
0.99
1.00
0.98
1.02
1.00
1.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.771
7.764
7.616
7.608
7.213
7.211
7.200
7.198
7.188
7.185
6.972
6.964
6.957
6.879
6.865
6.833
6.821
6.808
6.564
6.551
4.264
4.259
4.253
4.247
4.233
4.221
4.215
4.209
4.204
3.312
2.640
2.632
2.389
2.379
1.277
1.265
1.254
X : parts per Million : Proton

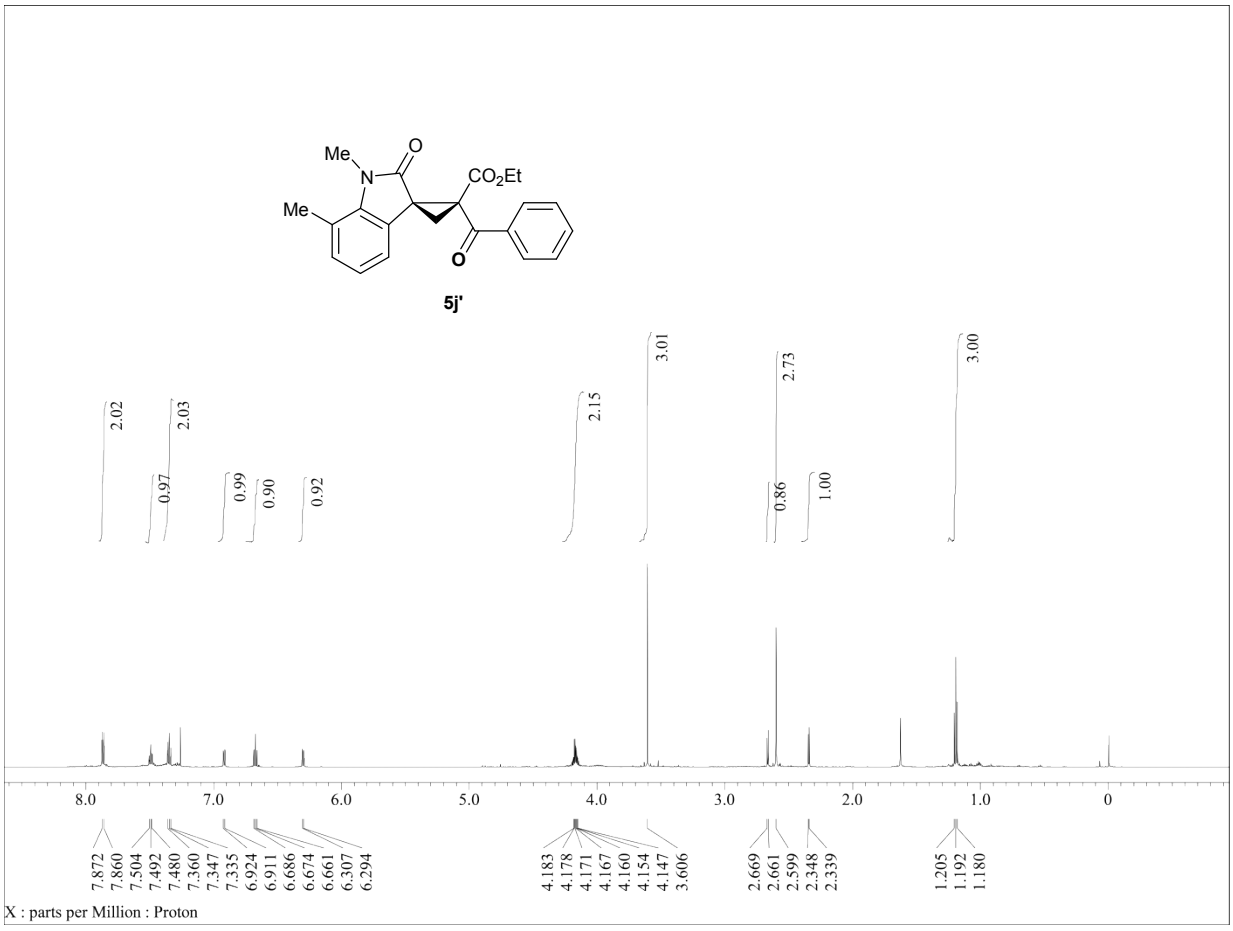

Me
N
O
CO2Et
S
O
5g' 2:1 d.r.
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
182.447
172.556
165.021
143.774
142.166
136.383
135.521
128.206
128.110
125.075
122.135
121.140
108.309
77.211
77.000
76.789
62.533
50.306
36.231
26.790
23.946
13.902
X : parts per Million : Carbon13

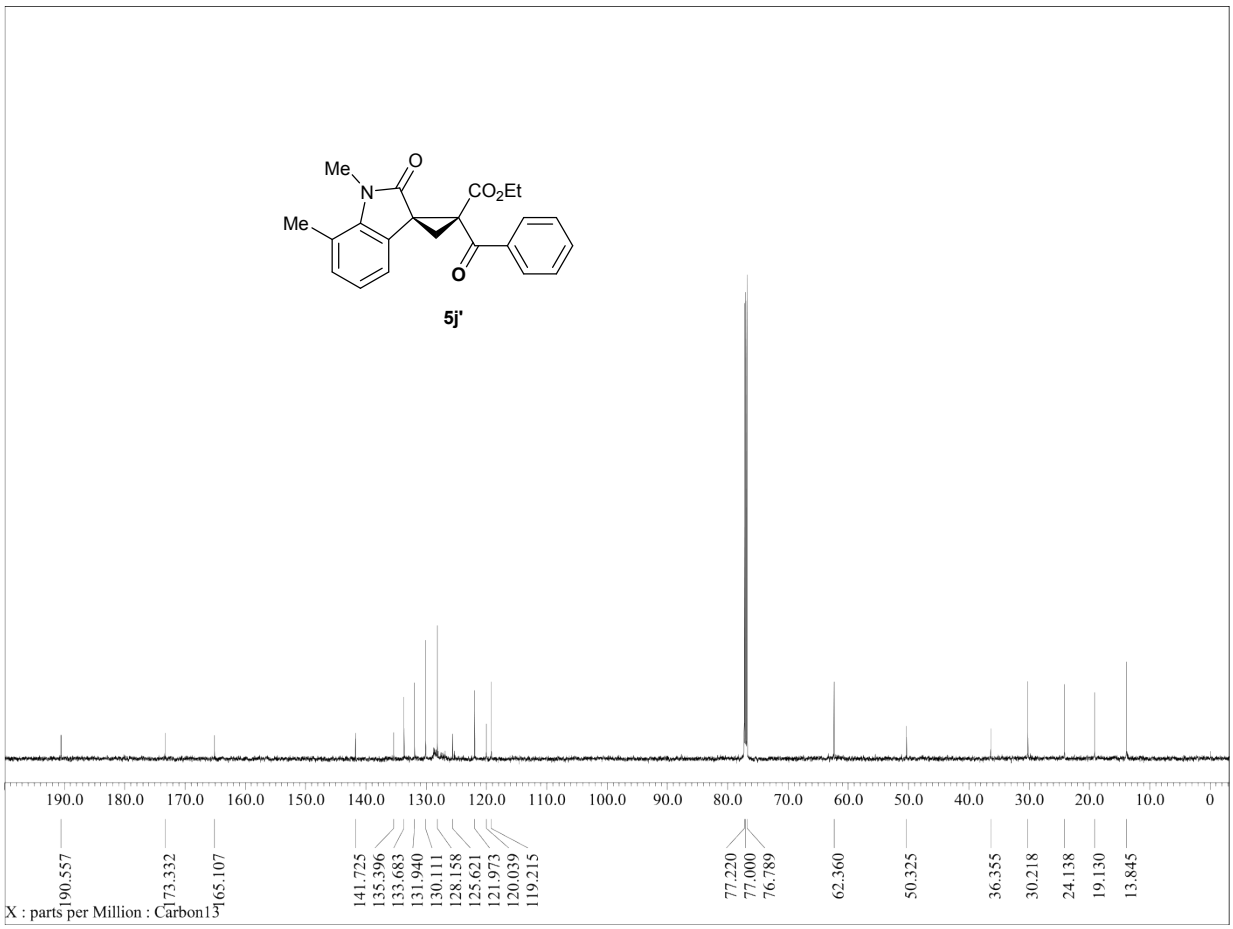

Me
N
O
CO2Et
O
F
5h'
1.98
1.98
0.95
0.96
0.95
0.93
2.13
3.05
1.00
1.01
2.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.891
7.877
7.533
7.520
7.508
7.382
7.369
7.356
6.934
6.930
6.919
6.916
6.904
6.901
6.817
6.810
6.803
6.796
6.292
6.287
6.278
6.274
4.191
4.185
4.180
4.173
4.167
4.161
4.155
4.150
3.312
2.695
2.686
2.382
2.374
1.195
1.184
1.172
X : parts per Million : Proton

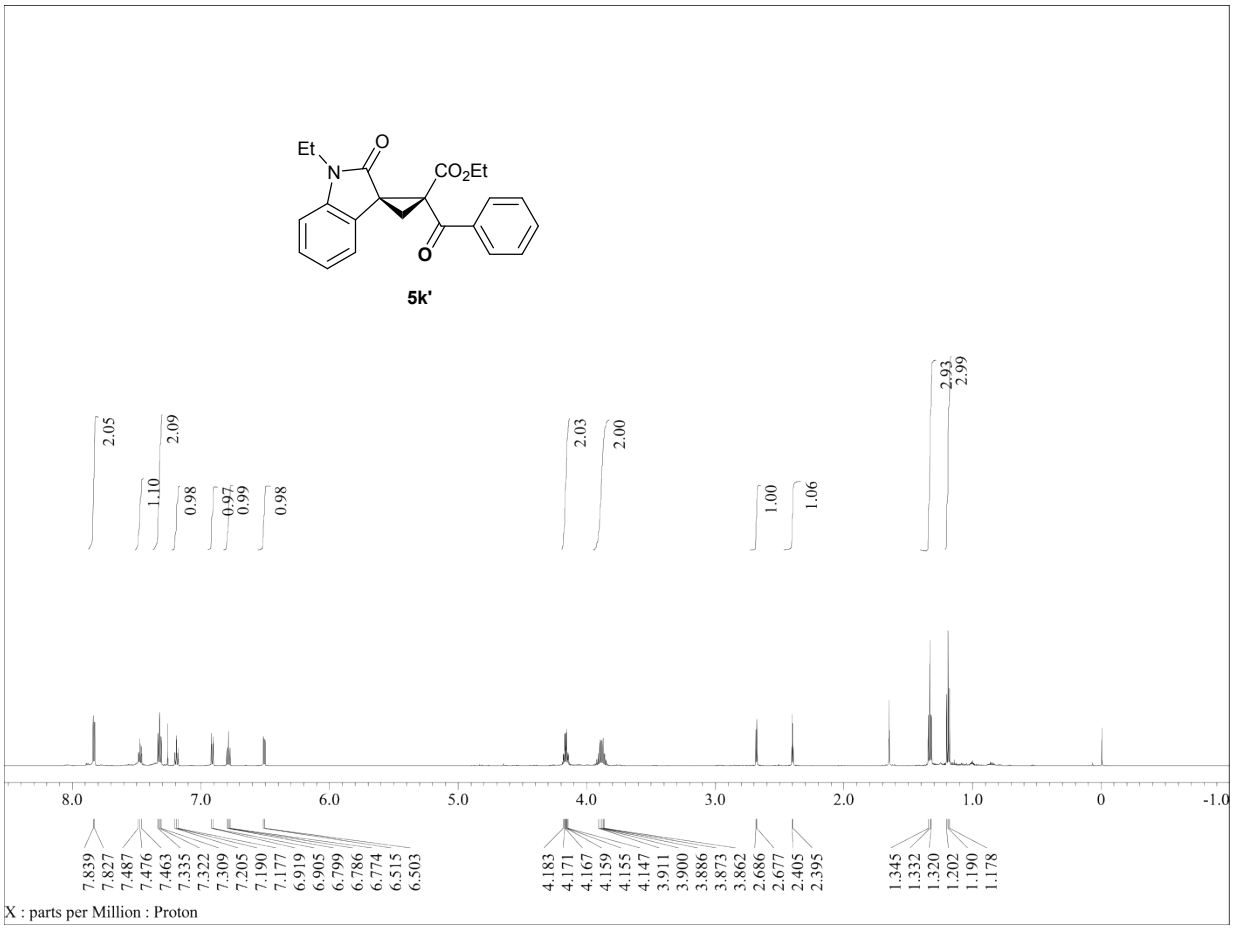

Me
N
O
CO2Et
O
F
5h'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.135
172.269
164.858
159.429
157.840
139.906
135.234
133.903
130.006
128.311
126.818
126.760
114.552
114.399
109.870
109.698
108.788
108.731
77.211
77.000
76.789
62.504
50.152
36.719
26.962
24.253
13.816
X : parts per Million : Carbon13

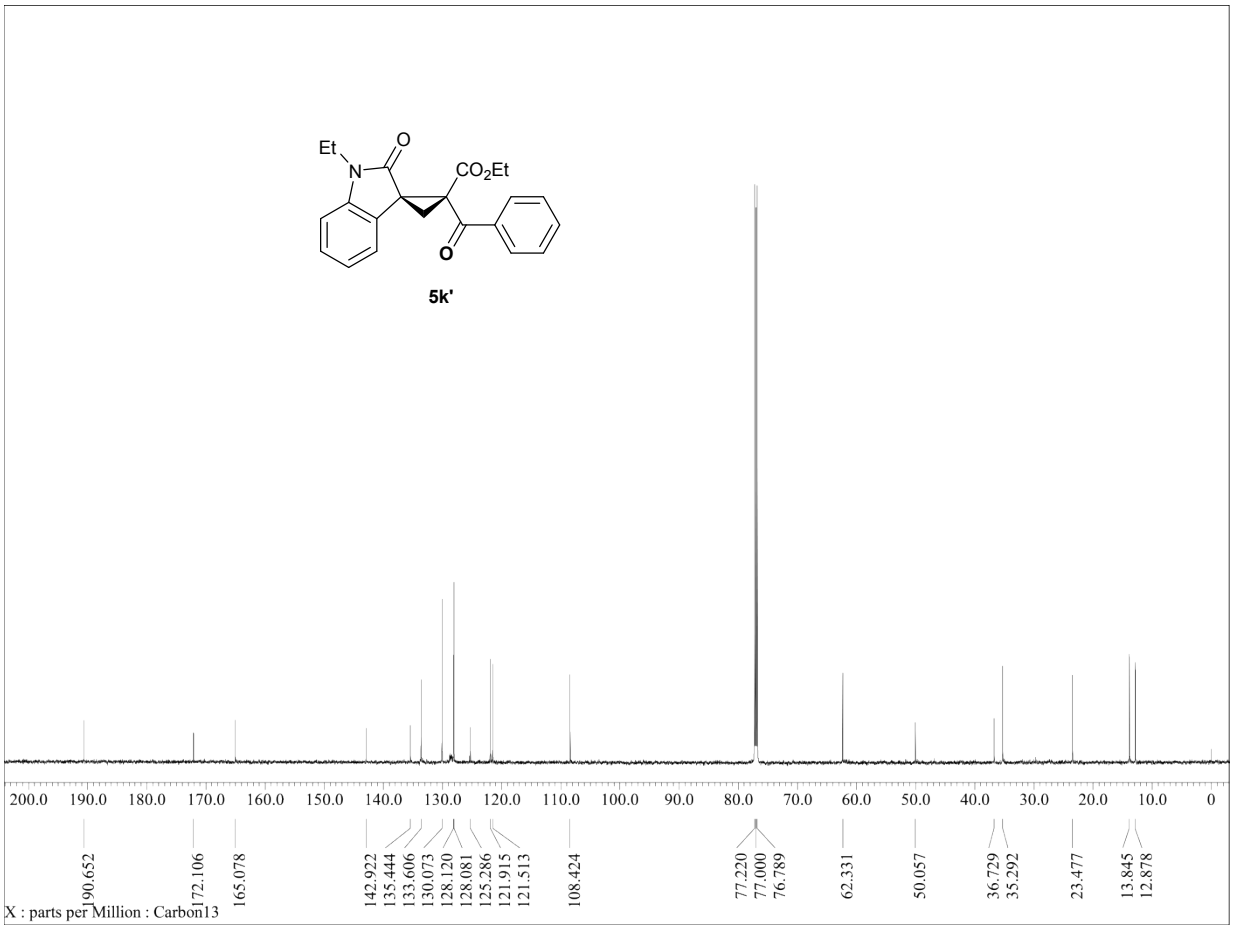

Me
N
O
CO2Et
O
Me
5i'
2.02
1.14
1.96
1.04
1.04
1.01
2.18
3.08
1.00
1.06
3.12
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.855
7.844
7.496
7.484
7.471
7.347
7.335
7.322
6.998
6.986
6.779
6.766
6.304
4.177
4.166
4.163
4.152
4.145
4.139
4.134
3.306
2.647
2.639
2.374
2.366
2.106
1.198
1.185
1.174
X : parts per Million : Proton

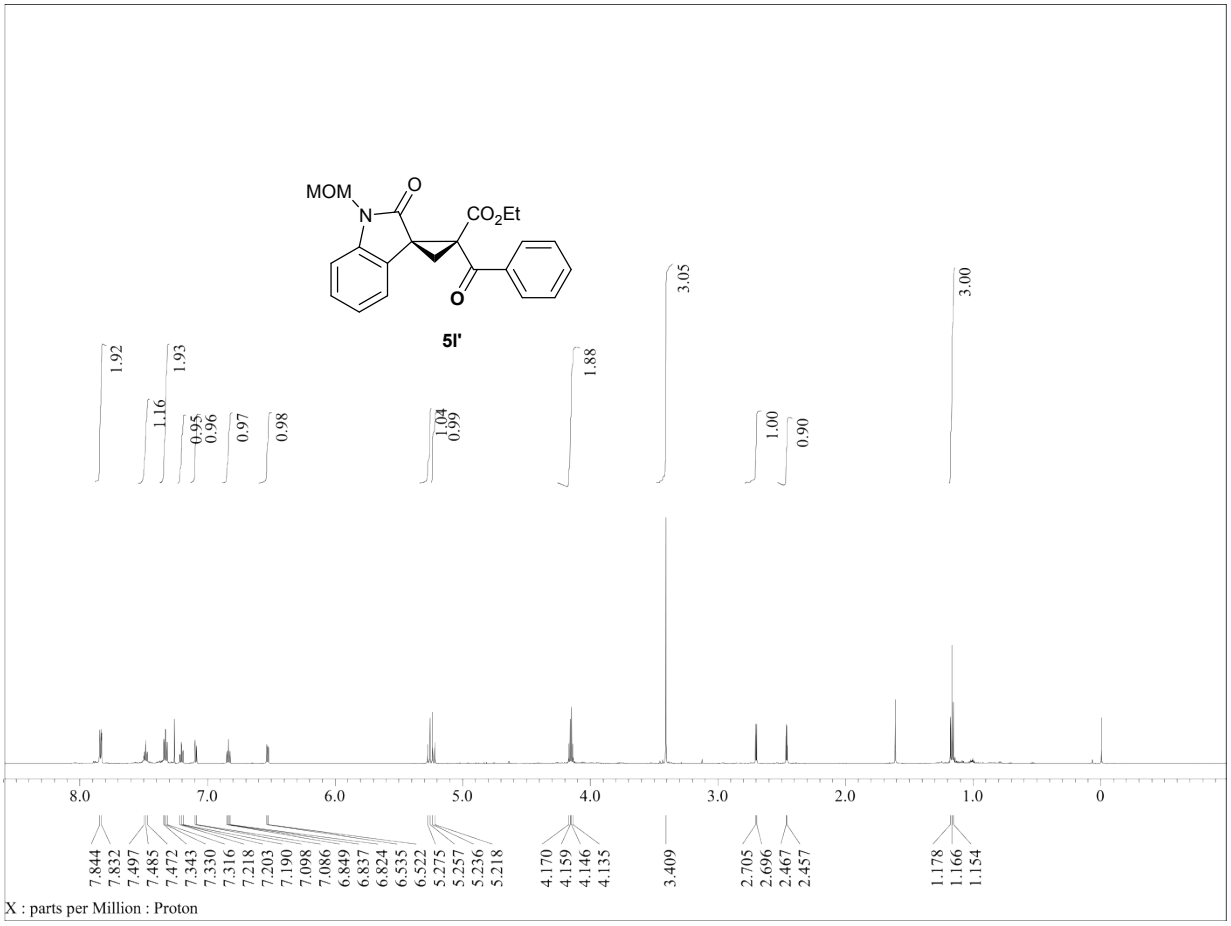

Me
N
O
CO2Et
O
Me
5i'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.748
172.499
165.145
141.572
135.502
133.596
131.672
130.054
128.484
128.110
125.084
122.126
108.061
77.211
77.000
76.789
62.331
49.923
36.709
26.857
23.611
20.978
13.826
X : parts per Million : Carbon13

