Supporting Information:

Direct Synthesis of Nitriles from Alcohols with Trialkylsilyl Cyanide Using Brønsted Acid Montmorillonite Catalysts

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Experimental:

1. Preparation of Sn-Mont and Ti-Mont:

Sn-Mont was prepared according to our previously reported protocol.[1] Na-Mont (8 g) was ion-exchanged with aq. $SnCl_4 \cdot 5H_2O$ (0.3 M, 80 mL) at room temperature for 2 h, and this exchange process was then repeated. The collected clay was washed twice with water (80 mL), with a mixture of water (40 mL) and methanol (40 ml) 6 times, and with absolute methanol (80 mL) once. Finally, Sn-Mont was dried in a vacuum (0.5 mmHg) at room temperature for 12 h, followed by being ground in a mortar with a pestle, passed through a 60-mesh screen and stored in a general glass bottle under ambient conditions.

Ti-Mont was prepared as follows:[2] Na-Mont (4.2 g) was ion-exchanged with aq. $TiCl_4$ (3.32×10^{-2} M, 80 mL) at 50 °C for 24 h. The collected clay was filtered and repeatedly washed with water until it was completely free of Cl ions via checking the filtrate by an $AgNO_3$ solution. The clay was then dried at 110 °C for 15 h, followed by being ground in a mortar with a pestle, passed through a 60-mesh screen and stored in a general glass bottle under ambient conditions.

The XRD analysis showed that Sn-Mont and Ti-Mont had large peaks at the lower angles of below 10 degrees than the pristine Na-Mont, indicating that the pore sizes of Sn-Mont and Ti-Mont expanded after the ion-exchange of Na-Mont with aqueous $SnCl_4$ and $TiCl_4$ solutions, respectively.

According to the nitrogen sorption data, the specific surface areas of Sn-Mont and Ti-Mont greatly increased to 280 $m^2\ g^{-1}$ and 125 $m^2\ g^{-1}$ from 12 $m^2\ g^{-1}$ of the presitine Na-Mont, respectively (Figure S2).

The elemental analysis by inductively coupled plasma (ICP) showed the tin content in Sn-Mont is 1.9 mmol g^{-1} and the titanium content in Ti-Mont is 0.68 mmol g^{-1}.

2. Preparation of other montmorillonite catalysts and control catalysts:

Iron ion-exchanged montmorillonite (Fe-Mont),[1,3,4] Sn-MCM-41 (Si/Sn = 20)[5] and Al-MCM-41 (Si/Al = 20) [6]were prepared according to the previously papers. Proton ion-exchanged montmorillonite (H-Mont)[7] and aluminum ion-exchanged montmorillonite (Al-Mont)[7] were synthesized according to the previous methods. $Sn(OH)_4$ was prepared by the hydrolysis of $SnCl_4 \cdot 5H_2O$ in aq. NH_3.

3. IR measurements of the montmorillonite catalysts with pyridine adsorption:

The IR spectra of the pyridine-adsorbed catalysts were obtained at room temperature in the transmission mode using a JASCO IR-630 spectrophotometer. The catalysts (0.1 g) were treated with 1 mmol of pyridine for 1 h. The excess of pyridine was removed by heating the sample at 150 ^oC in a vacuum for 3 h. The pyridine-adsorbing catalyst was mixed with KBr (3 mg catalyst and 100 mg KBr), and then was pressed into a disc (10 mm diameter). The spectra are found in Figure S5.

4. Preparation of TMSCN or TBDMSCN-treated Sn/Ti-Mont:

A solution of TMSCN or TBDMSCN (3 mmol) in dichloromethane (5 mL) was added to Sn-Mont or Ti-Mont

(200 mg), and the suspended solution was stirred for 1 h at room temperature. Then, the modified Sn/Ti-Mont was isolated by the filtration, washed with CH_2Cl_2, and then dried in a vacuum for 6 h. Sn/Ti-Mont-TMS and Sn/Ti-Mont-TBDMS are Sn/Ti-Mont treated with TMSCN and TBDMSCN, respectively. The obtained Sn/Ti-Mont-TMS and Sn/Ti-Mont-TBDMS are reddish brown, while the original Sn/Ti-Mont is grayish white.

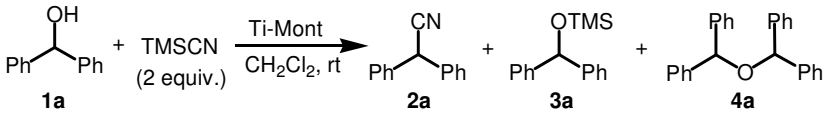
5. Synthesis of bis(diphenylmethyl) ether 4a (Eq. 5 in the main text):

A solution of benzhydrol **1a** (10 mmol) in crude dichloromethane (20 mL) was added to Ti-Mont (200 mg; 1.36 mol%), and the suspended solution was stirred for 1 h. Then, the catalyst was removed by the filtration through a Celite plug, and was washed with CH_2Cl_2. The combined solution was evaporated under reduced pressures to give crude solid products. The solids were further washed with hexane to afford the desired pure product (1.32 g, 75 %). The spectra data of the product were in good agreement with the reported data.

6. Reaction of bis(diphenylmethyl) ether 4a with TMSCN catalyzed by Ti-Mont (Eq. 6 in the main text):

Bis(diphenylmethyl) ether **4a** (1.0 mmol, 350 mg) and water (1 mmol) were added to a CH_2Cl_2 (2 mL) suspension of Ti-Mont (40 mg; 2.72 mol%), and TMSCN (3.0 mmol) was then added. The mixture was stirred at room temperature under nitrogen atmosphere for 24 h, and was analyzed by GC. No nitrile **2a** was detected, and **4a** was completely recovered.

Table S1. Optimization of the reaction conditions for the cyanation of **1a** catalyzed by Ti-Mont.[a]



1a **2a** **3a** **4a**

Entry	*t* (h)	Method[b]	Conv. (%)[c]	Yield (%)[c]		
				2a	**3a**	**4a**
1	0.1	A	Quant.	39	9	52
2	3	A	Quant.	47	0	53
3	8	A	Quant.	57	0	43
4	0.1	B	99%	75	24	0
5	1	B	Quant.	93	7	0
6	1.5	B	Quant.	98	2	0

[a]Ti-Mont (20 mg), **1a** (1 mmol), TMSCN (2 mmol), CH_2Cl_2 (2 mL), rt. [b]Method A: TMSCN was added to the suspension of **1a** and Ti-Mont; Method B: **1a** dissolved in CH_2Cl_2 was dropwise added to the suspension of Ti-Mont and TMSCN. [c]Determined by GC based on **1a**.

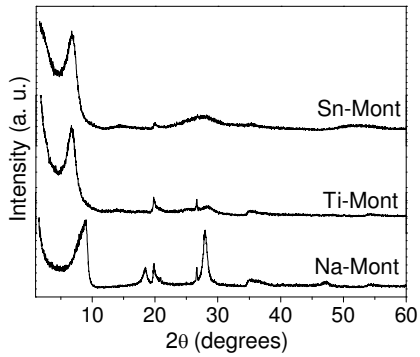


Figure S1. XRD patterns of Sn-Mont, Ti-Mont and Na-Mont.

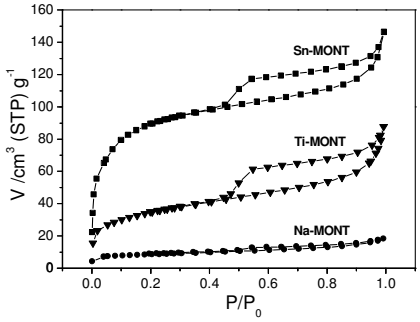


Figure S2. Nitrogen sorption isotherms of Sn-Mont, Ti-Mont, and Na-Mont.

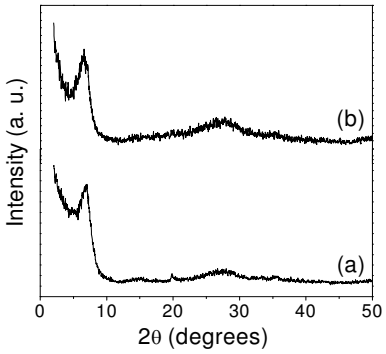


Figure S3. XRD patterns of Sn-Mont (a) and the recovered Sn-Mont after the cyanation of benzhydrol (b).

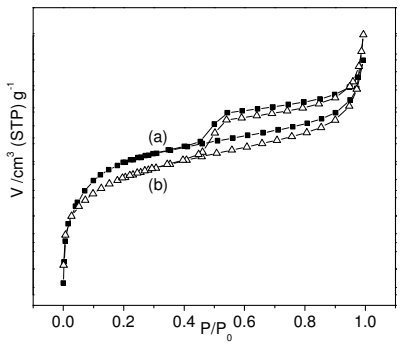


Figure S4. Nitrogen sorption isotherms of Sn-Mont (a) and the recovered Sn-Mont after the cyanation of benzhydrol (b).

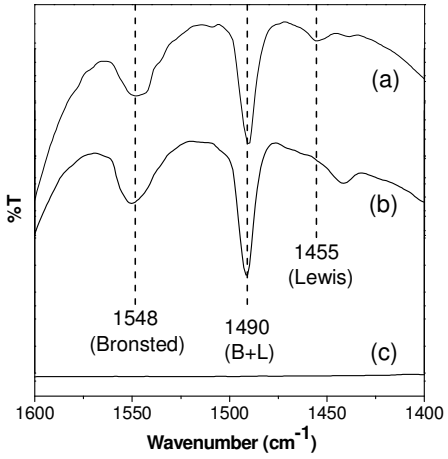


Figure S5. FT-IR spectra of the montmorillonite catalysts after pyridine adsorption: (a) Sn-Mont, (b) Ti-Mont, and (c) Na-Mont. The spectra of both Ti-Mont and Sn-Mont after pyridine adsorption showed one strong absorption band at 1548 cm^{-1}, indicating the presence of Brønsted acid sites.[8,9]

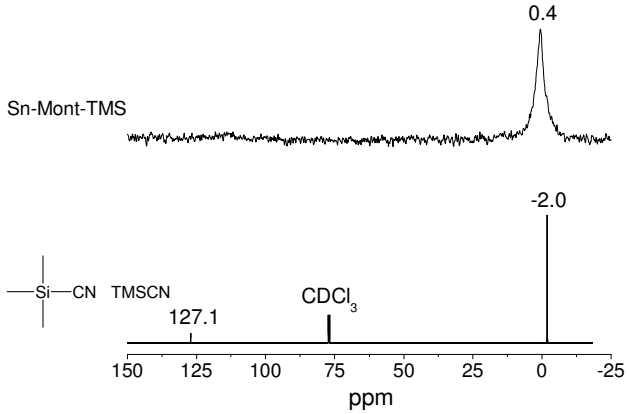


Figure S6. Comparison between liquid-state ^{13}C NMR spectrum of TMSCN and solid-state ^{13}C DDMAS NMR spectrum of TMSCN treated Sn-Mont (Sn-Mont-TMS).

In the spectrum of TMSCN, the signals at 127.1 and -2.0 ppm are assignable to the cyanide and methyl groups respectively in TMSCN.

In the spectrum of TMSCN-treated Sn-Mont (Sn-Mont-TMS), only one signal observed at 0.4 ppm should be due to the methyl groups of TMS attaching to the montmorillonite catalysts.

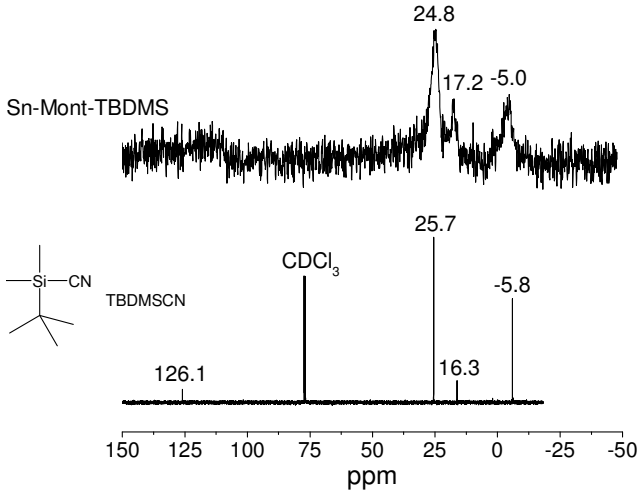


Figure S7. Comparison between liquid-state ^{13}C NMR spectrum of TBDMSCN and solid-state ^{13}C DDMAS NMR spectrum of TBDMSCN treated Sn-Mont (Sn-Mont-TBDMS).

In the spectrum of TBDMSCN, the signals at -5.8, 16.3, 25.7, and 126.1ppm are ascribed to $\underline{C}H_3Si$, $\underline{C}(CH_3)_3$, $(\underline{C}H_3)_3C$, and $\underline{C}N$, respectively.

In the spectrum of TBDMSCN-treated Sn-Mont (Sn-Mont-TBDMS), the signals at -5.0, 17.2, and 24.8 ppm are assignable to $\underline{C}H_3Si$, $\underline{C}(CH_3)_3$, $(\underline{C}H_3)_3C$ in a *t*-butyldimethylsilyl group attaching to the montmorillonite catalysts.

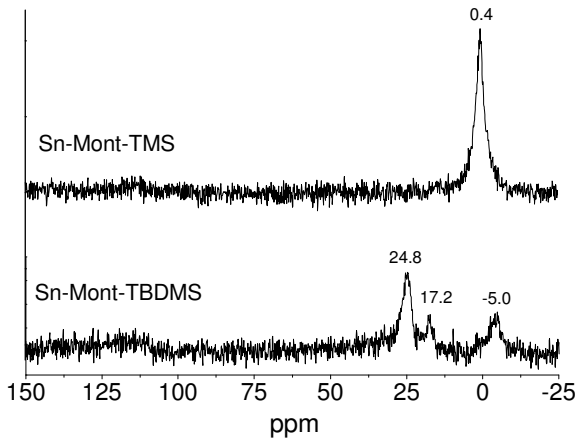


Figure S8. Solid-state ^{13}C DDMAS NMR spectra of Sn-Mont-TMS and Sn-Mont-TBDMS.

All nitriles are characterized by IR, $^{1}H/^{13}C$ NMR, HRMS, and melting point measurements. All characterization data are shown:

2,2-Diphenylacetonitrile (**2a**):[10-12] Light yellow solid; m.p. 72-73 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 – 7.30 (m, 10H), 5.14 ppm (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.9, 129.2, 128.3, 127.8, 119.7, 42.5 ppm; FTIR (neat, NaCl): *v* (C≡N) 2230 cm^{-1}; HRMS (EI): m/z calcd. for $C_{14}H_{11}N$ (M^+): 193.0891, found: 193.0885.

2-(4-Methylphenyl)-2-phenylacetonitrile (**2b**):[10] Yellow green solid; m.p. 61-62 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.43 – 7.30 (m, 5H), 7.20 (q, *J* = 8.3, 4H), 5.10 (s, 1H), 2.34 ppm (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 137.9, 135.9, 132.7, 129.6, 128.9, 127.9, 127.4 (double peaks), 119.6, 42.0, 20.8 ppm; FTIR (neat, NaCl): *v* (C≡N) 2233 cm^{-1}; HRMS (EI): m/z calcd. for $C_{15}H_{13}N$ (M^+): 207.1048, found: 207.1035.

2-(4-Methoxyphenyl)-2-phenylacetonitrile (**2c**):[10,13] Gray white solid; m.p. 123-124 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.43 – 7.30 (m, 5H), 7.25 (d, *J* = 8.8, 2H), 6.89 (d, *J* = 8.6, 2H), 5.10 (s, 1H), 3.80 ppm (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 159.2, 136.0, 128.9, 128.7, 127.9, 127.7, 127.4, 119.7, 114.3, 55.1, 41.6 ppm; FTIR (neat, NaCl): *v* (C≡N) 2238 cm^{-1}; HRMS (EI): m/z calcd. for $C_{15}H_{13}NO$ (M^+): 223.0997, found: 223.1003.

2-(3,4-Methylenedioxyphenyl)propanenitrile (**2d**):[14] Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.00 – 6.65 (m, 3H), 5.97 (d, *J* = 0.7, 2H), 3.81 (q, *J* = 7.3, 1H), 1.60 ppm (dd, *J* = 0.7, 7.3, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 148.0, 147.2, 130.5, 121.4, 119.8, 108.4, 107.0, 101.2, 30.7, 21.3 ppm; FTIR (neat, NaCl): *v* (C≡N) 2233 cm^{-1}; HRMS (EI): m/z calcd. for $C_{10}H_9NO_2$ (M^+): 175.0633, found: 175.0619.

2-(4-Methoxyphenyl)propanenitrile (**2e**):[12,15] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.5, 2H), 6.91 (d, *J* = 9.2, 2H), 3.85 (q, *J* = 7.3, 1H), 3.81 (s, 3H), 1.62 ppm (d, *J* = 7.3, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.4, 129.1, 127.9, 121.9, 114.5, 55.3, 30.4, 21.4 ppm; FTIR (neat, NaCl): *v* (C≡N) 2235 cm^{-1}; HRMS (EI): m/z calcd. for $C_{10}H_{11}NO$ (M^+): 161.0841, found: 161.0839.

2-(4-Methoxyphenyl)butanenitrile (**2f**):[14] Colorless oil; ^{1}H NMR (500 MHz, CDCL3): δ = 7.24 (d, *J* = 9.2, 2H), 6.90 (d, *J* = 8.5, 2H), 3.81 (s, 3H), 3.68 (t, *J* = 7.2, 1H), 1.99 – 1.79 (m, 2H), 1.06 ppm (t, *J* = 7.6, 3H); ^{13}C NMR (126 MHz, CDCL3): δ = 159.3, 128.4, 127.8, 121.0, 114.4, 55.3, 38.1, 29.2, 11.4 ppm; FTIR (neat, NaCl): *v* (C≡N) 2238 cm^{-1}; HRMS (EI): m/z calcd. for $C_{11}H_{13}NO$ (M^+): 175.0997, found: 175.1007.

2-(4-Methylphenyl)propanenitrile (**2g**):[16] Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.27 – 7.15 (m, 4H), 3.86 (q, *J* = 7.4, 1H), 2.35 (s, 3H), 1.62 ppm(d, *J* = 7.3, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.6, 133.9, 129.5, 126.4, 121.6, 30.6, 21.3, 20.8 ppm; FTIR (neat, NaCl): *v* (C≡N) 2239 cm^{-1}; HRMS (EI): m/z calcd. for $C_{10}H_{11}N$ (M^+): 145.0891, found: 145.0900.

2-(6-Methoxynaphthalen-2-yl)propanenitrile (**2h**):[11,12] White solid; m.p. 71-73 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.75 (t, *J* = 8.1, 3H), 7.39 (dd, *J* = 1.8, 8.7, 1H), 7.23 – 7.11 (m, 2H), 4.03 (q, *J* = 7.3, 1H), 3.92 (s, 3H), 1.71 ppm (d, *J* = 7.3, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 157.9, 133.8, 131.8, 129.1, 128.5, 127.7, 125.2, 124.7, 121.5, 119.4, 105.4, 55.1, 31.0, 21.2 ppm; FTIR (neat, NaCl): *v* (C≡N) 2240 cm^{-1}; HRMS (EI): m/z calcd. for $C_{14}H_{13}NO$ (M^+): 211.0997, found: 211.0979.

2-(9*H*-Fluoren-2-yl)propanenitrile (**2i**):[14] White solid; m.p. 103-105 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 2.3, 7.3, 2H), 7.55 (d, *J* = 4.9, 2H), 7.43 – 7.31 (m, 3H), 3.97 (dd, *J* = 7.3, 14.5, 1H), 3.91 (s, 2H), 1.69 ppm (d, *J* = 7.3, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 144.0, 143.1, 141.5, 140.7, 135.2, 126.9, 126.7, 125.2, 124.9, 123.2, 121.6, 120.1, 119.8, 36.6, 31.1, 21.5 ppm; FTIR (neat, NaCl): *v* (C≡N) 2236 cm^{-1}; HRMS (EI): m/z calcd. for $C_{16}H_{13}N$ (M^+): 219.1048, found: 219.1064.

2-(Naphthalen-2-yl)-2-phenylacetonitrile (**2j**): White solid; m.p. 75-76 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 7.9, 13.5, 4H), 7.62 – 7.46 (m, 2H), 7.45 – 7.30 (m, 6H), 5.29 ppm (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 135.6, 133.0, 132.9, 132.6, 129.0, 128.1, 127.8, 127.6, 127.5, 127.0, 126.6, 126.5, 125.0, 119.4, 42.5 ppm; FTIR (neat, NaCl): *v* (C≡N) 2241 cm^{-1}; HRMS (EI): m/z calcd. for $C_{18}H_{13}N$ (M^+): 243.1048, found: 243.1037.

2,2,2-Triphenylacetonitrile (**2k**):[12] White solid; m.p. 128-130 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.35 (dd, *J* = 1.9, 5.2, 9H), 7.22 ppm (dt, *J* = 2.1, 5.5, 6H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 140.0, 128.6, 128.5, 127.9, 123.3, 57.2 ppm; FTIR (neat, NaCl): *v* (C≡N) 2242 cm^{-1}; HRMS (EI): m/z calcd. for $C_{20}H_{15}N$ (M^+): 269.1204, found: 269.1197.

(*E*)-2-Methyl-4-phenylbut-3-enenitrile (**2l**):[17] Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.60 – 7.13 (m, 5H), 6.71 (d, *J* = 15.8, 1H), 6.06 (ddd, *J* = 1.0, 5.9, 15.8, 1H), 3.66 – 3.34 (m, 1H), 1.50 ppm (dd, *J* = 1.0, 7.3, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 135.4, 132.2, 128.5, 128.0, 126.3, 124.0, 120.6, 28.1, 18.8 ppm; FTIR (neat, NaCl): *v* (C≡N) 2242 cm^{-1}; HRMS (EI): m/z calcd. for $C_{11}H_{11}N$ (M^+): 157.0891, found: 157.0894.

(*E*)-2-Methyl-4-(4-methylphenyl)but-3-enenitrile (**2m**):[18] Viscous colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (d, *J*=8.1, 2H), 7.14 (d, *J*=7.9, 2H), 6.67 (dd, *J*=1.2, 15.8, 1H), 6.00 (dd, *J*=6.1, 15.8, 1H), 3.55 – 3.41 (m, 1H), 2.34 (s, 3H), 1.49 ppm (d, *J*=7.2, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.2, 132.9, 132.4, 129.4, 126.5, 123.3, 121.0, 28.4, 21.3, 19.1 ppm; FTIR (neat, NaCl): *v* (C≡N) 2241 cm^{-1}; HRMS (EI): m/z calcd. for $C_{12}H_{13}N$ (M^+): 171.1048, found: 171.1066.

(*E*)-4-(4-Methoxyphenyl)-2-methylbut-3-enenitrile (**2n**):[18] Viscous colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 – 7.28 (m, 2H), 6.92 – 6.81 (m, 2H), 6.65 (dd, *J*=1.3, 15.8, 1H), 5.92 (dd, *J*=6.2, 15.8, 1H), 3.81 (s, 3H), 3.56 – 3.39 (m, 1H), 1.49 ppm (d, *J*=7.2, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.7, 132.0, 128.5, 127.8, 122.1, 121.1,

114.1, 55.3, 28.4, 19.2 ppm; FTIR (neat, NaCl): ν (C≡N) 2239 cm^{-1}; HRMS (EI): m/z calcd. for $C_{12}H_{13}NO$ (M^+): 187.0997, found: 187.0989.

(*E*)-4-(4-Chlorophenyl)-2-methylbut-3-enenitrile (**2o**): Viscous golden oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (s, 4H), 6.67 (dd, *J*=1.6, 15.8, 1H), 6.04 (dd, *J*=6.0, 15.8, 1H), 3.61 – 3.41 (m, 1H), 1.51 ppm (d, *J*=7.2, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 134.2, 134.0, 131.4, 128.9, 127. 8, 125.0, 120.7, 28.4, 19.0 ppm; FTIR (neat, NaCl): ν (C≡N) 2240 cm^{-1}; HRMS (EI): m/z calcd. for $C_{11}H_{10}ClN$ (M^+): 191.0502, found: 191.0487.

