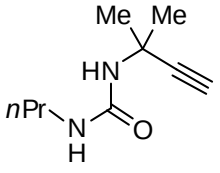
Electronic Supporting Information

General Information.

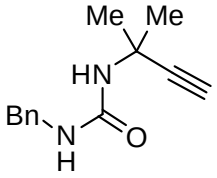
All melting points were measured on a Yanaco MP-3S micro melting point apparatus and are uncorrected. ^{1}H, ^{13}C NMR and HMBC spectra were recorded on JEOL AL 400 and JEOL Lambda 500 spectrometer spectrometers in $CDCl_3$ with Me_4Si as an internal reference. ^{13}C NMR spectra were recorded at 100 MHz. High-resolution mass spectra (HR-MS) were obtained with JEOL GC Mate II, JMS-SX102 and JEOL JMS 600H spectrometer. In the case of CD_2Cl_2, solvent peaks were used as a reference (5.32ppm for ^{1}H, and 53.8ppm for ^{13}C). IR spectra were recorded with JASCO FT/IR-300 spectrometer. All reagents were purchased from commercial sources and used without purification. All evaporations were performed under reduced pressure. For column chromatography, silica gel (Kieselgel 60) was employed.

Preparation of substrates 1.

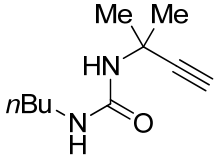
The substrates **1** was prepared according to the literature.[1] The ureas **1** except **1a** and **1b** are new compounds.[2]



1a[2]



1b[2]

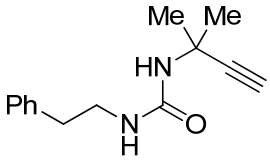


1c : colorless needles; mp 80-83 ℃.

^{1}H-NMR ($CDCl_3$) δ 0.92 (3 H, t, *J* = 7.2 Hz), 1.33-1.40 (2 H, m), 1.47-1.51 (2 H, m), 1.58 (6 H, s), 2.40 (1H, s), 3.19-3.23 (2 H, m), 4.93 (1 H, br-s), 5.32 (1 H, br-s); ^{13}C-NMR ($CDCl_3$) δ 13.8, 20.1, 30.2 (2C), 32.3, 40.0, 46.7, 70.1, 87.7, 157.6.

IR (KBr): 3360, 3241, 2968, 2105, 1632 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{10}H_{18}N_2O$: 182.1419; found: 182.1418.

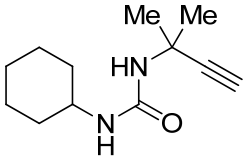


1d : colorless needles; mp 111-113 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.52 (6 H, s), 2.23 (1H, s), 2.82 (2 H, t, *J* = 7.0 Hz), 3.46-3.51 (2 H, m), 4.76 (1 H, br-s), 5.22 (1 H, br-s), 7.20-7.31 (5 H, m); ^{13}C-NMR ($CDCl_3$) δ 30.0 (2C), 36.2, 41.4, 46.6, 70.3, 87.2, 126.3, 128.5 (2C), 128.9 (2C), 139.2, 159.3.

IR (KBr): 3336, 3284, 2103, 1636, 1568, 1282, 1263, 642 cm^{-1}.

HRMS-EI:*m/z* [M$^+$] calcd for $C_{14}H_{18}N_2O$: 230.1419; found: 230.1415.

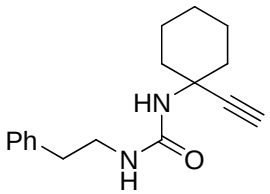


1e : colorless needles; mp 160-164 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.15-1.91 (10 H, m), 1.58 (6H, s), 2.43 (1 H, s), 3.61-3.67 (1 H, m), 4.60 (1 H, s), 5.15 (1 H, d, *J* = 6.8 Hz); ^{13}C-NMR ($CDCl_3$) δ 24.8 (2C), 25.6, 30.2 (2C), 33.7 (2C), 46.7, 48.8, 70.5, 87.5, 156.7.

IR (KBr): 3317, 3249, 2924, 2106, 1629, 1557, 695 cm^{-1}.

HRMS-EI:*m/z* [M$^+$] calcd for $C_{12}H_{20}N_2O$: 208.1576; found: 208.1572.

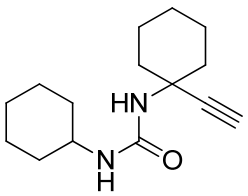


1f : colorless needles; mp 126-129 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.12-2.03 (10 H, m), 2.28 (1H, s), 2.83 (2 H, t, *J* = 6.8 Hz), 3.50 (2 H, q, *J* = 6.8 Hz), 4.53 (1 H, br-s), 5.25 (1 H, br-s), 7.20-7.31 (5H, m); ^{13}C-NMR ($CDCl_3$) δ 22.3 (2C), 25.2, 36.1, 38.1 (2C), 41.5, 50.9, 73.2, 85.6, 126.3, 128.5 (2C), 129.0 (2C), 139.4, 157.2.

IR (KBr): 3353, 3235, 2928, 2100, 1628, 1565 cm^{-1}.

HRMS-EI:*m/z* [M$^+$] calcd for $C_{17}H_{22}N_2O$: 270.1732; found: 270.1730.

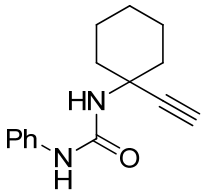


1g : colorless needles; mp 111-113 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.16-2.11 (20 H, m), 2.52 (1H, s), 3.64-3.69 (1 H, m), 4.57 (1 H, s), 5.25 (1 H, d, *J* = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) δ 22.4 (2C), 24.8 (2C), 25.2, 25.7, 33.7 (2C), 38.2 (2C), 48.8, 50.9, 73.2, 86.0, 156.6.

IR (KBr): 3308, 3278, 2931, 2854, 2103, 1637, 1560, 1254, 637 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{15}H_{24}N_2O$: 248.1889; found: 248.1890.

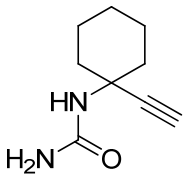


1h : colorless needles; mp 146-150 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.27-1.68 (8 H, m), 2.14-2.15 (2H, m), 2.54 (1 H, s), 5.00 (1 H, br-s), 7.02-7.05 (1 H, m), 7.21 (1 H, br-s), 7.25-7.36 (4 H, m); ^{13}C-NMR ($CDCl_3$) δ 22.4 (2C), 25.2, 38.0 (2C), 51.3, 73.0, 85.9, 120.3 (2C), 123.4, 129.1 (2C), 138.7, 154.7.

IR (KBr): 3347, 3305, 2934, 2859, 2109, 1656, 1603, 1554, 1500, 1312, 1242 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{15}H_{18}N_2O$: 242.1419; found: 242.1420.

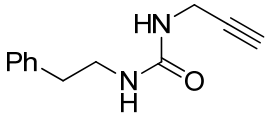


1i : colorless needles; mp 109-113℃.

^{1}H-NMR ($CDCl_3$) δ 1.28-1.67 (8 H, m), 2.11-2.13 (2H, m), 2.51 (1 H, s), 5.18 (2 H, br-s), 5.27 (1 H, br-s); ^{13}C-NMR ($CDCl_3$) δ 22.4 (2C), 25.2, 37.9 (2C), 51.1, 73.1, 85.7, 158.4.

IR (KBr): 3437, 3314, 2936, 2113, 1661, 1610, 1550, 1362 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_9H_{14}N_2O$: 166.1106; found: 166.1107.



1j : colorless needles; mp 96-99 ℃.

^{1}H-NMR ($CDCl_3$) δ 2.16 (1 H, t, *J* = 2.4 Hz), 2.79 (2 H, t, *J* = 6.8 Hz), 3.39-3.44 (2 H, m), 3.90 (2 H, dd, *J* = 2.4, 5.6 Hz), 5.03 (1 H, br-s), 5.12 (1 H, br-s), 7.17-7.30 (5H, m); ^{13}C-NMR ($CDCl_3$) δ 30.0, 36.4, 41.7, 71.0, 80.8, 126.4, 128.6 (2C), 128.8 (2C), 139.1, 157.9.

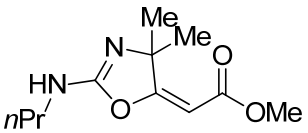
IR (KBr): 3353, 3322, 3277, 2116, 1620, 1594 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{12}H_{14}N_2O$: 202.1106; found: 202.1103.

General procedure for the CCC-coupling reaction of 1

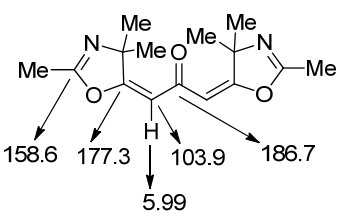
A 50-mL two-neck round-bottom flask containing a magnetic stirring bar, substrate **1** (0.5 mmol), *p*-benzoquinone (1.5 mmol) and MeOH (7 mL) was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with carbon monoxide. The apparatus was purged with carbon monoxide by pump-filling via the three-way stopcock. A MeOH (1 mL) suspension of [Pd(**L**)$(tfa)_2$] (0.025 mmol) was added to the stirred solution at an appropriate temperature using a syringe. The remaining [Pd(**L**)$(tfa)_2$] was washed in MeOH (1 mL) twice. After stirring at the appropriate temperature for a

period of time, the mixture was diluted with CH_2Cl_2 (50 mL) and washed with 3% NaOH (40 mL). The aqueous layer was extracted with CH_2Cl_2 (50 mL) twice and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel. The fraction eluted with hexane-AcOEt (10/1-1/2) afforded the dimeric ketone **4**. **4** was then precipitated from the reaction mixture and the resulting precipitate was collected by filtration and washed with cold MeOH (1 mL × 2). The filtrate was reprocessed via the above procedure to provide additional products after chromatography.

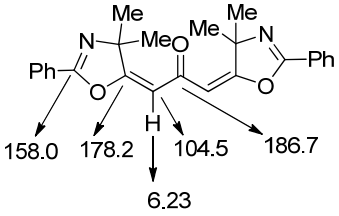


2a : Spectral data were identical to those described in the literature.[2]

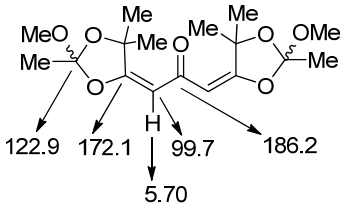
The structure of the dimeric ketone **4a** was confirmed by comparing the ^{1}H and ^{13}C-NMR data with those of similar oxazolines **A**, **B** and **C**. [3]



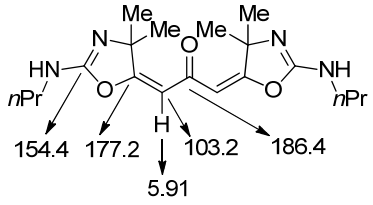
A



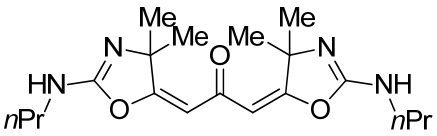
B



C



4a

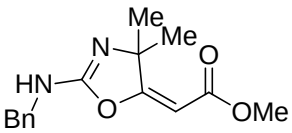


4a : colorless needles; mp 186-191 ℃.

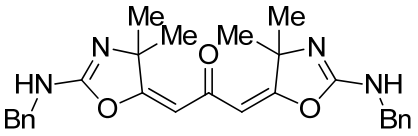
^{1}H-NMR ($CDCl_3$) δ 0.95 (6 H, t, *J* = 7.2 Hz), 1.55-1.65 (4 H, m), 1.63 (12 H, s), 3.20 (4 H, t, *J* = 7.2 Hz), 4.11 (2 H, br-s), 5.91 (2 H, s); ^{13}C-NMR ($CDCl_3$) δ 11.2 (2C), 22.9 (2C), 25.4 (4C), 44.6 (2C), 71.0 (2C), 103.2 (2C), 154.4 (2C), 177.2 (2C), 186.4

IR (KBr): 3203, 3114, 2963, 2877, 1724, 1629, 1370, 1183, 969, 930 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{19}H_{30}N_4O_3$: 362.2318; found: 362.2315.



2b : Spectral data were identical to those described in the literature.[2]

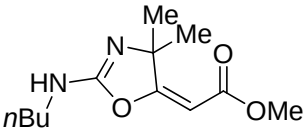


4b : colorless needles; mp 155-158℃

^{1}H-NMR ($CDCl_3$) δ 1.65 (12 H, s), 4.40 (2 H, s), 5.92 (2 H, s), 7.26-7.36 (10 H, m) ; ^{13}C-NMR ($CDCl_3$) δ 25.4 (4C), 46.8 (2C), 70.9 (2C), 103.5 (2C), 127.6 (4C), 127.7 (2C), 128.7 (4C), 137.8 (2C), 154.6 (2C), 176.9 (2C), 186.2

IR (KBr): 2930, 1730, 1630, 1182, 966, 933 cm^{-1}

HRMS-EI:*m/z* [M^+] calcd for $C_{27}H_{30}N_4O_3$: 458.2318; found: 458.2320.

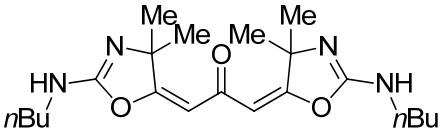


2c : colorless needles; mp 96-99 ℃.

^{1}H-NMR ($CDCl_3$) δ 0.94 (3 H, t, *J* = 7.2 Hz), 1.35-1.43 (2 H, m), 1.52-1.62 (8 H, m), 3.23 (2 H, t, *J* = 7.2 Hz), 3.69 (3 H, s), 4.13 (1 H, br-s), 5.54 (1 H, s); ^{13}C-NMR ($CDCl_3$) δ 13.7, 19.9, 25.9 (2C), 31.7, 42.6, 51.1, 70.7, 92.6, 154.3, 166.6, 178.5.

IR (KBr): 3179, 2967, 1723, 1708, 1689, 1656, 1172, 1095 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{12}H_{20}N_2O_3$: 240.1474; found: 240.1473.

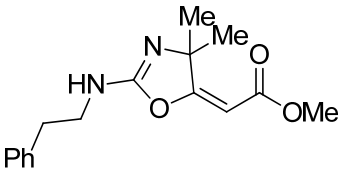


4c : colorless needles; mp 189-191 ℃.

^{1}H-NMR ($CDCl_3$) δ 0.94 (6 H, t, *J* = 7.2 Hz), 1.33-1.59 (8 H, m), 1.63 (12 H, s), 3.23 (4 H, t, *J* = 7.2 Hz), 4.07 (2 H, br-s), 5.91 (2 H, s); ^{13}C-NMR ($CDCl_3$) δ 13.8 (2C), 19.9 (2C), 25.4 (4C), 31.7(2C), 42.6 (2C), 71.0 (2C), 103.2 (2C), 154.4 (2C), 177.1 (2C), 186.4

IR (KBr): 3206, 2965, 1725, 1627, 1184, 929 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{21}H_{34}N_4O_3$: 390.2631; found: 390.2632.

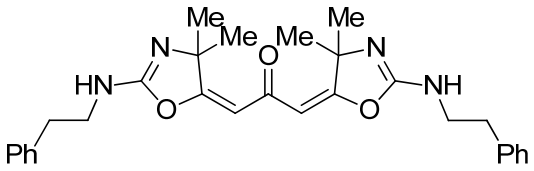


2d : brown oil.

^{1}H-NMR ($CDCl_3$) δ 1.62 (6 H, s), 2.89 (2 H, t, *J* = 6.8 Hz), 3.51 (2 H, t, *J* = 6.8 Hz), 3.68 (3 H, s), 4.35 (1 H, br-s), 5.52 (1 H, s), 7.19-7.31 (5 H, m); ^{13}C-NMR ($CDCl_3$) δ 25.9 (2C), 35.5, 43.6, 51.1, 70.7, 92.9, 126.7, 128.7 (2C), 128.8 (2C), 138.3, 154.3, 166.5, 178.2.

