Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Sustainable Oragnocatalytic Cyanosilylation of Ketones by PPM-Level Loading Triphenylcarbenium Tetrakis(pentafluorophenyl)borate

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1. General Information

■ **Chemical:** Chemicals were purchased from commercial retailers (*e.g.*, Aldrich, Alfa Aesar, Combi-Blocks, TCI) and used as received unless otherwise stated. HPLC grade solvents, anhydrous solvents, NMR solvents, and additional organic solvents were purchased from commercial retailers (*e.g.*, Aldrich, Alfa Aesar, CIL Inc., Merck, Wako) and used without further distillation or purification.

■ **Reaction:** Reaction mixtures were stirred magnetically in flame-dried glassware, under argon gas atmosphere associating standard Schlenk technique and the room temperature was maintained at 24 ± 1 °C consistently unless otherwise specified.

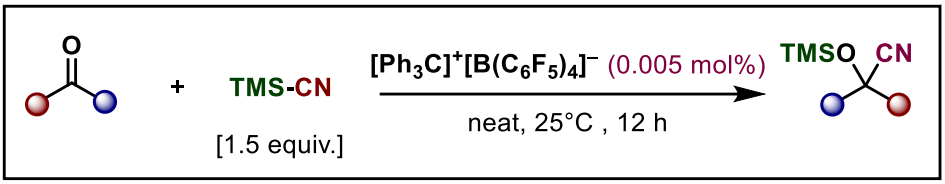
■ **Thin-Layer Chromatography (TLC):** TLC results were monitored using silica gel plates (Merck, Kieselgel 60 F254 0.25 mm). Visualization by staining methods (*e.g.*, p-Anisaldehyde Stain or $KMnO_4$ upon heating) was performed when if it was needed.

■ **Nuclear Magnetic Resonance (NMR) spectroscopy:** ^{1}H NMR (500 MHz), ^{13}C NMR (125.7 MHz), and ^{19}F NMR (470.4 MHz) spectra were recorded using Bruker Ascend™ 500 spectrometer at the Chiral Material Core Facility Center for Sungkyunkwan University. Chemical shifts (δ) were reported by using tetramethylsilane (TMS) as the internal standard for ^{1}H and ^{13}C NMR. Integration data were represented as follows; coupling constant (J = Hz), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). All analytical data and NMR spectra of known compounds are in accordance with reported literatures.

■ **Mass Spectroscopy (MS):** High-resolution mass spectra were analyzed in electron ionization (HR-EI-MS) option by using JMS-700.

2. Reaction Procedure

2.1. General procedure for catalytic cyanosilylation



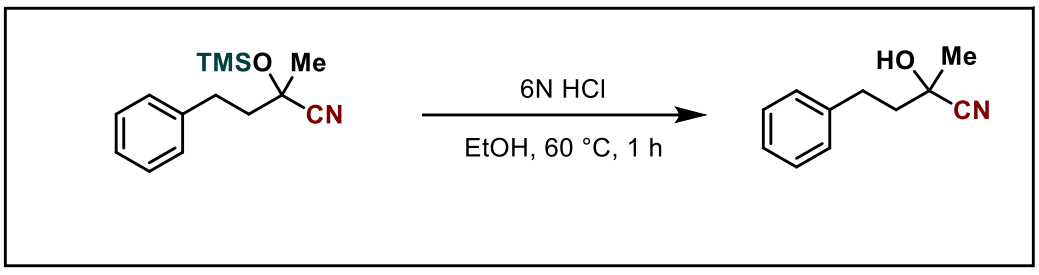
A flame dried 5.0 mL vial was charged, under Ar atmosphere, ketone (75 µL, 0.5 mmol, 1.0 equiv), and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (50 ppm = 0.005 mol%, 0.023 mg) were added (the stock solution was prepared using 0.005 mmol of $[Ph_3C]^+[B(C_6F_5)_4]^-$ in 2.0 mL of Et_2O). Lastly, TMS-CN (94 µL 0.75 mmol, 1.5 equiv) was introduced dropwise by micro syringe. The resultant mixture was then stirred at 25 °C for 12 h. After the completion of reaction, the volatiles were removed by rotary evaporator and dried under high vacuum without further purification which afforded the corresponding pure product.

*** Scale-up experiment (on 1.0 g scale)**

To a flame-dried 10.0 mL round bottom flask, equipped with a magnetic stirring bar, back filled with Ar gas (three times), 4-Phenyl-2-butanone, (1.00 g, 6.74 mmol), and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (50 ppm = 0.005 mol%, 0.310 mg) were added respectively. Then, TMS-CN (1.26 mL, 10.1 mmol, 1.5 equiv) was added dropwise via syringe. The resultant mixture was then stirred at room temperature for 12 h. After the completion of reaction, the volatiles were removed by rotary evaporator and dried under high vacuum without further purification which afforded the corresponding pure product **1** (1.65g, >99% yield).

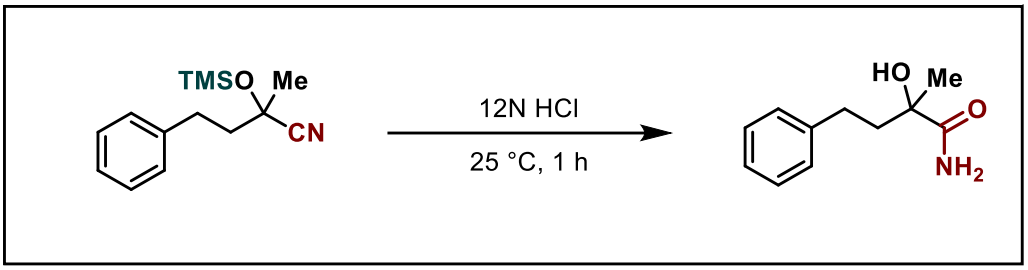
2.2. Procedures for the synthetic transformations

Synthesis of 2-hydroxy-2-methyl-4-phenylbutanenitrile (**33**)



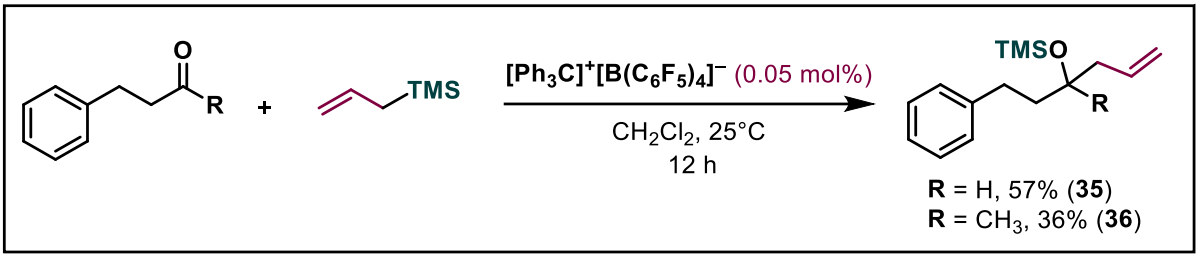
In a flamed-dried 10 mL schlenk tube equipped with a stir bar, cyanohydrin **1** (124mg, 0.5 mmol) was dissolved in 6N HCl/EtOH (1.0 mL, 1:1 vol/vol), and stirred at 60 °C for 1 h. After the reaction was completed, water was added, the aqueous layer was extracted with CH_2Cl_2 (3×5 ml, washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford product **33** (91%).

Synthesis of 2-hydroxy-2-methyl-4-phenylbutanamide (**34**)



To a flamed-dried 5 mL vial charged with a magnetic stir bar, cyanohydrin **1** (124mg, 0.5 mmol) and concentrated HCl (37%, 1.0 mL) were added at room temperature. The reaction mixture was stirred vigorously at 25 °C for 1 h. After the reaction was completed, water was added drops wise to reaction mixture in order to quench the reaction. The resulting solution was extracted with EtOAc (3×5 ml), washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporator. The crude product was purified by column chromatography using (petroleum ether/ethyl acetate = 1:1) as eluent to afford product **34** (88%).

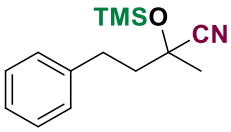
2.3. General procedure for catalytic Hosomi-Sakurai allylation



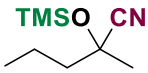
To a flame dried 5.0 mL vial charged with a magnetic bar, under nitrogen atmosphere, hydrocinnamaldehyde /4-phenyl-2-butanone (0.5 mmol, 1 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (500 ppm = 0.05 mol%, 0.23 mg) and 1 mL of anhydrous dichloromethane were added. Finally, Allyltrimethylsilane (0.75 mmol, 1.5 equiv) was introduced dropwise by micro syringe. The resultant mixture was the stirred at room temperature for 12 h. After the completion of reaction, the solvent was removed by rotary evaporator and purified by a short column on silica gel (Hexanes: EtOAc = 50:1) to afford the corresponding allylation-reaction products **35** (57%) and **36** (36%).

#Note: Partial decomposition was observed in both allylation reactions.

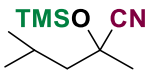
3. Analytical Data of the Products



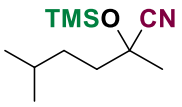
1, known compound[1], colorless oil, 122 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.23 – 7.22 (m, 3H), 2.93 – 2.87 (m, 1H), 2.84 – 2.78 (m, 1H), 2.10–2.00 (m, 2H), 1.65 (s, 3H), 0.29 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 140.85, 128.66, 128.49, 126.28, 122.01, 69.48, 45.36, 30.83, 29.14, 1.43.



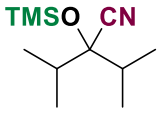
2, known compound[2], colorless oil, 92 mg, >99 yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.74 – 1.62 (m, 2H), 1.60 – 1.56 (m, 1H), 1.55 (s, 3H), 1.52 – 1.42 (m, 1H), 0.96 (t, J = 7.3 Hz, 3H), 0.22 (s, 9H).**^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 122.30, 69.70, 45.62, 29.04, 17.77, 13.91, 1.39.



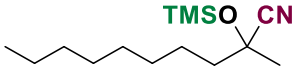
3, known compound[2], colorless oil, 99 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.98 – 1.89 (m, 1H), 1.67 – 1.59 (m, 2H), 1.56 (s, 3H), 0.99 (dd, J = 6.7, 5.2 Hz, 6H), 0.22 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 122.67, 69.27, 51.65, 29.92, 25.04, 23.91, 23.79, 1.43.



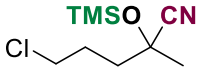
4, known compound[2], colorless oil, 106 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.75 – 1.64 (m, 2H), 1.59 – 1.55 (m, 1H), 1.54 (s, 3H), 1.44 – 1.37 (m, 1H), 1.35 – 1.27 (m, 1H), 0.90 (d, J = 6.8 Hz, 6H), 0.22 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 122.25, 69.86, 41.45, 33.23, 28.97, 28.00, 22.59, 22.52, 1.38.



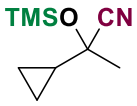
5, known compound[3], colorless oil, 106 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.04 – 1.96 (m, 2H), 1.04 (d, J = 6.9 Hz, 6H), 0.97 (d, J = 6.7 Hz, 6H), 0.23 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 120.23, 81.60, 34.98, 18.55, 16.68, 1.92.



6, known compound[4], colorless oil, 127 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.75– 1.64 (m, 2H), 1.55 (s, 3H), 1.53 – 1.38 (m, 2H), 1.32 – 1.27 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H), 0.22 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 122.28, 69.77, 43.50, 31.93, 29.49, 29.43, 29.28, 29.00, 24.38, 22.74, 14.17, 1.38.



7, known compound[2], colorless oil, 109 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.62 – 3.54 (m, 2H), 2.07 – 1.92 (m, 2H), 1.90 – 1.85 (m, 2H), 1.59 (s, 3H), 0.23 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 121.80, 69.19, 44.49, 40.84, 29.07, 27.60, 1.32.

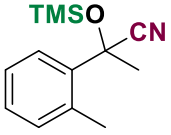


8, known compound[5], colorless oil, 90 mg, 98% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.62 (s, 3H), 1.19 – 1.13 (m, 1H), 0.63 – 0.54 (m, 4H), 0.22 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 121.12, 70.63, 29.60, 21.69, 2.60, 2.05, 1.40.

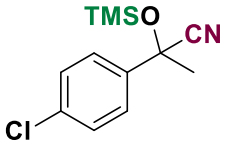
9, known compound[1], colorless oil, 109 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.42 – 7.35 (m, 3H), 1.87 (s, 3H), 0.20 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 142.09, 128.75, 128.73, 124.70, 121.71, 71.70, 33.65, 1.14.

10, known compound[1], colorless oil, 116 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.29 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H), 1.93 (s, 3H), 0.26 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 139.20, 138.61, 129.36, 124.69, 121.85, 71.61, 33.62, 21.15, 1.17.

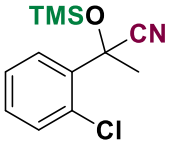
11, known compound[2], colorless oil, 115 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (d, J = 8.1 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 2.41 (s, 3H), 1.87 (s, 3H), 0.21 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 142.00, 138.42, 129.44, 128.60, 125.34, 121.79, 121.75, 71.70, 33.63, 21.54, 1.14.



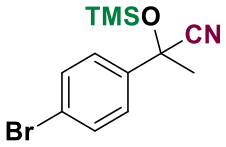
12, known compound[6], colorless oil, 115 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 1H), 7.32 – 7.24 (m, 3H), 2.64 (s, 3H), 2.02 (s, 3H), 0.26 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 138.49, 135.54, 132.73, 128.75, 126.05, 125.35, 121.67, 71.76, 30.58, 20.74, 1.17.



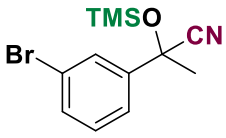
13, known compound[1], colorless oil, 126 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.38 – 7.35 (m, 2H), 1.83 (s, 3H), 0.19 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 140.83, 134.70, 128.94, 126.19, 121.34, 71.16, 33.61, 1.16.



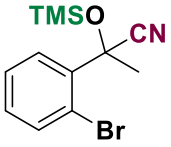
14, known compound[2], colorless oil, 126 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.4, 2.2 Hz, 1H), 7.41 (dd, J = 7.5, 1.7 Hz, 1H), 7.31 (pd, J = 7.3, 1.7 Hz, 2H), 2.00 (s, 3H), 0.29 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 138.07, 131.55, 131.25, 129.99, 127.13, 127.01, 120.45, 70.26, 29.84, 1.24.



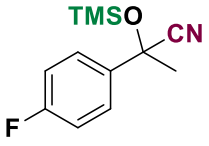
15, known compound[6], colorless oil, 147 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.43 – 7.41 (m, 2H), 1.83 (s, 3H), 0.19 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 141.36, 131.89, 126.48, 122.82, 121.25, 71.19, 33.57, 1.16.



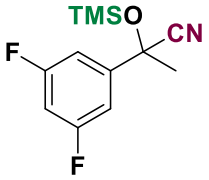
16, known compound[7], colorless oil, 147 mg >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (t, J = 1.8 Hz, 1H), 7.54 (dd, J = 7.9, 1.8 Hz, 2H), 7.32 (t, J = 7.9 Hz, 1H), 1.89 (s, 3H), 0.27 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 144.45, 131.90, 130.34, 127.92, 123.39, 122.86, 121.18, 71.01, 33.61, 1.17.



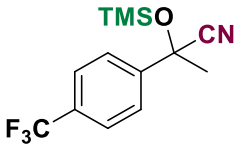
17, known compound[8], colorless oil, 145 mg 97% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.0, 1.6 Hz, 1H), 7.63 (dd, J = 7.9, 1.2 Hz, 1H), 7.37 (td, J = 7.9, 1.2 Hz, 1H), 7.21 (td, J = 7.7, 1.7 Hz, 1H), 2.03 (s, 3H), 0.29 (s, 9H**). ^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 139.34, 135.33, 130.21, 127.73, 127.39, 120.49, 120.23, 71.54, 29.98, 1.30.



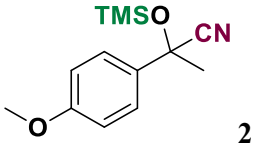
18, known compound[9], colorless oil, 117 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.07 (t, J = 8.6 Hz, 2H), 1.84 (s, 3H), 0.19 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 162.79 (d, $J_{C\text{-}F}$ = 247.9 Hz), 138.09 (d, $J_{C\text{-}F}$ = 3.2 Hz), 126.64 (d, $J_{C\text{-}F}$ = 8.4 Hz), 121.51, 115.63 (d, $J_{C\text{-}F}$ = 21.8 Hz), 71.14, 33.64, 1.11.



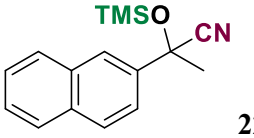
19, new compound, colorless oil, 126 mg, >99% yield. **R_f** = 0.41 (EtOAc:hexanes = 1:20 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 (dd, J = 8.1, 2.2 Hz, 2H), 6.82 – 6.77 (m, 1H), 1.83 (s, 3H), 0.24 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 164.17 (d, $J_{C\text{-}F}$ = 12.5 Hz), 162.18 (d, $J_{C\text{-}F}$ = 12.5 Hz), 146.47 (t, $J_{C\text{-}F}$ = 8.6 Hz), 120.84, 108.21 (d, $J_{C\text{-}F}$ = 6.8 Hz), 108.04 (d, $J_{C\text{-}F}$ = 6.8 Hz), 104.23 (t, $J_{C\text{-}F}$ = 25.3 Hz), 70.81 (t, $J_{C\text{-}F}$ = 2.4 Hz), 33.48, 1.11. **^{19}F NMR** (470.4 MHz, $CDCl_3$) δ -107.86 (t, J = 8.1 Hz). **HR-MS (EI+)**: [M]+ Calcd. for $C_{12}H_{15}F_2NOSi$: 255.0891; found : 255.0888.



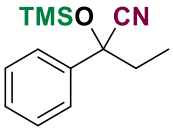
20, known compound[9], colorless oil, 142 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 4H), 1.86 (s, 3H), 0.22 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 146.22, 131.11 (q, $J_{C\text{-}F}$ = 32.7 Hz), 127.98 (d, $J_{C\text{-}F}$ = 195.8 Hz), 125.87 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.22, 123.96 (d, $J_{C\text{-}F}$ = 272.2 Hz), 121.16, 71.26, 33.64, 1.12.



21, known compound[6], colorless oil, 124 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 6.93 – 6.90 (m, 2H), 3.81 (s, 3H), 1.85 (s, 3H), 0.17 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 159.84, 134.04, 126.07, 121.81, 113.92, 71.29, 55.30, 33.41, 1.09.



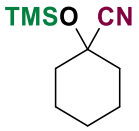
22, known compound[1], colorless oil, 132 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, J = 1.5 Hz, 1H), 7.93 – 7.86 (m, 3H), 7.64 (dd, J = 8.7, 1.9 Hz, 1H), 7.57 – 7.53 (m, 2H), 1.97 (s, 3H), 0.23 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 139.31, 133.32, 132.93, 128.87, 128.48, 127.77, 126.83, 126.79, 123.81, 122.46, 121.75, 71.94, 33.62, 1.23.



23, known compound[1], colorless oil, 115 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.51 (m, 2H), 7.41 – 7.35 (m, 3H), 2.10 – 2.03 (m, 1H), 1.99 – 1.91 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.15 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 141.00, 128.71, 128.61 125.25, 120.88, 76.37, 39.31, 8.81, 1.04.

24, known compound[10], colorless oil, 122 mg, 99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 2H), 7.41 – 7.32 (m, 3H), 2.05 – 1.97 (m, 1H), 1.91 – 1.85 (m, 1H), 1.58 – 1.49 (m, 1H), 1.41 – 1.31 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.13 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 141.33, 128.70, 128.63, 125.20, 121.11, 75.72, 48.27, 17.87, 13.75, 1.07.

25, known compound[7], colorless oil, 139 mg, >99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 4H), 7.40 – 7.34 (m, 6H), 0.19 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 142.07, 128.78, 128.67, 126.01, 120.83, 76.47, 1.04.

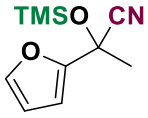


26, known compound[7], colorless oil, 97 mg, 98% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.04 – 2.01 (m, 2H), 1.74 – 1.70 (m, 2H), 1.63 – 1.49 (m, 5H), 1.26 – 1.20 (m, 1H), 0.22 (s, 9H).**^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 122.00, 70.70, 39.43, 24.59, 22.71, 1.48.

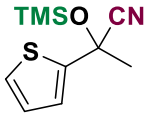
27, known compound[11], colorless oil, 120 mg, 98% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 1H), 7.31 – 7.27 (m, 2H), 7.15 – 7.12 (m, 1H), 2.90 – 2.80 (m, 2H), 2.39 – 2.34 (m, 1H), 2.26 – 2.21 (m, 1H), 2.13 – 2.05 (m, 1H), 2.04 – 1.96 (m, 1H), 0.26 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 136.16, 135.72, 129.33, 129.11, 128.04, 126.65, 122.15, 69.92, 37.78, 28.36, 18.74, 1.40.

28, known compound[12], colorless oil, 121 mg, 98% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ

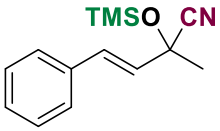
7.56 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 6.99 – 6.96 (m, 1H), 6.84 (dd, *J* = 8.3, 0.9 Hz, 1H), 4.38 – 4.30 (m, 2H), 2.46 – 2.34 (m, 2H), 0.17 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 153.66, 131.48, 128.83, 121.14, 120.91, 120.88, 117.68, 65.68, 61.40, 36.40, 1.30.



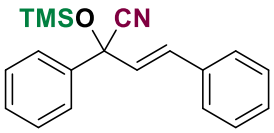
29, known compound[6], brown oil, 104 mg, >99% yield.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 – 7.41 (m, 1H), 6.49 (d, *J* = 3.3 Hz, 1H), 6.37 (dd, *J* = 3.3, 1.8 Hz, 1H), 1.92 (s, 3H), 0.08 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 151.75, 143.20, 120.29, 110.79, 108.24, 65.98, 28.96, 0.58.



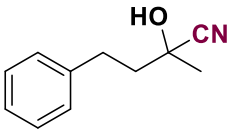
30, known compound[6], colorless oil, 106 mg, 94% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.20 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H), 1.98 (s, 3H), 0.18 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 146.53, 126.84, 126.20, 124.93, 121.06, 68.48, 33.63, 1.02.



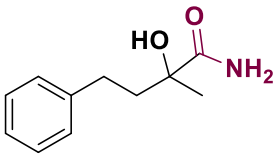
31, known compound[1], colorless oil, 113 mg, 92% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.34 – 7.31 (m, 1H), 6.92 (d, *J* = 15.9 Hz, 1H), 6.16 (d, *J* = 15.9 Hz, 1H), 1.77 (s, 3H), 0.28 (s, 9H).**^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 135.23, 131.07, 129.65, 128.88, 128.71, 127.00, 120.78, 70.07, 30.98, 1.48.



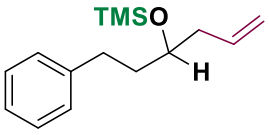
32, known compound[7], colorless oil, 139 mg, 90% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) 7.61 – 7.59 (m, 2H), 7.44 – 7.29 (m, 8H), 7.03 (d, *J* = 15.9 Hz, 1H), 6.21 (d, *J* = 15.8 Hz, 1H), 0.27 (s, 9H).**^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 140.49, 135.24, 131.04, 129.83, 129.01, 128.91, 128.87, 128.82, 127.20, 125.61, 119.81, 75.20, 1.43.



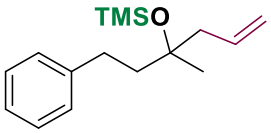
33, known compound[13], viscous oil, 80 mg, 91% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.22 – 7.20 (m, 3H), 3.12 (s, 1H), 2.94 – 2.80 (m, 2H), 2.09 – 2.05 (m, 2H), 1.64 (s, 3H).**^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 140.28, 128.80, 128.48, 121.89, 68.62, 43.40, 30.76, 28.00.



34, known compound[14], white solid, 85 mg, 88% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.28 (d, *J* = 7.3 Hz, 3H), 6.82 (s, 1H), 6.32 (s, 1H), 2.91 – 2.85 (m, 1H), 2.74 – 2.68 (m, 1H), 2.28 (ddd, *J* = 13.7, 12.1, 4.9 Hz, 1H), 2.00 (ddd, *J* = 13.8, 12.1, 5.2 Hz, 1H), 1.58 (s, 3H).**^{13}C NMR** (125.7 MHz, $CDCl_3$) 179.26, 141.69, 128.61, 128.50, 126.13, 75.84, 42.30, 30.18, 27.03.



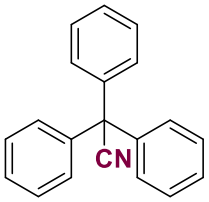
35, known compound[15], colorless oil, 60 mg, 57% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28– 7.25 (m, 2H), 7.23– 7.15 (m, 3H), 5.85 – 5.76 (m, 1H), 5.07– 5.03 (m, 2H), 3.76– 3.71 (m, 1H), 2.76– 2.70 (m, 1H), 2.59– 2.53 (m, 1H), 2.29 – 2.24 (m, 2H), 1.81 – 1.72 (m, 2H), 0.13 (s, 9H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 142.57, 135.22, 128.49, 128.46, 125.83, 117.13, 71.97, 42.32, 38.84, 32.23, 0.60.



36, known compound[16], colorless oil, 48 mg, 36% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.14 – 7.11 (m, 2H), 7.07– 7.03 (m, 3H), 5.74 – 5.66 (m, 1H), 4.94 – 4.91 (m, 2H), 2.53 – 2.49 (m, 2H), 2.16 (d, *J* = 7.3 Hz, 2H), 1.61 – 1.53 (m, 2H), 1.12 (s, 3H), -0.00 (s, 9H).**^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 143.21, 135.16, 128.51, 128.47, 125.72, 117.34, 75.67, 47.33, 44.34, 30.51, 27.56, 2.83.

4. Preliminary Mechanistic Studies

The pre-catalyst $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.05 mmol) and TMS-CN (0.05 mmol) were dissolved [1:1 ratio (mol/mol)] in 0.5 mL $CDCl_3$ at 25 °C. Then NMR was recorded of this crude mixture. The ^1H NMR and ^{13}C NMR spectra confirms the formation of 2,2,2-Triphenylacetonitrile.



2,2,2-Triphenylacetonitrile, known compound[17], (data from crude ^1H NMR and ^{13}C NMR). **^1H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 9H), 7.23 – 7.21 (m, 6H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 140.14, 128.92, 128.87, 128.39, 123.85, 57.63.

5. References

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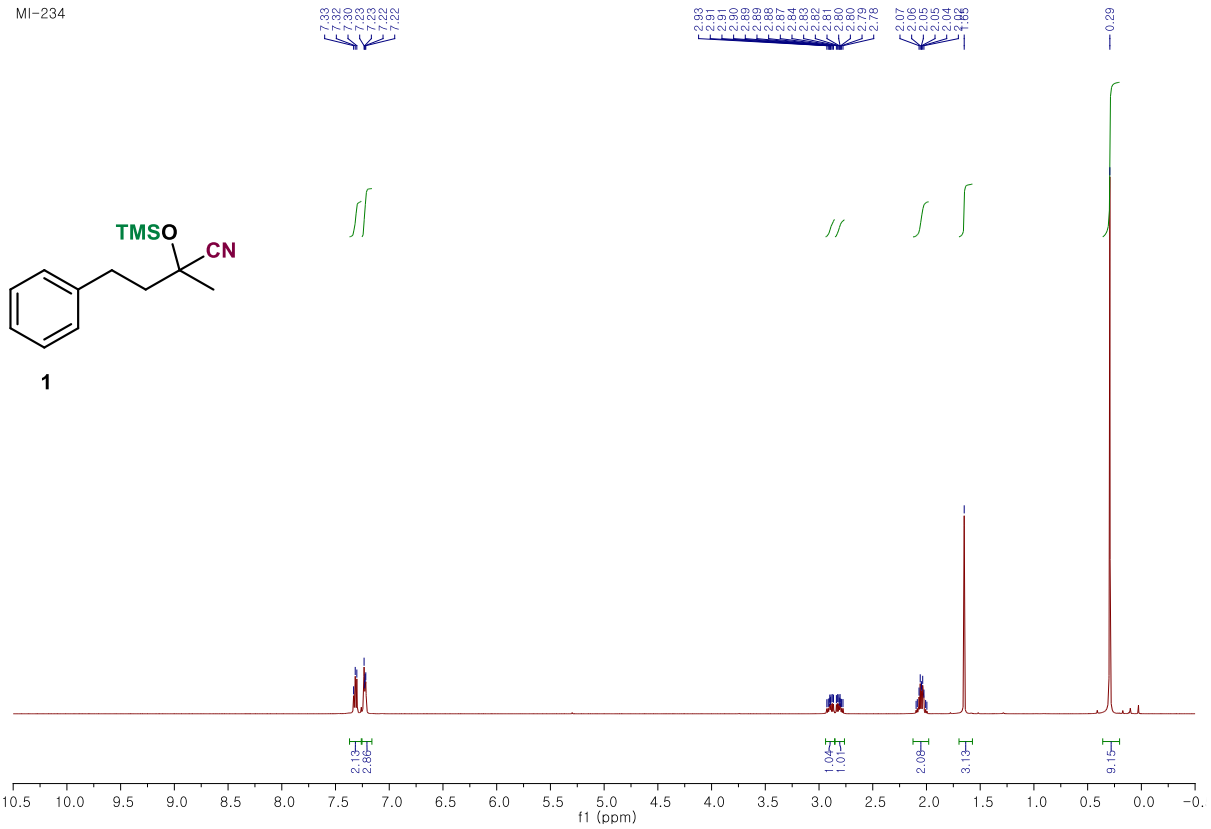
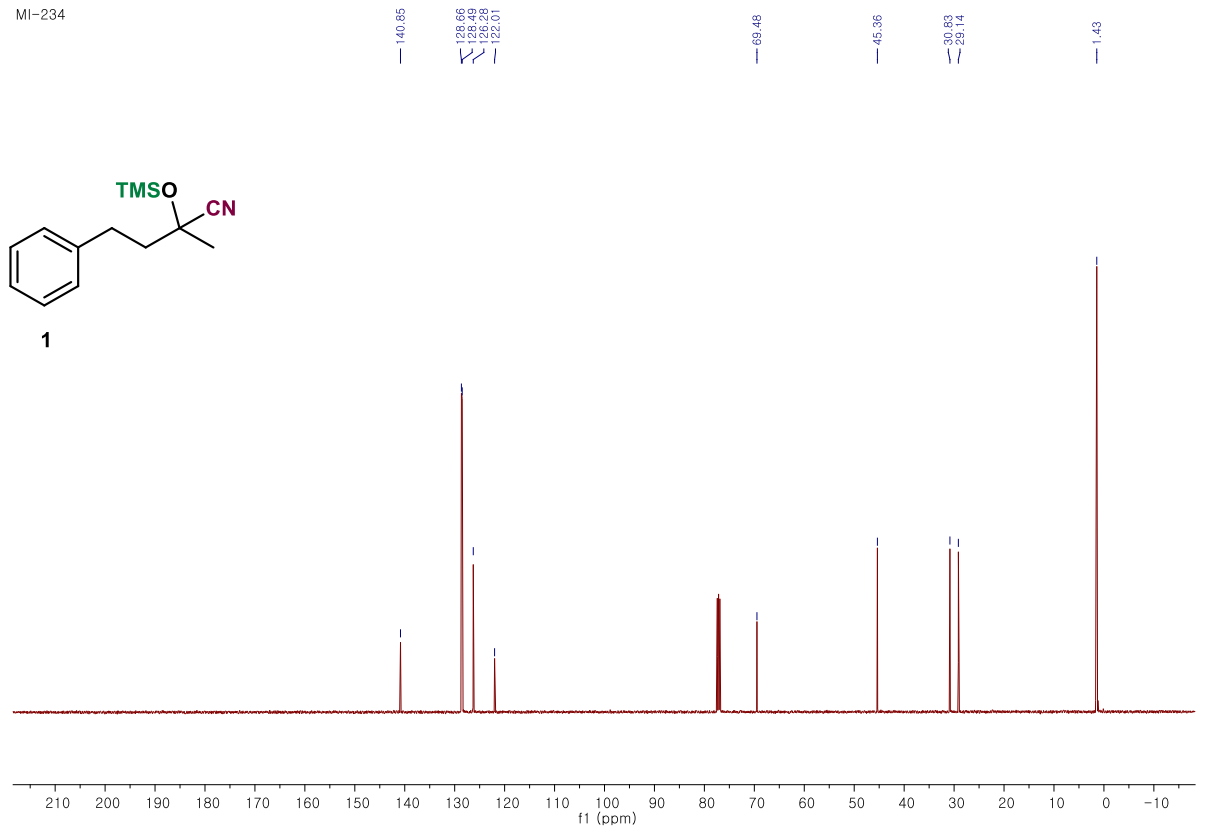
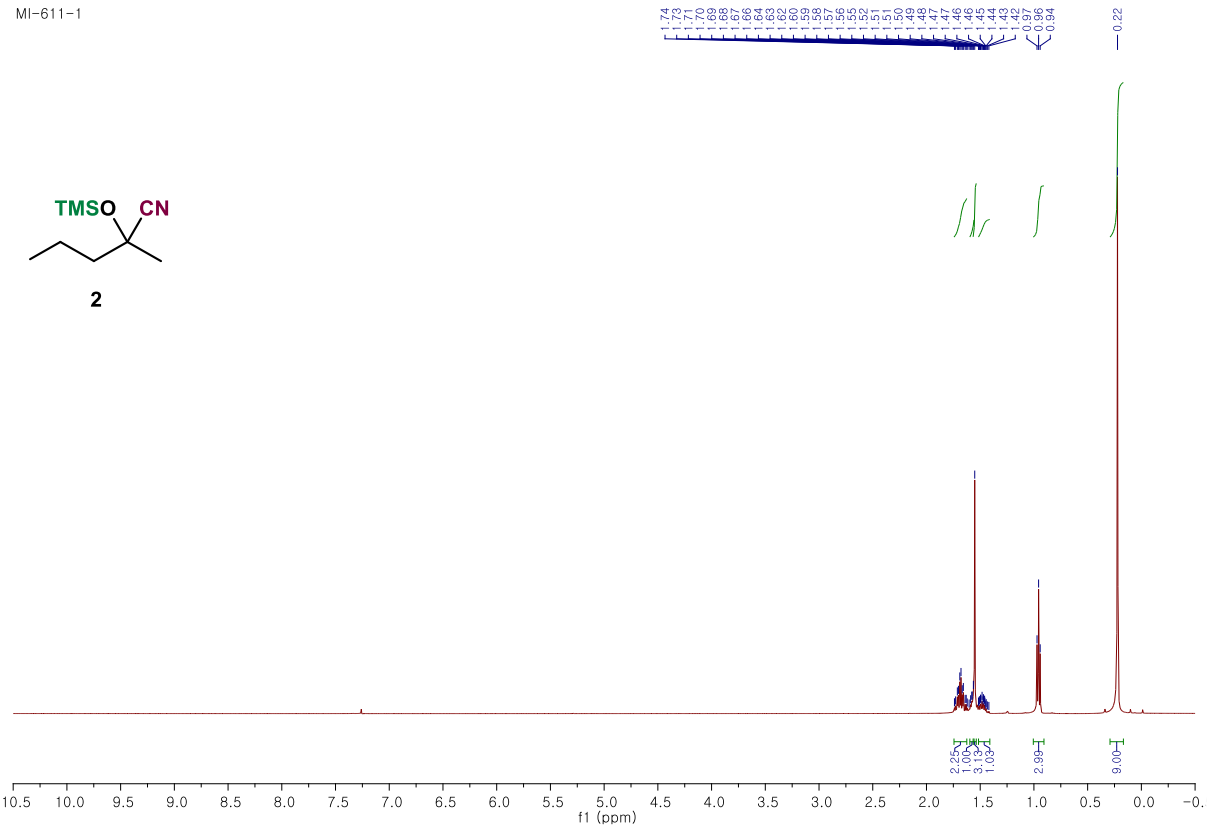
6. NMR Spectra of the Products



