Electronic Supplementary Material (ESI) for ChemComm.

Cu-Catalyzed direct cyanation of terminal alkynes with AMBN or AIBN as cyanation reagents

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Experimental Section

General experimental: Alkynes, AIBN or AMBN, and metal catalysts used in this reaction were obtained from commercial sources and used without further purification. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in $CDCl_3$ on a Varian Inova-400 NMR spectrometer (400 MHz); chemical shifts were reported in ppm with the solvent signals as reference, and coupling constants (J) were given in Hertz. The peak information was described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. Products were characterized by comparison of ^{1}H NMR, ^{13}C NMR and TOF-MS data in the literatures.

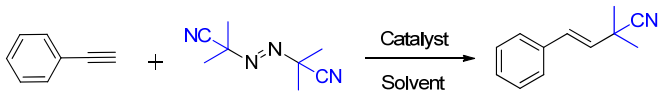
I. General procedure for the cyanation of alkynes.

To a Schlenk tube equipped with a magnetic stir bar was added alkynes (0.3 mmol), AMBN (0.6 mmol, 115.4 mg) or AIBN (0.6 mmol, 98.5 mg), $Cu(NO)_3 \cdot 3H_2O$ (20 mol%, 14.5 mg) and acetonitrile (4.0 ml). The Schlenk tube was then charged with an air balloon and the mixture was stirred at 80 ^{o}C for 12 hours. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 60:1) to afford the pure products.

II. General procedure for the synthesis of vinyl isobutyronitrile.

To a Schlenk tube equipped with a magnetic stir bar was added alkynes (0.6 mmol), AIBN (0.15 mmol, 24.6 mg) or AMBN (0.15 mmol, 28.8 mg), $Cu(OAc)_2 \cdot H_2O$ (20 mol%, 12.0 mg) and pyridine (2.0 ml). The mixture was stirred at 80 ^{o}C for 12 hours under argon atmosphere. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) to afford the pure products.

Table 1. Condition optimization of vinyl isobutyronitrile synthesis through the reaction between arylacetylene and AIBN[a]

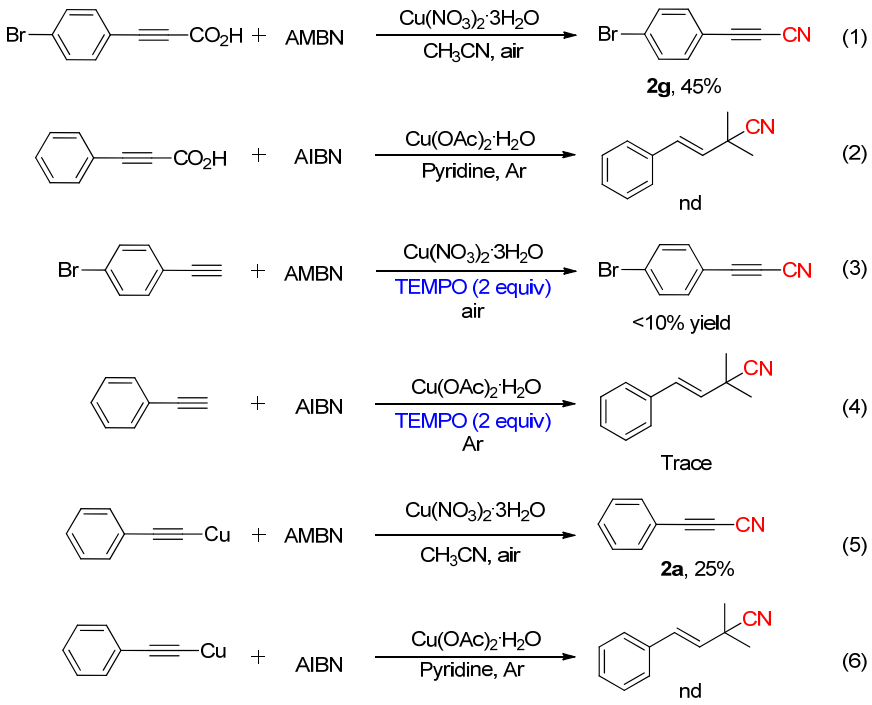


3a

entry	catalyst	temp (^{o} C)	solvent	yield (%)[b]
1	$Cu(OAc)_2{\cdot}H_2O$	80	CH_3CN	28
2[c]	$Cu(OAc)_2{\cdot}H_2O$	80	CH_3CN	nd
3	-	80	CH_3CN	nd
4	Cu	80	CH_3CN	nd
5	CuCl	80	CH_3CN	nd
6	$CuSO_4$	80	CH_3CN	nd
7	copper acrylate	80	CH_3CN	26
8	copper formate	80	CH_3CN	24
9	$Cu(TFA)_2$	80	CH_3CN	20
10	$Cu(OAc)_2{\cdot}H_2O$	80	DCE	trace
11	$Cu(OAc)_2{\cdot}H_2O$	80	DMSO	21
12	$Cu(OAc)_2{\cdot}H_2O$	80	dioxane	trace
13	$Cu(OAc)_2{\cdot}H_2O$	80	ethanol	trace
14	$Cu(OAc)_2{\cdot}H_2O$	80	toluene	<10
15	$Cu(OAc)_2{\cdot}H_2O$	80	pyridine	62
16[d]	$Cu(OAc)_2{\cdot}H_2O$	80	pyridine	46
17[e]	$Cu(OAc)_2{\cdot}H_2O$	80	pyridine	59
18	$Cu(OAc)_2{\cdot}H_2O$	90	pyridine	55
19	$Cu(OAc)_2{\cdot}H_2O$	70	pyridine	43

[a] *Reaction conditions:* phenylacetylene (2.0 equiv, 0.6 mmol), AIBN (0.15 mmol), catalyst (20 mol%), solvent (2 mL), Ar, 80 ^{o}C, 12 h. [b] Isolated yield; ND: Not Detected. [c] Air. [d] 1.5 equiv, 0.45 mmol of phenylacetylene was used; [e] 3 equiv, 0.9 mmol of phenylacetylene was used.

Scheme 1. Control experiments.

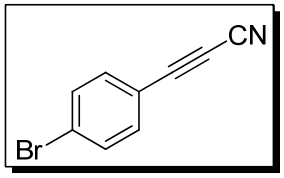


In order to further explore the applicability of the developed protocol, a few more reactions were conducted by using AMBN as cyanating reagent. Firstly, 3-(4-bromophenyl)propiolic acid can successfully afford **2g** in 45% yield through a decarboxylative cyanation process. However, no desired product was generated when phenylpropiolic was applied to react with AIBN (eq 2), nor the self-coupling byproduct. These results suggest that these two processes follow different reaction pathways.

A few reactions were conducted to investigate the mechanism.Both of the reactions under air or argon were significantly inhibited when TEMPO (2.0 equiv) was added (eq 3 and eq 4 respectively), which strongly suggests that these reactions proceeded through radical process. As expected, product **2a** was successfully obtained when (phenylethynyl)copper reacted with AMBN under standard condition (eq 5), indicating that (phenylethynyl)copper could be a very possible intermediate in this reaction. While no vinyl isobutyronitrile product was detected in the reaction of (phenylethynyl)copper with AIBN (eq 6). This reaction cann't proceed even stoichiometric amount of water or ethanol were added as protonation reagents, which suggests that another reaction pathway should be involved besides the (phenylethynyl)copper intermediate.

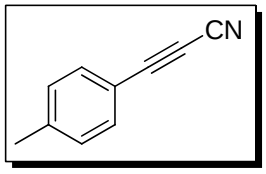
Characterization of the Corresponding Products:

3-(4-Bromophenyl)propiolonitrile (2a)[1]



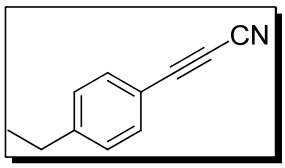
White solid (45.1 mg, 73%); mp: 116 – 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.57 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 134.8, 132.5, 127.2, 116.5, 105.4, 81.9, 64.2; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for C_9H_4BrNNa 227.9425, found 227.9414.

3-*p*-Tolylpropiolonitrile (2b)[1]



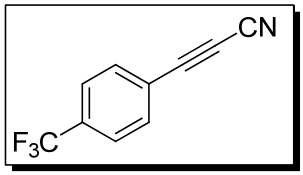
White solid (24.6 mg, 58%); mp: 44 – 46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.50 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.0, 133.6, 129.8, 114.5, 105.8, 83.6, 62.9, 22.0; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{10}H_7NNa$ 164.0476, found 164.0473.

3-(4-Ethylphenyl)propiolonitrile (2c)



Colorless liquid (25.6 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.63 – 7.42 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 149.1, 133.7, 128.6, 114.7, 105.8, 83.7, 62.8, 29.2, 15.2; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{11}H_9NNa$ 178.0633, found 178.0627.

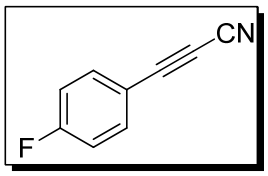
3-(4-(Trifluoromethyl)phenyl)propiolonitrile (2d)



White solid (45.7 mg, 78%); mp: 38 – 40 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.75 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 134.0, 133.6 (q, *J* = 33.0 Hz), 126.0 (q, *J* = 3.6 Hz), 123.4 (d, *J* = 272.8 Hz), 121.5, 105.1, 81.0, 65.0; HRMS (TOF

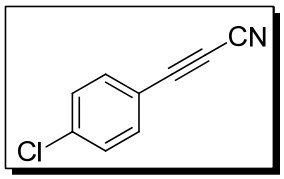
MS ESI$^+$) $[M+Na]^+$ calculated for $C_{10}H_4F_3NNa$ 218.0194, found 178.0192.

3-(4-Fluorophenyl)propiolonitrile (2e)[2]



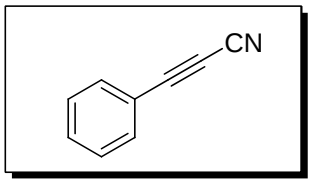
White solid (33.5 mg, 77%); mp: 64 – 66 ^oC; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.68 – 7.55 (m, 2H), 7.19 – 7.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 164.7 (d, J = 256.1 Hz), 136.1 (d, J = 9.1 Hz), 116.7 (d, J = 22.6 Hz), 113.8 (d, J = 3.6 Hz), 105.5, 82.0, 63.3; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for C_9H_4FNNa 168.0225, found 168.0219.

3-(4-Chlorophenyl)propiolonitrile (2f)[1]



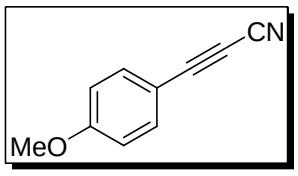
White solid (36.4 mg, 75%); mp: 84 – 86 ^oC; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.64 – 7.46 (m, 2H), 7.45 – 7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 138.7, 134.8, 129.5, 116.1, 105.4, 81.9, 64.1; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for C_9H_4ClNNa 183.9930, found 183.9932.

3-Phenylpropiolonitrile (2g)[2]



White solid (25.6 mg, 67%); mp: 38 – 40 ^oC; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.65 – 7.59 (m, 2H), 7.57 – 7.51 (m, 1H), 7.45 – 7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 133.6, 132.0, 129.0, 127.6, 105.6, 83.1, 63.2; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for C_9H_5NNa 150.0320, found 150.0312.

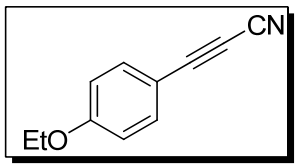
3-(4-Methoxyphenyl)propiolonitrile (2h)[2]



White solid (23.1 mg, 49%); mp: 78 – 80 ^oC; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.63 – 7.47 (m, 2H), 7.01 – 6.82 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 162.5, 135.6, 114.8, 109.2, 106.0, 83.8, 62.6, 55.6; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{10}H_7NNaO$

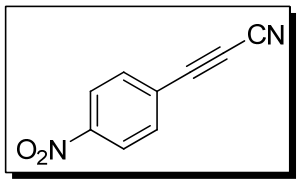
180.0425, found 180.0421.

3-(4-Ethoxyphenyl)propiolonitrile (2i)



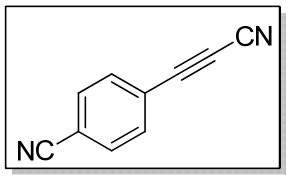
White solid (19.5 mg, 38%); mp: 74 – 76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.57 – 7.50 (m, 2H), 6.93 – 6.85 (m, 2H), 4.07 (q, *J* = 6.8 Hz, 2H), 1.44 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 161.9, 135.6, 115.2, 109.0, 106.0, 84.0, 64.0, 62.5, 14.7; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{11}H_9NNaO$ 194.0582, found 194.0580.

3-(4-Nitrophenyl)propiolonitrile (2j)[3]



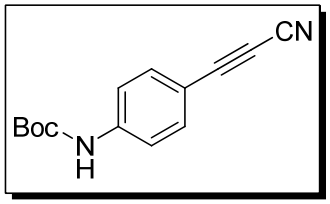
White solid (32.5 mg, 63%); mp: 142 – 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.32 – 8.26 (m, 2H), 7.84 – 7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 149.3, 134.6, 124.1, 104.8, 80.0, 66.7; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_9H_4N_2NaO_2$ 195.0170, found 195.0164.

4-(Cyanoethynyl)benzonitrile (2k)



White solid (40.2 mg, 88%); mp: 196 – 198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 134.0, 132.6, 122.3, 117.5, 115.5, 104.9, 80.4, 66.2; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{10}H_4N_2Na$ 175.0272, found 175.0270.

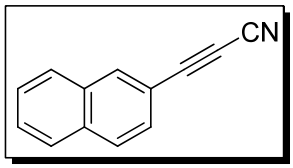
*t*ert-Butyl 4-(cyanoethynyl)phenylcarbamate (2l)



White solid (60%, 43.6 mg); mp: 168 – 170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.52 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 152.1, 142.0, 134.8, 118.1, 111.0, 105.9, 83.7, 81.7, 62.7, 28.3; HRMS (TOF MS ESI$^+$)

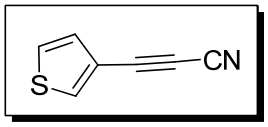
$[M+H]^+$ calculated for $C_{14}H_{15}N_2O_2$ 243.1134, found 243.1127.

3-(Nphthalen-2-yl)propiolonitrile (2m)



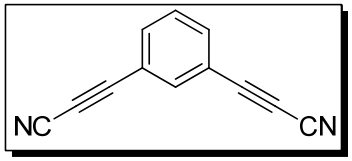
White solid (34.5 mg, 65%); mp: 68 – 70 ^oC; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.18 (s, 1H), 7.89 – 7.82 (m, 3H), 7.65 – 7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 135.5, 134.4, 132.5, 128.9, 128.8, 128.3, 128.1, 127.9, 127.6, 114.7, 105.7, 83.6, 63.3; HRMS (TOF MS ESI^+) $[M+H]^+$ calculated for $C_{13}H_8N$ 178.0657, found 178.0654.

3-(Thiophen-3-yl)propiolonitrile (2n)[2]



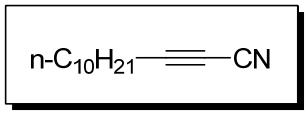
Yellow solid (21.6 mg, 54%); mp: 36 – 38 ^oC; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.87 (dd, J = 3.0, 1.2 Hz, 1H), 7.37 (dd, J = 5.1, 3.0 Hz, 1H), 7.25 (dd, J = 5.1, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 136.2, 130.3, 126.9, 117.0, 105.7, 78.5, 63.3; HRMS (TOF MS ESI^+) $[M+H]^+$ calculated for C_7H_4NS 134.0064, found 134.0067.

3,3'-(1,3-Phenylene)dipropiolonitrile (2o)



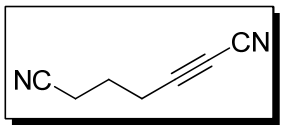
White solid (32.8 mg, 62%); mp: 96 – 98 ^oC; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.85 (dd, J = 1.6, 1.1 Hz, 1H), 7.76 (dd, J = 7.9, 1.6 Hz, 2H), 7.55 – 7.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 137.9, 136.3, 129.8, 119.1, 105.0, 80.4, 64.6; HRMS (TOF MS ESI^+) $[M+Na]^+$ calculated for $C_{12}H_4N_2S$ 199.0272, found 199.0268.

Tridec-2-ynenitrile (2p)[2]



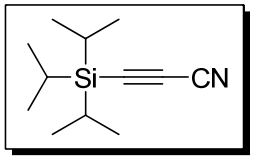
Colorless liquid (32.1 mg, 56%); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 2.35 (t, J = 7.1 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.43 – 1.36 (m, 2H), 1.27 (comp, 12H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 105.4, 87.6, 55.4, 32.0, 29.6, 29.5, 29.4, 29.0, 28.8, 27.2, 22.8, 18.9, 14.2; HRMS (TOF MS ESI^+) $[M+Na]^+$ calculated for $C_{13}H_{21}NNa$ 214.1572, found 214.1575.

Hept-2-ynedinitrile (2q)



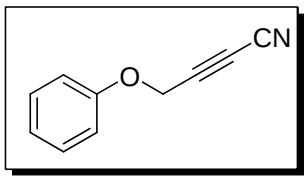
Colorless liquid (32.6 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 2.57 (t, *J* = 7.0 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 1.97 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 118.1, 104.9, 84.3, 56.9, 23.2, 18.0, 16.4; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_7H_6N_2Na$ 141.0429, found 141.0433.

3-(Triisopropylsilyl)propiolonitrile (2r)[2]



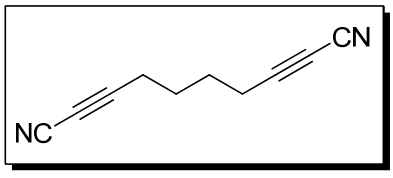
Colorless oil (26.1 mg, 42%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 1.18 – 1.12 (m, 3H), 1.10 (d, *J* = 5.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 105.1, 93.6, 77.8, 18.4, 11.0; HRMS (TOF MS ESI$^+$) $[M+H]^+$ calculated for $C_{12}H_{22}NSi$ 208.1522, found 208.1520.

4-Phenoxybut-2-ynenitrile (2s)[4]



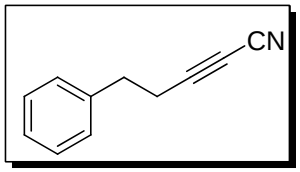
Colorless liquid (36.8 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.38 – 7.32 (m, 2H), 7.08 (m, 1H), 6.97 – 6.92 (m, 2H), 4.81 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 156.9, 129.9, 122.7, 114.9, 104.5, 79.9, 61.2, 55.5; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{10}H_7NNaO$ 180.0425, found 180.0419.

Deca-2,8-diynedinitrile (2t)



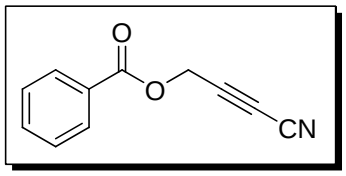
Colorless oil (23.4 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 2.47 – 2.39 (m, 4H), 1.77 – 1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 105.2, 86.0, 56.2, 26.1, 18.5; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{10}H_8N_2Na$ 179.0585, found 179.0587.

5-Phenylpent-2-ynenitrile (2u)



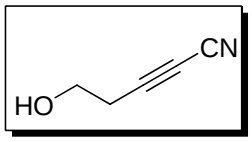
Colorless liquid (33.5 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.37 (tt, *J* = 8.1, 1.7 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.26 – 7.21 (m, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 138.7, 128.9, 128.4, 127.1, 105.3, 86.4, 56.1, 33.3, 21.2; HRMS (TOF MS ESI$^+$) $[M+H]^+$ calculated for $C_{11}H_{10}N$ 156.0813, found 156.0817.

3-Cyanoprop-2-ynyl benzoate (2v)



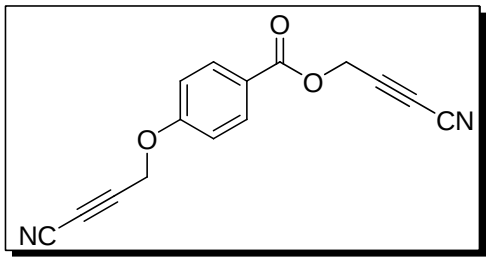
Colorless liquid (38.9 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.06 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.50 – 7.45 (m, 2H), 5.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 164.4, 133.1, 129.1, 127.8, 127.5, 103.5, 77.8, 59.7, 50.6; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{11}H_7NNaO_2$ 208.0374, found 208.0368.

5-Hydroxypent-2-ynenitrile (2w)[6]



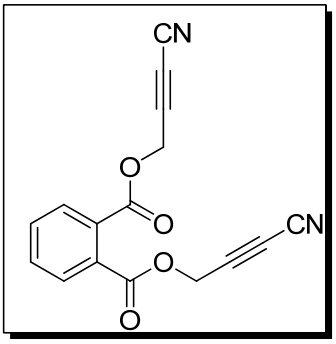
Colorless liquid (45%, 12.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 3.831= (t, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 6.4 Hz, 2H), 2.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 105.2, 84.7, 59.6, 57.7, 23.4.

3-Cyanoprop-2-ynyl 4-(3-cyanoprop-2-ynyloxy)benzoate (2x)



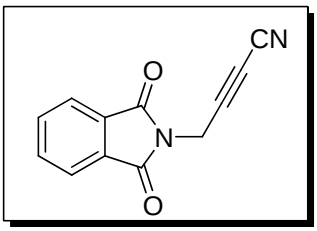
Colorless liquid (46.0 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.08 – 8.02 (m, 2H), 7.02 – 6.97 (m, 2H), 5.00 (s, 2H), 4.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 164.6, 161.1, 132.4, 122.7, 114.7, 104.5, 104.3, 78.8, 78.6, 61.8, 60.6, 55.5, 51.5; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{15}H_8N_2NaO_3$ 287.0433, found 287.0435.

Bis(3-cyanoprop-2-ynyl) phthalate (2y)



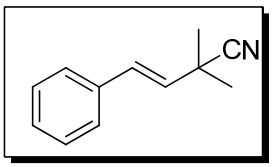
Colorless liquid (59.6 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.82 – 7.76 (m, 2H), 7.67 – 7.62 (m, 2H), 5.01 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 165.8, 132.3, 130.4, 129.5, 104.4, 78.1, 61.0, 52.2; HRMS (TOF MS ESI$^+$) $[M+Na]^+$ calculated for $C_{16}H_8N_2NaO_4$ 315.0382, found 315.0380.

4-(1,3-Dioxoisoindolin-2-yl)but-2-ynenitrile (2z)



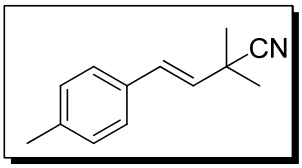
White solid (54.2 mg, 86%); mp: 118 – 120 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): δ 7.90 (dd, J = 5.5, 3.1 Hz, 2H), 7.78 (dd, J = 5.5, 3.1 Hz, 2H), 4.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 166.4, 134.8, 131.7, 124.0, 104.5, 78.5, 57.7, 27.1; HRMS (TOF MS ESI$^+$) $[M+H]^+$ calculated for $C_{12}H_7N_2O_2$ 211.0508, found 211.0512.

(*E*)-2,2-Dimethyl-4-phenylbut-3-enenitrile (3a)[5]



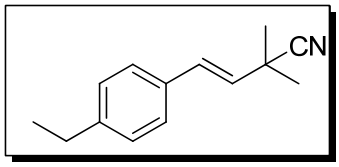
Colorless oil (31.8 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.41 – 7.37 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 6.76 (d, J = 15.9 Hz, 1H), 6.04 (d, J = 15.9 Hz, 1H), 1.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 135.9, 130.5, 130.0, 128.8, 128.3, 126.7, 123.6, 35.1, 27.8;

(*E*)-2,2-Dimethyl-4-p-tolylbut-3-enenitrile (3b)



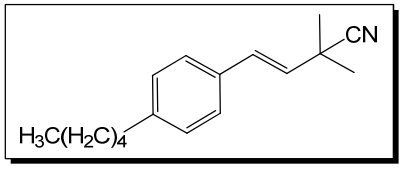
White solid (35.0 mg, 63%); mp: 56 – 58 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.29 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 1.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 138.2, 133.1, 129.8, 129.5, 126.6, 123.7, 35.0, 27.8, 21.3; HRMS (TOF MS CI$^+$) $[M+H]^+$ calculated for $C_{13}H_{16}N$ 186.1283, found 186.1281.

(*E*)-4-(4-Ethylphenyl)-2,2-dimethylbut-3-enenitrile (3c)



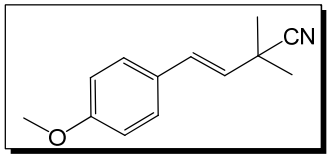
Yellow oil (34.7, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.32 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.00 (d, *J* = 15.9 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.54 (s, 6H), 1.24 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 144.6, 133.3, 129.8, 129.6, 128.3, 126.7, 123.7, 35.0, 28.7, 27.8, 15.6; HRMS (TOF MS CI$^+$) $[M+H]^+$ calculated for $C_{14}H_{18}N$ 200.1439, found 200.1443.

(*E*)-2,2-Dimethyl-4-(4-pentylphenyl)but-3-enenitrile (3d)



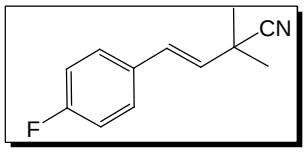
Yellow oil (41.3 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.33 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 15.9 Hz, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.57 (s, 6H), 1.39 – 1.31 (comp, 4H), 0.93 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.3, 133.3, 129.8, 129.5, 128.9, 126.6, 123.7, 35.7, 35.0, 31.5, 31.2, 27.8, 22.6, 14.1; HRMS (TOF MS CI$^+$) $[M+H]^+$ calculated for $C_{17}H_{24}N$ 242.1909, found 242.1916.

(*E*)-4-(4-Methoxyphenyl)-2,2-dimethylbut-3-enenitrile (3e)



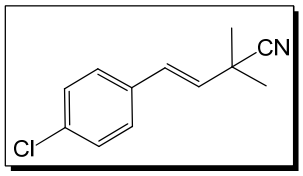
Colorless oil (30.2 mg, 50%); mp: ; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.34 – 7.30 (m, 2H), 6.89 – 6.85 (m, 2H), 6.69 (d, *J* = 15.9 Hz, 1H), 5.90 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H), 1.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 159.7, 129.4, 128.6, 128.3, 127.9, 123.8, 114.2, 55.4, 35.0, 27.9; HRMS (TOF MS CI$^+$) $[M+H]^+$ calculated for $C_{13}H_{16}NO$ 202.1232, found 202.1237.

(*E*)-4-(4-Fluorophenyl)-2,2-dimethylbut-3-enenitrile (3f)



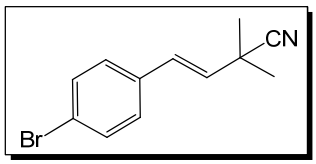
Colorless liquid (25.5 mg, 45%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.38 – 7.32 (m, 2H), 7.06 – 6.99 (m, 2H), 6.72 (d, *J* = 15.9 Hz, 1H), 5.95 (d, *J* = 15.9 Hz, 1H), 1.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 162.7 (d, *J* = 247.6 Hz), 132.0 (d, *J* = 3.4 Hz), 130.3 (d, *J* = 2.2 Hz), 128.9, 128.2 (d, *J* = 8.1 Hz), 123.5, 115.8 (d, *J* = 21.5 Hz), 35.0, 27.8; HRMS (TOF MS CI$^+$) $[M+H]^+$ calculated for $C_{12}H_{13}FN$ 190.1032, found 190.1030.

(*E*)-4-(4-Chlorophenyl)-2,2-dimethylbut-3-enenitrile (3g)



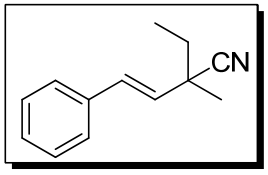
White solid (36.4 mg, 59%); mp: 36 – 38 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.30 (s, 4H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.00 (d, *J* = 15.9 Hz, 1H), 1.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 134.4, 134.0, 131.2, 129.0, 128.9, 127.9, 123.4, 35.1, 27.7; HRMS (TOF MS CI$^+$) $[M+H]^+$ calculated for $C_{12}H_{13}ClN$ 206.0737, found 206.0736.

(*E*)-4-(4-Bromophenyl)-2,2-dimethylbut-3-enenitrile (3h)



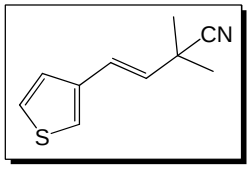
White solid (39.0 mg, 52%); mp: 48 – 50 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.47 – 7.44 (m, 2H), 7.26 – 7.22 (m, 2H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 1.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 134.8, 131.9, 131.3, 128.9, 128.2, 123.3, 122.1, 35.1, 27.7; HRMS (TOF MS CI$^+$) $[M+H]^+$ calculated for $C_{12}H_{13}BrN$ 250.0231, found 250.0235.