IR (KBr): 3360, 3193, 2972, 1724, 1657, 1106, 1048 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{16}H_{20}N_2O_3$: 288.1474; found: 288.1471.

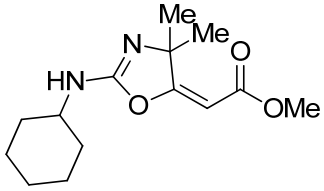


4d : colorless needles; mp 180-182 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.63 (12 H, s), 2.89 (4 H, t, *J* = 6.8 Hz), 3.51 (4 H, t, *J* = 6.8 Hz), 4.01 (2 H, br-s), 5.87 (2 H, s), 7.19-7.33 (10 H, m); ^{13}C-NMR ($CDCl_3$) δ 25.4 (4C), 35.4 (2C), 43.7 (2C), 71.0 (2C), 103.3 (2C), 126.7 (2C), 128.7 (4C), 128.8 (4C), 138.4 (2C), 154.2 (2C), 177.0 (2C), 186.4.

IR (KBr): 3211, 3108, 2942, 1736, 1626, 1180, 966, 931 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{29}H_{34}N_4O_3$: 486.2631; found: 486.2631.

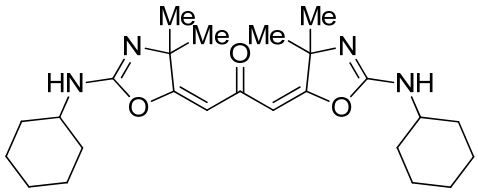


2e : colorless needles; mp 125-127 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.15-2.06 (10 H, m), 1.62 (6 H, s), 3.46 (1 H, m), 3.69 (3 H, s), 4.04 (1 H, br-s), 5.53 (1 H, s); ^{13}C-NMR ($CDCl_3$) δ 24.6, 25.5 (2C), 25.9 (2C), 33.3 (2C), 51.0, 51.3, 70.8, 92.4, 153.3, 166.6, 178.5.

IR (KBr): 3206, 2934, 2856, 1717, 1658, 1538, 1102 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{14}H_{22}N_2O_3$: 266.1631; found: 266.1633.

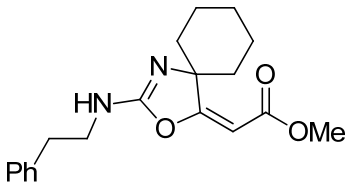


4e : colorless needles; mp 243-246 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.19-1.95 (22 H, m), 1.85 (12 H, s), 3.55 (2 H, m), 6.25 (2 H, s); ^{13}C-NMR ($CDCl_3$) δ 24.5 (4C), 24.7 (4C), 24.7 (2C), 32.7 (4C), 53.2 (2C), 64.9 (2C), 107.0 (2C), 156.4 (2C), 170.5 (2C), 184.1.

IR (KBr): 3205, 2933, 2857, 1729, 1625, 1367, 1182, 990, 928 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{25}H_{38}N_4O_3$: 442.2944; found: 442.2943.

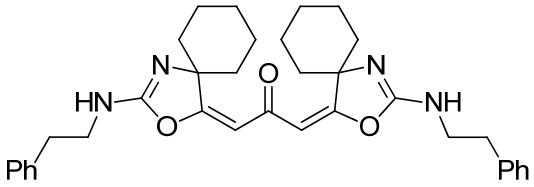


2f : colorless needles; mp 104-106 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.37-1.82 (8 H, m), 2.55-2.62 (2 H, m), 2.89 (2 H, t, *J* = 6.8 Hz), 3.51 (2 H, t, *J* = 6.8 Hz), 3.68 (3 H, s), 4.09 (1 H, br-s), 5.52 (1 H, s); ^{13}C-NMR ($CDCl_3$) δ 22.2 (2C), 25.1, 33.6 (2C), 35.6, 43.9, 51.1, 74.2, 92.6, 126.6, 128.7, 128.8, 138.6, 153.5, 166.7, 179.2..

IR (KBr): 3111, 2969, 1732, 1655, 1127, 1065 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{19}H_{24}N_2O_3$: 328.1787; found: 328.1786.

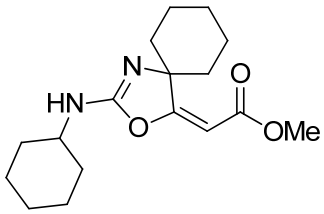


4f : colorless needles; mp 186-190 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.32-1.80 (16 H, m), 2.65-2.72 (4 H, m), 2.89 (4 H, t, *J* = 6.8 Hz), 3.51 (4 H, t, *J* = 6.8 Hz), 4.06 (2 H, br-s), 5.88 (2 H, s), 7.19-7.31 (10 H, m); ^{13}C-NMR ($CDCl_3$) δ 22.3 (4C), 25.2 (2C), 32.9 (4C), 35.7 (2C), 43.9 (2C), 74.4 (2C), 103.6 (2C), 126.6 (2C), 128.7 (4C), 128.9 (4C), 138.6 (2C), 153.6 (2C), 177.3 (2C), 186.3.

IR (KBr): 3418, 2930, 2860, 1720, 1625, 1014, 976, 931 cm^{-1}.

HRMS-EI:*m/z* [M$^+$] calcd for $C_{35}H_{42}N_4O_3$: 566.3257; found: 566.3260.

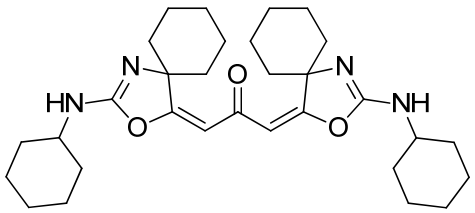


2g :colorless needles; mp 133-135 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.12-2.05 (18 H, m), 2.55-2.62 (2 H, m), 3.42-3.50 (1 H, m), 3.69 (3 H, s), 3.96 (1 H, br-s), 5.54 (1 H, s); ^{13}C-NMR ($CDCl_3$) δ 22.2 (2C), 24.6 (2C), 25.2, 25.6, 33.2 (2C), 33.4 (2C),51.1, 51.4, 74.2, 92.4, 152.8, 166.8, 179.3.

IR (KBr): 3358, 2932, 2857, 1707, 1644, 1518, 1125, 1066 cm^{-1}.

HRMS-EI:*m/z* [M$^+$] calcd for $C_{17}H_{26}N_2O_3$: 306.1944; found: 306.1945.

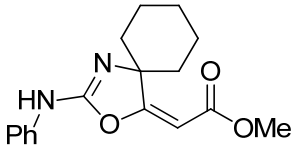


4g : colorless needles; mp 189-191 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.11-1.79 (32 H, m), 2.00-2.03 (4 H, m), 2.65-2.72 (4 H, m), 3.40-3.47 (2 H, m), 3.94 (2 H, br-s), 5.91 (2 H, s); ^{13}C-NMR ($CDCl_3$) δ 22.3 (4C), 24.6 (4C), 25.1 (2C), 25.5 (2C), 32.8 (4C), 33.2 (4C), 51.3 (2C), 74.2 (2C), 103.4 (2C), 153.0 (2C), 177.3 (2C), 186.3.

IR (KBr): 3430, 2928, 2855, 1710, 1624, 1498, 996, 927 cm^{-1}.

HRMS-EI:*m/z* [M$^+$] calcd for $C_{31}H_{46}N_4O_3$: 522.3570; found: 522.3568.



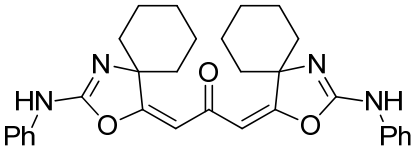
2h : colorless needles; mp 121-124 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.42-1.89 (8 H, m), 2.62-2.70 (2 H, m), 3.71 (3 H, s), 5.62 (1 H, s), 6.23 (1H, br-s), 7.03 (1 H, t, *J* = 7.6 Hz), 7.32 (2 H, t, *J* = 7.6 Hz), 7.51 (2 H, d, *J* = 7.6 Hz); ^{13}C-NMR (CD_2Cl_2) δ 22.7 (2C), 25.6, 33.6 (2C), 51.4, 75.4, 93.4,

118.2 (2C), 122.9, 129.3 (2C), 139.1, 149.5, 166.7, 177.4.

IR (KBr): 3298, 2929, 1688, 1605, 1552, 1315, 1151, 1064 cm^{-1}.

HRMS-EI:*m/z* [M^+] calcd for $C_{17}H_{20}N_2O_3$: 300.1474; found: 300.1472.



4h : colorless needles; mp 300 ℃.

^{1}H-NMR ($CDCl_3$) δ 1.46-1.91 (16 H, m), 2.67-2.73 (4 H, m), 6.30 (2 H, s), 7.16-7.56 (10 H, m), 8.65 (2H, br-s); ^{13}C-NMR ($CDCl_3$) δ 21.4 (4C), 23.9 (2C), 31.9 (4C), 69.4 (2C), 108.4 (2C), 122.5 (4C), 127.8 (2C), 129.8 (4C), 133.2 (2C), 155.9 (2C), 169.3 (2C), 183.7

IR (KBr): 3411, 2928, 2859, 1715, 1628, 1603, 1535, 996 cm^{-1}.

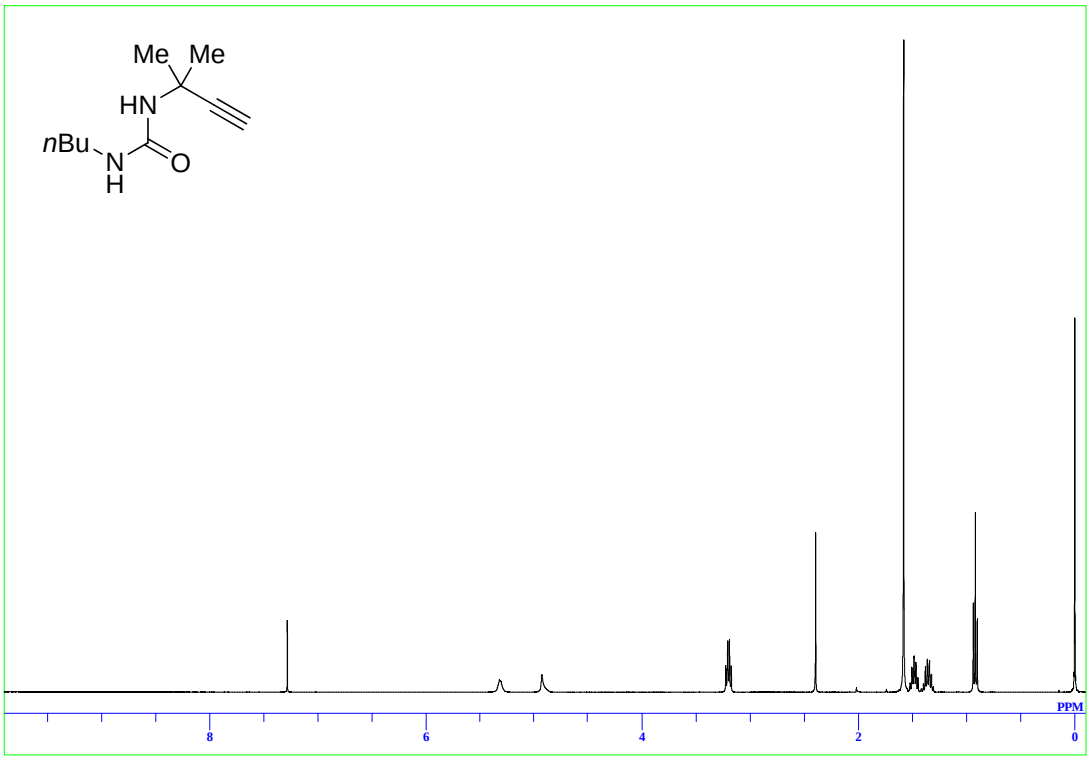
HRMS-EI:*m/z* [M^+] calcd for $C_{31}H_{34}N_4O_3$: 510.2631; found: 510.2629.

Ref

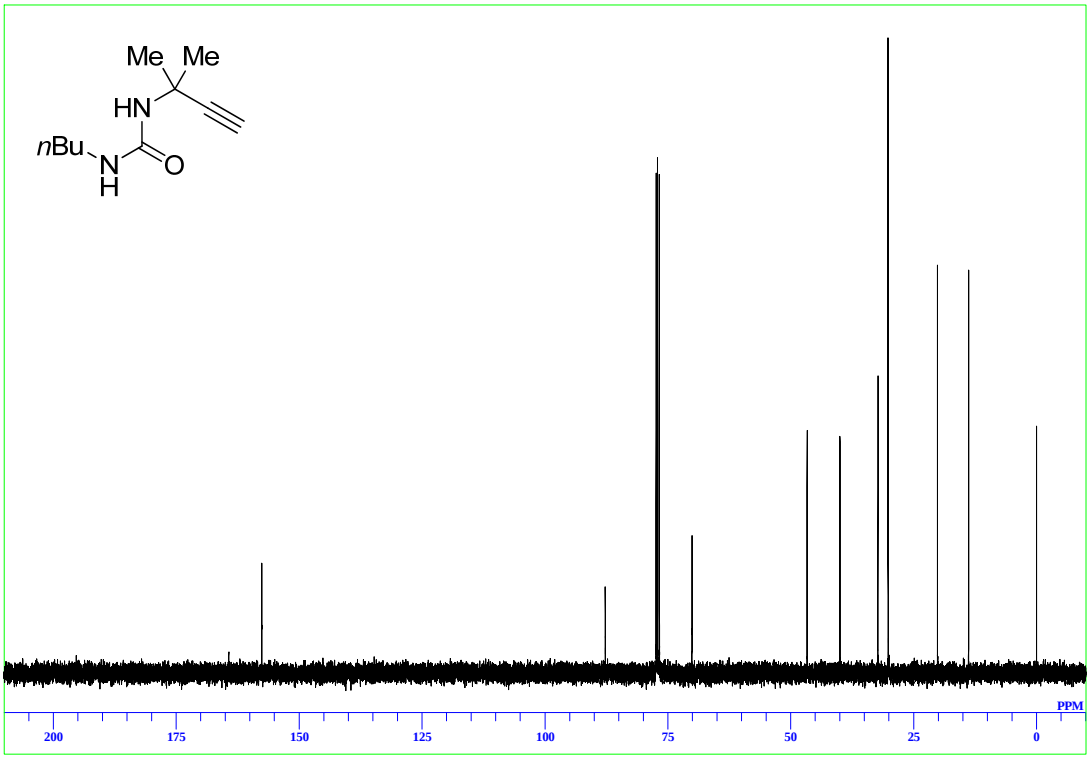
1) F. E. Michael, P. A. Sibbald, B. M. Cochran, *Org. Lett*. **2008**, *10*, 793.

2) A. Bacchi, G. P. Chiusoli, M. Costa, C. Sani, B. Gabriele, G. Salerno, *J. Organomet. Chem.* **1998**, *562*, 35.