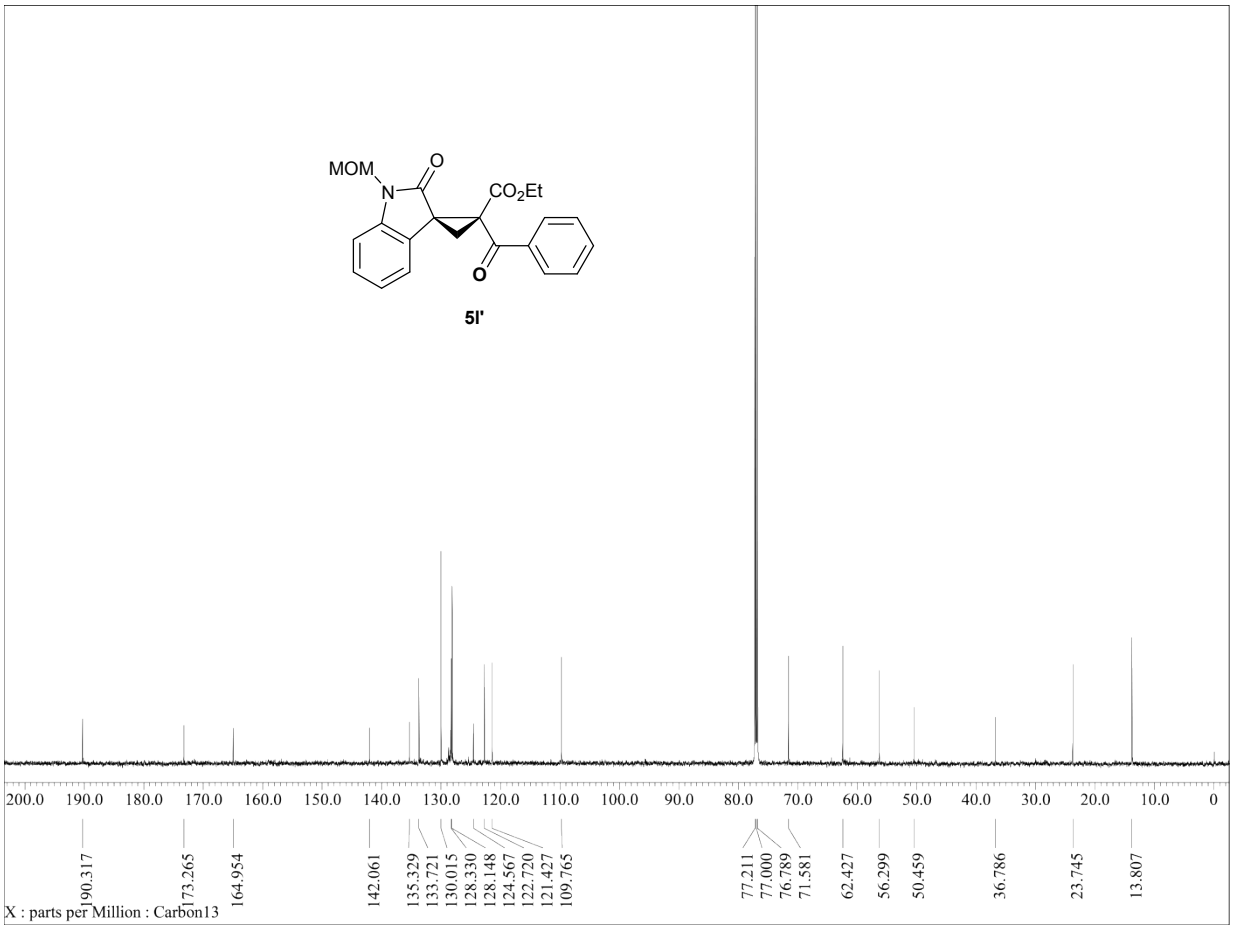

Me
N
O
CO2Et
Me
O
5j'
2.02
2.03
0.97
0.99
0.90
0.92
2.15
3.01
2.73
0.86
1.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.872
7.860
7.504
7.492
7.480
7.360
7.347
7.335
6.924
6.911
6.686
6.674
6.661
6.307
6.294
4.183
4.178
4.171
4.167
4.160
4.154
4.147
3.606
2.669
2.661
2.599
2.348
2.339
1.205
1.192
1.180
X : parts per Million : Proton

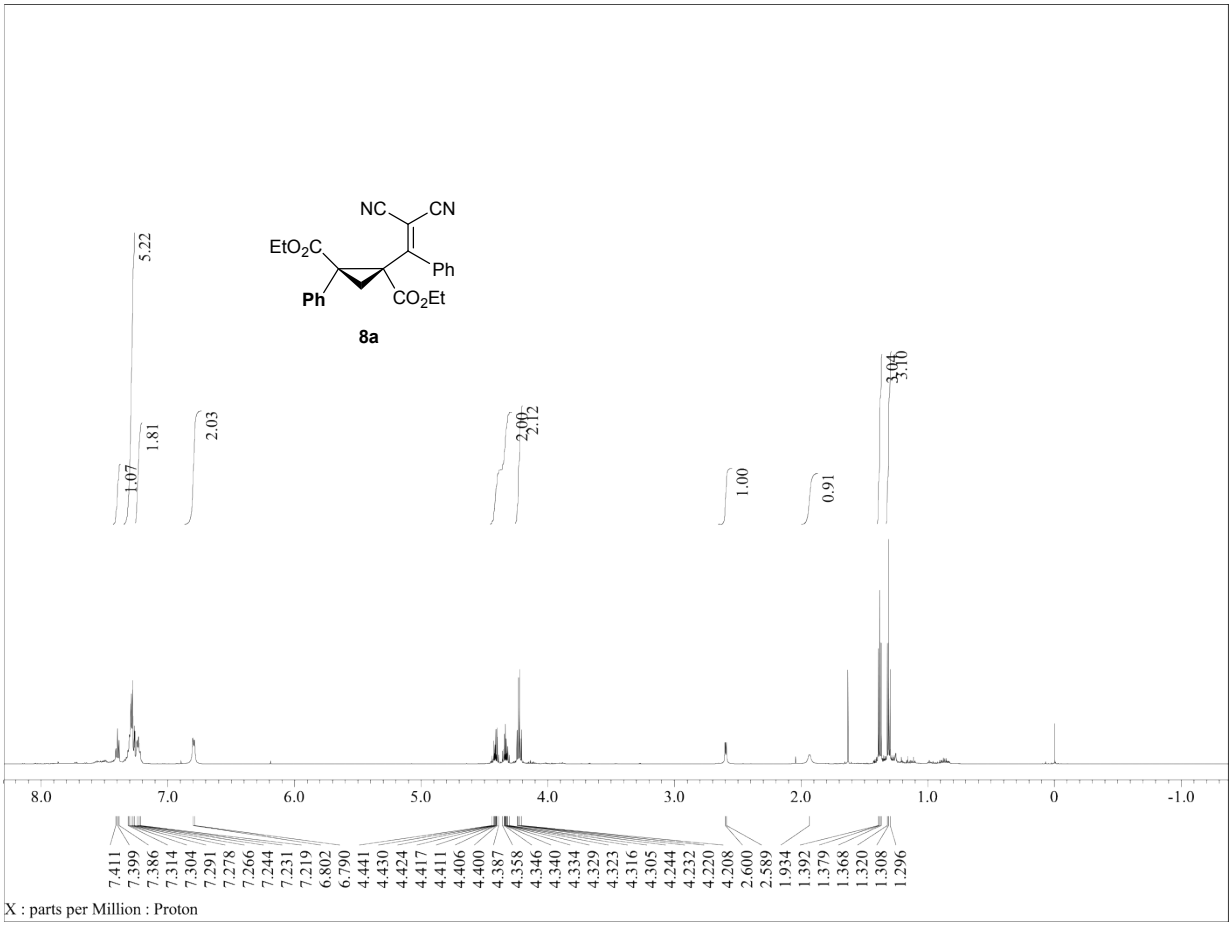

Me
N
O
CO2Et
Me
O
5j'
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.557
173.332
165.107
141.725
135.396
133.683
131.940
130.111
128.158
125.621
121.973
120.039
119.215
77.220
77.000
76.789
62.360
50.325
36.355
30.218
24.138
19.130
13.845
X : parts per Million : Carbon13

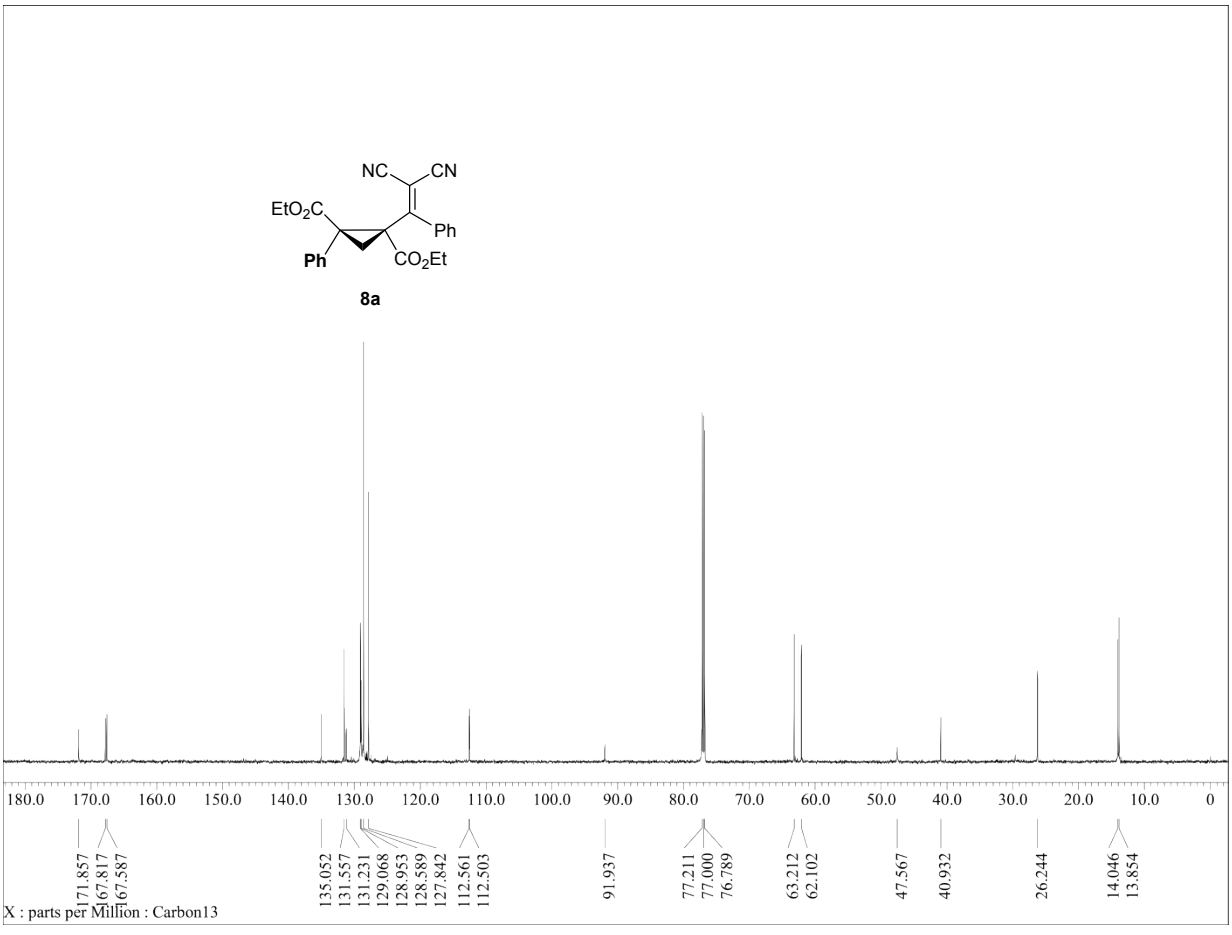

Et
N
O
CO2Et
O
5k'
2.05
2.09
1.10
0.98
0.97
0.99
0.98
2.03
2.00
1.00
1.06
2.93
2.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.839
7.827
7.487
7.476
7.463
7.335
7.322
7.309
7.205
7.190
7.177
6.919
6.905
6.799
6.786
6.774
6.515
6.503
4.183
4.171
4.167
4.159
4.155
4.147
3.911
3.900
3.886
3.873
3.862
2.686
2.677
2.405
2.395
1.345
1.332
1.320
1.202
1.190
1.178
X : parts per Million : Proton

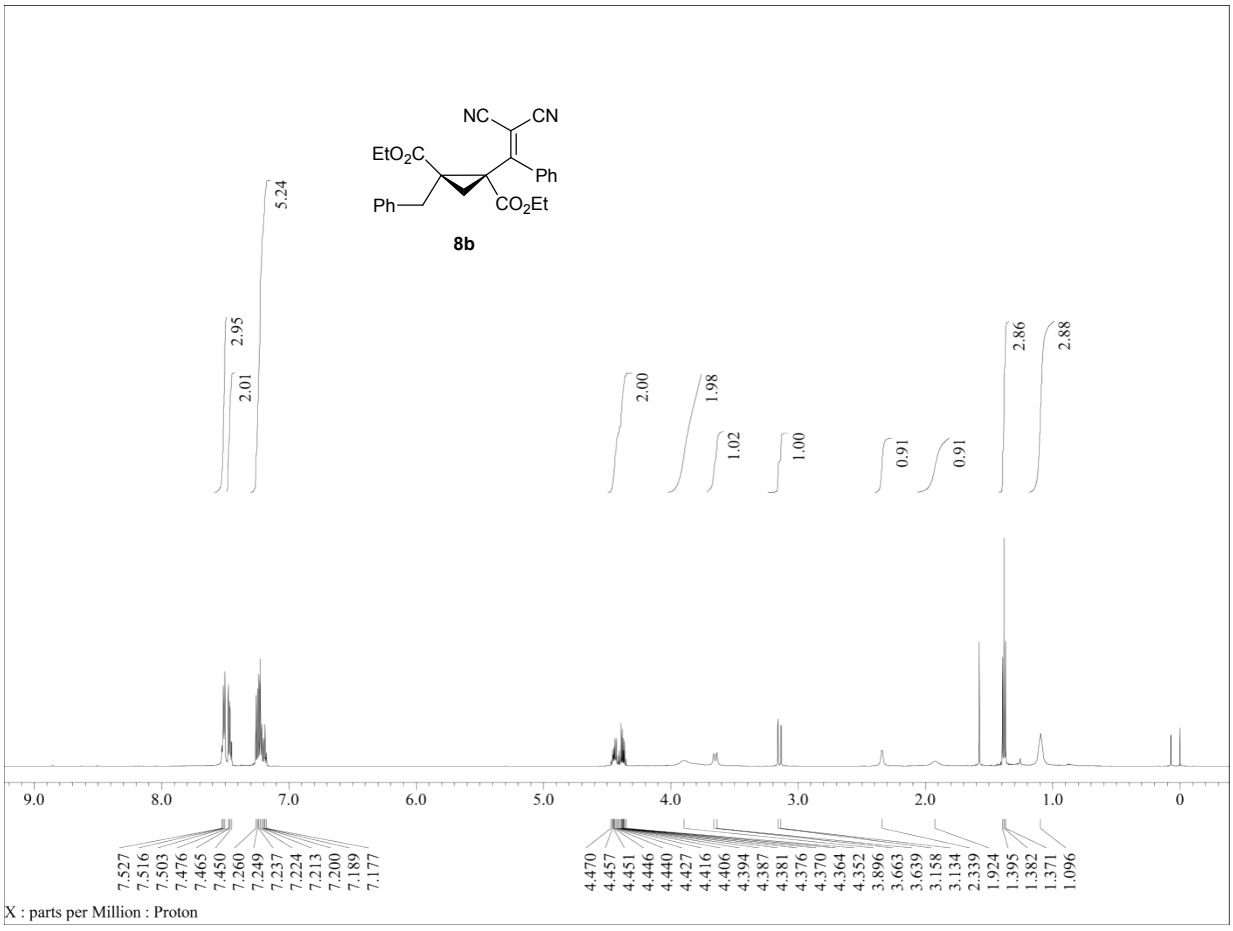

Et
N
O
CO2Et
O
5k'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.652
172.106
165.078
142.922
135.444
133.606
130.073
128.120
128.081
125.286
121.915
121.513
108.424
77.220
77.000
76.789
62.331
50.057
36.729
35.292
23.477
13.845
12.878
X : parts per Million : Carbon13

