Electronic Supplementary Information (ESI)

Bismuth(III)-catalyzed bis-cyclization of propargylic diol-esters: a unified approach for the synthesis of [5,5]- and [6,5]-oxaspirolactones

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1. *General information*:

All reactions were performed under argon atmosphere with oven (80 ºC) or flame-dried glassware with septum seal. Tetrahydrofuran (THF) was distilled from sodium-benzophenone under argon atmosphere immediately prior to use. Dichloromethane and ethanol were freshly distilled over calcium hydride under argon atmosphere; 27 °C corresponds to the room temperature (rt) of the laboratory when the experiments were carried out. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. Analytical thin layer chromatography (TLC) was performed on TLC Silica gel 60 F254. Visualization was accomplished with short wave UV light, anisaldehyde or $KmnO_4$ staining solutions followed by heating. Chromatography was performed on silica gel (100-200 mesh) by standard techniques eluting with solvents as indicated. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 200, 400 and 500 MHz spectrometers in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ H = 7.27 ppm, δ C = 77.00 ppm), the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; AB q, AB quartet; dd, doublet of doublet; td, triplet doublet; and br. broad. HRMS data were recorded on Q Exactive Hybrid™ Quadrupole-Orbitrap™ mass spectrometer (Thermo Scientific,™ Accela 1250 pump).

Experimental procedures for all new compounds and known compounds without published experimental procedures are described below. Compounds that are not presented in the main text (manuscript) are numbered starting from **S1**.

2. Figure S1.

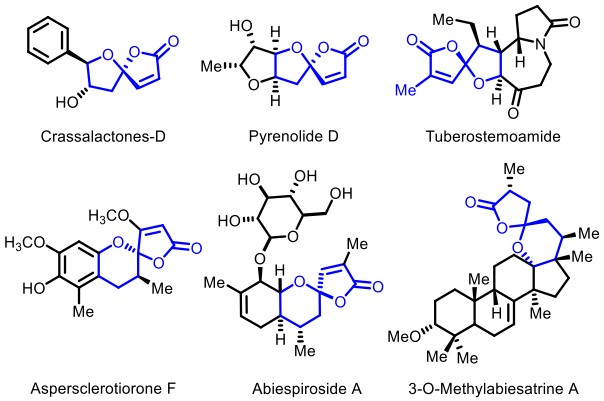
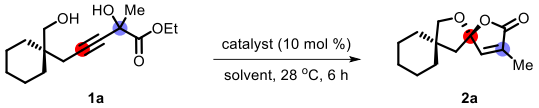


Figure S1. Representative natural products possessing [5,5]- and [6,6]-oxaspirolactone skeleton

3. Table S1.

Table S1. Reaction optimization[a]



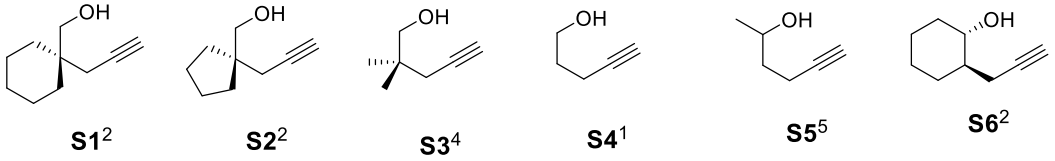
entry	catalyst	solvent	yield (%)[b]
1	$Bi(OTf)_3$	CH_2Cl_2	85
2	AgOTf	CH_2Cl_2	82
3	PPh_3AuCl+AgOTf	CH_2Cl_2	84
4	AgOTf	THF	16
5	AuCl	CH_2Cl_2	36
6	$FeCl_3$	CH_2Cl_2	12
7[c]	$FeCl_3$	CH_3CN	-
8	$Cu(OTf)_2$	CH_2Cl_2	18
9	$In(OTf)_3$	CH_2Cl_2	55
10	$In(OTf)_3$	CH_3CN	51
11[c]	$Sc(OTf)_3$	CH_2Cl_2	-
12	$HgCl_2$	CH_3CN	34
13	$Hg(OTf)_2$	CH_3CN	36
14	$Hg(OTf)_2$	$CH_3CN:H_2O$	16
15[c]	$Pd(PPh_3)Cl_2$	THF	-
16[c]	*p*-TSA	CH_2Cl_2	-
17	*p*-TSA, reflux	DCE	36
18	TfOH	CH_2Cl_2	16
19[c]	$Bi(OTf)_3$, MS-4 Å	CH_2Cl_2	-
20[c]	No catalyst	CH_2Cl_2	-

[a]Reaction condition unless otherwise specified: **1a** (0.25 mmol), catalyst (10 mol %) in the indicated solvent (anhydrous, 2 mL) at rt (28 °C). [b]Isolated yield of **2a**. MS = Molecular Sieves. [c]No conversion was observed.

4. *Synthesis of alkynols and α-ketoesters*

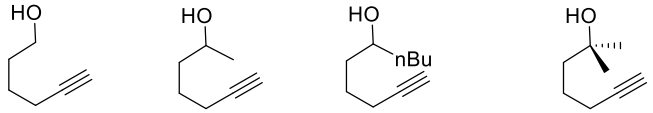
All the alkynols and α-ketoesters were synthesised by using known literature reports (entries A-C, Figure S1).[1,2,3,4,5,6,7,8,9,10]

A. List of 4-pentyn-ols obtained using known procedures



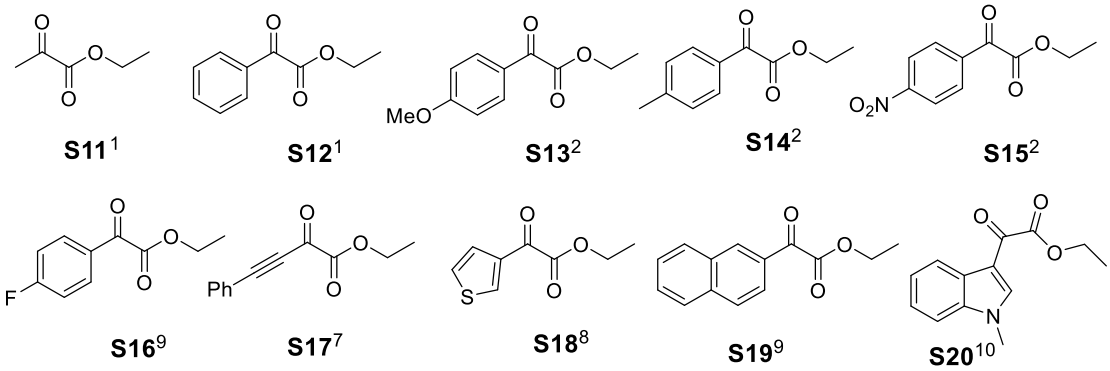
S1[2] **S2**[2] **S3**[4] **S4**[1] **S5**[5] **S6**[2]

B. List of 5-hexyn-ols obtained using known procedures



S7[1] **S8**[3] **S9**[6] **S10**[3]

C. List of α-ketoeseters obtained using known procedures



S11[1] **S12**[1] **S13**[2] **S14**[2] **S15**[2]

S16[9] **S17**[7] **S18**[8] **S19**[9] **S20**[10]

Figure S1.Structural details of building blocks **S1**-**S20**.

[1]**S4, S7, S11 and S12** were purchased from commercial sources.

[2]Kambale, D. A.; Thorat, S. S.; Pratapure, M. S.; Gonnade, R. G.; Kontham, R. *Chem. Commun*. **2017**, *53*, 6641−6644

[3]Thorat S. S.; Kataria P.; Kontham, R. *Org. Lett.***2018**, *20*, 3, 872-875

[4]Magnus, P.;Principe, L. M.;Slater, M. J.*J. Org. Chem.* **1987**, *52*, 8, 1483-1486

[5]Ojima, D.; Yasui, A.; Tohyama, K.; Tokuzumi, K.;Toriihara, E.; Ito, K.; Iwasaki, A.; Tomura, T.; Ojika, M.; Suenaga, K. *J. Org. Chem.* **2016**, *81*, 20, 9886-9894

[6]Kamijo, S. ;Dudley, G. B. *Tetrahedron Lett*., **2006**, *47*, 32, 5629-5632

[7]Sinha, D.; Biswas, A.; Singh, V. K.*Org. Lett*. **2015**, *17*, 3302-3305

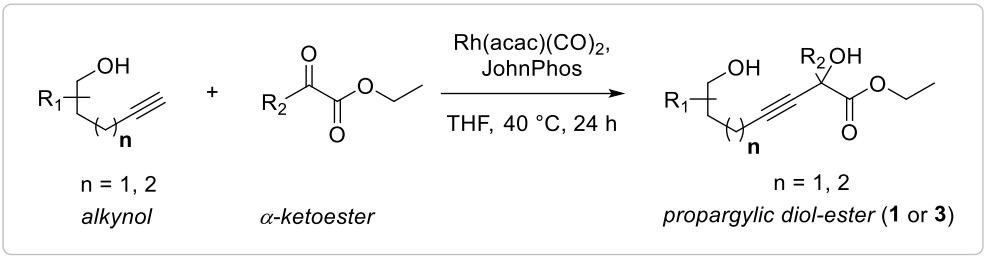
[8]Jeffries, A. T.; Moore, K. C.; Ondeyka, D. M.; Springsteen A. W. ; MacDowell, D. H. W. *J. Org. Chem.* **1981**, *46*, 14, 2885-2889

[9]Hayashi, M.; Nakamura, S. *Angew. Chem. Int. Ed.* **2011**, *50*, 2249 –2252

[10]Yang, L.; Liu, Z.; Li, Y.; Lei, N.; Shen, Y.; Zheng, K.*Org. Lett.* **2019,** *21***,** 7702−7707.

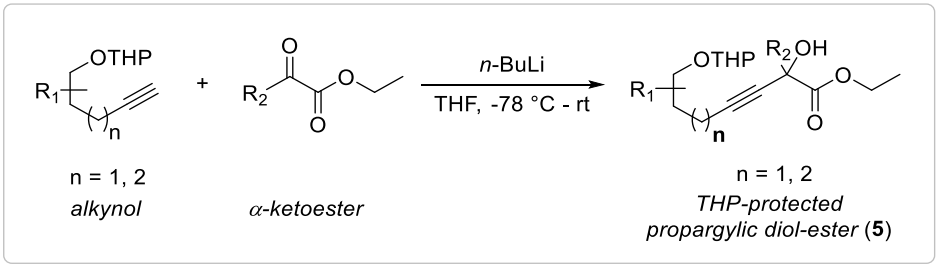
5. ***Synthesis of propargylic diol esters and General procedures A-E***

General procedure A for the synthesis of propargylic diol esters (**1** or **3**):



Propargylic diol esters were obtained by using known literature procedure.[11]A solution of alkynol (1.31 mmol) and α-ketoester (3.94 mmol) in 3.0 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.01g, 0.04 mmol, 3 mol%) and JohnPhos (0.035g, 0.12 mmol, 9.0 mol%) under argon atmosphere at room temperature, then the reaction mixture was warmed to 40 °C. After 24h at 40 °C, the mixture was allowed to cool to room temperature, diluted and extracted with CH_2Cl_2, concentrated under reduced pressure and purified by silica gel column chromatography (using ethyl acetate/petroleum ether) to afford propargylic diol ester (**1** or **3**).

General procedure B for the synthesis of THP- protected propargylic diol esters (**5**):

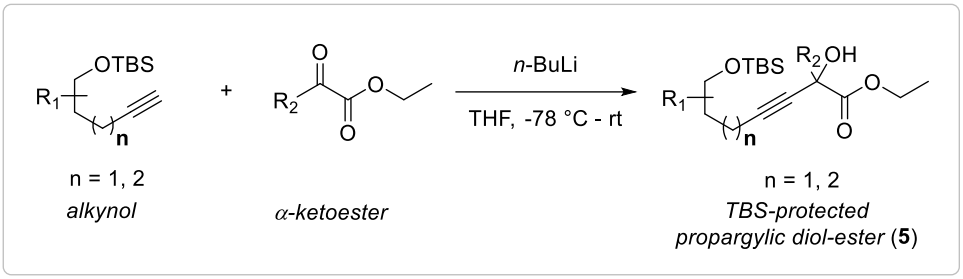


To a solution alkynol (16.9 mmol) in an anhydrous THF (30 mL) under argon atmosphere was added *n*-BuLi solution (1.6 M in hexane, 25.35 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of α-ketoester (2.2 mL, 18.6 mmol) in an anhydrous THF (10 mL) was added at the same temperature and stirred the reaction mixture for 30 min. Then the reaction mixture was allowed to warm tort and stirred until completion of reaction monitored by TLC. Reaction was quenched through the slow addition of saturated aqueous NH_4Cl solution at 0 ºC, extracted with ethyl acetate, dried over an anhydrous Na_2SO_4, filtered, and concentrated

[11]Dhondi, P. D.; Carberry, P.; Choi, L. B.; Chisholm, J. D. *J. Org. Chem.*, **2005,** *72*(25), 9590-9596

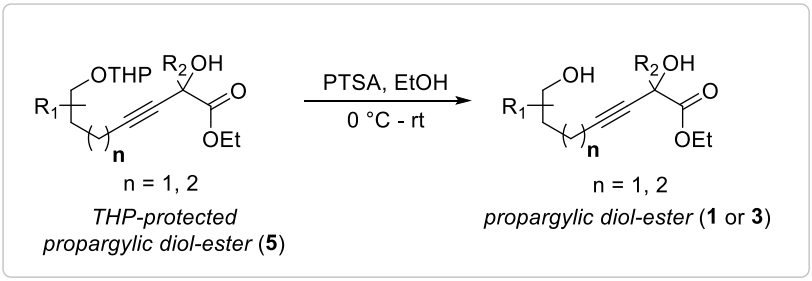
under vacuum. Purification by column chromatography (SiO_2, EtOAc/hexane) afforded THP-protected propargylic diol ester (**5**).

General procedure C for the synthesis of TBS-protected propargylic diol ester (**5**):



To a solution of *tert*-butyldimethyl silyl protected alkynol (1.87 mmol) in an anhydrous THF (10 mL) under argon was added *n*-BuLi (1.6 M in hexane, 2.81 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of α-ketoester in an anhydrous THF was added at the same temperature and stirred it for 30 min. Then the reaction mixture was allowed to warm to rt and stirred till the complete conversion of starting material monitored by TLC. Reaction was quenched with saturated aqueous NH_4Cl solution at 0 ºC, warmed to rt, extracted with ethyl acetate, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. Purification by flash column chromatography (SiO_2, EtOAc/hexane) afforded TBS-protected propargylic diol ester (**5**).

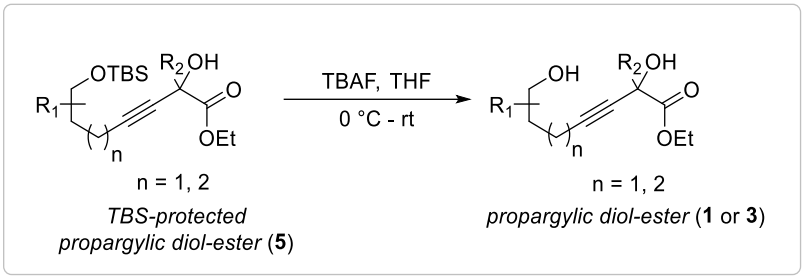
General procedure D for the synthesis of propargylic diol ester (**1** or **3**) from THP-protected propargylic diol ester (**5**):



To a solution of THP-protected propargylic diol ester (8.5mmol) in ethanol was added *p*-toluenesulfonic acid (0.85 mmol) at 0°C and then it was slowly warmed to rt. The resulting reaction mixture was stirred at rt till the complete conversion of starting material. Then the ethanol was evaporated under reduced pressure, diluted with ethyl acetate and quenched with saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate (3x25 mL). Combined

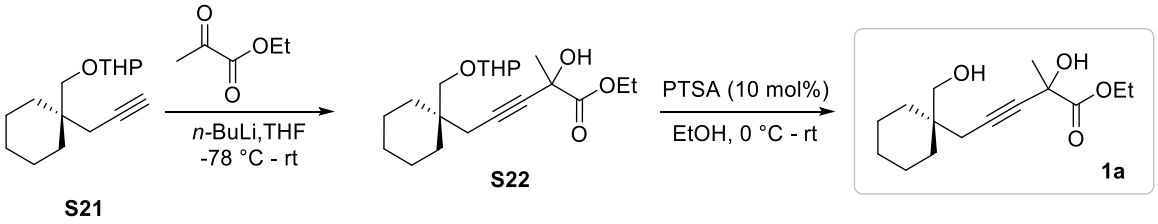
organic layers were dried over an anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude product, which was purified by silica gel column chromatography (SiO_2, EtOAc/hexanes) to afford propargylic diol ester (**1** or **3**).

General procedure E for the synthesis of propargylic diol ester from TBS-protected propargylic diol ester (**5**):



TBS-protected propargylic diol ester (**5**) (0.85 mmol) was placed in a flame-dried, two-neck, round-bottom flask under argon. To this was added an anhydrous THF (10 mL), and the mixture was cooled to 0 ºC. TBAF (1.0 M in THF, 0.94 mmol) was then added slowly at 0 ºC. The cooling bath was removed, and the system was allowed to stir at rt for 2h. After complete conversion of starting material, the reaction mixture was concentrated under reduced pressure and subjected for column chromatography (SiO_2, EtOAc/hexanes) to afford the propargylic diol ester (**1** or **3**).

Synthesis of 1a:

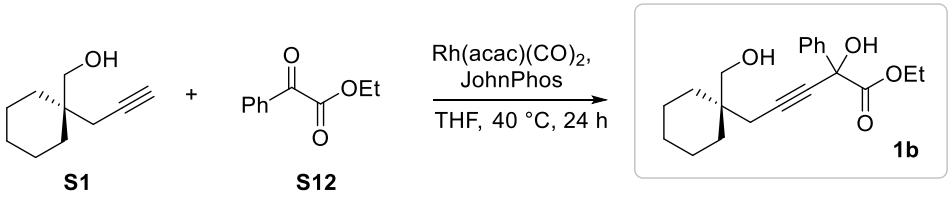


Ethyl 2-hydroxy-2-methyl-5-(1-(((tetrahydro-2*H*-pyran-2-yl) oxy) methyl) cyclohexyl) pent-3-ynoate (S22): Following *General Procedure B*, a solution of ((1-(prop-2-yn-1-yl) cyclohexyl)methoxy) tetrahydro-2*H*-pyran[2] (**S21**) (4g, 16.9 mmol) in anhydrous THF (30 mL) under argon was treated with *n*-BuLi (1.6 M in hexane, 26.5 mL, 42.35 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl pyruvate (**S11**) (2.2 mL, 18.6

mmol) in an anhydrous THF (10 mL) was added to give ethyl 2-hydroxy-2-methyl-5-(1-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)cyclohexyl)pent-3-ynoate (**S22**) (3.0 g,68%) as yellow oil. TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.63-4.51 (m, 1H), 4.38-4.14 (m, 2H), 3.93-3.78 (m, 1H), 3.71-3.57 (m 1H), 3.56-3.4 (m, 2H), 3.27-3.11 (m, 1H), 2.29 (s, 2H), 1.84-1.73 (m, 2H), 1.7-1.64 (m, 4H), 1.6-1.51 (m, 4H), 1.45-1.4 (m, 9H), 1.32 (t, *J* = 6.87 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz):δ173.2, 98.8, 82.9, 81.7, 72.1, 67.9, 62.6, 61.6, 37.3, 32.3, 32.2, 30.5, 27.3, 26.1, 25.8, 25.5, 21.6, 19.2, 14.0; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{20}H_{32}O_5Na$ 375.2142; found 375.2135.

Ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-methylpent-3-ynoate (1a): Following *General Procedure C*, to a solution of ethyl 2-hydroxy-2-methyl-5-(1-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)cyclohexyl)pent-3-ynoate (**S22**) (3 g, 8.5 mmol) in ethanol was added *p*-toluenesulfonic acid (0.16g, 0.85 mmol) to afford ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-methylpent-3-ynoate (**1a**) (1.25 g, 66%) as a colourless liquid. TLC: R_f = 0.4 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.36-4.15 (m, 2H), 3.95 (s, 1H), 3.47 (s, 2H), 2.40 (br. s, 1H), 2.24 (s, 2H), 1.63 (s, 3H), 1.47-1.25 (m, 13H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 173.0, 82.6, 81.9, 68.2, 68.0, 62.6, 37.9, 31.9, 27.4, 26.1, 25.2, 21.5, 14.0; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{15}H_{24}O_4Na$ 291.1567; found 291.1563.

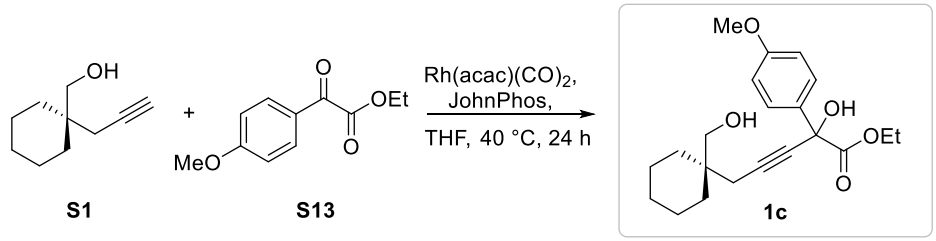
Synthesis of 1b:



Ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-phenylpent-3-ynoate (1b): Following *General Procedure A*, a solution of (1-(prop-2-yn-1-yl)cyclohexyl)methanol (**S1**) (0.2 g, 1.31 mmol) and ethyl phenyl glyoxylate (**S12**) (0.7 g, 3.94mmol) in 3mL of THF was added to a mixture of Rh(acac)$(CO)_2$ (0.01 g, 0.04 mmol, 3 mol%) and JohnPhos (0.035 g, 0.12 mmol, 9 mol%) to afford ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-phenylpent-3-ynoate (**1b**) (0.107 g, 62%) as colourless liquid. TLC: R_f = 0.4 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73-7.59 (m, 2H), 7.42-7.27 (m, 3H), 4.35-4.08 (m, 3H), 3.57 (s, 2H), 2.39 (s, 2H), 1.51-1.38 (m, 10H), 1.27-1.18 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 172.2,

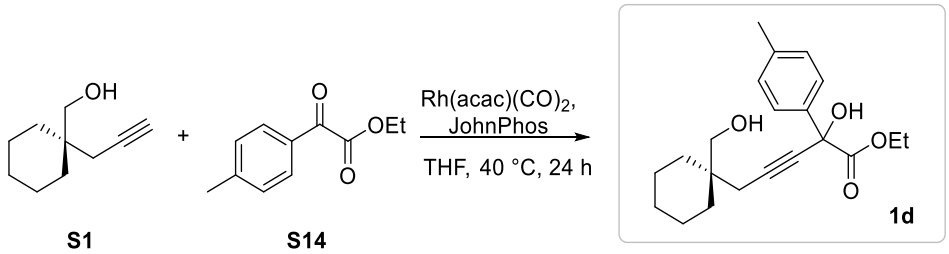
139.8, 128.6, 128.3, 126.1, 84.9, 80.7, 72.9, 68.7, 63.4, 38.2, 32.0, 31.9, 26.1, 25.6, 25.4, 21.5, 13.9;HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{20}H_{26}O_4Na$ 353.1721; found 353.1723.

Synthesis of 1c:



Ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-(4-methoxyphenyl) pent-3-ynoate (1c): Following *General Procedure A*, to a solution of (1-(prop-2-yn-1-yl)cyclohexyl)methanol (**S1**) (0.2 g, 1.13 mmol) and ethyl anisylglyoxylate (**S13**) (0.82 g, 3.94 mmol) in 3 mL of THF was added $Rh(acac)(CO)_2$ (0.1 g, 0.039 mmol, 3 mol%) and JohnPhos (0.035g, 0.118mmol, 9 mol%) to afford ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-(4-methoxyphenyl) pent-3-ynoate (**1c**) (0.128 g, 27% (54% brsm) as a colourless liquid. TLC: R_f = 0.2 (SiO_2, 30% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66-7.50 (m, 2H), 6.96-6.81 (m, 2H), 4.38-4.08 (m, 3H), 3.81 (s, 3H), 3.56 (s, 2H), 2.38 (s, 2H), 1.56-1.36 (m, 10H), 1.26-1.2 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.3, 159.7, 131.9, 127.4, 113.6, 84.7, 80.8, 72.5, 68.6, 63.3, 55.3, 38.2, 32.0, 26.1, 25.5, 21.5, 13.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{21}H_{28}O_5Na$ 383.1829; found 383.1829.

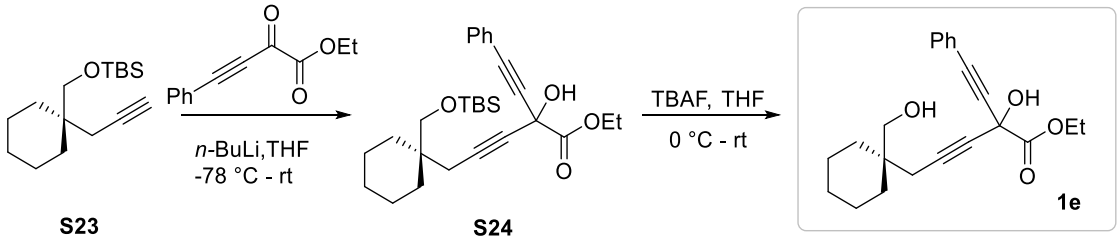
Synthesis of 1d:



Ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-(*p*-tolyl)pent-3-ynoate (1d): Following *General Procedure A*, to a solution of (1-(prop-2-yn-1-yl)cyclohexyl)methanol (**S1**) (0.2 g, 1.32mmol) and ethyl *p*-tolylglyoxylate (**S14**) (0.76 g, 3.96 mmol) in 5 mL of THF was added to $Rh(acac)(CO)_2$ (0.01 g, 0.039 mmol, 3 mol%) and JohnPhos (0.035 g, 0.119 mmol, 9 mol%) to

afford ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-(*p*-tolyl)pent-3-ynoate (**1d**) (0.074 g, 16% (32% brsm) as a colourless liquid. TLC: R_f = 0.2 (SiO_2, 30% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54 (d, *J* = 8.39 Hz, 2H), 7.16 (d, *J* = 8.39 Hz, 2H), 4.48 (br. s, 1H), 4.34-4.09 (m, 2H), 3.53 (s, 2H), 2.39-2.32 (m, 5H), 1.51-1.34 (m, 10H), 1.22 (t, *J* = 6.87 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.1, 138.2, 136.9, 128.9, 125.9, 84.8, 80.6, 72.8, 68.3, 63.12, 38.1, 31.9, 26.1, 25.3, 21.4, 21.0, 13.8; HRMS (ESI) m/z:[M+Na]$^+$ calcd for $C_{21}H_{28}O_4Na$ 367.1880; found 367.1876.

Synthesis of 1e:

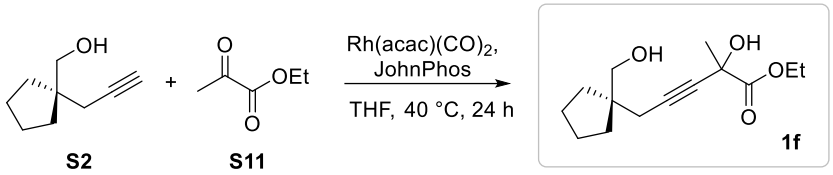


Ethyl-5-(1-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclohexyl)-2-hydroxy-2-(phenyl ethynyl)pent-3-ynoate (S24): Following *General procedure C*, to a solution of *tert*-butyldimethyl((1-(prop-2-yn-1-yl)cyclohexyl)methoxy)silane[12] (**S23**) (0.5 g, 1.87 mmol) in an anhydrous THF (5 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 1.7 mL, 2.81 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl 2-oxo-4-phenylbut-3-ynoate (**S17**) (0.45 g, 2.2 mmol) in an anhydrous THF (5 mL) was added at the same temperature to give ethyl 5-(1-(((*tert*-butyldimethylsilyl) oxy) methyl) cyclohexyl)-2-hydroxy-2-(phenylethynyl)pent-3-ynoate (**S24**) (0.43 g, 49%) as a colourless liquid. TLC : R_f = 0.6 (SiO_2, 10% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72-7.62 (m, 1H), 7.5-7.44 (m, 2H), 7.35-7.31 (m, 2H), 4.44- 4.37 (m, 2H), 3.87 (br. s, 1H), 3.49-3.41 (m, 2H), 2.3 (s, 2H), 1.44-1.38 (m, 13H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.2, 133.8, 132.0, 128.9, 128.8, 128.2, 121.7, 85.4, 84.2, 83.5, 78, 67.5, 63.9, 63.5, 63.3, 38.5, 31.8, 31.7, 26.2, 25.9, 21.6, 18.2, 14.0, -5.5; HRMS (ESI) m/z:[M+Na]$^+$ calcd for $C_{28}H_{40}O_4NaSi$ 491.2588; found 491.2588.

[12]Aponick, A.; Li, C. Y.; Palmes, J. A.*Org. Lett*, **2009,** *11*(1), 121-124

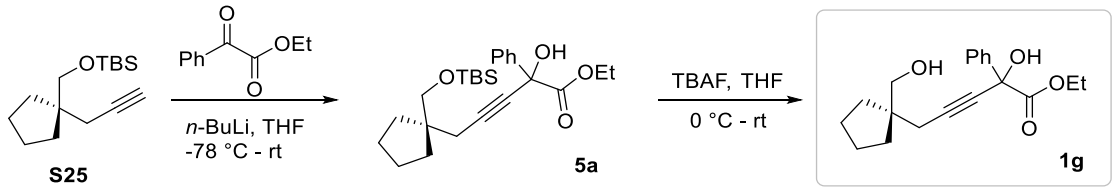
Ethyl-2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-(phenylethynyl)pent-3 ynoate (1e): Following *General procedure E*, to a stirred solution of ethyl 5-(1-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclohexyl)-2-hydroxy-2-(phenylethynyl)pent-3-ynoate (**S24**) (0.4 g, 0.85 mmol) in an anhydrous THF at 0 °C, solution of TBAF (1.0 M in THF, 1 mL, 0.94 mmol) was added to afford ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-(phenylethynyl)pent-3-ynoate(**1e**)(0.187 g, 62%) as colourless liquid. TLC: R_f= 0.40 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.5-7.45 (m, 2H), 7.37-7.29 (m, 3H), 4.46-4.33 (m, 2H), 3.98 (br. s, 1H), 3.56 (s, 2H), 2.34 (s, 2H), 1.49-1.37 (m, 13H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169, 132, 129.1, 128.9, 128.3, 127.9, 121.5, 85.2, 83.8, 83.7, 78.6, 68.5, 64.1, 63.5, 38.3, 32, 26.1, 21.6, 14;HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{22}H_{27}O_4$ 355.1904; found 355.1893.

Synthesis of 1f:



Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclopentyl)-2-methylpent-3-ynoate(1f): Following *General procedure A*, to a solution of (1-(prop-2-yn-1-yl)cyclopentyl)methanol (**S2**) (0.2 g , 1.5 mmol) and ethyl pyruvate (**S11**) (0.17 g, 1.5 mmol) in 2 mL of THF was added to a mixture of Rh(acac)$(CO)_2$(0.011 g, 0.043 mmol) and JohnPhos (0.0038 g, 0.13 mmol) under argon to afford ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclopentyl)-2-methylpent-3-ynoate (**1f**) (0.25 g, 68%) as a colourless liquid. TLC: R_f = 0.39 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.29 (q, *J* = 6.7 Hz, 2H), 3.53 (s, 1H), 3.48 (s, 2H), 2.3 (s, 2H), 1.82 (br. s, 1H), 1.66 (s, 3H), 1.65-1.55 (m, 4H), 1.54-1.42 (m, 4H), 1.33 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.1, 83.4, 80.9, 68.9, 67.9, 62.8, 47.3, 34.1, 27.4, 26.9, 25.2, 14; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{14}H_{23}O_4$ 255.1591, found 255.1586.

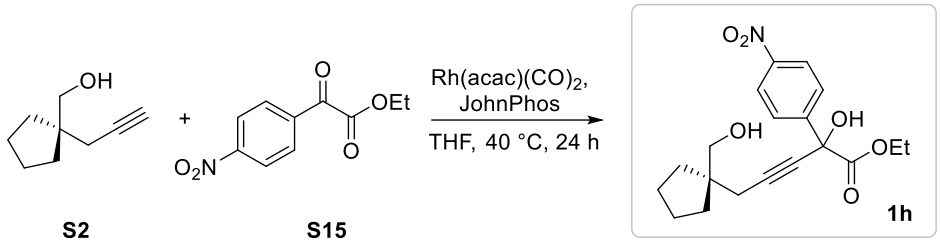
Synthesis of 1g:



Ethyl-5-(1-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclopentyl)-2-hydroxy-2-phenylpent-3-ynoate (5a): Following *General procedure C*, to a solution of *tert*-butyldimethyl((1-(prop-2-yn-1-yl)cyclopentyl)methoxy)silane (**S25**) (0.3 g, 1.2 mmol) in anhydrous THF (5 mL) under argon was added *n*-BuLi solution (1.6 M in hexane1.1 ml, 1.78mmol), then resultant mixture was stirred at -78 ºC for 45 min. Next, the solution of ethyl phenyl glyoxylate(**S12**) (0.25 g, 1.4 mmol) in anhydrous THF was added at the same temperature to afford ethyl 5-(1-(((*tert*-butyldimethylsilyl) oxy) methyl) cyclopentyl)-2-hydroxy-2-phenylpent-3-ynoate (**5a**) (0.276 g, 54%) as yellowish oil.TLC: R_f = 0.5 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, *J* = 7.32 Hz, 2H), 7.41-7.3 (m, 3H), 4.32-4.13 (m, 3H), 3.44 (s, 2H), 2.4(s, 2H), 1.68-1.48 (m, 8H), 1.22 (t, *J* = 7.32 Hz, 3H), 0.91 (s, 9H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 172.3, 139.9, 128.4, 128.1, 126.3, 86.3, 78.9, 72.9, 68.3, 68.3, 47.6, 33.9, 33.9, 26.9, 25.9, 25.4, 18.2, 13.8,-5.5; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{25}H_{39}O_4Si$ 431.2612; found 431.2609.

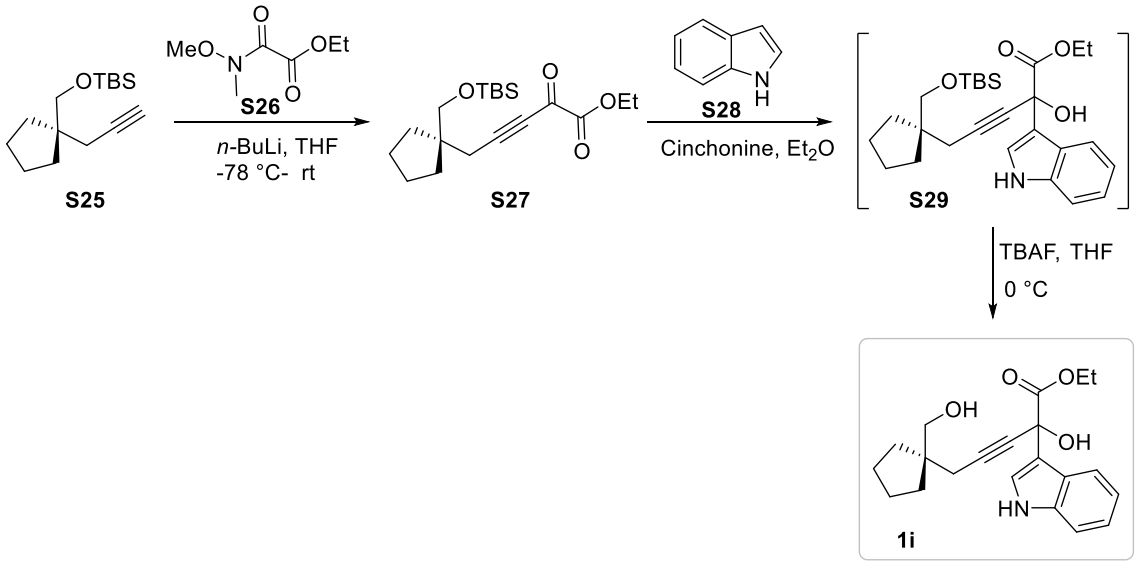
Ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclopentyl)-2-phenylpent-3-ynoate (1g): Following *General procedure E*, to a solution of ethyl 5-(1-(((*tert*-butyldimethylsilyl) oxy) methyl) cyclopentyl)-2-hydroxy-2-phenylpent-3-ynoate (**5a**) (0.1 g, 0.23 mmol) was added anhydrous THF (1.0 mL) and the mixture was cooled to 0 ºC. Then TBAF (1.0 M in THF 0.072 mL, 0.28 mmol) was added slowly at 0ºC to obtain the ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclopentyl)-2-phenylpent-3-ynoate (**1g**) (0.07 g, 96%) as a viscous liquid. TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.7-7.62 (m, 2H), 7.41-7.3 (m, 3H), 4.34-4.24 (m, 1H), 4.23-4.12 (m, 1H), 3.54 (s, 2H), 2.42 (s, 2H), 1.71-1.5 (m, 8H), 1.23 (t, *J* = 7.32 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 172.1, 139.7, 128.5, 128.2, 126.1, 85.7, 79.5, 72.9, 68.9, 63.4, 47.4, 34.2, 27.1, 25.2, 13.8; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{19}H_{25}O_4$ 317.1747; found 317.1764.

Synthesis of 1h:



Ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclopentyl)-2-(4-nitrophenyl) pent-3-ynoate (1h): Following *General procedure A*, to a solution of(1-(prop-2-yn-1-yl)cyclopentyl)methanol (**S2**) (0.2 g, 1.45mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (**S15**) (0.323 g 1.45 mmol) in 5mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.011g, 0.04 mmol, and JohnPhos (0.038g, 0.13 mmol, under argon to afford ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclopentyl)-2-(4-nitrophenyl) pent-3-ynoate (**1h**) as a yellowish liquid (0.075 g, 14 %). TLC: R_f = 0.4(SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.3-8.17 (m, 2H), 7.94-7.79 (m, 2H), 4.37-4.13 (m, 3H), 3.53 (s, 2H), 2.44 (s, 2H), 1.73-1.47 (m, 8H), 1.24 (t, J = 7.2Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.8, 147.9, 146.5, 127.5, 123.4, 86.8, 78.8, 72.4, 68.6, 63.9, 47.4, 34.3, 26.9, 25.2, 13.8; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{19}H_{24}O_6N$ 362.1598; found 362.1596.

Synthesis of 1i:



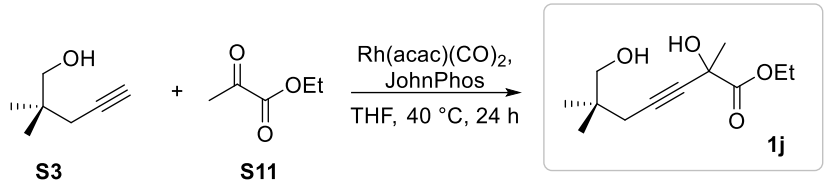
Ethyl 5-(1-(((*tert*-butyldimethylsilyl) oxy) methyl) cyclopentyl)-2-oxopent-3-ynoate (S27): To a solution of *tert*-butyldimethyl((1-(prop-2-yn-1-yl)cyclopentyl)methoxy)silane (**S25**) (0.9 g, 3.56 mmol) in an anhydrous THF (10 mL) under argon was added *n*-BuLi (1.6 M in hexane 3.3 ml, 5.35 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl 2-(methoxy(methyl)amino)-2-oxoacetate[13] (**S26**)(1.4 g, 11.8 mmol) in anhydrous THF was added at the same temperature and stirred it for 30 min. The reaction mixture was warmed to rt and stirred till the completion of reaction monitored by TLC. Reaction was quenched with saturated aqueous NH_4Cl solution at 0 ºC, warmed to rt and diluted with water. The reaction mixture was extracted with EtOAc, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. Purification by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded ethyl 5-(1-(((*tert*-butyldimethylsilyl) oxy) methyl) cyclopentyl)-2-oxopent-3-ynoate (**S27**) (0.2 g, 16%) as a yellowish oil.TLC: R_f = 0.5 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400MHz): δ 4.36 (q, *J* = 6.87 Hz, 2H), 3.42 (s, 2H), 2.58 (s, 2H), 1.67-1.51 (m, 8H), 1.38 (t, *J* = 6.87 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.6, 159.2, 102.3, 80.4, 68.1, 63.0, 47.8, 34.1, 27.6, 25.8, 25.2, 18.2, 13.9, -5.5; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{19}H_{33}O_4Si$ 353.2143; found 353.2144.

Ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclopentyl)-2-(1*H*-indol-3-yl) pent-3-ynoate (1i):To a solution of ethyl 5-(1-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclopentyl)-2-oxopent-3-ynoate (**S27**) (0.15 g, 0.42 mmol) in anhydrous diethyl ether (3 mL) was added indole (**S28**) (0.1 g. 0.85 mmol) and cinchonide (0.012 g, 0.043 mmol) and stirred it at rt for 67h. After complete conversion, the reaction mixture was concentrated and filtered by using a short-pad of silica-gel to afford the crude **S29** (0.04 g, 76% (crude)) as a viscous liquid. TLC: R_f= 0.3 (SiO_2, 20% EtOAc/hexane), which was forwarded for the next step without purification. To a THF (2 mL) solution of **S29** (0.03 g, 0.064 mmol) under argon was added TBAF (1.0 M in THF, 0.03 ml) 0 slowly at 0 ºC. Then the cooling bath was removed, and the system was allowed to stir at rt for 2h. After complete conversion, the reaction mixture was as such concentrated and subjected column chromatography (SiO_2, 30% EtOAc/hexane) to afford the ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclopentyl)-2-(1*H*-indol-3-yl) pent-3-ynoate (**1i**) (0.012 g, 76%) as a viscous liquid. TLC: R_f = 0.3 (SiO_2, 40% EtOAc/ hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.22 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.47-7.42 (m, 1H), 7.37-7.32 (m, 1H), 7.22-7.16 (m, 1H), 7.14-7.09 (m,

[13]Honda, K.; Ohkura, S.; Hayashi, Y.; Kawauchi, S.; Mikami, K. *Chemistry - An Asian Journal*, **2018**, *13* (19), 2842-2846

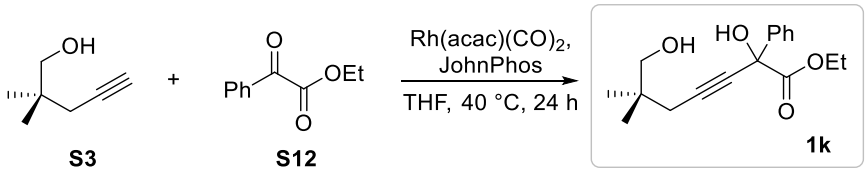
1H), 4.36-4.27 (m, 1H), 4.23-4.09 (m, 2H), 3.52 (s, 2H), 2.41(s, 2H), 1.70-1.58 (m, 4H), 1.55-1.51 (m, 3H), 1.29-1.23 (m, 2H), 1.21 (t, *J* = 7.25 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.3, 136.8, 124.4, 123.9, 122.4, 120.2, 115.9, 111.3, 84.3, 79.8, 69.1, 68.9, 63.3, 47.4, 34.3, 29.7, 27.1, 25.2, 13.9; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{21}H_{25}NO_4$ 355.1778; found 355.1727.

Synthesis of 1j:



Ethyl 2,7-dihydroxy-2,6,6-trimethylhept-3-ynoate(1j): Following *General procedure A,* a solution of 2,2-dimethylpent-4-yn-1-ol(**S3**) (0.3 g, 2.67mmol) and ethyl pyruvate (**S11**) (0.93 g, 8.02 mmol) in 5 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.020 g, 0.08 mmol, 3 mol%) and JohnPhos (0.071 g, 0.24 mmol, 9 mol%) under argon to afford ethyl 2,7-dihydroxy-2,6,6-trimethylhept-3-ynoate (**1j**) (0.11g, 18% (30% brsm) as colourless oil. TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.38-4.14 (m, 3H), 3.39 (s, 2H), 2.16 (s, 2H), 1.65 (s, 3H), 1.32 (t, *J* = 6.87 Hz, 3H), 0.95 (s, 6H); ^{13}C NMR ($CDCl_3$, 101MHz): δ 173.0, 82.7, 81.8, 70.7, 67.9, 62.7, 35.7, 28.4, 27.5, 23.7, 14.0; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{12}H_{20}O_4Na$ 251.1254; found 251.1249.

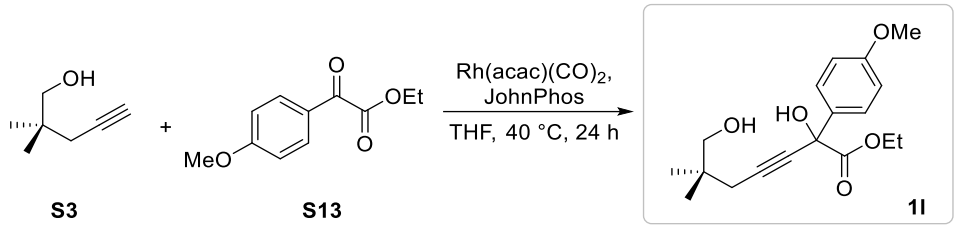
Synthesis of 1k:



Ethyl 2,7-dihydroxy-6,6-dimethyl-2-phenylhept-3-ynoate (1k): Following *General procedure A*,a solution of 2,2-dimethylpent-4-yn-1-ol(**S3**) (0.3 g, 2.67 mmol) and ethyl phenylglyoxylate(**S12**) (1.4 g, 8.02 mmol) in 5 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.02 g, 0.08 mmol, 3 mol%) and JohnPhos(0.071g, 0.24 mmol, 9 mol%) under argon to afford ethyl 2,7-dihydroxy-6,6-dimethyl-2-phenylhept-3-ynoate(**1k**)(0.106g, 9% (35%brsm) as a yellowish oil. TLC: R_f = 0.4 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.70-7.59 (m, 2H), 7.40-7.32 (m, 3H), 4.34-4.09 (m, 3H), 3.4 5(s, 2H), 2.30 (s, 2H),

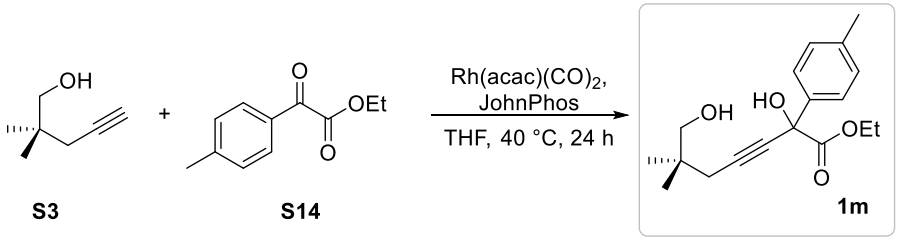
1.23 (t, *J* = 6.87 Hz, 3H), 1.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.1, 139.7, 128.5, 128.2, 126.1, 85.0, 80.4, 72.9, 70.8, 63.3, 36.0, 28.6, 23.8, 13.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{17}H_{22}O_4Na$ 313.141; found 313.1404.

Synthesis of 1l:



Ethyl 2,7-dihydroxy-2-(4-methoxyphenyl)-6,6-dimethylhept-3-ynoate (1l): Following *General procedure A,* a solution of 2,2-dimethylpent-4-yn-1-ol (**S3**) (0.2 g, 1.78 mmol) and ethyl anisylglyoxylate (**S13**) (1.11 g, 5.34 mmol) in 5 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.014 g, 0.053 mmol, 3 mol%) and JohnPhos (0.048 g, 0.16 mmol, 9 mol%) under argon to obtain ethyl 2,7-dihydroxy-2-(4-methoxyphenyl)-6,6-dimethylhept-3-ynoate(**1l**)(0.079 g, 14% (34%brsm) as colourless oil. TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.5 (m, 2H), 6.9-6.8 (m, 2H), 4.3-4.1 (m, 3H), 3.79 (s, 3H), 3.42 (s, 2H), 2.27 (s, 2H), 1.3-1.15 (m, 3H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz); δ 172.4, 159.8, 132.1, 127.5, 113.7, 85.0, 80.7, 72.7, 70.9, 63.3, 55.4, 38.9, 36.1, 28.7, 24.0, 14; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{18}H_{24}O_5Na$ 343.1516; found 343.1511.

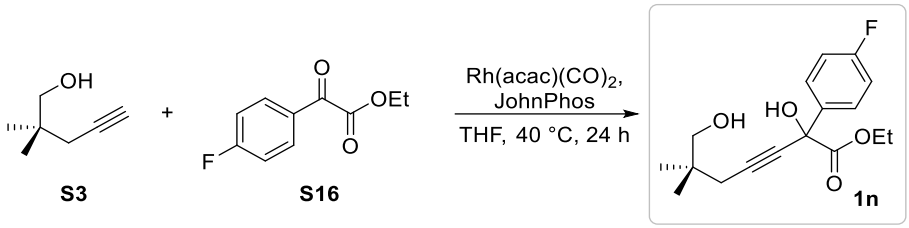
Synthesis of 1m:



Ethyl 2,7-dihydroxy-6,6-dimethyl-2-(*p*-tolyl)hept-3-ynoate (1m): Following *General procedure A,* a solution of 2,2-dimethylpent-4-yn-1-ol (**S3**)(0.2 g, 0.018 mmol) and ethyl *p*-tolylglyoxylate (**S14**) (1.03g, 5.34 mmol) in 5 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.014 g, 0.053 mmol, 3 mol%) and JohnPhos (0.048 g, 0.16 mmol, 9 mol%) under argon to afford ethyl 2,7-dihydroxy-6,6-dimethyl-2-(*p*-tolyl)hept-3-ynoate (**1m**) (0.096g,

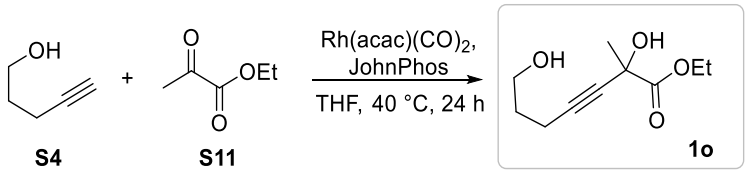
18% (37% brsm) as a viscous liquid. TLC: R_f= 0.4 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60-7.49 (m, 2H), 7.22-7.12 (m, 2H), 4.37-4.10 (m, 3H), 3.46 (s, 2H), 2.36 (s, 3H), 2.30 (s, 2H), 1.24(t, *J* = 7.63 Hz, 3H), 1.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.3, 138.4, 136.9, 129.0, 126.0, 84.8, 80.5, 72.8, 71.0, 63.4, 36.0, 29.8, 28.8, 23.9, 21.1, 13.9; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{18}H_{24}O_4Na$ 327.1567; found 327.1562.

Synthesis of 1n:



Ethyl 2-(4-fluorophenyl)-2,7-dihydroxy-6,6-dimethylhept-3-ynoate(1n): Following *General procedure A*,a solution of 2,2-dimethylpent-4-yn-1-ol (**S3**) (0.3 g, 2.67 mmol) and ethyl 2-(4-fluorophenyl)-2-oxoacetate (**S16**) (1.57 g, 8.02 mmol) in 5 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.021g, 0.08 mmol, 3 mol%) and JohnPhos (0.072 g, 0.24 mmol, 9 mol%) under argon to obtain ethyl 2-(4-fluorophenyl)-2,7-dihydroxy-6,6-dimethylhept-3-ynoate (**1n**) (0.088 g, 11% (31% brsm) as yellowish oil. TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ7.71-7.6 (m, 2H), 7.11-7.99 (m, 2H), 4.34-4.13 (m, 3H), 3.45 (s, 2H), 2.30 (s, 2H), 1.23 (t, *J* = 6.87 Hz, 3H), 1.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.0, 135.5, 128.1, 128.0, 115.2, 115.0, 85.2, 80.3, 72.3, 70.9, 70.7, 63.5, 36.1, 36.0, 29.7, 29.0, 28.6, 23.9, 13.9; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{17}H_{21}O_4FNa$ 331.1316; found 331.1308.

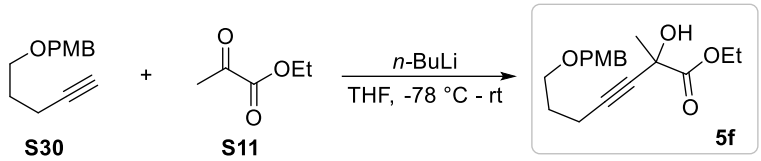
Synthesisof 1o:



Ethyl 2,7-dihydroxy-2-methylhept-3-ynoate (1o): Following *General procedure A* ,a solution of 4-pentyn-1-ol (**S4**) (0.2 g , 2.4 mmol) and ethyl pyruvate (**S11**) (0.17 g, 1.5 mmol) in 2 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.018 g, 0.07 mmol) and JohnPhos (0.063 g,

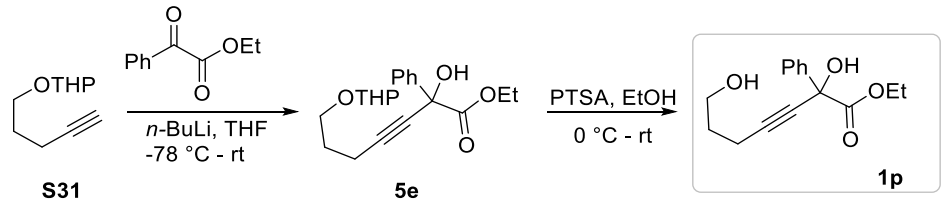
0.21 mmol) under argon to afford ethyl 2, 7-dihydroxy-2-methylhept-3-ynoate (**1o**) (0.29 g, 60%) as a viscous liquid. TLC: R_f= 0.4 (SiO_2, 40% EtOAc/ hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.3(q, *J* = 6.87 Hz, 2H), 3.74 (t, *J* = 6.1 Hz, 2H), 2.35 (t, *J* = 6.87 Hz, 2H), 1.8-1.73 (m, 2H), 1.66 (s, 3H), 1.34 (t, *J* = 6.87 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 173.3, 84.4, 80.7, 67.9, 62.8, 61.6, 30.9, 27.4, 15.3, 14.0; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{10}H_{16}O_4Na$ 223.0941; found 223.0939.

Synthesis of 5f:



Ethyl 2-hydroxy-7-((4-methoxybenzyl)oxy)-2-methylhept-3-ynoate (5f): Following *General procedure C,* to a solution of 1-methoxy-4-((pent-4-yn-1-yloxy)methyl)benzene[14] (**S30**) (0.5 g, 2.44 mmol) in anhydrous THF (20 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 2.29 mL, 3.67mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl pyruvate (**S11**) (0.34 g, 2.93 mmol) in anhydrous THF was added at the same temperature to afford ethyl 2-hydroxy-7-((4-methoxybenzyl)oxy)-2-methylhept-3-ynoate (**5f**) (0.4 g, 61%) as colourless oil. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (d, *J* = 9.13 Hz, 2H), 6.88 (d, *J* = 8.76 Hz, 2H), 4.43 (s, 2H), 4.28 (q, *J* = 7.13 Hz, 2H), 3.8 (s, 3H), 3.51(t, *J* = 6.13 Hz, 2H), 3.45 (br. s, 1H), 2.32 (t, *J* = 7.13 Hz, 2H), 1.83-1.73 (m, 2H), 1.64 (s, 3H), 1.32 (t, *J* = 7.13 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.1, 159.2, 130.5, 129.2, 113.8, 84.3, 80.1, 72.6, 68.4, 67.9, 62.7, 55.3, 28.5, 27.4, 15.6, 14; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{18}H_{24}O_5Na$ 343.1516; found 343.1511.

Synthesis of 1p:

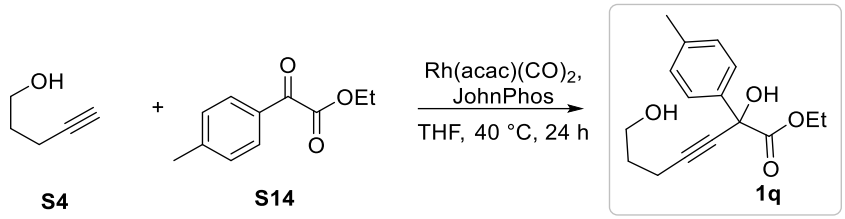


[14]Chandrasekhar, S.; Rao, C. L.; Seenaiah, M.; Naresh, P.; Jagadeesh, B.; Manjeera, D.; Sarkar, A.; Bhadra, M. P.*J. Org. Chem*,**2009**, *74* (1), 401-404.

Ethyl 2-hydroxy-2-phenyl-7-((tetrahydro-2*H*-pyran-2-yl)oxy)hept-3-ynoate (5e): Following *General procedure C*, to as olution of 2-(pent-4-yn-1-yloxy)tetrahydro-2*H*-pyran[15] (**S31**) (2 g, 11.9 mmol) in anhydrous THF (20 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 11.13 mL, 17.8 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl phenyl glyoxylate (**S12**) (2.5 mL, 14.2mmol) in anhydrous THF was added at the same temperature to afford ethyl 2-hydroxy-2-phenyl-7-((tetrahydro-2*H*-pyran-2-yl)oxy)hept-3-ynoate (**5e**)(1.86 g, 62%) as a colourless liquid. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.5-7.4 (m, 2H), 7.36-7.26 (m, 3H), 4.58 (s, 1H), 4.38 (q, *J* = 6.71Hz, 2H), 4.21 (br. s, 1H), 3.88-3.7 (m, 2H), 3.54-3.36 (m, 2H), 2.3 (t, *J* = 7.32 Hz, 2H), 1.71-1.49 (m, 8H), 1.36(t, *J* = 7.32 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.9, 132, 129, 128.2, 121.6, 98.7, 85.5, 85.4, 83.6, 66.8, 63.9, 63.5, 62.2, 30.6, 28.8, 25.4, 24.9, 19.5, 18.6, 13.9; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{20}H_{27}O_5$ 347.1853, found 347.1863.

Ethyl 2,7-dihydroxy-2-phenylhept-3-ynoate (1p): Following *General procedure D,* to a solution of ethyl 2-hydroxy-2-phenyl-7-((tetrahydro-2*H*-pyran-2-yl)oxy)hept-3-ynoate (**5e**) (1.8 g, 0.52 mmol) in ethanol was added *p*-toluenesulfonic acid (0.5g, 0.26 mmol) at 0 °C and then it was slowly warmed to rt to afford ethyl 2,7-dihydroxy-2-phenylhept-3-ynoate (**1p**) (1.25 g, 92%) as a colourless liquid. TLC: R_f = 0.4 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72-7.60 (m, 2H), 7.43-7.29 (m, 3H), 4.35-4.14 (m, 3H), 3.79 (t, *J* = 6.10 Hz, 2H), 2.46 (t, *J* = 6.87 Hz, 2H), 1.89-1.77 (m, 3H), 1.22(t, *J* = 6.87 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.1, 139.6, 128.5, 128.2, 126.1, 86.5, 79.05, 72.8, 63.4, 61.6, 30.9, 15.5, 13.9; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{15}H_{18}O_4Na$ 285.1097; found 285.1089.

Synthesis of 1q:

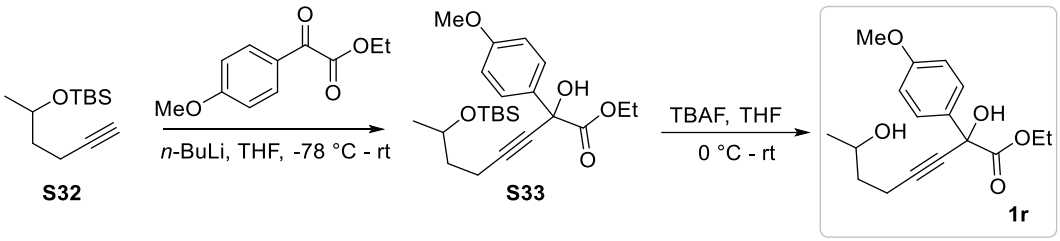


Ethyl 2,7-dihydroxy-2-(*p*-tolyl)hept-3-ynoate (1q): Following *General procedure A*, a solution of pent-4-yn-1-ol (**S4**) (0.2 g, 2.37 mmol) and ethyl *p*-tolylglyoxylate (**S14**) (1.37 g, 7.13 mmol)

[15]Marino, J. P.; Nguyen, H. N.*J. Org. Chem.* **2002**, *67* (18), 6291-6296.

in 5 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.018 g, 0.071 mmol, 3 mol%) and JohnPhos (0.064g, 0.21 mmol, 9 mol%) to afford ethyl 2,7-dihydroxy-2-(*p*-tolyl)hept-3-ynoate (**1q**) (0.072g, 11% (27% brsm) as colourless oil. TLC: R_f = 0.4 (40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69-7.55 (m, 2H), 7.10-7.95 (m, 2H), 4.38-4.02 (m, 3H), 3.73-3.58 (m, 2H), 2.64 (t, *J* = 6.87 Hz, 2H), 2.35 (s, 3H), 1.77-1.57 (m, 2H), 1.2 (t, *J* = 7.33 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): 172.4, 136.9, 129.1, 126.1, 86.4, 79.3, 76.8, 72.8, 63.5, 61.8, 31.1, 15.6, 13.9;HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{16}H_{20}O_4Na$ 299.1254; found 299.1250.

Synthesis of 1r:

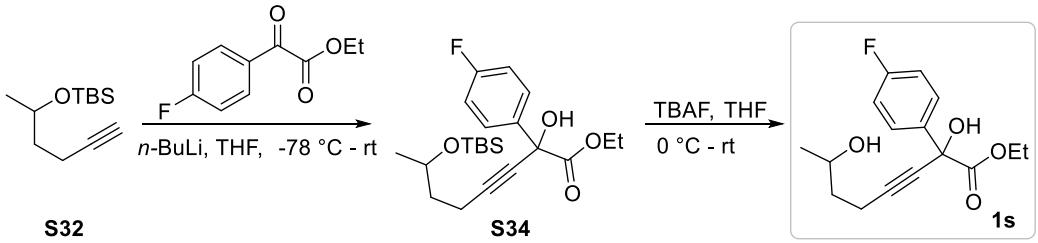


Ethyl-7-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-(4-methoxyphenyl)oct-3-ynoate (S33): Following *General procedure C,* to a solution of *tert*-butyl(hex-5-yn-2-yloxy)dimethylsilane[16] (**S32**) (0.5 g, 2.3 mmol) in an anhydrous THF (10 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 2.2 mL, 3.53 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl anisylglyoxylate (**S13**) (0.58 g, 2.82 mmol) in anhydrous THF was added at the same temperature to afford ethyl 7-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-(4-methoxyphenyl)oct-3-ynoate (**S33**) (0.35 g, 59% brms). TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57(d, *J* = 9.1 Hz, 2H), 6.88(d, *J* = 8.88 Hz, 2H), 4.31-4.12(m, 3H), 4.0-3.87(m, 1H), 3.81(s, 3H), 2.47-2.26 (m, 2H), 1.71-1.66 (m, 2H), 1.22-1.20 (m, 3H), 1.16 (d, *J* = 6 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR ($CDCl_3$,101 MHz): δ 172.4, 159.7, 132.1, 127.5, 113.5, 87.1, 78.6, 72.5, 67.2, 66.9, 64.4, 63.2, 55.3, 38.1, 30.3, 25.9, 25.3, 23.7, 18.8, 18.1, 15.3, 13.8, 13.6, -4.3, -4.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{23}H_{36}O_5NaSi$ 443.222; found 443.2216.

[16]Mulzer, J.;Berger,M.*J.Org.Chem*, **2004**, *69*(3), 891-898

Ethyl 2,7-dihydroxy-2-(4-methoxyphenyl)oct-3-ynoate (1r): Following *General procedure E,* to a solution ofethyl-7-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-(4-methoxyphenyl)oct-3-ynoate (S**33**) (0.3 g, 0.71mmol) was added an anhydrous THF (5 mL), and the mixture was cooled to 0 ºC. TBAF (1.0 M in THF, 1mL, 0.85 mmol) was then added to afford ethyl 2,7-dihydroxy-2-(4-methoxyphenyl)oct-3-ynoate (**1r**) (0.1 g, 57%brsm) as a viscous liquid, TLC: R_f = 0.4 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.63-7.5 (m, 2H), 6.95-6.8 (m, 2H), 4.34-4.13(m, 2H), 4.05-3.88 (m, 1H), 3.81 (s, 3H), 2.45 (t, *J* = 6.69 Hz, 2H), 1.82 (br. s, 1H), 1.78-1.64 (m, 2H), 1.3-1.2 (m, 6H); ^{13}C NMR ($CDCl_3$, 56 MHz): δ172.3, 159.8, 131.9, 127.5, 113.6, 86.6, 79.2, 72.5, 67.1, 63.3, 55.3, 37.3, 29.7, 23.4, 15.5, 13.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{17}H_{22}O_5Na$ 329.1359; found 329.1354.

Synthesis of 1s:

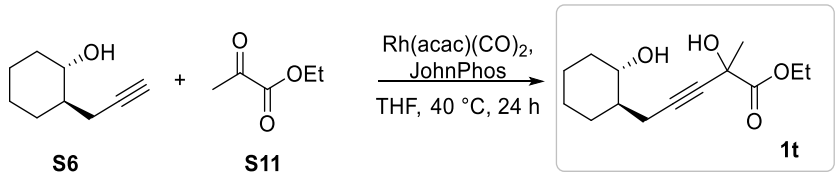


Ethyl 7-((*tert*-butyldimethylsilyl)oxy)-2-(4-fluorophenyl)-2-hydroxyoct-3-ynoate (S34):

Following *General procedure C,* to a solution of *tert*-butyl(hex-5-yn-2-yloxy)dimethylsilane[15] (**S32**) (0.5 g, 2.35 mmol) in anhydrous THF (10 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 2.2 mL, 3.53 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl 2-(4-fluorophenyl)-2-oxoacetate (**S16**) (0.58 g, 2.82 mmol) in anhydrous THF was added at the same temperature and again stirred it for 30 min to afford ethyl 7-((*tert*-butyldimethylsilyl)oxy)-2-(4-fluorophenyl)-2-hydroxyoct-3-ynoate (**S34**) (0.437 g, 74% brsm). TLC: R_f = 0.3 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.57(m, 2H), 7.10-6.97 (m, 2H), 4.28-4.10 (m, 3H), 3.95-3.87 (m, 1H), 2.41-2.34 (m, 2H), 1.68-1.65 (m, 1H), 1.58-1.54 (m, 1H), 1.16 (d, *J* = 6.10 Hz, 3H), 0.90-0.86 (m, 12H), 0.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ172.1, 164.0, 161.6, 135.6, 128.2, 128.1, 115.1, 114.9, 87.3, 78.3, 72.3, 67.1, 38.0, 30.2, 25.8, 23.7, 18.7, 18.0, 15.3,13.5, -4.28, -4.74; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{22}H_{34}O_4FSi$ 409.2205; found 409.2203.

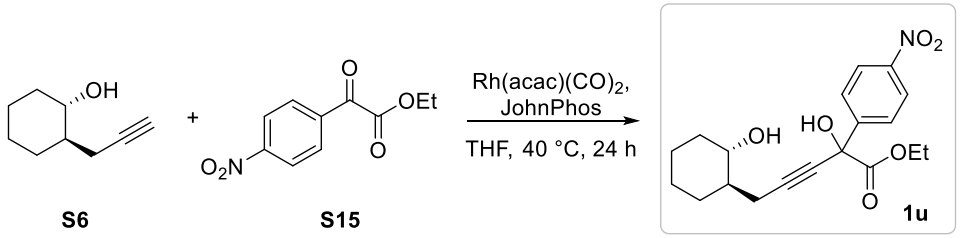
Ethyl 2-(4-fluorophenyl)-2,7-dihydroxyoct-3-ynoate (1s): Following *General procedure E*, to a solution ethyl 7-((*tert*-butyldimethylsilyl)oxy)-2-(4-fluorophenyl)-2-hydroxyoct-3-ynoate (**S34**) (0.4 g, 0.98 mmol)in anhydrous THF (5 mL) was added TBAF (1.0 M in THF, 1mL, 1.07 mmol) at 0 ºC to afford ethyl 2-(4-fluorophenyl)-2,7-dihydroxyoct-3-ynoate (**1s**) (0.131 g, 57% brsm). TLC: R_f = 0.4 (SiO_2. 40% EtOAc/ hexanes) as a viscous liquid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69-7.57(m, 2H), 7.1-6.96 (m, 2H), 4.35-4.17 (m, 3H), 4.02-3.86 (m 1H), 2.5-2.37 (m, 2H), 1.77-1.64 (m, 2H), 1.27-1.15 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ171.9, 164.1, 161.6, 161.3, 135.6, 128.2, 128.1, 115.2, 115.0, 86.9, 78.9, 72.4, 67.1, 63.5, 37.2, 23.4, 15.4, 13.8;HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{16}H_{19}O_4FNa$ 317.1160; found 317.1154.

Synthesis of 1t:



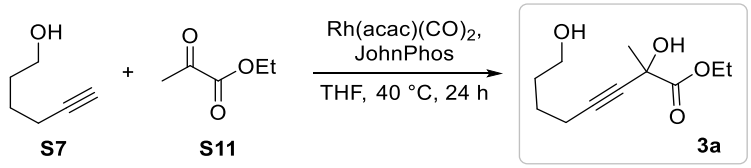
Ethyl 2-hydroxy-5-(2-hydroxycyclohexyl)-2-methylpent-3-ynoate (1t): Following *General procedure A*, a solution of 2-(prop-2-yn-1-yl)cyclohexan-1-ol) (**S6**) (0.15 g, 1.1 mmol) and ethyl pyruvate (**S11**) (0.13 g, 1.1mmol) in 0.5 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.0083 g, 0.0033 mmol) and JohnPhos (0.029 g, 0.1 mmol) under argon to afford ethyl 2-hydroxy-5-(2-hydroxycyclohexyl)-2-methylpent-3-ynoate (**1t**) (0.16 g, 57%) as a colourless liquid. TLC: R_f = 0.4 (50% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.34-4.24(m, 2H), 3.48 (br. s, 1H), 3.36-3.21 (m, 1H), 2.55-2.49 (m, 1H), 2.34-2.21 (m, 1H), 2.02-1.93 (m, 1H), 1.88-1.71 (m, 2H), 1.66 (s, 3H), 1.5-1.37 (m, 1H), 1.36-1.23 (m, 8H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.1, 83.3, 81.4, 73.6, 68, 62.7, 44.1, 35.5, 30.4, 27.4, 25.4, 24.9, 22.06, 14.03; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{14}H_{22}O_4Na$ 277.1410; found 277.1409.

Synthesis of 1u:



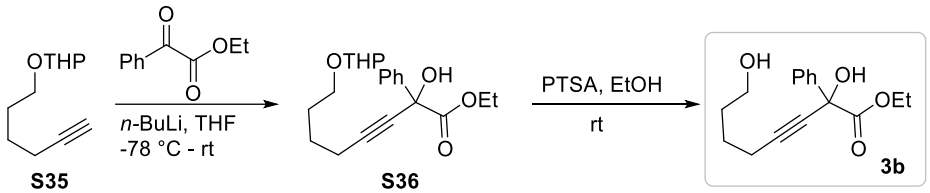
Ethyl 2-hydroxy-5-(2-hydroxycyclohexyl)-2-(4-nitrophenyl)pent-3-ynoate (1u): Following *General procedure A*, a solution of 2-(prop-2-yn-1-yl)cyclohexan-1-ol (**S6**) (0.15 g, 1.1 mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (**S15**) (0.242 g, 1.1 mmol) in 1 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.008 g, 0.032 mmol) and JohnPhos (0.028 mg, 0.1 mmol) under argon to afford ethyl 2-hydroxy-5-(2-hydroxycyclohexyl)-2-(4-nitrophenyl)pent-3-ynoate (**1u**) (0.25 g, 62%) as yellowish oil. TLC: R_f = 0.4 (40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.22 (d, *J* = 8.77 Hz, 2H), 7.88 (d, *J* = 8.39 Hz, 2H), 4.49 (br. s, 1H), 4.35-4.25 (m, 1H), 4.23-4.13 (m, 1H), 3.41-3.28 (m, 1H), 2.62 (dd, *J* = 4.20, 16.78 Hz, 1H), 2.44 (dd, *J* = 7.25, 16.78 Hz, 1H), 2.0-1.88 (m, 2H), 1.77-1.67 (m, 2H), 1.55-1.43 (m, 1H), 1.29-1.18 (m, 8H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.0, 148.0, 146.6, 127.6, 123.4, 86.8, 79.1, 73.6, 72.4, 63.9, 44.1, 35.7, 30.5, 25.4, 24.9, 22.2, 13.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{19}H_{23}O_6NNa$ 384.1418; found 384.1440.

Synthesis of 3a:



Ethyl 2, 8-dihydroxy-2-methyloct-3-ynoate (3a): Following *General procedure A*, a solution of hex-5-yn-1-ol (**S7**) (0.2 g, 2.04 mmol) and ethyl pyruvate (**S11**) (0.71 g, 6.1 mmol) in 3 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.016 g, 0.061 mmol, 3 mol%) and JohnPhos (0.055 g, 0.18 mmol, 9 mol%) under argon to afford ethyl 2,8-dihydroxy-2-methyloct-3-ynoate (**3a**) (0.119 g, 52%) as a colourless liquid. TLC: R_f = 0.2 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.29 (q, *J* = 6.87 Hz, 2H), 3.66 (t, *J* = 6.1 Hz, 2H), 2.25 (t, *J* = 6.87 Hz, 2H), 1.67-1.58 (m, 7H), 1.33 (t, *J* = 7.63 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 173.1, 84.5, 80.2, 67.9, 62.7, 62.2, 31.6, 27.3, 24.5, 18.4, 14.0; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{11}H_{18}O_4Na$ 237.1097; found 237.1091.

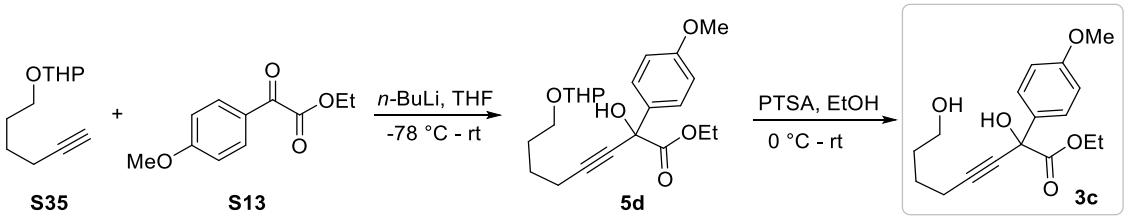
Synthesis of 3b:



Ethyl 2-hydroxy-2-phenyl-8-((tetrahydro-2*H*-pyran-2-yl) oxy) oct-3-ynoate (S36): Following *General procedure B,* to a solution of 2-(hex-5-yn-1-yloxy)tetrahydro-2*H*-pyran[16] (**S35**) (1.5 g, 8.23 mmol) in anhydrous THF (20 mL) under argon was added *n*-BuLi solution (1.6M in hexane, 6.18 mL, 9.9mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl phenyl glyoxylate (**S12**) (1.76 g, 9.9 mmol) in anhydrous THF was added at the same temperature and stirred it for 30 min to afford ethyl 2-hydroxy-2-phenyl-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (**S36**) (1.2 g, 40%) as a yellowish oil. TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, *J* = 7.63 Hz, 2H), 7.4-7.26 (m, 3H), 4.6 (s, 1H), 4.37-4.25 (m, 2H), 4.35 (br. s, 1H), 3.82-3.76 (m, 2H), 3.55-3.39 (m, 2H), 2.3 (t, *J* = 6.87Hz, 2H), 1.89-1.49 (m, 10H), 1.22(t, *J* = 6.87 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 168.9, 132.0, 129.0, 128.2, 121.6, 98.7, 85.5, 83.6, 66.8, 63.8, 63.5, 62.2, 30.6, 28.8, 25.4, 24.9, 19.5, 18.6, 13.9; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{21}H_{28}O_5Na$ 383.1829; found 383.1823.

Ethyl 2,8-dihydroxy-2-phenyloct-3-ynoate (3b): Following *General procedure D,* to a solution of ethyl 2-hydroxy-2-phenyl-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (**S36**) (1.1 g, 3.05 mmol)in ethanol was added *p*-toluenesulfonic acid(0.052g, 0.305mmol) at 0 °C and then it was slowly warmed to rt to afford ethyl 2,8-dihydroxy-2-phenyloct-3-ynoate (**3b**) (0.58 g, 68%) as a colourless liquid. TLC: R_f = 0.4 (SiO_2, 40%EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72-7.62 (m, 2H), 7.40-7.28 (m, 3H), 4.35 (br. s, 1H), 4.25-4.05 (m, 2H), 3.67 (t, *J* = 6.13 Hz, 2H), 2.36 (t, *J* = 6.88 Hz, 2H), 1.90 (br. s, 1H), 1.71-1.66 (m, 2H), 1.6-1.5 (m, 2H), 1.29-1.17 (m, 2H), 0.84 (t, *J* = 7.25 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 172.2,139.7, 128.4, 128.1, 126.1, 86.9, 78.8, 72.8, 67.0, 62.2, 31.7, 30.2, 24.6, 18.7, 18.5, 13.4; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{16}H_{20}O_4Na$ 299.1254; found 299.1250.

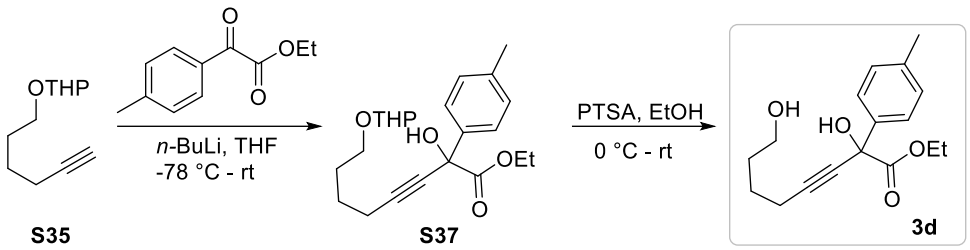
Synthesis of 5d and 3c:



Ethyl 2-hydroxy-2-(4-methoxyphenyl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (5d):Following *General procedure B,* to a solution of 2-(hex-5-yn-1-yloxy)tetrahydro-2*H*-pyran (**S35**) (0.5 g, 2.74mmol) in anhydrous THF (20 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 2.5 mL, 4.11mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl anisylglyoxylate (**S13**) (0.68 g, 3.29 mmol) in anhydrous THF was added at the same temperature and stirred it for 30 min to afford ethyl 2-hydroxy-2-(4-methoxyphenyl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (**5d**) (0.412 g, 52%) as a yellowish oil. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 8.77 Hz, 2H), 6.88 (d, *J* = 8.77 Hz, 2H), 4.62-4.54 (m, 1H), 4.33-4.24 (m, 1H), 4.22-4.12 (m, 2H), 3.89-3.75 (m, 5H), 3.53-3.40 (m, 2H), 2.37 (d, *J* = 6.87 Hz, 2H), 1.88-1.80 (m, 1H), 1.76-1.66 (m, 5H), 1.60-1.50 (m, 4H), 1.22 (t, *J* = 6.87 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 172.4, 159.7, 132.1, 127.5, 113.5, 98.8, 87, 79, 72.5, 66.9, 63.2, 62.3, 55.3, 30.7, 28.9, 25.5, 25.2, 19.6, 18.7, 13.9; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{22}H_{30}O_6Na$ 413.1935; found 413.1927.

Ethyl 2,8-dihydroxy-2-(4-methoxyphenyl)oct-3-ynoate(3c): Following *General procedure D,* to a solution of ethyl 2-hydroxy-2-(4-methoxyphenyl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate(**5d**) (0.15 g, 0.384mmol)in ethanol was added *p*-toluenesulfonic acid (0.007 g, 0.038 mmol) at 0°C and then it was slowly warmed to rt to afford ethyl 2,8-dihydroxy-2-(4-methoxyphenyl)oct-3-ynoate (**3c**) (0.087 g, 74%) as a colourless liquid. TLC: R_f = 0.4 (SiO_2, 40%EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62-7.5 (m, 2H), 6.94-6.82 (m, 2H), 4.13-4.11 (m, 3H), 3.8 (s, 3H), 3.67 (t, *J* = 6.13 Hz, 2H), 2.36 (t, *J* = 6.88 Hz, 2H), 1.78-1.6 (m, 4H), 1.21 (t, *J* = 7.13 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.3, 159.7, 132.03, 127.5, 113.6, 86.9, 79.05, 72.6, 63.2, 62.2, 55.3, 31.7, 24.6, 18.6, 13.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{17}H_{22}O_5Na$ 329.1359; found 329.1354.

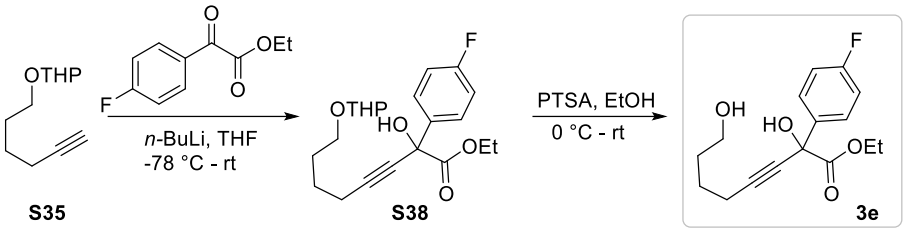
Synthesis of 3d:



Ethyl2-hydroxy-8-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-(*p*-tolyl)oct-3-ynoate(S37): Following *General procedure B,* to a solution of 2-(hex-5-yn-1-yloxy)tetrahydro-2*H*-pyran (**S35**) (0.3 g, 1.64 mmol) in anhydrous THF (20 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 1.54 mL, 2.46 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl *p*-tolylglyoxylate (**S14**) (0.37 g, 1.57 mmol) in anhydrous THF was added at the same temperature and stirred it for 30 min to afford ethyl 2-hydroxy-8-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-(*p*-tolyl)oct-3-ynoate (**S37**) (0.338 g, 55%) as a yellowish oil. TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.48 (m, 2H), 7.21-7.08 (m. 2H), 4.61-4.56 (m, 1H), 4.31-4.14 (m, 3H), 3.90-3.82 (m, 1H), 3.81-3.74 (m, 1H), 3.54-3.47 (m, 1H), 3.46-3.39 (m, 1H), 2.39-2.33 (m, 2H), 2.33 (s, 3H), 1.87-1.79 (m, 1H), 1.76-1.67 (m, 5H), 1.60-1.50 (m, 4H), 1.22(t, *J* = 6.87 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 172.3, 138.2, 136.9, 128.9, 126.1, 98.7, 86.9, 78.8, 72.7, 66.8, 63.2, 62.2, 30.7, 28.9, 25.4, 25.2, 21.1, 19.5, 18.6, 13.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{22}H_{30}O_5Na$ 397.1985; found 397.1978.

Ethyl 2,8-dihydroxy-2-(*p*-tolyl)oct-3-ynoate(3d): Following *General procedure D,* to a solution of ethyl 2-hydroxy-8-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-(*p*-tolyl)oct-3-ynoate (**S37**) (0.1 g, 0.267 mmol)in ethanol was added *p*-toluenesulfonic acid (0.004 g, 0.027 mmol) at 0 ºC and then it was slowly warmed to rt to afford ethyl 2,8-dihydroxy-2-(*p*-tolyl)oct-3-ynoate (**3d**) (0.062 g, 80%) as a colourless liquid. TLC: R_f = 0.4 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.57 (m, 2H), 7.10-7.97 (m, 2H), 4.34-4.09 (m, 2H), 3.78 (s, 1H), 3.78-3.60 (m, 2H), 2.65 (s, 3H), 2.43-2.31 (m, 2H), 1.79-1.59 (m, 4H), 1.22 (t, *J* = 7.33 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 172.0, 135.5, 128.2, 128.1, 115.2, 114.9, 87.1, 78.7, 72.3, 63.4, 62.2, 31.7, 24.6, 18.6, 13.8; HRMS (ESI) m/z:$[M+Na]^+$calcd for $C_{17}H_{22}O_4Na$ 313.1410; found 313.1402.

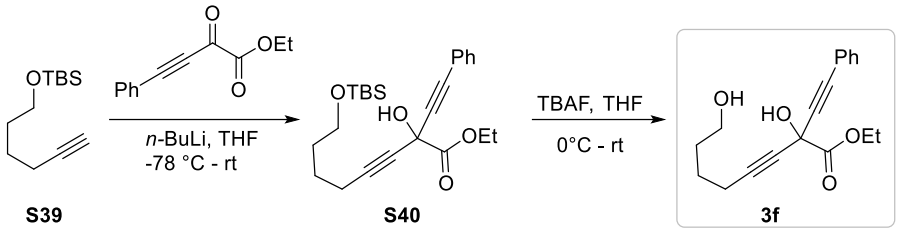
Synthesis of 3e:



Ethyl 2-(4-fluorophenyl)-2-hydroxy-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (S38):Following *General procedure B*,to a solution of 2-(hex-5-yn-1-yloxy)tetrahydro-2*H*-pyran(**S35**)(0.3 g, 1.64mmol) in anhydrous THF (20 mL) under argon was added*n*-BuLi solution (1.6M in hexane, 1.54 mL, 2.46mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl 2-(4-fluorophenyl)-2-oxoacetate (**S16**) (0.39 mL, 1.97 mmol) in anhydrous THF was added at the same temperature and again stirred it for 30 min to afford ethyl 2-(4-fluorophenyl)-2-hydroxy-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (**S38**) (0.324 g, 52%) as a yellowish oil. TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72-7.57 (m, 2H), 7.12-6.97 (m, 2H), 4.63-4.52 (m, 1H), 4.31-4.15 (m, 3H), 3.90-3.73 (m, 2H), 3.54-3.38 (m, 2H), 2.37 (t, *J* = 6.87 Hz, 2H), 1.75-1.67 (m, 5H), 1.61-1.49 (m, 5H), 1.21(t, *J* = 7.33 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.0, 164.0, 135.6, 128.2,128.1, 115.1, 114.9, 98.8, 87.2, 78.6, 72.3, 66.8, 63.3, 62.3, 30.7, 28.9, 25.4, 25.1, 19.5, 18.6, 13.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{21}H_{27}O_5FNa$ 401.1735; found 401.1722.

Ethyl 2-(4-fluorophenyl)-2,8-dihydroxyoct-3-ynoate (3e): Following *General procedure D*, to a solution of ethyl 2-(4-fluorophenyl)-2-hydroxy-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (**S38**) (0.1 g, 8.5 mmol) in ethanol was added *p*-toluenesulfonic acid (0.008 g, 0.85 mmol) at 0 °C and then it was slowly warmed to rt to afford ethyl 2-(4-fluorophenyl)-2,8-dihydroxyoct-3-ynoate (**3e**) (0.057 g, 73%) as a colourless liquid. TLC: R_f = 0.4 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70-7.56 (m, 2H), 7.11-6.97 (m, 2H), 4.39-4.08 (m, 2H), 3.8 (s, H), 3.69(t, *J* = 5.95 Hz, 2H), 2.65 (s, 3H), 2.37 (m, 2H), 1.73-1.66 (m, 3H), 1.22 (t, *J* = 7.33 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.9, 164.03, 135.5, 128.27, 128.20, 115.17, 114.95, 87.1, 78.7, 72.3,63.4, 62.2, 31.7, 24.6, 18.5, 13.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{16}H_{19}O_4FNa$ 317.1160; found 317.1152.