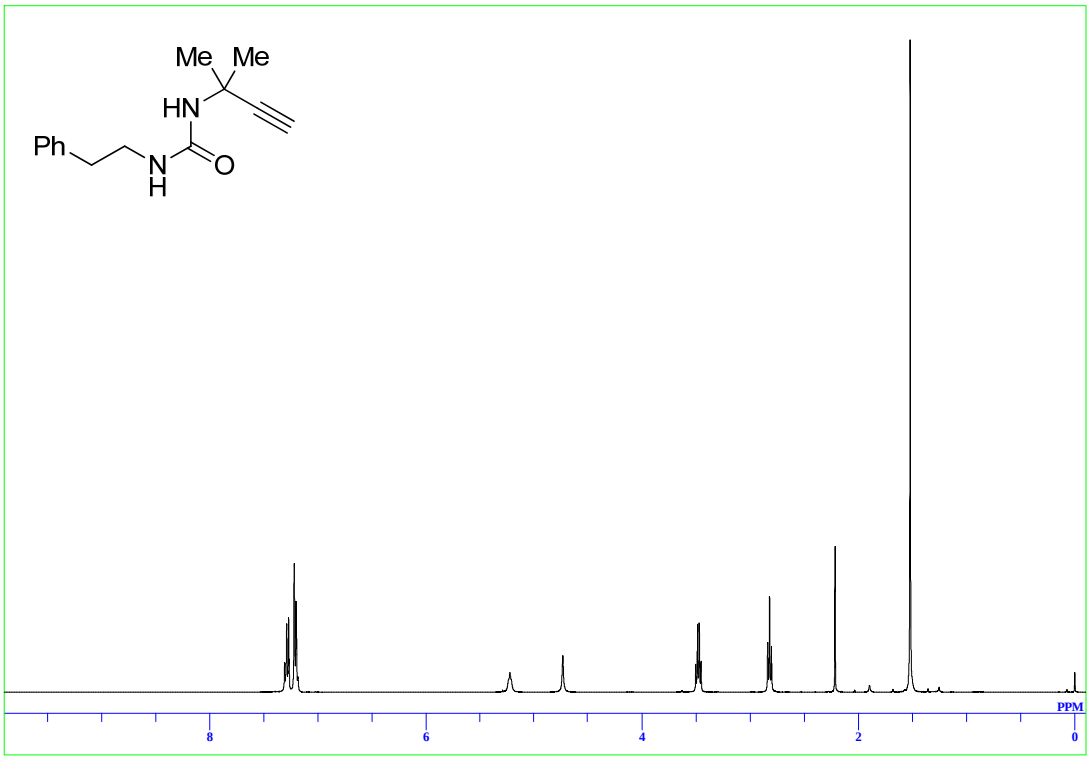
1c proton



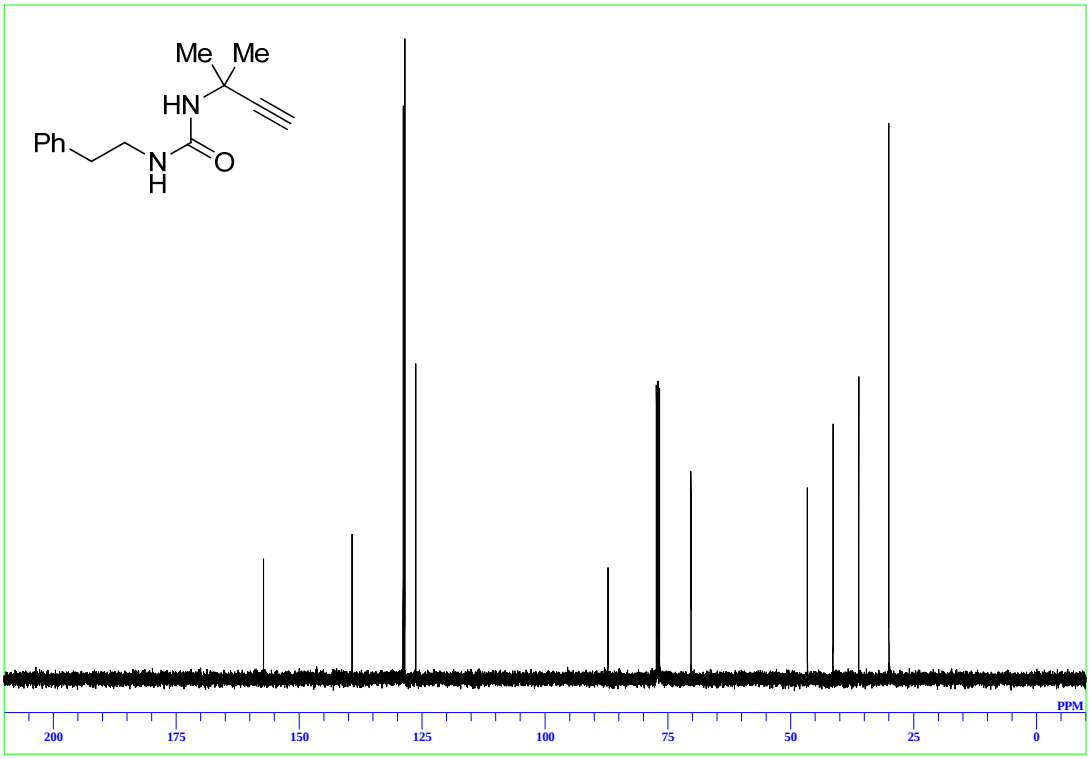
1c carbon



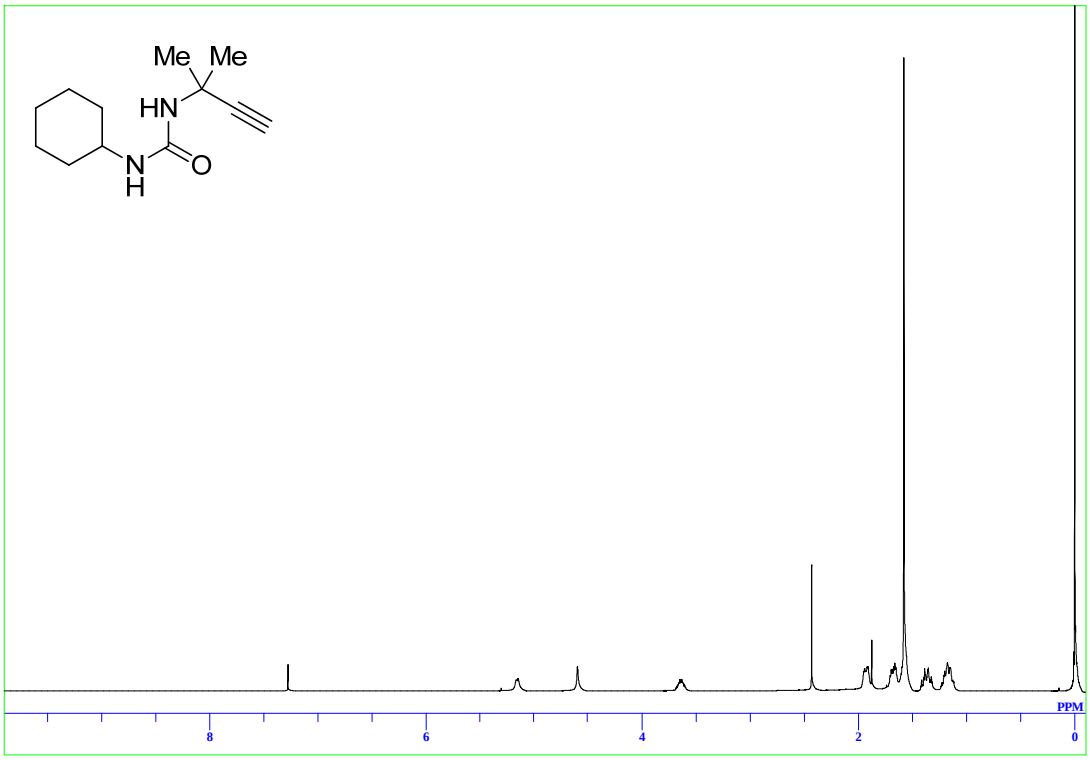
1d proton



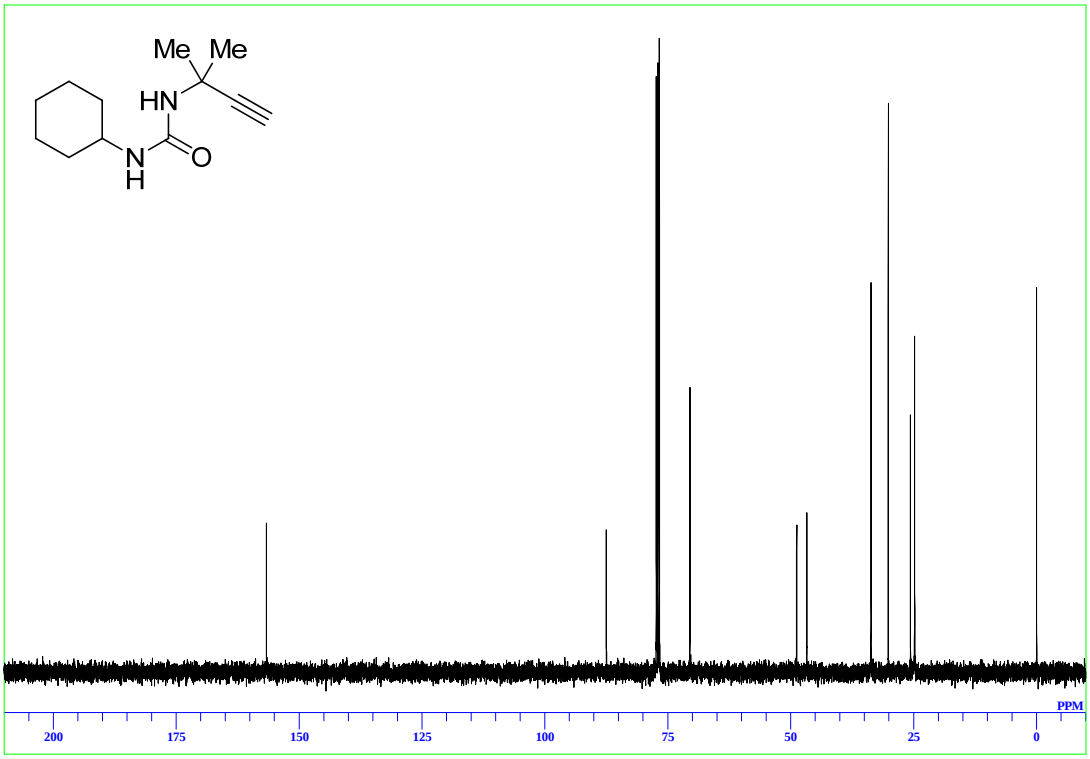
1d carbon



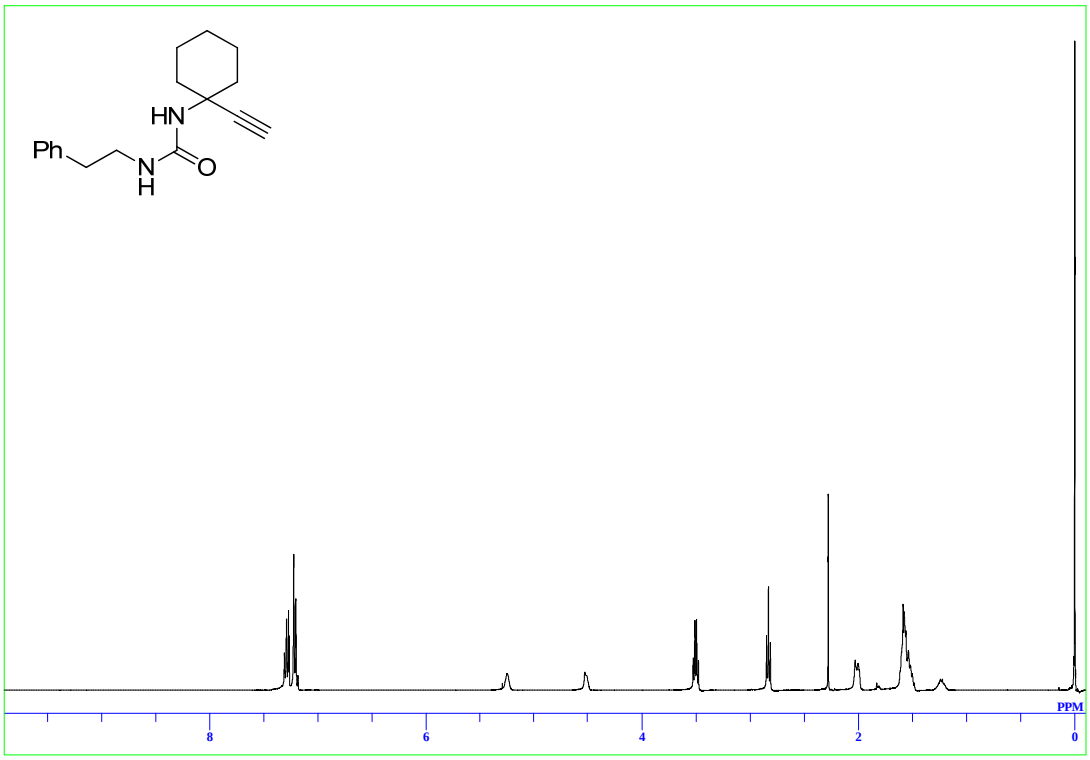
1e proton



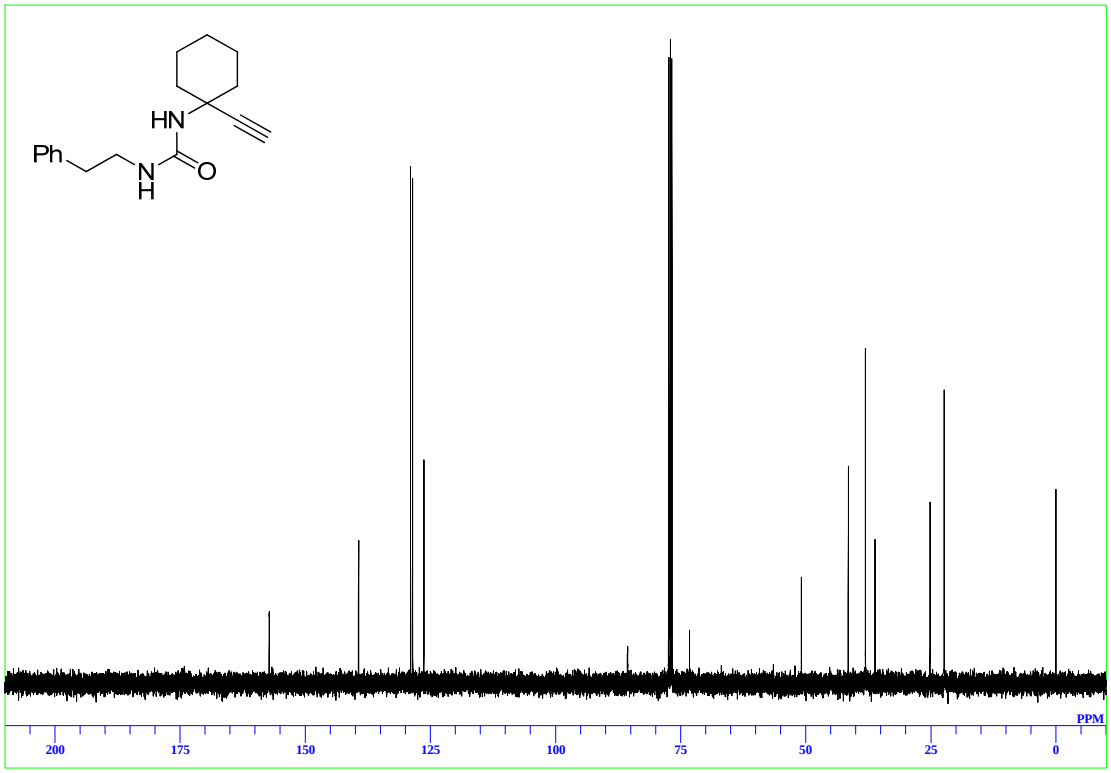
1e carbon



1f proton

