

Supporting Information

Diboron-Promoted Iron-Catalyzed Denitrative Vinylation of β -Nitrostyrenes with Cycloketoximes

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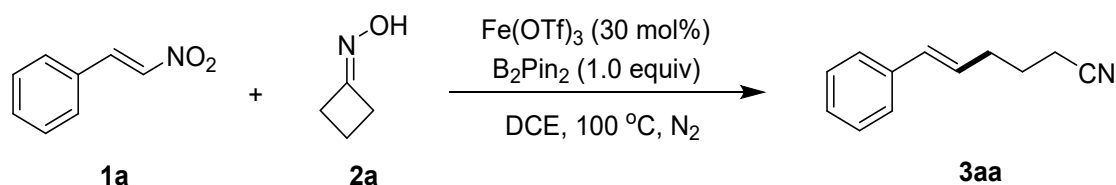
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General Information:

Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were obtained with an Agilent Technologies 400 or 500 spectrometer in CDCl_3 with TMS as an internal standard. Mass spectra were obtained on a Bruker Dalton maXis instrument. All reactions were carried out under an nitrogen atmosphere. Unless otherwise noted, materials obtained from commercial suppliers without further purification. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. Flash column chromatograph was carried out using 300–400 mesh silica gel at medium pressure. The β -nitrostyrene derivatives **1a-1t** and the cycloketoimes derivatives **2a-2l** were synthesized according to known literature.^[1,2,3,4]

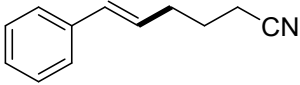
General Procedures for Alkenylation



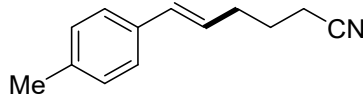
Flame-dried 25 mL Schlenk tube filled with nitrogen, (*E*)-(2-nitrovinyl)benzene (**1a**, 29.8 mg, 0.2 mmol), cyclobutanone oxime (**2a**, 85.1 mg, 1 mmol), $\text{Fe}(\text{OTf})_3$ (30.2 mg, 30 mol%), B_2Pin_2 (50.8 mg, 0.2 mmol) absolute dry DCE (2.0 mL) were added under nitrogen. The formed mixture was stirred at 100 °C under nitrogen for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by flash column chromatography on silica gel to afford 24 mg (70%) of **3aa** as a yellow oil.

Characterization of Products

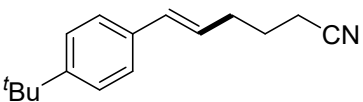
(E)-6-phenylhex-5-enenitrile (**3aa**).

 Yellow oil (24 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.20 (m, 5H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.8, 1.6 Hz, 1H), 2.42 – 2.36 (m, 4H), 1.85 (qt, *J* = 7.2, 1.5 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 132.0, 128.6, 127.6, 127.3, 126.1, 119.5, 31.6, 25.0, 16.4; HRMS *m/z* (ESI) calcd for C₁₂H₁₄N (M + H)⁺ 172.1126, found 172.1118.

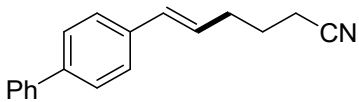
(E)-6-(*p*-tolyl)hex-5-enenitrile (**3ba**).

 Yellow oil (19.4 mg, 52%). ¹H NMR (400 MHz, CDCl₃) δ 7.24 (dt, *J* = 8.3, 1.9 Hz, 2H), 7.13 – 7.10 (m, 2H), 6.42 (d, *J* = 16.4 Hz, 1H), 6.11 – 6.02 (m, 1H), 2.40 – 2.35 (m, 4H), 2.33 (s, 3H), 1.87 – 1.80 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 134.3, 131.9, 129.2, 126.5, 125.9, 119.6, 31.6, 25.0, 21.1, 16.4; HRMS *m/z* (ESI) calcd for C₁₃H₁₆N (M + H)⁺ 186.1283, found 186.1277.

(E)-6-(4-(*tert*-butyl)phenyl)hex-5-enenitrile (**3ca**).

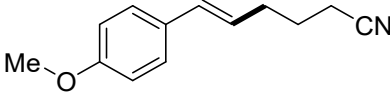
 Yellow oil (24.6 mg, 54%). ¹H NMR (400 MHz, CDCl₃) δ 7.24 (dt, *J* = 8.3, 1.9 Hz, 2H), 7.13 – 7.10 (m, 2H), 6.42 (d, *J* = 16.4 Hz, 1H), 6.11 – 6.02 (m, 1H), 2.40 – 2.35 (m, 4H), 2.33 (s, 3H), 1.87 – 1.80 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 134.3, 131.9, 129.2, 126.5, 125.9, 119.6, 31.6, 25.0, 21.1, 16.4; HRMS *m/z* (ESI) calcd for C₁₃H₁₆N (M + H)⁺ 228.1752, found 228.1744.

(E)-6-([1,1'-biphenyl]-4-yl)hex-5-enenitrile (**3da**).

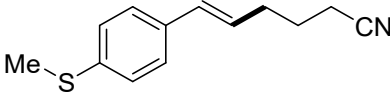
 White solid (25.3 mg, 51%). ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.54 (m, 4H), 7.46 – 7.41 (m, 4H), 7.36 – 7.32 (m, 1H), 6.51 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.18 (dt, *J* = 15.8, 7.0 Hz, 1H), 2.44 – 2.39 (m, 4H), 1.86 (p, *J* = 7.2 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 140.7, 140.1, 136.1, 131.6, 128.8, 127.7, 127.3, 127.3, 126.9, 126.5, 119.6, 31.7, 25.0, 16.5; HRMS *m/z* (ESI) calcd for C₁₈H₁₈N (M + H)⁺ 248.1439,

found 248.1428.

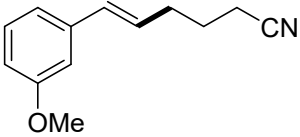
(E)-6-(4-methoxyphenyl)hex-5-enenitrile (3ea).

 Yellow oil (16.6 mg, 41%). ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.25 (m, 2H), 6.86– 6.82 (m, 2H), 6.42 – 6.37 (m, 1H), 5.97 (dt, *J* = 15.8, 7.1 Hz, 1H), 3.80 (s, 3H), 2.39 – 2.33 (m, 4H), 1.84 – 1.79 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 159.0, 131.4, 129.9, 127.2, 125.3, 119.6, 114.0, 55.3, 31.6, 25.1, 16.4; HRMS *m/z* (ESI) calcd for C₁₃H₁₆NO (M + H)⁺ 202.1232, found 202.1227.

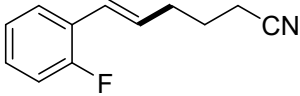
(E)-6-(4-(methylthio)phenyl)hex-5-enenitrile (3fa).

 Yellow oil (21.8 mg, 50%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.25 (m, 2H), 7.20 – 7.18 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.12 – 6.04 (m, 1H), 2.47 (s, 3H), 2.39 – 2.34 (m, 4H), 1.83 (p, *J* = 7.2 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 137.4, 134.1, 131.4, 127.1, 126.8, 126.5, 119.5, 77.4, 77.1, 76.7, 31.7, 25.0, 16.4, 15.9; HRMS *m/z* (ESI) calcd for C₁₃H₁₆NS (M + H)⁺ 218.1003, found 218.0991.

(E)-6-(3-methoxyphenyl)hex-5-enenitrile (3ga).

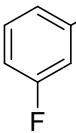
 Yellow oil (19.3 mg, 48%). ¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.95 – 6.93 (m, 1H), 6.88 (t, *J* = 2.1 Hz, 1H), 6.78 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.45 – 6.41 (m, 1H), 6.12 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.81 (s, 3H), 2.40 – 2.35 (m, 4H), 1.87 – 1.80 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 159.8, 138.5, 131.9, 129.5, 128.0, 119.5, 118.7, 112.9, 111.5, 55.2, 31.6, 25.0, 16.4; HRMS *m/z* (ESI) calcd for C₁₃H₁₆NO (M + H)⁺ 202.1232, found 202.1228.

(E)-6-(2-fluorophenyl)hex-5-enenitrile (3ha).

 Yellow oil (26.9 mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.38 (m, 1H), 7.21 – 7.16 (m, 1H), 7.10 – 6.99 (m, 2H), 6.62 – 6.57 (m, 1H), 6.22 (dt, *J* = 16.0, 7.0 Hz, 1H), 2.43 – 2.37 (m, 4H), 1.89 – 1.82

(m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.0 (d, $J = 248.7$ Hz), 130.5 (d, $J = 4.8$ Hz), 128.5 (d, $J = 8.4$ Hz), 127.2 (d, $J = 3.9$ Hz), 124.8 (d, $J = 12.2$ Hz), 124.5 (d, $J = 3.4$ Hz), 124.1 (d, $J = 3.5$ Hz), 119.5, 115.7 (d, $J = 22.2$ Hz), 32.1, 24.9, 16.5; ^{19}F NMR (471 MHz, CDCl_3) δ -118.42; HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{FN}$ ($M + H$) $^+$ 190.2414, found 190.2405.

***(E)*-6-(3-fluorophenyl)hex-5-enenitrile (3ia).**

 Yellow oil (22.7 mg, 60%). ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.23 (m, 1H), 7.10 – 7.02 (m, 2H), 6.93 – 6.89 (m, 1H), 6.42 (d, $J = 15.9$ Hz, 1H), 6.18 – 6.10 (m, 1H), 2.41 – 2.36 (m, 4H), 1.81 – 1.81 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.1 (d, $J = 245.3$ Hz), 139.4, 131.0 (d, $J = 2.6$ Hz), 130.0 (d, $J = 8.4$ Hz), 129.1, 122.0 (d, $J = 2.7$ Hz), 119.4, 114.1 (d, $J = 21.4$ Hz), 112.5 (d, $J = 21.8$ Hz), 31.6, 24.8, 16.5; ^{19}F NMR (471 MHz, CDCl_3) δ -113.56; HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{FN}$ ($M + H$) $^+$ 190.2414, found 190.2405.

***(E)*-6-(4-fluorophenyl)hex-5-enenitrile (3ja).**

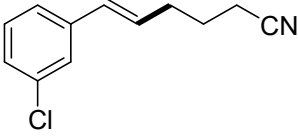
 Yellow oil (23 mg, 61%). ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.28 (m, 2H), 7.02 – 6.96 (m, 2H), 6.44 – 6.39 (m, 1H), 6.04 (dt, $J = 15.8, 7.0$ Hz, 1H), 2.40 – 2.34 (m, 4H), 1.84 (p, $J = 7.2$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.1 (d, $J = 246.4$ Hz), 133.2 (d, $J = 3.4$ Hz), 130.8, 127.5 (d, $J = 8.0$ Hz), 127.3, 119.5, 115.4 (d, $J = 21.5$ Hz), 31.6, 25.0, 16.5; ^{19}F NMR (471 MHz, CDCl_3) δ -114.9; HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{FN}$ ($M + H$) $^+$ 190.2414, found 190.2405.

***(E)*-6-(2-chlorophenyl)hex-5-enenitrile (3ka).**

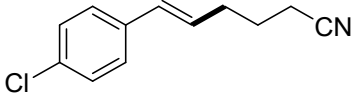
 Yellow oil (29.9 mg, 73%). ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.47 (m, 1H), 7.35 – 7.32 (m, 1H), 7.23 – 7.13 (m, 2H), 6.83 (dt, $J = 15.9, 1.5$ Hz, 1H), 6.16 – 6.08 (m, 1H), 2.45 – 2.39 (m, 4H), 1.91 – 1.85 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 138.9, 134.5, 130.7, 129.8, 129.2, 127.3, 126.0, 124.3, 119.4, 31.6, 24.8, 16.5; HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{ClN}$ ($M + H$) $^+$

206.0737, found 206.0735.

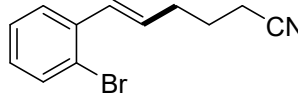
***(E)*-6-(3-chlorophenyl)hex-5-enenitrile (3la).**

 Yellow oil (27.4 mg, 67%). **¹H NMR (400 MHz, CDCl₃)** δ 7.33 – 7.17 (m, 4H), 6.40 (dt, *J* = 15.8, 1.8 Hz, 1H), 6.18 – 6.10 (m, 1H), 2.42 – 2.35 (m, 4H), 1.88 – 1.81 (m, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 138.9, 134.5, 130.7, 129.8, 129.2, 127.3, 126.0, 124.3, 119.4, 31.6, 24.8, 16.5; **HRMS *m/z* (ESI)** calcd for C₁₂H₁₃ClN (*M* + *H*)⁺ 206.0737, found 206.0735.

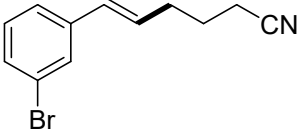
***(E)*-6-(4-chlorophenyl)hex-5-enenitrile (3ma).**

 Yellow oil (25.8 mg, 63%). **¹H NMR (400 MHz, CDCl₃)** δ 7.26 (s, 4H), 6.41 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.10 (dt, *J* = 15.8, 7.0 Hz, 1H), 2.37 (qd, *J* = 7.4, 1.4 Hz, 4H), 1.83 (p, *J* = 7.2 Hz, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 135.6, 132.9, 130.8, 128.7, 128.4, 127.3, 119.5, 31.6, 24.9, 16.5; **HRMS *m/z* (ESI)** calcd for C₁₂H₁₃ClN (*M* + *H*)⁺ 206.0737, found 206.0732.

***(E)*-6-(2-bromophenyl)hex-5-enenitrile (3na).**

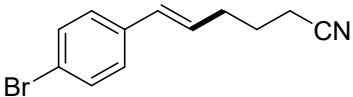
 Yellow oil (20.9 mg, 42%). **¹H NMR (400 MHz, CDCl₃)** δ 7.54 – 7.52 (m, 1H), 7.48 – 7.45 (m, 1H), 7.27 – 7.23 (m, 1H), 7.11 – 7.06 (m, 1H), 6.78 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.07 (dt, *J* = 15.7, 7.0 Hz, 1H), 2.45 – 2.39 (m, 4H), 1.87 (p, *J* = 7.2 Hz, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 137.0, 132.9, 130.9, 130.8, 128.7, 127.5, 126.9, 123.3, 119.5, 31.7, 24.8, 16.5; **HRMS *m/z* (ESI)** calcd for C₁₂H₁₃BrN (*M* + *H*)⁺ 250.0231, found 250.0221.

***(E)*-6-(3-bromophenyl)hex-5-enenitrile (3oa).**

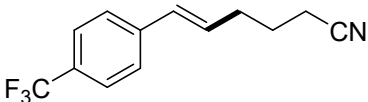
 Yellow oil (19.9 mg, 40%). **¹H NMR (400 MHz, CDCl₃)** δ 7.49 (t, *J* = 1.8 Hz, 1H), 7.35 – 7.33 (m, 1H), 7.25 – 7.23 (m, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.39 (dt, *J* = 15.7, 1.5 Hz, 1H), 6.14 (dt, *J* = 15.8, 7.0 Hz, 1H), 2.42 – 2.36 (m, 4H), 1.88 – 1.81 (m, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 139.2, 130.7, 130.2, 130.1, 129.3, 128.9, 124.8, 122.8, 119.4,

31.6, 24.8, 16.5; **HRMS m/z (ESI)** calcd for C₁₂H₁₃BrN (M + H)⁺ 250.0231, found 250.0222.

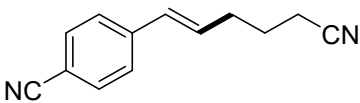
(E)-6-(4-bromophenyl)hex-5-enenitrile (3pa).

 Yellow oil (20.9 mg, 42%). **¹H NMR (400 MHz, CDCl₃)** δ 7.43 – 7.40 (m, 2H), 7.21 – 7.18 (m, 2H), 6.39 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.12 (dt, *J* = 15.8, 7.0 Hz, 1H), 2.37 (dt, *J* = 7.8, 6.5 Hz, 4H), 1.83 (p, *J* = 7.2 Hz, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 136.0, 131.6, 130.9, 128.5, 127.6, 121.0, 119.4, 31.6, 24.8, 16.5; **HRMS m/z (ESI)** calcd for C₁₂H₁₃BrN (M + H)⁺ 250.0231, found 250.0221.

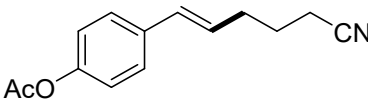
(E)-6-(4-(trifluoromethyl)phenyl)hex-5-enenitrile (3qa).

 Yellow oil (25.3 mg, 53%). **¹H NMR (400 MHz, CDCl₃)** δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.44 (s, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.8, 7.0 Hz, 1H), 2.44 – 2.38 (m, 4H), 1.87 (q, *J* = 7.2 Hz, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 140.5 (d, *J* = 1.8 Hz), 130.6 (d, *J* = 29.0 Hz), 129.1 (d, *J* = 32.4 Hz), 126.2, 125.5, 125.5, 122.8, 119.4, 31.7, 24.8, 16.5; **¹⁹F NMR (471 MHz, CDCl₃)** δ -62.47; **HRMS m/z (ESI)** calcd for C₁₃H₁₃F₃N (M + H)⁺ 240.1000, found 240.0992.

(E)-4-(5-cyanopent-1-en-1-yl)benzonitrile (3ra).

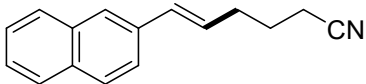
 Yellow oil (14.2 mg, 36%). **¹H NMR (400 MHz, CDCl₃)** δ 7.59 – 7.57 (m, 2H), 7.42 – 7.40 (m, 2H), 6.47 (dt, *J* = 15.7, 1.5 Hz, 1H), 6.32 – 6.24 (m, 1H), 2.45 – 2.38 (m, 4H), 1.88 – 1.84 (m, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 141.5, 132.4, 131.9, 130.6, 126.6, 119.3, 118.9, 110.6, 31.7, 24.7, 16.6; **HRMS m/z (ESI)** calcd for C₁₃H₁₃N₂ (M + H)⁺ 197.1079, found 197.1074.

(E)-4-(5-cyanopent-1-en-1-yl)phenyl acetate (3sa).

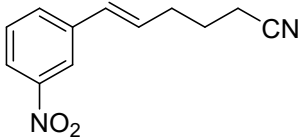
 Yellow oil (17 mg, 37%). **¹H NMR (400 MHz, CDCl₃)** δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.03 – 7.01 (m, 2H), 6.44 (d,

$J = 15.8$ Hz, 1H), 6.13 – 6.05 (m, 1H), 2.37 (q, $J = 7.0$ Hz, 4H), 2.29 (d, $J = 1.1$ Hz, 3H), 1.84 (p, $J = 7.1$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.5, 149.8, 134.9, 131.1, 127.9, 127.0, 121.7, 119.5, 31.6, 24.9, 21.1, 16.4; HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{NO}_2$ ($M + \text{H}$) $^+$ 230.1181, found 230.1173.

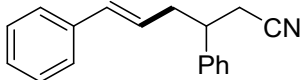
***(E)*-6-(naphthalen-2-yl)hex-5-enenitrile (3ta).**

 White solid (27 mg, 62%). ^1H NMR (400 MHz, CDCl_3) δ 7.81 – 7.77 (m, 3H), 7.69 – 7.68 (m, 1H), 7.57 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.48 – 7.41 (m, 2H), 6.62 (dt, $J = 15.9, 1.6$ Hz, 1H), 6.26 (dt, $J = 15.8, 7.0$ Hz, 1H), 2.47 – 2.39 (m, 4H), 1.88 (p, $J = 7.2$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 134.5, 133.6, 132.8, 132.1, 128.2, 128.0, 127.9, 127.6, 126.3, 125.8, 125.8, 123.4, 119.6, 31.8, 25.0, 16.5; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{N}$ ($M + \text{H}$) $^+$ 222.1283, found 222.1280.

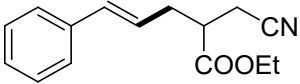
***(E)*-6-(3-nitrophenyl)hex-5-enenitrile (3ua)**

 Yellow oil (9.1 mg, 21%). ^1H NMR (500 MHz, CDCl_3) δ 8.22 (t, $J = 2.0$ Hz, 1H), 8.08 (ddd, $J = 8.2, 2.3, 1.0$ Hz, 1H), 7.65 (dt, $J = 7.6, 1.4$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 1H), 6.55 (dt, $J = 15.9, 1.5$ Hz, 1H), 6.33 (dt, $J = 15.8, 7.0$ Hz, 1H), 2.49 – 2.42 (m, 4H), 1.91 (p, $J = 7.1$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 147.4, 138.9, 132.1, 131.2, 129.9, 129.5, 121.9, 120.6, 119.3, 31.6, 24.7, 16.6; HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_2$ ($M + \text{H}$) $^+$ 217.0977, found 217.0967.

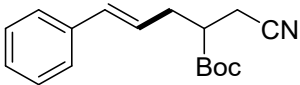
***(E)*-3,6-diphenylhex-5-enenitrile (3ab).**

 Yellow oil (31 mg, 63%). ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.35 (m, 2H), 7.32 – 7.25 (m, 8H), 6.48 (dt, $J = 15.7, 1.4$ Hz, 1H), 6.04 (dt, $J = 15.8, 7.3$ Hz, 1H), 3.13 (p, $J = 7.1$ Hz, 1H), 2.73 – 2.66 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 141.3, 137.0, 133.2, 128.9, 128.6, 127.6, 127.5, 127.2, 126.1, 126.1, 118.5, 42.1, 38.4, 23.9; HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{N}$ ($M + \text{H}$) $^+$ 248.1439, found 248.1433.

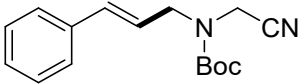
***ethyl (E)*-2-(cyanomethyl)-5-phenylpent-4-enoate (3ac).**


 Yellow oil (27.7 mg, 57%). **¹H NMR (400 MHz, CDCl₃)** δ 7.36 – 7.27 (m, 4H), 7.25 – 7.21 (m, 1H), 6.56 – 6.46 (m, 1H), 6.11 – 5.99 (m, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.88 (p, *J* = 6.7 Hz, 1H), 2.73 – 2.59 (m, 4H), 1.28 (t, *J* = 7.2 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ 171.9, 136.6, 134.2, 128.6, 127.7, 126.2, 124.0, 117.8, 61.5, 41.4, 34.4, 18.6, 14.2; **HRMS m/z (ESI)** calcd for C₁₅H₁₈NO₂ (M + H)⁺ 244.1338, found 244.1326.

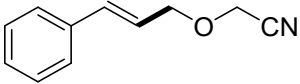
tert-butyl (E)-2-(cyanomethyl)-5-phenylpent-4-enoate (3ad).


 Yellow oil (36 mg, 67%). **¹H NMR (400 MHz, CDCl₃)** δ 7.35 – 7.29 (m, 4H), 7.25 – 7.21 (m, 1H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.10 – 6.03 (m, 1H), 2.82 – 2.75 (m, 1H), 2.68 – 2.54 (m, 4H), 1.47 (s, 9H); **¹³C NMR (101 MHz, CDCl₃)** δ 192.4, 136.7, 133.9, 128.6, 127.6, 126.2, 124.3, 117.9, 82.2, 42.2, 34.6, 28.0, 18.7; **HRMS m/z (ESI)** calcd for C₁₇H₂₂NO₂ (M + H)⁺ 272.1651, found 272.1641.

tert-butyl cinnamyl(cyanomethyl)carbamate (3ae).


 Yellow oil (25 mg, 46%). **¹H NMR (400 MHz, CDCl₃)** δ 7.33 – 7.23 (m, 5H), 6.50 (dd, *J* = 15.8, 1.4 Hz, 1H), 6.10 – 6.03 (m, 1H), 2.82 – 2.75 (m, 1H), 2.67 – 2.52 (m, 4H), 1.49 (d, *J* = 1.1 Hz, 9H); **¹³C NMR (101 MHz, CDCl₃)** δ 171.1, 136.7, 133.9, 128.6, 127.6, 126.2, 124.4, 117.9, 82.2, 42.2, 34.6, 28.0, 27.9; **HRMS m/z (ESI)** calcd for C₁₆H₂₁N₂O₂ (M + H)⁺ 273.1603, found 273.1594.

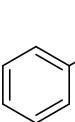
2-(cinnamyloxy)acetonitrile (3af).


 Yellow oil (13.8 mg, 40%). **¹H NMR (400 MHz, CDCl₃)** δ 7.42 – 7.26 (m, 5H), 6.69 (dt, *J* = 16.0, 1.5 Hz, 1H), 6.22 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.34 – 4.29 (m, 4H); **¹³C NMR (101 MHz, CDCl₃)** δ 135.9, 135.4, 128.7, 128.3, 126.7, 123.0, 121.3, 71.7, 54.6; **HRMS m/z (ESI)** calcd for C₁₁H₁₂NO (M + H)⁺ 174.0919, found 174.0912.

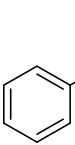
2-(cinnamylthio)acetonitrile (3ag).

 Yellow oil (14 mg, 38%). **¹H NMR (400 MHz, CDCl₃)** δ 7.42 – 7.25 (m, 5H), 6.58 (dt, *J* = 15.7, 1.7 Hz, 1H), 6.16 – 6.08 (m, 1H), 3.54 – 3.51 (m, 2H), 3.25 – 3.24 (m, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 135.9, 134.4, 128.7, 128.1, 126.5, 122.9, 117.3, 34.4, 15.5; **HRMS m/z (ESI)** calcd for C₁₁H₁₂NS (M + H)⁺ 190.0690, found 190.0709.

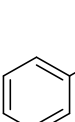
(S,E)-4-methyl-6-phenylhex-5-enenitrile (3ah).

 Yellow oil (26.7 mg, 72%). **¹H NMR (400 MHz, CDCl₃)** δ 7.37 – 7.29 (m, 4H), 7.25 – 7.20 (m, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.99 – 5.93 (m, 1H), 2.50 – 2.42 (m, 1H), 2.39 – 2.28 (m, 2H), 1.83 – 1.64 (m, 2H), 1.15 (dd, *J* = 6.7, 1.4 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ 137.0, 133.4, 130.5, 128.6, 127.4, 126.1, 119.8, 36.7, 32.2, 20.5, 15.3; **HRMS m/z (ESI)** calcd for C₁₃H₁₆N (M + H)⁺ 186.1283, found 186.1277.

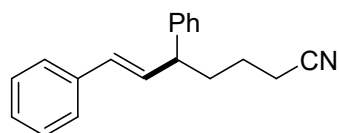
(S,E)-5-methyl-4-styrylhex-5-enenitrile (3ai).

 Yellow oil (22 mg, 52%). **¹H NMR (400 MHz, CDCl₃)** δ 7.36 – 7.29 (m, 4H), 7.25 – 7.20 (m, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 5.86 (dd, *J* = 15.8, 9.2 Hz, 1H), 4.79 – 4.72 (m, 2H), 2.56 – 2.47 (m, 1H), 2.41 – 2.29 (m, 2H), 2.17 (d, *J* = 7.4 Hz, 2H), 1.73 (t, *J* = 1.2 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ 142.7, 136.9, 131.7, 131.7, 128.6, 127.5, 126.2, 119.7, 112.9, 43.9, 40.4, 30.0, 22.3, 15.3; **HRMS m/z (ESI)** calcd for C₁₅H₁₈N (M + H)⁺ 212.1439, found 212.1439.

(E)-5-methyl-7-phenylhept-6-enenitrile (3aj).