Synthesis of 3f:

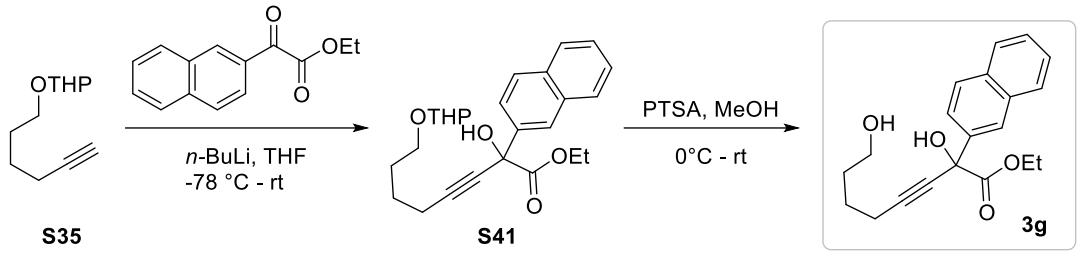


Ethyl 8-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-(phenylethynyl)oct-3-ynoate (S40): Following *General procedure B* ,to a solution of *tert*-butyl(hex-5-yn-1-yloxy)dimethylsilane[17] (**S39**) (0.5 g, 2.35 mmol) in anhydrous THF (10 mL) under argon was added *n*-BuLi solution (1.6M in hexane, 2.2 mL, 3.53mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl 2-oxo-4-phenylbut-3-ynoate (**S17**) (0.571 g, 2.82mmol) in anhydrous THF was added at the same temperature and again stirred it for 30 min to afford ethyl 8-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-(phenylethynyl)oct-3-ynoate (**S40**) (0.18 g, 49%) as a yellowish oil. TLC: R_f = 0.7 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.40 (m, 2H), 7.31-7.25 (m, 3H), 4.36 (q, *J* = 7.13 Hz, 2H), 3.87 (br. s, 1H), 3.62-3.55 (m, 2H), 2.29-2.22 (m, 2H), 1.60-1.55 (m, 4H), 1.34 (t, *J* = 7.13 Hz, 3H), 0.84 (s, 9H), 0.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ169.1, 132.0, 129.0, 128.3, 128.2, 121.7, 85.5, 85.4, 83.7, 64.0, 63.5, 61.4, 31.2, 29.7, 25.9, 25.6, 18.3, 15.2, 13.9, -5.37; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{24}H_{35}O_4Si$ 415.2299; found 415.2294.

Ethyl 2,8-dihydroxy-2-(phenylethynyl)oct-3-ynoate(3f): Following *General procedure D,* to a solution of ethyl 8-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-(phenylethynyl)oct-3-ynoate (**S40**) (0.15 g, 0.36 mmol)in dry THF was added TBAF in THF (0.5 mL, 0.85 mmol) at 0 °C and then it was slowly warmed to rt to afford ethyl 2,8-dihydroxy-2-(phenylethynyl)oct-3-ynoate (**3f**) (0.1 g, 66%) as a colourless liquid. TLC: R_f = 0.4 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51-7.44 (m, 2H), 7.35-7.29 (m, 3H), 4.41 (q, *J* = 7.13 Hz, 2H), 3.69 (t, *J* = 6.0 Hz, 2H), 2.33 (t, *J* = 6.75 Hz, 2H), 1.70-1.64 (m, 4H), 1.39 (t, *J* = 7.13 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.9, 132.0, 129.1, 128.23, 121.5, 85.1, 85.0, 83.7, 64.1, 63.5, 61.5, 30.6, 29.7, 15.4, 13.9; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{18}H_{21}O_4$ 301.1434; found 301.1421.

[17]Skotnitzki, J.; Kremsmair, A.; Keefer, D.; Gong, Y.; Vivie-Riedle, R. D.; Knochel, P. *Angew. Chem. Int. Ed*. **2020**, *59*, 320 – 324.

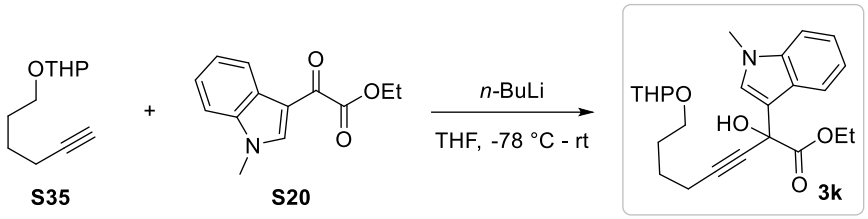
Synthesis of 3g:



Ethyl 2-hydroxy-2-(naphthalene-2-yl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (S41): Following *General procedure B,* to a solution of 2-(hex-5-yn-1-yloxy)tetrahydro-2*H*-pyran (**S35**) (0.5 g, 2.74 mmol) in an anhydrous THF (20 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 2.57 mL, 4.11 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl 2-(naphthalene-2-yl)-2-oxoacetate (**S19**) (0.625 g, 2.74 mmol) in an anhydrous THF was added at the same temperature and stirred it for 30 min to afford ethyl 2-hydroxy-2-(naphthalene-2-yl)-8-((tetrahydro-2*H*-pyran-2-yl) oxy) oct-3-ynoate (**S41**) (0.3g, 45% brsm) as yellowish oil.TLC: R_f = 0.4 (SiO_2, 30% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27-8.06 (m, 2H), 7.97-7.77 (m, 2H), 7.59-7.36 (m, 3H), 4.61 (s, 1H), 4.30-4.13 (m, 2H), 3.92-3.76 (m, 2H), 3.58-3.34 (m, 2H), 2.52-2.39 (t, *J* = 6.7 Hz, 2H), 1.88-1.67 (m, 6H), 1.62-1.50 (m, 4H), 1.08 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.1, 134.3, 133.9, 130.4, 130.1, 128.9, 127.2, 126.4, 125.7, 124.8, 98.9, 89.6, 78.9, 74.5, 67.0, 63.2, 62.4, 30.8, 29.1, 25.5, 25.3, 19.7, 18.9, 13.8; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{25}H_{30}O_5Na$ 433.1985; found 433.1973.

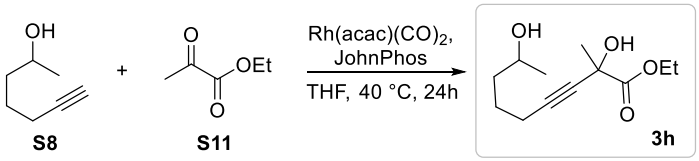
Ethyl 2, 8-dihydroxy-2-(naphthalene-2-yl) oct-3-ynoate (3g): Following *General procedure D,* to a solution of ethyl 2-hydroxy-2-(naphthalene-2-yl)-8-((tetrahydro-2*H*-pyran-2-yl) oxy) oct-3-ynoate (**S41**)(0.3g, 7.3 mmol)in ethanol (5 mL) was added *p*-toluenesulfonic acid (0.14 g, 7.3 mmol) at 0°C and then it was slowly warmed to rt to afford ethyl 2, 8-dihydroxy-2-(naphthalene-2-yl) oct-3-ynoate (**3g**) (0.15 g, 63%) as a colourless liquid. TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.21-8.1 (m, 2H), 7.91-7.81 (m, 2H), 7.53-7.44 (m, 3H), 4.29-4.11 (m, 3H), 3.75-3.67 (m, 2H), 2.47-2.41 (m, 2H), 1.76-1.7 (m, 4H), 1.09 (t, *J* =7 .25 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 173.1, 134.3, 133.9, 130.3, 130.1, 128.9, 127.1, 126.3, 125.6, 124.7, 89.4, 79.05, 74.5, 63.2, 62.3, 31.8, 24.6, 18.8, 13.7; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{20}H_{22}O_4Na$ 349.1410; found 349.1405.

Synthesis of 3k:



Ethyl 2-hydroxy-2-(1-methyl-1*H*-indol-3-yl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (3k): Following *General procedure B,* to a solution of 2-(hex-5-yn-1-yloxy)tetrahydro-2*H*-pyran (**S35**) (0.5 g, 2.74 mmol) in anhydrous THF (10 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 2.6 mL, 4.11mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl 2-(1-methyl-1*H*-indol-3-yl)-2-oxoacetate (**S20**) (0.761 g, 3.29 mmol) in anhydrous THF was added at the same temperature and stirred it for 30 min to afford ethyl 2-hydroxy-2-(1-methyl-1*H*-indol-3-yl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (**3k**) (0.67g, 59%) as a yellowish oil. TLC: R_f = 0.3 (SiO_2, 30% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.77-7.68 (m, 1H), 7.36-7.33 (m, 1H), 7.32-7.28 (m, 1H), 7.25-7.20 (m, 1H), 7.15-7.09(m, 1H), 4.62-4.56 (m, 1H), 4.37-4.14 (m, 2H), 3.91-3.84 (m, 2H), 3.78 (s, 3H), 3.52-3.42 (m, 2H), 2.38 (t, J = 7.0 Hz, 2H), 1.91-1.45 (m, 10H), 1.22 (t, J = 7.13 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ172.5, 137.7, 128.5, 124.9, 121.9, 120.3, 119.6, 114.2, 109.4, 98.9, 85.6, 79.0, 69.0, 67.0, 63.2, 62.3, 32.9, 30.7, 29.0, 25.5, 25.3, 19.6, 18.7, 14.0; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{24}H_{31}O_5NNa$ 436.2094; found 436.2096.

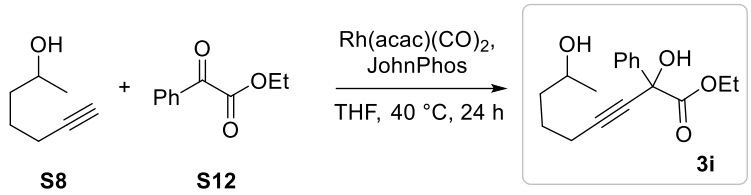
Synthesis of 3h:



Ethyl 2,8-dihydroxy-2-methylnon-3-ynoate (3h): Following *General procedure A,* a solution of hept-6-yn-2-ol(**S8**) (0.2 g, 2.04 mmol) and ethyl pyruvate (**S11**) (0.71 g, 6.1 mmol) in 3 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.016 g, 0.061 mmol, 3.0 mol%) and JohnPhos (0.055g, 0.18 mmol, 9.0 mol%) under argon to ethyl 2,8-dihydroxy-2-methyloct-3-ynoate (**3h**) (0.119g, 52%) as a colourless liquid. TLC: R_f = 0.2 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR

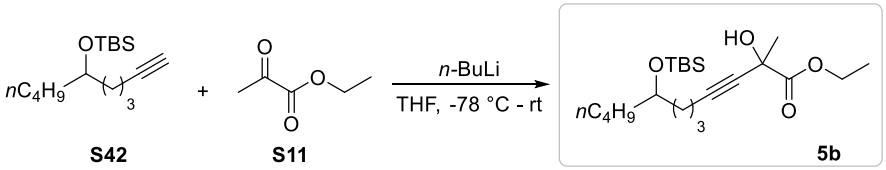
($CDCl_3$, 500 MHz): δ 4.28 (q, *J* = 6.87 Hz, 2H), 3.87-3.763 (m, 1H), 3.45 (s, 1H), 2.25 (t, *J* = 6.87 Hz, 2H), 1.53 (s, 3H), 1.6-1.43 (m, 4H), 1.33 (t, *J* = 7.63 Hz, 3H), 1.17 (d, *J* = 6.87 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 173.2, 84.7, 80.3,68.0, 67.7, 62.8, 38.3, 27.5, 24.6, 23.7, 18.7, 14.1; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{12}H_{20}O_4Na$ 251.1254; found 251.1245.

Synthesis of 3i:



Ethyl 2,8-dihydroxy-2-phenylnon-3-ynoate(3i): Following *General procedure A*, a solution of hept-6-yn-2-ol (**S8**) (0.3 g, 2.67mmol) and ethyl phenyl glyoxylate (**S12**) (1.4 g, 8.02 mmol) in 5 mL of THF was added to a mixture of $Rh(acac)(CO)_2$ (0.02 g, 0.080mmol, 3 mol%) and JohnPhos (0.071 g, 2.4mmol, 9 mol%) under argon to obtain ethyl 2,8-dihydroxy-2-phenylnon-3-ynoate (**3i**) (0.24 g, 22%; 54% brsm) as a colourless liquid. TLC: R_f = 0.2 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.58 (m, 2H), 7.41-7.3 (m, 3H), 4.33-4.08 (m, 3H), 3.89-3.80 (m, 1H), 2.4-2.32 (m, 2H), 1.78-1.48 (m, 4H), 1.29-1.16 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ172.3, 139.8, 128.5, 128.2, 126.2, 87.0, 78.9, 72.9, 67.6, 67.06, 63.3, 38.3, 30.3, 24.6, 23.6, 18.8, 18.7, 13.8, 13.5; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{17}H_{22}O_4Na$ 313.1410; found 313.1404.

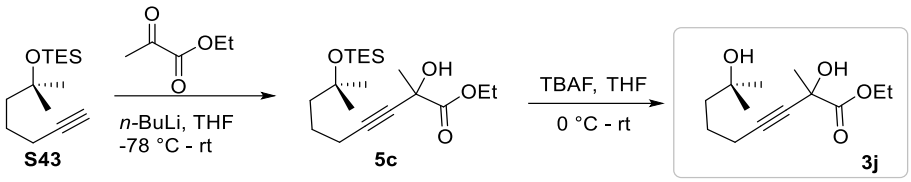
Synthesis of 5b:



Ethyl 8-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-methyldodec-3-ynoate (5b): Following *General procedure C*, to a solution of *tert*-butyl(dec-9-yn-5-yloxy)dimethylsilane (**S42**) (0.5 g, 1.86 mmol) in an anhydrous THF (20 mL) under argon was added *n*-BuLi solution (1.6 M in

hexane, 1.74 mL, 2.79 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl pyruvate (**S11**) (0.26 g, 2.23mmol) in an anhydrous THF was added at the same temperature and stirred it for 30 min to afford ethyl 8-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-methyldodec-3-ynoate (**5b**) (0.427 g, 60%) as yellowish oil. TLC: R_f= 0.4 (SiO_2, 10% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.28(q, *J* = 6.87 Hz, 2H), 3.67-3.55 (m, 1H), 2.25-2.16 (m, 2H), 1.64 (s, 3H), 1.56-1.39 (m, 7H), 1.35-1.24 (m, 7H), 0.87 (s, 12H), 0.03 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ173.1, 84.8, 79.9, 71.7, 67.8, 6.6, 36.7, 36.0,30.4, 27.4, 27.3, 25.8, 24.05, 22.8, 18.8, 18.06, 14.06, 13.9, -4.5; HRMS (ESI) m/z:[M+Na]$^+$ calcd for $C_{21}H_{40}O_4NaSi$ 407.2588; found 407.2580.

Synthesis of 3j:



Triethyl((2-methylhept-6-yn-2-yl)oxy)silane (S43): To a solution of 2-methylhept-6-yn-2-ol (**S10**) (1.6 g, 12.67 mmol) in anhydrous DMF (15 mL) under argon was added imidazole (1.72 g, 25.34 mmol) and chlorotriethylsilane(4.7 mL, 13.16 mmol)was added at 0 °C. The resultant reaction mixture was warmed to rt and monitored by TLC, then the reaction was quenched with ice-cold water and extracted with diethyl ether to afford triethyl((2-methylhept-6-yn-2-yl)oxy)silane (**S43**) (1.8 g, 56%). TLC: R_f = 0.8 (SiO_2, 10% EtOAc/hexanes)as a yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.22-2.15 (m, 2H), 1.96-1.91(m, 1H), 1.62-1.49(m, 4H), 1.21 (s, 6H), 0.96-0.92 (m, 9H), 0.61-0.54 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 84.8, 73.1, 68.1, 44.2, 29.9, 23.6, 18.9, 7.1, 6.8, 6.4; HRMS (ESI) m/z:[M+H]$^+$ calcd for $C_{14}H_{29}OSi$ 241.1982; found 241.1983.

Ethyl 2-hydroxy-2,8-dimethyl-8-((triethylsilyl)oxy)non-3-ynoate(5c): To a solution of triethyl((2-methylhept-6-yn-2-yl)oxy)silane (**S43**) (0.3 g, 1.25mmol) in anhydrous THF (10 mL) under argon was added *n*-BuLi solution (1.6 M in hexane, 1.19 mL, 1.9 mmol). The resultant mixture was stirred at -78 ºC for 45 min. Then the solution of ethyl pyruvate(**S11**) (0.18 g, 1.5 mmol) in anhydrous THF was added at the same temperature and again stirred it for 30 min to

afford ethyl 2-hydroxy-2,8-dimethyl-8-((triethylsilyl)oxy)non-3-ynoate(**5c**)(0.32 g, 73%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes) as a yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.30 (q, *J* = 7.13 Hz, 2H), 3.42(s, 1H), 2.20 (d, *J* = 6.88 Hz, 2H), 1.66 (s, 3H), 1.59-1.47 (m, 4H), 1.34 (t, *J* = 7.13 Hz, 3H), 1.20 (s, 6H), 0.94 (t. *J* = 8.0 Hz, 9H), 0.57 (q, *J* = 7.75 Hz, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ173.2, 85.1, 79.9, 73.1, 67.9, 62.7, 44.2, 29.9, 27.3, 23.4, 19.1, 14.0, 7.12, 6.7; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{19}H_{36}O_4NaSi$ 379.2275; found 379.2270.

Ethyl 2,8-dihydroxy-2,8-dimethylnon-3-ynoate (3j): Following *General procedure D,* to a solution of ethyl 2-hydroxy-2,8-dimethyl-8-((triethylsilyl)oxy)non-3-ynoate (**S43**) (0.15 g, 0.36 mmol) in dry THF was added TBAF in THF (0.5 mL, 0.85 mmol) at 0 °C and then it was slowly warmed to rt to afford ethyl 2,8-dihydroxy-2,8-dimethylnon-3-ynoate (**3j**) (0.1 g, 66%) as a colourless liquid. TLC: R_f = 0.7 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.3 (q, *J* = 7.13 Hz, 2H), 2.23(t, *J* = 6.63 Hz, 2H), 1.66 (s, 3H), 1.62-1.52 (m, 4H), 1.34 (t, *J* = 7.13Hz, 3H), 1.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.1, 84.7, 80.2, 76.7, 70.8, 67.9, 62.7, 42.9, 29.3, 27.4, 23.4, 19.1, 14.04; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{13}H_{22}O_4Na$ 265.1410; found 265.1411.

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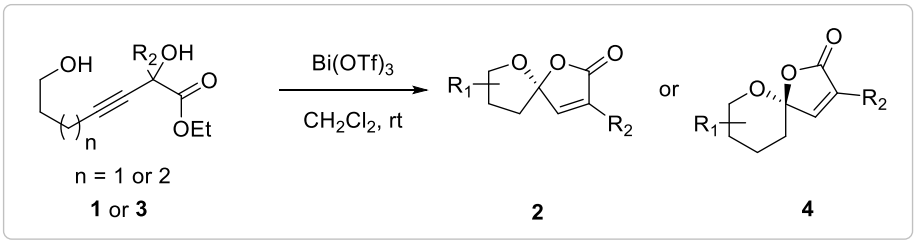
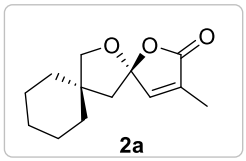
6. ***Synthesis of [5,5]-unsaturated oxaspirolactones from propargylic diol esters***



General Procedure F for the synthesis of [5,5] and [6,5]-α,β-unsaturated oxaspirolactones (**2** and **4**) from propargylic diol esters (**1** and **3**): To a stirred solution of **1** or **2** (0.25 mmol) in anhydrous CH_2Cl_2 (2.0 mL) was added $Bi(OTf)_3$ (0.024 mmol, 10 mol%) at room temperature under argon atmosphere, and the reaction mixture was stirred at rt until complete conversion monitored by TLC. The reaction was quenched by the addition of saturated aqueous solution of $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2 (2x5 mL) and combined organic layers were washed with brine solution. The combined extracts were dried over an anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by

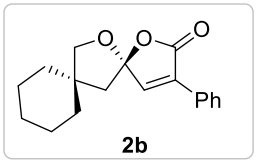
silica gel column chromatography (elution with EtOAc/hexanes) to afford [5,5] or [6,5]-α,β-unsaturated oxaspirolactones (**2** or **4**).

3-Methyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (2a):



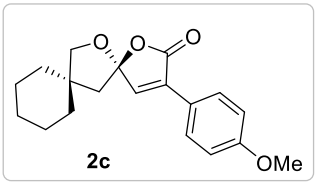
Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-methylpent-3-ynoate (**1a**) (0.05 g, 0.19 mmol) in an anhydrous CH_2Cl_2 (1.0 mL) was added $Bi(OTf)_3$ (0.012 g, 0.019 mmol) under argon atmosphere to obtain 3-methyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**2a**) (0.035 g, 85%) as a colourless liquid. TLC: R_f = 0.7 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.69-6.67 (m, 1H), 3.95 (d, *J* = 8.39 Hz, 1H), 3.86 (d, *J* = 8.39 Hz, 1H), 2.12 (d, *J* = 14.5 Hz, 1H), 2.01 (d, *J* = 14.5 Hz, 1H), 1.91 (s, 3H), 1.72-1.64 (m, 2H), 1.53-1.38 (m, 8H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.6, 145.1, 132.5, 113.2, 80.4, 47.1, 43.6, 37.4, 35.5, 25.6, 23.8, 23.7, 10.4; FTIR (cm^{-1}) 2928, 2857, 1767, 1669, 1447, 1329, 1123, 1008, 972, 870, 763; HRMS (ESI) m/z:[M+H]$^+$calcd for $C_{13}H_{19}O_3$ 223.1329; found 223.1333.

3-Phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (2b):



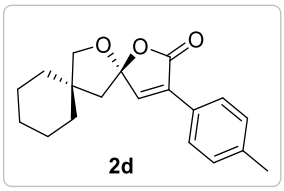
Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-phenylpent-3-ynoate (**1b**) (0.05 g, 0.15 mmol) in an anhydrous CH_2Cl_2 (2 mL) was added $Bi(OTf)_3$ (0.01 g, 0.015 mmol) under argon atmosphere to obtain 3-phenyl-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (**2b**) (0.035 g, 81%). TLC: R_f = 0.7 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.75 (m, 2H), 7.5-7.37 (m, 3H), 7.17 (s, 1H), 4.04(d, *J* = 8.46 Hz, 1H), 3.93 (d, *J* = 8.46 Hz, 1H), 2.24 (d, *J* = 13.89 Hz, 1H), 2.13(d, *J* = 13.77 Hz, 1H), 1.81-1.68 (m, 2H), 1.64-1.39 (m, 8H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.3, 143.7, 133.6, 129.7, 129, 128.7, 127.5, 112.4, 80.5, 47.4, 43.8, 37.4, 35.5, 25.6, 23.9, 23.8; FTIR (cm^{-1}) 3023, 2928, 2858, 1761, 1647, 1451, 1216, 1123, 1037, 944, 847, 762, 671; HRMS (ESI) m/z:[M+H]$^+$ calcd for $C_{18}H_{21}O_3$ 285.1485; found 285.1483.

3-(4-Methoxyphenyl)-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (2c):



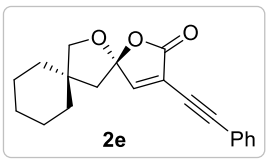
Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-(4-methoxyphenyl) pent-3-ynoate (**1c**)(0.1 g, 0.277 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.018g, 0.0277mmol) under argon atmosphere to obtain 3-(4-methoxyphenyl)-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (**2c**) (0.072 g, 83%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.75 (m, 2H), 7.06 (s, 1H), 7.04-6.92 (m, 2H), 4.04(d, *J* = 8.46 Hz, 1H), 3.93 (d, *J* = 8.46 Hz, 1H), 3.86 (s, 3H), 2.24 (d, *J* = 13.89 Hz, 1H), 2.13(d, *J* = 13.77 Hz, 1H), 1.81-1.68 (m, 2H), 1.64-1.39 (m, 8H); ^{13}C NMR ($CDCl_3$,101 MHz): δ 169.6, 160.7, 141.3, 132.9, 129.0, 121.5, 114.1, 112.4, 80.5, 55.4, 47.4, 43.8, 37.4, 35.6, 25.6, 23.87, 23.76; FTIR (cm^{-1}) 3022, 2927, 2856, 1761, 1610, 1512, 1455, 1252, 1216, 1171, 1124, 1033, 909, 838, 761, 666; HRMS (ESI) m/z:[M+H]$^+$ calcd for $C_{19}H_{23}O_4$ 315.1591; found 315.1582.

3-(p-tolyl)-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (2d):



Following *General Procedure F*,to the mixture of ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclohexyl)-2-(*p*-tolyl)pent-3-ynoate (**1d**) (0.05 g, 0.15 mmol) in an anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.009, 0.015 mmol) under argon atmosphere to obtain 3-(*p*-tolyl)-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (**2d**) (0.034 g, 79%).TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76-7.70 (m, 2H), 7.23-7.18 (m, 2H), 7.11 (s, 1H), 4.0 (d, *J* = 8.46 Hz, 1H), 3.91 (d, *J* = 8.46 Hz, 1H), 2.36 (s, 3H), 2.21 (d, *J* = 13.89 Hz, 1H), 2.12 (d, *J* = 13.77 Hz, 1H), 1.74-1.69 (m, 2H), 1.56-1.42 (m, 8H); ^{13}C NMR ($CDCl_3$,101 MHz): δ 169.4, 142.6, 139.8, 133.3, 129.3, 127.3, 126.0, 112.3, 80.4, 47.3, 43.7, 37.3, 35.5, 25.5, 23.8, 23.7, 21.3; HRMS (ESI) m/z:[M+H]$^+$calcd for $C_{19}H_{23}O_3$ 299.1642; found 299.1643.

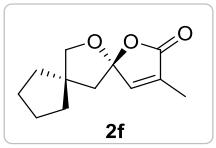
3-(Phenylethynyl)-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (2e):



Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-(phenylethynyl)pent-3-ynoate (**1e**) (0.1 g, 0.282 mmol) in an anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.018 g, 0.028 mmol) under argon atmosphere to obtain 3-(phenylethynyl)-1,14-

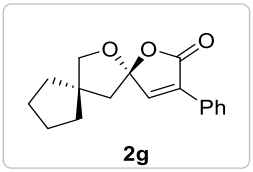
dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one] (**2e**) (0.071 g, 82%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57-7.52 (m, 2H), 7.4-7.34 (m, 3H), 7.14-7.09 (m, 1H), 4.01(d, *J* = 8.39 Hz, 1H), 3.92 (d, *J* = 8.39 Hz, 1H), 2.21 (d, *J* = 13.73 Hz, 1H), 2.1(d, *J* = 13.73 Hz, 1H), 1.73-1.68 (m, 2H), 1.53-1.44 (m, 8H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 167.3, 150.4, 133.8, 132.1, 129.6, 128.4, 121.5, 120.1, 113.8, 97.9, 80.8, 78.1, 43.8, 37.3, 35.5, 25.5, 23.9, 23.7; HRMS (ESI) m/z:[M+H]$^+$ calcd for $C_{20}H_{21}O_3$ 309.1485; found 309.1483.

3-Methyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (2f):



Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclopentyl)-2-methylpent-3-ynoate (**1f**) (0.05 g, 0.2 mmol)in anhydrous CH_2Cl_2 (1 mL) was added $Bi(OTf)_3$ (0.013 g, 0.02 mmol) under argon atmosphere to obtain 3-methyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (**2f**) (0.032 g, 78%) as white solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.71 (s, 1H), 4.01(d, *J* = 8.4 Hz, 1H), 3.85 (d, *J* = 8.4 Hz, 1H), 2.18 (s, 2H), 1.92 (s, 3H), 1.86-1.81(m, 2H), 1.7-1.58 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.6, 145.1, 132.5, 113.3, 81.1, 50.3, 47.4, 38.01, 37.2, 24.6, 24.4, 10.4;FTIR (cm^{-1}) 3020, 2931, 2866, 1764, 1659, 1447, 1397, 1330, 1222, 1115, 1006, 758, 672; HRMS (ESI) m/z:[M+H]$^+$ calcd for $C_{12}H_{17}O_3$ 209.1172; found 209.1176.

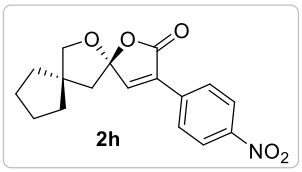
3-Phenyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (2g):



Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclopentyl)-2-phenylpent-3-ynoate(**1g**) (0.05 g, 1.6 mmol) in anhydrous CH_2Cl_2 (1 mL) was added $Bi(OTf)_3$ (0.0103 g, 0.016 mmol) under argon atmosphere to obtain 3-phenyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (**2g**) (0.37 g, 86 %) as a white solid; TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz):δ 7.88-7.8 (m, 2H), 7.46-7.37 (m, 3H), 7.19 (s, 1H), 4.08 (d, *J* = 8.1 Hz, 1H), 3.92 (d, *J* = 8.39 Hz, 1H), 2.4-2.2 (m, 2.37-2.25 (m, 2H), 1.93-1.84 (m, 2H), 1.79-1.62 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.3, 143.7, 133.6, 129.7, 129.0, 128.7, 127.6, 112.4, 81.3, 50.5, 47.7, 38.01, 37.2, 24.7,24.4; FTIR (cm^{-1}) 3023, 2955, 2403,

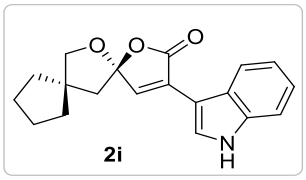
1763, 1647, 1439, 1334, 1216, 1116, 1034, 942, 852, 760, 669; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{17}H_{19}O_3$ 271.1329; found 271.1333.

3-(4-Nitrophenyl)-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (2h):



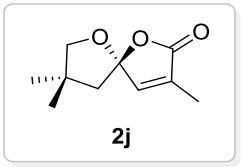
Following *General Procedure F*,to the mixture of ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclopentyl)-2-(4-nitrophenyl)pent-3-ynoate (**1h**) (0.05 g, 0.14 mmol) in anhydrous CH_2Cl_2 (1 mL) was added $Bi(OTf)_3$ (0.009 g, 0.014 mmol) under argon atmosphere to obtain 3-(4-nitrophenyl)-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (**2h**) (0.032 g, 73%) as a yellowish solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 9.2 Hz, 2H), 7.39 (s, 1H), 4.11 (d, *J* = 8.5 Hz, 1H), 3.94 (d, *J* = 7.9 Hz, 1H), 2.39-2.27 (m, 2H), 1.95-1.83 (m, 2H), 1.81-1.62 (m, 6H); ^{13}C NMR ($CDCl_3$, 101MHz): δ 168.3, 148.3, 147.0, 135.0, 131.7, 128.5, 123.9, 112.6, 81.5, 50.6, 47.6, 37.9, 37.1, 24.6, 24.4; FTIR (cm^{-1}) 3023, 2949, 1756, 1650, 1521, 1350, 1215, 1350, 1215, 1118, 1047, 760; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{17}H_{18}O_5N$ 316.1179; found 316.1187.

3-(1*H*-Indol-3-yl)-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (2i):



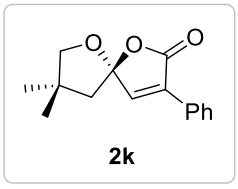
Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-5-(1-(hydroxymethyl) cyclopentyl)-2-(1-methyl-1*H*-indol-3-yl) pent-3-ynoate (**1i**) (0.012 g, 0.034 mmol) in anhydrous CH_2Cl_2 (1 mL) was added $Bi(OTf)_3$ (0.002 g. 0.003 mmol) under argon atmosphere to obtain 3-(1-methyl-1*H*-indol-3-yl)-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (**2i**) (0.0074 g,71%) as a yellowish solid. TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.5(br. s, 1H), 8.32-8.21(m, 1H), 7.85-7.73(m, 1H), 7.50-7.40(m, 1H), 7.3-7.2(m, 2H), 7.18(s, 1H), 4.09(d, *J* = 8.39Hz, 1H), 3.93(d, *J* = 7.63Hz, 1H), 2.34 (dd, *J* = 12.97, 2.29Hz, 2H), 1.94-1.84(m, 2H), 1.8-1.65(m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.8, 136.4, 136.2, 128.0, 127.2, 125.6, 123.0, 121.1, 119.7, 114.0, 111.8, 105.9, 81.1, 64.5, 50.4, 48.0, 38.2, 37.3, 24.7, 24.4; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{19}H_{20}O_3N$310.1438; found 310.1438.

3,8,8-Trimethyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2j):



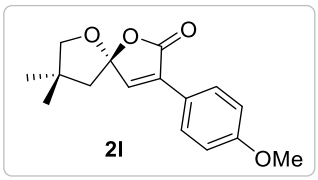
Following *General Procedure F*, to the mixture of ethyl 2,7-dihydroxy-2,6,6-trimethylhept-3-ynoate (**1j**) (0.1 g, 0.44 mmol)in an anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.029 g, 0.044 mmol) under argon atmosphere to obtain 3,8,8-trimethyl-1,6-dioxaspiro[4.4]non-3-en-2-one (**2j**) (0.068 g, 86%) as a yellowish oil. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.63 (s, 1H), 3.8 (d, *J* = 8.39 Hz, 1H), 3.66 (d, *J* = 8.39 Hz, 1H), 1.99 (s, 2H), 1.81 (s, 3H), 1.18 (s, 3H), 1.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 101MHz): δ 171.3, 145.2, 131.8, 113.4, 81.8, 48.8, 39.3, 27.5, 25.9, 10.1; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{10}H_{15}O_3$183.1016; found 183.1015.

8,8-Dimethyl-3-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one(2k):



Following *General Procedure F*, to the mixture of ethyl 2,7-dihydroxy-6,6-dimethyl-2-phenylhept-3-ynoate(**1k**)(0.1 g, 0.34 mmol)in an anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.023g, 0.034mmol) under argon atmosphere to obtain 8,8-dimethyl-3-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (**2k**) (0.071 g, 84%) as a white solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86-7.77 (m, 2H), 7.43-7.33 (m, 3H), 7.16 (s, 1H), 3.96 (d, *J* = 8.39 Hz, 1H), 3.8 (d, *J* = 8.39Hz, 1H), 2.19 (s, 2H), 1.31 (s, 3H), 1.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.2, 143.8, 133.3, 129.7, 128.9, 128.6, 127.5, 112.7, 82.2, 49.4, 39.7, 27.8, 26.1; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{15}H_{17}O_3$ 245.1172; found 245.1172.

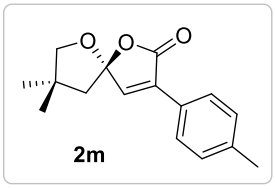
3-(4-Methoxyphenyl)-8,8-dimethyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2l):



Following *General Procedure F*, to the mixture of ethyl 2,7-dihydroxy-2-(4-methoxyphenyl)-6,6-dimethylhept-3-ynoate (**1l**) (0.05 g, 0.15mmol) in an anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.010 g, 0.015 mmol) under argon atmosphere to obtain 3-(4-methoxyphenyl)-8,8-dimethyl-1,6-dioxaspiro[4.4]non-3-en-2-one (**2l**) (0.038 g, 90%) as a white

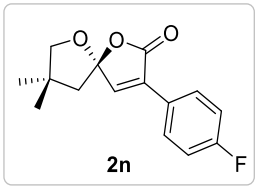
solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.89-7.76 (m, 2H), 7.06 (s, 1H), 6.97-6.85 (m, 2H), 3.97 (d, *J* = 8.24 Hz, 1H), 3.84 (s, 3H), 3.81 (d, *J* = 8.24 Hz, 1H), 2.23- 2.14 (m, 2H), 1.32 (s, 3H), 1.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.5, 160.7, 141.4, 132.7, 128.9, 121.4, 114.0, 112.7, 82.1, 55.3, 49.5, 39.7, 27.9, 26.2; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{16}H_{19}O_4$ 275.1278; found 275.1274.

8,8-Dimethyl-3-(*p*-tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one(2m):



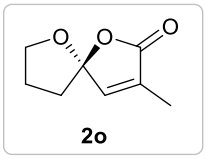
Following *General Procedure F*, to the mixture of ethyl 2,7-dihydroxy-6,6-dimethyl-2-(*p*-tolyl)hept-3-ynoate (**1m**) (0.08g, 0.26 mmol) in an anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.017 g, 0.026 mmol) under argon atmosphere to obtain 8,8-dimethyl-3-(*p*-tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one (**2m**) (0.054 g, 80%) as a white solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.69 (m, 2H), 7.2-7.15 (m, 2H), 7.11(s, 1H), 3.93 (d, *J* = 8.39 Hz, 1H), 3.78 (d, *J* = 8.39 Hz, 1H), 2.34 (s, 3H), 2.15 (s, 2H), 1.29 (s, 3H), 1.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.3, 142.8, 139.7, 132.9, 129.2, 127.2, 125.9, 112.6, 82.0, 49.2, 39.6, 27.6, 26.0, 21.2; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{16}H_{19}O_3$ 259.1329; found 259.1328.

3-(4-Fluorophenyl)-8,8-dimethyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2n):



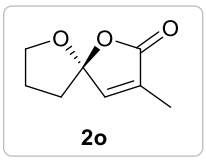
Following *General Procedure F*, to the mixture of ethyl 2-(4-fluorophenyl)-2,7-dihydroxy-6,6-dimethylhept-3-ynoate (**1n**)(0.07 g, 0.23 mmol) in an anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.0145 g, 0.023mmol) under argon atmosphere to obtain 8,8-dimethyl-3-(4-nitrophenyl)-1,6-dioxaspiro[4.4]non-3-en-2-one (**2n**) (0.041g, 77%) as a white solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90-7.79 (m, 2H), 7.16-7.06 (m, 3H), 3.98 (d, *J*= 8.39 Hz, 1H), 3.82 (d, *J*= 8.39 Hz, 1H), 2.26-2.15 (m, 2H), 1.33 (s, 3H), 1.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.1, 163.6 (*J* = 251 Hz), 143.3 (*J* = 1.53 Hz), 132.3, 129.6 (*J* = 8.39 Hz), 125.1 (*J* = 3.05 Hz), 115.8 (*J* = 23.36 Hz), 112.7, 82.3, 49.4, 39.8, 27.9, 26.2; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -110.4 ; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{16}FO_3$ 263.1078; found 263.1082.

3-Methyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (2o):



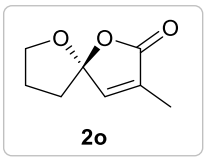
Following *General Procedure F*, to the mixture of ethyl 2,7-dihydroxy-2-methylhept-3-ynoate(**1o**)(0.05 g, 0.25 mmol) in anhydrous CH_2Cl_2 (1 mL) was added $Bi(OTf)_3$ (0.0164 g ,0.025 mmol) under argon atmosphere to obtain 3-methyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (**2o**) (0.27 g, 71 %) as a yellowish oil.TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.74-6.67 (m, 1H), 4.24-4.17 (m, 1H), 4.08-4.01 (m, 1H), 2.35-2.08 (m, 4H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.3, 144.3, 133.2, 112.6, 70.2, 35.2, 24.1, 10.4; FTIR (cm^{-1}) 3023, 2928, 2404, 1729, 1655, 1452, 1263, 1216, 1050, 844, 760, 670; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_8H_{11}O_3$ 155.0703; found 155.1313.

3-Methyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (2o):



Following *General Procedure F*,to the mixture of ethyl 2-hydroxy-7-((4-methoxybenzyl)oxy)-2-methylhept-3-ynoate (**5f**) (1g, 3.12 mmol) in anhydrous CH_2Cl_2 (10 mL) was added $Bi(OTf)_3$ (0.204 g , 0.31mmol) under argon atmosphere to obtain 3-methyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (**2o**) (0.340 g, 71 %) as a yellowish oil. TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400MHz): δ 6.77-6.65(m, 1H), 4.23-4.16 (m, 1H), 4.13-3.97(m, 1H), 2.39-2.05 (m, 4H), 1.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.4, 144.3, 133.4, 112.7, 70.3, 35.3, 24.2, 10.6.

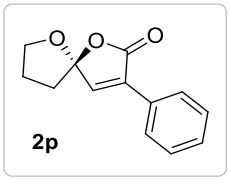
3-methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2o):



The reaction of 2N-HCl (1.5 equiv) with 3-methyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (2o): To the mixture of 3-methyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (**2o**) (0.1 g, 3.12 mmol) in anhydrous CH_2Cl_2 (2 mL) was added 2N HCl (0.5 mL , 0.97 mmol) under argon atmosphere and stirred for 12 h, no conversion was observed through TLC monitoring. Hence, quenched with saturated aqueous $NaHCO_3$ solution and extracted with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to obtain the crude product. Purification by silica-gel column chromatography gave unreacted 3-methyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (**2o**) (0.091 g, 91 %) as a yellowish oil. TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.77-6.65 (m, 1H), 4.23-4.16 (m, 1H), 4.13-3.97 (m, 1H), 2.39-2.05 (m, 4H), 1.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.4,

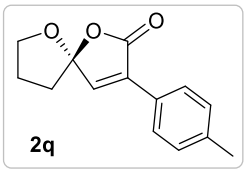
144.3, 133.4, 112.7, 70.3, 35.3, 24.2, 10.6; HRMS (ESI) m/z: $[M+H]^+$calcd for $C_8H_{11}O_3$155.0703; found 155.1313.

3-Phenyl-1, 6-dioxaspiro [4, 4] non-3-en-2-one (2p):



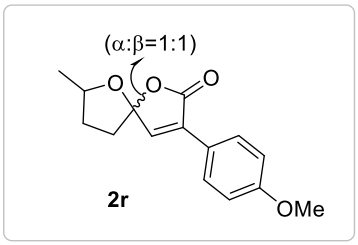
Following *General Procedure F*,to the mixture of ethyl 2,7-dihydroxy-2-phenylhept-3-ynoate (**1p**) (1.0 g, 3.81 mmol)in an anhydrous CH_2Cl_2 (10 mL) was added $Bi(OTf)_3$ (0.250 g, 0.38 mmol) under argon atmosphere to obtain 3-phenyl-1, 6-dioxaspiro [4, 4] non-3-en-2-one (**2p**) (0.62 g, 75%) as a yellow oil.TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92-7.76 (m, 2H), 7.50-7.36 (m, 3H), 7.21 (s, 1H), 4.37-4.25 (m, 1H), 4.20-4.05 (m, 1H), 2.47-2.10(m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ169.1, 142.9, 134.4, 129.8, 129.0, 128.7, 127.5, 111.9, 70.5, 35.5, 24.3; FTIR (cm^{-1}) 3074, 2976, 2899, 1762, 1643, 1590, 1491, 1449, 1340, 1231, 1175, 1094, 1017, 955, 932, 876, 756, 695, 658; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{13}H_{13}O_3$217.0859; found 217.0864.

3-(*p*-Tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one(2q):



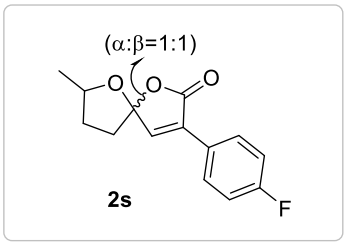
Following *General Procedure F*, to the mixture of ethyl 2,7-dihydroxy-2-(*p*-tolyl)hept-3-ynoate (**1q**) (0.1 g, 0.36 mmol)in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.023 g, 0.036mmol) under argon atmosphere to obtain 3-(*p*-tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one (**2q**) (0.065 g, 78%) as a yellow solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75 (d, *J* = 8.13 Hz, 2H), 7.22 (d, *J* = 8 Hz, 2H), 7.15 (s, 1H), 4.33-4.24 (m, 1H), 4.16-4.07 (m, 1H), 2.38 (s, 3H), 2.36-2.15 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.3, 141.9, 140, 134.2, 129.4, 127.4, 126.2, 111.8, 70.4, 35.7, 24.3, 21.4; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{14}H_{15}O_3$ 231.1016; found 231.1019.

3-(4-Methoxyphenyl)-7-methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2r):



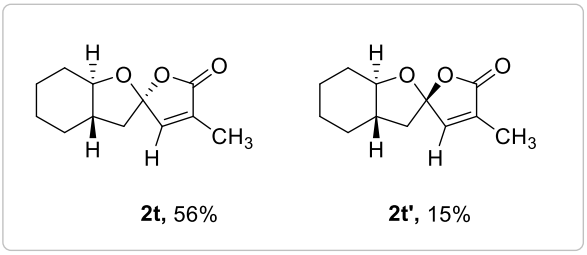
Following *General Procedure F*, to the mixture of ethyl 2,7-dihydroxy-2-(4-methoxyphenyl)oct-3-ynoate (**1r**)(0.05 g, 0.16 mmol)in an anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.01 g, 0.016 mmol) under argon atmosphere to obtain 3-(4-methoxyphenyl)-7-methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (**2r**) (0.38 g, 80%) as a inseparable mixture of diastereomers (*dr*, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.77 (m,, 2H), 7.06 (d, *J* = 14.38 Hz, 1H), 6.96-6.89 (m, 2H), 4.63-4.55 (m, 0.44 H), 4.48-4.41(m, 0.45H), 3.84 (s, 3H), 2.49-2.25(m, 2.8H), 2.05-1.9(m, 0.7H), 1.79-1.71 (0.52 H)1.43 (d, *J* = 6.13 Hz, 1.5H), 1.33(d, *J* = 6.25 Hz, 1.5H);^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.5, 160.7, 140.9, 140.8, 133.7, 133.4, 129.0, 121.7, 121.6, 114.1, 112.0, 111.8, 79.7, 78.1, 55.3, 37.3, 35, 32.2, 31.4, 22, 21.2;FTIR (cm^{-1}) 3020, 2926, 2856, 1759, 1008, 1511, 1456, 1378, 1337, 1222, 1178, 1101, 939, 837, 758, 668; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{15}H_{17}O_4$261.1121; found 261.1125.

3-(4-Fluorophenyl)-7-methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2s):



Following *General Procedure F*, to the mixture of ethyl 2-(4-fluorophenyl)-2,7-dihydroxyoct-3-ynoate (**1s**) (0.1 g, 0.34 mmol)in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.022 g, 0.034 mmol) under argon atmosphere to obtain 3-(4-fluorophenyl)-7-methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (**2s**) (0.049 g, 74%)as a inseparable mixture of diastereomers (*dr*, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94-7.78 (m, 2H), 7.19-7.04 (m, 3H), 4.67-4.55 (m, 0.42H), 4.51-4.43 (m, 0.41H), 2.60-2.22 (m, 3H), 2.08-1.86 (m, 1H), 1.82-1.72 (m, 0.58H), 1.44 (d, *J* = 6.13 Hz, 1.44H), 1.34 (d, *J* = 6.25Hz, 1.56H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.1, 163.6 (*J* = 250.24 Hz), 142.8 (*J* = 11.44 Hz), 129.5 (*J* = 8.39 Hz), 125.2, 115.8 (*J* = 22.12 Hz), 111.9, 111.8, 79.9, 78.3, 44.0, 42.6, 37.2, 35.0, 32.1, 31.3,22.0, 21.1; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -110.5; HRMS (ESI) m/z:$[M+Na]^+$ calcd for $C_{14}H_{13}O_3FNa$ 271.0741; found 271.0739.

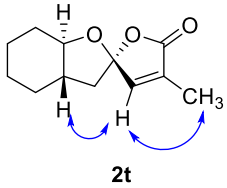
4'-Methyl-3a, 4, 5, 6, 7, 7a-hexahydro-3*H*, 5'*H*-spiro [benzofuran-2, 2'-furan]-5'-one (2t):



2t, 56% **2t'**, 15%

Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-5-(2-hydroxycyclohexyl)-2-methylpent-3-ynoate (**1t**) (0.05 g, 0.2 mmol)in anhydrous CH_2Cl_2 (0.5 mL) was added $Bi(OTf)_3$ (0.02 g, 0.02 mmol) under argon atmosphere to obtain 4'-methyl-3a, 4, 5, 6, 7, 7a-hexahydro-3H, 5'*H*-spiro [benzofuran-2, 2'-furan]-5'-one (**2t**) as two separable diastereomers (**2**t and **2t'**) in 8:2 ratio (0.023 g, 56% and 0.006 g, 15%) as a solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); relative stereochemistry was assigned based on NOE analysis.

Major diastereomer (**2t**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.72(s, 1H), 3.66-3.53 (m, 1H), 2.35 (dd, *J* = 13.4, 7.9 Hz, 1H), 2.2-2.06 (m, 2H), 1.99-1.8 (m, 5H), 1.81-1.74 (m, 1H), 1.62-1.53 (m, 1H), 1.43-1.21 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.9, 145.8, 131.2, 111.8, 84.7, 46.3, 39.8, 30.5, 28.5, 25.5, 24.0, 10.3; FTIR (cm^{-1}) 3017, 2940, 2841, 1759, 1643, 1456, 1216, 1023, 927, 846, 760, 668; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{12}H_{17}O_3$ 209.1172; found 209.1176.

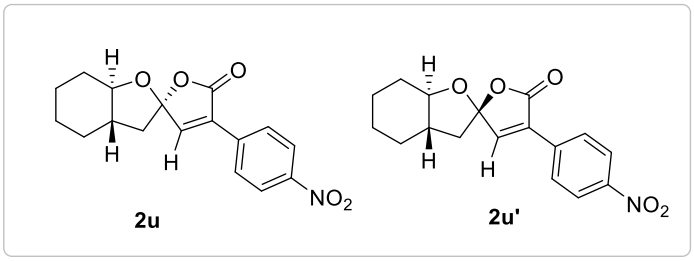


2t

Key NOE interactions in Compound **2t**

Minor diastereomer (**2t'**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.71(s, 1H), 3.39 (td, *J* = 10.7, 3.8 Hz, 1H), 2.17-2.11 (m, 2H), 2.1-1.94 (m, 1H), 1.93-1.8 (m, 5H), 1.78-1.69 (m, 1H), 1.57-1.42 (m, 1H), 1.4.-1.21(m, 3H), 1.19-1.08 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ171.3, 145.9, 132.3, 111.4, 86.7, 43.7, 41.5, 31.3, 28.5, 25.5, 24.2, 10.4; FTIR (cm^{-1}) 2926, 2858, 1767, 1662, 1454, 1375, 1312, 1253, 1158, 1113, 1056, 973, 928, 863, 759; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{12}H_{17}O_3$ 209.1172; found 209.1176.

4'-(4-Nitrophenyl)-3a,4,5,6,7,7a-hexahydro-3*H*,5'*H*-spiro[benzofuran-2,2'-furan]-5'-one (2u):



Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-5-(2-hydroxycyclohexyl)-2-(4-nitrophenyl)pent-3-ynoate (**1u**) (0.05 g, 0.14 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added $Bi(OTf)_3$ (0.009 g, 0.014 mmol) under argon atmosphere to obtain 4'-methyl-3a, 4, 5, 6, 7, 7a-hexahydro-3H, 5'*H*-spiro [benzofuran-2, 2'-furan]-5'-one (**2u**) as two separable diastereomers (**2u** and **2u'**) in 7:3 ratio (yield: 0.023 g, 52% and 0.01g , 23% isolated yield) as a white solid.TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes).

Major diastereomer **2u**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32-8.22 (m, 2H), 8.09-7.97 7.38 (s, 1H), 3.69 (td, *J* = 3.75, 10.63 Hz, 1H), 2.50 (dd, *J* = 7.5, 13.63 Hz 1H), 2.28-2.17 (m, 2H), 2.04-1.88 (m, 2H), 1.85-1.76 (m, 1H), 1.74-1.61 (m, 1H), 1.49-1.28 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.6, 148.3, 147.4, 135.0, 130.6, 128.5, 123.9, 111.1, 85.3, 46.5, 40.1, 30.6, 28.5, 25.4, 24.0; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{17}H_{18}O_5N$ 316.1179; found 316.1187.

Minor diastereomer **2u'**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.34-8.21 (m, 2H), 8.10-7.98 (m, 2H), 7.42 (s, 1H), 3.55-3.40 (m, 1H), 2.36-2.25 (m, 1H), 2.24-2.15 (m, 1H), 2.11-1.98 (m, 3H), 1.97-1.88 (m, 1H), 1.85-1.76 (m, 1H), 1.62-1.54 (m, 1H), 1.37-1.21 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.1, 148.3, 147.9, 135.0, 131.7, 128.4, 123.9, 110.8, 87.3, 43.8, 41.8, 31.3, 28.5, 24.4, 24.2; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{17}H_{18}O_5N$ 316.1179; found 316.1178.

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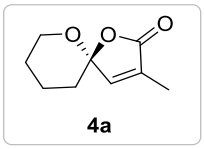
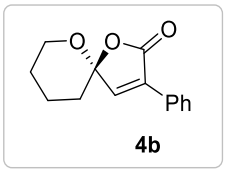
7. *Synthesis of [6,5]-unsaturated oxaspirolactones from propargylic diol esters*

3-Methyl-1, 6-dioxaspiro [4.5] dec-3-en-2-one (4a):



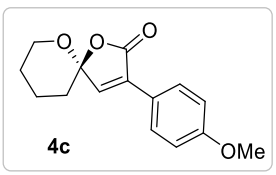
Following *General Procedure F*, to the mixture of ethyl 2, 8-dihydroxy-2-methyloct-3-ynoate (**3a**) (0.086 g, 0.4 mmol) in an anhydrous CH_2Cl_2 (2 mL) was added $Bi(OTf)_3$ (0.026 g, 0.04 mmol) under argon atmosphere to obtain 3-methyl-1,6-dioxaspiro[4.5]dec-3-en-2-one(**4a**) (0.0.047 g, 70%) as a colourless liquid. TLC: R_f = 0.2 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.81-6.67(m, 1H), 4.02 (td, *J* = 3.81, 11.4Hz, 1H), 3.95-3.84 (m, 1H), 2-1.93 (m, 1H), 1.91 (s, 3H), 1.87-1.79 (m, 2H), 1.73-1.66 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ171.9, 147.2, 131.9, 104.8, 65.0, 32.3, 24.1, 19.1, 10.5; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_9H_{13}O_3$ 169.1459; found 169.0869.

3-Phenyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4b):



Following *General Procedure F*, to the mixture of ethyl 2,8-dihydroxy-2-phenyloct-3-ynoate (**3b**) (0.1 g, 0.36 mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.024 g, 0.036 mmol) under argon atmosphere to obtain 3-phenyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4b**) (0.063 g, 75%). TLC: R_f = 0.40 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.90-7.77 (m, 2H), 7.47-7.35(m, 3H), 7.22 (s, 1H), 4.09 (td, *J* = 3.05, 11.44 Hz, 1H), 4.0-3.90 (m, 1H), 2.05-1.69 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.6, 145.6, 133.2, 129.7, 129.1, 128.7, 127.5, 104.0, 65.0, 32.5, 24.1, 19.1; FTIR (cm^{-1}) 3074, 3022, 2946, 1760, 1645, 1484, 1448, 1367, 1305, 1261, 1222, 1112, 1051, 1006, 947, 927, 850, 754, 691; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{14}H_{15}O_3$ 231.1016; found 231.1019.

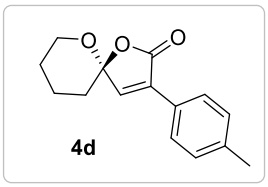
3-(4-Methoxyphenyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4c):



Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-2-(4-methoxyphenyl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (**5d**) (0.2 g, 0.652 mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$

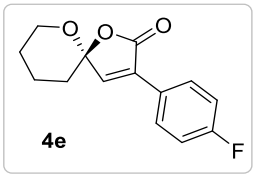
(0.043 g, 0.0652 mmol) under argon atmosphere to obtain 3-(4-methoxyphenyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4c**) (0.118 g, 70%). TLC: R_f = 0.40 (SiO_2, 20% EtOAc/hexanes);^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J*= 9.16 Hz, 2H), 7.11 (s, 1H), 6.93 (d, *J*= 9.16 Hz, 2H), 4.08 (td, *J*= 3.21, 11.45 Hz, 1H), 3.97-3.91(m, 1H), 3.84 (s, 3H), 2.05-1.73 (m, 6H);^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.9, 160.7, 143.3, 132.5, 128.9, 121.6, 114.1, 103.9, 65.0, 55.3, 32.6, 24.2, 19.2; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{15}H_{17}O_4$261.1121; found 261.1125.

3-(*p*-Tolyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one(4d):



Following *General Procedure F*, to the mixture of ethyl 2,8-dihydroxy-2-(*p*-tolyl)oct-3-ynoate (**3d**) (0.1 g, 0.34 mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.023 g, 0.034mmol) under argon atmosphere to obtain 3-(*p*-tolyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4d**) (0.068 g, 81%). TLC: R_f = 0.40 (SiO_2, 20% EtOAc/hexanes);^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.68, (m, 2H), 7.22-7.17(m, 2H), 7.15(s, 1H), 4.06 (td, *J* = 3.81, 11.44 Hz, 1H), 3.96-3.89 (m, 1H), 2.35 (s, 3H), 2.05-1.62 (m, 6H); ^{13}C NMR ($CDCl_3$,101 MHz): δ 169.7, 144.6, 139.8, 132.8, 129.3, 127.3, 126.1, 103.9, 64.9, 32.4, 24.1, 21.3, 19.1; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{15}H_{17}O_3$ 245.1172; found 245.1170.

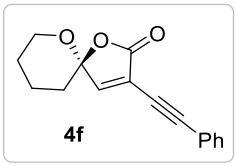
3-(4-Fluorophenyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4e):



Following *General Procedure F*, to the mixture of ethyl 2-(4-fluorophenyl)-2,8-dihydroxyoct-3-ynoate (**3e**) (0.1 g, 0.34 mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$(0.02 g, 0.034 mmol) under argon atmosphere to obtain 3-(4-fluorophenyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4e**) (0.058 g, 69%). TLC: R_f = 0.40 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$,400 MHz): δ 7.93-7.74 (m, 2H), 7.18 (s, 1H), 7.14-7.05 (m, 2H), 4.08 (td, *J* = 3.66, 11.45 Hz, 1H), 4.01-3.88 (m, 1H), 2.09-1.71 (m, 6H); ^{13}C NMR ($CDCl_3$,101 MHz): δ 169.5, 163.7 (*J* = 250.24 Hz), 145.1 (*J* = 2.29 Hz), 132.1, 129.5 (*J* = 8.39 Hz), 125.2, 115.8 (*J* = 21.36 Hz), 104.0, 65.0,

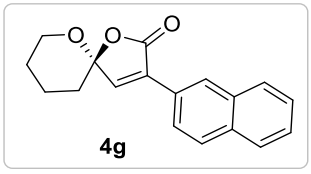
32.4, 24.1, 19.1; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -110.5; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{14}H_{14}O_3F$ 249.0921; found 249. 0919.

3-(Phenylethynyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4f):



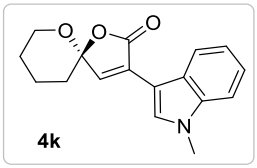
Following *General Procedure F*, to the mixture of ethyl 2,8-dihydroxy-2-(phenylethynyl)oct-3-ynoate (**3f**) (0.1 g, 0.33mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.021 g, 0.033 mmol) under argon atmosphere to obtain 3-(phenylethynyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4f**) (0.064 g, 76%). TLC: R_f = 0.40 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.50 (m, 2H), 7.41-7.33 (m, 3H), 7.16 (s, 1H), 4.29 (td, *J* = 3.81, 8.39 Hz, 1H), 4.16-4.08 (m, 1H), 2.39-2.14 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 167.2, 149.6, 132.1, 129.6, 128.4, 121.5, 120.8, 113.3, 97.9, 78.1, 70.8, 35.8, 31.9, 24.2, 22.7, 14.1; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{16}H_{15}O_3$ 255.1016; found 255.1006.

3-(Naphthalene-2-yl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4g):



Following *General Procedure F*, to the mixture of ethyl 2,8-dihydroxy-2-(naphthalene-2-yl)oct-3-ynoate (**3g**) (0.1 g, 0.31 mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.02 g, 0.031 mmol) under argon atmosphere to obtain 3-phenyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4g**) (0.071 g, 83%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$,400 MHz): δ 7.89-7.81(m, 3H), 7.58-7.51(m, 1H), 7.5-7.37(m, 3H), 7.2(s, 1H), 4.17-4.02(m, 1H), 4.01-3.87(m, 1H), 2.06-1.66(m, 6H); ^{13}C NMR ($CDCl_3$,101 MHz): δ 170.2, 150.4, 133.6, 133.5, 131.1, 129.8, 128.6, 127.7, 126.7, 126.6, 126.1, 125.1, 124.4, 104.8, 65.1, 32.6, 24.1, 19.1; FTIR (cm^{-1}) 3019, 2944, 1764, 1650, 1592, 1508, 1448, 1367, 1298, 1225, 1130, 1051, 998, 921, 862, 760, 664; HRMS (ESI) m/z:$[M+H]^+$calcd for $C_{18}H_{17}O_3$281.1172; found 281.1178.

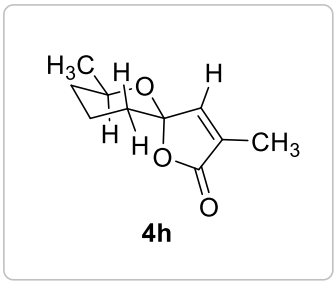
3-(1-Methyl-1*H*-indol-3-yl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4k):



4k

Following *General Procedure F*, to the mixture of ethyl 2-hydroxy-2-(1-methyl-1*H*-indol-3-yl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (**3k**) (0.1 g, 0.24 mmol) in anhydrous EtOH (5 mL) was add PTSA (0.046 g, 0.024 mmol) under argon atmosphere to obtain 3-(1-methyl-1*H*-indol-3-yl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4k**) (0.051 g, 75%). TLC: R_f = 0.40 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17 (s, 1H), 7.8 (d, *J* = 8.1 Hz, 1H), 7.4 (d, *J* = 8.37 Hz, 1H), 7.36-7.31 (m, 1H), 7.3-7.24 (m, 1H),7.2 (s, 1H), 4.18-4.08 (m, 1H), 4.03-3.96 (m, 1H), 3.86 (s, 3H), 2.1-1.98 (m, 2H), 1.94-1.85 (m, 2H), 1.82-1.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.2, 137.8, 131.6, 126.3, 122.6, 120.8, 119.8, 110.0, 105.4, 65.1, 33.2, 33.02, 24.3, 19.4; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{17}H_{18}O_3N$ 284.1281; found 284.1281.

3,7-Dimethyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4h):

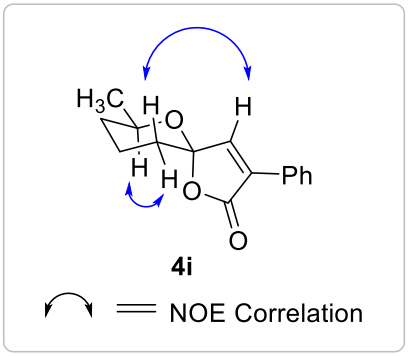


4h

Following *General Procedure F*, to the mixture of ethyl 2,8-dihydroxy-2-methyloct-3-ynoate (**3h**) (0.1 g, 0.44 mmol) in an anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.029 g, 0.044 mmol) under argon atmosphere to obtain 3,7-dimethyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4h**) (0.07 g, 88%) as a colourless liquid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.76 (q, *J* = 1.63 Hz, 1H), 4.15-4.06 (m, 1H), 2.09-1.94 (m, 1H), 1.92 (d, *J* = 1.63 Hz, 3H), 1.85-1.78 (m, 1H), 1.77-1.68 (m, 3H), 1.22 (d, *J* = 6.13 Hz, 1H), 1.19 (d, *J* = 6.25Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.1, 147.5, 131.9, 105.4, 70.9, 31.8, 31.6, 29.7, 25.4, 21.7, 19.4, 10.5; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{10}H_{15}O_3$183.1016; found 183.1015.

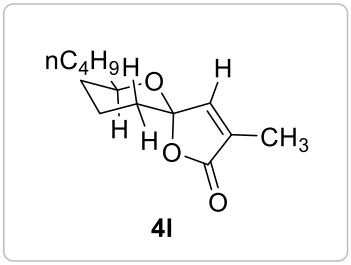
7-Methyl-3-phenyl-1, 6-dioxaspiro [4.5] dec-3-en-2-one (4i):

Following *General Procedure F*, to the mixture of ethyl 2,8-dihydroxy-2-phenylnon-3-ynoate (**3i**) (0.1 g, 0.34 mmol) in an anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.023 g, 0.034 mmol) under argon atmosphere to obtain 3-phenyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4i**) (0.071 g,



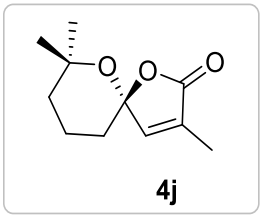
84%) as a colourless liquid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); relative stereochemistry was assigned based on NOE analysis. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.89 - 7.81 (m, 2H), 7.44 - 7.38 (m, 3H), 7.23 (s, 1H), 4.21 - 4.13 (m, 1H), 2.08 - 1.99 (m, 1H), 1.90 - 1.82 (m, 2H), 1.80 - 1.74 (m, 2H), 1.42 - 1.33 (m, 1H), 1.22 (d, *J* = 6.49 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.6, 145.8, 132.9, 129.6, 129.1, 128.6, 127.4, 104.5, 70.9, 32.0, 31.5, 21.7, 19.4; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{15}H_{17}O_3$ 245.1172; found 275.1174.

7-Butyl-3-methyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4l):



Following *General Procedure F*, to the mixture of ethyl 8-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-methyldodec-3-ynoate. (**5b**) (0.1 g, 0.26 mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.0 g, 0.026 mmol) under argon atmosphere to obtain 3-phenyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4l**) (0.045 g, 78%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.75 (q, *J* = 1.63 Hz, 1H), 3.99-3.87 (m, 1H), 2.01-1.92 (m, 1H), 1.91 (d, *J* = 1.63 Hz, 3H), 1.85-1.67 (m, 4H), 1.41-1.18 (m, 7H), 0.91-0.85 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.2, 147.6, 131.7, 105.5, 74.7, 35.7, 32.2, 29.7, 27.3, 22.7, 19.5, 14.0, 10.5; HRMS (ESI) m/z:$[M+Na]^+$calcd for $C_{13}H_{20}O_3Na$ 247.1305; found 247.1304.

3,7,7-Trimethyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4j):



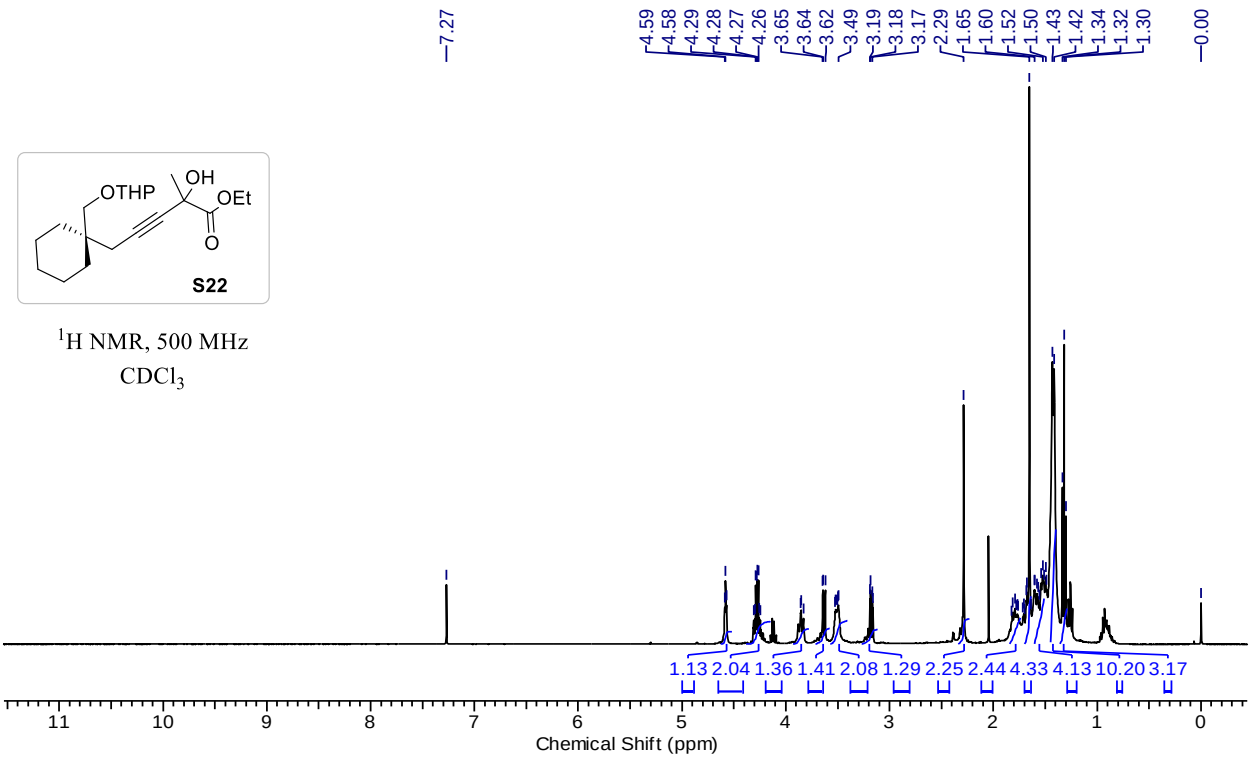
Following *General Procedure F*, to the mixture of ethyl 2,8-dihydroxy-2,8-dimethylnon-3-ynoate (**3j**) (0.1 g, 0.41mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.027 g, 0.041 mmol) under argon atmosphere to obtain 3-phenyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (**4j**) (0.04 g, 50%); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.72-6.69 (m, 1H), 1.90 (s, 3H), 1.72-1.68 (m, 3H), 1.39-1.38 (m,

3H), 1.25 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ172.2, 148.3, 131.7, 105.6, 75.4, 35.1, 32.1, 31.8, 26.4, 16.1, 10.5; HRMS (ESI) m/z:$[M+H]^+$ calcd for $C_{11}H_{16}O_3$197.1172; found 197.1172.

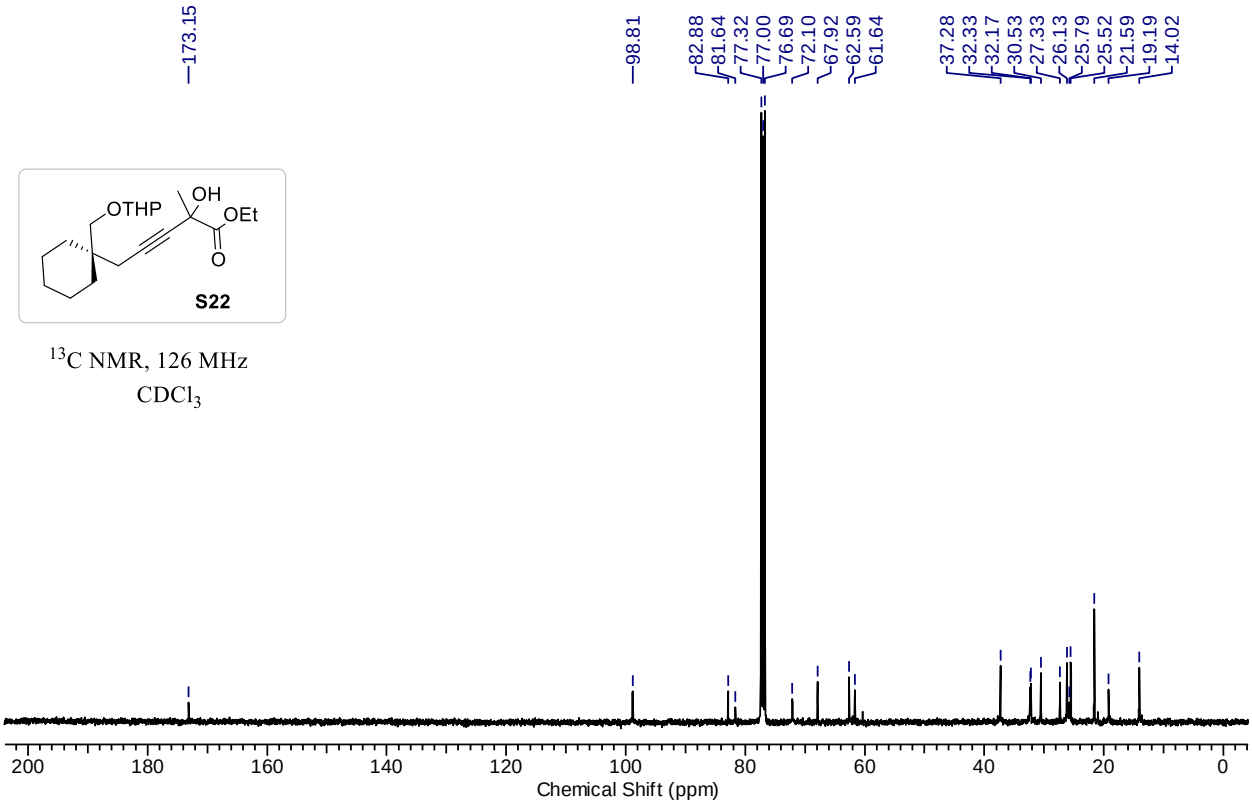
8.

^{1}H, ^{13}C and 2D-NMR Spectra

Ethyl 2-hydroxy-2-methyl-5-(1-(((tetrahydro-2*H*-pyran-2-yl) oxy) methyl) cyclohexyl) pent-3-ynoate (S22):

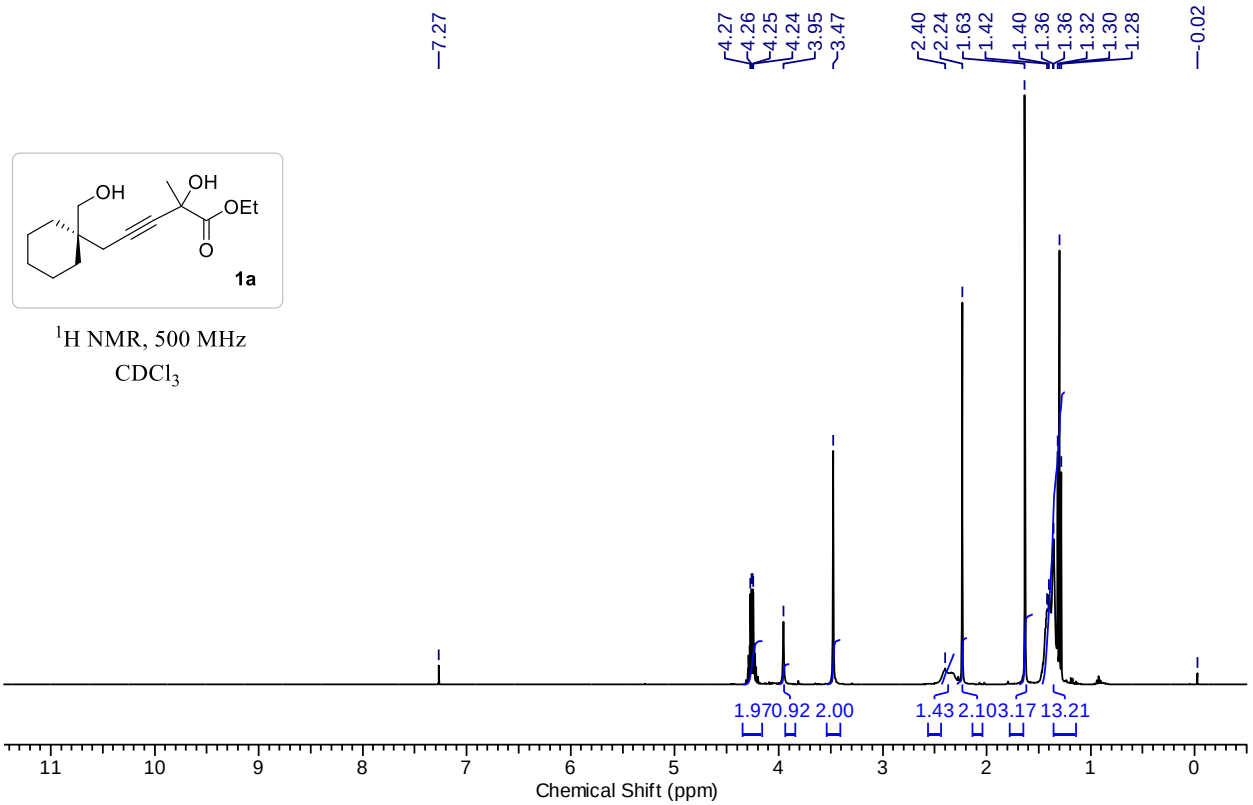


^{1}H NMR, 500 MHz
$CDCl_3$

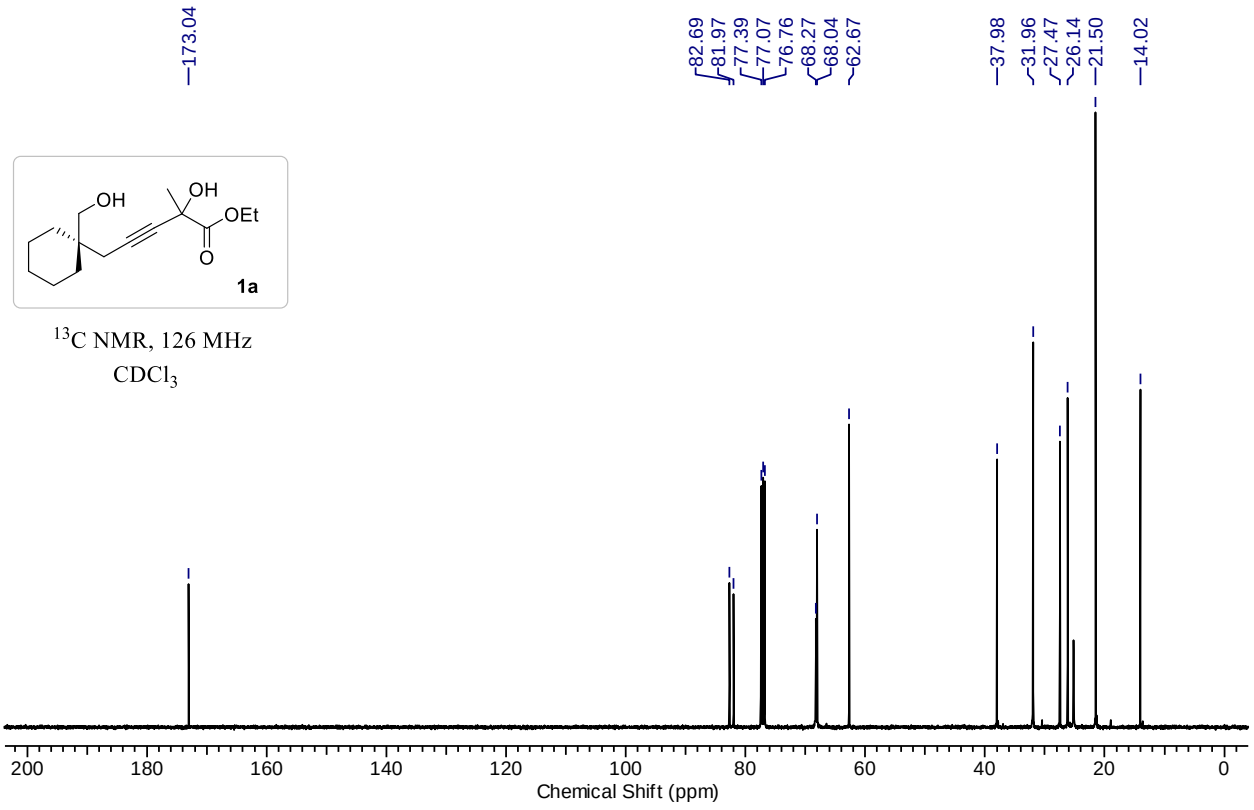


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-methylpent-3-ynoate (1a):

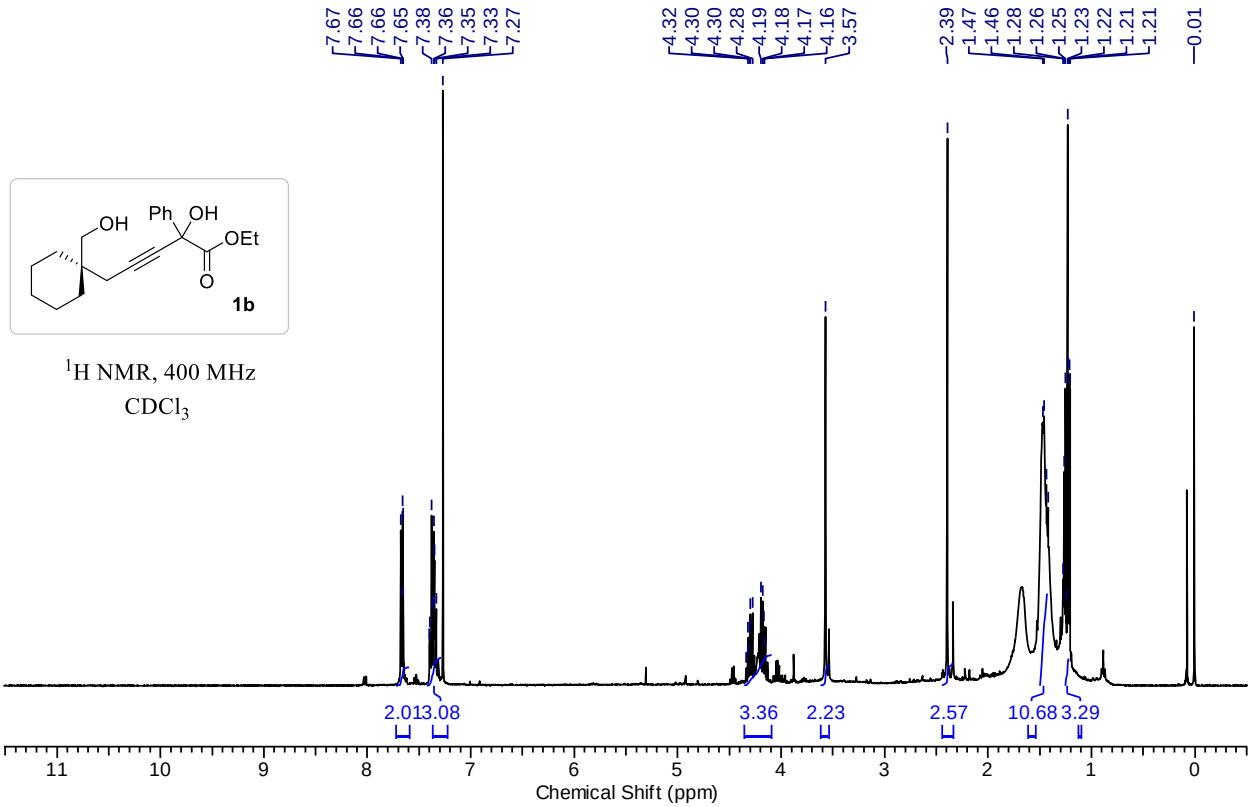


^{1}H NMR, 500 MHz
$CDCl_3$

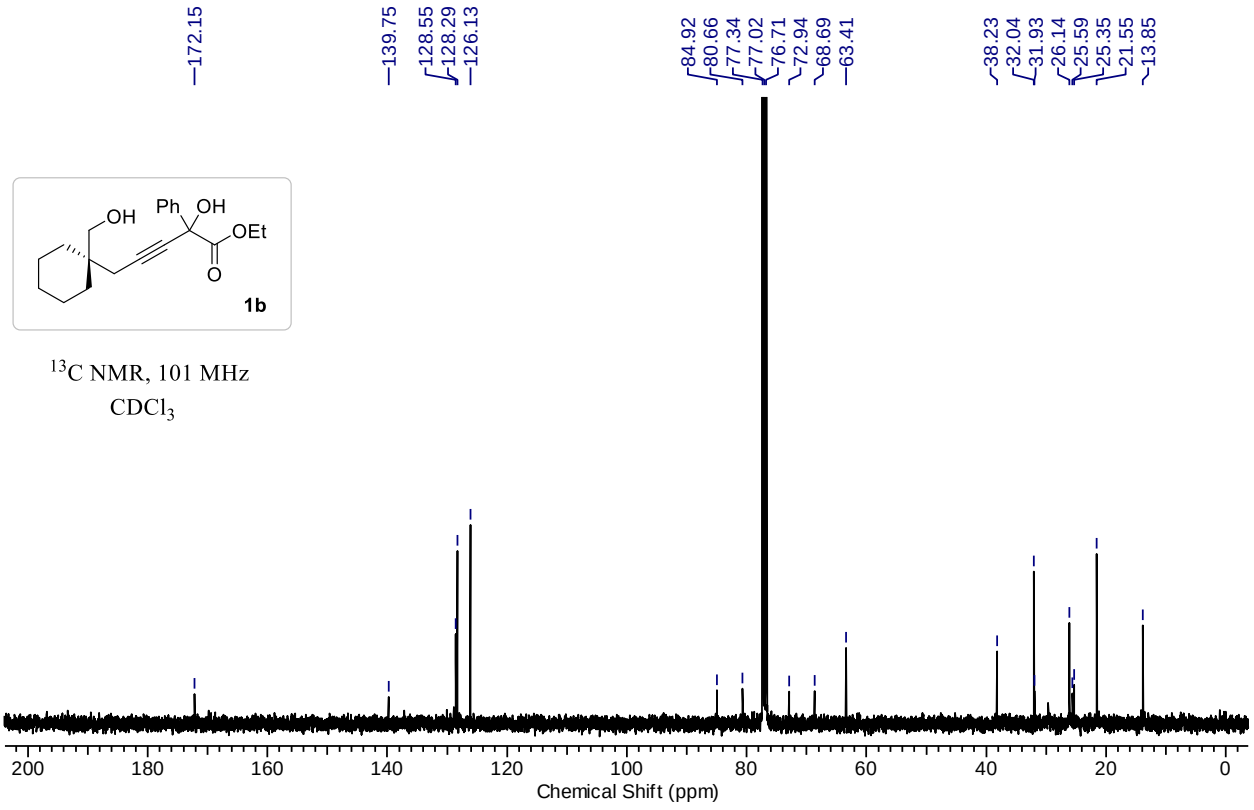


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-phenylpent-3-ynoate (1b):