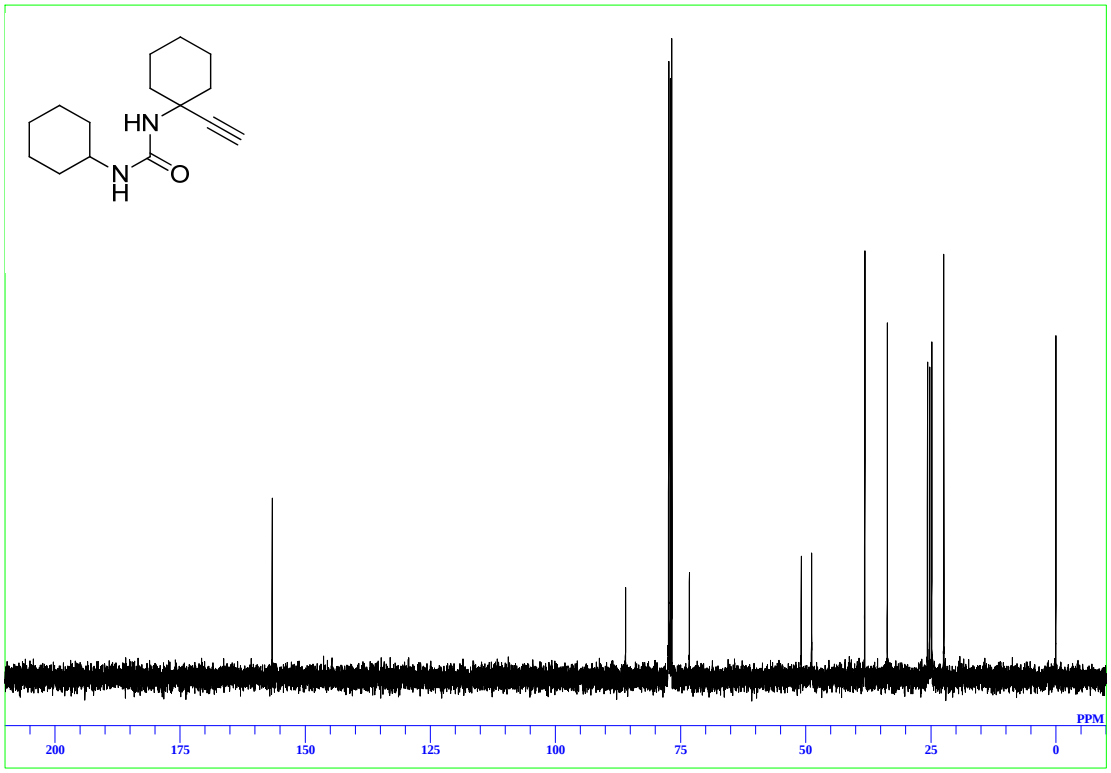


1f carbon

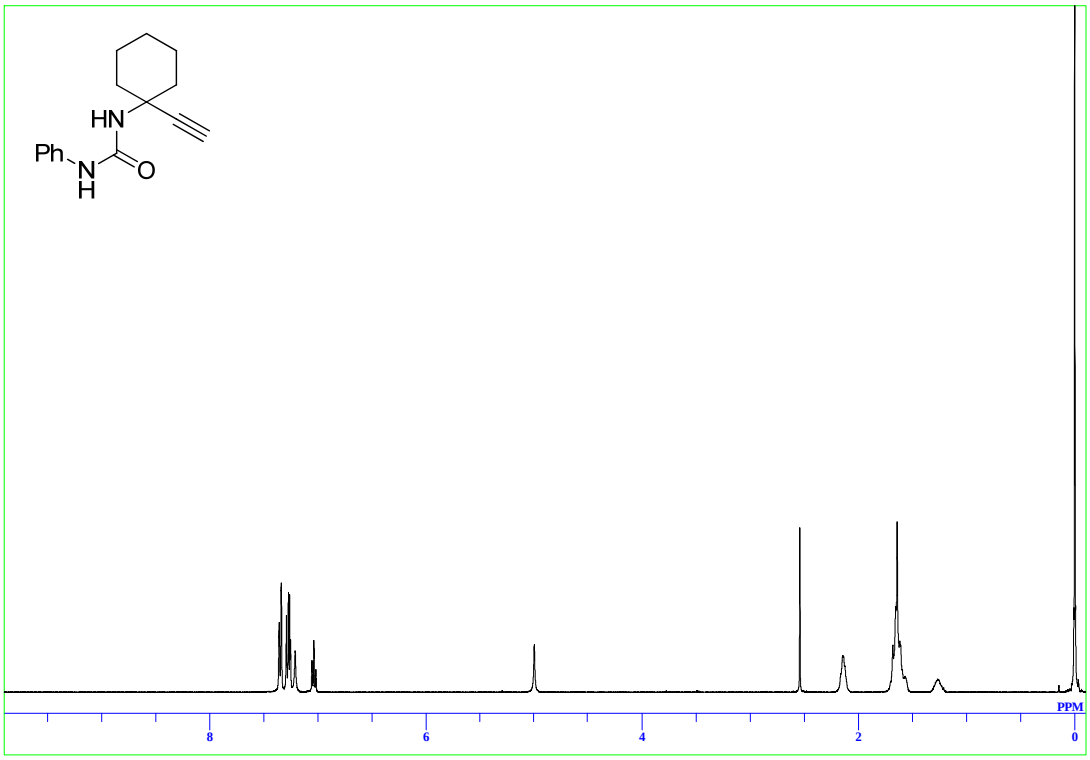


1g proton

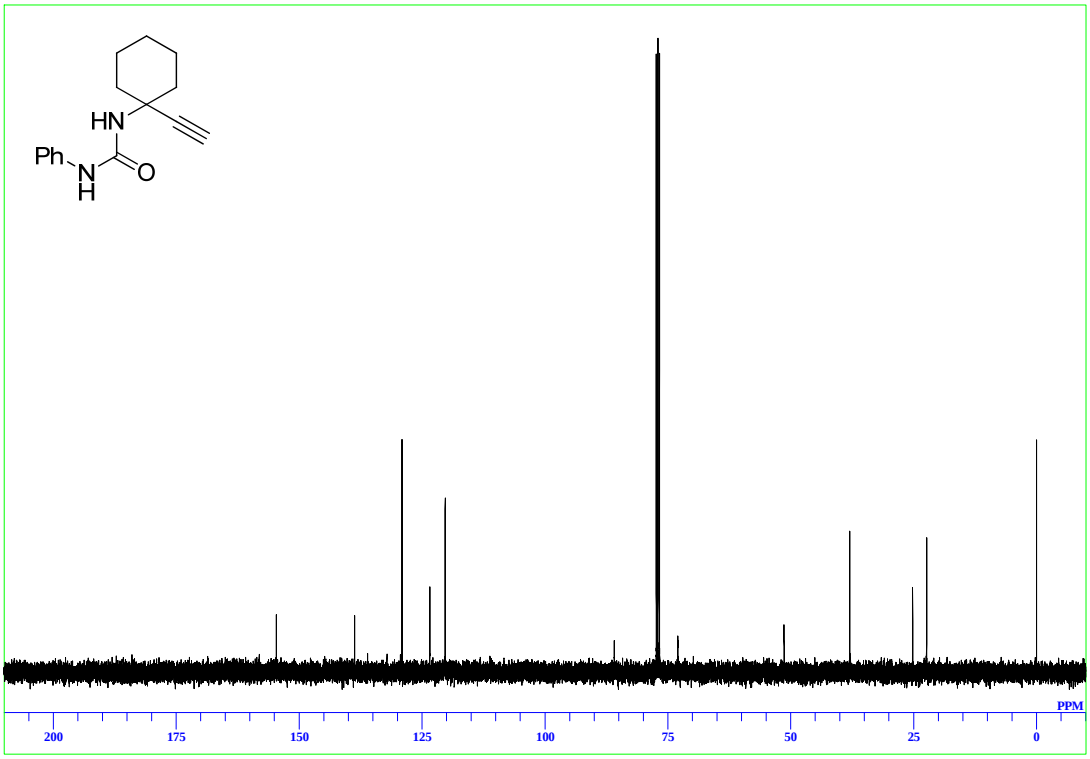
1g carbon



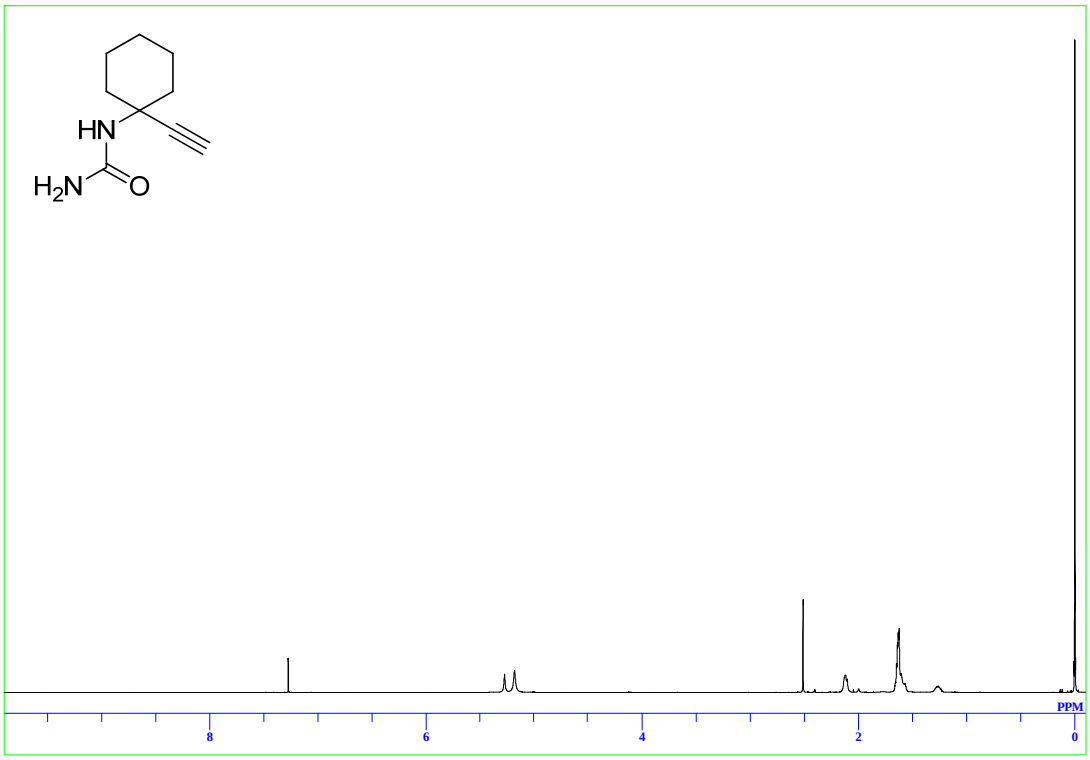
1h proton



1h carbon



1i proton



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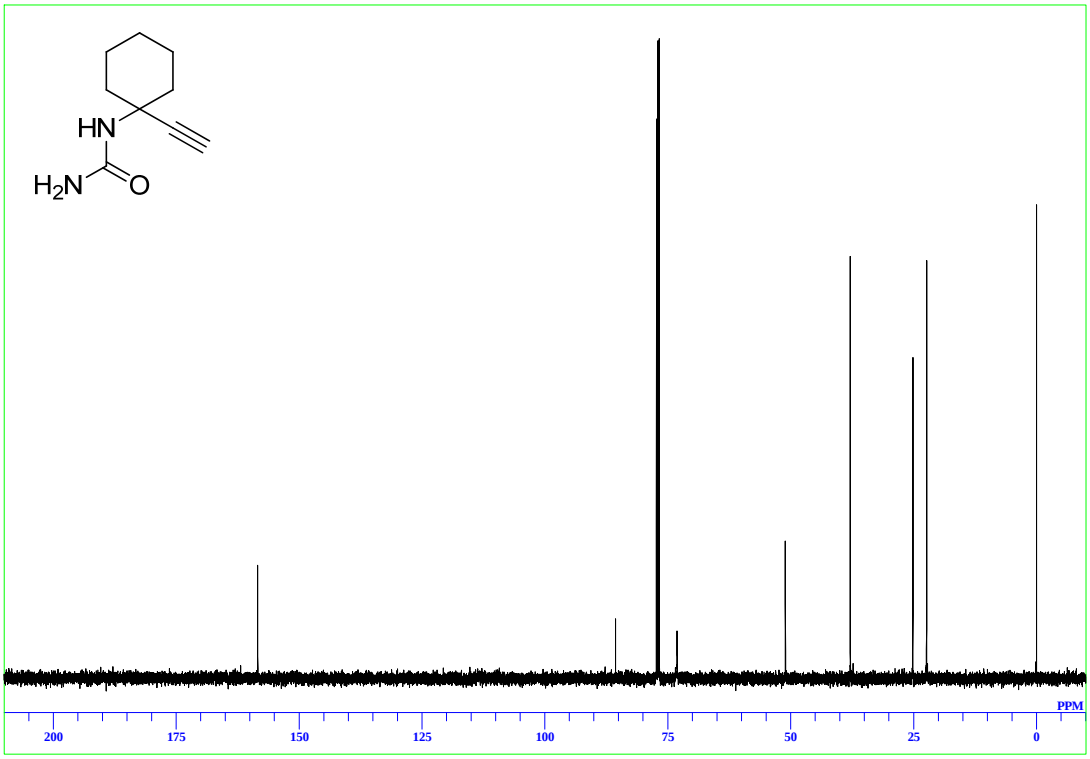