(*E*)-2-Ethyl-2-methyl-4-phenylbut-3-enenitrile (3i)



Colorless liquid (31.7 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.41 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 5.90 (d, *J* = 16.0 Hz, 1H), 1.85 – 1.64 (m, 2H), 1.51 (s, 3H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 136.0, 131.0, 129.5, 128.8, 128.2, 126.7, 122.6, 40.9, 33.8, 26.0, 9.8; HRMS (TOF MS CI$^+$) $[M+H]^+$ calculated for $C_{13}H_{16}N$ 186.1283, found 186.1286.

(*E*)-2,2-Dimethyl-4-(thiophen-3-yl)but-3-enenitrile (3j)



Colorless liquid (29.2 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.30 (m, 1H), 7.22 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.19 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.77 (d, *J* = 15.9 Hz, 1H), 5.90 (d, *J* = 15.9 Hz, 1H), 1.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 138.4, 130.3, 126.5, 124.9, 124.2, 123.5, 123.3, 34.9, 27.8; HRMS (TOF MS CI^+) $[M+H]^+$ calculated for $C_{10}H_{12}NS$ 178.0690, found 178.0692.

Reference

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3 J.-G. Kim, E. H. Lee, D. O. Jang, *Tetrahedron Lett.,* 2007, **48**, 2299.
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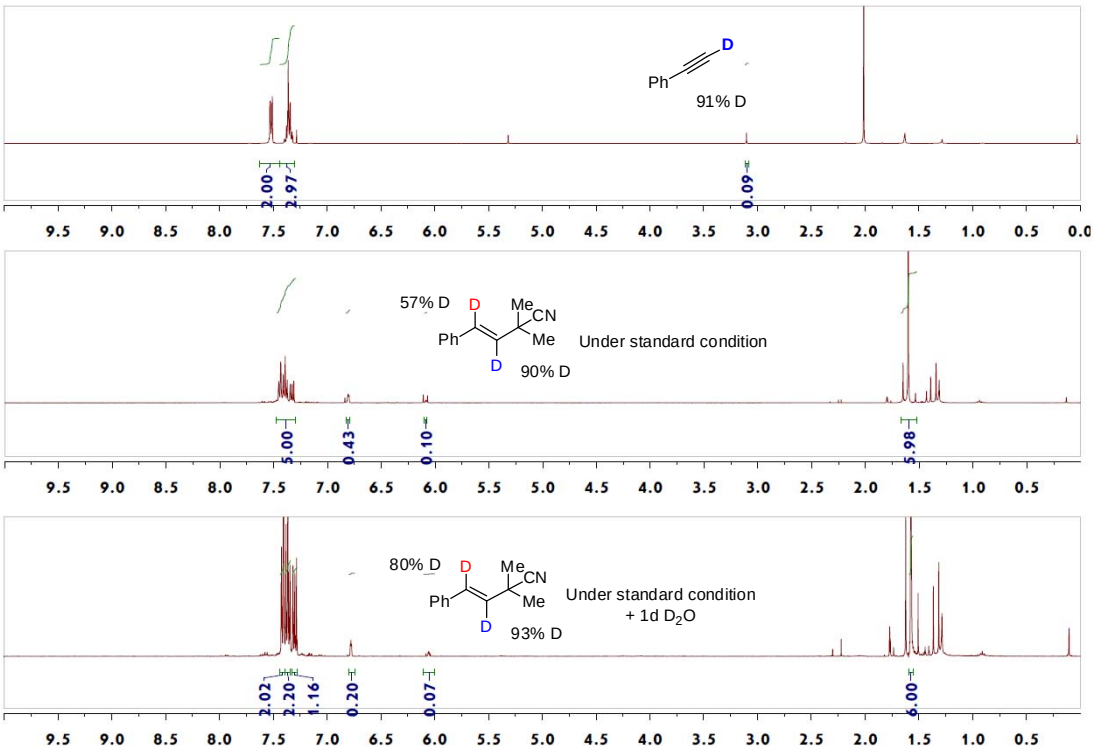
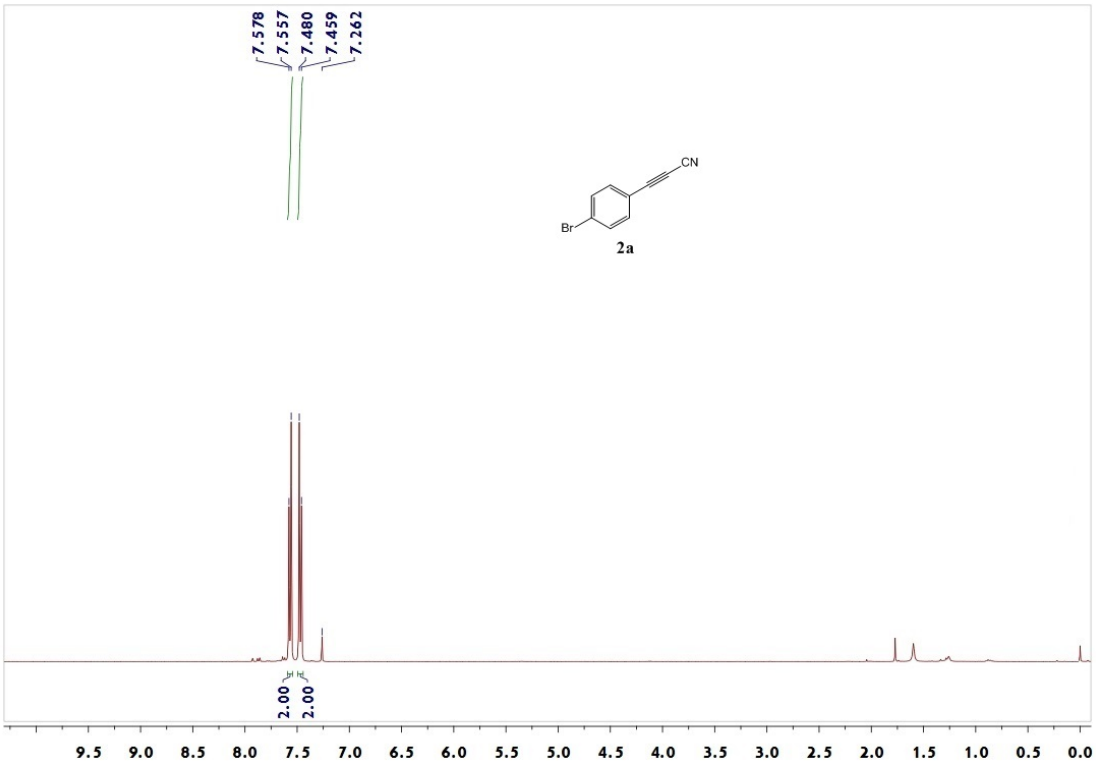
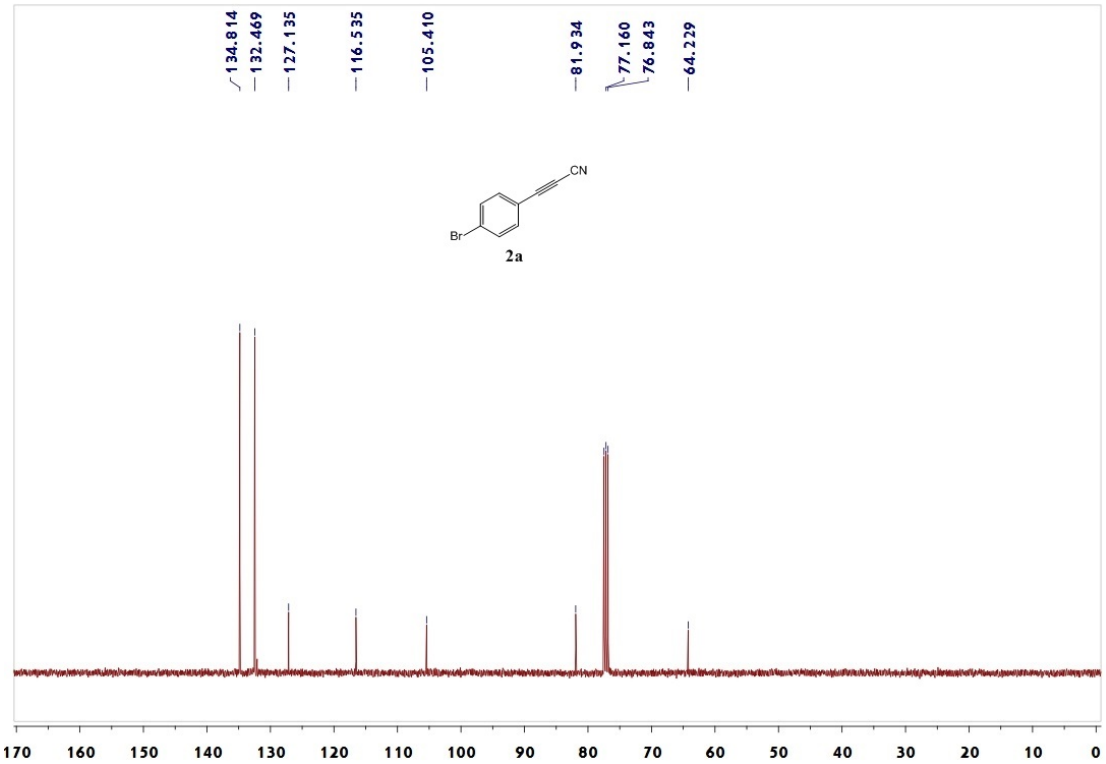
6 F. F. Fleming, V. Gudipati, O. W. Steward, *Tetrahedron*, 2003, **59**, 5585.

