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Supporting Information

Iron-Catalyzed Peroxidation-Carbamoylation of Alkenes with Hydroperoxides and Formamides via Formyl C(sp^2)-H Functionalization

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General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received.

The *tert*-butyl hydroperoxide solution (5.5 M in decane, over molecular sieve 4Å) and iron(III) chloride (reagent grade, 97%) were purchased from Sigma-Aldrich.

Thin layer chromatography was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. Other visualization method was staining with a basic solution of potassium permanganate, followed by heating.

Flash column chromatography was performed using Merck silica gel 60 with analytical grade solvents as eluents.

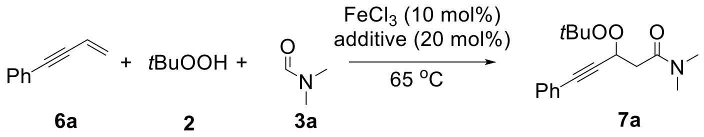
^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Corresponding chemical shifts are reported in ppm downfield relative to TMS and were referenced to the signal of chloroform-d (δ=7.26, singlet). Multiplicities were given as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, dd=doublets of doublet, td= triplet of doublet. Values of coupling constant are reported as J in Hz.

HRMS spectra were recorded on a Waters Q–Tof Permier Spectrometer.

CAUTION: No safety issue was encountered in handling the compounds described in this work. However, extra precaution should be taken when working with peroxides as mixture of peroxides and metal salts or metals may cause explosion. Exposure of neat peroxides with heat should be avoided, too.

Optimization of Reaction Condition:

Table S1 Effect of additives on the reaction of **6a** with DMF [a,b]



entry	additive (20 mol%)	time (h)	yield (%)
1	-	1	42
2	**$PhCO_2H$**	**1.25**	**51**
3	$Zn(OTf)_2$	3	36
4	$AlCl_3$	3	40
5	$InCl_3$	1	38
6	LiOAc	1.5	42
7	K_2CO_3	3	37
8	$HNEt_2$	3	38
9	DBU	3	34
10	4,-nitrobenzoic acid	1.25	35
11	2,4-dimethoxybenzoic acid	1.25	46
12	PivOH	8	<10

[a]Reaction conditions: enyne **6a** (0.30 mmol), **2** (1.2 mmol), **3a** (1.0 mL), 65 ℃, air. [b]Isolated yields.

General procedure for the synthesis of *β*-peroxy amides 4a-4e, 4g, 5a-5g, 7k&7k' (GP1):

To a mixture of the alkene (0.50 mmol, 1 equiv.) in 1.6 mL of formamide was added the iron (III) chloride (0.05 mmol, 10 mol%) and PhCOOH (0.10 mmol, 20 mol%). TBHP (5.5 M in decane, 2.0 mmol, 4 equiv.) was then added dropwise to the stirring reaction mixture. The reaction mixture was stirred at 65 ℃ until the starting material spot was observed to disappear from TLC. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and washed with water. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine before removal of the solvent under reduced pressure. The crude reaction mixture was subjected to flash column chromatography and the pure product was isolated with hexane /ethyl acetate.

General procedure for the synthesis of *β*-peroxy amides 4f, 4h (GP2):

To a mixture of the styrene (0.5 mmol, 1 equiv.) in 1.6 mL of DMSO was added the iron (III) chloride (0.05 mmol, 10 mol%), $PhCO_2H$ (0.10 mmol, 20 mol%) and formamide (6.0 mmol, 12 equiv.). TBHP (5.5 M in decane, 2.0 mmol, 4 equiv.) was then added dropwise to the stirring reaction mixture. The reaction mixture was stirred at 65 ℃. Upon completion of reaction and cooling to room temperature, the reaction mixture was diluted with ethyl acetate and washed with water. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine before removal of the solvent under reduced pressure. The crude reaction mixture was subjected to flash column chromatography and the pure product was isolated with hexane / ethyl acetate.

General procedure for the synthesis of ***β***-peroxy amides 7a-7j, 7l-7o, 7q (GP3):

To a mixture of the enyne (0.3 mmol, 1 equiv.) in 1.0 mL of formamide was added the iron (III) chloride (0.03 mmol, 10 mol%) and $PhCO_2H$ (0.06 mmol, 20 mol%). TBHP (5.5 M in decane, 1.2 mmol, 4 equiv.) was then added dropwise to the stirring reaction mixture. The reaction mixture was stirred at 65 ℃ until the starting material spot was observed to disappear from TLC (i.e. 1.25 h). After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and washed with water. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine before removal of the solvent under reduced pressure. The crude reaction mixture was subjected to flash column chromatography and the pure product was isolated with hexane / ethyl acetate.

General Procedure for the synthesis of ***β***-peroxy amides 7p, 7r (GP4):

To a mixture of the enyne (0.3 mmol, 1 equiv.) in 1.0 mL of DMSO was added the iron (III) chloride (0.03 mmol, 10 mol%), $PhCO_2H$ (0.06 mmol, 20 mol%) and formamide (3.6 mmol, 12 equiv.). TBHP (5.5 M in decane, 1.2 mmol, 4 equiv) was then added dropwise to the stirring reaction mixture. The reaction mixture was stirred at 65 ℃ until the starting material spot was observed to disappear from TLC (i.e. 1.25 h). After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and washed with water. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine before removal of the solvent under reduced pressure. The crude reaction mixture was subjected to flash column chromatography and the pure product was isolated with hexane / ethyl acetate.

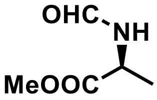
Procedure for the preparation of *N*-formyl-L-alanine methyl ester:[1,2]

Acetic formic anhydride was first prepared by heating the stirring solution of acetic anhydride (30.8 mmol, 1 equiv.) and formic acid (33.9 mmol, 1.1 equiv.) at 55 ℃ overnight. The resulting solution was used directly after cooling to room temperature.

The solution of L-alanine methyl ester hydrochloride salt (14 mmol) in $CHCl_3$ (10 mL) was added dropwise a solution of NEt_3 (14 mmol) in $CHCl_3$ (10 mL). The reaction mixture was then stirred at room temperature for 5 h before heated at 70 ℃ for 1 h. After cooling to room temperature, the volatiles were removed in vacuo to give white solid, which was then diluted with diethyl ether. The mixture was then filtered with with further washing using diethyl ether. Removal of the ether filtrate in vacuo gave the L-alanine methyl ester as yellow oil, which was used for next step without further purification.

To a stirring solution of L-alanine methyl ester (14 mmol) in DCM (35 mL) cooled to 0 ℃ in ice water bath, acetic formic anhydride was added dropwise, after which the mixture was stirred for overnight at room temperature. All volatiles were removed in vacuo to give N-formyl-L-alanine methyl ester as yellow oil in 78% yield.

Methyl formyl-L-alaninate



^{1}H NMR: (CDCl$_3$, 400 MHz): δ 8.14 (s, 1H); 6.60 (br, 1H); 4.70-4.59 (m, 1H); 3.73 (s, 3H); 1.40 (d, J = 7.2, 3H)

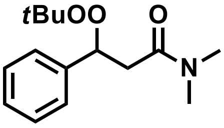
^{13}C NMR: (CDCl$_3$, 100 MHz): δ 173.07, 160.73, 52.56, 46.74, 18.28

HRMS (ESI): $C_5H_{10}NO_3$: Calculated: 132.0661; found: 132.0663

$[\alpha]_D^{22.6} = -30.5^\circ\ (c = 0.65, EtOAc)$; {lit.[3] $[\alpha]_D^{20} = -35.6^\circ\ (c = 0.65, EtOAc)$}

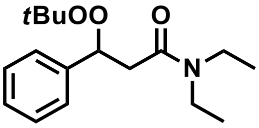
Spectral data for 4a-4i, 5a-5g, 7a-7R

3-(*tert*-Butylperoxy)-*N*,*N*-dimethyl-3-phenylpropanamide (4a)



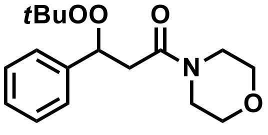
The title compound was prepared according to **GP1** and isolated as slowly solidifying colourless oil after purification by flash column chromatography. 63% (5 h). **^{1}H NMR:** (CDCl$_3$, 400 MHz): δ 7.44-7.26 (m, 5H); 5.44 (t, J = 6.8 Hz, 1H); 3.08 (dd, J = 7.2, 14.8 Hz, 1H); 3.12-2.90 (m, 6H); 2.63 (dd, J = 6.4, 14.8 Hz, 1H); 1.22 (s, 9H). **^{13}C NMR:** (CDCl$_3$, 100 MHz): δ 170.15, 140.40, 128.34, 127.97, 126.97, 83.33, 80.75, 38.87, 37.58, 35.50, 26.41. **HRMS (ESI):** $C_{15}H_{24}NO_3$: Calculated: 266.1756; found: 266.1757

3-(*tert*-Butylperoxy)-*N*,*N*-diethyl-3-phenylpropanamide (4b)



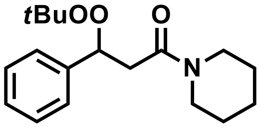
The title compound was prepared according to **GP1** and was obtained after flash column chromatography as colourless oil. 74% (3 h). **^{1}H NMR:** (CDCl$_3$, 400 MHz): δ 7.42-7.26 (m, 5H); 5.49 (t, J= 6.8 Hz, 1H); 3.47-3.13 (m, 4H); 3.01 (dd, J = 7.6, 14.8 Hz, 1H); 2.58 (dd, J = 6.2, 14.6 Hz, 1H); 1.22 (s, 9H); 1.14-1.05 (m, 6H). **^{13}C NMR:** (CDCl$_3$, 100 MHz): δ 169.18, 140.61, 128.31, 127.85, 126.86, 83.38, 80.82, 42.23, 40.45, 38.91, 26.42, 14.39, 13.05. **HRMS (ESI):** $C_{17}H_{28}NO_3$: Calculated: 294.2069; found: 294.2068.

3-(*tert*-Butylperoxy)-1-morpholino-3-phenylpropan-1-one (4c)



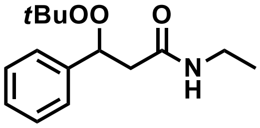
The title compound was prepared according to **GP1** and was obtained after flash column chromatography as colourless oil. 47% (3 h). **^{1}H NMR:** (CDCl$_3$, 400 MHz): δ 7.40-7.26 (m, 5H); 5.42 (t, *J* = 6.8 Hz, 1H); 3.73-3.32 (m, 8H); 3.08 (dd, *J* = 7.0, 14.6 Hz, 1H); 2.65 (dd, *J* = 6.6, 14.6 Hz, 1H); 1.22 (s, 9H). **^{13}C NMR:** (CDCl$_3$, 100 MHz): δ 168.81, 139.92, 128.41, 128.17, 126.96, 83.28, 80.84, 66.76, 66.50, 46.42, 42.01, 38.29, 26.42. **HRMS (ESI):** $C_{17}H_{26}NO_4$: Calculated: 308.1862; found: 308.1860.

3-(*tert*-Butylperoxy)-3-phenyl-1-(piperidin-1-yl)propan-1-one (4d)



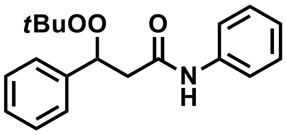
The title compound was prepared according to **GP1** and was obtained after flash column chromatography as colourless oil. 47% (4 h). **^{1}H NMR:** (CDCl$_3$, 400 MHz): δ 7.42-7.22 (m, 5H); 5.44 (t, *J* = 6.6 Hz, 1H); 3.61-3.53 (m, 1H); 3.50-3.34 (m, 3H); 3.07 (dd, *J* = 7.2, 14.8 Hz, 1H); 2.65 (dd, *J* = 6.8, 14.8 Hz, 1H); 1.62-1.32 (m, 6H); 1.22 (s, 9H). **^{13}C NMR:** (CDCl$_3$, 100 MHz): δ 168.11, 140.32, 128.24, 127.87, 126.95, 83.25, 80.63, 47.00, 42.70, 38.39, 26.37, 26.28, 25.43, 24.43. **HRMS (ESI):** $C_{18}H_{28}NO_3$: Calculated: 306.2069; found: 306.2075.

3-(*tert*-Butylperoxy)-*N*-ethyl-3-phenylpropanamide (4e)



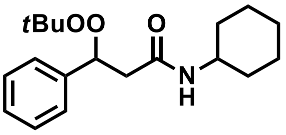
The title compound was prepared according to **GP1** and was obtained after flash column chromatography as colourless oil. 73% (4 h) **^{1}H NMR:** (CDCl$_3$, 400 MHz): δ 7.37-7.26 (m, 5H); 5.79 (br, 1H); 5.32 (dd, *J* = 5.0, 8.2 Hz, 1H); 3.33-3.22 (m, 2H); 2.76 (dd, *J* = 8.4, 14.8 Hz, 1H); 2.55 (dd, *J* = 5.0, 14.6 Hz, 1H); 1.21 (s, 9H); 1.08 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR:** (CDCl$_3$, 100 MHz): δ 169.74, 139.83, 128.23, 127.91, 126.64, 82.46, 80.69, 42.44, 34.26, 26.28, 14.56. **HRMS (ESI):** $C_{15}H_{24}NO_3$: Calculated: 266.1756; found: 266.1762.

3-(*tert*-Butylperoxy)-*N*,3-diphenylpropanamide (4f)



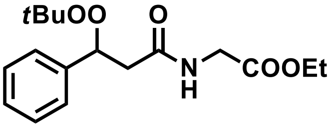
The title compound was prepared according to **GP2** and was obtained after flash column chromatography as pale yellow solid. 48% (3 h); m.p.: 92-93 ℃. **^{1}H NMR:** (CDCl$_3$, 400 MHz): δ 7.80 (br, 1H); 7.50-7.45 (m, 2H); 7.44-7.26 (m, 7H); 7.15-7.05 (m, 1H); 5.39 (dd, *J* = 4.4, 8.0 Hz, 1H); 2.97 (dd, *J* = 8.0, 14.8 Hz, 1H); 2.82 (dd, *J* = 4.4, 15.2 Hz, 1H); 1.23 (s, 9H). **^{13}C NMR:** (CDCl$_3$, 100 MHz): δ 168.37, 139.30, 137.94, 128.93, 128.48, 128.30, 126.84, 124.18, 119.91, 82.49, 81.06, 43.21, 26.42. **HRMS (ESI):** $C_{19}H_{24}NO_3$: Calculated: 314.1756; found: 314.1755.

3-(*tert*-Butylperoxy)-*N*-cyclohexyl-3-phenylpropanamide (4g)



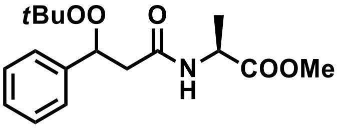
The title compound was prepared according to **GP1** and was obtained after flash column chromatography as white solid. 65% (5 h); m.p.: 105-106 ℃. **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 7.37-7.24 (m, 5H); 5.73 (br, 1H); 5.30 (dd, *J* = 5.0, 8.2 Hz, 1H); 3.78-3.66 (m, 1H); 2.74 (dd, *J* = 8.2, 14.6 Hz, 1H); 2.53 (dd, *J* = 5.2, 14.8 Hz, 1H); 1.94-1.87 (m, 1H); 1.80-1.54 (m, 4H); 1.40-0.94 (m, 14 H) **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 168.73, 139.89, 128.29, 127.98, 126.73, 82.53, 80.74, 48.01, 42.74, 33.02, 32.91, 26.39, 25.48, 24.72, 24.68 **HRMS (ESI):** $C_{19}H_{30}NO_3$: Calculated: 320.2226; found: 320.2223.

Ethyl (3-(*tert*-butylperoxy)-3-phenylpropanoyl)glycinate (4h)



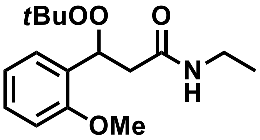
The title compound was prepared according to **GP2** and was obtained after flash column chromatography as colourless oil. 54% (5 h) **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 7.37-7.26 (m, 5H); 6.39 (br, 1H); 5.33 (dd, *J* = 5.2, 8.0 Hz, 1H); 4.20 (q, *J* = 7.1 Hz, 2H); 4.01 (d, *J* = 4.8 Hz, 2H); 2.89 (dd, *J* = 8.0, 14.8 Hz, 1H); 2.66 (dd, *J* = 5.0, 15.0 Hz, 1H); 1.27 (t, *J* = 7.2 Hz, 3H); 1.20 (s, 9H) **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 170.06, 169.77, 139.56, 128.41, 128.18, 126.87, 82.23, 80.83, 61.49, 41.95, 41.53, 26.38, 14.14 **HRMS (ESI):** $C_{17}H_{26}NO_5$: Calculated: 324.1811; found: 324.1818.

Methyl (3-(*tert*-butylperoxy)-3-phenylpropanoyl)alaninate (4i)



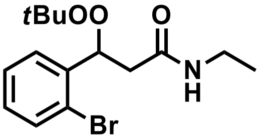
The title compound was prepared according to **GP2** and was obtained after flash column chromatography as pale yellow oil. d.r. was approximated as 1:1 from ^{13}C NMR. 40% (5 h). **^{1}H NMR:** ($CDCl_3$, 400 MHz, 2 diastereomers): δ 7.40-7.26 (m, 5H); 6.48-6.34 (br, 1H); 5.34-5.29 (m, 1H); 4.62-4.53 (m, 1H); 3.74-3.72 (2s, 3H); 2.89 (dd, *J* = 7.6, 14.4 Hz, 1H, 1 diastereomer); 2.81 (dd, *J* = 8.8, 14.8 Hz, 1H, 1 diastereomer); 2.64-2.59 (m, 1H); 1.41 (d, *J* = 7.2 Hz, 3H, 1 diastereomer); 1.27 (d, *J* = 7.2 Hz, 3H, 1 diastereomer); 1.21-1.20 (2s, 9H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 173.32, 169.40, 169.25, 139.72, 139.53, 128.33, 128.11, 128.06, 126.83, 126.79, 82.27, 82.23, 80.80, 80.74, 52.36, 48.03, 47.93, 42.27, 42.09, 26.34, 18.49, 18.36. **HRMS (ESI):** $C_{17}H_{26}NO_5$: Calculated: 324.1181; found: 324.1805.

3-(*tert*-Butylperoxy)-*N*-ethyl-3-(2-methoxyphenyl)propanamide (5a)



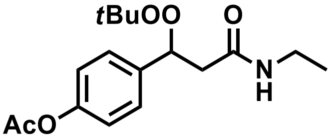
The title compound was prepared according to **GP1** and was obtained after flash column chromatography as white solid. 59% (3.5 h); m.p.: 116-117 ℃ **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 7.39 (dd, *J* = 1.4, 7.4 Hz, 1H); 7.25 (td, *J* = 1.5, 7.8 Hz, 1H); 6.96 (t, *J* = 7.6 Hz, 1H); 6.86 (d, *J* = 8.0 Hz, 1H); 6.03 (br, 1H); 5.69 (dd, *J* = 5.0, 8.2 Hz, 1H); 3.82 (s, 3H); 3.32-3.25 (m, 2H); 2.68 (dd, *J* = 4.2, 15.0 Hz, 1H); 2.61 (dd, *J* = 8.6, 15.0 Hz, 1H); 1.23 (s, 9H); 1.12 (t, *J* = 7.2 Hz, 3H) **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 170.14, 156.38, 128.78, 128.26, 127.08, 120.43, 110.47, 80.68, 55.34, 41.36, 34.33, 26.43, 14.77 **HRMS (ESI):** $C_{16}H_{26}NO_4$: Calculated: 296.1862; found: 296.1859.

3-(2-Bromophenyl)-3-(*tert*-butylperoxy)-*N*-ethylpropanamide (5b)



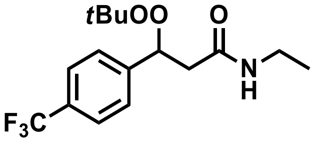
The title compound was prepared according to **GP1** and was obtained after flash column chromatography as white solid. 71% (2.5 h); m.p.: 104-105 ℃. **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 7.52-7.46 (m, 2H); 7.31 (t, J = 7.6 Hz, 1H); 7.13 (dt, *J* = 1.7, 7.7 Hz, 1H); 5.95 (br, 1H); 5.69 (dd, *J* = 3.6, 9.6 Hz, 1H); 3.35-3.26 (m, 2H); 2.65 (dd, *J* = 3.6, 15.2 Hz, 1H); 2.47 (dd, *J* = 9.6, 15.2 Hz, 1H); 1.22 (s, 9H); 1.13 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.07, 139.40, 132.80, 129.20, 127.86, 127.47, 122.32, 81.25, 81.08, 41.47, 34.46, 26.39, 14.80. **HRMS (ESI):** $C_{15}H_{23}NO_3Br$: Calculated: 346.0841; found: 346.0841.

4-(1-(*tert*-Butylperoxy)-3-(ethylamino)-3-oxopropyl)phenyl acetate (5c)



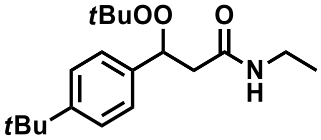
The title compound was prepared according to **GP1** and was obtained after flash column chromatography as white solid. 75% (2 h); m.p.: 86-88 ℃. **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 7.35 (d, *J* = 8.4 Hz, 2H); 7.05 (d, *J* = 8.4 Hz, 2H); 5.78 (br, 1H); 5.33 (dd, *J* = 5.0, 8.2 Hz, 1H); 3.45-3.21 (m, 2H); 2.72 (dd, *J* = 8.2, 14.6 Hz, 1H); 2.51 (dd, *J* = 5.0, 14.6 Hz,1H); 2.28 (s, 3H); 1.20 (s, 9H); 1.08 (t, *J* = 7.2 Hz,3H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.53, 169.42, 150.34, 137.59, 127.79, 121.47, 81.95, 80.93, 42.72, 34.43, 26.40, 21.14, 14.72. **HRMS (ESI):** $C_{17}H_{26}NO_5$: Calculated: 324.1811; found: 324.1807.

3-(*tert*-Butylperoxy)-*N*-ethyl-3-(4-(trifluoromethyl)phenyl)propanamide (5d)



The title compound was prepared according to **GP1** and was obtained after flash column chromatography as white solid. 77% (2 h); m.p.: 110-111 ℃. **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 7.59 (d, *J* = 8.4 Hz, 2H); 7.47 (d, *J* = 8.0 Hz, 2H); 5.80 (br, 1H); 5.40 (dd, *J* = 5.0, 8.4 Hz, 1H); 3.32-3.22 (m, 2H); 2.68 (dd, *J* = 8.4, 14.8 Hz, 1H); 2.50 (dd, *J* = 5.0, 14.6 Hz, 1H); 1.21 (s, 9H); 1.09 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.02, 144.32, 130.13 (q, $J_{C\text{-}F}$ = 32.3 Hz), 126.91, 125.36 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.10 (q, $J_{C\text{-}F}$ = 270.3 Hz), 81.84, 81.12, 42.64, 34.48, 26.36, 14.74. **HRMS (ESI):** $C_{16}H_{23}NO_3F_3$: Calculated: 334.1630; found: 334.1627.

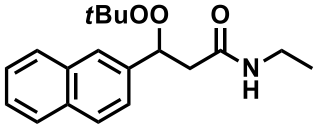
3-(4-(*tert*-Butyl)phenyl)-3-(*tert*-butylperoxy)-*N*-ethylpropanamide (5e)



The title compound was prepared according to **GP1** and was obtained after flash column chromatography as white solid. 68% (2 h); m.p.: 112-114 ℃. **^{1}H NMR:** (CDCl3, 400 MHz): δ 7.36 (d, *J* = 8.4 Hz); 7.27 (d, *J* = 8.0 Hz); 5.76 (br, 1H); 5.30 (dd, *J* = 4.8, 8.4 Hz, 1H); 3.28-3.23 (m, 2H); 2.76 (dd, *J* = 8.2, 14.6 Hz, 1H); 2.57 (dd, *J* = 5.0, 14.6 Hz, 1H); 1.31 (s, 9H); 1.22 (s, 9H); 1.06

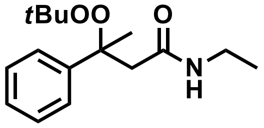
(t, J = 7.4 Hz). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.88, 150.88, 136.64, 126.42, 125.24, 82.40, 80.78, 42.54, 34.49, 34.29, 31.29, 26.38, 14.66. **HRMS (ESI):** $C_{19}H_{32}NO_3$: Calculated: 322.2382; found: 322.2379.

3-(*tert*-Butylperoxy)-*N*-ethyl-3-(naphthalen-2-yl)propanamide (5f)



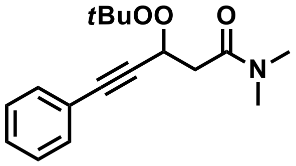
The title compound was prepared according to **GP1** and was obtained after flash column chromatography as white solid. 56% (2.5 h); m.p.: 107-109 ℃. **^{1}H NMR:** (CDCl3, 400 MHz): δ 7.85-7.81 (m, 4H); 7.50-7.44 (m, 3H); 5.89 (br, 1H); 5.51 (dd, J = 5.0, 8.2 Hz, 1H); 3.27-3.23 (m, 2H); 2.84 (dd, J = 8.2, 14.6 Hz, 1H); 2.62 (dd, J = 5.0, 14.6 Hz, 1H); 1.23 (s, 9H); 1.06 (t, J = 7.2 Hz, 3H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.63, 137.47, 133.18, 133.14, 128.17, 128.06, 127.64, 126.10, 126.00, 125.91, 124.42, 82.68, 80.88, 42.73, 34.39, 26.42, 14.70. **HRMS (ESI):** $C_{19}H_{26}NO_3$: Calculated: 316.1913; found: 316.1905.

3-(*tert*-Butylperoxy)-*N*-ethyl-3-phenylbutanamide (5g)



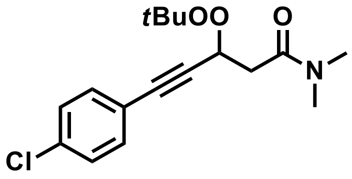
The title compound was prepared according to **GP1** and was obtained after flash column chromatography colourless oil. 64% (2 h). **^{1}H NMR:** (CDCl3, 400 MHz): δ 7.45-7.40 (m, 2H); 7.36-7.23 (m, 3H); 6.42 (br, 1H); 3.22-3.14 (m, 1H); 2.97 (d, J = 14.8 Hz, 1H); 2.89 (d, J = 14.8 Hz, 1H); 1.63 (s, 3H); 1.28 (s, 9H); 0.99 (t, J = 7.2 Hz, 3H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.92, 143.21, 128.08, 127.37, 125.27, 82.55, 79.91, 44.84, 33.98, 26.64, 25.99, 14.51. **HRMS (ESI):** $C_{16}H_{26}NO_3$: Calculated: 280.1913; found: 280.1913.

3-(*tert*-Butylperoxy)-*N*,*N*-dimethyl-5-phenylpent-4-ynamide (7a)



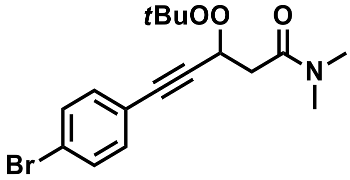
The title compound was prepared according to **GP3** and isolated as yellow oil after purification by flash column chromatography. 51% (1.25 h). **^{1}H NMR**: ($CDCl_3$, 400 MHz): δ 7.46-7.42 (m, 2H); 7.30-7.27 (m, 3H); 5.36-5.32 (m, 1H); 3.07-3.02 (m, 4H); 2.97 (s, 3H); 2.77 (dd, J = 6.2, 15.0 Hz, 1H); 1.28 (s, 9H). **^{13}C NMR**: ($CDCl_3$, 100 MHz): δ 169.13, 131.84, 128.41, 128.19, 122.64, 87.05, 85.48, 81.08, 71.71, 37.78, 37.61, 35.59, 26.43. **HRMS (ESI):** $C_{17}H_{24}NO_3$: Calculated: 290.1756; found: 290.1763.

3-(*tert*-Butylperoxy)-5-(4-chlorophenyl)-*N*,*N*-dimethylpent-4-ynamide (7b)



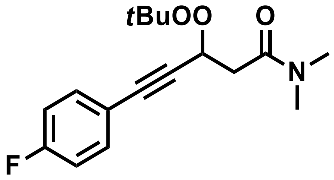
The title compound was prepared according to **GP3** and isolated as pale yellow solid after purification by flash column chromatography. 39% (1.25 h); m.p.: 78-79 ℃. **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 7.36 (d, J = 8.4 Hz, 2H); 7.26 (d, J = 8.4 Hz, 2H); 5.33 (t, J = 6.6 Hz, 1H); 3.07-3.00 (m, 4H); 2.97 (s, 3H); 2.76 (dd, J = 6.2, 15.0 Hz, 1H); 1.27 (s, 9H). **^{13}C NMR**: ($CDCl_3$, 100 MHz): δ 168.97, 134.47, 133.09, 128.55, 121.15, 88.13, 84.31, 81.15, 71.61, 37.67, 37.55, 35.58, 26.41. **HRMS (ESI):** $C_{17}H_{23}NO_3Cl$: Calculated: 324.1366; found: 324.1370.

5-(4-Bromophenyl)-3-(*tert*-butylperoxy)-*N*,*N*-dimethylpent-4-ynamide (7c)



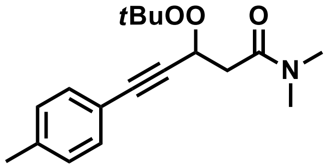
The title compound was prepared according to **GP3** and was obtained after flash column chromatography as pale yellow solid. 41% (1.25 h); m.p.: 84-85 ℃. **^{1}H NMR**: ($CDCl_3$, 400 MHz): δ 7.43 (d, J = 8.4 Hz, 2H); 7.30 (d, J = 8.4 Hz, 2H); 5.35-5.31 (m, 1H); 3.07-3.01 (m, 4H); 2.98 (s, 3H); 2.76 (dd, J = 6.0, 15.2 Hz, 1H); 1.27 (s, 9H). **^{13}C NMR:** ($CDCl_3$, 100 MHz,): δ 168.99, 133.33, 131.50, 122.73, 121.62, 88.32, 84.39, 81.20, 71.64, 37.66, 37.58, 35.61, 26.43. **HRMS (ESI):** $C_{17}H_{23}NO_3Br$: Calculated: 368.0861; found: 368.0874.

3-(*tert*-Butylperoxy)-5-(4-fluorophenyl)-*N*,*N*-dimethylpent-4-ynamide (7d)



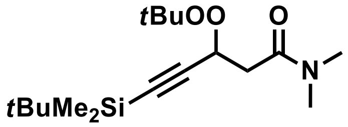
The title compound was prepared according to **GP3** and isolated as pale yellow solid after purification by flash column chromatography. 41% (1.25 h); m.p.: 51-53 ℃. **^{1}H NMR**: ($CDCl_3$, 400 MHz): δ 7.44-7.40 (m, 2H); 7.01-6.96 (m, 2H); 5.33 (t, J = 6.8 Hz, 1H); 3.07-2.97 (m, 7H); 2.76 (dd, J = 6.2, 15.0 Hz, 1H); 1.28 (s, 9H). **^{13}C NMR**: ($CDCl_3$, 100 MHz): δ 169.07, 162.59 (d, $J_{C\text{-}F}$ = 248 Hz), 133.79 (d, $J_{C\text{-}F}$ = 8.0 Hz), 118.73 (d, $J_{C\text{-}F}$ = 3.0 Hz), 115.49 (d, $J_{C\text{-}F}$ = 21.0 Hz), 86.78, 84.42, 81.14, 71.66, 37.74, 37.58, 35.59, 26.42. **HRMS (ESI):** $C_{17}H_{23}NO_3F$: Calculated: 308.1662; found: 308.1664.

3-(*tert*-Butylperoxy)-*N*,*N*-dimethyl-5-(*p*-tolyl)pent-4-ynamide (7e)



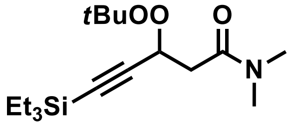
The title compound was prepared according to **GP3** and isolated as pale yellow solid after purification by flash column chromatography. 50% (1.25 h); m.p.:93-94 ℃. **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 7.33 (d, 2H, J = 8.4 Hz); 7.09 (d, 2H, J = 8.0 Hz); 5.33 (t, 1H, J = 6.6 Hz); 3.08-3.00 (m, 4H); 2.97 (s, 3H); 2.77 (dd, J = 6.0, 14.8 Hz, 1H); 2.33 (s, 3H); 1.27 (s, 9H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.18, 138.51, 131.72, 128.93, 119.54, 86.27, 85.65, 81.03, 71.77, 37.83, 37.61, 35.56, 26.42, 21.46. **HRMS (ESI):** $C_{18}H_{26}NO_3$: Calculated: 304.1913; found: 304.1909.

5-(*tert*-Butyldimethylsilyl)-3-(*tert*-butylperoxy)-*N*,*N*-dimethylpent-4-ynamide (7f)



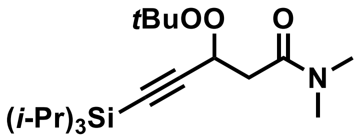
The title compound was prepared according to **GP3** and isolated as yellow oil after purification by flash column chromatography. 61% (1.25 h). **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 5.12 (dd, J = 6.0, 7.6 Hz, 1H); 3.05 (s, 3H); 2.98-2.91 (m, 4H); 2.66 (dd, J = 6.0, 14.8 Hz, 1H); 1.23 (s, 9H); 0.92 (s, 9H); 0.09 (s, 6H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.16, 103.83, 88.76, 80.79, 71.56, 37.72, 37.69, 35.58, 26.41, 26.01, 16.55, -4.76. **HRMS (ESI):**$C_{17}H_{34}NO_3Si$: Calculated: 328.2308; found: 328.2309.

3-(*tert*-Butylperoxy)-*N*,*N*-dimethyl-5-(triethylsilyl)pent-4-ynamide (7g)



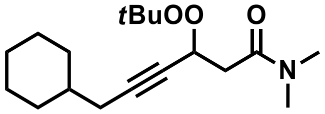
The title compound was prepared according to **GP3** and isolated as colourless oil after purification by flash column chromatography. 52% (1.25 h). **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 5.12 (dd, J = 6.0, 7.6 Hz, 1H); 3.05 (s, 3H); 2.97-2.91 (m, 4H); 2.67 (dd, J = 6.0, 14.8 Hz, 1H); 1.23 (s, 9H); 0.97 (t, J = 7.8 Hz, 9H); 0.58 (q, J = 8.0 Hz, 6H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.13, 104.38, 87.79, 80.69, 71.53, 37.74, 37.66, 35.51, 26.35, 7.30, 4.18. **HRMS (ESI):** $C_{17}H_{34}NO_3Si$: Calculated: 328.2308; found: 328.2310.

3-(*tert*-Butylperoxy)-*N*,*N*-dimethyl-5-(triisopropylsilyl)pent-4-ynamide (7h)



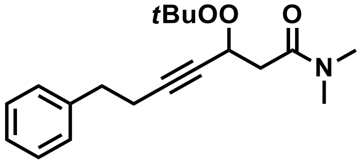
The title compound was prepared according to **GP3** and isolated as colourless solid after purification by flash column chromatography. 61% (1.25 h); m.p.: 87-88 °C. **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 5.14 (dd, J = 6.2, 7.4 Hz, 1H); 3.05 (s, 3H); 2.98-2.91 (m, 4H); 2.68 (dd, J = 6.4, 14.8 Hz, 1H); 1.23 (s, 9H); 1.06-1.04 (m, 21H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.23, 105.13, 86.72, 80.61, 71.60, 37.82, 37.72, 35.55, 26.39, 18.51, 11.11 **HRMS (ESI):** $C_{20}H_{40}NO_3Si$: Calculated: 370.2777; found: 370.2777.

3-(*tert*-Butylperoxy)-6-cyclohexyl-*N*,*N*-dimethylhex-4-ynamide (7i)



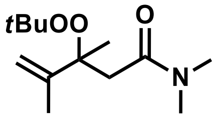
The title compound was prepared according to **GP3** and isolated as yellow oil after purification by flash column chromatography. 45% (1.25 h). **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 5.12-5.07 (m, 1H); 3.05 (s, 3H); 2.97-2.90 (m, 4H); 2.64 (dd, J = 6.4, 14.4 Hz, 1H); 2.09 (dd, J = 2.0, 6.8 Hz, 1H); 1.80-1.74 (m, 2H); 1.70-1.62 (m, 3H); 1.50-1.39 (m, 1H); 1.27-1.18 (m, 12H); 1.02-0.90(m, 2H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.41, 85.49, 80.80, 78.55, 71.71, 38.06, 37.61, 37.19, 35.48, 32.61, 26.60, 26.34, 26.24, 26.10. **HRMS (ESI):** $C_{18}H_{32}NO_3$: Calculated: 310.2382; found: 310.2386.

3-(*tert*-Butylperoxy)-*N*,*N*-dimethyl-7-phenylhept-4-ynamide (7j)



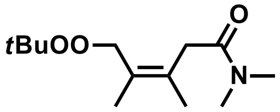
The title compound was prepared according to **GP3** and isolated as light yellow oil after purification by flash column chromatography. 42% (1.25 h). **^{1}H NMR:** ($CDCl_3$, 400 MHz): δ 7.30-7.25 (m, 2H); 7.22-7.17 (m, 3H); 5.11-5.06 (m, 1H); 3.01 (s, 3H); 2.97-2.87 (m, 4H); 2.82 (t, J = 7.6 Hz, 2H); 2.60 (dd, J = 6.4, 14.8 Hz, 1H); 2.51 (td, J = 1.6, 7.6 Hz, 2H); 1.24 (s, 9H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 169.24, 140.59, 128.45, 128.26, 126.18, 85.60, 80.91, 78.53, 71.54, 37.94, 37.46, 35.44, 34.81, 26.32, 21.03. **HRMS (ESI):** $C_{19}H_{28}NO_3$: Calculated: 318.2069; found: 318.2062.

3-(*tert*-Butylperoxy)-*N*,*N*,3,4-tetramethylpent-4-enamide (7k)



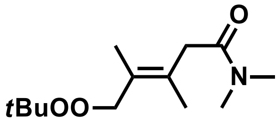
The title compound was prepared according to **GP1** with 2,3-dimethyl-1,3-butadiene and isolated as colourless oil together with **7k'** and **7k''**after purification by flash column chromatography. 14% (3 h). ^{1}**H NMR:** ($CDCl_3$, 400 MHz): δ 4.97-4.91 (m, 2H); 3.09 (s, 3H); 2.93 (s, 3H); 2.82 (d, J = 14.0 Hz, 1H); 2.53 (d, J = 14.0 Hz, 1H); 1.84 (s, 3H); 1.57 (s, 3H); 1.20 (s, 9H). ^{13}**C NMR:** ($CDCl_3$, 100 MHz): δ 170.02, 148.27, 111.81, 83.68, 40.75, 38.37, 35.58, 26.65, 22.09, 19.16 **HRMS (ESI):** $C_{13}H_{26}NO_3$: Calculated: 244.1913; found: 244.1910.