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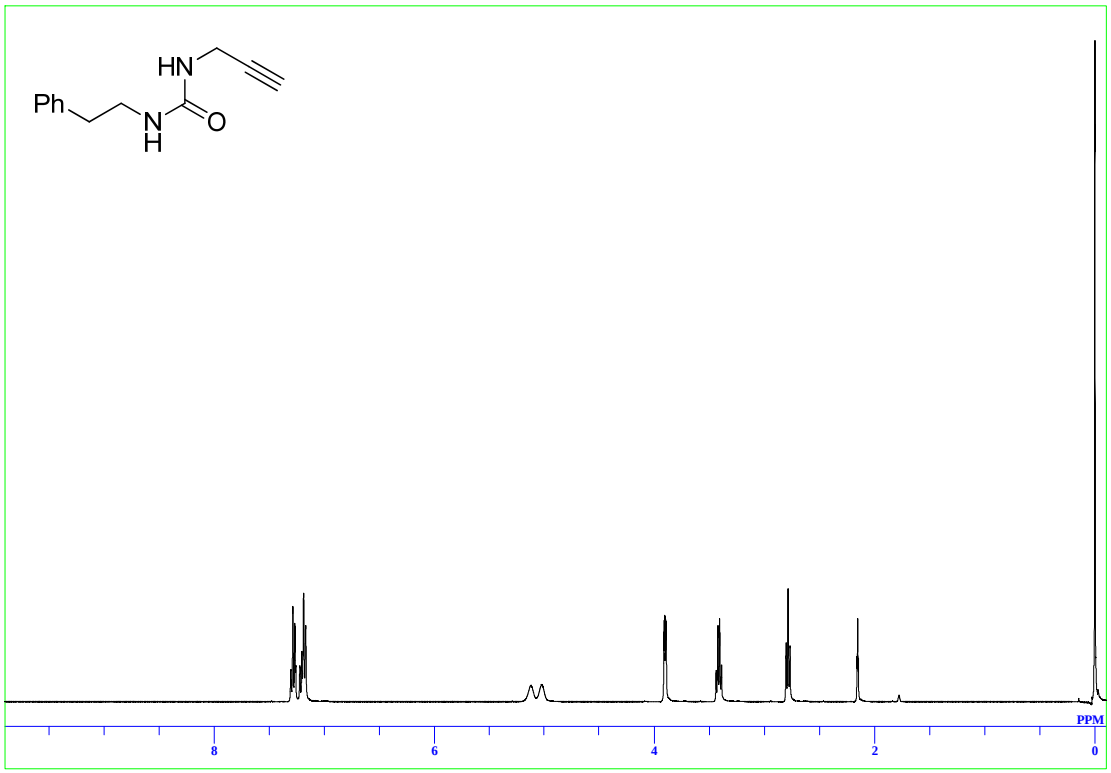
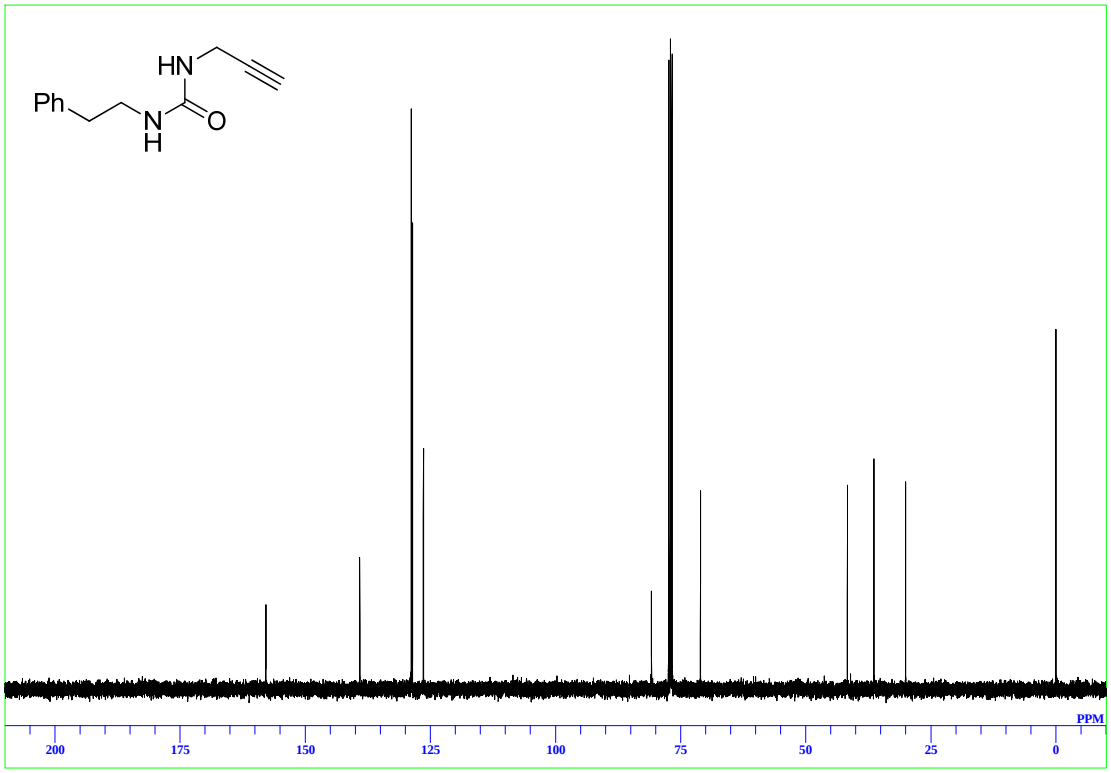
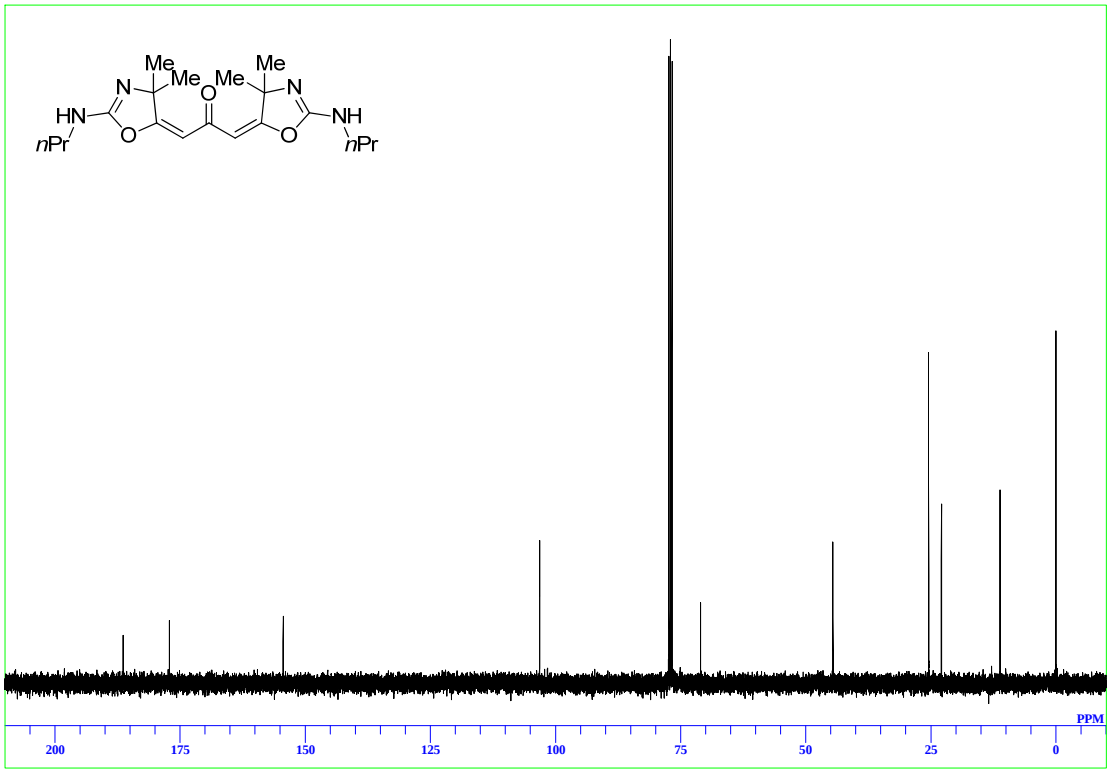