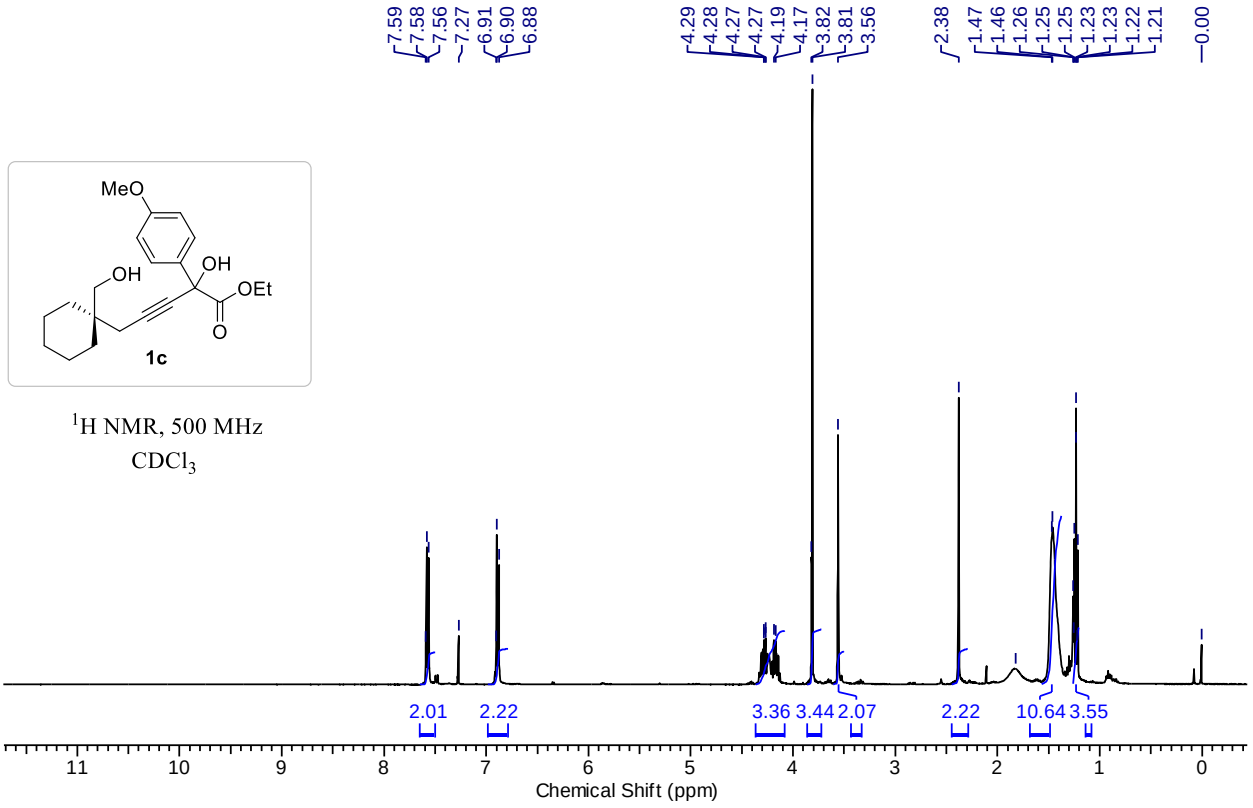


^{1}H NMR, 400 MHz
$CDCl_3$

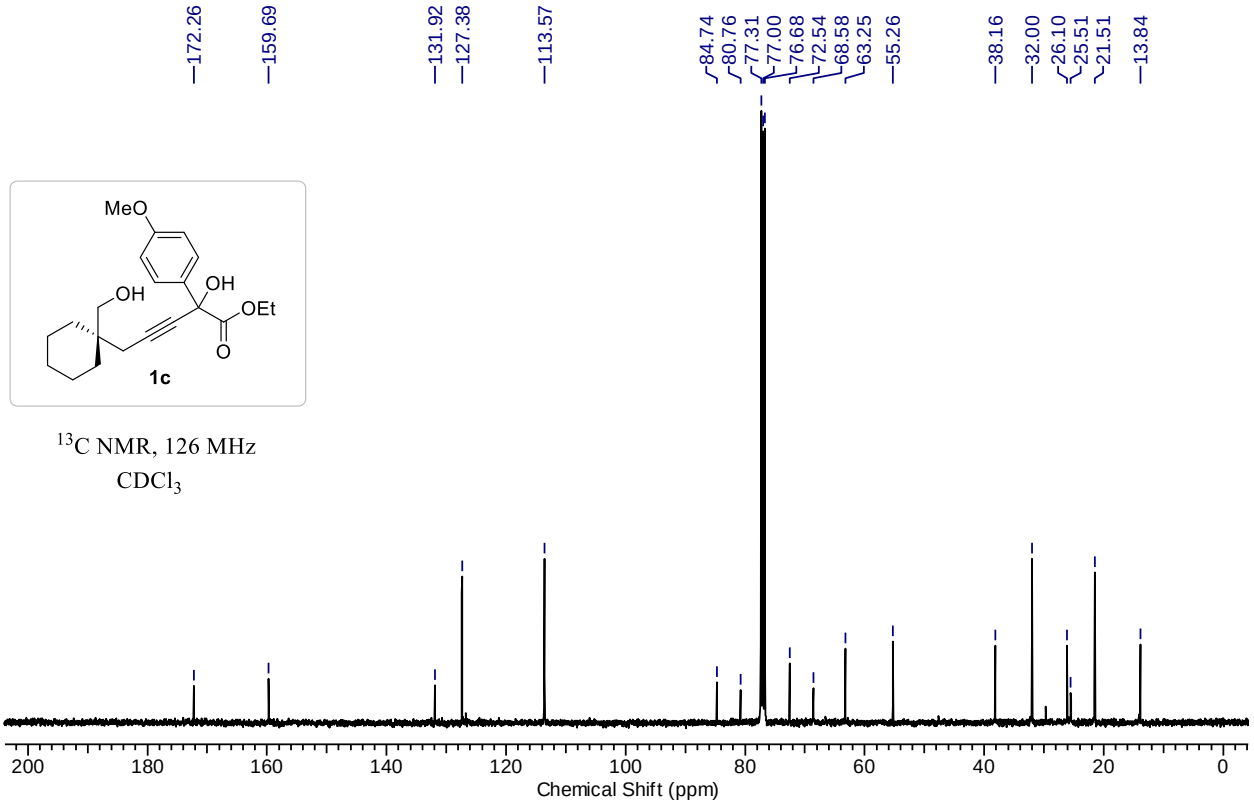


^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-(4-methoxyphenyl)pent-3-ynoate (1c):

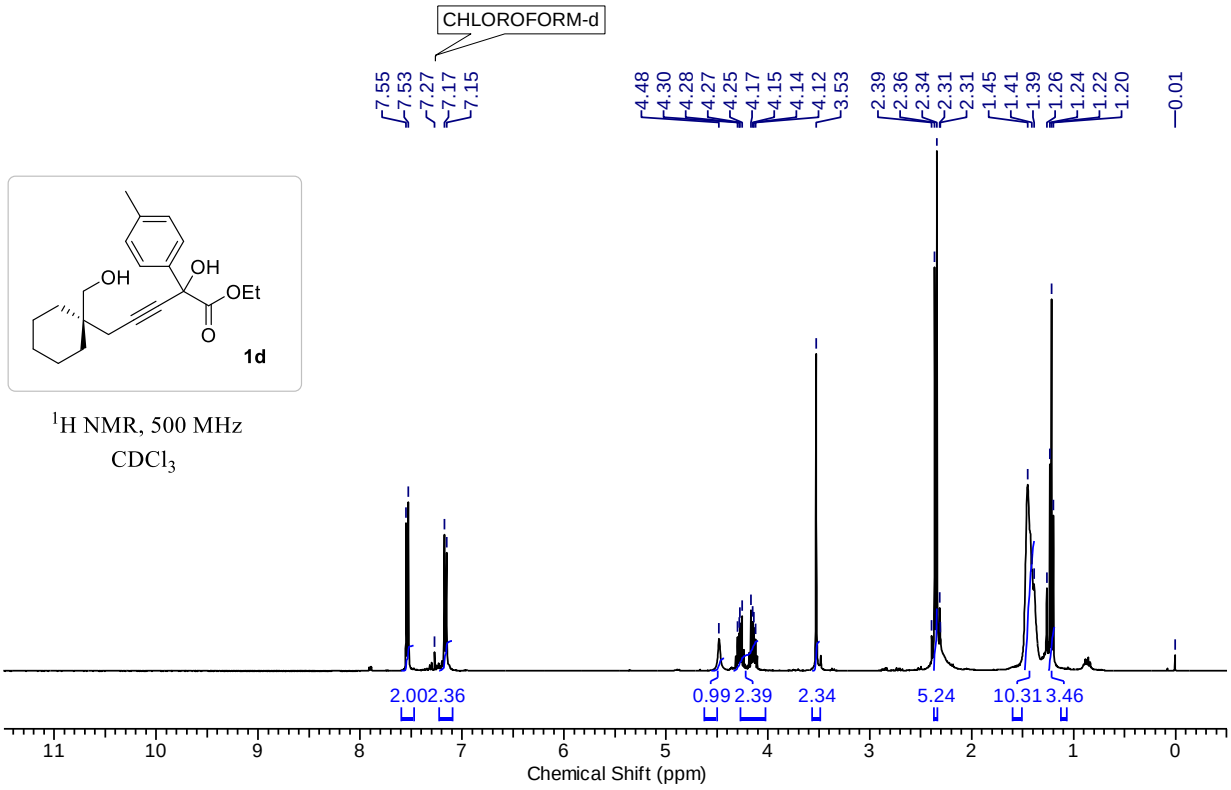


^{1}H NMR, 500 MHz
$CDCl_3$

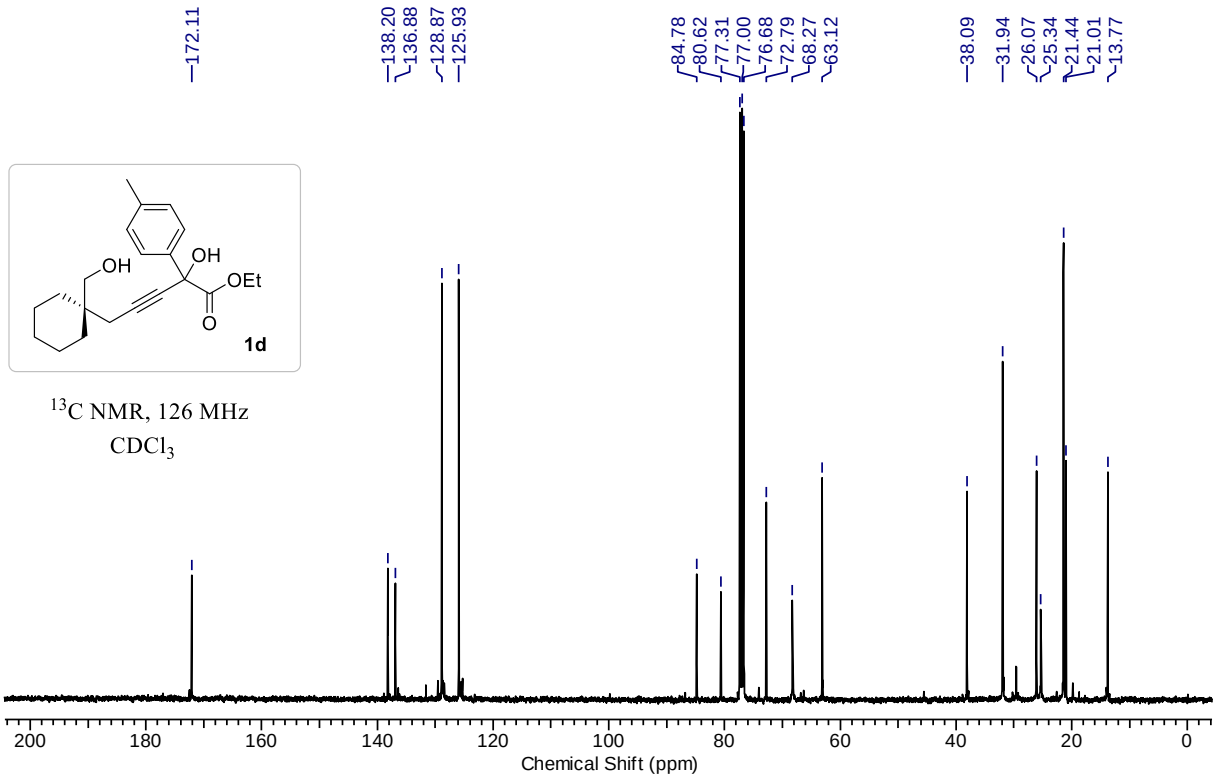


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-(*p*-tolyl)pent-3-ynoate (1d):

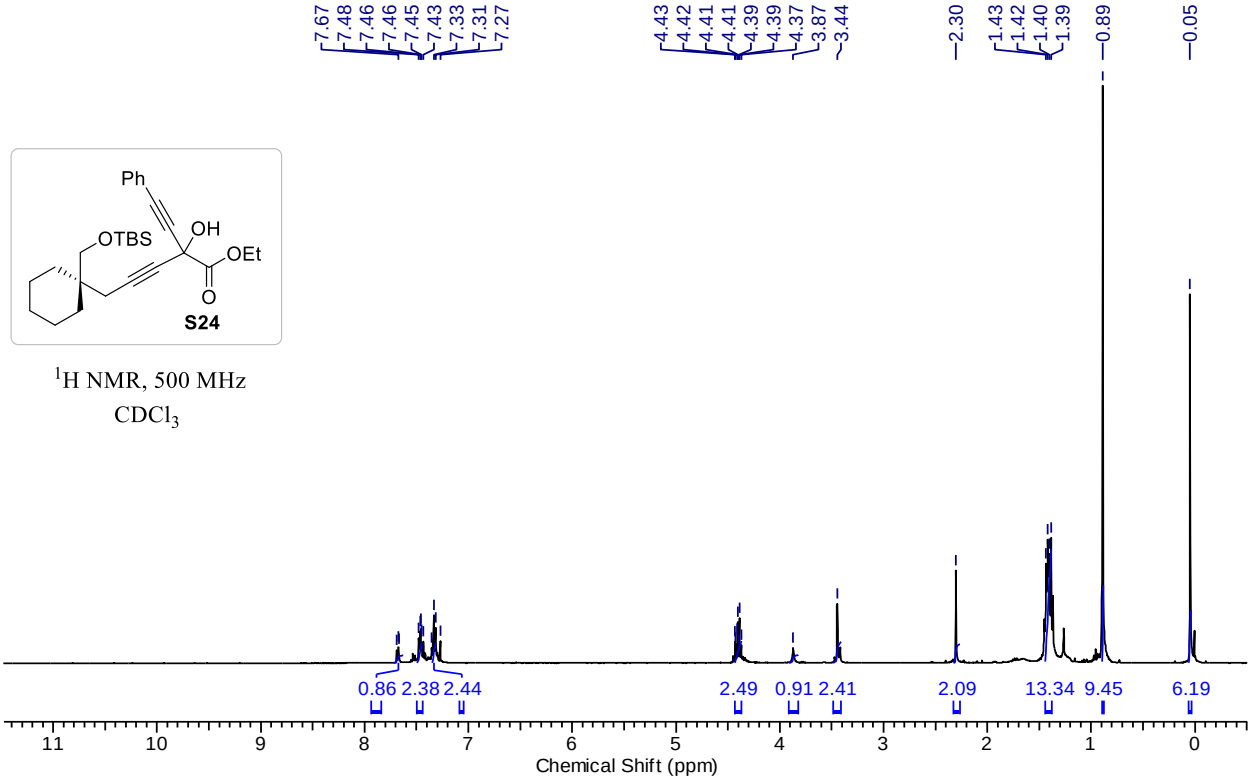


^{1}H NMR, 500 MHz
$CDCl_3$

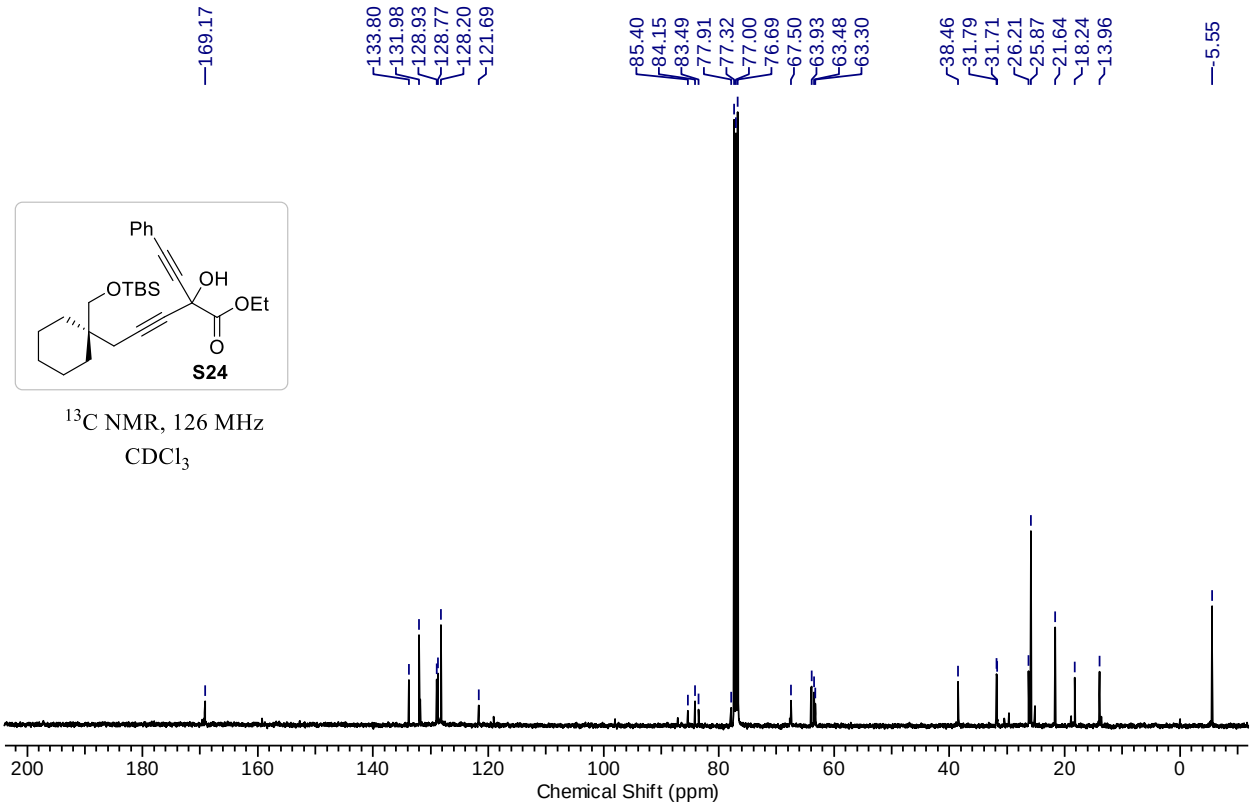


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 5-(1-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclohexyl)-2-hydroxy-2-(phenylethynyl) pent-3-ynoate (S24):

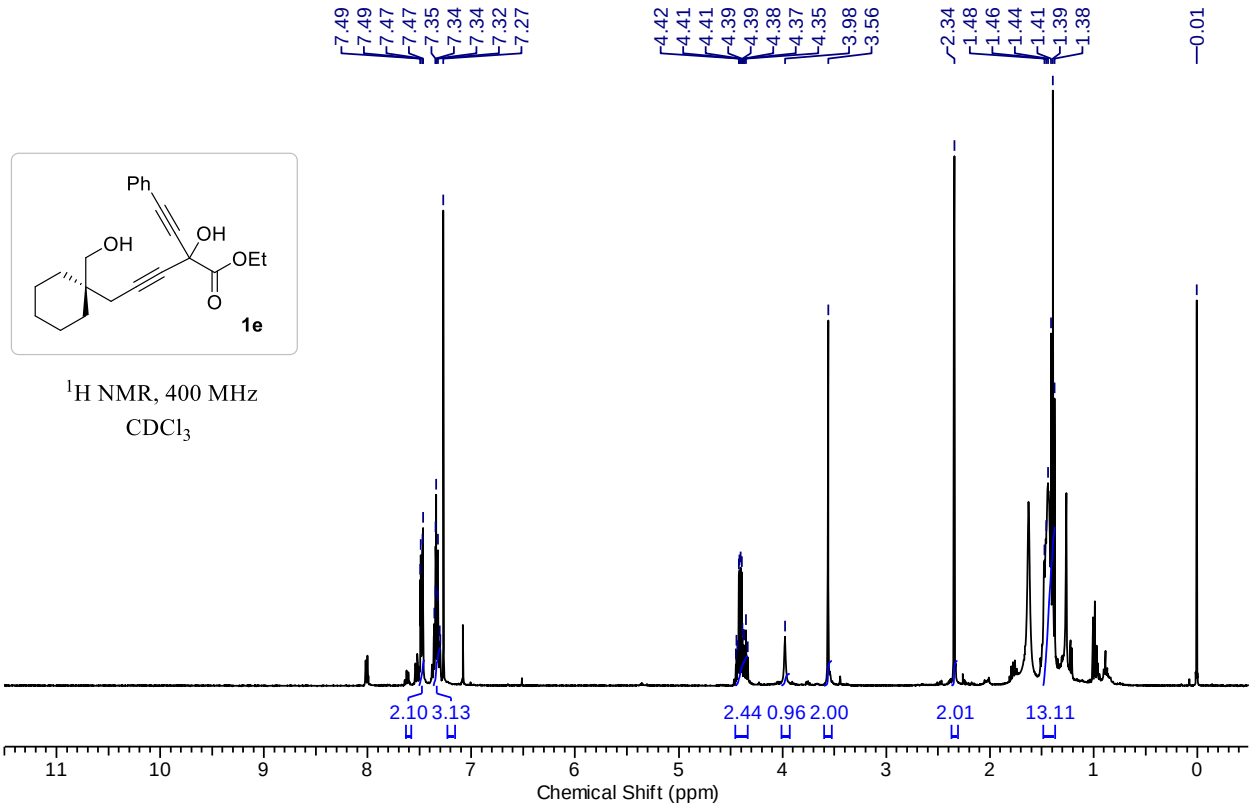


^{1}H NMR, 500 MHz
$CDCl_3$

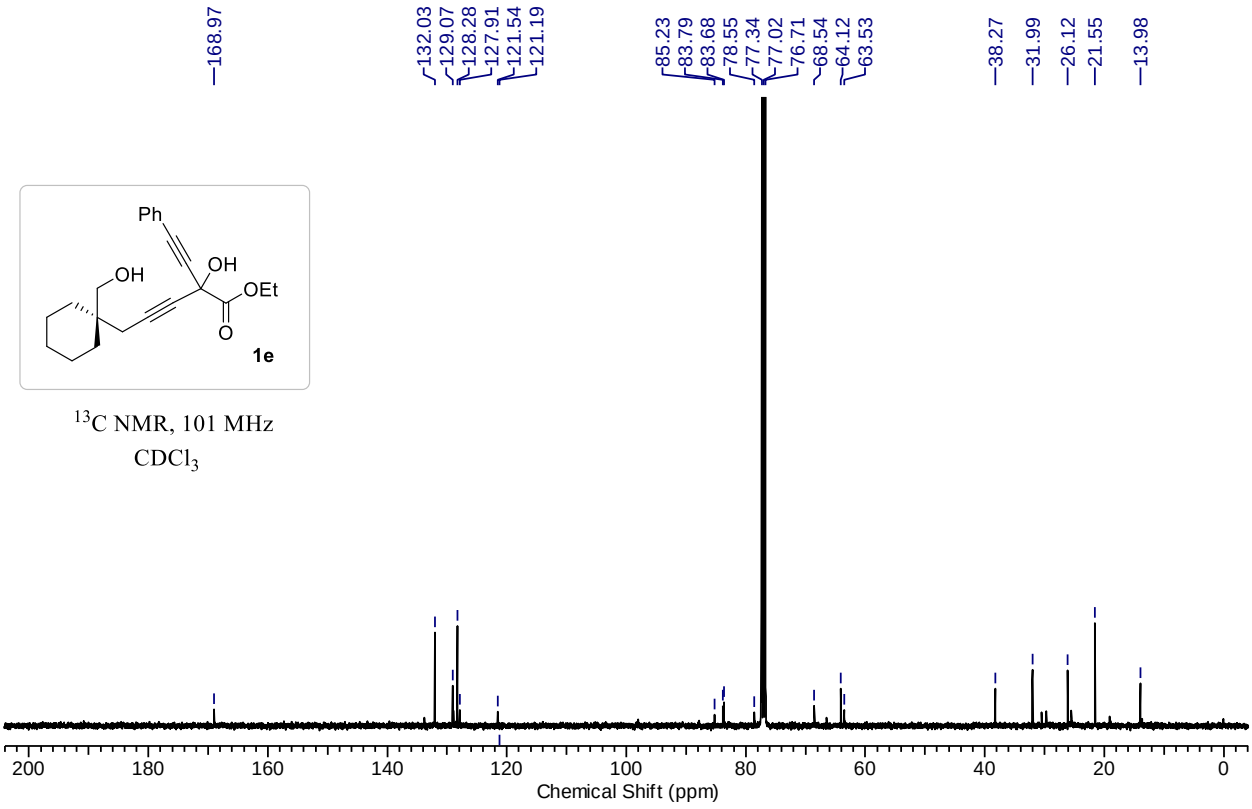


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclohexyl)-2-(phenylethynyl)pent-3-ynoate (1e):

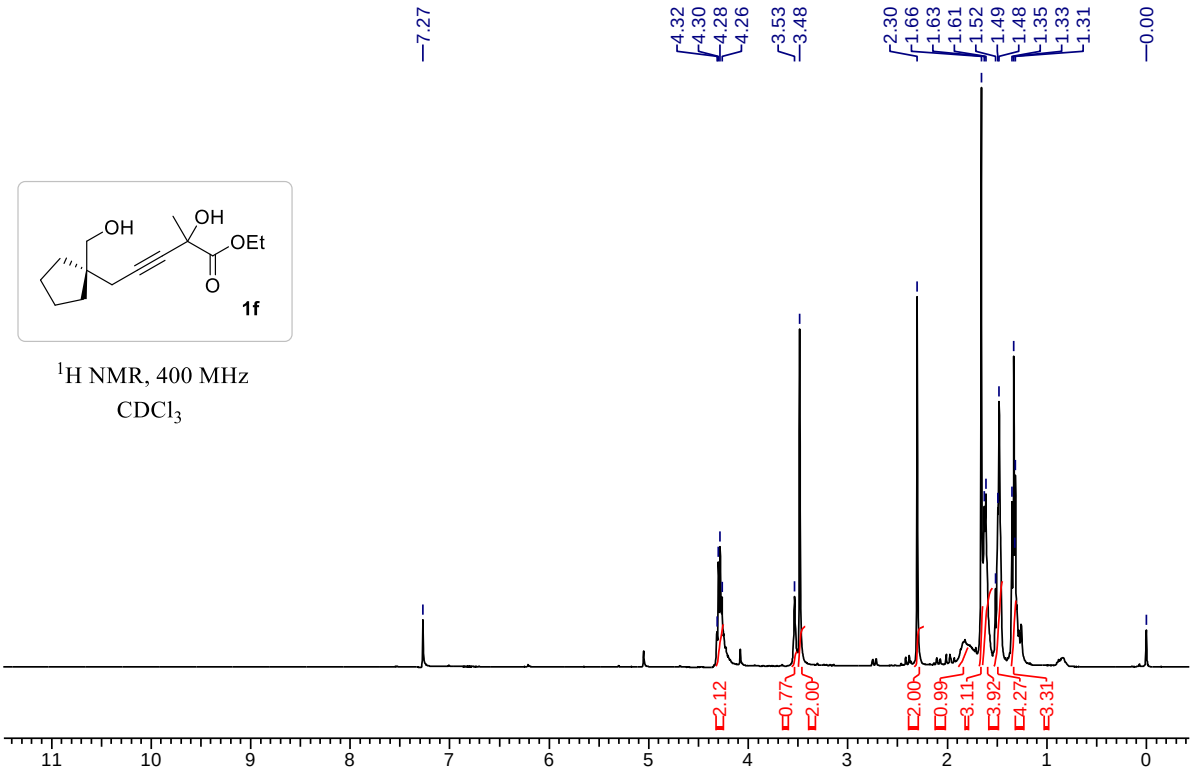


^{1}H NMR, 400 MHz
$CDCl_3$

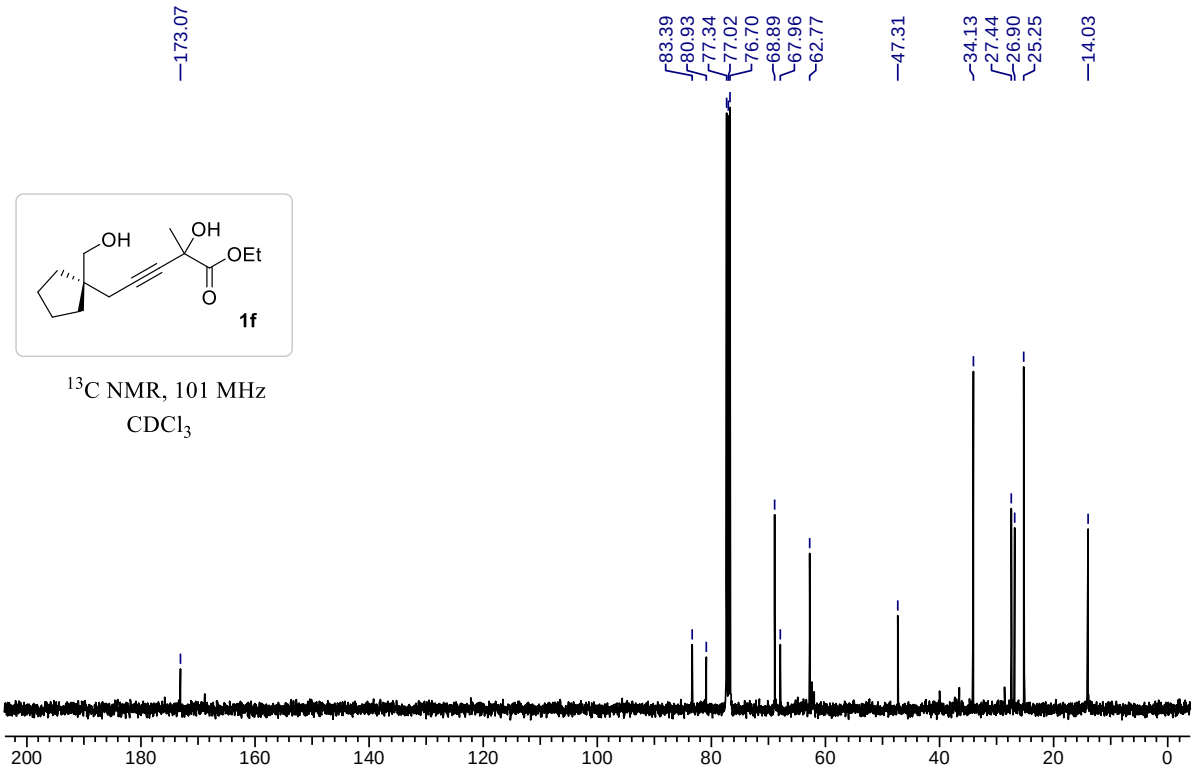


^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclopentyl)-2-methylpent-3-ynoate (1f):

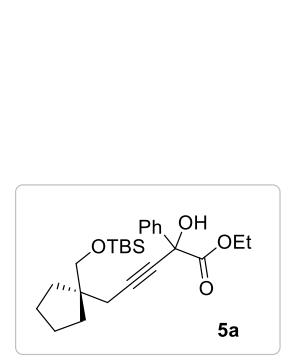


^{1}H NMR, 400 MHz
$CDCl_3$

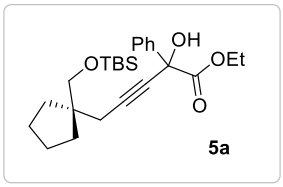


^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 5-(1-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclopentyl)-2-hydroxy-2-phenylpent-3-ynoate (5a):

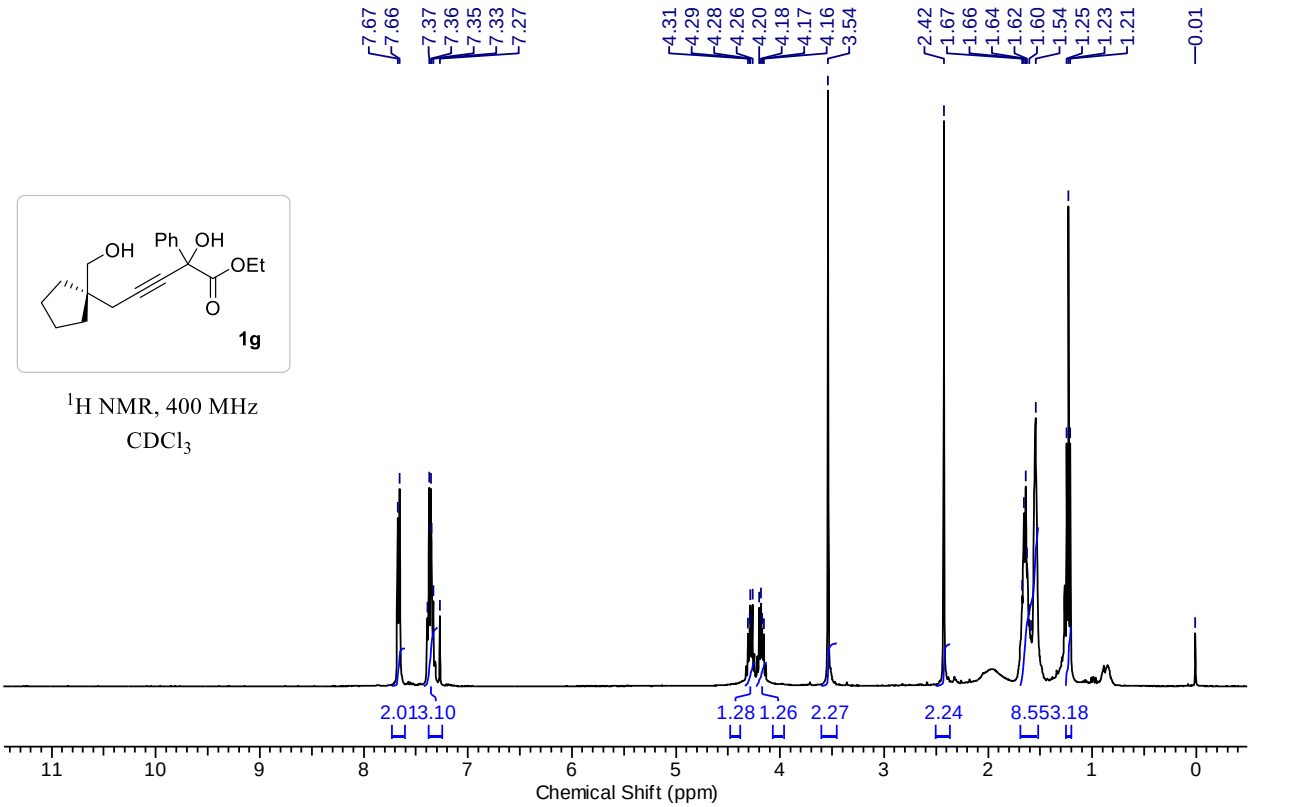


^{1}H NMR, 400 MHz
$CDCl_3$

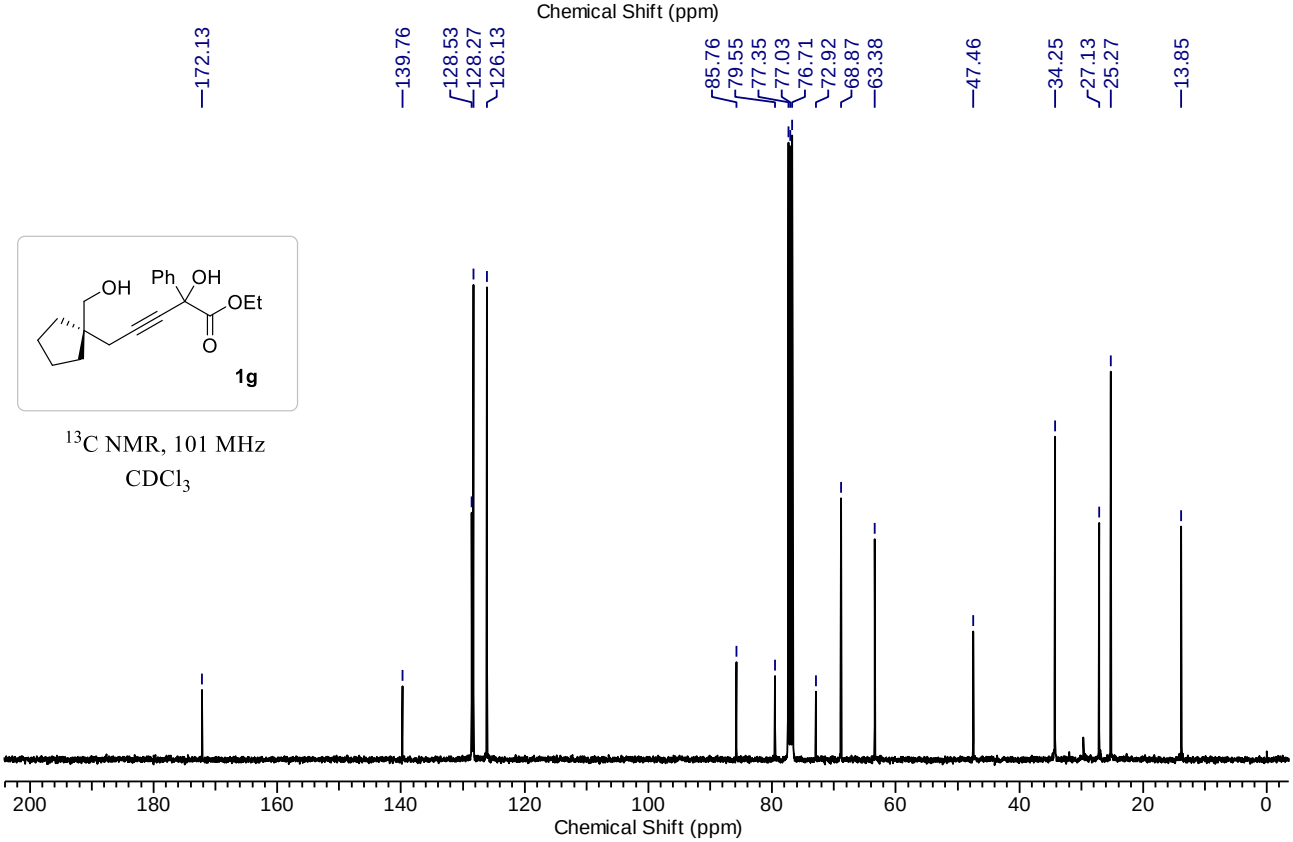


^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclopentyl)-2-phenylpent-3-ynoate (1g):

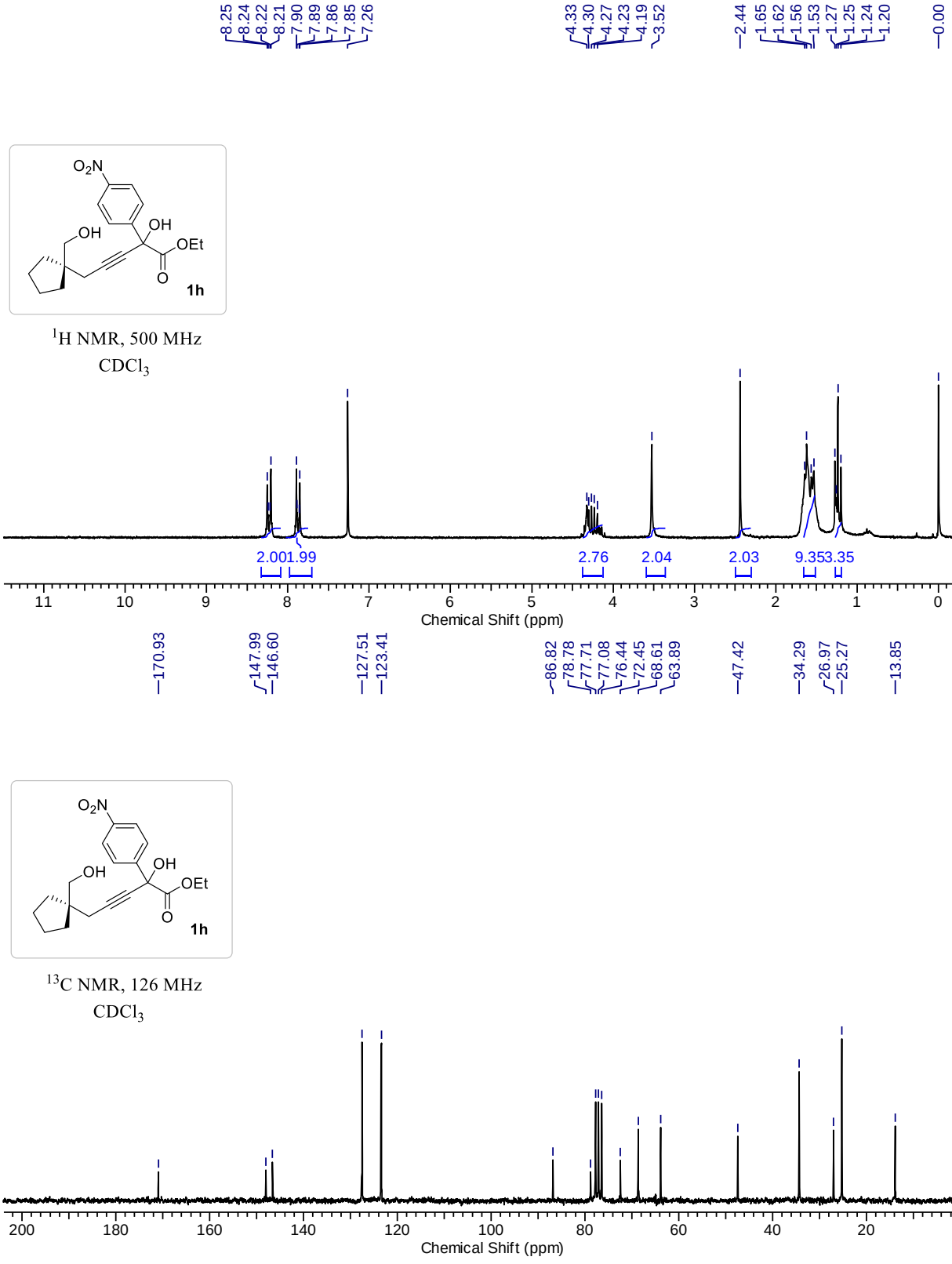


^{1}H NMR, 400 MHz
$CDCl_3$

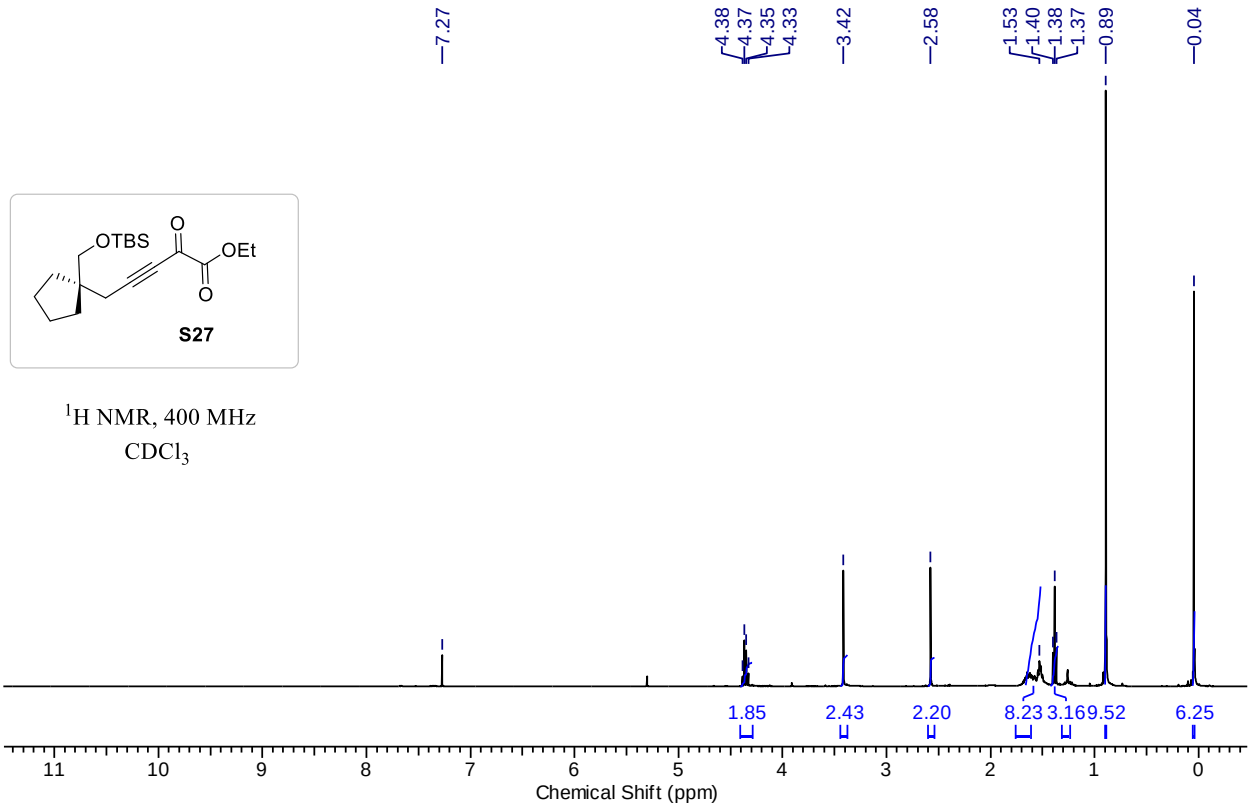


^{13}C NMR, 101 MHz
$CDCl_3$

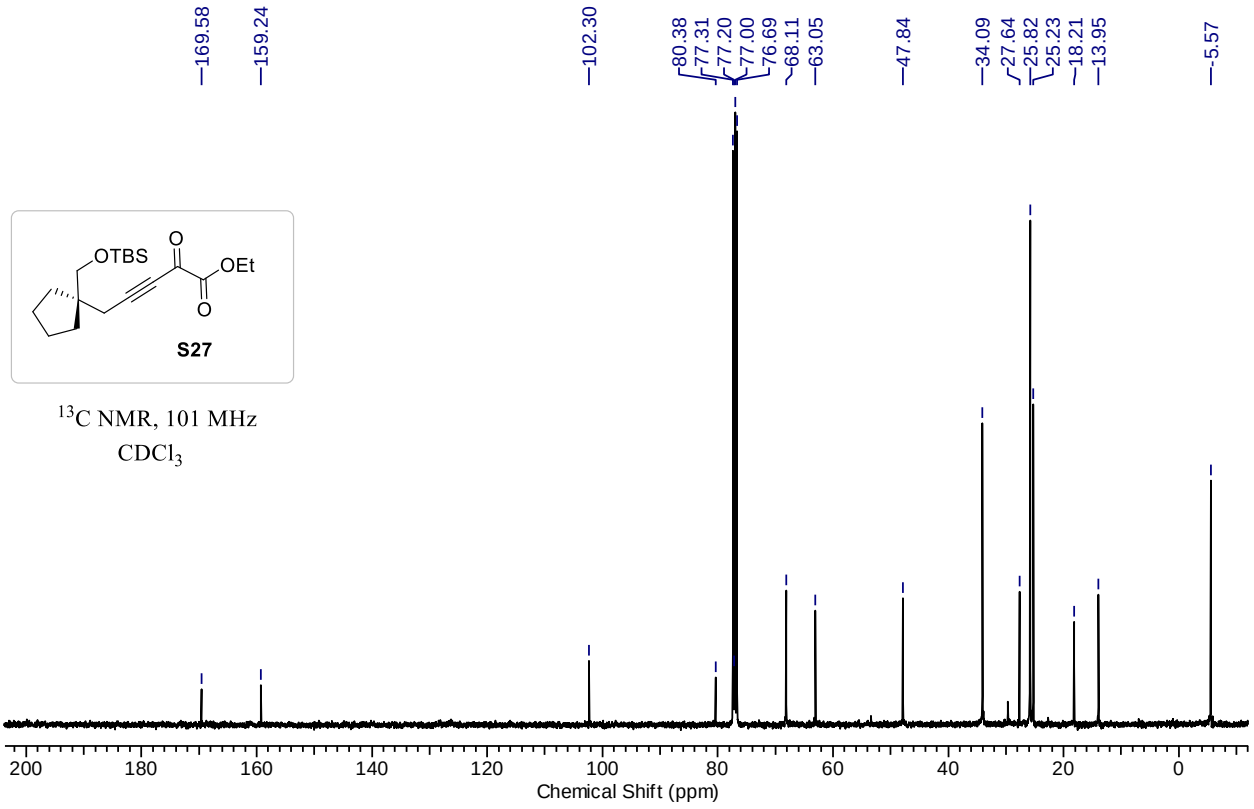
Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclopentyl)-2-(4-nitrophenyl)pent-3-ynoate(1h):



Ethyl 5-(1-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclopentyl)-2-oxopent-3-ynoate (S27):

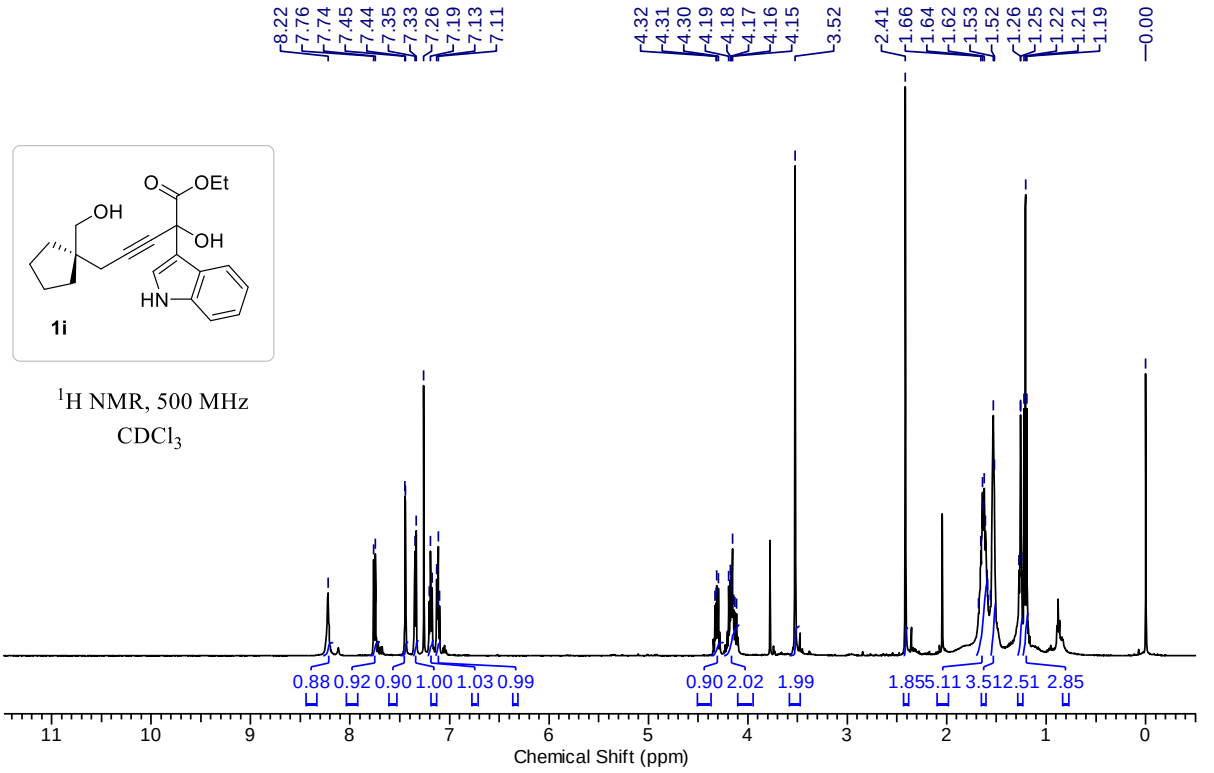


^{1}H NMR, 400 MHz
$CDCl_3$

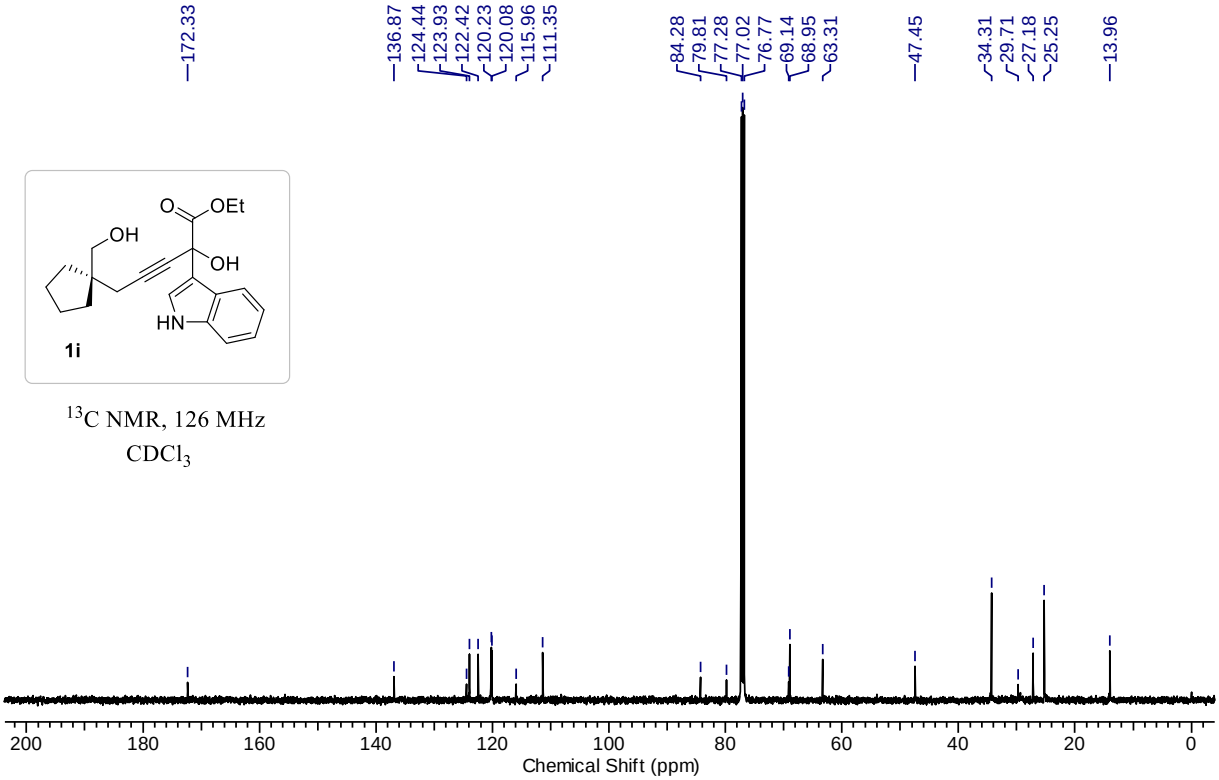


^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(1-(hydroxymethyl)cyclopentyl)-2-(1*H*-indol-3-yl)pent-3-ynoate (1i):

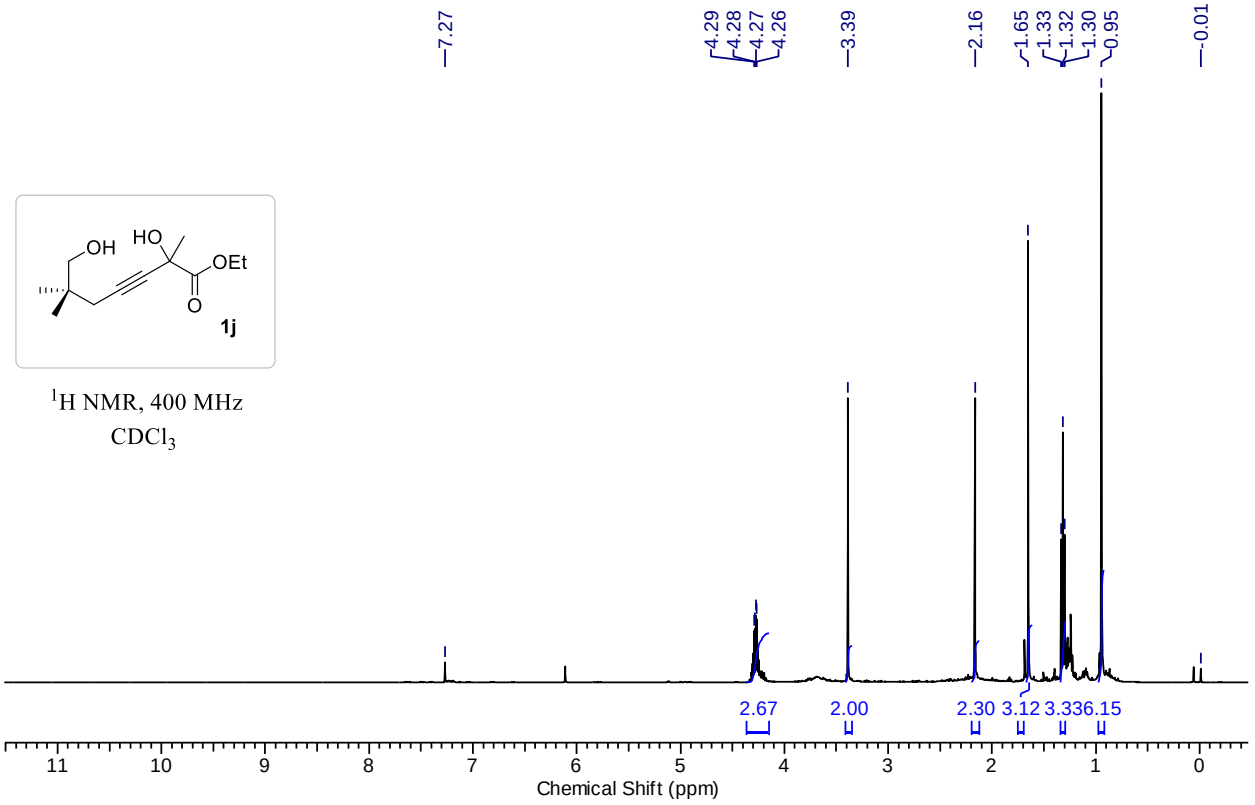


^{1}H NMR, 500 MHz
$CDCl_3$

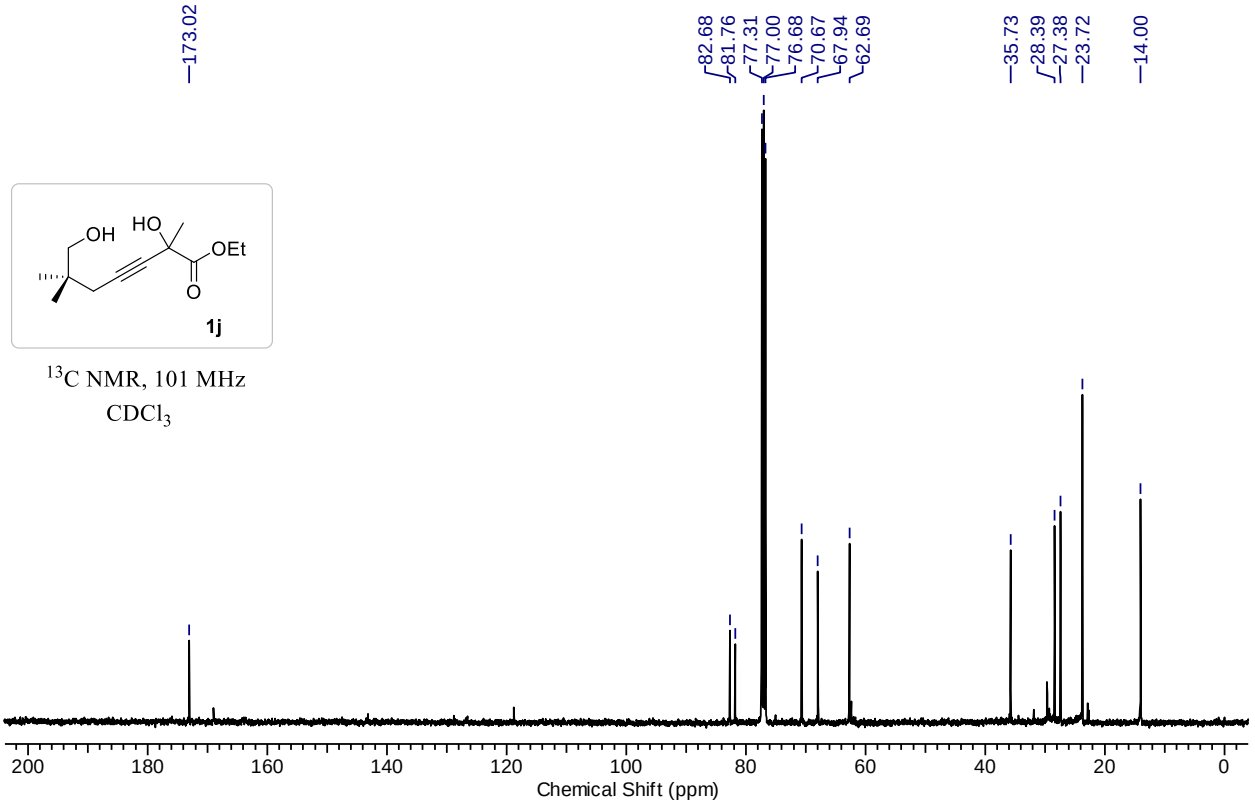


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2,7-dihydroxy-2,6,6-trimethylhept-3-ynoate (1j):

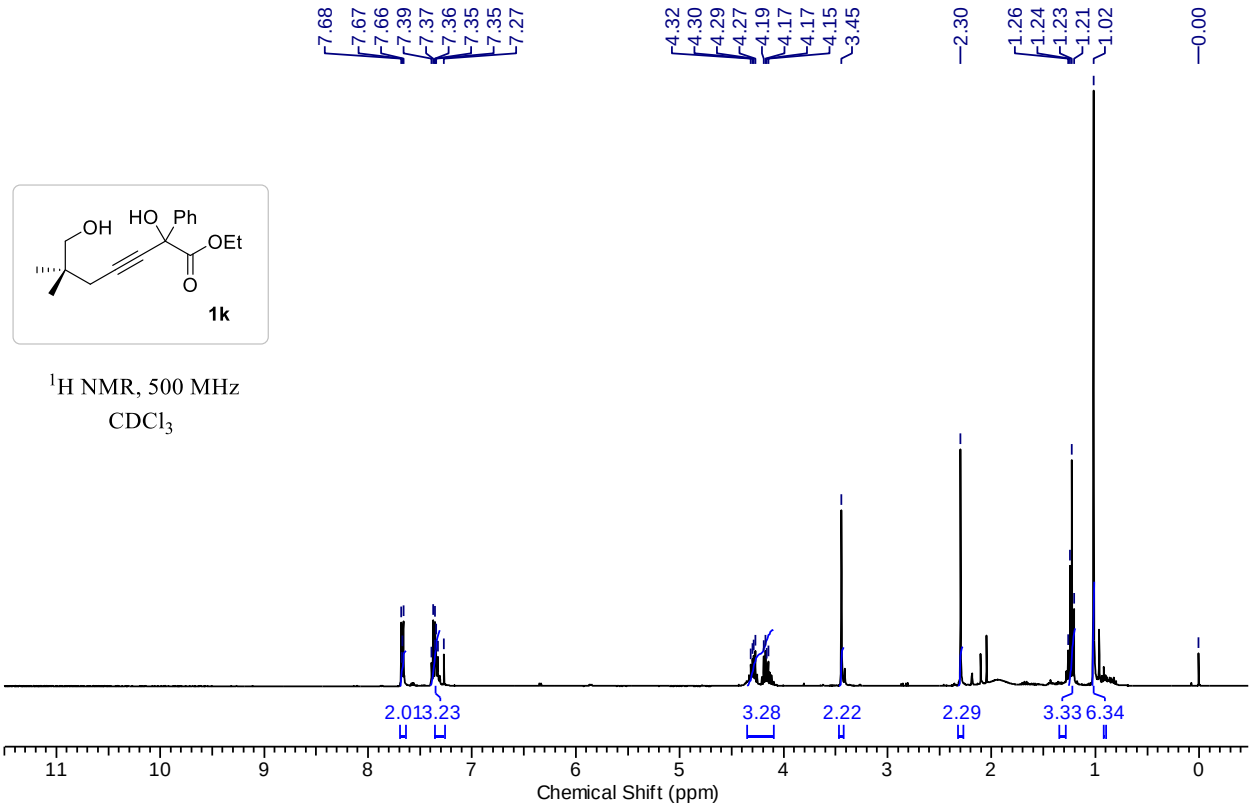


^{1}H NMR, 400 MHz
$CDCl_3$

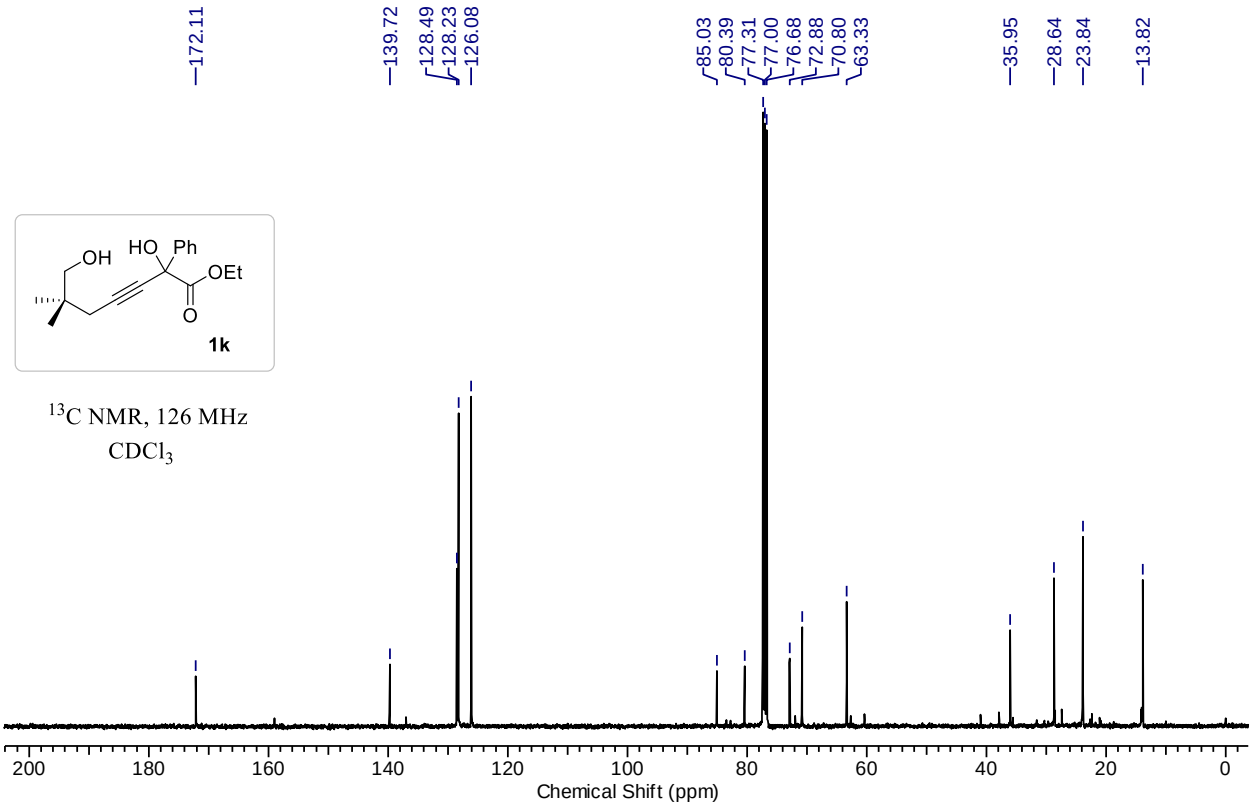


^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 2,7-dihydroxy-6,6-dimethyl-2-phenylhept-3-ynoate (1k):

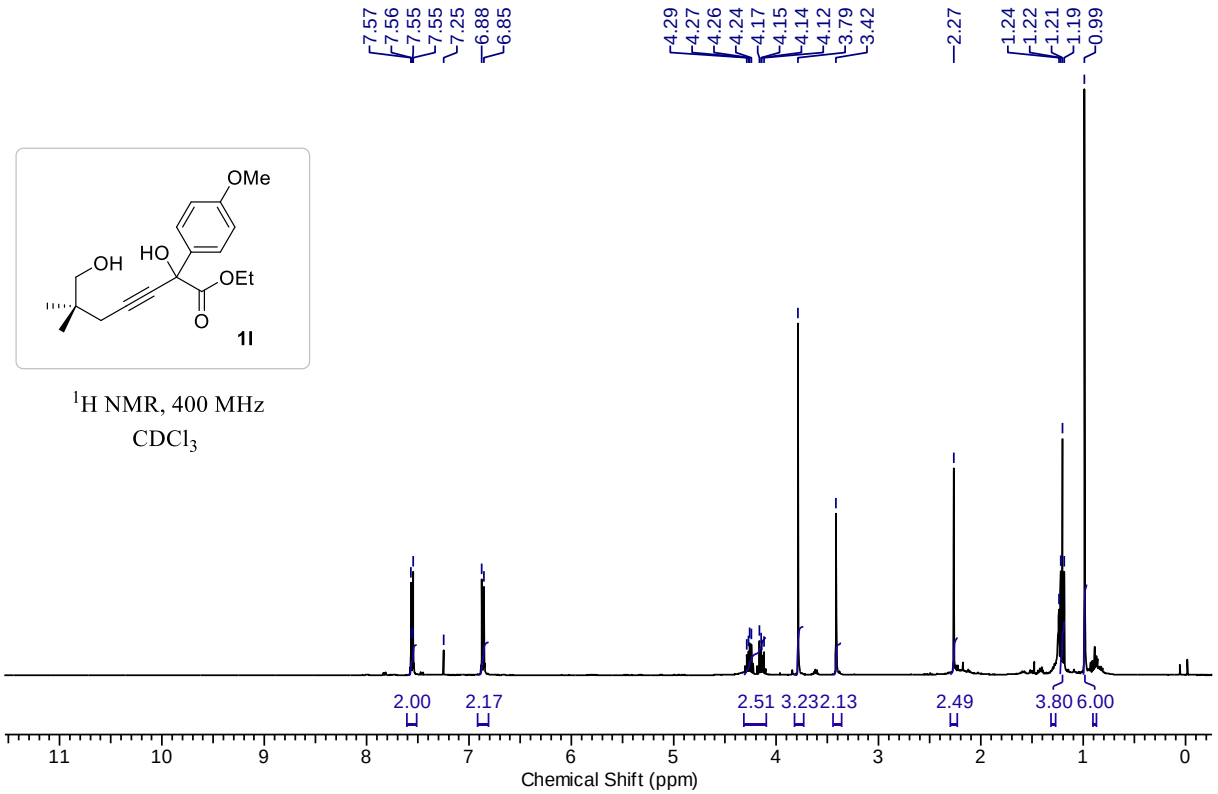


^{1}H NMR, 500 MHz
$CDCl_3$

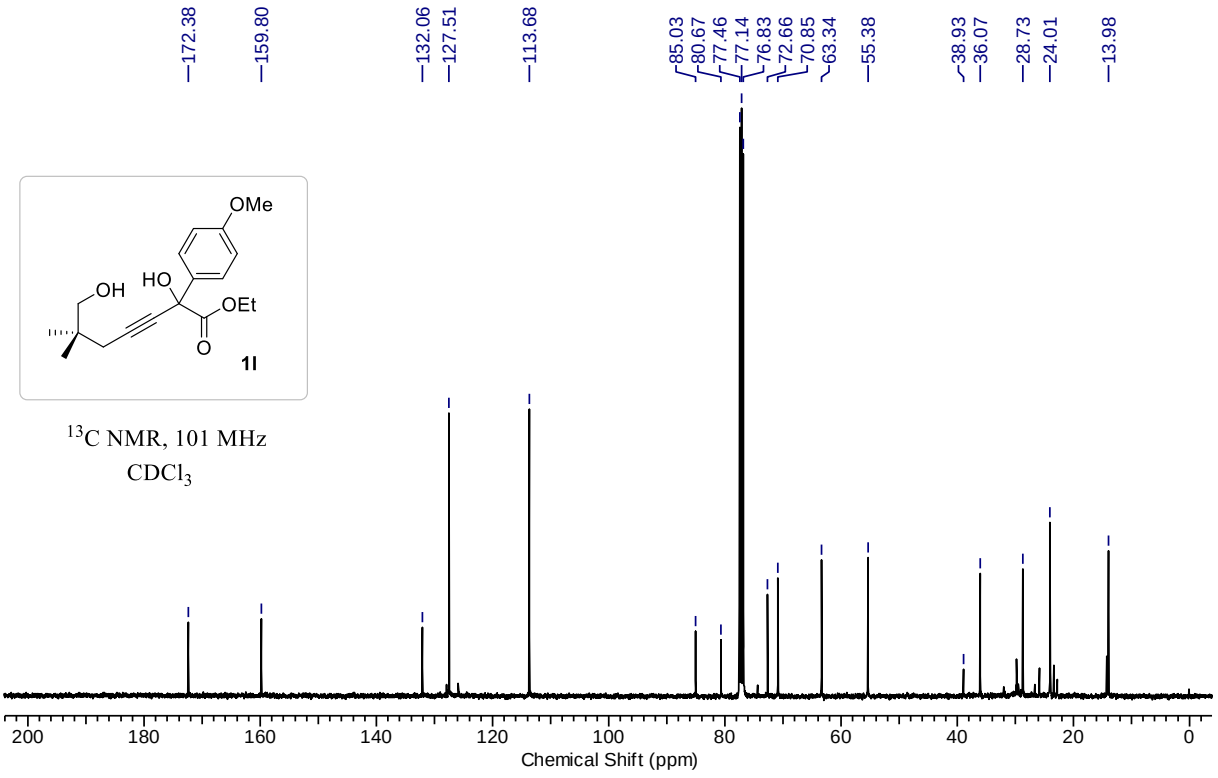


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2,7-dihydroxy-2-(4-methoxyphenyl)-6,6-dimethylhept-3-ynoate (1l):

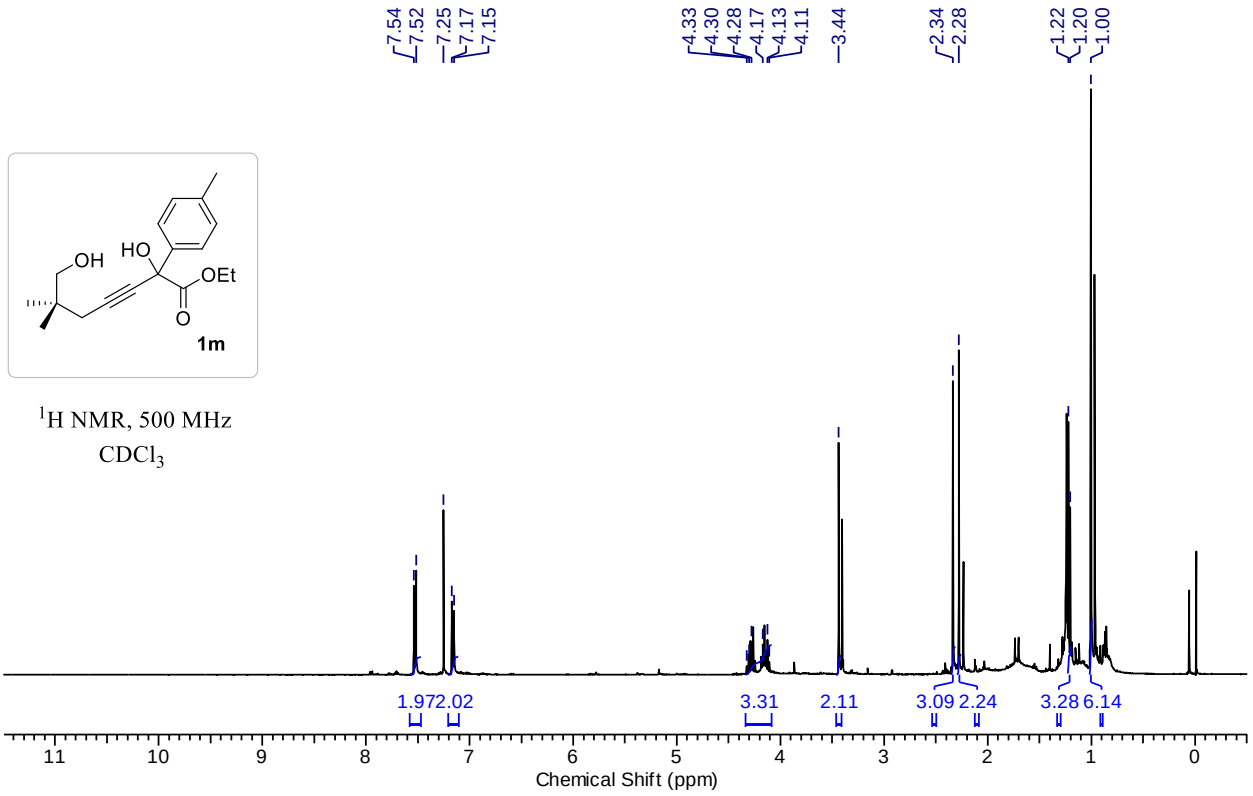


^{1}H NMR, 400 MHz
$CDCl_3$

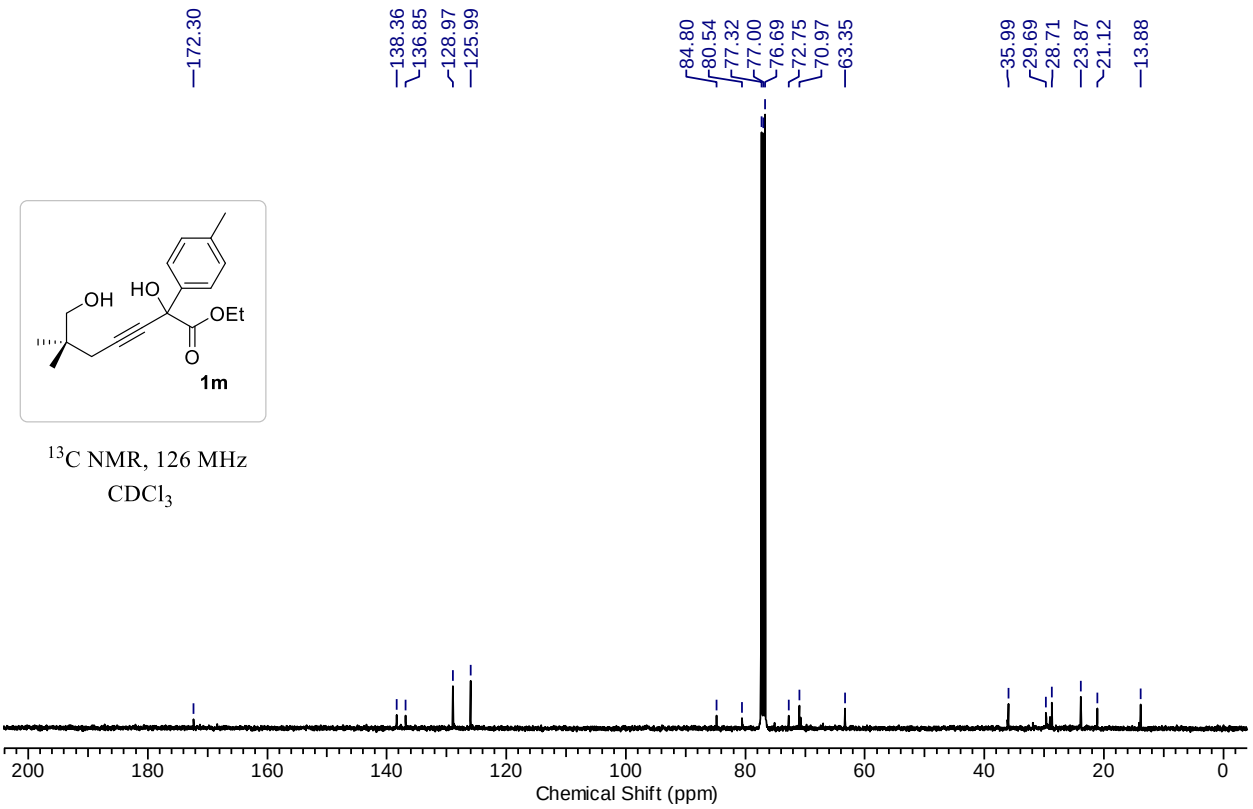


^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 2,7-dihydroxy-6,6-dimethyl-2-(*p*-tolyl)hept-3-ynoate (1m):

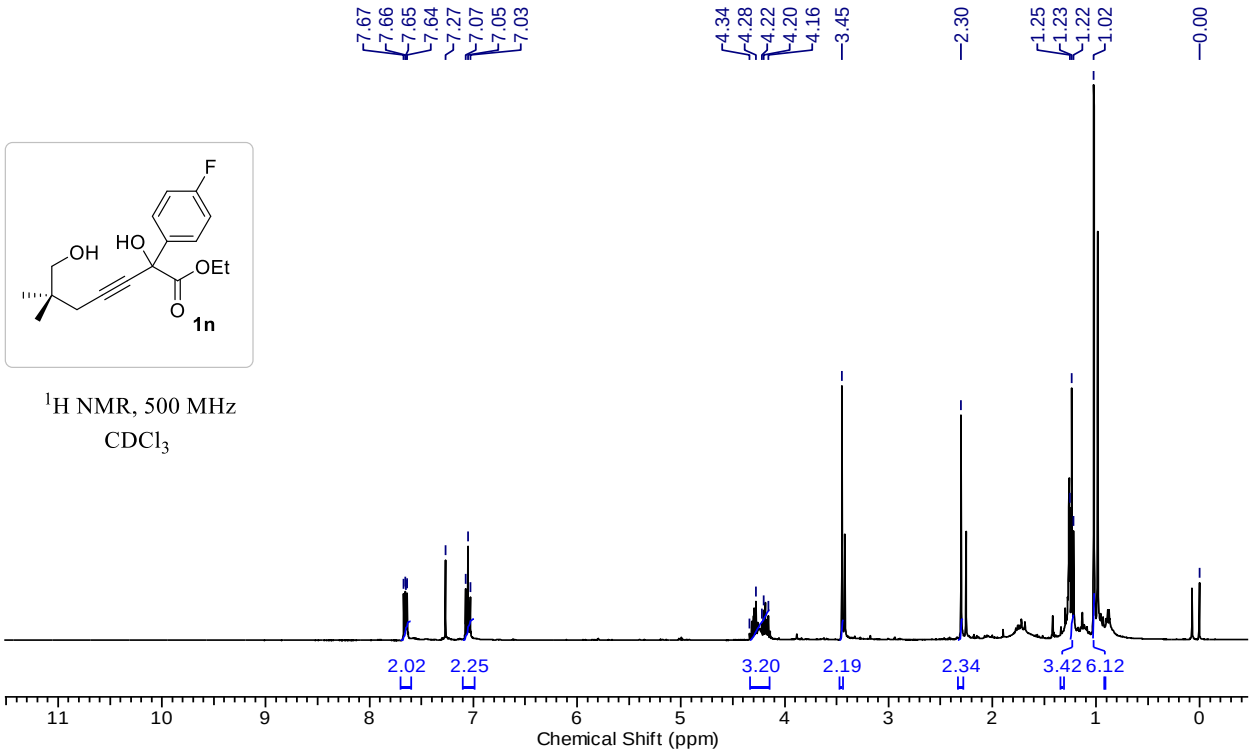


^{1}H NMR, 500 MHz
$CDCl_3$

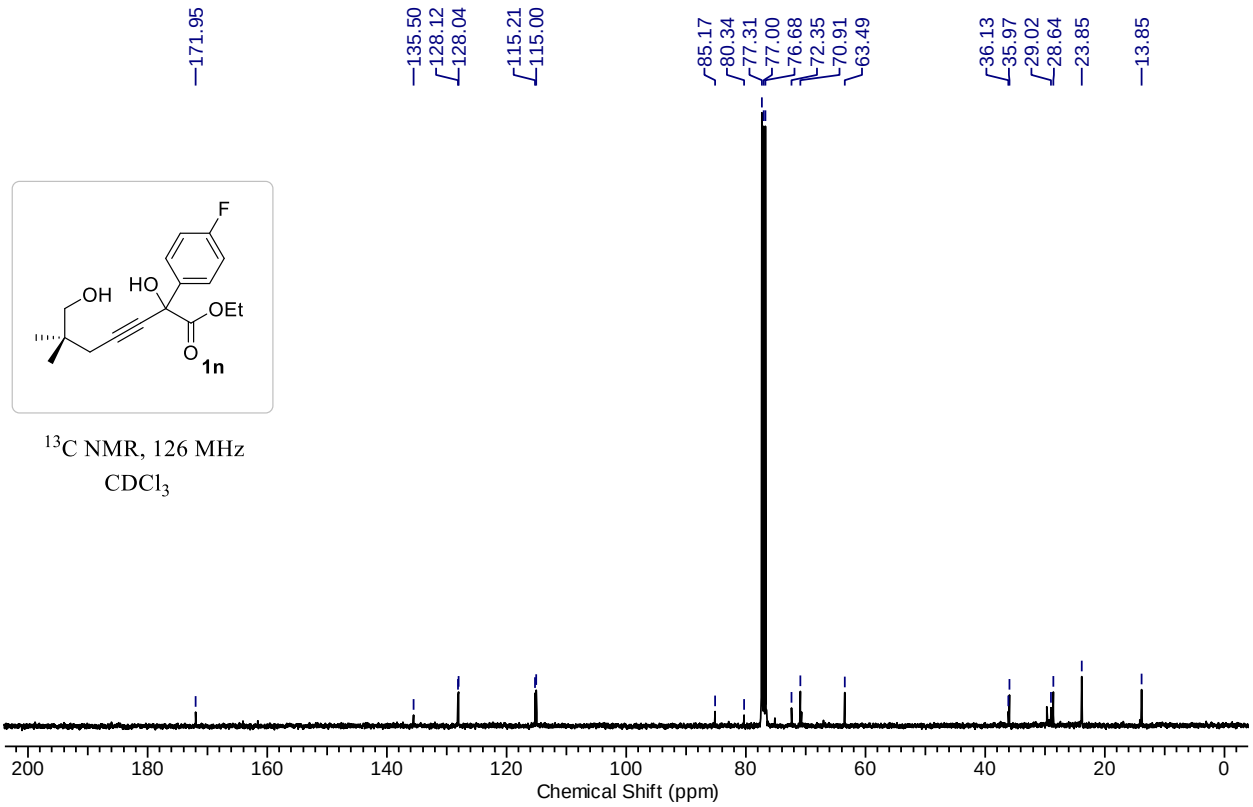


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2-(4-fluorophenyl)-2,7-dihydroxy-6,6-dimethylhept-3-ynoate (1n):