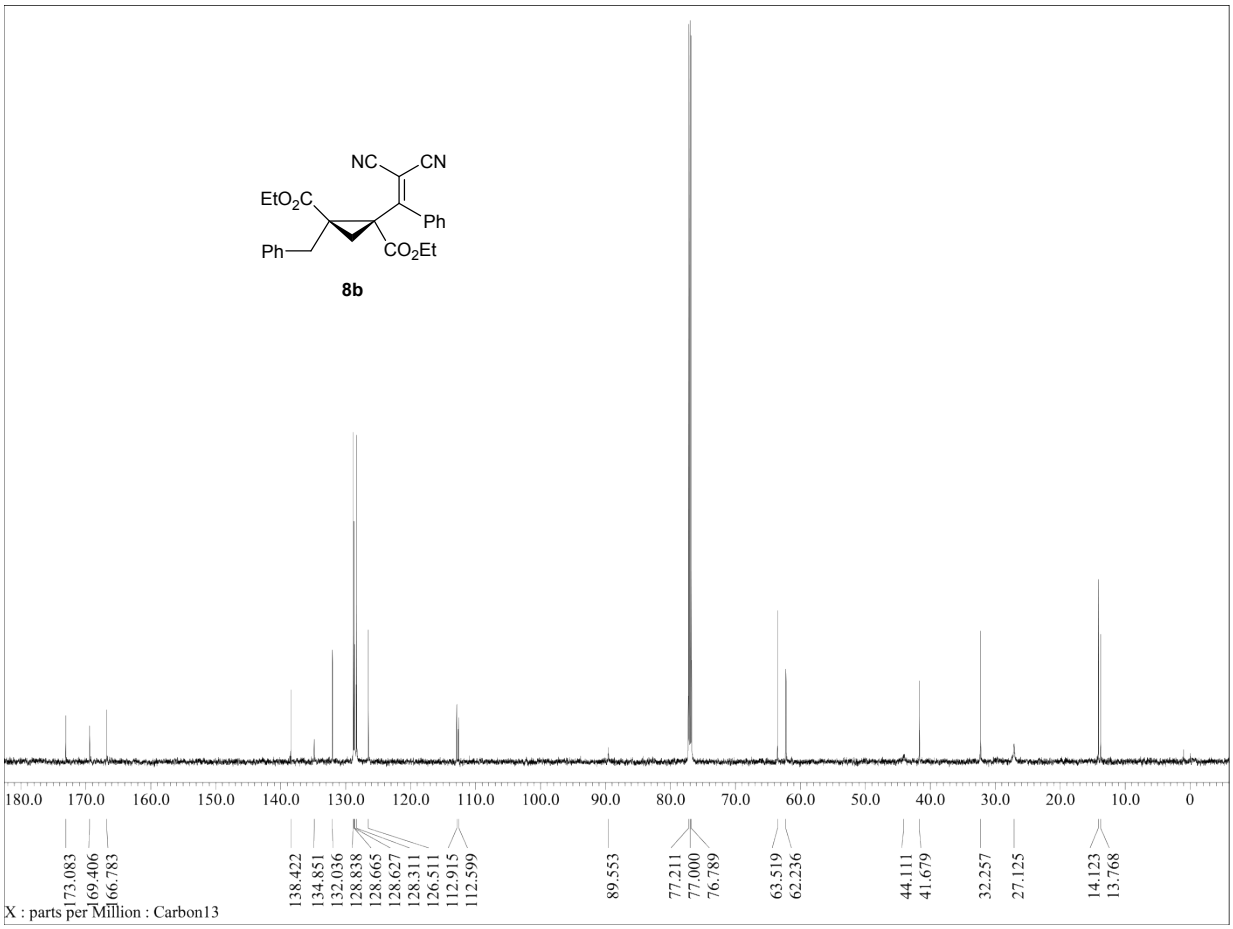

MOM
N
O
CO2Et
O
5l'
1.92
1.93
1.16
0.95
0.96
0.97
0.98
1.04
0.99
1.88
3.05
1.00
0.90
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.844
7.832
7.497
7.485
7.472
7.343
7.330
7.316
7.218
7.203
7.190
7.098
7.086
6.849
6.837
6.824
6.535
6.522
5.275
5.257
5.236
5.218
4.170
4.159
4.146
4.135
3.409
2.705
2.696
2.467
2.457
1.178
1.166
1.154
X : parts per Million : Proton

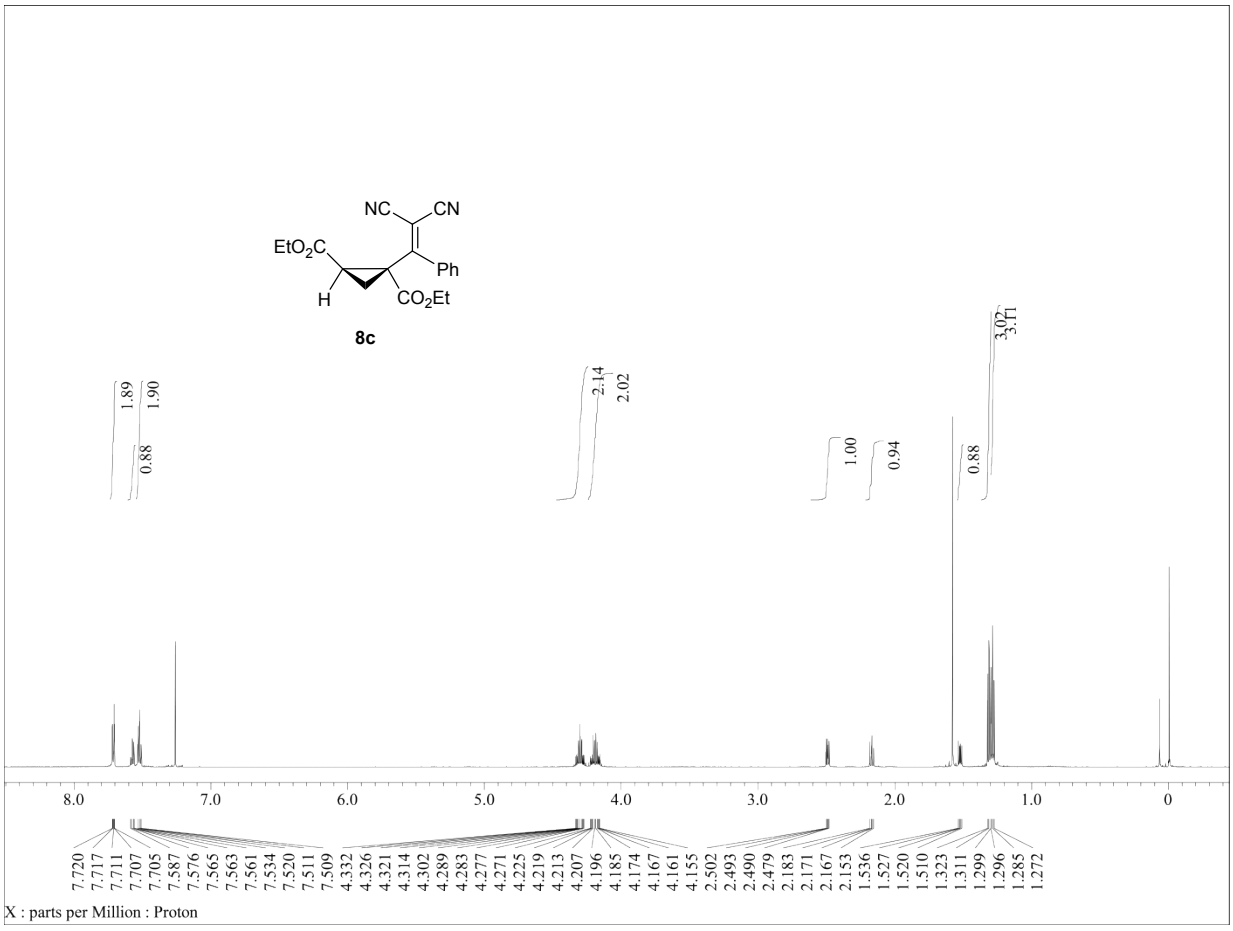

MOM
N
O
CO2Et
O
5l'
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.317
173.265
164.954
142.061
135.329
133.721
130.015
128.330
128.148
124.567
122.720
121.427
109.765
77.211
77.000
76.789
71.581
62.427
56.299
50.459
36.786
23.745
13.807
X : parts per Million : Carbon13

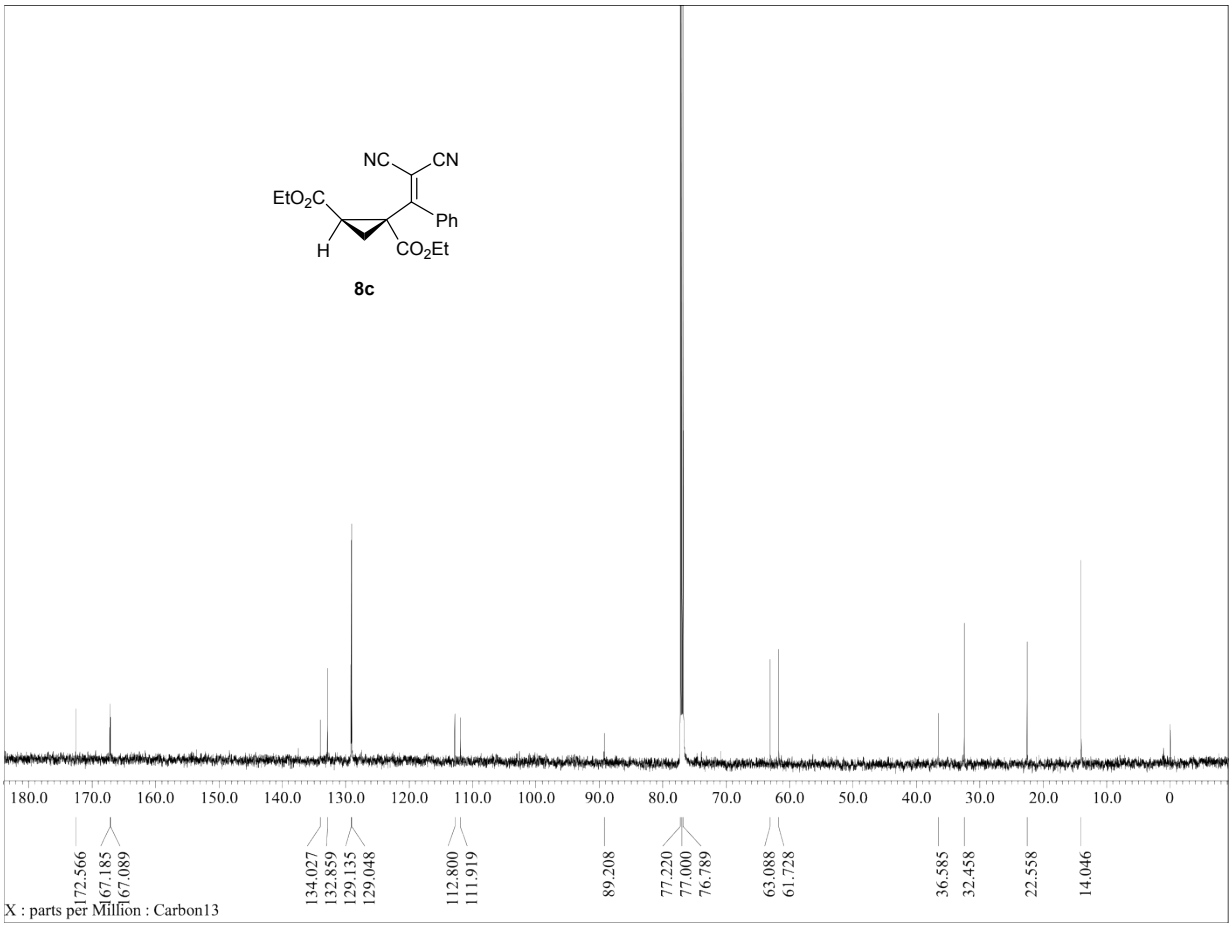

NC
CN
EtO2C
Ph
Ph
CO2Et
8a
5.22
1.81
2.03
1.07
2.00
2.12
1.00
0.91
3.04
3.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.411
7.399
7.386
7.314
7.304
7.291
7.278
7.266
7.244
7.231
7.219
6.802
6.790
4.441
4.430
4.424
4.417
4.411
4.406
4.400
4.387
4.358
4.346
4.340
4.334
4.329
4.323
4.316
4.305
4.244
4.232
4.220
4.208
2.600
2.589
1.934
1.392
1.379
1.368
1.320
1.308
1.296
X : parts per Million : Proton

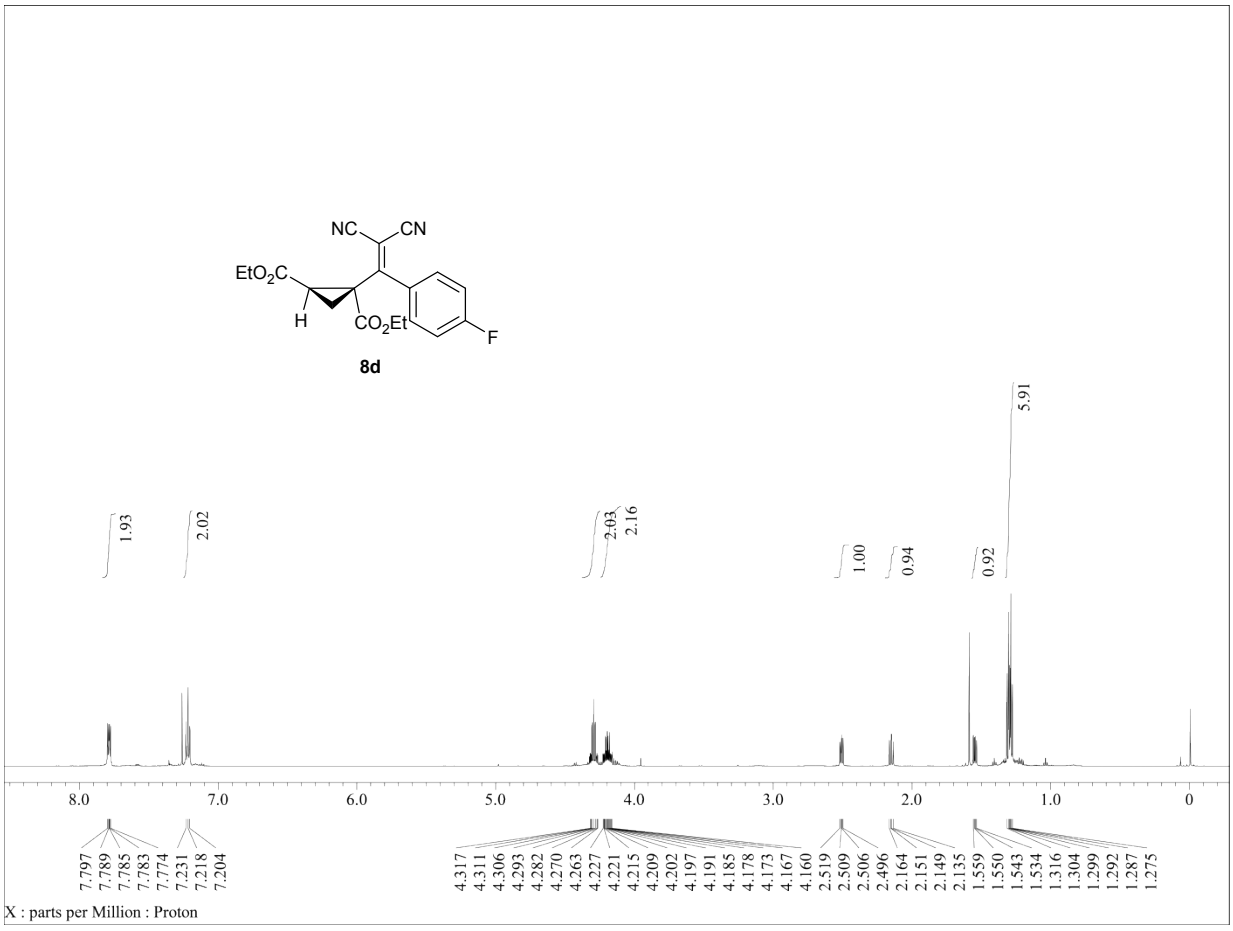

NC
CN
EtO2C
Ph
Ph
CO2Et
8a
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.857
167.817
167.587
135.052
131.557
131.231
129.068
128.953
128.589
127.842
112.561
112.503
91.937
77.211
77.000
76.789
63.212
62.102
47.567
40.932
26.244
14.046
13.854
X : parts per Million : Carbon13

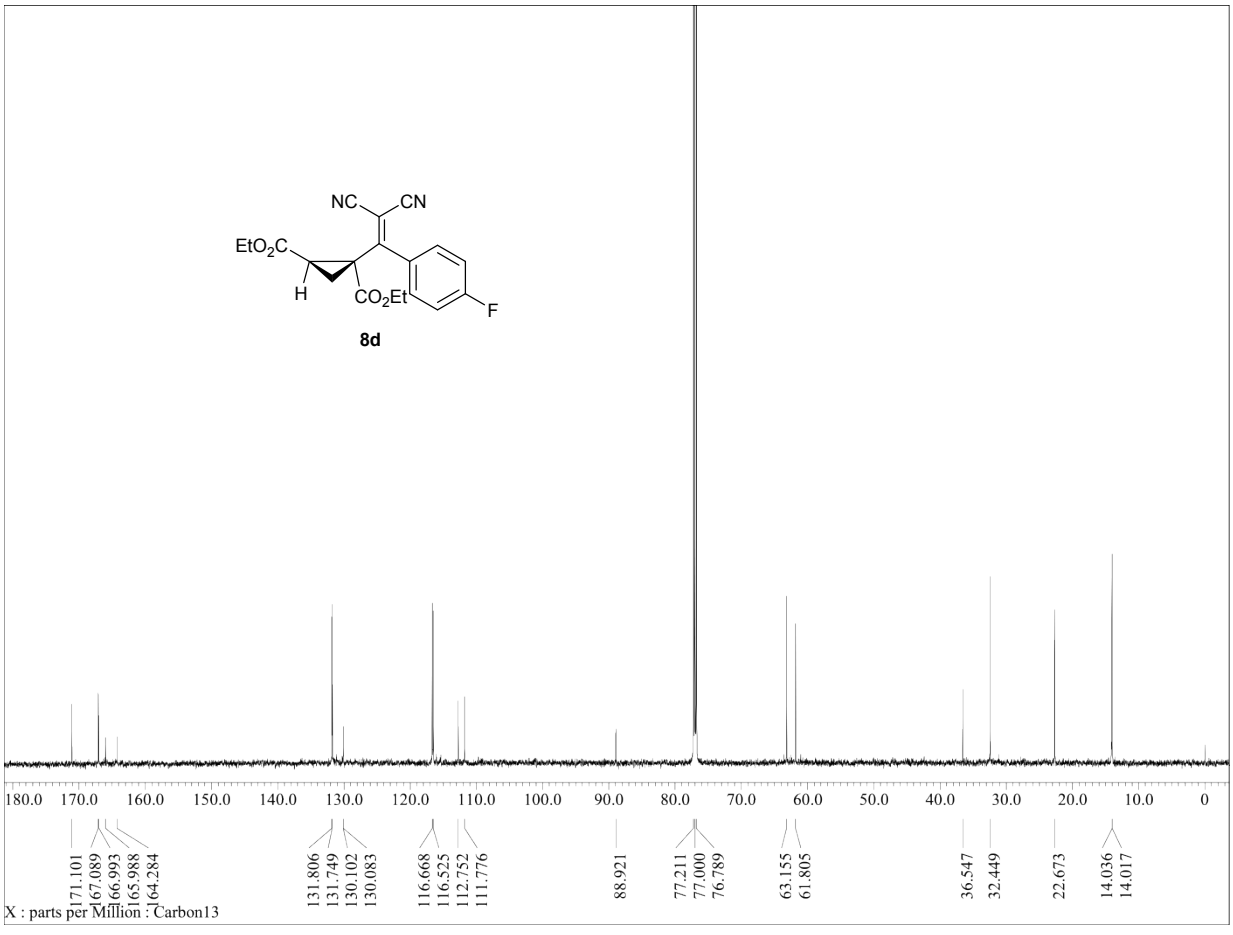

NC
CN
EtO2C
Ph
Ph
CO2Et
8b
5.24
2.95
2.01
2.00
1.98
1.02
1.00
0.91
0.91
2.86
2.88
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.527
7.516
7.503
7.476
7.465
7.450
7.260
7.249
7.237
7.224
7.213
7.200
7.189
7.177
4.470
4.457
4.451
4.446
4.440
4.427
4.416
4.406
4.394
4.387
4.381
4.376
4.370
4.364
4.352
3.896
3.663
3.639
3.158
3.134
2.339
1.924
1.395
1.382
1.371
1.096
X : parts per Million : Proton