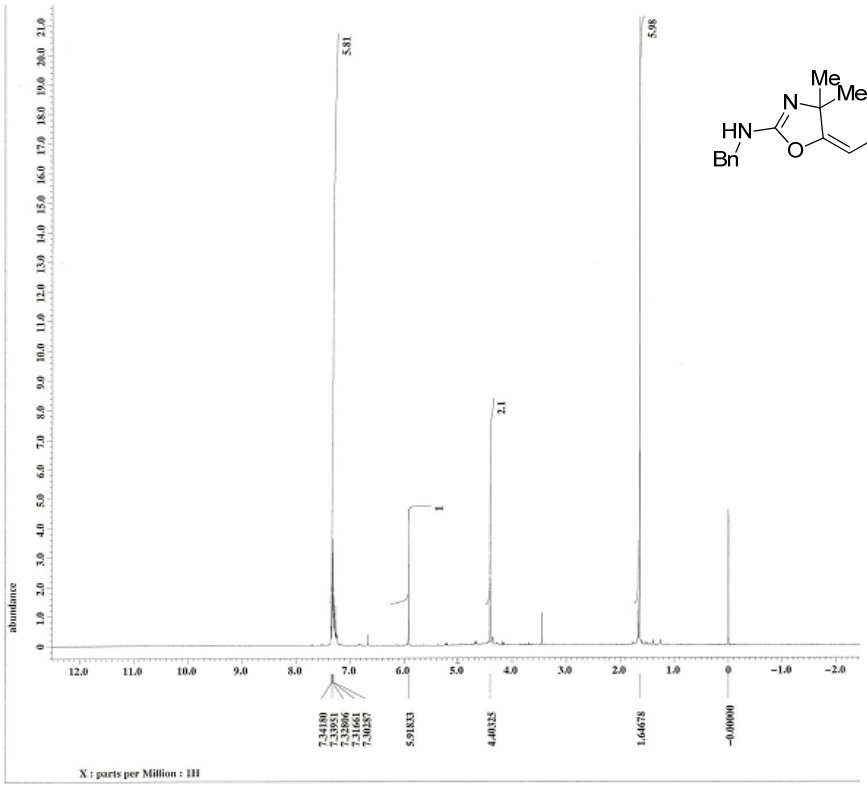
1j carbon

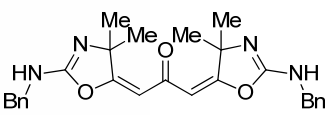


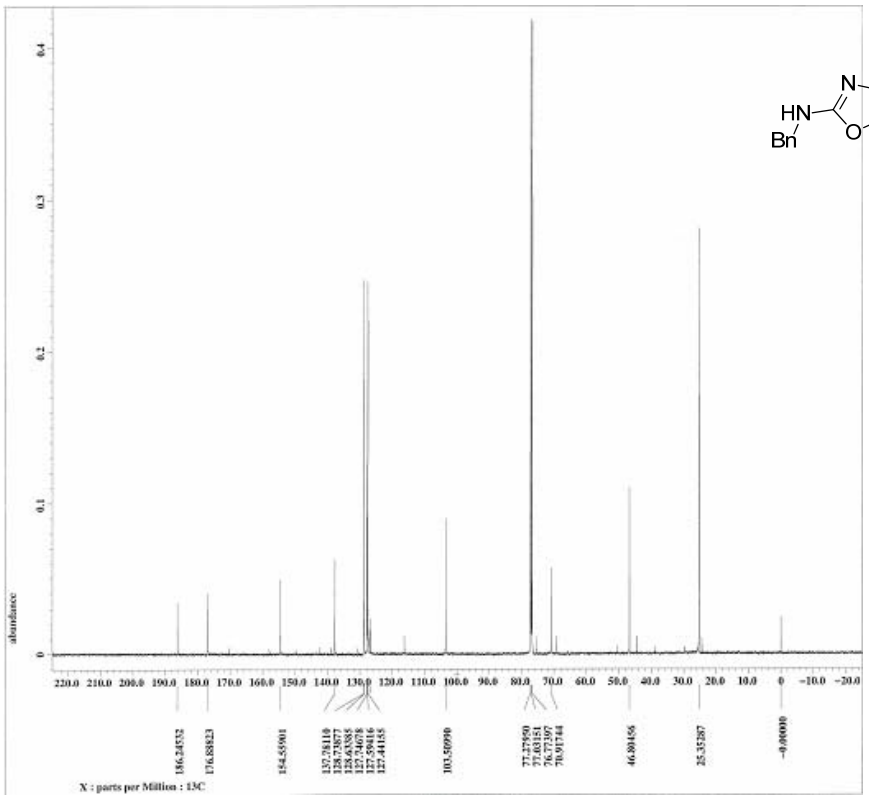
4a proton

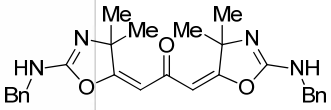
4a carbon



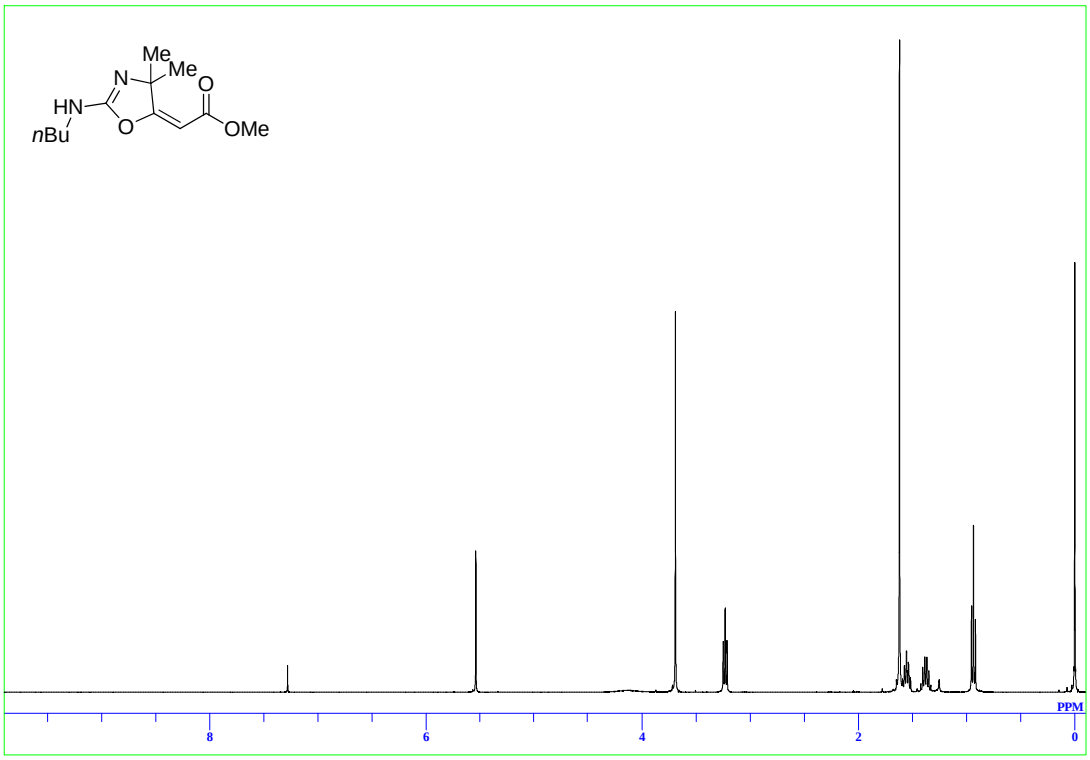

5.81
5.98
2.1
1
abundance
X : parts per Million : 1H


Me
Me
Me
Me
N
N
O
HN
NH
Bn
Bn
O
O

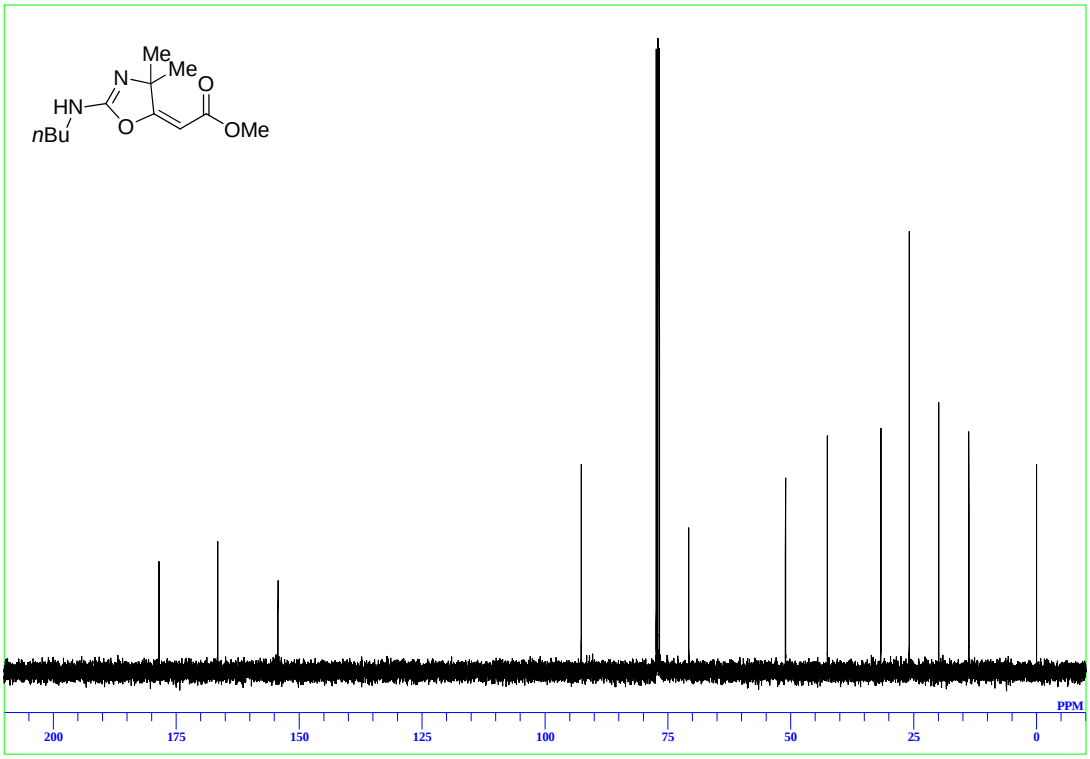

abundance
X : parts per Million : 13C


Me
Me
Me
Me
N
N
O
HN
NH
Bn
Bn
O
O

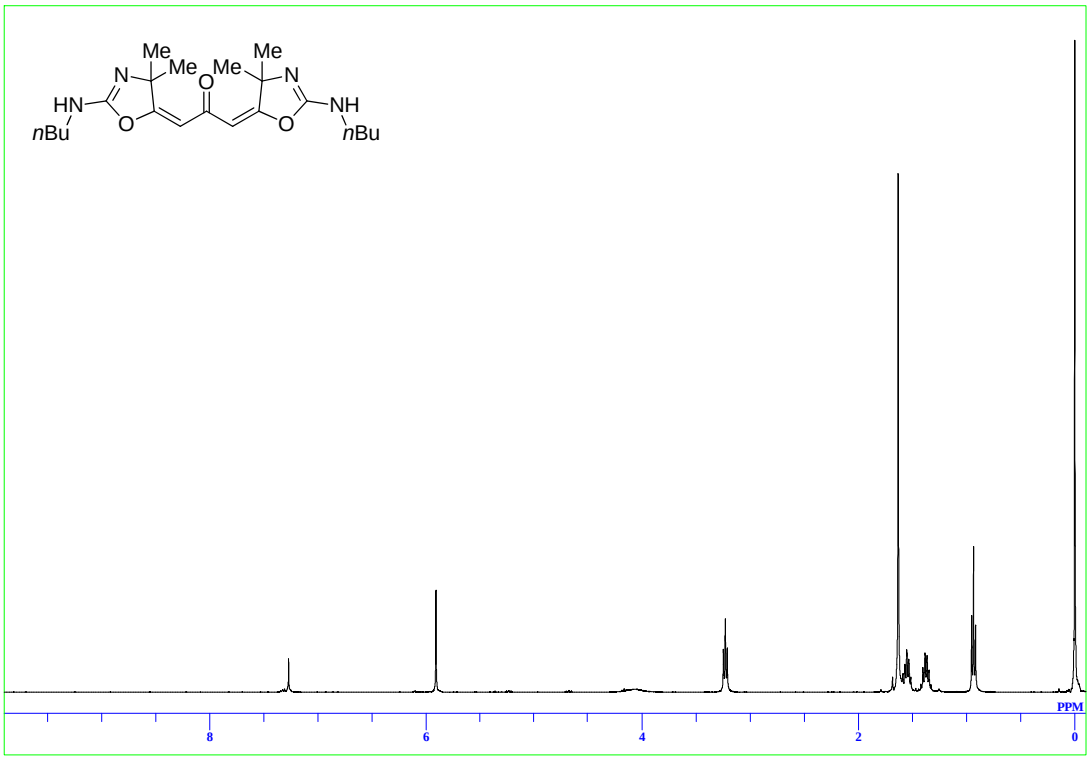