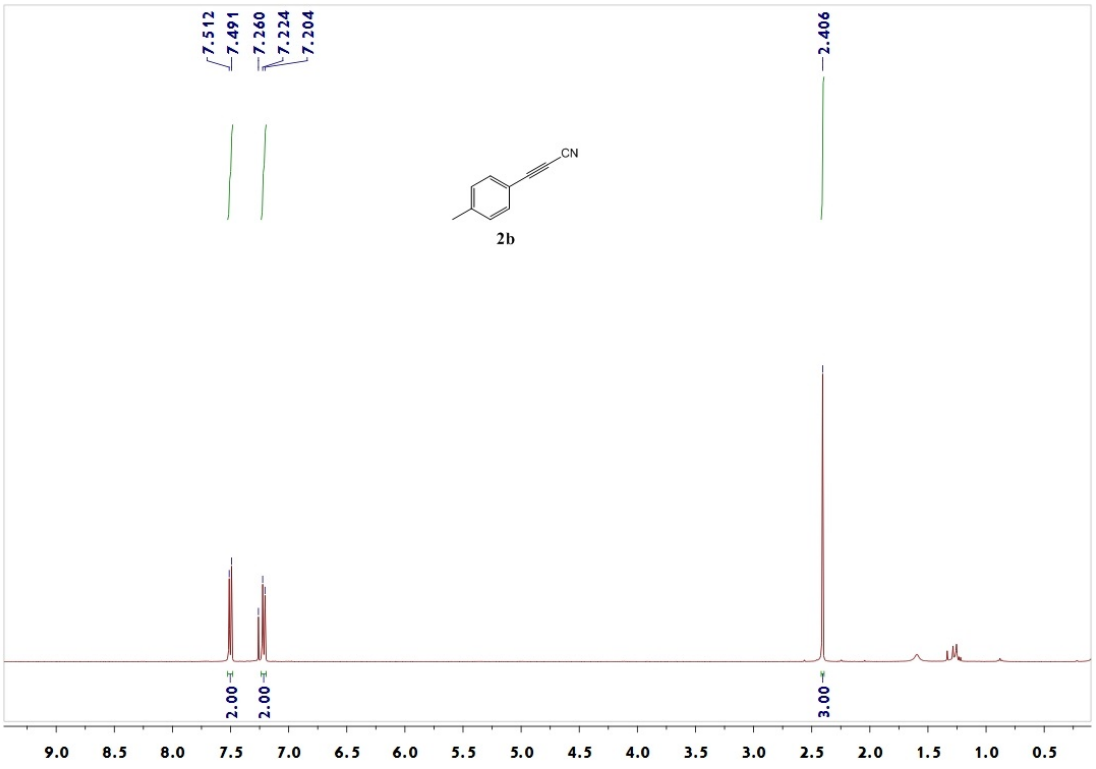
Deuterium Labeling Experiment Results



Copy of NMR Spectra for desired products



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7.491
7.260
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2.406
CN
2b
2.00
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
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3.5
3.0
2.5
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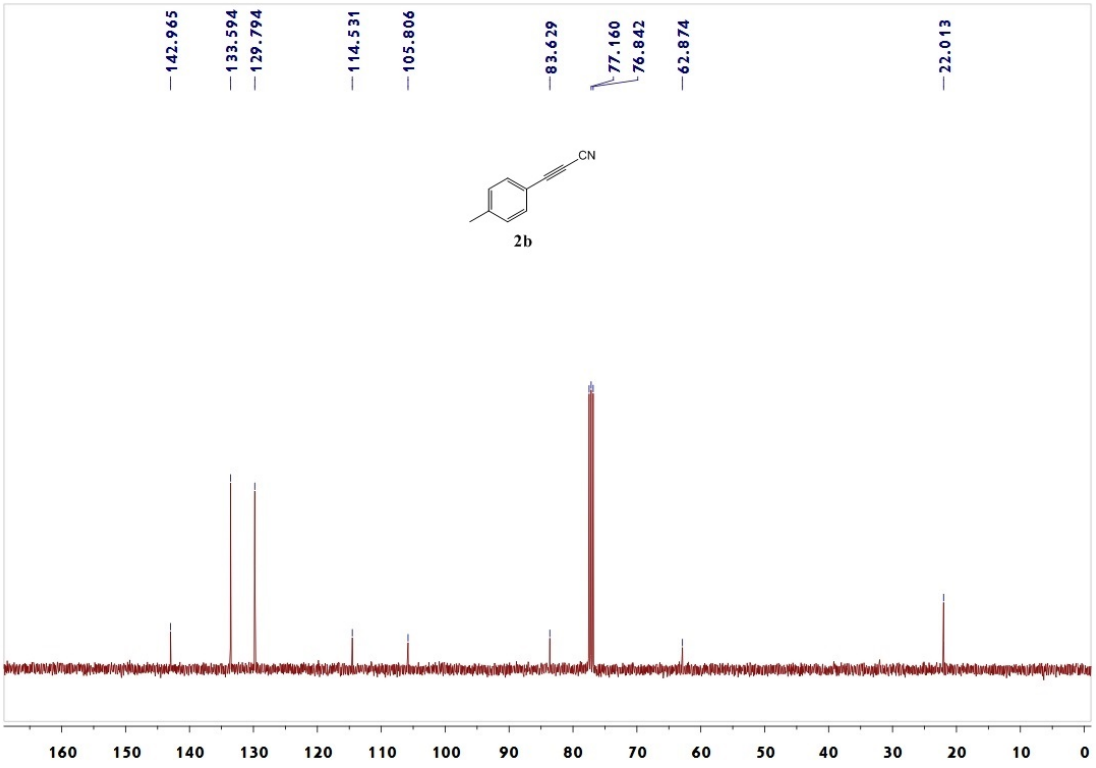
0.5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80
70
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30
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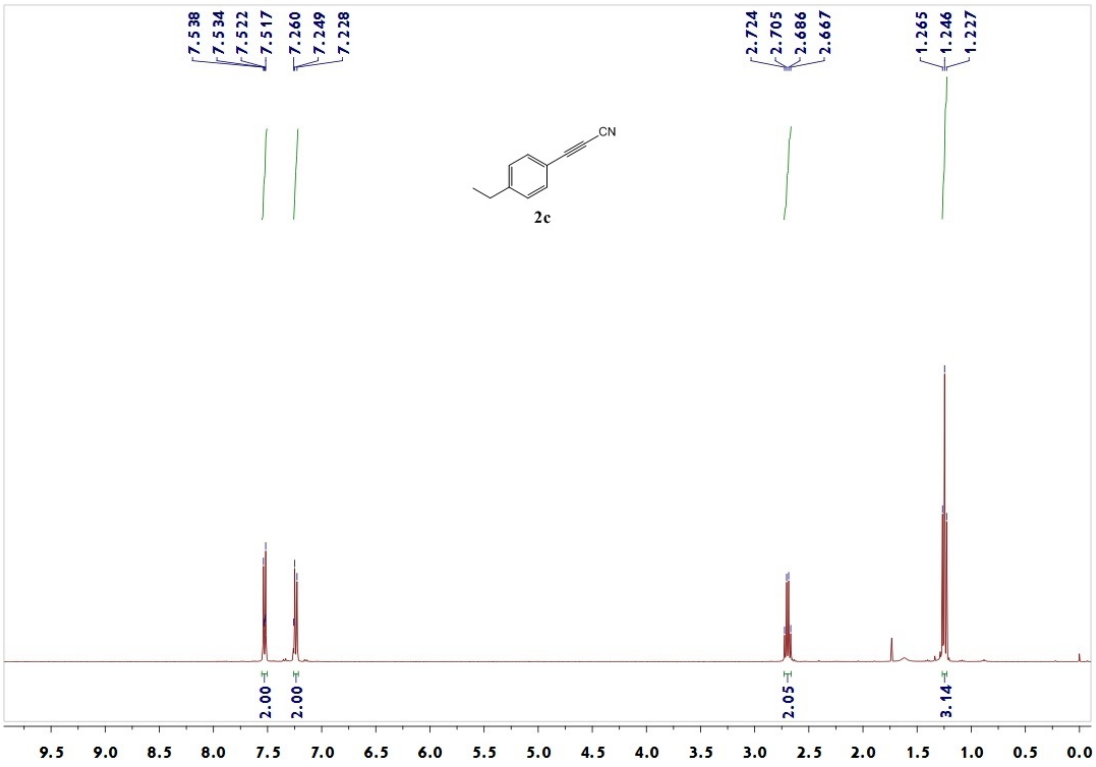
10
0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1.246
1.227
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2c
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2.00
2.05
3.14
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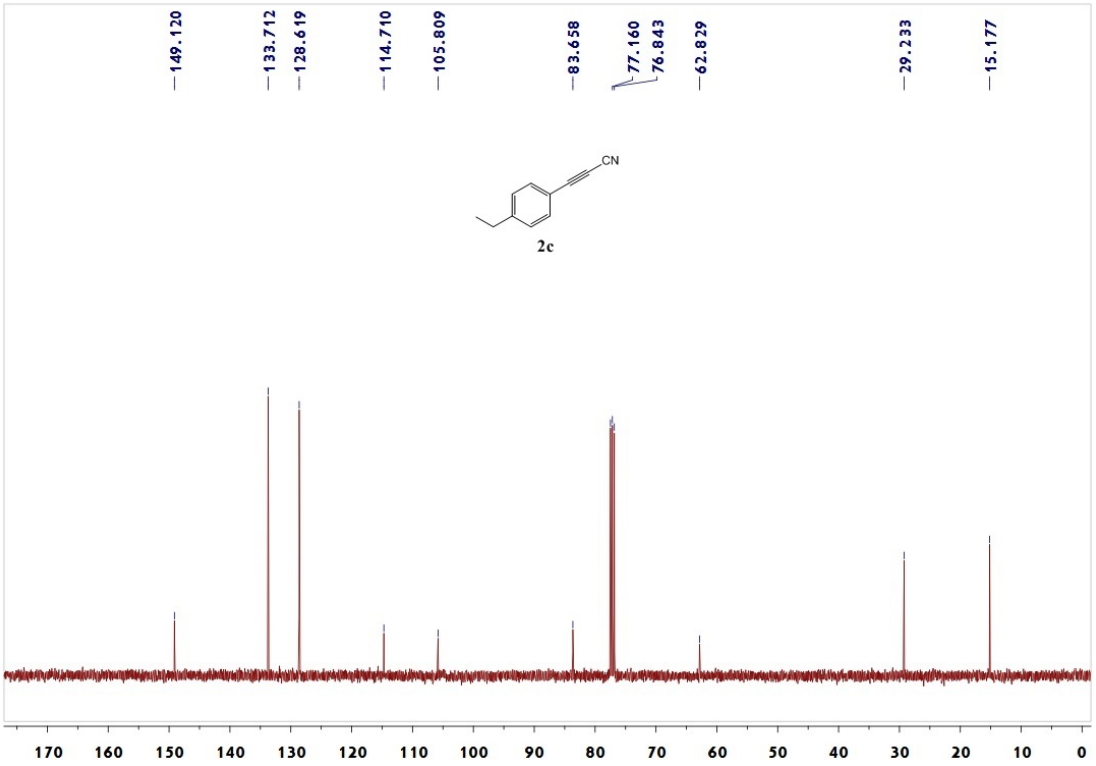
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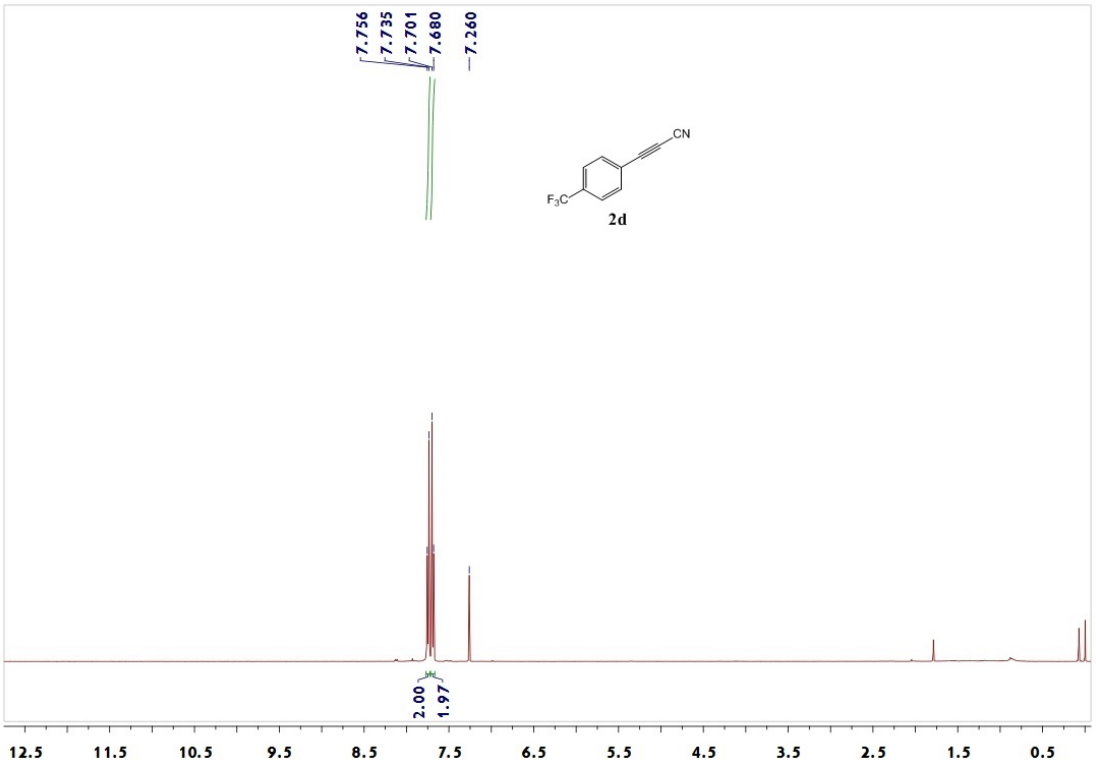
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6.5
5.5
4.5
3.5
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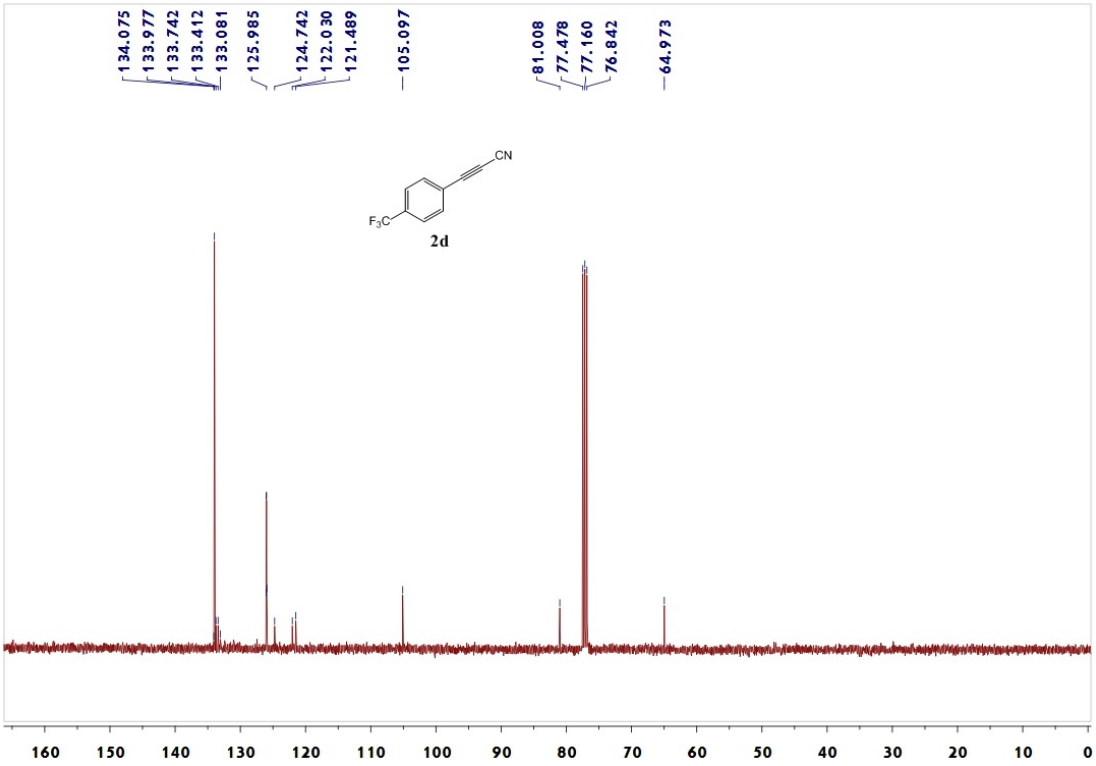
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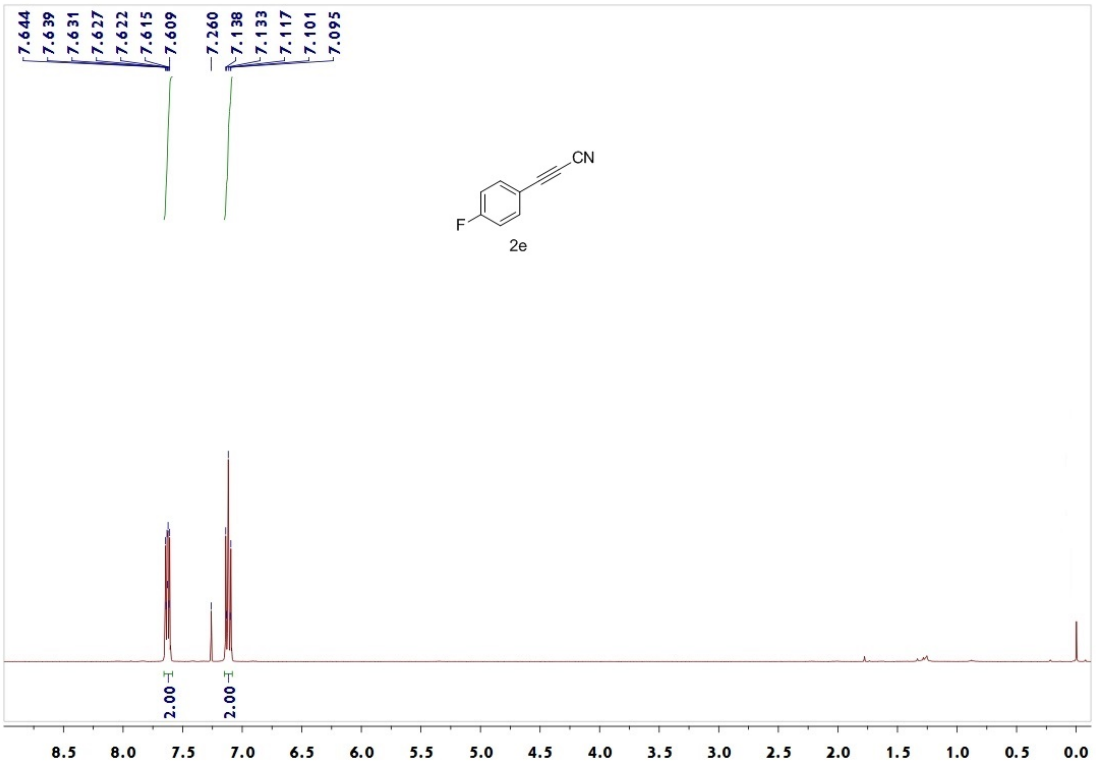
