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Supporting Information for

Rh(I)-Catalyzed Intramolecular [2+2+1] Cycloaddition of Diyne with the *N*-Terminal of Diazo Group

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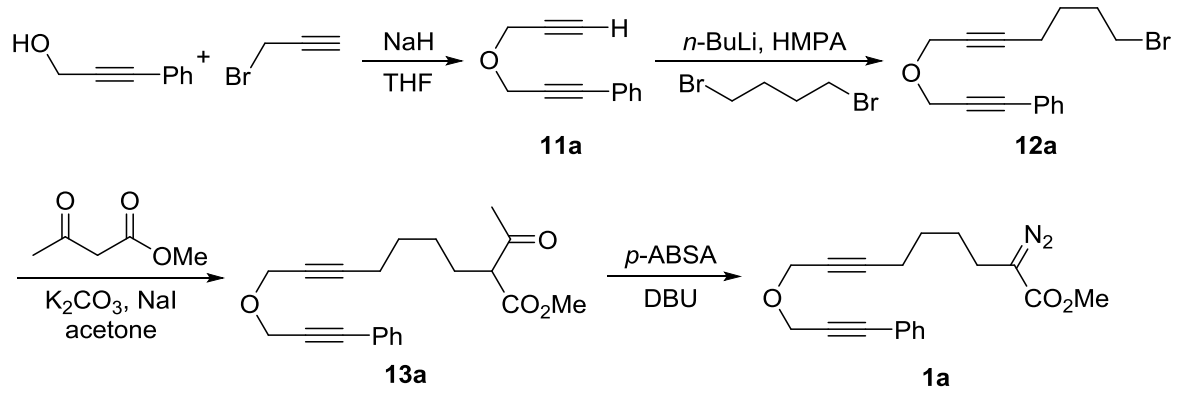
Table of Contents

I. General

Air- and moisture-sensitive reaction were carried out in oven-dried glassware sealed with rubber septa under nitrogen atmosphere. THF were distilled from sodium with benzophenone as indicator. $[Rh(cod)_2]BF_4$ and other metal salts were commercially available. Purification of products was carried out by flash chromatography on silica gel (200-300 mesh, from Qingdao, China). NMR spectra were measured on a Bruker ARX400 (^1H at 400 MHz, ^{13}C at 100 MHz) magnetic resonance spectrometer. Chemical shifts are reported in *ppm* using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet). IR spectra were recorded on a Nicolet Avatar 330 Fourier transform spectrometer (FT-IR) and are reported in wave numbers (cm^{-1}). HRMS data were obtained on a VG ZAB-HS mass spectrometer, Brucker Apex IV FTMS spectrometer. PE: petroleum ether; EA: ethyl acetate.

II. The preparation of the diazo substrates 1a-v

1. Procedures for the preparation of **1a**.



(3-(Prop-2-yn-1-yloxy)prop-1-yn-1-yl)benzene (**11a**)[1]

To a solution of NaH (4.0 g, 60%, 100 mmol) in 120 mL dry THF was added 3-phenylprop-2-yn-1-ol (13.21 g, 100 mmol) dropwise. After being stirred for about 30 minutes, 3-bromoprop-1-yne (11.896 g, 100 mmol) was added. Then the mixture was stirred overnight. The reaction was quenched with sat. *aq*. NH_4Cl solution and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under

reduced pressure. The crude product was then purified by silica gel column chromatography with PE/EtOAc (100:1v/v) to afford **11a** (14.1982 g, 83%) as a colorless oil. R_f = 0.1 (PE:EA = 100:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.46 (m, 2H), 7.29-7.33 (m, 3H), 4.49 (s, 2H), 4.33 (d, *J* = 2.4 Hz, 2H), 2.47 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.6, 128.3, 122.4, 86.9, 84.1, 79.0, 75.0, 57.4, 56.6.

(3-((7-Bromohept-2-yn-1-yl)oxy)prop-1-yn-1-yl)benzene (**12a**)

To a stirred solution of **11a** (3.40 g, 20 mmol, 1.0 equiv) in dry THF (50 mL) under nitrogen at -78 ^{o}C was added *n*-BuLi (2.5 M in hexane, 8.8 mL, 22 mmol, 1.1 eq.) dropwise. After addition the reaction mixture was warm to room temperature and stirred for 30 minutes. The mixture was cooled to -78 ^{o}C and hexamethylphosphoramide (7.16 g, 40 mmol, 2.0 eq.) was added. Then 1,4-dibromobutane (8.64 g, 40 mmol, 2.0 equiv) was added. The mixture was stirred for 2 h at -78 ^{o}C before warmed to room temperature. The reaction was quenched with sat. *aq*. NH_4Cl solution and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography with PE/EtOAc (100:1v/v) to afford **12a** (4.70 g, 77%) as a colorless oil. R_f = 0.38 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.46 (m, 2H), 7.31-7.32 (m, 3H), 4.46 (s,2H), 4.30 (t, *J* = 2.1 Hz, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.30 (tt, J_1= 2.1 Hz, J_2 = 6.9 Hz), 1.95-2.02 (m, 2H), 1.65-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.5, 128.3, 122.5, 86.7, 86.6, 84.4, 76.0, 57.3, 33.2, 31.7, 27.0, 18.0; IR (film) 1490, 1442, 1349, 1253 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{16}H_{18}BrO$ $[M+H]^+$ 305.0541, found 305.0536.

Methyl 2-acetyl-9-((3-phenylprop-2-yn-1-yl)oxy)non-7-ynoate (**13a**)

To a stirred solution of K_2CO_3 (4.25 g, 30.8 mmol, 2.0 eq.) and NaI (0.23 g, 1.54 mmol, 0.1 equiv) in acetone was added methyl acetoacetate (3.58 g, 30.8 mmol, 2.0 equiv). The mixture was stirred at room temperature for 2 h before **12a** (4.70 g, 15.4 mmol, 1.0 equiv) was added. The reaction was then reflux for 24 h. After cooled to room temperature, the reaction was quenched with sat. *aq*. NH_4Cl solution and extracted with EtOAc. The combined

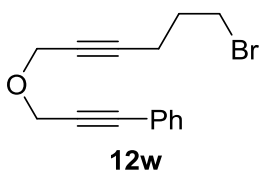
organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography with PE/EtOAc (10:1v/v) to afford **13a** (74%) as a colorless oil. R_f = 0.22 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.46 (m, 2H), 7.31-7.32 (m, 3H), 4.45 (s,2H), 4.29 (t, *J* = 2.1 Hz, 2H), 3.74 (s, 3H), 3.44 (t, *J* = 7.4 Hz, 1H), 2.25 (tt, J_1 = 2.1 Hz, J_2 = 7.0 Hz, 2H), 2.23 (s, 3H), 1.83-1.90 (m, 2H), 1.51-1.59 (m, 2H), 1.36-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.3, 131.8, 128.5, 128.3, 122.6, 87.0, 86.6, 84.5, 75.6, 59.5, 57.3, 57.2, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1744, 1716, 1490, 1442, 1356, 1274, 1245, 1202, 1147, 1074 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{25}O_4$ $[M+H]^+$ 341.1753, found 341.1747.

Methyl 2-diazo-9-((3-phenylprop-2-yn-1-yl)oxy)non-7-ynoate (**1a**)

To a solution of **13a** (1.3916 g, 4.1 mmol, 1.0 equiv) and *p*-ABSA (1.1785 g, 4.9 mmol, 1.2 eq.) in MeCN (30 mL) at 0 ^{o}C was added DBU (0.8114 g, 5.33 mmol, 1.3 equiv). The mixture was stirred overnight at room temperature. The reaction mixture was quenched with sat. *aq*. NH_4Cl solution, extracted with Et_2O, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography with PE/EtOAc (30:1v/v) to afford **1a** (0.8386 g, 63%) as an orange oil. R_f = 0.38 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.46 (m, 2H), 7.29-7.33(m, 3H), 4.46 (s, 2H), 4.30 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.28 (tt, J_1 = 2.1 Hz, J_2 = 6.8 Hz, 2H), 1.55-1.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.5, 128.3, 122.6, 86.9, 86.6, 84.5, 75.8, 57.3, 57.2, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2081, 1693, 1438, 1351, 1158, 1116, 1074 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{21}N_2O_3$ $[M+H]^+$ 325.1552, found 325.1547.

1w, **1x** were prepared with the same procedures.

(3-((6-Bromohex-2-yn-1-yl)oxy)prop-1-yn-1-yl)benzene (**12w**)

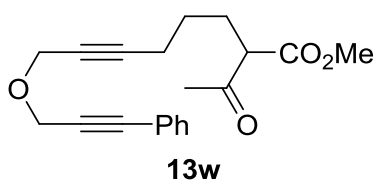


12w

colorless oil; R_f = 0.32 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.46 (m, 2H), 7.31-7.33 (m, 3H), 4.46 (s, 2H), 4.30 (t, *J* = 2.1 Hz, 2H), 3.53 (t, J = 6.4 Hz, 2H), 2.45 (tt, J_1 = 2.1 Hz, J_2 = 6.8 Hz, 2H),

2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.6, 128.3, 122.5, 86.7, 85.5, 84.4, 76.5, 57.3, 57.2, 32.4, 31.3, 17.5; IR (film) 1490, 1442, 1349, 1248, 1076 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{15}H_{16}BrO$ $[M+H]^+$ 291.0385, found 291.0379.

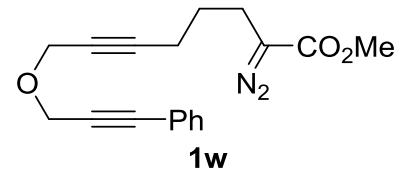
Methyl 2-acetyl-8-((3-phenylprop-2-yn-1-yl)oxy)oct-6-ynoate (**13w**)



13w

colorless oil; R_f = 0.23 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.46 (m, 2H), 7.30-7.32 (m, 3H), 4.46 (s, 2H), 4.29 (t, *J* = 2.1 Hz, 2H), 3.74 (s, 3H), 3.46 (t, *J* = 7.4 Hz, 1H), 2.28 (tt, J_1 = 2.0 Hz, J_2 = 7.0 Hz, 2H), 2.23 (s, 3H), 1.93-1.99 (m, 2H), 1.48-1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 170.1, 131.8, 128.5, 128.3, 122.5, 86.6, 86.5, 84.4, 76.0 59.1, 57.2, 52.5, 28.9, 27.3, 26.3, 25.6, 18.6; IR (film) 1745, 1717, 1359, 1153, 1076 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}O_4$ $[M+H]^+$ 327.1596, found 327.1591.

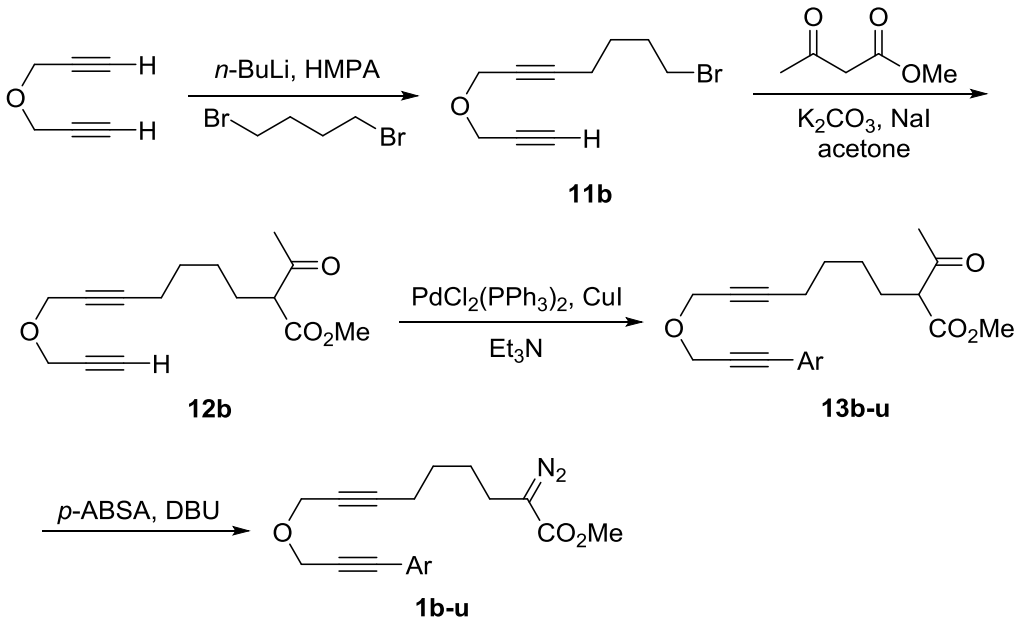
Methyl 2-diazo-8-((3-phenylprop-2-yn-1-yl)oxy)oct-6-ynoate (**1w**)



1w

orange oil; R_f = 0.35 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.46 (m, 2H), 7.30-7.32 (m, 3H), 4.46 (s, 2H), 4.30 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.33 (tt, J_1 = 2.1 Hz, J_2 = 6.9 Hz), 1.75 (p, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.5, 128.3, 122.5, 86.6, 86.1, 84.4, 76.3, 57.2, 57.2, 51.9, 26.6, 22.6, 18.0; IR (film) 2084, 1692, 1438, 1350, 1167, 1116, 1075 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$ 311.1396, found 311.1390.

2. General procedures for the preparation of **1b**-**1u**.



7-Bromo-1-(prop-2-yn-1-yloxy)hept-2-yne (**11b**)

To a stirred solution of dipropargyl ether (4.58 g, 48.7 mmol) in dry THF (100 mL) under nitrogen at -78 ^{o}C was added *n*-BuLi (2.5 M in hexane, 19.5 mL, 48.7 mmol) dropwise. After addition the reaction mixture was warm to room temperature and stirred for 30 minutes. The mixture was cooled to -78 ^{o}C and hexamethylphosphoramide (8.72 g, 48.7 mmol, 1.0 equiv) was added. Then 1,4-dibromobutane (21.02 g, 97.3 mmol, 2.0 equiv) was added. The mixture was stirred for 2 h at -78 ^{o}C before warmed to room temperature. The reaction was quenched with sat. *aq*. NH_4Cl solution and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography with PE/EtOAc (100:1v/v) to afford **11b** (4.20 g, 37.6%) as a colorless oil. R_f = 0.38 (PE:EA = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (m, 4H), 3.44 (t, J = 6.6 Hz, 2H), 2.45 (t, J = 2.4 Hz, 1H), 2.28 (tt, J_1 = 2.0 Hz, J_2 = 6.9 Hz, 2H), 1.94-2.02 (m, 2H), 1.64-1.72 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.7, 79.1, 75.7, 74.8, 57.1, 56.3, 33.2, 31.7, 26.9, 18.0; IR (film) 3296, 1444, 1347, 1291, 1251, 1137, 1078 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{10}H_{14}BrO$ $[M+H]^+$ 229.0228, found 229.0223.

Methyl 2-acetyl-9-(prop-2-yn-1-yloxy)non-7-ynoate (**12b**)

To a stirred solution of K_2CO_3 (5.058 g, 36.6 mmol, 2.0 equiv) and NaI (0.274 g, 1.83

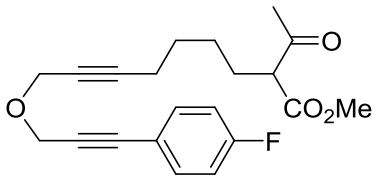
mmol, 0.1 equiv) in acetone (50 mL) was added methyl acetoacetate (4.25 g, 36.6 mmol, 2.0 equiv). The mixture was stirred at room temperature for 2 h before **12b** (4.20 g, 18.3 mmol, 1.0 equiv) was added. The reaction was then reflux for 24 hours. After cooled to room temperature, the reaction was quenched with sat. *aq*. NH_4Cl solution and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography with PE/EtOAc (10:1v/v) to afford **12b** (4.1577 g, 86%) as a colorless oil. R_f = 0.21 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23-4.24 (m, 4H), 3.74 (s, 3H), 3.44 (t, *J* = 7.4 Hz, 1H), 2.45 (t, *J* = 2.4 Hz, 1H), 2.21-2.26 (m, 5H), 1.83-1.88 (m, 2H), 1.50-1.56 (m, 2H), 1.38-1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 87.1, 79.7, 74.8, 59.5, 57.1, 56.3, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1745, 1717, 1446, 1359, 1246, 1149, 1079 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{15}H_{21}O_4$ $[M+H]^+$ 265.1440, found 265.1434.

General procedures for the preparation of **13b-u** and **1b-u**

To a solution of $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol, 0.05 equiv), CuI (38.1 mg, 0.2 mmol, 0.10 equiv), *i*-Pr_2NH (0.4048 g, 4 mmol, 2.0 equiv) and ArI (2.4 mmol, 1.2 equiv) in 20 mL THF under nitrogen was added a solution of **11b** (2 mmol, 1.0 equiv, in 2 mL THF) dropwise over 30 minutes. The brown reaction mixture was stirred at rt for 1.5 h. Then the reaction was quenched with sat. *aq*. NH_4Cl solution and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography with PE/EtOAc (10:1v/v) to afford **13b-u**.

To a solution of **13b-u** (1.0 equiv) and *p*-ABSA (1.2 equiv) in MeCN (0.25 M) at 0 ^{o}C was added DBU (1.5 equiv). The mixture was stirred overnight at room temperature. The reaction mixture was quenched with sat. *aq*. NH_4Cl solution, extracted with Et_2O, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography with PE/EtOAc (30:1v/v) to afford **1b-u**.

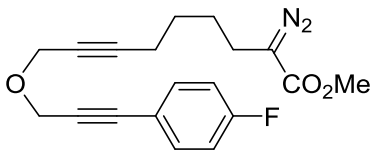
Methyl 2-acetyl-9-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13b**)



13b

colorless oil; R_f = 0.21 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.45 (m, 2H), 6.99-7.03 (m, 2H), 4.43 (s, 2H), 4.28 (t, *J* = 2.1 Hz, 2H), 3.74 (s, 3H), 3.44(t, *J* = 7.4 Hz, 1H), 2.25 (tt, J_1 = 2.1 Hz, J_2 = 7.0 Hz, 2H), 2.23 (s, 3H), 1.83-1.88 (m, 2H), 1.51-1.59 (m, 2H), 1.35-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 162.6 (d, *J* = 249.6 Hz), 133.7 (d, *J* = 8.4 Hz), 118.6 (d, *J* = 3.5 Hz), 115.6 (d, *J* = 22.1 Hz), 87.1, 85.5, 84.2, 75.6, 59.5, 57.3, 57.1, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1744, 1716, 1507, 1356, 1222, 1157, 1076 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{24}FO_4$ $[M+H]^+$ 359.1659, found 359.1653.

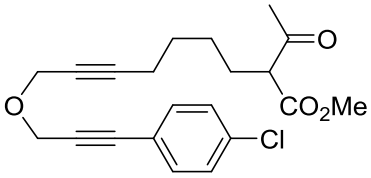
Methyl 2-diazo-9-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1b**)



1b

orange oil; R_f = 0.39 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.45 (m, 2H), 6.99-7.03 (m, 2H), 4.44 (s, 2H), 4.28 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.34 (t, *J* = 7.1 Hz), 2.28 (tt, J_1 = 2.0 Hz, J_2 = 6.7 Hz, 2H), 1.56-1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 249.8 Hz), 133.7 (d, *J* = 8.5 Hz), 118.6 (d, *J* = 3.6 Hz), 115.6 (d, *J* = 22.0 Hz), 87.0, 85.5, 84.2, 75.7, 57.3, 57.1, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2081, 1693, 1507, 1438, 1353, 1222, 1158, 1117, 1076 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}FN_2O_3$ $[M+H]^+$ 343.1458, found 343.1452.

Methyl 2-acetyl-9-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13c**)

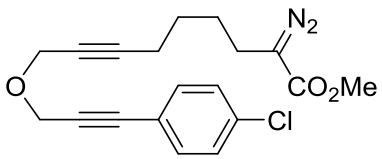


13c

colorless oil; R_f = 0.22 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.39 (m, 2H), 7.28-7.30 (m, 2H), 4.44 (s, 2H), 4.27(t, *J* = 2.1 Hz, 2H) 3.74 (s, 3H), 3.43 (t, *J* = 7.4 Hz, 1H), 2.23-2.26 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 134.6, 133.0, 128.7, 121.0, 87.2, 85.6, 85.4, 75.5, 59.5, 57.4, 57.1, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1743, 1716, 1489, 1461, 1436, 1356,

1259, 1205, 1146, 1074, 1015 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{24}ClO_4$ $[M+H]^+$ 375.1363, found 375.1358.

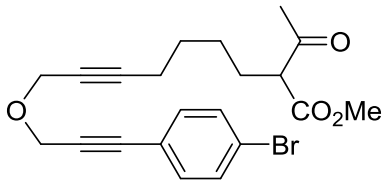
Methyl 9-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)-2-diazonon-7-ynoate (**1c**)



1c

orange oil; R_f = 0.36 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.38 (m, 2H), 7.28-7.30 (m, 2H), 4.44 (s, 2H), 4.28 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.34 (t, *J* = 7.1 Hz, 2H), 2.28 (tt, J_1 = 2.0 Hz, J_2 = 6.4 Hz, 2H), 1.55-1.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 133.0, 128.7, 121.0, 87.1, 85.5, 85.4, 75.7, 57.4, 57.1, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2081, 1693, 1489, 1437, 1352, 1158, 1117, 1075 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}ClN_2O_3$ $[M+H]^+$ 359.1162, found 359.1157.

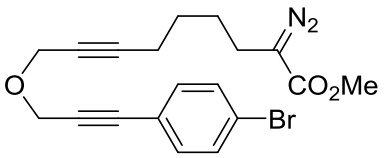
Methyl 2-acetyl-9-((3-(4-bromophenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13d**)



13d

colorless oil; R_f = 0.22 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.46 (m, 2H), 7.29-7.31 (m, 2H), 4.43 (s, 2H), 4.27 (s, 2H), 3.74 (s, 3H), 3.43 (t, *J* = 7.4 Hz, 1H), 2.23-2.26 (m, 5H), 1.82-1.88 (m, 2H), 1.51-1.58 (m, 2H), 1.39-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 170.2, 133.2, 131.6, 122.8, 121.5, 87.2, 85.8, 85.5, 75.5, 59.5, 57.4, 57.1, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1743, 1716, 1486, 1437, 1352, 1257, 1203, 1151, 1072, 1011 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{24}BrO_4$ $[M+H]^+$ 419.0858, found 419.0852.

Methyl 9-((3-(4-bromophenyl)prop-2-yn-1-yl)oxy)-2-diazonon-7-ynoate (**1d**)

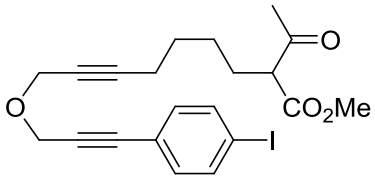


1d

orange oil; R_f = 0.37 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.45 (m, 2H), 7.29-7.31 (m, 2H), 4.43 (s, 2H), 4.28 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.28 (tt, J_1 = 2.1 Hz, J_2 = 6.8 Hz, 2H), 1.52-1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2, 131.6, 122.8, 121.5, 87.1,

85.7, 85.5, 75.7, 57.4, 57.1, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2080, 1692, 1486, 1438, 1351, 1159, 1116, 1071, 1011 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}BrN_2O_3$ $[M+H]^+$ 403.0657, found 403.0652.

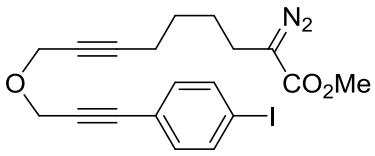
Methyl 2-acetyl-9-((3-(4-iodophenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13e**)



13e

colorless oil; R_f = 0.23 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.66 (m, 2H), 7.16-7.18 (m ,2H), 4.42 (s, 2H), 4.27 (t, *J* = 2.1 Hz, 2H), 3.74 (s, 3H), 3.43 (t, *J* = 7.4 Hz, 1H), 2.23-2.27 (m, 5H), 1.84-1.87 (m, 2H), 1.51-1.58 (m, 2H), 1.33-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.96, 170.23, 137.50, 133.3, 122.1, 94.5, 87.2, 86.0, 85.6, 75.5, 59.5, 57.4, 57.1, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1746, 1716, 1484, 1435, 1356, 1258, 1202, 1146, 1074, 1007 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{24}IO_4$ $[M+H]^+$ 467.0719, found 467.0714.

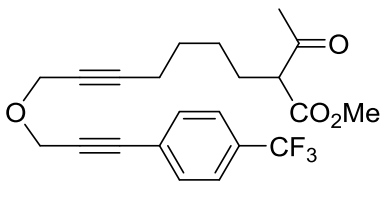
Methyl 2-diazo-9-((3-(4-iodophenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1e**)



1e

orange oil; R_f = 0.36 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.66 (m, 2H), 7.15-7.17 (m, 2H), 4.43 (s, 2H), 4.28 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.28 (tt, J_1 = 2.0 Hz, J_2 = 6.4 Hz, 2H), 1.54-1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.3, 122.1, 94.5, 87.1, 86.0, 85.6, 75.7, 57.4, 57.1, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2080, 1692, 1484, 1436, 1350, 1190, 1158, 1116, 1076, 1007 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}IN_2O_3$ $[M+H]^+$ 451.0519, found 451.0513.

Methyl 2-acetyl-9-((3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13f**)

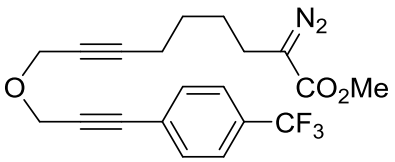


13f

colorless oil; R_f = 0.25 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.59 (m, 4H), 4.46 (s, 2H), 4.29 (t, *J* = 1.9 Hz, 2H), 3.74 (s, 3H), 3.43 (t, *J* = 7.3 Hz, 1H), 2.23-2.27 (m, 5H), 1.85-1.88 (m, 2H), 1.52-1.59 (m, 2H), 1.33-1.41 (m, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 132.0, 130.3 (q, J = 32.7 Hz), 126.4, 125.3 (q, J = 3.7 Hz), 124.4 , 87.3, 87.1, 85.1, 75.4, 59.5, 57.5, 57.0, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1744, 1720, 1325, 1129, 1067 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{24}F_3O_4$ $[M+H]^+$ 409.1627, found 409.1621.

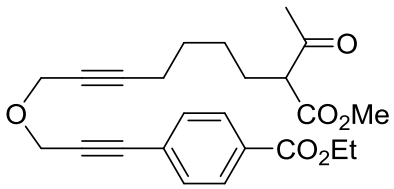
Methyl 2-diazo-9-((3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1f**)



1f

orange oil; R_f = 0.41 (PE:EA = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.59 (m, 4H), 4.47 (s, 2H), 4.30 (t, J = 2.1 Hz, 2H), 3.76 (s, 3H), 2.34 (t, J = 7.1 Hz, 2H), 2.29 (tt, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 2H), 1.51-1.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 130.3 (q, J = 32.7 Hz), 126.4, 125.3 (q, J = 3.6 Hz), 122.5 Hz, 87.2, 87.1, 85.2, 75.6, 57.5, 57.0, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2084, 1686, 1439, 1350, 1324, 1169, 1133, 1107, 1067 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{20}F_3N_2O_3$ $[M+H]^+$ 393.1426, found 393.1421.

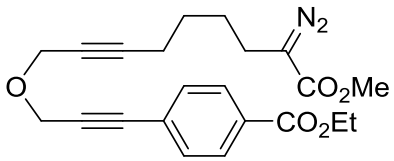
Ethyl 4-(3-((8-(methoxycarbonyl)-9-oxodec-2-yn-1-yl)oxy)prop-1-yn-1-yl)benzoate (**13g**)



13g

colorless oil; R_f = 0.27 (PE:EA = 3:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-8.00 (m, 2H), 7.49-7.51 (m, 2H), 4.47 (s, 2H), 4.38 (q, J = 7.1 Hz, 2H), 4.29 (t, J = 2.1 Hz, 2H), 3.74 (s, 3H), 3.44 (t, J = 7.4 Hz, 1H), 2.23-2.27 (m, 5H), 1.83-1.90 (m, 2H), 1.52-1.59 (m, 2H), 1.38-1.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 166.0, 131.6, 130.2, 129.4, 127.1, 87.5, 87.3, 85.8, 75.5, 61.2, 59.5, 57.4, 57.1, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5, 14.3; IR (film) 1742, 1716, 1602, 1362, 1274, 1176, 1107, 1077 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{24}H_{29}O_6$ $[M+H]^+$ 413.1964, found 413.1959.

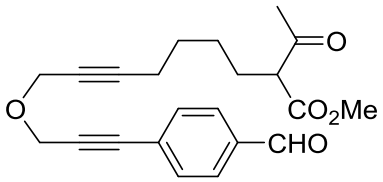
Ethyl 4-(3-((8-diazo-9-methoxy-9-oxonon-2-yn-1-yl)oxy)prop-1-yn-1-yl)benzoate (**1g**)



1g

orange oil; R_f = 0.22 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-8.00 (m, 2H), 7.49-7.51 (m, 2H), 4.47 (s, 2H), 4.38 (q, J = 7.1 Hz, 2H), 4.30 (t, J = 2.1 Hz, 2H), 3.76 (s, 3H), 2.34 (t, J = 7.1 Hz, 2H), 2.29 (tt, J_1 = 2.0 Hz, J_2 = 6.3Hz, 2H), 1.54-1.69 (m, 4H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0; 131.6, 130.2, 129.4, 127.1, 87.5, 87.1, 85.8, 75.6, 61.2, 57.4, 57.1, 51.9, 27.5, 26.8, 22.7, 18.5, 14.3; IR (film) 2081, 1716, 1694, 1273, 1106, 1078 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{25}N_2O_5$ $[M+H]^+$ 397.1763, found 397.1757.

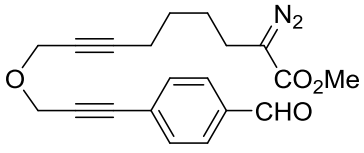
Methyl 2-acetyl-9-((3-(4-formylphenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13h**)



13h

colorless oil; R_f = 0.31 (PE:EA = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.83-7.85 (m, 2H), 7.59-7.61 (m ,2H), 4.48 (s, 2H), 4.29 (t, J =2.1 Hz, 2H), 3.74 (s, 3H), 3.43 (t, J = 7.4 Hz, 1H), 2.23-2.28 (m, 5H), 1.83-1.88 (m, 2H), 1.53-1.59 (m, 2H), 1.39-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 191.4, 170.2, 135.7, 132.3, 129.5, 128.8, 88.7, 87.4, 85.6, 75.4, 59.5, 57.5, 57.0, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 2922, 1737, 1703, 1601, 1209, 1075 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{28}NO_5$ $[M+NH_4]^+$ 386.1967, found 386.1962.

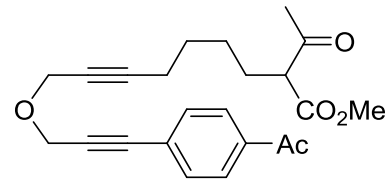
Methyl 2-diazo-9-((3-(4-formylphenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1h**)



1h

orange oil; R_f = 0.26 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.83-7.85 (m, 2H), 7.59-7.61 (m, 2H), 4.48 (s, 2H), 4.30 (t, J = 2.1 Hz, 2H), 3.76 (s, 3H), 2.34 (t, J = 7.0 Hz, 2H), 2.29 (tt, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 2H), 1.55-1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 135.7, 132.3, 129.5, 128.8, 88.7, 87.2, 85.6, 75.5, 57.5, 57.1, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2081, 1700, 1603, 1352, 1206, 1165, 1076 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{21}N_2O_4$ $[M+H]^+$ 353.1501, found 353.1496.

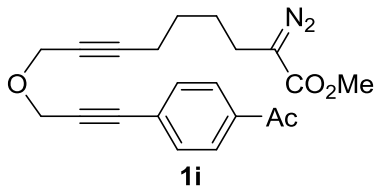
Methyl 2-acetyl-9-((3-(4-acetylphenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13i**)



13i

colorless oil; R_f = 0.28 (PE:EA = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.92 (m, 2H), 7.52-7.54 (m, 2H), 4.47 (s, 2H), 4.29 (t, *J* = 1.7 Hz, 2H), 3.74 (s, 3H), 3.44 (t, *J* = 7.4 Hz, 1H), 2.60 (s, 3H), 2.23-2.27 (m, 5H), 1.83-1.89 (m, 2H), 1.51-1.59 (m, 2H), 1.27-1.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 197.3, 170.2, 136.5, 131.9, 128.2, 127.4, 87.9, 87.3, 85.7, 75.4, 59.5, 57.5, 57.1, 52.4, 28.9, 28.2, 27.7, 26.6, 26.6, 18.5; IR (film) 1744, 1715, 1685, 1602, 1358, 1263, 1148, 1074 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{23}H_{27}O_5$ $[M+H]^+$ 383.1858, found 383.1853.

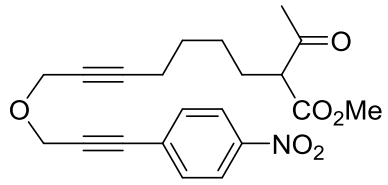
Methyl 9-((3-(4-acetylphenyl)prop-2-yn-1-yl)oxy)-2-diazonon-7-ynoate (**1i**)



1i

orange oil; R_f = 0.26 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.92 (m, 2H), 7.52-7.54 (m, 2H), 4.48 (s, 2H), 4.30 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.60 (s, 3H), 2.34 (t, *J* = 7.1 Hz, 2H), 2.29 (tt, J_1 = 2.1 Hz. J_2 = 6.7 Hz, 2H), 1.55-1.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 136.5, 131.9, 128.2, 127.4, 87.9, 87.2, 85.7, 75.6, 57.4, 57.1, 51.9, 27.5, 26.8, 26.6, 22.7, 18.5; IR (film) 2082, 1686, 1437, 1356, 1262, 1160, 1116, 1078 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{23}N_2O_4$ $[M+H]^+$ 367.1658, found 367.1652.

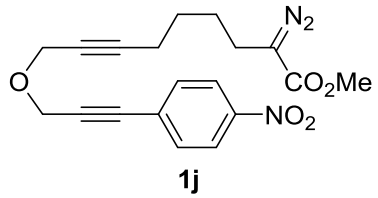
Methyl 2-acetyl-9-((3-(4-nitrophenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13j**)



13j

colorless oil; R_f = 0.18 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.20 (m, 2H), 7.59-7.61 (m, 2H), 4.48 (s, 2H), 4.29 (t, *J* = 2.1 Hz, 2H), 3.74 (s, 3H), 3.44 (t, *J* = 7.4 Hz, 1H), 2.23-2.28 (m, 5H), 1.83-1.90 (m, 2H), 1.52-1.59 (m, 2H), 1.33-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 170.2, 147.3, 132.5, 129.4, 123.6, 90.1, 87.5, 84.6, 75.3, 59.5, 57.6, 56.9, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1747, 1716, 1594, 1520, 1344, 1167, 1116, 1075 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{24}NO_6$ $[M+H]^+$ 386.1604, found 386.1598.

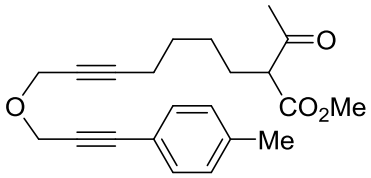
Methyl 2-diazo-9-((3-(4-nitrophenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1j**)



1j

yellow oil; R_f = 0.32 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.20 (m, 2H), 7.58-7.60 (m, 2H), 4.49 (s, 2H), 4.30 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.34 (t, *J* = 7.1 Hz, 2H), 2.29 (tt, J_1 = 2.0 Hz, J_2 = 6.7 Hz, 2H), 1.53-1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 132.5, 129.4, 123.6, 90.1, 87.4, 84.6, 75.4, 57.6, 56.9, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2081, 1693, 1594, 1520, 1437, 1344, 1159, 1115, 1077 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}N_3O_5$ $[M+H]^+$ 370.1403, found 370.1397.

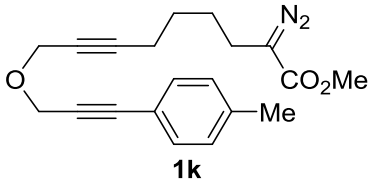
Methyl 2-acetyl-9-((3-(*p*-tolyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13k**)



13k

colorless oil; R_f = 0.24 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.35 (m, 2H), 7.11-7.13 (m, 2H), 4.44 (s, 2H), 4.28 (t, *J* = 2.1 Hz, 2H), 3.74 (s, 3H), 3.44 (t, *J* = 7.4 Hz, 1H), 2.35 (s, 3H), 2.23-2.27 (m, 5H), 1.81-1.89 (m, 2H), 1.51-1.57 (m, 2H), 1.33-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.3, 138.7, 131.7, 129.1, 119.5, 86.9, 86.7, 83.7, 75.7, 59.5, 57.3, 57.2, 52.4, 28.9, 28.2, 27.7, 26.6, 21.5, 18.6; IR (film) 1743, 1717, 1357, 1152, 1076 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{27}O_4$ $[M+H]^+$ 355.1909, found 355.1904.

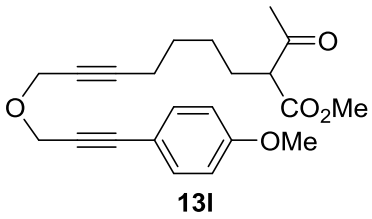
Methyl 2-diazo-9-((3-(*p*-tolyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1k**)



1k

orange oil; R_f = 0.39 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.35 (m, 2H), 7.10-7.12 (m, 2H), 4.44 (s, 2H), 4.29 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.32-2.35 (m, 5H), 2.28 (tt, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 2H), 1.56-1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 131.7, 129.1, 119.5, 86.8, 86.7, 83.7, 75.8, 57.3, 57.2, 51.9, 27.5, 26.8, 22.7, 21.5, 18.5; IR (film) 2080, 1693, 1510, 1437, 1351, 1191, 1158, 1133, 1116, 1075 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}N_2O_3$ $[M+H]^+$ 339.1709, found 339.1703.

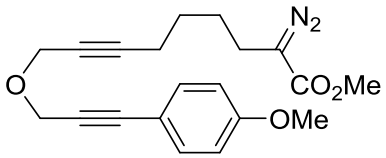
Methyl 2-acetyl-9-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13l**)



13l

colorless oil; R_f = 0.21 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.39 (m, 2H), 6.83-6.84 (m, 2H), 4.43 (s, 2H), 4.28 (t, *J* = 2.1 Hz, 2H), 3.81 (s, 3H), 3.74 (s, 3H), 3.44 (t, *J* = 7.4 Hz, 1H), 2.23-2.26 (m, 5H), 1.84-1.87 (m, 2H), 1.52-1.58 (m, 2H), 1.33-1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 159.8, 133.3, 114.6, 113.9, 86.9, 86.5, 83.1, 75.7, 59.5, 57.3, 57.2, 55.3, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1746, 1716, 1607, 1510, 1437, 1357, 1292, 1249, 1174, 1153, 1074, 1033 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{27}O_5$ $[M+H]^+$ 371.1858, found 371.1853.

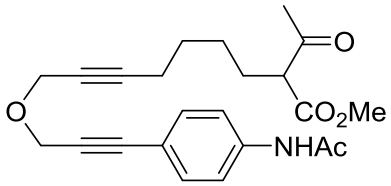
Methyl 2-diazo-9-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1l**)



1l

orange oil; R_f = 0.35 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.40 (m, 2H), 6.82-6.84 (m, 2H), 4.44 (s, 2H), 4.28 (t, *J* = 2.0 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 2.33 (t, *J* = 7.0 Hz, 2H), 2.26-2.30 (m, 2H), 1.51-1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 133.3, 114.6, 113.9, 86.8, 86.5, 83.1, 75.9, 57.3, 57.2, 55.3, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2081, 1695, 1601, 1510, 1440, 1351, 1293, 1250, 1117, 1073, 1032 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}N_2O_4$ $[M+H]^+$ 355.1658, found 355.1652.

Methyl 9-((3-(4-acetamidophenyl)prop-2-yn-1-yl)oxy)-2-acetylnon-7-ynoate (**13m**)

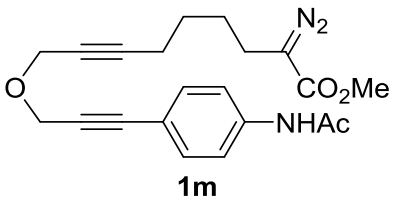


13m

colorless oil; R_f = 0.15 (PE:EA = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.48-7.50 (m, 2H), 7.37-7.39 (m, 2H), 4.44 (s, 2H), 4.28 (t, *J* = 2.0 Hz, 2H), 3.74 (s, 3H), 3.44 (t, *J* = 7.4 Hz, 1H), 2.23-2.26 (m, 5H), 2.16 (s, 3H), 1.81-1.87 (m, 2H), 1.50-1.58 (m, 2H), 1.33-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 170.3, 168.6, 138.4, 132.6, 119.3, 118.0, 87.1. 86.3, 84.0, 75.6, 59.5, 57.3, 57.2, 52.4, 28.9, 28.2, 27.7, 26.6, 24.6, 18.5; IR (film) 1741, 1718, 1653, 1525, 1353, 1315, 1253, 1077 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{23}H_{28}NO_5$ $[M+H]^+$ 398.1967, found

398.1962.

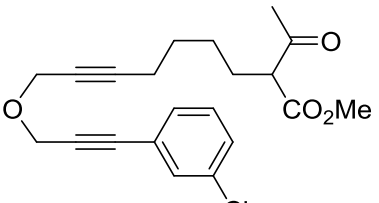
Methyl 9-((3-(4-acetamidophenyl)prop-2-yn-1-yl)oxy)-2-diazonon-7-ynoate (**1m**)



1m

orange oil; R_f = 0.14 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.49-7.51 (m, 2H), 7.36-7.38 (m, 2H), 4.44 (s, 2H), 4.29 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.27 (tt, J_1 = 2.1 Hz, J_2 = 6.8 Hz, 2H), 2.16 (s, 3H), 1.53-1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 138.4, 132.5, 119.4, 117.9, 87.0, 86.4, 84.0, 75.8, 57.3, 52.0, 27.5, 26.8, 24.5, 22.7, 18.5; IR (film) 2082, 1691, 1594, 1523, 1512, 1438, 1353, 1314, 1296, 1254, 1160, 1117, 1073 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{24}N_3O_4$ $[M+H]^+$ 382.1767, found 382.1761.

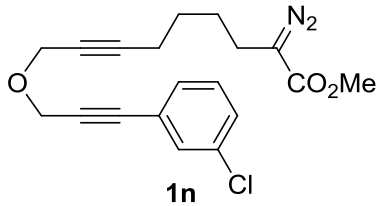
Methyl 2-acetyl-9-((3-(3-chlorophenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13n**)



13n

colorless oil; R_f = 0.23 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 1H), 7.29-7.33 (m, 2H), 7.22-7.36 (m, 1H), 4.44 (s, 2H), 4.28 (t, *J* = 2.0 Hz, 2H), 3.74 (s, 3H), 3.43 (t, *J* = 7.4 Hz, 1H), 2.23-2.29 (m, 5H), 1.83-1.90 (m, 2H), 1.51-1.59 (m, 2H), 1..35-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 134.1, 131.7, 129.9, 129.6, 128.8, 124.3, 87.2, 85.8, 85.1, 75.5, 59.5, 57.3, 57.0, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1744, 1716, 1356, 1246, 1150, 1076 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{27}ClNO_4$ $[M+NH_4]^+$ 392.1629, found 392.1623.

Methyl 9-((3-(3-chlorophenyl)prop-2-yn-1-yl)oxy)-2-diazonon-7-ynoate (**1n**)

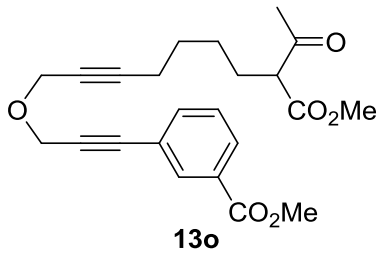


1n

orange oil; R_f = 0.35 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 1H), 7.29-7.33 (m, 2H), 7.22-7.26 (m, 1H), 4.44 (s, 2H), 4.28 (t, *J* = 1.9 Hz, 2H), 3.76 (s, 3H), 2.34 (t, *J* = 6.9 Hz, 2H), 2.27-2.30 (m, 2H), 1.54-1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 131.7, 129.9, 129.6, 128.8, 124.3, 87.1, 85.8, 85.1, 75.6,

57.4, 57.0, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2082, 1694, 1439, 1355, 1078 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}ClN_2O_3$ $[M+H]^+$ 359.1162, found 359.1157.

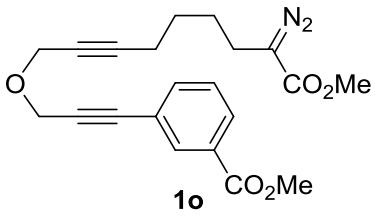
Methyl 3-(3-((8-(methoxycarbonyl)-9-oxodec-2-yn-1-yl)oxy)prop-1-yn-1-yl)benzoate (**13o**)



13o

colorless oil; R_f = 0.23 (PE:EA = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 4.46 (s, 2H), 4.29 (t, *J* = 2.1 Hz, 2H), 3.92 (s, 3H), 3.74 (s, 3H), 3.44 (t, *J* = 7.4 Hz, 1H), 2.23-2.27 (m, 5H), 1.83-1.89 (m, 2H), 1.51-1.59 (m, 2H), 1.33-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 166.3, 135.9, 132.9, 130.4, 129.5, 128.5, 123.0, 87.2, 85.5, 85.5, 75.5, 59.5, 57.3, 57.0, 52.4, 52.3, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1724, 1439, 1356, 1300, 1231, 1148, 1108, 1077 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{23}H_{27}O_6$ $[M+H]^+$ 399.1808, found 399.1802.

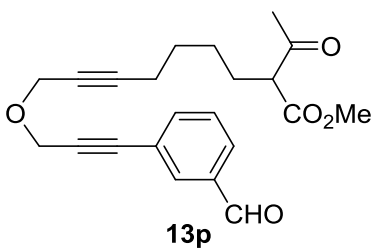
Methyl 3-(3-((8-diazo-9-methoxy-9-oxonon-2-yn-1-yl)oxy)prop-1-yn-1-yl)benzoate (**1o**)



1o

orange oil; R_f = 0.26 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 4.46 (s, 2H), 4.30 (t, *J* = 1.8 Hz, 2H), 3.92 (s, 3H), 3.76 (s, 3H), 2.34 (t, *J* = 6.9 Hz, 2H), 2.29 (t, *J* = 6.4 Hz, 2H), 1.51-1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 135.9, 132.9, 130.4, 129.5, 128.5, 123.0, 87.1, 85.5, 75.7, 57.3, 57.0, 52.3, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2081, 1726, 1692, 1438, 1351, 1300, 1230, 1158, 1111, 1077 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{23}N_2O_5$ $[M+H]^+$ 383.1607, found 383.1601.

Methyl 2-acetyl-9-((3-(3-formylphenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13p**)

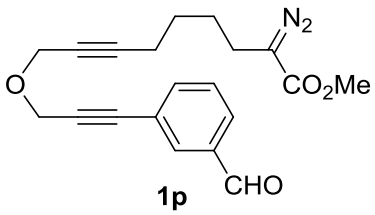


13p

colorless oil; R_f = 0.14 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.95 (s, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 4.47 (s, 2H), 4.30 (t, *J* = 1.9 Hz, 2H), 3.74 (s, 3H), 3.44 (t, *J* = 7.4 Hz, 1H),

2.23-2.26 (m, 5H), 1.81-1.91 (m, 2H), 1.52-1.59 (m, 2H), 1.33-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 191.4, 170.2, 137.3, 136.4, 133.1, 129.2, 129.1, 123.8, 87.3, 86.3, 85.1, 75.4, 59.5, 57.4, 57.0, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1744, 1707, 1436, 1360, 1277, 1160, 1077 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{28}NO_5$ $[M+NH_4]^+$ 386.1967, found 386.1962.

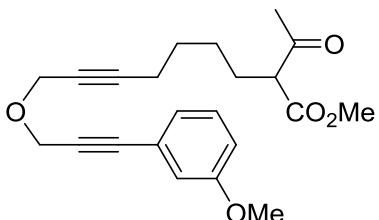
Methyl 2-diazo-9-((3-(3-formylphenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1p**)



1p

orange oil; R_f = 0.24 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.95 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 4.48 (s, 2H), 4.31 (t, *J* = 1.9 Hz, 2H), 3.76 (s, 3H), 2.34 (t, *J* = 7.0 Hz, 2H), 2.28-2.32 (m, 2H), 1.55-1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 137.3, 136.4 133.1, 129.2, 129.1, 123.8, 87.1, 86.2, 85.1, 75.6, 57.4, 57.0, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2082, 1697, 1437, 1352, 1159, 1116, 1075 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{21}N_2O_4$ $[M+H]^+$ 353.1501, found 353.1496.

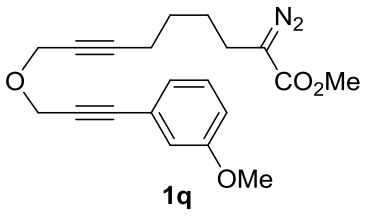
Methyl 2-acetyl-9-((3-(3-methoxyphenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13q**)



13q

colorless oil; R_f = 0.23 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.88 (dd, J_1 = 2.5 Hz, J_2 = 8.3 Hz, 1H), 4.44 (s, 2H), 4.28 (s, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 3.43 (t, *J* = 7.4 Hz, 1H), 2.22-2.26 (m, 5H), 1.79-1.87 (m, 2H), 1.51-1.58 (m, 2H), 1.35-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 159.3, 129.4, 124.3, 123.5, 116.6, 115.1, 87.1, 86.5, 84.3, 75.6, 59.5, 57.3, 57.1, 55.3, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1741, 1717, 1291, 1207, 1165, 1076 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{30}NO_5$ $[M+NH_4]^+$ 388.2124, found 388.2118.

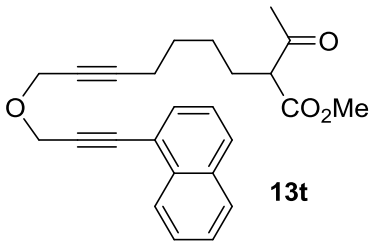
Methyl 2-diazo-9-((3-(3-methoxyphenyl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1q**)



1q

orange oil; R_f = 0.32 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.98 (m, 1H), 6.88 (dd, J_1 = 2.5 Hz, J_2 = 8.3 Hz, 1H), 4.45 (s, 2H), 4.29 (t, *J* = 2.1 Hz, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 2.34 (t, *J* = 7.1 Hz, 2H), 2.27-2.31 (m, 2H), 1.55-1.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 129.4, 124.3, 123.5, 116.6, 115.1, 87.0, 86.5, 84.3, 75.8, 57.3, 57.2, 55.3, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2082, 1695, 1438, 1354, 1290, 1164, 1076 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}N_2O_4$ $[M+H]^+$ 355.1658, found 355.1652.

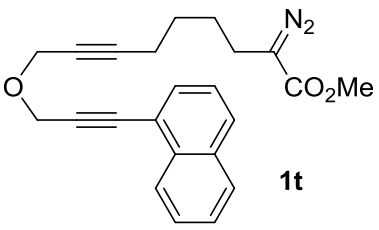
Methyl 2-acetyl-9-((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13t**)



13t

colorless oil; R_f = 0.23 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.2 Hz, 1H), 7.82-7.85 (m, 2H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.50-7.59 (m, 2H), 7.42 (t. *J* = 7.7 Hz, 1H), 4.61 (s, 2H), 4.37 (t, *J* = 1.9 Hz, 2H), 3.72 (s, 3H), 3.42 (t, *J* = 7.4 Hz, 1H), 2.25-2.28 (m, 2H), 2.21 (s, 3H), 1.84-1.87 (m, 2H), 1.52-1.59 (m, 2H), 1.39-1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 133.3, 133.1, 130.8, 129.0, 128.3, 126.9, 126.4, 126.1, 125.2, 120.2, 89.4, 87.2, 84.7, 75.7, 59.5, 57.4, 57.3, 52.4, 28.9, 28.2, 27.7, 26.6, 18.6; IR (film) 1745, 1716, 1434, 1354, 1247, 1211, 1148, 1098, 1072 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{25}H_{27}O_4$ $[M+H]^+$ 391.1909, found 391.1904.

Methyl 2-diazo-9-((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1r**)

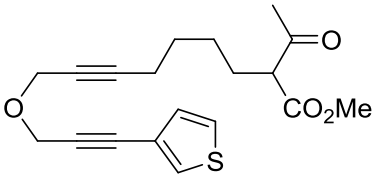


1t

orange oil; R_f = 0.33 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.82-7.85 (m, 2H), 7.68 (dd, J_1 = 0.9 Hz, J_2 = 7.1 Hz, 1H), 7.49-7.58 (m, 2H), 7.41 (dd, J_1 = 7.3 Hz, J_2 = 8.2 Hz, 1H), 4.62 (s, 2H), 4.38 (t, *J* = 2.1 Hz, 2H), 3.74 (s, 3H), 2.28-2.34 (m, 4H), 1.53-1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1333, 133.1, 130.8, 129.0, 128.3, 126.8, 126.5, 126.1, 125.2, 120.2, 89.4, 87.0, 84.7, 75.8, 57.4, 57.3, 51.9, 27.5, 26.8, 22.7, 18.6; IR (film) 2081, 1693, 1437, 1351,

1191, 1156, 1116, 1073 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{23}H_{23}N_2O_3$ $[M+H]^+$ 375.1709, found 375.1703.

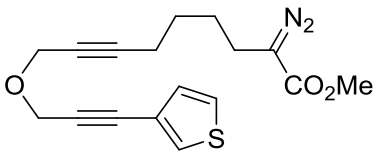
Methyl 2-acetyl-9-((3-(thiophen-3-yl)prop-2-yn-1-yl)oxy)non-7-ynoate (**13s**)



13u

colorless oil; R_f = 0.24 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 1H), 7.25-7.26 (m, 1H), 7.11-7.12 (m, 1H), 4.43 (s, 2H), 4.27 (s, 2H), 3.74 (s, 3H), 3.44 (t, *J* = 7.3 Hz, 1H), 2.23-2.26 (m, 5H), 1.81-1.89 (m, 2H), 1.51-1.58 (m, 2H), 1.35-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 129.9, 129.3, 125.3, 121.6, 87.1, 84.2, 81.7, 75.6, 59.5, 57.2, 57.1, 52.4, 28.9, 28.2, 27.7, 26.6, 18.5; IR (film) 1743, 1715, 1359, 1247, 1206, 1179, 1145, 1073 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{23}O_4S$ $[M+H]^+$ 347.1317, found 347.1312.

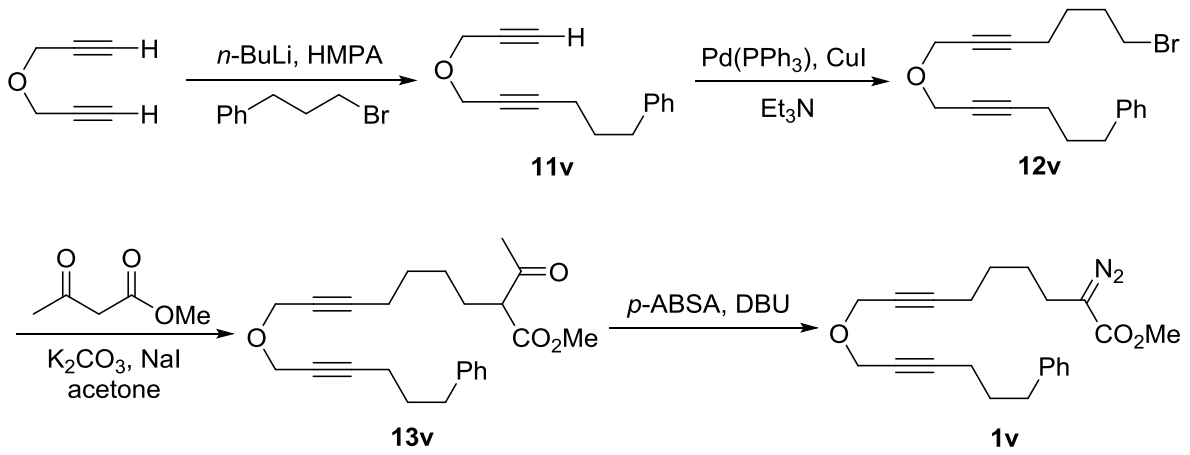
Methyl 2-diazo-9-((3-(thiophen-3-yl)prop-2-yn-1-yl)oxy)non-7-ynoate (**1s**)



1u

orange oil; R_f = 0.40 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J_1 = 0.9 Hz, J_2 = 2.9 Hz, 1H), 7.25-7.26 (m, 1H), 7.11 (dd, J_1 = 1.0 Hz, J_2 = 5.0 Hz, 1H), 4.43 (s, 2H), 4.28 (t, *J* = 2.1 Hz, 2H), 3.76 (s, 3H), 2.33 (t, *J* = 7.1 Hz. 2H), 2.28 (tt, J_1 = 2.1 Hz, J_2 = 6.8 Hz), 1.55-1.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.9, 129.3, 125.3, 121.6, 86.9, 84.2, 81.7, 75.8, 57.3, 57.2, 51.9, 27.5, 26.8, 22.7, 18.5; IR (film) 2081, 1693, 1438, 1352, 1192, 1158, 1117, 1073 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{17}H_{19}N_2O_3S$ $[M+H]^+$ 331.1116, found 331.1111.

3. Procedures for the preparation of **1v**

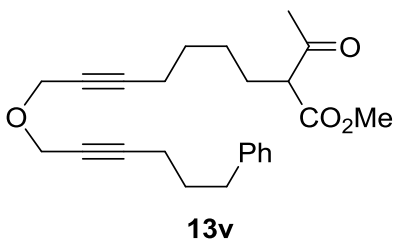


(6-(Prop-2-yn-1-yloxy)hex-4-yn-1-yl)benzene (**11v**)

To a stirred solution of dipropargyl ether (1.882 g, 20 mmol, 1.0 equiv) in dry THF (60 mL) under nitrogen at -78 ^{o}C was added *n*-BuLi (2.5 M in hexane, 8.0 mL, 20 mmol, 1.0 equiv) dropwise. After addition the reaction mixture was warm to room temperature and stirred for 30 minutes. The mixture was cooled to -78 ^{o}C and hexamethylphosphoramide (3.584 g, 20 mmol, 1.0 equiv) was added. Then (3-bromopropyl)benzene (7.964 g, 40 mmol, 2.0 equiv) was added. The mixture was stirred for 2 h at -78 ^{o}C before warmed to room temperature. The reaction was quenched with sat. *aq*. NH_4Cl solution and extracted with Et_2O. The combined organic layer was dried by anhydrous Na_2SO_4 and concentrated under reduced pressure. Because there is a by-product which has the same R_f which **11d**, only crude product (2.8620 g, R_f = 0.37, PE:EA = 20:1) can be generated. Considering that the by-product is stable in the next reactions, the crude product was used directly for the next step. The ^{1}H NMR yield of **11b** is 41%. The by-product was removed in the preparation of **13t**.

12d, **13t** and **1t** was prepared with the same procedures as **12a**, **13a** and **1a**.

Methyl 2-acetyl-9-((6-phenylhex-2-yn-1-yl)oxy)non-7-ynoate (**13v**)

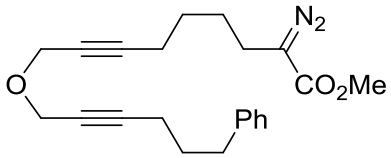


13v

colorless oil; R_f = 0.26 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.30 (m, 2H), 7.18-7.19 (m, 3H), 4.21-4.23 (m, 4H), 3.73 (s, 3H), 3.43 (t, *J* = 7.4 Hz, 1H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.22-2.27 (m, 7H), 1.80-1.87 (m, 4H),

1.50-1.57 (m, 2H), 1.35-1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.2, 141.5, 128.5, 128.4, 125.9, 86.9, 86.7, 75.8, 75.7, 59.5, 57.0, 56.9, 52.4, 34.8, 30.2, 28.9, 28.2, 27.7, 26.6, 18.5, 18.2; IR (film) 1745, 1717, 1438, 1352, 1164, 1071 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{24}H_{34}NO_4$ $[M+NH_4]^+$ 400.2488, found 400.2482.

Methyl 2-diazo-9-((6-phenylhex-2-yn-1-yl)oxy)non-7-ynoate (**1v**)



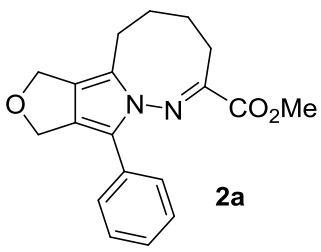
1v

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.30 (m, 2H), 7.18-7.20 (m, 3H), 4.22-4.23 (m, 4H), 3.75 (s, 3H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.0 Hz, 2H), 2.17-2.28 (m, 4H), 1.80-1.87 (m, 2H), 1.53-1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 128.5, 128.4, 125.9, 87.0, 86.6, 75.9, 75.8, 57.0, 56.9, 51.9, 34.8, 30.2, 27.5, 26.8, 22.7, 18.5, 18.2; IR (film) 2080, 1437, 1350, 1156, 1116, 1073 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{27}N_2O_3$ $[M+H]^+$ 367.2022, found 367.2016.

III. General Procedure for the Rh(I)-Catalyzed [2+2+1] Reactions

A 25 mL oven-dried Schlenk flask was charged with $[Rh(cod)_2]BF_4$ (6.0 mg, 0.015 mmol, 5 mol%) and BINAP (11.8 mg, 0.018mmol, 6 mol%) under nitrogen. Then dry THF (6.0 mL) was added using a syringe. The solution was stirred till the catalysts dissolved. Then **1a** (0.3 mmol) was added by syringe and the reaction was heated at 80 ^{o}C while maintaining stirring for 12 h. After cooling to room temperature, the solvent was removed in vacuo to leave a crude mixture, which was purified by silica gel column chromatography to afford pure product **2a**.

Methyl (*E*)-10-phenyl-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2a**)

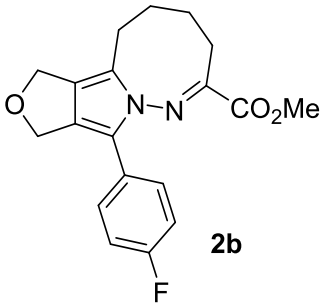


2a

yellow solid (mp = 152-156 ^{o}C); yield 65.2 mg (67%); R_f = 0.17 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.36 (m, 4H), 7.14-7.18 (m, 1H), 5.08 (s, 2H), 4.92 (s, 2H), 3.95 (s, 3H), 2.68-2.71 (m, 2H), 2.38-2.40 (m, 2H), 1.81-1.85 (m, 2H),

1.67-1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.5, 132.0, 128.5, 126.6, 125.9, 125.8, 123.7, 122.2, 120.8, 68.8, 67.3, 53.3, 28.2, 26.9, 24.5, 24.1; IR (film) 1726, 1440, 1290, 1254, 1199, 1169, 1105, 1048 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{21}N_2O_3$ $[M+H]^+$ 325.1552, found 325.1547.

