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Supporting Information for:

Carboallylation of Electron-Deficient Alkenes by Palladium/Copper Catalysis

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General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard schlenk technique under an argon atmosphere or in a glove box under a nitrogen atmosphere. Medium pressure liquid chromatography (MPLC) was performed using Kanto Chemical silica gel 60 (spherical, 40–50 μm) or Biotage® SNAP Ultra. Analytical thin layer chromatography (TLC) was performed on Merck TLC silica gel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating.

Apparatus. Proton, carbon, and fluorine nuclear magnetic resonance spectra (^{1}H, ^{13}C, and ^{19}F NMR) were recorded on a JEOL ECS-400 (^{1}H NMR, 400 MHz; ^{13}C NMR 101 MHz; ^{19}F NMR 376 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CHCl_3$ at 7.26 ppm, C_6H_6 at 7.16 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm, C_6D_6 at 128.0 ppm; ^{19}F NMR, C_6F_6 at –162.0 ppm). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with Thermo Scientific Exactive (ESI or APCI) and JEOL JMX-SX102A (EI). Medium pressure liquid chromatography (MPLC) was performed with a Yamazen EPLC-W-Prep 2XY. Preparative recycling silica gel chromatography was performed on a Shimadzu Prominence chromatograph quipped with COSMOSIL 5SL-II (Nacalai Tesque, 20 mm x 250 mm, spherical, 5 μm). GC analysis was performed on a Shimadzu GC-2014 equipped with a BP1 column (SGE Analytical Science, 0.25 mm x 30 m, pressure = 149.0 kPa, detector = FID, 290 °C) with helium gas as a carrier. Chiral HPLC analyses were performed with a Shimadzu Prominence chromatograph. Optical rotations were measured on a HORIBA SEPA-200.

Chemicals. Unless otherwise noted, commercially available chemicals were used without purification. Alkenes (**1b**,[1b] **1c**,[1b] **1d**,[1a] **1e**,[1c] **1f**[1d]), HOMSi® reagents (**2a**,[2a] **2b**,[2b] **2c**,[2b] **2d**,[2c] **2e**,[2a] **2f**,[2d] **2g**–**2i**,[2a] **2j**,[2e] **2k**[2e]), allylic carbonates (**3a**,[3b] **3b**,[3d] **3c**,[3b] **3d**,[3d] **3e**,[3a] **3f**[3c]), (IPr)CuCl,[4] (SIPr)CuCl,[4] (IMes)CuCl,[4] and (SIMes)CuCl[4] were prepared according to the literature. Superdehydrated 1,4-dioxane was purchased from Wako Chemical and used as received.

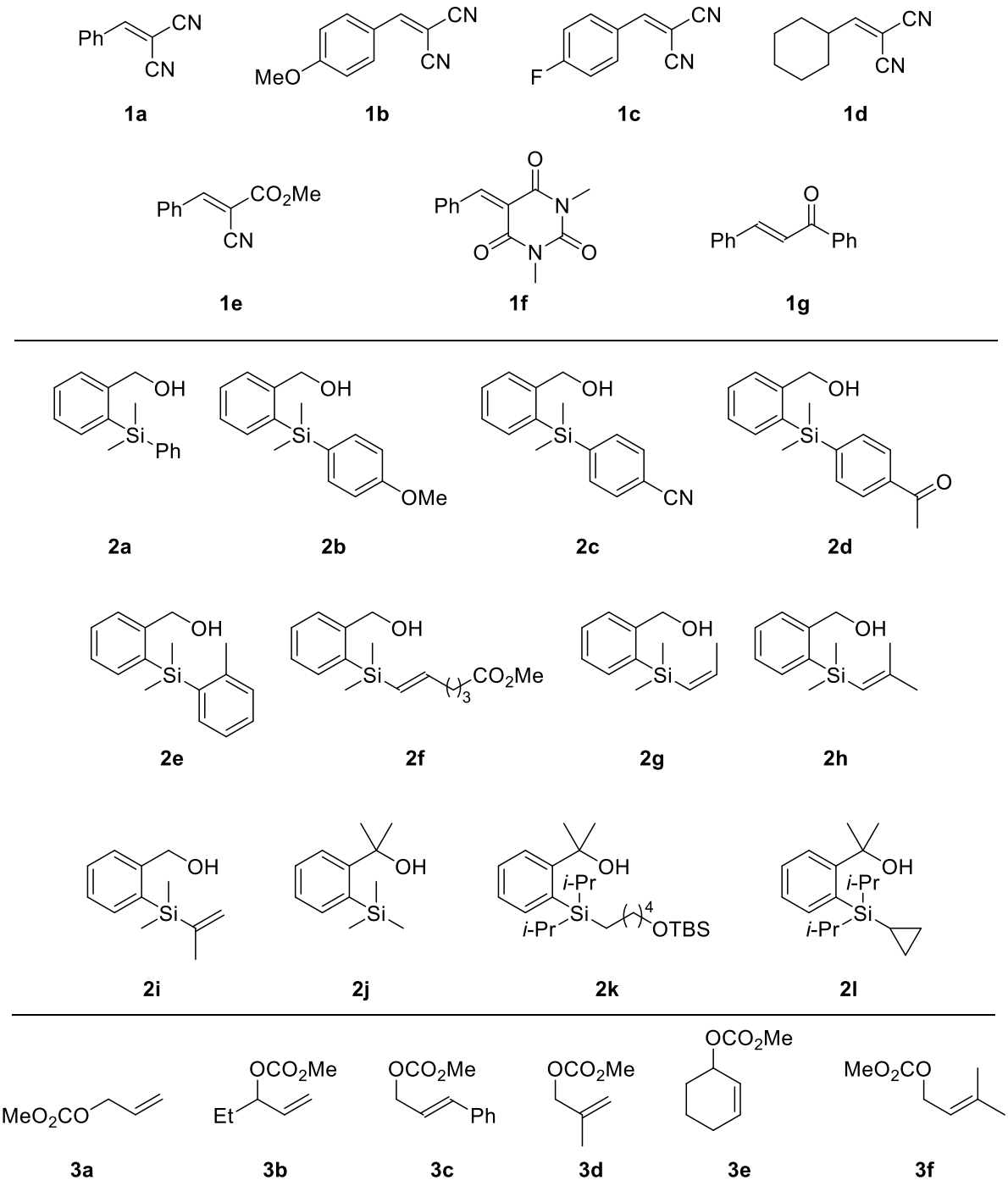
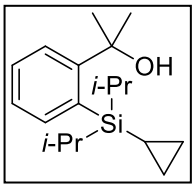
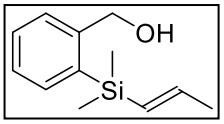


Figure S1. List of alkenes, HOMSi® reagents and allylic carbonates

Preparation of the substrate.

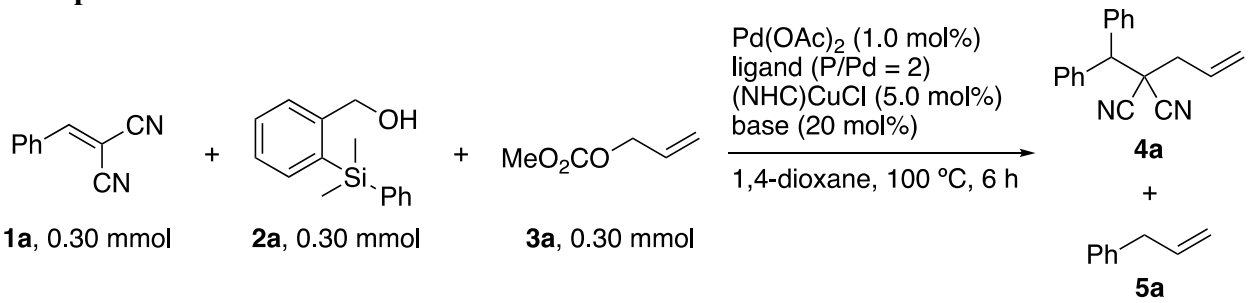


Preparation of 2l. Following the reported procedure,[2d] a 0.56 M solution of cyclopropyllithium in Et_2O (10 mL, 5.6 mmol) was added dropwise to a THF (5.0 mL) solution of 3,3-dimethyl-1,1-diisopropyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1.24 g, 5.0 mmol) at –78 °C, and the resulting mixture was stirred at –78 °C. After stirring for 1 h, the reaction mixture was quenched with a 2M HCl aqueous solution and saturated $NaHCO_3$ aqueous solution. The aqueous phase was extracted with Et_2O, and the combined organic phases were washed with brine, dried over anhydrous $MgSO_4$, and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane:ethyl acetate = 30:1) to give the title compound (1.07 g, 74%) as a light yellow solid (mp = 46.4–49.7 °C), R_f 0.50 (*n*-hexane:ethyl acetate = 20:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (d, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.24–7.17 (m, 2H), 2.21 (s, 1H), 1.61 (s, 6H), 1.34–1.21 (m, 2H), 1.02 (d, *J* = 7.3 Hz, 6H), 0.98 (d, *J* = 7.3 Hz, 6H), 0.82–0.75 (m, 2H), 0.51–0.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 154.9, 137.9, 132.0, 128.3, 125.6, 125.1, 74.1, 33.7, 19.9, 19.3, 12.6, 3.4, –4.8; HRMS [APCI(–)] calcd for $C_{18}H_{29}OSi$ [M–H]$^-$: 289.1993. Found: *m*/*z* 289.1994.



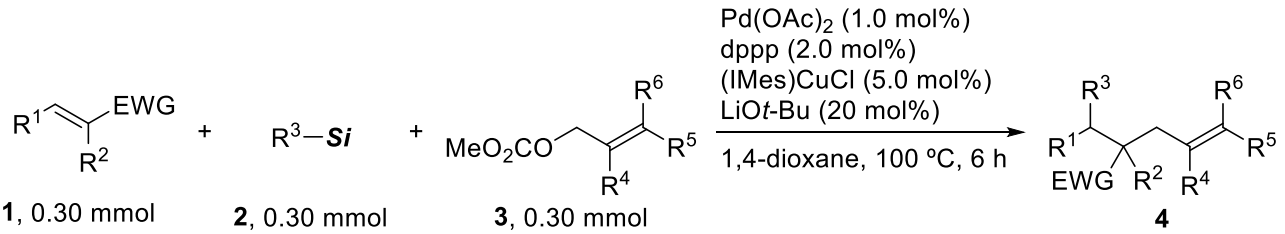
Preparation of (*E*)-2-(hydroxymethyl)phenyl]dimethyl(propen-1-yl)silane. Following the reported procedure,[2a] a solution of (*E*)-propen-1-ylmagnesium bromide in THF (8.0 mL) [prepared from (*E*)-1-bromo-1-propene (0.69 g, 5.7 mmol) and Mg (0.17 g, 6.9 mmol)] was added to a THF (3.0 mL) solution of 1,1-dimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (0.67 g, 4.1 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with a saturated NH_4Cl aqueous solution and the organic layer washed with a brine and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel to give the title compound (0.20 g, 24%, *E*:*Z* = 81:19 as estimated by ^{1}H NMR analysis) as a colorless oil, R_f 0.26 (*n*-hexane:ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, *J* = 6.9 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.40 (dt, *J* = 1.2 Hz, 7.5 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 6.17 (dq, *J* = 6.1 Hz, 19 Hz, 1H), 5.87 (dd, *J* = 1.6 Hz, 19 Hz, 1H), 4.74 (s, 2H), 1.86 (dd, *J* = 1.6 Hz, 6.2 Hz, 3H), 0.39 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 146.4, 144.2, 137.0, 135.1, 130.2, 129.6, 128.0, 127.0, 65.4, 22.7, –1.3; Anal. Calcd for $C_{12}H_{18}OSi$; C, 69.84; H, 8.79. Found: C, 69.64; H, 8.85.

General procedures for Table 1.



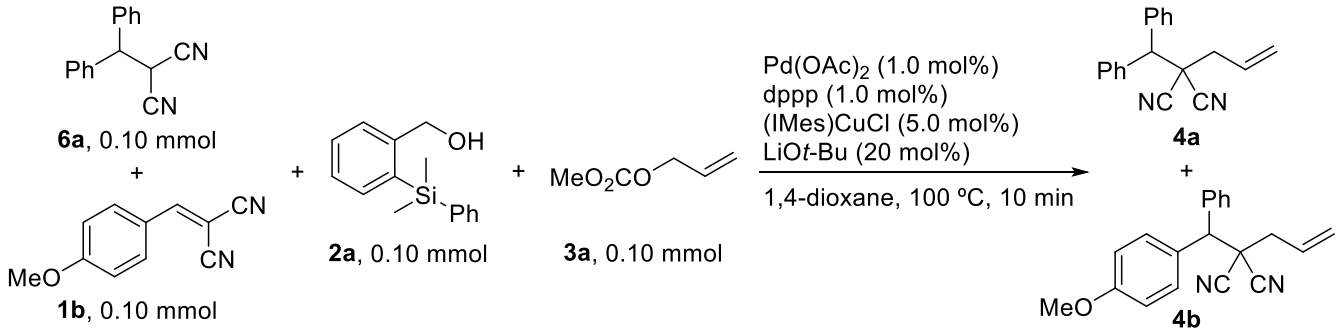
In the air, a vial (Vial **A**) was charged with (NHC)CuCl (15 μmol). A vial (Vial **B**) was charged with **1a** (46 mg, 0.30 mmol) and **2a** (73 mg, 0.30 mmol). A vial (Vial **C**) was charged with $Pd(OAc)_2$ (0.7 mg, 3.0 μmol) and phosphine ligand (P/Pd = 2). These vials were transferred into a glove box. In the glove box, base (60 μmol) and *n*-tridecane (50 μL) were added to Vial **A**. 1.95 mL of 1,4-dioxane was added into Vial **B** and 0.60 mL of 1,4-dioxane was added into Vial **C**. **3a** (35 mg, 0.30 mmol) was added to Vial **C**. Then, the solution in Vial **B** and **C** were added to Vial **A**. The resulting mixture was stirred for 6 h at 100 ºC. After the reaction, the yield of **4a** and **5a** were determined by GC with *n*-tridecane as an internal standard.

General procedures for Tables 2 and 3.



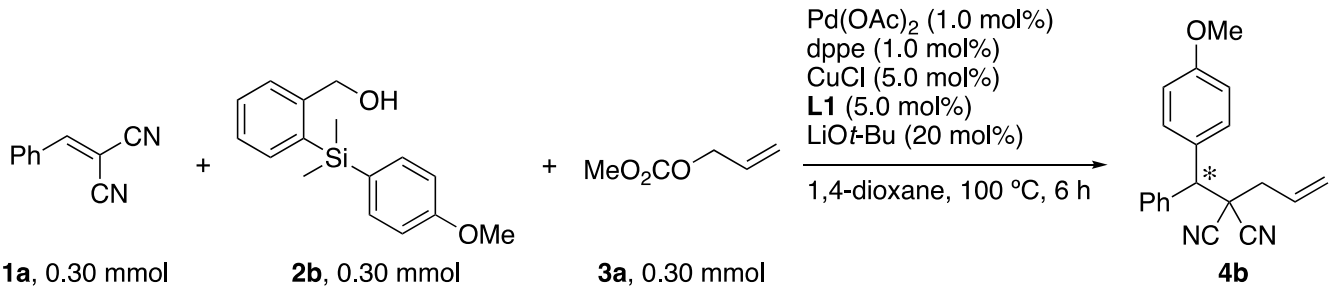
In the air, a vial (Vial **A**) was charged with (IMes)CuCl (20 mg, 50 μmol). A vial (Vial **B**) was charged with alkene (1.0 mmol) and HOMSi® reagent (1.0 mmol). A vial (Vial **C**) was charged with $Pd(OAc)_2$ (2.3 mg, 10 μmol) and dppp (4.1 mg, 10 μmol). These vials were transferred into a glove box. In the glove box, LiO*t*-Bu in 1.0 M THF solution (200 μL, 0.20 mmol) was added to Vial **A**. 6.5 mL of 1,4-dioxane was added into Vial **B** and 2.0 mL of 1,4-dioxane was added into Vial **C**. Allylic carbonate (1.0 mmol) was added to Vial **C**. Then, the solution in Vial **B** and **C** were added to Vial **A**. The resulting mixture was stirred for 6 h at 100 ºC. After the reaction, the mixture was filtered through a short pad of silica gel and Celite®, and all of the volatiles were removed in *vacuo*. The product was purified by MPLC on silica gel to give the corresponding products.

Procedures for Eq. 4.



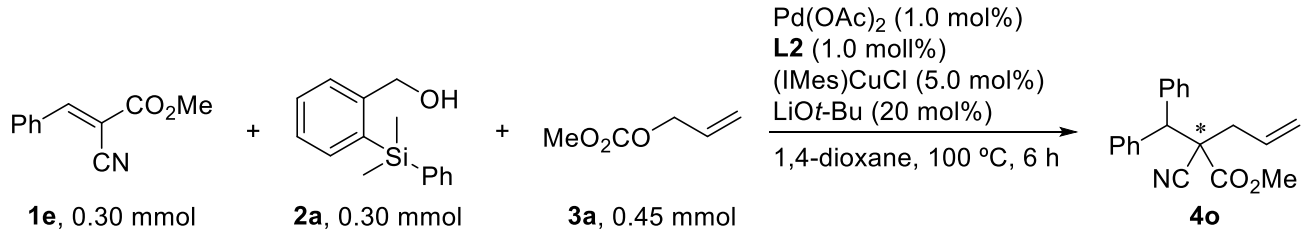
In the air, a vial (Vial **A**) was charged with (IMes)CuCl (2.0 mg, 5.0 μmol). A vial (Vial **B**) was charged with **1b** (18.4 mg, 0.10 mmol), **2a** (24 mg, 0.10 mmol) and 1,1-dicyano-2,2-diphenylethane (**6a**) (24 mg, 0.10 mmol). A vial (Vial **C**) was charged with $Pd(OAc)_2$ (0.2 mg, 1.0 μmol) and dppp (0.4 mg, 1.0 μmol). These vials were transferred into a glove box. In the glove box, LiO*t*-Bu in 1.0 M THF solution (20 μL, 20 μmol) and *n*-tridecane (30 μL) were added to Vial **A**. 0.65 mL of 1,4-dioxane was added into Vial **B** and 0.20 mL of 1,4-dioxane was added into Vial **C**. **3a** (11.6 mg, 0.10 mmol) was added to Vial **C**. Then, the solution in Vial **B** and **C** were added to Vial **A**. The resulting mixture was stirred for 10 min at 100 ºC. After the reaction, the yields of **4a** and **4b** were determined by GC with *n*-tridecane as an internal standard.

Procedures for Eq. 5.



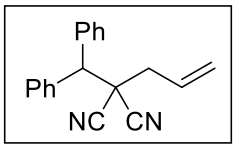
In the air, a vial (Vial **A**) was charged with **1a** (46 mg, 0.30 mmol) and **2b** (82 mg, 0.30 mmol). A vial (Vial **B**) was charged with $Pd(OAc)_2$ (0.7 mg, 3.0 μmol) and dppp (1.2 mg, 3.0 μmol). These vials were transferred into a glove box. In the glove box, CuCl (1.5 mg, 15 μmol), **L1** (10.5 mg, 15 μmol) in 1,4-dioxane (0.50 mL) and LiO*t*-Bu in 1.0 M THF solution (60 μl, 60 μmol) were added to a vial (Vial **C**). 1.45 mL of 1,4-dioxane was added into Vial **A** and 0.60 mL of 1,4-dioxane was added into Vial **B**. **3a** (35 mg, 0.30 mmol) was added to Vial **B**. Then, the solution in Vial **A** and **B** were added to Vial **C**. The resulting mixture was stirred for 6 h at 100 ºC. After the reaction, the mixture was filtered through a short pad of silica gel and Celite®, and all of the volatiles were removed in *vacuo*. The product was purified by MPLC on silica gel to give **4b** (17.2 mg, 57 μmol, 19%).

Procedures for Eq. 6.

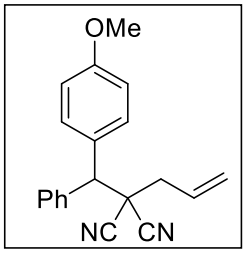


In the air, a vial (Vial **A**) was charged with (IMes)CuCl (6.1 mg, 15 μmol). A vial (Vial **B**) was charged with **1a** (46 mg, 0.30 mmol) and **2a** (73 mg, 0.30 mmol). A vial (Vial **C**) was charged with $Pd(OAc)_2$ (0.7 mg, 3.0 μmol). These vials were transferred into a glove box. In the glove box, LiO*t*-Bu in 1.0 M THF solution (60 μL, 60 μmol) was added to Vial **A**. **L2** (2.1 mg, 3.0 μmol) was added to the Vial **C**. 1.95 mL of 1,4-dioxane was added into Vial **B** and 0.60 mL of 1,4-dioxane was added into Vial **C**. **3a** (52 mg, 0.45 mmol) was added to Vial **C**. Then, the solution in Vial **B** and **C** were added to Vial **A**. The resulting mixture was stirred for 6 h at 100 ºC. After the reaction, the mixture was filtered through a short pad of silica gel and Celite®, and all of the volatiles were removed in *vacuo*. The product was purified by MPLC on silica gel to give **4n** (74 mg, 0.24 mmol, 81%).

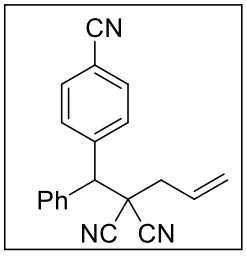
Characterization of the products



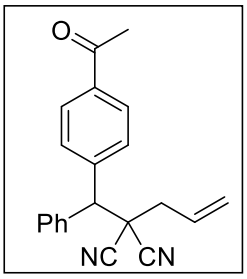
2,2-dicyano-1,1-diphenyl-4-pentene (4a). The reaction of **1a** (154 mg, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 96:4 to 84:16) gave the title compound (0.25 g, 0.92 mmol, 92%) as white solid (mp 88.9 °C), R_f 0.43 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, *J* = 7.4 Hz, 4H), 7.47–7.33 (m, 6H), 6.05–5.92 (m, 1H), 5.45 (d, *J* = 10.0 Hz, 1H), 5.35 (dd, *J* = 1.3 Hz, 16.8 Hz, 1H), 4.34 (s, 1H), 2.70 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 136.6, 129.0, 128.8, 128.4, 123.3, 115.0, 56.4, 42.4, 41.4, a signal for sp^2-carbon overlap with others; All the resonances of ^{1}H NMR spectrum were consist with reported values.[5] HRMS [APCI(+)] calcd for $C_{19}H_{17}N_2$ $[M+H]^+$: 273.1386. Found: *m*/*z* 273.1380.



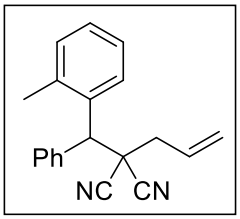
2,2-dicyano-1-phenyl-1-(4-methoxyphenyl)-4-pentene (4b). The reaction of **1a** (154 mg, 1.0 mmol), **2b** (0.27 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 94:6 to 76:24) gave the title compound (191 mg, 0.63 mmol, 63%) as light yellow solid (mp 67.4 °C), R_f 0.43 (*n*-hexane:ethyl acetate = 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.38–7.28 (m, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.05–5.90 (m, 1H), 5.44 (d, *J* = 10.1 Hz, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 4.30 (s, 1H), 3.80 (s, 3H), 2.68 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.5, 137.0, 130.0, 129.0, 128.6, 128.53, 128.49, 128.3, 123.2, 115.1, 114.3, 55.7, 55.1, 42.7, 41.3; HRMS [APCI(+)] calcd for $C_{20}H_{19}N_2O$ $[M+H]^+$: 303.1492. Found: *m*/*z* 303.1481.



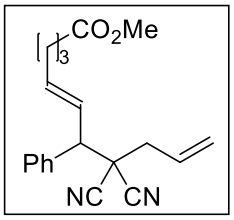
2,2-dicyano-1-phenyl-1-(4-cyanophenyl)-4-pentene (4c). The reaction of **1a** (77 mg, 0.50 mmol), **2c** (134 mg, 0.50 mmol) and **3a** (58 mg, 0.50 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 92:8 to 68:32) gave the title compound (59 mg, 0.20 mmol, 40%) as colorless oil, R_f 0.46 (*n*-hexane:ethyl acetate = 5:2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73–7.64 (m, 4H), 7.53–7.46 (m, 2H), 7.46–7.35 (m, 3H), 6.00–5.86 (m, 1H), 5.46 (d, *J* = 10.1 Hz, 1H), 5.33 (d, *J* = 16.9 Hz, 1H), 4.34 (s, 1H), 2.68 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.9, 135.0, 132.8, 129.6, 129.5, 129.1, 128.8, 127.9, 123.9, 118.0, 114.6, 114.5, 112.6, 56.1, 41.9, 41.2; HRMS [APCI(+)] calcd for $C_{20}H_{16}N_3$ $[M+H]^+$: 298.1339. Found: *m*/*z* 298.1337.



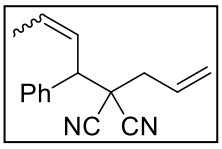
2,2-dicyano-1-phenyl-1-(4-acetylphenyl)-4-pentene (4d). The reaction of **1a** (77 mg, 0.50 mmol), **2d** (142 mg, 0.50 mmol) and **3a** (58 mg, 0.50 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 92:8 to 68:32) gave the title compound (57 mg, 0.18 mmol, 36%) as yellow oil, R_f 0.19 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 6.9 Hz, 2H), 7.45–7.33 (m, 3H), 6.01–5.88 (m, 1H), 5.45 (d, *J* = 10.1 Hz, 1H), 5.33 (dd, *J* = 1.1 Hz, 16.7 Hz, 1H), 4.36 (s, 1H), 2.68 (d, *J* = 7.3 Hz, 2H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 197.2, 141.7, 137.0, 135.7, 129.3, 129.14, 129.07, 128.9, 128.2, 123.8, 114.8, 114.7, 56.3, 42.1, 41.4, 26.6; HRMS [APCI(+)] calcd for $C_{21}H_{18}N_2O$ $[M+H]^+$: 315.1492. Found: *m*/*z* 315.1498..



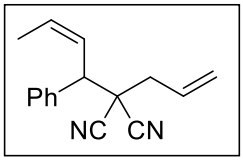
2,2-dicyano-1-phenyl-1-(2-methylphenyl)-4-pentene (4e). The reaction of **1a** (154 mg, 1.0 mmol), **2e** (0.26 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) using dppe (1,2-Bis(diphenylphosphino)ethane) as a ligand followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 100:0 to 94:6) gave the title compound (0.21 g, 0.72 mmol, 72%) as white solid (mp 83.0 °C), R_f 0.57 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.48–7.44 (m, 2H), 7.40–7.30 (m, 4H), 7.24 (dd, *J* = 0.9 Hz, 7.3 Hz, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.01–5.89 (m, 1H), 5.43 (d, *J* = 9.6 Hz, 1H), 5.29 (dd, *J* = 0.9 Hz, 16.9 Hz, 1H), 4.52 (s, 1H), 2.79 (dd, *J* = 7.6 Hz, 14.0 Hz, 1H), 2.73 (dd, *J* = 7.1 Hz, 14.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 136.6, 135.6, 131.7, 129.9, 129.1, 128.71, 128.66, 128.3, 126.9, 126.6, 123.6, 115.5, 115.3, 51.7, 42.7, 41.5, 20.1; HRMS [APCI(+)] calcd for $C_{20}H_{19}N_2$ $[M+H]^+$: 287.1543. Found: *m*/*z* 287.1536.



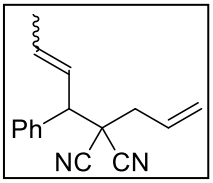
methyl (*E*)-8,8-dicyano-7-phenylundeca-5,10-dienoate (4f). The reaction of **1a** (77 mg, 0.50 mmol), **2f** (146 mg, 0.50 mmol) and **3a** (58 mg, 0.50 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 95:5 to 80:20) gave the title compound (77 mg, 0.24 mmol, 48%) as light yellow oil, R_f 0.33 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44–7.33 (m, 5H), 5.99–5.84 (m, 2H), 5.79 (dt, *J* = 7.2 Hz, 15.5 Hz, 1H), 5.41 (d, *J* = 10.1 Hz, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 3.65 (s, 3H), 3.61 (d, *J* = 9.4 Hz, 1H), 2.61 (dd, *J* = 7.1, 13.8 Hz, 1H), 2.48 (dd, *J* = 7.1, 13.8 Hz, 1H), 2.32 (t, *J* = 7.4 Hz, 2H), 2.18 (q, *J* = 7.2 Hz, 2H), 1.75 (quintet, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.6, 137.0, 136.1, 129.0, 128.7, 128.6, 128.4, 125.4, 123.0, 114.7, 114.3, 54.3, 51.4, 43.6, 40.2, 33.1, 31.7, 23.9; HRMS [APCI(+)] calcd for $C_{20}H_{23}N_2O_2$ $[M+H]^+$: 323.1754. Found: *m*/*z* 323.1743.



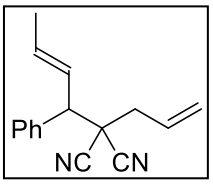
4,4-dicyano-5-phenyl-oct-1,6-diene (4g). The reaction of **1a** (77 mg, 0.50 mmol), **2g** (103 mg, 0.50 mmol) and **3a** (58 mg, 0.50 mmol) using dppe as a ligand followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 99:1 to 96:4) gave the title compound (79 mg, 0.34 mmol, 67%, *E*:*Z* = 4:96) as colorless oil, R_f 0.24 (*n*-hexane:ethyl acetate = 98:2). The ratio of *E*/*Z* isomers was determined by ^{1}H NMR analysis.



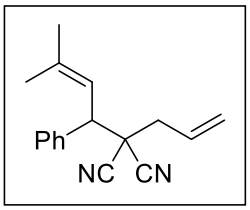
(*Z*)-4,4-dicyano-5-phenyl-oct-1,6-diene. Purification by HPLC (*n*-hexane:ethyl acetate = 10:1) gave the title compound as colorless oil, R_f 0.24 (*n*-hexane:ethyl acetate = 98:2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48–7.32 (m, 5H), 6.05–5.84 (m, 3H), 5.42 (d, *J* = 10.1 Hz, 1H), 5.37 (dd, *J* = 1.4 Hz, 16.9 Hz, 1H), 4.01 (d, *J* = 10.1 Hz, 1H), 2.68 (dd, *J* = 6.9 Hz, 13.7 Hz, 1H), 2.53 (dd, *J* = 7.3 Hz, 14.2 Hz, 1H), 1.70 (dd, *J* = 1.4 Hz, 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 136.5, 130.6, 129.1, 128.8, 128.75, 128.66, 125.1, 123.1, 114.7, 114.5, 48.3, 43.8, 40.4, 13.5; HRMS [EI(+)] calcd for $C_{16}H_{16}N_2$ $[M]^+$: 236.1313. Found: *m*/*z* 236.1306. The (*Z*)-configuration was determined by NOE experiments.



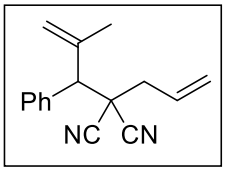
4,4-dicyano-5-phenyl-oct-1,6-diene. The reaction of **1a** (77 mg, 0.50 mmol), (*E*)-2-(hydroxymethyl)phenyl]dimethyl(propen-1-yl)silane (103 mg, 0.50 mmol) and **3a** (58 mg, 0.50 mmol) using dppe as a ligand followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 99:1 to 96:4) gave the title compound (46 mg, 0.19 mmol, 39%, *E*:*Z* = 66:34) as colorless oil, R_f 0.24 (*n*-hexane:ethyl acetate = 98:2). The ratio of *E*/*Z* isomers was determined by ^{1}H NMR analysis.



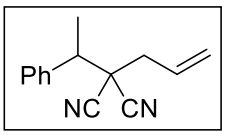
(*E*)-4,4-dicyano-5-phenyl-oct-1,6-diene. Purification by HPLC (*n*-hexane:ethyl acetate = 10:1) gave the title compound as colorless oil, R_f 0.24 (*n*-hexane:ethyl acetate = 98:2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44–7.32 (m, 5H), 5.98–5.87 (m, 2H), 5.82 (dq, *J* = 6.4 Hz, 15.1 Hz, 1H), 5.41 (d, *J* = 10.1 Hz, 1H), 5.35 (d, *J* = 16.9 Hz, 1H), 3.60 (d, *J* = 9.2 Hz, 1H), 2.62 (dd, *J* = 7.1 Hz, 14.0 Hz, 1H), 2.48 (dd, *J* = 7.3 Hz, 14.2 Hz, 1H), 1.79 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 136.5, 133.2, 129.1, 128.8, 128.7, 128.5, 125.7, 123.0, 114.9, 114.5, 54.6, 43.7, 40.5, 18.1; HRMS [APCI(+)] calcd for $C_{16}H_{17}N_2$ $[M+H]^+$: 237.1386. Found: *m*/*z* 237.1390. The (*E*)-configuration was determined by a coupling constant of a vinylic proton and NOE experiments.



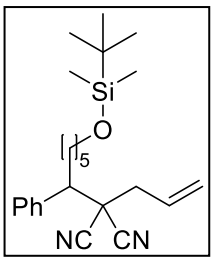
5,5-dicyano-2-methyl-4-phenyl-oct-2,7-diene (4h). The reaction of **1a** (154 mg, 1.0 mmol), **2h** (0.22 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 98:2 to 92:8) gave the title compound (0.20 g, 0.81 mmol, 81%) as white solid (mp 81.5 °C), R_f 0.65 (*n*-hexane:ethyl acetate = 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44–7.32 (m, 5H), 5.98–5.86 (m, 1H), 5.72 (d, *J* = 10.1 Hz, 1H), 5.41 (d, *J* = 10.1 Hz, 1H), 5.35 (d, *J* = 16.8 Hz, 1H), 3.89 (d, *J* = 10.1 Hz, 1H), 2.65 (dd, *J* = 7.1 Hz, 13.8 Hz, 1H), 2.50 (dd, *J* = 7.4 Hz, 14.1Hz, 1H), 1.84 (s, 3H), 1.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.9, 136.9, 128.8, 128.4, 128.3, 122.7, 119.3, 114.7, 114.5, 49.4, 43.8, 40.2, 25.9, 18.4; HRMS [APCI(+)] calcd for $C_{17}H_{19}N_2$ $[M+H]^+$: 251.1543. Found: *m*/*z* 251.1537.



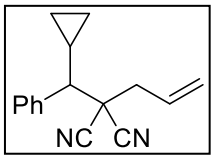
4,4-dicyano-2-methyl-3-phenyl-hept-1,6-diene (4i). The reaction of **1a** (154 mg, 1.0 mmol), **2i** (0.21 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 98:2 to 92:8) gave the title compound (159 mg, 0.67 mmol, 67%) as pale yellow oil, R_f 0.63 (*n*-hexane:ethyl acetate = 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46–7.35 (m, 5H), 6.00–5.87 (m, 1H), 5.55 (s, 1H), 5.43 (d, *J* = 10.1 Hz, 1H), 5.35 (d, *J* = 16.8 Hz, 1H), 5.30 (s 1H), 3.56 (s 1H), 2.65 (dd, *J* = 7.4 Hz, 14.1 Hz, 1H), 2.58 (dd, *J* = 7.1 Hz, 13.8 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 140.9, 134.3, 129.2, 128.90, 128.86, 128.5, 123.2, 115.1, 114.8, 114.7, 56.8, 41.4, 40.5, 23.1; HRMS [APCI(+)] calcd for $C_{16}H_{17}N_2$ $[M+H]^+$: 237.1386. Found: *m*/*z* 237.1382.



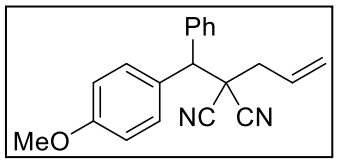
3,3-dicyano-2-phenyl-5-hexene (4j). The reaction of **1a** (154 mg, 1.0 mmol), **2j** (0.21 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 99:1 to 96:4) gave the title compound (116 mg, 0.55 mmol, 55%) as yellow oil, R_f 0.59 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43–7.34 (m, 5H), 5.97–5.83 (m, 1H), 5.40 (dd, *J* = 0.9 Hz, 10.1 Hz, 1H), 5.34 (dd, *J* = 0.9 Hz, 16.9 Hz, 1H), 3.21 (q, *J* = 7.0 Hz, 1H), 2.54 (dd, *J* = 7.3 Hz, 13.7 Hz, 1H), 2.43 (dd, *J* = 7.1 Hz, 14.0 Hz, 1H), 1.71 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 137.5, 129.1, 129.00, 128.97, 128.5, 123.1, 115.3, 114.6, 45.8, 44.2, 40.4, 17.8; All the resonances of ^{1}H NMR spectrum were consist with reported values.[5] HRMS [APCI(+)] calcd for $C_{14}H_{15}N_2$ $[M+H]^+$: 211.1230. Found: *m*/*z* 211.1224.



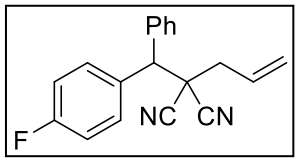
2-allyl-2-(6-((tert-butyldimethylsilyl)oxy)-1-phenylhexyl)malononitrile (4k). The reaction of **1a** (154 mg, 1.0 mmol), **2k** (0.45 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 97:3 to 88:12) gave the title compound (0.30 g, 0.76 mmol, 76%) as colorless oil, R_f 0.77 (*n*-hexane:ethyl acetate = 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43–7.36 (m, 3H), 7.36–7.30 (m, 2H), 5.94–5.81 (m, 1H), 5.38 (d, *J* = 10.1 Hz, 1H), 5.30 (d, *J* = 16.8 Hz, 1H), 3.53 (t, *J* = 6.0 Hz, 2H), 2.98 (t, *J* = 7.7 Hz, 1H), 2.47 (dd, *J* = 7.4 Hz, 13.4 Hz, 1H), 2.35 (dd, *J* = 6.7 Hz, 14.1 Hz, 1H), 2.15 (d, *J* = 8.1 Hz, 1H), 2.11 (d, *J* = 8.1 Hz, 1H), 1.49–1.21 (m, 4H), 1.21–1.09 (m, 2H), 0.87 (s, 9H), 0.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 135.4, 128.9, 128.8, 128.6, 122.7, 115.3, 114.4, 62.6, 51.1, 43.4, 40.2, 32.2, 31.5, 26.7, 25.8, 25.2, 18.1, –5.5; HRMS [APCI(+)] calcd for $C_{24}H_{37}N_2OSi$ $[M+H]^+$: 397.2670. Found: *m*/*z* 397.2663.