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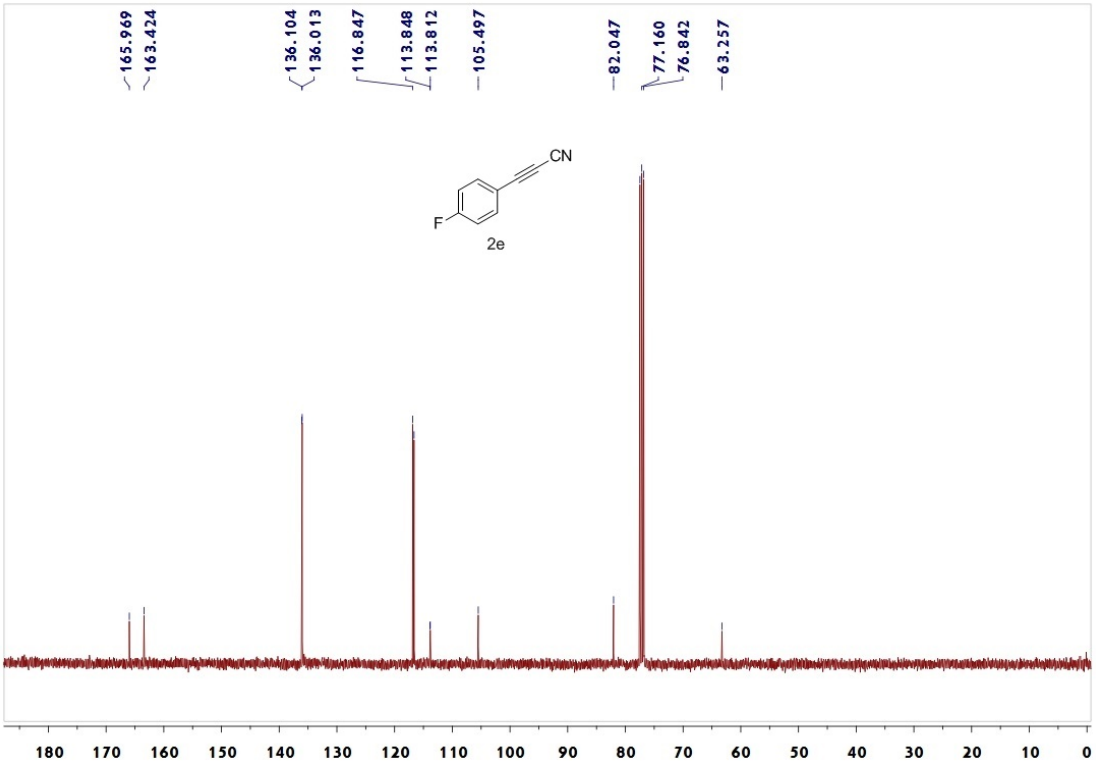
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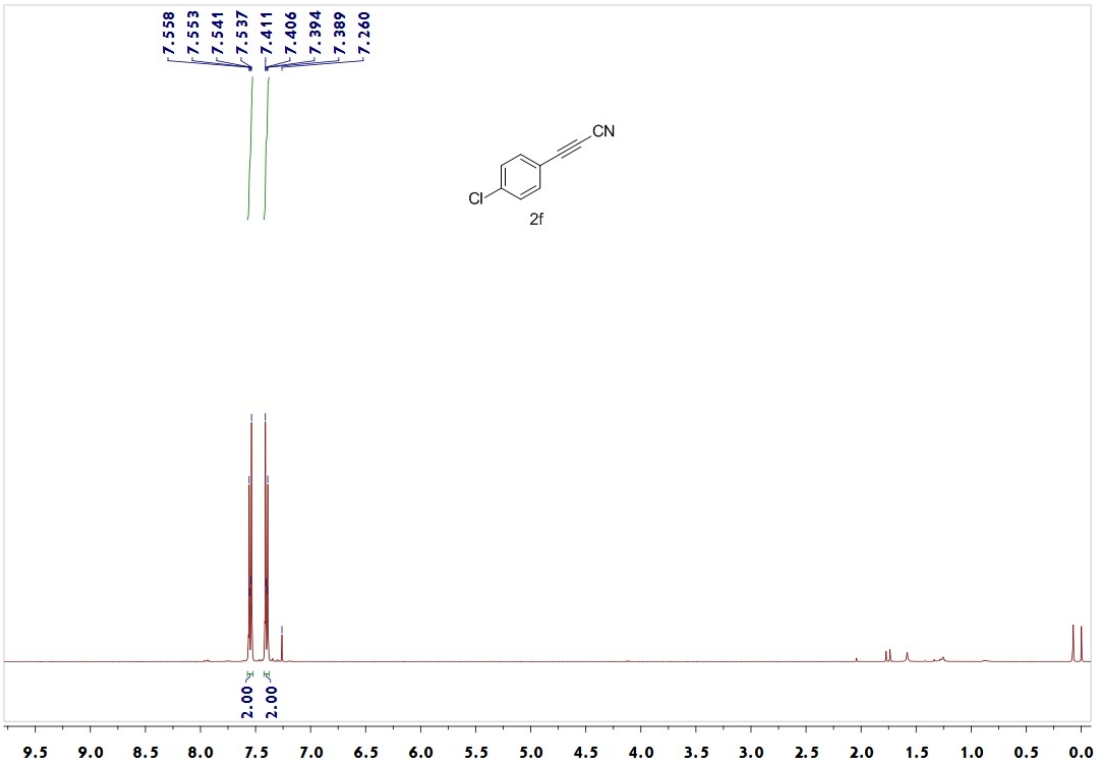
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2.00
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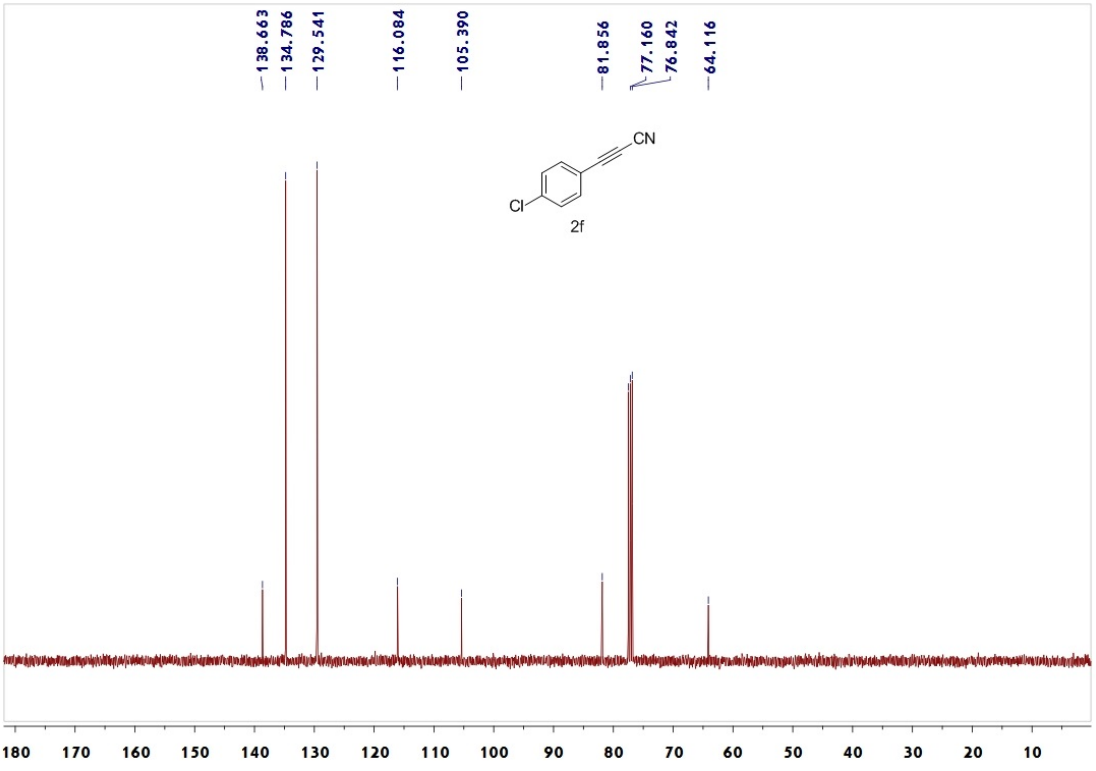
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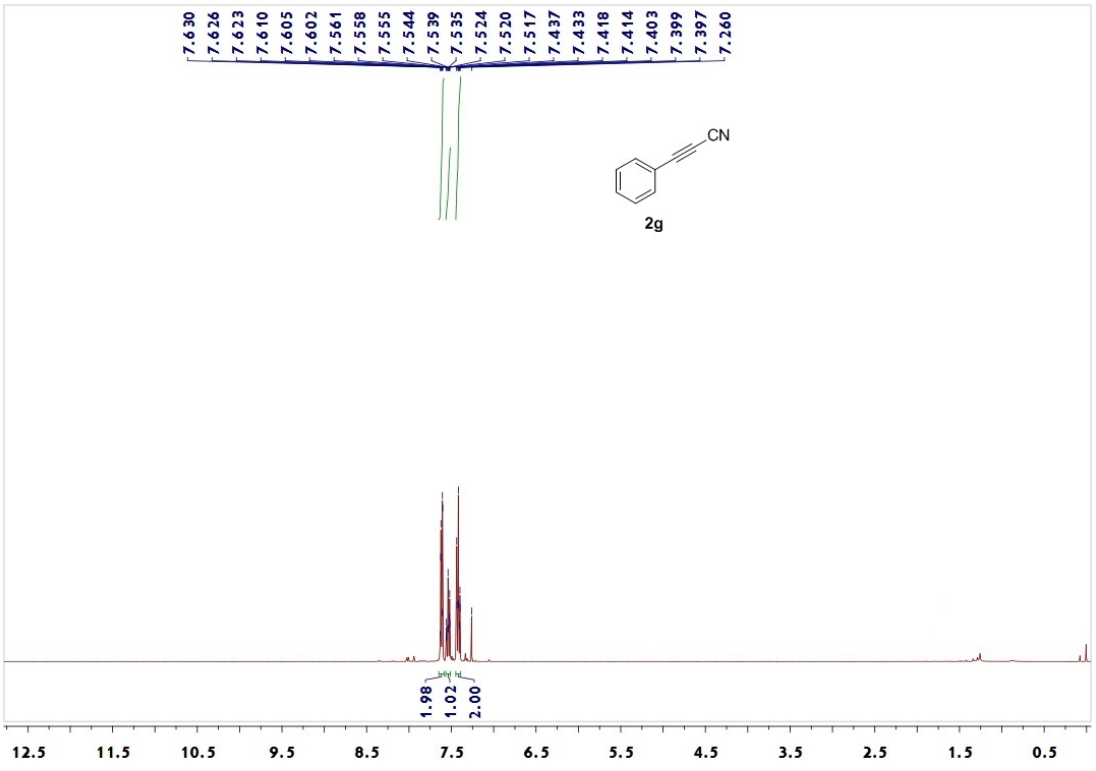
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7.403
7.399
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1.02
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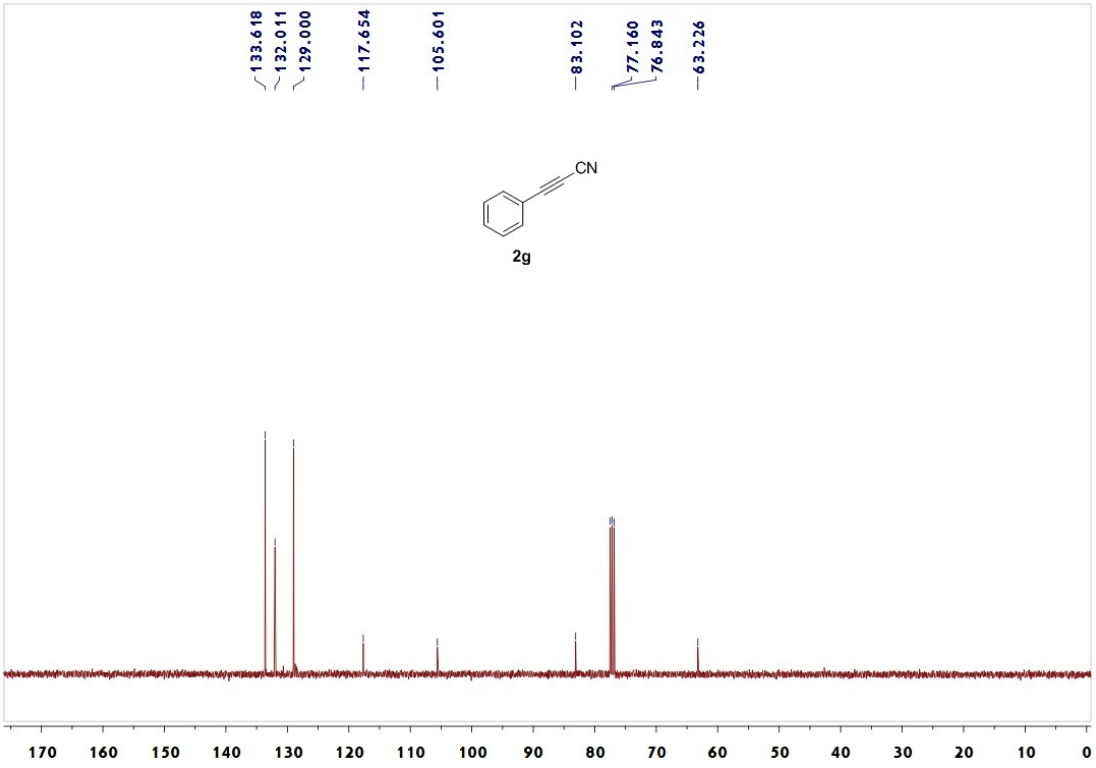
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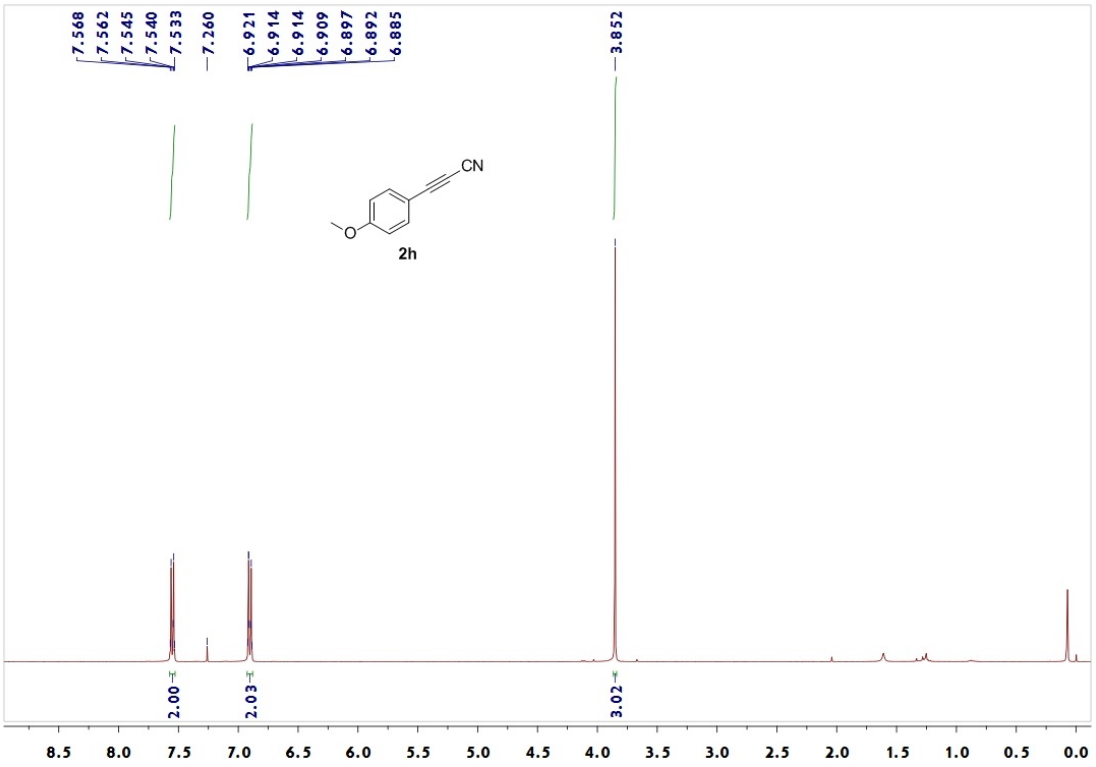
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3.852
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O
2h
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2.03
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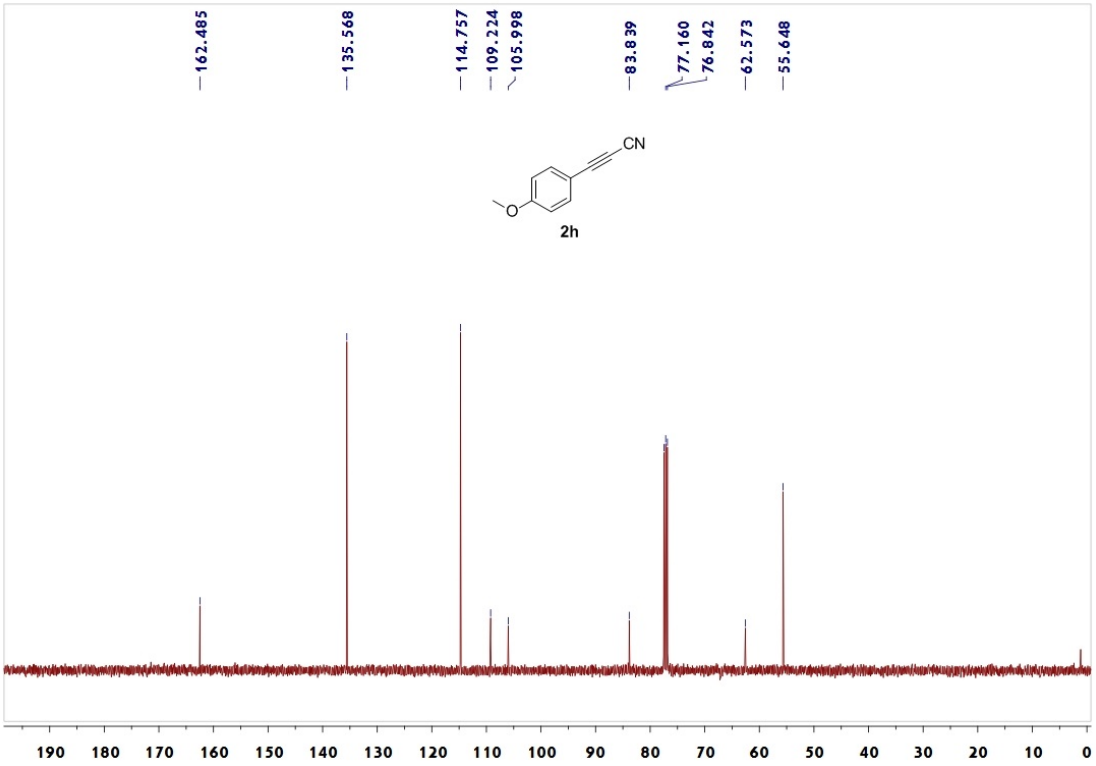
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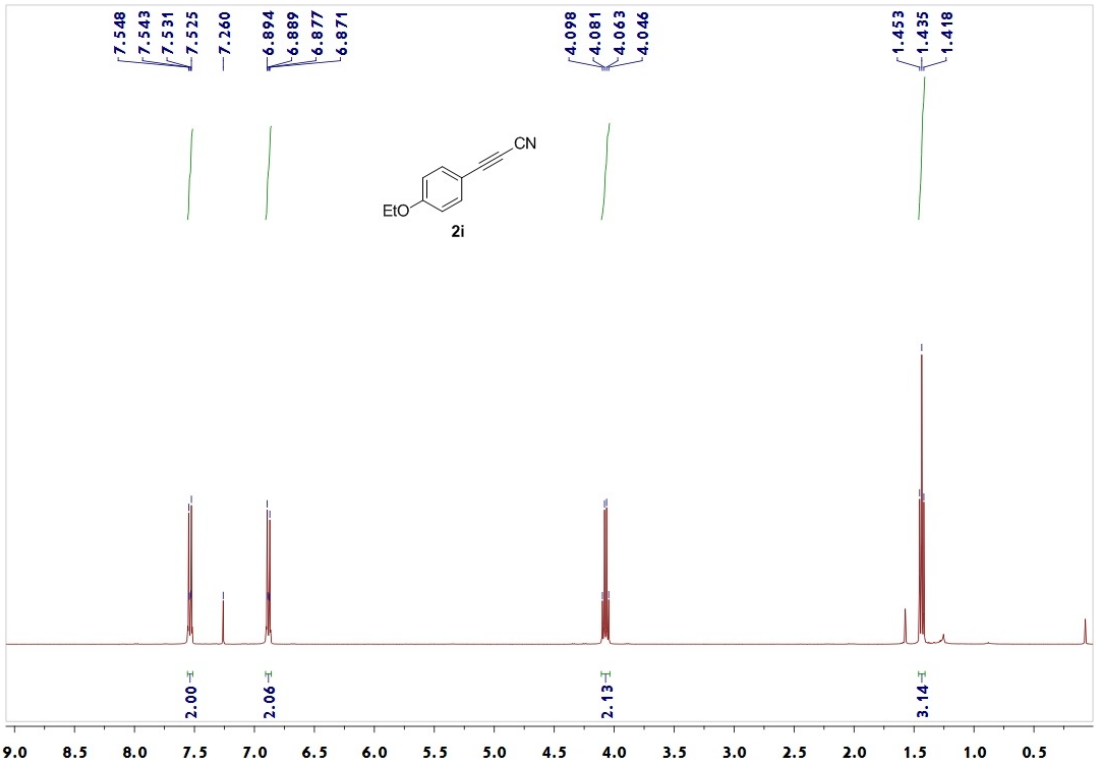
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7.0
6.5
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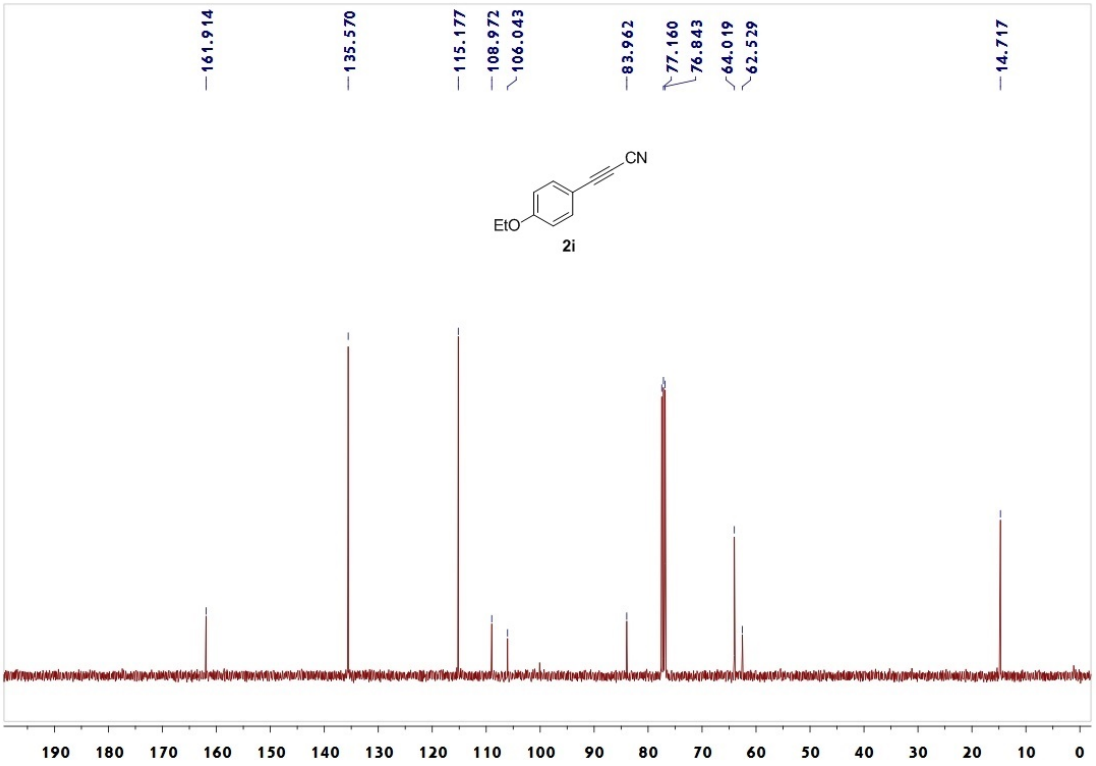
