Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

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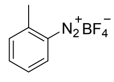
1. General information

Except for the tetrafluoroborate diazonium salt, all reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques, and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ^{1}H and ^{13}C NMR spectra were taken on 400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ as solvent. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV.

The tetrafluoroborate diazonium salt (**1a-1i**) used here were synthesized according to the reported methods.[1]



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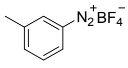

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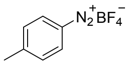

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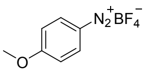

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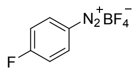

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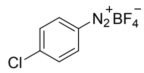

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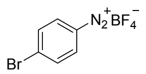

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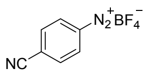

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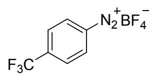

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2. Optimization of the Reaction Condition

Table 1. Screening of the solvent.[a]

Entry	Pd	Ligand	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	TFP	THF/DMSO	42%
2	$Pd(OAc)_2$	TFP	toluene	22%
3	$Pd(OAc)_2$	TFP	DMSO	44%
4	$Pd(OAc)_2$	TFP	DMF	21%
5	$Pd(OAc)_2$	TFP	THF	23%
6	$Pd(OAc)_2$	TFP	CH_3CN	0%
7	$Pd(OAc)_2$	TFP	Dioxane	39%

[a] Reaction condition: phenyl diazonium tetrafluoroborate (0.5 mmol), phenylacetylene (1.0 mmol), $Pd(OAc)_2$ (3 mol%), TFP (6 mol%), 2,3-Dimethylbuta-1,3-diene (0.75 mmol), formic acid (1.0 mmol), DCC (1.0 mmol), solvent (2 mL), 20 h. [b] GC yield, with dodecane as the internal standard.

Table 2. Screening of the ligand.[a]

Entry	Pd	Ligand	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	PPh_3	DMSO	72%[c]
2	$Pd(OAc)_2$	TFP	DMSO	44%
3	$Pd(OAc)_2$	Xphos	DMSO	44%

4	$Pd(OAc)_2$	PCy_3	DMSO	52%
5	$Pd(OAc)_2$	$P(o\text{-}tolyl)_3$	DMSO	31%
6	$Pd(OAc)_2$	$BuPAd_2$	DMSO	32%
7	$Pd(OAc)_2$	Tri(naphthalen-1-yl)phosphine	DMSO	40%
8	$Pd(OAc)_2$	2-(di-tert-butylphosphine) biphenyl	DMSO	23%
9	$Pd(OAc)_2$	$(t\text{-}Bu)_3P \cdot HBF_4$	DMSO	43%
10	$Pd(OAc)_2$	DPPF	DMSO	10%
11	$Pd(OAc)_2$	Xantphos	DMSO	63%
12	$Pd(OAc)_2$	Tris (4-methoxyphenyl) phosphine	DMSO	39%
13	$Pd(OAc)_2$	DPPE	DMSO	0%
14	$Pd(OAc)_2$	DPPB	DMSO	55%
15	$Pd(OAc)_2$	DPEphos	DMSO	37%

[a] Reaction condition: phenyl diazonium tetrafluoroborate (0.5 mmol), phenylacetylene (1.0 mmol), $Pd(OAc)_2$ (3 mol%), P:Pd = 2:1, 2,3-Dimethylbuta-1,3-diene (0.75 mmol), formic acid (1.0 mmol), DCC (1.0 mmol), DMSO (2 mL), 20 h. [b] GC yield, with dodecane as the internal standard. [c] Isolated yield.

Table 3. Screening of the Palladium catalyst.[a]

Entry	Cat.	Ligand	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	PPh_3	DMSO	72%[c]
2	$(CF_3COO)_2Pd$	PPh_3	DMSO	63%
3	$PdCl_2$	PPh_3	DMSO	15%
4	$Pd_2(dba)_3$	PPh_3	DMSO	5%
5	$Pd(PPh_3)_4$	PPh_3	DMSO	25%

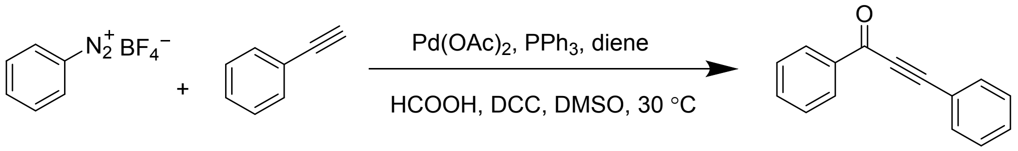
[a] Reaction condition: phenyl diazonium tetrafluoroborate (0.5 mmol), phenylacetylene (1.0 mmol), Pd (3 mol%), PPh_3 (6 mol%), 2,3-Dimethylbuta-1,3-diene (0.75 mmol), formic acid (1.0 mmol), DCC (1.0 mmol), DMSO (2 mL), 20 h. [b] GC yield, with dodecane as the internal standard. [c] Isolated yield.

Table 4. Screening of the additives.[a]

Entry	additive	Yield (%)[b]
1	4Å MS	43%
2	$(n\text{-}Bu)_4NI$ (10 mol%).	29%

[a] Reaction condition: phenyl diazonium tetrafluoroborate (0.5 mmol), phenylacetylene (1.0 mmol), $Pd(OAc)_2$ (3 mol%), PPh_3 (6 mol%), 2,3-Dimethylbuta-1,3-diene (0.75 mmol), formic acid (1.0 mmol), DCC (1.0 mmol), DMSO (2 mL), 20 h. [b] GC yield, with dodecane as the internal standard.

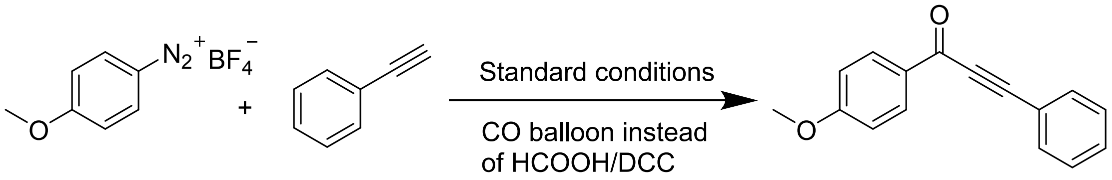
Table 5. The amount loading of diene.



Diene	Yield (%)
1.5 equiv	72[b]
1.0 equiv	41
0.5 equiv	38
0.2 equiv	33

[a] Reaction condition: Benzenediazonium tetrafluoroborate (0.5 mmol), phenylacetylene (1 mmol), $Pd(OAc)_2$ (3 mol%), PPh_3 (6 mol%), 2,3-dimethylbuta-1,3-diene (x equiv.),formic (1 mmol), DCC (1 mmol), DMSO (2 mL), 20 h. [b] Isolated yields.

Table 6. Control experiments.



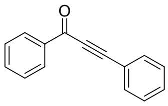
Entry	condition	Yield (%)[b]
1	CO balloon, No diene	50
2	CO balloon, diene	63
3	CO balloon, No diene, DCU[d]	trace
4	CO balloon, diene, DCU	trace
5	CO balloon, No diene, Et_3N (2 equiv.)	trace
6	CO balloon, diene, Et_3N (2 equiv.)	trace
7	CO balloon, diene, HCOOH, DCU	39
8	CO balloon, No diene, HCOOH, DCU	24
9	CO balloon, diene, HCOOH (2 equiv.)	99 (91) [c]
10	CO balloon, No diene, HCOOH (2 equiv.)	46
11	diene, HCOOH (2 equiv.)	None
12	DCC (40 mol%), diene, HCOOH (2 equiv.)	trace
13	CO balloon, diene, HCOOH (2 equiv.)	No reaction[e]

[a] Reaction condition: *p*-methoxybenzenediazonium tetrafluoroborate (0.5 mmol), phenylacetylene (1 mmol), $Pd(OAc)_2$ (3 mol%), PPh_3 (6 mol%), 2,3-dimethylbuta-1,3-diene (0.75 mmol),CO balloon, DMSO (2 mL), 20 h. [b] Yield was determined by NMR. [c] Isolated yields. [d] DCU is 1,3-dicyclohexylurea. [e] No phenylacetylene.

3. General Procedure

$Pd(OAc)_2$ (3.4 mg, 3 mol%), PPh_3 (7.8 mg, 6 mol%), benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and DCC (206.1 mg, 1 mmol) were transferred into an oven-dried tube which was filled with nitrogen. DMSO (2.0 mL), 1,3-butadiene (375 uL, 2 mol/L) and phenylacetylene (110 uL, 1 mmol) were added to the reaction tube. After formic acid (38 uL, 1 mmol) were added, the tube was sealed and the mixture was stirred at 30 °C for 20 h. After the reaction finished, the reaction mixture was extracted with ethyl acetate three times and dried with sodium sulfate. The crude product was filtered and concentrated under vacuum and was purified by column chromatography on silica gel column EtOAc/petroleum ether (1/200 to 1/50) to give the desired product.

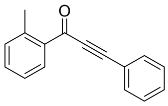
4. Spectroscopic Data of Products



1,3-Diphenylprop-2-yn-1-one (**3a**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3a** (95.2 mg, 90% yield) as a red oil.

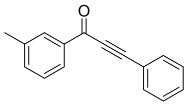
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, *J* = 7.1 Hz, 2H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.65 (d, *J* = 6.8 Hz, 1H), 7.54 (dd, *J* = 16.8, 10.2 Hz, 3H), 7.46 (d, *J* = 7.4 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.01, 136.97, 134.09, 133.07, 130.78, 129.59, 128.69, 128.63, 120.21, 93.09, 86.93.



3-Phenyl-1-(*o*-tolyl)prop-2-yn-1-one (**3b**)

Prepared with 2-Methylbenzenediazonium tetrafluoroborate (103 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3b** (70.4 mg, 64% yield) as a red oil.

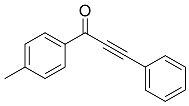
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, *J* = 7.7 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.53 – 7.46 (m, 2H), 7.46 – 7.38 (m, 3H), 7.31 (d, *J* = 7.5 Hz, 1H), 2.71 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 179.81, 140.51, 135.74, 133.22, 133.18, 132.94, 132.20, 130.61, 128.66, 125.91, 120.37, 91.83, 88.40, 21.97.



3-Phenyl-1-(*m*-tolyl)prop-2-yn-1-one (**3c**)

Prepared with 3-Methylbenzenediazonium tetrafluoroborate (103 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3c** (90.2 mg, 82% yield) as a red oil.

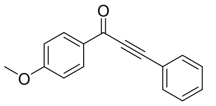
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 – 8.00 (m, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 4H), 2.48 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.27, 138.53, 136.94, 135.01, 133.08, 130.76, 129.82, 128.70, 128.54, 127.16, 120.24, 92.90, 87.03, 21.36.



3-Phenyl-1-(*p*-tolyl)prop-2-yn-1-one (**3d**)

Prepared with 4-Methylbenzenediazonium tetrafluoroborate (103 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3d** (81.4 mg, 74% yield) as a yellow oil.

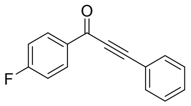
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.49 (dd, *J* = 6.2, 4.0 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 177.78, 145.27, 134.64, 133.06, 130.70, 129.74, 129.38, 128.69, 120.30, 92.63, 86.99, 21.87.



1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (**3e**)

Prepared with 4-Methoxybenzenediazonium tetrafluoroborate (111 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:20) to give **3e** (103.8 mg, 88% yield) as a red oil.

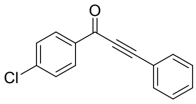
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.29 – 8.14 (m, 2H), 7.69 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.51 – 7.40 (m, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.69, 164.52, 132.98, 132.00, 130.63, 130.31, 128.68, 120.35, 113.92, 92.35, 86.95, 55.62.



1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-one (**3f**)

Prepared with 4-Fluorobenzenediazonium tetrafluoroborate (105 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3f** (87.4 mg, 78% yield) as a red oil.

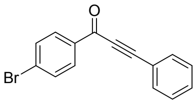
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.73 – 7.68 (m, 2H), 7.55 – 7.50 (m, 1H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 8.5 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.43, 167.77, 133.08, 132.21, 130.93, 128.75, 119.99, 116.01, 115.79, 93.39, 86.61.



1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-one (**3g**)

Prepared with 4-Chlorobenzenediazonium tetrafluoroborate (113 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3g** (88.8 mg, 74% yield) as a yellow oil.

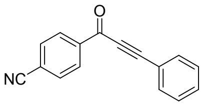
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (d, *J* = 8.6 Hz, 2H), 7.72 – 7.68 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 3H), 7.44 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.70, 140.75, 135.31, 133.14, 131.01, 130.89, 129.04, 128.77, 119.90, 93.68, 86.60.



1-(4-Bromophenyl)-3-phenylprop-2-yn-1-one (**3h**)

Prepared with 4-Bromobenzenediazonium tetrafluoroborate (135 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3h** (88.0 mg, 62% yield) as a yellow oil.

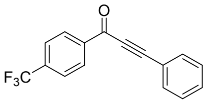
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, *J* = 8.6 Hz, 2H), 7.68 (t, *J* = 8.3 Hz, 4H), 7.53 – 7.48 (m, 1H), 7.44 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.87, 135.71, 133.15, 132.02, 131.03, 130.96, 129.60, 128.78, 119.88, 93.73, 86.60.



4-(3-Phenylpropioloyl)benzonitrile (**3i**)

Prepared with 4-Cyanobenzenediazonium tetrafluoroborate (108.5 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:20) to give **3i** (63.5 mg, 55% yield) as a white solid.

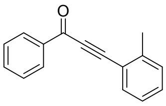
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.22, 139.65, 133.27, 132.53, 131.41, 129.84, 128.86, 119.46, 117.90, 117.17, 95.17, 86.44.



3-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (**3j**)

Prepared with 4-(Trifluoromethyl)benzenediazonium tetrafluoroborate (130 mg, 0.5 mmol) and phenylacetylene (110 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3j** (57.5 mg, 42% yield) as a yellow solid.

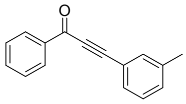
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.35 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.77 – 7.69 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.76, 149.01, 139.39, 133.22, 131.23, 129.82, 128.82, 125.72, 119.68, 94.51, 88.19, 86.59.



1-Phenyl-3-(*o*-tolyl)prop-2-yn-1-one (**3k**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 1-Ethynyl-2-methylbenzene (126 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3k** (81.4 mg, 74% yield) as a red oil.

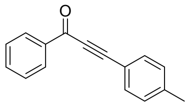
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.72 – 7.65 (m, 2H), 7.52 – 7.46 (m, 1H), 7.42 (dd, *J* = 11.4, 4.4 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 2.54 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.09, 142.20, 137.06, 134.07, 133.69, 130.84, 129.91, 129.57, 128.66, 125.97, 120.02, 92.21, 90.77, 20.92.



1-Phenyl-3-(*m*-tolyl)prop-2-yn-1-one (**3l**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 1-Ethynyl-3-methylbenzene (125 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3l** (92.4 mg, 84% yield) as a red oil.

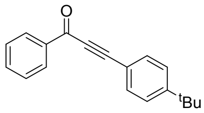
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.35 – 8.21 (m, 2H), 7.72 – 7.62 (m, 2H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 2.62 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.08, 142.20, 137.07, 134.08, 133.70, 130.86, 129.92, 129.57, 128.67, 125.97, 120.02, 92.22, 90.79, 20.92.



1-Phenyl-3-(*p*-tolyl)prop-2-yn-1-one (**3m**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 1-Ethynyl-4-methylbenzene (127 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3m** (96.8 mg, 88% yield) as a red oil.

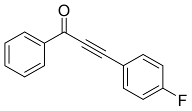
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, *J* = 7.1 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (dd, *J* = 13.1, 7.4 Hz, 4H), 7.34 (dd, *J* = 10.3, 3.6 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.08, 138.56, 136.96, 133.59, 131.80, 130.27, 129.60, 128.65, 119.94, 93.56, 86.70, 21.21.



3-(4-(*tert*-Butyl)phenyl)-1-phenylprop-2-yn-1-one (**3n**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 1-(*tert*-Butyl)-4-ethynylbenzene (180 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3n** (93.0 mg, 71% yield) as a red oil.

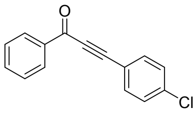
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 3H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.06, 154.61, 137.02, 134.07, 133.05, 129.57, 128.65, 125.81, 117.04, 93.86, 86.81, 35.10, 31.08.



3-(4-Fluorophenyl)-1-phenylprop-2-yn-1-one (**3o**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 1-Ethynyl-4-fluorobenzene (114 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3o** (90.7 mg, 81% yield) as a yellow solid.

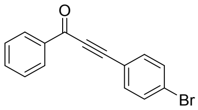
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.64 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 8.7 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 177.89, 165.30, 162.77, 136.79, 135.44, 135.35, 134.22, 129.56, 128.68, 116.38, 116.27, 116.15, 92.03, 86.83.



3-(4-Chlorophenyl)-1-phenylprop-2-yn-1-one (**3p**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 1-Chloro-4-ethynylbenzene (118 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3p** (76.8 mg, 64% yield) as a yellow solid.