(*E*)-2,2-Dimethyl-4-phenylbut-3-enenitrile (**2p**):[19] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 – 7.50 (m, 5H), 7.10 (d, *J* = 16.0, 1H), 6.35 (dd, *J* =16.0, 1H), 1.88 ppm (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.8, 130.4, 129.9, 128.7, 128.2, 126.6, 121.8, 35.0, 27.7 ppm; FTIR (neat, NaCl): ν (C≡N) 2241 cm^{-1}; HRMS (EI): m/z calcd. for $C_{12}H_{13}N$ (M^+): 171.1048, found: 171.1052.

(*E*)-2,4-Diphenylbut-3-enenitrile (**2q**):[14,19] White solid; m.p. 70-71 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 – 7.27 (m, 10H), 6.82 (dd, *J* = 1.2, 15.9, 1H), 6.20 (dd, *J* = 6.1, 15.9, 1H), 4.70 ppm (dd, *J* = 1.5, 6.4, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.5, 134.6, 133.4, 129.3, 128.8, 128.5, 127.6, 126.8, 123.3, 118.8, 40.0 ppm; FTIR (neat, NaCl): ν (C≡N) 2245 cm^{-1}; HRMS (EI): m/z calcd. for $C_{16}H_{13}N$ (M^+): 219.1048, found: 219.1062.

(3*E*, 5*E*)-2,6-Diphenylhexa-3,5-dienenitrile (**2r**): White solid; m.p. 100-102 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.50 – 7.27 (m, 10H), 6.50 – 7.27 (m, 3H), 5.81 (dd, *J*=6.3, 15.0, 1H), 4.63 ppm (d, *J*=6.2, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 136.7, 134.8, 134.7, 133.6, 129.3, 128.7, 128.4, 128.1, 127.6, 126.7, 126.6 (double peaks), 118.8, 39.9 ppm; FTIR (neat, NaCl): ν (C≡N) 2242 cm^{-1}; HRMS (EI): m/z calcd. for $C_{18}H_{15}N$ (M^+): 245.1204, found: 245.1223.

(3*E*, 5*E*)-2,6-Bis(4-methylphenyl)hexa-3,5-dienenitrile (**2t**): White solid; m.p. 131-133 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (dd, *J*=2.1, 8.2, 2H), 7.25 – 7.10 (m, 6H), 6.77 – 6.53 (m, 3H), 5.76 (dd, *J*=6.3, 15.0, 1H), 4.58 (d, *J*=6.3, 1H), 2.36 (s, 3H), 2.34 ppm (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.3, 138.1, 134.6, 133.9, 133.6, 129.9, 129.4, 127.4, 126.6, 126.5, 126.2, 125.9, 119.0, 39.5, 21.3, 21.1 ppm; FTIR (neat, NaCl): ν (C≡N) 2238 cm^{-1}; HRMS (EI): m/z calcd. for $C_{20}H_{19}N$ (M^+): 273.1517, found: 273.1505.

(3*E*, 5*E*)-2,6-Bis(4-methoxyphenyl)hexa-3,5-dienenitrile (**2u**): White solid; m.p. 150-152 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 – 7.23 (m, 4H), 6.95 – 6.82 (m, 4H), 6.66 – 6.49 (m, 3H), 5.72 (dd, *J*=6.3, 14.6, 1H), 4.56 (d, *J*=6.2, 1H), 3.81 ppm (double peaks, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.6 (double peaks), 134.2, 133.6, 129.5, 128.7, 127.8, 126.8, 125.7, 124.8, 119.1, 114.6, 114.2, 55.4, 55.3, 39.1 ppm; FTIR (neat, NaCl): ν (C≡N) 2239 cm^{-1}; HRMS (EI): m/z calcd. for $C_{20}H_{19}NO_2$ (M^+): 305.1416, found: 305.1442.

(3*E*, 5*E*)-2,6-Bis(4-chlorophenyl)hexa-3,5-dienenitrile (**2v**): White solid; m.p. 157-159 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 – 7.36 (m, 2H), 7.34 – 7.27 (m, 6H), 6.77 – 6.52 (m, 3H), 5.78 (dd, *J*=6.3, 14.9, 1H), 4.61 ppm (d, *J*=5.9, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.0, 134.6, 133.9, 133.8, 133.7, 133.0, 129.5, 128.9 (double peaks), 127.7, 127.1, 126.4, 118.2, 39.3 ppm; FTIR (neat, NaCl): *v* (C≡N) 2240 cm^{-1}; HRMS (EI): m/z calcd. for $C_{18}H_{13}Cl_2N$ (M^+): 313.0425, found: 313.0425.

(3-Benzylidenecyclohex-1-enyl)phenylacetonitrile (**2w**): White solid; m.p. 190-192 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 – 7.19 (m, 10H), 6.42 (s, 1H), 6.40 (s, 1H), 4.52 (s, 1H), 2.64 – 2.56 (m, 2H), 2.16 – 1.95 (m, 2H), 1.72 – 1.64 ppm (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.4, 136.2, 134.6, 134.1, 131.0, 129.1 (double peaks), 128.8, 128.4, 128.2, 127.8, 126.7, 118.8, 44.8, 26.5, 26.2, 22.6 ppm; FTIR (neat, NaCl): *v* (C≡N) 2235 cm^{-1}; HRMS (EI): m/z calcd. for $C_{21}H_{19}N$ (M^+): 285.1517, found: 285.1521.

[3-(4-Methylbenzylidene)cyclohex-1-enyl](4-methylphenyl)acetonitrile (**2x**): Light yellow green solid; m.p. 212-214 ^{o}C ; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 – 7.09 (m, 8H), 6.39 (s, 1H), 6.36 (s, 1H), 4.46 (s, 1H), 2.64 – 2.53 (m, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 2.14 – 1.93 (m, 2H), 1.71 – 1.62 ppm (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.2, 136.4, 135.6, 134.6, 134.3, 131.1, 130.9, 129.8, 129.1, 129.0, 128.7, 127.7, 119.0, 44.4, 26.5, 26.3, 22.6, 21.3, 21.2 ppm; FTIR (neat, NaCl): *v* (C≡N) 2237 cm^{-1}; HRMS (EI): m/z calcd. for $C_{23}H_{23}N$ (M^+): 313.1830, found: 313.1856.

[3-(4-Methoxybenzylidene)cyclohex-1-enyl](4-methoxyphenyl)acetonitrile (**2y**): Light yellow green solid; m.p. 245-247 ^{o}C ; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 – 7.21 (m, 4H), 6.92 – 6.84 (m, 4H), 6.37 (s, 1H), 6.34 (s, 1H), 4.47 (s, 1H), 3.81 (double peaks, 6H), 2.63 – 2.53 (m, 2H), 2.12 – 1.95 (m, 2H), 1.72 – 1.65 ppm (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.6, 158.3, 134.6, 133.9, 130.8, 130.3, 130.1, 128. 9, 128.3, 126.1, 119.1, 114. 5, 113.7, 55.4, 55.3, 44.0, 26.4, 26.2, 22.6 ppm; FTIR (neat, NaCl): *v* (C≡N) 2236 cm^{-1}; HRMS (EI): m/z calcd. for $C_{23}H_{23}NO_2$ (M^+): 345.1729, found: 345.1700.

[3-(4-Fluorobenzylidene)cyclohex-1-enyl](4-fluorophenyl)acetonitrile (**2z**): White solid; m.p. 192-194 ^{o}C ; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 – 7.31 (m, 2H), 7.28 – 7.21 (m, 2H), 7.13 – 6.99 (m, 4H), 6.39 (s, 1H), 6.35 (s, 1H), 4.51 (s, 1H), 2.63 – 2.50 (m, 2H), 2.16 – 1.92 (m, 2H), 1.74 – 1.65 ppm (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.6, 160.5, 134.4, 133.3, 130.9, 130.7, 130.6, 129.5, 129.4, 127.8, 118.6, 116.0, 115.1, 44.0, 26.5, 26.0, 22.5 ppm; FTIR (neat, NaCl): *v* (C≡N) 2238 cm^{-1}; HRMS (EI): m/z calcd. for $C_{21}H_{17}F_2N$ (M^+): 321.1329, found: 321.1330.

[3-(4-Chlorobenzylidene)cyclohex-1-enyl](4-chlorophenyl)acetonitrile (**2aa**): White solid; m.p. 258-260 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42 – 7.17 (m, 8H), 6.39 (s, 1H), 6.34 (s, 1H), 4.50 (s, 1H), 2.62 – 2.50 (m, 2H), 2.15 – 1.93 (m, 2H), 1.73 – 1.66 ppm (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 136.5, 135.6, 134.6, 134.5, 132.5, 132.4,

131.0, 130.3, 129.4, 129.1, 128.4, 127.9, 118.3, 44.1, 26.5, 26.1, 22.4 ppm; FTIR (neat, NaCl): ν (C≡N) 2242 cm^{-1}; HRMS (EI): m/z calcd. for $C_{21}H_{17}Cl_2N$ (M^+): 353.0738, found: 353.0738.

(3*E*, 5*E*, 7*E*)-2,8-Diphenylocta-3,5,7-trienenitrile (**2bb**): White solid; m.p. 124-126 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 – 7.37 (m, 4H), 7.37 – 7.29 (m, 5H), 7.25 – 7.21 (m, 1H), 6.80 (dd, *J*=10.7, 15.5, 1H), 6.61 (d, *J*=15.6, 1H), 6.57 – 6.44 (m, 2H), 6.32 (dd, *J*=10.8, 14.8, 1H), 5.73 (dd, *J*=6.4, 15.0, 1H), 4.61 ppm (d, *J*=6.1, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.0, 135.3, 134.7, 134.1, 133.5, 130.7, 129.3, 128.7, 128.4, 128.3, 127.9, 127.5, 126.5, 126.3, 118.8, 39.9 ppm; FTIR (neat, NaCl): ν (C≡N) 2241 cm^{-1}; HRMS (EI): m/z calcd. for $C_{20}H_{17}N$ (M^+): 271.1361, found: 271.1366.

(3*E*, 5*E*, 7*E*, 9*E*)-2,10-Diphenyldeca-3,5,7,9-tetraenenitrile (**2cc**): White solid; m.p. 145-147 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 – 7.37 (m, 4H), 7.37 – 7.29 (m, 5H), 7.22 (ddd, *J*=1.1, 3.9, 7.3, 1H), 6.83 (dd, *J*=10.6, 15.5, 1H), 6.60 (d, *J*=15.6, 1H), 6.54 – 6.32 (m, 4H), 6.25 (dd, *J*=10.7, 14.0, 1H), 5.71 (dd, *J*=6.4, 15.0, 1H), 4.60 ppm (d, *J*=6.3, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.2, 135.2, 134.8, 134.7, 133.6, 133.5, 132.6, 130.6, 129.3, 128.8, 128.7, 128.4, 127.7, 127.5, 126.5, 126.2, 118.7, 39.9; FTIR (neat, NaCl): ν (C≡N) 2242 cm^{-1}; HRMS (EI): m/z calcd. for $C_{22}H_{19}N$ (M^+): 297.1597, found: 297.1578.

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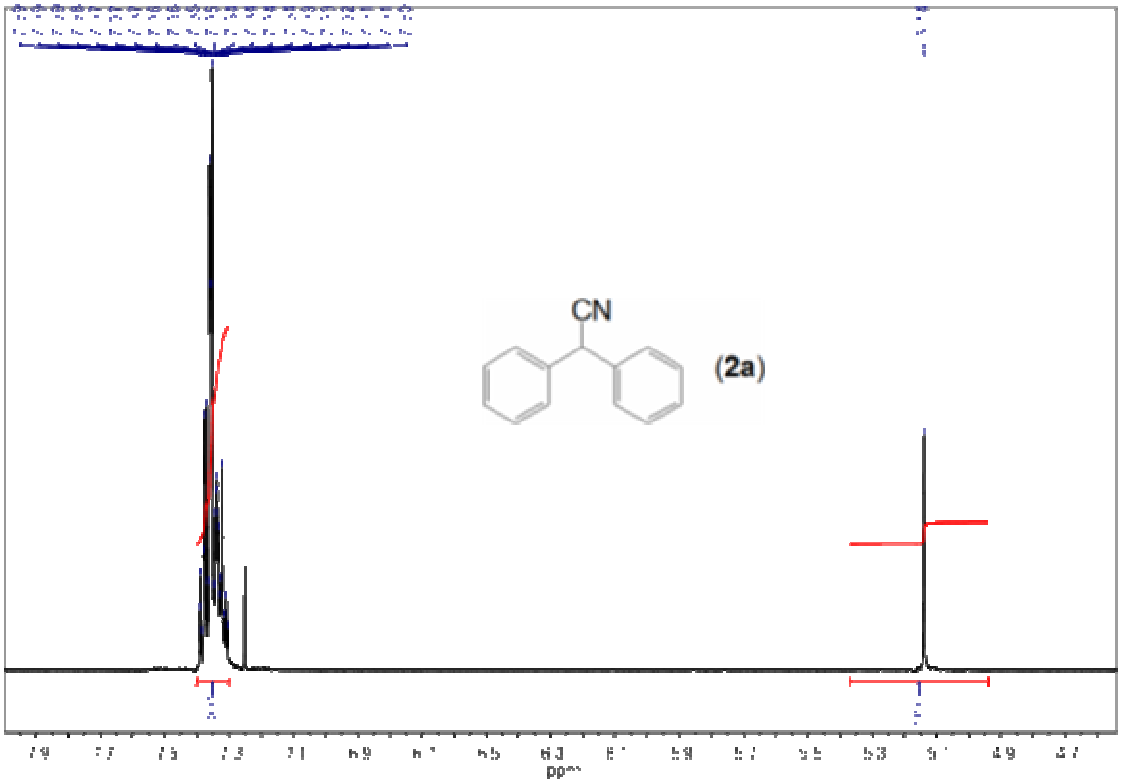