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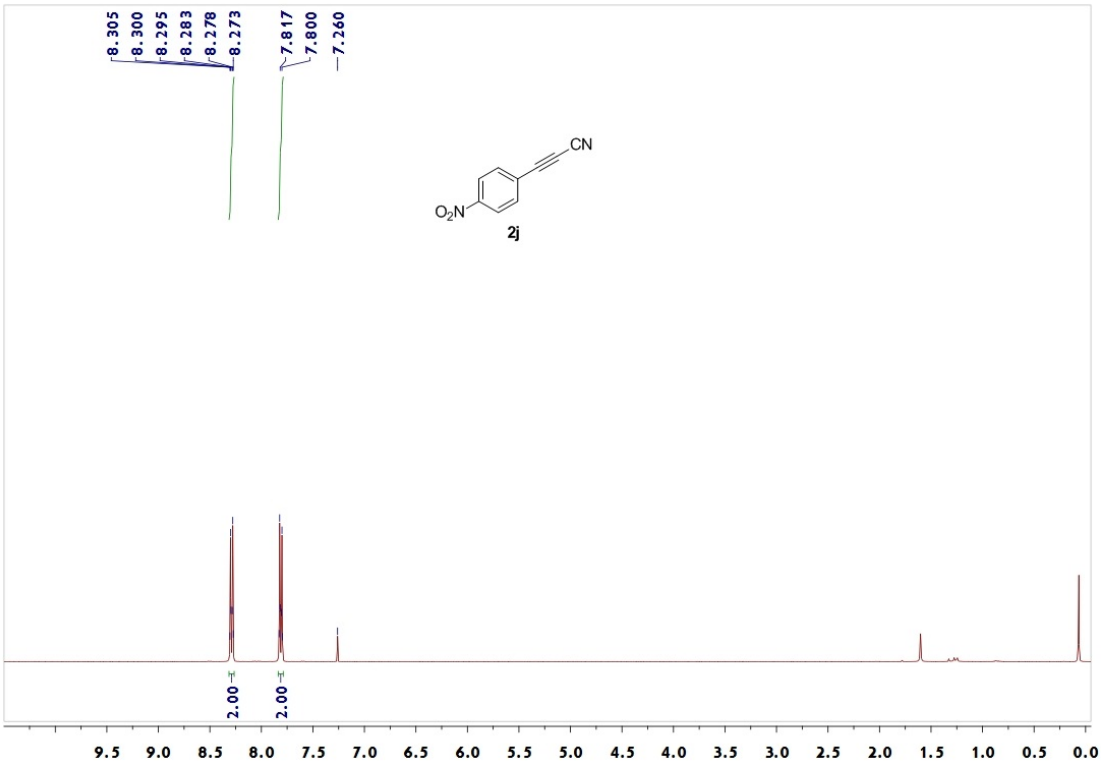
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2.00
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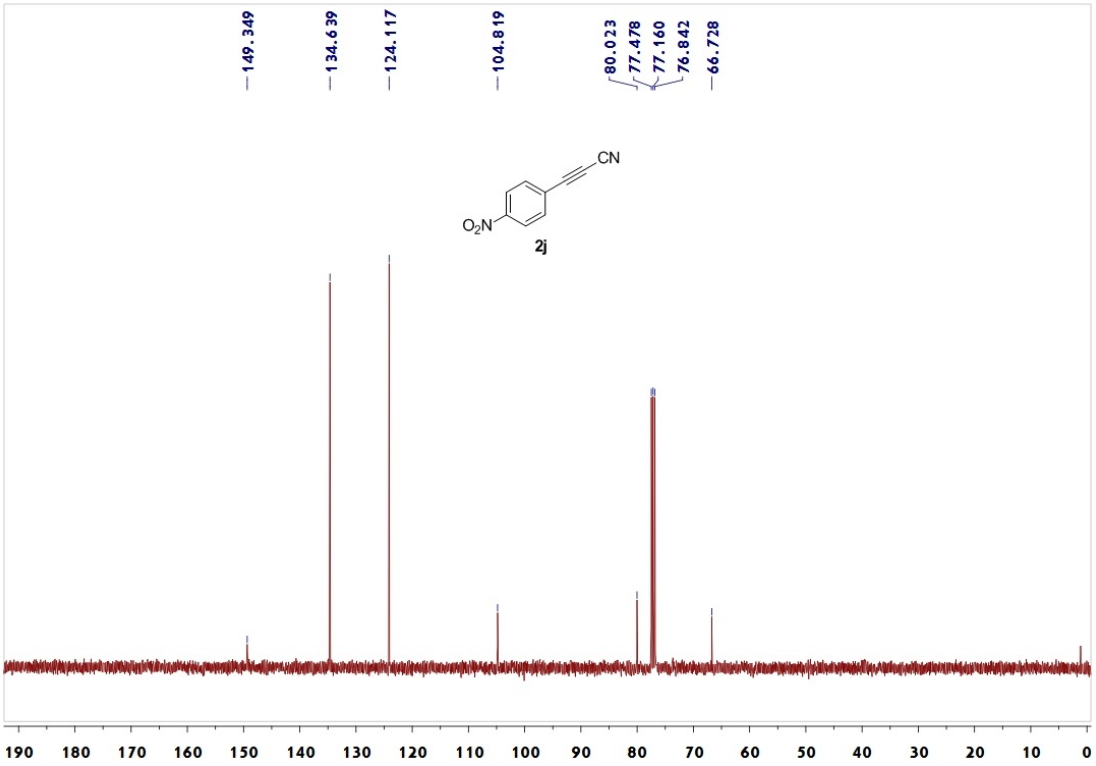
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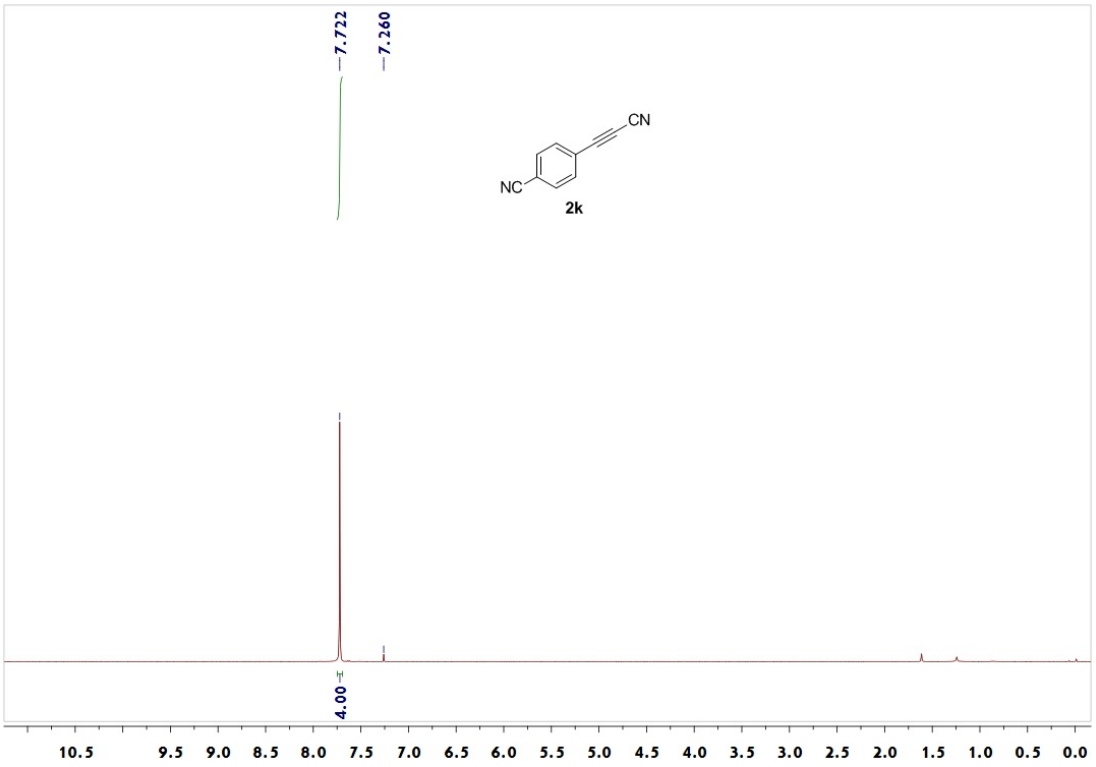
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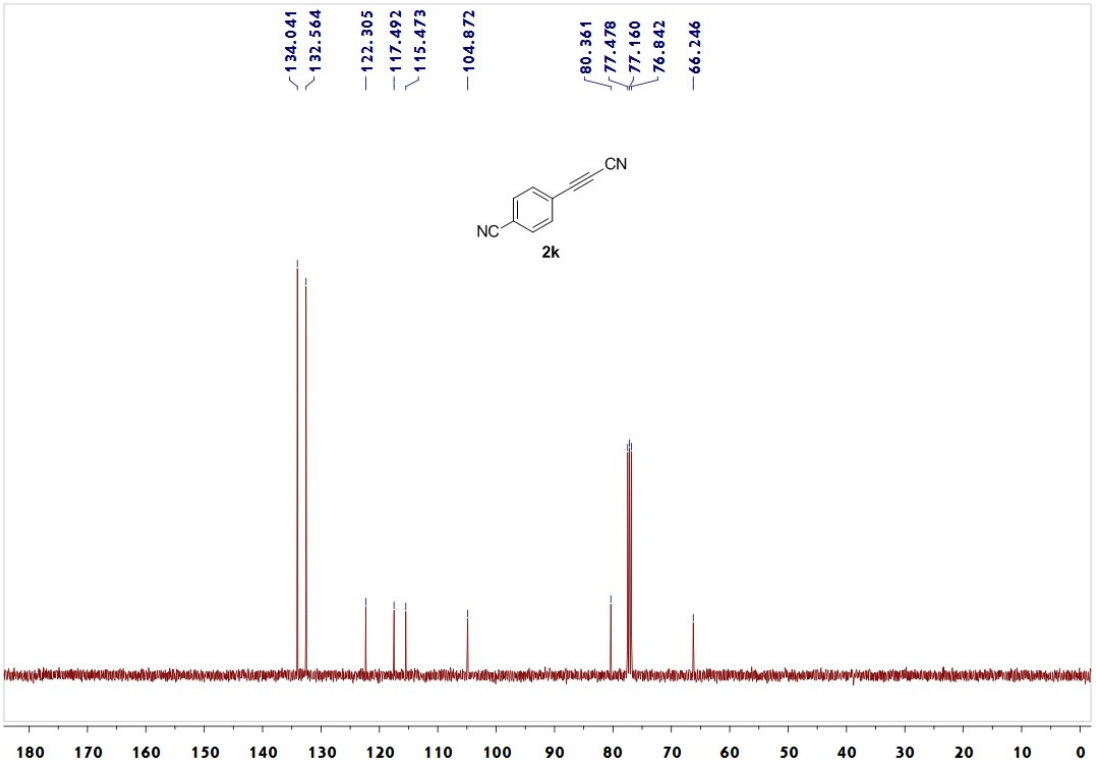
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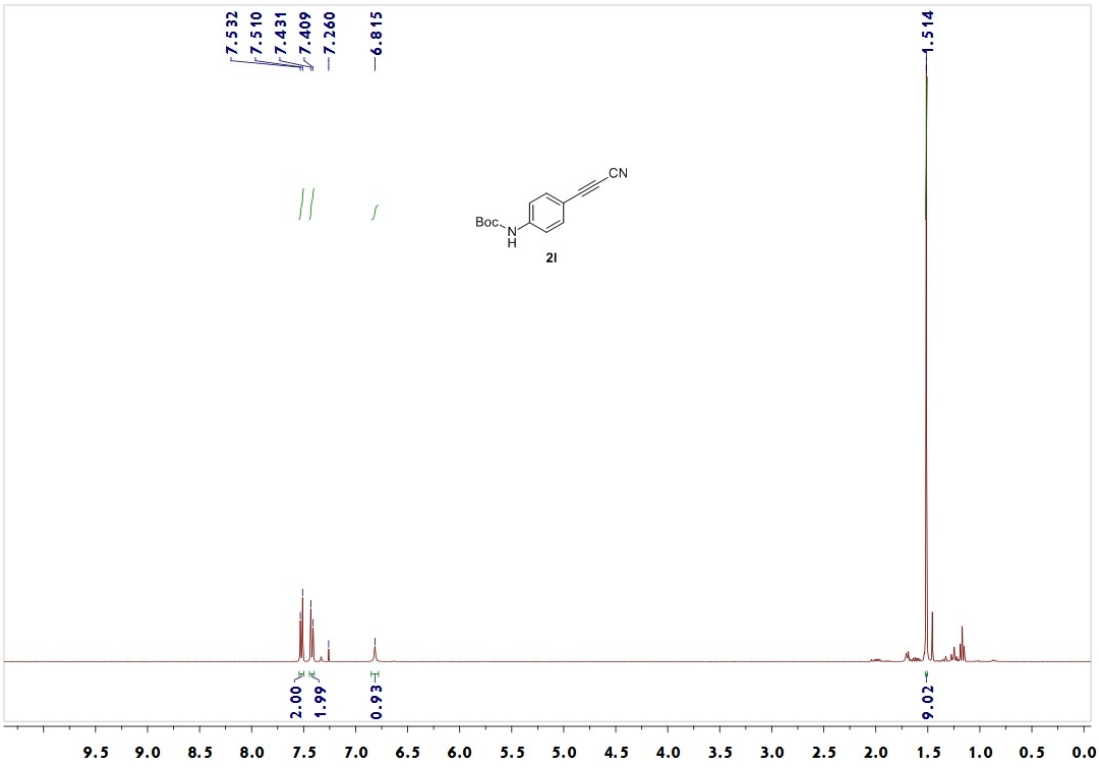
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9.02
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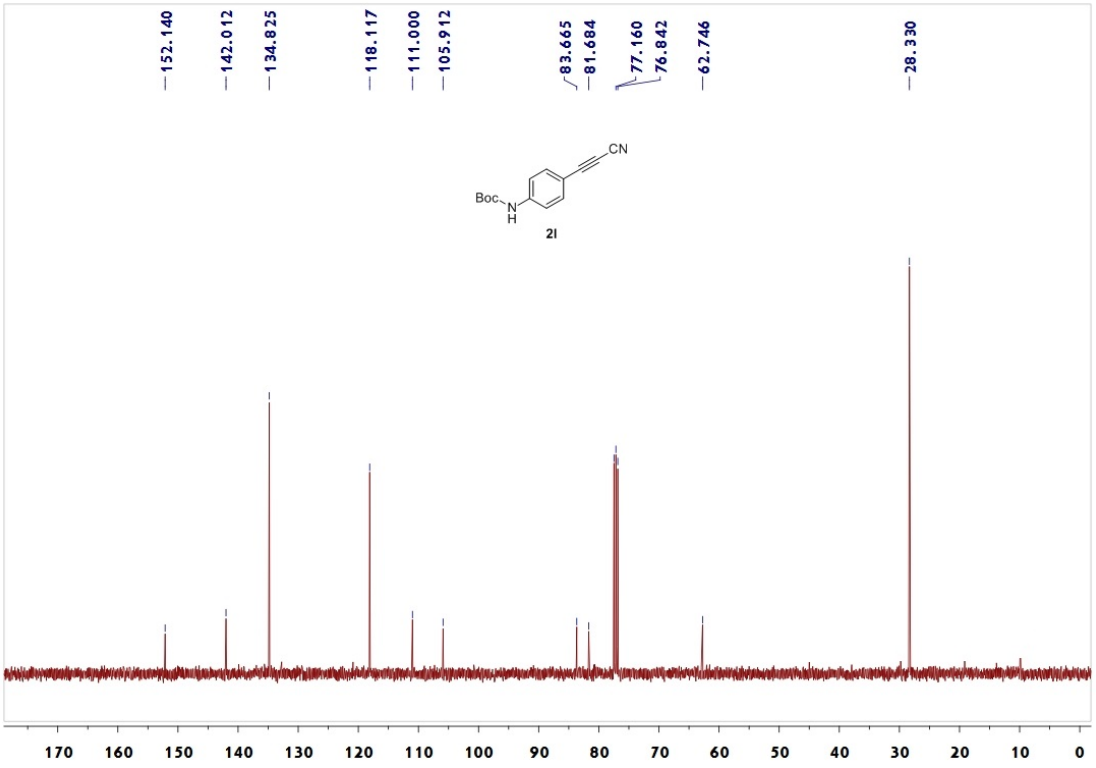
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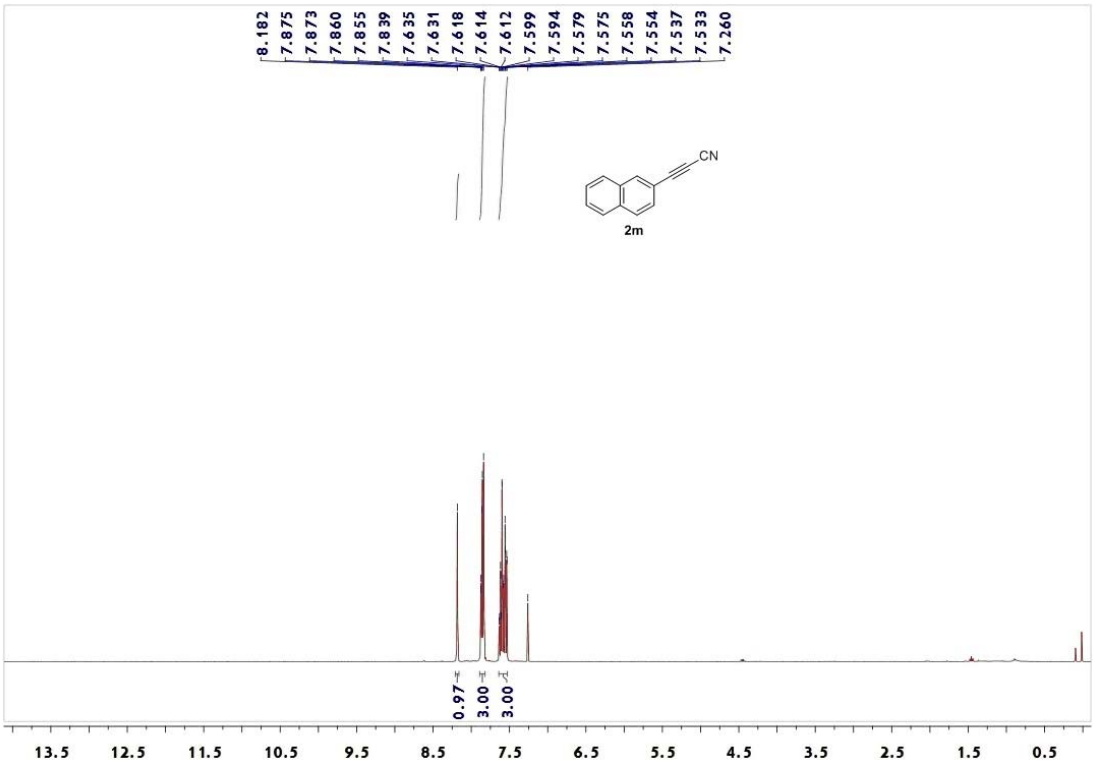
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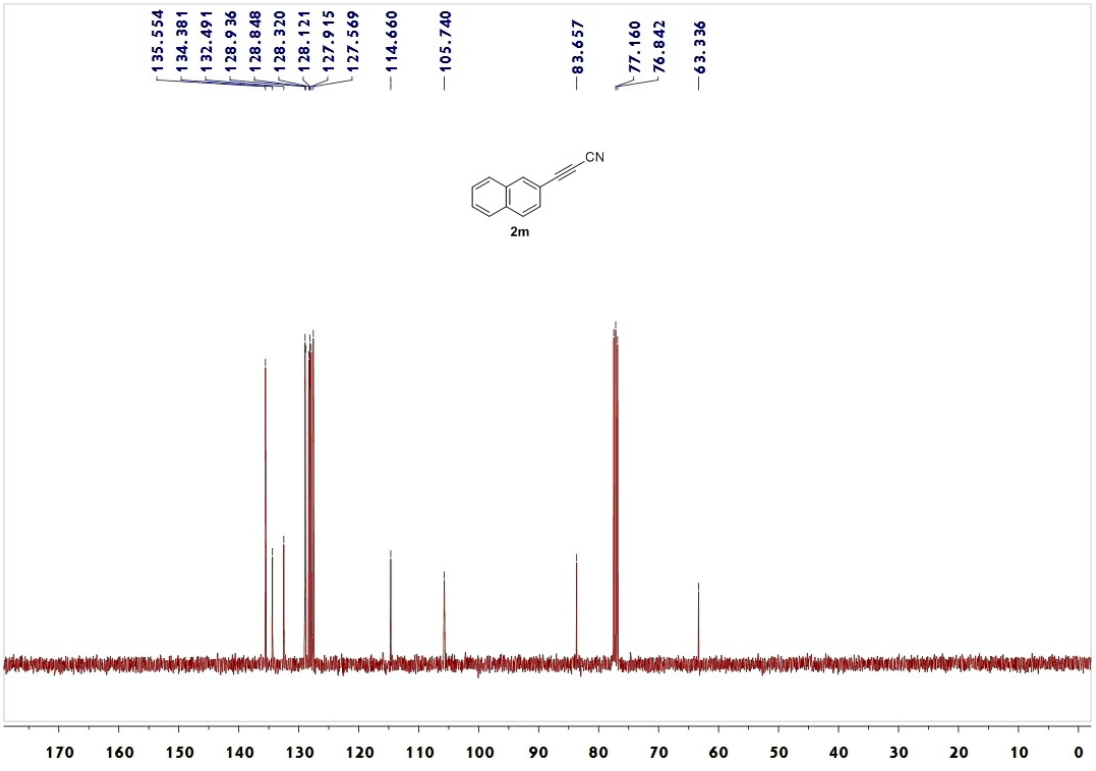
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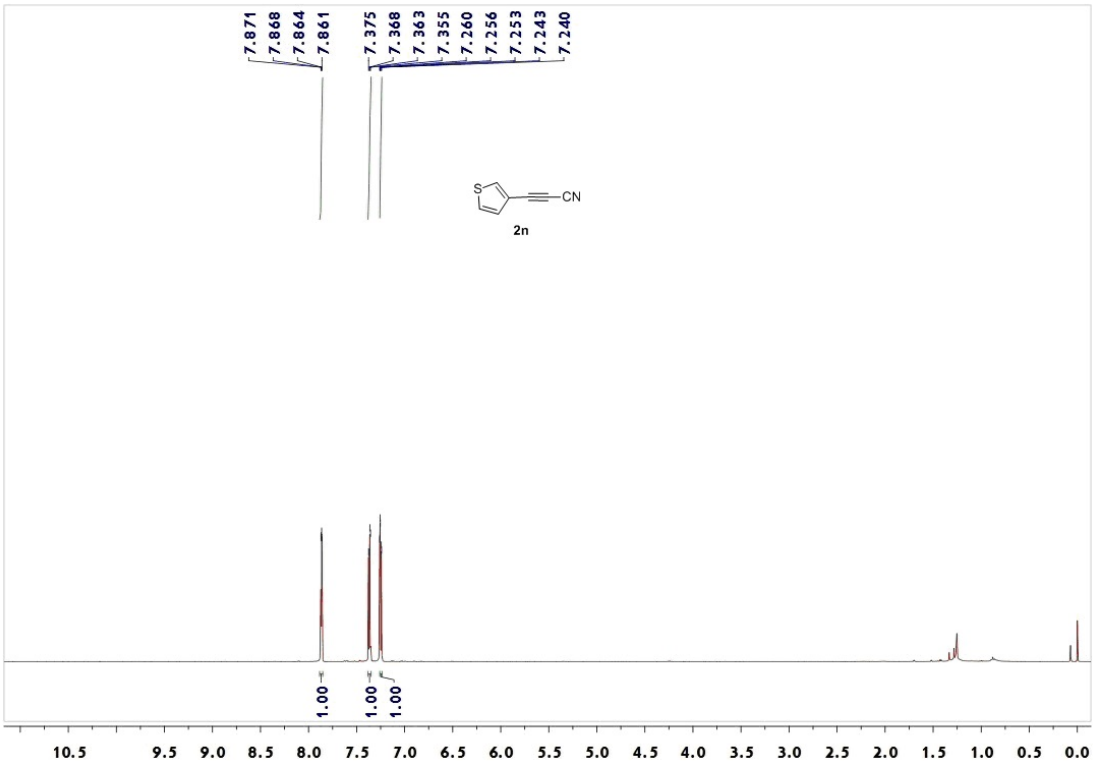
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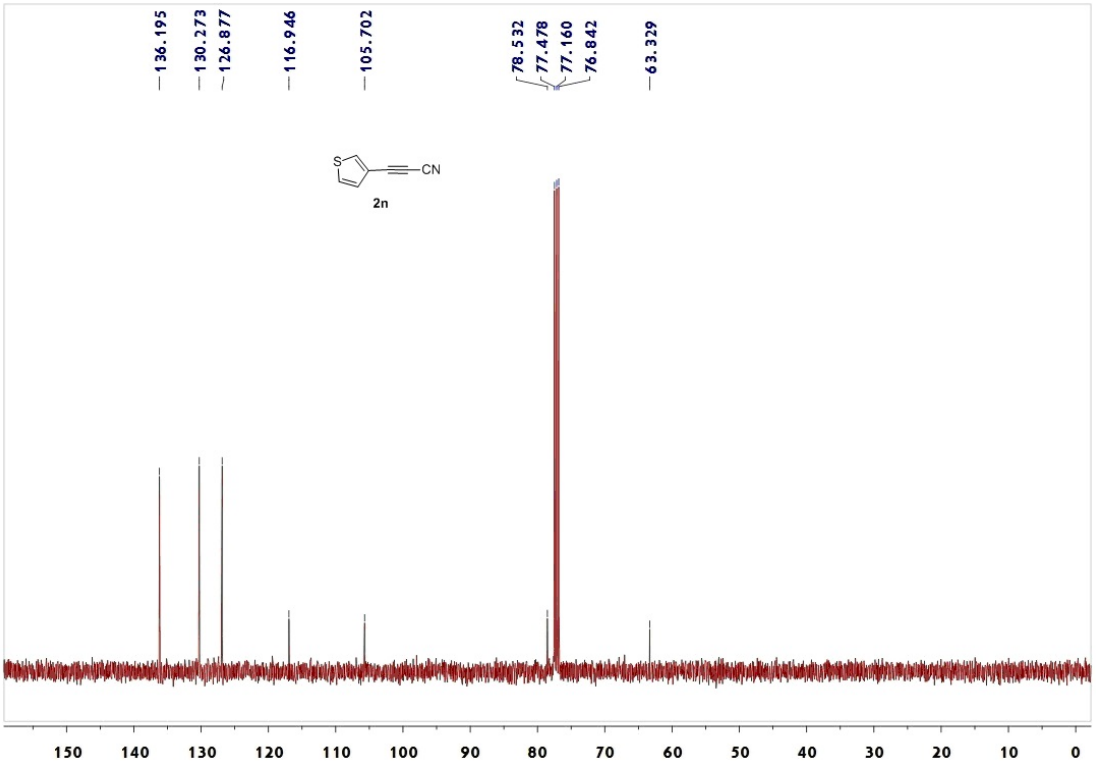
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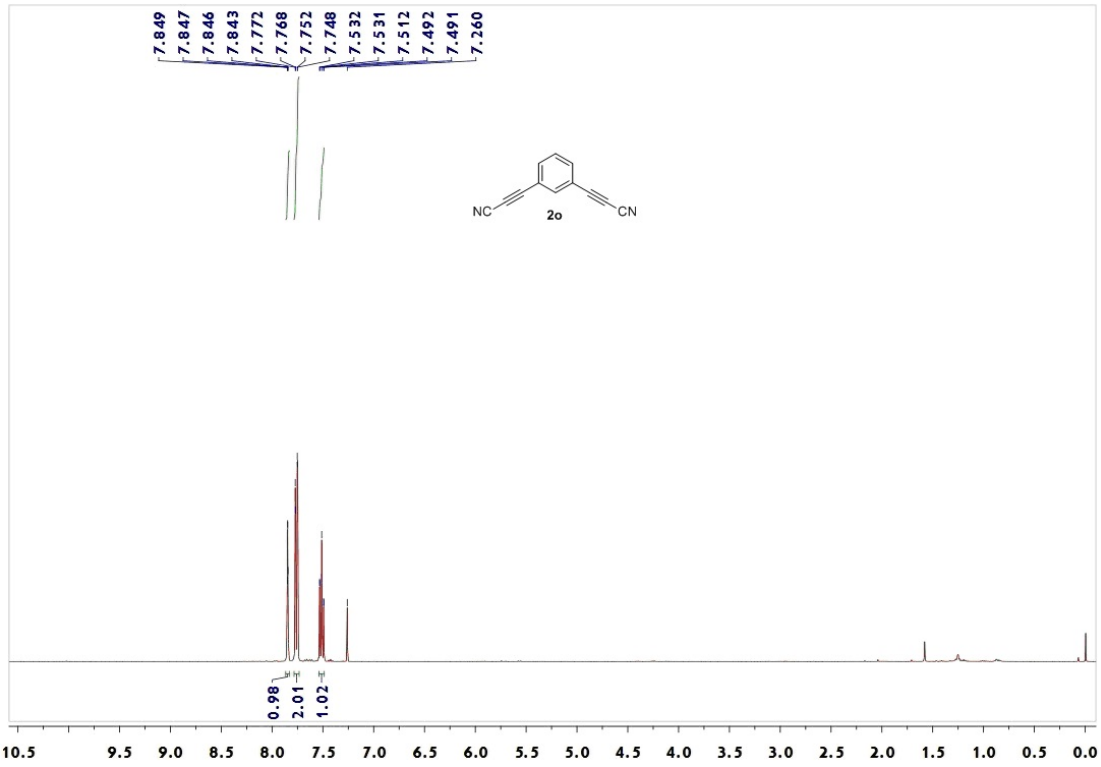
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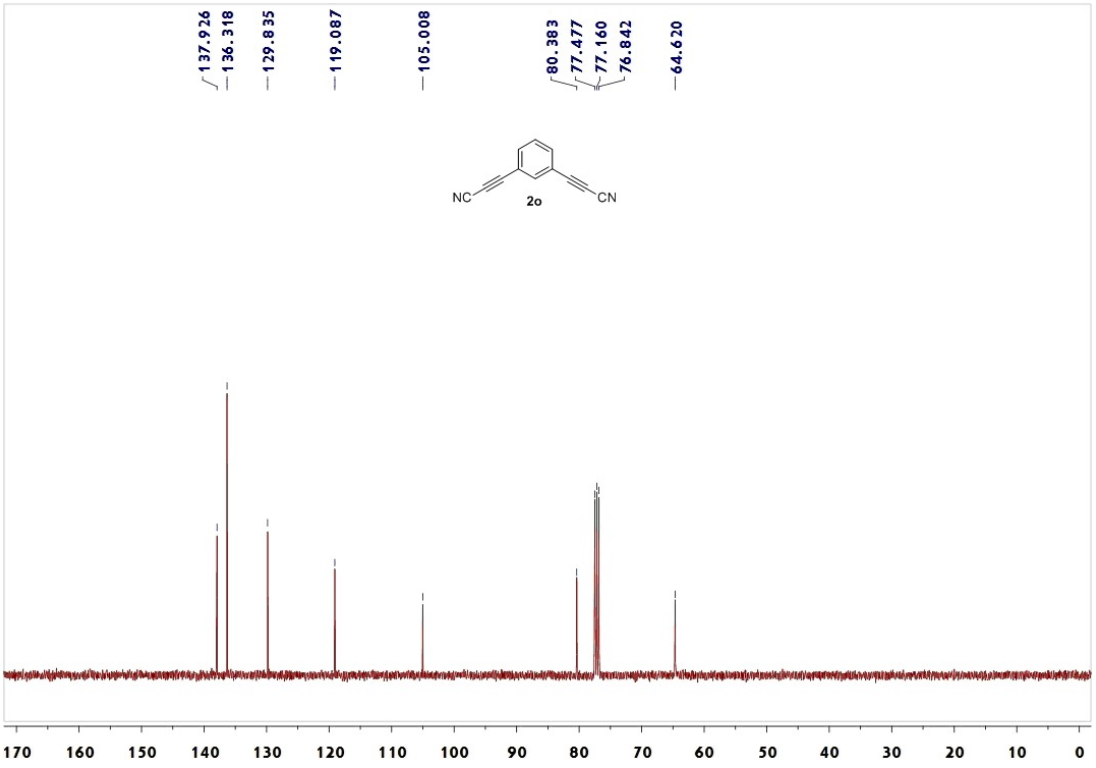
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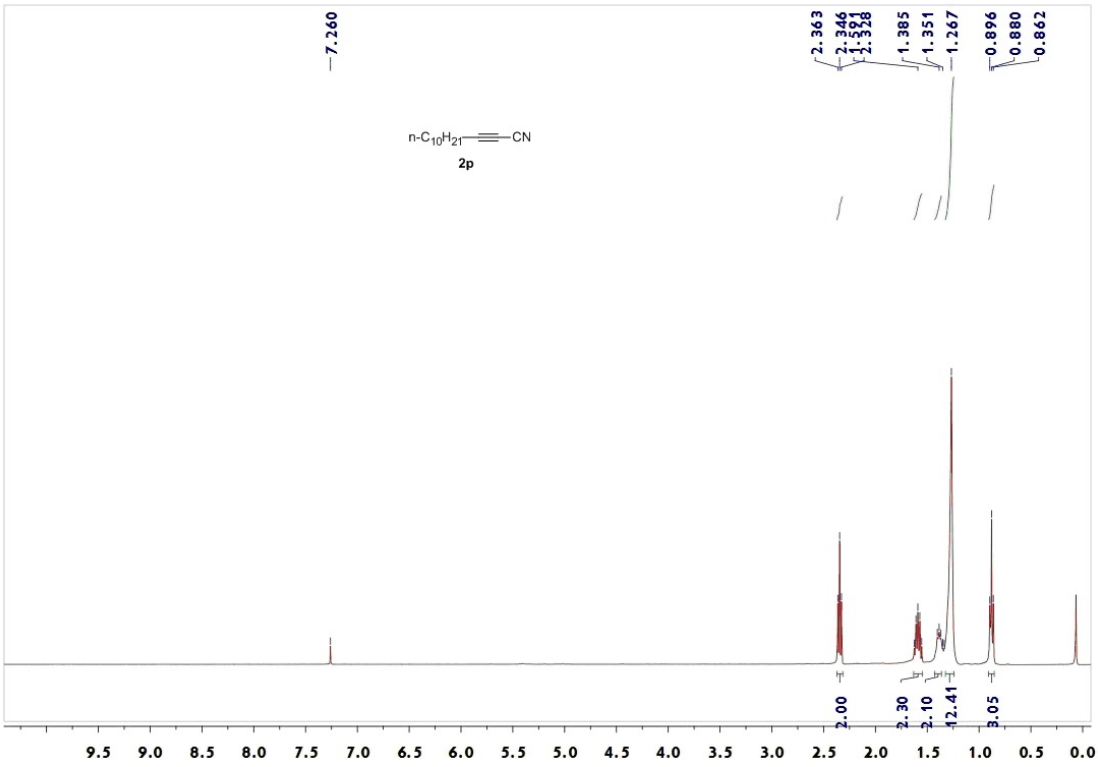