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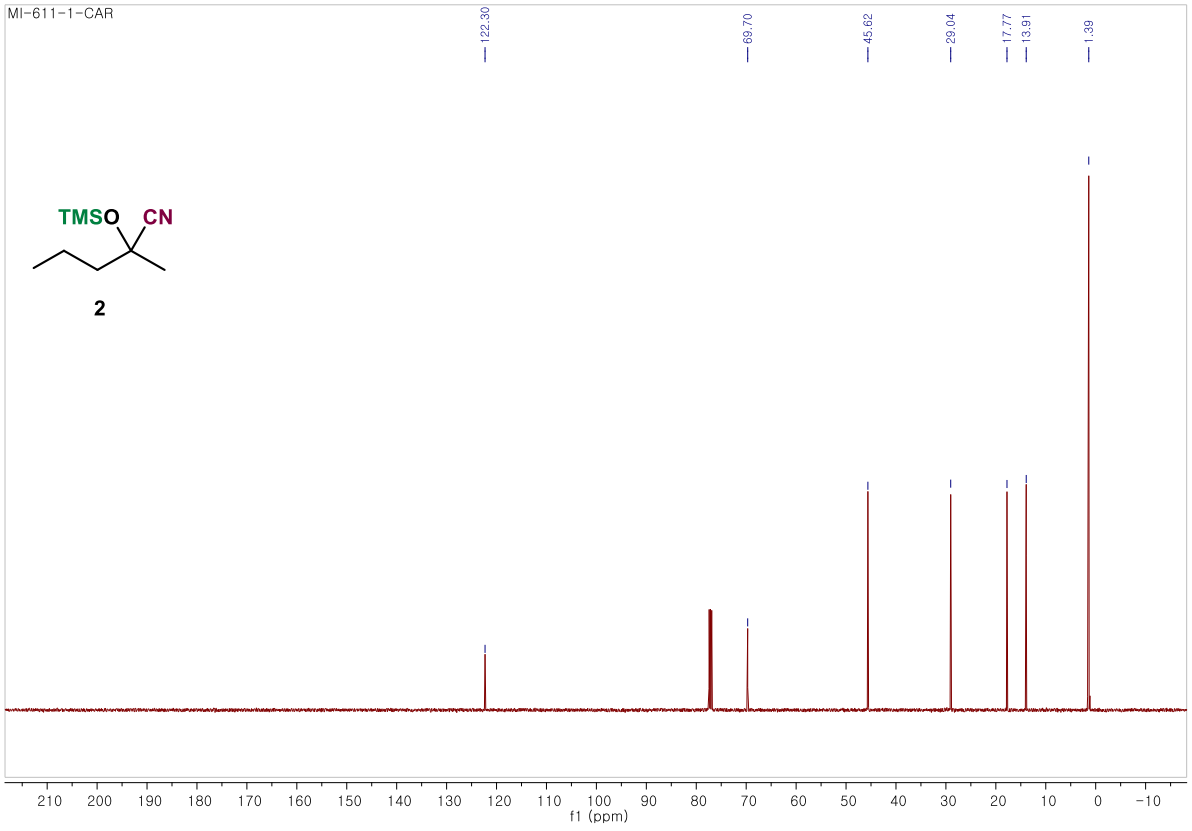
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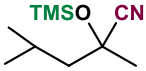
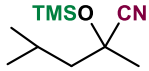
13.91
1.39
TMSO CN
2
f1 (ppm)

MI-613--



3

MI-613-N



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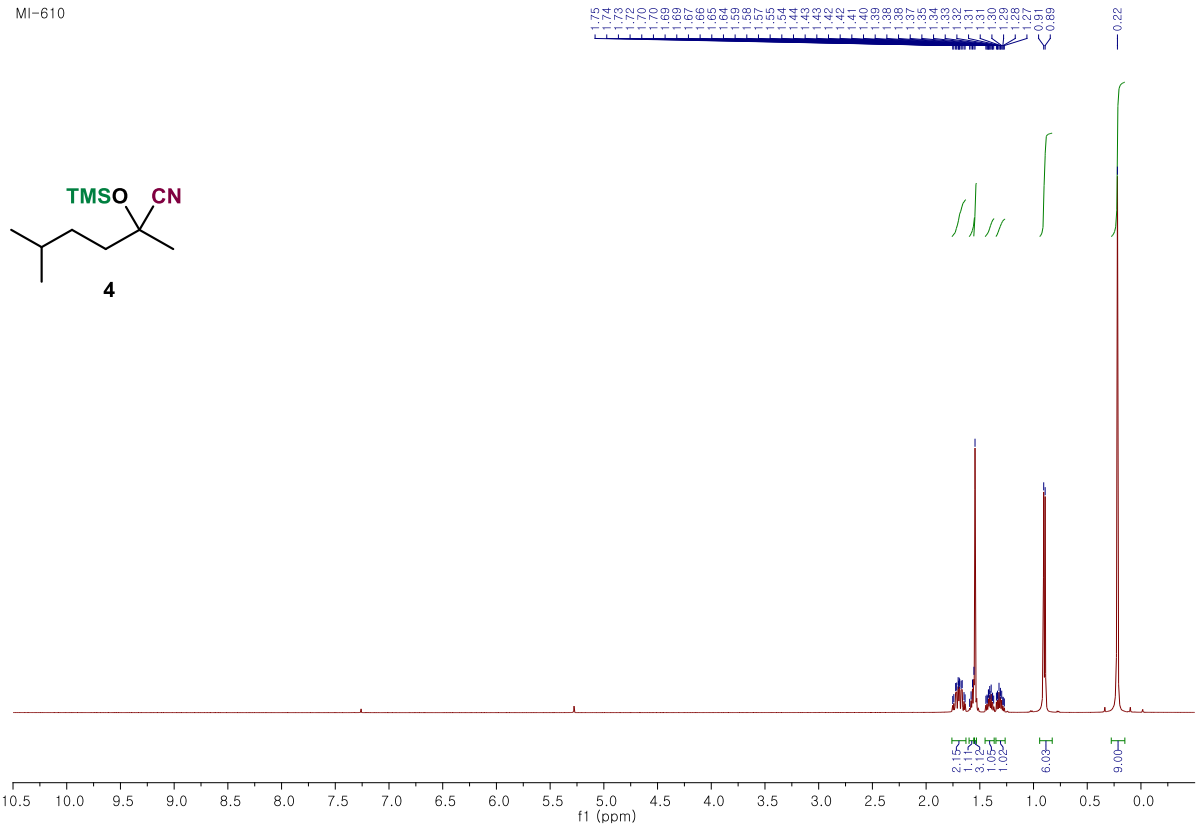

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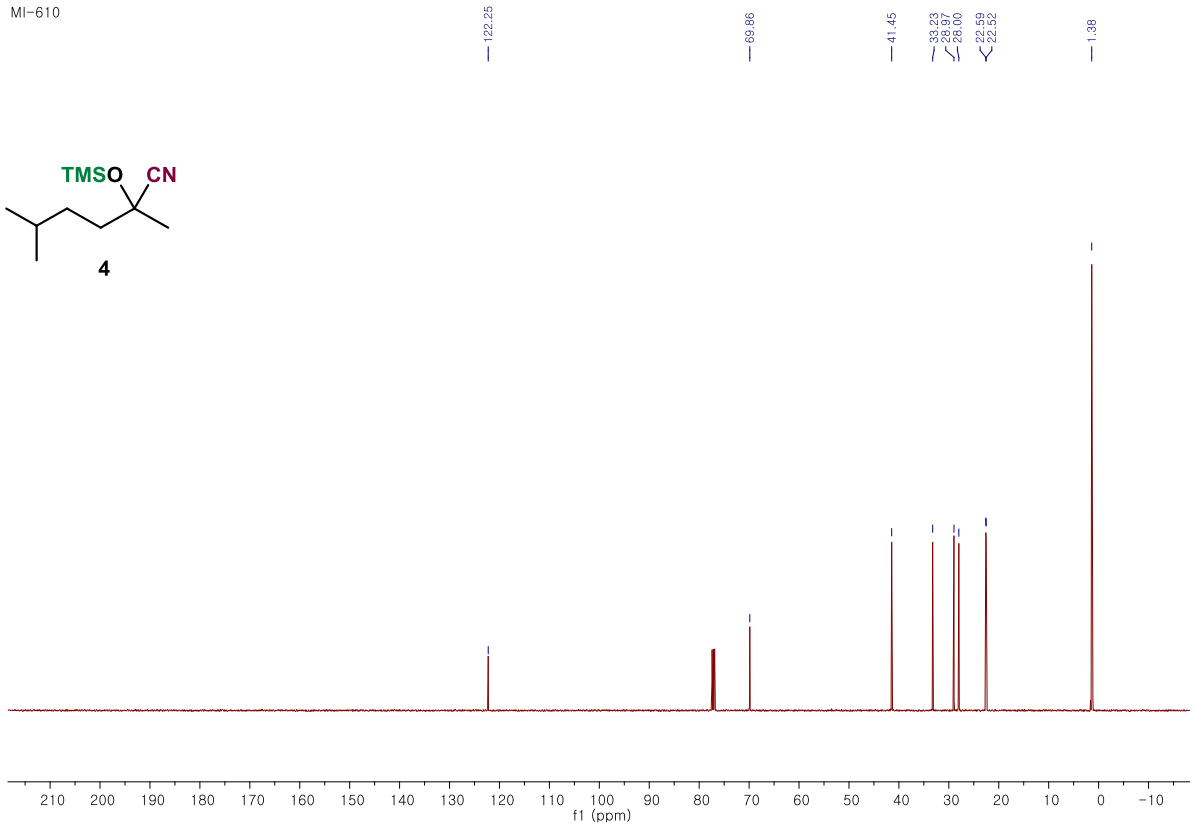

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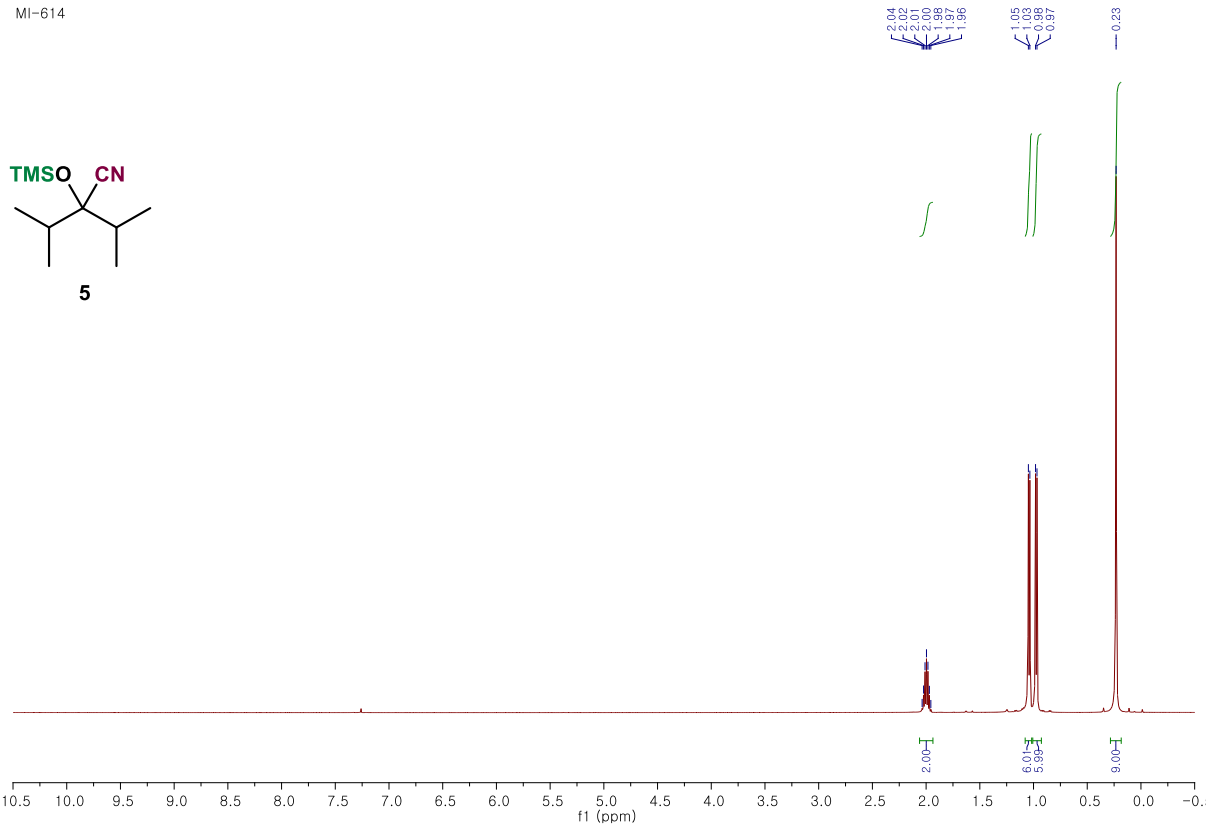
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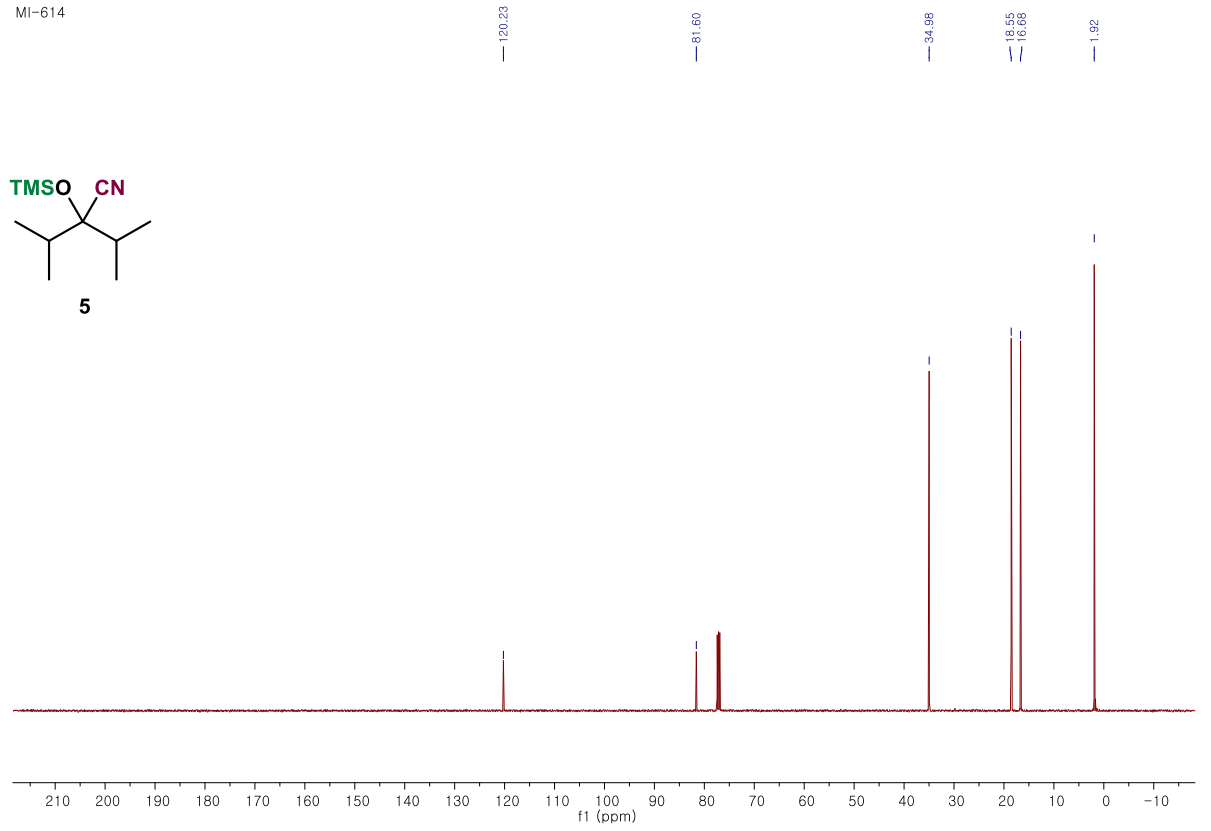
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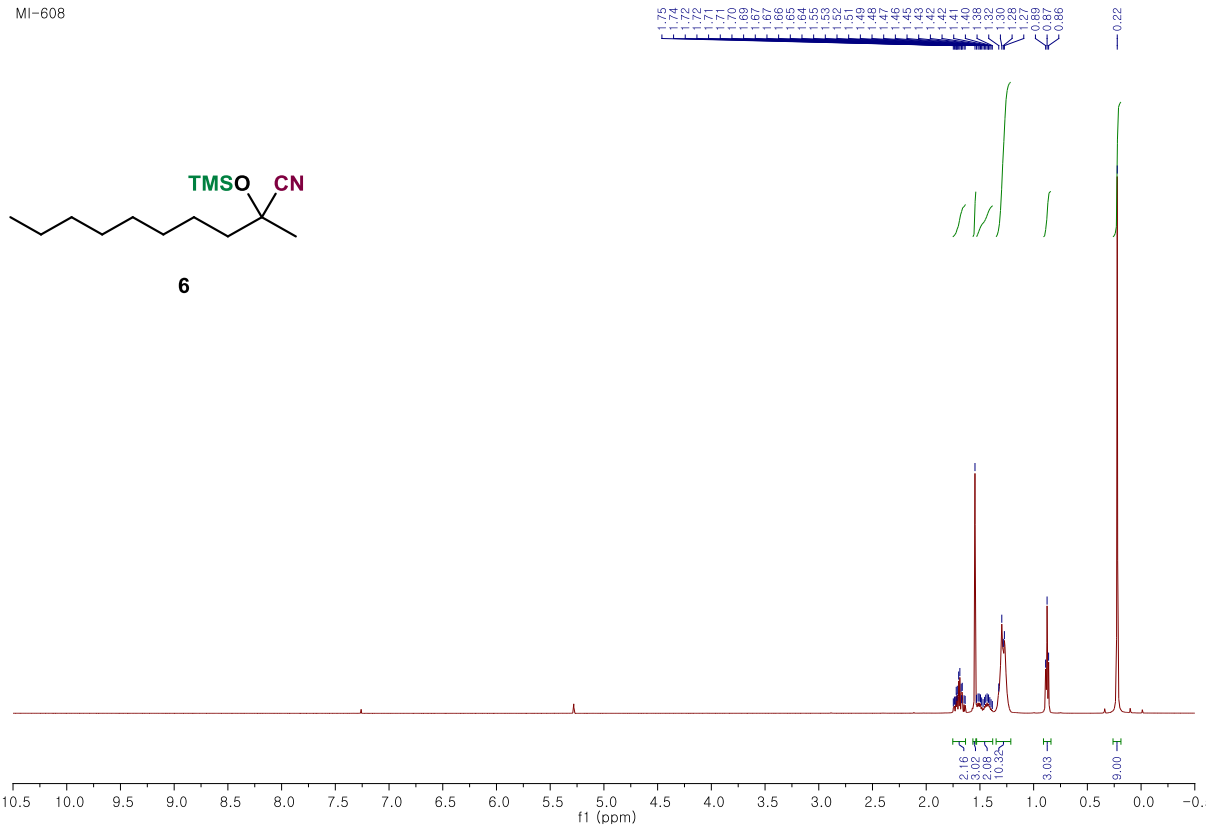
f1 (ppm)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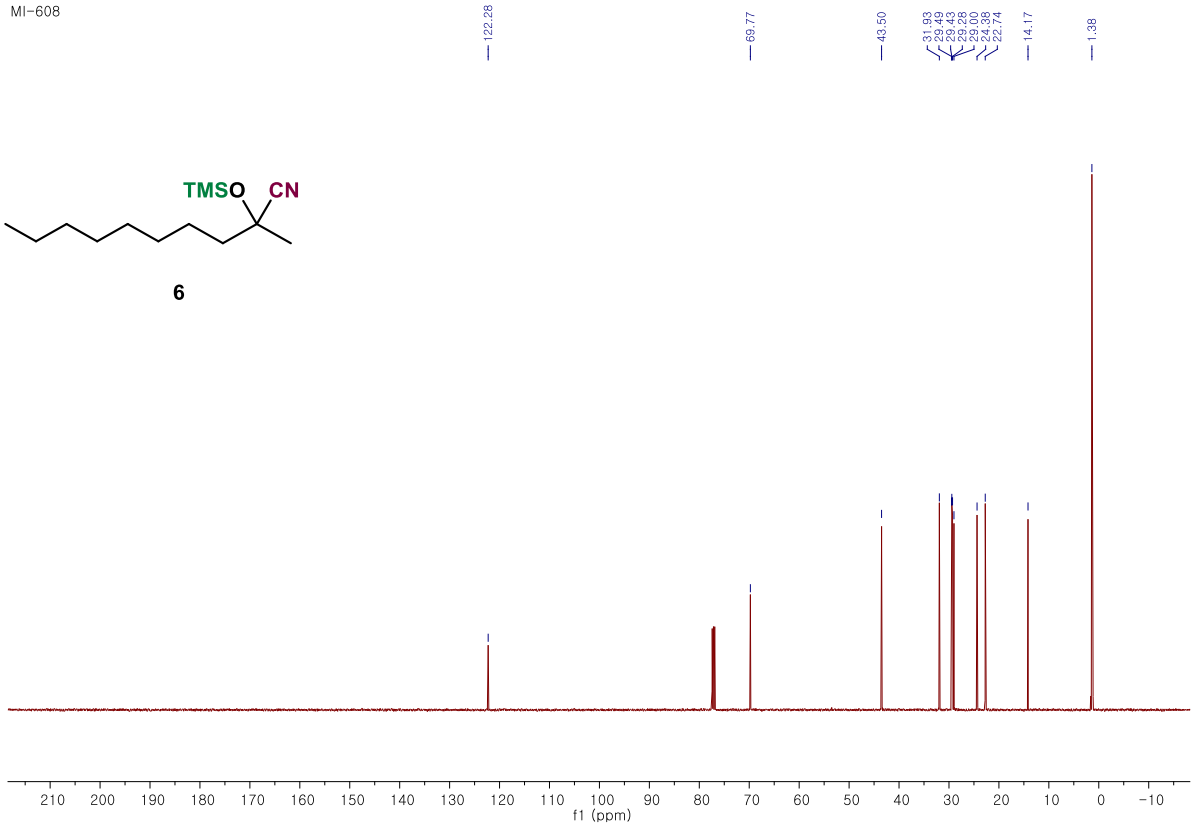
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CN
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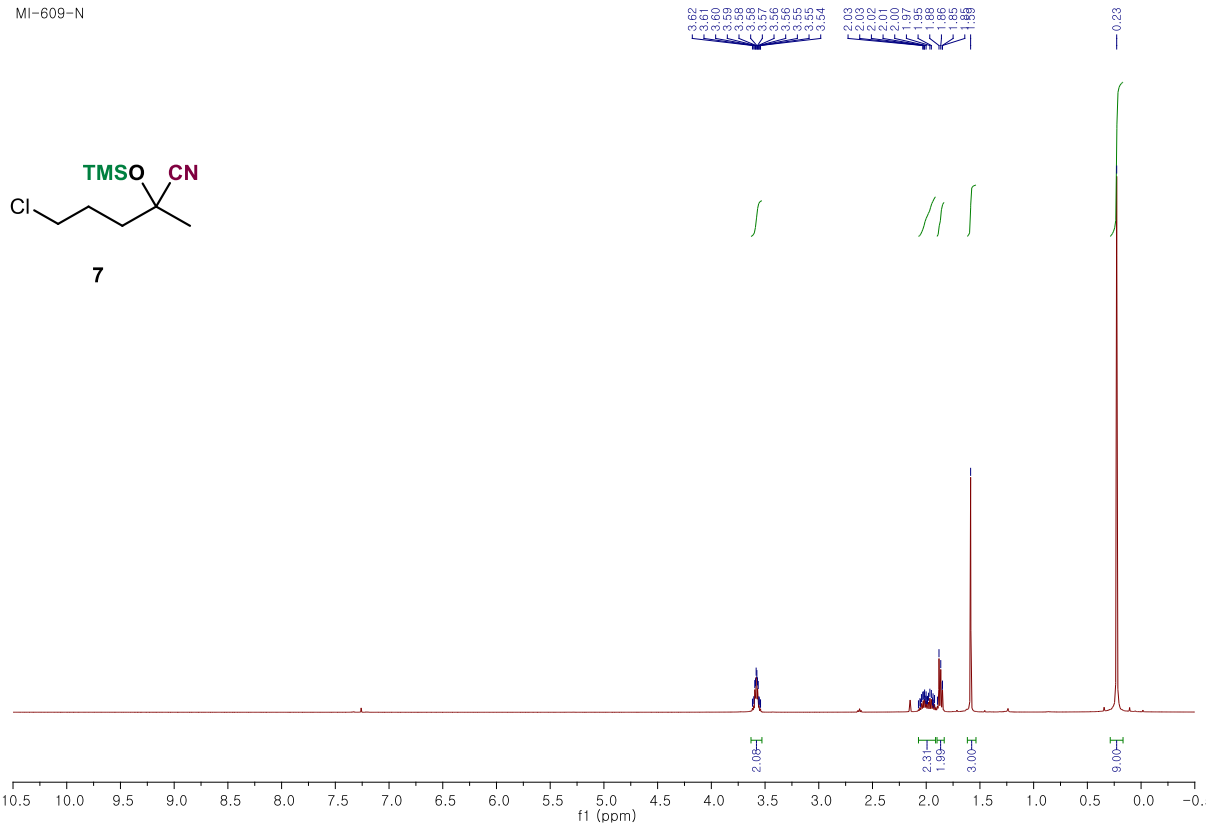
f1 (ppm)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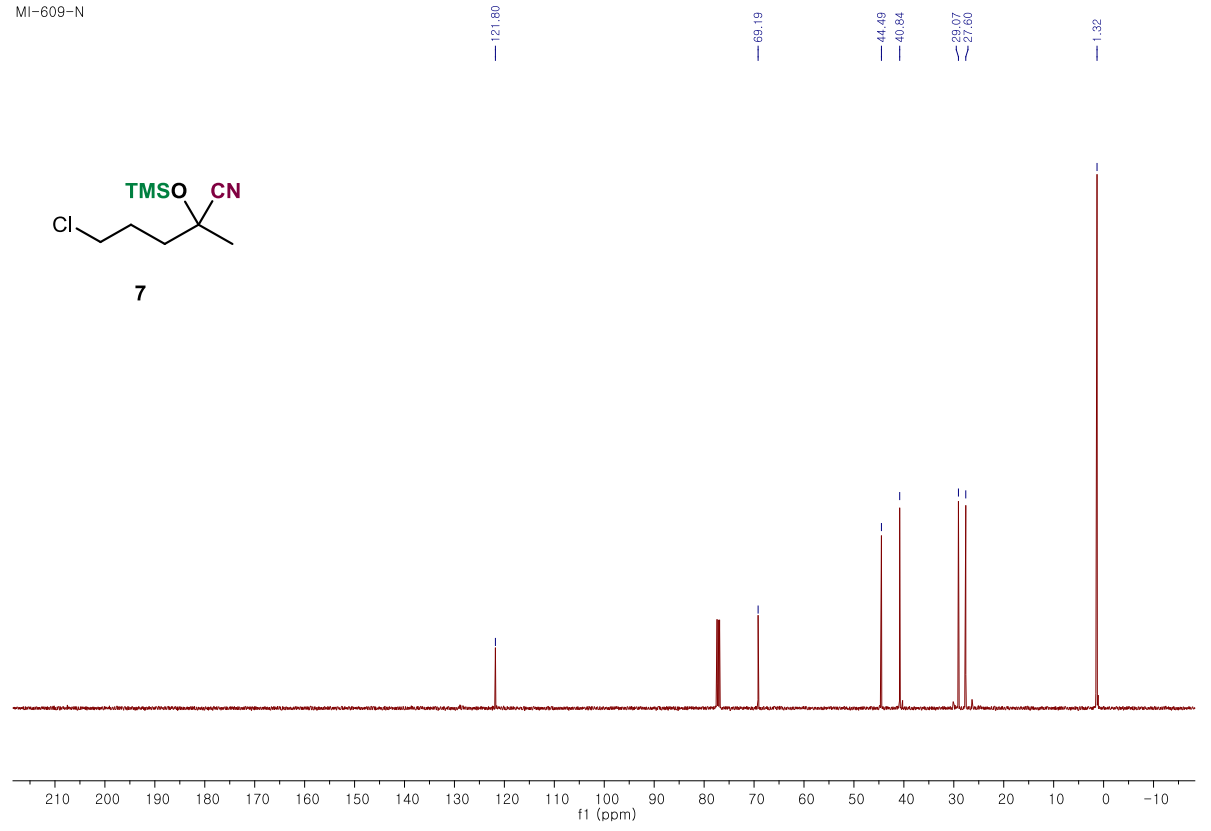
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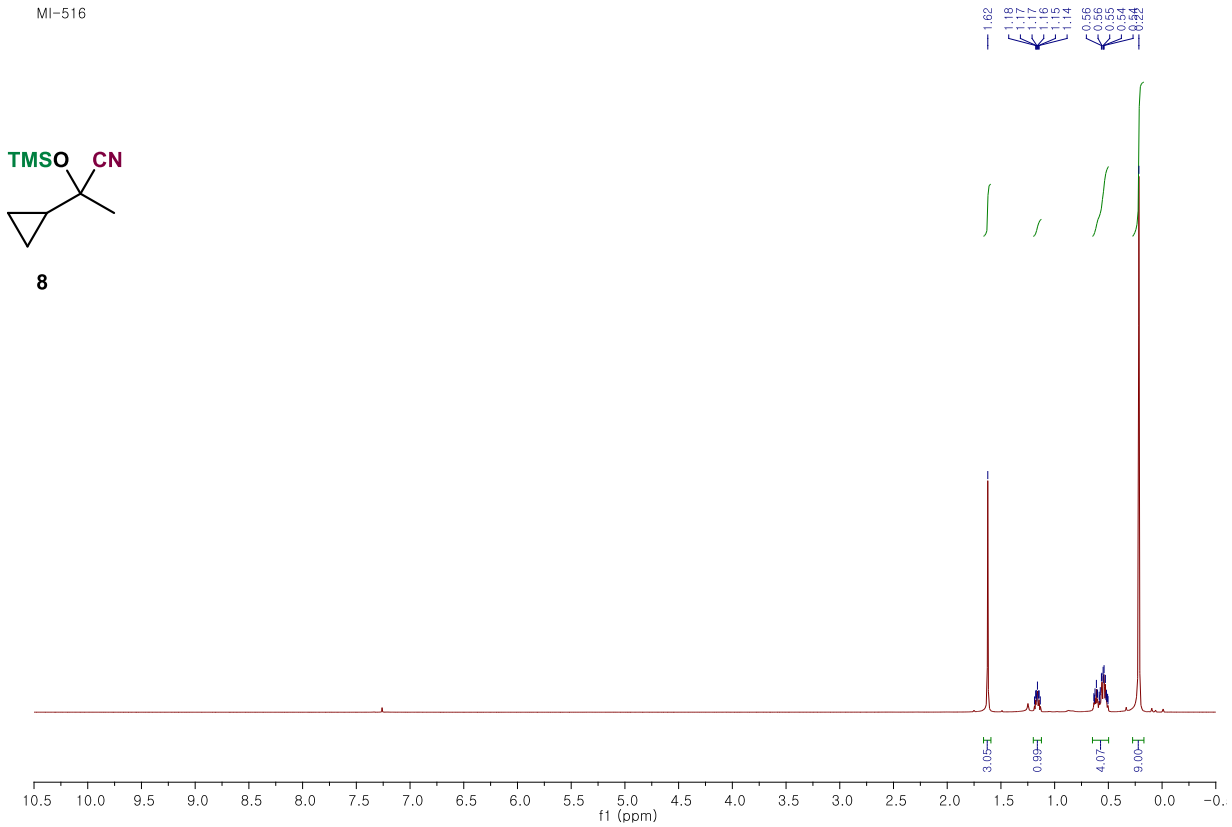
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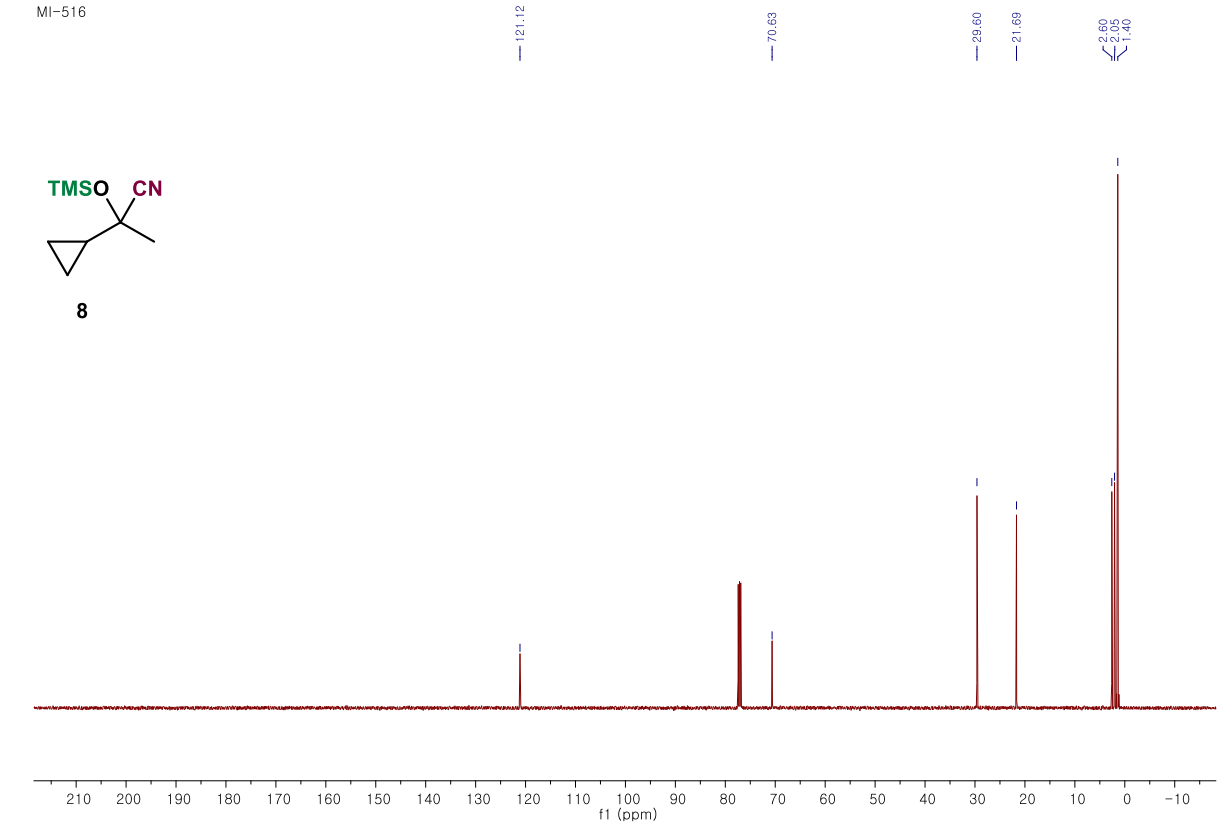
9.00
f1 (ppm)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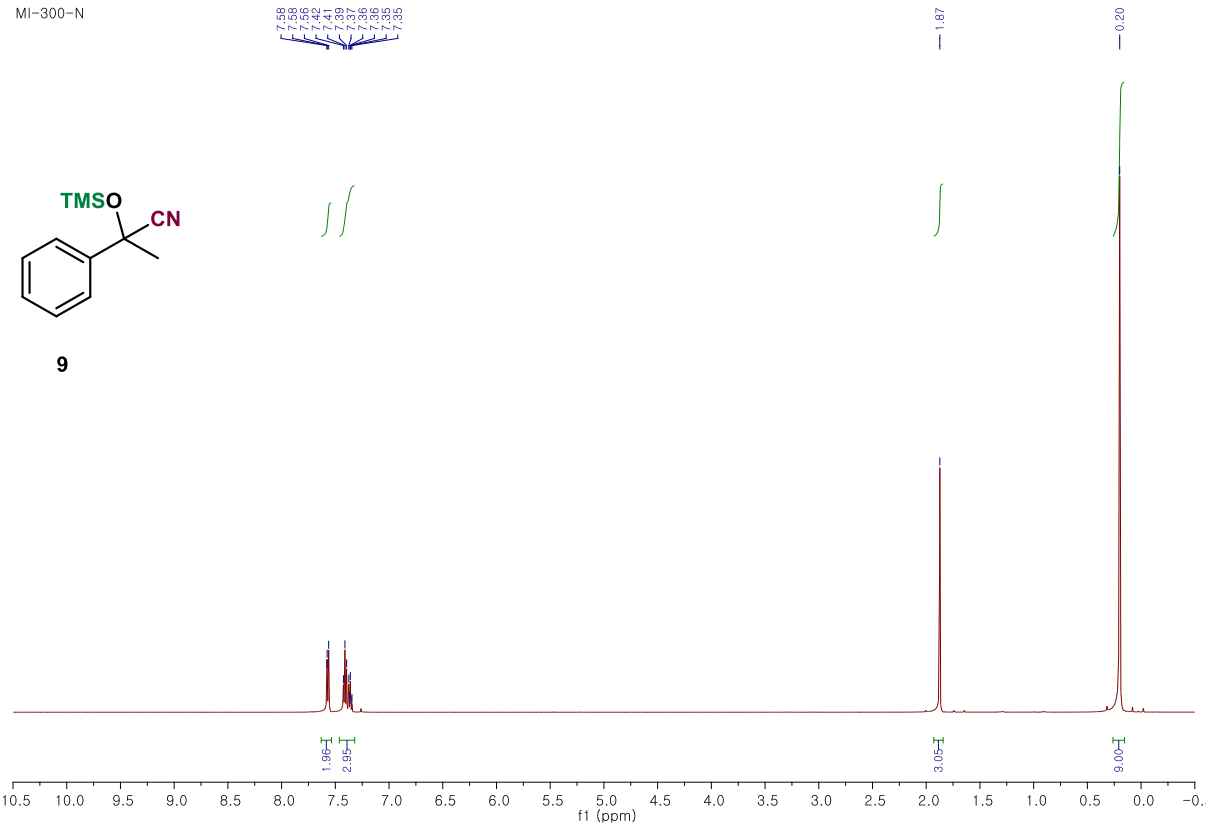
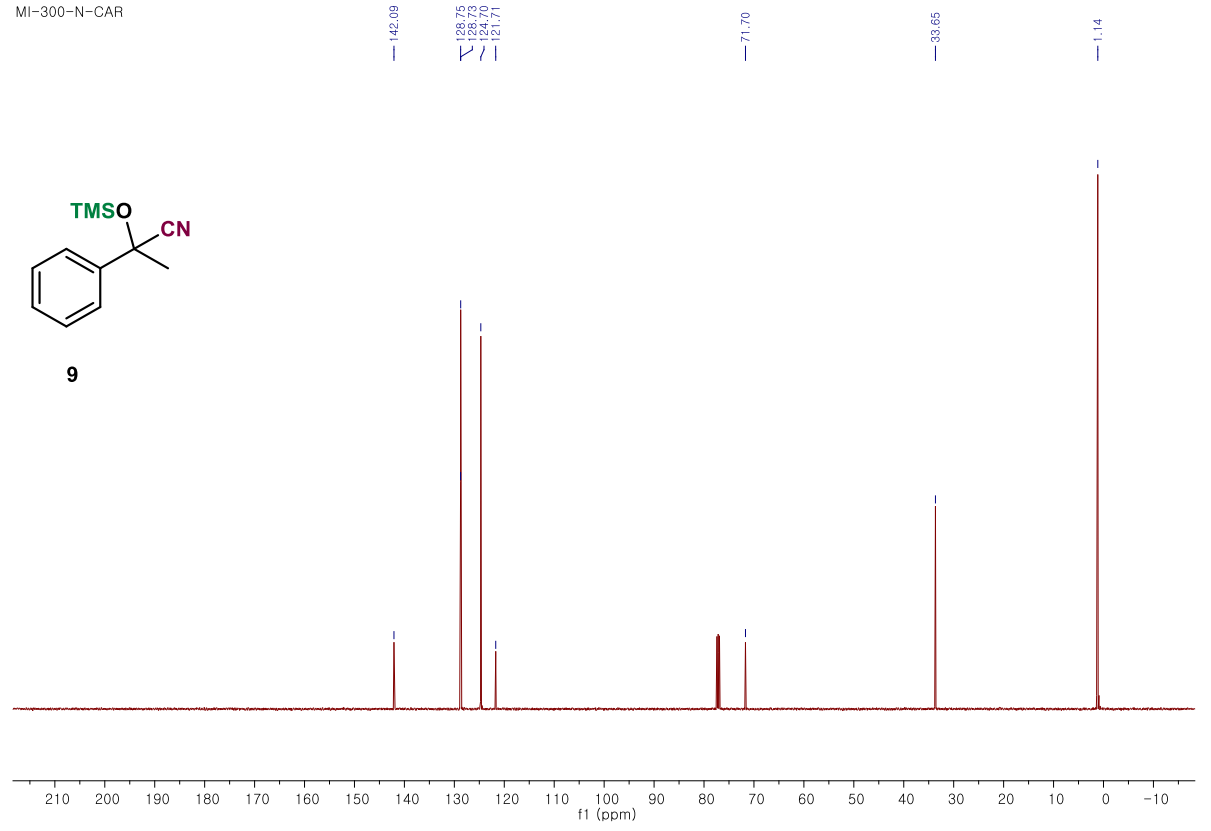
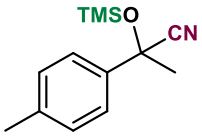
1.40
f1 (ppm)