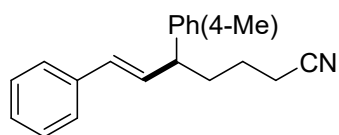
 Yellow oil (14 mg, 35%). **¹H NMR (400 MHz, CDCl₃)** δ 7.35 – 7.29 (m, 4H), 7.22 – 7.18 (m, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 6.03 (dd, *J* = 15.8, 8.2 Hz, 1H), 2.36 – 2.31 (m, 3H), 1.11 (d, *J* = 6.7 Hz, 3H), 0.89 – 0.83 (m, 4H); **¹³C NMR (101 MHz, CDCl₃)** δ 135.3, 129.1, 128.5, 127.1, 126.0, 119.7, 36.9, 35.8, 23.4, 20.8, 17.2; **HRMS m/z (ESI)** calcd for C₁₄H₁₈N (M + H)⁺ 200.1439, found 200.1429.

(E)-5,7-diphenylhept-6-enenitrile (3ak).



Yellow oil (30.3 mg, 58%). **¹H NMR (400 MHz, CDCl₃)** δ 7.40 – 7.35 (m, 3H), 7.32 – 7.27 (m, 3H), 7.25 – 7.20 (m, 4H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.8, 7.7 Hz, 1H), 3.43 (q, *J* = 7.6 Hz, 1H), 2.36 – 2.32 (m, 2H), 2.00 – 1.93 (m, 2H), 1.77 – 1.60 (m, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 143.3, 137.1, 133.0, 130.0, 128.8, 128.5, 127.5, 127.3, 126.7, 126.2, 119.5, 48.5, 34.7, 23.6, 17.1; **HRMS m/z (ESI)** calcd for C₁₉H₂₀N (M + H)⁺ 262.1596, found 262.1586.

(*S,E*)-7-phenyl-5-(*p*-tolyl)hept-6-enitrile (3al).



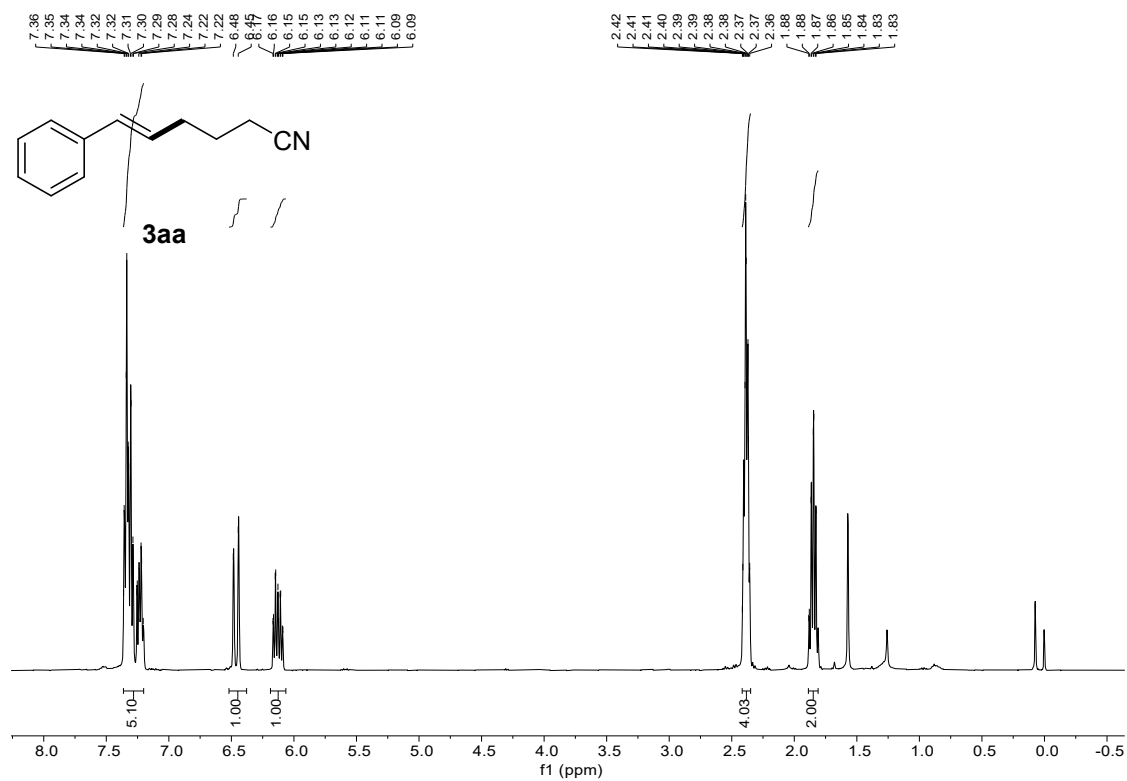
Yellow oil (29.7 mg, 54%). **¹H NMR (400 MHz, CDCl₃)** δ 7.36 – 7.27 (m, 4H), 7.22 – 7.17 (m, 1H), 7.13 (s, 4H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.29 (dd, *J* = 15.9, 7.6 Hz, 1H), 3.43 – 3.33 (m, 1H), 2.35 – 2.32 (m, 6H), 1.98 – 1.91 (m, 2H), 1.74 – 1.60 (m, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ 140.2, 137.2, 136.2, 133.2, 129.8, 129.4, 128.5, 127.3, 127.3, 126.2, 119.6, 48.1, 34.7, 23.6, 21.0, 17.1; **HRMS m/z (ESI)** calcd for C₂₀H₂₂N (M + H)⁺ 276.1752, found 276.1741.

References

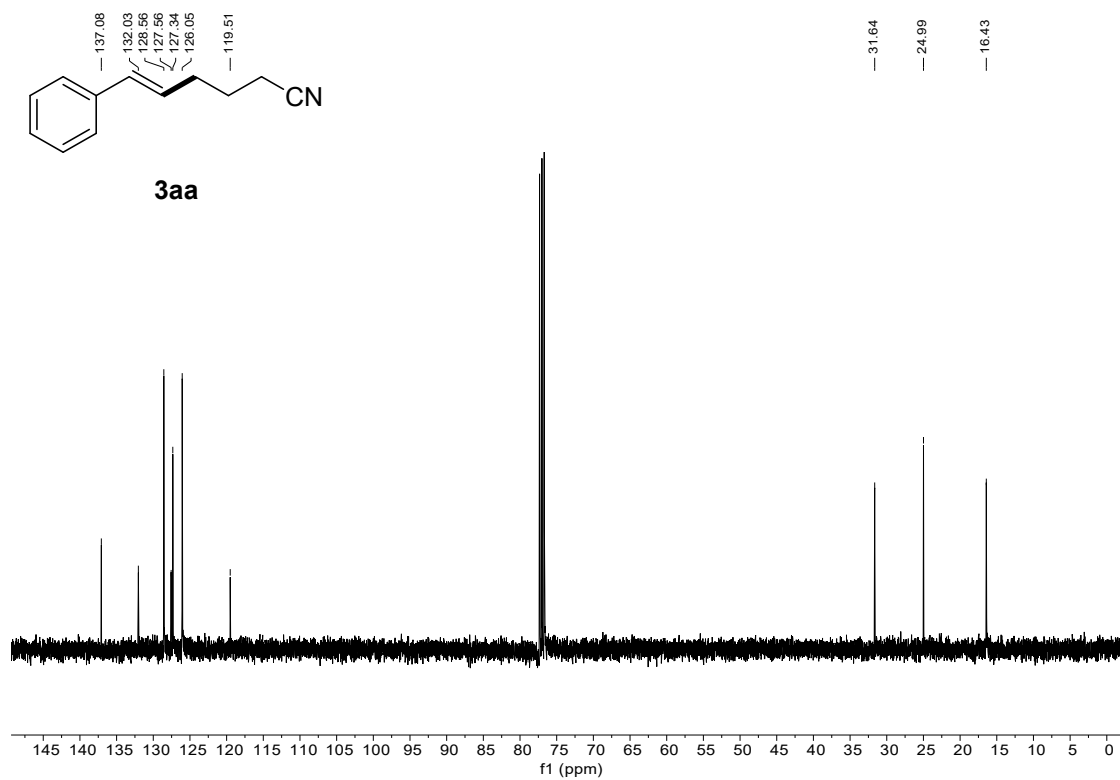
- [1] L. Friedman, E. Kosower, *Org. Synth. Coll.* **1955**, 3, 510.
- [2] B. Zhao, Z. Shi, *Angew. Chem. Int. Ed.* **2017**, 56, 12727-12731; *Angew. Chem.* **2017**, 129, 12901-12905.
- [3] H.-D. Zuo, S.-S. Zhu, W.-J. Hao, S.-C. Wang, S.-J. Tu, B. Jiang, *ACS Catal.* **2021**, 11, 6010-6019.
- [4] Y. Xu, T.-S. Su, Z.-X. Huang, G. Dong, *Angew. Chem. Int. Ed.* **2016**, 55, 2559-2563; *Angew. Chem.* **2016**, 128, 2605-2609.