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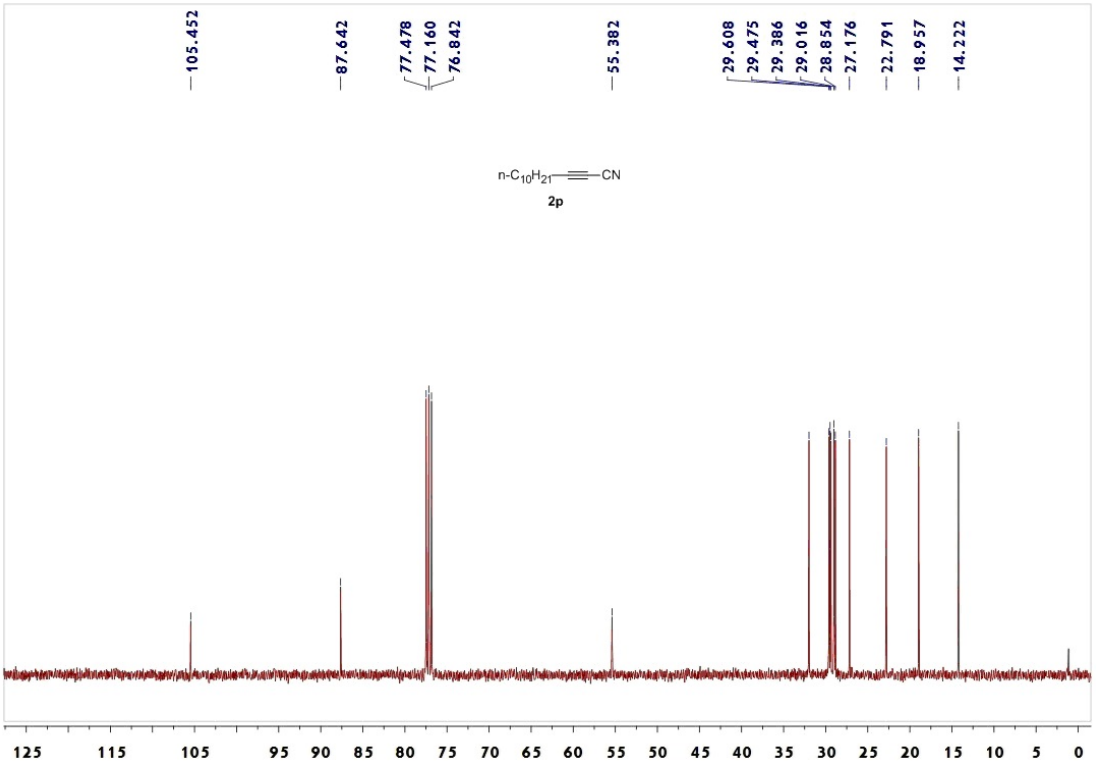
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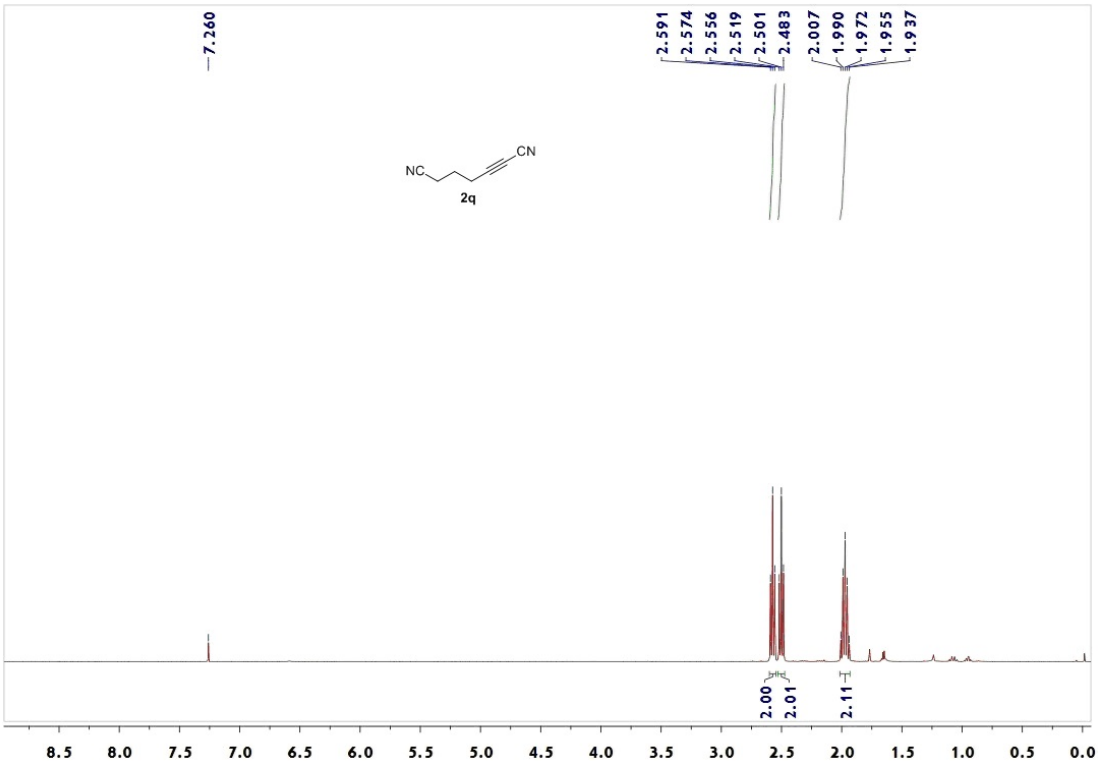
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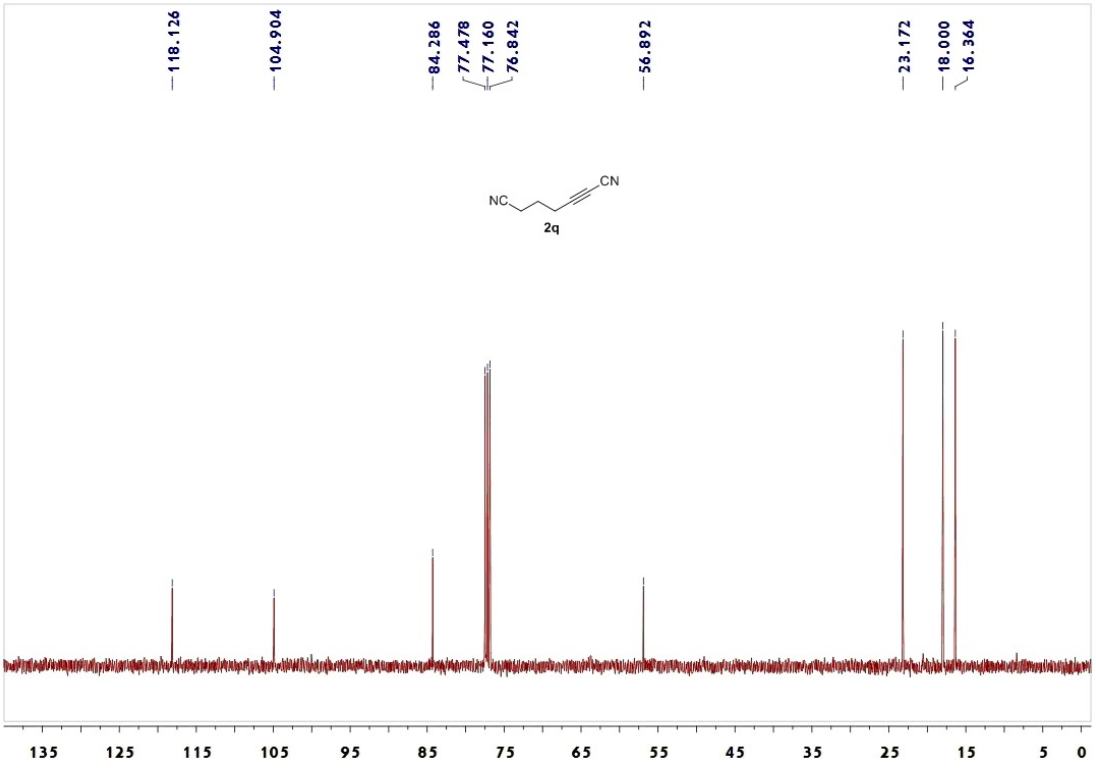
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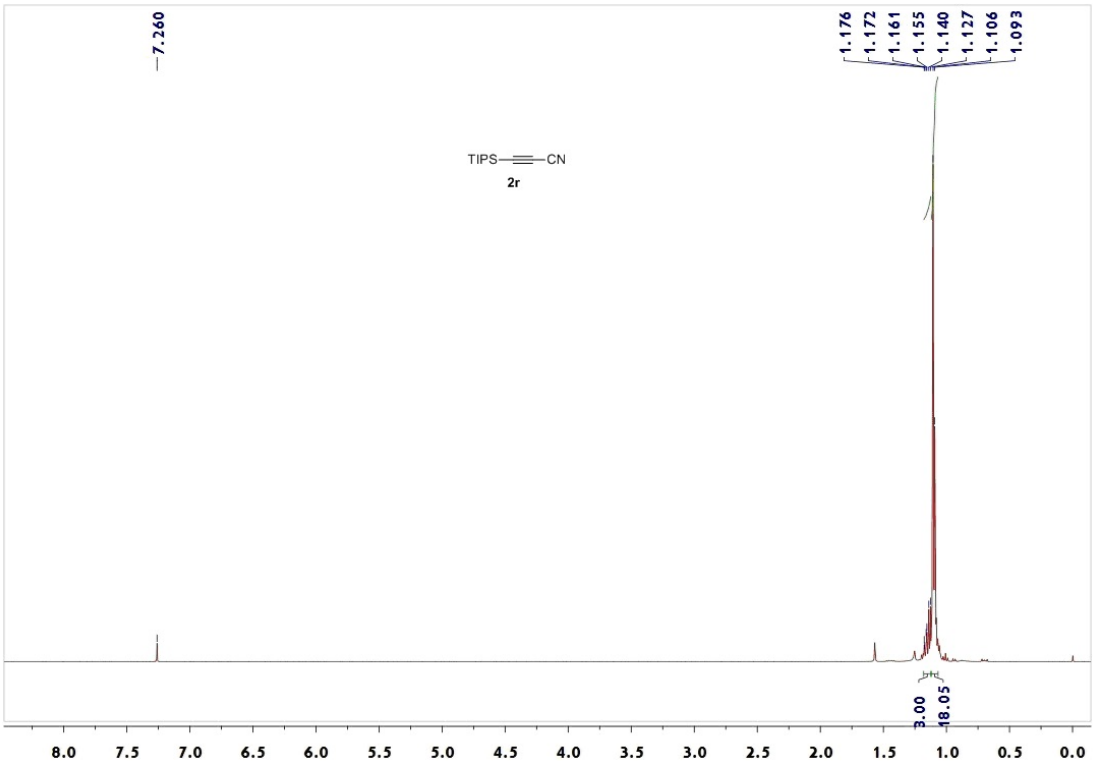
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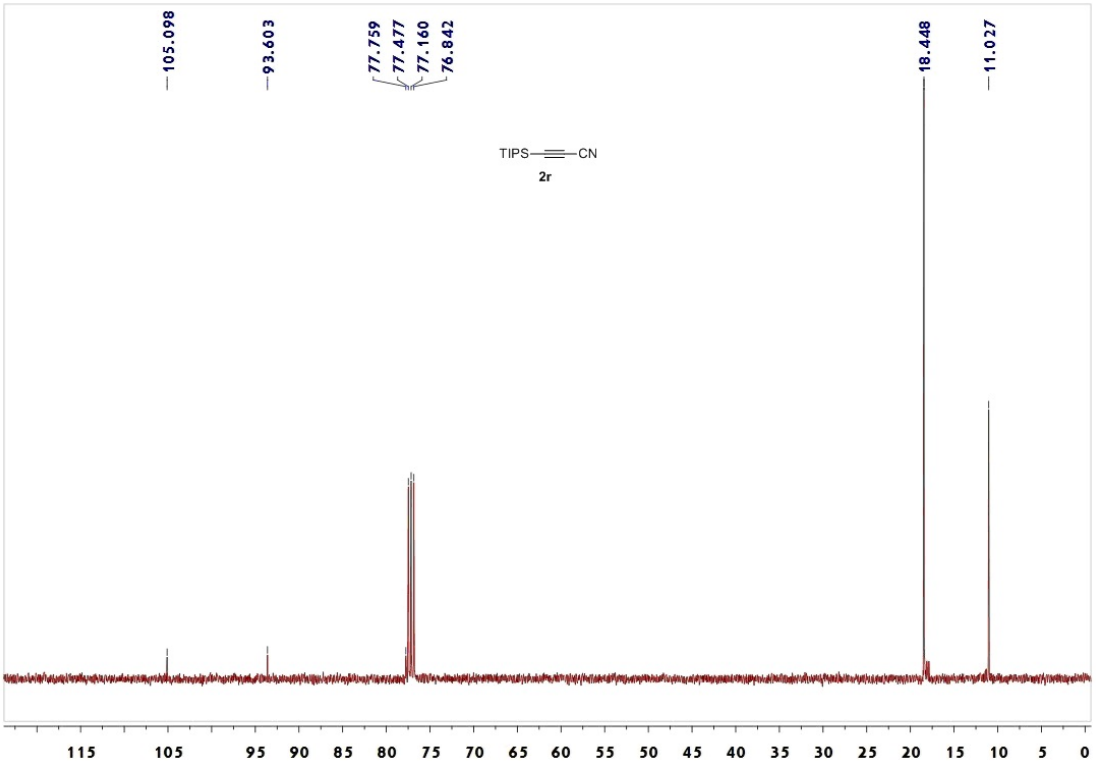
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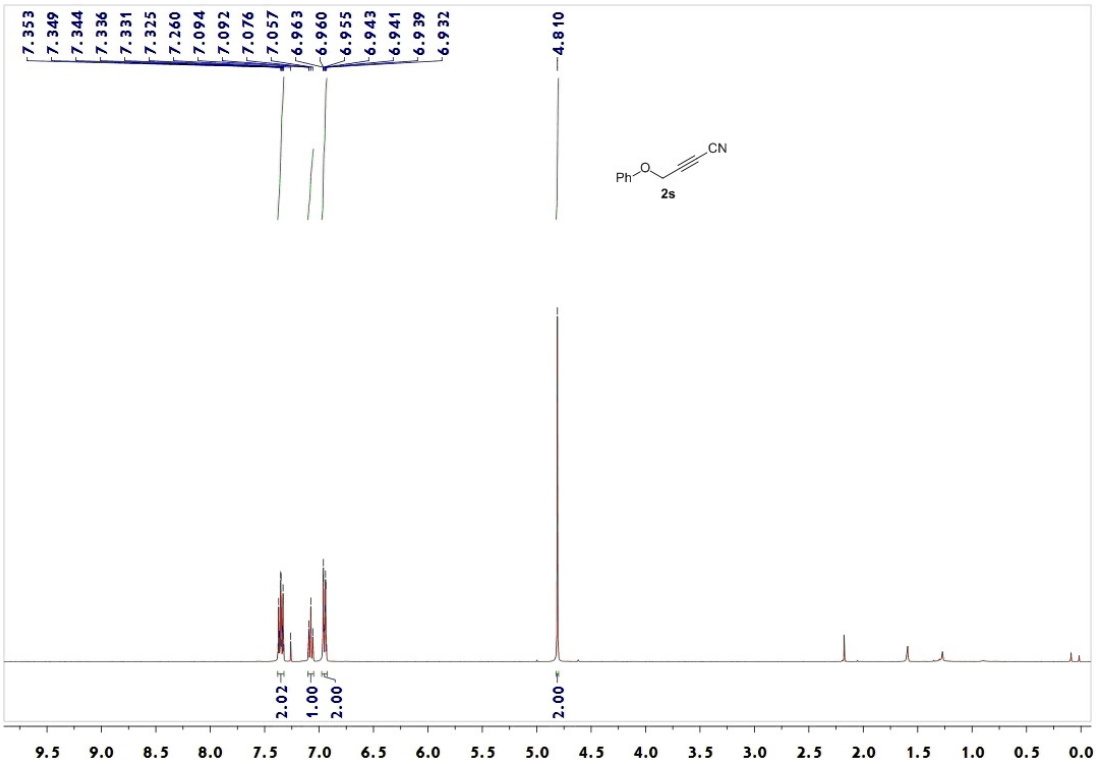
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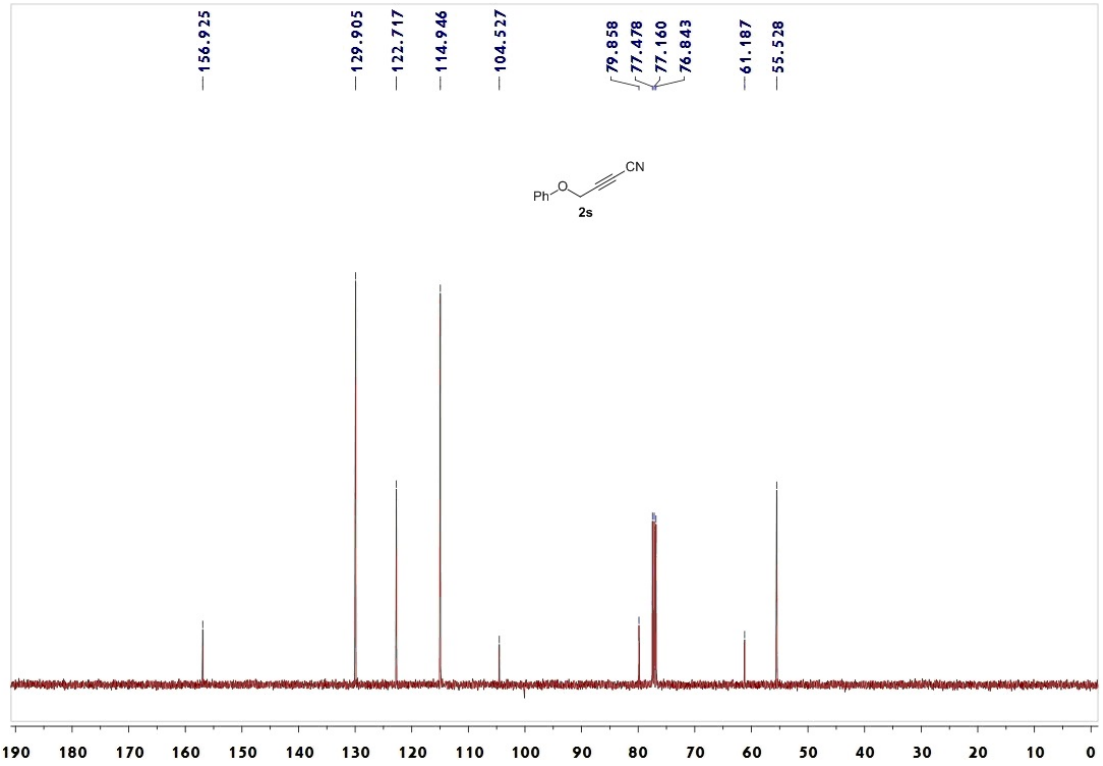
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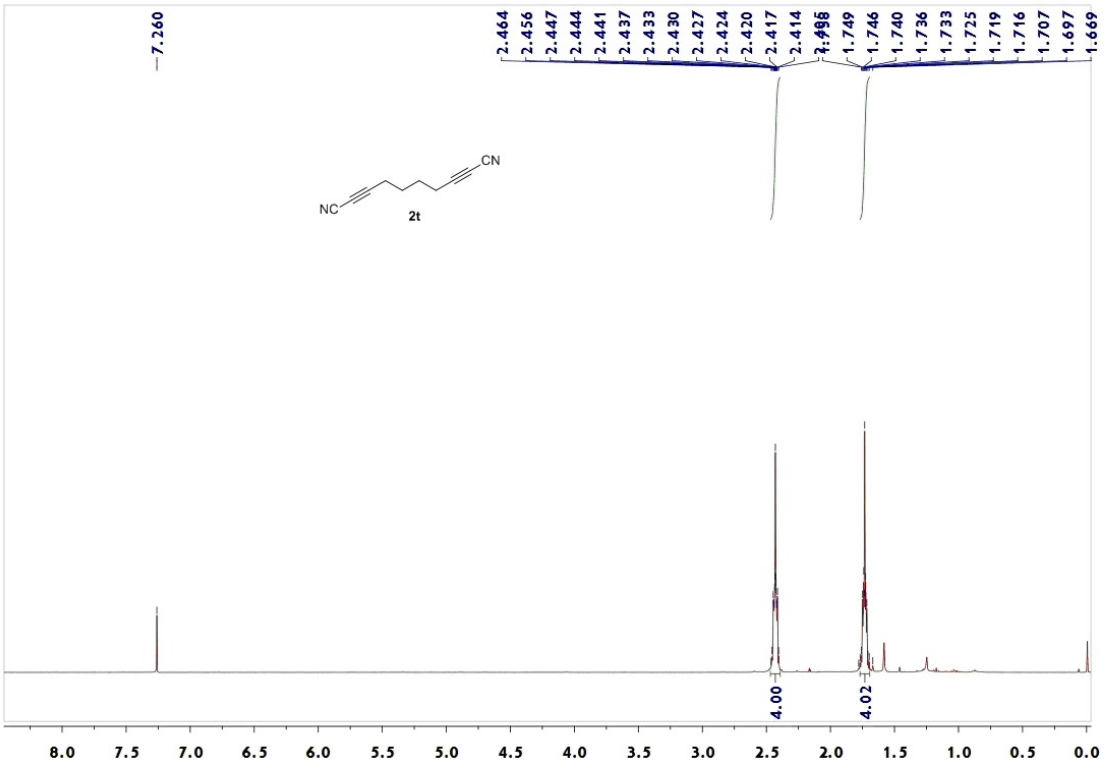
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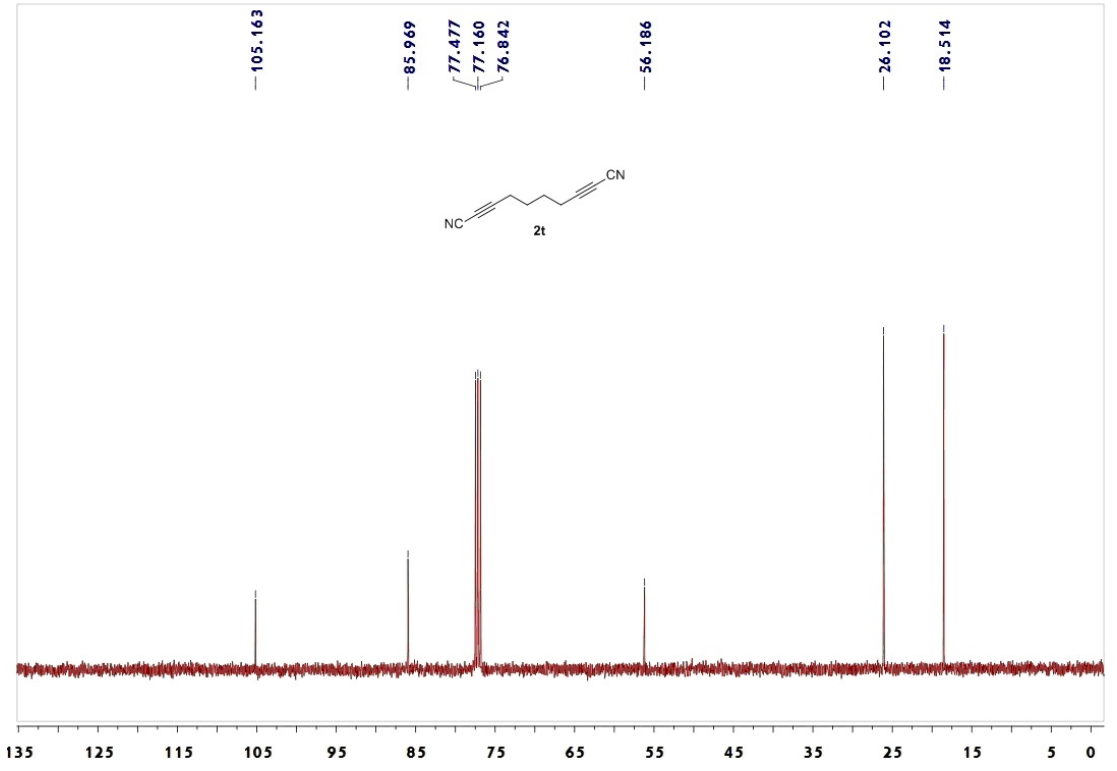
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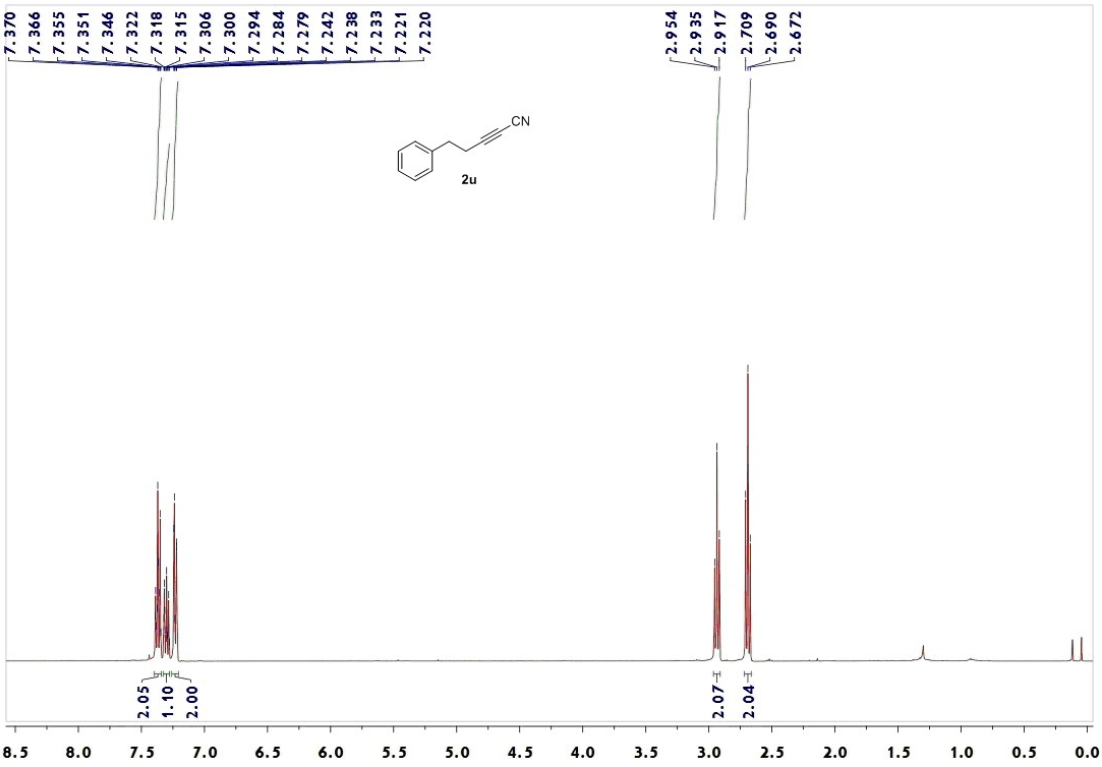
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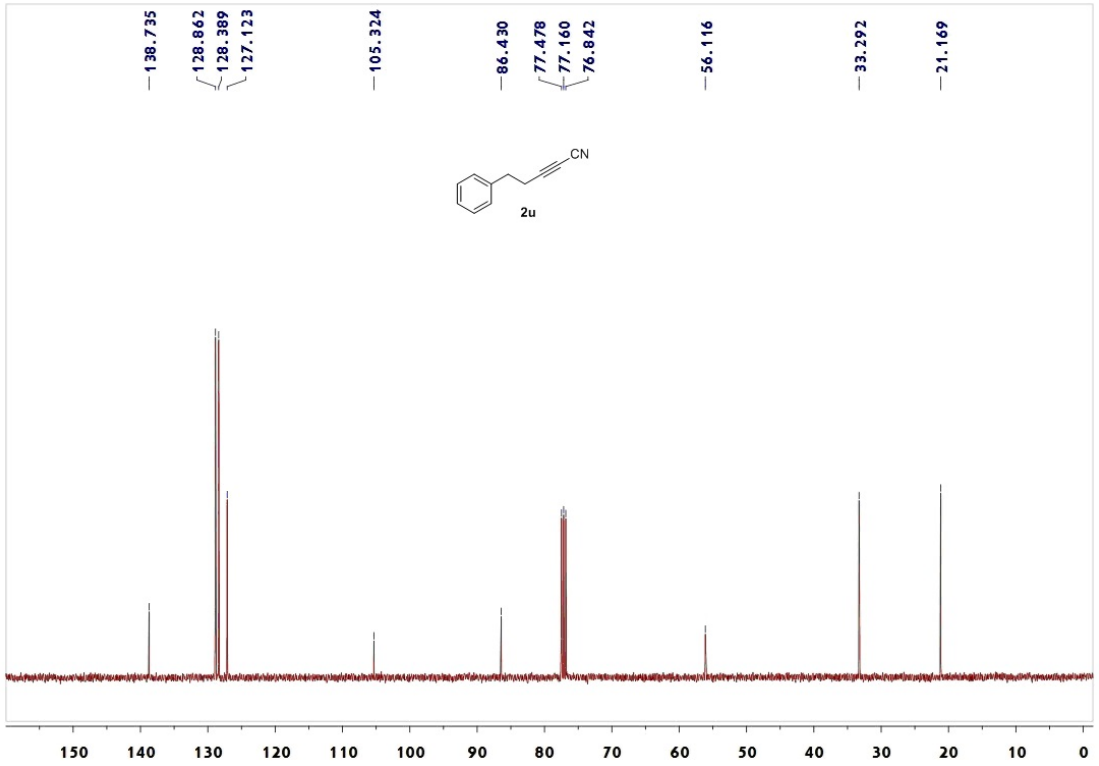
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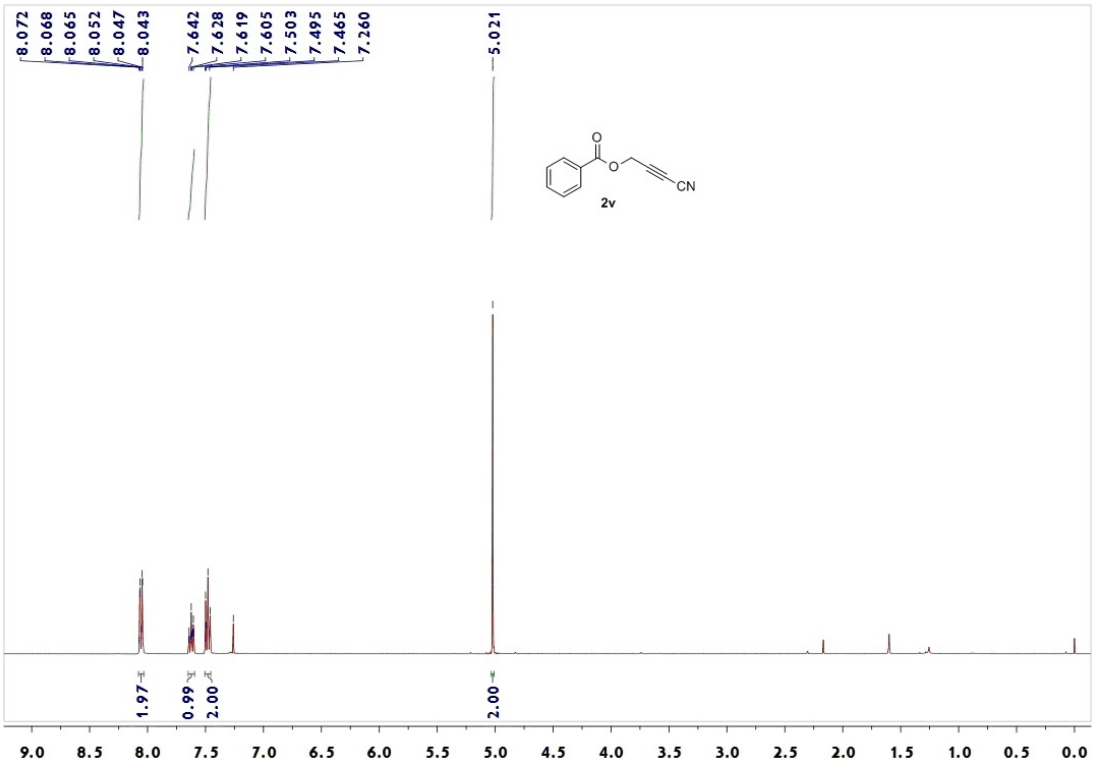
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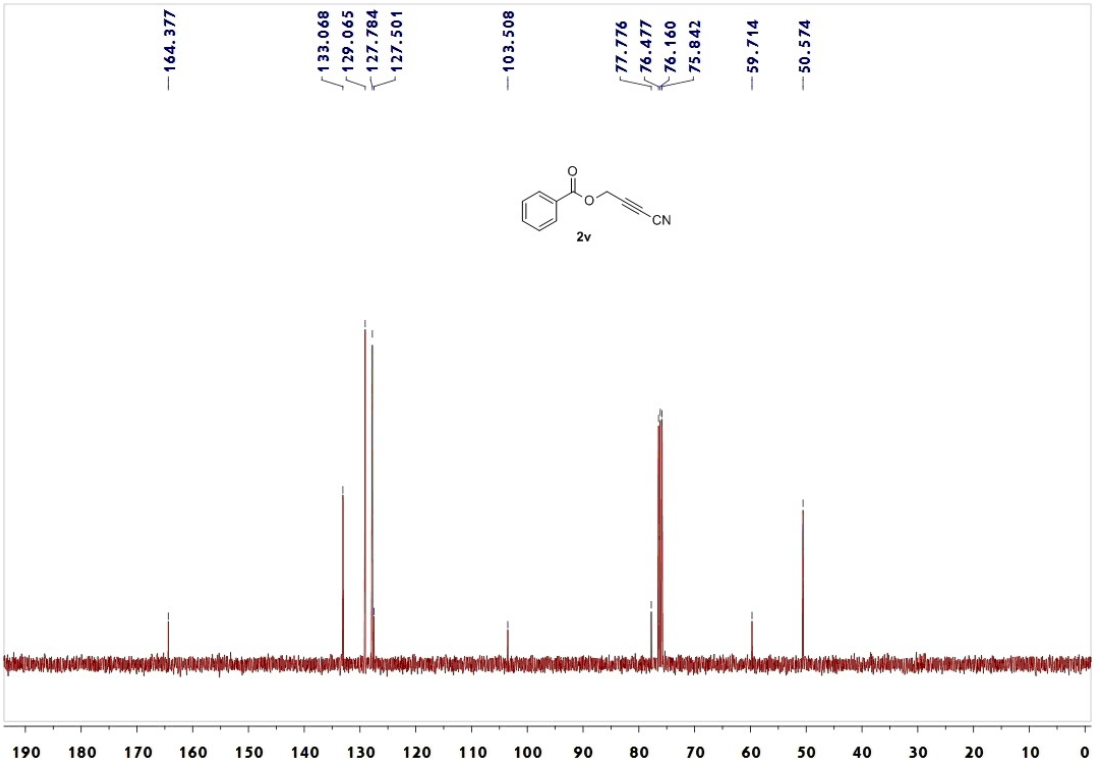
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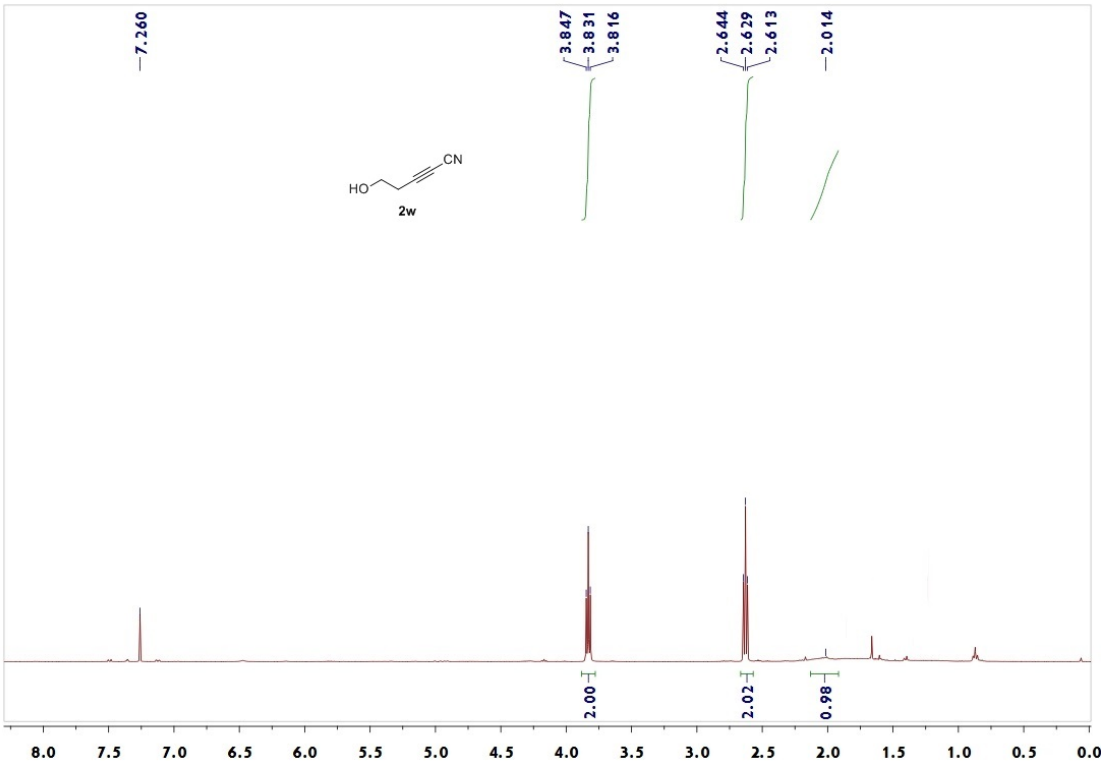
