# Supporting Information

## Synthesis of trisubstituted olefin by Ni-Catalyzed hydroalkylation of internal alkynes with cycloketone oxime esters

## Table of Contents

# I. General Information

## (a). Materials

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity ≥99.999%). The following chemicals were purchased and used as received: $NiBr_2$.diglyme (Aldrich, CAS: 312696-09-6), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbpy, CAS: 72914-19-3, Energy-Chemical), DMAc (Hengyue Chemical Technology Co., Ltd., 4 Å molecular sieves). N-methylpyrrolidin-2-one (Hengyue Chemical Technology Co., Ltd., 4 Å molecular sieves). Diethoxymethyl-silan (CAS: 2031-62-1, DEMS, Adamas), Polymethylhydrosiloxane (CAS: 9004-73-3, Adamas), $(EtO)_3SiH$ (CAS: 998-30-1, Adamas), $(Me_2SiH)_2O$ (CAS: 3277-26-7, Adamas).

All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

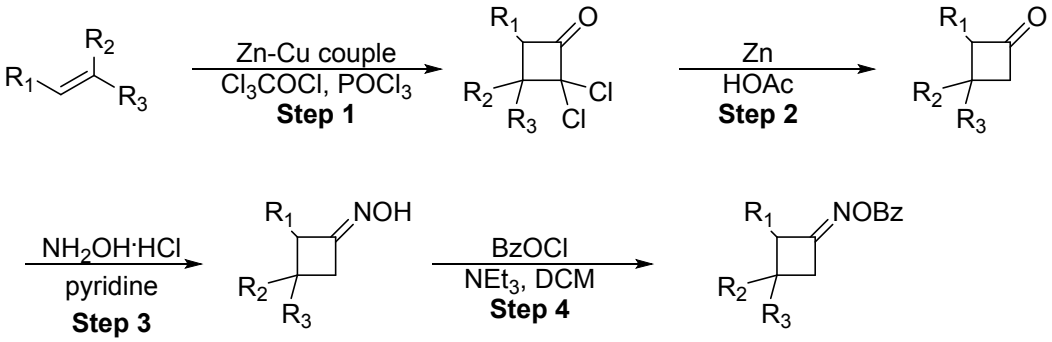
## (b). Analytical Methods

$^1$H-NMR, $^{13}$C-NMR and $^{19}$F-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted; Data for $^1$H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for $^{13}$C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. Chiralpak IC, AD, AS, KM columns were purchased from Daicel Chemical Industries, LTD. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

# II. Preparation of Substrates

## (a).Synthesis of Cycloketone oxime esters

### Method 1:




**Step 1:** To a 50 mL three-necked flask under argon were added alkene derivative (5.0 mmol, 1.0 equiv), zinc-copper couple (960 mg, 15.0 mmol, 3.0 equiv), and anhydrous ether (10 mL). To the mixture was added a solution of trichloroacetyl chloride (1.12 mL, 10.0 mmol, 2.0 equiv) and phosphorus oxychloride (0.51 mL, 5.5 mmol, 1.1 equiv) in ether (10 mL) over 1 h through an addition funnel. The suspension was stirred overnight at reflux. The resulting mixture was filtered through a pad of Celite and was washed with ether (20 mL). The organic solution was successively washed with water (30 mL), a saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (30 mL), and dried over $MgSO_4$. Then the solution was filtered, concentrated and used in the next step without further purification.[1]

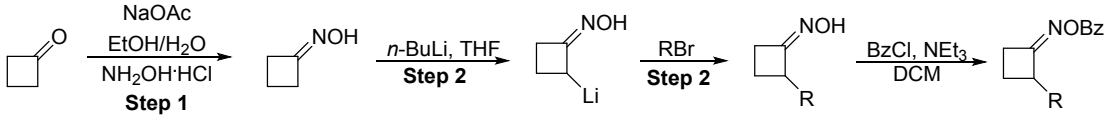
**Step 2:** A mixture of 2,2-dichlorocyclobutanones (1.0 equiv) and zinc dust (4.0 equiv) in acetic acid (10 mL) was stirred at room temperature for 2 h and then heated at 80 °C for 5 h. The resulting mixture was allowed to cool to room temperature, followed by diluting with water (30 mL) and extracted with ether. The organic phase was washed successively with a saturated solution of aqueous $NaHCO_3$, water (30 mL) and brine (30 mL), then dried over $MgSO_4$ and concentrated in vacuum. The residue was then purified by flash chromatography with a mixture of petroleum ether and ethyl acetate to afford various cyclobutanones.

**Step 3:** To a stirred solution of cyclobutanones (1.0 equiv) in pyridine (0.5 M) was added hydroxylamine hydrochloride (2.0 equiv) at room temperature. After stirring for 2 h, pyridine was removed under reduced pressure. The residue was diluted with water and extracted with EtOAc.

The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure to give the crude material, which were used in the next step without further purification.[1]

**Step 4:** To a mixture of cyclobutanone oxime (1.0 equiv), triethylamine (2.0 equiv) and DCM (0.5 M) in a 30mL two-necked flask was added benzoyl chloride (1.5 equiv) at 0 °C. After 6 h, water was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was subjected to column chromatography with EtOAc-PE as an eluent to give cyclobutanone oxime esters.[1]

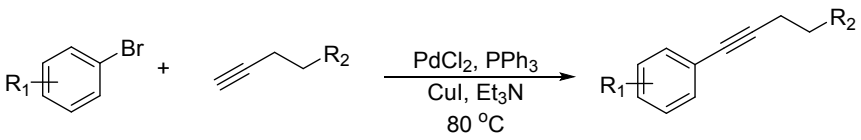
## Method 2:




**Step1**: To a mixture of hydroxylamine hydrochloride (18.0 mmol), sodium acetate (22.5 mmol), ethanol (10.5 mL) and water (4.5 mL) in a 30 mL two-necked flask was added cyclobutanone (15 mmol) and the mixture was stirred at 100 °C for 12 h. The reaction mixture was cooled to room temperature and then ethanol was removed under reduced pressure and the resulting mixture was extracted with diethyl ether. The organic layer was washed with water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was subjected to column chromatography to give cyclobutanone oxime as a white solid.[1]

**Step2**: Cyclobutanone oxime (1.0 equiv) in absolute THF (0.5 M) was added n-BuLi (2.0 equiv) slowly at 0 °C, and the resulting mixture was stirred for another 15 min at this temperature for the formation of syn dianion. RBr (1.0 equiv) was added dropwise at 0 °C and the mixture was warmed to r.t. for 2 h. Subsequently, the reaction was quenched by cold water, and the mixture was diluted with EA. The organic layer was washed with water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was subjected to column chromatography with EtOAc-PE as an eluent to give a-substituted oximes in quantitative yield.[1]

## (b).Synthesis of alkynes




A $Et_3N$ solution (30 mL) of Ar-Br (10.0 mmol), alkynes (12 mmol), palladium chloride (0.20 mmol), copper (I) iodide (0.30 mmol), and triphenylphosphine (0.4 mmol) was stirred at 80 $^oC$ temperature for 24 h, saturated, aqueous $NH_4Cl$ was added, the phases were separated and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried ($Na_2SO_4$), concentrated, and then the crude reaction mixture was purified by silica gel column chromatography to afford the product.[2]

**References**

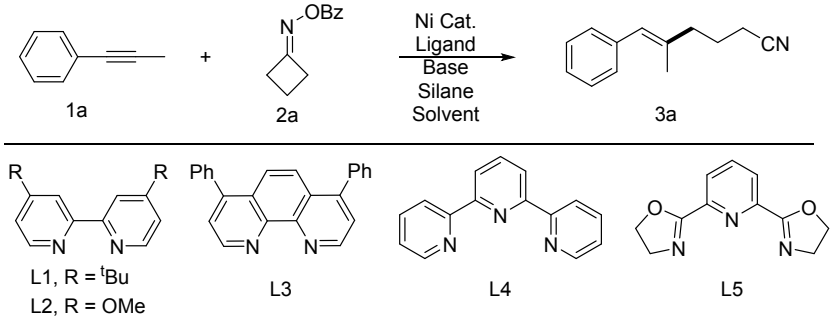
[1] (a) M.-M. Zhang, S.-H. Li, J.-L. Tu, Q.-Q. Min and F. Liu, *Org. Chem. Front.*, **2020**, 7, 622; (b) J. Lou, Y. He, Y. Li and Z. Yu, *Adv. Synth. Catal.*, **2019**, 361, 3787.

[2] X. Yang, D. Nath and F. F. Fleming, *Org. Lett*., **2015**, 17, 4906.

# III. General Experimental Procedures

## Experimental Procedures for Examples Described in Table 1.

In air, Catalyst (8 mol%), Ligand (10 mol%), Cycloketone oxime esters (0.25 mmol), base (2.5 equiv) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent (0.8 mL), 1-Phenylpropyne (2.5 equiv) and silane (3.0 equiv) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at the mentioned temperature for the indicated amount of time. Biphenyl was added as internal standard. The product was yielded by GC.




| Entry | Cat. | Lig. | Silane | Base | Solvent | Temperature | Yield % |
|---|---|---|---|---|---|---|---|
| 1 | $NiBr_2$·diglyme | L1 | DEMS | $K_2CO_3$ | DMAc | r.t. | 40 |
| 2 | $NiBr_2$·diglyme | L1 | DEMS | $Na_2CO_3$ | DMAc | r.t | 12 |
| 3 | $NiBr_2$·diglyme | L1 | DEMS | NaOAc | DMAc | r.t | 16 |
| 4 | $NiBr_2$·diglyme | L1 | DEMS | $K_3PO_4$ | DMAc | r.t | 45 |
| 5 | $NiBr_2$·diglyme | L1 | DEMS | $C_SF$ | DMAc | r.t | 17 |
| 6 | $NiBr_2$·diglyme | L1 | DEMS | $Ga(OAc)_2$ | DMAc | r.t | 6 |
| 7 | $NiBr_2$·diglyme | L1 | DEMS | $Mg(OAc)_2$ | DMAc | r.t | 13 |
| 8 | $NiBr_2$·diglyme | L1 | DEMS | KF | DMAc | r.t | 28 |
| 9 | $NiBr_2$·diglyme | L1 | PMHS | $K_2CO_3$ | DMAc | r.t. | 21 |
| 10 | $NiBr_2$·diglyme | L1 | $(EtO)_3SiH$ | $K_2CO_3$ | DMAc | r.t. | 5 |
| 11 | **$NiBr_2$·diglyme** | **L1** | **$(Me_2SiH)_2O$** | **$K_2CO_3$** | **DMAc** | **r.t.** | **70** |
| 12 | $NiBr_2$·diglyme | L1 | $(Me_2SiH)_2O$ | $K_2CO_3$ | NMP | r.t. | 46 |
| 13 | $NiBr_2$·diglyme | L1 | $(Me_2SiH)_2O$ | $K_2CO_3$ | DMF | r.t. | 35 |
| 14 | $NiBr_2$·diglyme | L1 | $(Me_2SiH)_2O$ | $K_2CO_3$ | $CH_3CN$ | r.t. | 22 |
| 15 | $NiBr_2$·diglyme | L1 | $(Me_2SiH)_2O$ | $K_2CO_3$ | THF | r.t. | 15 |
| 16 | $NiBr_2$·diglyme | L1 | $(Me_2SiH)_2O$ | $K_2CO_3$ | Dio. | r.t. | 23 |
| 17 | $NiBr_2$·diglyme | L2 | $(Me_2SiH)_2O$ | $K_2CO_3$ | DMAc | r.t. | 43 |
| 18 | $NiBr_2$·diglyme | L3 | $(Me_2SiH)_2O$ | $K_2CO_3$ | DMAc | r.t. | 5 |
| 19 | $NiBr_2$·diglyme | L4 | $(Me_2SiH)_2O$ | $K_2CO_3$ | DMAc | r.t. | 3 |
| 20 | $NiBr_2$·diglyme | L5 | $(Me_2SiH)_2O$ | $K_2CO_3$ | DMAc | r.t. | trace |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 21 | $NiBr_2$·diglyme | L1 | $(Me_2SiH)_2O$ | $K_2CO_3$ | DMAc | 0°C | 20 |
| 22 | $NiBr_2$·diglyme | L1 | $(Me_2SiH)_2O$ | $K_2CO_3$ | DMAc | 40 °C | 78 |
| 23 | **$NiBr_2$·diglyme** | **L1** | **$(Me_2SiH)_2O$** | **$K_3PO_4$** | **DMAc** | **40°C** | **83** |
| 24 | $NiBr_2$·diglyme | L1 | $(Me_2SiH)_2O$ | $K_3PO_4$ | DMAc | 50°C | 67 |
| 25[b] | - | L1 | $(Me_2SiH)_2O$ | $K_3PO_4$ | DMAc | 40°C | 0 |

[a] **Reaction conditions:** 1a (2.5 equiv), 2a (0.25 mmol), catalyst (8 mol%), Base (2.5 equiv), ligand (10 mol%), and Silane (3.0 equiv) in 0.8 mL for 12 h under Ar atmosphere. [b] **Reaction conditions:** no catalyst. The yield was determined by GC (average of two GC runs). PMHS = Poly(methylhydrosiloxane), DEMS = diethoxymethyl-silan (CAS: 2031-62-1), PMHS = Polymethylhydrosiloxane (CAS: 9004-73-3), Dio. = dioxane.

## General procedure：Experimental Procedures for Examples Described in Table 2

In air, $NiBr_2$·diglyme (8 mol%), L1 (10 mol%), $K_3PO_4$ (2.5 equiv), and Cycloketone oxime esters (0.25 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). To these solids, DMAc (0.8 mL), alkynes and $(Me_2SiH)_2O$ (3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 40 °C for 12 h. The mixture was purified by column chromatography to afford the desired products.

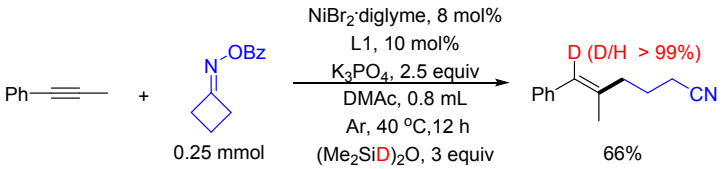
## General procedure：Experimental Procedures for Examples Described in Table 3

In air, $NiBr_2$·diglyme (10 mol%), L1 (12 mol%), $K_3PO_4$ (2.5 equiv), and Cycloketone oxime esters (0.25 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). To these solids, DMAc (1.0 mL), alkynes and $(Me_2SiH)_2O$ (3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 40 °C for 12 h. The mixture was purified by column chromatography to afford the desired products.

## Experimental Procedures for Examples Described in Scheme 2

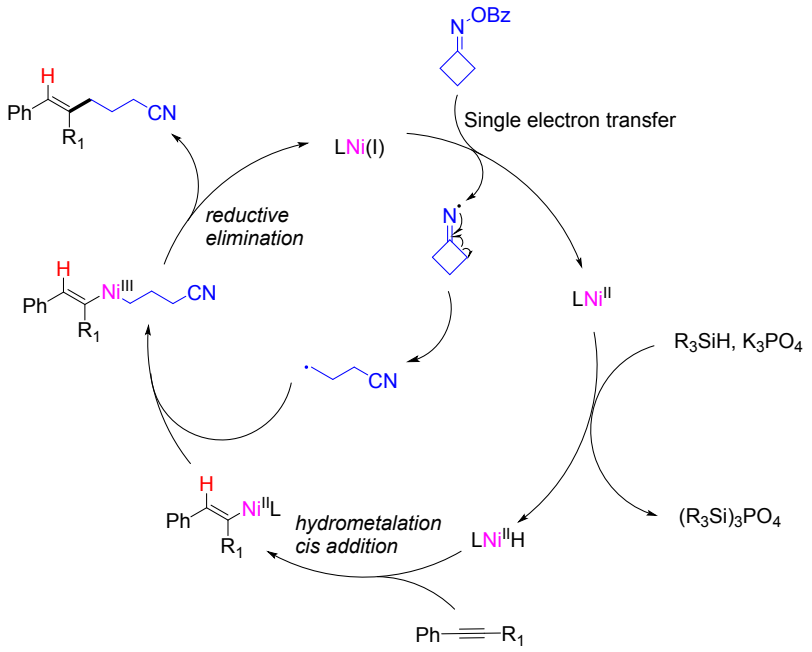
In air, $NiBr_2$·diglyme (8 mol%), L1 (10 mol%), $K_3PO_4$ (2.5 equiv), and Cycloketone oxime esters (5 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). To these solids, DMAc (12 mL), alkynes and $(Me_2SiH)_2O$ (3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 40 °C for 12 h. The mixture was purified by column chromatography to afford the desired products.

## Experimental Procedures for Examples Described in Scheme 3

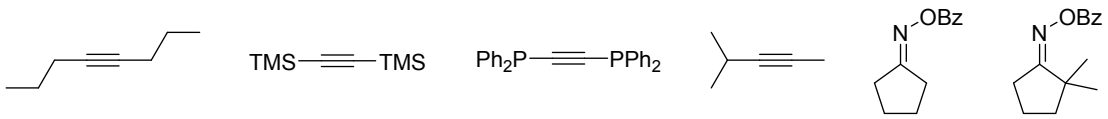



In air, $NiBr_2$·diglyme (8 mol%), L1 (10 mol%), $K_3PO_4$ (2.5 equiv), and Cycloketone oxime esters (0.25 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). To these solids, DMAc (0.8 mL), alkynes and $(Me_2SiD)_2O$ (3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 40 °C for 12 h. The mixture was purified by column chromatography to afford the desired products (Refer to this literature for the synthesis of the $(Me_2SiD)_2O$: *J. Am. Chem. Soc.* **2020**, 142, 8109-8115).

## Proposed Catalytic Cycle

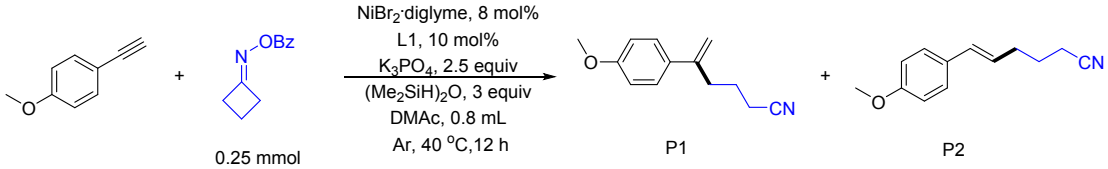



## Incompatible substrate




< 5% yield

## An example of phenylacetylene substrate



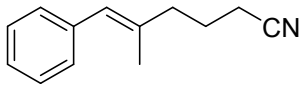

0.25 mmol

P1

P2

26% yield, P1 : P2 = 1.2 : 1

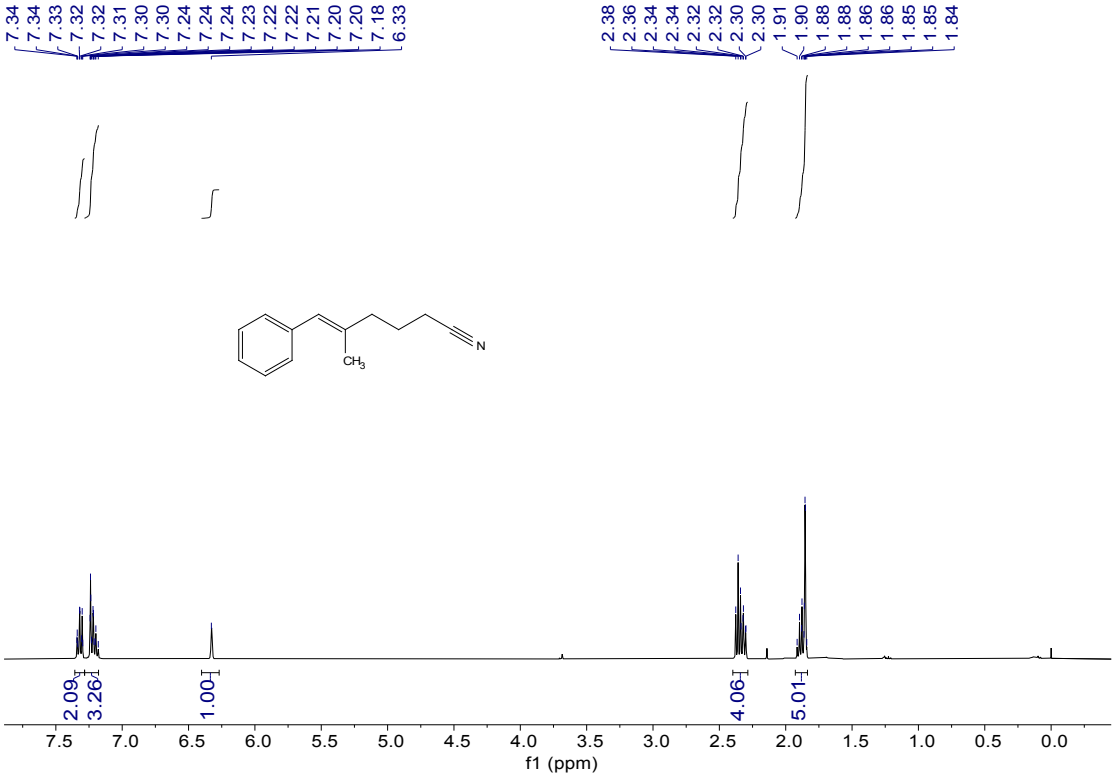
# Ⅳ. Substrate Scope, Spectral Data and NMR Spectra

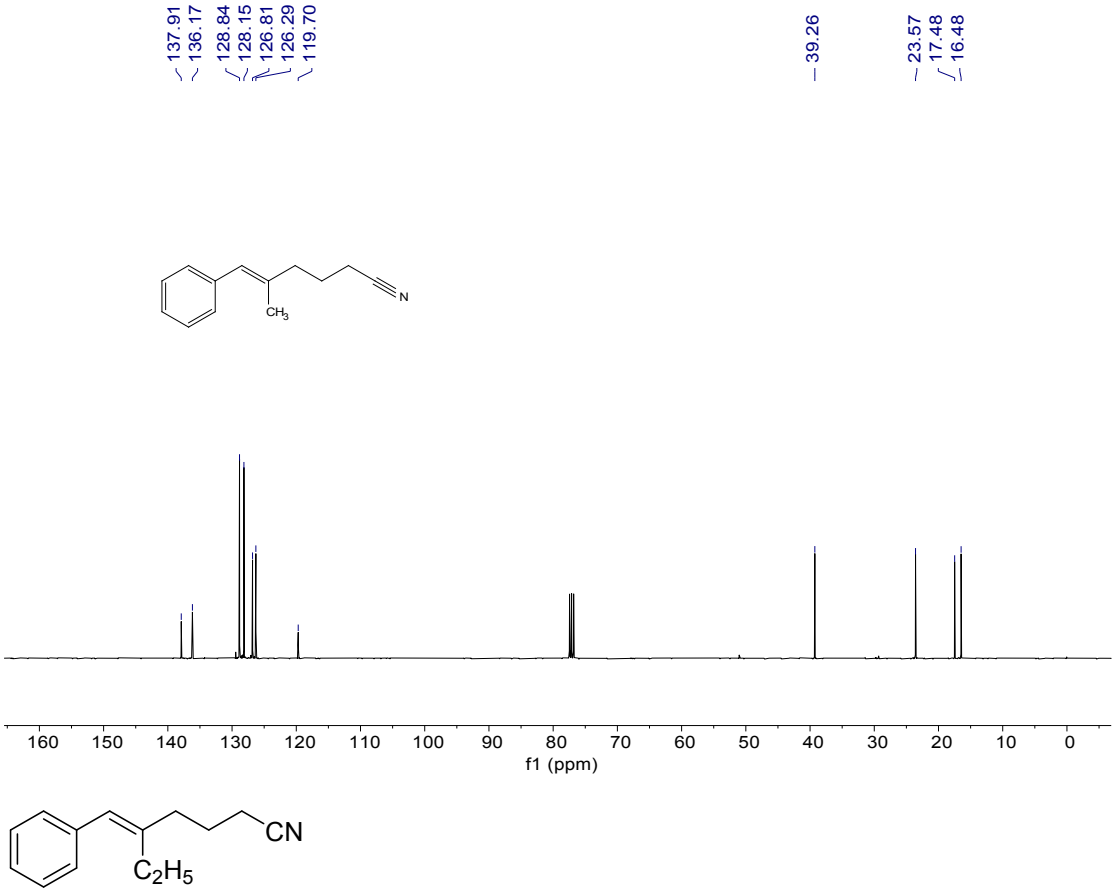



**(E)-5-methyl-6-phenylhex-5-enenitrile (3a)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.26 – 7.17 (m, 3H), 6.33 (s, 1H), 2.40 – 2.27 (m, 4H), 1.92 – 1.83 (m, 5H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.91, 136.17, 128.84, 128.15, 126.81, 126.29, 119.70, 39.26, 23.57, 17.48, 16.48.

**HRMS** (APCI) calcd for $C_{13}H_{16}N$ ($M+H^+$): 186.1277; found: 186.1278.





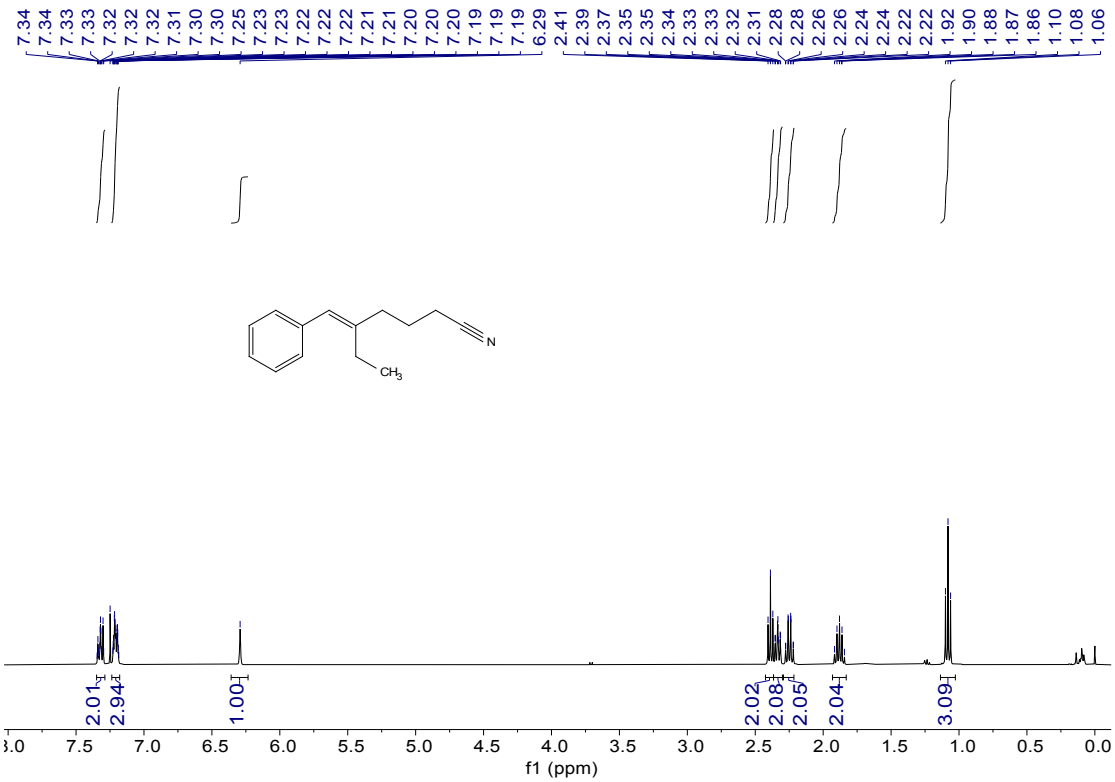


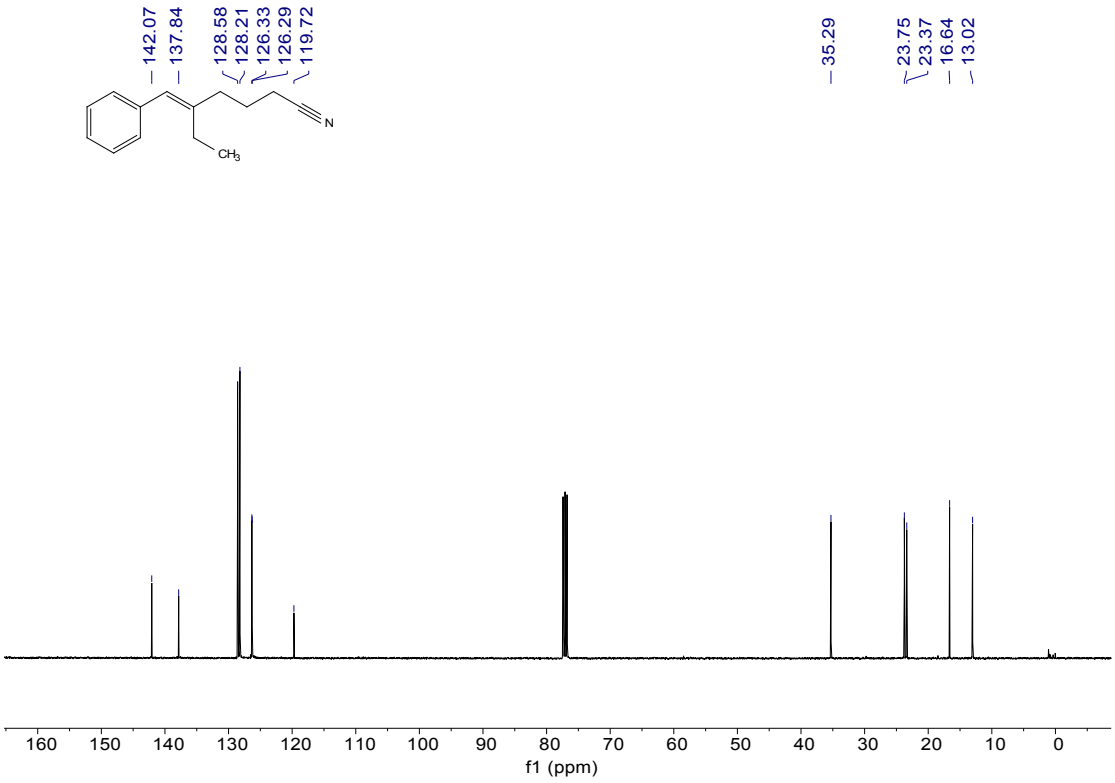


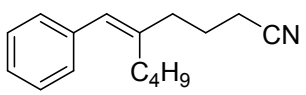
**(E)-5-benzylideneheptanenitrile (3b)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.29 (m, 2H), 7.24 – 7.18 (m, 3H), 6.29 (s, 1H), 2.39 (t, *J* = 7.1 Hz, 2H), 2.36 – 2.30 (m, 2H), 2.24 (td, *J* = 7.5, 0.7 Hz, 2H), 1.96 – 1.83 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.07, 137.84, 128.58, 128.21, 126.33, 126.29, 119.72, 35.29, 23.75, 23.37, 16.64, 13.02.

**HRMS** (APCI) calcd for $C_{14}H_{18}N$ ($M+H^+$): 200.1434; found: 200.1431.



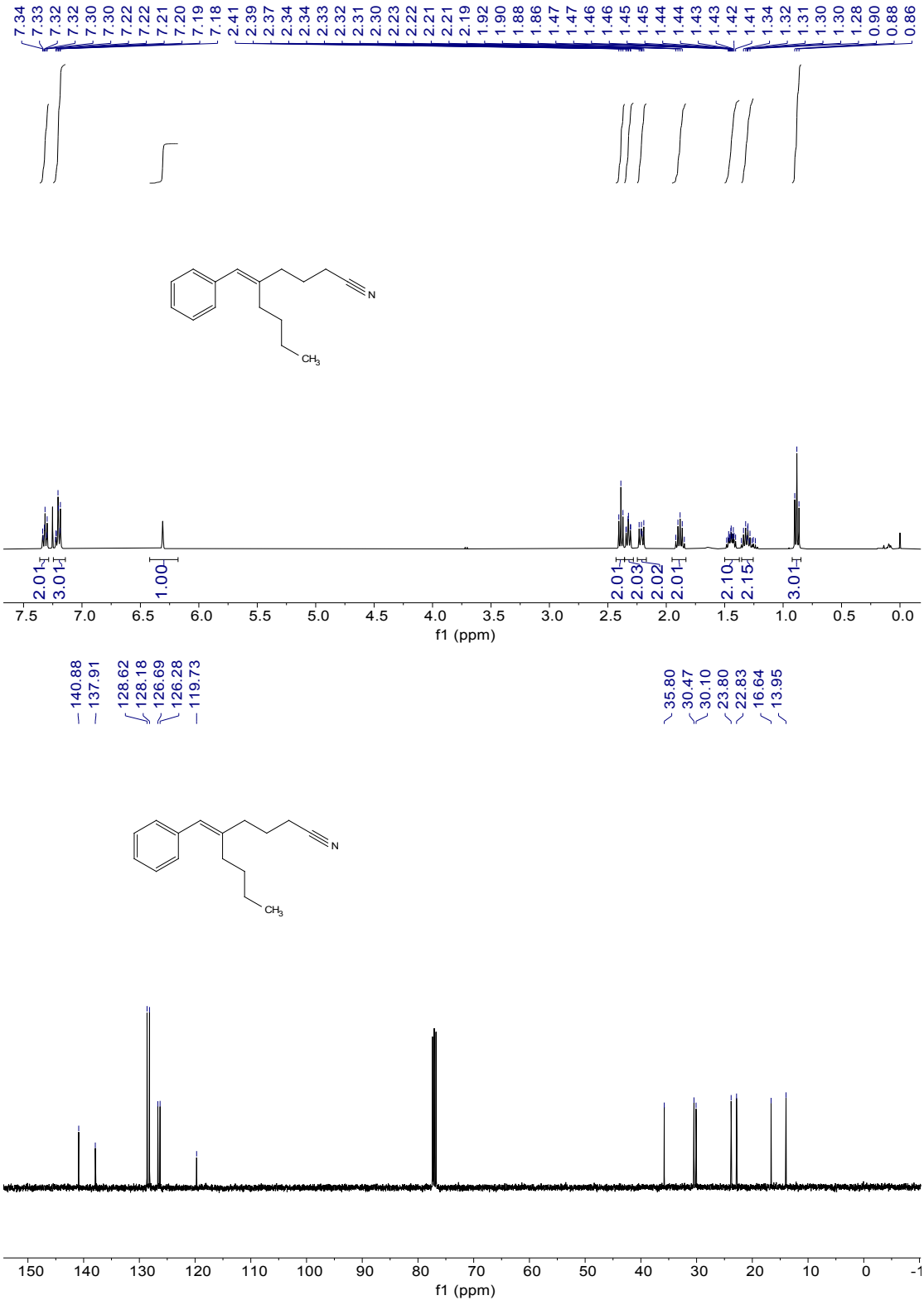

**(E)-5-benzylidenenonanenitrile (3c)**

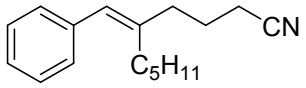
Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.24 – 7.17 (m, 3H), 6.31 (s, 1H), 2.39 (t, *J* = 7.1 Hz, 2H), 2.32 (td, *J* = 7.4, 1.2 Hz, 2H), 2.25

– 2.19 (m, 2H), 1.94 – 1.83 (m, 2H), 1.51 – 1.40 (m, 2H), 1.36 – 1.23 (m, 2H), 0.88 (t, $J$ = 7.3 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 140.88, 137.91, 128.62, 128.18, 126.69, 126.28, 119.73, 35.80, 30.47, 30.10, 23.80, 22.83, 16.64, 13.95.