Spectra of the Products

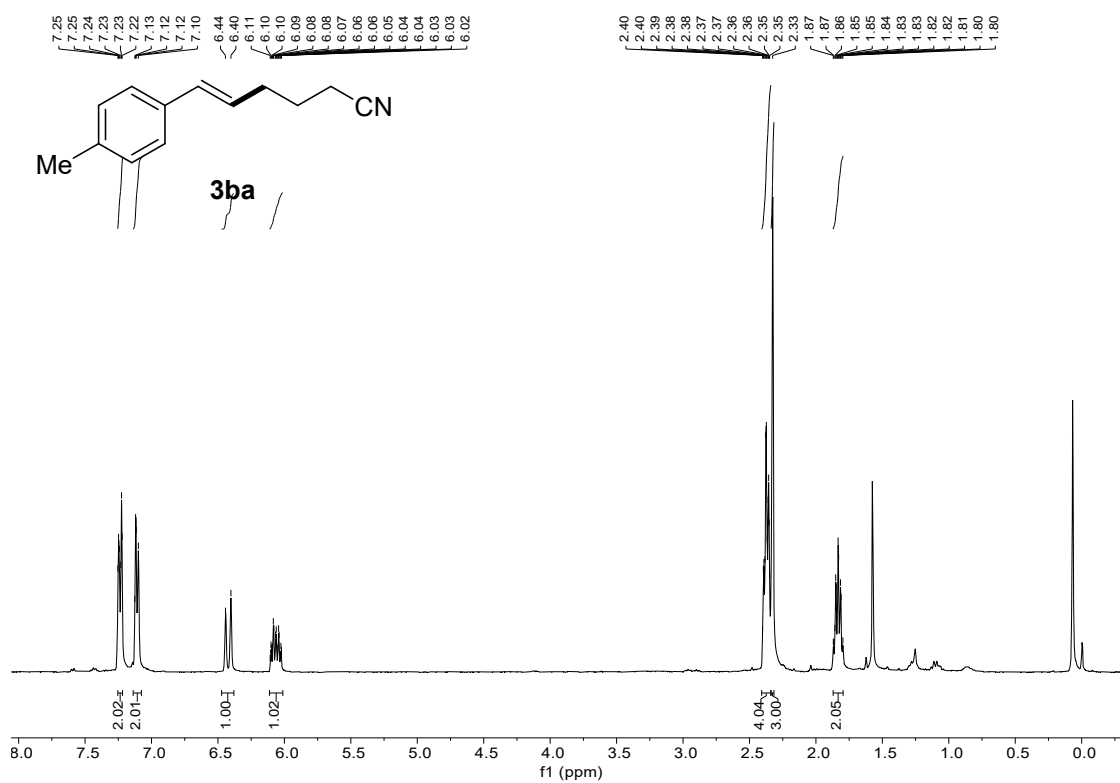
^1H NMR spectra of compound **3aa**



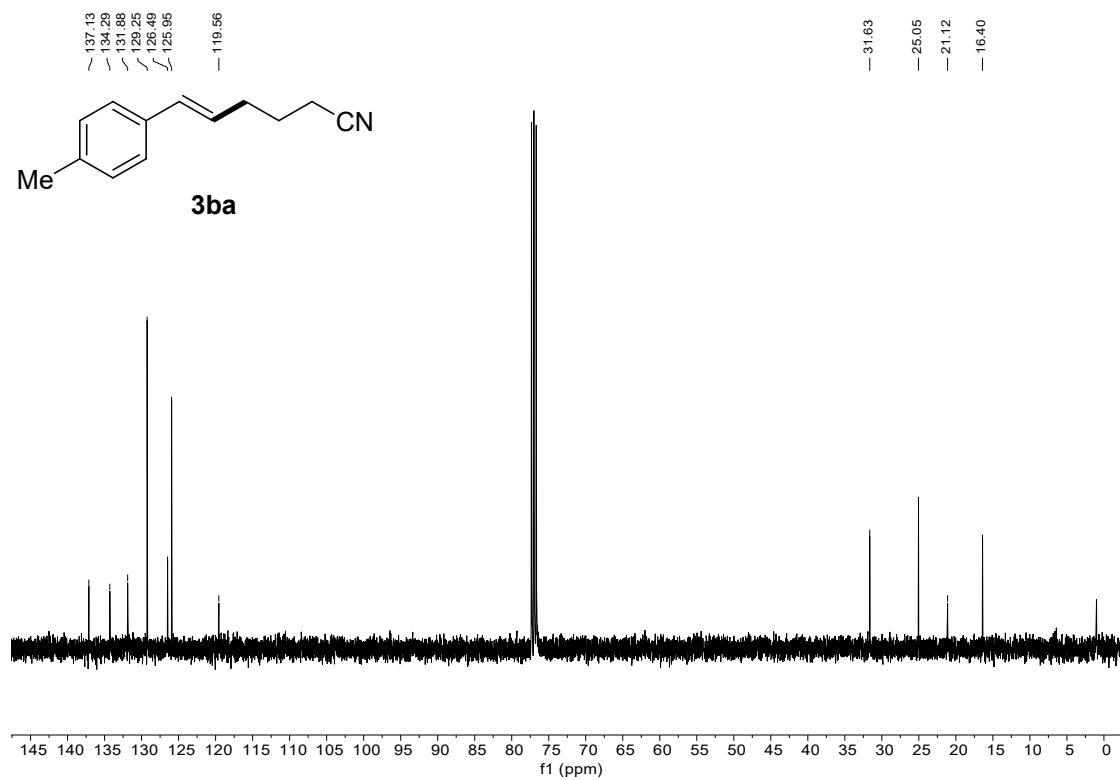
^{13}C NMR spectra of compound **3aa**



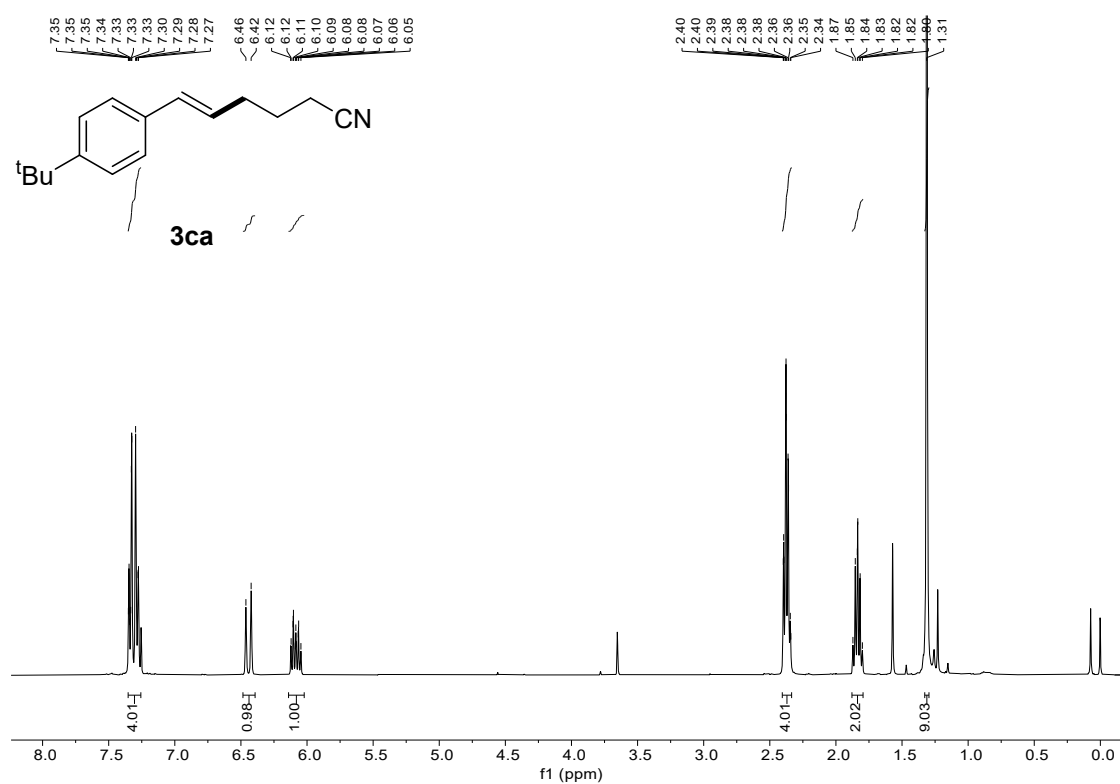
¹H NMR spectra of compound **3ba**



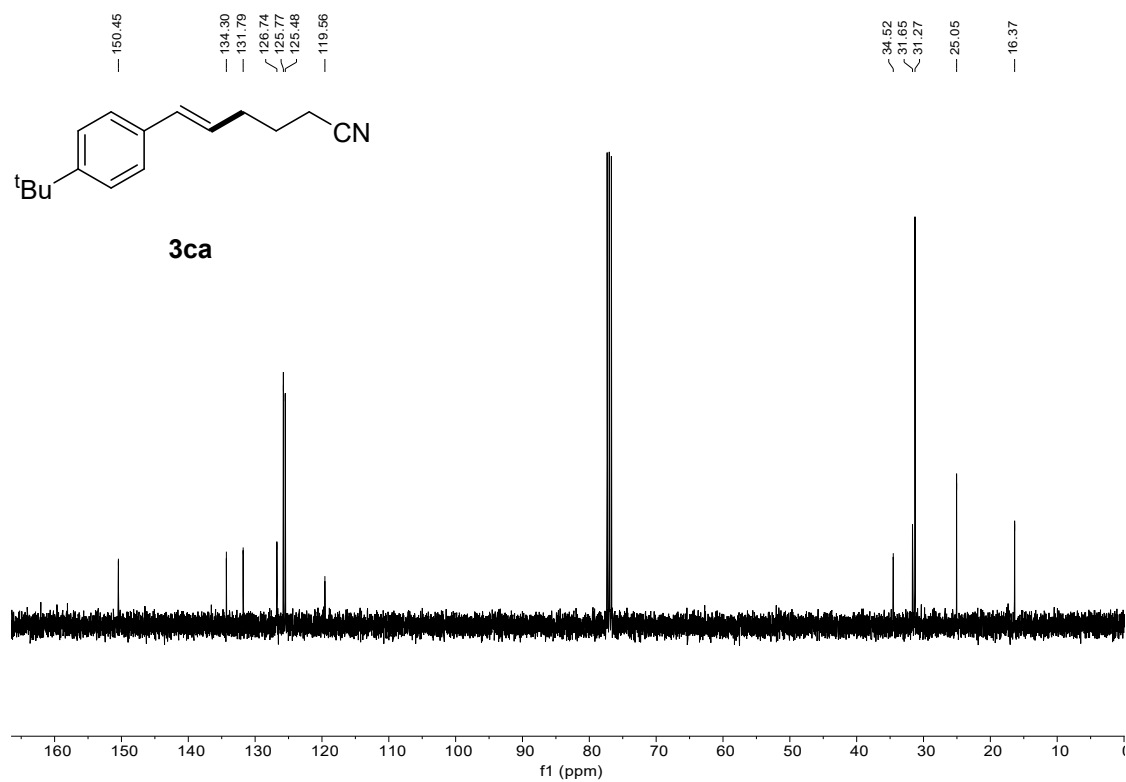
¹³C NMR spectra of compound **3ba**



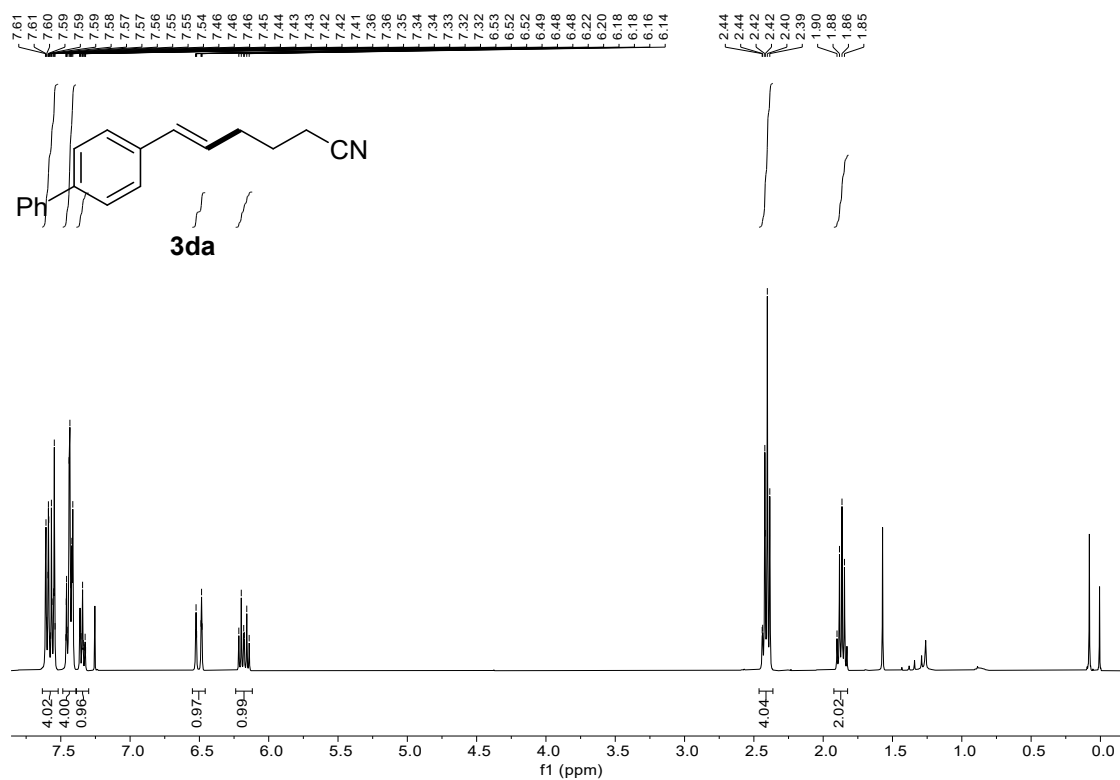
¹H NMR spectra of compound **3ca**



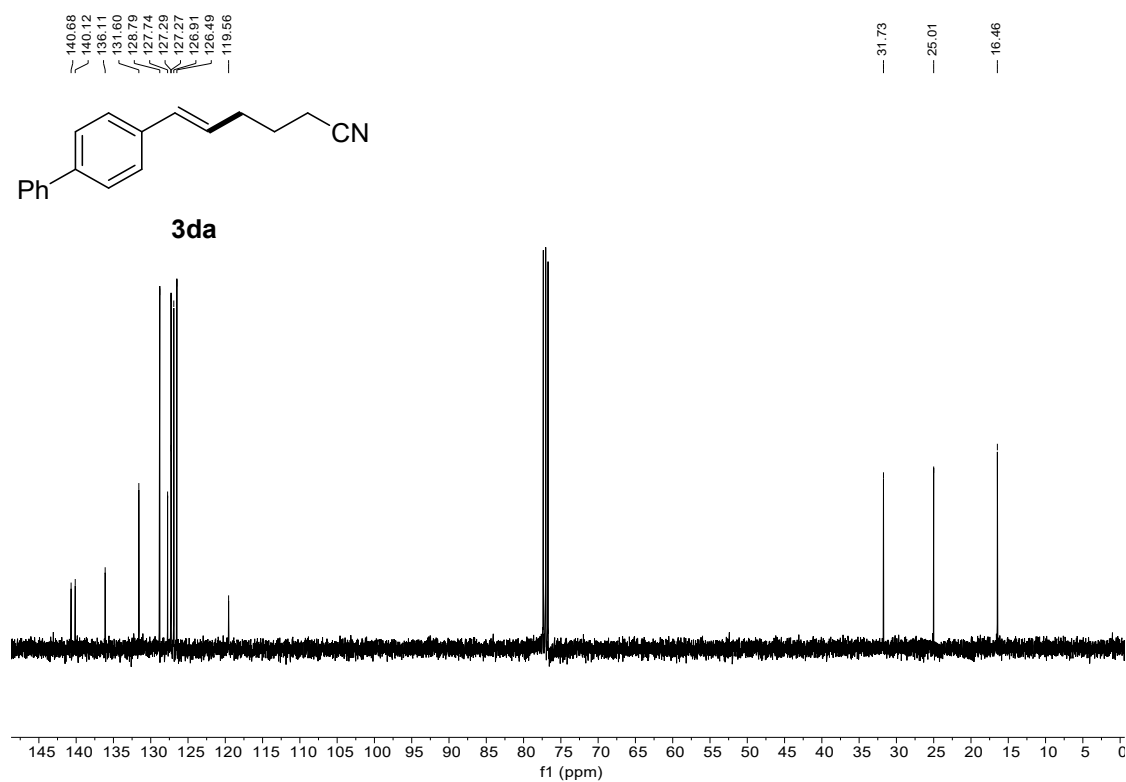
¹³C NMR spectra of compound **3ca**



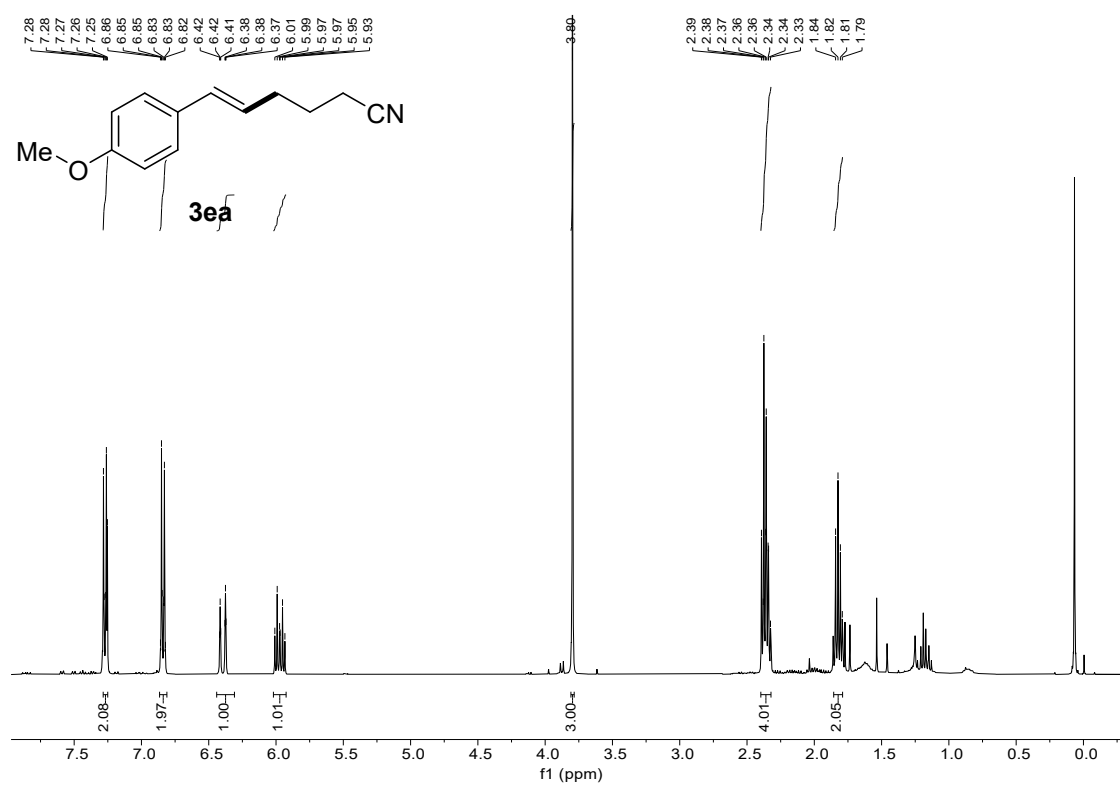
¹H NMR spectra of compound **3da**



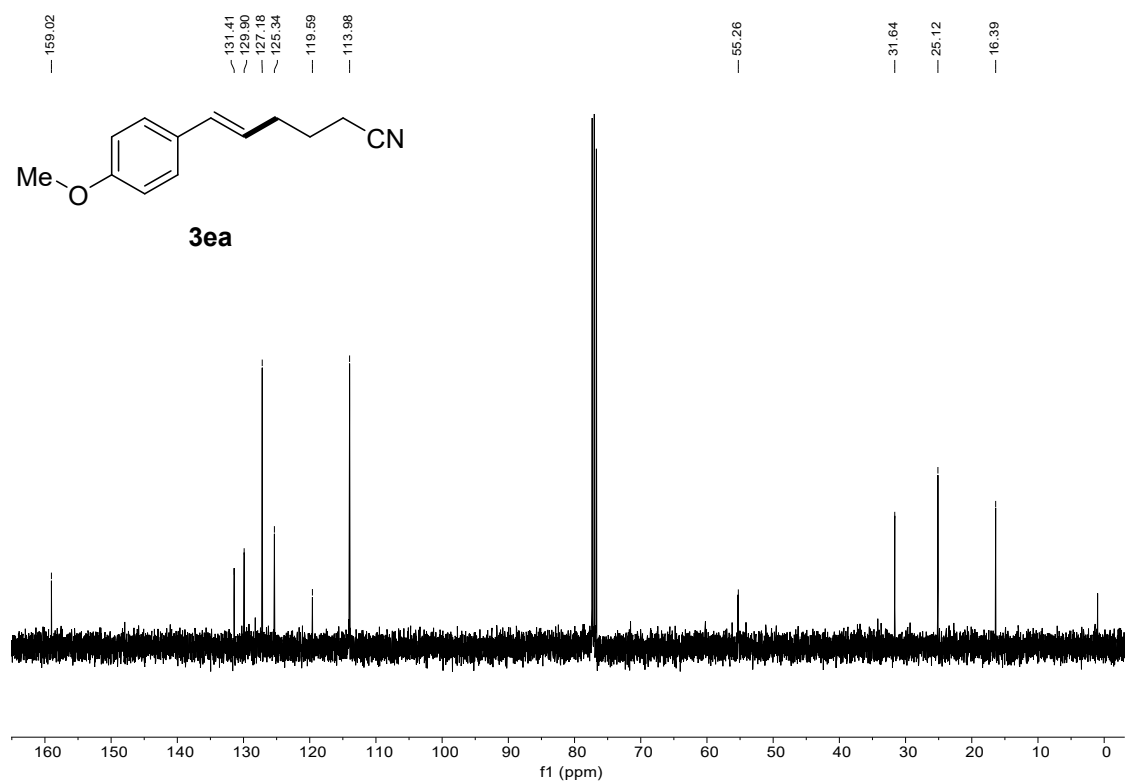
¹³C NMR spectra of compound **3da**



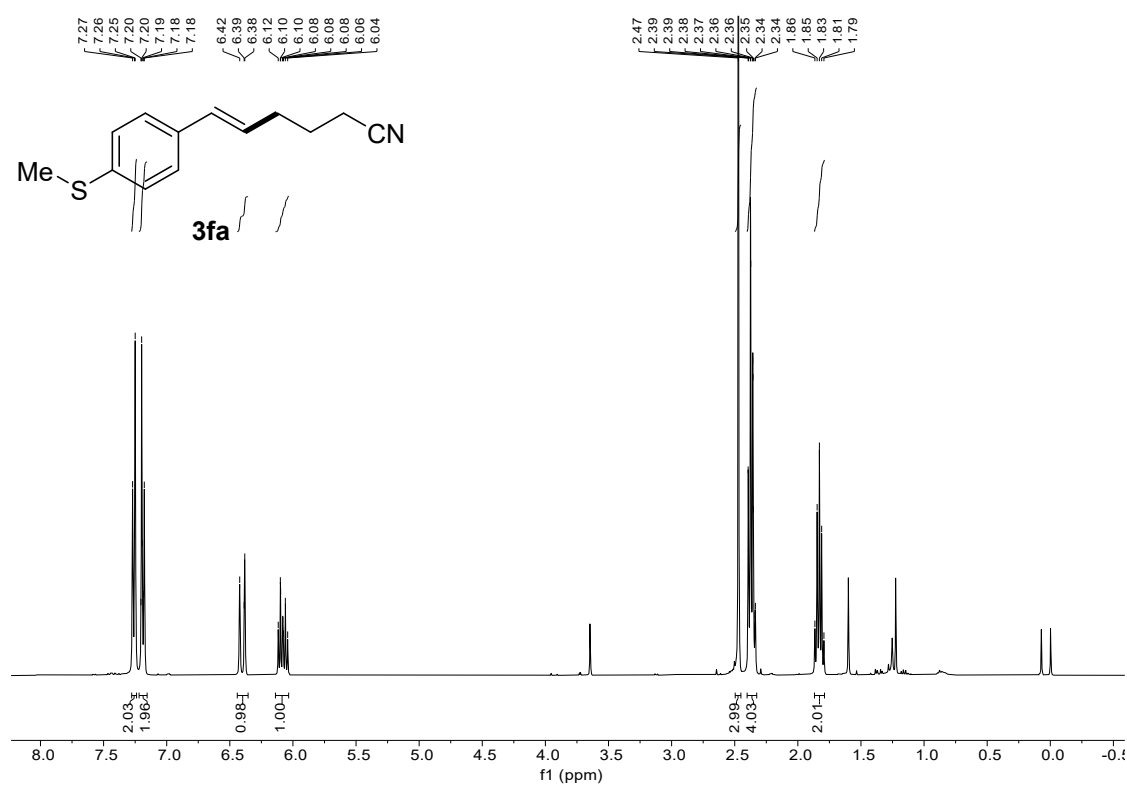
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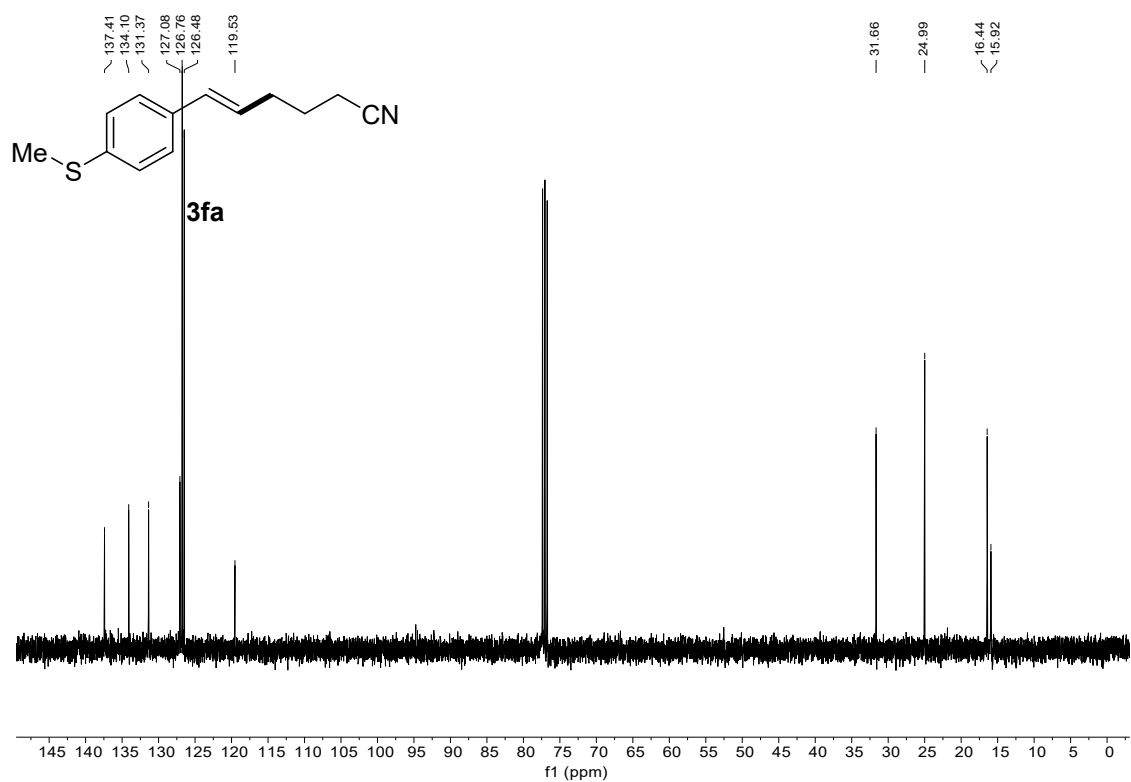
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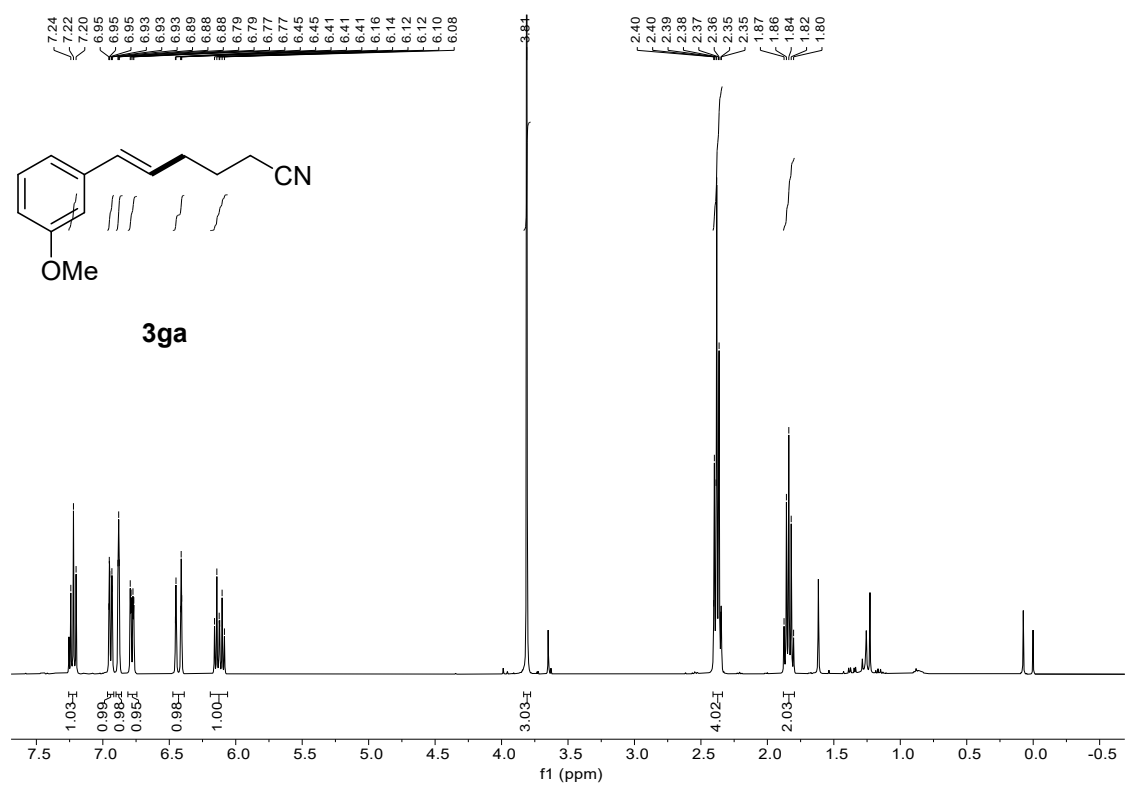
¹H NMR spectra of compound 3fa



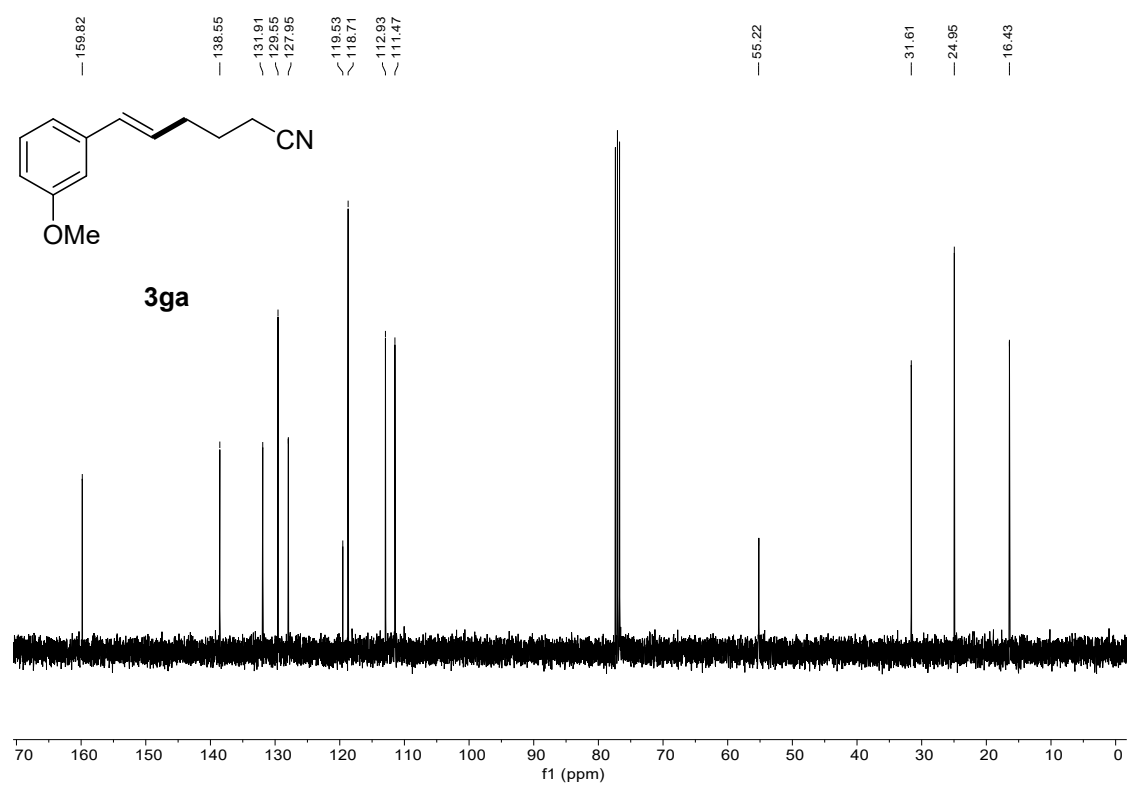
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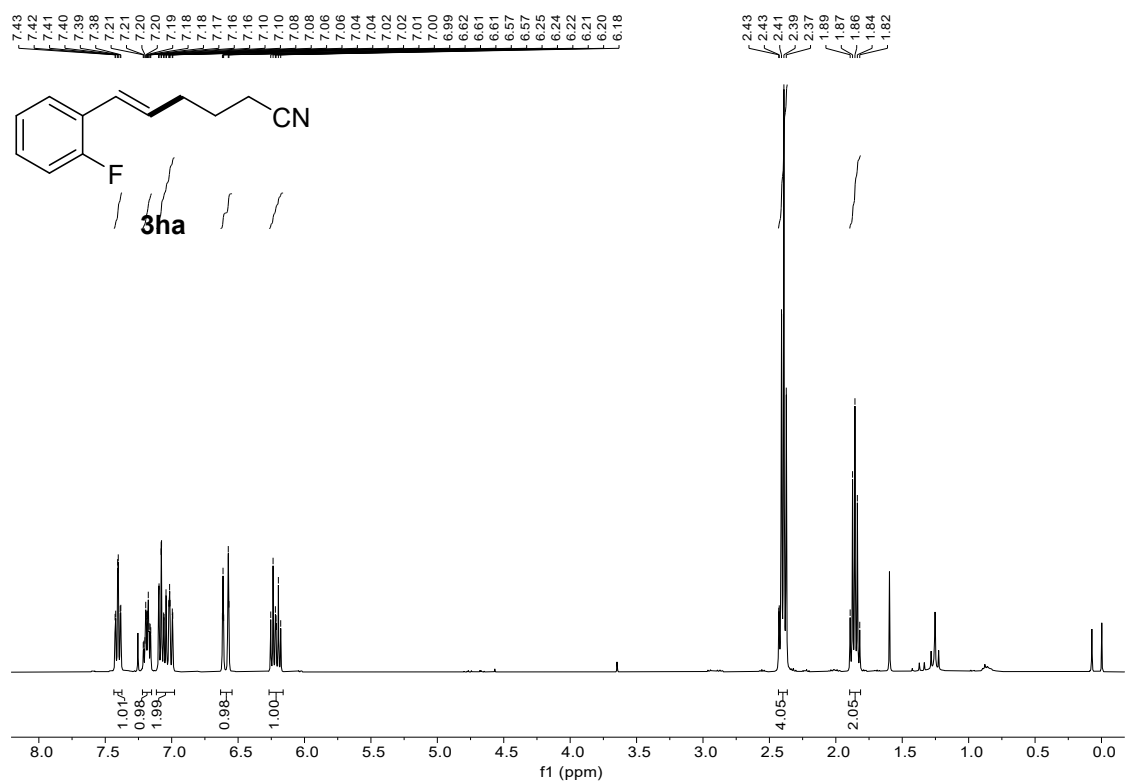
¹H NMR spectra of compound 3ga