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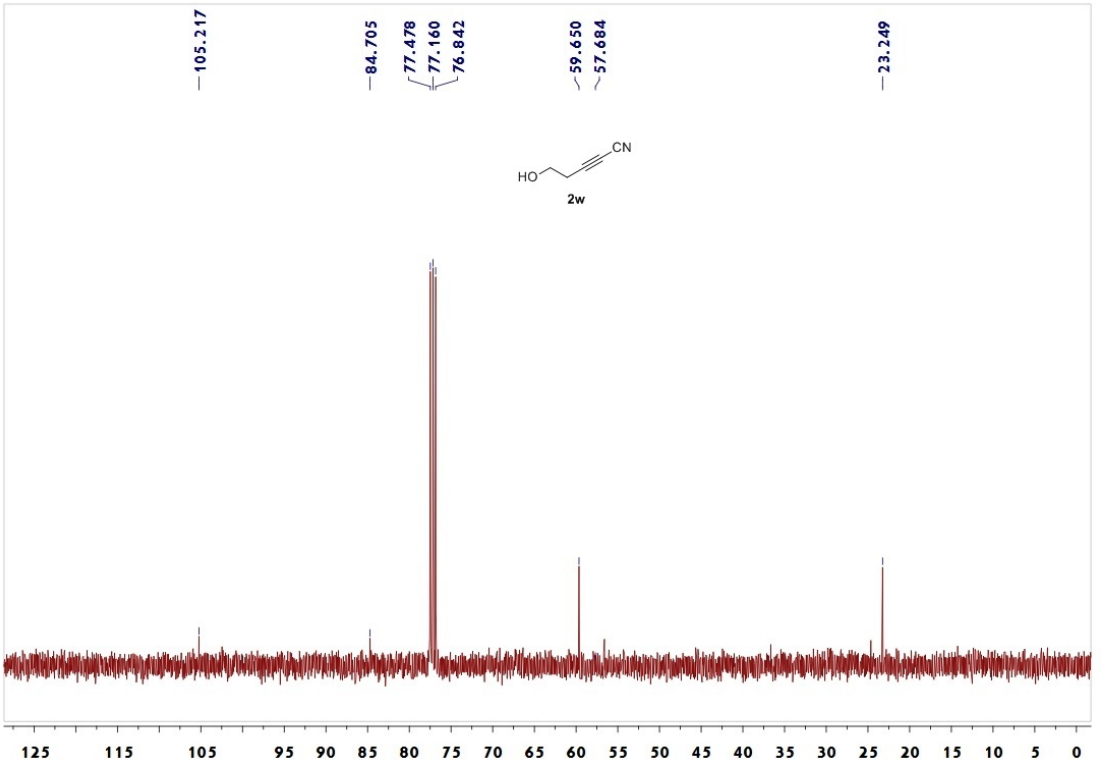
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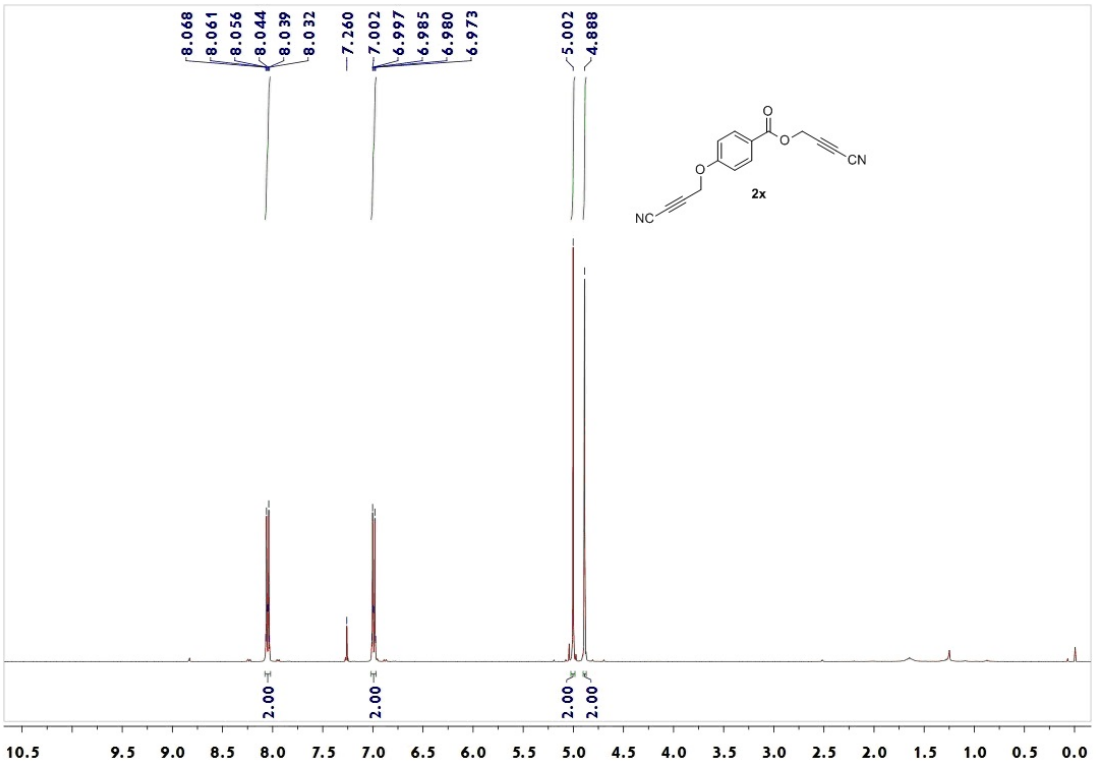
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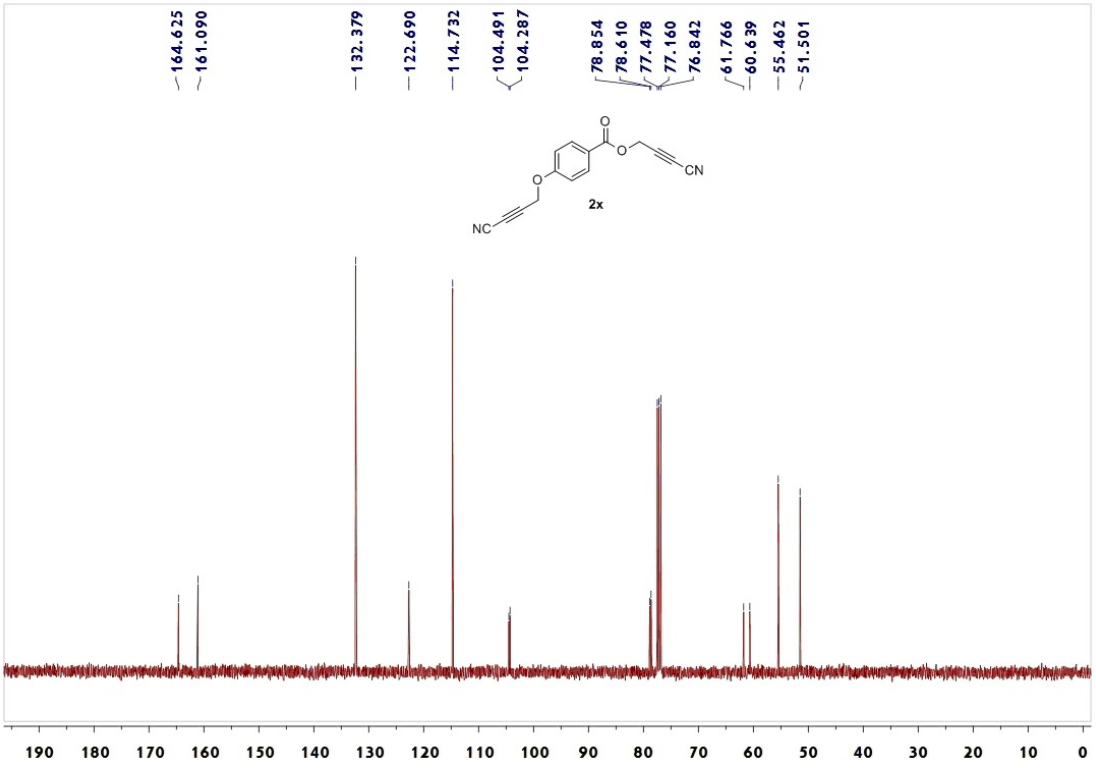
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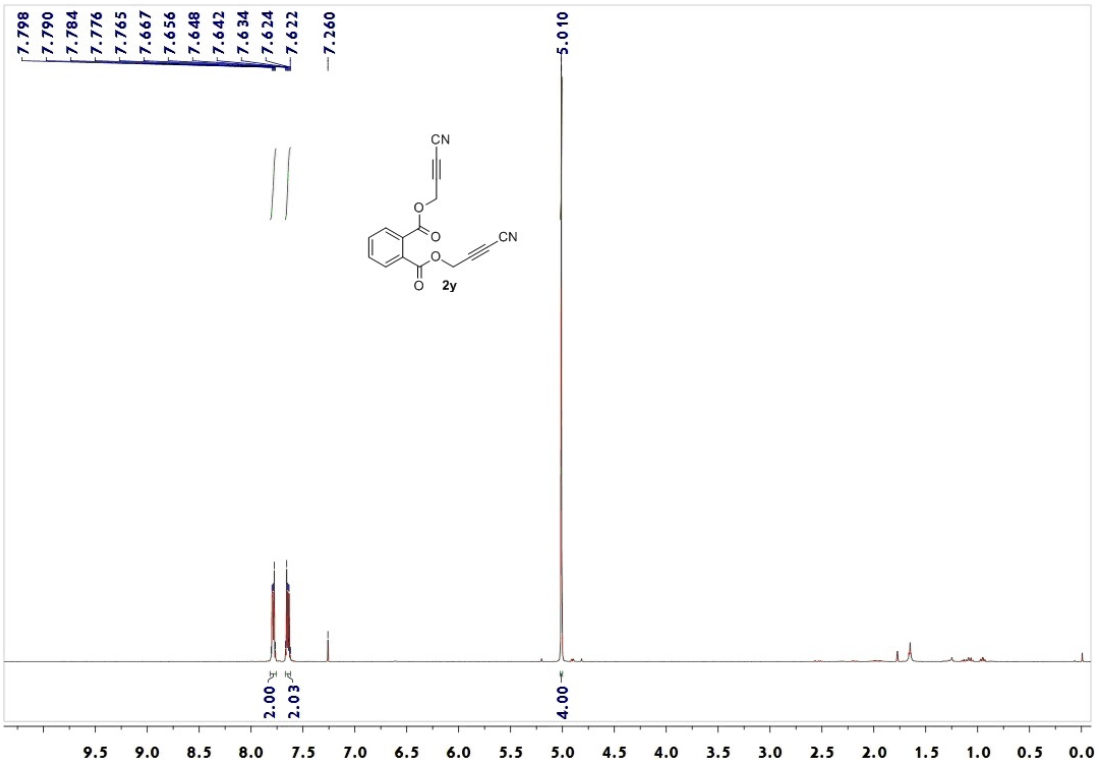
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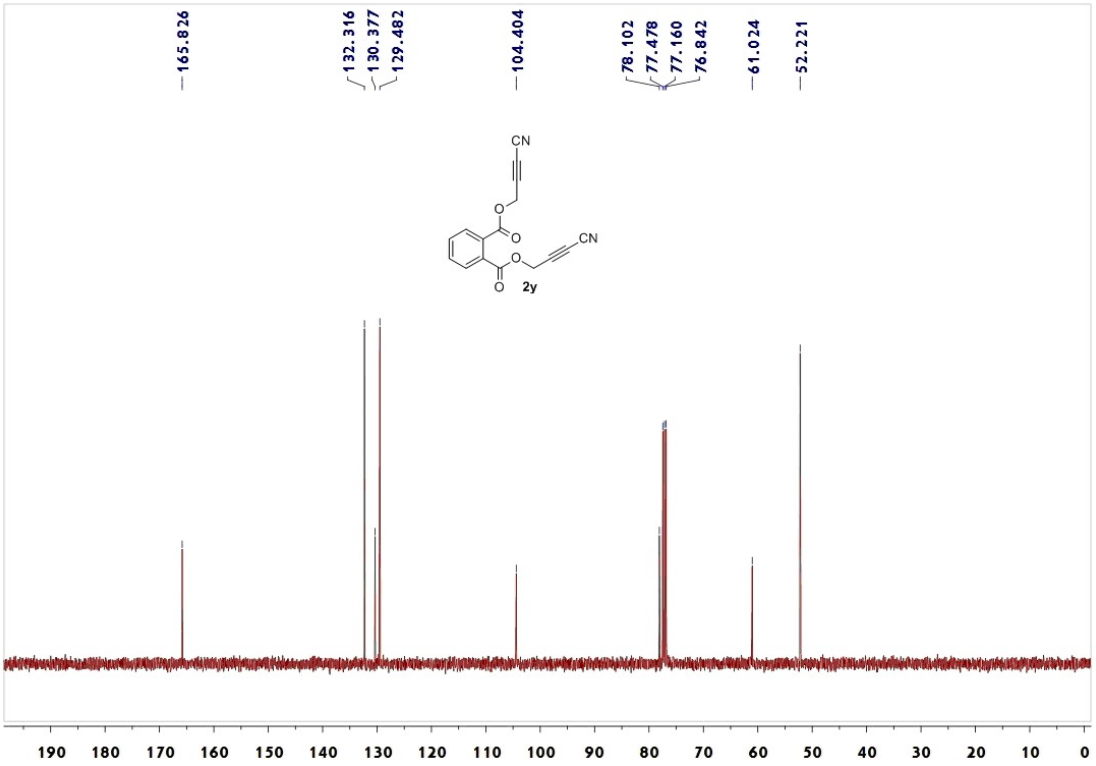
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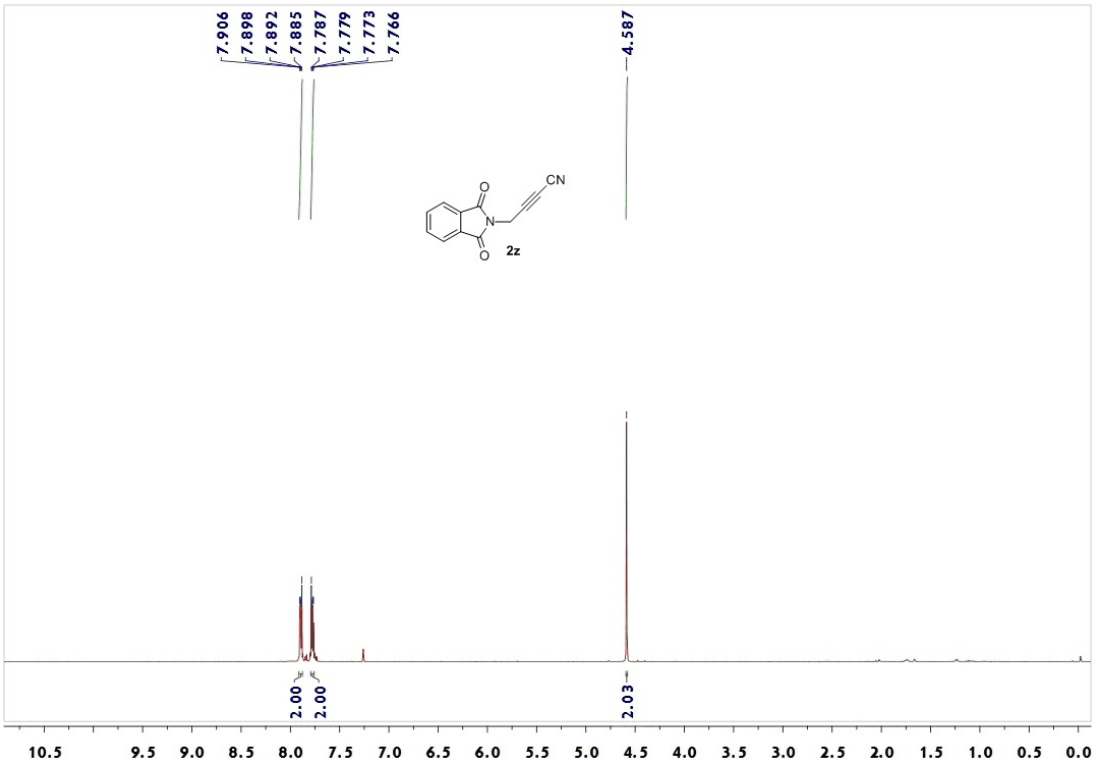
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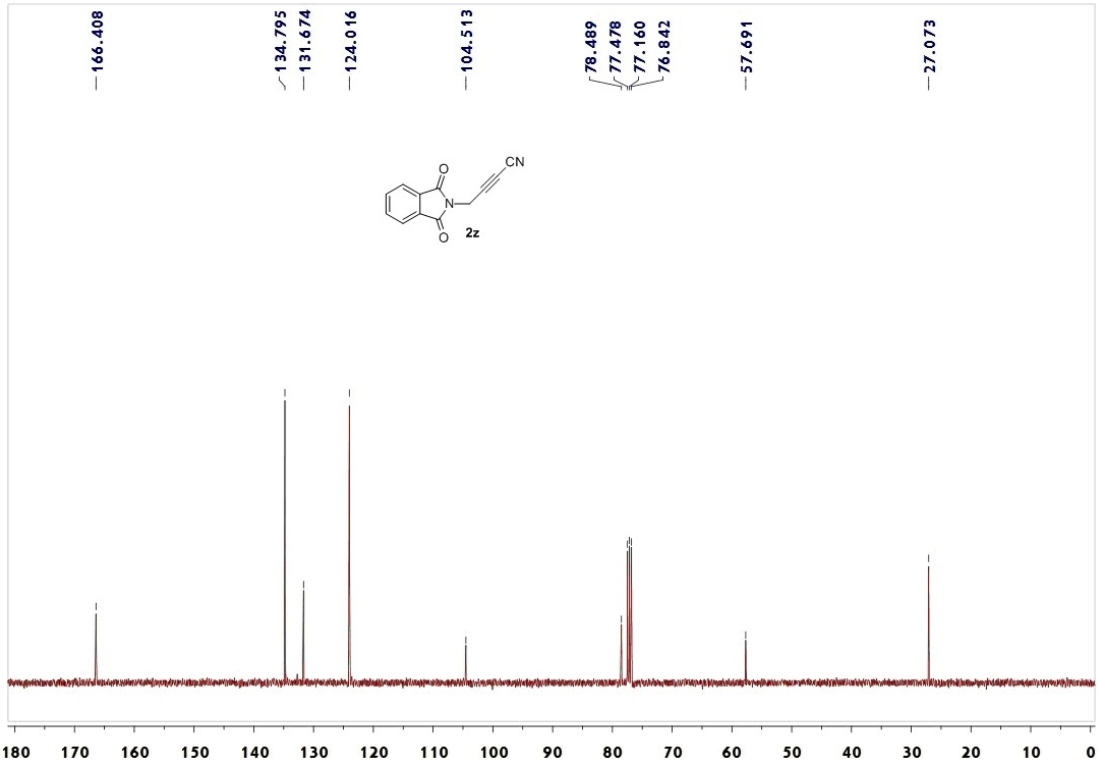
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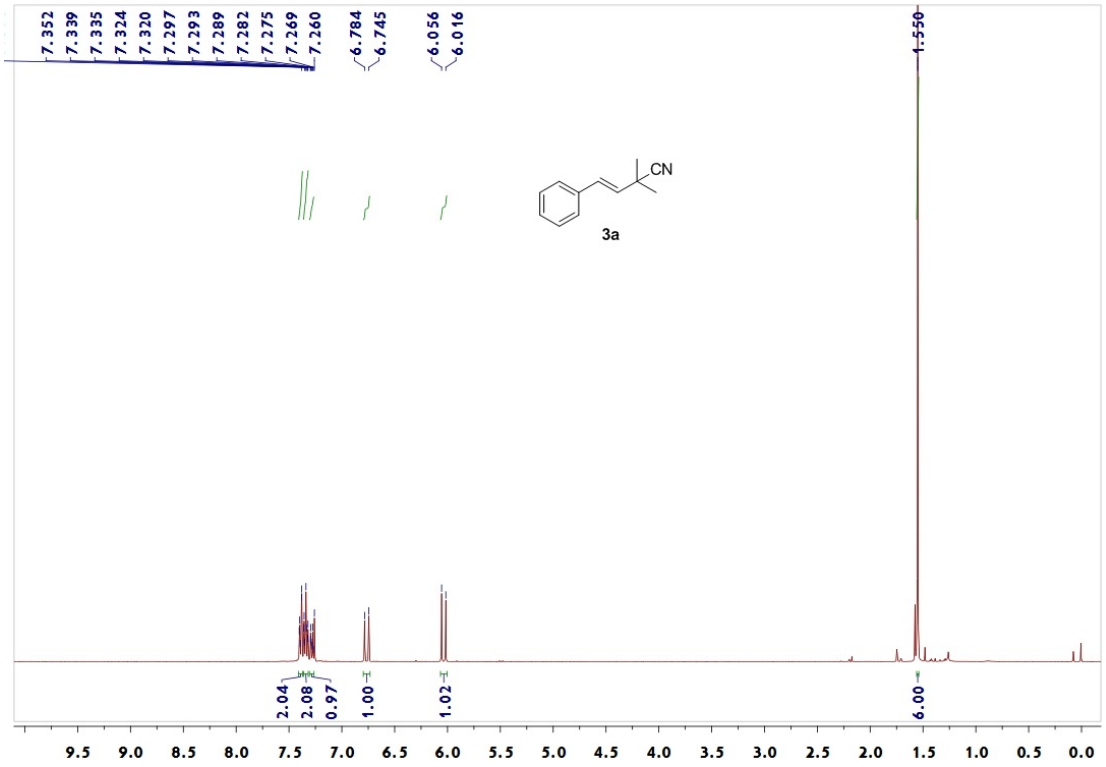
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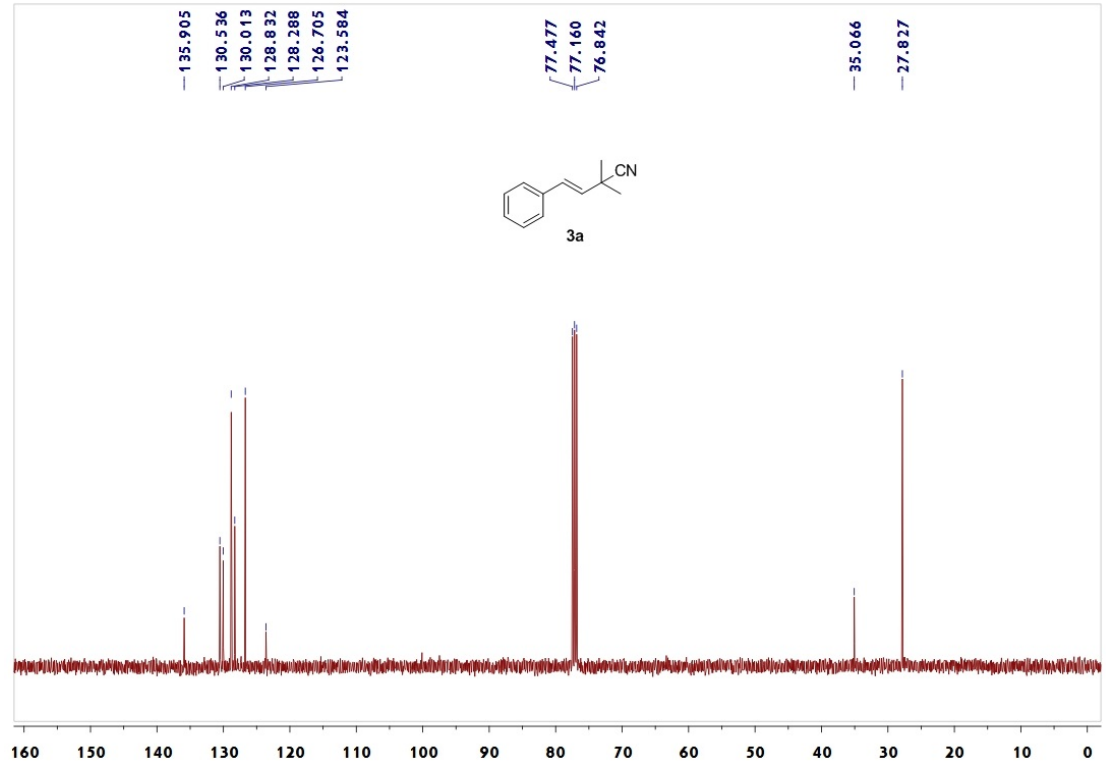
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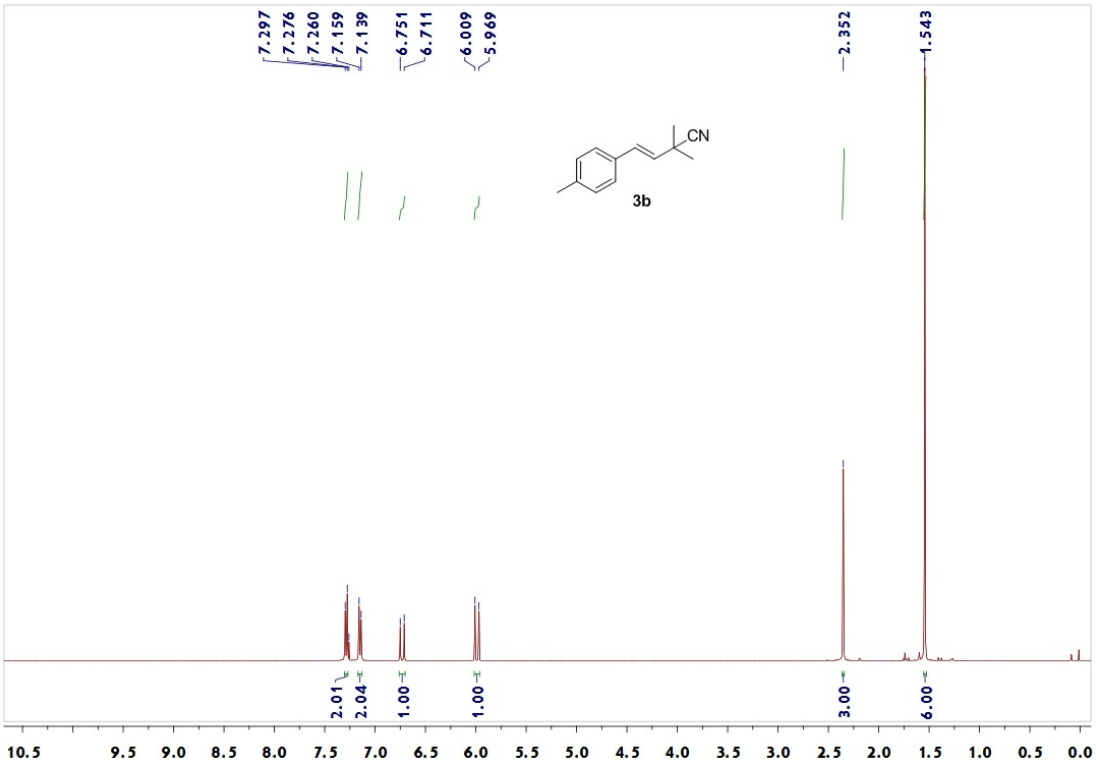
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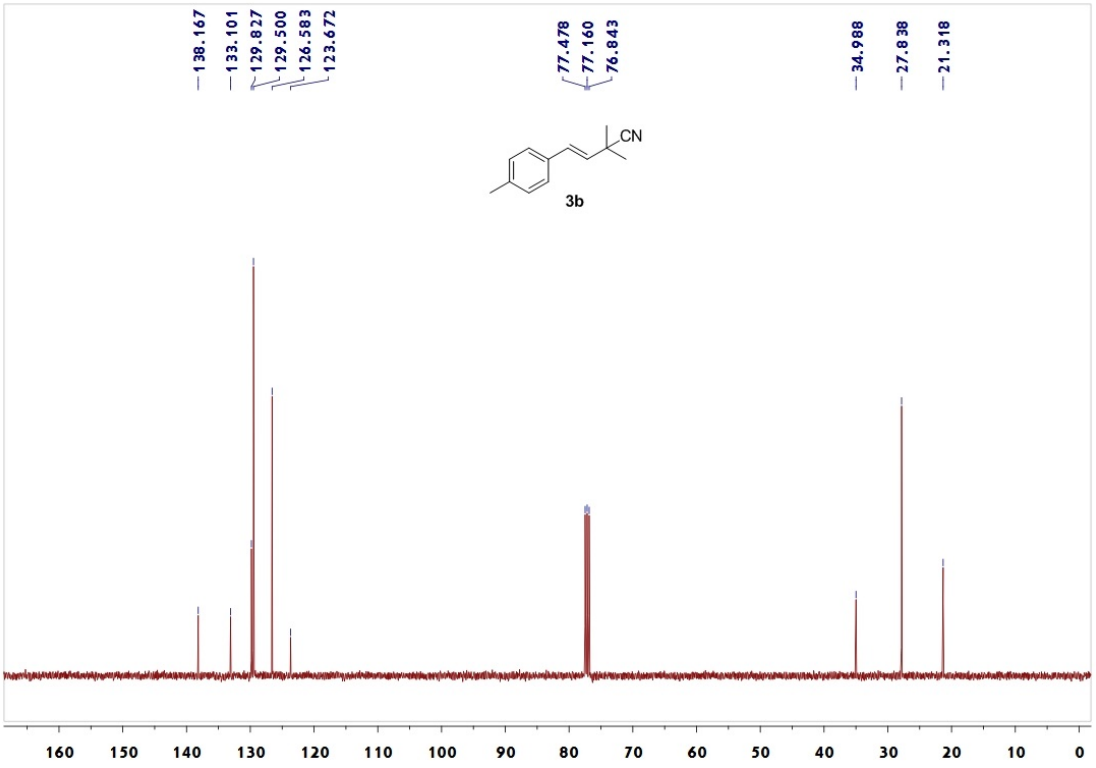
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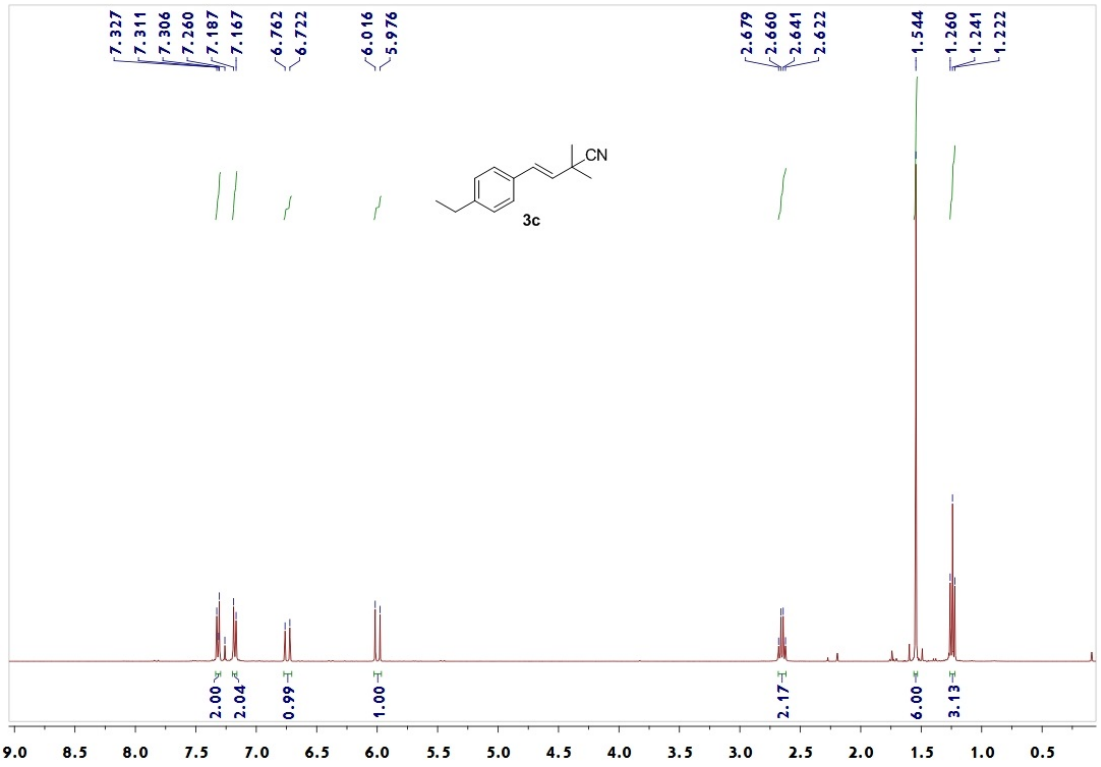
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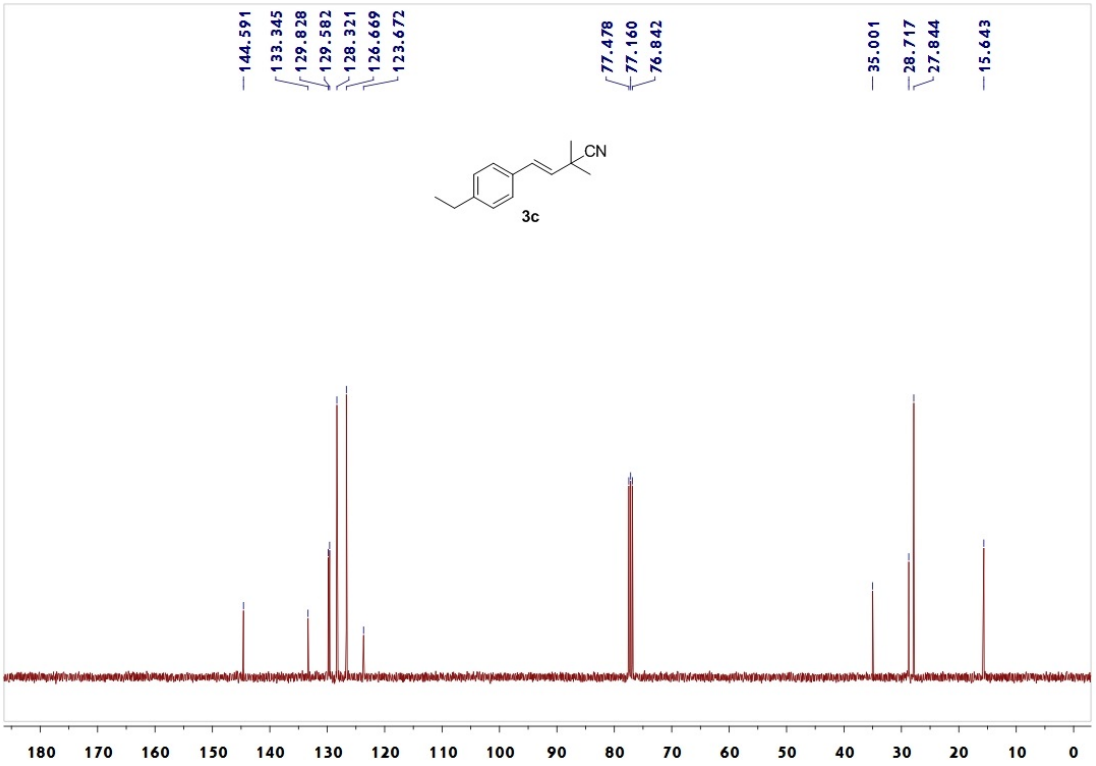
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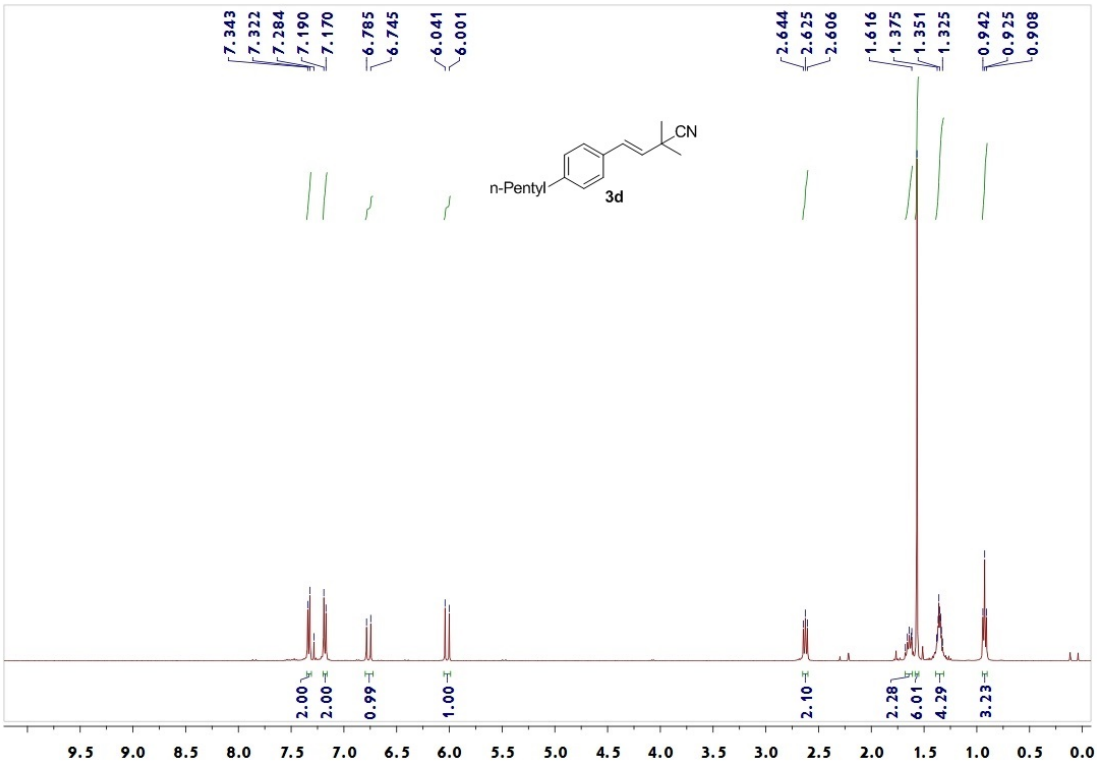