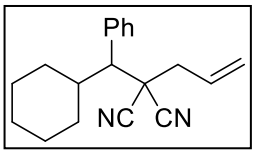
2,2-dicyano-1-cyclopropyl-1-phenyl-4-pentene (4l). The reaction of **1a** (154 mg, 1.0 mmol), **2l** (0.29 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 97:3 to 88:12) gave the title compound (162 mg, 0.69 mmol, 69%) as yellow oil, R_f 0.56 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45–7.33 (m, 5H), 5.98–5.83 (m, 1H), 5.40 (d, *J* = 10.8 Hz, 1H), 5.33 (d, *J* = 16.8 Hz, 1H), 2.63 (dd, *J* = 7.4 Hz, 13.4 Hz, 1H), 2.50 (dd, *J* = 7.1 Hz, 13.8 Hz, 1H), 2.27 (d, *J* = 10.8 Hz, 1H), 1.60–1.48 (m, 1H), 1.08–0.97 (m, 1H), 0.77–0.67 (m, 1H), 0.65–0.54 (m, 1H), 0.16–0.06 (m, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 137.0, 128.8, 128.7, 128.6, 128.5, 122.8, 115.1, 114.6, 55.6, 43.8, 40.5, 13.4, 8.5, 3.3. HRMS [APCI(+)] calcd for $C_{16}H_{17}N_2$ $[M+H]^+$: 237.1386. Found: *m*/*z* 237.1382.



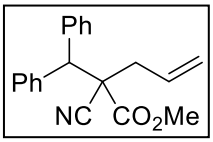
2,2-dicyano-1-phenyl-1-(4-methoxyphenyl)-4-pentene (4b). The reaction of **1b** (92 mg, 0.50 mmol), **2a** (121 mg, 0.50 mmol) and **3a** (58 mg, 0.50 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 94:6 to 76:24) gave the title compound (97 mg, 0.32 mmol, 64%) as white solid, R_f 0.43 (*n*-hexane:ethyl acetate = 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.36–7.30 (m, 1H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.01–5.88 (m, 1H), 5.43 (d, *J* = 10.1 Hz, 1H), 5.32 (d, *J* = 16.9 Hz, 1H), 4.24 (s, 1H), 3.80 (s, 3H), 2.66 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.6, 137.0, 130.1, 129.1, 128.72, 128.66, 128.6, 128.4, 123.4, 115.1, 114.5, 56.0, 55.3, 42.8, 41.5.; HRMS [APCI(+)] calcd for $C_{20}H_{19}N_2O$ $[M+H]^+$: 303.1492. Found: *m*/*z* 303.1480.



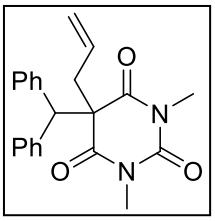
2,2-dicyano-1-phenyl-1-(4-fluorophenyl)-4-pentene (4m). The reaction of **1c** (172 mg, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 96:4 to 84:16) gave the title compound (0.21 g, 0.73 mmol, 73%) as pale yellow oil, R_f 0.38 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56–7.49 (m, 4H), 7.44–7.33 (m, 3H), 7.12–7.05 (m, 2H), 6.00–5.88 (m, 1H), 5.44 (d, *J* = 10.1 Hz, 1H), 5.32 (d, *J* = 16.1 Hz, 1H), 4.28 (s 1H), 2.66 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.4 (d, *J* = 249 Hz), 136.3, 132.5 (d, *J* = 3.8 Hz), 130.6 (d, *J* = 8.6 Hz), 129.1, 128.61, 128.55, 128.3, 123.4, 116.0 (d, *J* = 22 Hz), 114.9, 114.8, 55.5, 42.5, 41.2; ^{19}F NMR ($CDCl_3$, 376 MHz): δ –113.2. HRMS [EI(+)] calcd for $C_{19}H_{15}FN_2$ $[M]^+$: 290.1214. Found: *m*/*z* 290.1218.



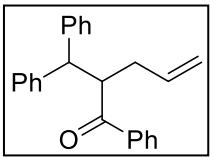
2,2-dicyano-1-cyclohexyl-1-phenyl-4-pentene (4n). The reaction of **1d** (160 mg, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 98:2 to 92:8) gave the title compound (145 mg, 0.52 mmol, 52%) as white solid (mp 60.1 °C), R_f 0.80 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42–7.23 (m, 5H), 5.92–5.78 (m, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.22 (d, *J* = 16.8 Hz, 1H), 2.83 (d, *J* = 8.1 Hz, 1H), 2.35–2.07 (m, 4H), 1.90–1.81 (m, 1H), 1.70–1.56 (m, 3H), 1.44–1.31 (m, 1H), 1.31–1.03 (m, 3H), 0.97–0.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 136.4, 129.0, 128.8, 128.4, 122.9, 116.3, 115.1, 57.3, 42.1, 42.0, 39.7, 32.4, 30.9, 26.2, 26.0, 25.8; All the resonances of ^{1}H NMR spectrum were consist with reported values.[5] HRMS [APCI(+)] calcd for $C_{19}H_{23}N_2$ $[M+H]^+$: 279.1856. Found: *m*/*z* 279.1850.



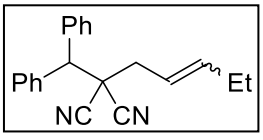
methyl 2-cyano-2-(diphenylmethyl)pent-4-enoate (4o). The reaction of **1e** (187 mg, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 96:4 to 84:16) gave the title compound (0.21 g, 0.70 mmol, 70%) as white solid (mp 86.5 °C), R_f 0.27 (*n*-hexane:ethyl acetate = 9:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.33–7.20 (m, 4H), 5.84–5.69 (m, 1H), 5.21–5.12 (m, 2H), 4.41 (s, 1H), 3.59 (s, 3H), 2.65 (dd, *J* = 8.2 Hz, 13.7 Hz, 1H), 2.50 (dd, *J* = 6.2 Hz, 13.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.6, 139.0, 137.8, 130.4, 129.5, 128.8, 128.7, 128.3, 127.9, 127.6, 120.8, 118.6, 57.0, 54.7, 53.1, 42.1; HRMS [APCI(+)] calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1489. Found: *m*/*z* 306.1488.



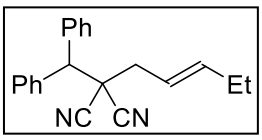
5-allyl-1,3-dimethyl-5-(diphenylmethyl)pyrimidine-2,4,6(1H,3H,5H)-trione (4p). The reaction of **1f** (0.24 g, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 96:4 to 84:16) gave the title compound (151 mg, 0.42 mmol, 42%) as white solid (mp 146.2 °C), R_f 0.52 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41–7.36 (m, 4H), 7.32–7.22 (m, 6H), 5.51–5.39 (m, 1H), 5.05 (dd, *J* = 1.4 Hz, 16.9 Hz, 1H), 4.99 (dd, *J* = 1.6 Hz, 10.3 Hz, 1H), 4.56 (s, 1H), 3.12 (s, 6H), 2.71 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.7, 150.2, 137.9, 131.2, 129.4, 128.3, 127.7, 120.5, 61.7, 61.2, 41.0, 28.2; HRMS [APCI(+)] calcd for $C_{22}H_{23}N_2O_3$ $[M+H]^+$: 363.1703. Found: *m*/*z* 363.1693.



1-phenyl-2-diphenylmethyl-4-pentene-1-one (4q). The reaction of **1g** (0.21 g, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3a** (116 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 99:1 to 96:4) and preparative recycling HPLC (*n*-hexane:ethyl acetate = 95:5) gave the title compound (21 mg, 0.064 mmol, 6%) as white solid (mp 97.1 °C), R_f 0.64 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86–7.76 (m, 2H), 7.53–7.45 (m, 1H), 7.43–7.28 (m, 6H), 7.25–7.17 (m, 3H) 7.11–7.02 (m, 2H), 7.01–6.93 (m, 1H), 5.68–5.54 (m, 1H), 4.91–4.82 (m, 2H), 4.54–4.45 (m, 1H), 4.41 (d, *J* =11.5 Hz, 1H), 2.49–2.28 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 203.1, 142.8, 142.5, 138.3, 134.6, 132.7, 128.7, 128.4, 128.3, 128.0, 127.8, 126.6, 126.2, 117.3, 53.7, 50.1, 36.4, a signal for sp^2-carbon overlap with others; HRMS [APCI(+)] calcd for $C_{24}H_{23}O$ $[M+H]^+$: 327.1743. Found: *m*/*z* 327.1727.

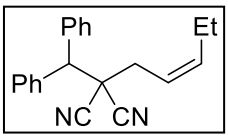


2,2-dicyano-1,1-diphenyl-4-heptene (4r). The reaction of **1a** (154 mg, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3b** (144 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 96:4 to 84:16) gave the title compound (0.21 g, 0.69 mmol, 69%, *E*:*Z* = 91:9) as colorless oil, R_f 0.48 (*n*-hexane:ethyl acetate = 5:1). The ratio of *E*/*Z* isomers was determined by ^{1}H NMR analysis.

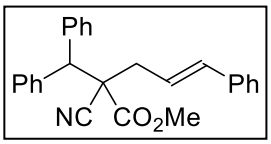


***trans*-2,2-dicyano-1,1-diphenyl-4-heptene.** Purification by HPLC (*n*-hexane:ethyl acetate = 8:1) gave the title compound as colorless oil, R_f 0.48 (*n*-

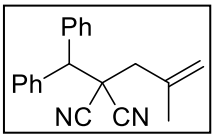
hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, *J* = 7.8 Hz, 4H), 7.44–7.30 (m, 6H), 5.75 (dt, *J* = 6.0 Hz, 15.6 Hz, 1H), 5.54 (dt, *J* = 7.3 Hz, 15.1 Hz, 1H), 4.27 (s, 1H), 2.61 (d, *J* = 6.9 Hz, 2H), 2.12 (quint, *J* = 7.1 Hz, 2H), 1.02 (t, *J* =7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.7, 136.8, 129.07, 128.88, 128.4, 118.8, 115.3, 56.5, 43.0, 40.6, 25.6, 13.3.; HRMS [APCI(+)] calcd for $C_{21}H_{21}N_2$ $[M+H]^+$: 301.1699. Found: *m*/*z* 301.1694.



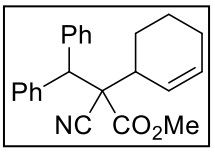
***cis*-2,2-dicyano-1,1-diphenyl-4-heptene.** Purification by HPLC (*n*-hexane:ethyl acetate = 8:1) gave the title compound as colorless oil, R_f 0.48 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, *J* = 7.8 Hz, 4H), 7.43–7.30 (m, 6H), 5.80 (dt, *J* = 7.8 Hz, 10.1 Hz, 1H), 5.53 (dt, *J* = 8.0 Hz, 9.2 Hz, 1H), 4.30 (s, 1H), 2.71 (d, *J* = 7.3 Hz, 2H), 1.92 (quint, *J* = 7.4 Hz, 2H), 0.95 (t, *J* =7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.7, 136.8, 129.10, 128.86, 128.5, 118.5, 115.3, 56.4, 42.6, 35.2, 21.0, 13.8.; HRMS [APCI(+)] calcd for $C_{21}H_{21}N_2$ $[M+H]^+$: 301.1699. Found: *m*/*z* 301.1693.



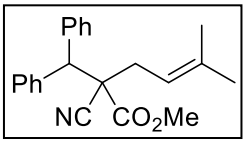
***trans*-2-cyano-2-methoxycarbonyl-1,1,5-triphenyl-4-pentene (4s).** The reaction of **1e** (187 mg, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3c** (192 mg, 1.0 mmol) using dppe as a ligand followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 96:4 to 84:16) gave the title compound (0.26 g, 0.67 mmol, 67%) as white solid (mp 120.7 °C), R_f 0.45 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.34–7.27 (m, 7H), 7.26–7.19 (m, 2H), 6.46 (d, *J* = 16.1 Hz, 1H), 6.19–6.08 (m, 1H), 4.49 (s, 1H), 3.53 (s, 3H), 2.81 (dd, *J* = 8.7 Hz, 13.4 Hz, 1H), 2.67 (dd, *J* = 6.4 Hz, 13.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.6, 138.9, 137.7, 136.3, 135.5, 129.5, 128.8, 128.6, 128.4, 128.3, 127.9, 127.8, 127.5, 126.4, 121.3, 118.7, 56.9, 54.8, 53.2, 41.4; HRMS [APCI(+)] calcd for $C_{26}H_{24}NO_2$ $[M+H]^+$: 382.1802. Found: *m*/*z* 382.1792.



2,2-dicyano-4-methyl-1,1-diphenyl-4-pentene (4t). The reaction of **1a** (154 mg, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3d** (130 mg, 1.0 mmol) followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 96:4 to 84:16) gave the title compound (0.20 g, 0.71 mmol, 71%) as white solid (119.7 °C), R_f 0.52 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 7.4 Hz, 4H), 7.43–7.32 (m, 6H), 5.14 (s, 1H), 5.03 (s, 1H), 4.29 (s, 1H), 2.61 (s, 2H), 1.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ137.2, 136.7, 129.0, 128.8, 128.4, 118.6, 115.4, 58.0, 45.0, 41.8, 23.1; HRMS [APCI(+)] calcd for $C_{20}H_{19}N_2$ $[M+H]^+$: 287.1543. Found: *m*/*z* 287.1536.



methyl 2-cyano-2-(cyclohex-2-en-1-yl)-3,3-diphenylpropanoate (4u). The reaction of **1e** (187 mg, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3e** (156 mg, 1.0 mmol) using dppe as a ligand for 20 h at 130 ºC followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 96:4 to 84:16) gave the title compound (130 mg, 0.38 mmol, 38%) as pale yellow oil, R_f 0.60 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.56 Hz, 2H), 7.31–7.18 (m, 4H), 5.85–5.78 (m, 1H), 5.71–5.65 (m, 1H), 4.68 (s, 1H), 3.58 (s, 3H), 2.86–2.77 (m, 1H), 1.98–1.90 (m, 2H), 1.88–1.79 (m, 1H), 1.79–1.69 (m, 2H), 1.38–1.24 (m, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 167.4, 139.3, 138.2, 131.2, 129.0, 128.81, 128.77, 128.5, 127.6, 127.3, 125.1, 119.6, 57.6, 53.2, 52.8, 42.0, 24.6, 23.2, 21.6; HRMS [APCI(+)] calcd for $C_{23}H_{24}NO_2$ $[M+H]^+$: 346.1802. Found: *m*/*z* 346.1794.



2-cyano-2-methoxycarbonyl-5-methyl-1,1-diphenyl-4-hexene (4v). The reaction of **1e** (187 mg, 1.0 mmol), **2a** (0.24 g, 1.0 mmol) and **3f** (144 mg, 1.0 mmol) using dppe as a ligand for 20 h at 130 ºC followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 96:4 to 84:16) gave the title compound (179 mg, 0.54 mmol, 54%) as colorless oil, R_f 0.56 (*n*-hexane:ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 7.79 Hz, 2H), 7.33–7.19 (m, 4H), 5.12 (t, *J* = 7.1 Hz, 1H), 4.42 (s, 1H), 3.57 (s, 3H), 2.67 (dd, *J* = 8.2 Hz, 14.2 Hz, 1H), 2.46 (dd, *J* = 6.6 Hz, 14.0 Hz, 1H), 1.70 (s, 3H), 1.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.9, 139.1, 137.93, 137.87, 129.3, 128.6, 128.5, 128.2, 127.7, 127.4, 119.0, 115.9, 56.8, 54.5, 53.0, 36.5, 25.8, 17.8; HRMS [APCI(+)] calcd for $C_{22}H_{24}NO_2$ $[M+H]^+$: 334.1802. Found: *m*/*z* 334.1792.

Procedure for time-course study. Under air, a vial (Vial **A**) was charged with (IMes)CuCl (6.1 mg, 15 μmol) and fluorene (16.7 mg, 0.10 mmol) as an internal standard. A vial (Vial **B**) was charged with **1a** (46 mg, 0.30 mmol) and **2a** (73 mg, 0.30 mmol). A vial (Vial **C**) was charged with $Pd(OAc)_2$ (0.7 mg, 3.0 μmol) and dppp (1.2 mg, 3.0 μmol). These vials were transferred into a glove box. In the glove box, LiO*t*-Bu in 1.0 M THF solution (60 μL, 60 μmol) was added to Vial **A**. 1.95 mL of 1,4-dioxane was added into Vial **B** and 0.60 mL of 1,4-dioxane was added into Vial **C**. **3a** (35 mg, 0.30 mmol) was added to Vial **C**. Then, the solution in Vial **B** and **C** were added to Vial **A**. The resulting mixture was stirred at 100 ºC. 100 μL of sample was taken every 10 minutes from 0 to 1 h and every 30 minutes from 1 to 6 h. All of the volatiles in the samples were removed in *vacuo* and filtered through a short pad of silica gel and Celite®. The resulting samples were measured by ^{1}H NMR spectroscopy to calculate yields of the hydroarylation product **5a** and **4a**.

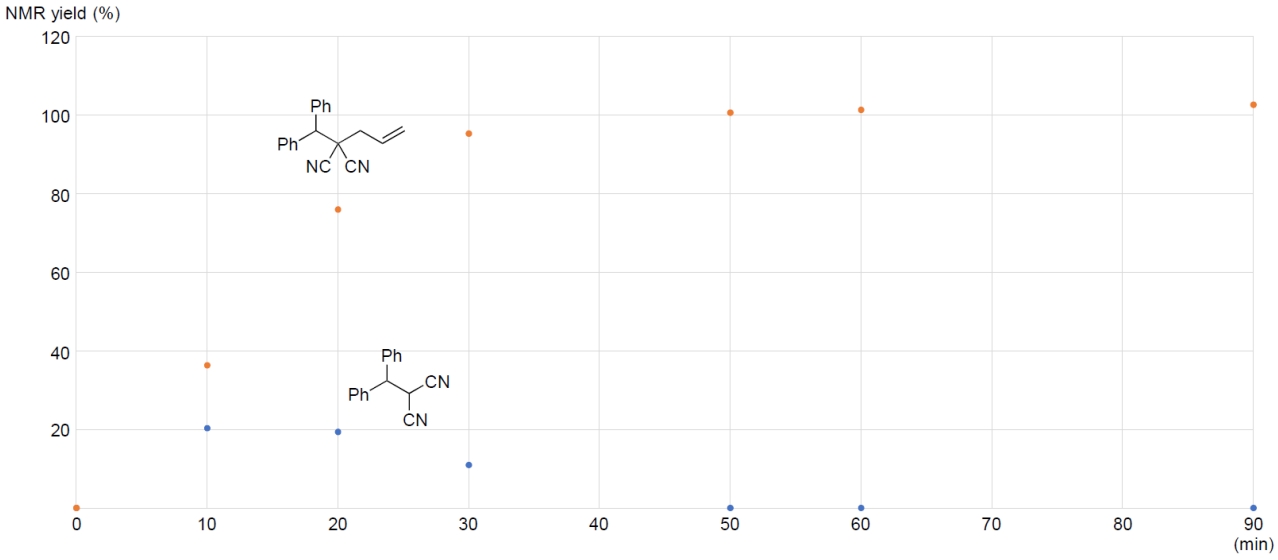
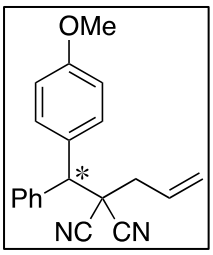
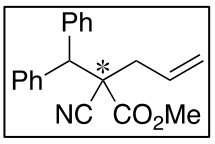


Figure S2. A time-course of the allylarylation of **1a** with **2a** and **3a**.



Enantioselective allylarylation of 4b. The reaction of **1a** (56 mg, 0.30 mmol), **2b** (82 mg, 0.30 mmol) and **3a** (35 mg, 0.30 mmol) using **L1** as a ligand followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 95:5 to 80:20) gave the title compound (17.2 mg, 57 μmol, 19%) as pale yellow oil. The resonance is of ^{1}H and ^{13}C NMR spectra of the product were consist with those of **4b** in Table 2. The ee was determined on a Daicel Chiralpak AS-H column with *n*-hexane–2-propanol = 99:1, flow = 1.0 mL/min, detection at 220 nm. Retention times: 9.2 min (major enantiomer), 11.1 min (minor enantiomer). $[\alpha]^{19}_{D}$ –0.746 (*c* 0.0067, CH_2Cl_2).



Enantioselective allylarylation of 4o. The reaction of **1e** (56 mg, 0.30 mmol), **2a** (73 mg, 0.30 mmol) and **3a** (52 mg, 0.45 mmol) using **L2** as a ligand followed by purification by MPLC (25 g Biotage® SNAP Ultra, *n*-hexane:ethyl acetate = 95:5 to 80:20) gave the title compound (74 mg, 0.24 mmol, 81%) as white solid. The resonance is of ^{1}H and ^{13}C NMR spectra of the product were consist with those of **4o** in Table 3. The ee was determined on a Daicel Chiralpak AD-H column with *n*-hexane–2-propanol = 99:1, flow = 1.0 mL/min, detection at 254 nm. Retention times: 8.7 min (major enantiomer), 10.2 min (minor enantiomer). $[\alpha]^{19}_{D}$ 6.47 (*c* 0.0056, CH_2Cl_2).

==== Shimadzu LCsolution 分析レポート ====

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バイアル番号	: 1
注入量	: 10 uL
データファイル	: 6429-06-06-142-a-racemi-1.0-1.0-2.lcd
メソッドファイル	: ohta.lcm
バッチファイル	:
レポートファイル	: Default.lcr
分析日時	: 2016/04/29 14:28:06
解析日時	: 2017/07/21 16:24:24

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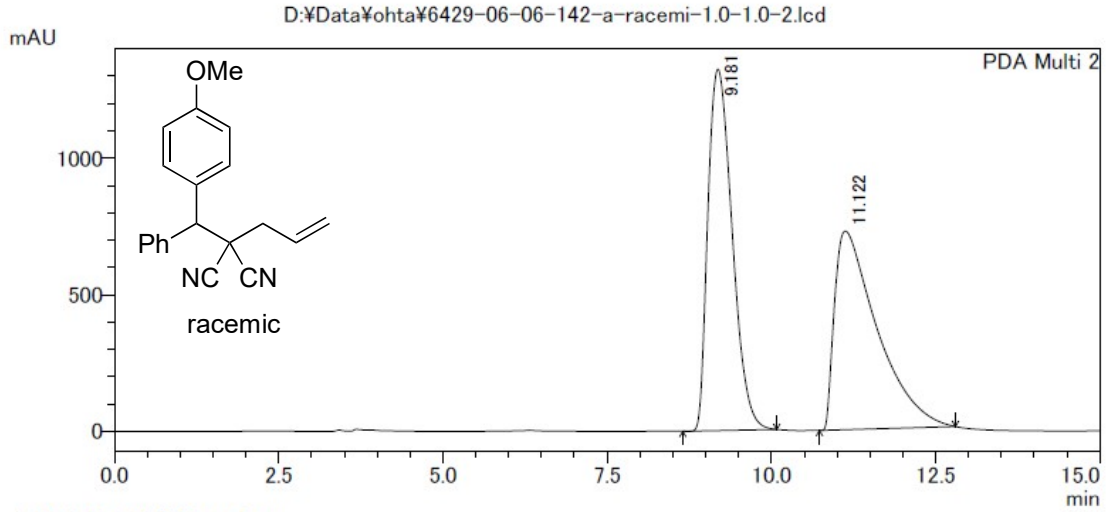

1 PDA Multi 2/220nm 4nm

ピークテーブル

PDA Ch2 220nm 4nm

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==== Shimadzu LCsolution 分析レポート ====

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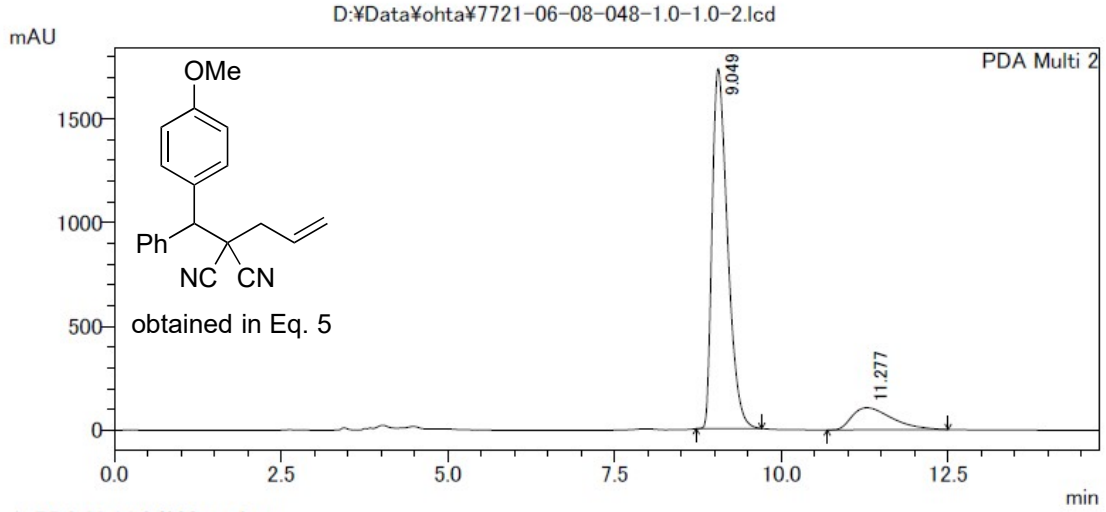

1 PDA Multi 2/220nm 4nm

ピークテーブル

PDA Ch2 220nm 4nm

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2	11.277	4428750	106312	13.705	5.773
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==== Shimadzu LCsolution 分析レポート ====

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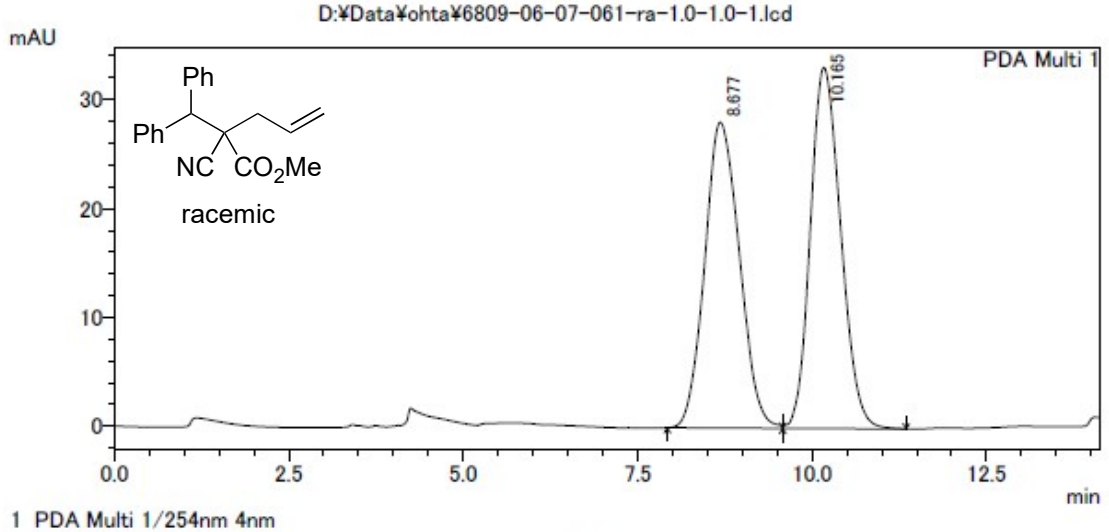

1 PDA Multi 1/254nm 4nm

ピークテーブル

PDA Ch1 254nm 4nm

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2	10.165	1004797	33134	50.823	54.125
合計		1977063	61218	100.000	100.000

==== Shimadzu LCsolution 分析レポート ====

分析者	: System Administrator
サンプル名	: 6809-06-07-061-1.0-1.0-1
サンプルID	: 6809-06-07-061-1.0-1.0-1
トレイ番号	: 1
バイアル番号	: 2
注入量	: 10 uL
データファイル	: 6809-06-07-061-1.0-1.0-1.lcd
メソッドファイル	: ohta.lcm
バッチファイル	:
レポートファイル	: Default.lcr
分析日時	: 2016/08/08 18:30:52
解析日時	: 2016/08/13 14:36:57

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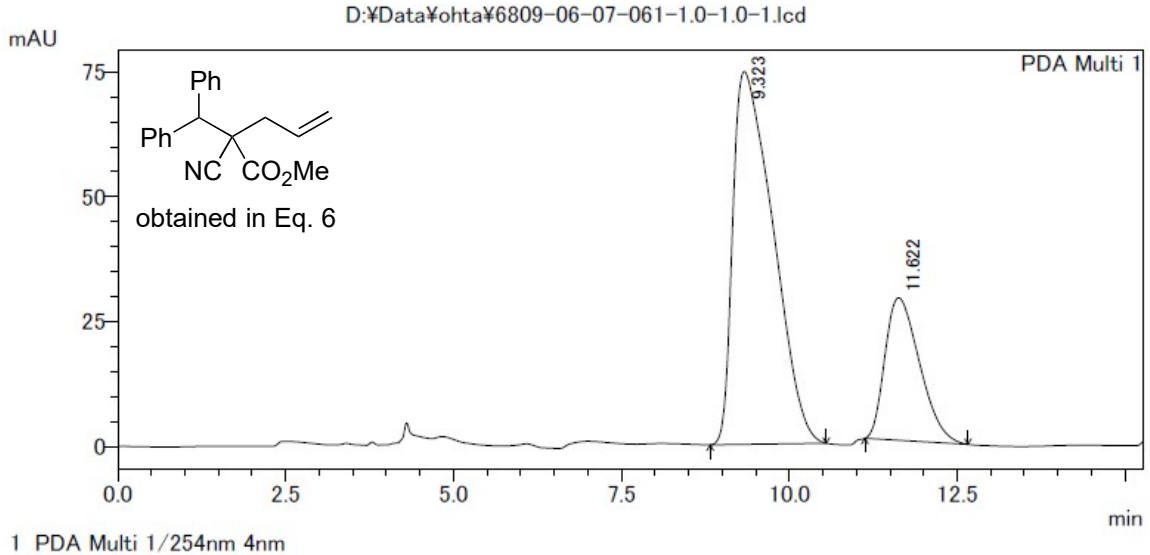

1 PDA Multi 1/254nm 4nm

ピークテーブル

PDA Ch1 254nm 4nm

ピーク#	保持時間	面積	高さ	面積%	高さ%
1	9.323	3103936	74690	75.174	72.351
2	11.622	1025065	28543	24.826	27.649
合計		4129002	103233	100.000	100.000

References

[1] (a) G. B. Kharas, K. Watson, *Macromolecules* 1989, **22,** 3871–3877; (b) D. E. Q. Jimenez, I. M. Ferreira, W. G. Birolli, L. P. Fonseca, A. L. M. Porto, *Tetrahedron* 2016, **72,** 7317–7322; (c) M. A. Camerino, M. Liu, S. Moriya, T. Kitahashi, A. Mahgoub, S. J. Mountford, D. K. Chalmers, T. Soga, I. S. Parhar, P. E. Thompson, *J. Pept. Sci.* 2016, **22,** 406–414; (d) Y. Liu, W. Yang, Y. Wu, B. Mao, X. Gao, H. Liu, Z. Sun, Y. Xiao, H. Guo, *Adv. Synth. Catal.* 2016, **358,** 2867–2872.

[2] (a) Y. Nakao, H. Imanaka, A. K. Sahoo, A. Yada, T. Hiyama, *J. Am. Chem. Soc.* 2005, **127,** 6952–6953; (b) Y. Nakao, J. Chen, H. Imanaka, T. Hiyama, Y. Ichikawa, W.-L. Duan, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* 2007, **129,** 9137–9143; (c) M. Iizuka, Y. Kondo, *Eur. J. Org. Chem.* 2008, 1161–1163; (d) Y. Nakao, H. Imanaka, J. Chen, A. Yada, T. Hiyama, *J. Organomet. Chem.* 2007, **692,** 585–603; (e) Y. Nakao, M. Takeda, T. Matsumoto, T. Hiyama, *Angew. Chem., Int. Ed.* 2010, **49,** 4447–4450.

[3] (a) T. R. Ramadhar, J. Kawakami, A. J. Lough, R. A. Batey, *Org. Lett.* 2010, **12,** 4446–4449; (b) X. Qian, A. Auffrant, A. Felouat, C. Gosmini, *Angew. Chem., Int. Ed.* 2011, **50,** 10402–10405; (c) S. Ghosh, S. Chaudhuri, A. Bisai, *Org. Lett.* 2015, **17,** 1373–1376; (d) H. Chen, X. Jia, Y. Yu, Q. Qian, H. Gong, *Angew. Chem., Int. Ed.* 2017, **56,** 13103–13106.