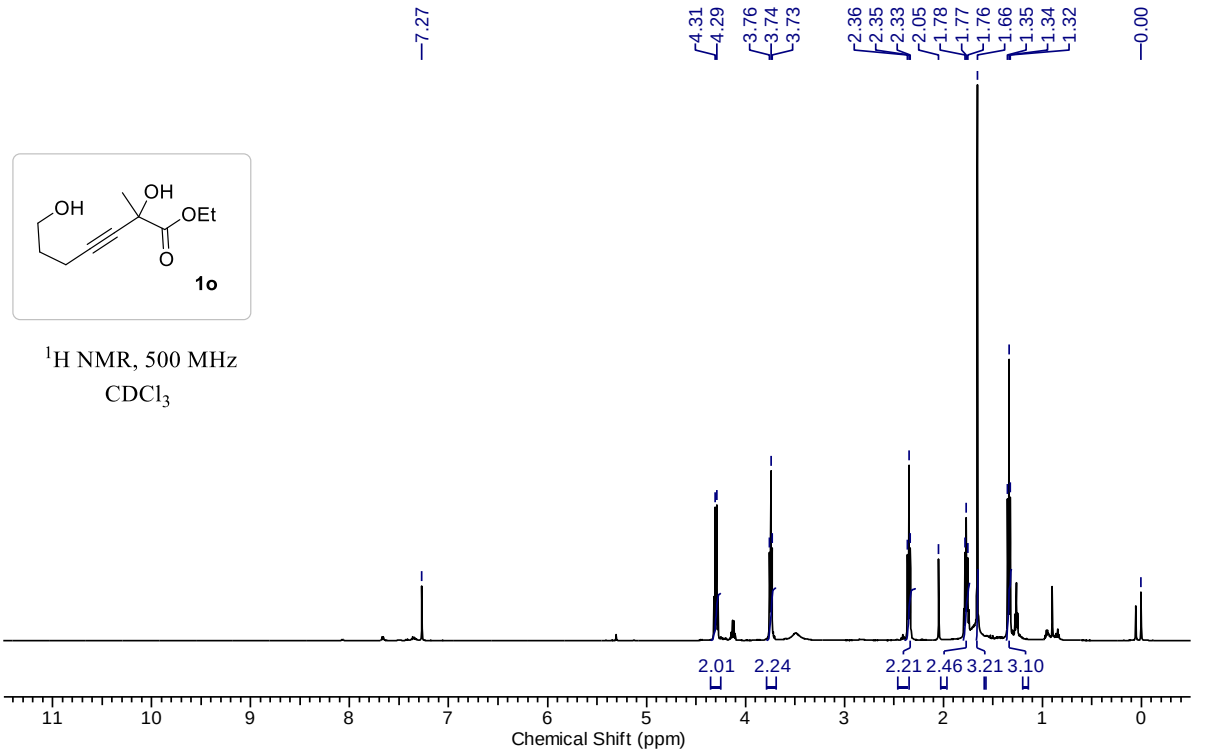


^{1}H NMR, 500 MHz
$CDCl_3$

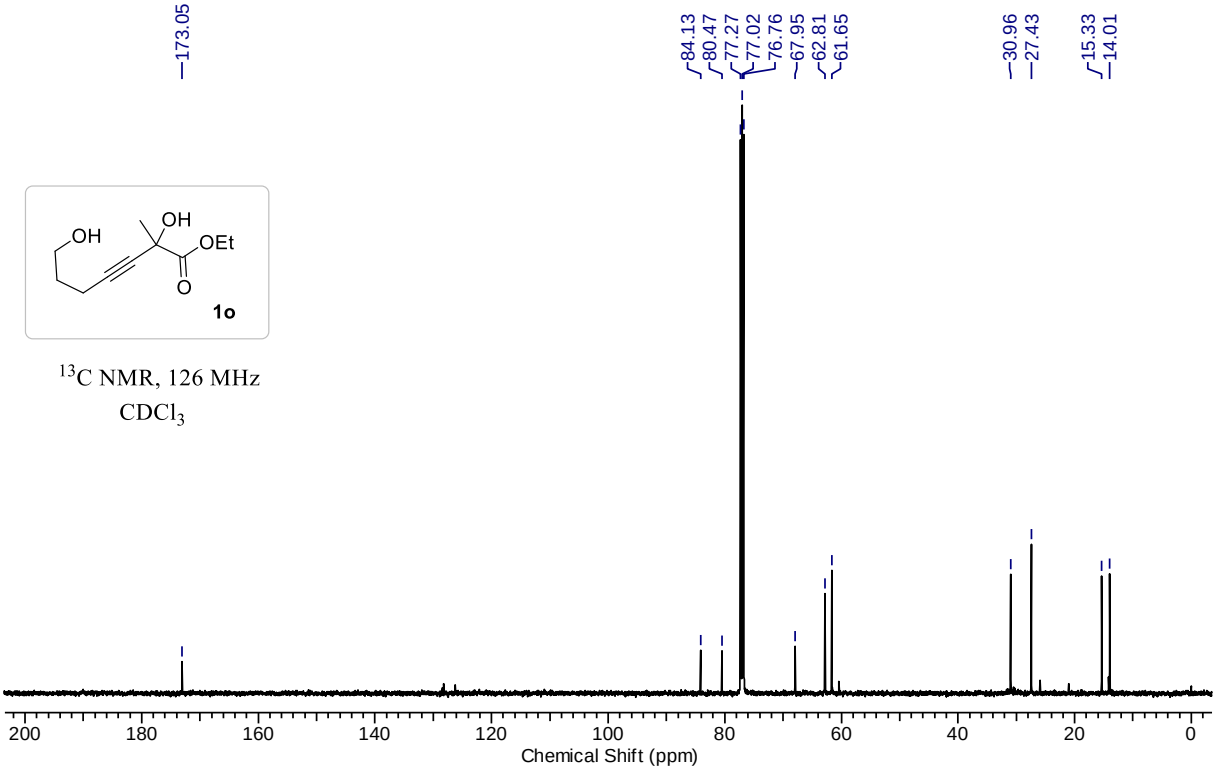


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2,7-dihydroxy-2-methylhept-3-ynoate (1o):

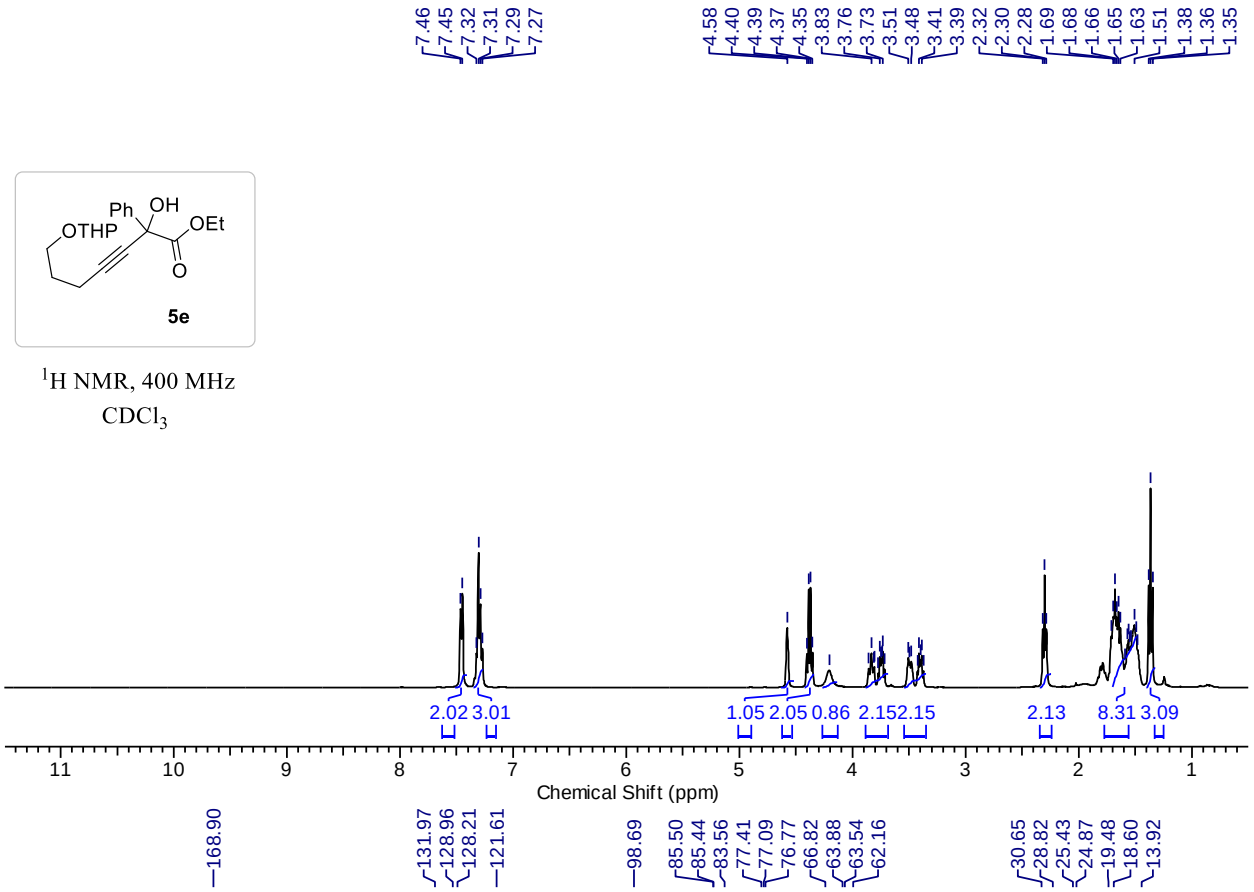


^{1}H NMR, 500 MHz
$CDCl_3$



^{13}C NMR, 126 MHz
$CDCl_3$

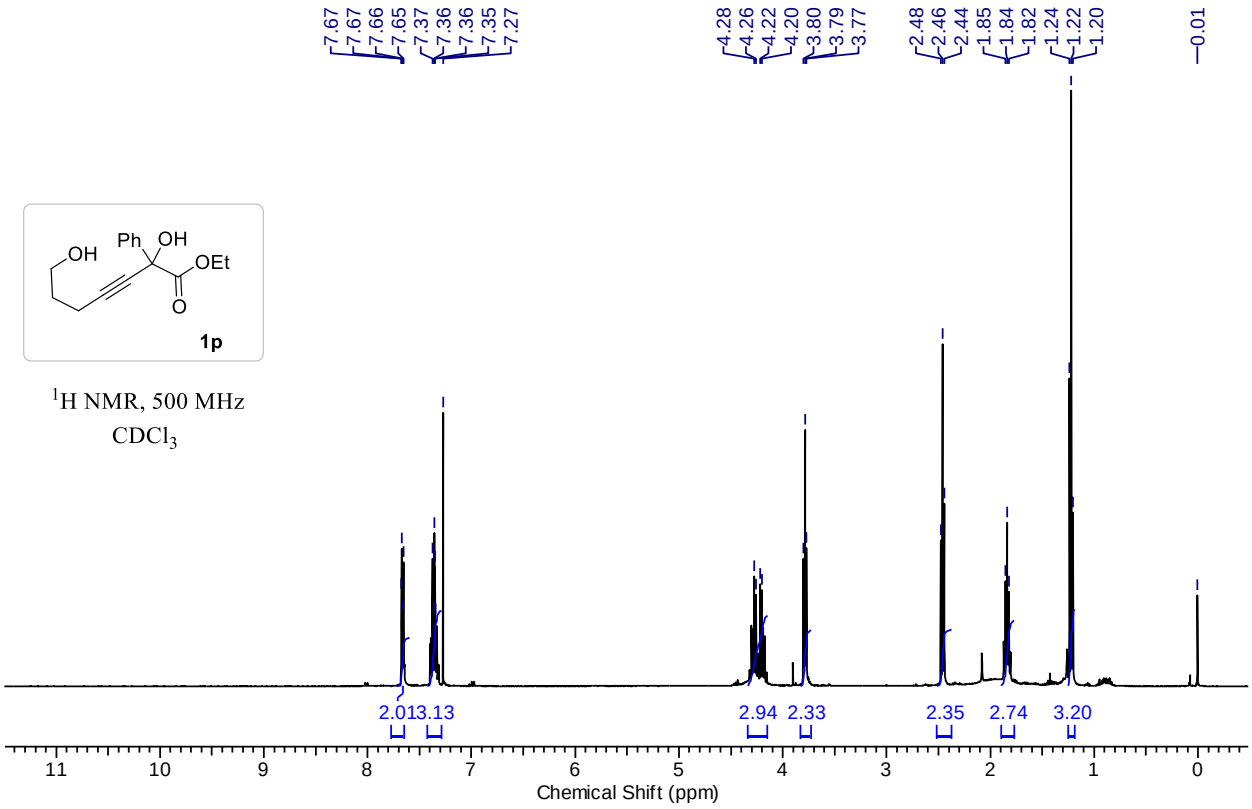
Ethyl 2-hydroxy-2-phenyl-7-((tetrahydro-2*H*-pyran-2-yl)oxy)hept-3-ynoate (5e):



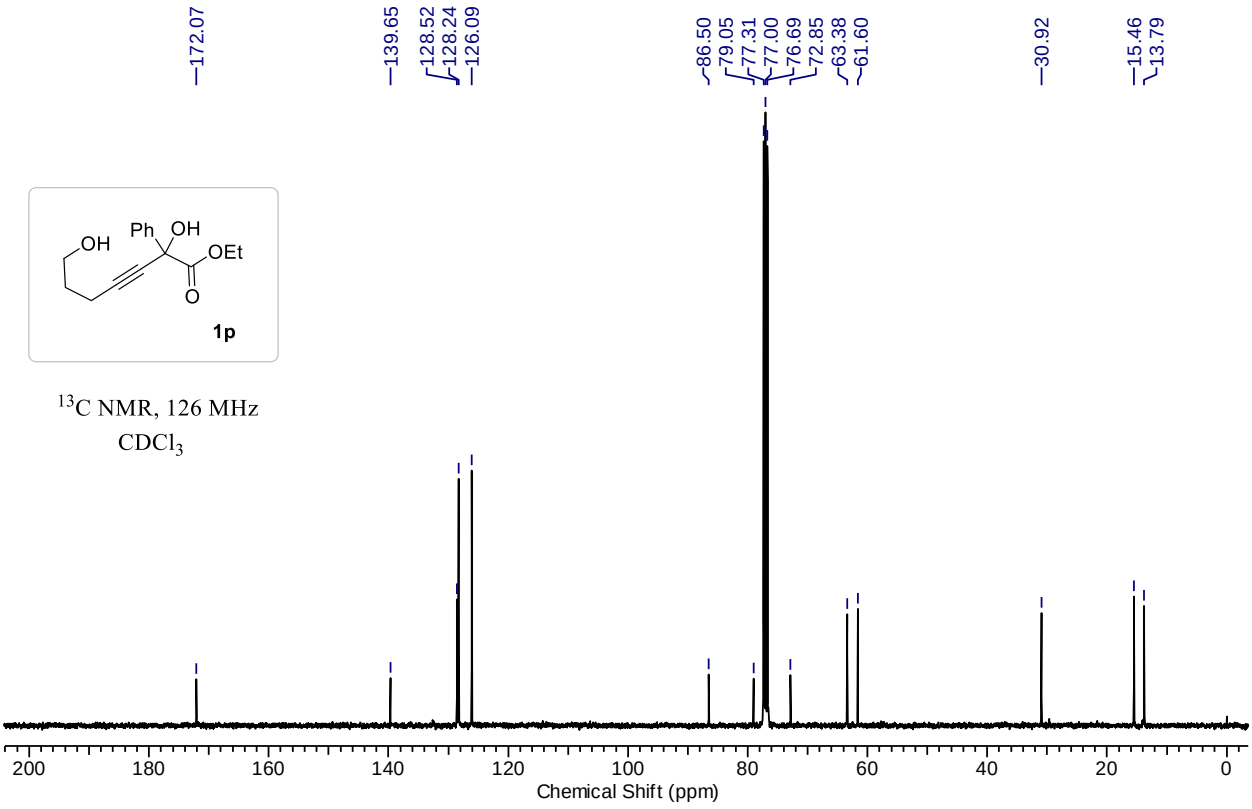
^{1}H NMR, 400 MHz
$CDCl_3$

^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 2,7-dihydroxy-2-phenylhept-3-ynoate(1p):

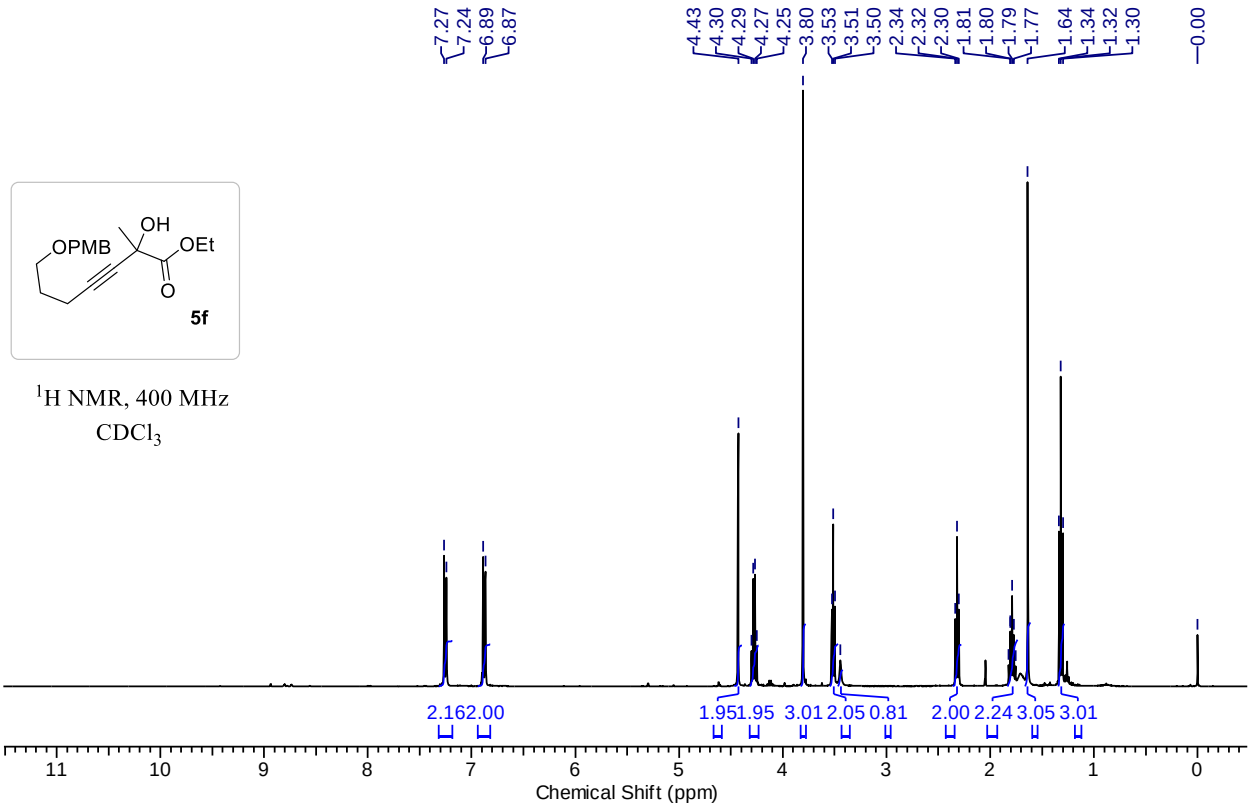


^{1}H NMR, 500 MHz
$CDCl_3$

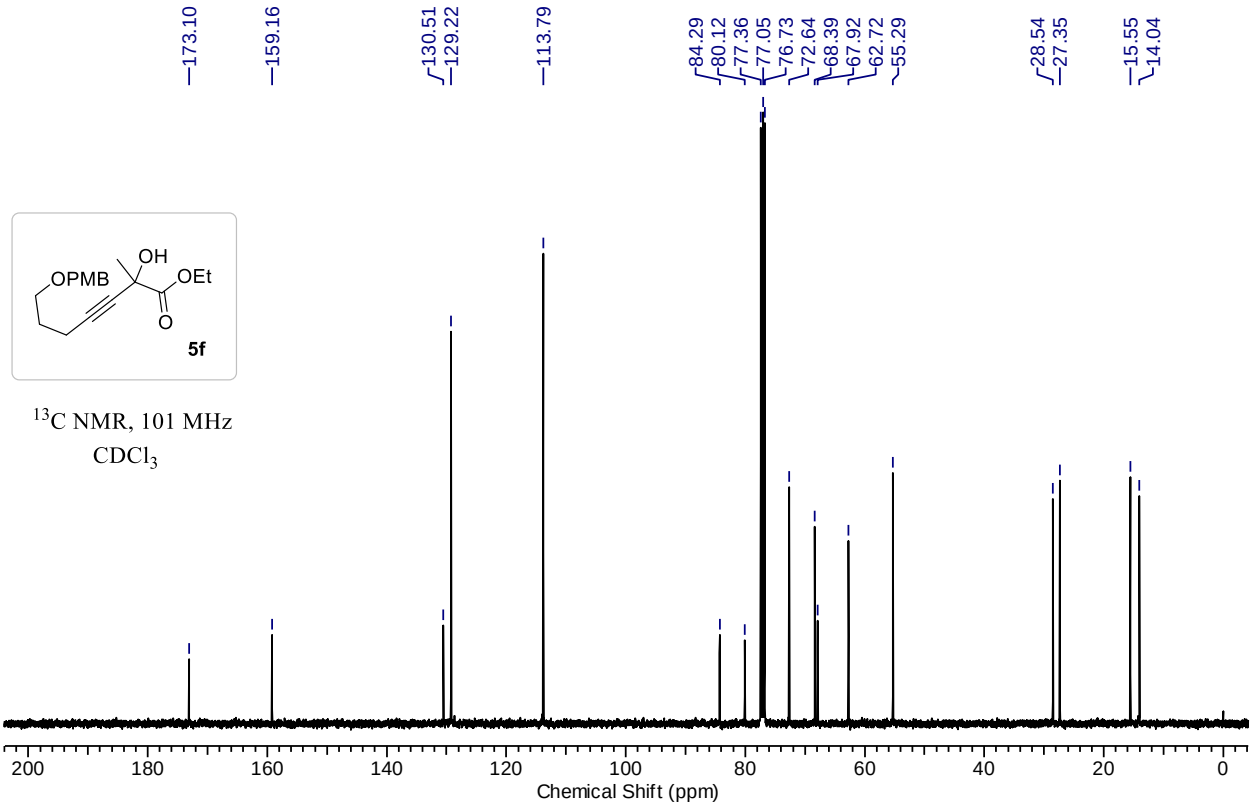


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2-hydroxy-7-((4-methoxybenzyl)oxy)-2-methylhept-3-ynoate (5f):

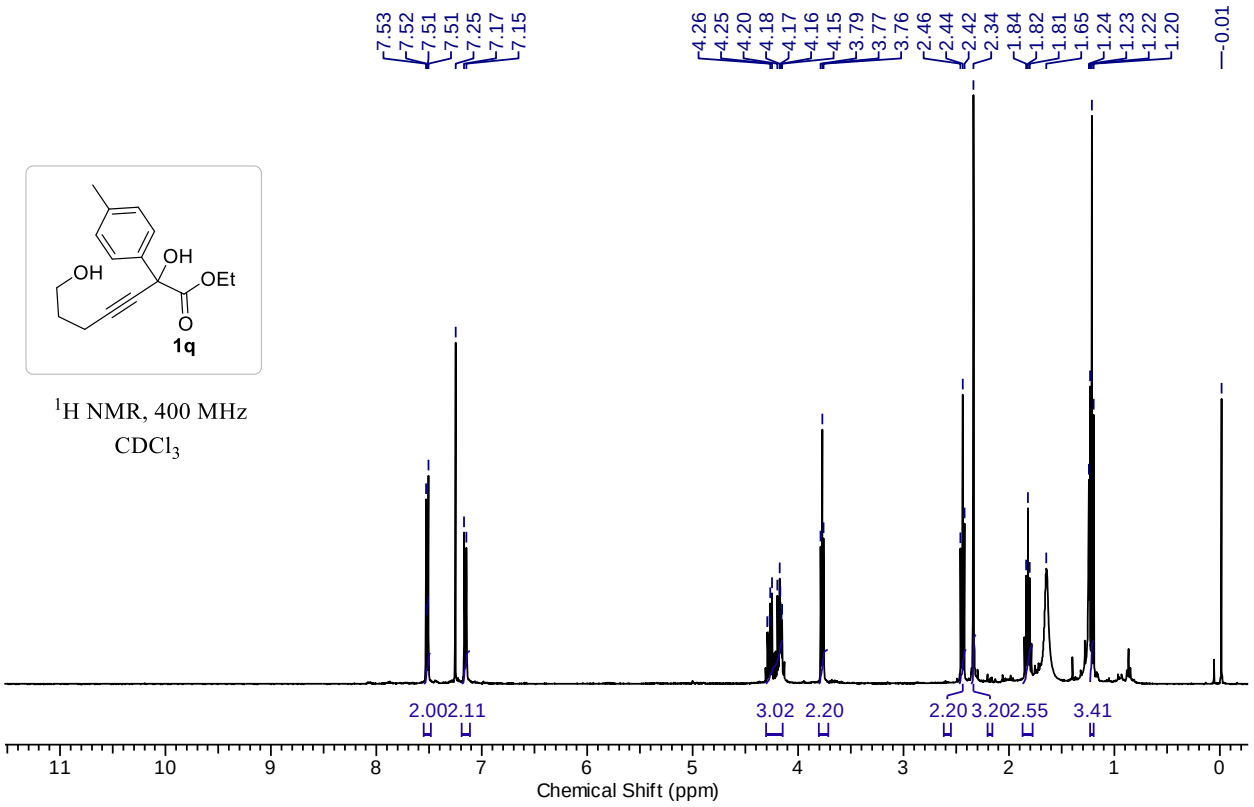


^{1}H NMR, 400 MHz
$CDCl_3$

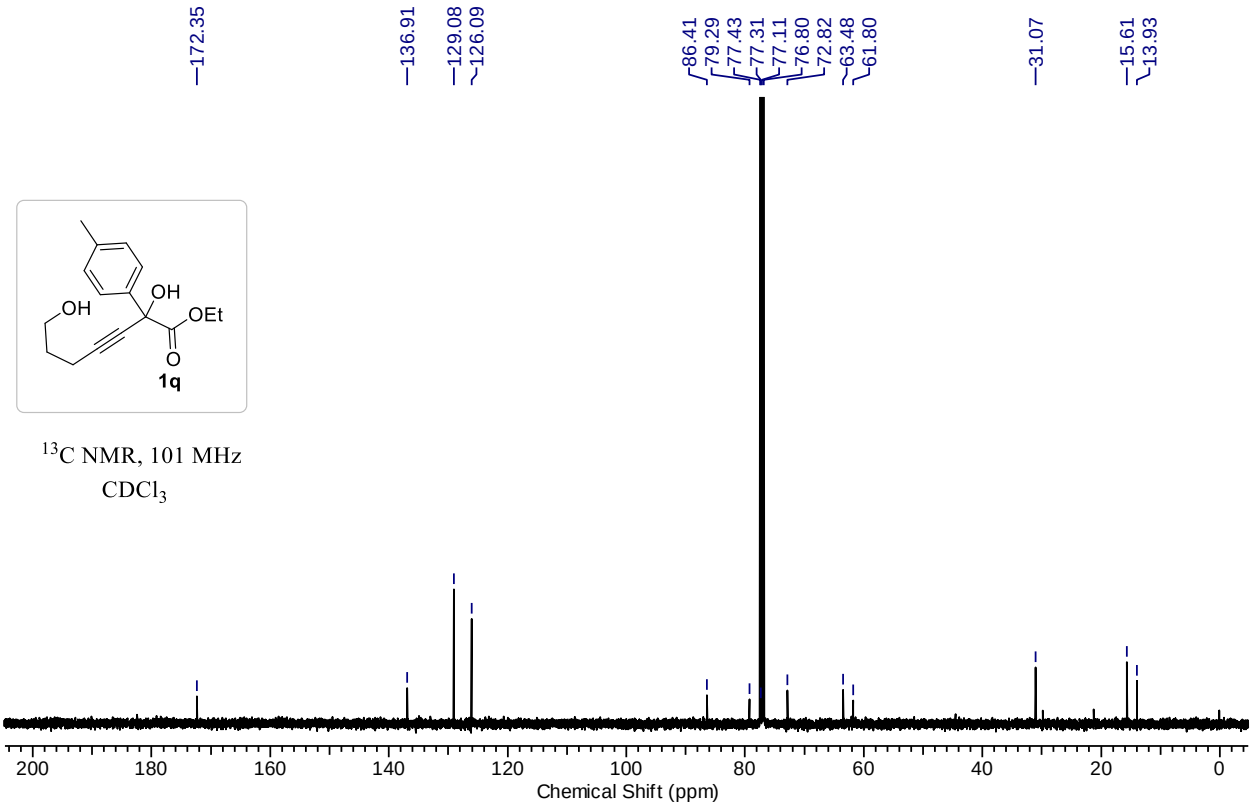


^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 2,7-dihydroxy-2-(*p*-tolyl)hept-3-ynoate (1q):

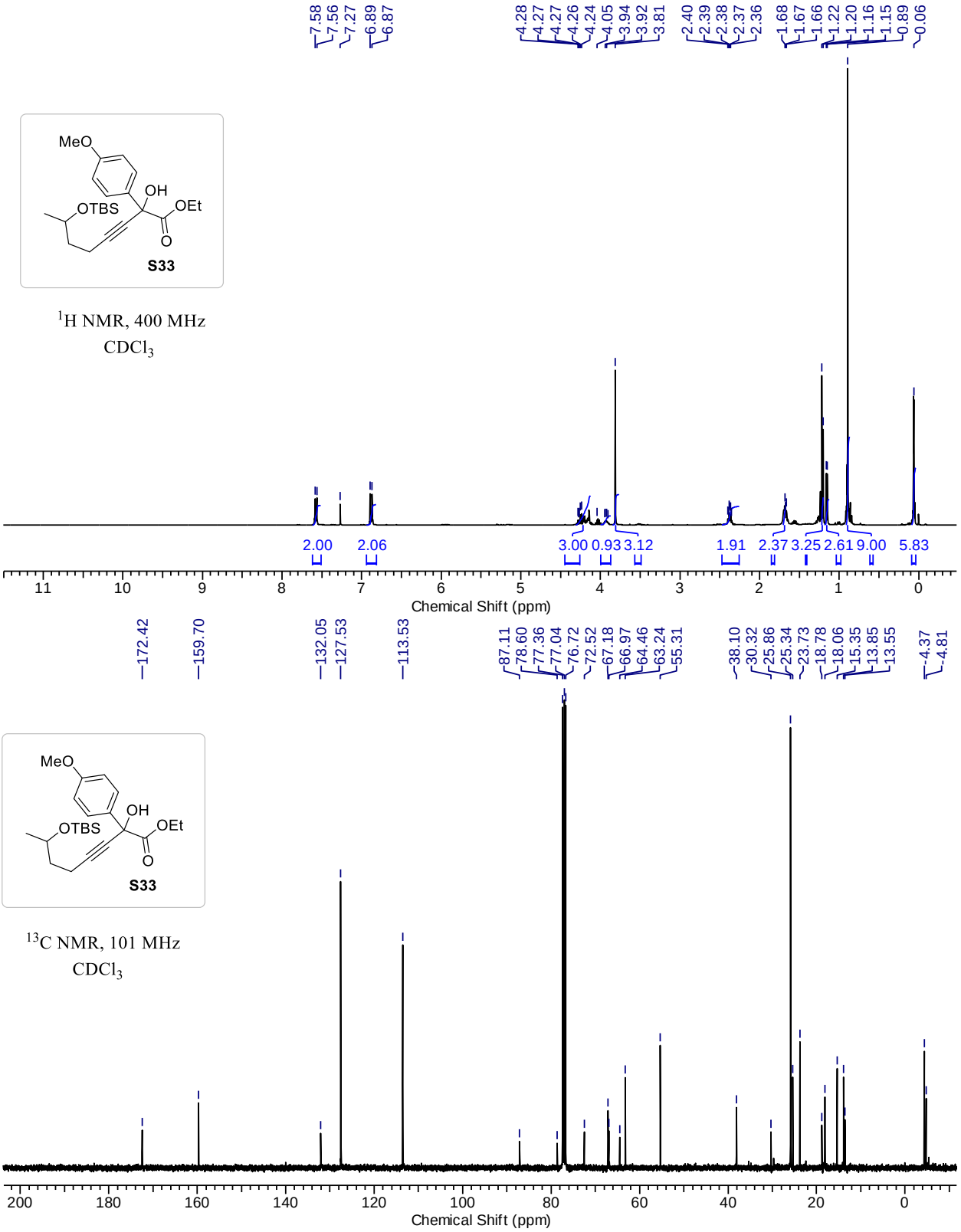


^{1}H NMR, 400 MHz
$CDCl_3$

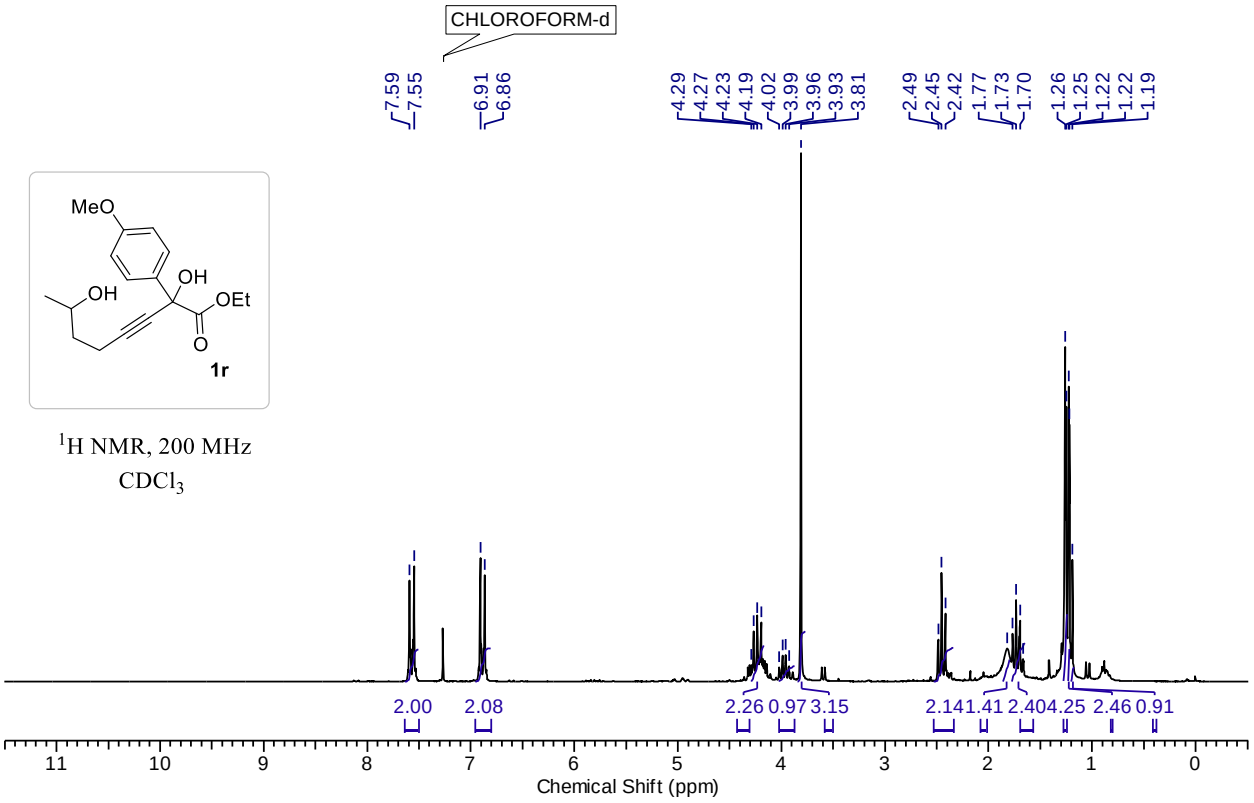


^{13}C NMR, 101 MHz
$CDCl_3$

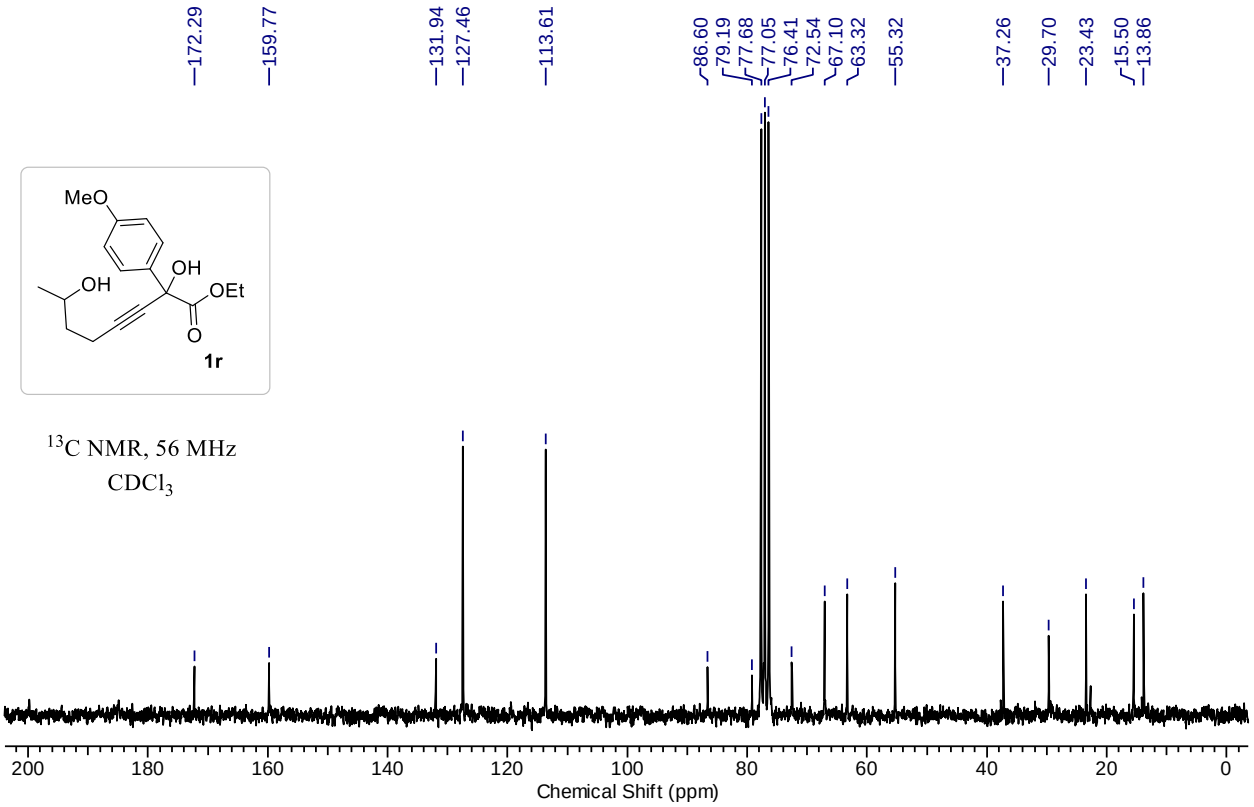
Ethyl7-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-(4-methoxyphenyl)oct-3-ynoate (S33):



Ethyl 2,7-dihydroxy-2-(4-methoxyphenyl)oct-3-ynoate (1r):

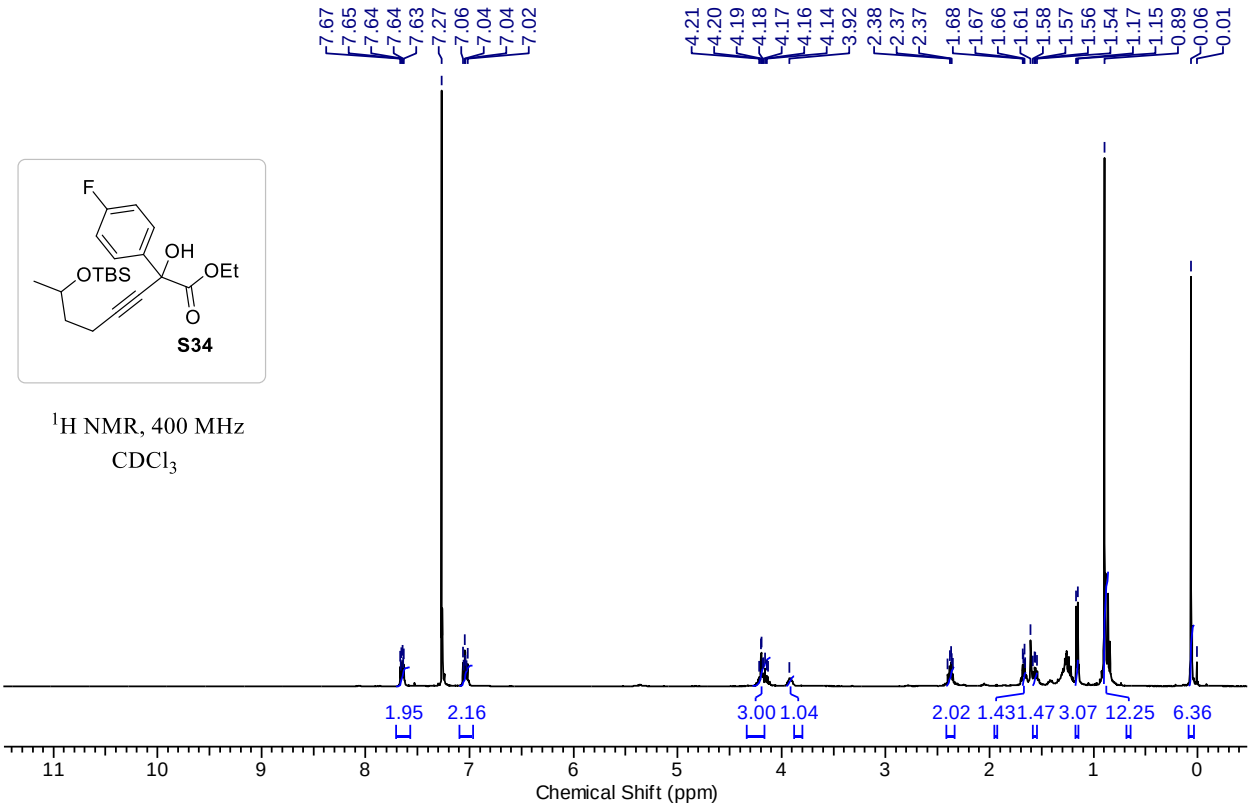


^{1}H NMR, 200 MHz
$CDCl_3$

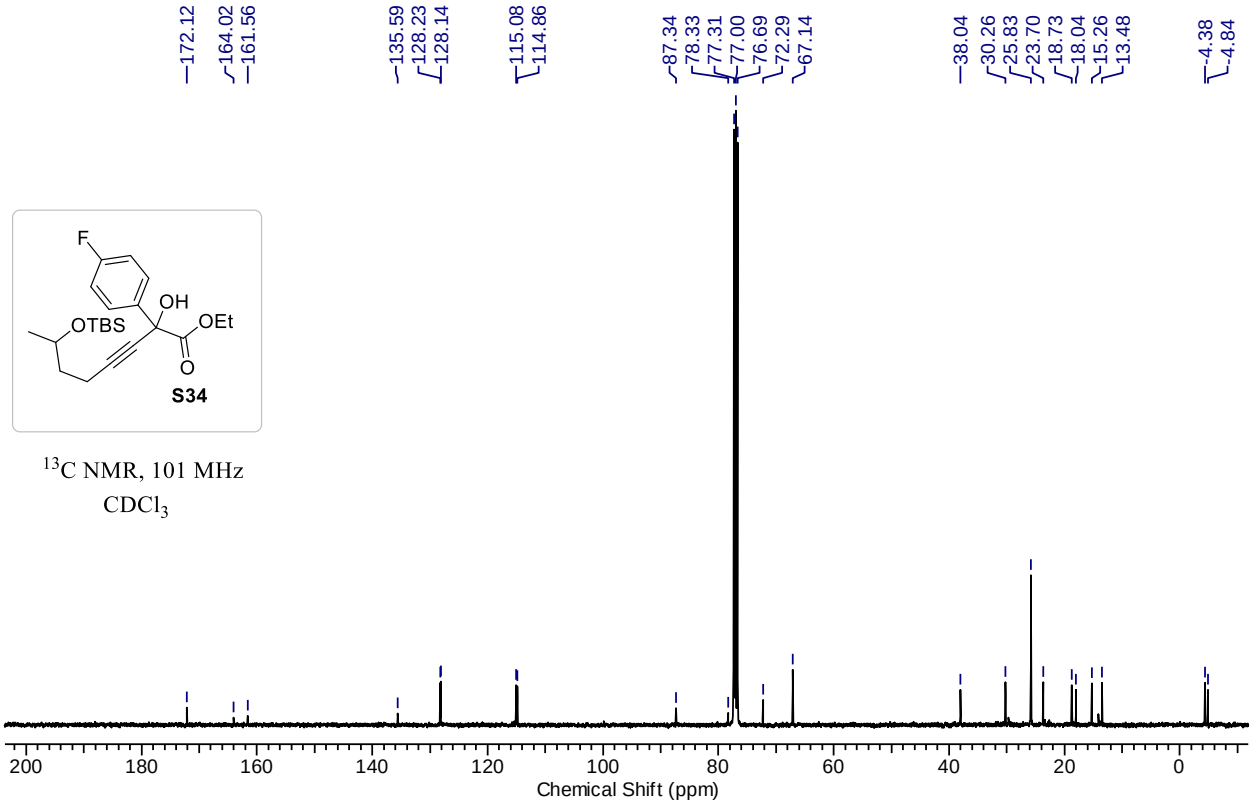


^{13}C NMR, 56 MHz
$CDCl_3$

Ethyl 7-((*tert*-butyldimethylsilyl)oxy)-2-(4-fluorophenyl)-2-hydroxyoct-3-ynoate (S34):

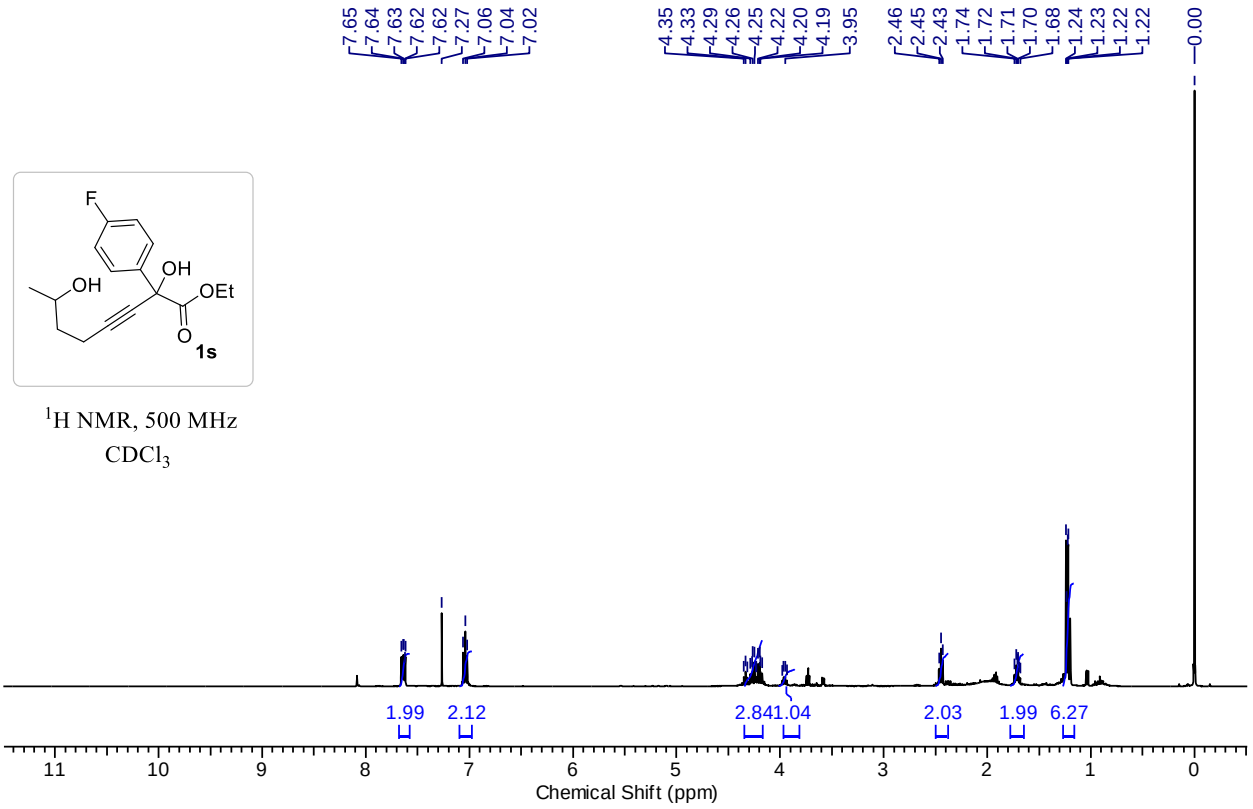


^{1}H NMR, 400 MHz
$CDCl_3$

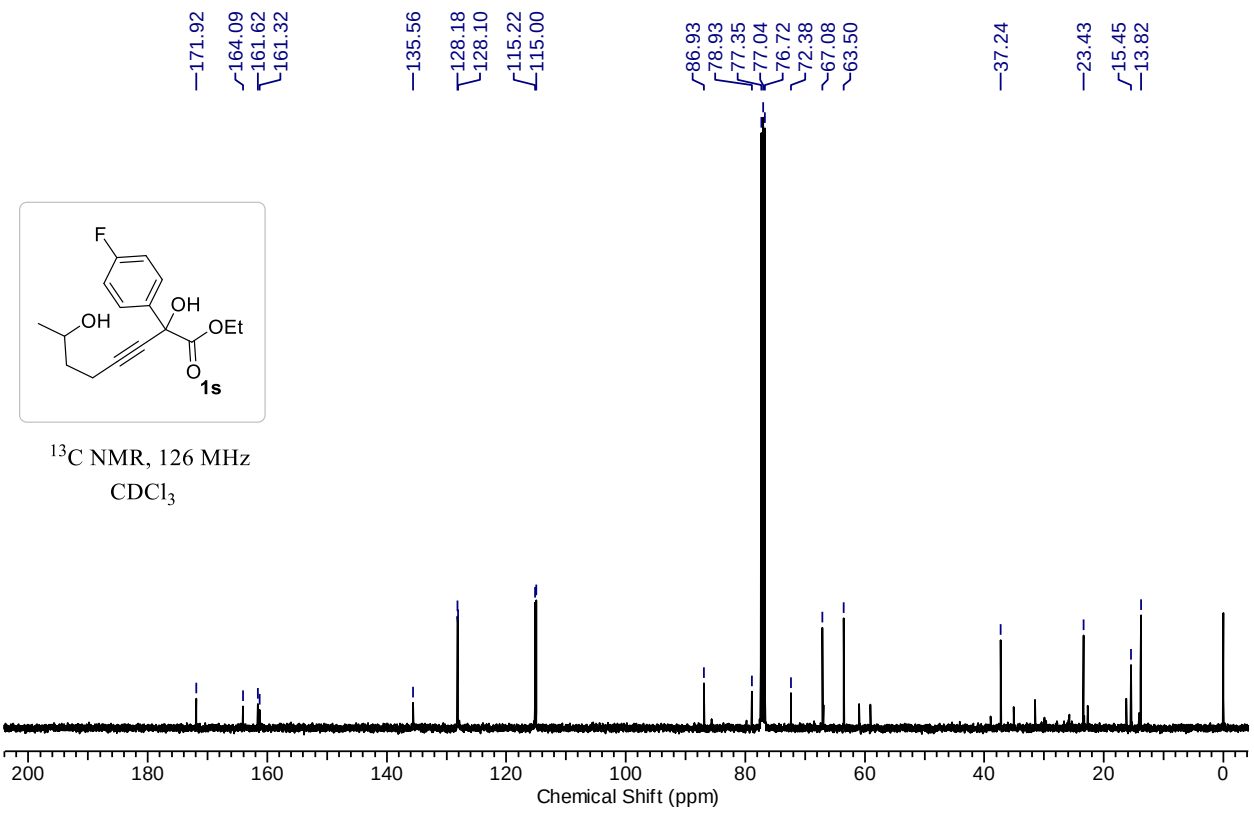


^{13}C NMR, 101 MHz
$CDCl_3$

Ethyl 2-(4-fluorophenyl)-2,7-dihydroxyoct-3-ynoate(1s):

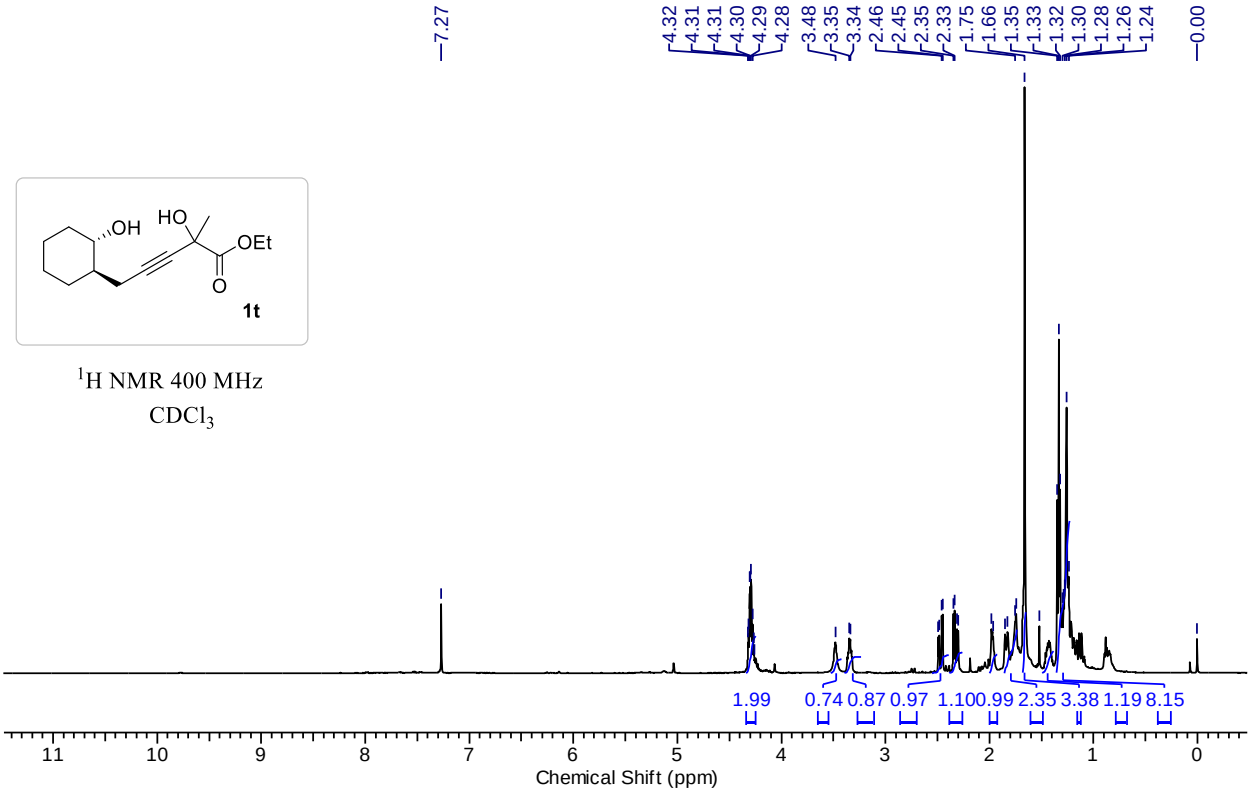


^{1}H NMR, 500 MHz
$CDCl_3$

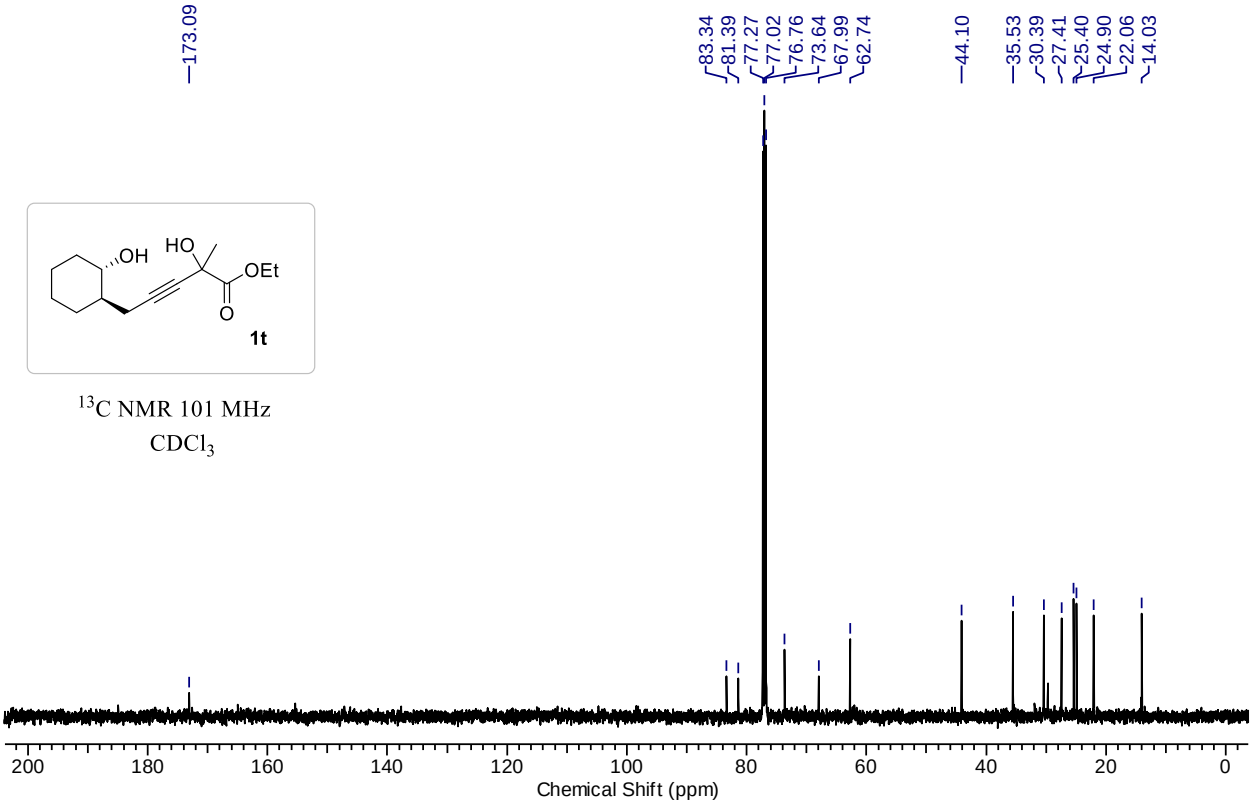


^{13}C NMR, 126 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(2-hydroxycyclohexyl)-2-methylpent-3-ynoate (1t):

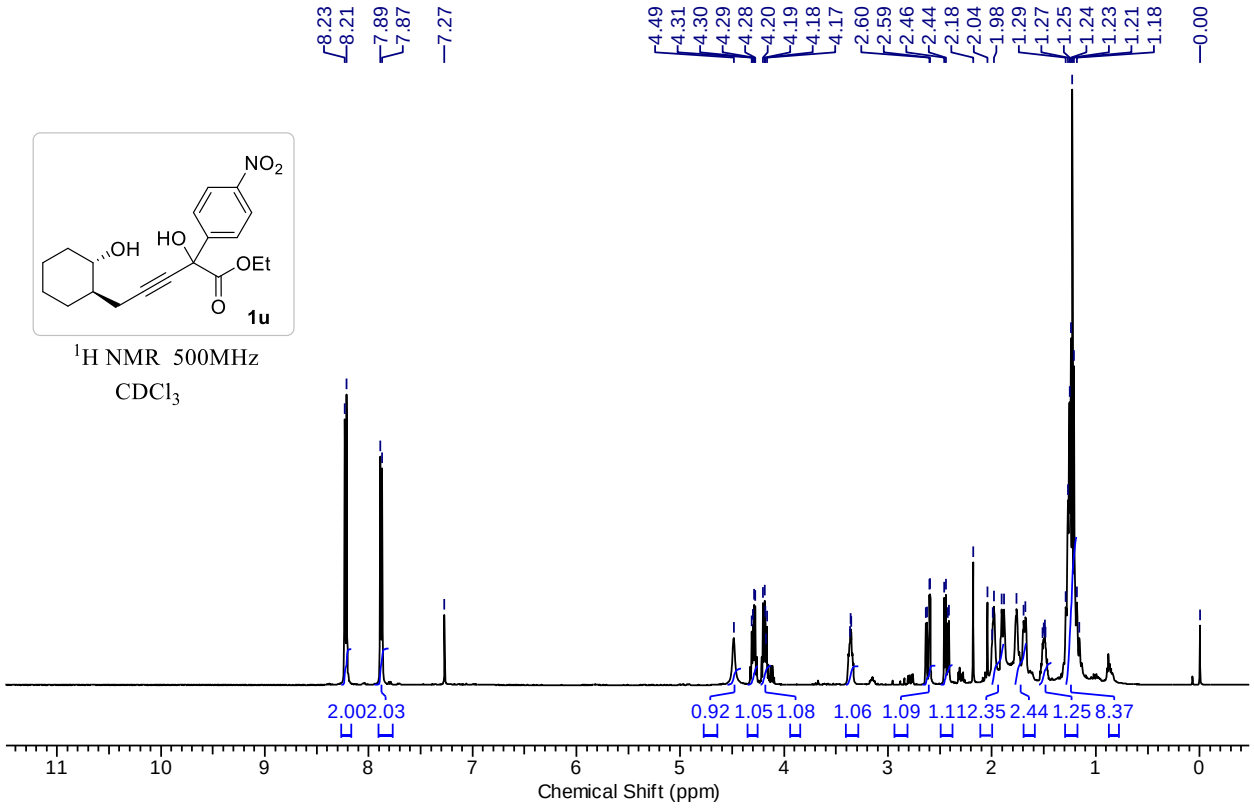


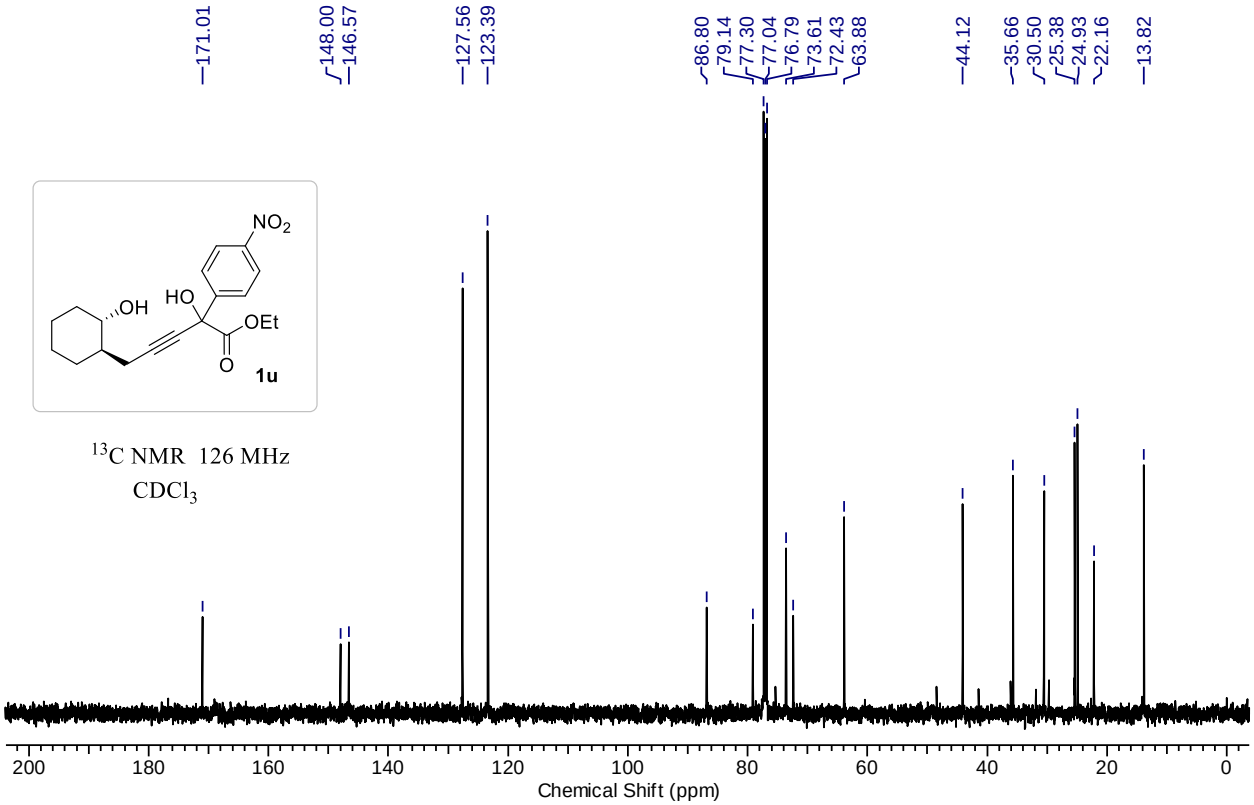
^{1}H NMR 400 MHz
$CDCl_3$



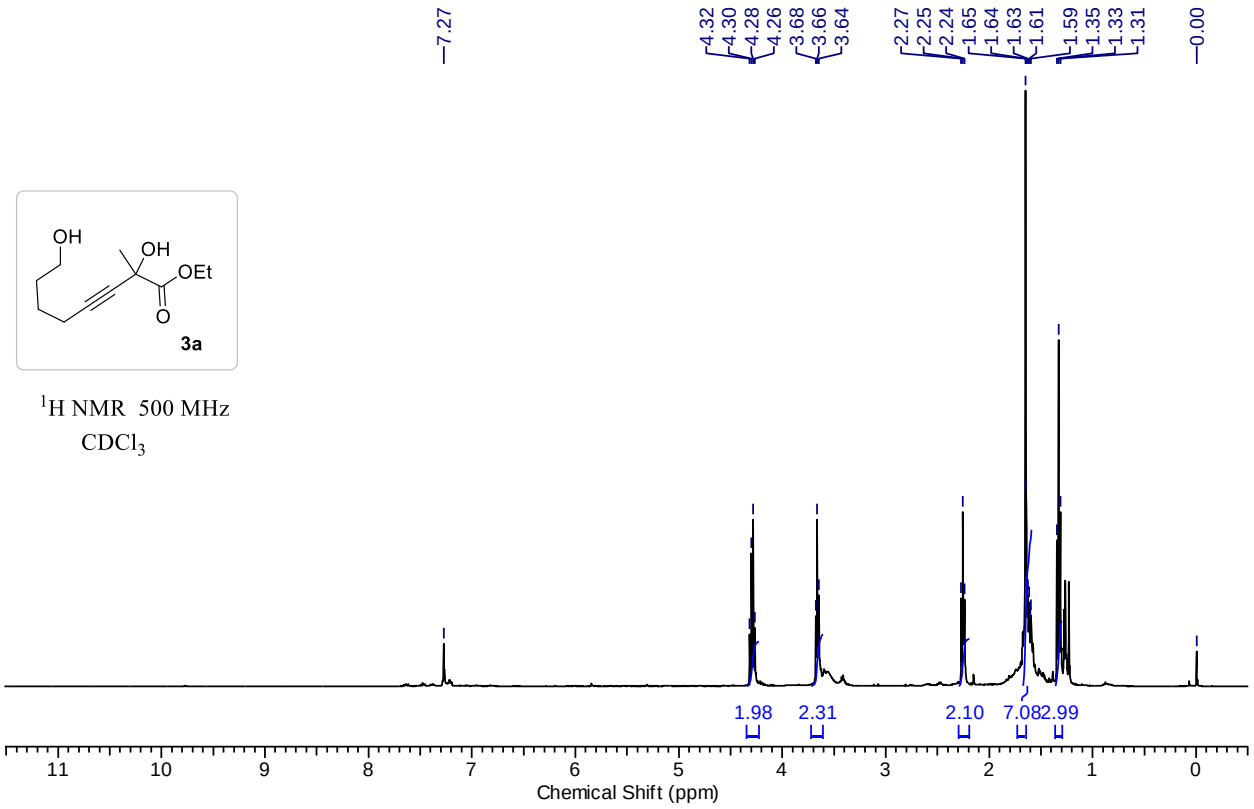
^{13}C NMR 101 MHz
$CDCl_3$

Ethyl 2-hydroxy-5-(2-hydroxycyclohexyl)-2-(4-nitrophenyl) pent-3-ynoate (1u):

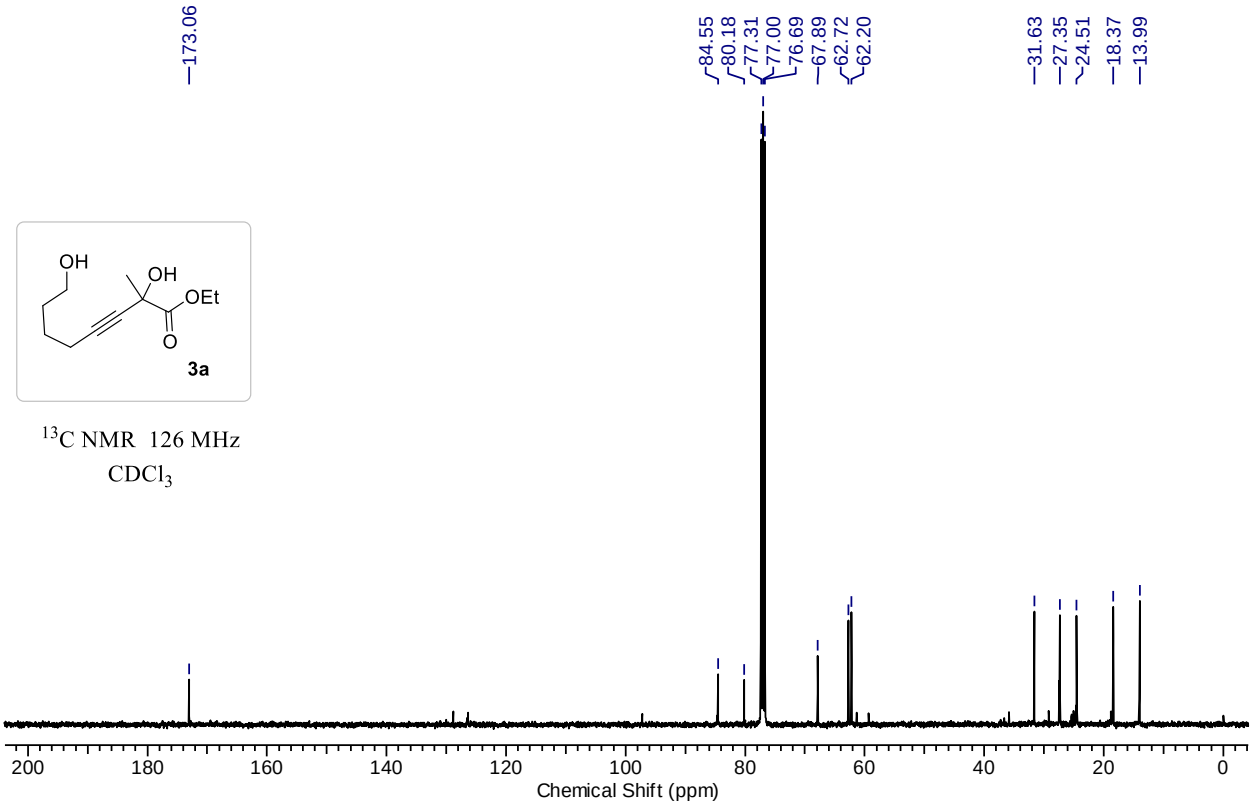




Ethyl 2, 8-dihydroxy-2-methyloct-3-ynoate (3a):

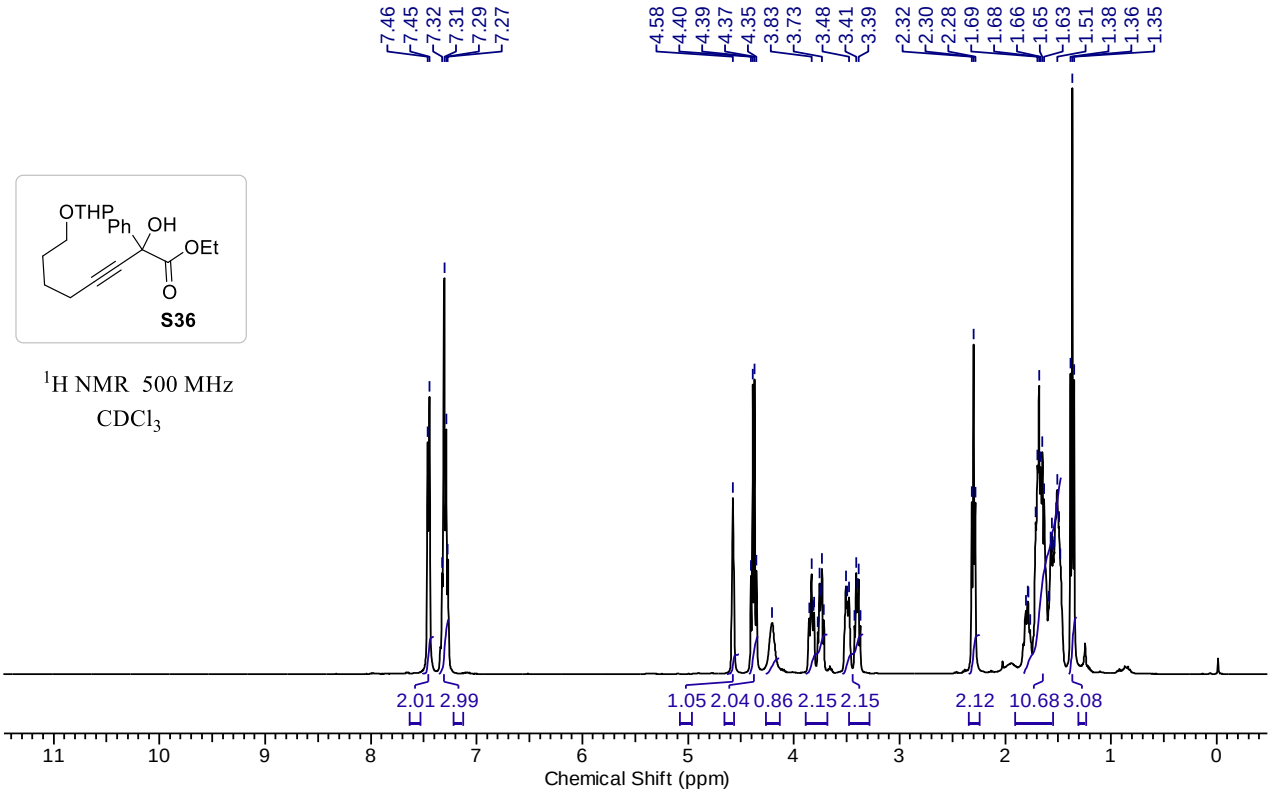


^{1}H NMR 500 MHz
$CDCl_3$

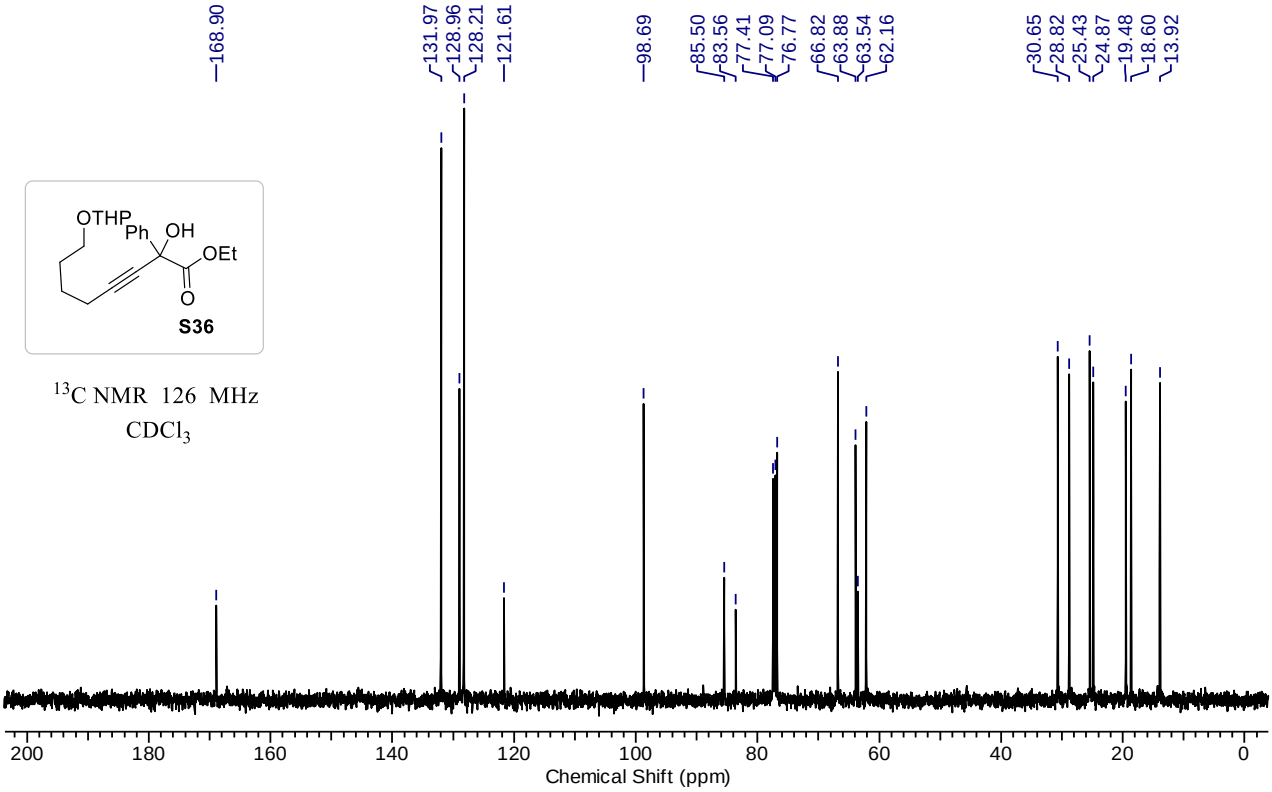


^{13}C NMR 126 MHz
$CDCl_3$

Ethyl 2-hydroxy-2-phenyl-8-((tetrahydro-2*H*-pyran-2-yl) oxy) oct-3-ynoate (S36):

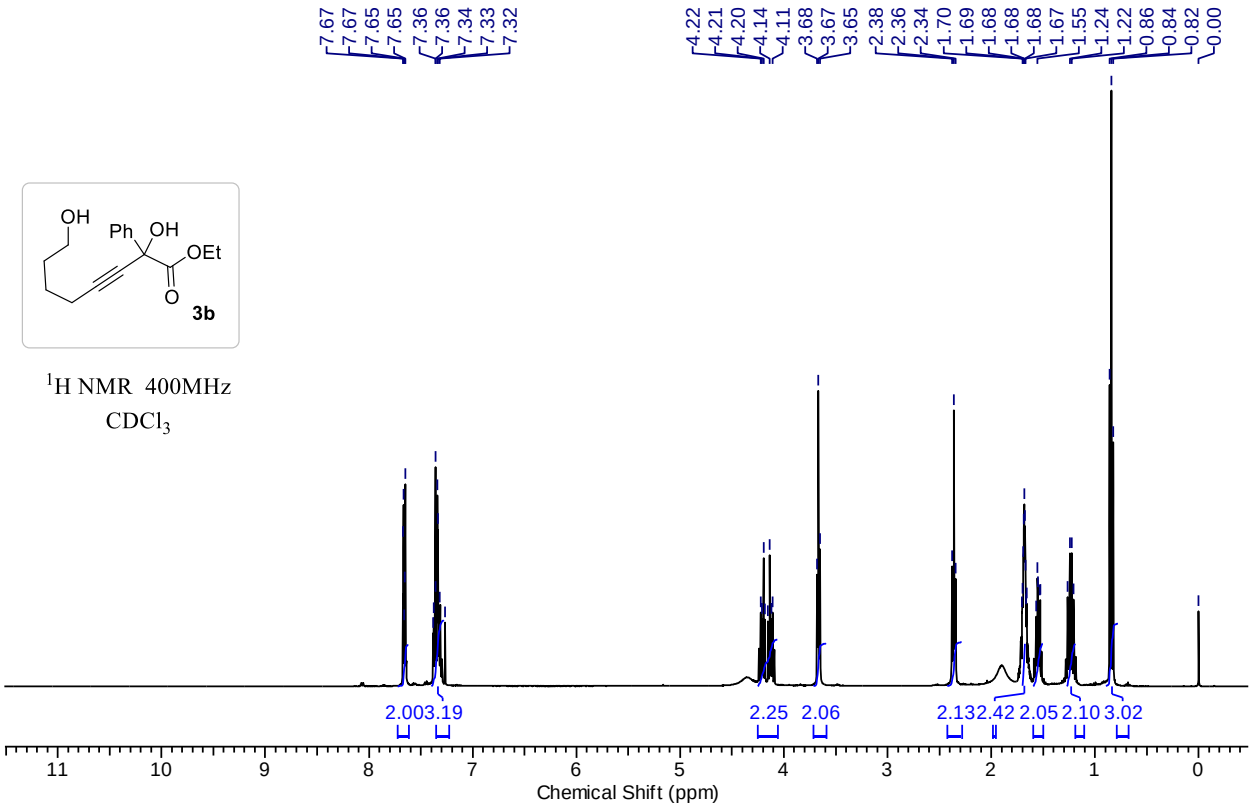


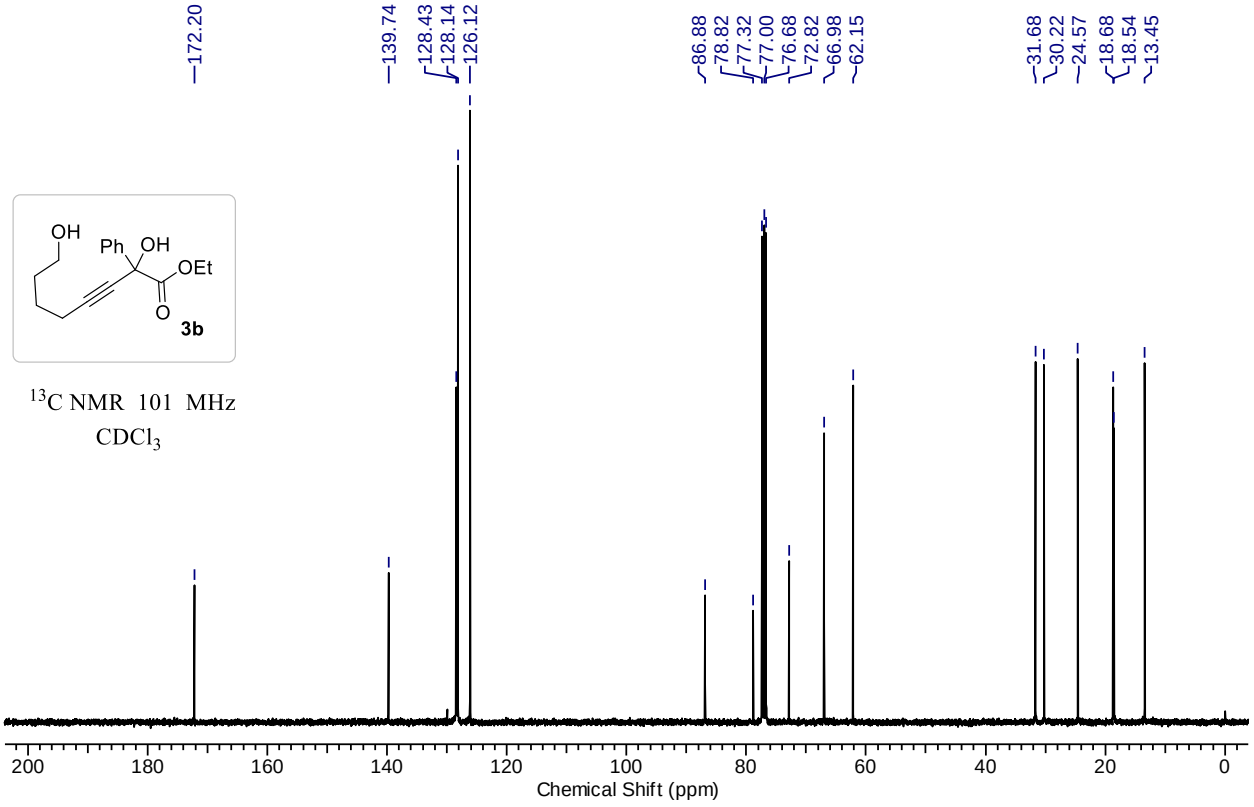
^{1}H NMR 500 MHz
$CDCl_3$



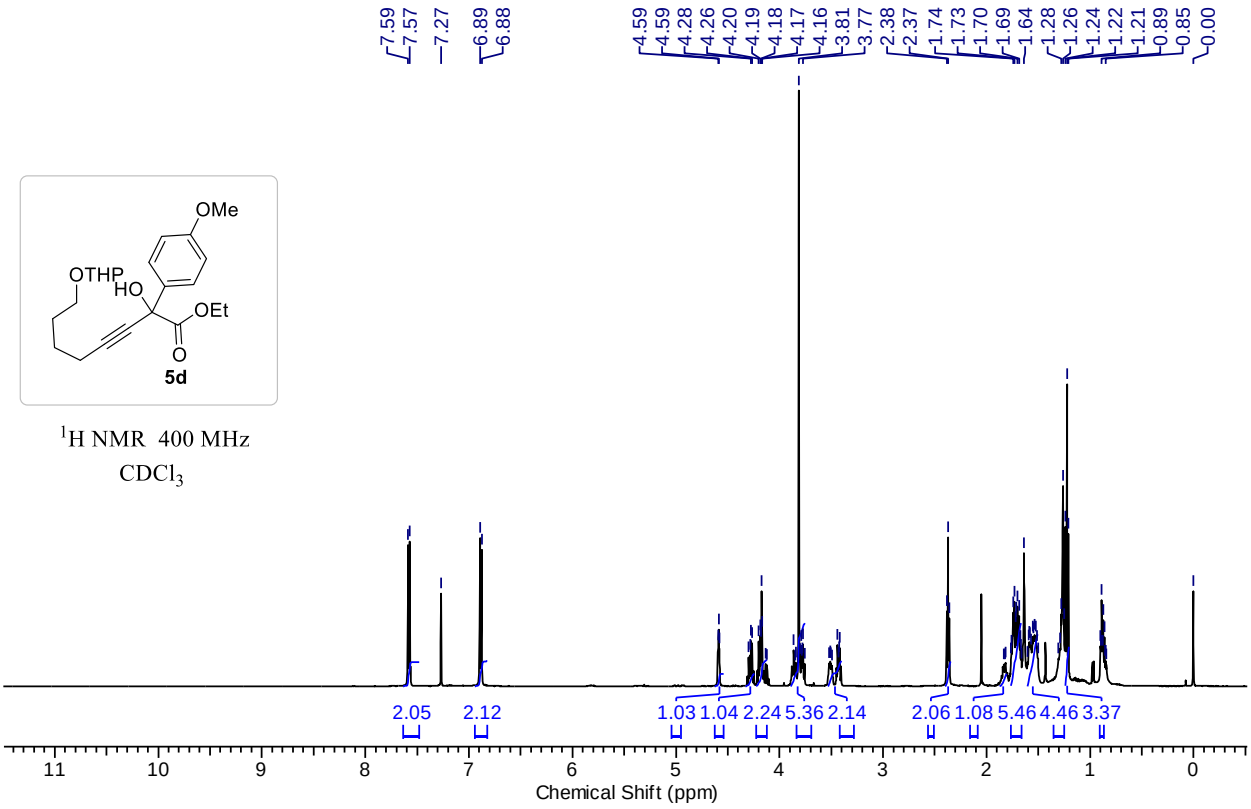
^{13}C NMR 126 MHz
$CDCl_3$

Ethyl 2,8-dihydroxy-2-phenyloct-3-ynoate (3b):