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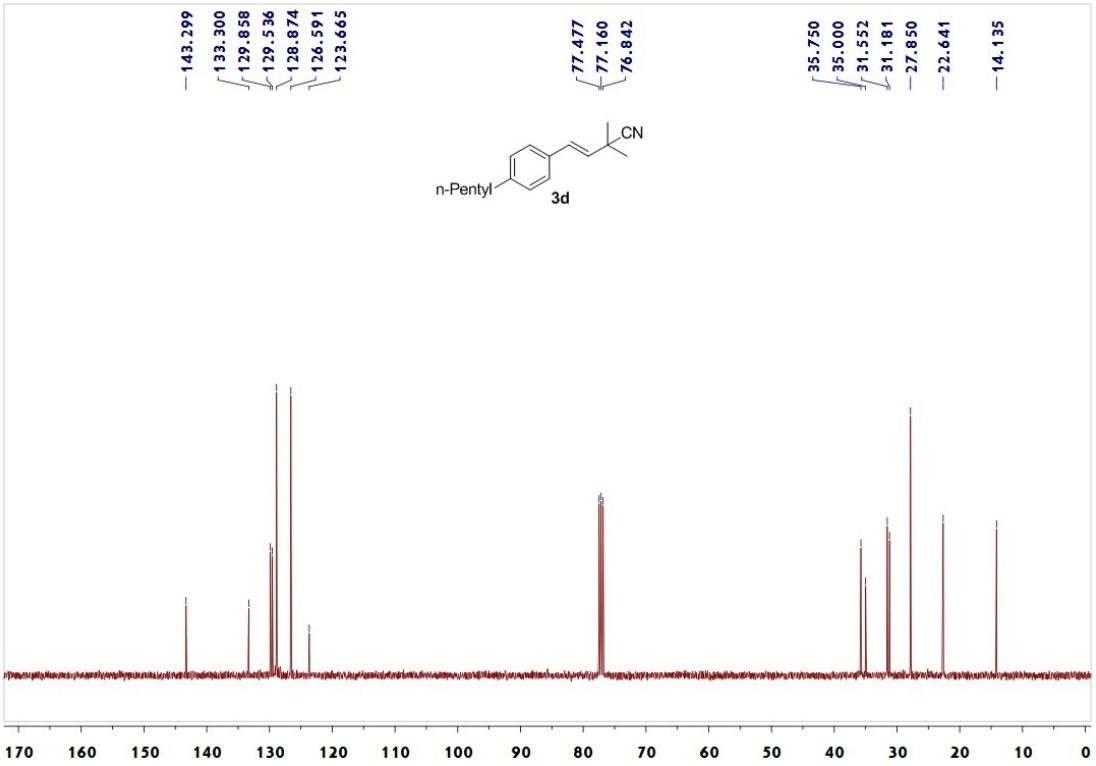
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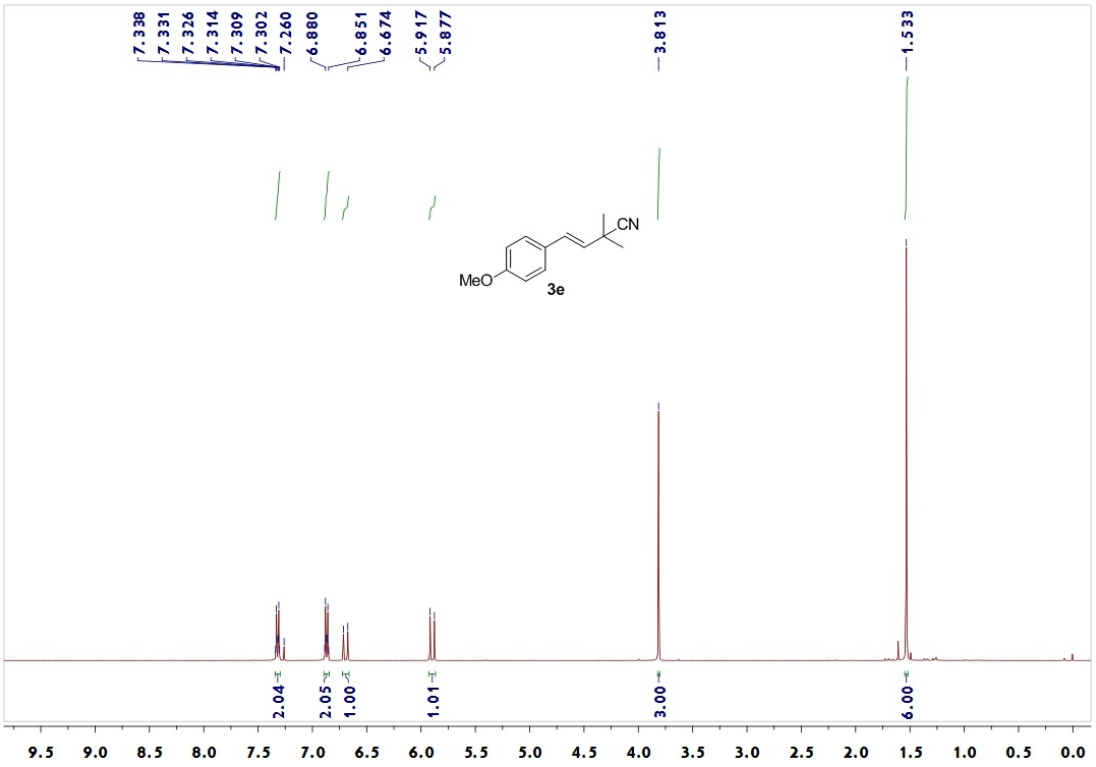
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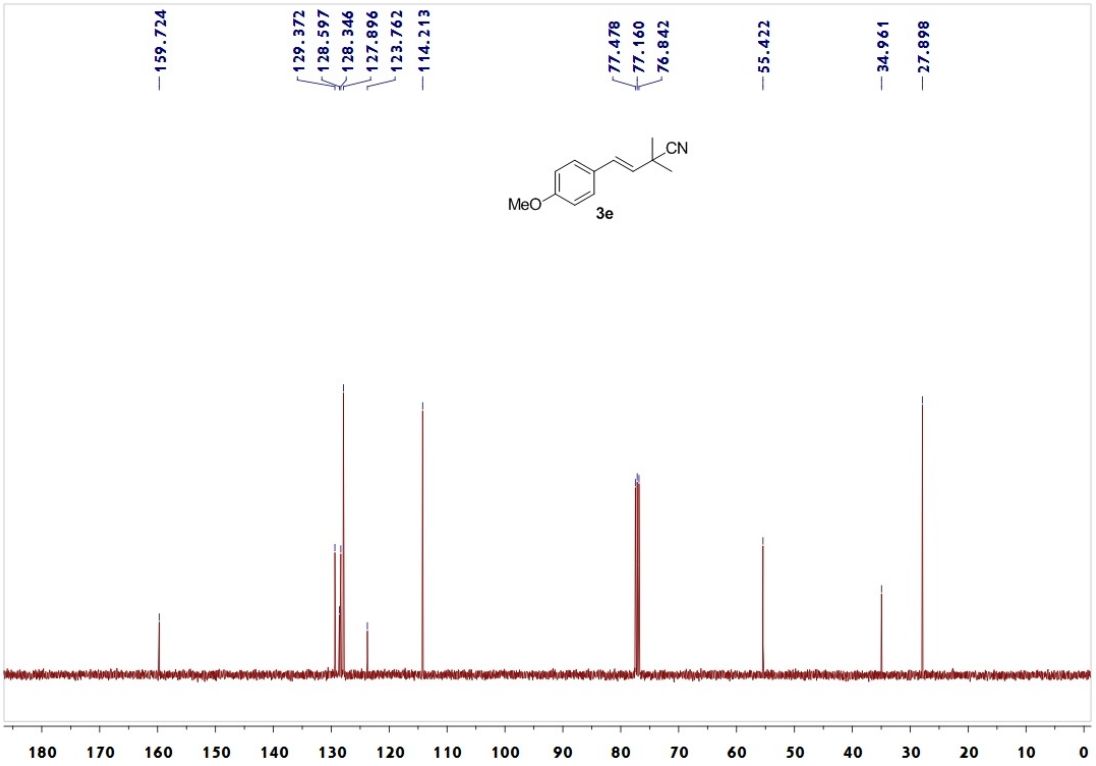
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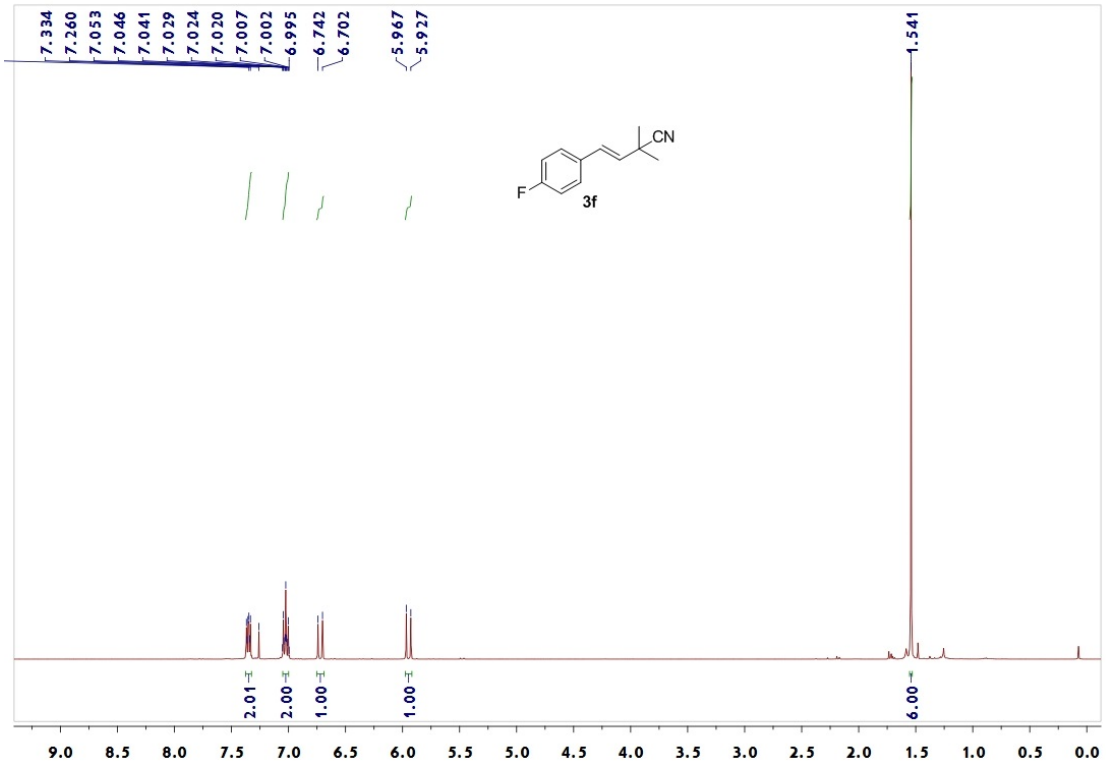
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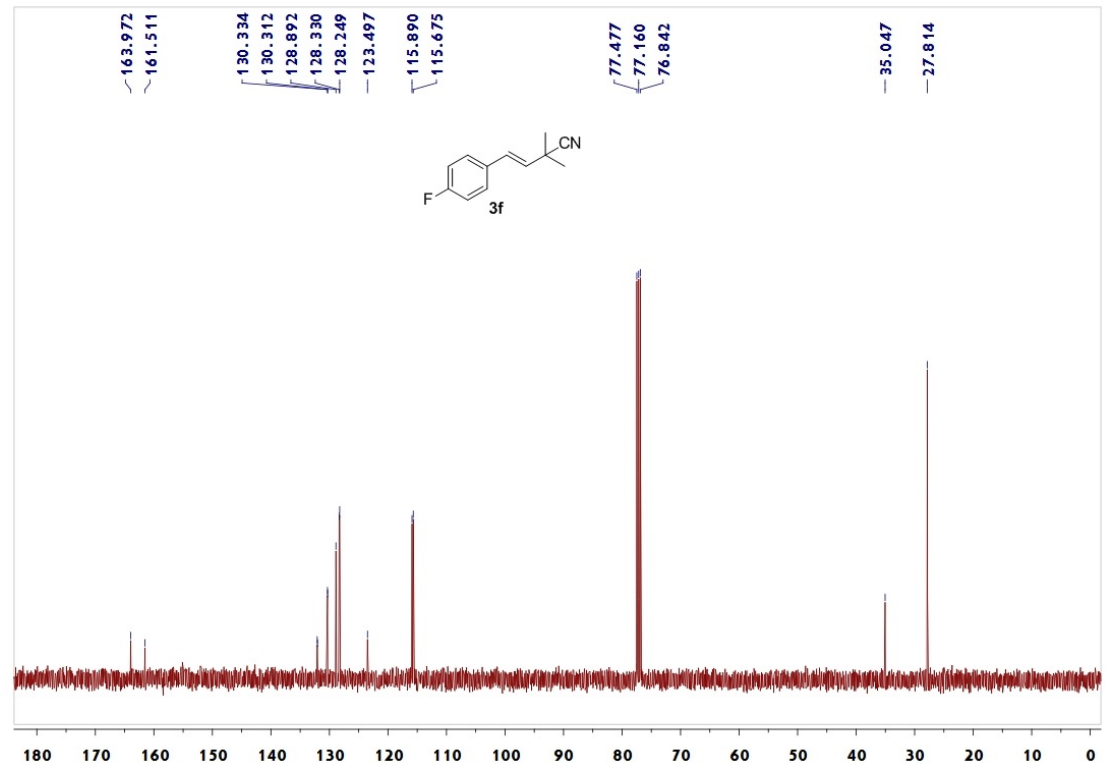
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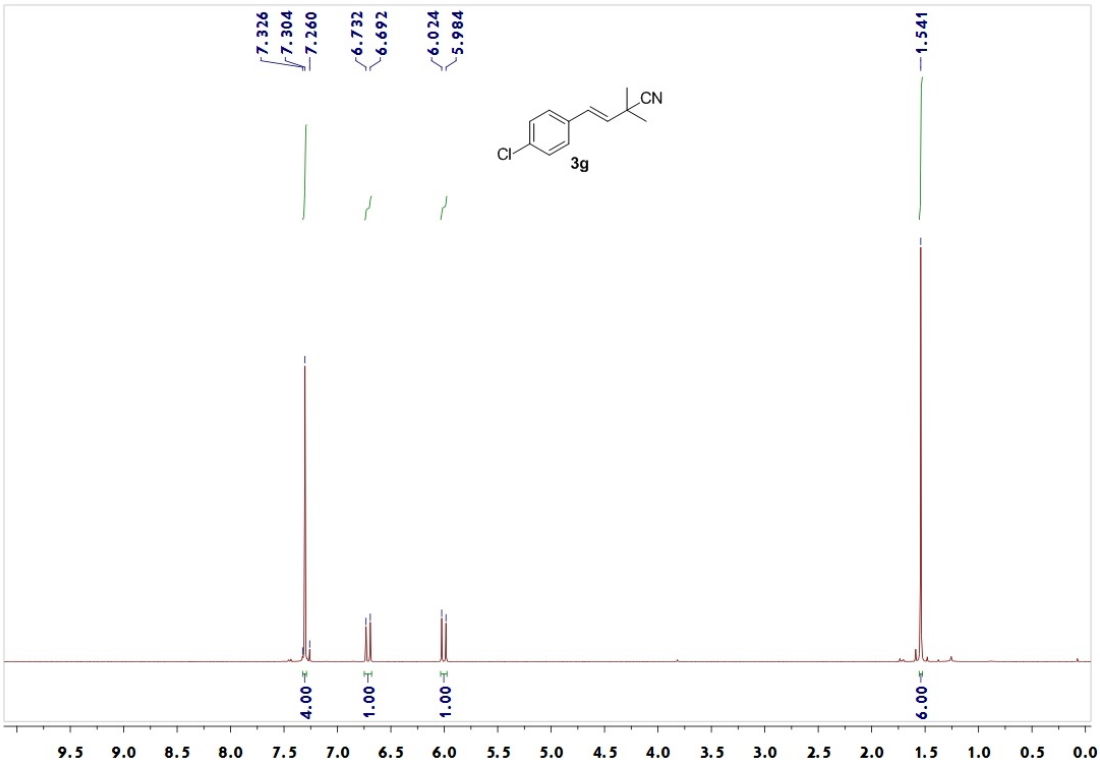
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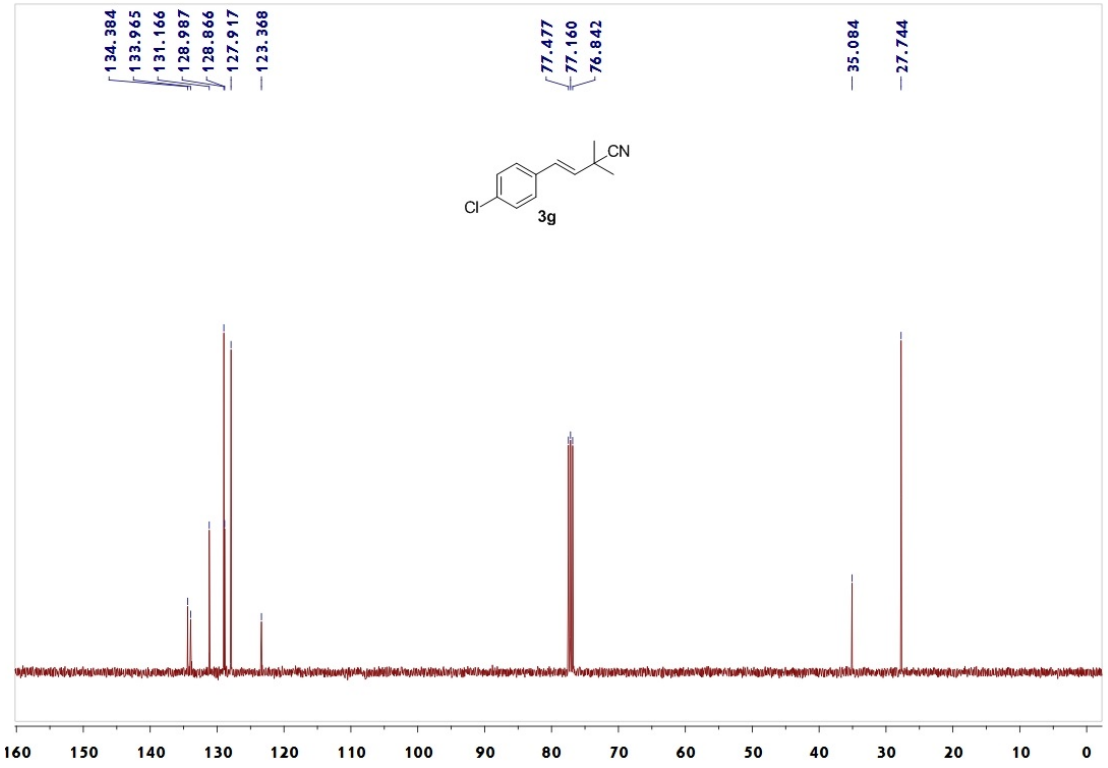
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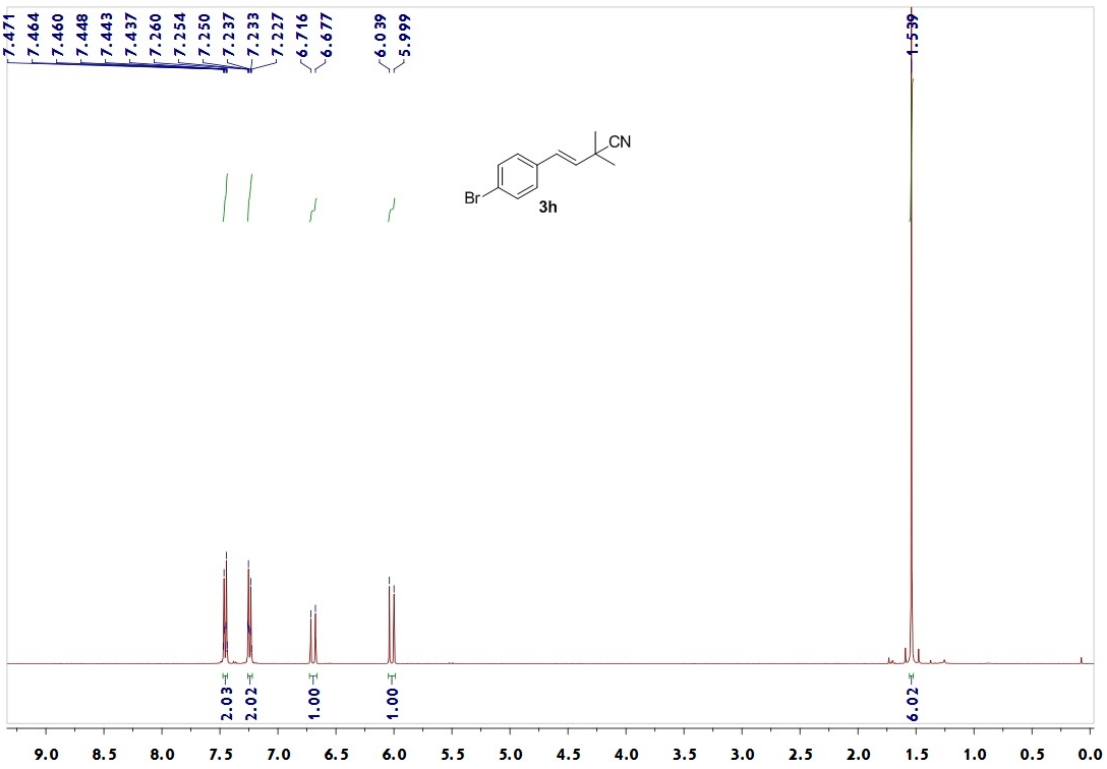
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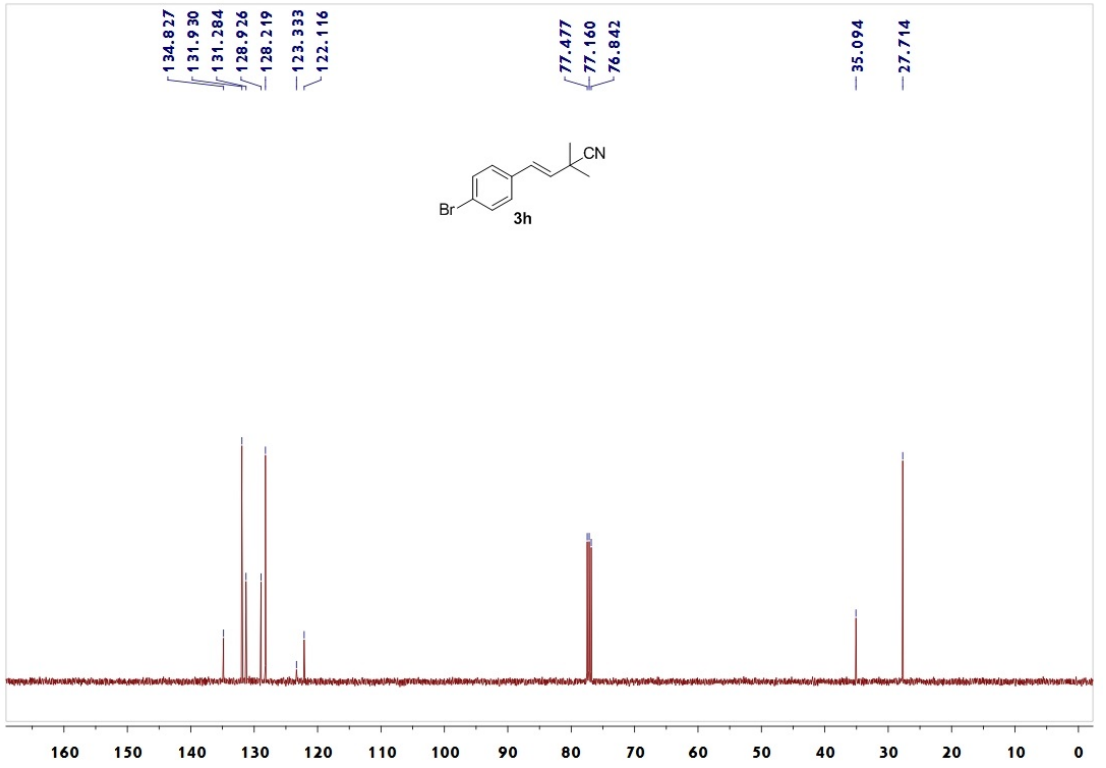
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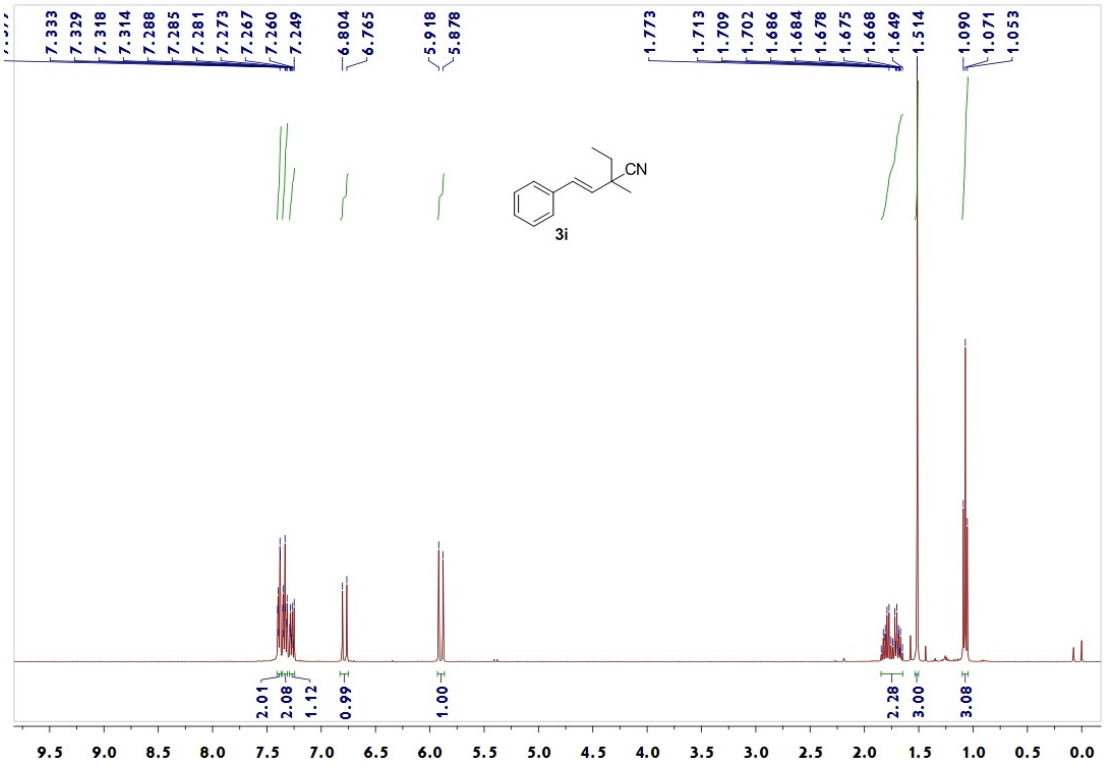
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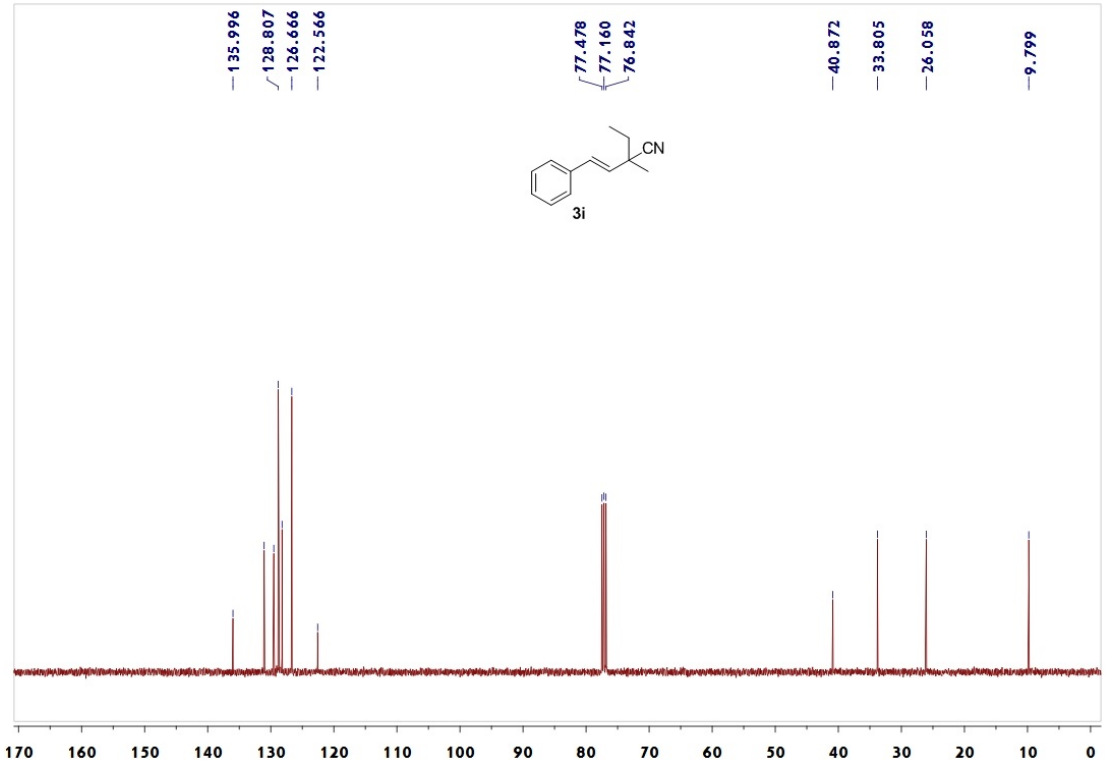
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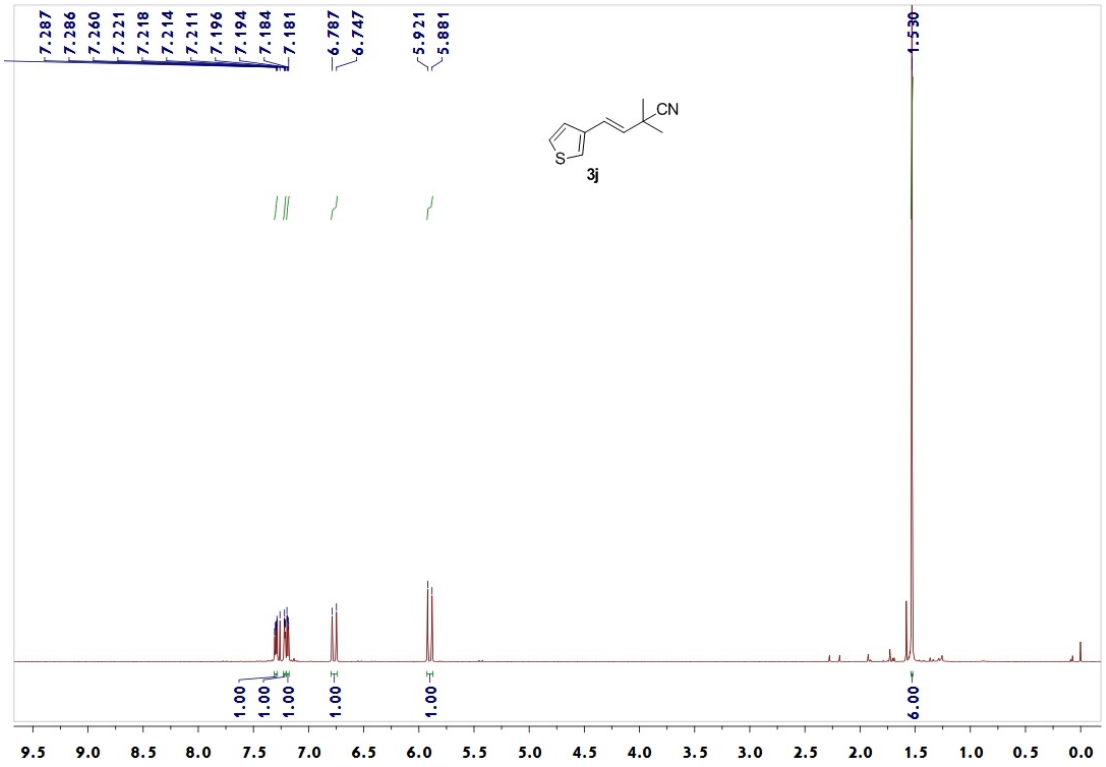
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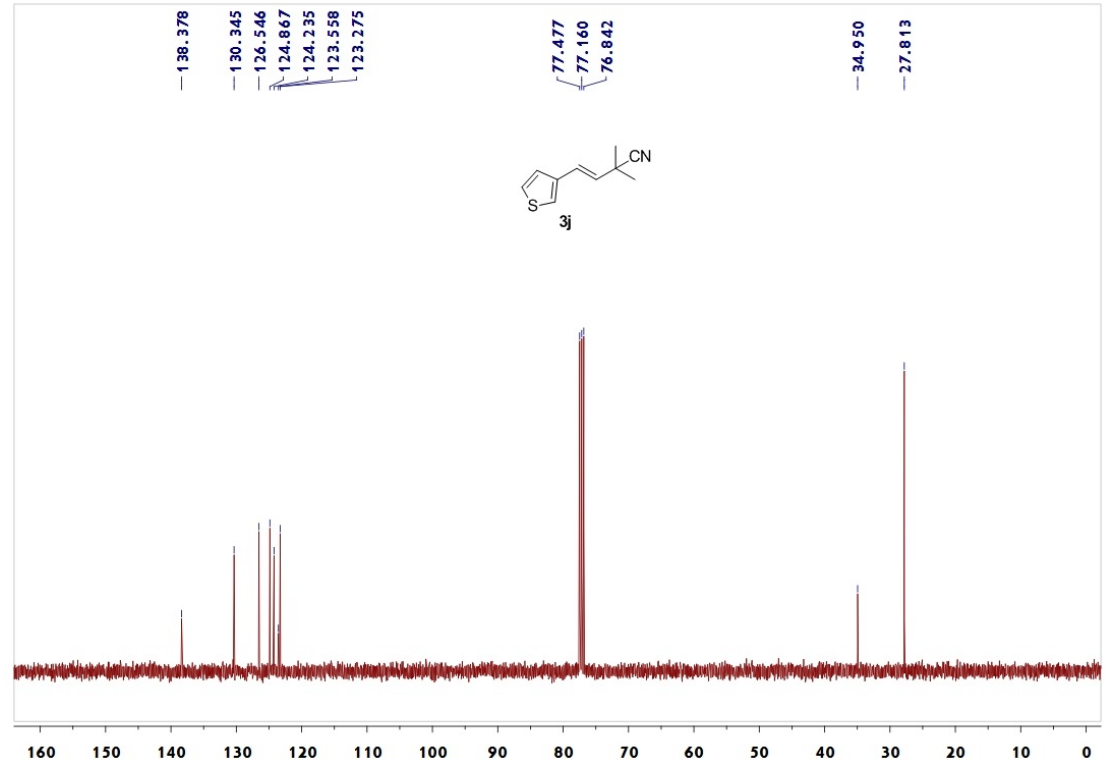
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