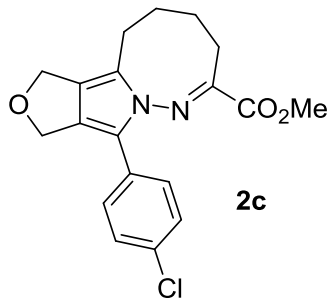
Methyl (*E*)-10-(4-fluorophenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2b**)



2b

yellow solid (mp = 140-141 °C); yield 78.1 mg (76%); R_f = 0.21 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.33 (m, 2H), 7.00-7.04 (m, 2H), 5.05 (s, 2H), 4.91 (s, 2H), 3.95 (s, 3H), 2.67-2.70 (m, 2H), 2.37-2.40 (m, 2H), 1.80-1.86 (m, 2H), 1.66-1.72 (m, 2H); 1.83-1.90 (m, 2H), 1.51-1.59 (m, 2H), 1.39-1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.4, 161.1 (d, *J* = 246.2 Hz), 128.3 (d, *J* = 7.6 Hz), 128.2 (d, *J* = 3.2 Hz), 125.5, 123.7, 122.1, 119.9, 115.4 (d, *J* = 21.7 Hz), 68.6, 67.3, 53.4, 28.3, 26.9, 24.6, 24.1; IR (film) 1727, 1504, 1290, 1254, 1230, 1199, 1106 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}FN_2O_3$ $[M+H]^+$ 343.1458, found 343.1452.

Methyl (*E*)-10-(4-chlorophenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2c**)

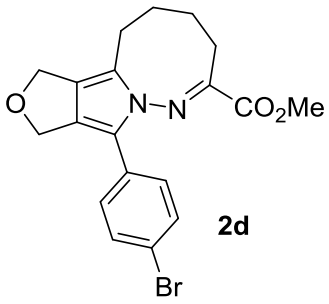


2c

yellow solid (mp = 150-151 °C); yield 86.2 mg (80%); R_f = 0.17 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 5.06 (s, 2H), 4.91 (s, 2H), 3.96 (s, 3H), 2.66-2.69 (m, 2H), 2.37-2.40 (m, 2H), 1.80-1.86 (m, 2H), 1.66-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.3, 131.5, 130.5, 128.7, 127.8, 126.1, 123.9, 122.6, 119.7, 68.6, 67.3, 53.4, 28.3, 26.8, 24.6, 24.1; IR (film) 1728, 1489, 1439, 1303, 1289, 1254, 1199, 1170, 1105, 1094, 1049 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}ClN_2O_3$ $[M+H]^+$ 359.1162, found 359.1157.

Methyl (*E*)-10-(4-bromophenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*]

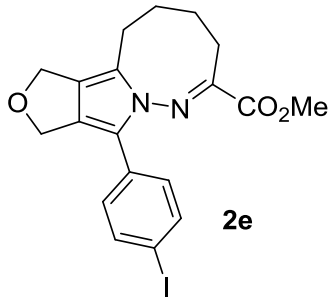
[1,2]diazocine-2-carboxylate (**2d**)



2d

yellow solid (mp = 158-160 ^{o}C); yield 87.1 mg (72%); R_f = 0.20 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.45 (m, 2H), 7.21-7.24 (m, 2H), 5.05 (s, 2H), 4.91 (s, 2H), 3.96 (s, 3H), 2.65-2.86 (m, 2H), 2.37-2.39 (m, 2H), 1.80-1.86 (m, 2H), 1.66-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.3, 131.6, 130.9, 128.0, 126.2, 123.9, 122.7, 119.7, 119.5, 68.6, 67.2, 53.4, 28.3, 26.8, 24.6, 24.0; IR (film) 1727, 1485, 1438, 1289, 1252, 1199, 1169, 1105, 1075, 1048 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}BrN_2O_3$ $[M+H]^+$ 403.0657, found 403.0652.

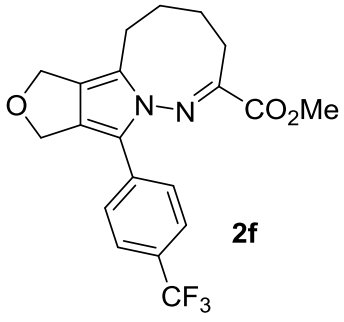
Methyl (*E*)-10-(4-iodophenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*] [1,2]diazocine-2-carboxylate (**2e**)



2e

yellow solid (mp = 163-165 ^{o}C); yield 89.2 mg (66%); R_f = 0.20 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.65 (m, 2H), 7.09-7.11 (m ,2H), 5.05 (s, 2H), 4.91 (s, 2H), 3.96 (s, 3H), 2.65-2.68 (m, 2H), 2.37-2.39 (m, 2H), 1.80-1.87 (m, 2H), 1.66-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.3, 131.5, 128.3, 126.3, 124.0, 122.8, 119.8, 90.7, 68.7, 67.2, 53.4, 28.3, 26.8, 24.5, 24.0; IR (film) 1728, 1484, 1289, 1200, 1105, 1048 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}IN_2O_3$ $[M+H]^+$ 451.0519, found 451.0513.

Methyl (*E*)-10-(4-(trifluoromethyl)phenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo [1,2-*b*][1,2]diazocine-2-carboxylate (**2f**)

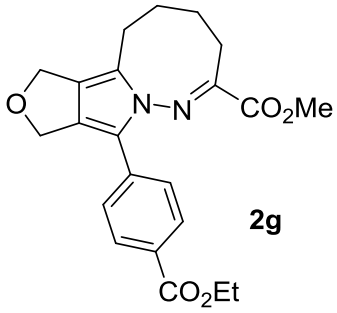


2f

yellow solid (mp = 143-144 ^{o}C); yield 63.6 mg (54%); R_f = 0.38 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.58 (m, 2H), 7.45-7.47 (m, 2H), 5.10 (s, 2H), 4.92 (s, 2H), 3.97 (s, 3H), 2.66-2.69 (m, 2H), 2.39-2.41 (m, 2H), 1.82-1.88 (m, 2H), 1.68-1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 164.3, 135.3, 127.5, 126.3, 125.5 (q, *J* = 3.8 Hz), 124.2, 123.4, 119.4,

68.7, 67.3, 53.4, 28.3, 26.7, 24.5, 24.0; IR (film) 1729, 1614, 1439, 1324, 1296, 1199, 1166, 1114, 1073 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{20}F_3N_2O_3$ $[M+H]^+$ 393.1426, found 393.1421.

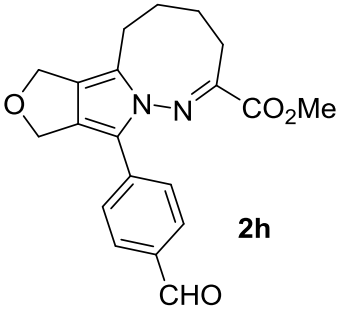
Methyl (*E*)-10-(4-(ethoxycarbonyl)phenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo [1,2-*b*][1,2]diazocine-2-carboxylate (**2g**)



2g

yellow solid (mp = 168-170 ^oC); yield 50.1 mg (42%); R_f = 0.08 (PE:EA = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-8.00 (m, 2H), 7.40-7.42 (m, 2H), 5.11 (s, 2H), 4.92 (s, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 3H), 2.67-2.70 (m, 2H), 2.39-2.41 (m, 2H), 1.81-1.89 (m, 2H), 1.67-1.75 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.6, 164.3, 136.2, 129.9, 127.7, 127.1, 125.8, 124.3, 123.6, 119.9, 68.9, 67.2, 60.8, 53.4, 28.3, 26.7, 24.5, 24.0, 14.4; IR (film) 1712, 1605, 1274, 1199, 1184, 1107, 1024 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{25}N_2O_5$ $[M+H]^+$ 397.1763, found 397.1757.

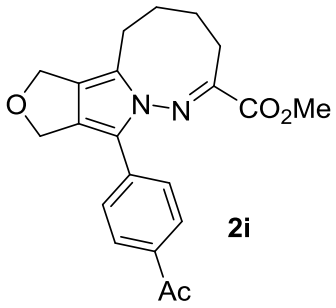
Methyl (*E*)-10-(4-formylphenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*] [1,2]diazocine-2-carboxylate (**2h**)



2h

yellow solid (mp = 160-162 ^oC); yield 25.4 mg (24%); R_f = 0.23 (PE:EA = 3:1); ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.81-7.84 (m, 2H), 7.49-7.51 (m, 2H), 5.13 (s, 2H), 4.93 (s, 2H), 3.99 (s, 3H), 2.68-2.70 (m, 2H), 2.40-2.42 (m, 2H), 1.83-1.89 (m, 2H), 1.70-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 165.9, 164.2, 137.8, 133.2, 130.2, 128.6, 126.2, 124.5, 124.3, 119.8, 69.0, 67.3, 53.5, 28.4, 26.6, 24.6, 24.0; IR (film) 1727, 1693, 1599, 1200, 1170, 1062 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{21}N_2O_4$ $[M+H]^+$ 353.1501, found 353.1496.

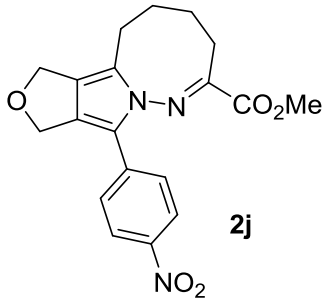
Methyl (*E*)-10-(4-acetylphenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*] [1,2]diazocine-2-carboxylate (**2i**)



2i

yellow solid (mp = 170-171 ^{o}C); yield 24.2 mg (22%); R_f = 0.18 (PE:EA = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.93 (m, 2H), 7.43-7.45 (m, 2H), 5.12 (s, 2H), 4.93 (s, 2H), 3.98 (s, 3H), 2.67-2.70 (m, 2H), 2.58 (s, 3H), 2.39-2.41 (m, 2H), 1.84-1.86 (m, 2H), 1.69-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 165.7, 164.3, 136.5, 133.8, 128.8, 128.0, 125.9, 124.4, 123.8, 119.8, 68.9, 67.3, 53.5, 28.3, 26.7, 26.5, 24.5, 24.0; IR (film) 1727, 1676, 1599, 1438, 1361, 1272, 1199 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{23}N_2O_4$ $[M+H]^+$ 367.1658, found 367.1652.

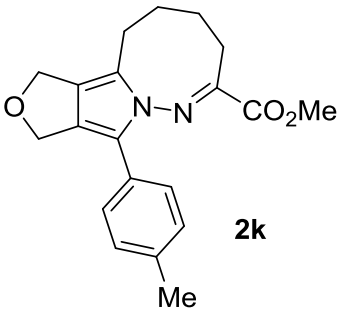
Methyl (*E*)-10-(4-nitrophenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2j**)



2j

yellow solid (mp = 201-202 ^{o}C); yield 49.9 mg (45%); R_f = 0.11 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.19 (m, 2H), 7.48-7.51 (m, 2H), 5.13 (s, 2H), 4.93 (s, 2H), 4.00 (s, 3H), 2.66-2.68 (m, 2H), 2.40-2.43 (m, 2H), 1.84-1.88 (m, 2H), 1.70-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 164.1, 144.7, 138.1, 129.3, 126.0, 124.9, 124.8, 124.2, 118.9, 68.9, 67.3, 53.6, 28.4, 26.5, 24.6, 23.9; IR (film) 1730, 1590, 1534, 1508, 1327, 1199, 1108, 1062, 1048 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}N_3O_5$ $[M+H]^+$ 370.1403, found 370.1397.

Methyl (*E*)-10-(p-tolyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2k**)

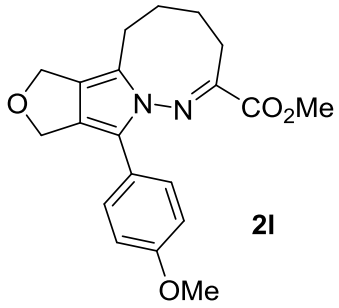


2k

yellow solid (mp = 117-119 ^{o}C); yield 64.0 mg (63%); R_f = 0.18 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.26 (m, 2H), 7.13-7.15 (m, 2 H), 5.06 (s, 2H), 4.91 (s, 2H), 3.94 (s, 3H), 2.67-2.69 (m, 2H), 2.37-2.39 (m, 2H), 2.33 (s, 3H); 1.79-1.85 (m, 2H), 1.67-1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.5, 135.6, 129.2, 129.2, 126.6, 125.2, 123.6, 121.8, 120.8, 68.7, 67.2, 53.3, 28.2, 26.9, 24.6, 24.2, 21.1; IR (film) 1726, 1437, 1289, 1255, 1199, 1169,

1105, 1048, 1023 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}N_2O_3$ $[M+H]^+$ 339.1709, found 339.1703.

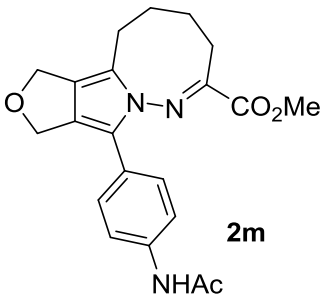
Methyl (*E*)-10-(4-methoxyphenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2l**)



2l

yellow solid (mp = 171-174 °C); yield 70.2 mg (66%); R_f = 0.15 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.30 (m, 2H), 6.87-6.89 (m, 2H), 5.05 (s, 2H), 4.91 (s, 2H), 3.94 (s, 3H), 3.81 (s, 3H); 2.67-2.70 (m, 2H), 2.36-2.39 (m, 2H), 1.79-1.85 (m, 2H), 1.66-1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 164.5, 157.8, 128.1, 124.8, 124.6, 123.6, 121.5, 120.6, 114.0, 68.6, 67.3, 55.3, 53.3, 28.2, 27.0, 24.6, 24.2; IR (film) 1726, 1506, 1439, 1294, 1249, 1198, 1180, 1105, 1030 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}N_2O_4$ $[M+H]^+$ 355.1658, found 355.1652.

Methyl (*E*)-10-(4-acetamidophenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2m**)

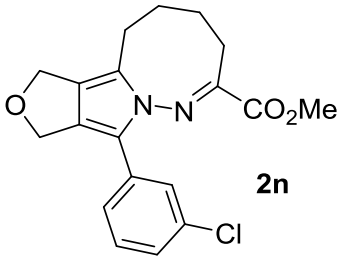


2m

yellow solid (mp = 214-216 °C); yield 80.1 mg (70%); R_f = 0.11 (PE:EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.41-7.43 (m, 2H), 7.24-7.27 (m, 2H), 5.05 (s, 2H), 4.91 (s, 2H), 3.95 (s, 3H), 2.69-2.72 (m, 2H), 2.36-2.38 (m, 2H), 2.10 (s, 3H), 1.79-1.87 (m, 2H), 1.66-1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 165.2, 164.4, 135.9, 127.9, 127.2, 125.5, 123.8, 122.1, 120.7, 119.9, 68.6, 67.2, 53.4, 28.2, 26.9, 24.6, 24.5, 24.2; IR (film) 1728, 1672, 1596, 1528, 1509, 1319, 1299, 1288, 1257, 1200 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{24}N_3O_4$ $[M+H]^+$ 382.1767, found 382.1761.

Methyl (*E*)-10-(3-chlorophenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2n**)

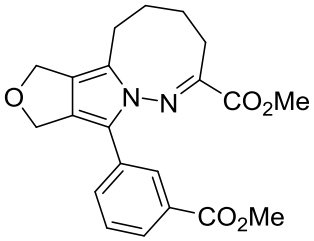
yellow solid (mp = 118-119 °C); yield 42.0 mg (39%); R_f = 0.15 (PE:EA = 5:1); ^{1}H NMR



2n

(400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 1.8 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.20 (td, J_1 = 1.4 Hz, J_2 = 7.9 Hz, 1H), 7.11-7.14 (m, 1H), 5.08 (s, 2H), 4.91 (s, 2H), 3.97 (s, 3H), 2.65-2.68 (m, 2H), 2.38-2.40 (m, 2H), 1.81-1.87 (m, 2H), 1.66-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.4, 134.4, 133.7, 129.7, 126.7, 126.4, 125.7, 124.6, 124.0, 122.8, 119.3, 68.7, 67.2, 53.4, 28.3, 26.7, 24.5, 24.0; IR (film) 1728, 1592, 1482, 1433, 1290, 1255, 1199 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}ClN_2O_3$ $[M+H]^+$ 359.1162, found 359.1157.

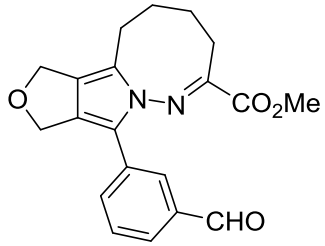
Methyl (*E*)-10-(3-(methoxycarbonyl)phenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4] pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2o**)



2o

yellow solid (mp = 136-138 °C); yield 82.6 mg (72%); R_f = 0.10 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (t, *J* = 1.6 Hz, 1H), 7.81-7.84 (m, 1H), 7.55 (ddd, J_1 = 1.2 Hz, J_2 = 1.8Hz, J_3 = 7.9 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 5.12 (s, 2H), 4.92 (s, 2H), 3.97 (s, 3H), 3.91 (s, 3H), 2.67-2.70 (m, 2H), 2.39-2.41 (m, 2H), 1.79-1.87 (m, 2H), 1.67-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.4, 164.4, 132.3, 130.6, 130.4, 128.6, 127.6, 126.7, 126.5, 124.0, 122.7, 119.7, 68.7, 67.2, 53.3, 52.2, 28.3, 26.8, 24.5, 24.1; IR (film) 1723, 1437, 1296, 1275, 1254, 1234, 1199, 1106 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{21}H_{23}N_2O_5$ $[M+H]^+$ 383.1607, found 383.1601.

Methyl (*E*)-10-(3-formylphenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2] diazocine-2-carboxylate (**2p**)

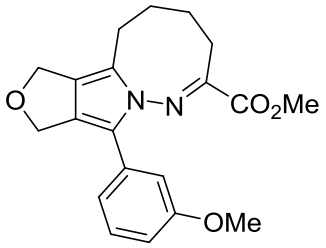


2p

yellow solid (mp = 120-122 °C); yield 42.3 mg (40%); R_f = 0.30 (PE:EA = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.98 (s, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 5.13 (s, 2H), 4.93 (s, 2H), 3.98 (s, 3H), 2.67-2.69 (m, 2H), 2.40-2.42 (m, 2H), 1.79-1.89 (m, 2H), 1.65-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 165.4, 164.3, 136.7, 133.0, 132.1,

129.2, 127.8, 126.8, 126.6, 124.1, 123.0, 119.3, 68.7, 67.3, 53.4, 28.3, 26.7, 24.6, 24.1; IR (film) 1728, 1698, 1295, 1257, 1201, 1169 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{21}N_2O_4$ $[M+H]^+$ 353.1501, found 353.1496.

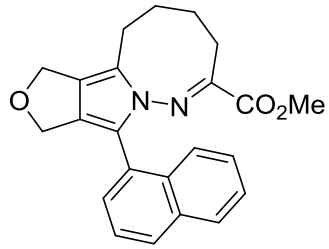
Methyl (*E*)-10-(3-methoxyphenyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2q**)



2q

yellow solid (mp = 128-130 °C); yield 64.8 mg (61%); R_f = 0.16 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 1H), 7.07-7.08 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.73 (dd, J_1 = 2.5 Hz, J_2 = 8.2 Hz, 1H), 5.09 (s, 2H), 4.92 (s, 2H), 3.95 (s, 3H), 3.81 (s, 3H), 2.64-2.67 (m, 2H), 2.38-2.40 (m, 2H), 1.79-1.87 (m, 2H), 1.65-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.4, 159.6, 133.2, 129.5, 126.1, 123.7, 122.3, 120.4, 119.3, 111.8, 111.7, 68.8, 67.3, 55.1, 53.3, 28.2, 26.9, 24.5, 24.1; IR (film) 1728, 1599, 1293, 1263, 1200, 1048 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}N_2O_4$ $[M+H]^+$ 355.1658, found 355.1652.

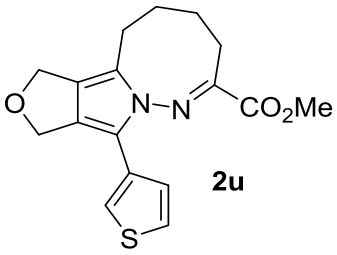
Methyl (*E*)-10-(naphthalen-1-yl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2t**)



2t

yellow solid (mp = 172-174 °C); yield 28.1 mg (25%); R_f = 0.19 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.93 (m, 1H), 7.84-7.86 (m, 1H), 7.78-7.80 (m, 1H), 7.42-747 (m, 3H), 7.27 (m, 1H), 4.98 (s, 2H), 4.82 (s, 2H), 3.77 (s, 3H), 2.80-2.82 (m, 2H), 2.44-2.46 (m, 2H), 1.75-1.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.3, 133.8, 131.7, 129.3, 128.4, 128.3, 127.8, 127.2, 126.1, 126.0, 125.8, 125.2, 123.3, 121.8, 119.3, 68.6, 67.4, 53.4, 28.3, 27.0, 24.7, 24.3; IR (film) 1726, 1433, 1289, 1250, 1201, 1171, 1102, 1019 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{23}H_{23}N_2O_3$ $[M+H]^+$ 375.1709, found 375.1703.

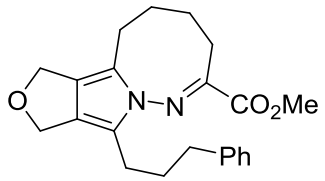
Methyl (*E*)-10-(thiophen-3-yl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2u**)



2u

yellow solid (mp = 126-127 ^{o}C); yield 64.4 mg (65%); R_f = 0.20 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 1H), 7.29-7.30 (m, 1H), 7.08-7.09 (m, 1H), 5.08 (s, 2H), 4.92 (s, 2H), 3.99 (s, 3H), 2.59-2.62 (m, 2H), 2.37-2.39 (m, 2H), 1.80-1.88 (m, 2H), 1.64-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 132.2, 126.5, 125.3, 124.4, 123.4, 121.3, 118.6, 117.1, 68.7, 67.3, 53.4, 28.1, 26.8, 24.5, 24.2; IR (film) 1727, 1437, 1288, 1254, 1197, 1182, 1169, 1106, 1049, 1024 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{17}H_{19}N_2O_3S$ $[M+H]^+$ 331.1116, found 331.1111.

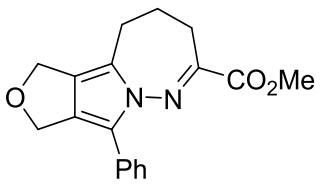
Methyl (*E*)-10-(3-phenylpropyl)-4,5,6,7-tetrahydro-3*H*,9*H*-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazocine-2-carboxylate (**2v**)



2v

yellow solid (mp = 83-85 ^{o}C); yield 28.6 mg (26%); R_f = 0.28 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.29 (m, 2H), 7.15-7.19 (m, 3H), 4.87 (s, 2H), 4.83 (s, 2H), 3.95 (s, 3H), 2.55-2.65 (m, 6H), 2.30-2.32 (m, 2H), 1.82-1.86 (m, 2H), 1.73-1.79 (m, 2H), 1.55-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.7, 142.0, 128.4, 128.3, 125.8, 122.7, 122.6, 120.5, 119.4, 67.8, 67.1, 53.2, 35.5, 29.9, 27.8, 27.0, 25.4, 24.6, 24.3; IR (film) 1726, 1433, 1283, 1197, 1173 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{22}H_{27}N_2O_3$ $[M+H]^+$ 367.2022, found 367.2016.

Methyl 9-phenyl-3,4,5,6-tetrahydro-8H-furo[3',4':3,4]pyrrolo[1,2-*b*][1,2]diazepine-2-carboxylate (**2w**)



2w

yellow solid (mp = 149-151 ^{o}C); yield 58.7 mg (63%); R_f = 0.17 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.45 (m, 2H), 7.33-7.37 (m, 2H), 7.18-7.22 (m, 1H), 5.06 (s, 2H), 4.89 (s, 2H), 3.91 (s, 3H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.66 (t, *J* = 6.9 Hz, 2H), 2.18 (p, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 155.5, 131.6, 128.4, 127.4, 126.2,

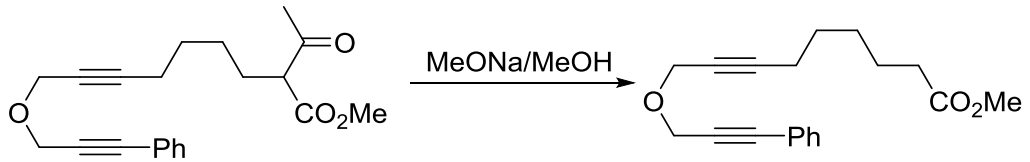
125.9, 124.6, 123.8, 119.9, 68.6, 67.0, 53.1, 29.3, 27.2, 25.0; IR (film) 1720, 1439, 1286, 1250, 1209, 1109, 1031 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$ 311.1396, found 311.1390.

IV. Mechanistic Experiments

All the mechanism experiments were carried out under standard conditions.

Experiment (a)

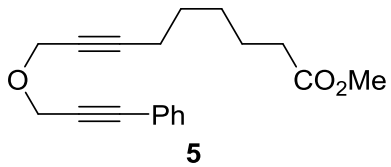
The preparation of the **5**



13a **5**

To a solution of MeONa (37.8 mg, 0.7 mmol, 0.1 equiv) in MeOH (2.0 mL) was added **13a** (2.55 g, 7.5 mmol, 1.0 equiv), the reaction mixture was reflux for 48 h. The reaction was quenched with sat. *aq*. NH_4Cl solution and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography with PE/EtOAc (100:1v/v) to afford **5** (1.05 g, 47%) as a colorless oil.

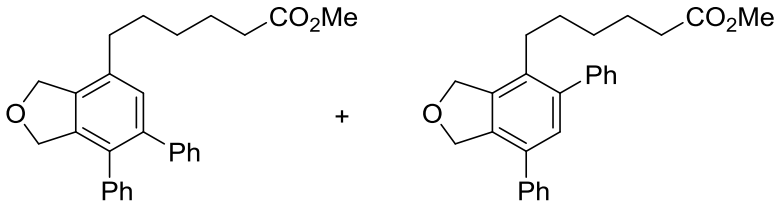
Methyl 9-((3-phenylprop-2-yn-1-yl)oxy)non-7-ynoate (**5**)



5

R_f = 0.45 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.46 (m, 2H), 7.30-7.32 (m, 3H), 4.46 (s, 2H), 4.30 (s, 2H), 3.67 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.25(t, *J* = 6.4 Hz, 2H), 1.61-1.68 (m, 2H), 1.51-1.58 (m, 2H), 1.39-1.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 131.8, 128.5, 128.3, 122.6, 87.4, 86.6, 84.5, 75.4, 57.3, 57.2, 51.5, 33.9, 28.3, 24.5, 18.7; IR (film) 1738, 1498, 1442, 1359, 1075 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{19}H_{23}O_3$ $[M+H]^+$ 299.1647, found 299.1642.

Methyl 5-(6,7-diphenyl-1,3-dihydroisobenzofuran-4-yl)pentanoate (**6a**) and Methyl 5-(5,7-diphenyl-1,3-dihydroisobenzofuran-4-yl)pentanoate (**6b**)

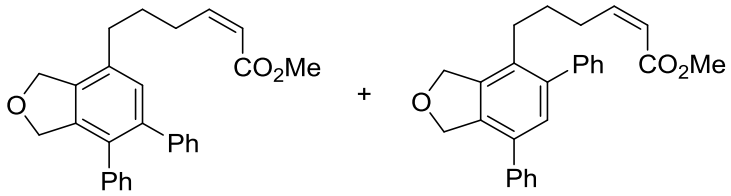


6a **6b**

Colorless oil; R_f = 0.28 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-7.42 (m, 11H), 5.02-5.28 (m, 4H), 3.64-3.66 (m, 3H), 2.60 (t, *J* = 7.7 Hz, 0.75 H), 2.50-2.54 (m, 1.25H), 2.33 (t, *J* = 7.4 Hz, 0.75 H), 2.18 (t, *J* = 7.5 Hz, 1.25 H), 1.18-1.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 174.0, 142.1, 141.2, 141.0, 140.6, 139.9, 139.3, 139.1, 138.9, 137.1, 136.1, 135.0, 133.3, 132.8, 132.1, 130.0, 129.9, 129.6, 129.3, 128.7, 128.2, 128.1, 127.8, 127.7, 127.3, 127.0, 126.7, 126.4, 74.1, 73.9, 73.3, 73.2, 51.5, 34.0, 33.8, 33.1, 30.3, 29.7, 29.5, 29.1, 29.0, 24.8, 24.4; IR (film) 1738, 1471, 1442, 1054 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{27}H_{29}O_3$ $[M+H]^+$ 401.2117, found 401.2111.

Experiment (b)

Methyl (*Z*)-6-(6,7-diphenyl-1,3-dihydroisobenzofuran-4-yl)hex-2-enoate (**7a**) and Methyl (*Z*)-6-(5,7-diphenyl-1,3-dihydroisobenzofuran-4-yl)hex-2-enoate (**7b**)



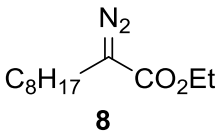
7a **7b**

Colorless oil; R_f = 0.26 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.42 (m, 6H), 7.04-7.23 (m, 5H), 6.26 (td, J_1 = 7.4 Hz, J_2 = 11.1 Hz, 0.40 H), 5.95 (td, J_1 = 7.4 Hz, J_2 = 11.5 Hz, 0.56 H), 5.83 (d, *J* = 11.5 Hz, 0.40 H), 5.69 (d, J = 11.4 Hz, 0.56 H), 5.02-5.28 (m, 4H), 3.68-3.70 (m, 3H), 2.63-2.79 (m, 2H), 2.53-2.55 (m, 2H), 1.78-1.86 (m, 0.82 H), 1.48-1.56 (m, 1.22H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 149.8, 149.7, 142.1, 141.1, 141.0, 140.6, 139.9, 139.4, 139.1, 138.9, 137.1, 136.2, 134.5, 133.4, 132.4, 132.2, 130.0, 129.9, 129.6, 129.3,

128.7, 128.2, 128.1, 127.8, 127.7, 127.4, 127.1, 126.7, 126.4, 120.0, 119.8, 74.2, 74.0, 73.3, 73.2, 51.1, 51.0, 32.9, 30.2, 29.4, 29.2, 28.9, 28.8; IR (film) 1722, 1648, 1471, 1442, 1197, 1177 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{27}H_{27}O_3$ $[M+H]^+$ 399.1960, found 399.1955.

Experiment (c)

Ethyl 2-diazodecanoate (**8**) was prepared with literature procedures.[2]

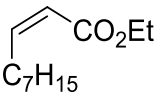


8

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (q, *J* = 7.1 Hz, 2H), 2.29 (t, *J* = 7.4 Hz, 2H), 1.26-1.53 (m, 15H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.7, 31.8, 29.3, 29.2, 28.8, 27.6, 23.0, 22.7, 14.5, 14.1;

We have isolated a product in 58% yield. HRMS results demonstrate that the molecular formula of the product is $C_{38}H_{44}O_6$. It's exactly two **5**. Considering the reactions conditions, we speculate it's dimerized through [2+2+2] reaction of alkynes catalyzed by Rh(I). However, because there are two alkynes in **5** and both alkynes are not symmetric. There are four possible structures of the dimer of **5**. As a result, the ^{1}H NMR spectrum and ^{13}C NMR spectrum are not discernable. HRMS (ESI, *m/z*) calcd for $C_{38}H_{48}NO_6$ $[M+NH_4]^+$ 614.3482, found 614.3479.

Methyl (*Z*)-dec-2-enoate (**10**)



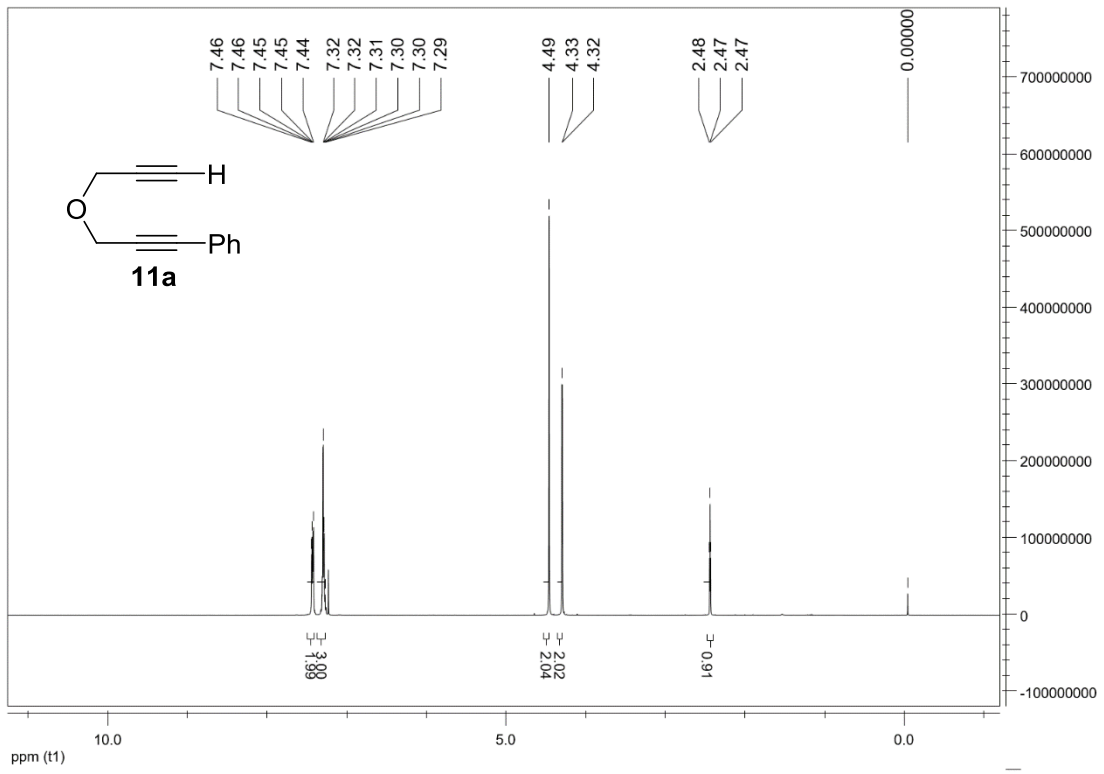
10

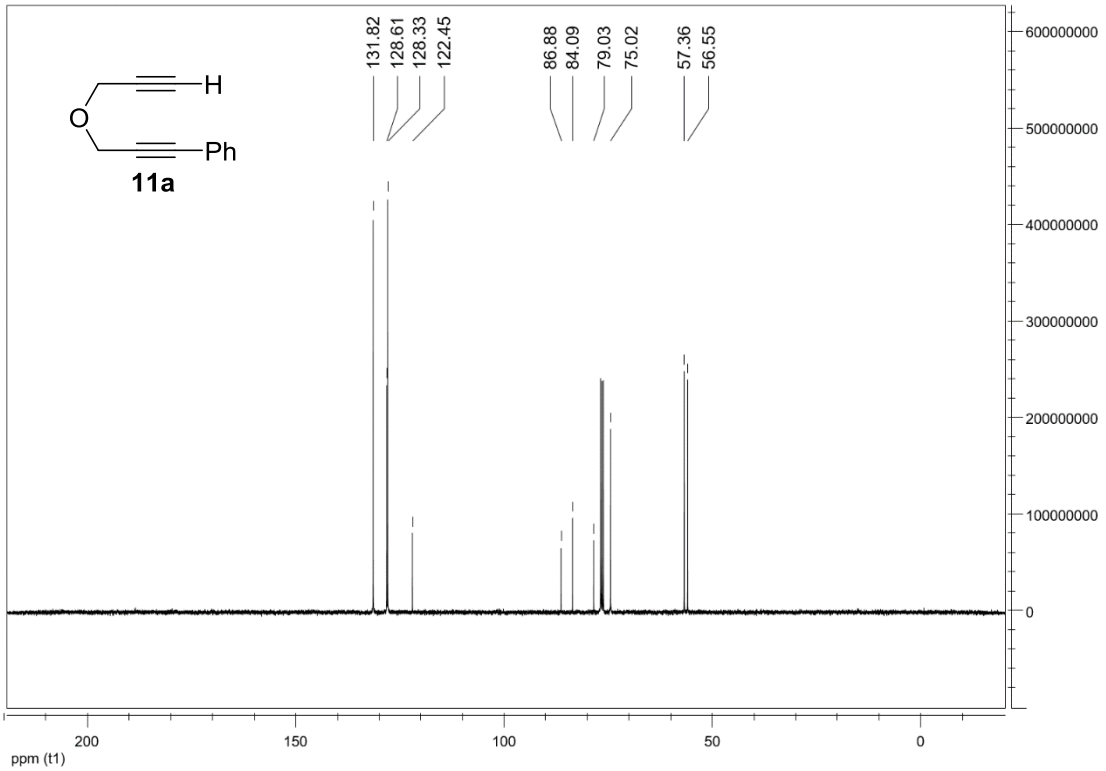
Colorless oil; R_f = 0.33 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (td, J_1 = 7.5 Hz, J_2 = 11.5 Hz, 1H), 5.75 (d, *J* = 11.5 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.64(q, *J* = 7.4 Hz, 2H), 1.40-1.45 (m, 2H), 1.27-1.31 (m, 11H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 150.7, 119.6, 59.8, 31.8, 29.3, 29.2, 29.1, 29.0, 22.7, 14.3, 14.1; IR (film) 1724, 1644, 1191 cm^{-1}; HRMS (ESI, *m/z*) calcd for $C_{12}H_{23}O_2$ $[M+H]^+$ 199.1698, found 199.1693.

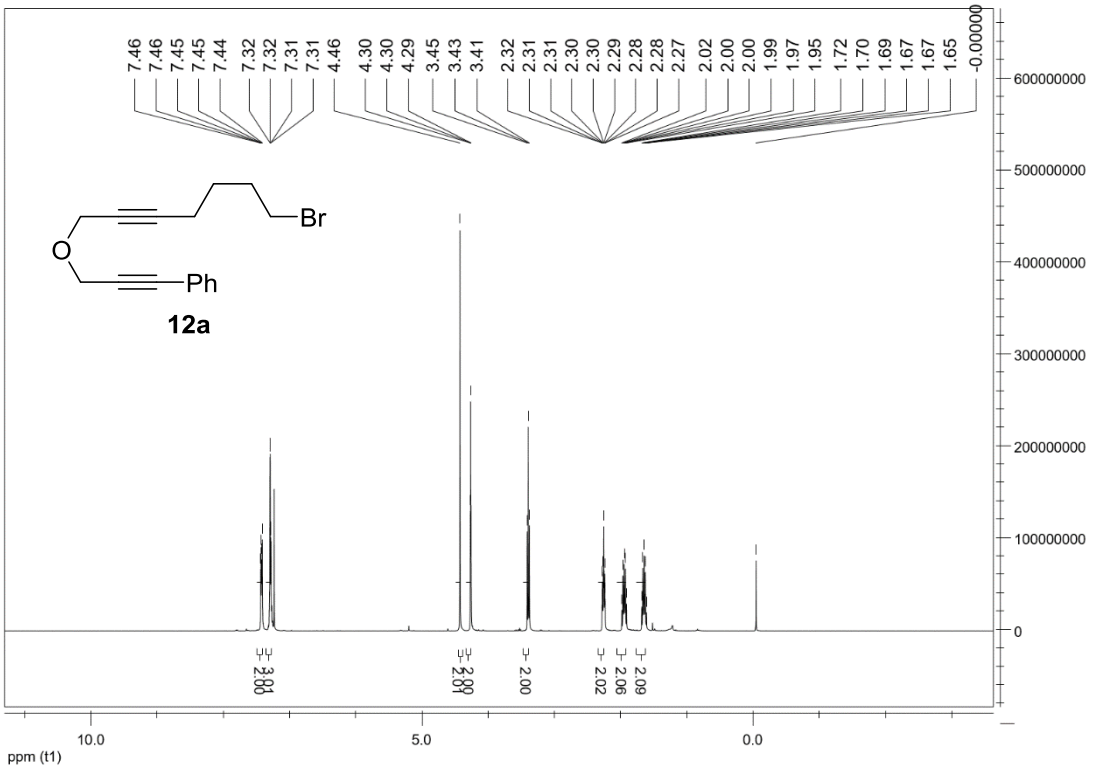
V. References

1. Kudoh, T.; Mori, T.; Shirahama, M.; Yamada, M.; Ishikawa, T.; Saito, S.; Kobayashi, H. *J. Am. Chem. Soc.* **2007**, *129*, 4939-4947.
2. Hu, M.; Rong, J.; Miao, W.; Ni, C.; Han, Y.; Hu, J. *Org. Lett.* **2014**, *16*, 2030-2033.