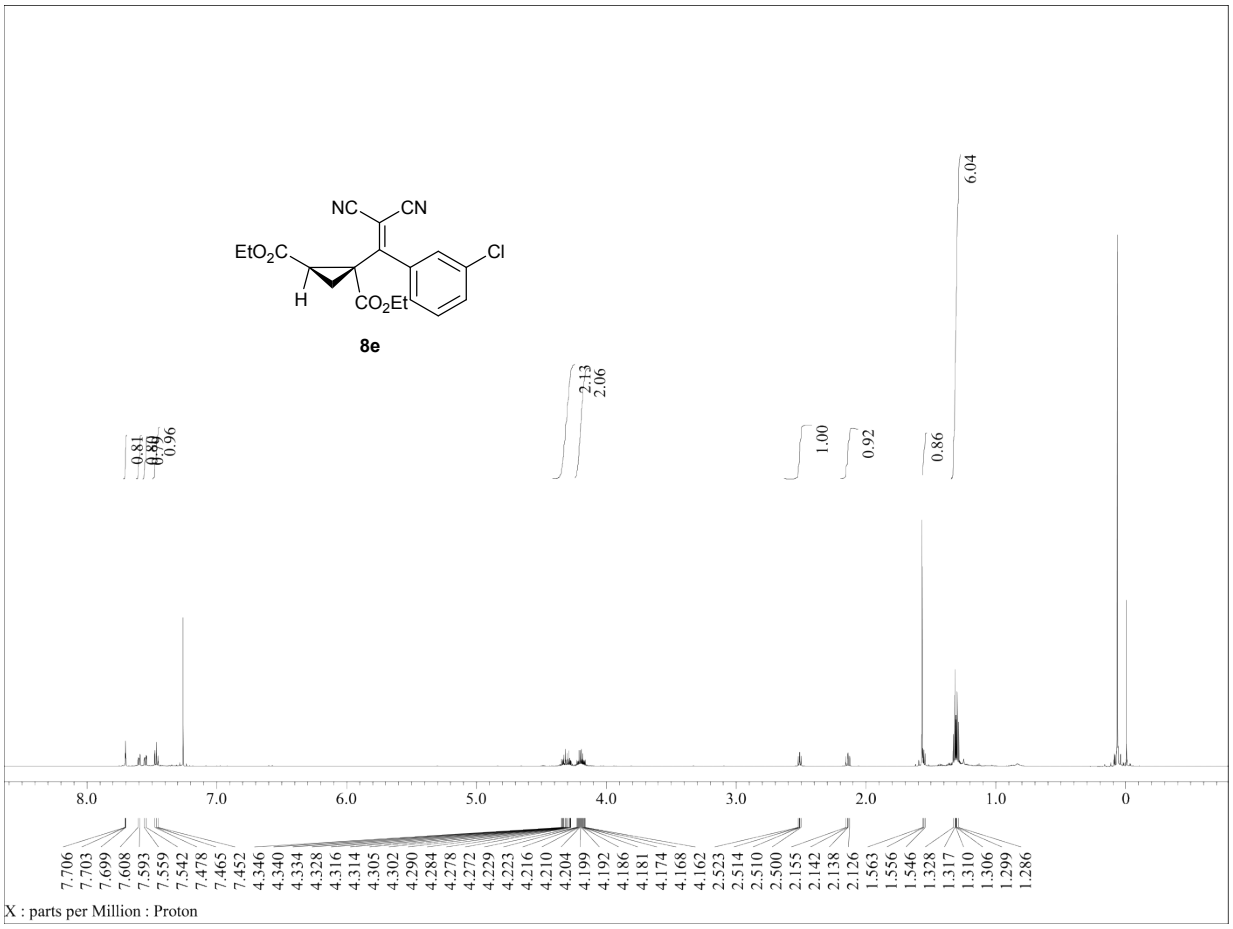

NC
CN
EtO2C
Ph
Ph
CO2Et
8b
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.083
169.406
166.783
138.422
134.851
132.036
128.838
128.665
128.627
128.311
126.511
112.915
112.599
89.553
77.211
77.000
76.789
63.519
62.236
44.111
41.679
32.257
27.125
14.123
13.768
X : parts per Million : Carbon13

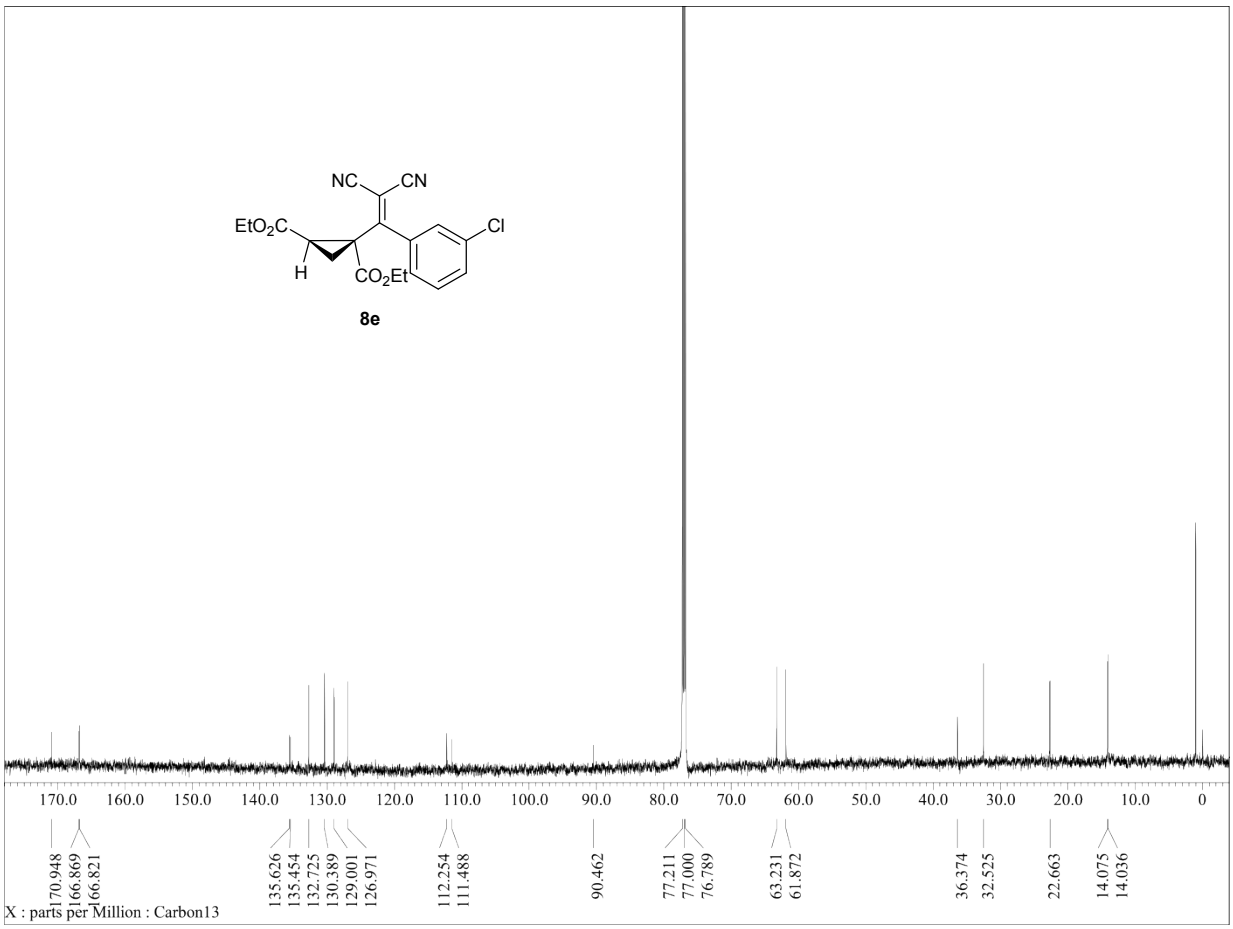

NC
CN
EtO2C
Ph
H
CO2Et
8c
1.89
1.90
0.88
2.14
2.02
1.00
0.94
0.88
3.07
3.11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.720
7.717
7.711
7.707
7.705
7.587
7.576
7.565
7.563
7.561
7.534
7.520
7.511
7.509
4.332
4.326
4.321
4.314
4.302
4.289
4.283
4.277
4.271
4.225
4.219
4.213
4.207
4.196
4.185
4.174
4.167
4.161
4.155
2.502
2.493
2.490
2.479
2.183
2.171
2.167
2.153
1.536
1.527
1.520
1.510
1.323
1.311
1.299
1.296
1.285
1.272
X : parts per Million : Proton

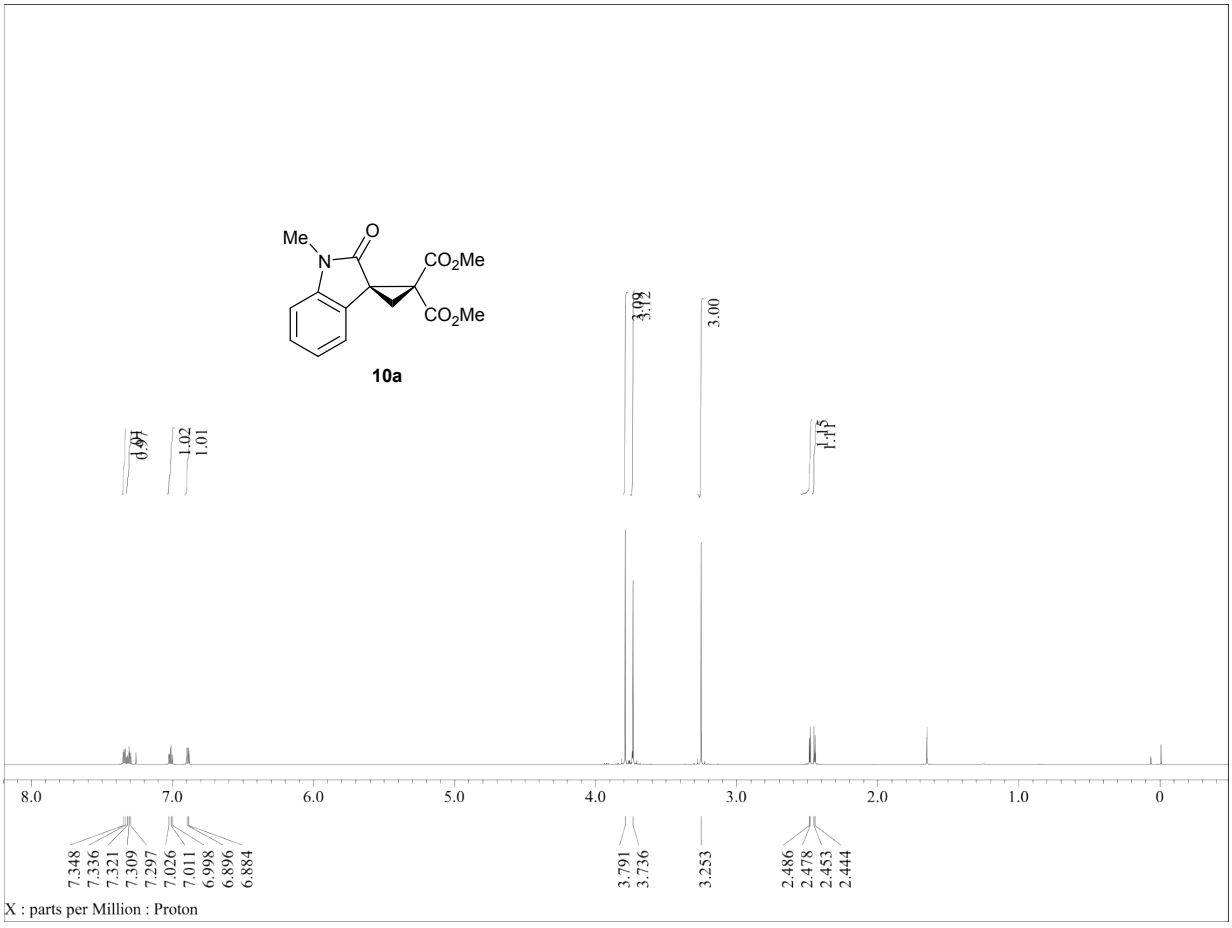

NC
CN
EtO2C
Ph
H
CO2Et
8c
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.566
167.185
167.089
134.027
132.859
129.135
129.048
112.800
111.919
89.208
77.220
77.000
76.789
63.088
61.728
36.585
32.458
22.558
14.046
X : parts per Million : Carbon13

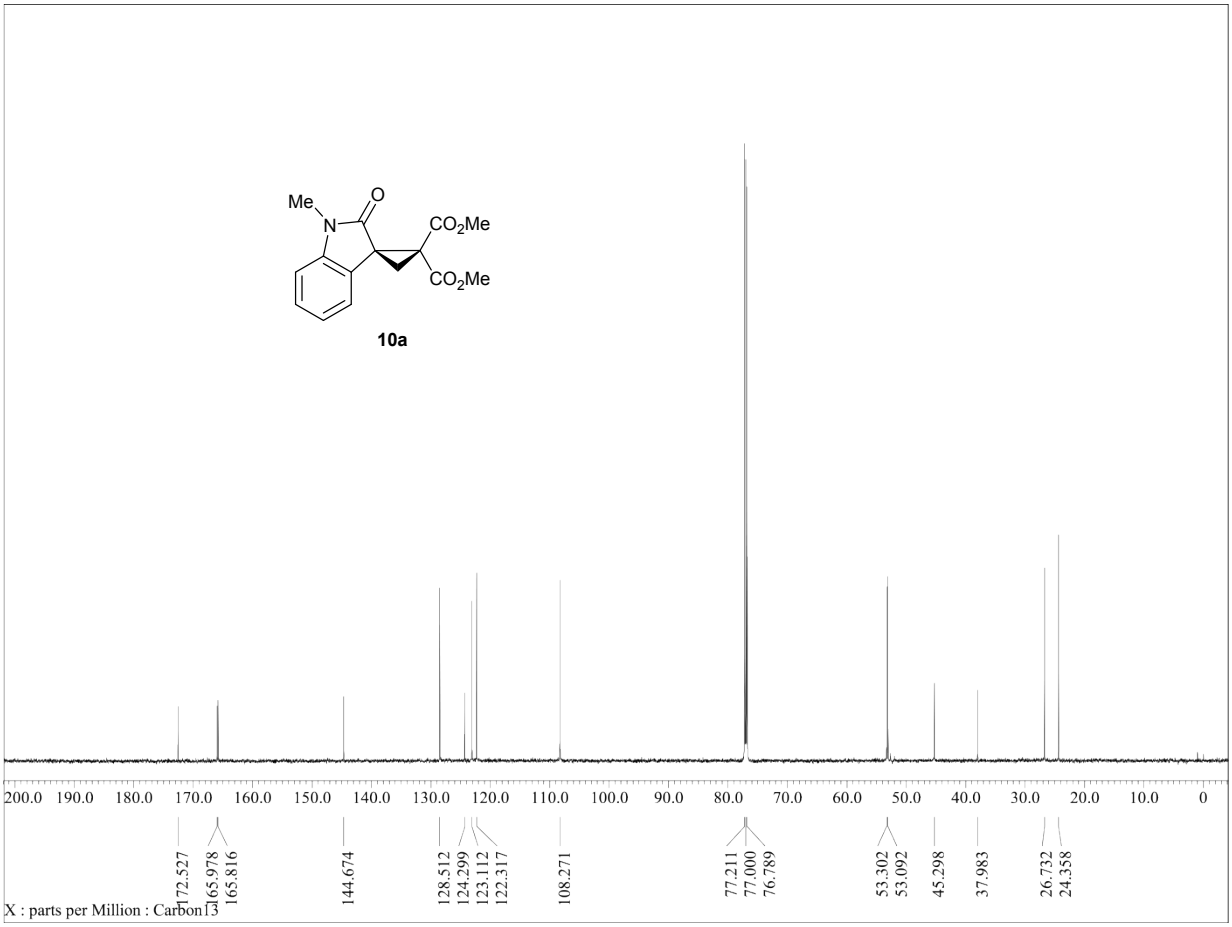

NC
CN
EtO2C
H
CO2Et
F
8d
1.93
2.02
2.03
2.16
1.00
0.94
0.92
5.91
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.797
7.789
7.785
7.783
7.774
7.231
7.218
7.204
4.317
4.311
4.306
4.293
4.282
4.270
4.263
4.227
4.221
4.215
4.209
4.202
4.197
4.191
4.185
4.178
4.173
4.167
4.160
2.519
2.509
2.506
2.496
2.164
2.151
2.149
2.135
1.559
1.550
1.543
1.534
1.316
1.304
1.299
1.292
1.287
1.275
X : parts per Million : Proton

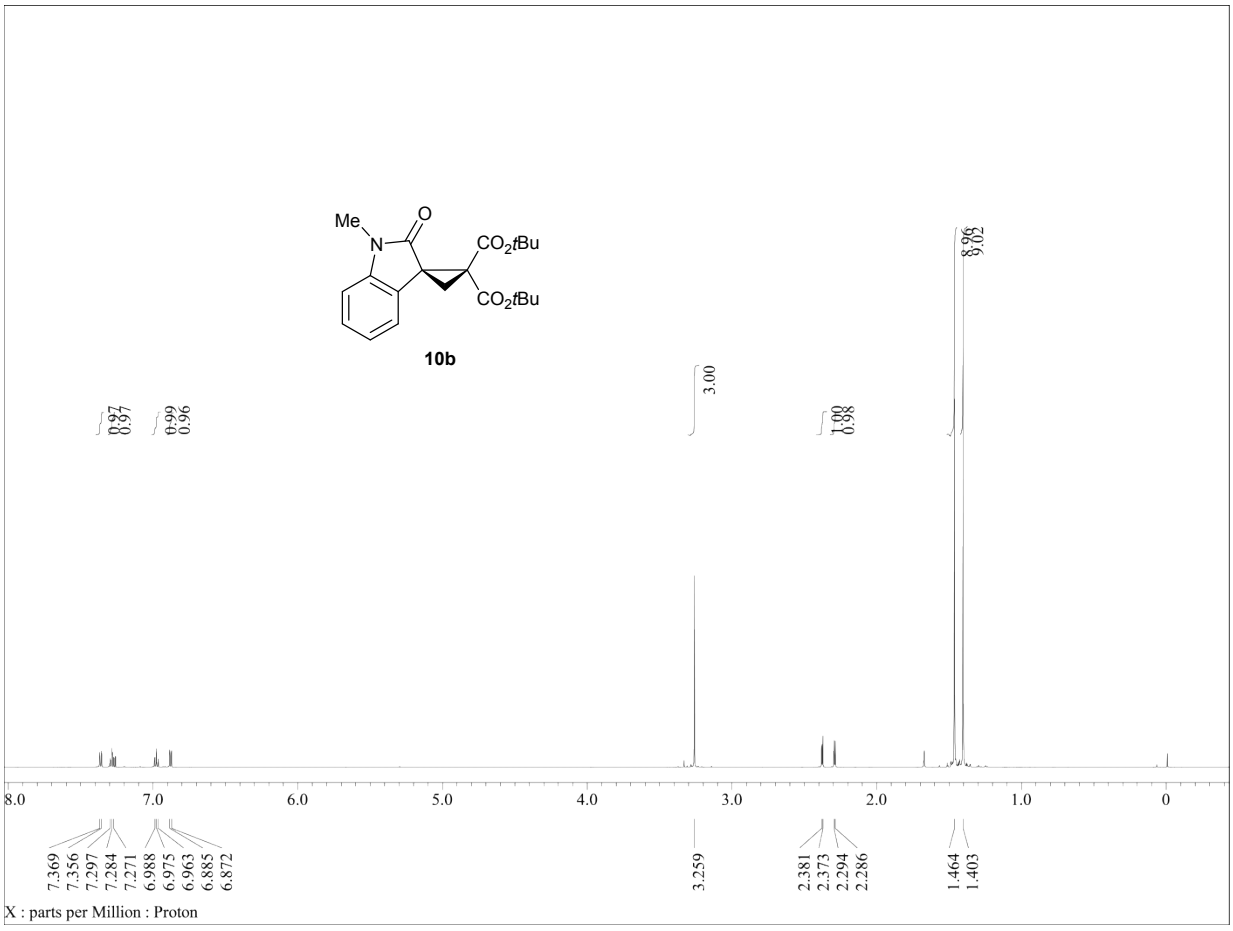

NC
CN
EtO2C
H
CO2Et
F
8d
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.101
167.089
166.993
165.988
164.284
131.806
131.749
130.102
130.083
116.668
116.525
112.752
111.776
88.921
77.211
77.000
76.789
63.155
61.805
36.547
32.449
22.673
14.036
14.017
X : parts per Million : Carbon13