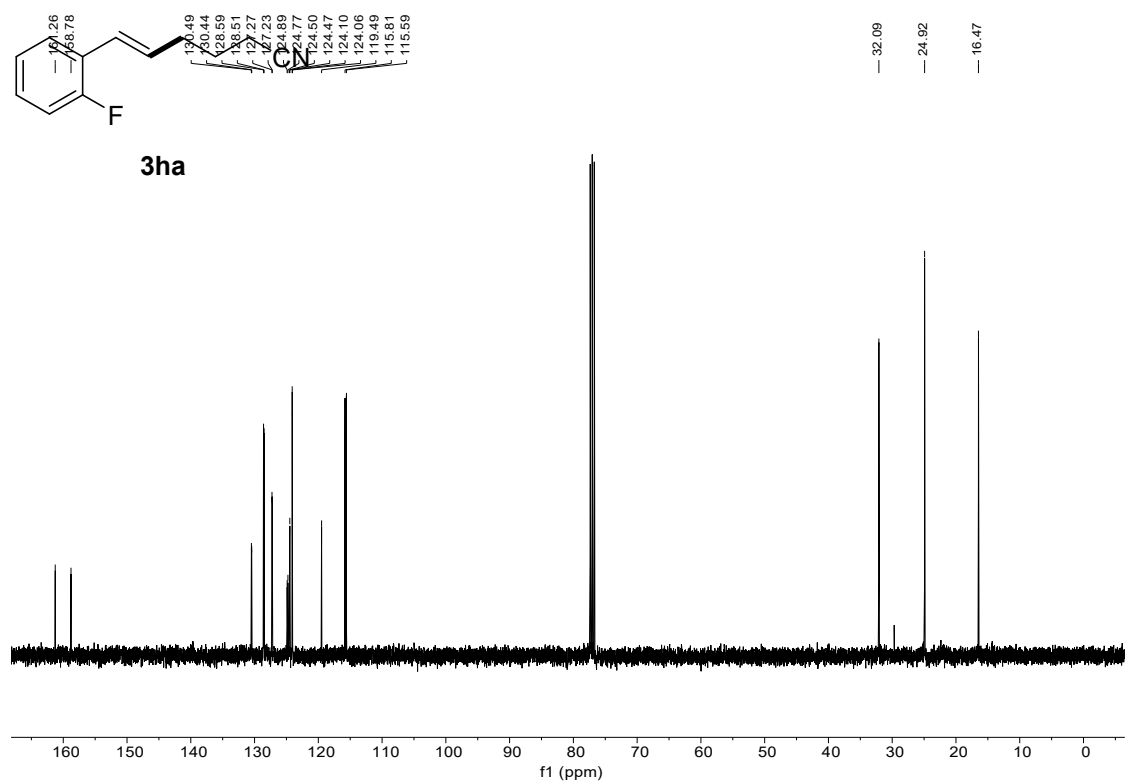
¹³C NMR spectra of compound **3ga**



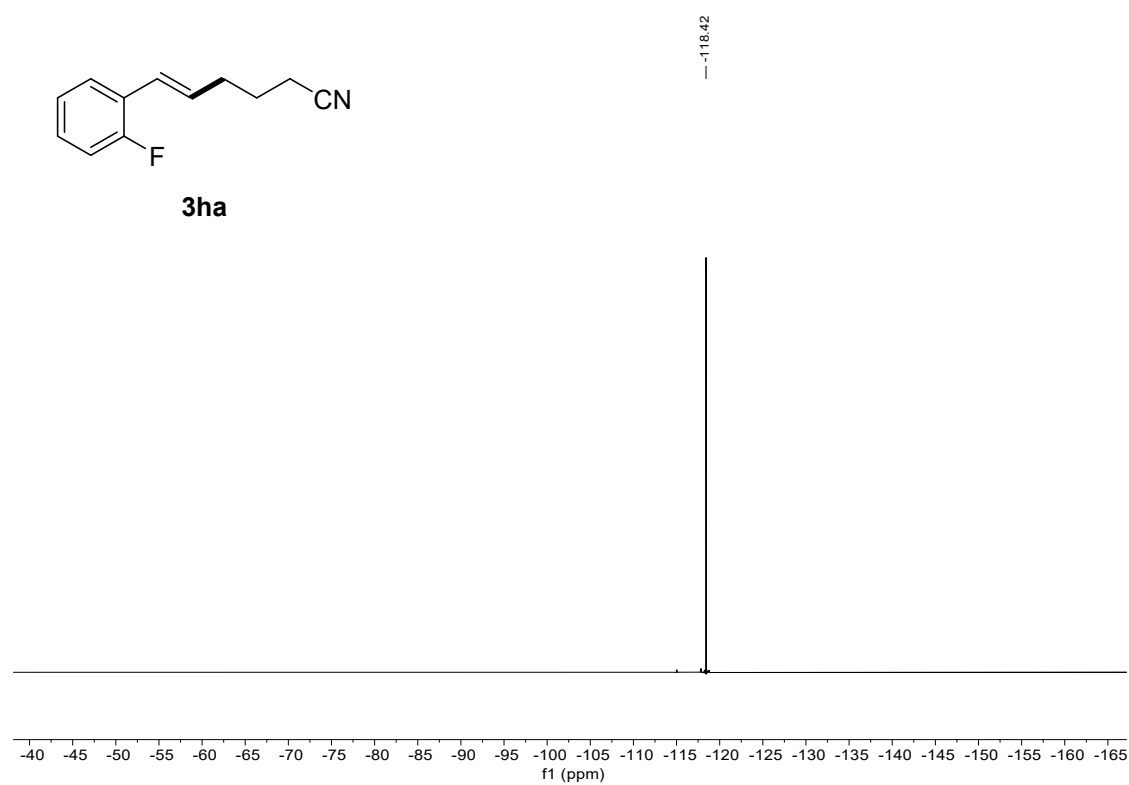
¹H NMR spectra of compound **3ha**



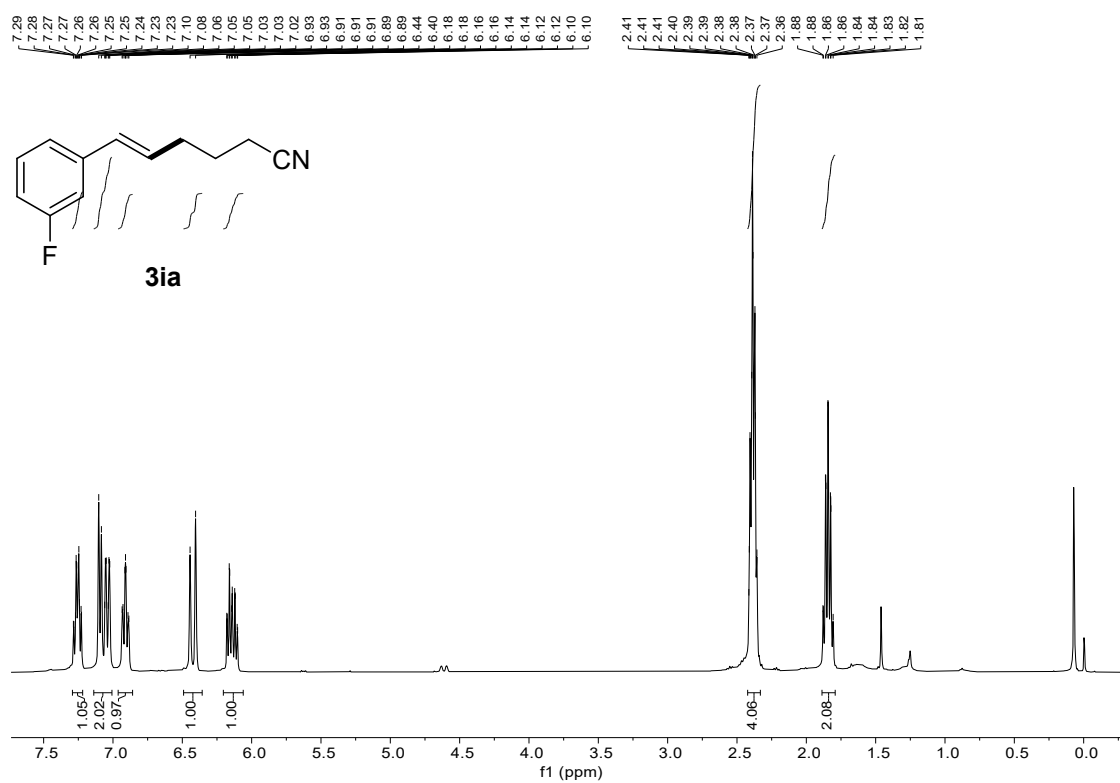
¹³C NMR spectra of compound 3ha



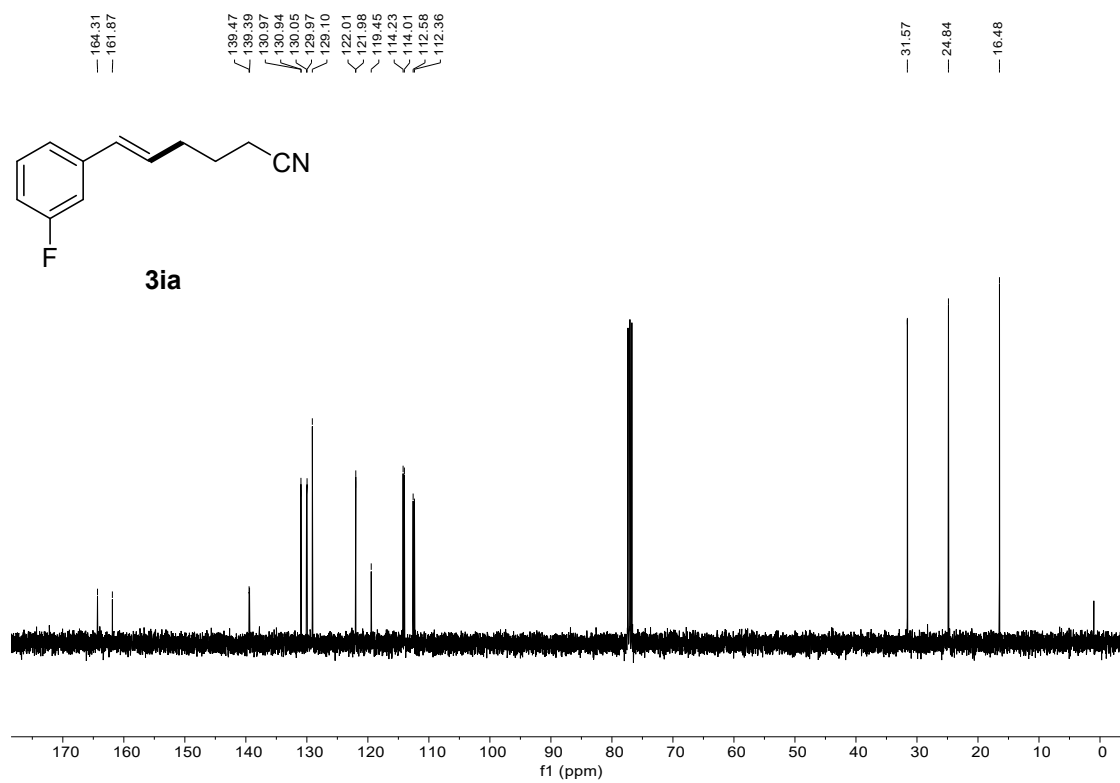
^{19}F NMR spectra of compound **3ha**



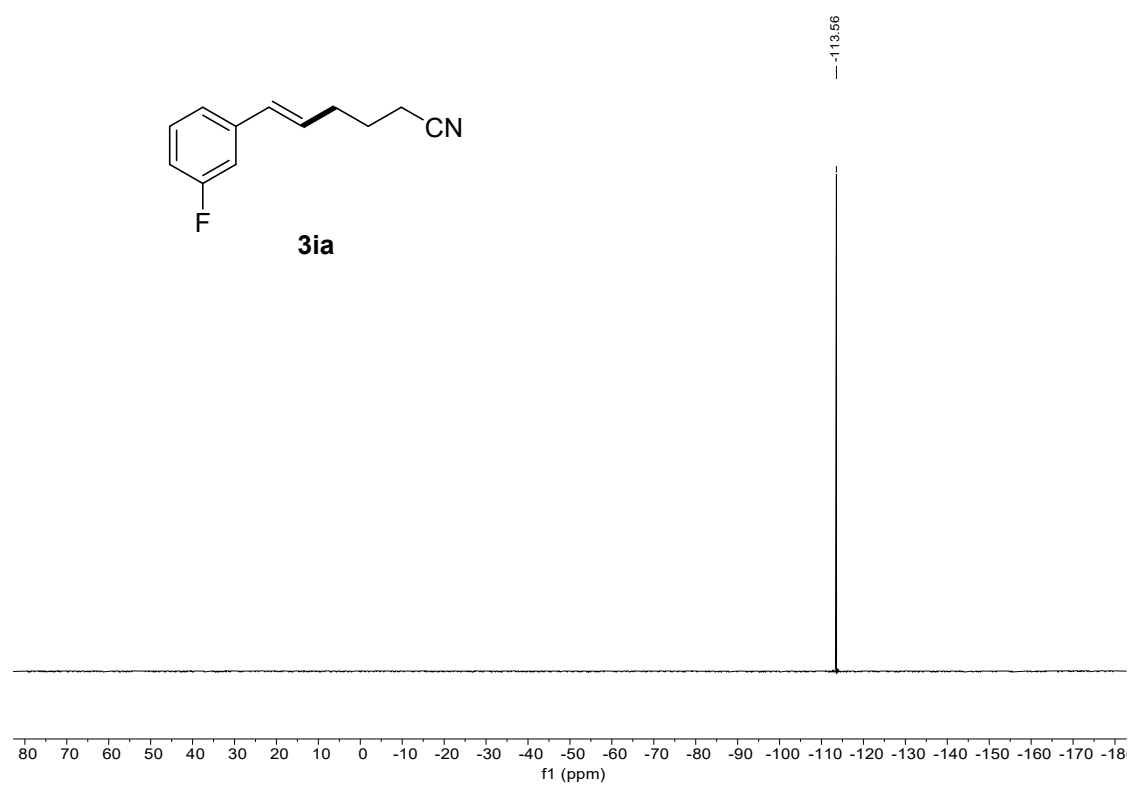
¹H NMR spectra of compound **3ia**



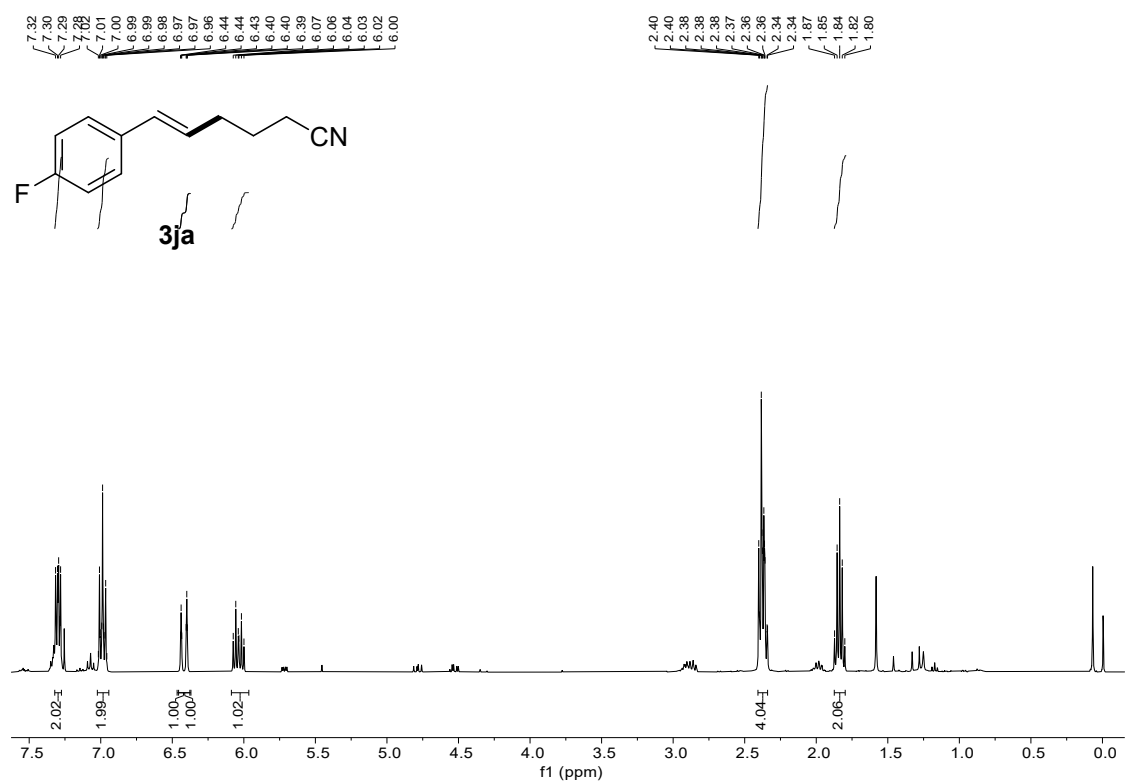
¹³C NMR spectra of compound **3ia**



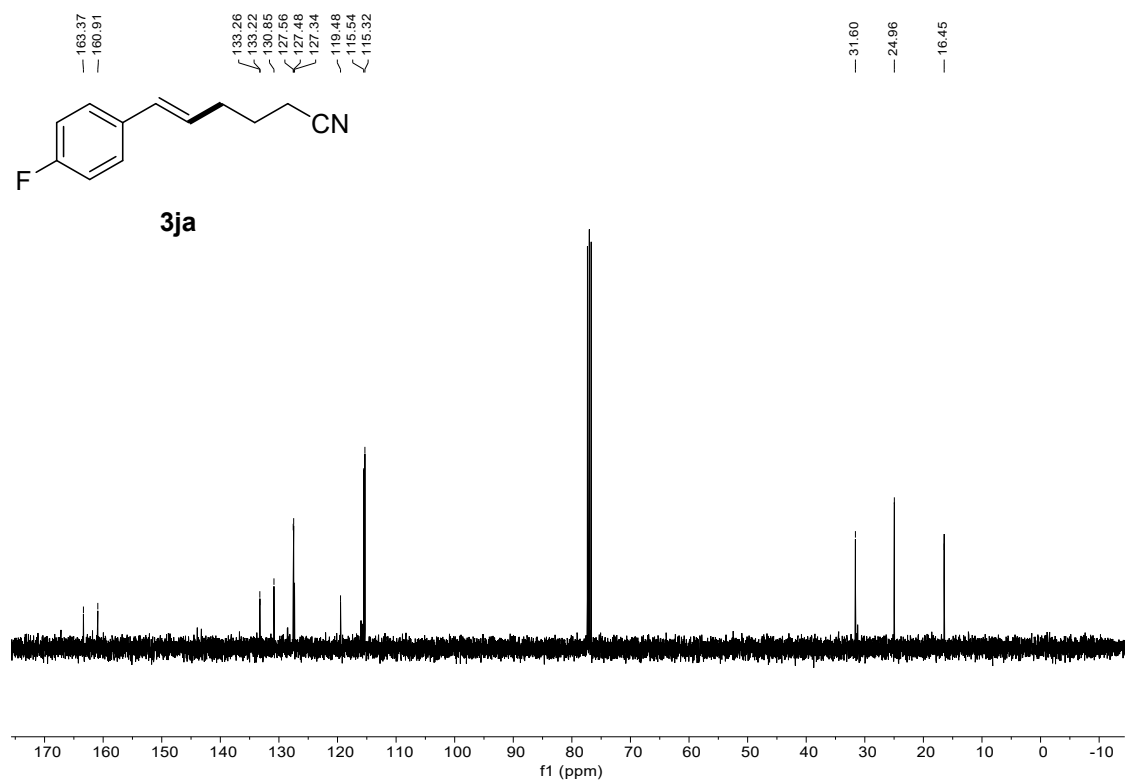
^{19}F NMR spectra of compound **3ia**



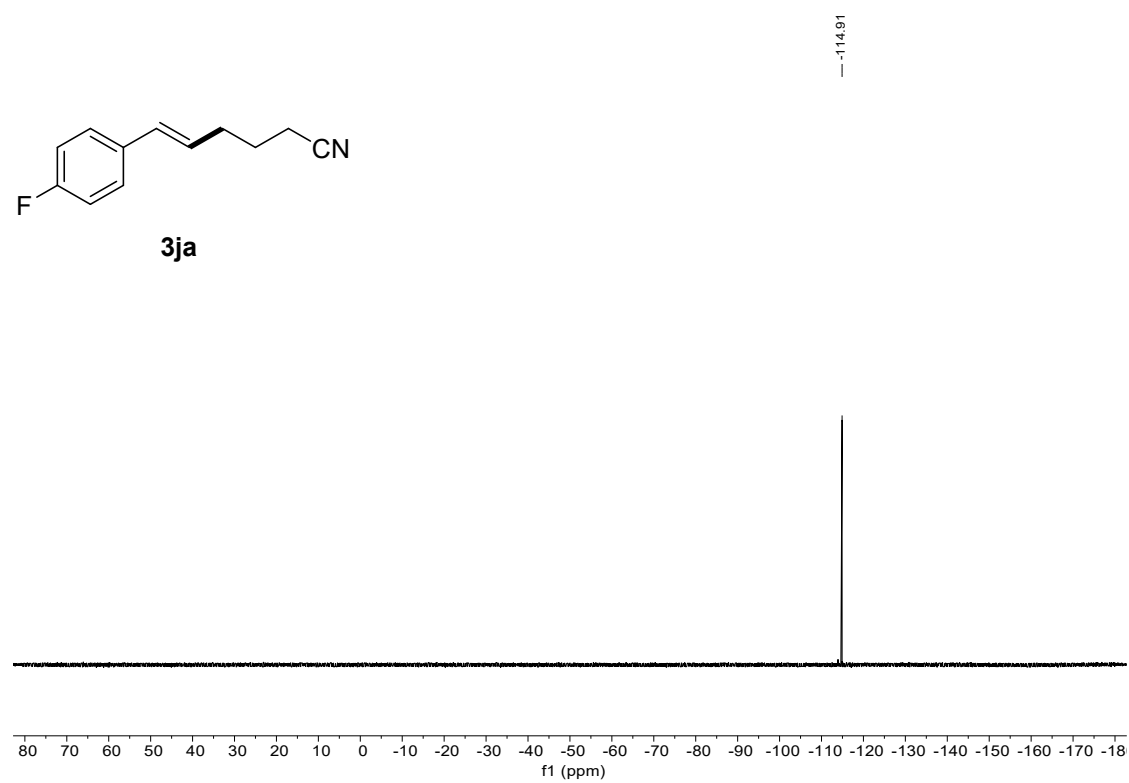
¹H NMR spectra of compound **3ja**



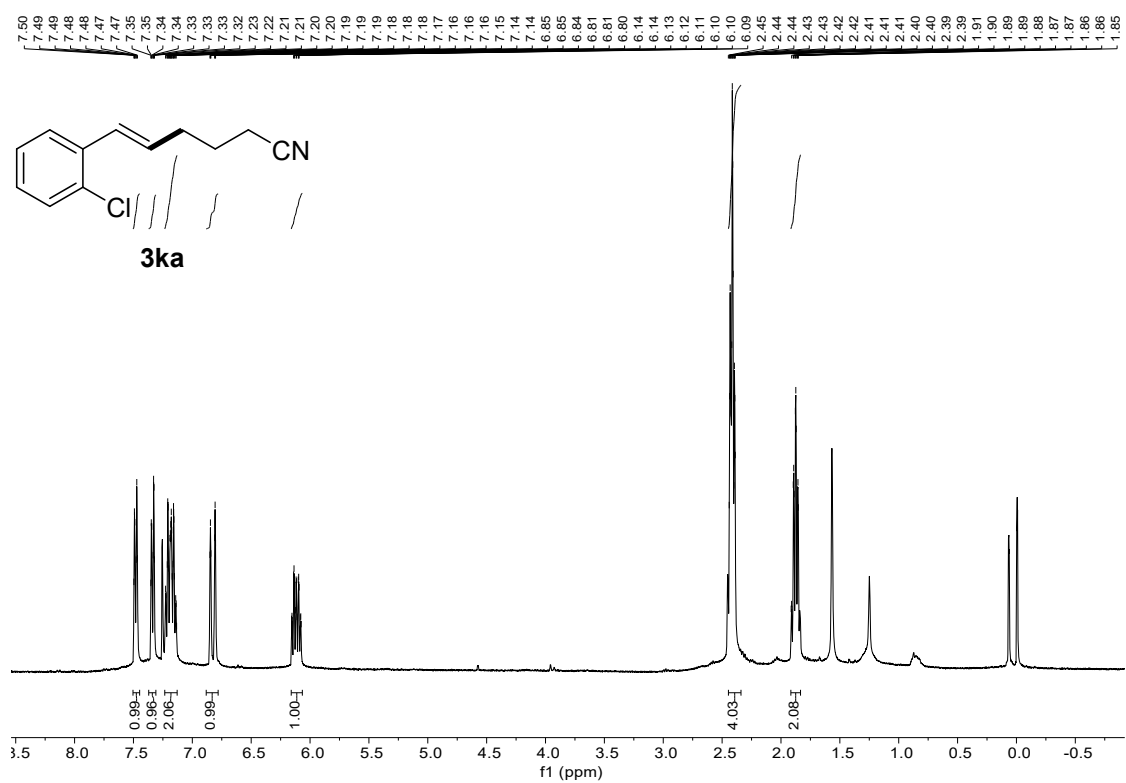
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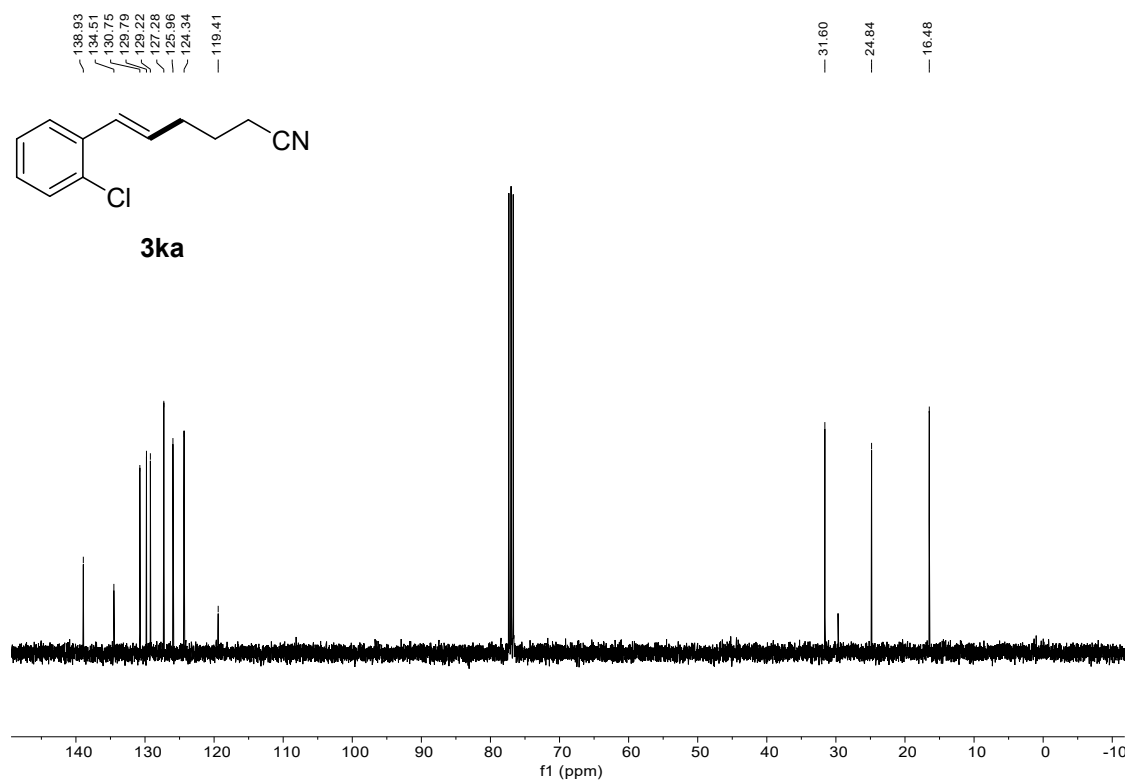
¹⁹F NMR spectra of compound **3ja**