VI. ^{1}H and ^{13}C NMR of the diazo substrate and the products



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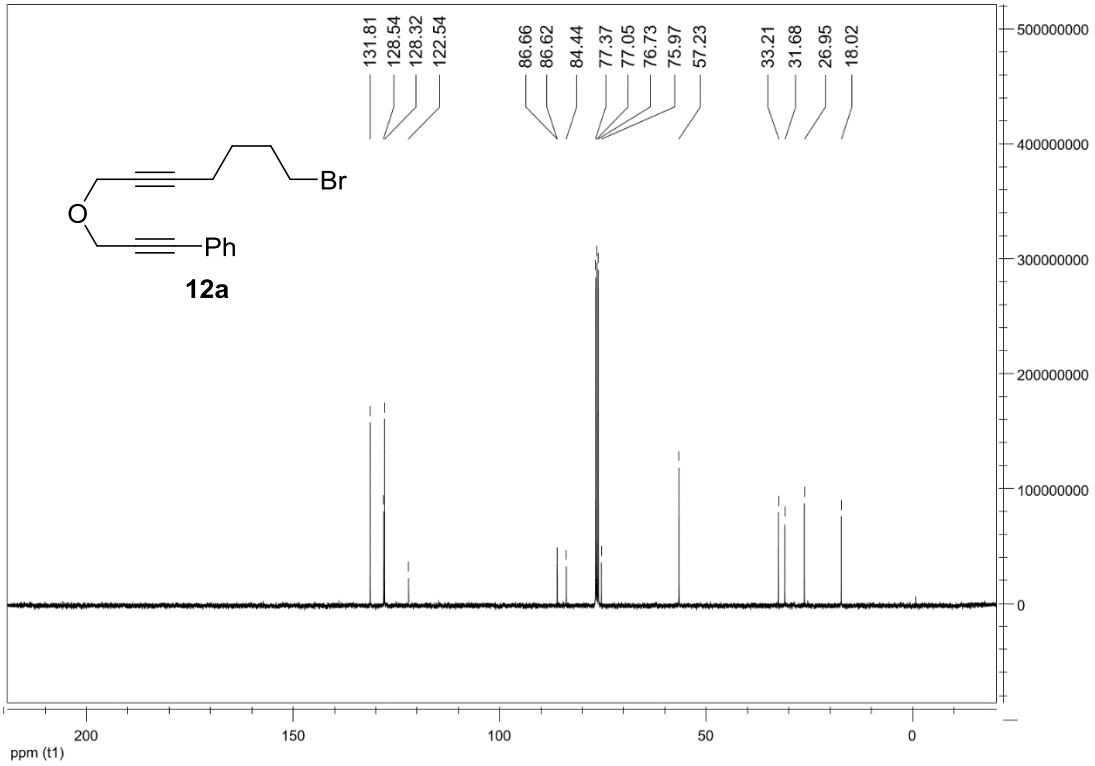
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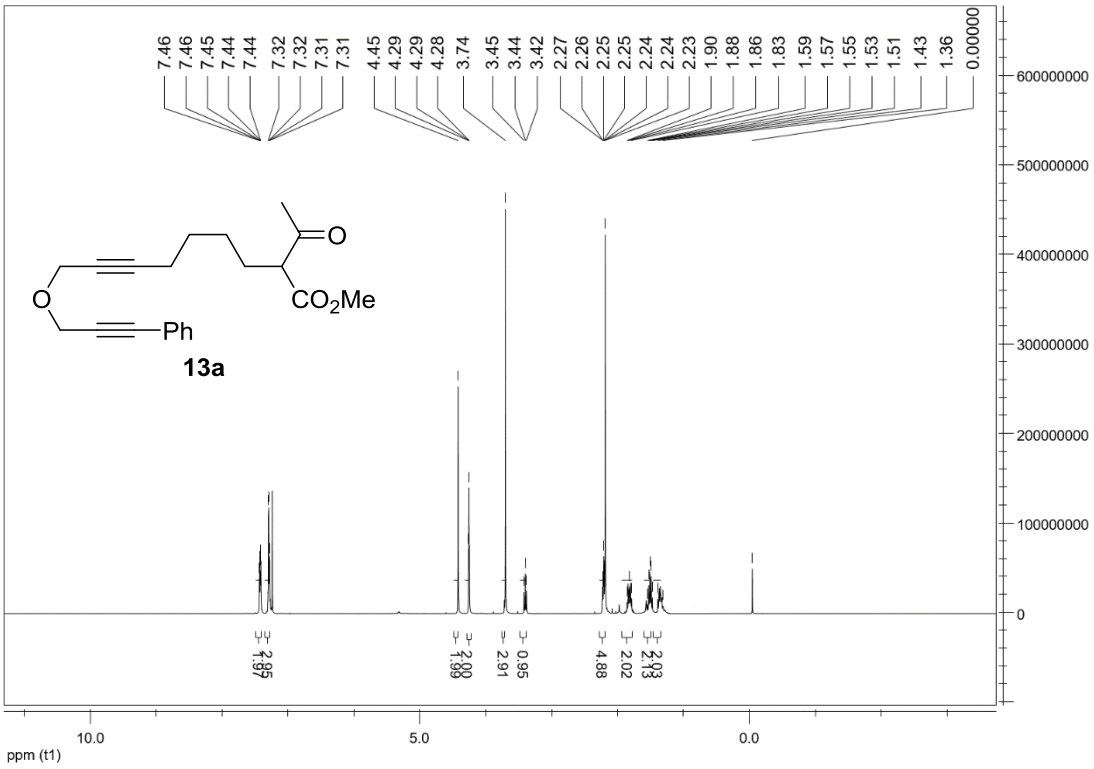
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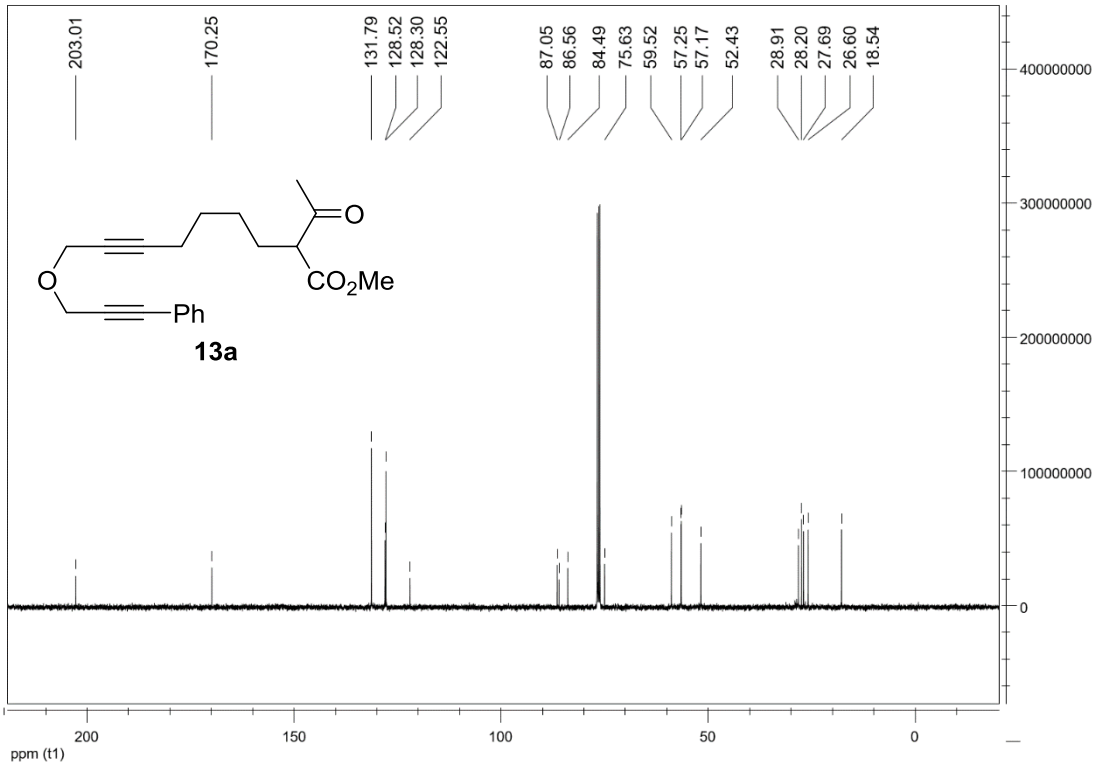
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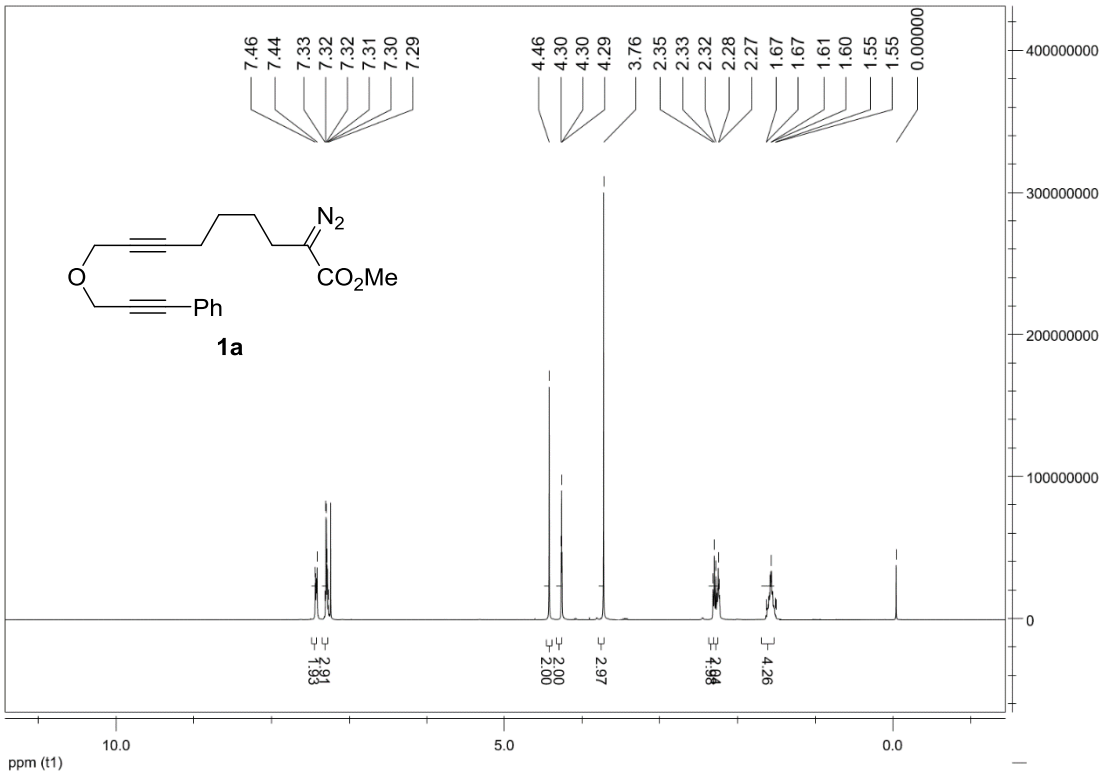
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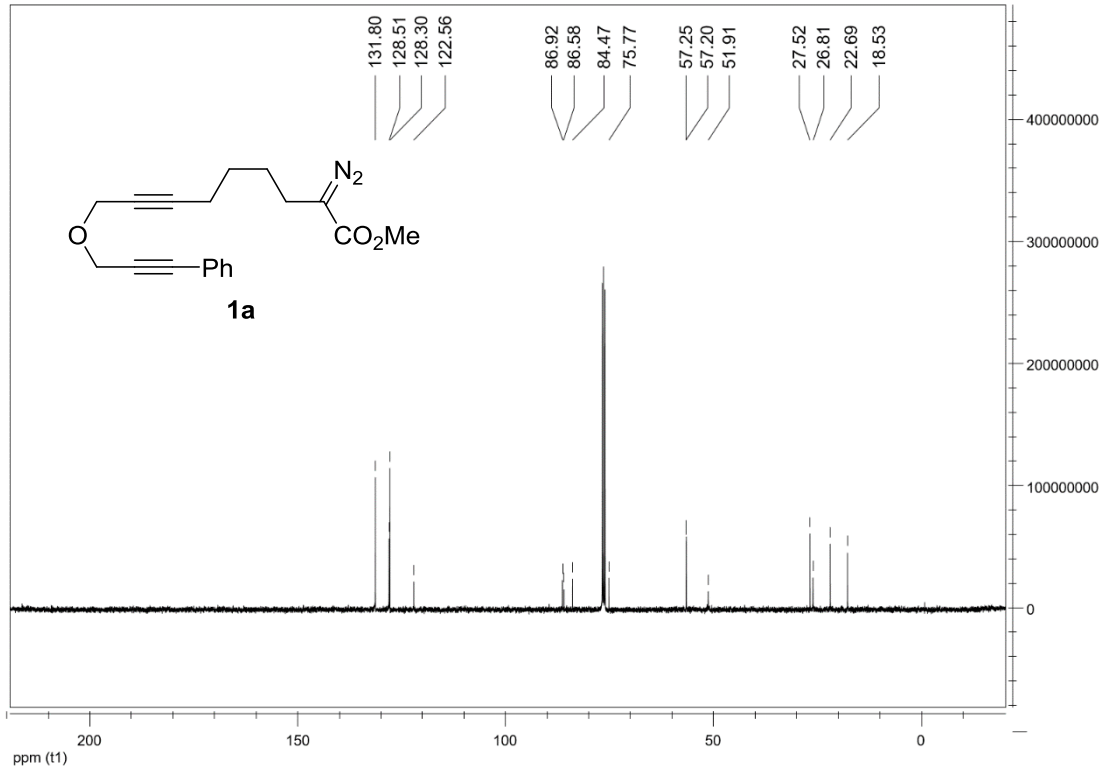
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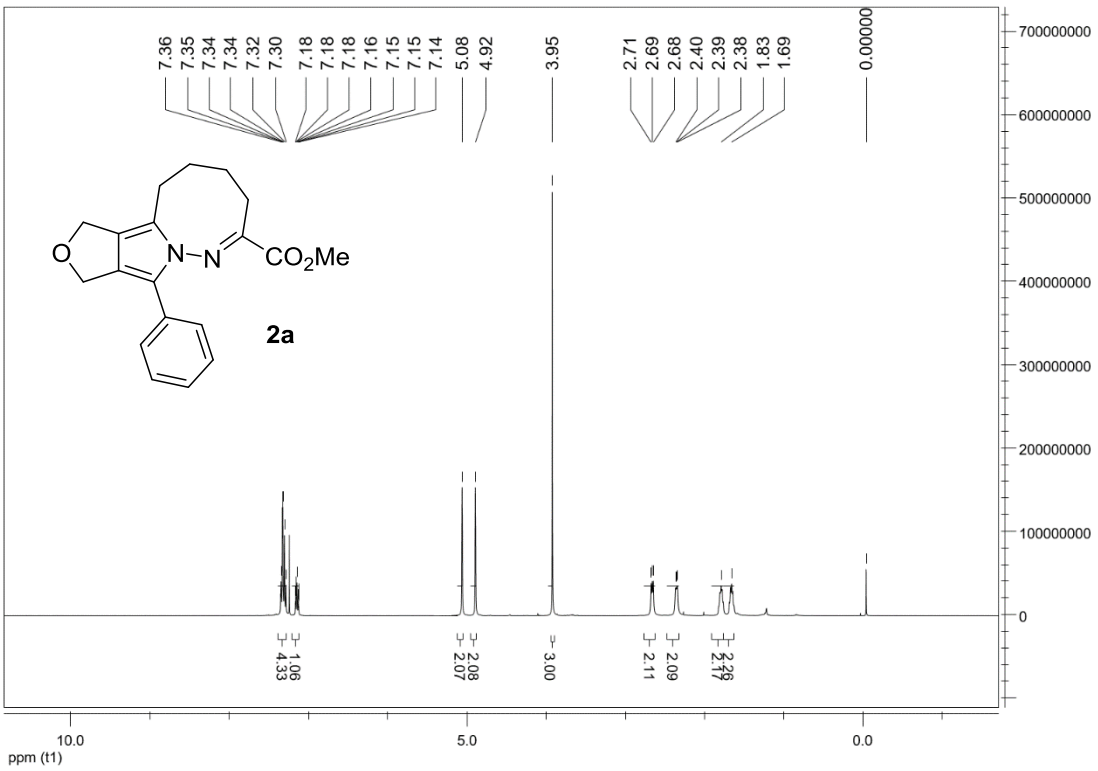
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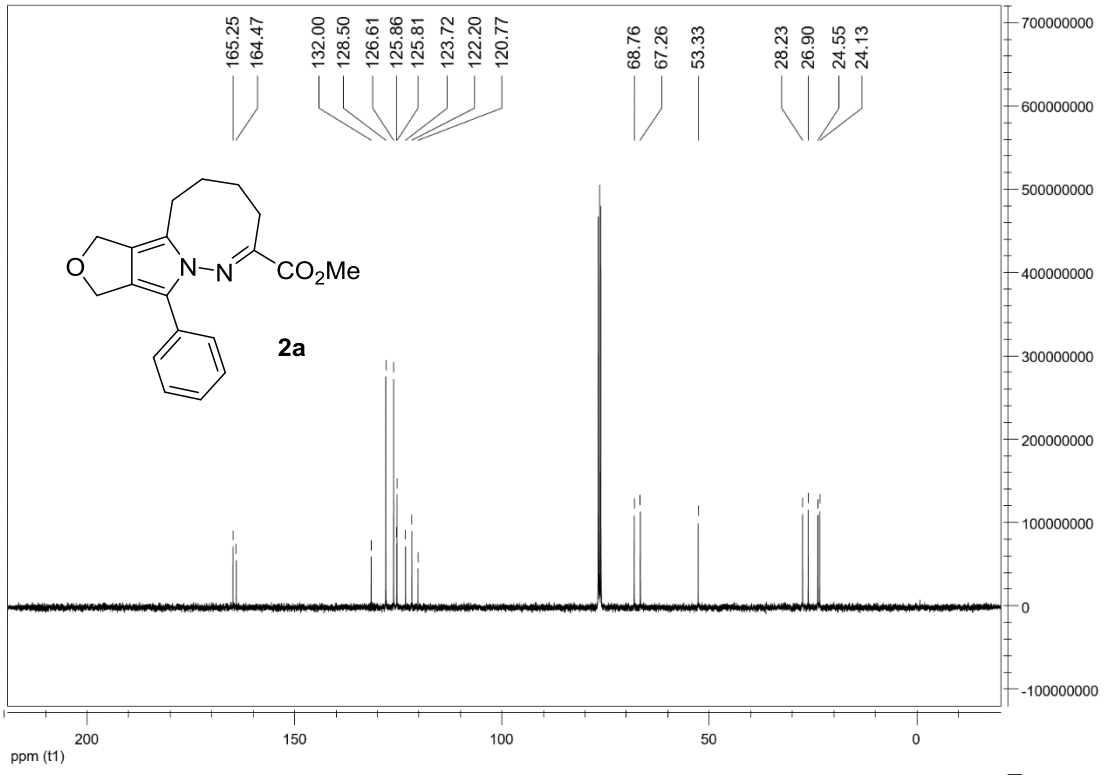
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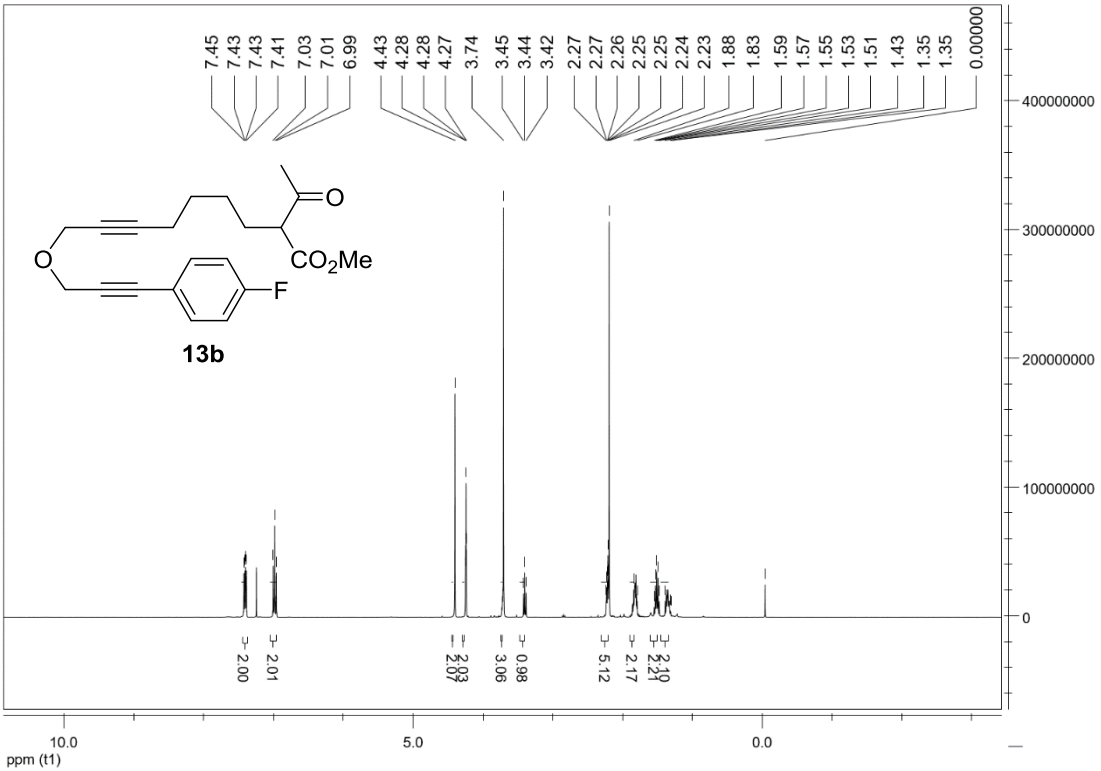
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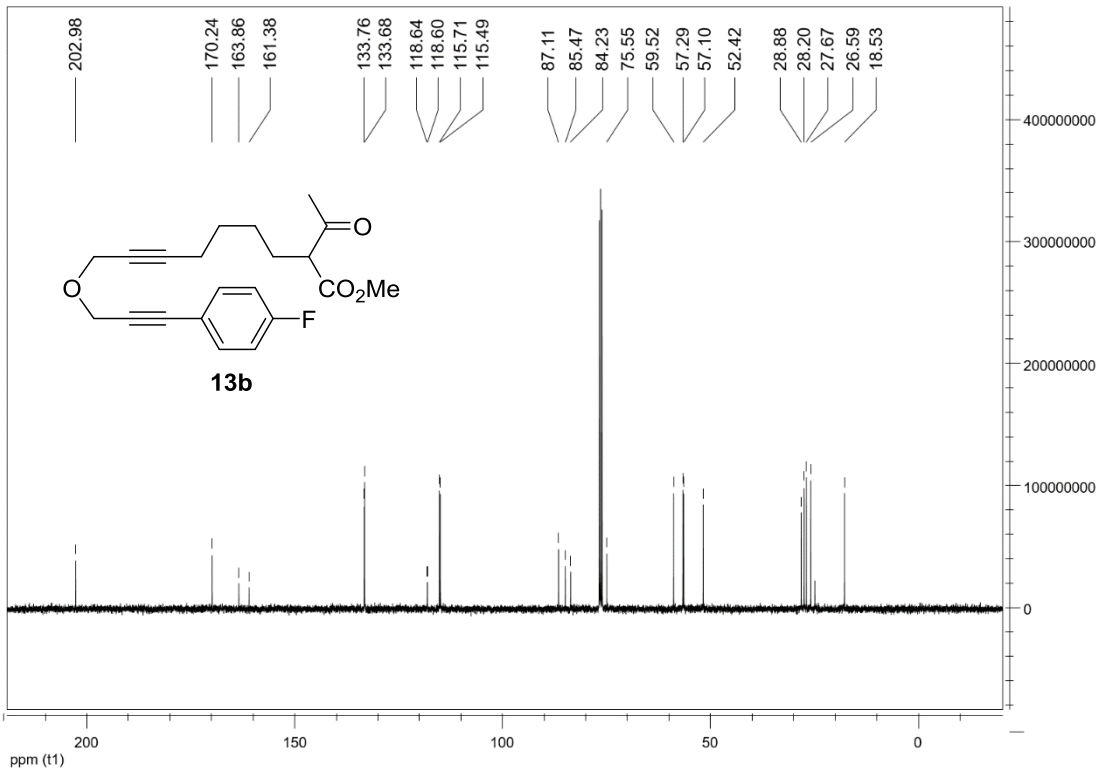
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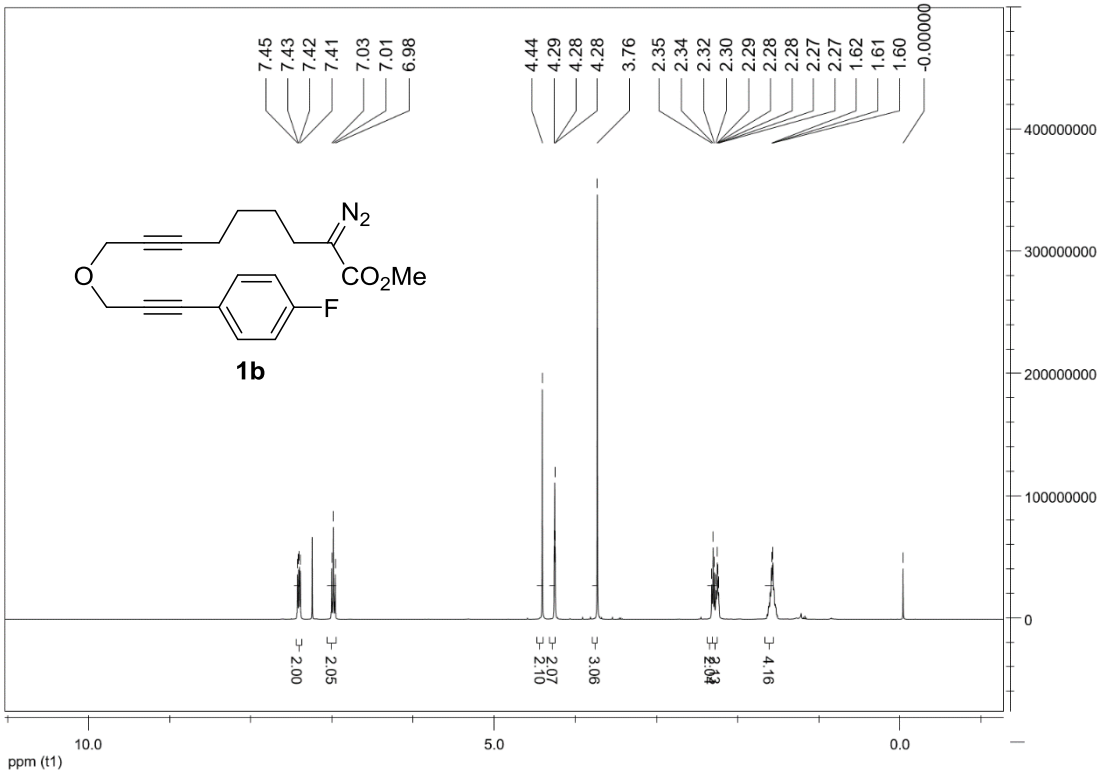
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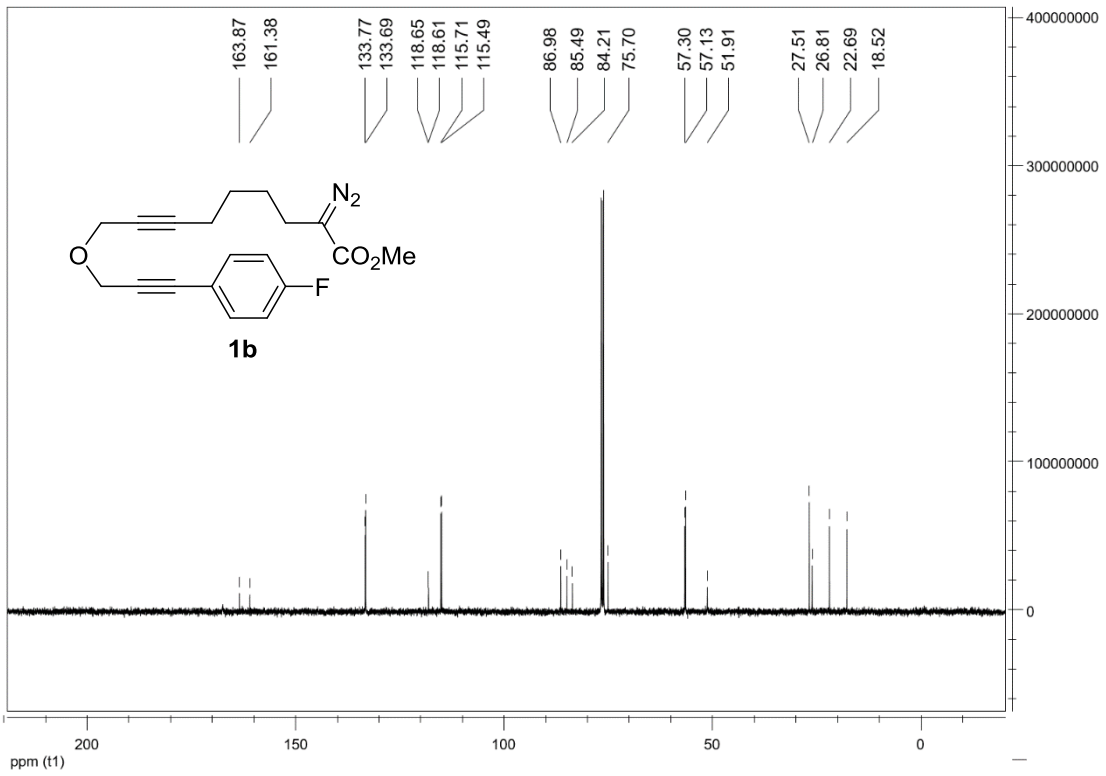
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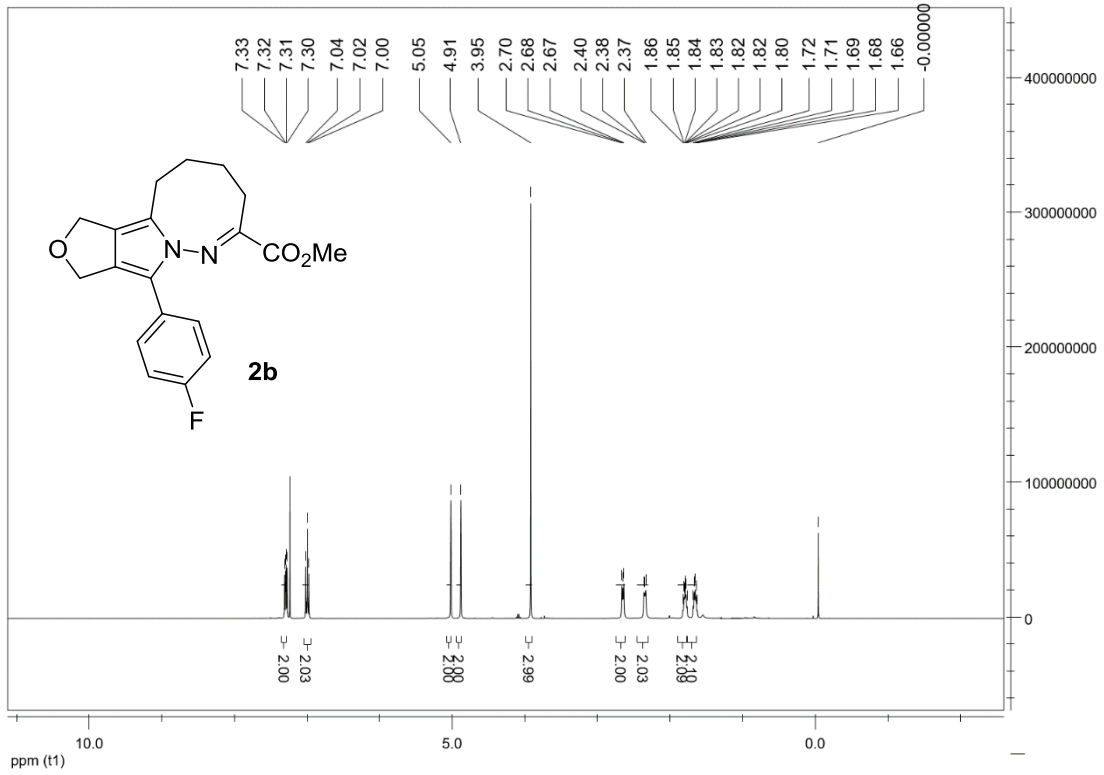
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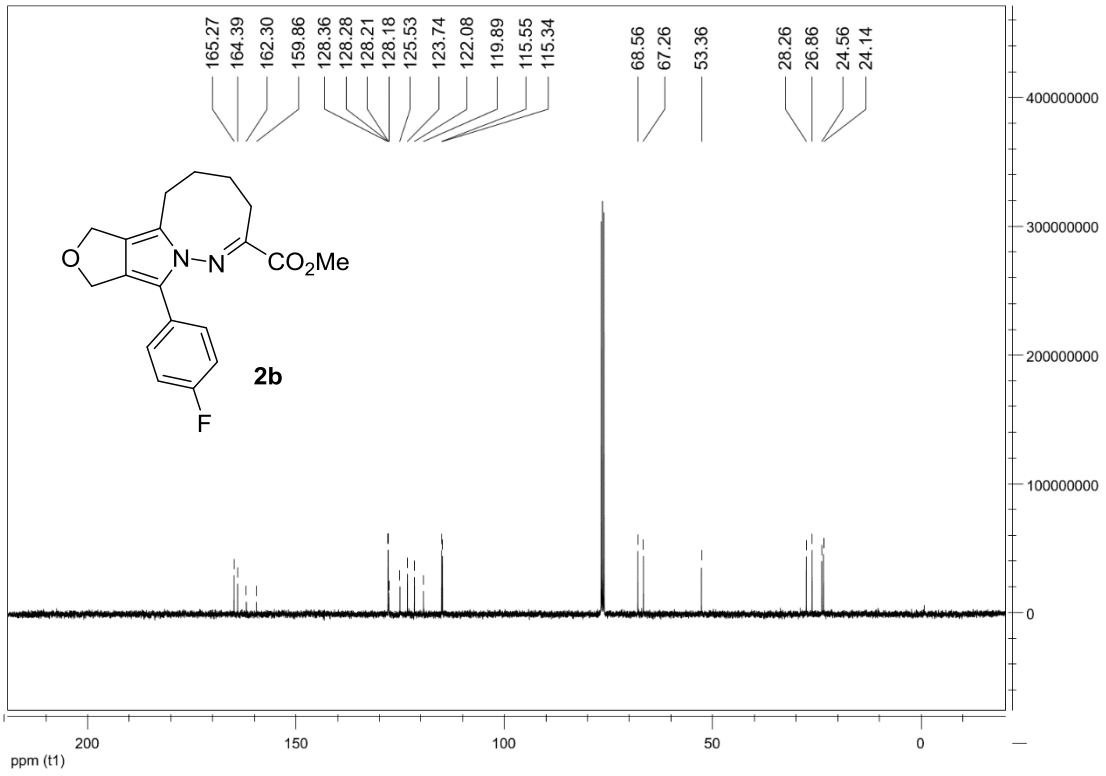
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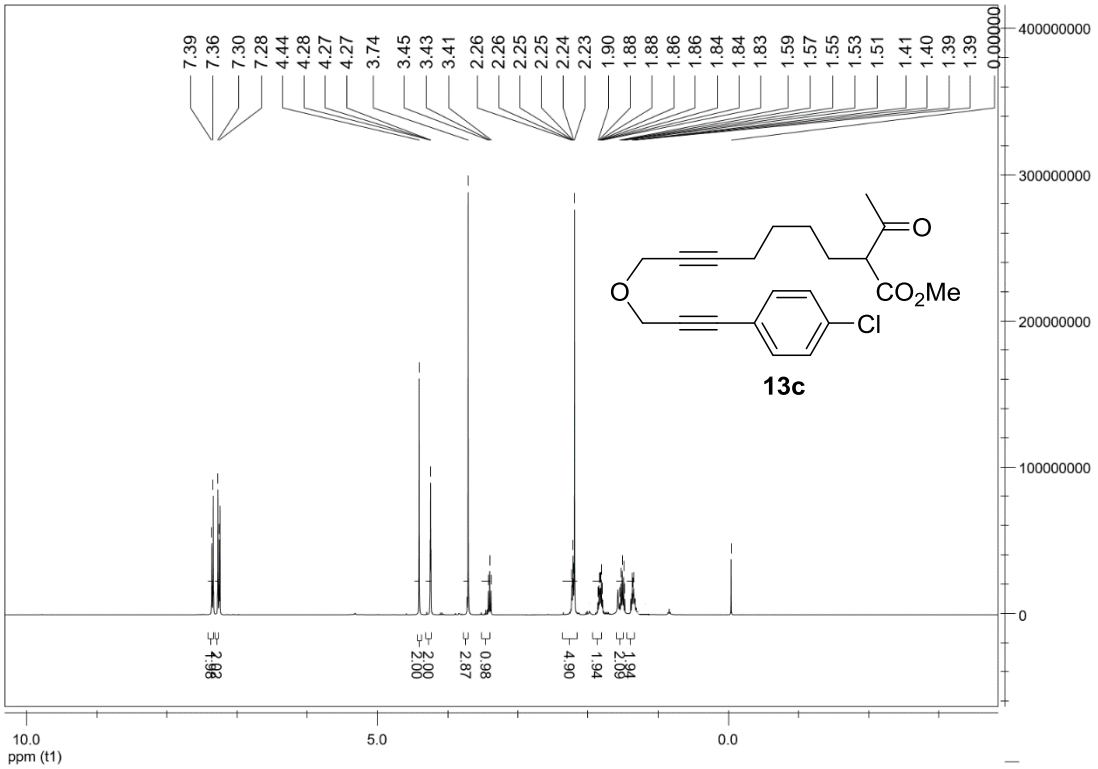
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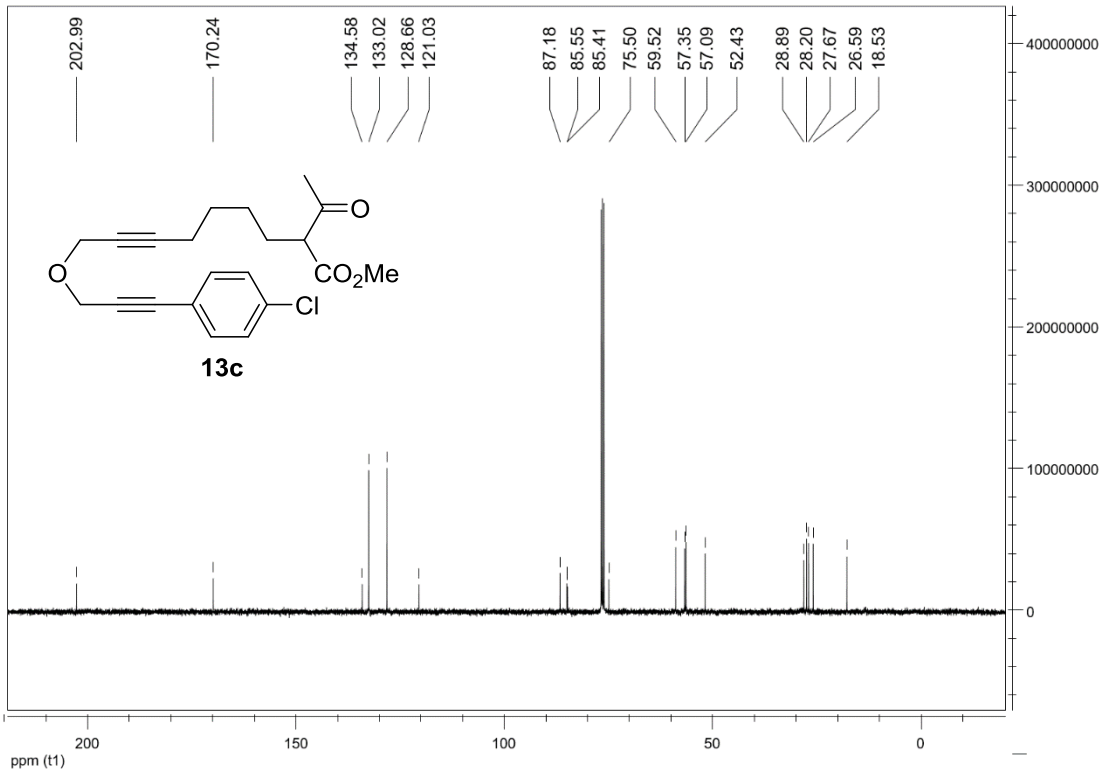
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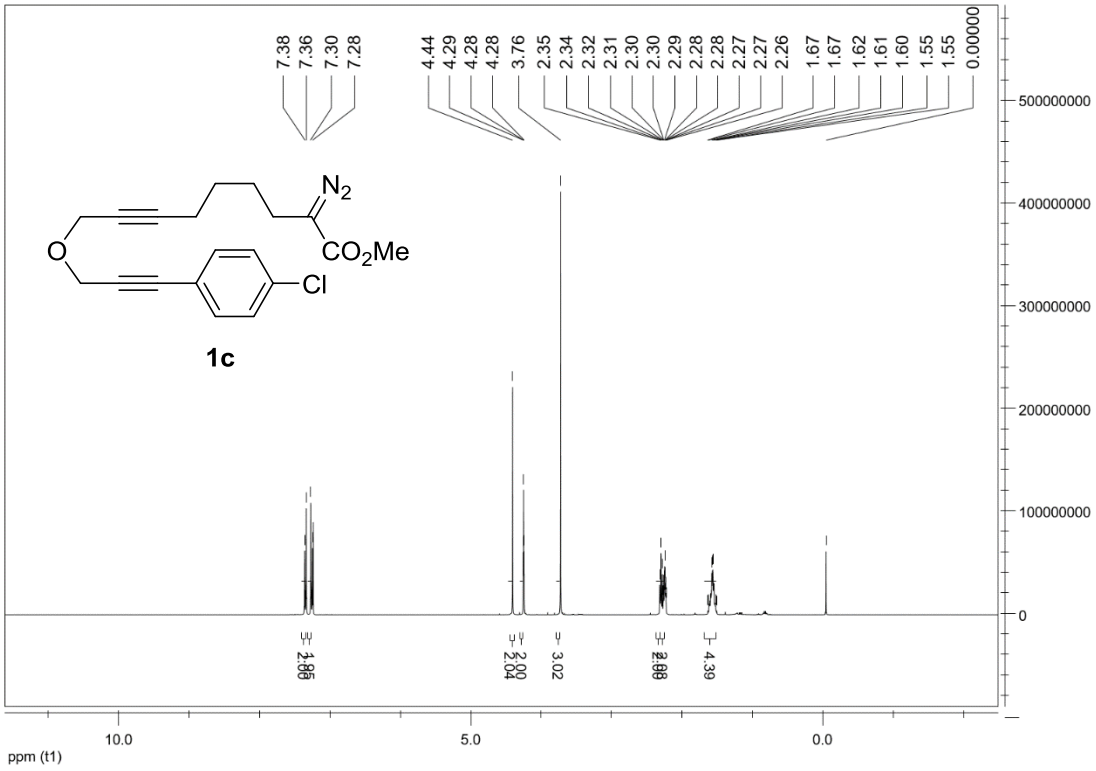
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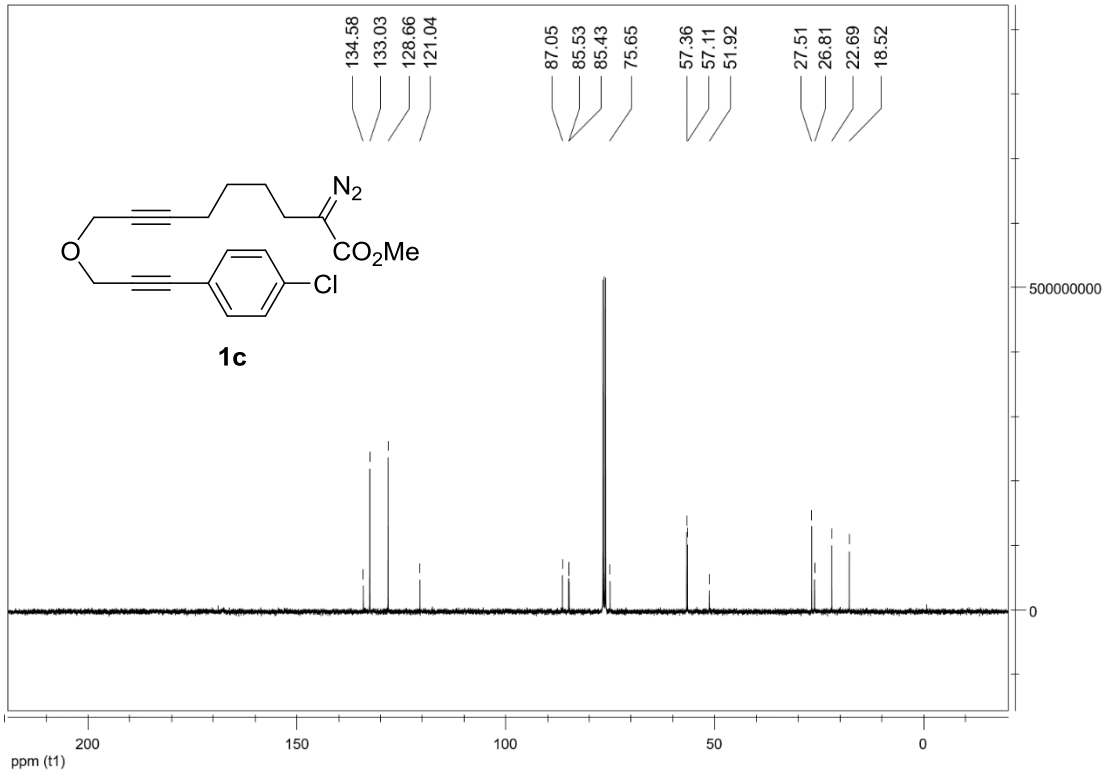
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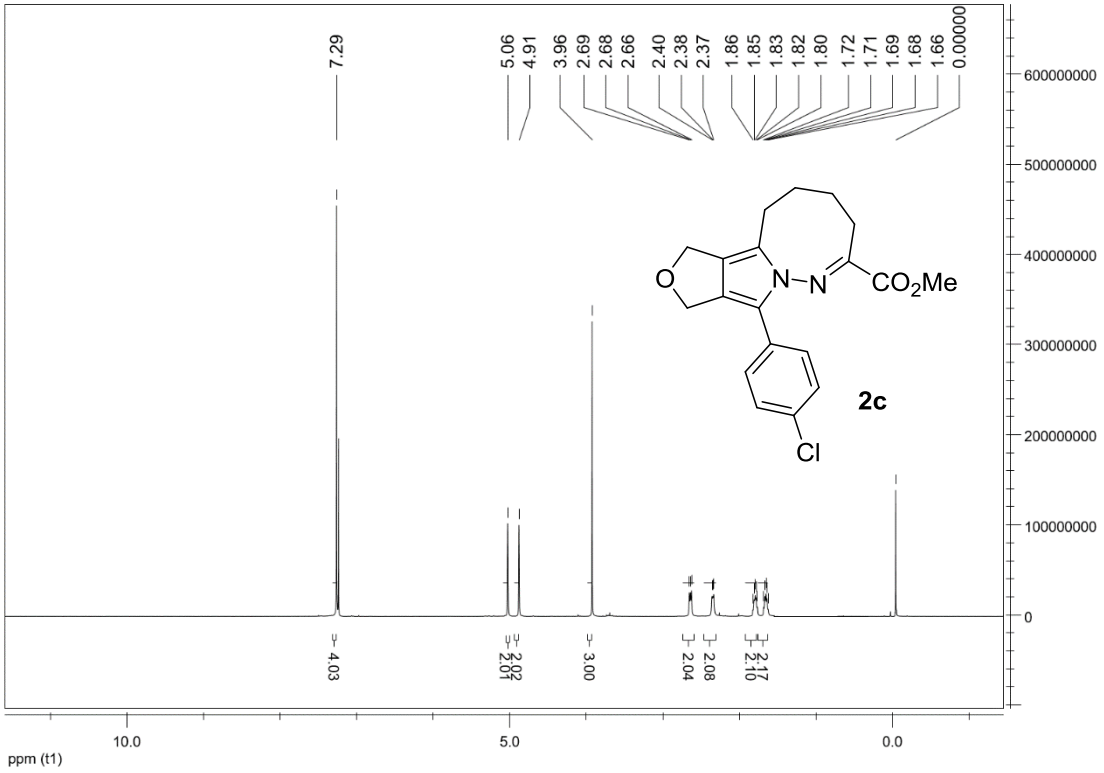
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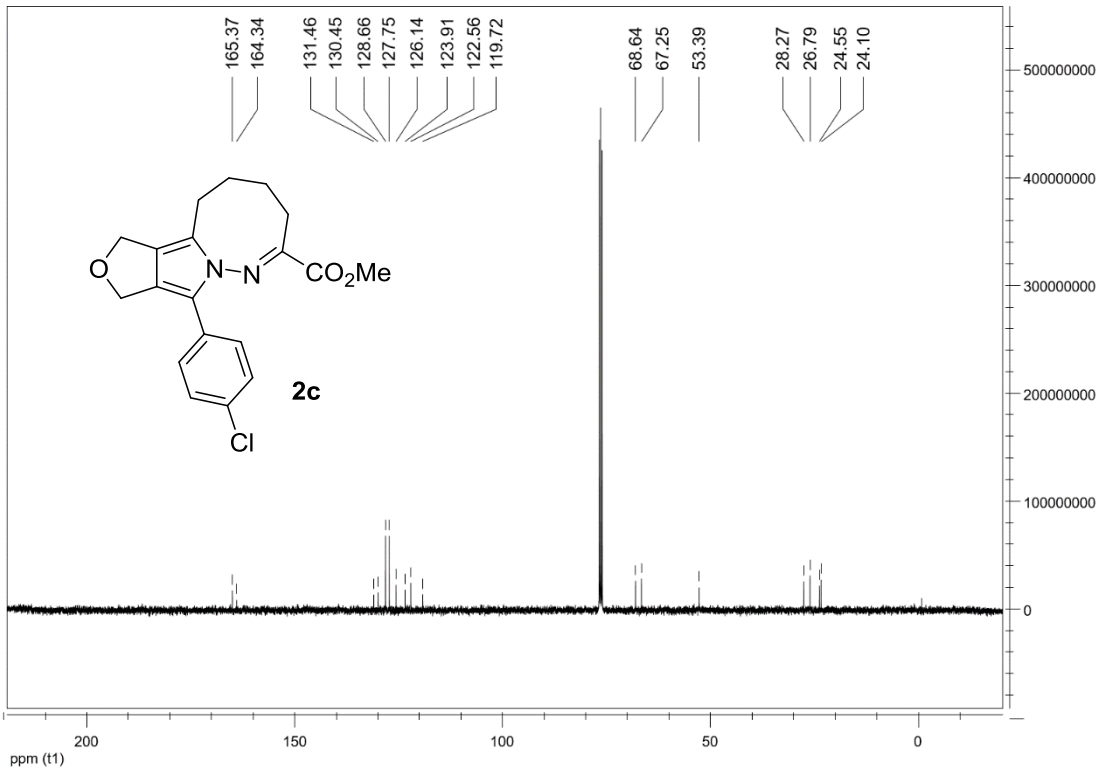
CO2Me
Cl
2c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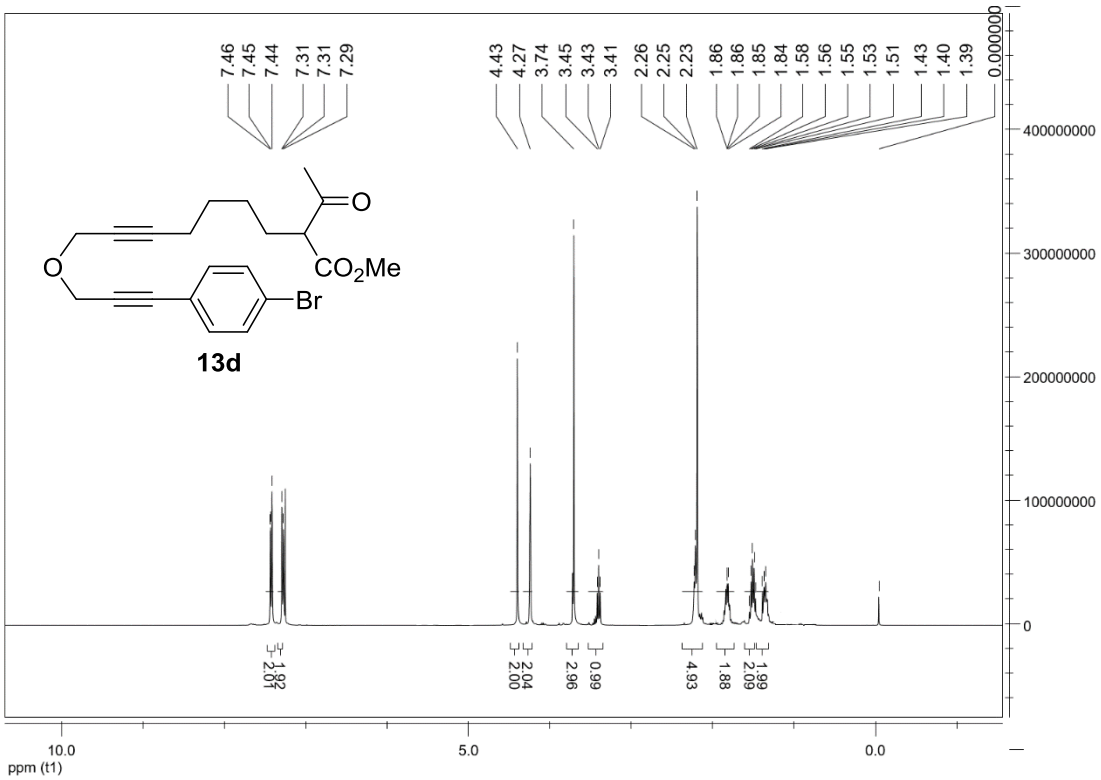
2c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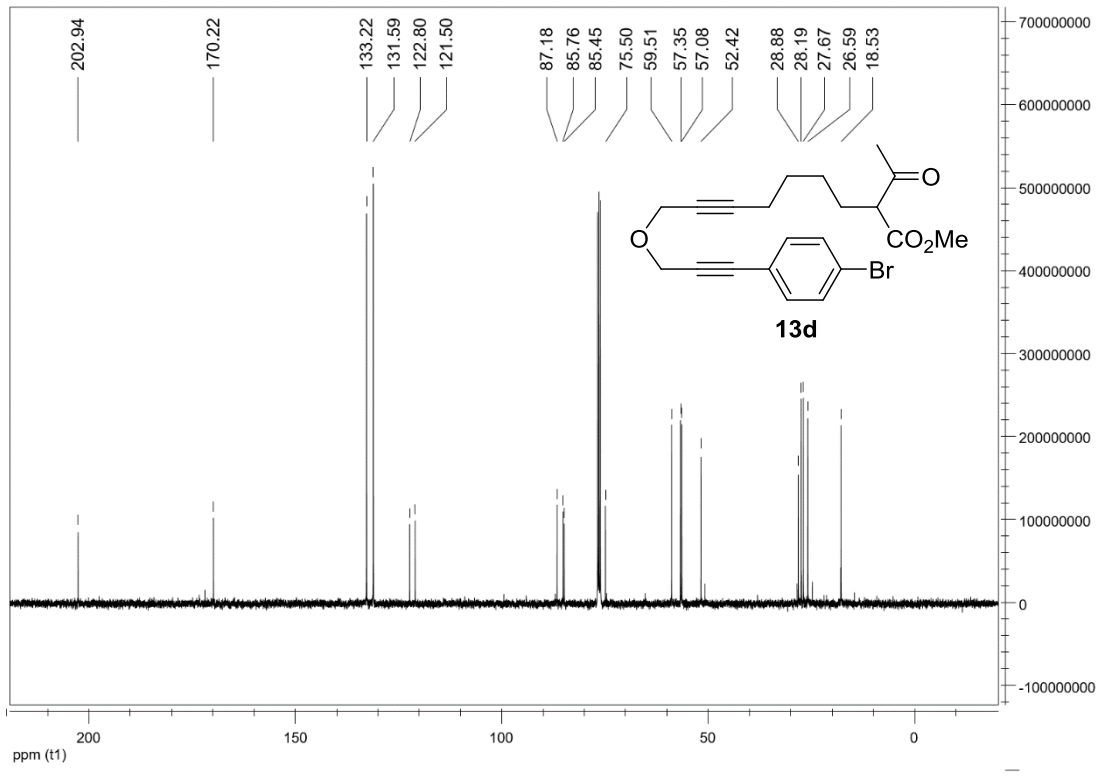
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Br
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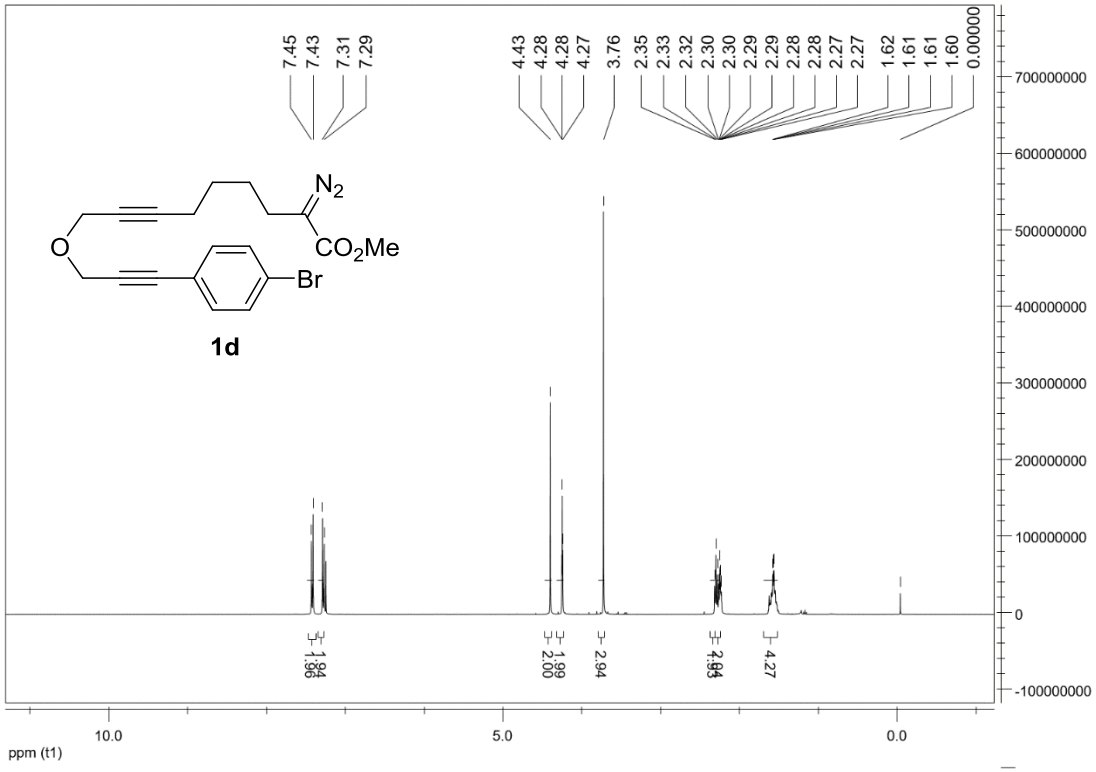
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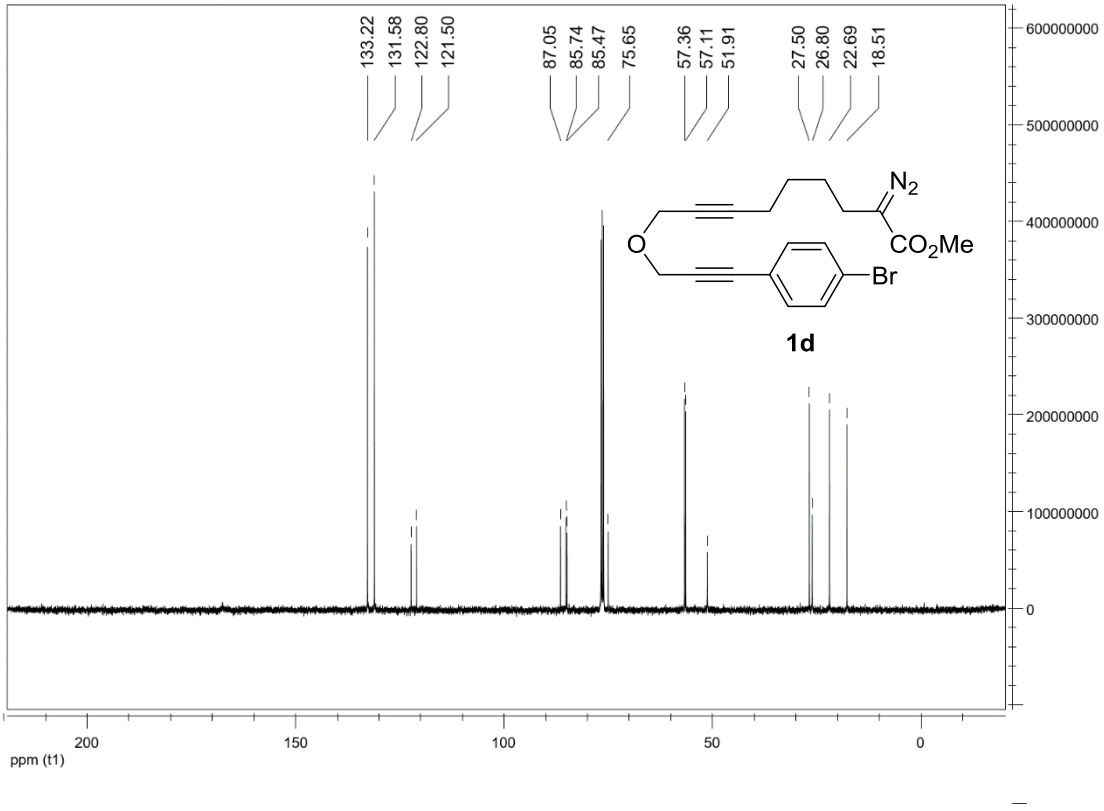
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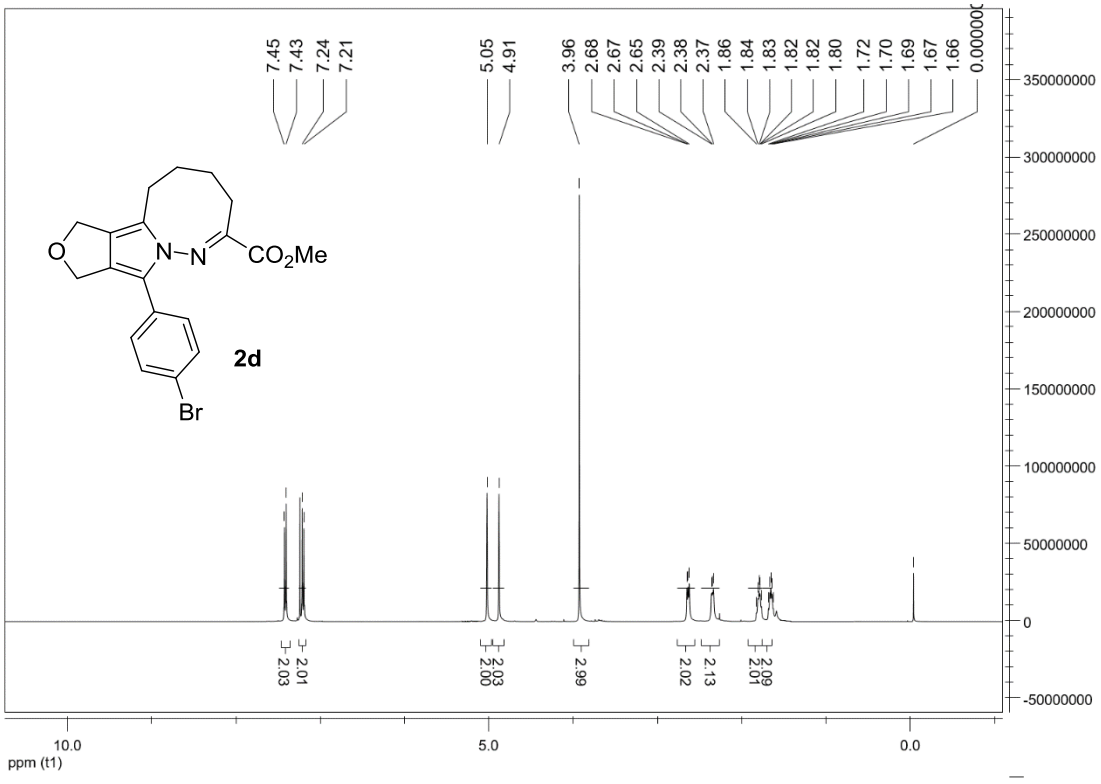
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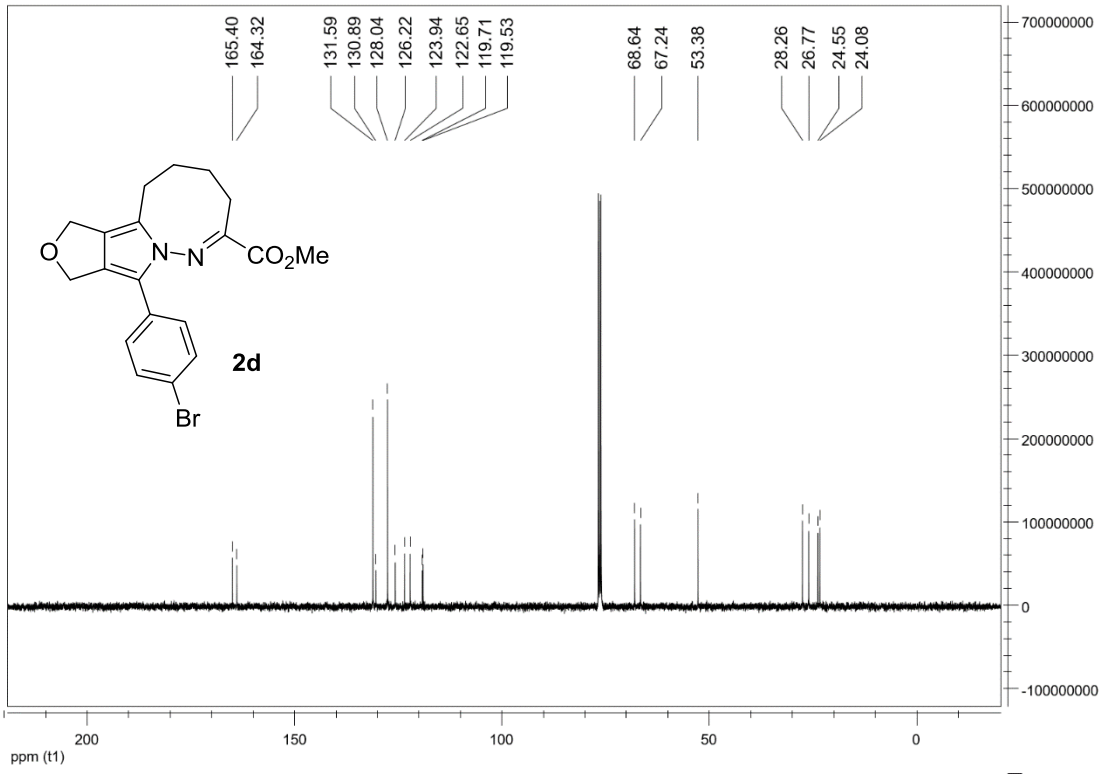
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26.77
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2d
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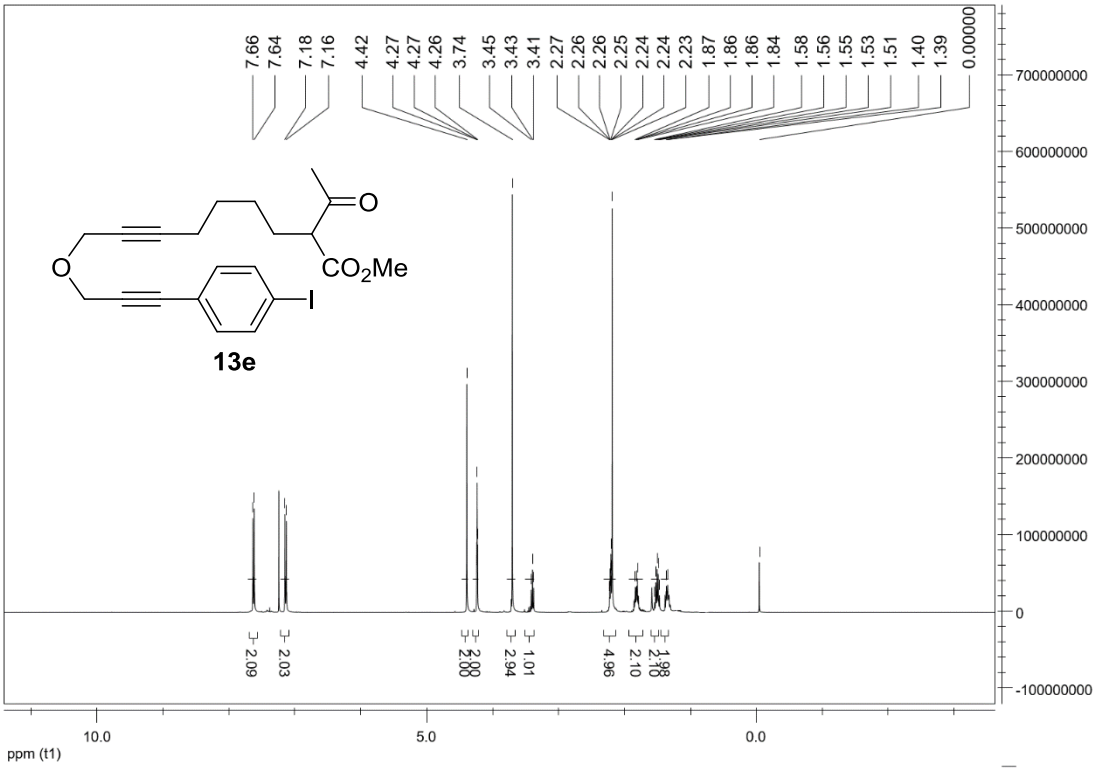
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1.86
1.84
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1.53
1.51
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CO2Me
I
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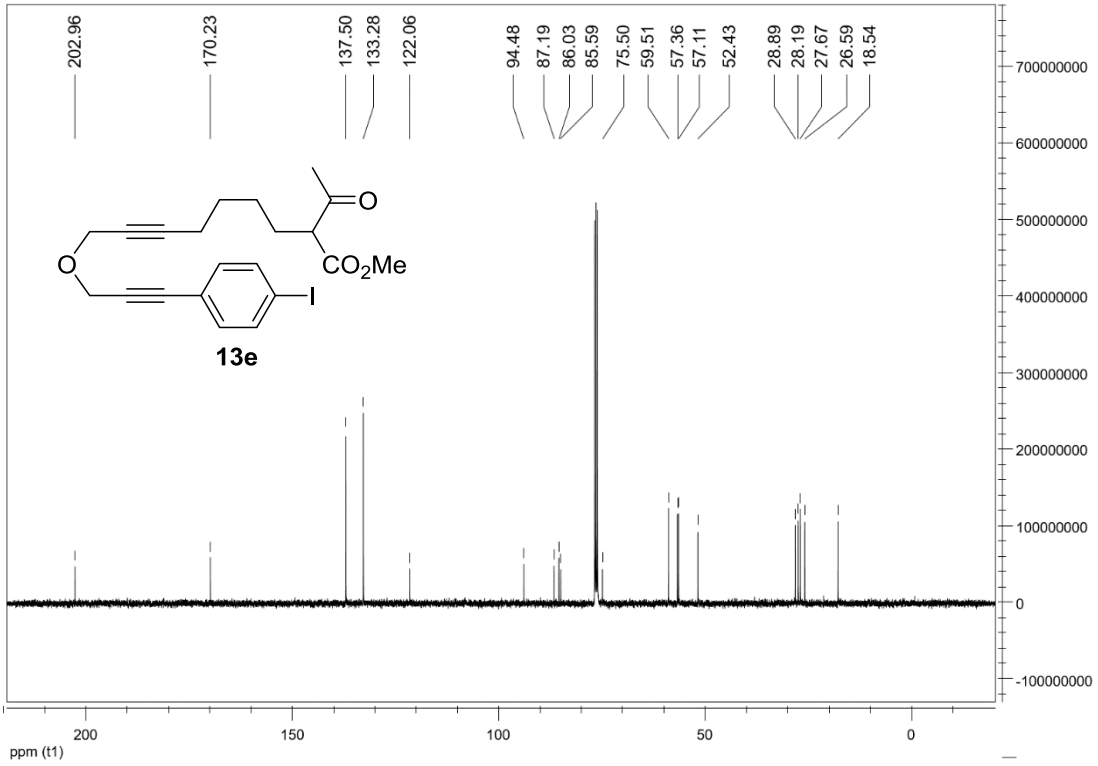
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27.67
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O
CO2Me
I
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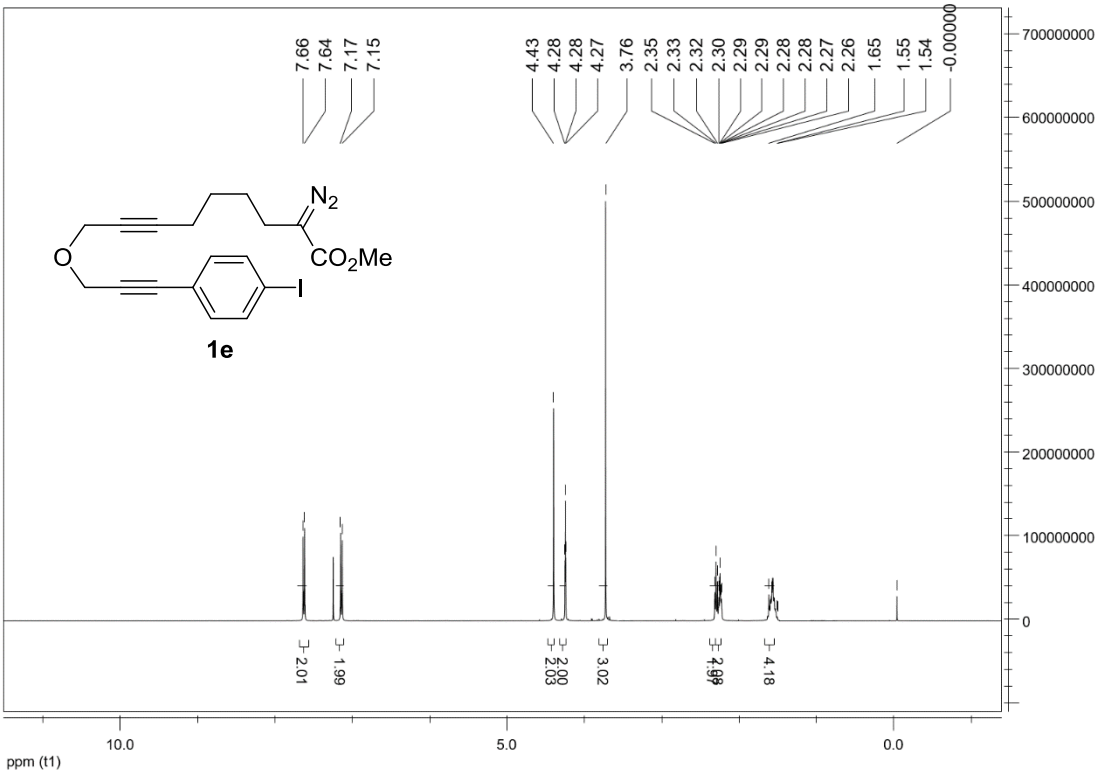
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2.29
2.29
2.28
2.28
2.27
2.26
1.65
1.55
1.54
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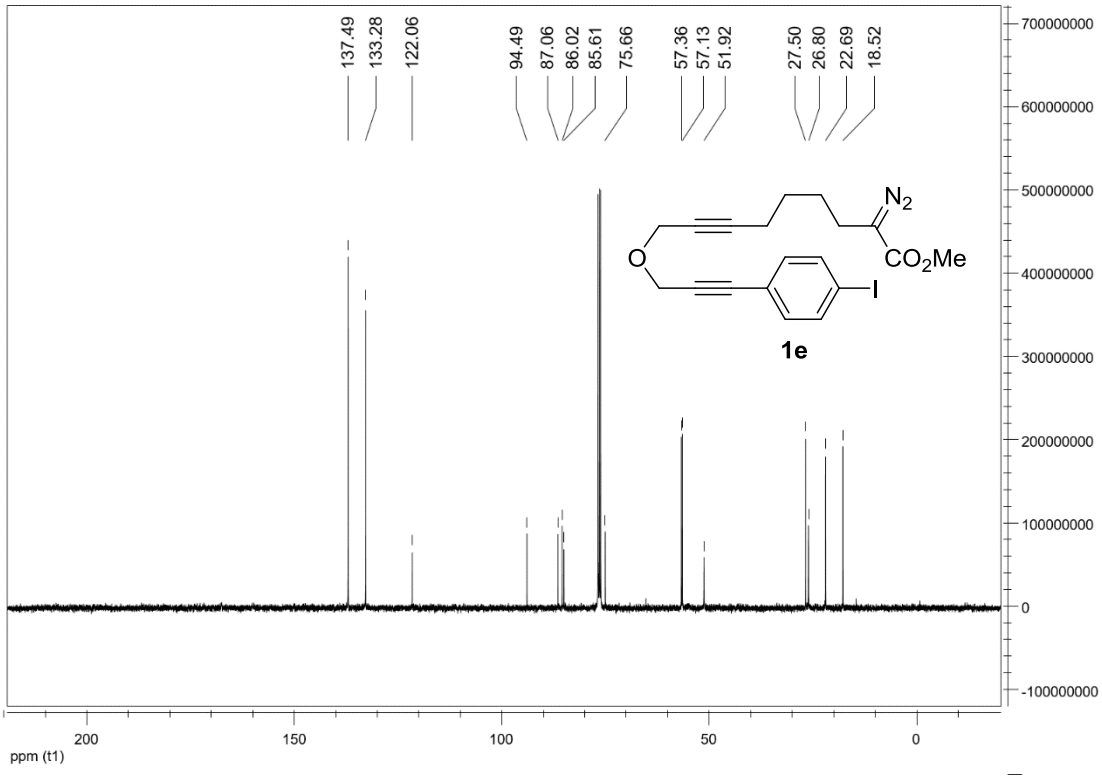
ppm (t1)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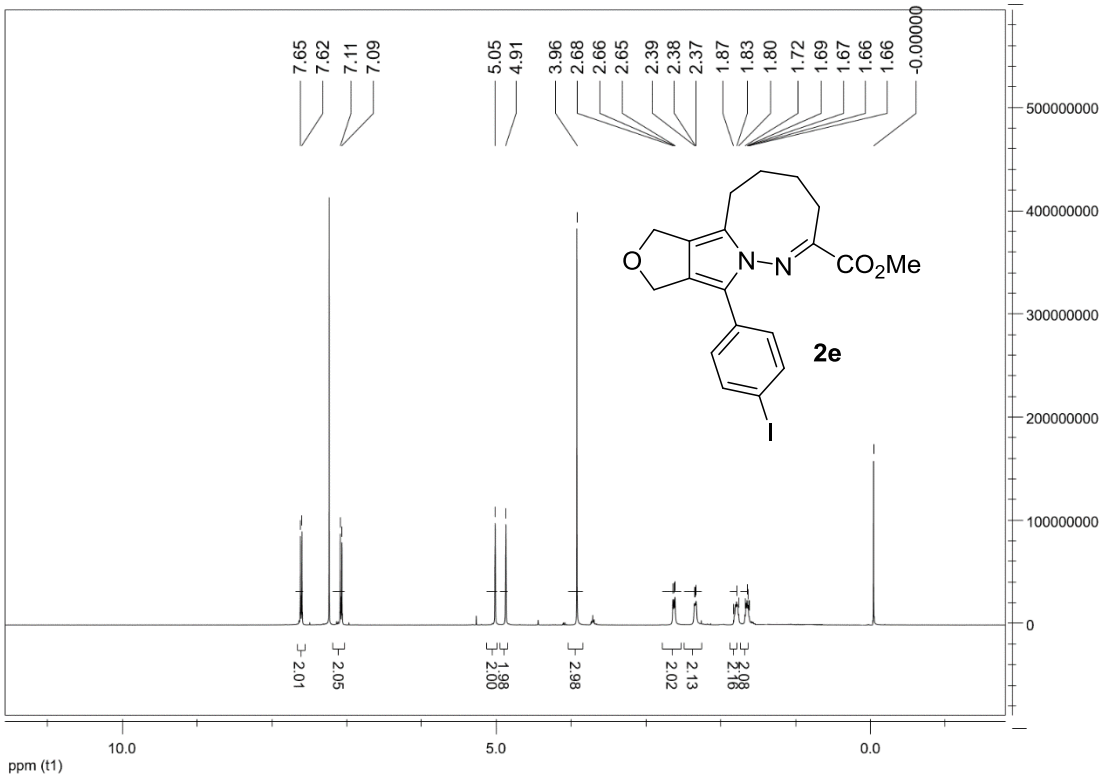
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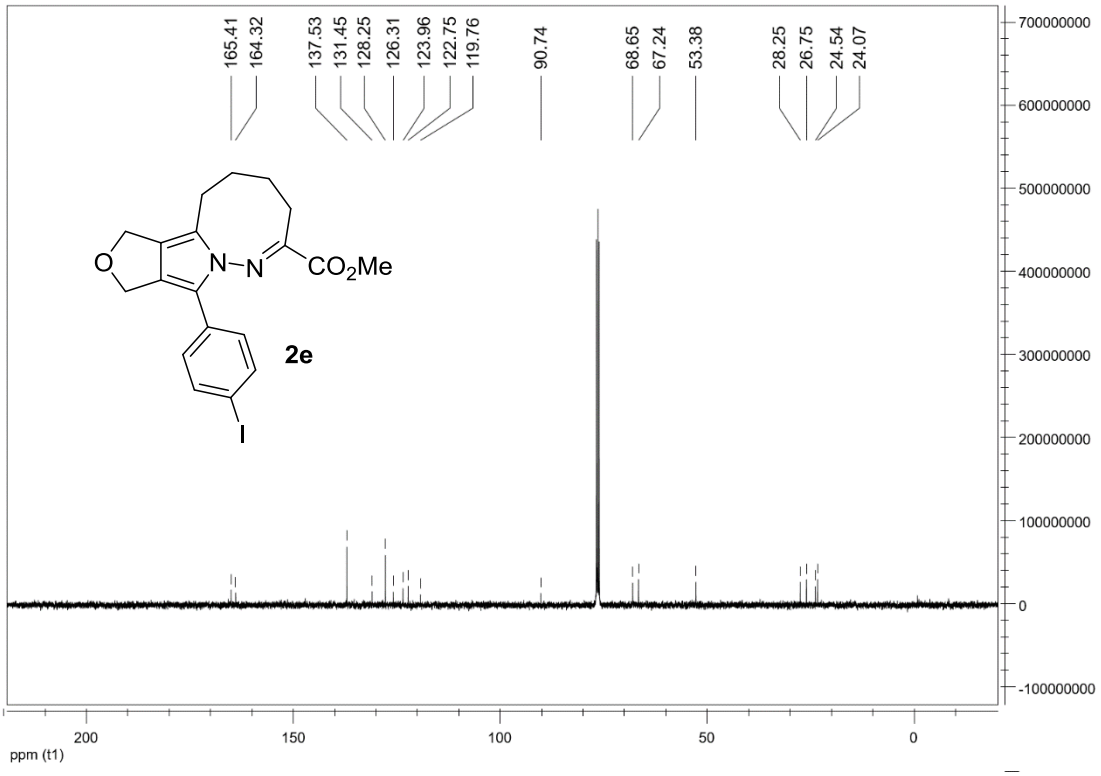
ppm (t1)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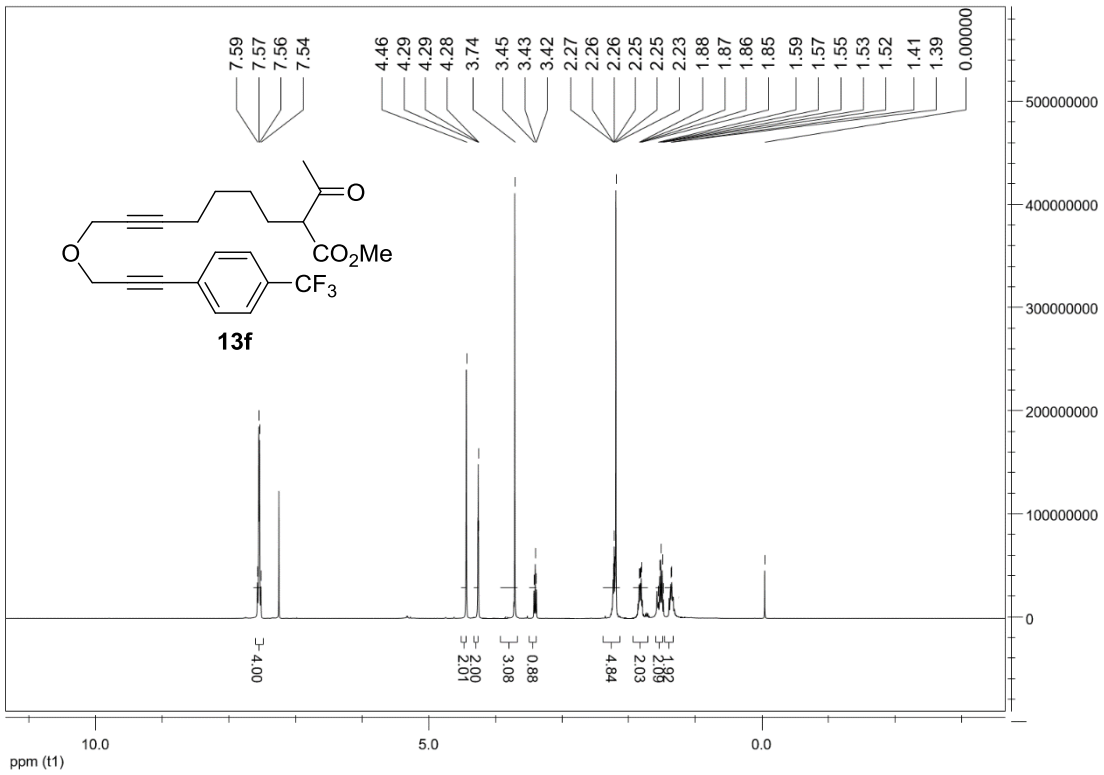
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O
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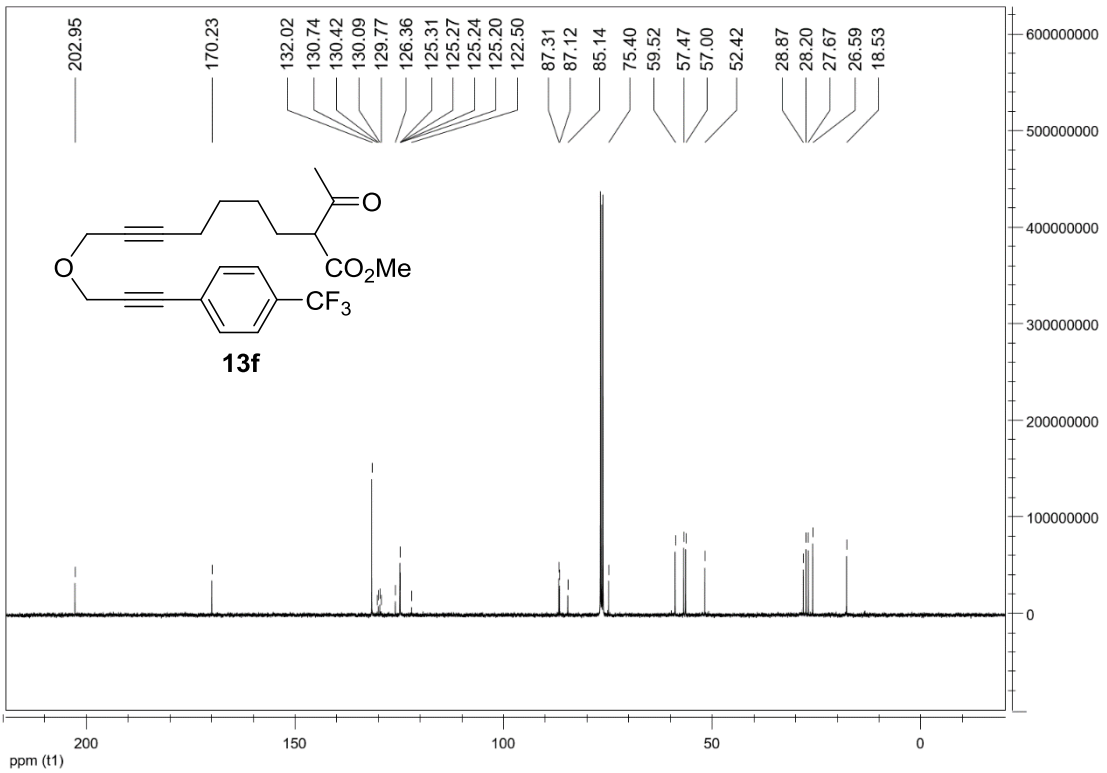
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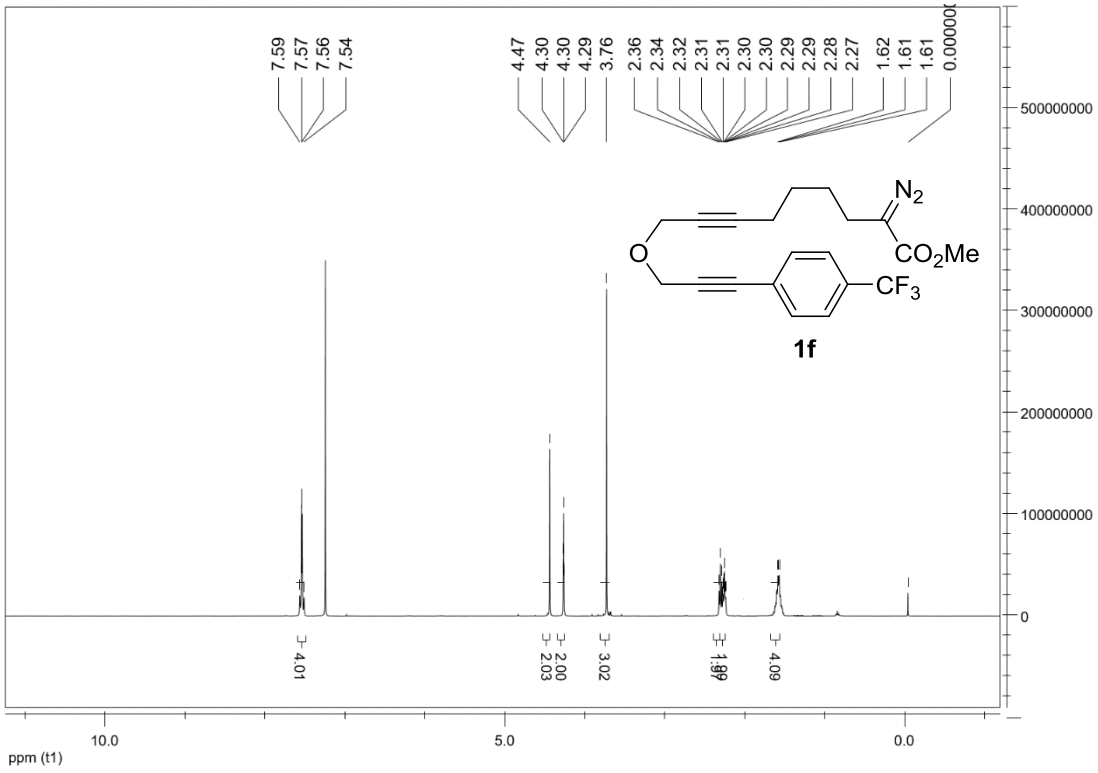
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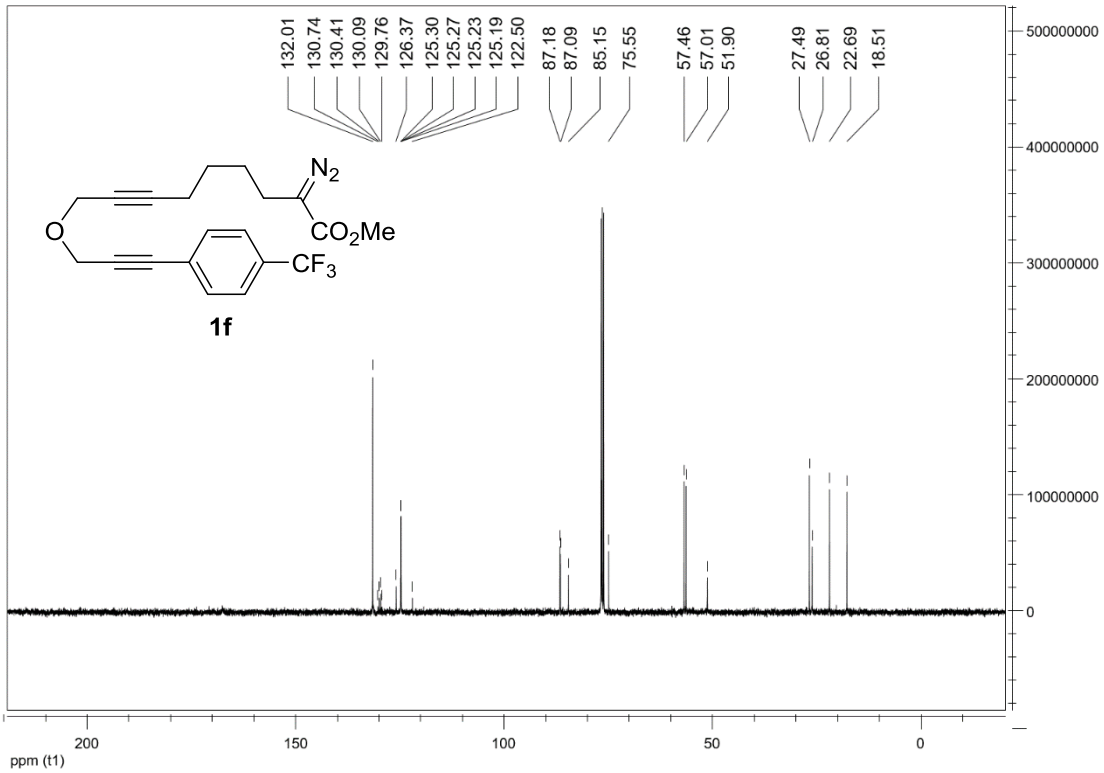
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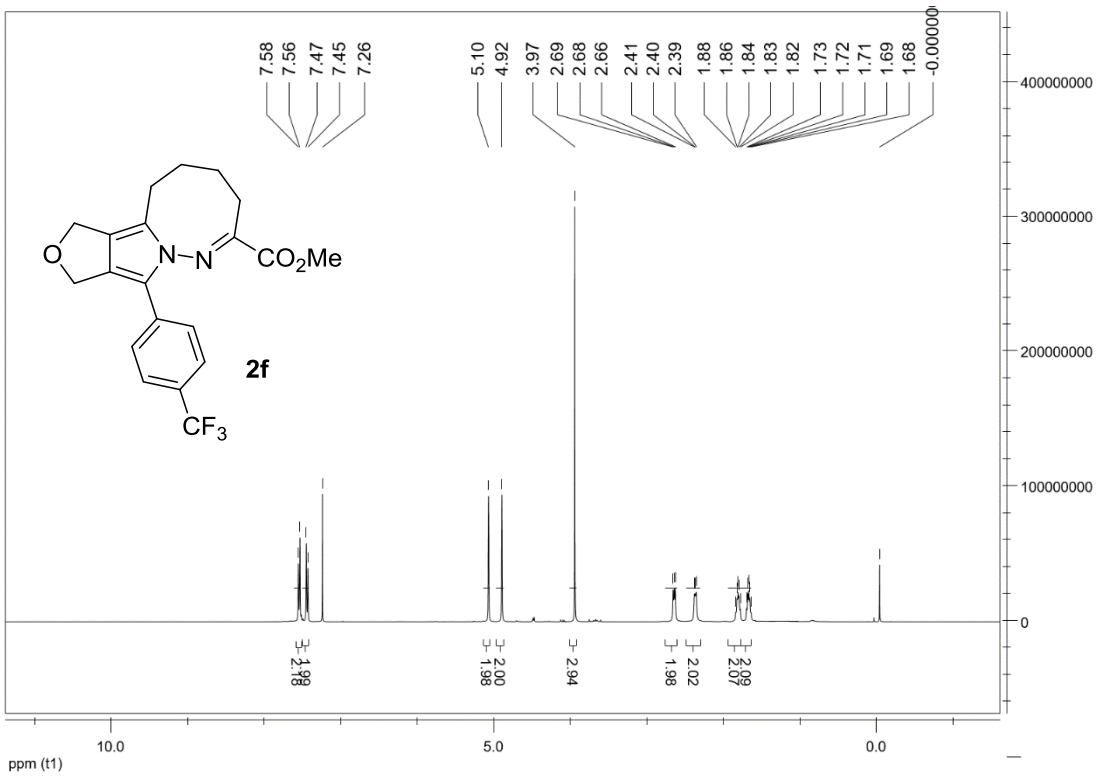
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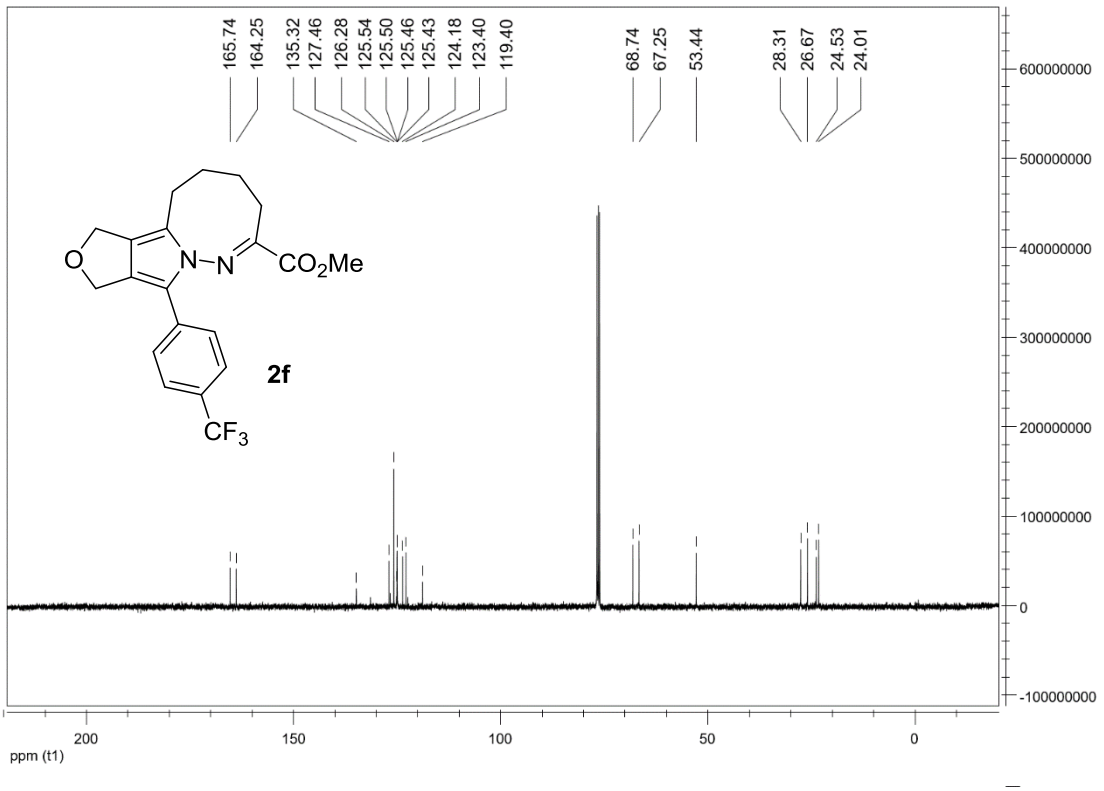
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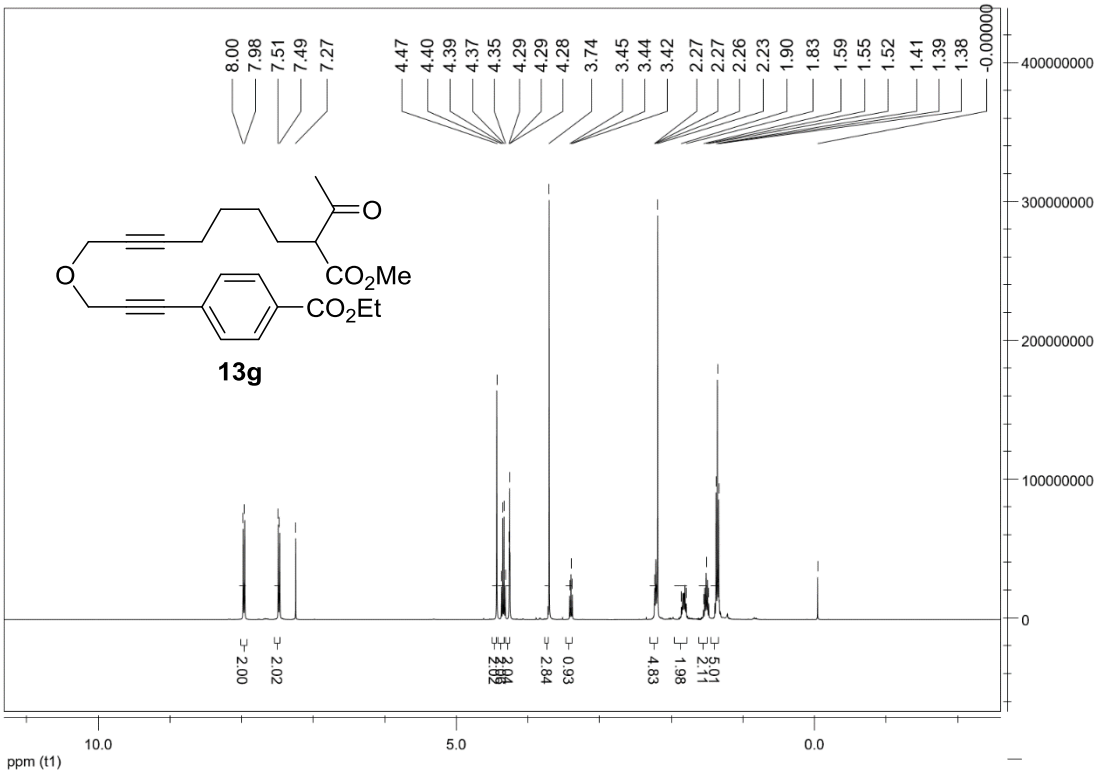
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1.52
1.41
1.39
1.38
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O
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CO2Et
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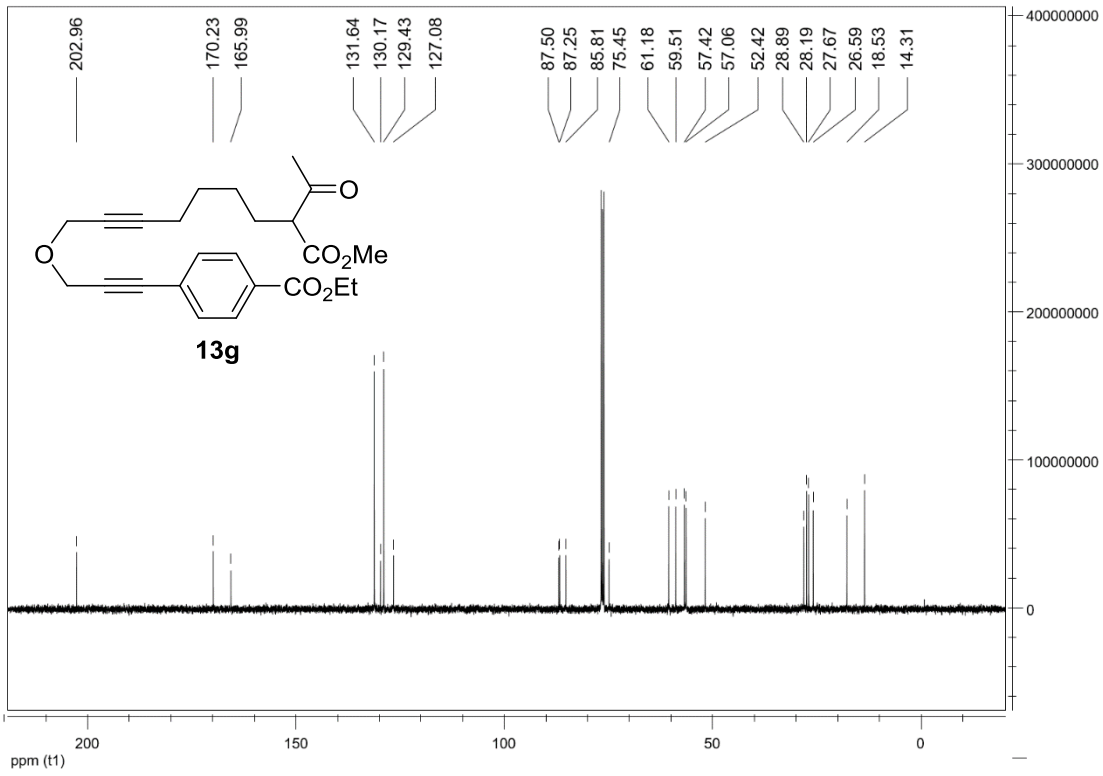
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18.53
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CO2Et
13g
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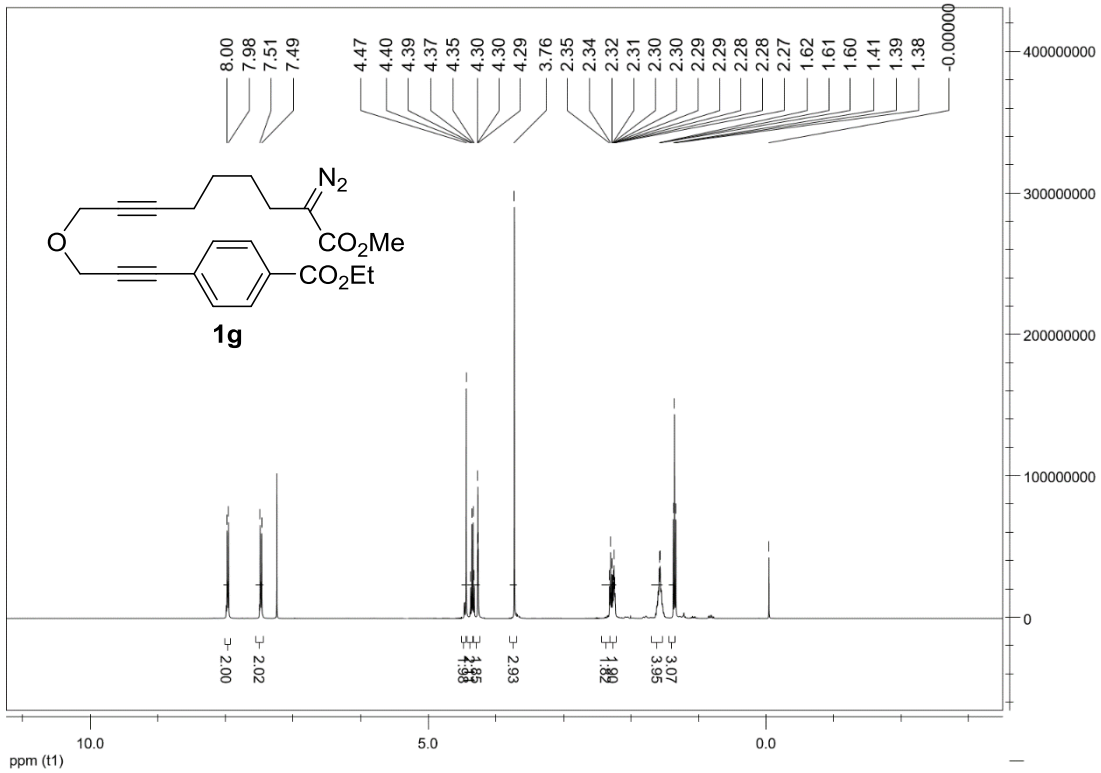
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O
CO2Et
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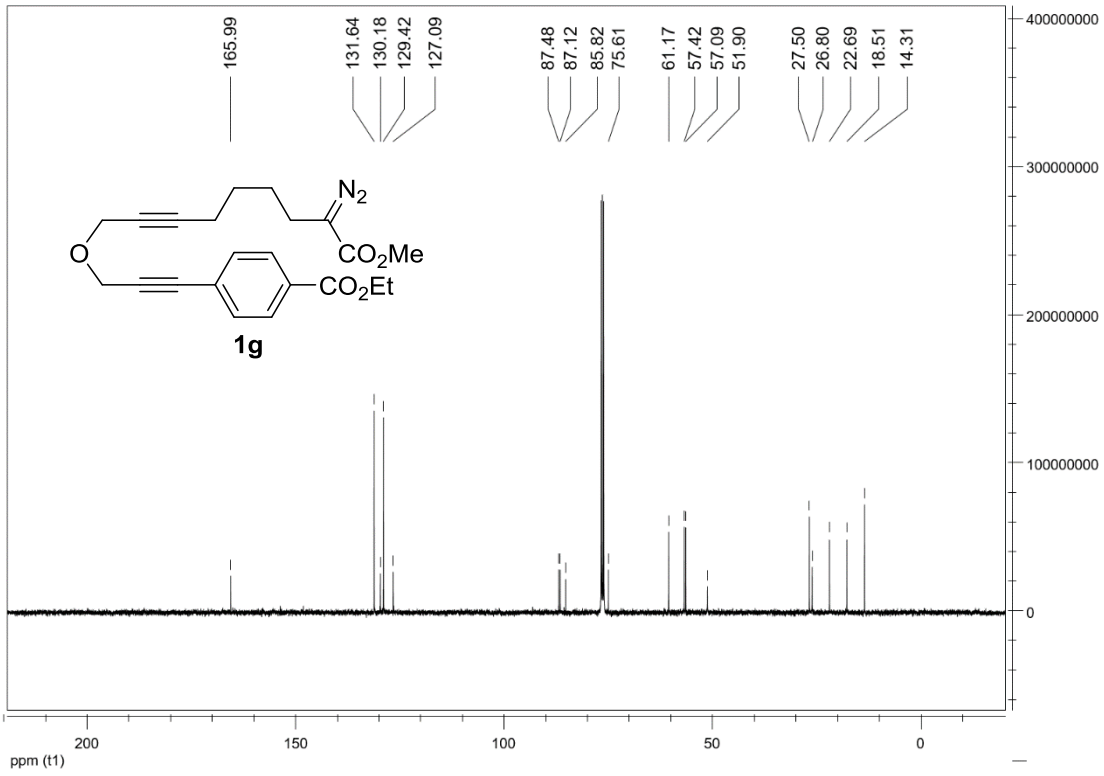
ppm (t1)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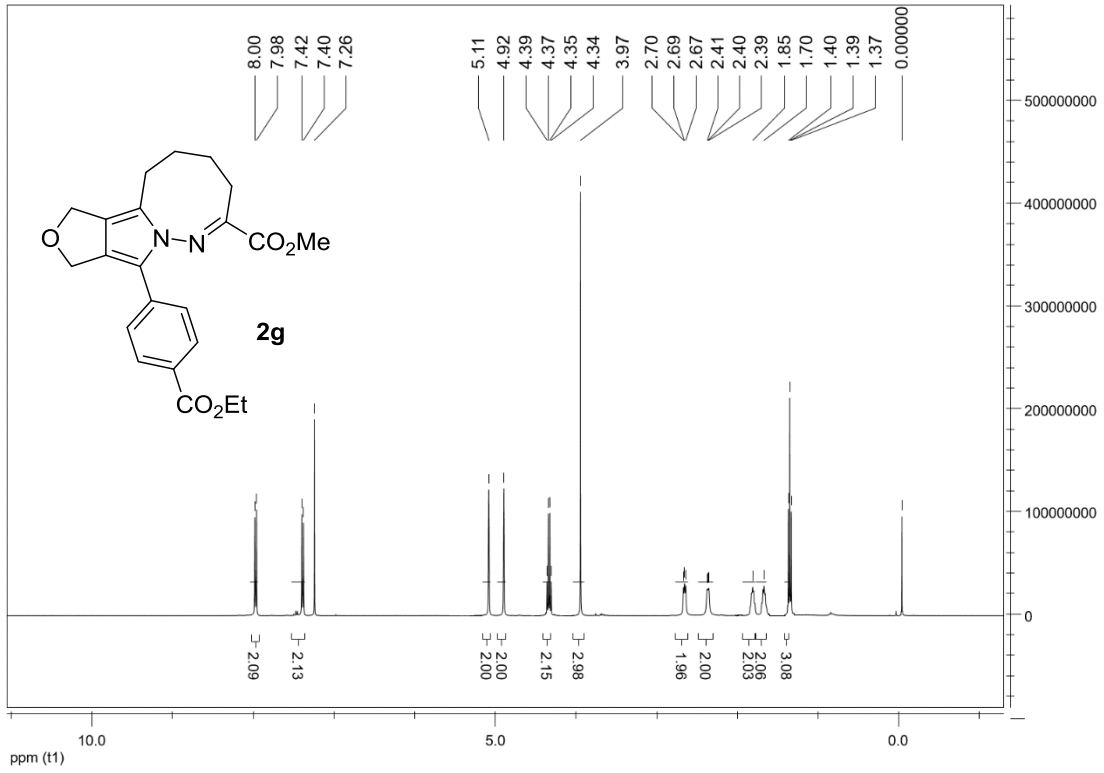
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N
N
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2g
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2.13
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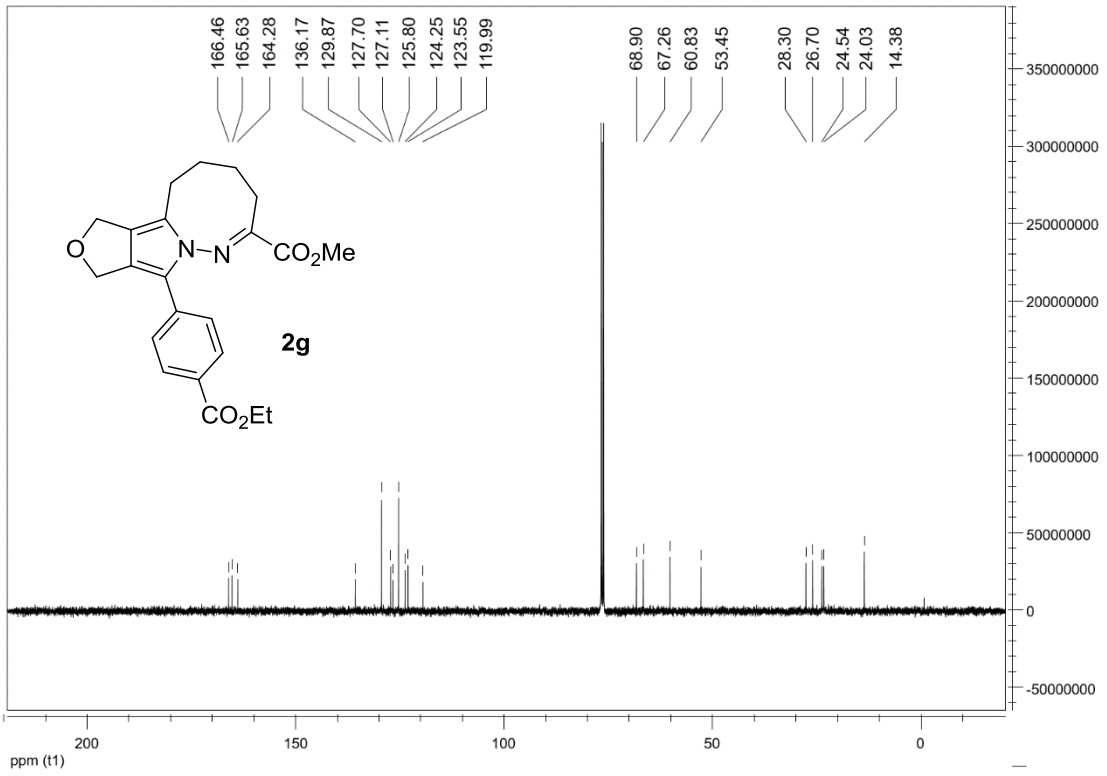
ppm (t1)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24.03
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O
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CO2Me
2g
CO2Et
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50000000
0
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100
50
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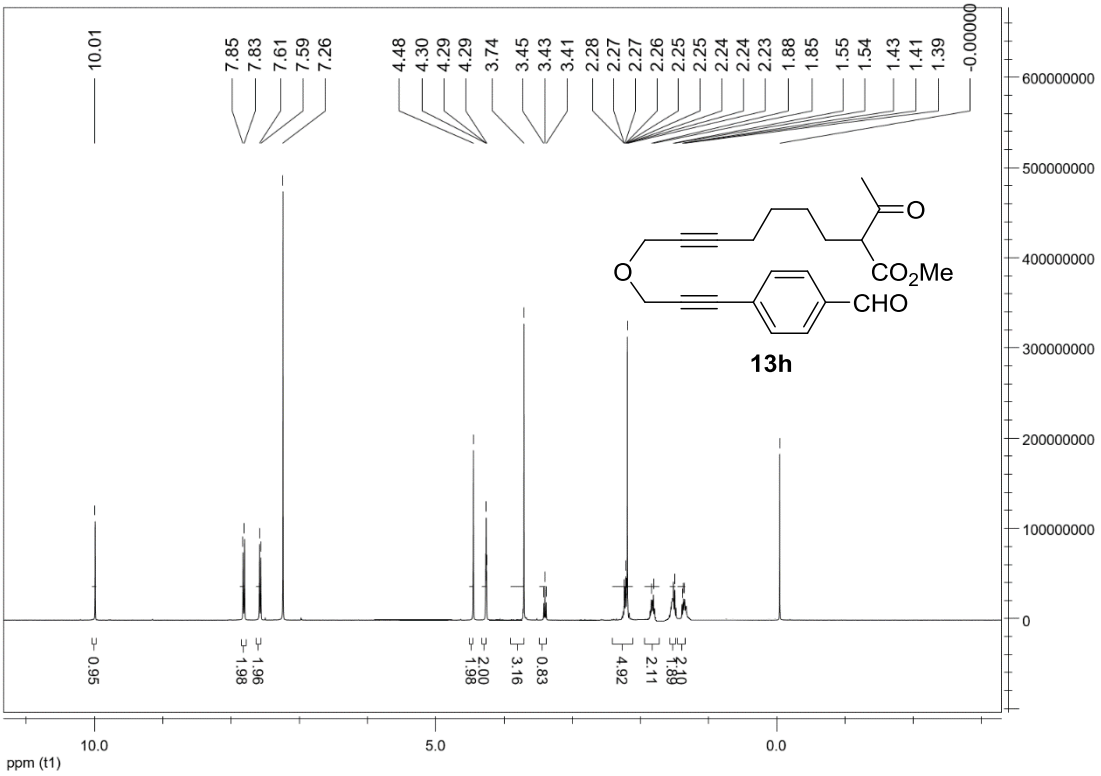
ppm (t1)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3.43
3.41
2.28
2.27
2.27
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2.25
2.25
2.24
2.24
2.23
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1.85
1.55
1.54
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1.41
1.39
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CO2Me