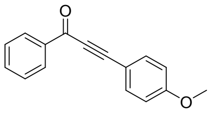
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.64 (dd, *J* = 14.7, 7.9 Hz, 3H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.44 (dd, *J* = 23.7, 21.9 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 177.81, 137.22, 136.73, 134.29, 134.28, 129.59, 129.18, 128.71, 118.59, 91.65, 87.61.



3-(4-Bromophenyl)-1-phenylprop-2-yn-1-one (**3q**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 1-Bromo-4-ethynylbenzene (120 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3q** (103.7 mg, 73% yield) as a yellow solid.

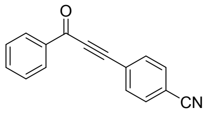
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.61 – 7.52 (m, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 177.84, 136.73, 134.36, 134.30, 132.13, 129.60, 128.71, 125.63, 119.07, 91.67, 87.70.



3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-one (**3r**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 1-Ethynyl-4-methoxybenzene (130 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:50) to give **3r** (89.7 mg, 76% yield) as a yellow solid.

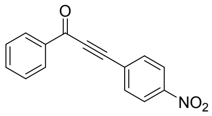
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.08 (m, 2H), 7.64 (ddd, *J* = 12.7, 8.3, 4.7 Hz, 3H), 7.53 (t, *J* = 7.6 Hz, 2H), 6.96 – 6.92 (m, 2H), 3.86 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.08, 161.78, 137.05, 135.18, 133.95, 129.50, 128.59, 114.46, 111.87, 94.42, 86.91, 55.46.



4-(3-Oxo-3-phenylprop-1-yn-1-yl)benzonitrile (**3s**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 4-Ethynylbenzonitrile (118 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:20) to give **3s** (83.2 mg, 72% yield) as a yellow solid.

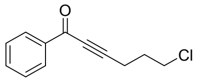
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.48, 136.45, 134.63, 133.30, 132.33, 129.66, 128.82, 124.97, 117.90, 114.07, 89.65, 89.40.



3-(4-Nitrophenyl)-1-phenylprop-2-yn-1-one (**3t**)

Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 1-Ethynyl-4-nitrobenzene (0.1470 g, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:20) to give **3t** (80.3 mg, 64% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.72 – 7.67 (m, 1H), 7.57 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.41, 148.54, 136.39, 134.70, 133.69, 129.68, 128.85, 126.81, 123.87, 89.87, 89.21.



3-(4-(3-Chloropropyl)phenyl)-1-phenylprop-2-yn-1-one (**3u**)

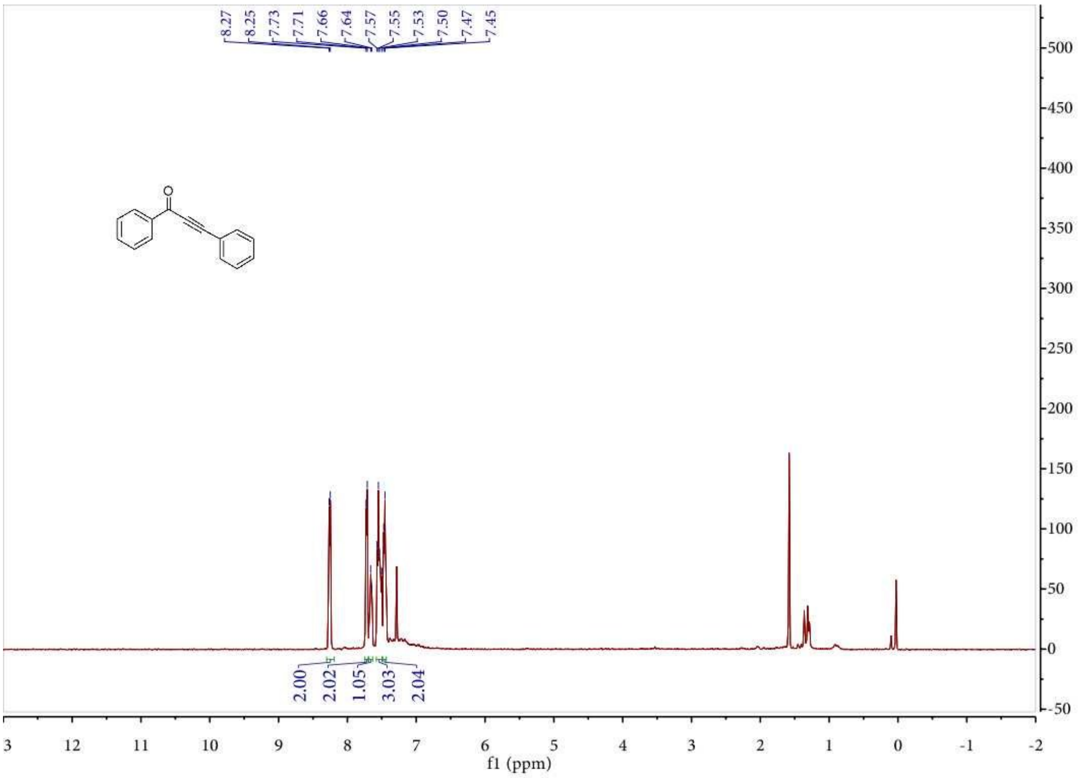
Prepared with Benzenediazonium tetrafluoroborate (96 mg, 0.5 mmol) and 5-Chloropent-1-yne (107 uL, 1 mmol) using the general procedure. The crude material was purified by chromatography column (EtOAc/petroleum ether = 1:20) to give **3u** (84.6 mg, 60% yield) as a red oil.

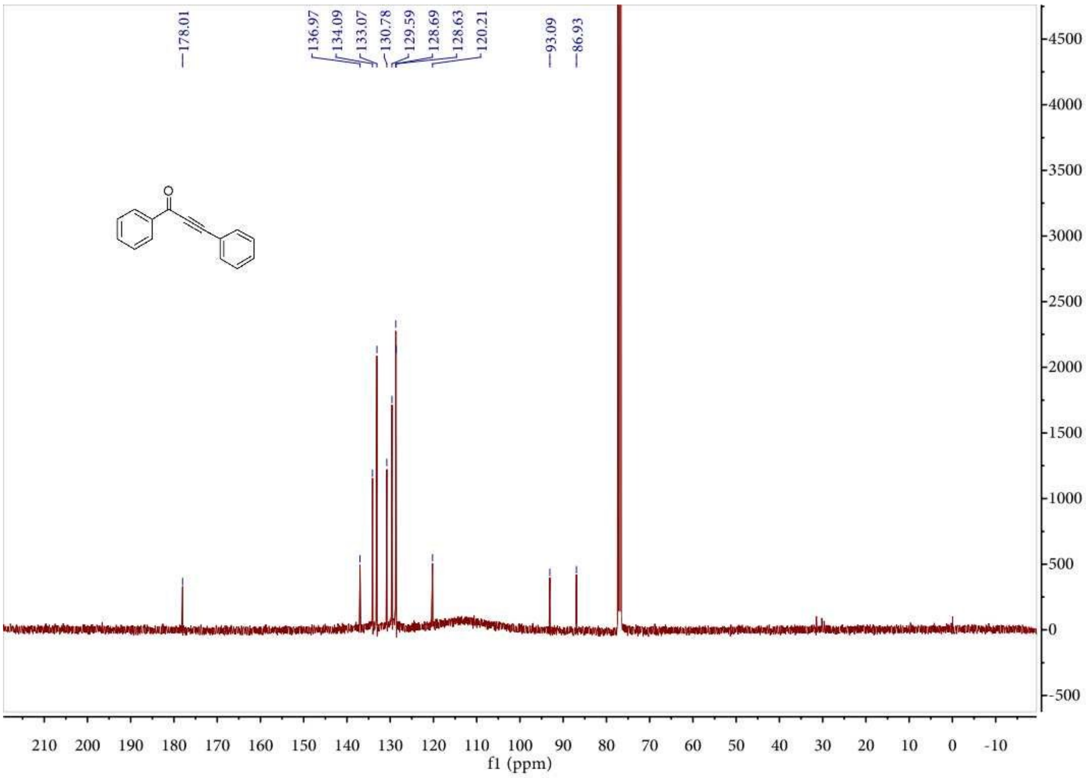
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 3.74 (t, *J* = 6.2 Hz, 2H), 2.74 (t, *J* = 6.9 Hz, 2H), 2.16 (p, *J* = 6.7 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.99, 136.74, 134.08, 129.57, 128.58, 94.17, 80.24, 43.38, 30.48, 16.65.

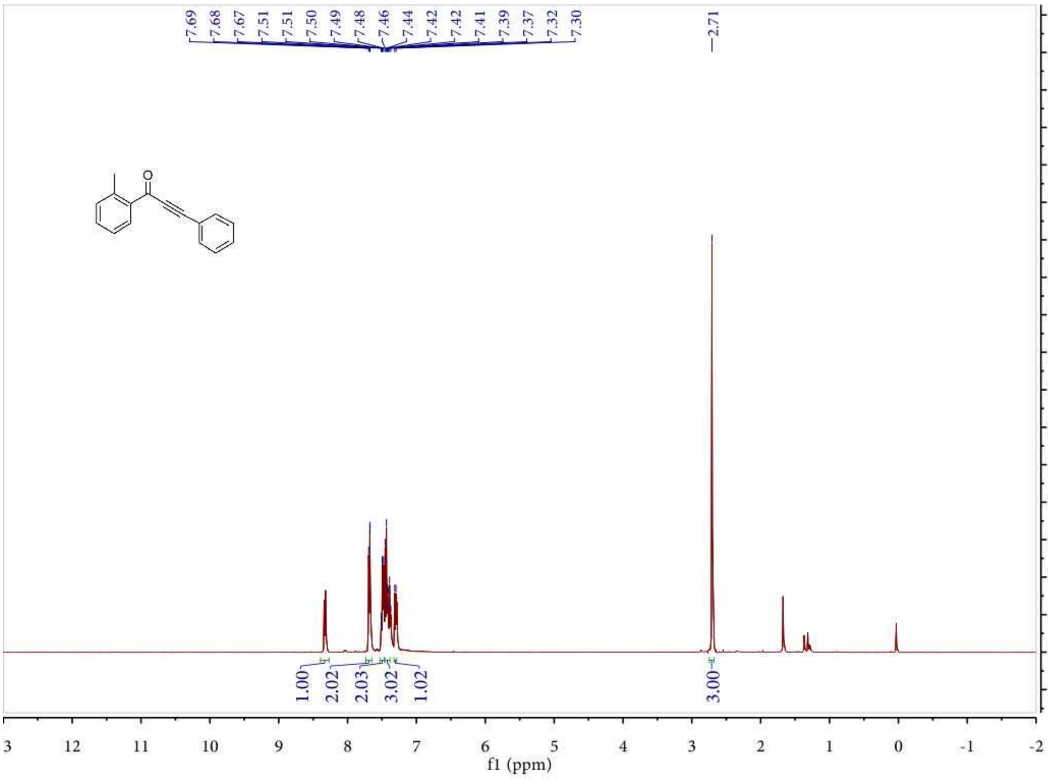
5. References

1. N. Zhang, Z.-J. Quan, Z. Zhang, Y.-X. Da and X.-C. Wang, *Chem. Commun.*, 2016, **52**, 14234.

6. Copy of ^{1}H and ^{13}C NMR Spectra of Products



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2.03
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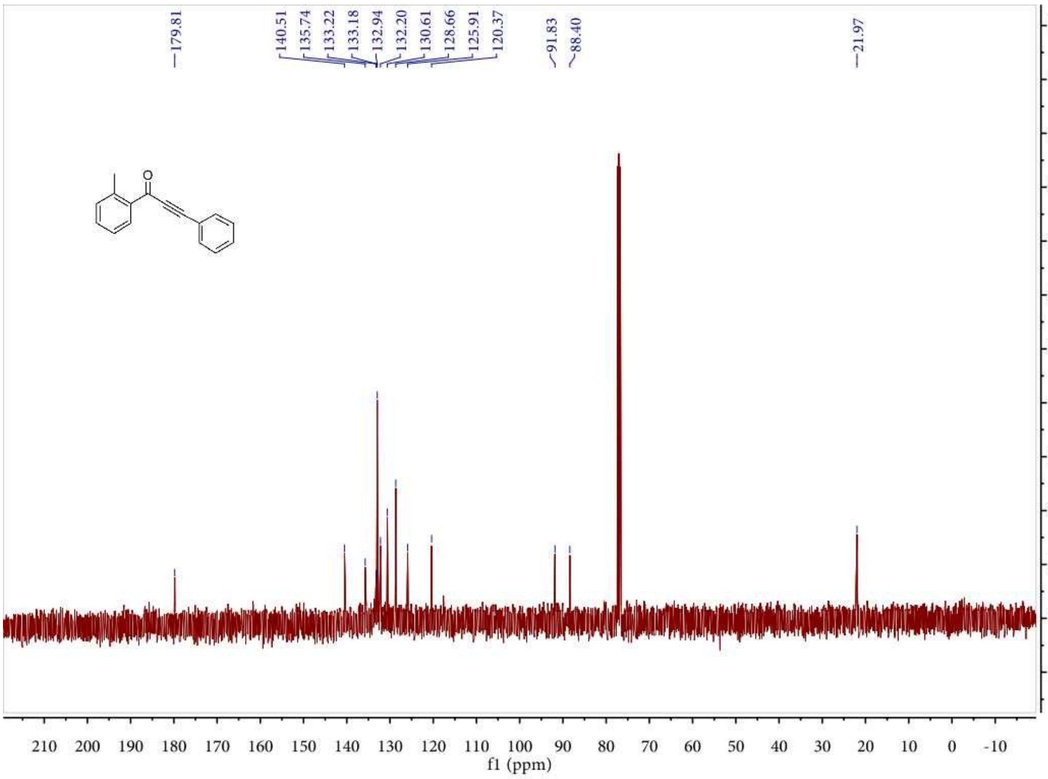
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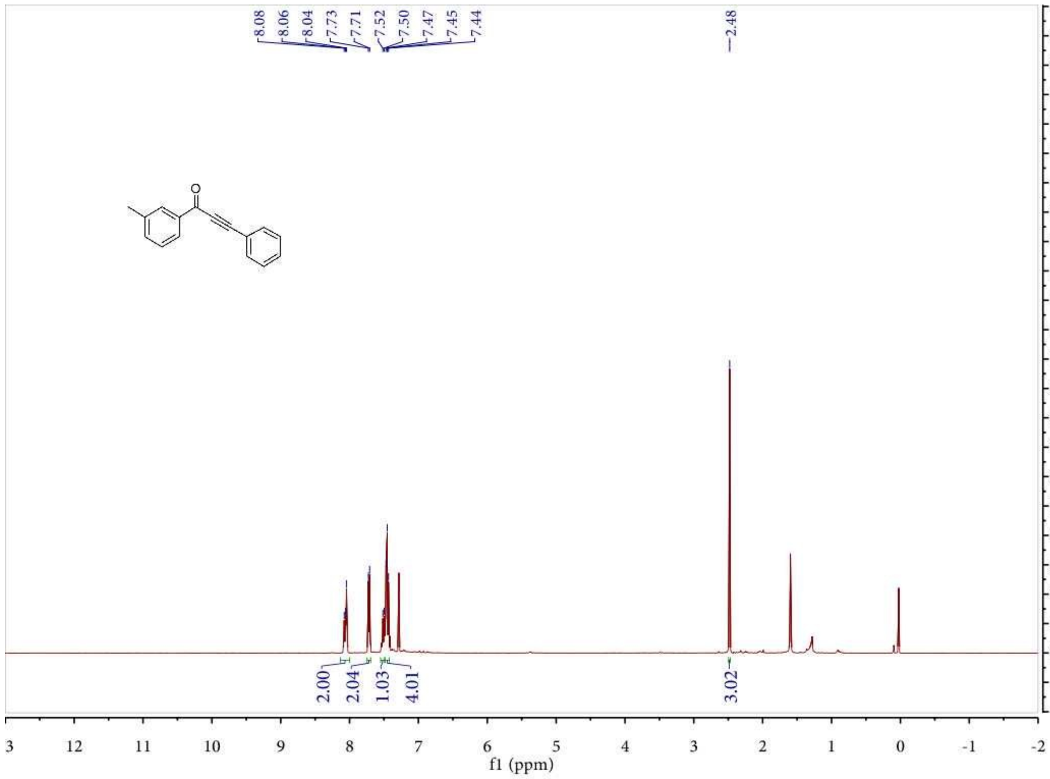
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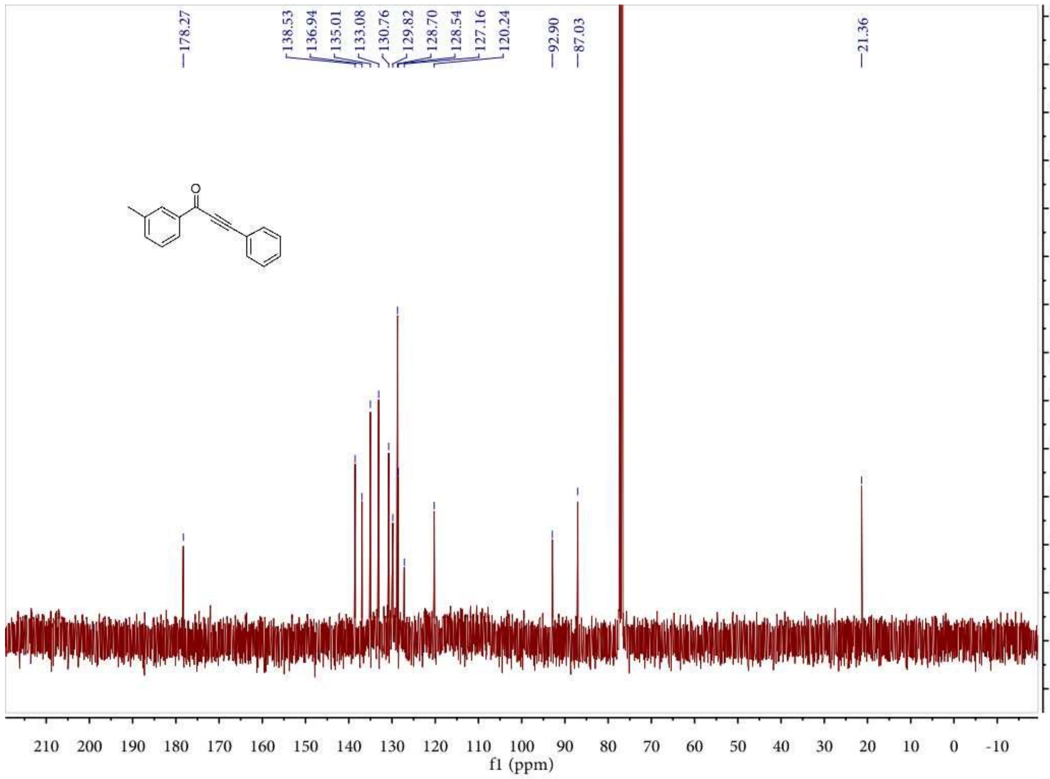
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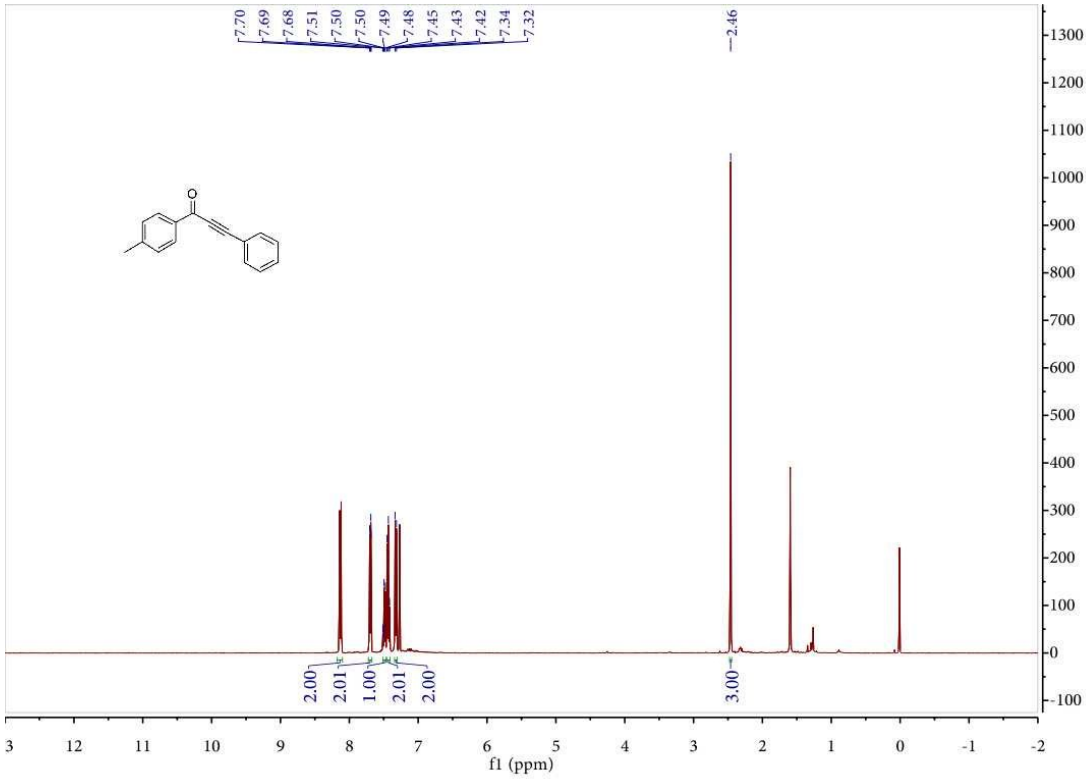