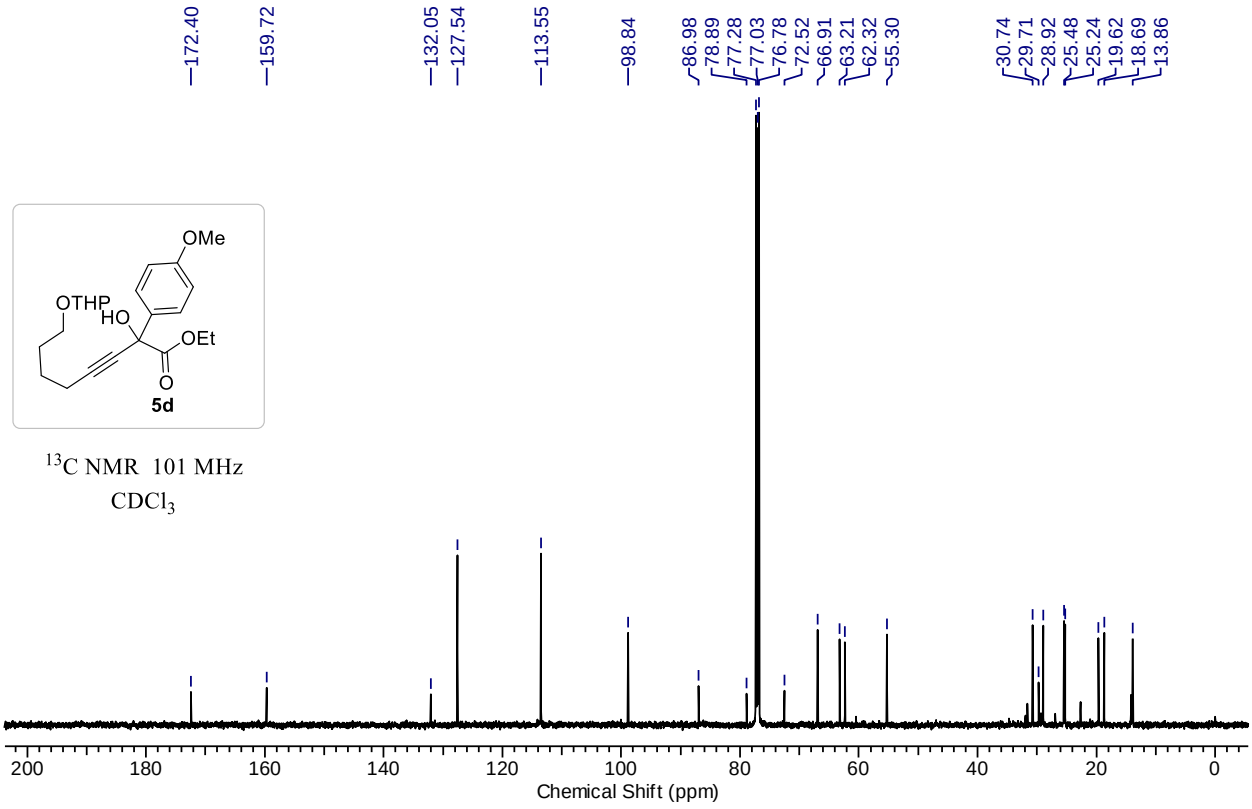




Ethyl 2-hydroxy-2-(4-methoxyphenyl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (5d):

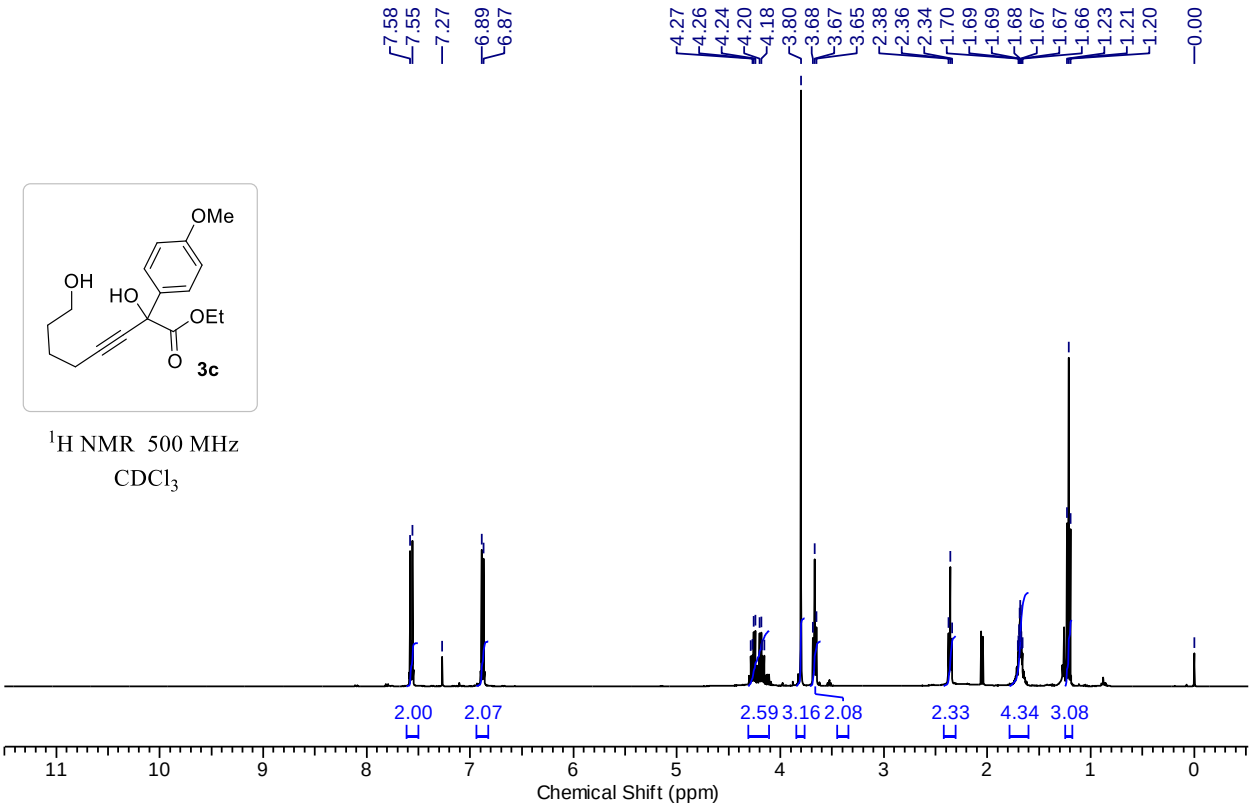


^{1}H NMR 400 MHz
$CDCl_3$

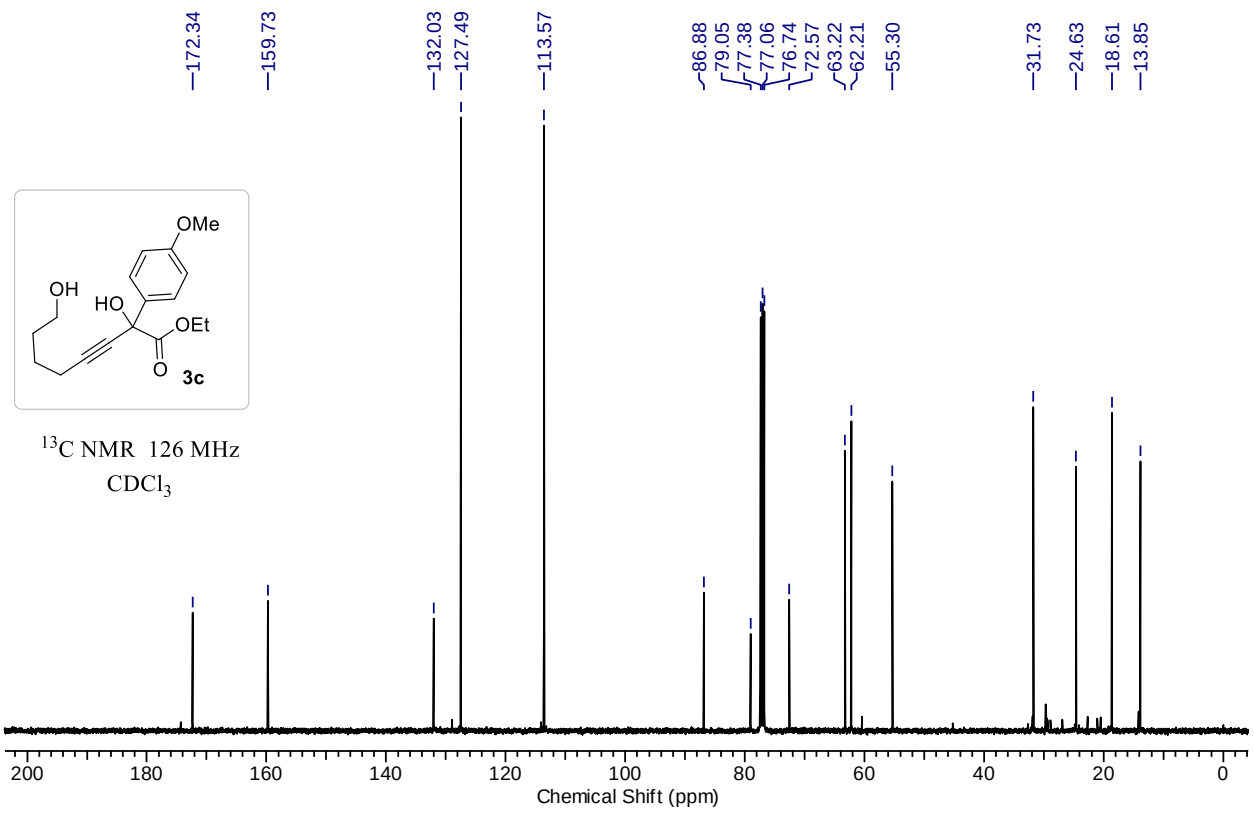


^{13}C NMR 101 MHz
$CDCl_3$

Ethyl 2,8-dihydroxy-2-(4-methoxyphenyl)oct-3-ynoate (3c):

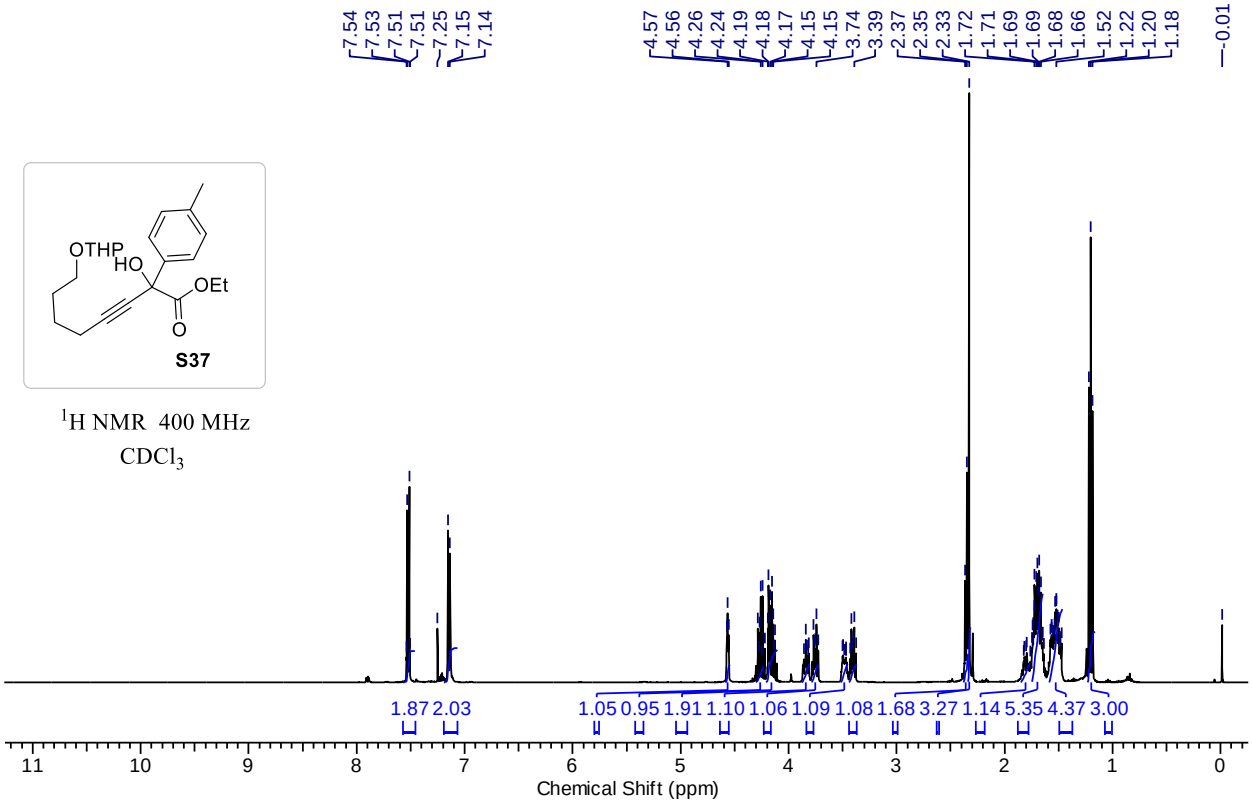


^{1}H NMR 500 MHz
$CDCl_3$

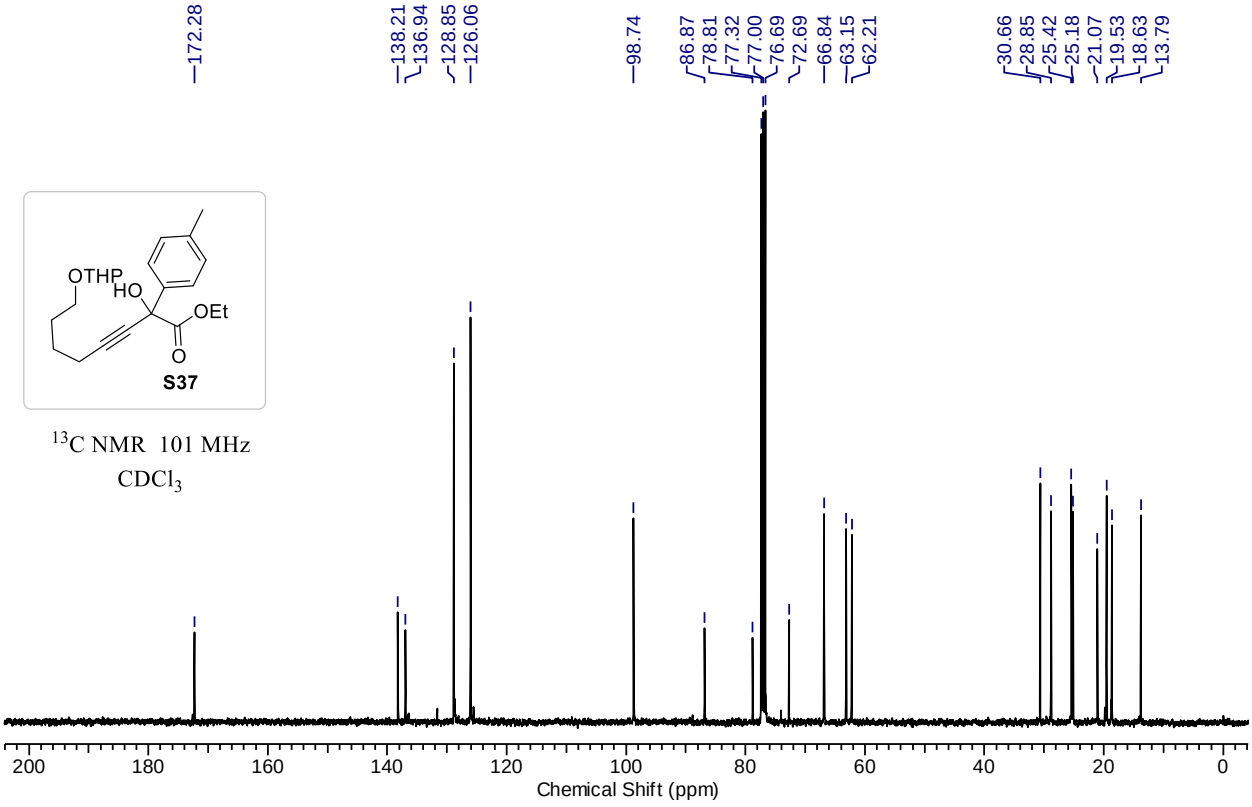


^{13}C NMR 126 MHz
$CDCl_3$

Ethyl 2-hydroxy-8-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-(*p*-tolyl)oct-3-ynoate (S37):

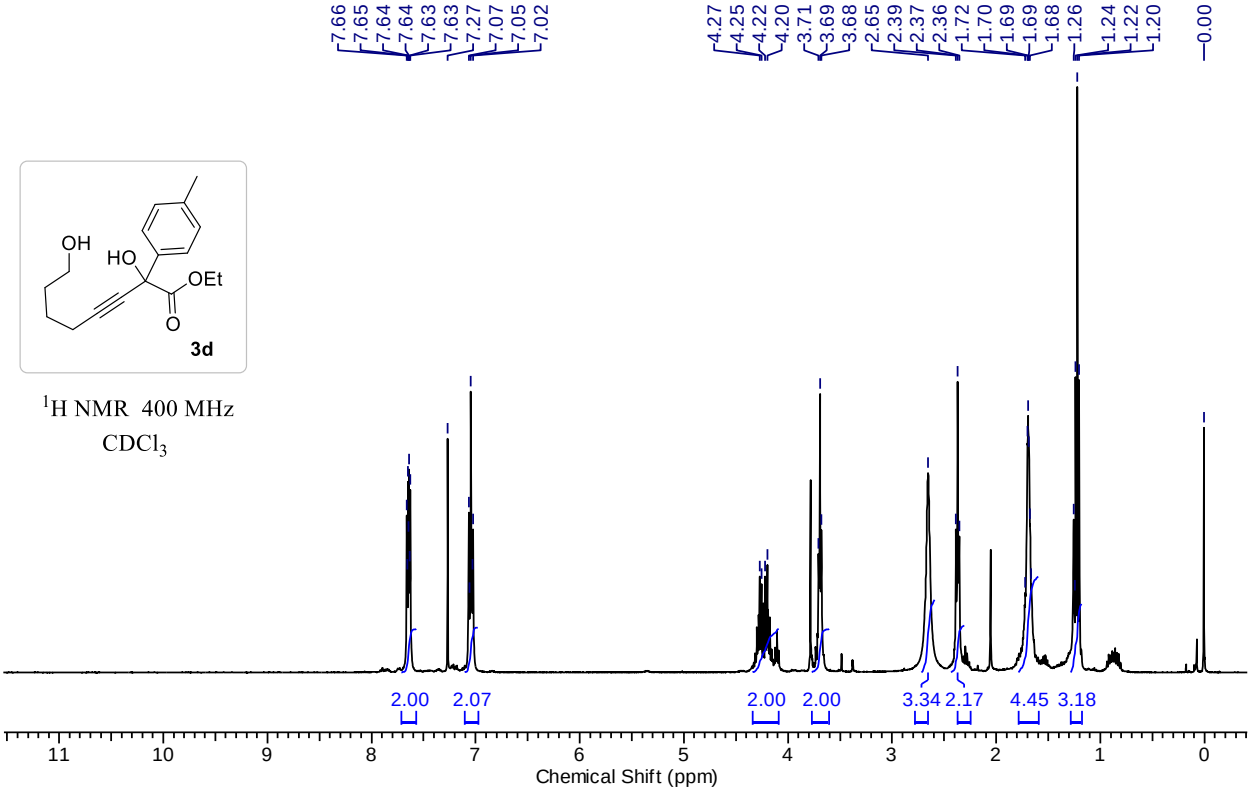


^{1}H NMR 400 MHz
$CDCl_3$

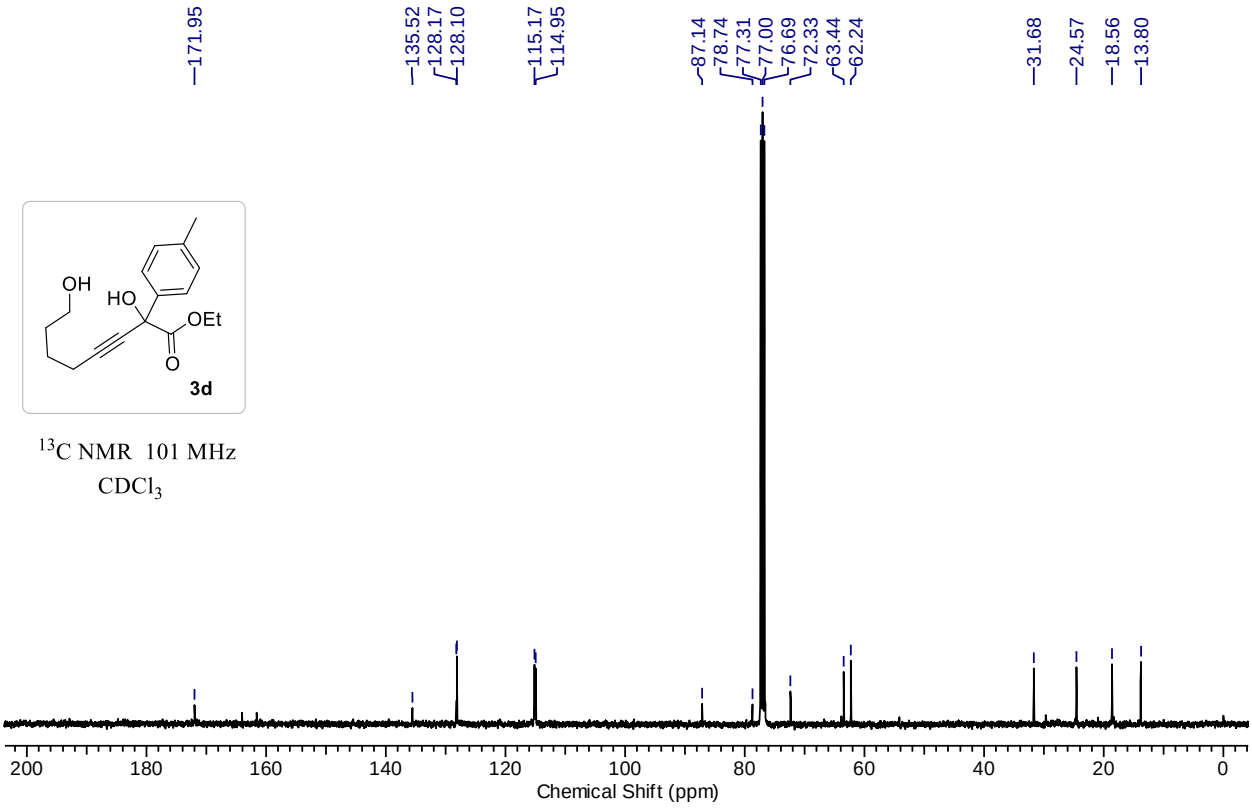


^{13}C NMR 101 MHz
$CDCl_3$

Ethyl 2,8-dihydroxy-2-(*p*-tolyl)oct-3-ynoate (3d):

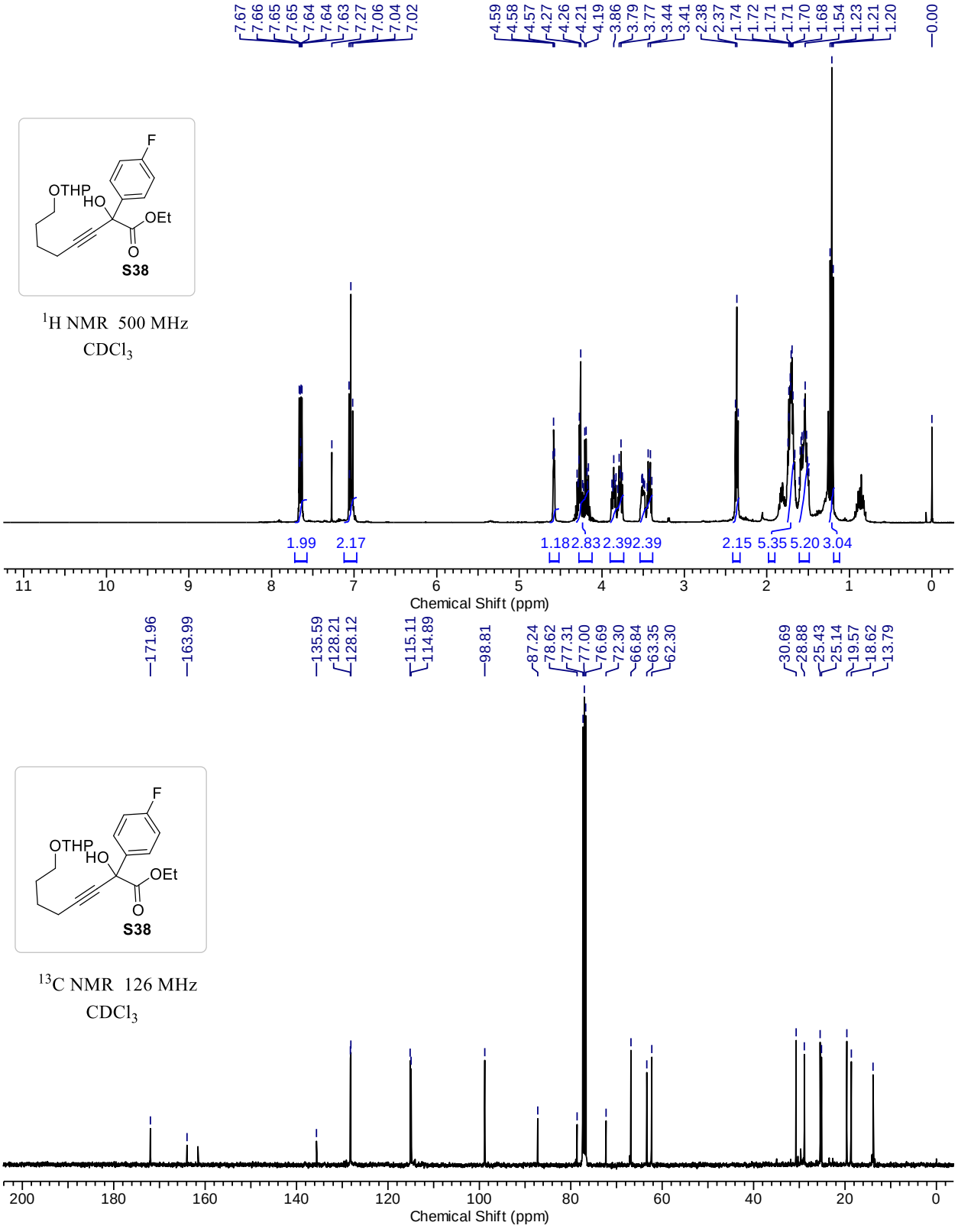


^{1}H NMR 400 MHz
$CDCl_3$

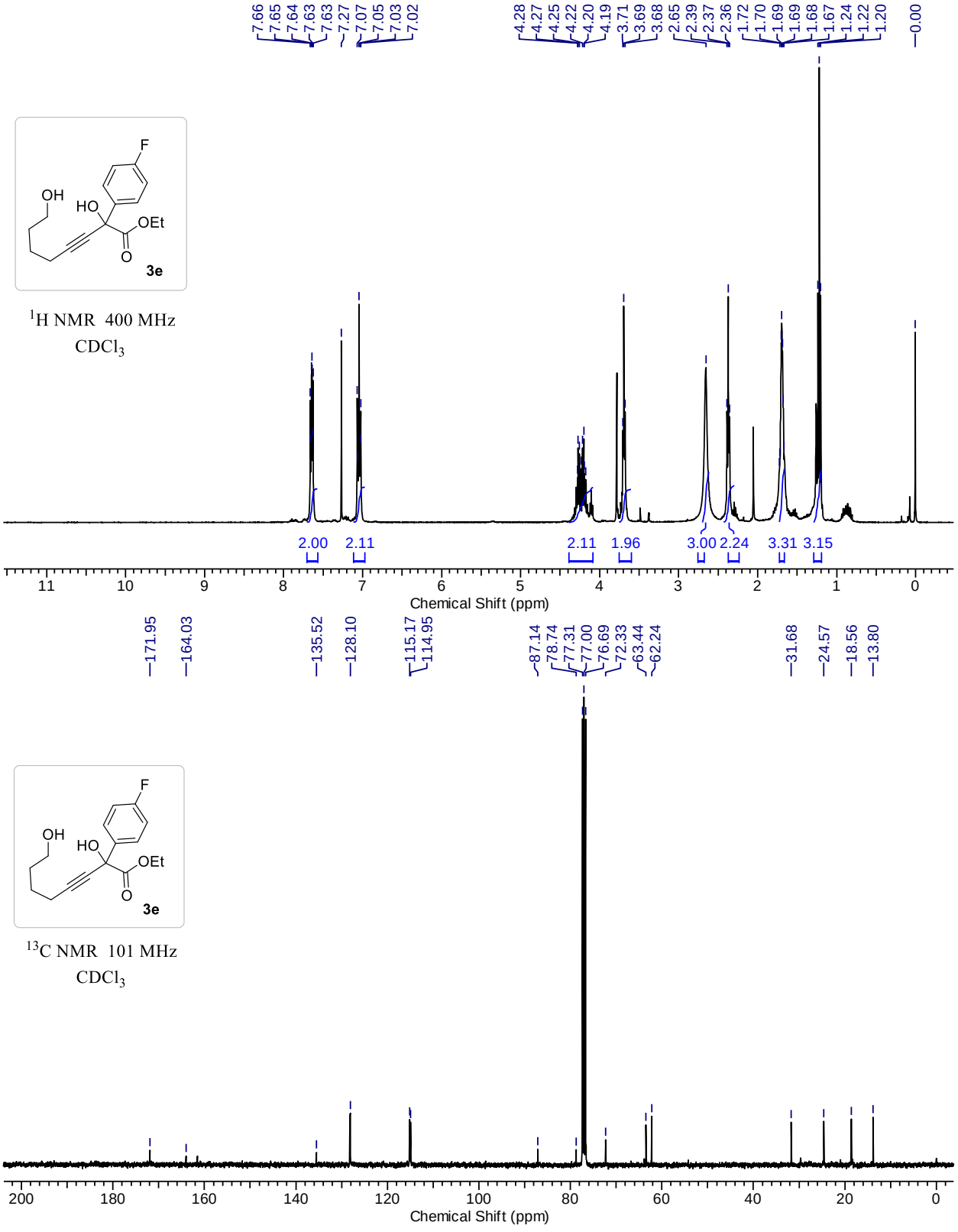


^{13}C NMR 101 MHz
$CDCl_3$

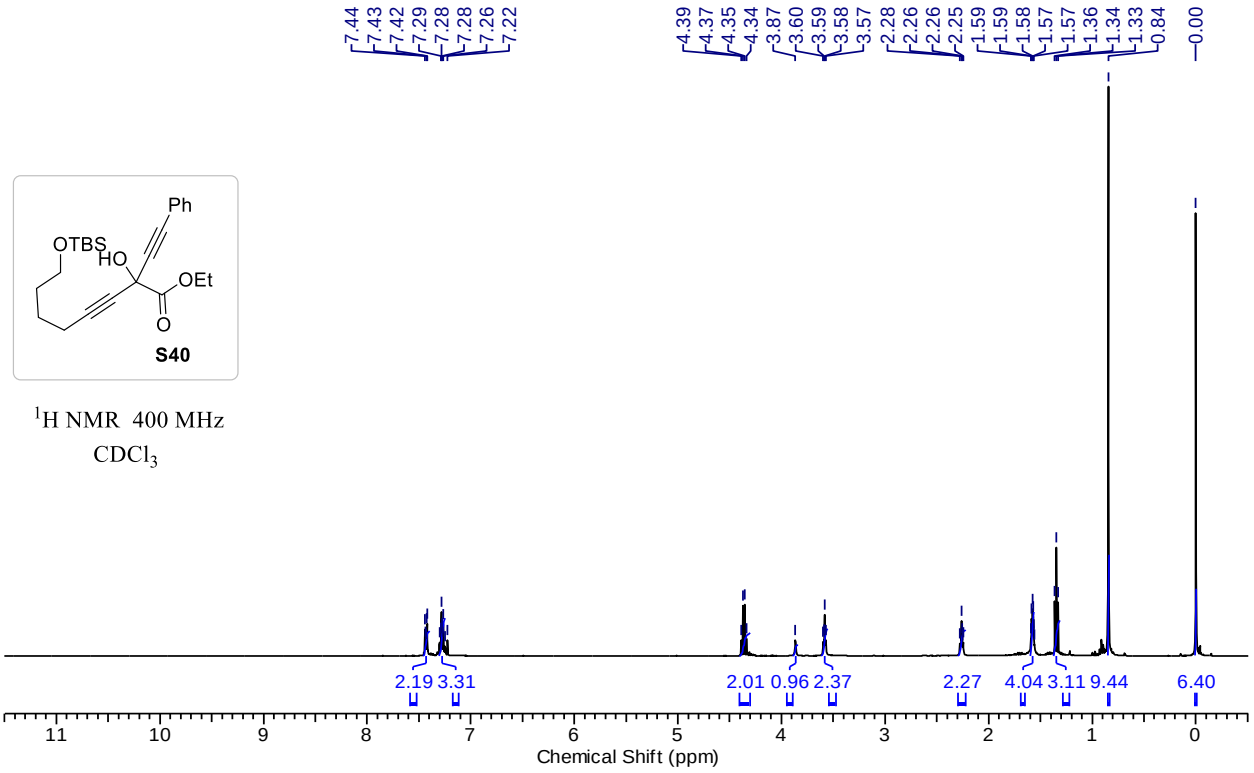
Ethyl 2-(4-fluorophenyl)-2-hydroxy-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (S38):



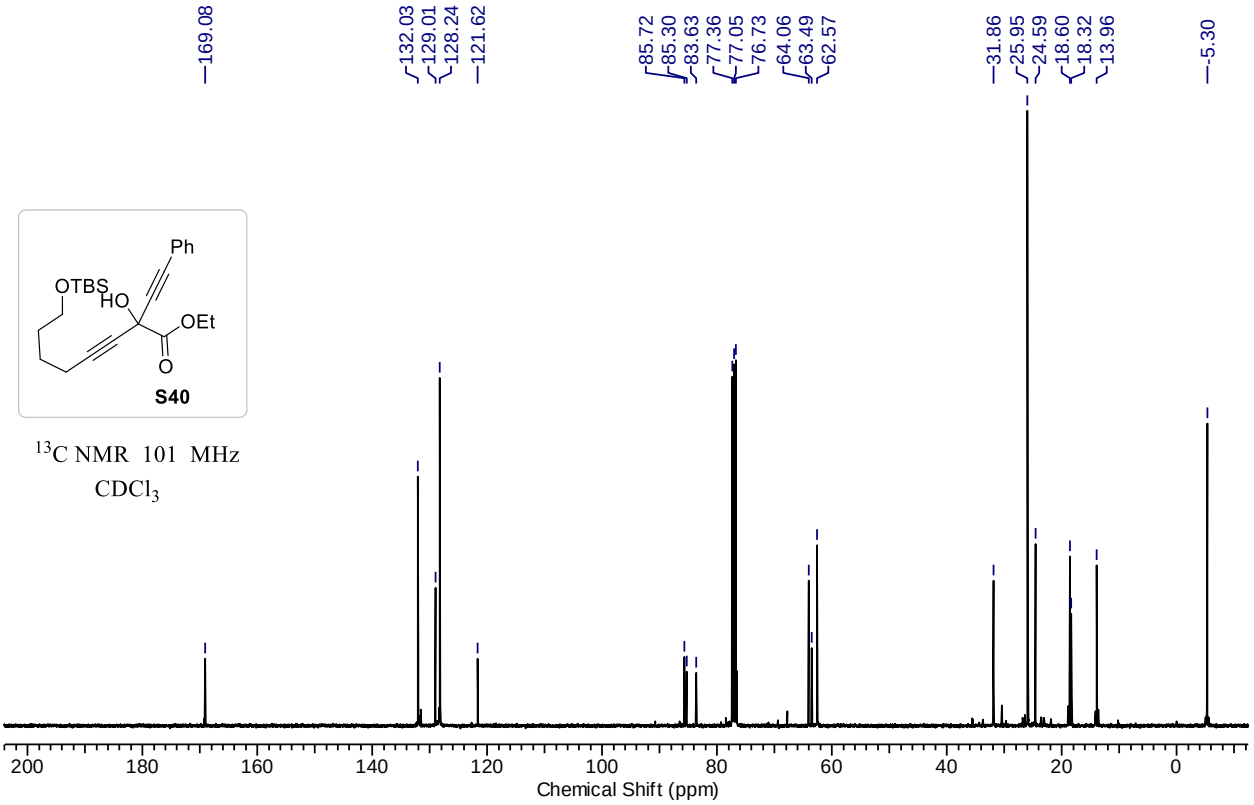
Ethyl 2-(4-fluorophenyl)-2,8-dihydroxyoct-3-ynoate (3e):



Ethyl 8-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-(phenylethynyl)oct-3-ynoate (S40):

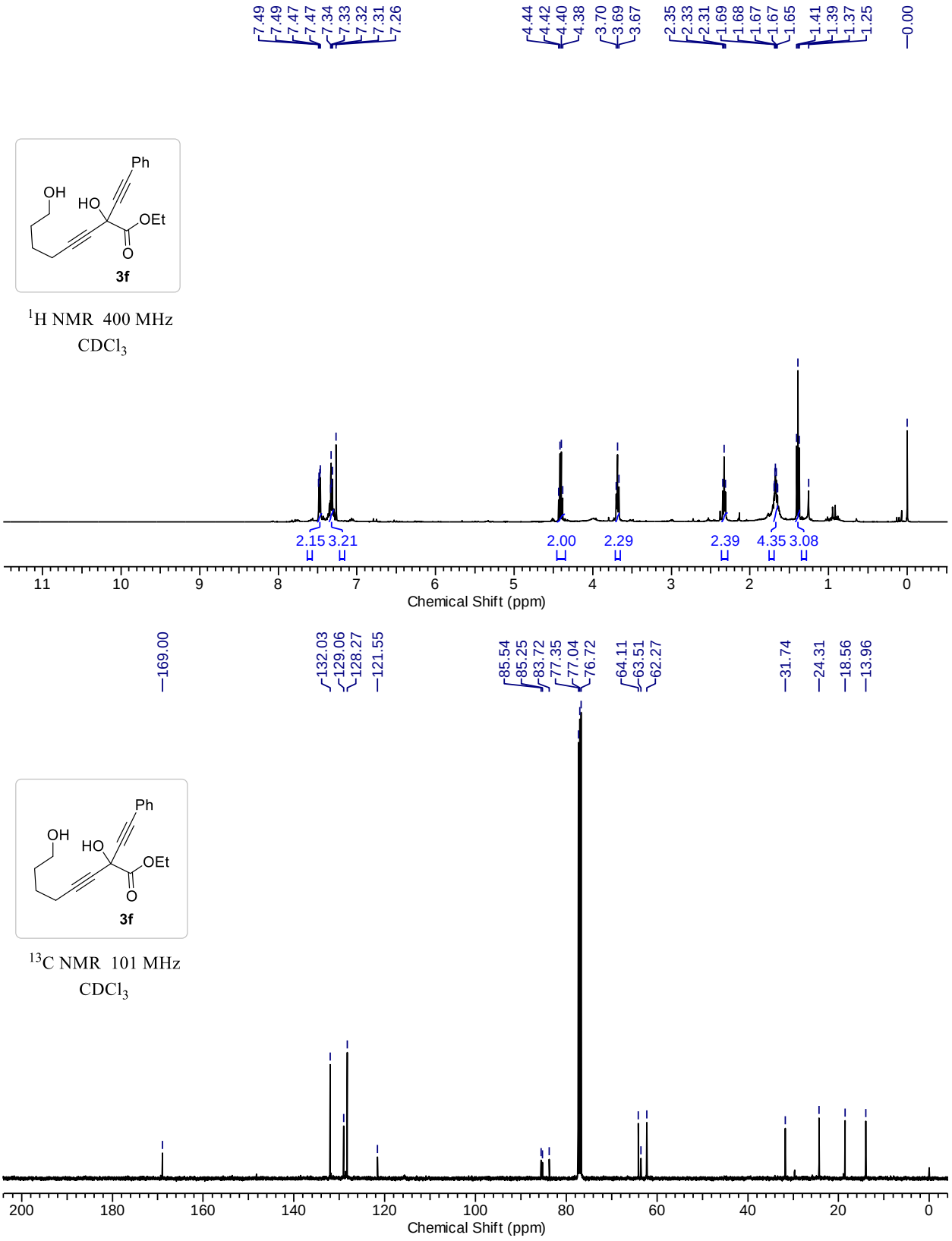


^{1}H NMR 400 MHz
$CDCl_3$



^{13}C NMR 101 MHz
$CDCl_3$

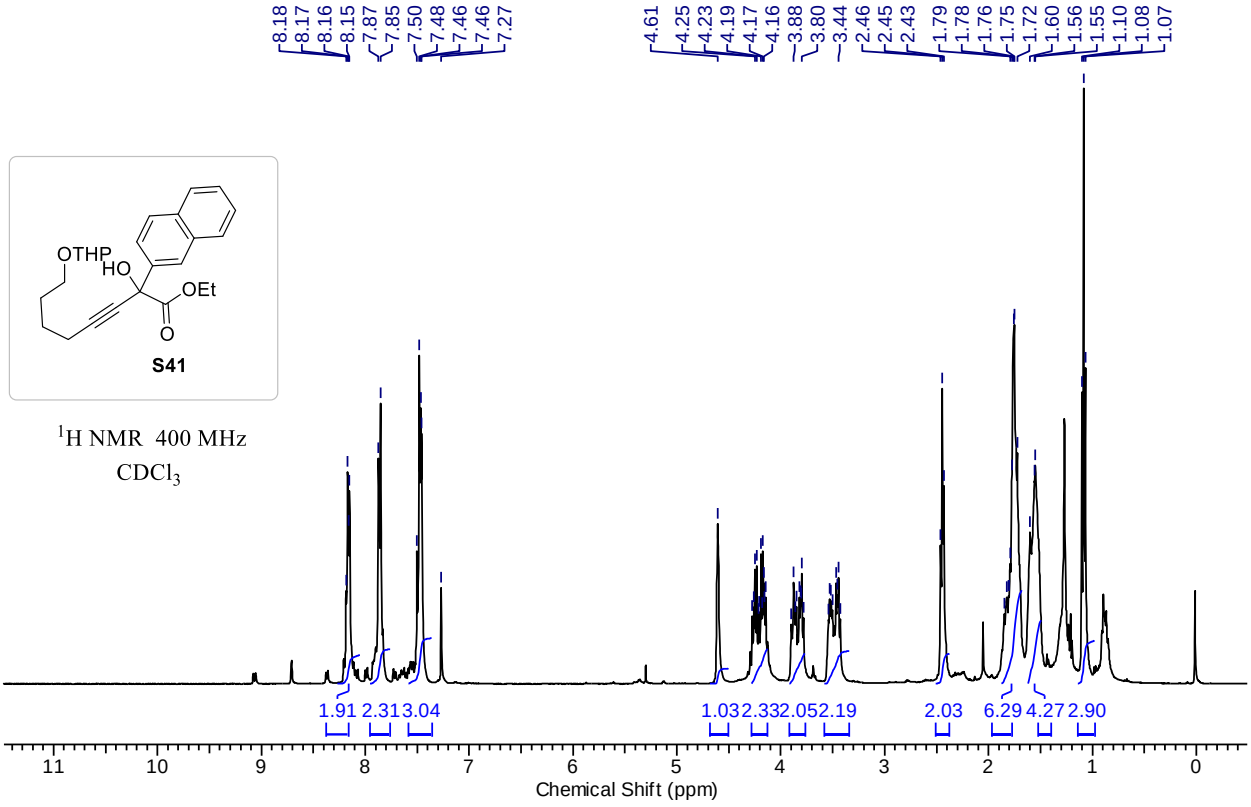
Ethyl 2,8-dihydroxy-2-(phenylethynyl)oct-3-ynoate (3f):



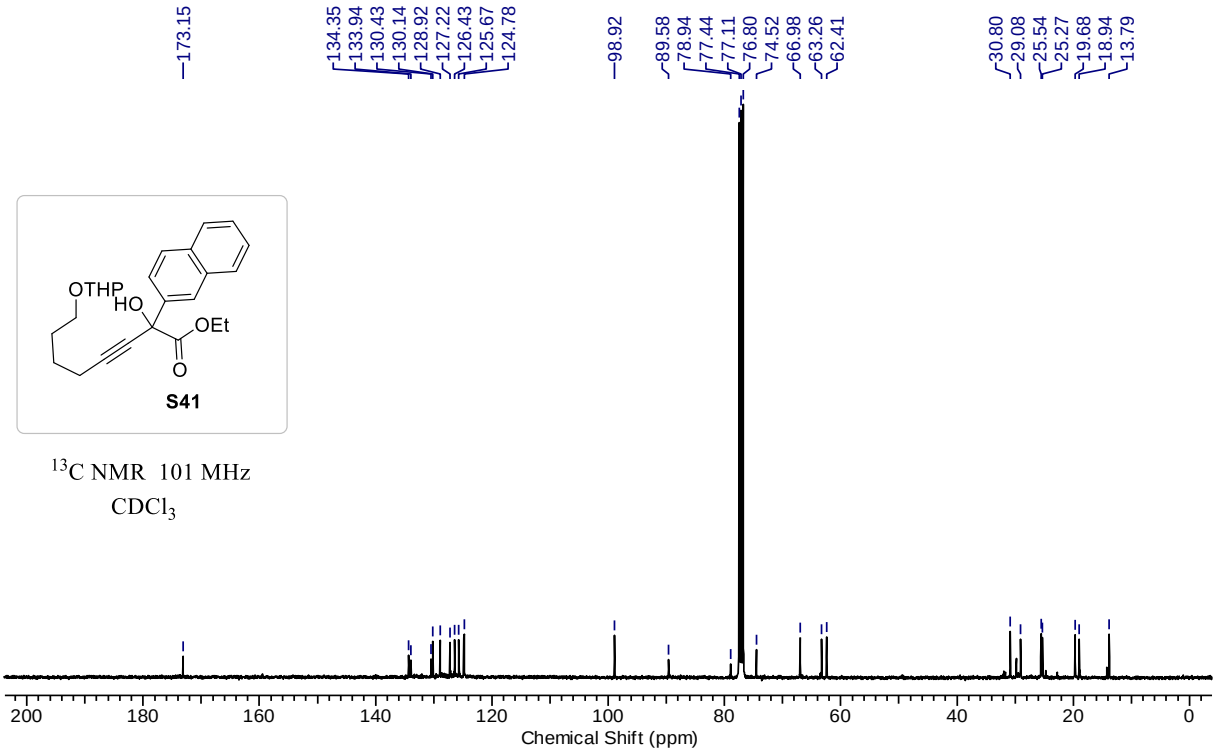
^{1}H NMR 400 MHz
$CDCl_3$

^{13}C NMR 101 MHz
$CDCl_3$

Ethyl2-hydroxy-2-(naphthalen-2-yl)-8-((tetrahydro-2*H*-pyran-2-yl) oxy) oct-3-ynoate (S41):

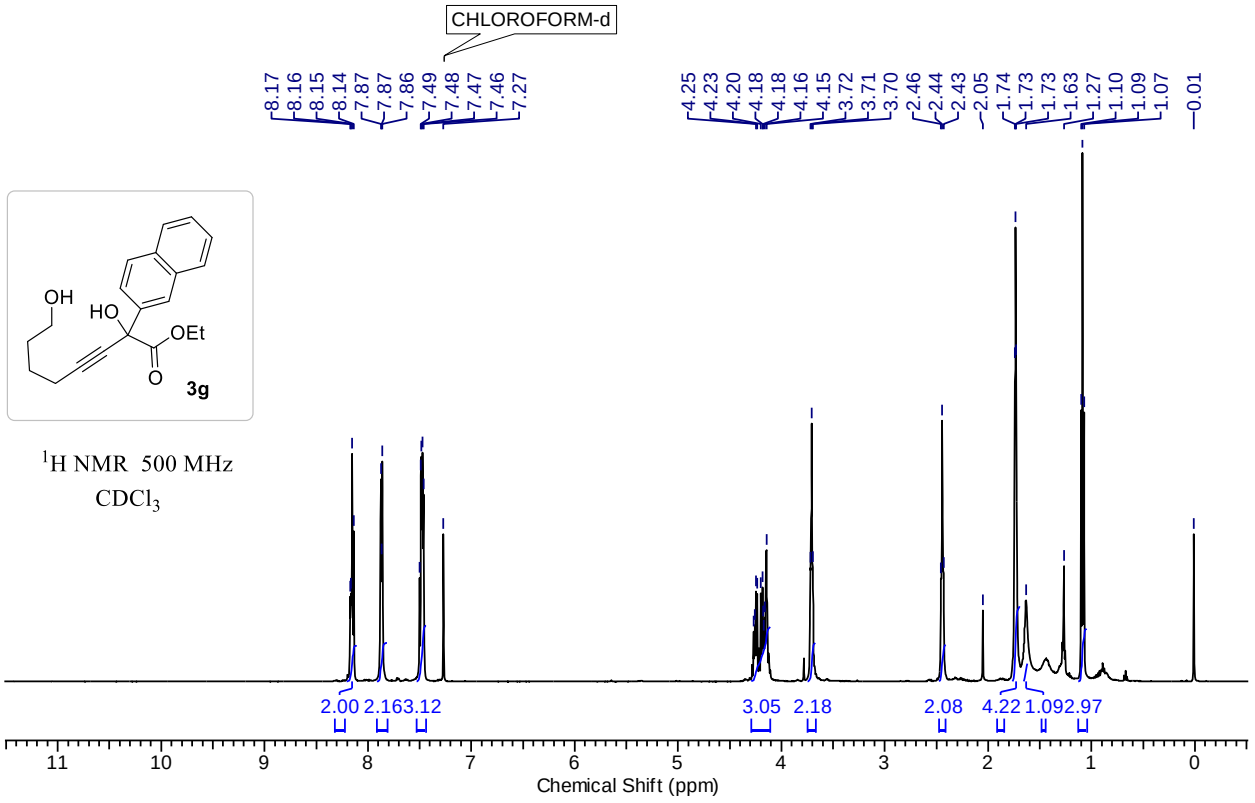


^{1}H NMR 400 MHz
$CDCl_3$

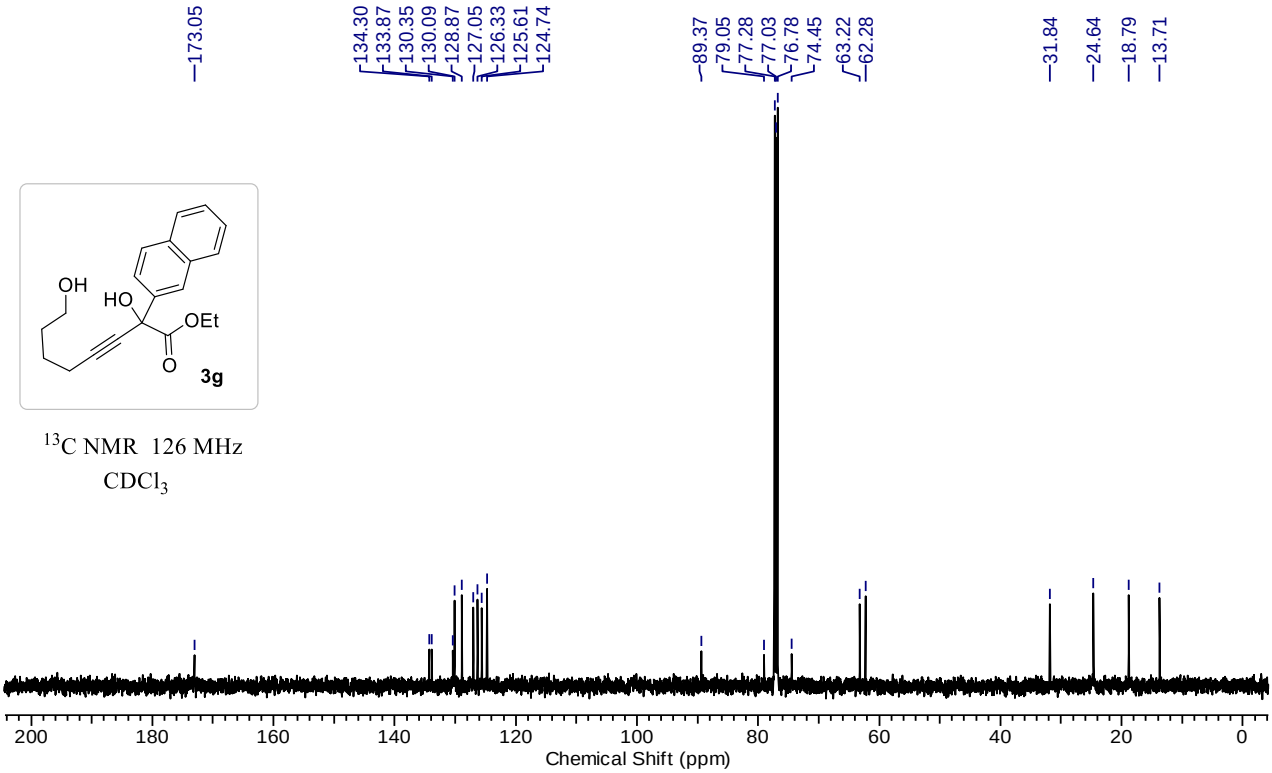


^{13}C NMR 101 MHz
$CDCl_3$

Ethyl 2, 8-dihydroxy-2-(naphthalen-2-yl) oct-3-ynoate (3g):

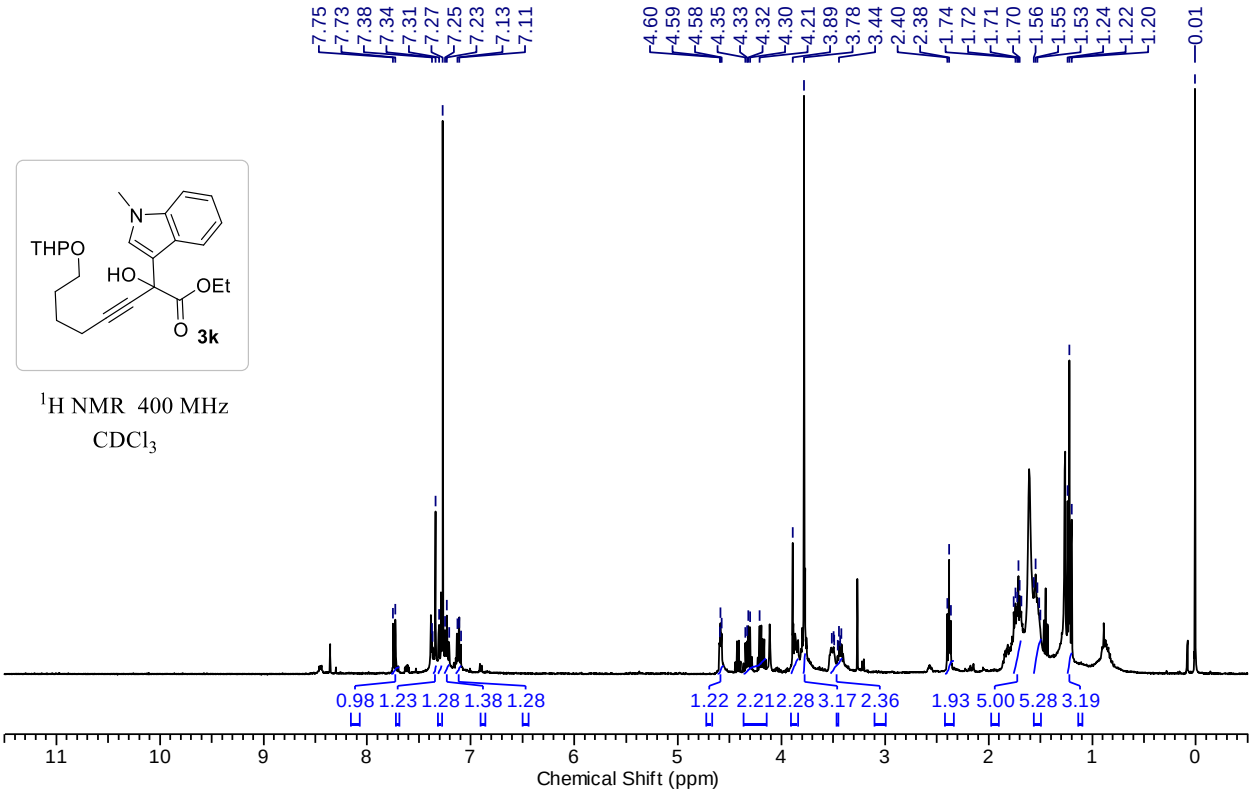


^{1}H NMR 500 MHz
$CDCl_3$

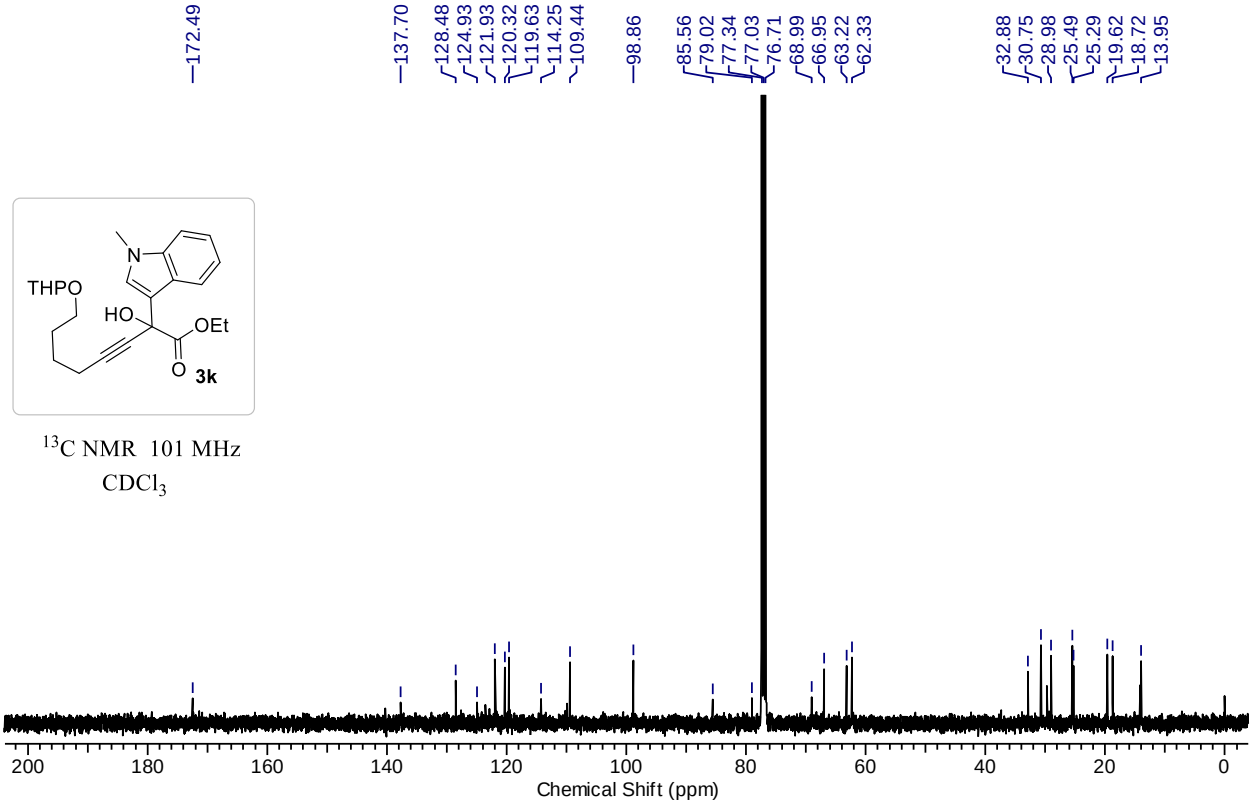


^{13}C NMR 126 MHz
$CDCl_3$

Ethyl 2-hydroxy-2-(1-methyl-1*H*-indol-3-yl)-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-3-ynoate (3k):

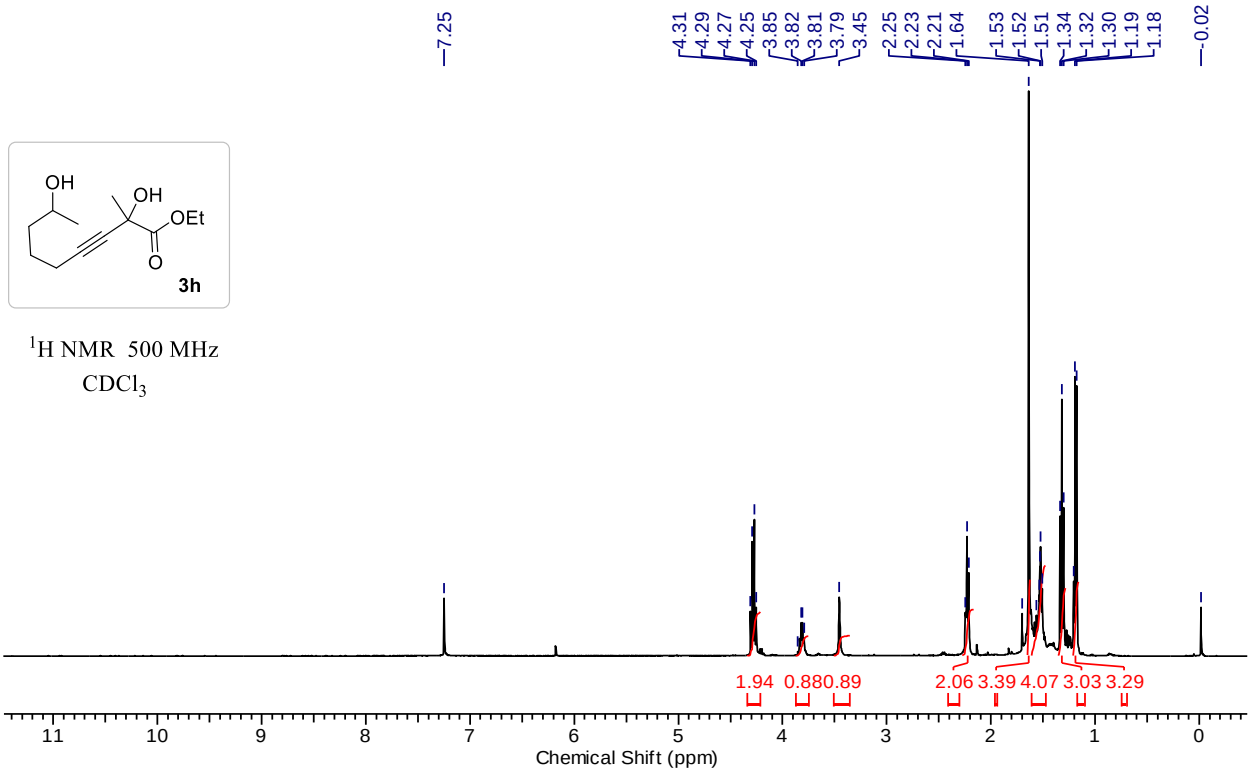


^{1}H NMR 400 MHz
$CDCl_3$

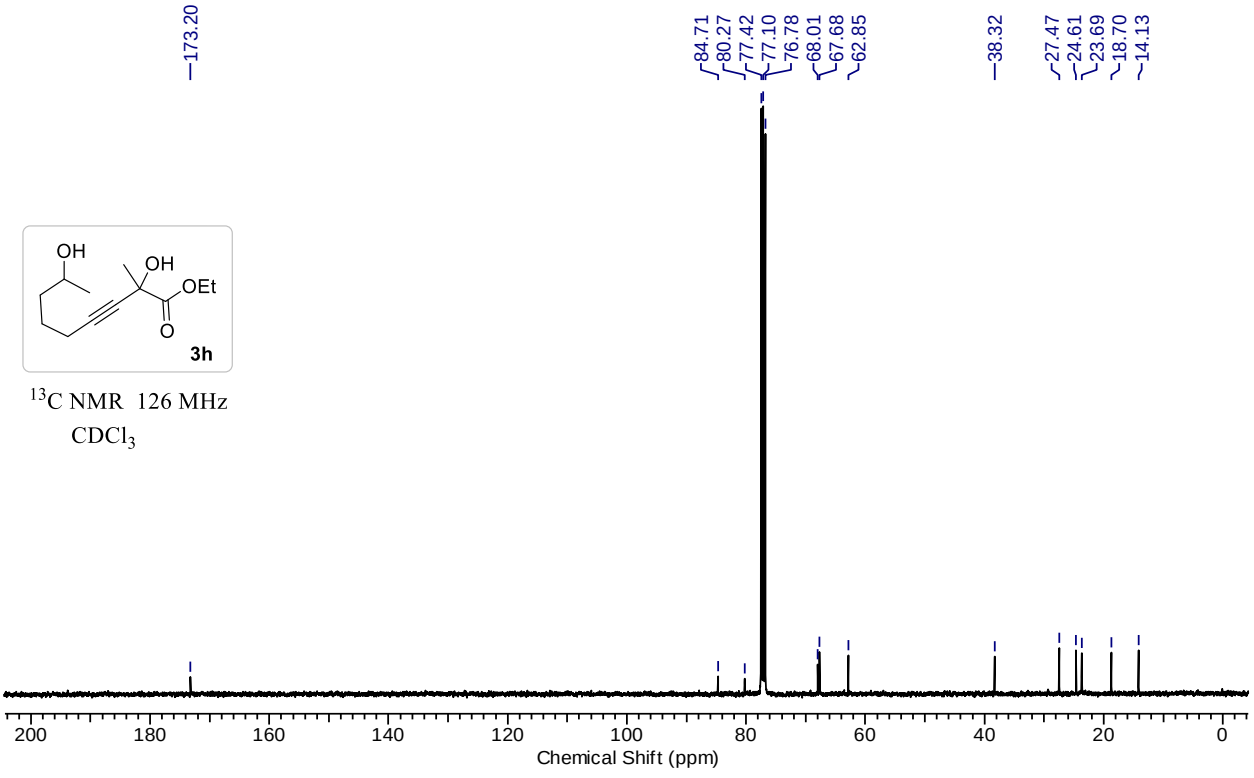


^{13}C NMR 101 MHz
$CDCl_3$

Ethyl 2,8-dihydroxy-2-methylnon-3-ynoate (3h):

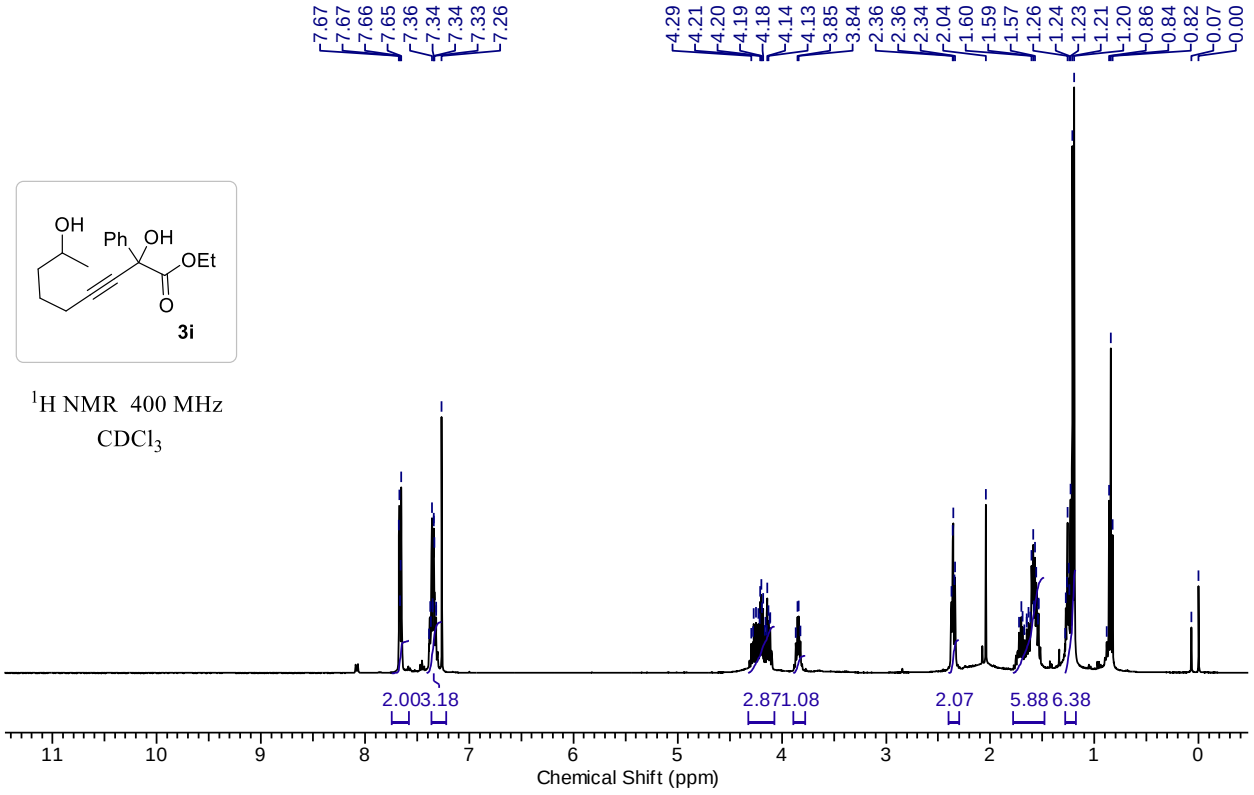


^{1}H NMR 500 MHz
$CDCl_3$

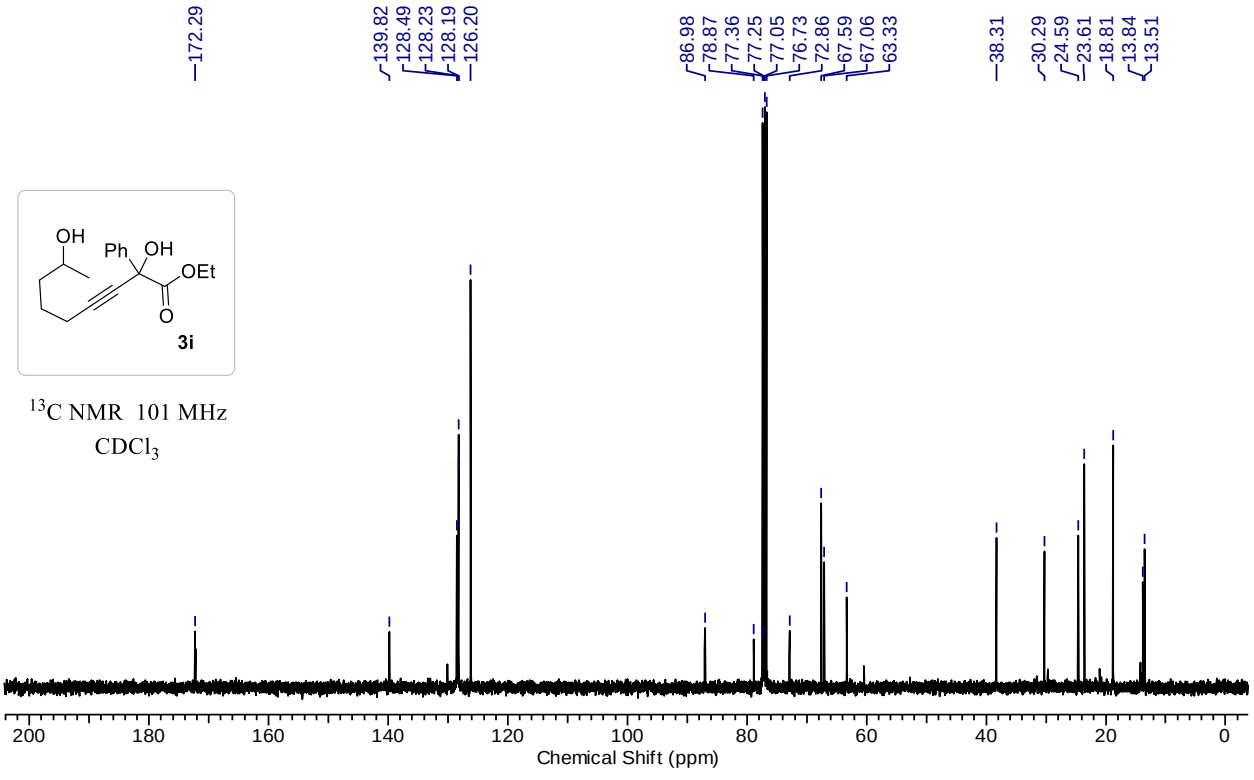


^{13}C NMR 126 MHz
$CDCl_3$

Ethyl 2,8-dihydroxy-2-phenylnon-3-ynoate (3i):

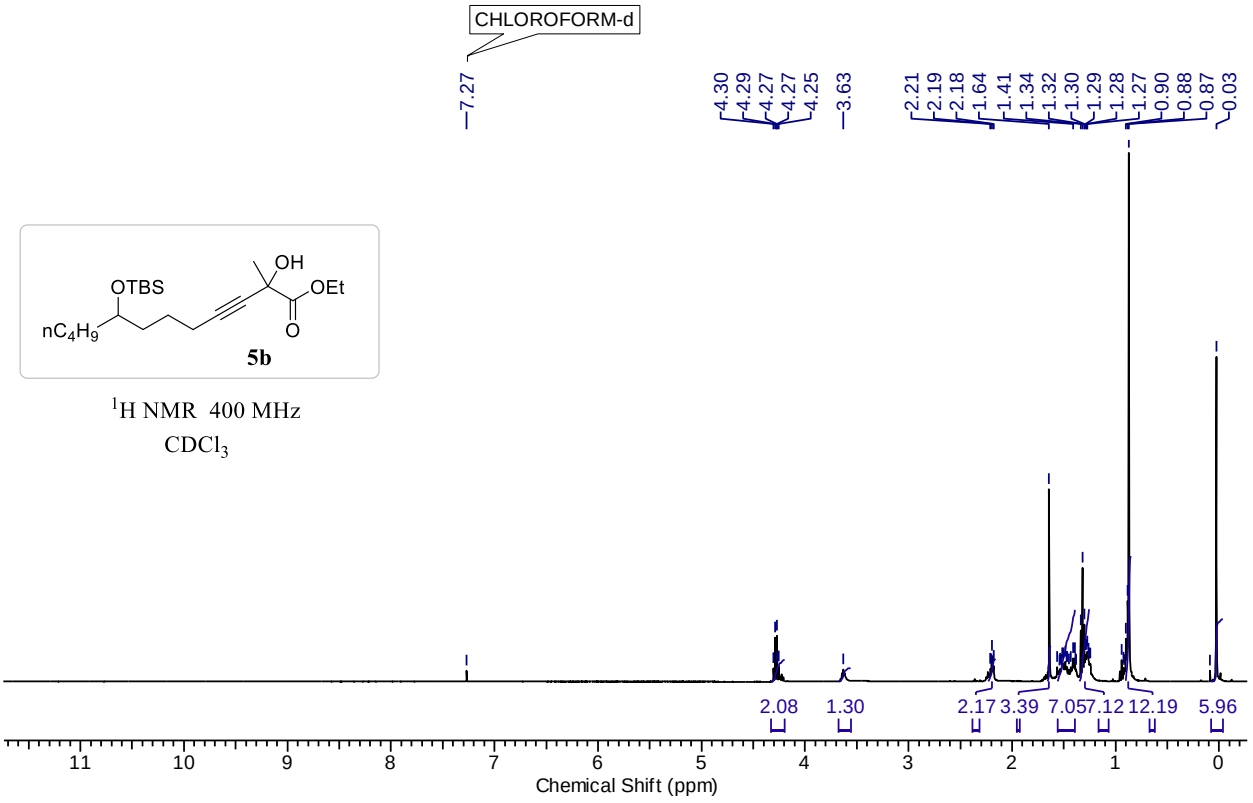


^{1}H NMR 400 MHz
$CDCl_3$

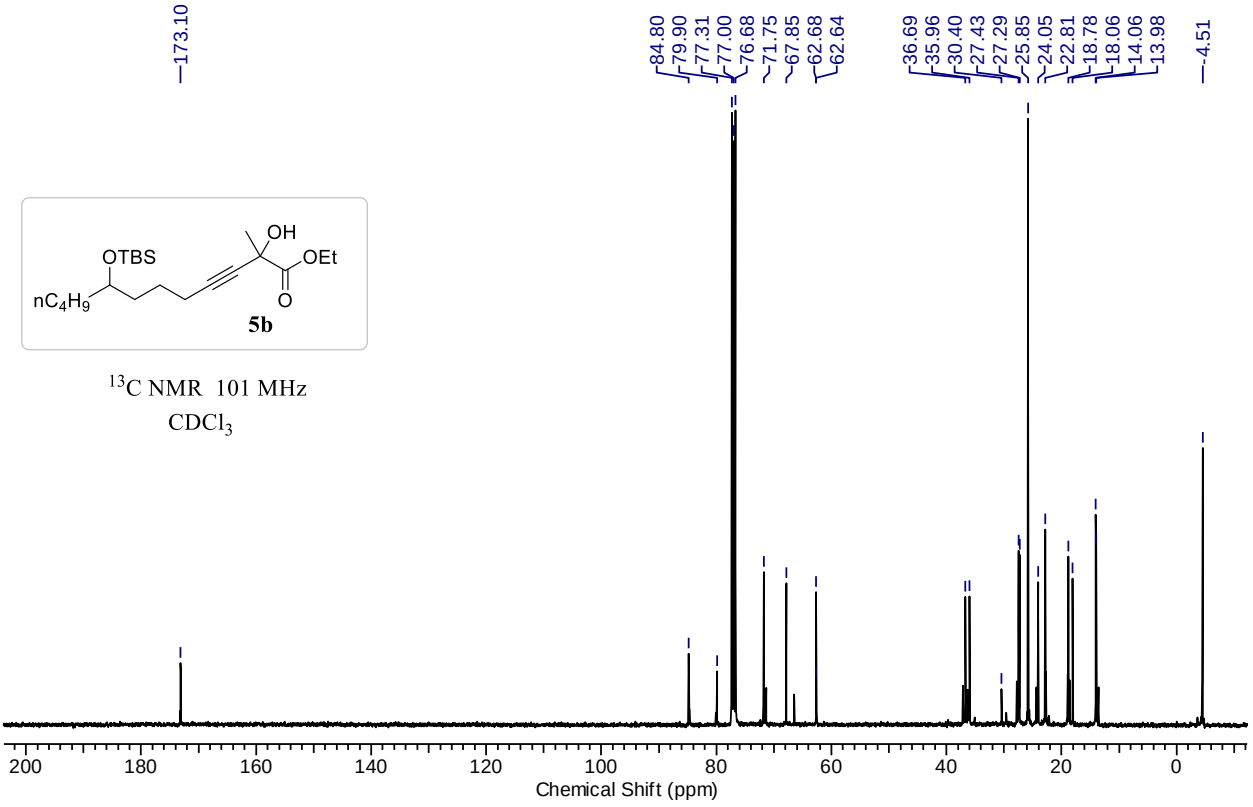


^{13}C NMR 101 MHz
$CDCl_3$

Ethyl 8-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-methyldodec-3-ynoate (5b):

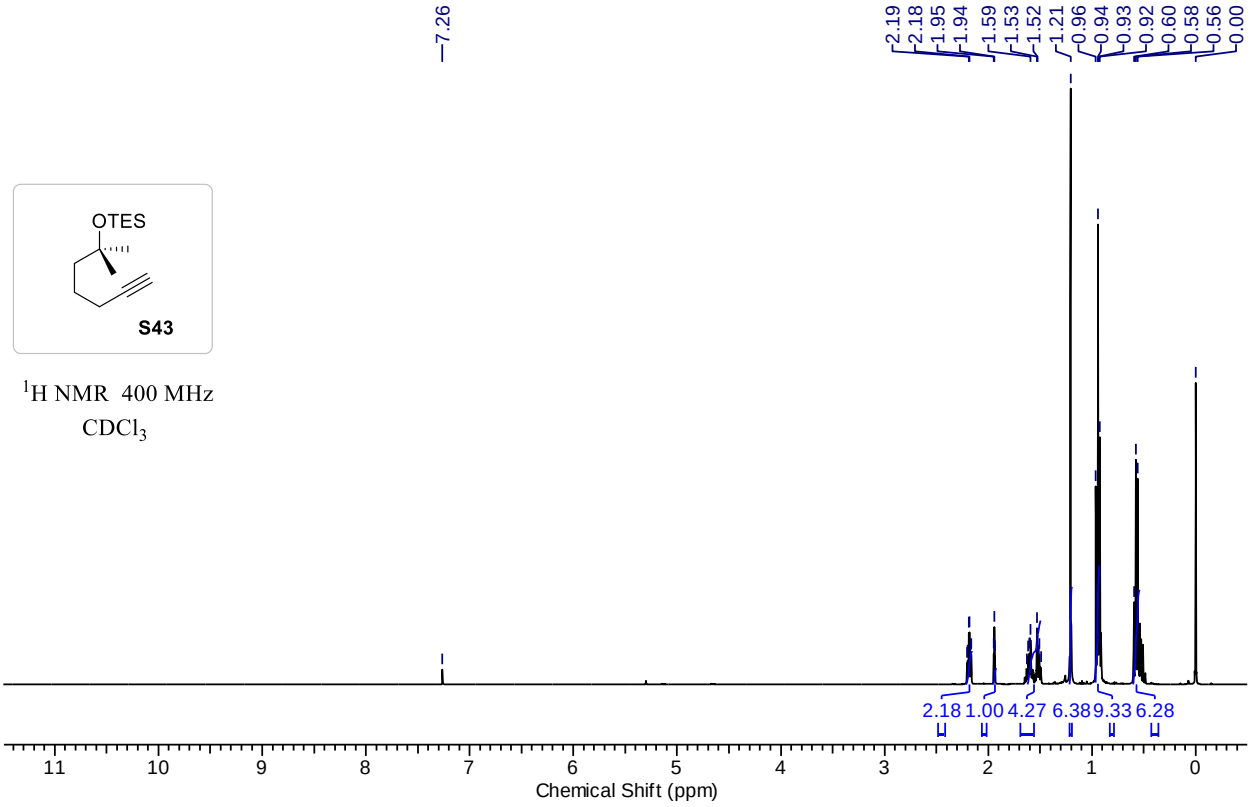


^{1}H NMR 400 MHz
$CDCl_3$

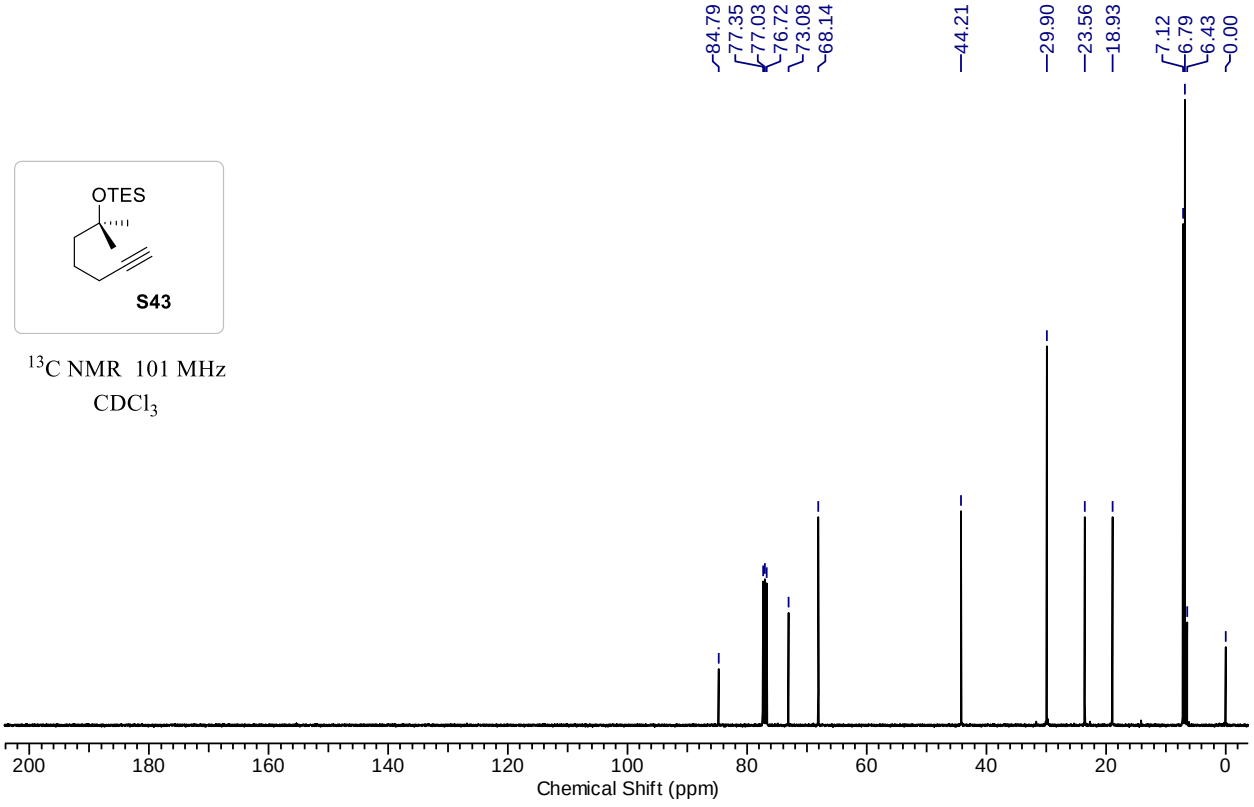


^{13}C NMR 101 MHz
$CDCl_3$

Triethyl((2-methylhept-6-yn-2-yl)oxy)silane (S43):