O
CHO
13h
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1.98
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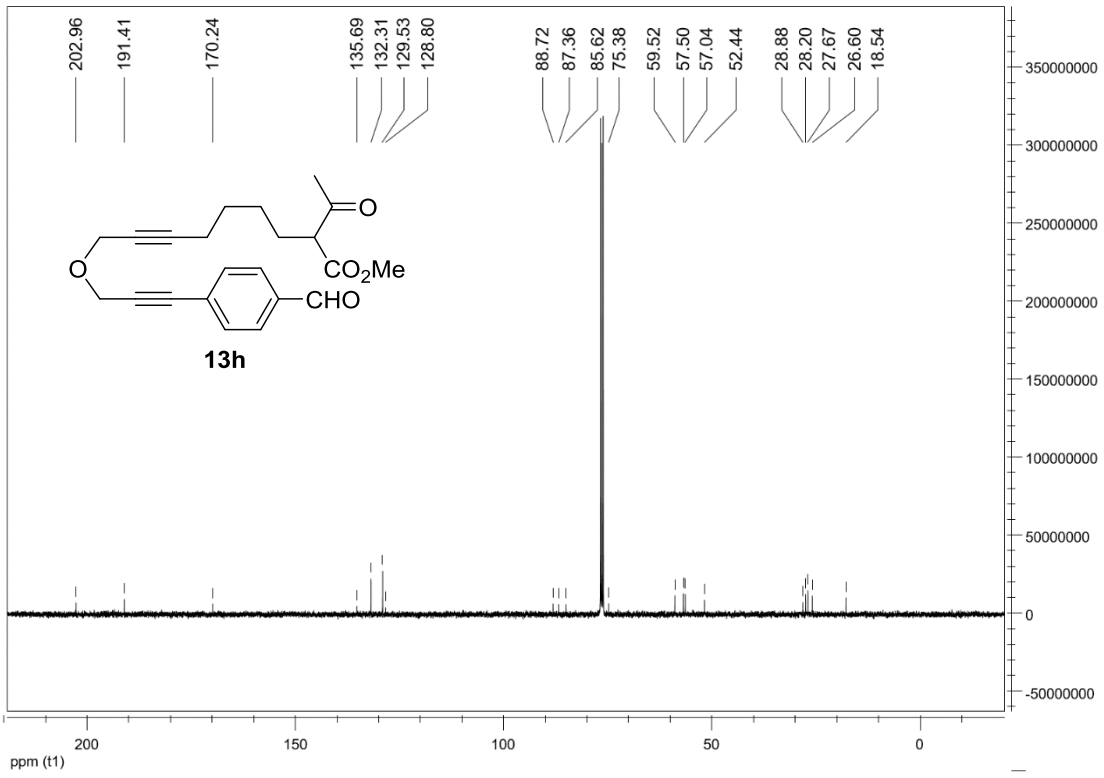
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57.04
52.44
28.88
28.20
27.67
26.60
18.54
O
CO2Me
O
CHO
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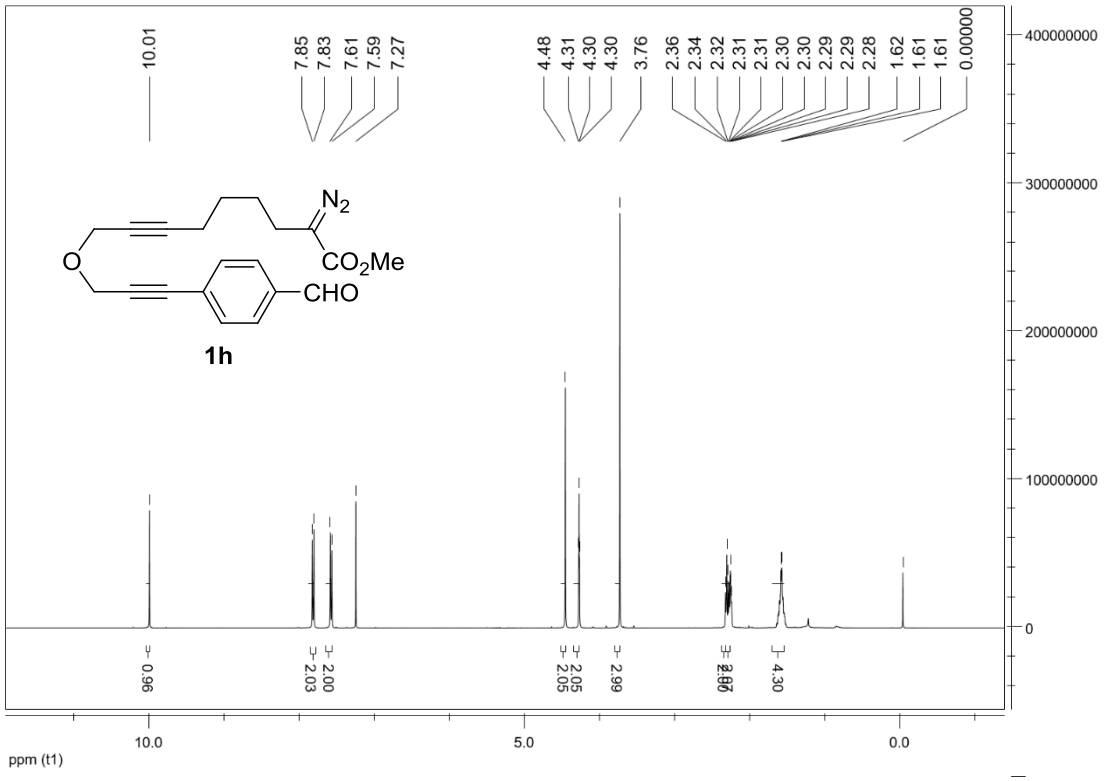
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2.30
2.29
2.29
2.28
1.62
1.61
1.61
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O
CHO
1h
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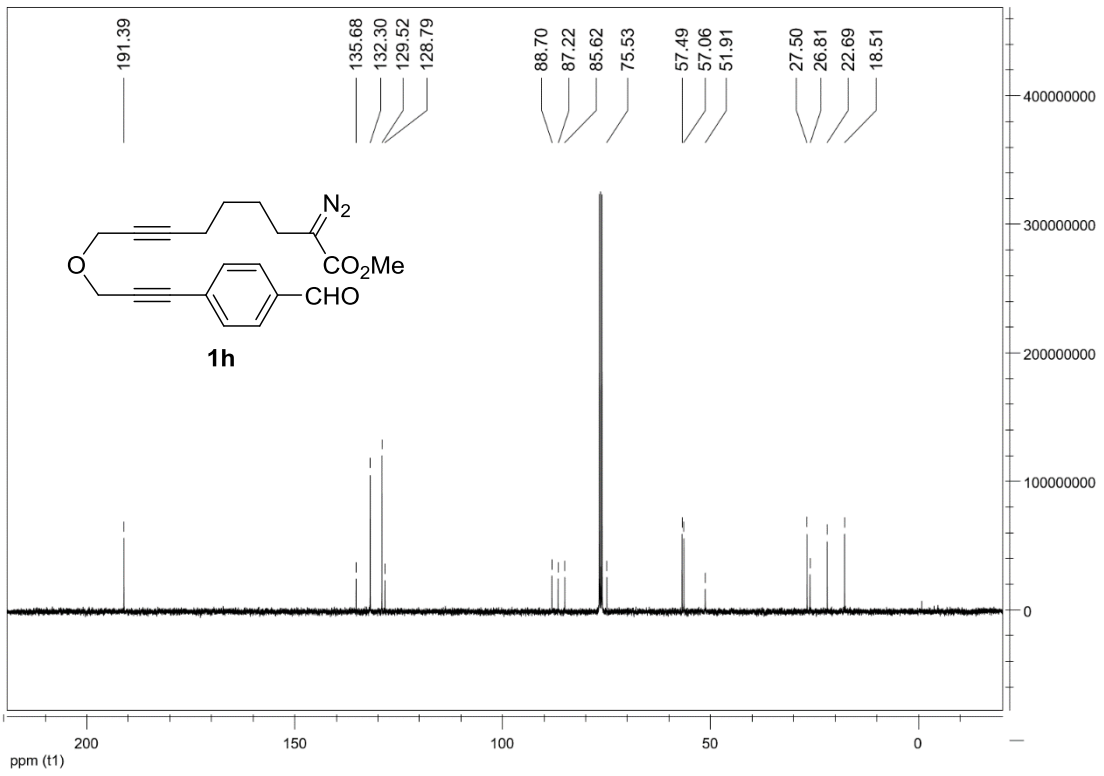
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22.69
18.51
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CHO
1h
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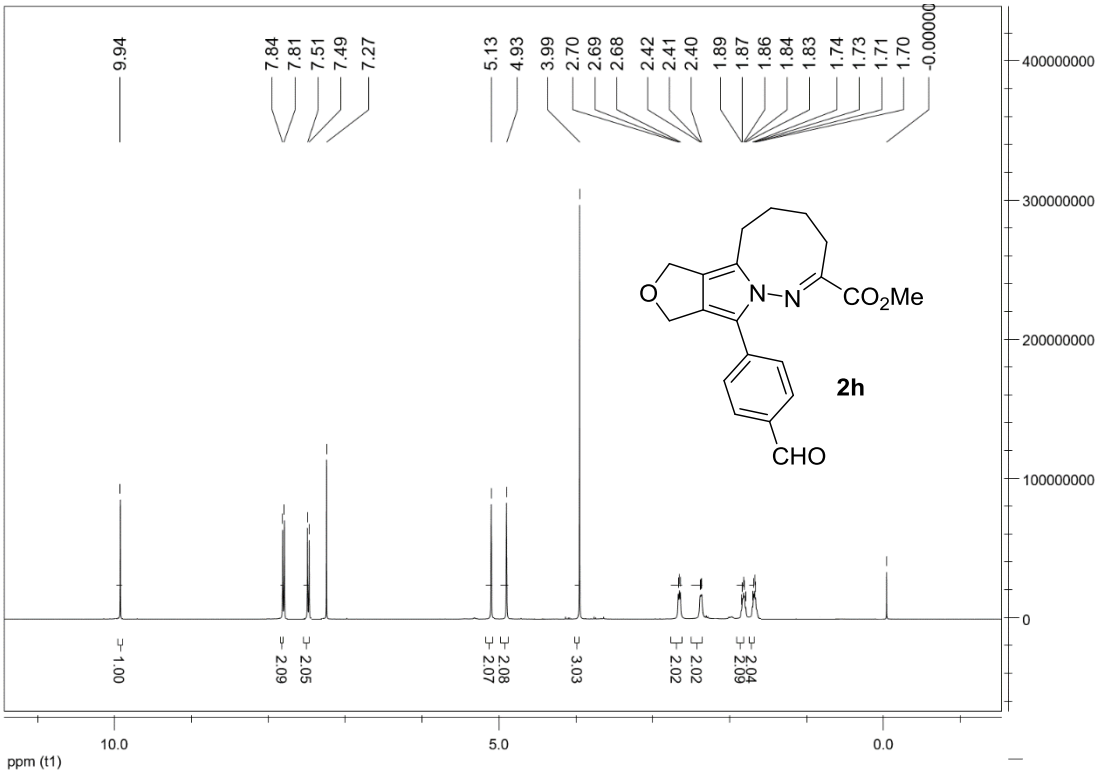
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2.41
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1.89
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1.70
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CO2Me
2h
CHO
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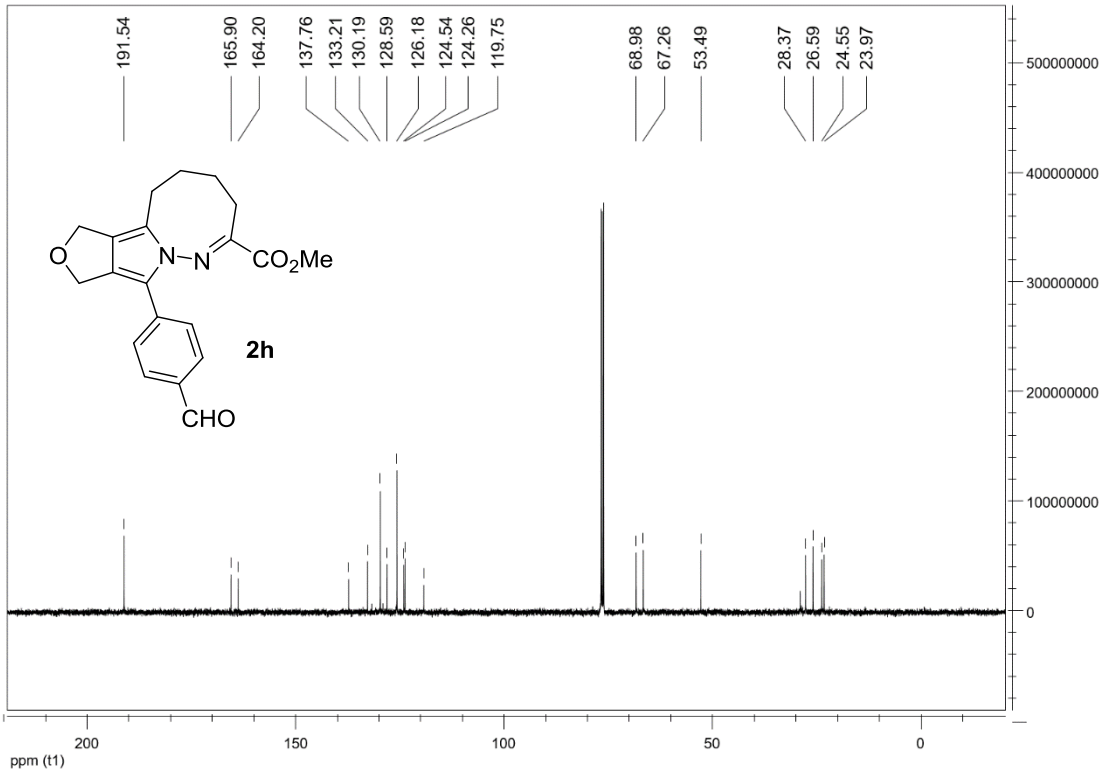
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68.98
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28.37
26.59
24.55
23.97
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CHO
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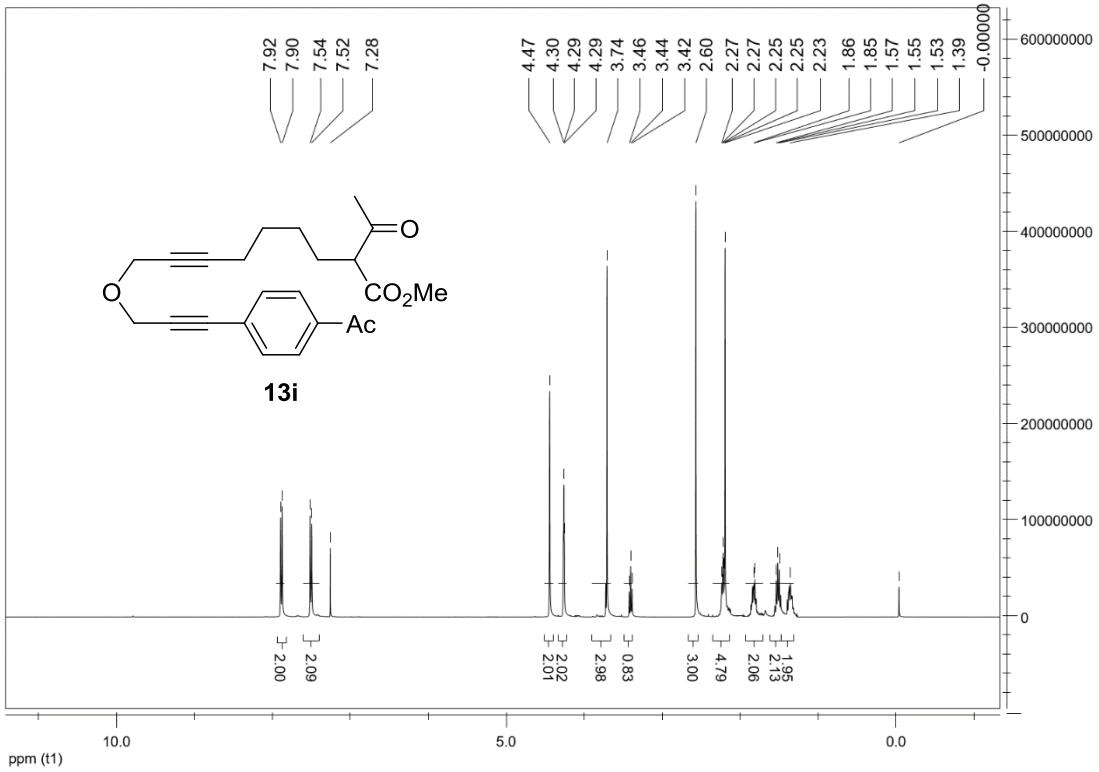
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3.74
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3.44
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2.27
2.27
2.25
2.25
2.23
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1.85
1.57
1.55
1.53
1.39
-0.00000
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O
CO2Me
Ac
13i
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2.09
2.02
2.01
2.98
0.83
3.00
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2.06
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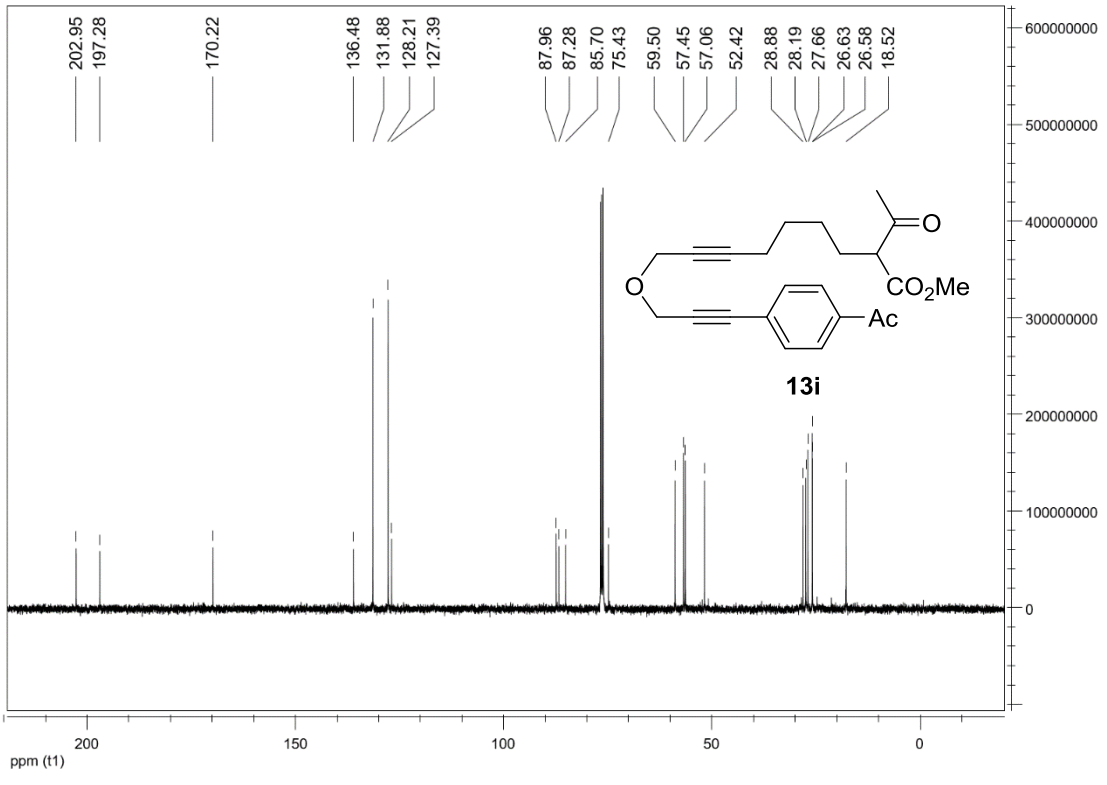
ppm (t1)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87.28
85.70
75.43
59.50
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57.06
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27.66
26.63
26.58
18.52
O
O
CO2Me
Ac
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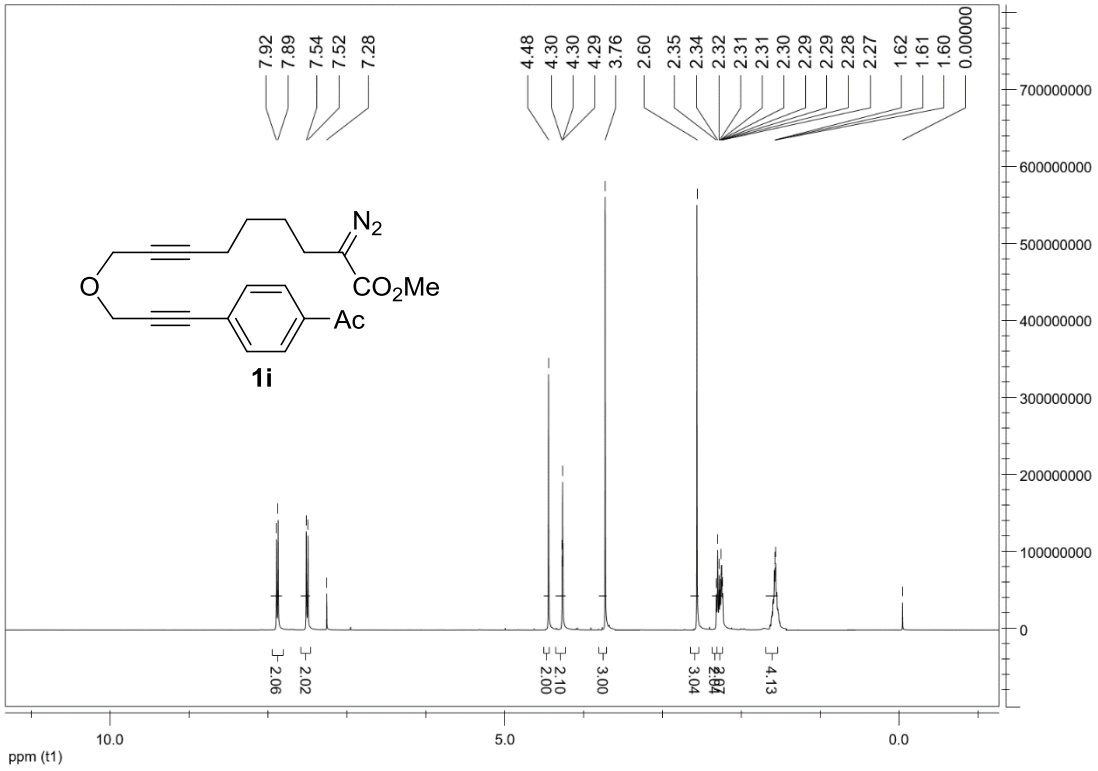
150
100
50
0
ppm (t1)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2.31
2.31
2.30
2.29
2.29
2.28
2.27
1.62
1.61
1.60
0.00000
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CO2Me
O
Ac
1i
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2.10
2.00
3.00
3.04
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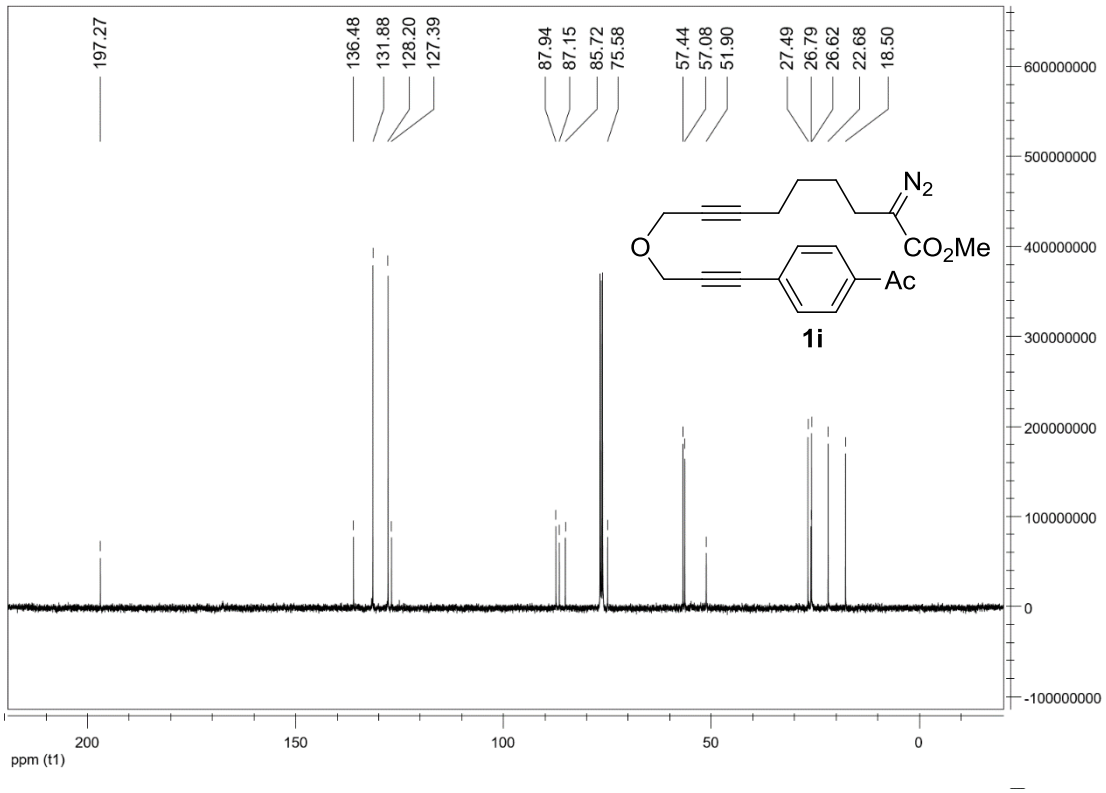
0.0
ppm (t1)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87.94
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75.58
57.44
57.08
51.90
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Ac
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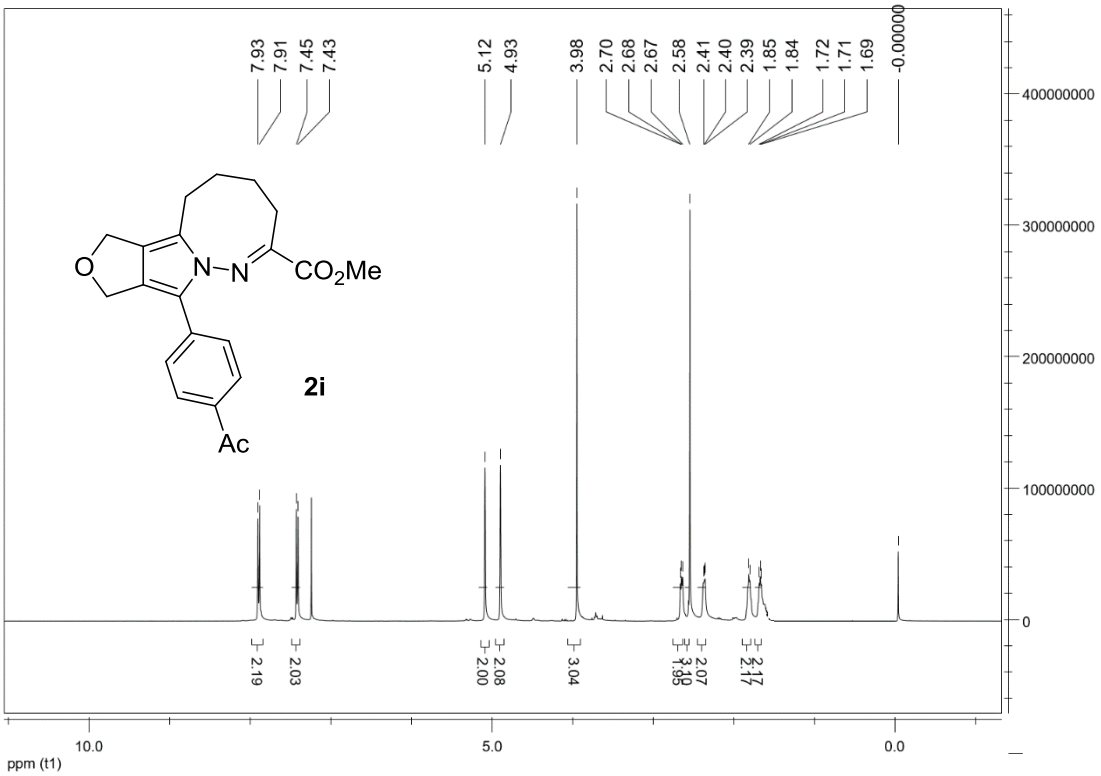
ppm (t1)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2.39
1.85
1.84
1.72
1.71
1.69
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3.04
3.00
3.05
2.07
2.17
2.17
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5.0
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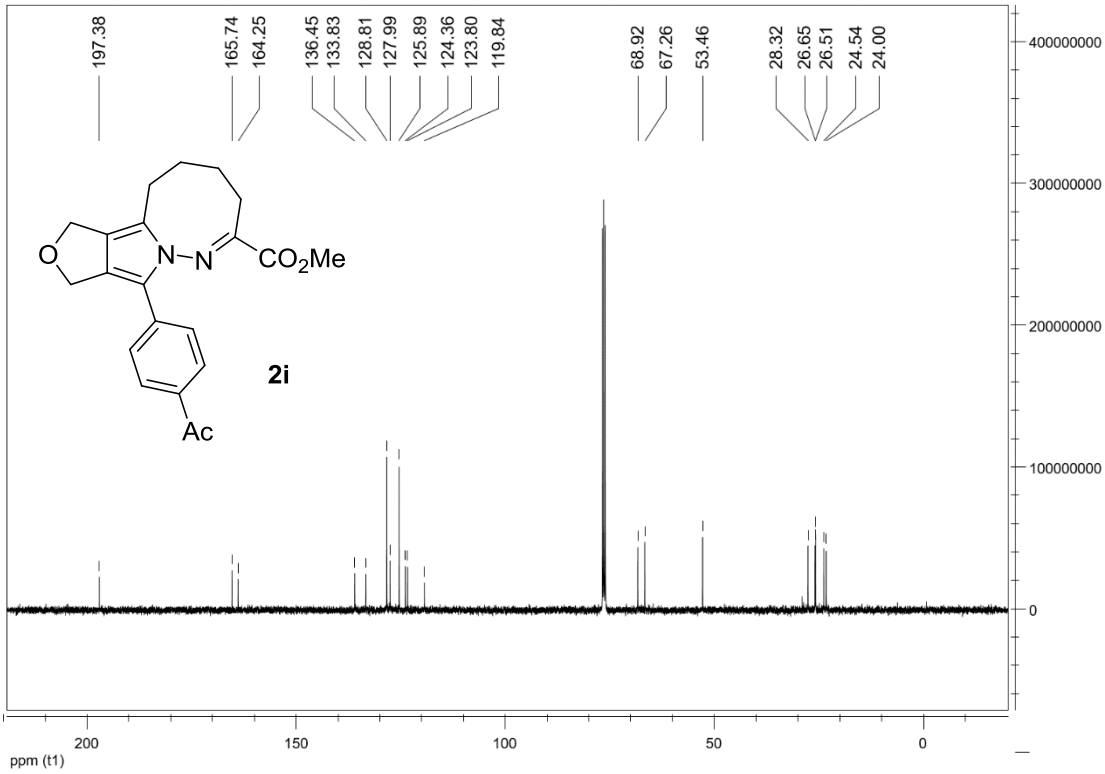
N
N
CO2Me
Ac
2i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26.65
26.51
24.54
24.00
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100
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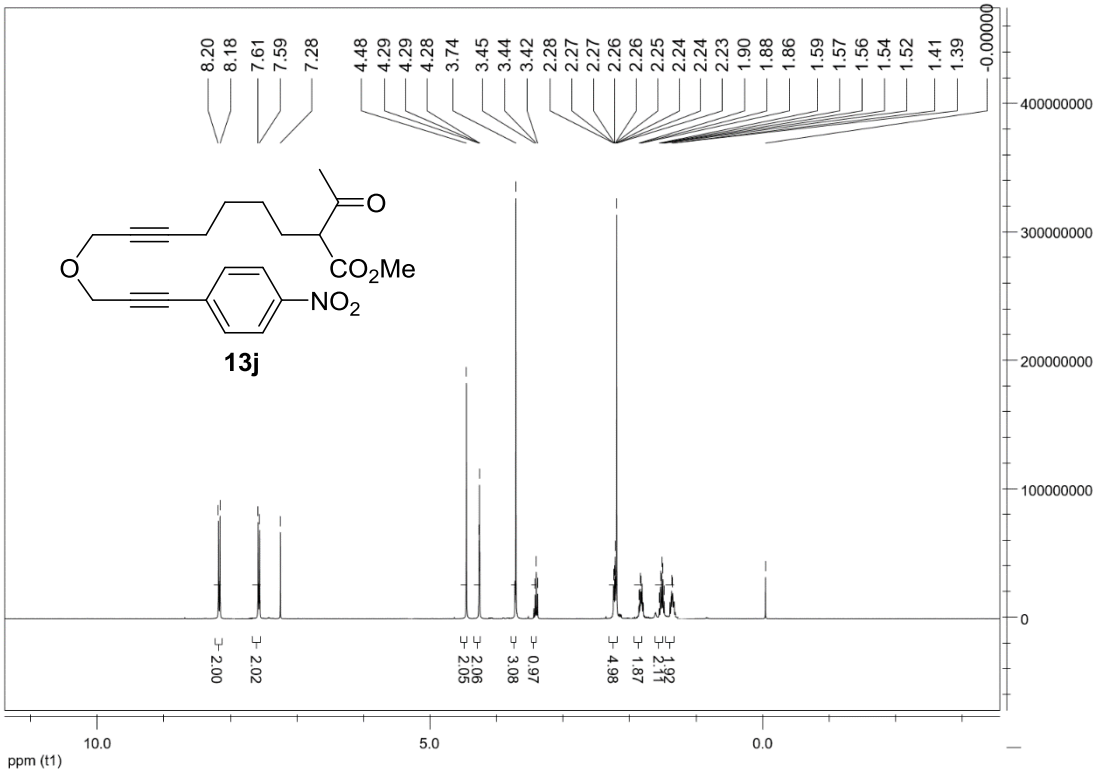
N
N
CO2Me
Ac
2i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3.45
3.44
3.42
2.28
2.27
2.27
2.26
2.26
2.25
2.24
2.24
2.23
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1.86
1.59
1.57
1.56
1.54
1.52
1.41
1.39
-0.00000
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O
CO2Me
NO2
13j
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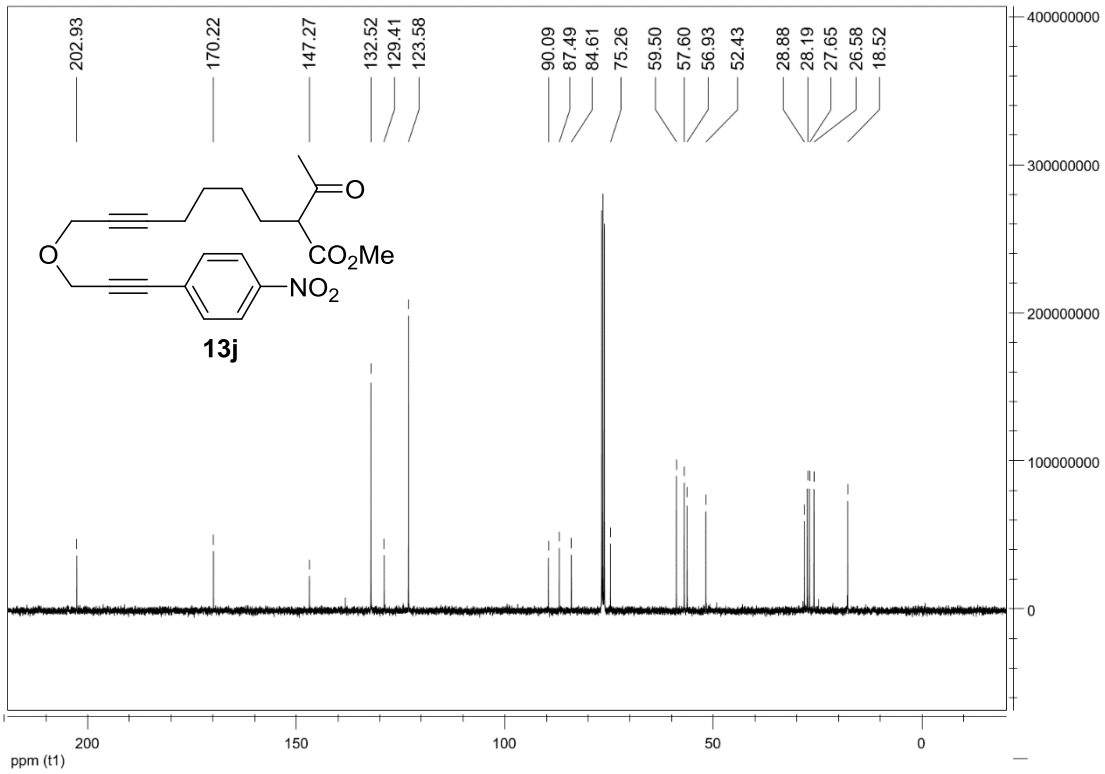
ppm (t1)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52.43
28.88
28.19
27.65
26.58
18.52
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NO2
13j
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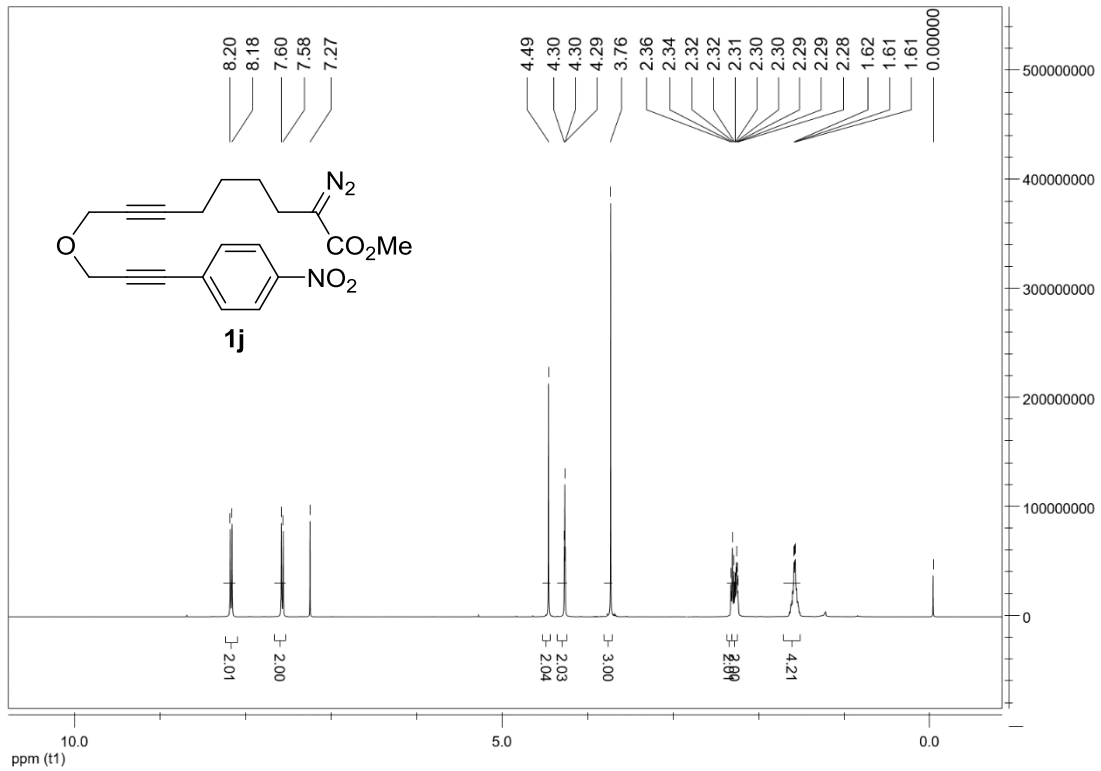
150
100
50
0
ppm (t1)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4.29
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2.32
2.31
2.30
2.30
2.29
2.29
2.28
1.62
1.61
1.61
0.00000
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CO2Me
O
NO2
1j
2.01
2.00
2.04
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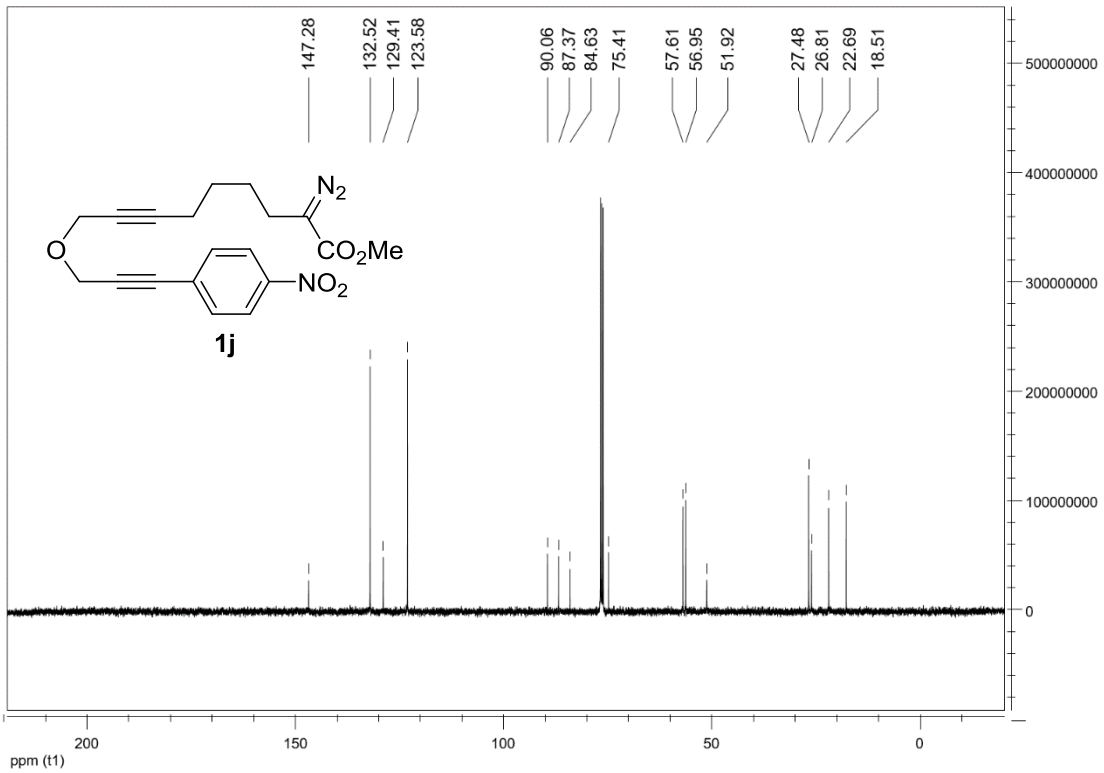
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27.48
26.81
22.69
18.51
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O
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1j
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50
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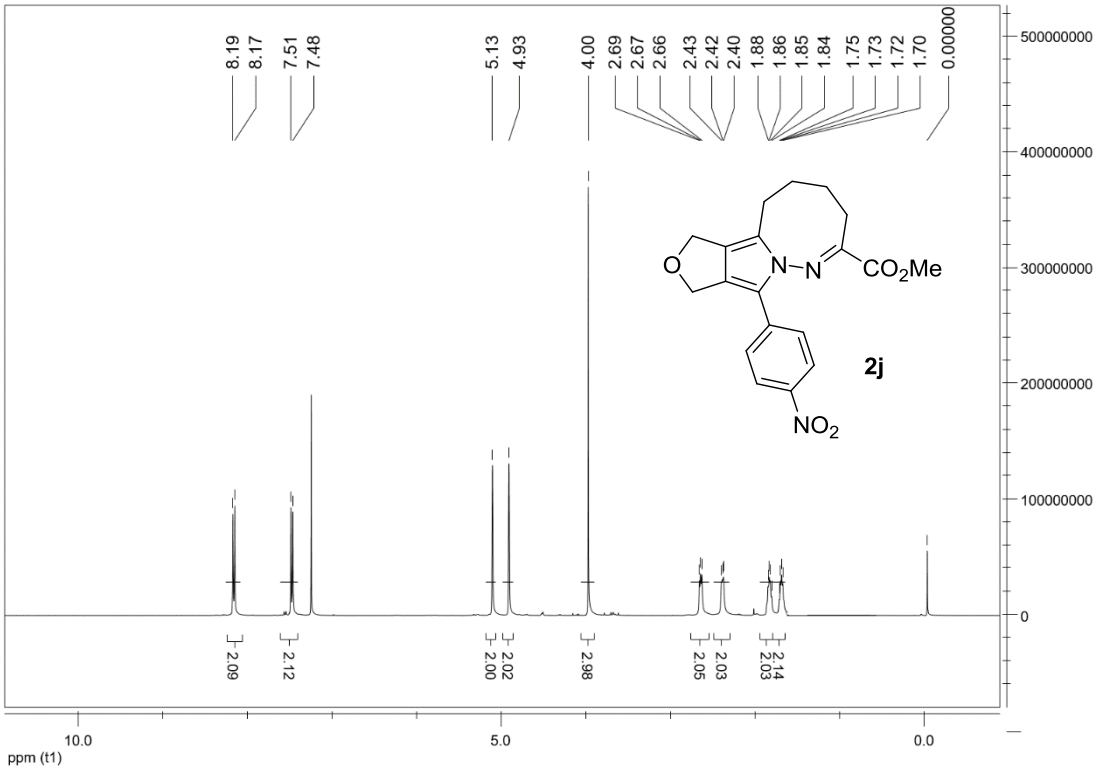
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1.88
1.86
1.85
1.84
1.75
1.73
1.72
1.70
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2.09
2.12
2.00
2.02
2.98
2.05
2.03
2.14
2.03
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100000000
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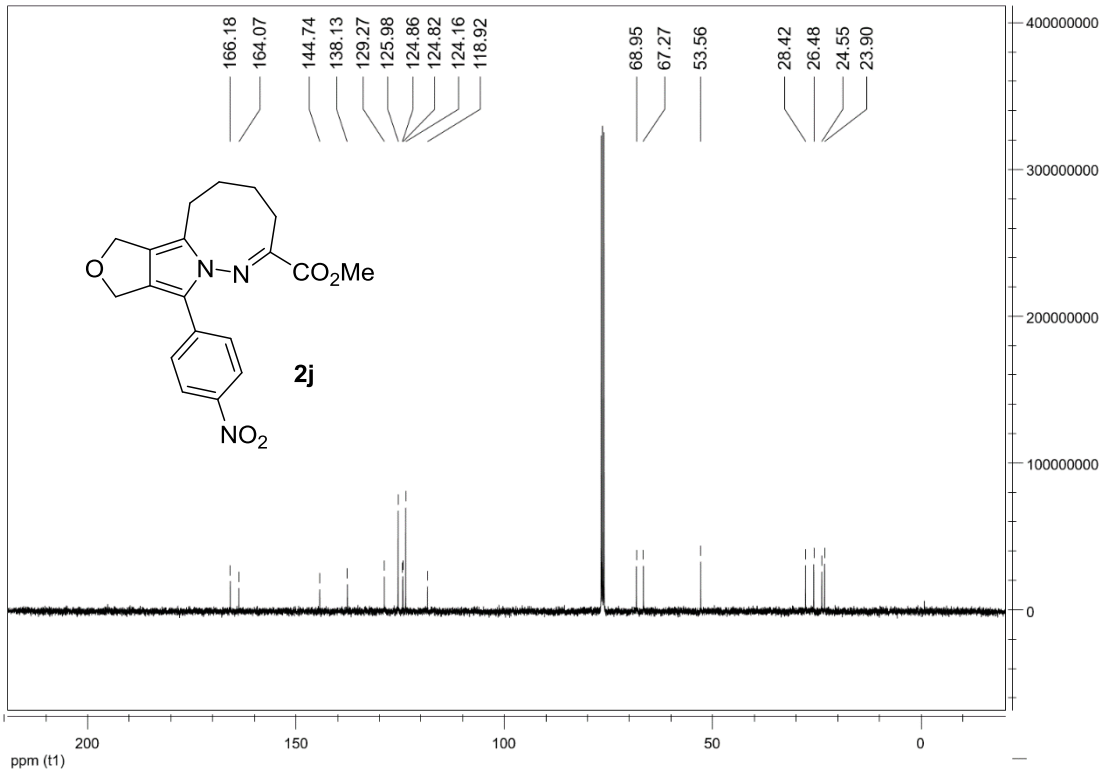
5.0
0.0
ppm (t1)
O
N–N
CO2Me
NO2
2j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124.82
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53.56
28.42
26.48
24.55
23.90
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50
0
ppm (t1)
O
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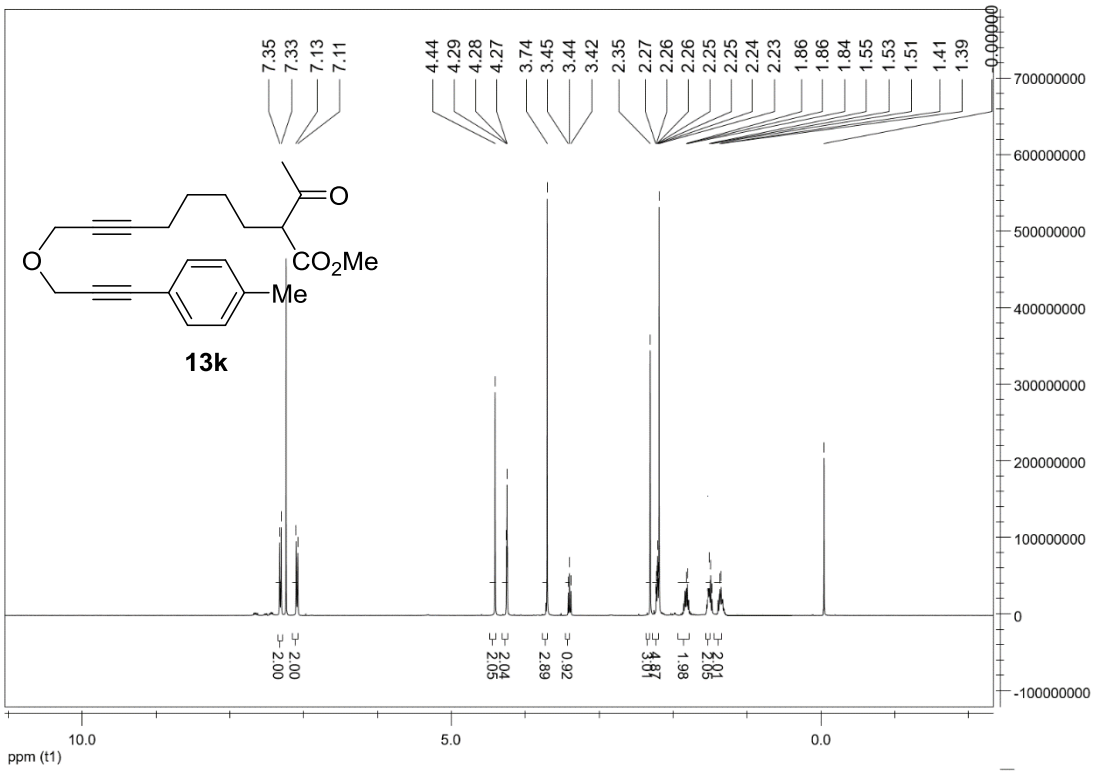
CO2Me
NO2
2j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3.44
3.42
2.35
2.27
2.26
2.26
2.25
2.25
2.24
2.23
1.86
1.86
1.84
1.55
1.53
1.51
1.41
1.39
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O
CO2Me
Me
13k
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2.00
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2.05
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3.87