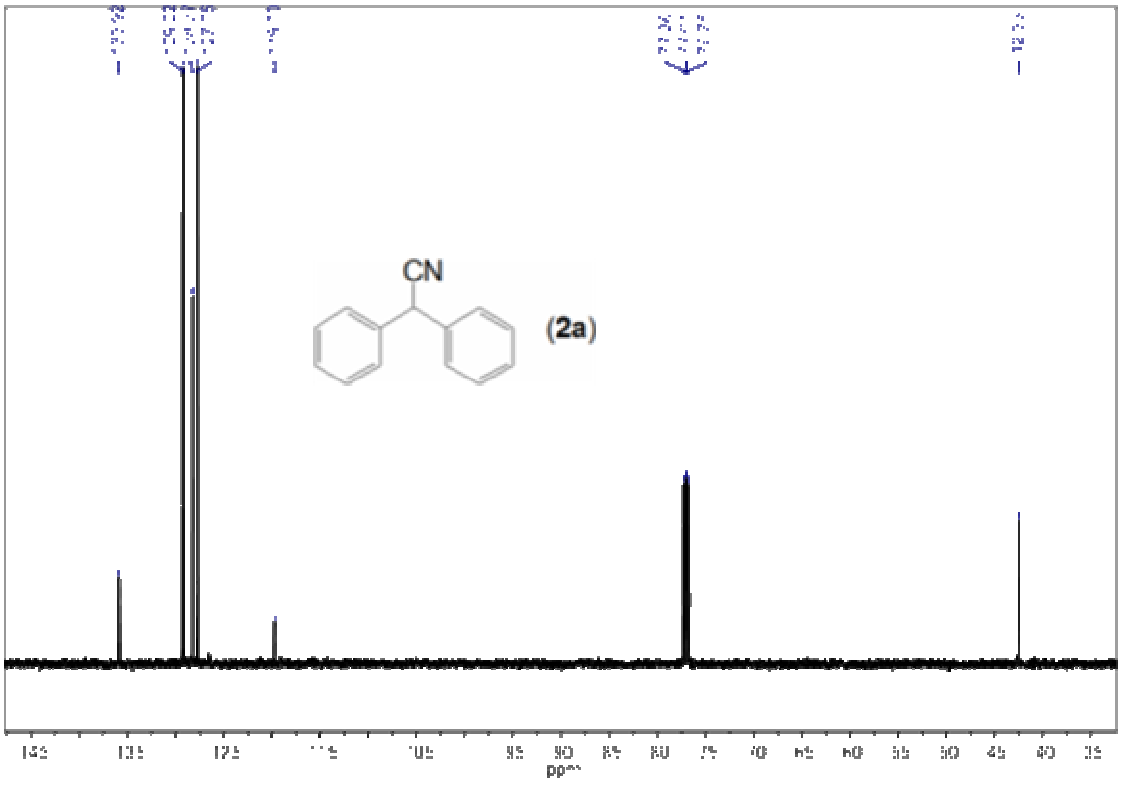

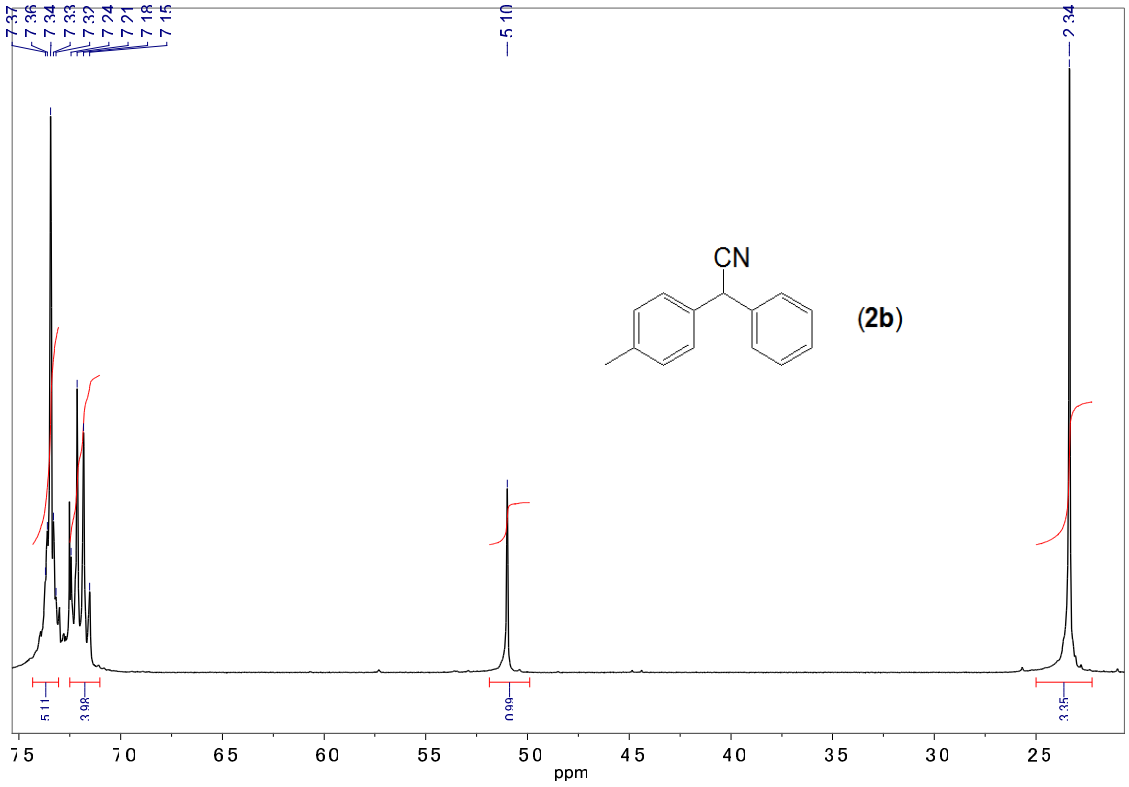
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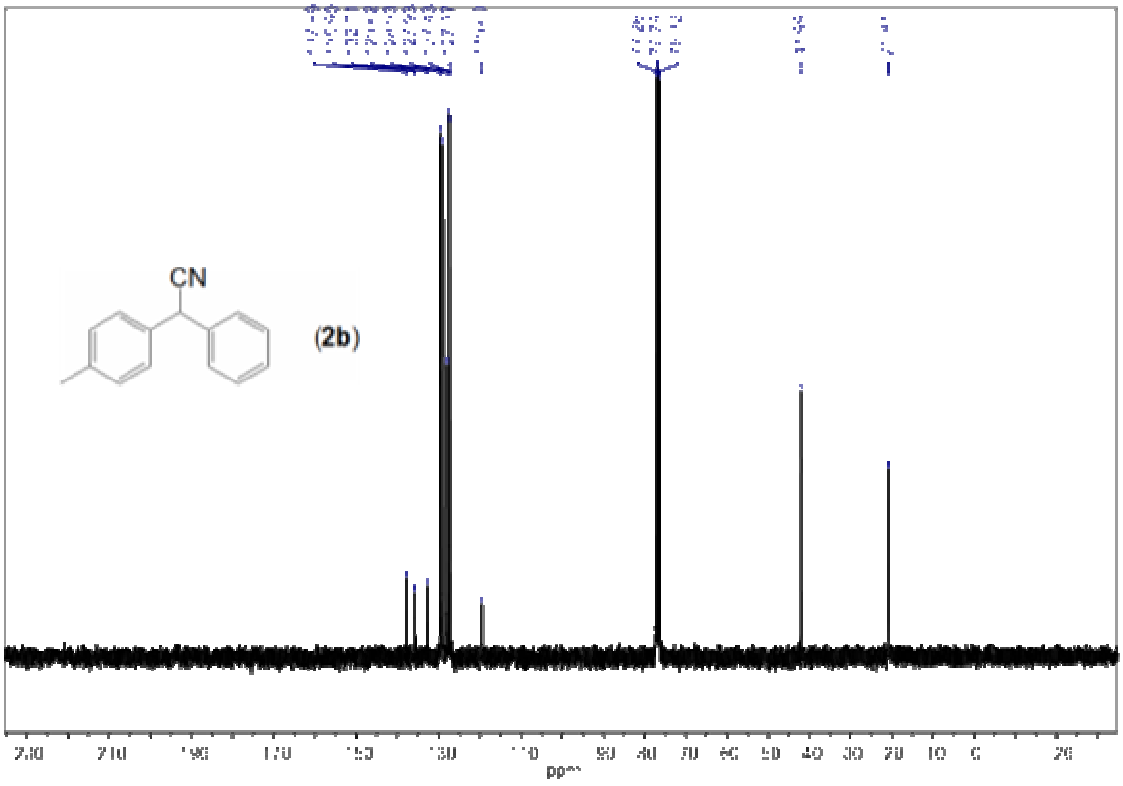
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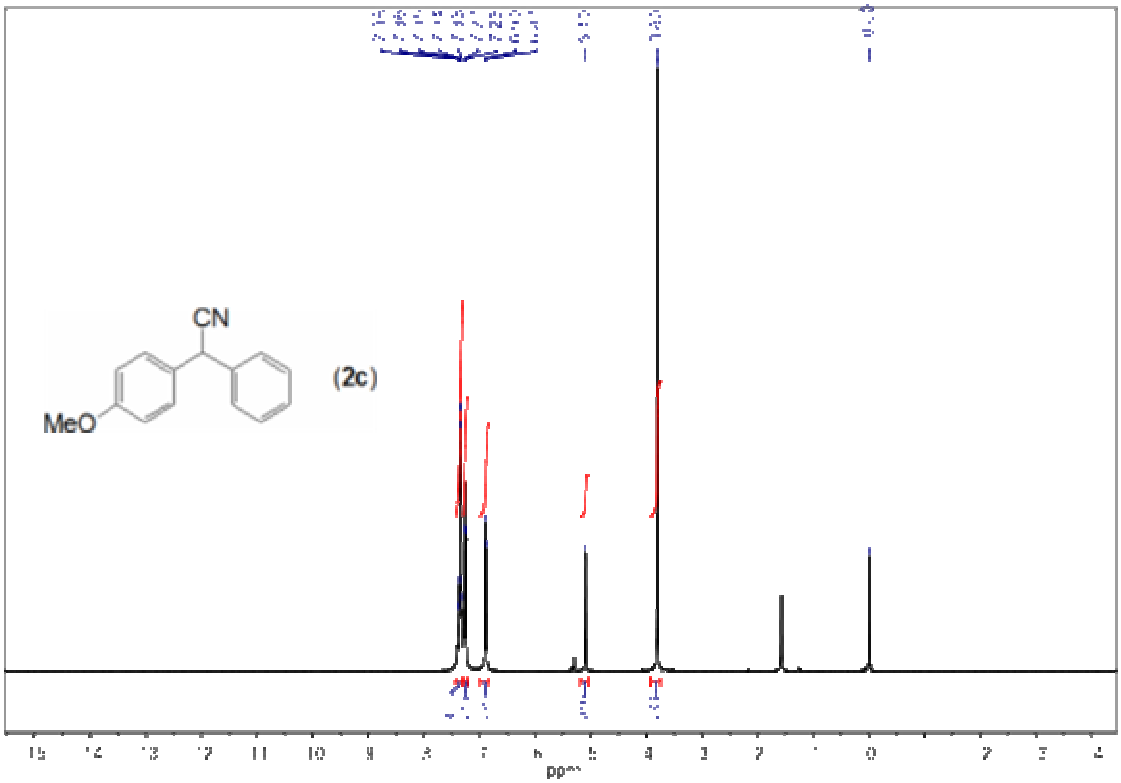
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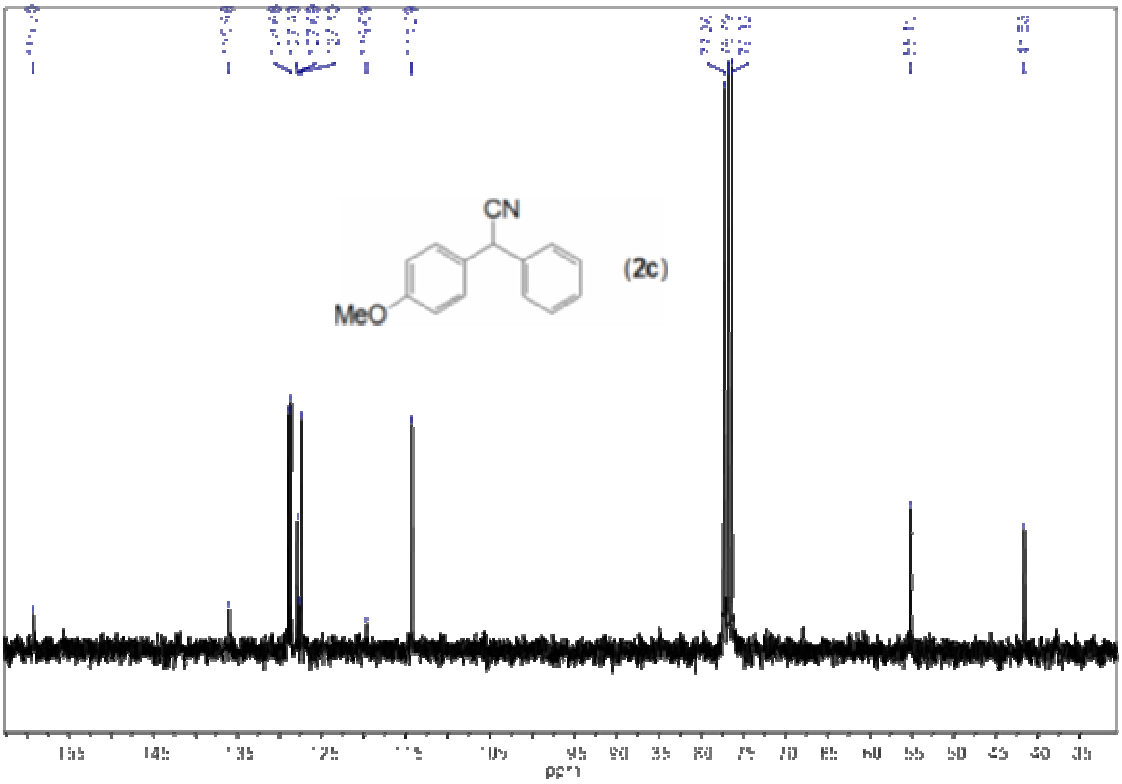
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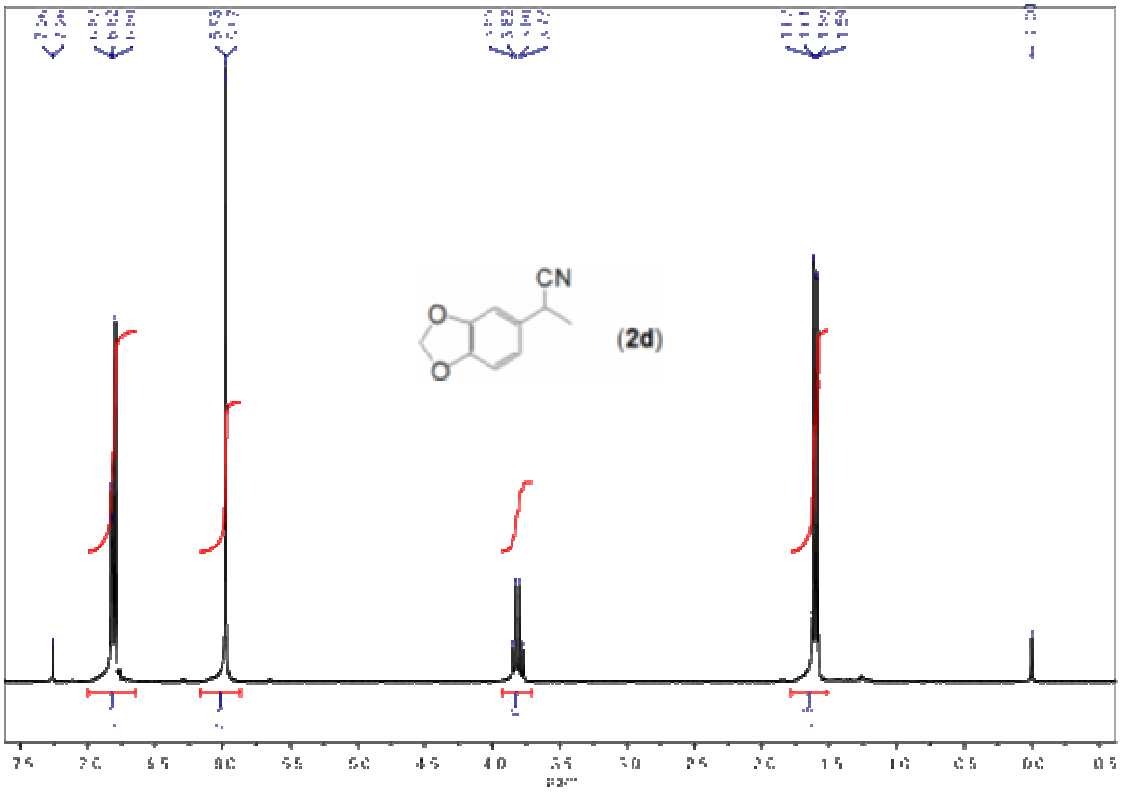
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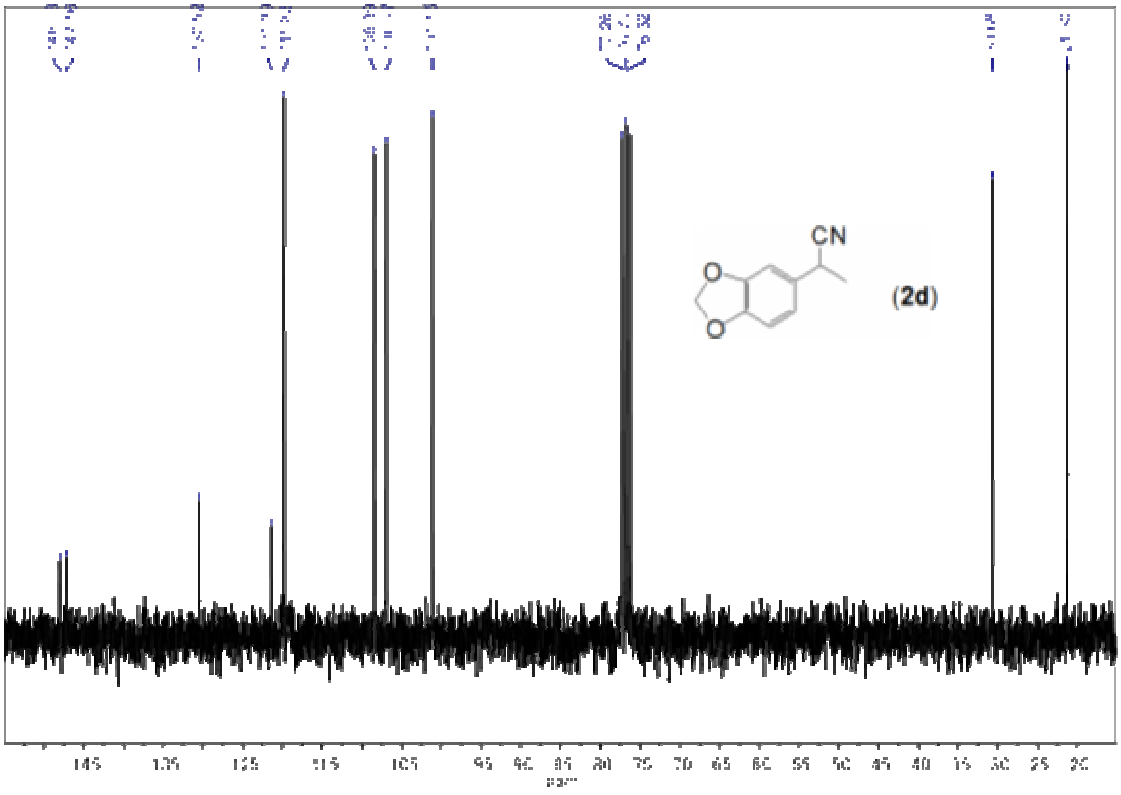
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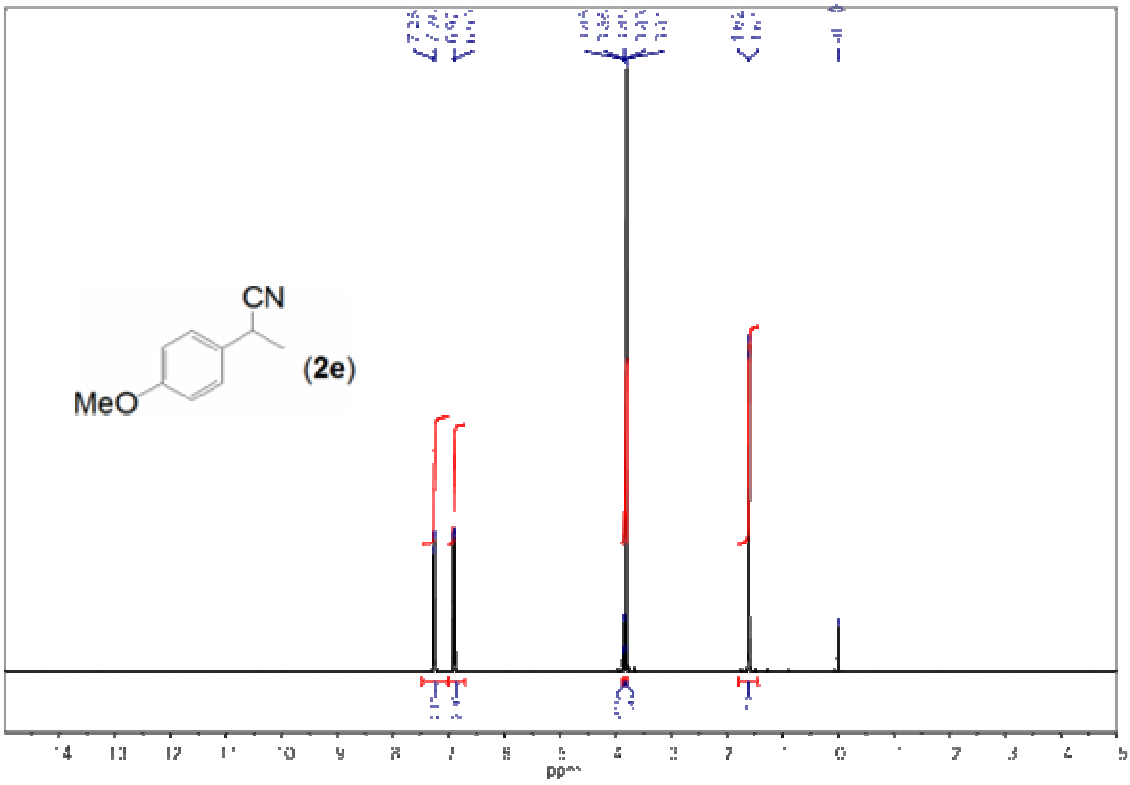
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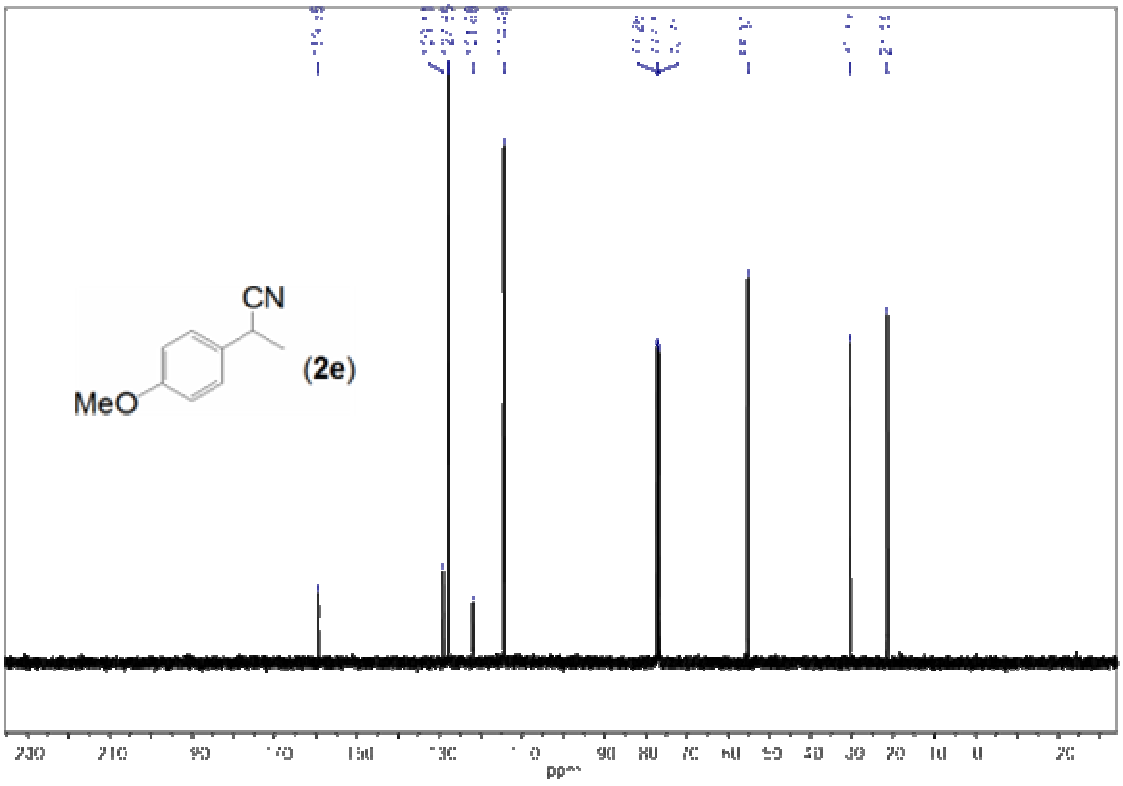
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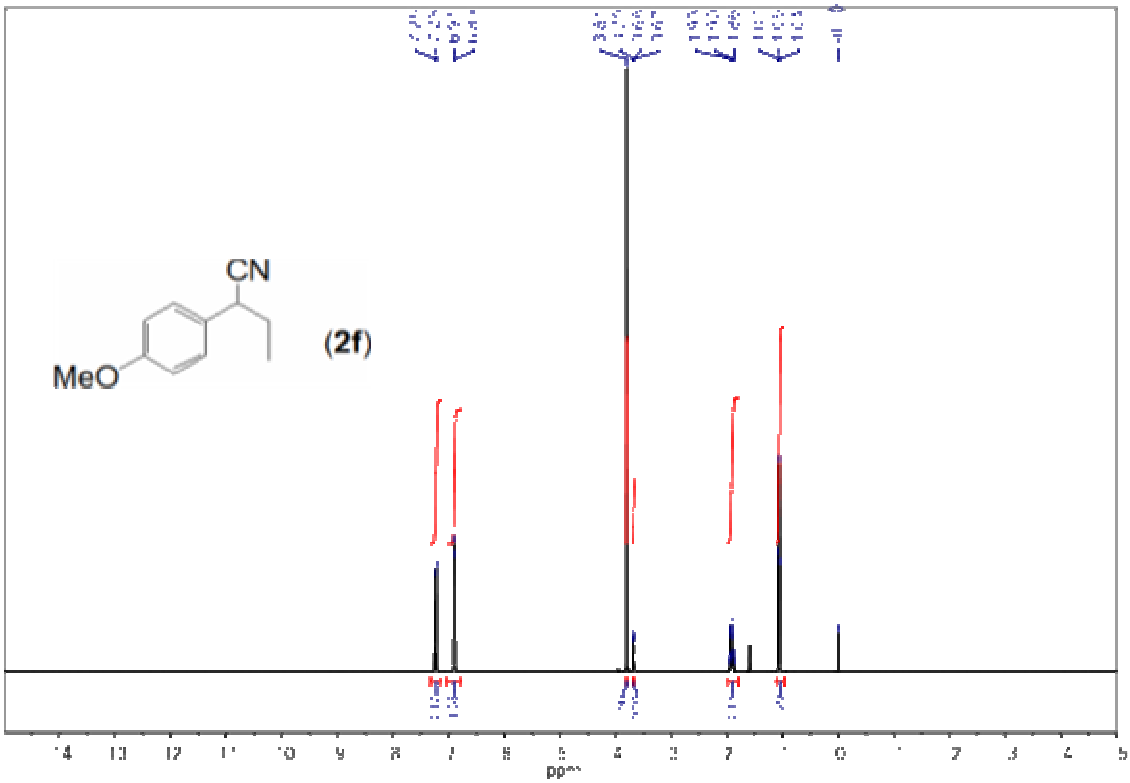
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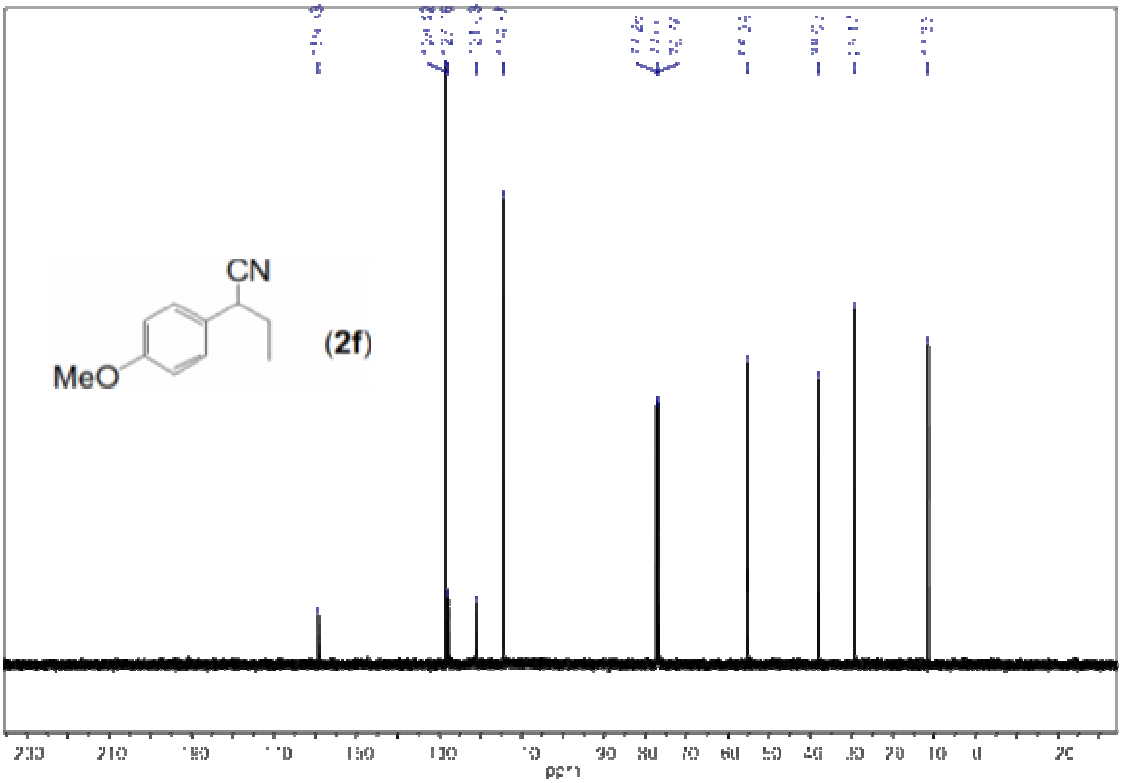