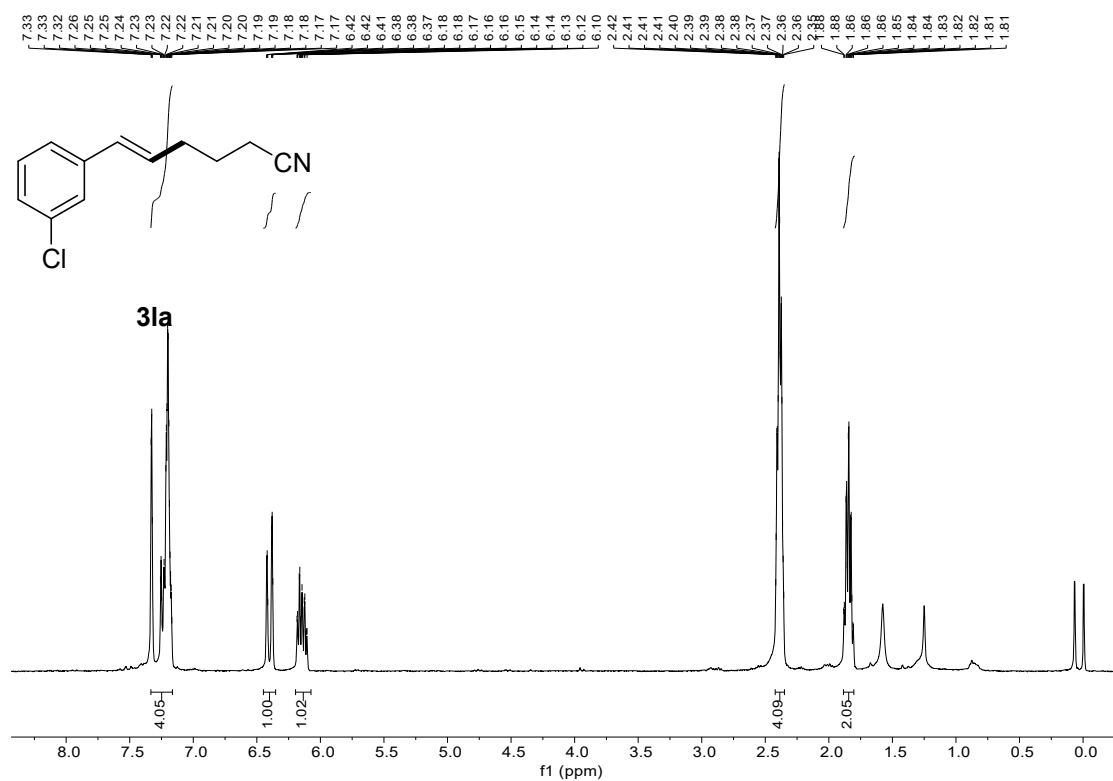
¹H NMR spectra of compound **3ka**



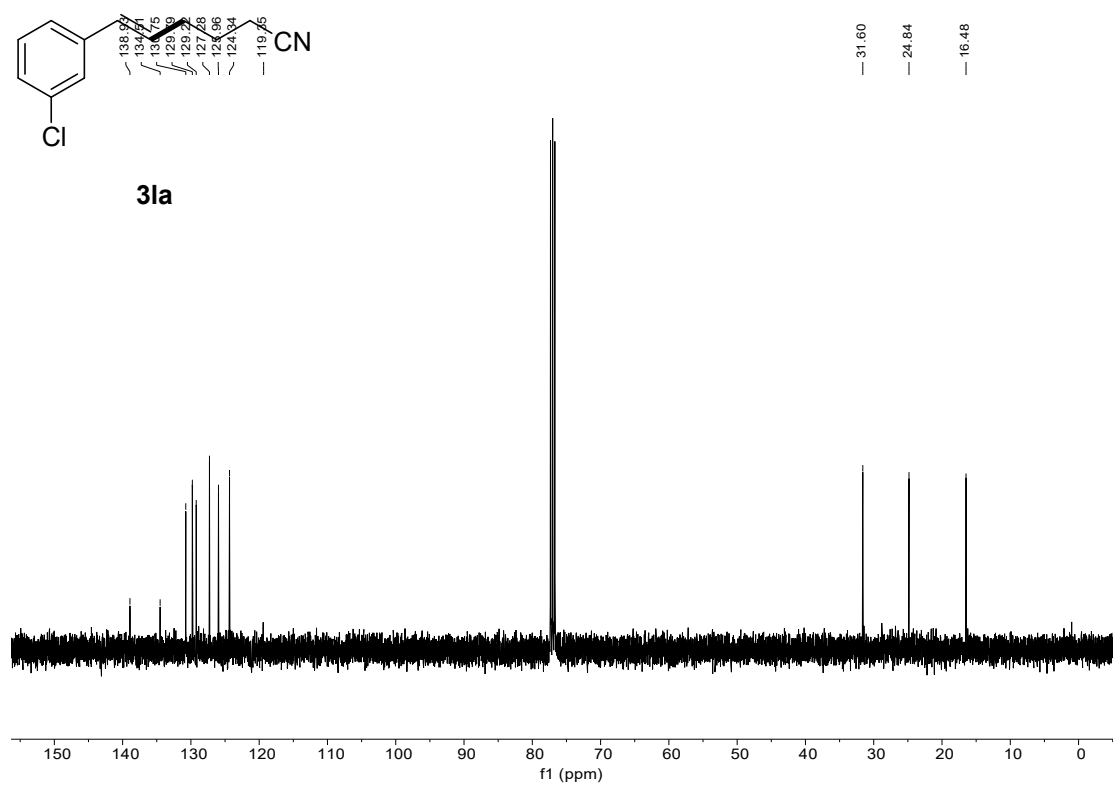
¹³C NMR spectra of compound **3ka**



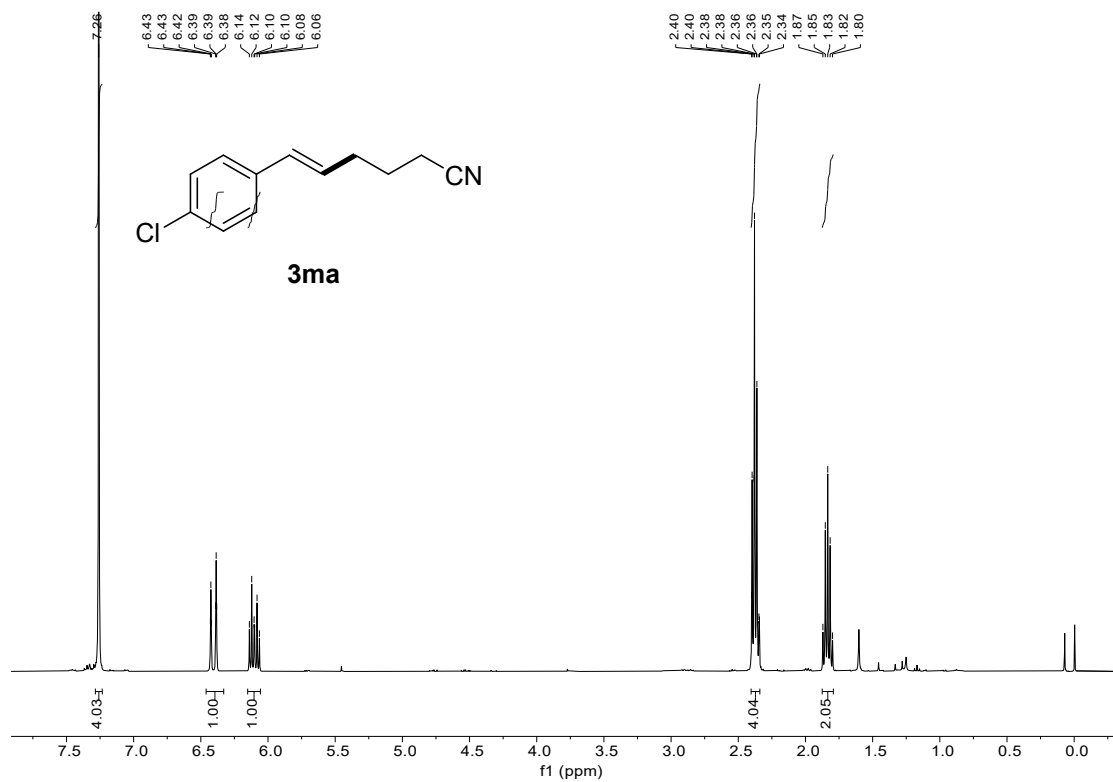
¹H NMR spectra of compound **3la**



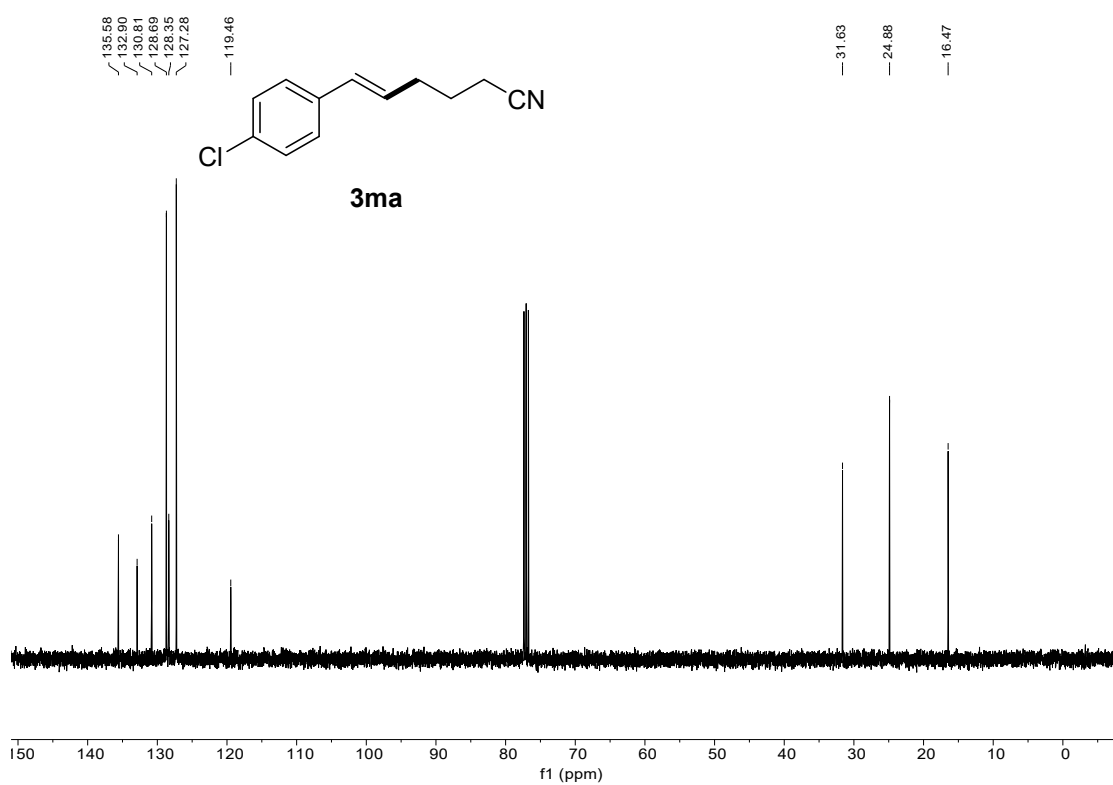
¹³C NMR spectra of compound **3la**



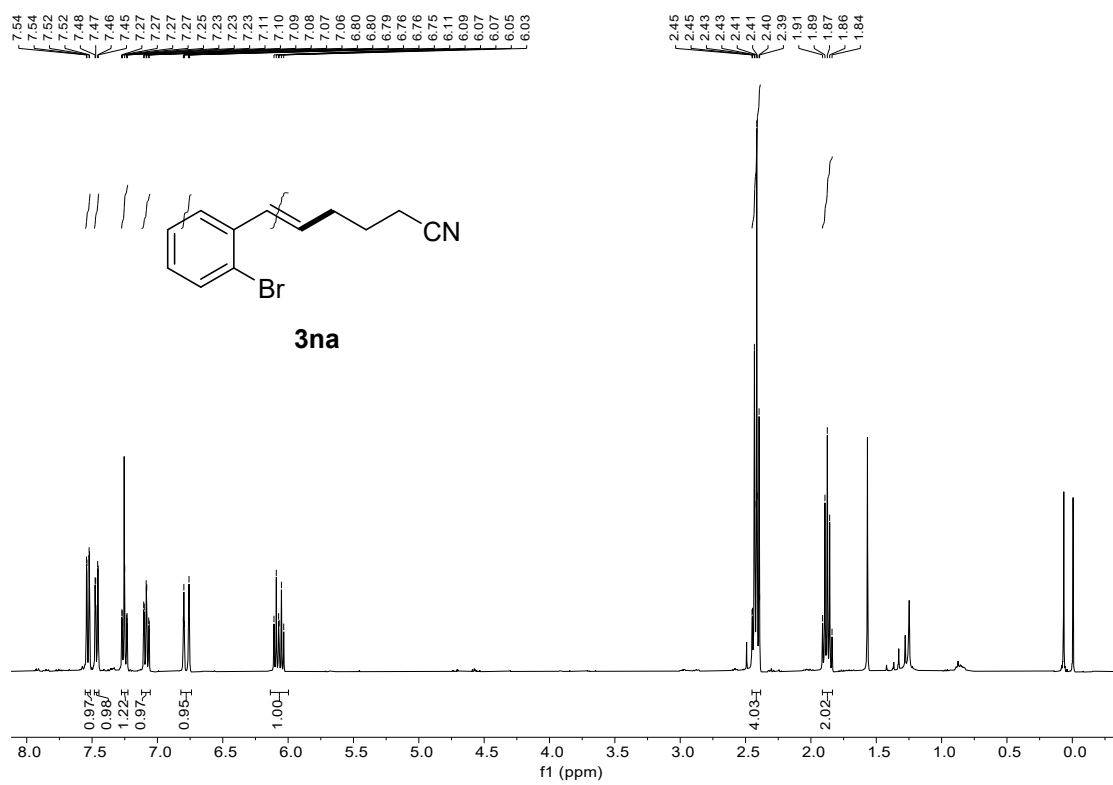
^1H NMR spectra of compound **3ma**



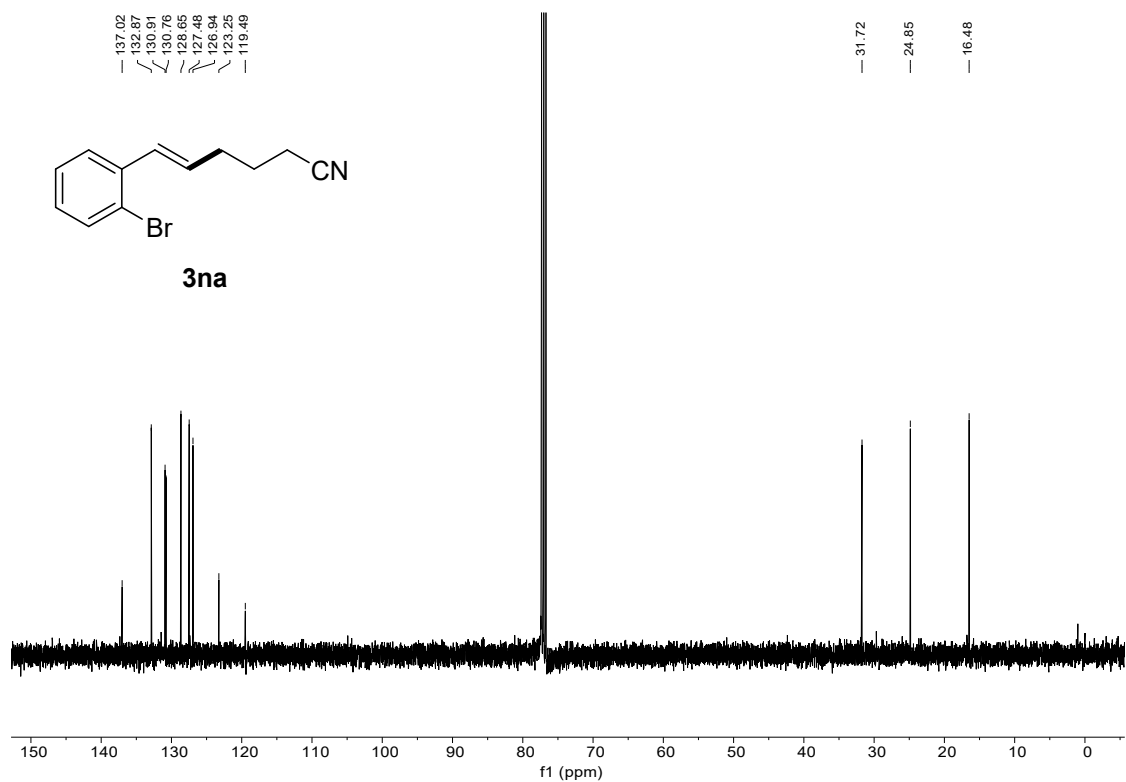
^{13}C NMR spectra of compound **3ma**



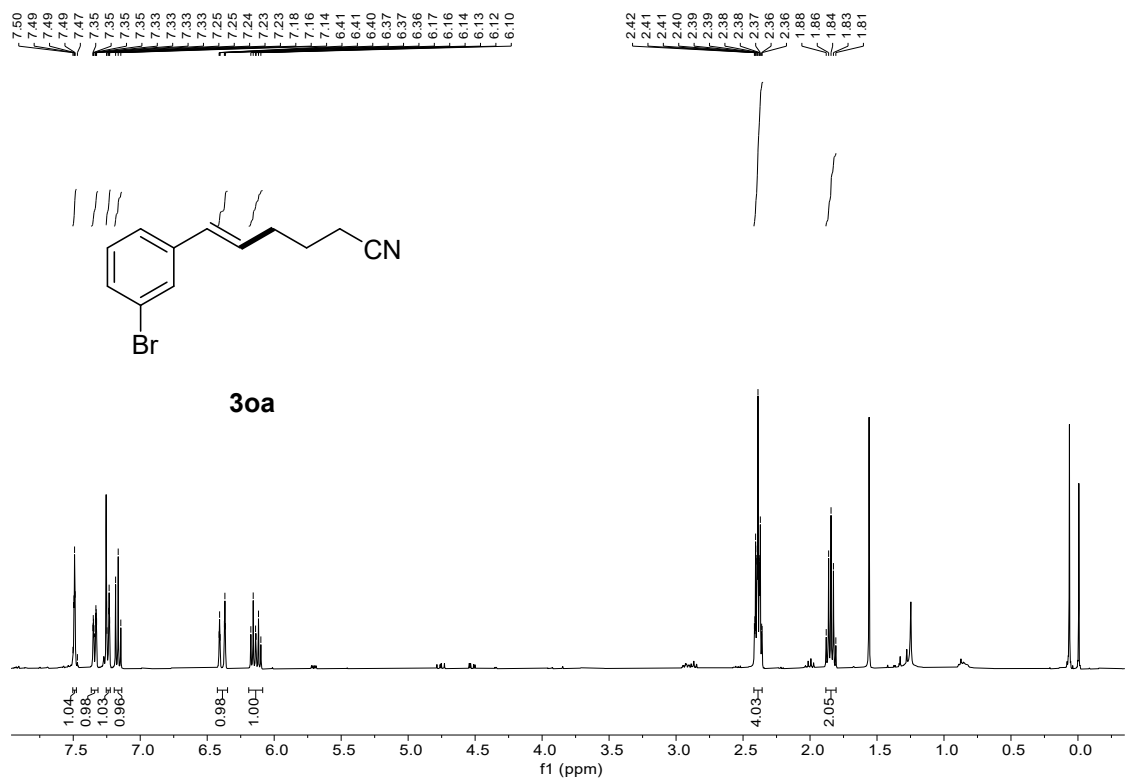
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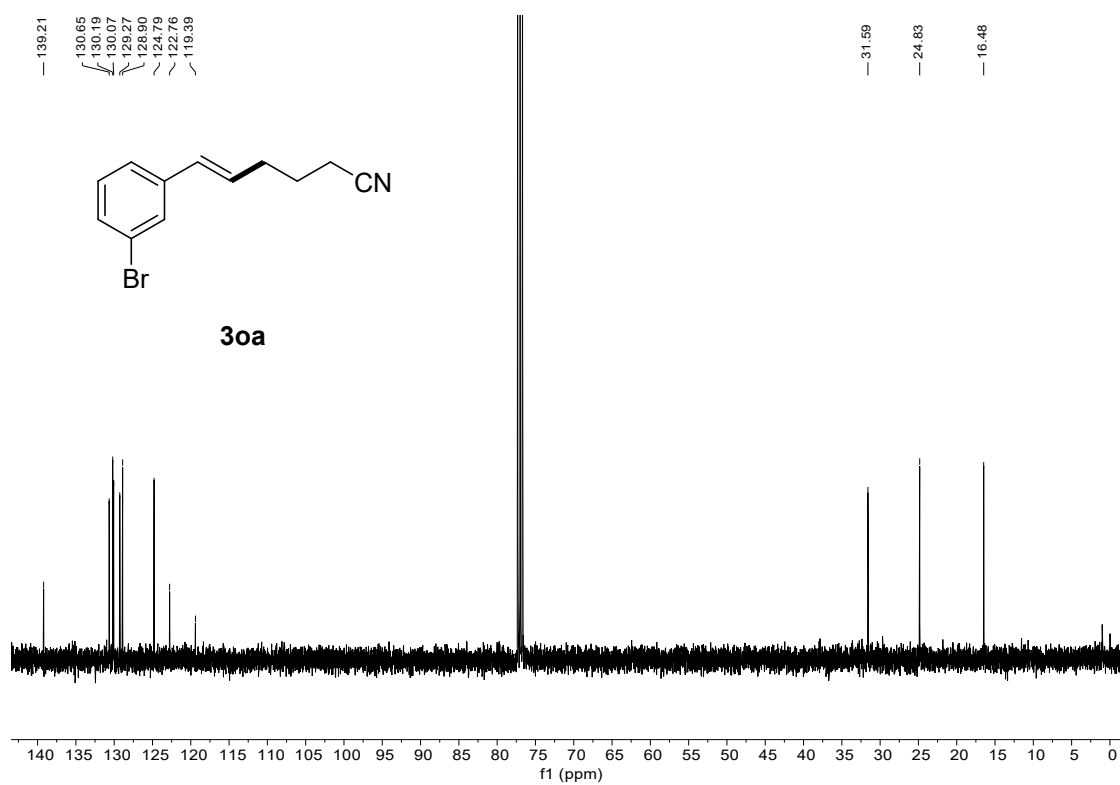
¹³C NMR spectra of compound **3na**



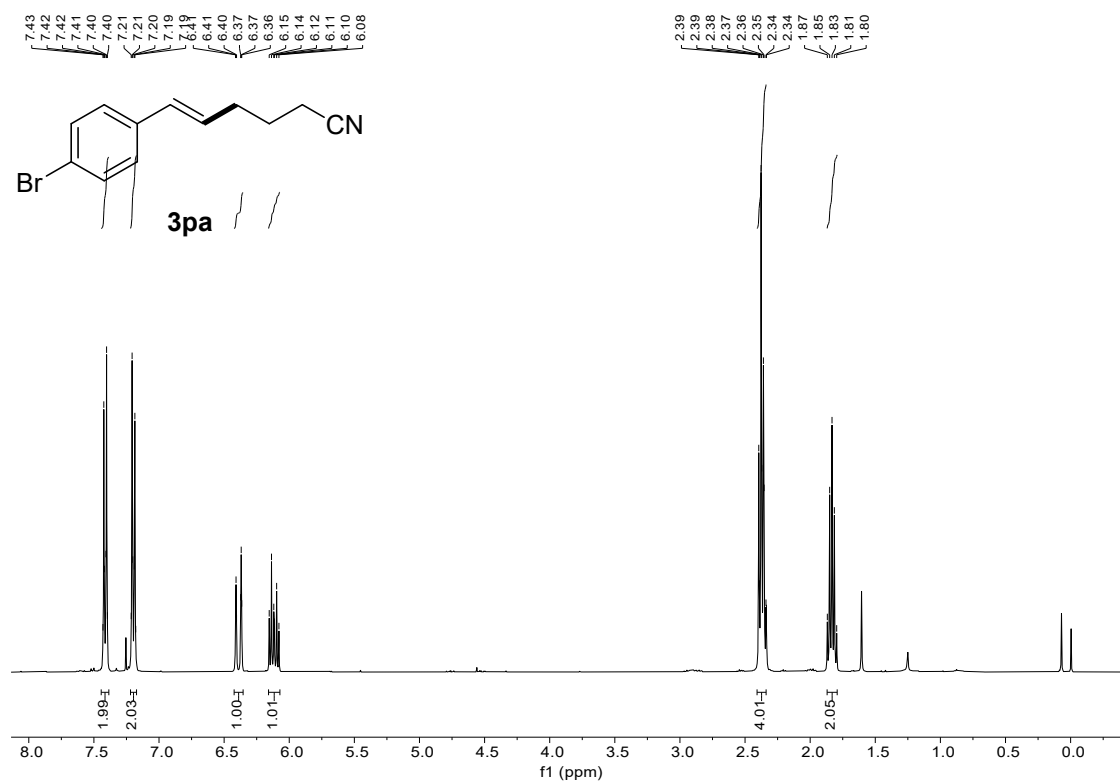
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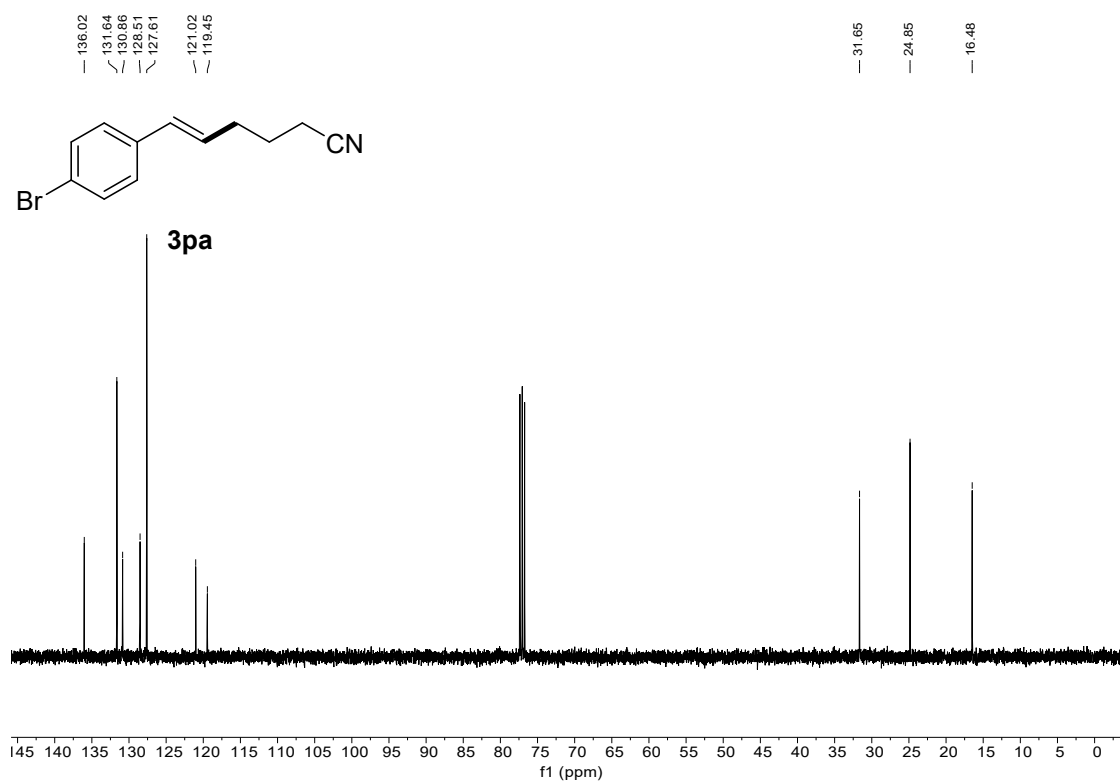
^{13}C NMR spectra of compound **3oa**



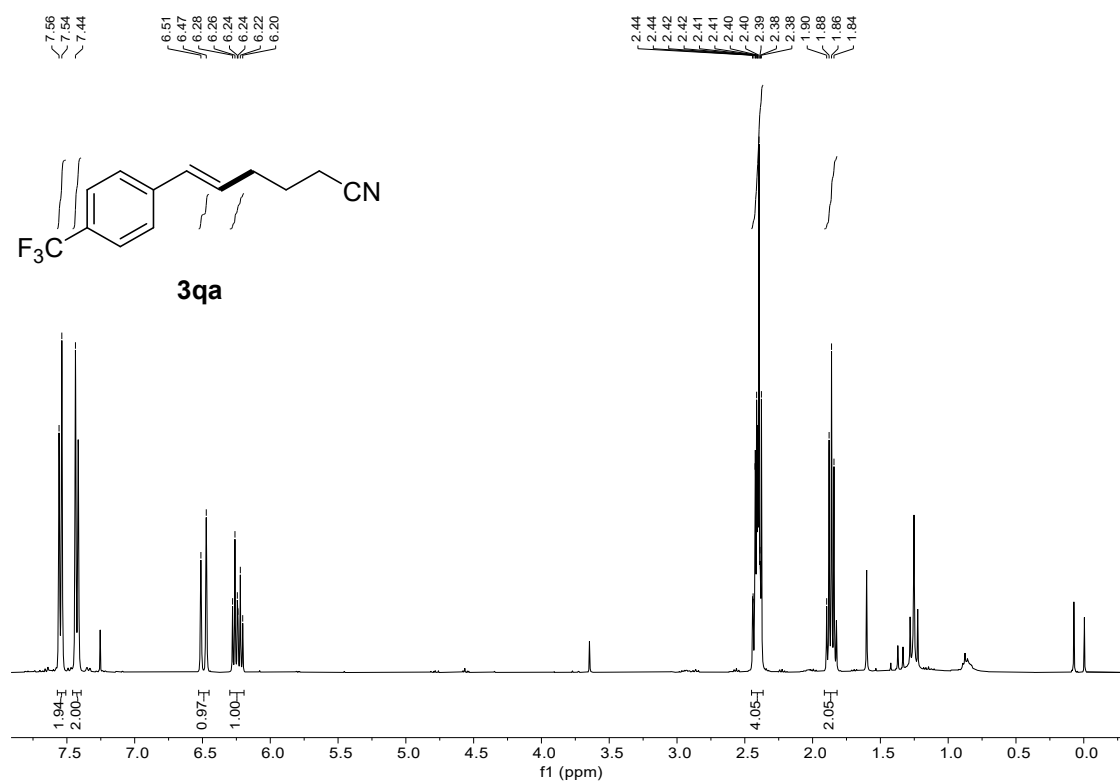
^1H NMR spectra of compound **3pa**



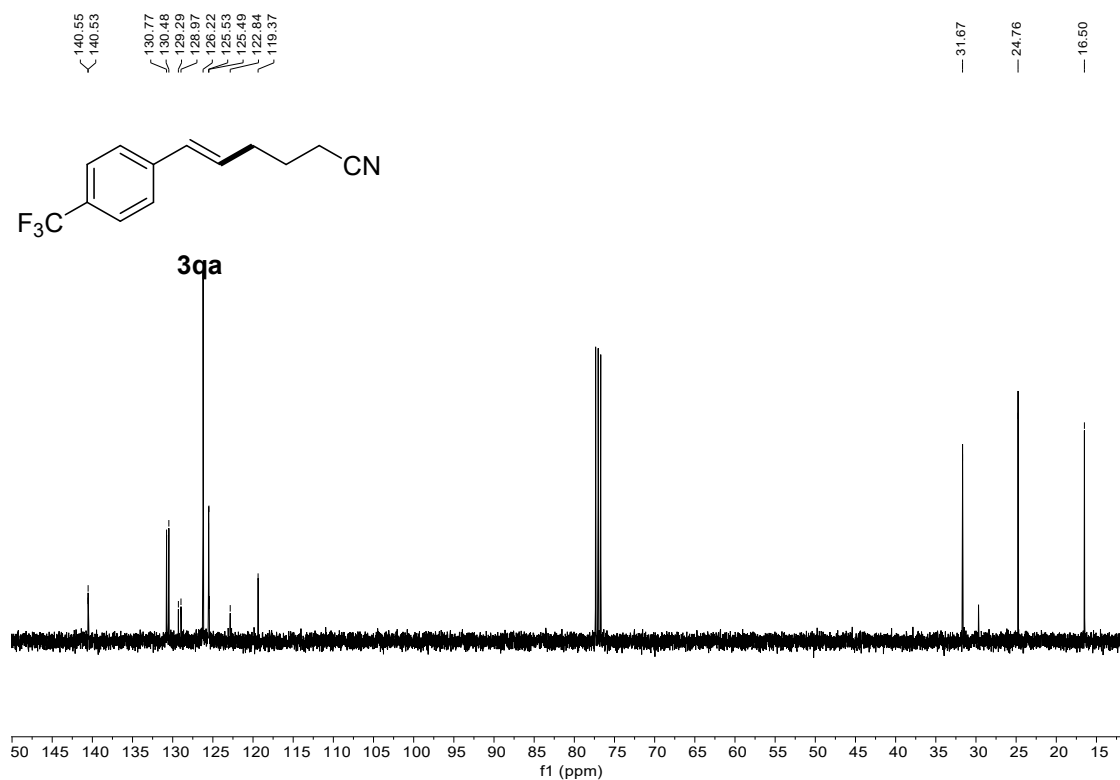
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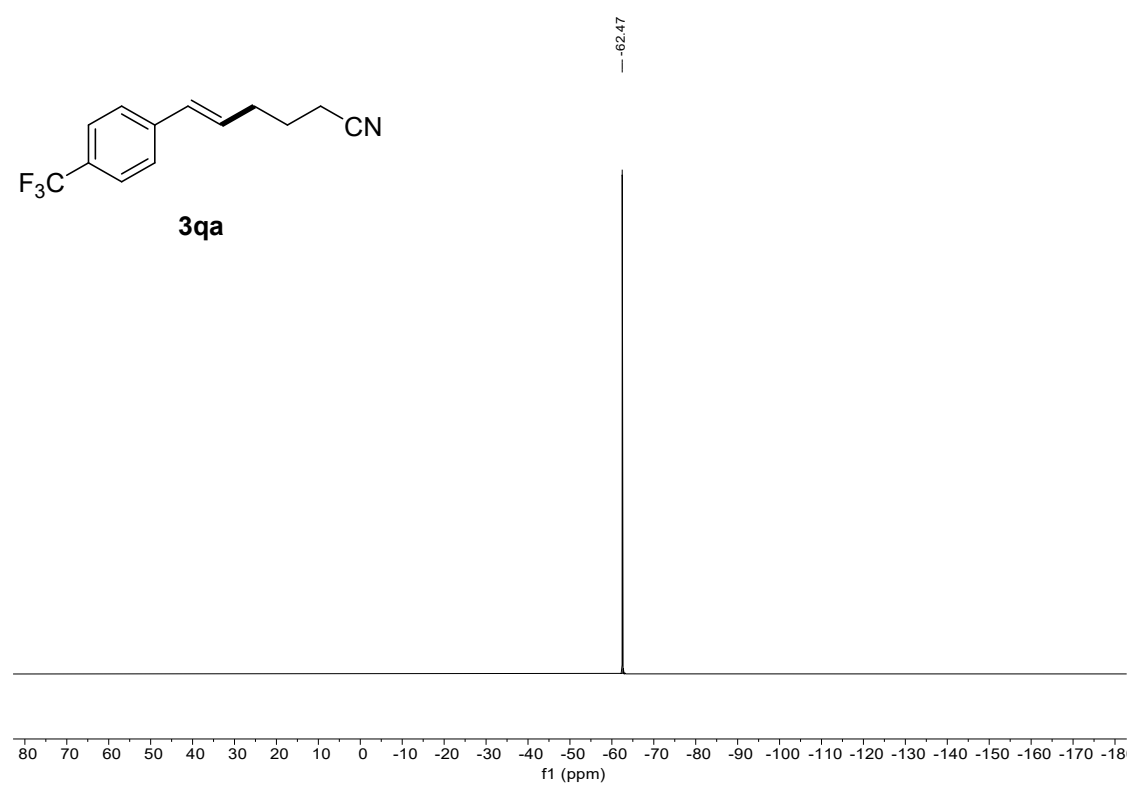
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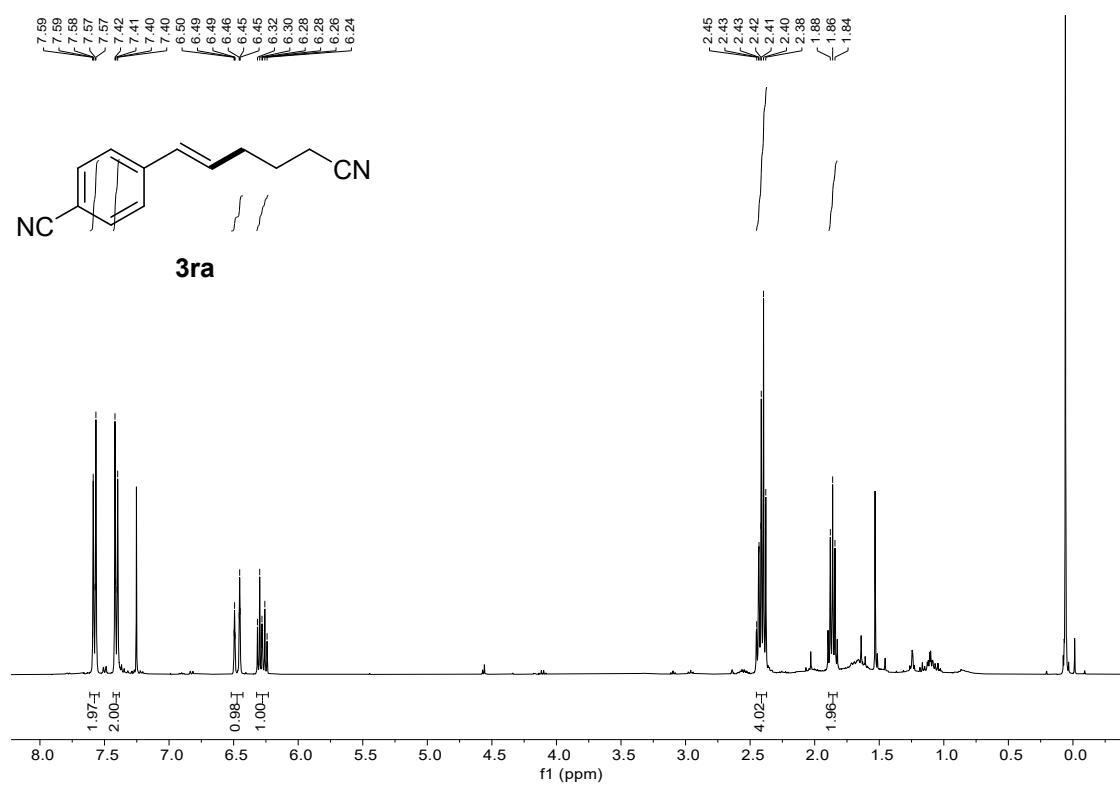
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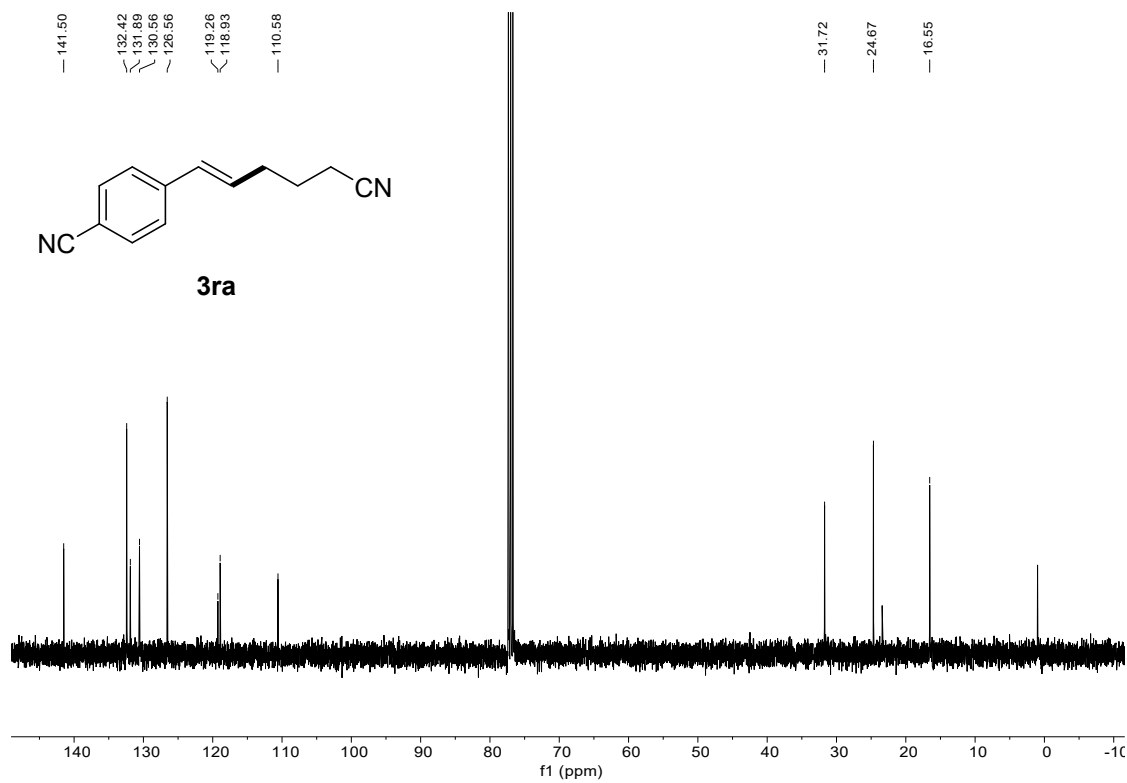
¹⁹F NMR spectra of compound **3qa**