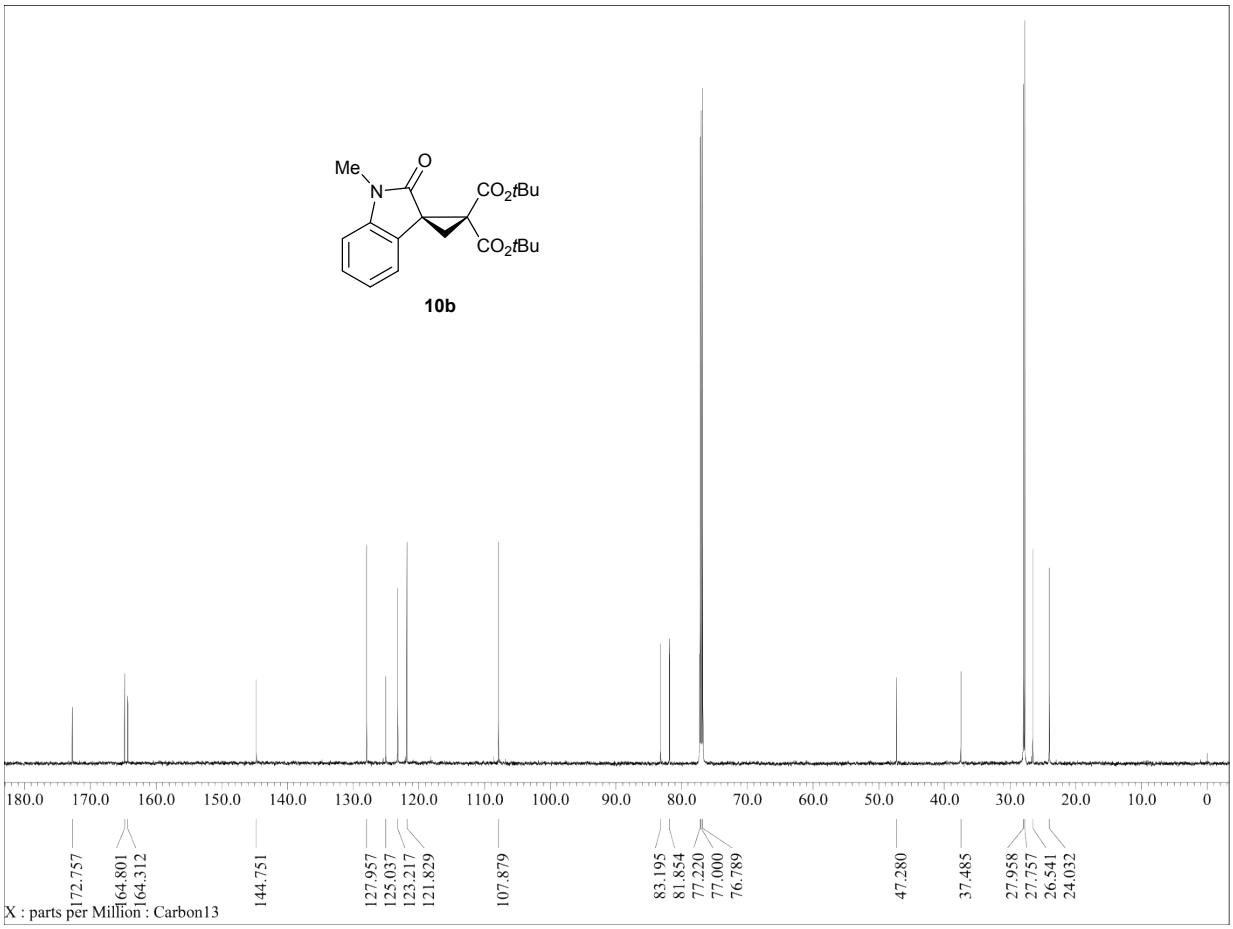

NC
CN
EtO2C
Cl
H
CO2Et
8e
6.04
2.13
2.06
1.00
0.92
0.86
0.81
0.89
0.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.706
7.703
7.699
7.608
7.593
7.559
7.542
7.478
7.465
7.452
4.346
4.340
4.334
4.328
4.316
4.314
4.305
4.302
4.290
4.284
4.278
4.272
4.229
4.223
4.216
4.210
4.204
4.199
4.192
4.186
4.181
4.174
4.168
4.162
2.523
2.514
2.510
2.500
2.155
2.142
2.138
2.126
1.563
1.556
1.546
1.328
1.317
1.310
1.306
1.299
1.286
X : parts per Million : Proton

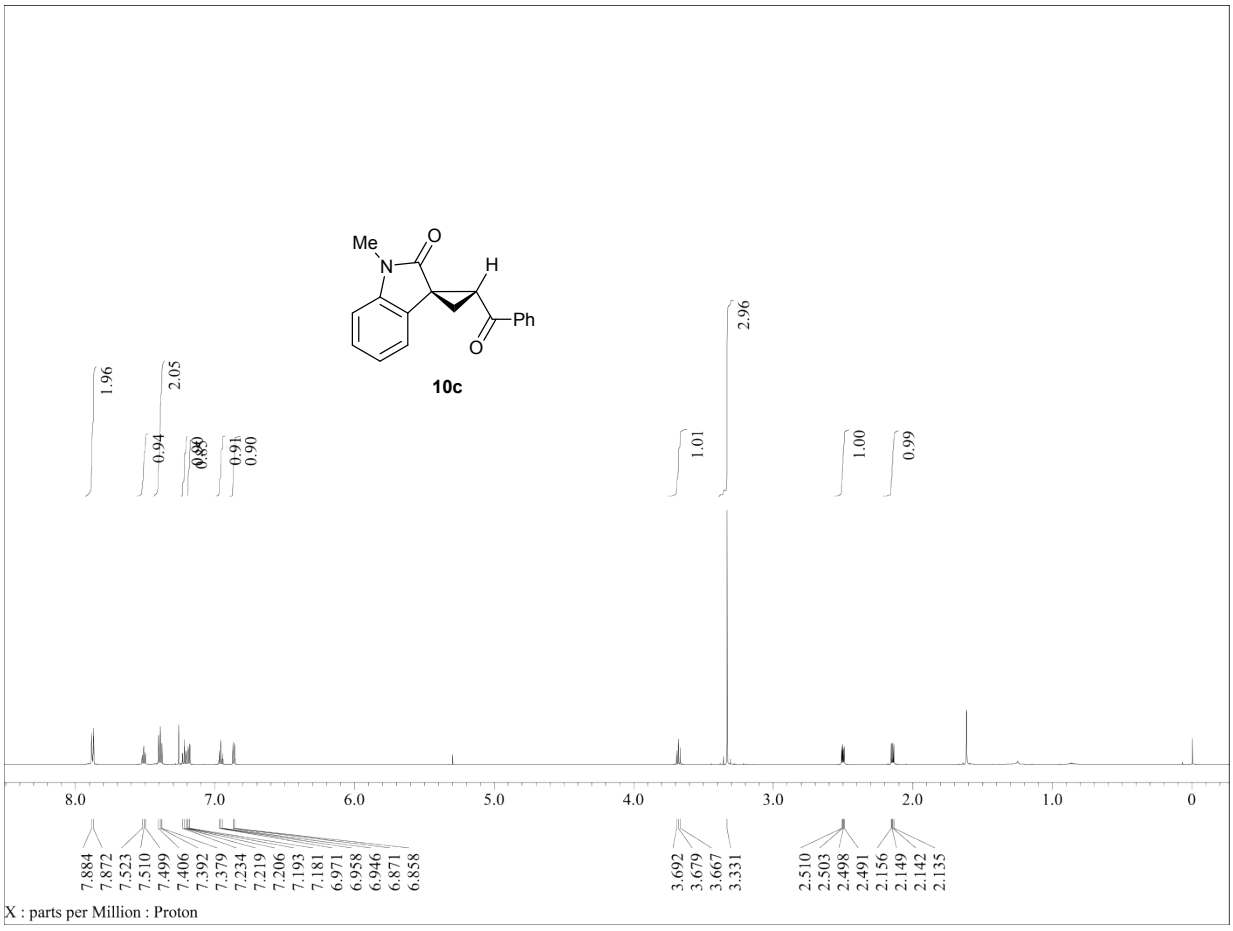

NC
CN
EtO2C
Cl
H
CO2Et
8e
170.948
166.869
166.821
135.626
135.454
132.725
130.389
129.001
126.971
112.254
111.488
90.462
77.211
77.000
76.789
63.231
61.872
36.374
32.525
22.663
14.075
14.036
X : parts per Million : Carbon13

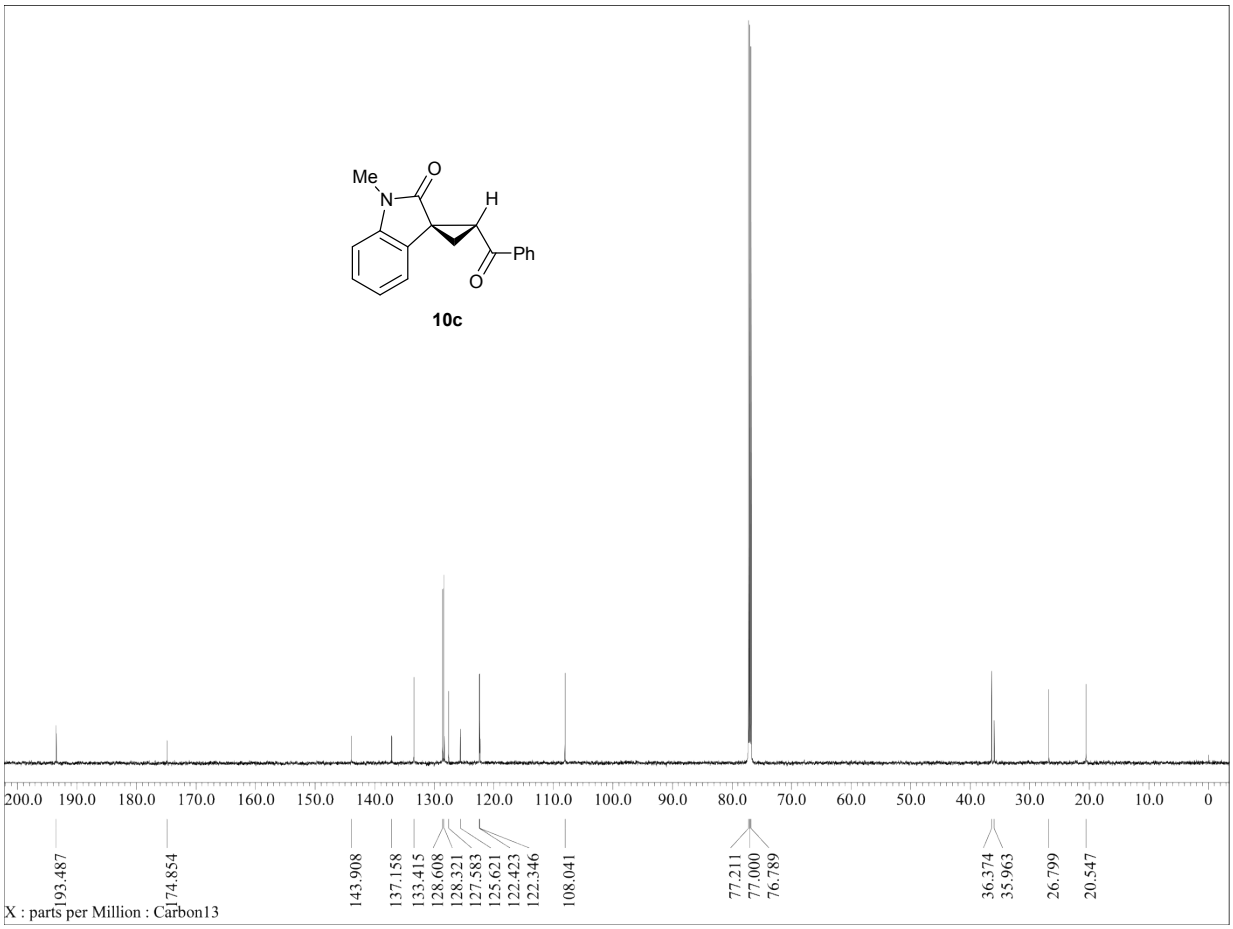

Me
N
O
CO2Me
CO2Me
10a
3.09
3.00
1.02
1.01
1.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.348
7.336
7.321
7.309
7.297
7.026
7.011
6.998
6.896
6.884
3.791
3.736
3.253
2.486
2.478
2.453
2.444
X : parts per Million : Proton

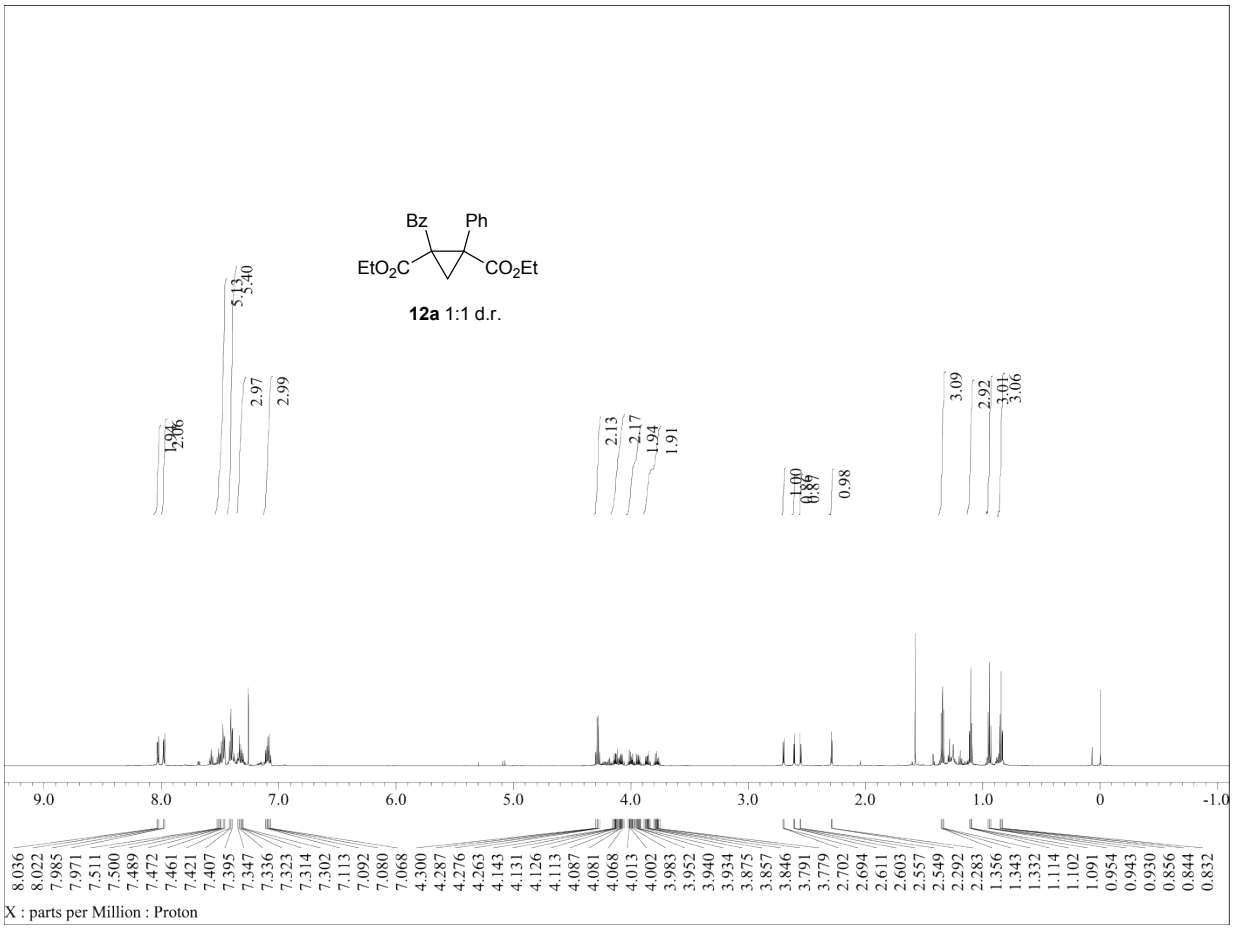

Me
N
O
CO2Me
CO2Me
10a
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.527
165.978
165.816
144.674
128.512
124.299
123.112
122.317
108.271
77.211
77.000
76.789
53.302
53.092
45.298
37.983
26.732
24.358
X : parts per Million : Carbon13

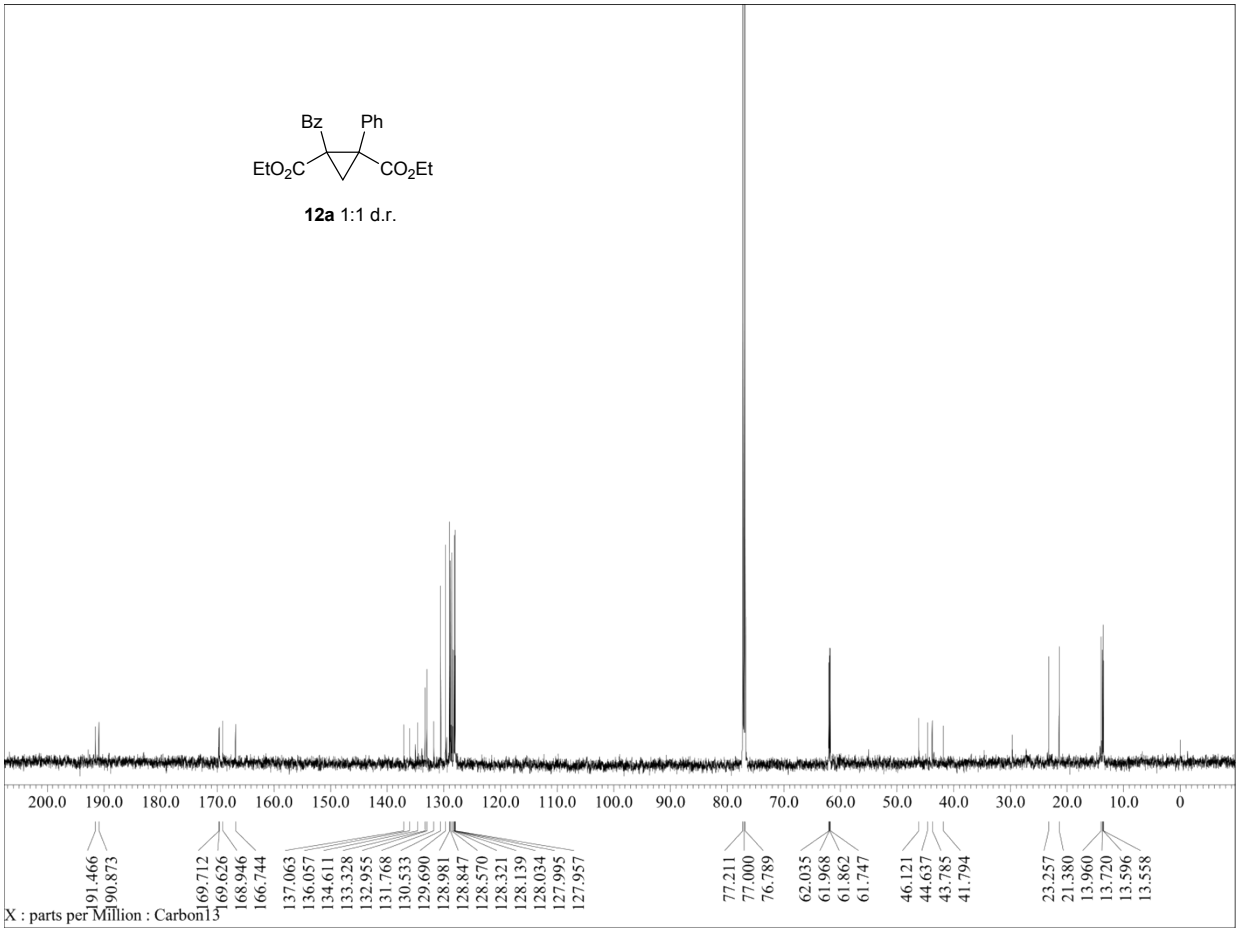

Me
N
O
CO2tBu
CO2tBu
10b
8.96
9.02
3.00
1.00
0.98
0.97
0.97
0.99
0.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.369
7.356
7.297
7.284
7.271
6.988
6.975
6.963
6.885
6.872
3.259
2.381
2.373
2.294
2.286
1.464
1.403
X : parts per Million : Proton