1.98
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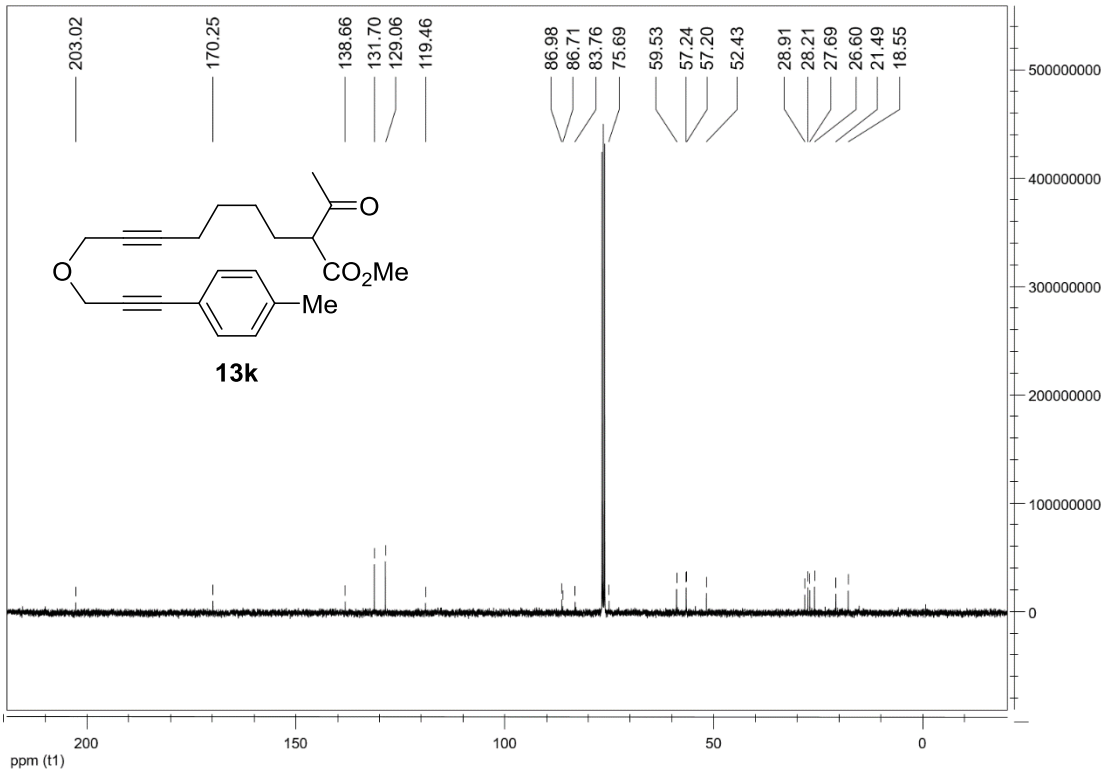
ppm (t1)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57.24
57.20
52.43
28.91
28.21
27.69
26.60
21.49
18.55
O
O
CO2Me
Me
13k
500000000
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50
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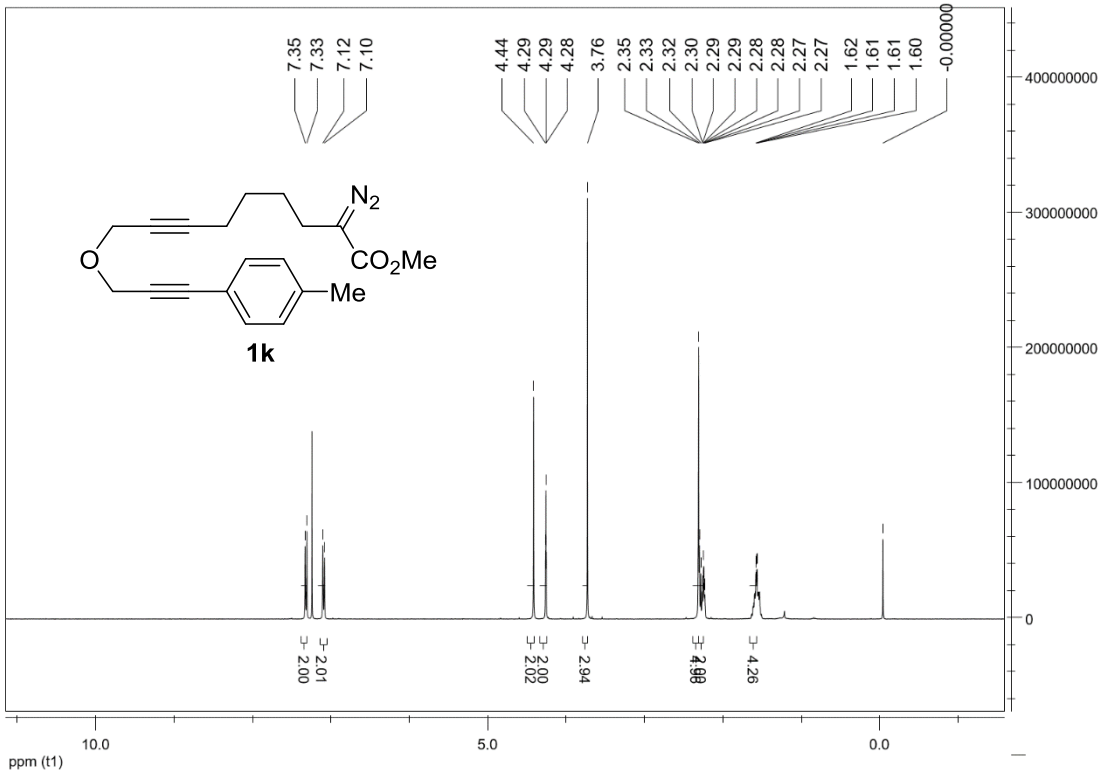
ppm (t1)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2.29
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2.28
2.28
2.27
2.27
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1.61
1.61
1.60
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O
Me
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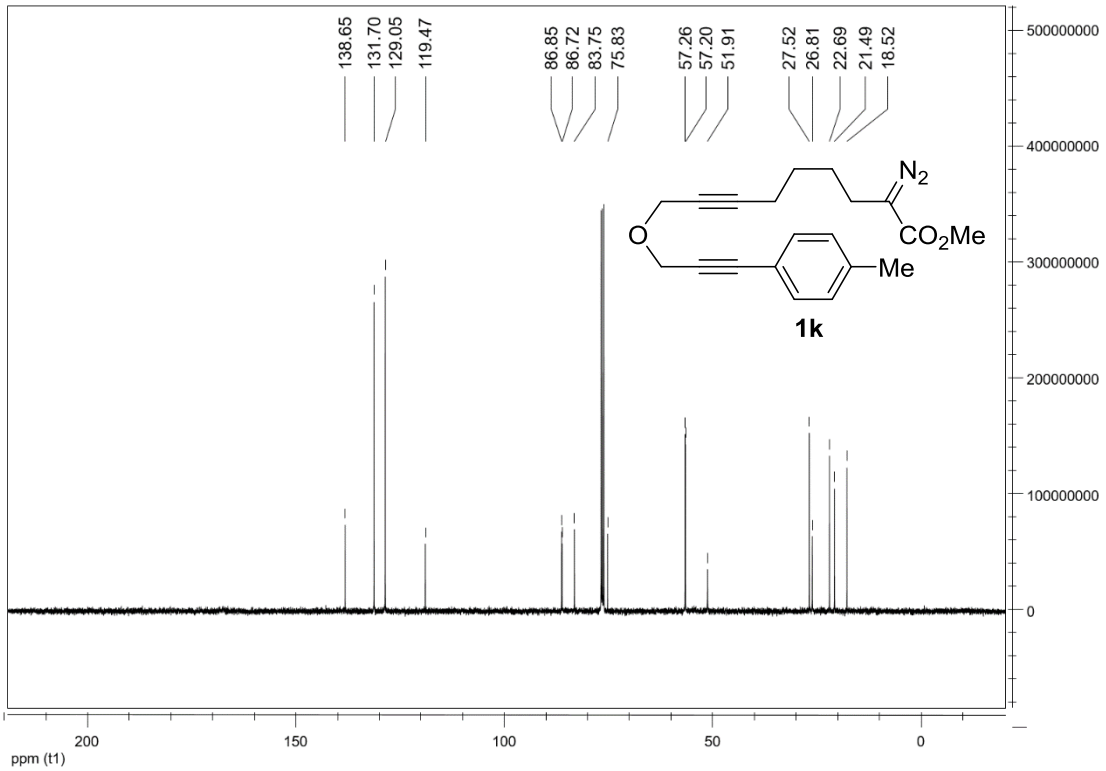
ppm (t1)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57.20
51.91
27.52
26.81
22.69
21.49
18.52
N2
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O
Me
1k
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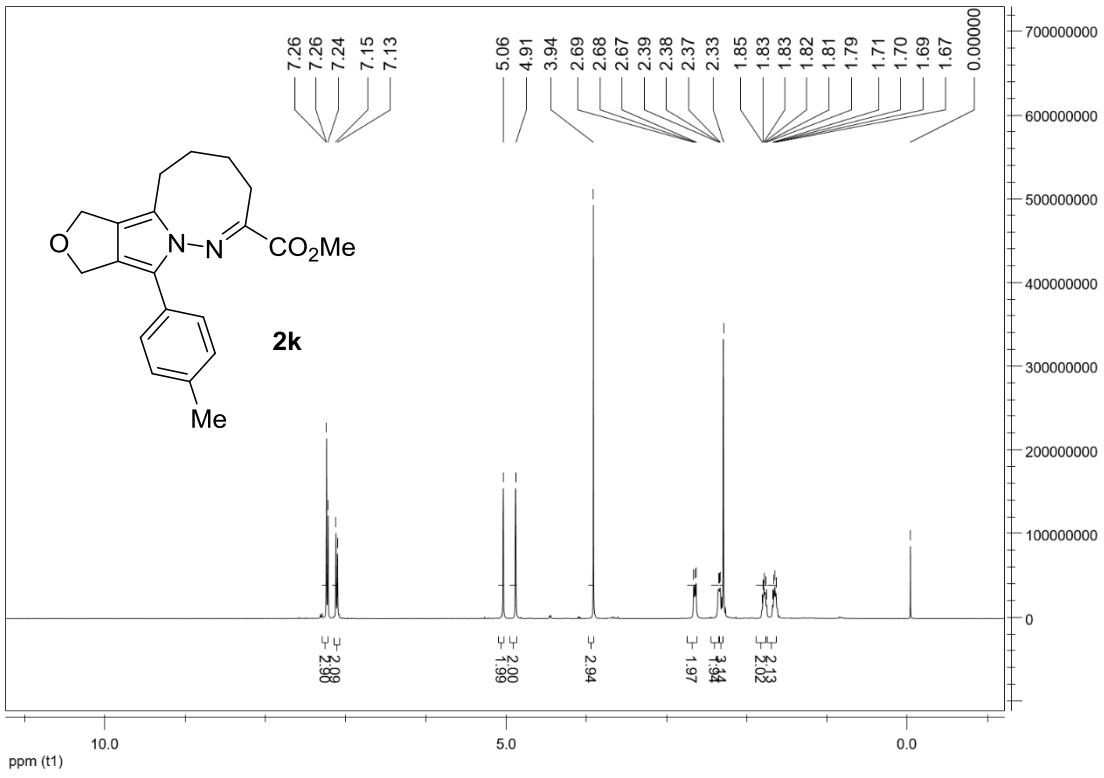
100
50
0
ppm (t1)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2.67
2.39
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2.37
2.33
1.85
1.83
1.83
1.82
1.81
1.79
1.71
1.70
1.69
1.67
0.00000
O
N–N
CO2Me
2k
Me
2.08
2.00
1.99
2.94
1.97
3.14
3.04
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2.02
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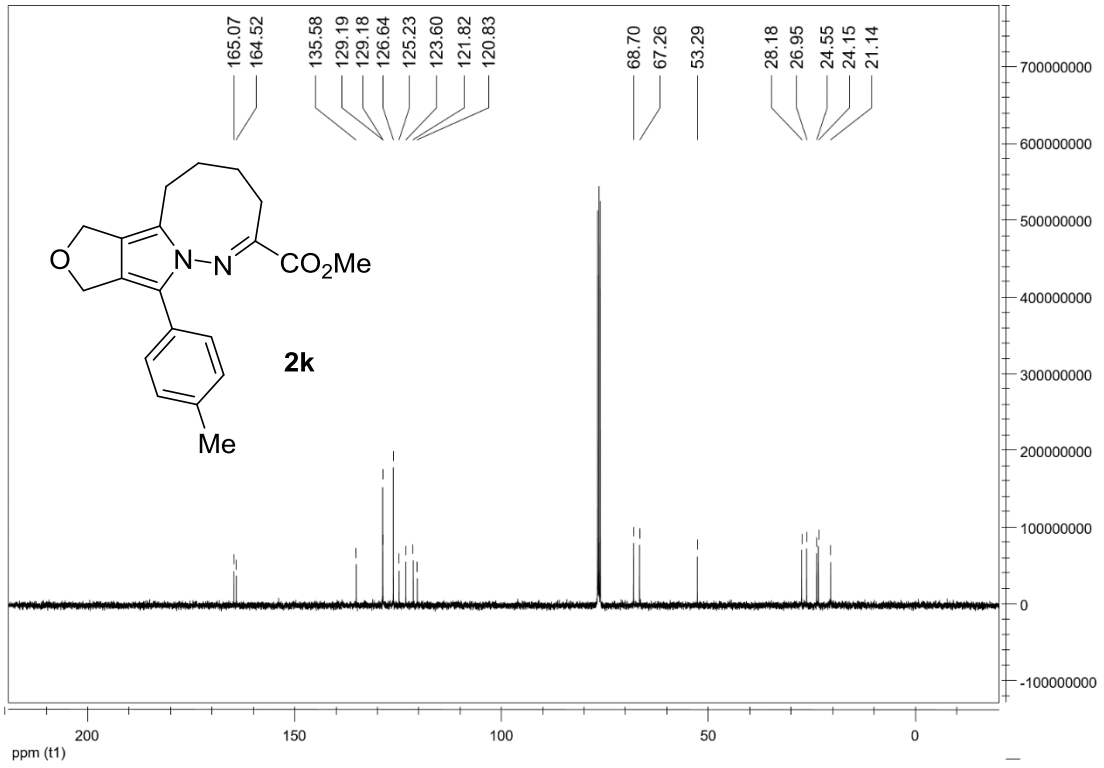
0.0
ppm (t1)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125.23
123.60
121.82
120.83
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67.26
53.29
28.18
26.95
24.55
24.15
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O
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CO2Me
2k
Me
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400000000
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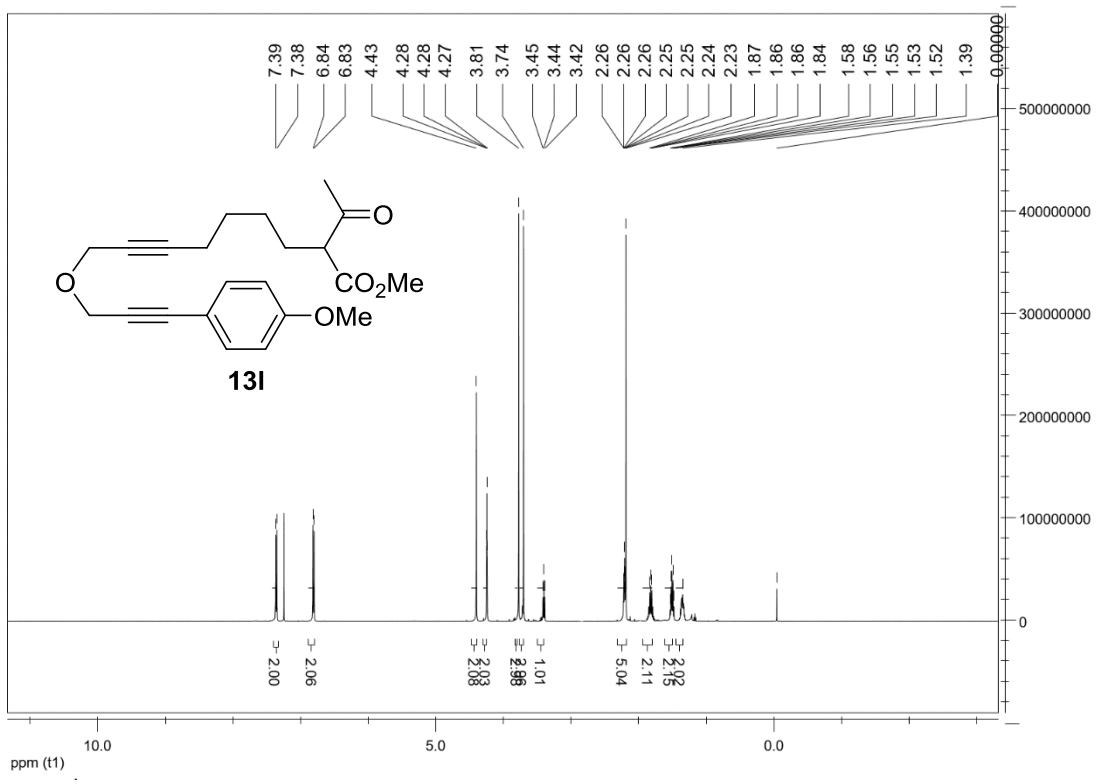
100000000
0
-100000000
200
150
100
50
0
ppm (t1)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3.42
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2.26
2.26
2.25
2.25
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2.23
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1.86
1.86
1.84
1.58
1.56
1.55
1.53
1.52
1.39
0.00000
O
O
CO2Me
OMe
13l
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2.06
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2.08
1.01
5.04
2.11
2.02
2.15
500000000
400000000
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200000000
100000000
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10.0
5.0
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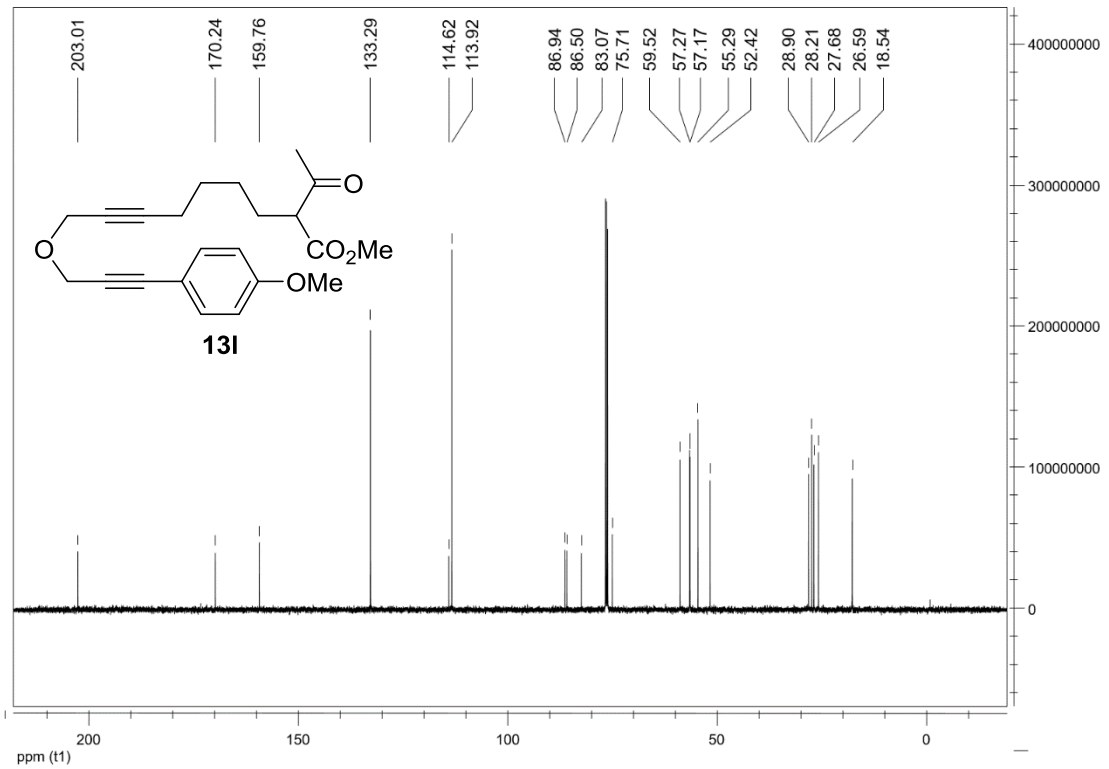
ppm (t1)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113.92
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86.50
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59.52
57.27
57.17
55.29
52.42
28.90
28.21
27.68
26.59
18.54
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O
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OMe
13l
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300000000
200000000
100000000
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50
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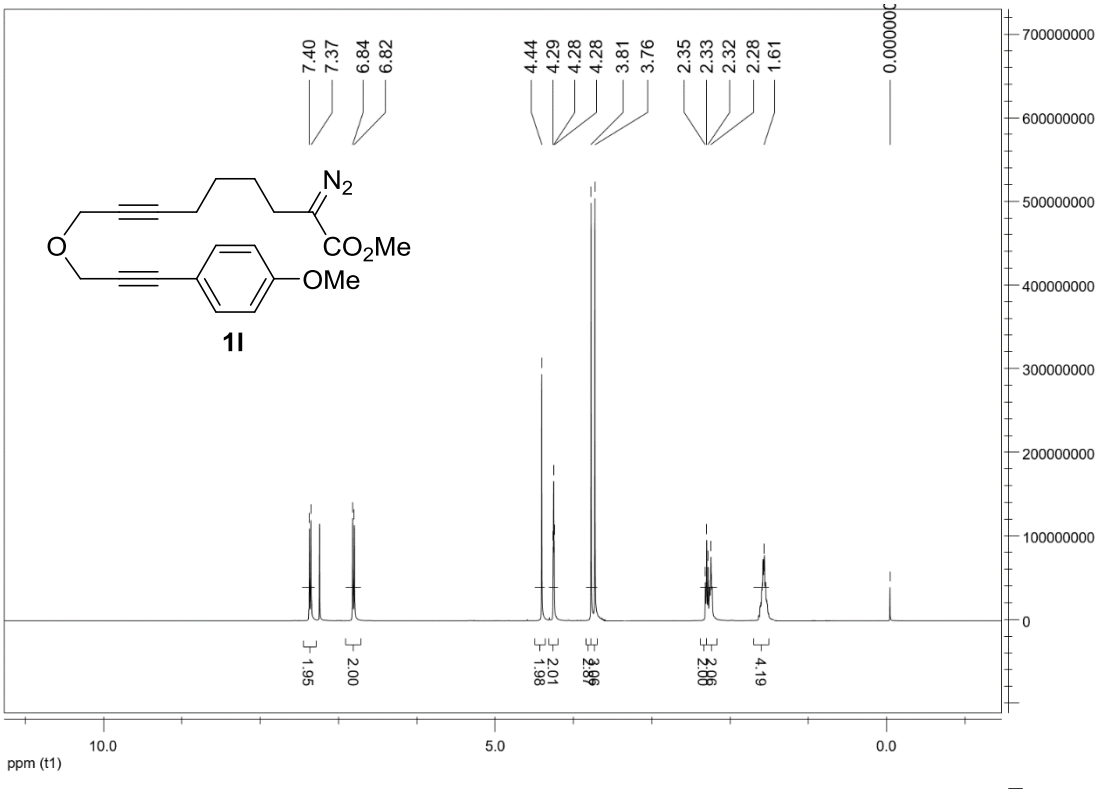
ppm (t1)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3.76
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2.33
2.32
2.28
1.61
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CO2Me
O
OMe
1l
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2.00
1.98
2.01
2.00
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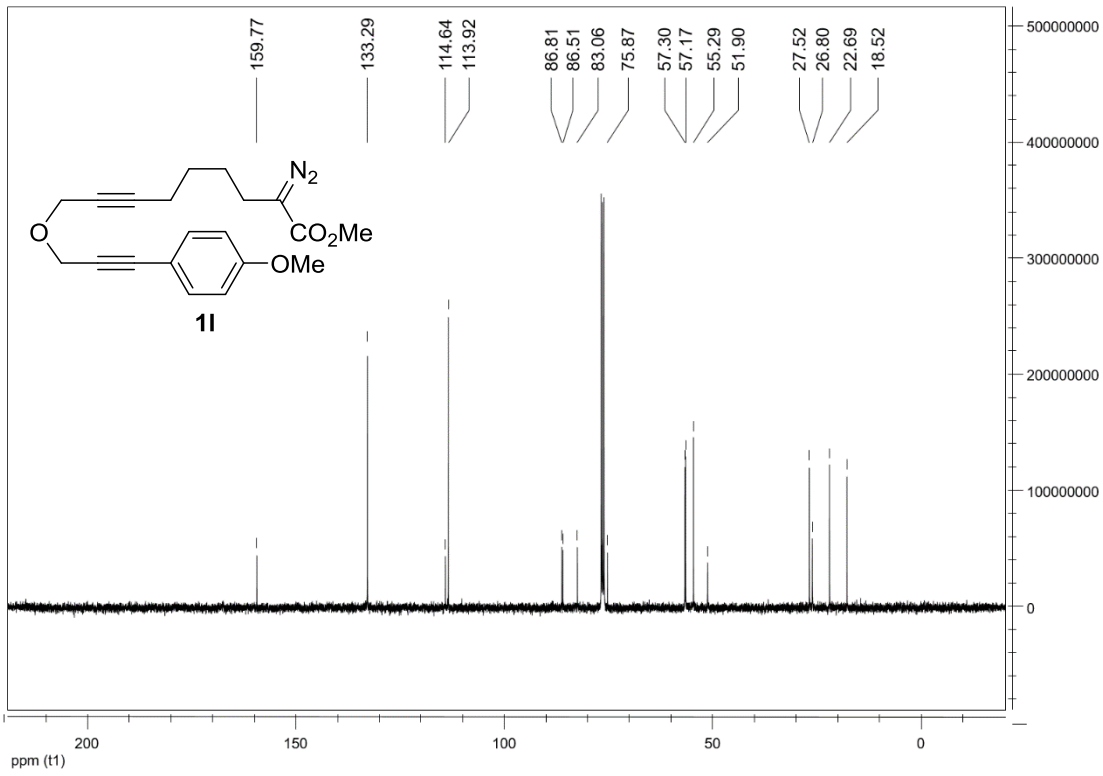
ppm (t1)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27.52
26.80
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18.52
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OMe
1l
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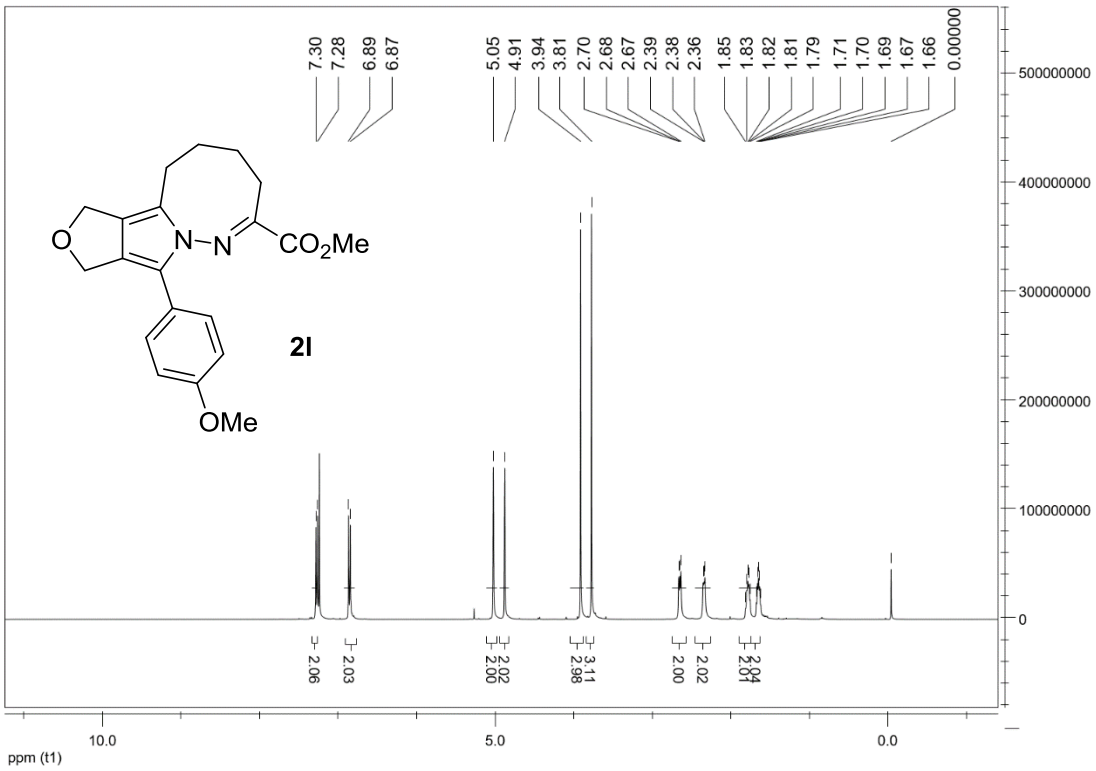
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2.39
2.38
2.36
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1.83
1.82
1.81
1.79
1.71
1.70
1.69
1.67
1.66
0.00000
O
N–N
CO2Me
OMe
2l
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2.03
2.00
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2.00
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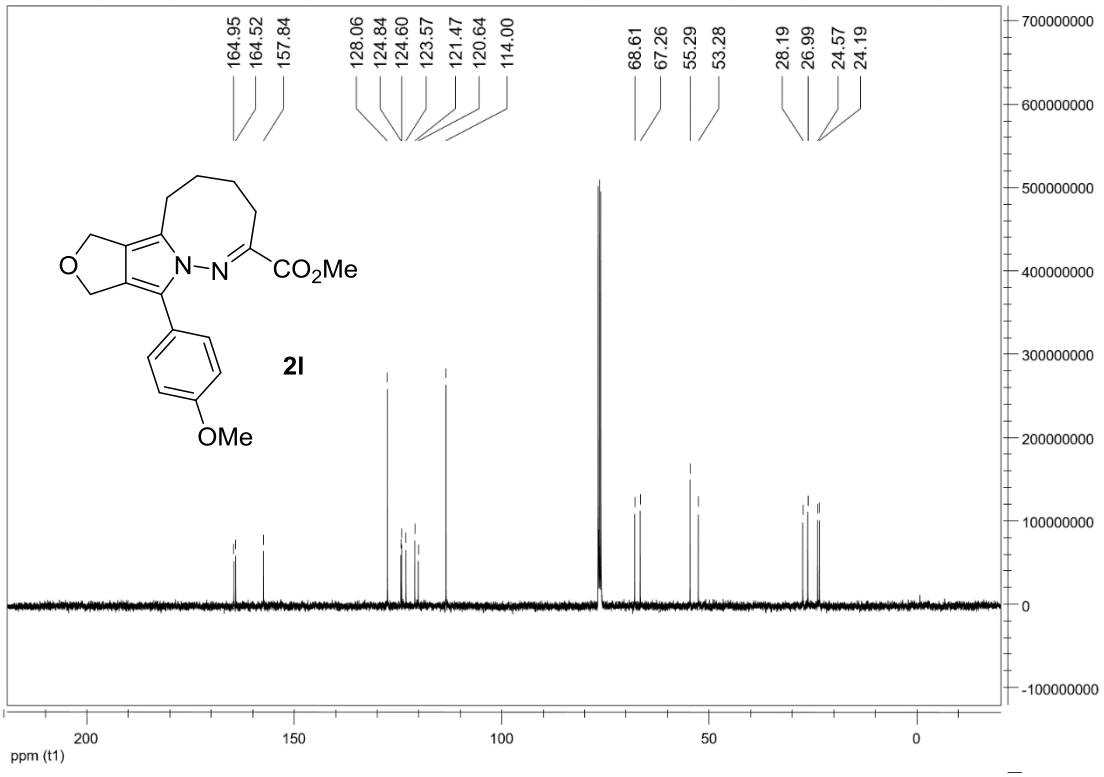
ppm (t1)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55.29
53.28
28.19
26.99
24.57
24.19
O
N–N
CO2Me
OMe
2l
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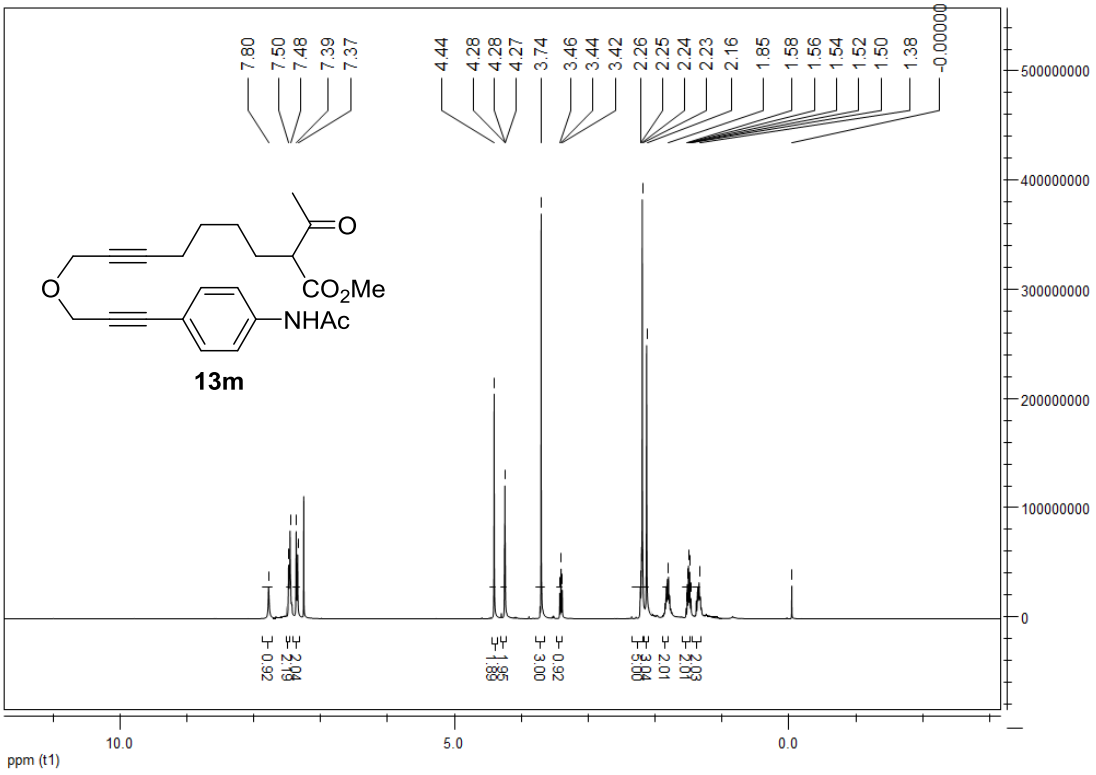
0
ppm (t1)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2.25
2.24
2.23
2.16
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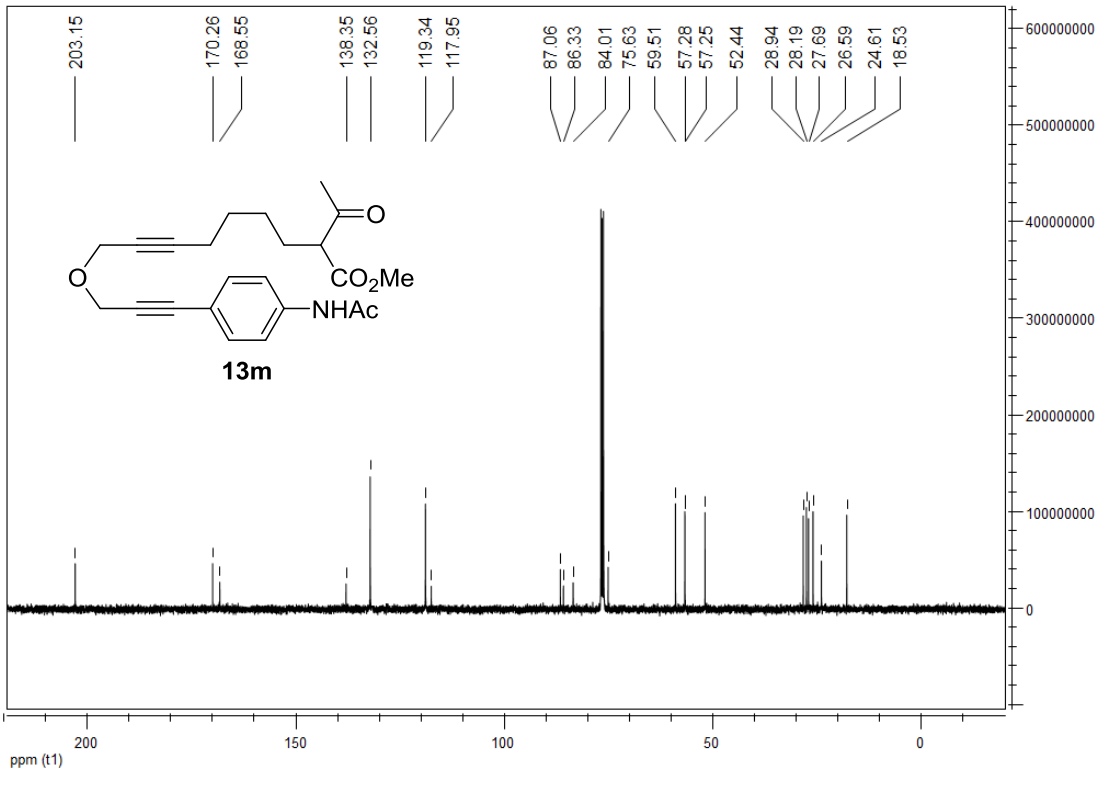
O
CO2Me
NHAc
13m
ppm (t1)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27.69
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24.61
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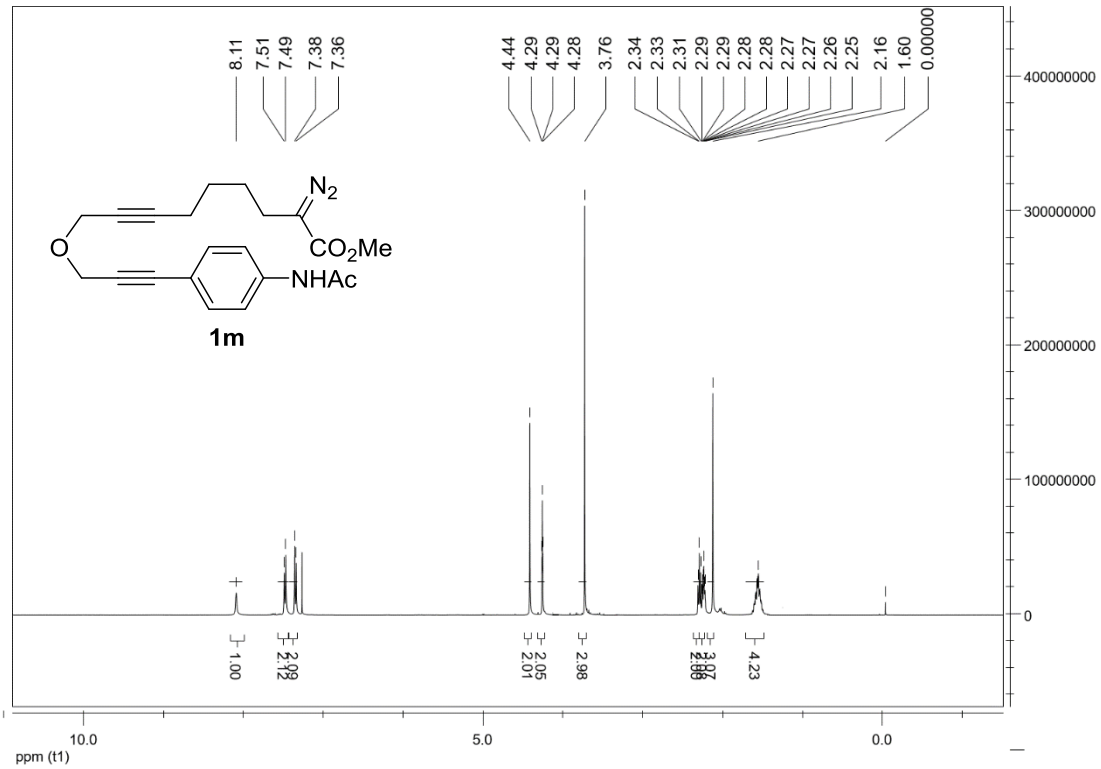
O
CO2Me
NHAc
13m
ppm (t1)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4.29
4.28
3.76
2.34
2.33
2.31
2.29
2.29
2.28
2.28
2.27
2.27
2.26
2.25
2.16
1.60
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CO2Me
O
NHAc
1m
1.00
2.09
2.12
2.05
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2.98
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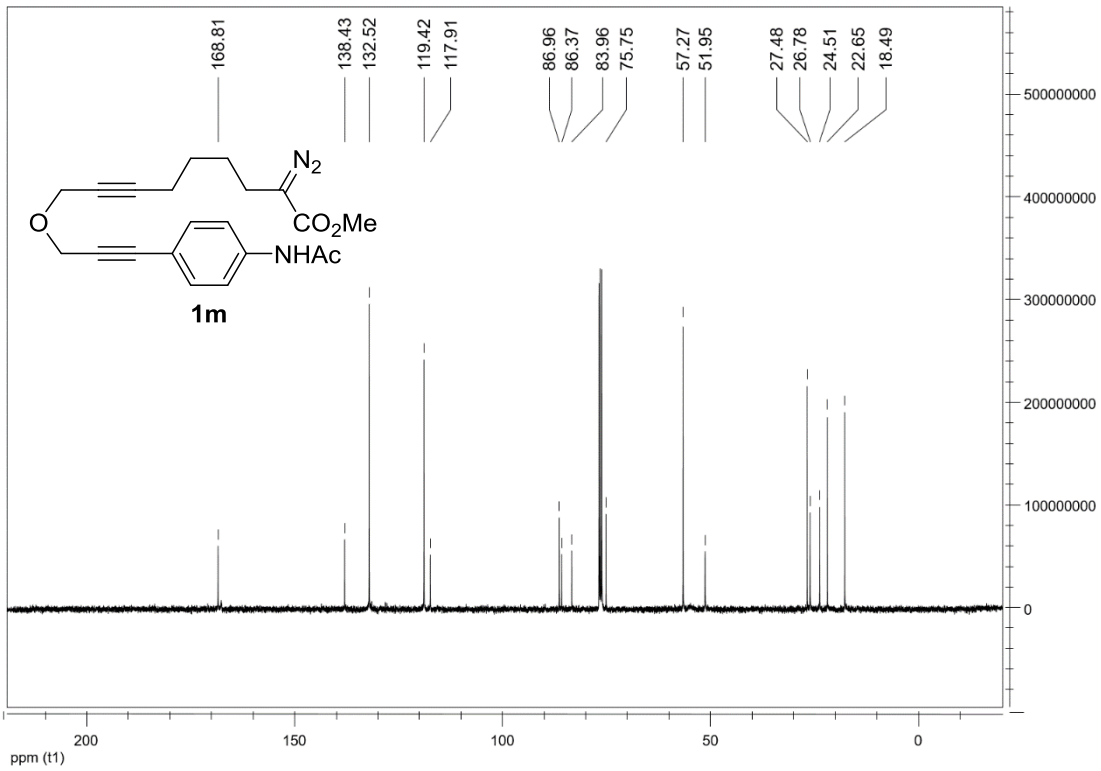
0.0
ppm (t1)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86.37
83.96
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57.27
51.95
27.48
26.78
24.51
22.65
18.49
N2
CO2Me
O
NHAc
1m
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100
50
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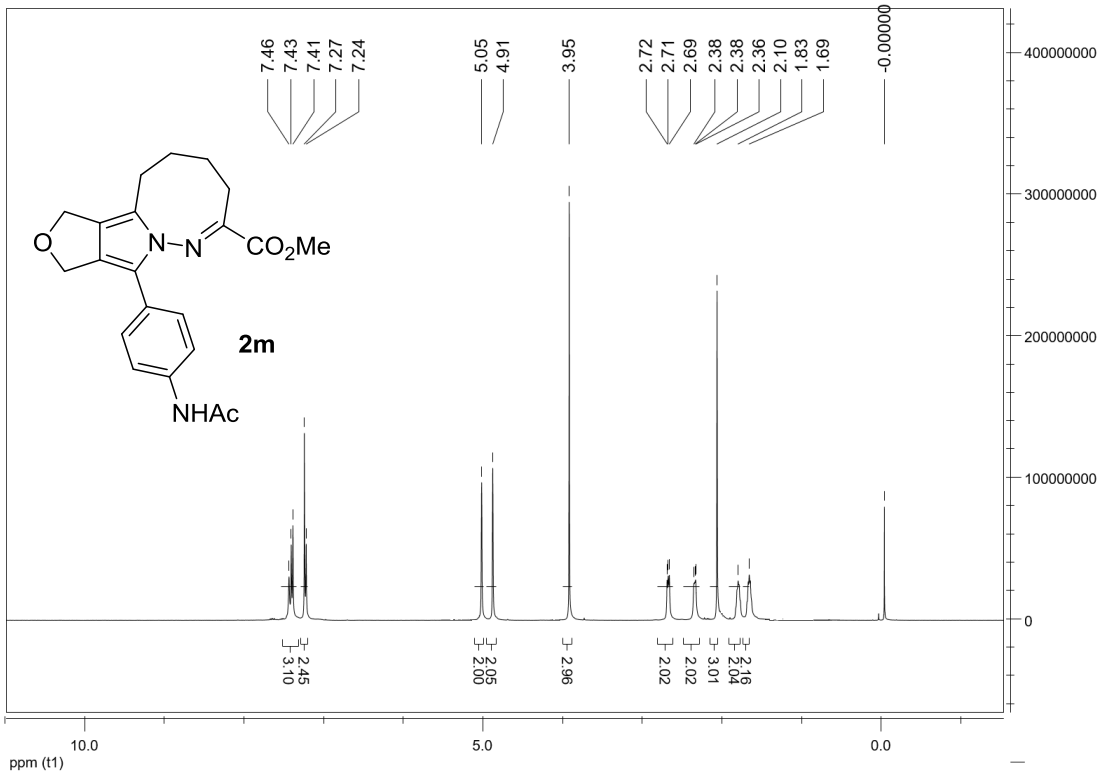
ppm (t1)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2.69
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2.38
2.36
2.10
1.83
1.69
-0.00000
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N
N
CO2Me
2m
NHAc
3.10
2.45
2.00
2.05
2.96
2.02
2.02
3.01
2.04
2.16
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100000000
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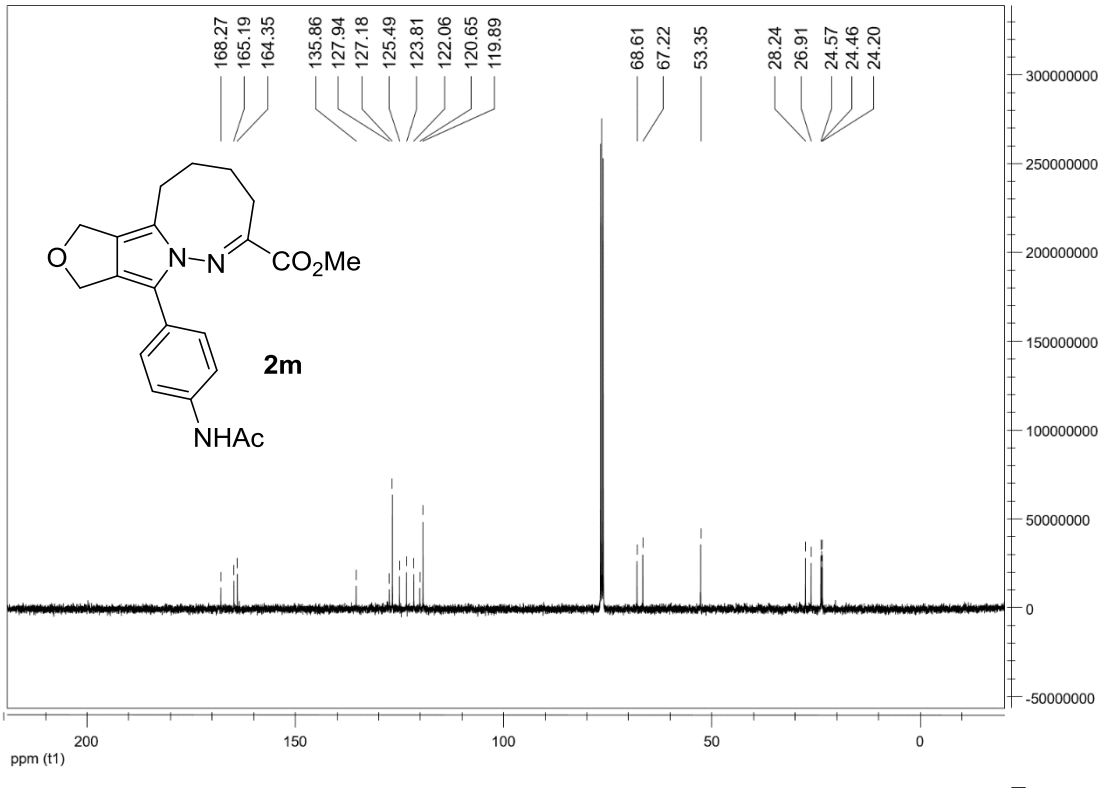