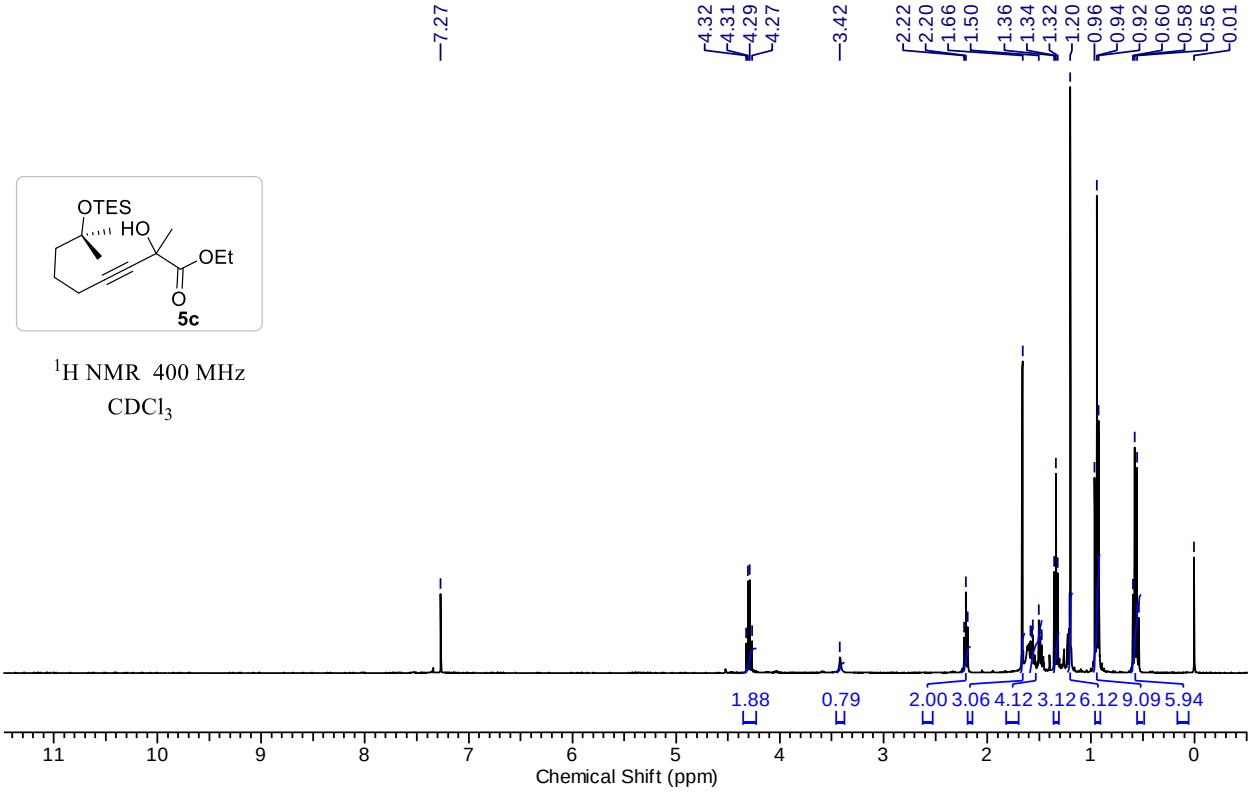


^{1}H NMR 400 MHz
$CDCl_3$

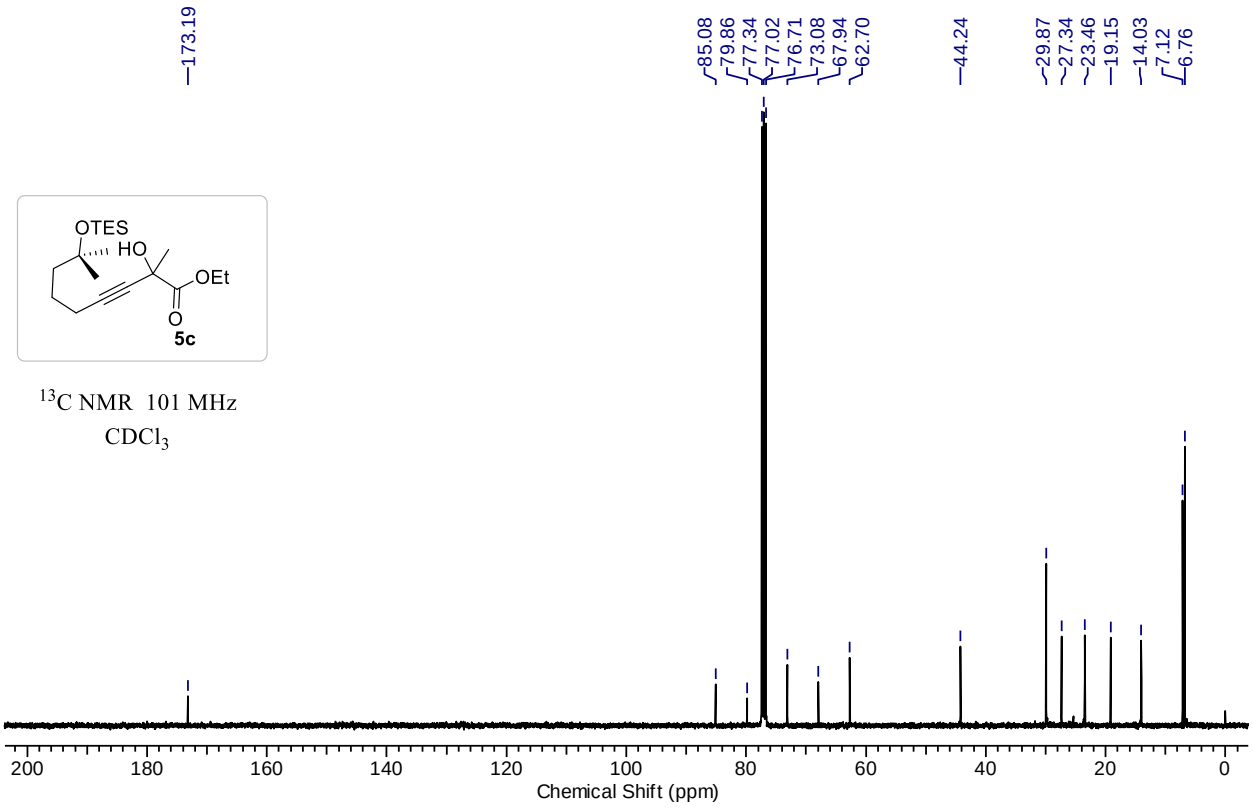


^{13}C NMR 101 MHz
$CDCl_3$

Ethyl 2-hydroxy-2,8-dimethyl-8-((triethylsilyl)oxy)non-3-ynoate (5c):

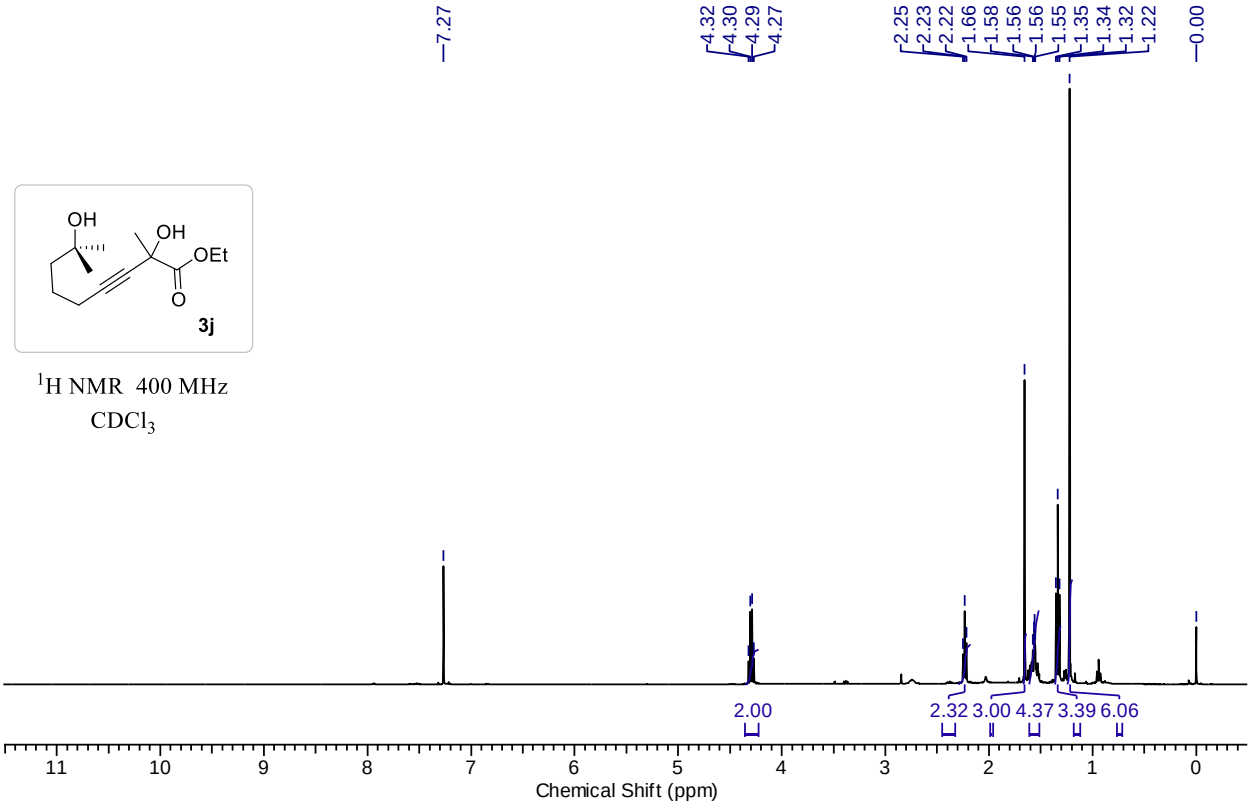


^{1}H NMR 400 MHz
$CDCl_3$

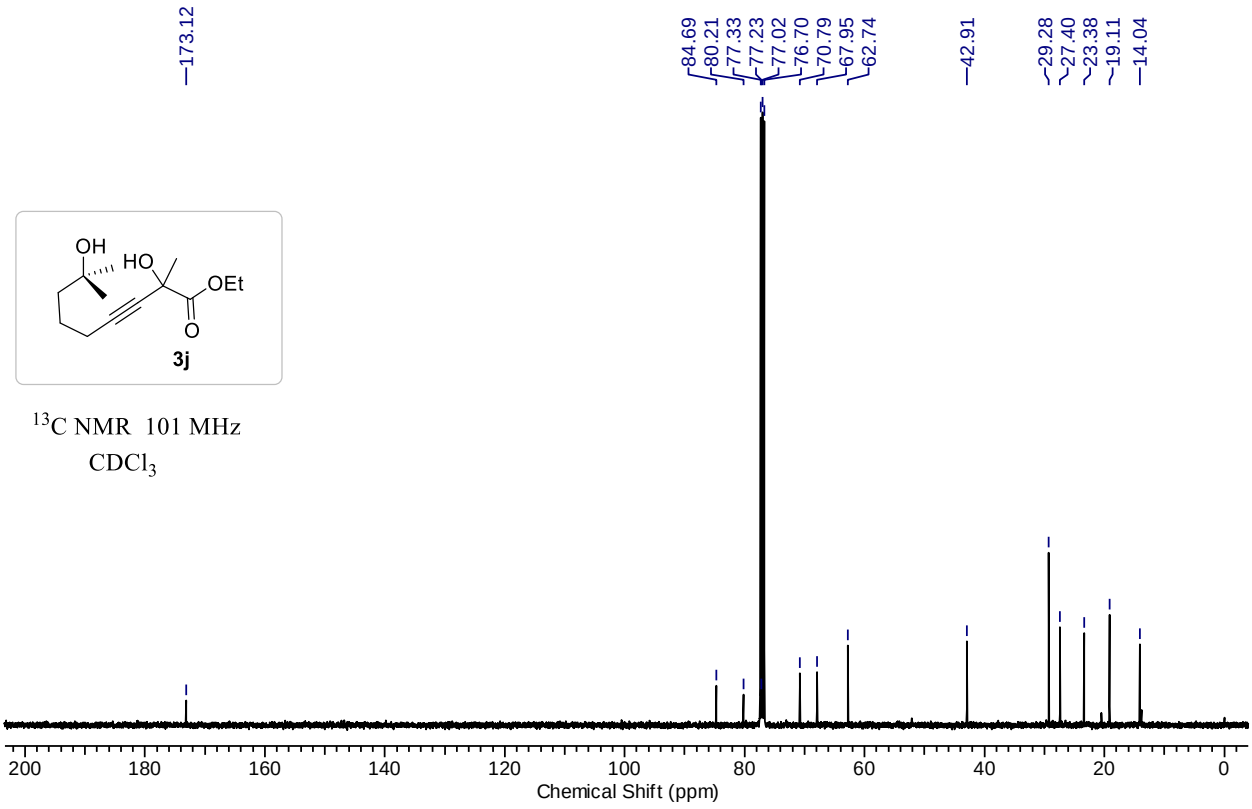


^{13}C NMR 101 MHz
$CDCl_3$

Ethyl 2,8-dihydroxy-2,8-dimethylnon-3-ynoate (3j):

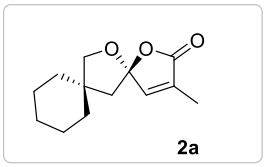


^{1}H NMR 400 MHz
$CDCl_3$

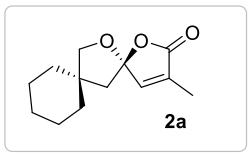


^{13}C NMR 101 MHz
$CDCl_3$

3-Methyl-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (2a):

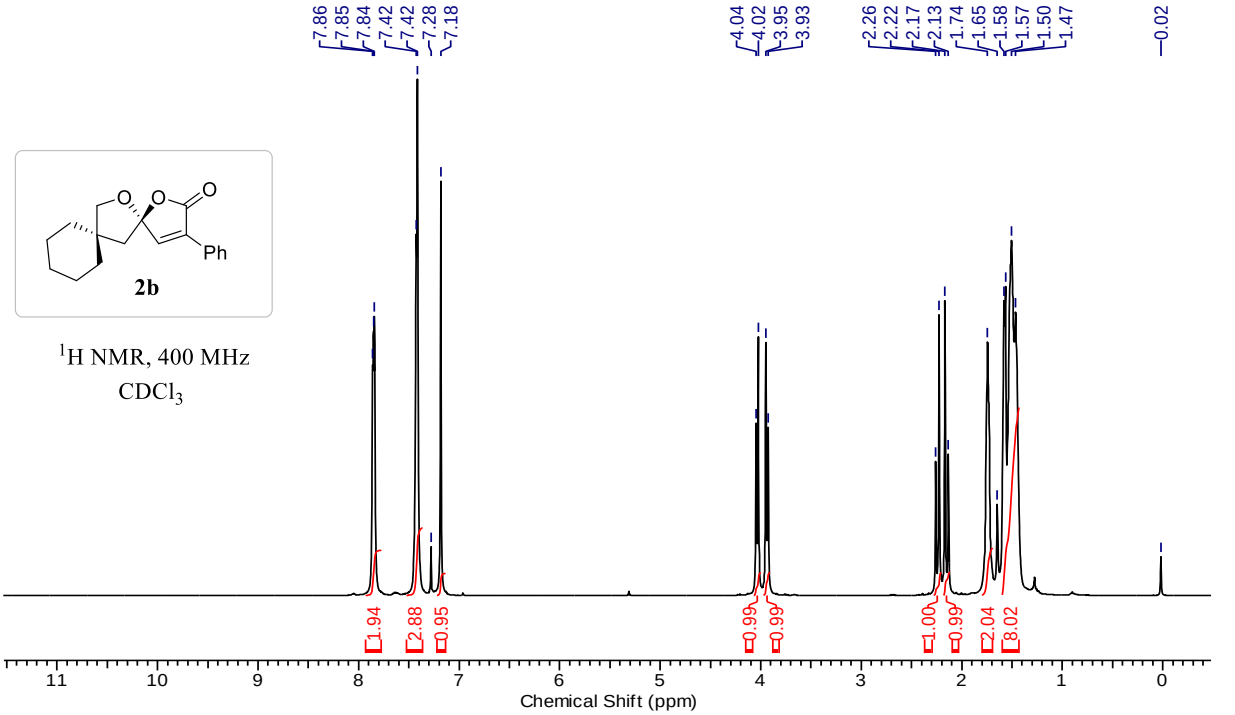


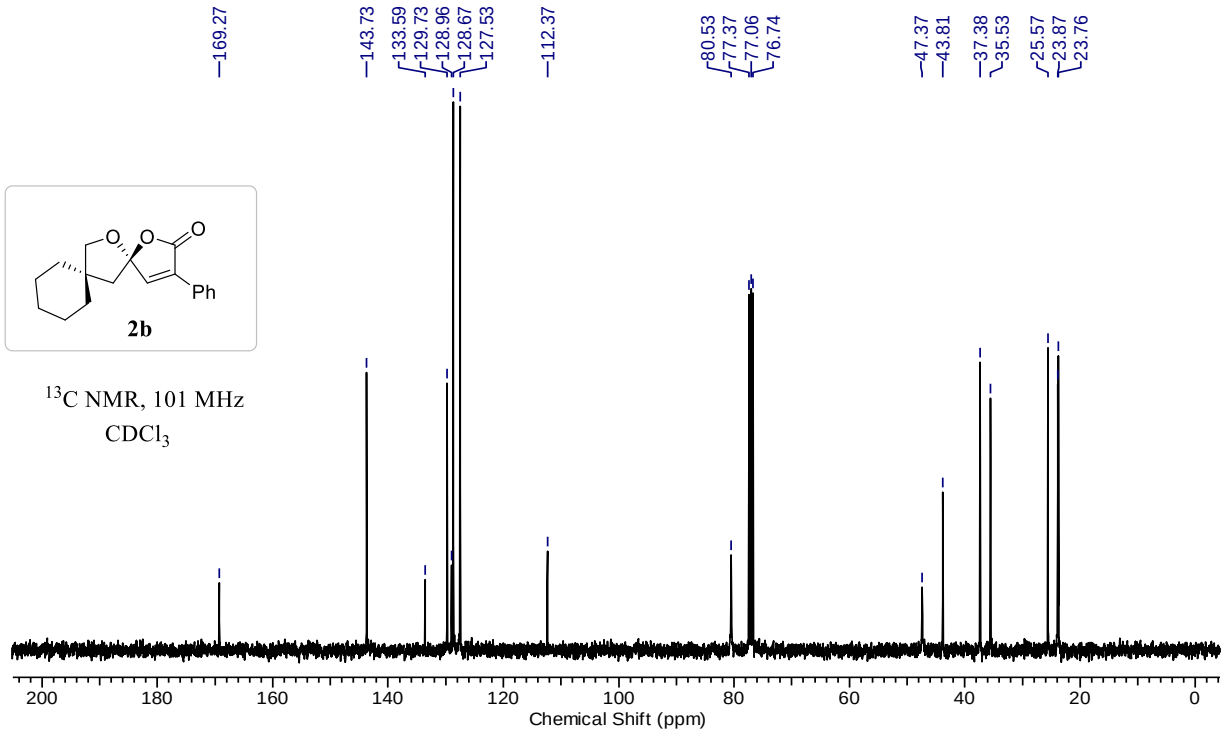
^{1}H NMR, 400 MHz
$CDCl_3$



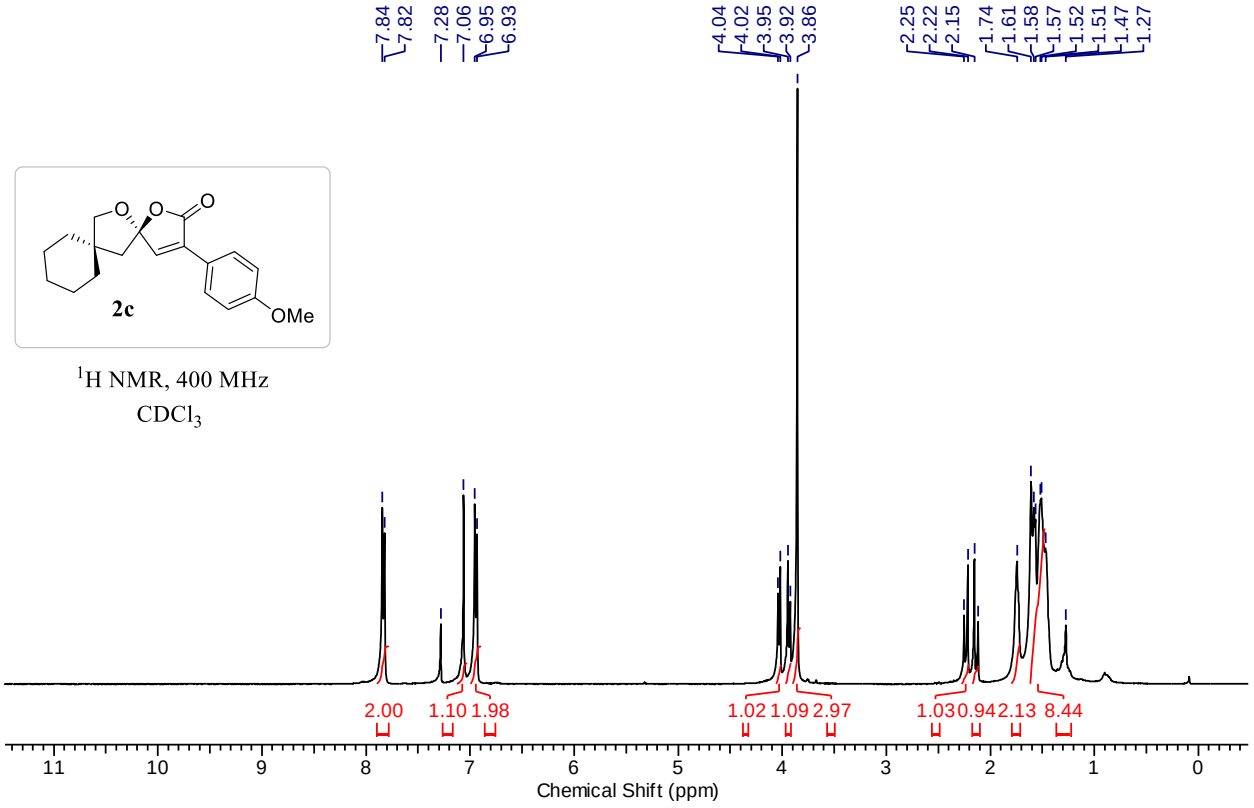
^{13}C NMR, 101 MHz
$CDCl_3$

3-Phenyl-1, 14-dioxadispiro [4.4.5^7.2^5] tetradec-3-en-one (2b):

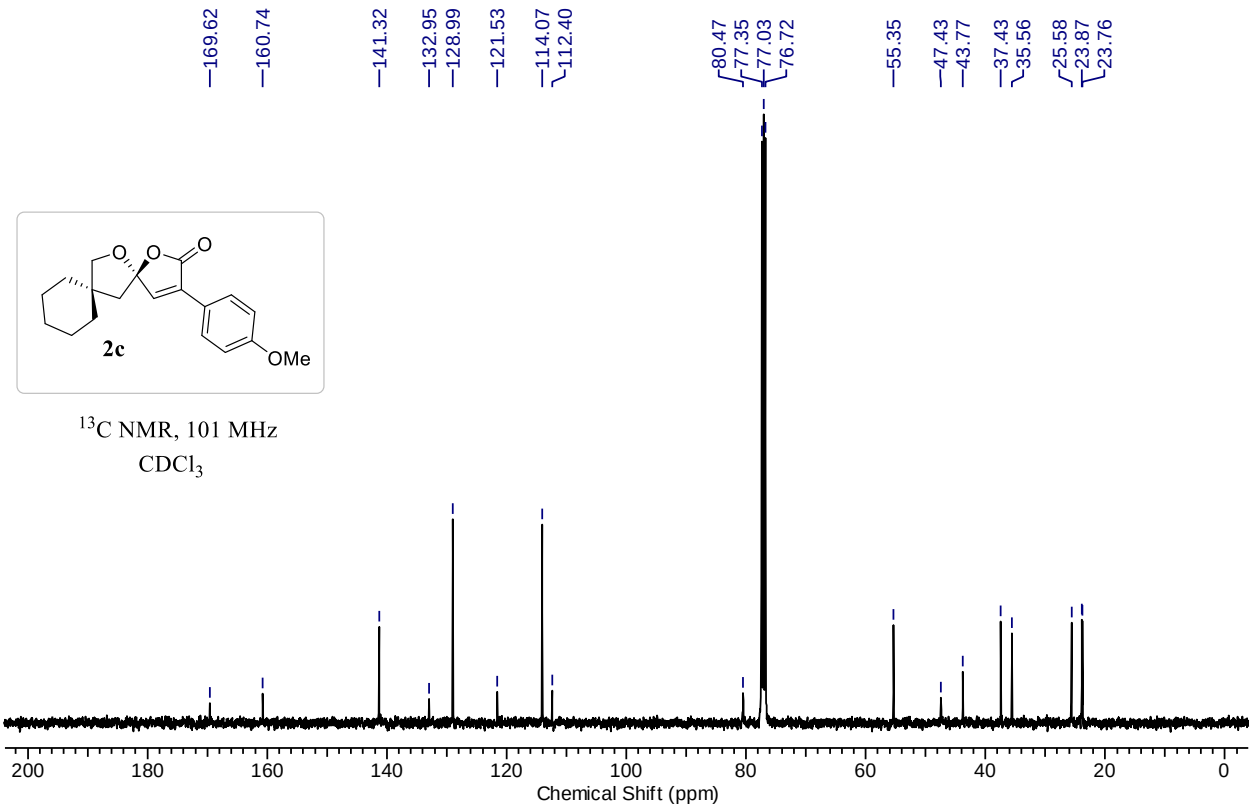




3-(4-Methoxyphenyl)-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (2c):

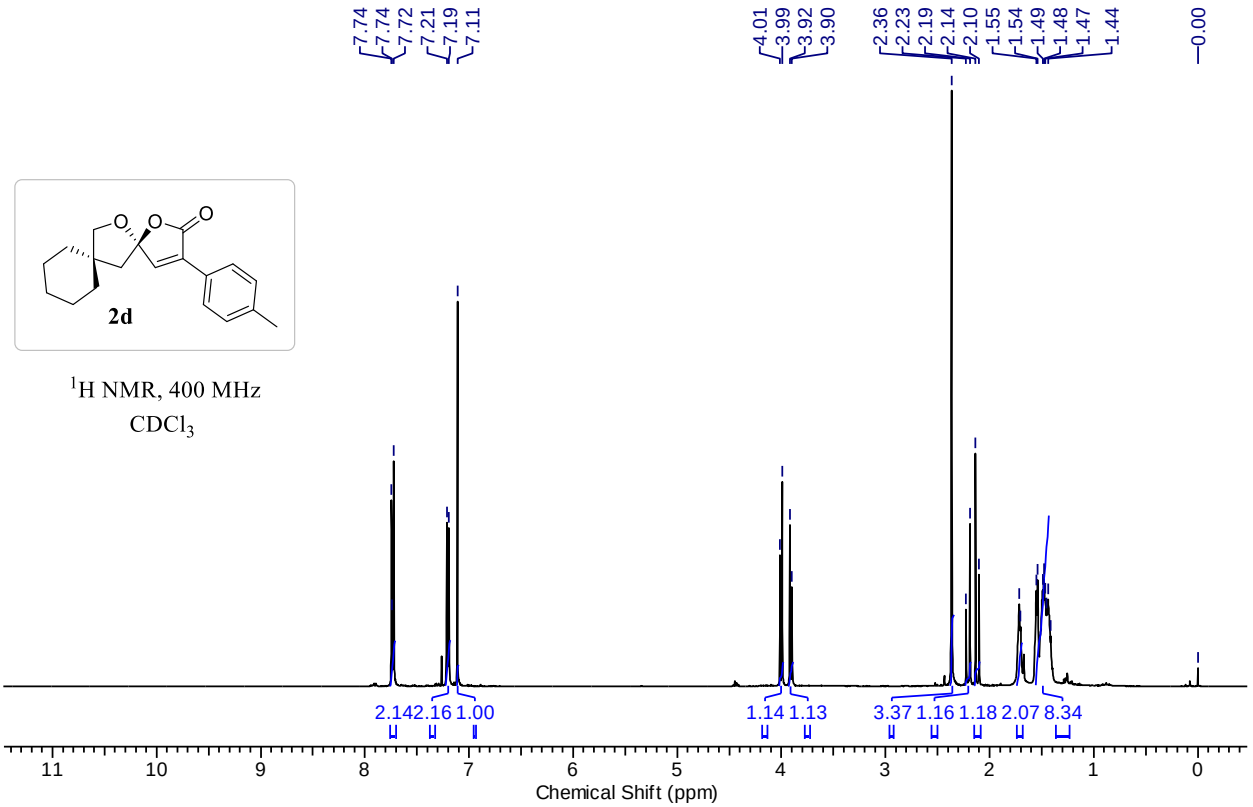


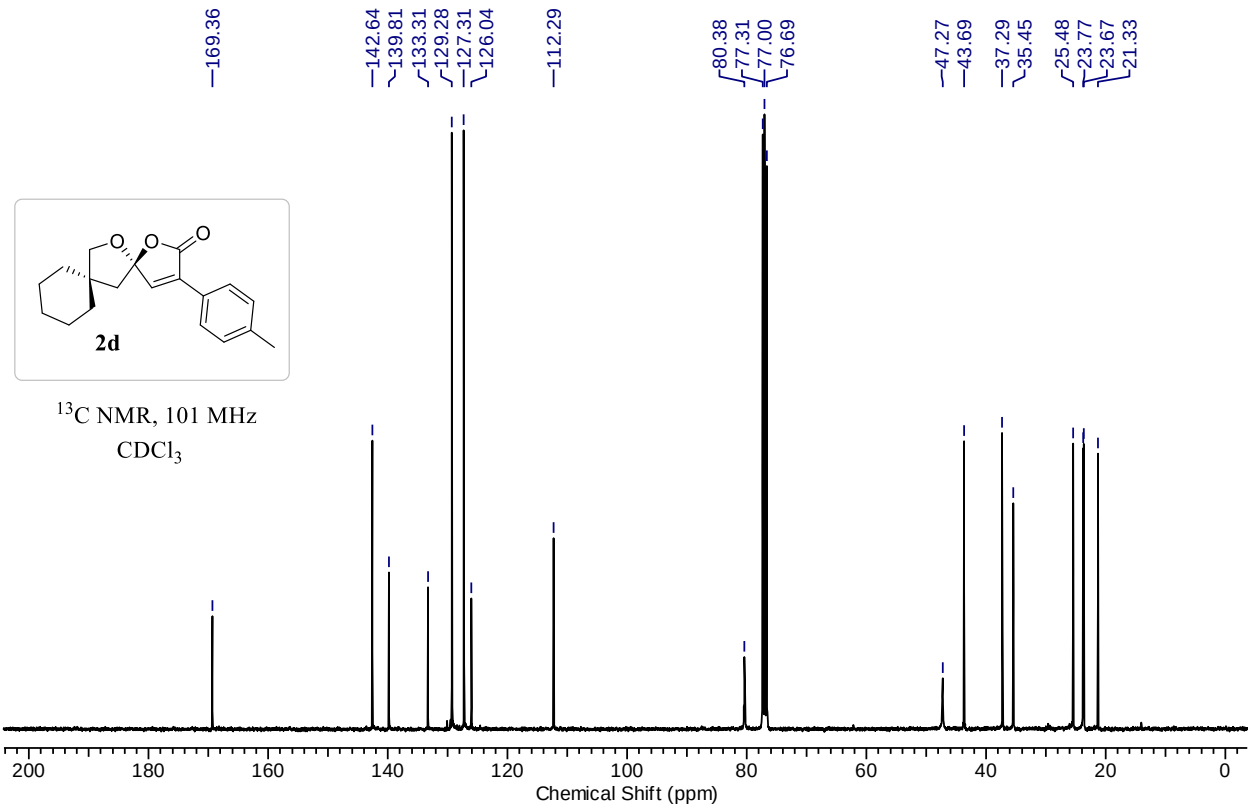
^{1}H NMR, 400 MHz
$CDCl_3$



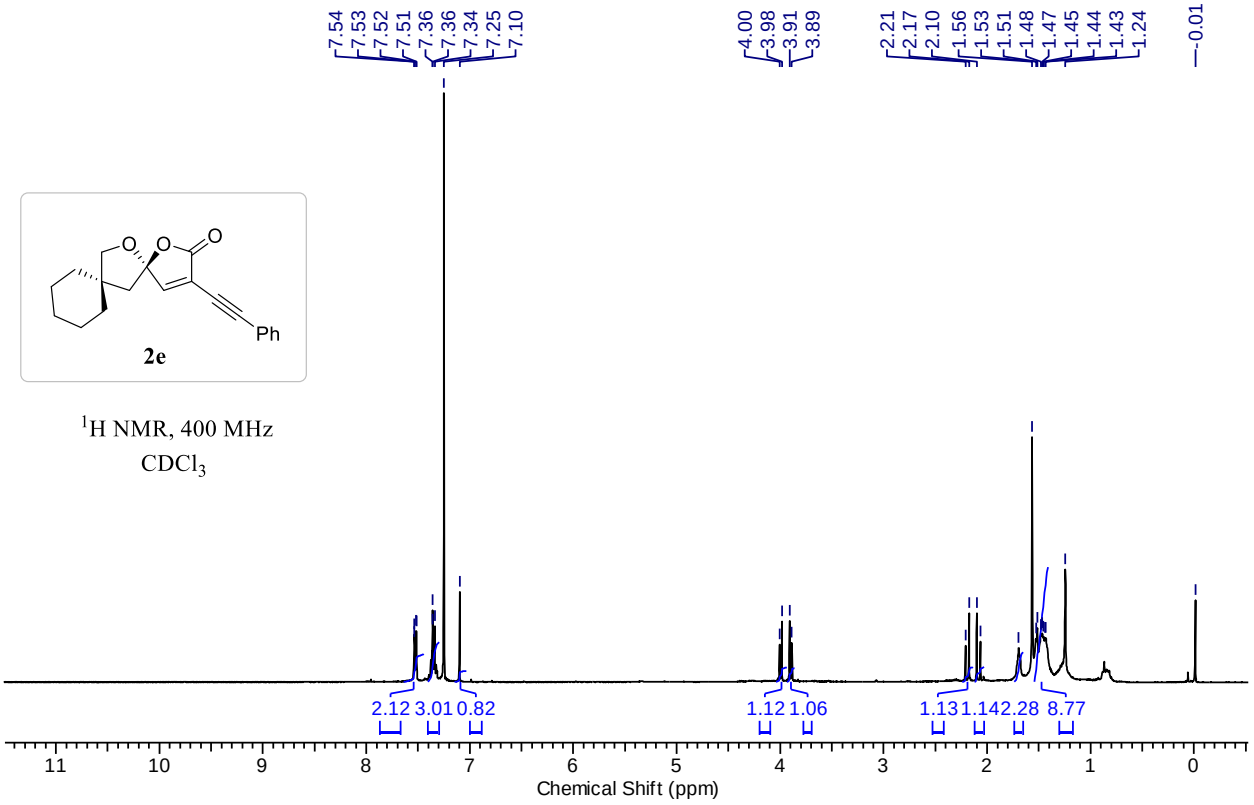
^{13}C NMR, 101 MHz
$CDCl_3$

3-(*p*-Tolyl)-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (2d):

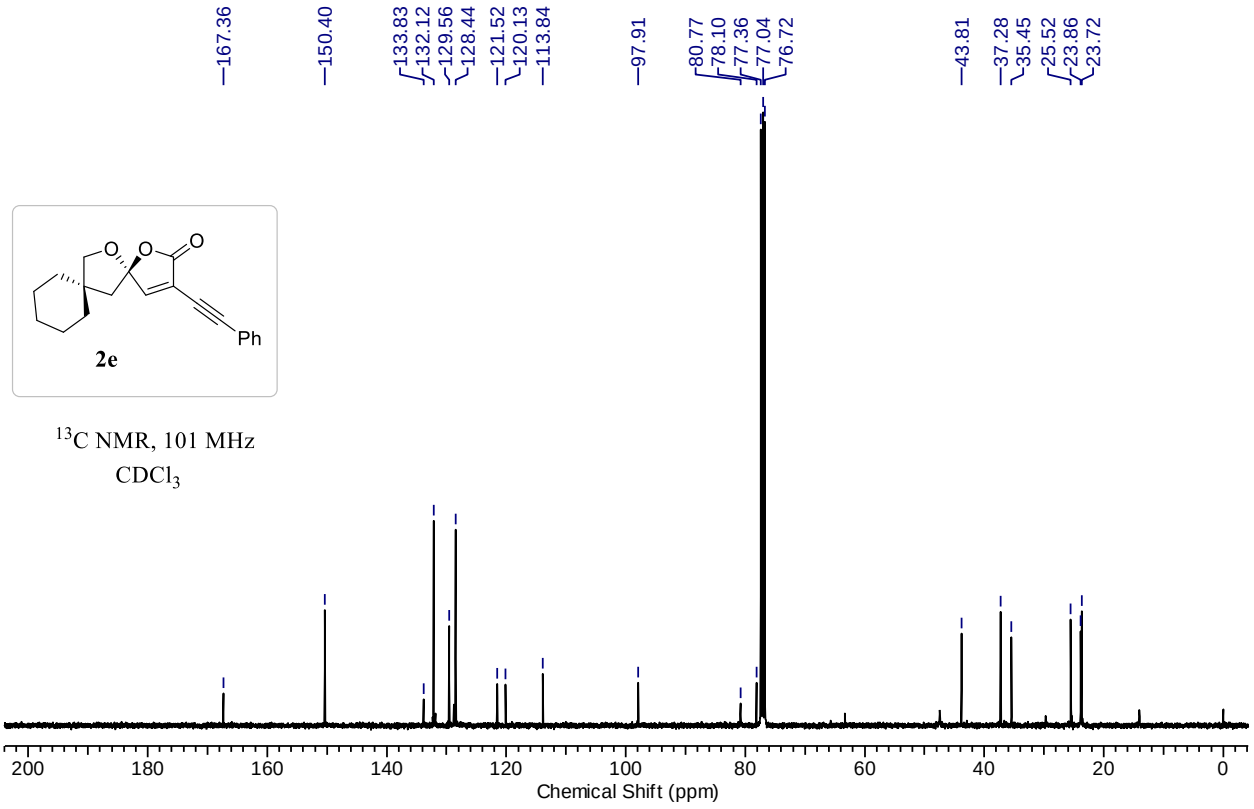




3-(Phenylethynyl)-1,14-dioxadispiro[4.1.5^{7}.2^{5}]tetradec-3-en-2-one (2e):

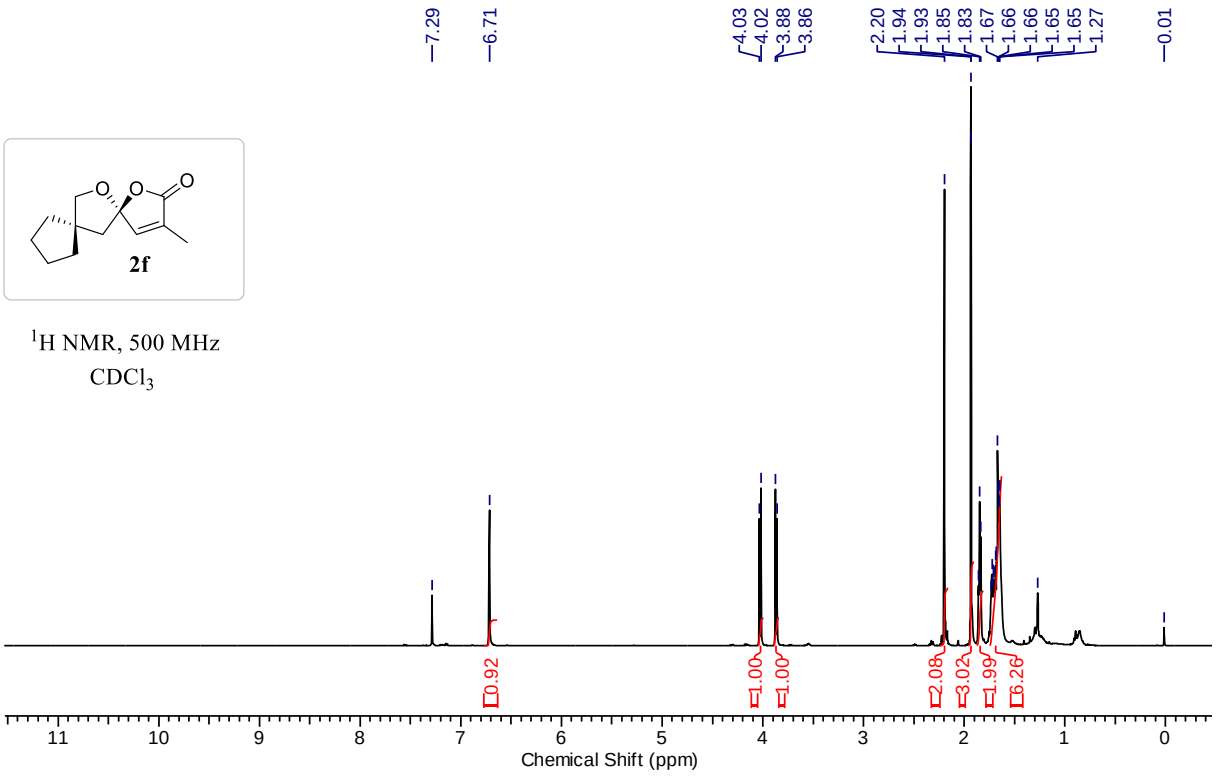


^{1}H NMR, 400 MHz
$CDCl_3$

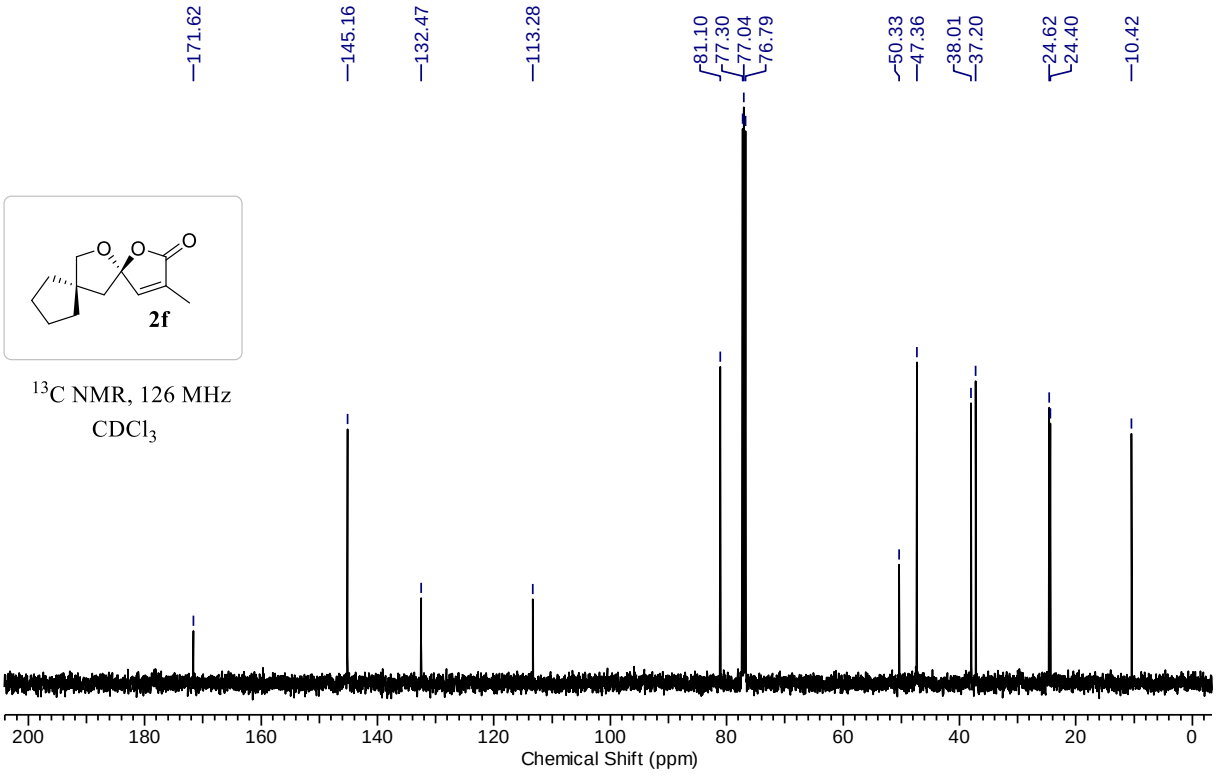


^{13}C NMR, 101 MHz
$CDCl_3$

3-Methyl-1,13-dioxadispiro[4.1.4^{7}.2^{5}]tridec-3-en-2-one (2f):

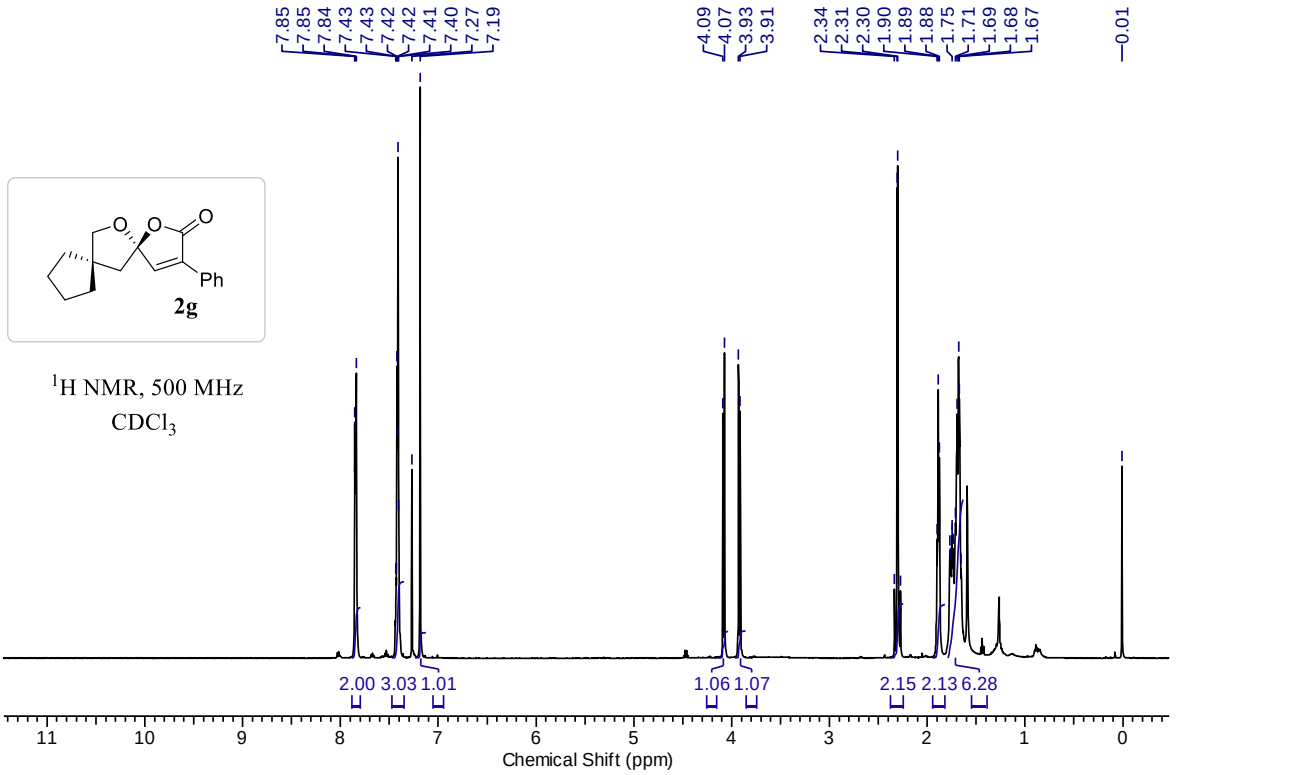


^{1}H NMR, 500 MHz
$CDCl_3$

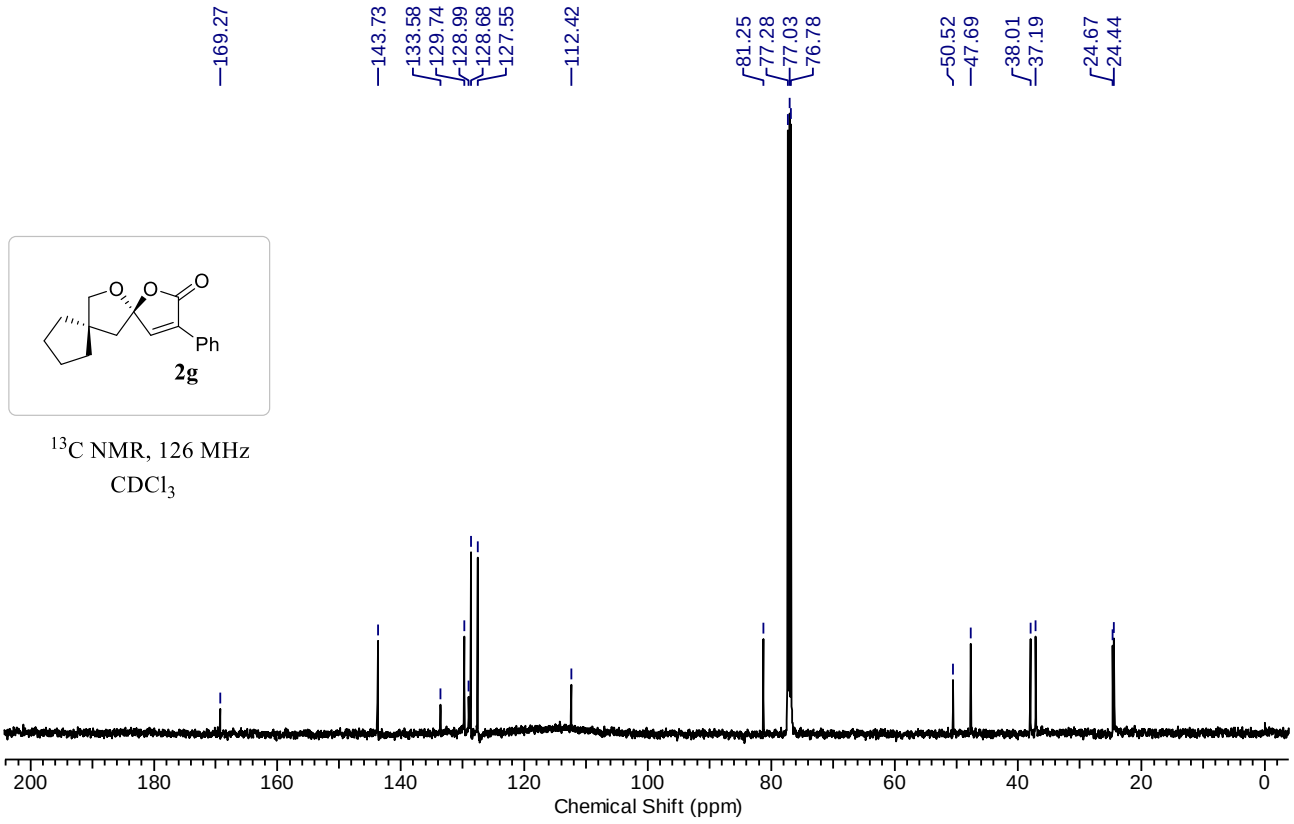


^{13}C NMR, 126 MHz
$CDCl_3$

3-Phenyl-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (2g) :

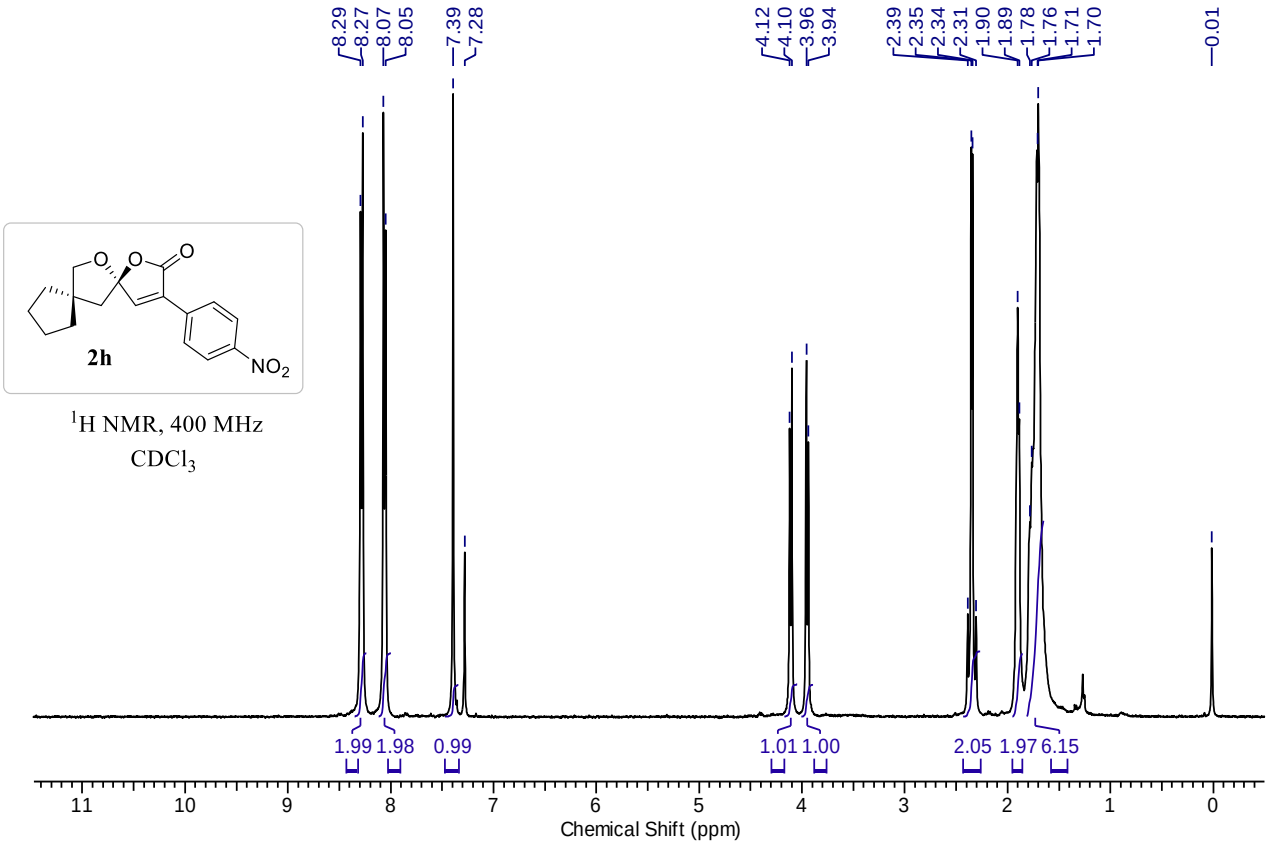


^{1}H NMR, 500 MHz
$CDCl_3$

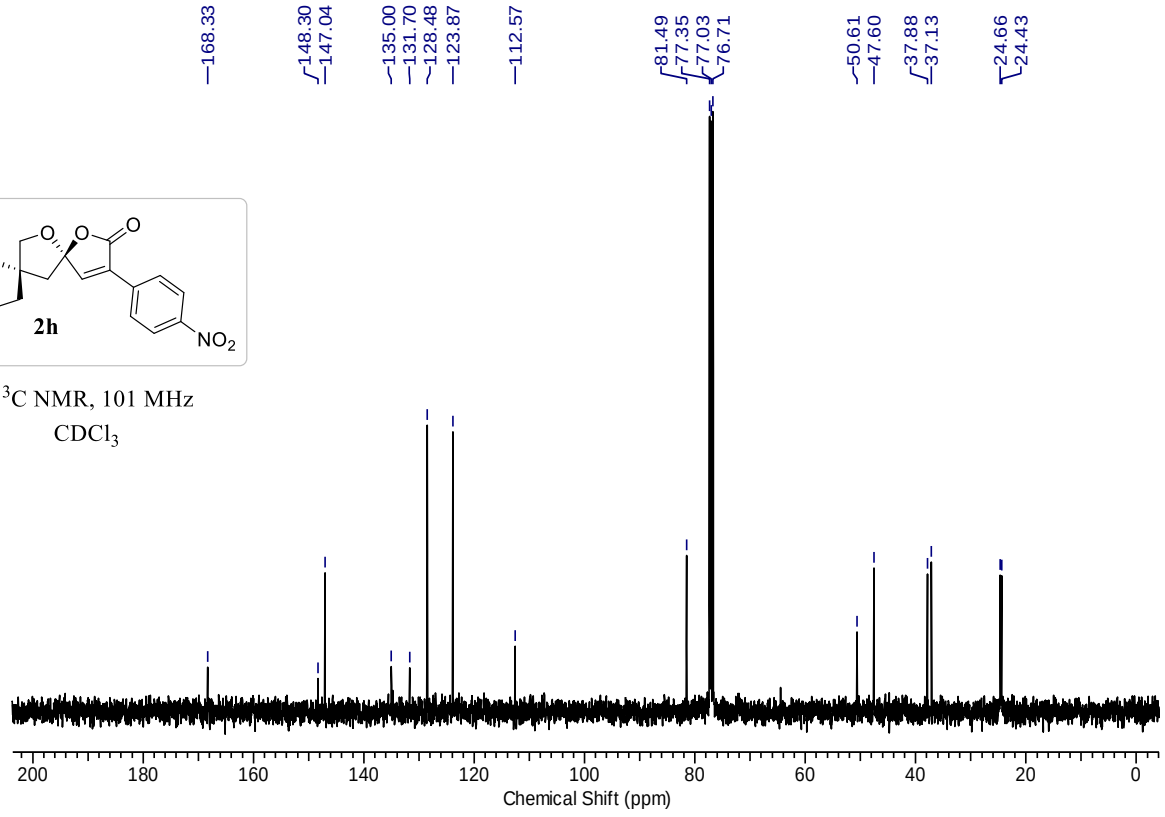


^{13}C NMR, 126 MHz
$CDCl_3$

3-(4-Nitrophenyl)-1,13-dioxadispiro[4.1.4^{7}.2^{5}]tridec-3-en-2-one (2h):

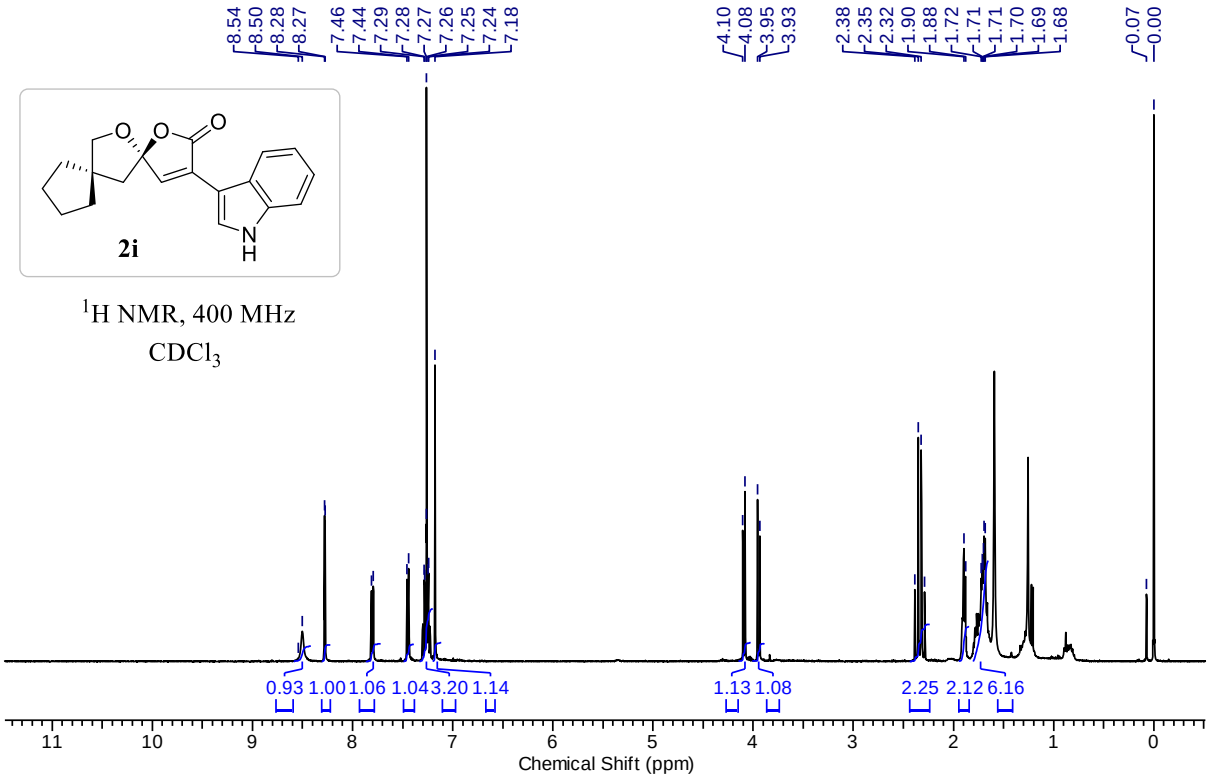


^{1}H NMR, 400 MHz
$CDCl_3$

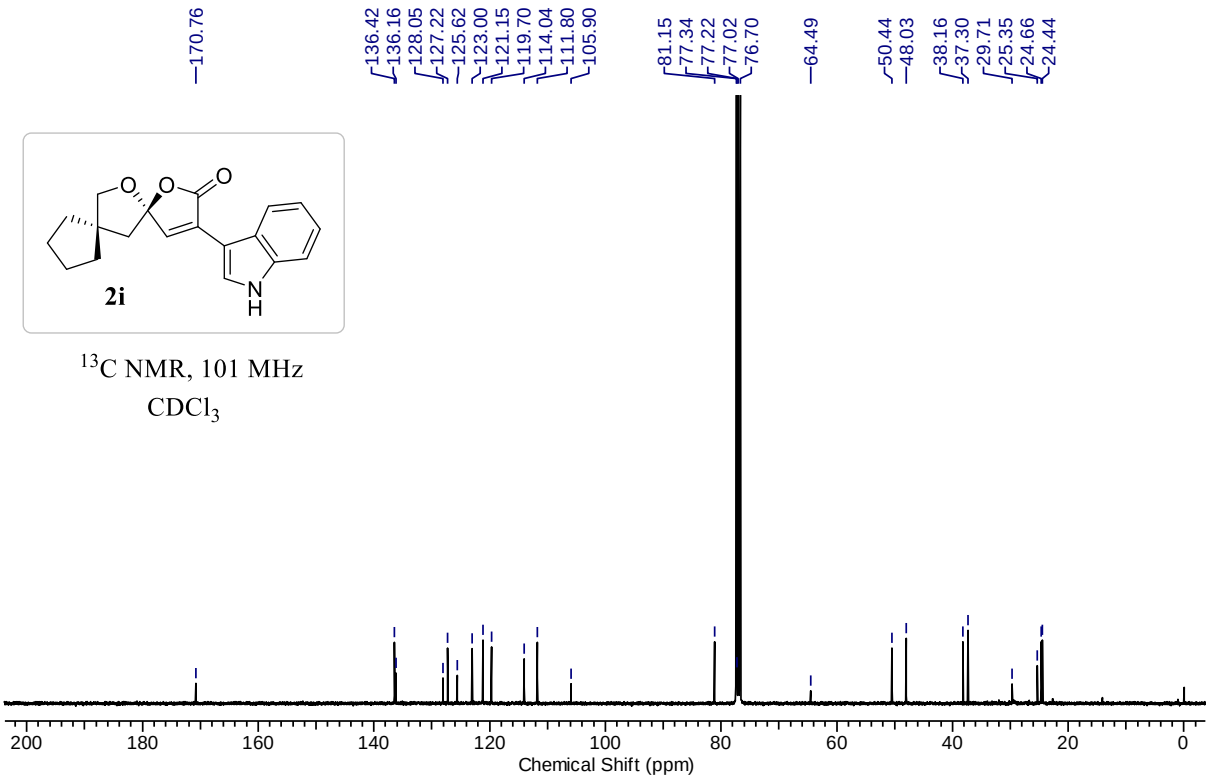


^{13}C NMR, 101 MHz
$CDCl_3$

3-(1*H*-indol-3-yl)-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (2i):

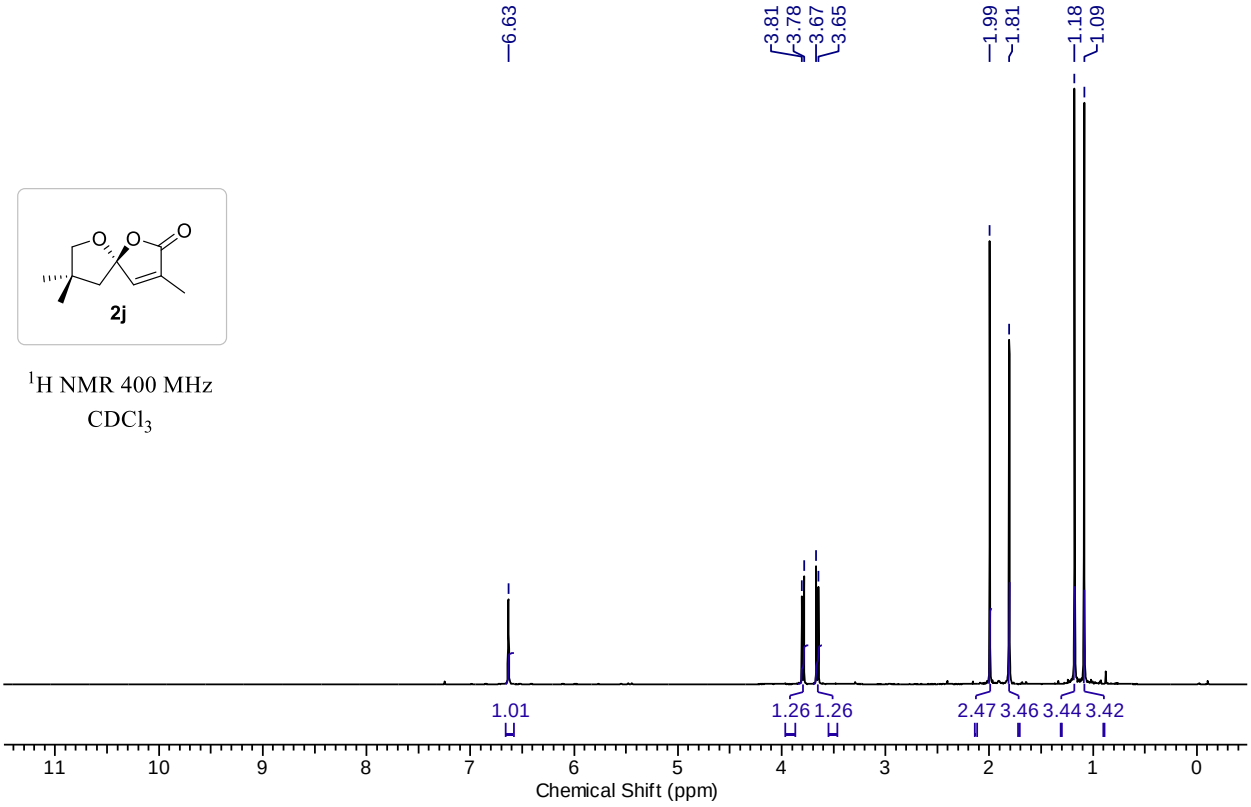


^{1}H NMR, 400 MHz
$CDCl_3$

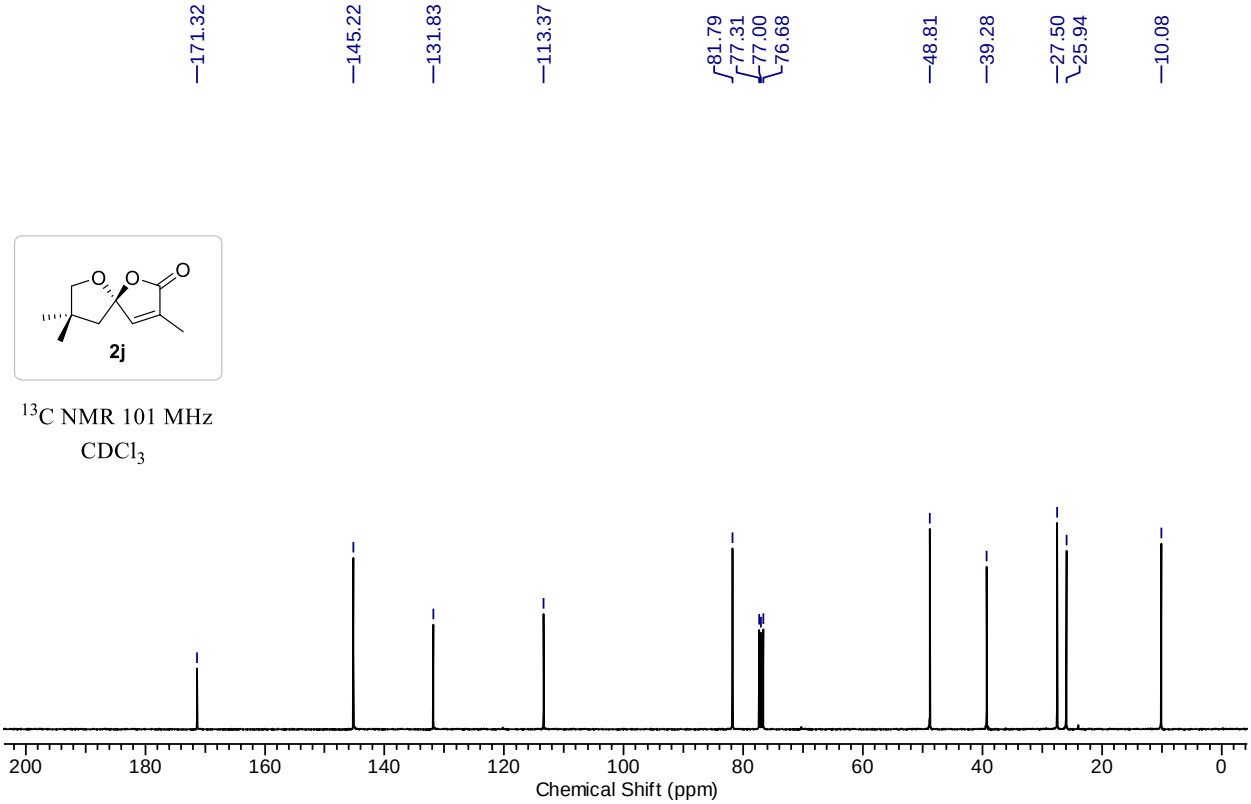


^{13}C NMR, 101 MHz
$CDCl_3$

3,8,8-Trimethyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2j):

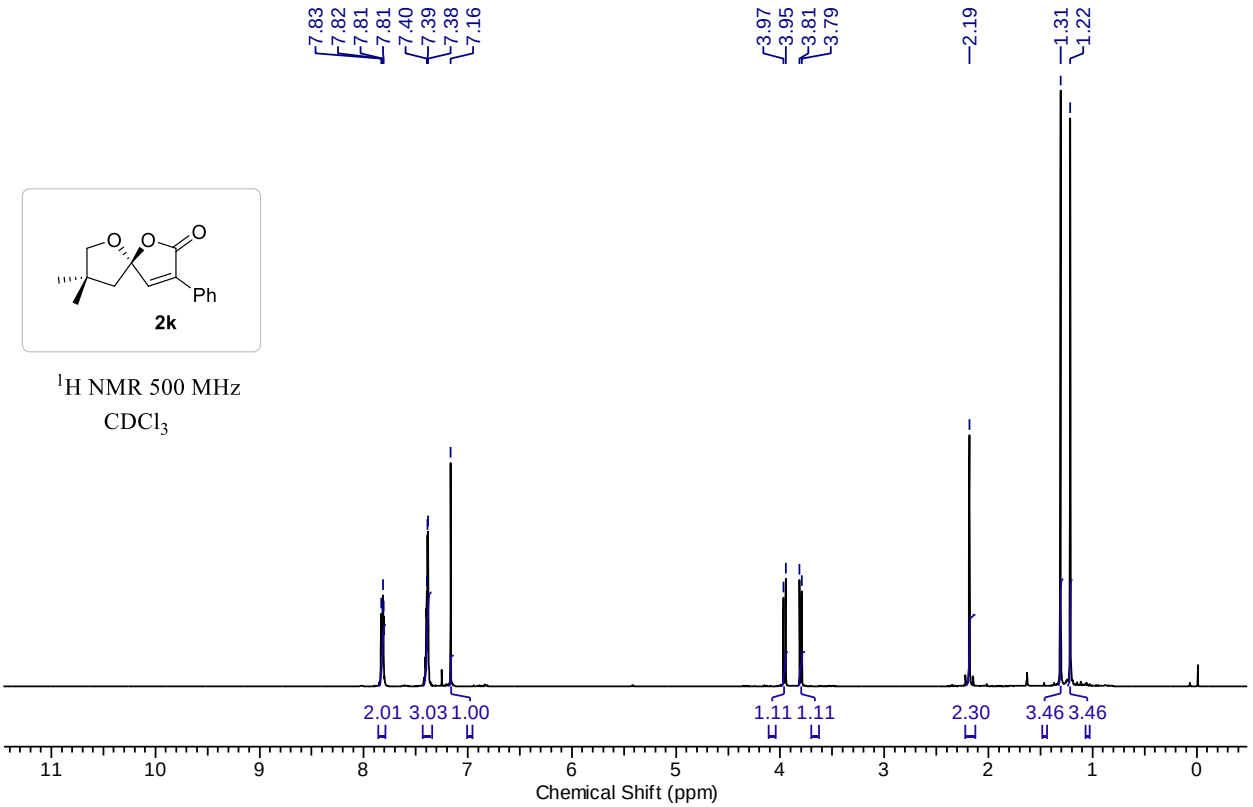


^{1}H NMR 400 MHz
$CDCl_3$

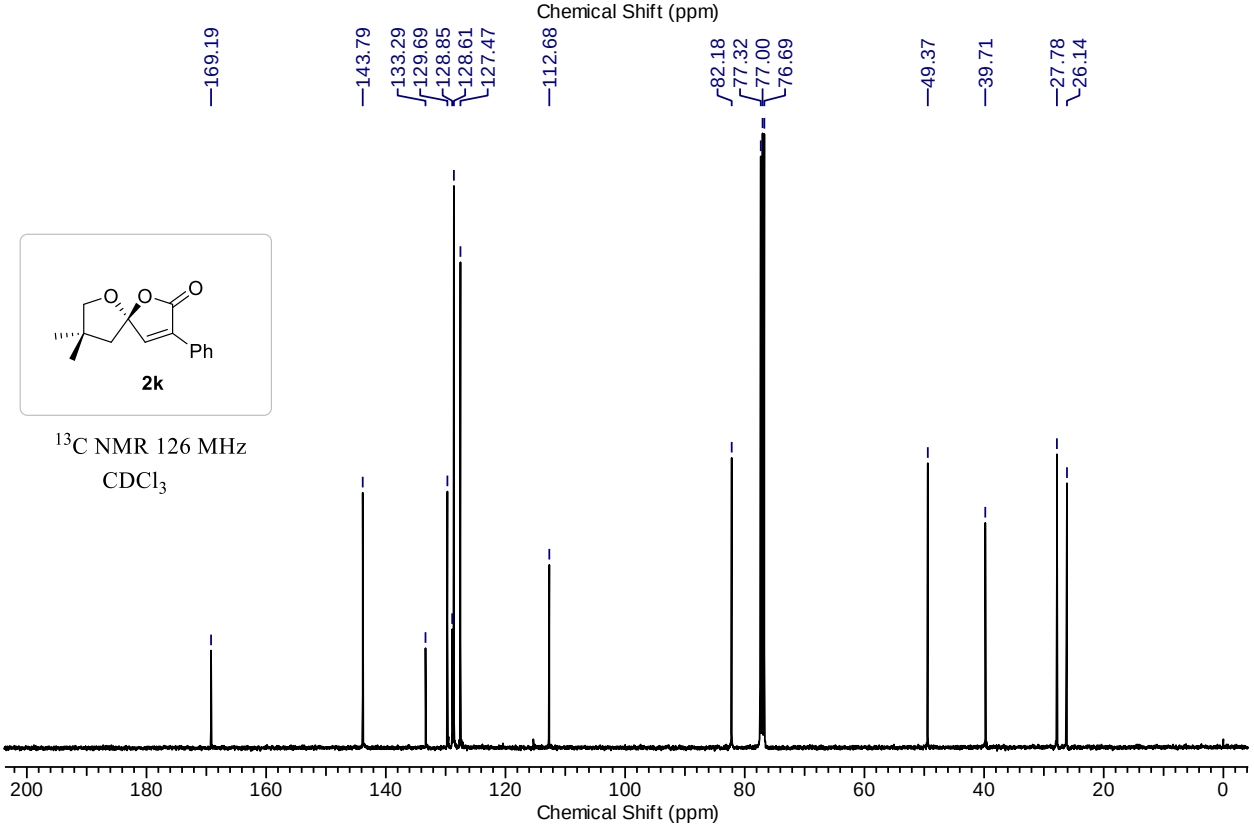


^{13}C NMR 101 MHz
$CDCl_3$

8,8-Dimethyl-3-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2k):

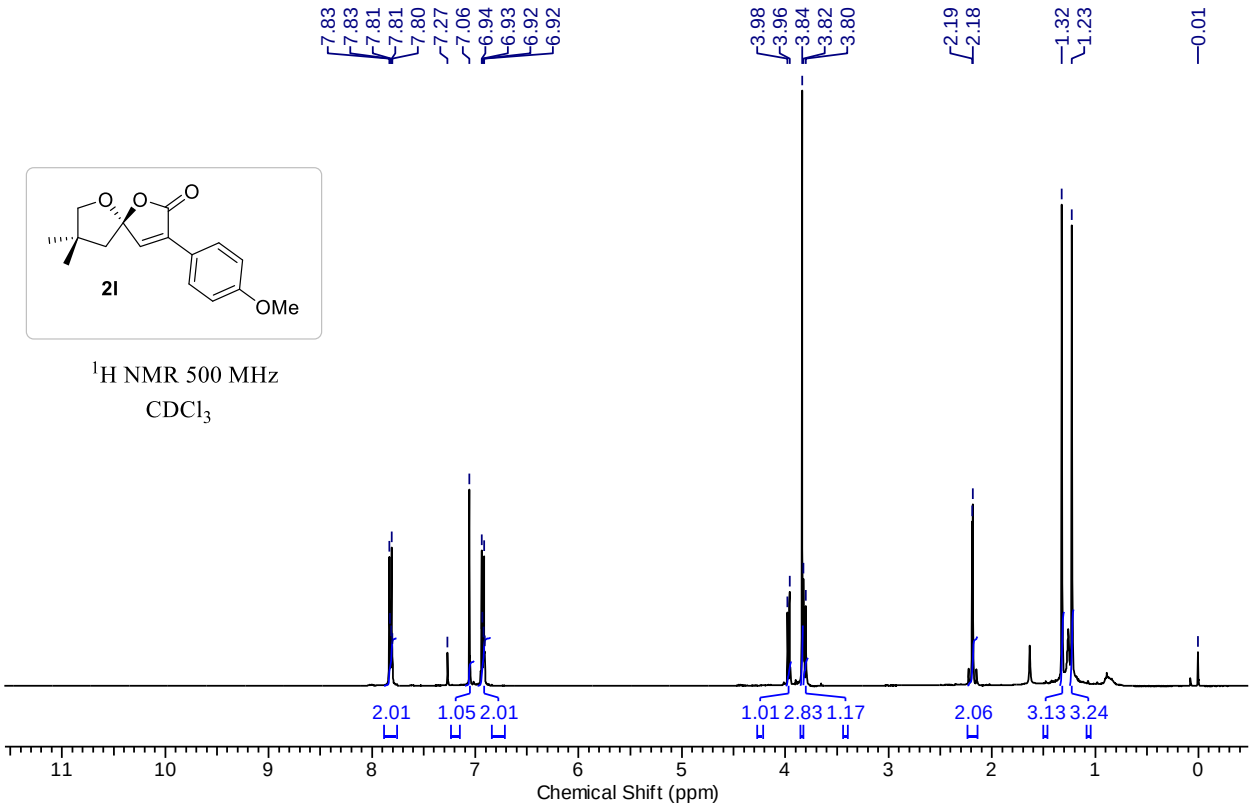


^{1}H NMR 500 MHz
$CDCl_3$

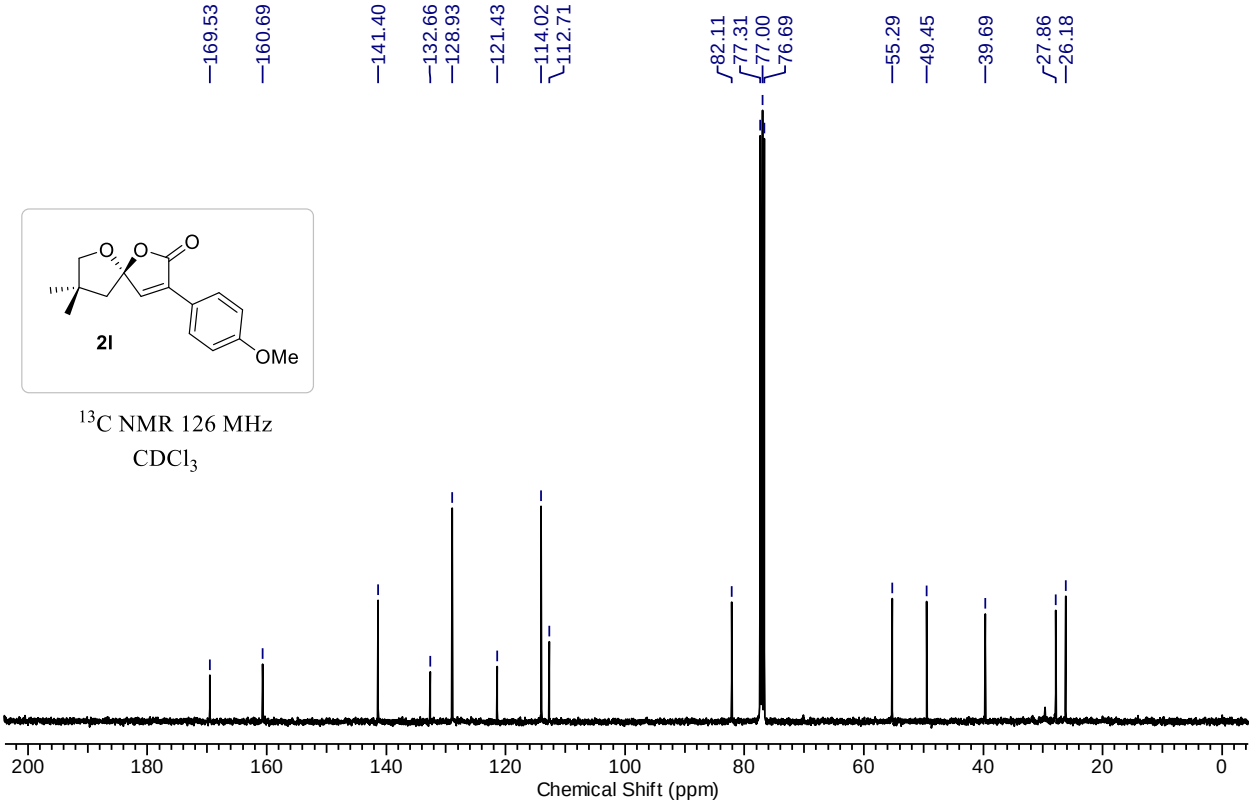


^{13}C NMR 126 MHz
$CDCl_3$

3-(4-Methoxyphenyl)-8,8-dimethyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2l):

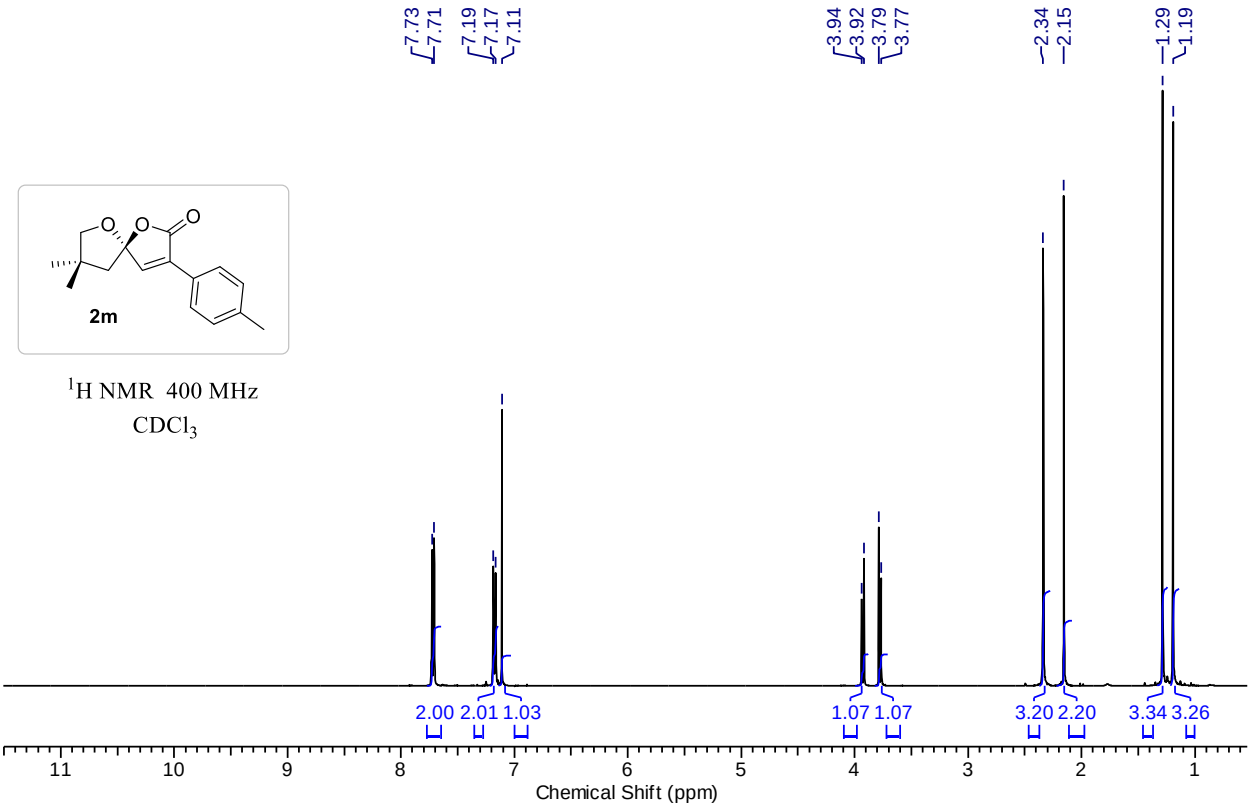


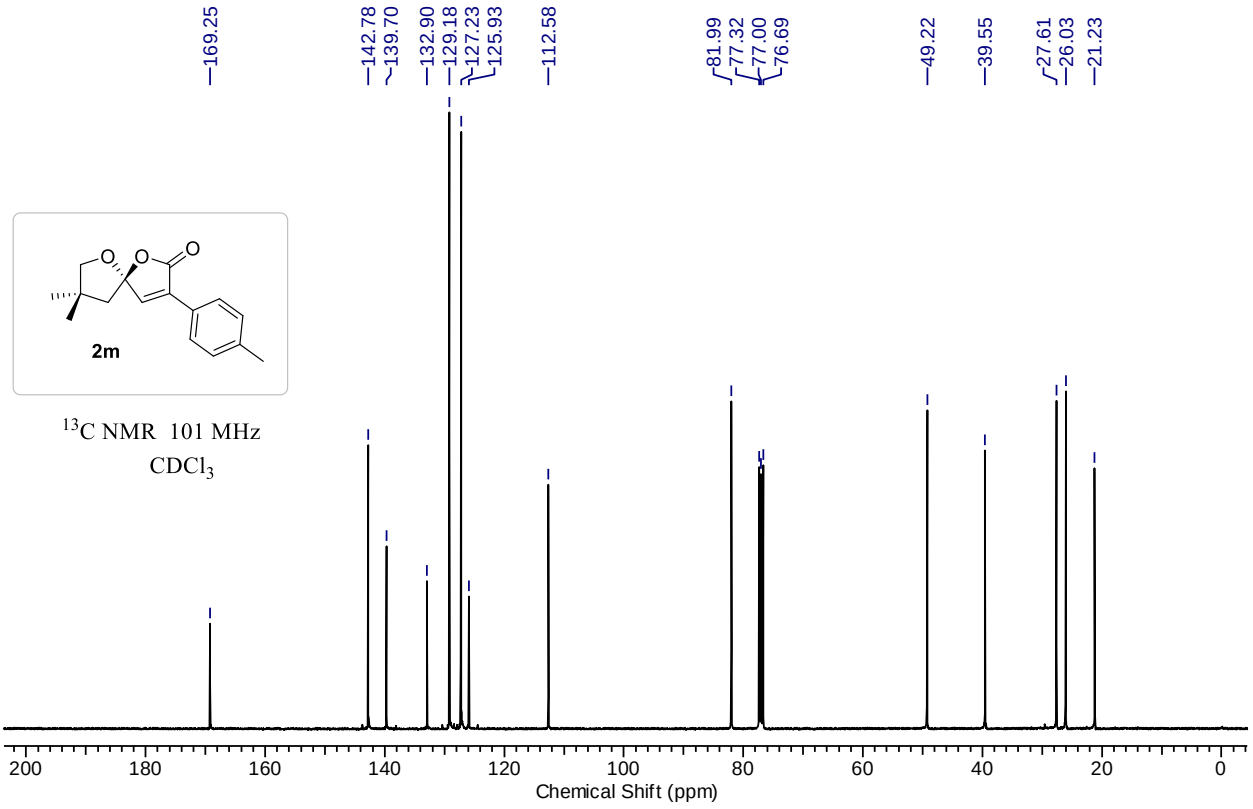
^{1}H NMR 500 MHz
$CDCl_3$



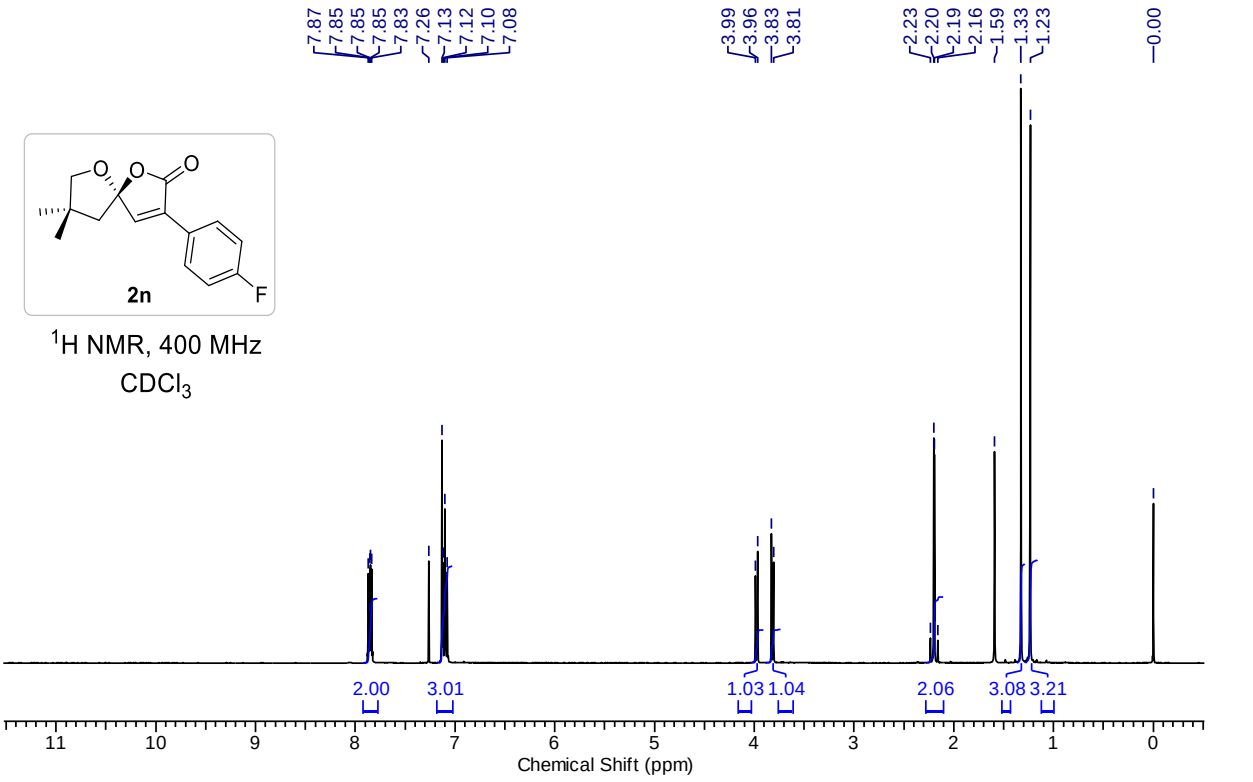
^{13}C NMR 126 MHz
$CDCl_3$

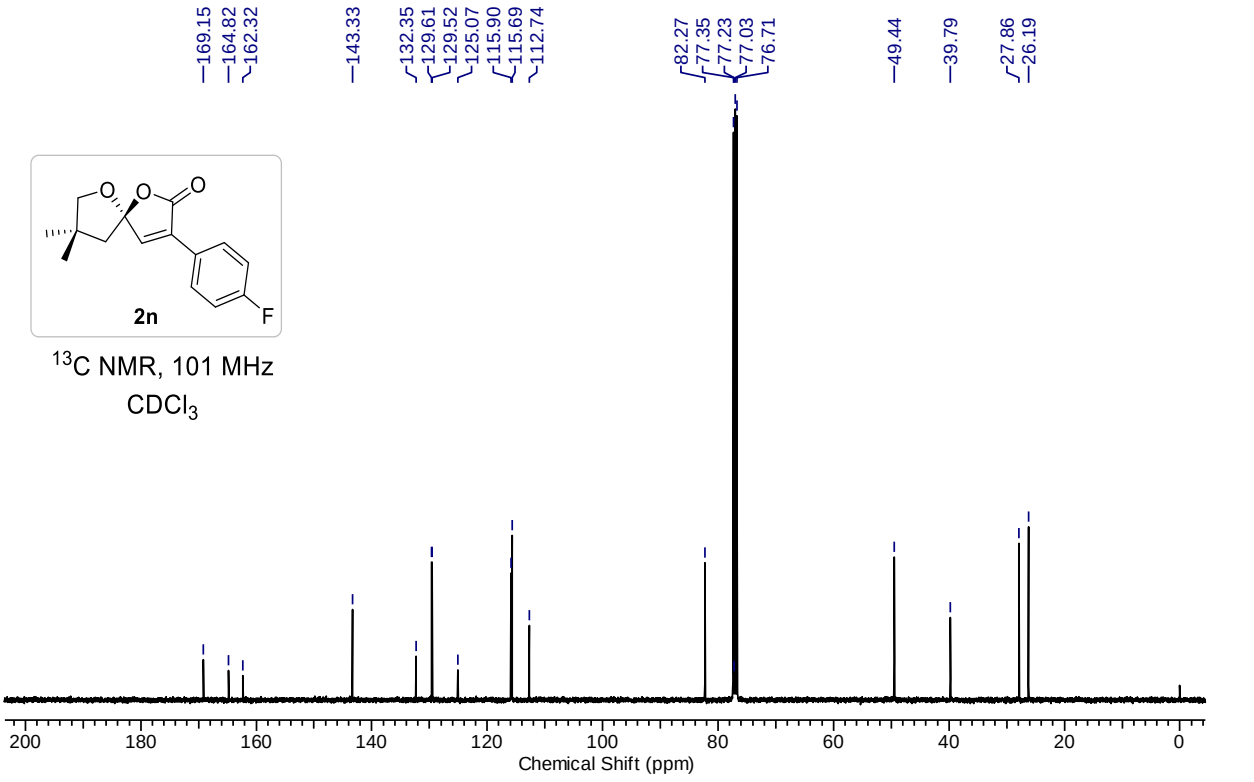
8,8-Dimethyl-3-(*p*-tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one (2m):