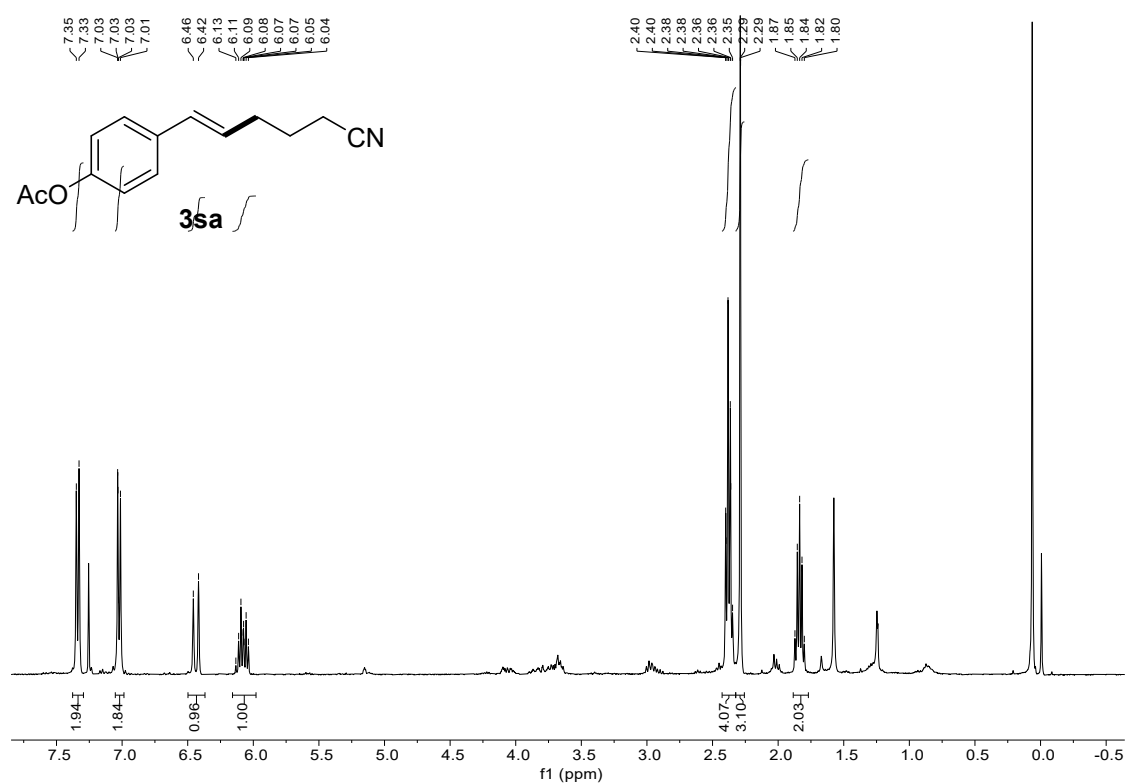
^1H NMR spectra of compound **3ra**



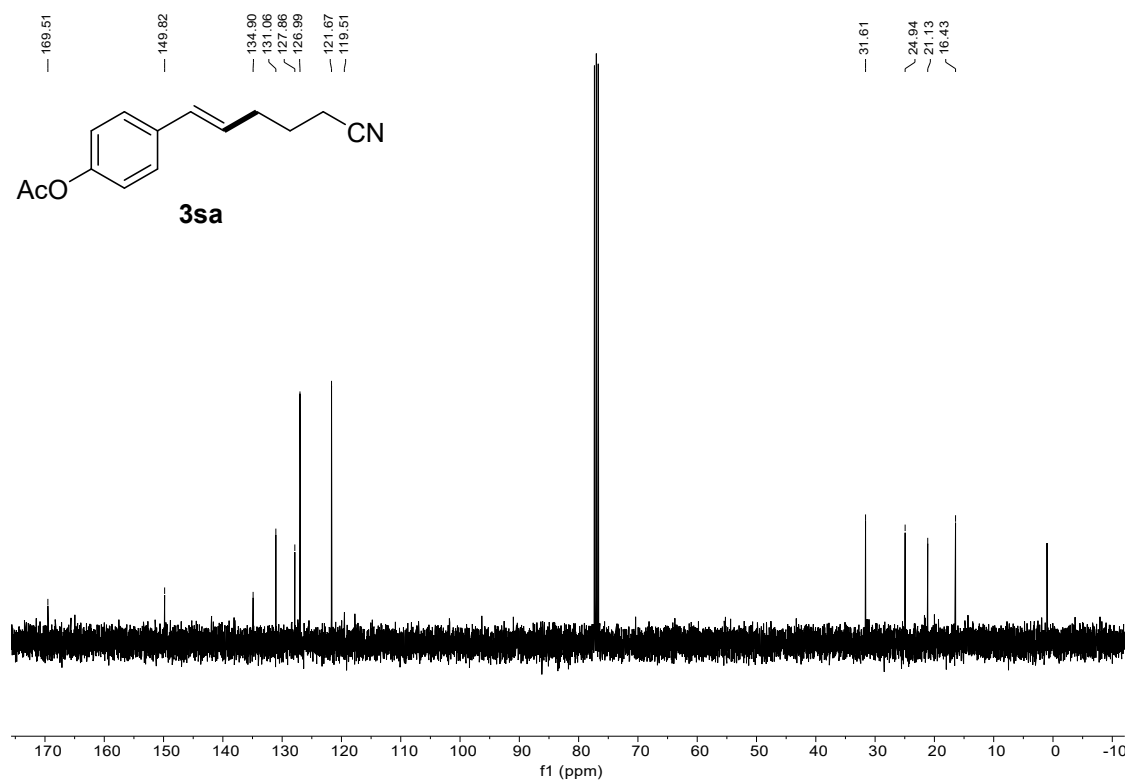
^{13}C NMR spectra of compound **3ra**



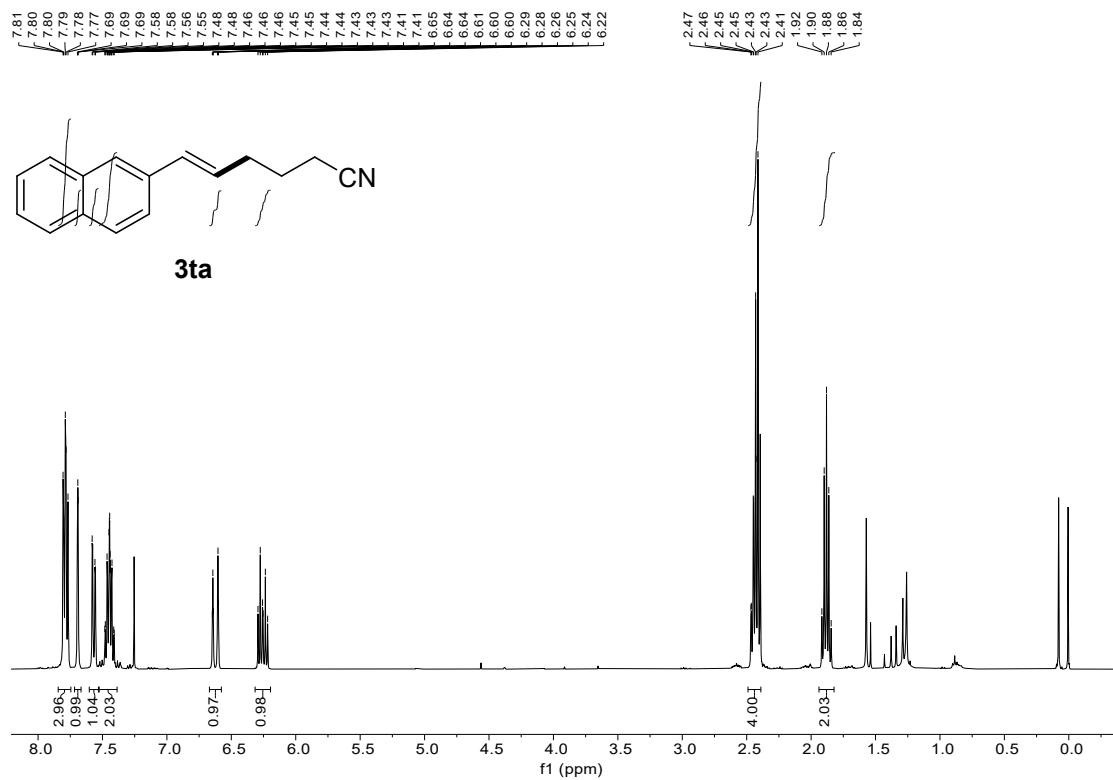
¹H NMR spectra of compound **3sa**



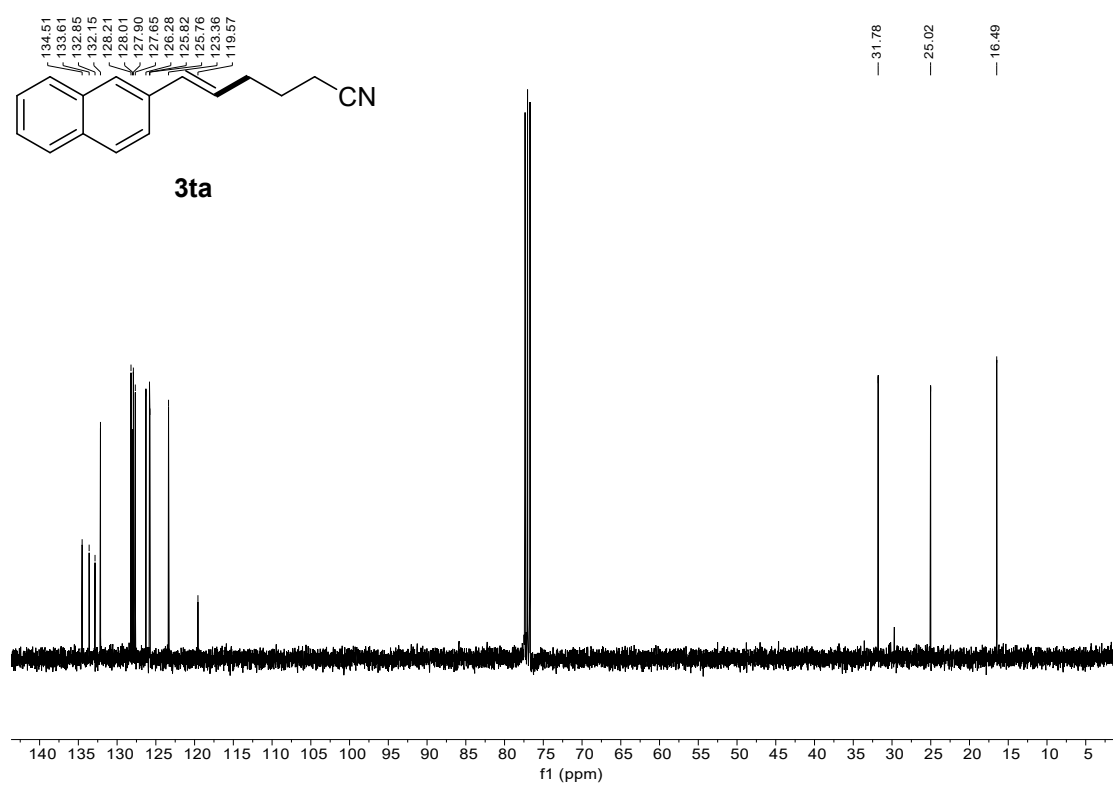
¹³C NMR spectra of compound **3sa**



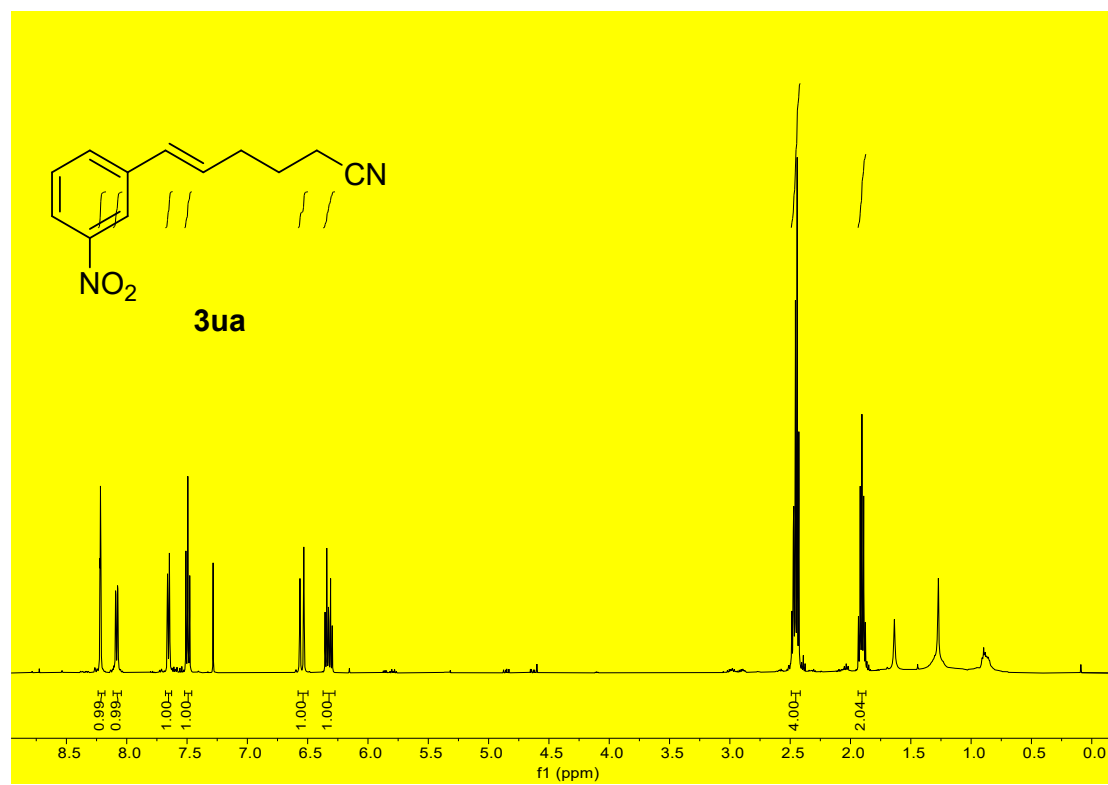
¹H NMR spectra of compound **3ta**



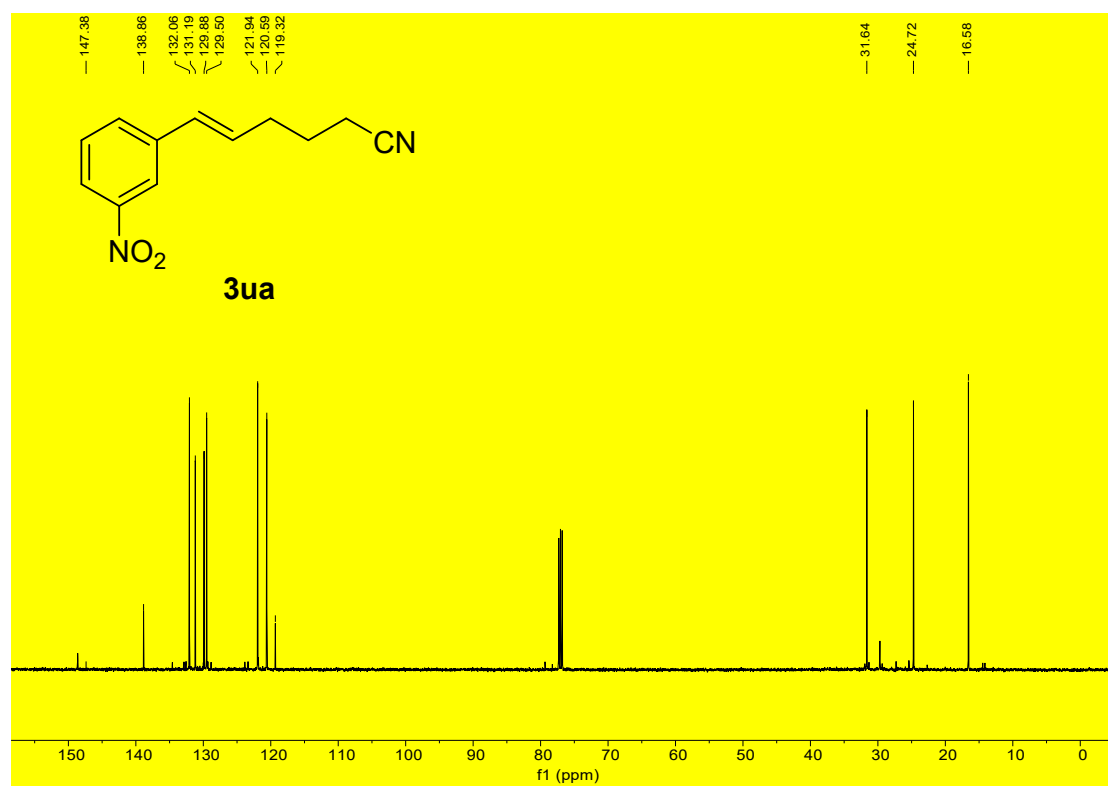
¹³C NMR spectra of compound **3ta**



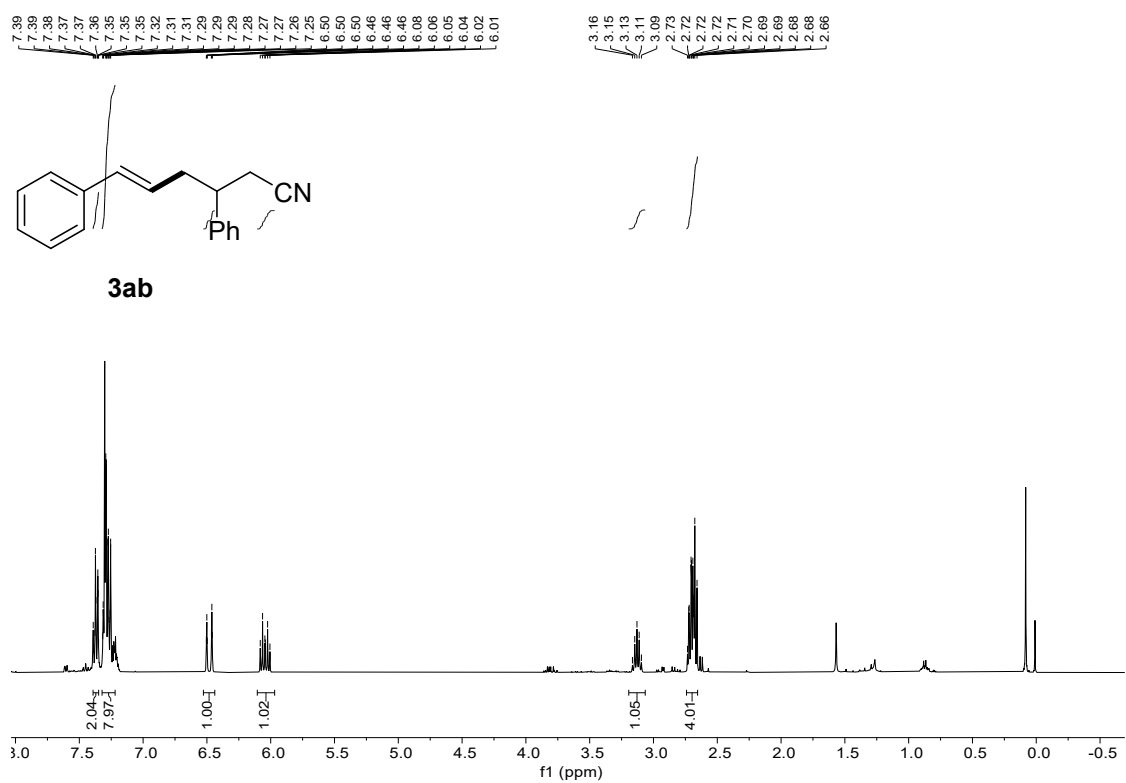
¹H NMR spectra of compound **3ua**



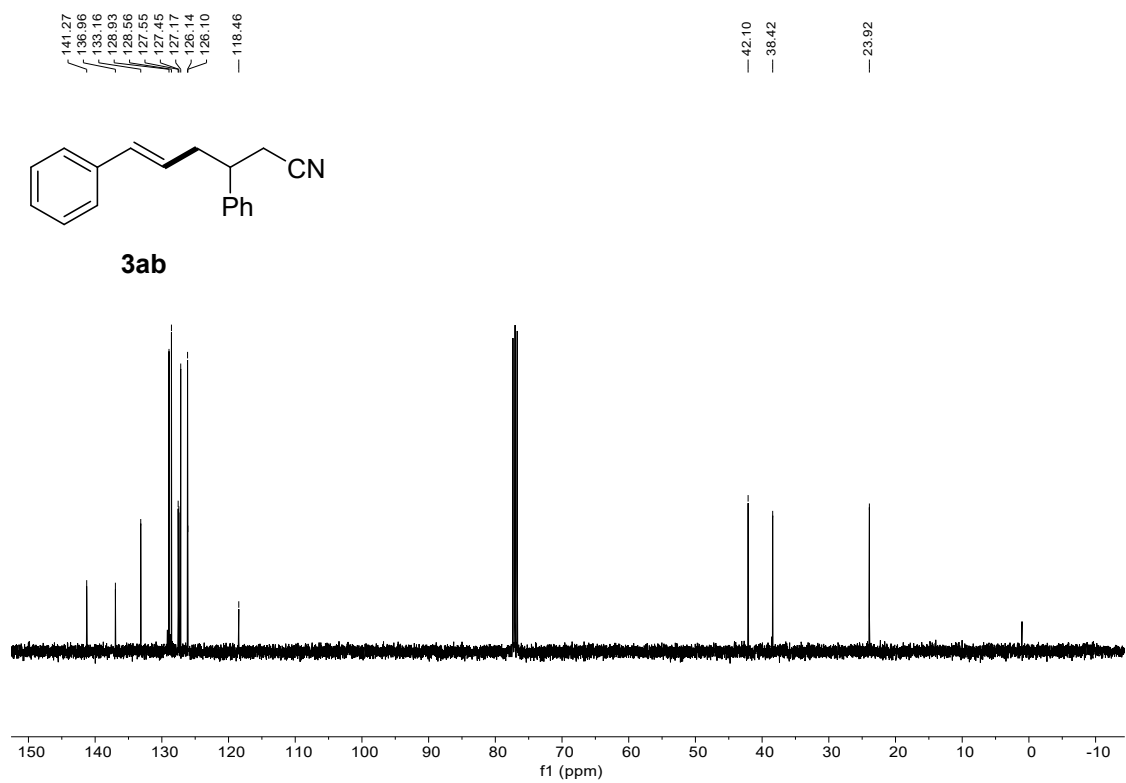