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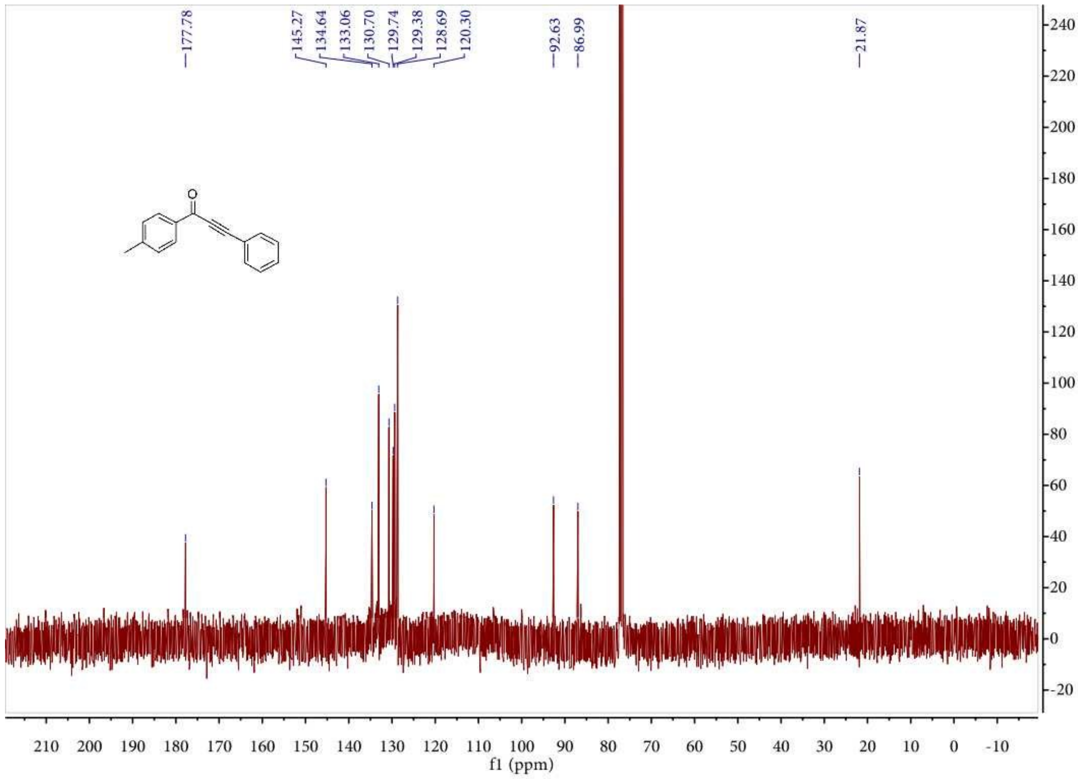