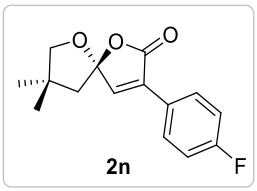




3-(4-Fluorophenyl)-8,8-dimethyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2n):





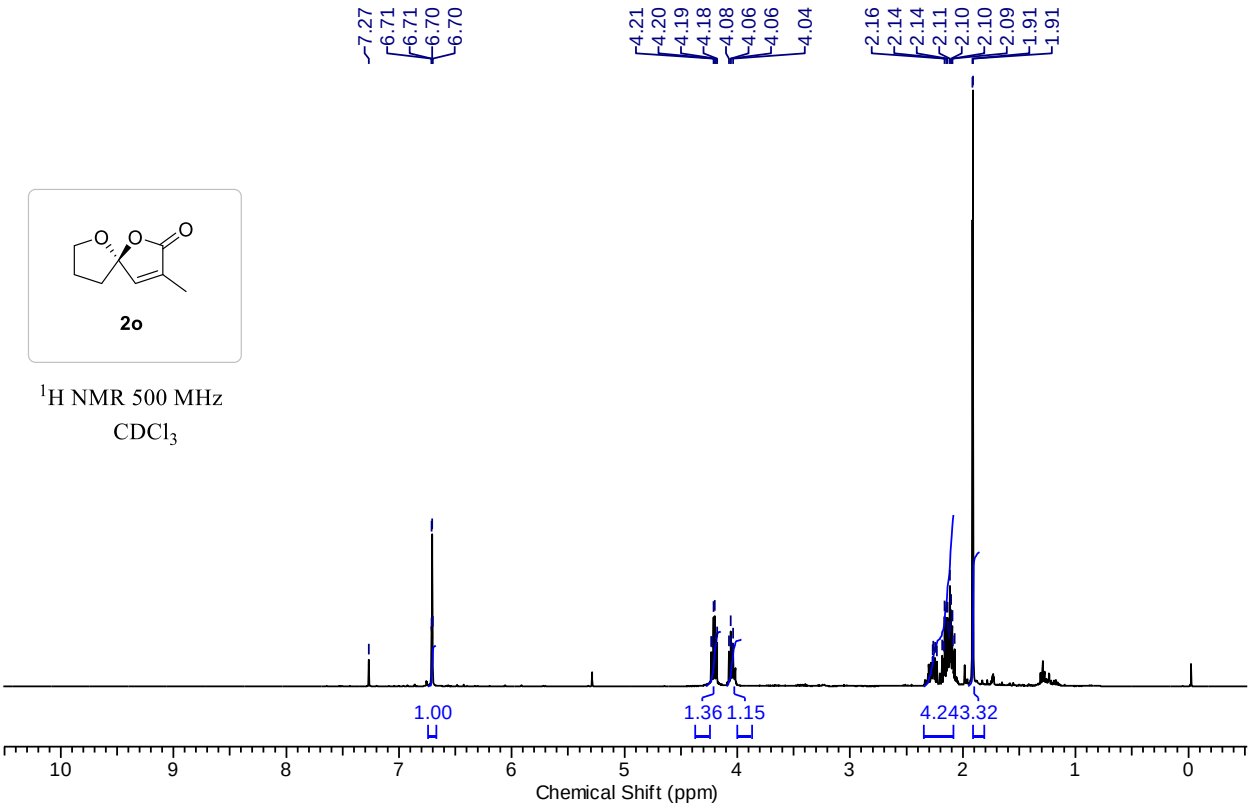


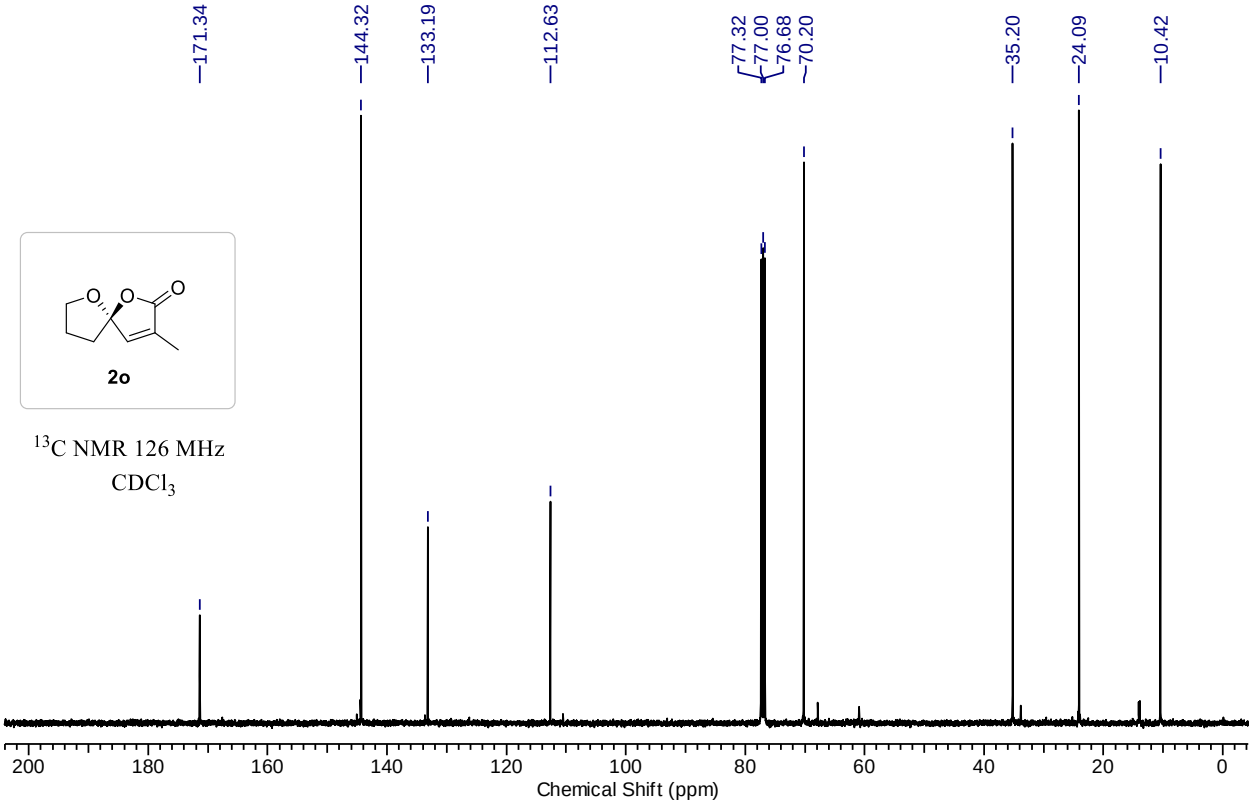
2n

^{19}F NMR, 376 MHz

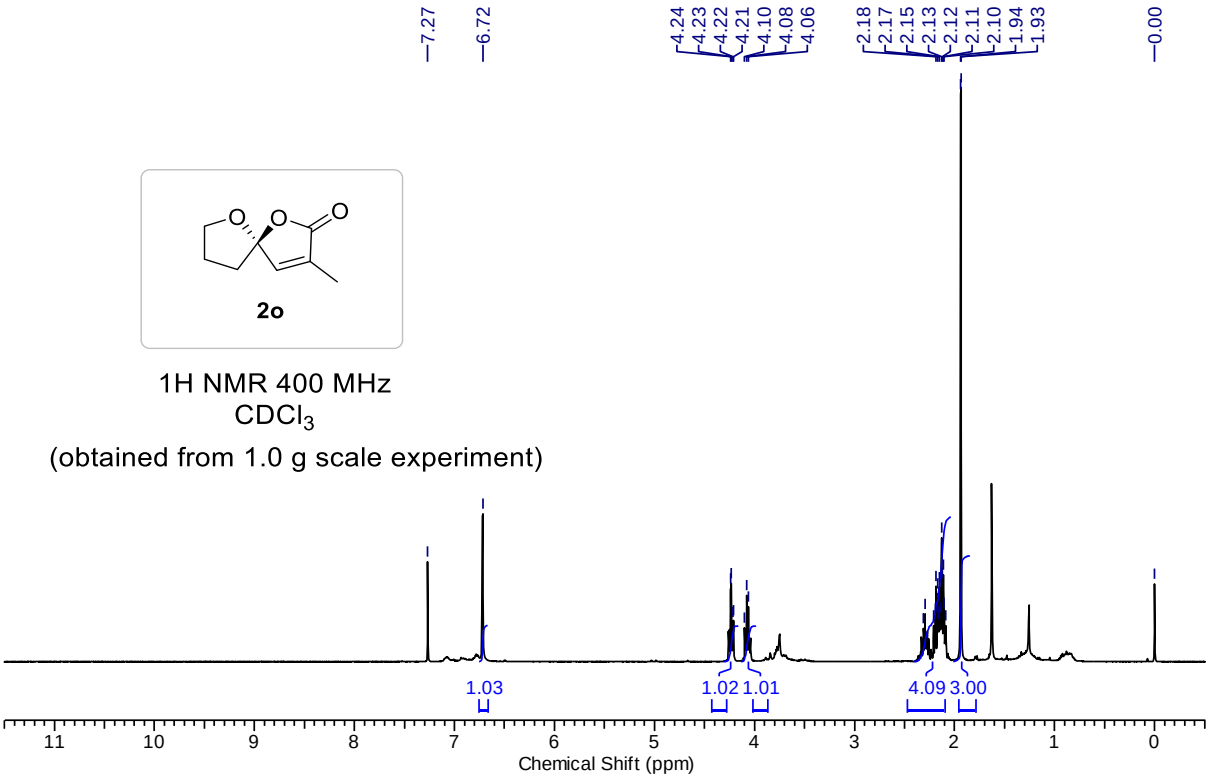
$CDCl_3$

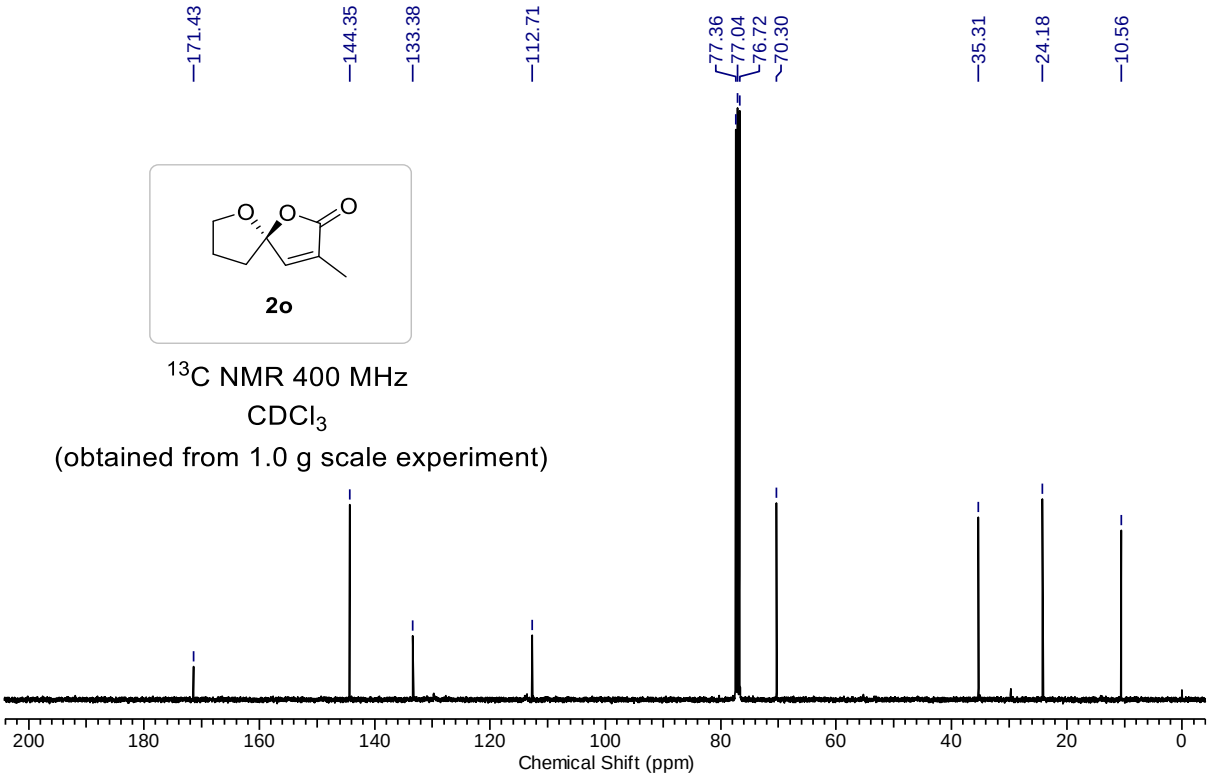
3-Methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2o):



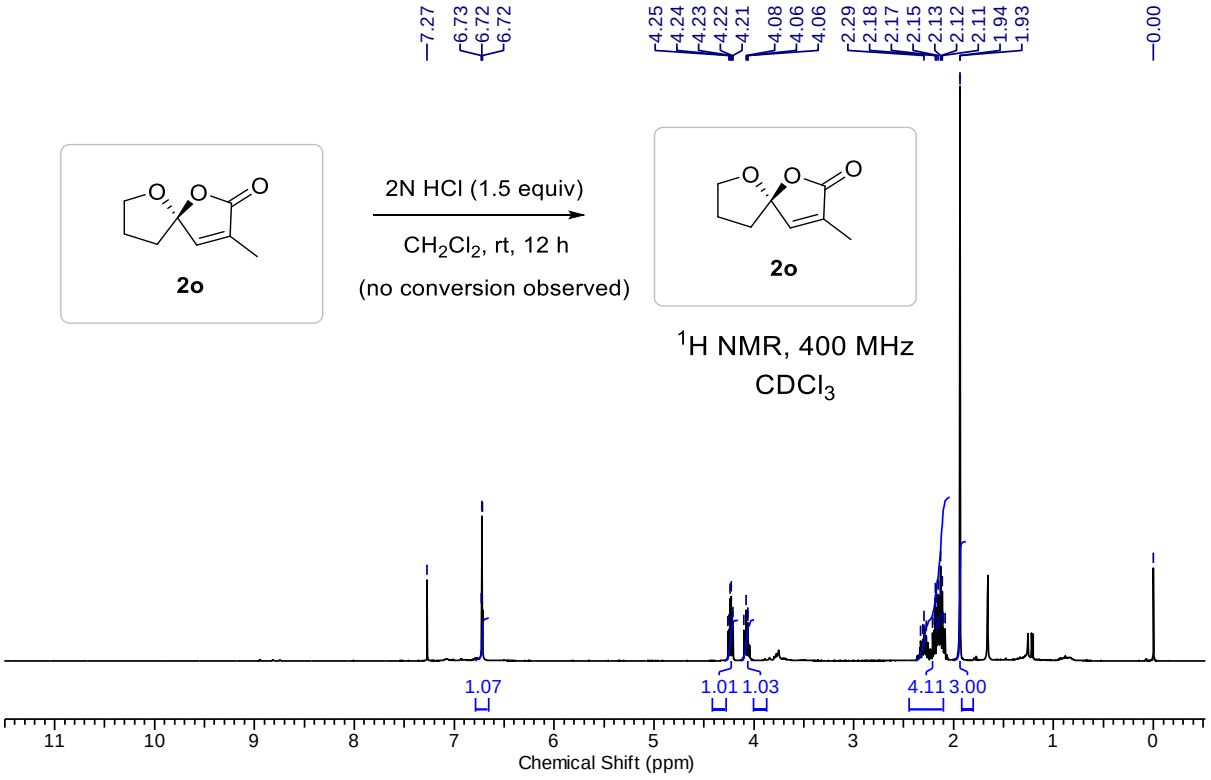


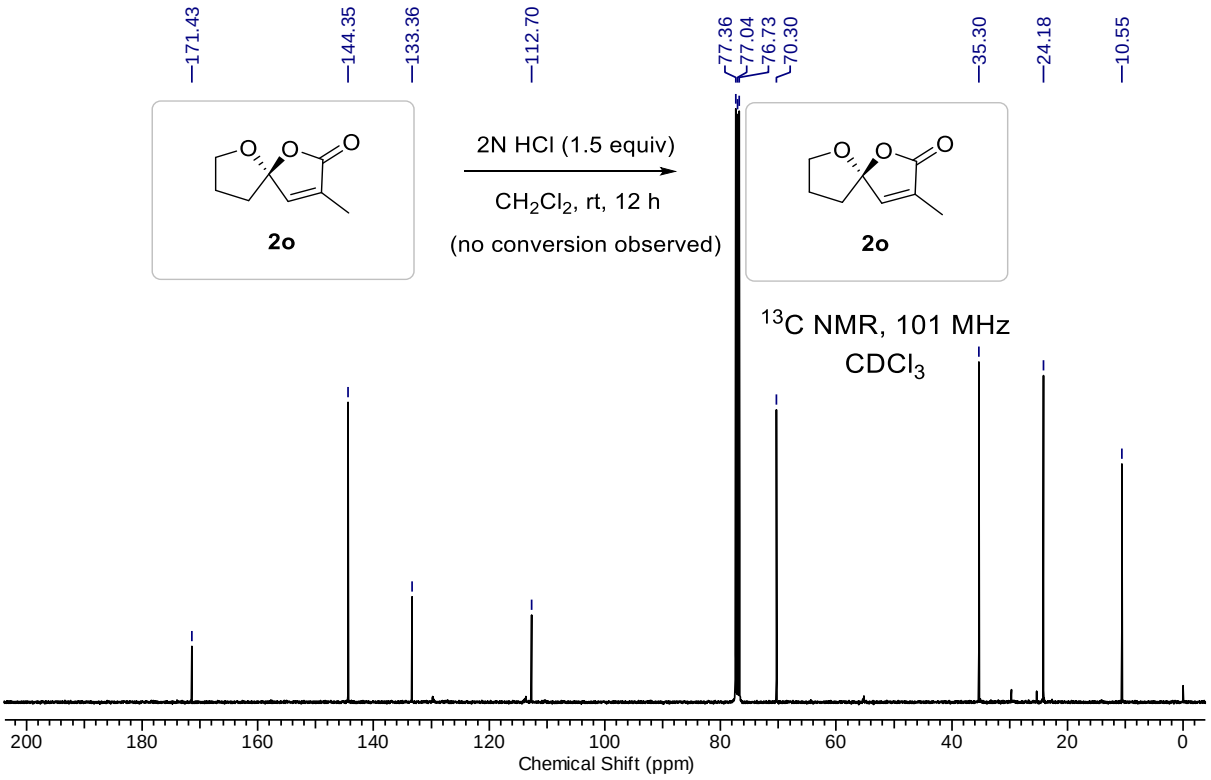
3-Methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2o):



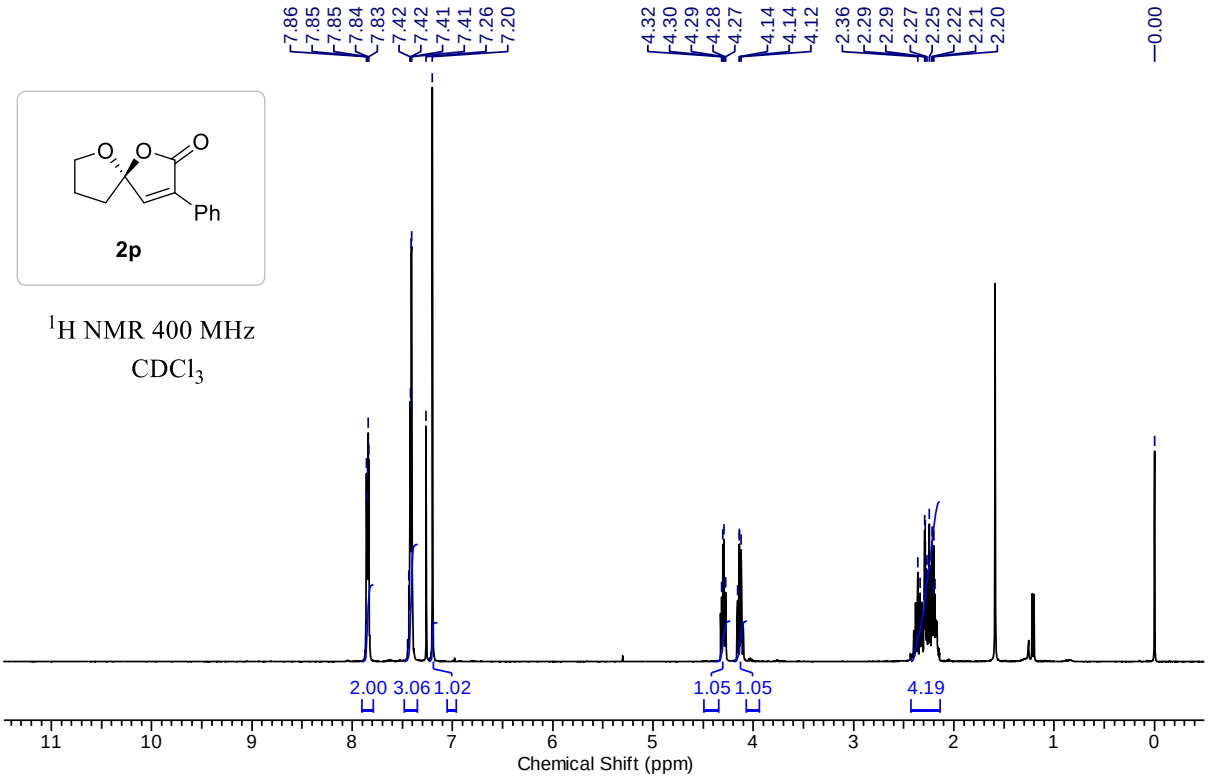


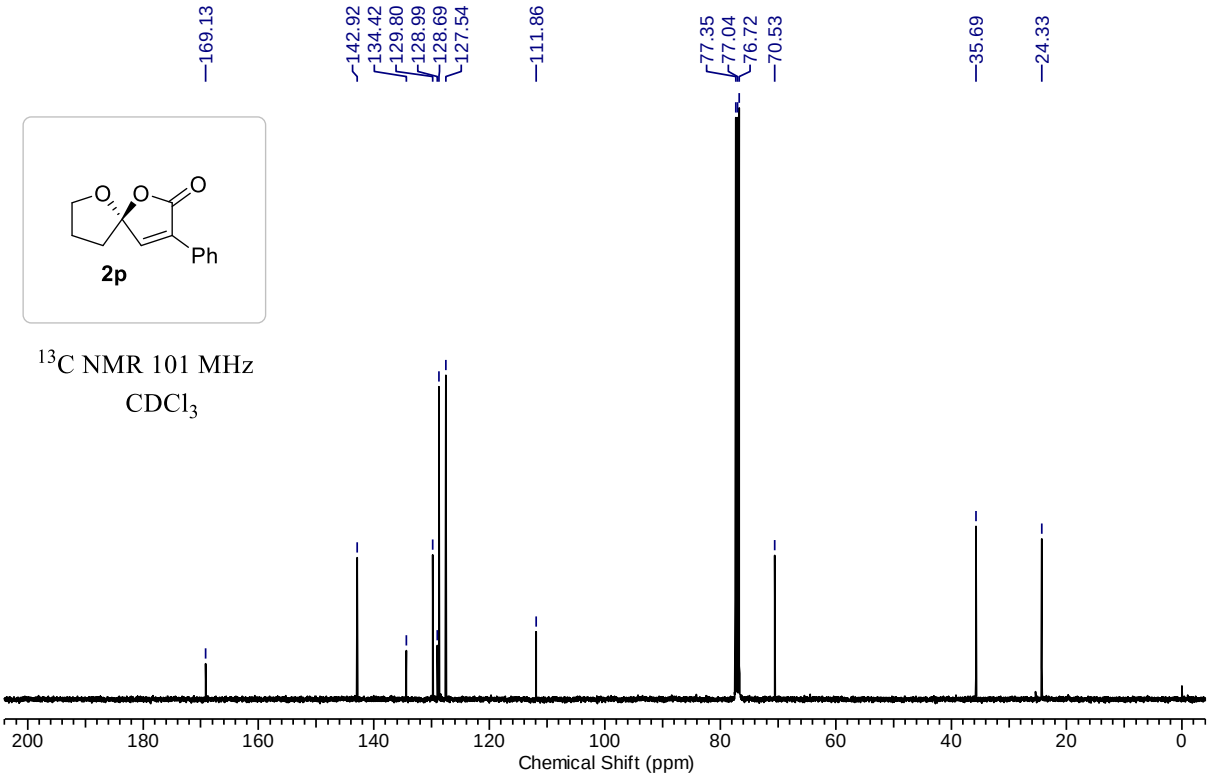
3-Methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2o):



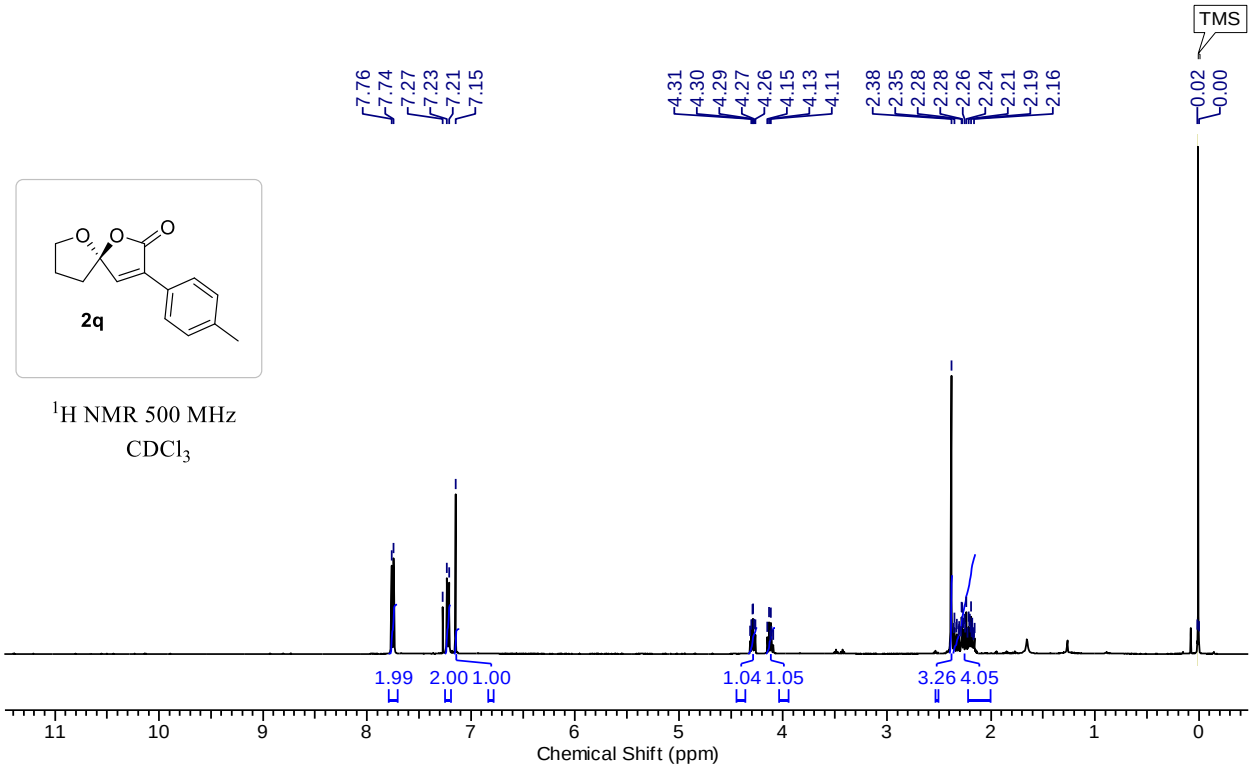


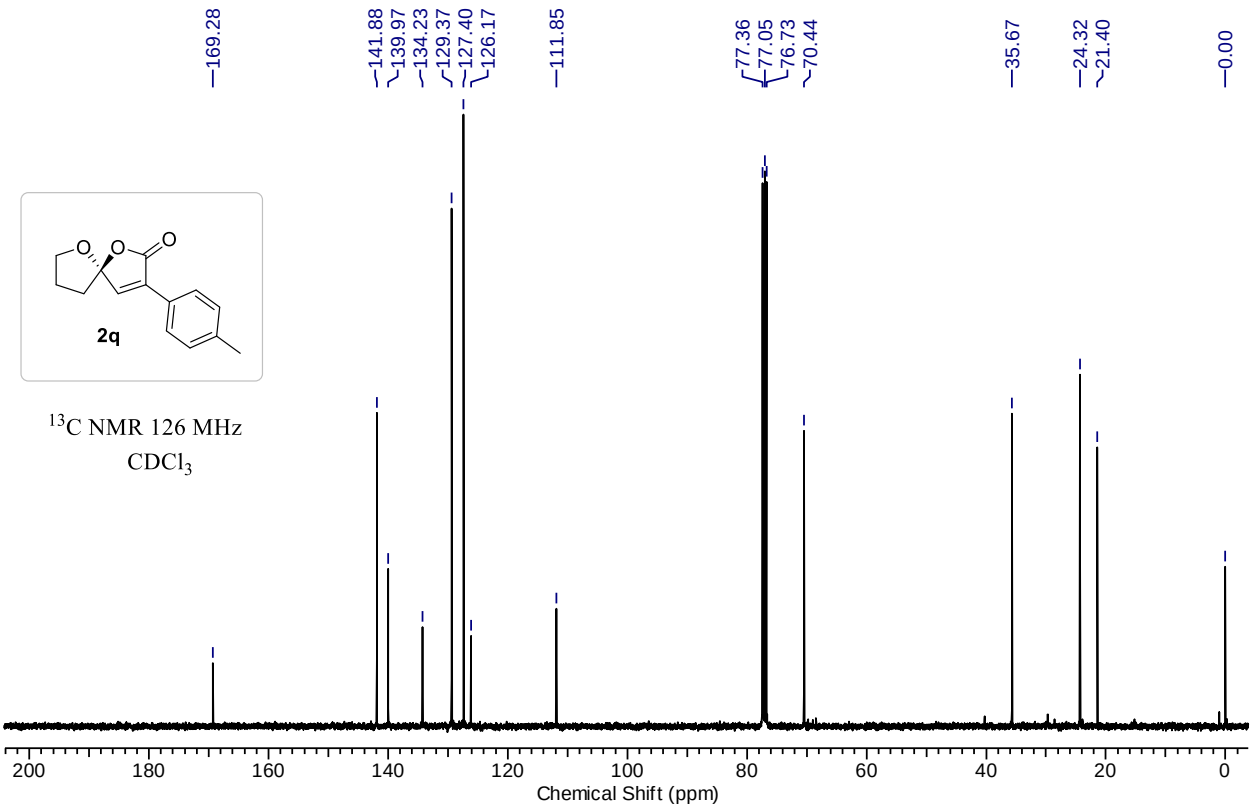
3-Phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2p):



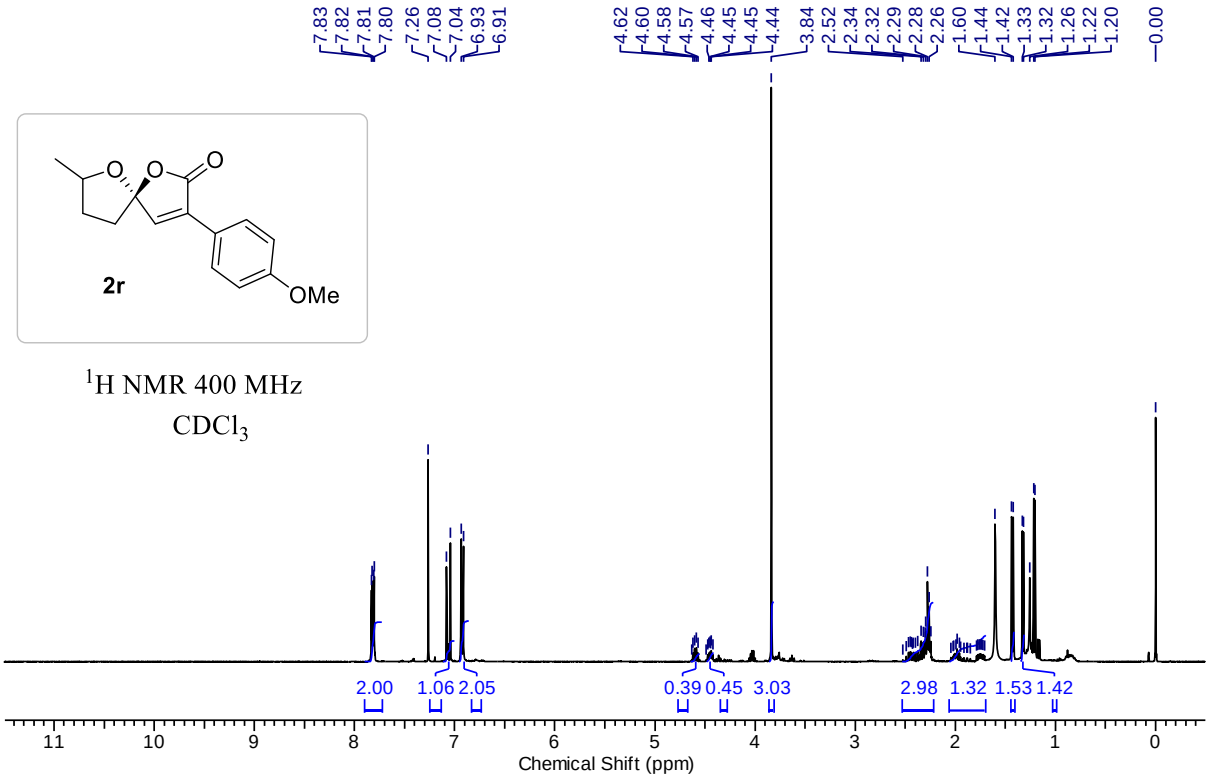


3-(*p*-Tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one (2q):

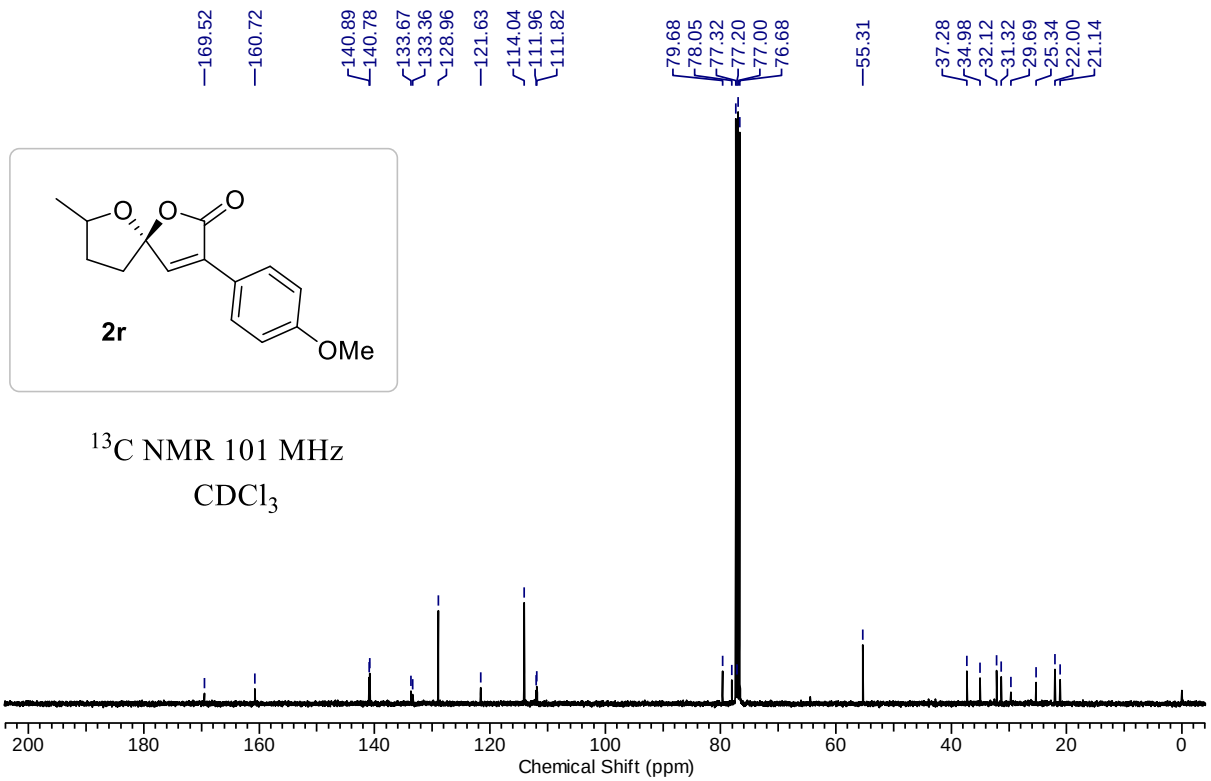




3-(4-Methoxyphenyl)-7-methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2r):

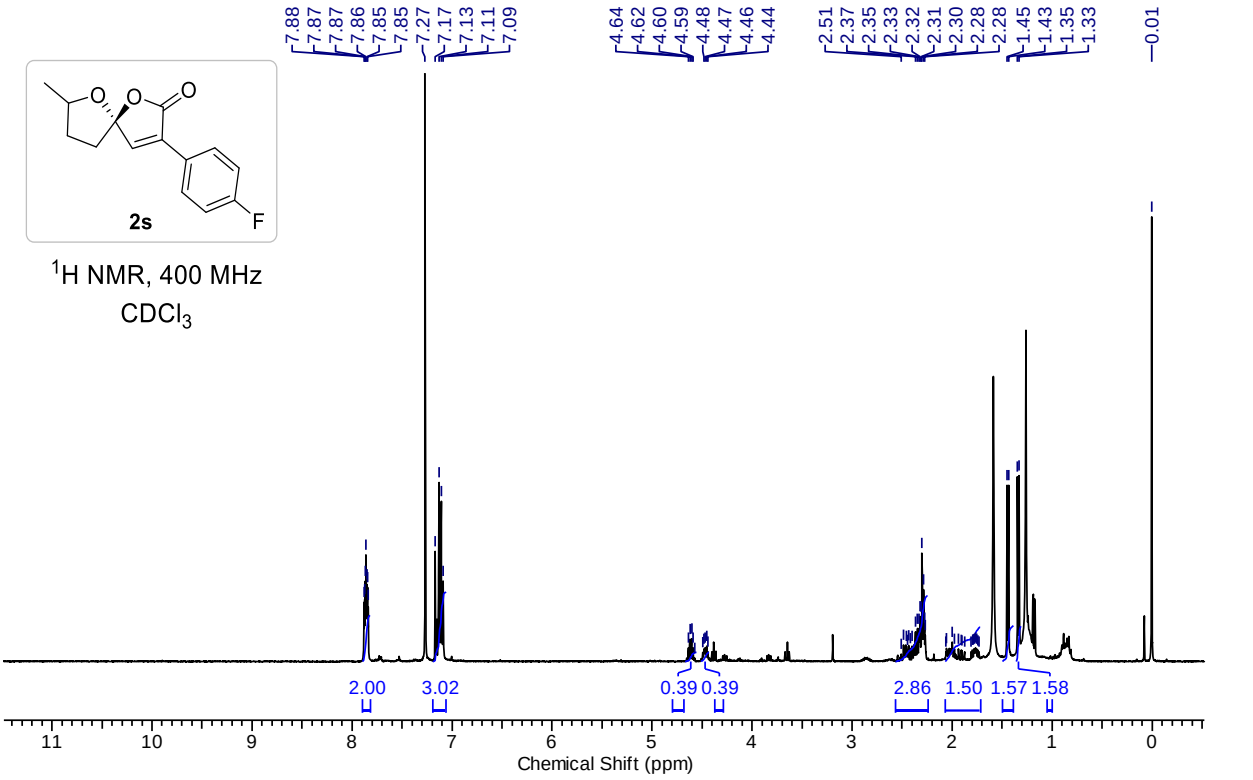


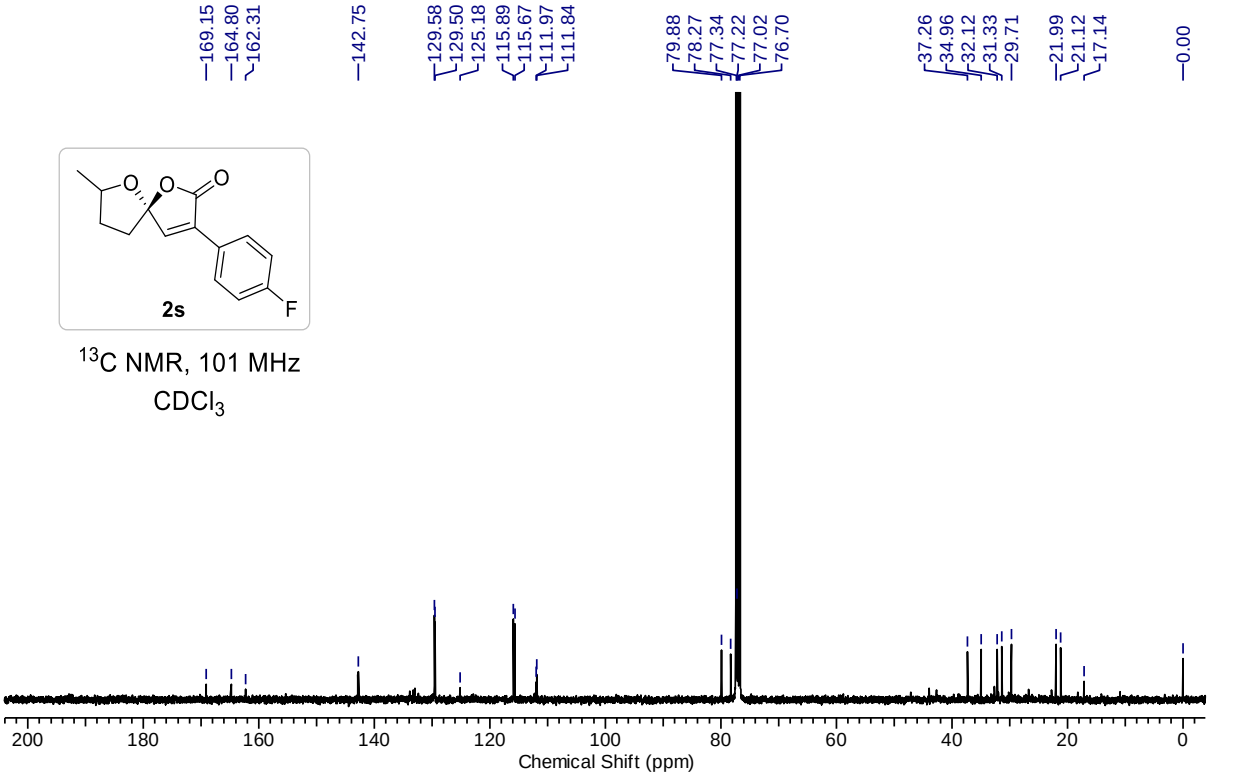
^{1}H NMR 400 MHz
$CDCl_3$

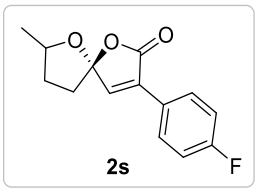


^{13}C NMR 101 MHz
$CDCl_3$

3-(4-Fluorophenyl)-7-methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (2s):







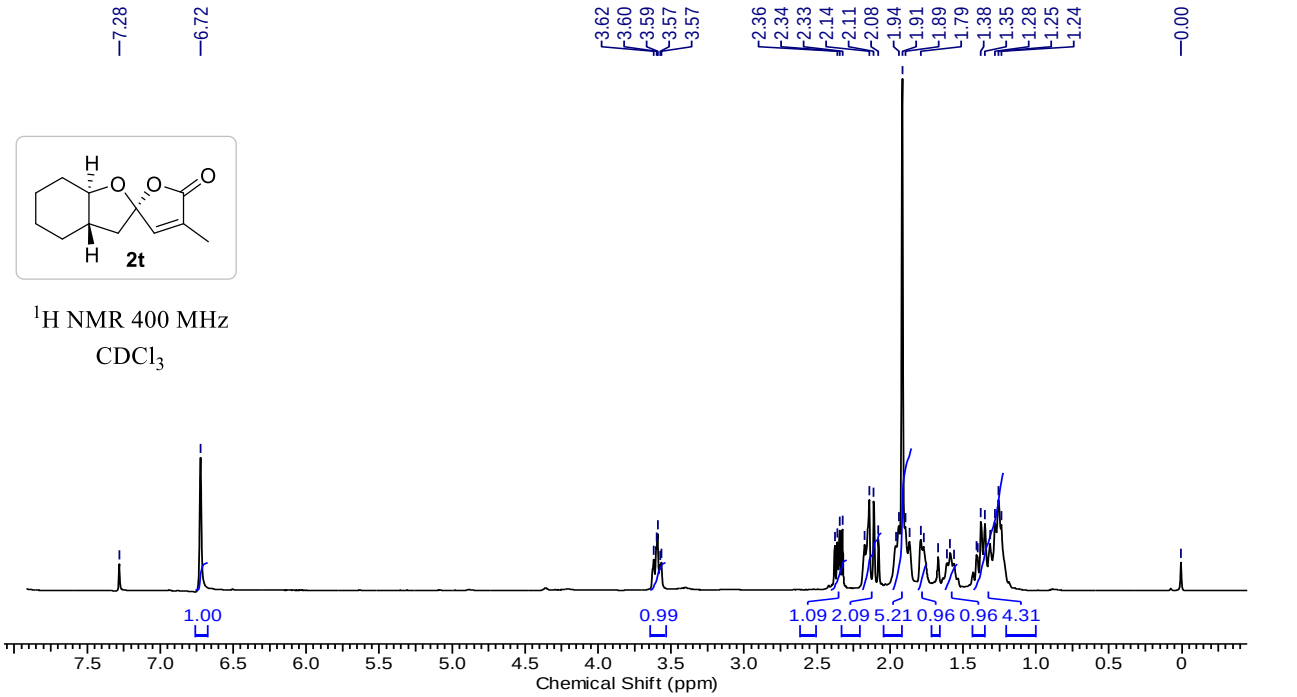
2s

^{19}F NMR, 376 MHz

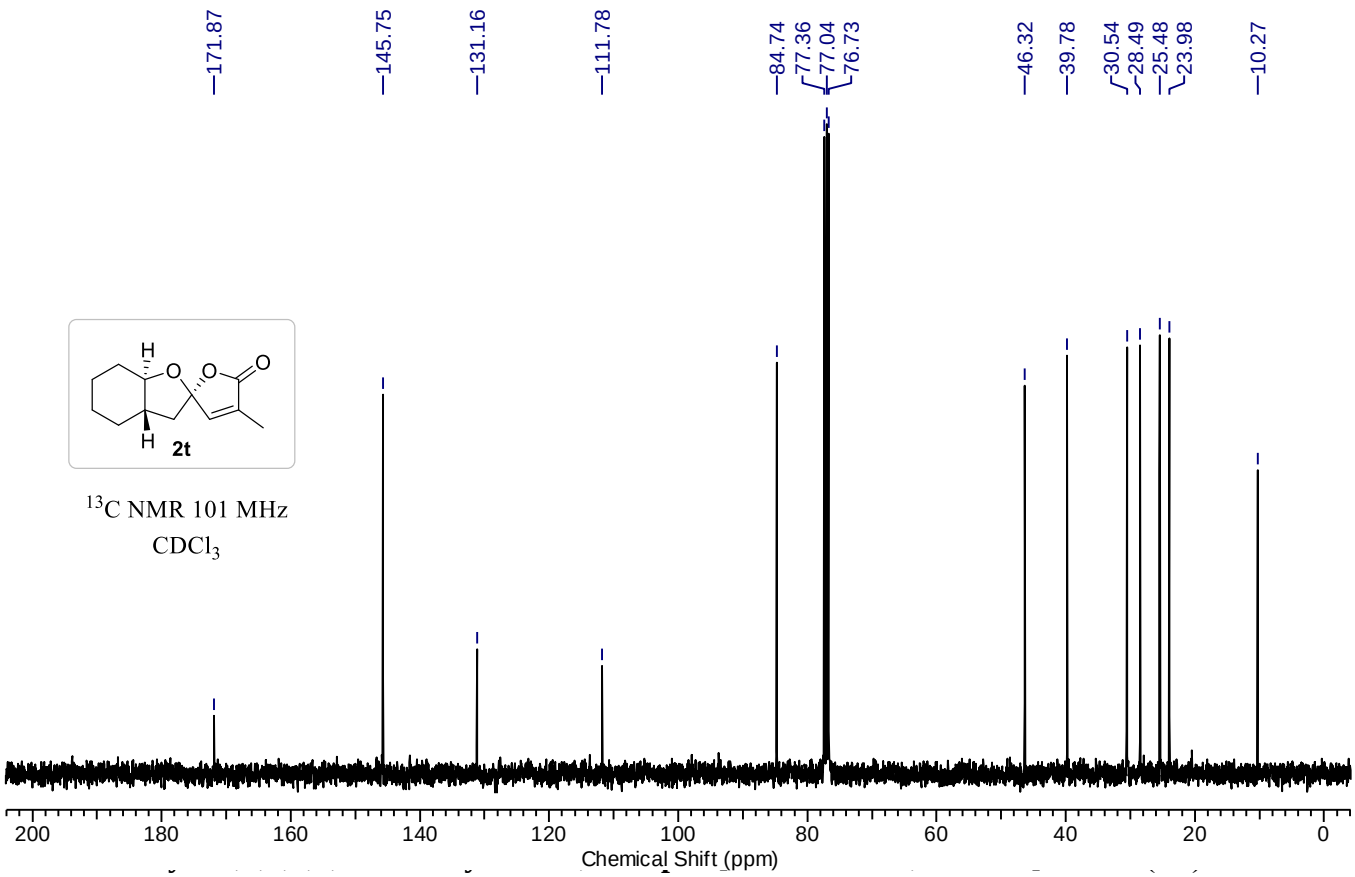
$CDCl_3$

4'-

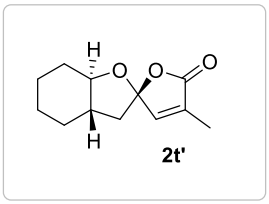
Methyl-3a,4,5,6,7,7a-hexahydro-3H,5'*H*-spiro[benzofuran-2,2'-furan]-5'-one (2t):



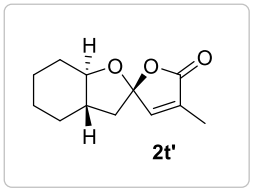
^{1}H NMR 400 MHz
$CDCl_3$



^{13}C NMR 101 MHz
$CDCl_3$

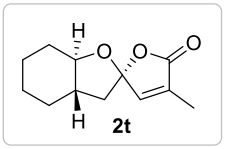


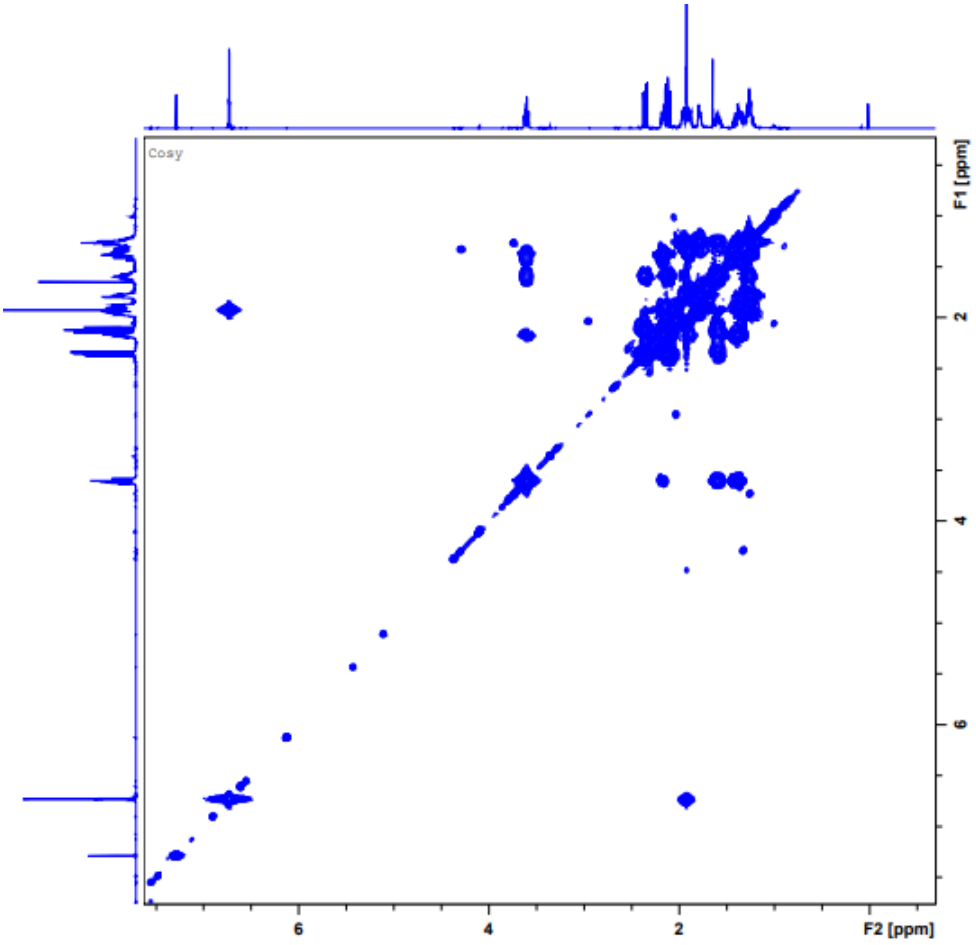
^{1}H NMR 500 MHz
$CDCl_3$



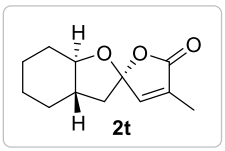
^{13}C NMR 126 MHz
$CDCl_3$

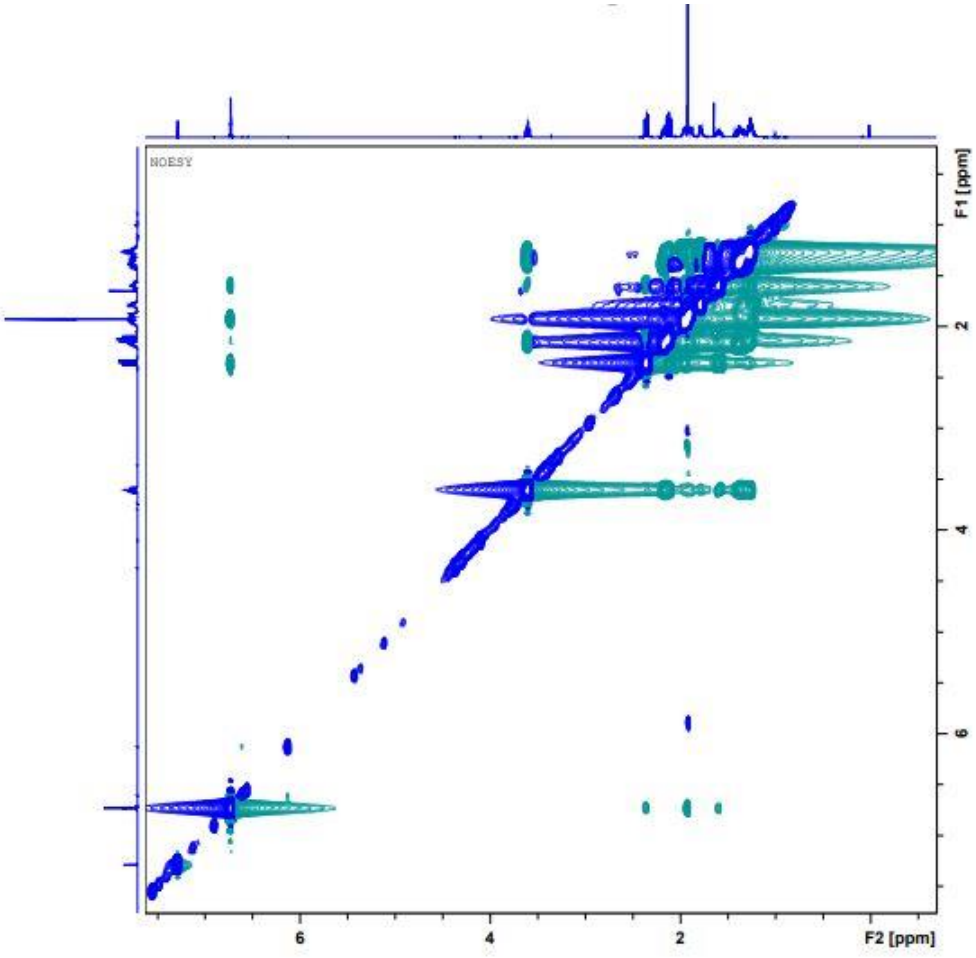
COSY: (2t)



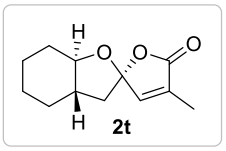


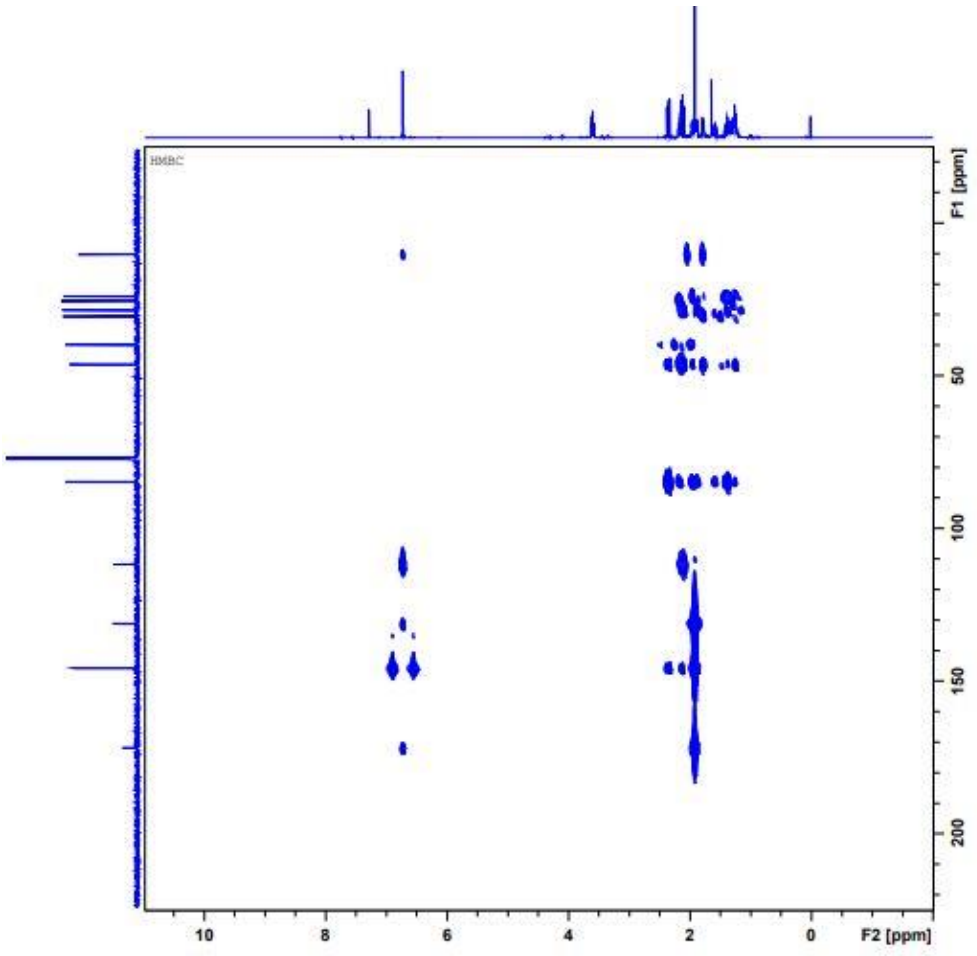
NOESY: (2t)



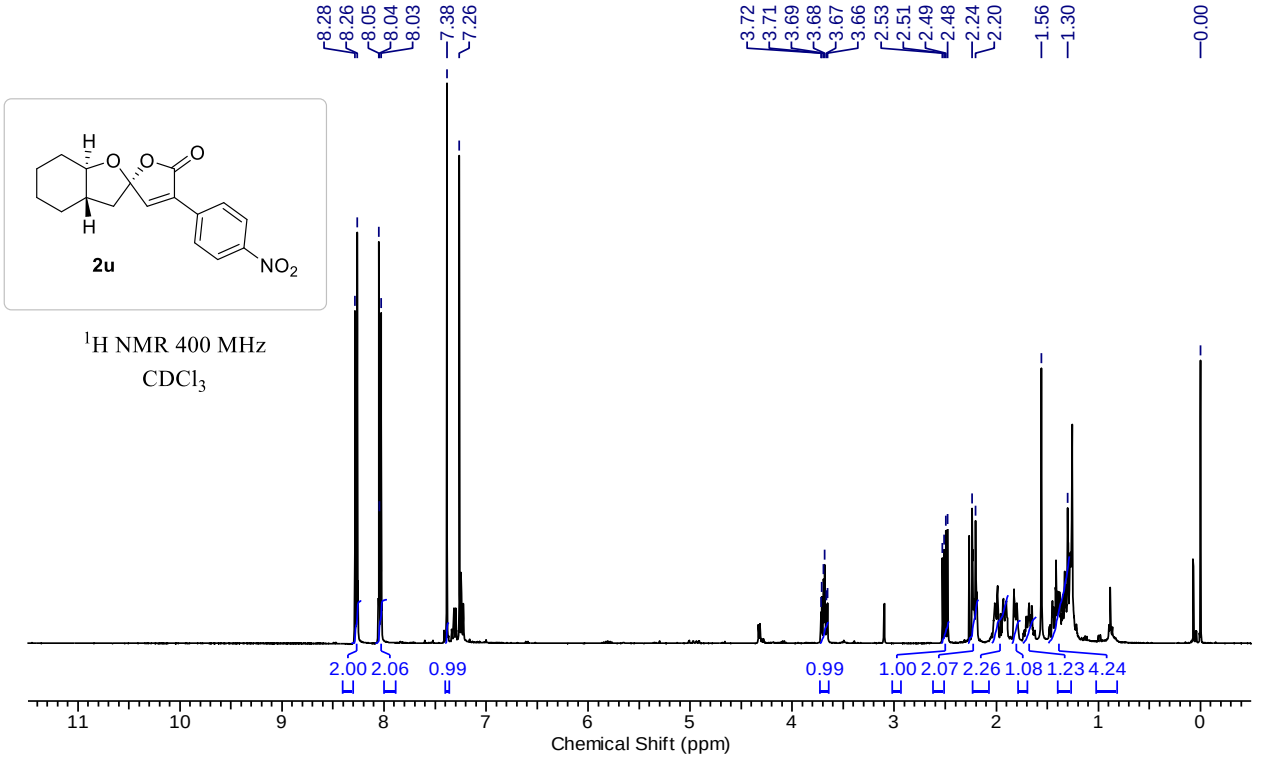


HMBC: (2t)

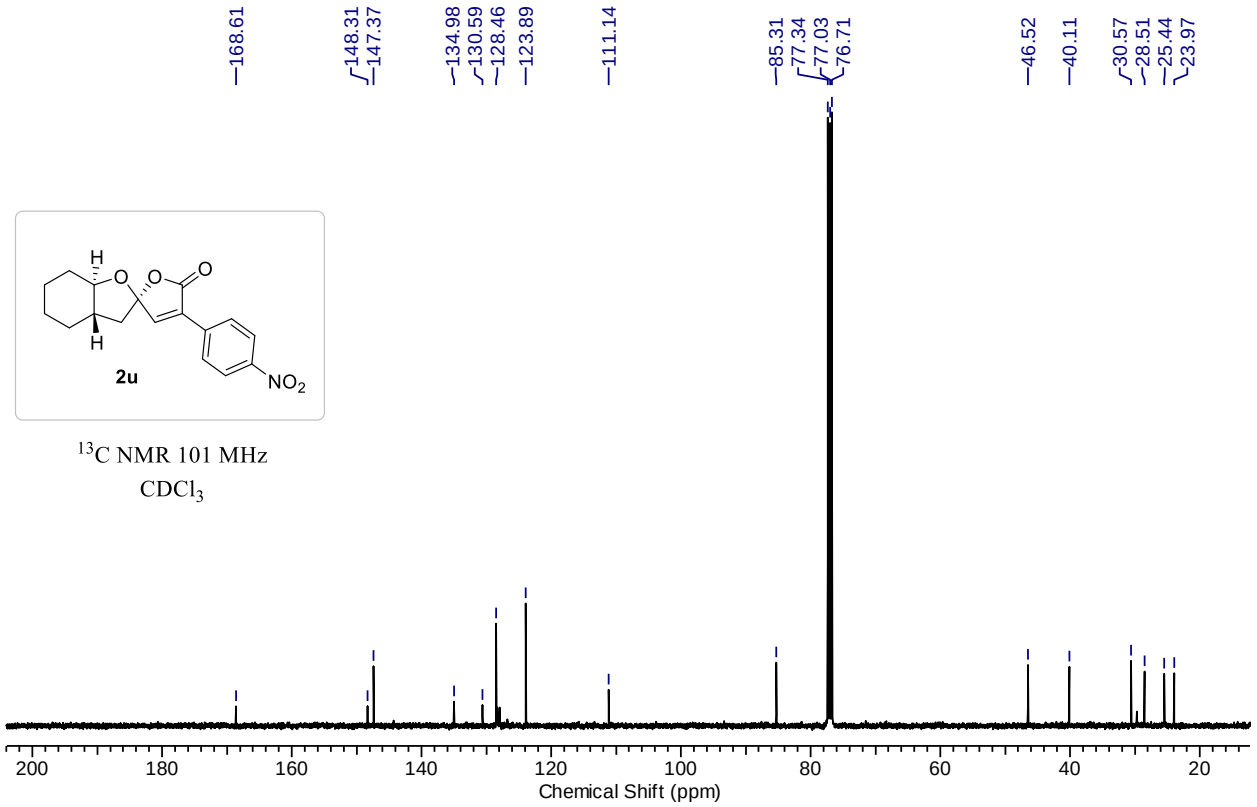




4'-(4-Nitrophenyl)-3a,4,5,6,7,7a-hexahydro-3H,5'*H*-spiro[benzofuran-2,2'-furan]-5'-one (2u):

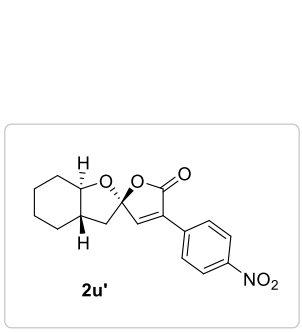


^{1}H NMR 400 MHz
$CDCl_3$

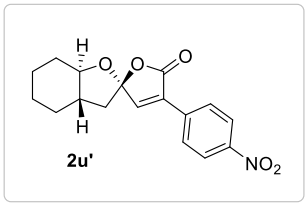


^{13}C NMR 101 MHz
$CDCl_3$

4'-(4-Nitrophenyl)-3a,4,5,6,7,7a-hexahydro-3*H*,5'*H*-spiro[benzofuran-2,2'-furan]-5'-one (2u'):

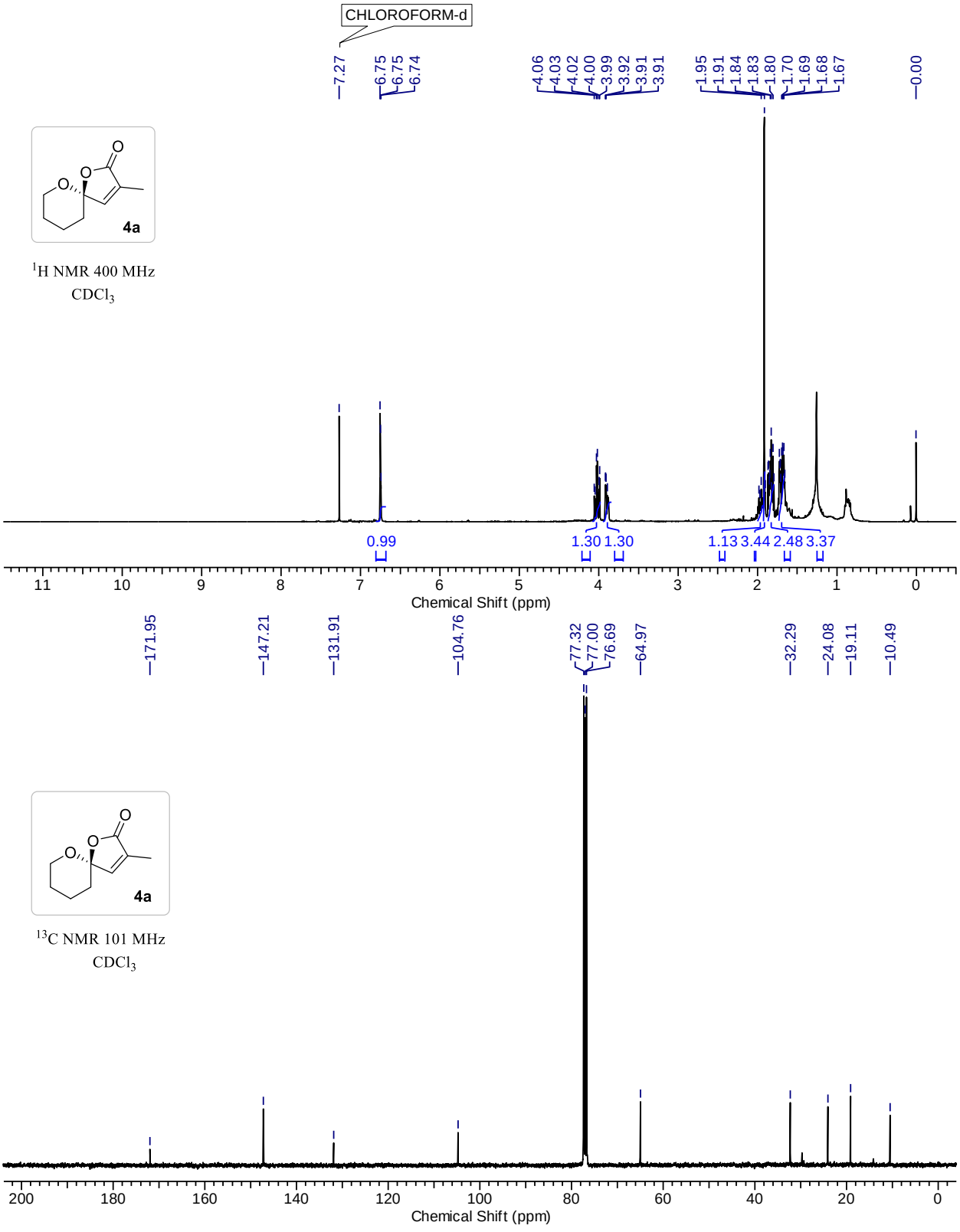


^{1}H NMR 400 MHz
$CDCl_3$

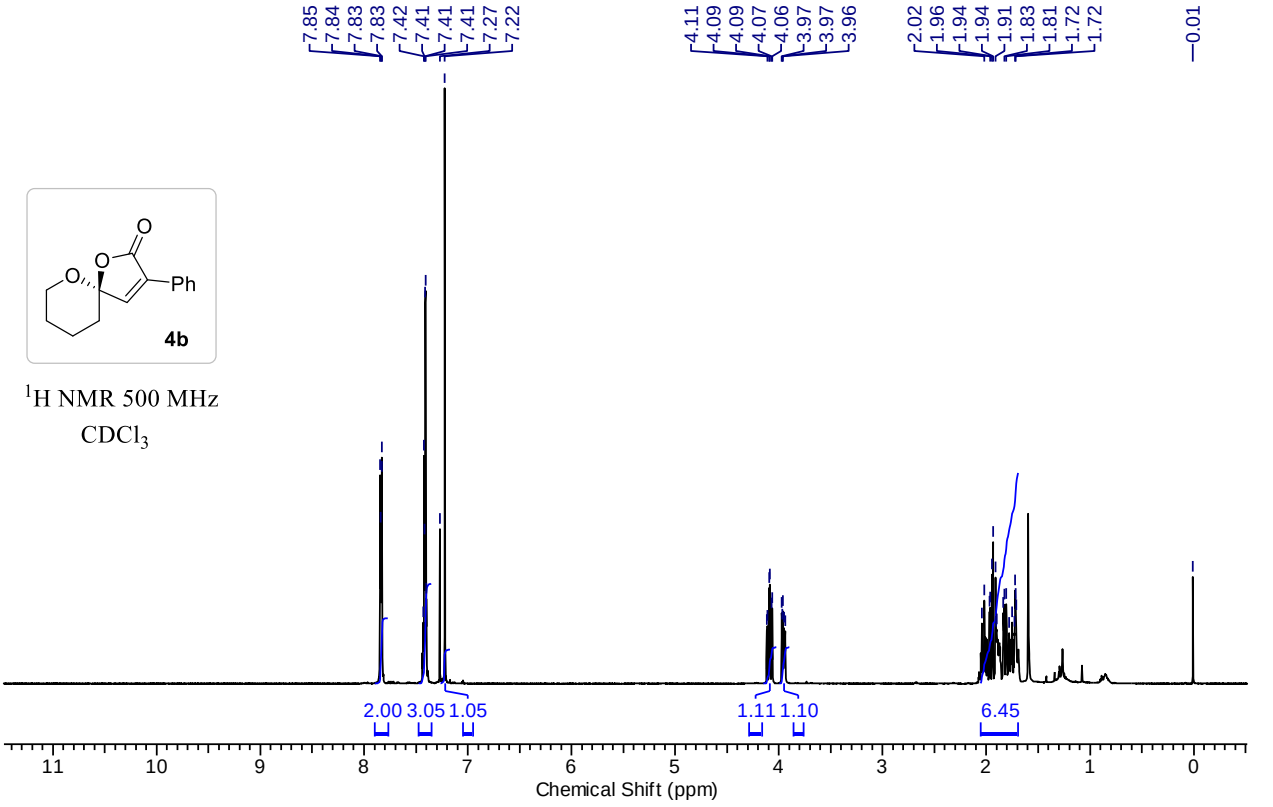


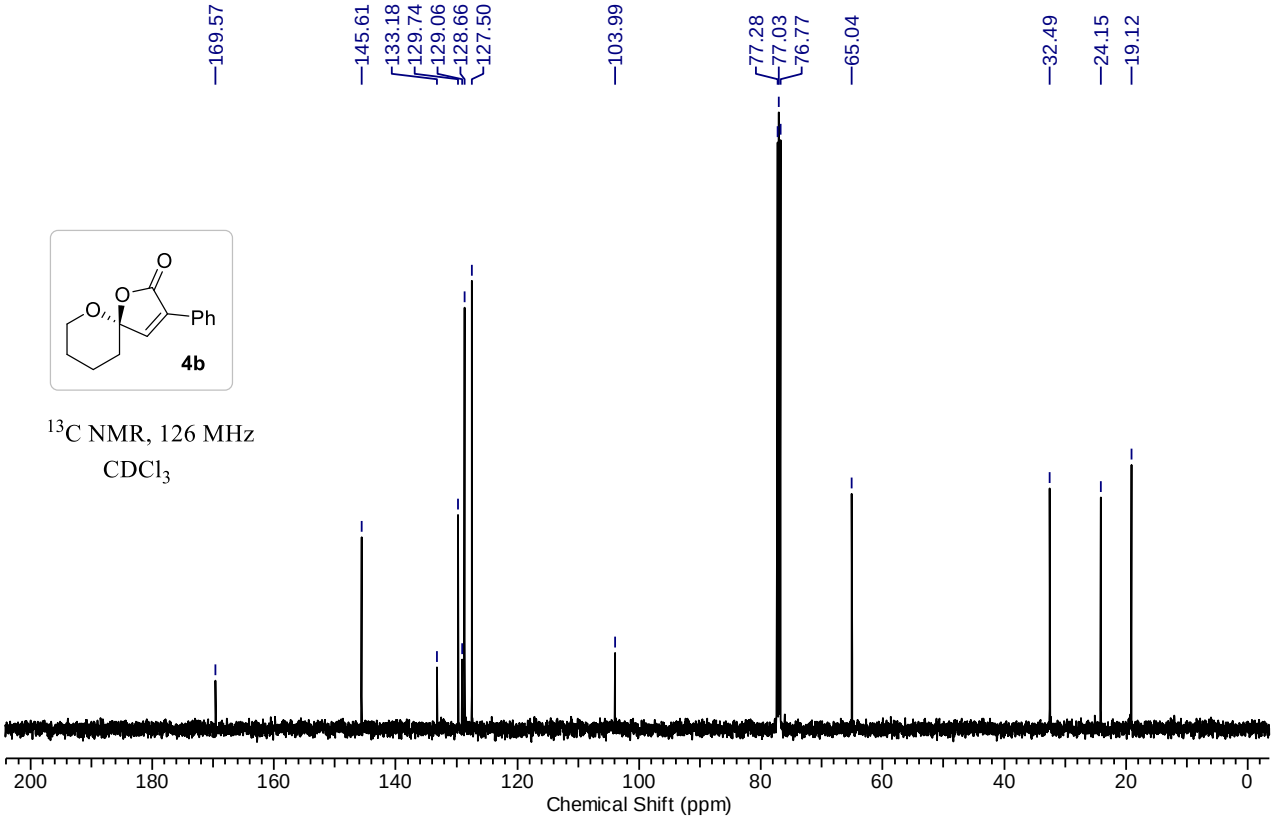
^{13}C NMR 101 MHz
$CDCl_3$

3-Methyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4a):

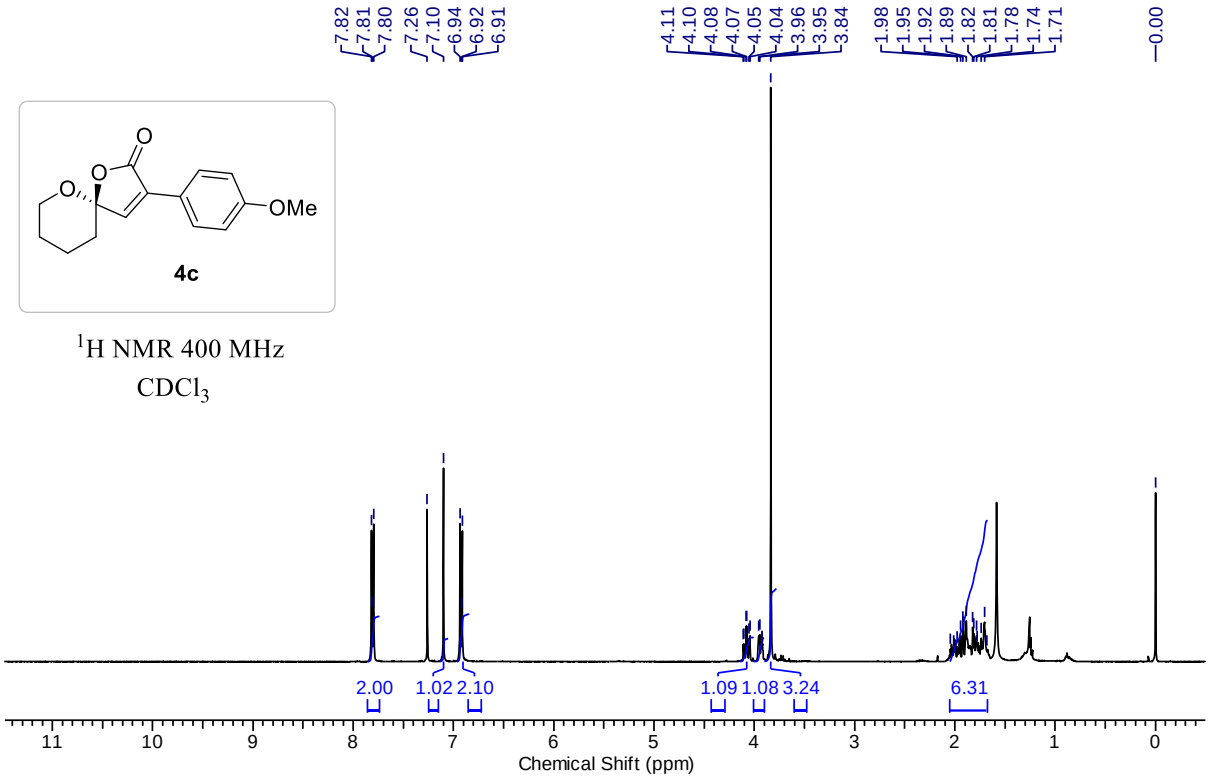


3-Phenyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4b):