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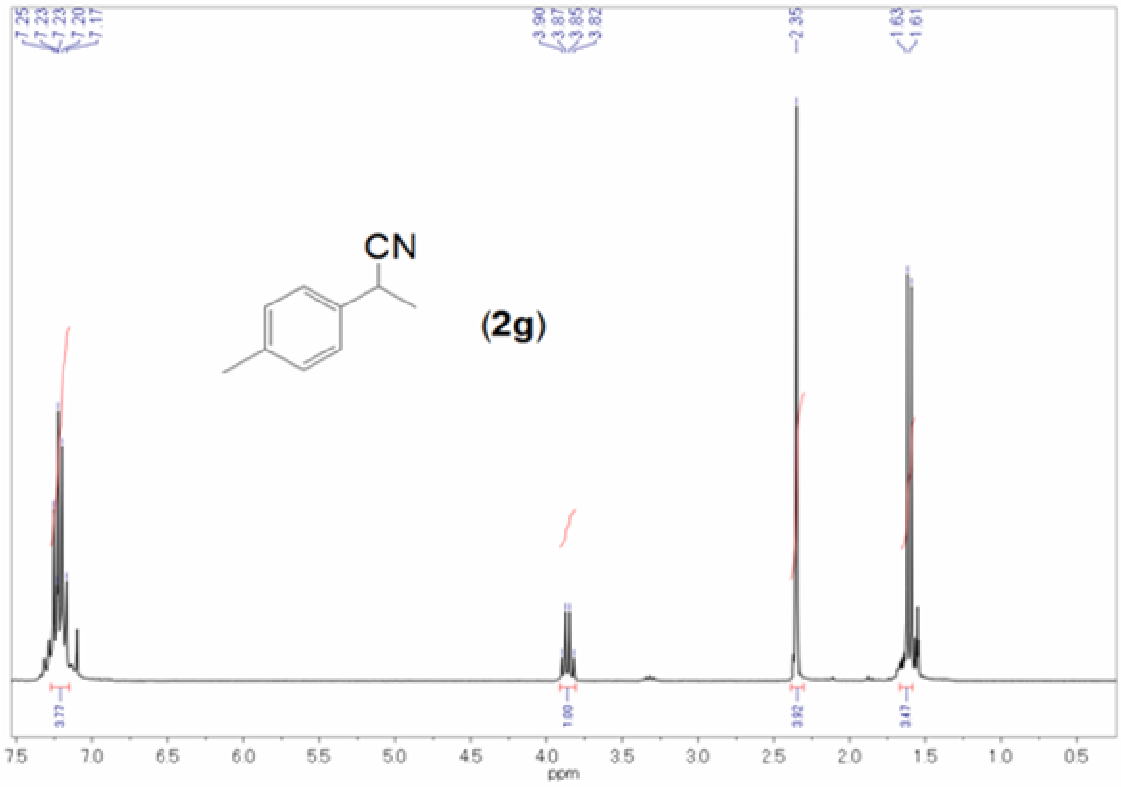
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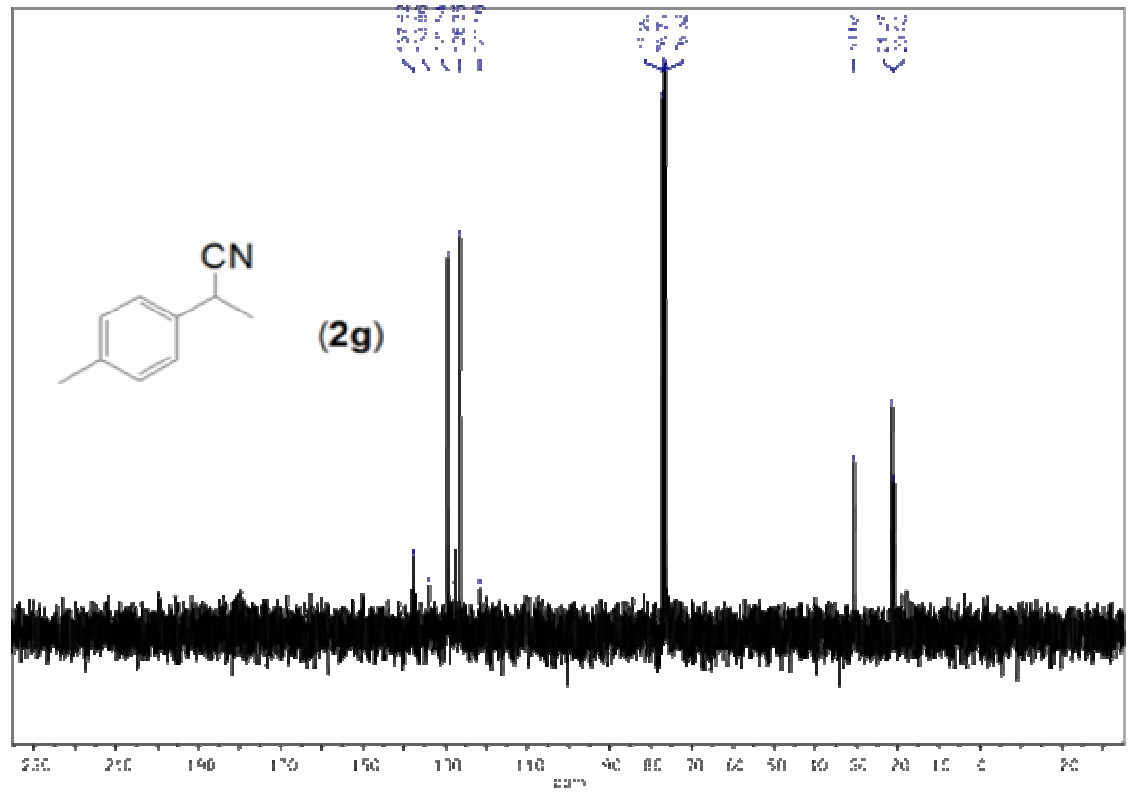
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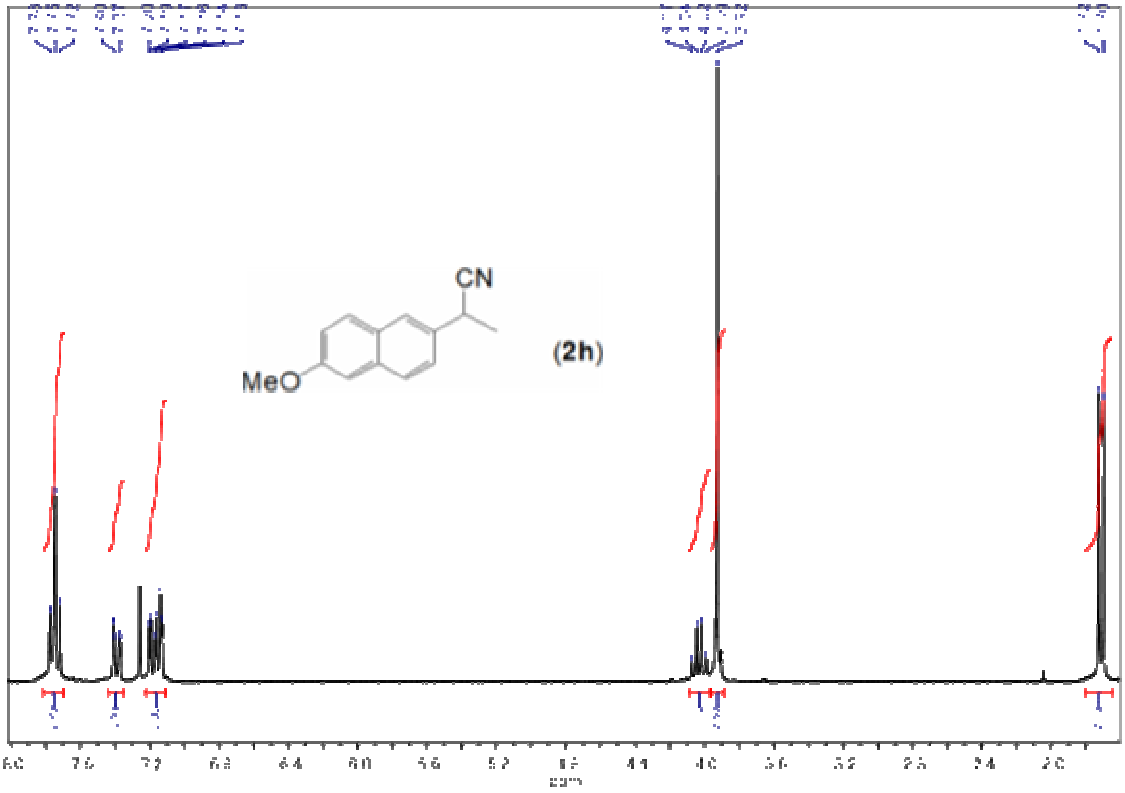
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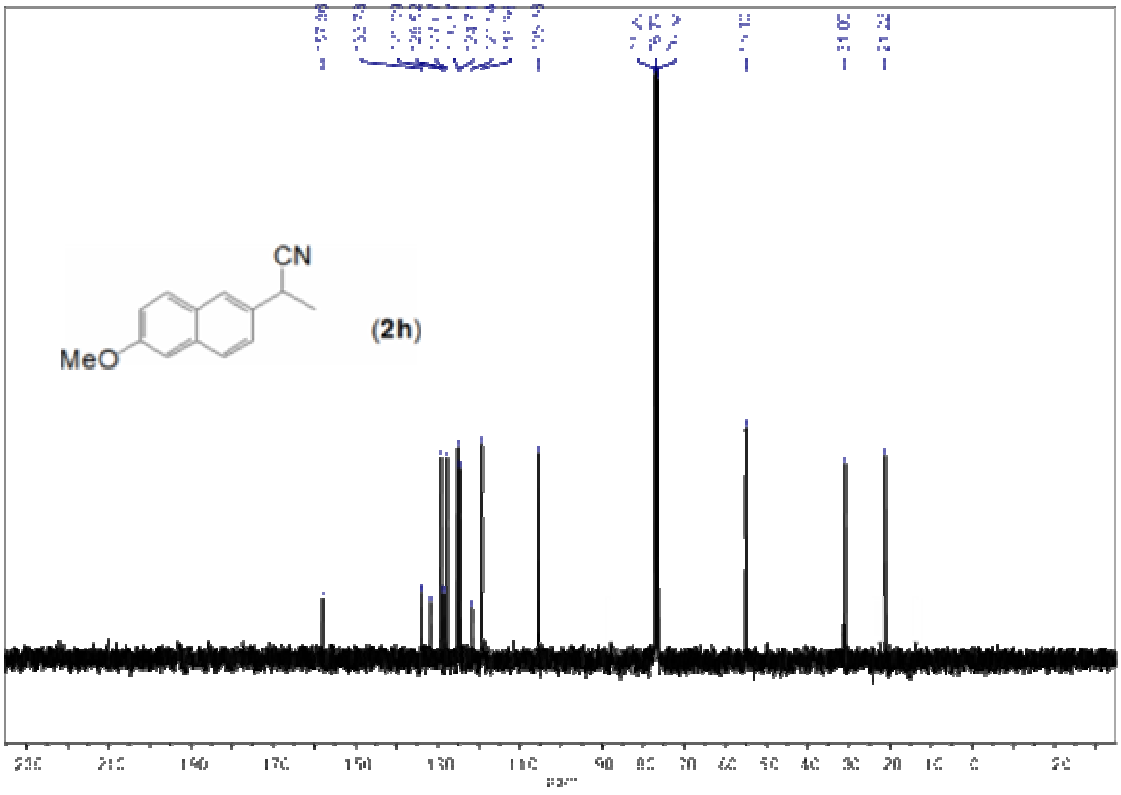
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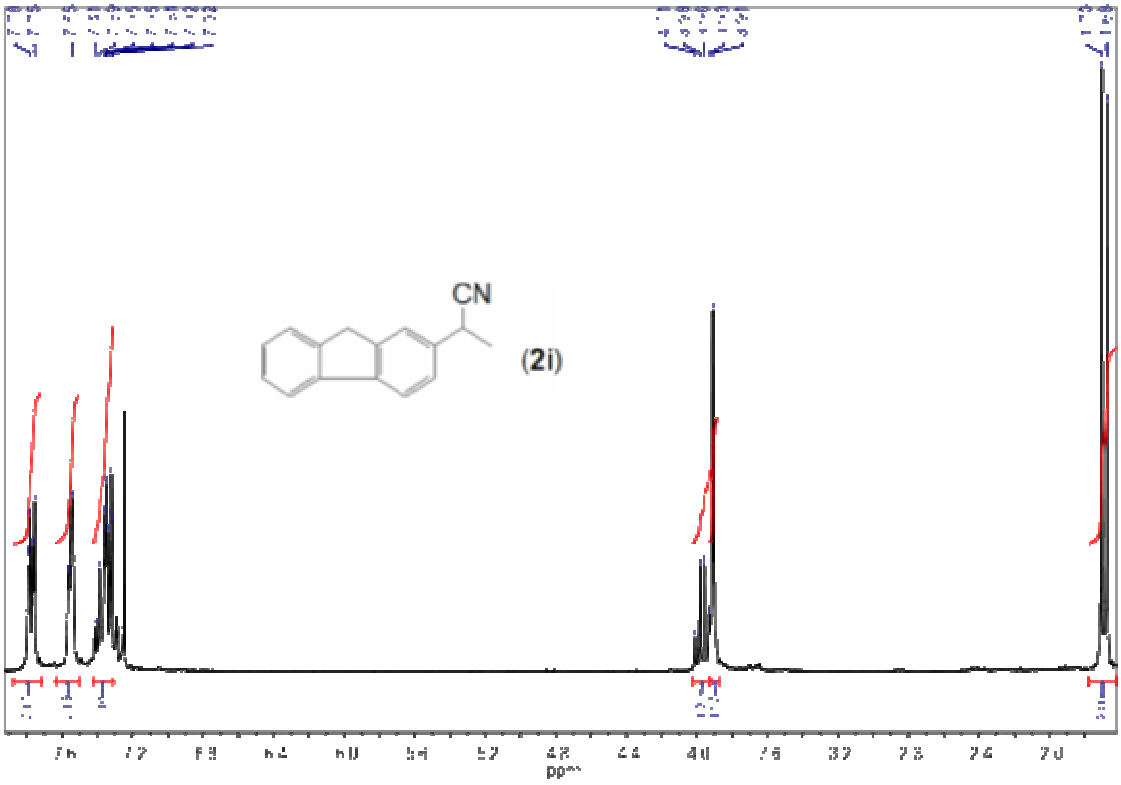
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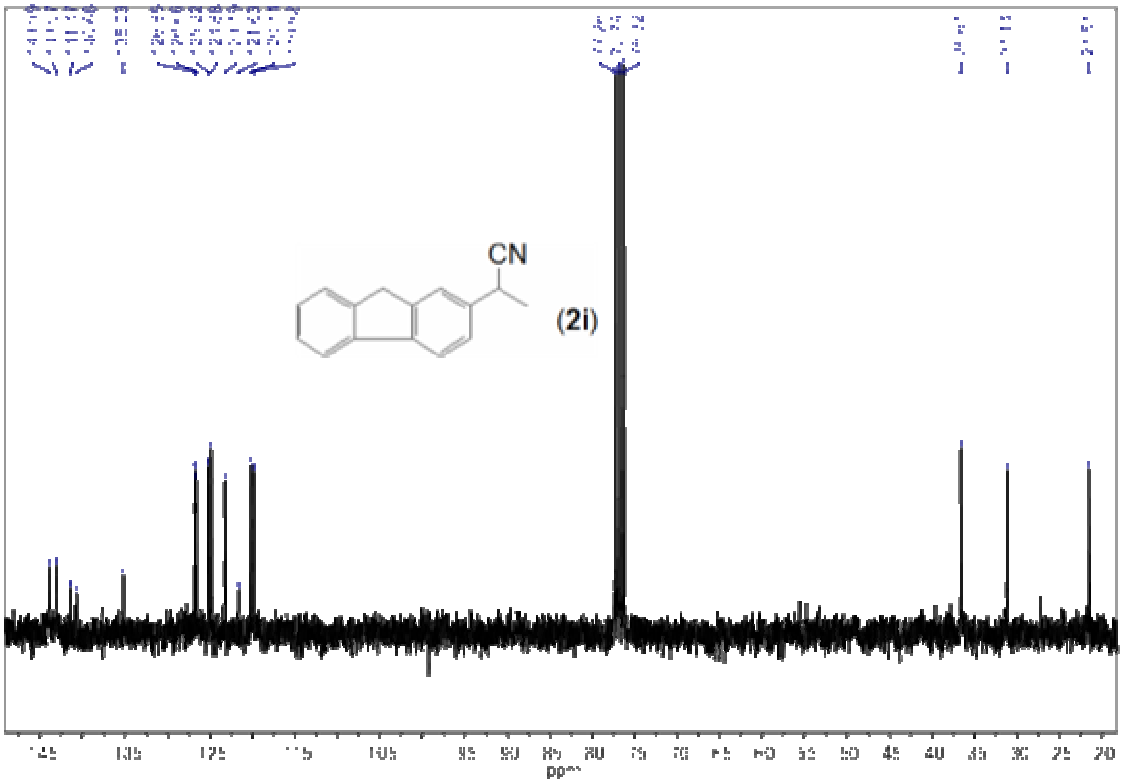
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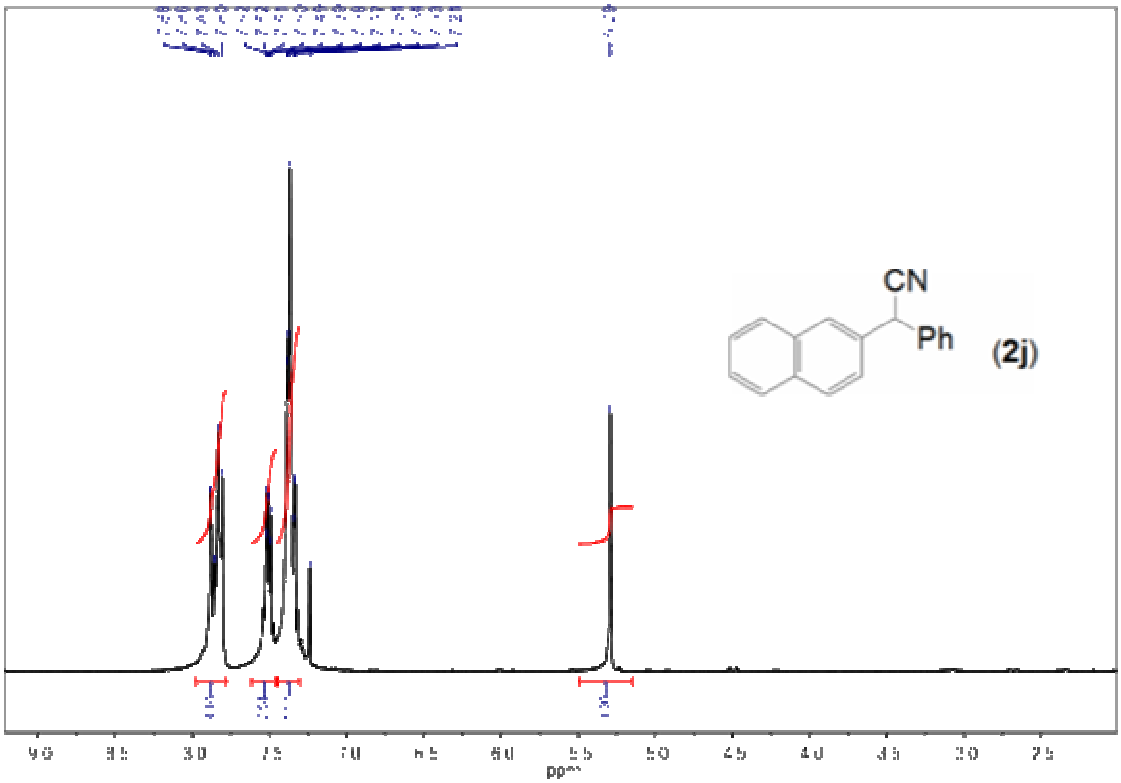
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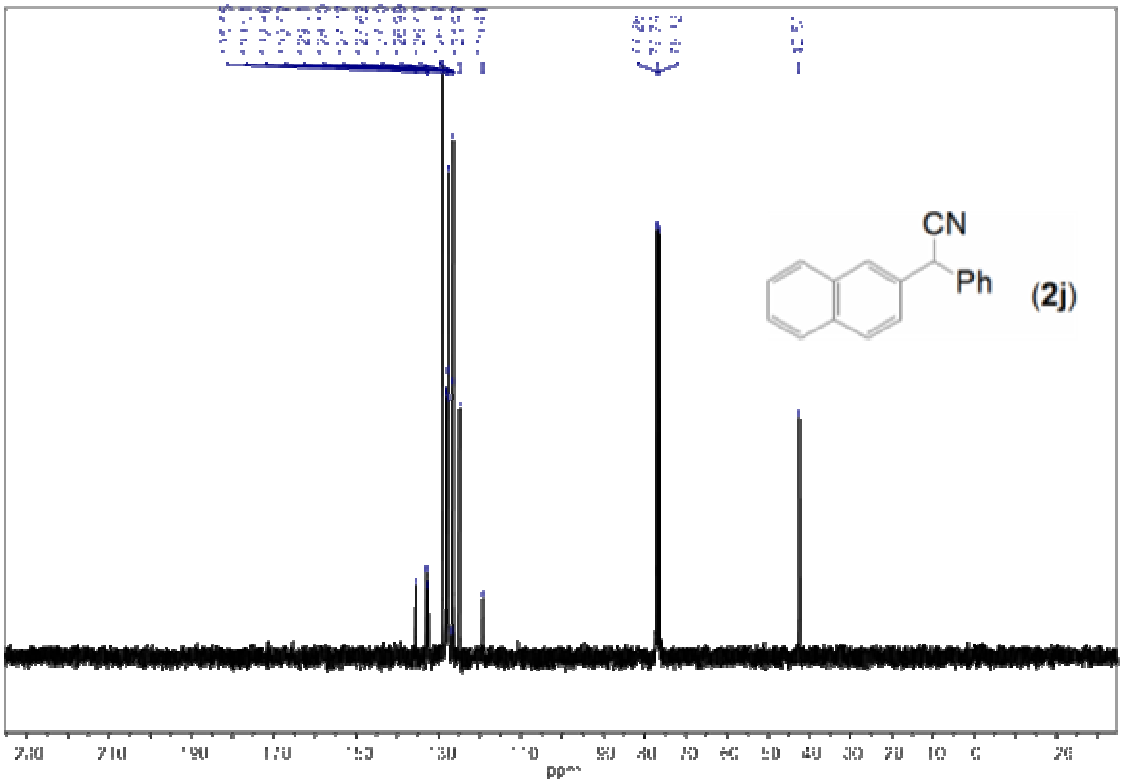
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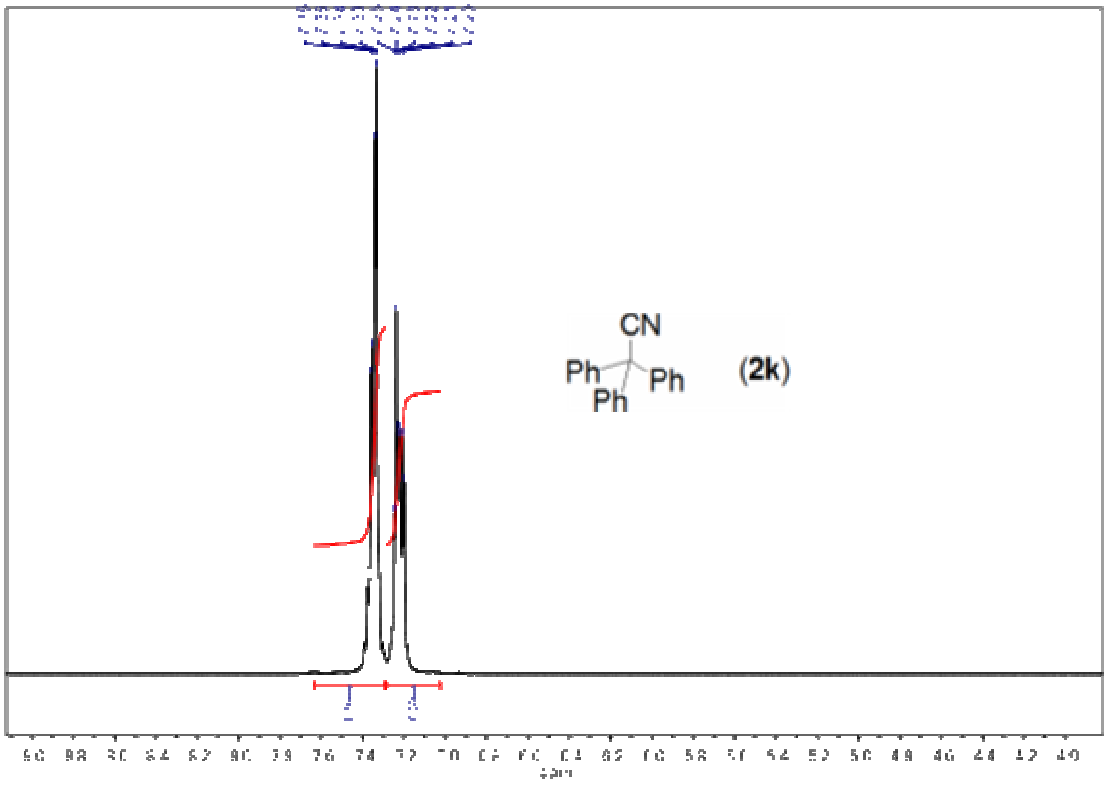