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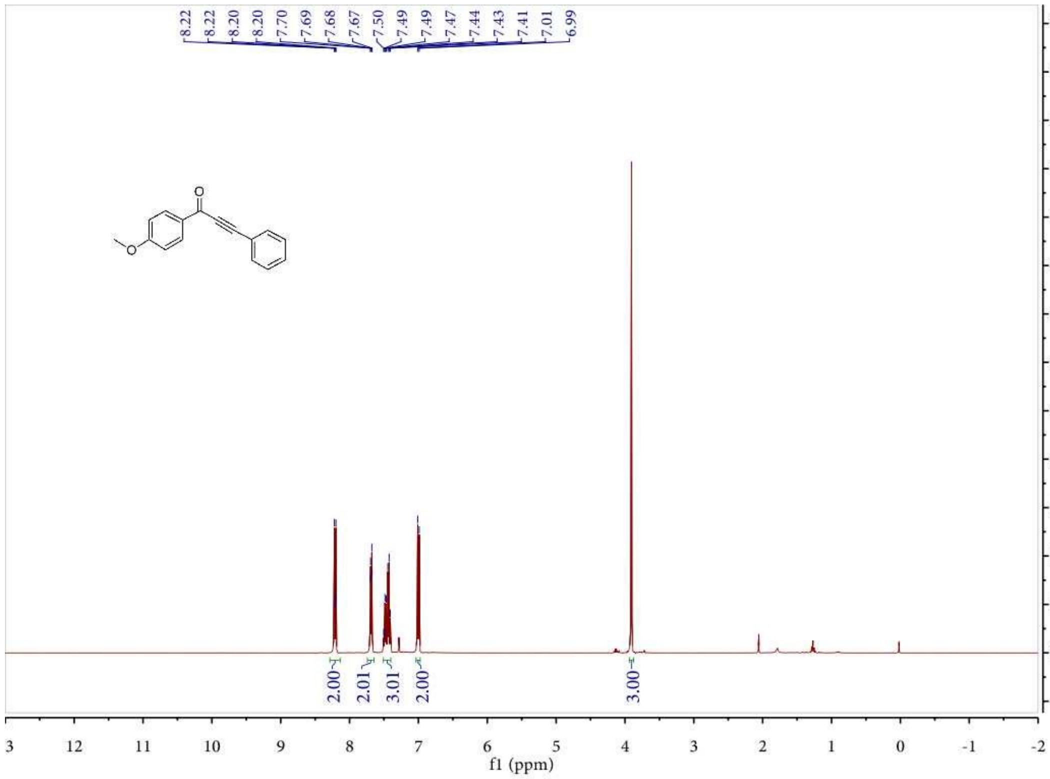
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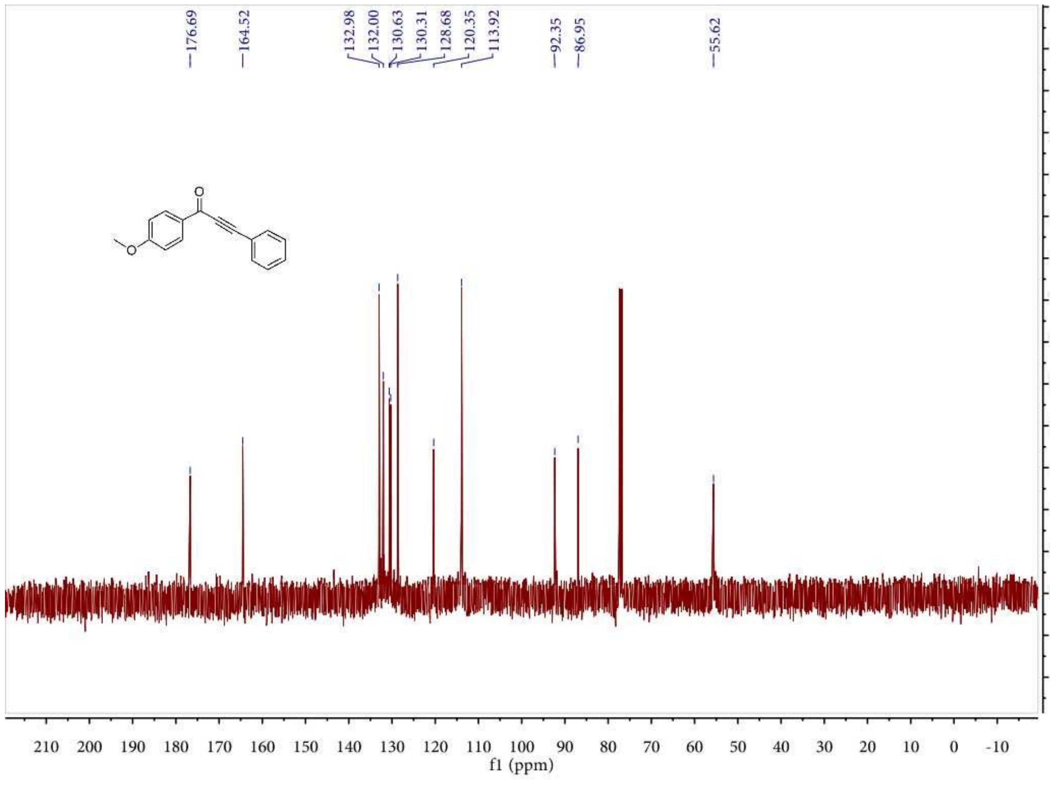
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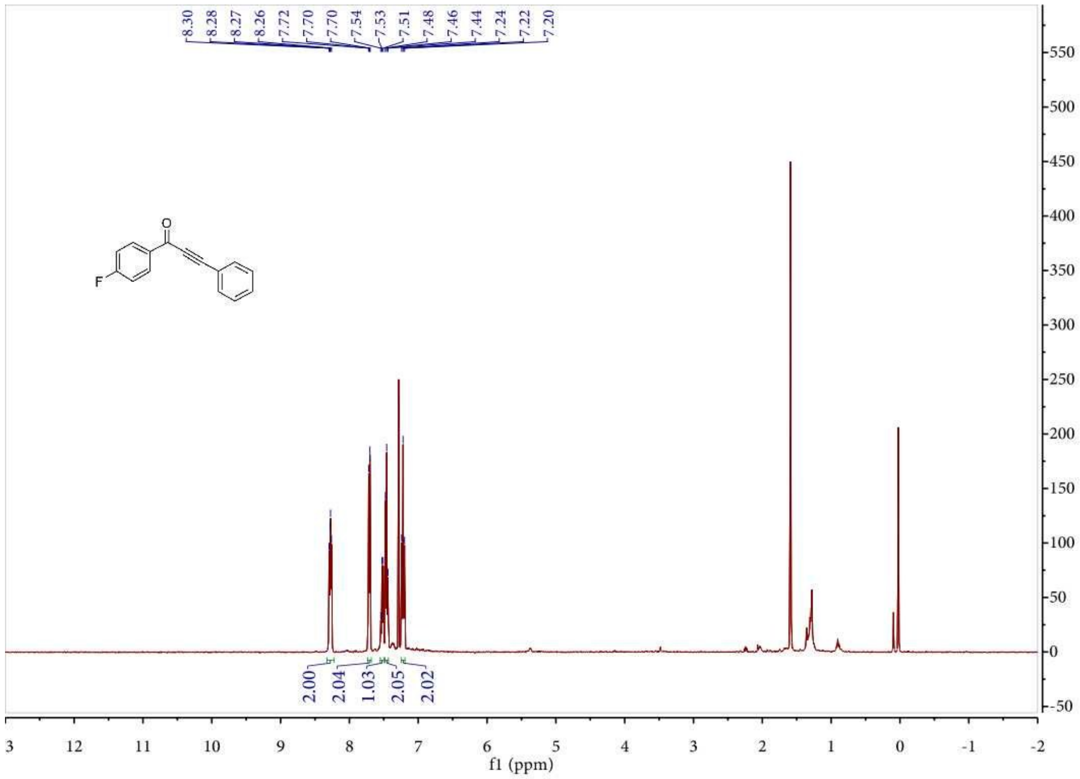
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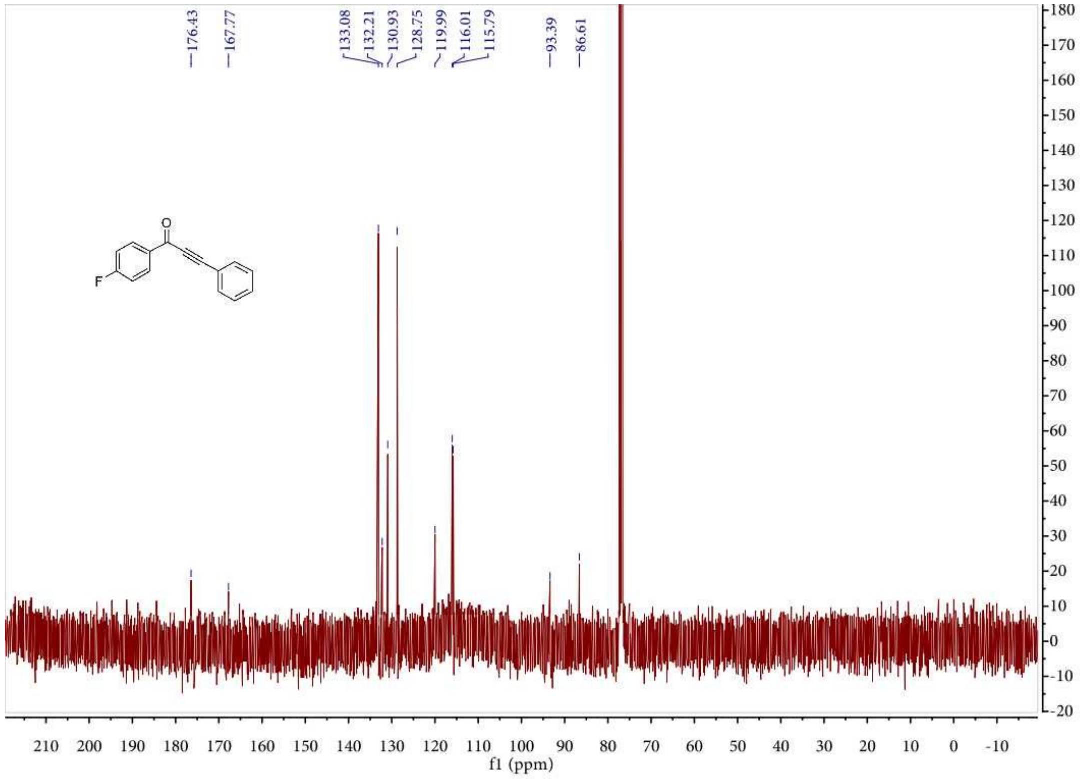
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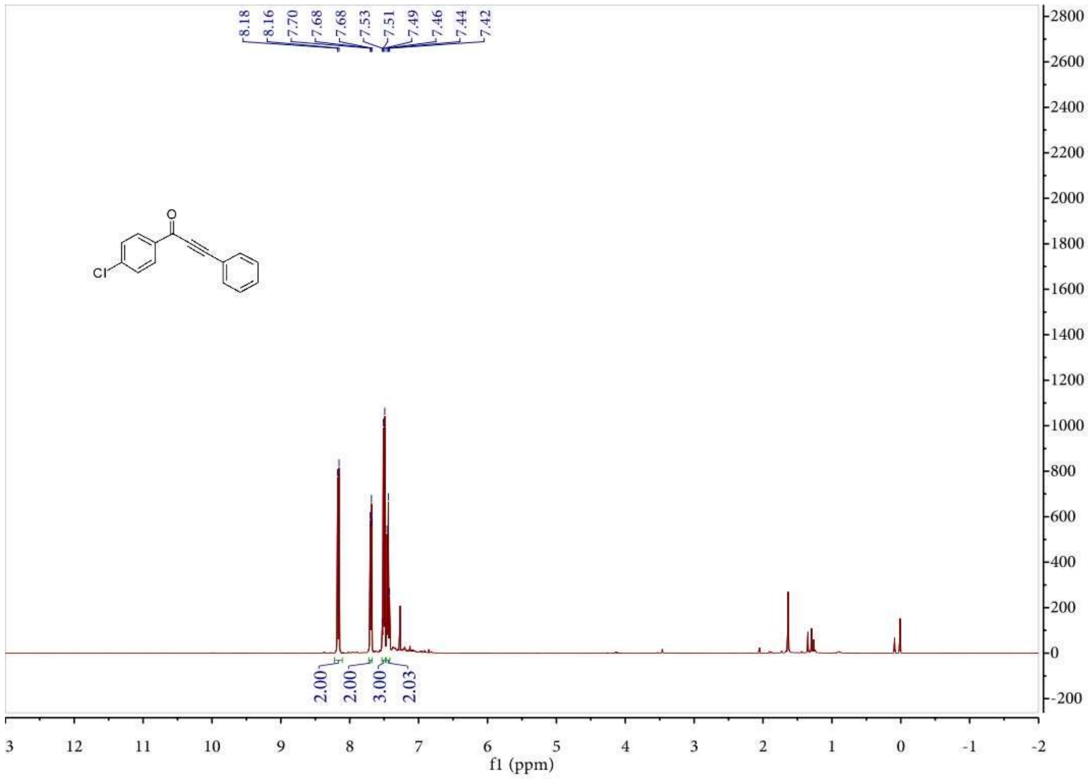
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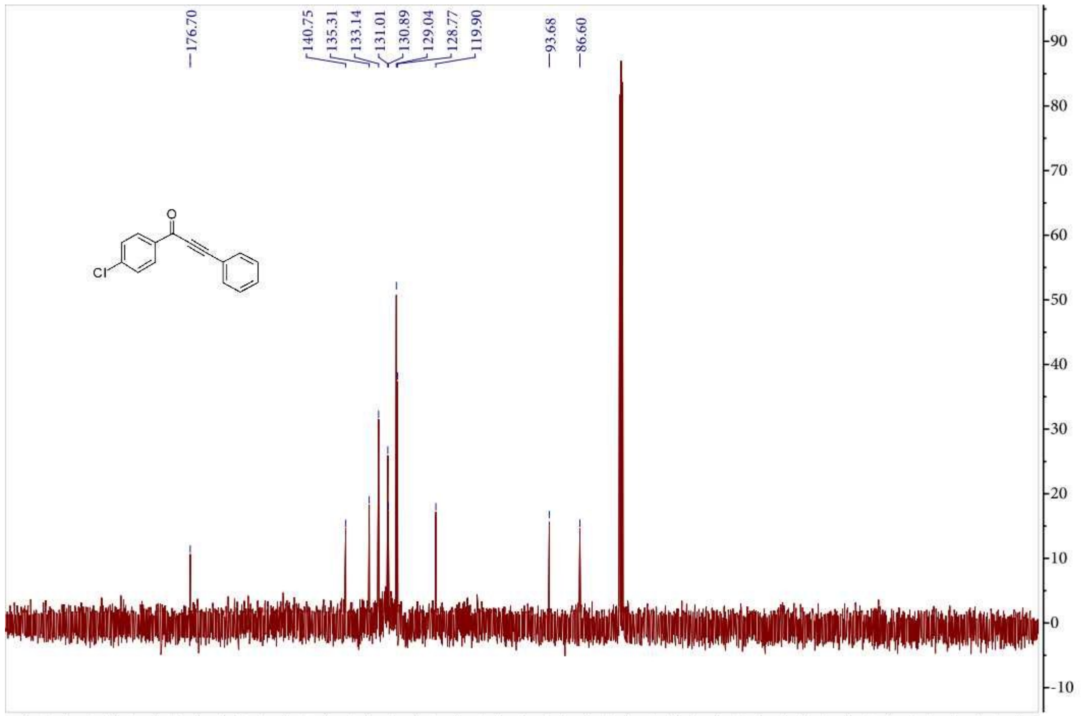
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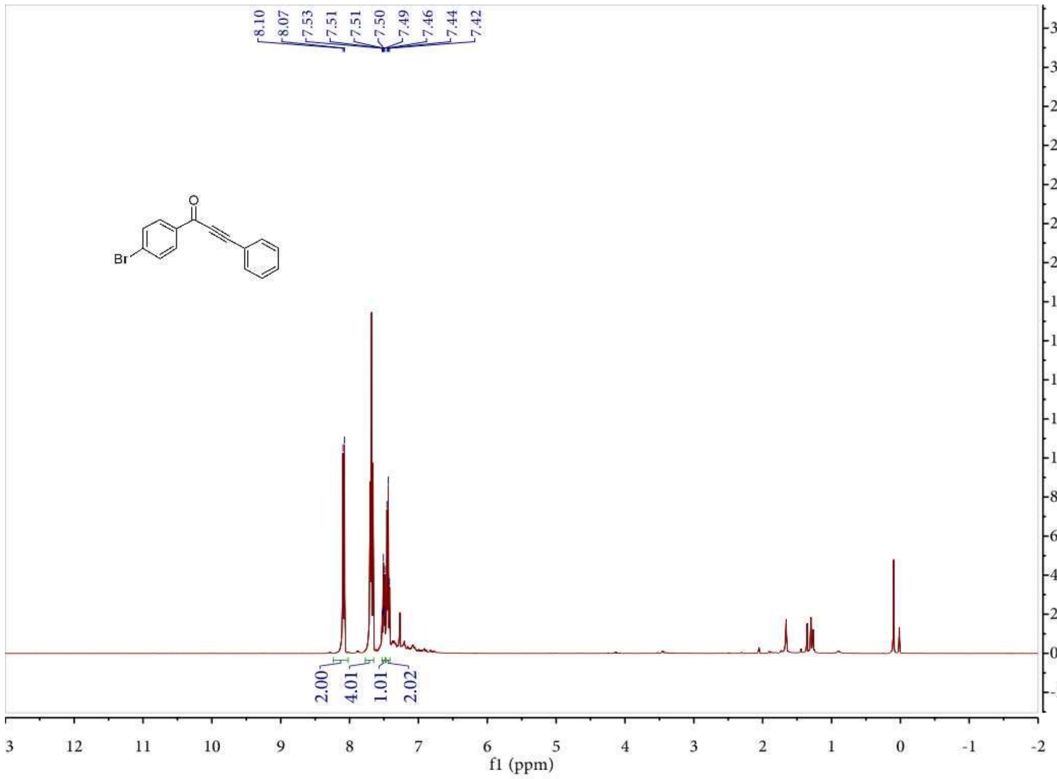
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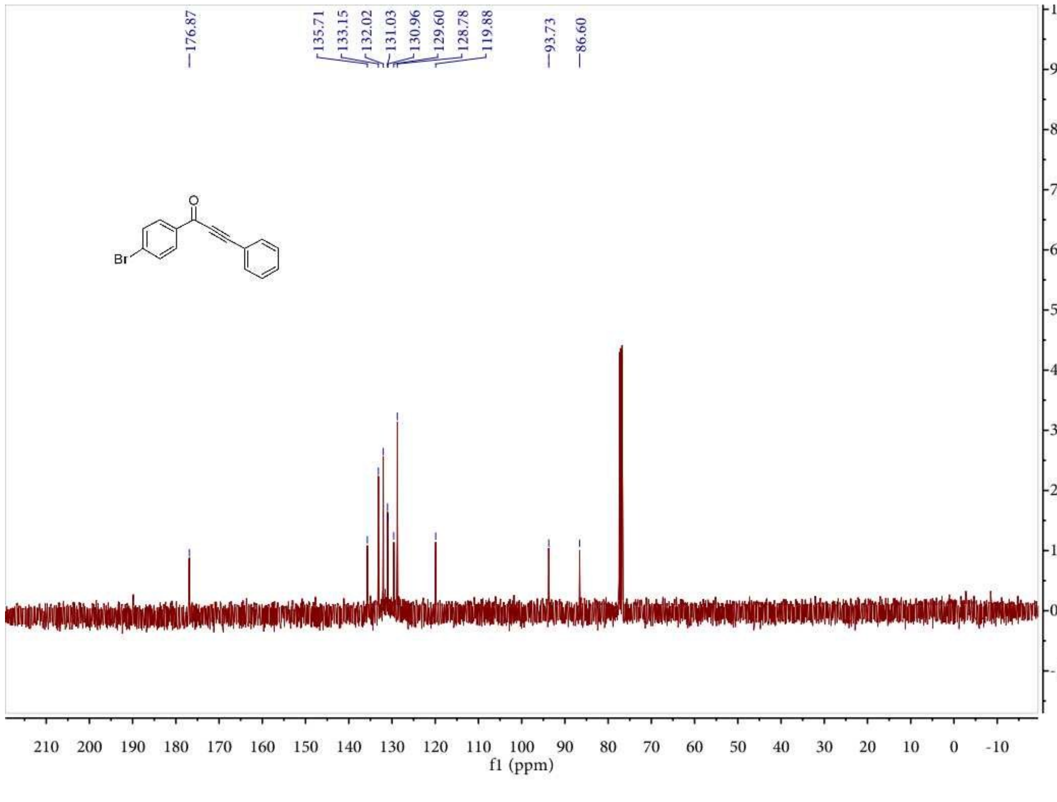
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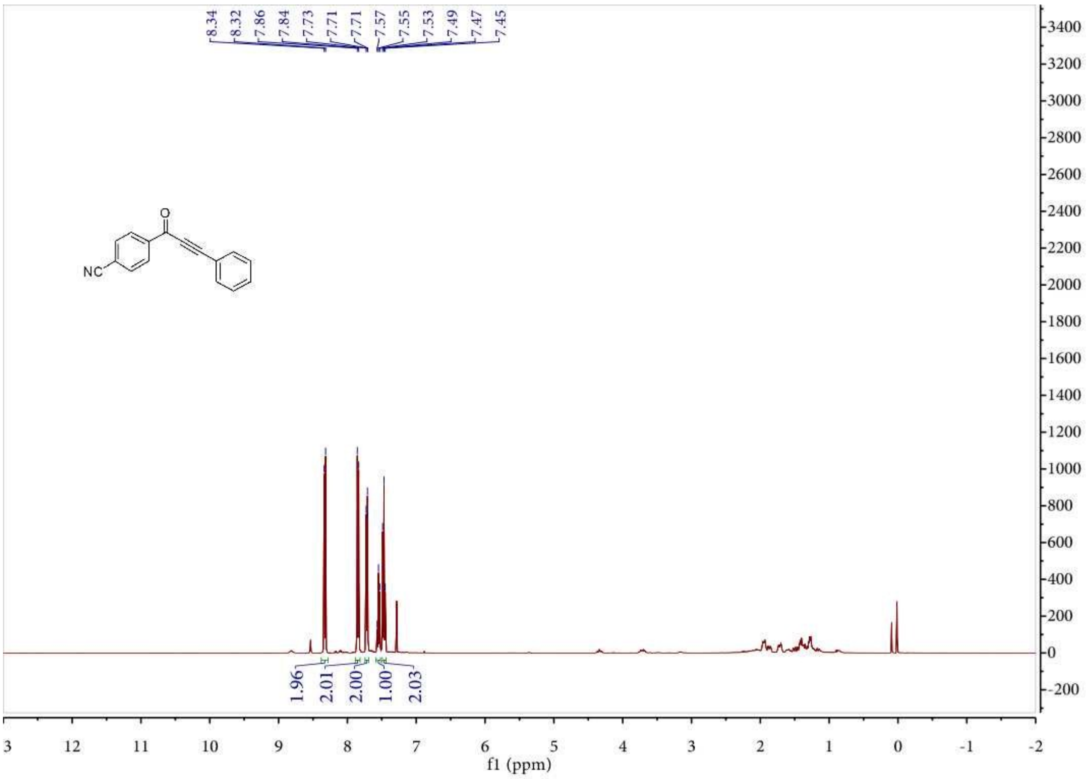
f1 (ppm)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8.32
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7.73
7.71
7.71
7.57
7.55
7.53
7.49
7.47
7.45
O
NC
1.96
2.01
2.00
1.00
2.03
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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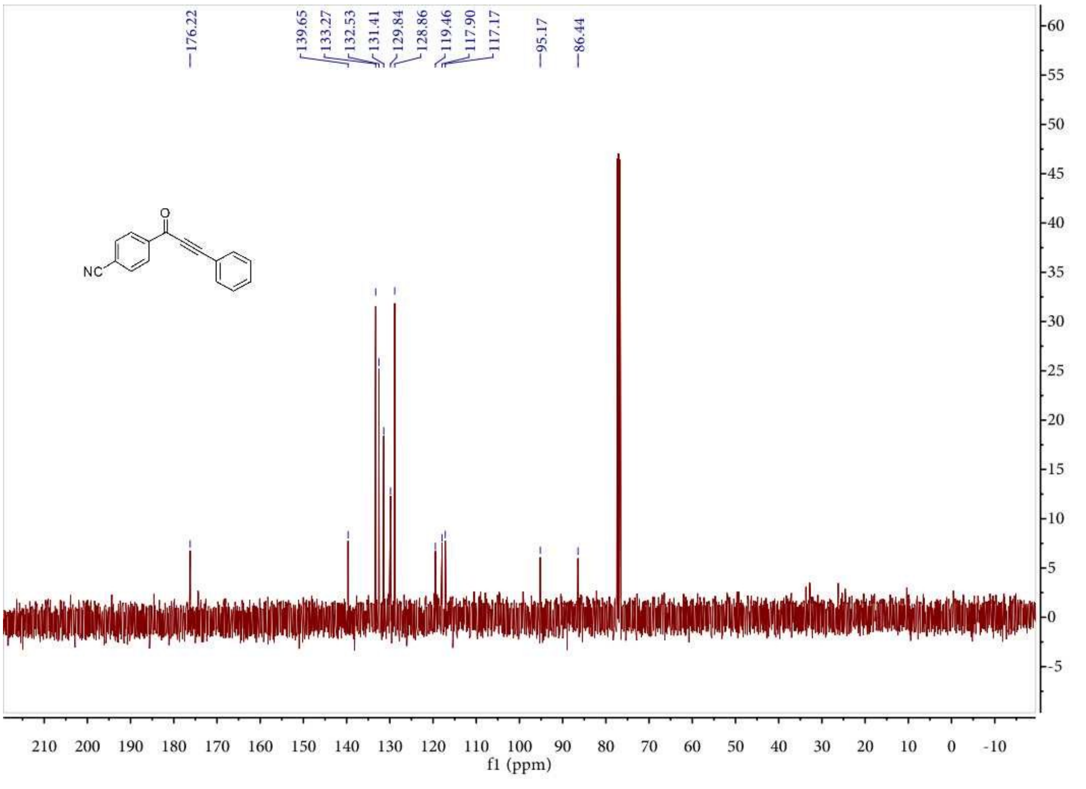
f1 (ppm)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129.84
128.86
119.46
117.90
117.17
95.17
86.44
O
NC
60
55
50
45
40
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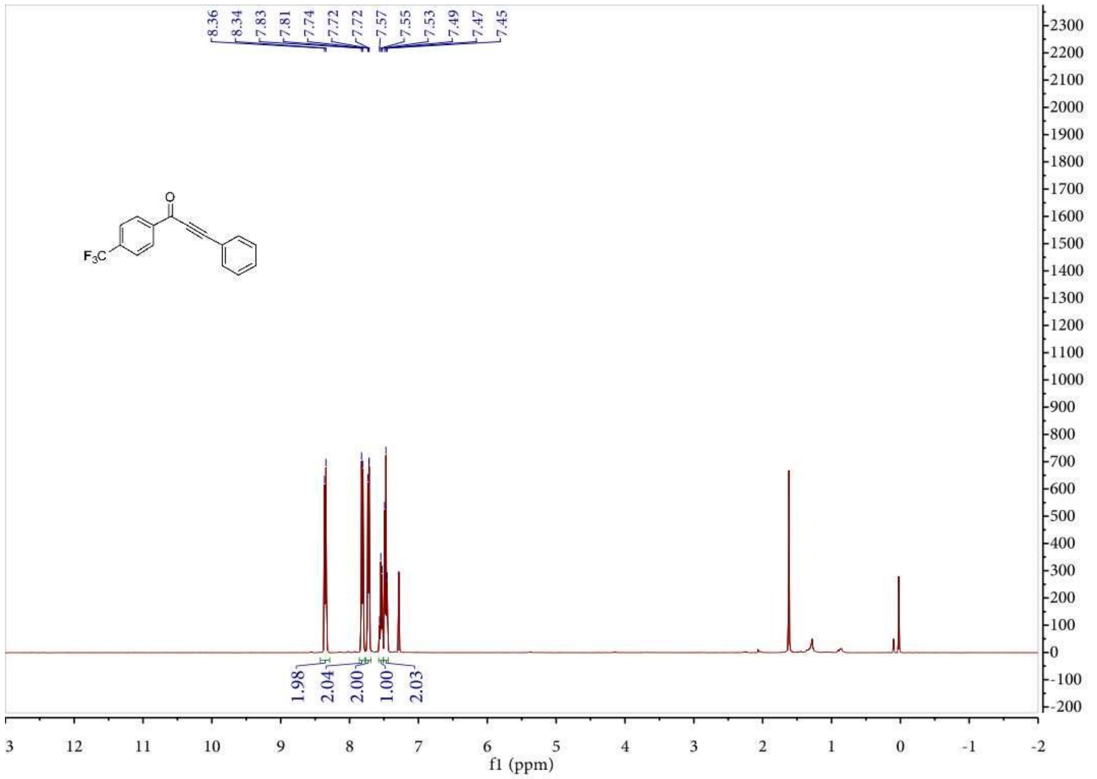
15
10
5
0
-5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.72
7.57
7.55
7.53
7.49
7.47
7.45
O
F3C
1.98
2.04
2.00
1.00
2.03
3
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
2300
2200
2100
2000
1900
1800
1700
1600
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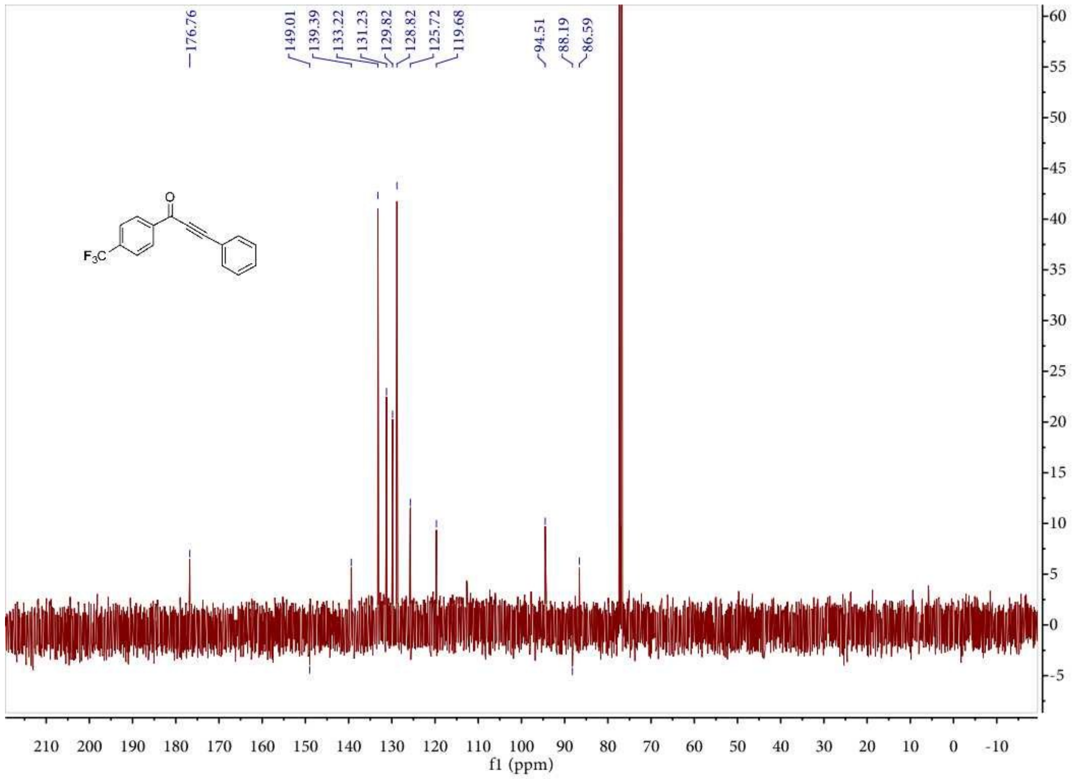
-200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88.19
86.59
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F3C
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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f1 (ppm)
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50
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30
25
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10
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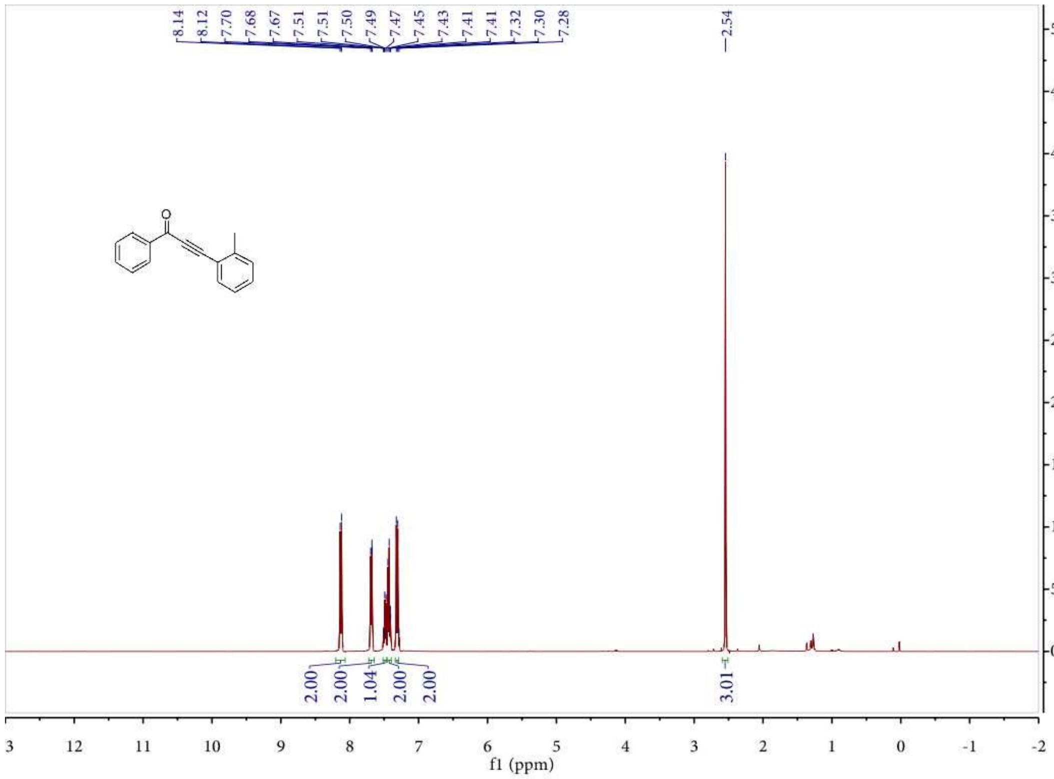
-5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7.47
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7.41
7.41
7.32
7.30
7.28
2.54
O
2.00
2.00
1.04
2.00
2.00
3.01
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