(*E*)-5-(*tert*-Butylperoxy)-*N*,*N*,3,4-tetramethylpent-3-enamide (7k')



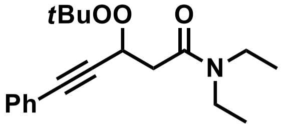
The title compound was prepared to **GP1** with 2,3-dimethyl-1,3-butadiene and isolated as colourless oil together with **7k** and **7k''** after purification by flash column chromatography. 13% (3 h). ^{1}**H NMR:** ($CDCl_3$, 400 MHz): δ 4.41 (s, 2H); 3.24 (s, 2H); 3.01 (s, 3H); 2.94 (s, 3H); 1.81 (s, 3H); 1.74 (s, 3H); 1.24 (s, 9H). ^{13}**C NMR:** ($CDCl_3$, 100 MHz): δ 171.04, 130.60, 126.46, 80.20, 76.01, 39.00, 37.32, 35.57, 26.41, 19.10, 18.11. **HRMS (ESI):** $C_{13}H_{26}NO_3$: Calculated: 244.1913; found: 244.1914.

(*Z*)-5-(*tert*-Butylperoxy)-*N*,*N*,3,4-tetramethylpent-3-enamide (7k'')



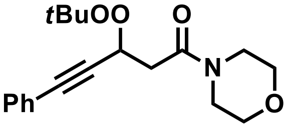
The title compound was prepared according to **GP1** with 2,3-dimethyl-1,3-butadiene and isolated as colourless oil together with **7k** and **7k'** after purification by flash column chromatography. 21% (3 h). ^{1}**H NMR:** ($CDCl_3$, 400 MHz): δ 4.48 (s, 2H); 3.15 (s, 2H); 2.97 (s, 3H); 2.93 (s, 3H); 1.78-1.76 (2s, 6H); 1.24 (s, 9H). ^{13}**C NMR:** ($CDCl_3$, 100 MHz): δ 170.90, 130.21, 126.37, 80.18, 76.03, 39.78, 37.25, 35.58, 26.39, 18.30, 17.79. **HRMS (ESI):** $C_{13}H_{26}NO_3$: Calculated: 244.1913; found: 244.1911.

3-(*tert*-Butylperoxy)-*N*,*N*-diethyl-5-phenylpent-4-ynamide (7l)



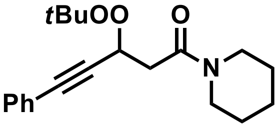
The title compound was prepared according to **GP3** and isolated as yellow oil after purification by flash column chromatography. 32% (1.25 h). ^{1}**H NMR:** ($CDCl_3$, 400 MHz): δ 7.46-7.42 (m, 2H); 7.32-7.25 (m, 3H); 5.39 (dd, *J* = 6.2, 7.4 Hz, 1H); 3.46-3.36 (m, 4H); 3.02 (dd, J = 14.6, 7.6 Hz, 1H); 2.74 (dd, J = 14.8, 6.2 Hz, 1H); 1.28 (s, 9H); 1.21 (t, *J* = 7.2 Hz, 3H); 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR:** ($CDCl_3$, 100 MHz): δ 168.15, 131.76, 128.34, 128.14, 122.63, 87.07, 85.43, 81.07, 71.85, 42.31, 40.53, 37.50, 26.38, 14.48, 13.05. **HRMS (ESI):** $C_{19}H_{28}NO_3$: Calculated: 318.2069; found: 318.2071.

3-(*tert*-Butylperoxy)-1-morpholino-5-phenylpent-4-yn-1-one (7m)



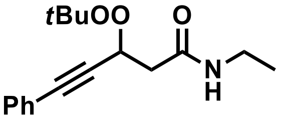
The title compound was prepared according to **GP3** and isolated as slowly solidifying colourless oil after purification by flash column chromatography. 34% (1.25 h). **^{1}H NMR:** ($CDCl_3$, 400 MHz): *δ* 7.48-7.42 (m, 2H); 7.33-7.25 (m, 3H); 5.34 (dd, J = 6.0, 7.2 Hz, 1H); 3.72-3.54 (m, 8H); 3.06 (dd, *J* = 7.4, 15.0 Hz, 1H); 2.78 (dd, *J*= 6.2, 15.0 Hz, 1H); 1.29 (s, 9H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): *δ* 167.88, 131.83, 128.56, 128.27, 122.48, 86.72, 85.84, 81.20, 71.68, 66.88, 66.73, 46.50, 42.20, 37.40, 26.50. **HRMS (ESI):** $C_{19}H_{26}NO_4$: Calculated: 332.1862; found: 332.1862.

3-(*tert*-Butylperoxy)-5-phenyl-1-(piperidin-1-yl)pent-4-yn-1-one (7n)



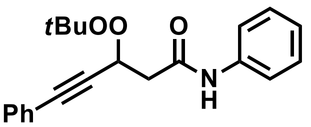
The title compound was prepared according to **GP3** and isolated as slowly solidifying colourless oil after purification by flash column chromatography. 44% (1.25 h). **^{1}H NMR:** ($CDCl_3$, 400 MHz): *δ* 7.46-7.41 (m, 2H); 7.31-7.26 (m, 3H); 5.37-5.33 (m, 1H); 3.65-3.57 (m, 2H); 3.53-3.42 (m, 2H); 3.05 (dd, *J* = 15.2, 7.2 Hz, 1H); 2.77 (dd, *J* = 15.0, 6.2 Hz, 1H); 1.67-1.53 (m, 6H); 1.29 (s, 9H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): *δ* 167.25, 131.84, 128.37, 128.18, 122.71, 87.25, 85.46, 81.06, 71.75, 47.12, 42.97, 37.50, 26.52, 26.48, 25.58, 24.54. **HRMS (ESI):** $C_{20}H_{28}NO_3$: Calculated: 330.2069; found: 330.2073.

3-(*tert*-Butylperoxy)-*N*-ethyl-5-phenylpent-4-ynamide (7o)



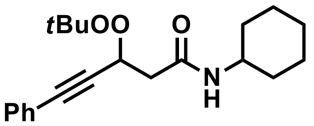
The title compound was prepared according to **GP3** and isolated as yellow oil after purification by flash column chromatography. 40% (1.25 h). **^{1}H NMR:** ($CDCl_3$, 400 MHz): *δ* 7.44- 7.38 (m, 2H); 7.30-7.25 (m, 3H); 6.11 (br, 1H); 5.18 (dd, *J* = 5.4, 7.4 Hz, 1H); 3.35-3.25 (m, 2H); 2.81-2.66 (m, 2H); 1.28 (s, 9H); 1.13 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): *δ* 168.70, 131.74, 128.55, 128.21, 122.28, 86.12, 86.10, 81.22, 71.12, 41.16, 34.44, 26.38, 14.76. **HRMS (ESI):** $C_{17}H_{24}NO_3$: Calculated: 290.1756; found: 290.1757.

3-(*tert*-Butylperoxy)-*N*,5-diphenylpent-4-ynamide (7p)



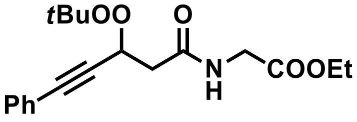
The title compound was prepared according to **GP4** and isolated as yellow oil after purification by flash column chromatography. 43% (1.25 h). **^{1}H NMR:** ($CDCl_3$, 400 MHz): *δ* 7.94 (br, 1H); 7.54-7.50 (m, 2H); 7.45-7.41 (m, 2H); 7.34-7.26 (m, 5H); 7.16-7.07 (m, 1H); 5.27-5.24 (m, 1H); 3.04-2.91 (m, 2H); 1.33 (s, 9H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): *δ* 167.29, 137.88, 131.83, 128.97, 128.72, 128.27, 124.31, 122.07, 119.98, 86.74, 85.55, 81.52, 71.10, 42.09, 26.47. **HRMS (ESI):** $C_{21}H_{24}NO_3$: Calculated: 338.1756; found: 338.1747.

3-(*tert*-Butylperoxy)-*N*-cyclohexyl-5-phenylpent-4-ynamide (7q)



The title compound was prepared according to **GP3** and isolated as white solid after purification by flash column chromatography. 37 % (1.25 h); m.p.: 84-85 ℃. **^{1}H NMR:** (CDCl$_3$, 400 MHz): 7.47-7.41 (m, 2H); 7.36-7.26 (m, 3H); 5.95-5.85 (br, 1H); 5.19-5.15 (m, 1H); 3.85-3.78 (m, 1H); 2.75-2.70 (m, 2H); 1.94-1.90 (m, 2H); 1.73-1.64 (m, 2H); 1.61-1.56 (m, 1H); 1.42-1.10 (m, 14H). **^{13}C NMR:** (CDCl$_3$, 100 MHz): δ 167.86, 131.80, 128.61, 128.27, 122.37, 86.21, 86.16, 81.25, 71.19, 48.14, 41.40, 33.06, 33.02, 26.48, 25.56, 24.69. **HRMS (ESI):** $C_{21}H_{30}NO_3$: Calculated: 344.2226; found: 344.2230.

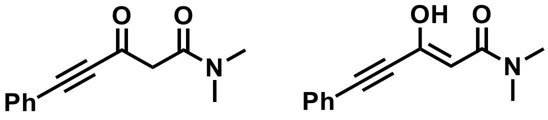
Ethyl (3-(*tert*-butylperoxy)-5-phenylpent-4-ynoyl)glycinate (7r)



The title compound was prepared according to **GP4** and isolated as yellow oil after purification by flash column chromatography. 33% (1.25 h). **^{1}H NMR:** (CDCl$_3$, 400 MHz): δ 7.46-7.41 (m, 2H); 7.32-7.26 (m, 3H); 6.54 (br, 1H); 5.20 (dd, *J* = 5.2, 7.2 Hz, 1H); 4.21 (q, J = 7.1 Hz, 2H); 4.07 (d, *J* = 4.8 Hz); 2.90 (dd, J = 15.0, 7.4 Hz, 1H); 2.80 (dd, *J* = 5.2, 14.0 Hz, 1H); 1.30-1.25 (m, 12H). **^{13}C NMR:** (CDCl$_3$, 100 MHz): δ 169.69, 169.02, 131.85, 128.61, 128.23, 122.28, 86.30, 85.90, 81.28, 70.83, 61.50, 41.61, 40.84, 26.42, 14.12. **HRMS (ESI):** $C_{19}H_{26}NO_5$: Calculated: 348.1811; found: 348.1815.

Transformation of *β*-Peroxy Amide 4a:

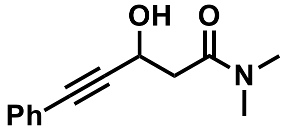
N,*N*-Dimethyl-3-oxo-5-phenylpent-4-ynamide (8)



1 : 2.7

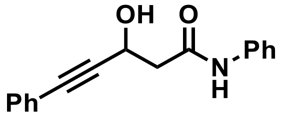
In a screw cap vial, **7a** (63.7mg, 0.22 mmol, 1 equiv) was dissolved in 1.5 mL of ethyl acetate, to which TMEDA (0.22 mmol) was added. The reaction mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then subjected to flash column chromatography with hexane/ethyl acetate (5:1) to give **8** (33.1 mg, clear oil) in 70% yield. Analysis of the product showed the keto and the enol form in a 1:2.7 ratio. **^{1}H NMR:** (CDCl3, 400 MHz): δ 7.61-7.31 (m, 5H, both keto and enol form); 5.63 (s, 1H, enol form); 3.80 (s, 2H, keto form); 3.04-2.99 (m, 6H, both keto and enol form). **^{13}C NMR:** (CDCl$_3$, 100 MHz): δ 180.31 (keto), 171.36 (enol), 165.54 (keto), 155.17 (enol), 133.26 (keto), 132.09 (enol), 131.08 (keto), 129.56 (enol), 128.64 (keto), 128.44 (enol), 121.16 (enol), 119.48 (keto), 94.39 (enol), 92.75 (keto), 91.60 (enol), 87.44 (keto), 84.53 (enol), 51.45 (keto), 37.92, 35.54. **HRMS (ESI):** $C_{13}H_{14}NO_2$: Calculated: 216.1025; found: 216.1025.

3-Hydroxy-*N*,*N*-dimethyl-5-phenylpent-4-ynamide (9)



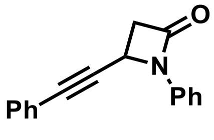
In a screw cap vial, **7a** (49.0 mg, 0.17 mmol, 1 equiv) was dissolved in 1.0 mL of acetic acid, to which zinc dust (0.85 mmol) was added. The reaction mixture was allowed to stir at 70 ℃ for 13 h. The reaction was diluted with ethyl acetate and washed with saturated sodium bicarbonate solution, brine and dried over sodium sulphate. The organic layers were evaporated in vacuo and the residue was purified by flash column chromatography with hexane/ethyl acetate (3:2) to give **9** (29.0 mg, pale yellow solid) in 79% yield. m.p.: 79-81 ℃.
^{1}H NMR: ($CDCl_3$, 400 MHz): δ 7.46-7.42 (m, 2H); 7.34-7.25 (m, 3H); 5.06-5.01 (m, 1H); 4.62 (br, 1H); 3.03-2.94 (2s, 6H); 2.58-2.78 (m, 2H) **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 171.32, 131.74, 128.39, 128.22, 122.55, 88.64, 84.53, 59.51, 39.96, 37.10, 35.24 **HRMS (ESI):** $C_{13}H_{16}NO_2$: Calculated: 218.1181; found: 218.1177

3-Hydroxy-*N*,5-diphenylpent-4-ynamide (10)



In a screw cap vial, **7p** (30.7 mg, 0.091 mmol) was dissolved in 1.0 mL of acetic acid, to which zinc dust (0.46 mmol) was added. The reaction mixture was allowed to stir at 70 ˚C for 3.5 hours. The reaction was diluted with ethyl acetate and washed with saturated sodium bicarbonate solution, brine and dried over sodium sulphate. The organic layers were evaporated in vacuo and the residue was purified by flash column chromatography with hexane/ethyl acetate (3:1) to give **10** (18.3mg, pale yellow solid) in 76% yield. The analytical data are in accordance with the literature.[4] m.p.: 131-132 ℃. **^{1}H NMR:** (CD_3OD, 400 MHz): δ 7.55 (d, J = 8.0 Hz, 2H); 7.40-7.24 (m, 7H); 7.08 (t, J = 7.4 Hz, 1H); 5.08 (t, J = 6.8 Hz, 1H); 2.88-2.76 (m, 2H). **^{13}C NMR:** (CD_3OD, 100 MHz): δ 170.64, 139.68, 132.56, 129.78, 129.51, 129.42, 125.32, 123.99, 121.38, 90.37, 85.52, 60.38, 46.44. **HRMS (ESI):** $C_{17}H_{16}NO_2$: Calculated: 266.1181; found: 266.1183.

1-phenyl-4-(phenylethynyl)azetidin-2-one (11)



To a stirring solution of **10** (30.5 mg, 0.11 mmol) in 1.2 mL of THF was added triethylphosphite (0.15 mmol) dropwise, which was then followed by diisopropylazodicarboxylate (0.17 mmol). The resulting yellow solution was stirred for 24.The resulting reaction mixture was then then evaporated in vacuo, after which the crude residue was purified by flash chromatography (Cyclohexane/EtOAc) to afford **11** (17.3 mg, white solid) in 61% yield. The analytical data are in accordance with the literature.[4] m.p.: 92-93 ℃. **^{1}H NMR:** (CDCl3, 400 MHz): δ 7.59-7.54 (m, 2H); 7.44-7.28 (m, 7H); 7.12 (t, *J* = 7.4 Hz, 1H); 4.81 (dd, *J* = 2.8, 5.6 Hz, 1H); 3.51 (dd, *J* = 5.8, 15.0 Hz, 1H); 3.29 (dd, *J* = 2.8, 14.8 Hz, 1H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 163.20, 137.59, 131.83, 129.17, 128.97, 128.40, 124.17, 121.81, 116.66, 86.70, 84.71, 44.91, 41.09. **HRMS (ESI):** $C_{17}H_{14}NO$: Calculated: 248.1075; found: 248.1080.

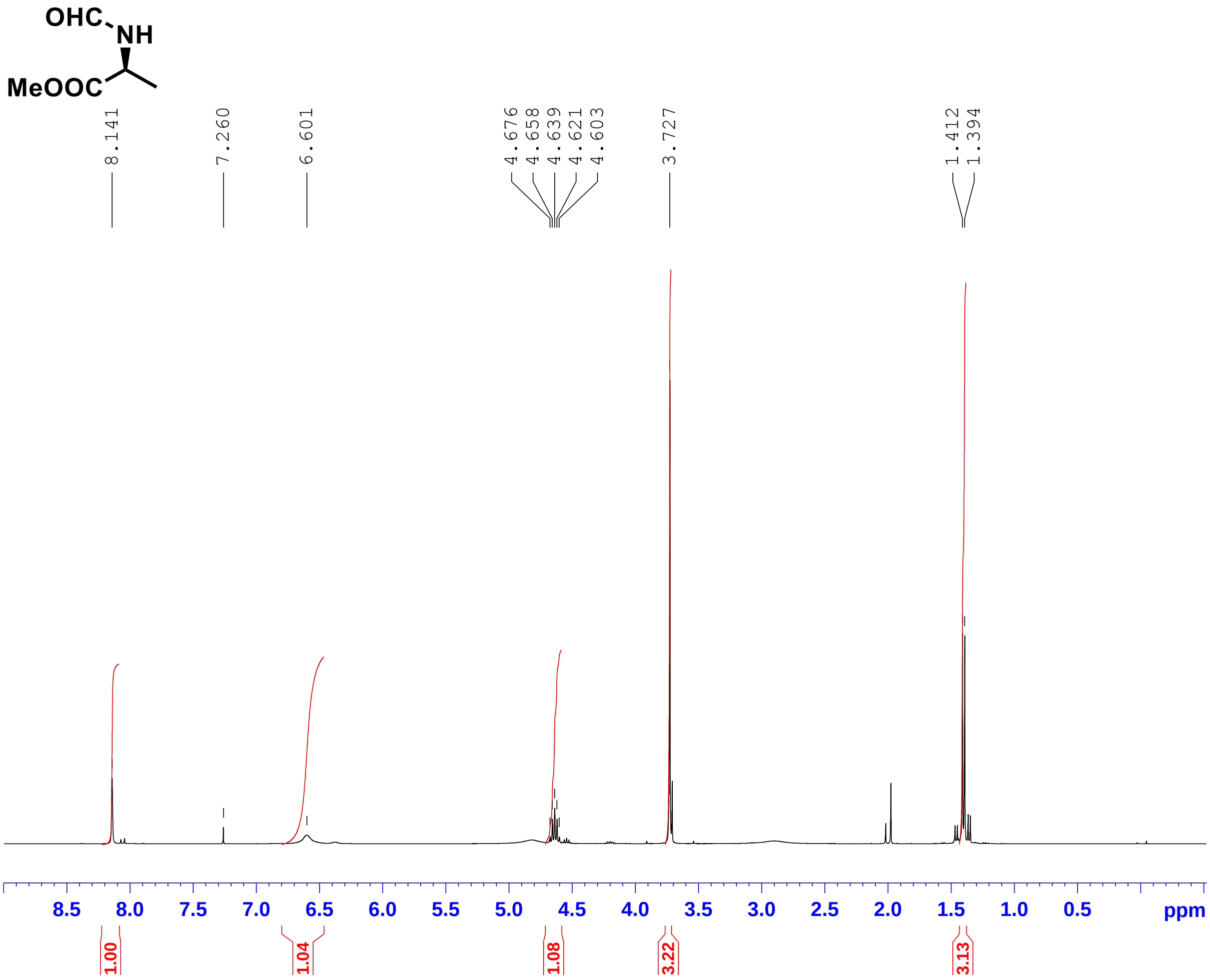
References:

1. Elders, N.; Schmitz, R. F.; de Kanter, F. J. J.; Ruijter, E.; Groen, M. B.; Orru, R. V. A. *J. Org. Chem.* **2007**, *72*, 6135.