5.0
0.0
ppm (t1)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127.18
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119.89
68.61
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53.35
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24.57
24.46
24.20
O
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N
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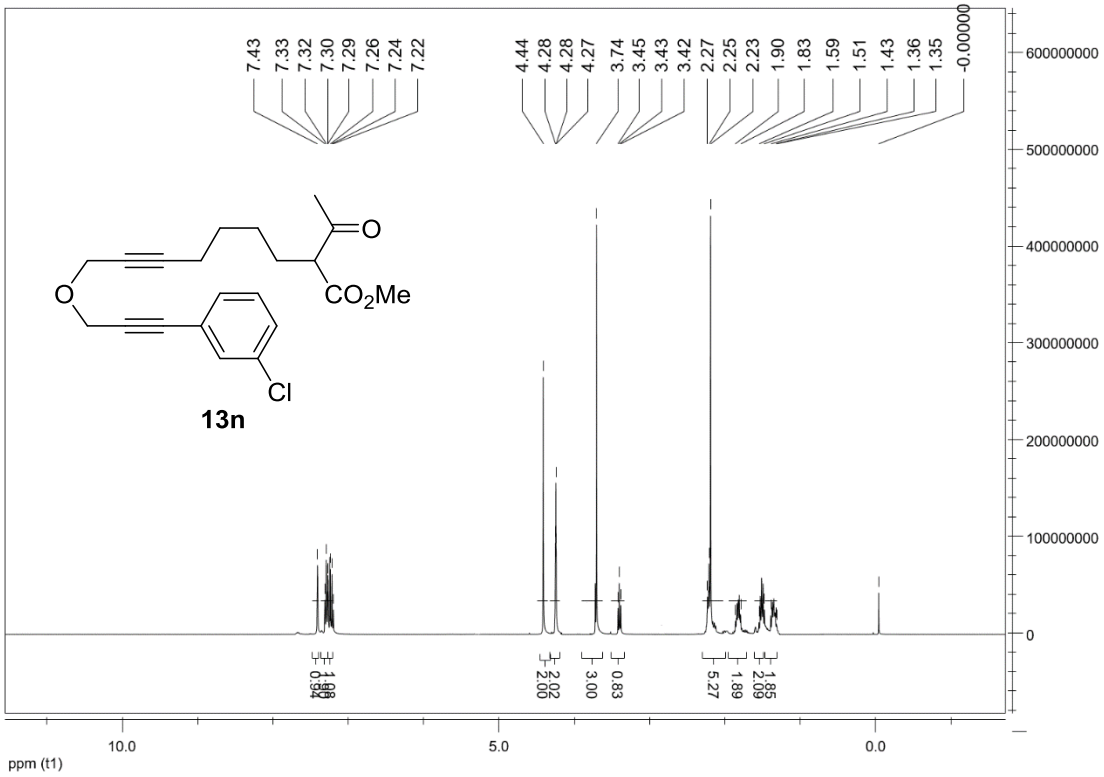
ppm (t1)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4.28
4.28
4.27
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3.45
3.43
3.42
2.27
2.25
2.23
1.90
1.83
1.59
1.51
1.43
1.36
1.35
-0.00000
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O
CO2Me
Cl
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500000000
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300000000
200000000
100000000
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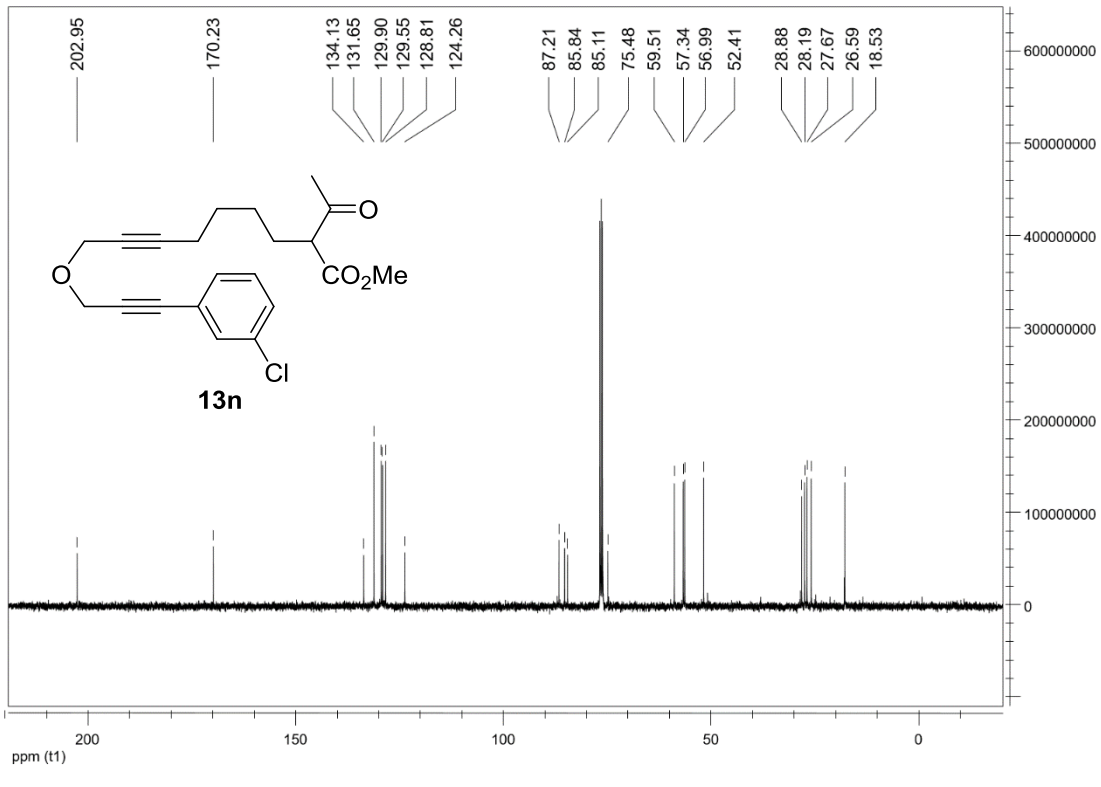
ppm (t1)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28.19
27.67
26.59
18.53
O
O
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Cl
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50
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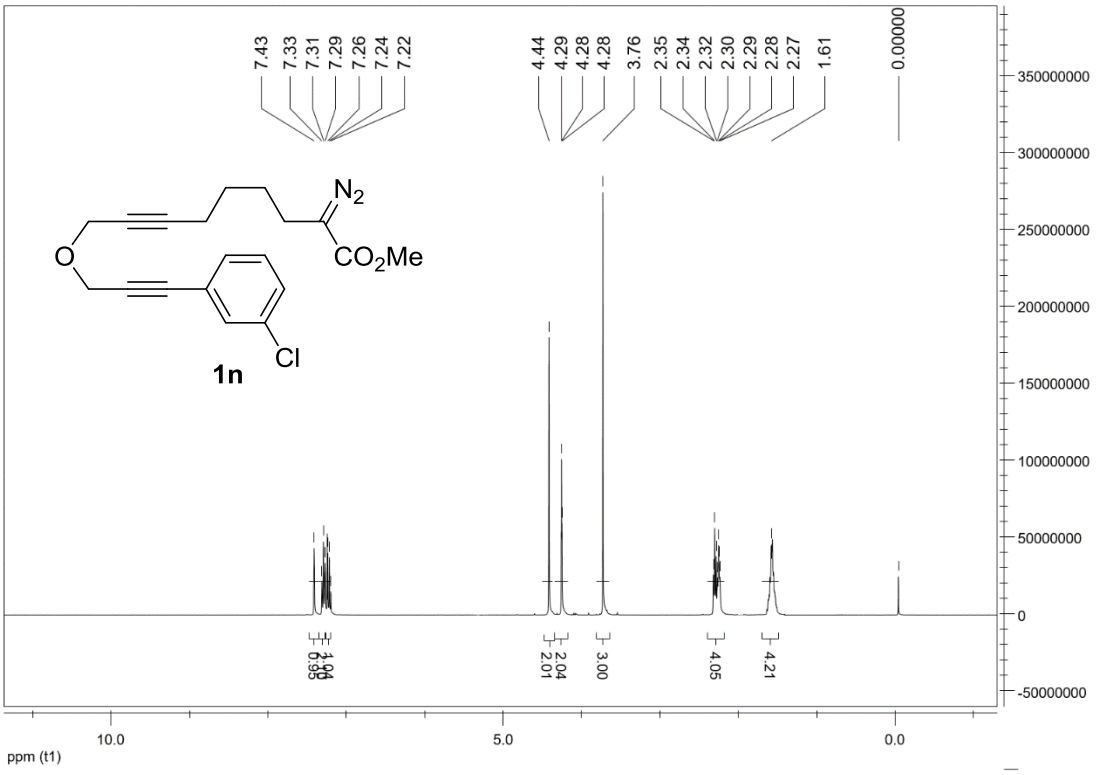
ppm (t1)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4.28
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2.34
2.32
2.30
2.29
2.28
2.27
1.61
0.00000
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CO2Me
O
Cl
1n
1.00
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2.01
3.00
4.05
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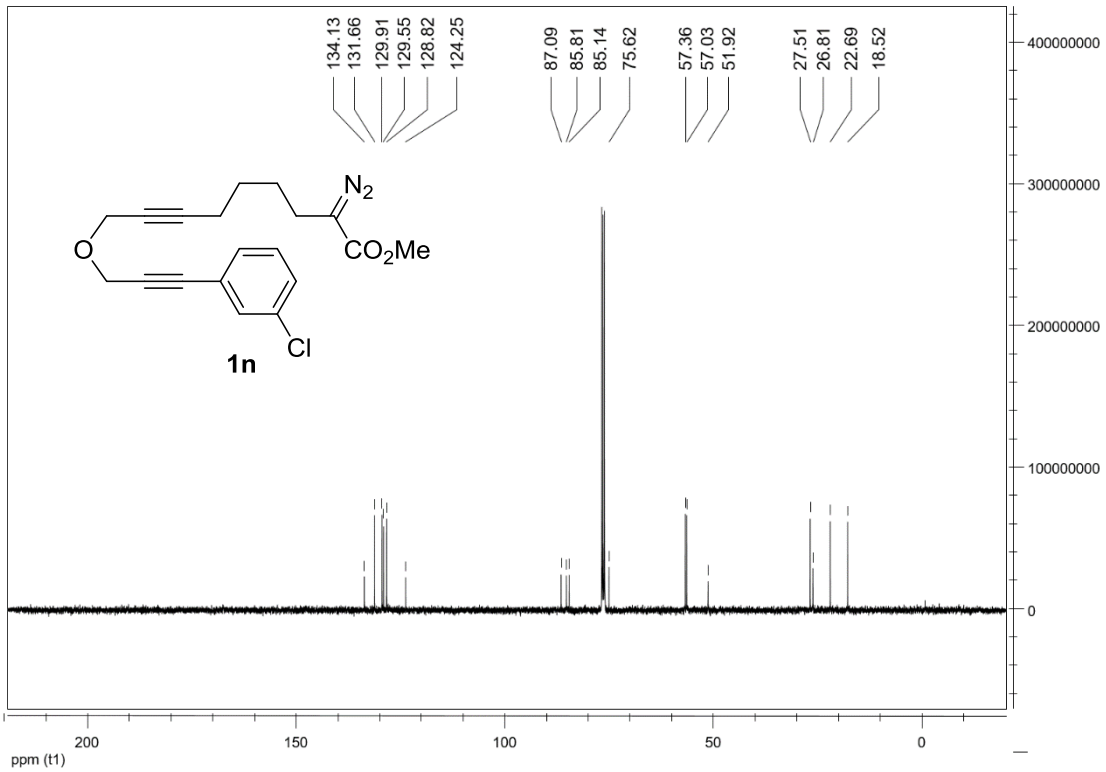
ppm (t1)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26.81
22.69
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Cl
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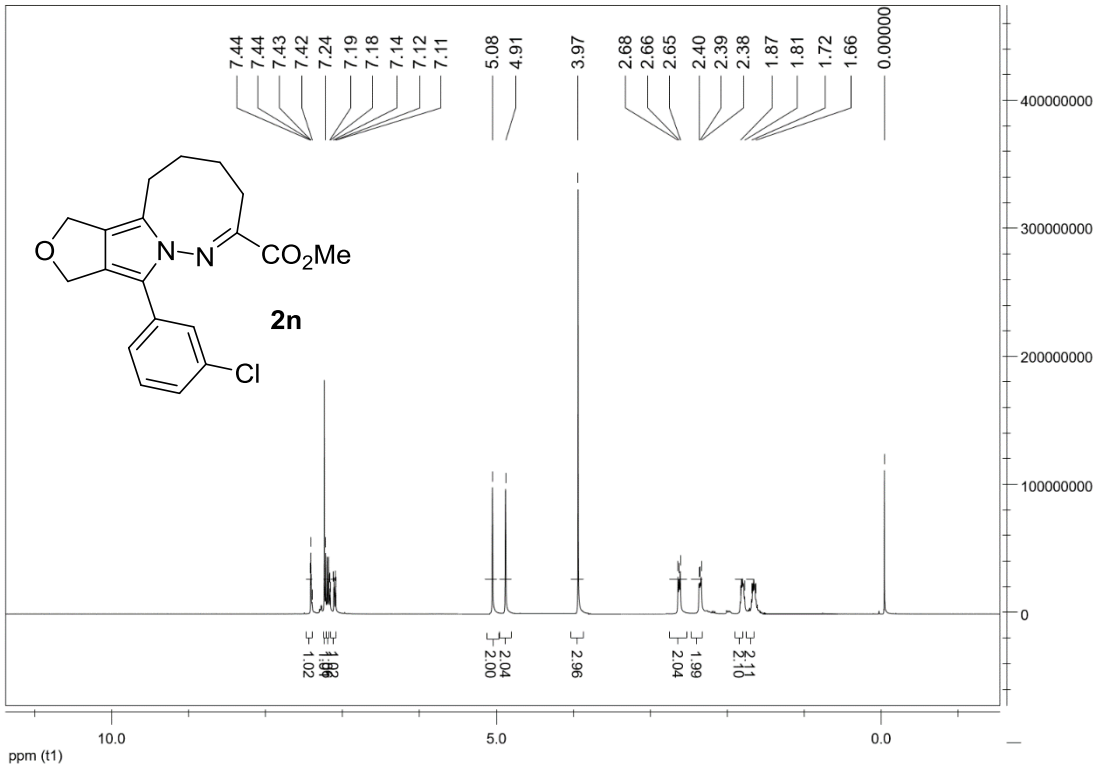
ppm (t1)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4.91
3.97
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2.66
2.65
2.40
2.39
2.38
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1.81
1.72
1.66
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CO2Me
2n
Cl
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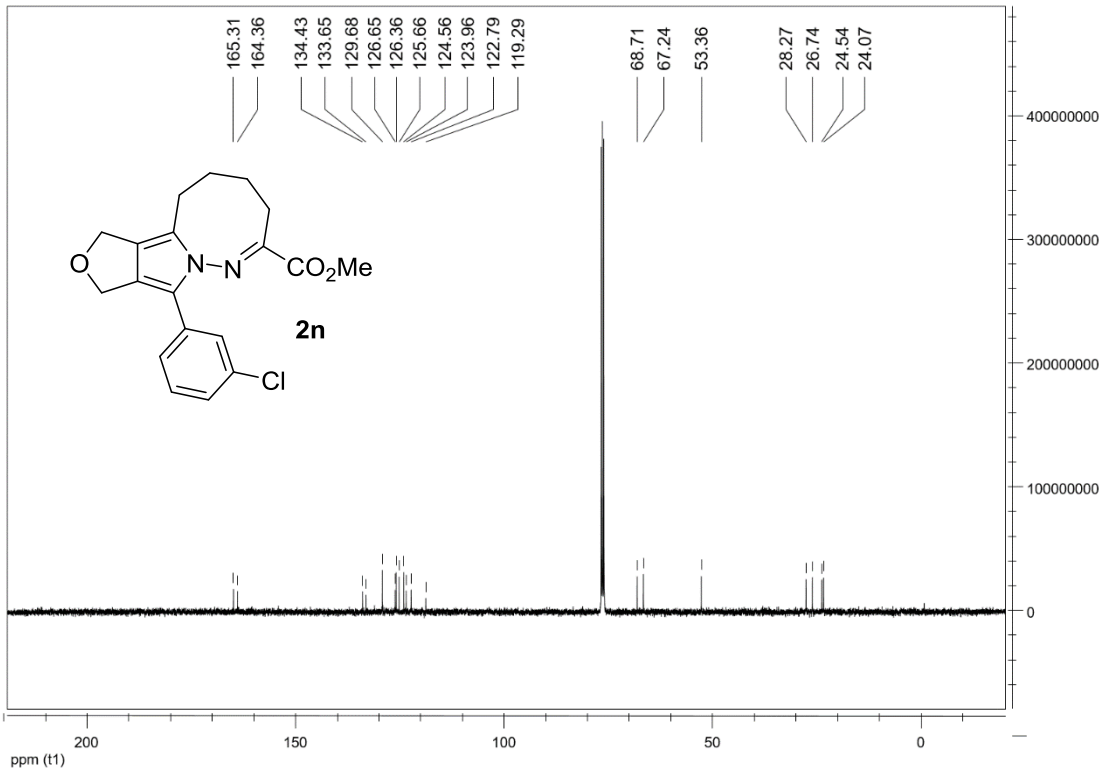
ppm (t1)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67.24
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28.27
26.74
24.54
24.07
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2n
Cl
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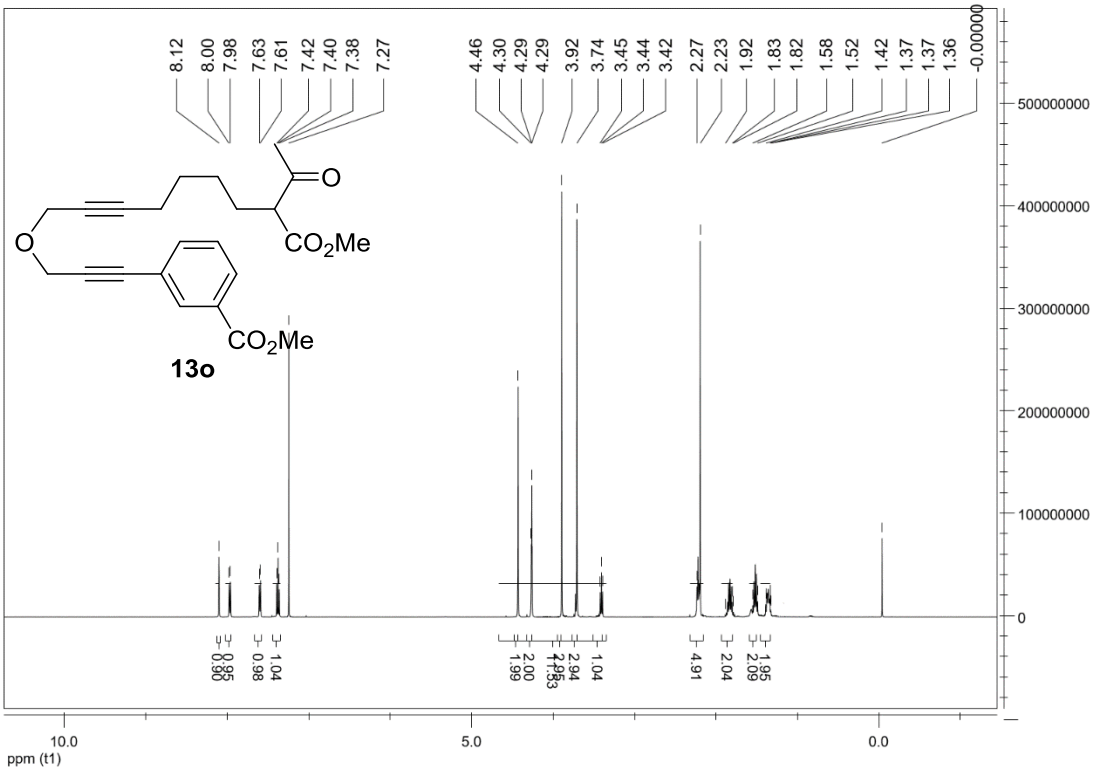
50
0
ppm (t1)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4.29
3.92
3.74
3.45
3.44
3.42
2.27
2.23
1.92
1.83
1.82
1.58
1.52
1.42
1.37
1.37
1.36
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CO2Me
O
CO2Me
13o
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100000000
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0.90
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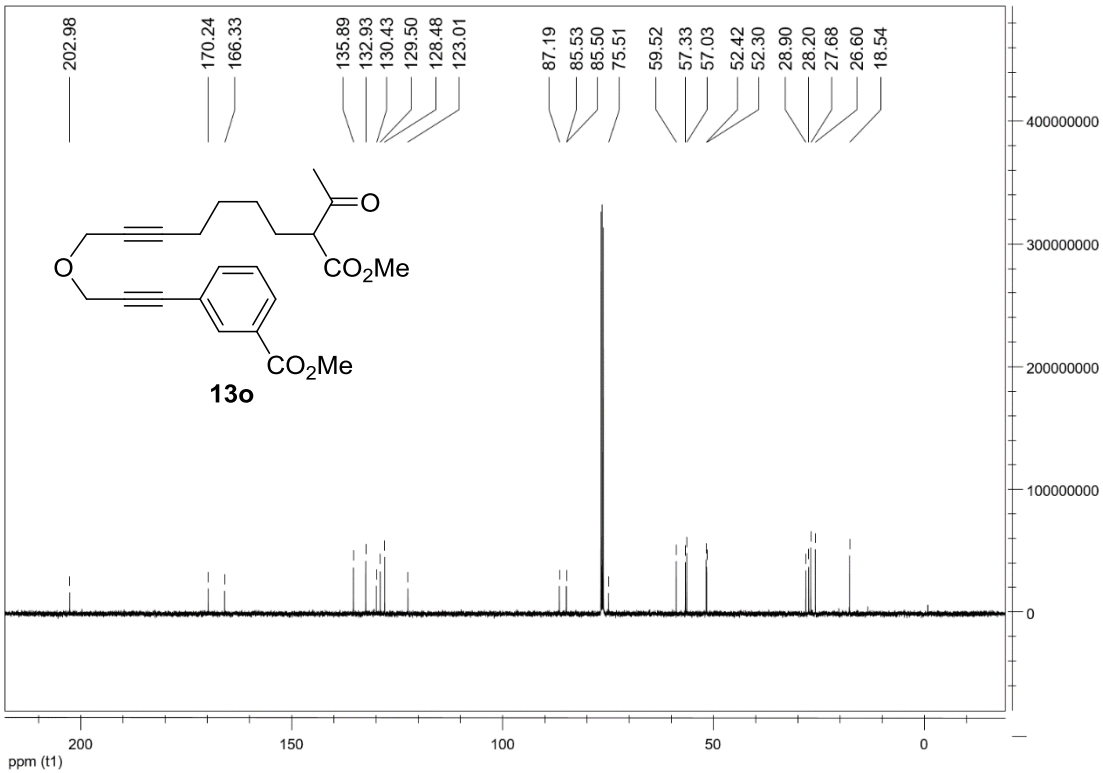
ppm (t1)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85.50
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59.52
57.33
57.03
52.42
52.30
28.90
28.20
27.68
26.60
18.54
O
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O
CO2Me
13o
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300000000
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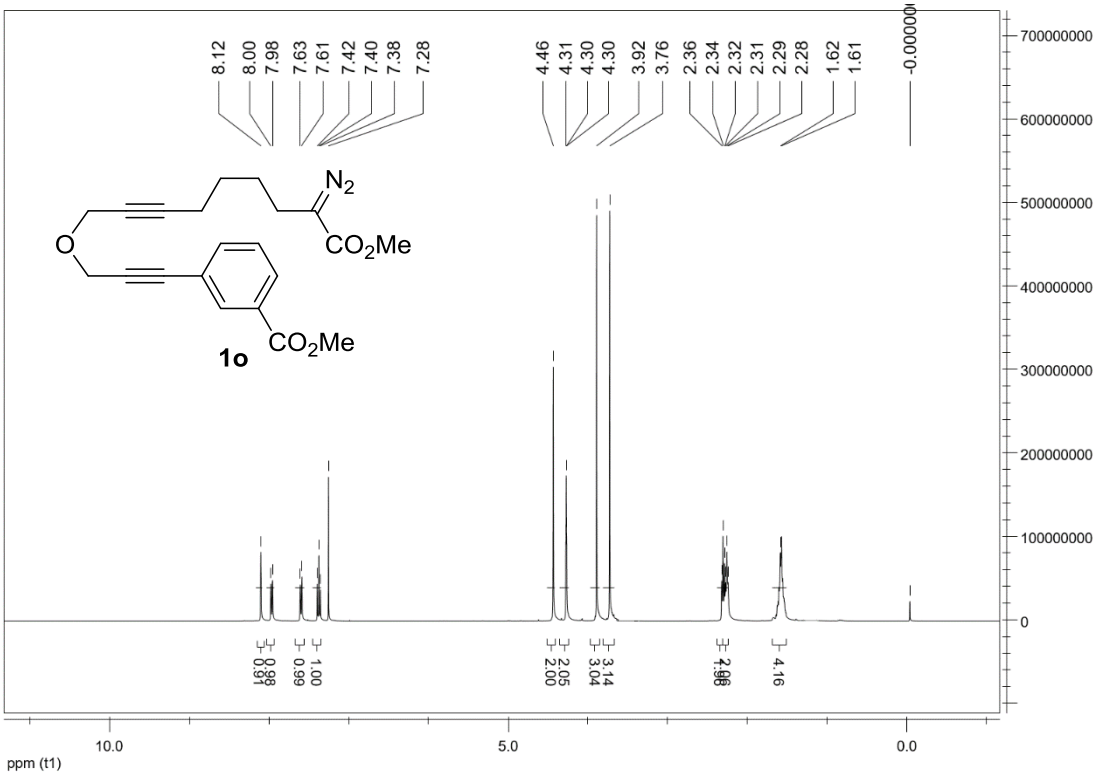
50
0
ppm (t1)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4.30
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3.76
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2.32
2.31
2.29
2.28
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1.61
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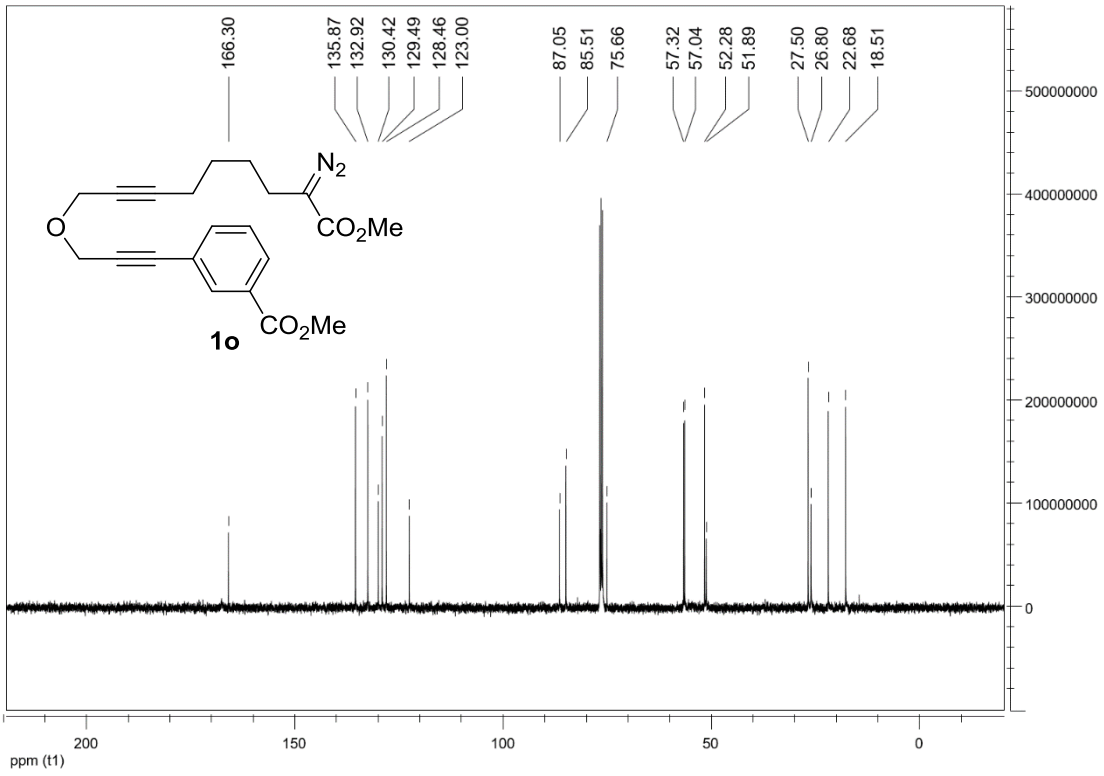
O
CO2Me
1o
ppm (t1)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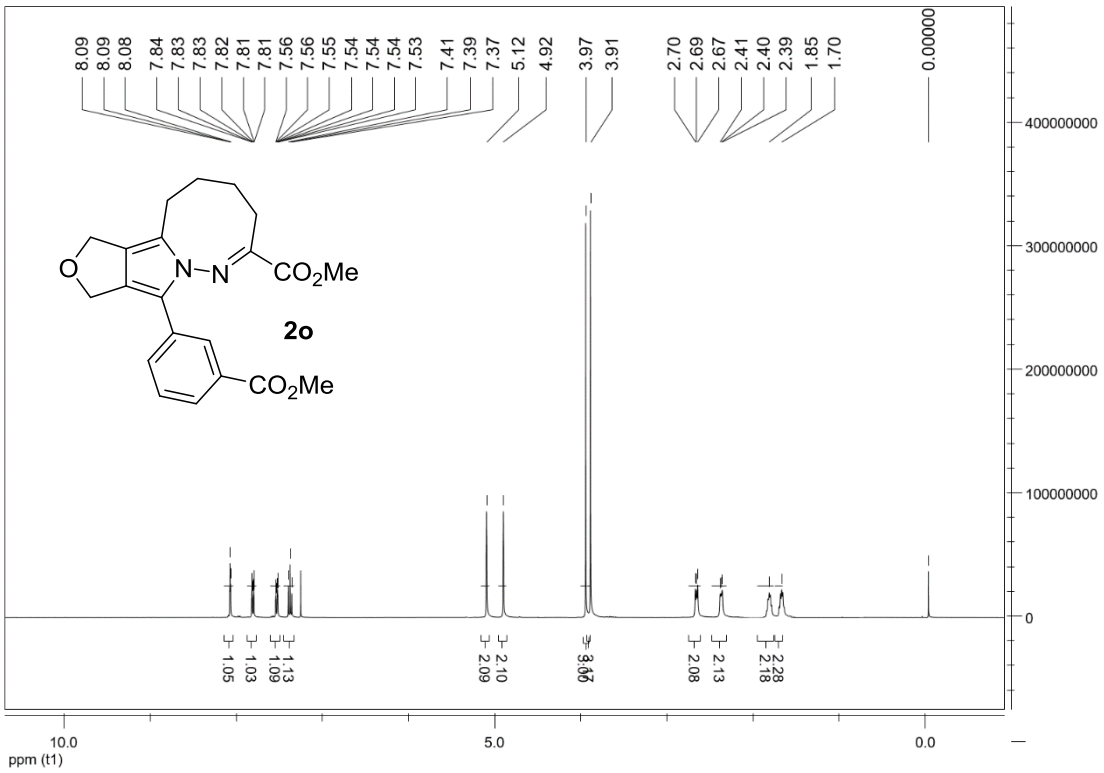
O
CO2Me
1o
ppm (t1)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7.54
7.53
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2.69
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CO2Me
2o
CO2Me
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1.03
1.09
1.13
2.09
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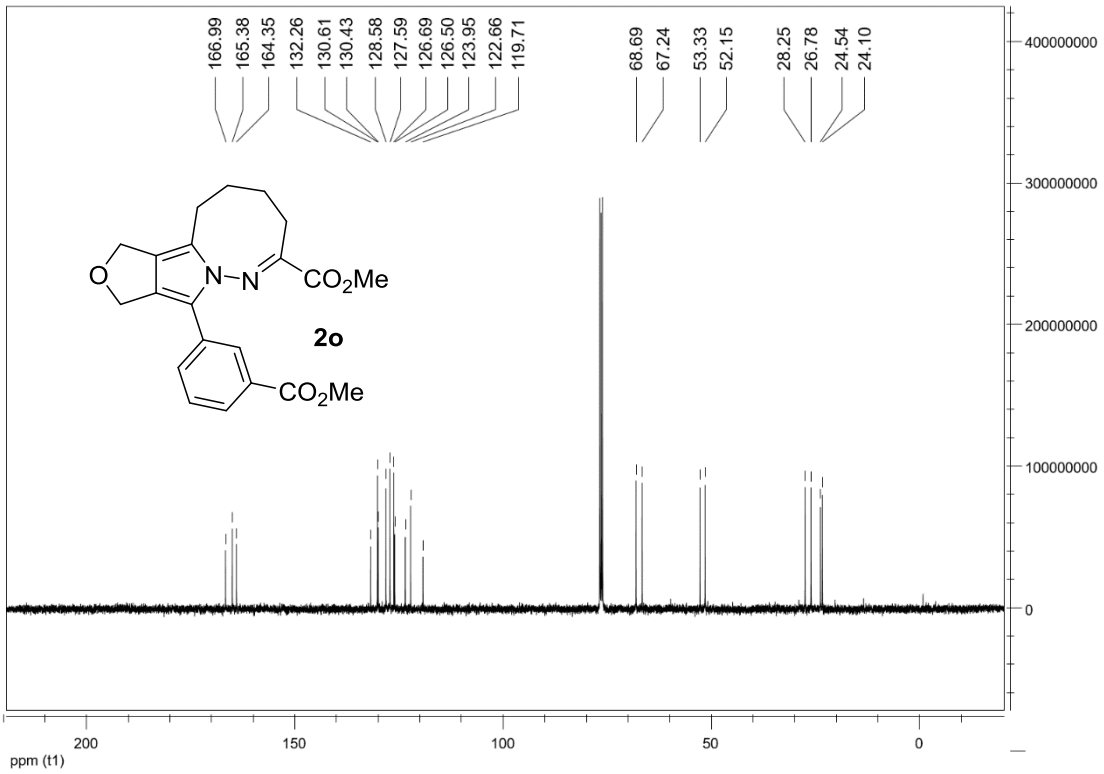
ppm (t1)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119.71
68.69
67.24
53.33
52.15
28.25
26.78
24.54
24.10
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2o
CO2Me
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200000000
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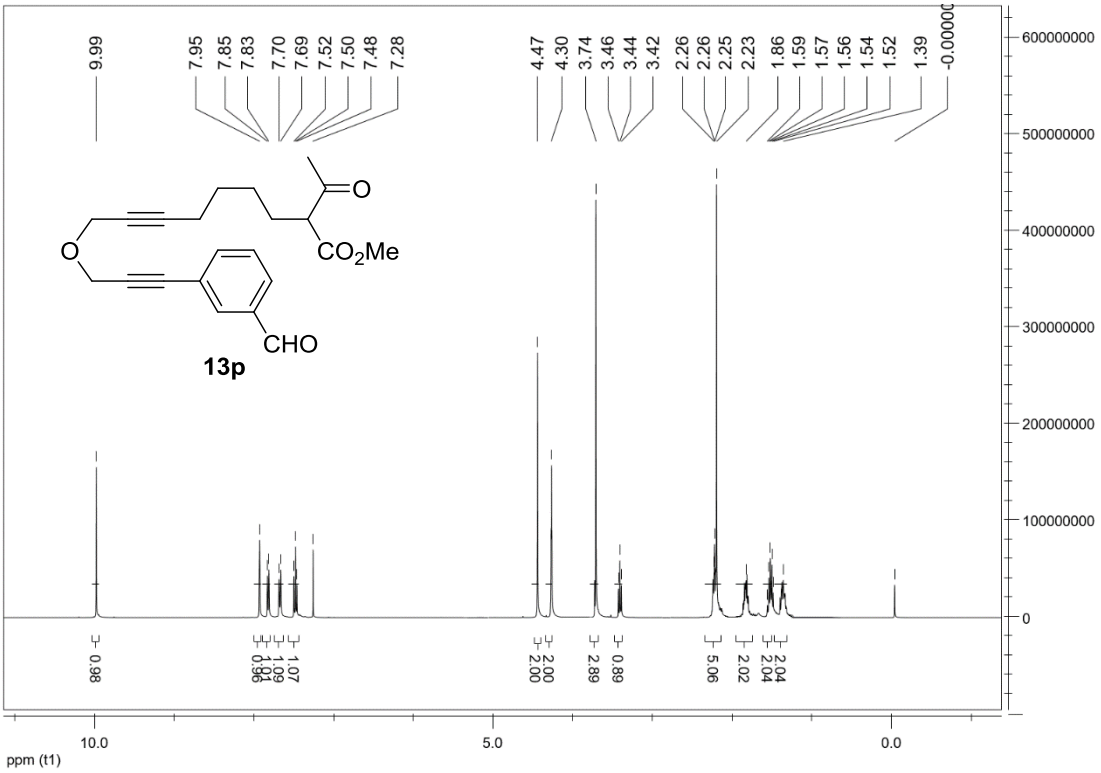
100
50
0
ppm (t1)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3.74
3.46
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2.23
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1.56
1.54
1.52
1.39
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O
CHO
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1.09
1.07
2.00
2.00
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2.02
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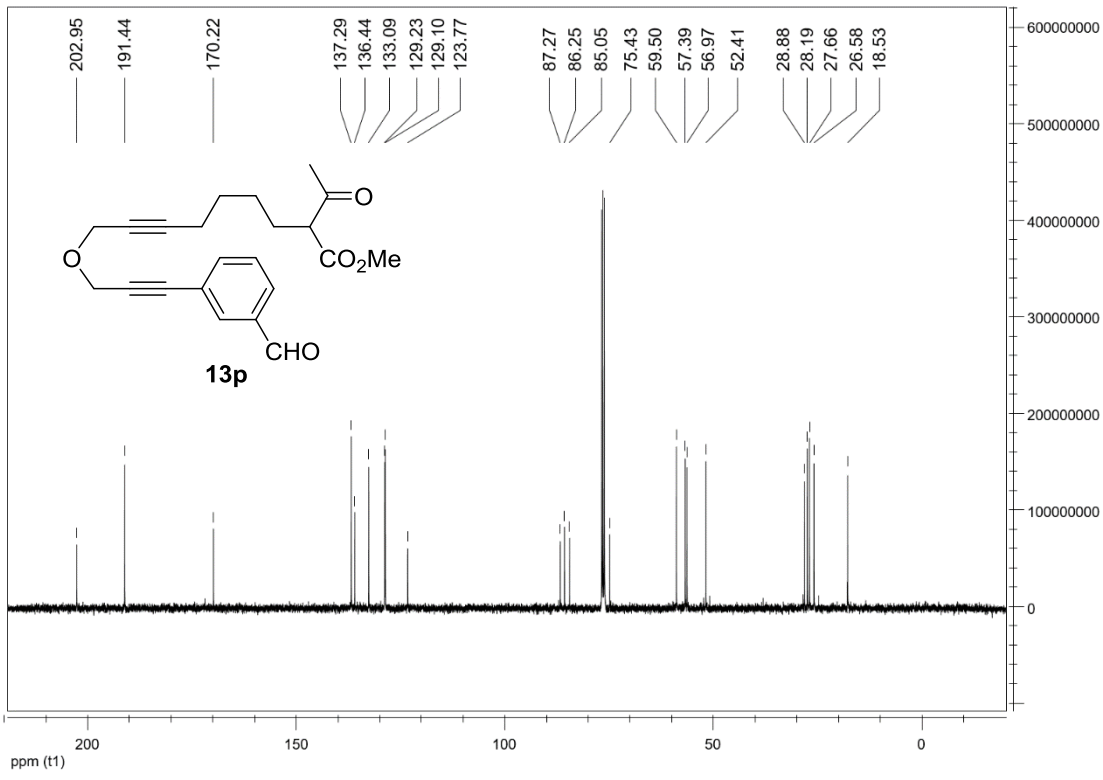
ppm (t1)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57.39
56.97
52.41
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28.19
27.66
26.58
18.53
O
CO2Me
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CHO
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50
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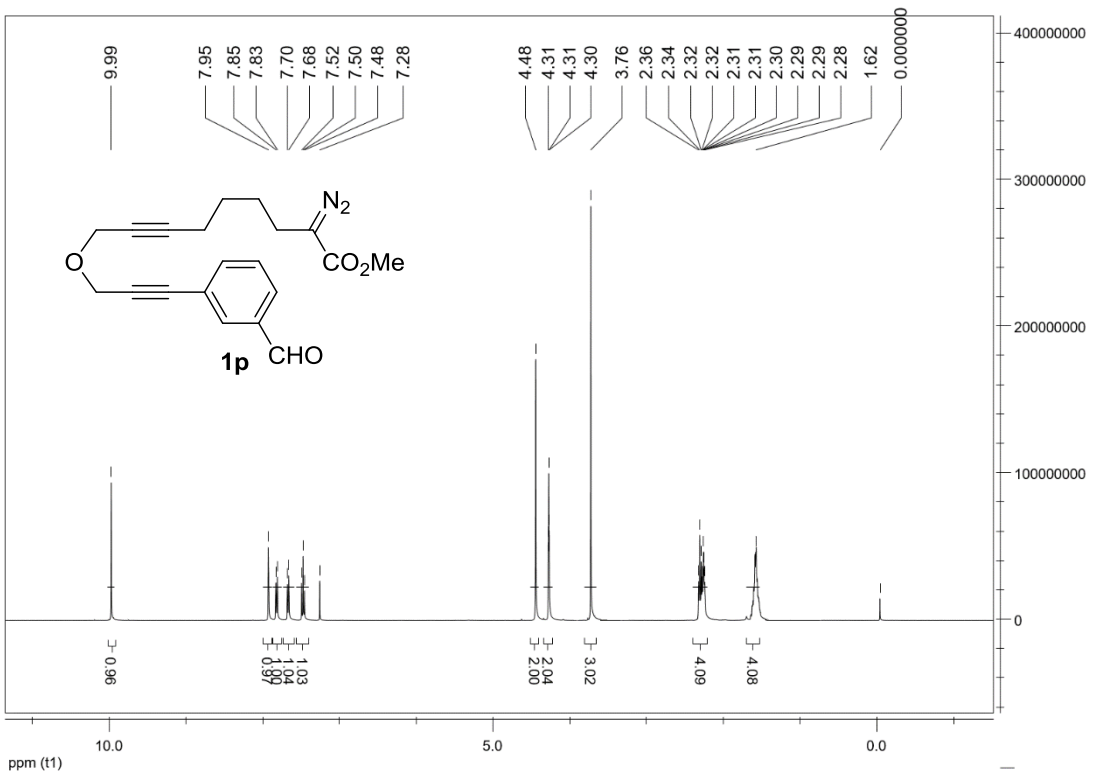
ppm (t1)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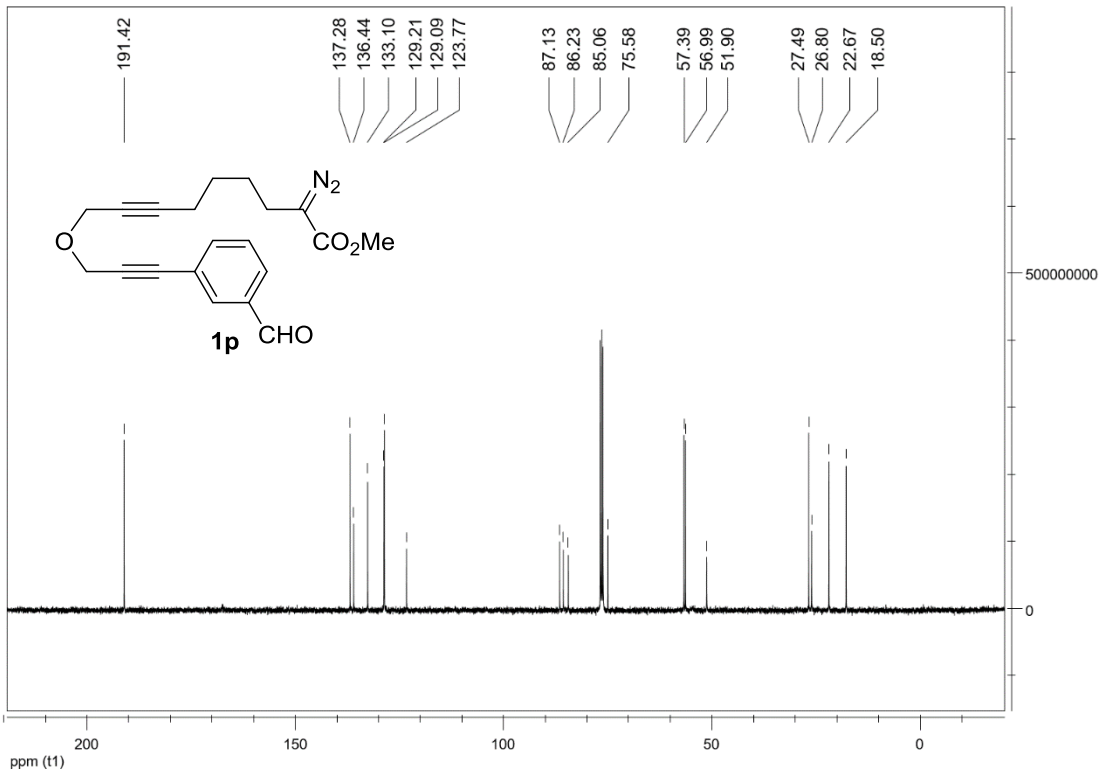
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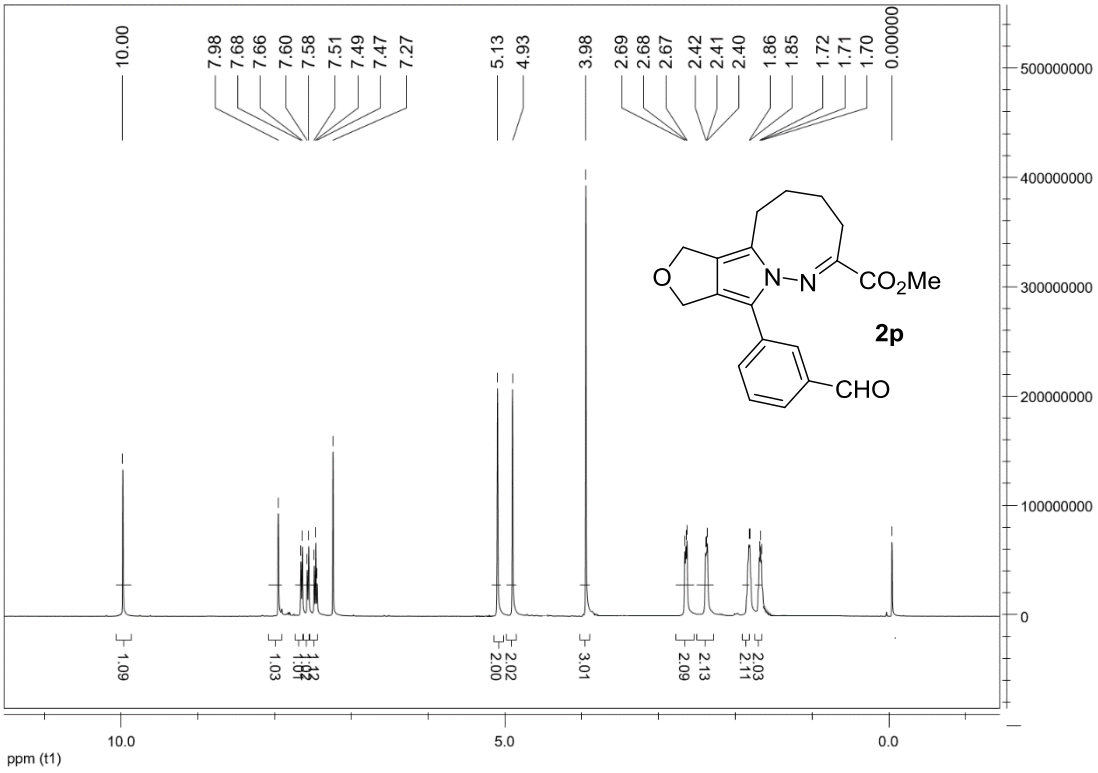
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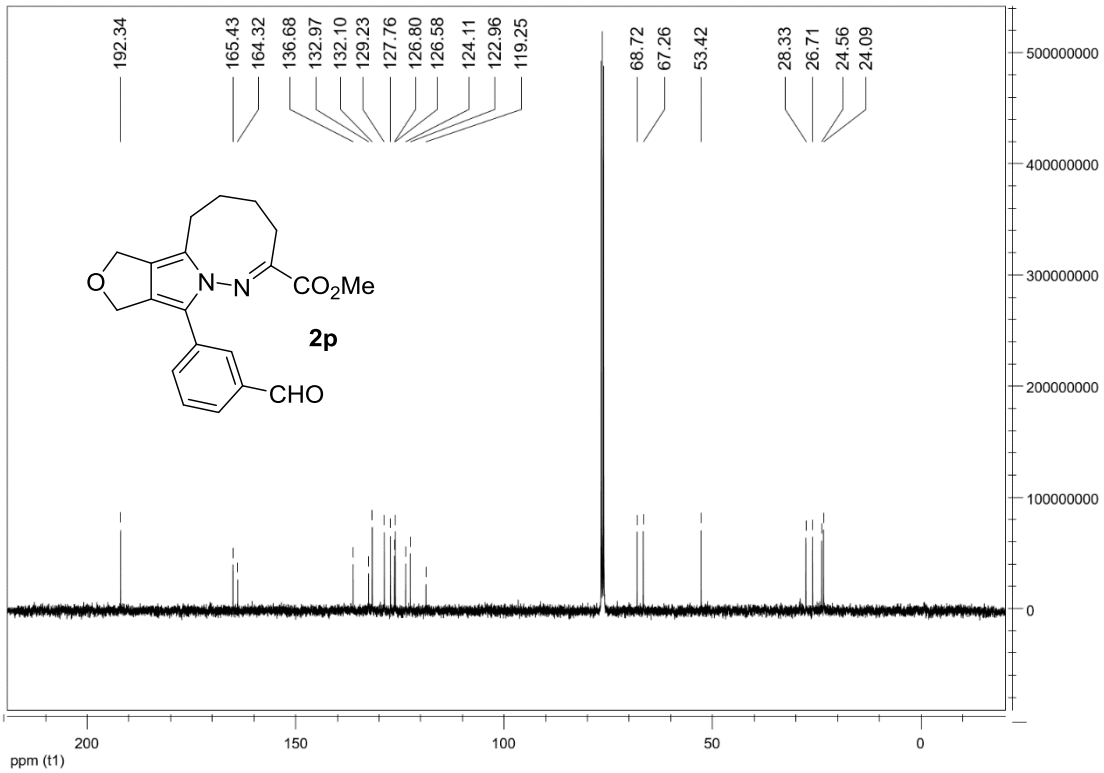
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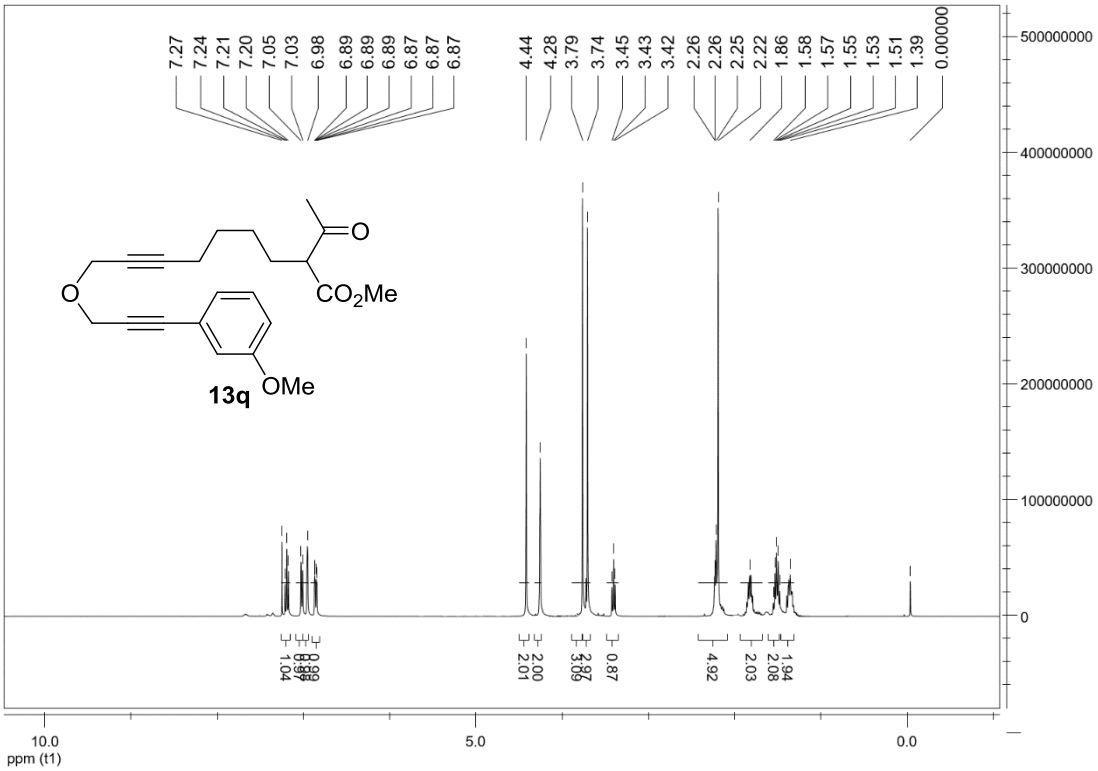
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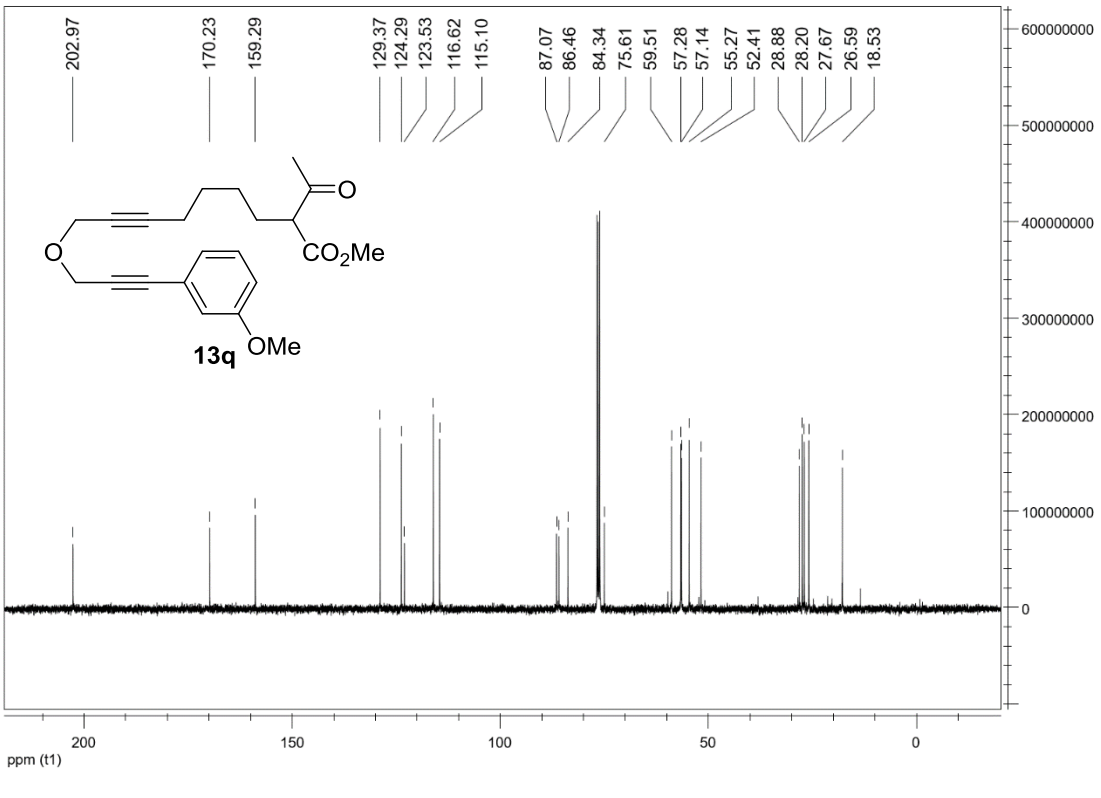
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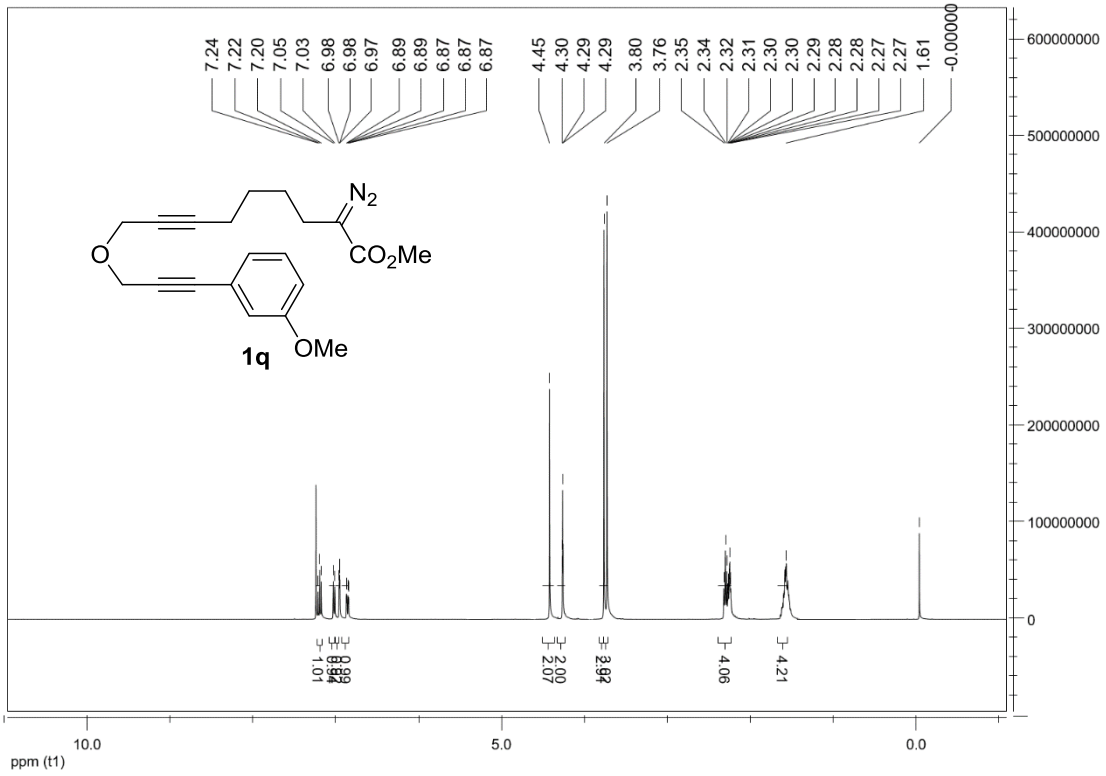
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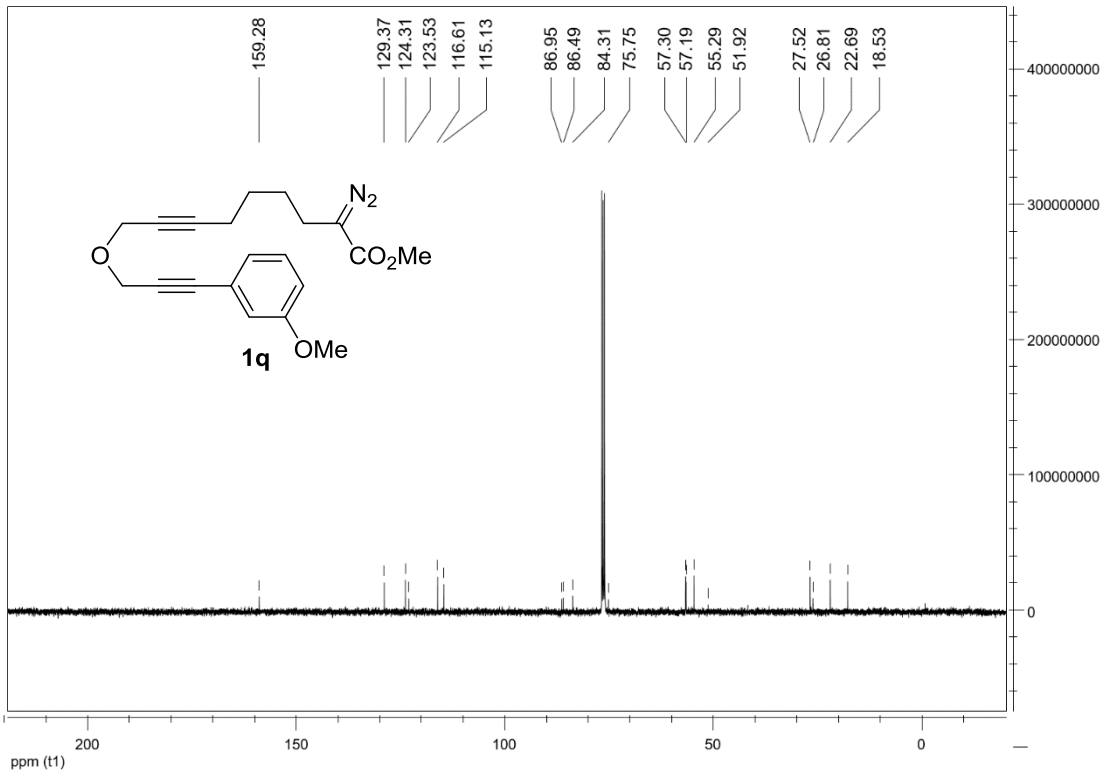