2c proton



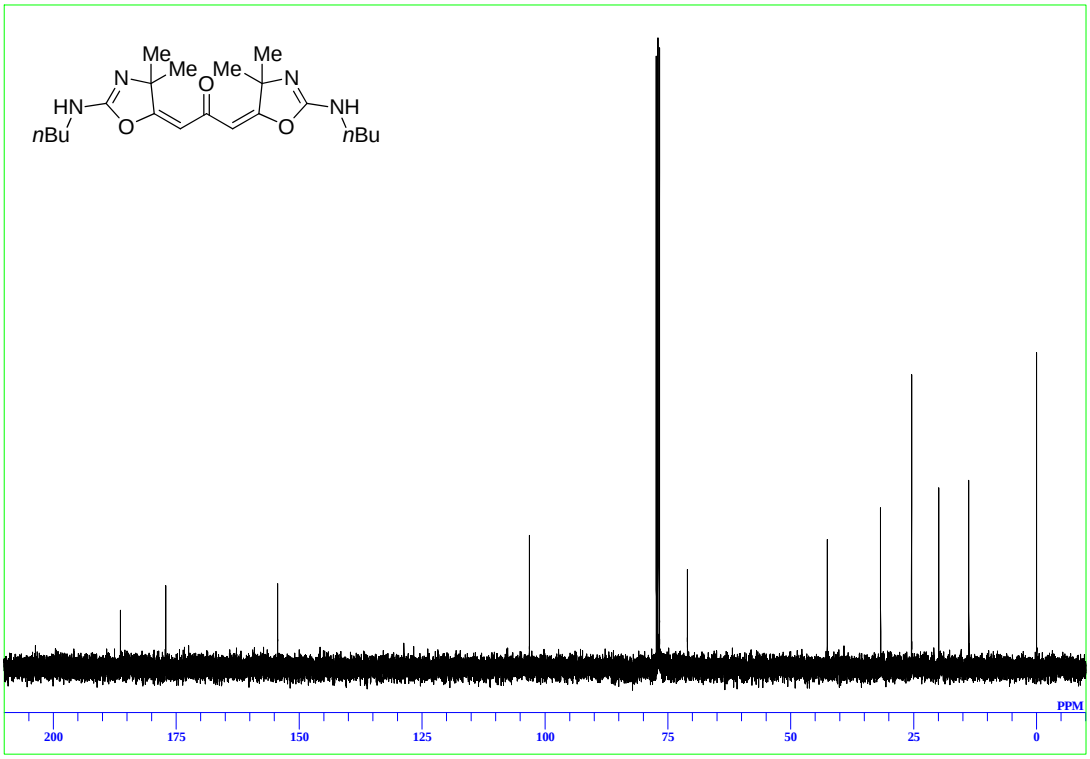
2c carbon



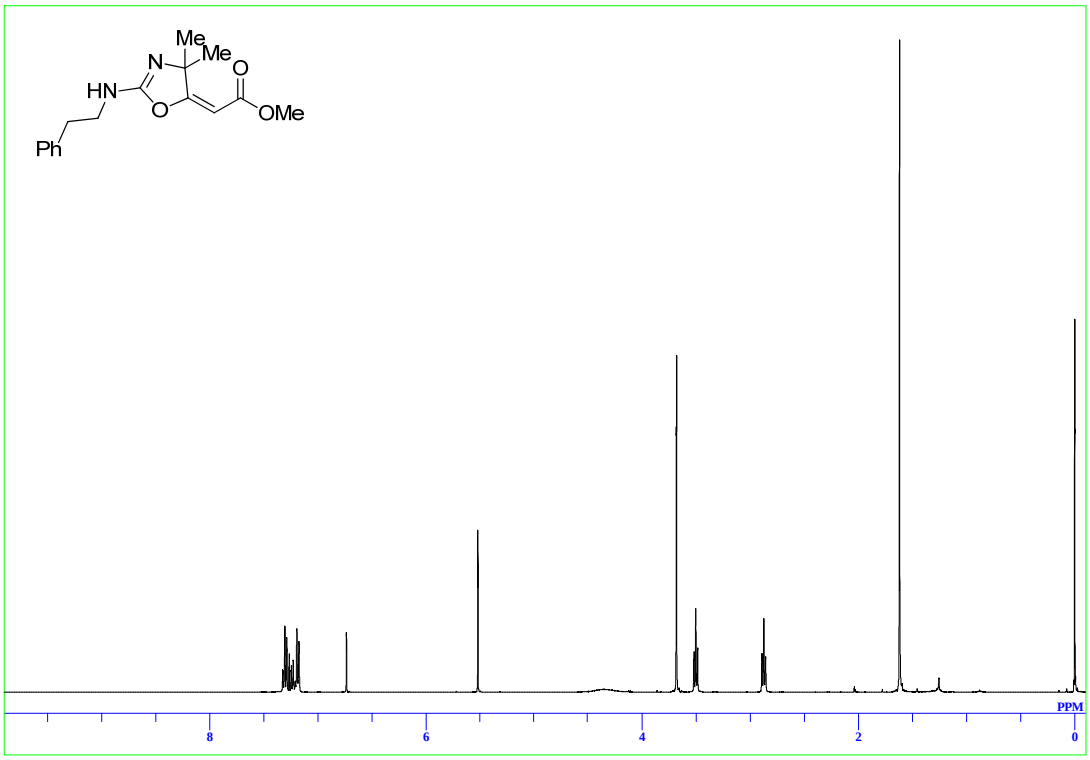
4c proton



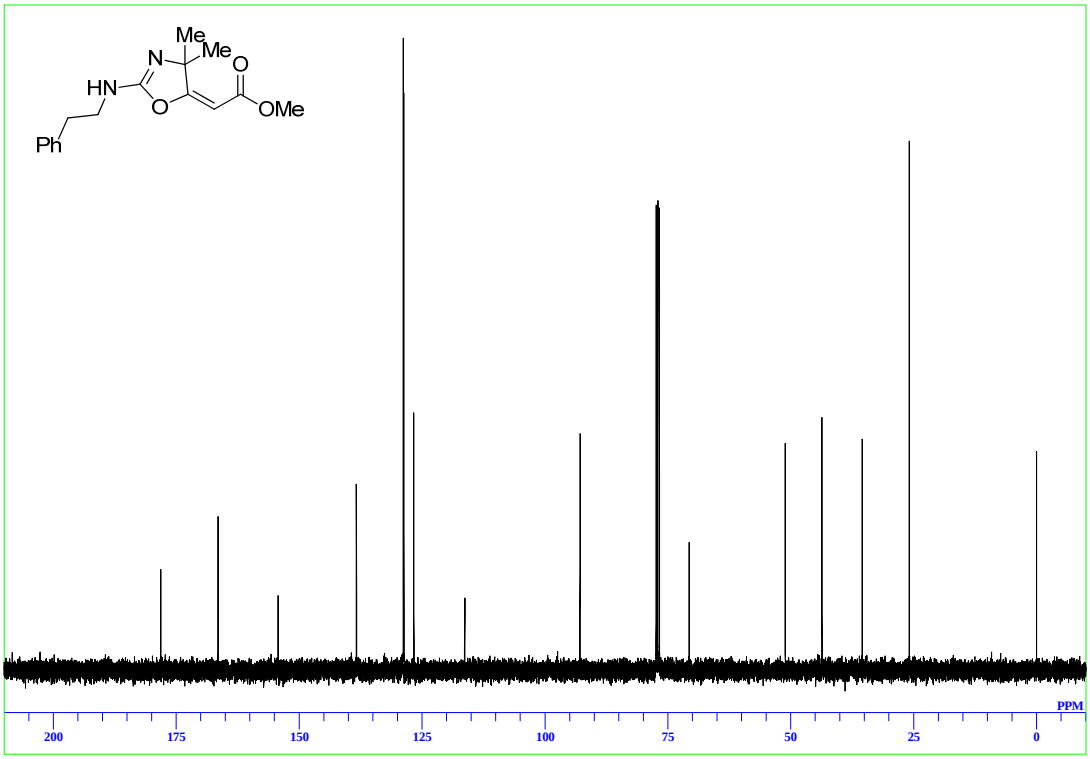
4c carbon



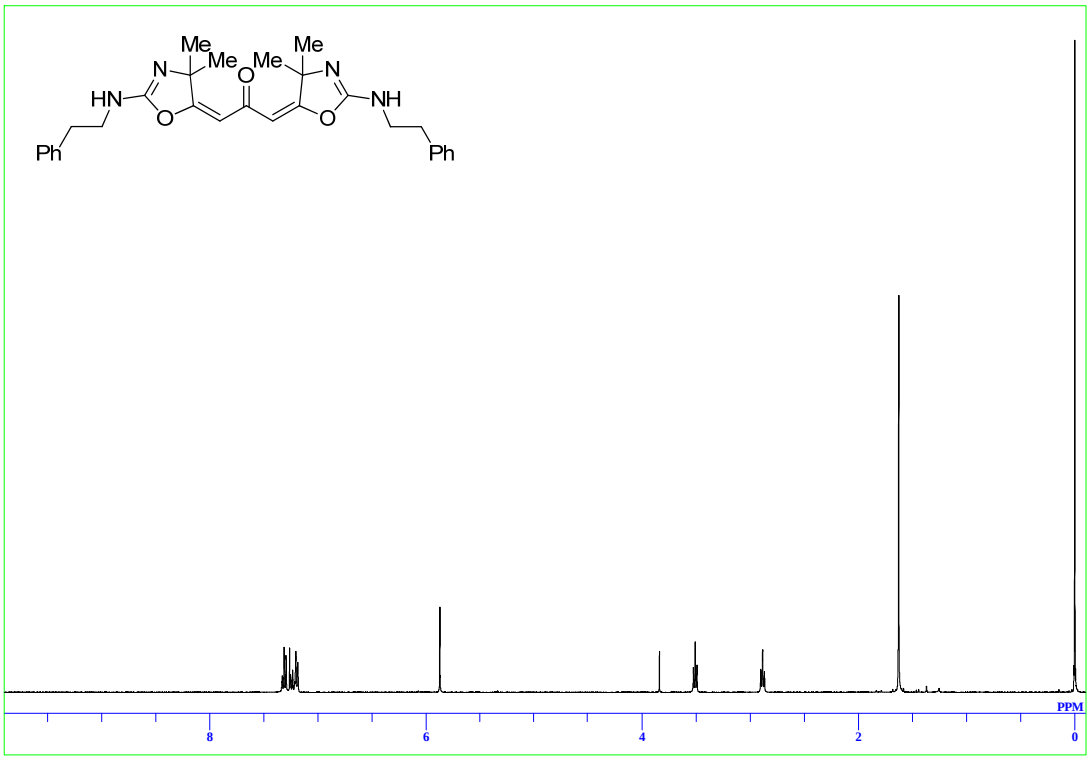
2d proton



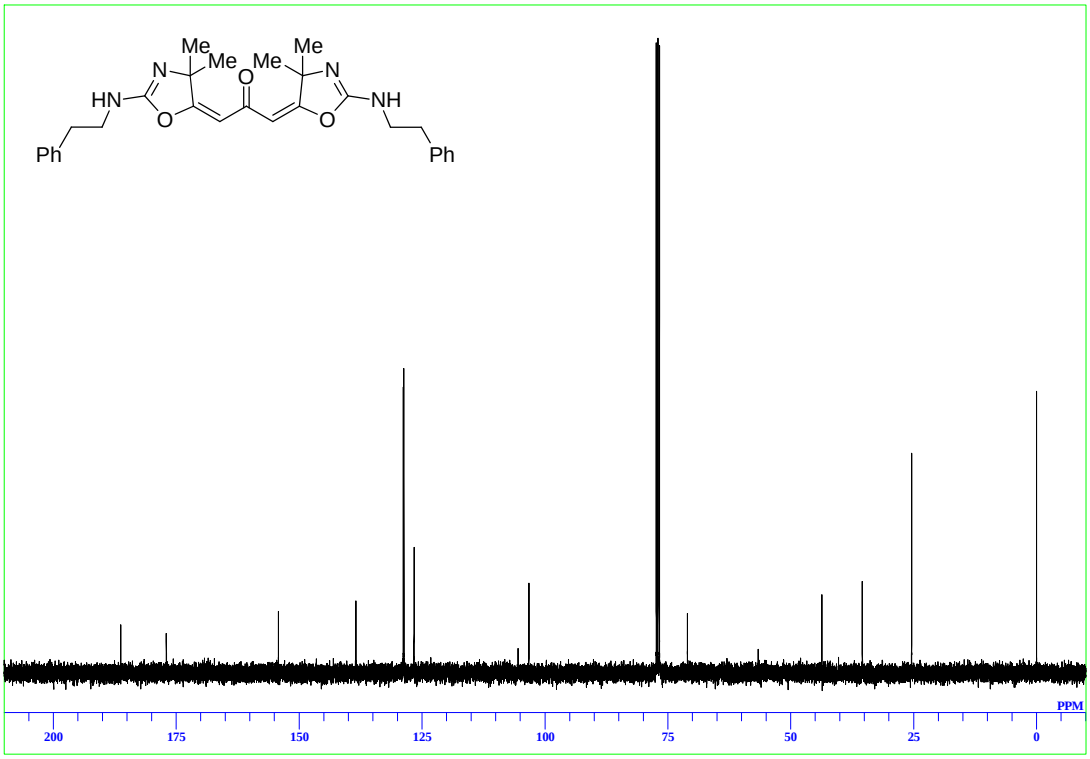
2d carbon



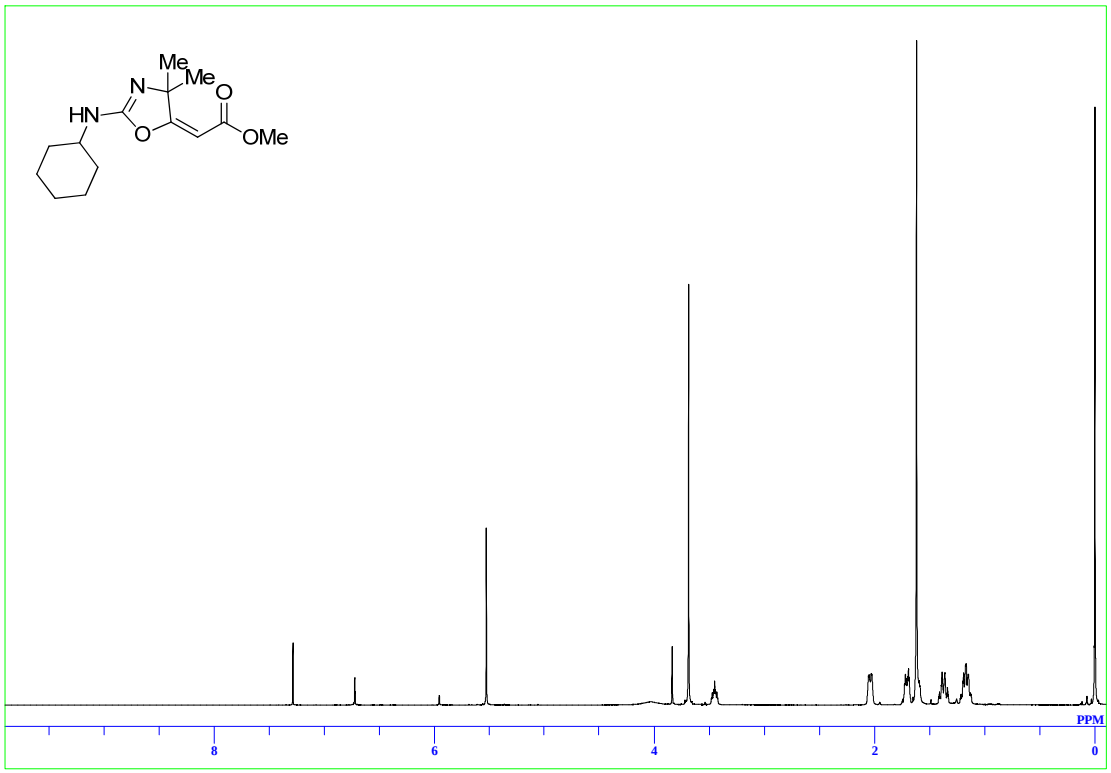
4d proton



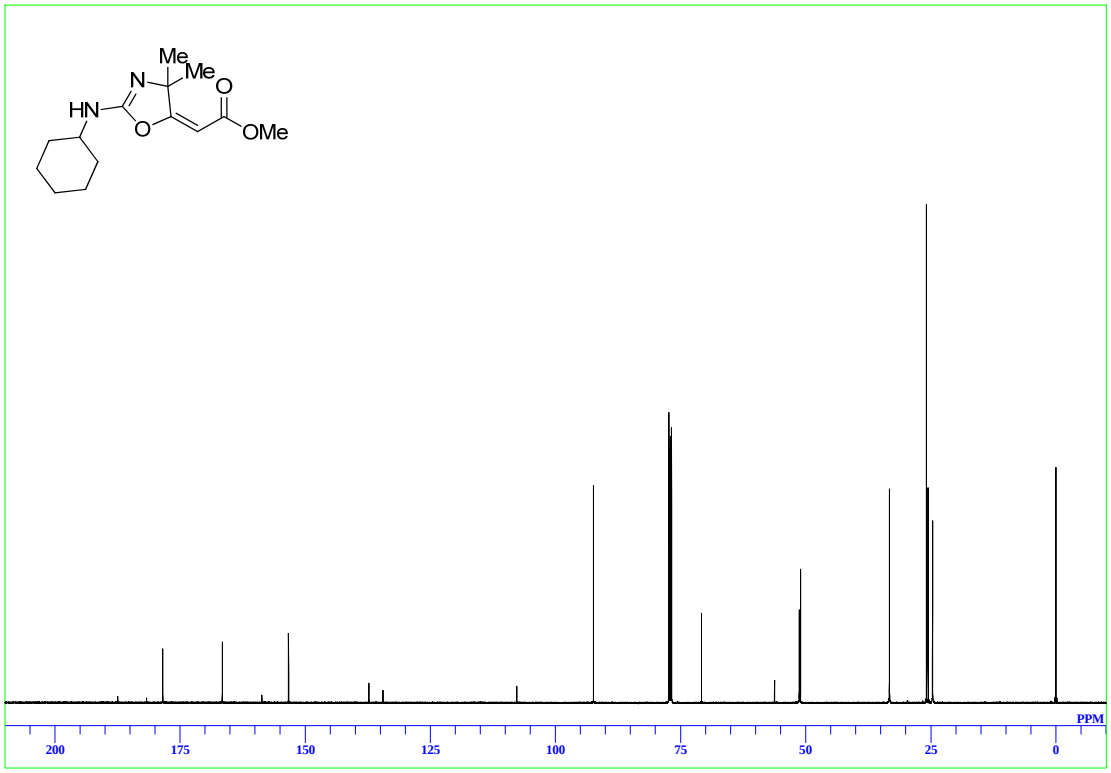
4d carbon



2e protpn

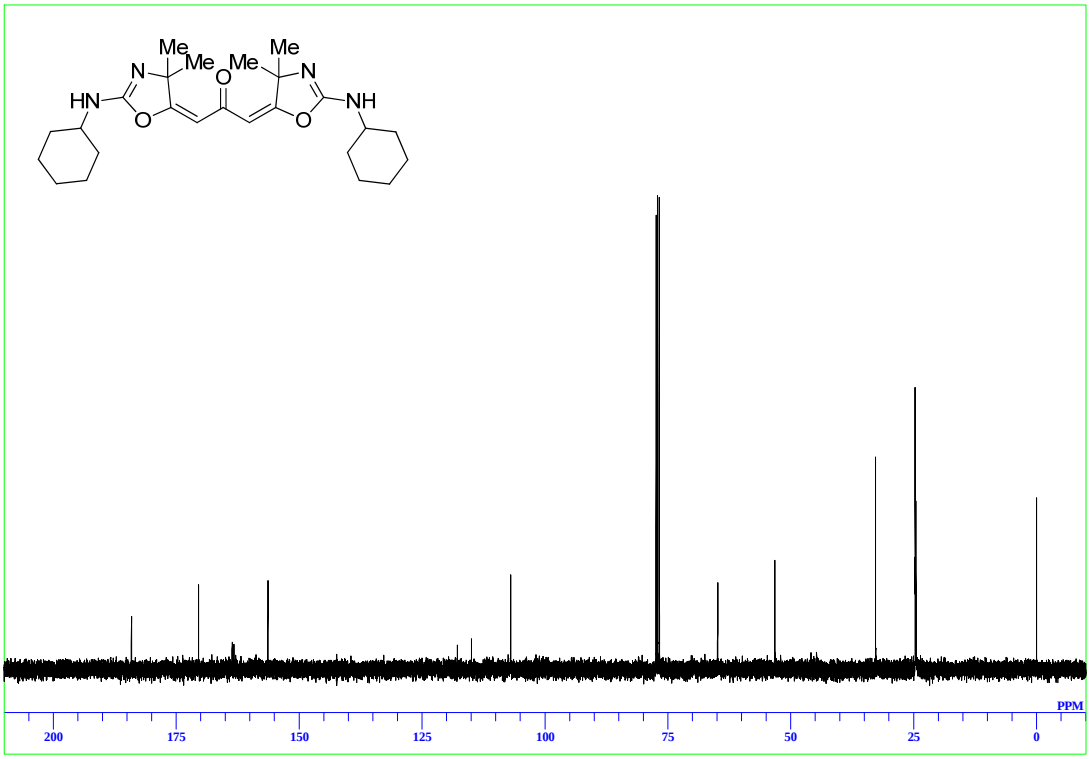


2e carbon



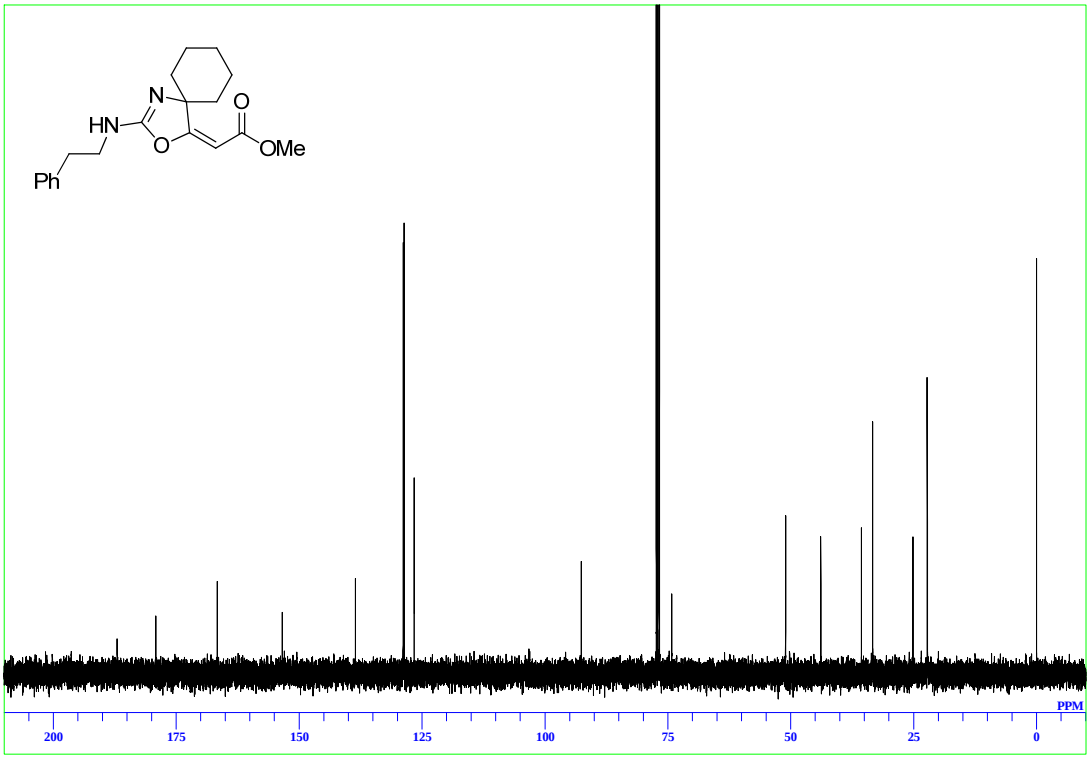