MI-300-N
7.58
7.58
7.56
7.42
7.41
7.39
7.37
7.36
7.36
7.35
7.35
1.87
0.20
TMSO
CN
9
1.96
2.95
3.05
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

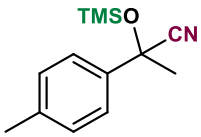

MI-300-N-CAR
142.09
128.75
128.73
124.70
121.71
71.70
33.65
1.14
TMSO
CN
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

MI-299-11

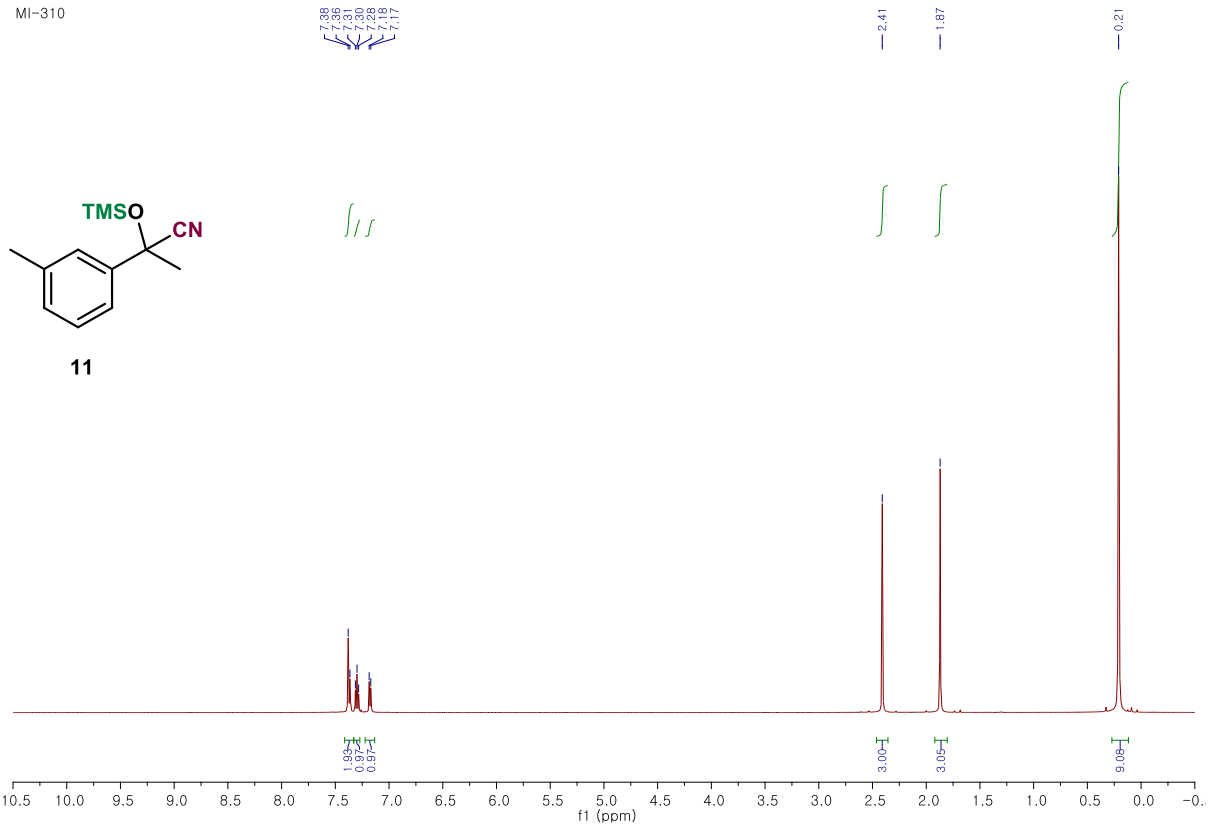


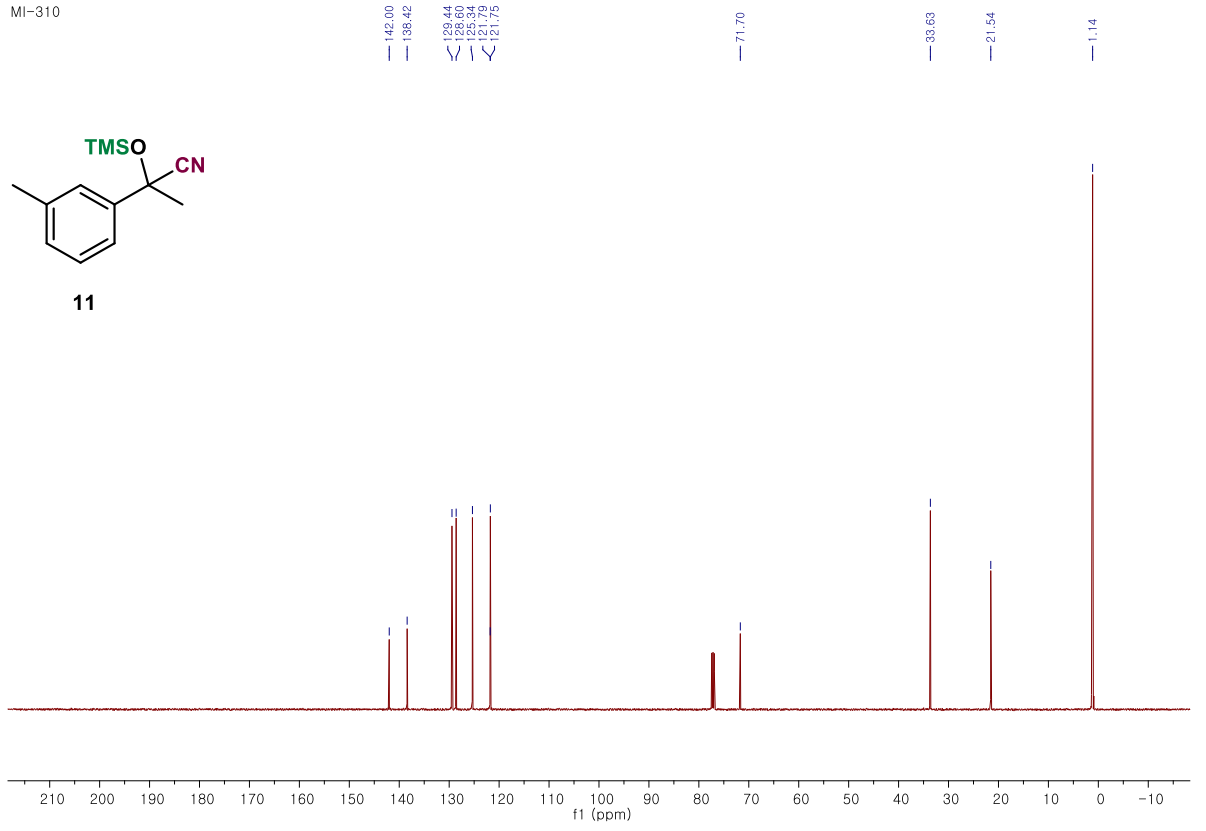
10

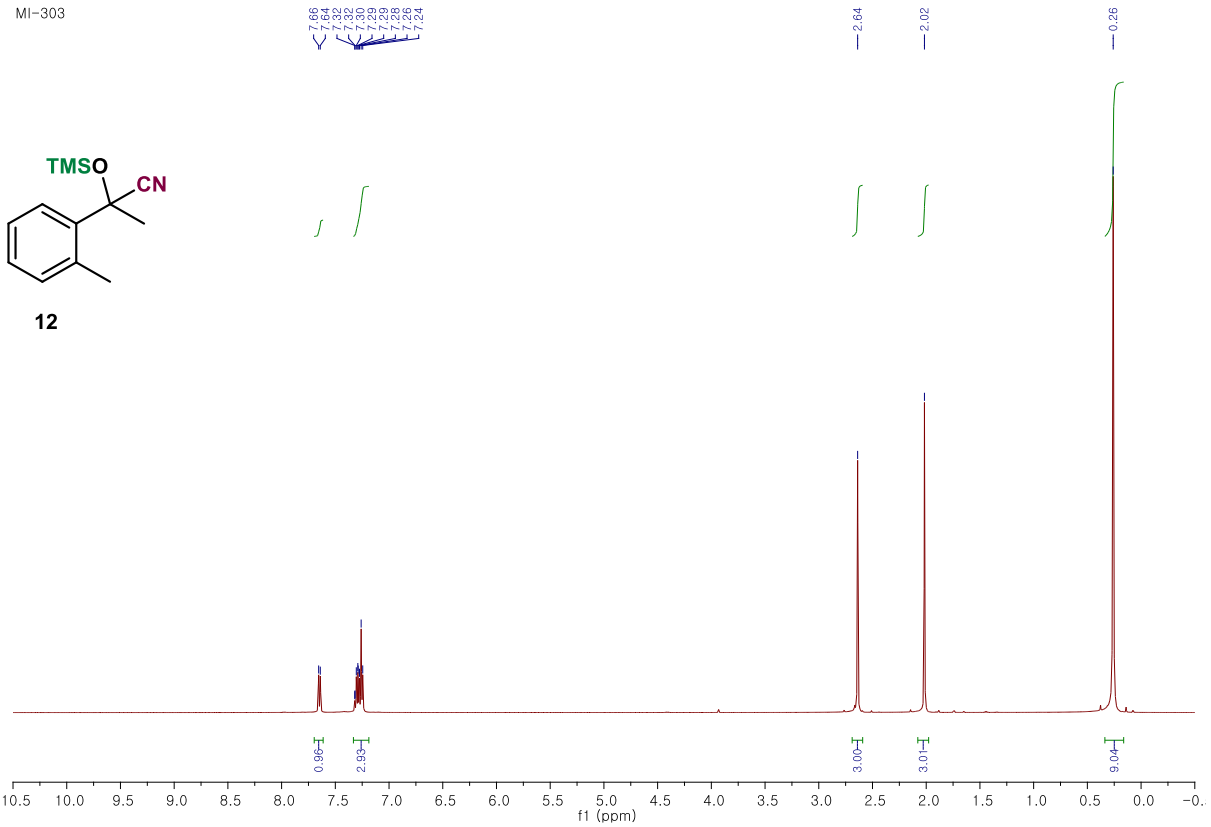
MI-299-1 CAR

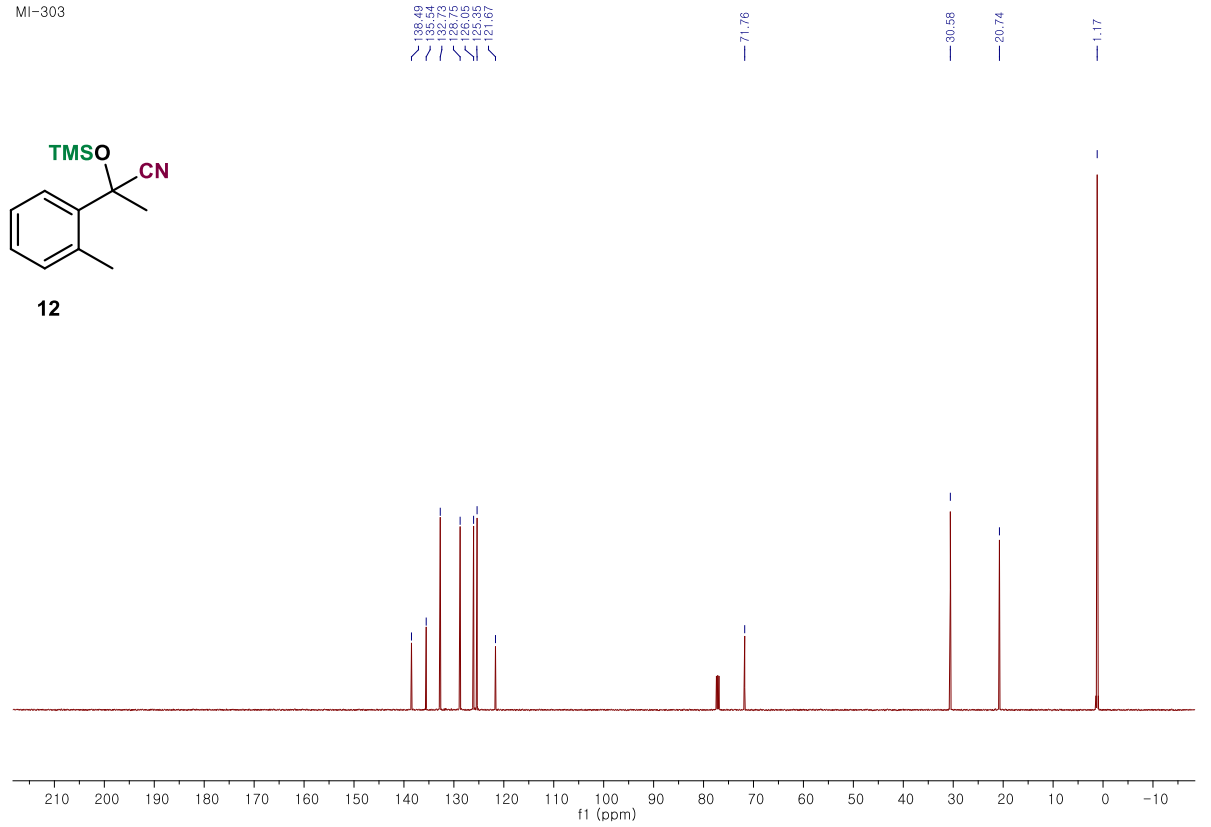


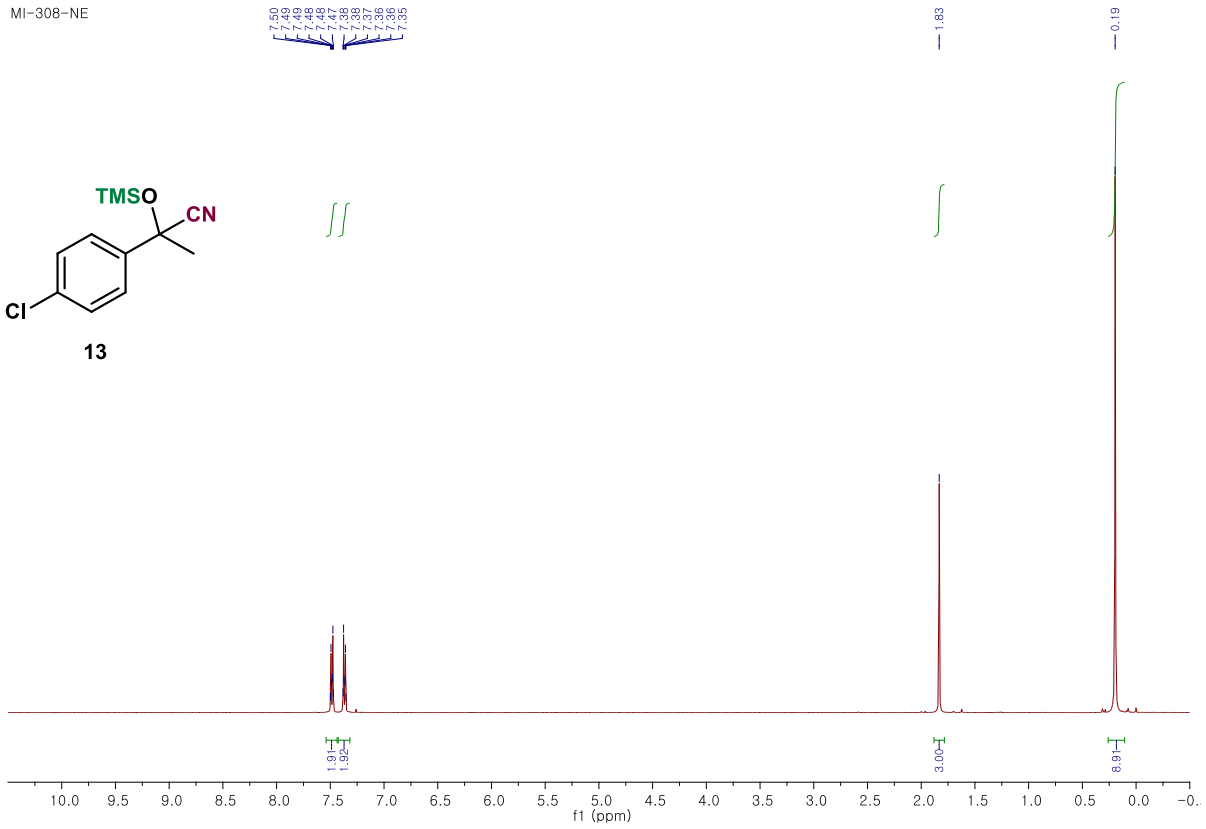
10

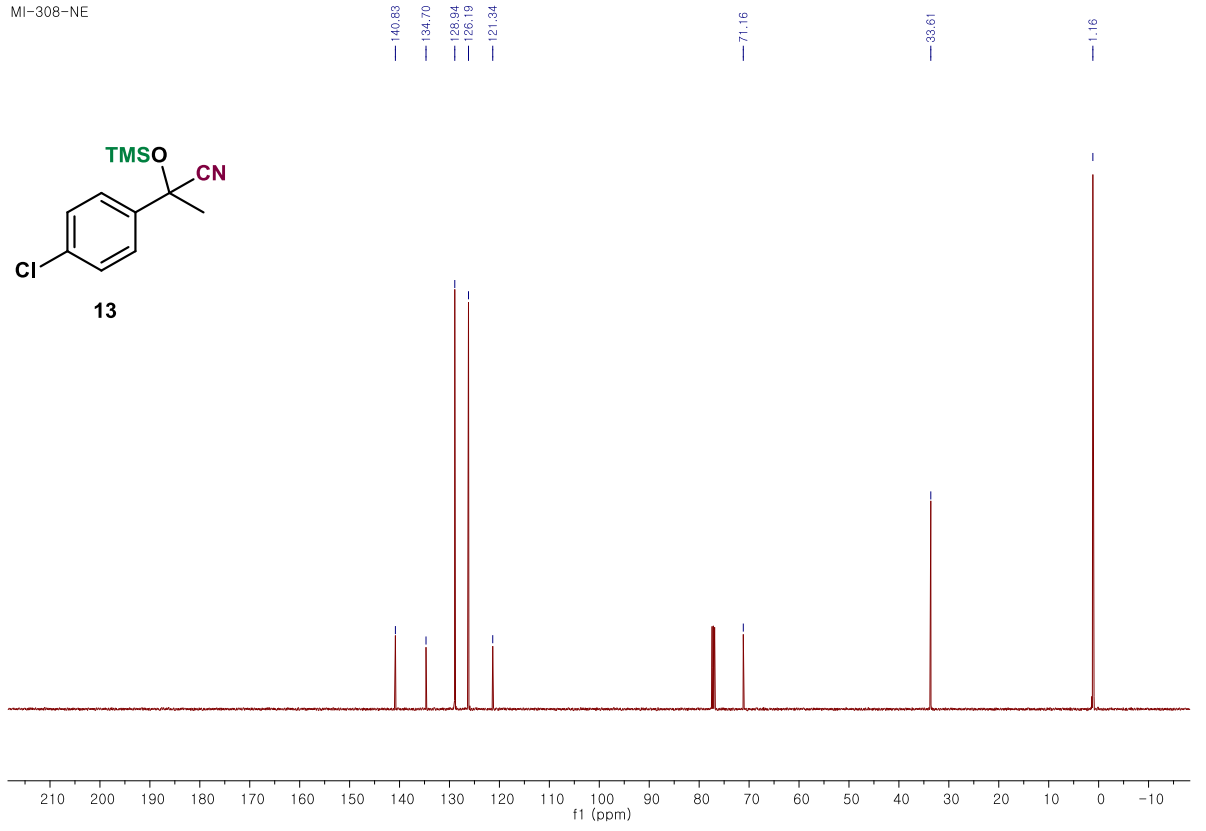

MI-310
7.38
7.36
7.31
7.30
7.28
7.19
7.17
2.41
1.87
0.21
TMSO
CN
11
1.93
0.97
0.97
3.00
3.05
9.08
f1 (ppm)