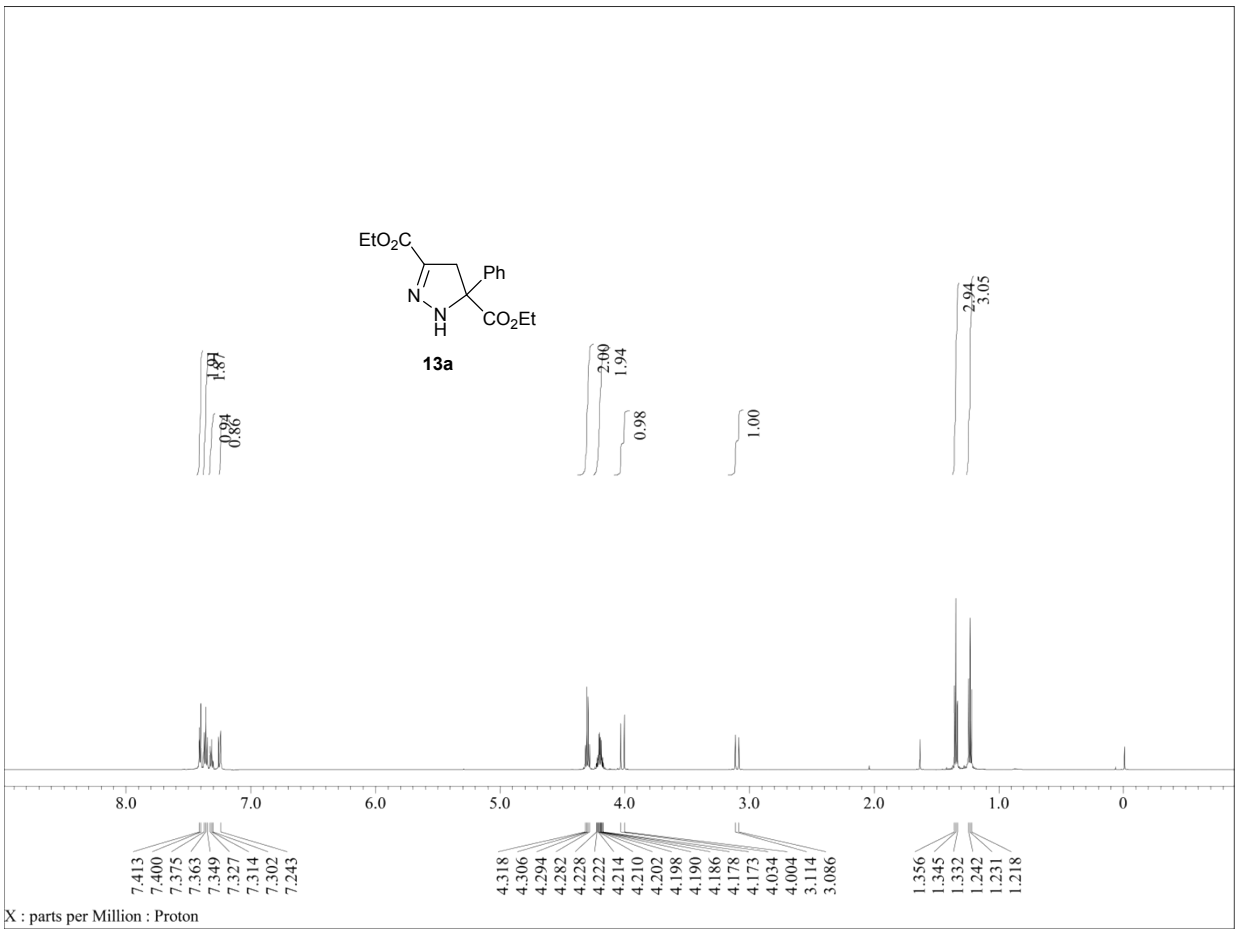

Me
N
O
CO2tBu
CO2tBu
10b
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.757
164.801
164.312
144.751
127.957
125.037
123.217
121.829
107.879
83.195
81.854
77.220
77.000
76.789
47.280
37.485
27.958
27.757
26.541
24.032
X : parts per Million : Carbon13

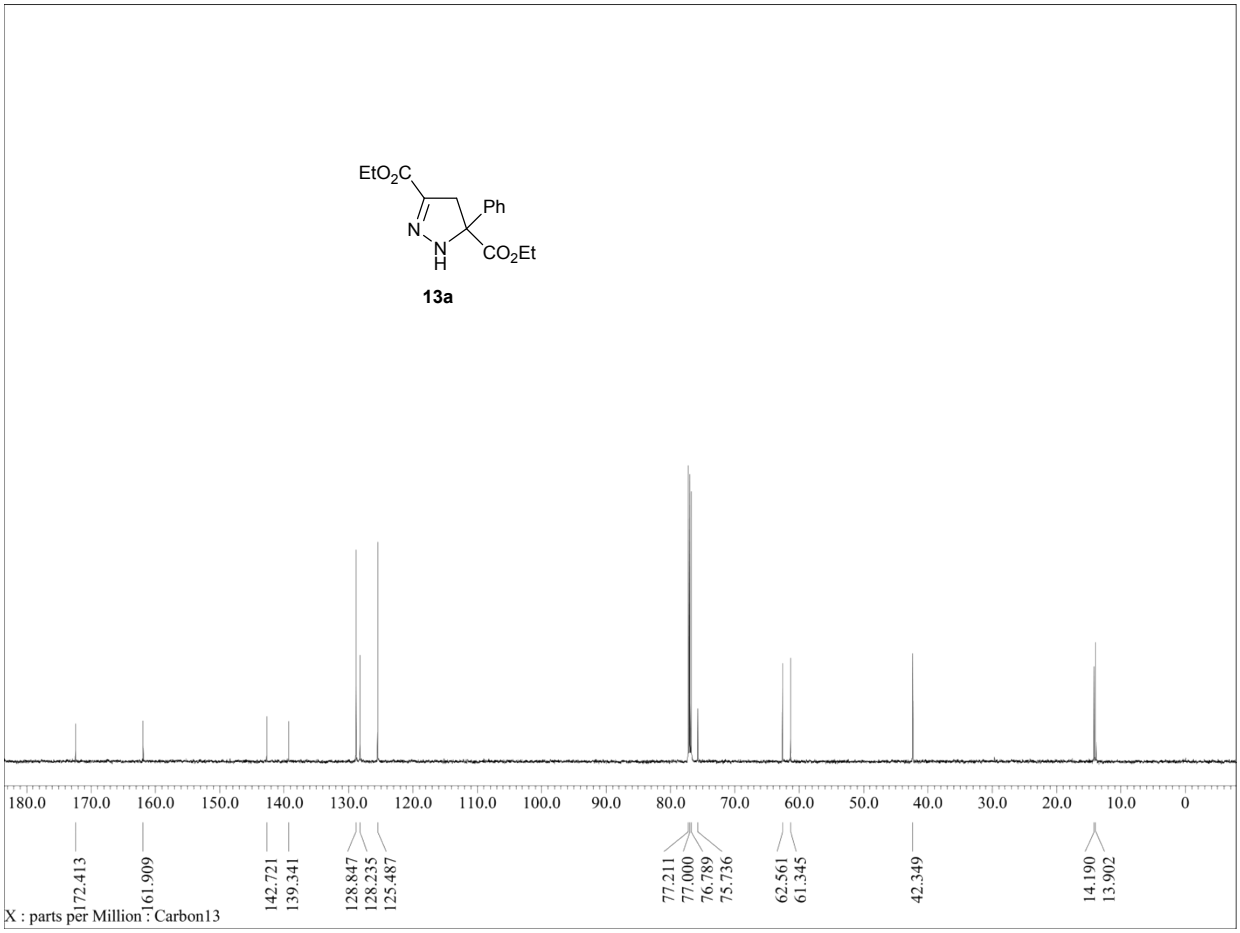

Me
N
O
H
Ph
O
10c
1.96
2.05
0.94
0.91
0.90
1.01
2.96
1.00
0.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.884
7.872
7.523
7.510
7.499
7.406
7.392
7.379
7.234
7.219
7.206
7.193
7.181
6.971
6.958
6.946
6.871
6.858
3.692
3.679
3.667
3.331
2.510
2.503
2.498
2.491
2.156
2.149
2.142
2.135
X : parts per Million : Proton

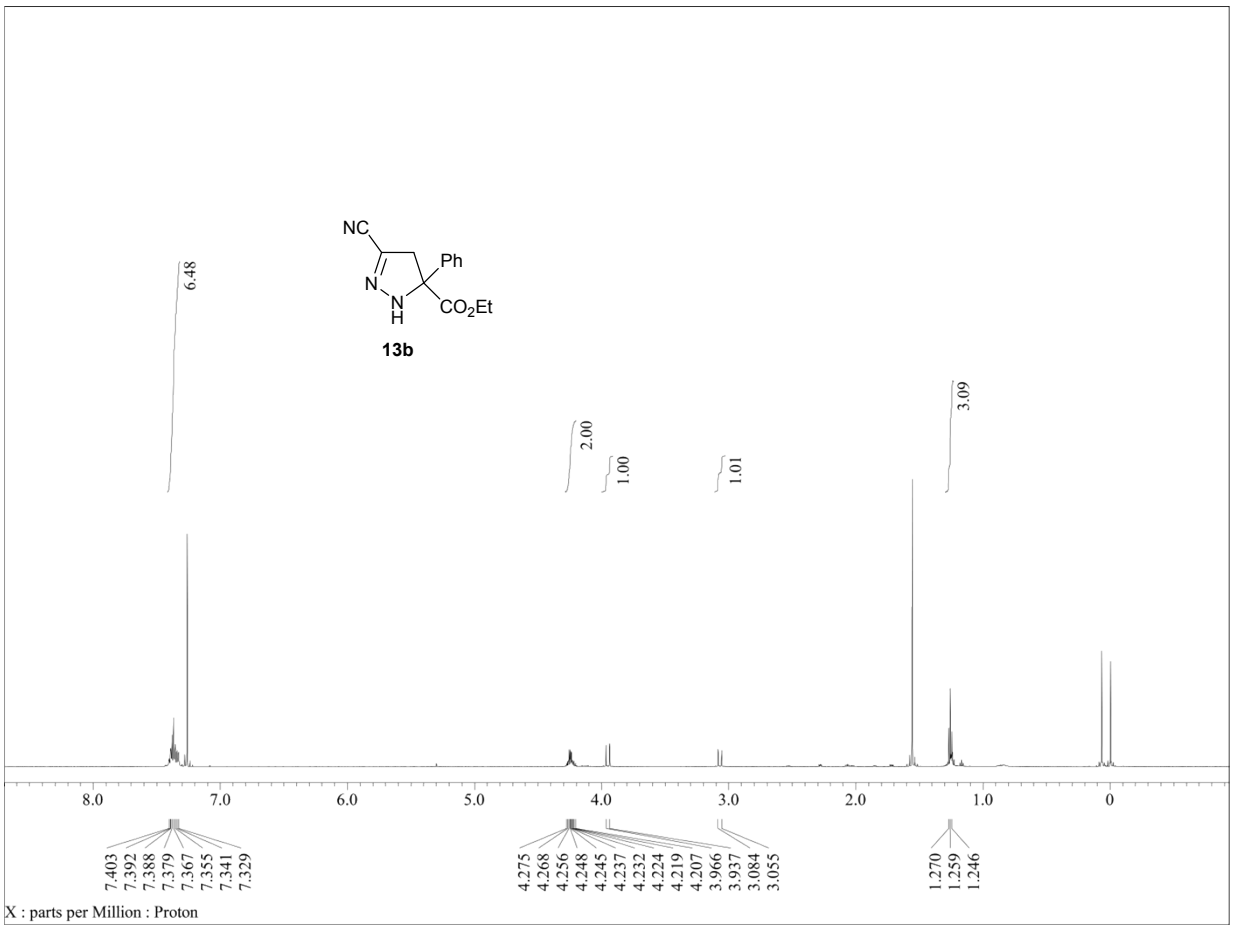

Me
N
O
H
Ph
O
10c
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
193.487
174.854
143.908
137.158
133.415
128.608
128.321
127.583
125.621
122.423
122.346
108.041
77.211
77.000
76.789
36.374
35.963
26.799
20.547
X : parts per Million : Carbon13