2. Mckerrow, J. D.; Al-Rawi, J. M. A.; Brooks, P. *Synth. Commun.* **2010**, *40*, 1161.

3. Chancellor, T.; Morton, C. *Synthesis* **1994**, *10,* 1023.

4. Kern, N.; Hoffmann, M.; Blanc, A.; Weibel, J.-M. Pale, P. *Org. Lett.* **2013**, *15,* 836.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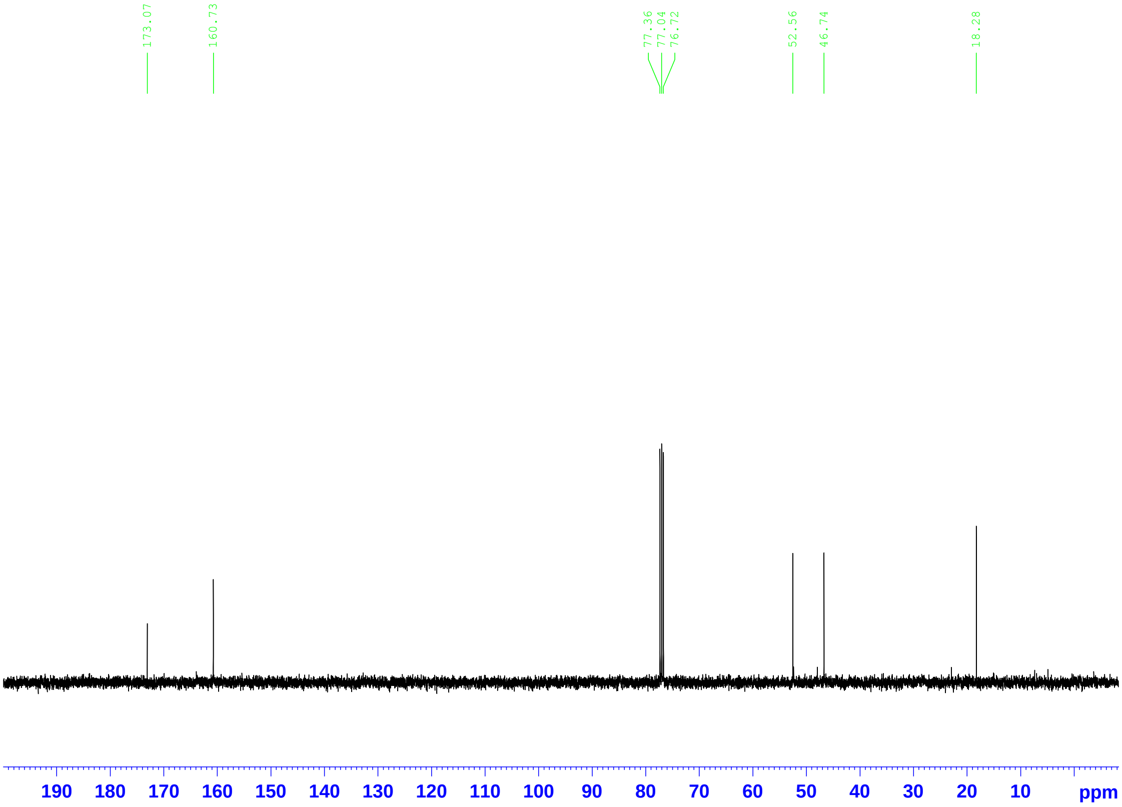
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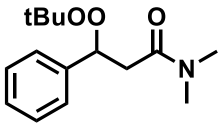
ppm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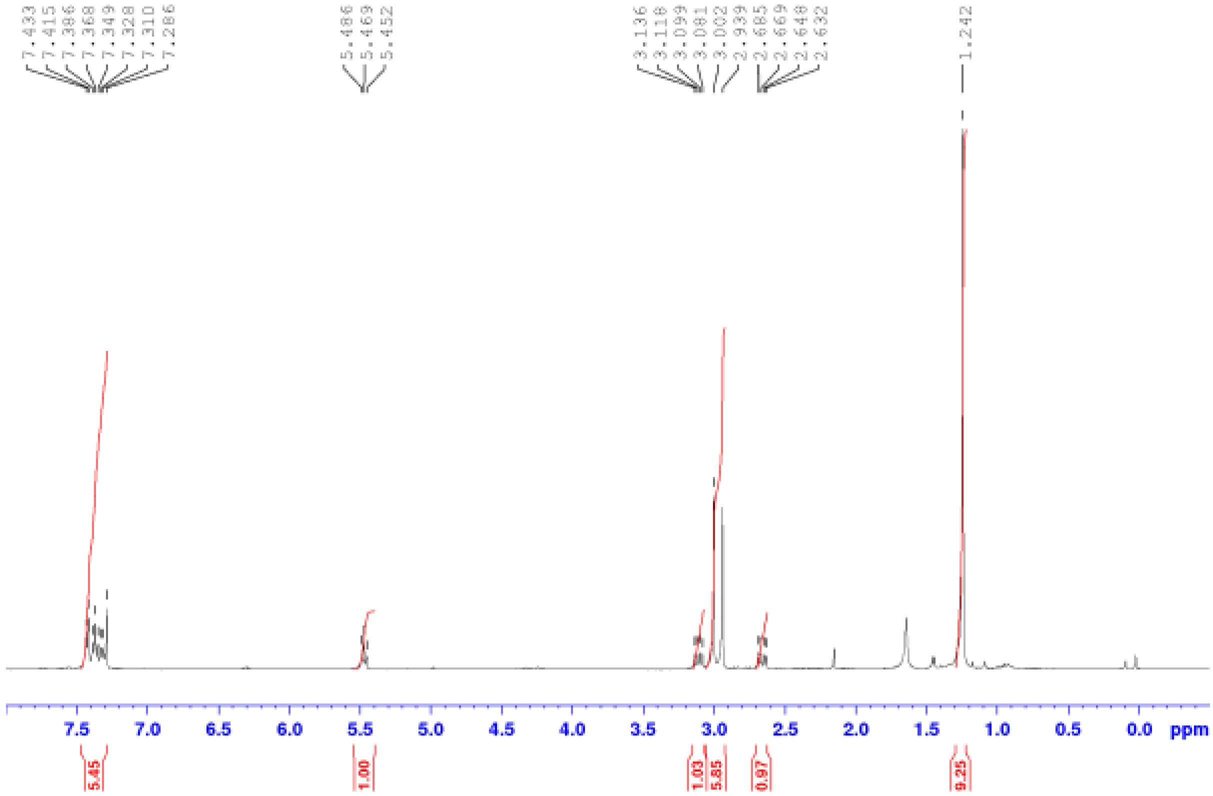
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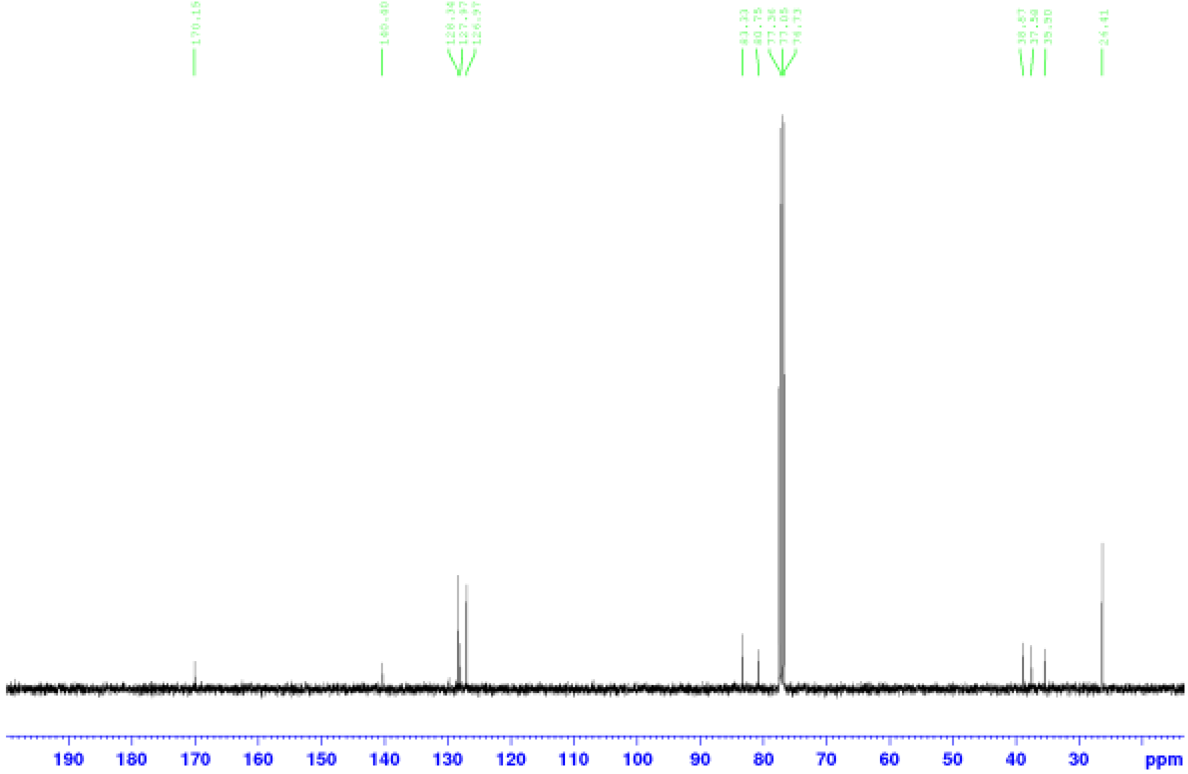
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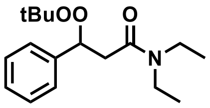
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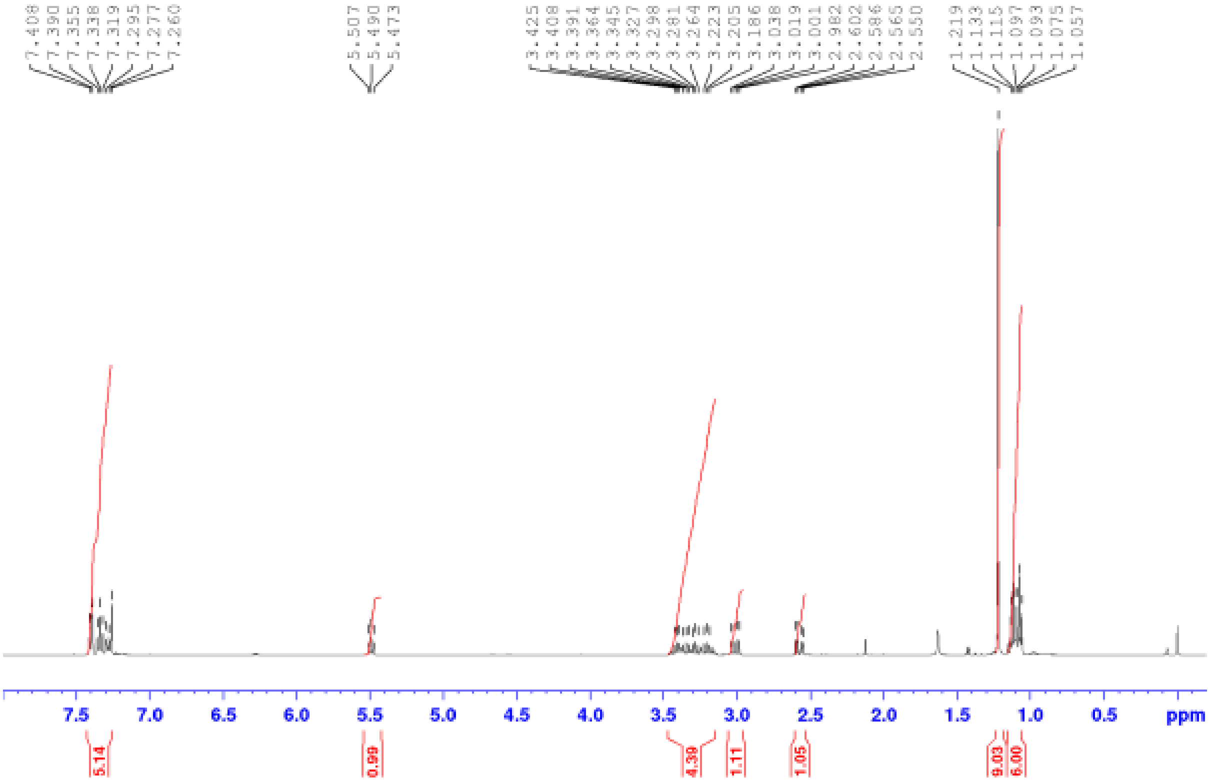
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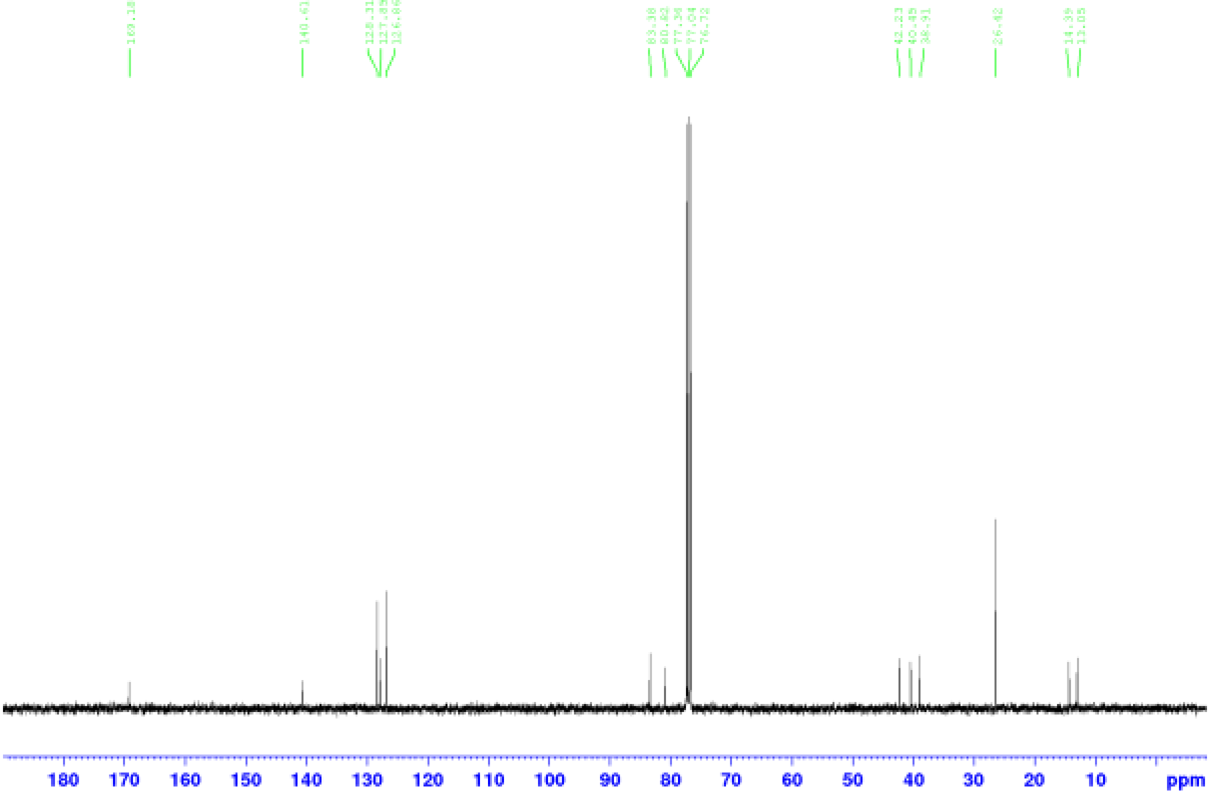
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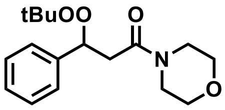
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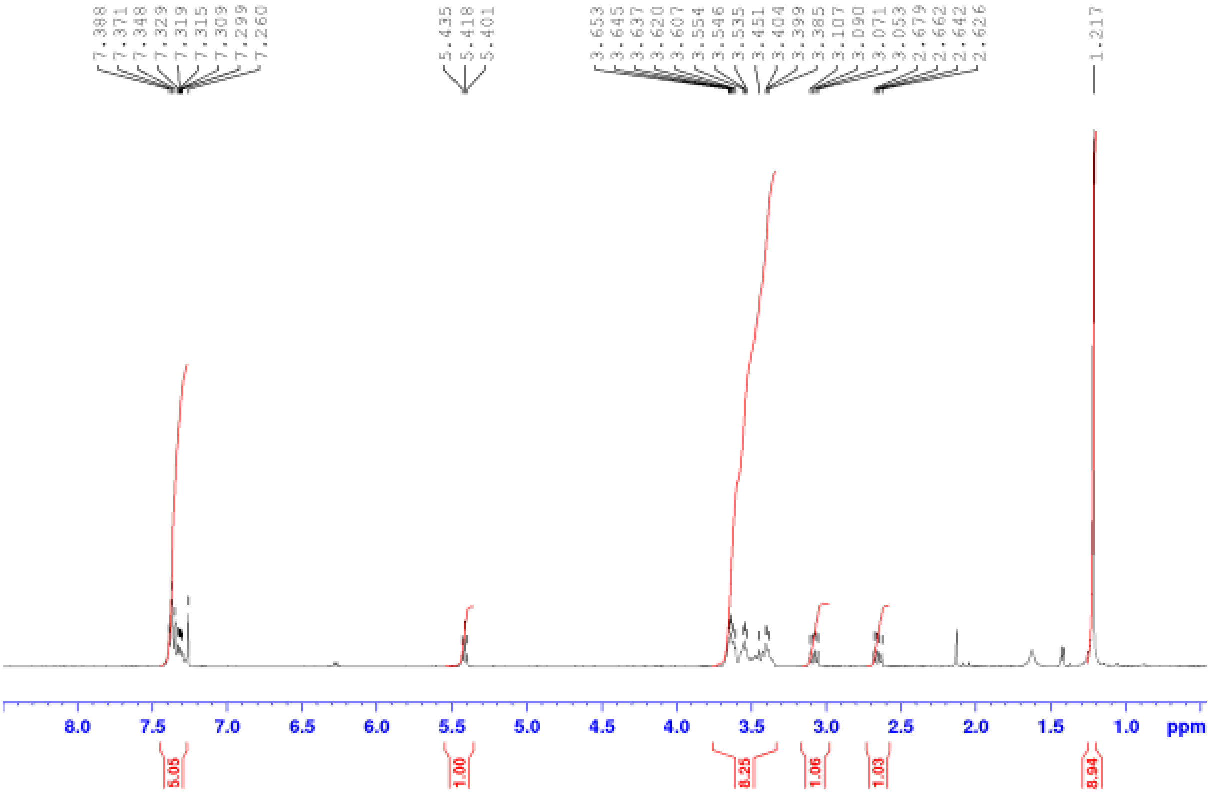
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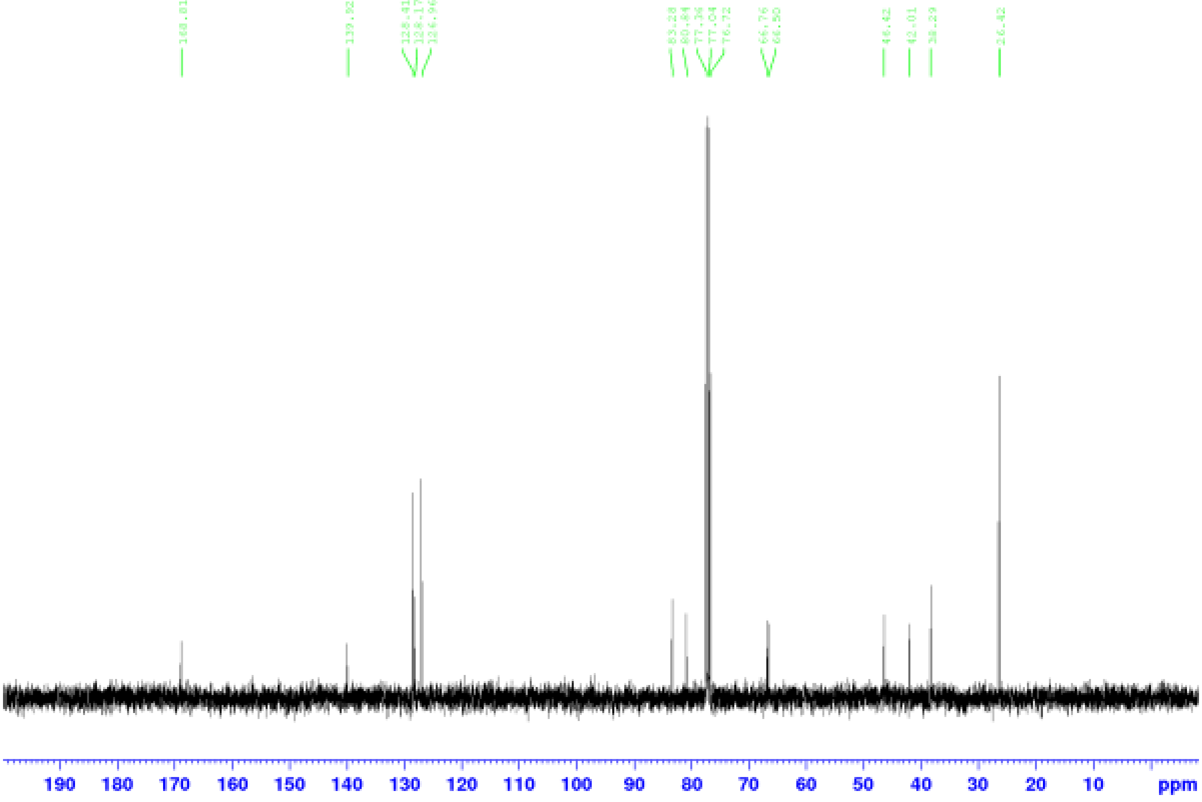
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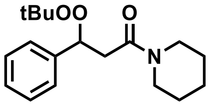
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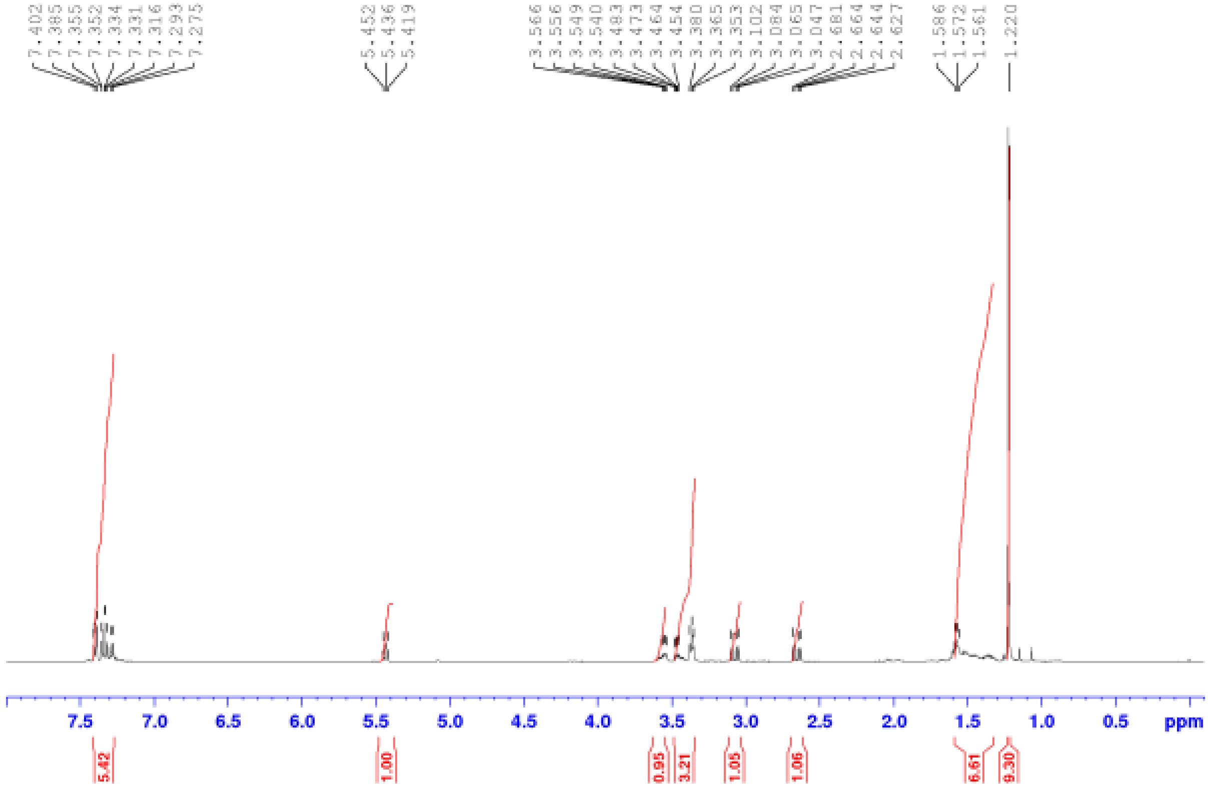
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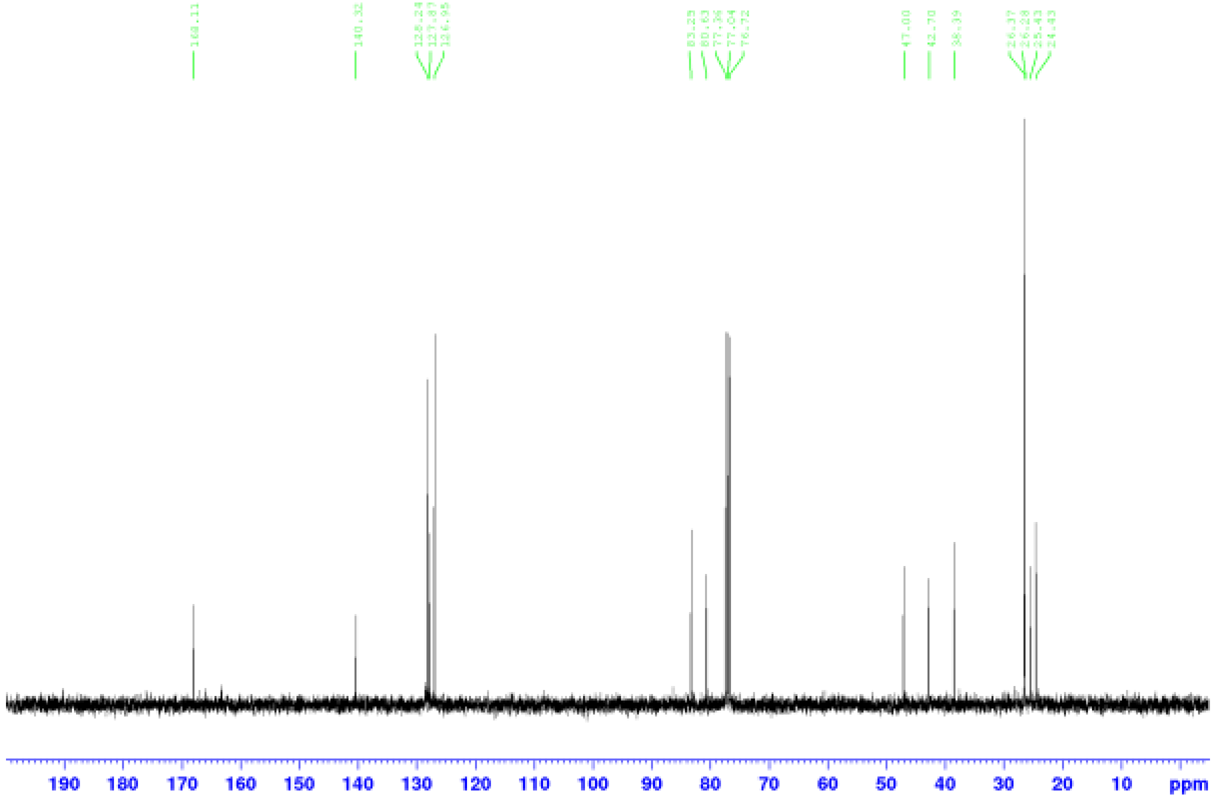
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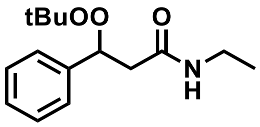
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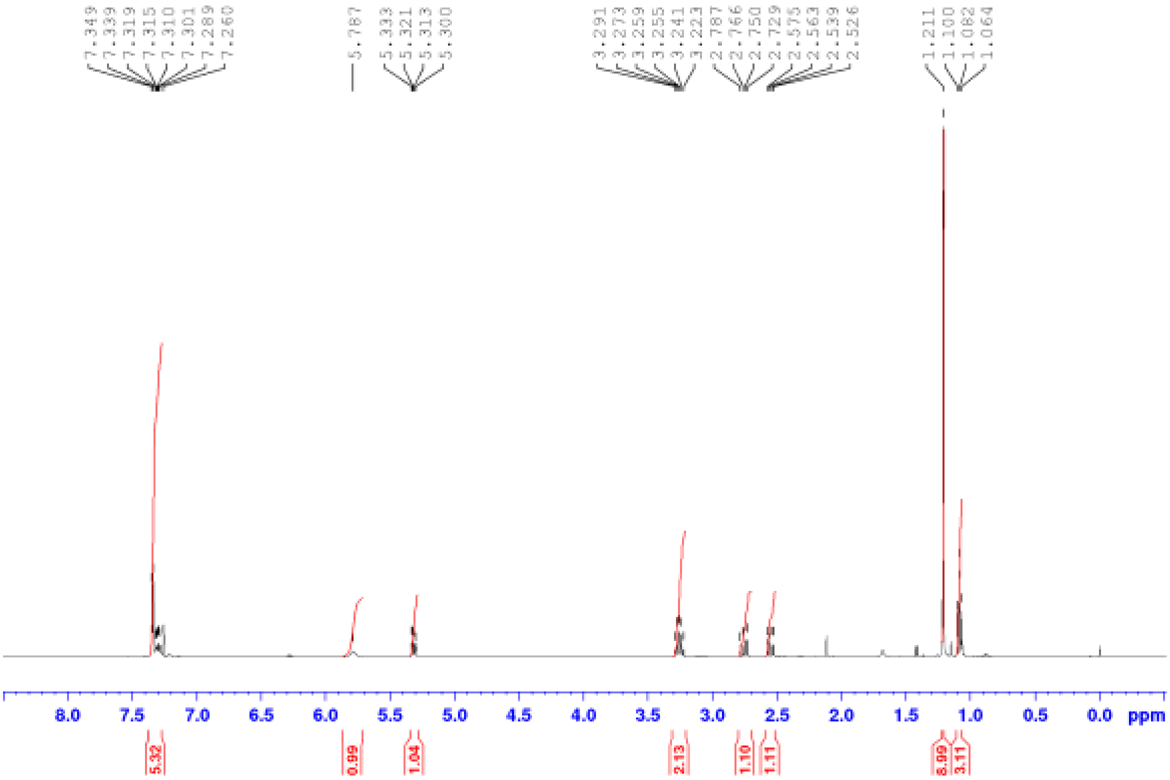
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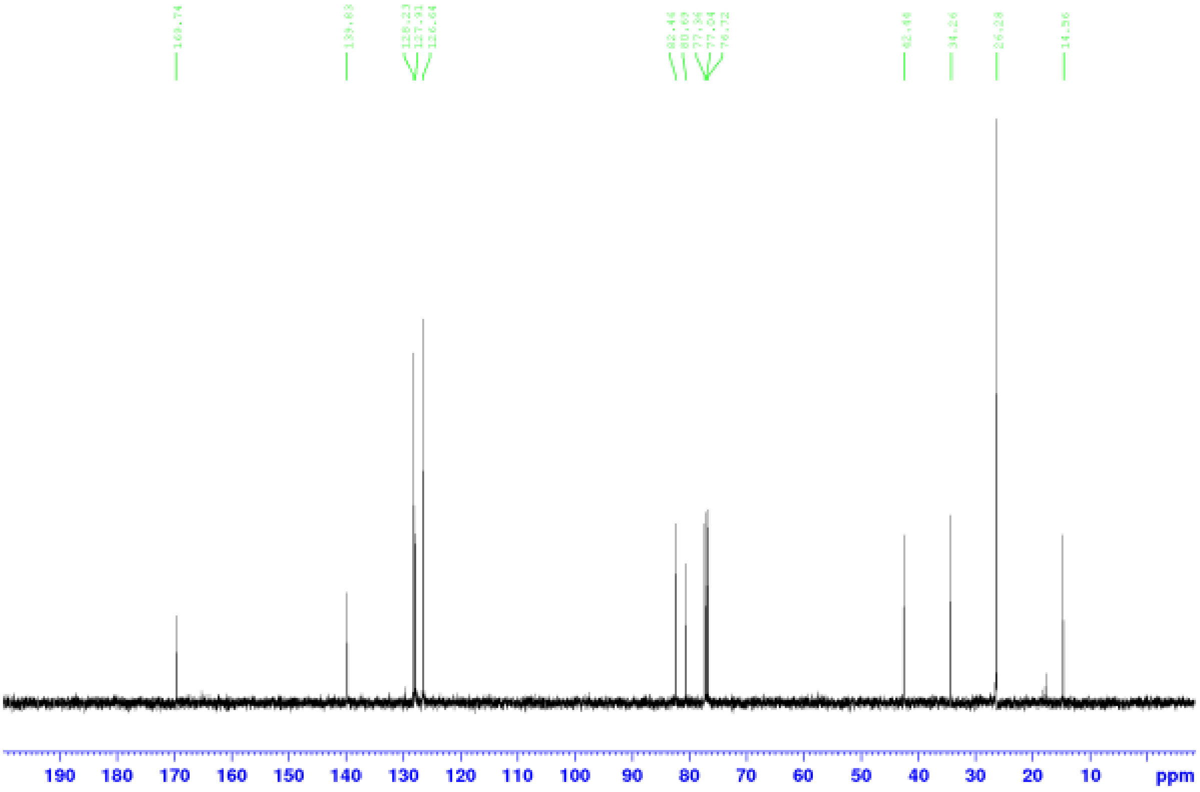
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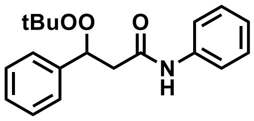
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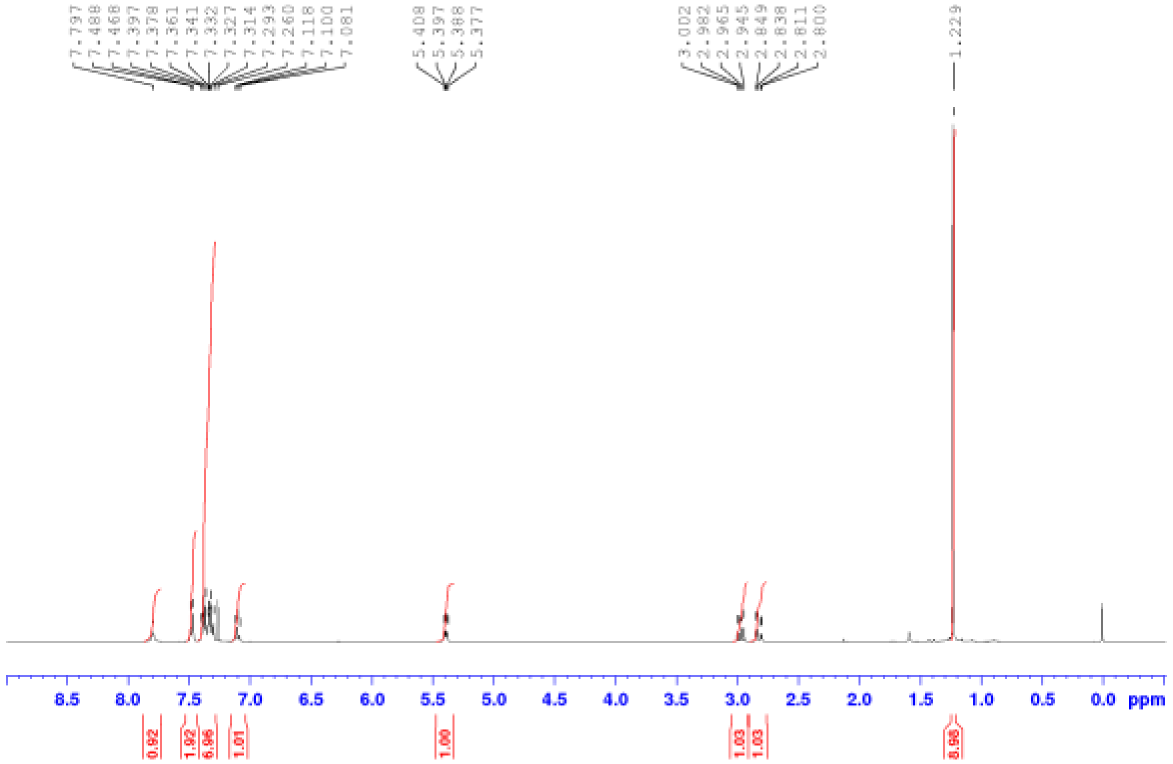
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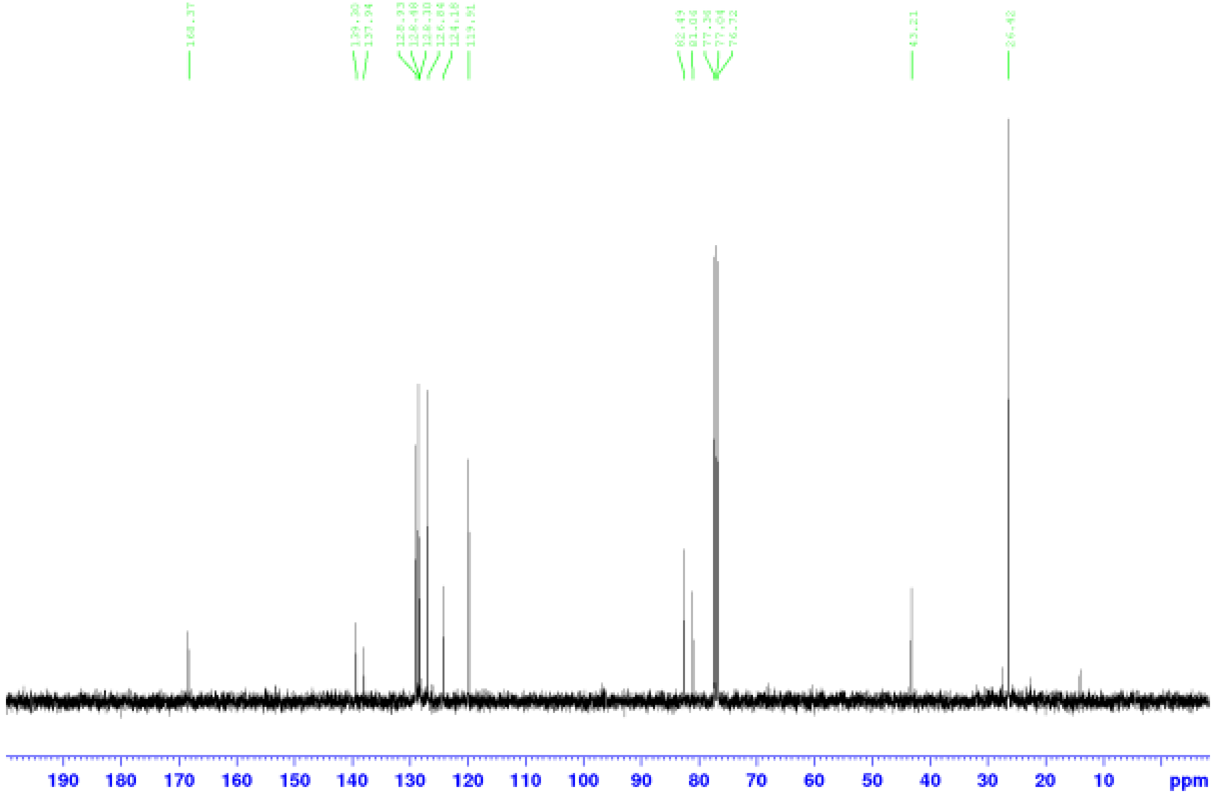
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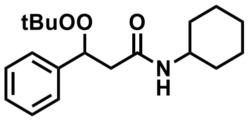
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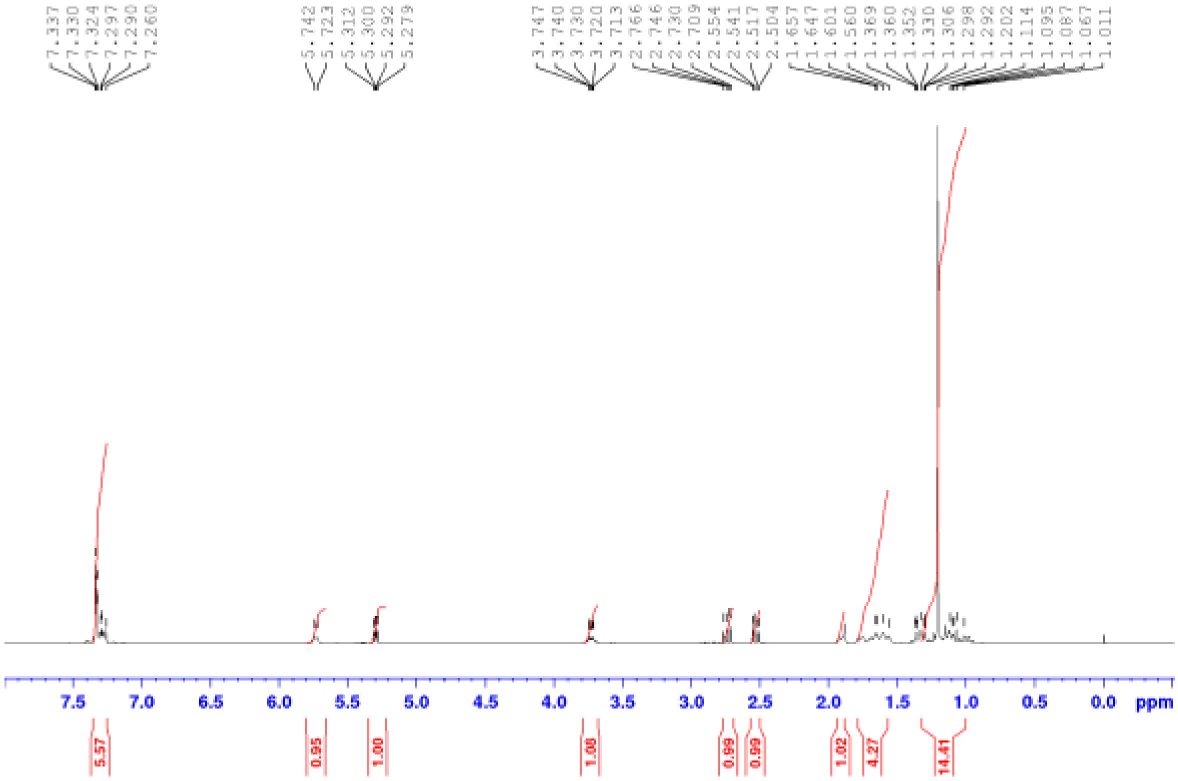
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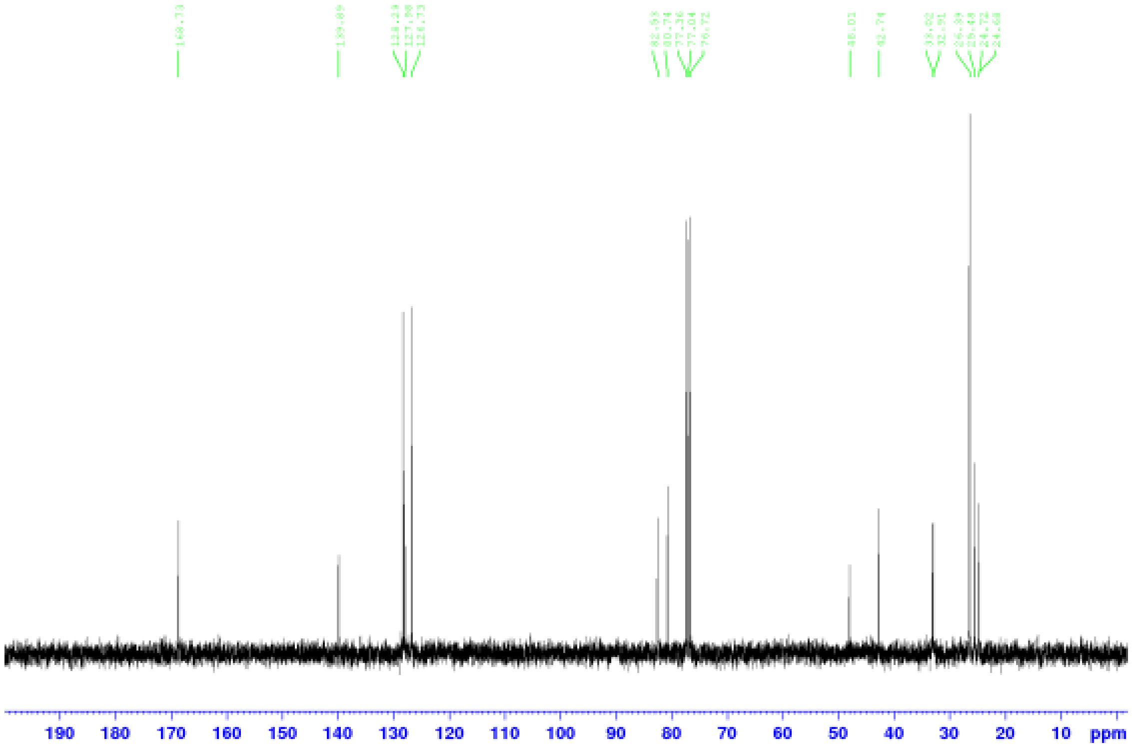
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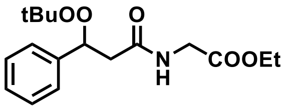
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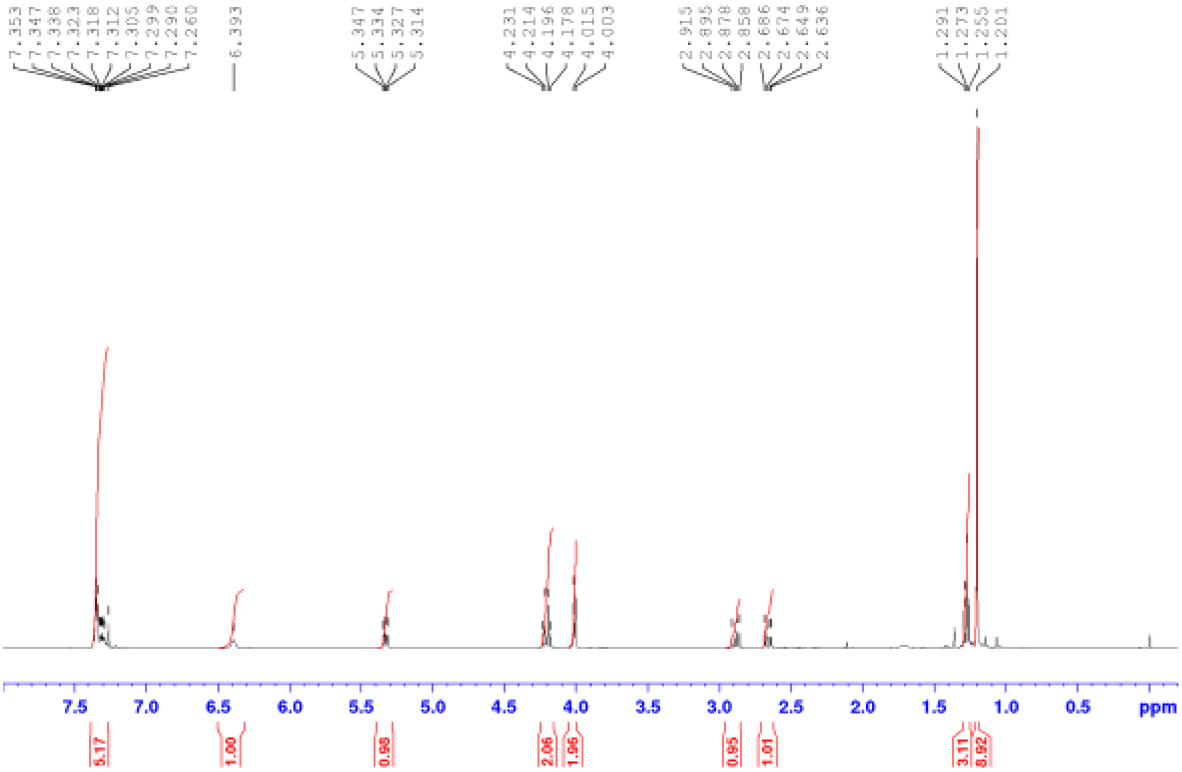
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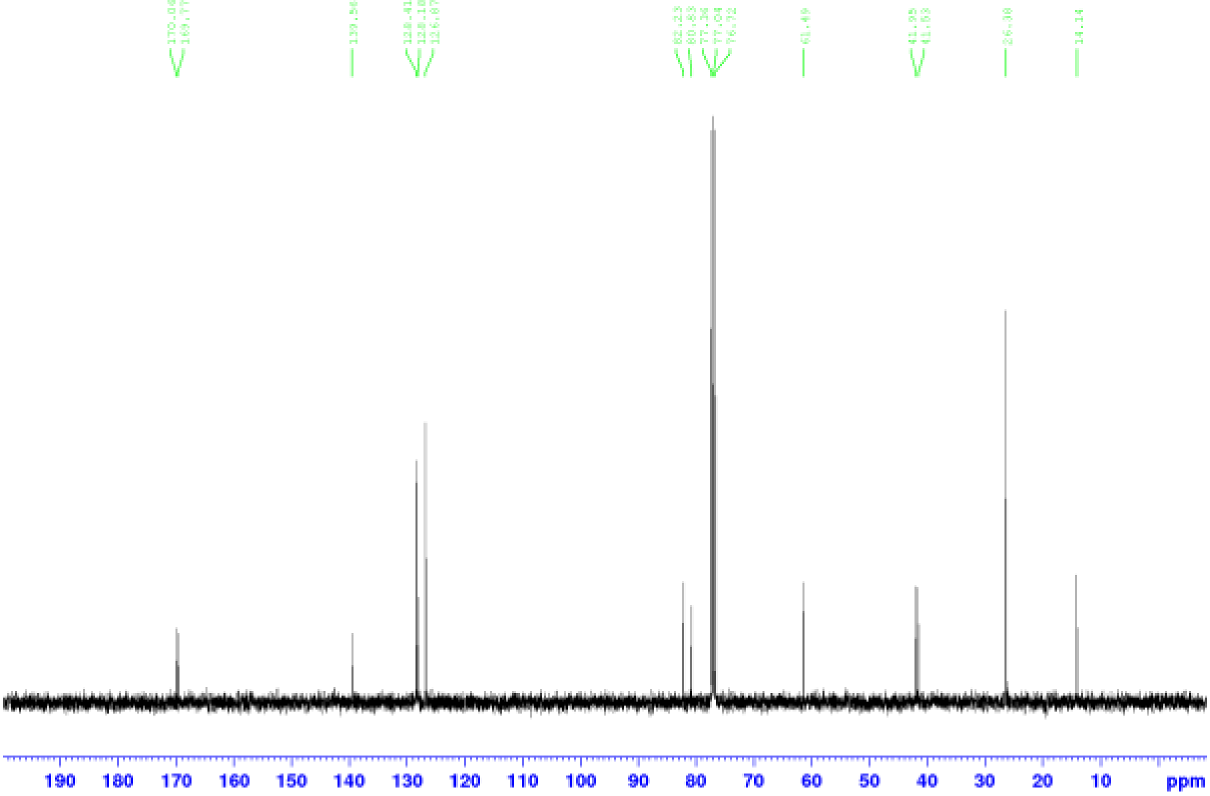
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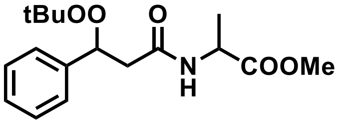
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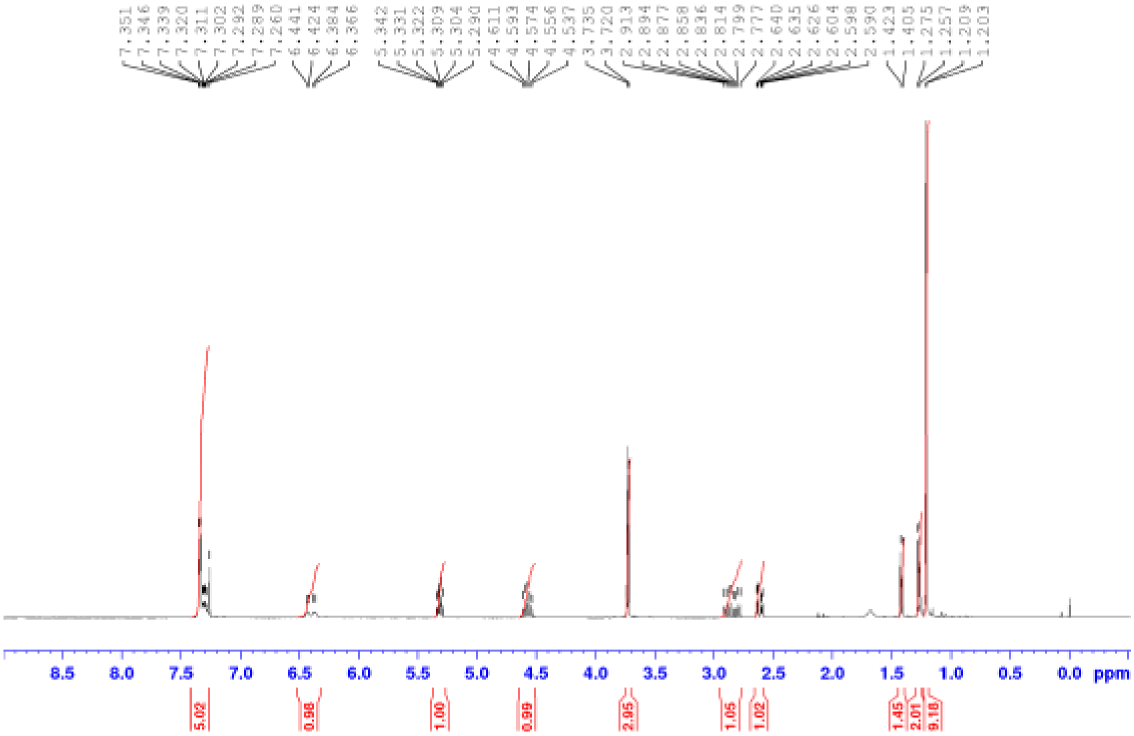
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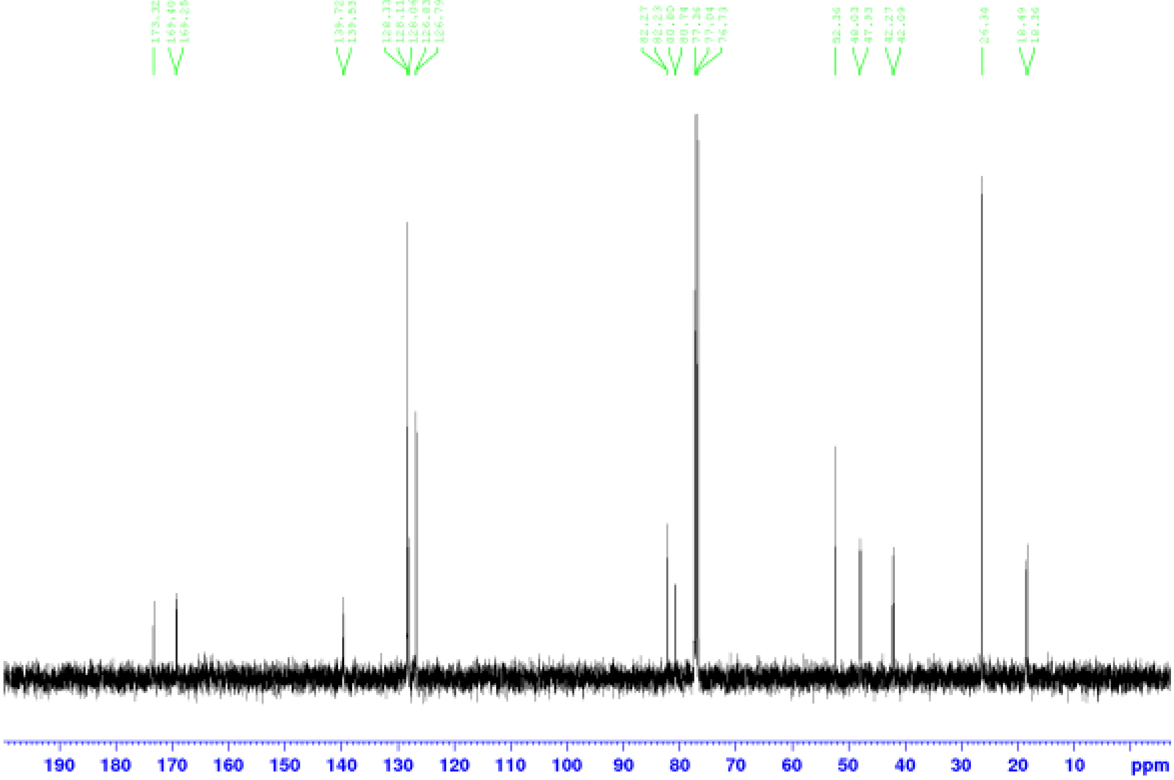
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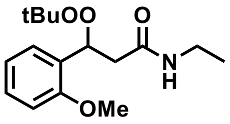
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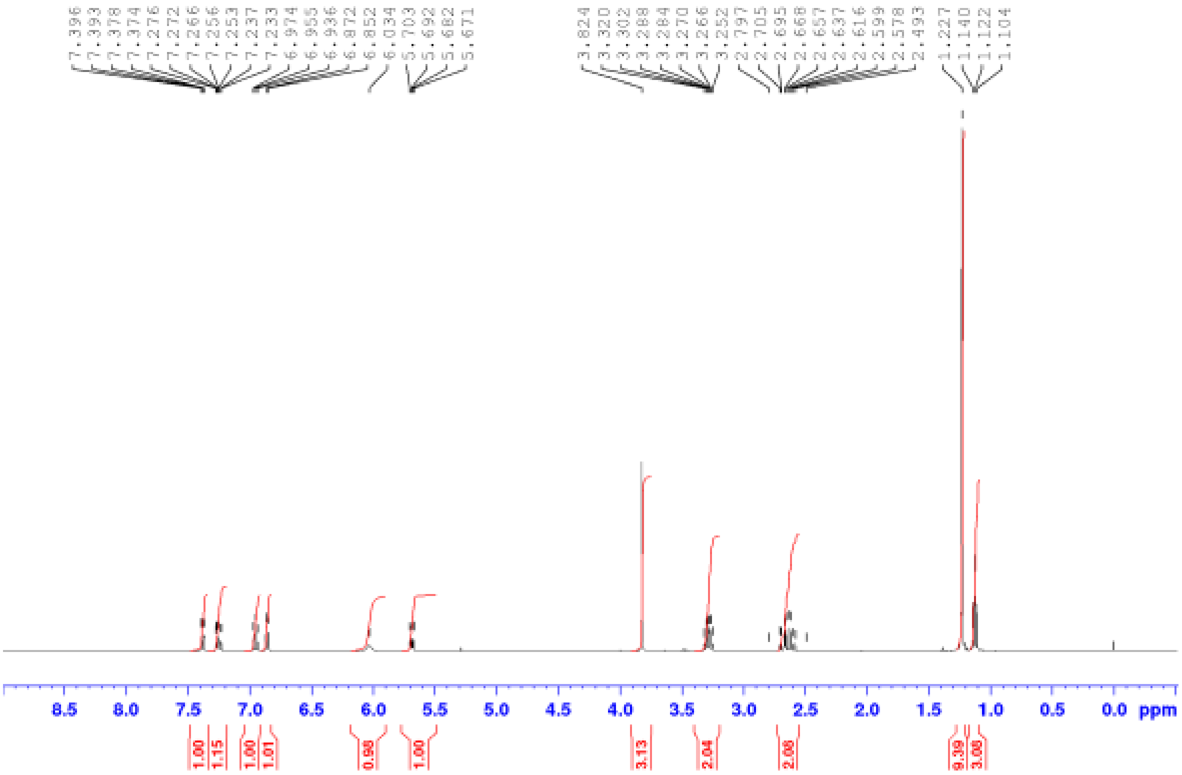
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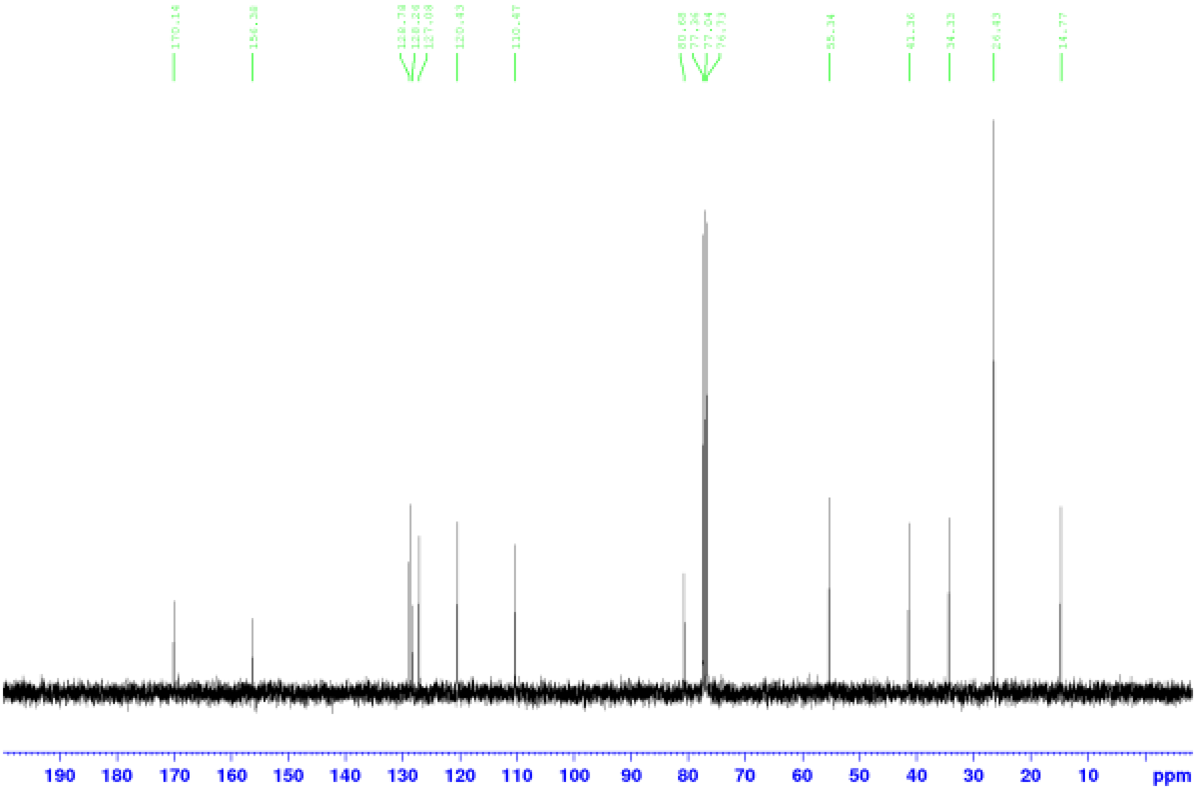
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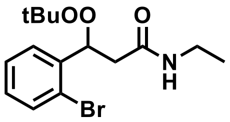
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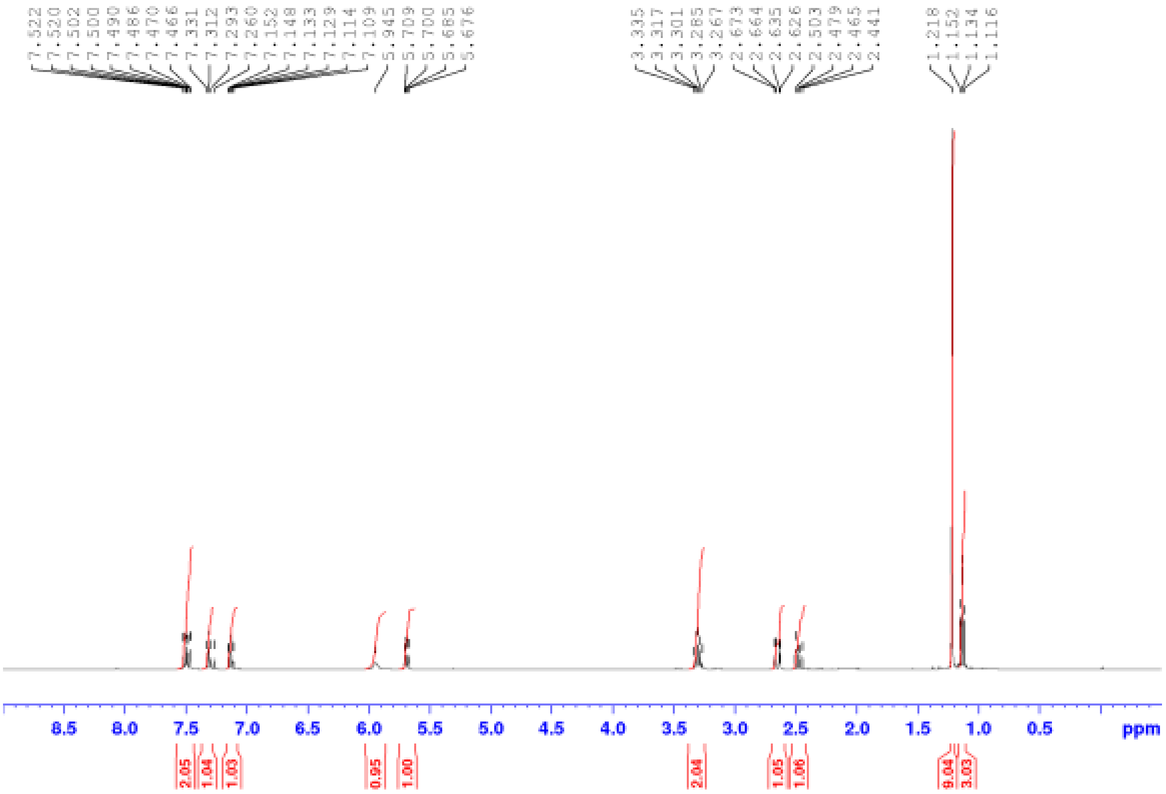
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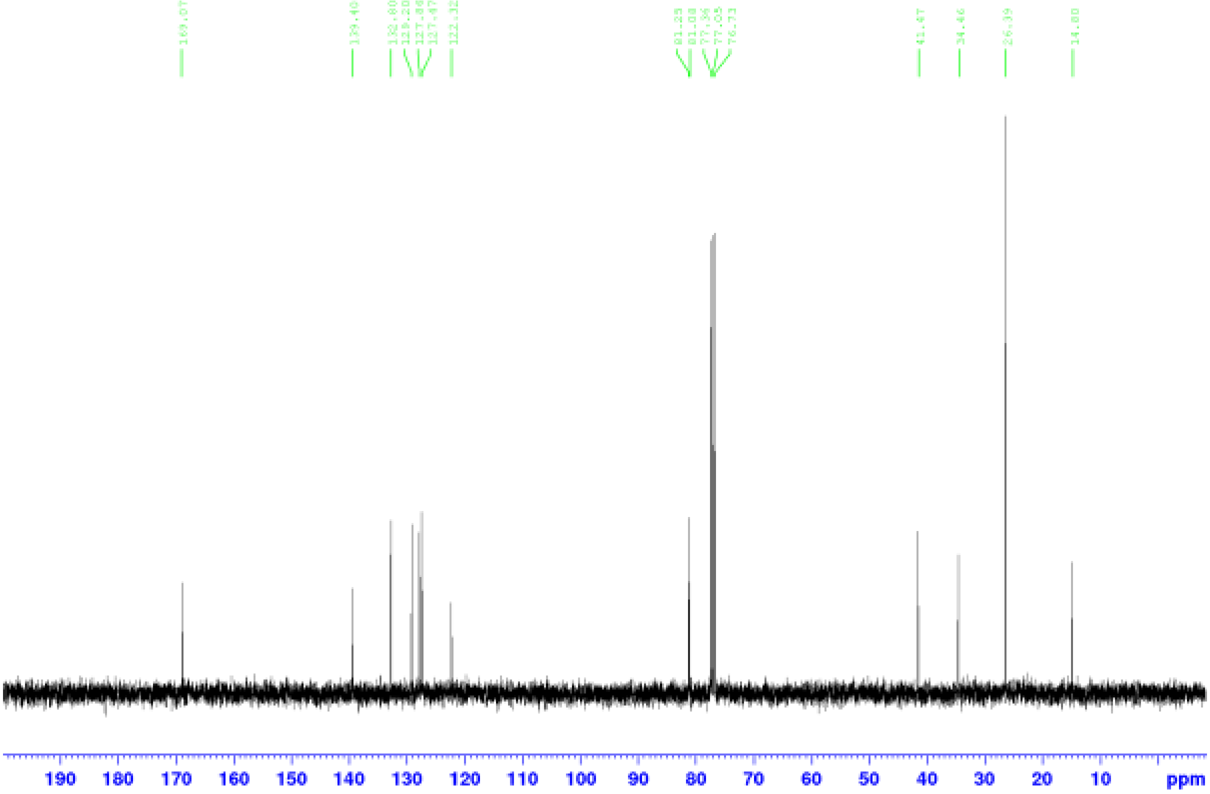
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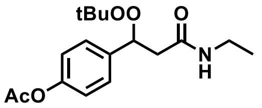
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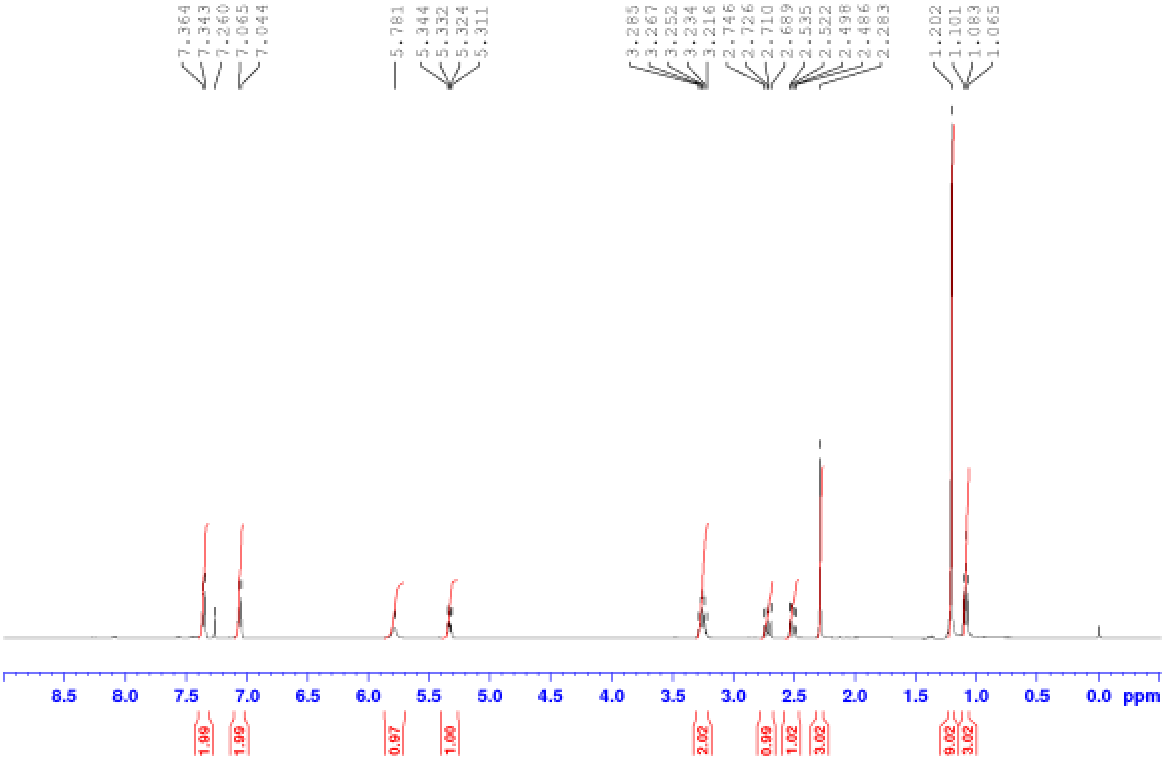
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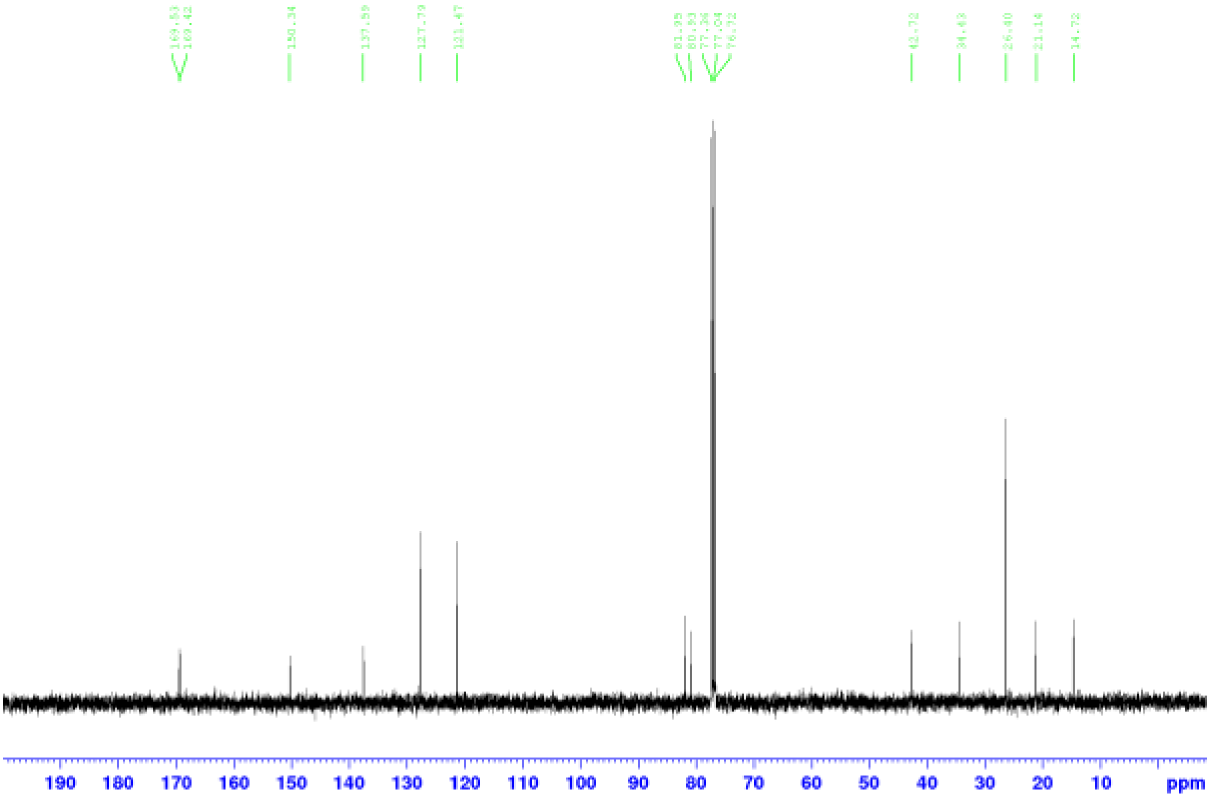
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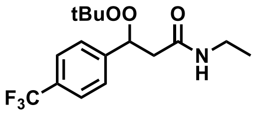
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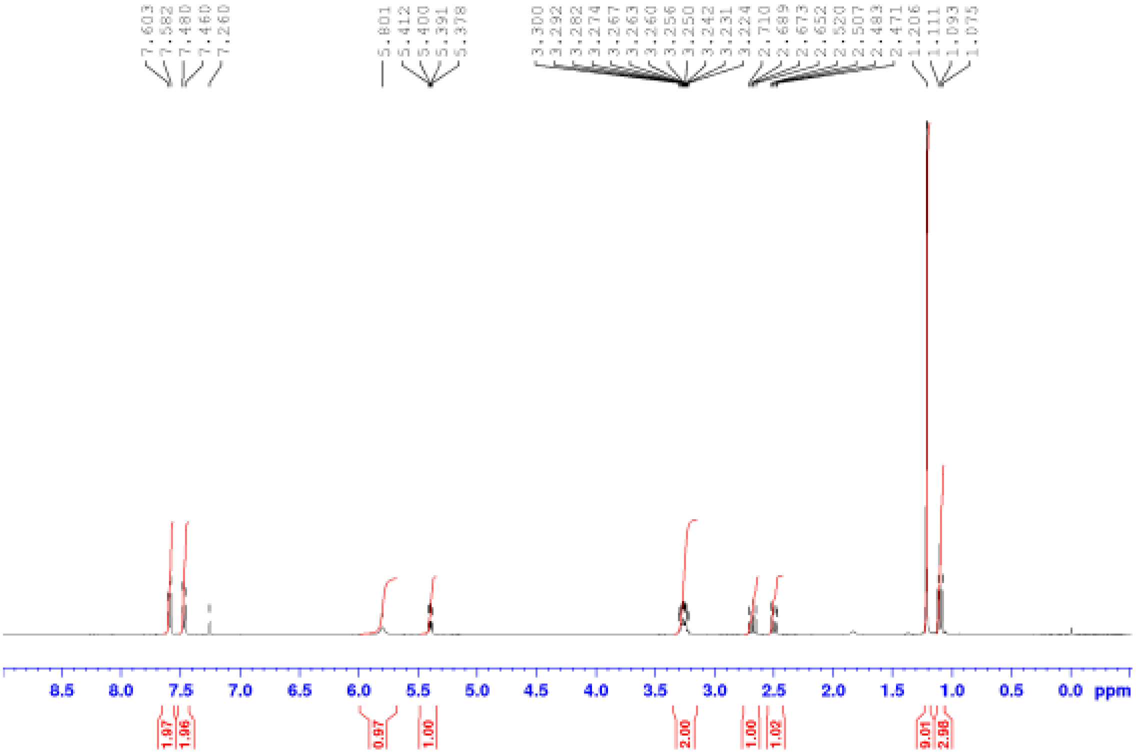
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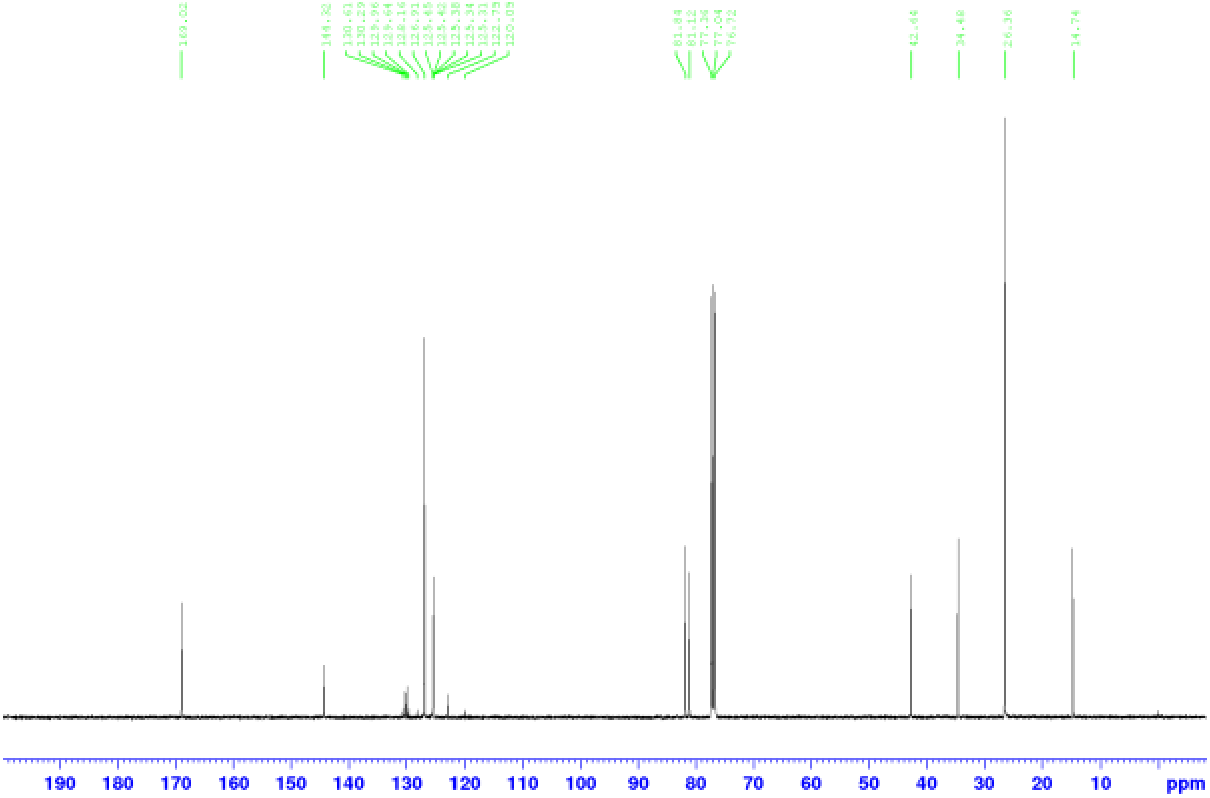
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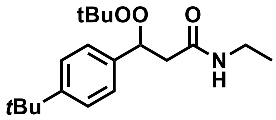
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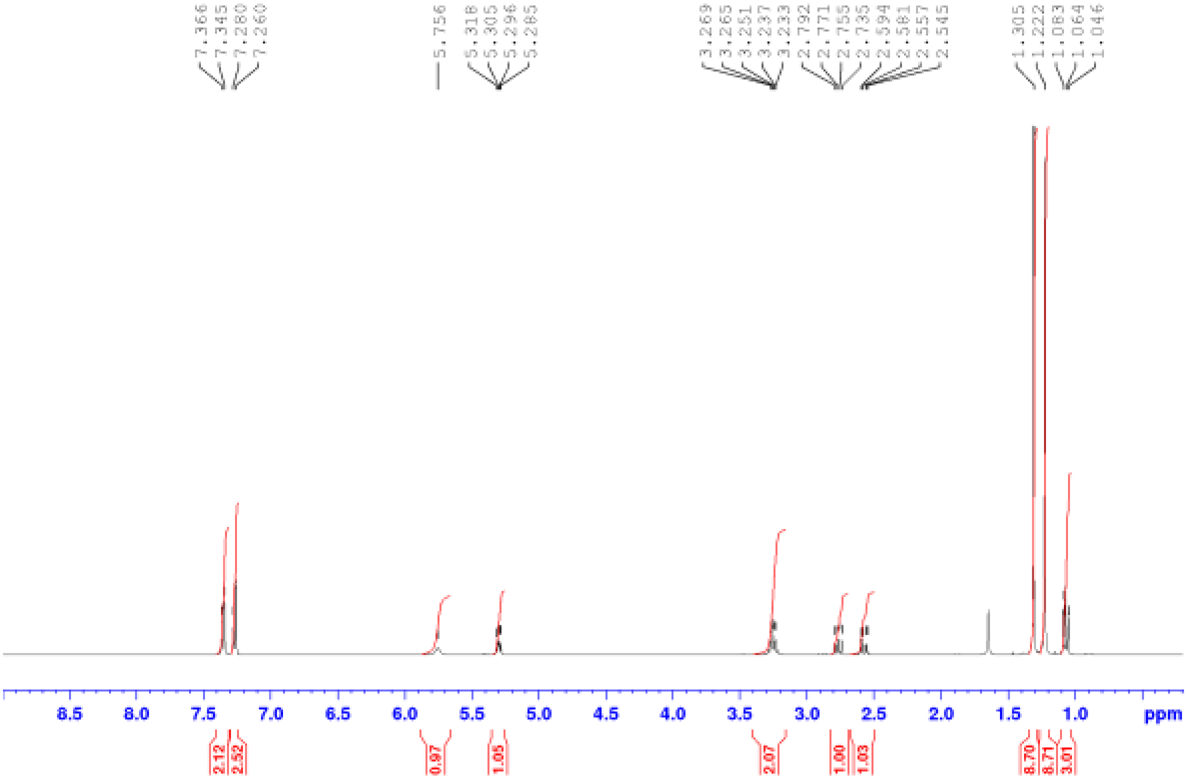
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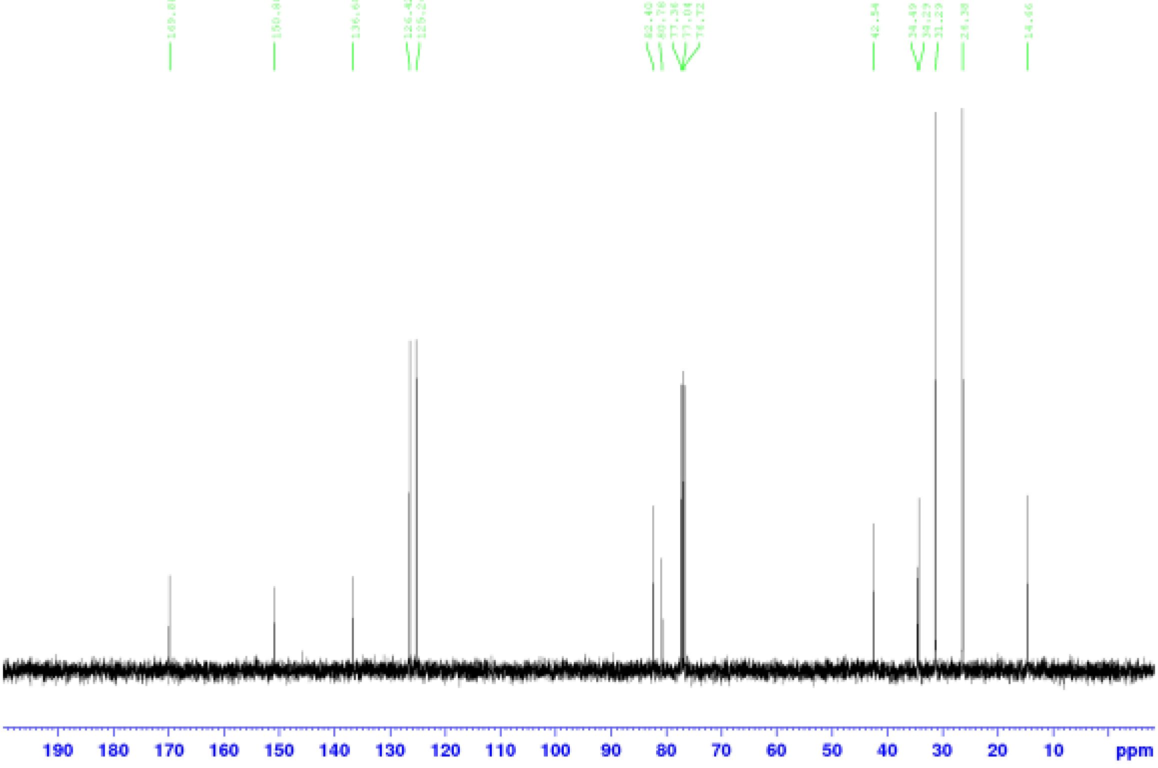
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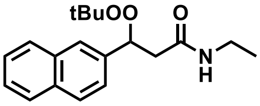
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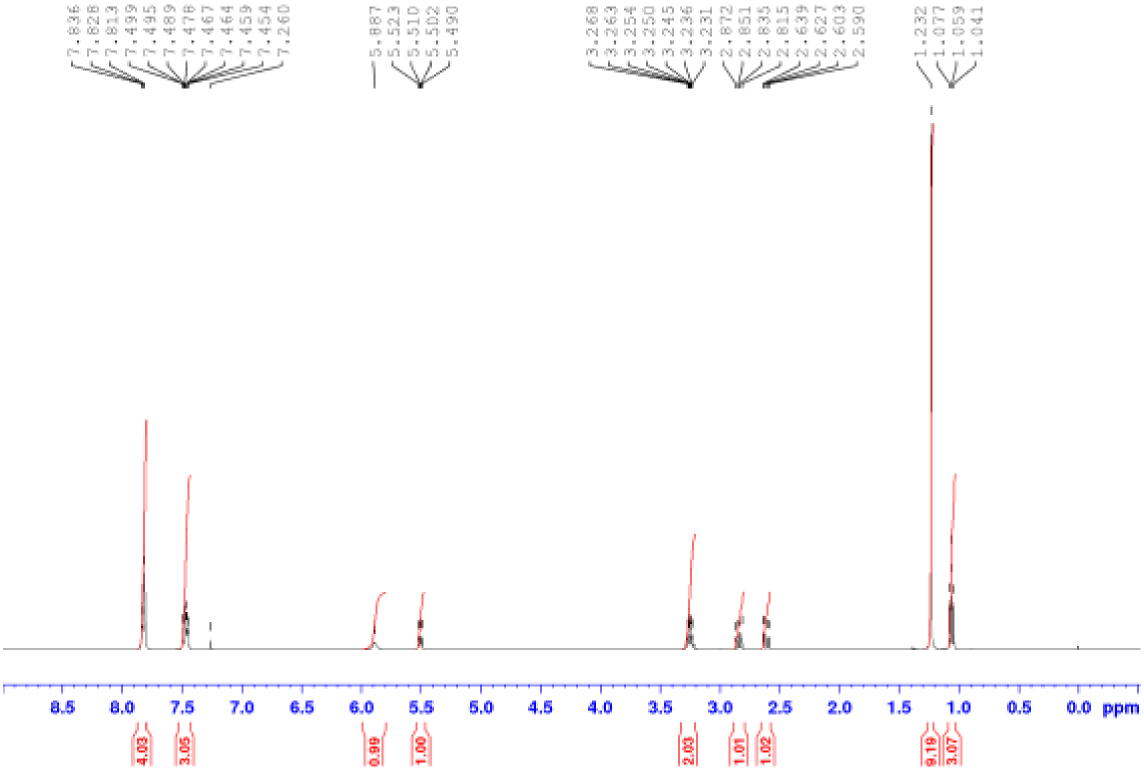
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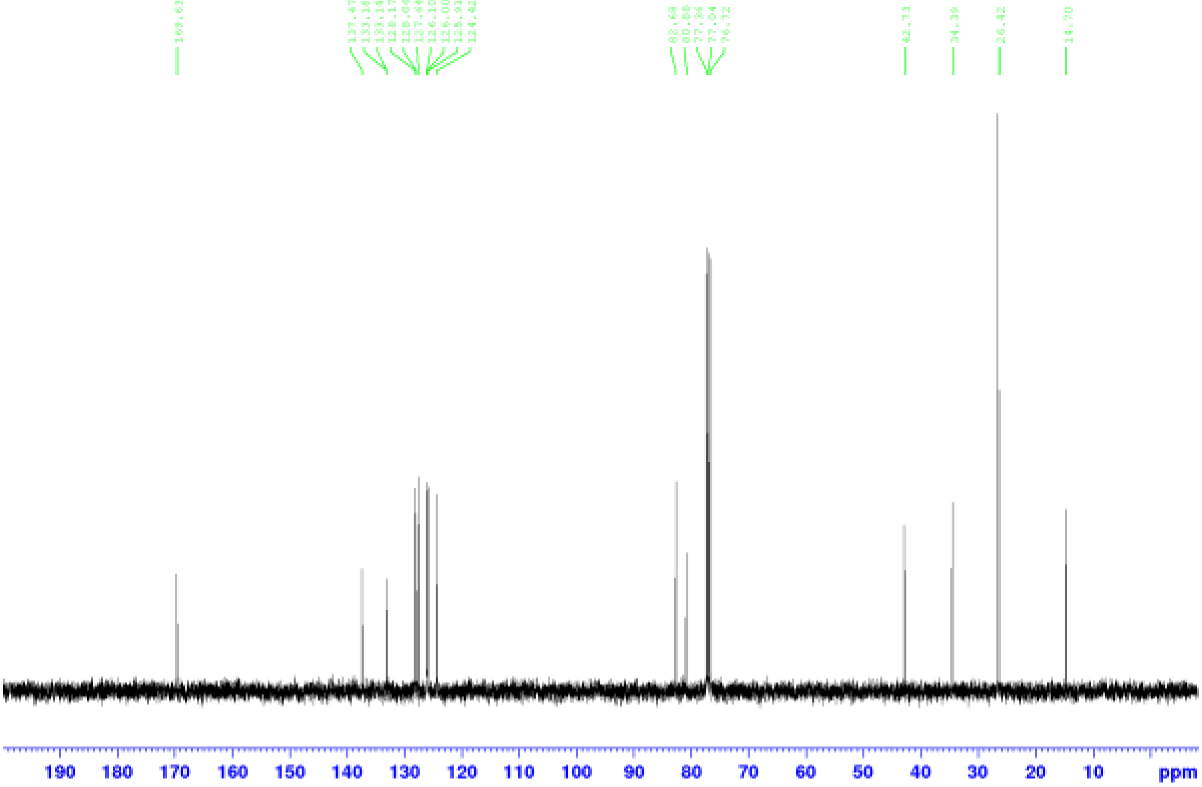
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26.42
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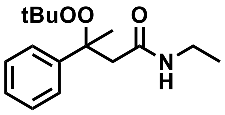
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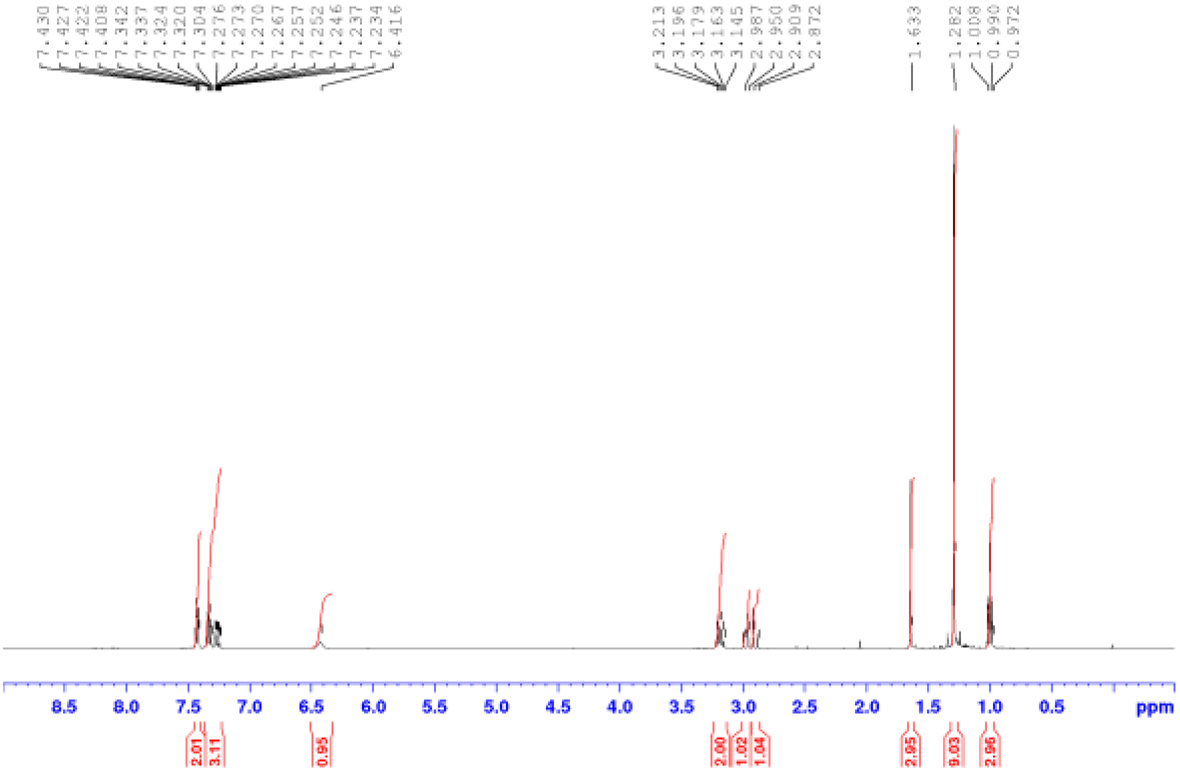