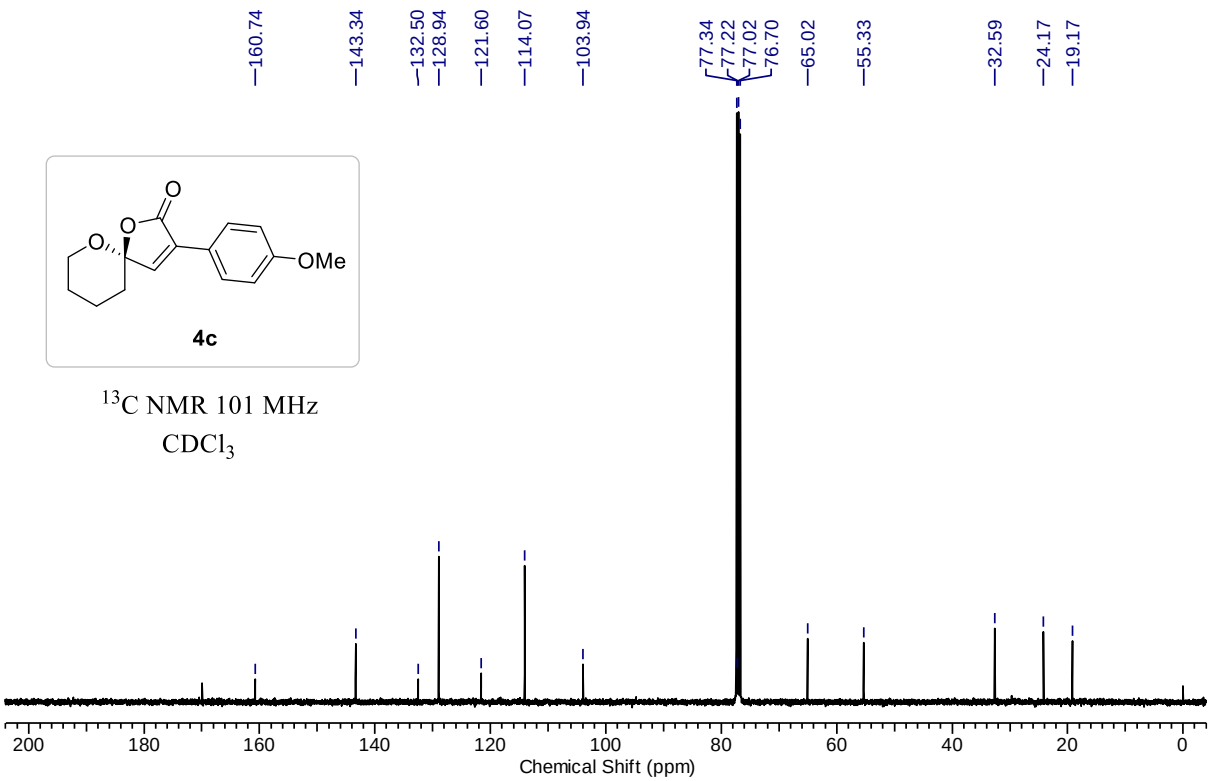




3-(4-Methoxyphenyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4c):

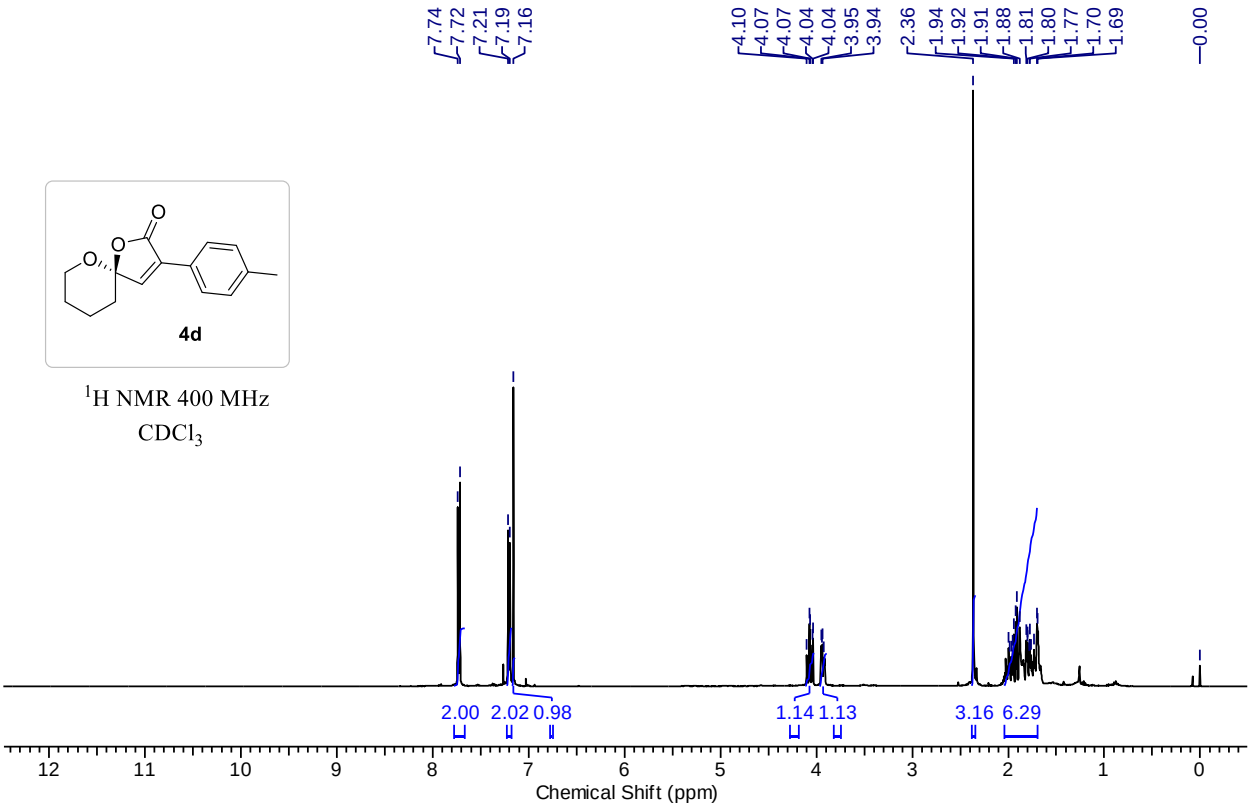


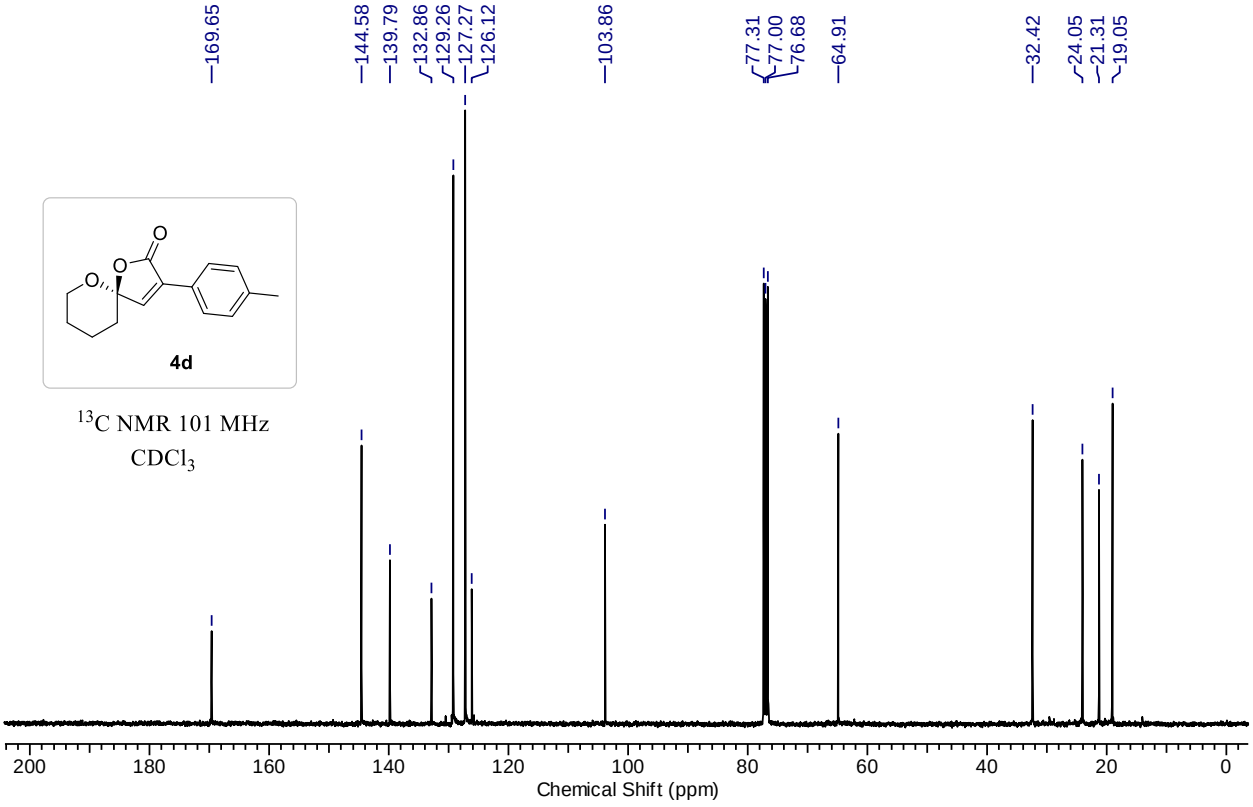
^{1}H NMR 400 MHz
$CDCl_3$



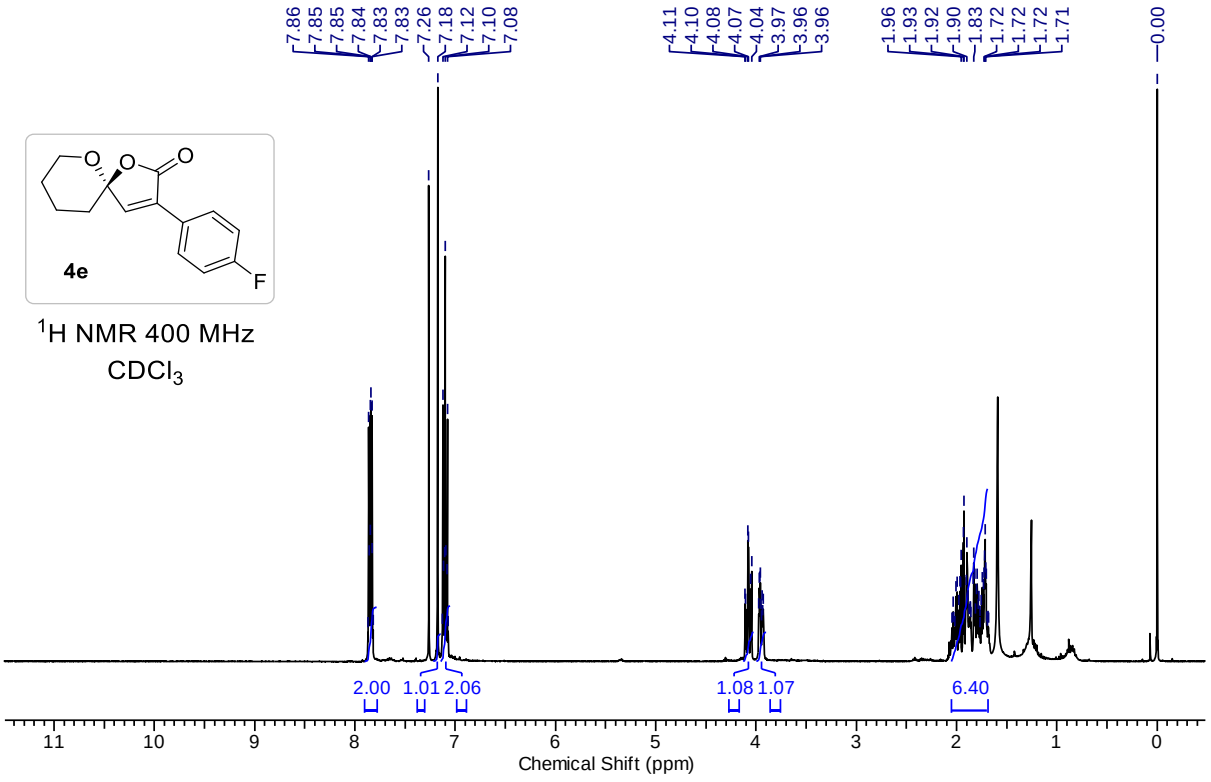
^{13}C NMR 101 MHz
$CDCl_3$

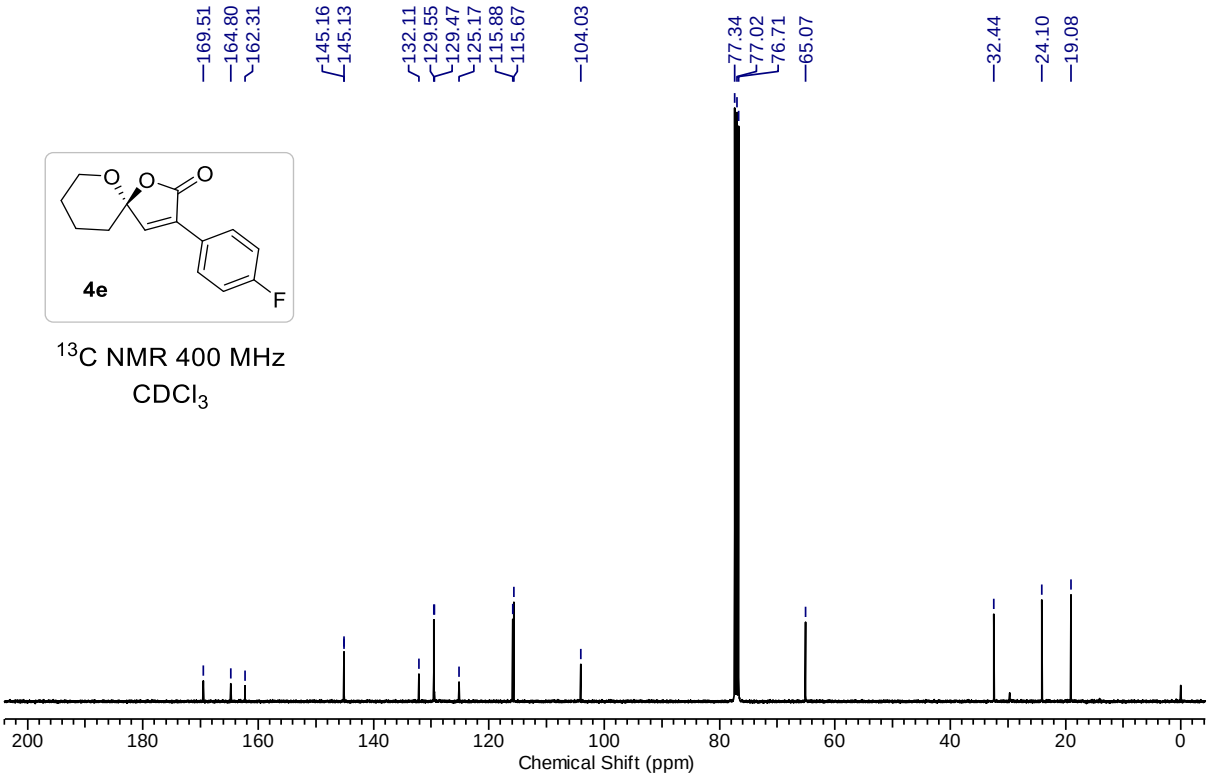
3-(*p*-Tolyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4d):

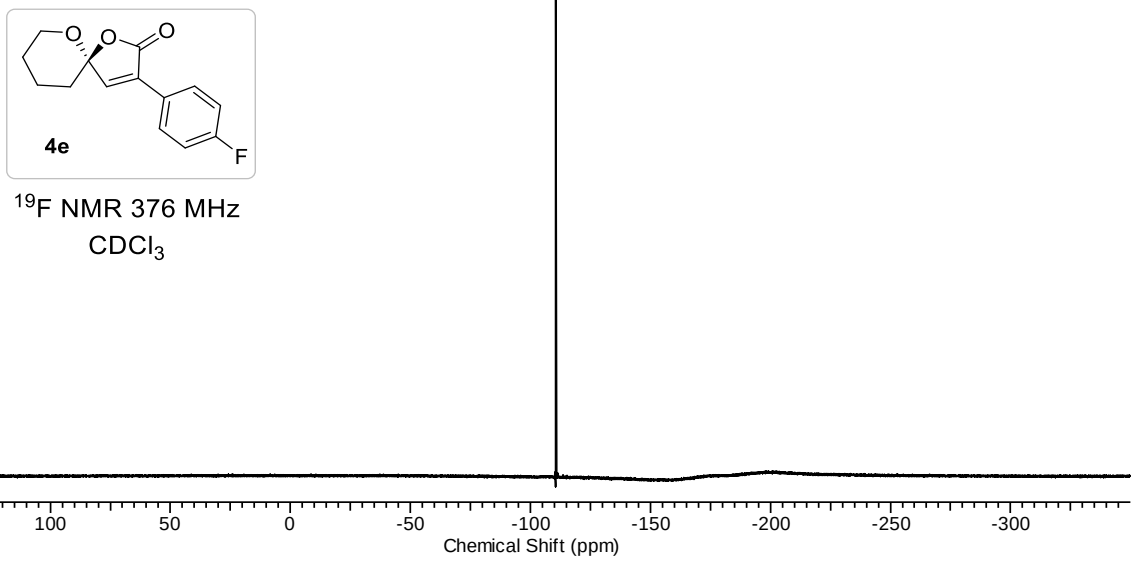




3-(4-Fluorophenyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4e):





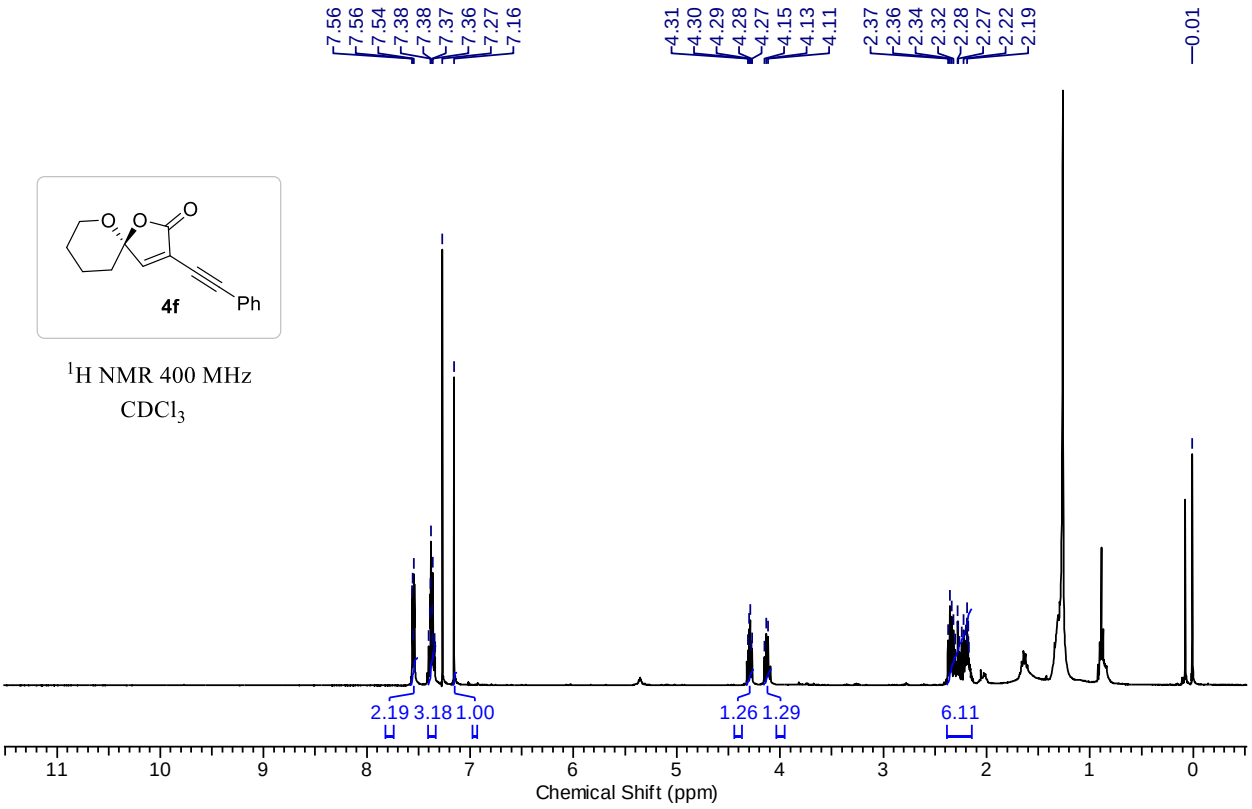


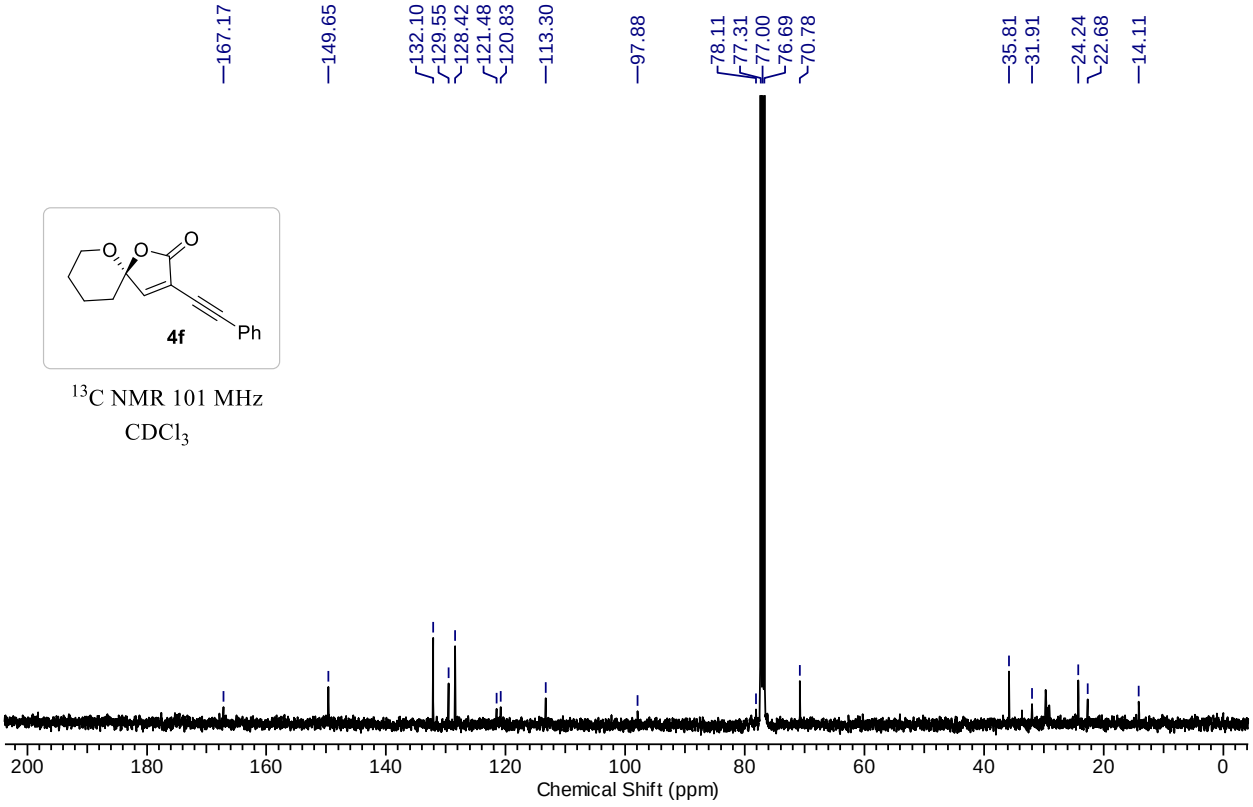
4e

^{19}F NMR 376 MHz

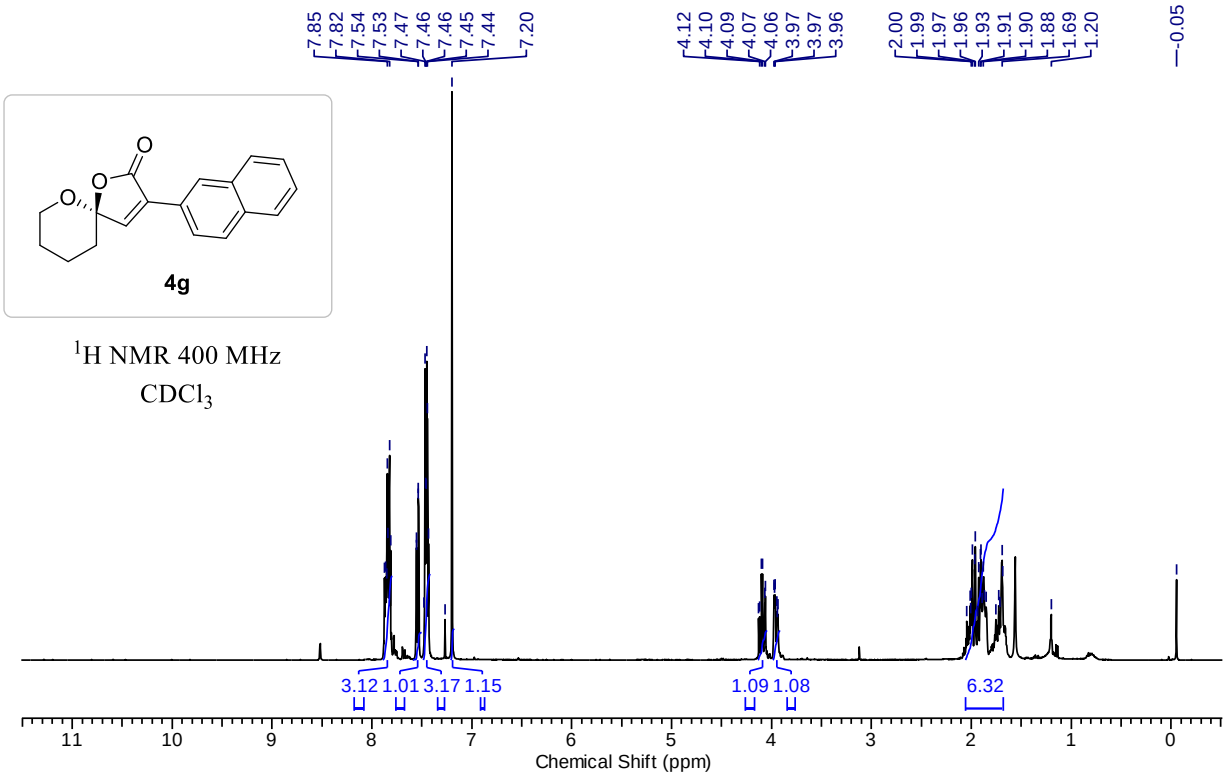
$CDCl_3$

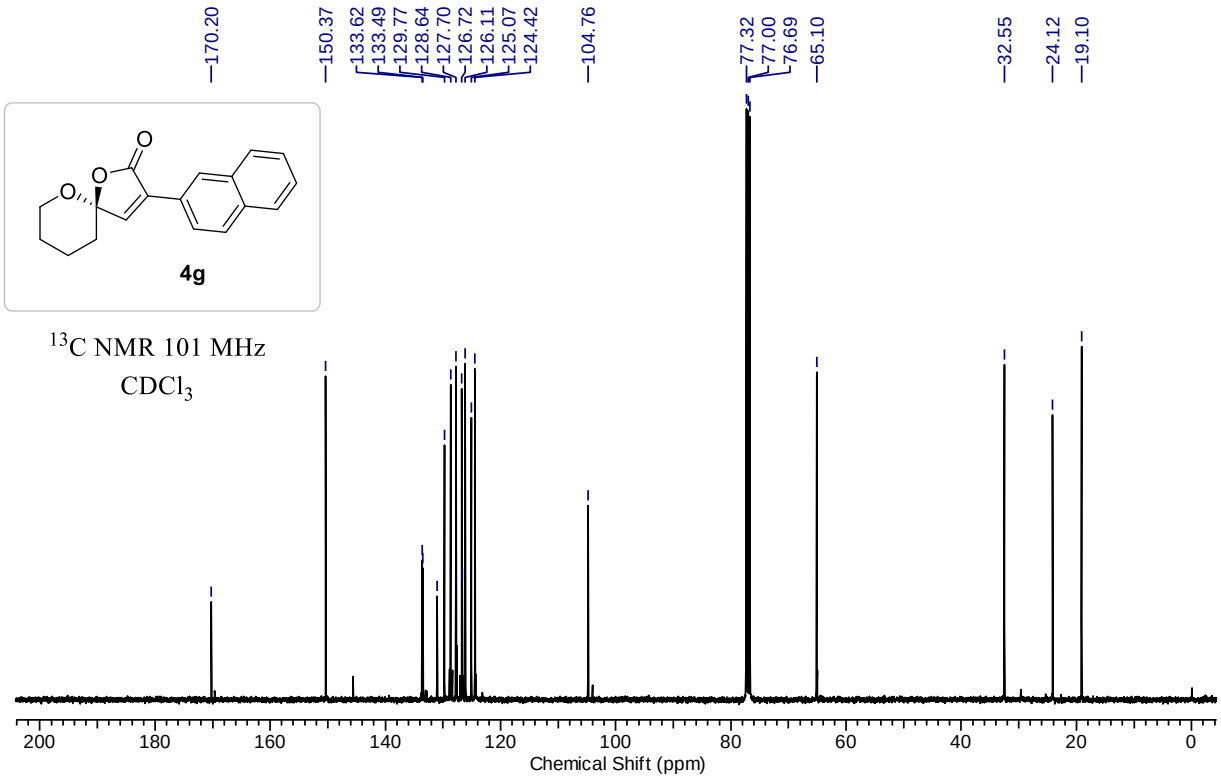
3-(Phenylethynyl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4f):



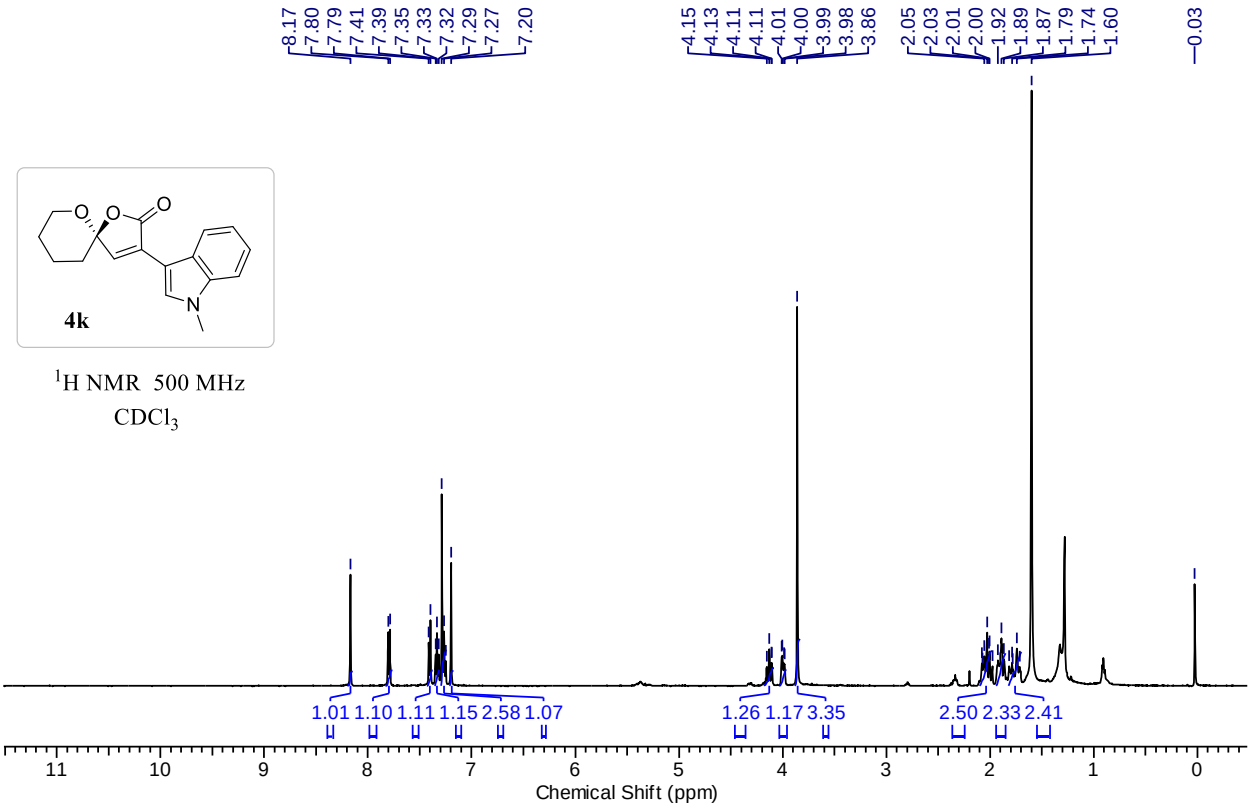


3-(Naphthalen-2-yl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4g):

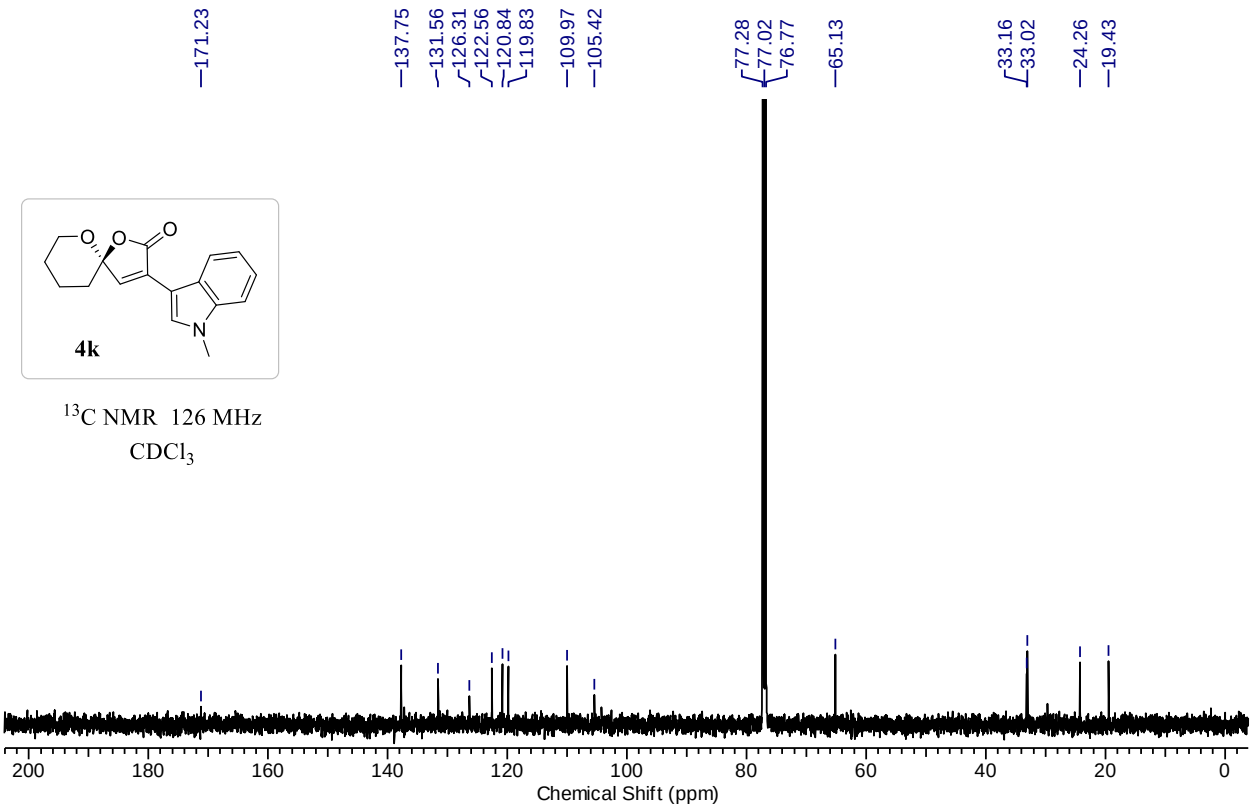




3-(1-Methyl-1*H*-indol-3-yl)-1,6-dioxaspiro[4.5]dec-3-en-2-one (4k):

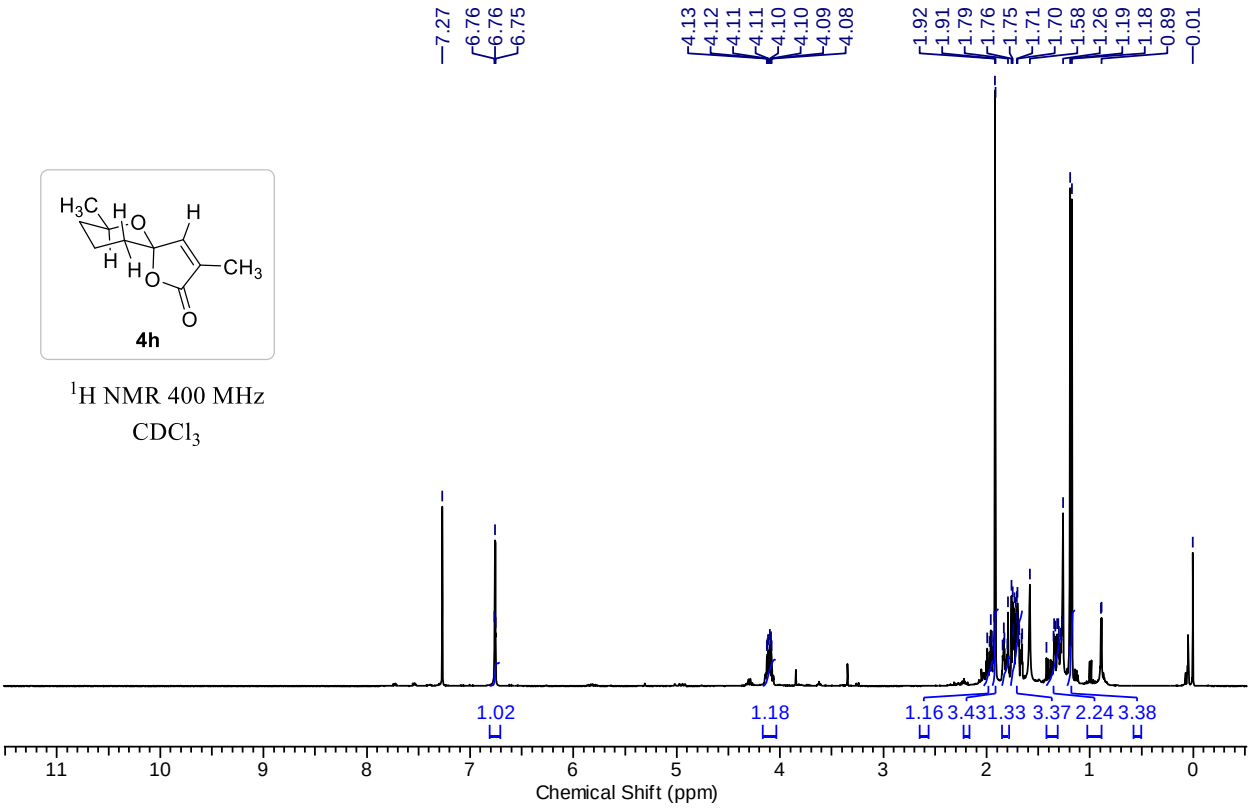


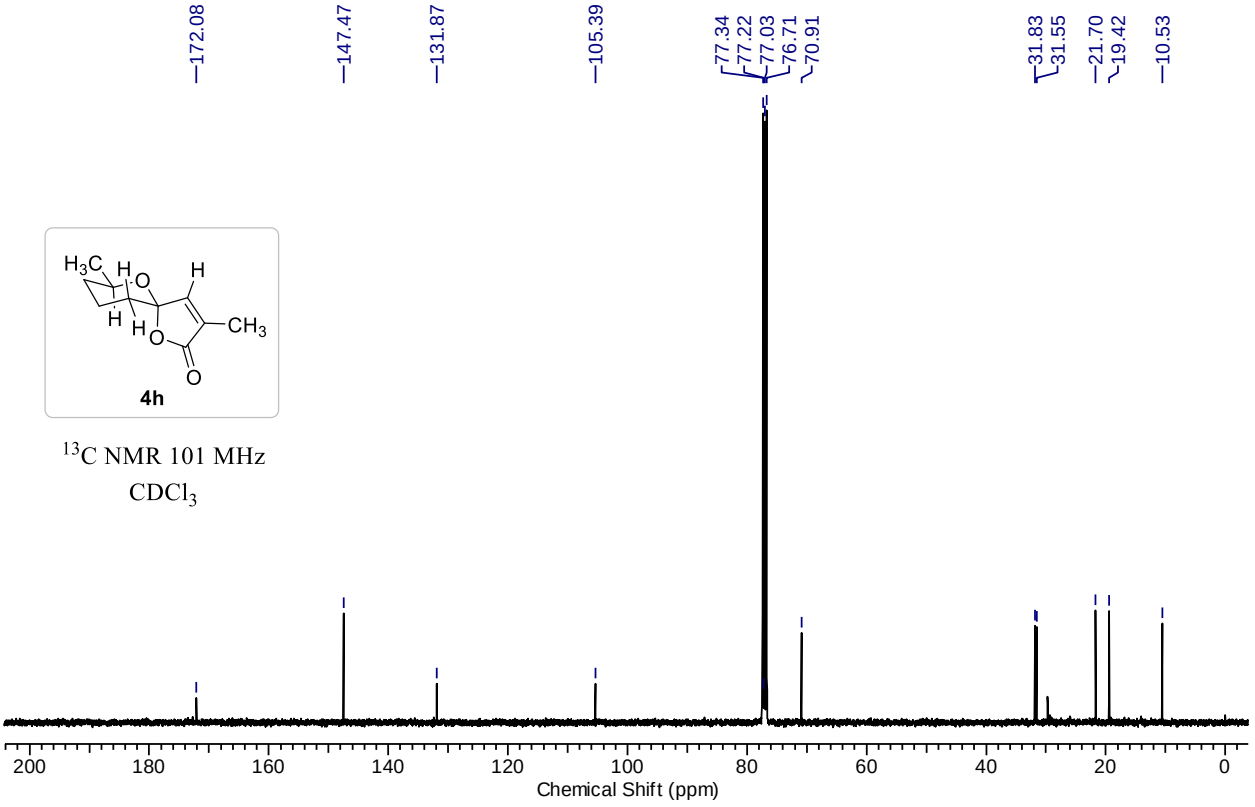
^{1}H NMR 500 MHz
$CDCl_3$



^{13}C NMR 126 MHz
$CDCl_3$

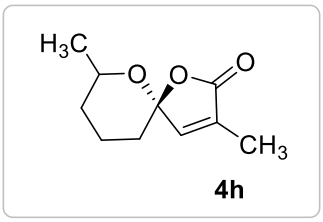
3,7-Dimethyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4h):



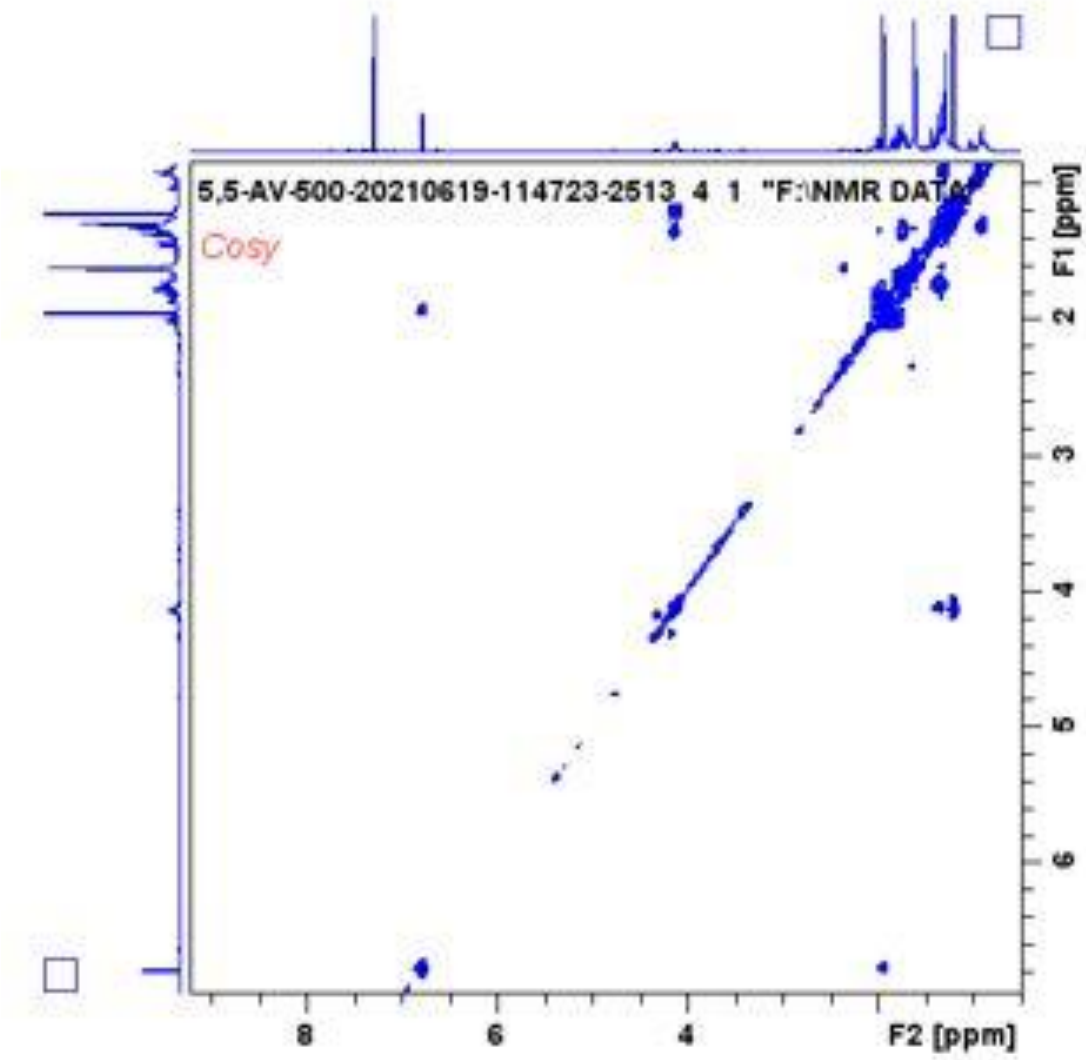


2D NMR analysis of 4h:

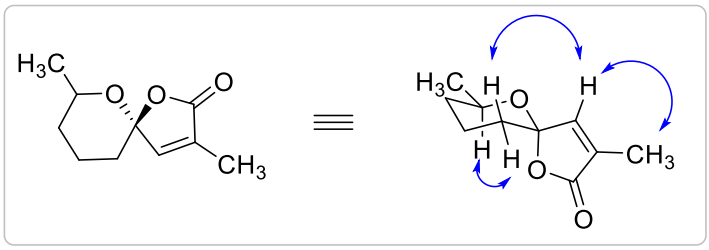
COSY: (4h)

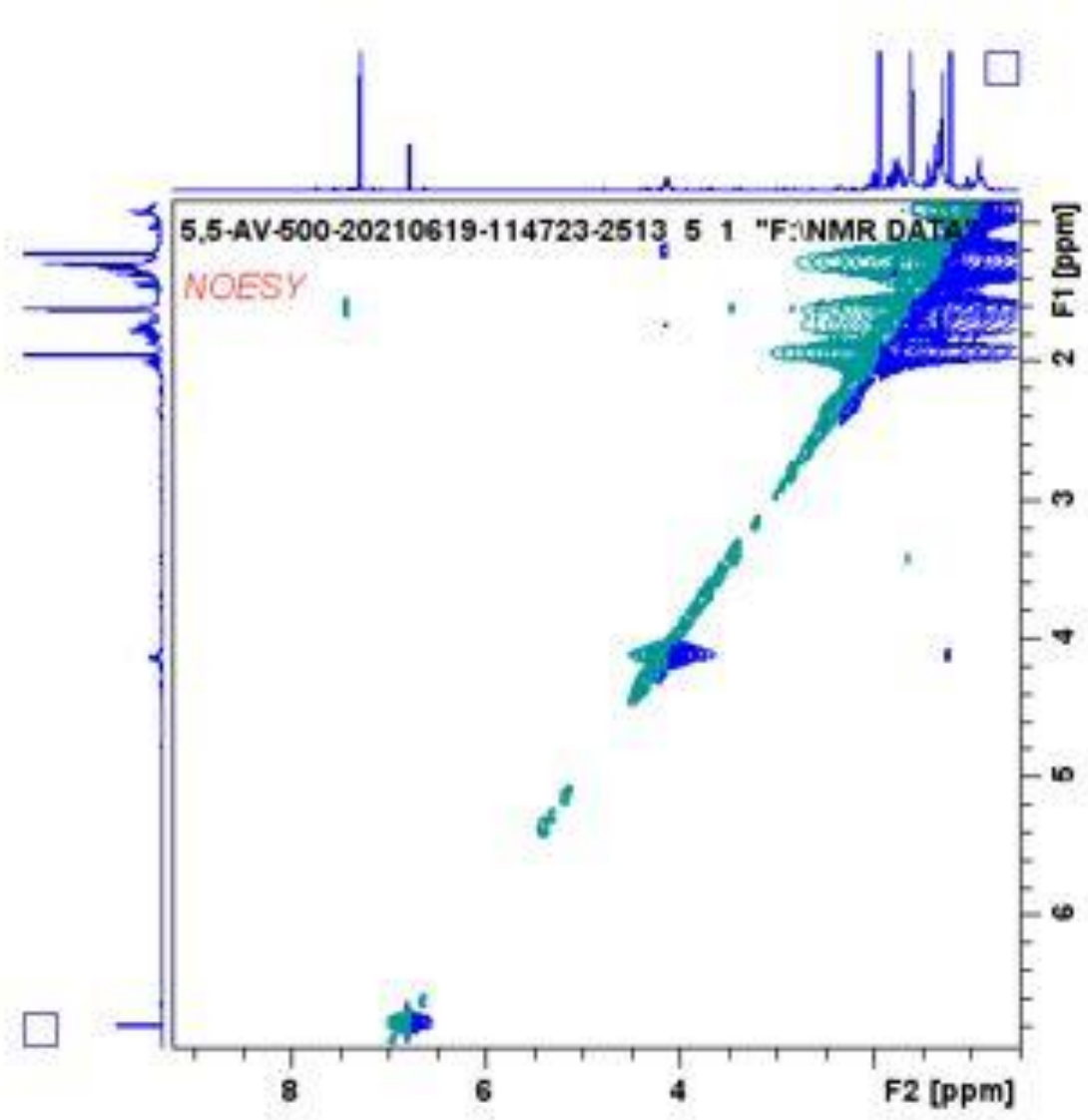


4h

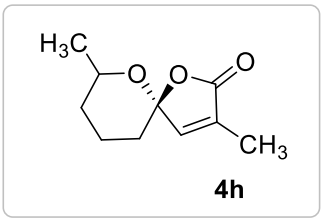


NOESY: (4h)

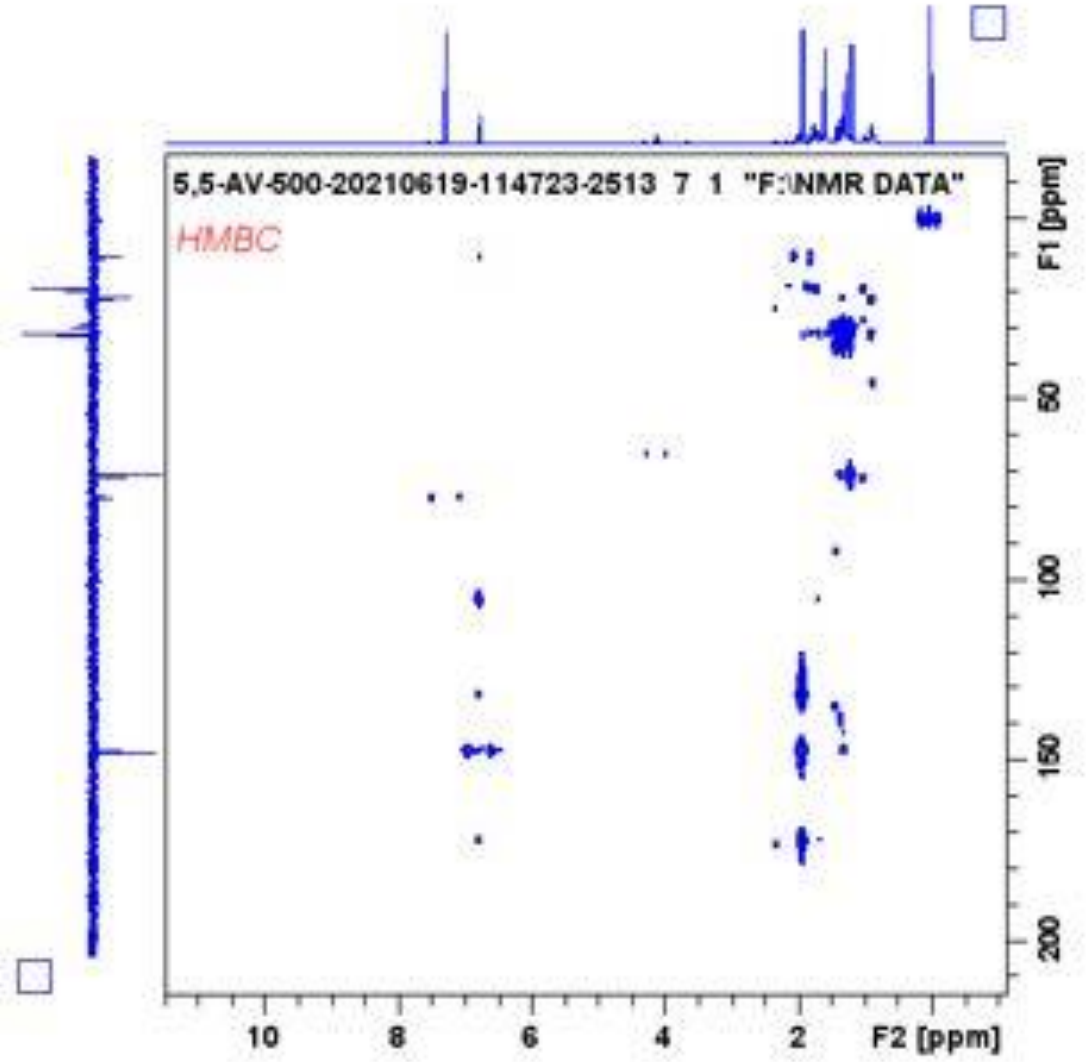

H3C
O
O
O
CH3
H3C
H
O
H
H
H
O
CH3
O


5,5-AV-500-20210619-114723-2513 5 1 "F:\NMR DATA
NOESY
F1 [ppm]
2
3
4
5
6
8
6
4
F2 [ppm]

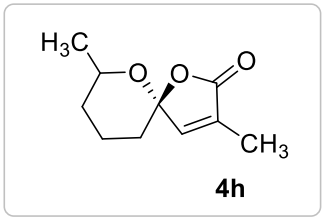
HMBC: (4h)


H3C
O
O
O
CH3

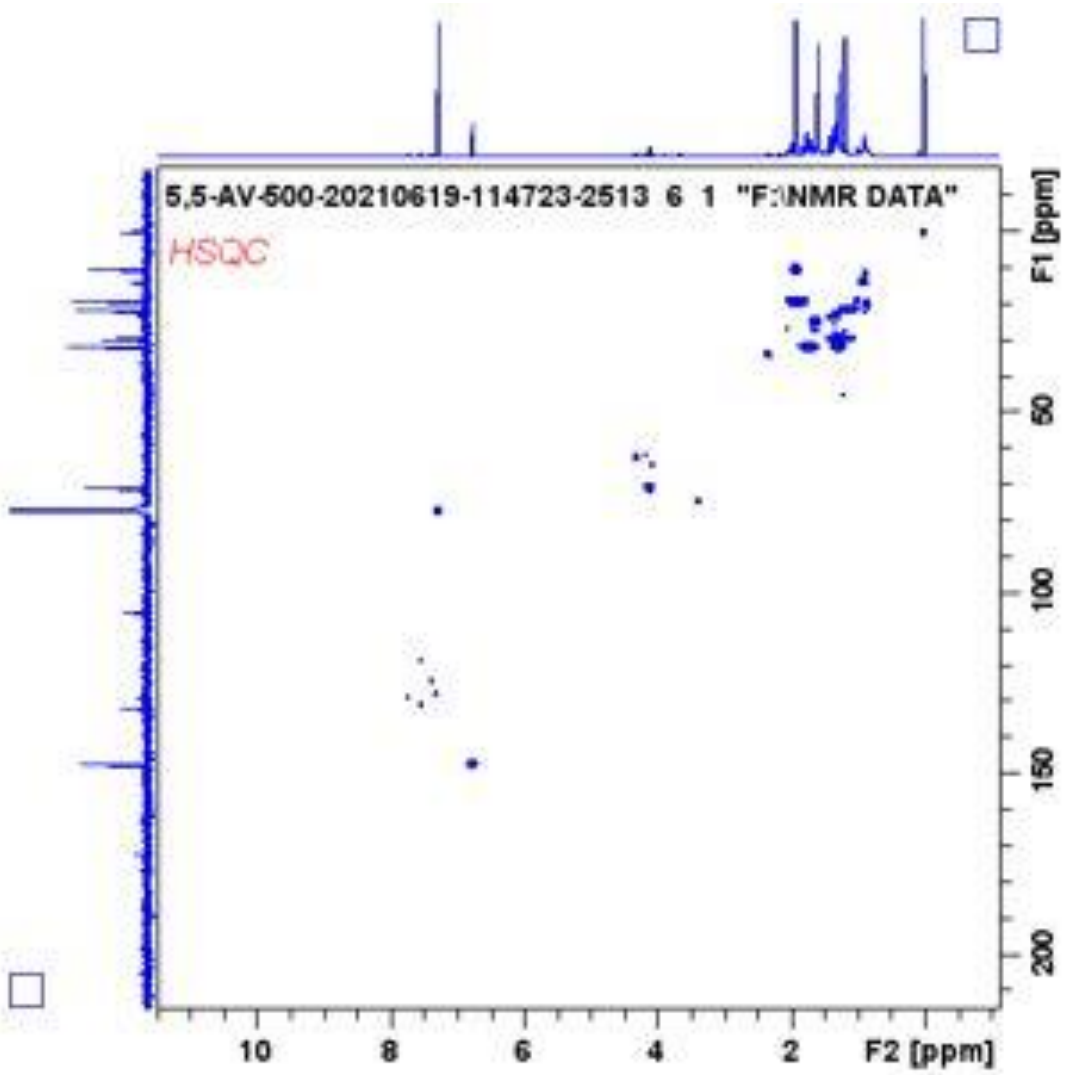
4h


5,5-AV-500-20210619-114723-2513 7 1 "F:\NMR DATA"
HMBC
F1 [ppm]
50
100
150
200
10
8
6
4
2
F2 [ppm]

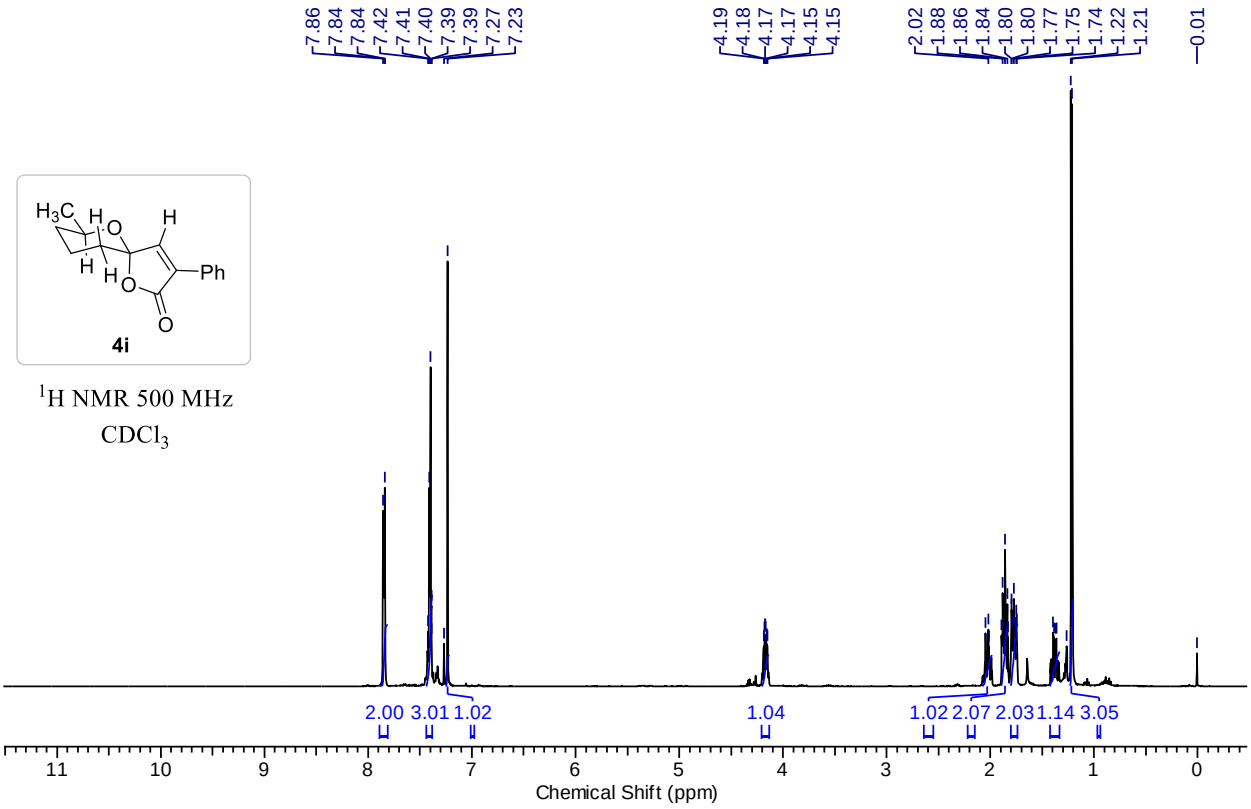
HSQC: (4h)


H3C
O
O
O
CH3

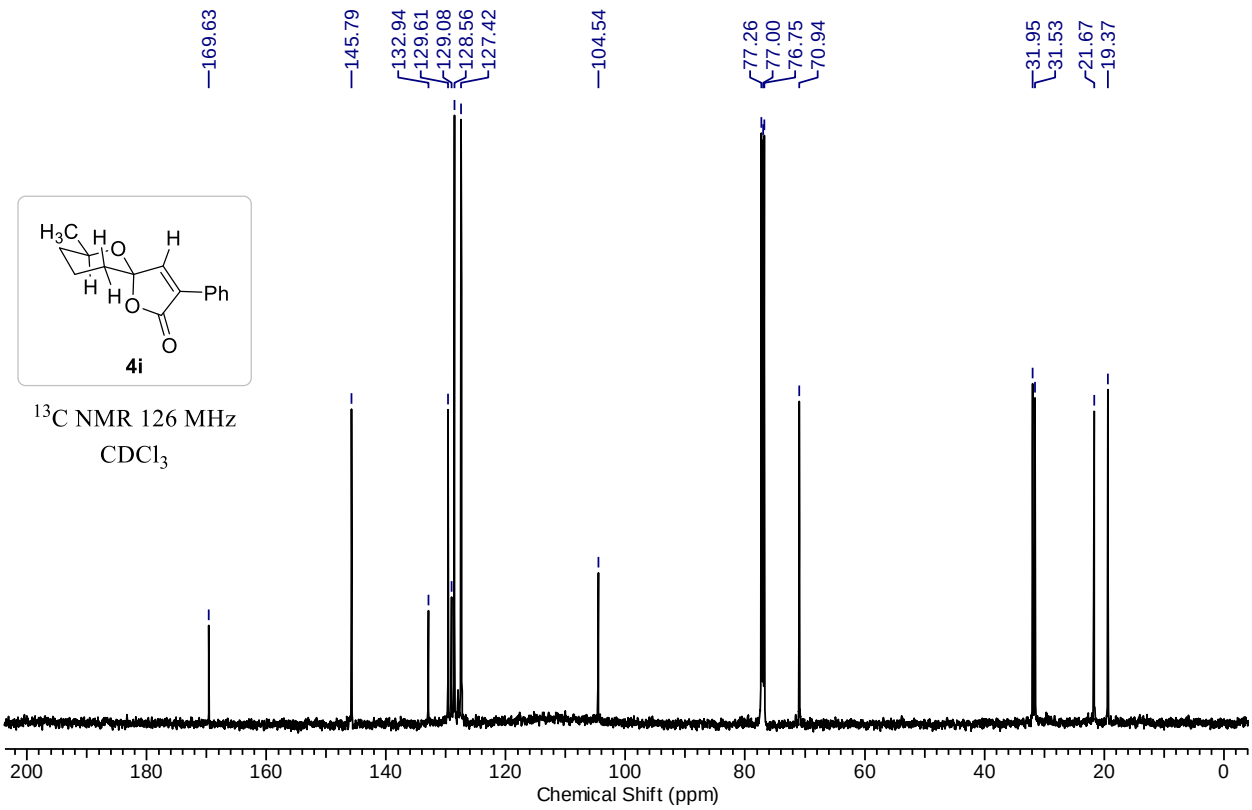
4h


5,5-AV-500-20210619-114723-2513 6 1 "F:\NMR DATA"
HSQC
F1 [ppm]
50
100
150
200
10
8
6
4
2
F2 [ppm]

7-Methyl-3-phenyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4i):

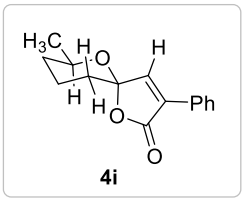


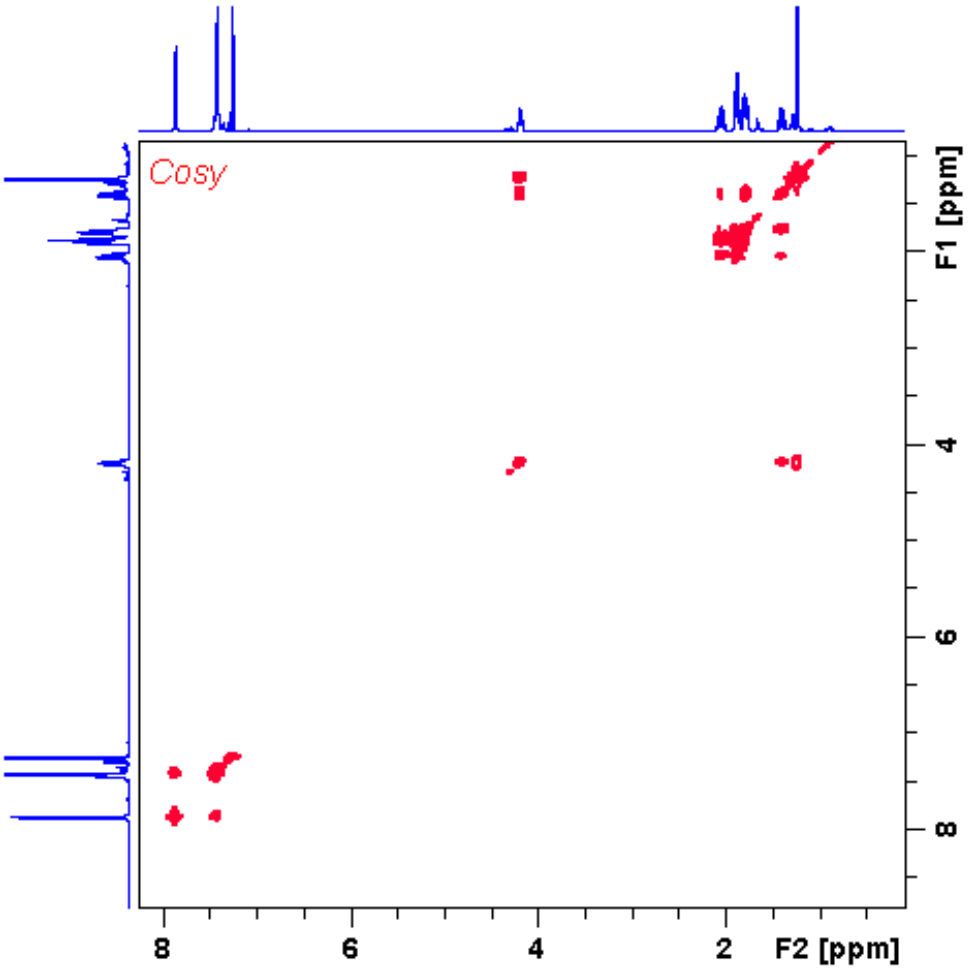
^{1}H NMR 500 MHz
$CDCl_3$



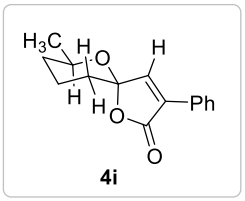
^{13}C NMR 126 MHz
$CDCl_3$

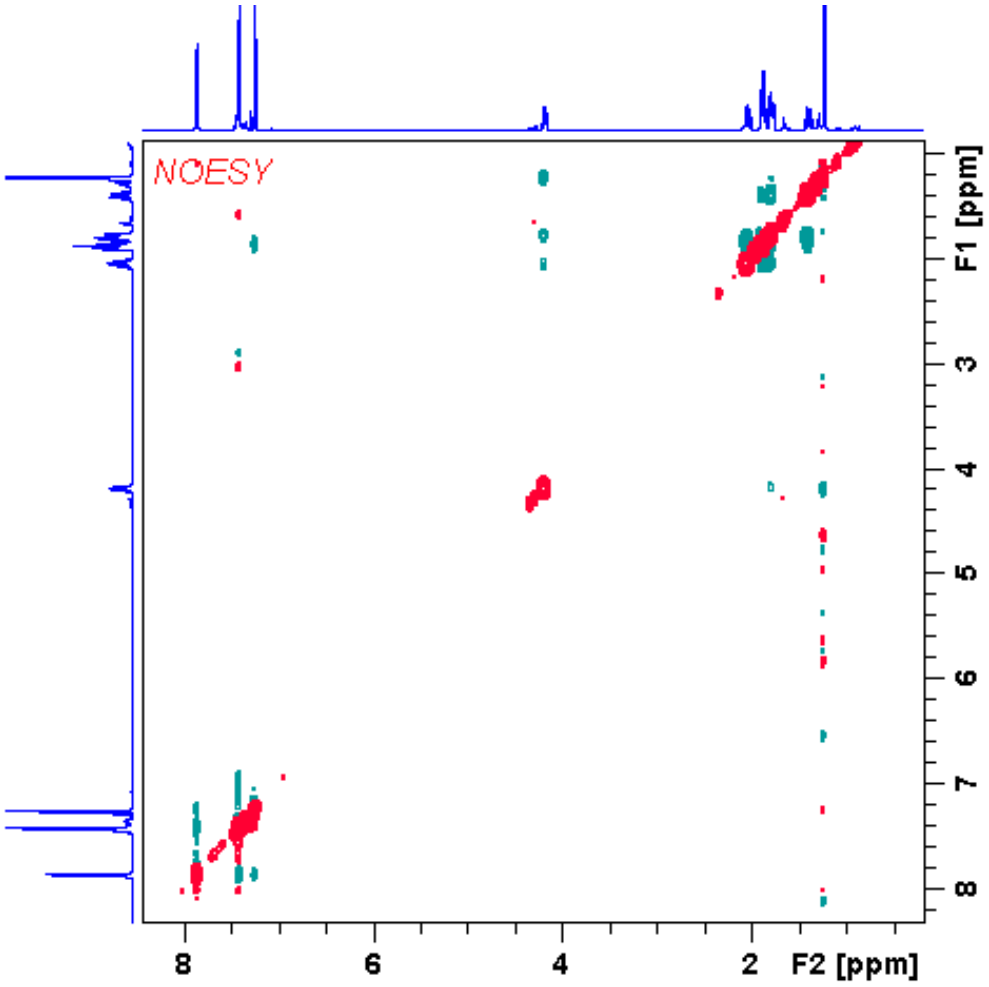
COSY: (4i)



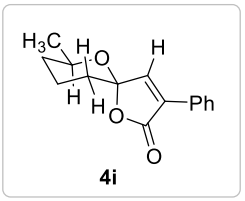


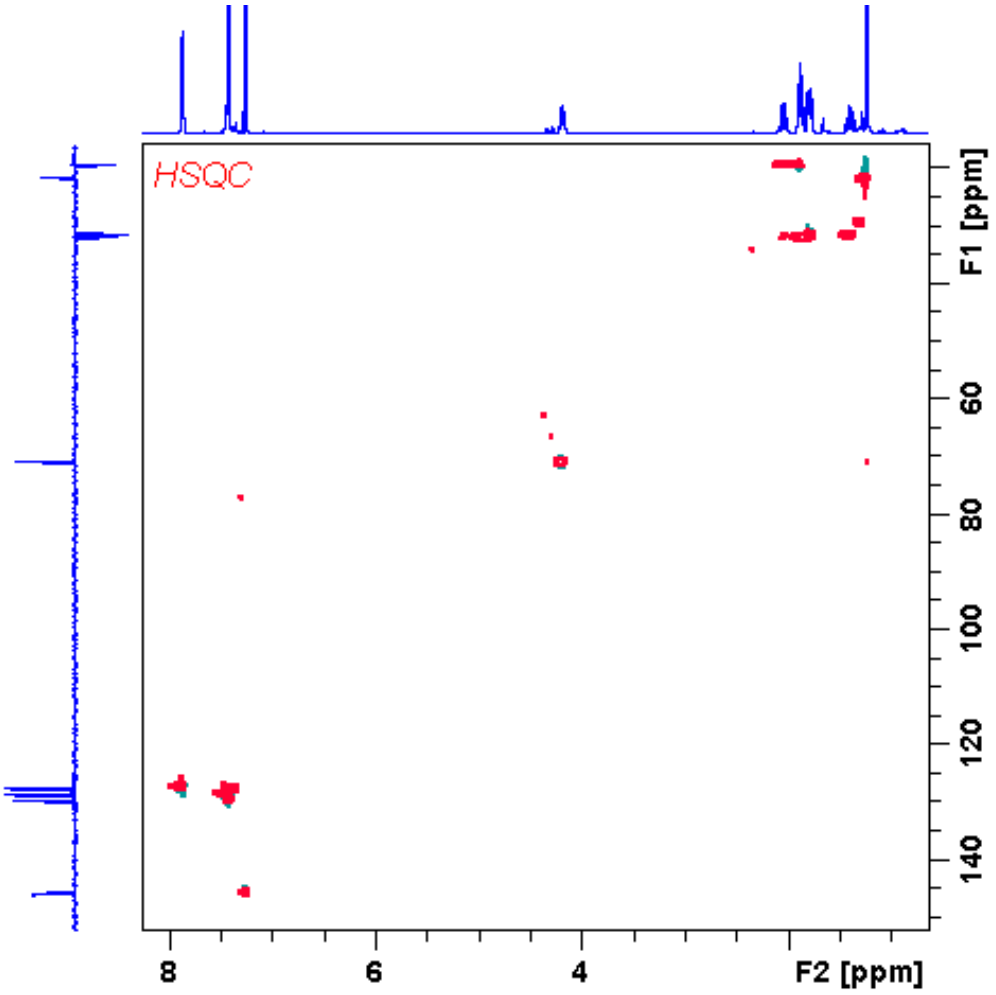
NOESY: (4i)



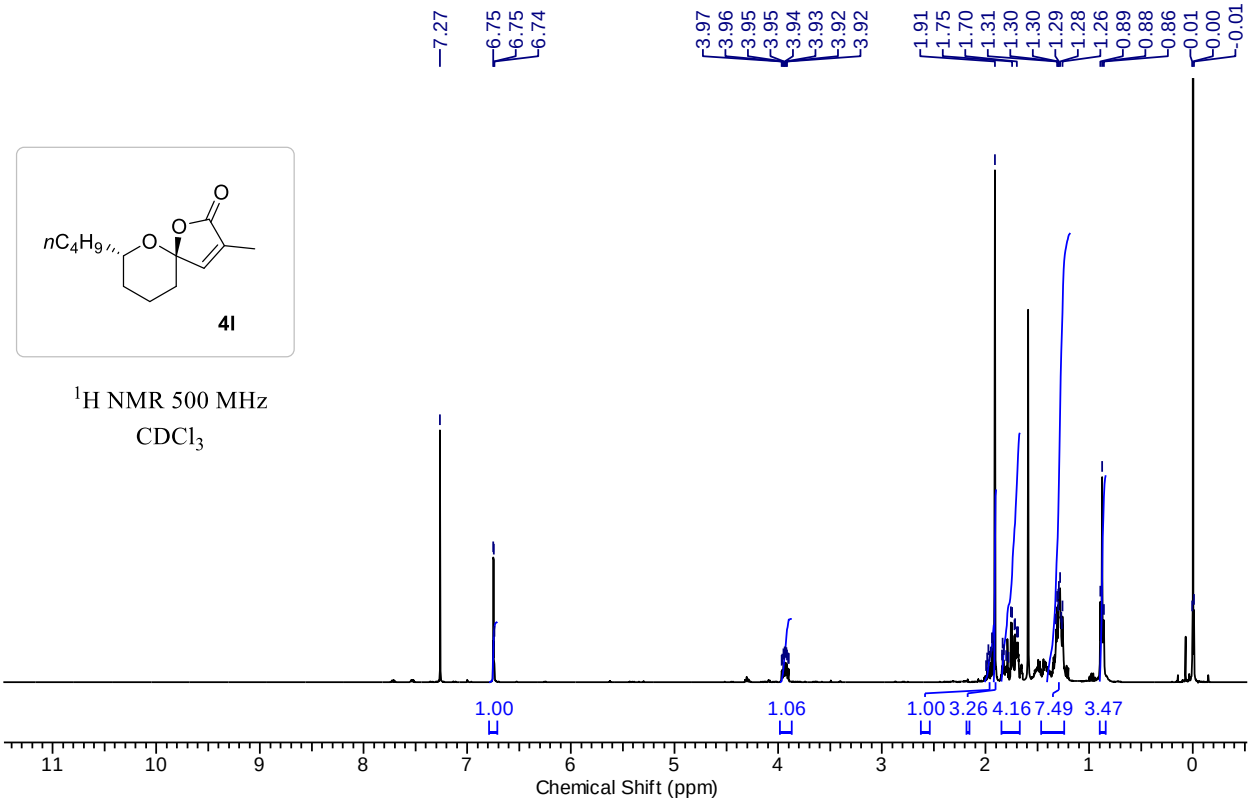


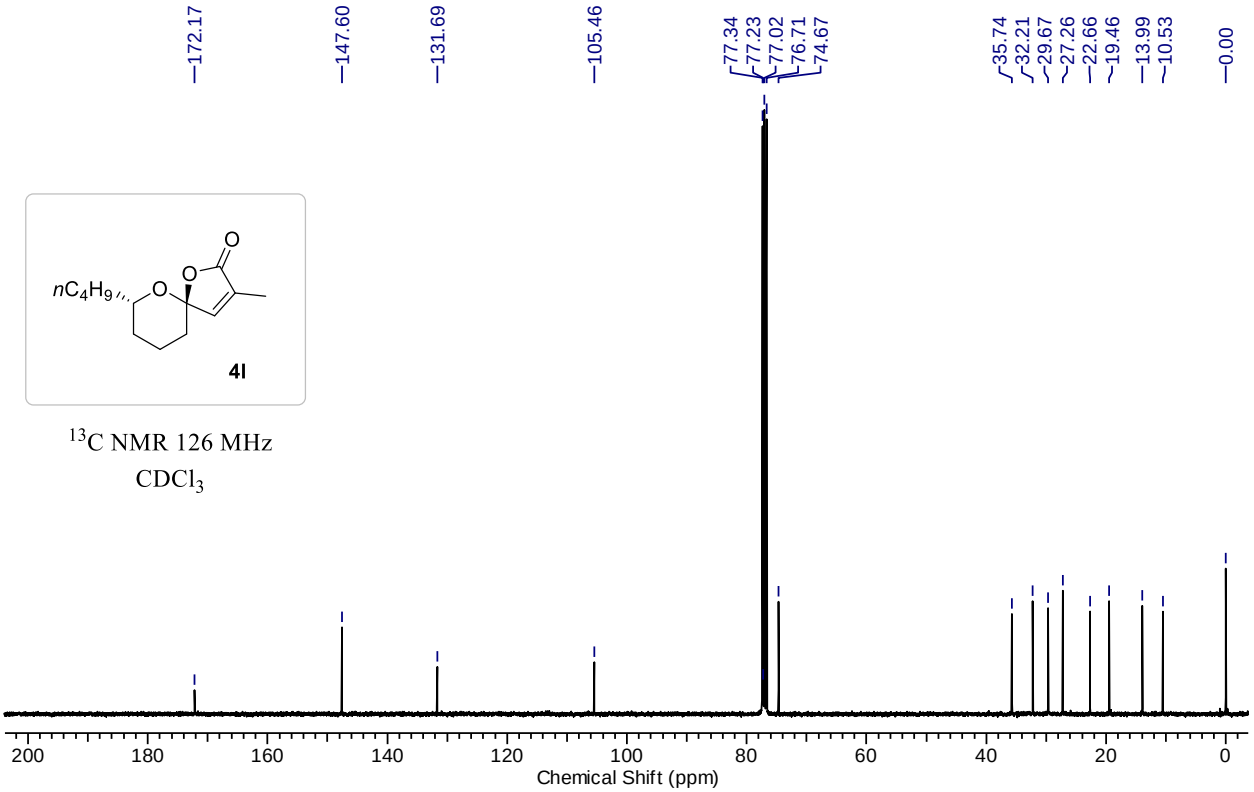
HSQC: (4i)



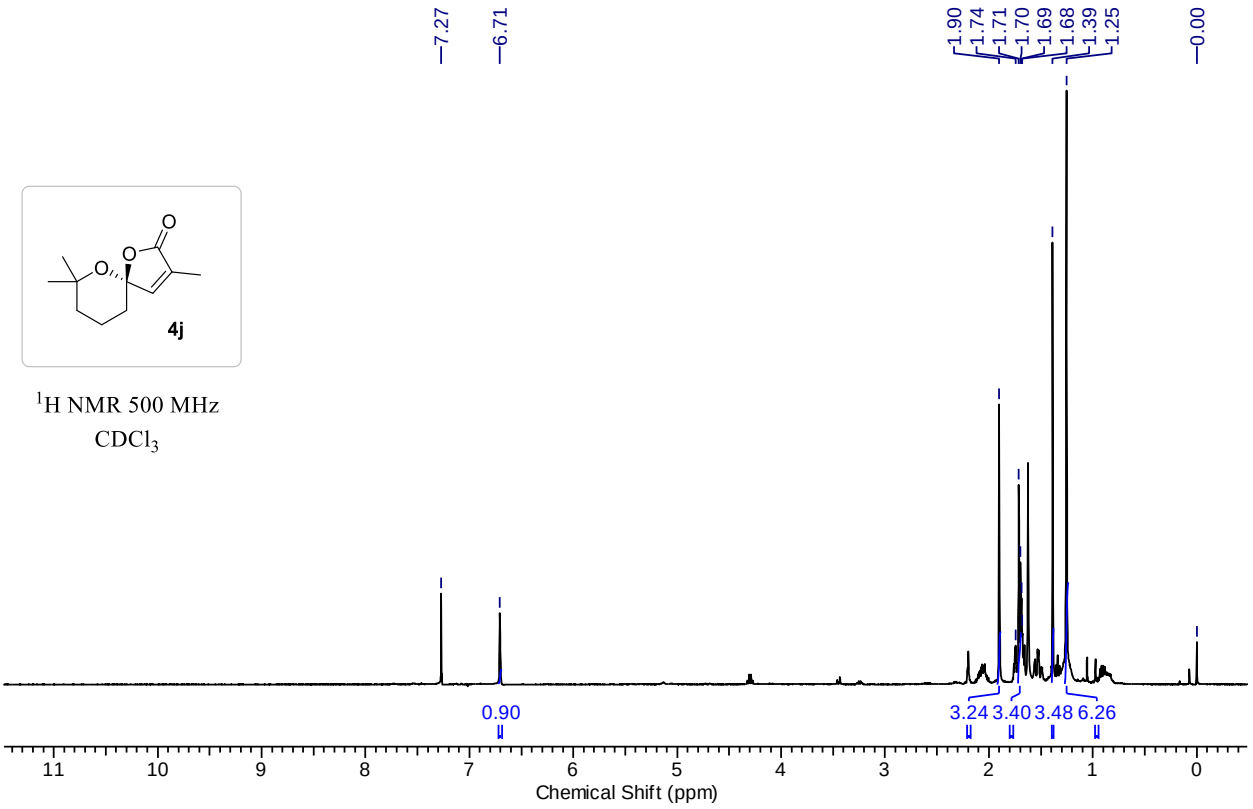


7-Butyl-3-methyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4l):

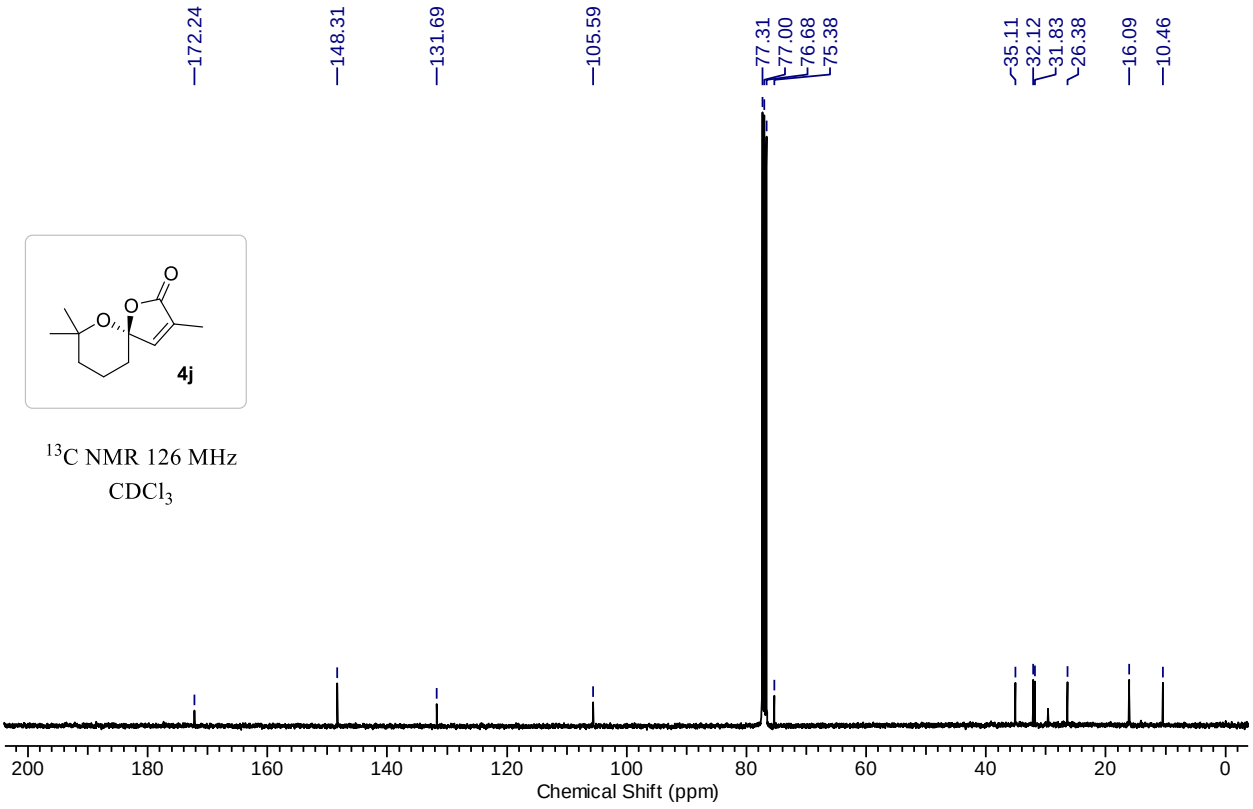




3,7,7-Trimethyl-1,6-dioxaspiro[4.5]dec-3-en-2-one (4j):



^{1}H NMR 500 MHz
$CDCl_3$



^{13}C NMR 126 MHz
$CDCl_3$