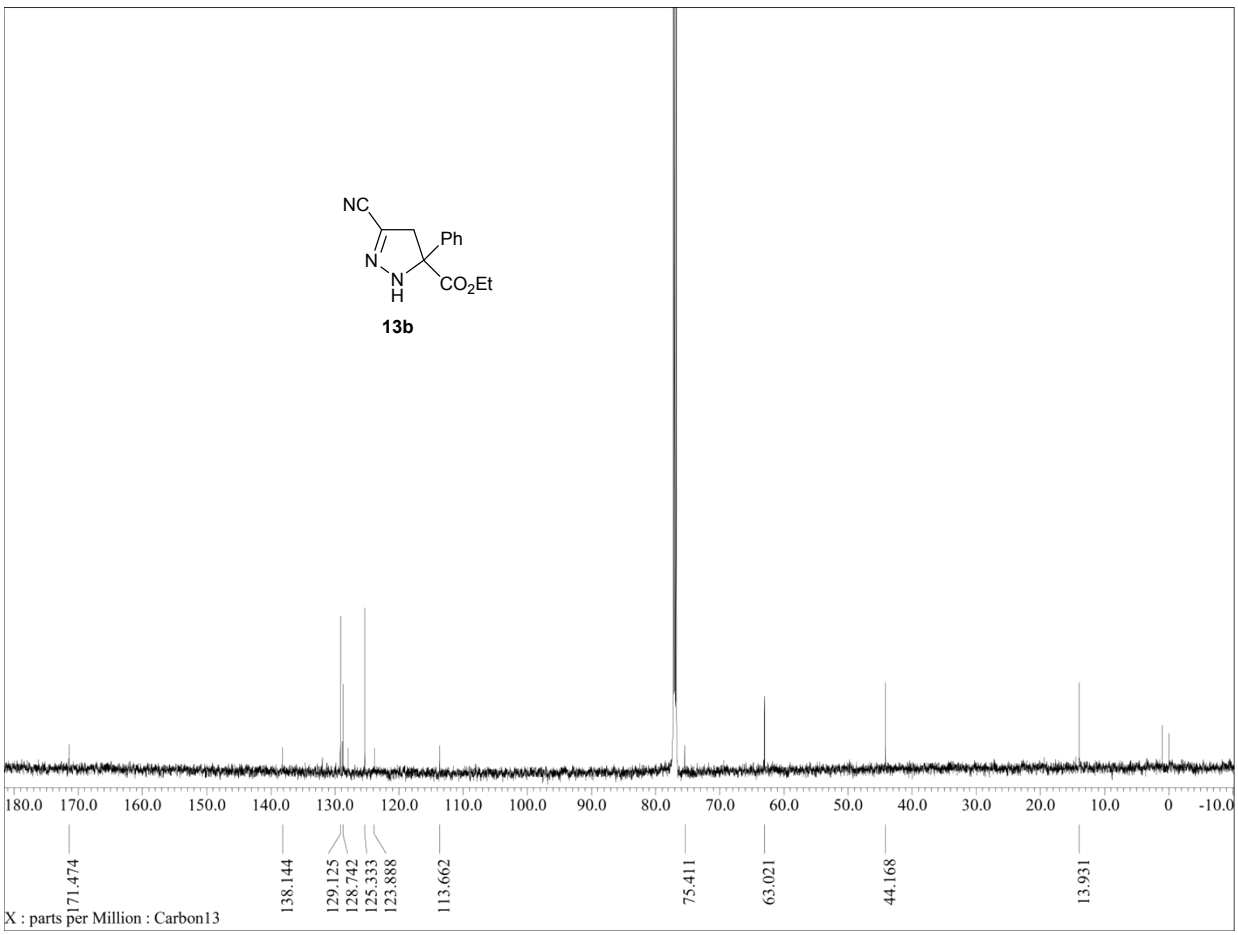

Bz
Ph
EtO2C
CO2Et
12a 1:1 d.r.
X : parts per Million : Proton

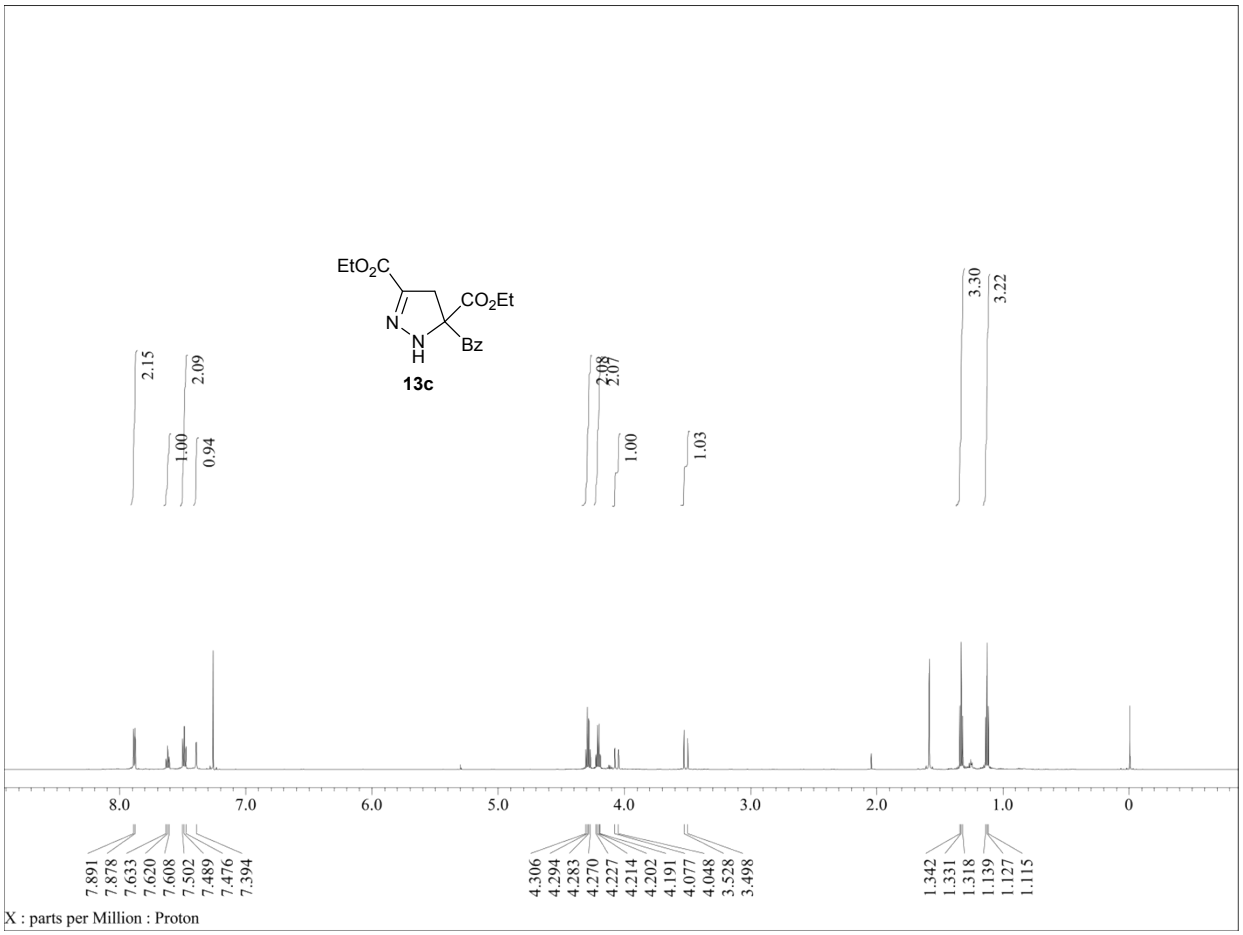

Bz
Ph
EtO2C
CO2Et
12a 1:1 d.r.
X : parts per Million : Carbon13

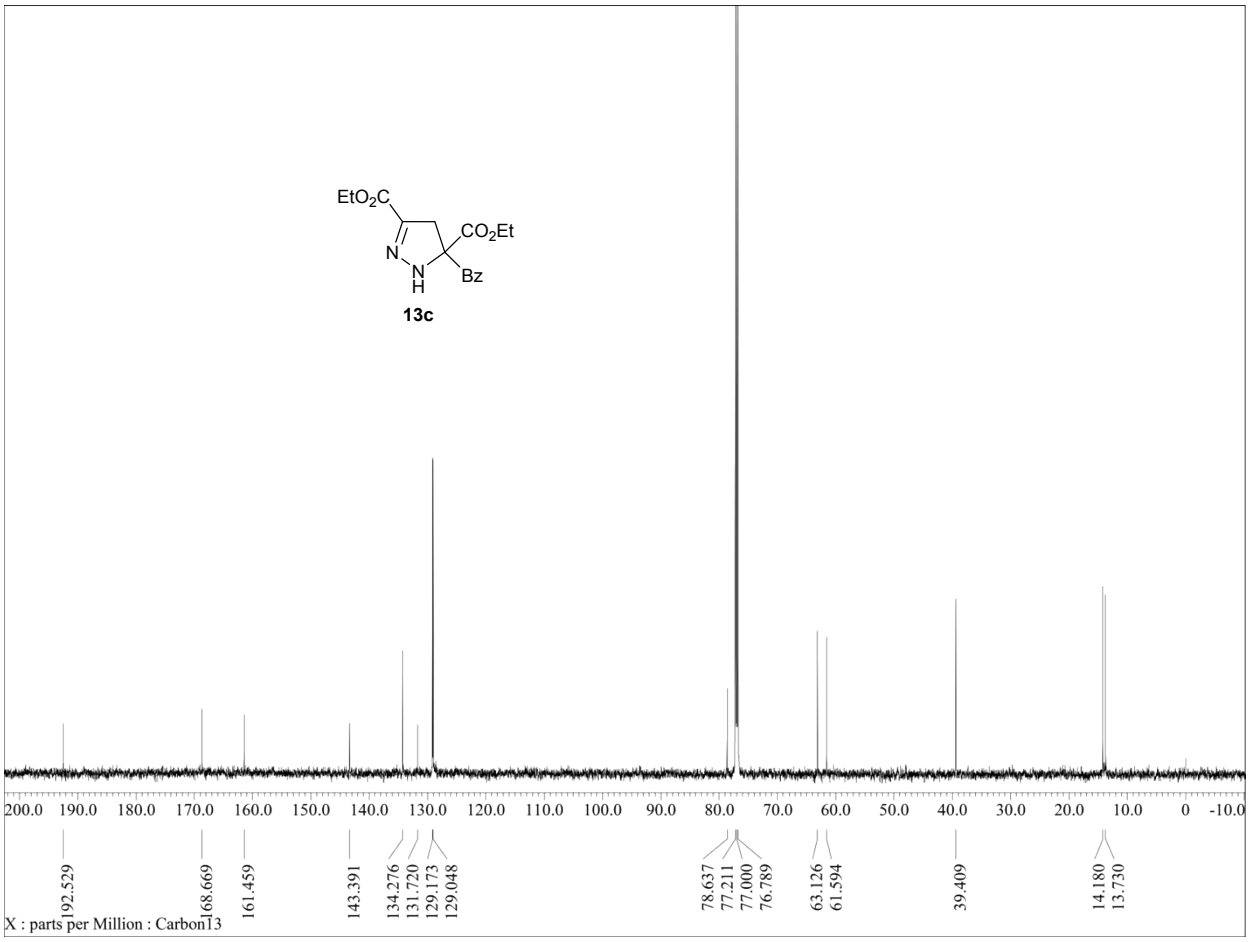

EtO2C
Ph
N
N
H
CO2Et
13a
1.97
1.87
0.94
0.86
2.00
1.94
0.98
1.00
2.94
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.413
7.400
7.375
7.363
7.349
7.327
7.314
7.302
7.243
4.318
4.306
4.294
4.282
4.228
4.222
4.214
4.210
4.202
4.198
4.190
4.186
4.178
4.173
4.034
4.004
3.114
3.086
1.356
1.345
1.332
1.242
1.231
1.218
X : parts per Million : Proton

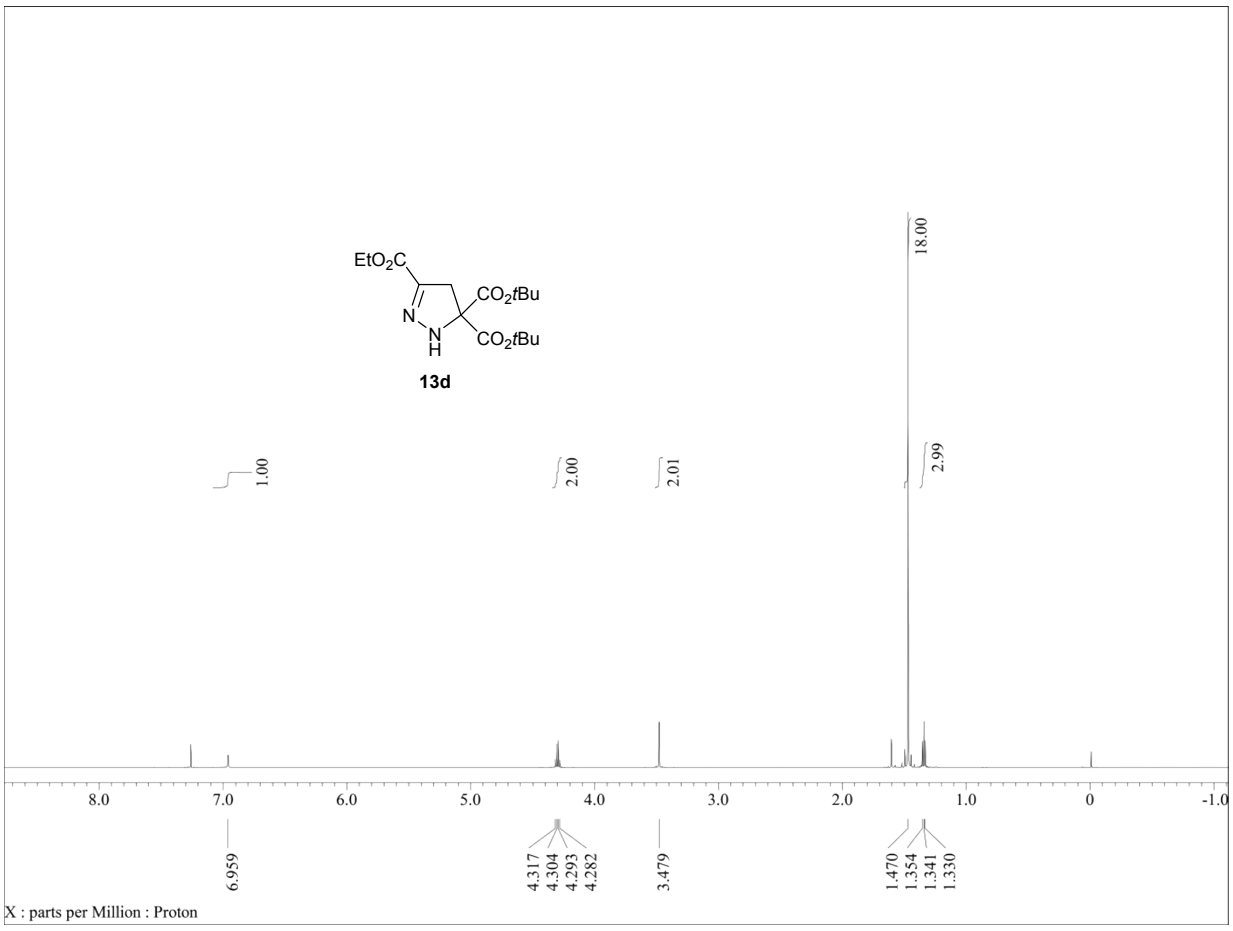

EtO2C
Ph
N
N
H
CO2Et
13a
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.413
161.909
142.721
139.341
128.847
128.235
125.487
77.211
77.000
76.789
75.736
62.561
61.345
42.349
14.190
13.902
X : parts per Million : Carbon13

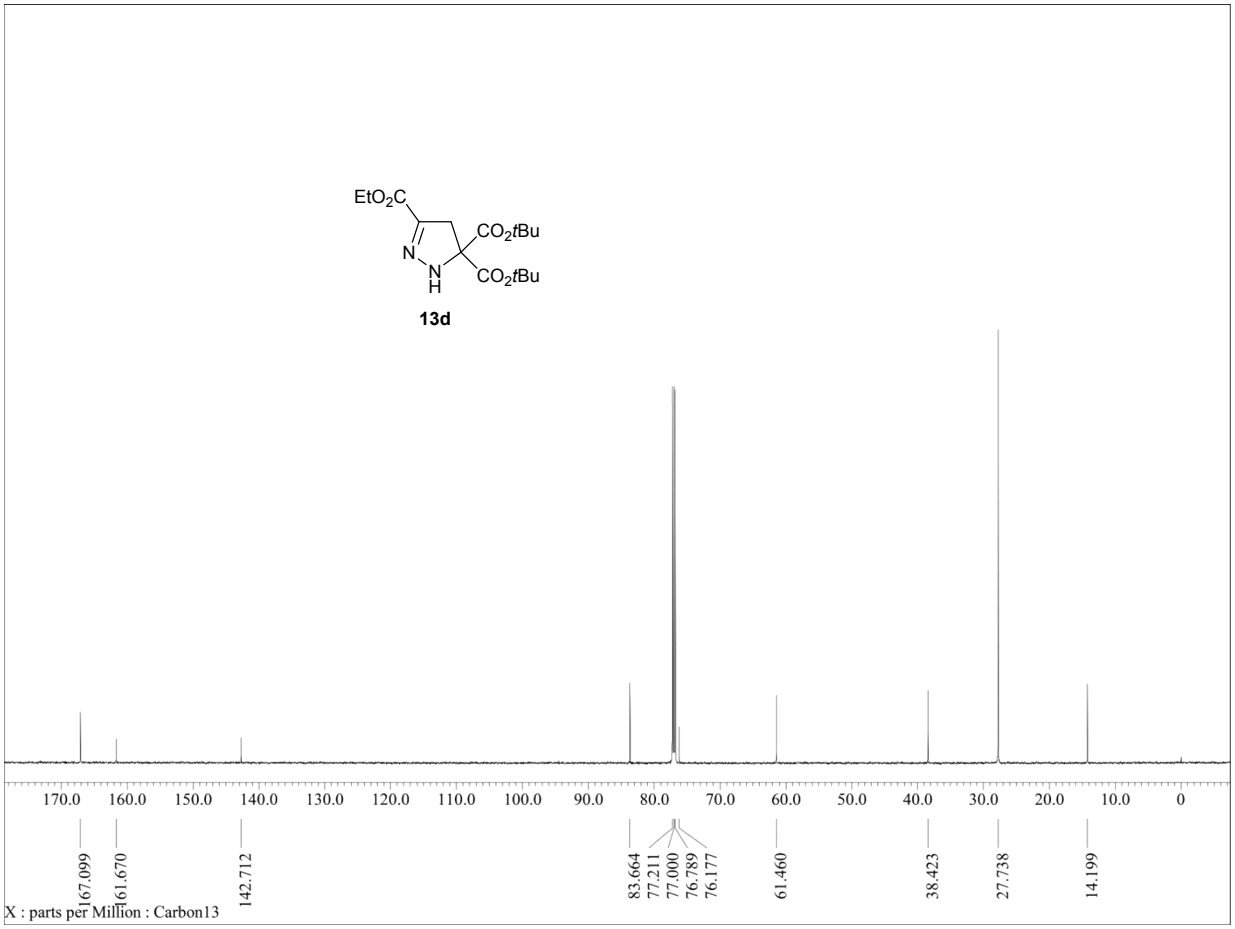

NC
Ph
N
N
H
CO2Et
13b
6.48
2.00
1.00
1.01
3.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.403
7.392
7.388
7.379
7.367
7.355
7.341
7.329
4.275
4.268
4.256
4.248
4.245
4.237
4.232
4.224
4.219
4.207
3.966
3.937
3.084
3.055
1.270
1.259
1.246
X : parts per Million : Proton

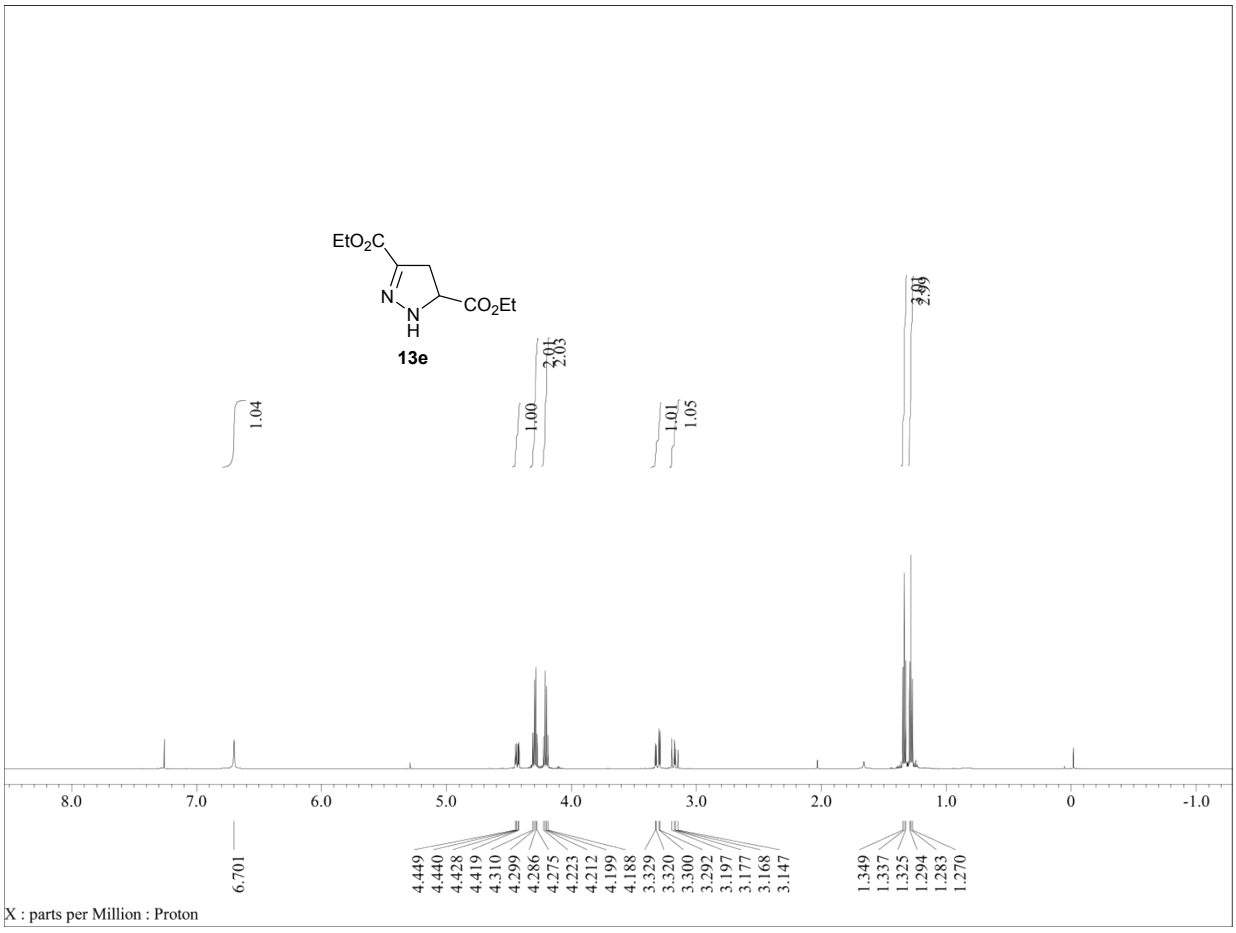

NC
Ph
N
N
H
CO2Et
13b
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
171.474
138.144
129.125
128.742
125.333
123.888
113.662
75.411
63.021
44.168
13.931
X : parts per Million : Carbon13