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7.267
7.257
7.252
7.246
7.237
7.234
6.416
3.213
3.196
3.179
3.163
3.145
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2.950
2.909
2.872
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1.282
1.008
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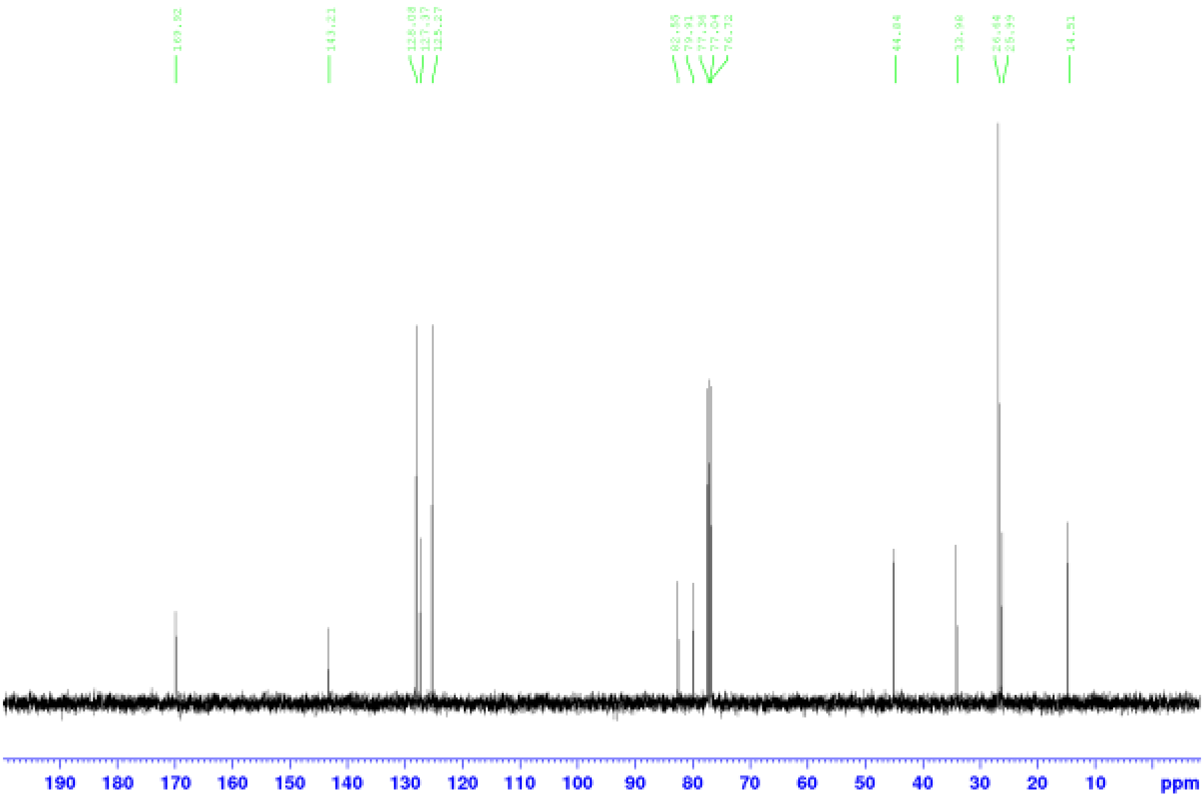
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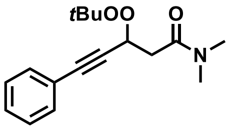
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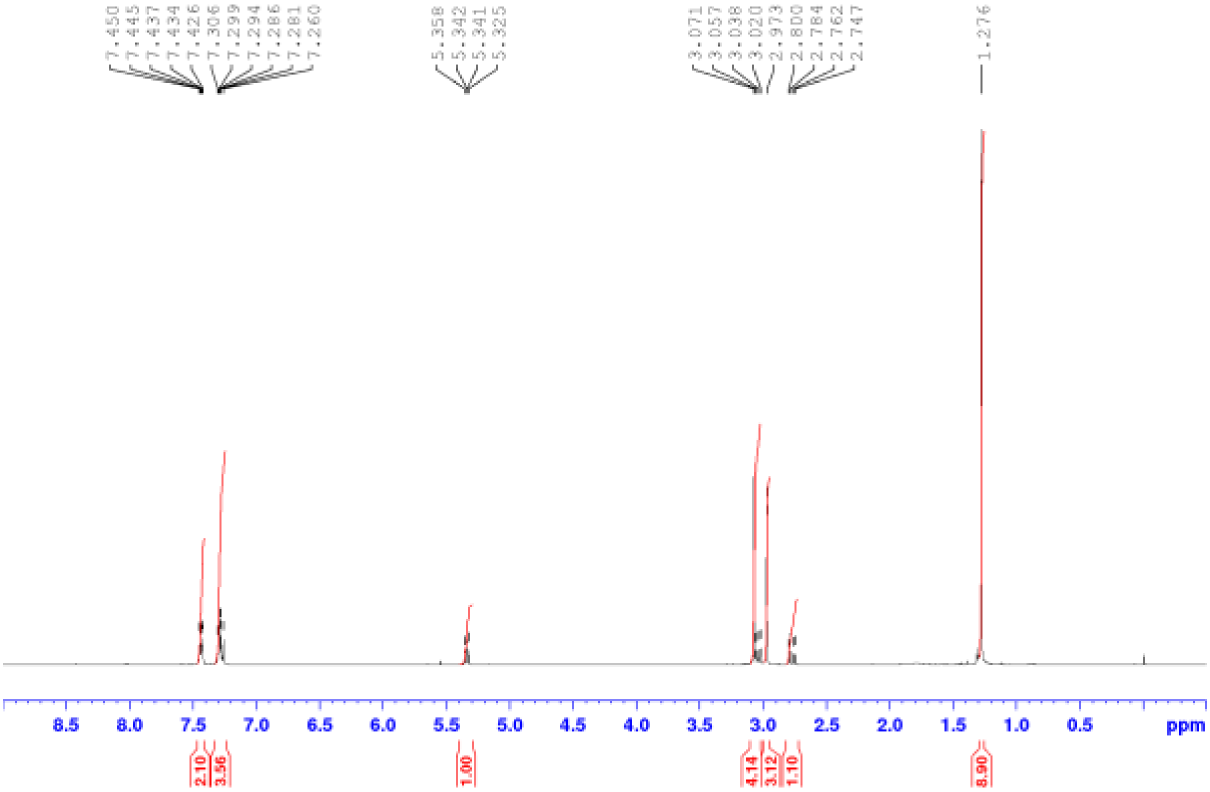
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3.038
3.020
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2.747
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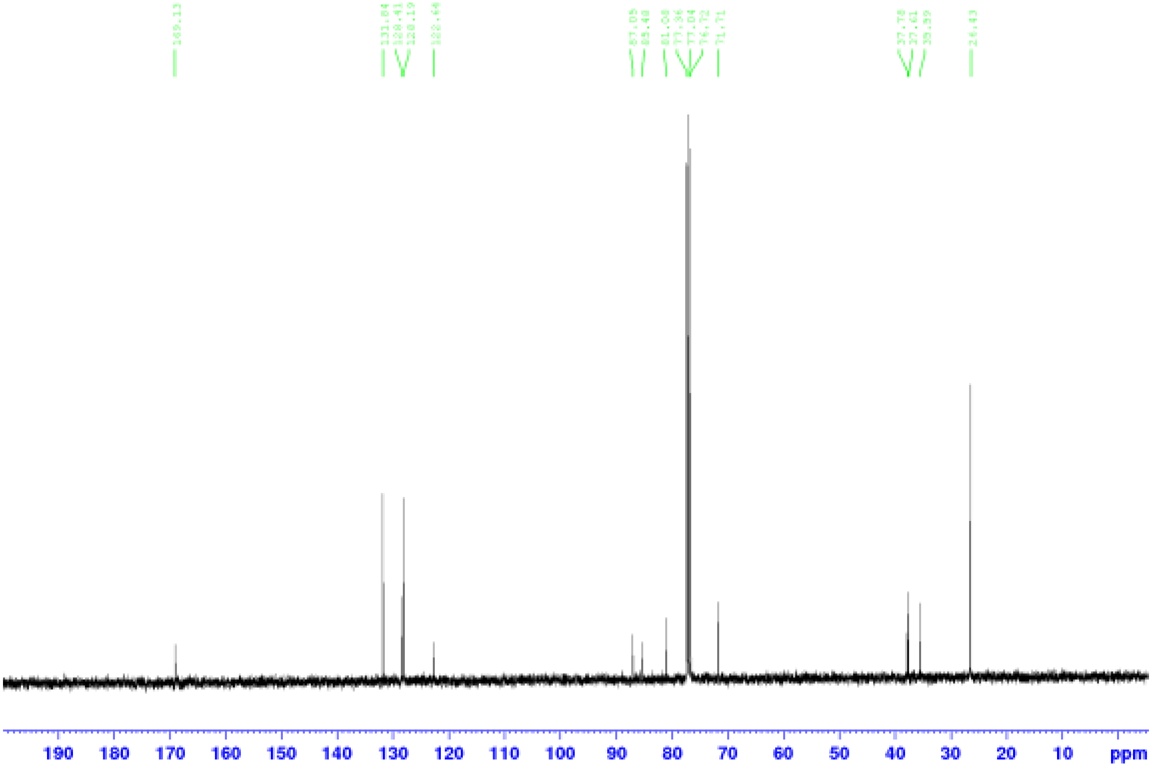
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35.39
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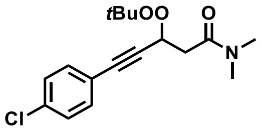
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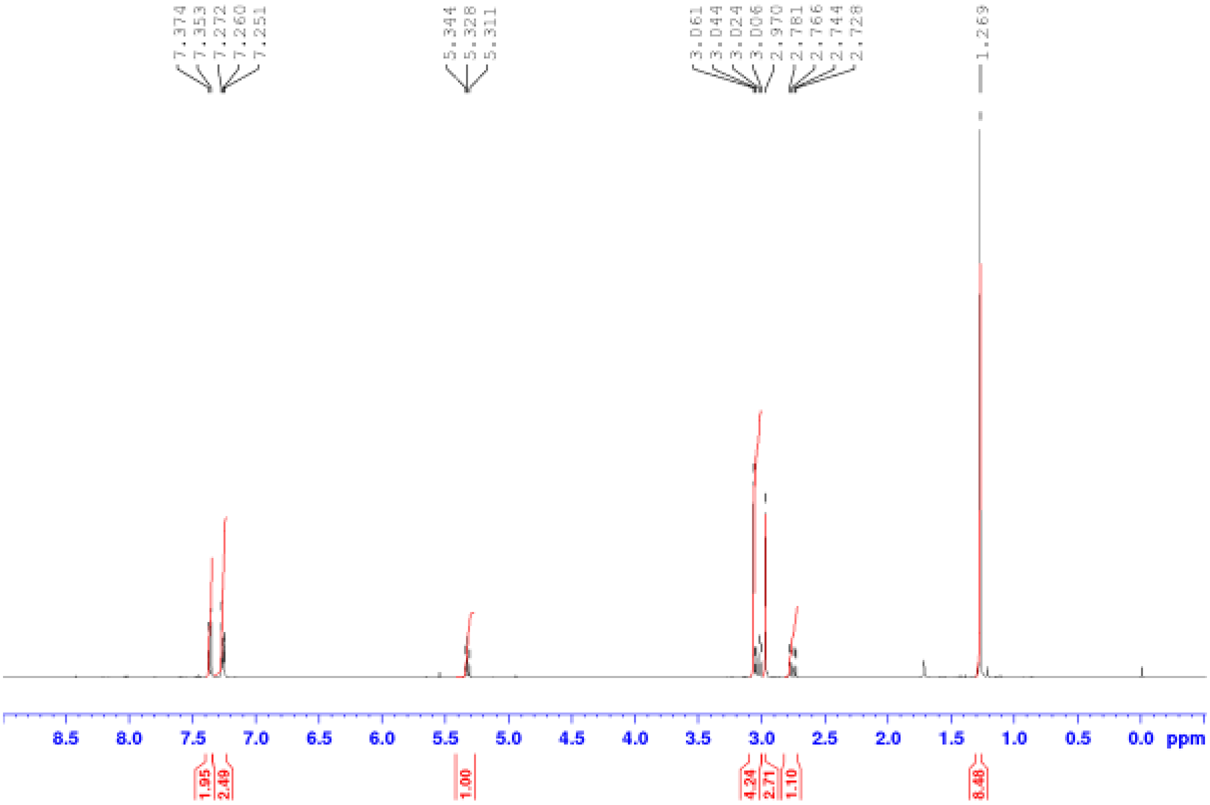
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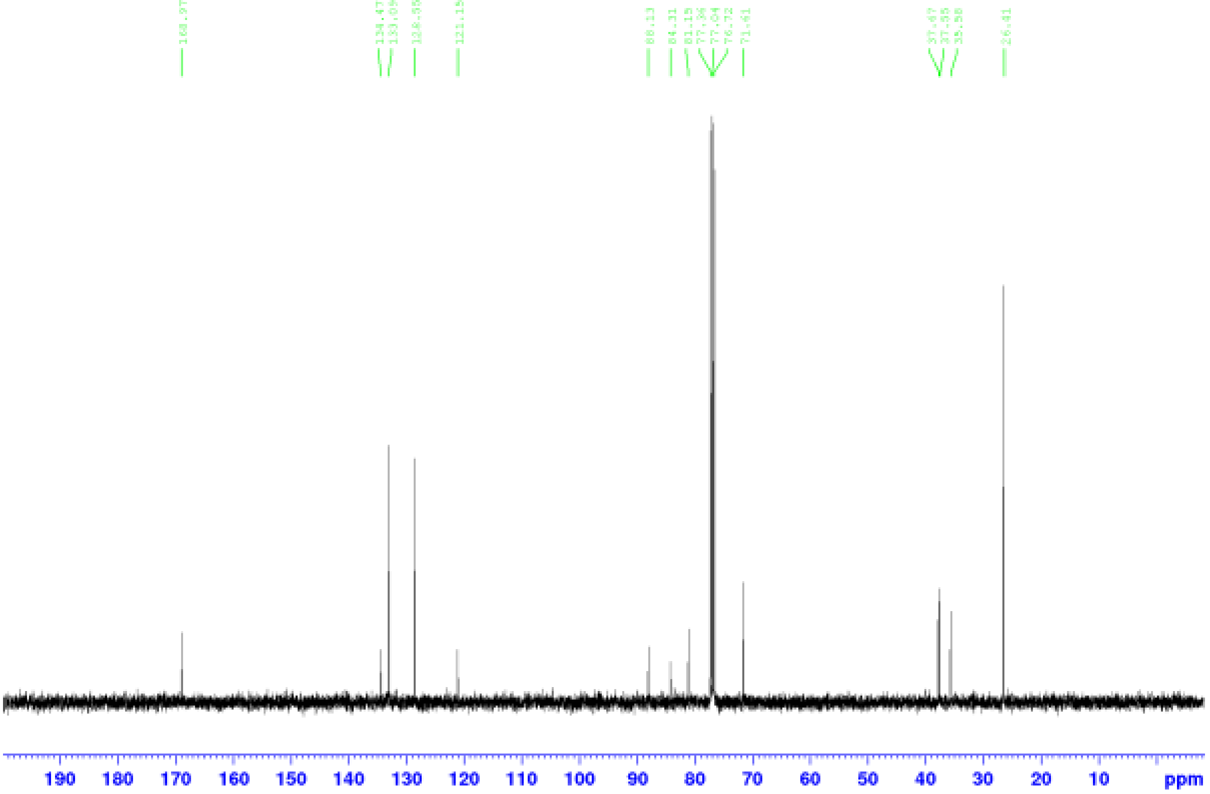
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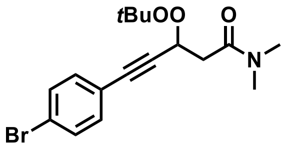
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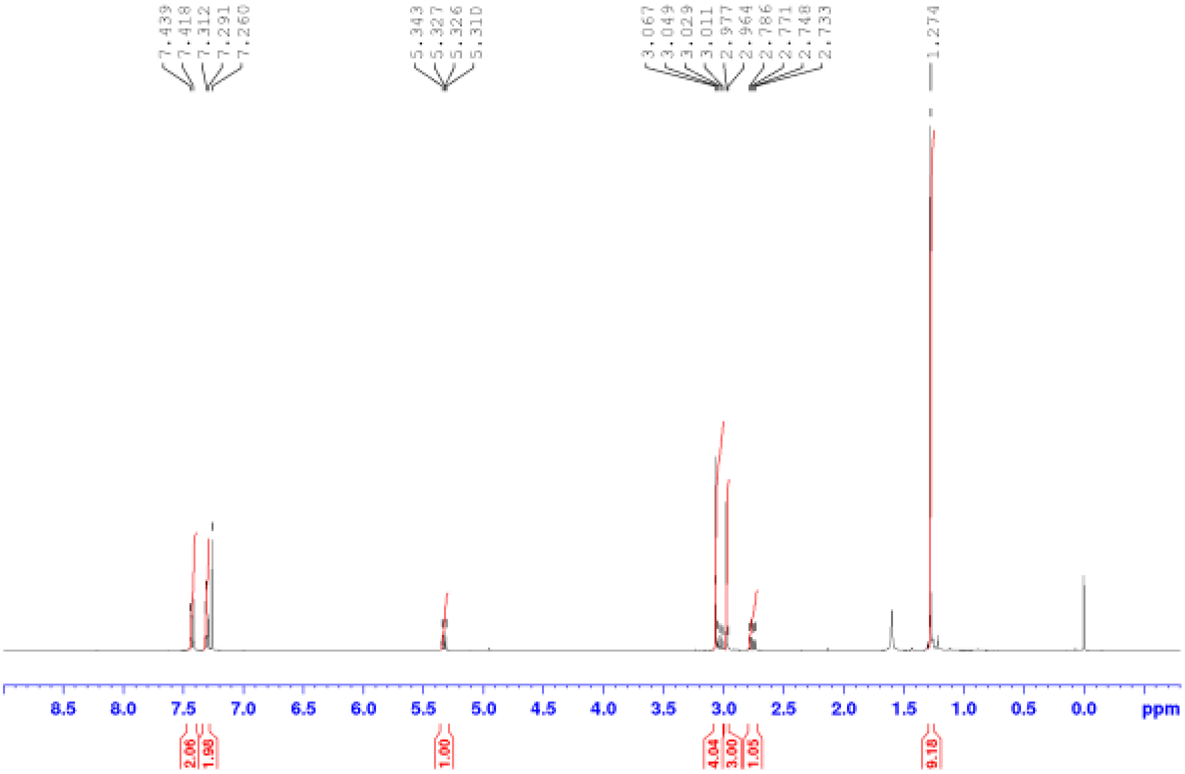
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3.029
3.011
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2.964
2.786
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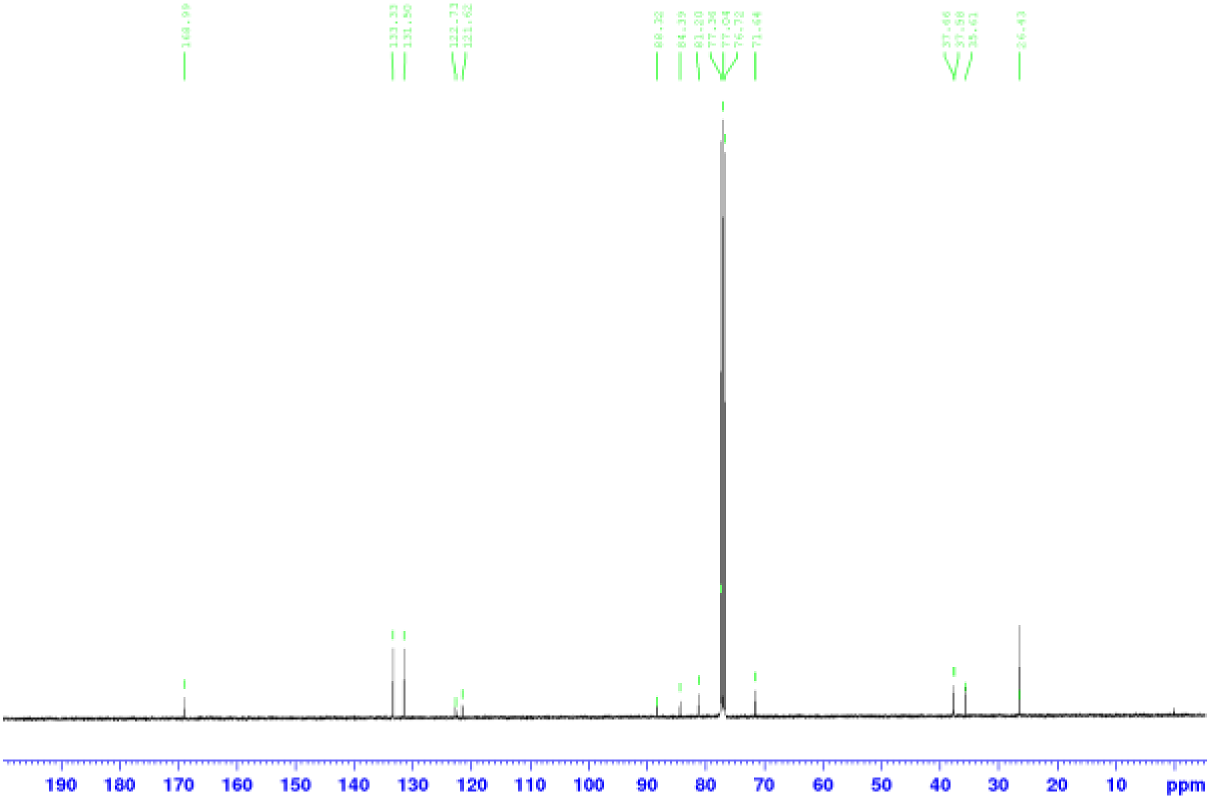
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30
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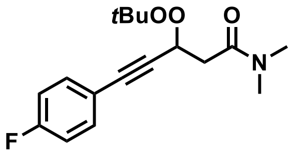
10
ppm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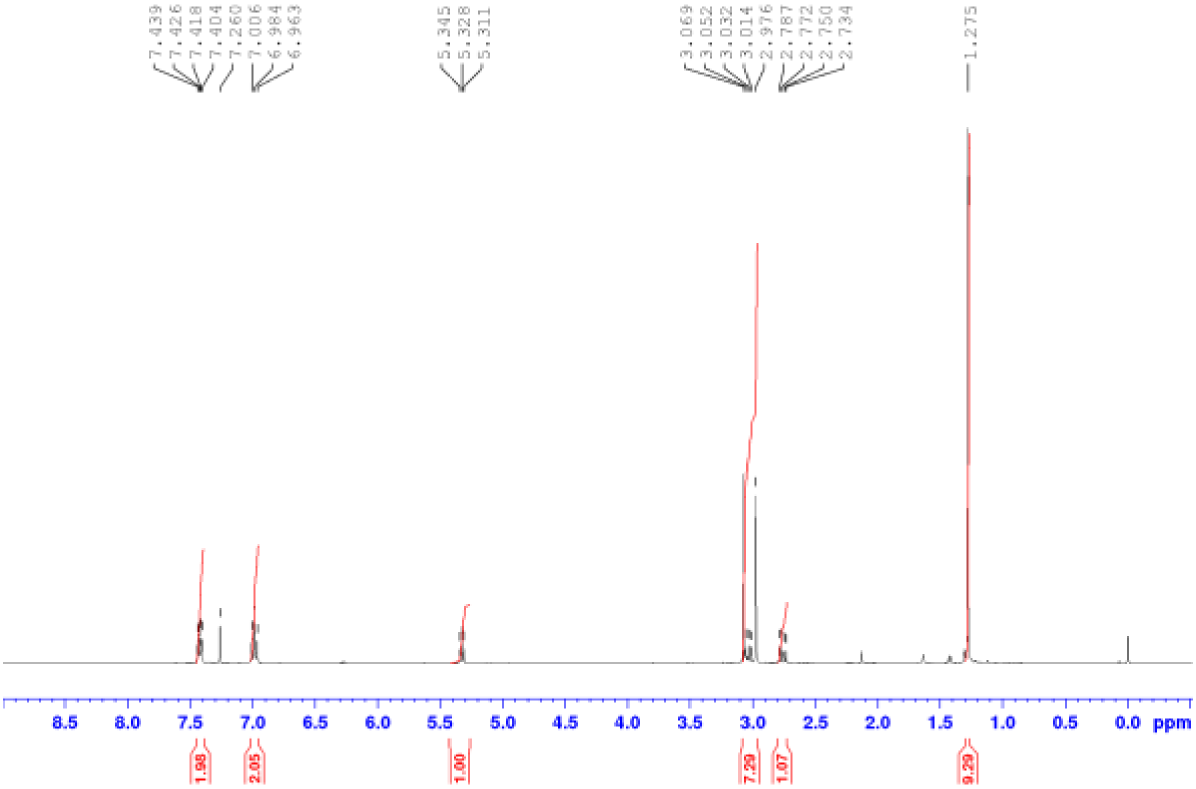
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3.032
3.014
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2.787
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7.0
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6.0
5.5
5.0
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4.0
3.5
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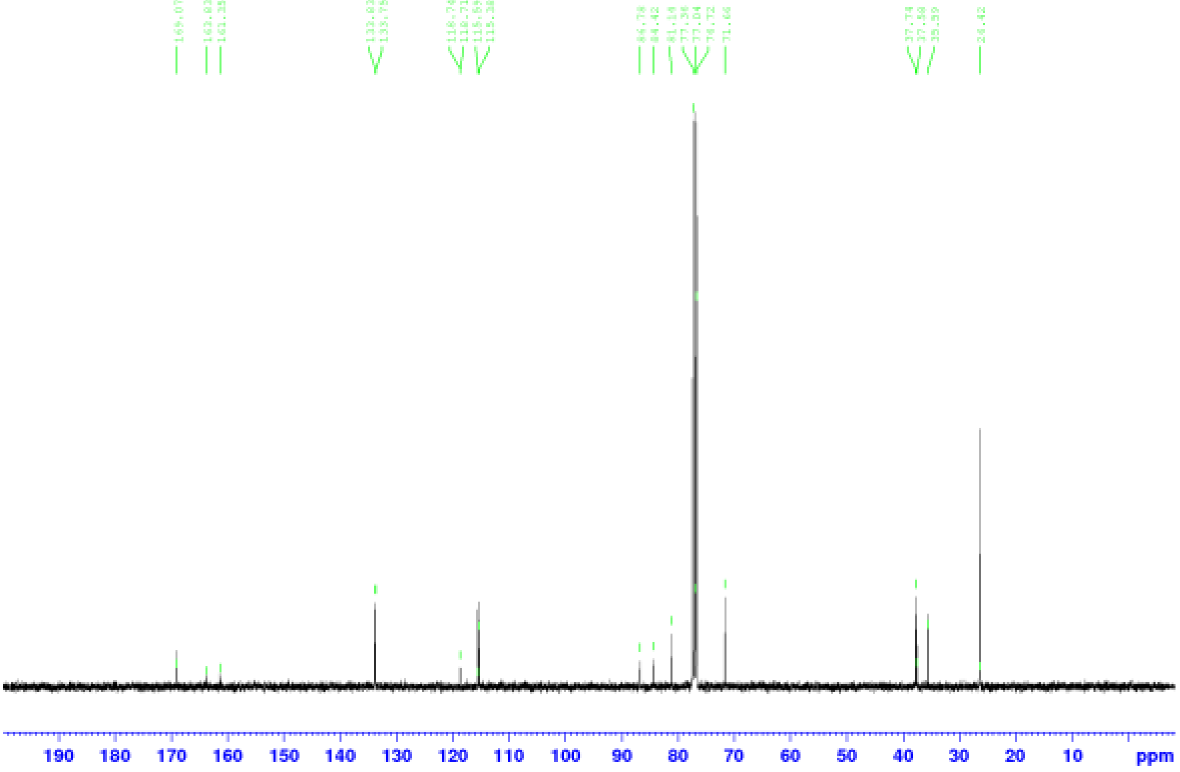
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77.04
76.72
71.66
37.74
37.58
35.59
26.42
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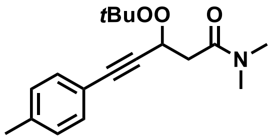
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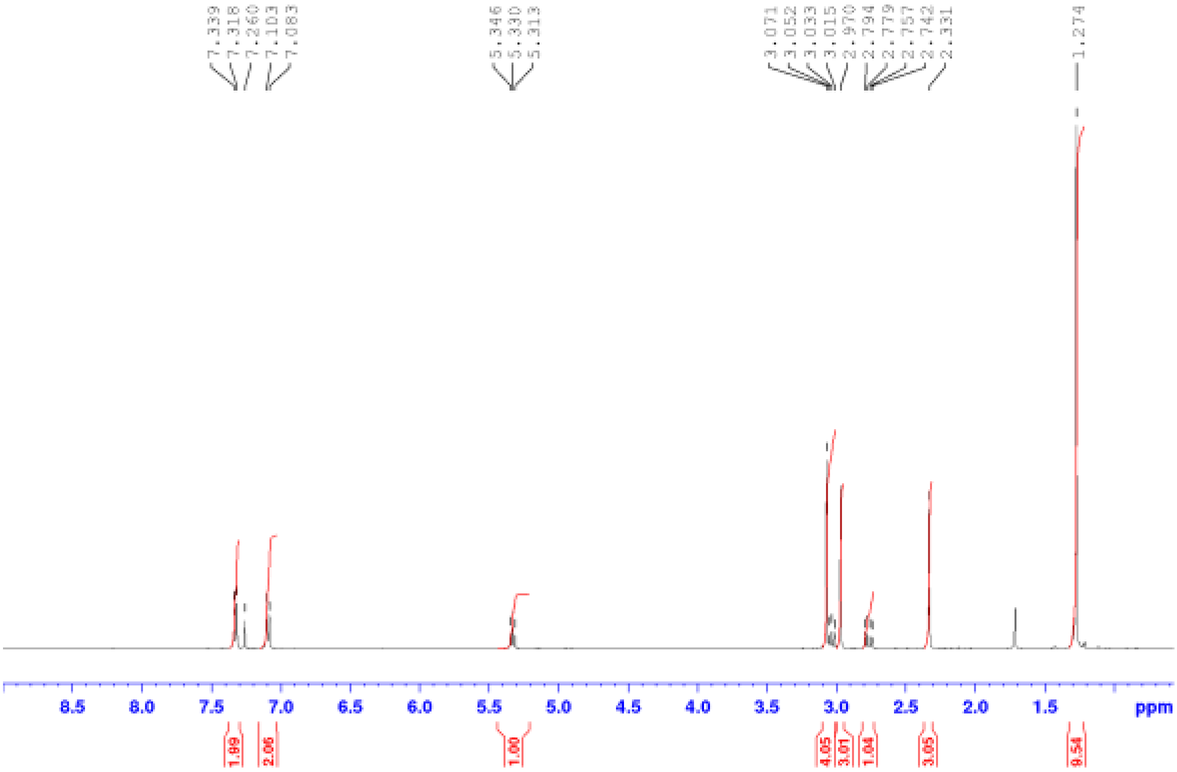
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3.033
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2.779
2.757
2.742
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6.5
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5.0
4.5
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3.05
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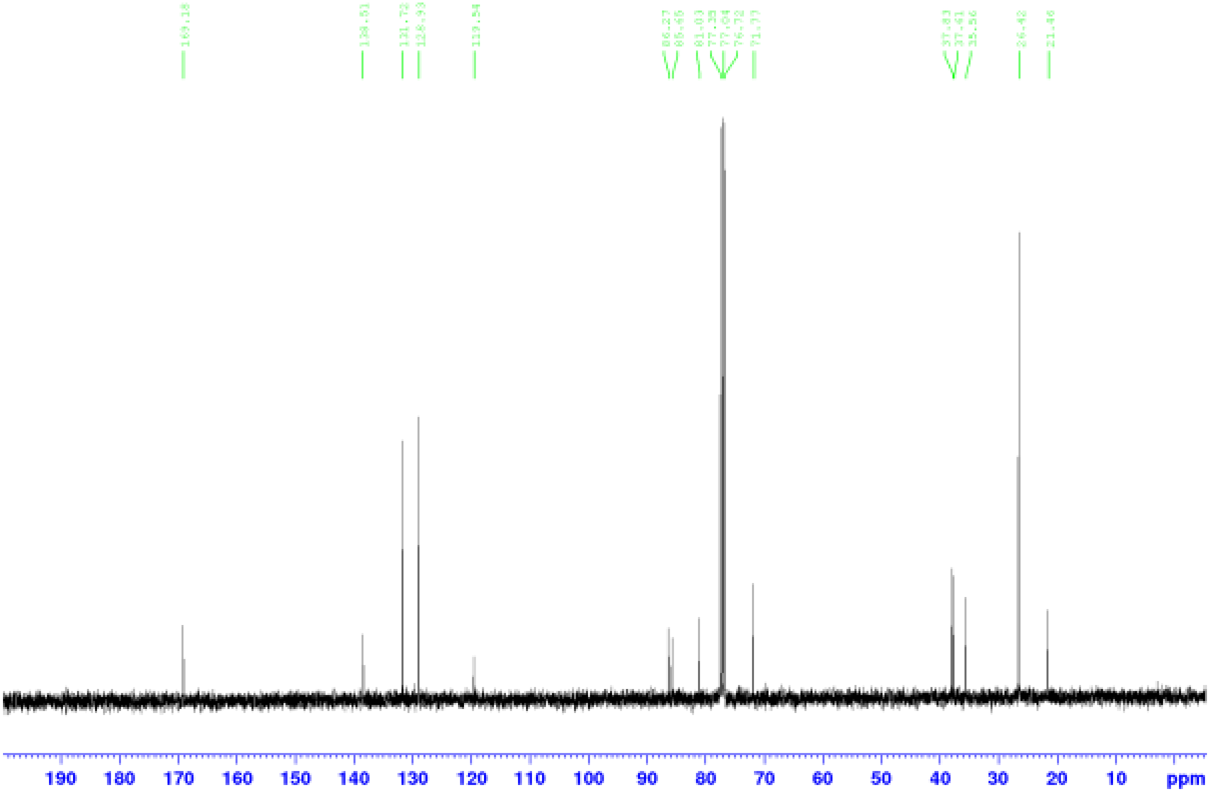
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26.42
21.46
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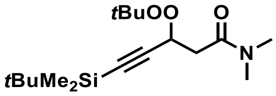
ppm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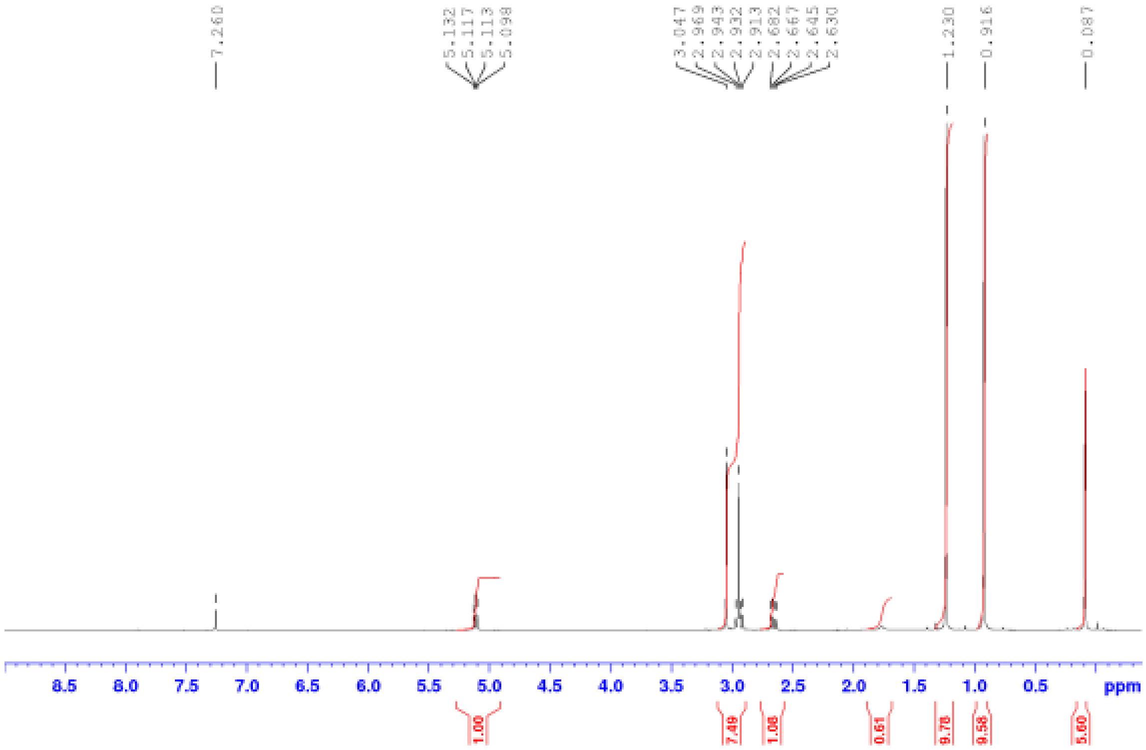
tBuMe$_2$Si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0.087
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6.0
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3.5
3.0
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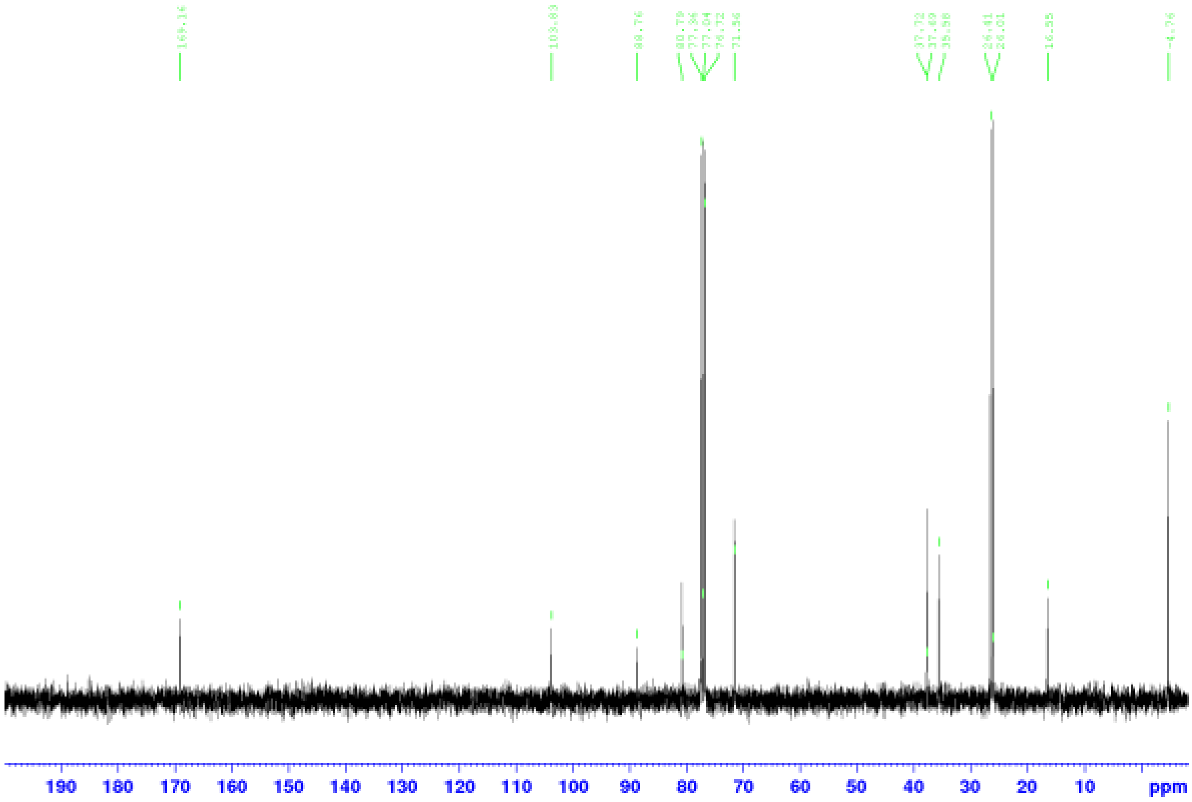
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-4.76
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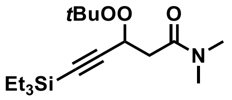
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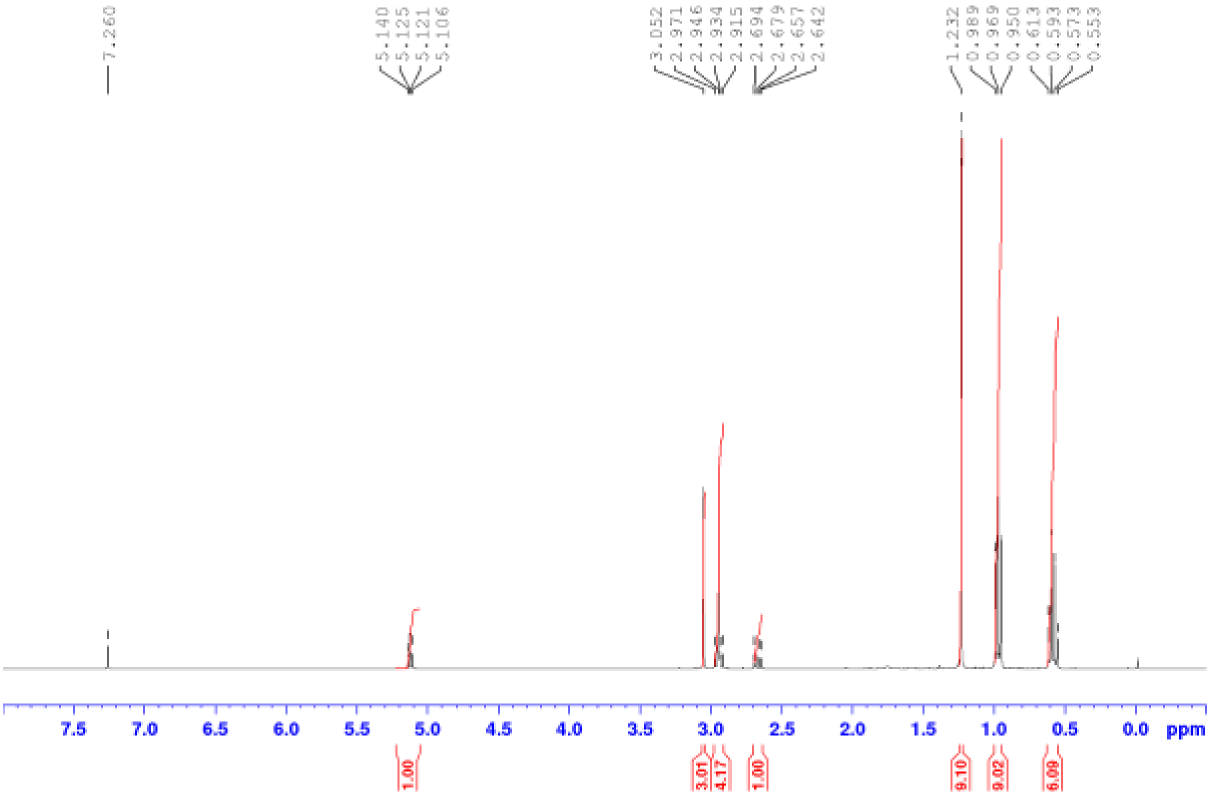
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2.657
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1.232
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0.969
0.950
0.613
0.593
0.573
0.553
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6.5
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5.5
5.0
4.5
4.0
3.5
3.0
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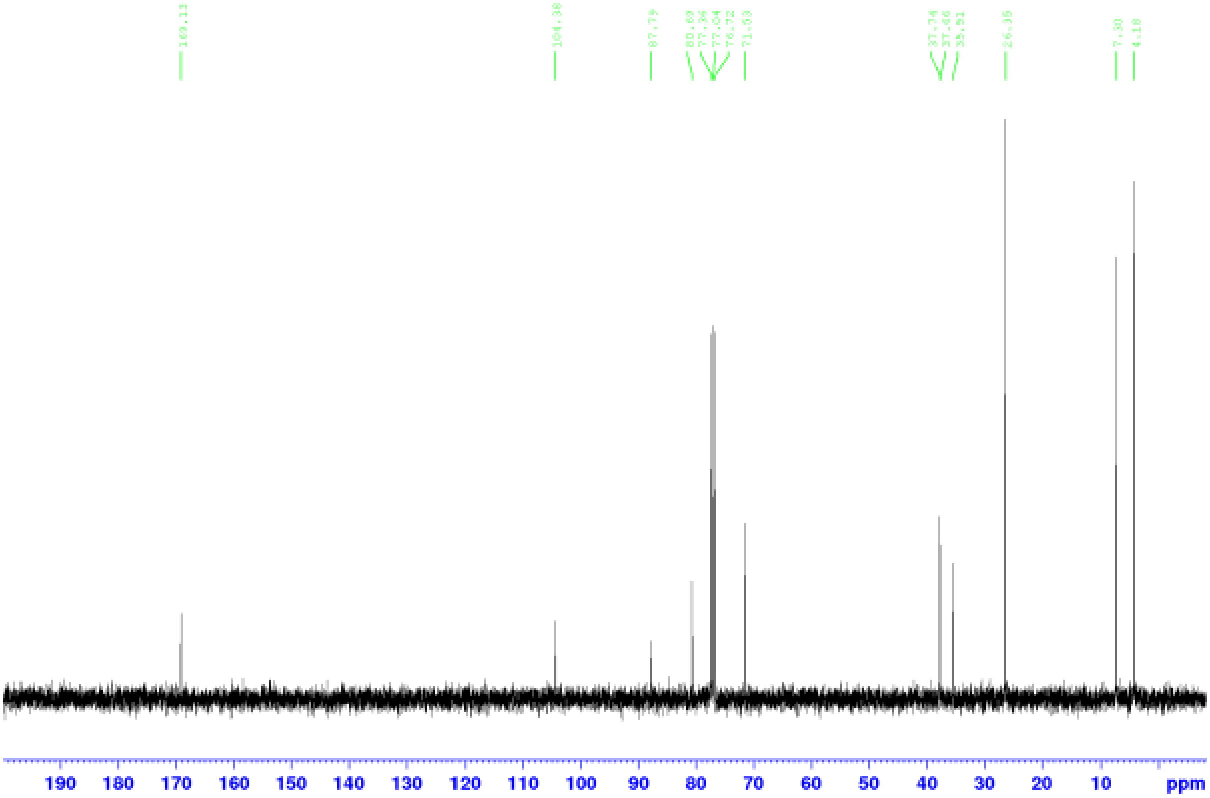
6.09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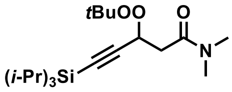
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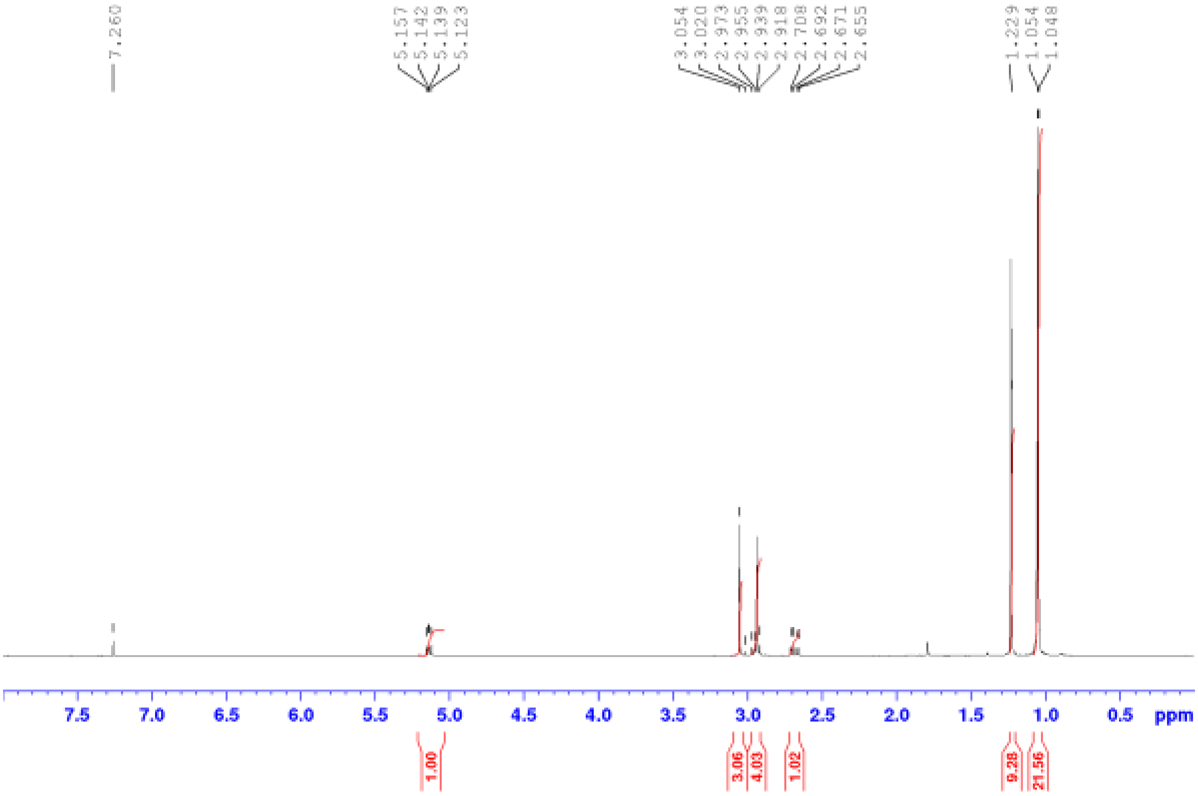
(i-Pr)3Si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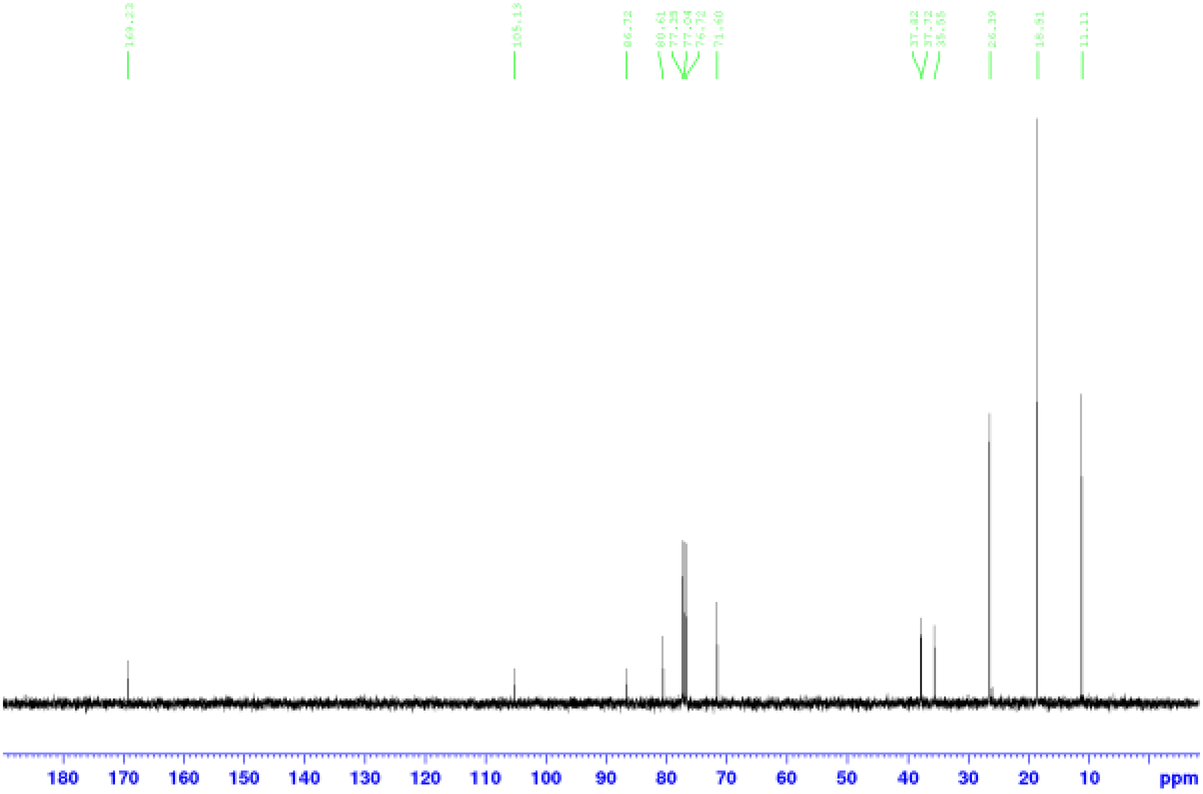
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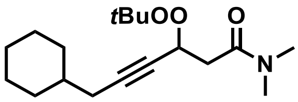
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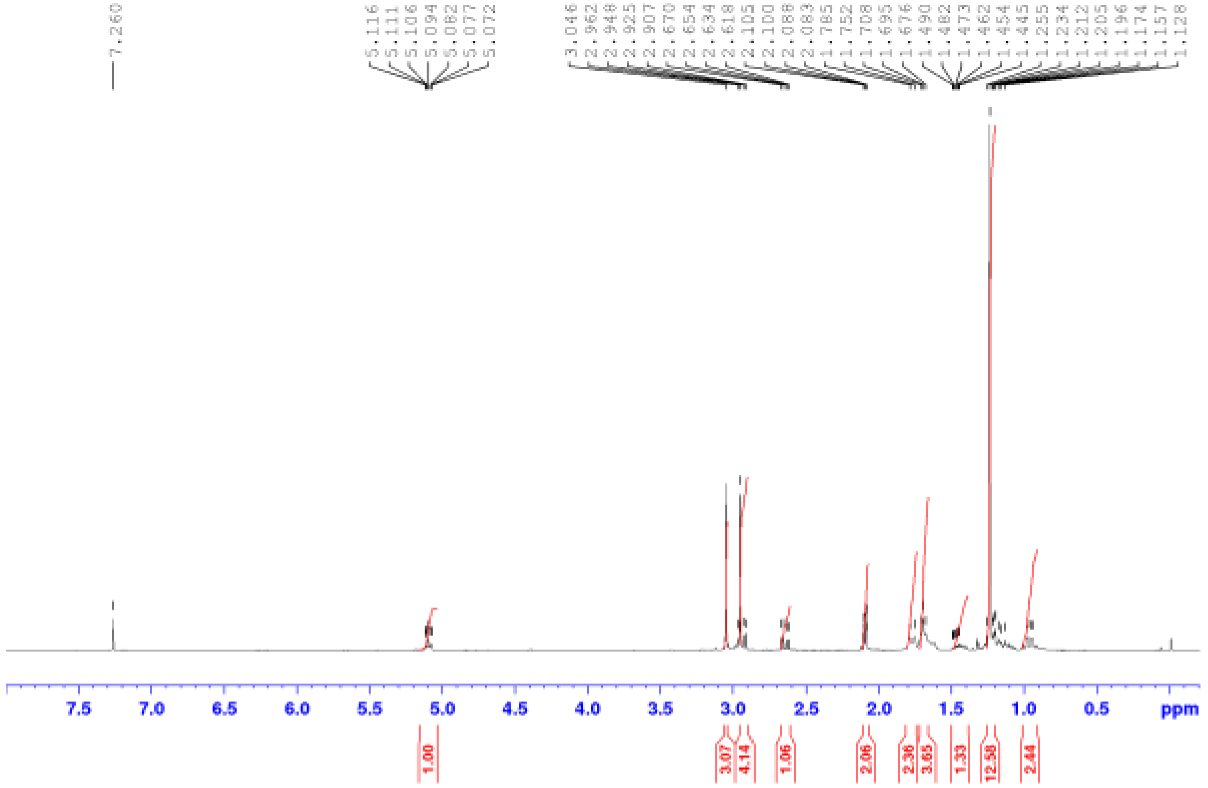
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1.708
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1.676
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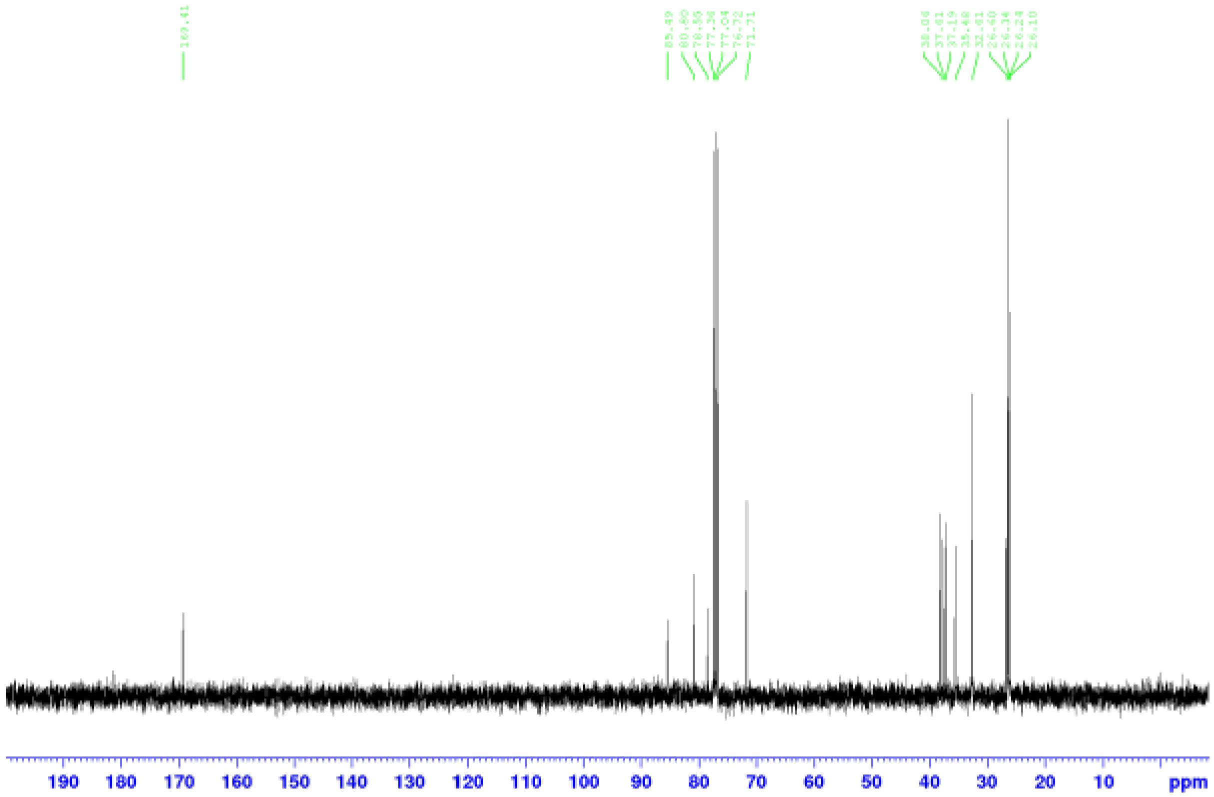
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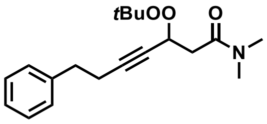