**HRMS** (APCI) calcd for $C_{16}H_{22}N$ ($M+H^+$): 228.1747; found: 228.1745.

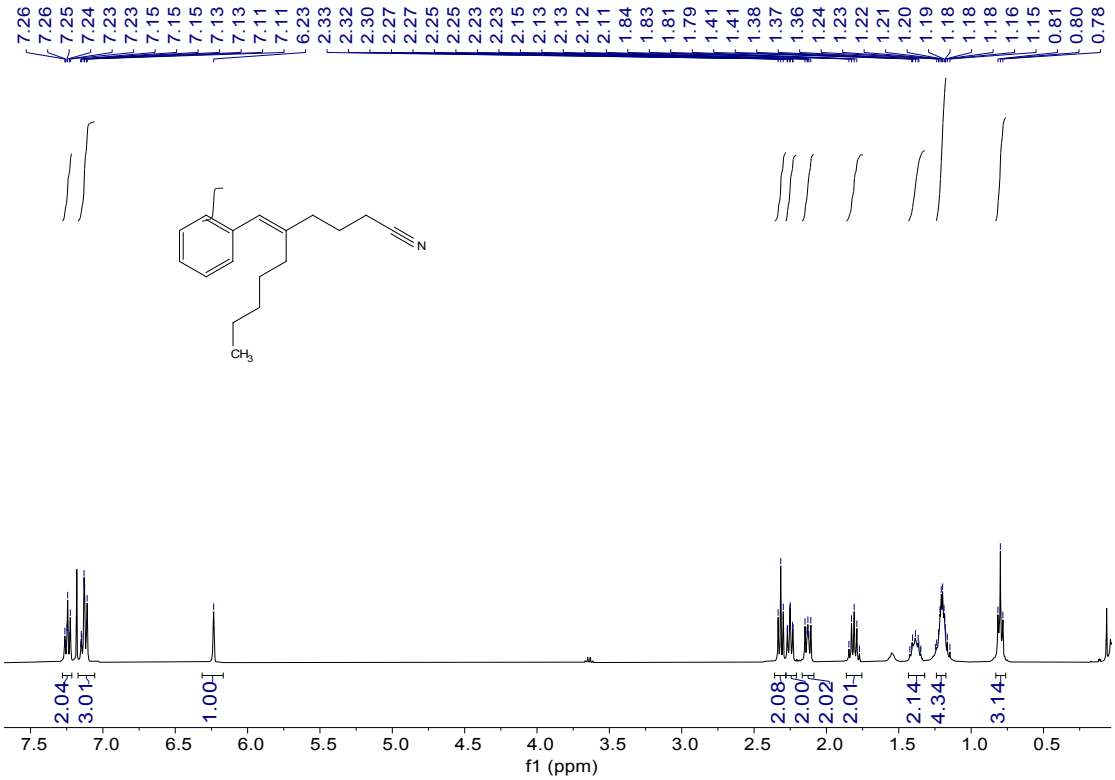


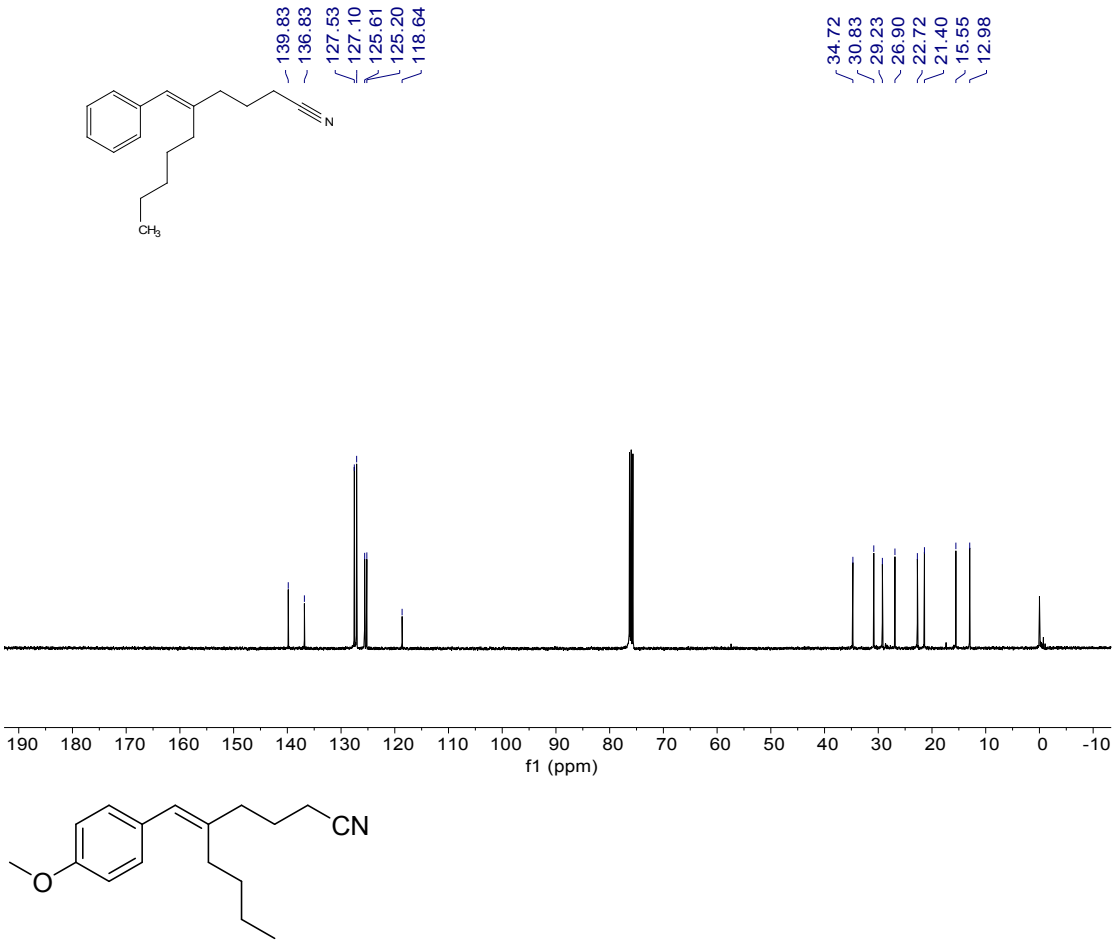



**(E)-5-benzylidenedecanenitrile (3d)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 8.6, 6.6 Hz, 2H), 7.13 (td, *J* = 7.3, 6.9, 1.5 Hz, 3H), 6.23 (s, 1H), 2.32 (t, *J* = 7.1 Hz, 2H), 2.28 – 2.23 (m, 2H), 2.18 – 2.09 (m, 2H), 1.88 – 1.74 (m, 2H), 1.39 (t, *J* = 7.8 Hz, 2H), 1.19 (td, *J* = 9.1, 8.2, 5.3 Hz, 4H), 0.80 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 139.83, 136.83, 127.53, 127.10, 125.61, 125.20, 118.64, 34.72, 30.83, 29.23, 26.90, 22.72, 21.40, 15.55, 12.98.

**HRMS** (APCI) calcd for $C_{17}H_{24}N$ ($M+H^+$): 242.1903; found: 242.1905.





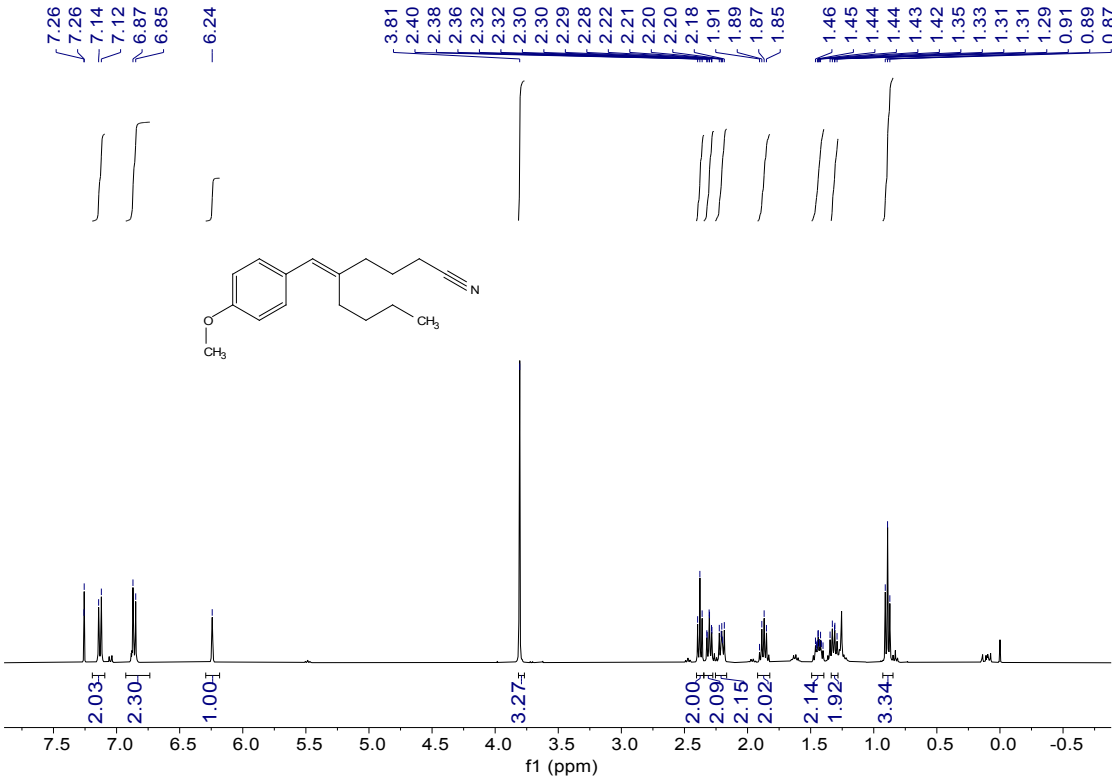


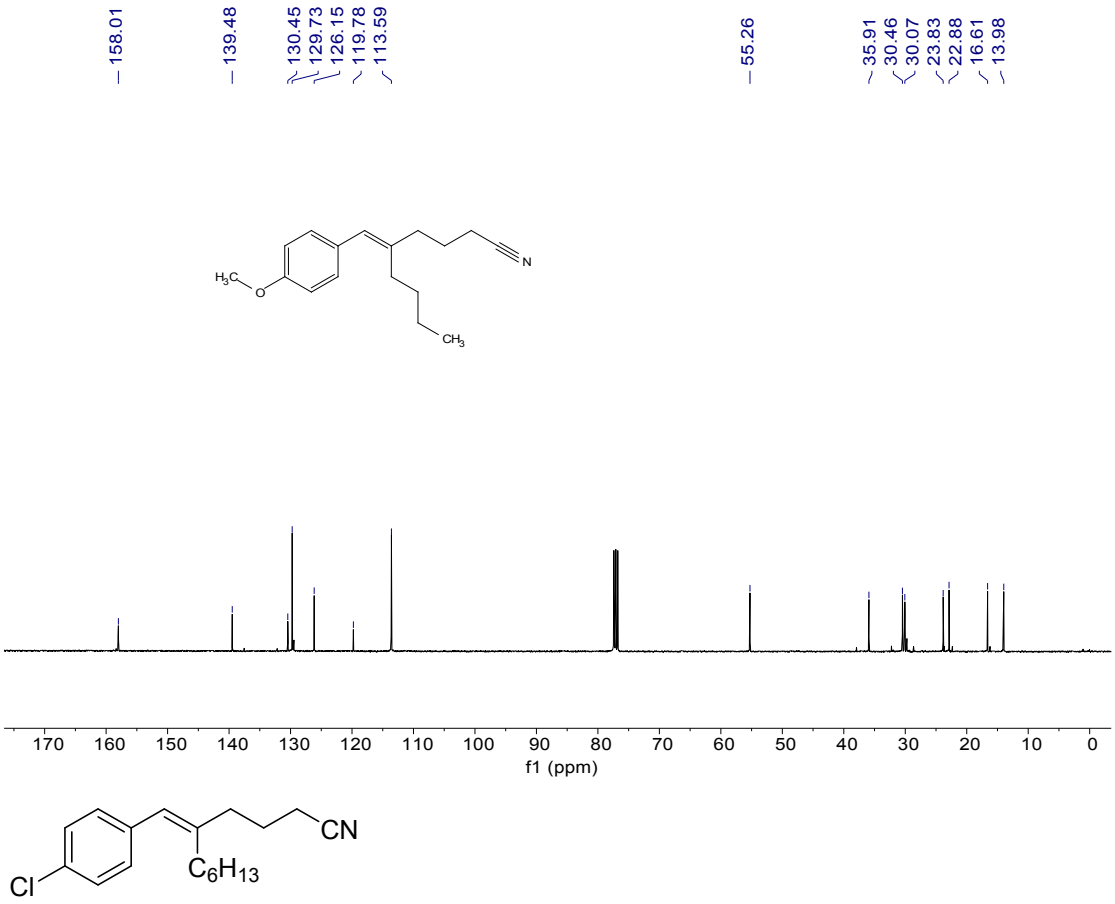


**(E)-5-(4-methoxybenzylidene)nonanenitrile (3e)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.24 (s, 1H), 3.81 (s, 3H), 2.38 (t, *J* = 7.1 Hz, 2H), 2.30 (td, *J* = 7.5, 1.2 Hz, 2H), 2.23 – 2.18 (m, 2H), 1.88 (q, *J* = 7.3 Hz, 2H), 1.49 – 1.40 (m, 2H), 1.35 – 1.29 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.01, 139.48, 130.45, 129.73, 126.15, 119.78, 113.59, 55.26, 35.91, 30.46, 30.07, 23.83, 22.88, 16.61, 13.98.

**HRMS** (APCI) calcd for $C_{17}H_{24}NO$ ($M+H^+$): 258.1852; found: 258.1856.





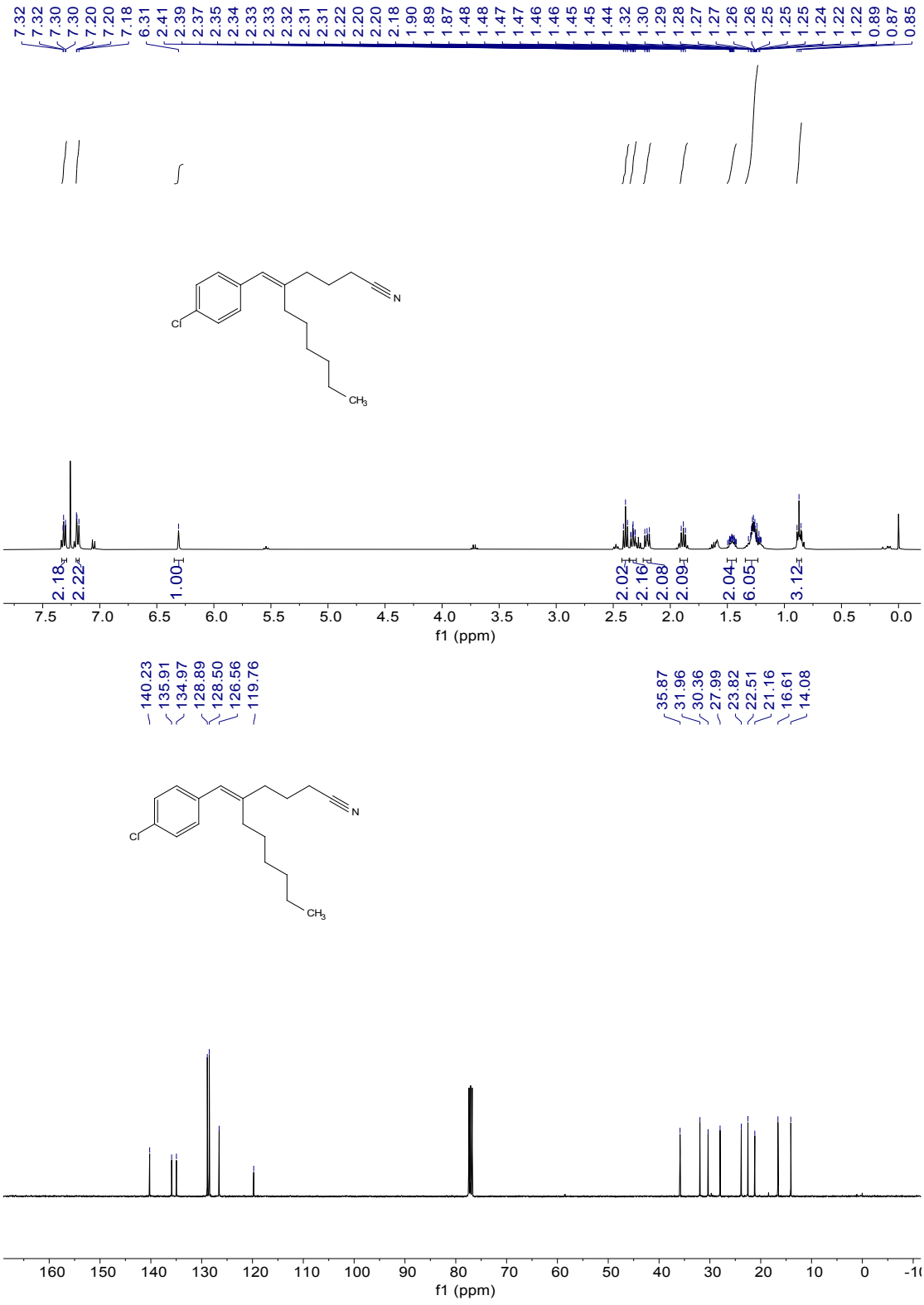


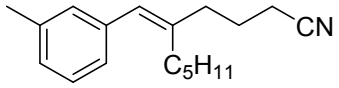
**(E)-5-(4-chlorobenzylidene)undecanenitrile (3f)**

Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 2H), 7.22 – 7.15 (m, 2H), 6.31 (s, 1H), 2.39 (t, *J* = 7.1 Hz, 2H), 2.36 – 2.28 (m, 2H), 2.24 – 2.15 (m,

2H), 1.92 – 1.85 (m, 2H), 1.51 – 1.42 (m, 2H), 1.33 – 1.21 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 140.23, 135.91, 134.97, 128.89, 128.50, 126.56, 119.76, 35.87, 31.96, 30.36, 27.99, 23.82, 22.51, 21.16, 16.61, 14.08.

**HRMS** (APCI) calcd for $C_{18}H_{25}ClN$ ($M+H^+$): 290.1670; found: 290.1672.

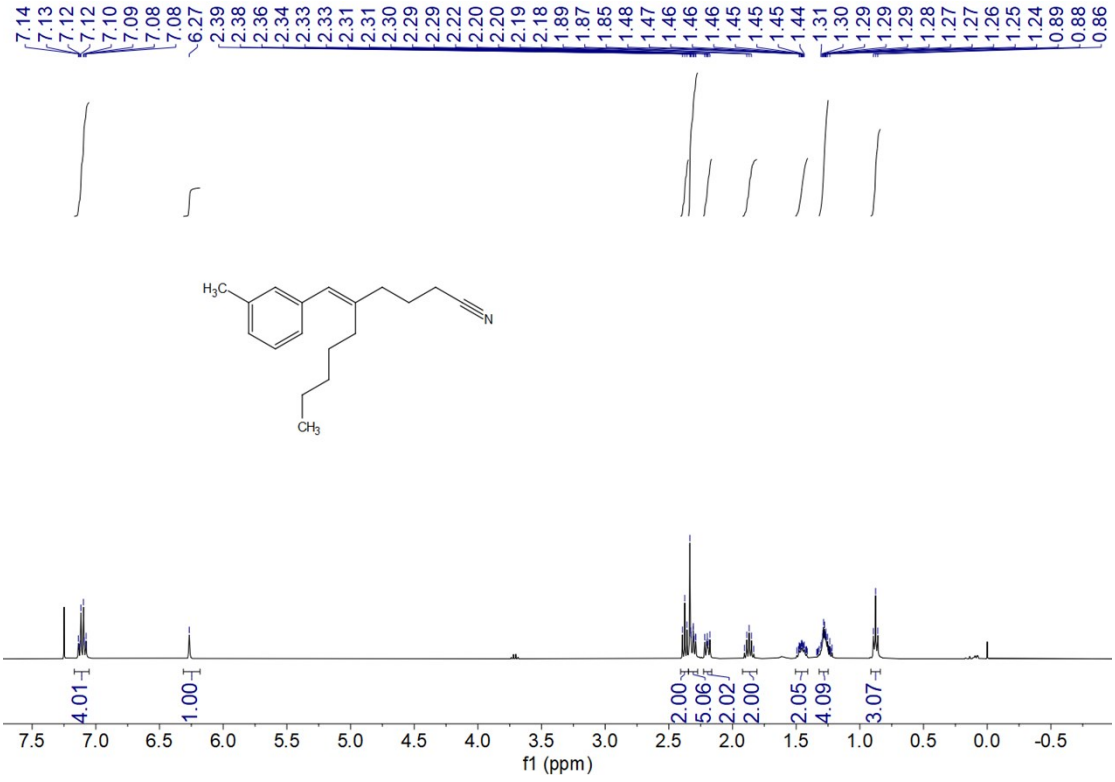


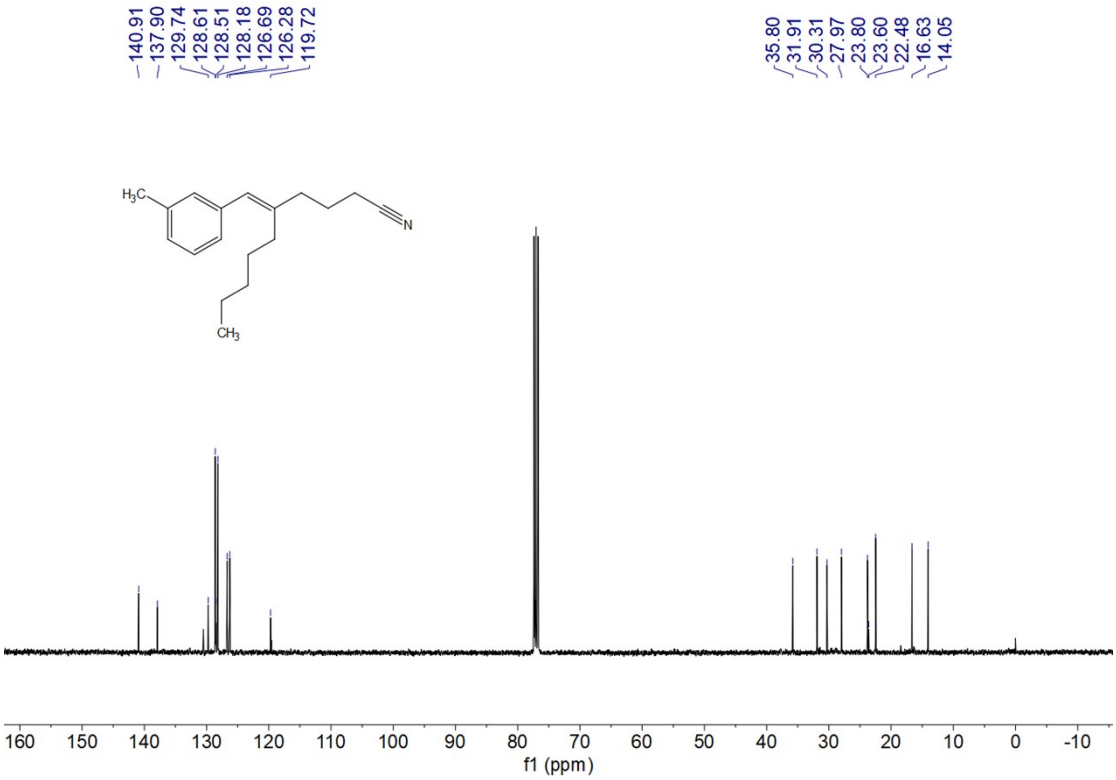


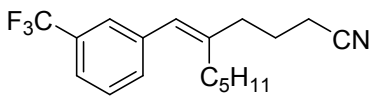

**(E)-5-(3-methylbenzylidene)decanenitrile (3g)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.19 – 7.01 (m, 4H), 6.27 (s, 1H), 2.38 (t, *J* = 7.1 Hz, 2H), 2.34 – 2.29 (m, 5H), 2.22 – 2.17 (m, 2H), 1.92 – 1.83 (m, 2H), 1.51 – 1.41 (m, 2H), 1.32 – 1.22 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 140.91, 137.90, 129.74, 128.61, 128.51, 128.18, 126.69, 126.28, 119.72, 35.80, 31.91, 30.31, 27.97, 23.80, 23.60, 22.48, 16.63, 14.05.

**HRMS** (APCI) calcd for $C_{18}H_{26}N$ ($M+H^+$): 256.2060; found: 256.2063.



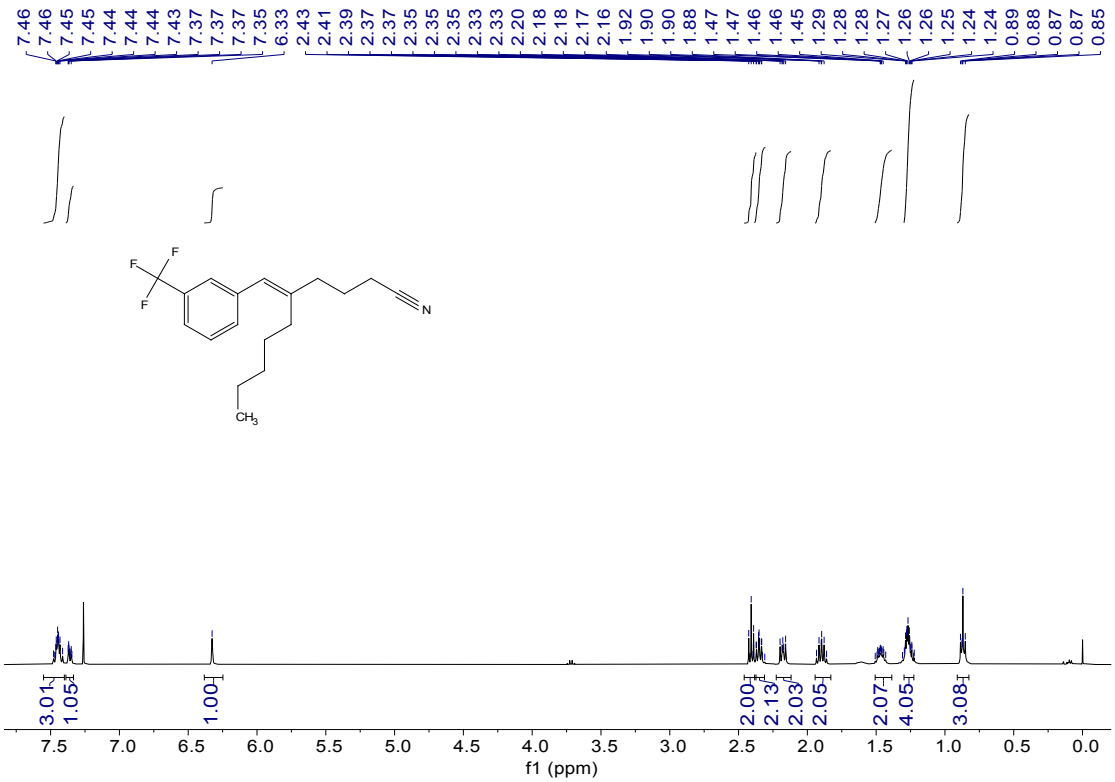


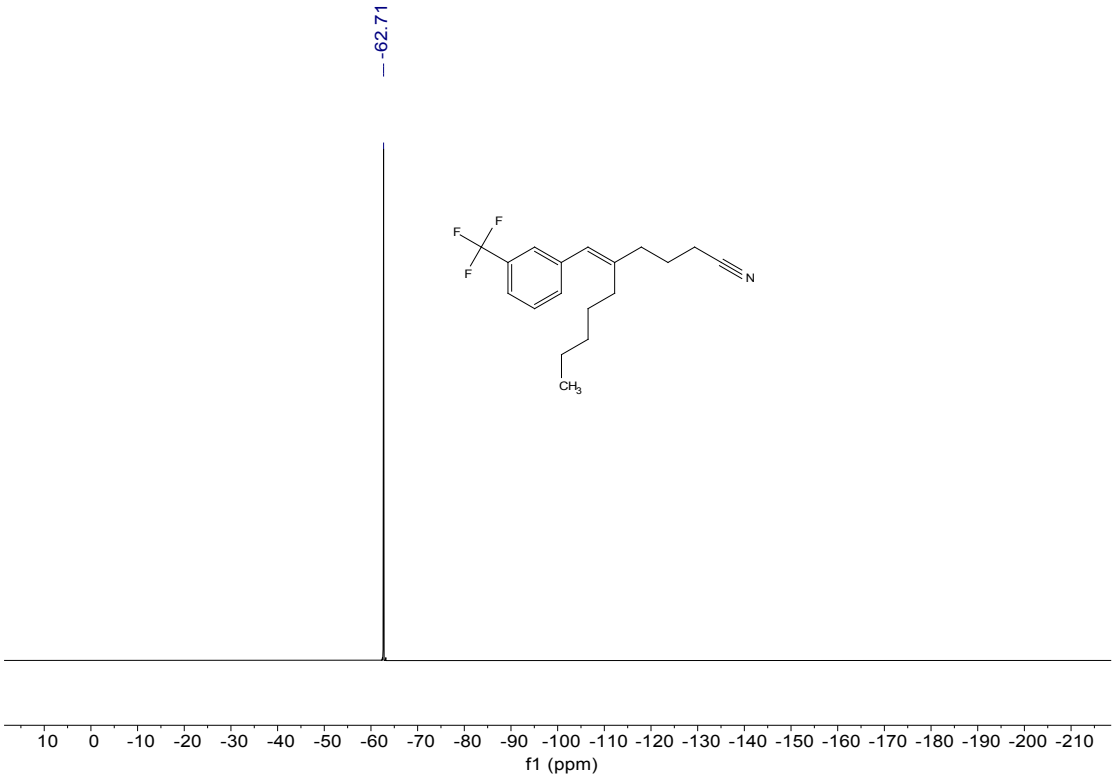



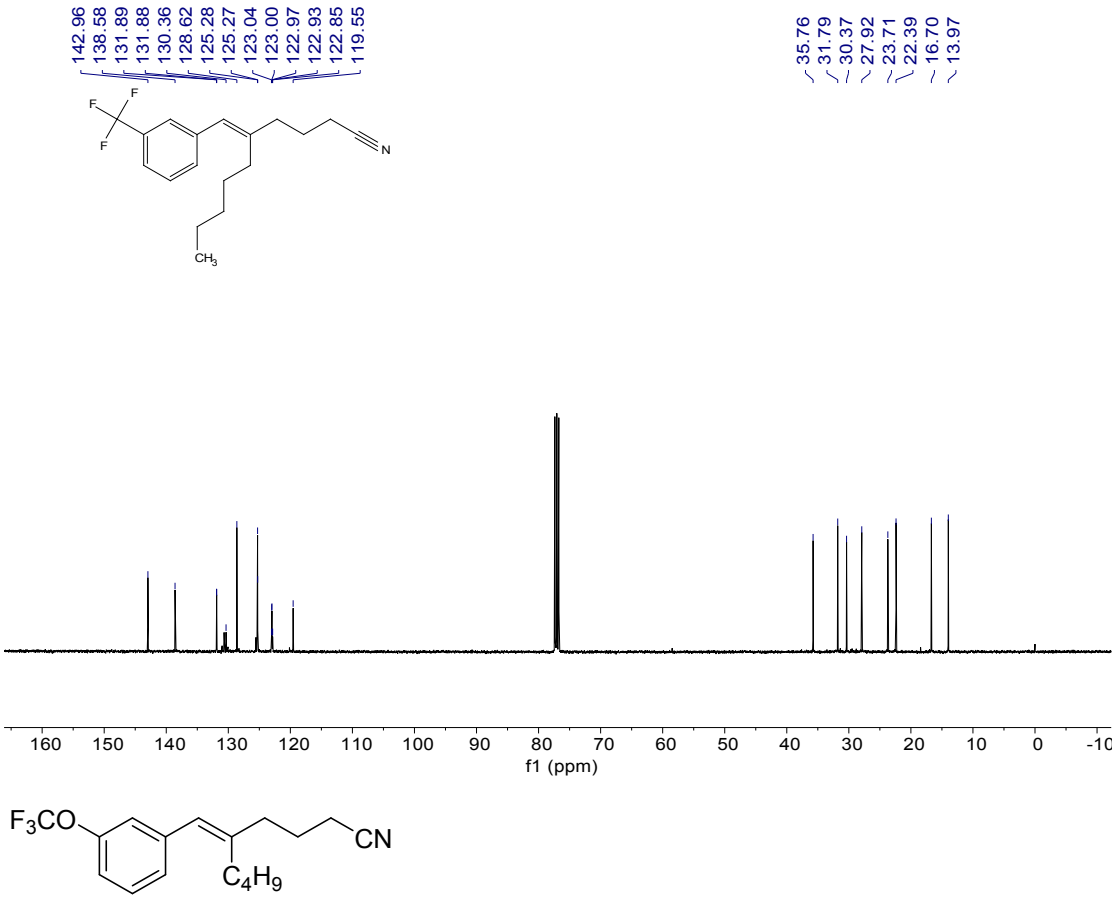

**(E)-5-(3-(trifluoromethyl)benzylidene)decanenitrile (3h)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 3H), 7.39 – 7.34 (m, 1H), 6.33 (s, 1H), 2.41 (t, *J* = 7.1 Hz, 2H), 2.38 – 2.31 (m, 2H), 2.23 – 2.15 (m, 2H), 1.96 – 1.85 (m, 2H), 1.53 – 1.41 (m, 2H), 1.35 – 1.19 (m, 4H), 0.87 (t, J= 7.0 HZ, 3H). **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -62.71. **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 142.96, 138.58, 131.89, 131.88, 130.52 (q, *J* = 32.0 Hz), 128.62, 125.27 (q, *J* = 3.7, 3.0 Hz), 124.21 (q, *J* = 272.2 Hz), 122.99 (q, *J* = 3.8 Hz), 119.55, 35.76, 31.79, 30.37, 27.92, 23.71, 22.39, 16.70, 13.97.