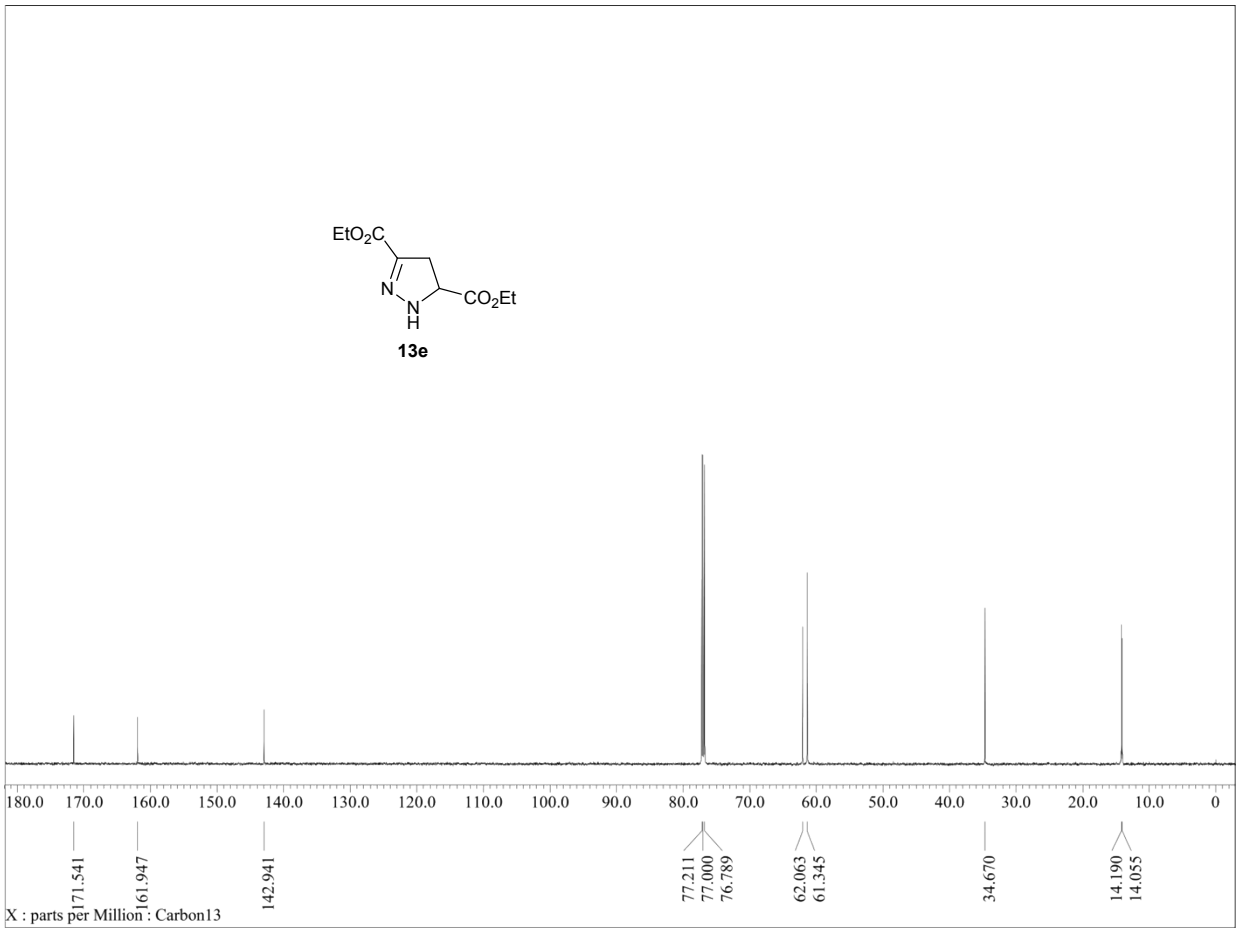

EtO2C
CO2Et
N
N
H
Bz
13c
2.15
2.09
1.00
0.94
2.08
2.07
1.00
1.03
3.30
3.22
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.891
7.878
7.633
7.620
7.608
7.502
7.489
7.476
7.394
4.306
4.294
4.283
4.270
4.227
4.214
4.202
4.191
4.077
4.048
3.528
3.498
1.342
1.331
1.318
1.139
1.127
1.115
X : parts per Million : Proton

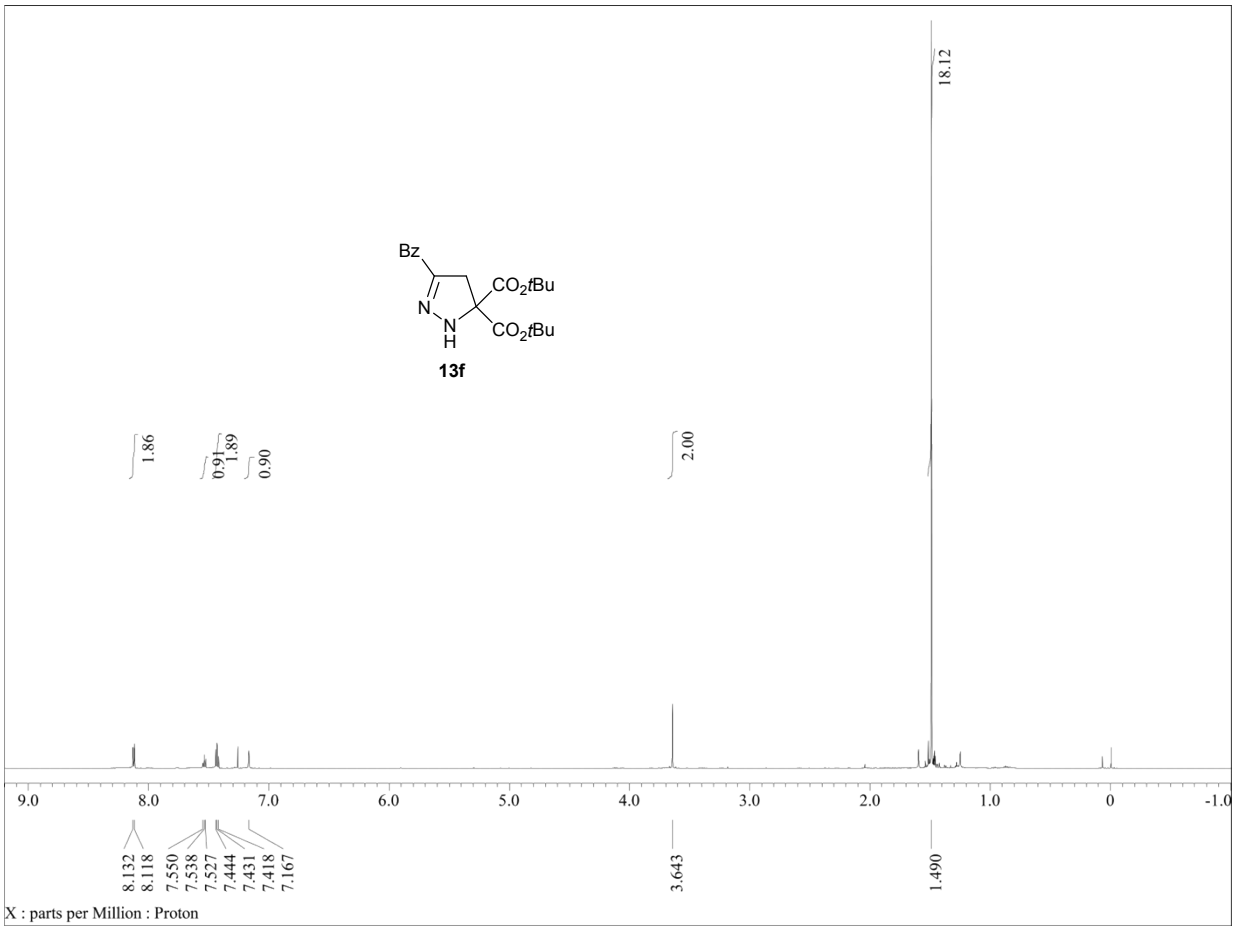

EtO2C
CO2Et
N
N
H
Bz
13c
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
192.529
168.669
161.459
143.391
134.276
131.720
129.173
129.048
78.637
77.211
77.000
76.789
63.126
61.594
39.409
14.180
13.730
X : parts per Million : Carbon13

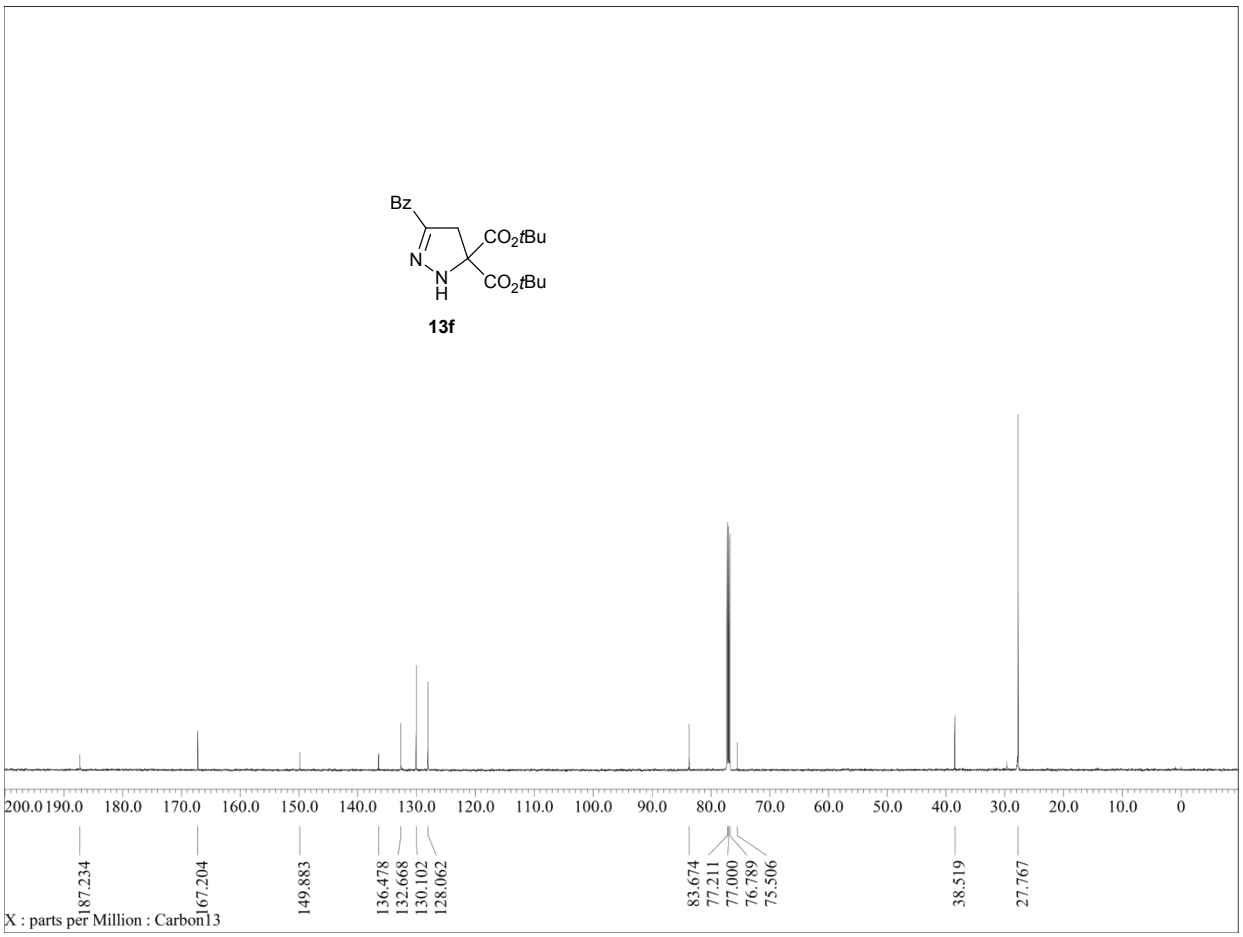

EtO2C
CO2tBu
CO2tBu
N
N
H
13d
18.00
2.99
2.01
2.00
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.959
4.317
4.304
4.293
4.282
3.479
1.470
1.354
1.341
1.330
X : parts per Million : Proton

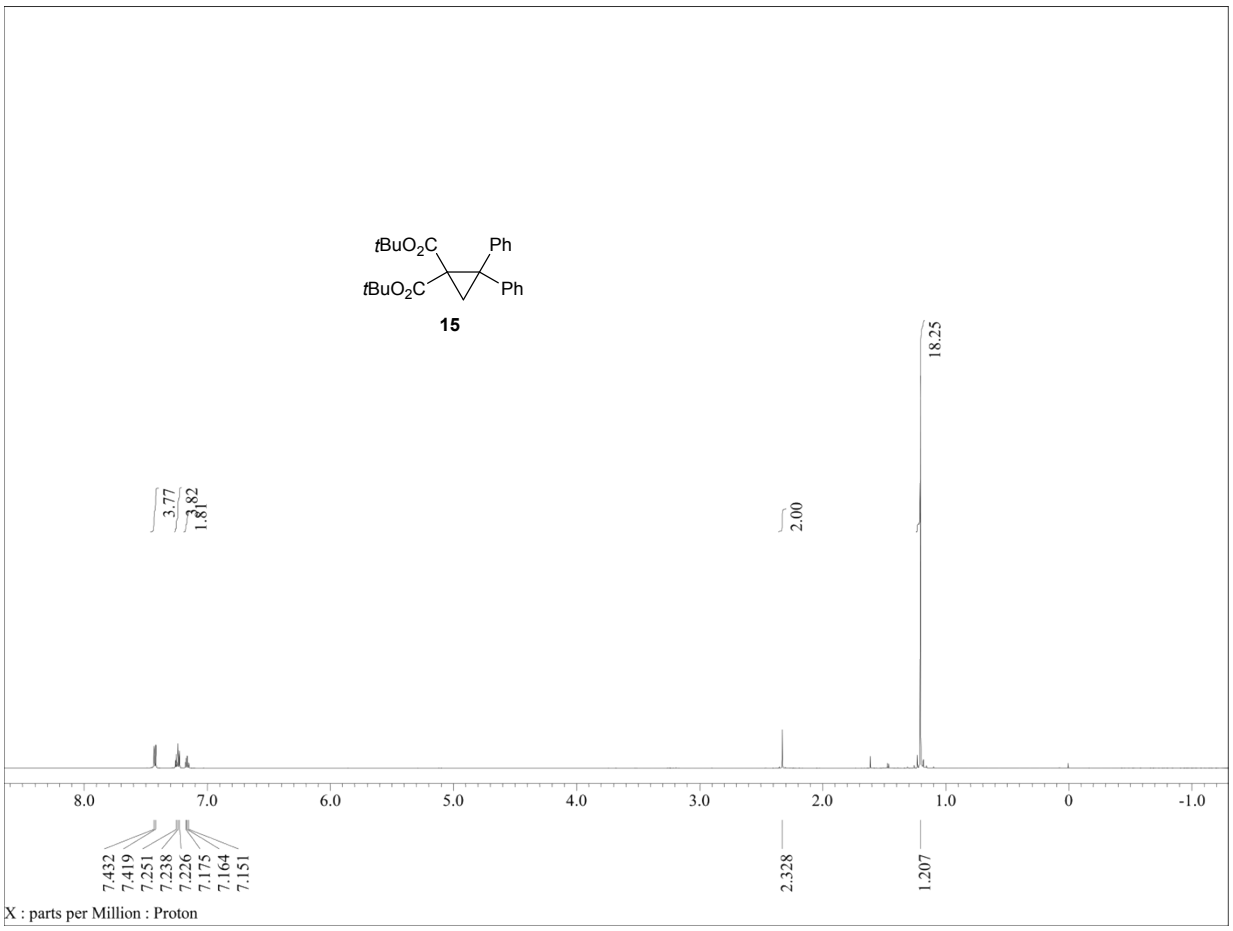

EtO2C
CO2tBu
CO2tBu
N
N
H
13d
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.099
161.670
142.712
83.664
77.211
77.000
76.789
76.177
61.460
38.423
27.738
14.199
X : parts per Million : Carbon13

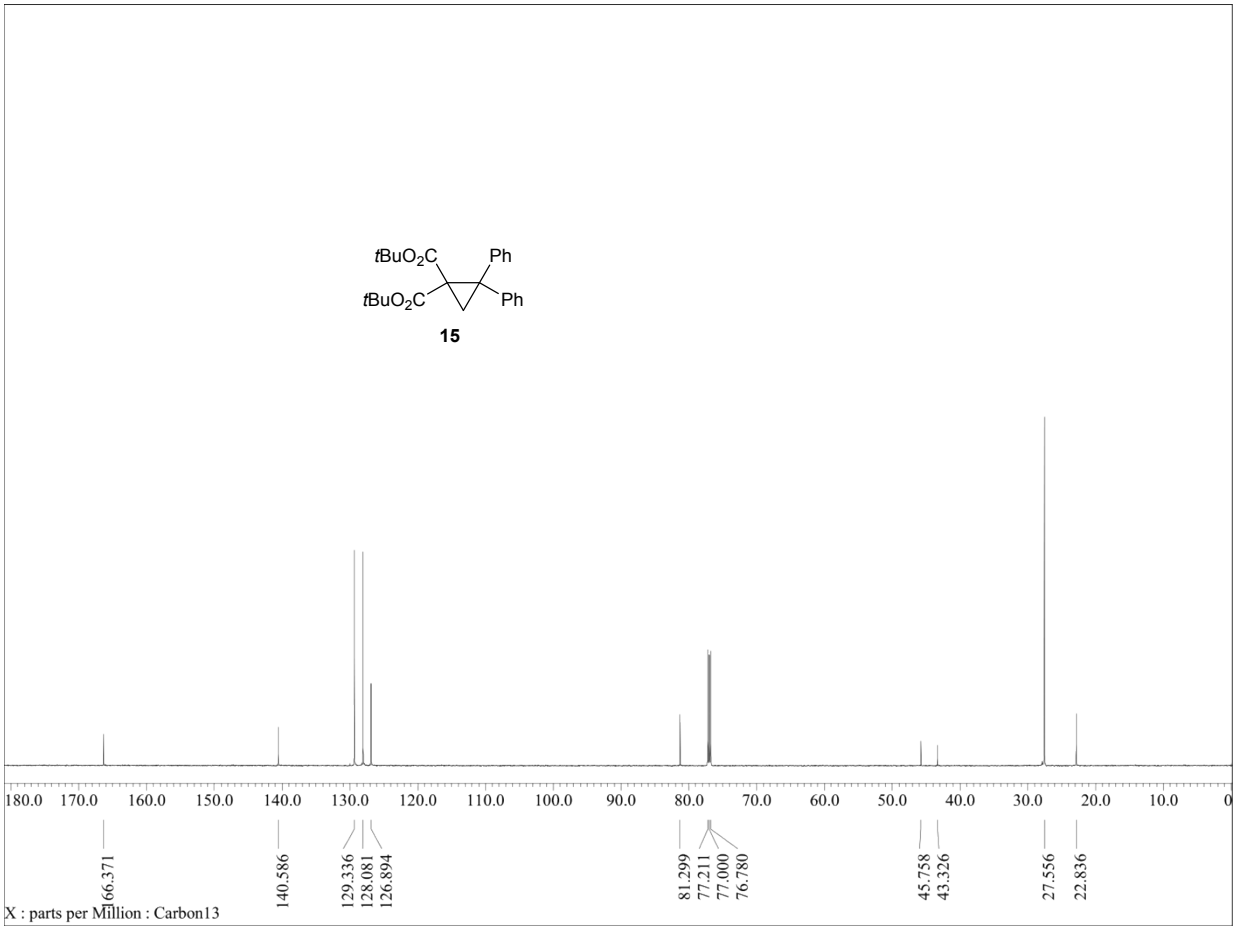

EtO2C
CO2Et
13e
1.04
1.00
2.01
2.03
1.01
1.05
2.93
2.96
2.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.701
4.449
4.440
4.428
4.419
4.310
4.299
4.286
4.275
4.223
4.212
4.199
4.188
3.329
3.320
3.300
3.292
3.197
3.177
3.168
3.147
1.349
1.337
1.325
1.294
1.283
1.270
X : parts per Million : Proton


EtO2C
CO2Et
13e
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
171.541
161.947
142.941
77.211
77.000
76.789
62.063
61.345
34.670
14.190
14.055
X : parts per Million : Carbon13


Bz
CO2tBu
CO2tBu
N
N
H
13f
18.12
1.86
0.91
1.89
0.90
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
8.132
8.118
7.550
7.538
7.527
7.444
7.431
7.418
7.167
3.643
1.490
X : parts per Million : Proton


Bz
CO2tBu
CO2tBu
N
N
H
13f
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
187.234
167.204
149.883
136.478
132.668
130.102
128.062
83.674
77.211
77.000
76.789
75.506
38.519
27.767
X : parts per Million : Carbon13


tBuO2C
Ph
tBuO2C
Ph
15
18.25
3.77
3.82
1.81
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.432
7.419
7.251
7.238
7.226
7.175
7.164
7.151
2.328
1.207
X : parts per Million : Proton


tBuO2C
Ph
tBuO2C
Ph
15
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
166.371
140.586
129.336
128.081
126.894
81.299
77.211
77.000
76.780
45.758
43.326
27.556
22.836
X : parts per Million : Carbon13