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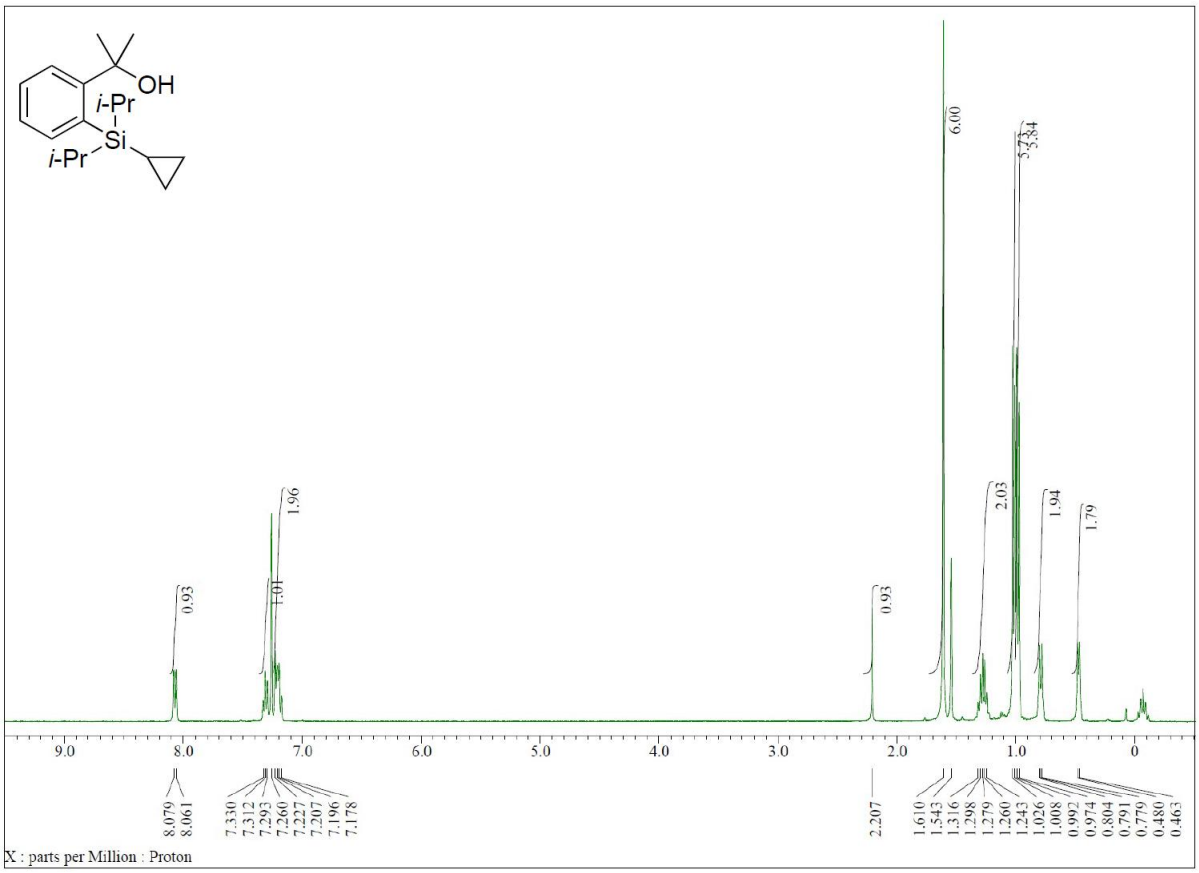
[5] K. Mizuno, M. Ikeda, S. Toda, Y. Otsuji, *J. Am. Chem. Soc.* 1988, **110,** 1288–1290.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i-Pr
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5.84
2.03
1.94
1.79
1.96
1.01
0.93
0.93
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.079
8.061
7.330
7.312
7.293
7.260
7.227
7.207
7.196
7.178
2.207
1.610
1.543
1.316
1.298
1.279
1.260
1.243
1.026
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0.791
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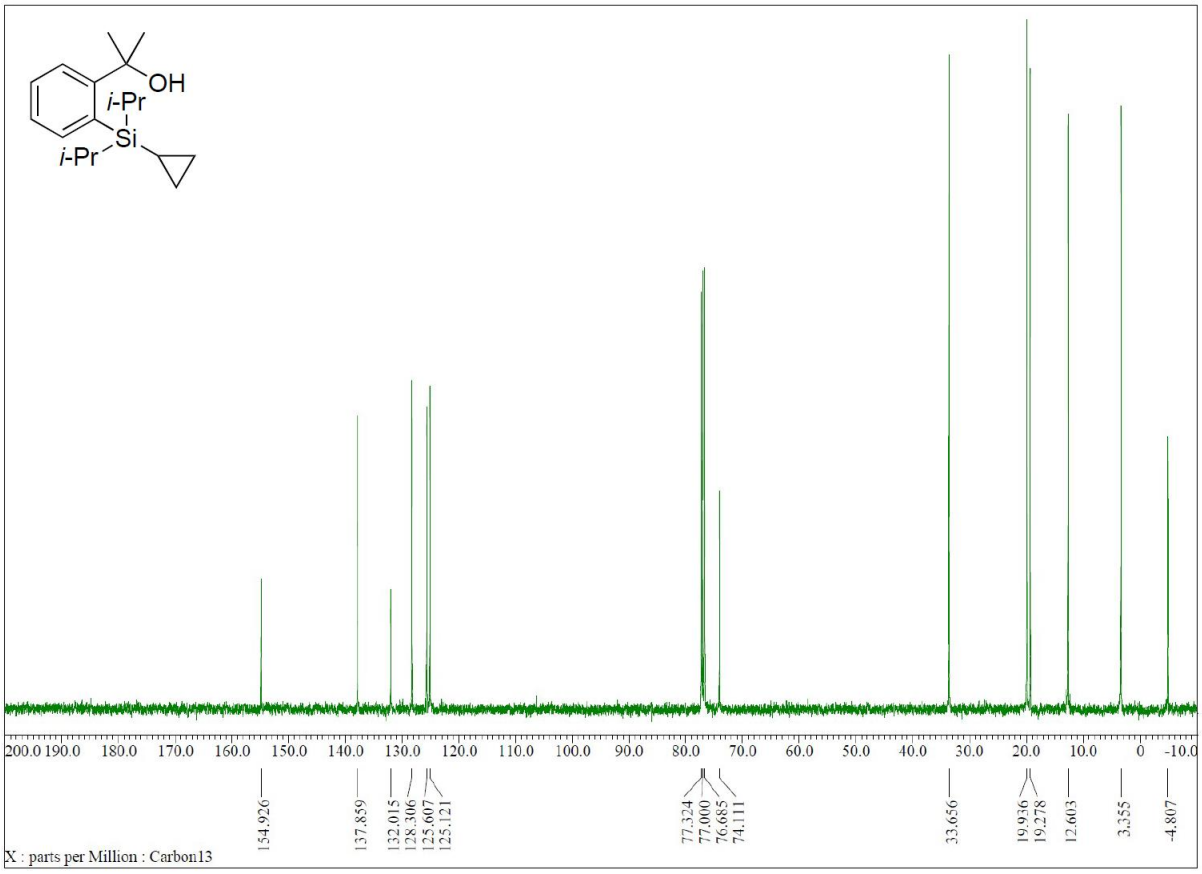
0.463
X : parts per Million : Proton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Si
i-Pr
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180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
154.926
137.859
132.015
128.306
125.607
125.121
77.324
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76.685
74.111
33.656
19.936
19.278
12.603
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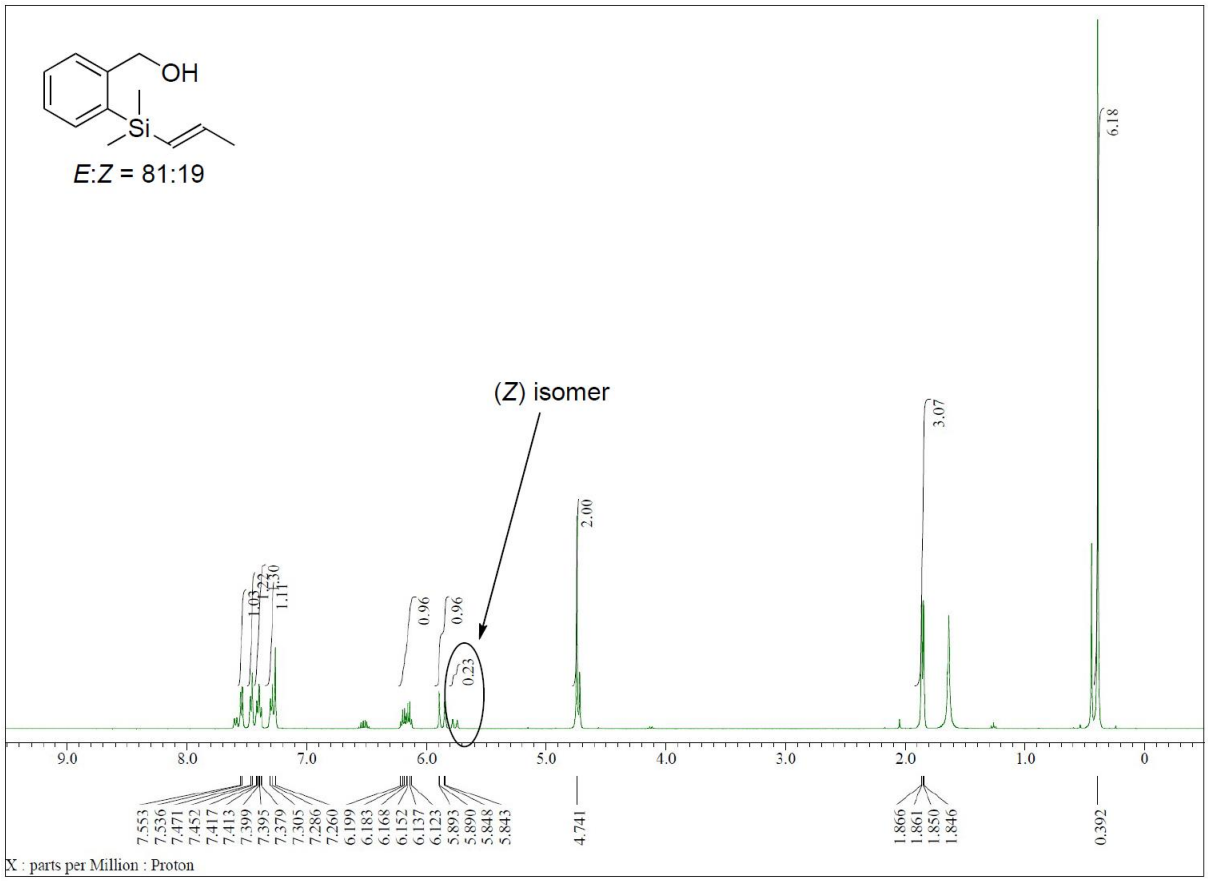
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(Z) isomer
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3.07
2.00
1.03
1.11
0.96
0.96
0.23
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.553
7.536
7.471
7.452
7.417
7.413
7.399
7.395
7.379
7.305
7.286
7.260
6.199
6.183
6.168
6.152
6.137
6.123
5.893
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5.843
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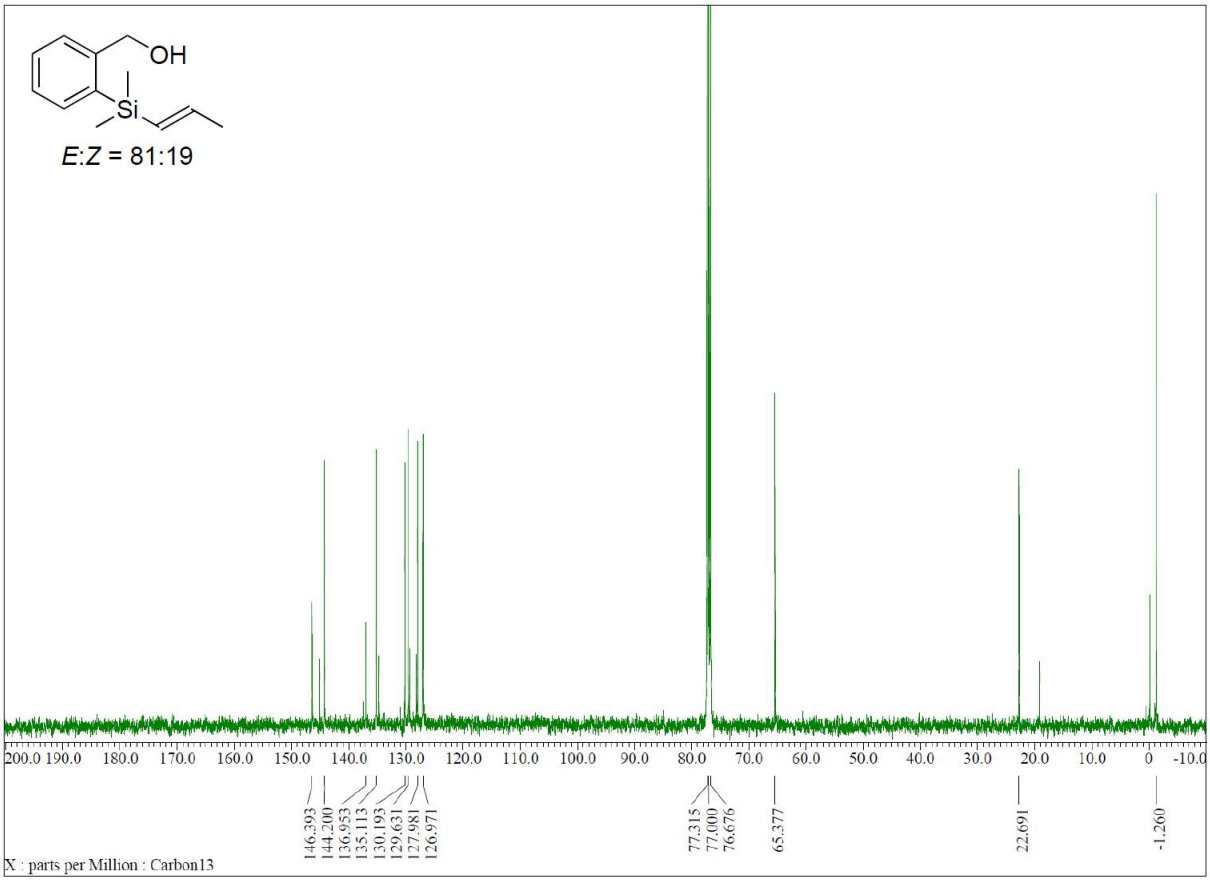
1.861
1.850
1.846
0.392
X : parts per Million : Proton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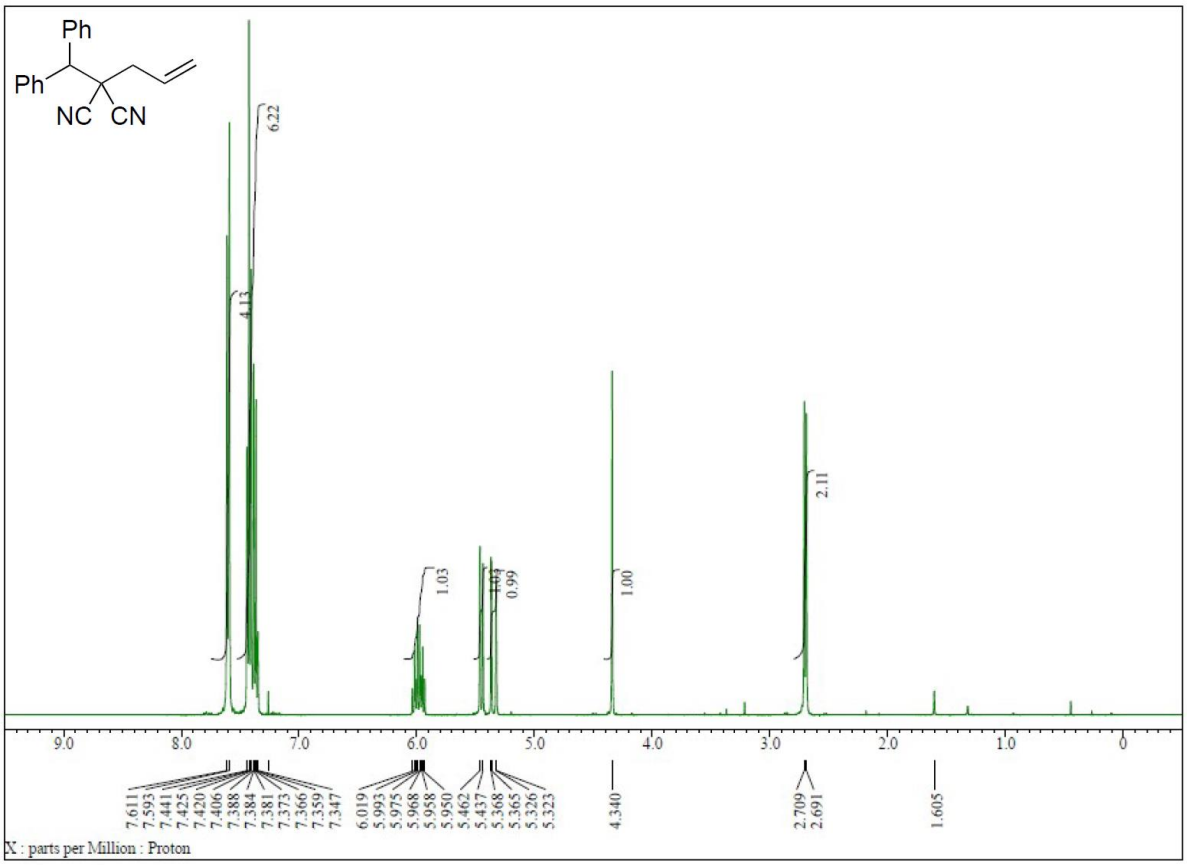
Si
E:Z = 81:19
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
146.393
144.200
136.953
135.113
130.193
129.631
127.981
126.971
77.315
77.000
76.676
65.377
22.691
-1.260
X : parts per Million : Carbon13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Ph
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CN
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1.03
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1.00
2.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.611
7.593
7.441
7.425
7.420
7.406
7.388
7.384
7.381
7.373
7.366
7.359
7.347
6.019
5.993
5.975
5.968
5.958
5.950
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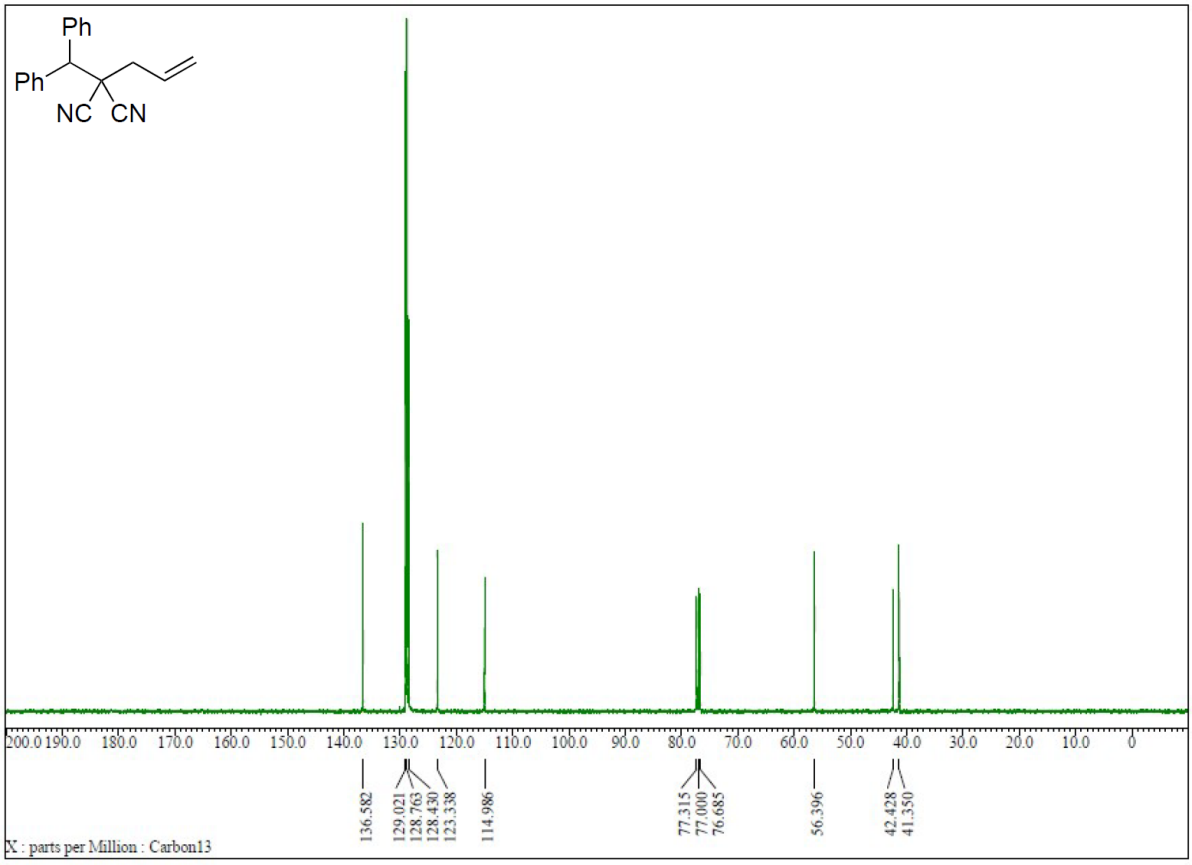
X : parts per Million : Proton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Ph
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CN
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180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
136.582
129.021
128.763
128.430
123.338
114.986
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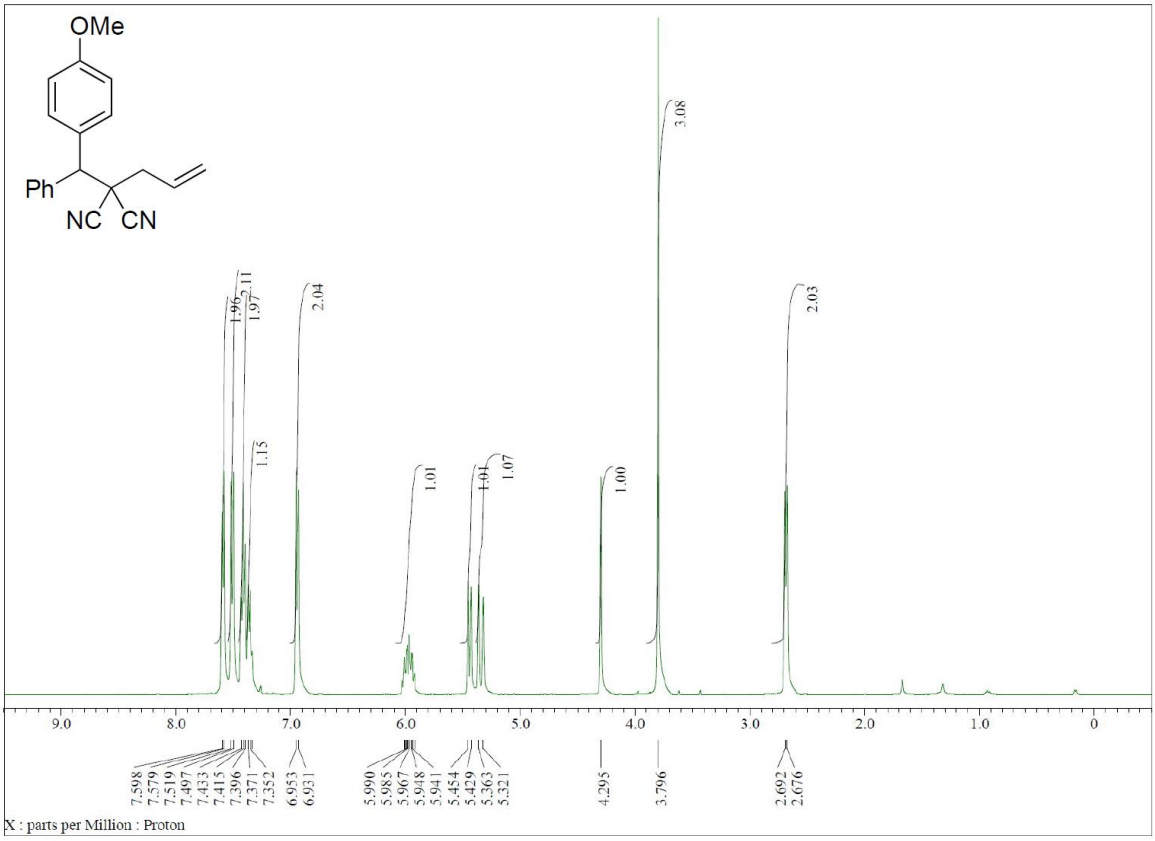
77.000
76.685
56.396
42.428
41.350
X : parts per Million : Carbon13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Ph
NC CN
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2.11
1.96
1.97
2.03
1.15
1.01
1.01
1.07
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.598
7.579
7.519
7.497
7.433
7.415
7.396
7.371
7.352
6.953
6.931
5.990
5.985
5.967
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5.429
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2.676
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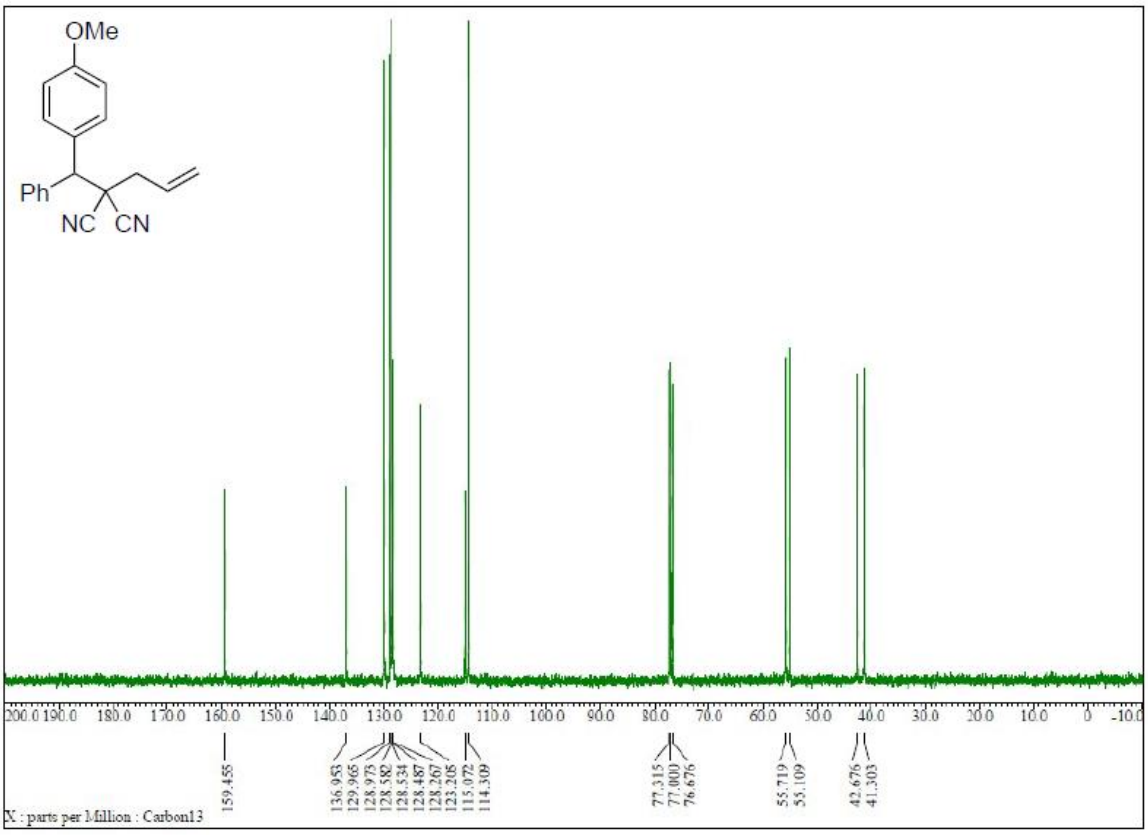
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128.973
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76.676
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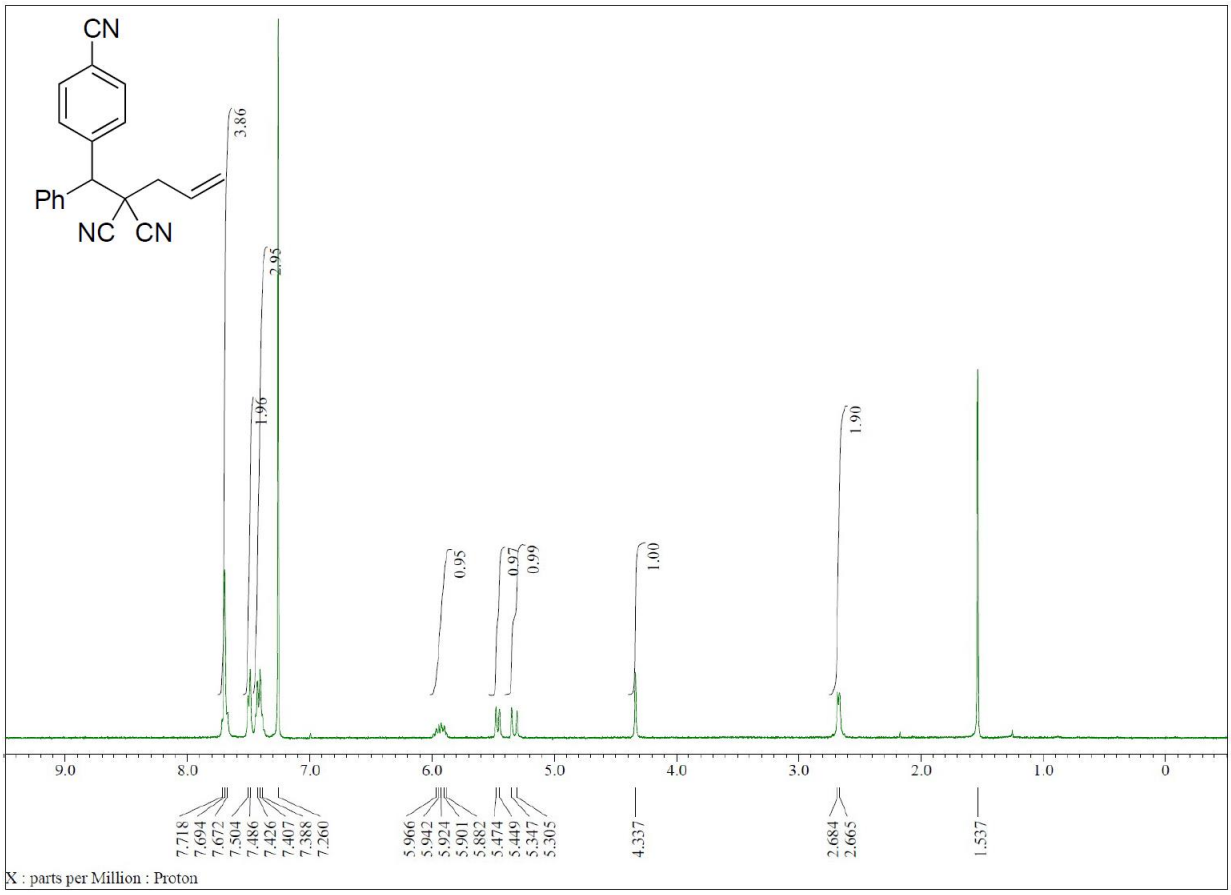
55.109
42.676
41.303
X : parts per Million : Carbon13


CN
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NC CN
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0.97
0.99
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.718
7.694
7.672
7.504
7.486
7.426
7.407
7.388
7.260
5.966
5.942
5.924
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5.305
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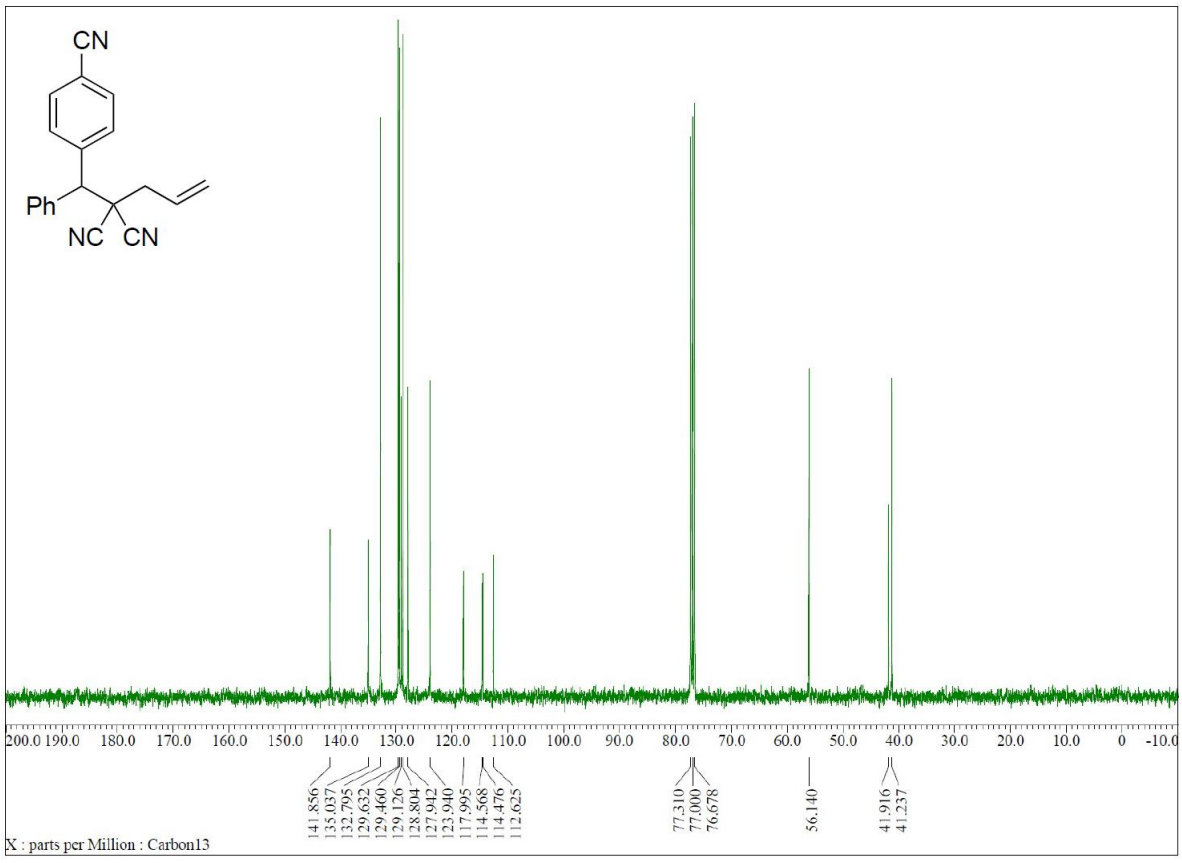
1.537
X : parts per Million : Proton