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OMe
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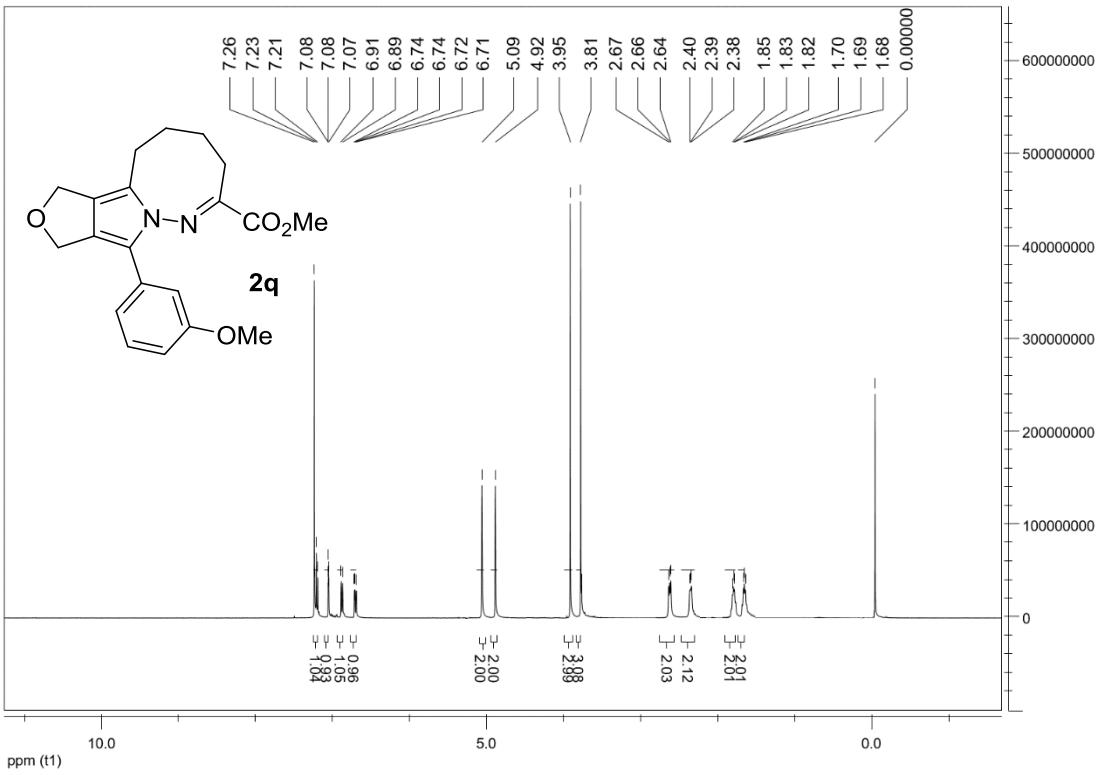
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OMe
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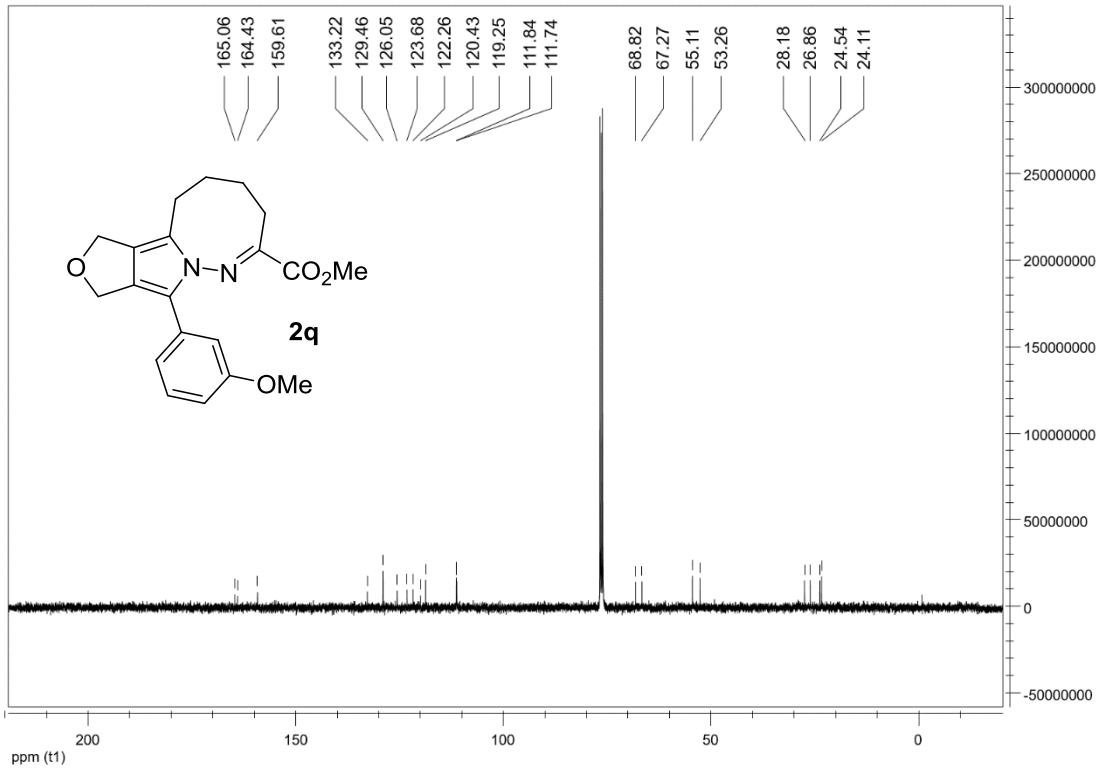
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N
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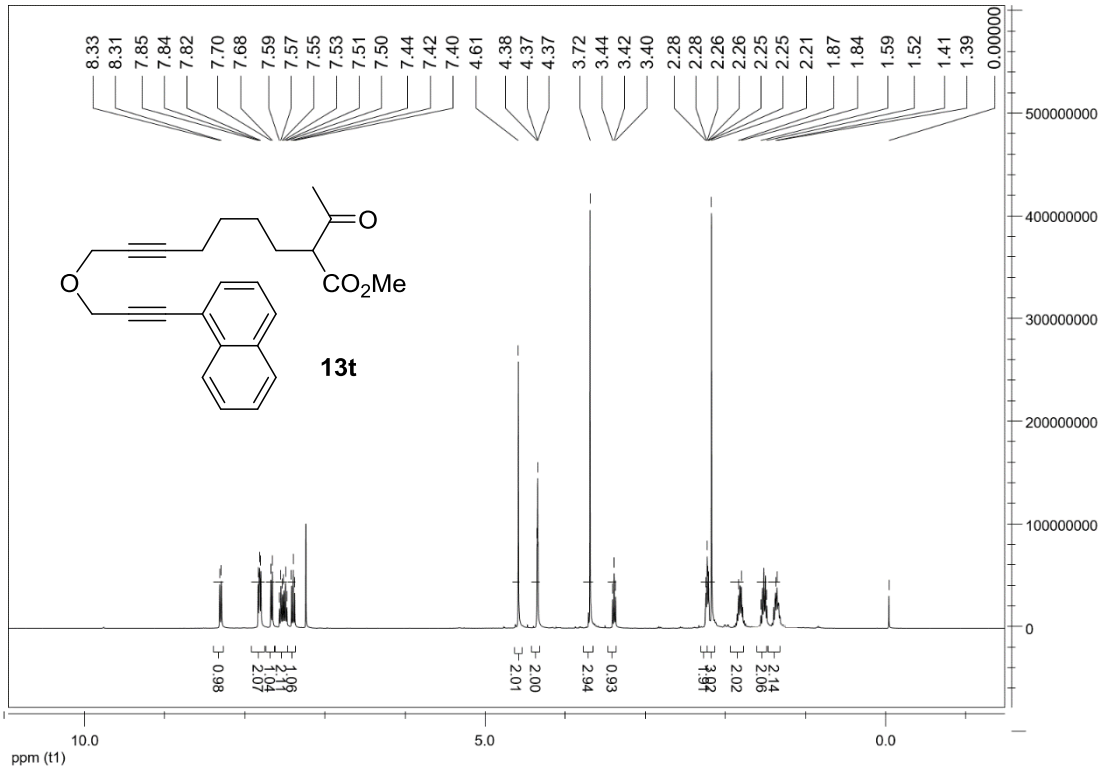
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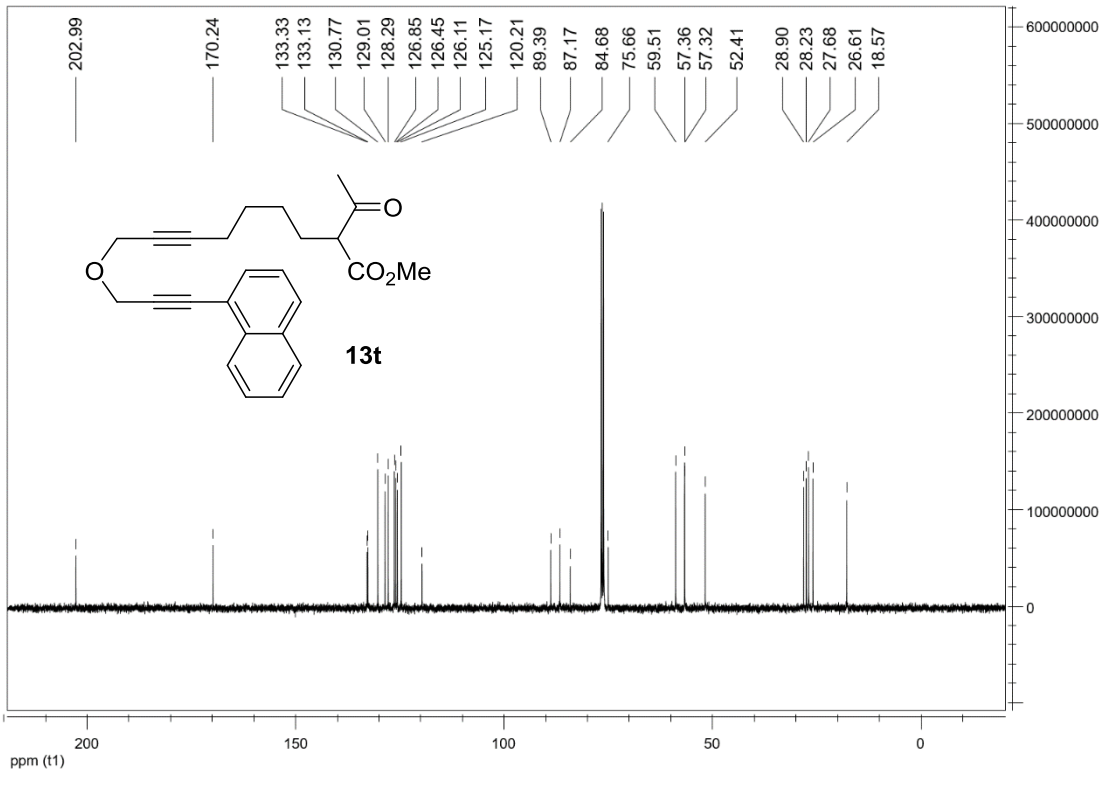
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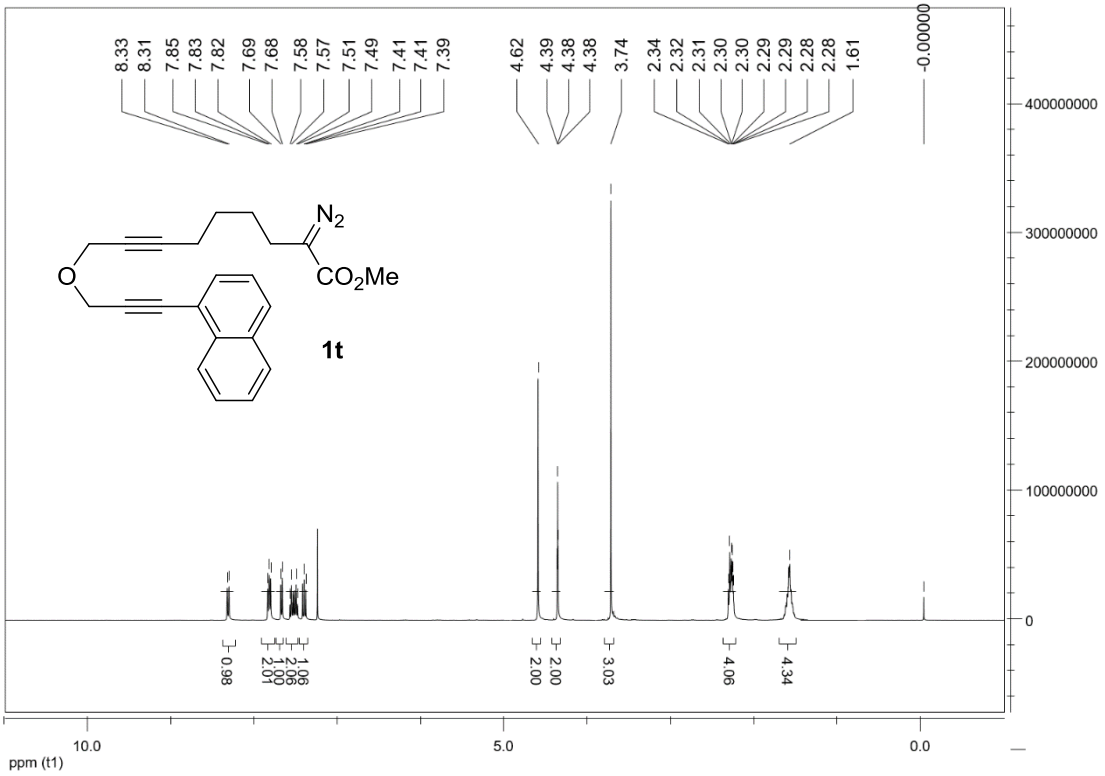
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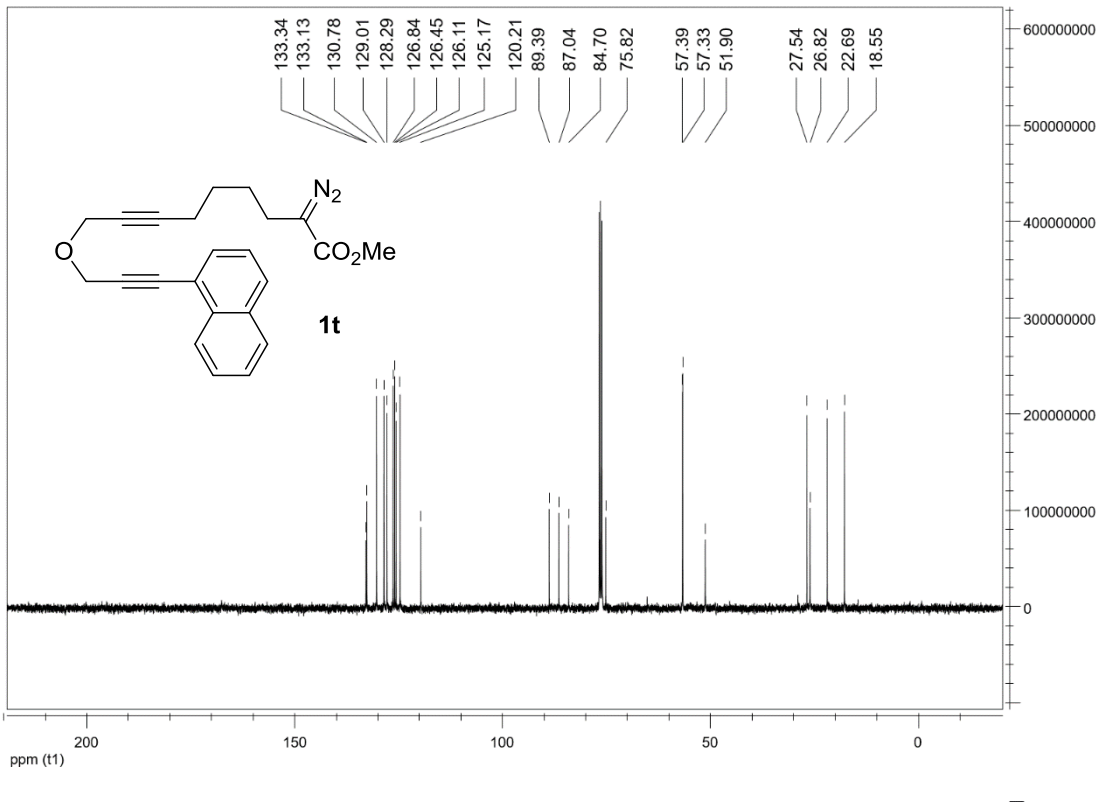
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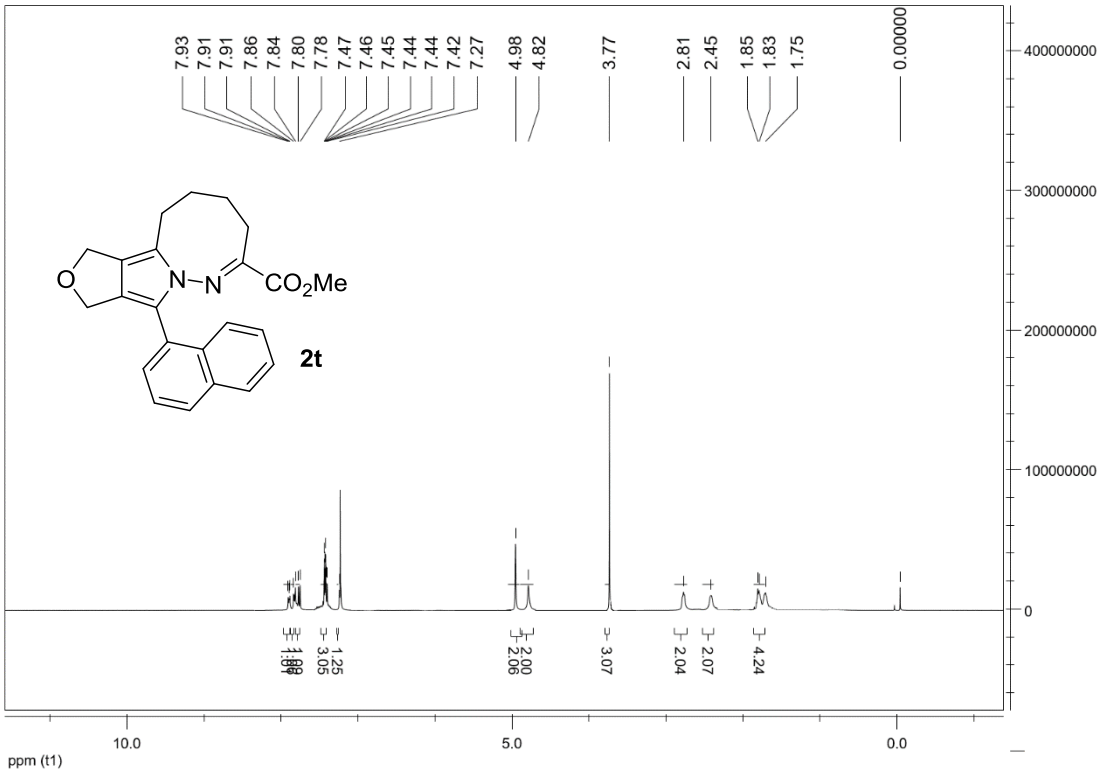
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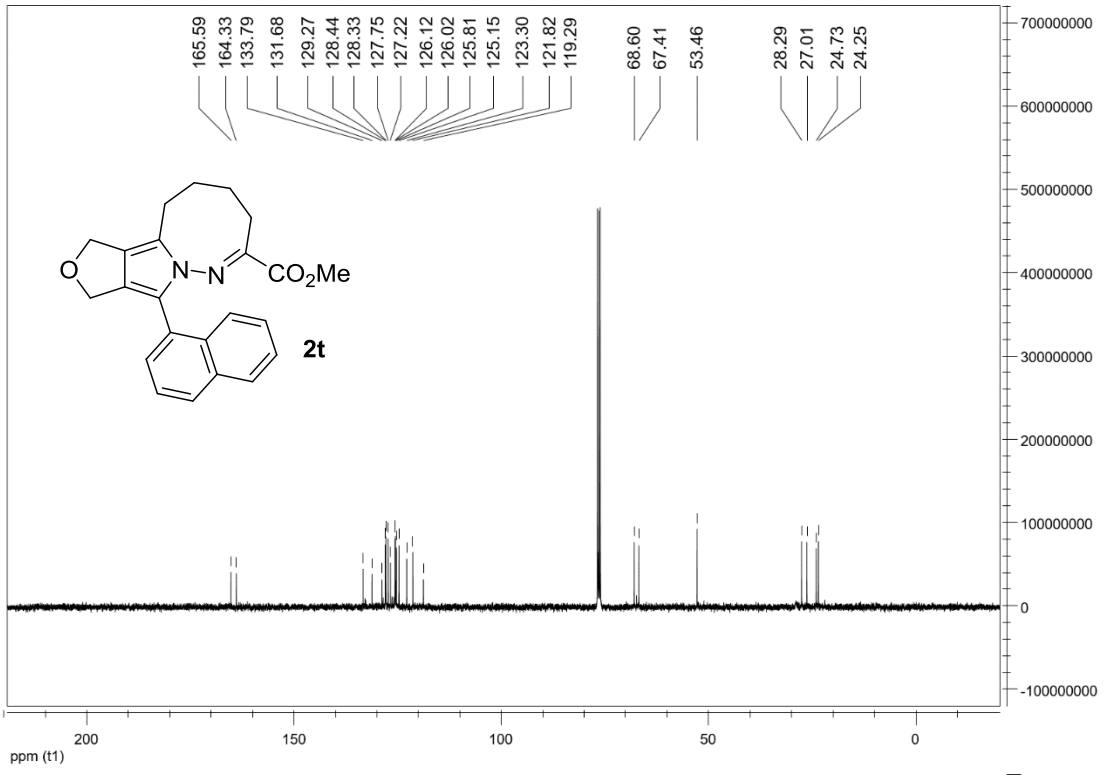
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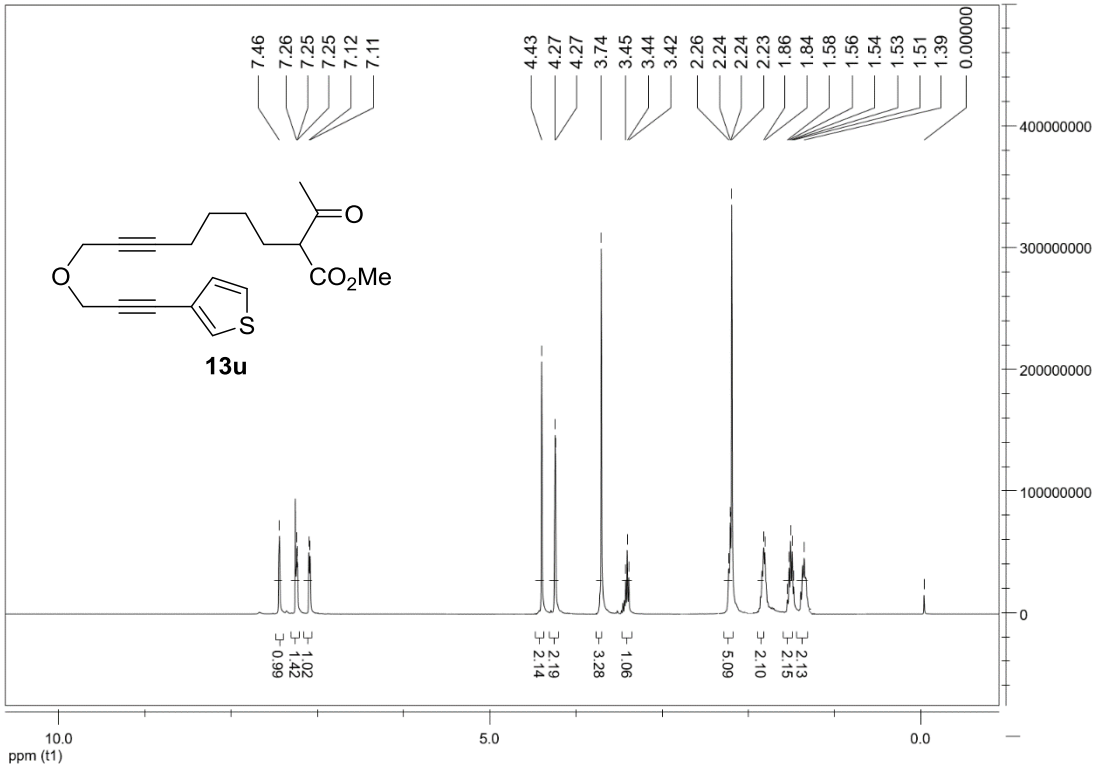
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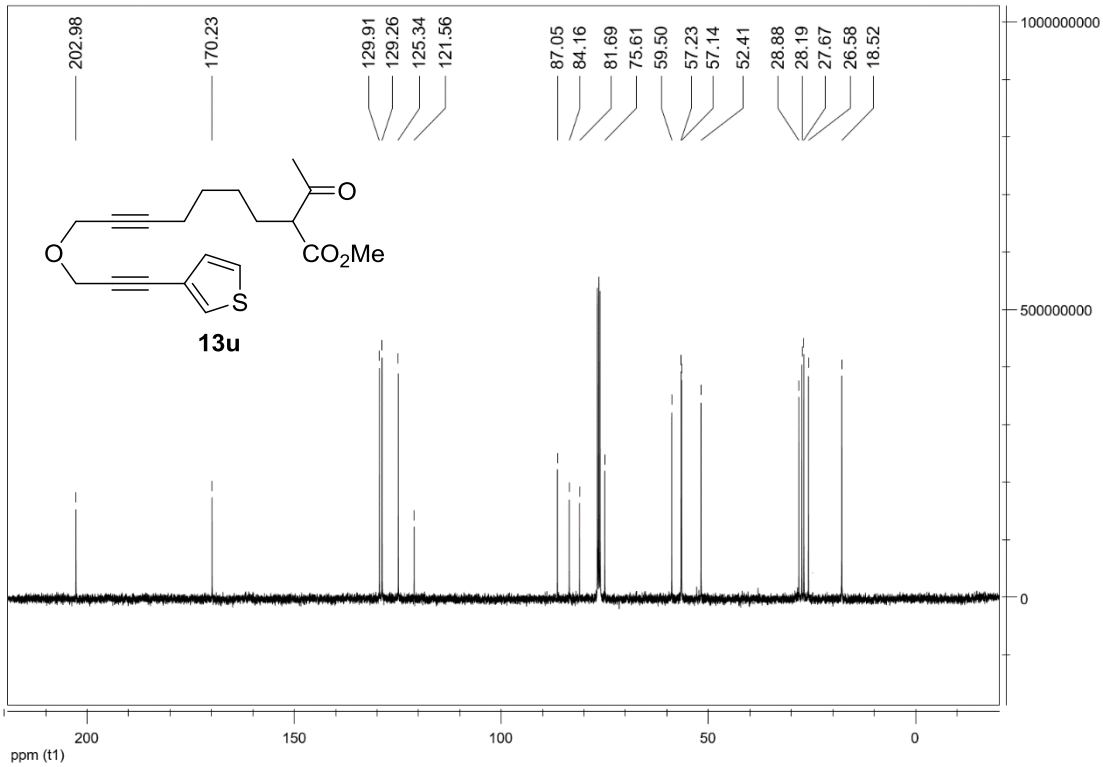
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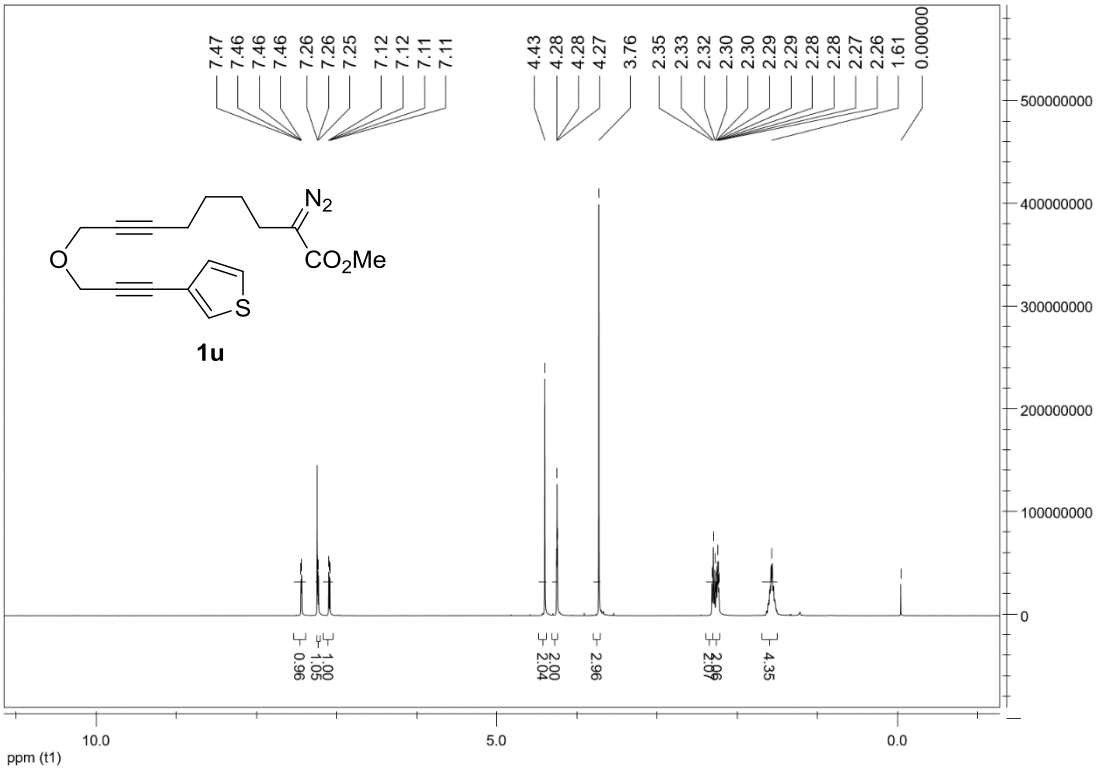
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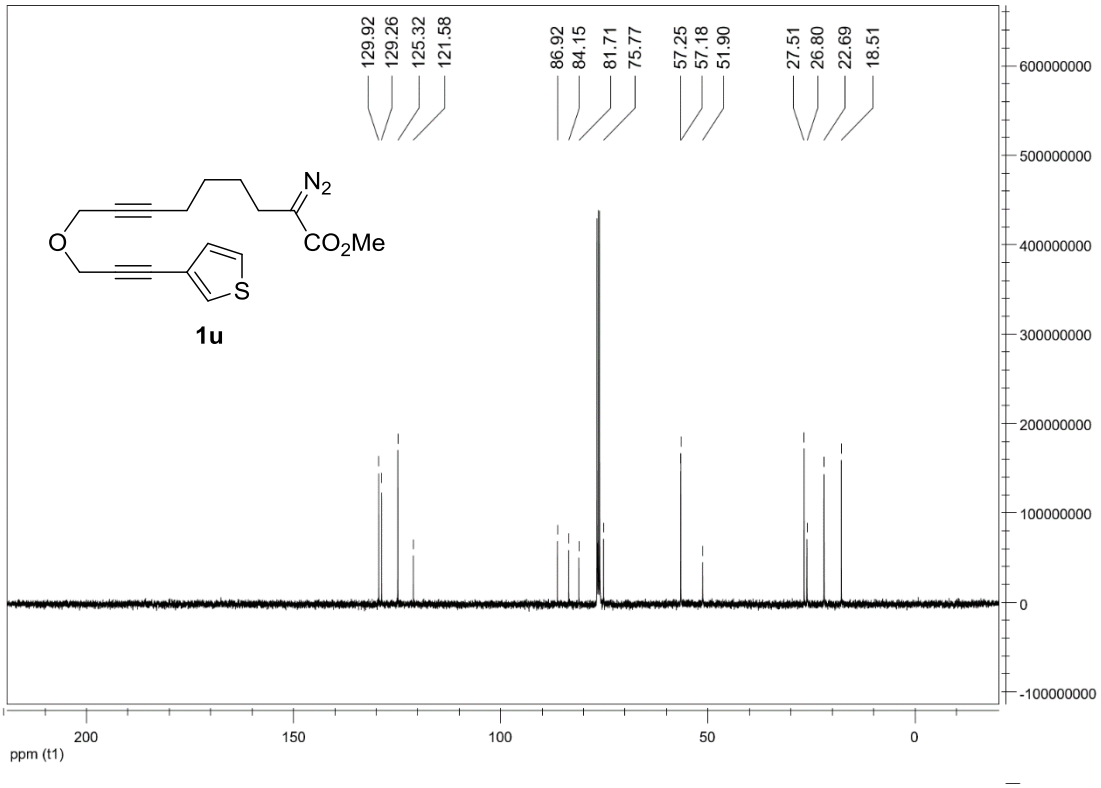
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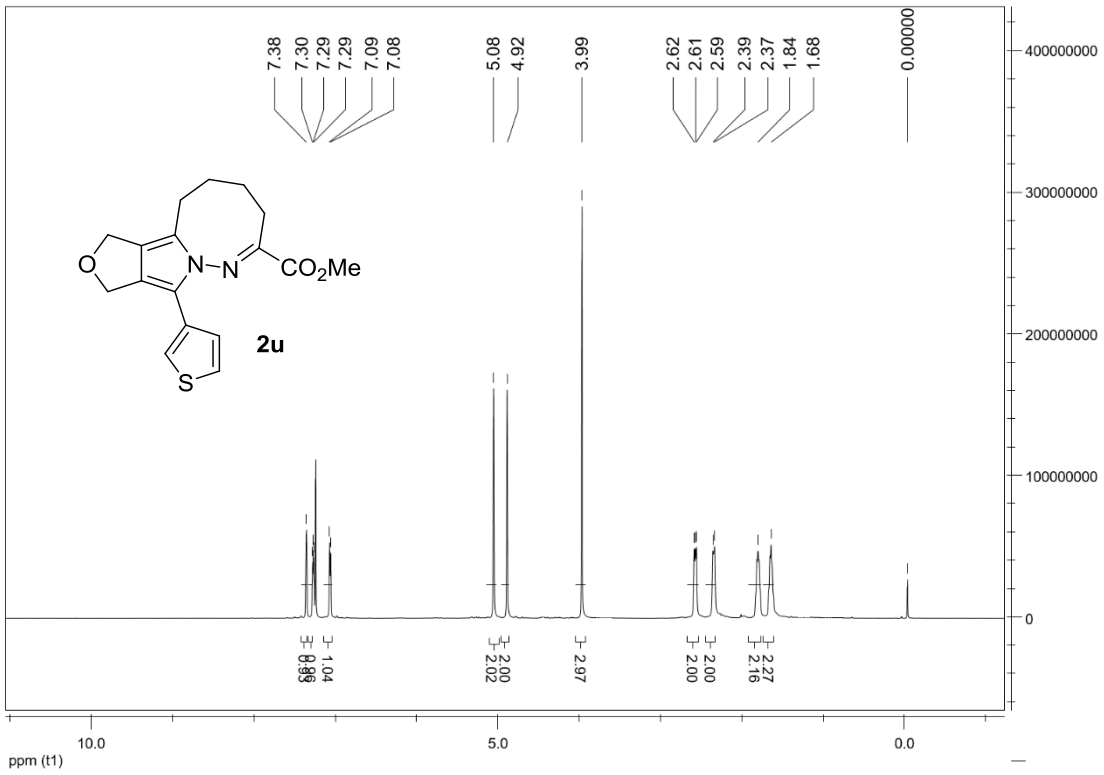
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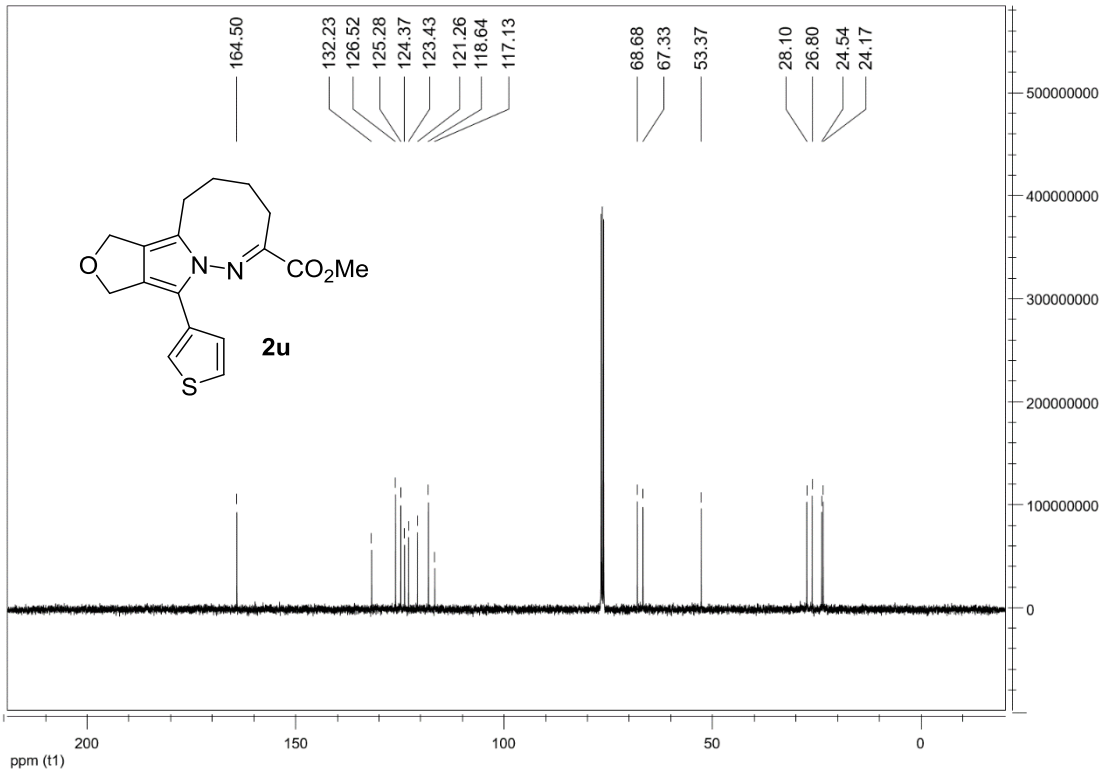
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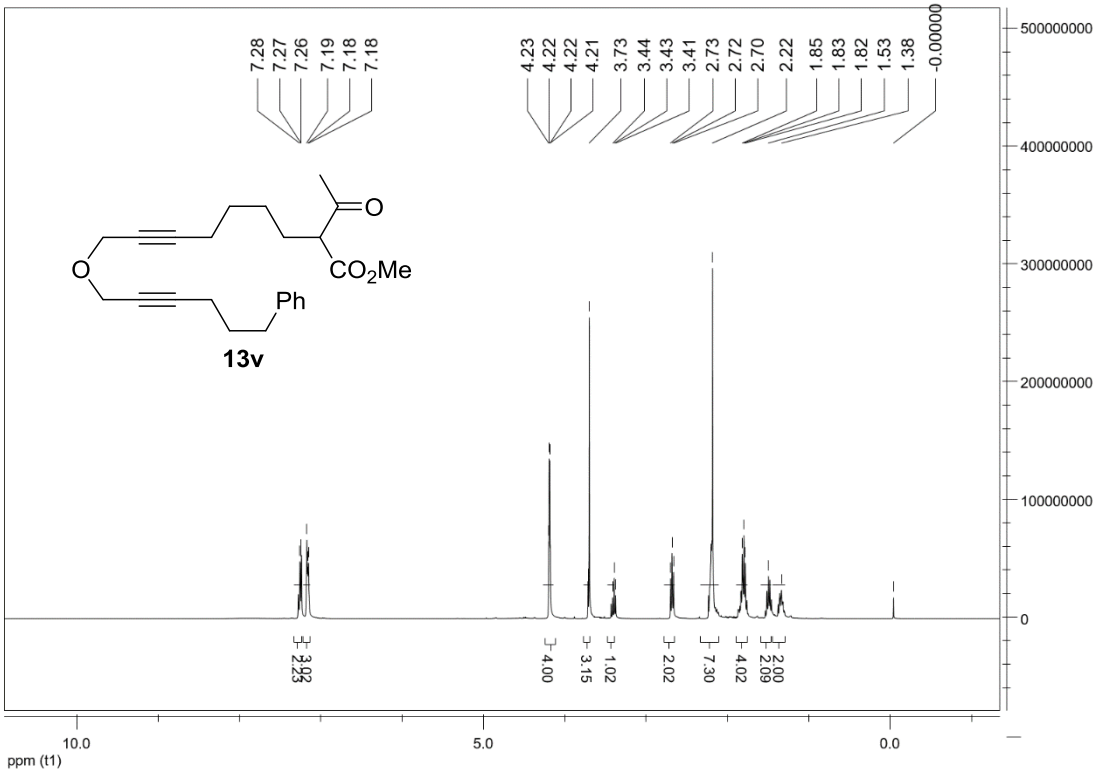
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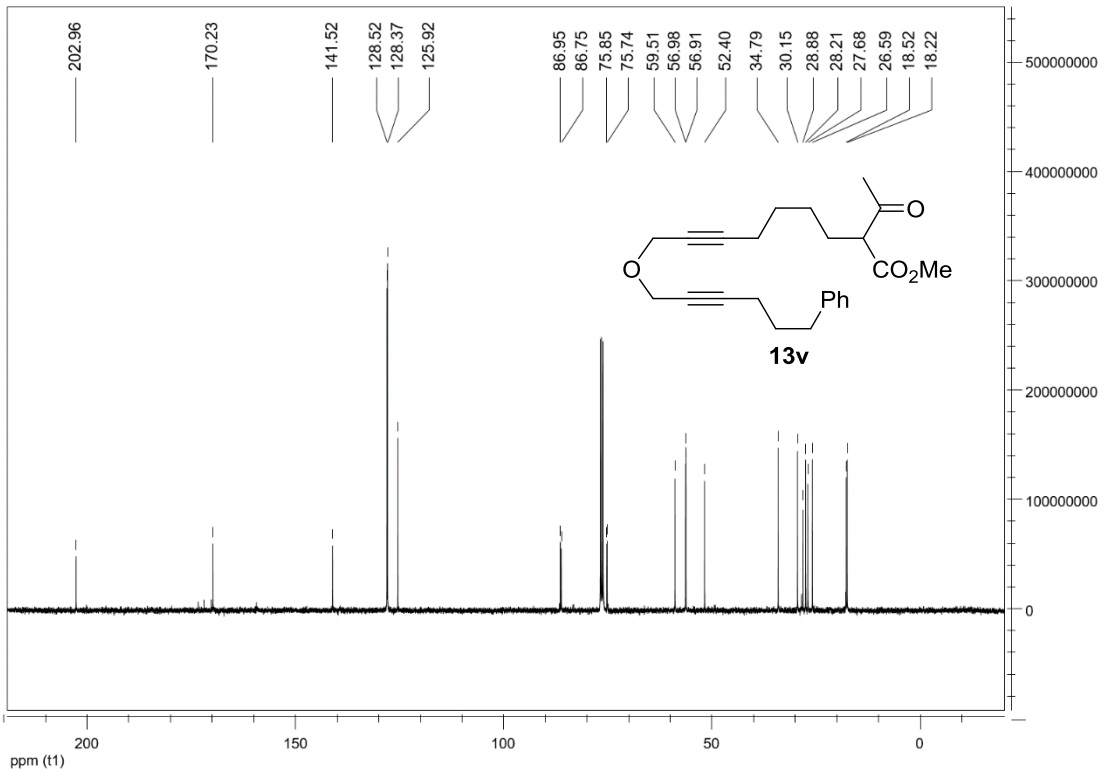
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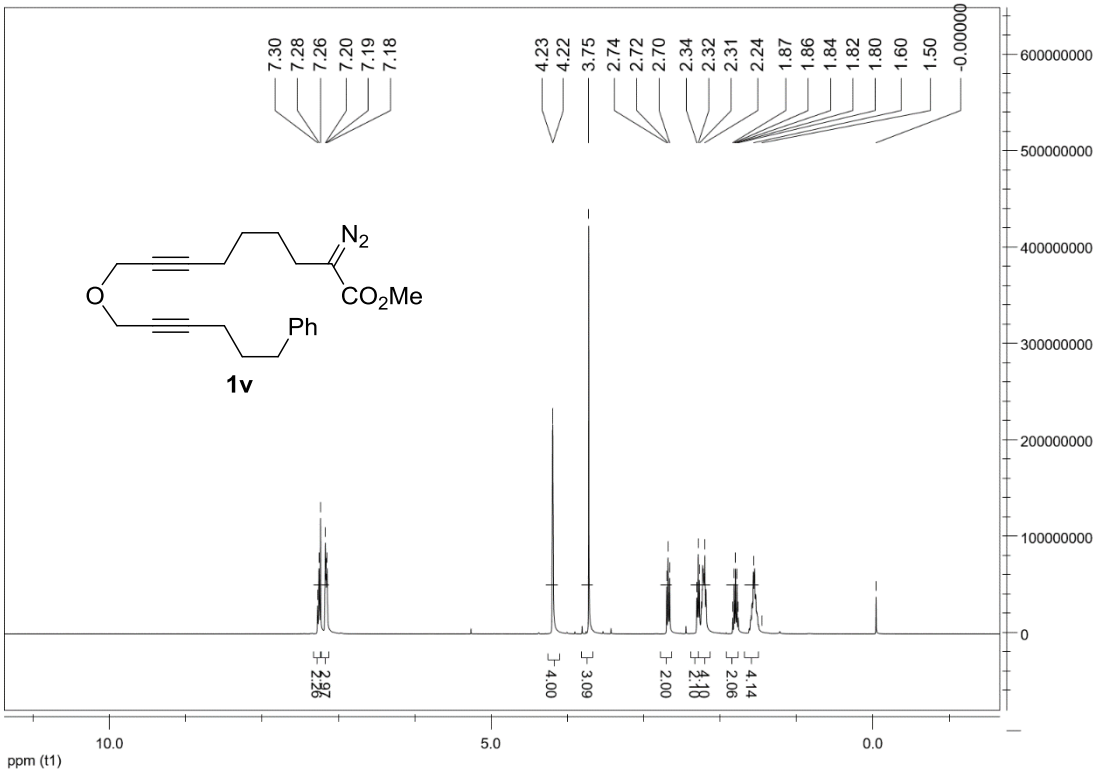
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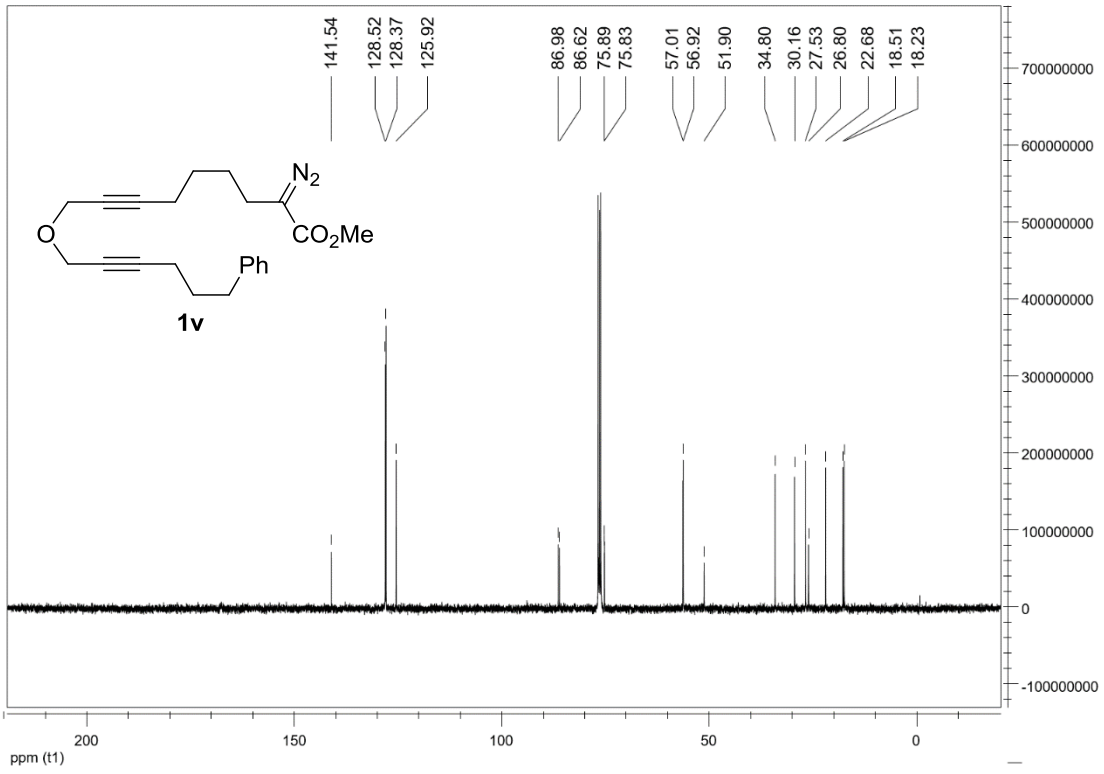
ppm (t1)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75.83
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56.92
51.90
34.80
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27.53
26.80
22.68
18.51
18.23
N2
CO2Me
O
Ph
1v
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400000000
300000000
200000000
100000000
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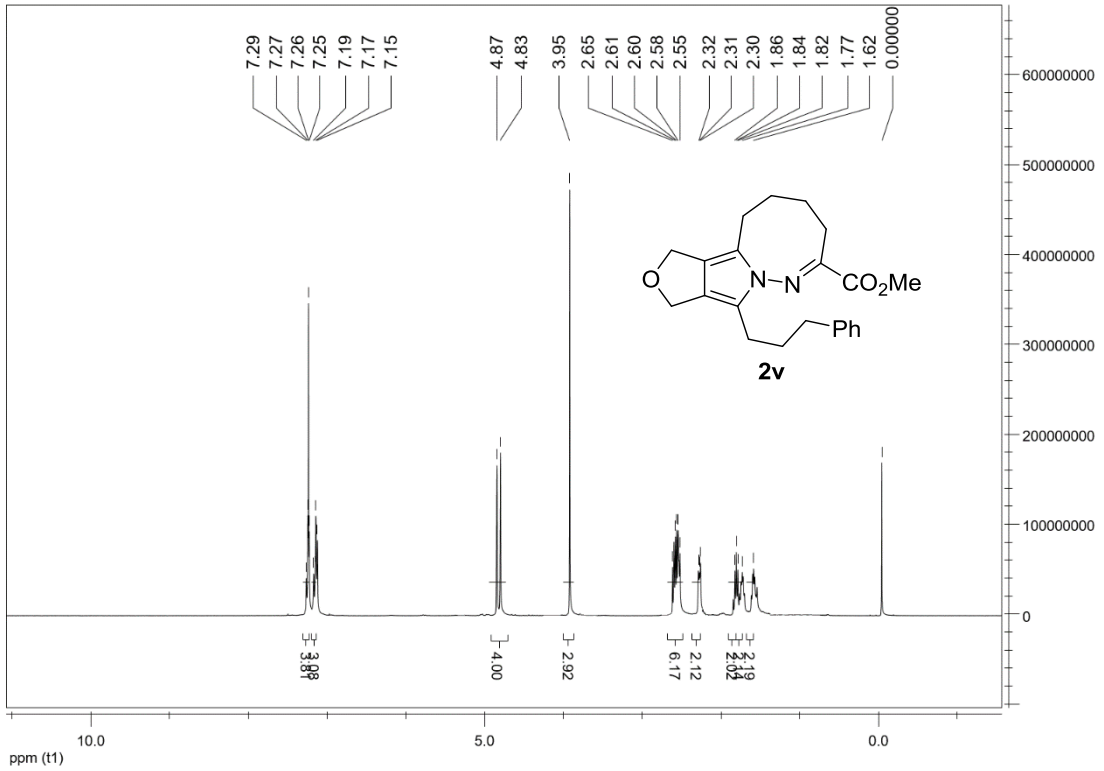
100
50
0
ppm (t1)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2.60
2.58
2.55
2.32
2.31
2.30
1.86
1.84
1.82
1.77
1.62
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500000000
400000000
300000000
200000000
100000000
0
3.08
4.00
2.92
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2.02
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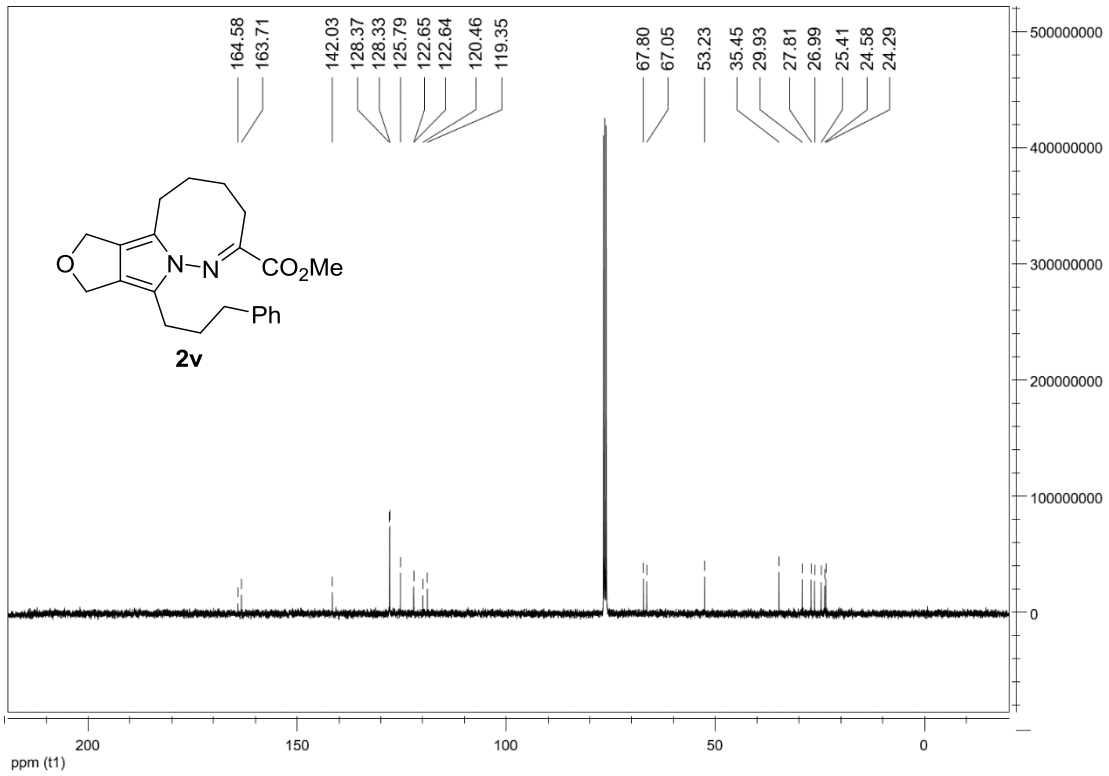
5.0
0.0
ppm (t1)
O
N
N
CO2Me
Ph
2v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122.64
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35.45
29.93
27.81
26.99
25.41
24.58
24.29
500000000
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100
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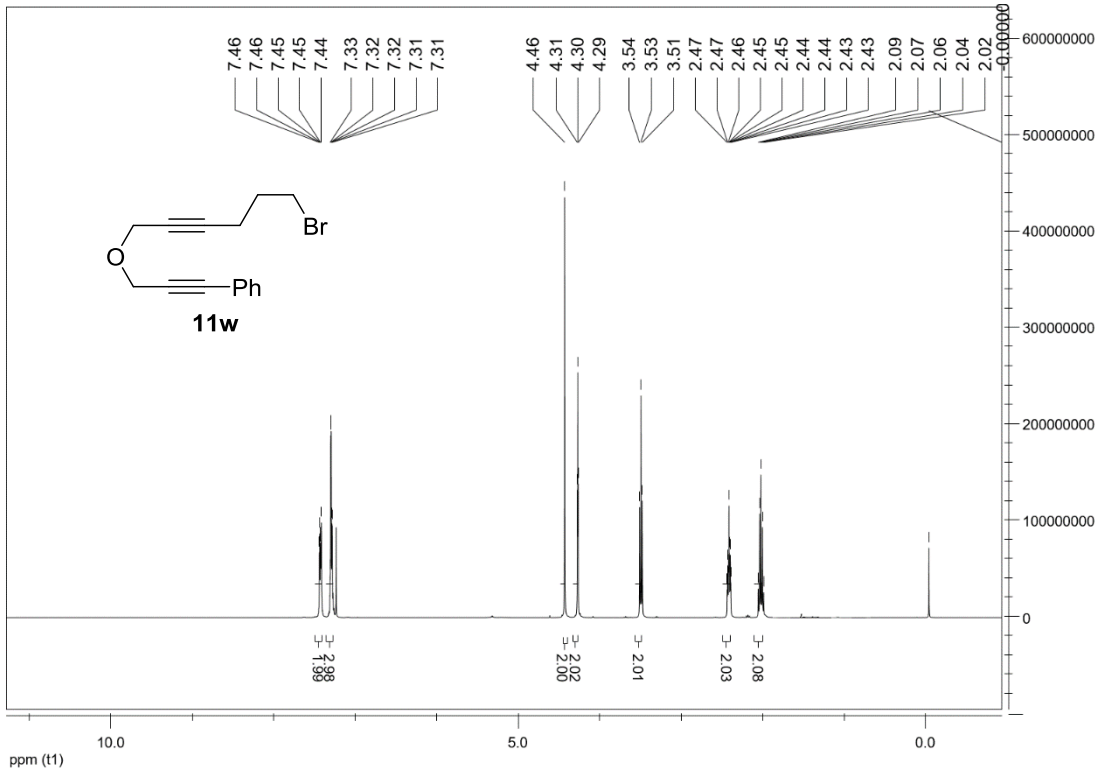
N
CO2Me
Ph
2v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7.45
7.45
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7.32
7.32
7.31
7.31
4.46
4.31
4.30
4.29
3.54
3.53
3.51
2.47
2.47
2.46
2.45
2.45
2.44
2.44
2.43
2.43
2.09
2.07
2.06
2.04
2.02
0.00000
Br
O
Ph
11w
1.98
1.99
2.02
2.00
2.01
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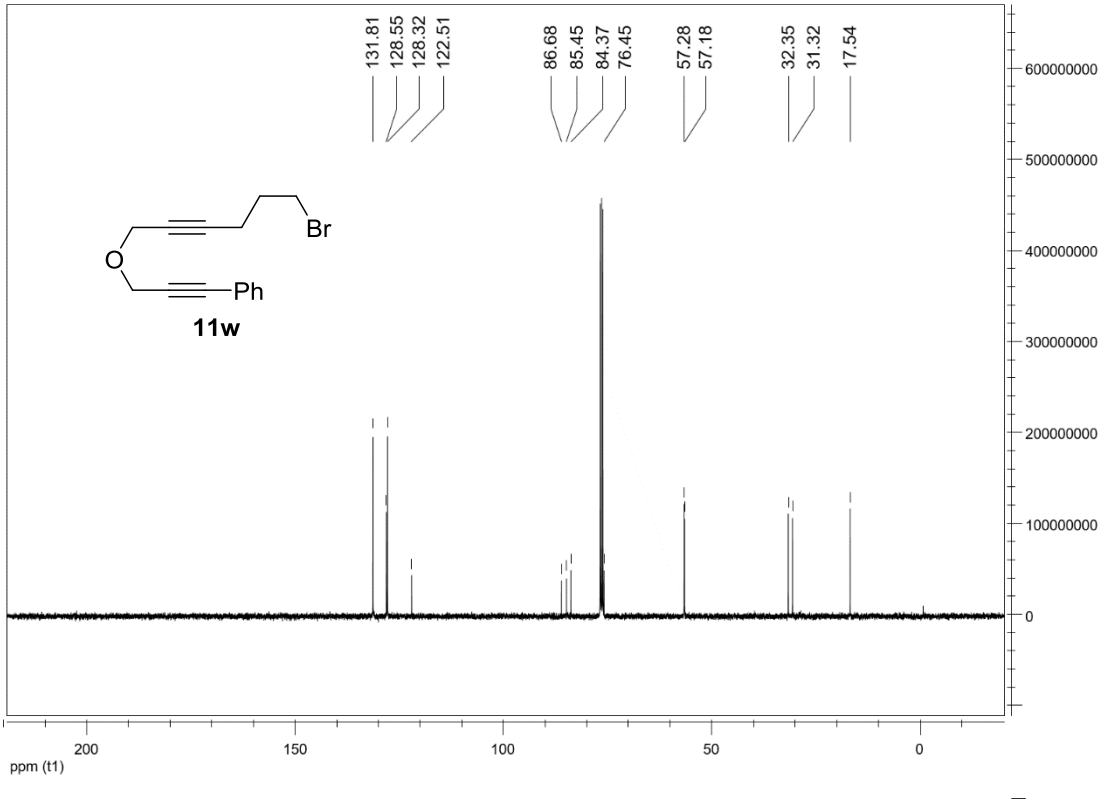
5.0
0.0
ppm (t1)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85.45
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32.35
31.32
17.54
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O
Ph
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400000000
300000000
200000000
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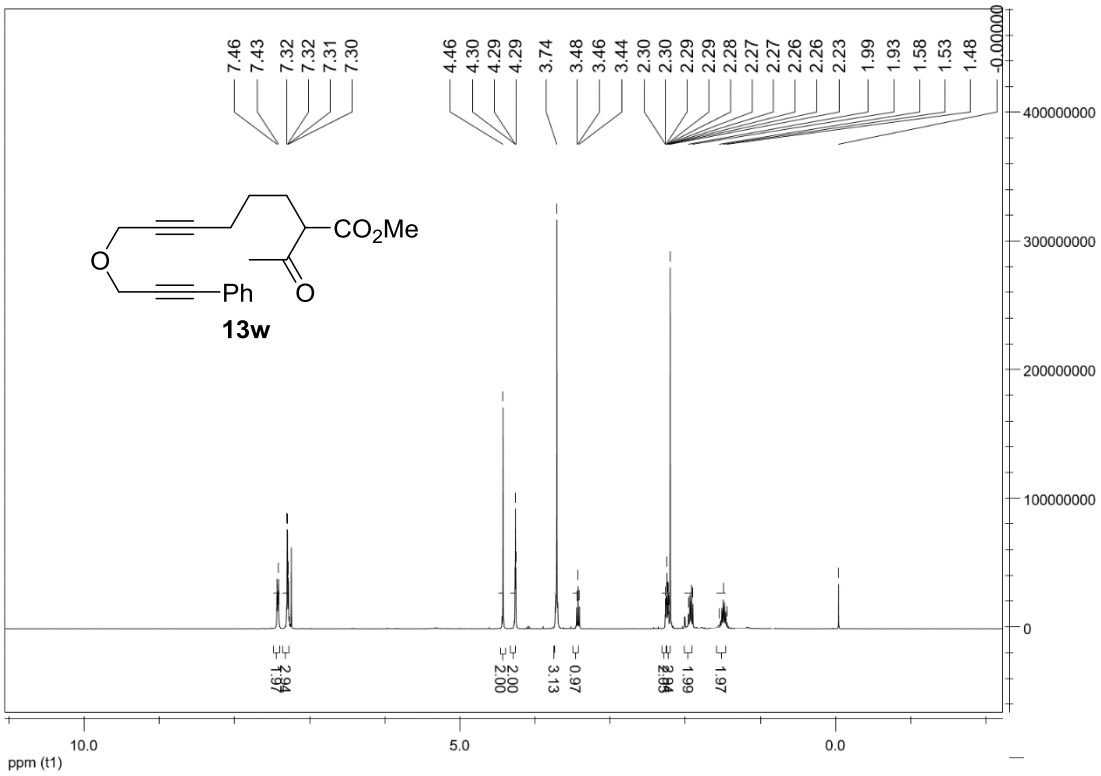
150
100
50
0
ppm (t1)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4.29
4.29
3.74
3.48
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3.44
2.30
2.30
2.29
2.29
2.28
2.27
2.27
2.26
2.26
2.23
1.99
1.93
1.58
1.53
1.48
0.00000
CO2Me
O
Ph
O
13w
400000000
300000000
200000000
100000000
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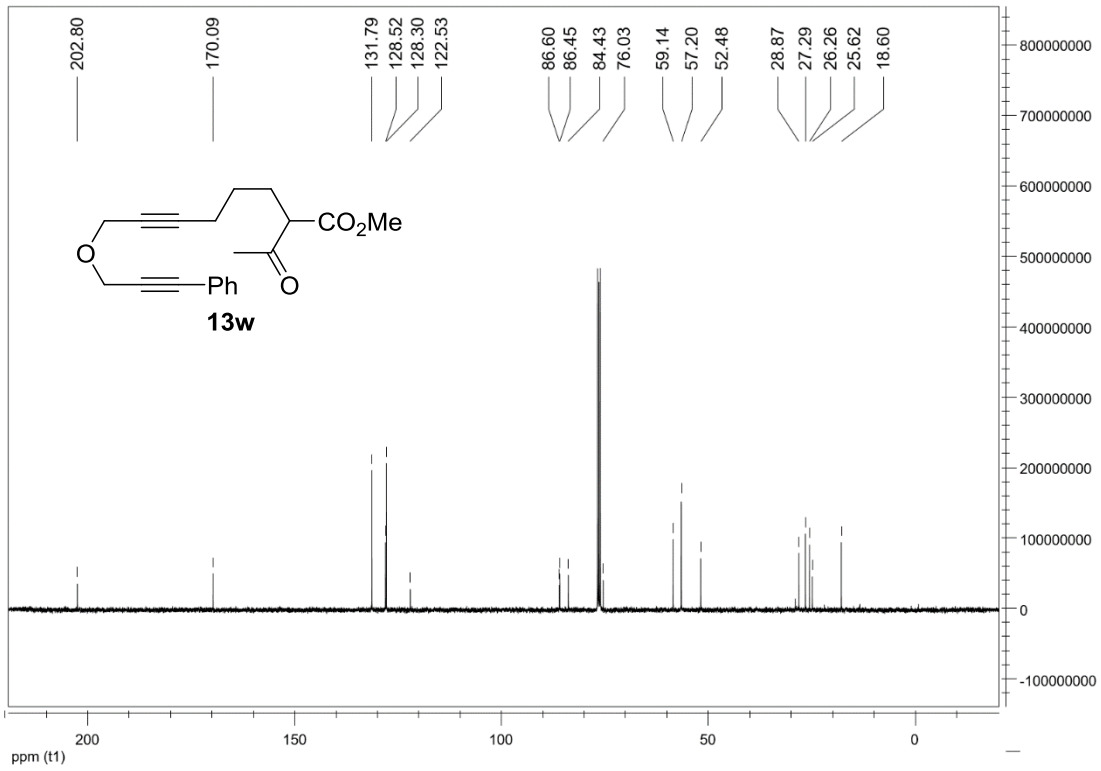
ppm (t1)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86.60
86.45
84.43
76.03
59.14
57.20
52.48
28.87
27.29
26.26
25.62
18.60
CO2Me
O
Ph
O
13w
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400000000
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150
100
50
0
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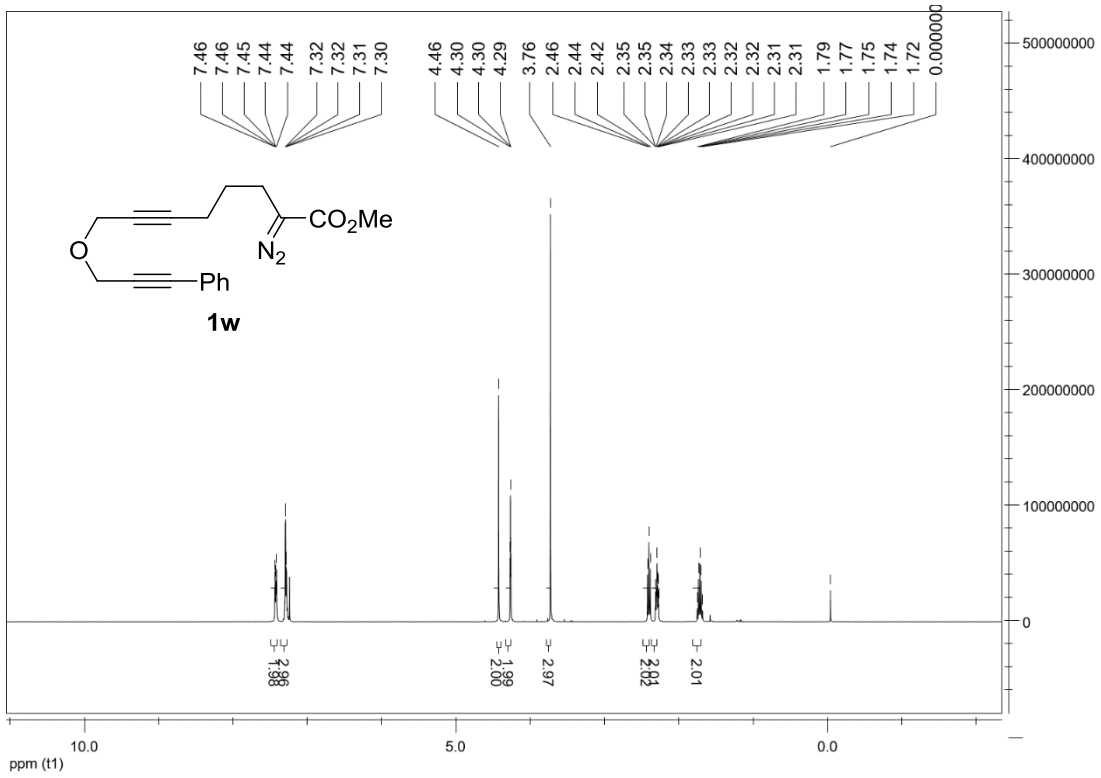
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7.32
7.31
7.30
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4.30
4.30
4.29
3.76
2.46
2.44
2.42
2.35
2.35
2.34
2.33
2.33
2.32
2.32
2.31
2.31
1.79
1.77
1.75
1.74
1.72
0.000000
CO2Me
N2
O
Ph
1w
2.88
2.88
1.99
2.00
2.97
2.02
2.01
500000000
400000000
300000000
200000000
100000000
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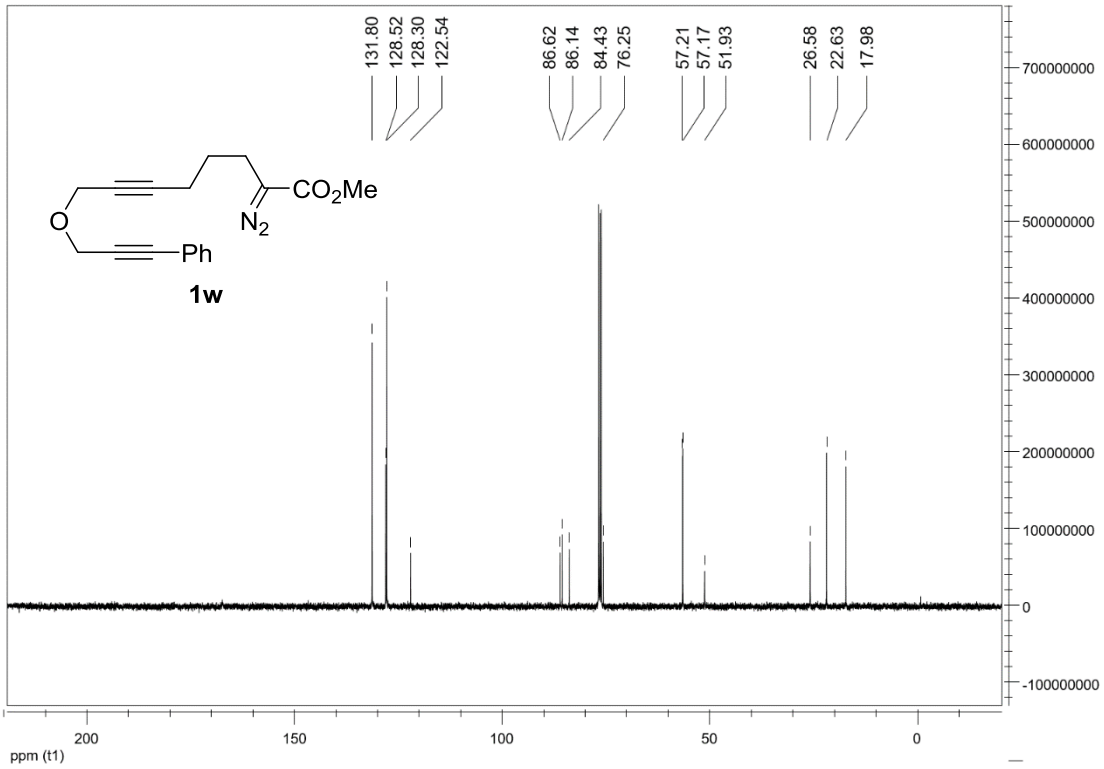
5.0
0.0
ppm (t1)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86.14
84.43
76.25
57.21
57.17
51.93
26.58
22.63
17.98
CO2Me
N2
O
Ph
1w
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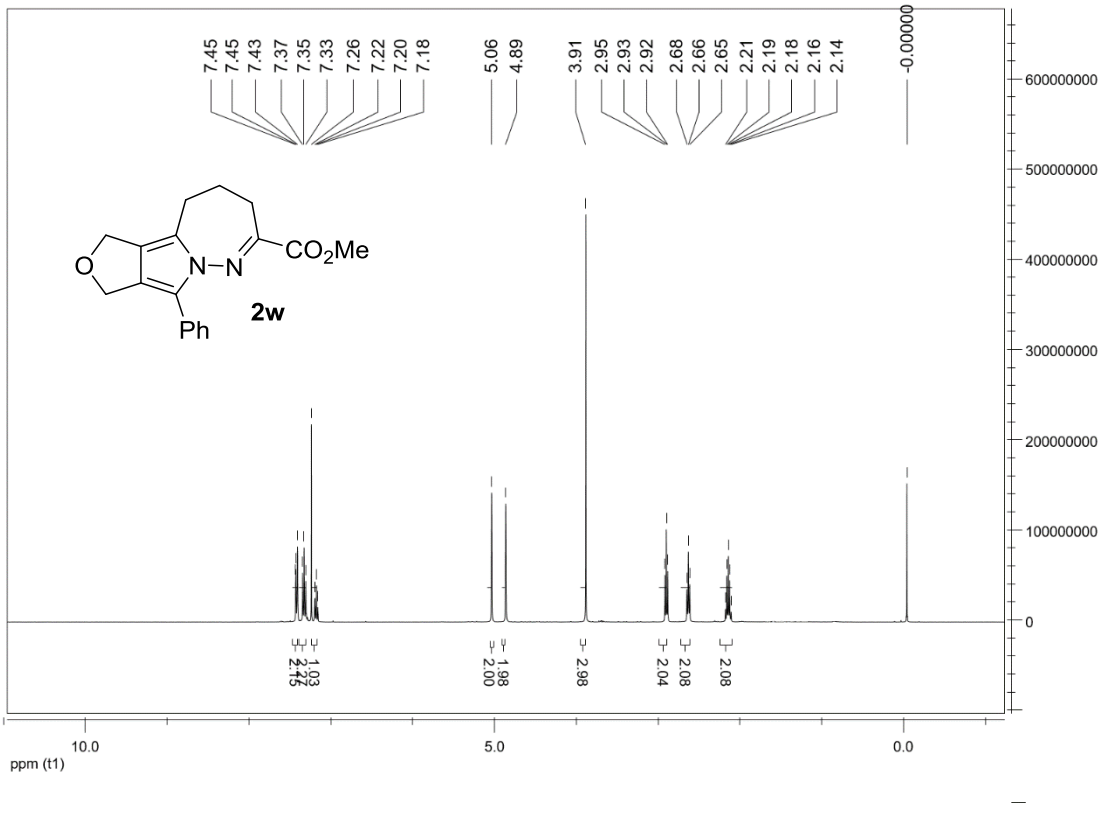
500000000
400000000
300000000
200000000
100000000
0
-100000000
200
150
100
50
0
ppm (t1)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7.45
7.43
7.37
7.35
7.33
7.26
7.22
7.20
7.18
5.06
4.89
3.91
2.95
2.93
2.92
2.68
2.66
2.65
2.21
2.19
2.18
2.16
2.14
-0.00000
CO2Me
N–N
O
Ph
2w
1.03
2.45
1.68
2.00
2.98
2.04
2.08
2.08
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500000000
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300000000
200000000
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10.0
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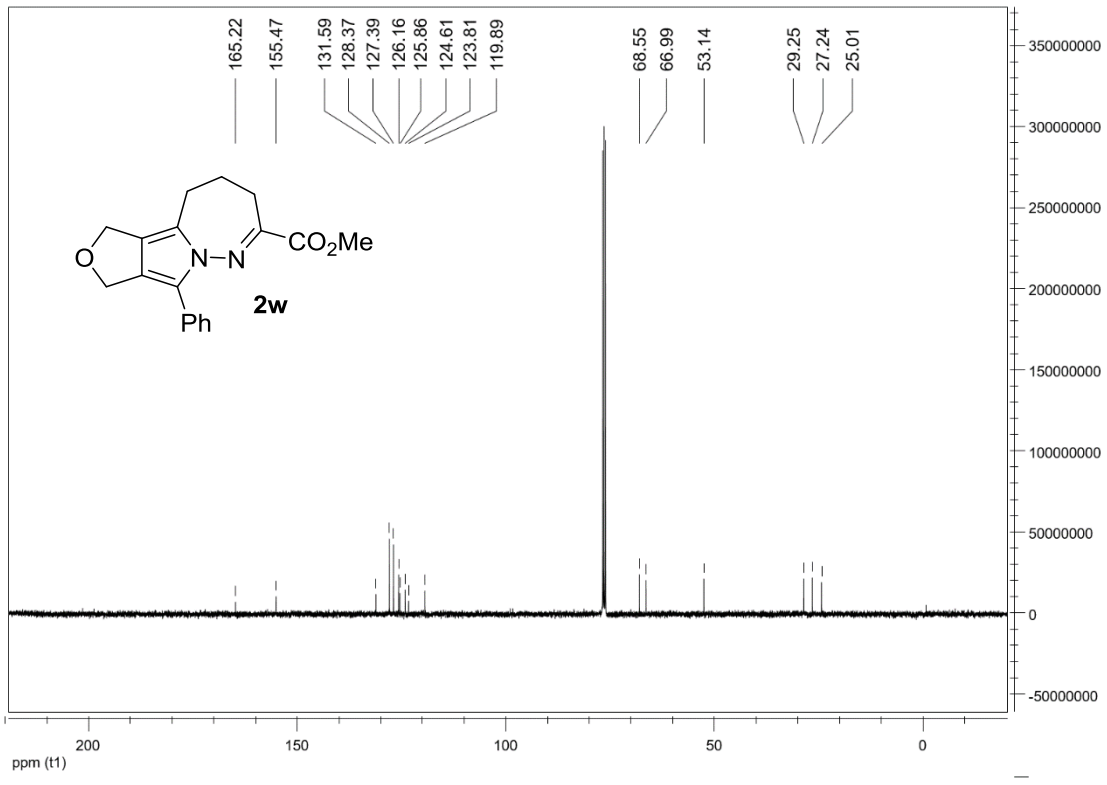
0.0
ppm (t1)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126.16
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124.61
123.81
119.89
68.55
66.99
53.14
29.25
27.24
25.01