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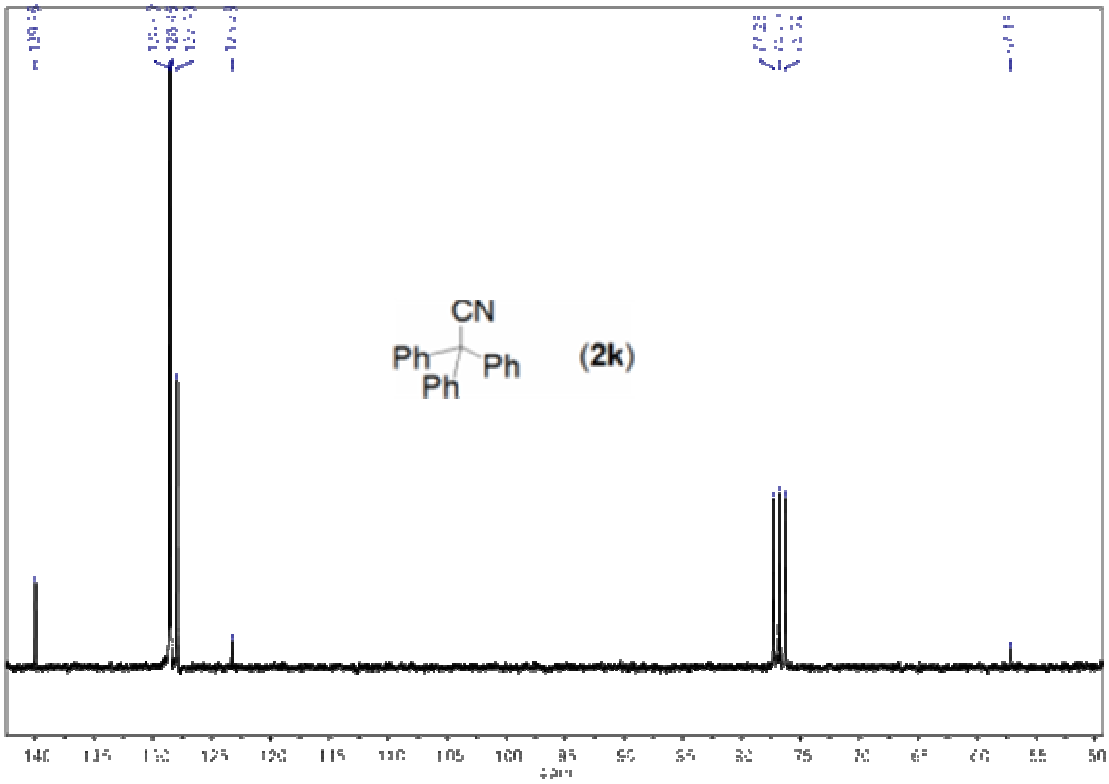
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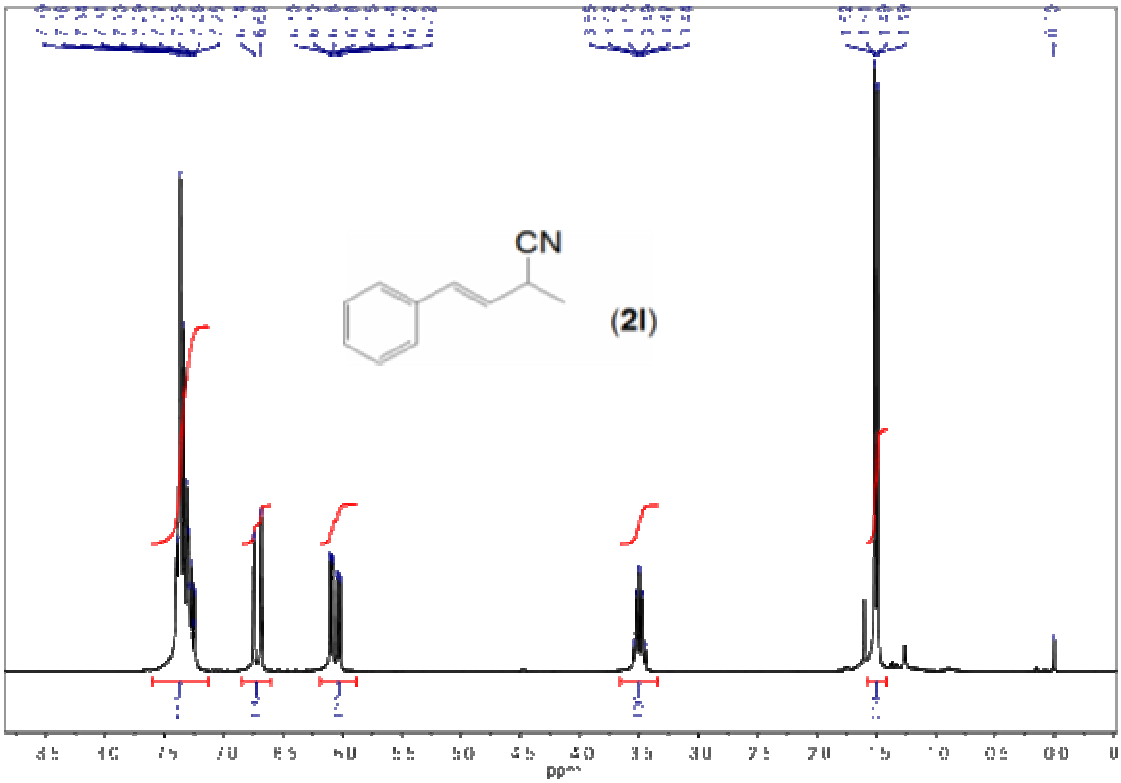
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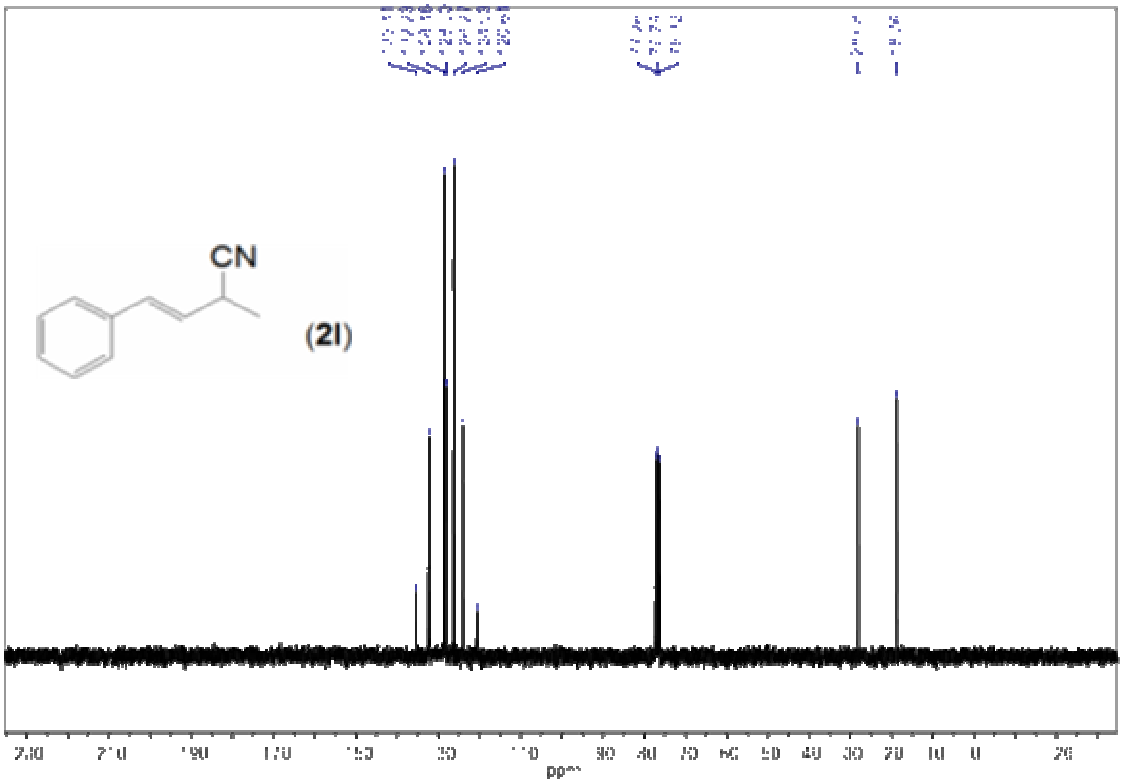
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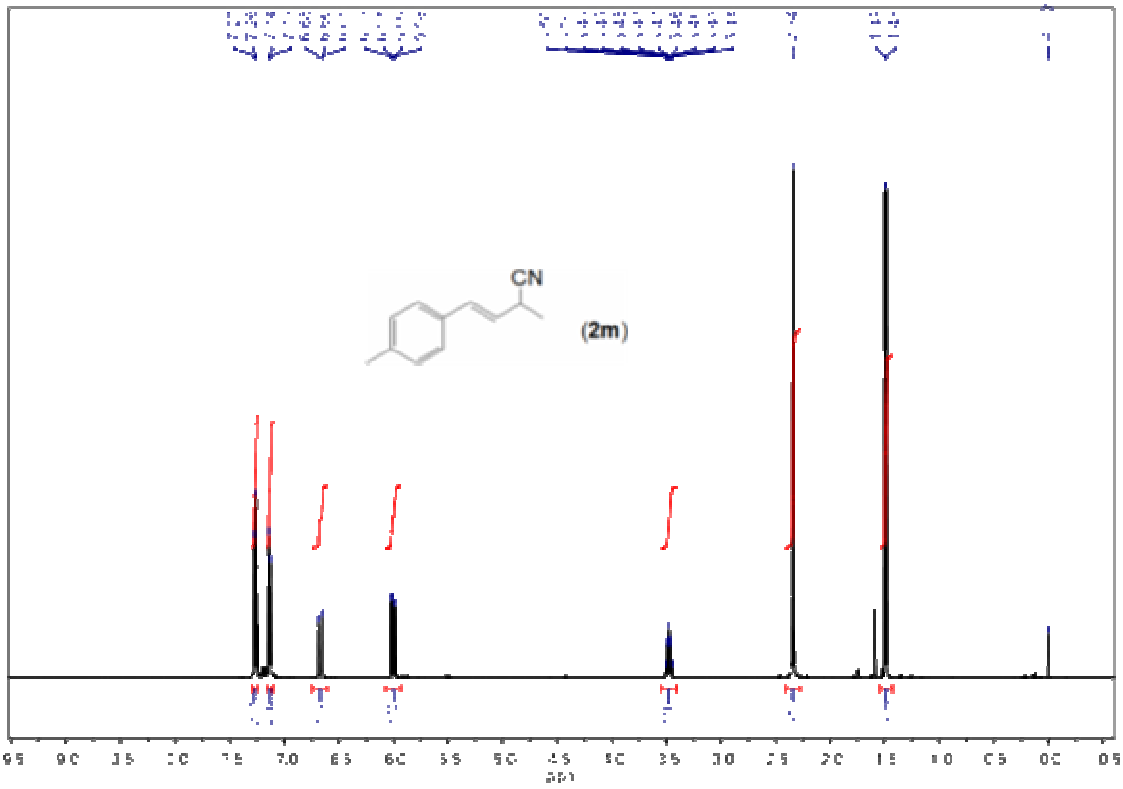
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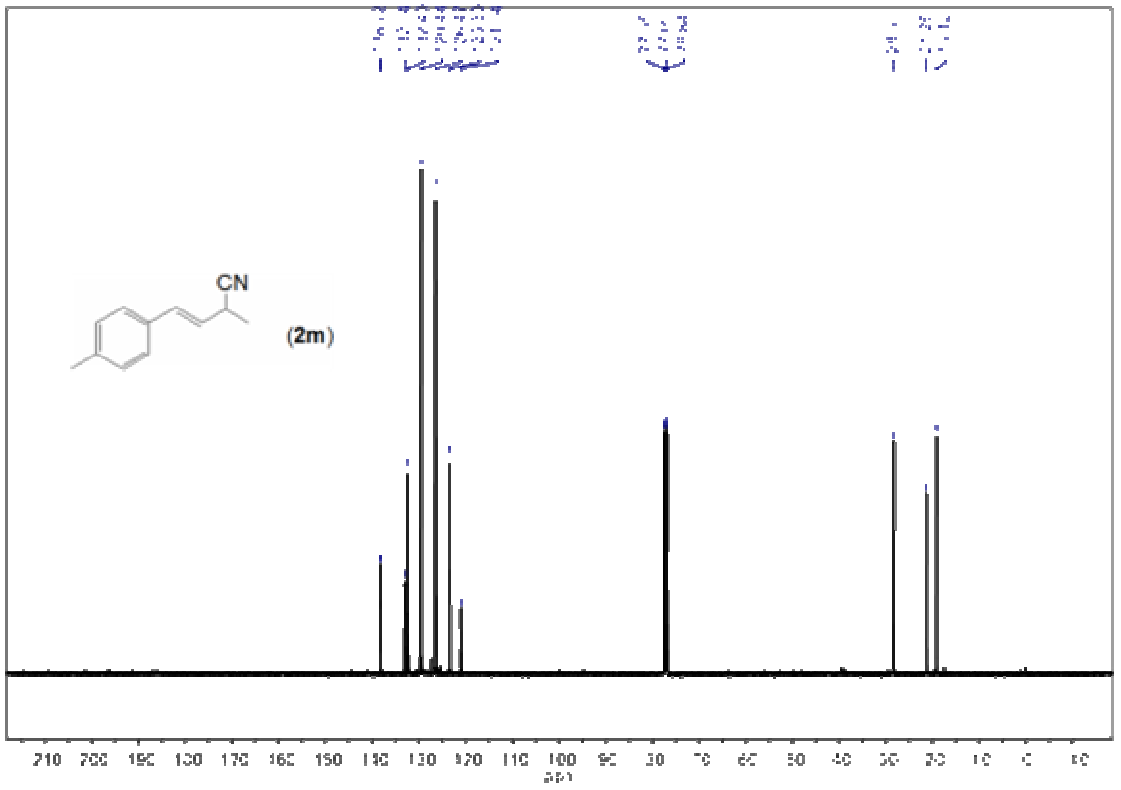
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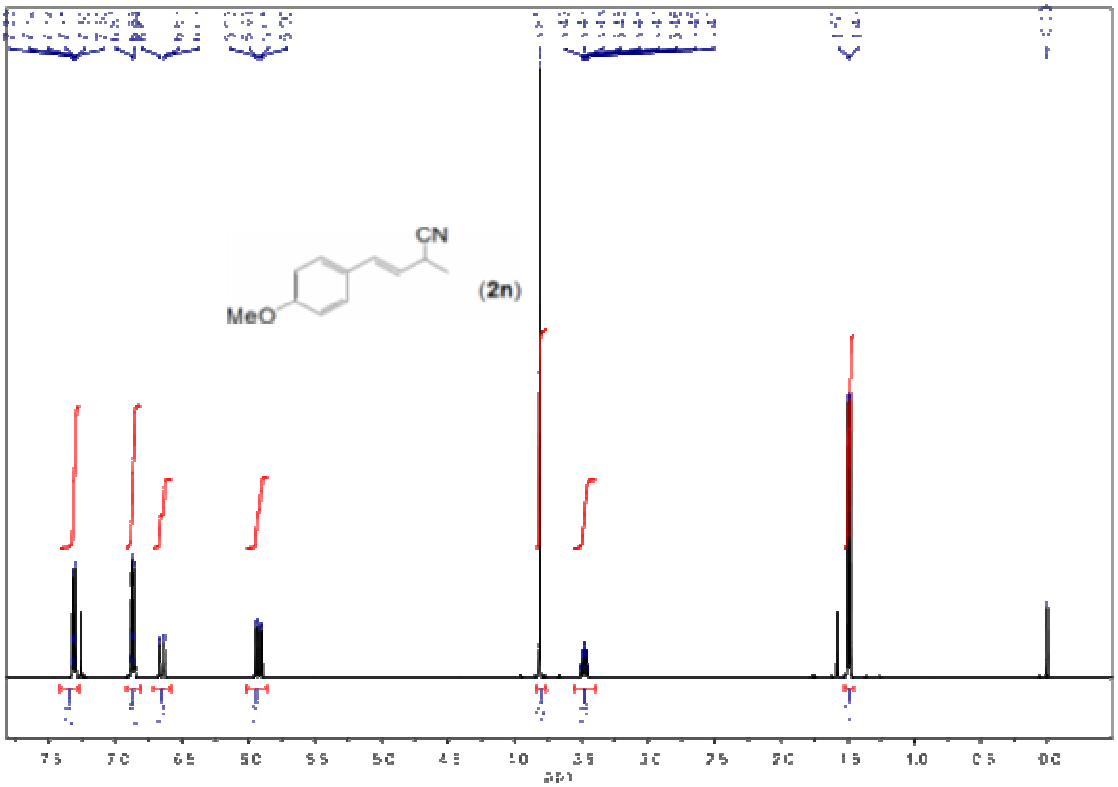
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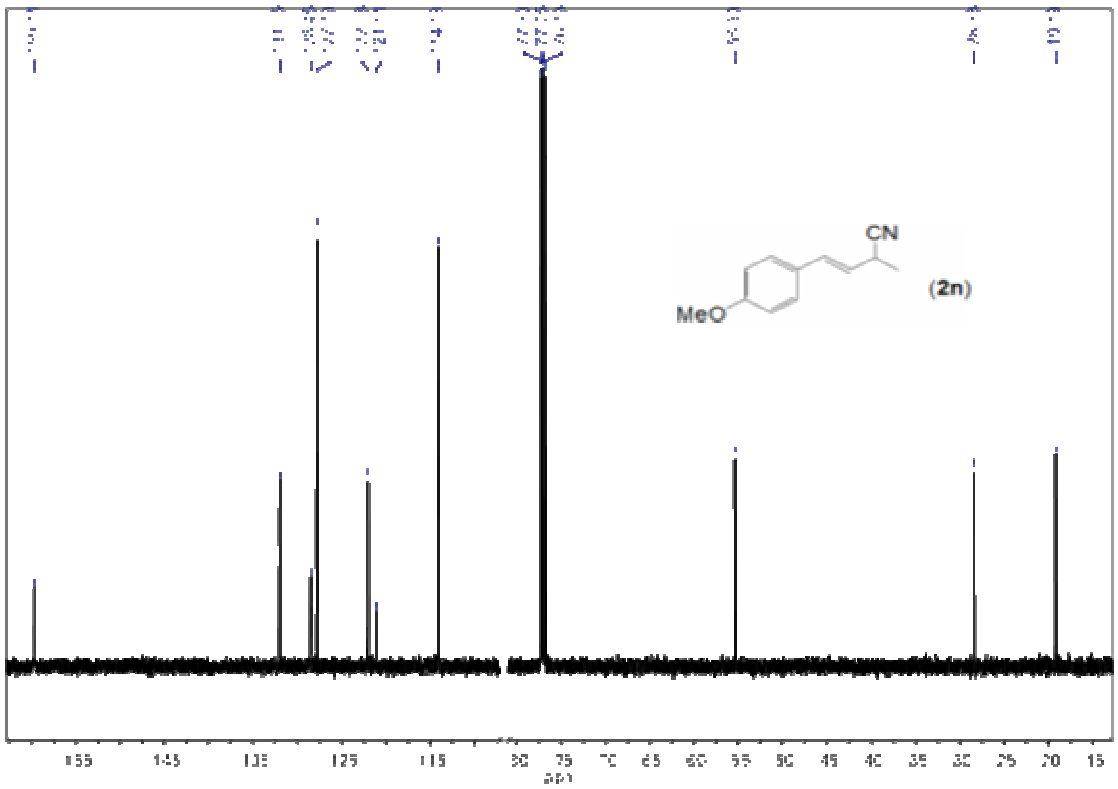
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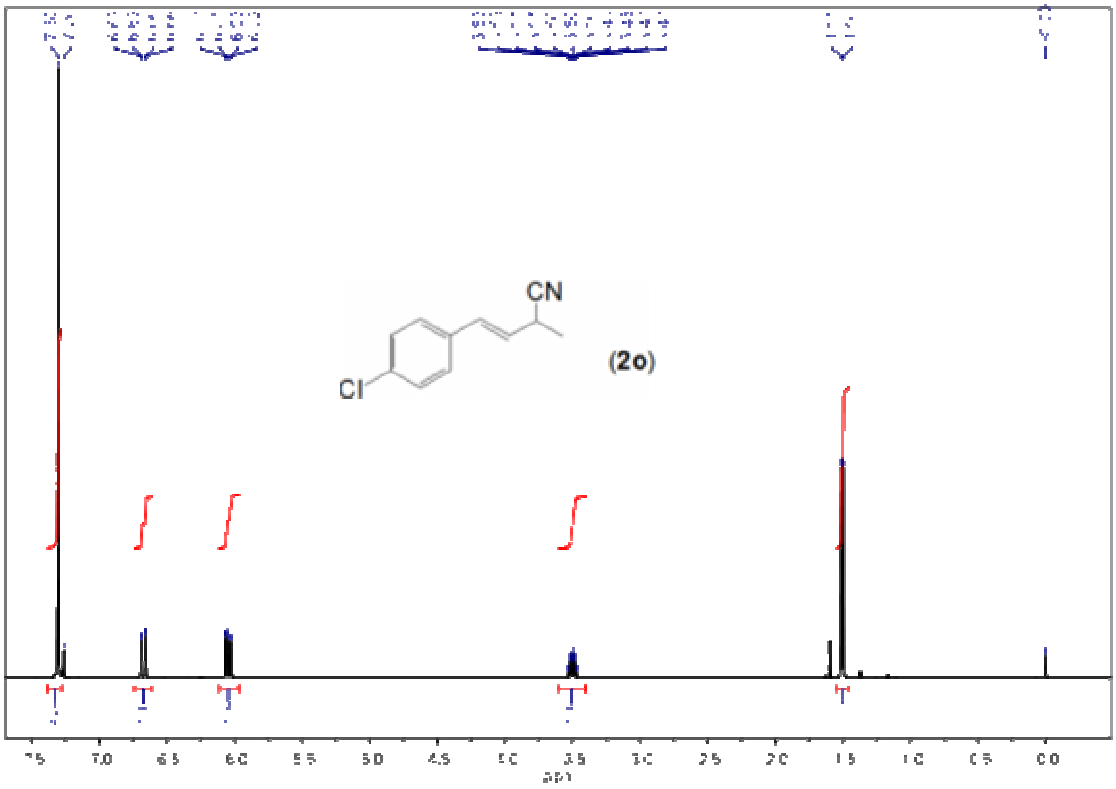
(2n)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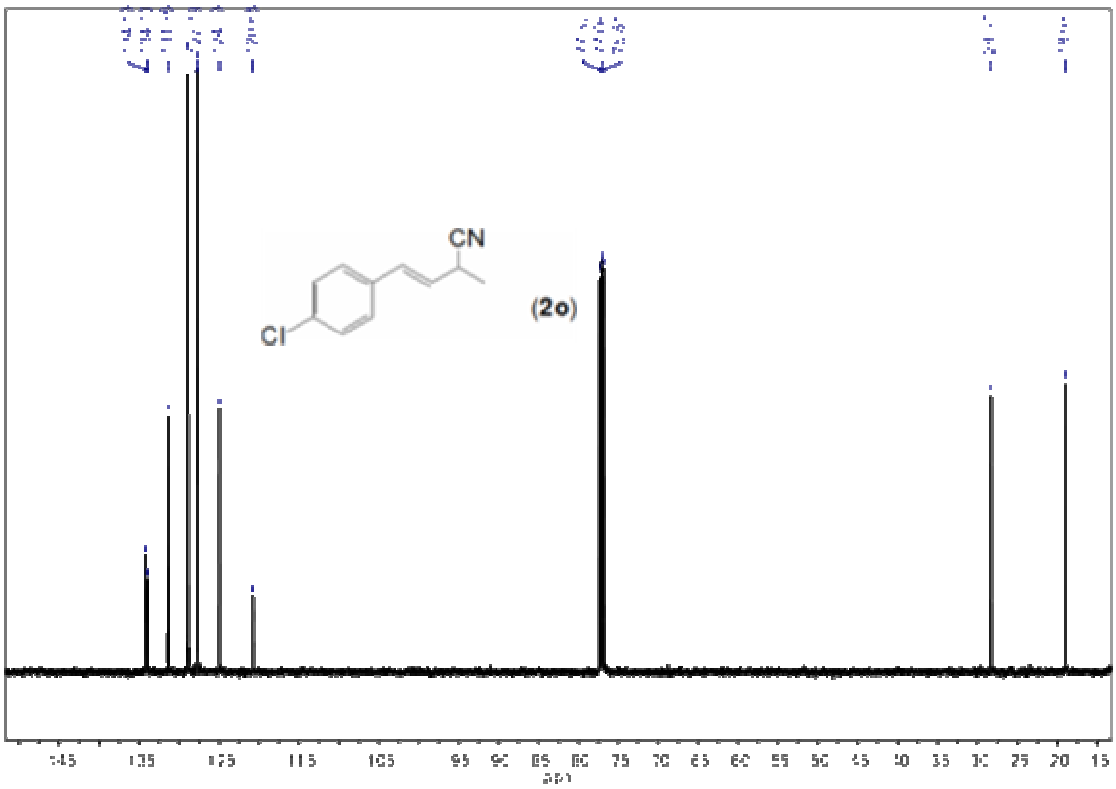
(2o)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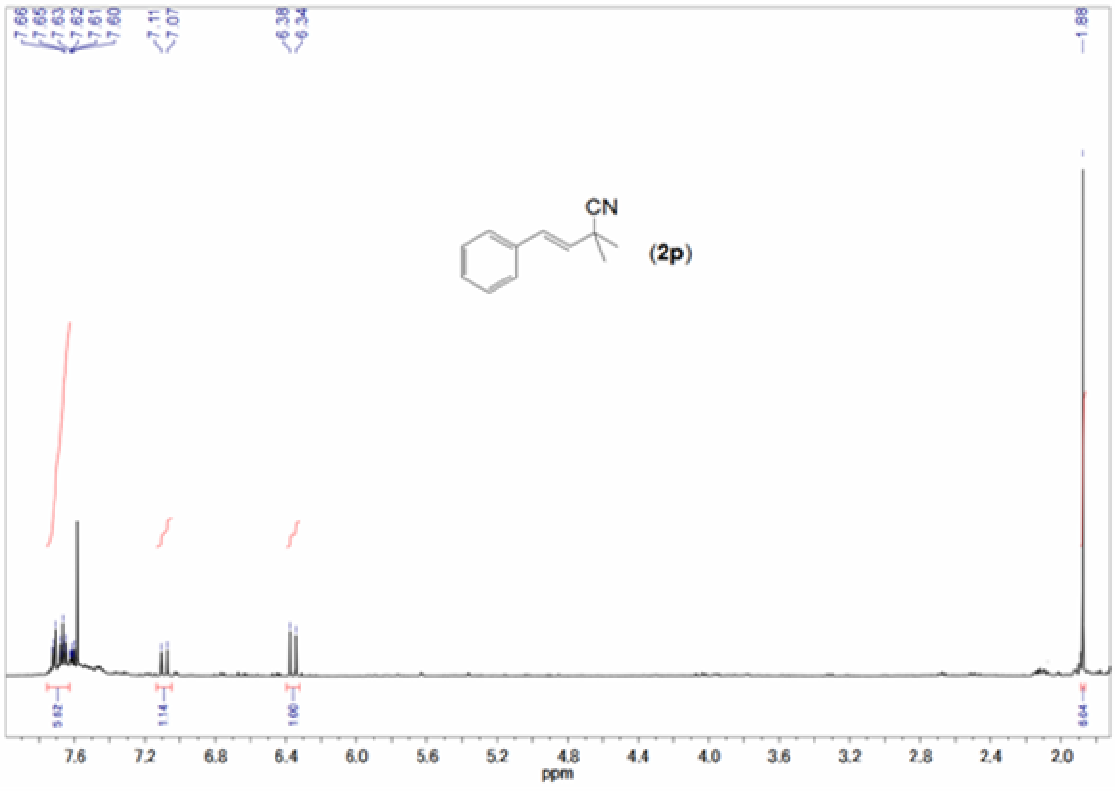