¹³C NMR spectra of compound **3ua**



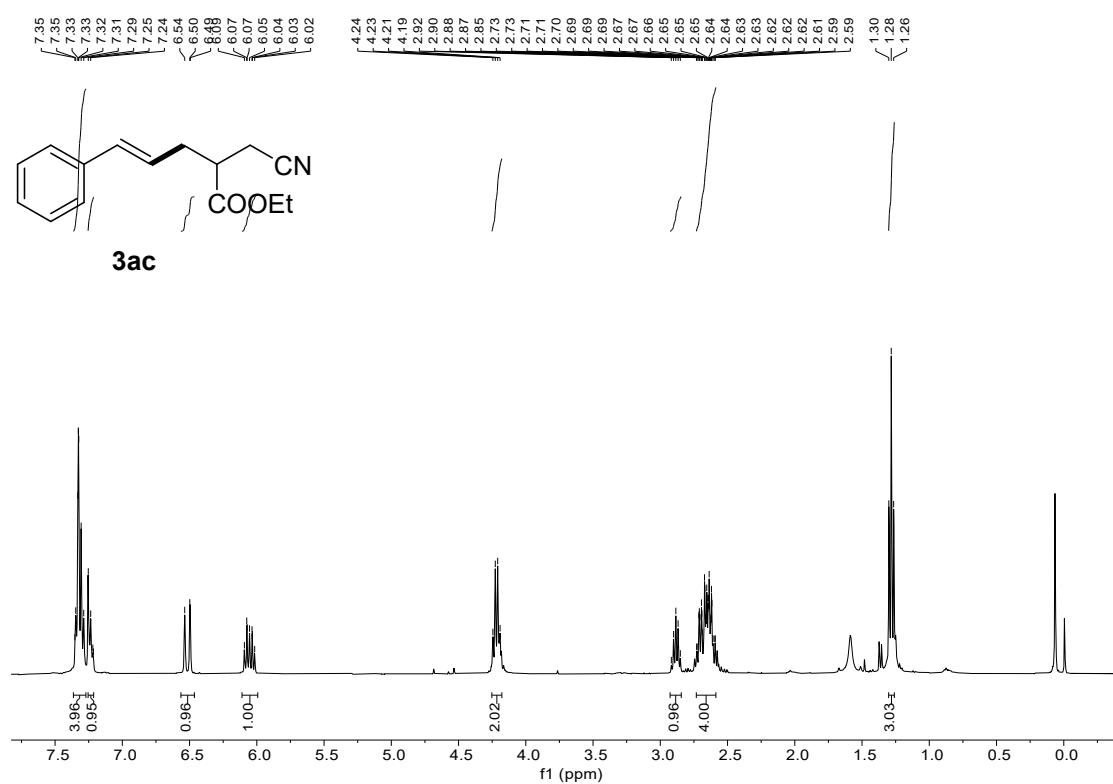
¹H NMR spectra of compound **3ab**



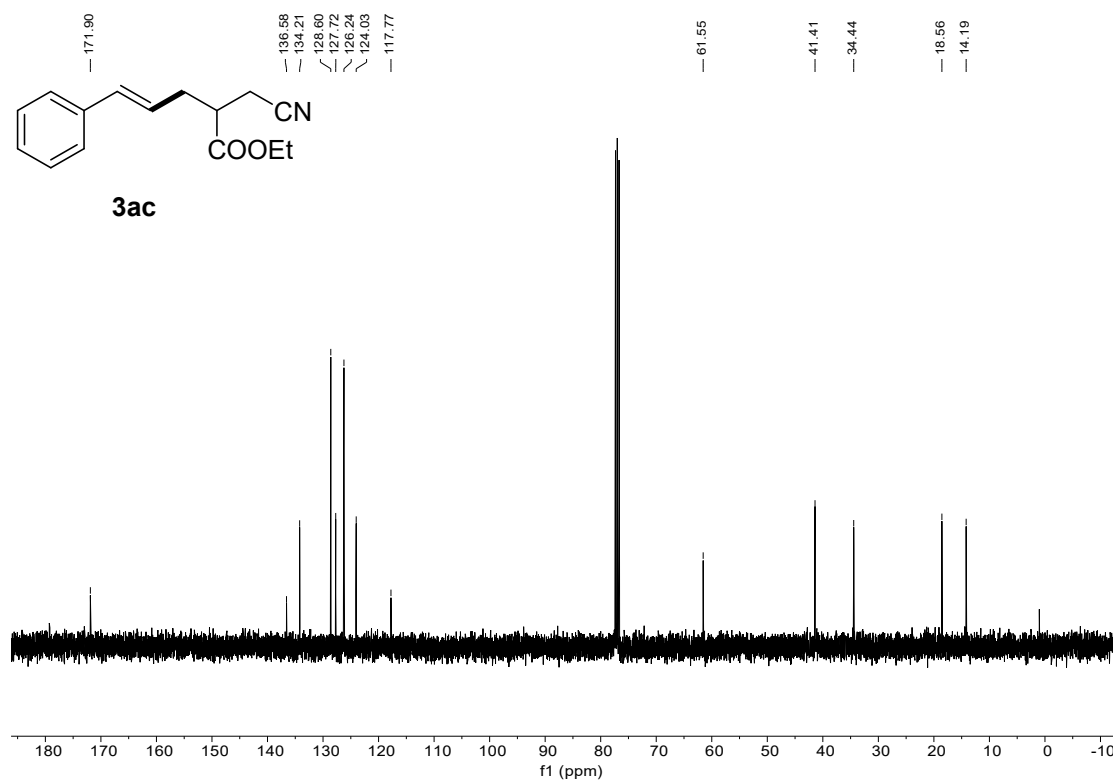
¹³C NMR spectra of compound **3ab**



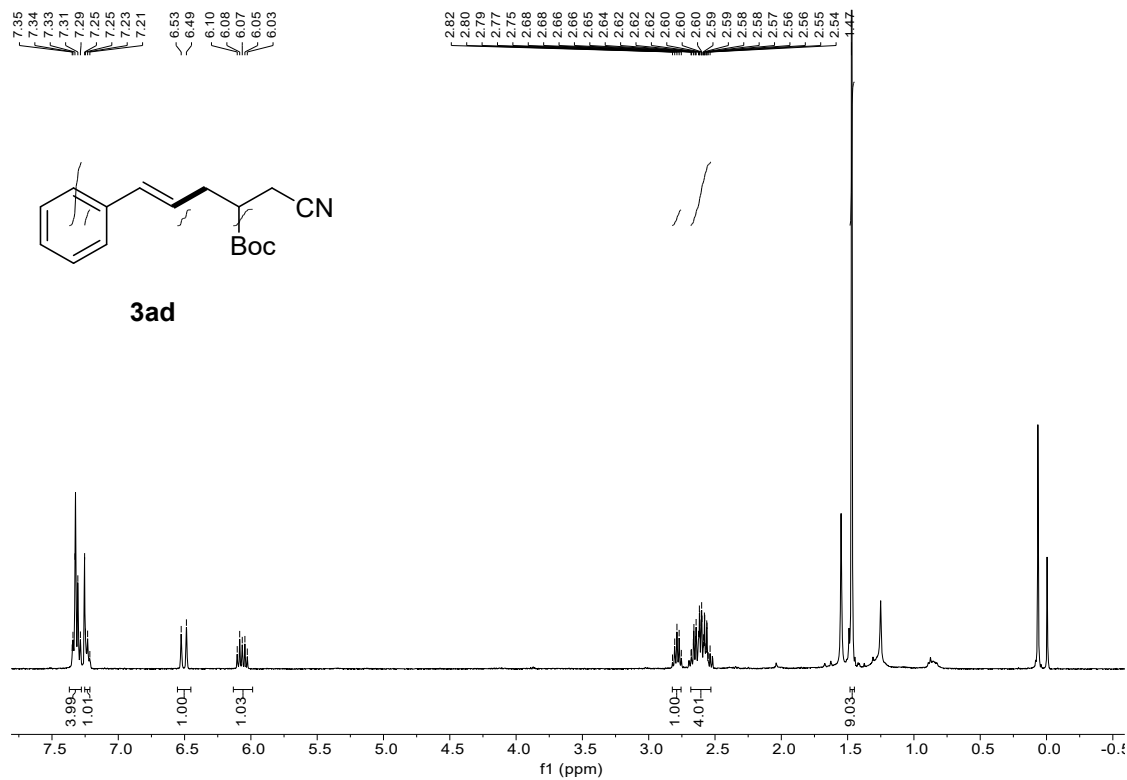
¹H NMR spectra of compound **3ac**



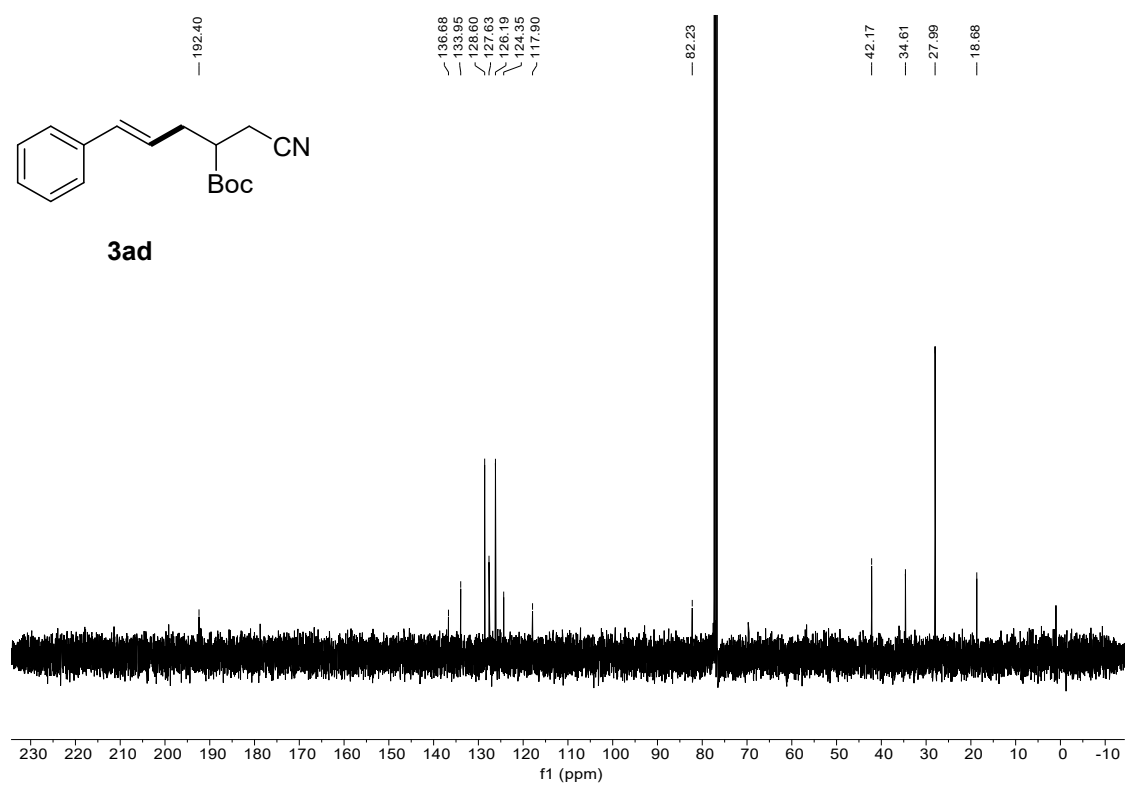
¹³C NMR spectra of compound **3ac**



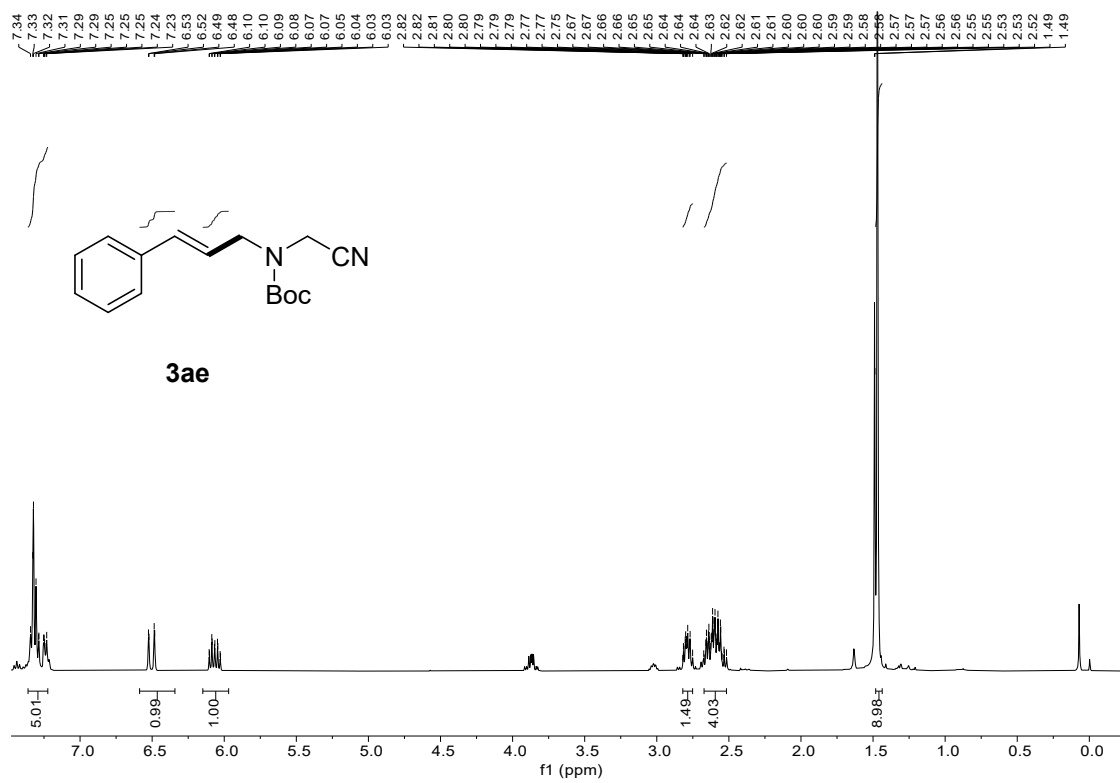
¹H NMR spectra of compound **3ad**



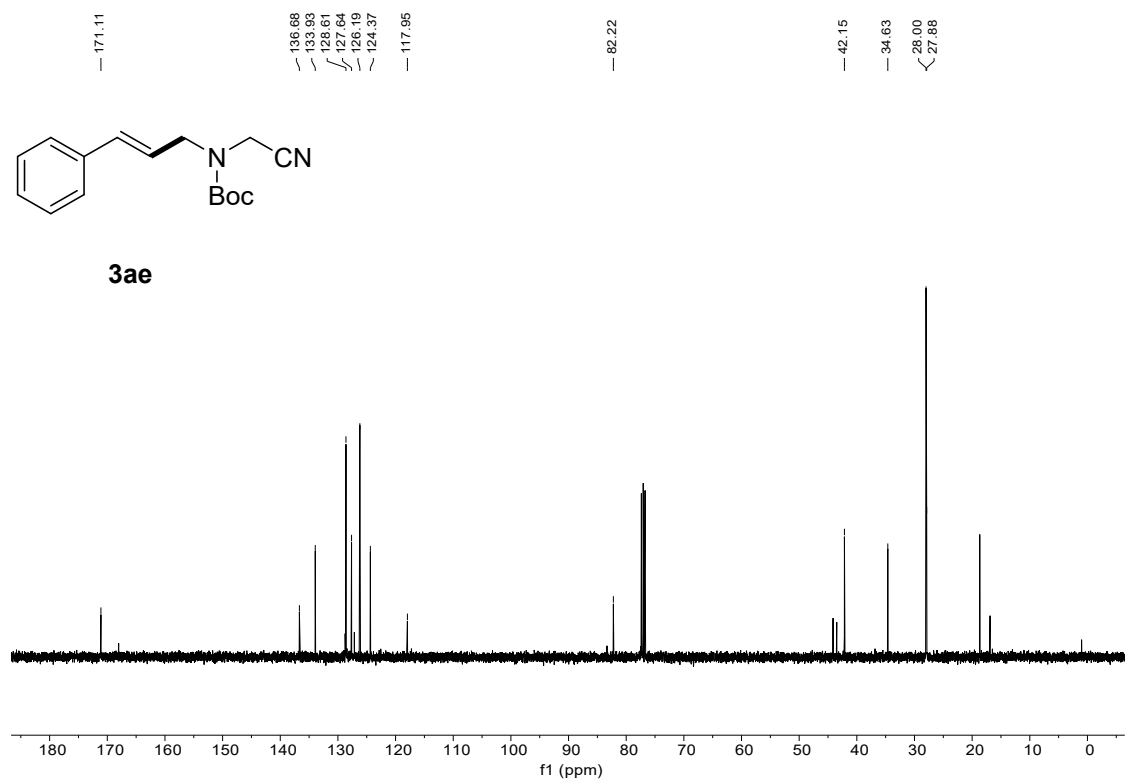
¹³C NMR spectra of compound **3ad**



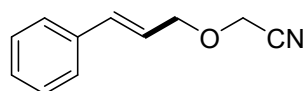
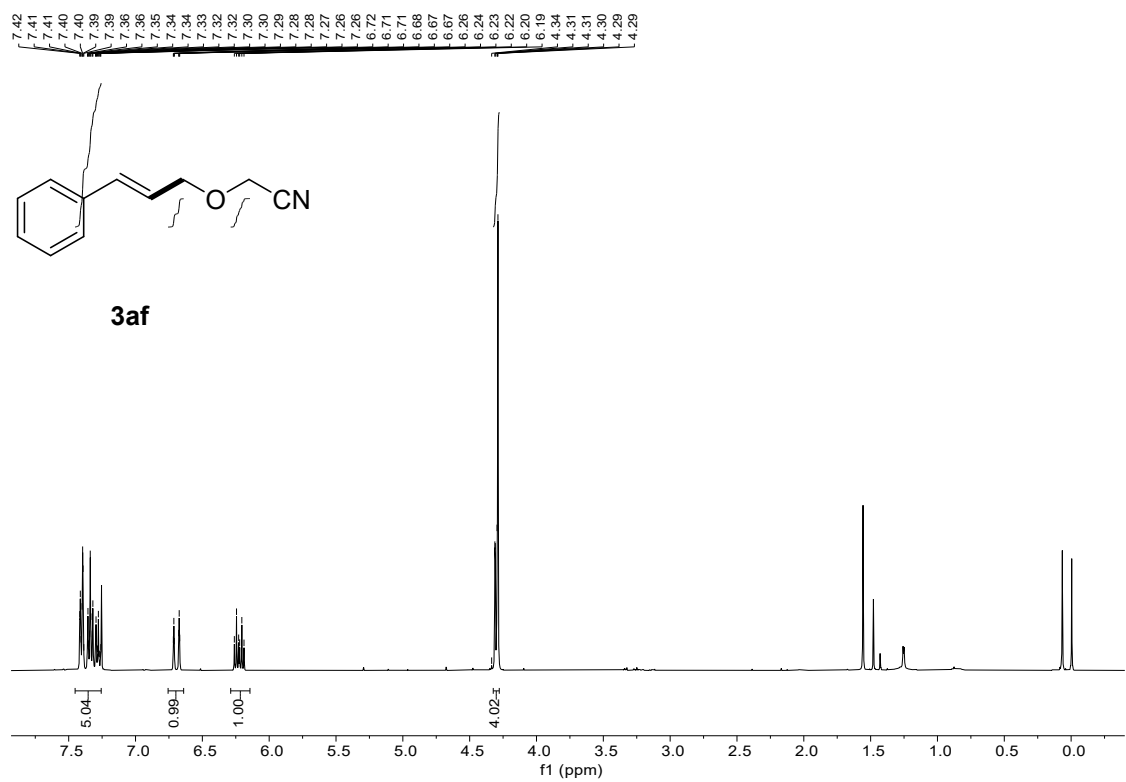
¹H NMR spectra of compound **3ae**