CN
Ph
NC CN
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
141.856
135.037
132.795
129.632
129.460
129.126
128.804
127.942
123.940
117.995
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112.625
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56.140
41.916
41.237
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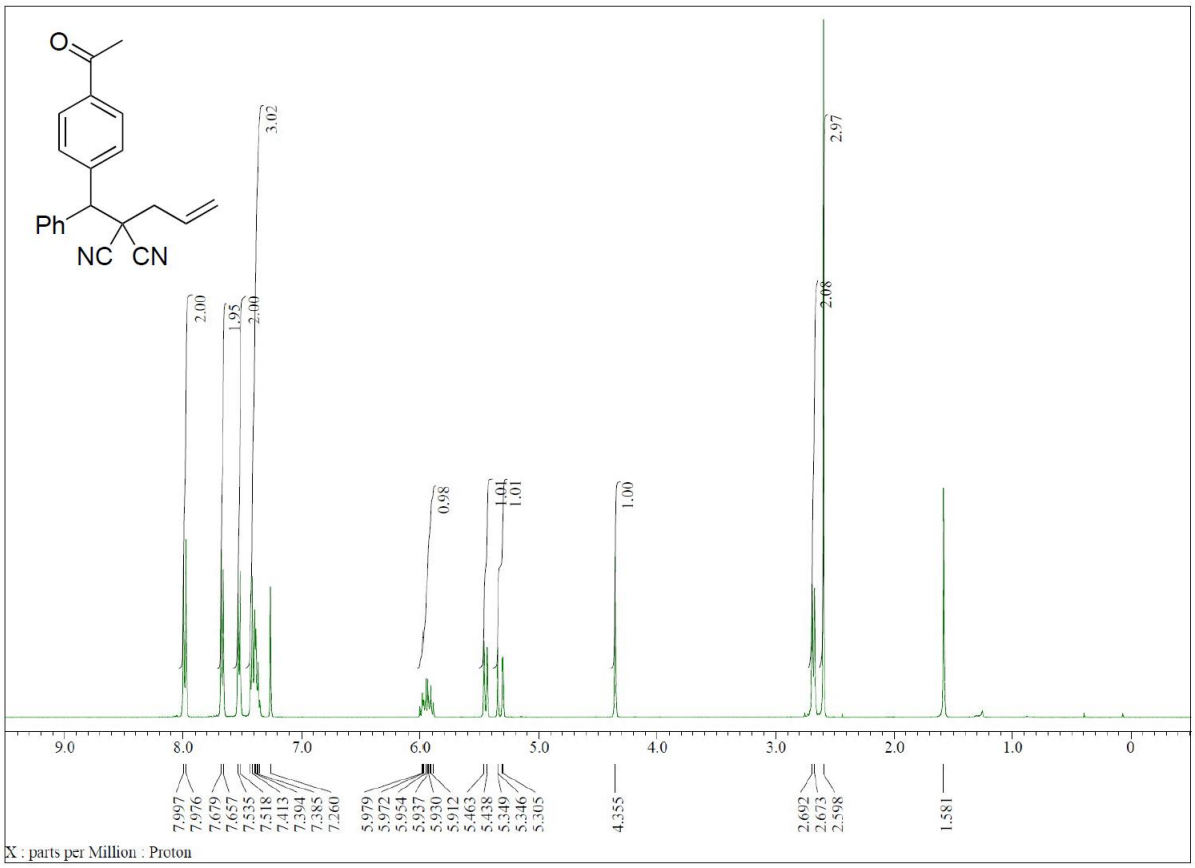
O
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1.01
1.00
2.08
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.976
7.679
7.657
7.535
7.518
7.413
7.394
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7.260
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5.930
5.912
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2.692
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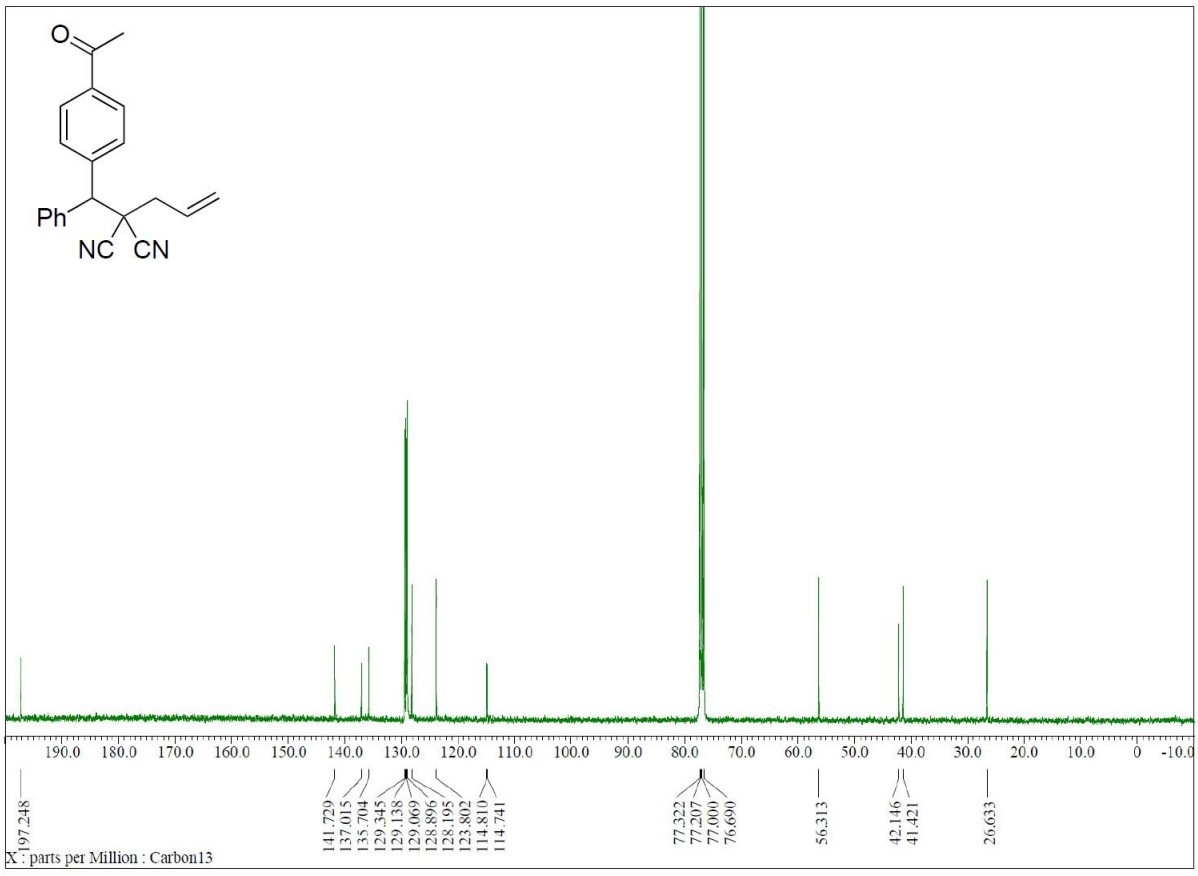
1.581
X : parts per Million : Proton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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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135.704
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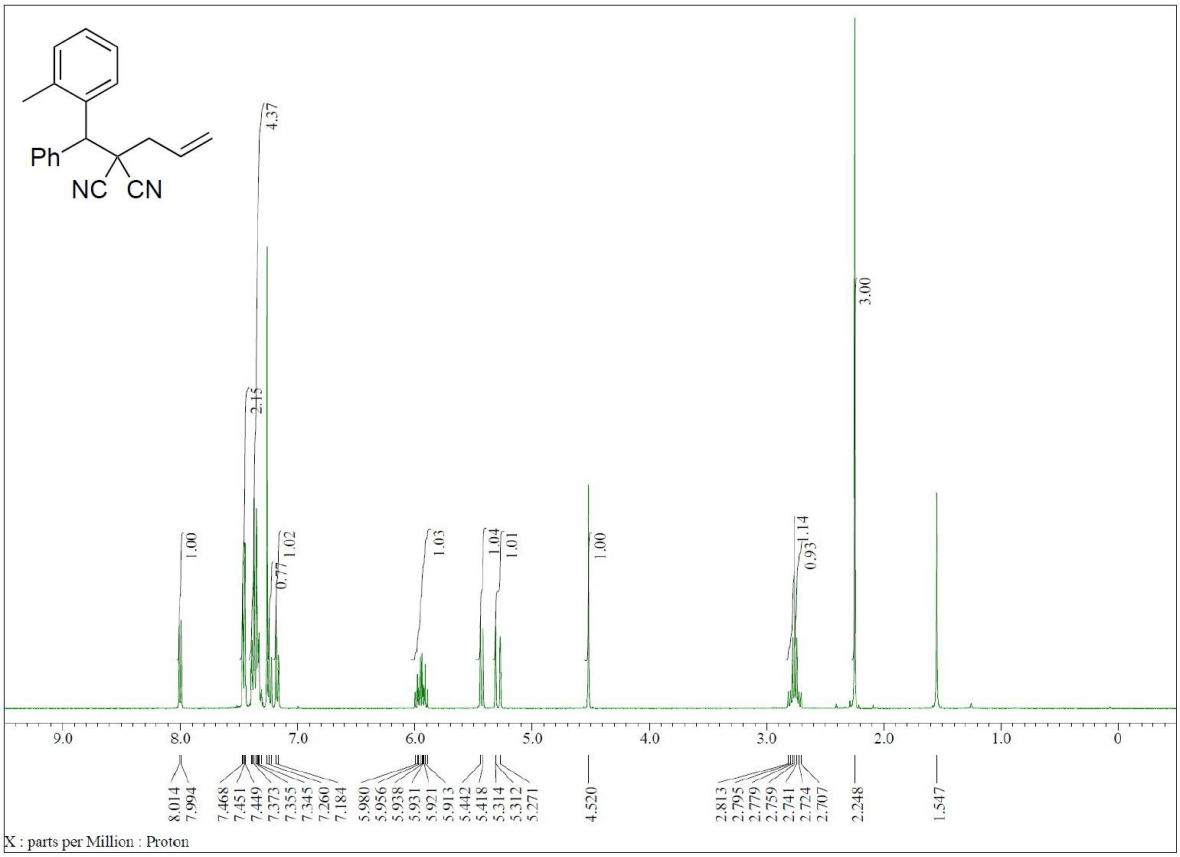
X : parts per Million : Carbon13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1.14
0.93
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.014
7.994
7.468
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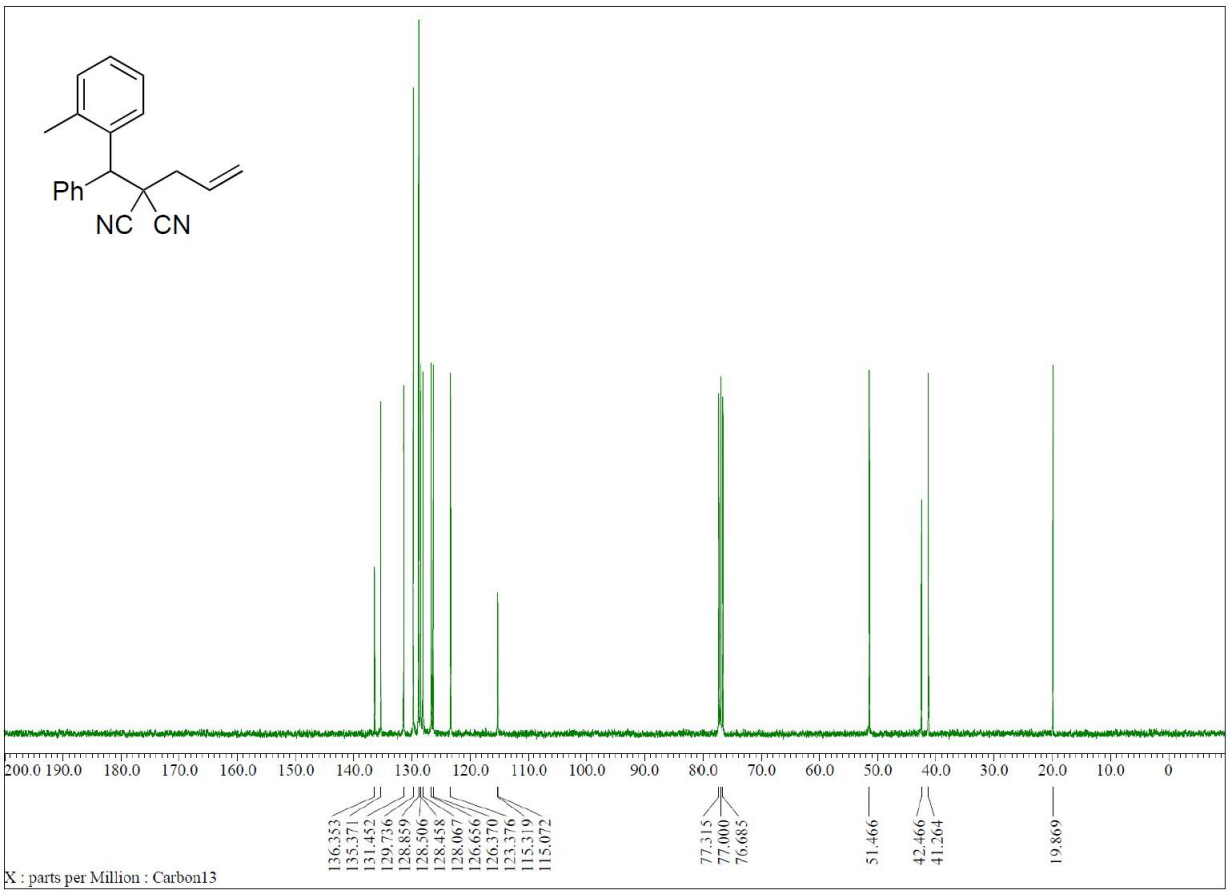
Ph
NC CN
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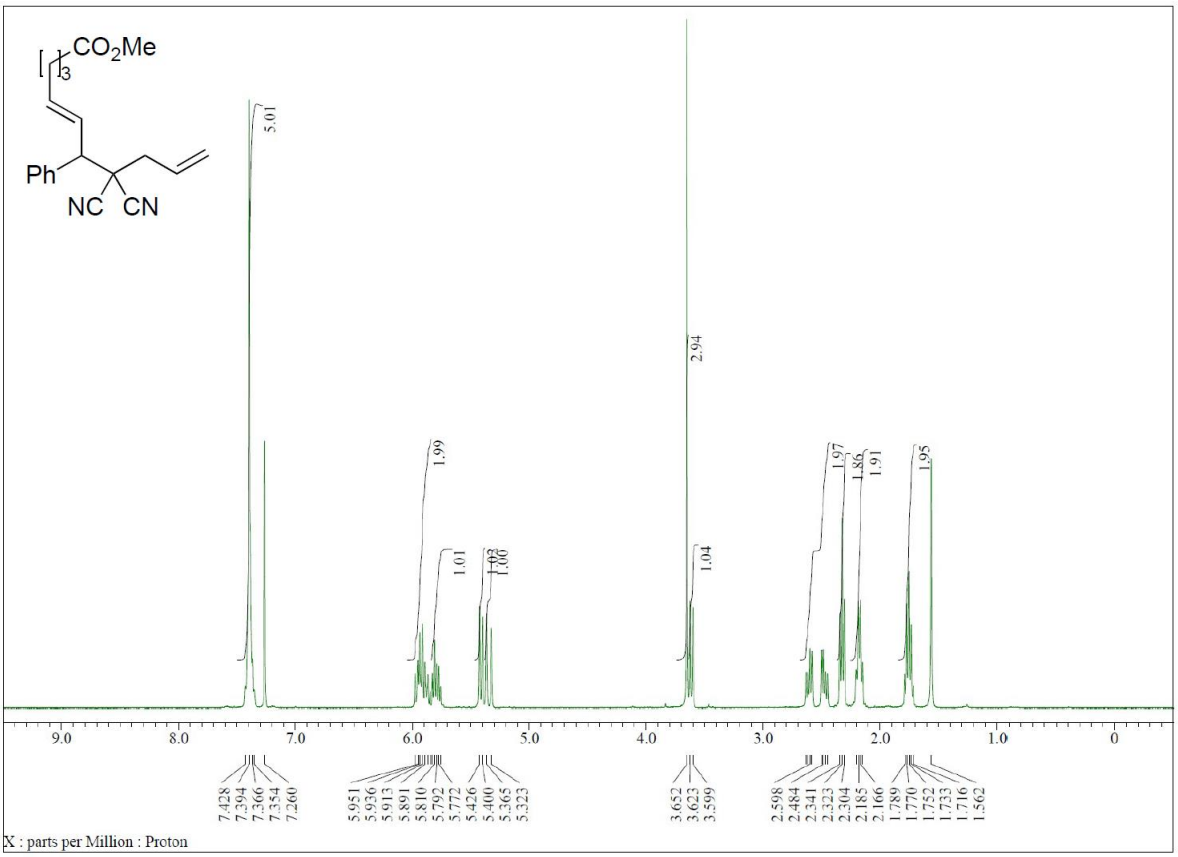
136.353
135.371
131.452
129.736
128.859
128.506
128.458
128.067
126.656
126.370
123.376
115.319
115.072
77.315
77.000
76.685
51.466
42.466
41.264
19.869
X : parts per Million : Carbon13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1.99
1.01
1.03
1.00
1.04
1.97
1.86
1.91
1.95
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.428 7.394 7.366 7.354 7.260
5.951 5.936 5.913 5.891 5.810 5.792 5.772 5.426 5.400 5.365 5.323
3.652 3.623 3.599
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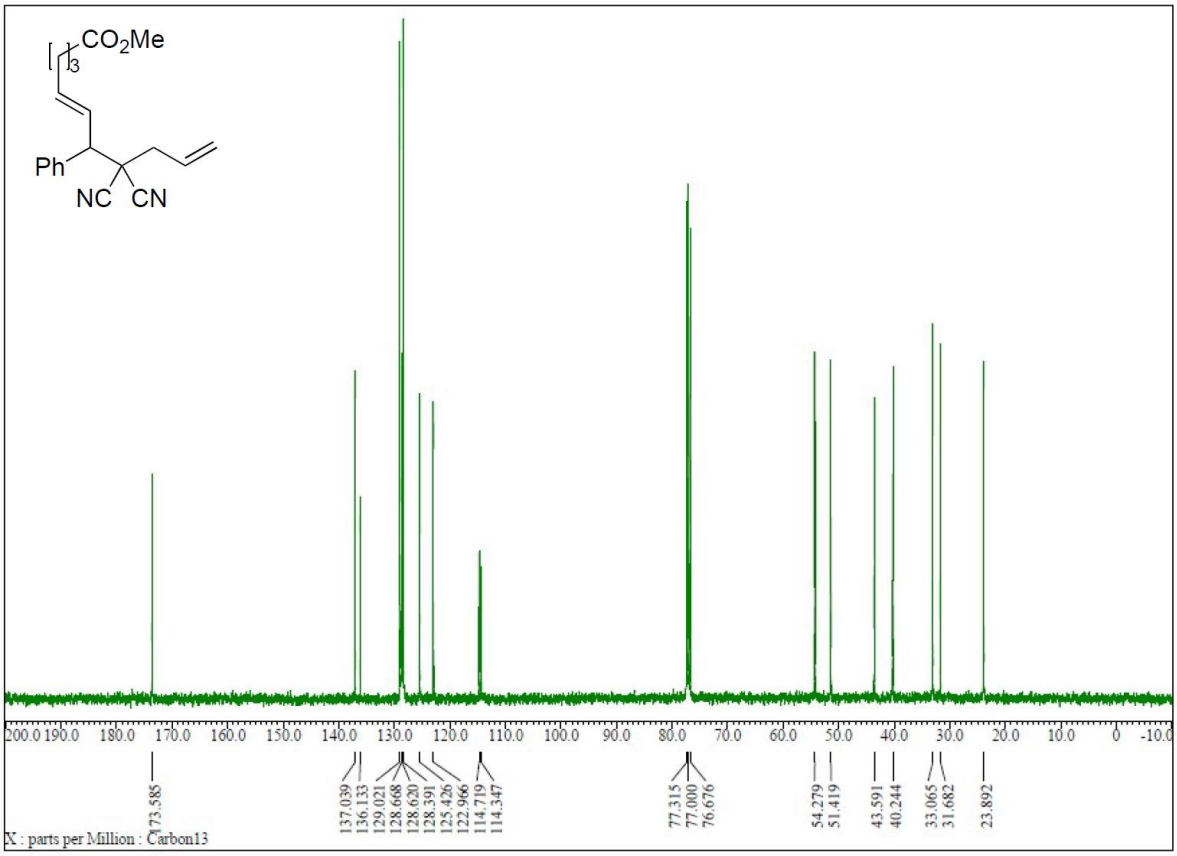
X : parts per Million : Proton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173.585
137.039 136.133 129.021 128.668 128.620 128.391 125.426 122.966 114.719 114.347
77.315 77.000 76.676
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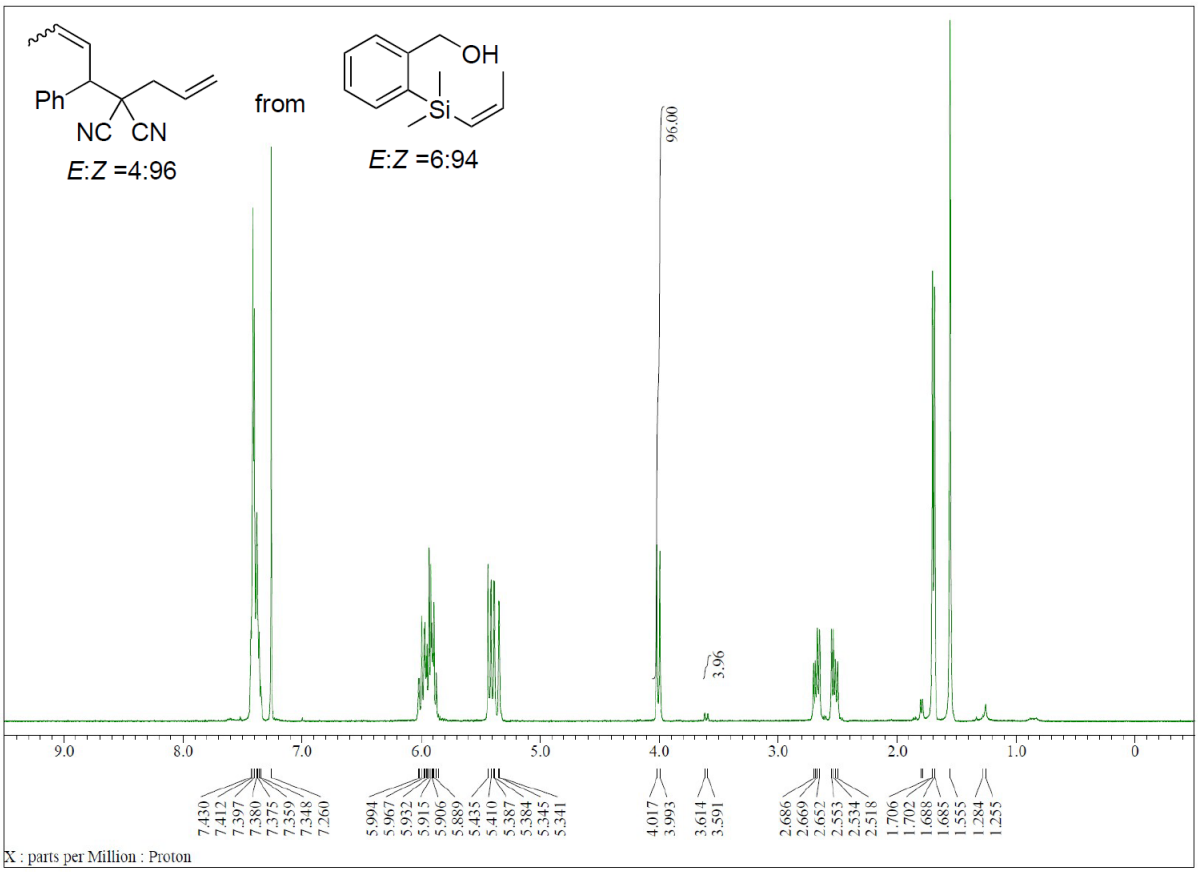
X : parts per Million : Carbon13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E:Z =4:96
from
OH
Si
E:Z =6:94
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.430
7.412
7.397
7.380
7.375
7.359
7.348
7.260
5.994
5.967
5.932
5.915
5.906
5.889
5.435
5.410
5.387
5.384
5.345
5.341
4.017
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2.669
2.652
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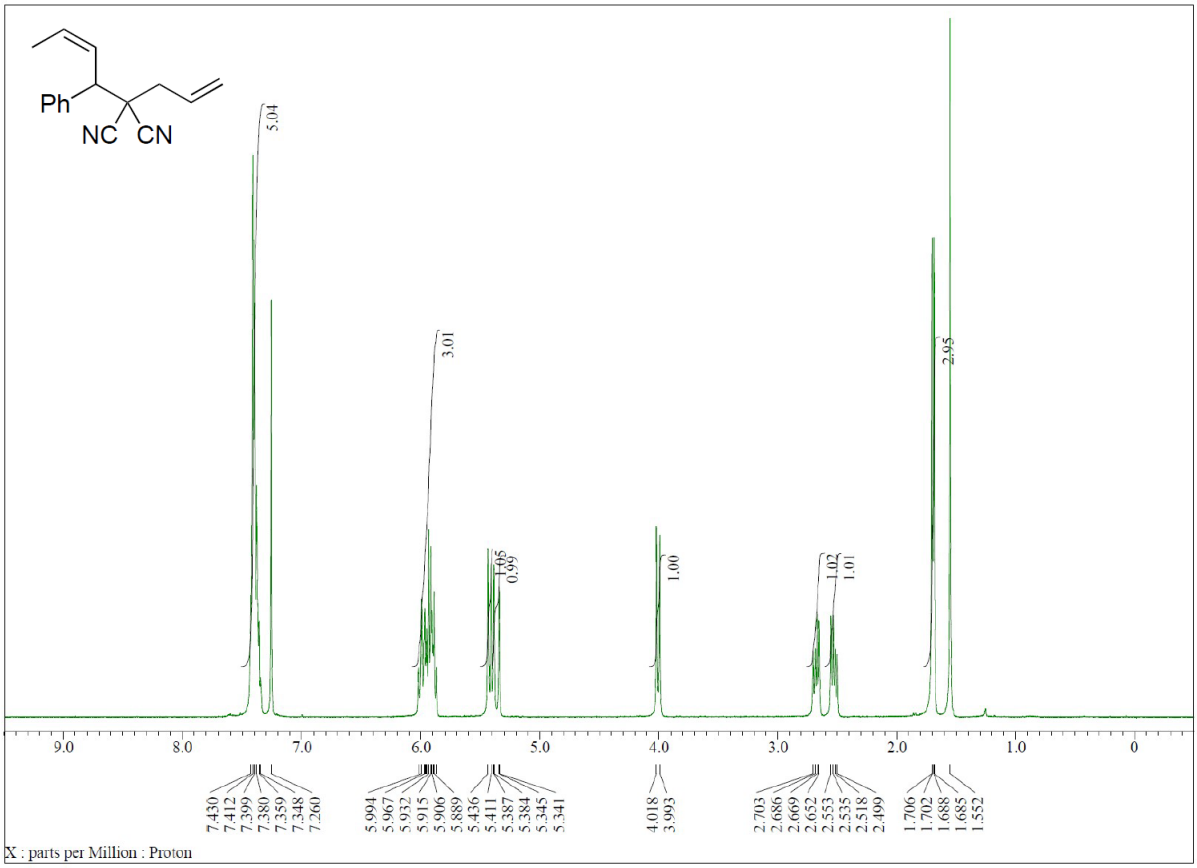
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0
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7.359
7.348
7.260
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5.967
5.932
5.915
5.906
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5.436
5.411
5.387
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5.345
5.341
4.018
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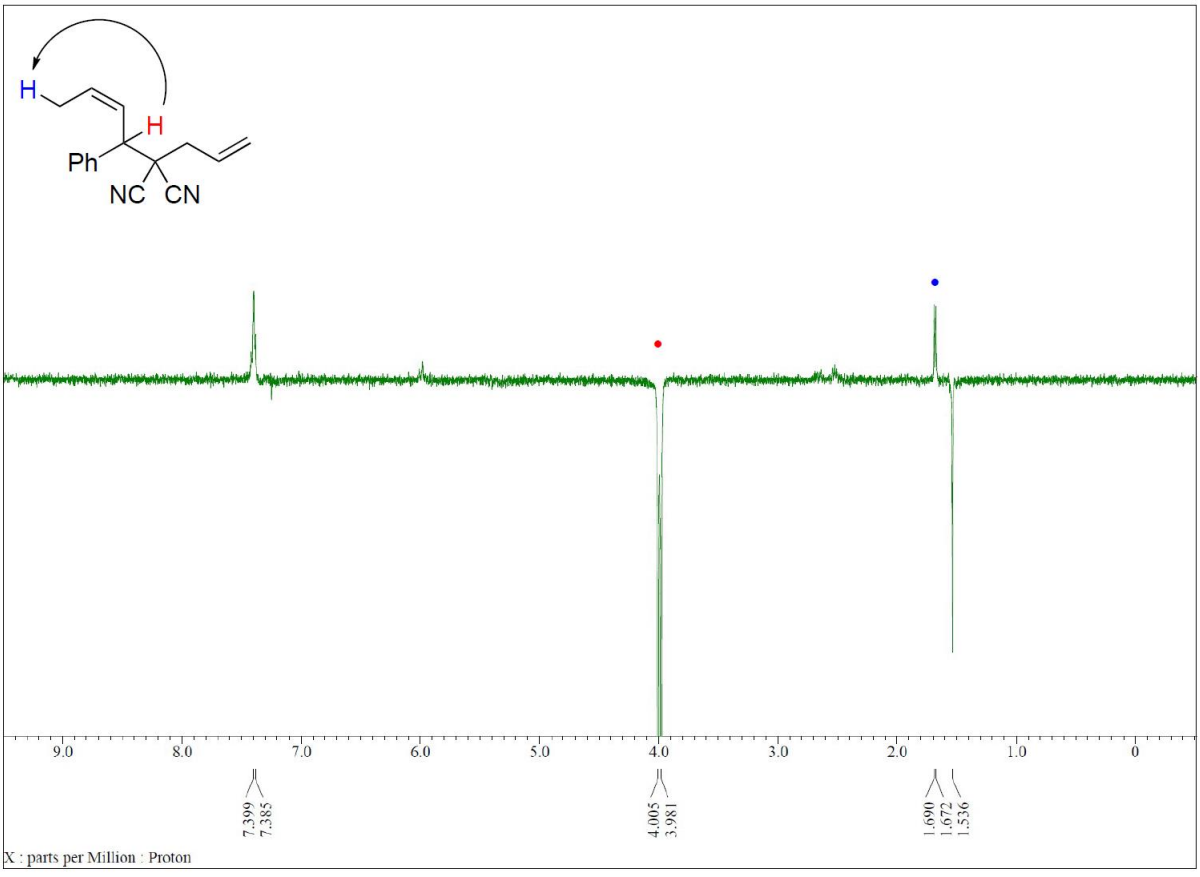
X : parts per Million : Proton


H
H
Ph
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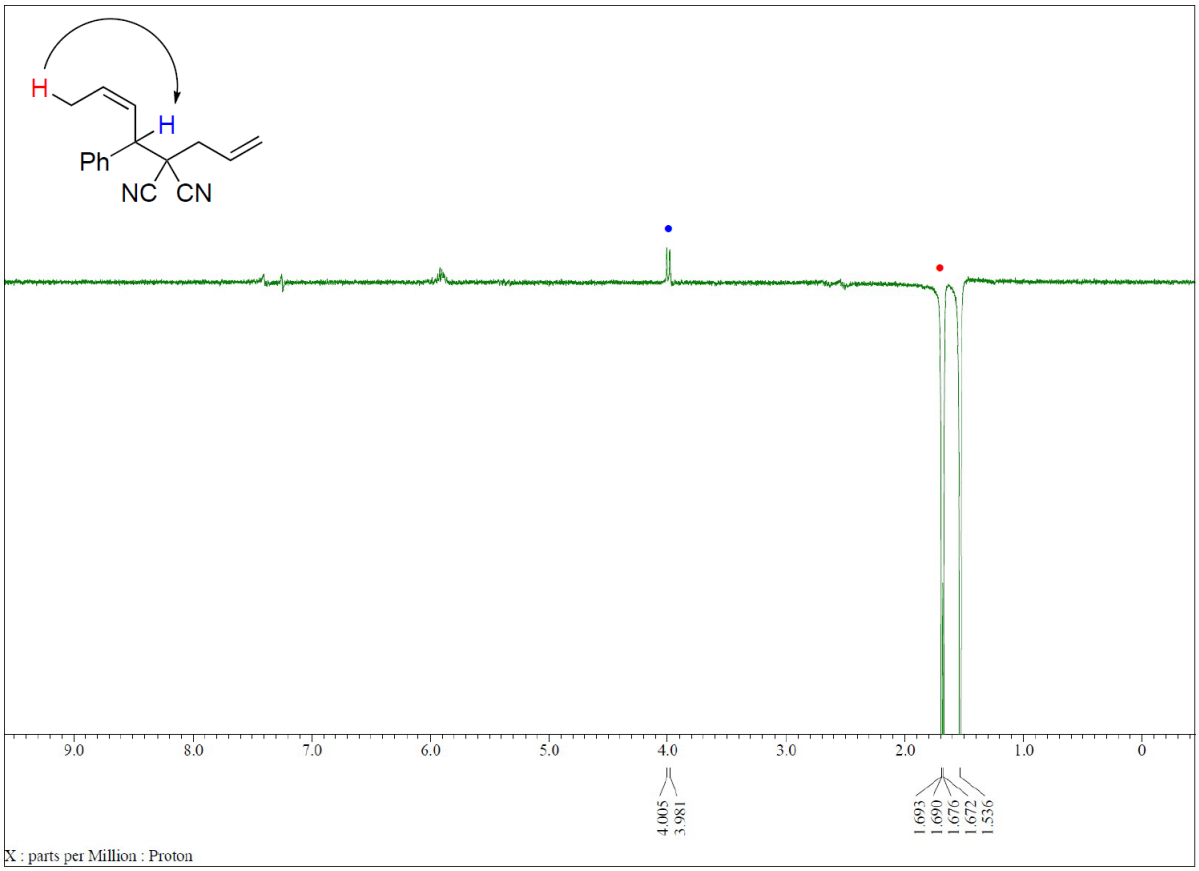
0
7.399
7.385
4.005
3.981
1.690
1.672
1.536
X : parts per Million : Proton


H
H
Ph
NC CN
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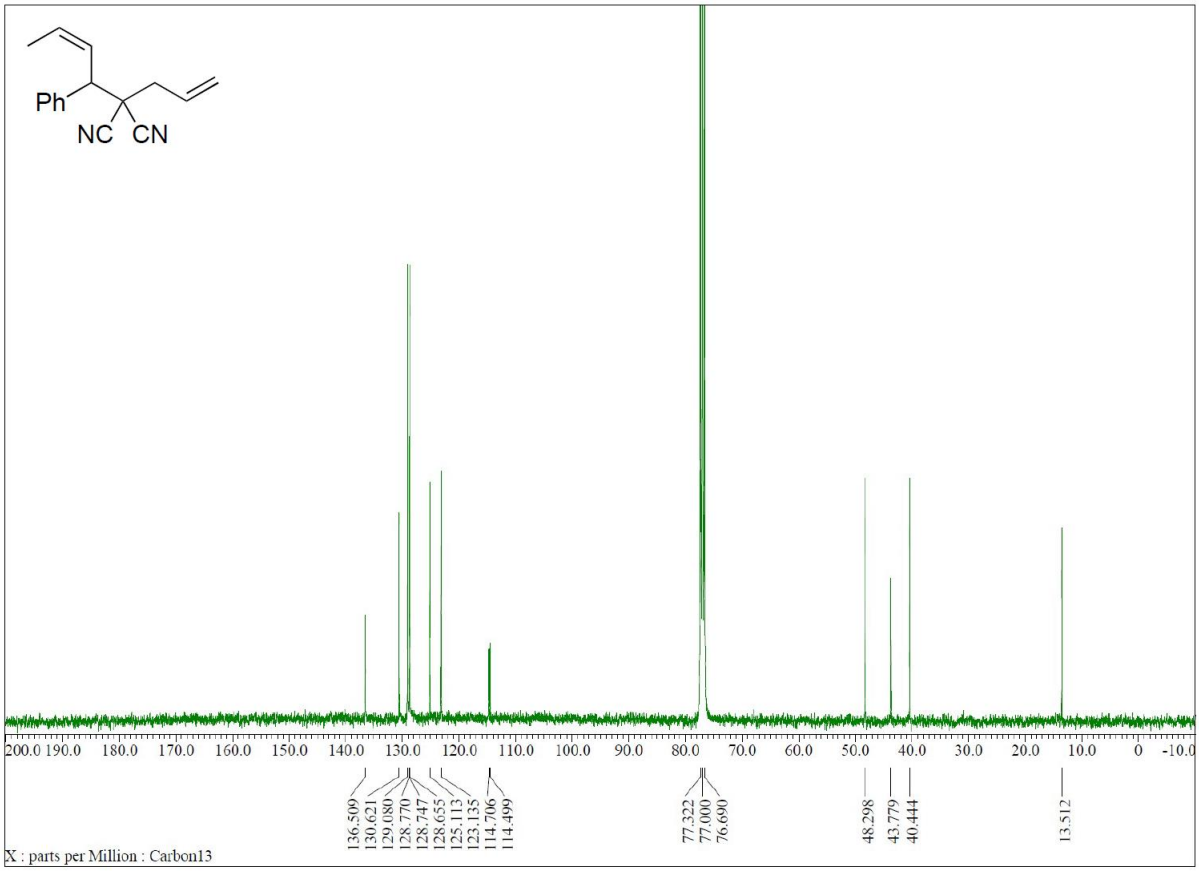
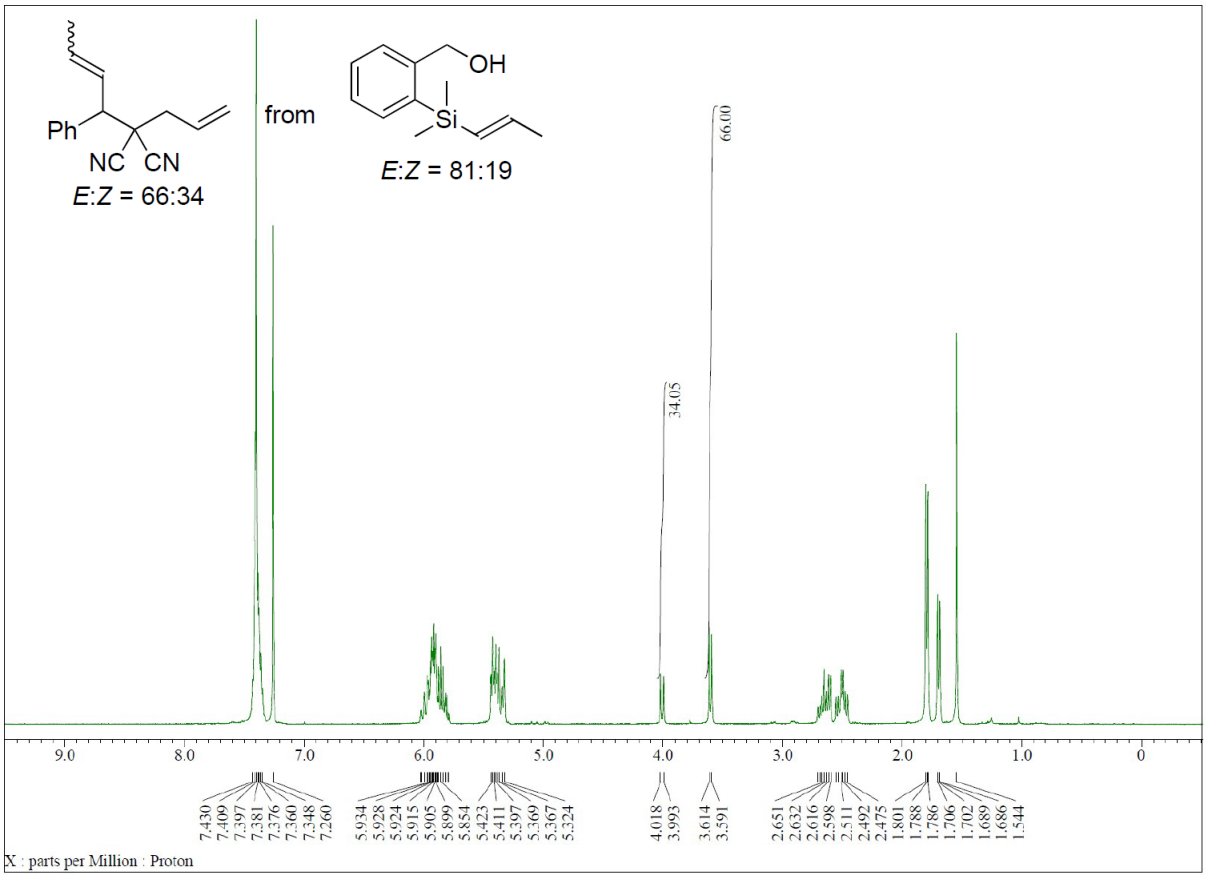
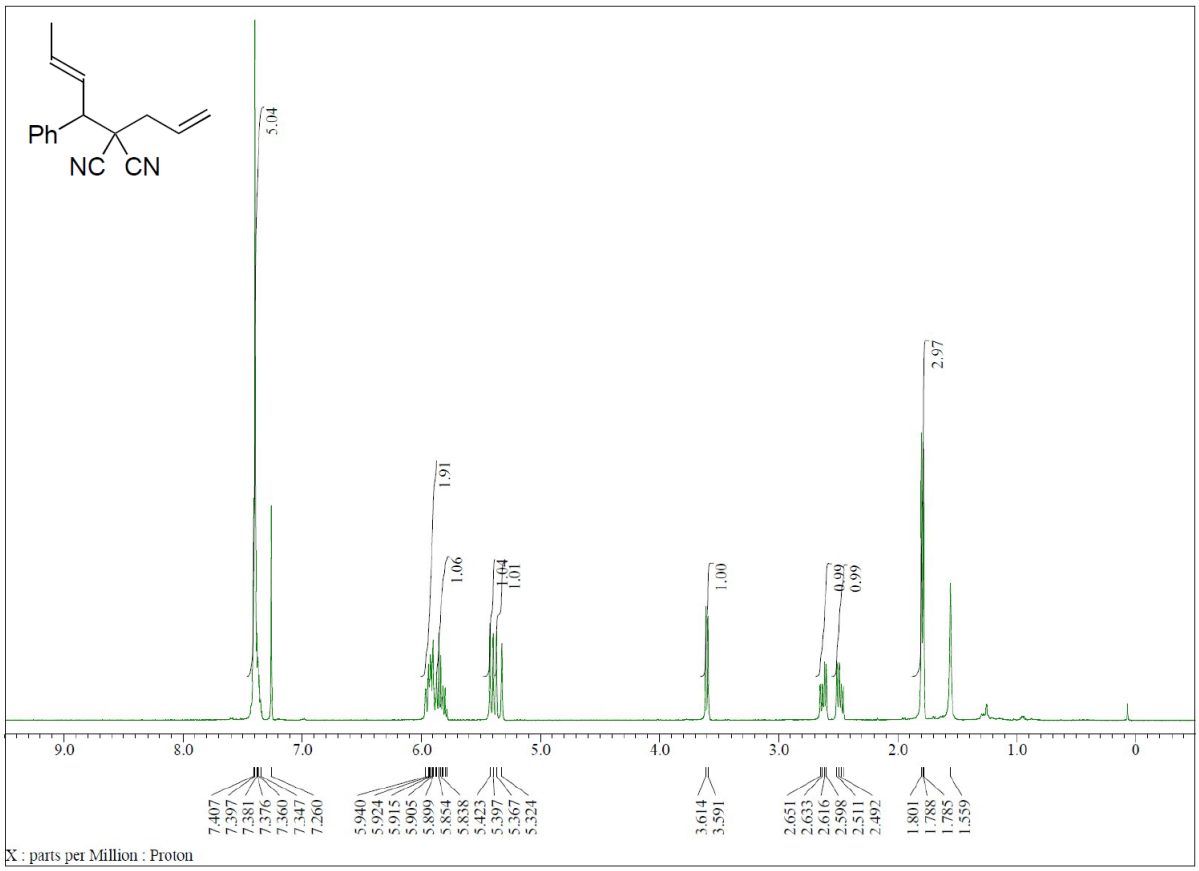
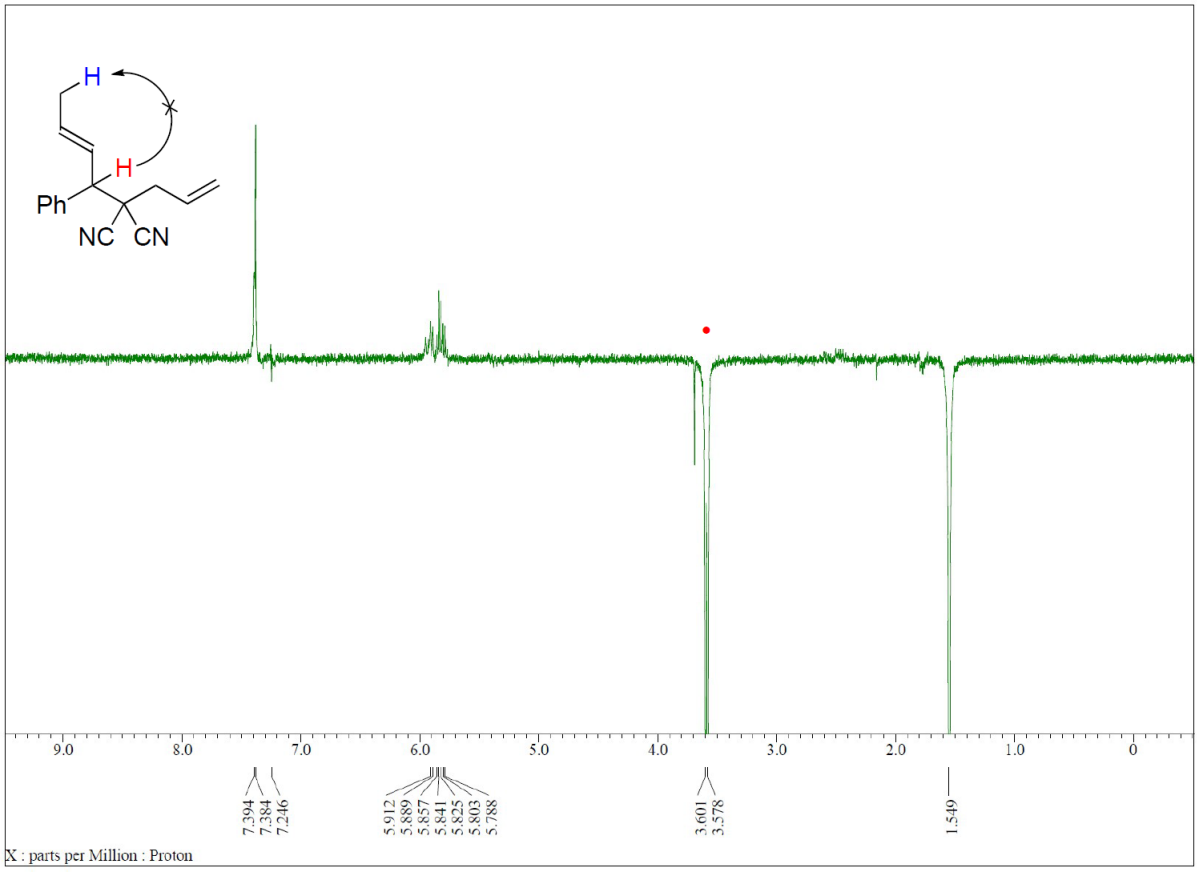
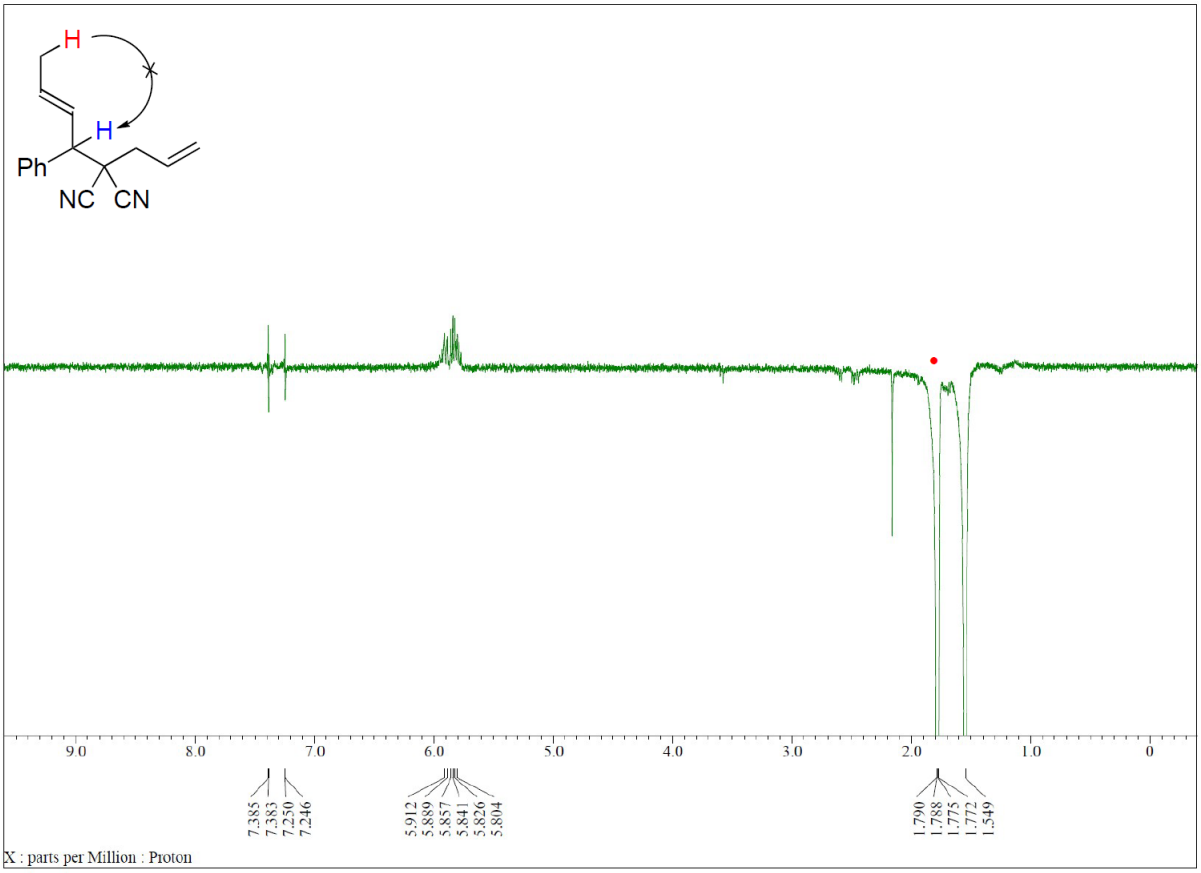
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4.005
3.981
1.693
1.690
1.676
1.672
1.536
X : parts per Million : Proton