**HRMS** (APCI) calcd for $C_{18}H_{23}F_3N$ ($M+H^+$): 310.1777; found: 310.1775.


7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.37 7.37 7.37 7.35 6.33
2.43 2.41 2.39 2.37 2.37 2.35 2.35 2.35 2.33 2.33 2.20 2.18 2.18 2.17 2.16 1.92 1.90 1.90 1.88 1.47 1.47 1.46 1.46 1.45 1.29 1.28 1.28 1.27 1.26 1.26 1.25 1.24 1.24 0.89 0.88 0.87 0.87 0.85
F
F
F
N
CH3
3.01 1.05 1.00 2.00 2.13 2.03 2.05 2.07 4.05 3.08
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)


-62.71
F
F
F
N
CH3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



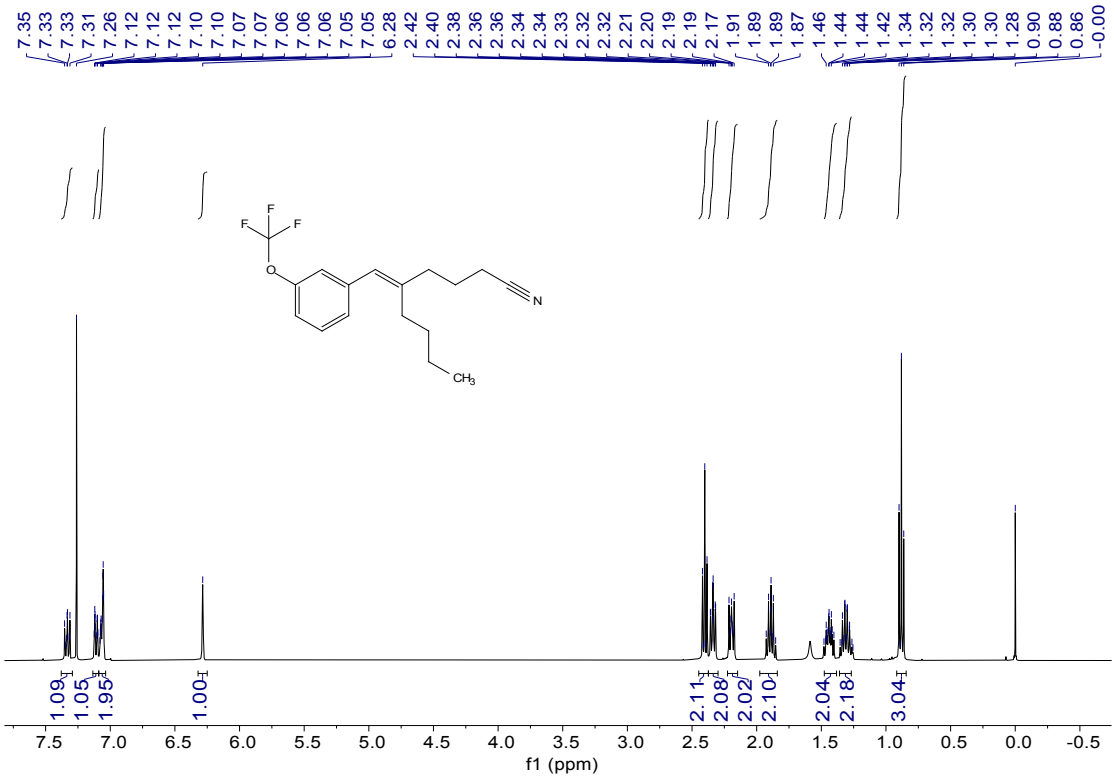


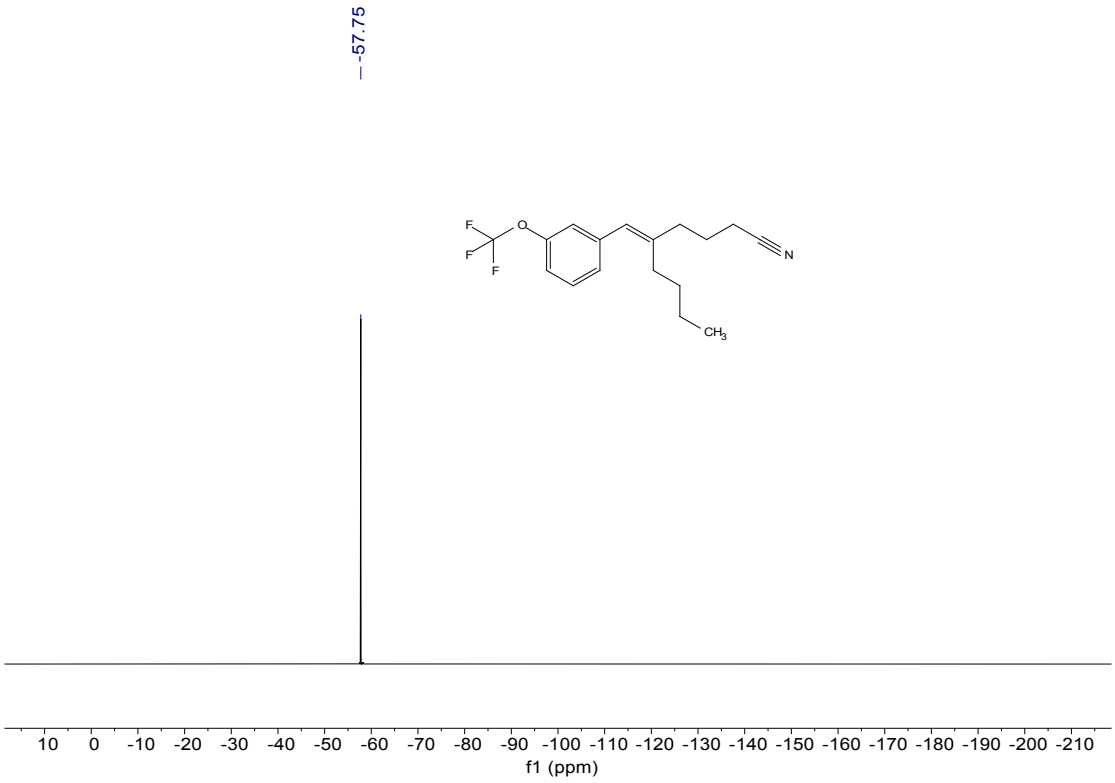


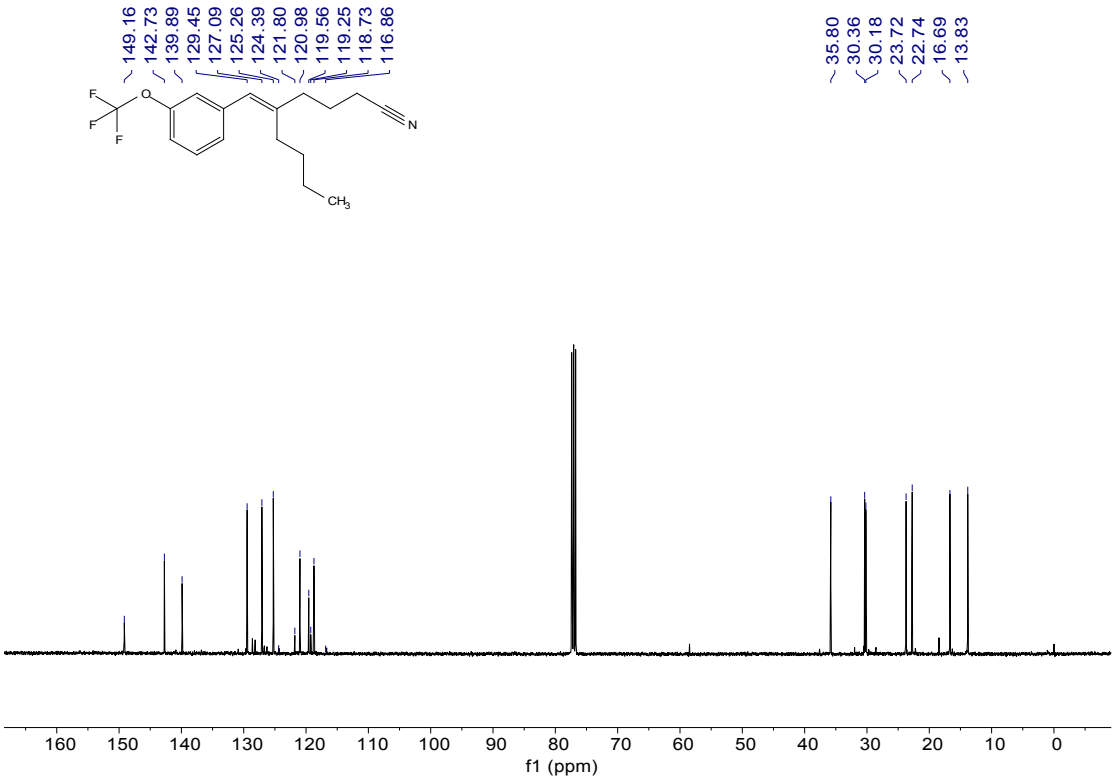
**(E)-5-(3-(trifluoromethoxy)benzylidene)nonanenitrile (3i)**

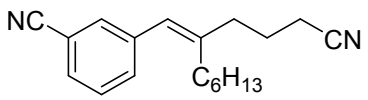
Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 1H), 7.14 – 7.09 (m, 1H), 7.09 – 7.03 (m, 2H), 6.29 (s, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.37 – 2.30 (m, 2H), 2.24 – 2.14 (m, 2H), 1.89 (p, *J* = 7.2 Hz, 2H), 1.49 – 1.39 (m, 2H), 1.37 – 1.27 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -57.75. **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ149.16, 142.73, 139.89, 129.45, 127.09, 125.26, 120.98, 120.52 (q, *J* = 256.9 Hz), 119.56, 118.73, 35.80, 30.36, 30.18, 23.72, 22.74, 16.69, 13.83.

**HRMS** (APCI) calcd for $C_{17}H_{21}F_3NO$ ($M+H^+$):312.1570; found: 312.1573.


7.35 7.33 7.33 7.31 7.26 7.12 7.12 7.12 7.10 7.10 7.07 7.07 7.06 7.06 7.06 7.05 7.05 6.28 2.42 2.40 2.38 2.36 2.36 2.34 2.34 2.33 2.32 2.32 2.21 2.20 2.19 2.19 2.17 1.91 1.89 1.89 1.87 1.46 1.44 1.44 1.42 1.34 1.32 1.30 1.30 1.28 0.90 0.88 0.86 -0.00
F
F
F
O
N
CH3
1.09 1.05 1.95 1.00 2.11 2.08 2.02 2.10 2.04 2.18 3.04
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 -0.5
f1 (ppm)


-57.75
F
F
F
O
N
CH3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

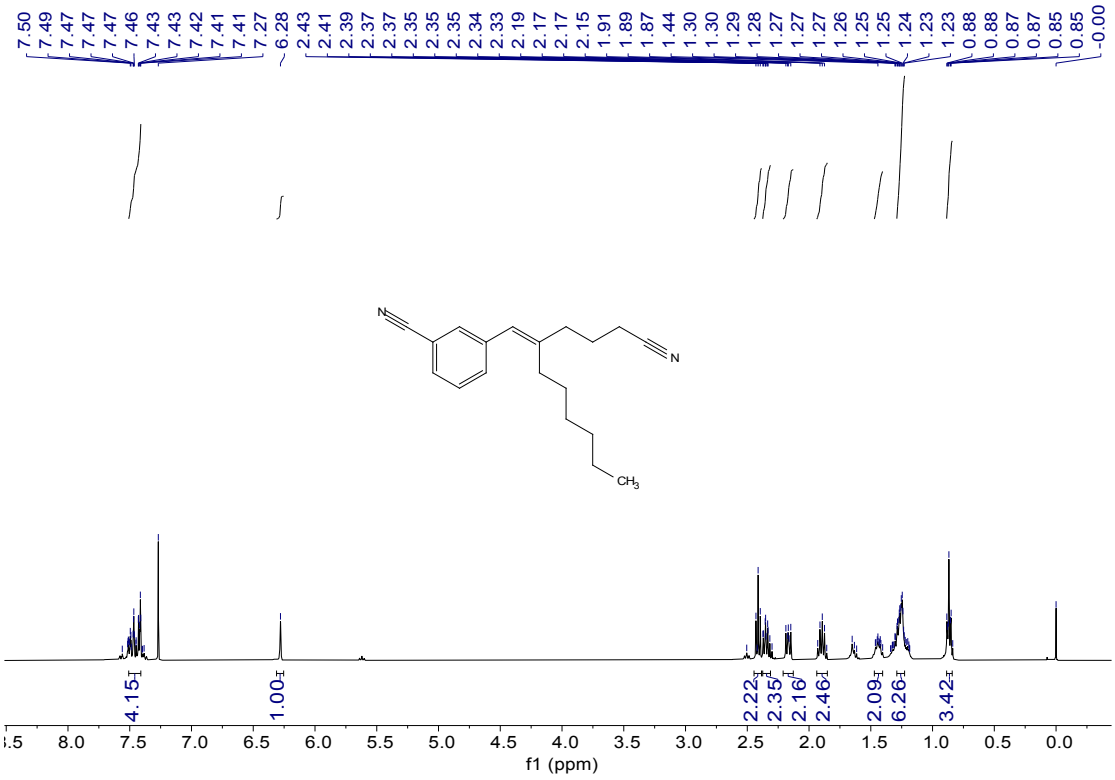


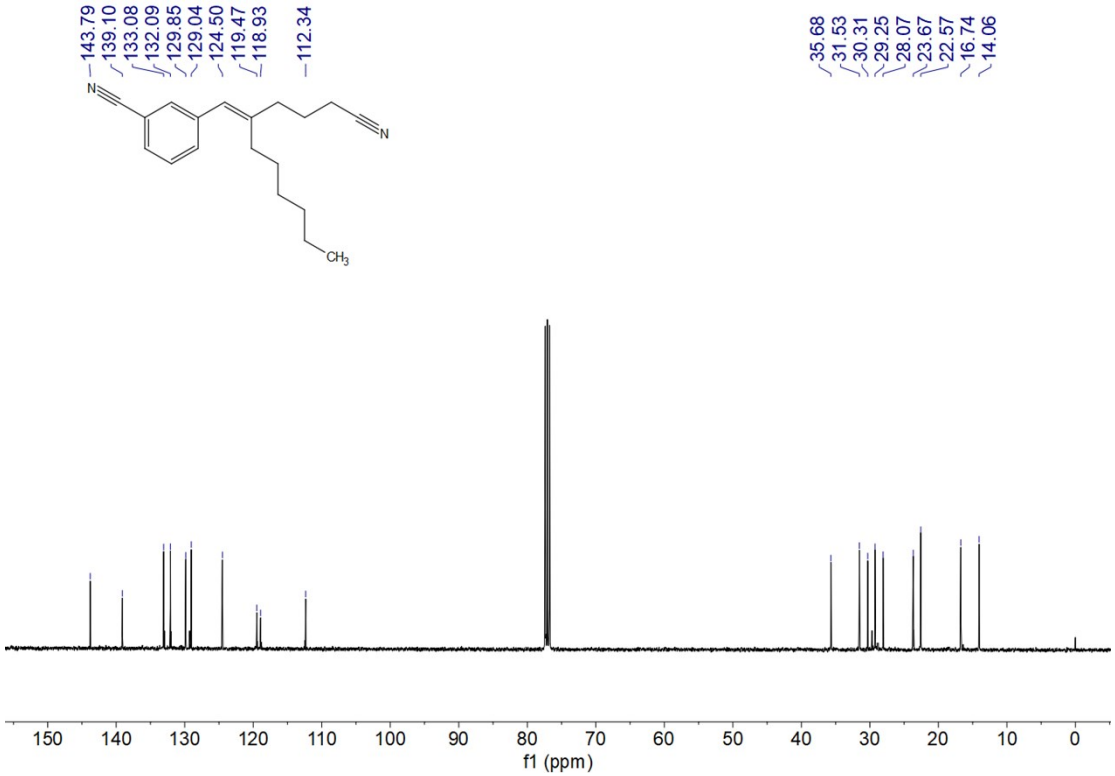



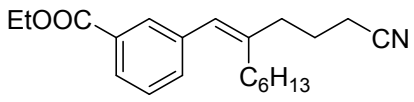

**(E)-3-(2-(3-cyanopropyl)oct-1-en-1-yl)benzonitrile (3j)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 7.38 (m, 4H), 6.28 (s, 1H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.37 – 2.31 (m, 2H), 2.20 – 2.13 (m, 2H), 1.98 – 1.85 (m, 2H), 1.43 (d, *J* = 7.3 Hz, 2H), 1.34 – 1.19 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.79, 139.10, 133.08, 132.09, 129.85, 129.04, 124.50, 119.47, 118.93, 112.34, 35.68, 31.53, 30.31, 29.25, 28.07, 23.67, 22.57, 16.74, 14.06.

**HRMS** (APCI) calcd for $C_{19}H_{25}N_2$ ($M+H^+$): 281.2012; found: 281.2016.



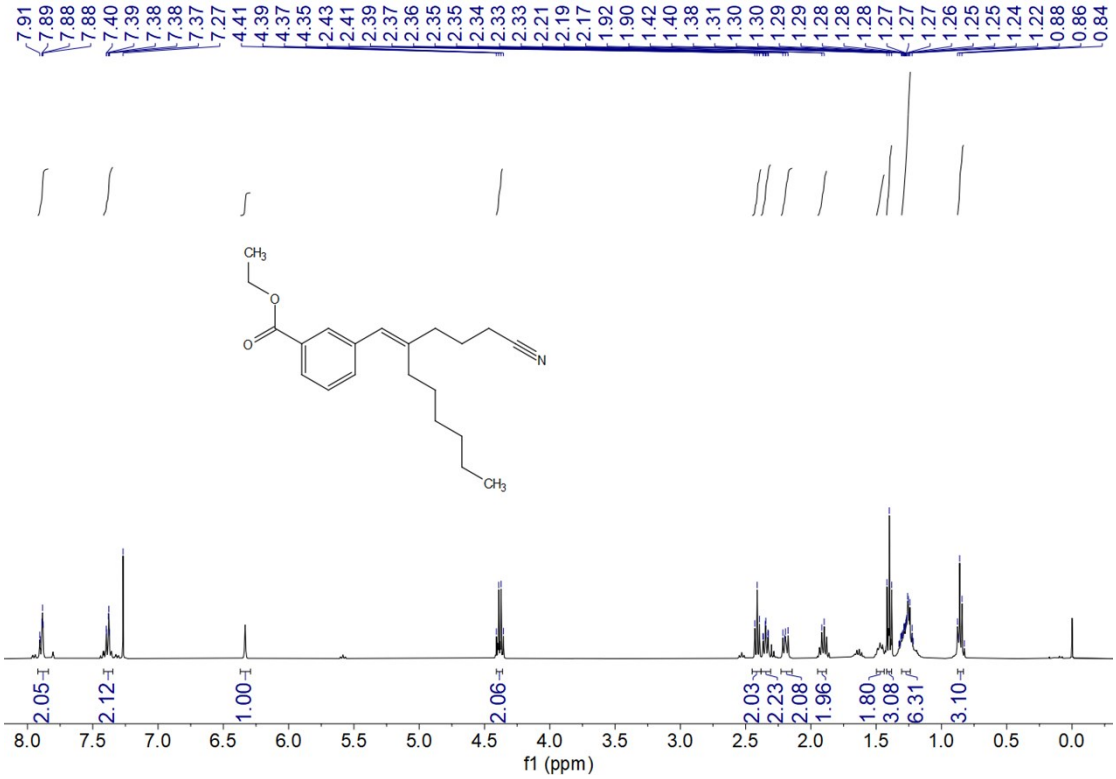



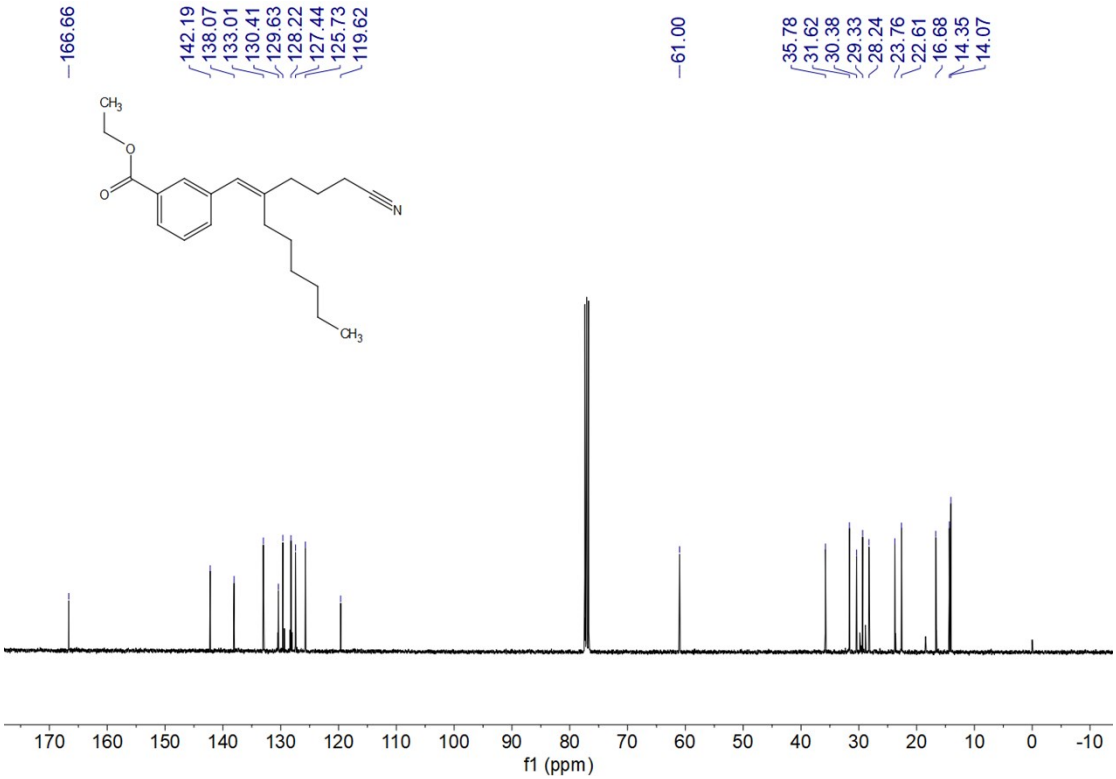

**ethyl (E)-3-(2-(3-cyanopropyl)oct-1-en-1-yl)benzoate (3k)**

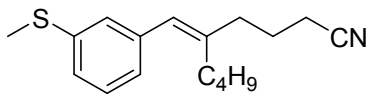
Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.95 – 7.85 (m, 2H), 7.48 – 7.36 (m, 2H), 6.33 (s, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.1 Hz, 2H), 2.35 (td, *J* =

7.5, 1.2 Hz, 2H), 2.26 – 2.16 (m, 2H), 1.98 – 1.81 (m, 2H), 1.50 – 1.44 (m, 2H), 1.40 (t, $J$ = 7.1 Hz, 3H), 1.33 – 1.21 (m, 6H), 0.86 (t, $J$ = 6.9 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.66, 142.19, 138.07, 133.01, 130.41, 129.63, 128.22, 127.44, 125.73, 119.62, 61.00, 35.78, 31.62, 30.38, 29.33, 28.24, 23.76, 22.61, 16.68, 14.35, 14.07.

**HRMS** (APCI) calcd for $C_{21}H_{30}NO_2$ ($M+H^+$):328.2271; found: 328.2270.

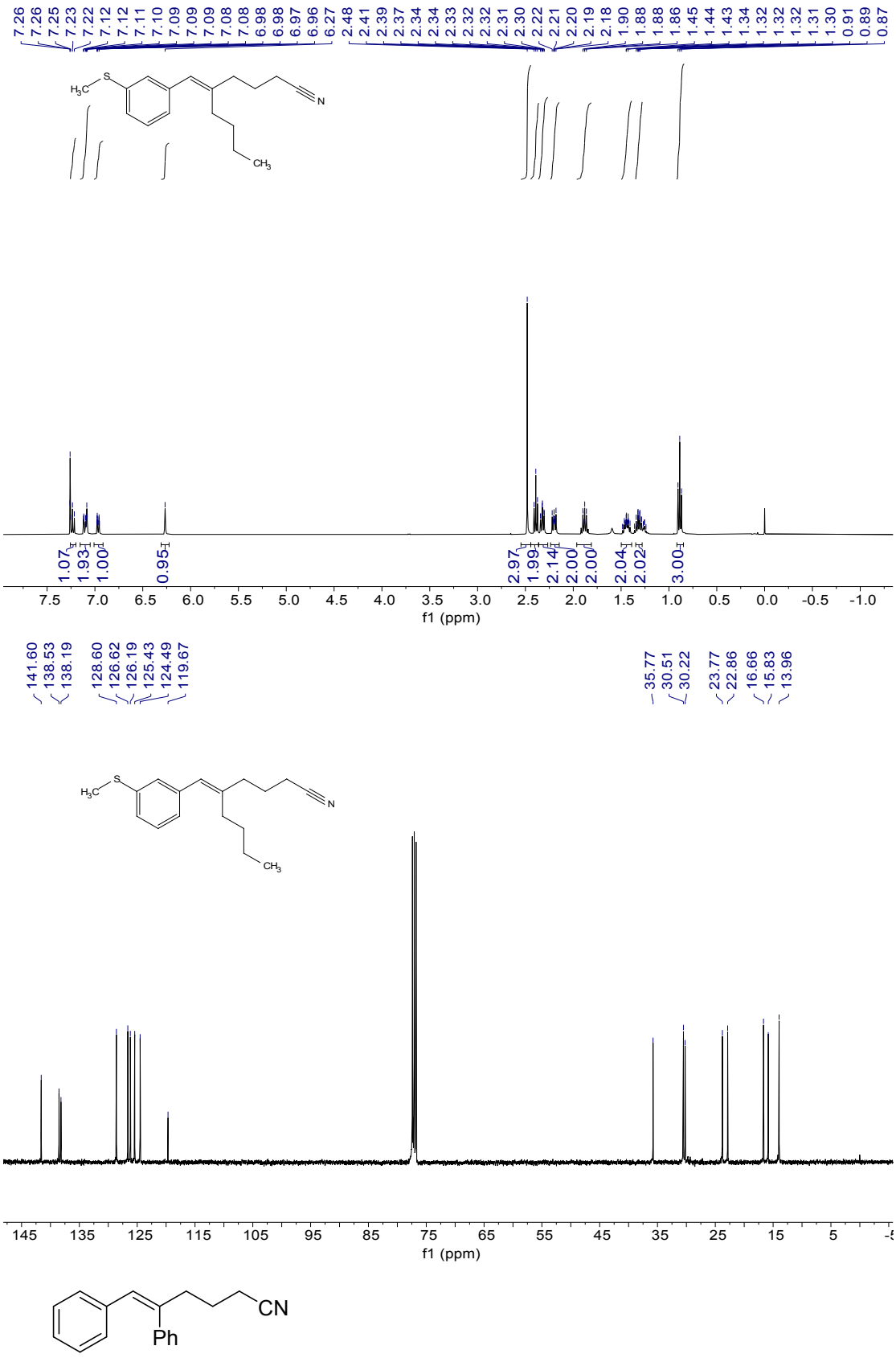





**(E)-5-(3-(methylthio)benzylidene)nonanenitrile (3l)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.7 Hz, 1H), 7.14 – 7.06 (m, 2H), 7.02 – 6.93 (m, 1H), 6.27 (s, 1H), 2.48 (s, 3H), 2.39 (t, *J* = 7.1 Hz, 2H), 2.32 (td, *J* = 7.5, 1.2 Hz, 2H), 2.25 – 2.17 (m, 2H), 1.88 (dd, *J* = 7.9, 6.9 Hz, 2H), 1.49 – 1.38 (m, 2H), 1.36 – 1.27 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 141.60, 138.53, 138.19, 128.60, 126.62, 126.19, 125.43, 124.49, 119.67, 35.77, 30.51, 30.22, 23.77, 22.86, 16.66, 15.83, 13.96. **HRMS** (APCI) calcd for $C_{17}H_{24}NS$ ($M+H^+$): 274.1624; found: 274.1620.

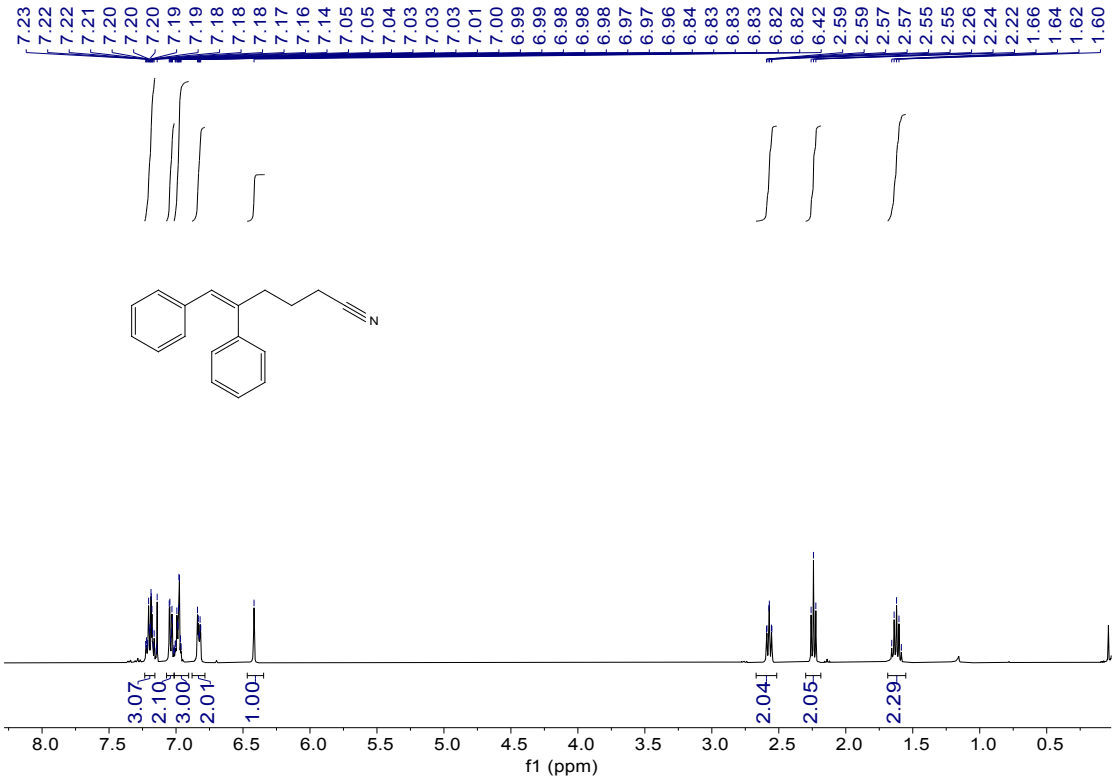


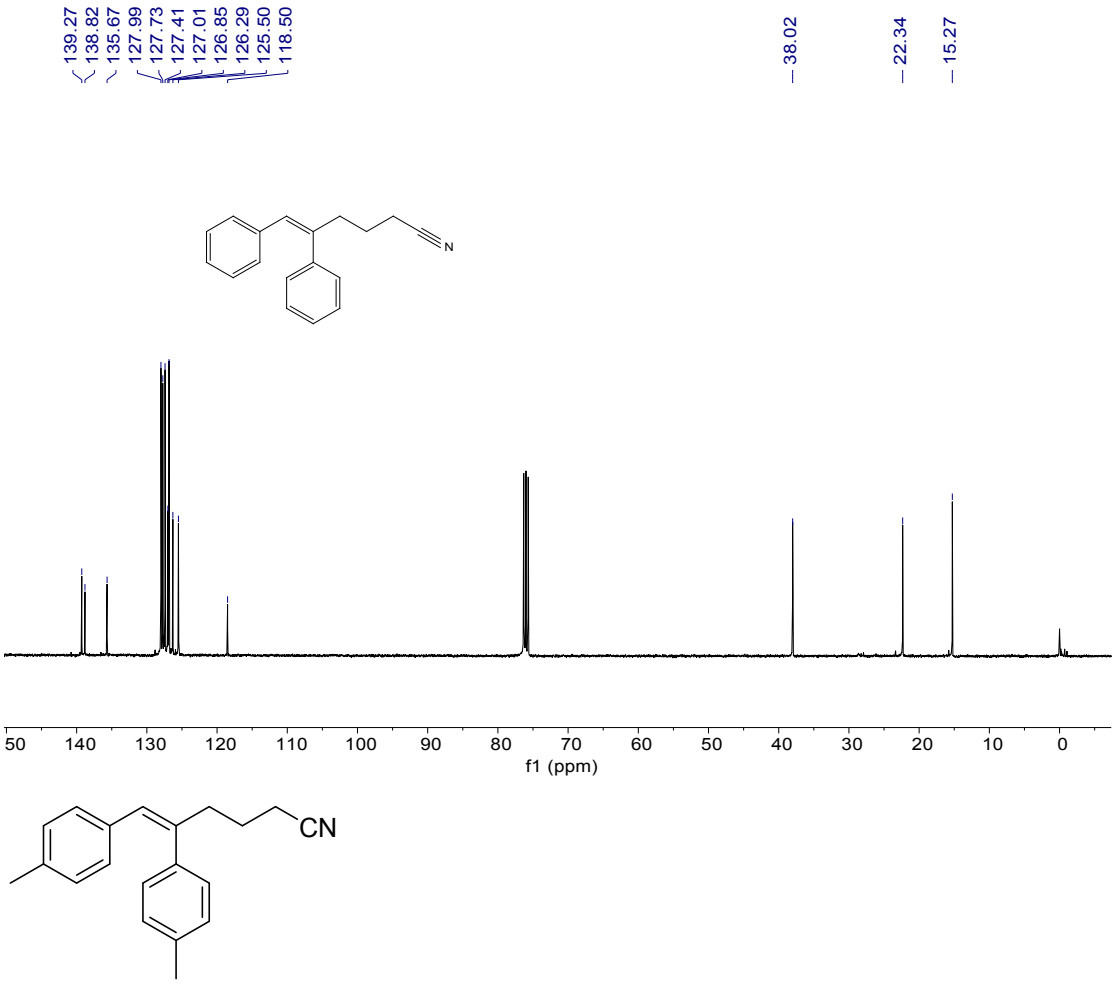

**(Z)-5,6-diphenylhex-5-enenitrile (3m)**

Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.23 –

7.16 (m, 3H), 7.07 – 7.02 (m, 2H), 7.01 – 6.94 (m, 3H), 6.83 (dd, *J* = 7.5, 2.2 Hz, 2H), 6.42 (s, 1H), 2.57 (td, *J* = 7.4, 1.2 Hz, 2H), 2.24 (t, *J* = 7.1 Hz, 2H), 1.69 – 1.55 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 139.27, 138.82, 135.67, 127.99, 127.73, 127.41, 127.01, 126.85, 126.29, 125.50, 118.50, 38.02, 22.34, 15.27.