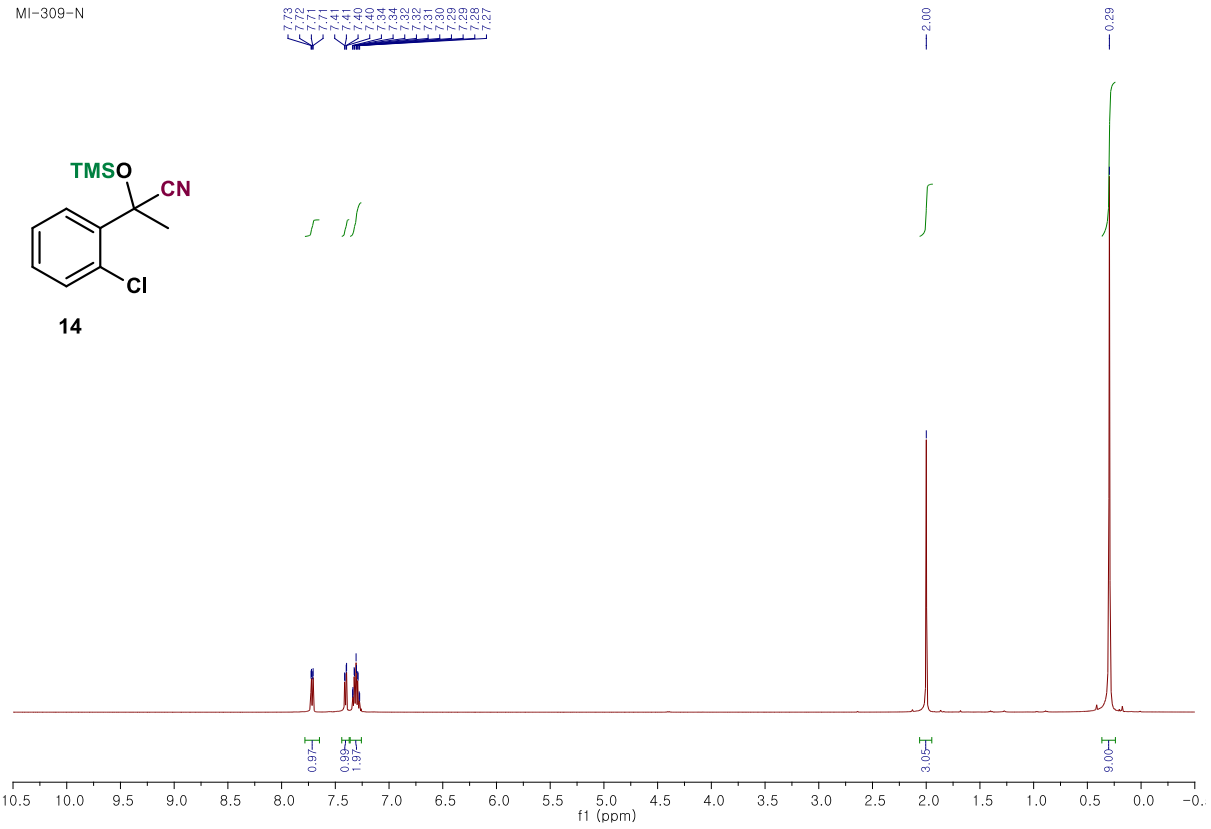

MI-310
142.00
138.42
129.44
128.60
125.34
121.79
121.75
71.70
33.63
21.54
1.14
TMSO
CN
11
f1 (ppm)

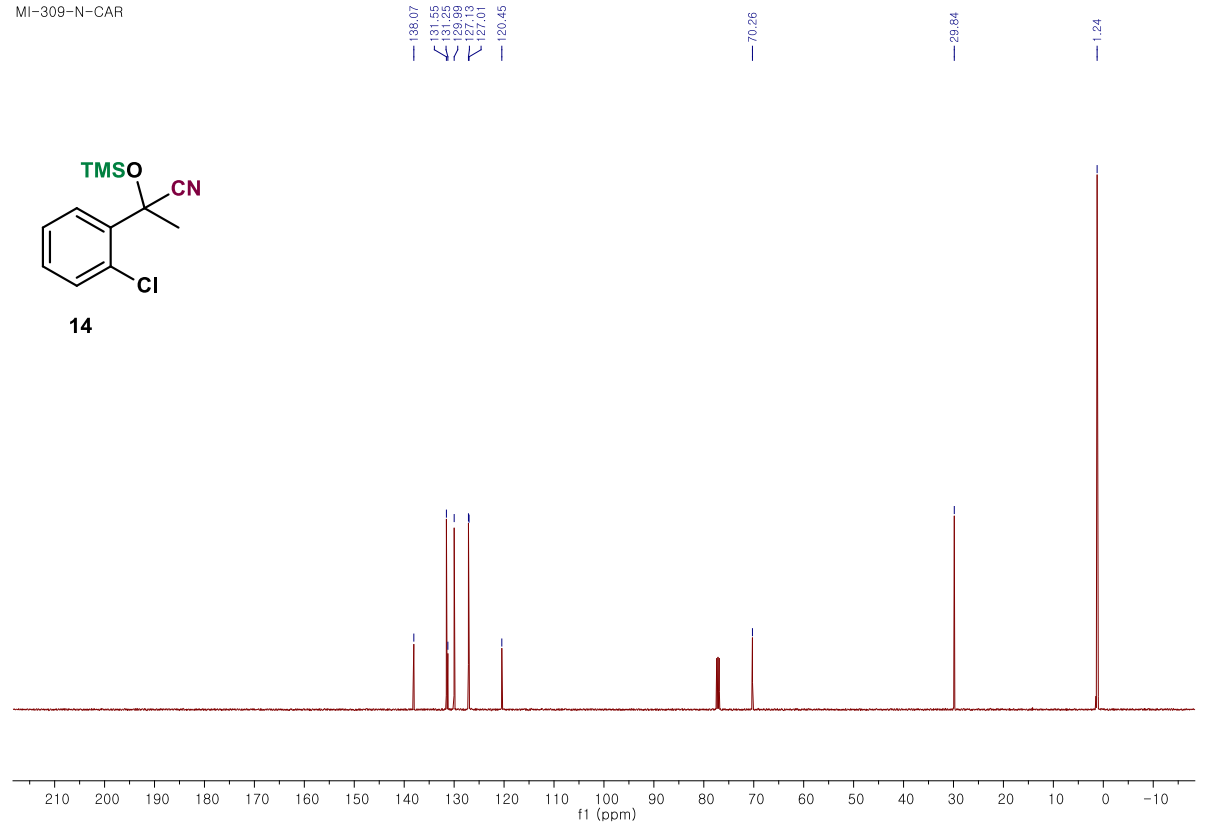

MI-303
7.66
7.64
7.32
7.32
7.30
7.29
7.29
7.28
7.26
7.24
2.64
2.02
0.26
TMSO
CN
12
0.96
2.93
3.00
3.01
9.04
f1 (ppm)

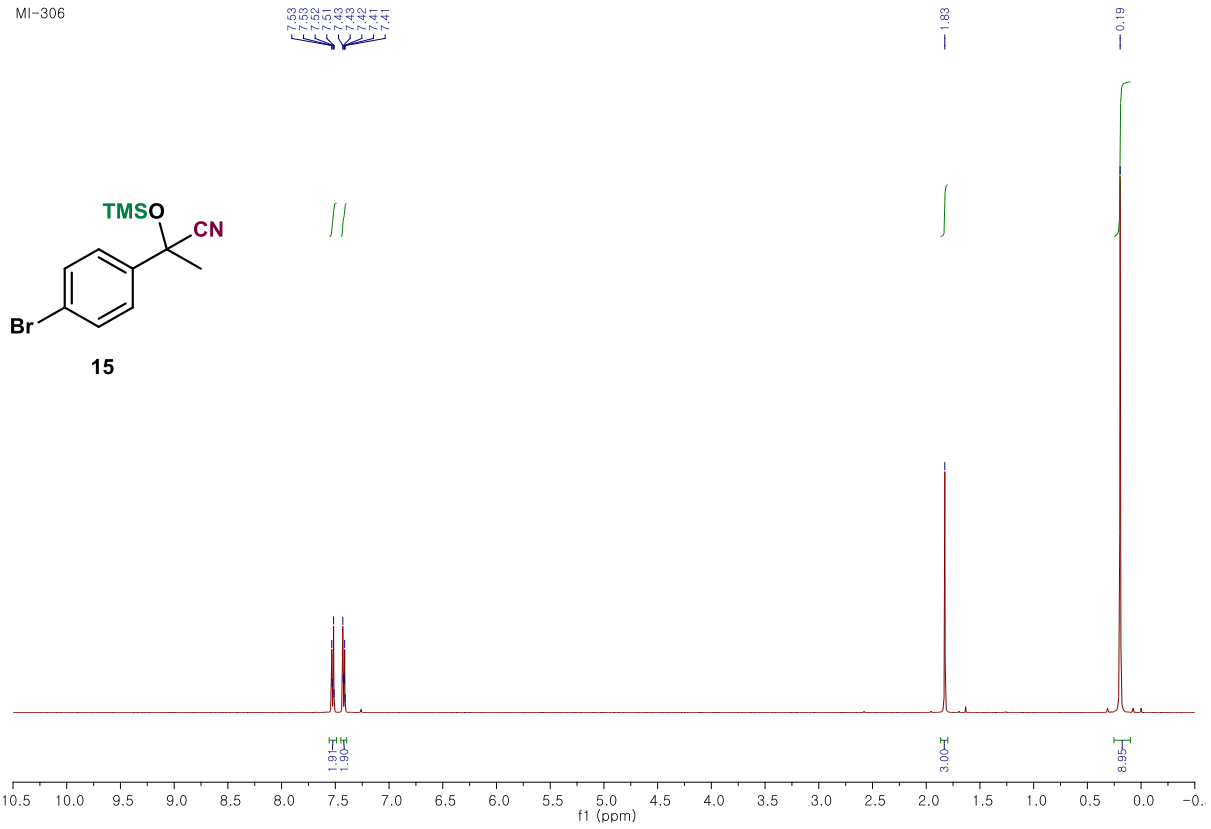

MI-303
138.49
135.54
132.73
128.75
126.05
125.35
121.67
71.76
30.58
20.74
1.17
TMSO
CN
12
f1 (ppm)

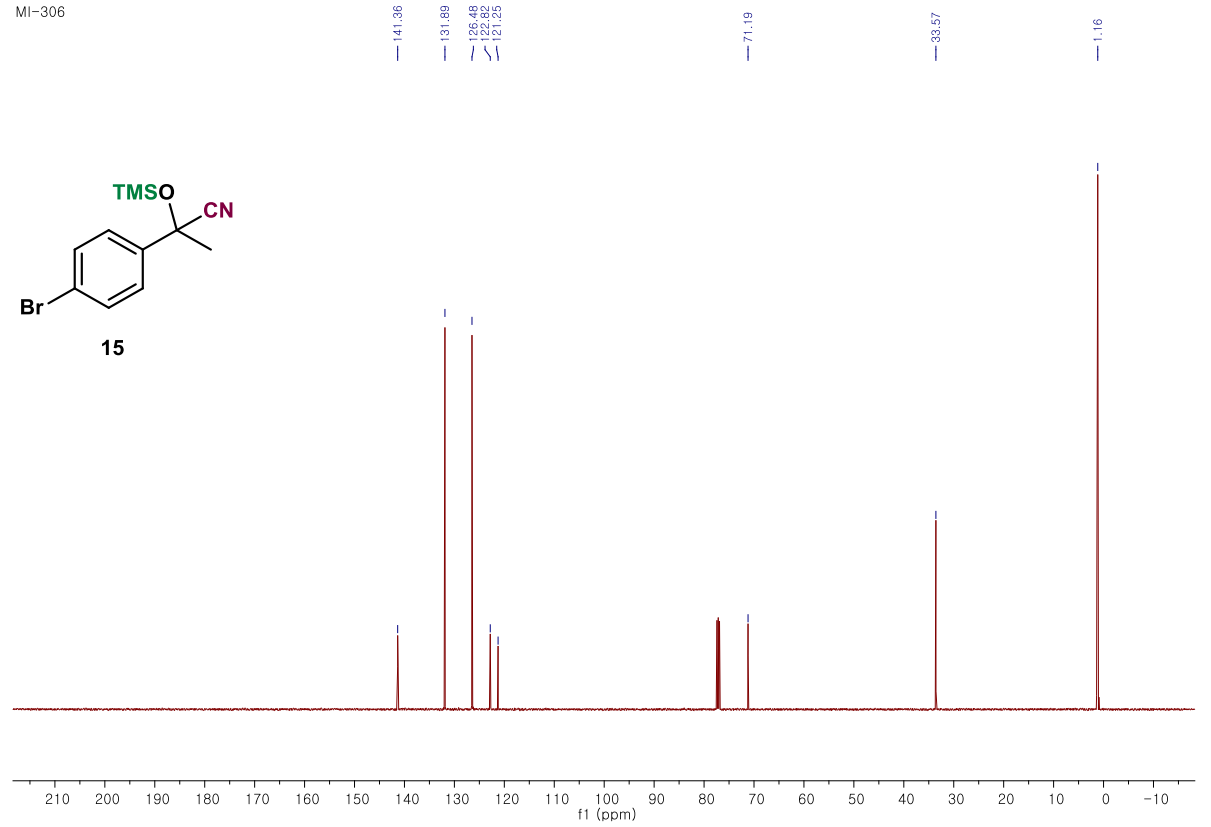

MI-308-NE
7.50
7.49
7.49
7.48
7.48
7.47
7.38
7.38
7.37
7.37
7.36
7.36
7.35
1.83
0.19
TMSO
CN
Cl
13
1.91
1.92
3.00
8.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

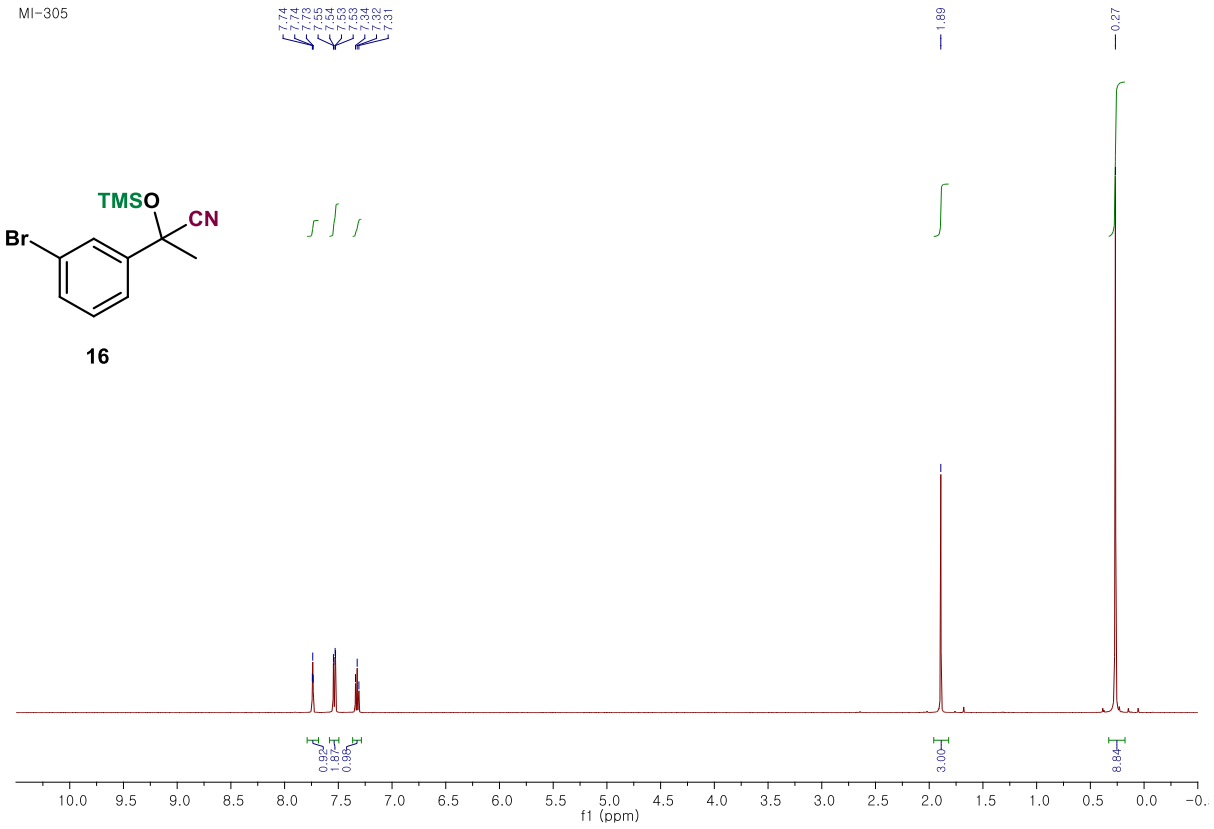

MI-308-NE
140.83
134.70
128.94
126.19
121.34
71.16
33.61
1.16
TMSO
CN
Cl
13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

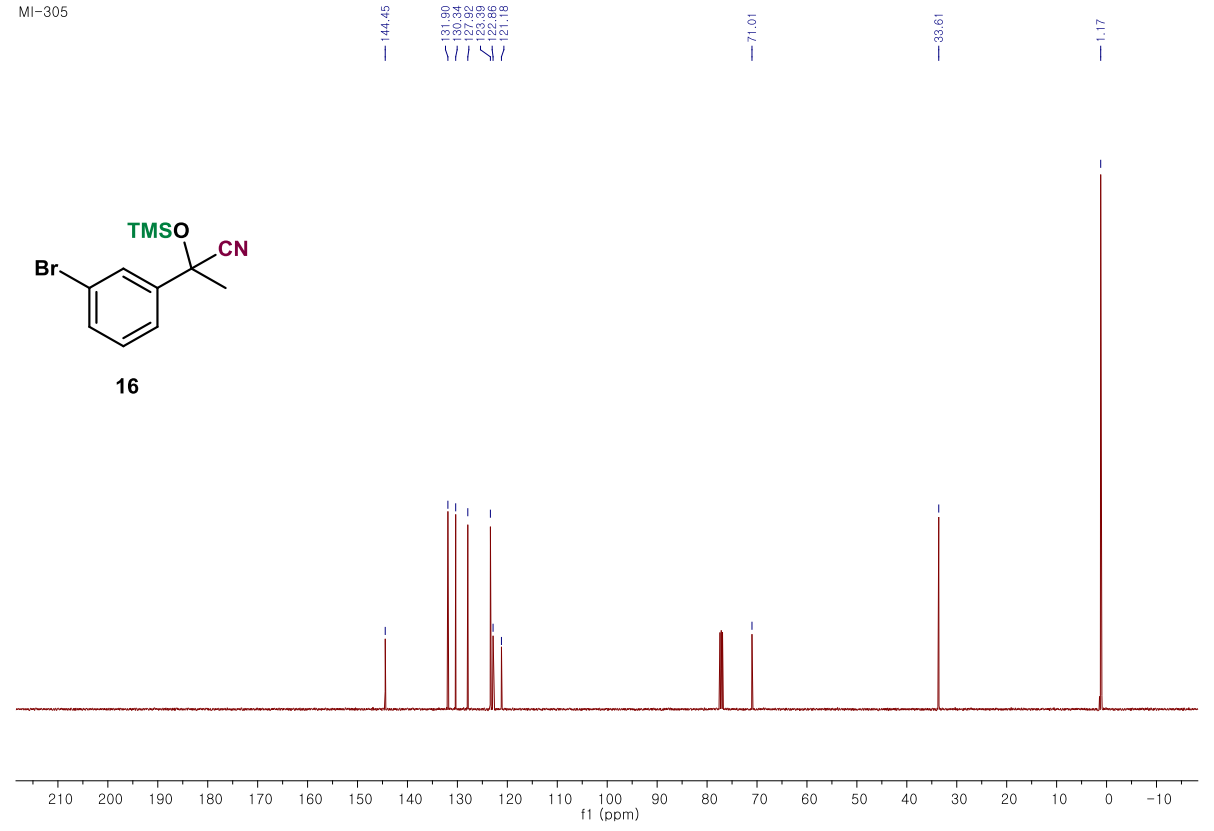

MI-309-N
7.73
7.72
7.71
7.71
7.41
7.41
7.40
7.40
7.34
7.34
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.27
2.00
0.29
TMSO
CN
Cl
14
0.97
0.99
1.97
3.05
9.00
f1 (ppm)

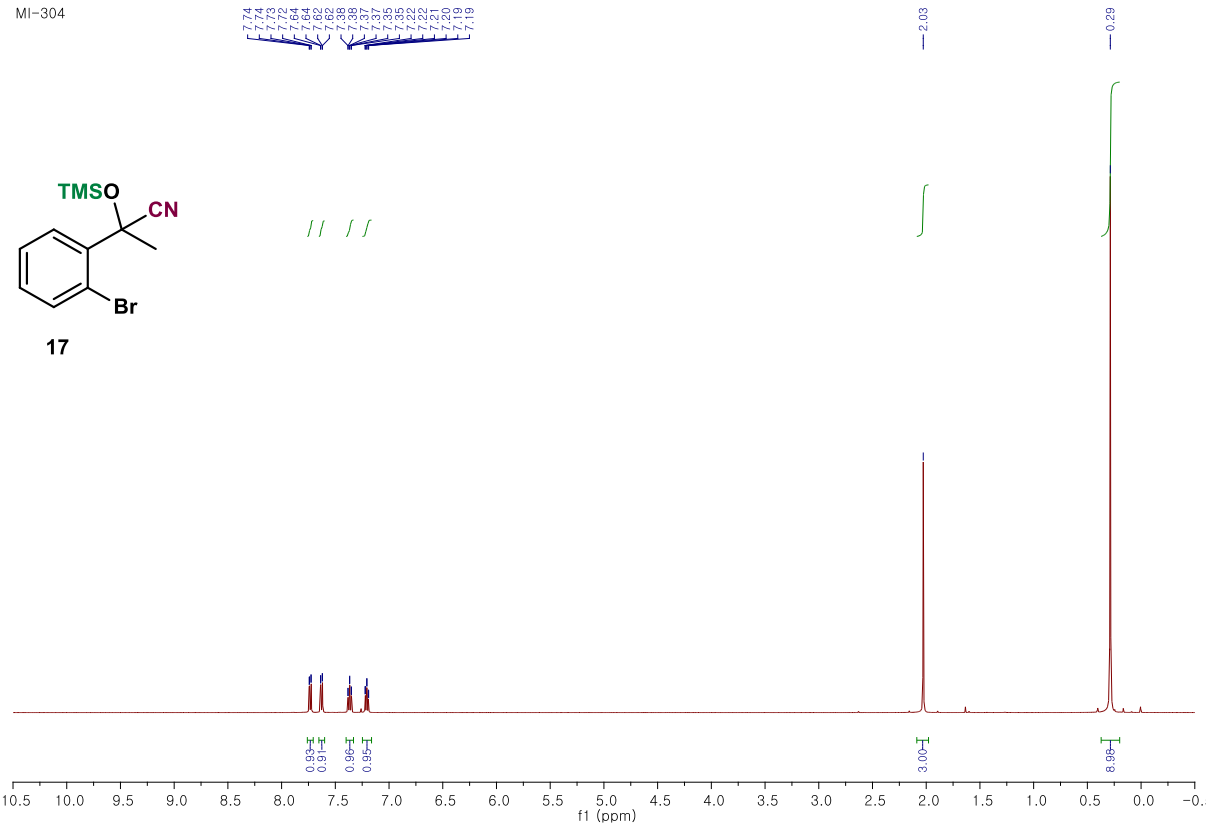

MI-309-N-CAR
138.07
131.55
131.25
129.99
127.13
127.01
120.45
70.26
29.84
1.24
TMSO
CN
Cl
14
f1 (ppm)

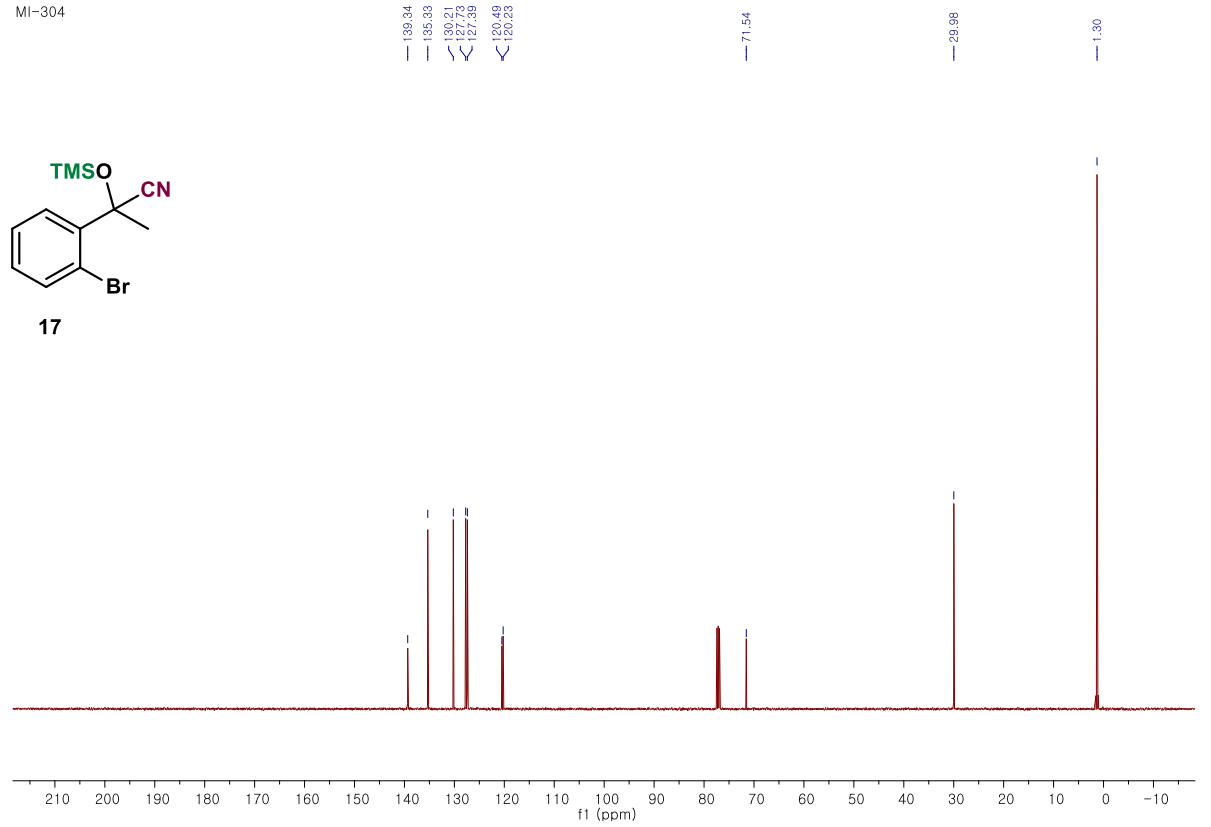

MI-306
7.53
7.53
7.52
7.51
7.43
7.43
7.42
7.41
7.41
1.83
0.19
TMSO
CN
Br
15
1.91
1.90
3.00
8.95
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

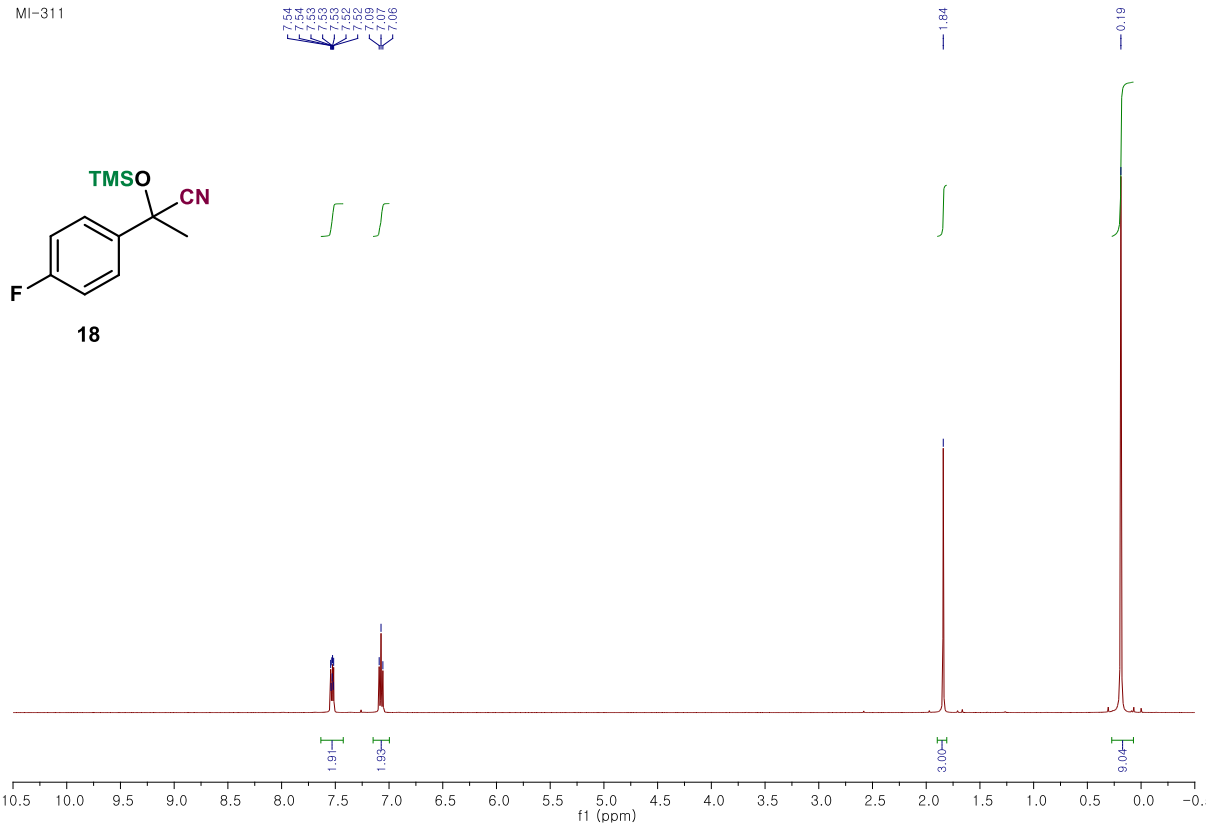

MI-306
141.36
131.89
126.48
122.82
121.25
71.19
33.57
1.16
TMSO
CN
Br
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