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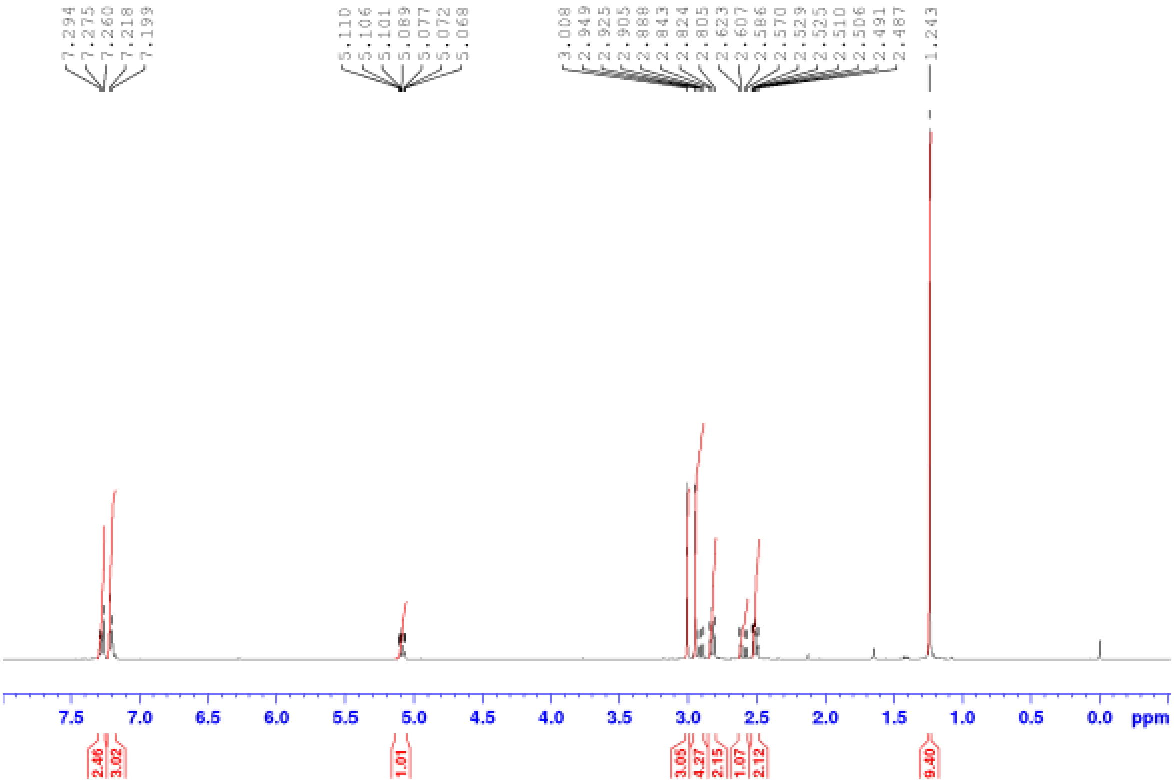