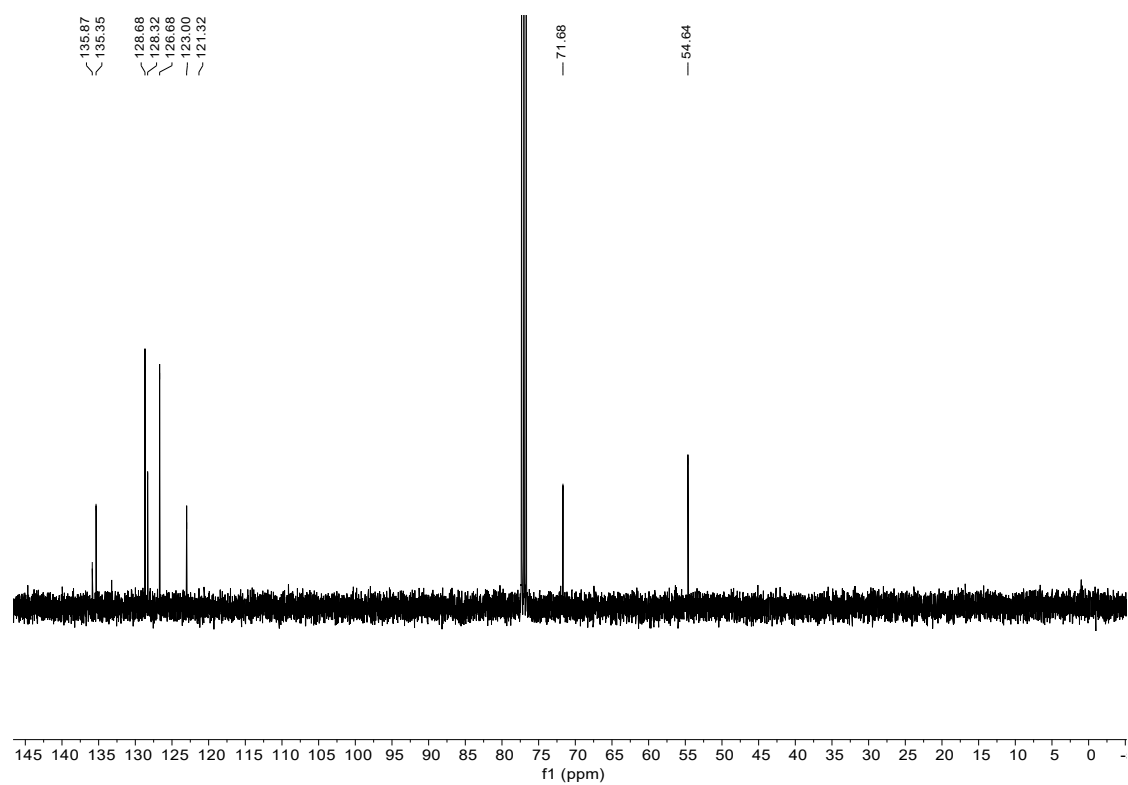
¹³C NMR spectra of compound **3ae**



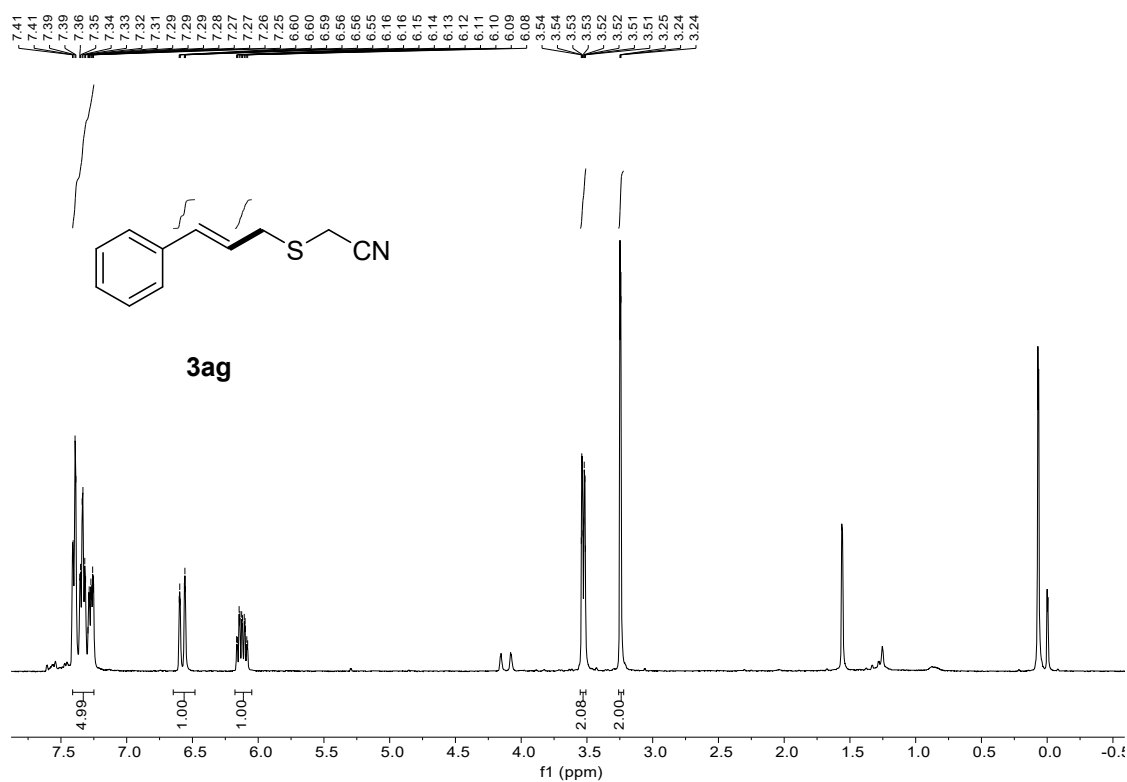
¹H NMR spectra of compound **3af**



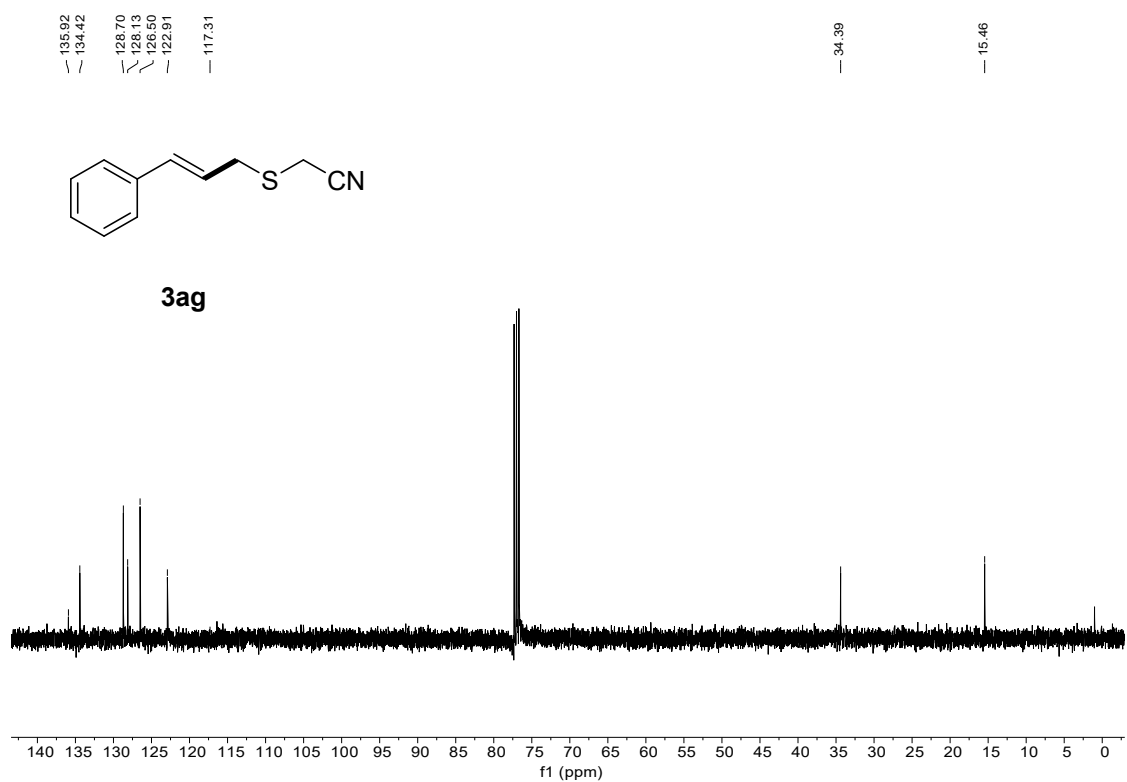
^{13}C NMR spectra of compound **3af**



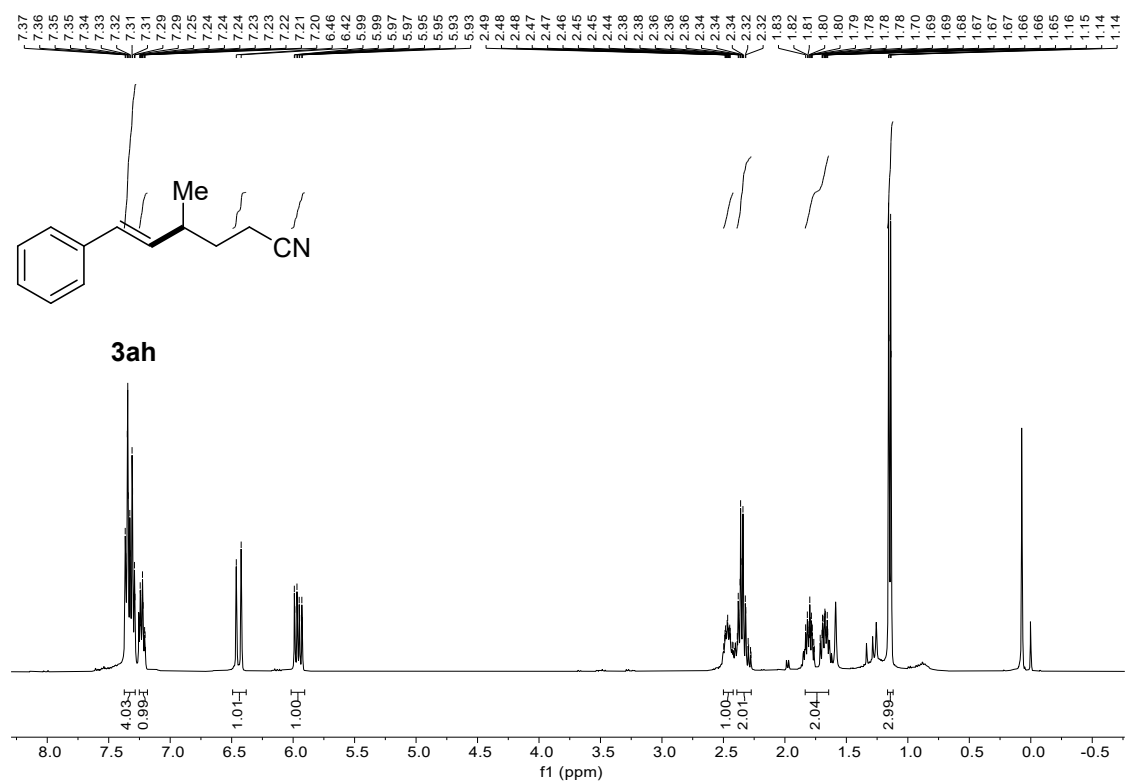
^1H NMR spectra of compound **3ag**



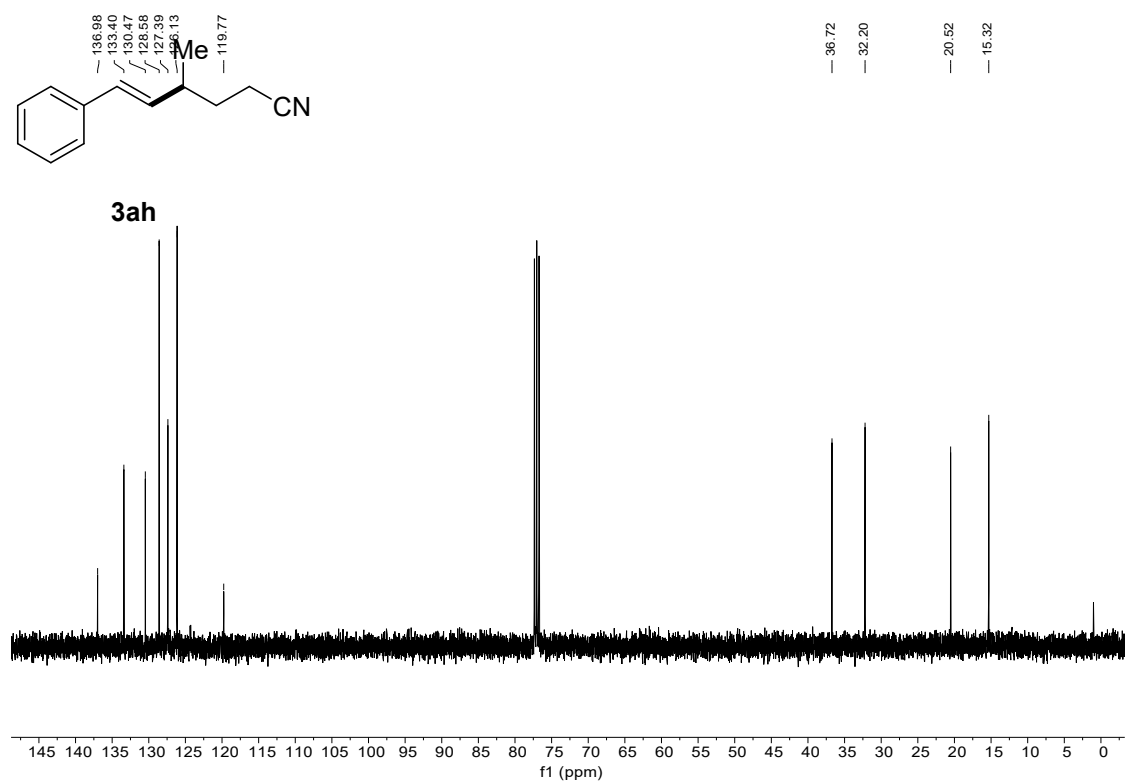
¹³C NMR spectra of compound **3ag**



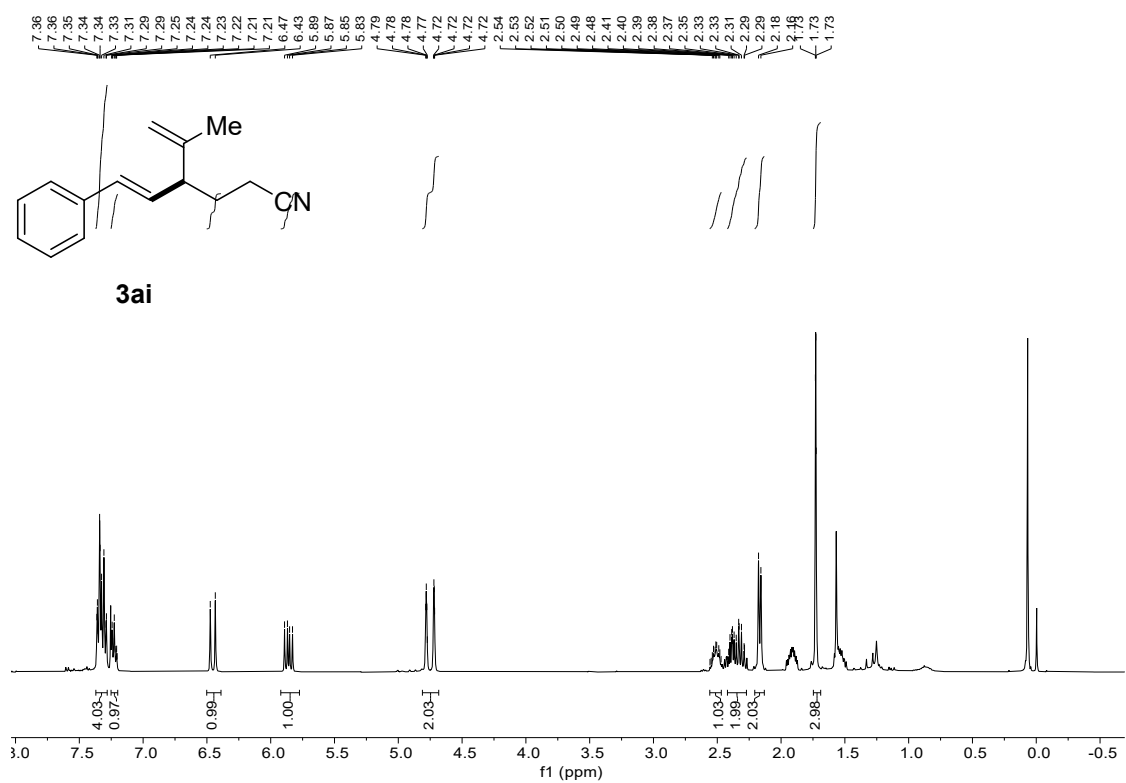
¹H NMR spectra of compound **3ah**



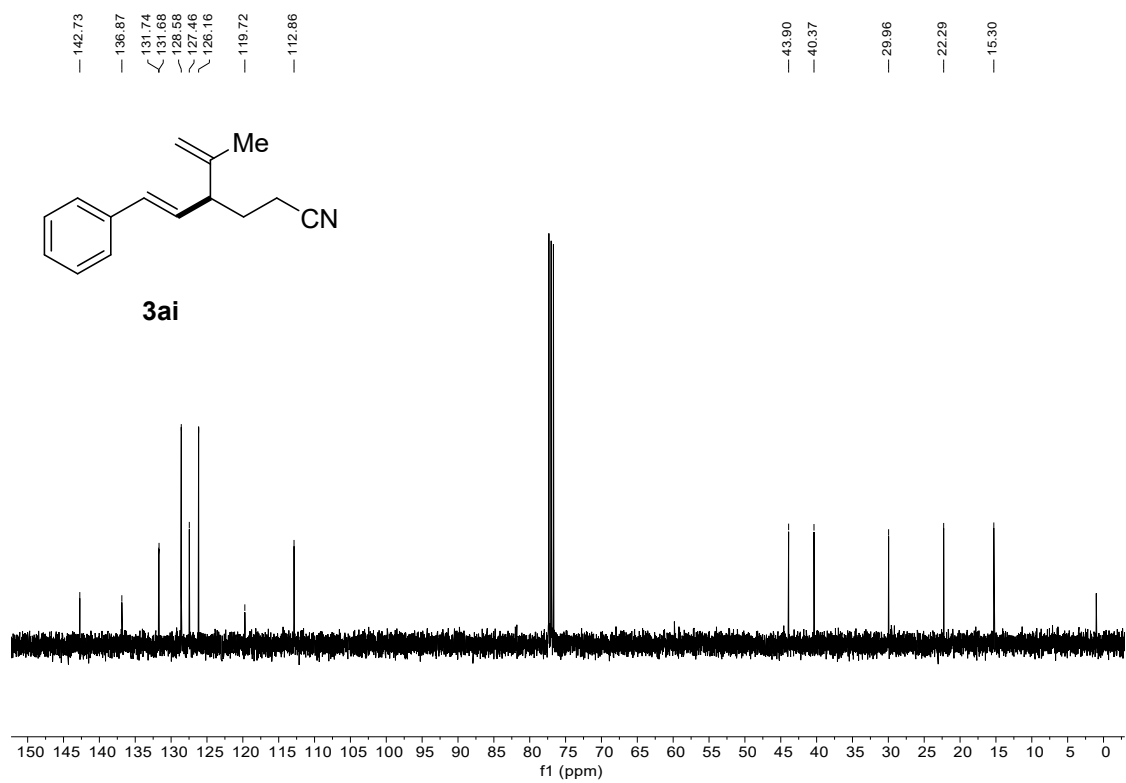
¹³C NMR spectra of compound 3ah



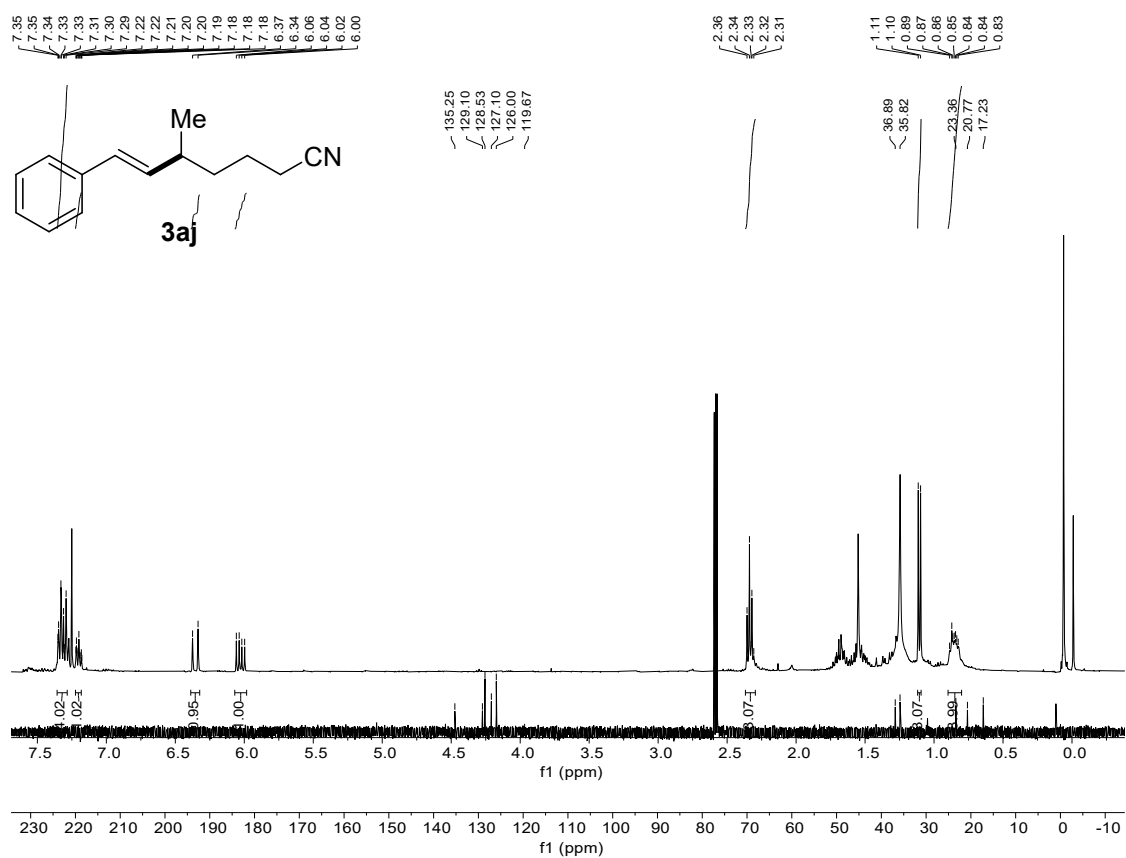
¹H NMR spectra of compound **3ai**



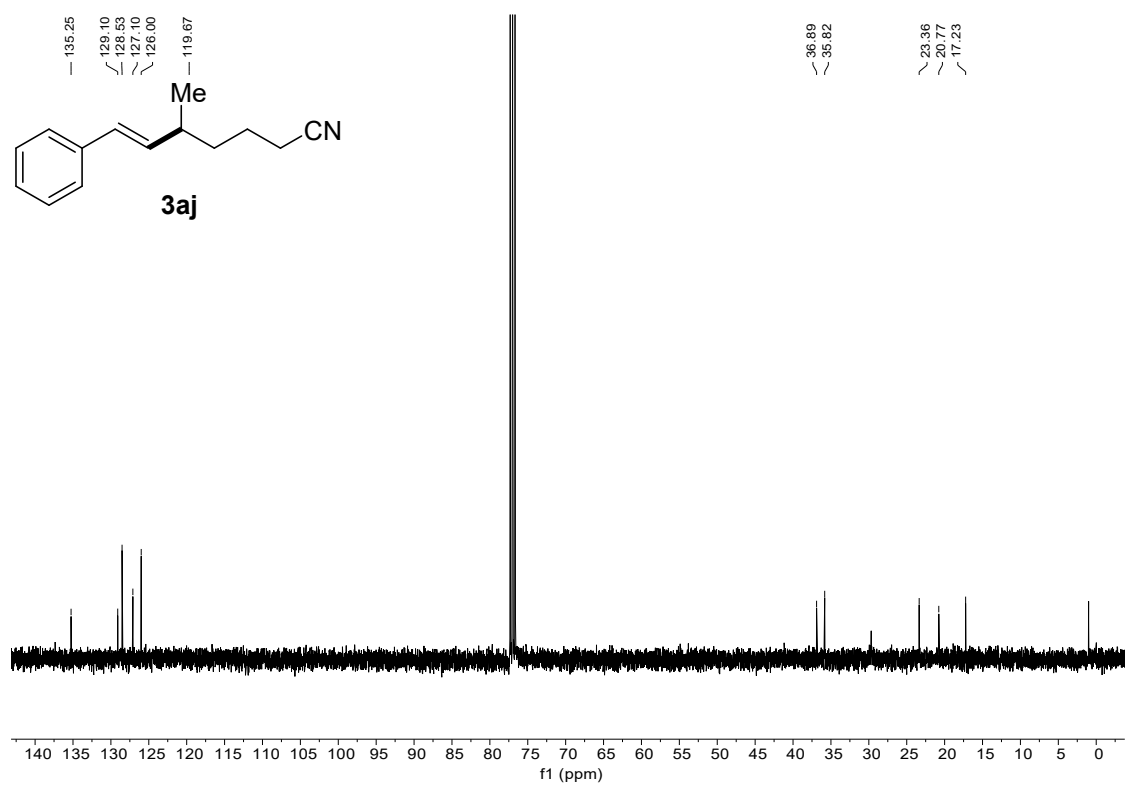
¹³C NMR spectra of compound **3ai**



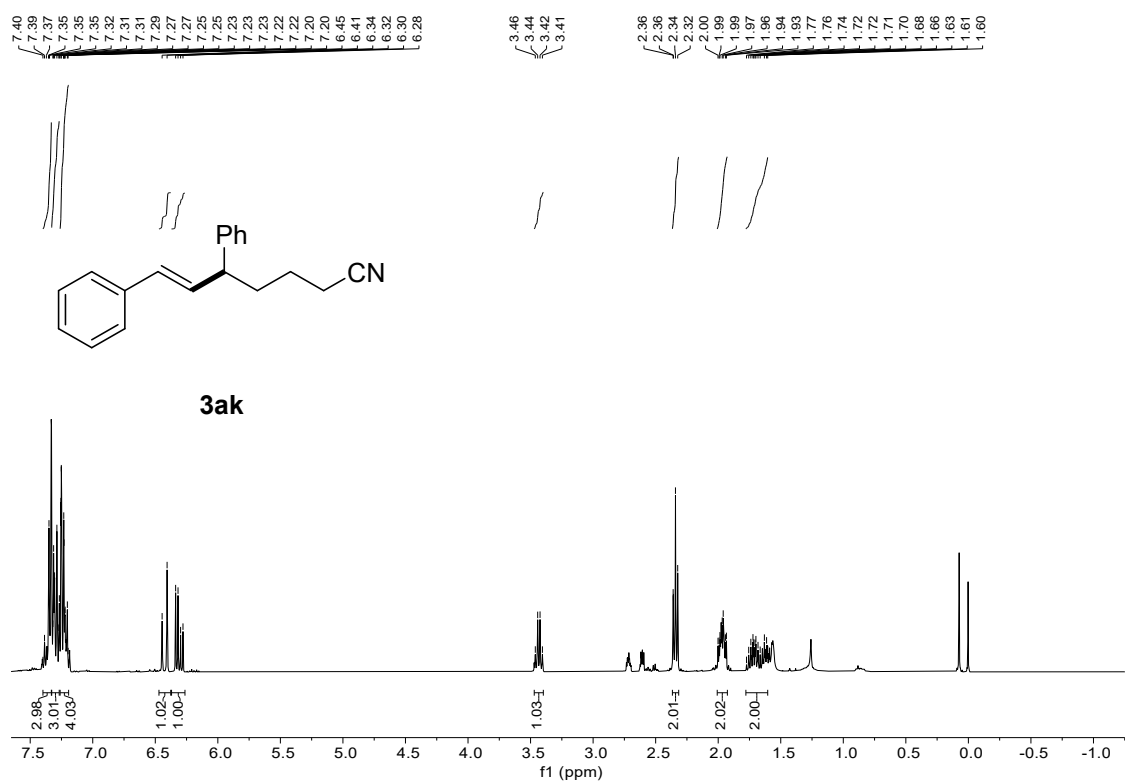
¹H NMR spectra of compound **3aj**



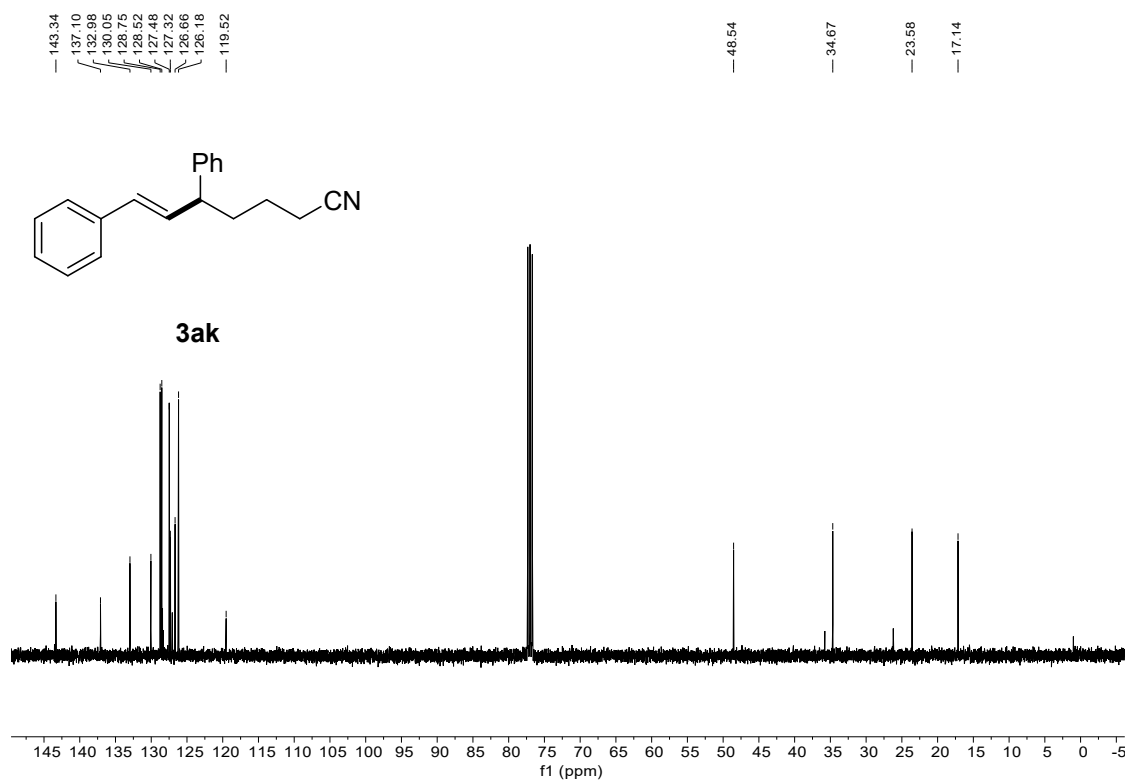
¹³C NMR spectra of compound **3aj**



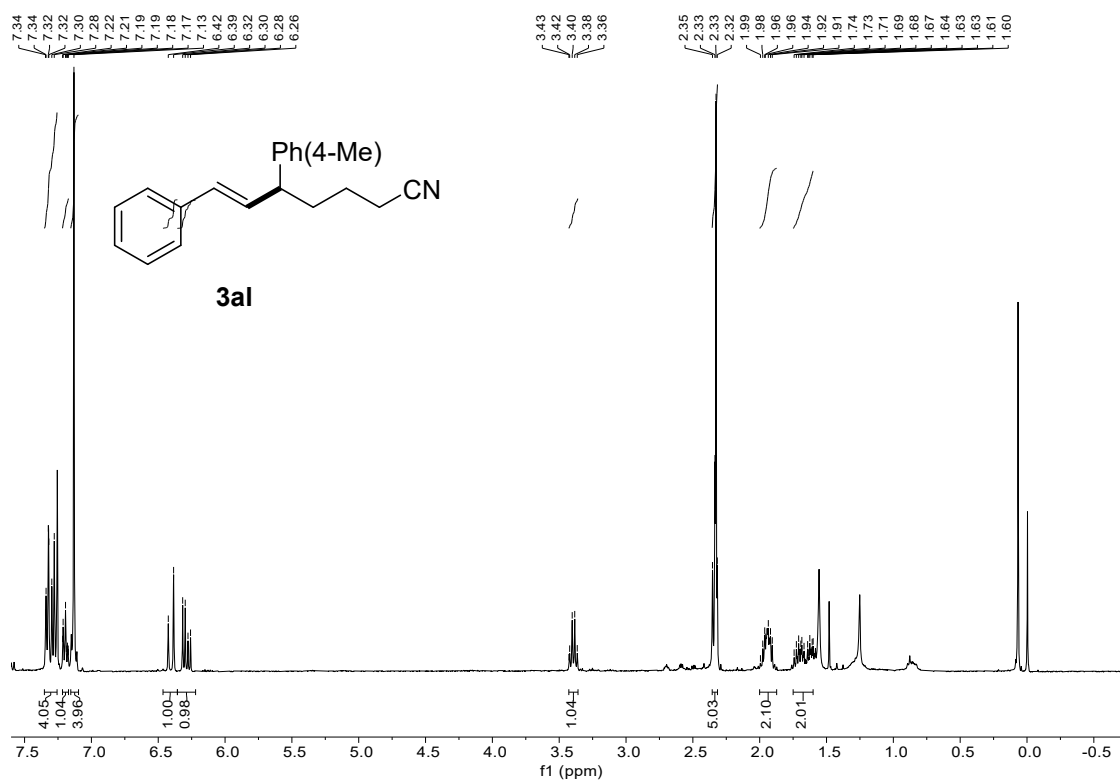
¹H NMR spectra of compound **3ak**



¹³C NMR spectra of compound **3ak**



¹H NMR spectra of compound **3al**



¹³C NMR spectra of compound **3al**