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2
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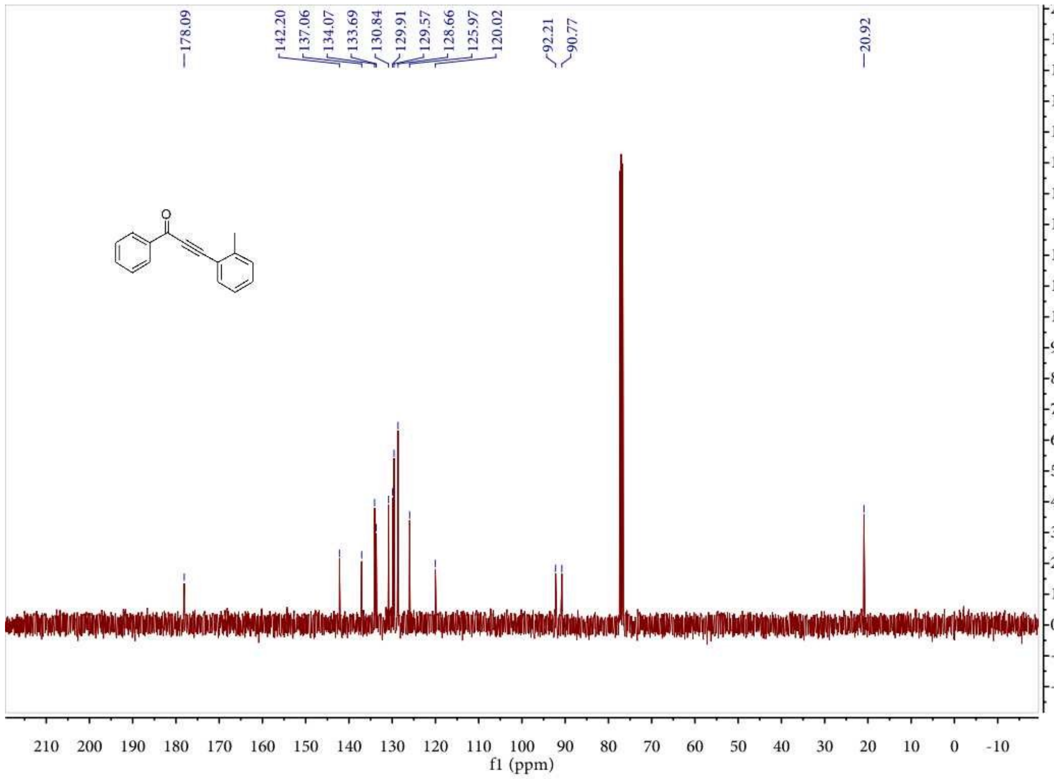
-2
f1 (ppm)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142.20
137.06
134.07
133.69
130.84
129.91
129.57
128.66
125.97
120.02
92.21
90.77
20.92
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
210
200
190
180
170
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100
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80
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60
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40
30
20
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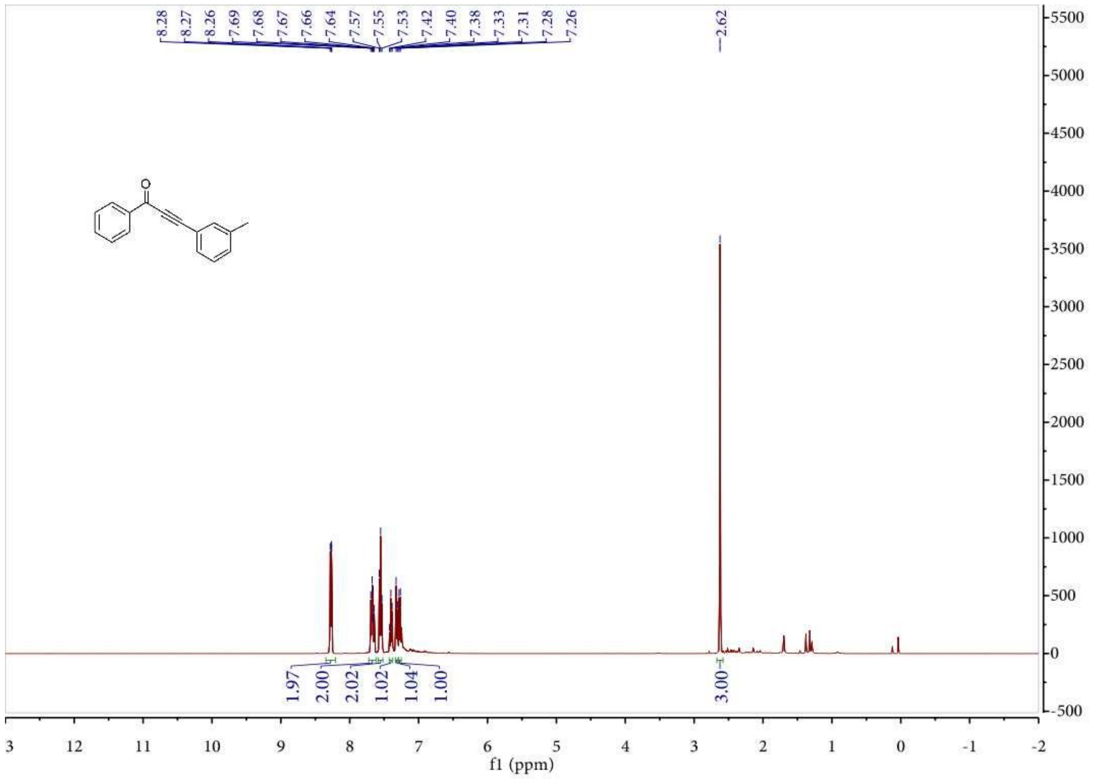
-10
f1 (ppm)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7.53
7.42
7.40
7.38
7.33
7.31
7.28
7.26
2.62
O
1.97
2.00
2.02
1.02
1.04
1.00
3.00
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
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3
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10
9
8
7
6
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4
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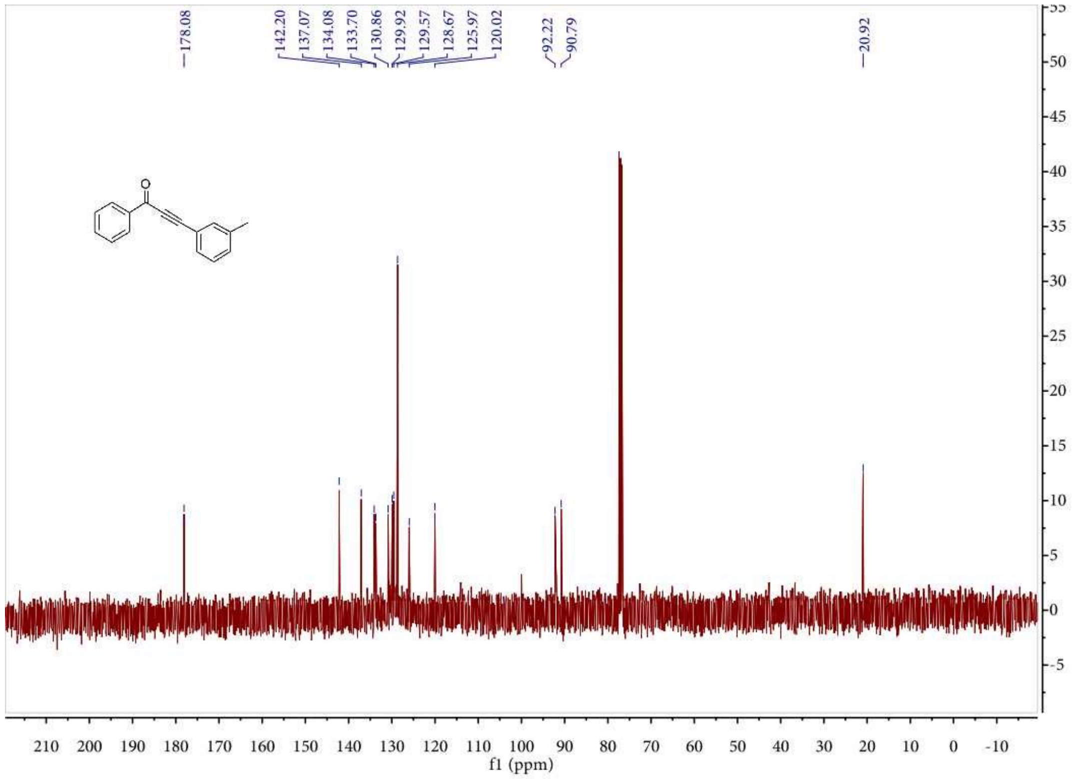
2
1
0
-1
-2
f1 (ppm)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129.57
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125.97
120.02
92.22
90.79
20.92
O
55
50
45
40
35
30
25
20
15
10
5
0
-5
210
200
190
180
170
160
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140
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100
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80
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60
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40
30
20
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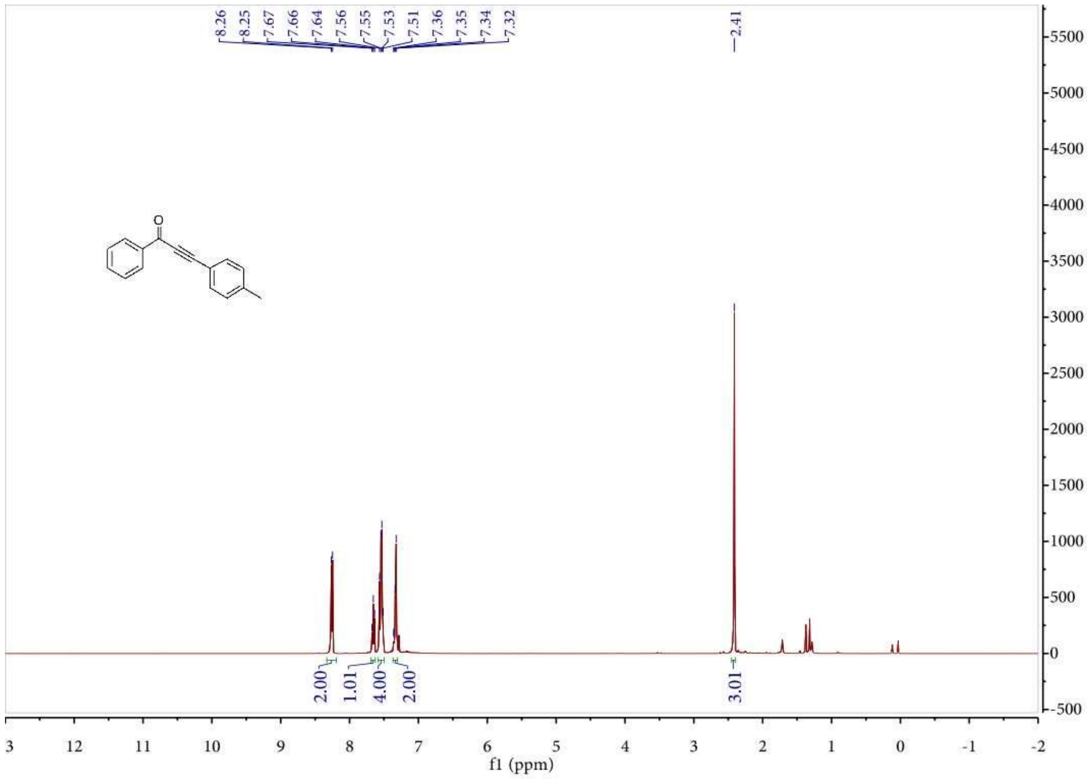
0
-10
f1 (ppm)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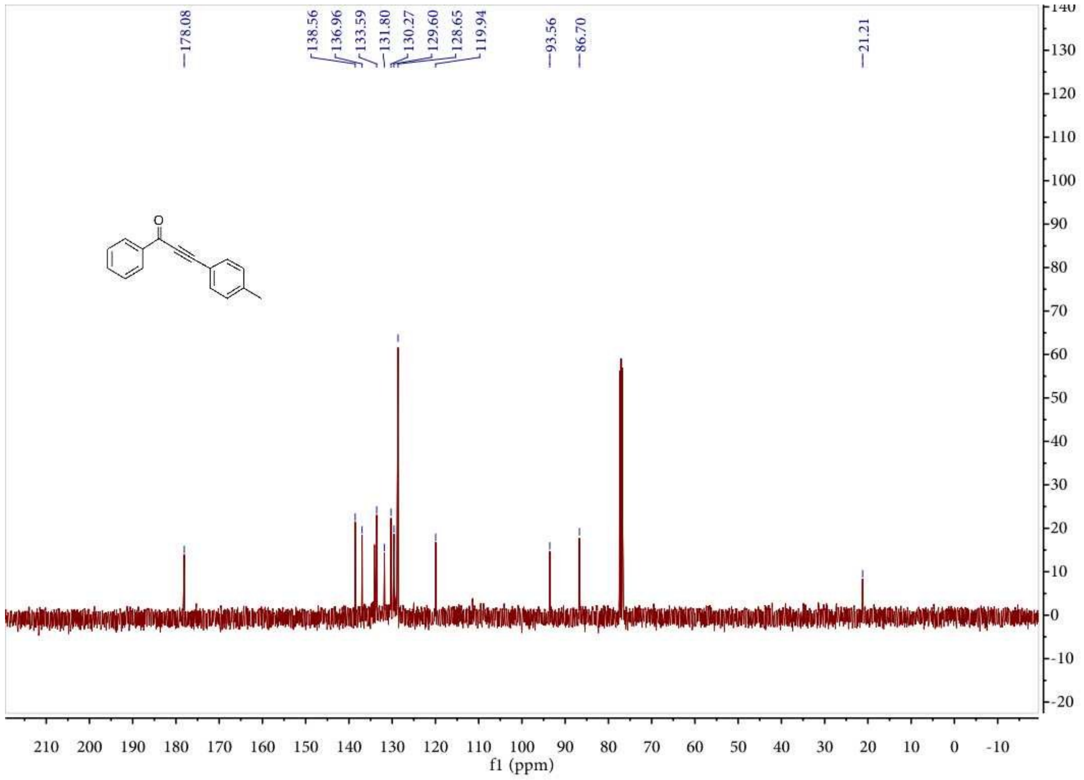
7.56
7.55
7.53
7.51
7.36
7.35
7.34
7.32
2.41
O
2.00
1.01
4.00
2.00
3.01
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
3
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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130.27
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93.56
86.70
21.21
O
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
210
200
190
180
170
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100
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80
70
60
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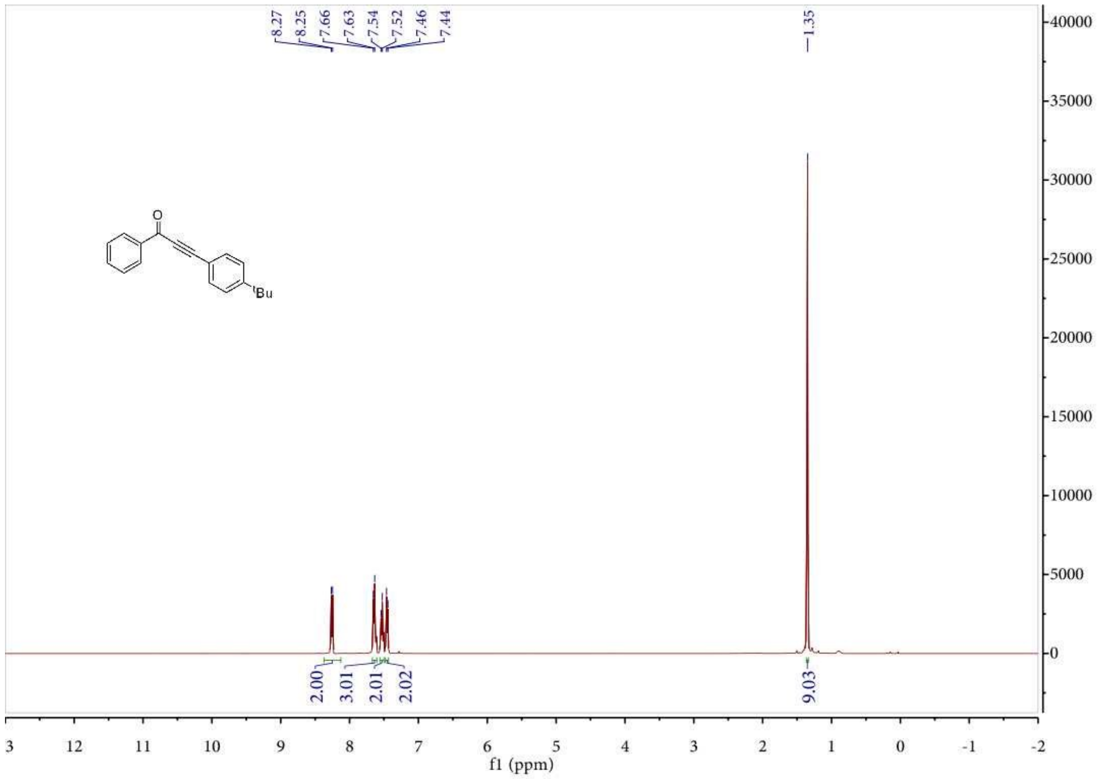