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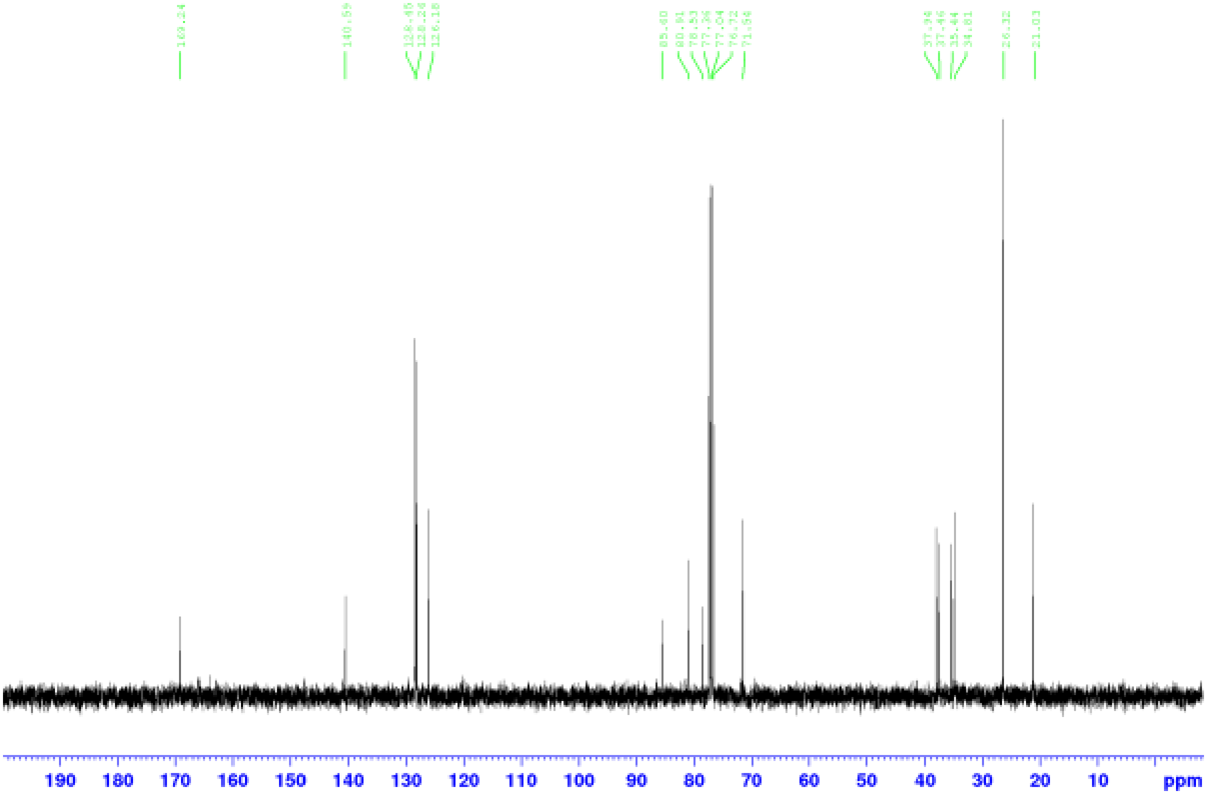