**HRMS** (APCI) calcd for $C_{18}H_{18}N$ ($M+H^+$): 248.1434; found: 248.1432.

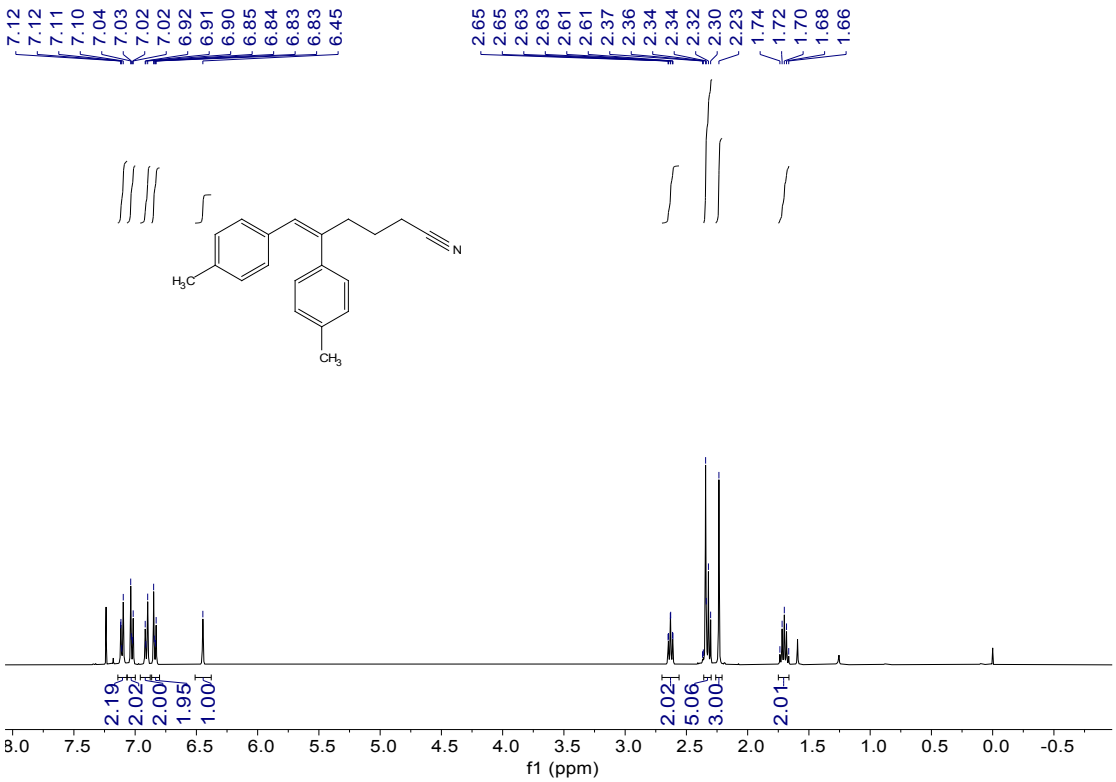


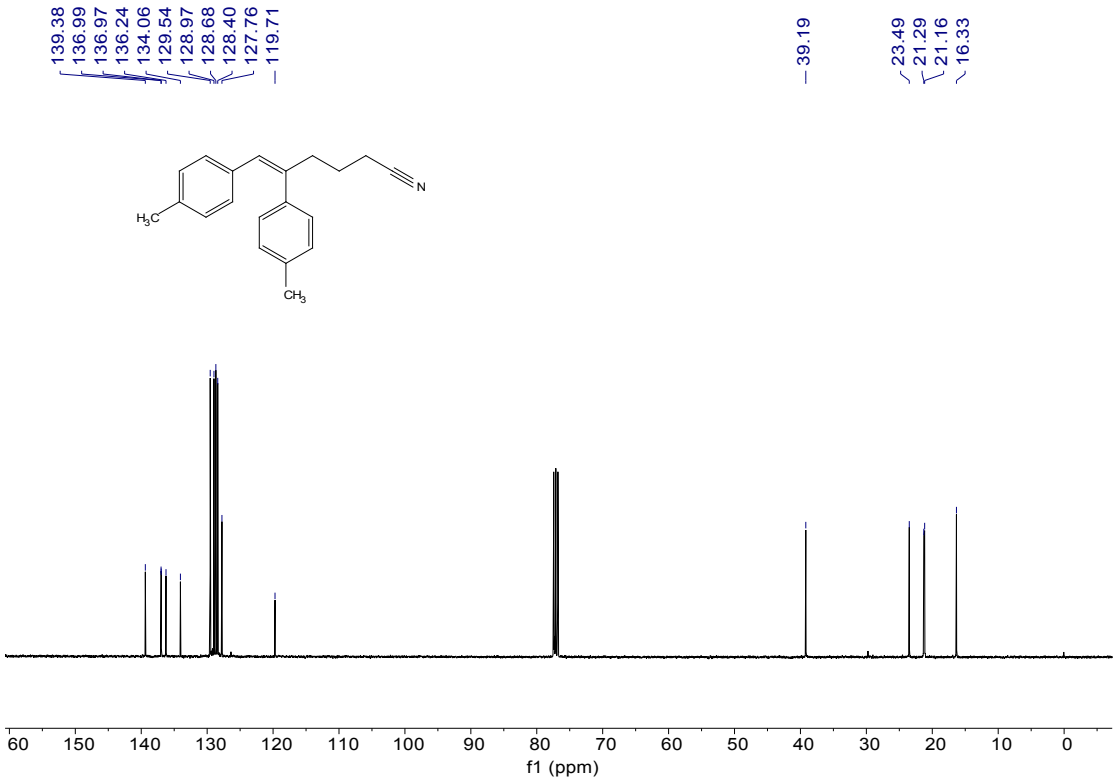


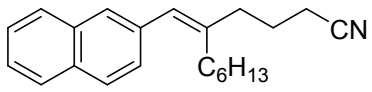

**(Z)-5,6-di-p-tolylhex-5-enenitrile (3n)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 7.6 Hz, 2H), 7.05 – 7.00 (m, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.45 (s, 1H), 2.63 (td, *J* = 7.3, 1.2 Hz, 2H), 2.36 – 2.29 (m, 5H), 2.23 (s, 3H), 1.76 – 1.66 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 139.38, 136.99, 136.97, 136.24, 134.06, 129.54, 128.97, 128.68, 128.40, 127.76, 119.71, 39.19, 23.49, 21.29, 21.16, 16.33.

**HRMS** (APCI) calcd for $C_{20}H_{22}N$ ($M+H^+$): 276.1747; found: 276.1752.



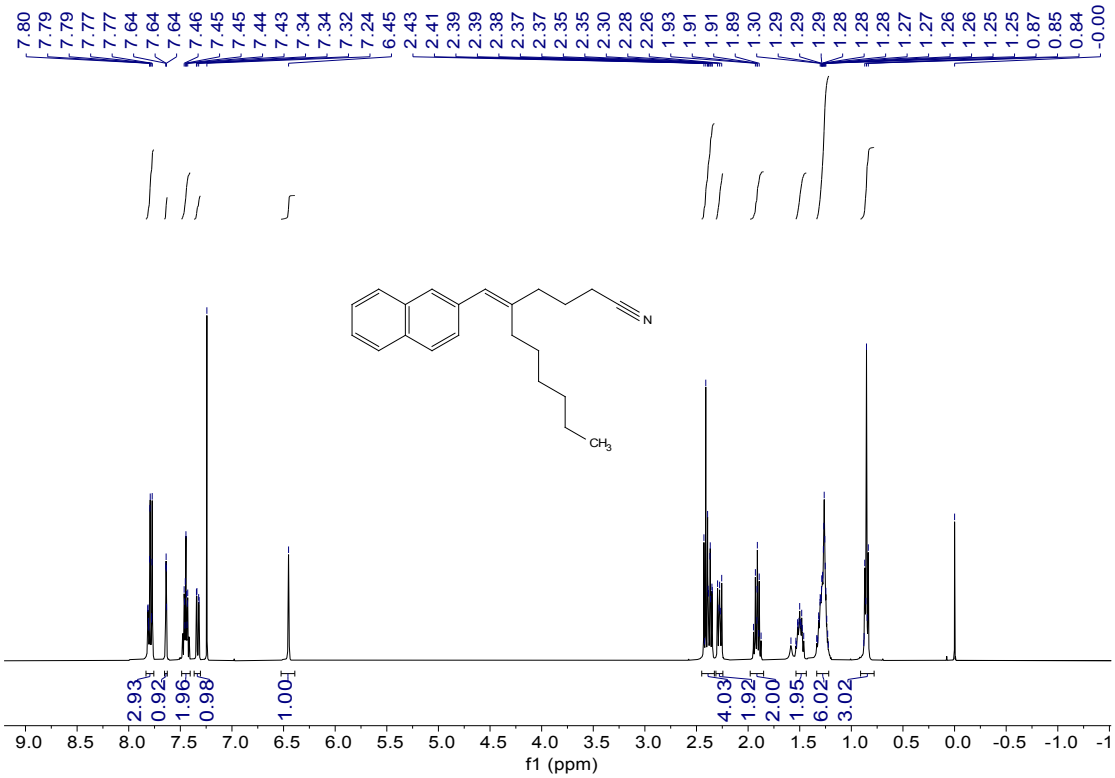



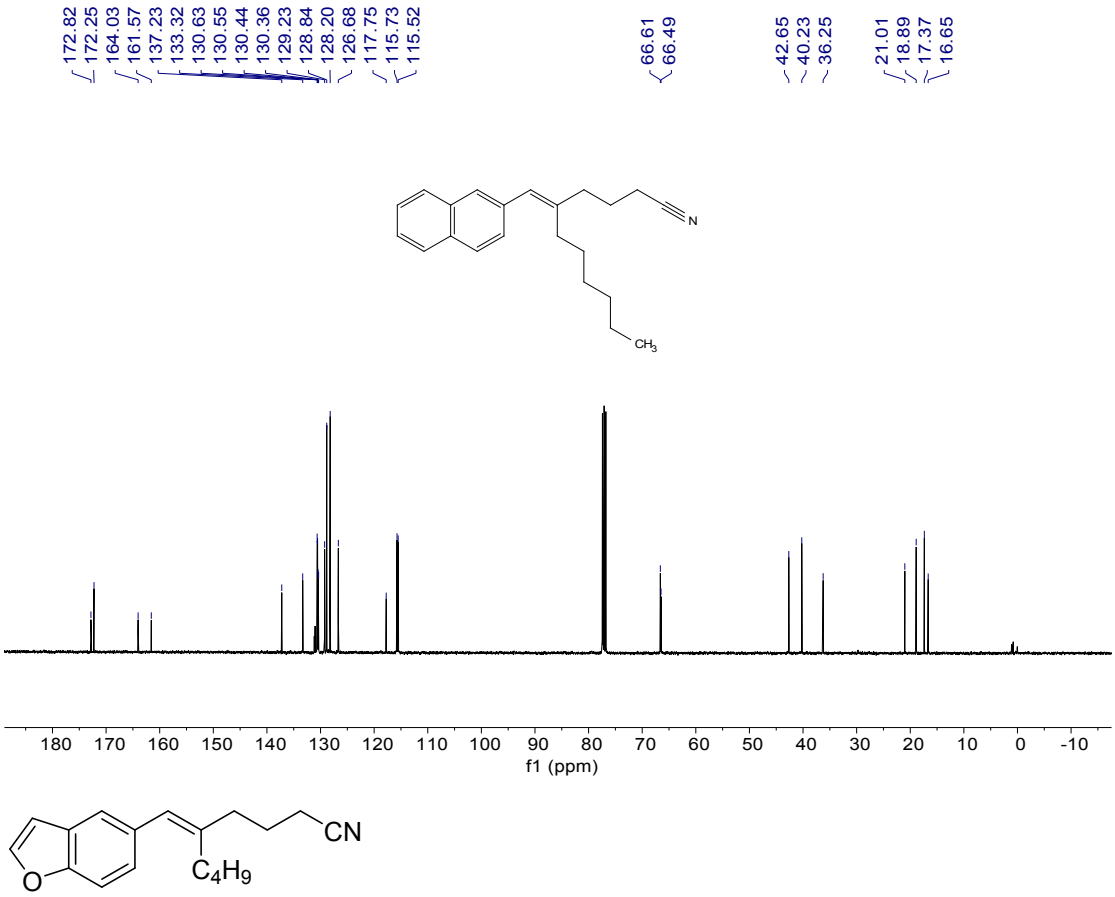

**(E)-5-(naphthalen-2-ylmethylene)undecanenitrile (3o)**

Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.84 – 7.72 (m, 3H), 7.69 – 7.59 (m, 1H), 7.49 – 7.37 (m, 2H), 7.34 (d, *J* = 1.7 Hz, 1H), 6.45 (s, 1H), 2.47 – 2.32

(m, 4H), 2.30 – 2.24 (m, 2H), 1.98 – 1.88 (m, 2H), 1.53 – 1.46 (m, 2H), 1.32 – 1.22 (m, 6H), 0.88 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 141.49, 135.45, 133.39, 132.03, 127.85, 127.64, 127.60, 127.30, 127.09, 126.70, 126.07, 125.62, 119.74, 35.92, 31.65, 30.49, 29.42, 28.32, 23.84, 22.65, 16.69, 14.10.

**HRMS** (APCI) calcd for $C_{22}H_{28}N$ ($M+H^+$): 306.2216; found: 306.2219.





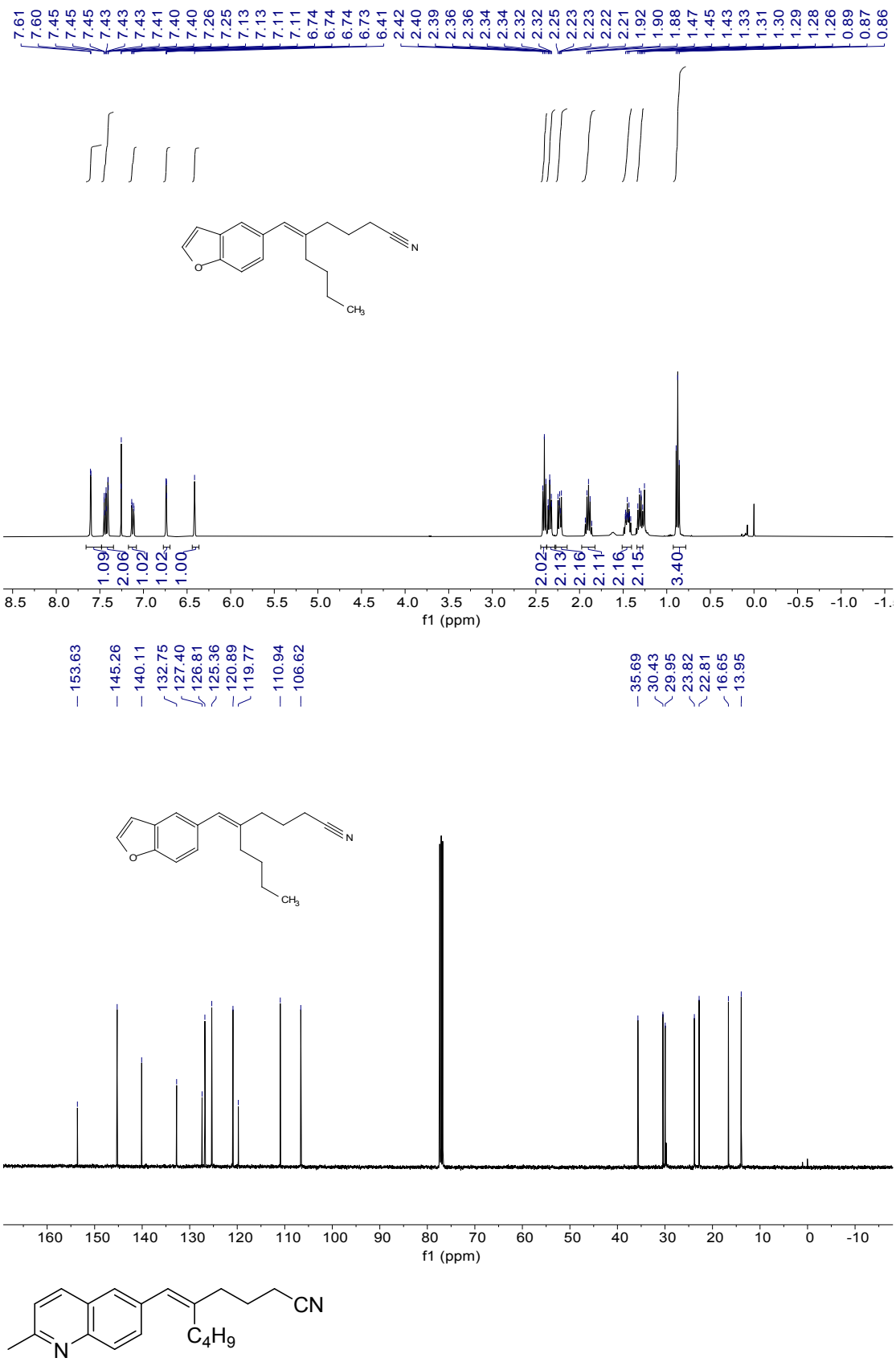




**(E)-5-(benzofuran-5-ylmethylene)nonanenitrile (3p)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.12 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.74 (dd, *J* = 2.1, 1.0 Hz, 1H), 6.41 (s, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.34 (td, *J* = 7.5, 1.2 Hz, 2H), 2.27 – 2.21 (m, 2H), 2.00 – 1.85 (m, 2H), 1.50 – 1.40 (m, 2H), 1.37 – 1.27 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.63, 145.26, 140.11, 132.75, 127.40, 126.81, 125.36, 120.89, 119.77, 110.94, 106.62, 35.69, 30.43, 29.95, 23.82, 22.81, 16.65, 13.95.

**HRMS** (APCI) calcd for $C_{18}H_{22}NO$ ($M+H^+$): 268.1696; found: 268.1697.

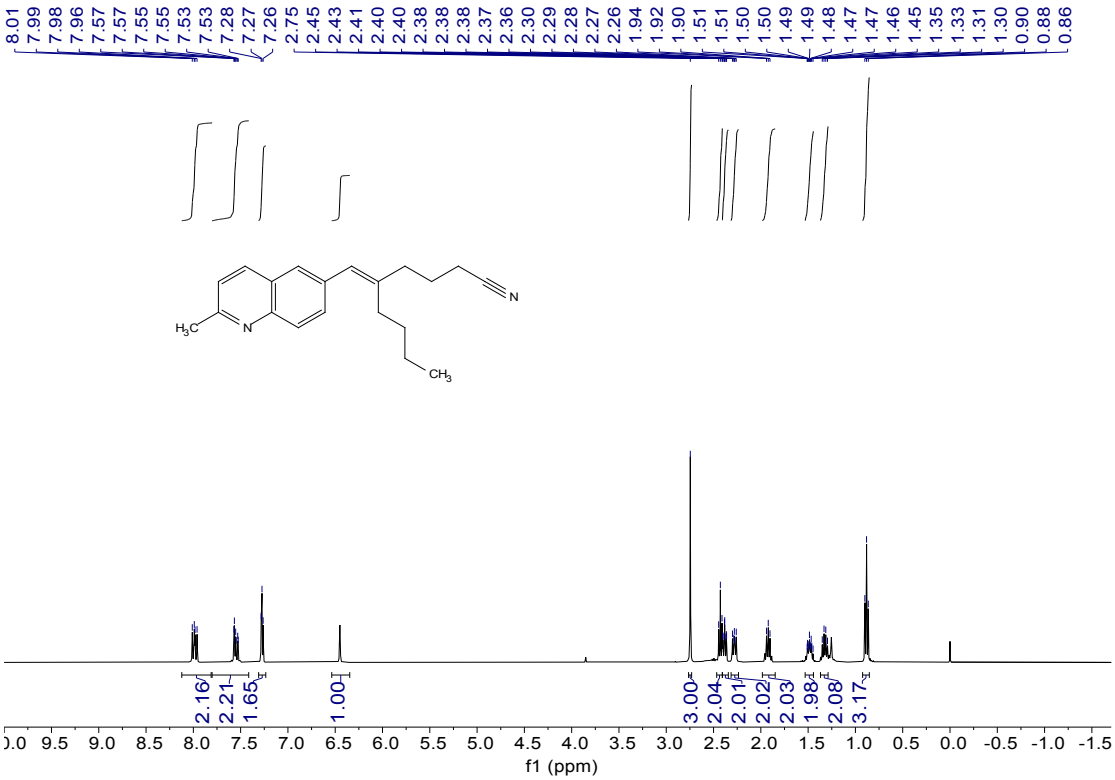


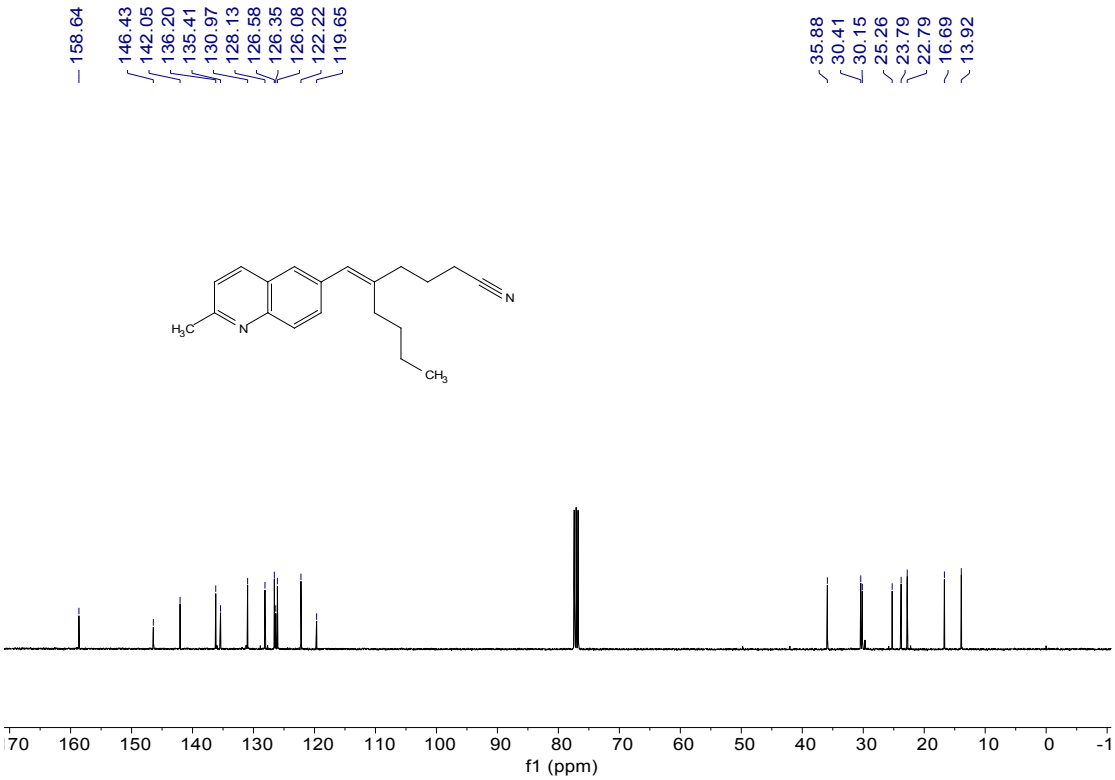

**(E)-5-((2-methylquinolin-6-yl)methylene)nonanenitrile (3q)**

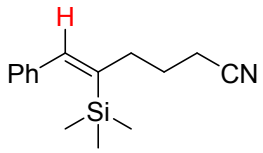
Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (dd, *J* =

11.7, 8.5 Hz, 2H), 7.63 – 7.49 (m, 2H), 7.27 (t, *J* = 4.2 Hz, 1H), 6.45 (s, 1H), 2.75 (s, 3H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.40 – 2.35 (m, 2H), 2.31 – 2.25 (m, 2H), 1.97 – 1.88 (m, 2H), 1.52 – 1.46 (m, 2H), 1.37 – 1.29 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.64, 146.43, 142.05, 136.20, 135.41, 130.97, 128.13, 126.58, 126.35, 126.08, 122.22, 119.65, 35.88, 30.41, 30.15, 25.26, 23.79, 22.79, 16.69, 13.92.

**HRMS** (APCI) calcd for $C_{20}H_{25}N_2$ ($M+H^+$): 293.2012; found: 293.2016.



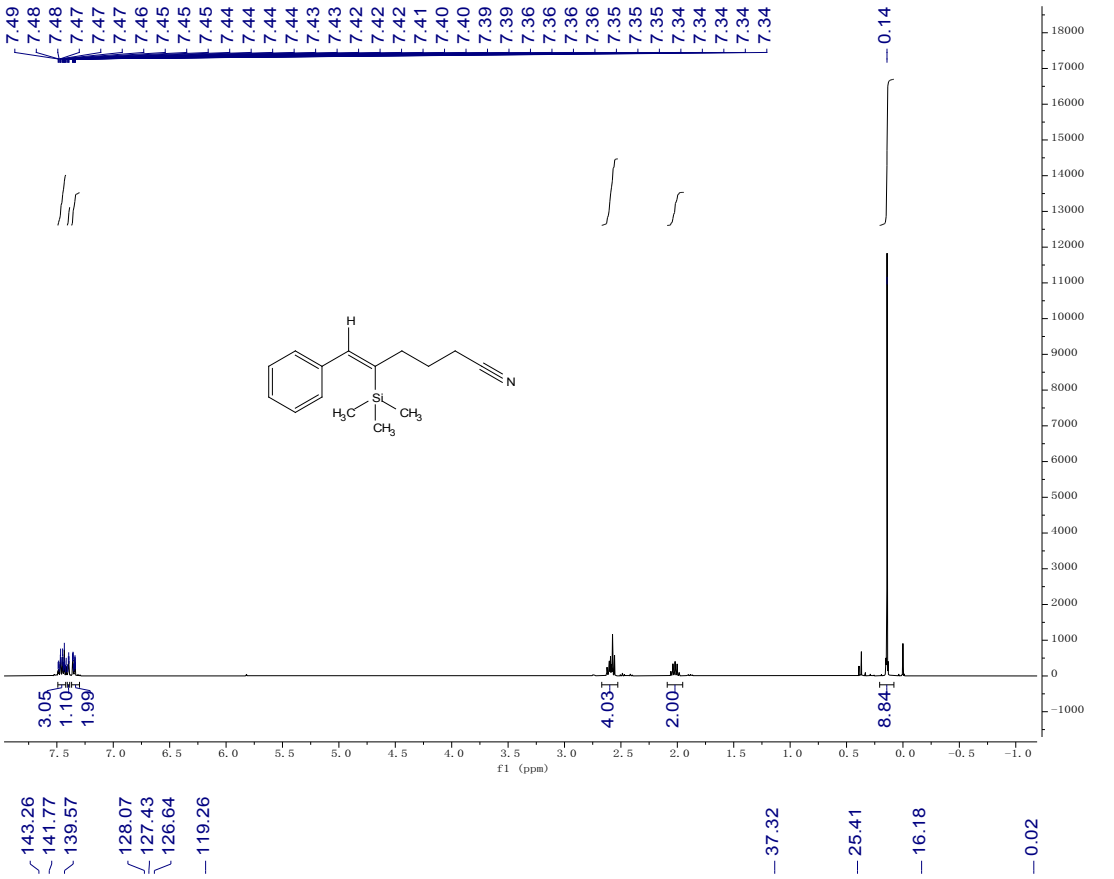


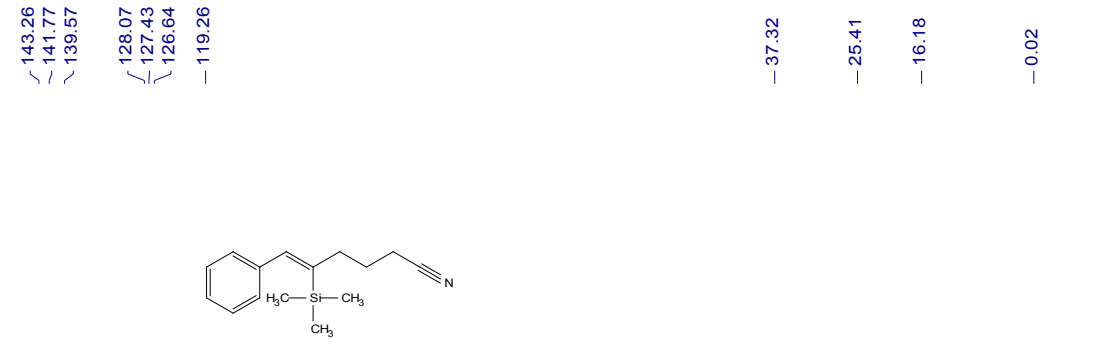



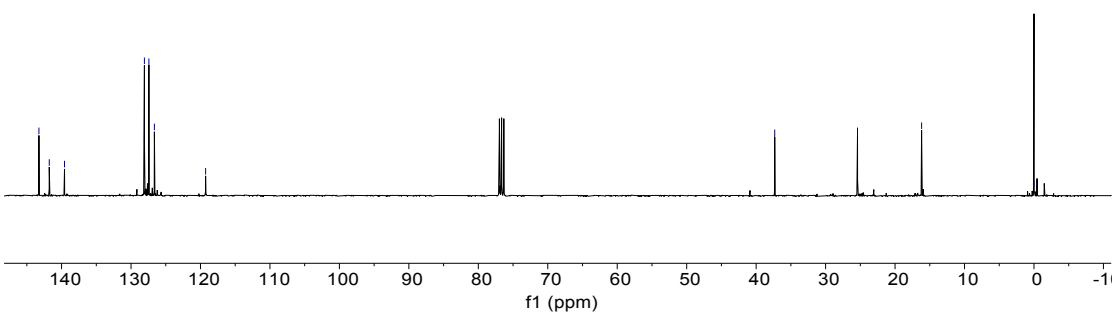

**(Z)-6-phenyl-5-(trimethylsilyl)hex-5-enenitrile (3r)**

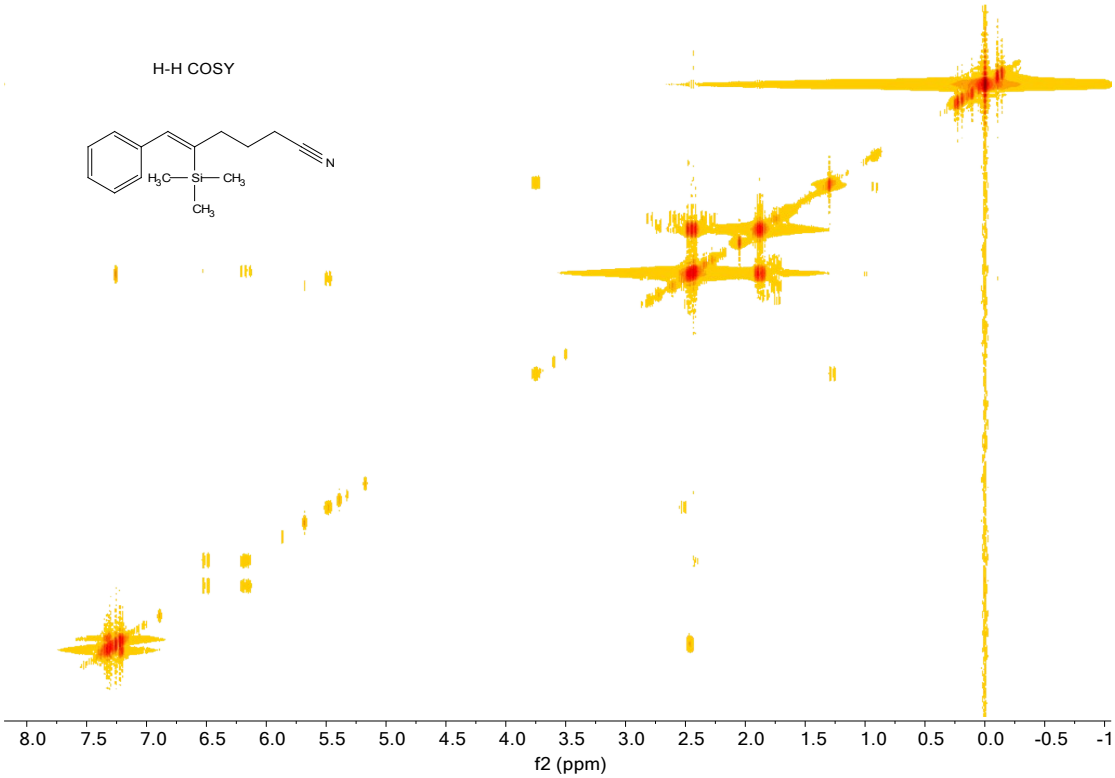
Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 3H), 7.25 (d, *J* = 1.7 Hz, 1H), 7.24 – 7.19 (m, 2H), 2.50 – 2.40 (m, 4H), 1.93 – 1.84 (m, 2H), 0.14 (s, 9H). **$^{13}$C NMR** (101 MHz, CDCl3) δ 143.26, 141.77, 139.57, 128.07, 127.43, 126.64, 119.26, 37.32, 25.41, 16.18, 0.02.