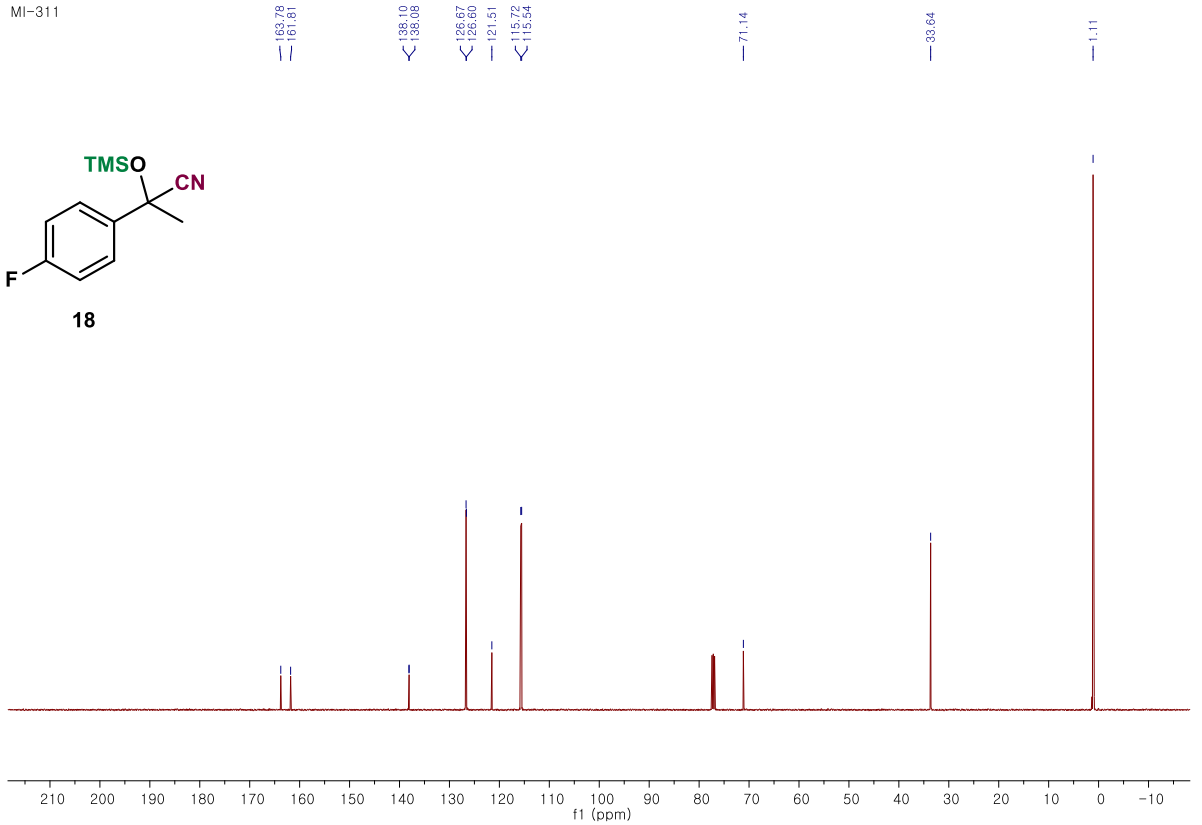

MI-305
7.74
7.74
7.73
7.55
7.54
7.53
7.53
7.34
7.32
7.31
1.89
0.27
TMSO
CN
Br
16
0.92
1.87
0.96
3.00
8.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

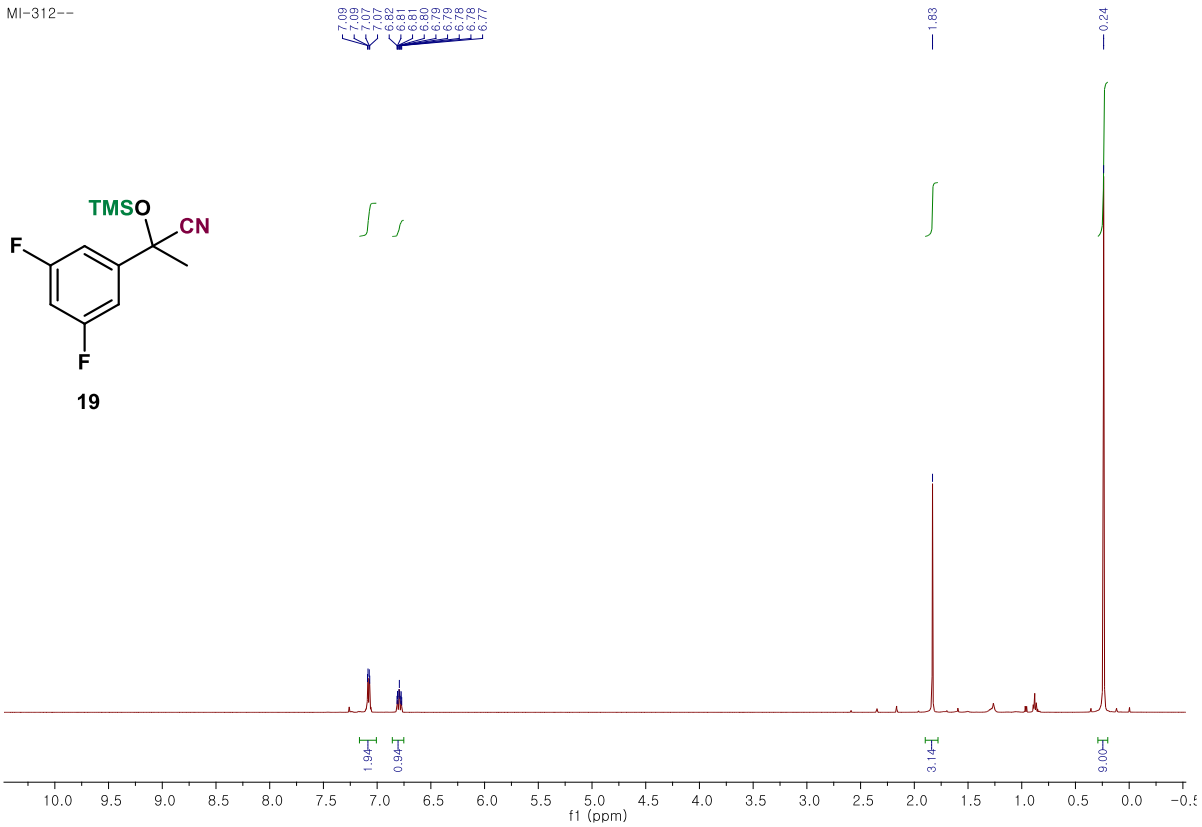

MI-305
144.45
131.90
131.34
127.92
123.39
122.86
121.18
71.01
33.61
1.17
TMSO
CN
Br
16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

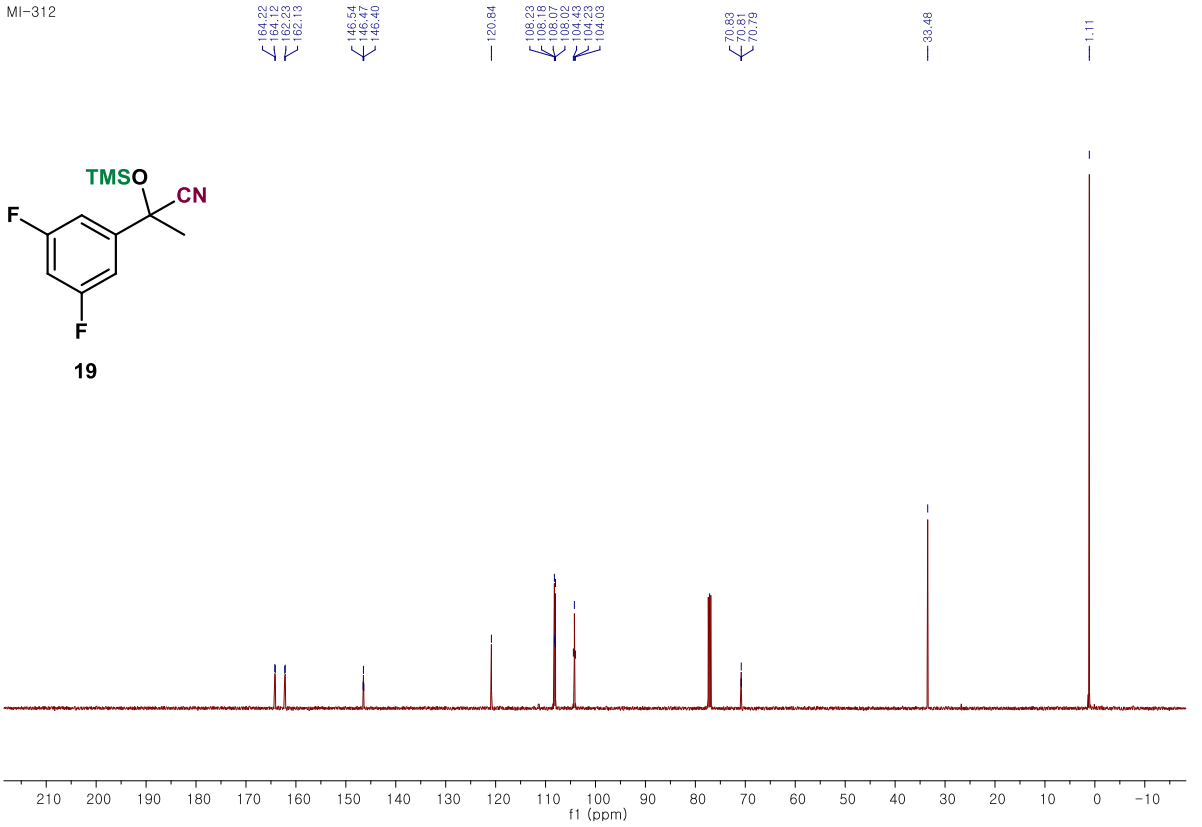

MI-304
7.74
7.74
7.73
7.72
7.64
7.64
7.62
7.62
7.38
7.38
7.37
7.37
7.35
7.35
7.22
7.21
7.20
7.19
7.19
2.03
0.29
TMSO
CN
Br
17
0.93
0.91
0.96
0.95
3.00
8.98
f1 (ppm)

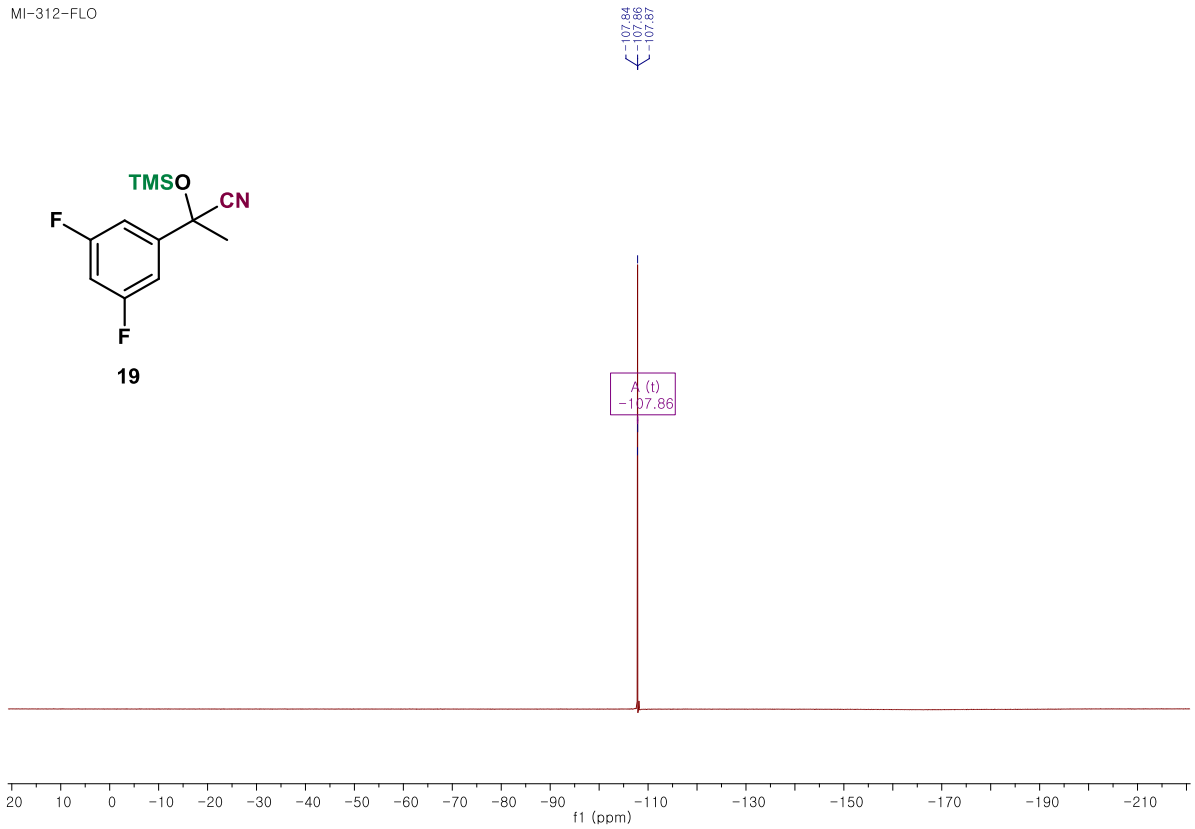

MI-304
139.34
135.33
130.21
127.73
127.39
120.49
120.23
71.54
29.98
1.30
TMSO
CN
Br
17
f1 (ppm)

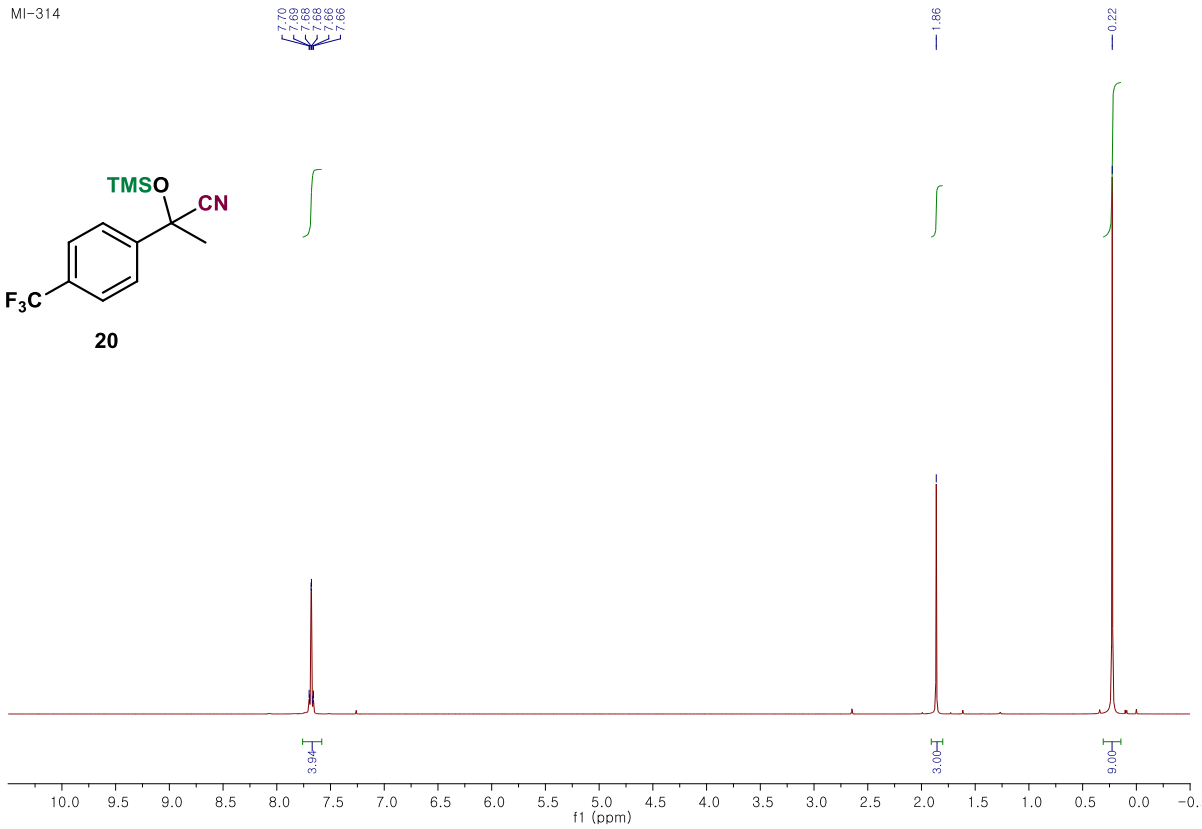

MI-311
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.09
7.07
7.06
1.84
0.19
TMSO
CN
F
18
1.91
1.93
3.00
9.04
f1 (ppm)

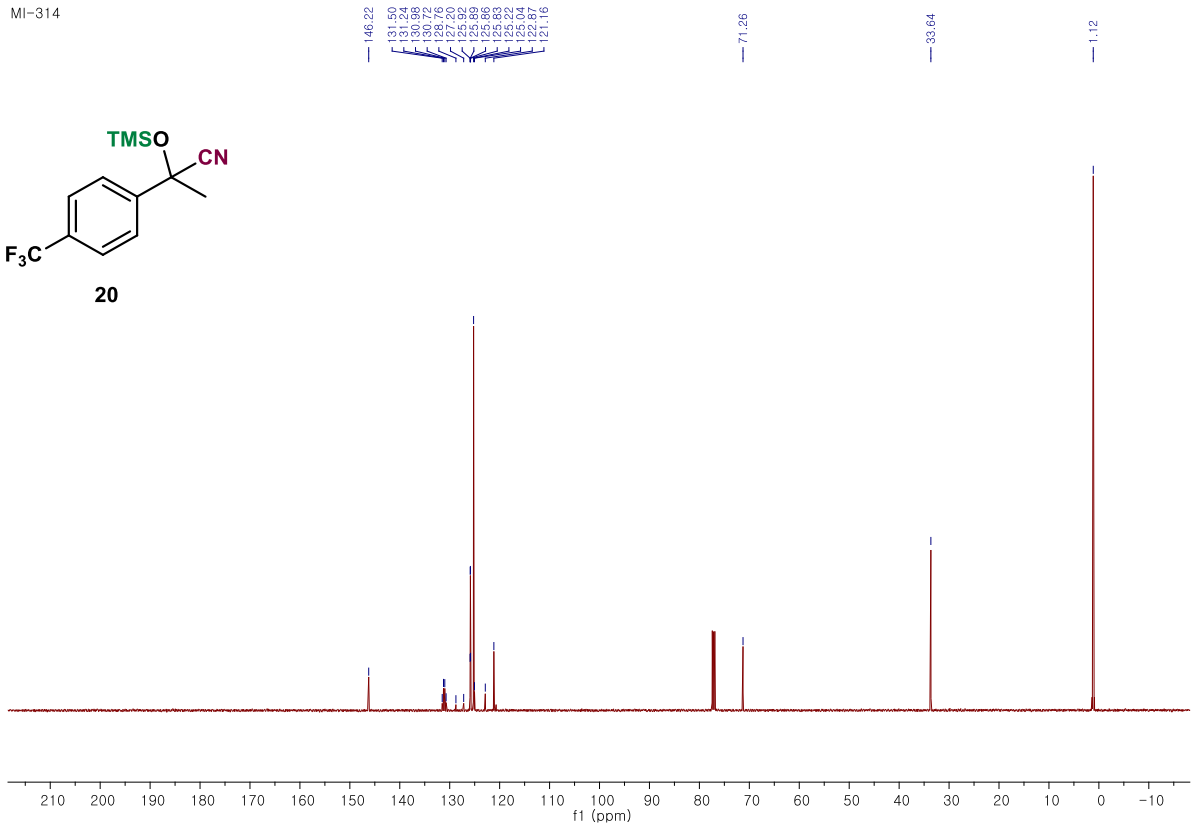

MI-311
163.78
161.81
138.10
138.08
126.67
126.60
121.51
115.72
115.54
71.14
33.64
1.11
TMSO
CN
F
18
f1 (ppm)

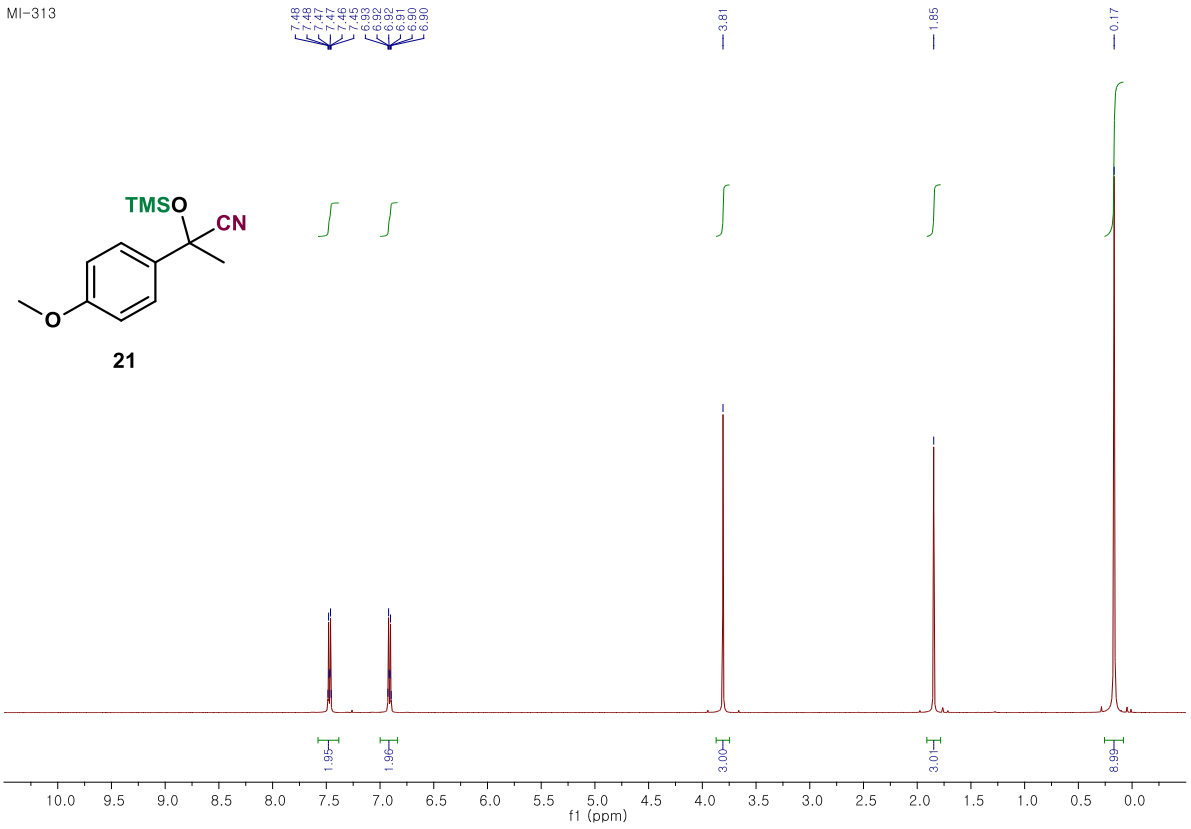

MI-312--
7.09
7.09
7.07
7.07
6.82
6.81
6.81
6.80
6.79
6.79
6.78
6.78
6.77
1.83
0.24
TMSO
CN
F
F
19
1.94
0.94
3.14
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

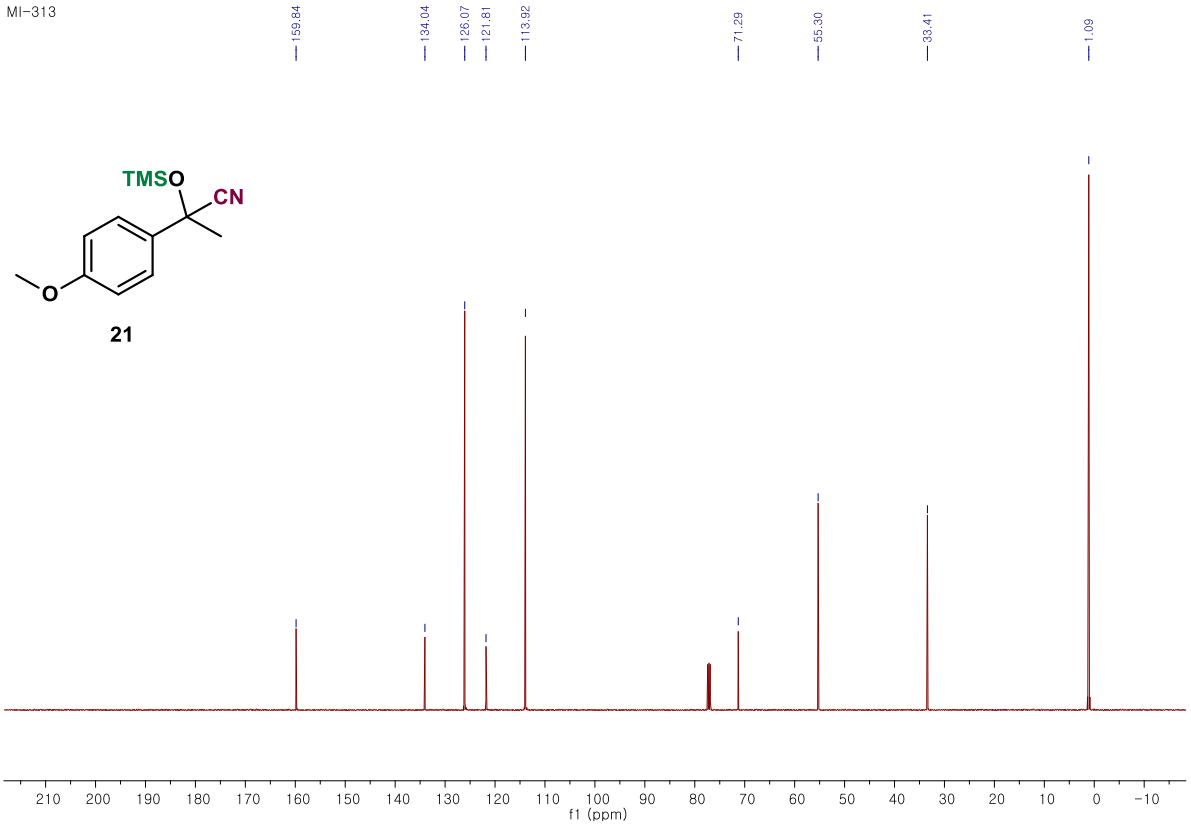

MI-312
164.22
164.12
162.23
162.13
146.54
146.47
146.40
120.84
108.23
108.18
108.07
108.02
104.43
104.23
104.03
70.83
70.81
70.79
33.48
1.11
TMSO
CN
F
F
19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

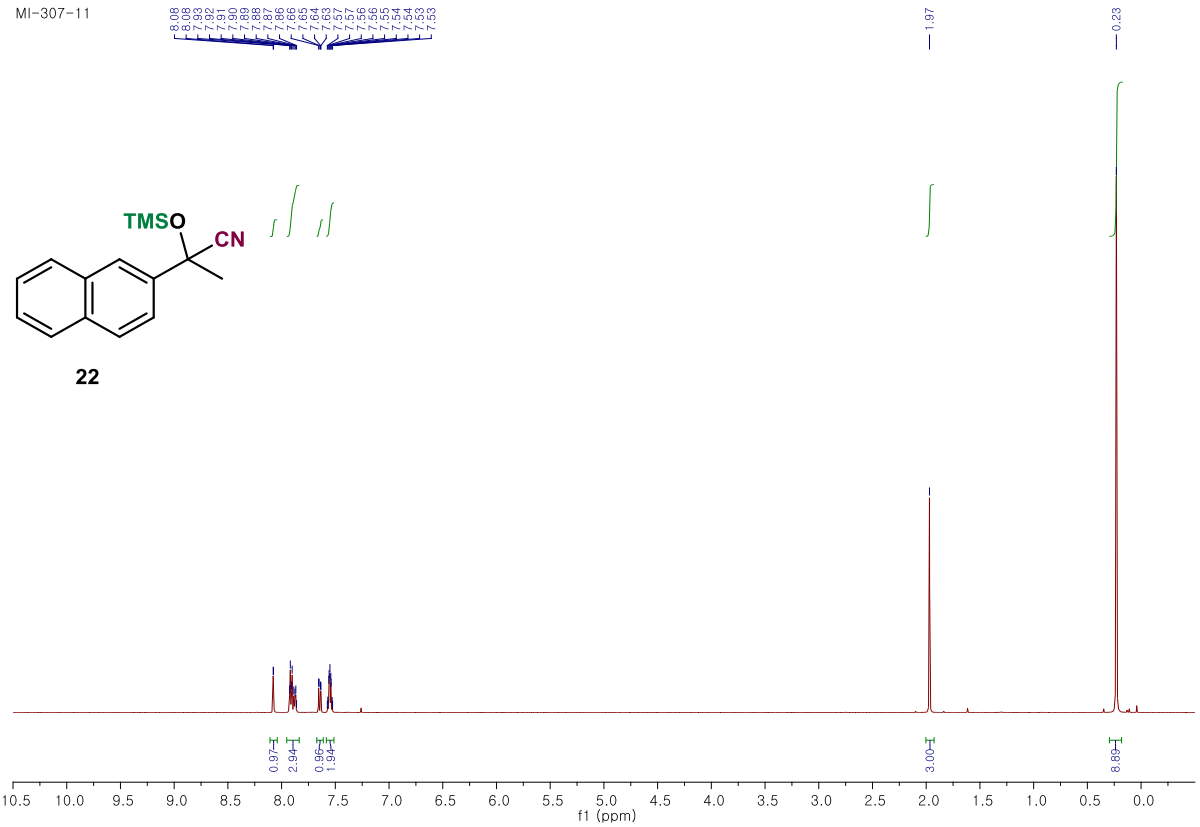

MI-312-FLO
-107.84
-107.86
-107.87
TMSO
CN
F
F
19
A (t)
-107.86
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