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20
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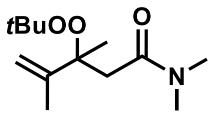
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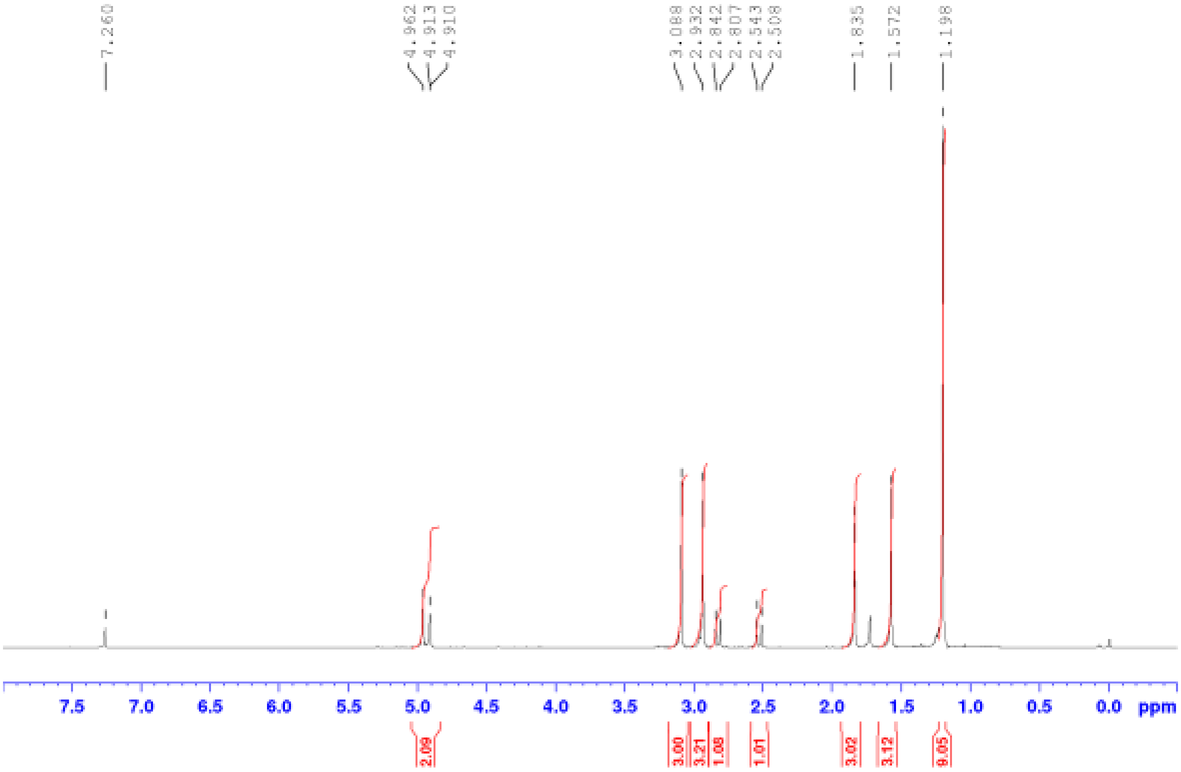
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2.807
2.543
2.508
1.835
1.572
1.198
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.08
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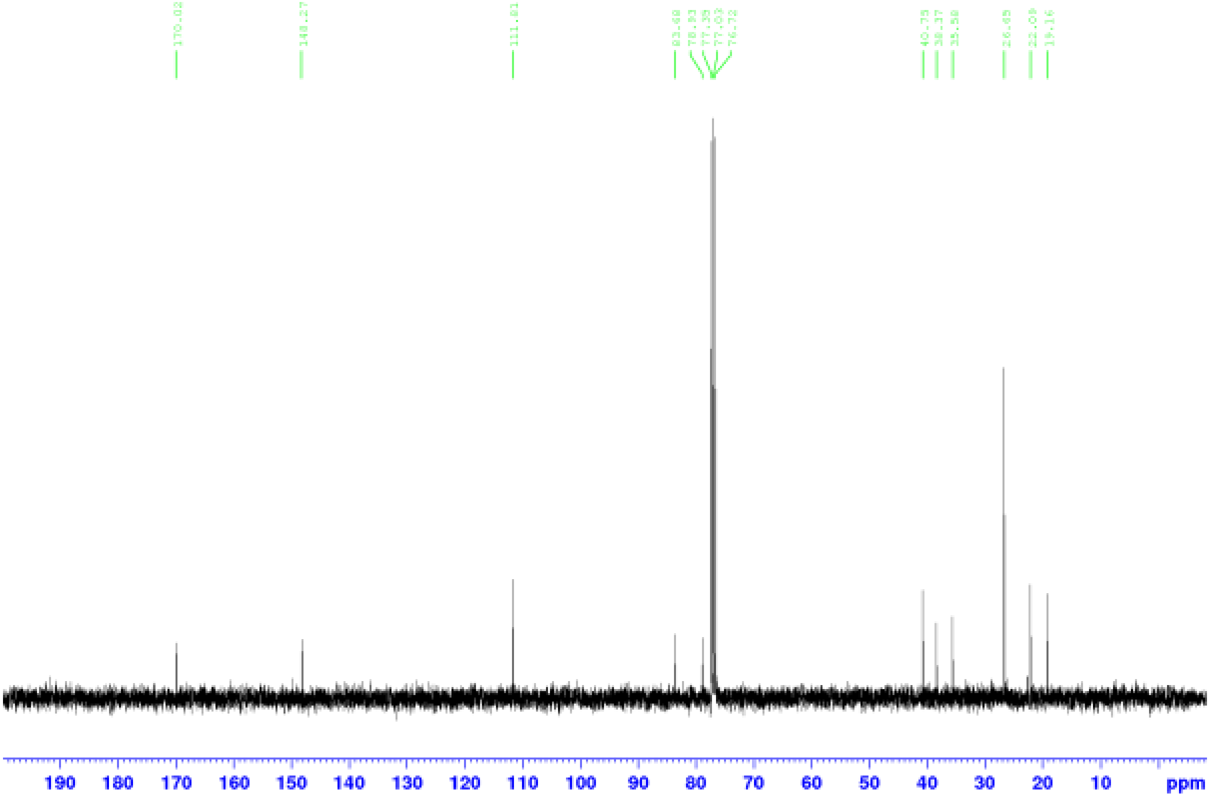
3.02
3.12
9.05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76.72
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26.65
22.09
19.16
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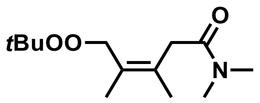
ppm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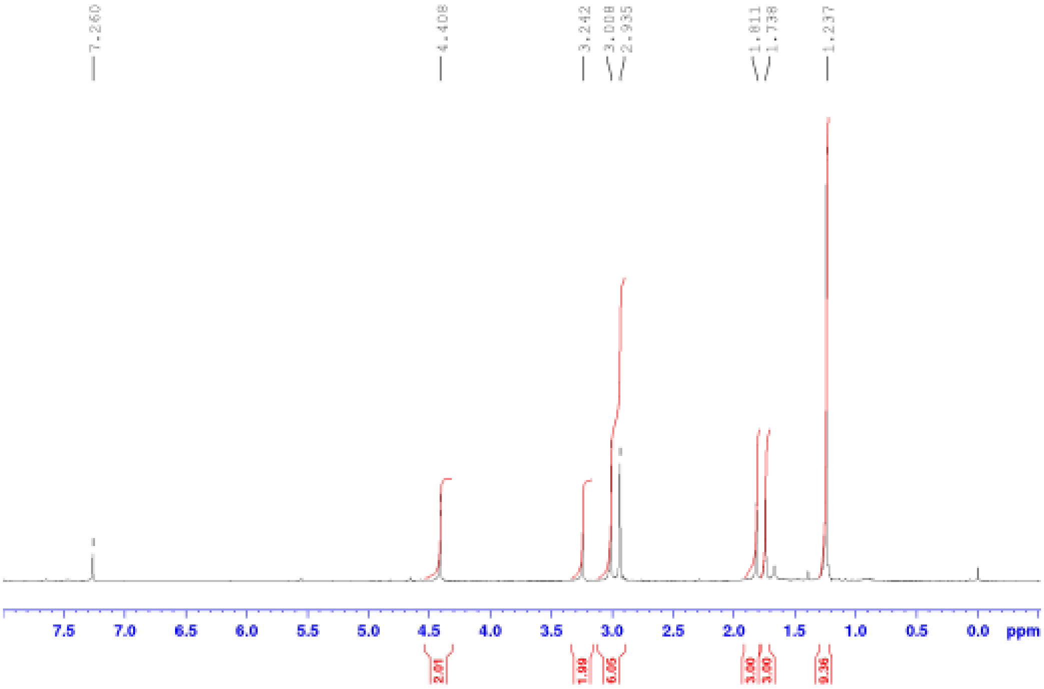
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5.0
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4.0
3.5
3.0
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0.0
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1.99
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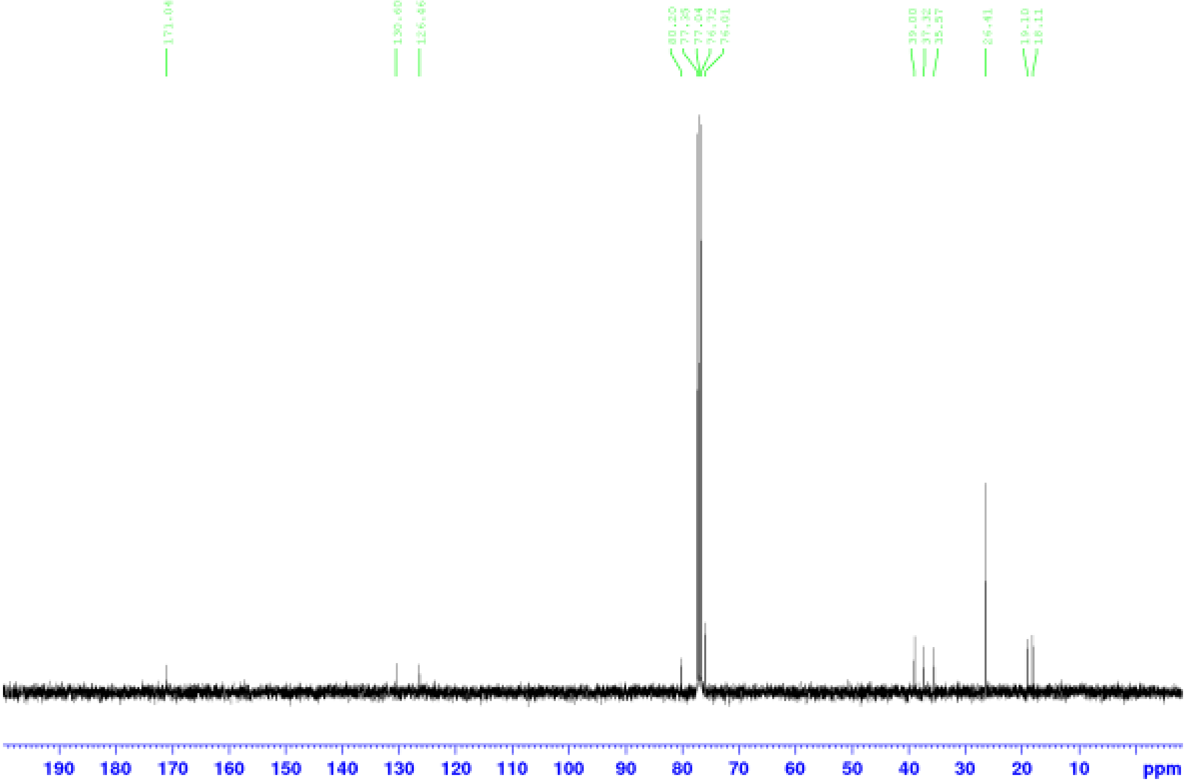
3.00
3.00
9.36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26.41
19.10
18.11
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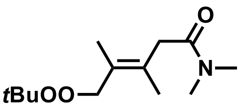
ppm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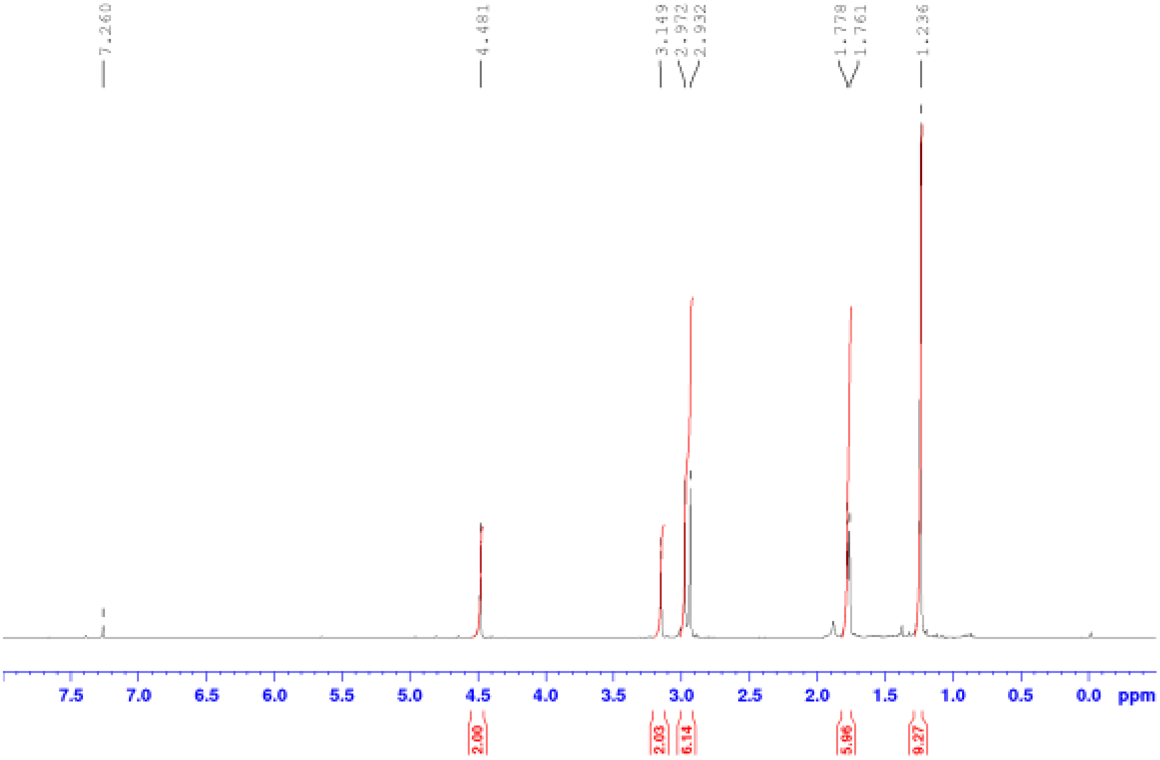
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5.0
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4.0
3.5
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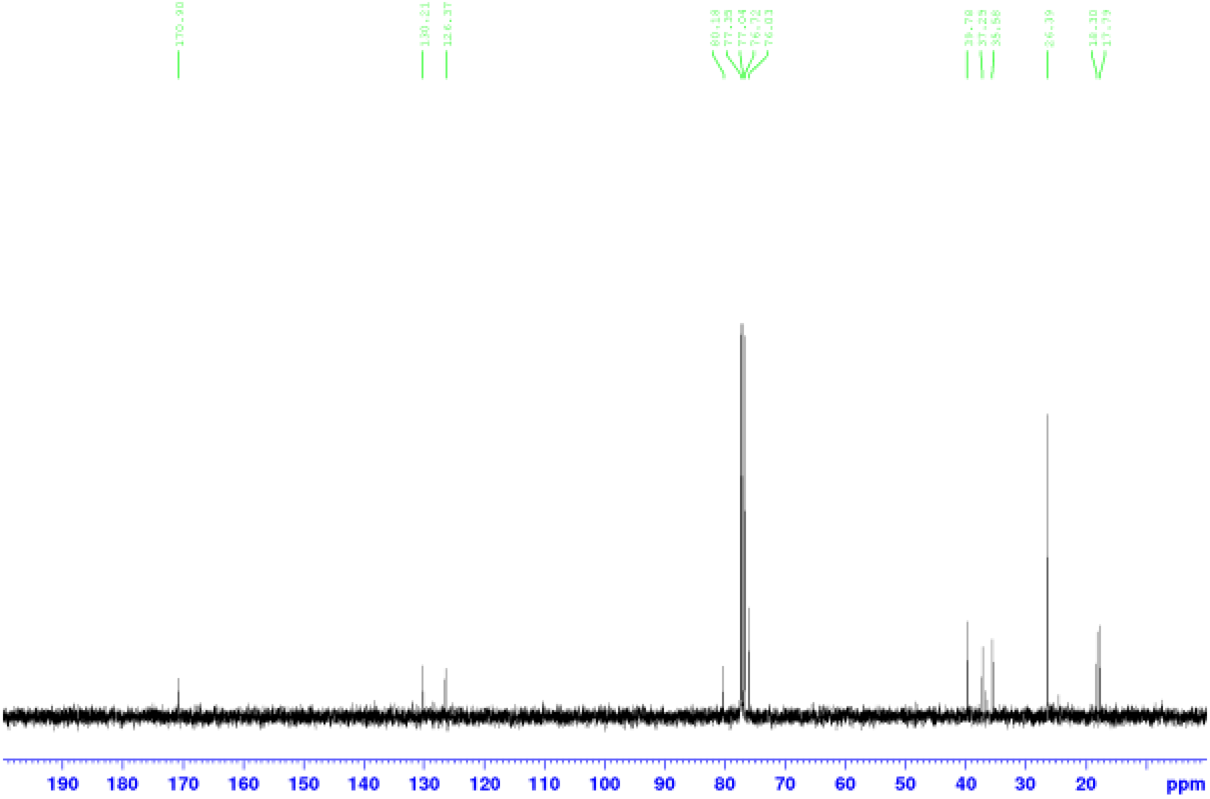
6.14
5.96
9.27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18.30
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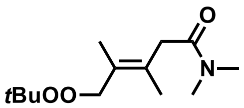
20
ppm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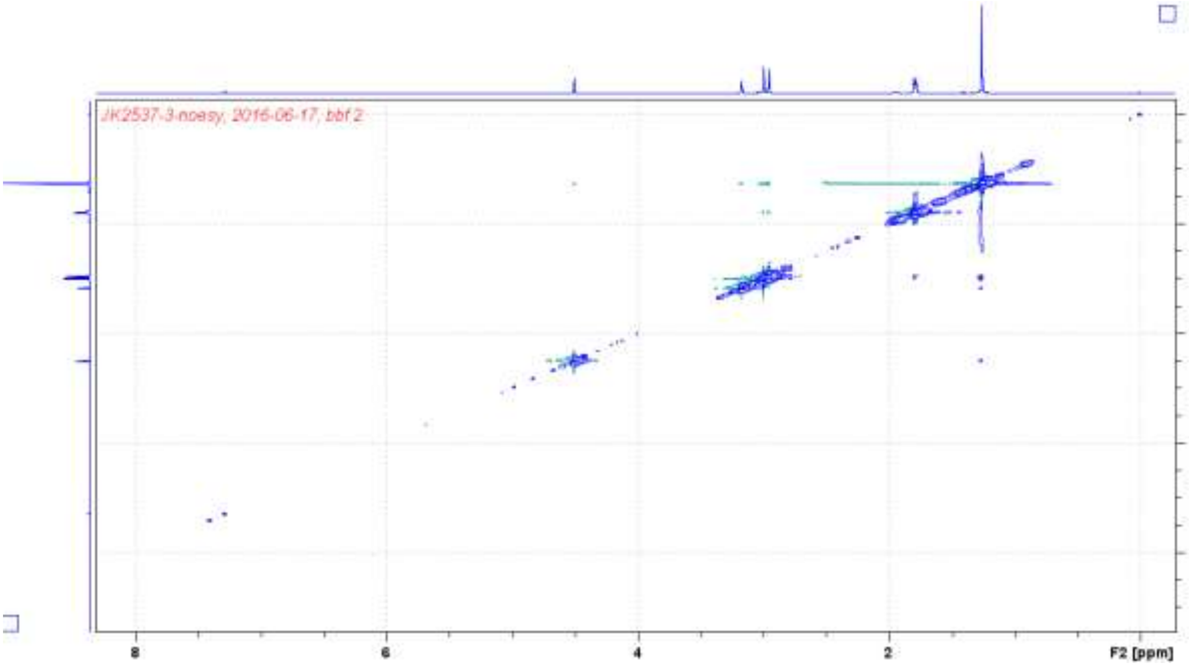
JK2537-3-noesy, 2016-06-17, bbf 2
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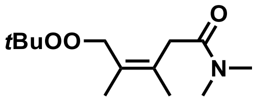
2
4
6
8
8
6
4
2
F2 [ppm]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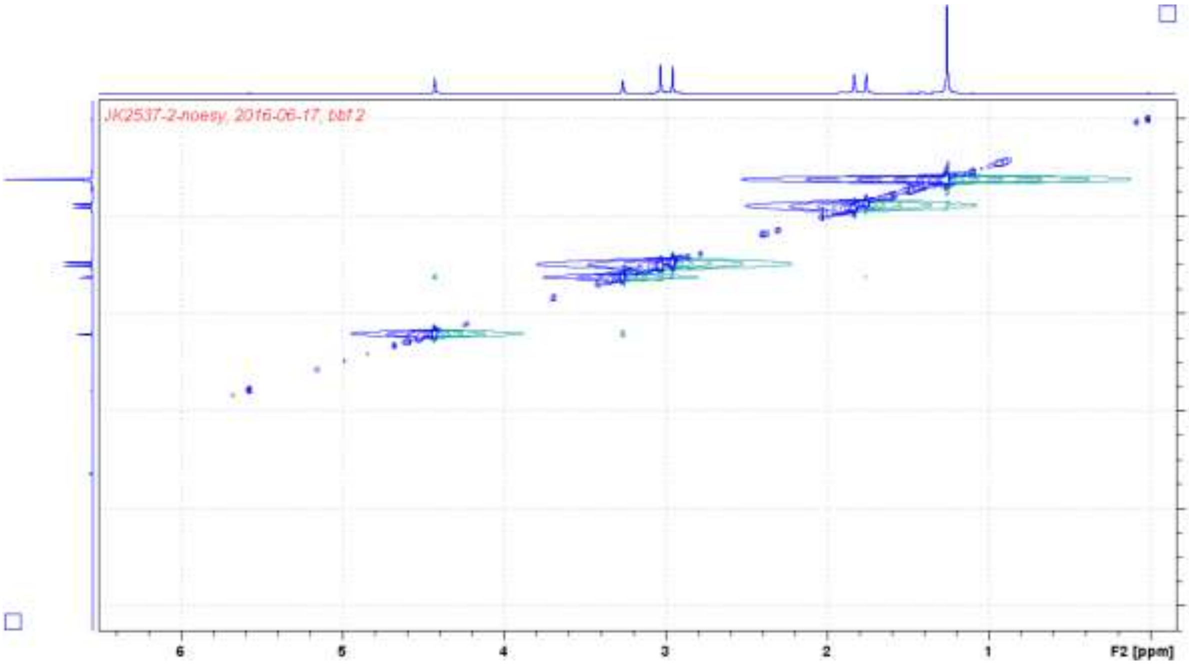
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4
6
8
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3
2
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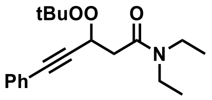
F2 [ppm]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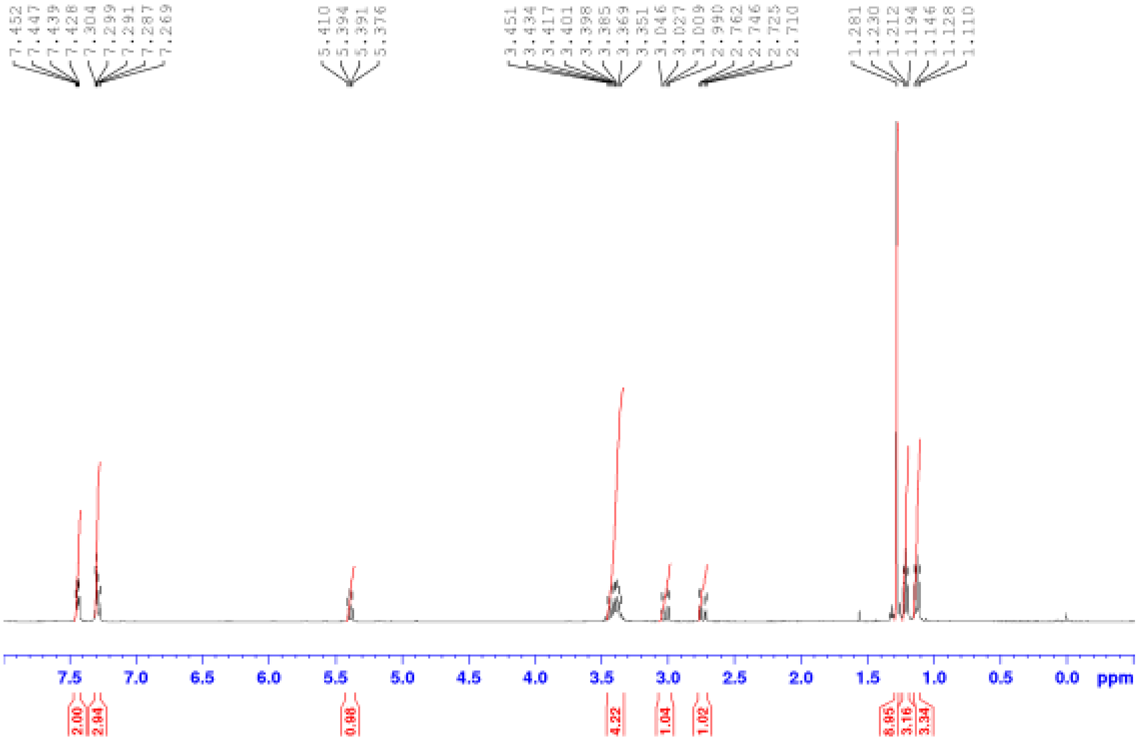
Ph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5.394
5.391
5.376
3.451
3.434
3.417
3.401
3.398
3.385
3.369
3.351
3.046
3.027
3.009
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2.746
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2.710
1.281
1.230
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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ppm
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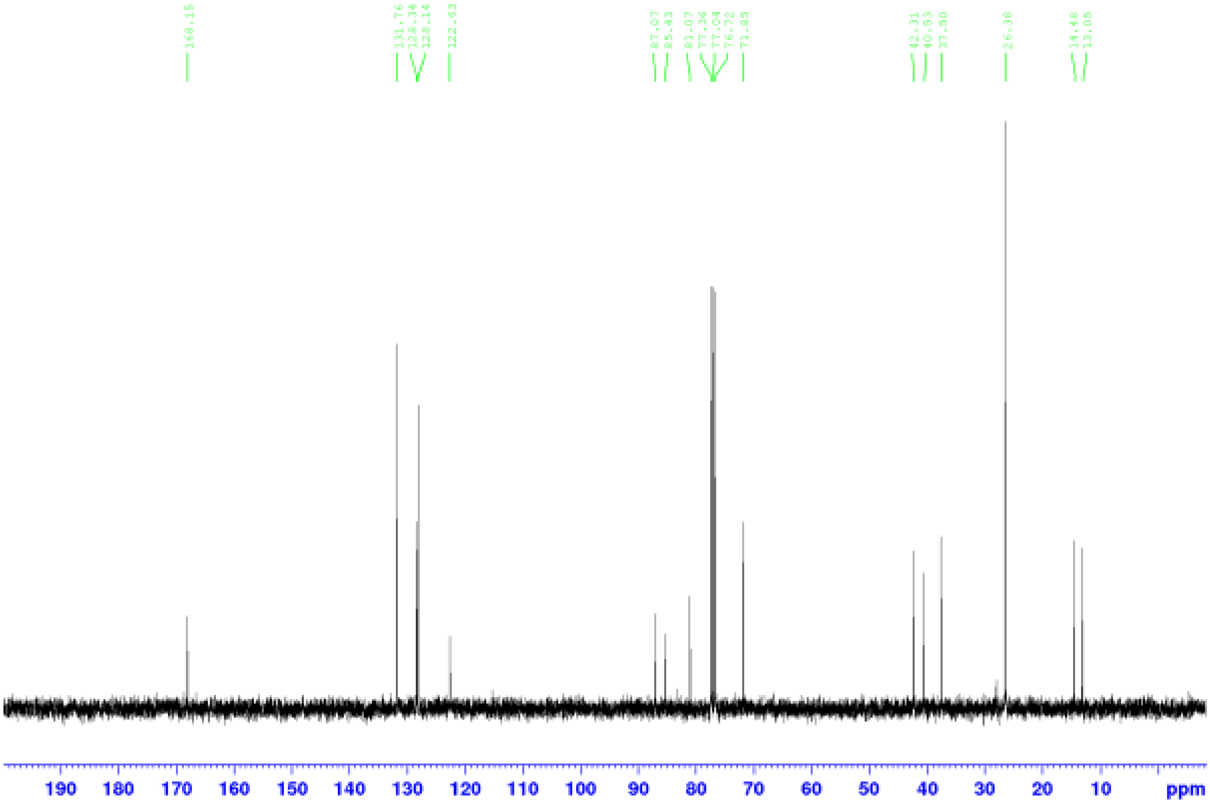
3.34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81.07
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77.04
76.72
71.85
42.31
40.53
37.50
26.38
14.48
13.05
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150
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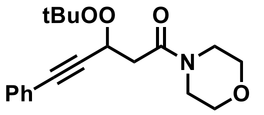
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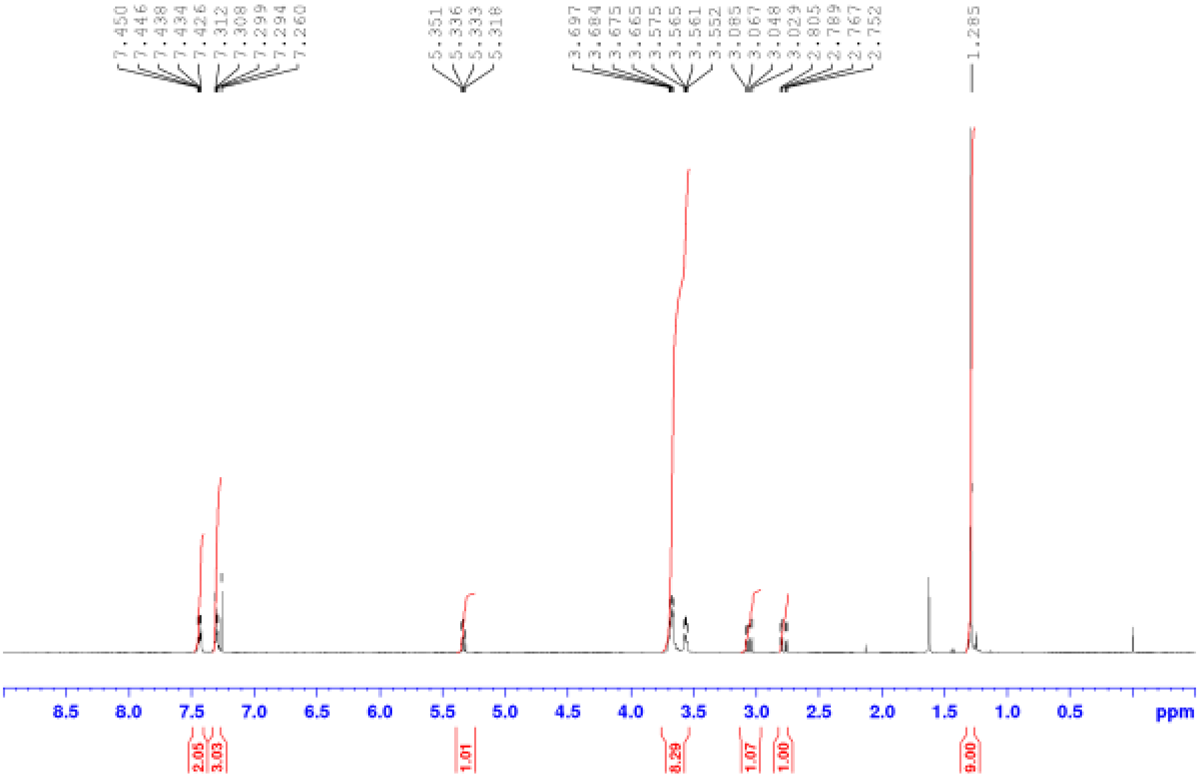
O
Ph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5.333
5.318
3.697
3.684
3.675
3.665
3.575
3.565
3.561
3.552
3.085
3.067
3.048
3.029
2.805
2.789
2.767
2.752
1.285
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
0.5
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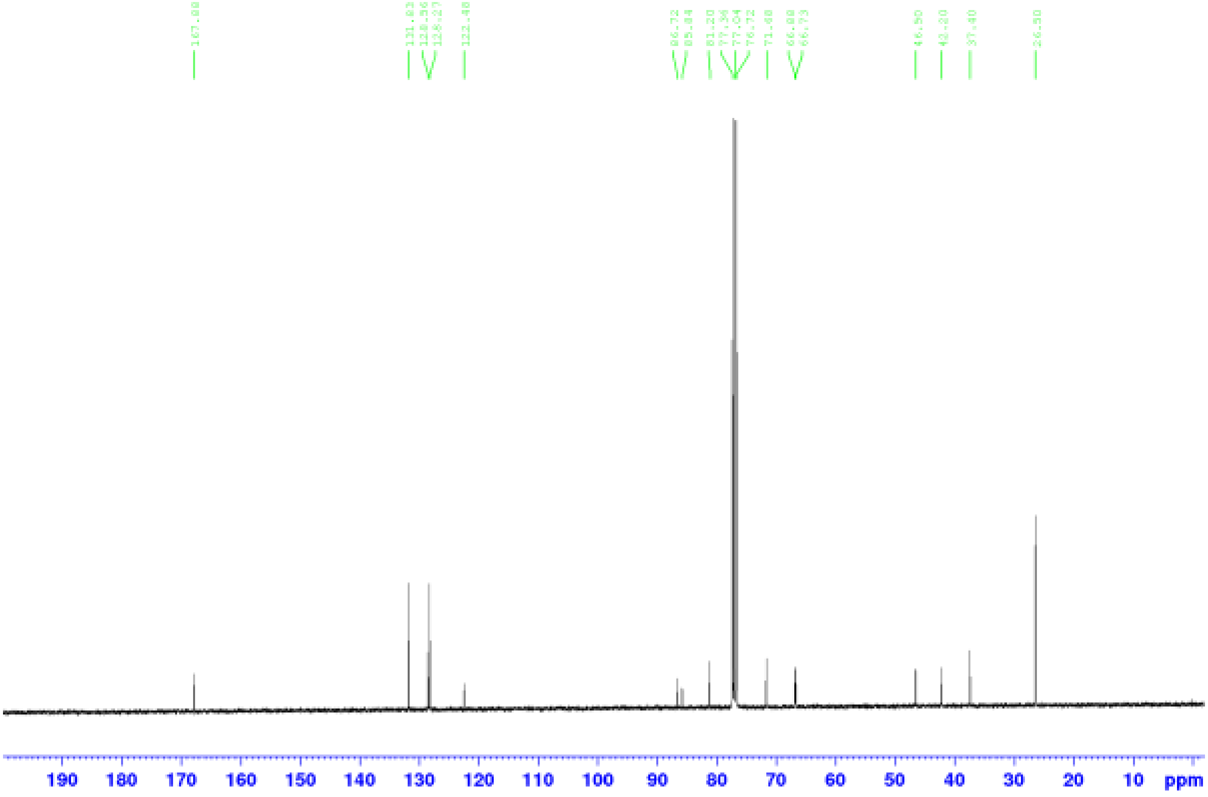
1.00
9.00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76.72
71.68
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42.20
37.40
26.30
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150
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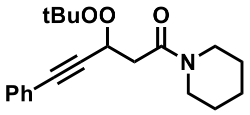
ppm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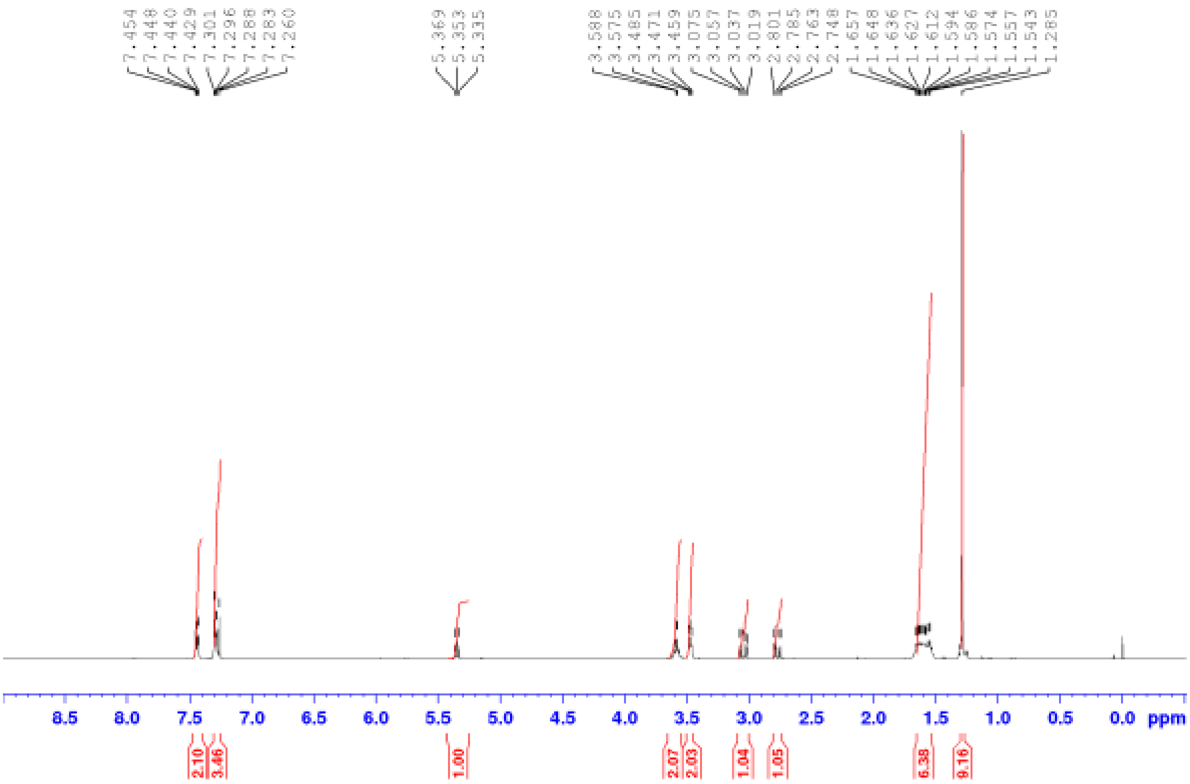
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5.335
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3.575
3.485
3.471
3.459
3.075
3.057
3.037
3.019
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1.648
1.636
1.627
1.612
1.594
1.586
1.574
1.557
1.543
1.285
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6.5
6.0
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5.0
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4.0
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2.0
1.5
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ppm
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1.04
1.05
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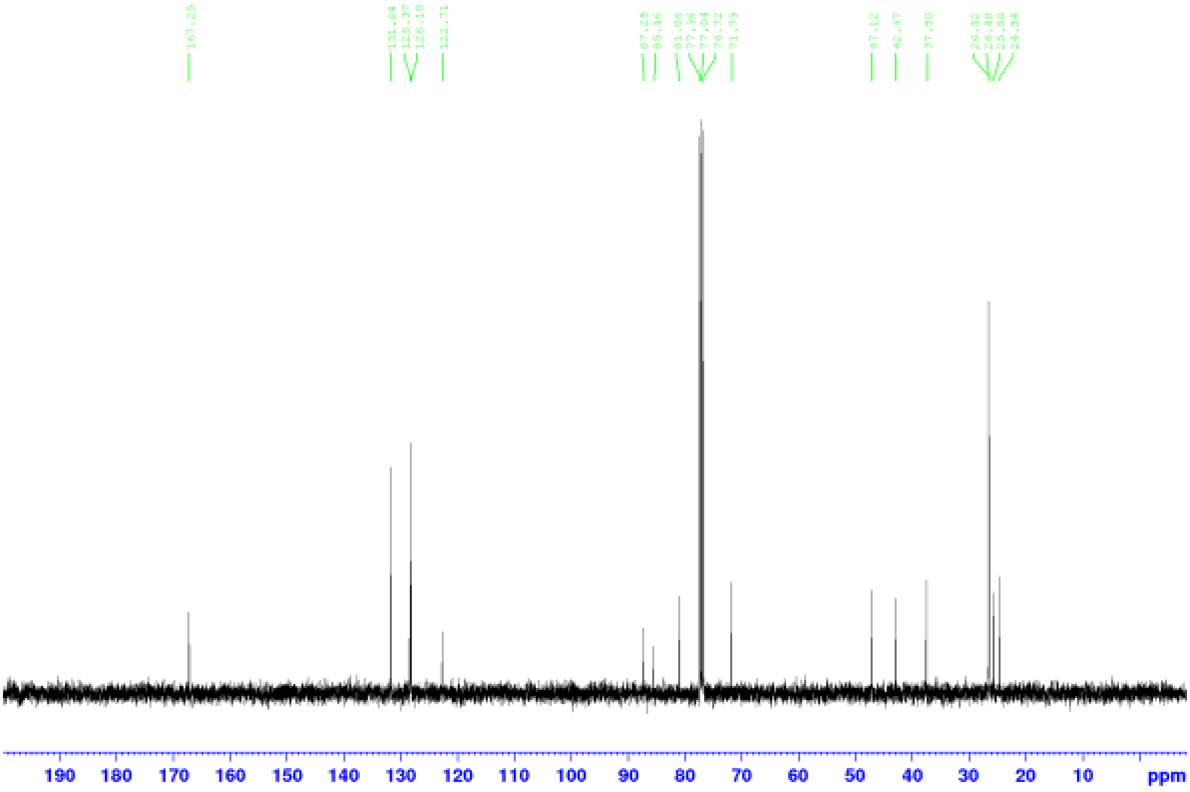
9.16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76.72
71.75
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25.50
24.54
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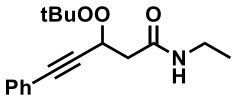
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H
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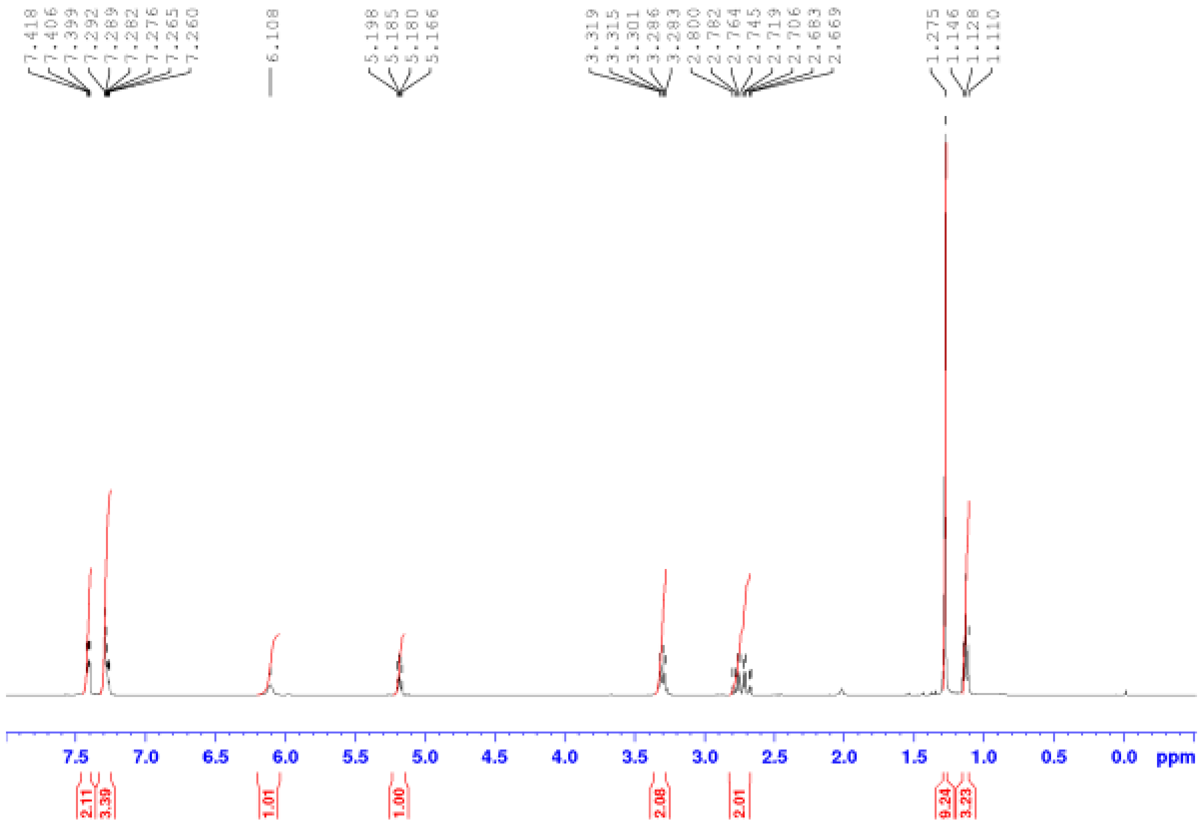
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5.180
5.166
3.319
3.315
3.301
3.296
3.283
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2.745
2.719
2.706
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2.669
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1.146
1.128
1.110
7.5
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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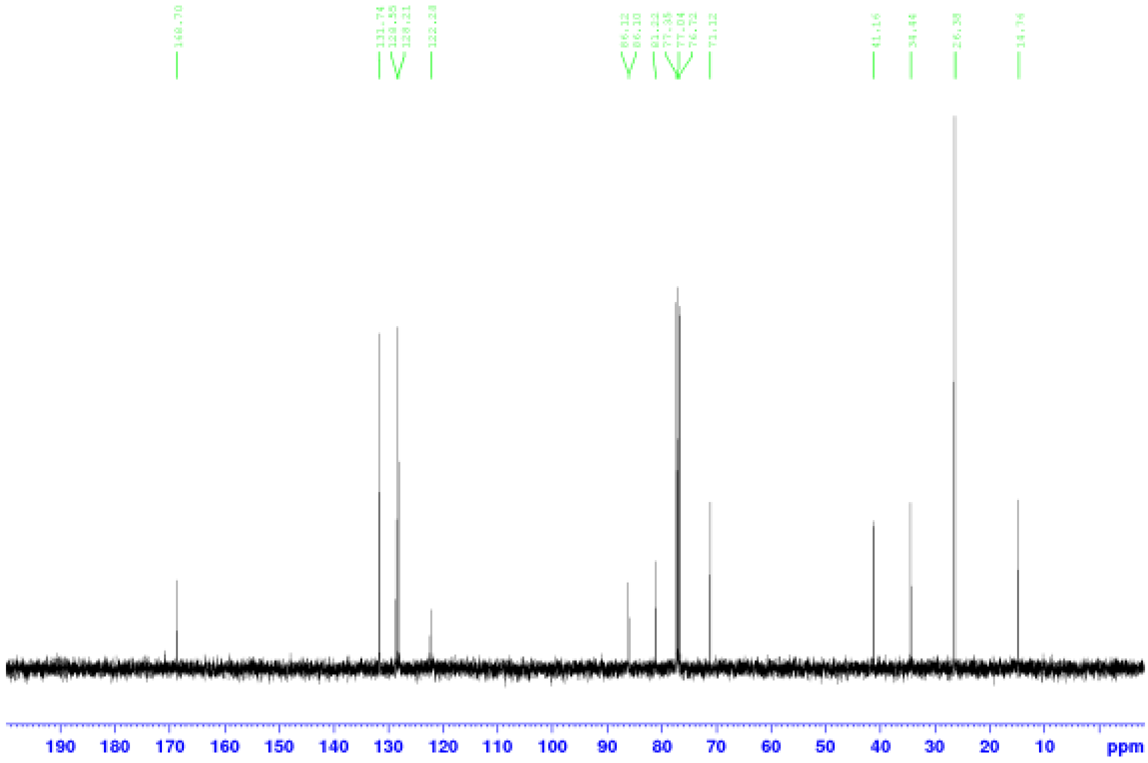
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26.38
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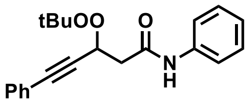
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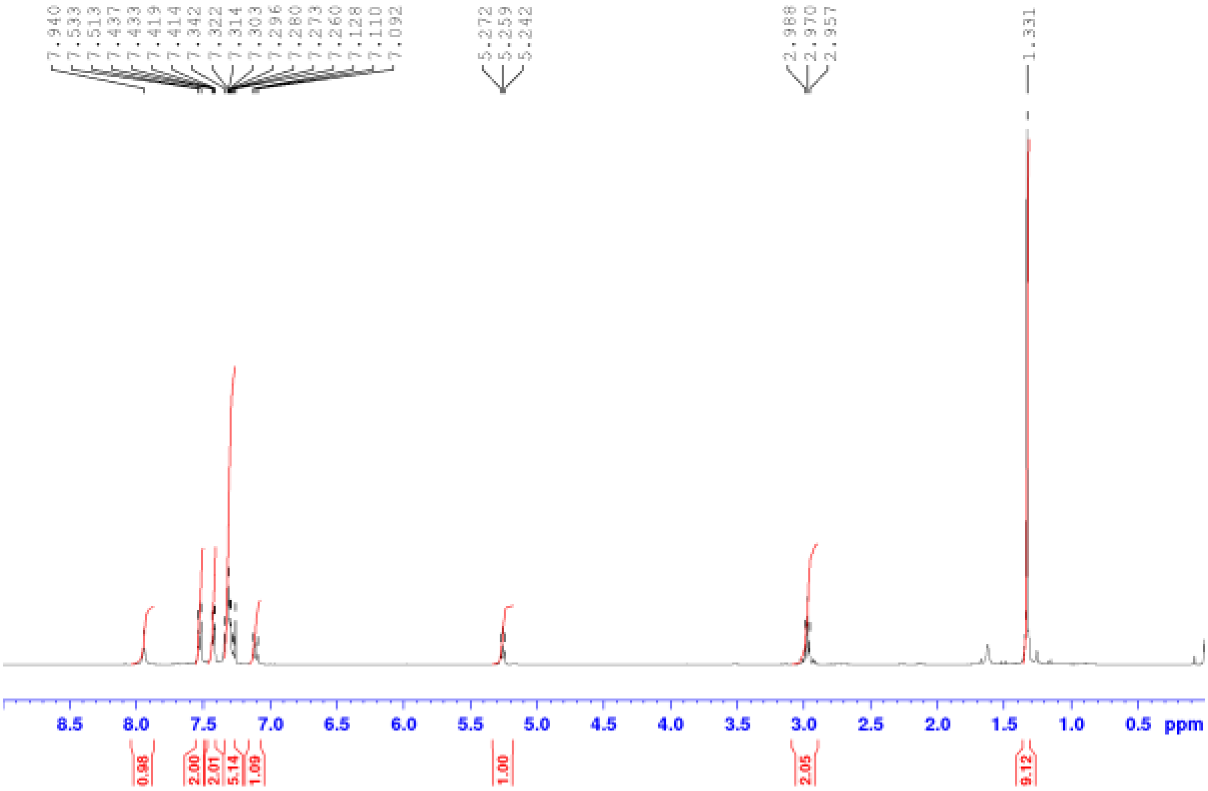
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7.273
7.260
7.128
7.110
7.092
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5.259
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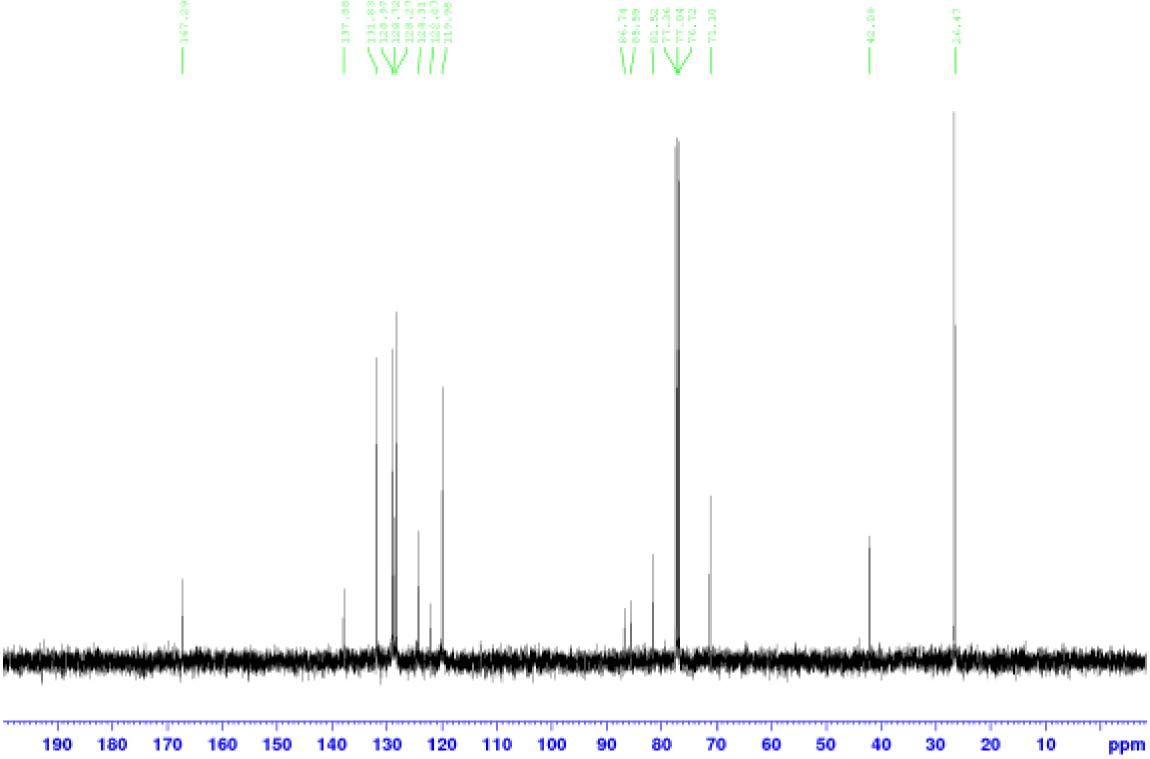
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122.07
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81.52
77.36
77.04
76.72
71.10
42.09
26.47
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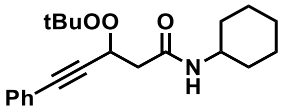
ppm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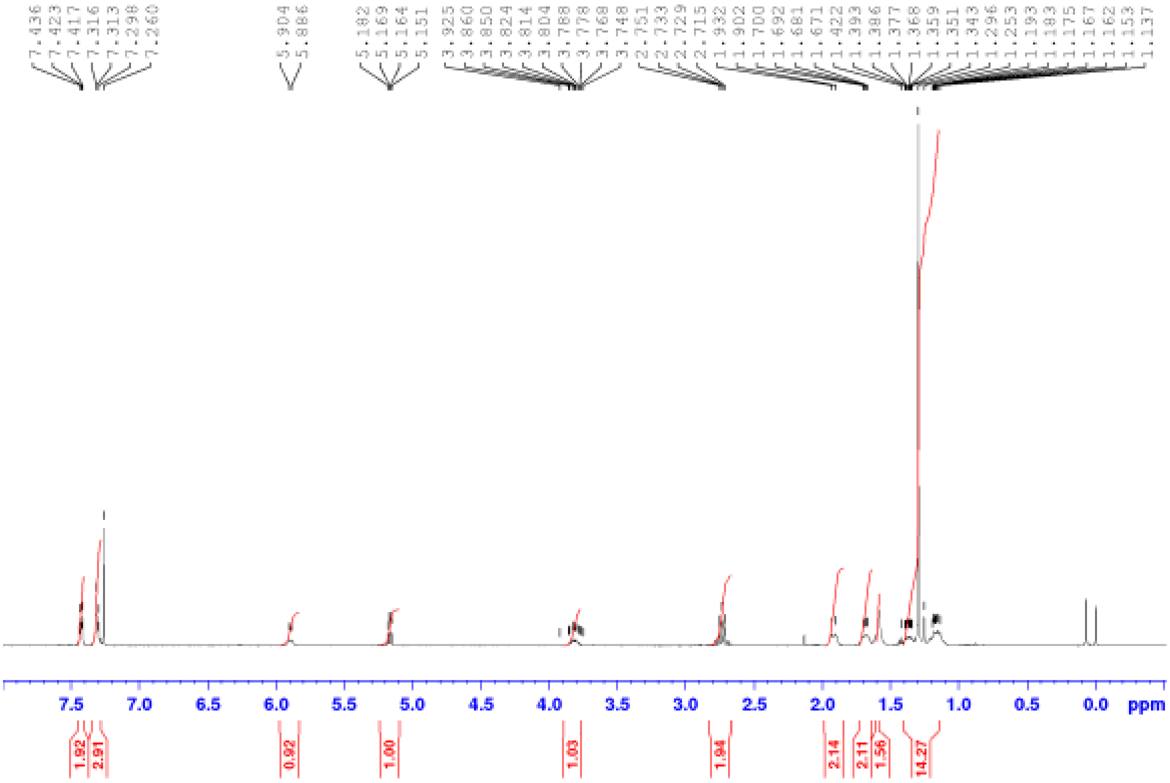
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3.778
3.768
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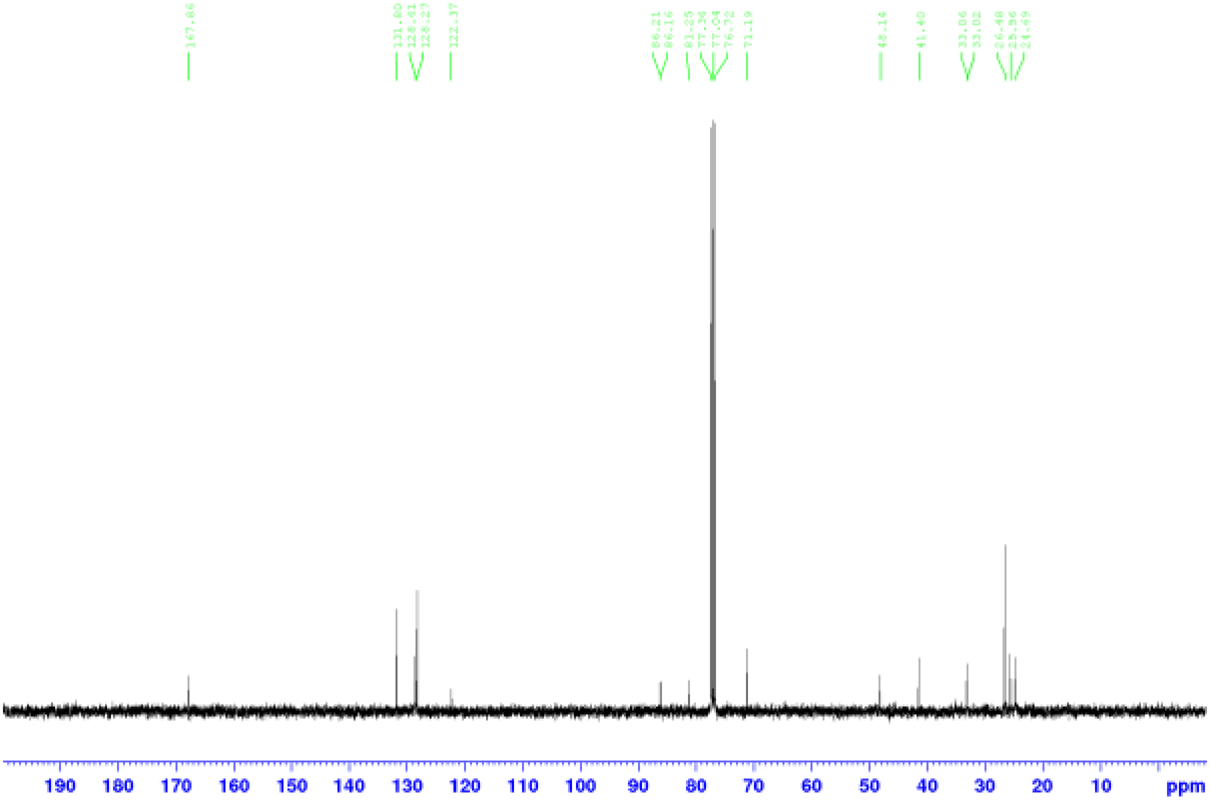
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25.56
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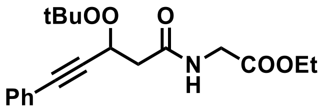
ppm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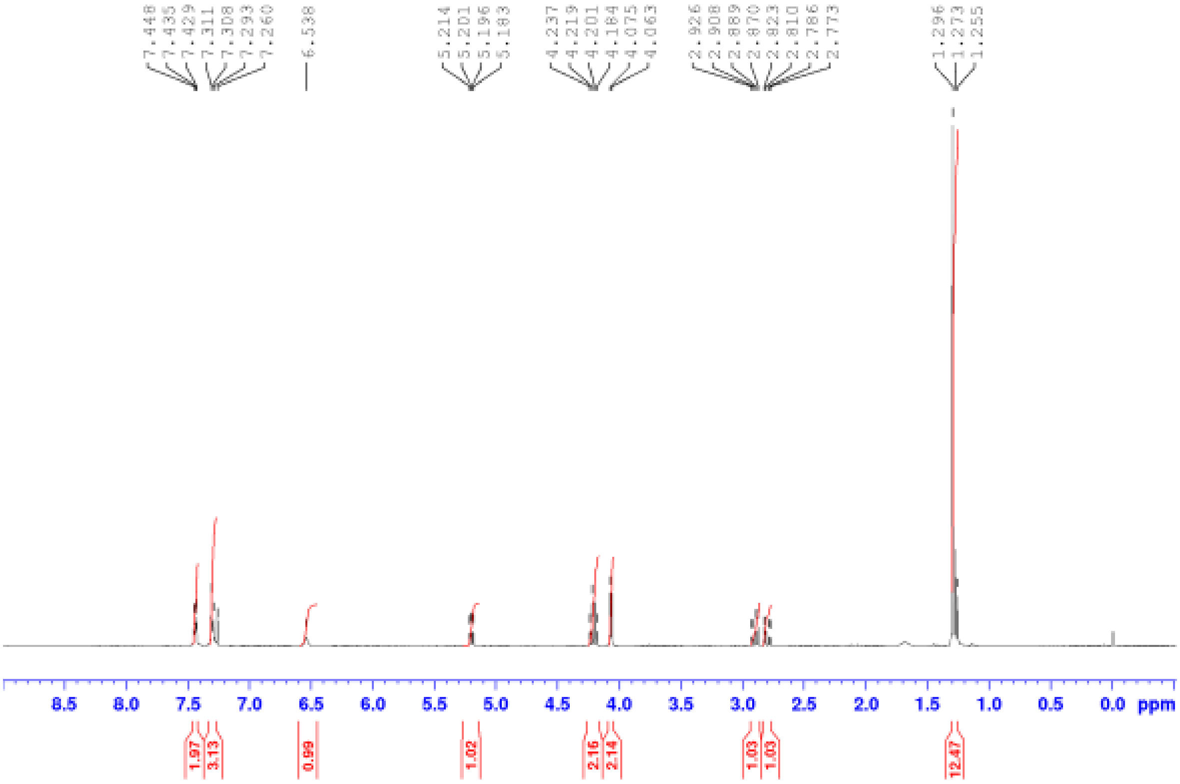
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4.219
4.201
4.184
4.075
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4.0
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2.0
1.5
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1.03
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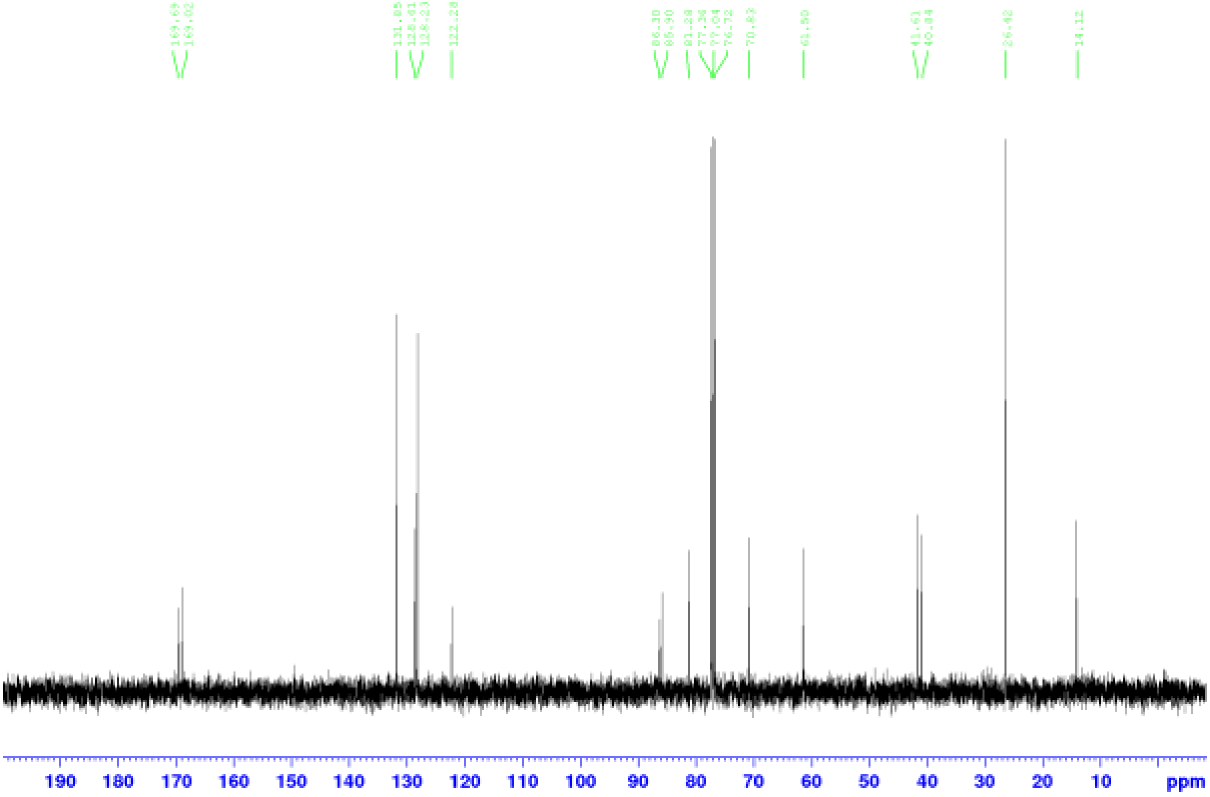
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77.34
77.04
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61.50
41.61
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30
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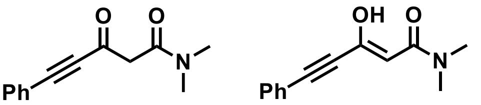
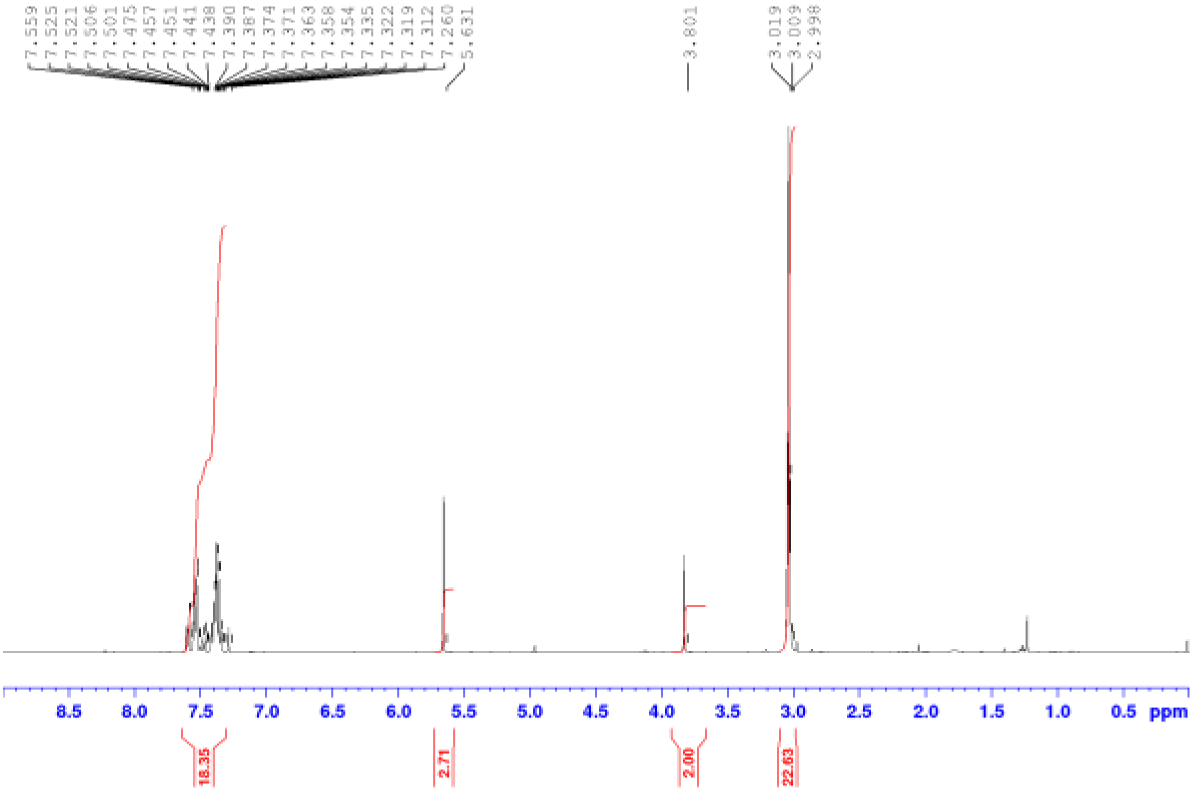
10
ppm