30
20
10
0
-10
f1 (ppm)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8.25
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7.52
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7.44
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2.00
3.01
2.01
2.02
9.03
O
tBu
40000
35000
30000
25000
20000
15000
10000
5000
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3
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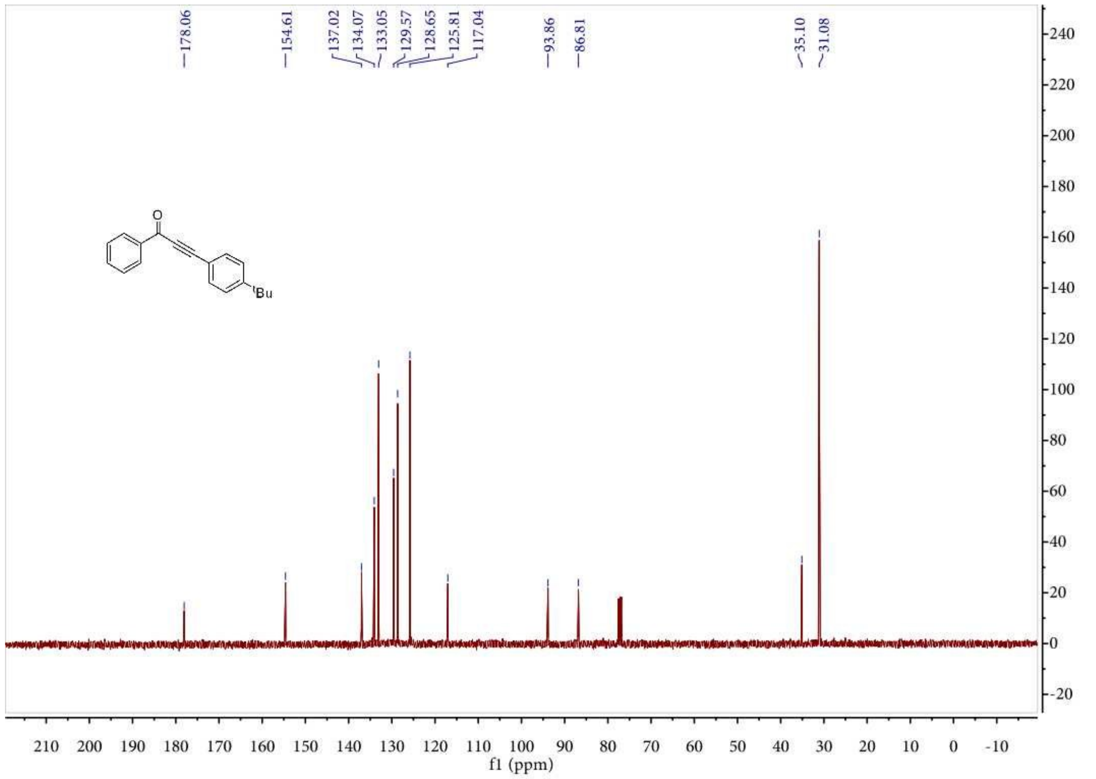
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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154.61
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133.05
129.57
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117.04
93.86
86.81
35.10
31.08
O
tBu
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210
200
190
180
170
160
150
140
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120
110
100
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80
70
60
50
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30
20
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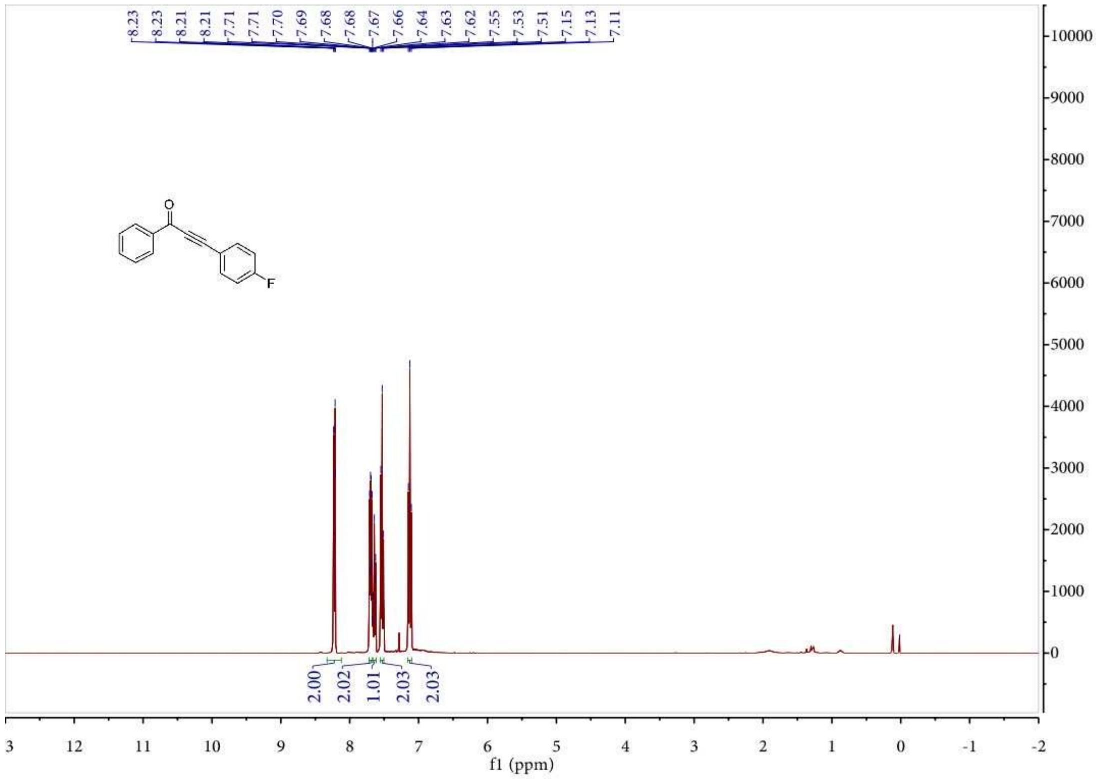
f1 (ppm)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7.69
7.68
7.68
7.67
7.66
7.64
7.63
7.62
7.55
7.53
7.51
7.15
7.13
7.11
O
F
2.00
2.02
1.01
2.03
2.03
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
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10
9
8
7
6
5
4
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2
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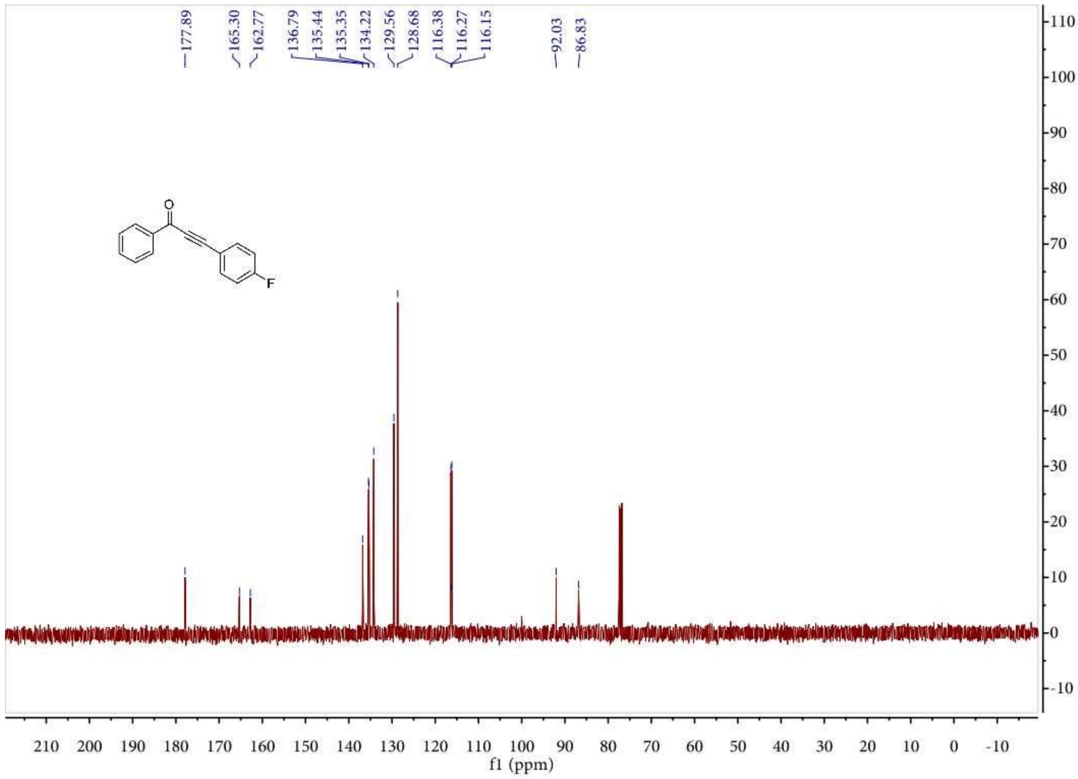
0
-1
-2
f1 (ppm)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135.35
134.22
129.56
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116.38
116.27
116.15
92.03
86.83
O
F
110
100
90
80
70
60
50
40
30
20
10
0
-10
210
200
190
180
170
160
150
140
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120
110
100
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80
70
60
50
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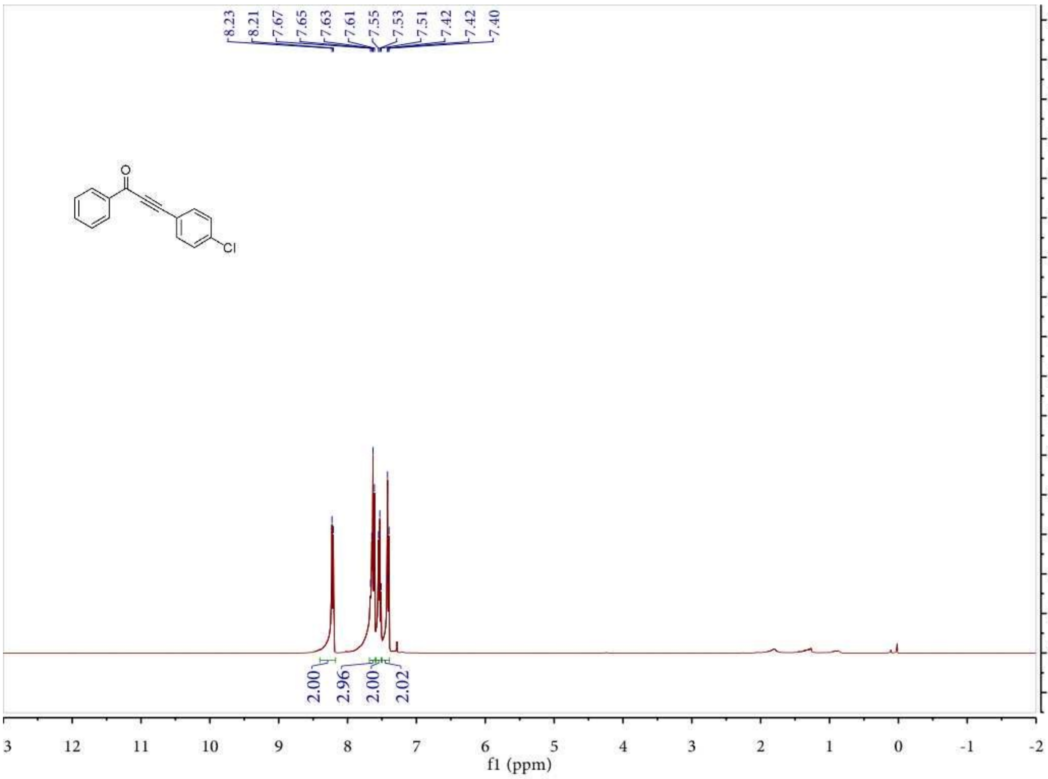
30
20
10
0
-10
f1 (ppm)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7.53
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7.42
7.42
7.40
O
Cl
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2.96
2.00
2.02
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
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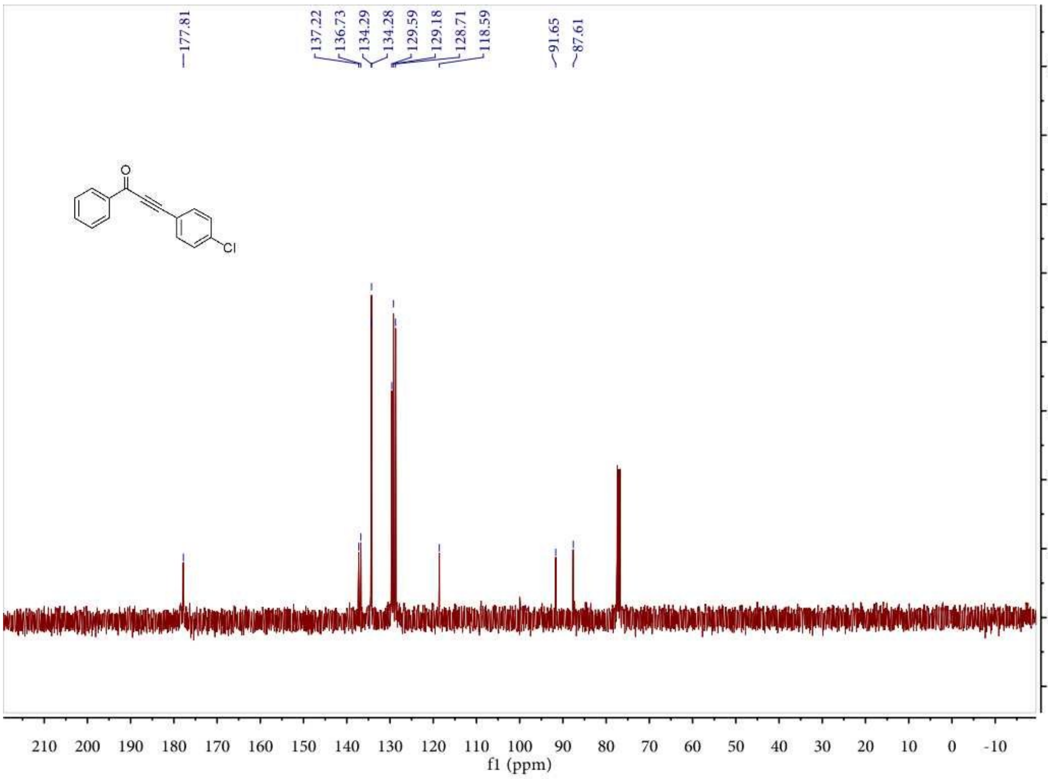
3