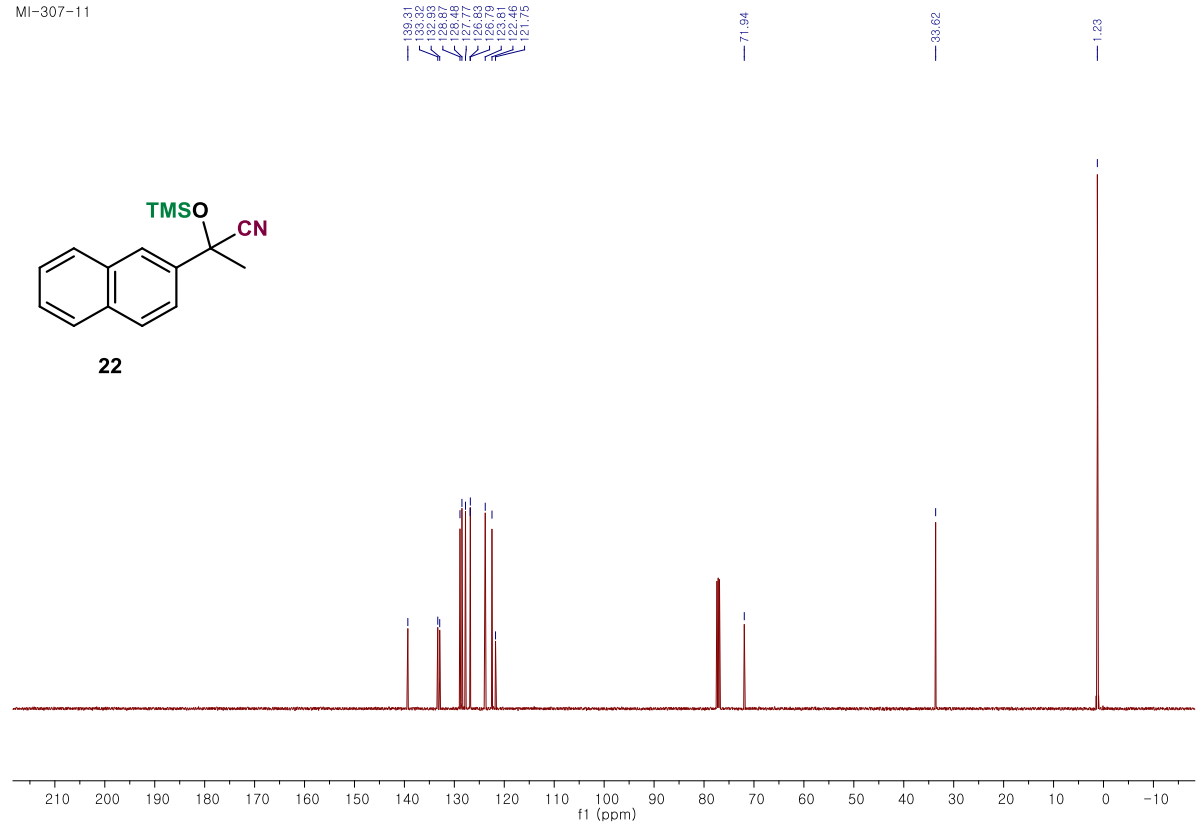

MI-314
7.70
7.69
7.68
7.68
7.66
7.66
1.86
0.22
TMSO
CN
F3C
20
3.94
3.00
9.00
f1 (ppm)

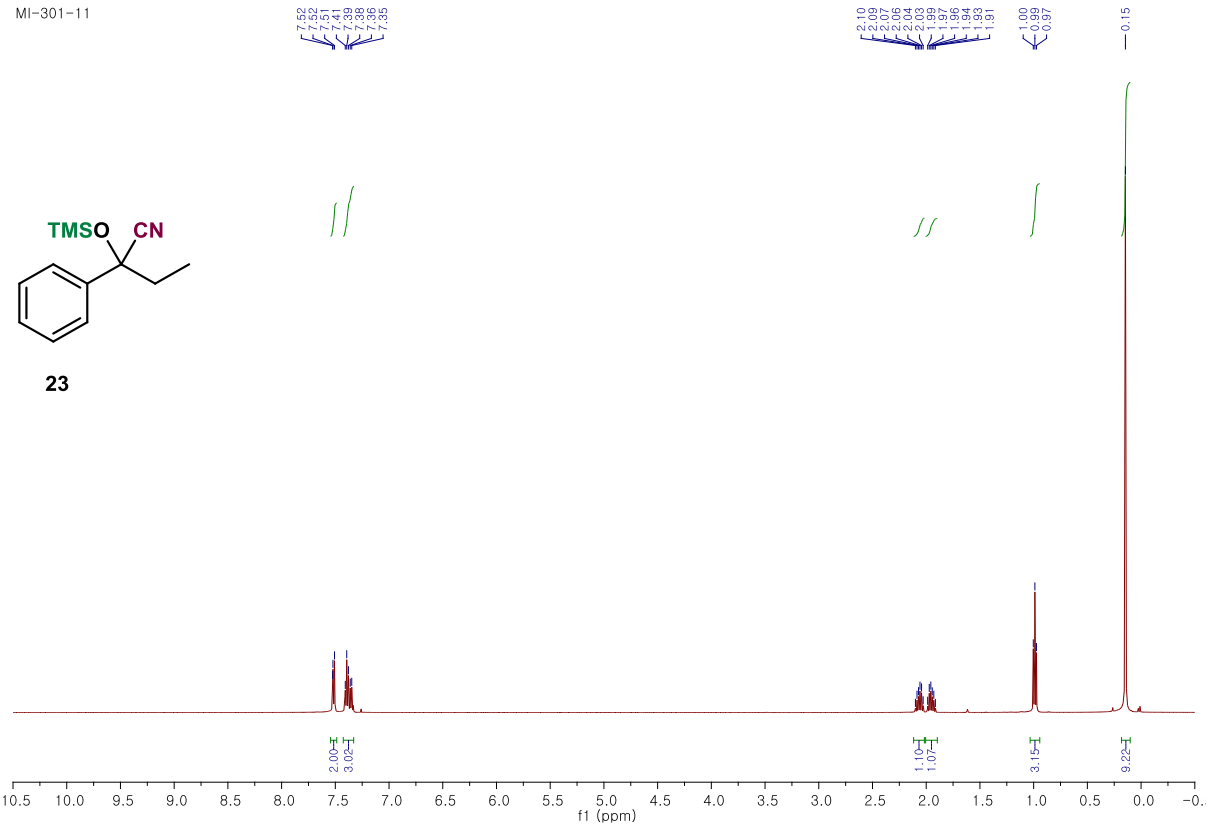

MI-314
146.22
131.50
131.24
130.98
130.72
128.76
127.20
125.92
125.89
125.86
125.83
125.22
125.04
122.87
121.16
71.26
33.64
1.12
TMSO
CN
F3C
20
f1 (ppm)

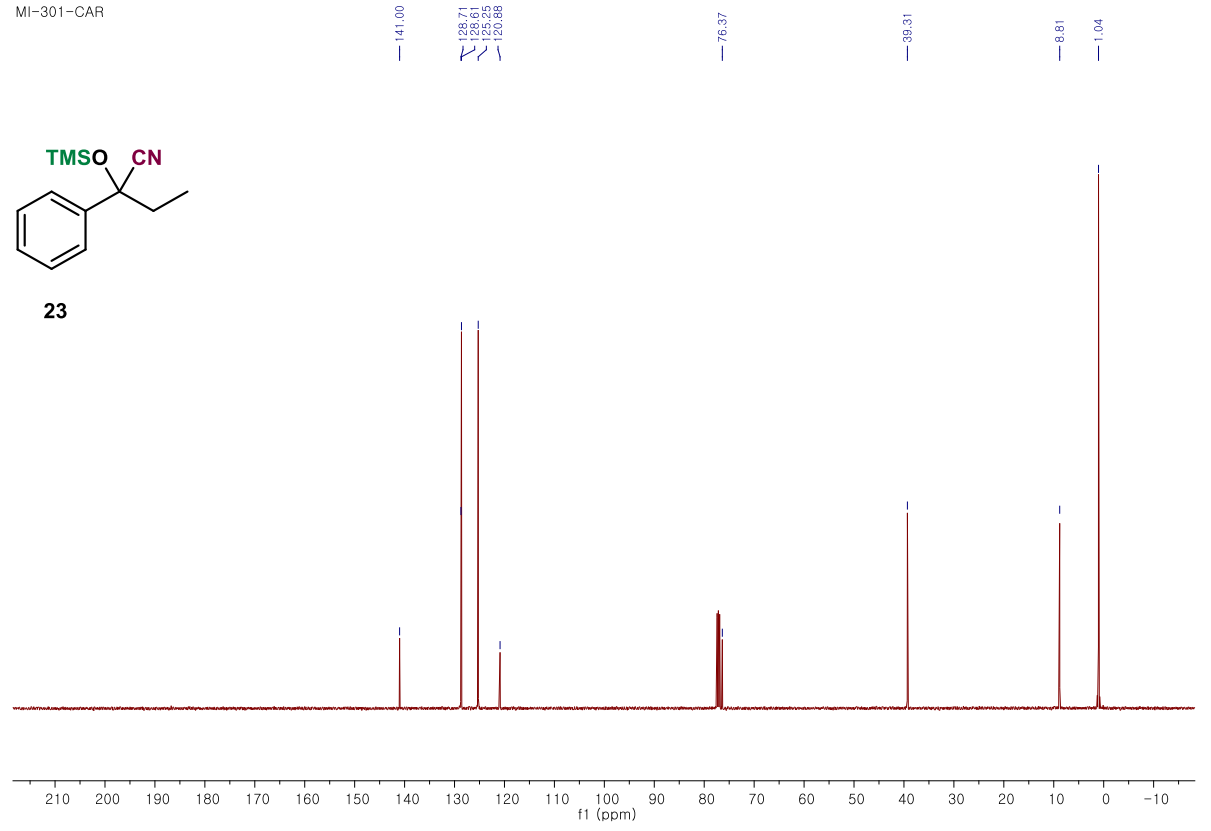

MI-313
7.48
7.48
7.47
7.47
7.46
7.45
6.93
6.92
6.91
6.91
6.90
6.90
3.81
1.85
0.17
TMSO
CN
O
21
1.95
1.96
3.00
3.01
8.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

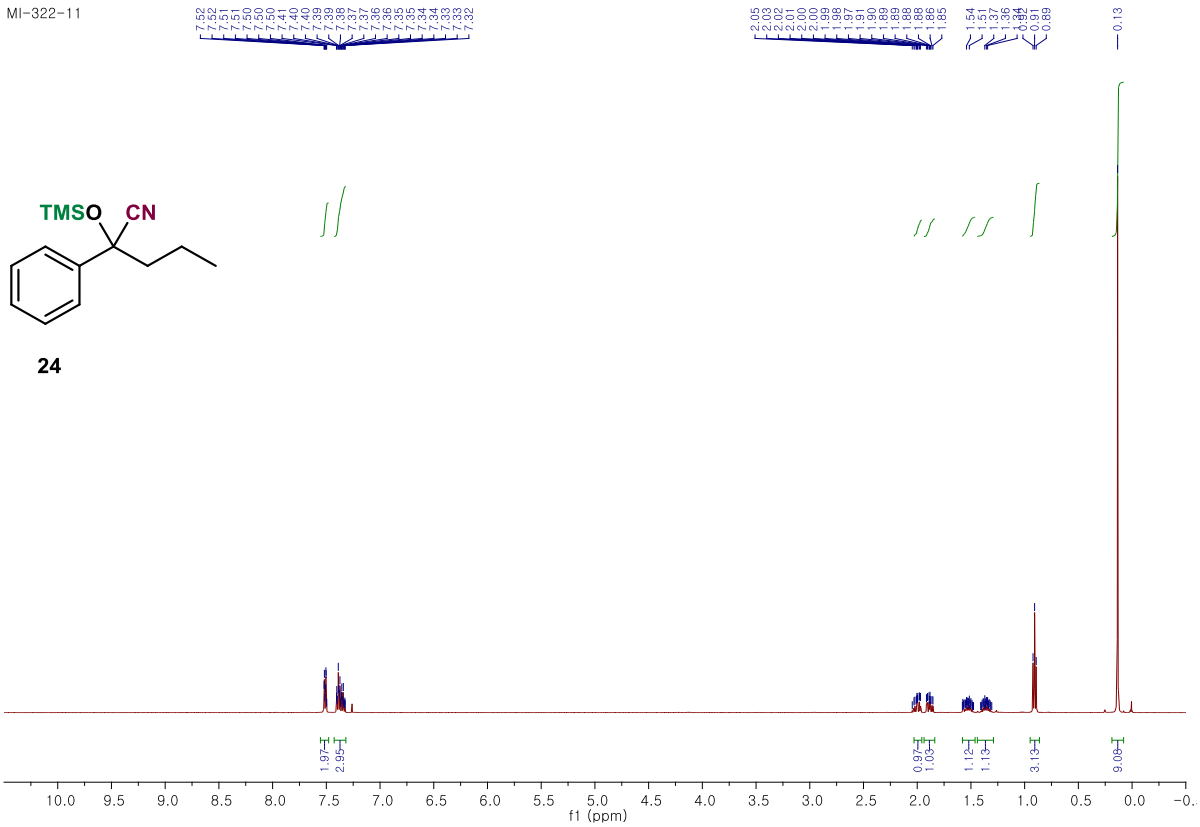

MI-313
159.84
134.04
126.07
121.81
113.92
71.29
55.30
33.41
1.09
TMSO
CN
O
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

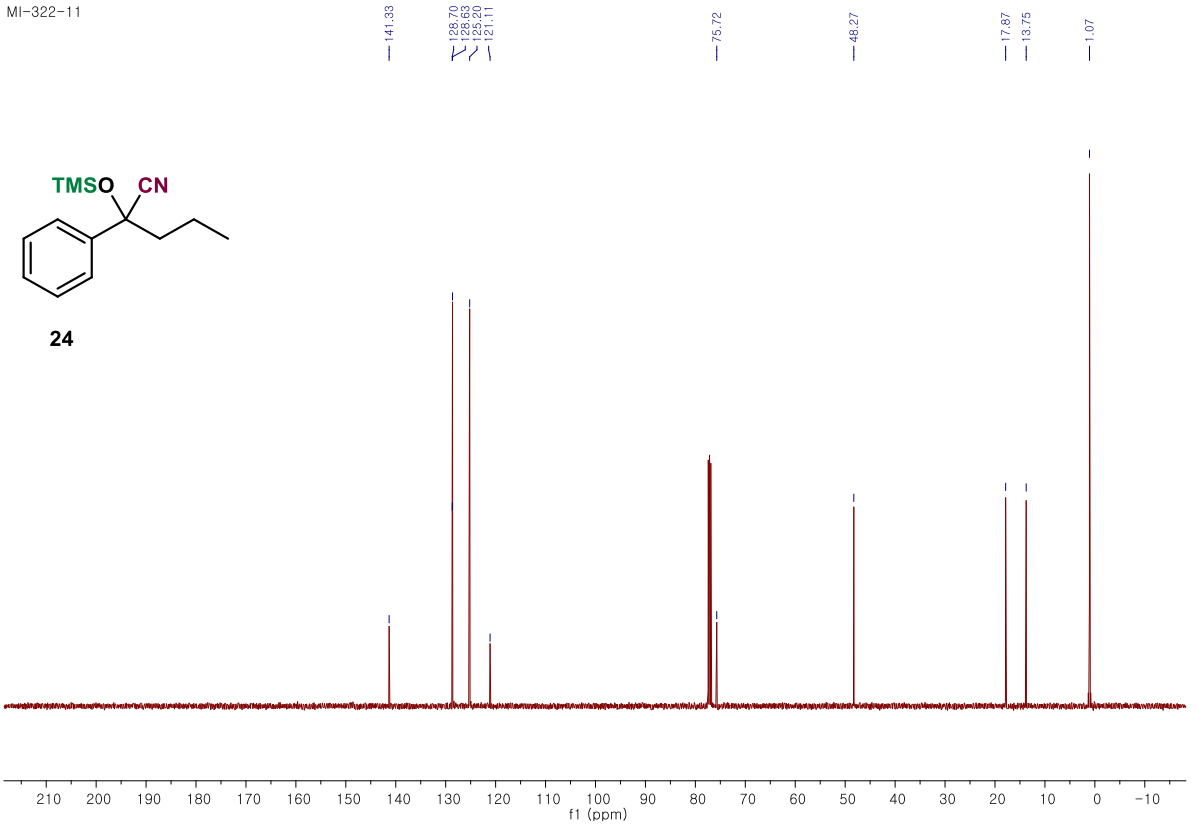

MI-307-11
8.08
8.08
7.93
7.92
7.91
7.90
7.88
7.88
7.87
7.86
7.66
7.65
7.64
7.63
7.57
7.57
7.56
7.56
7.55
7.54
7.54
7.53
7.53
1.97
0.23
TMSO
CN
22
0.97
2.94
0.96
1.94
3.00
8.89
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

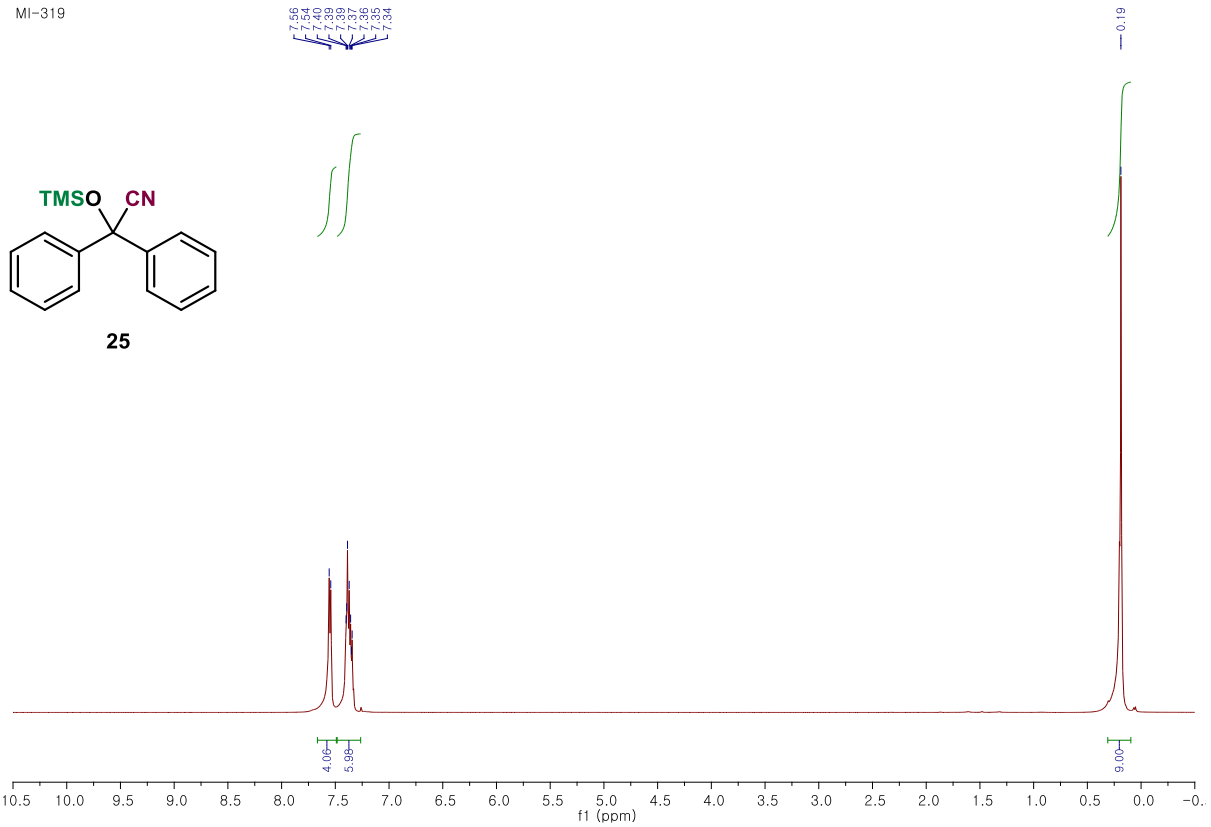

MI-307-11
139.31
133.32
132.93
128.87
128.49
127.77
126.83
126.79
123.81
122.46
121.75
71.94
33.62
1.23
TMSO
CN
22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

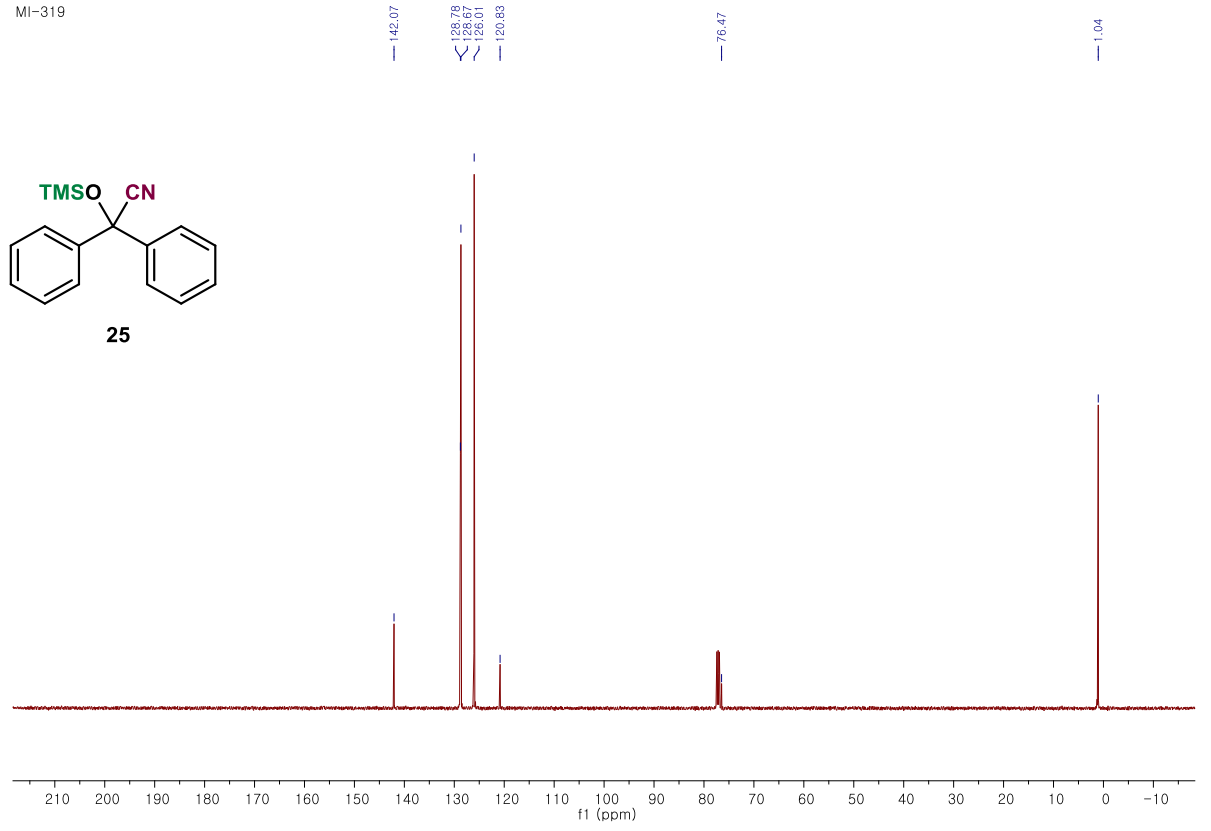

MI-301-11
TMSO CN
23
f1 (ppm)


MI-301-CAR
TMSO CN
23
f1 (ppm)

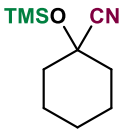

MI-322-11
TMSO CN
24
f1 (ppm)


MI-322-11
TMSO CN
24
f1 (ppm)


MI-319
7.56
7.54
7.40
7.39
7.39
7.37
7.36
7.35
7.34
0.19
TMSO
CN
25
4.06
5.99
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

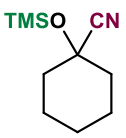

MI-319
142.07
128.78
128.67
128.01
120.83
76.47
1.04
TMSO
CN
25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