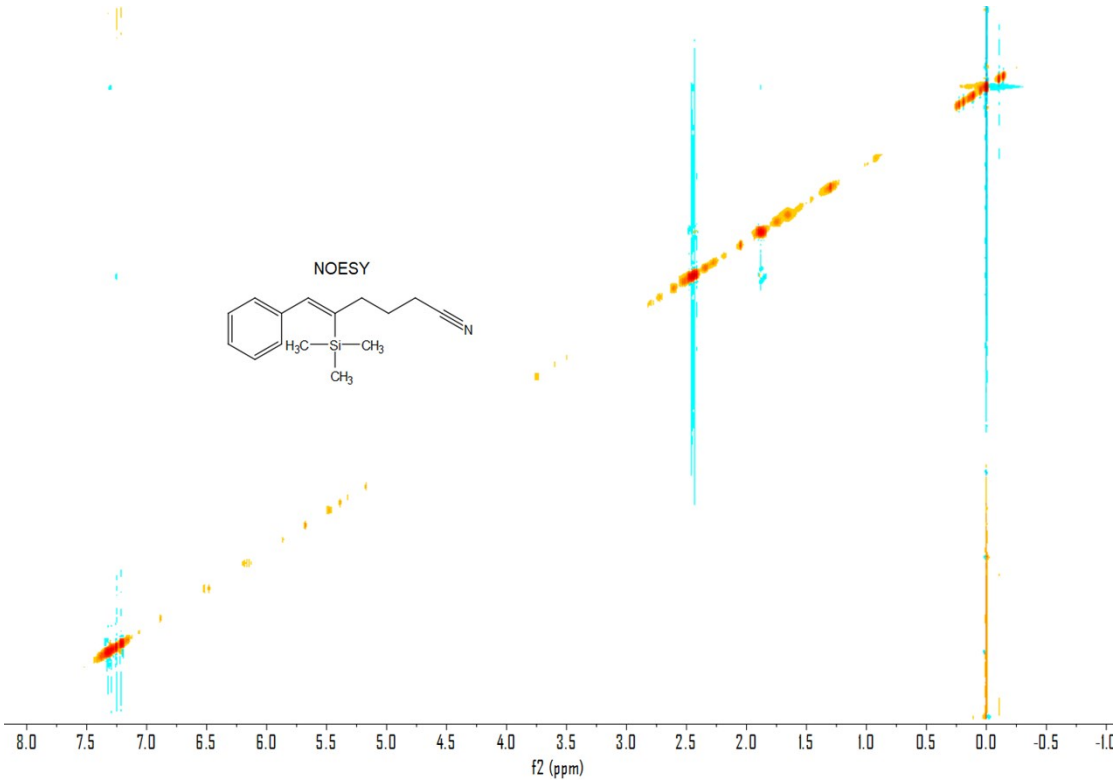
**HRMS** (APCI) calcd for $C_{15}H_{22}NSi$ ($M+H^+$): 244.1516; found: 244.1513.

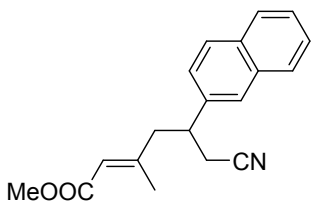

7.49 7.48 7.48 7.47 7.47 7.47 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.34
0.14
3.05
1.10
1.99
4.03
2.00
8.84
f1 (ppm)


143.26
141.77
139.57
128.07
127.43
126.64
119.26
37.32
25.41
16.18
0.02


f1 (ppm)



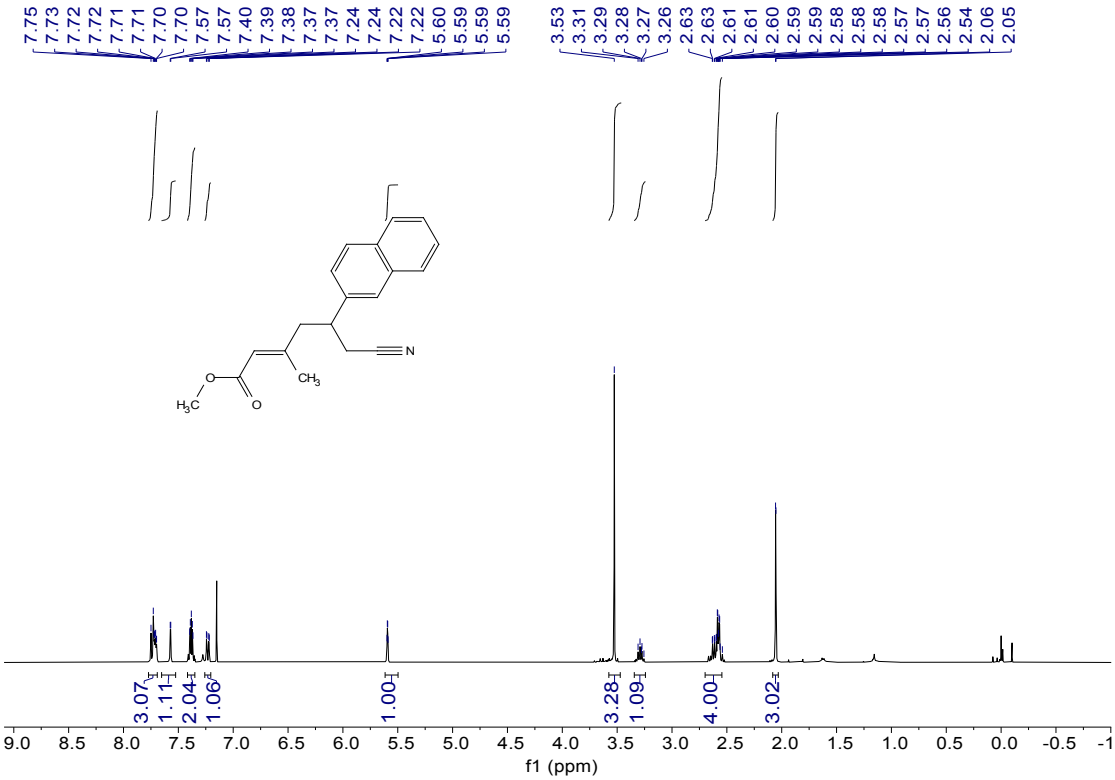



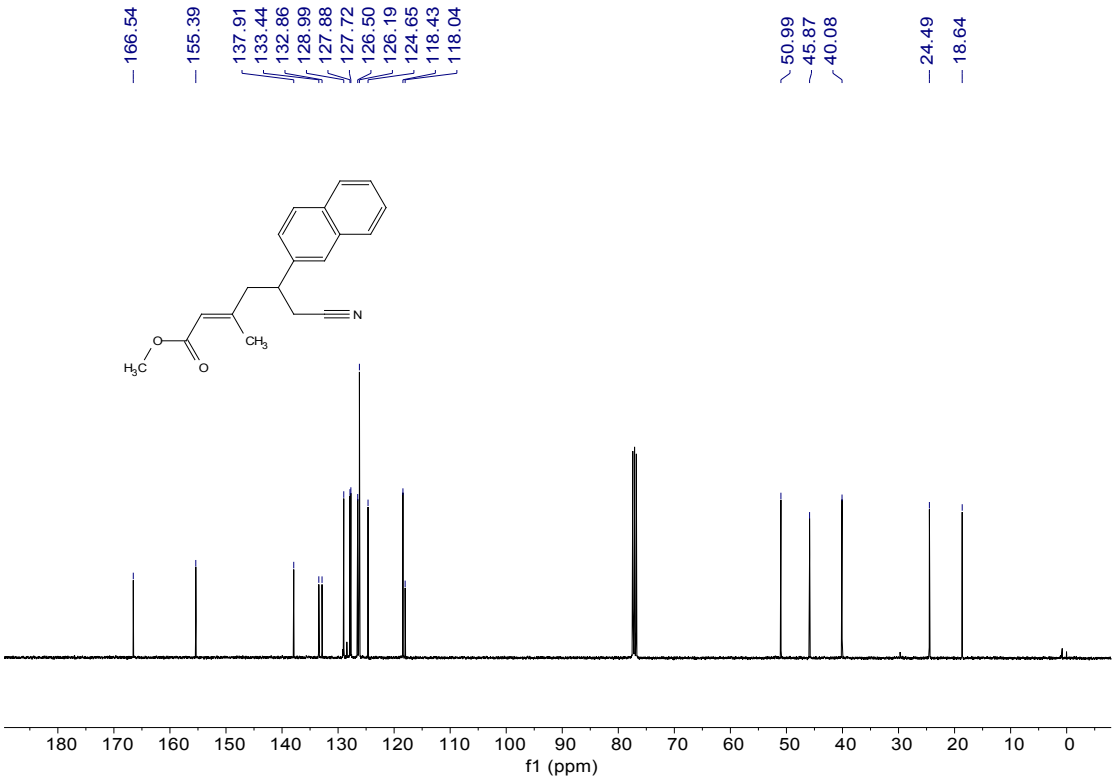



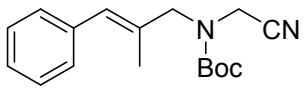

**methyl (E)-6-cyano-3-methyl-5-(naphthalen-2-yl)hex-2-enoate (3s)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 3H), 7.57 (d, *J* = 1.9 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.23 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.59 (q, *J* = 1.2 Hz, 1H), 3.53 (s, 3H), 3.34 – 3.22 (m, 1H), 2.71 – 2.54 (m, 4H), 2.05 (d, *J* = 1.3 Hz, 3H).**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.54, 155.39, 137.91, 133.44, 132.86, 128.99, 127.88, 127.72, 126.50, 126.19, 124.65, 118.43, 118.04, 50.99, 45.87, 40.08, 24.49, 18.64.

**HRMS** (APCI) calcd for $C_{19}H_{20}NO_2$ ($M+H^+$): 294.1489; found: 294.1487.



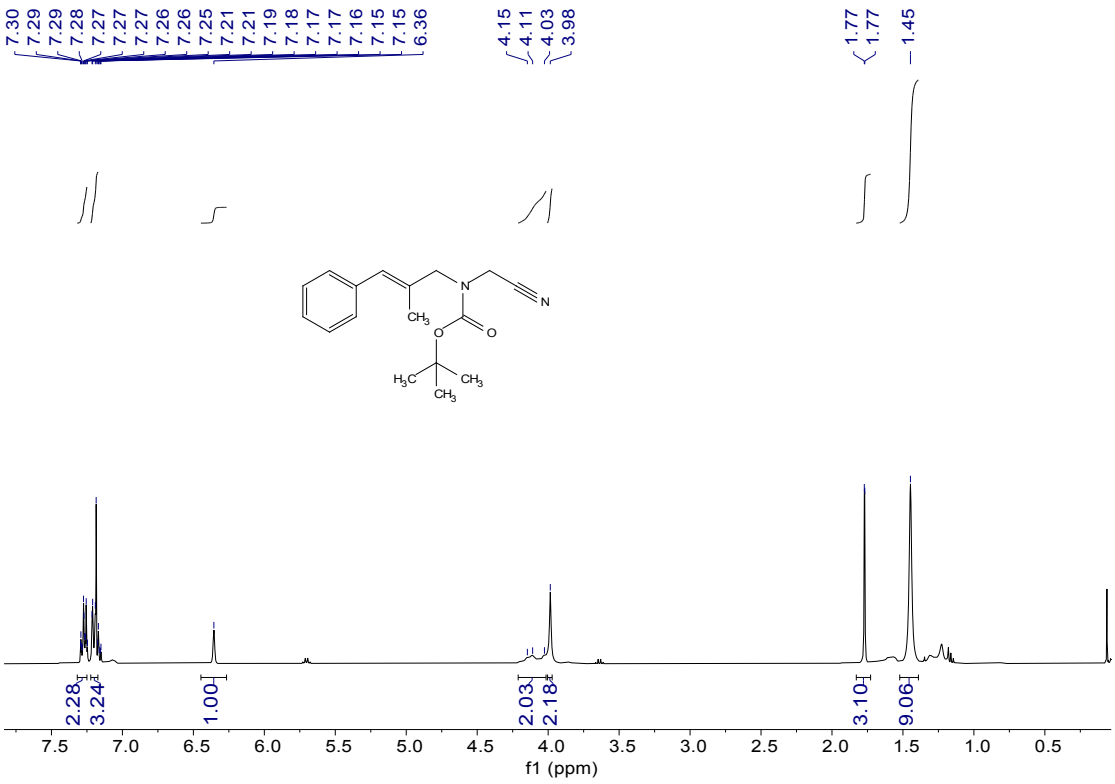


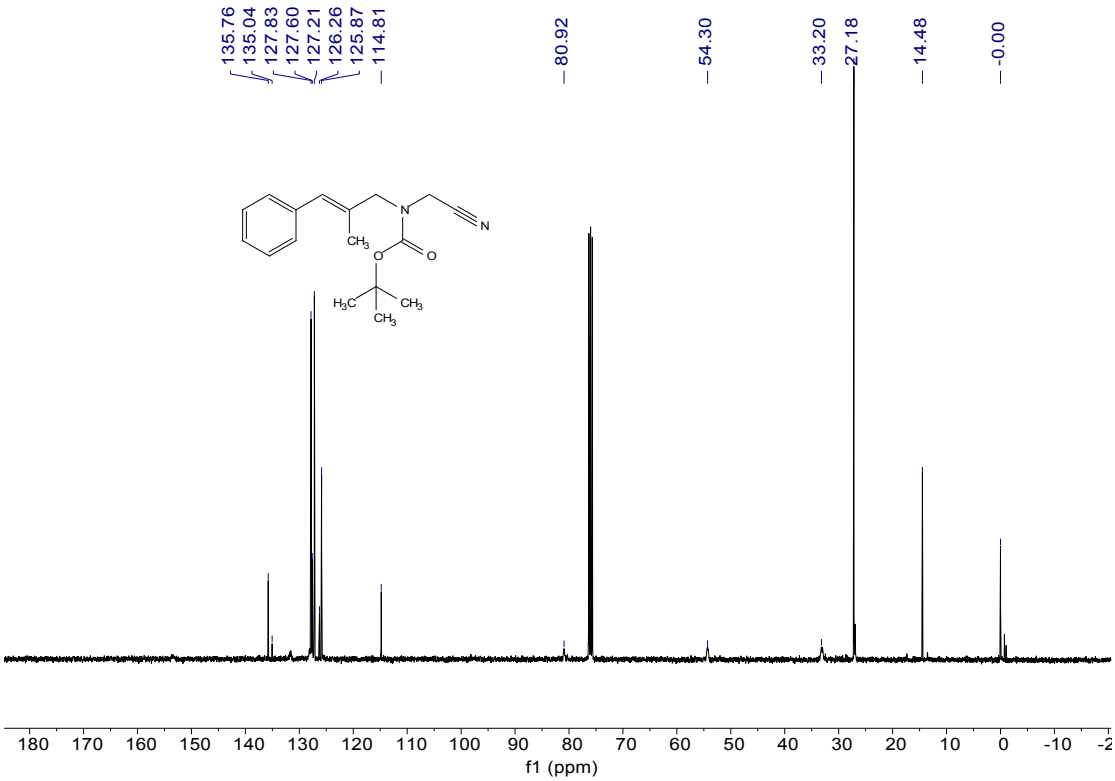



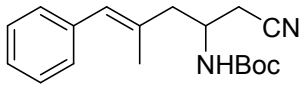

**tert-butyl (E)-(cyanomethyl)(2-methyl-3-phenylallyl)carbamate (3t)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 6.36 (s, 1H), 4.21 – 4.04 (m, 2H), 3.98 (s, 2H), 1.77 (d, *J* = 1.4 Hz, 3H), 1.45 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 135.76, 135.04, 127.83, 127.60, 127.21, 126.26, 125.87, 114.81, 80.92, 54.30, 33.20, 27.18, 14.48.

**HRMS** (APCI) calcd for $C_{17}H_{23}N_2O_2$ ($M+H^+$): 287.1754; found: 287.1757.



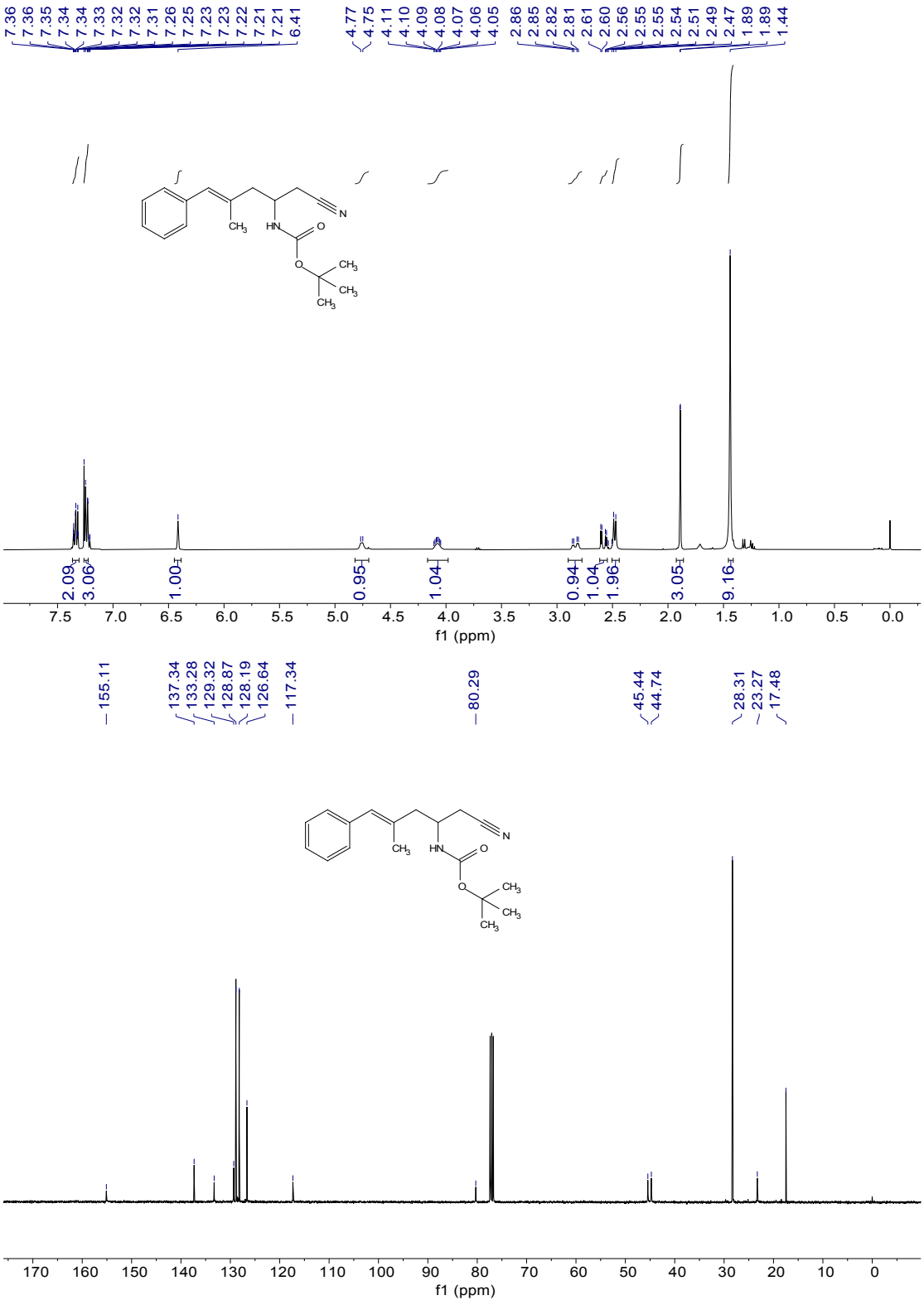



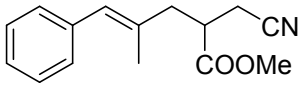

**tert-butyl (E)-(1-cyano-4-methyl-5-phenylpent-4-en-2-yl)carbamate (3u)**

Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 2H), 7.27 – 7.19 (m, 3H), 6.41 (s, 1H), 4.76 (d, *J* = 7.6 Hz, 1H), 4.15 – 4.02 (m, 1H), 2.89 – 2.76

(m, 1H), 2.63 – 2.54 (m, 1H), 2.48 (d, $J$ = 7.7 Hz, 2H), 1.89 (d, $J$ = 1.4 Hz, 3H), 1.44 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 155.11, 137.34, 133.28, 129.32, 128.87, 128.19, 126.64, 117.34, 80.29, 45.44, 44.74, 28.31, 23.27, 17.48.

**HRMS** (APCI) calcd for $C_{18}H_{25}N_2O_2$ ($M+H^+$): 301.1911; found: 301.1910.

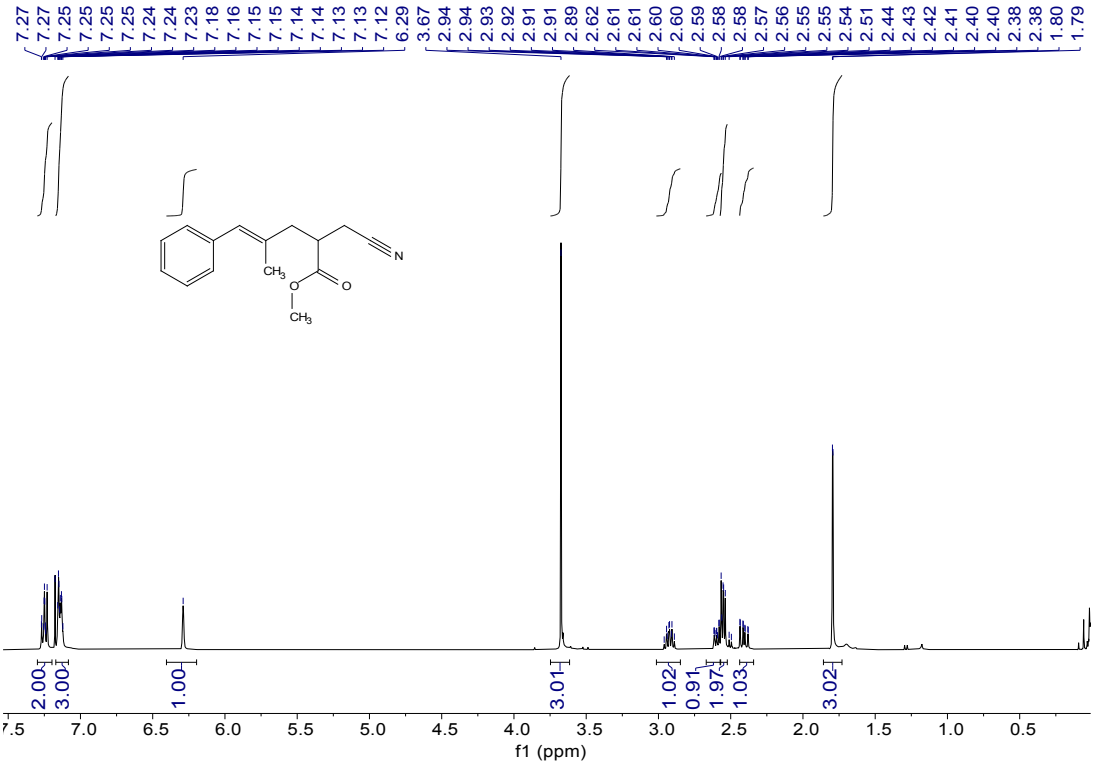


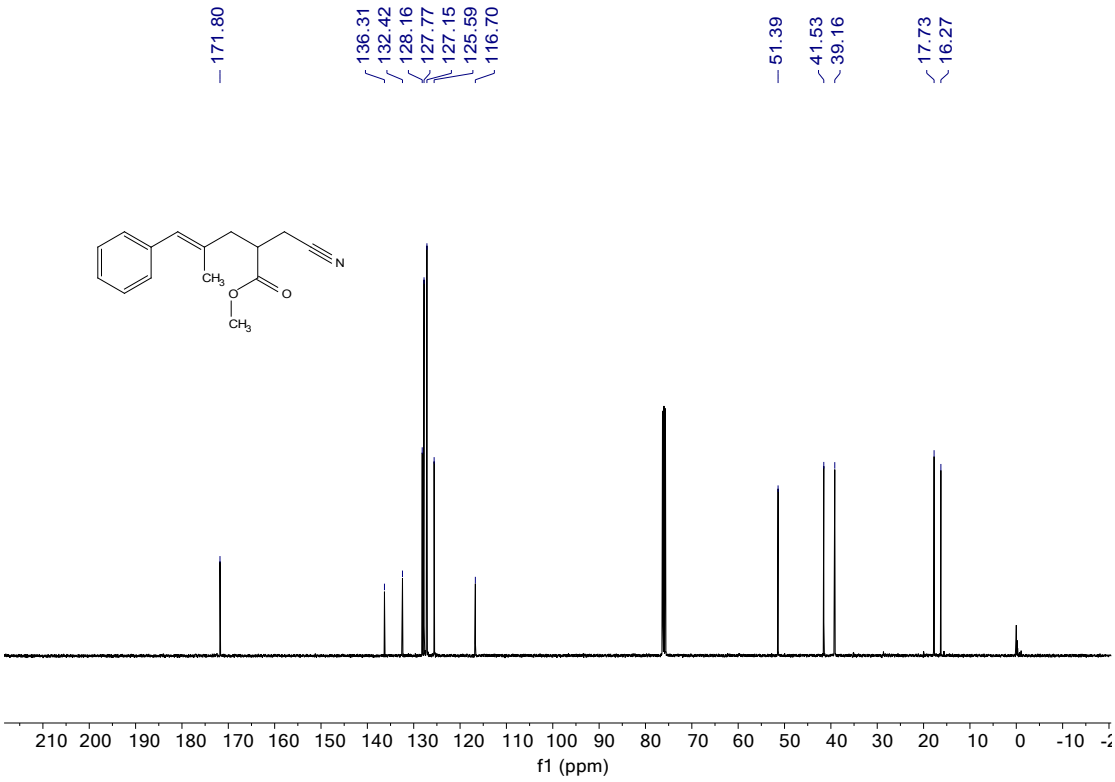


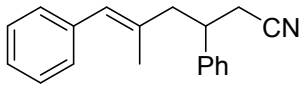

**methyl (E)-2-(cyanomethyl)-4-methyl-5-phenylpent-4-enoate (3v)**

Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.25 (dd, *J* = 8.0, 7.0 Hz, 2H), 7.18 – 7.08 (m, 3H), 6.29 (s, 1H), 3.67 (s, 3H), 3.00 – 2.87 (m, 1H), 2.58 (d, *J* = 1.1 Hz, 1H), 2.55 (dd, *J* = 6.6, 4.9 Hz, 2H), 2.45 – 2.35 (m, 1H), 1.79 (d, *J* = 1.4 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 171.80, 136.31, 132.42, 128.16, 127.77, 127.15, 125.59, 116.70, 51.39, 41.53, 39.16, 17.73, 16.27.

**HRMS** (APCI) calcd for $C_{15}H_{18}NO_2$ ($M+H^+$): 244.1332; found: 244.1336.



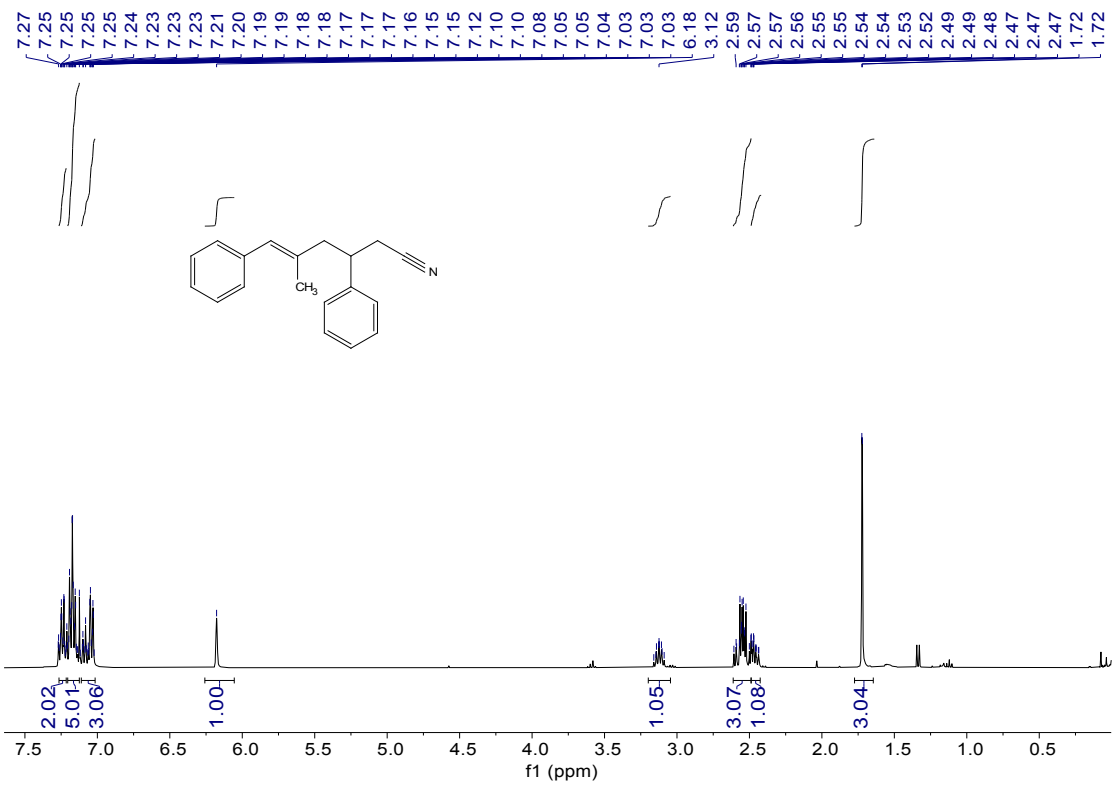


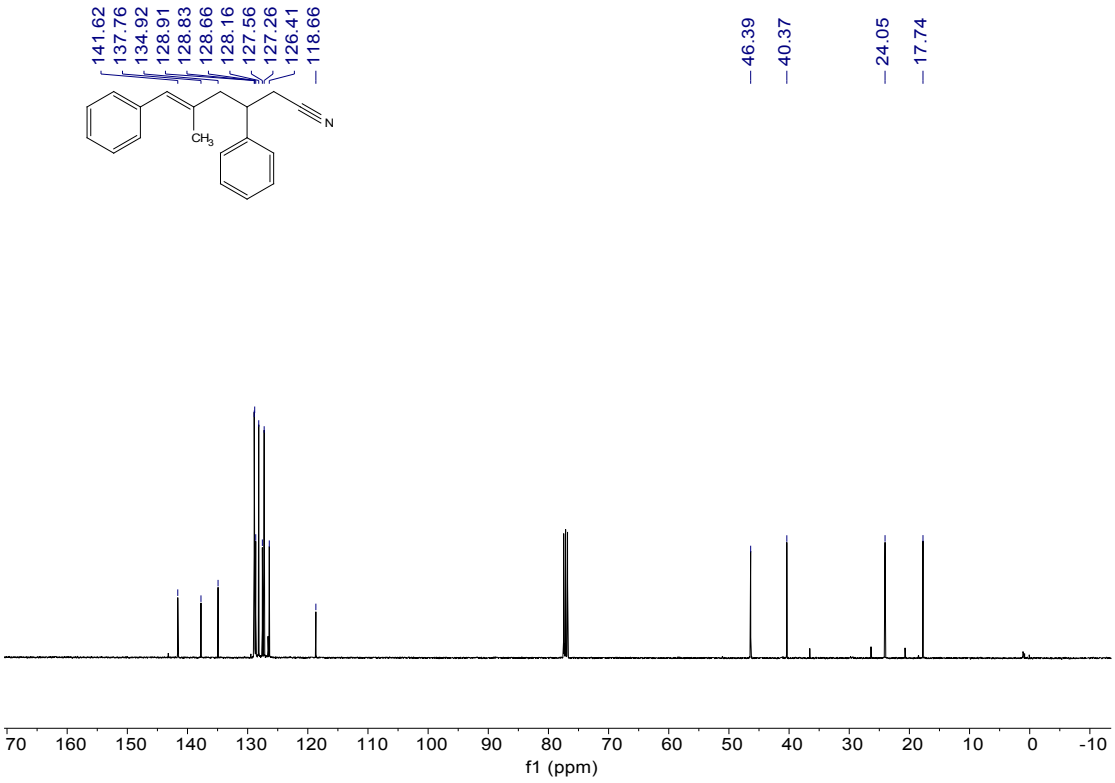



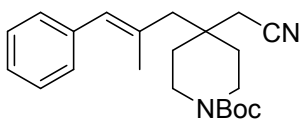

**(E)-5-methyl-3,6-diphenylhex-5-enenitrile (3w)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.28 – 7.22 (m, 2H), 7.21 – 7.13 (m, 5H), 7.11 – 7.01 (m, 3H), 6.18 (s, 1H), 3.19 – 3.07 (m, 1H), 2.62 – 2.52 (m, 3H), 2.51 – 2.42 (m, 1H), 1.72 (d, *J* = 1.4 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 141.62, 137.76, 134.92, 128.91, 128.83, 128.66, 128.16, 127.56, 127.26, 126.41, 118.66, 46.39, 40.37, 24.05, 17.74.