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7.07
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6.34
1.88
CN
(2p)
5.82
1.14
1.00
6.64
7.6
7.2
6.8
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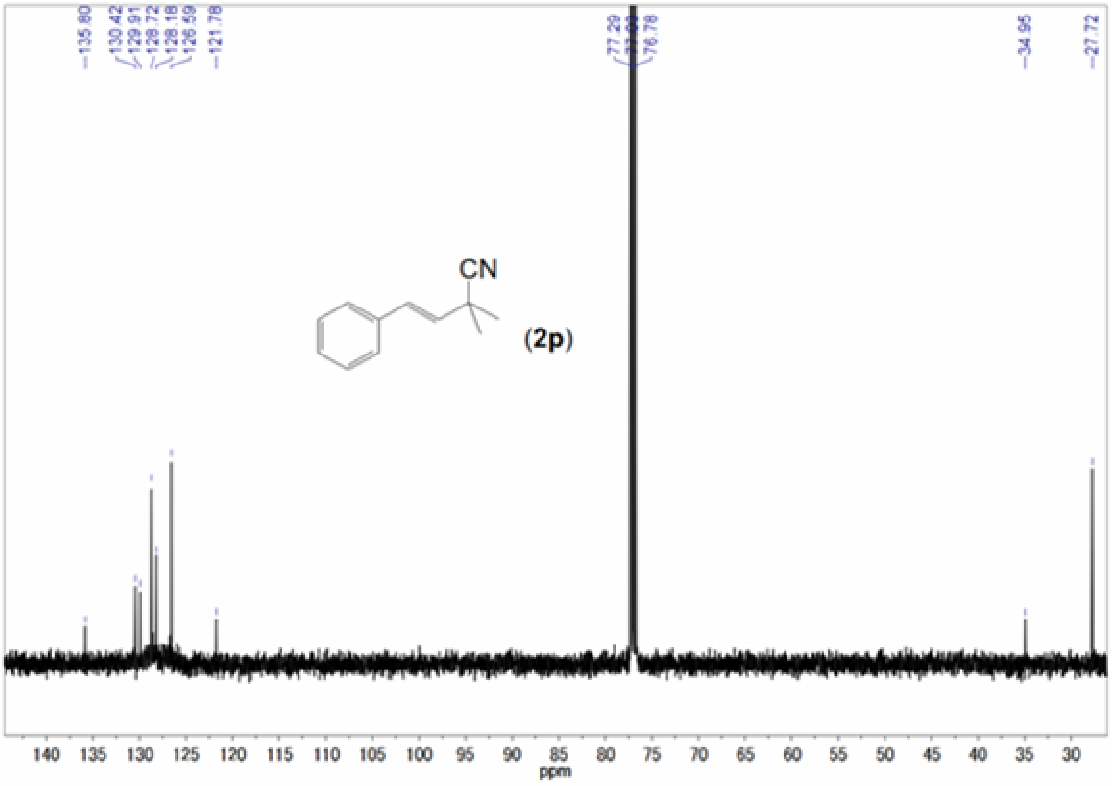
3.2
2.8
2.4
2.0
ppm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(2p)
140
135
130
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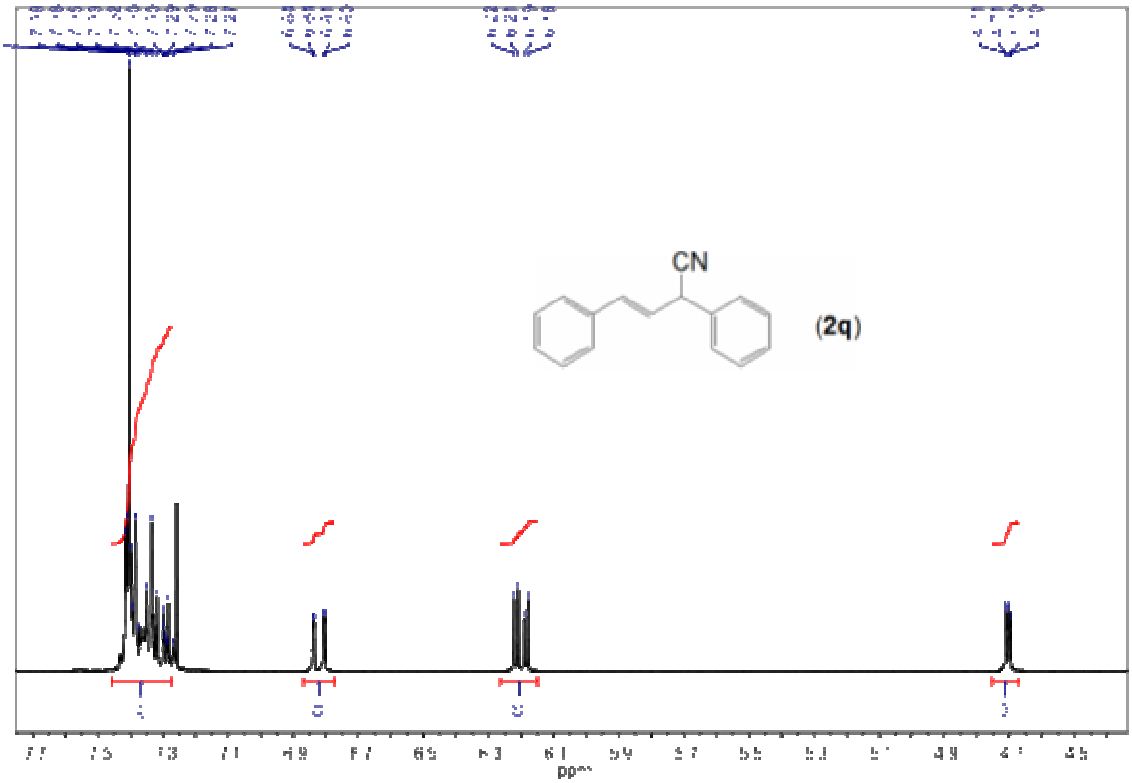
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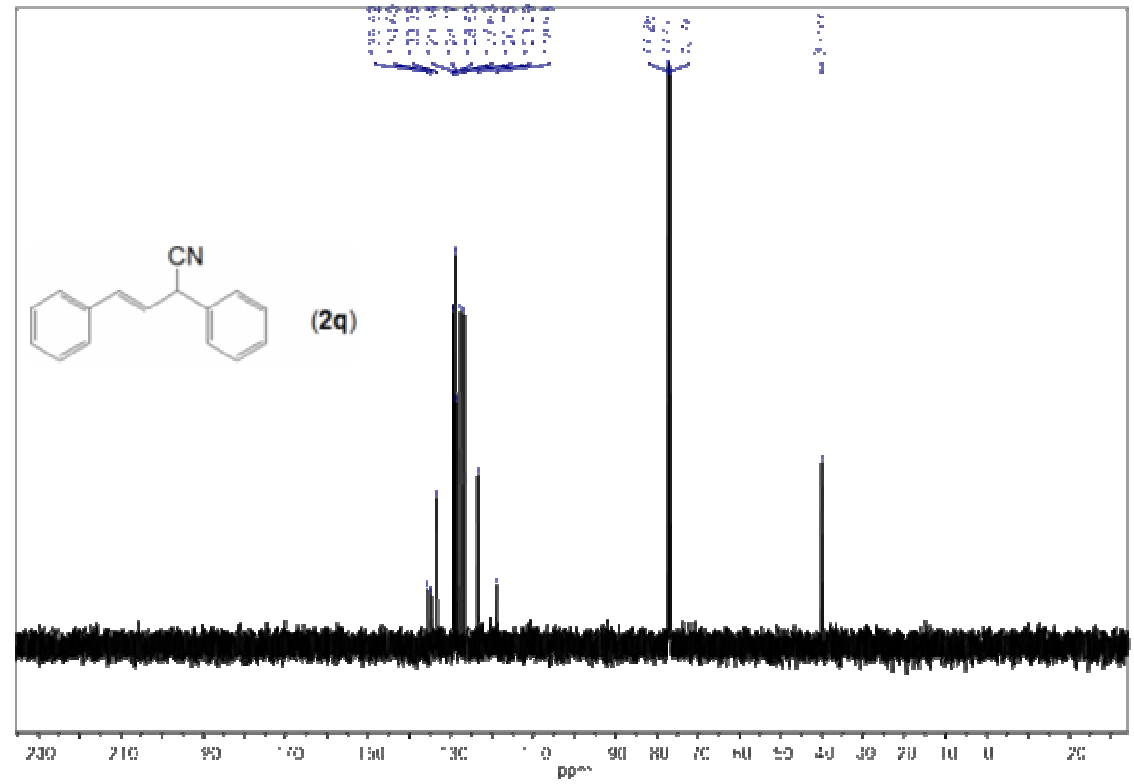
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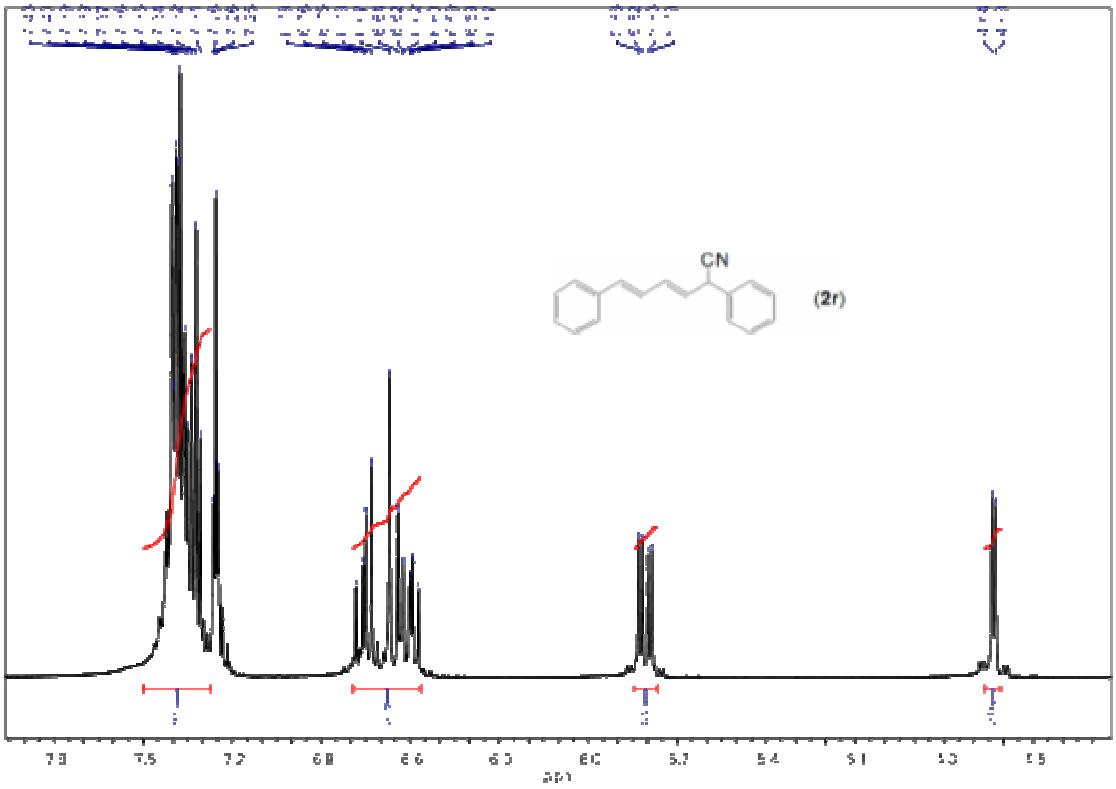
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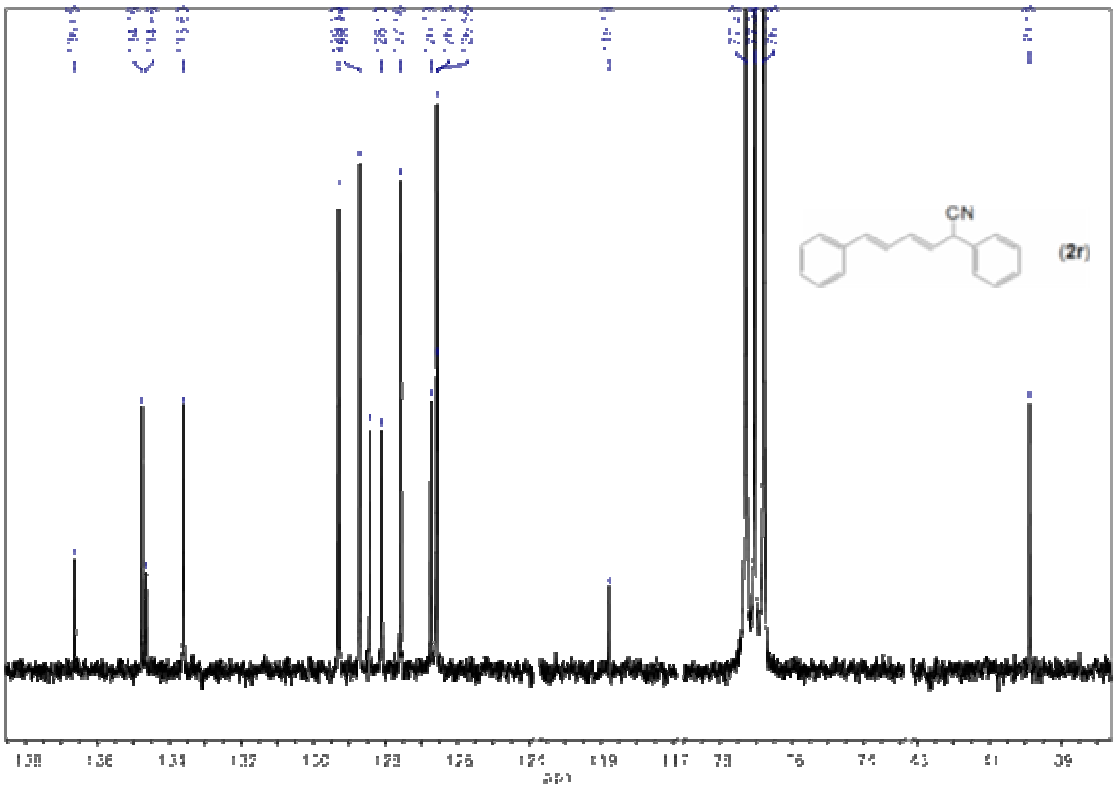
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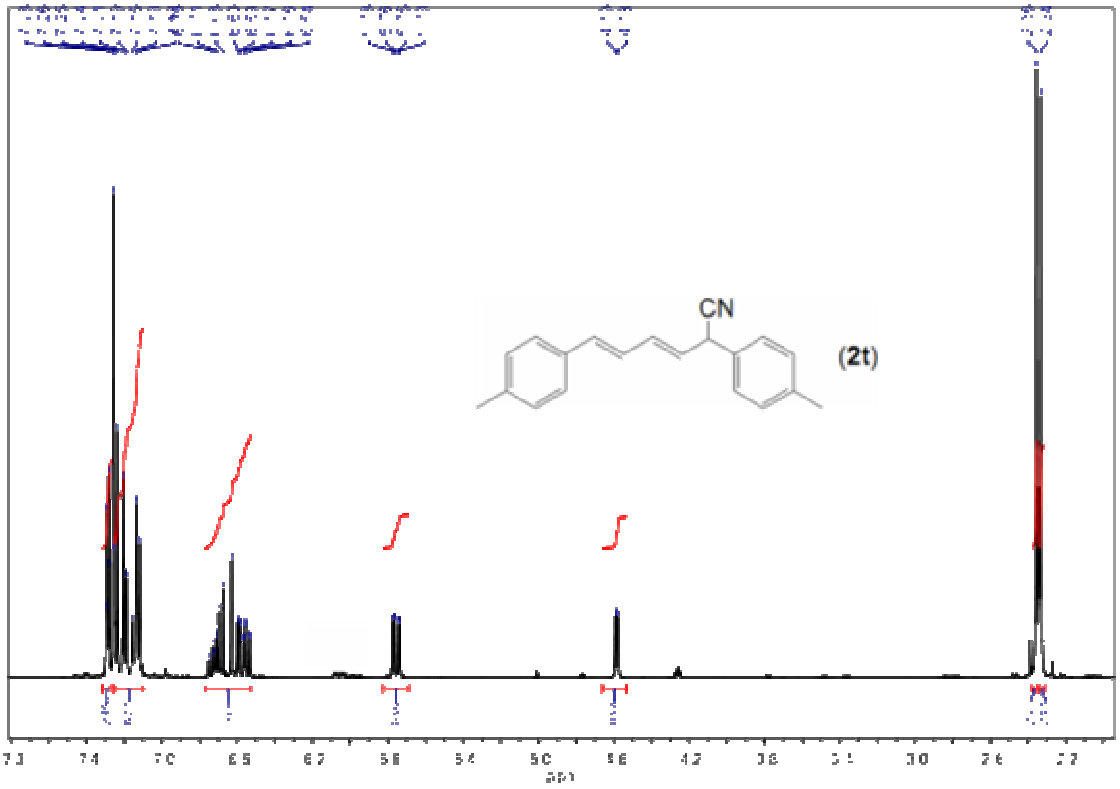
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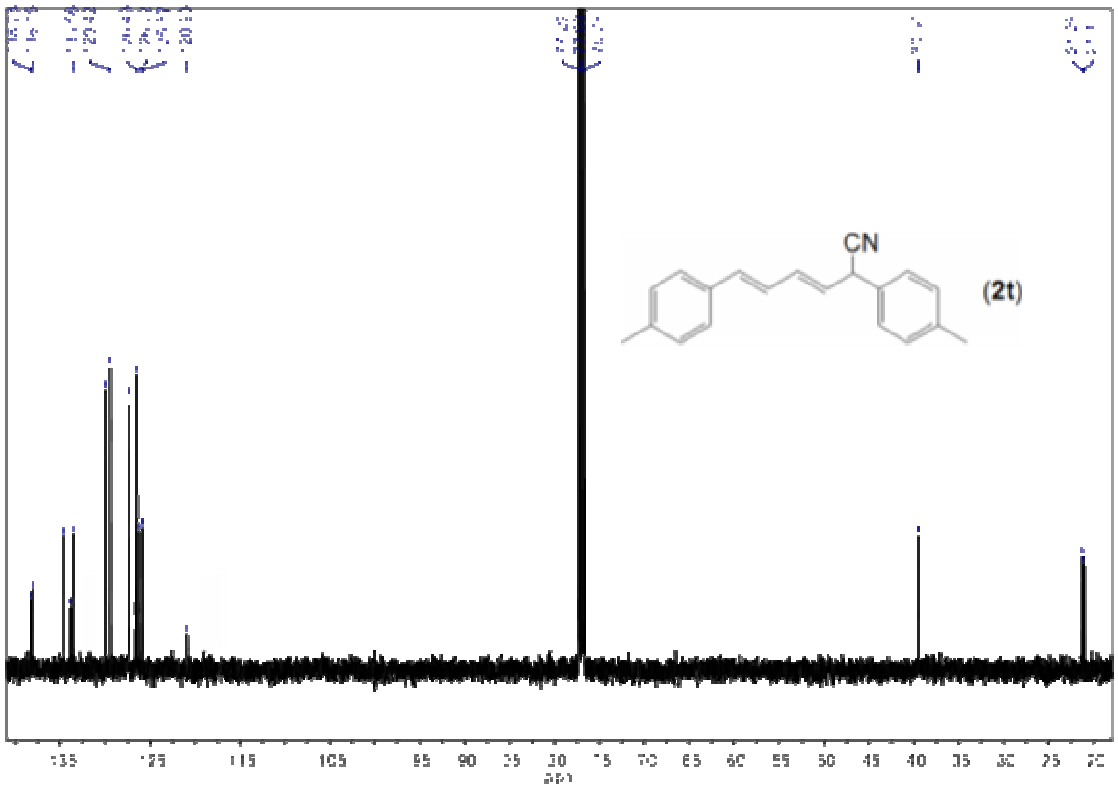