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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87.61
O
Cl
80
70
60
50
40
30
20
10
0
-10
210
200
190
180
170
160
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140
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120
110
100
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80
70
60
50
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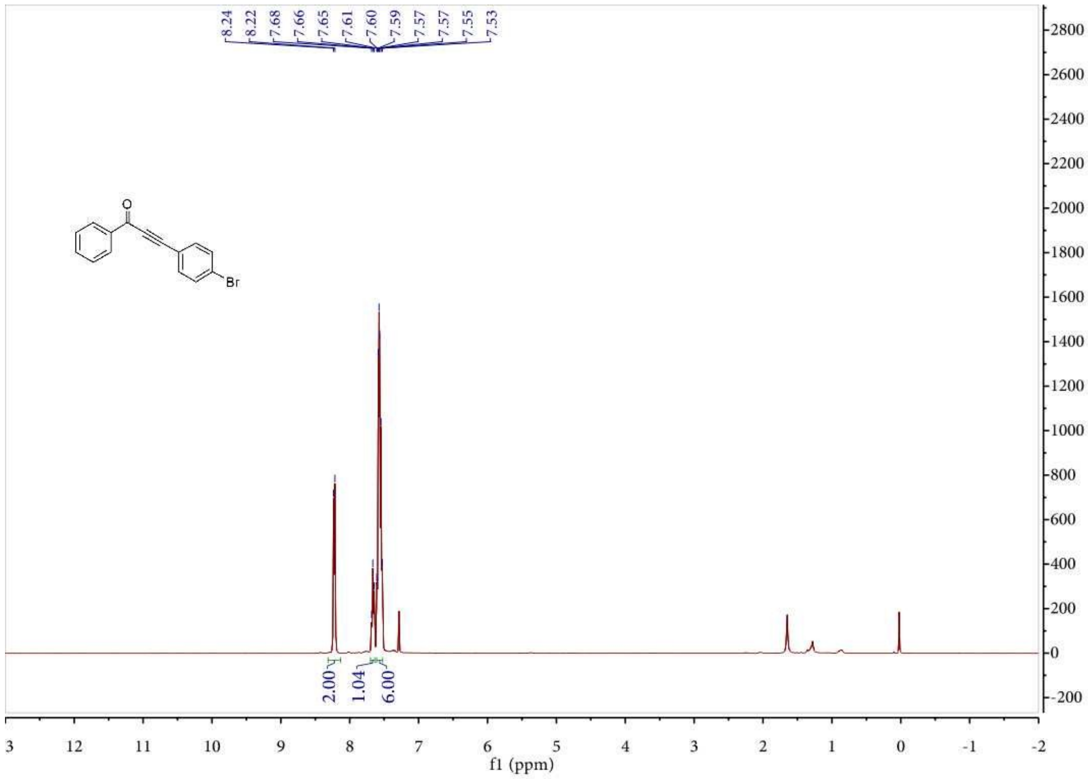
30
20
10
0
-10
f1 (ppm)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7.61
7.60
7.59
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7.57
7.55
7.53
O
Br
2.00
1.04
6.00
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
3
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11
10
9
8
7
6
5
4
3
2
1
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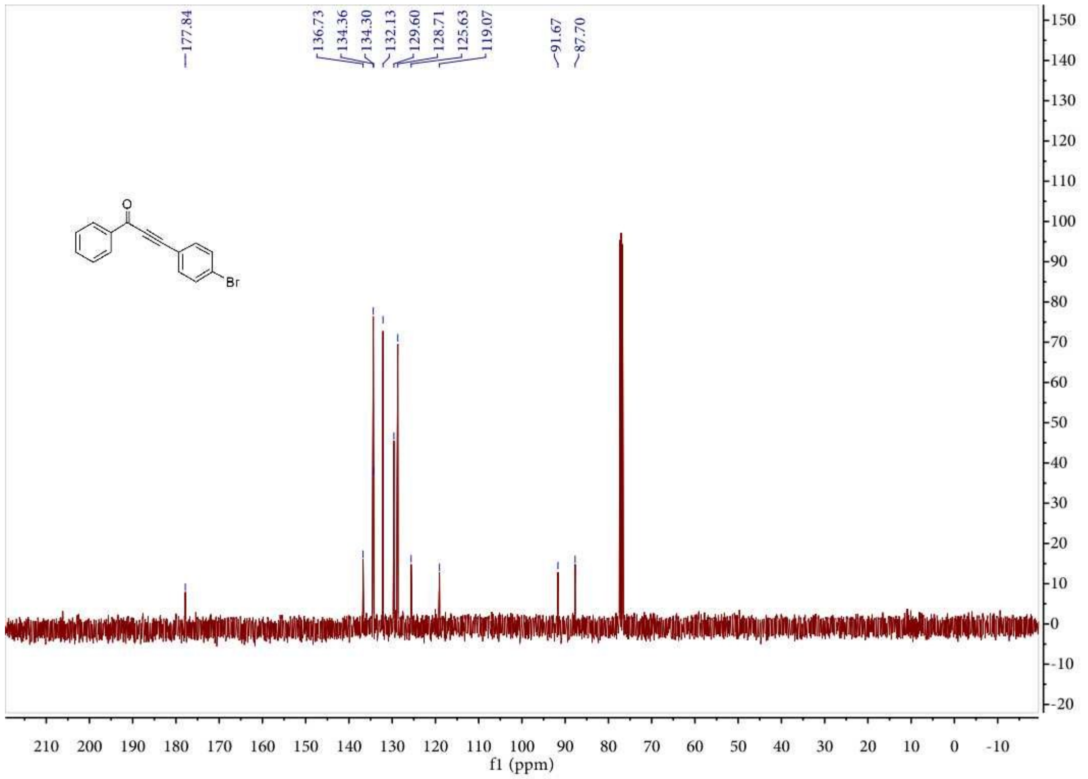
-2
f1 (ppm)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91.67
87.70
O
Br
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140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
210
200
190
180
170
160
150
140
130
120
110
100
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80
70
60
50
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30
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10
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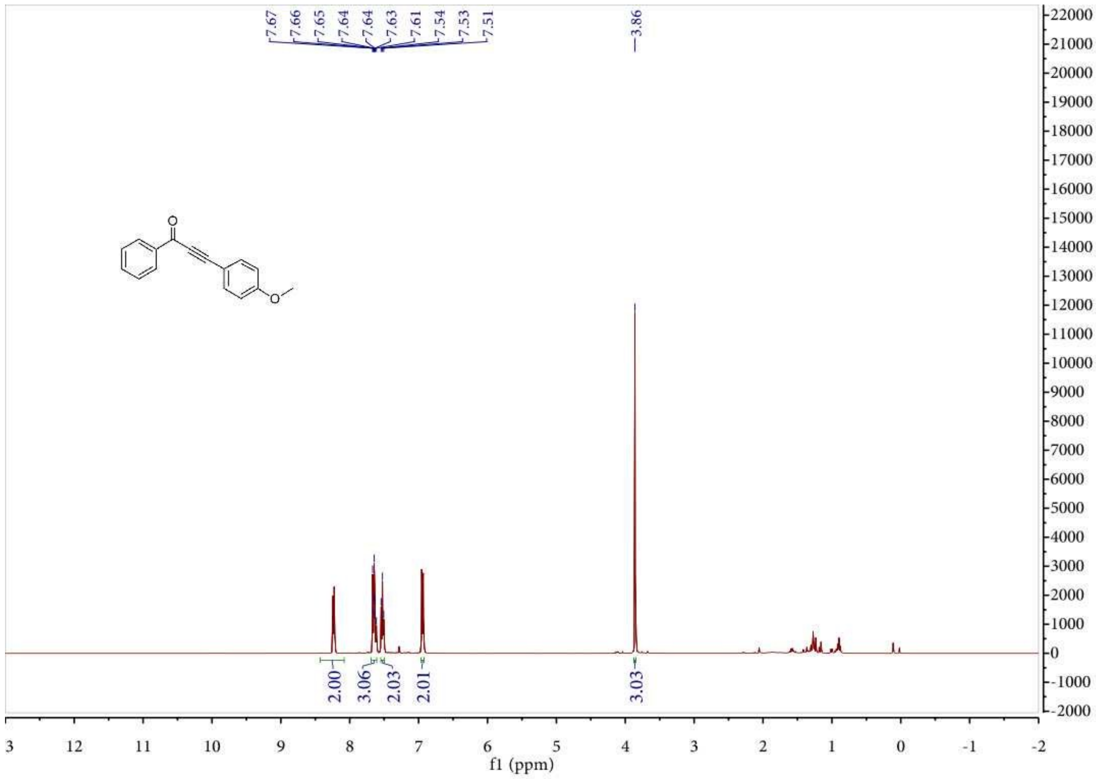
-10
f1 (ppm)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7.51
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O
2.00
3.06
2.03
2.01
3.03
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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3
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10
9
8
7
6
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4
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2
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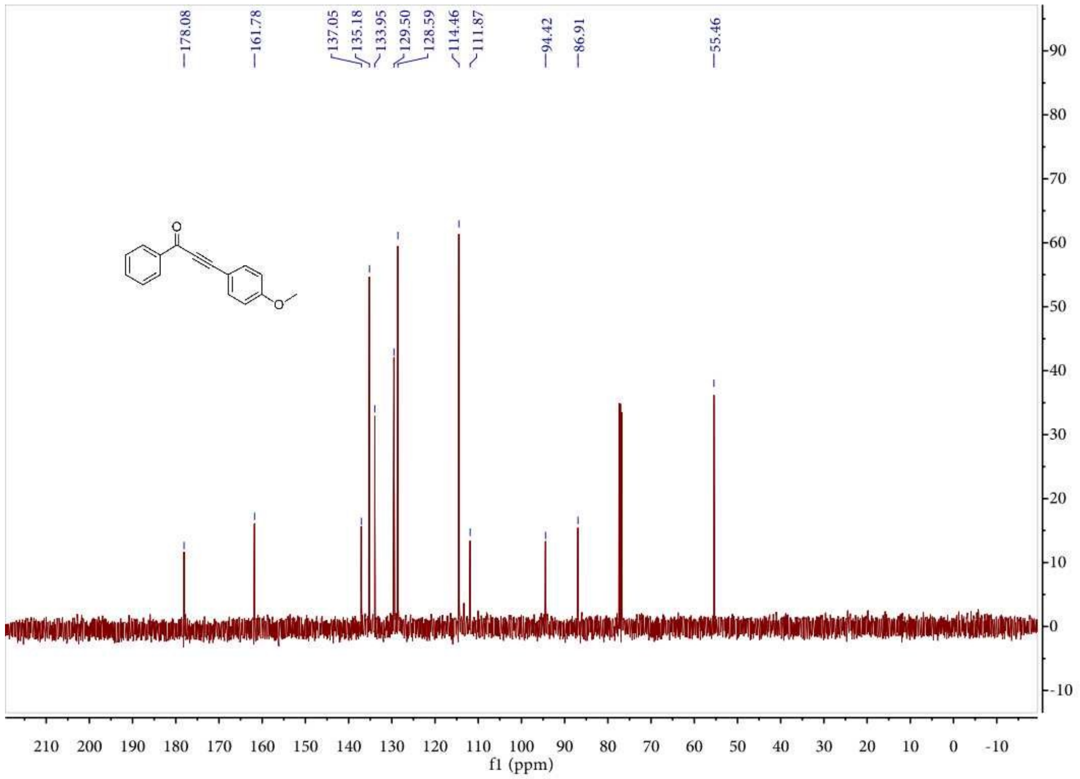
-2
f1 (ppm)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55.46
O
O
90
80
70
60
50
40
30
20
10
0
-10
210
200
190
180
170
160
150
140
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120
110
100
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80
70
60
50
40
30
20
10
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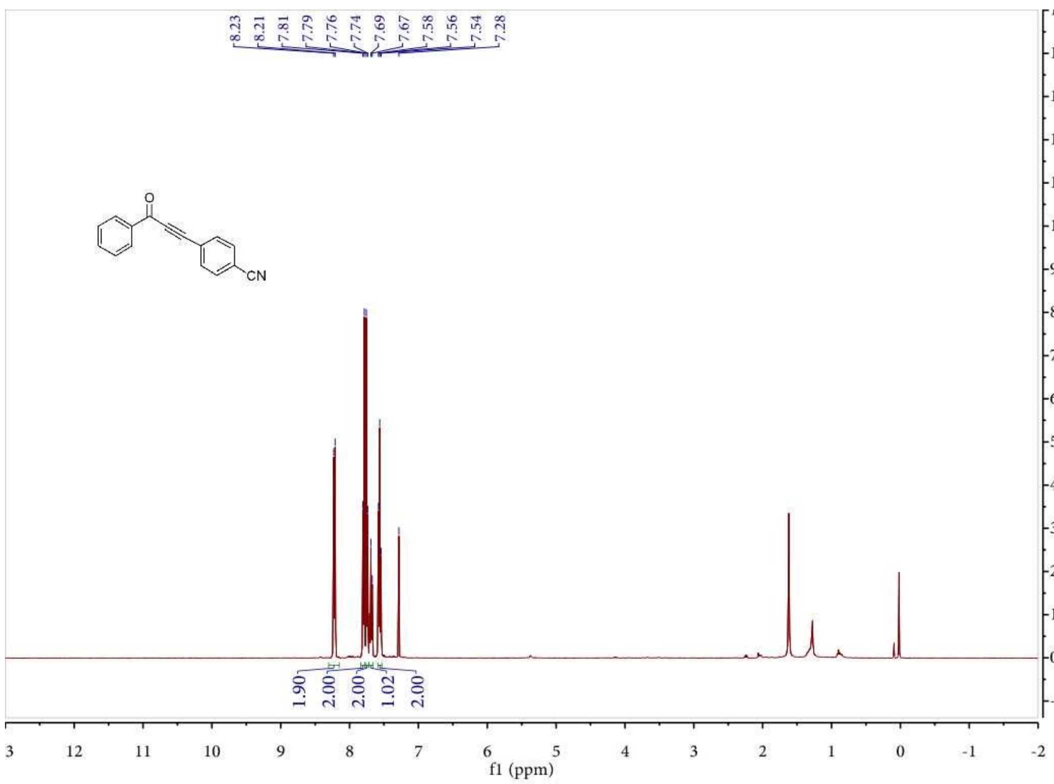
-10
f1 (ppm)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7.67
7.58
7.56
7.54
7.28
O
CN
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2.00
2.00
1.02
2.00
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