**HRMS** (APCI) calcd for $C_{19}H_{20}N$ ($M+H^+$): 262.1590; found: 262.1592.



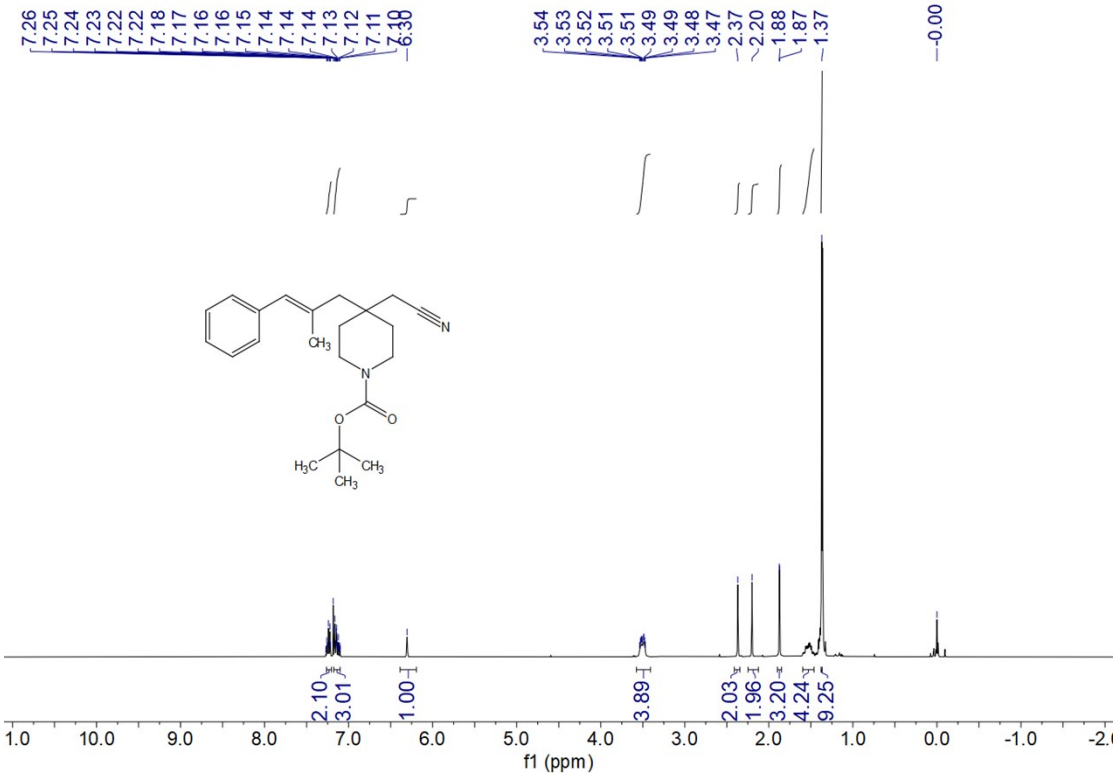



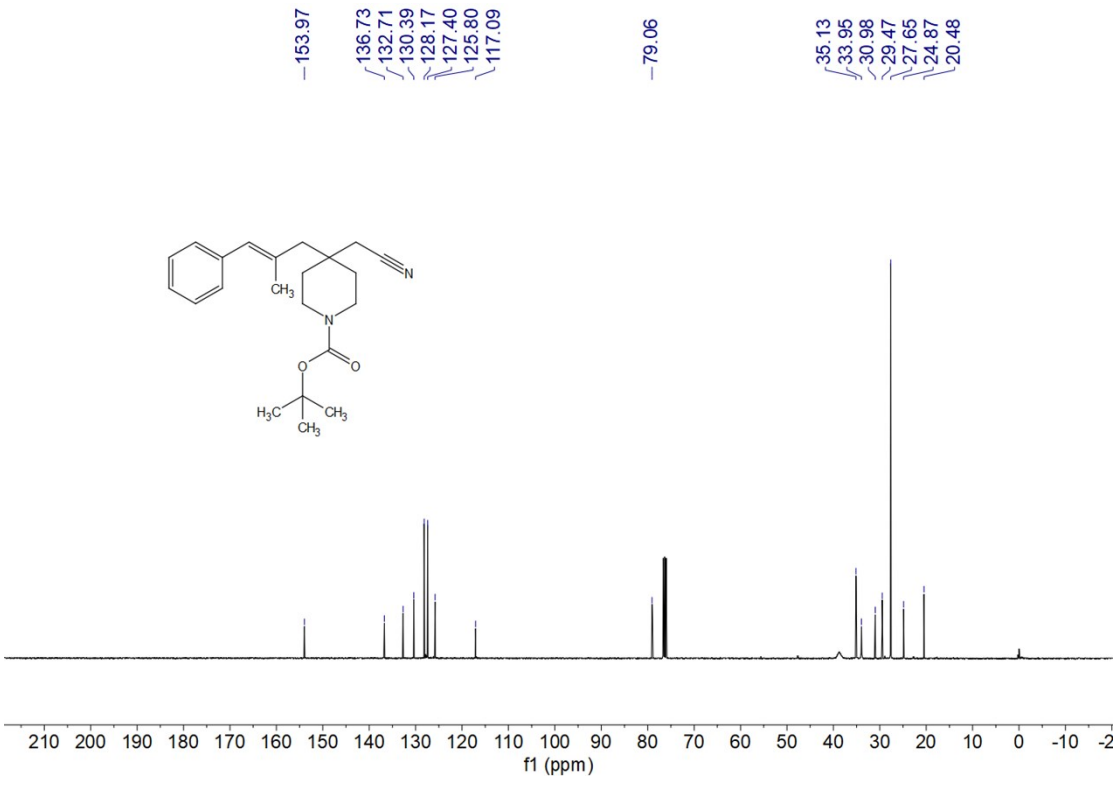

**tert-butyl (E)-4-(cyanomethyl)-4-(2-methyl-3-phenylallyl)piperidine-1-carboxylate (3x)**

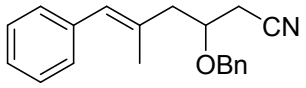
Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.07 (m, 3H), 6.30 (s, 1H), 3.57 – 3.45 (m, 4H), 2.37 (s, 2H), 2.20 (s, 2H), 1.87 (d, *J* =

1.4 Hz, 3H), 1.62 – 1.46 (m, 4H), 1.37 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.97, 136.73, 132.71, 130.39, 128.17, 127.40, 125.80, 117.09, 79.06, 35.13, 33.95, 30.98, 29.47, 27.65, 24.87, 20.48.

**HRMS** (APCI) calcd for $C_{22}H_{31}N_2O_2$ ($M+H^+$): 355.2380; found: 355.2385.



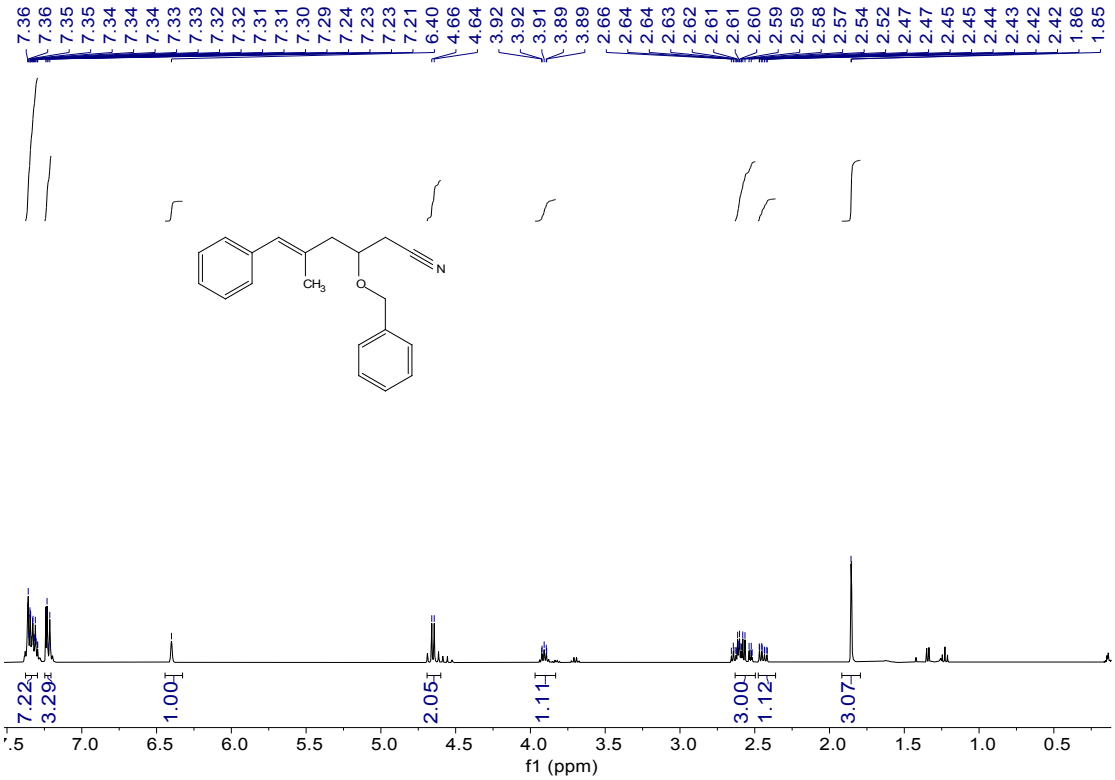



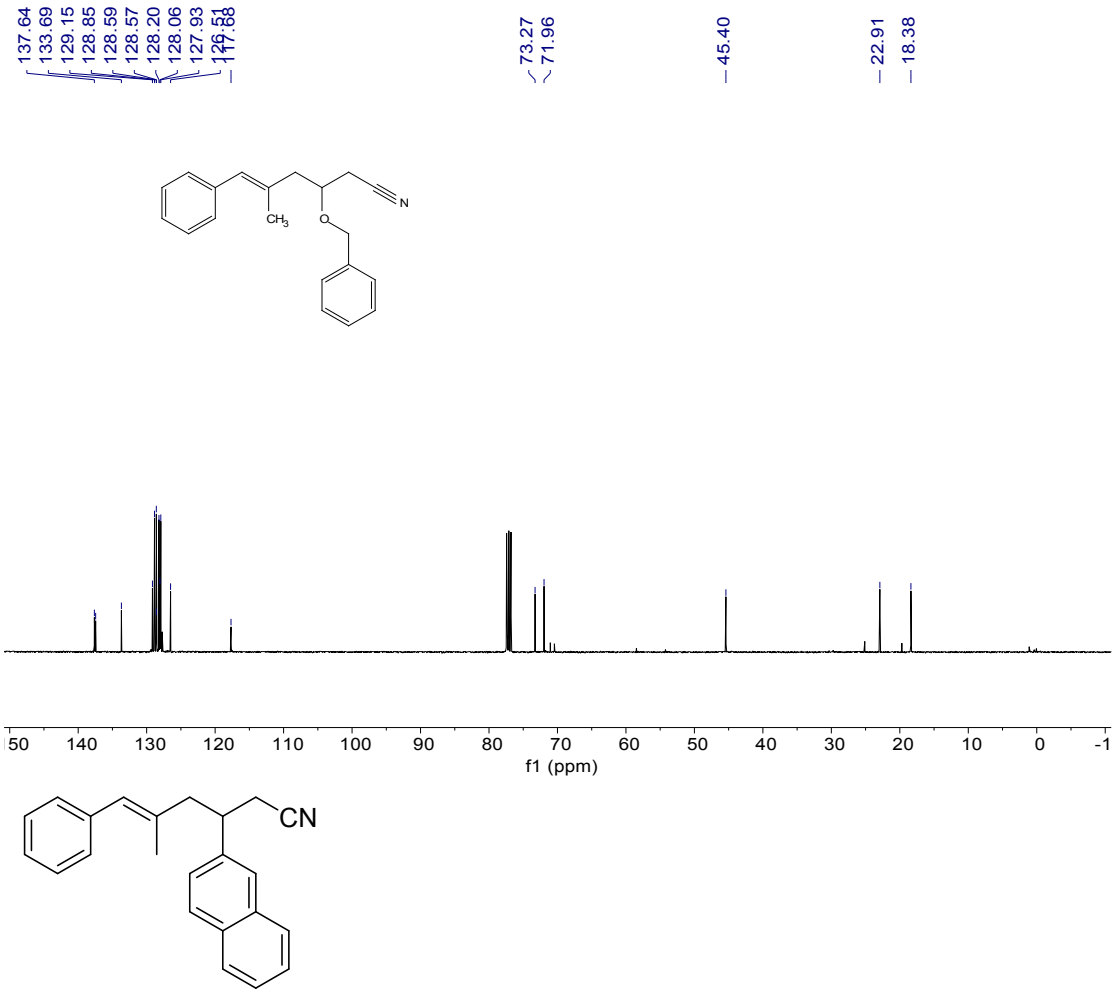



**(E)-3-(benzyloxy)-5-methyl-6-phenylhex-5-enenitrile (3y)**

Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.29 (m, 7H), 7.27 – 7.16 (m, 3H), 6.40 (s, 1H), 4.65 (d, *J* = 6.6 Hz, 2H), 3.96 – 3.85 (m, 1H), 2.66 – 2.53 (m, 3H), 2.49 – 2.38 (m, 1H), 1.85 (d, *J* = 1.4 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.64, 133.69, 129.15, 128.85, 128.59, 128.57, 128.20, 128.06, 127.93, 126.51, 117.68, 73.27, 71.96, 45.40, 22.91, 18.38.

**HRMS** (APCI) calcd for $C_{20}H_{22}NO$ ($M+H^+$): 292.1696; found: 292.1698.





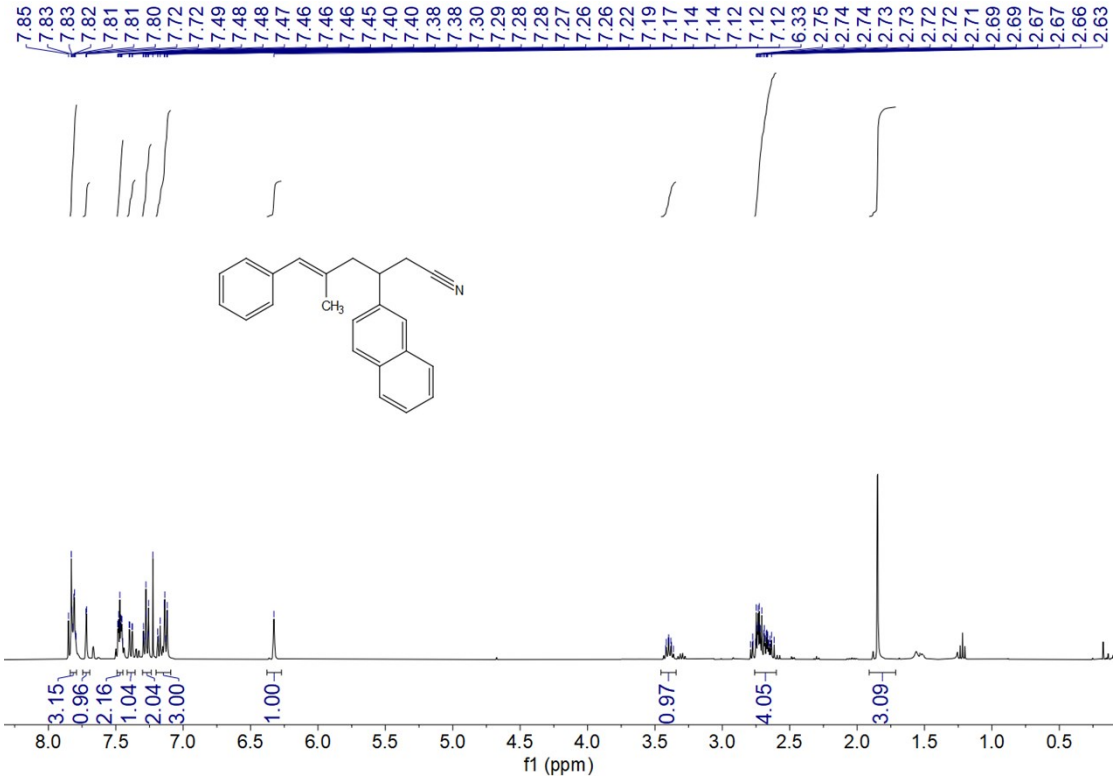


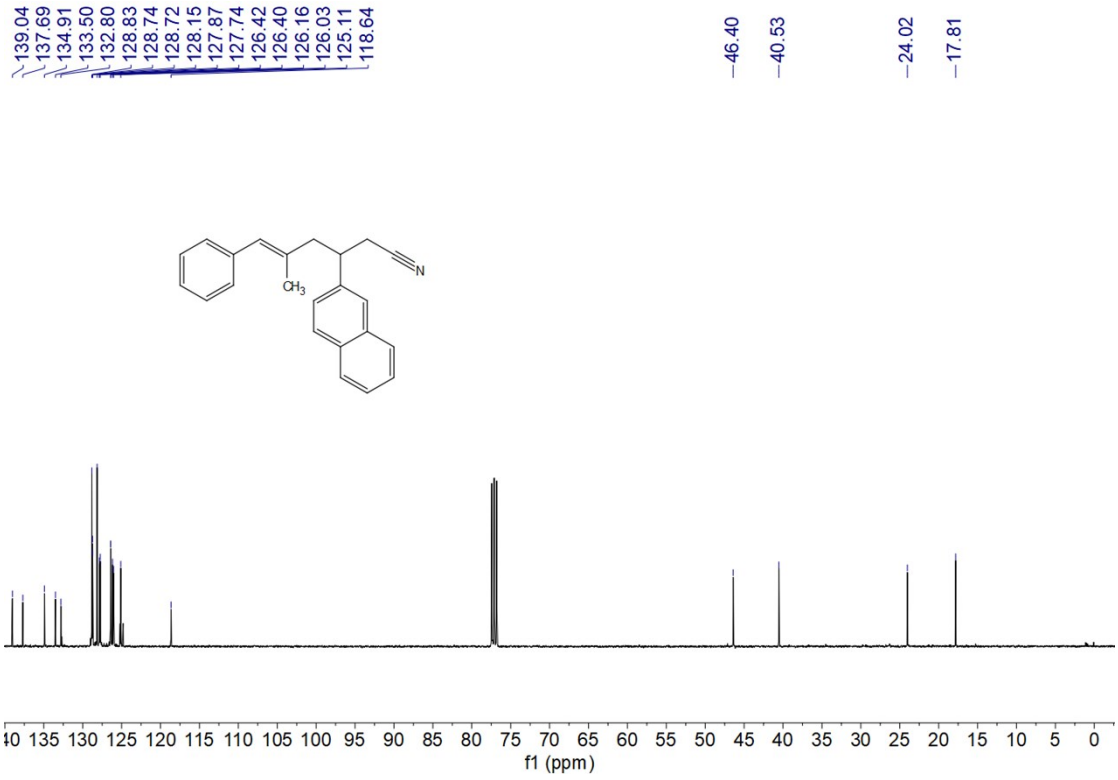


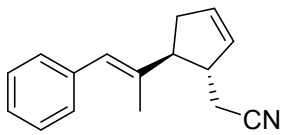
**(E)-5-methyl-3-(naphthalen-2-yl)-6-phenylhex-5-enenitrile (3z)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.85 – 7.79 (m, 3H), 7.72 (d, *J* = 1.8 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.39 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.19 – 7.10 (m, 3H), 6.33 (s, 1H), 3.44 – 3.35 (m, 1H), 2.76 – 2.61 (m, 4H), 1.85 (d, *J* = 1.4 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 139.04, 137.69, 134.91, 133.50, 132.80, 128.83, 128.74, 128.72, 128.15, 127.87, 127.74, 126.42, 126.40, 126.16, 126.03, 125.11, 118.64, 46.40, 40.53, 24.02, 17.81.

**HRMS** (APCI) calcd for $C_{23}H_{22}N$ ($M+H^+$): 312.1747; found: 312.1746.



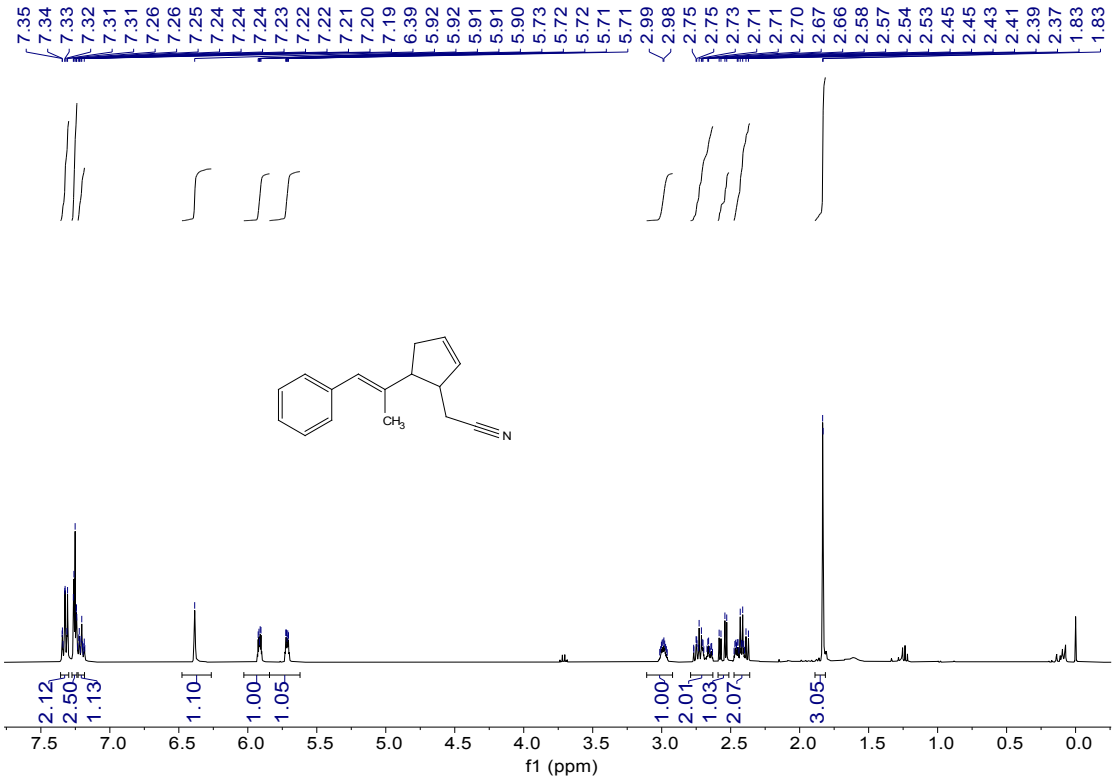



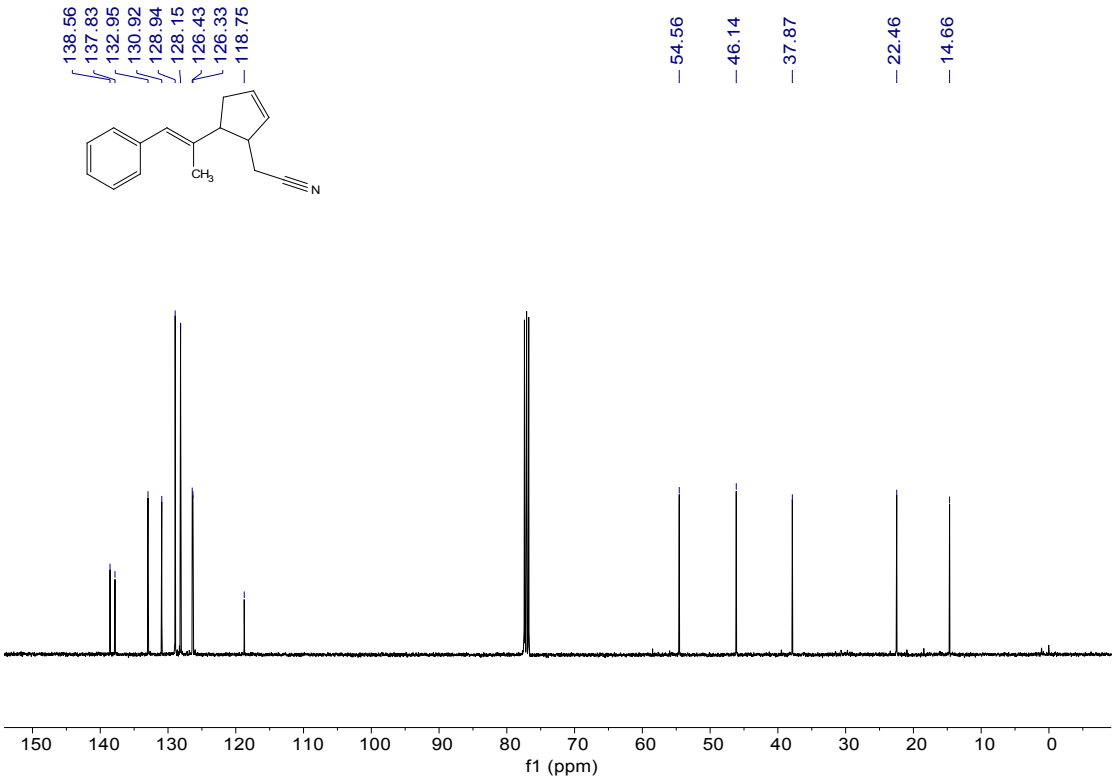



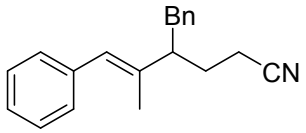

**(E)-2-(5-(1-phenylprop-1-en-2-yl)cyclopent-2-en-1-yl)acetonitrile (4a)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 2H), 7.28 – 7.23 (m, 2H), 7.23 – 7.17 (m, 1H), 6.39 (s, 1H), 5.96 – 5.87 (m, 1H), 5.77 – 5.65 (m, 1H), 2.99 (ddp, J = 7.3, 4.7, 2.5 Hz, 1H), 2.80 – 2.62 (m, 2H), 2.56 (dd, *J* = 16.7, 5.3 Hz, 1H), 2.48 – 2.36 (m, 2H), 1.83 (d, *J* = 1.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.56, 137.83, 132.95, 130.92, 128.94, 128.15, 126.43, 126.33, 118.75, 54.56, 46.14, 37.87, 22.46, 14.66.

**HRMS** (APCI) calcd for $C_{16}H_{18}N$ ($M+H^+$): 224.1434; found: 224.1435.



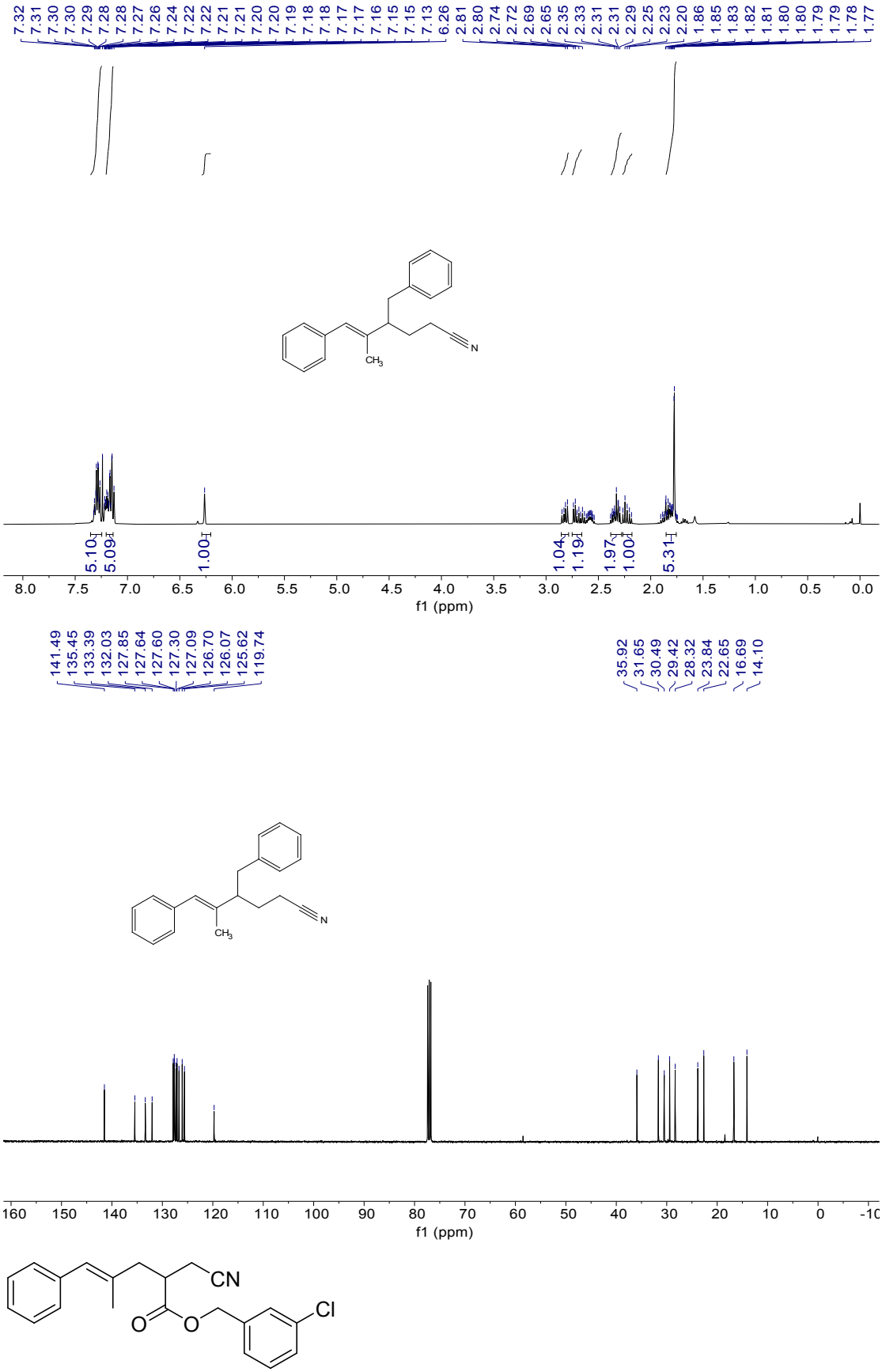



**(E)-4-benzyl-5-methyl-6-phenylhex-5-enenitrile (4b)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.24 – 7.16 (m, 5H), 7.13 – 7.02 (m, 5H), 6.16 (s, 1H), 2.72 (dd, *J* = 13.5, 7.8 Hz, 1H), 2.61 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.28 – 2.19 (m, 2H), 2.16 – 2.05 (m, 1H), 1.76 – 1.65 (m, 5H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.52, 136.50, 136.10, 127.91, 127.79, 127.66, 127.29, 127.02, 125.30, 125.18, 118.61, 49.54, 39.11, 26.72, 14.37, 12.72.