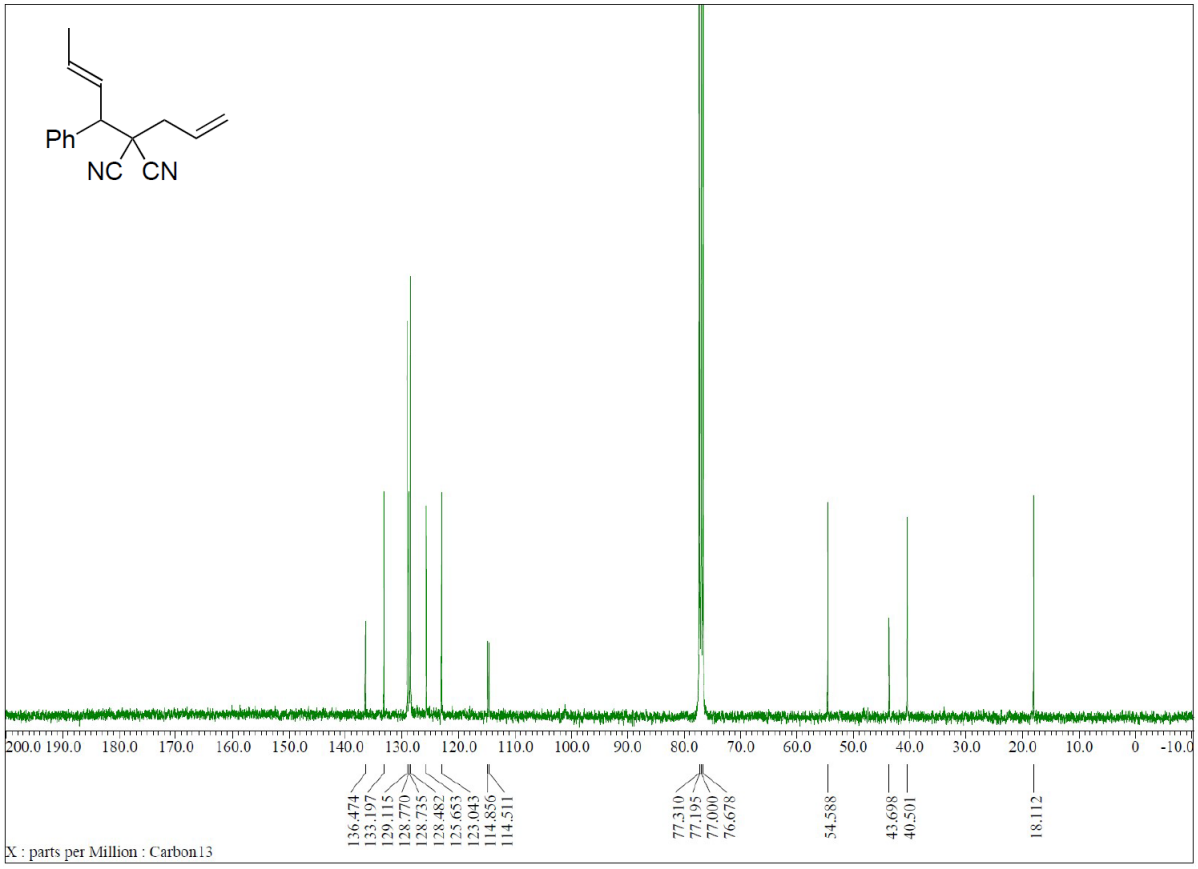

Ph
NC CN
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
136.509
130.621
129.080
128.770
128.747
128.655
125.113
123.135
114.706
114.499
77.322
77.000
76.690
48.298
43.779
40.444
13.512
X : parts per Million : Carbon13

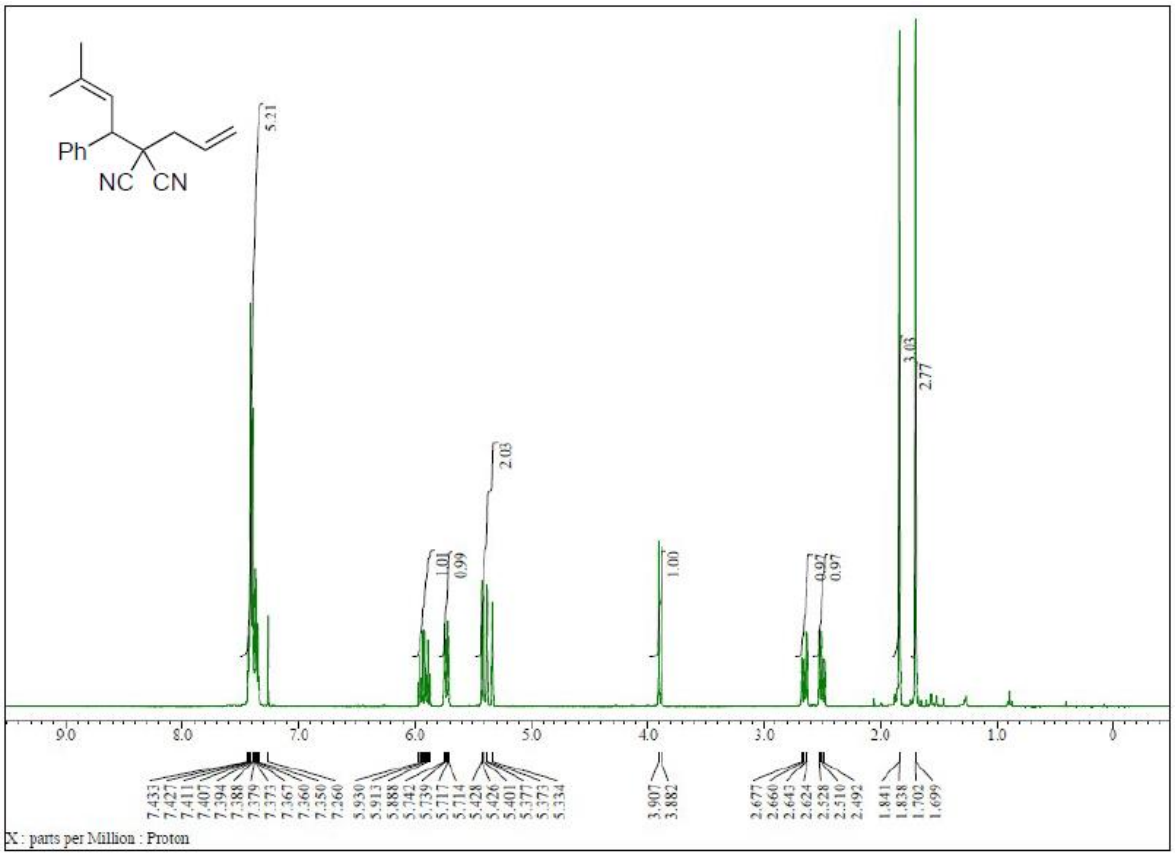

Ph
NC CN
E:Z = 66:34
from
OH
Si
E:Z = 81:19
66.00
34.05
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.430
7.409
7.397
7.381
7.376
7.360
7.348
7.260
5.934
5.928
5.924
5.915
5.905
5.899
5.854
5.423
5.411
5.397
5.369
5.367
5.324
4.018
3.993
3.614
3.591
2.651
2.632
2.616
2.598
2.511
2.492
2.475
1.801
1.788
1.786
1.706
1.702
1.689
1.686
1.544
X : parts per Million : Proton

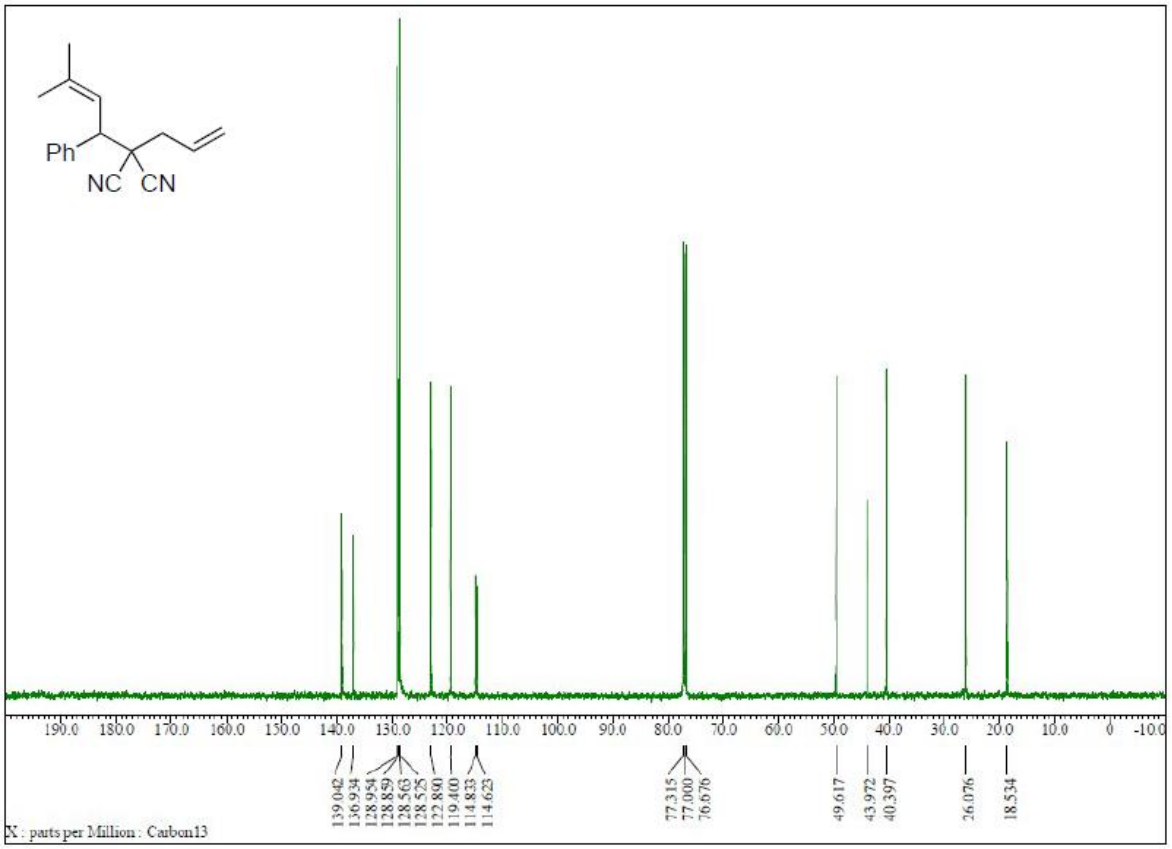

Ph
NC CN
5.04
1.91
1.06
1.64
1.01
1.00
0.99
0.99
2.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.407
7.397
7.381
7.376
7.360
7.347
7.260
5.940
5.924
5.915
5.905
5.899
5.854
5.838
5.423
5.397
5.367
5.324
3.614
3.591
2.651
2.633
2.616
2.598
2.511
2.492
1.801
1.788
1.785
1.559
X : parts per Million : Proton

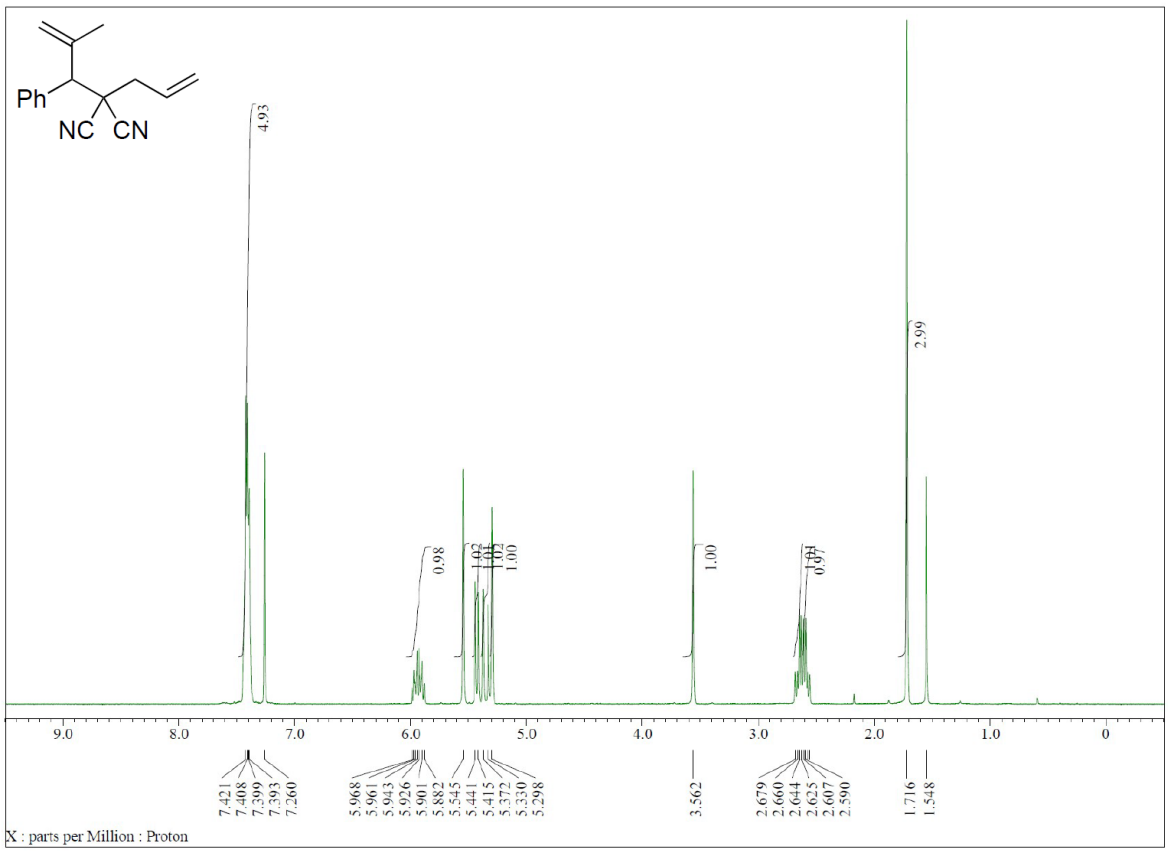

H
H
Ph
NC CN
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.394
7.384
7.246
5.912
5.889
5.857
5.841
5.825
5.803
5.788
3.601
3.578
1.549
X : parts per Million : Proton

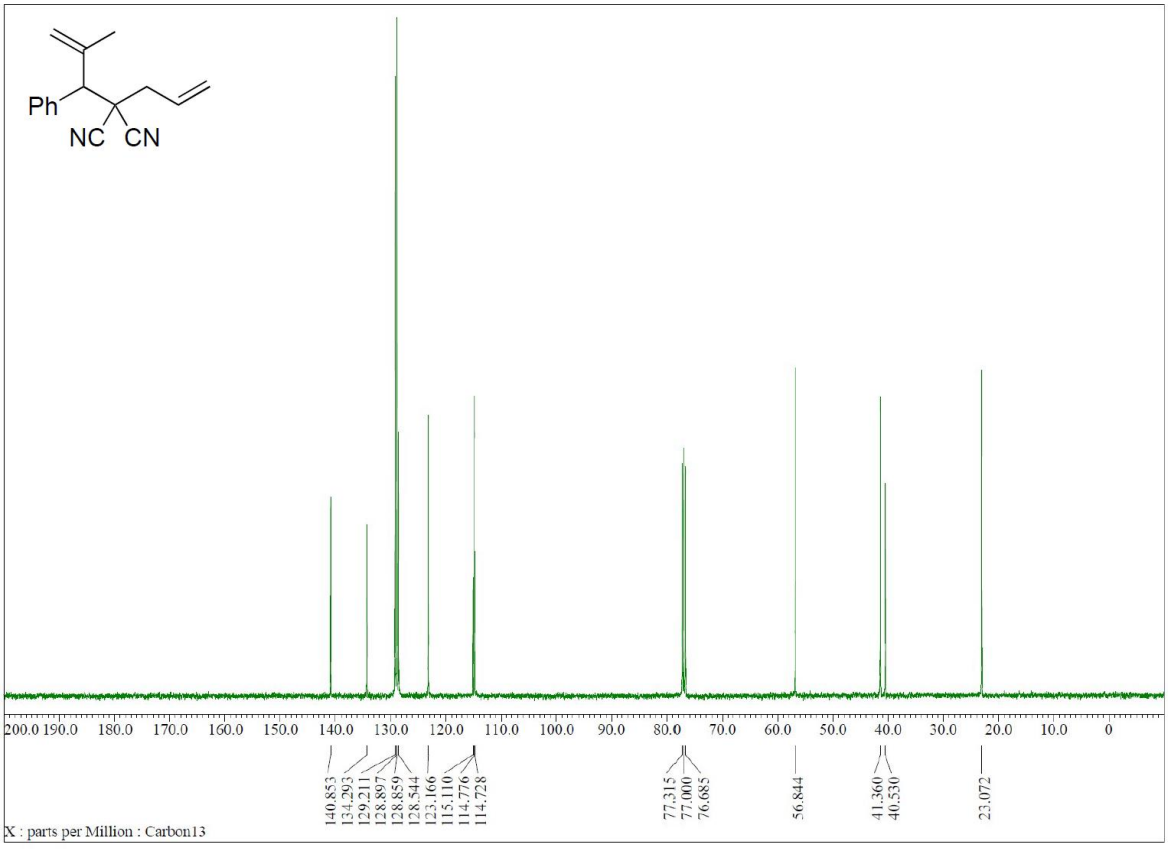

H
H
Ph
NC CN
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.385
7.383
7.250
7.246
5.912
5.889
5.857
5.841
5.826
5.804
1.790
1.788
1.775
1.772
1.549
X : parts per Million : Proton

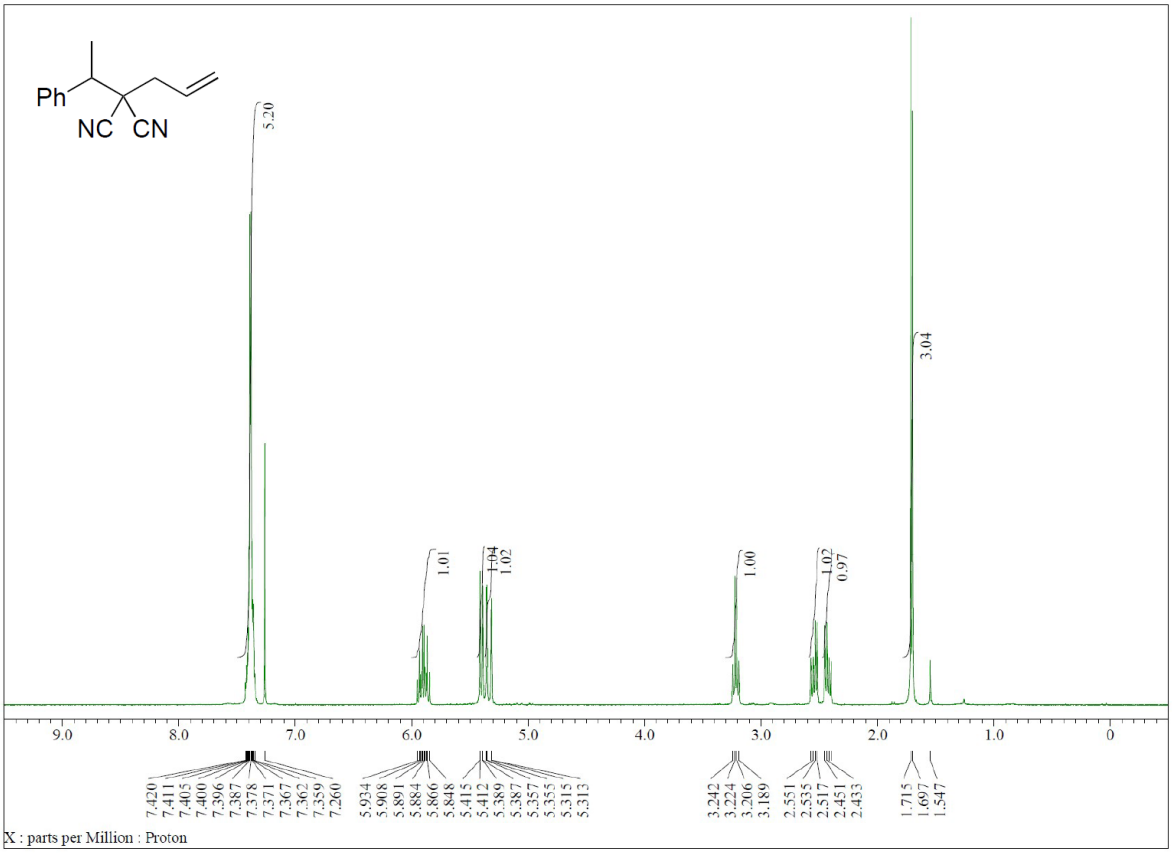

Ph
NC CN
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
136.474
133.197
129.115
128.770
128.735
128.482
125.653
123.043
114.856
114.511
77.310
77.195
77.000
76.678
54.588
43.698
40.501
18.112
X : parts per Million : Carbon13

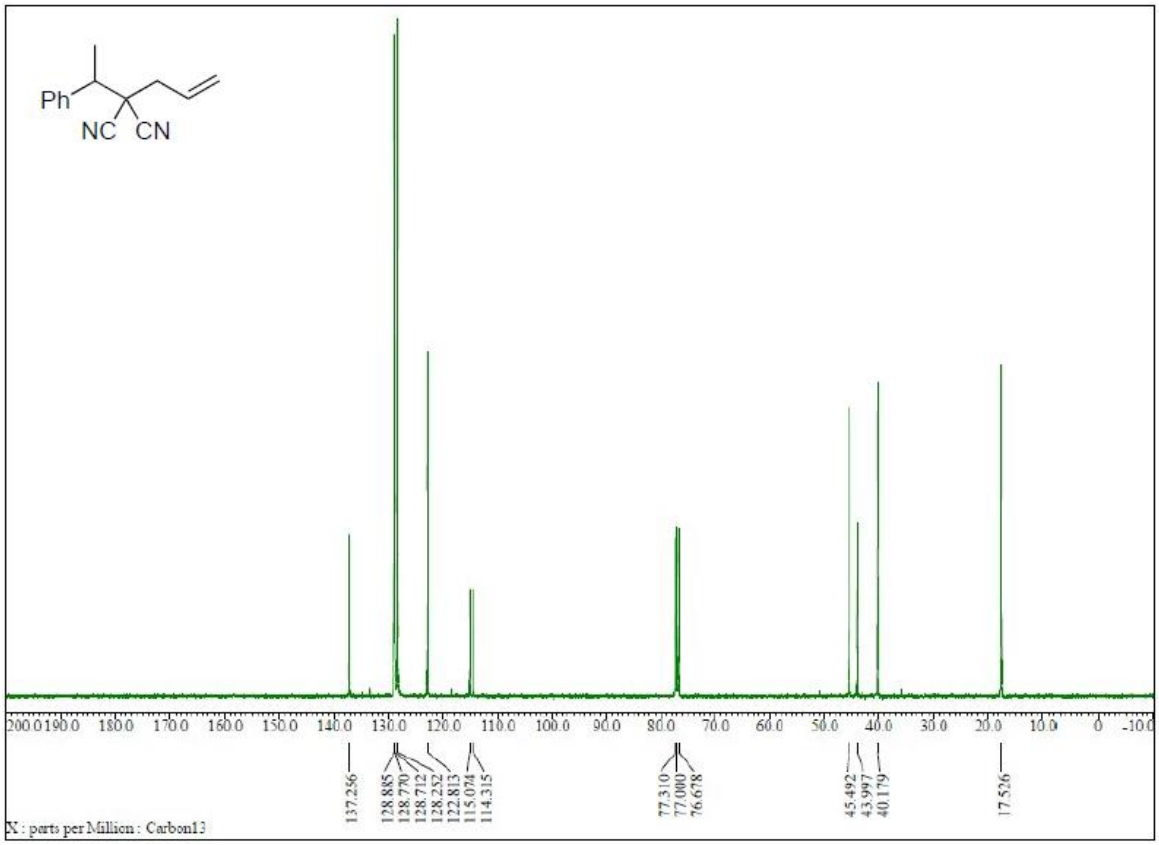

Ph
NC CN
5.21
2.03
1.01
0.99
1.00
0.97
0.97
3.03
2.77
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.433
7.427
7.411
7.407
7.394
7.388
7.379
7.373
7.367
7.360
7.350
7.260
5.930
5.913
5.888
5.742
5.739
5.717
5.714
5.428
5.426
5.401
5.377
5.373
5.334
3.907
3.882
2.677
2.660
2.643
2.624
2.528
2.510
2.492
1.841
1.838
1.702
1.699
X : parts per Million : Proton

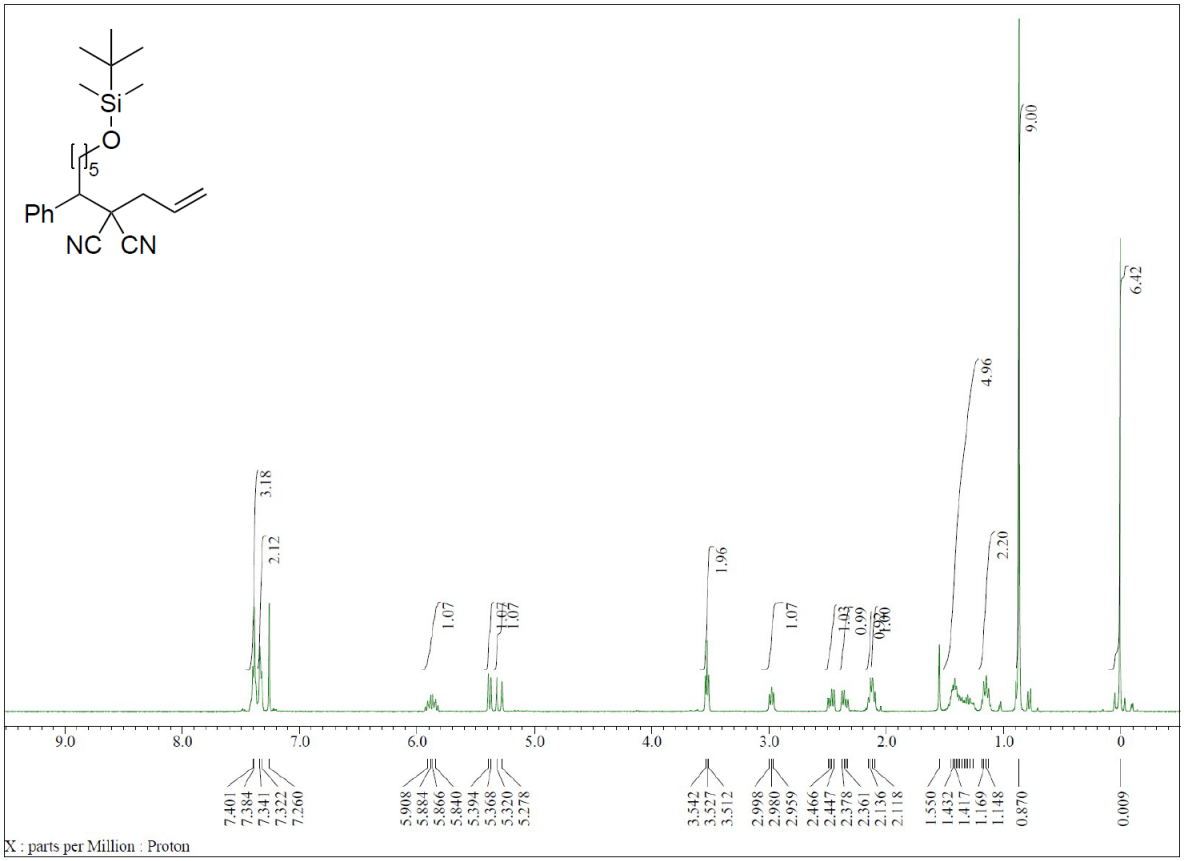

Ph
NC CN
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
139.042
136.934
128.954
128.859
128.565
128.525
122.800
119.400
114.833
114.623
77.315
77.000
76.676
49.617
43.972
40.397
26.076
18.534
X : parts per Million : Carbon13

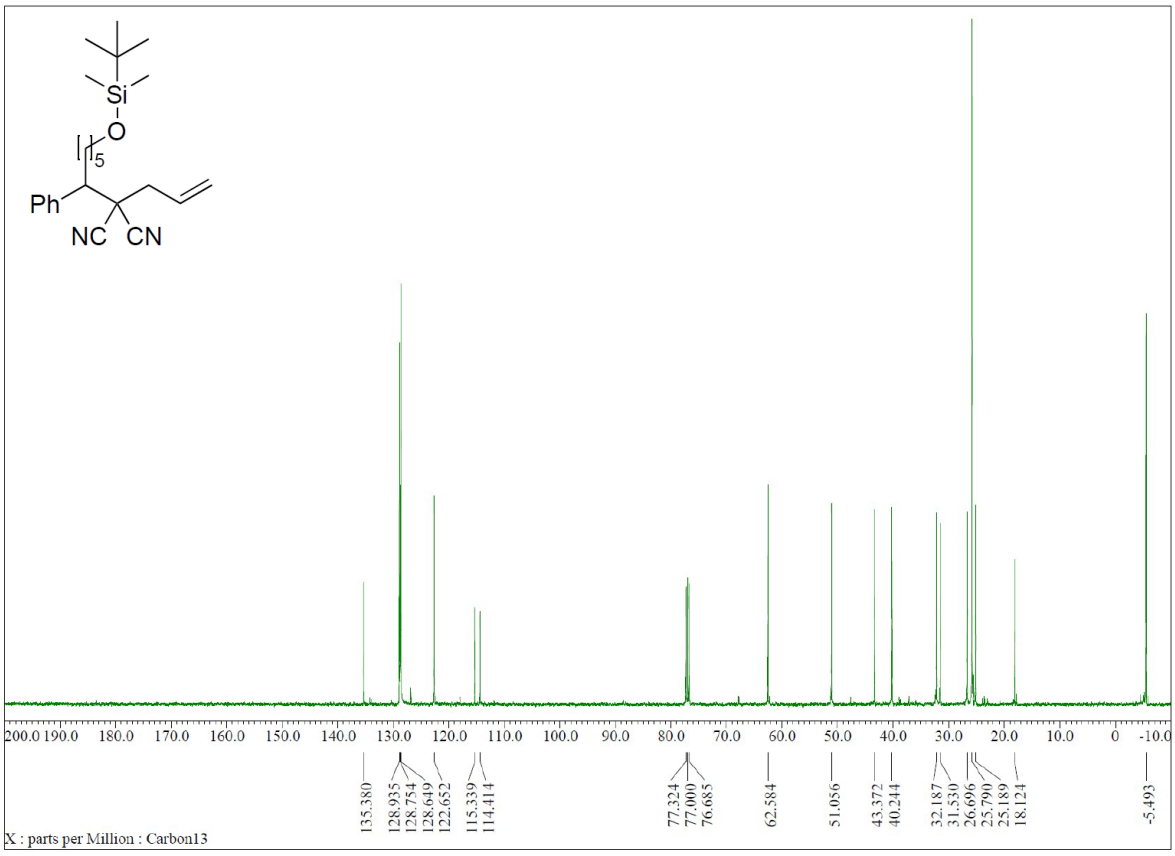

Ph
NC CN
4.93
2.99
0.98
1.02
1.01
1.02
1.00
1.00
0.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.421
7.408
7.399
7.393
7.260
5.968
5.961
5.943
5.926
5.901
5.882
5.545
5.441
5.415
5.372
5.330
5.298
3.562
2.679
2.660
2.644
2.625
2.607
2.590
1.716
1.548
X : parts per Million : Proton