4e proton

4e carbon

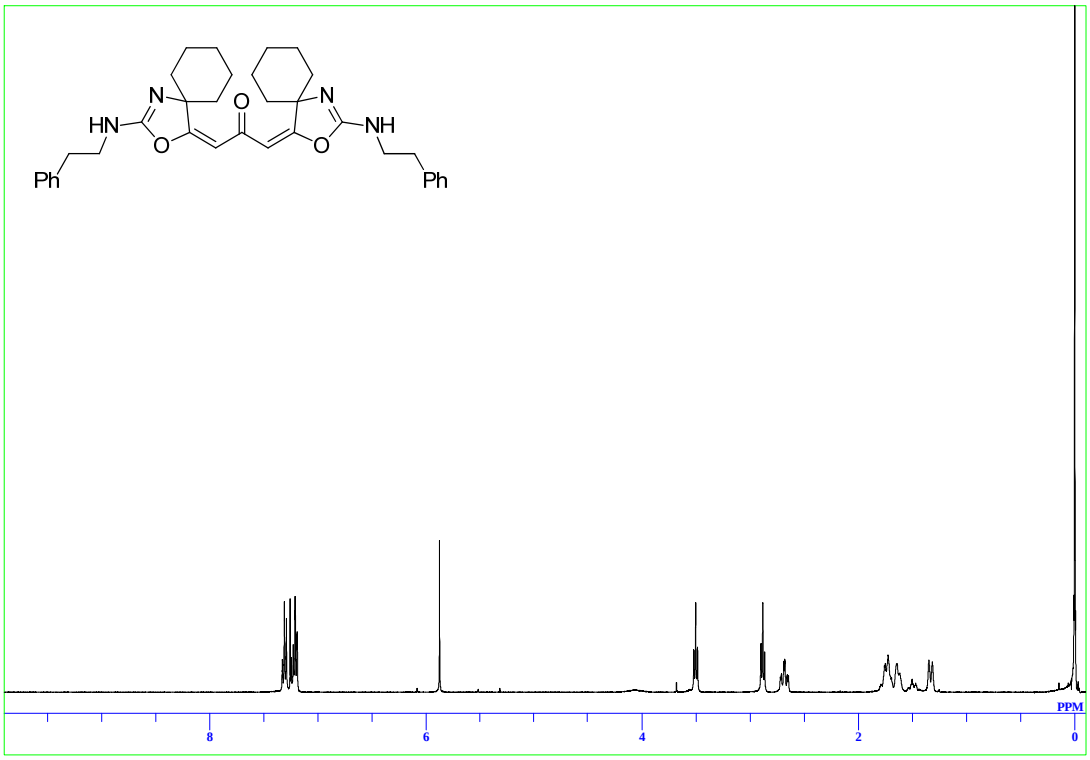


2f proton

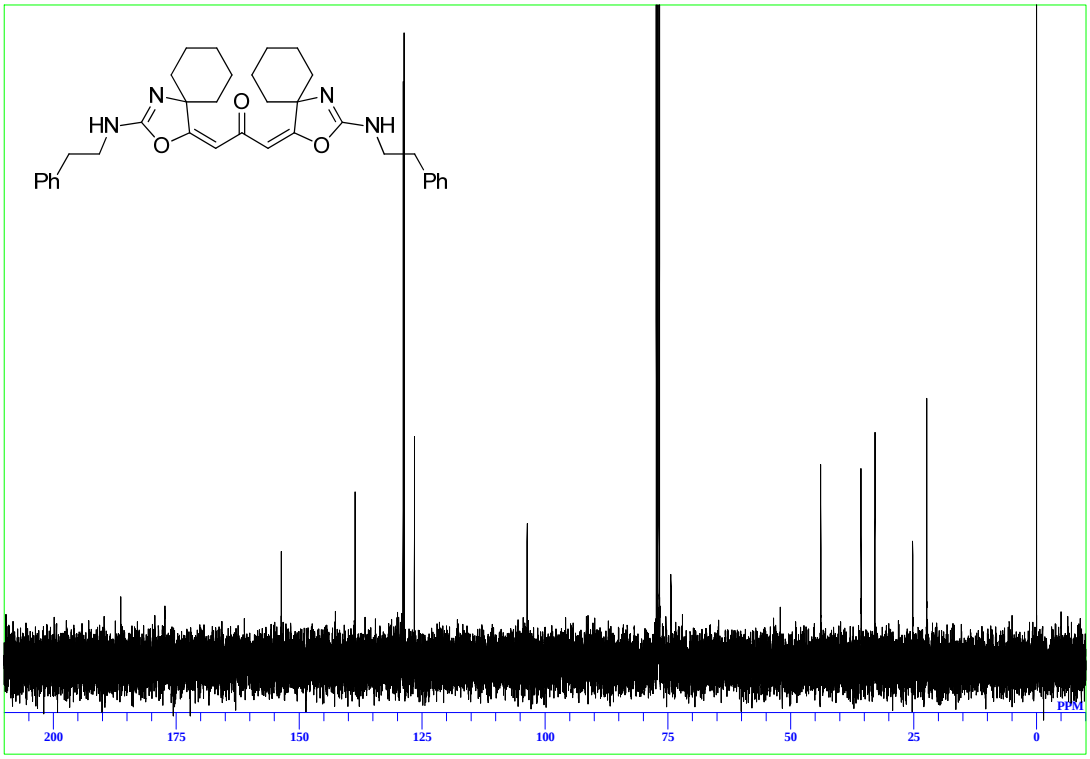
2f carbon



4f proton

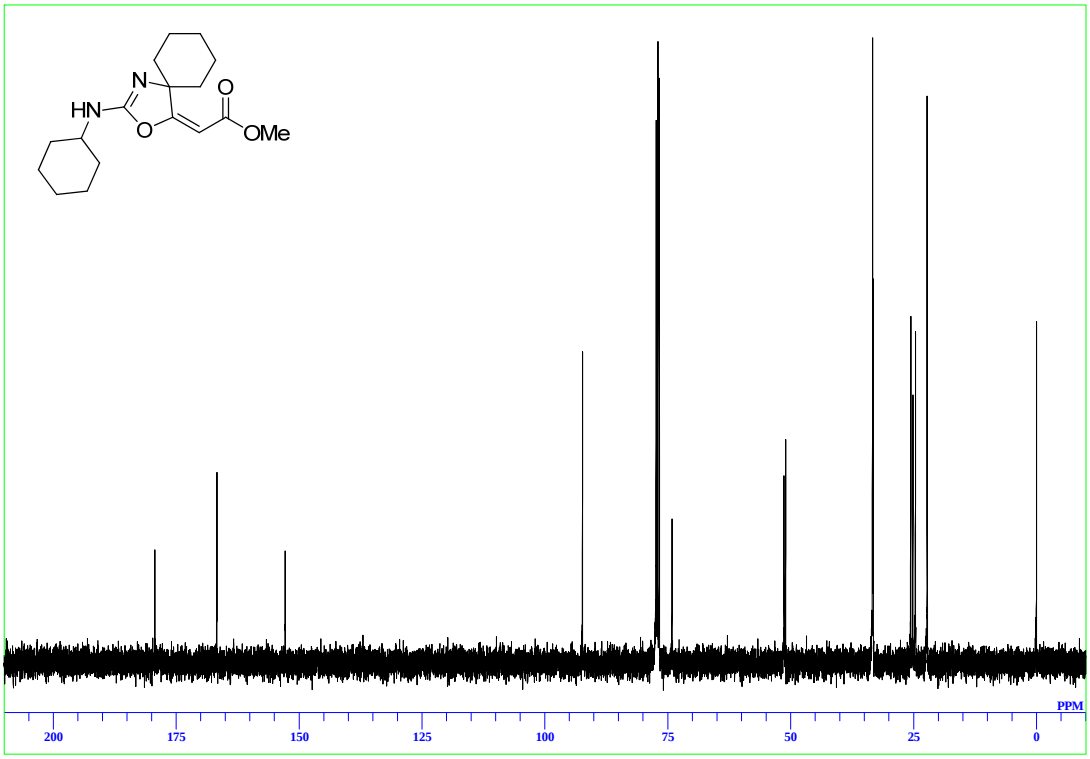


4f carbon

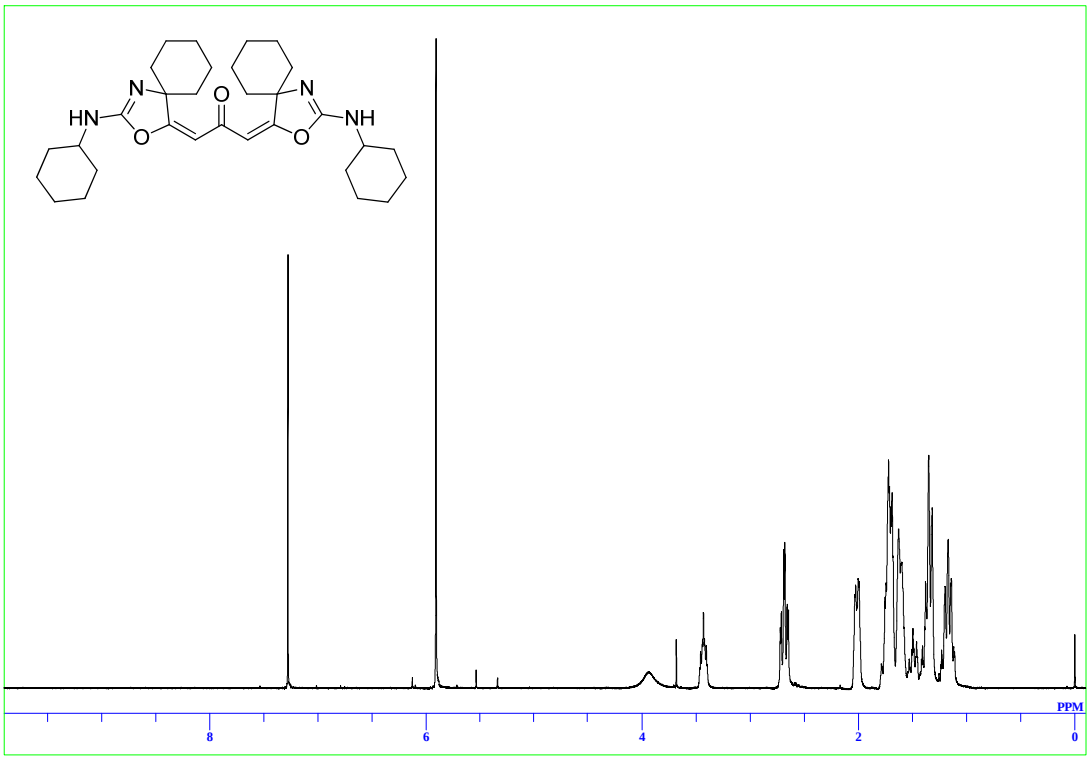


2g proton

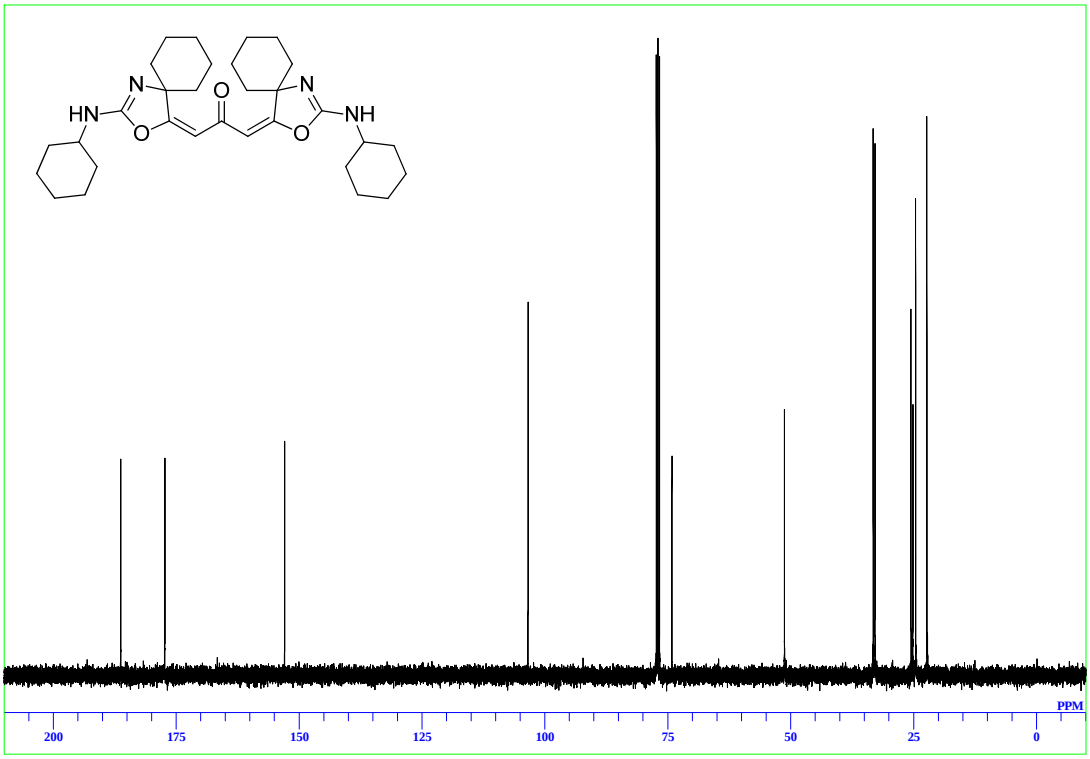
2g carbon



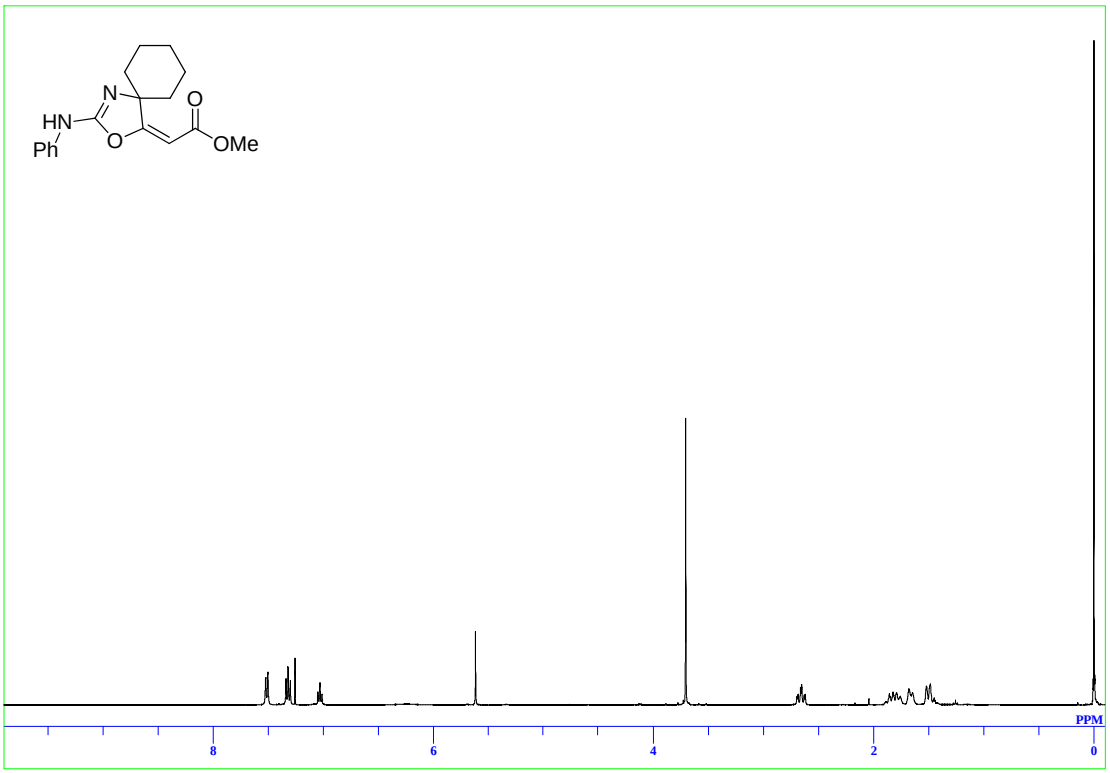
4g proton



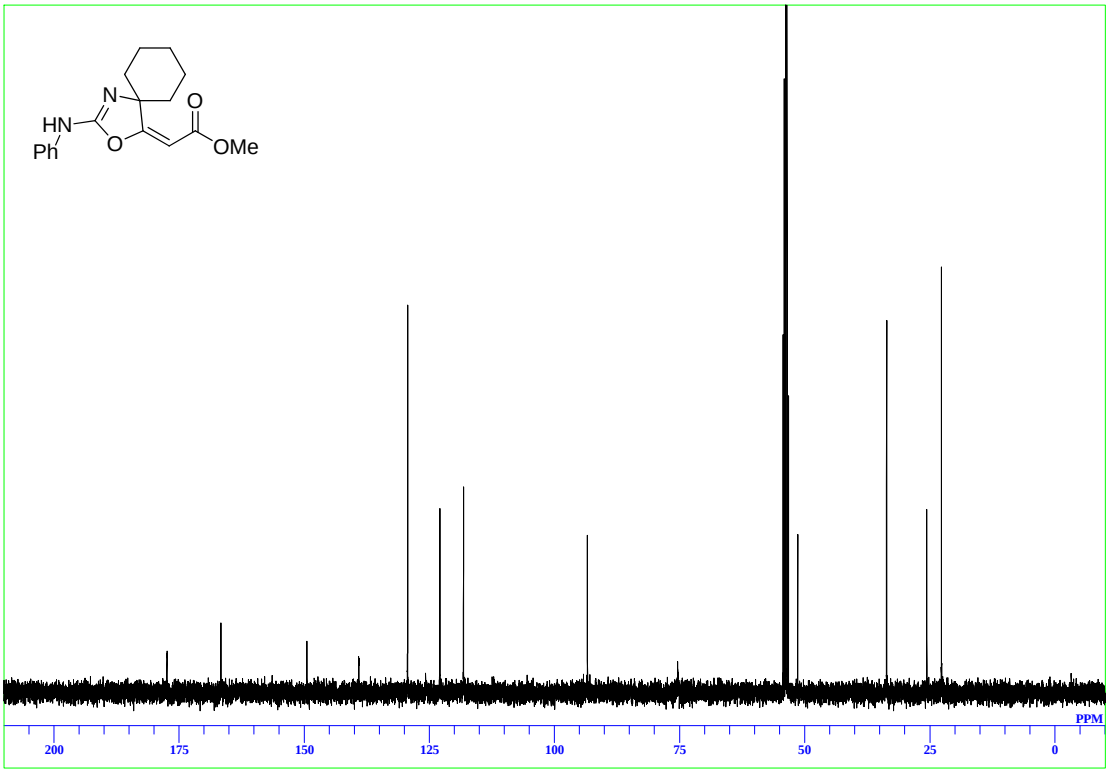
4g carbon



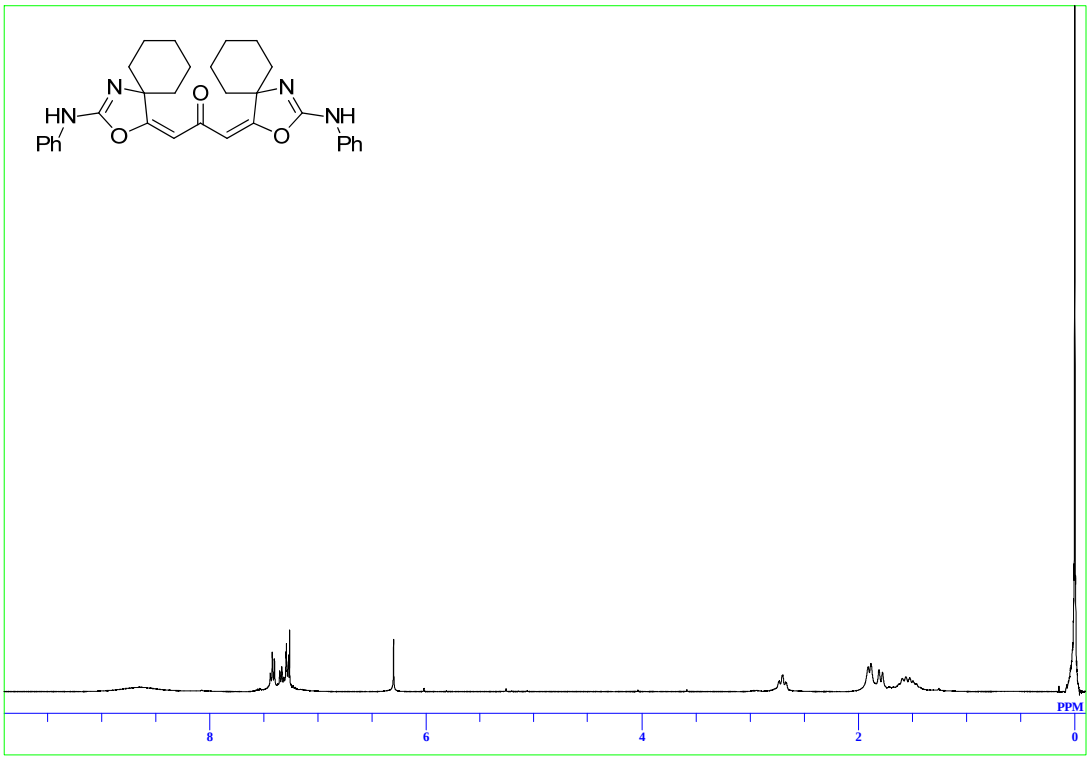
2g proton



2h carbon



4h proton



4h carbon