**HRMS** (APCI) calcd for $C_{20}H_{22}N$ ($M+H^+$): 276.1747; found: 276.1748.

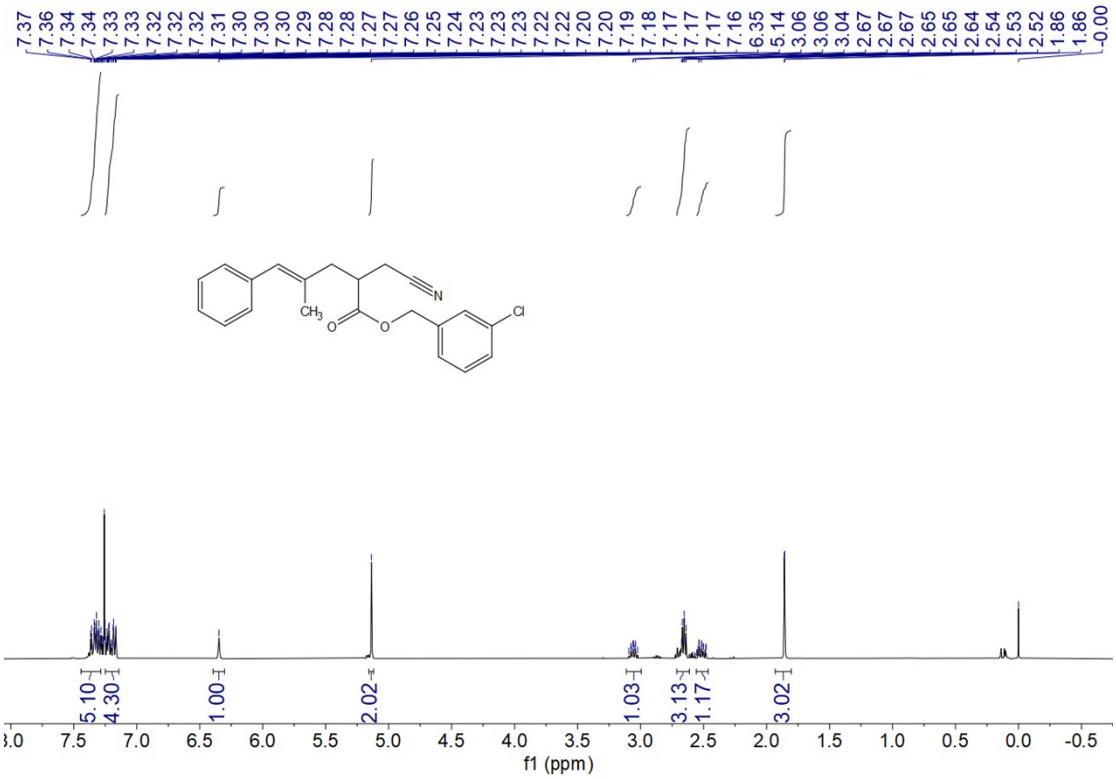


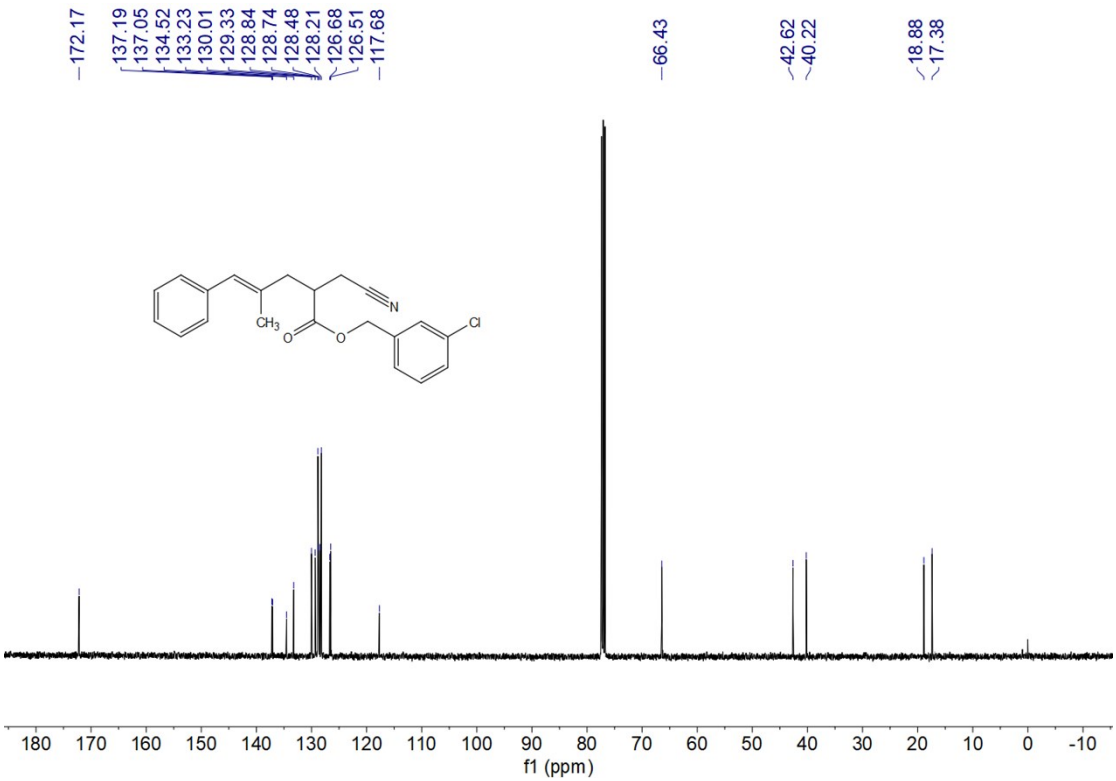

**3-chlorobenzyl (E)-2-(cyanomethyl)-4-methyl-5-phenylpent-4-enoate (4c)**

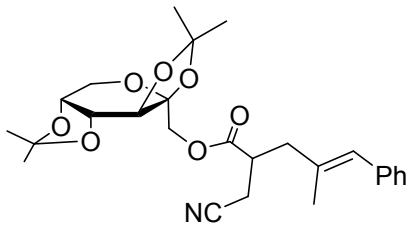
Following general procedure, as a sticky liquid. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m,

5H), 7.24 – 7.16 (m, 4H), 6.35 (s, 1H), 5.14 (s, 2H), 3.10 – 3.02 (m, 1H), 2.71 – 2.63 (m, 3H), 2.56 – 2.47 (m, 1H), 1.86 (d, $J$ = 1.5 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.17, 137.19, 137.05, 134.52, 133.23, 130.01, 129.33, 128.84, 128.74, 128.48, 128.21, 126.68, 126.51, 117.68, 66.43, 42.62, 40.22, 18.88, 17.38.

**HRMS** (APCI) calcd for $C_{21}H_{21}ClNO_2$ ($M+H^+$): 354.1255; found: 354.1259.



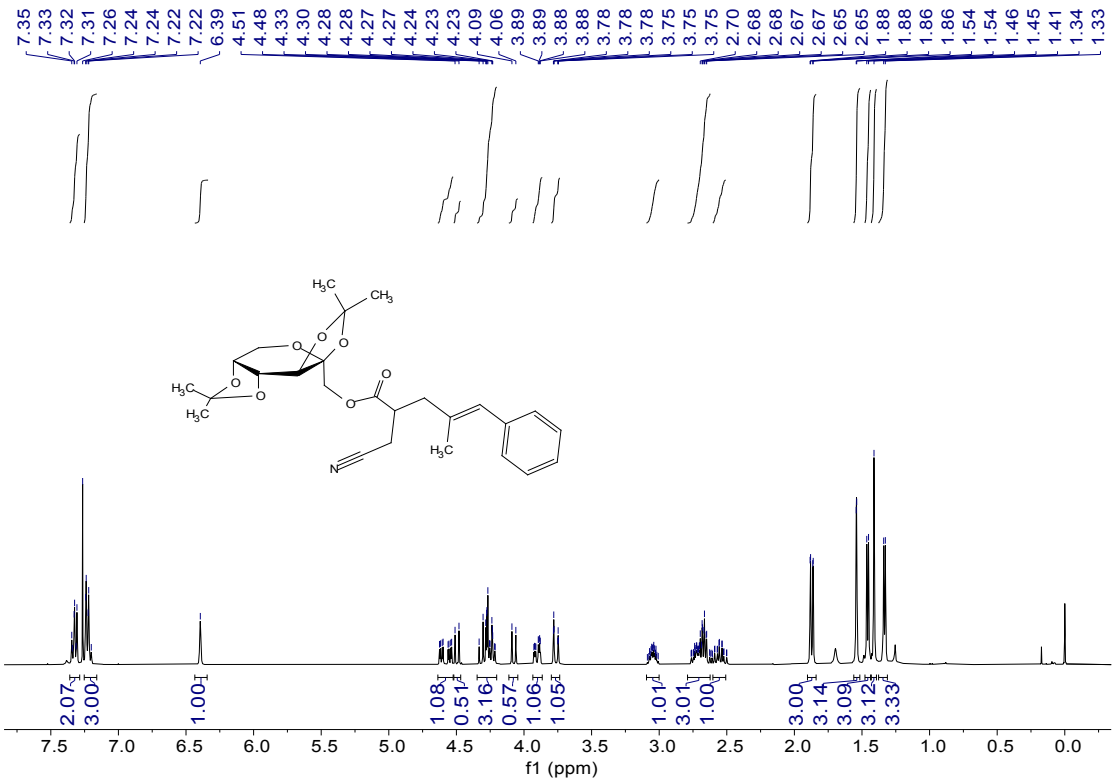


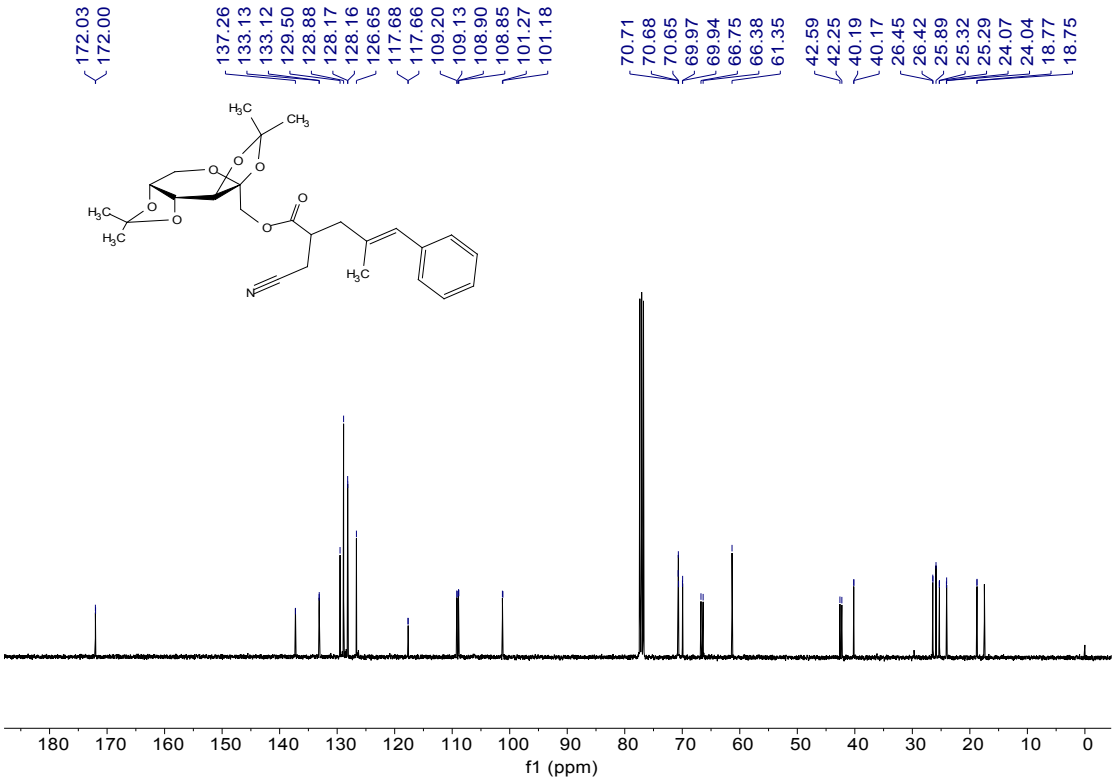



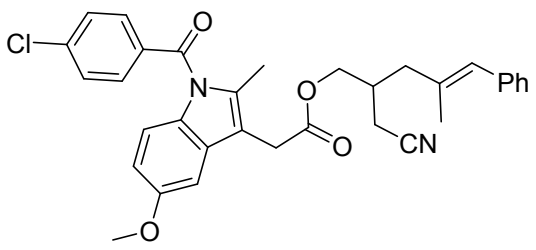

**((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl (E)-2-(cyanomethyl)-4-methyl-5-phenylpent-4-enoate (5a)**

Following general procedure, as a sticky liquid. ***d.r.* = 1:1**. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 6.39 (s, 1H), 4.64 – 4.53 (m, 1H), 4.50 (d, *J* = 11.7 Hz, 0.5 H), 4.35 – 4.20 (m, 3H), 4.07 (d, *J* = 11.6 Hz, 0.5 H), 3.94 – 3.87 (m, 1H), 3.79 – 3.73 (m, 1H), 3.09 – 3.00 (m, 1H), 2.77 – 2.63 (m, 3H), 2.61 – 2.50 (m, 1H), 1.90 – 1.84 (3H), 1.56 – 1.52 (3H), 1.48 – 1.44 (3H), 1.41 (s, 3H), 1.35 – 1.31 (3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.03, 172.00, 137.26, 133.13, 133.12, 129.50, 128.88, 128.17, 128.16, 126.65, 117.68, 117.66, 109.20, 109.13, 108.90, 108.85, 101.27, 101.18, 70.71, 70.68, 70.65, 69.97, 69.94, 66.75, 66.38, 61.35, 42.59, 42.25, 40.19, 40.17, 26.45, 26.42, 25.89, 25.32, 25.29, 24.07, 24.04, 18.77, 18.75.

**HRMS** (APCI) calcd for $C_{26}H_{34}NO_7$ ($M+H^+$): 472.2330; found: 472.2336.


7.35 7.33 7.32 7.31 7.26 7.24 7.24 7.22 7.22 6.39 4.51 4.48 4.33 4.30 4.28 4.28 4.27 4.27 4.24 4.23 4.23 4.09 4.06 3.89 3.89 3.88 3.88 3.78 3.78 3.78 3.75 3.75 3.75 2.70 2.68 2.68 2.67 2.67 2.65 2.65 1.88 1.88 1.86 1.86 1.54 1.54 1.46 1.45 1.41 1.34 1.33
2.07 3.00 1.00 1.08 0.51 3.16 0.57 1.06 1.05 1.01 3.01 1.00 3.00 3.14 3.09 3.12 3.33
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)

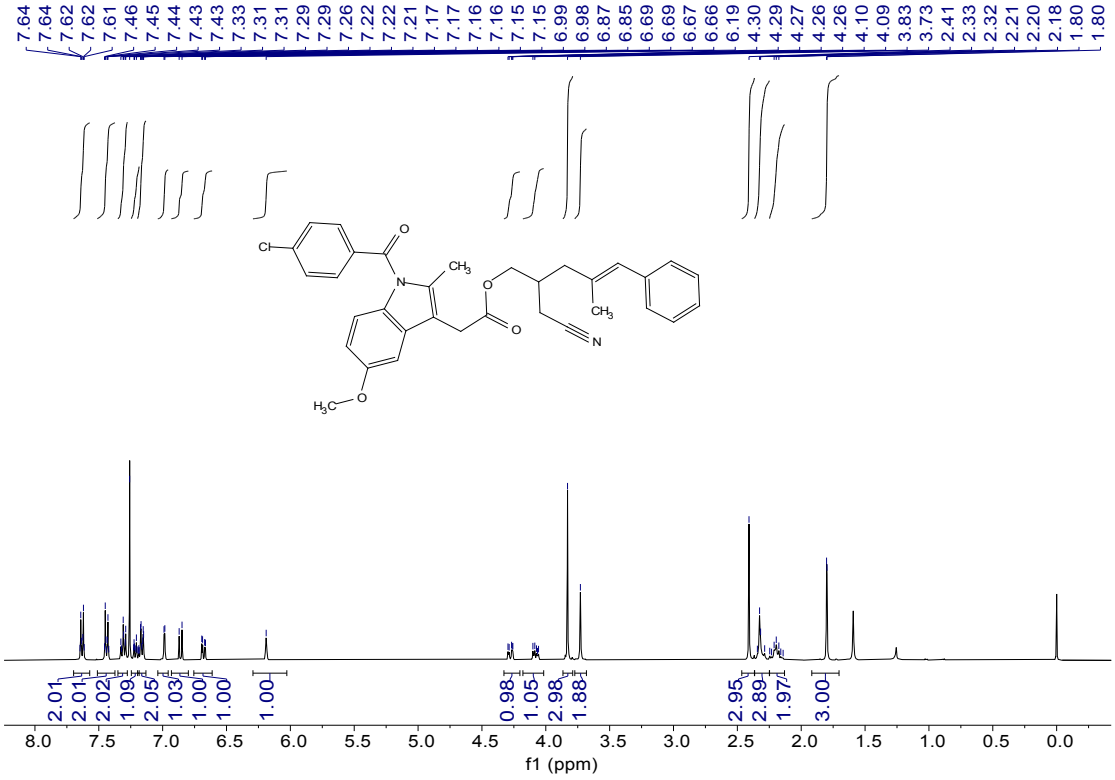

172.03 172.00 137.26 133.13 133.12 129.50 128.88 128.17 128.16 126.65 117.68 117.66 109.20 109.13 108.90 108.85 101.27 101.18 70.71 70.68 70.65 69.97 69.94 66.75 66.38 61.35 42.59 42.25 40.19 40.17 26.45 26.42 25.89 25.32 25.29 24.07 24.04 18.77 18.75
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

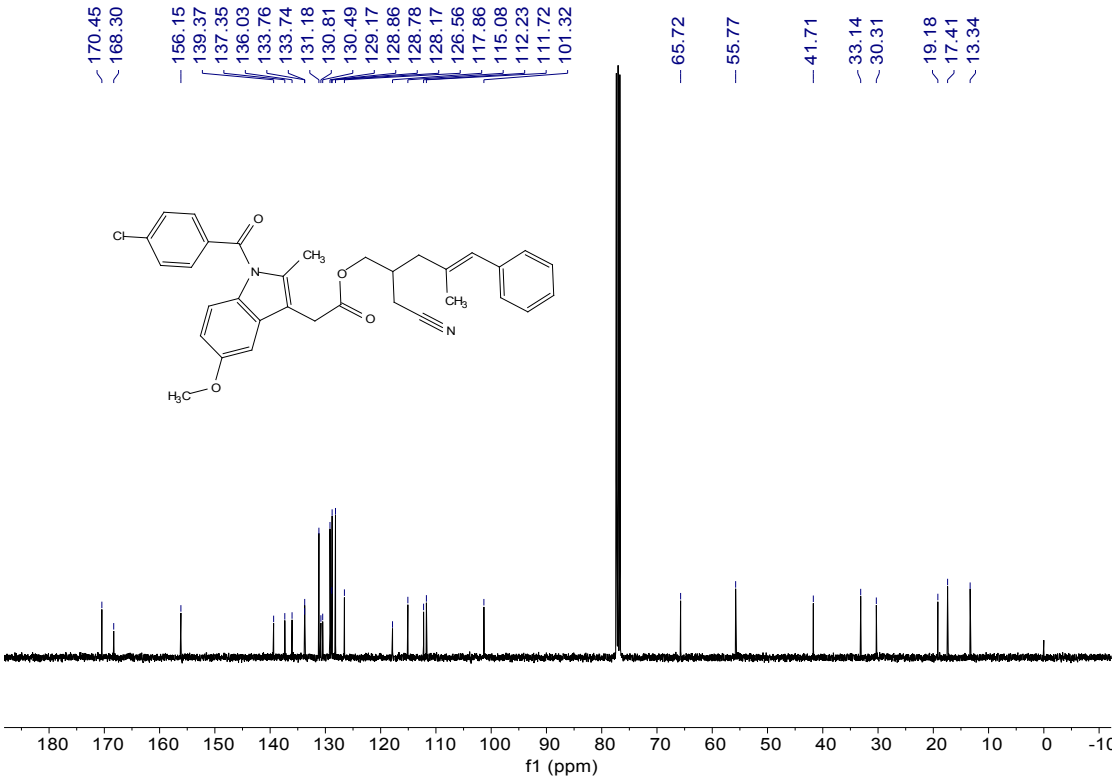

Cl
O
N
O
O
CN
Ph
O

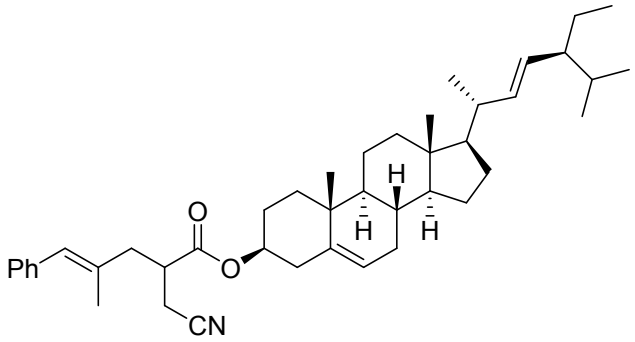
**(E)-2-(cyanomethyl)-4-methyl-5-phenylpent-4-en-1-yl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (5b)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.59 (m, 2H), 7.48 – 7.41 (m, 2H), 7.31 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.16 (dd, *J* = 8.1, 1.4 Hz, 2H), 6.99 (d, *J* = 2.6 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.19 (s, 1H), 4.34 – 4.24 (m, 1H), 4.08 (dd, *J* = 11.5, 6.2 Hz, 1H), 3.83 (s, 3H), 3.73 (s, 2H), 2.41 (s, 3H), 2.36 – 2.29 (m, 3H), 2.24 – 2.12 (m, 2H), 1.80 (d, *J* = 1.4 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 170.45, 168.30, 156.15, 139.37, 137.35, 136.03, 133.76, 133.74, 131.18, 130.81, 130.49, 129.17, 128.86, 128.78, 128.17, 126.56, 117.86, 115.08, 112.23, 111.72, 101.32, 65.72, 55.77, 41.71, 33.14, 30.31, 19.18, 17.41, 13.34.

**HRMS** (APCI) calcd for $C_{33}H_{32}ClN_2O_4$ ($M+H^+$): 555.2045; found: 555.2049.





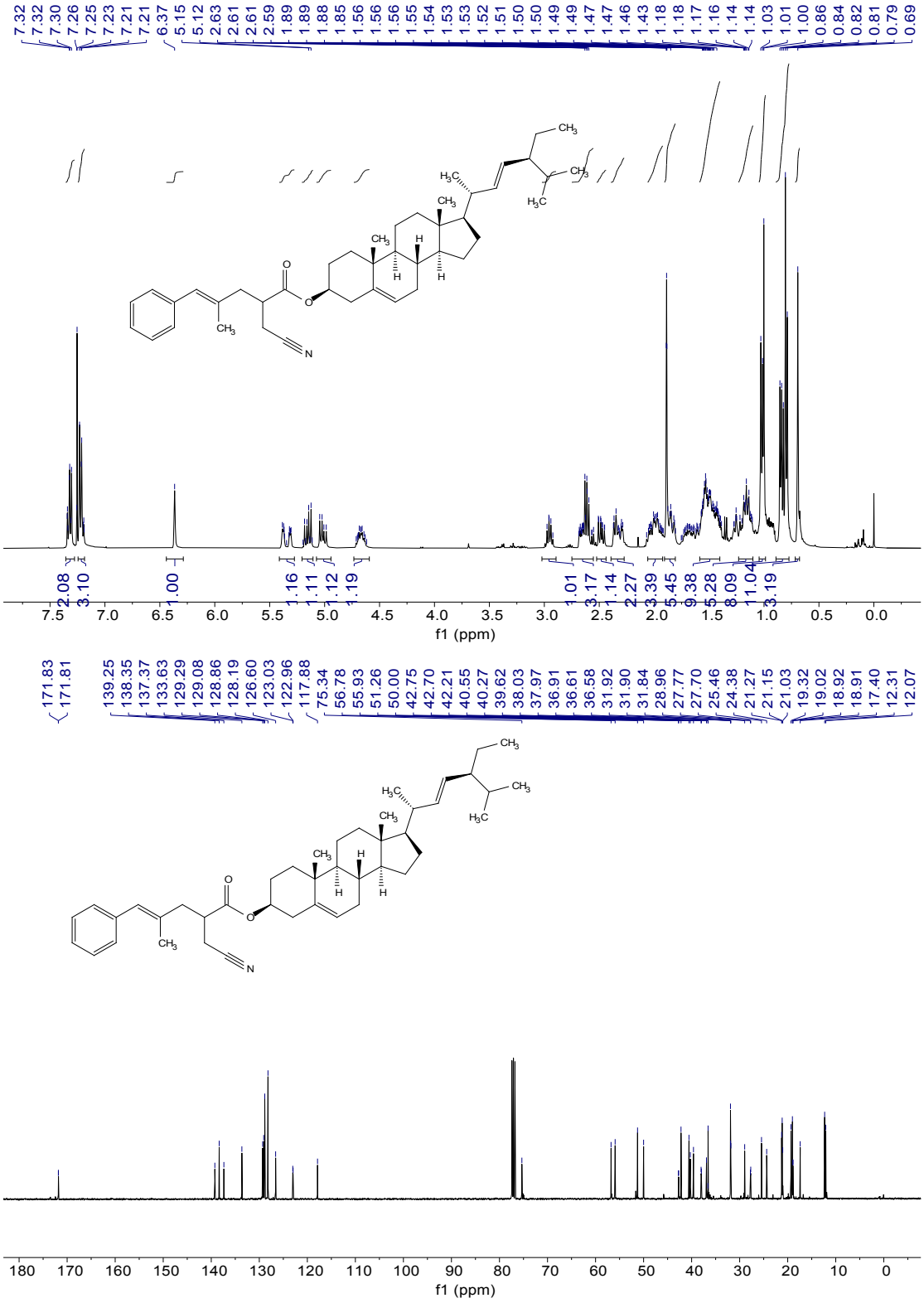



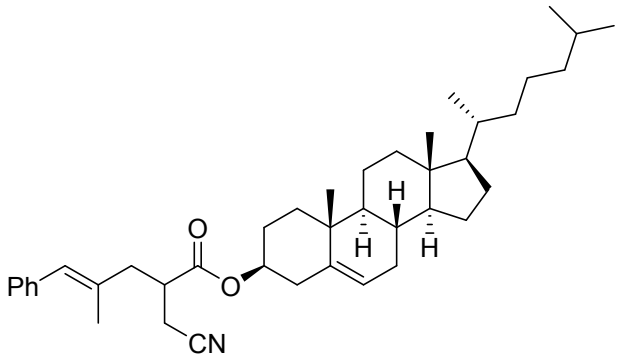

**(3S,8S,9S,10R,13R,14S,17R)-17-((2R,5S,E)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl-(E)-2-(cyanomethyl)-4-methyl-5-phenylpent-4-enoate (5c)**

Following general procedure, as a sticky solid. ***d.r.* = 1:1**. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 2H), 7.24 – 7.18 (m, 3H), 6.37 (s, 1H), 5.42 – 5.29 (m, 1H), 5.15 (dd, *J* = 15.1, 8.5 Hz, 1H), 5.01 (dd, *J* = 15.2, 8.6 Hz, 1H), 4.74 – 4.59 (m, 1H), 3.02 – 2.89 (m, 1H), 2.70 – 2.54 (m, 3H), 2.48 (ddd, *J* = 13.6, 8.2, 1.1 Hz, 1H), 2.39 – 2.28 (m, 2H), 2.08 – 1.92 (m, 3H), 1.90 – 1.81 (m, 5H), 1.60 – 1.39 (m, 9H), 1.23 – 1.10 (m, 5H), 1.06 – 0.98 (m, 8H), 0.89 – 0.76 (m, 11H), 0.69 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 171.83, 171.81, 139.25, 138.35, 137.37, 133.63, 129.29, 129.08, 128.86, 128.19, 126.60, 123.03, 122.96, 117.88, 75.34, 56.78, 55.93, 51.26, 50.00, 42.75, 42.70, 42.21, 40.55, 40.27, 39.62, 38.03, 37.97, 36.91, 36.61, 36.58, 31.92, 31.90, 31.84, 28.96, 27.77, 27.70, 25.46, 24.38, 21.27,

21.15, 21.03, 19.32, 19.02, 18.92, 18.91, 17.40, 12.31, 12.07.

**HRMS** (APCI) calcd for $C_{43}H_{62}NO_2$ ($M+H^+$): 624.4775; found: 624.4780.

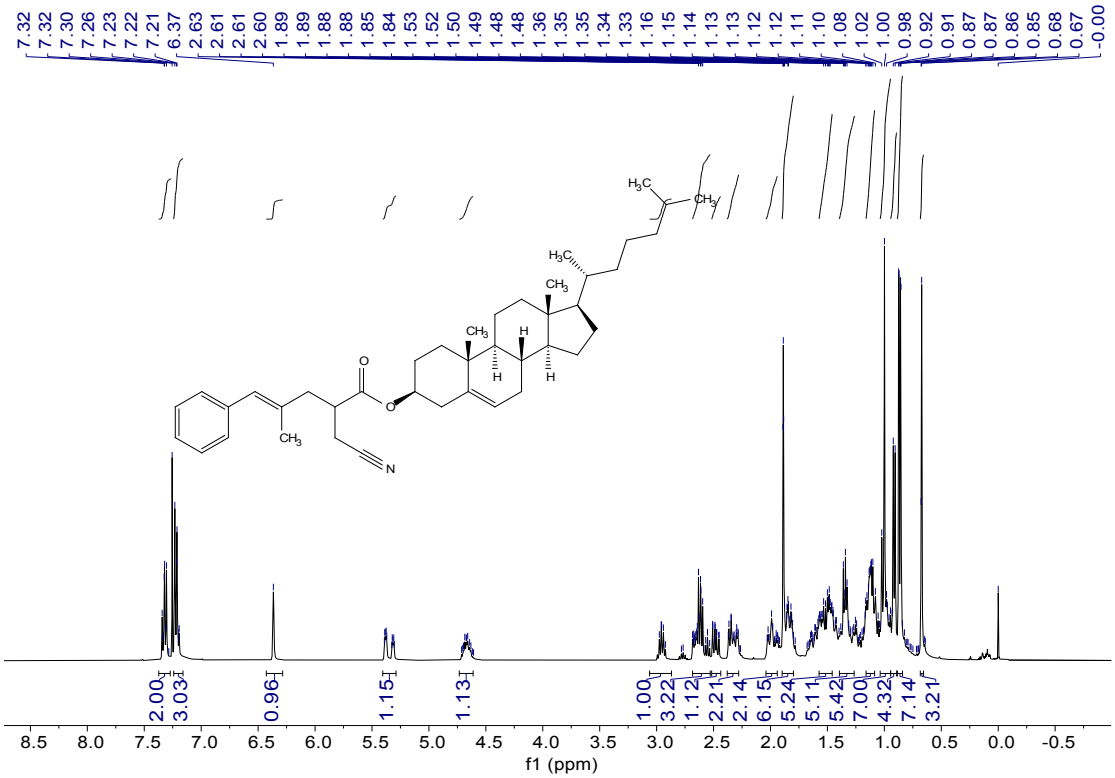


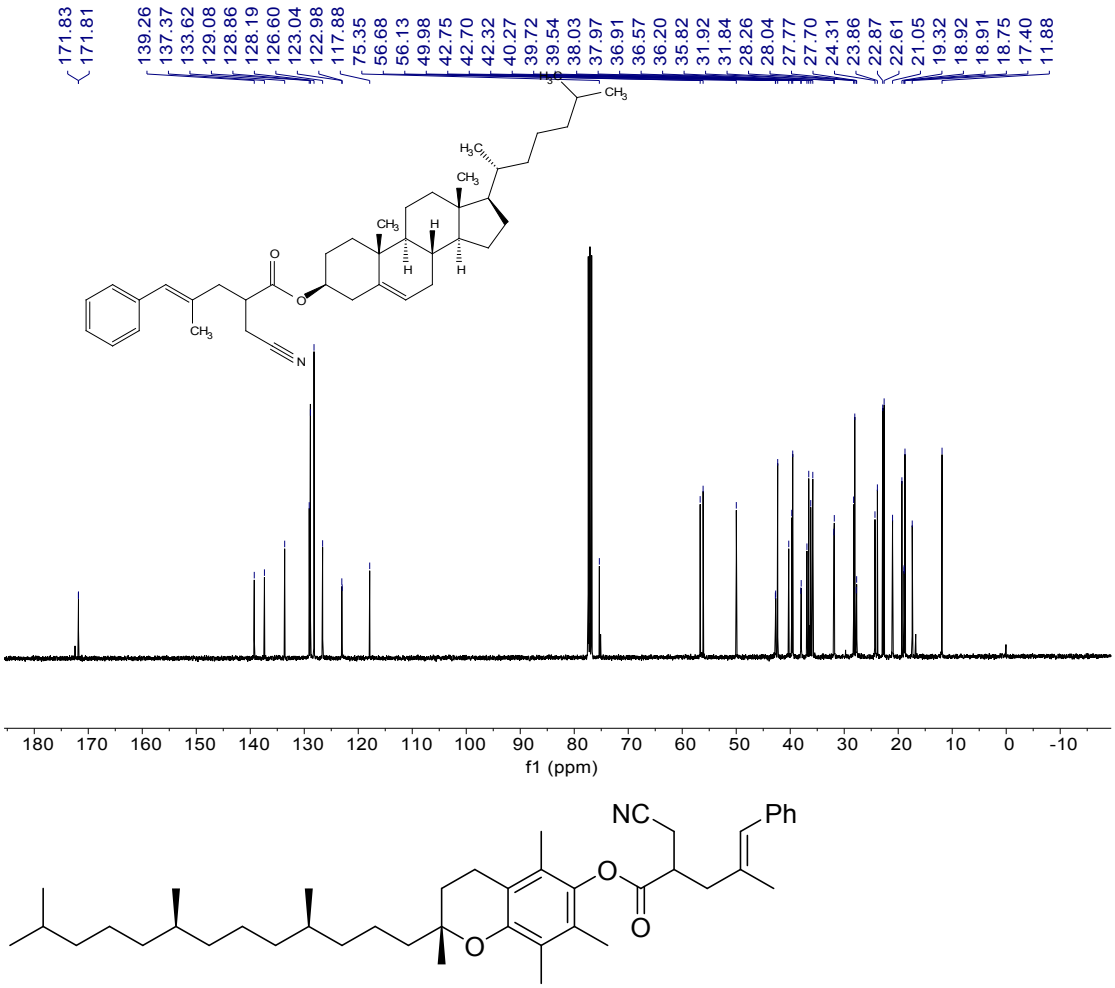



**(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl-(E)-2-(cyanomethyl)-4-methyl-5-phenylpent-4-enoate (5d)**

Following general procedure, as a sticky solid. ***d.r.* = 1:1**. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.25 – 7.13 (m, 3H), 6.37 (s, 1H), 5.41 – 5.29 (m, 1H), 4.73 – 4.59 (m, 1H), 3.02 – 2.90 (m, 1H), 2.70 – 2.57 (m, 3H), 2.52 – 2.44 (m, 1H), 2.39 – 2.26 (m, 2H), 2.06 – 1.92 (m, 2H), 1.90 – 1.78 (m, 6H), 1.60 – 1.43 (m, 5H), 1.38 – 1.24 (m, 5H), 1.18 – 1.05 (m, 5H), 1.04 – 0.96 (m, 7H), 0.91 (d, *J* = 6.5 Hz, 4H), 0.86 (dd, *J* = 6.6, 1.8 Hz, 7H), 0.67 (d, *J* = 2.0 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 171.83, 171.81, 139.26, 137.37, 133.62, 129.08, 128.86, 128.19, 126.60, 123.04, 122.98, 117.88, 75.35, 56.68, 56.13, 49.98, 42.75, 42.70, 42.32, 40.27, 39.72, 39.54, 38.03, 37.97, 36.91, 36.57, 36.20, 35.82, 31.92, 31.84, 28.26, 28.04, 27.77, 27.70, 24.31, 23.86, 22.87, 22.61, 21.05, 19.32, 18.92, 18.91, 18.75, 17.40, 11.88.