MI-612

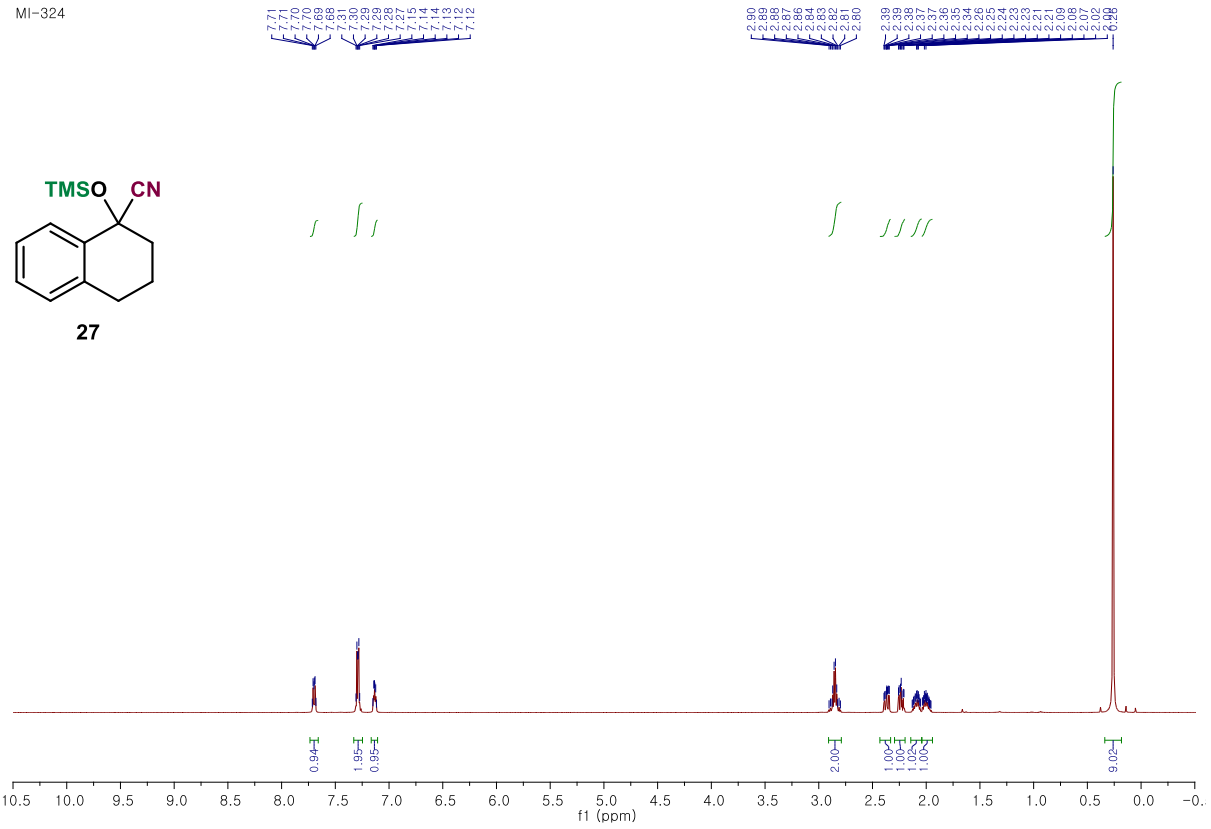


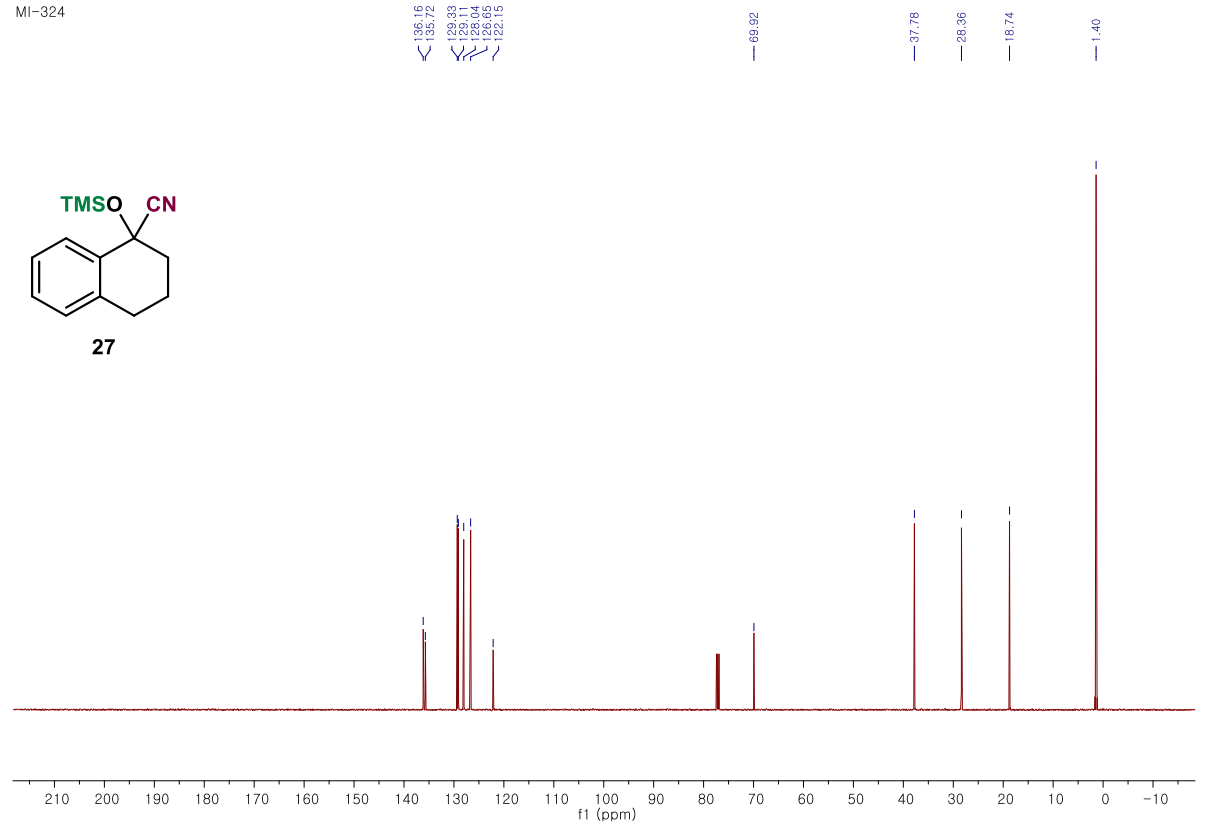
26

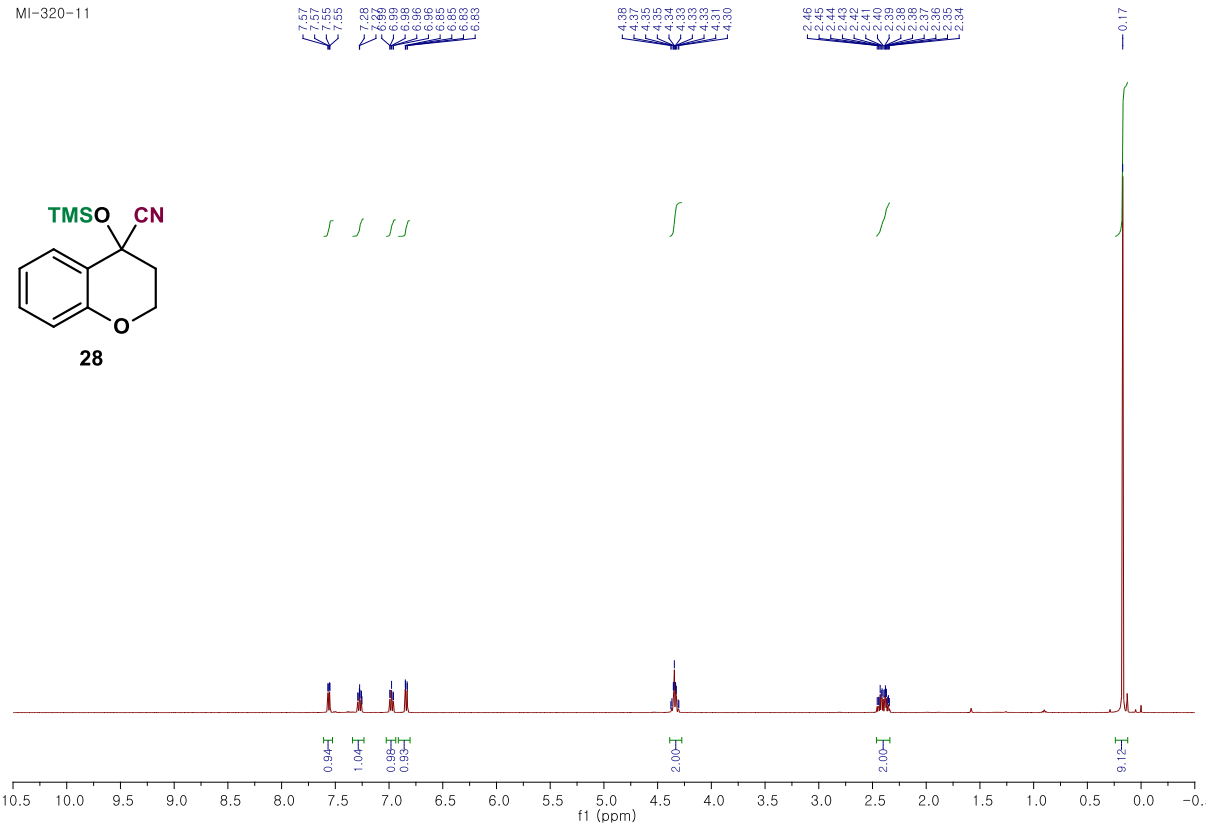
MI-612

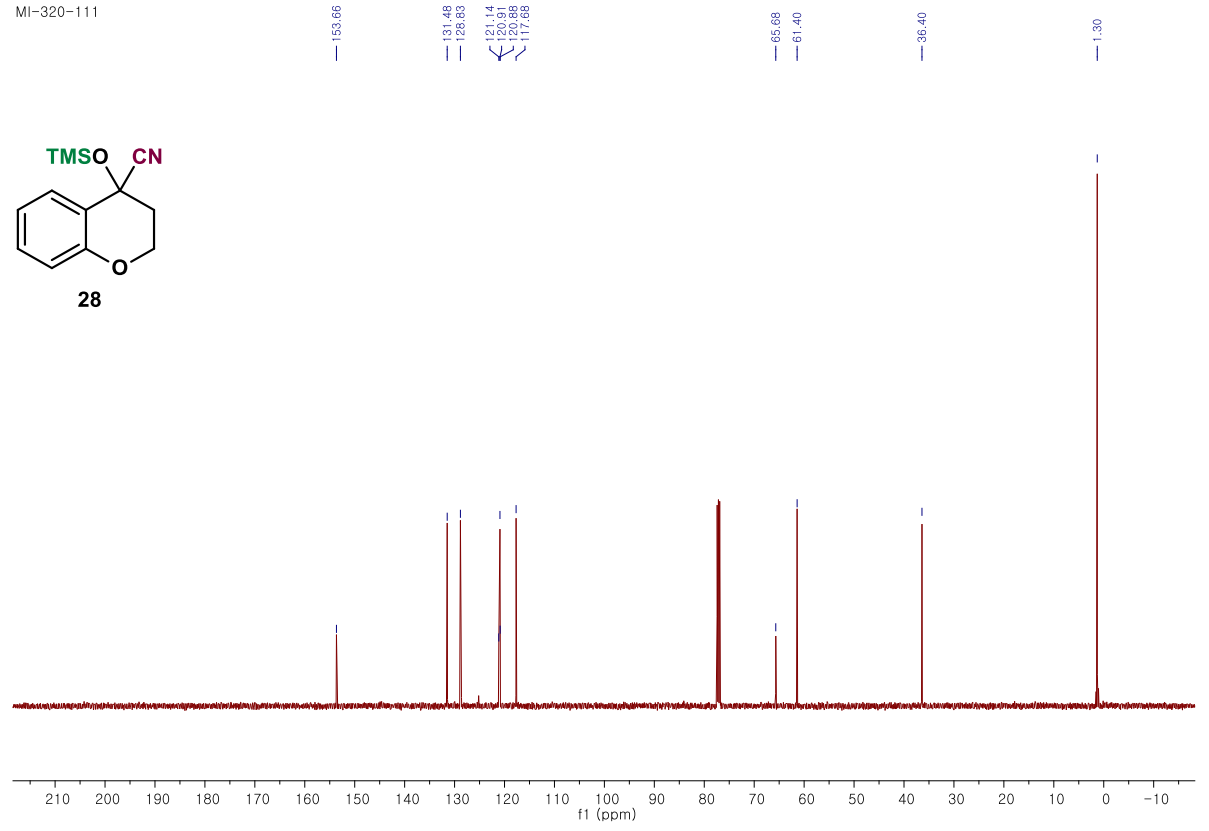


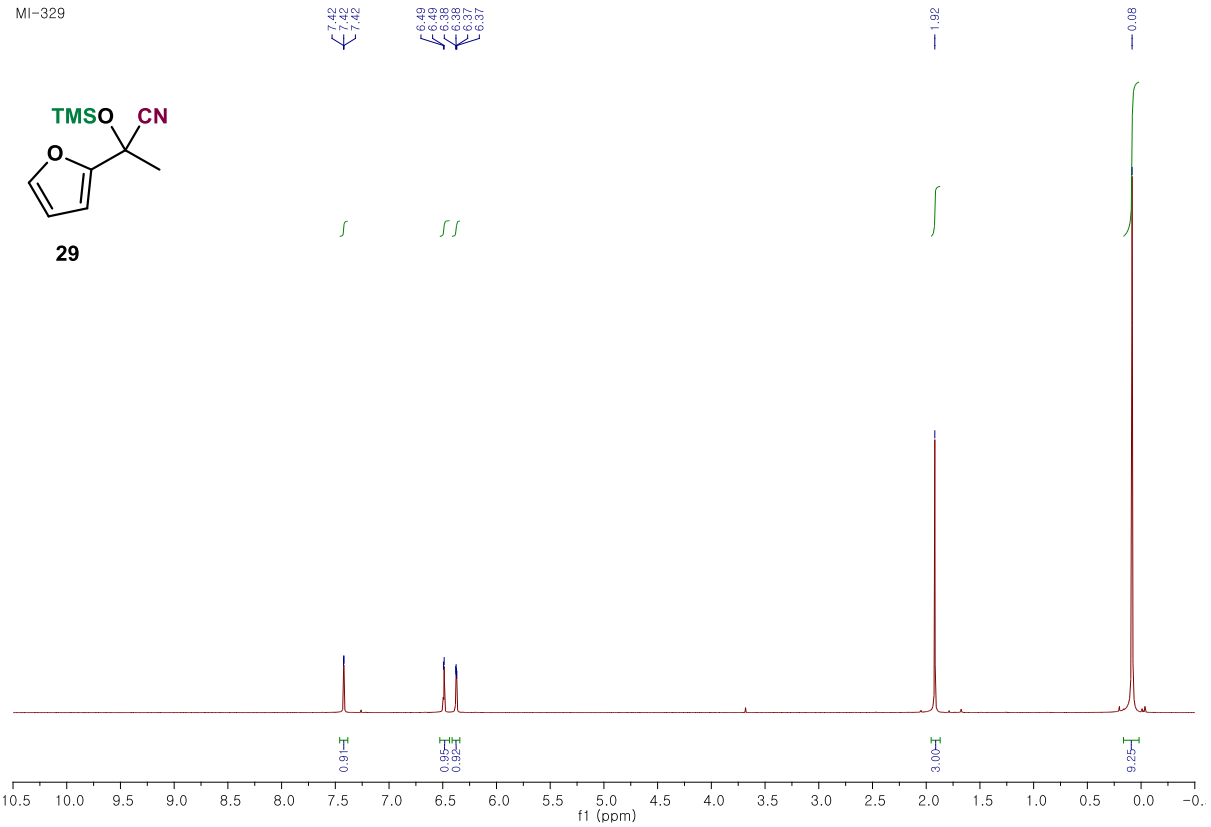
26

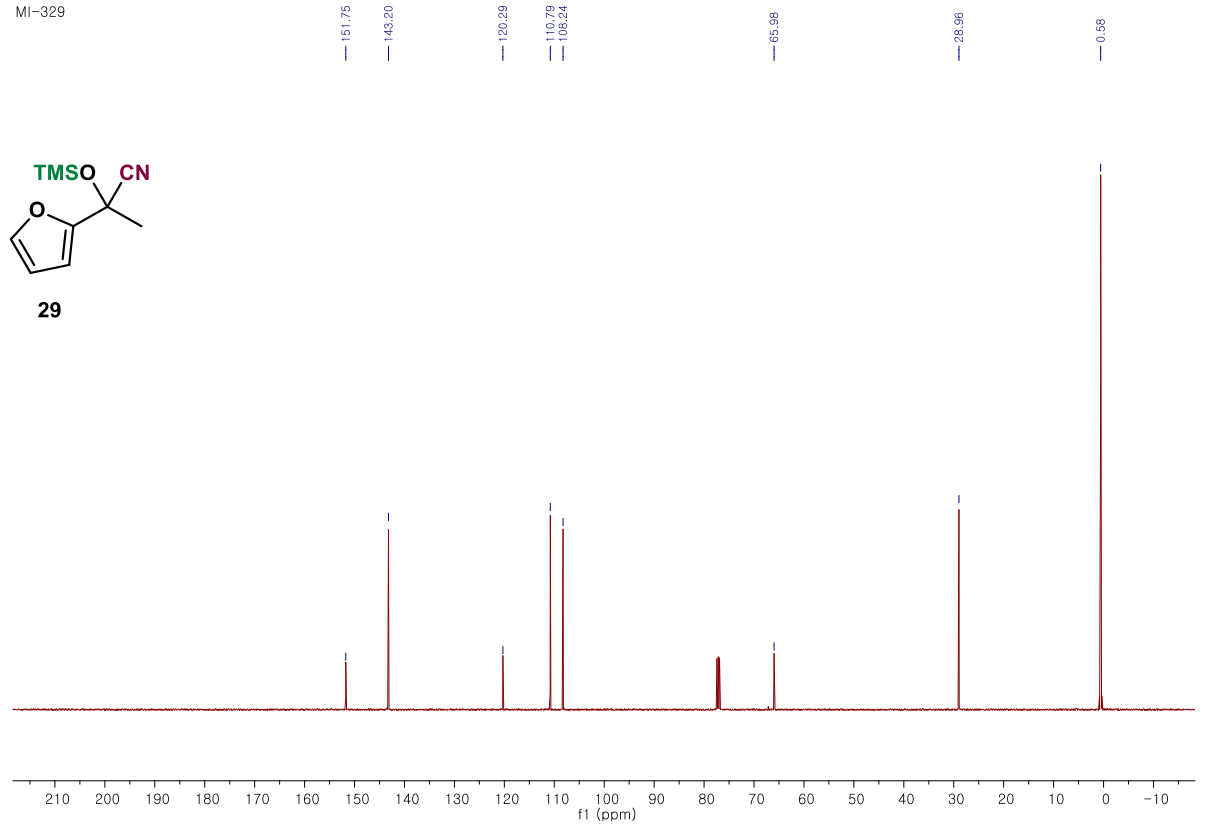

MI-324
TMSO CN
27
f1 (ppm)

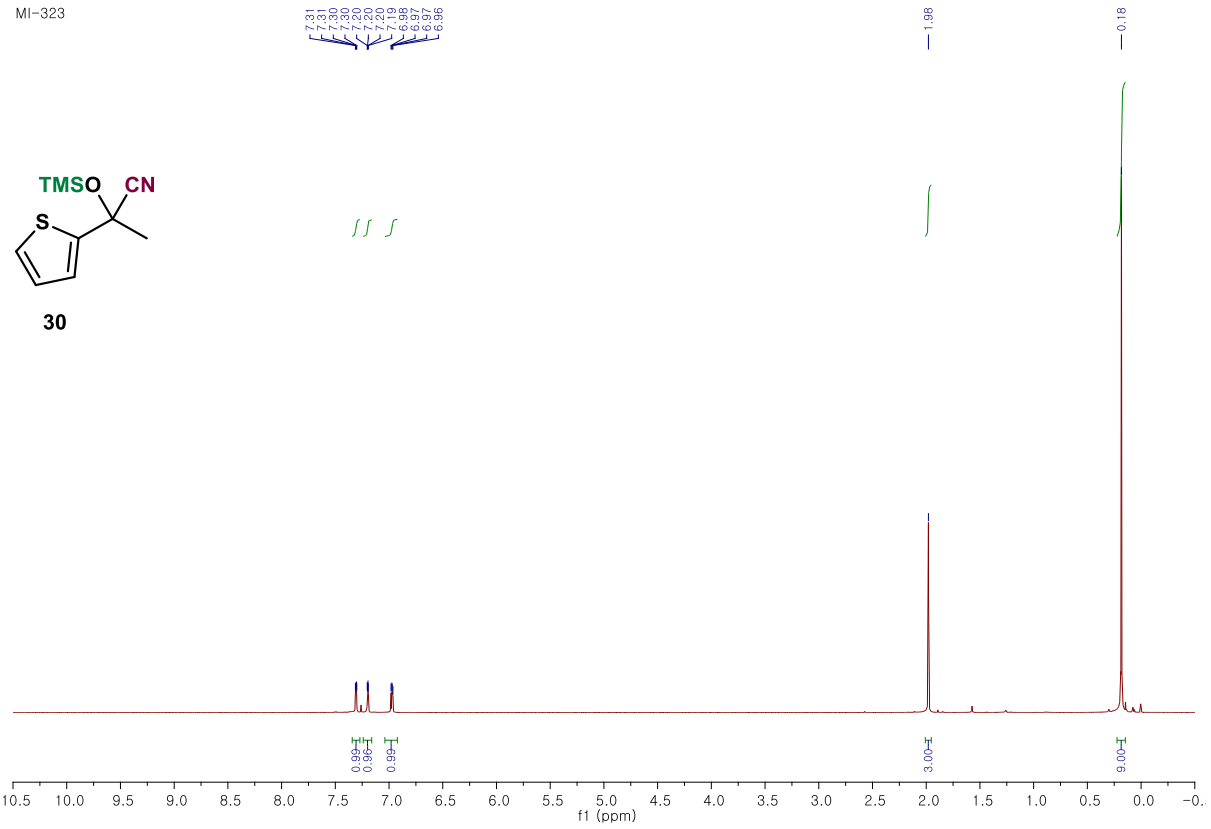

MI-324
TMSO CN
27
f1 (ppm)

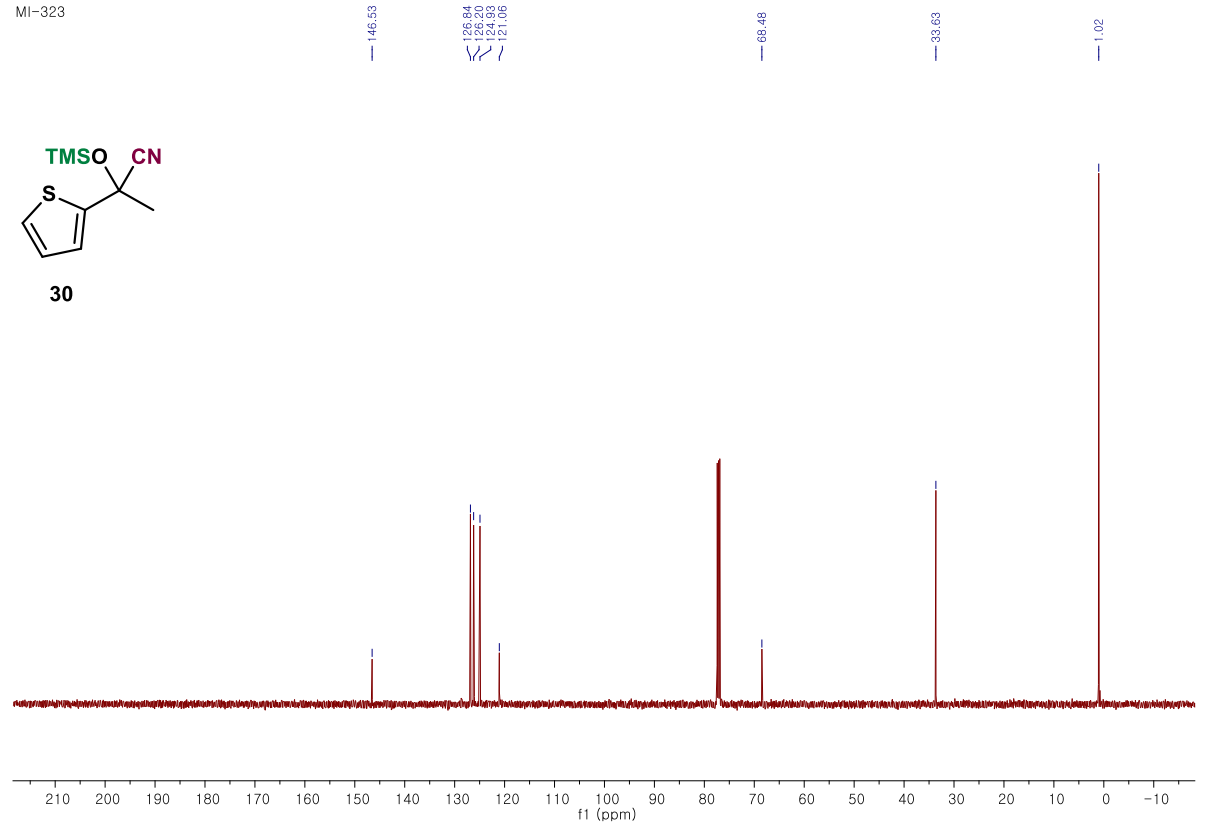

MI-320-11
TMSO CN
28
f1 (ppm)

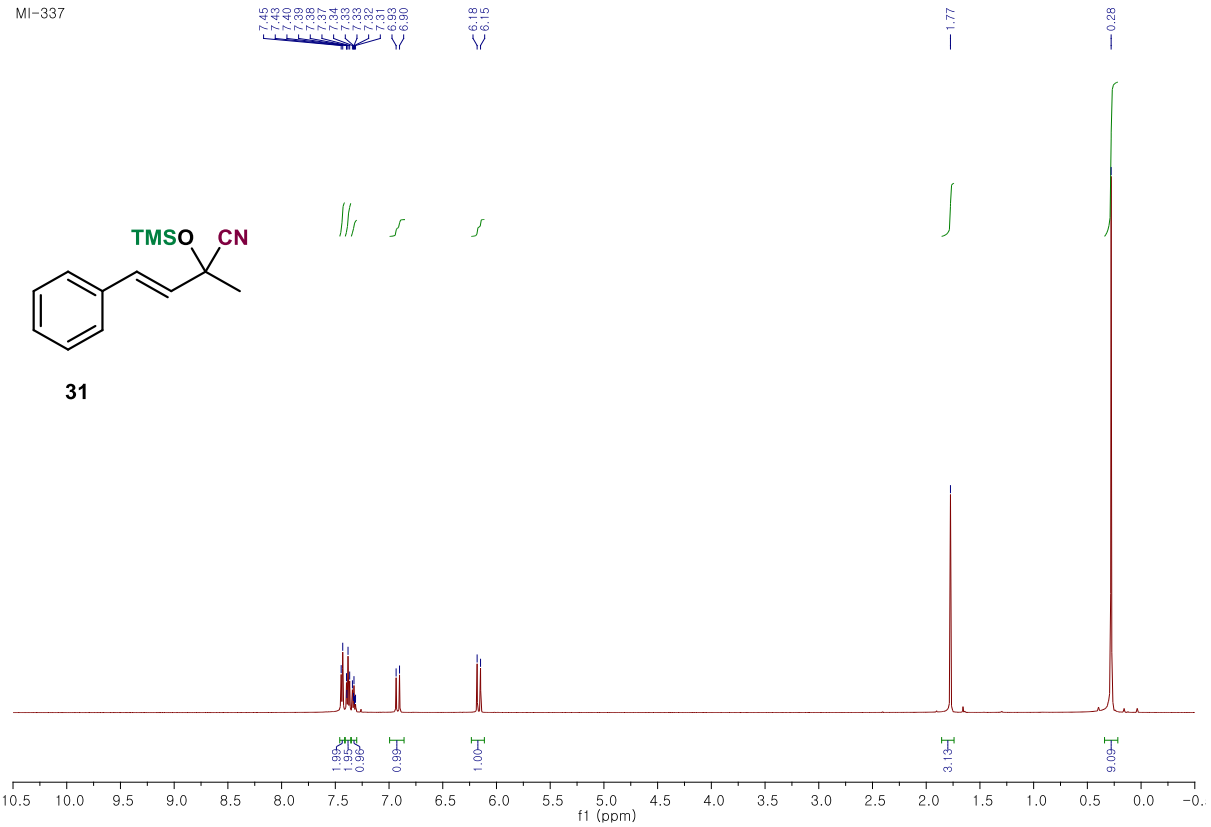

MI-320-111
TMSO CN
28
f1 (ppm)

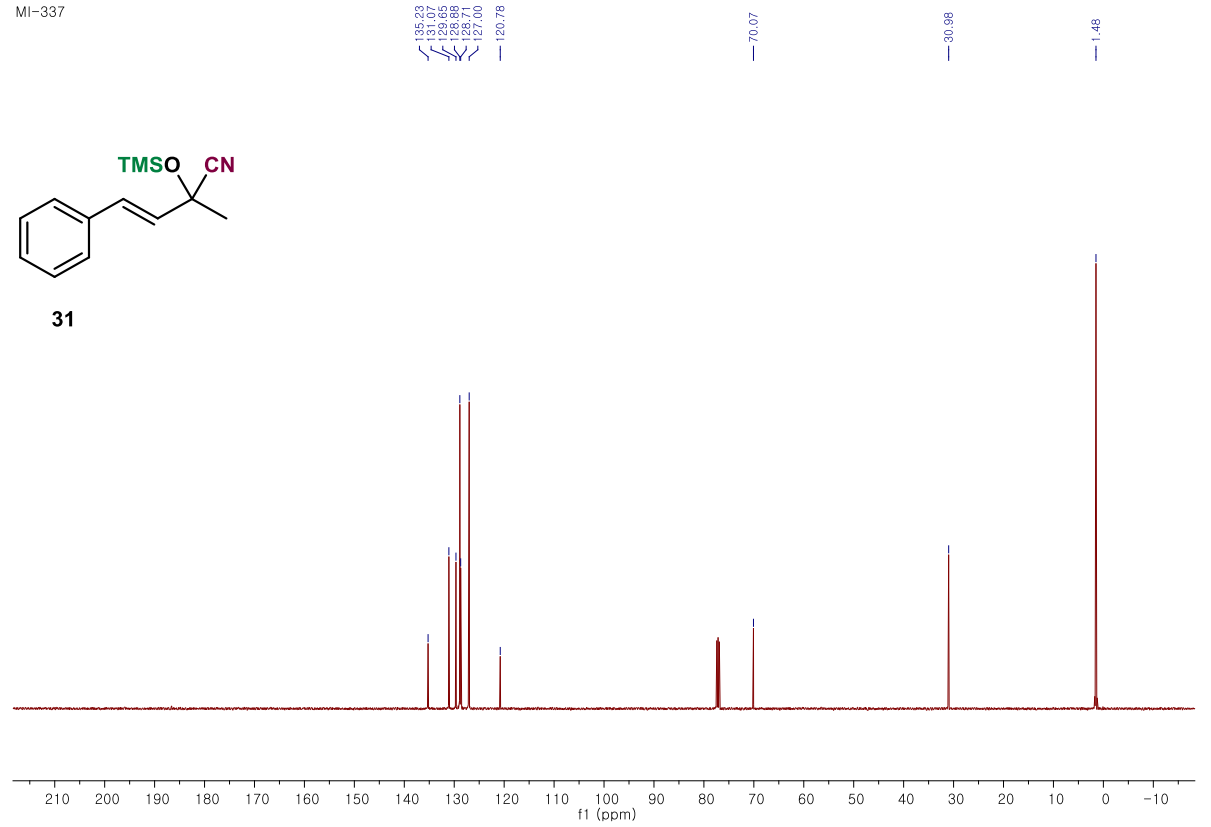

MI-329
7.42
7.42
7.42
6.49
6.49
6.38
6.38
6.37
6.37
1.92
0.08
TMSO
CN
O
29
0.91
0.95
0.92
3.00
9.25
f1 (ppm)

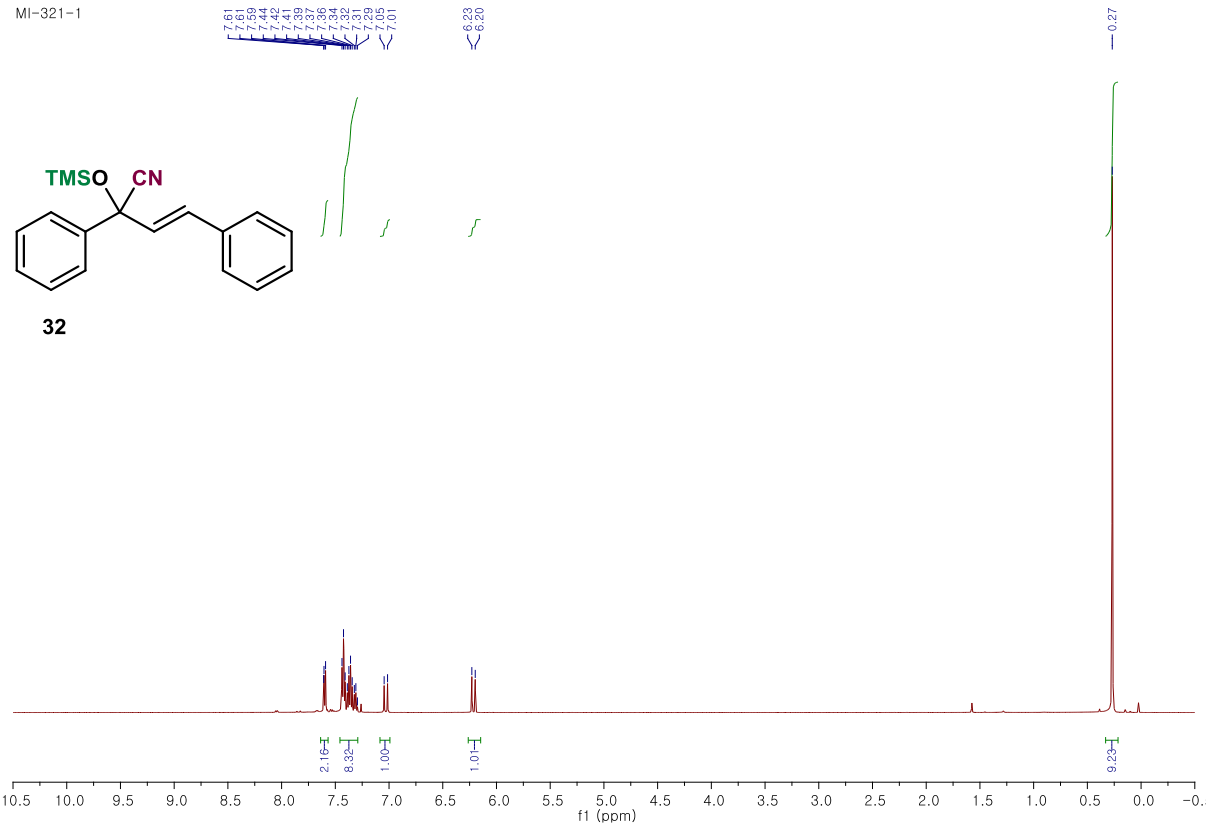

MI-329
151.75
143.20
120.29
110.79
108.24
65.98
28.96
0.58
TMSO
CN
O
29
f1 (ppm)


MI-323
7.31
7.31
7.30
7.30
7.20
7.20
7.19
6.98
6.97
6.97
6.96
1.98
0.18
TMSO
CN
S
30
0.99
0.96
0.99
3.00
9.00
f1 (ppm)

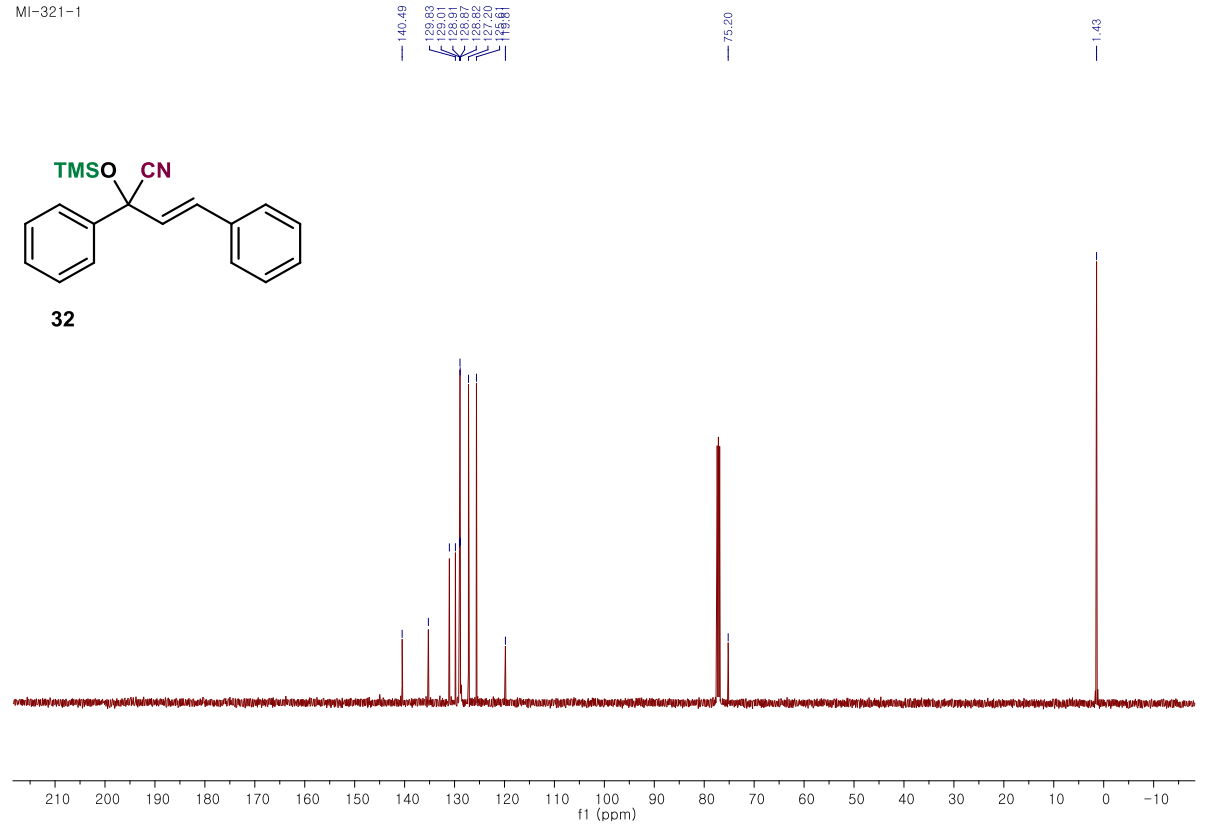

MI-323
146.53
126.84
126.20
124.93
121.06
68.48
33.63
1.02
TMSO
CN
S
30
f1 (ppm)


MI-337
7.45
7.43
7.40
7.38
7.38
7.37
7.34
7.33
7.33
7.32
7.31
6.93
6.90
6.18
6.15
1.77
0.28
TMSO
CN
31
1.99
1.95
0.96
0.99
1.00
3.13
9.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