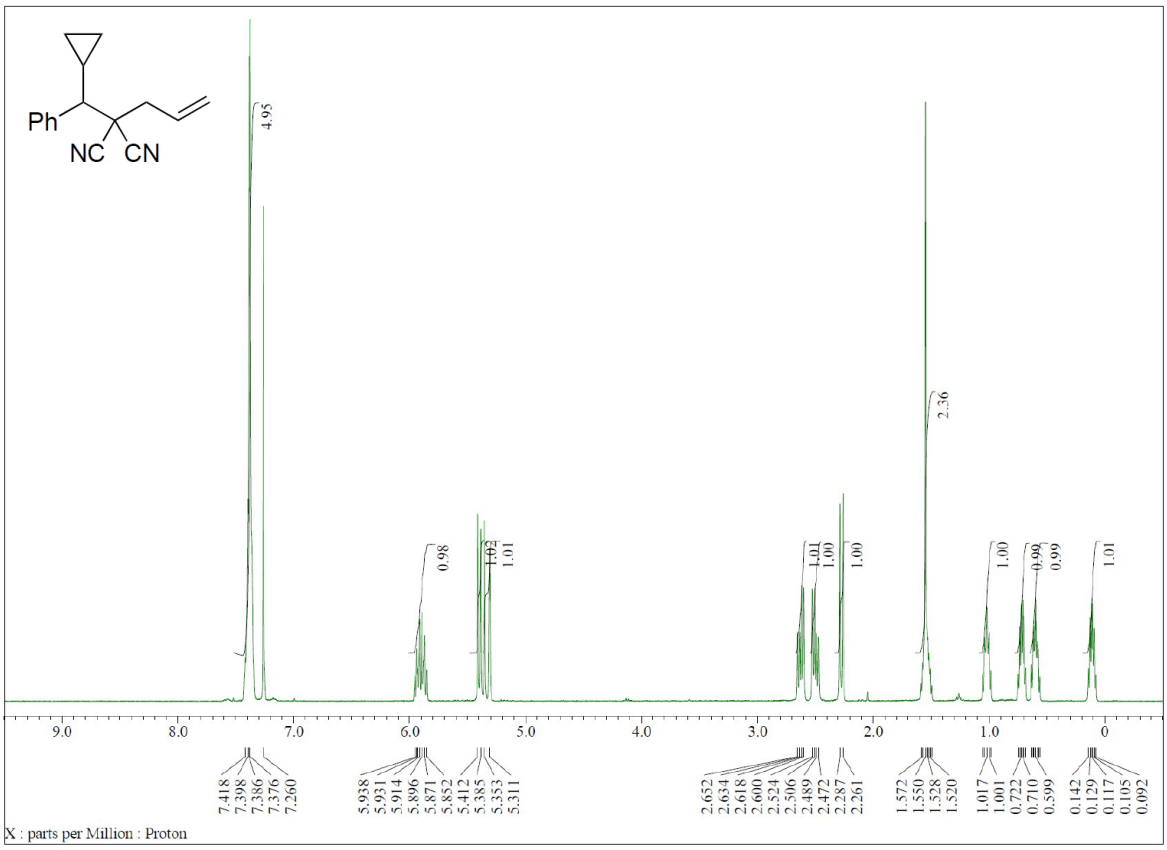

Ph
NC CN
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
140.853
134.293
129.211
128.897
128.859
128.544
123.166
115.110
114.776
114.728
77.315
77.000
76.685
56.844
41.360
40.530
23.072
X : parts per Million : Carbon13

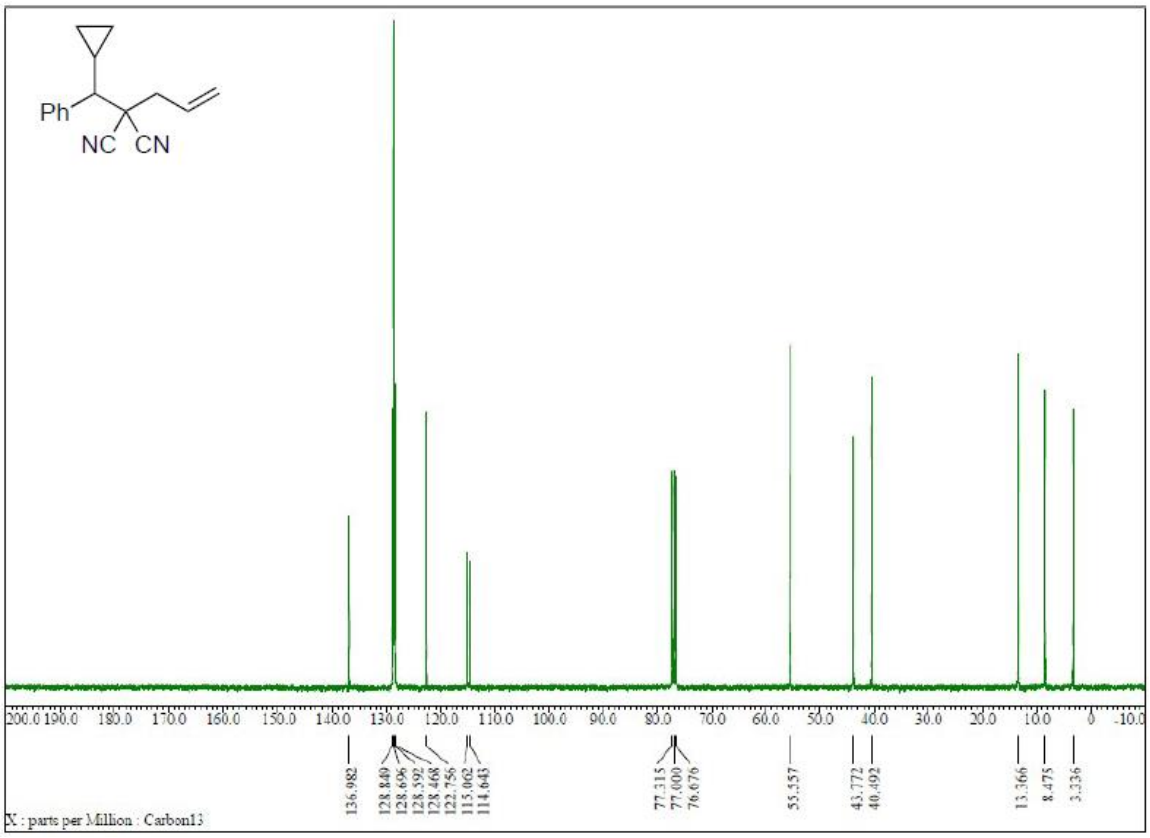

Ph
NC CN
5.20
1.01
1.04
1.02
1.00
1.02
0.97
3.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.420
7.411
7.405
7.400
7.396
7.387
7.378
7.371
7.367
7.362
7.359
7.260
5.934
5.908
5.891
5.884
5.866
5.848
5.415
5.412
5.389
5.387
5.357
5.355
5.315
5.313
3.242
3.224
3.206
3.189
2.551
2.535
2.517
2.451
2.433
1.715
1.697
1.547
X : parts per Million : Proton

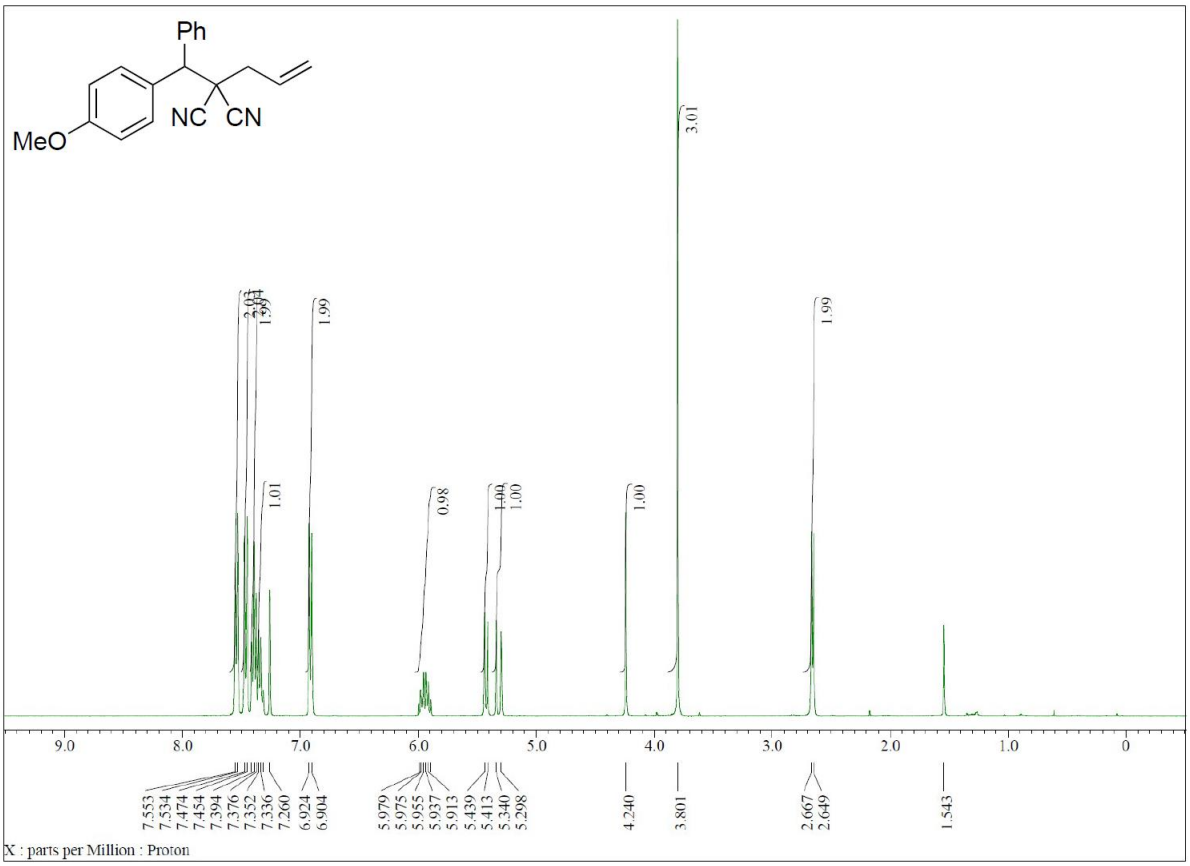

Ph
NC CN
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
137.256
128.885
128.770
128.712
128.252
122.813
115.074
114.315
77.310
77.000
76.678
45.492
43.997
40.179
17.526
X : parts per Million : Carbon13

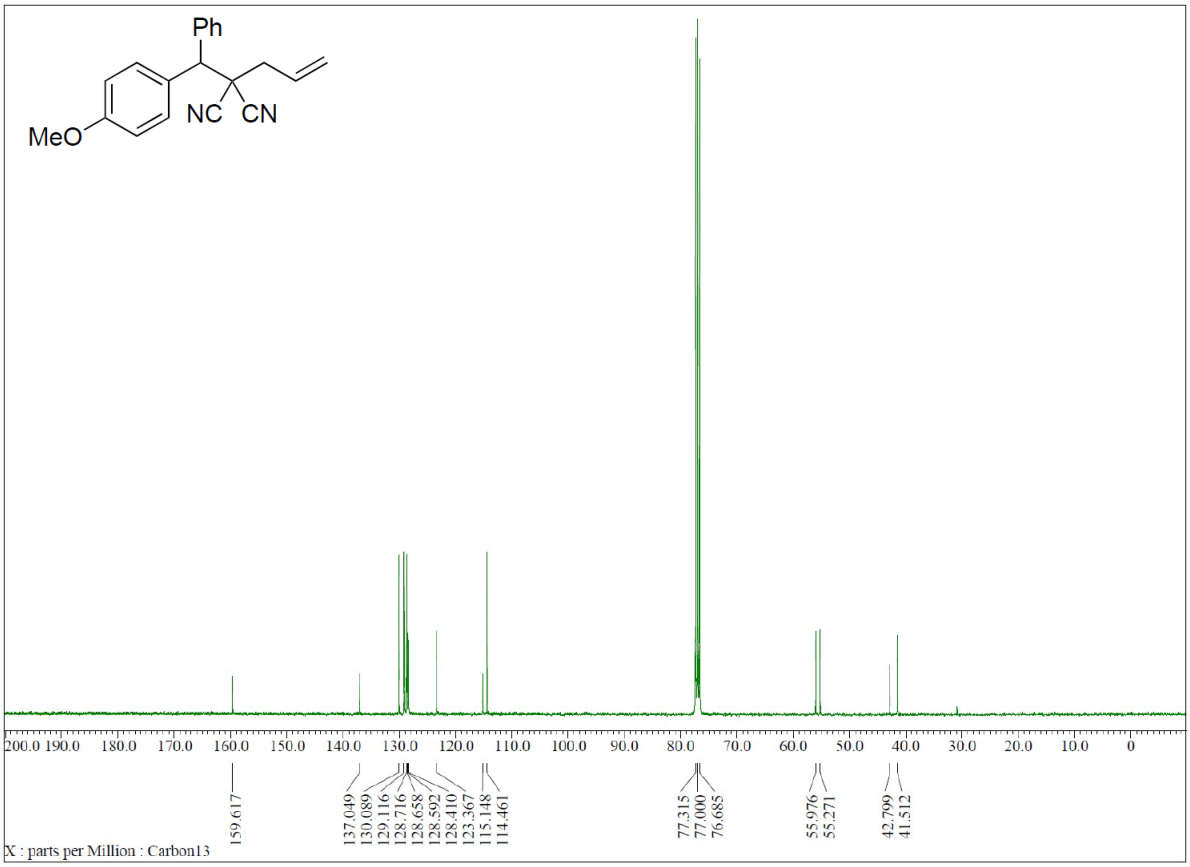

Si
O
5
Ph
NC CN
9.00
6.42
4.96
3.18
2.12
2.20
1.96
1.07
1.07
1.07
1.07
1.03
0.99
0.97
0.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.401
7.384
7.341
7.322
7.260
5.908
5.884
5.866
5.840
5.394
5.368
5.320
5.278
3.542
3.527
3.512
2.998
2.980
2.959
2.466
2.447
2.378
2.361
2.136
2.118
1.550
1.432
1.417
1.169
1.148
0.870
0.009
X : parts per Million : Proton

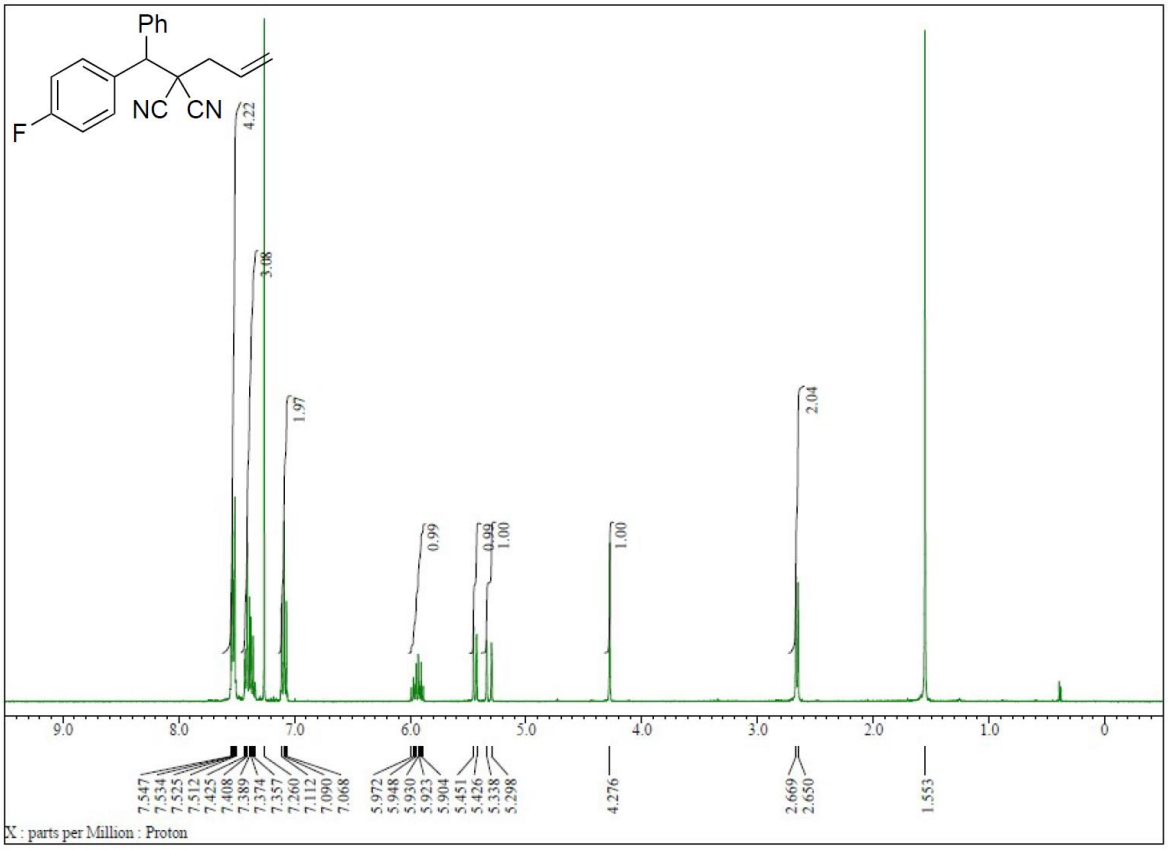

Si
O
5
Ph
NC CN
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
135.380
128.935
128.754
128.649
122.652
115.339
114.414
77.324
77.000
76.685
62.584
51.056
43.372
40.244
32.187
31.530
26.696
25.790
25.189
18.124
-5.493
X : parts per Million : Carbon13

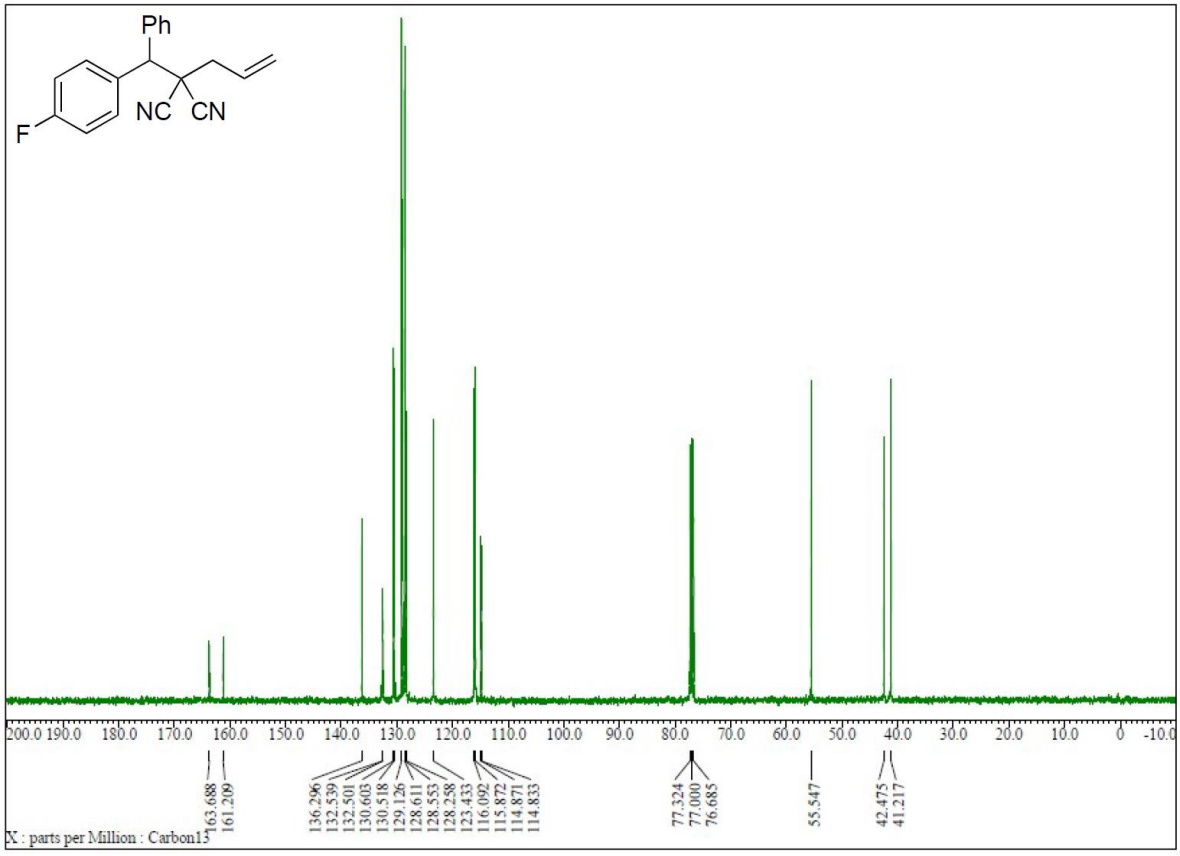

Ph
NC CN
4.95
0.98
1.02
1.01
1.01
1.00
1.00
2.36
1.00
0.99
0.99
1.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.418
7.398
7.386
7.376
7.260
5.938
5.931
5.914
5.896
5.871
5.852
5.412
5.385
5.353
5.311
2.652
2.634
2.618
2.600
2.524
2.506
2.489
2.472
2.287
2.261
1.572
1.550
1.528
1.520
1.017
1.001
0.722
0.710
0.599
0.142
0.129
0.117
0.105
0.092
X : parts per Million : Proton

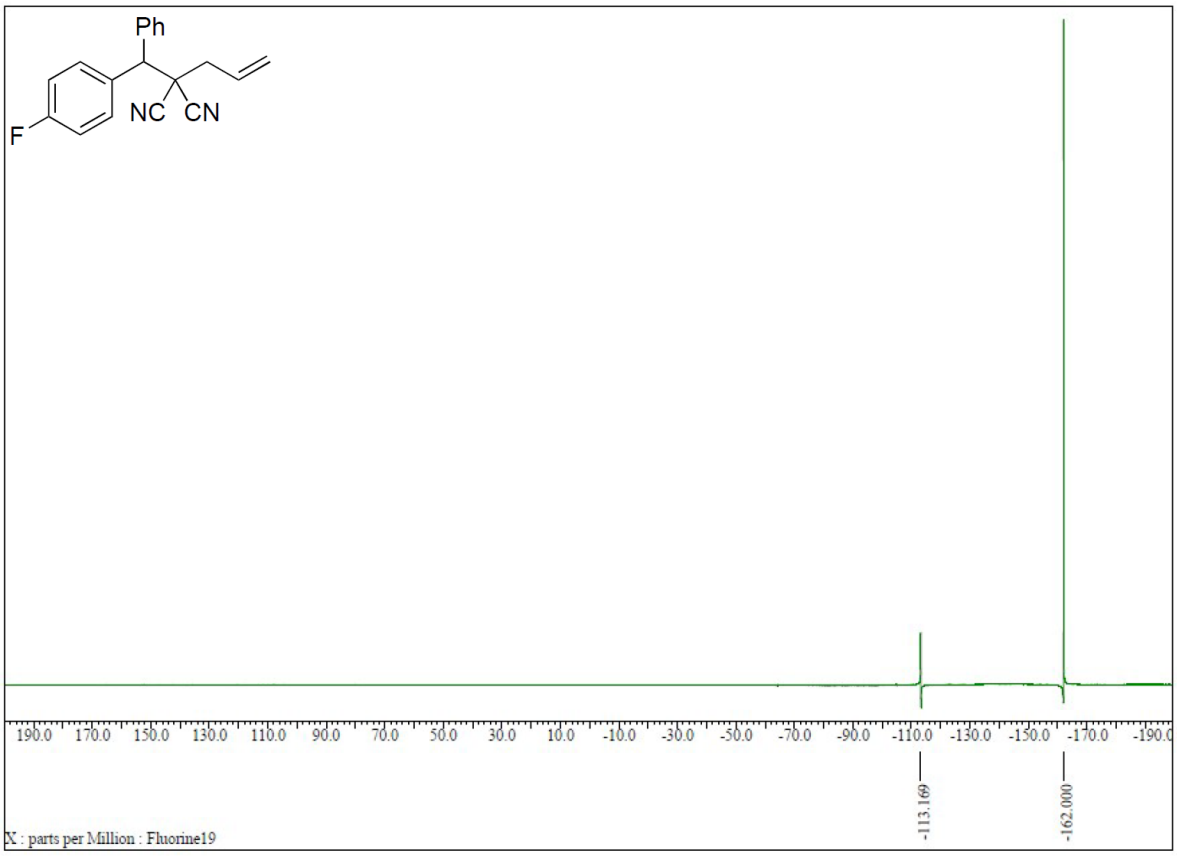

Ph
NC CN
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
136.982
128.849
128.696
128.592
128.468
122.756
115.062
114.643
77.315
77.000
76.676
55.557
43.772
40.492
13.366
8.475
3.336
X : parts per Million : Carbon13

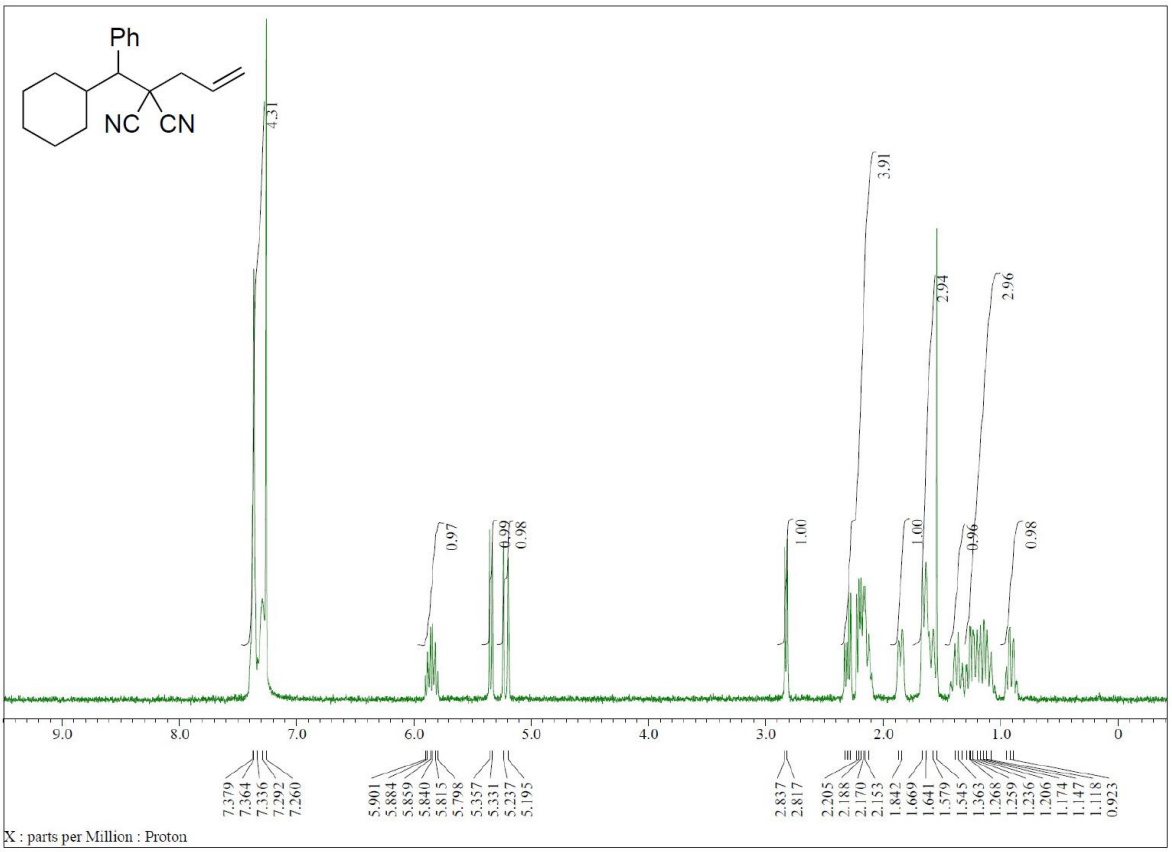

Ph
NC CN
MeO
3.01
1.99
1.99
1.01
0.98
1.00
1.00
1.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.553 7.534 7.474 7.454 7.394 7.376 7.352 7.336 7.260 6.924 6.904
5.979 5.975 5.955 5.937 5.913 5.439 5.413 5.340 5.298
4.240
3.801
2.667 2.649
1.543
X : parts per Million : Proton

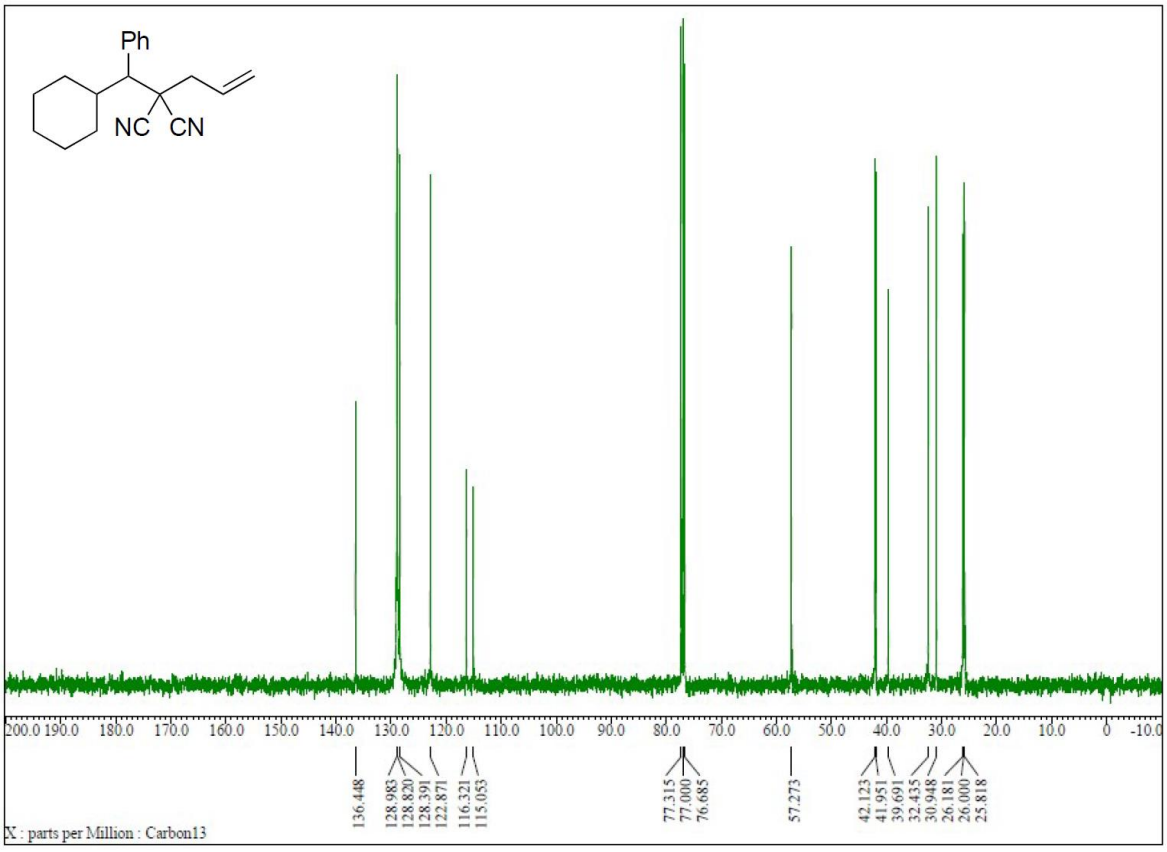

Ph
NC CN
MeO
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
159.617
137.049 130.089 129.116 128.716 128.658 128.592 128.410 123.367 115.148 114.461
77.315 77.000 76.685
55.976 55.271
42.799 41.512
X : parts per Million : Carbon13

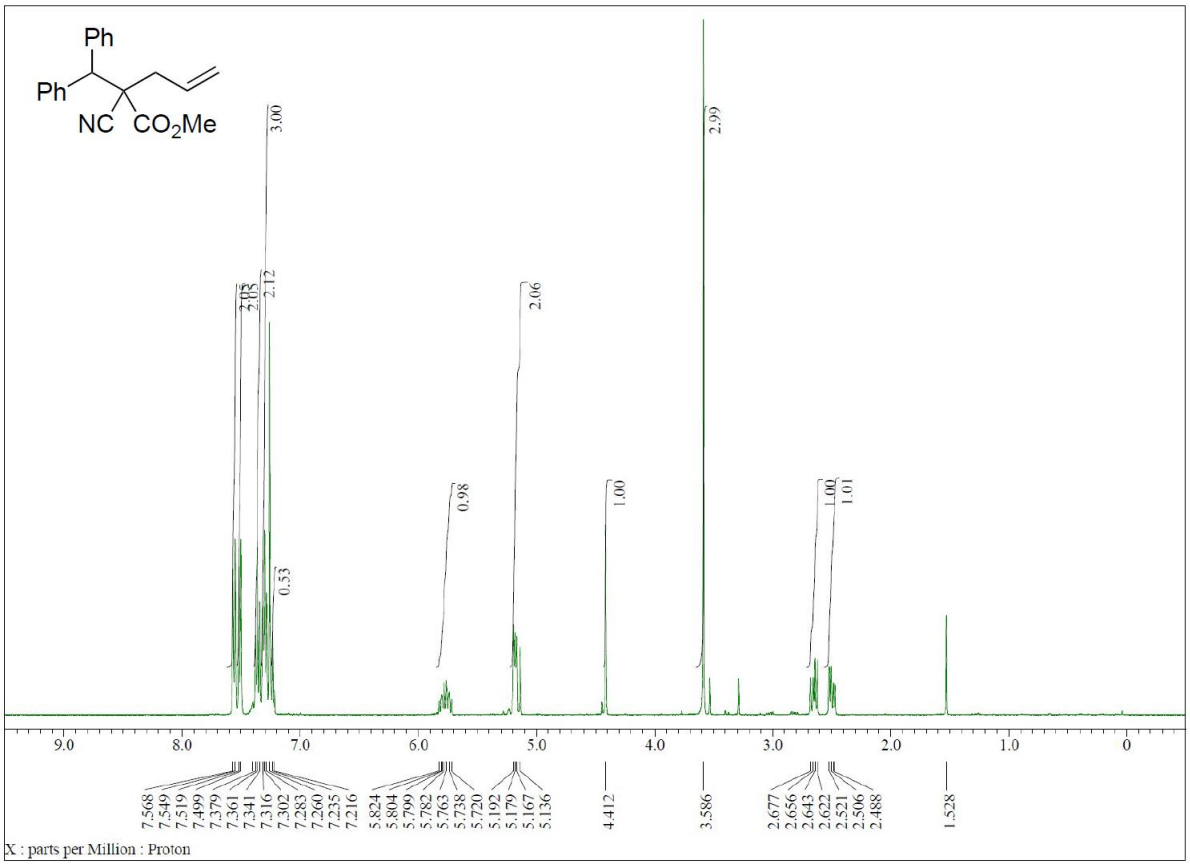

Ph
NC CN
F
4.22
3.08
1.97
0.99
0.99
1.00
1.00
2.04
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.547 7.534 7.525 7.512 7.425 7.408 7.389 7.374 7.357 7.260 7.112 7.090 7.068
5.972 5.948 5.930 5.923 5.904 5.451 5.426 5.338 5.298
4.276
2.669 2.650
1.553
X : parts per Million : Proton

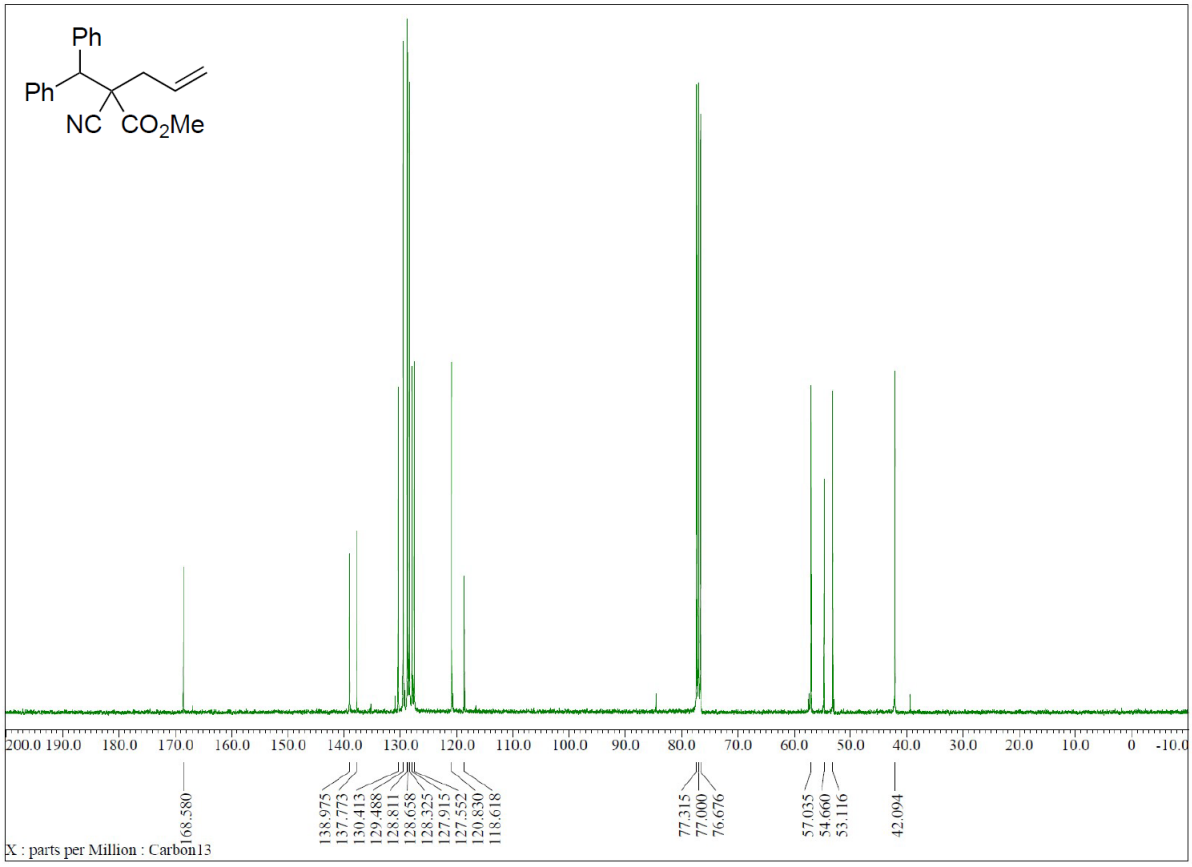

Ph
NC CN
F
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
163.688 161.209
136.296 132.539 132.501 130.603 130.518 129.126 128.611 128.553 128.258 123.433 116.092 115.872 114.871 114.833
77.324 77.000 76.685
55.547
42.475 41.217
X : parts per Million : Carbon13