CO2Me
N–N
O
Ph
2w
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200000000
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100000000
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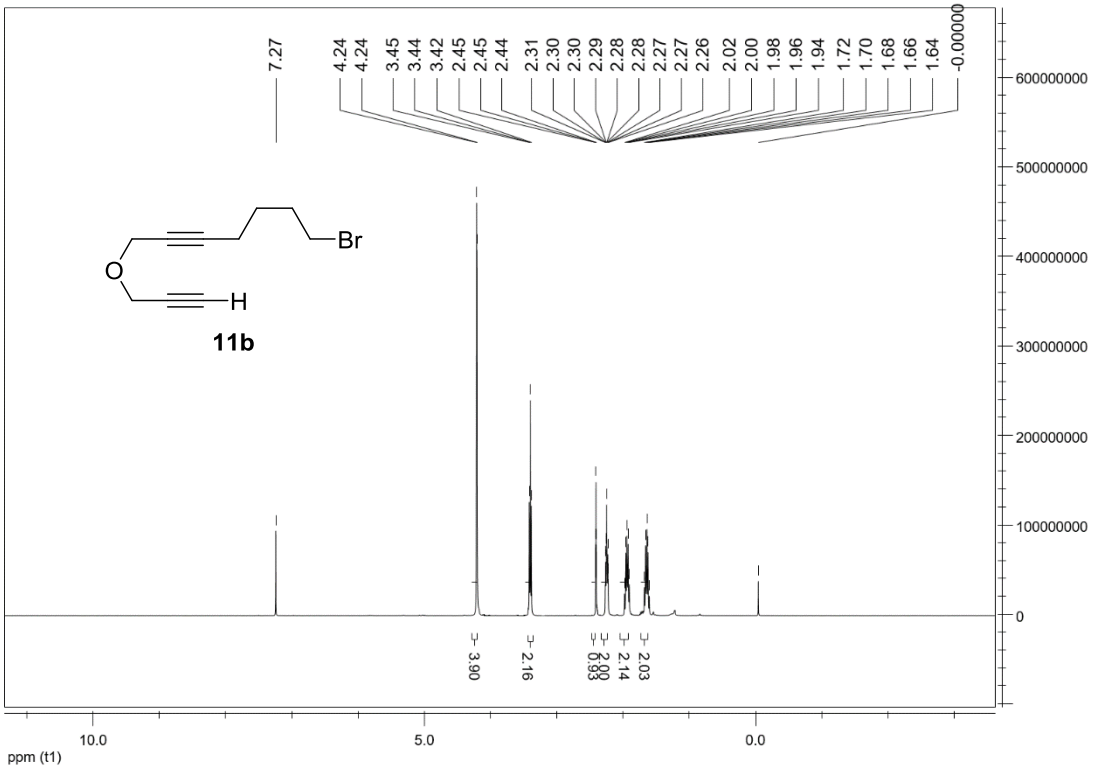
100
50
0
ppm (t1)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4.24
4.24
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3.44
3.42
2.45
2.45
2.44
2.31
2.30
2.30
2.29
2.28
2.28
2.27
2.27
2.26
2.02
2.00
1.98
1.96
1.94
1.72
1.70
1.68
1.66
1.64
-0.00000
Br
O
H
11b
3.00
2.16
2.00
2.03
2.14
2.03
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500000000
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200000000
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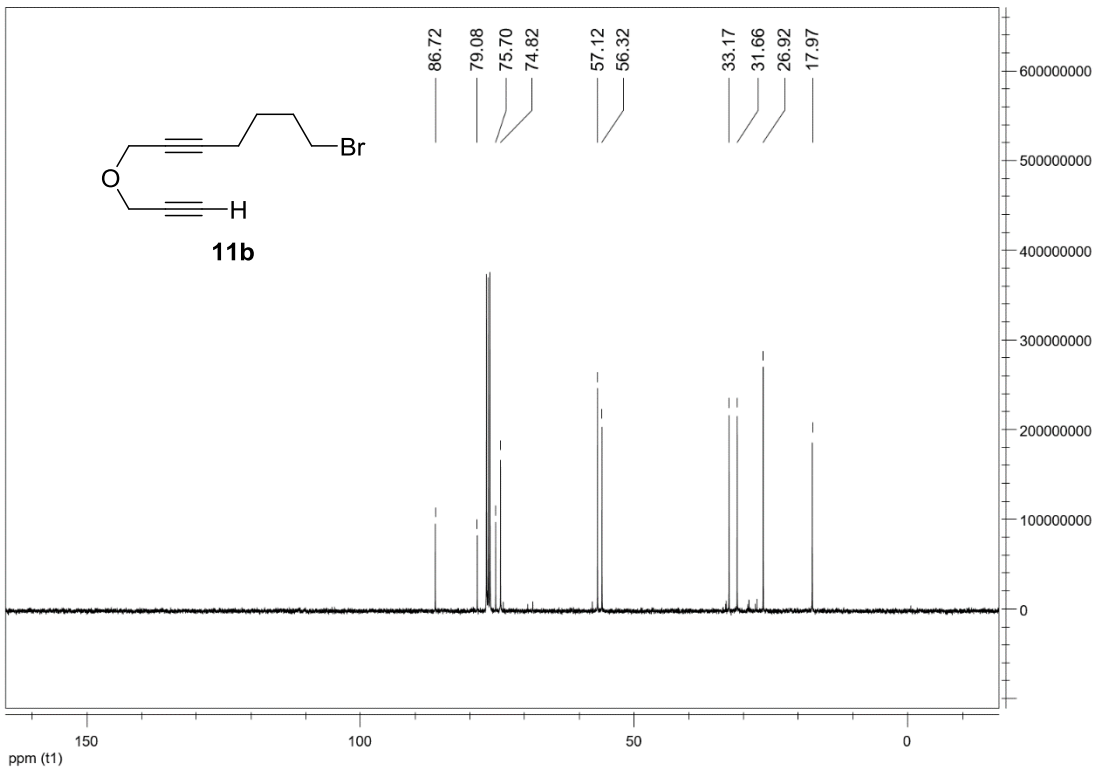
5.0
0.0
ppm (t1)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74.82
57.12
56.32
33.17
31.66
26.92
17.97
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O
H
11b
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400000000
300000000
200000000
100000000
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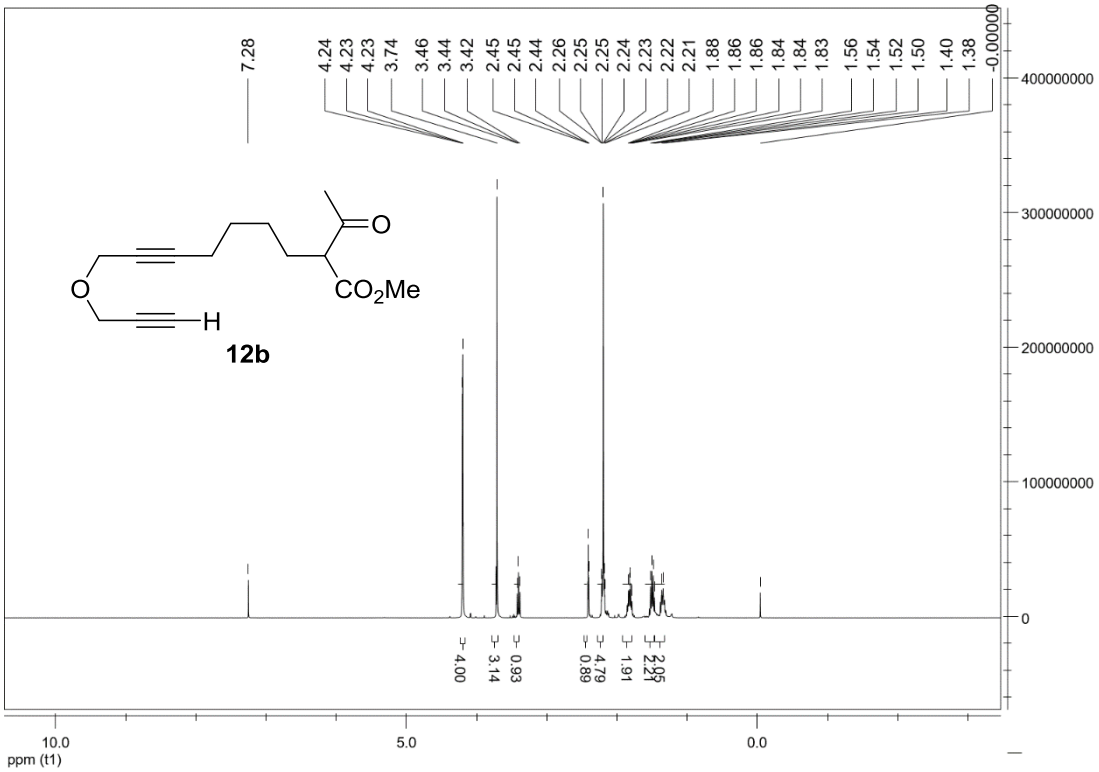
100
50
0
ppm (t1)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2.45
2.44
2.26
2.25
2.25
2.24
2.23
2.22
2.21
1.88
1.86
1.86
1.84
1.84
1.83
1.56
1.54
1.52
1.50
1.40
1.38
-0.00000
O
O
CO2Me
H
12b
4.00
3.14
0.93
0.89
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1.91
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2.05
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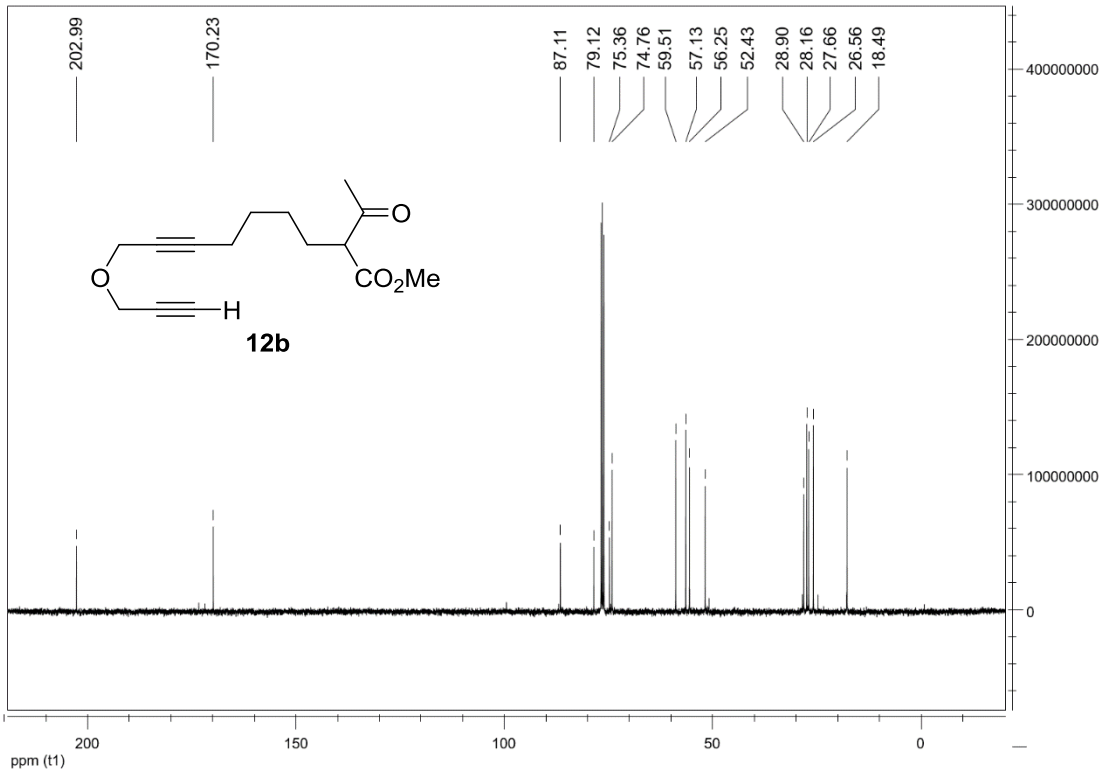
300000000
200000000
100000000
0
10.0
5.0
0.0
ppm (t1)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75.36
74.76
59.51
57.13
56.25
52.43
28.90
28.16
27.66
26.56
18.49
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O
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H
12b
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300000000
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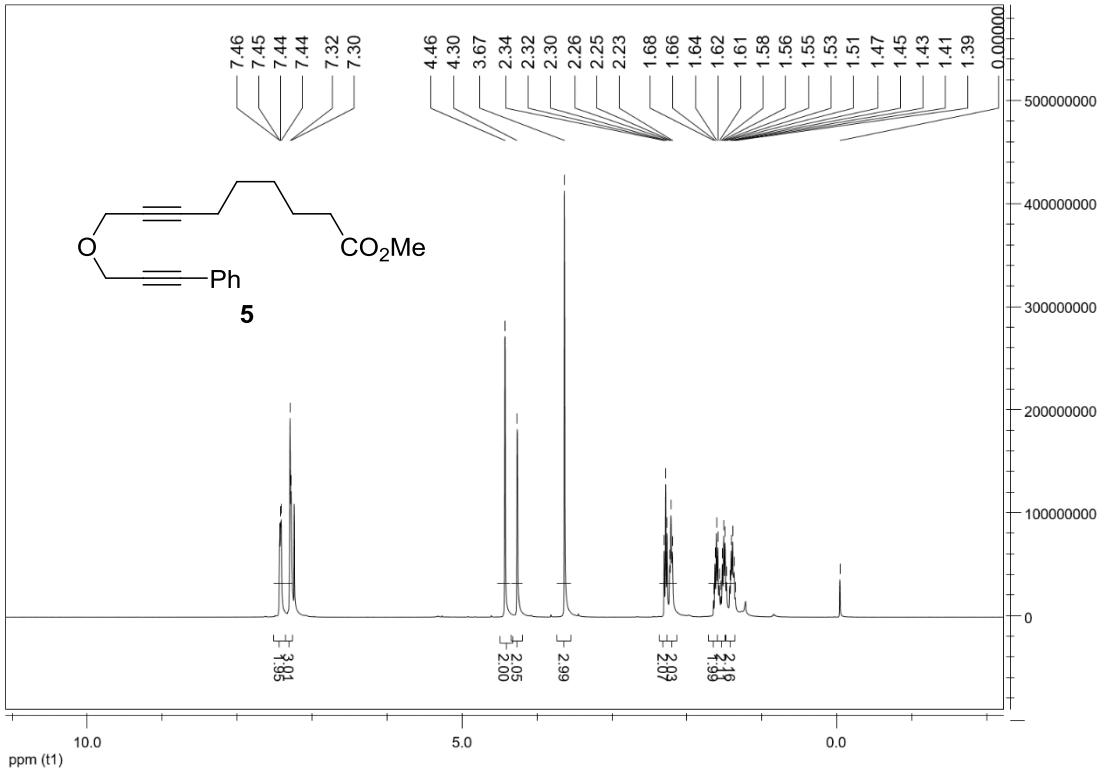
100
50
0
ppm (t1)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7.44
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4.30
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2.32
2.30
2.26
2.25
2.23
1.68
1.66
1.64
1.62
1.61
1.58
1.56
1.55
1.53
1.51
1.47
1.45
1.43
1.41
1.39
0.00000
O
CO2Me
Ph
5
3.01
2.00
2.05
2.99
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300000000
200000000
100000000
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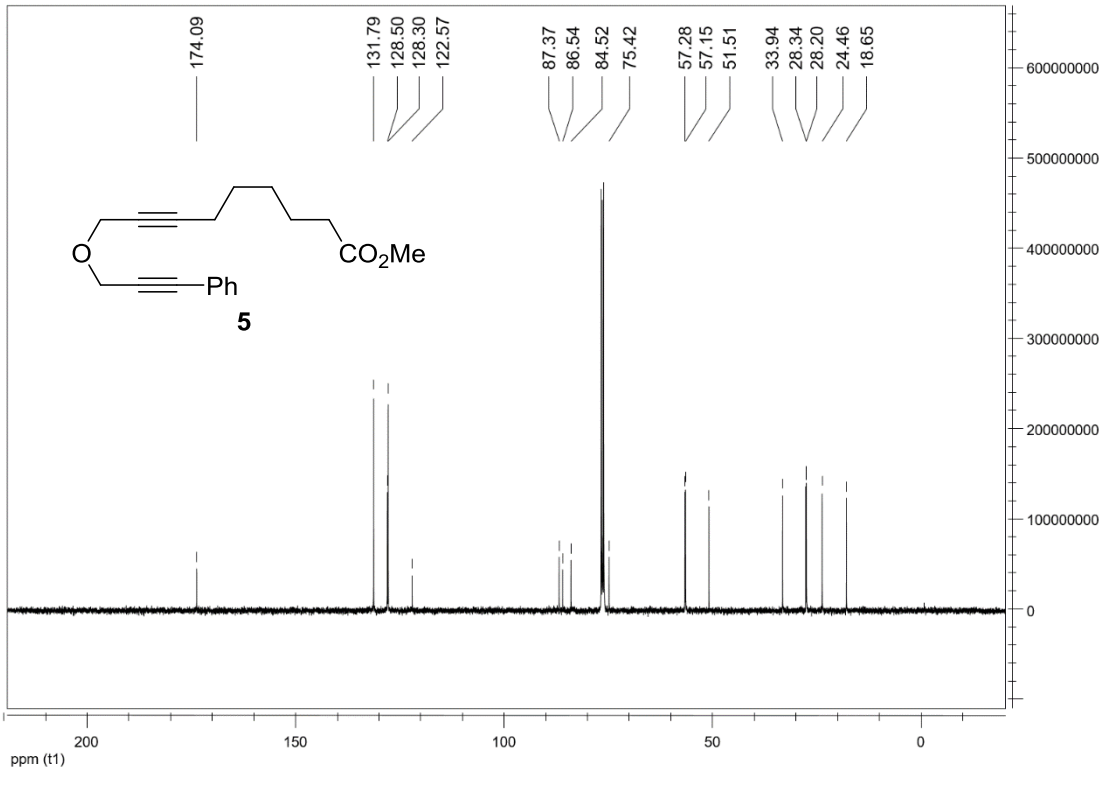
0.0
ppm (t1)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84.52
75.42
57.28
57.15
51.51
33.94
28.34
28.20
24.46
18.65
O
CO2Me
Ph
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600000000
500000000
400000000
300000000
200000000
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0
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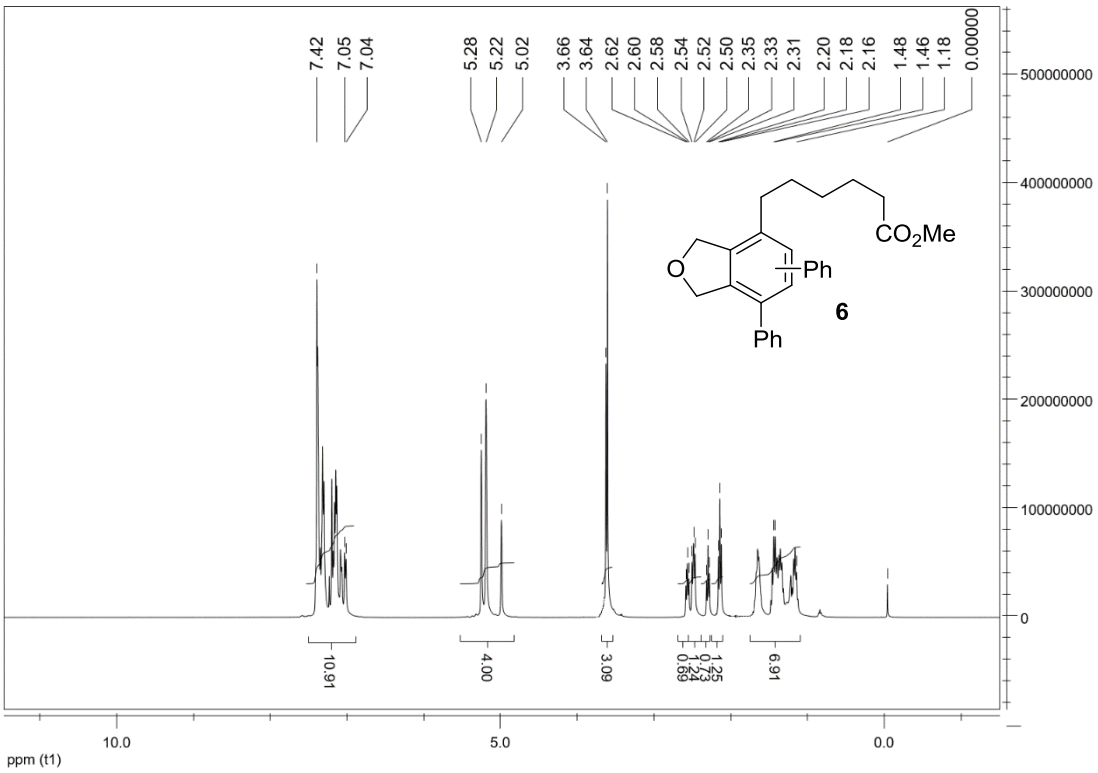
100
50
0
ppm (t1)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2.58
2.54
2.52
2.50
2.35
2.33
2.31
2.20
2.18
2.16
1.48
1.46
1.18
0.00000
CO2Me
O
Ph
Ph
6
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4.00
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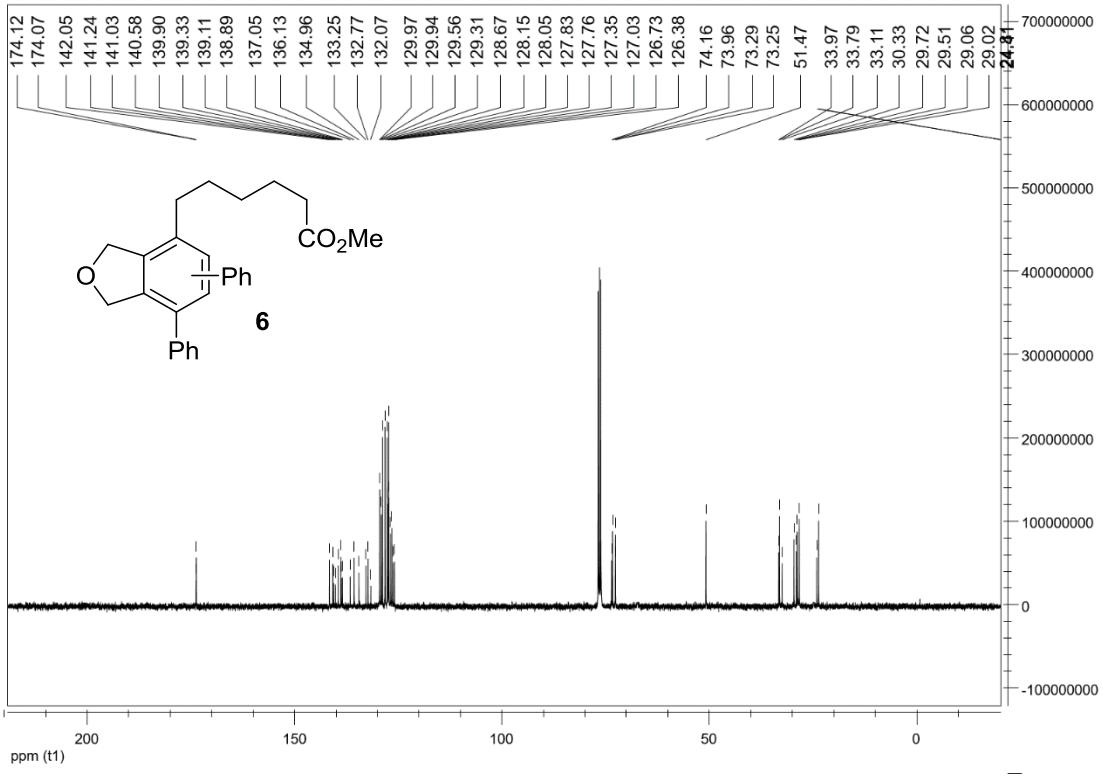
0.69
1.24
0.93
1.25
6.91
10.0
5.0
0.0
ppm (t1)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139.11
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136.13
134.96
133.25
132.77
132.07
129.97
129.94
129.56
129.31
128.67
128.15
128.05
127.83
127.76
127.35
127.03
126.73
126.38
74.16
73.96
73.29
73.25
51.47
33.97
33.79
33.11
30.33
29.72
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29.02
24.81
CO2Me
O
Ph
Ph
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50
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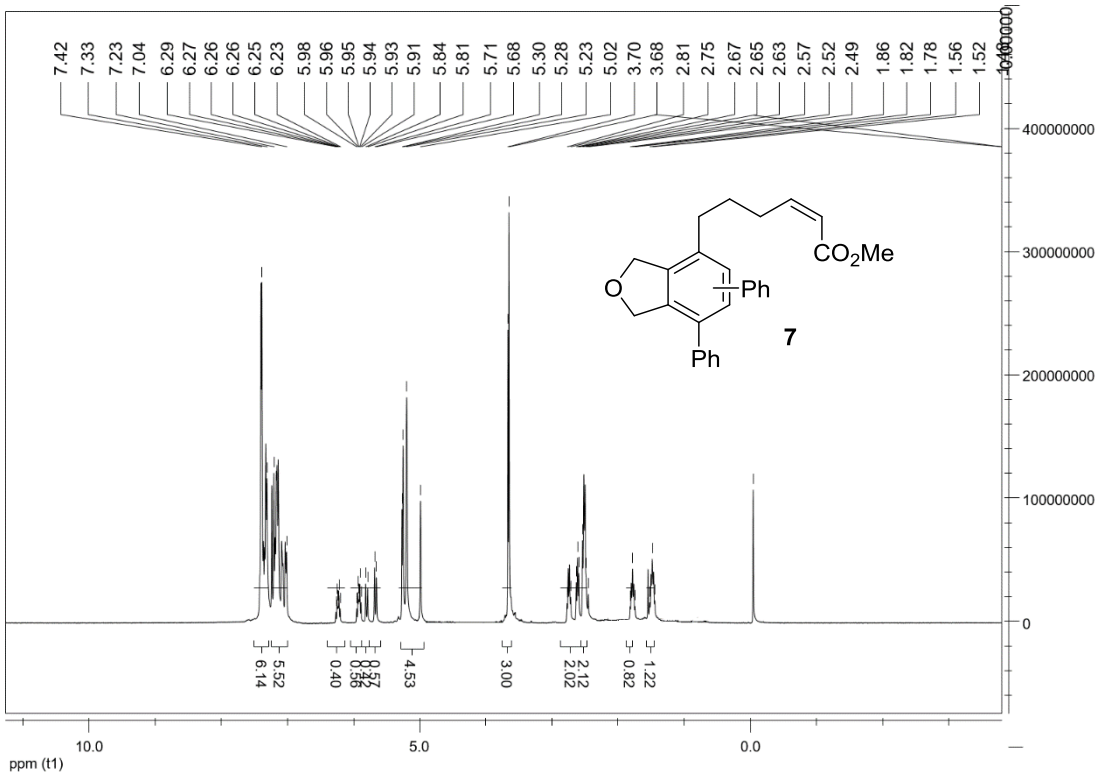
ppm (t1)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7.04
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6.27
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6.26
6.25
6.23
5.98
5.96
5.95
5.94
5.93
5.91
5.84
5.81
5.71
5.68
5.30
5.28
5.23
5.02
3.70
3.68
2.81
2.75
2.67
2.65
2.63
2.57
2.52
2.49
1.86
1.82
1.78
1.56
1.52
CO2Me
O
Ph
Ph
7
6.14
5.52
0.40
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3.00
2.12
2.02
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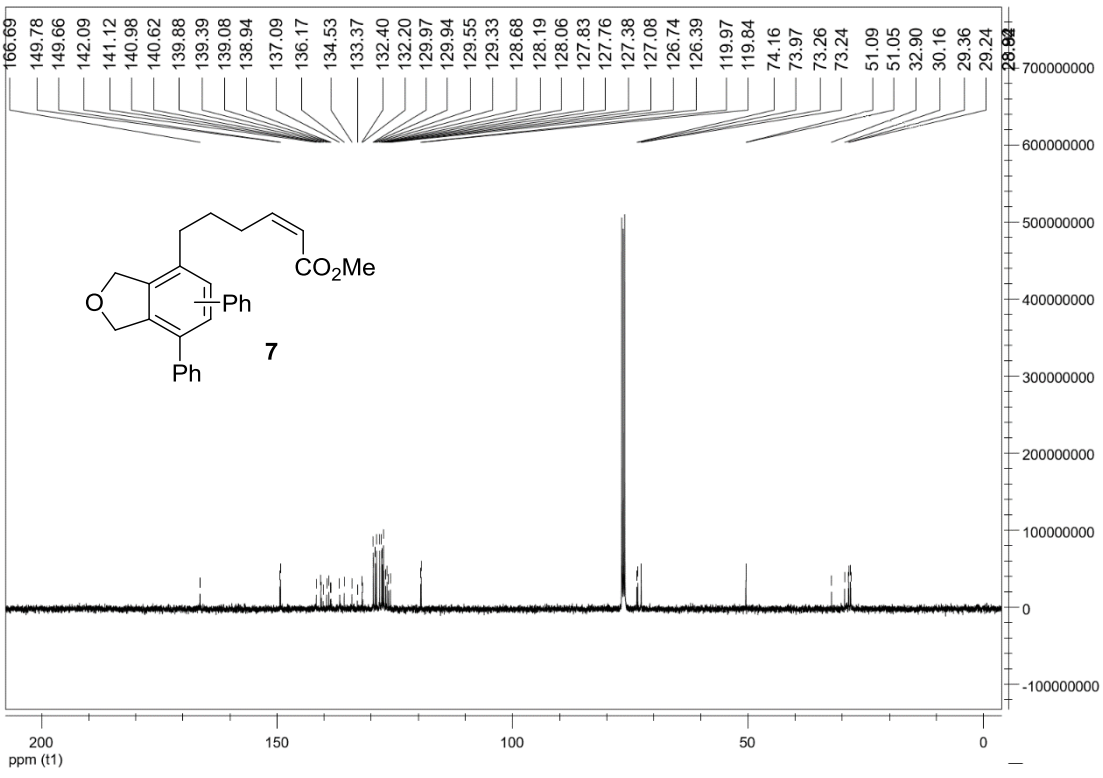
0.0
ppm (t1)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137.09
136.17
134.53
133.37
132.40
132.20
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129.94
129.55
129.33
128.68
128.19
128.06
127.83
127.76
127.38
127.08
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126.39
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119.84
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73.97
73.26
73.24
51.09
51.05
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29.36
29.24
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O
Ph
Ph
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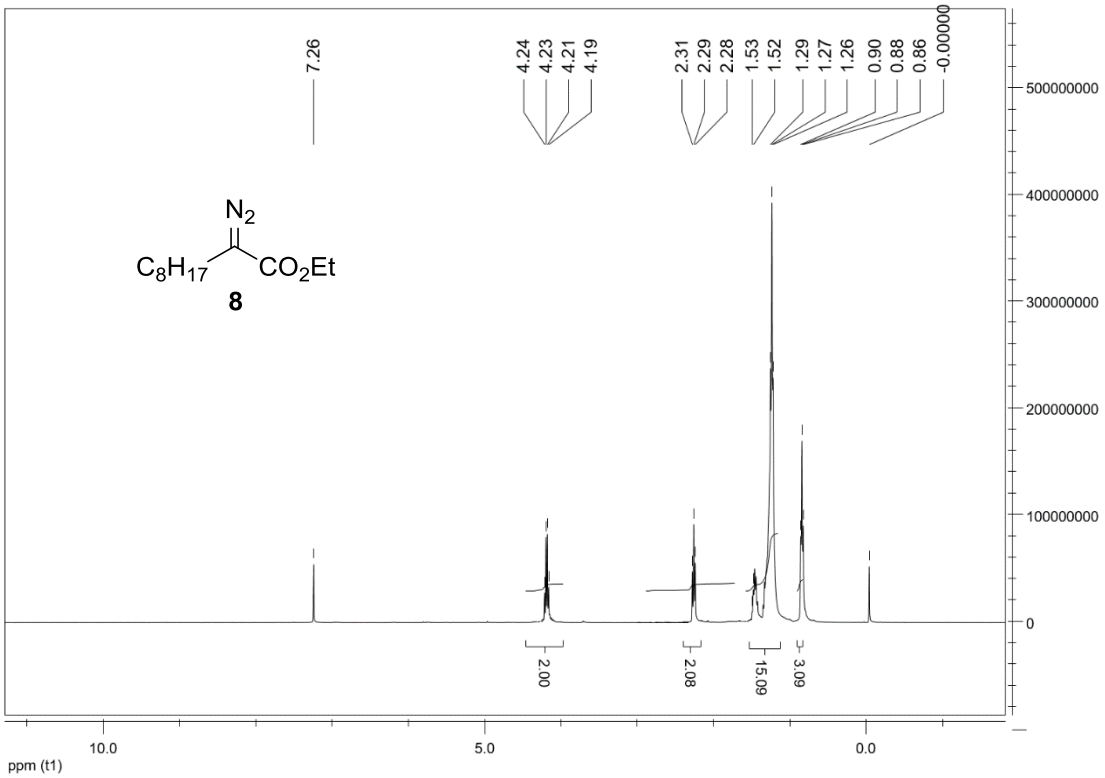
200
150
100
50
0
ppm (t1)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2.29
2.28
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1.52
1.29
1.27
1.26
0.90
0.88
0.86
-0.00000
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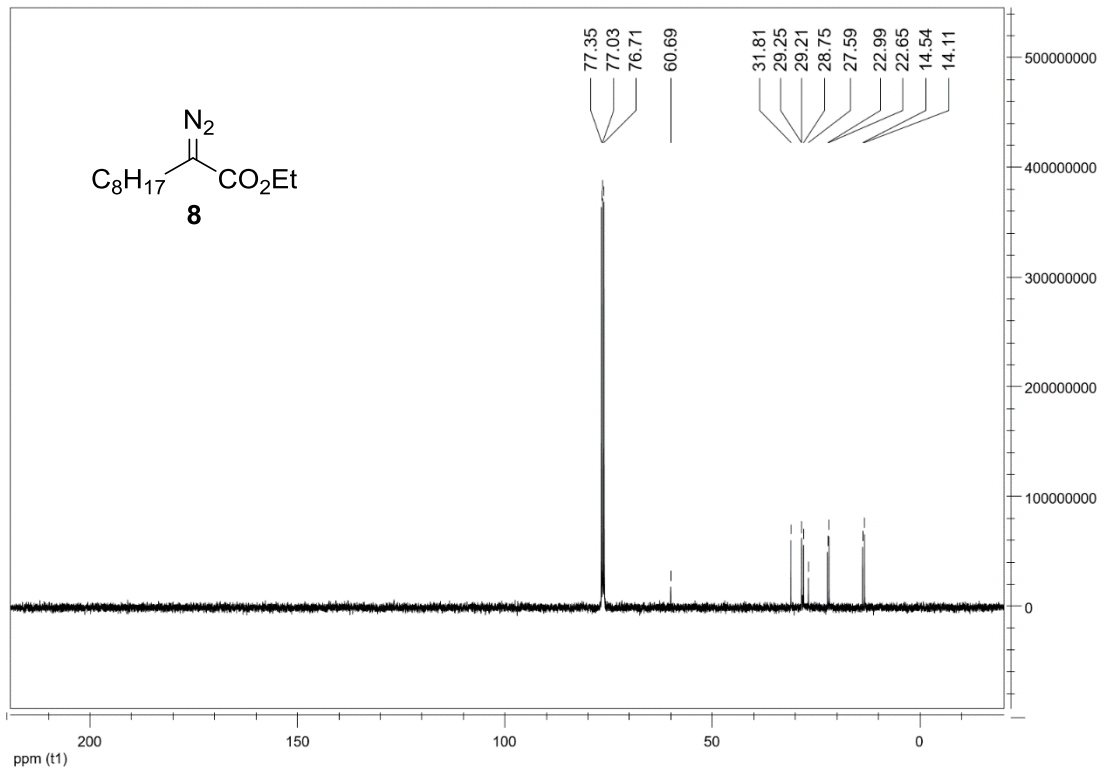
C8H17
CO2Et
8
2.00
2.08
15.09
3.09
10.0
5.0
0.0
ppm (t1)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27.59
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14.11
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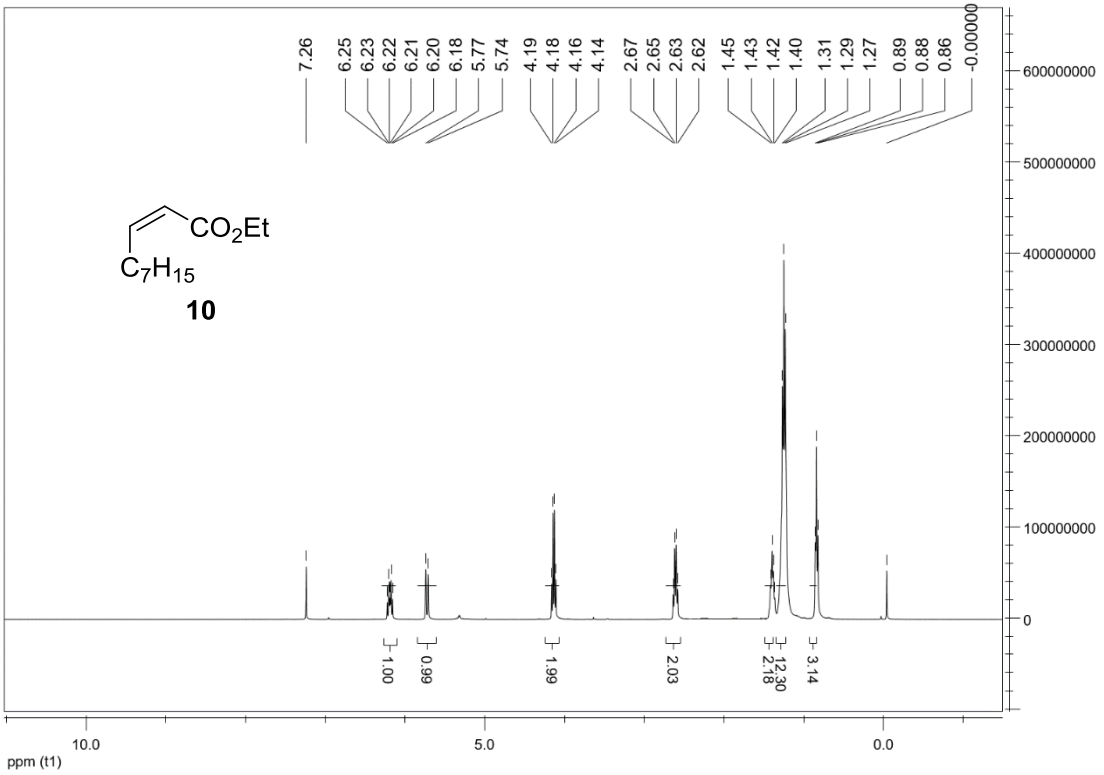
C8H17
CO2Et
8
200
150
100
50
0
ppm (t1)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5.74
4.19
4.18
4.16
4.14
2.67
2.65
2.63
2.62
1.45
1.43
1.42
1.40
1.31
1.29
1.27
0.89
0.88
0.86
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C7H15
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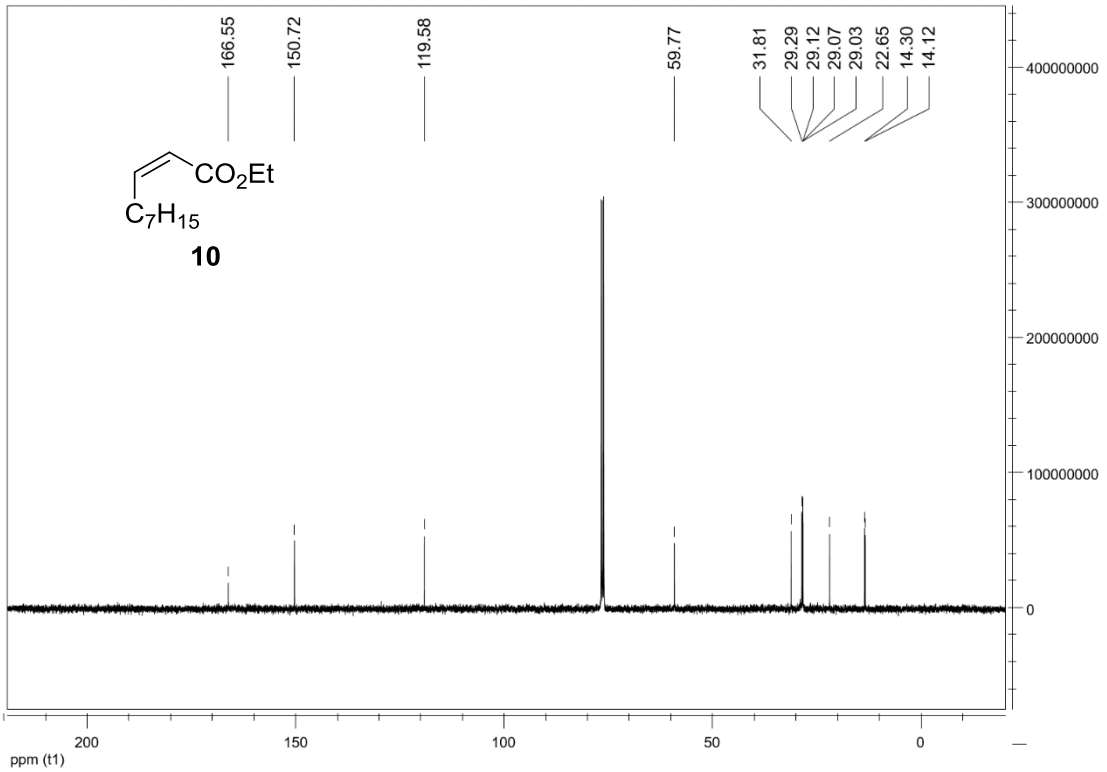
0.99
1.99
2.03
2.18
12.30
3.14
ppm (t1)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59.77
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29.29
29.12
29.07
29.03
22.65
14.30
14.12
CO2Et
C7H15
10
ppm (t1)