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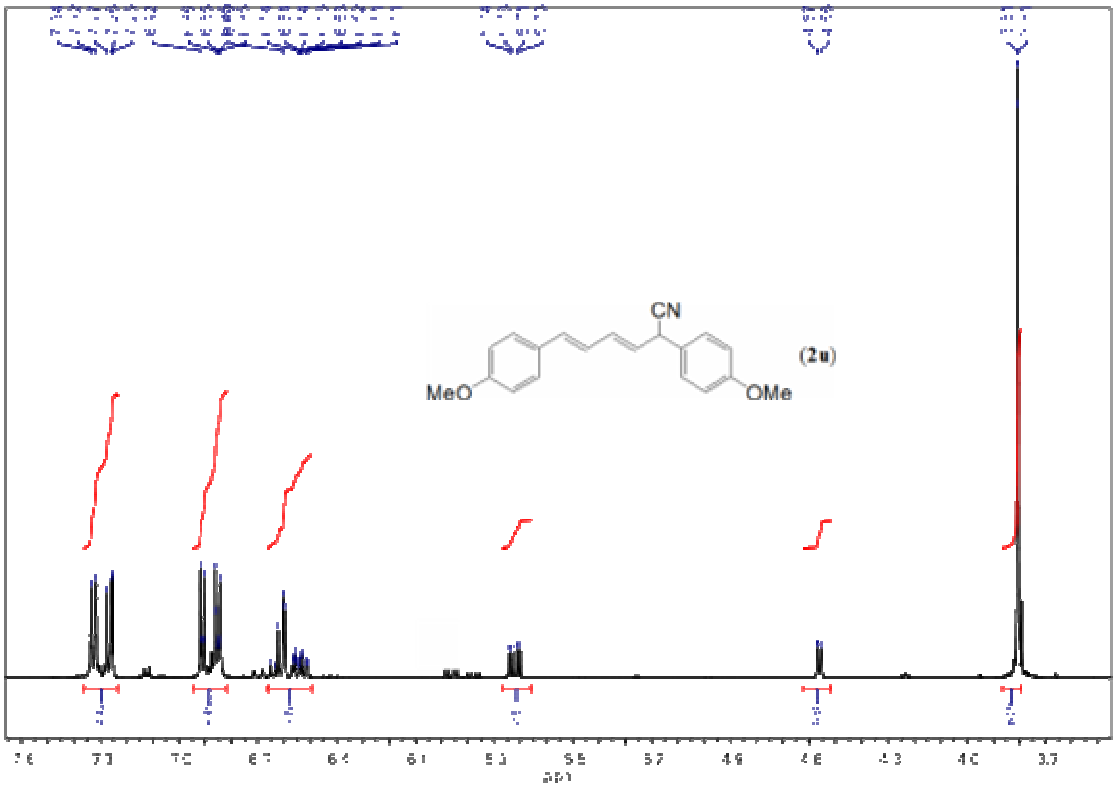
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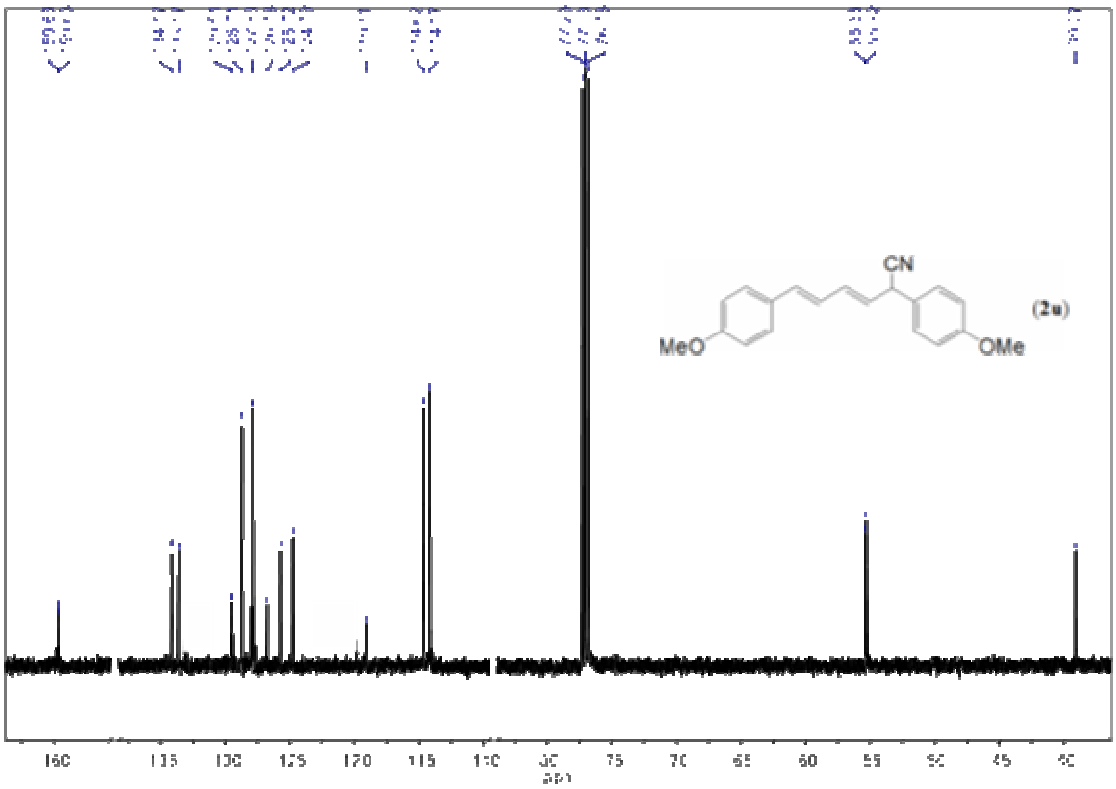
MeO
OMe
(2u)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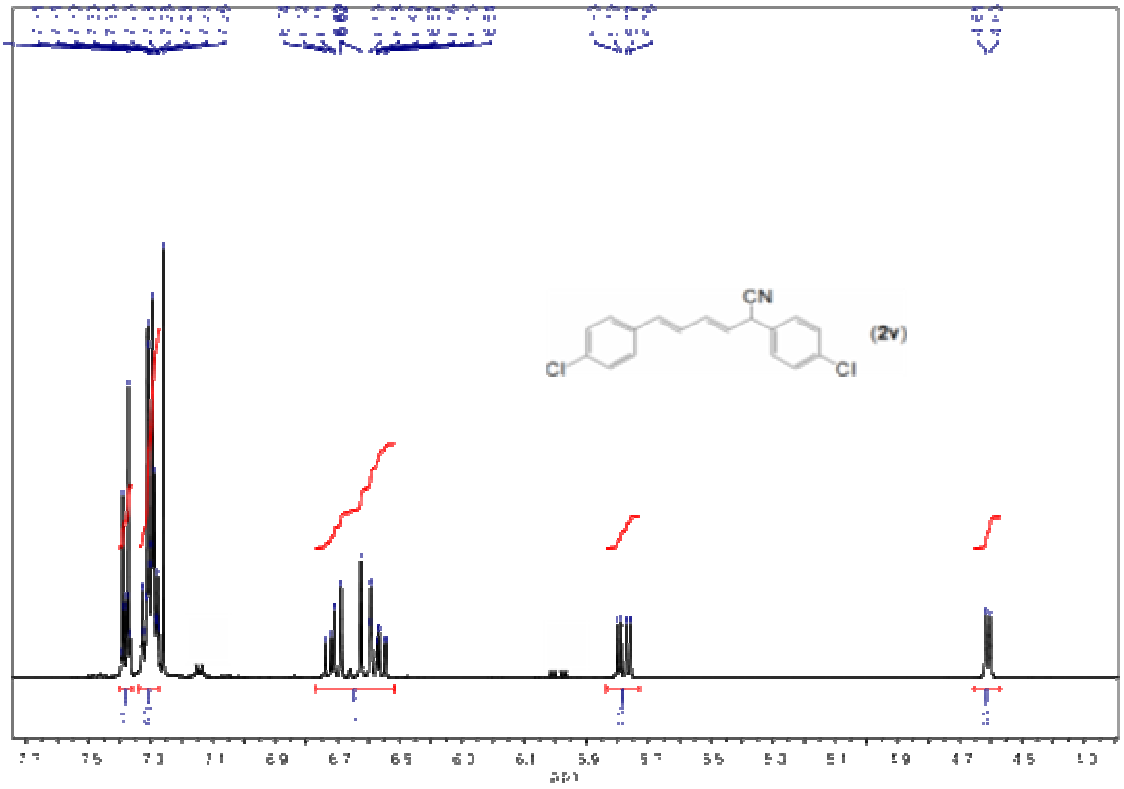
MeO
OMe
(2u)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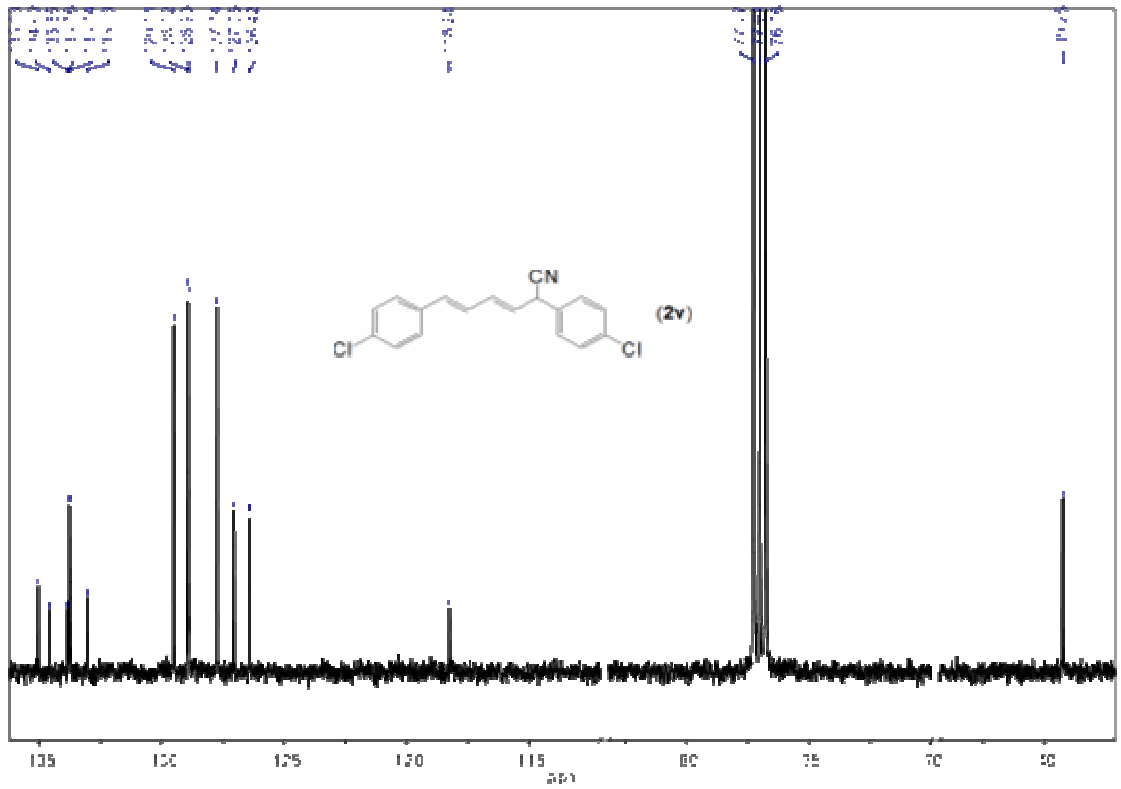
Cl
Cl
(2v)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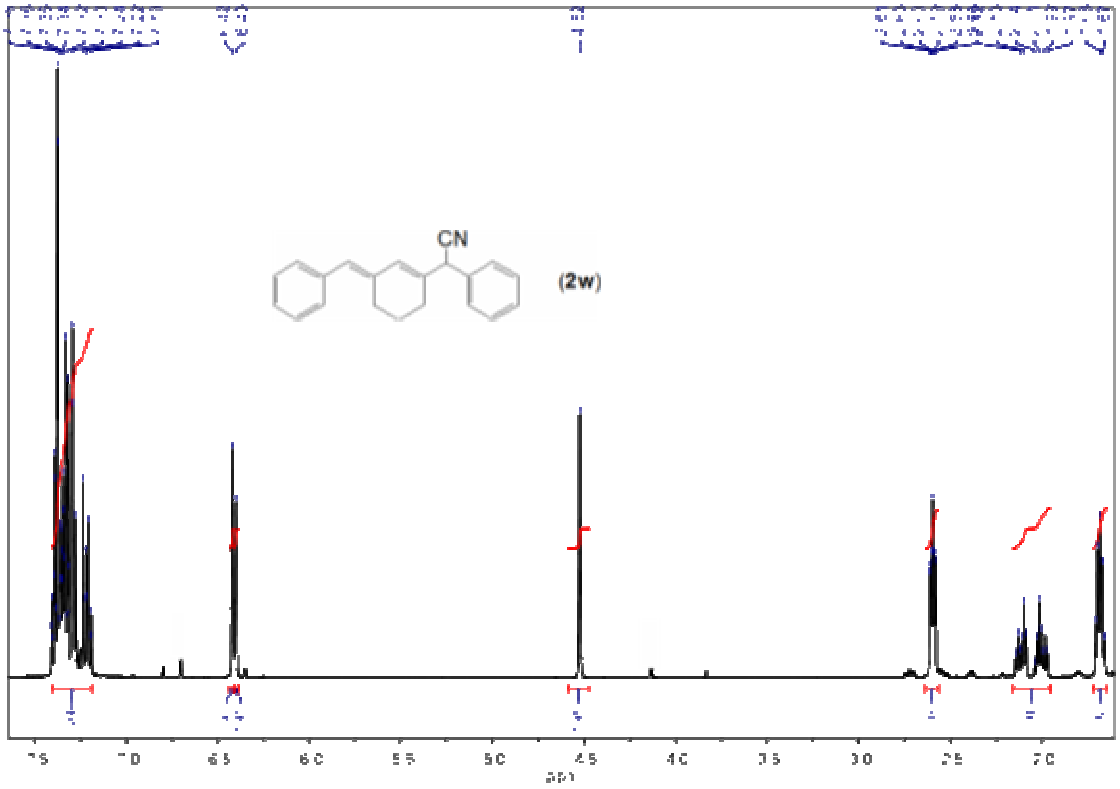
(2v)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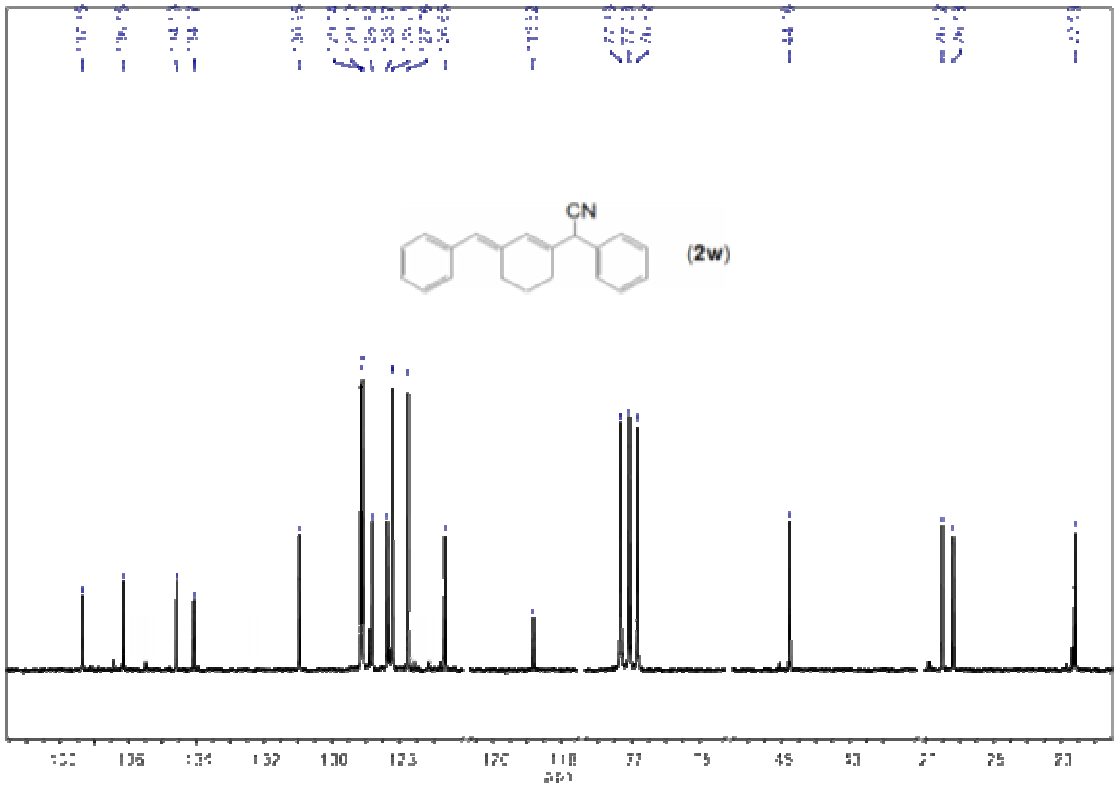
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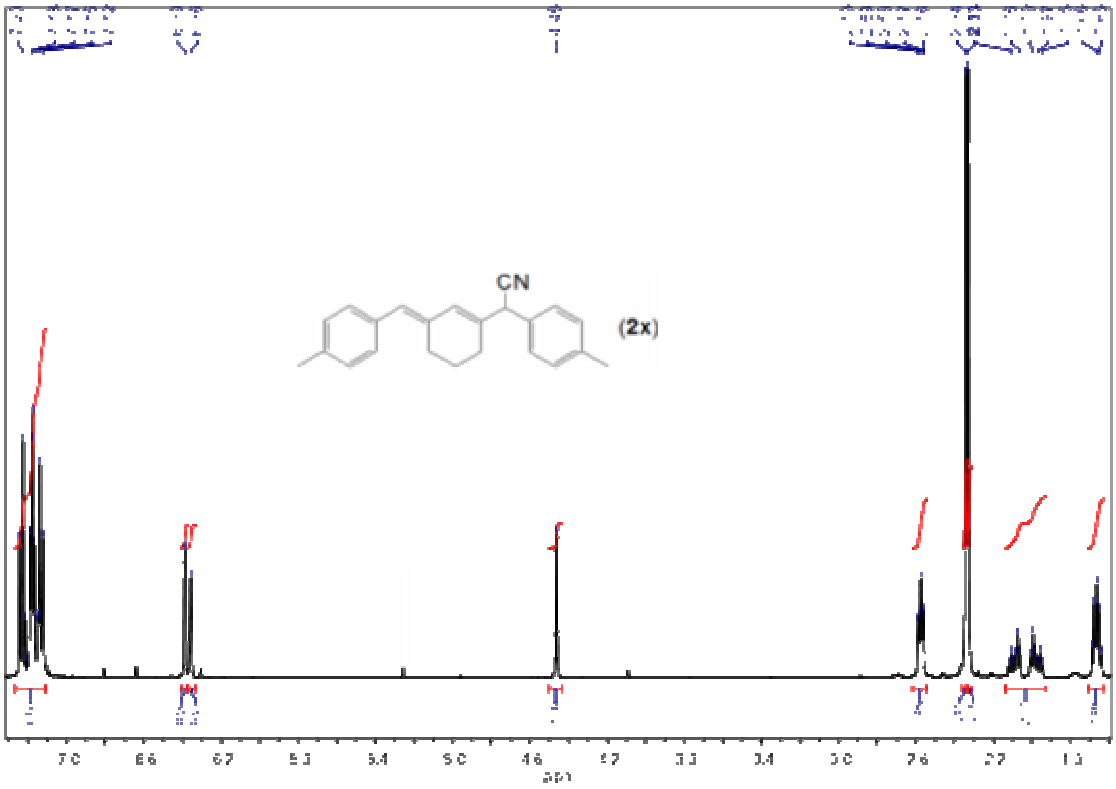
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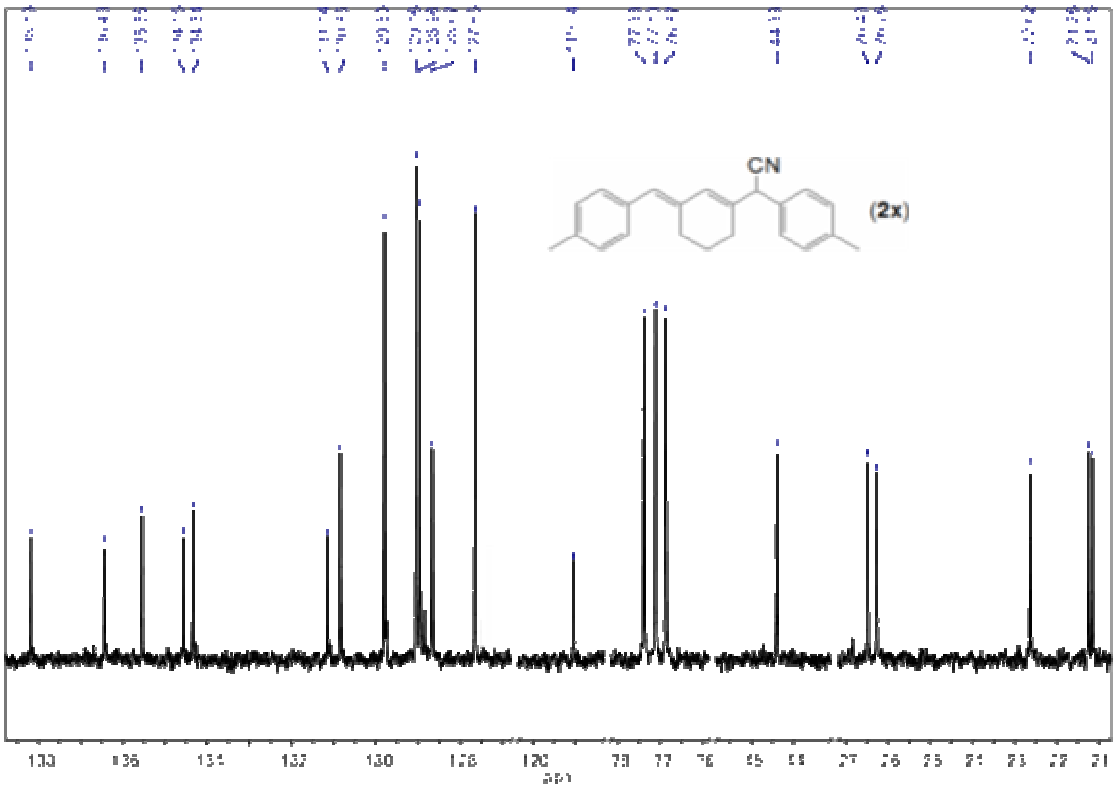
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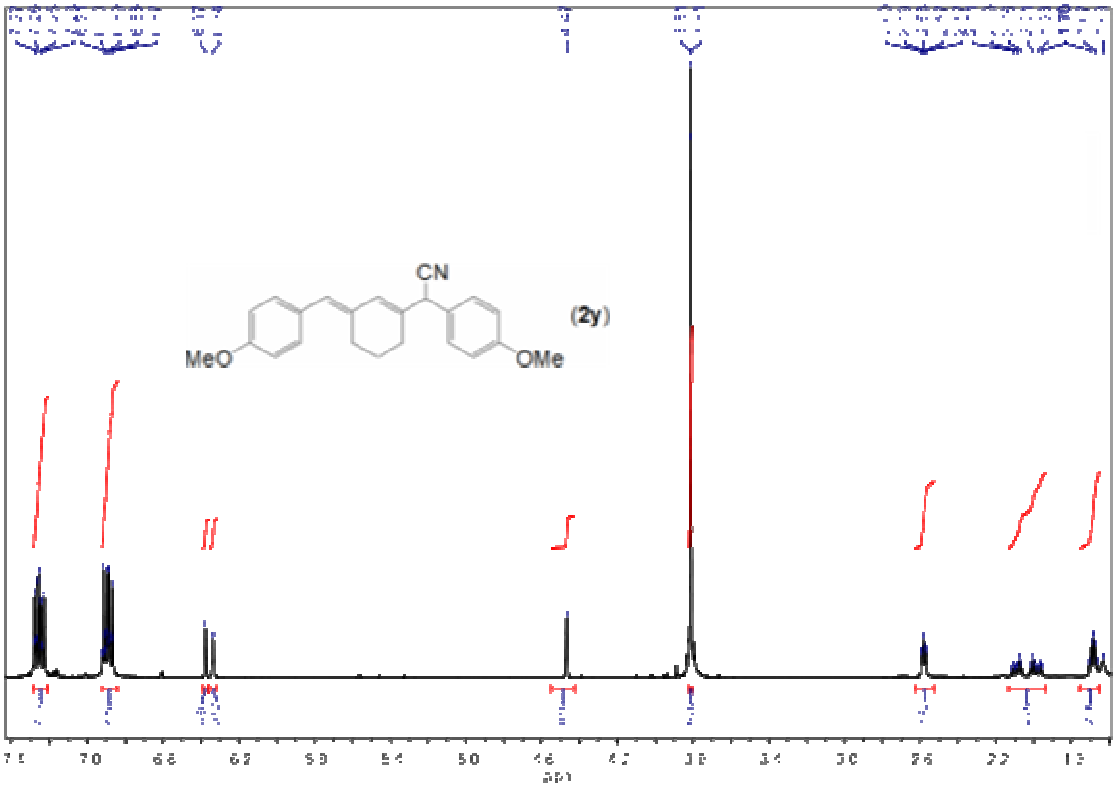