**HRMS** (APCI) calcd for $C_{41}H_{60}NO_2$ ($M+H^+$): 598.4619; found: 598.4625.





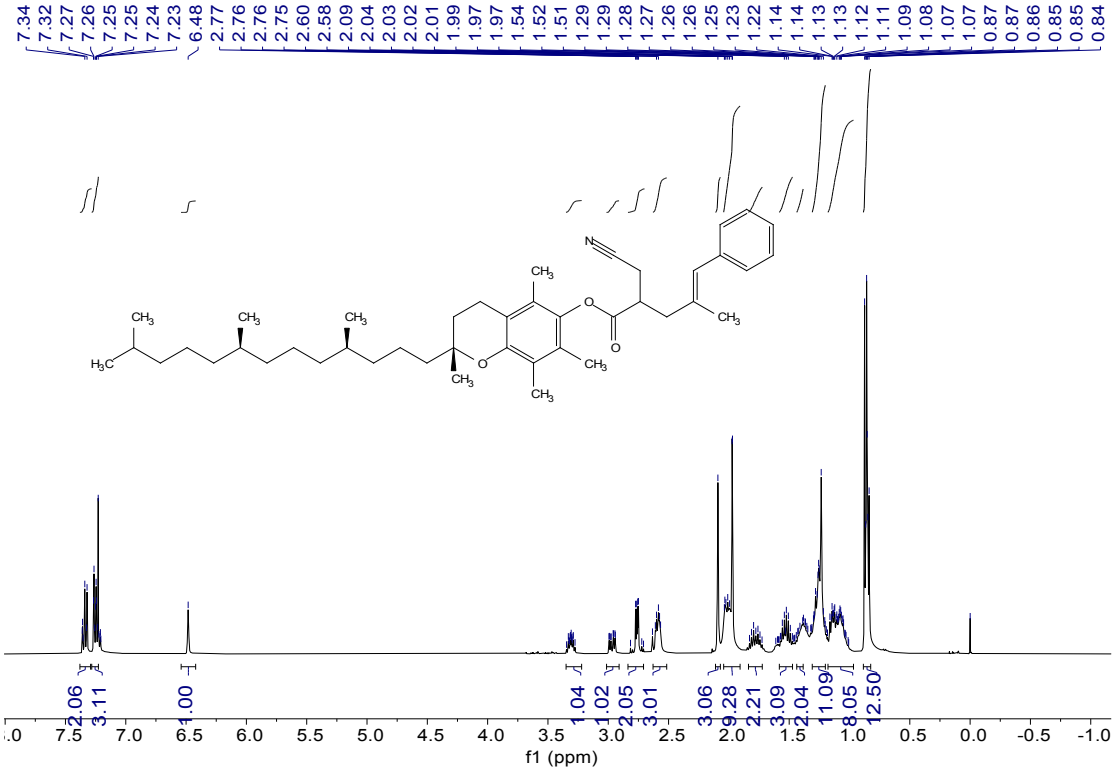


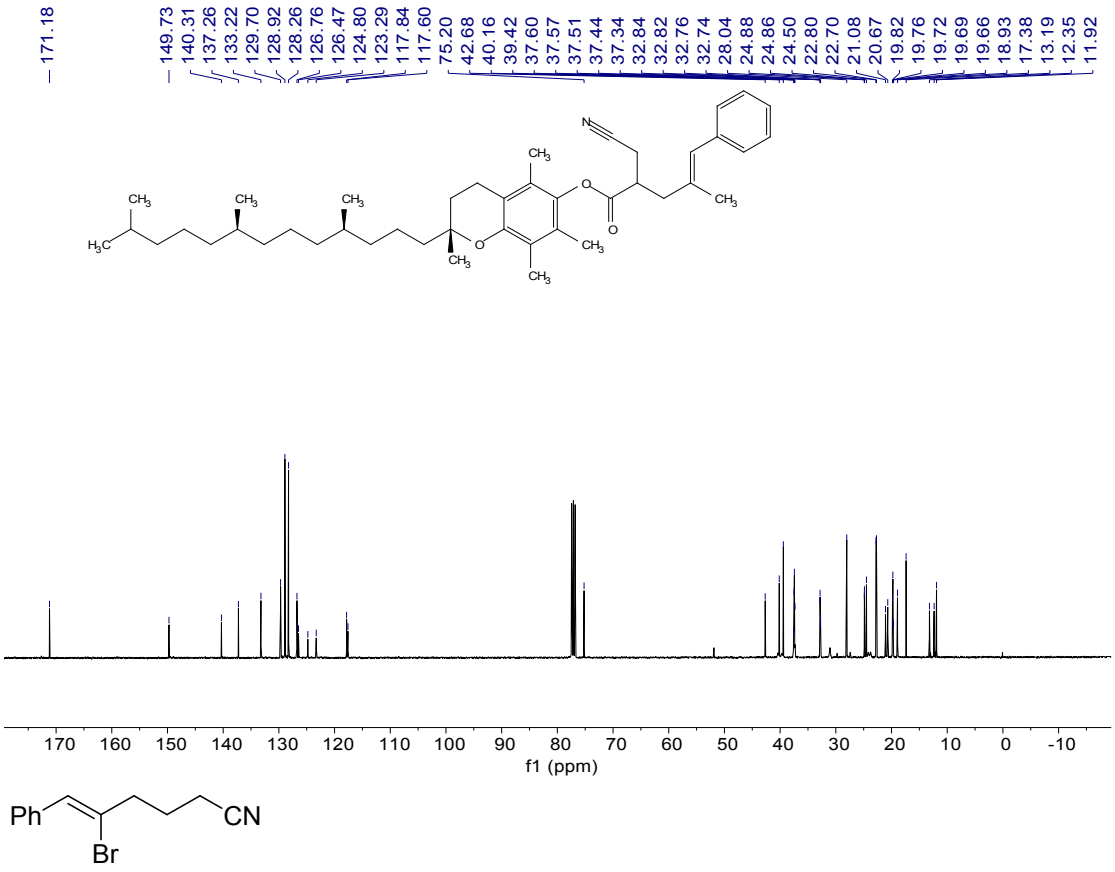
**(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl-(E)-2-**

**(cyanomethyl)-4-methyl-5-phenylpent-4-enoate (5e)**

Following general procedure, as a sticky liquid. ***d.r.* = 1:1**. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 2H), 7.29 – 7.20 (m, 3H), 6.48 (s, 1H), 3.36 – 3.23 (m, 1H), 2.95 (dd, *J* = 5.9, 1.2 Hz, 1H), 2.76 (dd, *J* = 6.4, 3.1 Hz, 2H), 2.66 – 2.53 (m, 3H), 2.09 (s, 3H), 2.06 – 1.91 (m, 9H), 1.85 – 1.70 (m, 2H), 1.60 – 1.47 (m, 3H), 1.44 – 1.34 (m, 2H), 1.31 – 1.18 (m, 11H), 1.16 – 1.00 (m, 8H), 0.92 – 0.78 (m, 12H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 171.18, 149.73, 140.31, 137.26, 133.22, 129.70, 128.92, 128.26, 126.76, 126.47, 124.80, 123.29, 117.84, 117.60, 75.20, 42.68, 40.16, 39.42, 37.60, 37.57, 37.51, 37.44, 37.34, 32.84, 32.82, 32.76, 32.74, 28.04, 24.88, 24.86, 24.50, 22.80, 22.70, 21.08, 20.67, 19.82, 19.76, 19.72, 19.69, 19.66, 18.93, 17.38, 13.19, 12.35, 11.92.

**HRMS** (APCI) calcd for $C_{43}H_{64}NO_3$ ($M+H^+$): 642.4881; found: 642.4886.





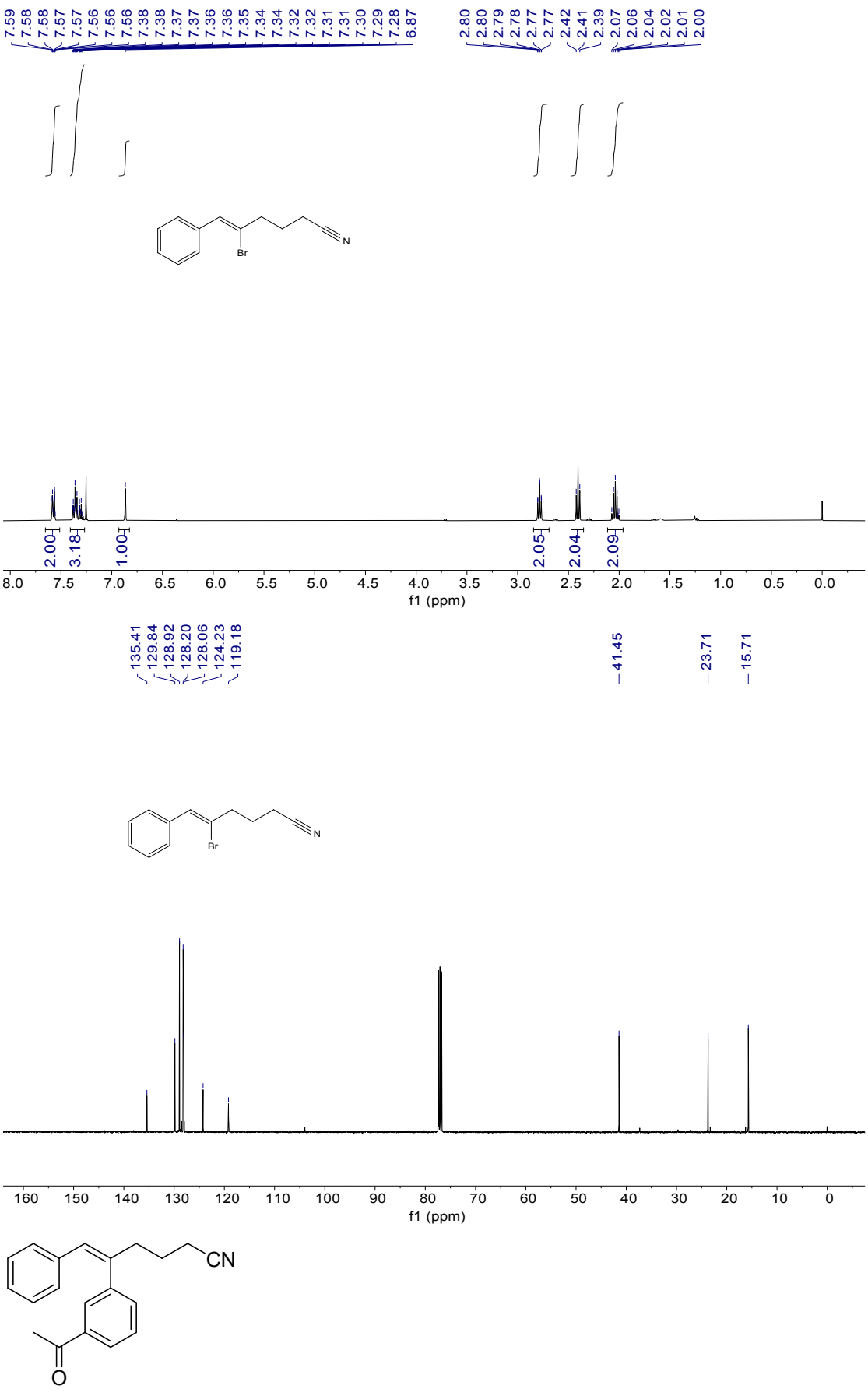




**(Z)-5-bromo-6-phenylhex-5-enenitrile (6a)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 2H), 7.41 – 7.27 (m, 3H), 6.87 (s, 1H), 2.78 (td, *J* = 7.0, 0.9 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.10 – 1.97 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 135.41, 129.84, 128.92, 128.20, 128.06, 124.23, 119.18, 41.45, 23.71, 15.71.

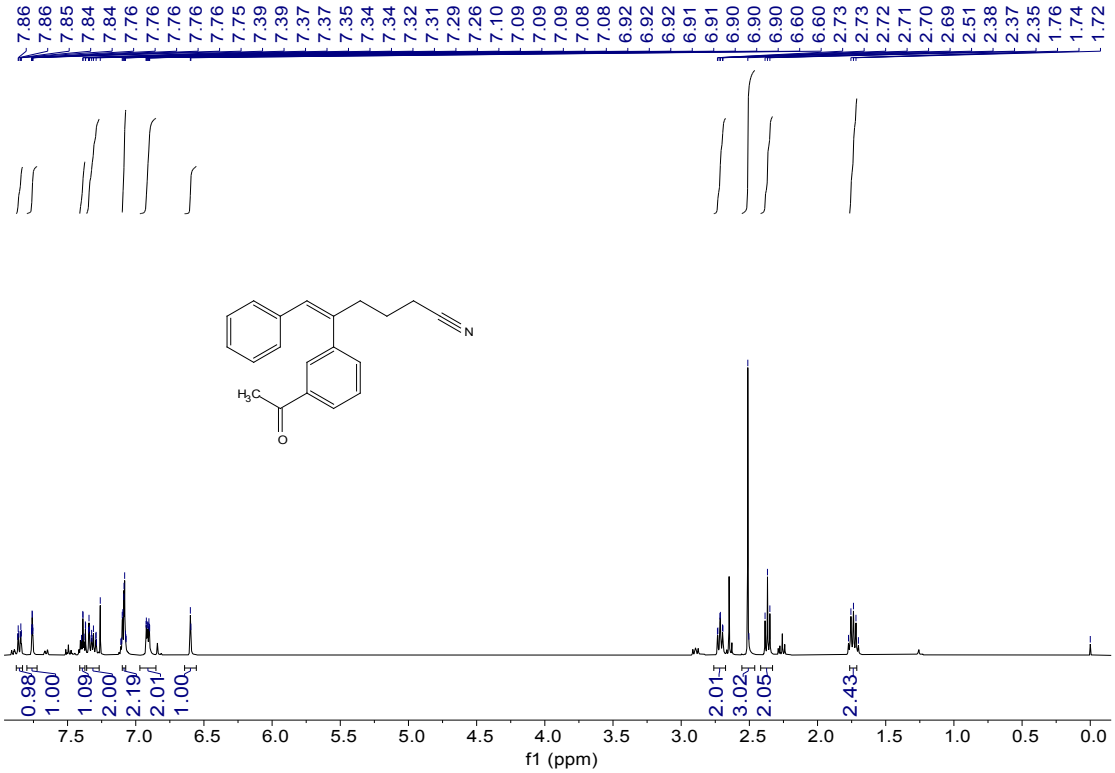
**HRMS** (APCI) calcd for $C_{12}H_{13}NBr$ ($M+H^+$): 250.0226; found: 250.0228.

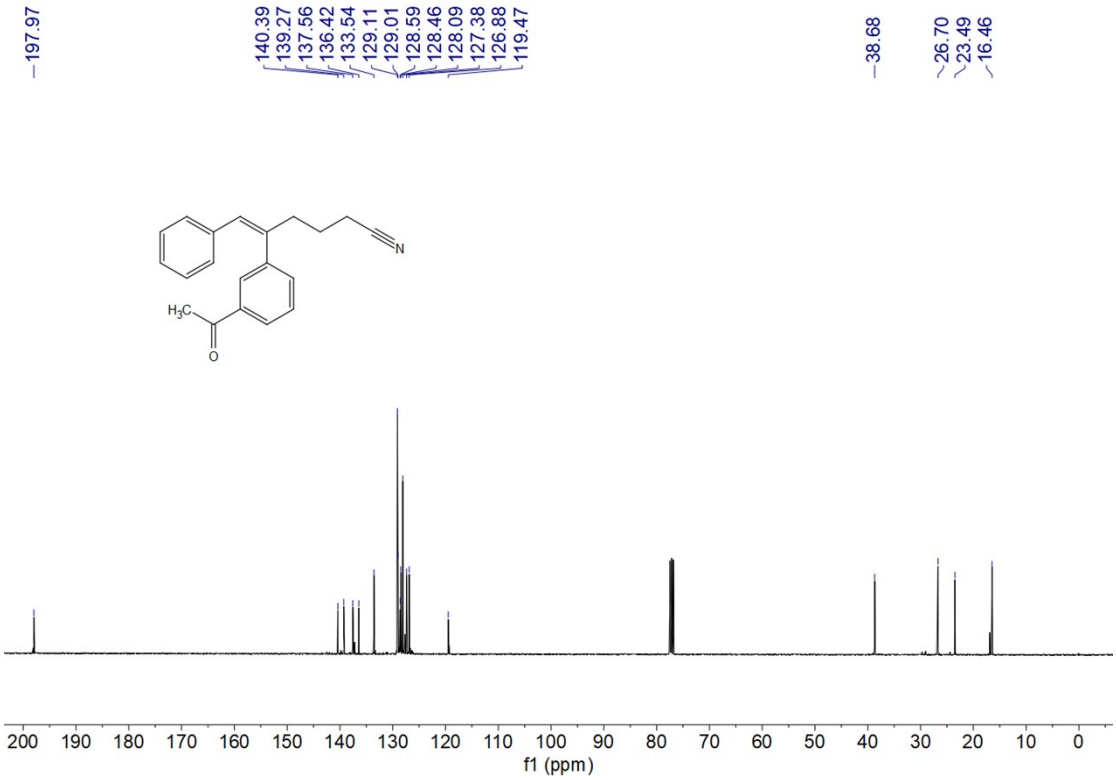


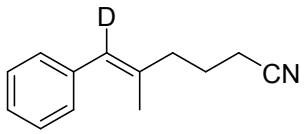

**(Z)-5-(3-acetylphenyl)-6-phenylhex-5-enenitrile (6b)**

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.88 – 7.83 (m, 1H), 7.79 – 7.72 (m, 1H), 7.43 – 7.37 (m, 1H), 7.35 – 7.28 (m, 2H), 7.16 – 7.05 (m, 2H), 6.95 – 6.88 (m, 2H), 6.60 (s, 1H), 2.75 – 2.68 (m, 2H), 2.51 (s, 3H), 2.37 (t, *J* = 7.1 Hz, 2H), 1.82 – 1.69 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.97, 140.39, 139.27, 137.56, 136.42, 133.54, 129.11, 129.01, 128.59, 128.46, 128.09, 127.38, 126.88, 119.47, 38.68, 26.70, 23.49, 16.46.

**HRMS** (APCI) calcd for $C_{20}H_{20}NO$ ($M+H^+$): 290.1539; found: 290.1541.



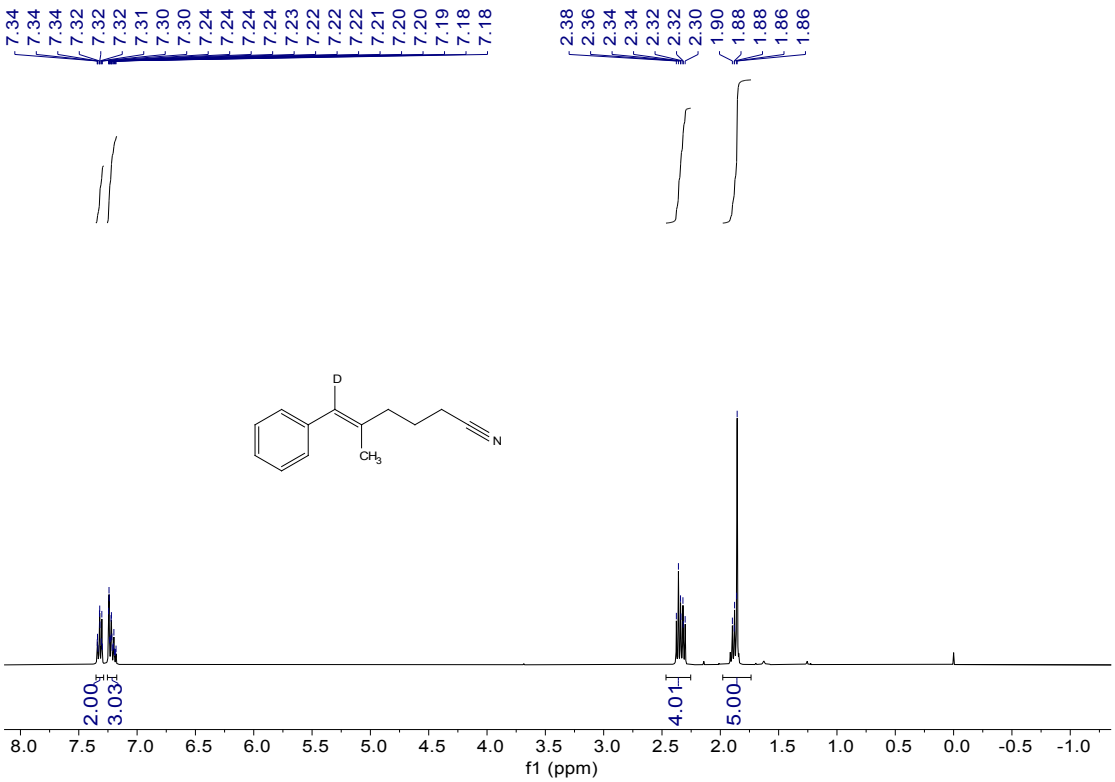


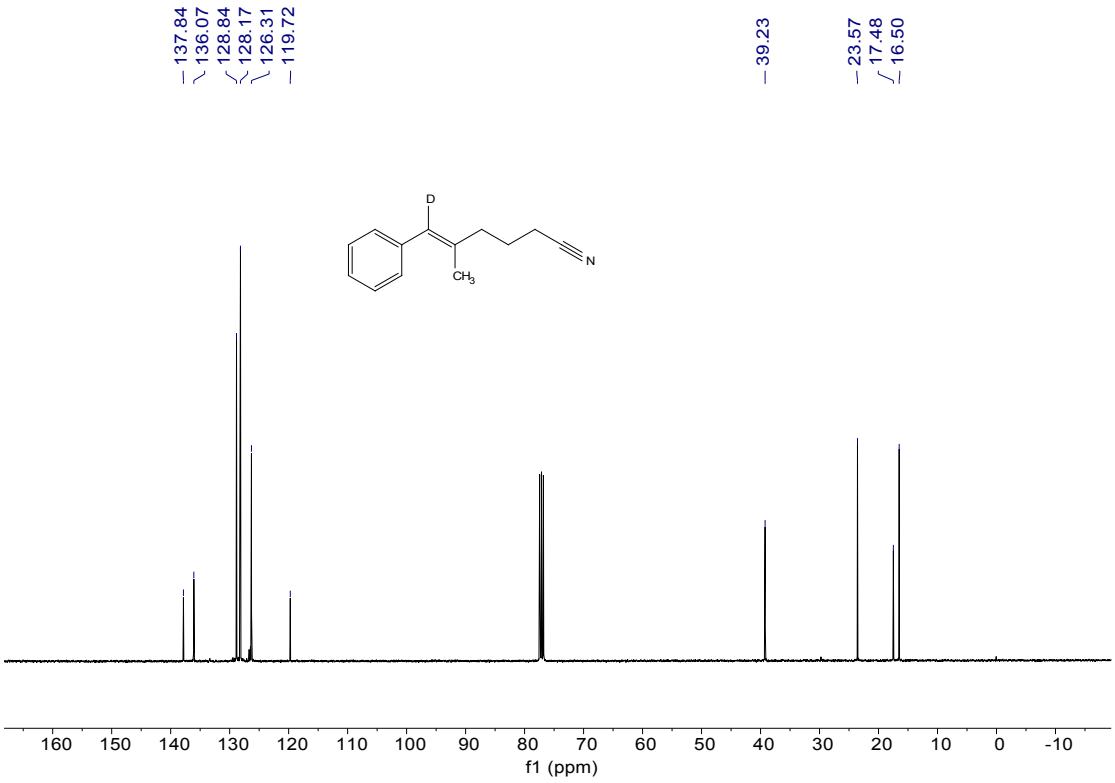



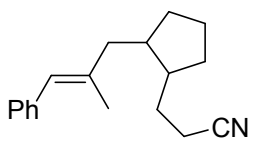

**(E)-5-methyl-6-phenylhex-5-enenitrile-6-d (7a)**

Following general procedure, as a sticky liquid. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.26 – 7.18 (m, 3H), 2.41 – 2.27 (m, 4H), 1.92 – 1.82 (m, 5H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.84, 136.07, 128.84, 128.17, 126.31, 119.72, 39.23, 23.57, 17.48, 16.50.

**HRMS** (APCI) calcd for $C_{13}H_{15}DN$ ($M+H^+$): 187.1340; found: 187.1345.



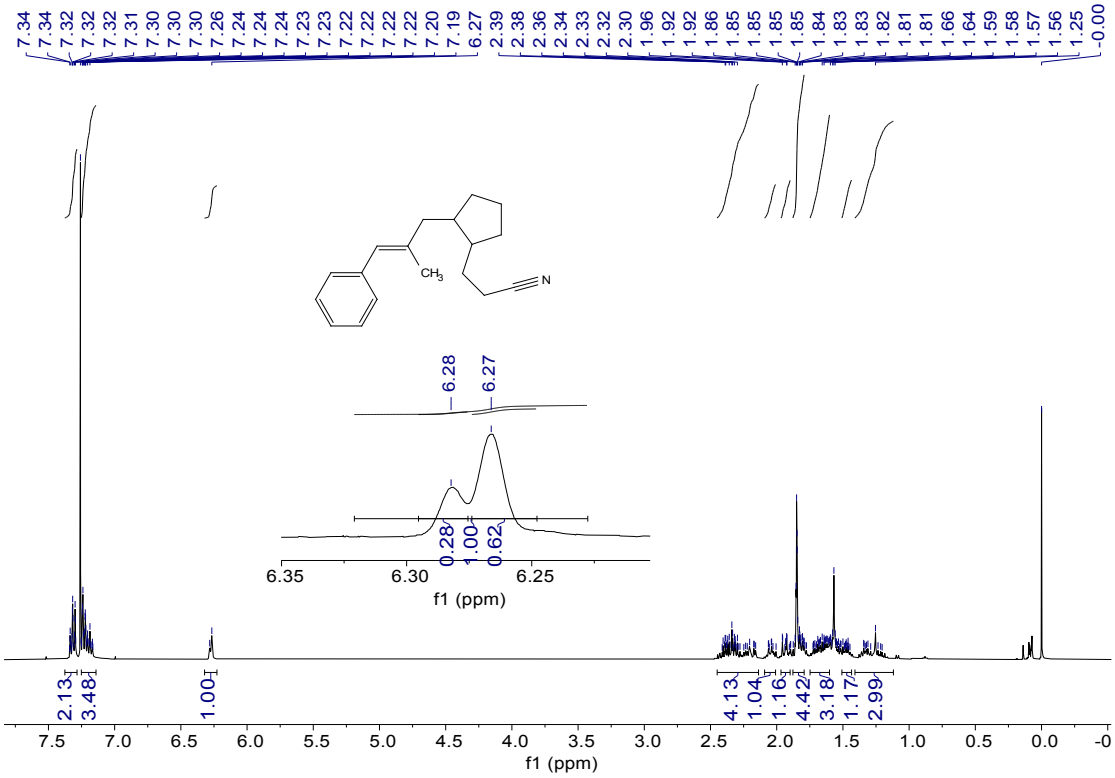



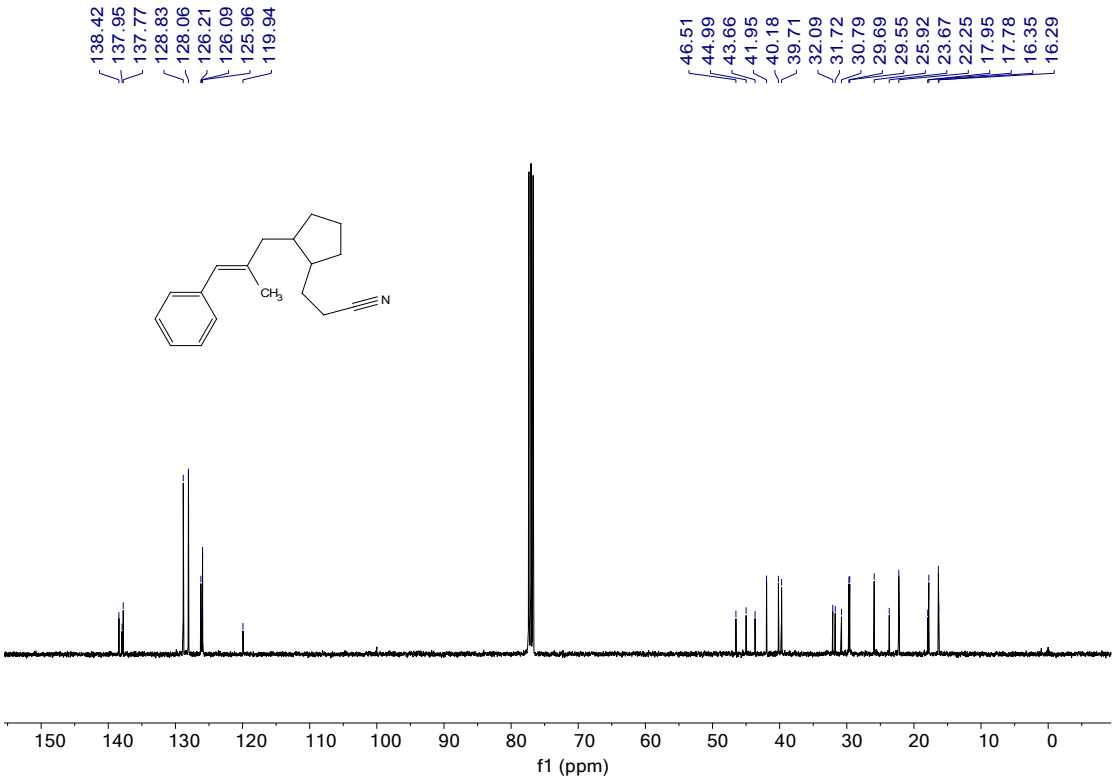



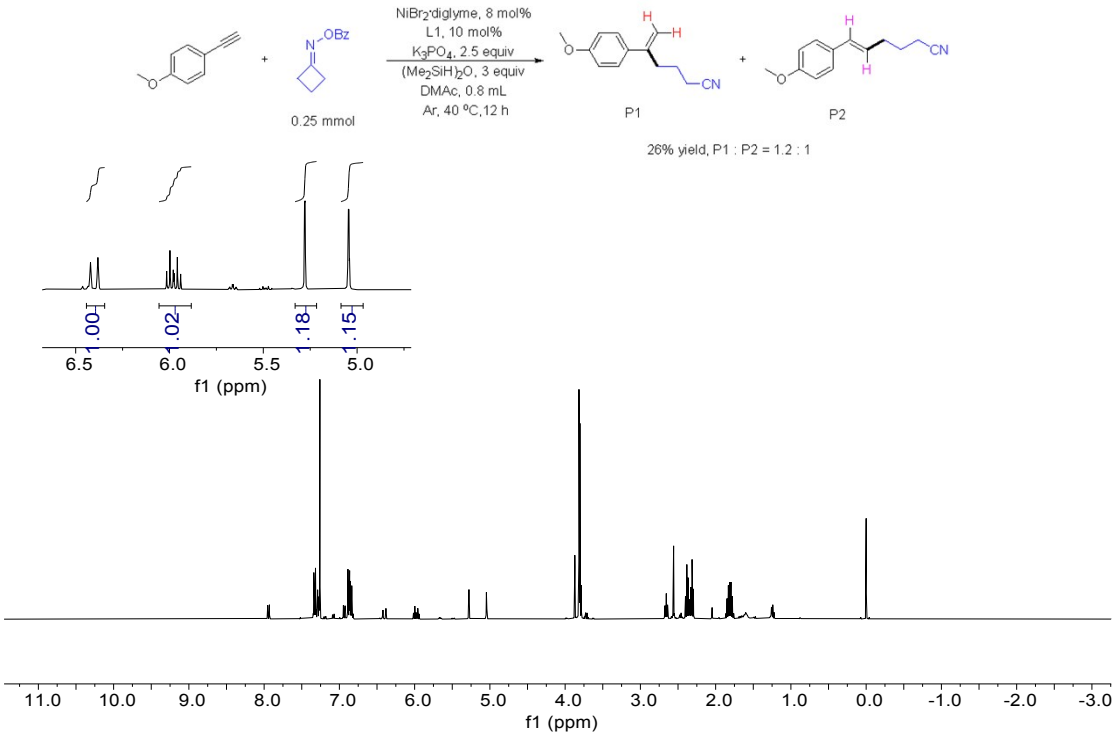

**(E)-3-(2-(2-methyl-3-phenylallyl)cyclopentyl)propanenitrile (8a)**

Following general procedure, as a sticky liquid. ***d.r.* = 2.2:1**. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H), 6.34 – 6.20 (m, 1H), 2.45 – 2.14 (m, 4H), 2.10 – 2.00 (m, 1H), 1.99 – 1.88 (m, 1H), 1.87 – 1.77 (m, 4H), 1.75 – 1.59 (m, 3H), 1.53 – 1.43 (m, 1H), 1.37 – 1.17 (m, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.42, 137.95, 137.77, 128.83, 128.06, 126.21, 126.09, 125.96, 119.94, 46.51, 44.99, 43.66, 41.95, 40.18, 39.71, 32.09, 31.72, 30.79, 29.69, 29.55, 25.92, 23.67, 22.25, 17.95, 17.78, 16.35, 16.29.

**HRMS** (APCI) calcd for $C_{18}H_{24}N$ ($M+H^+$): 254.1903; found: 254.1901.




138.42
137.95
137.77
128.83
128.06
126.21
126.09
125.96
119.94
46.51
44.99
43.66
41.95
40.18
39.71
32.09
31.72
30.79
29.69
29.55
25.92
23.67
22.25
17.95
17.78
16.35
16.29
CH3
N
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OBz
0.25 mmol
NiBr2·diglyme, 8 mol%
L1, 10 mol%
K3PO4, 2.5 equiv
(Me2SiH)2O, 3 equiv
DMAc, 0.8 mL
Ar, 40 °C,12 h
P1
P2
26% yield, P1 : P2 = 1.2 : 1
1.00
1.02
1.18
1.15
6.5 6.0 5.5 5.0
f1 (ppm)
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0 -3.0
f1 (ppm)