Ph
NC
CN
F
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
-50.0
-70.0
-90.0
-110.0
-130.0
-150.0
-170.0
-113.169
-162.000
X : parts per Million : Fluorine19


Ph
NC CN
4.31
3.91
2.94
2.96
0.97
0.99
0.98
1.00
1.00
0.96
0.98
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.379 7.364 7.336 7.292 7.260
5.901 5.884 5.859 5.840 5.815 5.798
5.357 5.331 5.237 5.195
2.837 2.817
2.205 2.188 2.170 2.153
1.842 1.669 1.641 1.579 1.545 1.363 1.268 1.259 1.236 1.206 1.174 1.147 1.118 0.923
X : parts per Million : Proton


Ph
NC CN
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
136.448
128.983 128.820 128.391 122.871
116.321 115.053
77.315 77.000 76.685
57.273
42.123 41.951 39.691 32.435 30.948 26.181 26.000 25.818
X : parts per Million : Carbon13


Ph
Ph
NC
CO2Me
3.00
2.99
2.12
2.06
0.98
1.00
1.00
1.01
0.53
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.568
7.549
7.519
7.499
7.379
7.361
7.341
7.316
7.302
7.283
7.260
7.235
7.216
5.824
5.804
5.799
5.782
5.763
5.738
5.720
5.192
5.179
5.167
5.136
4.412
3.586
2.677
2.656
2.643
2.622
2.521
2.506
2.488
1.528
X : parts per Million : Proton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Ph
NC
CO2Me
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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
168.580
138.975
137.773
130.413
129.488
128.811
128.658
128.325
127.915
127.552
120.830
118.618
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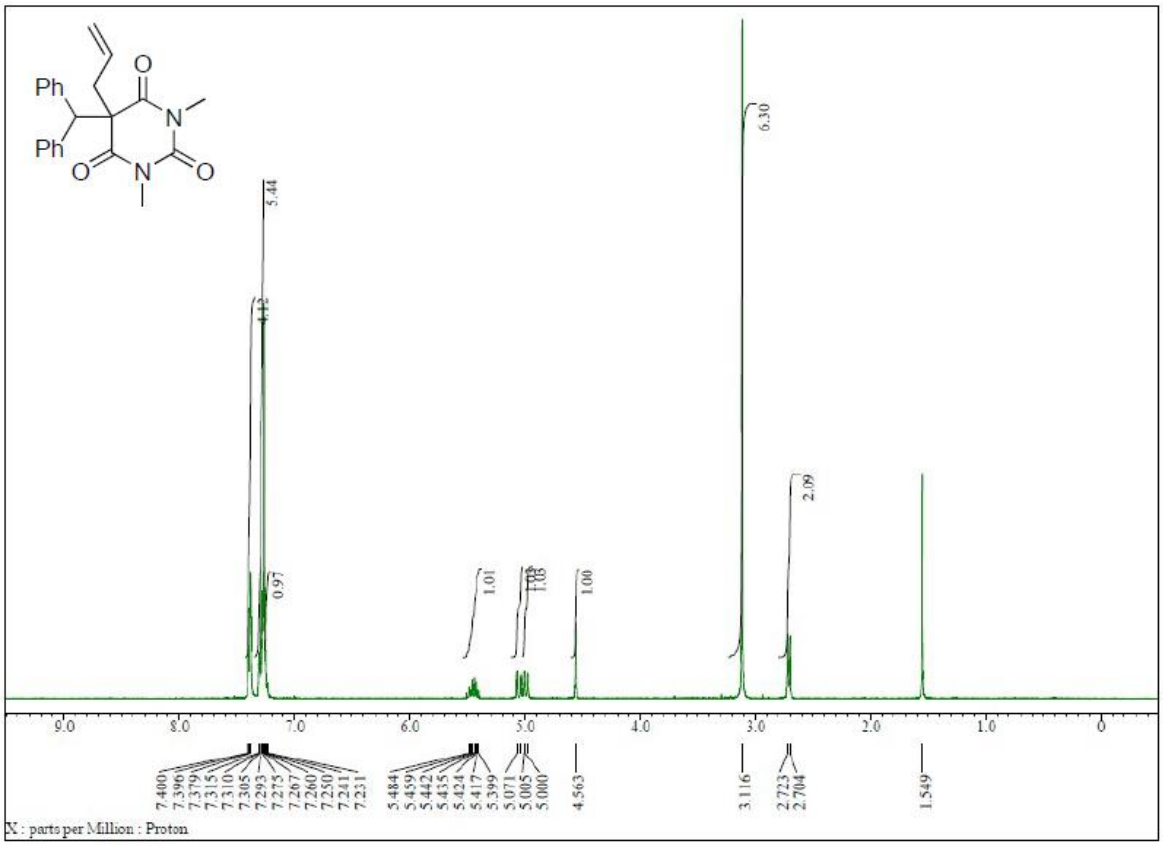
77.000
76.676
57.035
54.660
53.116
42.094
X : parts per Million : Carbon13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Ph
O
N
O
N
O
5.44
6.30
2.09
0.97
1.01
1.00
9.0
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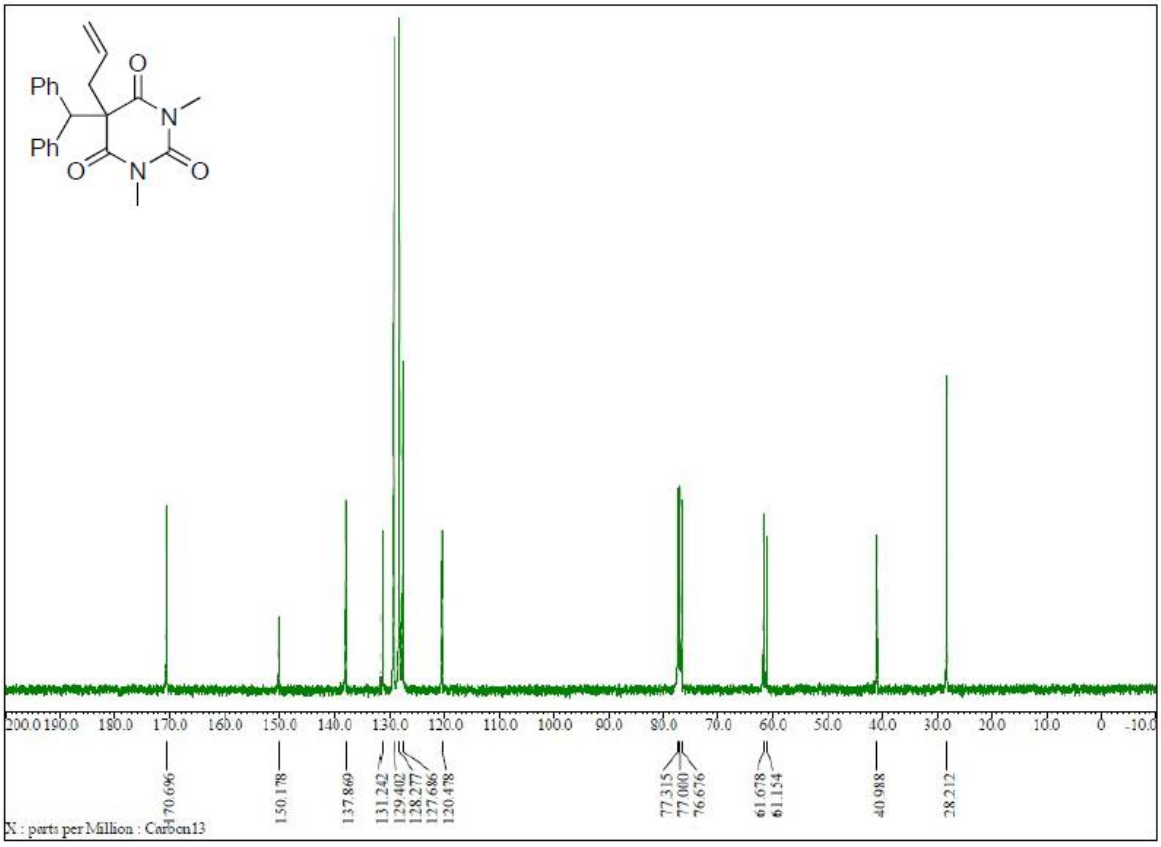
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.400
7.396
7.379
7.315
7.310
7.305
7.293
7.275
7.267
7.260
7.250
7.241
7.231
5.484
5.459
5.442
5.435
5.424
5.417
5.399
5.071
5.005
5.000
4.563
3.116
2.723
2.704
1.549
X : parts per Million : Proton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Ph
O
N
O
N
O
200.0
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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
-10.0
170.696
150.178
137.869
131.242
129.402
128.277
127.686
120.478
77.315
77.000
76.676
61.678
61.154
40.988
28.212
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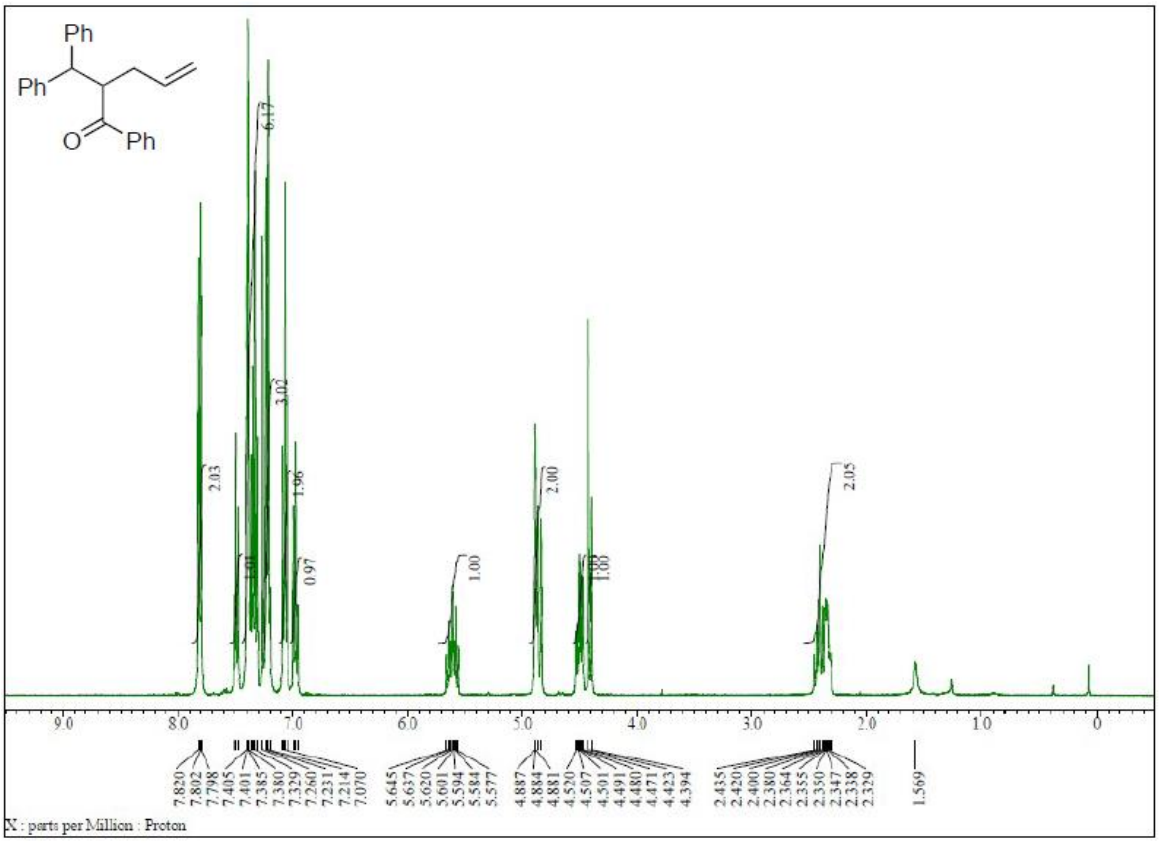
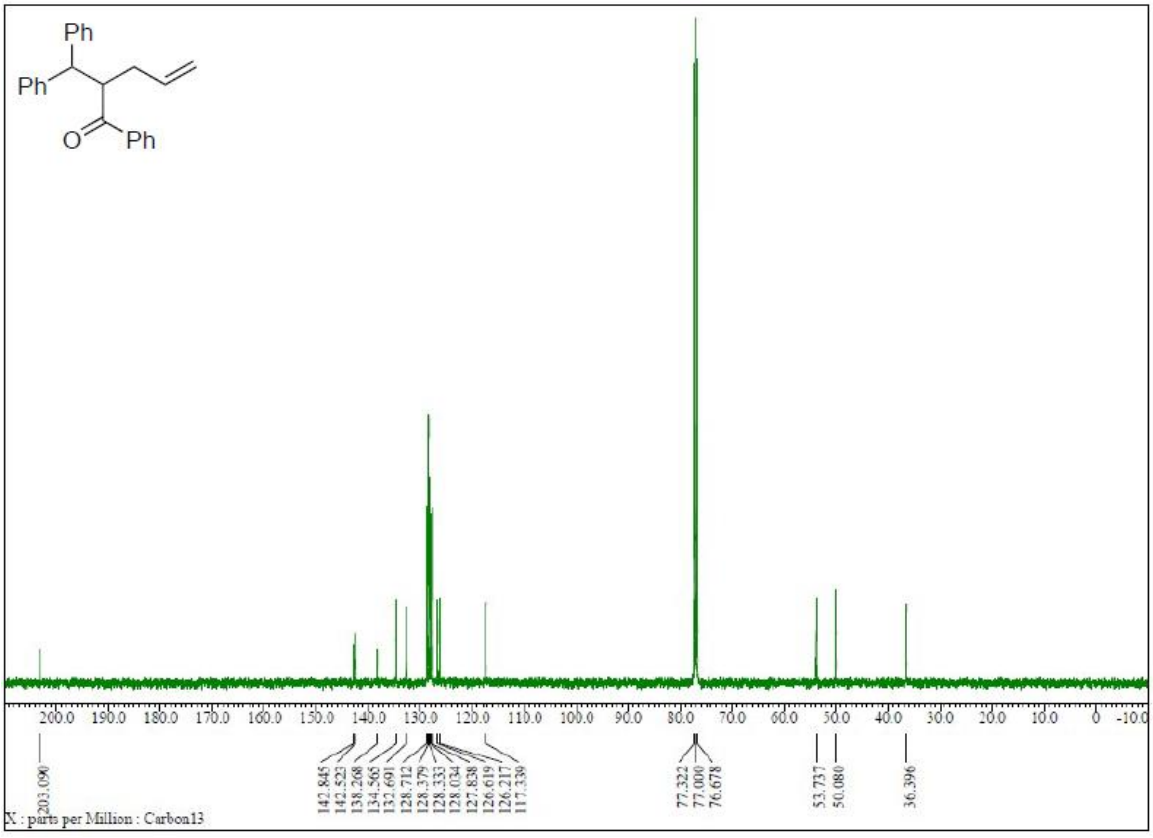
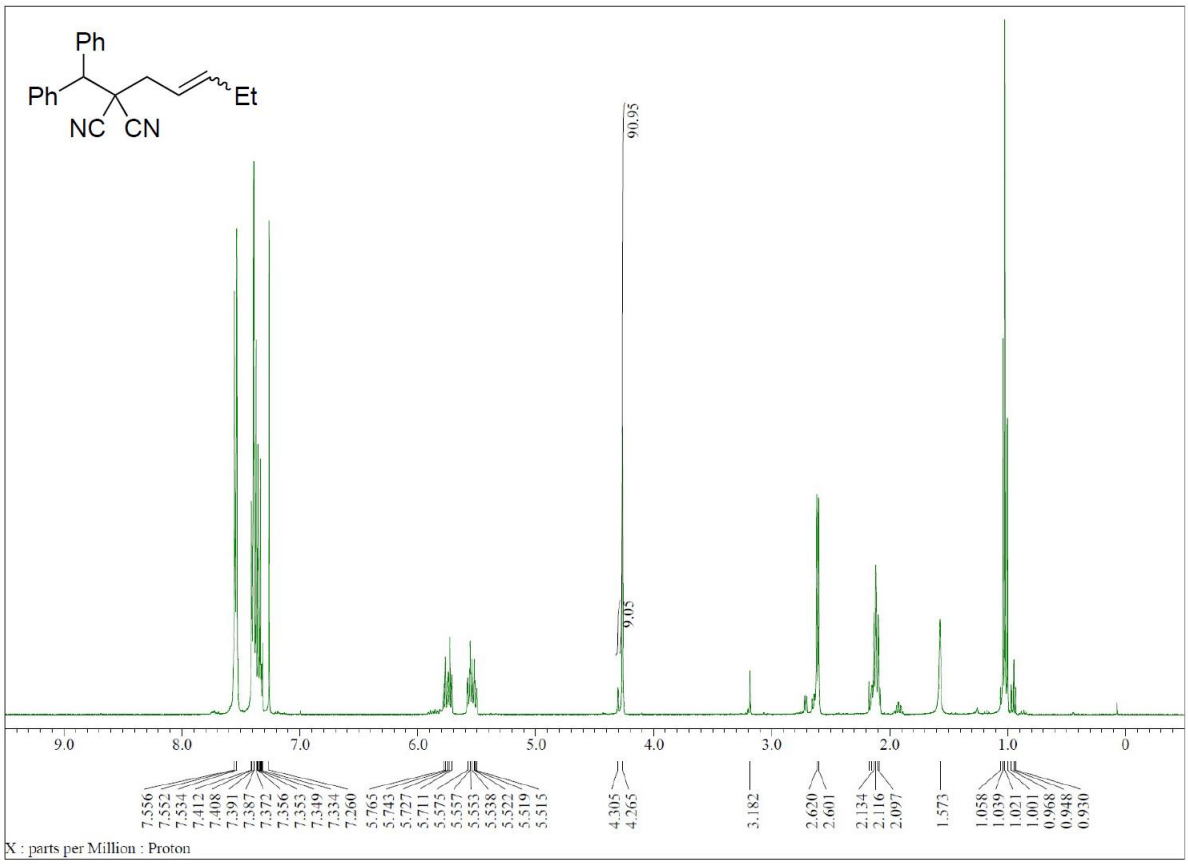
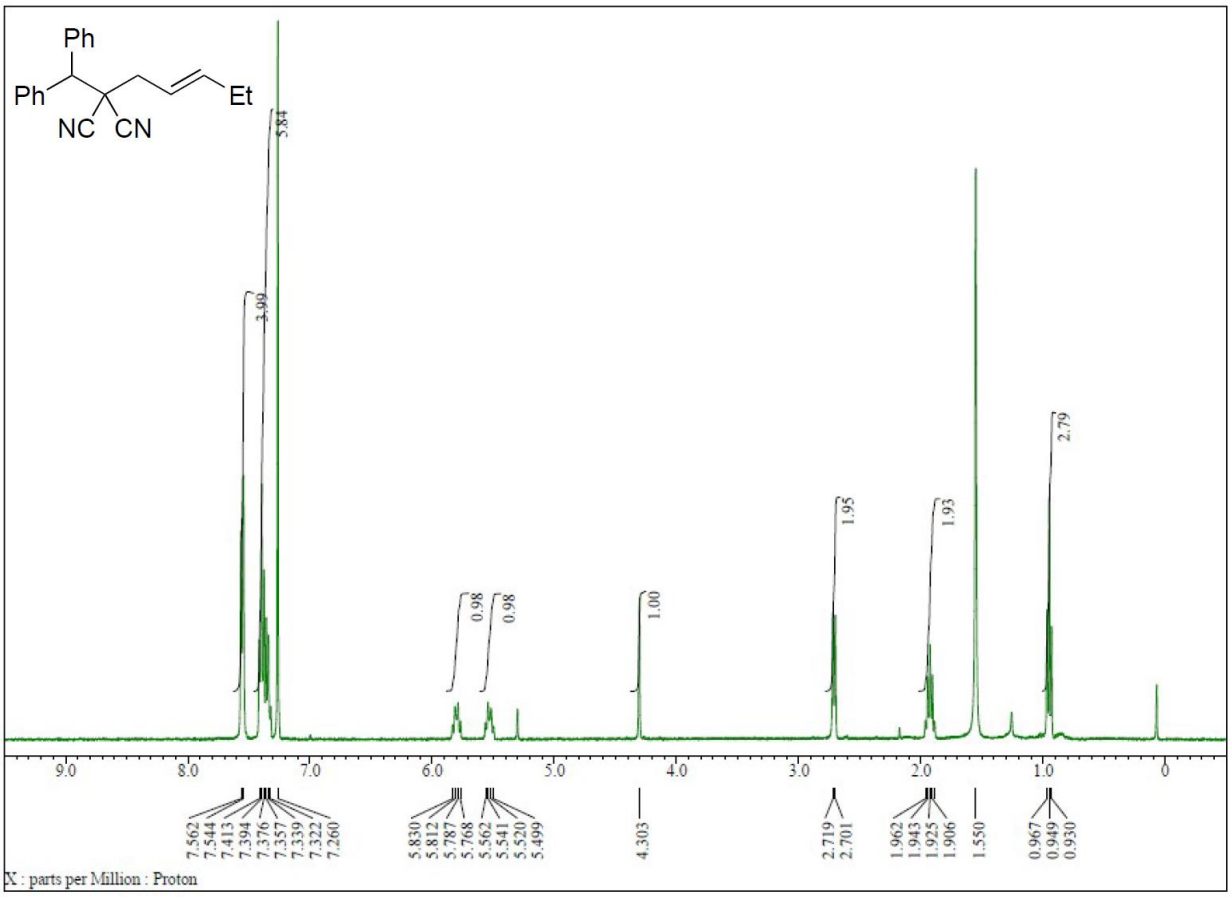

Ph
Ph
O
Ph
X : parts per Million : Proton


Ph
Ph
O
Ph
X : parts per Million : Carbon13


Ph
Ph
Et
NC
CN
90.95
9.05
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.556
7.552
7.534
7.412
7.408
7.391
7.387
7.372
7.356
7.353
7.349
7.334
7.260
5.765
5.743
5.727
5.711
5.575
5.557
5.553
5.538
5.522
5.519
5.515
4.305
4.265
3.182
2.620
2.601
2.134
2.116
2.097
1.573
1.058
1.039
1.021
1.001
0.968
0.948
0.930
X : parts per Million : Proton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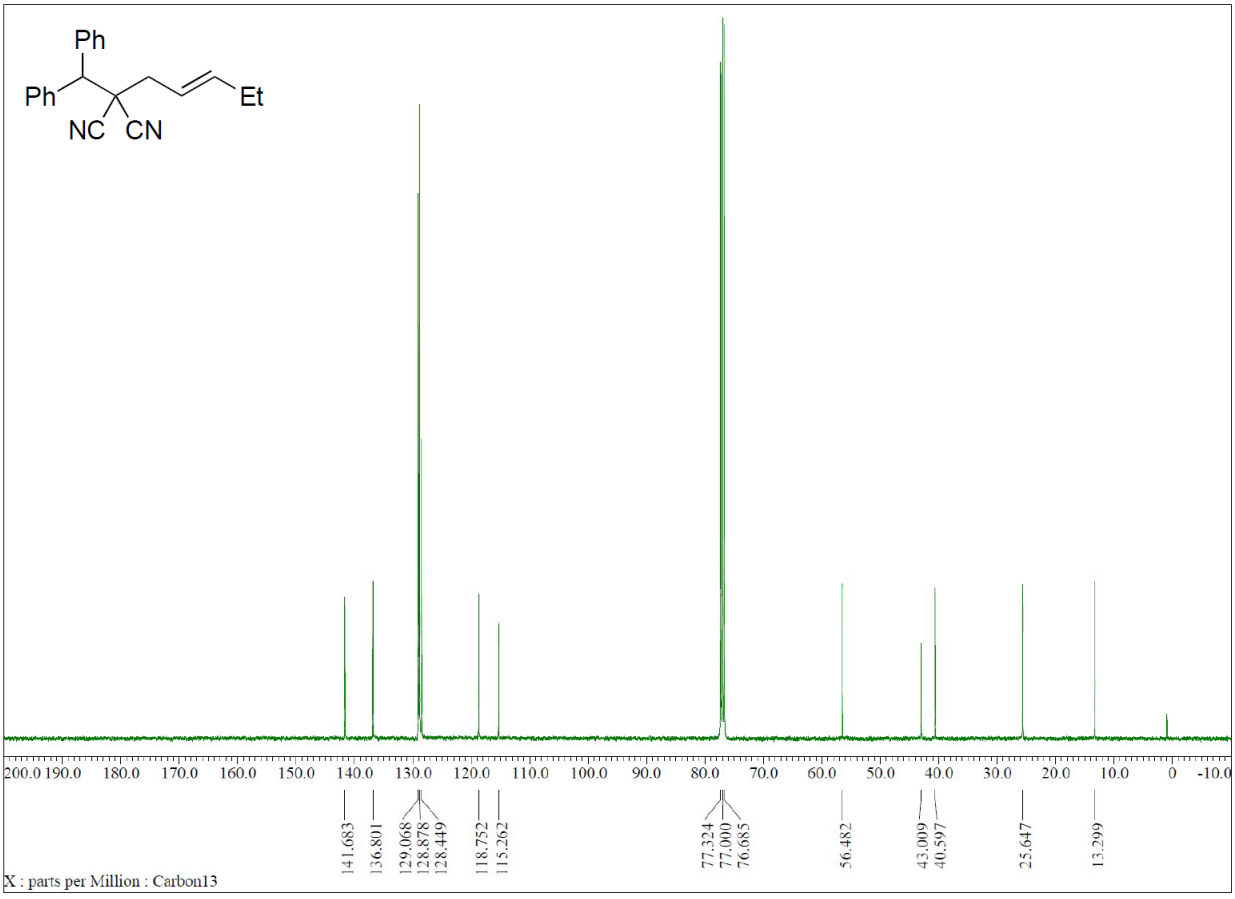
Ph
Et
NC
CN
5.84
3.99
0.98
0.98
1.00
1.95
1.93
2.79
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.562
7.544
7.413
7.394
7.376
7.357
7.339
7.322
7.260
5.830
5.812
5.787
5.768
5.562
5.541
5.520
5.499
4.303
2.719
2.701
1.962
1.943
1.925
1.906
1.550
0.967
0.949
0.930
X : parts per Million : Proton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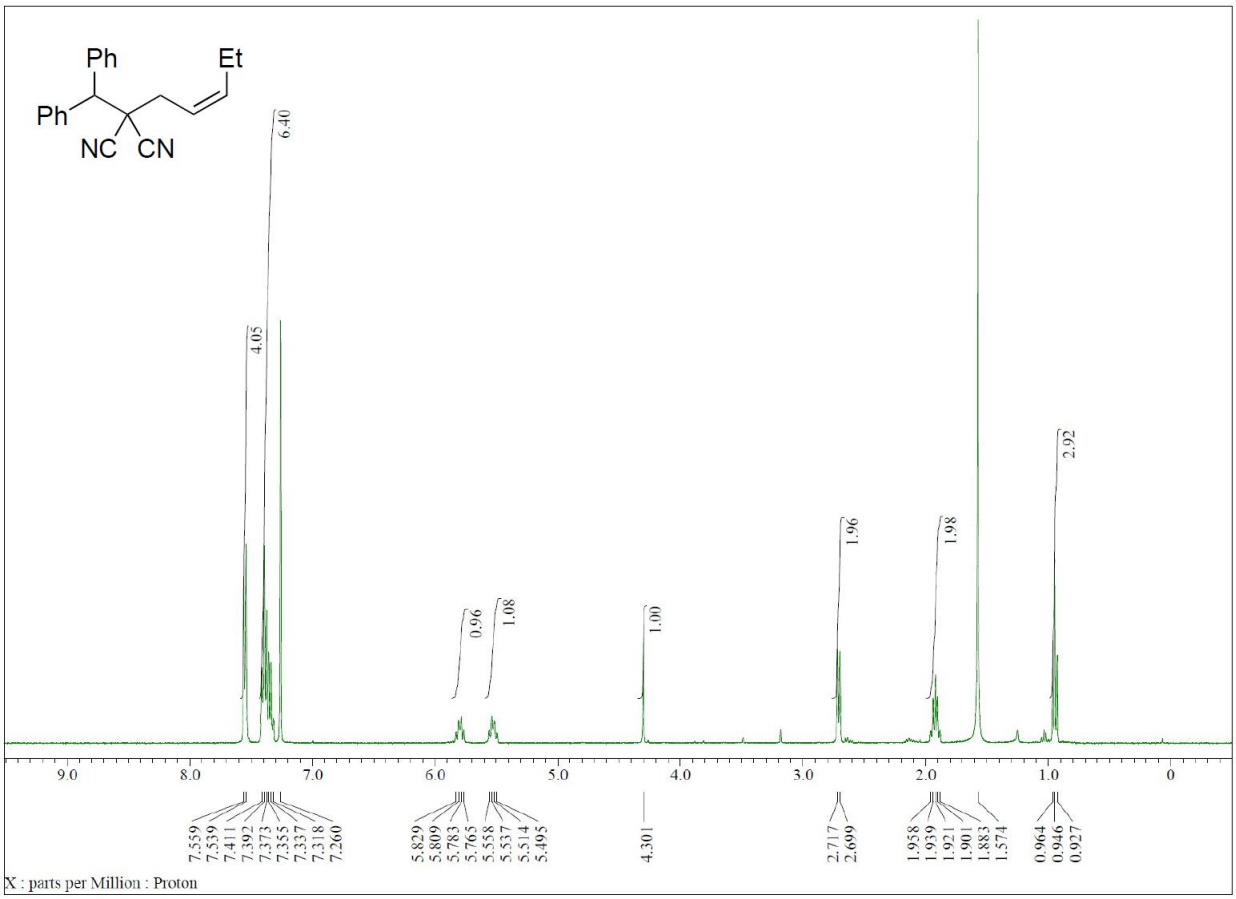
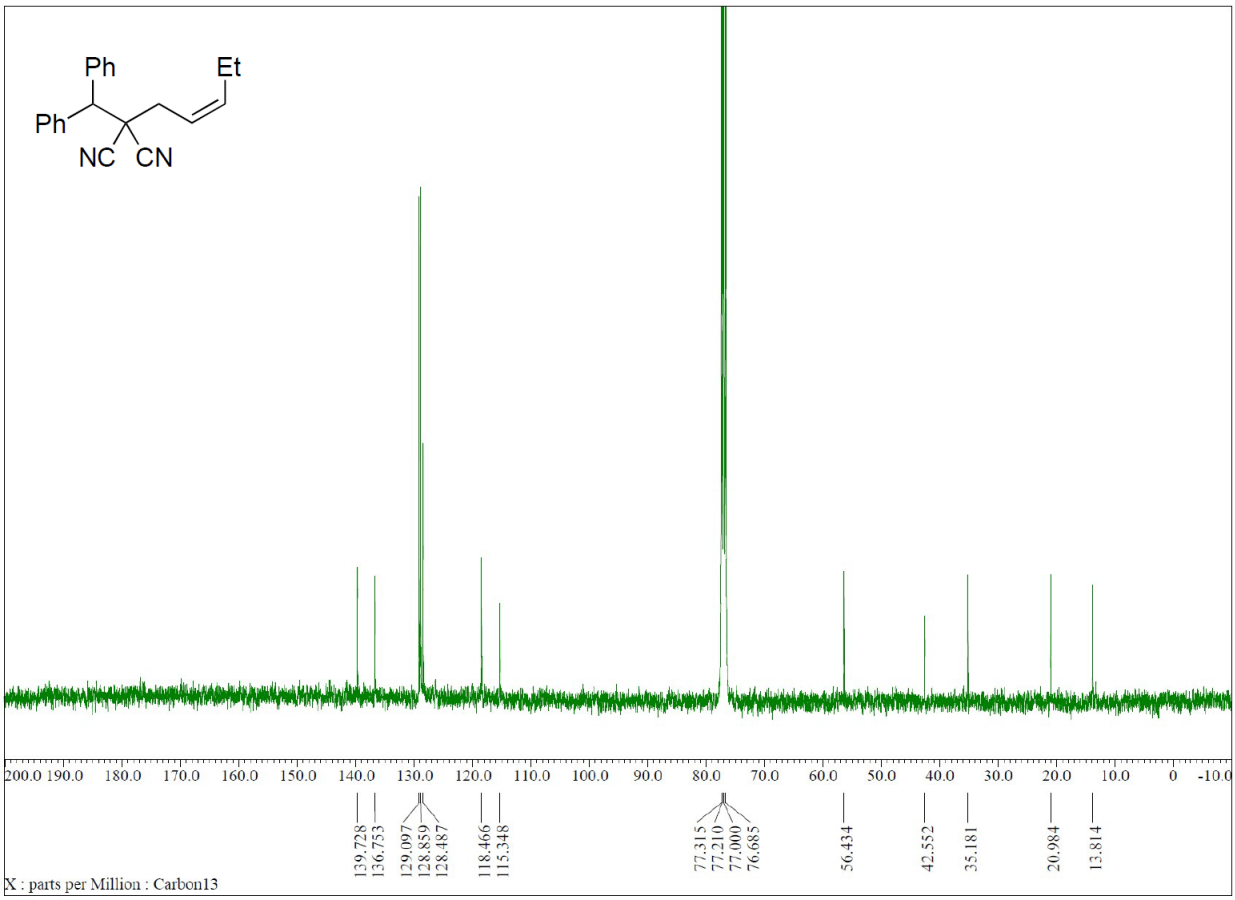
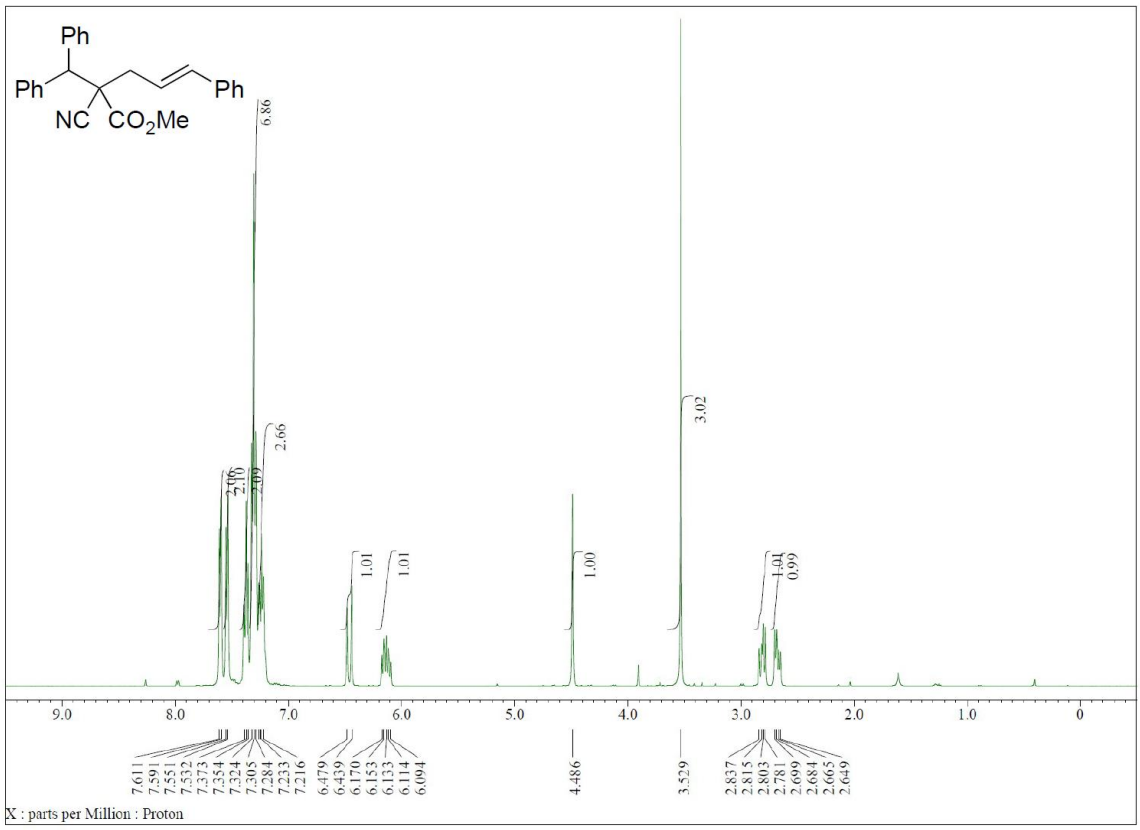
Ph
Et
NC
CN
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
141.683
136.801
129.068
128.878
128.449
118.752
115.262
77.324
77.000
76.685
56.482
43.009
40.597
25.647
13.299
X : parts per Million : Carbon13


Ph
Et
Ph
NC
CN
6.40
4.05
0.96
1.08
1.00
1.96
1.98
2.92
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.559
7.539
7.411
7.392
7.373
7.355
7.337
7.318
7.260
5.829
5.809
5.783
5.765
5.558
5.537
5.514
5.495
4.301
2.717
2.699
1.958
1.939
1.921
1.901
1.883
1.574
0.964
0.946
0.927
X : parts per Million : Proton


Ph
Et
Ph
NC
CN
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
139.728
136.753
129.097
128.859
128.487
118.466
115.348
77.315
77.210
77.000
76.685
56.434
42.552
35.181
20.984
13.814
X : parts per Million : Carbon13