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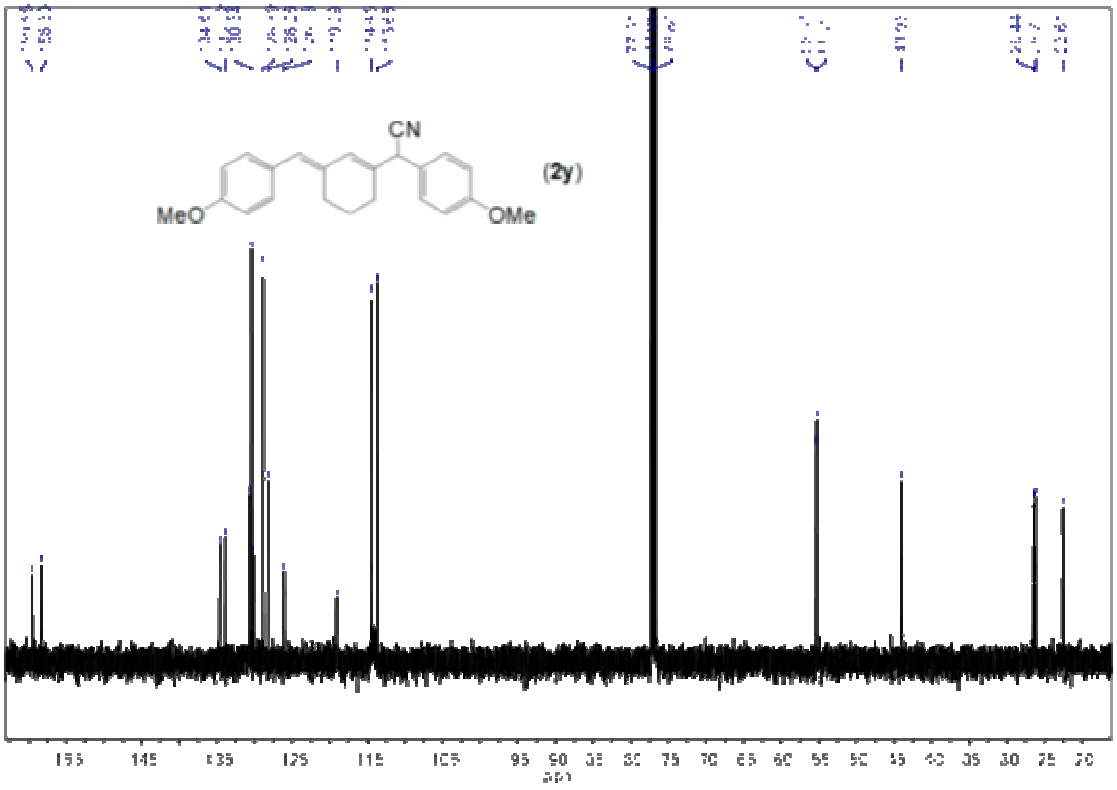
(2y)
MeO
OMe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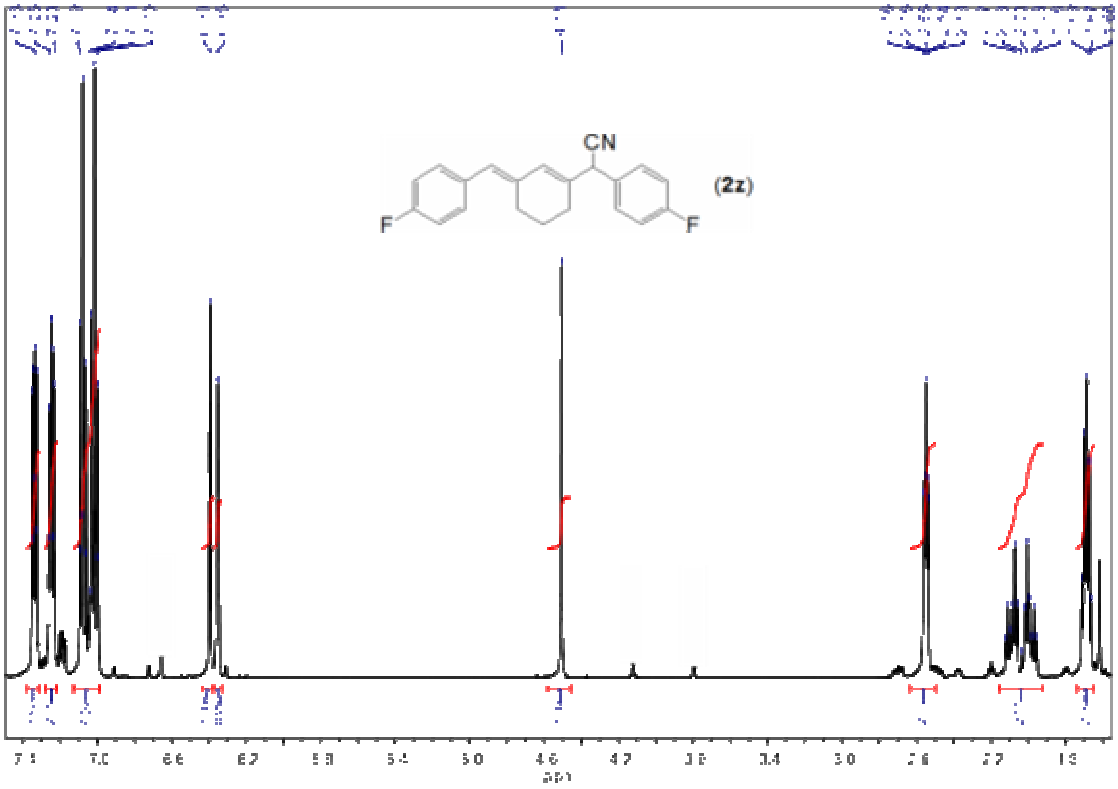
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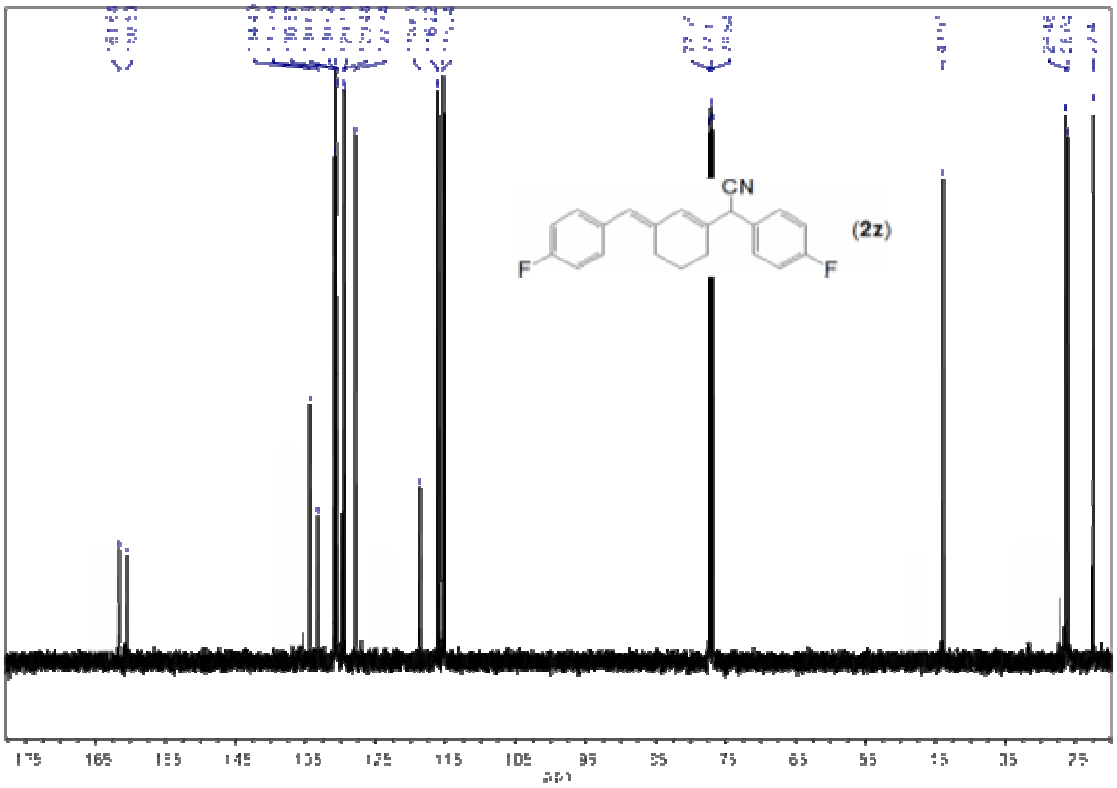
(2z)
F
F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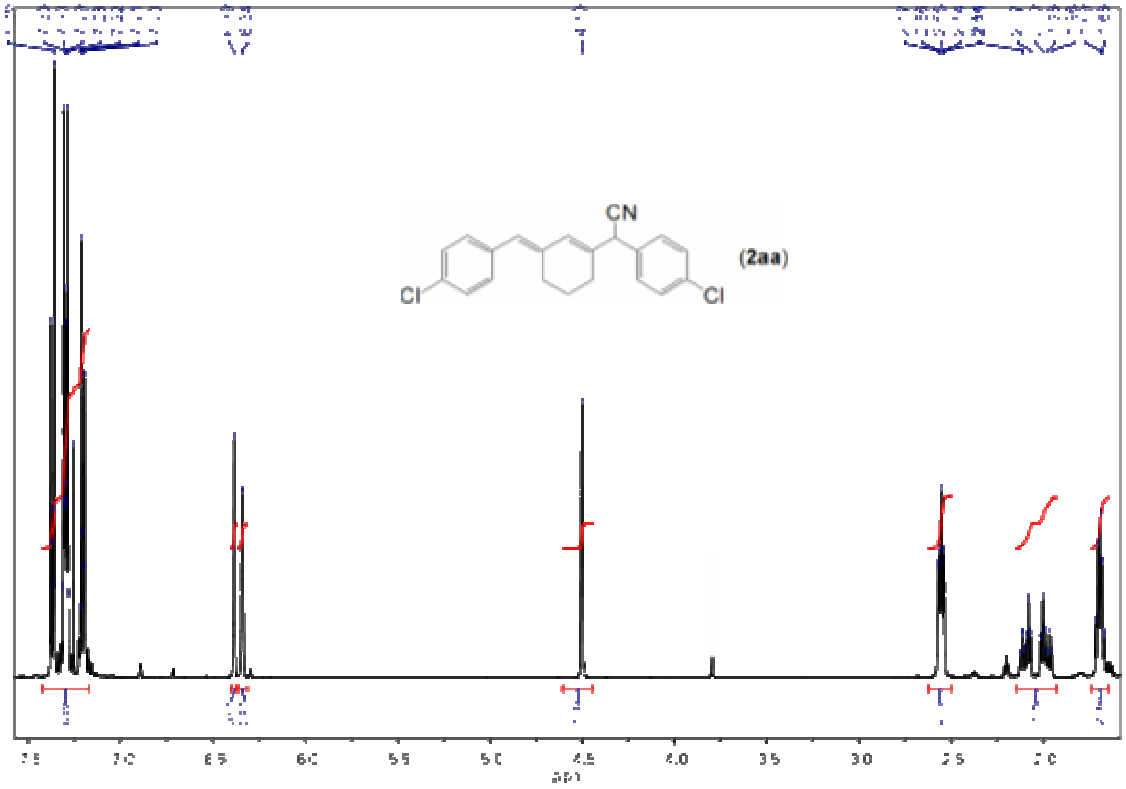
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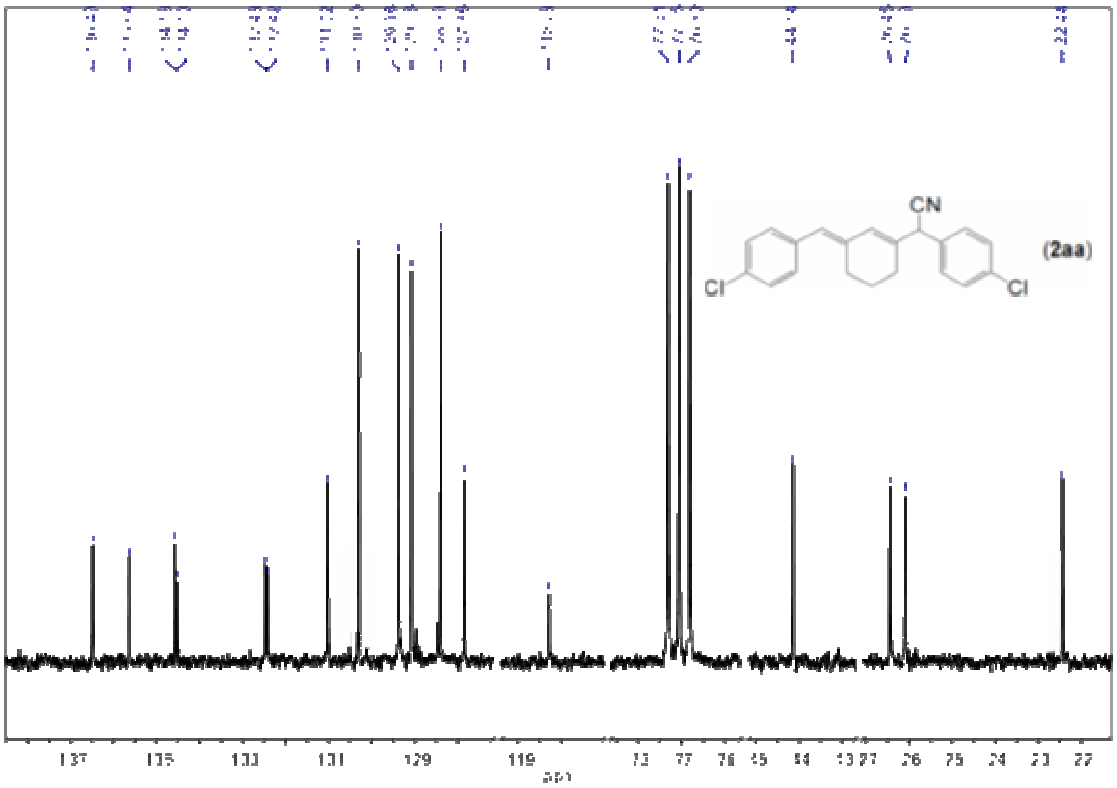
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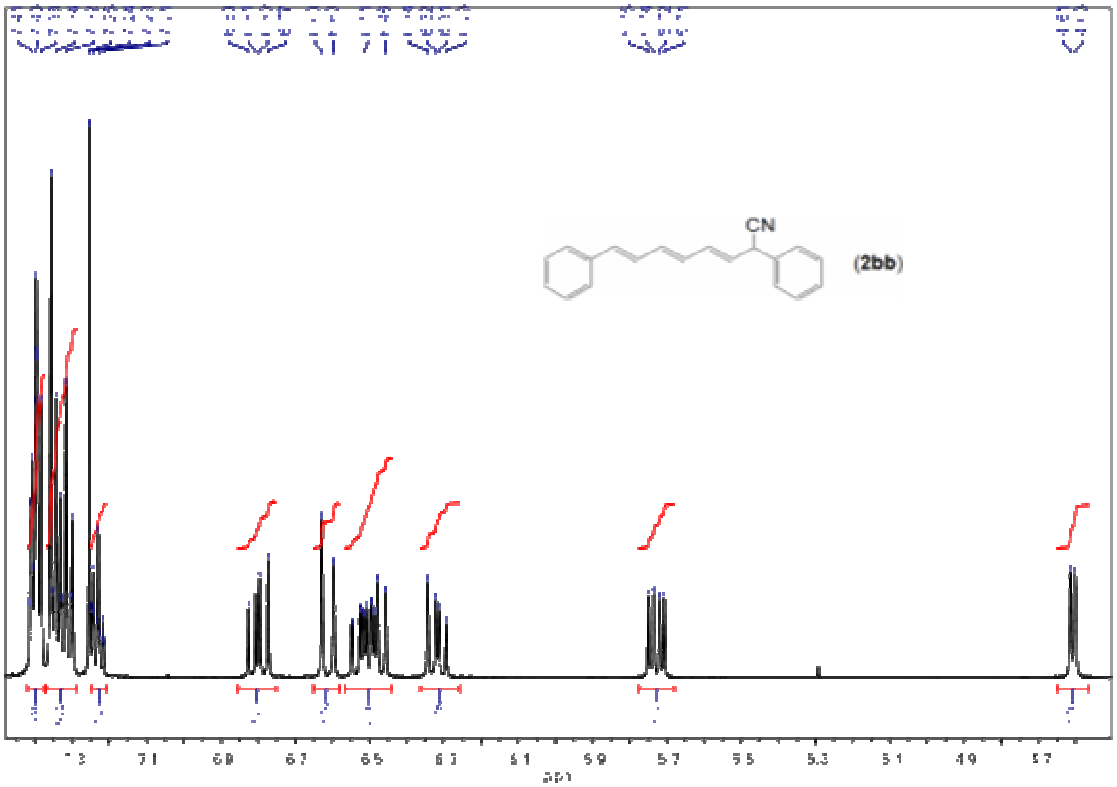
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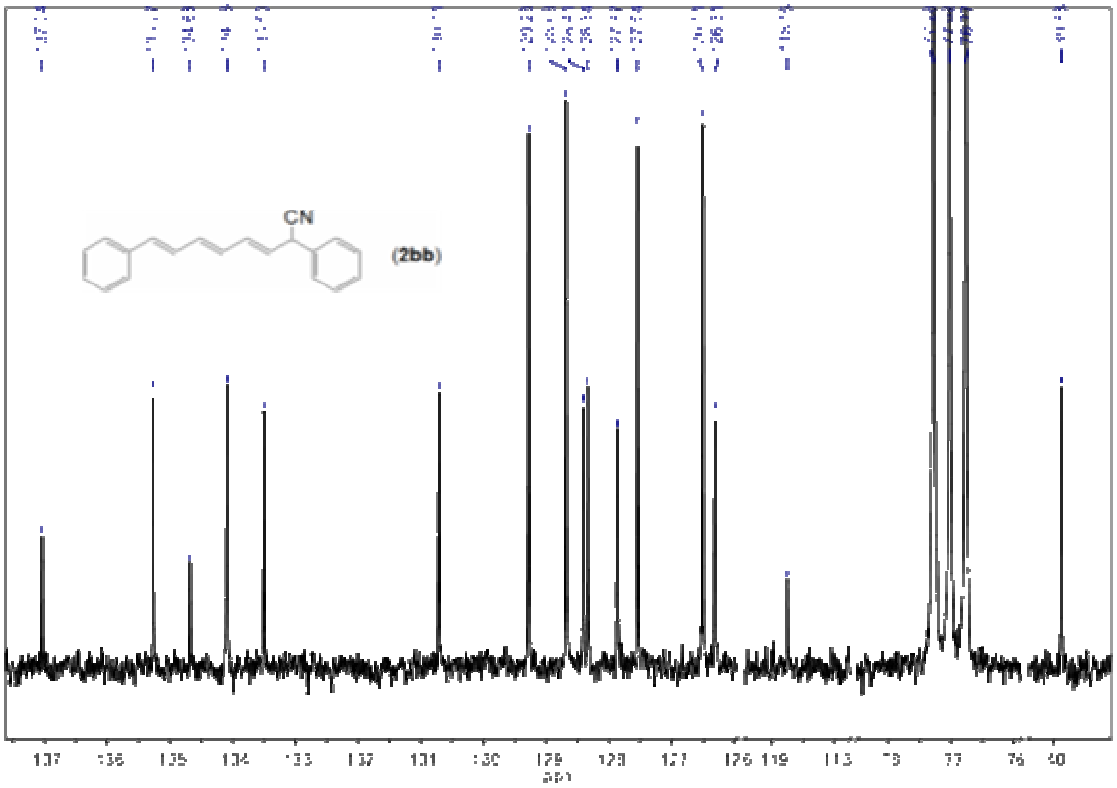
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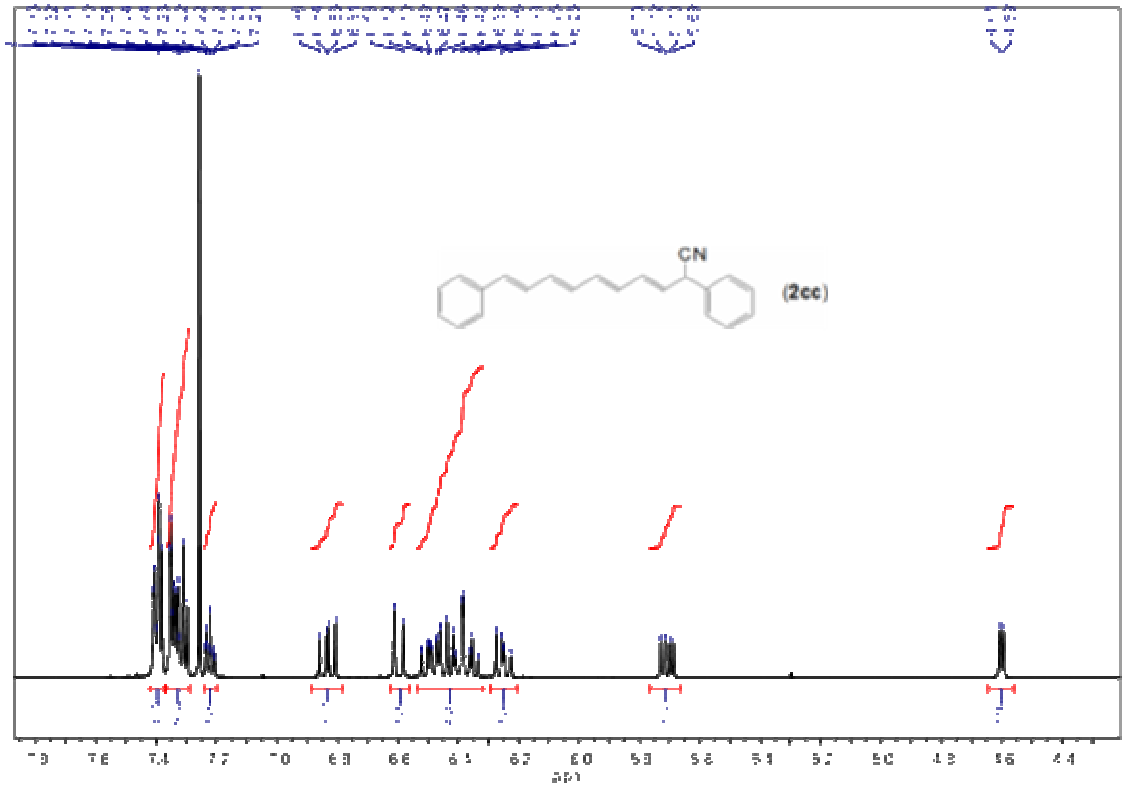
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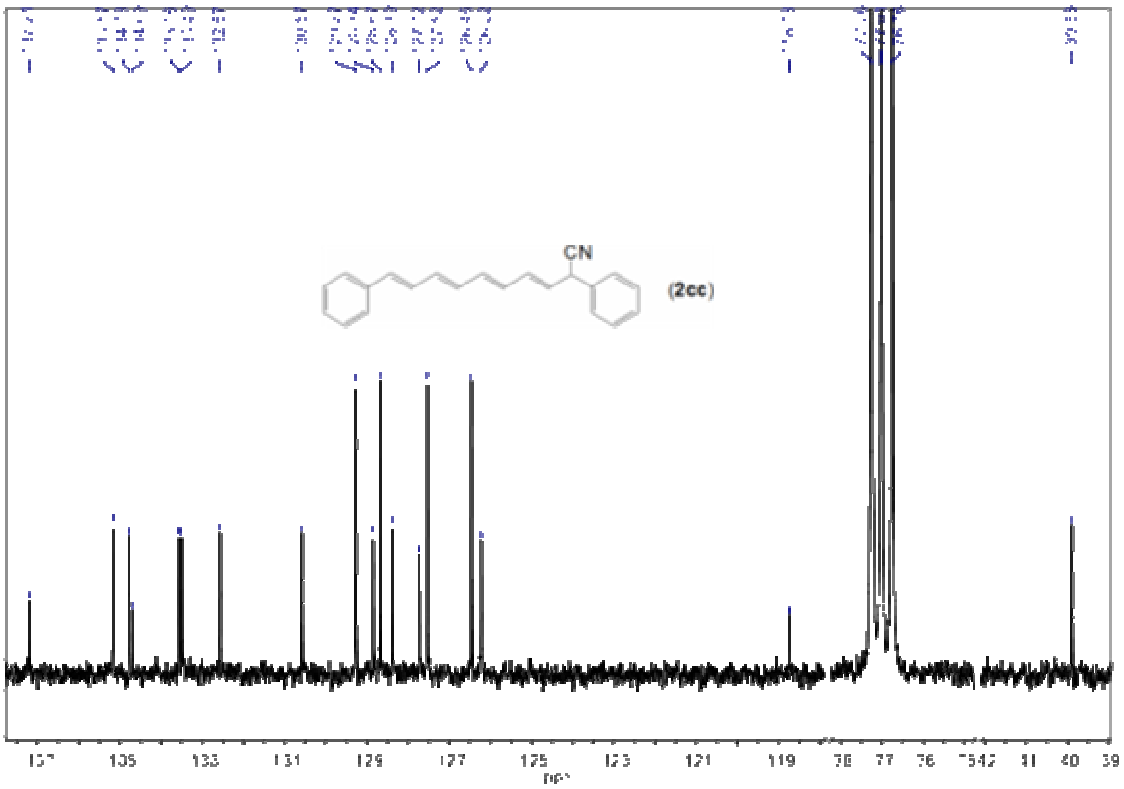
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