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3
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10
9
8
7
6
5
4
3
2
1
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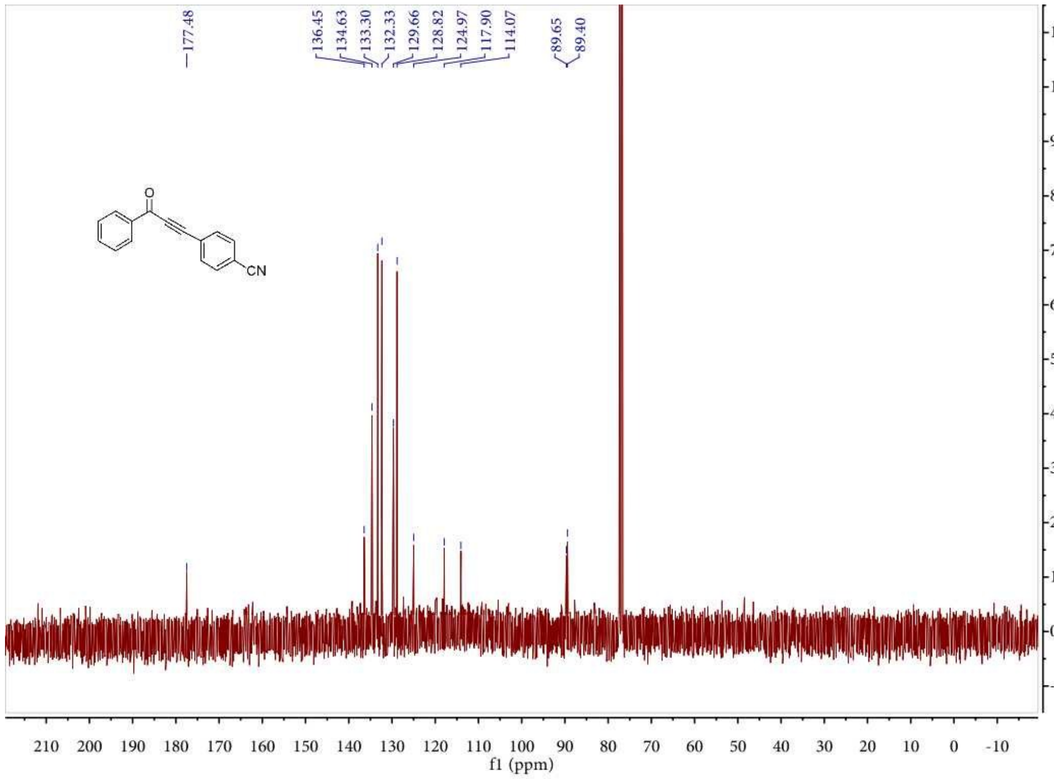
-2
f1 (ppm)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114.07
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89.40
O
CN
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100
90
80
70
60
50
40
30
20
10
0
-10
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200
190
180
170
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140
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100
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80
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60
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30
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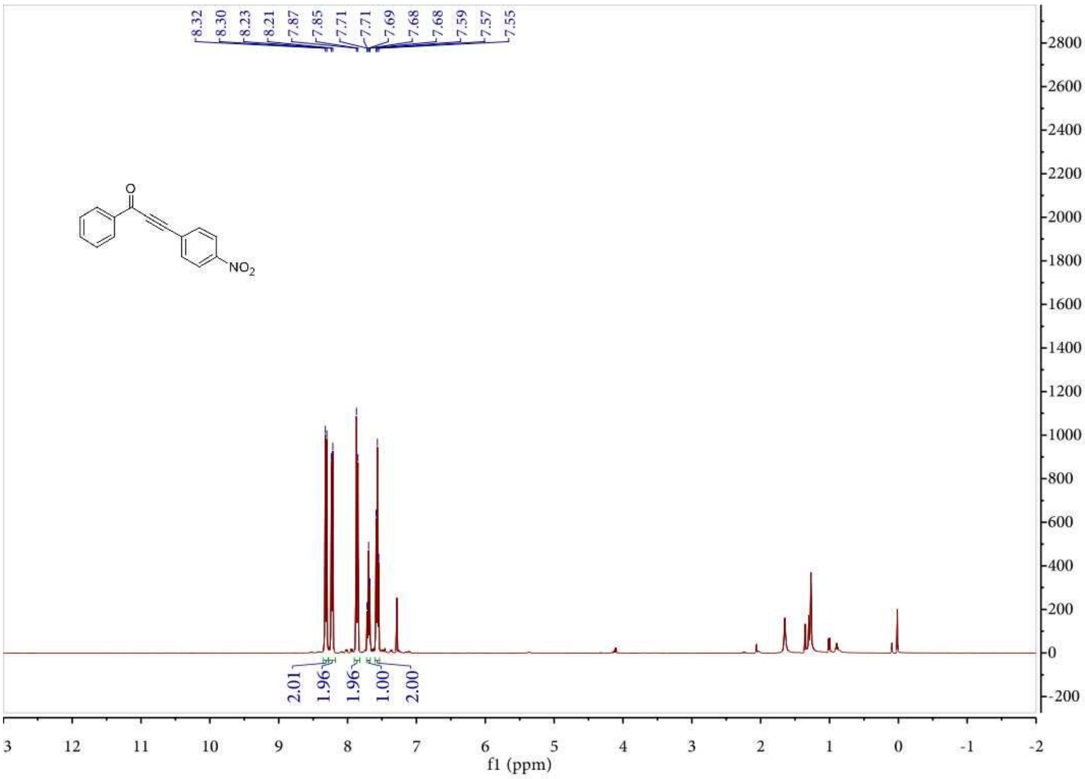
-10
f1 (ppm)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7.59
7.57
7.55
O
NO_2
2.01
1.96
1.96
1.00
2.00
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
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3
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10
9
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7
6
5
4
3
2
1
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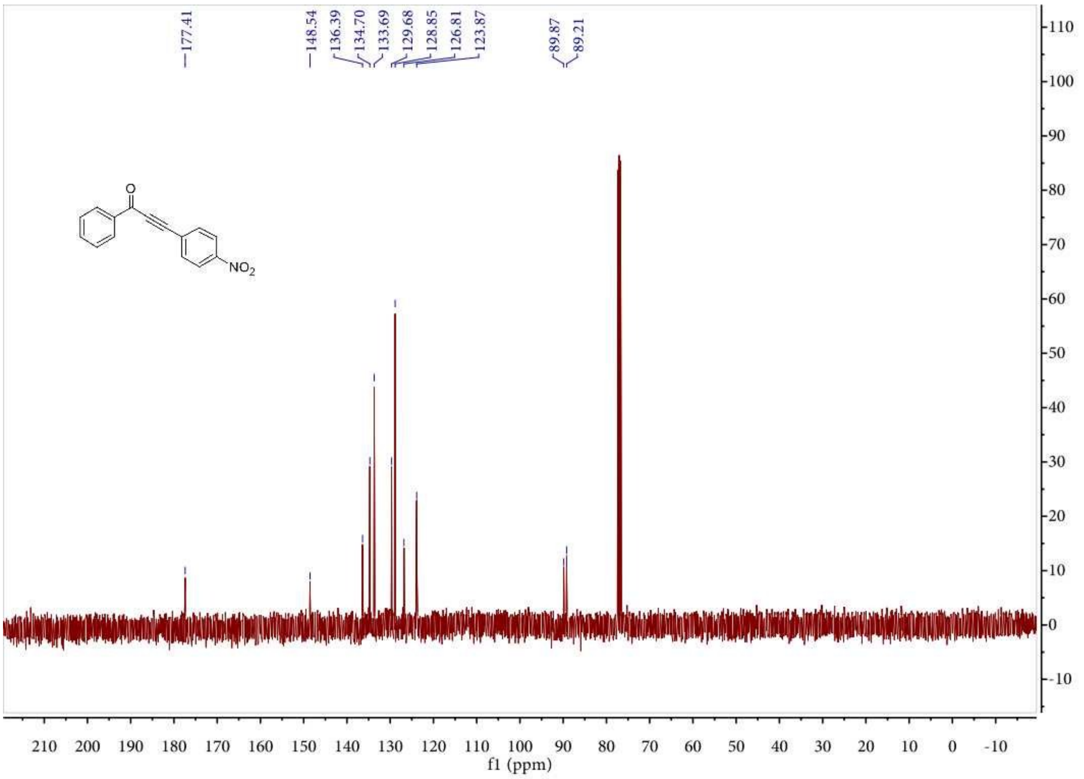
-1
-2
f1 (ppm)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89.87
89.21
O
NO_2
110
100
90
80
70
60
50
40
30
20
10
0
-10
210
200
190
180
170
160
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140
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120
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100
90
80
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60
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30
20
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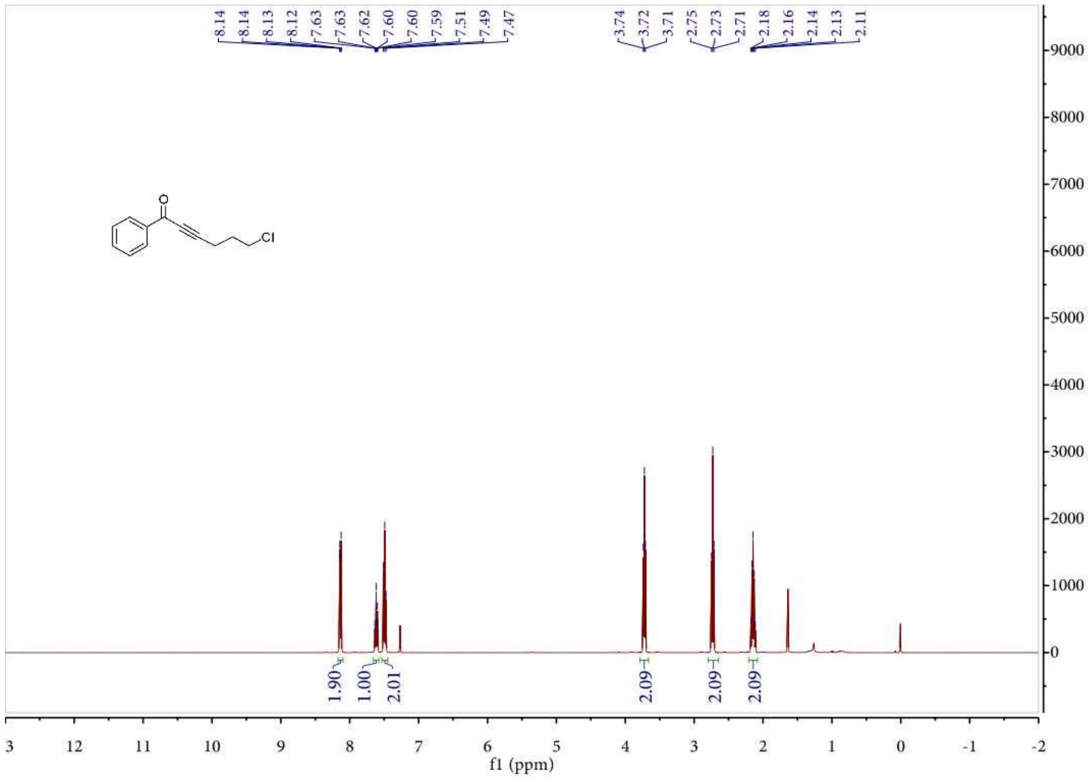
0
-10
f1 (ppm)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7.47
3.74
3.72
3.71
2.75
2.73
2.71
2.18
2.16
2.14
2.13
2.11
O
Cl
1.90
1.00
2.01
2.09
2.09
2.09
9000
8000
7000
6000
5000
4000
3000
2000
1000
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11
10
9
8
7
6
5
4
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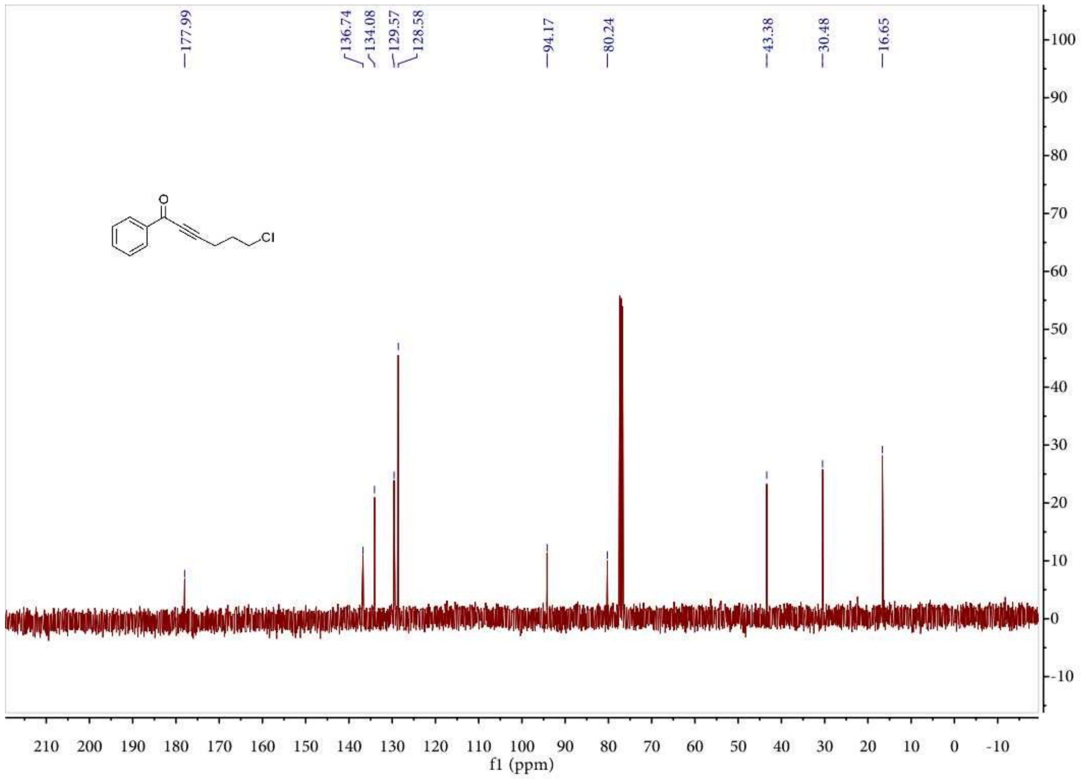
2
1
0
-1
-2
f1 (ppm)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80.24
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30.48
16.65
O
Cl
100
90
80
70
60
50
40
30
20
10
0
-10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)