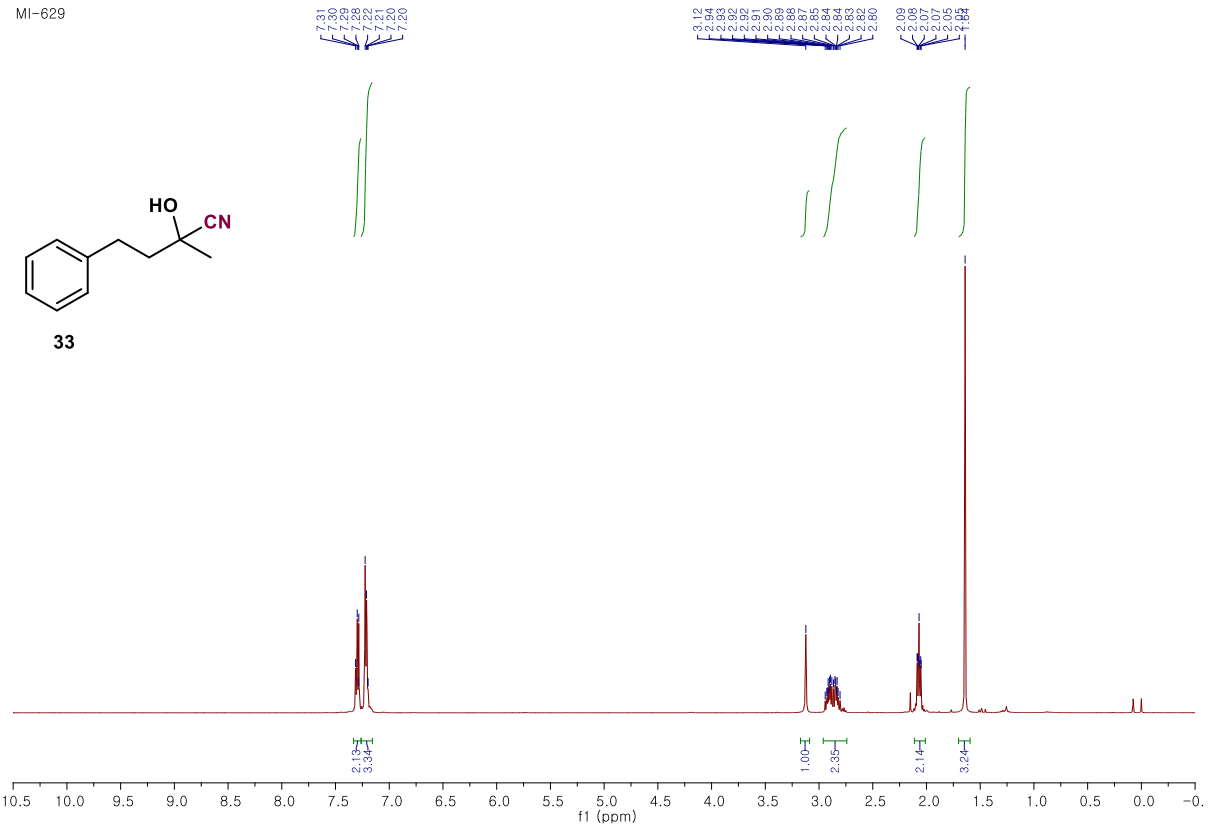

MI-337
135.23
131.07
129.65
128.88
128.71
127.00
120.78
70.07
30.98
1.48
TMSO
CN
31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

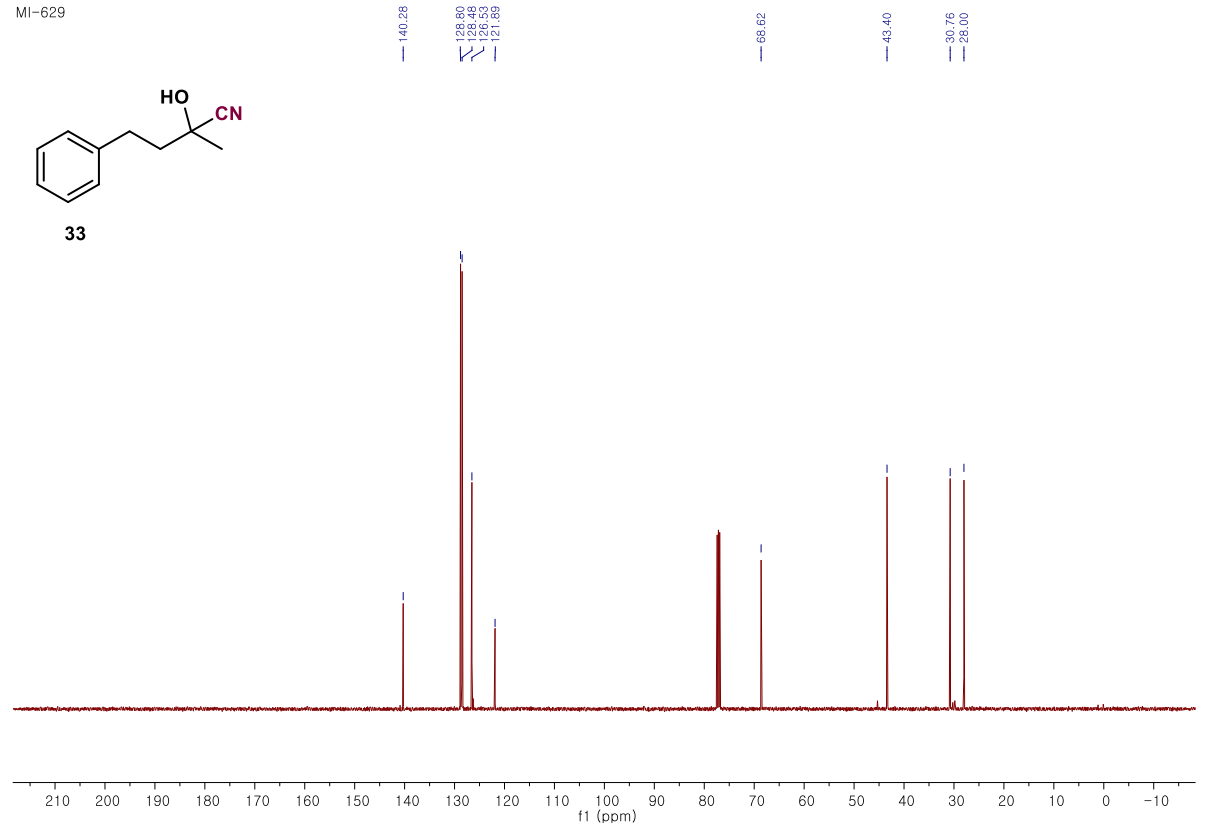

MI-321-1
7.61
7.61
7.59
7.44
7.42
7.41
7.39
7.37
7.36
7.34
7.32
7.31
7.29
7.05
7.01
6.23
6.20
0.27
TMSO
CN
2.16
8.32
1.00
1.01
9.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

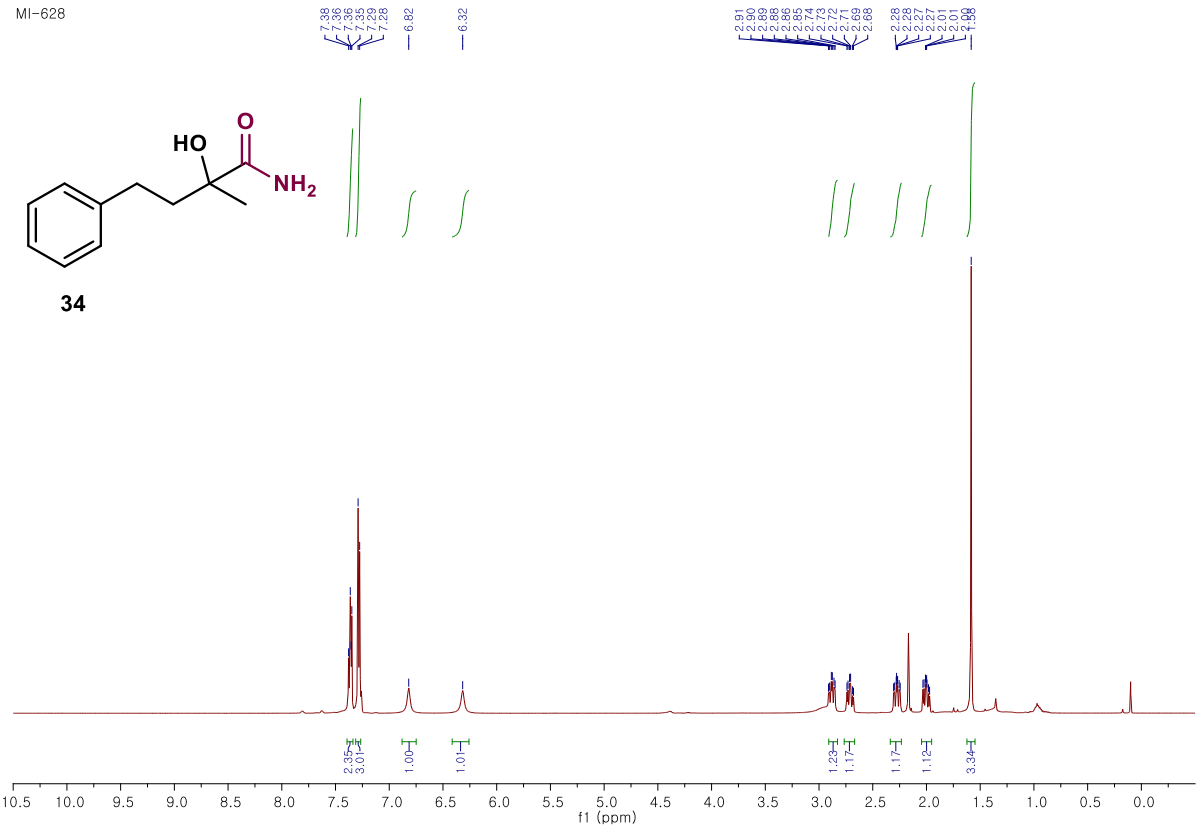
32

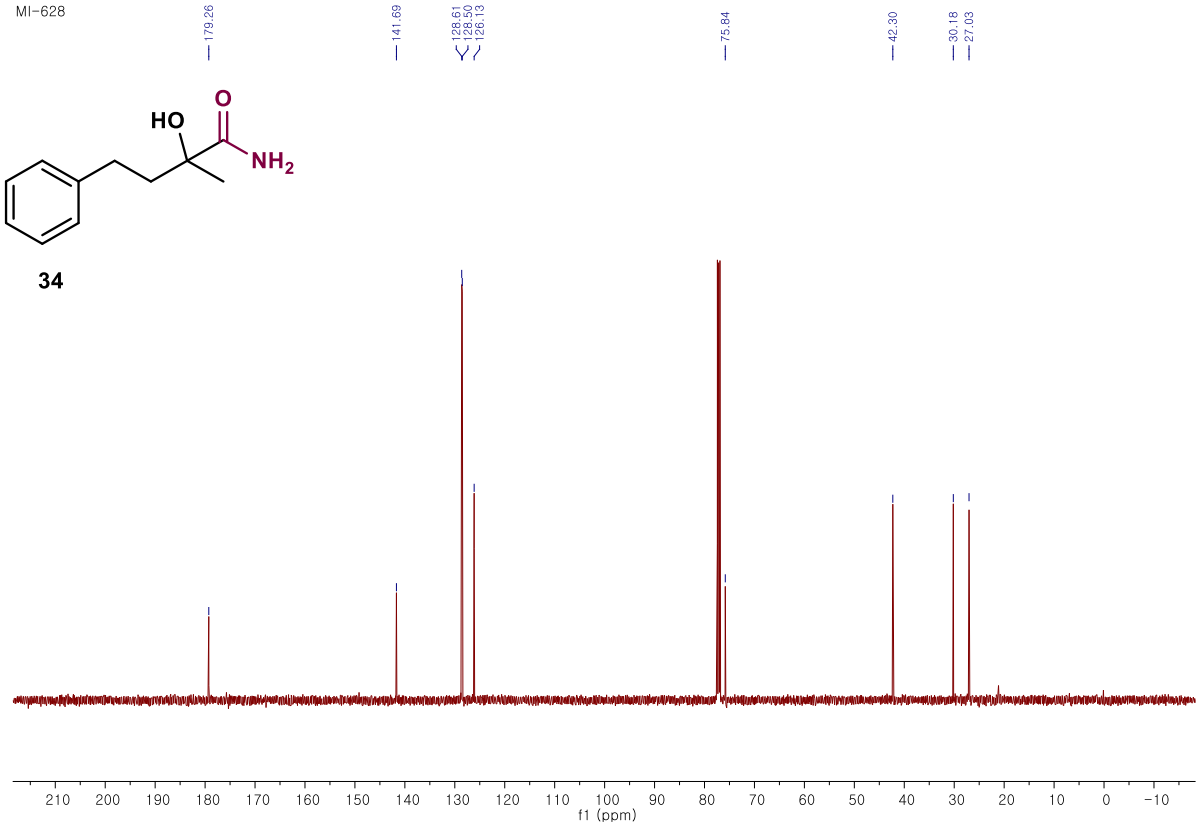

MI-321-1
140.49
129.83
129.01
128.91
128.87
128.82
127.20
75.20
1.43
TMSO
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

32

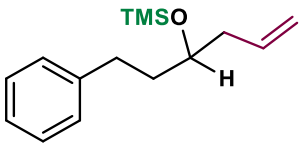

MI-629
HO
CN
33
f1 (ppm)


MI-629
HO
CN
33
f1 (ppm)

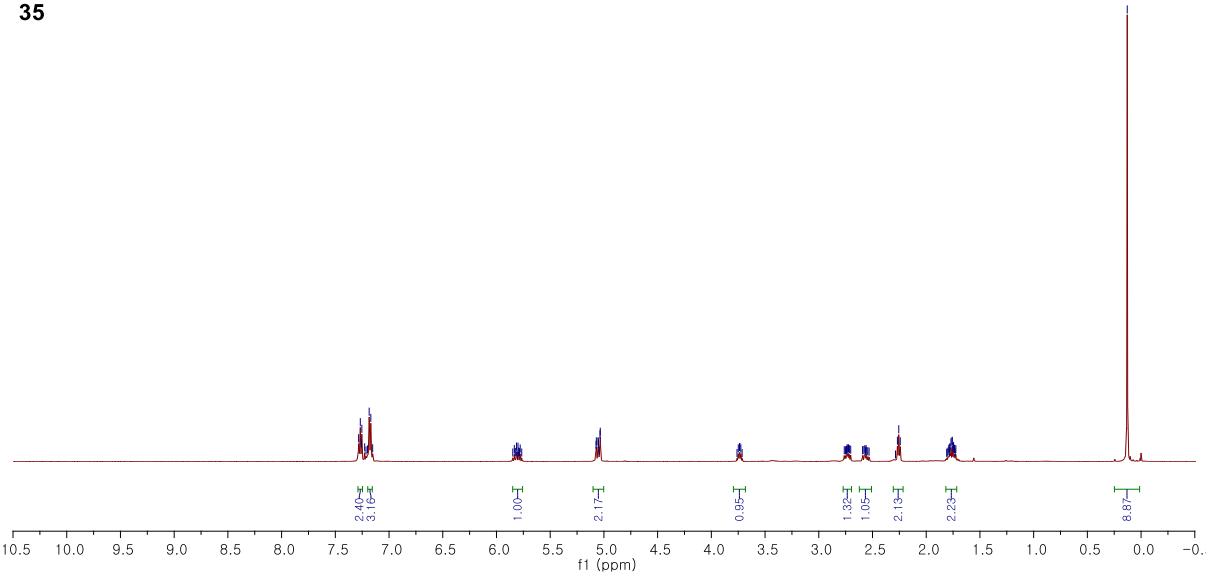

MI-628
7.38
7.36
7.36
7.35
7.29
7.28
6.82
6.32
2.91
2.90
2.88
2.88
2.86
2.85
2.74
2.73
2.72
2.71
2.69
2.68
2.28
2.28
2.27
2.27
2.01
2.01
1.99
1.98
HO
O
NH2
34
2.35
3.01
1.00
1.01
1.29
1.17
1.17
1.12
3.34
f1 (ppm)


MI-628
179.26
141.69
128.61
128.50
128.13
75.84
42.30
30.18
27.03
HO
O
NH2
34
f1 (ppm)

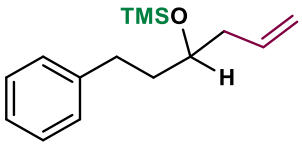
MI-274-H



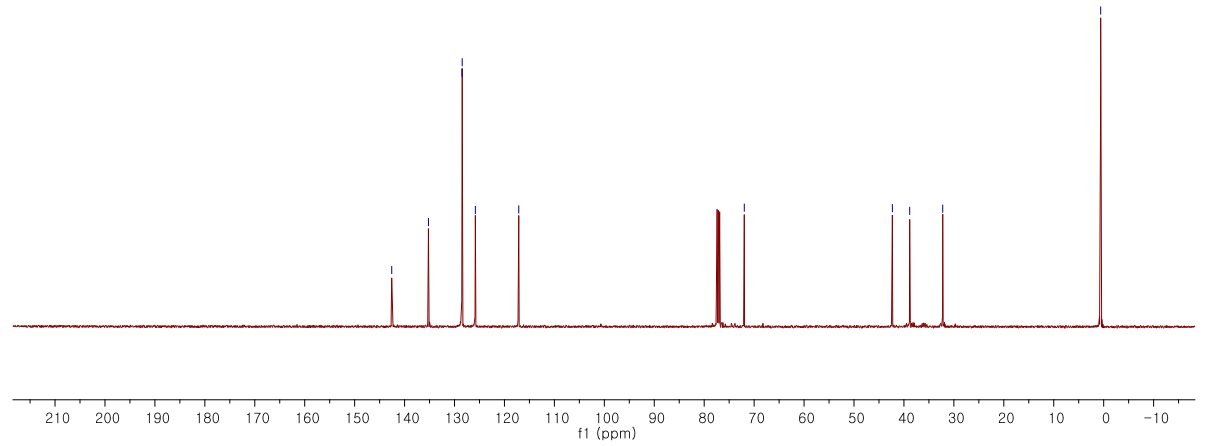
35

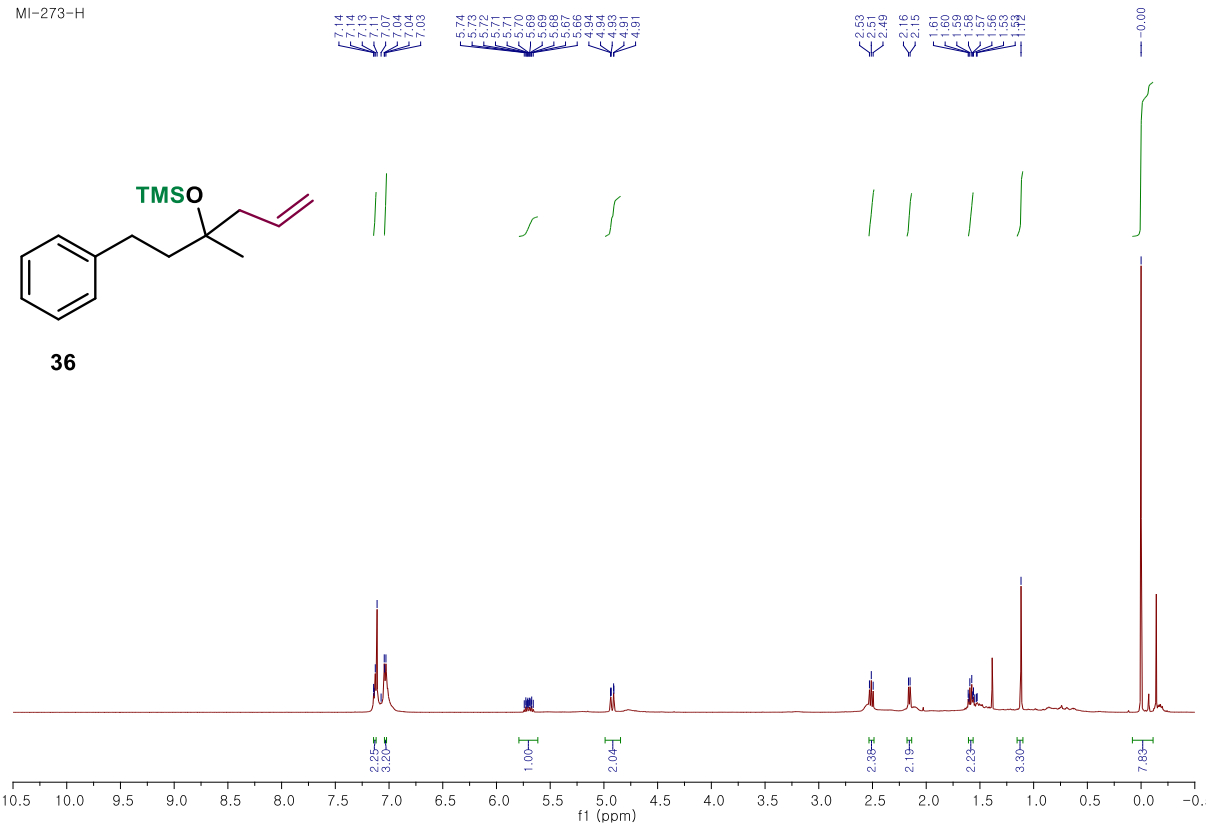


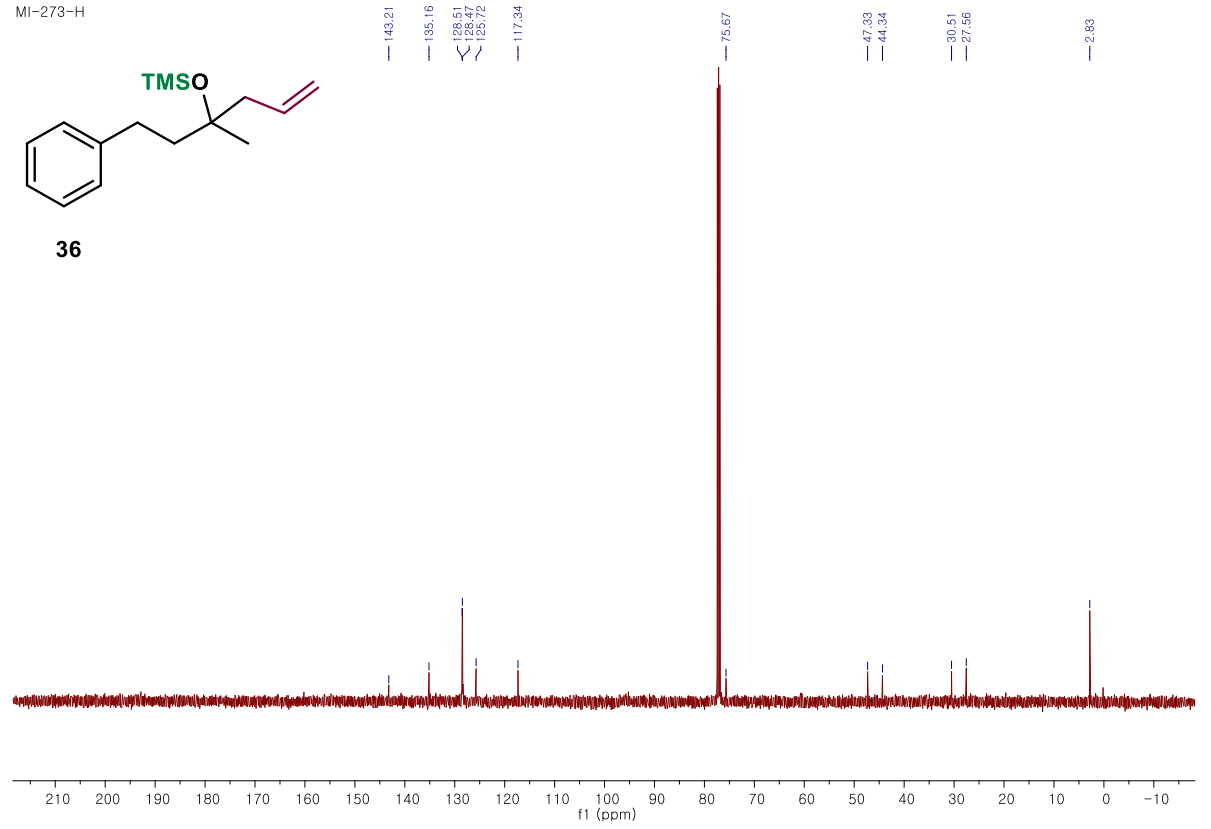
MI-274-CAR

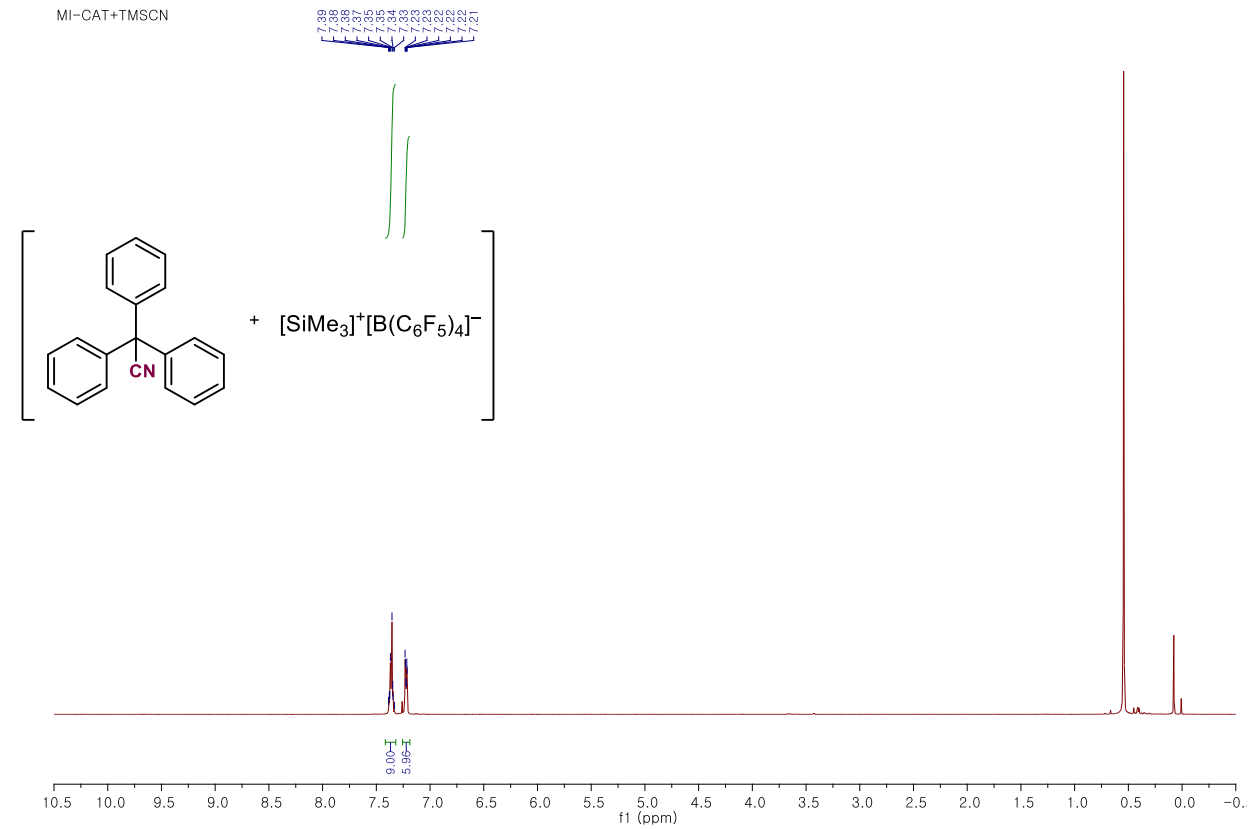


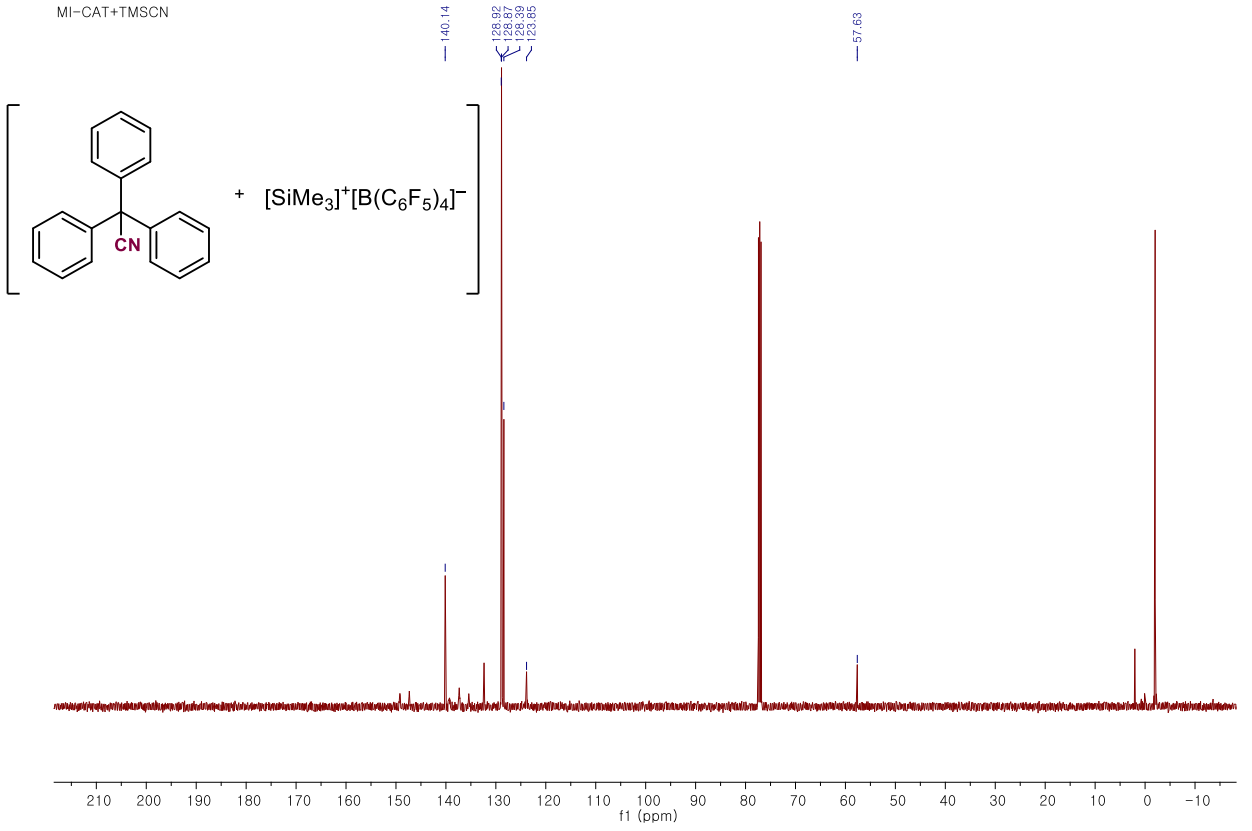
35




MI-273-H
TMSO
36
f1 (ppm)


MI-273-H
TMSO
36
f1 (ppm)


MI-CAT+TMSCN
7.39
7.38
7.38
7.37
7.35
7.35
7.34
7.33
7.23
7.22
7.22
7.22
7.21
CN
+ [SiMe3]+[B(C6F5)4]−
9.00
5.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


MI-CAT+TMSCN
140.14
128.92
128.87
128.39
123.85
57.63
CN
+ [SiMe3]+[B(C6F5)4]−
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)