Ph
Ph
Ph
NC
CO2Me
6.86
2.66
3.02
1.01
1.01
1.00
1.01
0.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.611
7.591
7.551
7.532
7.373
7.354
7.324
7.305
7.284
7.233
7.216
6.479
6.439
6.170
6.153
6.133
6.114
6.094
4.486
3.529
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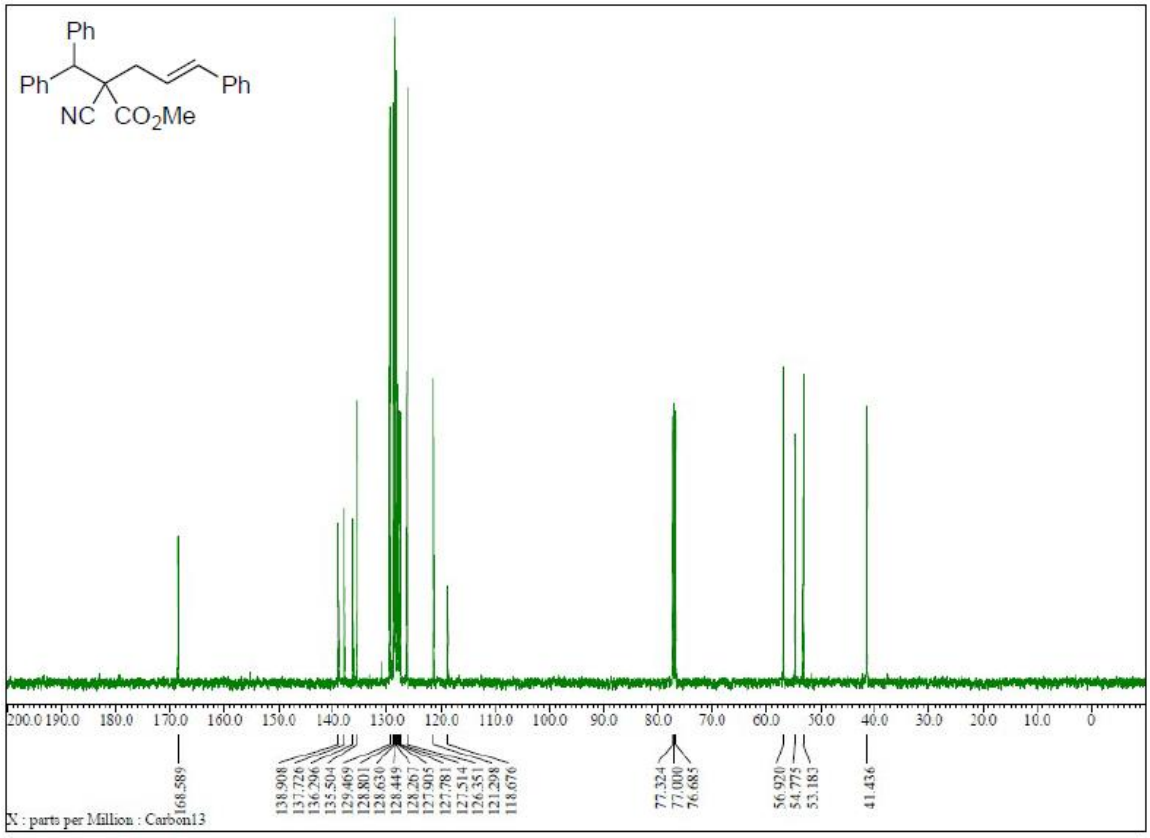
2.815
2.803
2.781
2.699
2.684
2.665
2.649
X : parts per Million : Proton


Ph
Ph
Ph
NC
CO2Me
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
168.589
138.908
137.726
136.296
135.504
129.469
128.801
128.630
128.449
128.267
127.905
127.781
127.514
126.351
121.298
118.676
77.324
77.000
76.685
56.920
54.775
53.183
41.436
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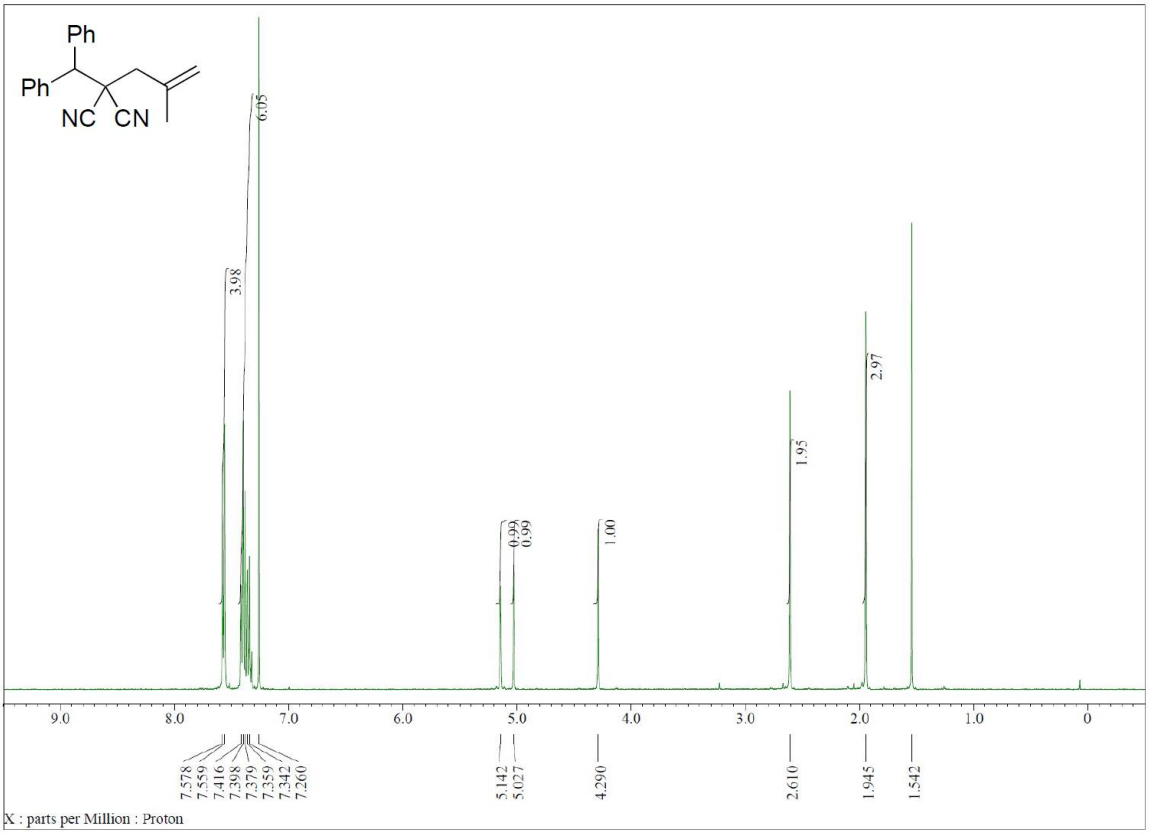
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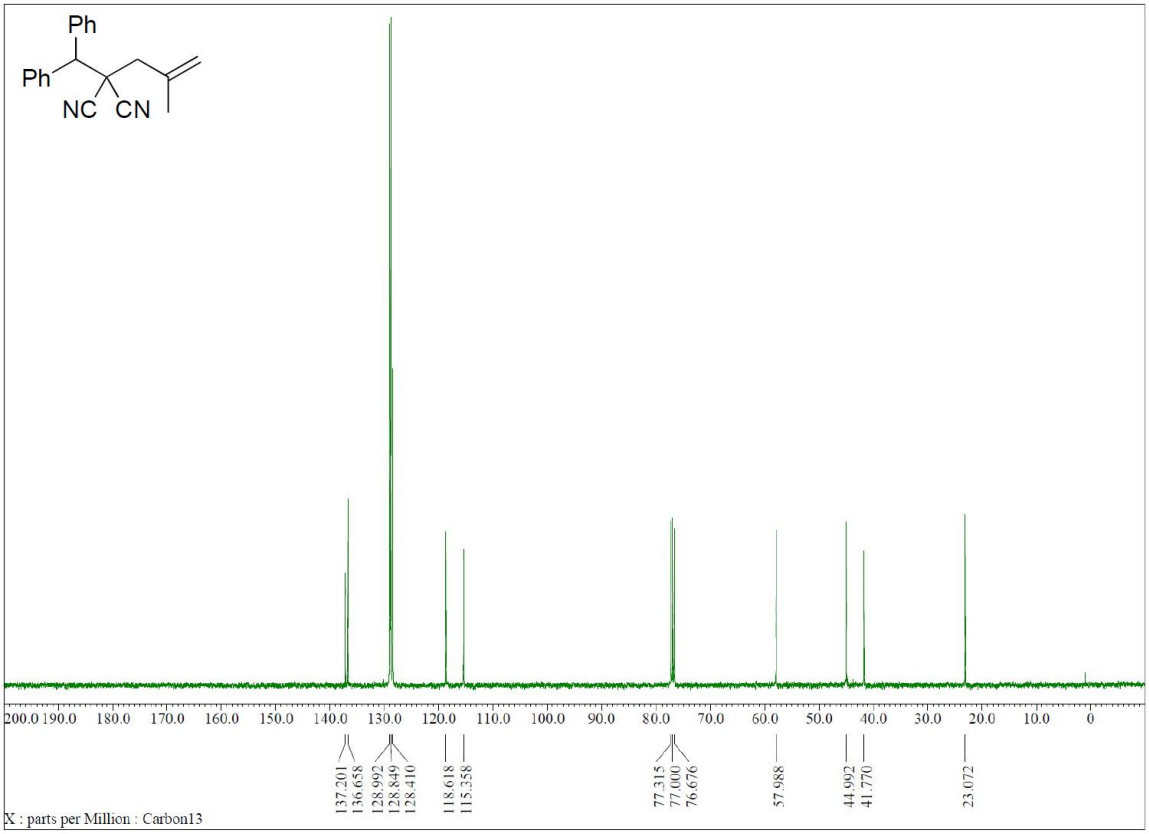
Ph
NC CN
6.05
3.98
2.97
1.95
1.00
0.99
0.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.578
7.559
7.416
7.398
7.379
7.359
7.342
7.260
5.142
5.027
4.290
2.610
1.945
1.542
X : parts per Million : Proton


Ph
Ph
NC CN
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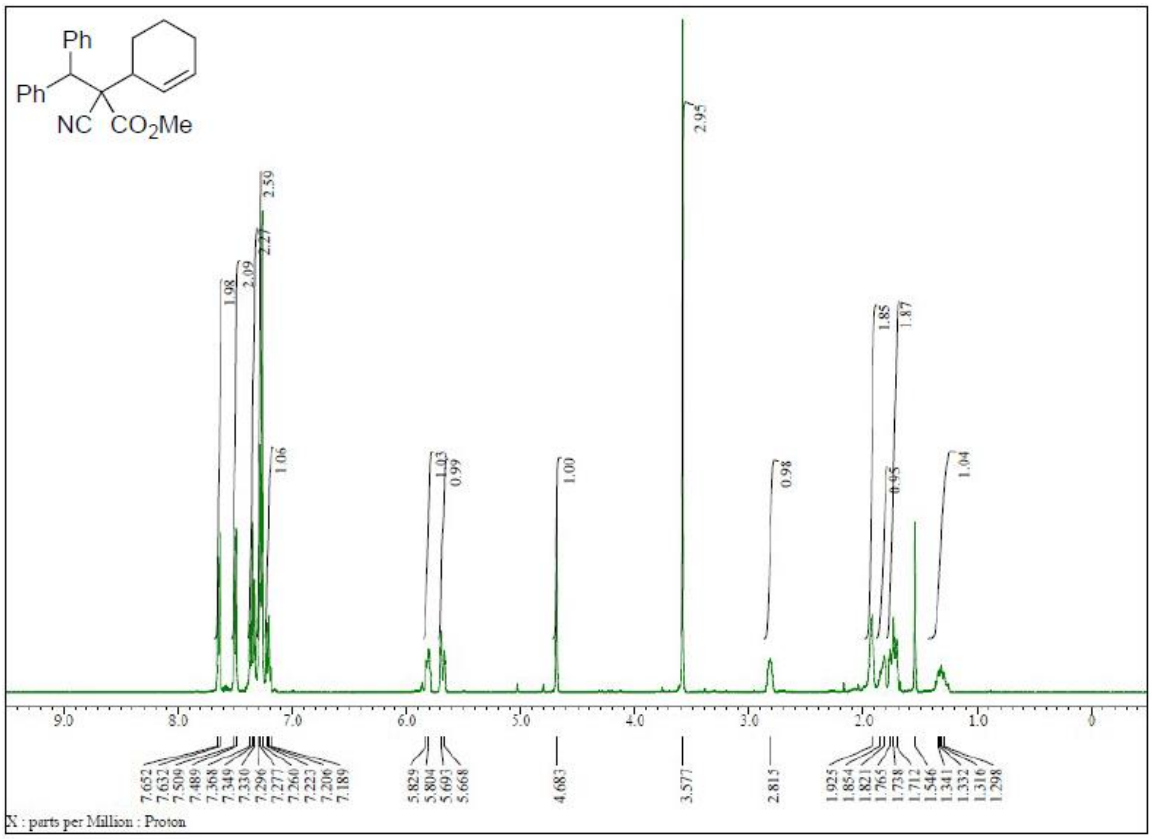
137.201
136.658
128.992
128.849
128.410
118.618
115.358
77.315
77.000
76.676
57.988
44.992
41.770
23.072
X : parts per Million : Carbon13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Ph
NC CO2Me
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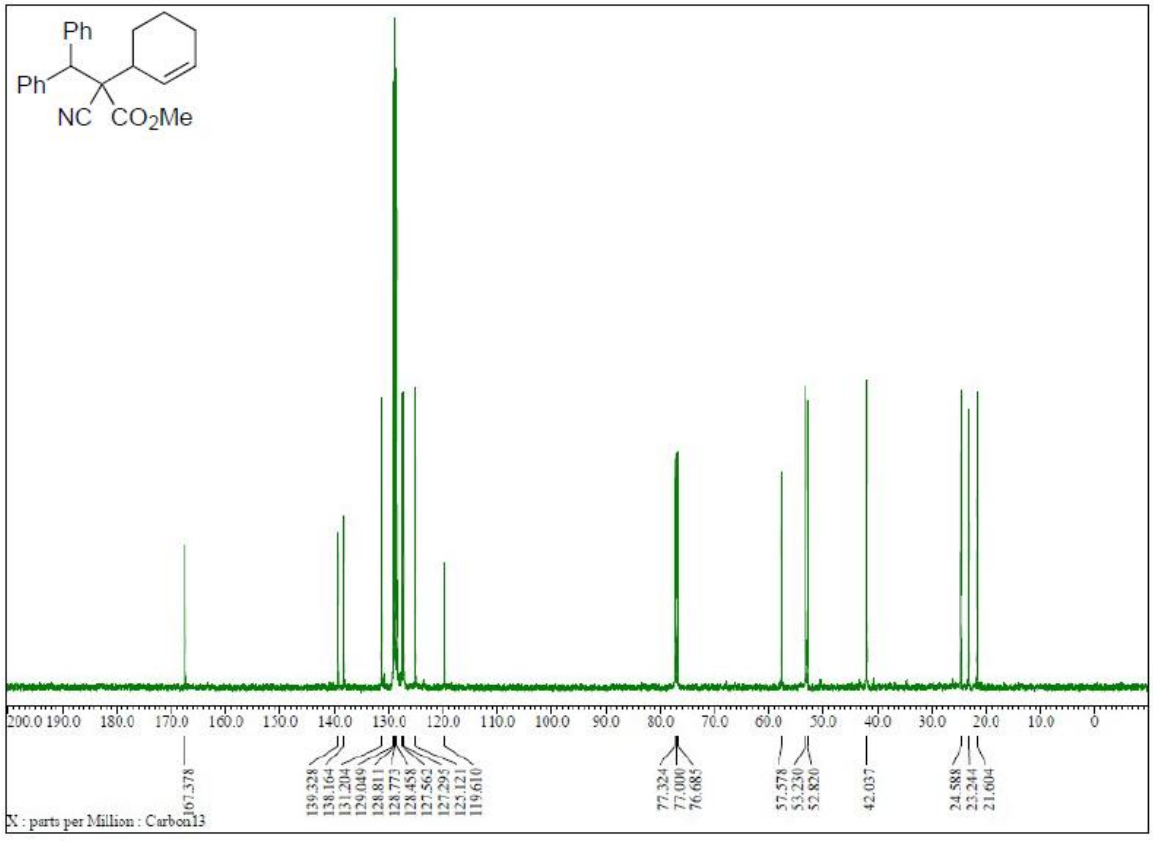
2.50
2.27
2.09
1.98
1.06
1.03
0.99
1.00
0.98
1.85
1.87
0.95
1.04
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.652 7.632 7.509 7.489 7.368 7.349 7.330 7.296 7.277 7.260 7.223 7.206 7.189
5.829 5.804 5.693 5.668
4.683
3.577
2.815
1.925 1.854 1.821 1.765 1.738 1.712 1.546 1.341 1.332 1.316 1.298
N : parts per Million : Proton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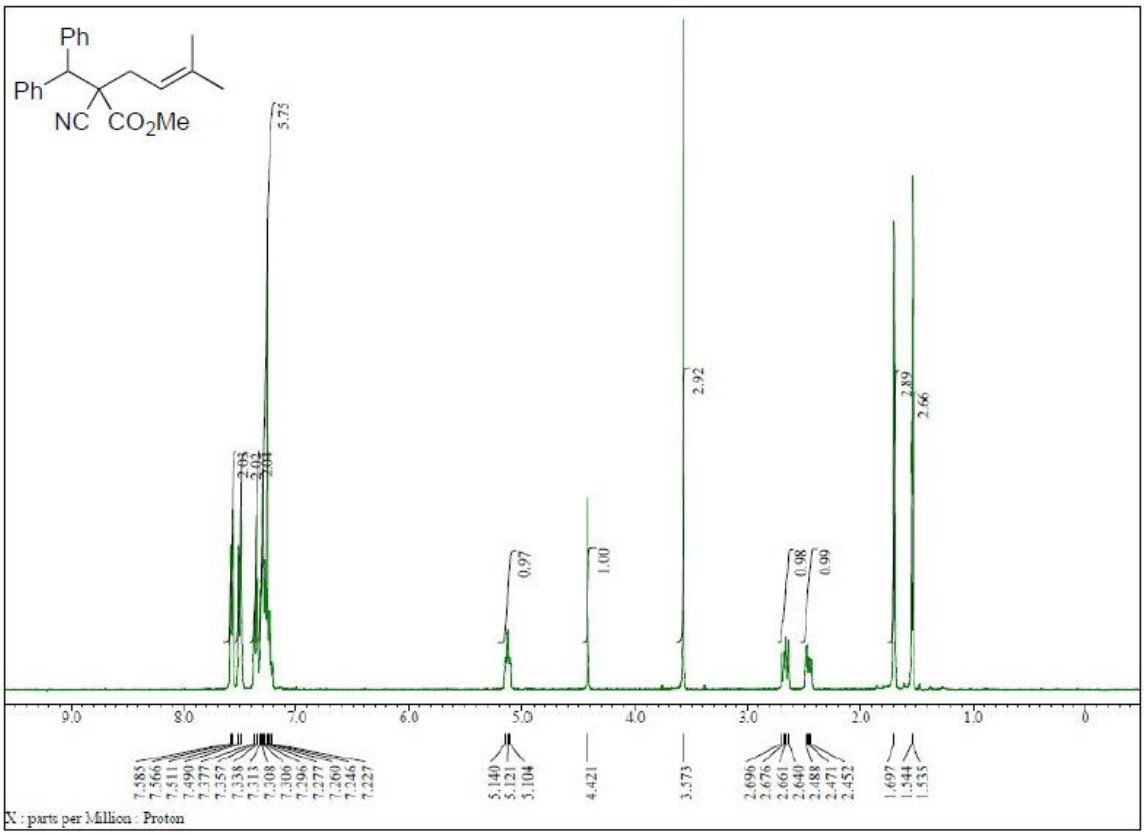
Ph
NC CO2Me
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
167.378
139.328 138.164 131.204 129.049 128.811 128.773 128.458 127.562 127.295 125.121 119.610
77.324 77.000 76.685
57.578 53.230 52.820
42.037
24.588 23.244 21.604
N : parts per Million : Carbon13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Ph
NC
CO2Me
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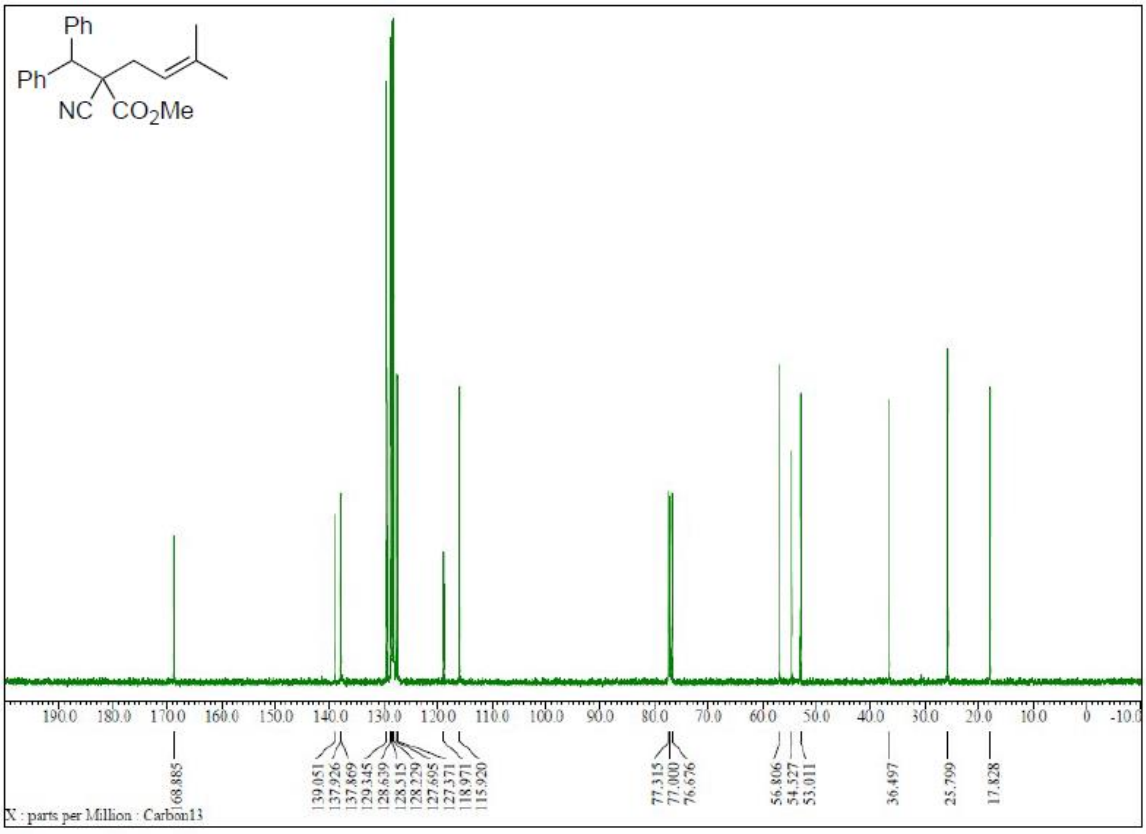
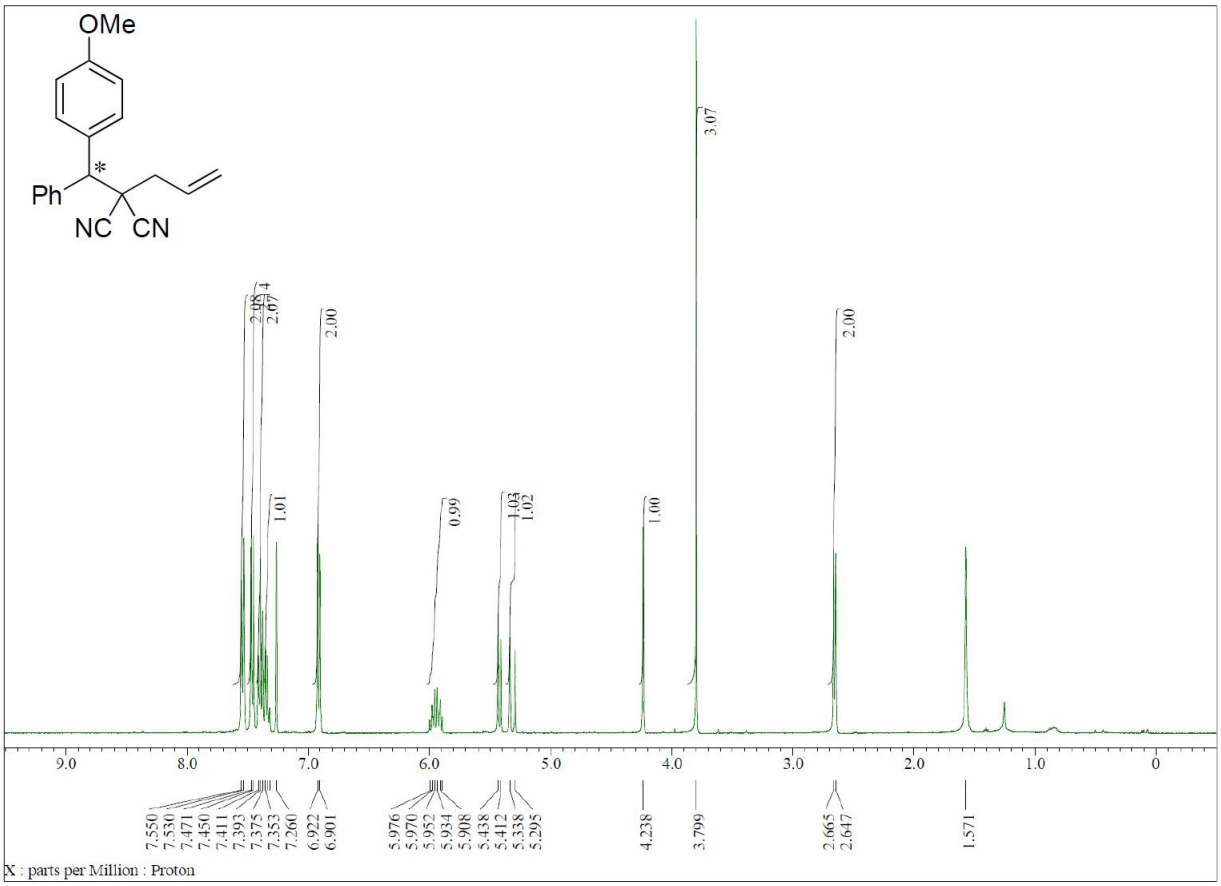
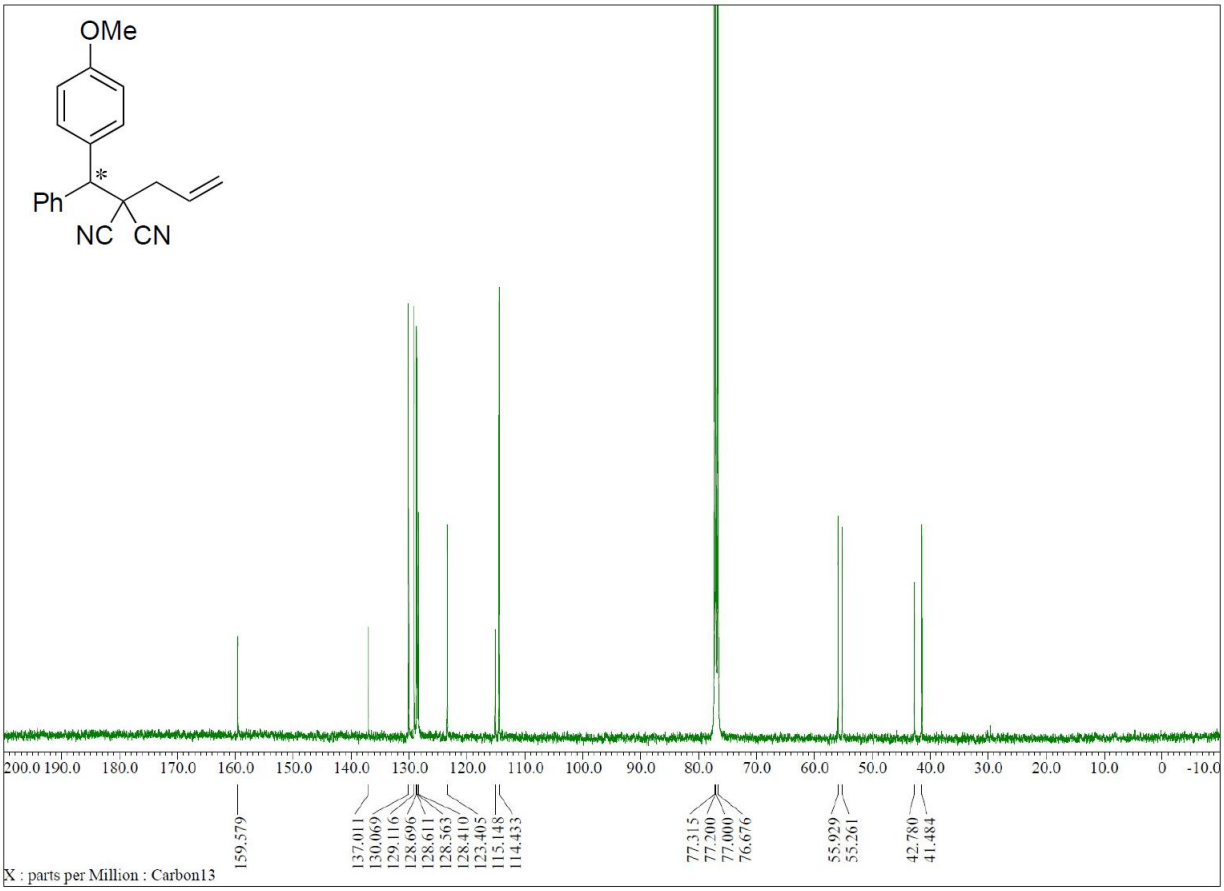
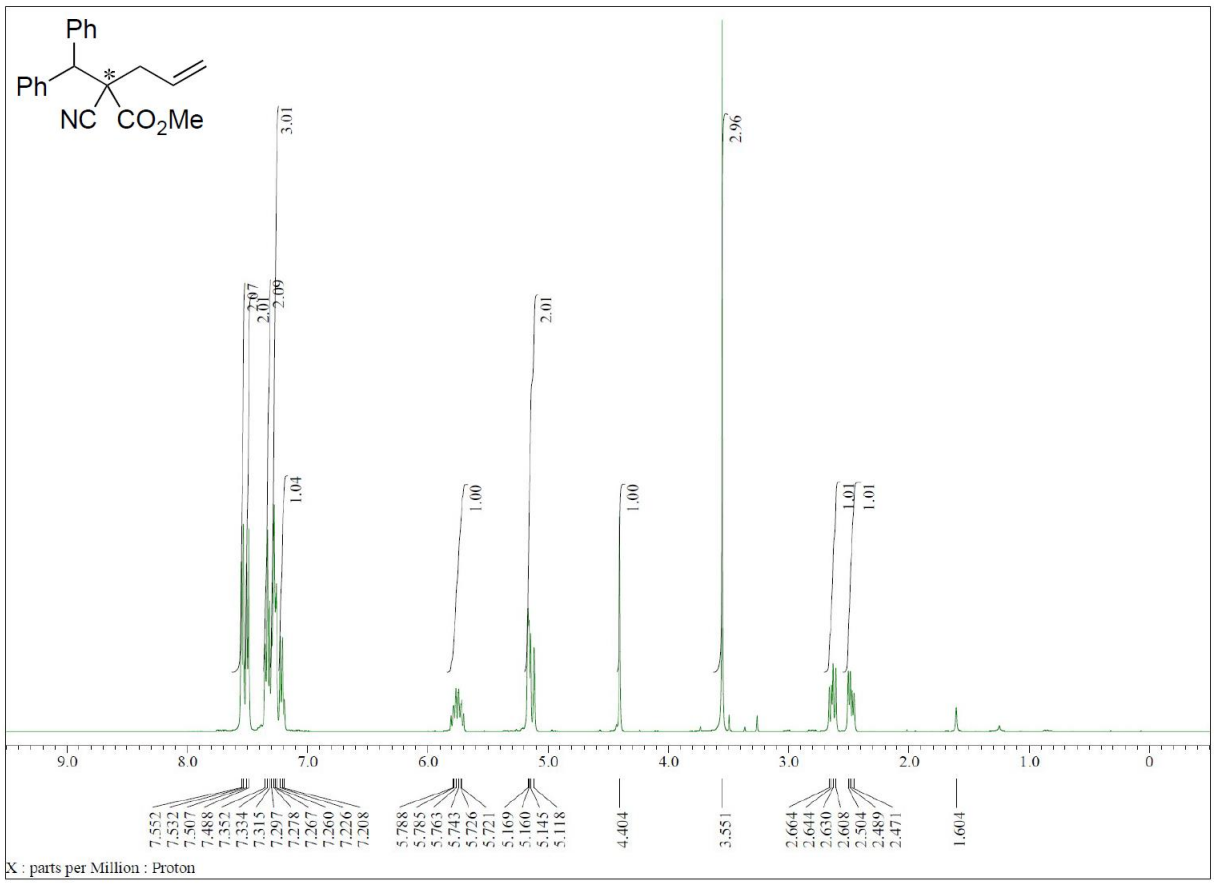
2.66
0.97
1.00
0.98
0.90
X : parts per Million : Proton


Ph
Ph
NC
CO2Me
X : parts per Million : Carbon13


OMe
Ph
NC CN
3.07
2.00
2.00
1.01
0.99
1.03
1.02
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.550
7.530
7.471
7.450
7.411
7.393
7.375
7.353
7.260
6.922
6.901
5.976
5.970
5.952
5.934
5.908
5.438
5.412
5.338
5.295
4.238
3.799
2.665
2.647
1.571
X : parts per Million : Proton


OMe
Ph
NC CN
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
159.579
137.011
130.069
129.116
128.696
128.611
128.363
128.410
123.405
115.148
114.433
77.315
77.200
77.000
76.676
55.929
55.261
42.780
41.484
X : parts per Million : Carbon13


Ph
Ph
NC
CO2Me
3.01
2.96
2.07
2.01
2.09
2.01
1.04
1.00
1.00
1.00
1.01
1.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.552
7.532
7.507
7.488
7.352
7.334
7.315
7.297
7.278
7.267
7.260
7.226
7.208
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5.726
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5.169
5.160
5.145
5.118
4.404
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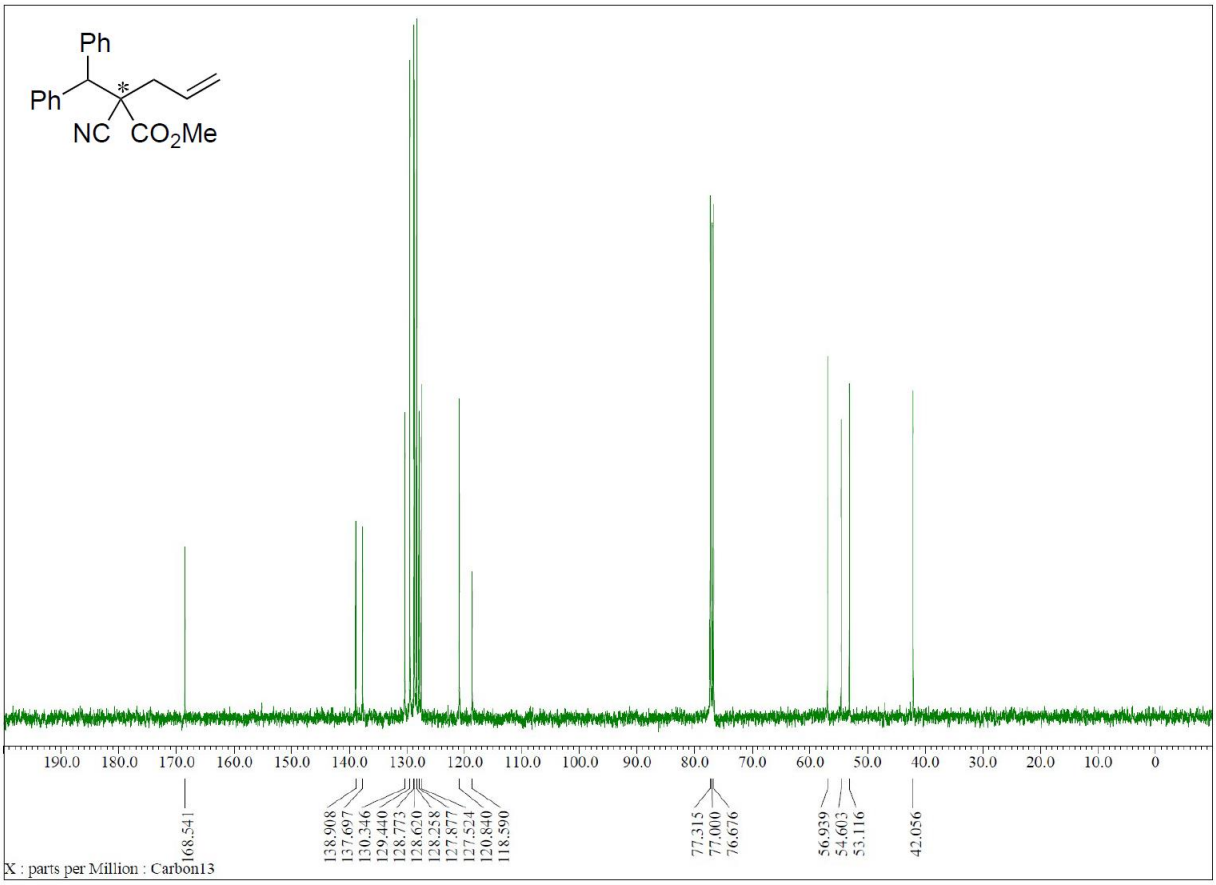
2.644
2.630
2.608
2.504
2.489
2.471
1.604
X : parts per Million : Proton


Ph
Ph
NC
CO2Me
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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
168.541
138.908
137.697
130.346
129.440
128.773
128.620
128.258
127.877
127.524
120.840
118.590
77.315
77.000
76.676
56.939
54.603
53.116
42.056
X : parts per Million : Carbon13