O
O
N
Ph
OH
O
N
Ph

1 : 2.7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7.438
7.390
7.387
7.374
7.371
7.363
7.358
7.354
7.335
7.322
7.319
7.312
7.260
5.631
3.801
3.019
3.009
2.998
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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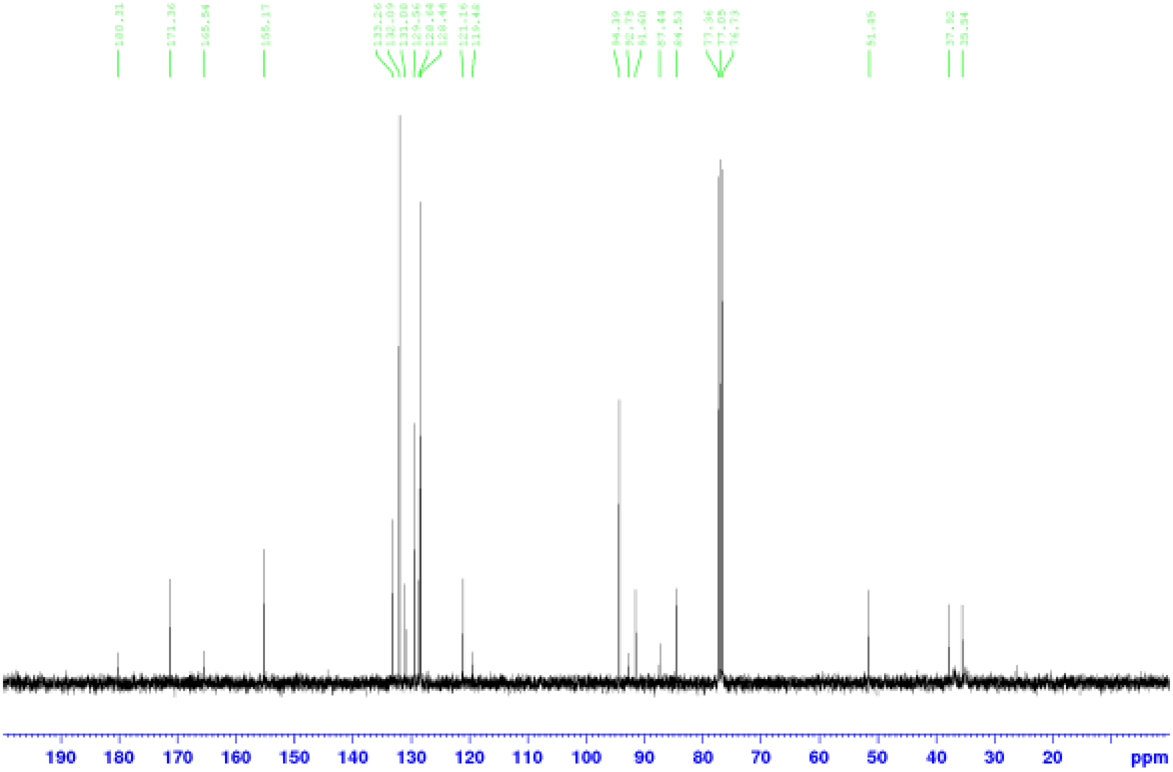
2.71
2.00
22.63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171.36
165.54
155.17
133.26
132.09
131.08
129.56
128.64
128.44
121.16
119.48
94.19
92.75
91.60
87.44
84.53
77.36
77.05
76.73
51.45
37.92
35.34
190
180
170
160
150
140
130
120
110
100
90
80
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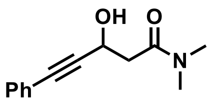
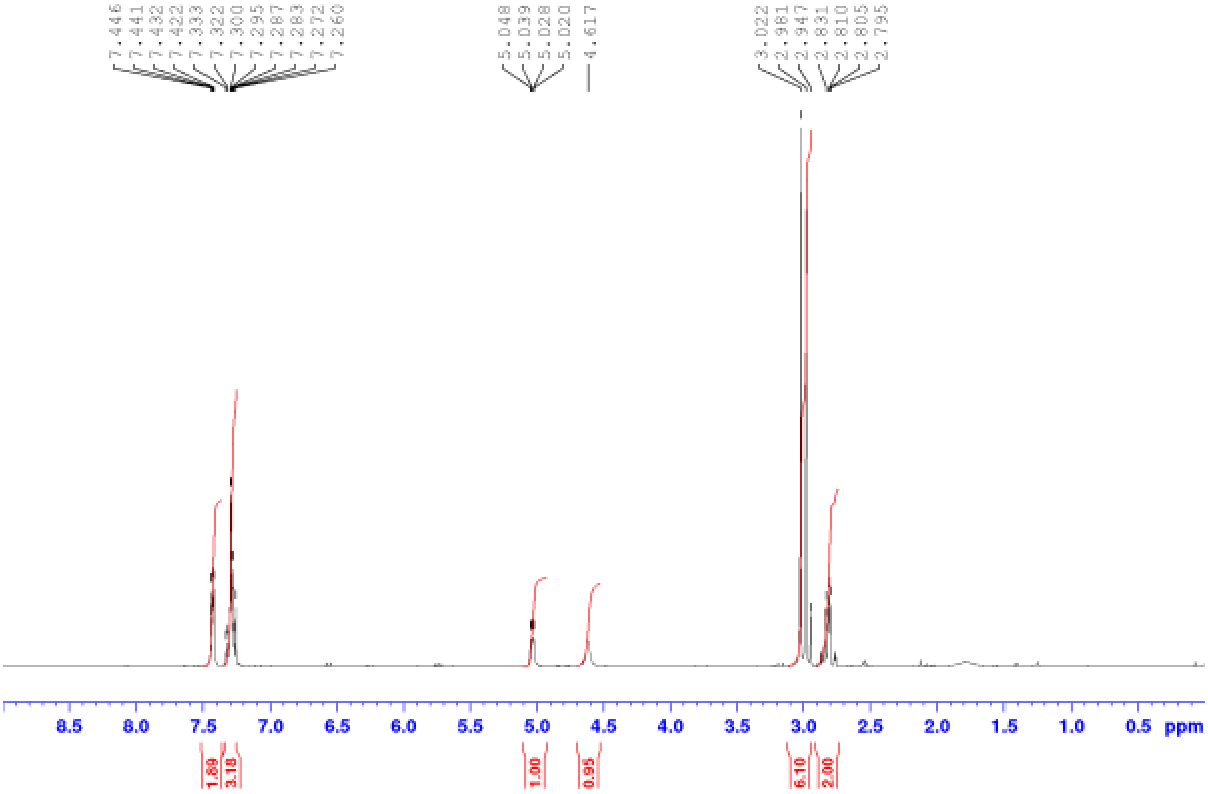
60
50
40
30
20
ppm


OH
O
N
Ph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7.432
7.422
7.333
7.322
7.300
7.295
7.287
7.283
7.272
7.260
5.048
5.039
5.028
5.020
4.617
3.022
2.981
2.947
2.831
2.810
2.805
2.795
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
1.0
0.5
ppm
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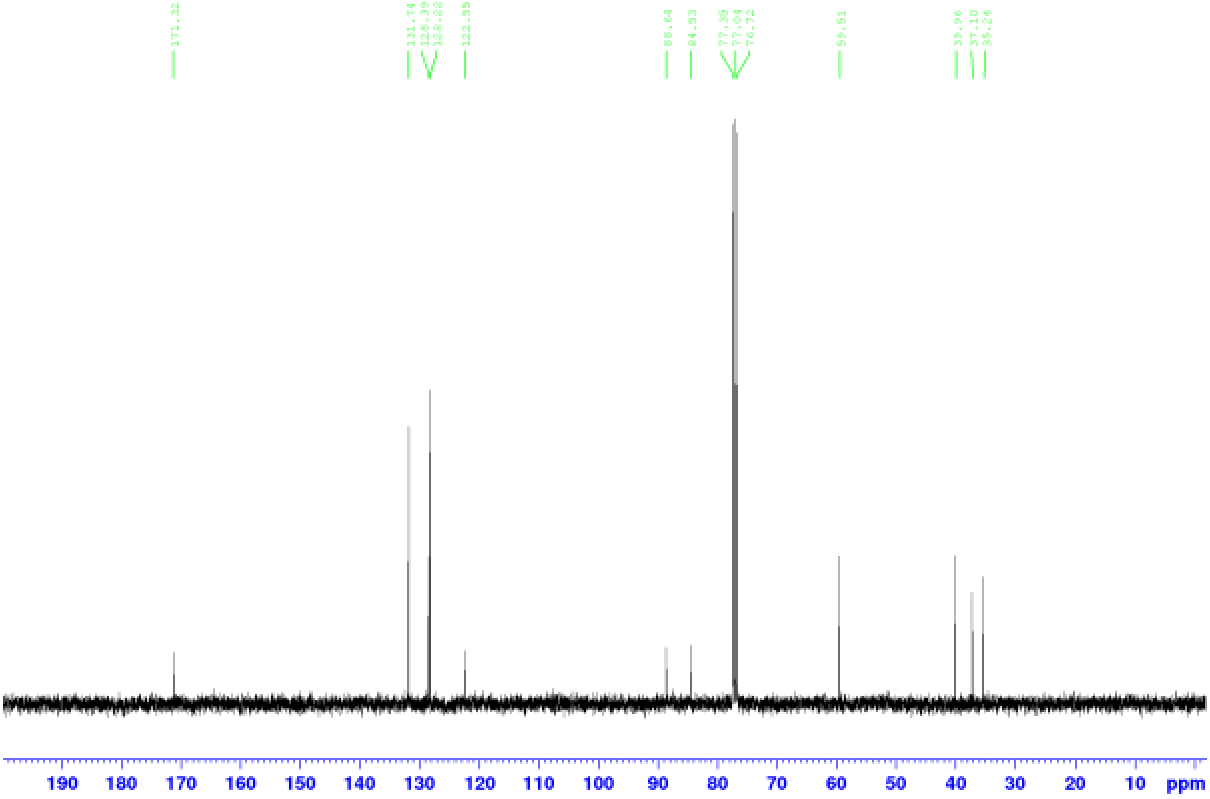
3.18
1.00
0.95
6.10
2.00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128.22
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88.64
84.33
77.35
77.04
76.72
59.51
39.96
37.10
35.24
190
180
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150
140
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120
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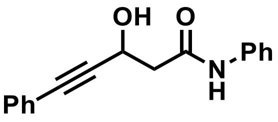
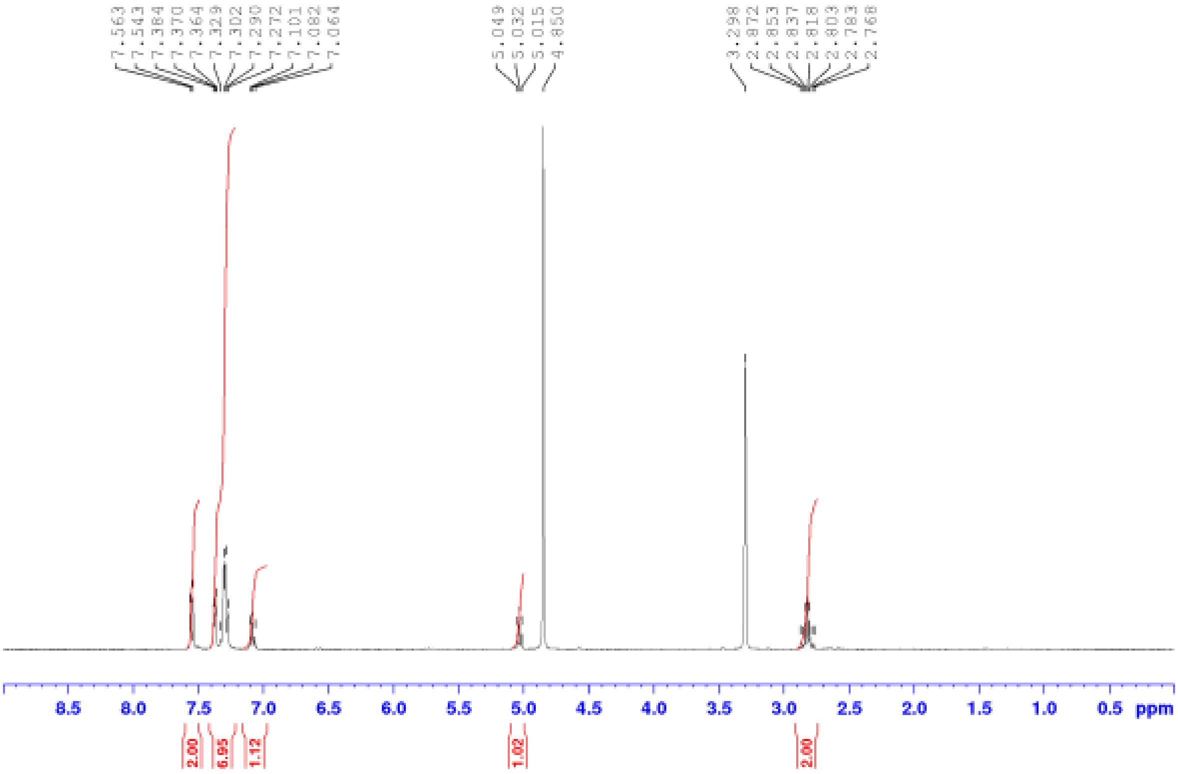
100
90
80
70
60
50
40
30
20
10
ppm


OH
O
N
H
Ph
Ph

in CD_3OD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7.290
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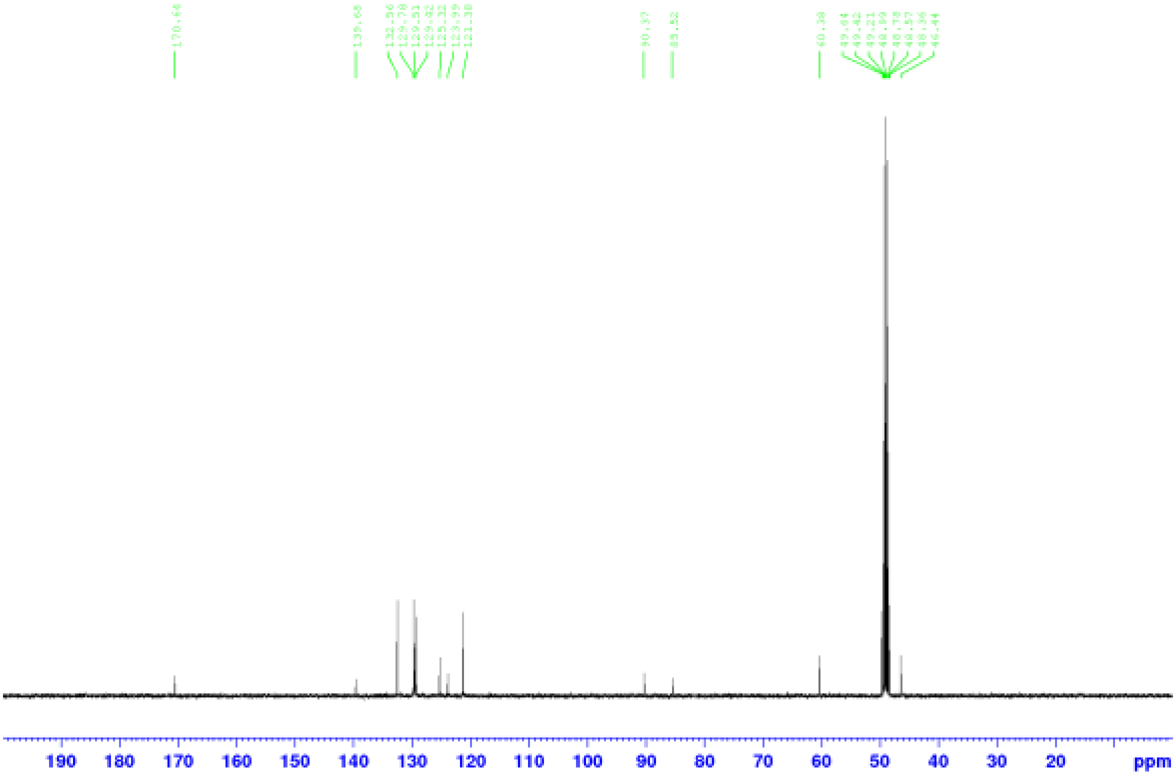
5.049
5.032
5.015
4.850
3.298
2.872
2.853
2.837
2.818
2.803
2.783
2.768
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
6.95
1.12
1.02
2.00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129.78
129.51
129.42
125.32
123.99
121.30
90.37
85.52
60.39
49.64
49.42
49.21
48.99
48.78
48.57
48.36
46.44
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180
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160
150
140
130
120
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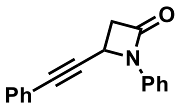
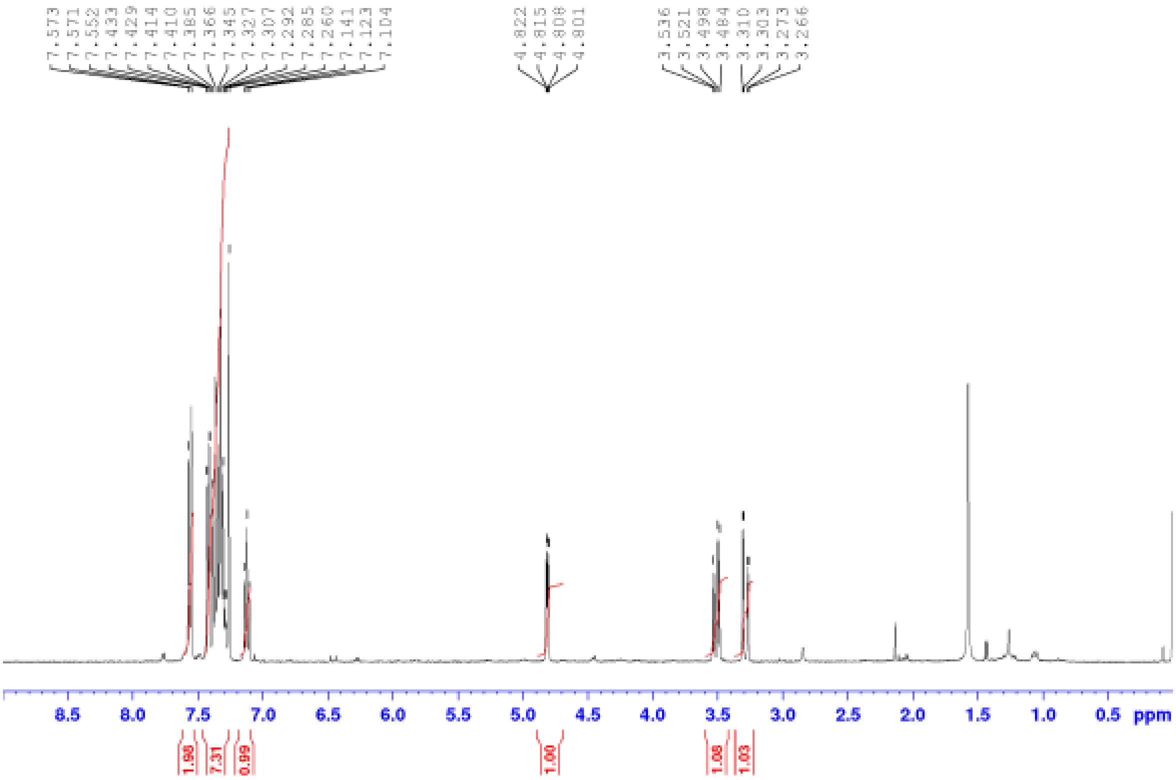
60
50
40
30
20
ppm


O
N
Ph
Ph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7.410
7.385
7.366
7.345
7.327
7.307
7.292
7.285
7.260
7.141
7.123
7.104
4.822
4.815
4.808
4.801
3.536
3.521
3.498
3.484
3.310
3.303
3.273
3.266
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
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ppm
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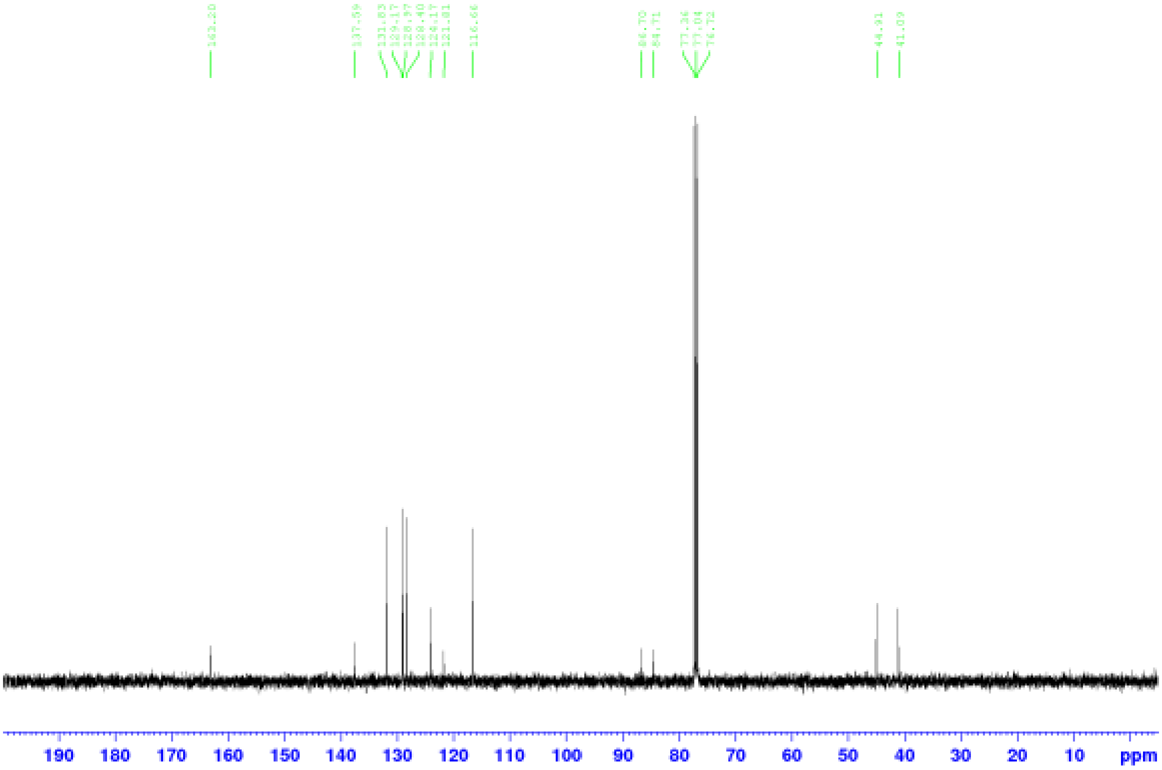
7.31
0.99
1.00
1.08
1.03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131.83
129.17
128.97
128.40
124.17
121.81
116.66
86.70
84.71
77.36
77.04
76.72
44.91
41.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm