Electronic Supplementary Material (ESI) for ChemComm.

Lewis acid catalyzed cascade annulation of alkynols with α-ketoesters: A facile access to γ-spiroketal-γ-lactones

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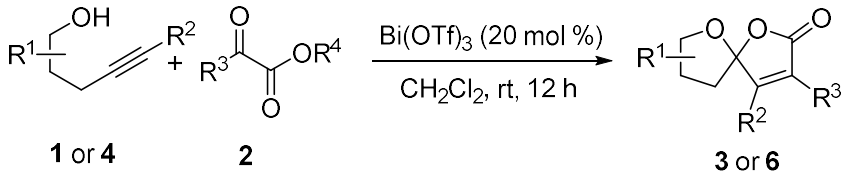
Electronic Supplementary Information (ESI)

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 acetonitrile were freshly distilled over calcium hydride under argon atmosphere. 30 °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 400 and 500 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 = 7.26 ppm, δ C = 77.16 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 a Thermo Scientific Q-Exactive, 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. *General Procedure* for the synthesis of unsaturated γ-spiroketal-γ-lactones from alkynols and α-ketoesters:



1 or **4** **2** **3** or **6**

Alkynol **1a (**0.66 mmol)/or **4** (0.66 mmol) and α-ketoester **2** (0.66 mmol) were taken in to a single neck round bottom flask, then dissolved in 5 mL of anhydrous CH_2Cl_2. $Bi(OTf)_3$ (0.13 mmol) was added under argon atmosphere at room temperature (rt). The resulting reaction mixture was stirred at rt for respective reaction time. After completion of the reaction (typically after 12 h, monitored by TLC, visualized using UV, anisaldehyde, and $KMnO_4$ staining solutions) the reaction was quenched with saturated aqueous-$NaHCO_3$ solution, then extracted with CH_2Cl_2 (2x10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified using silica-gel column chromatography (100-200 mesh) to afford the corresponding unsaturated γ-spiroketal-γ-lactone **3** or **6**.

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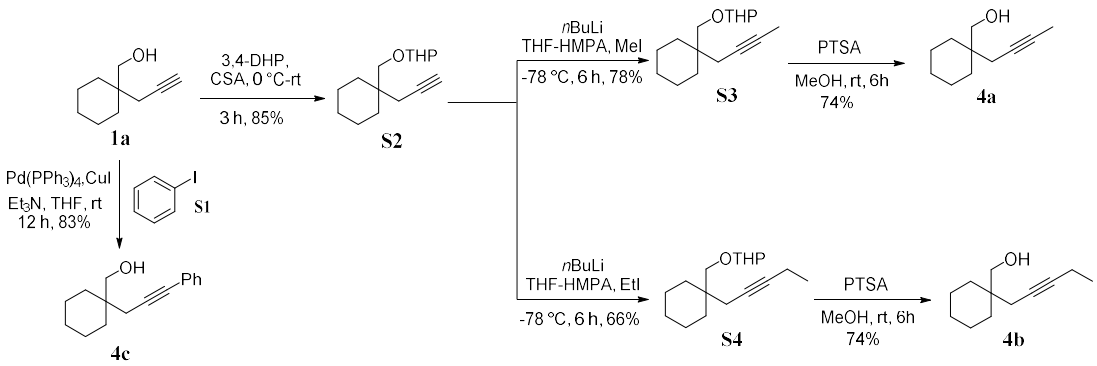
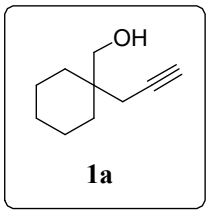
3. Synthesis of alkynols:



(see below experimental procedures)

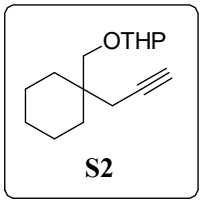
(1-(Prop-2-yn-1-yl) cyclohexyl) methanol (1a):



1a

(1-(prop-2-yn-1-yl) cyclohexyl) methanol (**1a**) was prepared using known procedure.[1] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.55 (s, 2H), 2.26 (d, J = 2.45 Hz, 2H), 2.01 (t, J = 2.69 Hz, 1H), 1.84 (br s, 1H), 1.35-1.51 (m, 10H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 82.0, 70.4, 68.5, 37.6, 31.8, 26.1, 25.1, 21.5, HRMS (ESI) m/z calcd for $C_{10}H_{17}O$ $[M+H]^+$ 153.1274, found 153.1280.

((1-(Prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S2):

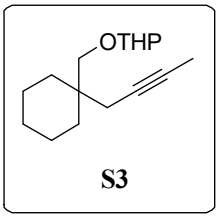


S2

To a cold (0 ^{o}C) mixture of (1-(prop-2-yn-1-yl)cyclohexyl) methanol (**1a**) (14 g, 100 mmol) and 3, 4-dihydro-2H-pyran (9.1 mL, 100 mmol) in 30 mL of anhydrous CH_2Cl_2 was added camphor sulfonic acid (CSA, 2 g, 10 mmol). The reaction mixture was warmed slowly to rt and stirred for 3 h. Then the reaction was quenched with saturated aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2 (2x50 mL). The combined organic layers were dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (SiO_2, 2% EtOAc/hexanes) to afford ((1-(prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (**S2**), (18.5 g, 85%) as colourless liquid. TLC: R_f = 0.40 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.64 - 4.57 (m, 1H), 3.96 - 3.85 (m, 1H), 3.65 (d, J = 9.8 Hz, 1H), 3.52 (d, J = 11.6 Hz, 1H), 3.21 (d, J = 9.2 Hz, 1H), 2.35-2.23 (m, 2H), 1.80 (t, J = 2.4 Hz, 3H), 1.84-1.79 (m, 1H), 1.74-1.51 (m, 5H), 1.5-1.36 (m, 10H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 98.8, 82.2, 72.1, 69.9, 61.7, 36.9, 32.3, 32.1, 30.6, 26.1, 25.6, 21.6, 19.2; HRMS (ESI) m/z calcd for $C_{15}H_{25}O_2$ $[M+H]^+$ 237.1849, found 237.1846

[1] N. T. Patil, R. D. Kavthe, V. S. Raut, V. N. Reddy. *J. Org. Chem*. **2009**, *74*, 6315-6318.

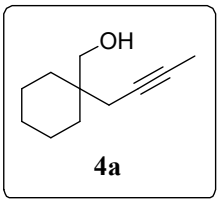
2-((1-(But-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S3):



S3

To a solution of ((1-(prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (**S2)** (1 g, 4.2 mmol) in anhydrous THF, *n*BuLi (1.6 M in hexane, 8.1 mL, 5.1 mmol) was added at -78 ^{o}C and stirred this reaction mixture for 45 min at -78 ^{o}C under argon atmosphere. Then the solution of CH_3I (1.8 mL, 12.7 mmol) in anhydrous HMPA (1 mL) was added at same temperature and resulting reaction mixture was slowly warmed to room temperature and further stirred for 6 h. Then the reaction mixture was quenched with saturated NH_4Cl solution at 0 ^{o}C and extracted with ethyl acetate (3x25 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by silica gel chromatography (SiO_2, 2% EtOAc/hexanes) to afford 2-((1-(but-2-yn-1-yl)cyclohexyl) methanol (**S3)** (1.23 g, 78%) as a colourless liquid. TLC: R_f = 0.5 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.62 (t, *J* = 3.43 Hz, 1H), 3.94-3.87 (m, 1H), 3.66 (d, *J* = 9.54 Hz, 1H), 3.56-3.49 (m, 1H), 3.22 (d, *J* = 9.16 Hz, 1H), 2.24-2.2 (m, 2H), 1.8 (t, *J* = 2.67 Hz, 3H), 1.89-1.37 (m, 16H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 98.9, 72.3, 61.6, 37.1, 32.3, 32.1, 30.6, 26.2, 25.9, 25.6, 21.7, 19.2, 3.5; HRMS (ESI) m/z calcd for $C_{16}H_{27}O_2$ $[M+H]^+$ 251.2006, found 251.2001.

(1-(But-2-yn-1-yl) cyclohexyl) methanol (4a):

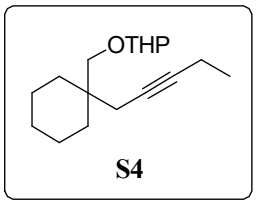


4a

To a solution of 2-((1-(but-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (**S3)** (1 g, 4 mmol) in methanol was added *p*-toluenesulfonic acid (PTSA, 0.075 g, 0.4 mmol) at 0 °C and then it was slowly warmed to rt. The resulting reaction mixture was stirred for 6 h at rt, then the methanol 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 anhydrous Na_2SO_4, filtered using sintered funnel, concentrated under reduced pressure to afford the crude product, which was purified by silica gel column chromatography (SiO_2, 10% EtOAc/hexanes) to afford (1-(but-2-yn-1-yl) cyclohexyl) methanol (**4a**), (0.59 g, 74%) as a colourless liquid. TLC: R_f= 0.2 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.54 (s, 2 H), 2.22-2.15 (m, 2 H), 1.82 (br. s., 1H), 1.8 (t, *J* = 2.44 Hz, 3H), 1.53 - 1.32 (m, 10 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 77.9, 76.4, 69.1, 37.7, 32.0, 26.2, 25.7, 21.6, 3.5; HRMS (ESI): m/z calcd for $C_{11}H_{19}O$ $[M+H]^+$ 167.2617, found 167.2619.

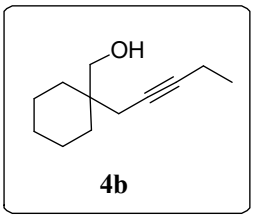
2-((1-(Pent-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S4):



S4

To a solution of ((1-(prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (**S2**) (1.5 g, 6.3 mmol) in anhydrous THF, *n*BuLi (1.6 M in hexane, 5 mL, 7.6 mmol) was added, and stirred this reaction mixture for 45 min at -78 °C under argon atmosphere. Then the solution of EtI (1.56 mL, 1.9 mmol) in anhydrous HMPA (1 mL) was added at -78 °C and resulting reaction mixture was stirred for 6 h at rt. The reaction mixture was quenched with saturated solution of NH_4Cl and extracted with ethyl acetate (2x25 mL). Combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, crude product was purified by silica gel column chromatography (SiO_2, 10% EtOAc/hexanes) to give 2-((1-(pent-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (**S4**) (1.1 g, 66%) as a colourless liquid. TLC: R_f = 0.45 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.60 (m, 1H), 3.95 - 3.79 (m, 1H), 3.64 (d, *J* = 9.8 Hz, 1H), 3.56-3.44 (m, 1H), 3.2 (d, *J* = 9.8 Hz, 1H), 2.25 - 2.2 (m, 2H), 2.2-2.11 (m, 2 H), 1.89-1.36 (m, 16H), 1.12 (t, *J* = 7.32 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 98.8, 83.3, 76.9, 72.3, 61.5, 37.0, 32.3, 32.1, 30.6, 26.3, 25.9, 25.6, 21.7, 19.2, 14.5, 12.5; HRMS (ESI): m/z calcd for $C_{17}H_{29}O_2$ $[M+H]^+$ 265.2162, found 265.2161.

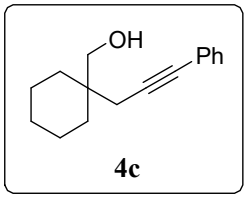
(1-(Pent-2-yn-1-yl) cyclohexyl) methanol (4b):



4b

To a solution of 2-((1-(pent-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (**S4**) (1.1 g, 4.16 mmol) in methanol was added PTSA at 0 °C and then it was warmed to room temperature, the resulting reaction mixture was stirred at rt for 6 h. Then methanol was evaporated under reduced pressure, diluted with ethyl acetate (25 mL) and washed with saturated solution of sodium bicarbonate and brine solution. The residue was dried over anhydrous sodium sulphate, filtered using sintered funnel, concentrated under reduced pressure, the crude product was purified by silica gel column chromatography (SiO_2, 10% EtOAc/hexanes) to afford (1-(pent-2-yn-1-yl) cyclohexyl) methanol **4b** (0.59 g, 78%) as a colourless liquid. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.53 (s, 2H), 2.24 - 2.11 (m, 4H), 1.85 (br. s., 1H), 1.51 - 1.32 (m, 10H), 1.12 (t, J = 7.32 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 84.2, 76.6, 69.2, 37.6, 32.0, 26.2, 25.8, 21.6, 14.3, 12.4; HRMS (ESI): m/z calcd for $C_{12}H_{20}ONa$ $[M+H]^+$ 203.1406, found 203.1405.

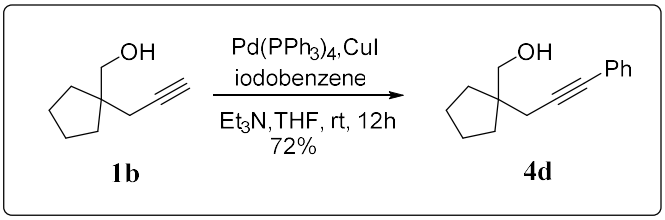
(1-(3-Phenylprop-2-yn-1-yl) cyclohexyl) methanol (4c):



4c

(1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (**4c)** was prepared according to the literature.[2] $Pd(PPh_3)_4$ (0.023 g, 0.019 mmol) and CuI (0.08 g, 0.039 mmol) were added to the solution of iodobenzene (**S1**) (0.45 ml, 3.94 mmol) and (1-(prop-2-yn-1-yl) cyclohexyl) methanol (0.3 g, 1.97 mmol) (**1a)** in triethylamine (2.76 mL, 19.7 mmol) and THF (10 mL) under argon atmosphere. The reaction mixture was stirred at rt for 12 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford the (1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (**4c)** as a brown oil (0.27 g, 60%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47-7.36 (m, 2H), 7.36-7.22 (m, 3H), 3.62

(s, 2H), 2.49 (s, 2H), 1.92 (br s, 1H), 1.61 - 1.34 (m, 10H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 131.6, 128.2, 127.6, 123.8, 87.6, 82.8, 68.7, 38.2, 32.0, 26.2, 26.1, 21.6; HRMS (ESI): m/z calcd for $C_{16}H_{21}O$ $[M+H]^+$ 229.1587, found 229.1586.

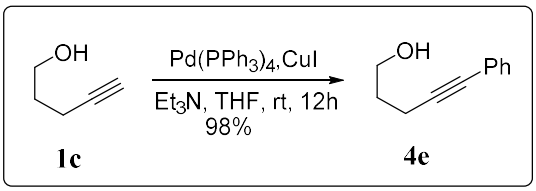


(1-(Prop-2-yn-1-yl) cyclopentyl) methanol (1b):[1]

(1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) was prepared using known procedure.[1] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (s, 2H), 2.35 (s, 1H), 2.27 (d, *J* = 2.45 Hz, 2H), 1.94 (t, *J* = 2.45 Hz, 1H), 1.68-1.54 (m, 4H), 1.53-1.42 (m, 4H), ^{13}C NMR ($CDCl_3$, 101 MHz): δ 82.9, 69.3, 68.5, 46.9, 34.0, 26.5, 25.2; HRMS (ESI) m/z calcd for $C_9H_{15}O$ $[M+H]^+$ 139.1117, found 139.116.

(1-(3-Phenylprop-2-yn-1-yl) cyclopentyl) methanol (4d):

(1-(3-phenylprop-2-yn-1- cyclopentyl) methanol (**4d)** was prepared according to the literature procedure.[1] $Pd(PPh_3)_4$ (0.042 g, 0.036 mmol) and CuI (0.014 g, 0.072 mmol) were added to the solution of iodobenzene (**S1**) (0.82 mL, 7.24 mmol) and (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.5 g, 3.62 mmol) in triethylamine (5 mL, 36.2 mmol) and THF (10 mL) under argon atmosphere. The reaction mixture was stirred at rt for 12 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford (1-(3-phenylprop-2-yn-1-cyclopentyl) methanol (**4d)** (0.5 g, 64%) as brownish oil, TLC: R_f = 0.5 (20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44-7.34 (m, 2H), 7.32 - 7.18 (m, 3H), 3.57 (s, 2H), 2.50 (s, 2H), 1.82-1.45 (m, 8H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 131.6, 128.2, 127.7, 123.8, 88.5, 81.7, 69.1, 47.6, 34.3, 27.7, 25.3; HRMS (ESI) m/z calcd for $C_{15}H_{19}O$ $[M+H]^+$ 215.1430, found 215.1426.



5-Phenylpent-4-yn-1-ol (4e):

5-phenylpent-4-yn-1-ol (**4e**) was prepared according to the literature procedure.[1] $Pd(PPh_3)_4$ (0.137 g, 0.12 mmol) and CuI (0.045 g, 0.24 mmol) were added to the solution of iodobenzene (**S1**) (2.7 mL, 23.77 mmol) and pent-4-yn-1-ol (**1c**) (1 g, 11.89 mmol) in triethylamine (16 mL, 118.9 mmol) and anhydrous THF (15 mL) under argon atmosphere. The reaction mixture was stirred at rt for 6 h. Then the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford 5-phenylpent-4-yn-1-ol (**4e**) (1.9 g, 98%) brown oil. TLC: R_f= 0.4 (20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46-7.38 (m, 2H), 7.34-7.25 (m, 3H), 3.89-3.68 (m, 2H), 2.59-2.51 (m, 2H), 2.1 (br. s., 1H), 1.93-1.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 131.6, 128.3, 127.7, 123.8, 89.4, 81.1, 61.7, 61.6, 31.4, 16.0; HRMS (ESI): m/z calcd for $C_{11}H_{13}O$ $[M+H]^+$ 161.0961, found 161.0958.

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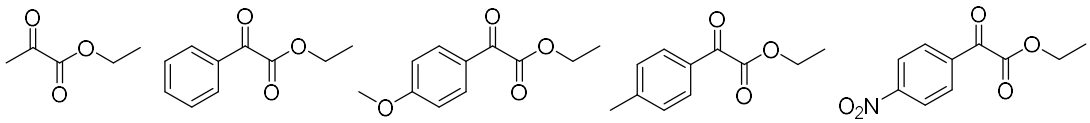
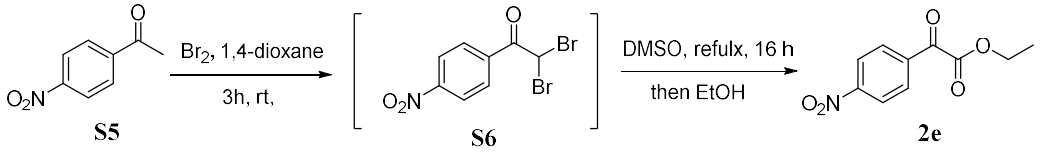
4. Synthesis of α-ketoesters:[2, 3,4,5]



2a[2] **2b**[2] **2c**[3] **2d**[4] **2e**[5]

[2] **2a** and **2b** were purchased from commercial sources.
[3] S. Kawashima, K. Aikawa, K. Mikami. *Eur. J. Org. Chem*. **2016**, 3166–3170
[4] H., M, S. Nakamura. *Angew. Chem. Int. Ed*., **2011**, *50*, 2249–2252.
[5] see the next page for preparation.

Ethyl 2-(4-nitrophenyl)-2-oxoacetate (2e)[6]:

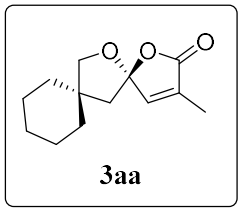


Bromine (3.51 mL, 68 mmol) was added drop wise over 20 min to anhydrous 1,4-dioxane (20 mL) at 25–30 °C under argon atmosphere and the mixture was kept under these conditions for 30 min. A solution of 1-(4-nitrophenyl)ethan-1-one (**S5**) (5 g, 34 mmol) in dioxane (20 mL) was added and the mixture was stirred for another 3 h. The reaction was then quenched with ice-cold water (400 mL, 10 volumes with respect to 1,4-dioxane) and the solid was filtered off and washed with chilled hexane to give 2,2-dibromo-1-(4-nitrophenyl)ethan-1-one (**S6**), which was used in the next step without further purification. The crude **S6** was dissolved in anhydrous DMSO (60 mL) under argon. The solution was then slowly heated to 70–75 °C and stirred at this temperature for 16 h. The mixture was then cooled to rt, then EtOH (3.97 mL, 0.6 mol) was added, and the mixture was stirred for 2 h at rt. The mixture was then diluted with H_2O (100 mL) and extracted with EtOAc (4 × 30 mL). The combined organic layers were washed successively with water (3×30 mL) and brine solution, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The pure product was isolated by silica gel column chromatography (12% EtOAc/hexanes) to give 3.21 g (47%) of **2e** as a yellow oil. TLC: R_f = 0.35 (20% EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (d, J = 8.55 Hz, 2H), 8.21 (d, J = 8.55 Hz, 2H), 4.47 (q, J = 7.32 Hz, 2H), 1.43 (t, J = 7.32 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 184.2, 162.3, 151.1, 137.0, 131.2, 123.9, 63.0, 14.0; HRMS (ESI): m/z calcd for $C_{10}H_{10}O_5N$ $[M+H]^+$ 224.0553, found 224.0549.

[6] A. Raghunadh, M. S. Babu, N. A. Kumar, G. S. Kumar, L. V. Rao, U. K. S. Kumar. *Synthesis*, **2012**, *44*, 283-289.

5. *Synthesis and Characterization* of unsaturated γ-spiroketal-γ-lactones from alkynols possessing terminal alkyne functionality:

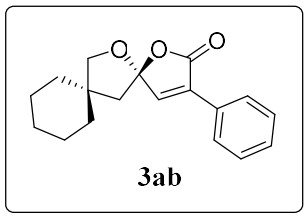
3-Methyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (3aa):



3aa

Following the *General Procedure*, to the mixture of (1-(prop-2-yn1 yl) cyclohexyl) methanol (**1a**) (0.100 g, 0.66 mmol) and ethyl pyruvate (**2a**) (0.104 g, 0.66 mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.090 g, 0.13 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc /hexanes) afforded 3-methyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**3aa**) (0.117 g, 80%). TLC: R_f = 0.40 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.74-6.65 (m, 1H), 3.95 (d, *J* = 8.8 Hz, 1H), 3.86 (d, *J* = 8.3 Hz, 1H), 2.12 (d, *J* = 13.7 Hz, 1H), 2.01 (d, *J* = 14.2 Hz, 1H), 1.91 (d, *J* = 0.98 Hz, 3H), 1.77-1.64 (m, 2H), 1.57-1.36 (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, 25.5, 23.8, 23.7, 10.4; HRMS (ESI) m/z calcd for $C_{13}H_{19}O_3$ $[M+H]^+$ 223.1329, found 223.1326.

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

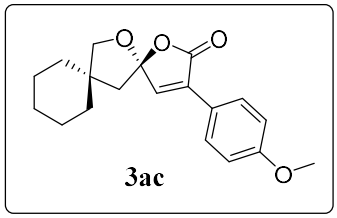


3ab

Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl) cyclohexyl) methanol (**1a**) (0.100 g, 0.66 mmol) and ethyl phenylglyoxylate (**2b**) (0.104 g, 0.66 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.09 g, 0.13 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 12 h. Purification of the crude product by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded 3-phenyl-

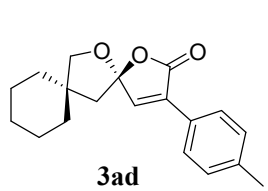
1,14-dioxadispiro[4.4.5^7.2^5]tetradec-3-en-one(**3ab**) as a crystalline solid (0.142 g, 76%). TLC: R_f = 0.75 (SiO_2, 20% EtOAc/hexanes)**;** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.79 (m, 2H), 7.42 (d, *J* = 3.7 Hz, 3H), 7.18 (s, 1H), 4.03 (d, *J* = 7.9 Hz, 1H), 3.94 (d, *J* = 8.5 Hz, 1H), 2.20 (dd, *J* = 36.01, 13.4 Hz, 2H), 1.81-1.69 (m, 2H), 1.62-1.38 (m, 8H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.3, 143.7, 133.6, 129.7, 129.0, 128.7, 127.5, 112.4, 80.5, 47.4, 43.8, 37.4, 35.5, 25.6, 23.9, 23.8; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1485, found 285.1483.

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

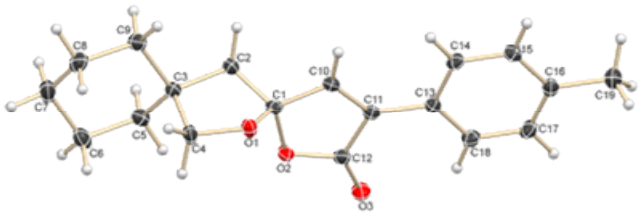


Following the *General Procedure*, to the mixture of (1-(prop- 2-yn-1-yl) cyclohexyl) methanol (**1a**) (0.05 g, 0.33 mmol) and ethyl anisylglyoxylate (**2c**) (0.054 g, 0.33 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.045 g, 0.066 mmol) under argon atmosphere at room temperature and stirred the reaction mixture for 12 h. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 3-(4-methoxyphenyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**3ac**) (0.06 g, 72%). TLC: R_f = 0.75 (SiO_2, 20% EtOAc/hexanes)**;** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.05 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.01 (d, *J* = 8.3 Hz, 1H), 3.92 (d, *J* = 8.3 Hz, 1H), 3.84 (s, 3H), 2.16 (dd, *J* = 38.15, 13.7 Hz, 2H), 1.77-1.69 (m, 2H), 1.59-1.40 (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, 55.3, 47.4, 43.8, 37.4, 35.5, 25.6, 23.9, 23.8; HRMS (ESI) m/z calcd for $C_{19}H_{23}O_4$ $[M+H]^+$ 315.1591, found 315.1588.

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



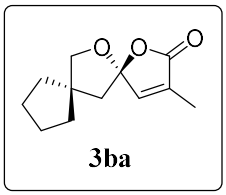
3ad



X-ray, CCDC No: 1510255 **ORTEP Diagram**

Following the *General Procedure*, to the reaction mixture of (1-(prop-2-yn-1-yl) cyclohexyl) methanol (**1a**) (0.05 g, 0.32 mmol) and ethyl p-tolylglyoxylate (**2d**) (0.063 g, 0.32 mmol) in anhydrous CH_2Cl_2 (4 mL) was added $Bi(OTf)_3$ (0.042 g, 0.064 mmol) under argon atmosphere at room temperature and stirred the reaction mixture for 12 h. Purification of the crude product by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded 3-(p-tolyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**3ad**) (0.067 g, 70%) as a crystalline solid. TLC: R_f = 0.60 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75 (d, J = 8.01 Hz, 2H), 7.22 (d, J = 8.01 Hz, 2H), 7.12 (s, 1H), 4.02 (d, J = 8.4 Hz, 1H), 3.93 (d, J = 8.4 Hz, 1H), 2.38 (s, 3H), 2.23 (d, J = 14.11 Hz, 1H), 2.13 (d, J = 13.73 Hz, 1H), 1.78-1.68 (m, 2H), 1.61-1.31 (m, 8H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.4, 142.7, 139.9, 133.5, 129.4, 127.4, 126.1, 112.3, 80.5, 43.8, 37.4, 35.6, 25.6, 23.9, 23.8, 21.4; HRMS (ESI) m/z calcd for $C_{19}H_{23}O_3$ $[M+H]^+$ 299.1642 found 299.1634.

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

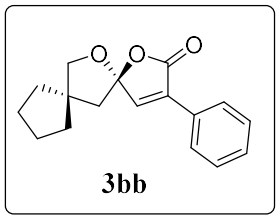


3ba

Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl)cyclopentyl)methanol (**1b**) (0.1 g, 0.72 mmol) and ethylpyruvate (**2a**) (0.083 g, 0.72 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.09 g, 0.144 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 3-

methyl-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (**3ba**) (0.117 g, 78%) as a white solid. TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.72-6.69 (m, 1H), 4.01 (d, *J* = 8.4 Hz, 1H), 3.85 (d, *J* = 8.4 Hz, 1H), 2.18 (s, 2H), 1.92 (d, *J* = 1.14 Hz, 3H), 1.86-1.81 (m, 2H), 1.74-1.58 (m, 6H)**;** ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.6, 145.2, 132.5, 113.3, 81.1, 50.3, 47.4, 38.0, 37.2, 24.6, 24.4, 10.4; HRMS (ESI): calcd for $C_{12}H_{17}O_3$ $[M+H]^+$ 209.1172, found 209.1171.

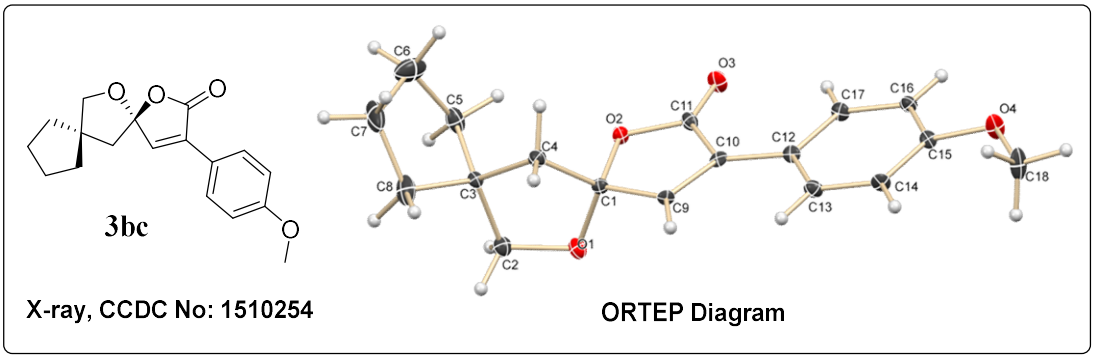
3-Phenyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-one (3bb):



3bb

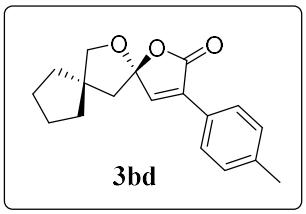
Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1- yl) cyclopentyl) methanol (**1b**) (0.1 g, 0.72 mmol) ethyl phenylglyoxylate (**2b**) (0.128 g, 0.72 mmol) in anhydrous CH_2Cl_2 (6 mL) was added $Bi(OTf)_3$ (0.09 g, 0.144 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc /hexanes) afforded 3-phenyl-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-one (**3bb**) (0.136 g, 70%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87-7.81 (m, 2H), 7.45-7.39 (m, 3H), 7.19 (s, 1H), 4.08 (d, *J* = 8.0 Hz, 1H), 3.92 (d, *J* = 8.0 Hz, 1H), 2.31 (dd, *J* = 17.55, 13.73 Hz, 2H), 1.91-1.87 (m, 2H), 1.79-1.63 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.3, 143.7, 133.6, 129.7, 129.0, 128.7, 127.5, 112.4, 81.2, 50.5, 47.7, 38.0, 37.2, 24.7, 24.4; HRMS (ESI): calcd for $C_{17}H_{19}O_3$ $[M+H]^+$ 271.1329, found 271.1328.

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



Following the *General Procedure*, to the reaction mixture of (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.1 g, 0.72 mmol) and ethyl anisylglyoxylate (**2c**) (0.15 g, 0.72 mmol) in anhydrous CH_2Cl_2 (2 mL) was added $Bi(OTf)_3$ (0.094 g, 0.14 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of crude product by column chromatography (SiO_2, 8% EtOAc /hexanes) afforded 3-(4-methoxyphenyl)-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (**3bc**) crystalline solid (0.151 g, 70%). TLC: R_f = 0.60 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.88-7.80 (m, 2H), 7.06 (s, 1H), 6.96-6.91 (m, 2H), 4.07 (d, J = 8.01 Hz, 1H), 3.91 (d, J = 8.01 Hz, 1H), 3.84 (s, 3H), 2.29 (dd, J = 13.35, 3.43 Hz, 2H), 1.91-1.85 (m, 2H), 1.78-1.63 (m, 6H); ^{13}C NMR (126MHz, $CDCl_3$): δ 169.6, 160.7, 141.3, 132.9, 129.0, 121.6, 114.1, 112.4, 81.2, 55.3, 50.5, 47.7, 38.1, 37.2, 29.7, 24.7, 24.4; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_4$ $[M+H]^+$ 300.1434 found 301.1425.

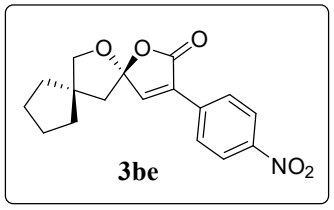
3-(p-Tolyl)-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (3bd):



Following the *General Procedure*, to the reaction mixture of (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.05 g, 0.36 mmol) and ethyl *p*-tolylglyoxylate (**2d**) (0.069 g, 0.36 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.042 g, 0.072 mmol) under argon atmosphere at room temperature and stirred for 12 h at rt. Purification of the crude

product by column chromatography (SiO_2, 2% EtOAc /hexanes) afforded 3-(p-tolyl)-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (**3bd**) (0.073 g, 72%) as a white solid. TLC: R_f = 0.60 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.13 (s, 1H), 4.07 (d, *J* = 8.5 Hz, 1H), 3.91 (d, *J* = 7.9 Hz, 1H), 2.39 (s, 3H), 2.29 (dd, *J* = 14.404, 1.22 Hz, 2H), 1.93-1.85 (m, 2H), 1.80-1.61 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.4, 142.7, 139.9, 133.4, 129.4, 127.4, 126.1, 112.4, 81.2, 50.5, 47.7, 38.0, 37.2, 24.7, 24.4, 21.4; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1485 found 285.1476.

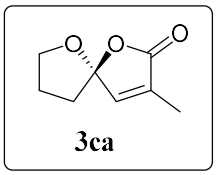
3-(4-Nitrophenyl)-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2 one (3be):



3be

Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.112 g, 0.811 mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (**2e**) (0.181 g, 0.811 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.106 g, 0.162 mmol) at room temperature under argon atmosphere and the mixture was stirred for 12 h at rt. Quenched with aqueous $NaHCO_3$ solution (5 mL), stirred for 5 min then extracted with CH_2Cl_2 (2x5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. Resulting solid was dissolved in hexanes (5 mL) and slowly added the minimum amount of CH_2Cl_2, then resulting solution was stand at room temperature until all solvents were evaporated to form crystalline product 3-(4-nitrophenyl)-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (**3be**) (0.144 g, 78%). TLC: R_f= 0.75 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, *J* = 8.5 Hz, 2H), 8.05 (d, *J* = 9.2 Hz, 2H), 7.38 (s, 1H), 4.10 (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 ($CDCl_3$, 101 MHz): 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, 24.7, 24.4; HRMS (ESI) m/z calcd for $C_{17}H_{18}O_5N$ $[M+H]^+$ 316.1179, found 316.1171.

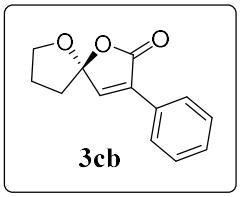
3-Methyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3ca):



3ca

Following the *General Procedure*, to the reaction mixture of pent-4-yn-1-ol (**1c**) (0.1 g, 1.1 mmol) and ethyl pyruvate (**2a**) (0.137 g, 1.1 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.154 g, 0.22 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 48 h at rt. Purification of crude product by column chromatography (SiO_2, 5% EtOAc /hexanes) afforded 3-methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (**3ca**) (0.106 g, 58%) as a yellow oily liquid. TLC: R_f = 0.60 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.73-6.70 (m, 1H), 4.65-4.19 (m, 1H), 4.10-4.03 (m, 1H), 2.34-2.23 (m, 1H), 2.22-2.06 (m, 3H), 1.93 (d, J = 1.91 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.4, 144.4, 133.3, 112.7, 70.3, 35.3, 24.2, 10.5; HRMS (ESI) m/z calcd for $C_8H_{11}O_3$ $[M+H]^+$ 154.0703 found 155.0699.

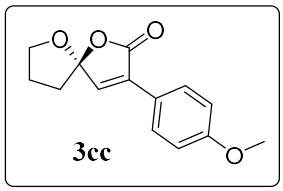
3-Phenyl-1, 6-dioxaspiro [4, 4] non-3-en-2-one (3cb):



3cb

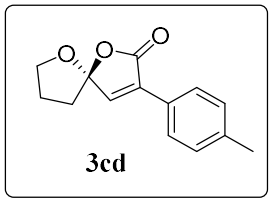
Following the *General Procedure*, to the mixture of 4-pentyne-1-ol (**1c**) (0.1 g, 1.19 mmol) and ethyl phenylglyoxylate (**2b**) (0.21 g, 1.19 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.249 g, 0.238 mmol) under argon atmosphere at room temperature and the resulting mixture was stirred for 48 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc/hexane) afforded 3-phenyl-1, 6-dioxaspiro [4, 4] non-3-en-2-one (**3cb**) (0.138 g, 54%). TLC: R_f = 0.45 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90-7.80 (m, 2H), 7.49-7.34 (m, 3H), 7.21 (s, 1H), 4.28 (td, J = 8.2, 3.7 Hz, 1H), 4.11 (q, J = 7.5 Hz, 1H), 2.42-2.14 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.2, 143.1, 134.3, 129.8, 129.0, 128.7, 128.2, 128.1, 127.7, 127.5, 127.3, 111.9, 70.5, 35.7, 24.3; HRMS (ESI) m/z calcd for $C_{13}H_{13}O_3$ $[M+H]^+$ 217.0859, found 217.0857.

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



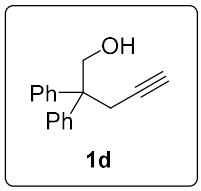
Following the *General Procedure*, to the mixture of 4-pentyne-1-ol (**1c**) (0.3 g, 3.57 mmol) and ethyl anisylglyoxylate (**2c**) (0.743 g, 3.57 mmol) in anhydrous CH_2Cl_2 (6 mL) was added $Bi(OTf)_3$ (0.465 g, 0.714 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 48 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc /hexanes) afforded 3-(4-methoxyphenyl)-1,6-dioxaspiro[4,4]non-3-en-2-one (**3cc**) (0.46 g, 52%). TLC: R_f = 0.40 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, J = 8.8 Hz, 2H), 7.07 (s, 1H), 6.92 (d, J = 8.8 Hz, 2H), 4.31-4.24 (m, 1H), 4.15-4.08 (m, 1H), 3.83 (s, 3H), 2.38-2.12 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.5, 160.8, 140.5, 133.7, 129.0, 121.6, 114.1, 111.9, 70.4, 55.3, 35.7, 24.3; HRMS (ESI): calcd for $C_{14}H_{15}O_4$ $[M+H]^+$ 247.0965, found 247.0964.

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



Following the *General Procedure*, to the reaction mixture of pent-4-yn-1-ol (**1c**) (0.1 g, 1.1 mmol) and ethyl p-tolylglyoxylate (**2d**) (0.228 g, 1.1 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.154 g, 0.22 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 48 h at rt. Purification of crude product by column chromatography (SiO_2, 8% EtOAc /hexanes) afforded 3-(p-tolyl)-1, 6-dioxaspiro [4.4] non-3-en-2-one (**3cd**) crystalline solid (0.084 g, 62%). TLC: R_f = 0.60 (SiO_2, 20% EtOAc /hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.15 (s, 1H), 4.33-4.25 (m, 1H), 4.17-4.08 (m, 1H), 2.38 (s, 3H), 2.43-2.12 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.3, 141.9, 140.0, 134.2, 129.4, 127.4, 126.2, 111.8, 70.4, 35.7, 24.3, 21.4; HRMS (ESI) m/z calcd for $C_{14}H_{15}O_3$ $[M+H]^+$ 230.1016 found 231.1009.

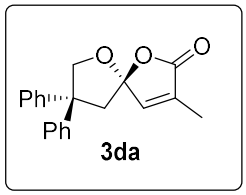
2, 2-diphenylpent-4-yn-1-ol (1d):



1d

Compound (**1d)** was prepared using known procedure.[7] ^{1}H NMR ($CDCl_3$, 500MHz) δ 7.33-7.27 (m, 4H), 7.25-7.20 (m, 6H), 4.30 (s, 2H), 3.08 (d, *J* = 2.29 Hz, 2H), 1.93 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 144. 4, 128.9, 128.02, 126.7, 81.4, 71.5, 68.3, 51.5, 27.4; HRMS (ESI) m/z calcd for $C_{17}H_{17}O$ $[M+H]^+$ 237.1274, found 237.1274.

3-methyl-8, 8-diphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3da):



3da

Following the *General Procedure*, to the mixture of 2, 2-diphenylpent-4-yn-1-ol (**1d**) (0.1 g, 0.42 mmol) and ethyl pyruvate (**2a**) (0.049 g, 0.42mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.055 g, 0.08 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc /hexanes) afforded3-methyl-8, 8-diphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (**3da**) (0.80 g, 62%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36-7.28 (m, 6H), 7.27-7.23 (m, 2H), 7.21-7.18 (m, 2H), 6.35 (d, *J* =1.53 Hz 1H), 4.86 (d, *J* =8.7 Hz, 1H), 4.49 (d, *J* = 9.1 Hz, 1H), 3.27 (d, *J* = 14.1Hz, 1H), 2.95 (d, *J* = 13.7 Hz, 1H), 1.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 171.4, 145.6, 145.2, 143.6, 131.7, 128.7, 128.3, 127.1, 127.0, 126.8, 112.9, 77.9, 56.3, 47.5, 10.3; HRMS (ESI) m/z calcd for $C_{20}H_{19}O_3$ $[M+H]^+$ 307.1329, found 307.1326.

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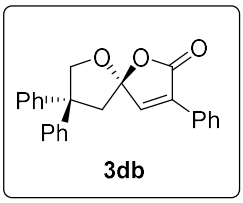
[7] Nakamura, I.; Chan, C. S.; Araki, T.; Terada, M, Yamamoto, Y. *Adv. Synth. Catal*. **2009**, *351*, 1089 – 1100.

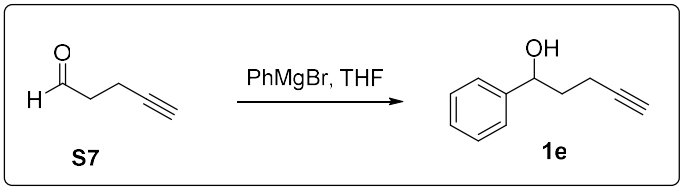
3, 8, 8-triphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3db):



3db

Following the *General Procedure*, to the mixture of 2, 2-diphenylpent-4-yn-1-ol (**1d**) (0.1 g, 0.42 mmol) and ethyl phenylglyoxylate (**2b**) (0.075 g, 0.42 mmol) in anhydrous CH_2Cl_2 (5 mL) was add $Bi(OTf)_3$ (0.055 g, 0.08 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc /hexanes) afforded3,8,8-triphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (**3db**) (0.109 g, 70%). TLC: R_f = 0.40 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR($CDCl_3$, 400 MHz) δ 7.80-7.71(m, 2H), 7.40-7.30 (m, 9H), 7.29-7.20 (m, 4H), 6.79 (s, 1H), 4.91(d, *J* = 9.1 Hz, 1H), 4.55 (d, *J* = 9.1 Hz, 1H), 3.36 (d, *J* = 14 Hz, 1H), 3.07 (d, *J* = 14 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 169, 145.5, 143.5, 132.7, 128.8, 129.8, 128.7, 128.6, 127.5, 127.1, 126.9, 126.8, 112.1, 78.1, 56.4, 47.8; HRMS (ESI) m/z calcd for $C_{25}H_{21}O_3$ $[M+H]^+$ 369.1485, found 369.1469.

1-phenylpent-4-yn-1-ol (1e):



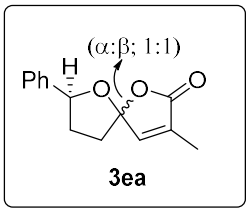
S7 **1e**

Compound **1e** was prepared using known procedure.[8] PhMgBr (1.0 M in THF, 18 mL, 1.82 mmol) was added drop wise to a solution of pent-4-ynal (**S7**) (0.5 g, 0.605 mmol) in THF (20 mL) at room temperature, the reaction mixture was stirred at rt for 2 h. Reaction was quenched by adding ice cold water (10 mL), then neutralized with 2N HCl (20 mL), extracted with EtOAc (20 mL), which was washed once with 2N HCl (20 mL) and brine solution (20 mL). Organic layer was dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent under reduced pressure afforded the desired product 1-phenylpent-4-yn-1-ol (**1e**) (0.72 g, 70 %).^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.45-7.11 (m, 5H), 4.77-4.64 (m, 1H), 2.96 (d,

[8] Ravindar, K.; Reddy, M. S.; Deslongchamps, P. *Org. Lett*. **2011**, *13*, 3178–3181.

J = 3.66 Hz, 1H), 2.36-2.06 (m, 2H), 2.03-1.66 (m, 3H); HRMS (ESI) m/z calcd for $C_{11}H_{13}O$ $[M+H]^+$ 161.0963, found 161.0961.

3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):



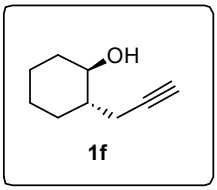
3ea

Following the *General Procedure*, to the mixture of 1-phenylpent-4-yn-1-ol (**1e**) (0.1 g, 0.062 mmol) and ethyl pyruvate (**2a**) (0.072 g, 0.062 mmol) in anhydrous CH_2Cl_2 (2 mL) was added $Bi(OTf)_3$ (0.081 g, 0.012 mmol), then reaction mixture was stirred under reflux conditions (40 ^oC) for 12 h. The reaction mixture was cooled to room temperature and quenched using aqueous $NaHCO_3$ solution. Extracted with dichloromethane (2x10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. Purification of the crude product by silica gel column chromatography (SiO_2, 6% EtOAc/hexanes) afforded two separable diastereomers of 3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (**3ea-Isomer-1**, 27% yield (0.038 g), **3ea-Isomer-2,** 29% yield (0.041 mg), in *dr* approx 1:1) as a yellow oil.

3ea-Isomer-1: TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.52-7.22 (m, 5H), 6.89 (s, 1H), 5.45 (t, *J* = 5.72 Hz, 1H), 2.81-2.69 (m, 1H), 2.37-2.26 (m, 2H), 2016-2.08 (m, 1H), 1.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 171.4, 144.3, 141.3, 133.3, 128.5, 127.8, 125.5, 112.8, 82.4, 34.4, 32.5, 10.5.

3ea-Isomer-2: TLC: R_f = 0.28 (SiO_2, 20% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.22 (m, 5H), 6.79 (s, 1H), 5.21 (t, *J* = 4.88 Hz, 1H), 2.57-244 (m, 1H), 2.41-2.21 (m, 3H), 1.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 171.4, 144.5, 141.0, 133.5, 128.6, 128.4, 128.1, 126.3, 112.7, 85.0, 37.2, 34.1, 10.6; HRMS (ESI) m/z calcd for $C_{14}H_{15}O_3$ $[M+H]^+$ 231.1016, found 231.1016.

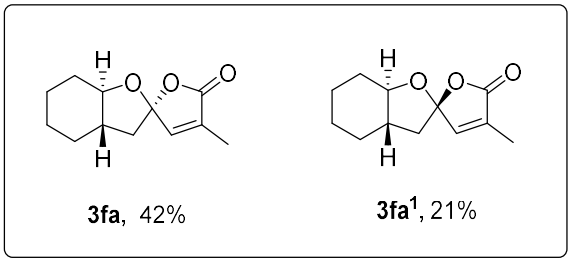
2-(prop-2-yn-1-yl)cyclohexan-1-ol (1f):



1f

Compound **1f** was prepared using analogous literature procedure:[9] **1f**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.38 (td, *J* = 9.9, 4.4 Hz, 1H), 2.50-2.42 (m, 1H), 2.32 (ddd, *J* = 16.8, 6.9, 2.7 Hz, 1H), 2.03-1.94 (m, 3H), 1.91-1.84 (m, 1H), 1.80-1.65 (m, 2H), 1.38-1.49 (m, 1H), 1.30-1.15 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 83.0, 73.5, 69.7, 43.9, 35.5, 30.3, 25.4, 24.9, 21.8; HRMS (ESI) m/z calcd for $C_9H_{15}O$ $[M+H]^+$ 139.1117, found 139.1114.

4'-methyl-3a,4,5,6,7,7a-hexahydro-3*H*,5'*H*-spiro[benzofuran-2,2'-furan]-5'-one (3fa and 3fa^1):



3fa, 42% **3fa^1**, 21%

Following the *General Procedure*, to the mixture of 2-(prop-2-yn-1-yl)cyclohexan-1-ol (**1f**) (0.15 g, 1.09 mmol) and ethyl pyruvate (**2a**) (0.12 g, 1.09 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.073g, 0.22 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 24 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 8% EtOAc/hexanes) afforded two separable diastereomers of 4'-methyl-3a,4,5,6,7,7a-hexahydro-3*H*,5'*H*-spiro[benzofuran-2,2'-furan]-5'-one (0.095 g of **3fa** (42%) and 0.048 g of **3fa^1** (21%); α:β = 7:3) as a white solid.

3fa: TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); Relative stereochemistry was assigned based on NOE analysis (see below). ^{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), 2.20-2.06 (m, 2H), 1.99-1.93 (m, 1H), 1.91 (s, 3H), 1.88 (d, *J* = 11.6 Hz, 1H), 1.78 (d, *J* = 7.3 Hz, 1H), 1.63-1.51 (m, 1H), 1.45-1.30

[9] Man, Z.; Dai, H.; Shi,Y.; Yang, D.; Li, C.Y. *Org. Lett.*, **2016**, *18*, 4962–4965.

(m, 2H), 1.28-1.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.9, 145.7, 131.2, 111.8, 84.7, 46.3, 39.8, 30.5, 28.5, 25.5, 24.0, 10.3; HRMS (ESI) m/z calcd for $C_{12}H_{17}O_3$ $[M+H]^+$ 209.1172, found 209.1173.

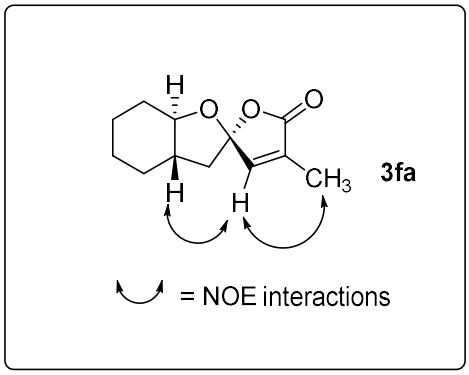
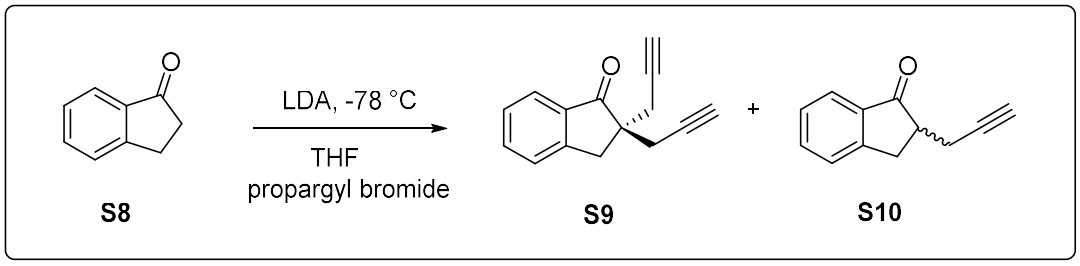


Figure 1. Key NOE interactions in compound **3fa**.

3fa[1]: R_f = 0.58 (SiO_2, 20% EtOAc/hexanes), Relative stereochemistry was assigned based on analogy to **3fa**; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.72 (d, *J* = 1.5 Hz, 1H), 3.39 (td, *J* = 10.7, 3.8 Hz, 1H), 2.17-2.11 (m, 2H), 2.0 (d, *J* = 14.1 Hz, 1H), 1.97-1.92 (m, 1H), 1.91 (d, *J* = 1.5 Hz, 3H), 1.88-1.85 (m, 1H), 1.78-1.73 (m, 1H), 1.50 (qd, *J* = 11.7, 3.8 Hz, 1H), 1.31-1.24 (m, 3H), 1.17 (td, *J* = 12.2, 3.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.3, 145.9, 132.4, 111.4, 86.7, 43.7, 41.5, 31.3, 28.5, 25.5, 24.2, 10.4; HRMS (ESI) m/z calcd for $C_{12}H_{17}O_3$ $[M+H]^+$ 209.1172, found 209.1174.

2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1*H*-inden-1-one (S9) and 2-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-inden-1-one (S10)

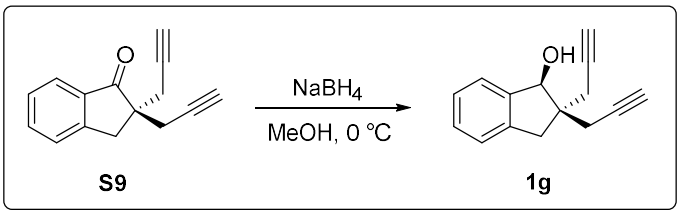


To a flame dried (100 mL) two neck round bottom flask, anhydrous THF (20 mL) was added under argon atmosphere and cooled it to 0 °C, to this diisopropylamine (0.42 mL, 4.16 mmol) followed by *n*-butyllithium (1.6 M in hexanes, 2.837 mL,) was added drop wise at 0

°C and stirred for 45 min at 0 °C to generate LDA solution. To this LDA solution was added 1-indanone (**S8**) (0.5 g, 3.78 mmol) in THF (20 mL) and stirred the reaction mixture at -78 °C for 30 min, then warmed to 0 °C and stirred for another 30 min. Reaction mixture was cooled back to -78 °C and propargyl bromide (80% in toluene, 0.2 mL, 3.78 mmol) was added drop wise. The resulting mixture was stirred at -78 °C for 1 h and warmed to 25 °C and stirred for overnight. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc (3x25 mL), combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1*H*-inden-1-one (**S9**) (0.2 g, 25%) and (**S10**) 2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (0.64 g, 42%) TLC: R_f = 0.6 and 0.59 (SiO_2, 20% EtOAc/hexanes); **S9**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.69-7.58 (m, 1H), 7.53-7.45 (m, 1H), 7.44-7.34 (m, 1H), 3.32 (s, 2H), 2.71-2.44 (m, 4H), 1.88 (t, *J* = 2.7 Hz, 2H); HRMS (ESI) m/z calcd for $C_{15}H_{12}NaO$ $[M+Na]^+$ 231.0780, found 231.0774.

S10: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (d, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 3.40 (dd, *J* = 17.7, 8.54 Hz, 1H), 3.10 (dd, *J* = 17.1, 4.3 Hz, 1H), 2.89-2.84 (m, 1H), 2.81-2.74 (m, 1H), 2.54 (ddd, *J* = 16.4, 7.9, 2.4 Hz, 1H), 1.90 (t, *J* = 2.7 Hz, 1H); HRMS (ESI) m/z calcd for $C_{12}H_{11}O$ $[M+H]^+$ 171.0804, found 171.0799.

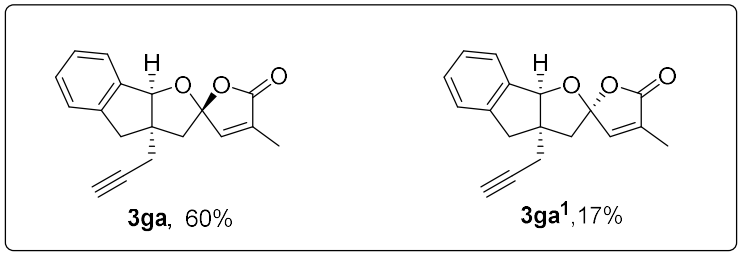
2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1*H*-inden-1-ol (1g):



To a solution of 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (**S9**) (0.13 g 0.66 mmol) in methanol (3 mL), sodium borohydride (0.015 g, 0.4 mmol) was slowly added at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then for 2.5 h at room temperature, after which the solvent was evaporated under reduced pressure. Aqueous NH_4Cl solution (5 mL) was added to the resulting suspension, and then extracted with EtOAc (3×5 mL). Organic phases were combined and dried over anhydrous Na_2SO_4, filtered and the

solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 6% EtOAc/hexanes) to afford 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1*H*-inden-1-ol **(1g)** (0.12 g, 87%) as a colourless liquid. TLC: R_f = 0.4 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46-7.36 (m, 1H), 7.32-7.22 (m, 3H), 5.13 (s, 1H), 3.09 (d, *J* = 15.9 Hz, 1H), 2.92 (d, *J* = 15.9 Hz, 1H), 2.66 (dd, *J* = 17.1, 2.4 Hz, 1H), 2.62-2.52 (m, 2H), 2.44 (dd, *J* = 17.1, 2.4 Hz, 1H), 2.28 (br s, 1H), 2.12 (t, *J* = 2.4 Hz, 1H), 2.05 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 142.8, 140.5, 128.6, 127.1, 125.2, 124.7, 81.9, 81.6, 80.7, 71.4, 70.6, 50.0, 40.1, 26.0, 22.1; HRMS (ESI) m/z calcd for $C_{15}H_{15}O$ $[M+H]^+$ 211.1117, found 211.1119.

4-methyl-3a'-(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5*H*-spiro[furan-2,2'-indeno[1,2-*b*]furan]-5-one (3ga, 3ga^1)



3ga, 60% **3ga^1**, 17%

Following the *General Procedure*, to the mixture of 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-ol **(1g)** (0.05 g, 0.24 mmol) and ethyl pyruvate **(2a)** (0.027 g, 0.24 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.032g, 0.05 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 4-methyl-3a'-(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5*H*-spiro[furan-2,2'-indeno[1,2-*b*]furan]-5-one and its diastereomer (77% yield,: 0.04 g of **3ga** (60%) and 0.011 g of **3ga^1** (17%) isolated yield *dr*: 8:2).

3ga: TLC: R_f = 0.4 (SiO_2, 20% EtOAc/hexanes); Relative stereochemistry was assigned based on NOE analysis (see below); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43-7.25 (m, 4H), 6.56 (s, 1H), 5.59 (s, 1H), 3.30 (d, *J* = 16.5 Hz, 1H), 3.10 (d, *J* = 17.1 Hz, 1H), 2.88 (AB q, *J* = 17.0, 3.0 Hz, 2H), 2.50 (d, *J* = 13.4 Hz, 1H), 2.21 (d, *J* = 14.0 Hz, 1H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.93 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.2, 144.5, 141.2, 140.8,

133.3, 129.4, 127.5, 125.7, 125.4, 113.2, 93.7, 81.4, 70.0, 52.6, 46.8, 43.0, 27.4, 10.5; HRMS (ESI) m/z calcd for $C_{18}H_{17}O_3$ $[M+H]^+$ 281.1172, found 281.1175.

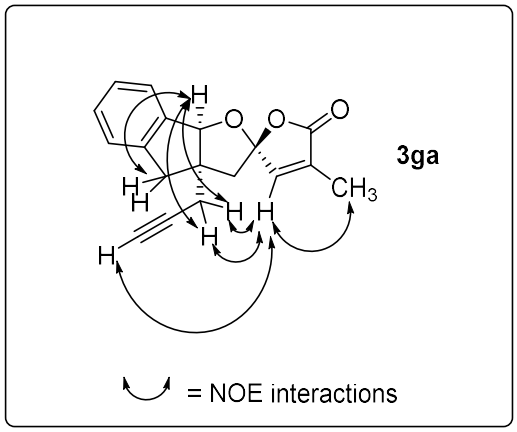
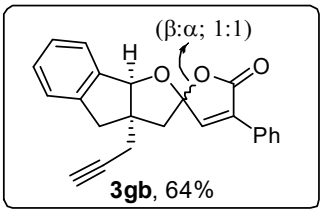


Figure 2. Key NOE interactions in compound **3ga**.

3ga[1]: TLC: R_f = 0.38 (SiO_2, 20% EtOAc/hexanes); Relative stereochemistry was assigned based on analogy to **3ga**; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, *J* = 7.3 Hz, 1H), 7.37-7.30 (m, 1H), 7.27-7.22 (m, 2H), 6.77 (s, 1H), 5.47 (s, 1H), 3.61 (d, *J* = 16.5 Hz, 1H), 3.04 (d, *J* = 16.5 Hz, 1H), 2.67-2.56 (m, 2H), 2.53-2.45 (m, 1H), 2.38 (d, *J* = 13.4 Hz, 1H), 2.06 (br s., 1H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.4, 144.6, 142.7, 139.6, 133.3, 129.6, 127.4, 126.1, 125.3, 113.9, 94.4, 80.8, 70.6, 52.6, 46.5, 43.7, 28.4, 10.4; HRMS (ESI) m/z calcd for $C_{18}H_{17}O_3$ $[M+H]^+$ 281.1172, found 281.1175.

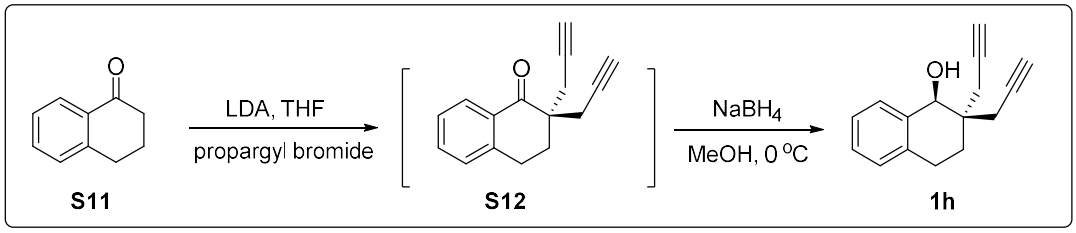
4-phenyl-3a'-(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5*H*-spiro[furan-2,2'-indeno[1,2-*b*]furan]-5-one (3gb)



Following the *General Procedure*, to the mixture of 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-ol **(1h)** (0.1 g, 0.48 mmol) and ethyl phenyl glyoxylate **(2b)**(0.08 g, 0.48 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.06 g, 0.1 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt.

Purification of the crude product by silica gel column chromatography (SiO_2, 3% EtOAc/hexanes) afforded inseparable diastereomeric mixture of 4-phenyl-3a'-(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5*H*-spiro[furan-2,2'-indeno[1,2-*b*]furan]-5-one (**3gb**) in 0.104 g (64% yield, *dr*: 1:1)) as a solid. TLC: R_f= 0.5 (SiO_2, 20% EtOAc/hexanes); (**3gb**; mixture of two diastereomers): Relative stereochemistry was assigned based on analogy to **3ga**[1]; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84-7.74 (m, 2H), 7.45-7.12 (m, 9H), 7.02 (s, 1H), 5.63 (s, 1H), 3.76-3.67 (m, 1H), 3.35-3.25 (m, 1H), 3.2-3.07 (m, 2H), 3.03-2.94 (m, 1H), 2.93-2.81 (m, 3H), 2.62-2.47 (m, 4H), 2.34-2.21 (m, 2H), 2.09-1.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.9, 143.1, 141.1, 140.8, 134.3, 129.9, 129.5, 128.8, 128.7, 127.6, 127.5, 127.4, 127.2, 125.8, 125.4, 125.3, 124.7, 112.4, 93.8, 81.4, 71.1, 70.2, 52.8, 50.6, 50.2, 48.8, 47.1, 43.7, 43.4, 42.9, 28.5, 27.4; HRMS (ESI) m/z calcd for $C_{23}H_{19}O_3$ $[M+H]^+$ 343.1329, found 343.1335.

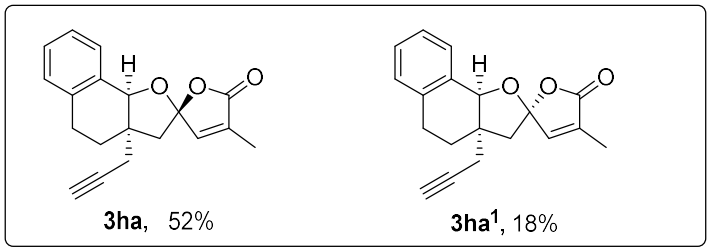
2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (1h)



To a flame dried (100 mL) two neck round bottom flask, anhydrous THF (50 mL) was added under argon atmosphere and cooled it to 0 °C, to this diisopropylamine (3.16 mL, 22.2 mmol) followed by *n*-butyllithium (1.6 M in hexanes, 12.82 mL,) was added drop wise at 0 °C and stirred for 45 min at 0 °C to generate LDA solution. To this LDA solution was added 1-tetralone (**S11**) (2.5 g, 17.1 mmol) in THF (10 mL) and stirred the reaction mixture at -78 °C for 30 min, then warmed to 0 °C and stirred for another 30 min. Reaction mixture was cooled back to -78 °C and propargyl bromide (80% in toluene, 1.2 mL, 17.1 mmol) was added drop wise. The resulting mixture was stirred at -78 °C for 1 h and warmed to 25 °C and stirred for overnight. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc (4x50 mL), combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure to give the crude product **S12** in (1 g, 26% yield), which was subjected to next reaction without further purification. To a solution of **S12** (0.3 g, 1.35 mmol) in methanol (10 mL), sodium borohydride (0.05 g, 1.35 mmol) was slowly

added at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then for 2.5 h at room temperature, after which the solvent was evaporated under reduced pressure. Aqueous NH_4Cl solution (5 mL) was added to the resulting suspension, and then extracted with EtOAc (3×10 mL). Organic phases were combined and dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 8% EtOAc/hexanes) to afford 2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol **(1h)** (0.28 g, 92%) as a solid as a colourless liquid. TLC: R_f = 0.35 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.46-7.40 (m, 1H), 7.26-7.20 (m, 2H), 7.17-7.11 (m, 1H), 4.68 (d, *J* = 5.3 Hz, 1H), 2.92-2.76 (m, 2H), 2.44 (AB q, *J* = 2.2 Hz, 16.7 Hz, 2H), 2.43 (AB q, *J* = 17.1, 2.2 Hz, 2H), 2.15 (d, *J* = 5.7 Hz, 1H), 2.09 (t, *J* = 2.7 Hz, 1H), 2.06 (t, *J* = 2.7 Hz, 1H), 1.98-1.90 (m, 1H), 1.90-1.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 136.7, 135.7, 129.4, 128.9, 127.9, 126.5, 81.1, 80.8, 72.6, 71.0, 70.9, 39.9, 26.6, 25.4, 23.8, 23.2; HRMS (ESI) m/z calcd for $C_{16}H_{17}O$ $[M+H]^+$ 225.1274, found 225.1268.

4-methyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'*H*,5*H*-spiro[furan-2,2'-naphtho[1,2-*b*]furan]-5-one (3ha, 3ha^1)



3ha, 52% **3ha^1**, 18%

Following the *General Procedure*, to the mixture of 2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol **(1h)** (0.1 g, 0.45 mmol) and ethyl pyruvate **(2a)** (0.05 g, 0.45 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.05 g, 0.09 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 4-methyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'*H*,5*H*-spiro[furan-2,2'-naphtho[1,2-*b*]furan]-5-one along with their partially separable diastereomer (70% yield,: 0.069 g (52%) and 0.023 g (18%) isolated yield (**3ha:3ha^1**; *dr*: β:α: 8.57:1.43)) as a solid.

3ha: TLC: R_f = 0.3 (SiO_2, 20% EtOAc/hexanes); Relative stereochemistry was assigned based on NOE analysis (see below); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, 7.3 Hz, 1H), 7.33-7.23 (m, 2H), 7.22-7.17 (m, 1H), 6.67 (s, 1H), 5.0 (s, 1H), 2.85-2.75 (m, 2H), 2.65-2.52 (m, 3H), 2.34 (d, J = 14.0 Hz, 1H), 2.07-1.97 (m, 2H), 1.97-1.87 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.5, 144.7, 137.2, 132.8, 132.3, 130.9, 128.7, 128.5, 126.7, 111.2, 83.9, 80.5, 70.8, 46.4, 43.9, 31.1, 26.6, 25.8, 10.4; HRMS (ESI) m/z calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1329, found 295.1318.

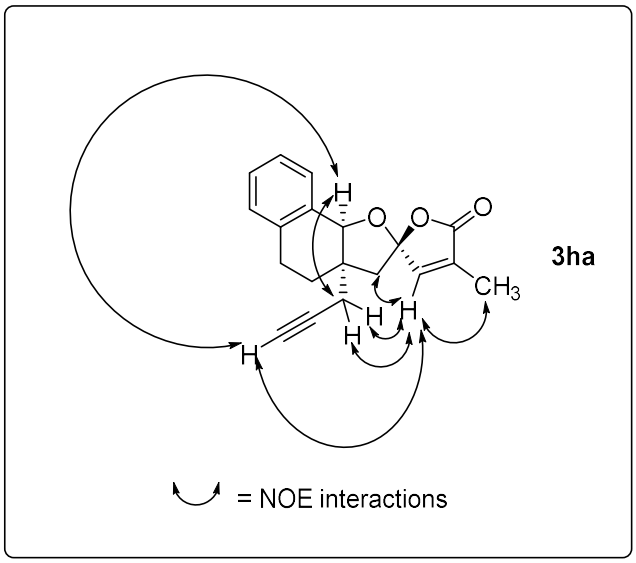
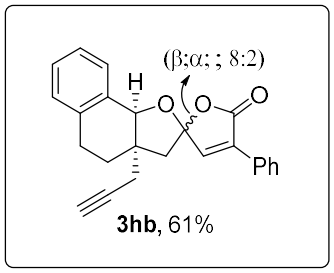


Figure 3. Key NOE interactions in compound **3ha**.

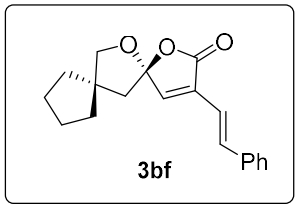
3ha[1] impure with **3ha** (**3ha+3ha**[1]; *dr*: β:α: 1 : 1.25): TLC: R_f = 0.3-0.29 (SiO_2, 20% EtOAc/hexanes); Relative stereochemistry was assigned based on analogy to **3ha**; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43-7.35 (m, 2H), 7.32-7.17 (m, 9H), 6.81 (d, J = 1.1 Hz, 1H), 6.67 (d, J = 1.5 Hz, 1H), 5.01 (s, 1H), 4.93 (s, 1H), 2.97- 2.31 (m, 13H), 2.13-1.9 (m, 10H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.5, 171.2, 145.7, 144.7, 137.2, 136.2, 132.9, 132.6, 132.3, 132.2, 130.9, 130.7, 128.7, 128.7, 128.5, 128.5, 126.7, 126.6, 111.9, 111.2, 83.9, 83.8, 80.5, 80.3, 71.5, 70.8, 46.6, 46.4, 43.9, 43.2, 31.2, 29.7, 28.3, 26.6, 25.8, 25.5, 10.4, 10.4; HRMS (ESI) m/z calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1329, found 295.1319.

4-phenyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'*H*,5*H*-spiro[furan-2,2'-naphtho[1,2-*b*]furan]-5-one (3hb)



Following the *General Procedure*, to the mixture of 2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol **(1h)** (0.1 g, 0.45 mmol) and ethyl phenylglyoxylate **(2b)** (0.08 g, 0.45 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.05 g, 0.09 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 0.097 g of inseparable diastereomeric mixture of 4-phenyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'*H*,5*H*-spiro[furan-2,2'-naphtho[1,2-*b*]furan]-5-one **3hb** (61% yield, (*dr*: 8:2)) as a solid. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.79 (m, 2H), 7.48-7.10 (m, 12H), 5.08 (s, 1H), 3.5-2.2 (m, 12H), 2.16-1.75 (m, 5H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.2, 144.2, 143.2, 137.2, 133.8, 132.2, 131.0, 130.8, 130.1, 129.8, 129.4, 128.8, 128.7, 128.6, 127.5, 126.8, 126.6, 126.5, 126.4, 110.4, 84.0, 83.9, 80.5, 71.4, 70.9, 51.1, 46.8, 46.7, 44.1, 42.8, 40.2, 31.2, 28.2, 26.6, 26.5, 25.8, 25.3; HRMS (ESI) m/z calcd for $C_{24}H_{21}O_3$ $[M+H]^+$ 357.1485, found 357.1473.

(*E*)-3-styryl-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (3bf)



Following the *General Procedure*, to the mixture of (1-(pent-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.1 g, 0.14 mmol) and ethyl (*E*)-2-oxo-4-phenylbut-3-enoate (**2f**)[10](0.294 g, 0.14 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.189 g, 0.028 mmol) under

[10]Dujardin, G.; Leconte, S.; Benard, A.; Brown, E. *Synlett*, **2001**, *1*, 147-149.

argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 5% EtOAc/hexanes) afforded (*E*)-3-styryl-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (**3bf**) (0.135 g, 63%) as a solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.71 (d, *J* = 16.44 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.39-7.30 (m, 3H), 6.90 (s, 1H), 6.81 (d, *J* = 14.44 Hz, 1H), 4.06 (d, *J* = 8.54 Hz, 1H), 3.9 (d, *J* = 8.54 Hz, 1H) 2.27 (s, 2H), 1.93-1.84 (m, 2H), 1.52.-1.78 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.4, 143.0, 136.6, 136.2, 131.4, 128.7, 127.1, 116.1, 113.1, 81.2, 50.5, 47.8, 38.0, 37.2, 24.6, 24.4; HRMS (ESI) m/z calcd for $C_{19}H_{21}O_3$ $[M+H]^+$ 297.1486, found 297.1485.

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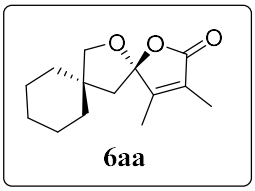
6. *Synthesis and Characterization* of unsaturated γ-spiroketal-γ-lactones from alkynols possessing internal alkyne functionality:

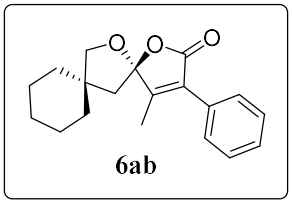
3, 4-Dimethyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6aa):



6aa

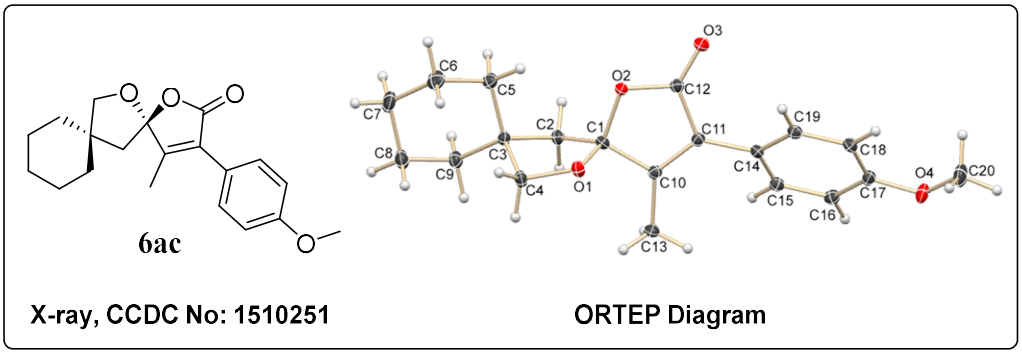
Following the *General Procedure*, to the mixture of (1-(but-2-yn-1-yl) cyclohexyl) methanol (**4a)** (0.05 g, 0.3 mmol) and ethyl pyruvate **2a** (0.05 g, 0.3 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.04 g, 0.06 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 5% EtOAc/hexanes) gave 3, 4-dimethyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**6aa**) (0.046 g, 65%) as a yellow oil. TLC: R_f = 0.7 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.95 (d, *J* = 8.8 Hz, 1H), 3.85 (d, *J* = 8.8 Hz, 1H), 2.04-1.94 (m, 2H), 1.90 (s, 3H), 1.80 (s, 3H), 1.72-1.65 (m, 2H), 1.53-1.39 (m, 8H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.7, 154.9, 126.0, 114.5, 80.6, 45.7, 43.4, 37.4, 35.6, 25.5, 23.8, 23.7, 10.5, 8.6; HRMS (ESI) m/z calcd for $C_{14}H_{21}O_3$ $[M+H]^+$ 237.1485, found 237.1486.

4-Methyl-3-phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6ab):



Following the *General Procedure*, to the mixture of (1-(but-2-yn-1-yl) cyclohexyl) methanol (**4a**) (0.05 g, 0.3 mmol) and ethyl phenylglyoxylate (**2b)** (0.054 g, 0.3 mmol) in dry CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.04 g, 0.066 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO_2, 3% EtOAc/hexanes) afforded 4-methyl-3-phenyl-1, 14-dioxadispiro[4.1.5^7.2^5] tetradec-3-en-2-one (**6ab**) (0.062 g, 68%) as a crystalline solid. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.34 (m, 5H), 4.06 (d, J = 8.5 Hz, 1H), 3.95 (d, J = 7.9 Hz, 1H), 2.23-2.05 (m, 2H), 2.13 (s, 3H), 1.83-1.72 (m, 2H), 1.60-1.45 (m, 8H); ^{13}C NMR ($CDCl_3$, 101 MHz); δ 169.9, 156.0, 129.6, 129.0, 128.98, 128.7, 128.5, 113.9, 80.9, 46.1, 43.7, 37.4, 35.6, 25.5, 23.9, 23.8, 11.5; HRMS (ESI) m/z calcd for $C_{19}H_{23}O_3$ $[M+H]^+$ 299.1642, found 299.1643.

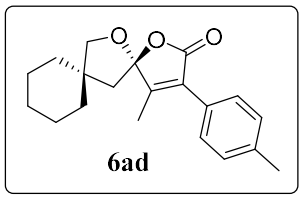
3-(4-Methoxyphenyl)-4-methyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6ac):



Following the *General Procedure*, to the mixture of (1-(but-2-yn-1-yl) cyclohexyl) methanol (**4a**) (0.050 g, 0.3 mmol) and ethyl anisylglyoxylate (**2c**) (0.063 g, 0.3 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.04 g, 0.066 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 3-(4-

methoxyphenyl)-4-methyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**6ac**) (0.062 g, 62%) as a crystalline solid. TLC: R_f = 0.45 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 4.05 (d, *J* = 7.9 Hz, 1H), 3.94 (d, *J* = 8.5 Hz, 1H), 3.85 (s, 3H), 2.12 (s, 3H), 2.21-2.04 (m, 2H), 1.76-1.7 (m, 2H), 1.61-1.41 (m, 8H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.2, 159.8, 154.3, 130.4, 128.4, 122.0, 113.9, 80.8, 55.3, 46.1, 43.6, 37.4, 35.7, 25.6, 23.9, 23.8, 11.6; HRMS (ESI) m/z calcd for $C_{20}H_{25}O_4$ $[M+H]^+$ 329.1747, found 329.1739.

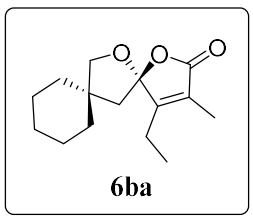
4-Methyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6ad):



6ad

Following the *General Procedure*, to the mixture of (1-(but-2-yn-1-yl) cyclohexyl) methanol (**4a**) (0.05 g, 0.3 mmol) and ethyl p-tolylglyoxylate (**2d**) (0.058 g, 0.3 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.04 g, 0.066 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 4% EtOAc/hexanes) gave 4-methyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**6ad**) (0.068 g, 72%) as a crystalline solid. TLC: R_f = 0.45 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 4.06 (d, *J* = 8.5 Hz, 1H), 3.94 (d, *J* = 8.5 Hz, 1H), 2.40 (s, 3H), 2.12 (s, 3H), 2.21-2.05 (m, 2H), 1.81-1.72 (m, 2H), 1.56-1.34 (m, 8H);^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.0, 155.1, 138.7, 129.2, 128.9, 126.7, 113.9, 80.8, 77.2, 46.1, 43.6, 37.4, 35.7, 25.6, 23.9, 23.8, 21.4, 11.5; HRMS (ESI) m/z calcd for $C_{20}H_{25}O_3$ $[M+H]^+$ 313.1798, found 313.1808.

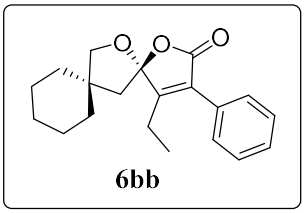
4-Ethyl-3-methyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6ba):



6ba

Following the *General Procedure*, to the mixture of (1-(pent-2-yn-1-yl) cyclohexyl) methanol (**4b**) (0.1 g, 0.55 mmol) and ethyl pyruvate (**2a**) (0.064 g, 0.55 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.073 g, 0.11 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 5% EtOAc/hexanes) provided 4-ethyl-3-methyl-1, 14-dioxadispiro [$4.1.5^7.2^5$] tetradec-3-en-2-one (**6ba**) (0.093 g, 68%) as a colourless oil. TLC: R_f = 0.45 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.96 (d, *J* = 8.5 Hz, 1H), 3.86 (d, *J* = 7.9 Hz, 1H), 2.44-2.31 (m, 1H), 2.31-2.2 (m, 1H), 2.06-1.96 (m, 2H), 1.84 (s, 3H), 1.74-1.67 (m, 2H), 1.55-1.39 (m, 8H), 1.17 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.9, 159.4, 126.0, 114.9, 80.5, 45.9, 43.3, 37.6, 35.7, 25.5, 23.9, 23.7, 18.9, 12.3, 8.6; HRMS (ESI) m/z calcd for $C_{15}H_{23}O_3$ $[M+H]^+$ 251.1642, found 251.1644.

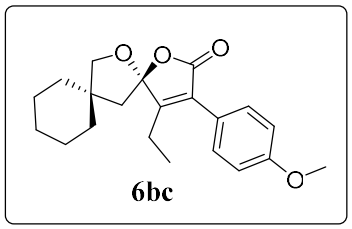
4-Ethyl-3-phenyl-1, 14-dioxadispiro [$4.1.5^7.2^5$] tetradec-3-en-2-one (6bb):



6bb

Following the *General Procedure*, to the mixture of (1-(pent-2-yn-1-yl) cyclohexyl) methanol (**4b**) (0.1 g, 0.55 mmol) and ethyl phenylglyoxylate (**2b**) (0.099 g, 0.55 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.073 g, 0.11 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 3% EtOAc/hexanes) afforded 4-ethyl-3-phenyl-1, 14-dioxadispiro [$4.1.5^7.2^5$] tetradec-3-en-2-one (**6bb**) (0.122 g, 70%) as a solid. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55-7.34 (m, 5H), 4.06 (d, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 8.4 Hz, 1H), 2.68-2.58 (m, 1H), 2.46-2.37 (m, 1H), 2.18 (s, 2H), 1.81-1.74 (m, 2H), 1.62-1.43 (m, 8H), 1.18 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.1, 160.5, 129.8, 129.4, 129.1, 128.9, 128.7, 128.4, 114.6, 80.7, 46.3, 43.5, 37.6, 35.7, 25.6, 23.9, 23.8, 19.4, 12.5; HRMS (ESI) m/z calcd for $C_{20}H_{25}O_3$ $[M+H]^+$ 313.1798, found 313.1797.

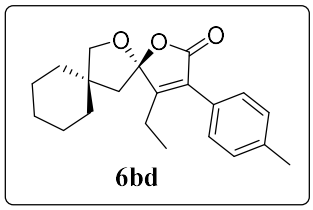
4-Ethyl-3-(4-methoxyphenyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6bc):



6bc

Following the *General Procedure*, to the mixture of (1-(pent-2-yn-1-yl) cyclohexyl) methanol (**4b**) (0.1 g, 0.55 mmol) and ethyl anisylglyoxylate (**2c**) (0.114 g, 0.55 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.073 g, 0.11 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 2% EtOAc/hexanes) gave 4-ethyl-3-(4-methoxyphenyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**6bc**) (0.146 g, 72%) as a solid. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 4.03 (d, *J* = 8.5 Hz, 1H), 3.93 (d, *J* = 8.5 Hz, 1H), 3.84 (s, 3H), 2.69-2.54 (m, 1H), 2.47-2.32 (m, 1H), 2.15 (s, 2H), 1.82-1.71 (m, 2H), 1.60-1.41 (m, 8H), 1.18 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.4, 159.8, 159.0, 130.2, 128.7, 122.2, 114.5, 113.9, 80.6, 55.3, 46.3, 43.4, 37.6, 35.7, 25.6, 23.9, 23.8, 19.4, 12.5; HRMS (ESI) m/z calcd for $C_{21}H_{27}O_4$ $[M+H]^+$ 343.1904, found 343.1905.

4-Ethyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6bd):

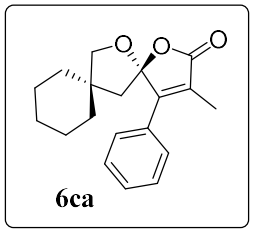


6bd

Following the *General Procedure*, to the mixture of (1-(pent-2-yn-1-yl) cyclohexyl) methanol (**4b**) (0.1 g, 0.55 mmol) and ethyl p-tolylglyoxylate (**2d**) (0.106 g, 0.55 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.073g, 0.11mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 2% EtOAc/hexanes) afforded 4-ethyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**6bd**) (0.13g, 76%) as a solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 4.05 (d, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 8.8 Hz, 1H), 2.68-

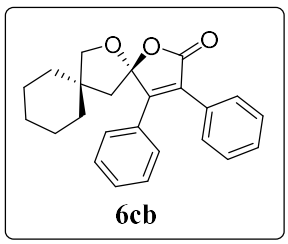
2.58 (m, 1H), 2.4 (s, 3H), 2.46-2.36 (m, 1H), 2.17 (s, 2H), 1.81-1.74 (m, 2H), 1.63-1.43 (m, 8H), 1.19 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.3, 159.8, 138.7, 129.3, 129.2, 128.8, 127.3, 126.9, 114.5, 80.6, 46.3, 43.4, 37.6, 35.8, 25.6, 23.9, 23.8, 21.3, 19.4, 12.5; HRMS (ESI) m/z calcd for $C_{21}H_{27}O_3$ $[M+H]^+$ 327.1955, found 327.1959.

3-Methyl-4-phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6ca):



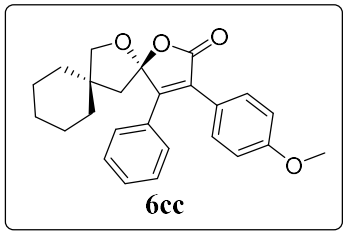
Following the *General Procedure*, to the mixture of (1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (**4c**) (0.1 g, 0.43 mmol) and ethyl pyruvate (**2a**) (0.052 g, 0.43 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 3% EtOAc/hexanes) afforded 3-methyl-4-phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**6ca**) (0.097g, 74%) as a white solid. TLC: R_f = 0.60 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.56-7.40 (m, 5H), 4.09 (d, J = 8.5 Hz, 1H), 3.94 (d, J = 8.5 Hz, 1H), 2.09 (d, J = 14.0 Hz, 1H), 2.0 (s, 3H), 1.86 (d, J = 14.0 Hz, 1H), 1.78-1.71 (m, 2H), 1.54-1.44 (m, 2H), 1.42-1.29 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.7, 154.8, 131.1, 129.6, 128.7, 128.4, 127.1, 115.0, 80.9, 43.3, 37.4, 35.8, 25.5, 23.9, 23.6, 9.9; HRMS (ESI) m/z calcd for $C_{19}H_{23}O_3$ $[M+H]^+$ 299.1642, found 299.1644.

3, 4-Diphenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6cb):



Following the *General Procedure*, to the mixture of (1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (**4c**) (0.1 g, 0.43 mmol) and ethyl phenylglyoxylate (**2b**) (0.078 g, 0.43 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature the reaction mixture was stirred for 12 h at rt. Purification of the crude product by crystallization (hexane:CH_2Cl_2 (8.2)) afforded 3, 4-diphenyl-1, 14-dioxadispiro [$4.1.5^7.2^5$] tetradec-3-en-2-one, (**6cb**) (0.187 g, 73%) as a solid. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.34 (m, 7H), 7.34-7.29 (m, 3H), 4.15 (d, *J* = 8.4 Hz, 1H), 3.98 (d, *J* = 8.4 Hz, 1H), 2.20 (d, *J* = 13.7 Hz, 1H), 1.93 (d, *J* = 13.7 Hz, 1H), 1.84-1.76 (m, 2H), 1.56-1.48 (m, 2H), 1.44-1.31 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.8, 155.2, 131.0, 129.7, 129.5, 129.4, 128.9, 128.73, 128.71, 128.4, 114.4, 81.0, 43.4, 37.3, 35.8, 25.5, 23.9, 23.7;HRMS (ESI) m/z calcd for $C_{24}H_{25}O_3$ $[M+H]^+$ 361.1798, found 361.1798.

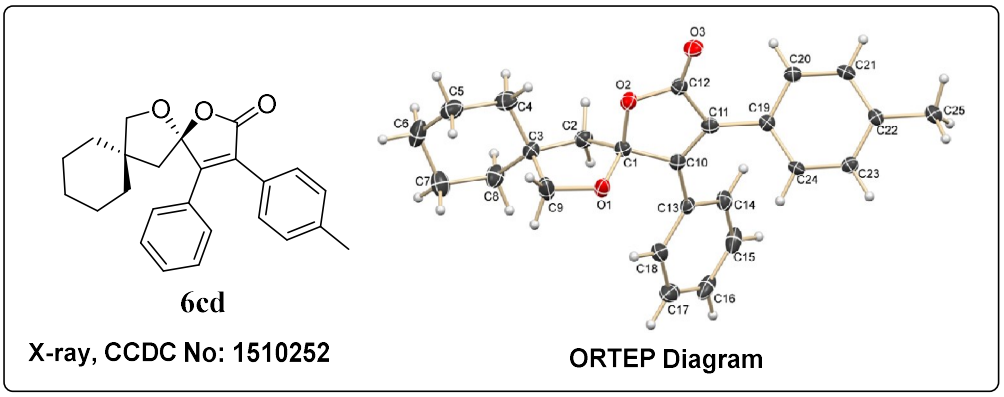
3-(4-Methoxyphenyl)-4-phenyl-1, 14-dioxadispiro [$4.1.5^7.2^5$] tetradec-3-en-2-one (6cc):



6cc

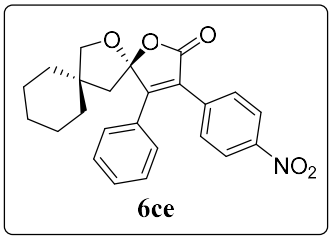
Following the *General Procedure*, to the mixture of (1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (**4c**) (0.1 g, 0.43 mmol) and ethyl anisylglyoxylate (**2c**) (0.091 g, 0.43 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 3-(4-methoxyphenyl)-4-phenyl-1, 14-dioxadispiro [$4.1.5^7.2^5$] tetradec-3-en-2-one (**6cc**) (0.116 g, 68%) as a solid. TLC: R_f = 0.45 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.33 (m, 7H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.13 (d, *J* = 8.5 Hz, 1H), 3.95 (d, *J* = 8.5 Hz, 1H), 3.81 (s, 3H), 2.17 (d, *J* = 13.4 Hz, 1H), 1.90 (d, *J* = 14.0 Hz, 1H), 1.82-1.74 (m, 2H), 1.54-1.47 (m, 2H), 1.43-1.25 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.2, 160.0, 153.5, 131.4, 130.9, 129.5, 128.7, 128.7, 128.3, 121.7, 114.4, 113.8, 80.9, 55.2, 43.4, 37.3, 35.8, 29.7, 25.5, 23.9, 23.7; HRMS (ESI) m/z calcd for $C_{25}H_{27}O_4$ $[M+H]^+$ 391.1904, found 391.1901.

4-Phenyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6cd):



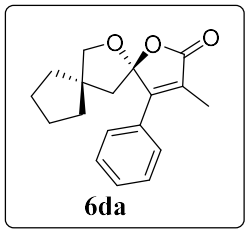
Following the *General Procedure*, to the mixture of (1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (**4c**) (0.1 g, 0.43 mmol) and ethyl p-tolylglyoxylate (**2d**) (0.084 g, 0.43 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature, the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 3% EtOAc/hexanes) afforded 4-phenyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (**6cd**) (0.088 g, 66%) as a white solid. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45-7.28 (m, 7H), 7.14-7.07 (m, 2H), 4.15 (d, J = 8.5 Hz, 1H), 3.96 (d, J = 8.5 Hz, 1H), 2.34 (s, 3H), 2.18 (d, J = 13.4 Hz, 1H), 1.91 (d, J = 14.0 Hz, 1H), 1.82-1.72 (m, 2H), 1.57-1.46 (m, 2H), 1.43-1.28 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.0, 154.4, 138.9, 131.2, 129.6, 129.4, 129.1, 128.8, 128.7, 126.4, 114.4, 81.0, 46.5, 43.4, 37.3, 35.8, 25.5, 24.0, 23.7, 21.4; HRMS (ESI) m/z calcd for $C_{25}H_{27}O_3$ $[M+H]^+$ 375.1955, found 375.1956.

3-(4-Nitrophenyl)-4-phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6ce):



Following the *General Procedure*, to the mixture of (1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (**4c**) (0.1 g, 0.43 mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (**2e**) (0.97 g, 0.43 mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature, the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 3% EtOAc/hexanes) afforded 3-(4-nitrophenyl)-4-phenyl-1, 14-dioxadispiro [$4.1.5^7.2^5$] tetradec-3-en-2-one (**6ce**) (0.125 g, 70%) as a yellow solid. TLC: R_f = 0.65 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16 (d, *J* = 8.54 Hz, 2H), 7.61 (d, *J* = 9.16 Hz, 2H), 7.51-7.35 (m, 5H), 4.17 (d, *J* = 8.55 Hz, 1H), 3.98 (d, *J* = 8.55 Hz, 1H), 2.22 (d, *J* = 14.04 Hz, 1H), 1.93 (d, *J* = 14.04 Hz, 1H), 1.84-1.74 (m, 2H), 1.56-1.48 (m, 2H), 1.44-1.25 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 168.8, 158.4, 147.8, 130.6, 130.5, 129.2, 128.5, 123.5, 114.6, 81.3, 53.4, 43.6, 37.2, 35.8, 25.5, 23.9, 23.6; HRMS (ESI) m/z calcd for $C_{24}H_{24}O_5N$ $[M+H]^+$ 406.1649, found 406.1640.

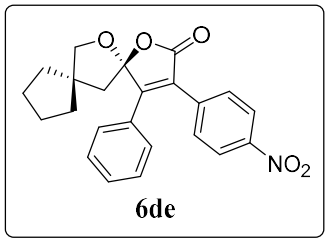
3-Methyl-4-phenyl-1, 13-dioxadispiro [$4.1.4^7.2^5$] tridec-3-en-2-one (6da):



6da

Following the *General Procedure*, to the mixture of (1-(3-phenylprop-2-yn-1-yl) cyclopentyl) methanol (**4d**) (0.05 gm, 0.23 mmol) and ethyl pyruvate (**2a**) (0.027 g, 0.23 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.03 g, 0.046 mmol) under argon atmosphere at room temperature the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 3% EtOAc/hexane) afforded 3-methyl-4-phenyl-1, 13-dioxadispiro [$4.1.4^7.2^5$] tridec-3-en-2-one one (**6da**) (0.036 g, 64%) as a solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz,): δ 7.55 - 7.44 (m, 5H), 4.14 (d, *J* = 8.0 Hz, 1H), 3.93 (d, *J* = 8.0 Hz, 1H), 2.15-2.04 (m, 2H), 2.01 (s, 3H), 1.95 - 1.85 (m, 2H), 1.73-1.53 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 171.7, 155.0, 131.1, 129.6, 128.7, 128.3, 127.1, 115.0, 81.5, 50.1, 47.0, 37.9, 37.7, 24.6, 24.3, 9.8; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_3$ [M+H] 285.1485, found 285.1482.

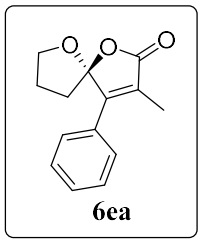
3-(4-Nitrophenyl)-4-phenyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (6de):



6de

Following the *General Procedure*, to the mixture of (1-(3-phenylprop-2-yn-1-yl) cyclopentyl) methanol (**4d**) (0.05 g, 0.23 mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (**2e**) (0.051 g, 0.23 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (0.03 g, 0.046 mmol) under argon atmosphere at room temperature, the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 3% EtOAc/hexanes) afforded 3-(4-nitrophenyl)-4-phenyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (**6de**) as a solid (0.05 g, 68%). TLC: R_f = 0.58 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (m, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.50-7.32 (m, 5H), 4.19 (d, *J* = 7.9 Hz, 1H), 3.96 (d, *J* = 7.9 Hz, 1H), 2.24 (d, *J* = 13.4 Hz, 1H), 2.12 (d, *J* = 14.0 Hz, 1H), 1.99-1.85 (m, 2H), 1.78-1.37 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.7, 158.6, 147.7, 136.0, 130.54, 130.47, 130.2, 129.2, 128.5, 126.8, 123.5, 114.6, 81.9, 50.3, 47.0, 37.8, 37.5, 24.7, 24.3; HRMS (ESI) m/z calcd for $C_{23}H_{22}O_5N$ $[M+H]^+$ 392.1492, found 392.1483.

3-Methyl-4-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6ea):

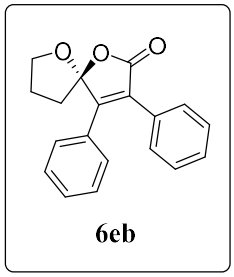


6ea

Following the *General Procedure*, to the mixture of 5-phenylpent-4-yn-1-ol (**4e**) (0.3 g, 1.87 mmol) and ethyl pyruvate (**2a**) (0.23 g, 1.87 mmol) in anhydrous CH_2Cl_2 (8 mL) was added $Bi(OTf)_3$ (0.09 g, 0.37 mmol) under argon atmosphere at room temperature, and the reaction mixture was stirred for 48 h at rt. Purification of the crude product by silica gel

column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 3-methyl-4-phenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (**6ea**) (0.038 g, 35%) as a solid. TLC: R_f = 0.45 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.49 (m, 2H), 7.48-7.42 (m, 3H), 4.33 (dt, *J* = 8.5, 4.3 Hz, 1H), 4.19-4.09 (m, 1 H), 2.39-2.27 (m, 1 H), 2.19-2.10 (m, 1 H), 2.08-1.96 (m, 5H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.5, 154.3, 131.1, 129.6, 128.7, 128.3, 127.3, 114.3, 70.4, 34.9, 24.4, 9.97; HRMS (ESI) m/z calcd for $C_{14}H_{15}O_3$ $[M+H]^+$ 231.1016, found 231.1013.

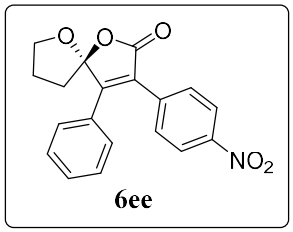
3,4-Diphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6eb):



6eb

Following the *General Procedure,* to the mixture of 5-phenylpent-4-yn-1-ol (**4e**) (0.3 g, 1.87 mmol) and ethyl phenylglyoxylate (**2b**) (0.333 g, 1.87 mmol) in anhydrous CH_2Cl_2 (8 mL) was added $Bi(OTf)_3$ (0.245 g, 0.37 mmol) under argon atmosphere at room temperature, and the reaction mixture was stirred for 48 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 3,4-diphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (**6eb**) (0.23 g, 42%) as a solid. TLC: R_f = 0.6 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.23 (m, 10H), 4.37 (td, *J* = 8.2, 3.7 Hz, 1H), 4.16 (m, 1H), 2.43-2.30 (m, 1H), 2.30-2.19 (m, 1H), 2.12-1.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.7, 154.8, 131.0, 129.8, 129.5, 129.4, 129.1, 128.9, 128.8, 128.7, 128.4, 113.7, 70.7, 34.9, 24.5; HRMS (ESI) m/z calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1172, found 293.1168.

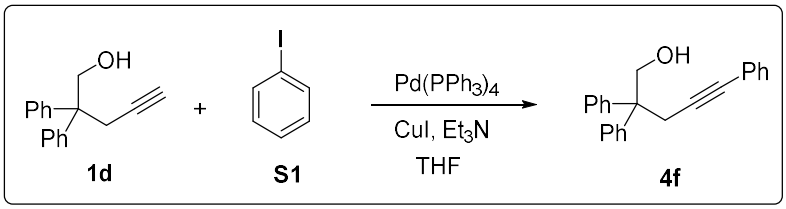
3-(4-Nitrophenyl)-4-phenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (6ee):



6ee

Following the *General Procedure*, to the mixture of 5-phenylpent-4-yn-1-ol (**4e**) (0.15 g, 0.72 mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (**2e**) (0.115 g, 0.72 mmol) in anhydrous CH_2Cl_2 (6 mL) was added $Bi(OTf)_3$ (0.095 g, 0.14 mmol) under argon atmosphere at room temperature, and the reaction mixture was stirred for 48 h at rt. Purification of the crude product by silica gel column chromatography (SiO_2, 5% EtOAc/hexanes) afforded 3-(4-nitrophenyl)-4-phenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (**6ee**) (0.052 g, 48%) as a solid. TLC: R_f = 0.45 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.48-7.42 (m, 1H), 7.42-7.35 (m, 4H), 4.42 (td, *J* = 8.4, 3.8 Hz, 1H), 4.21 (q, *J* = 8.0 Hz, 1H), 2.45-2.35 (m, 1H), 2.35-2.27 (m, 1H), 2.15-2.01 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 168.6, 157.9, 147.8, 136.0, 130.6, 130.5, 130.1, 129.2, 128.5, 127.1, 123.6, 113.9, 71.0, 34.9, 24.6; HRMS (ESI) m/z calcd for $C_{19}H_{16}O_5N$ $[M+H]^+$ 338.1023, found 338.1018.

2,2,5-triphenylpent-4-yn-1-ol (4f):



Compound (**4f**) was prepared using literature procedure.[11] $Pd(PPh_3)_4$ (0.015 g, 0.012 mmol) and CuI (0.048 g, 0.025 mmol) were added to the solution of iodobenzene (**S1**) (0.29 ml, 2.53 mmol) and 2,2-diphenylpent-4-yn-1-ol (**1d**) (0.3 g, 1.27 mmol) in triethylamine (1.78 mL, 12.7 mmol) and THF (10 mL) under argon atmosphere. The reaction mixture was stirred at rt for 12 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford the 2,2,5-triphenylpent-4-yn-1-ol (**4f**) as a brown oil (0.21 g, 53%).TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.23 (m , 15H), 4.39 (d, *J* = 6.1 Hz, 2H), 3.30 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.5, 131.5, 128.2, 128.1, 127.7, 126.7, 87.1, 83.7, 68.5, 52.2, 28.4; HRMS (ESI) m/z calcd for $C_{23}H_{21}O$ $[M+H]^+$ 313.1587, found 313.1587.

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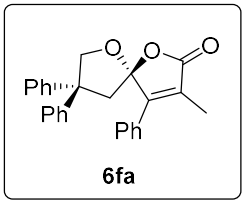
[11]Komeyama, K.; Yamada, T.; Igawa, R.; Takaki, K. *Chem. Commun*. 2**012**, *48*, 6372–6374.

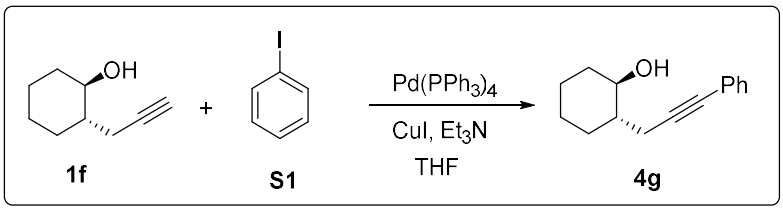
3-methyl-4, 8, 8-triphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (6fa):



6fa

Following the *General Procedure*, to the mixture of 2,2,5-triphenylpent-4-yn-1-ol (**4f**) (0.05 g, 0.16 mmol) and ethyl pyruvate (**2a**) (0.019 g, 0.16mmol) in anhydrous CH_2Cl_2 (2 mL) was added $Bi(OTf)_3$ (0.02 g, 0.032 mmol) under argon atmosphere at room temperature, the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc/hexanes) afforded3-methyl-4,8,8-triphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one(**6fa**) (0.038 g, 62%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.24 (m, 10H), 7.20-7.12 (m, 3H), 7.1-7.0 (m, 2H), 4.87 (d, *J* = 9.1 Hz, 1H), 4.77 (d, *J* = 9.7 Hz, 1H), 3.13 (d, *J* = 14 Hz, 1H), 2.90 (d, *J* = 14 Hz, 1H), 1.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) 171.3, 154.8, 146.1, 144.6, 130.4, 129.5, 128.6, 128.5, 128.3, 127.7, 127.4, 126.7, 126.4, 114.6, 79.3, 55.9, 48.2, 29.7, 9.8; HRMS (ESI) m/z calcd for $C_{26}H_{23}O_3$ $[M+H]^+$ 383.1642, found 383.1642.

2-(3-phenylprop-2-yn-1-yl) cyclohexan-1-ol (4g):

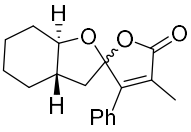


1f **S1** **4g**

2-(3-phenylprop-2-yn-1-yl)cyclohexan-1-ol (**4g**) was prepared according to the known procedure.[2] $Pd(PPh_3)_4$ (0.012 g, 0.011 mmol) and CuI (0.004 g, 0.021 mmol) were added to the solution of iodobenzene (**S1**) (0.24 ml, 2.17 mmol) and 2-(prop-2-yn-1-yl)cyclohexan-1-ol (0.15 g, 1.086 mmol) (**1f)** in triethylamine (1.5 mL, 10.86 mmol) and THF (10 mL) under argon atmosphere. The reaction mixture was stirred at rt for 12 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford 2-(3-phenylprop-2-yn-1-yl) cyclohexan-1-ol (**4g)** as brown oil (0.16 g, 69 %). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.39 (m, 2H), 7.33-7.26 (m, 3H), 3.53-

3.39 (m, 1H), 2.69 (dd, *J* = 16.4, 4.2 Hz, 1H), 2.56 (d, *J* = 17.1, 6.7 Hz, 1H), 2.05 – 1.91 (m, 2H), 1.87-1.65 (m, 3H), 1.64 - 1.48 (m, 1H), 1.35-1.22 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 131.5, 128.2, 127.6, 123.8, 88.5, 82.1, 73.8, 44.4, 35.5, 30.5, 25.5, 24.9, 22.8; HRMS (ESI) m/z calcd for $C_{15}H_{19}O$ $[M+H]^+$ 215.1430, found 215.1431.

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



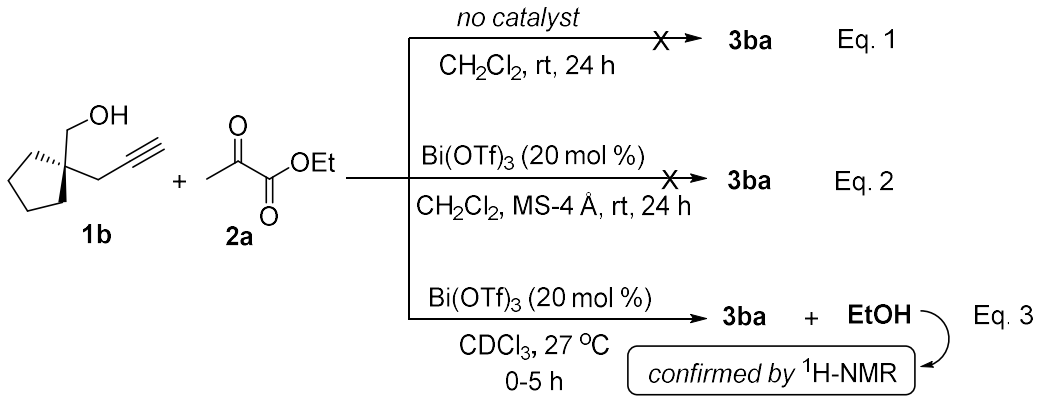
6ga + 6ga[1]

Following the *General Procedure*, to the mixture of 2-(3-phenylprop-2-yn-1-yl)cyclohexan-1-ol (**6ga**) (0.1 g, 0.46 mmol) and ethyl pyruvate (**2a**) (0.053g, 0.46mmol) in anhydrous CH_2Cl_2 (5 mL) was added $Bi(OTf)_3$ (0.060 g, 0.092 mmol) under argon atmosphere at room temperature, and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO_2, 5% EtOAc /hexanes) afforded separable 1:1 diastereomeric mixture of (3a,7a)-4'-methyl-3'-phenyl-3a,4,5,6,7,7a-hexahydro-3*H*,5'*H*-spiro[benzofuran-2,2'-furan]-5'-one (43 mg of **6ga** and 43.5 mg of **6ga[1]** (overall yield 64%).

6ga: TLC: R_f = 0.60 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44-7.38 (m, 5H), 3.25 (td, *J* = 3.81, 10.3 Hz, 1H), 2.82 (dd, *J* = 3.8, 12.9 Hz, 1H), 2.12-2.02 (m, 2H),1.97 (s, 3H), 1.84-1.73 (m, 2H), 1.7-1.62 (m, 1H), 1.57-1.37 (m, 3H), 1.24-1.17 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 171.5, 158.4, 136.0, 129.6, 129.0, 126.4, 123.3, 104.9, 78.1, 44.6, 31.7, 31.5, 31.2, 30.9, 25.2, 24.5, 8.5; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1486, found 285.1485.

6ga[1]: TLC: R_f = 0.53 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR($CDCl_3$, 500 MHz) δ 7.44-7.38 (m, 5H), 3.2 (td, *J* = 4.2, 10.7 1H),2.82 (dd, *J* = 4.2, 13.35, 1H), 2.18 (s, 2H), 2.1-2.02 (m, 2H), 1.97 (s, 3H), 1.85-1.73 (m, 2H), 1.7-1.6 (m, 1H), 1.53-1.4 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 171.5, 158.4, 136, 129.6, 129.0, ,126.4, 123.3, 104.92, 78.1, 44.6, 31.7, 31.5, 31.2, 25.2, 24.5, 8.5; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1487, found 285.1485.

7. Supporting experiments for the postulated reaction mechanism:



Eq. 1: To a dry 10 mL round bottom flask, equipped with a magnetic stir bar was added (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.1 g, 0.72 mmol) and ethyl pyruvate (**2a**) (0.083 g, 0.72 mmol) followed by anhydrous CH_2Cl_2 (5 mL) and stirred the reaction mixture at rt for 24 h under argon atmosphere without the addition of $Bi(OTf)_3$. Reaction monitored by TLC, which shown two starting materials (**1b** and **2a**) were remained intact even after 24 h. (This confirmed the role of the catalyst in the reaction).

Eq. 2: To a 10 mL round bottom flask, equipped with a magnetic stir bar was added activated molecular sieves (MS-4Å) powder and CH_2Cl_2 (5 mL). Then, added CH_2Cl_2 solution of (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.1 g, 0.72 mmol) and ethyl pyruvate (**2a**) (0.083 g, 0.72 mmol).Then $Bi(OTf)_3$ (0.09 g, 0.144 mmol) was added. The reaction mixture was stirred 24 h at rt under argon atmosphere. Interestingly, under these reaction conditions, the desired product was not observed (monitored by TLC). (This confirmed the role of in situ released water in the product (**3ba**) formation).

Eq. 3: **NMR-Scale Catalytic Reaction**: (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.01 g, 0.072 mmol) and ethyl pyruvate (**2a**) (0.0083 g, 0.072 mmol) were weighed in to a vial, and 500 μL $CDCl_3$ was added by syringe. The solution was mixed well and then transferred to a NMR tube, then $Bi(OTf)_3$ (0.009 g, 0.014 mmol) was added to the mixture in NMR tube, was monitored by ^1H NMR spectroscopy at 27 ^oC in between 0 to 5 h to identify reaction intermediates and by products to propose the reaction mechanism (Figure 1).

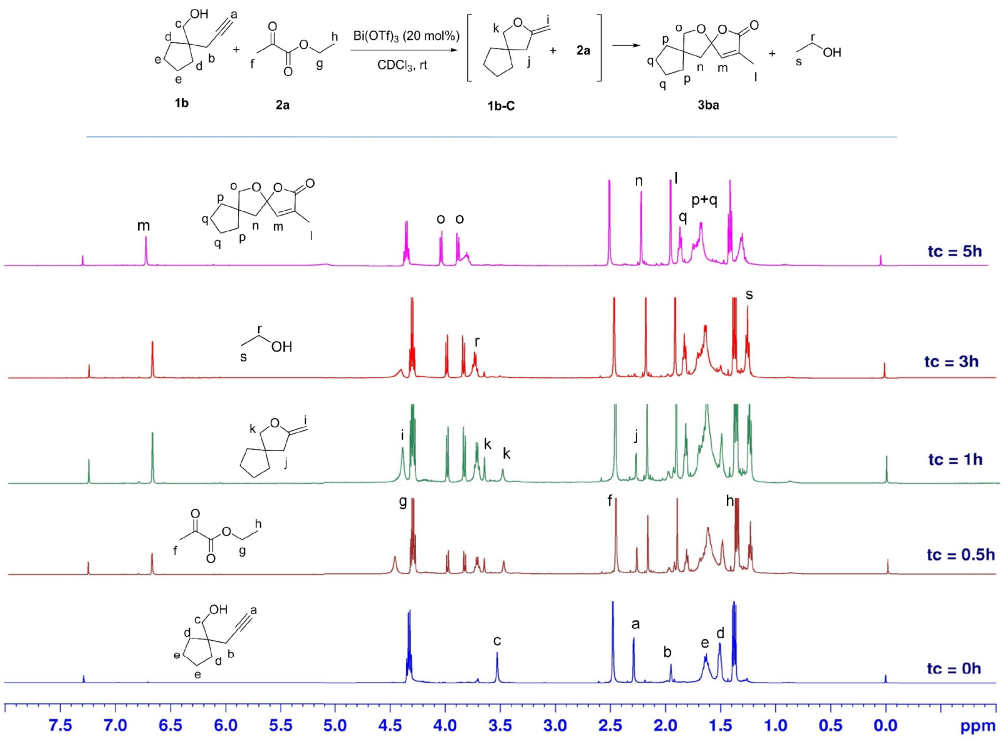


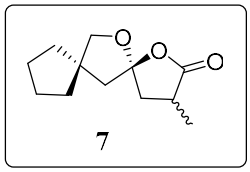
Figure 1. ^{1}H NMR spectra (500 MHz, $CDCl_3$): tc = o h, tc = 0.5 h, tc = 1 h, tc = 3 h and tc = 5 h are the spectrums belongs to respective reaction times.

An interesting observation in the above cascade annulation reaction is the various intermediates and products detected in the ^{1}H NMR spectroscopy as shown in Figure 1. Through, careful ^{1}H NMR analysis and by comparing with reported literature, we confirmed that this reaction proceeds through immediate formation of exocyclic-enolether (**1b-C**), which then reacts slowly with ethylpyruvate (**2a**) and gives the unsaturated γ-spiroketal-γ-lactone and EtOH as reaction products. These observations are consistent with Marks's reports (Eq 3. Figure 1).[12]

[12] S. –Y. Seo, X. Yu, T. J. Marks. *J. Am. Chem. Soc*. **2009**, *131*, 263-276.

8. Synthetic utility of unsaturated γ-spiroketal γ-lactones

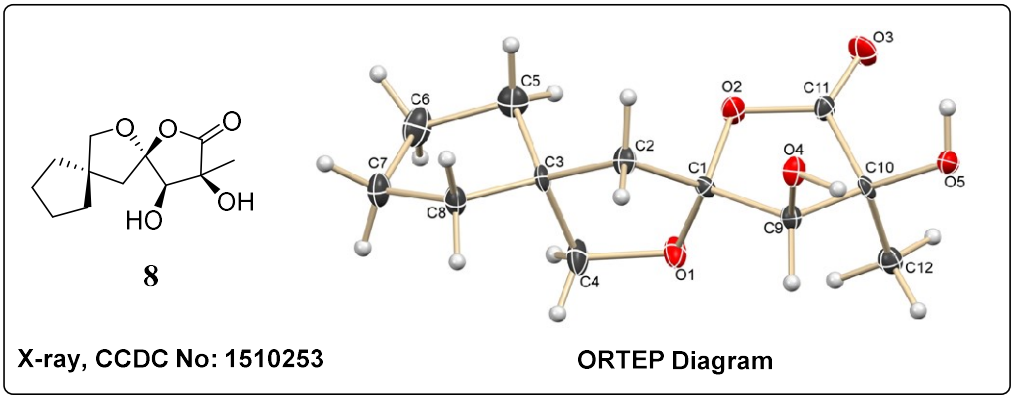
3-Methyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridecan-2-one (7):



7

To the mixture of 3-methyl-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (**3ba**) (0.05 g, 0.24 mmol) and Pd/C (0.025 g, 0.024 mmol) in anhydrous CH_2Cl_2 (5 mL) was added Et_3N (0.005 g, 0.048 mmol) at 0 °C under argon atmosphere, then argon was replaced with H_2 (in a balloon) and stirred the reaction mixture at room temperature for 3 h. After completion of the reaction, H_2 atmosphere was removed and the mixture passed through Celite-sintered glass funnel, filtrate was concentrated under reduced pressure. Purification of the crude product by silica gel column chromatography (5% EtOAc/hexane) afforded 3-methyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridecan-2-one (**7**) as crystalline solid (mixture of two diastereomers) (0.038 g, 76%). TLC: R_f = 0.65 (20% EtOAc/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (mixture of two diastereomers) 3.96-3.85 (m, 1H), 3.83 - 3.72 (m, 1H), 3.01 - 2.86 and 2.77-2.63 (m, 1H), 2.54-2.42 (m, 1H), 2.34-2.22 (m, 1H), 2.12-1.92 (m, 2H), 1.83-1.50 (m, 8H), 1.35 (minor isomer) (d, J = 7.32 Hz,) and 1.26 (major isomer) (d, J = 6.71 Hz) for 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ (mixture of two diastereomers) 179, 115.5, 114.1, 80.4, 80.0, 49.75, 49.67, 49.63, 48.86, 41.16, 40.14, 38.58, 38.49, 37.10, 37.05, 36.01, 34.97, 24.47, 24.31, 16.55, 15.01; HRMS (ESI) m/z calcd for $C_{12}H_{19}O_3$ $[M+H]^+$ 211.1329, found 211.1324.

3, 4-Dihydroxy-3-methyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridecan-2-one (8):

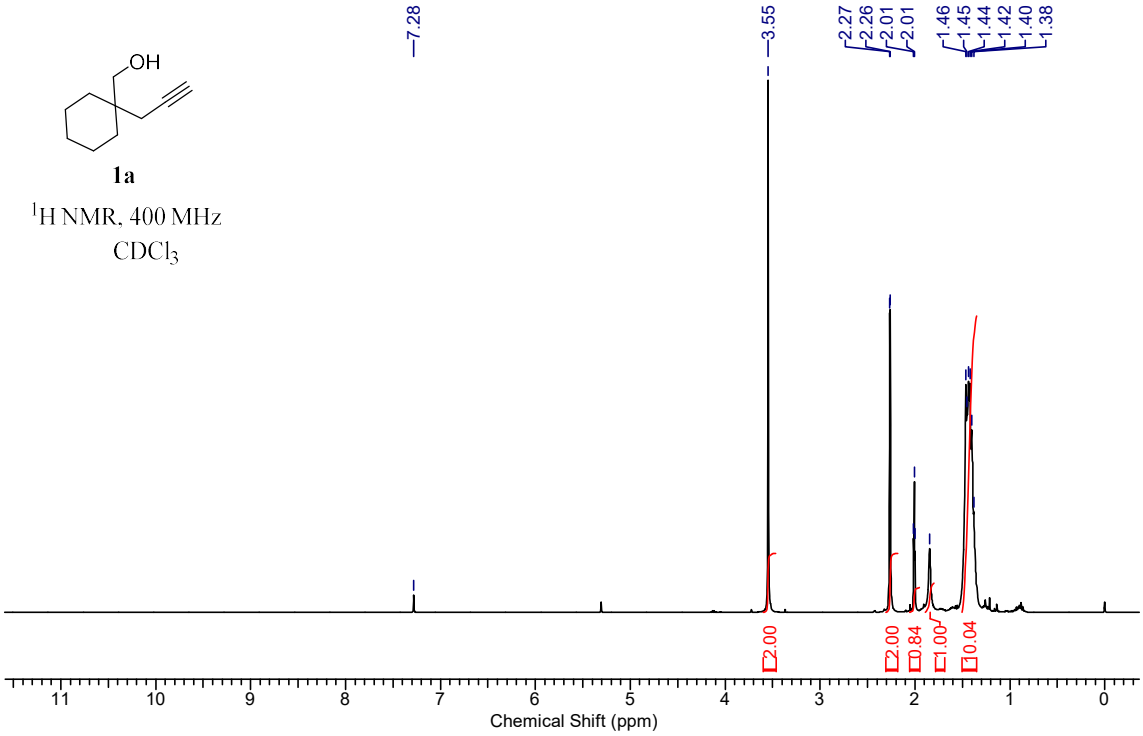


To a solution of 3-methyl-1,13-dioxadispiro[4.1.4^7.2^5]tridec-3-en-2-one (**3ba**) (0.15 g, 0.721 mmol) in 5:1 mixture of THF/H_2O (10 mL) was added *N*-methylmorphiline *N*-oxide hydrate (0.25 g, 2.16 mmol) and osmium tetroxide (0.1 M in toluene, 0.36 mL, 0.036 mmol). The reaction mixture was stirred at rt for 12 h. The resulting black mixture was quenched by saturated sodium sulphite solution and stirred at room temperature for 1 h. The aqueous layer was extracted with EtOAc (3x15 mL) and the combined organic layers were dried over anhydrous sodium sulphate, concentrated under reduced pressure and purified by silica gel column chromatography (SiO_2, 25% EtOAc/hexanes) to afford 3, 4-dihydroxy-3-methyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridecan-2-one (**8**) as a white crystalline solid (0.124 g, 71%). TLC: R_f = 0.5 (SiO_2, 50% EtOAc/hexanes);); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.98 (d, J = 8.5 Hz, 1H), 3.88 (s, 1H), 3.83 (d, J = 8.5 Hz, 1H), 3.48 (br. s., 1H), 3.25 (br. s, 1H), 2.48 (d, J = 14.6 Hz, 1H), 2.21 (d, J = 14.0 Hz, 1H), 1.64 (s, 3H), 1.84-1.54 (m, 8H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 177.9, 116.8, 81.3, 78.1, 77.2, 74.7, 48.7, 45.2, 37.8, 36.9, 24.6, 24.3, 23.0; HRMS (ESI): m/z calcd for $C_{12}H_{19}O_5$ $[M+H]^+$ 243.1227, found 243.1222.

9.

^{1}H and ^{13}C NMR Spectra

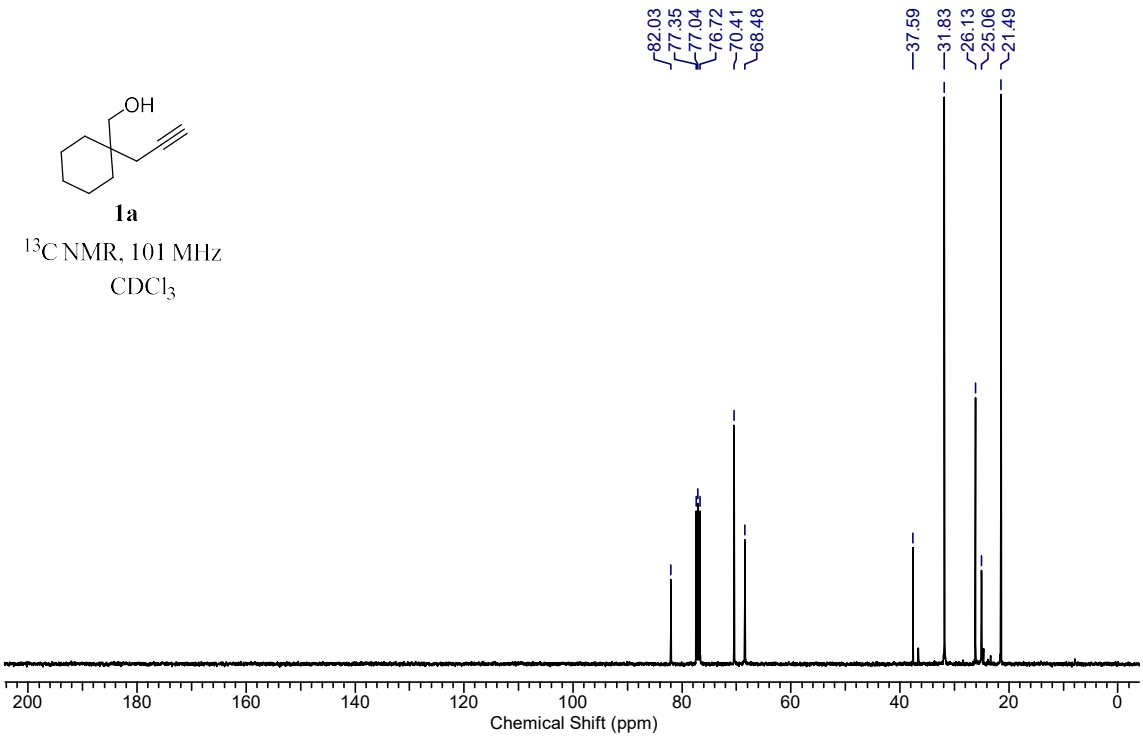
(1-(Prop-2-yn-1-yl)cyclohexyl)methanol (1a):



1a

^{1}H NMR, 400 MHz

$CDCl_3$

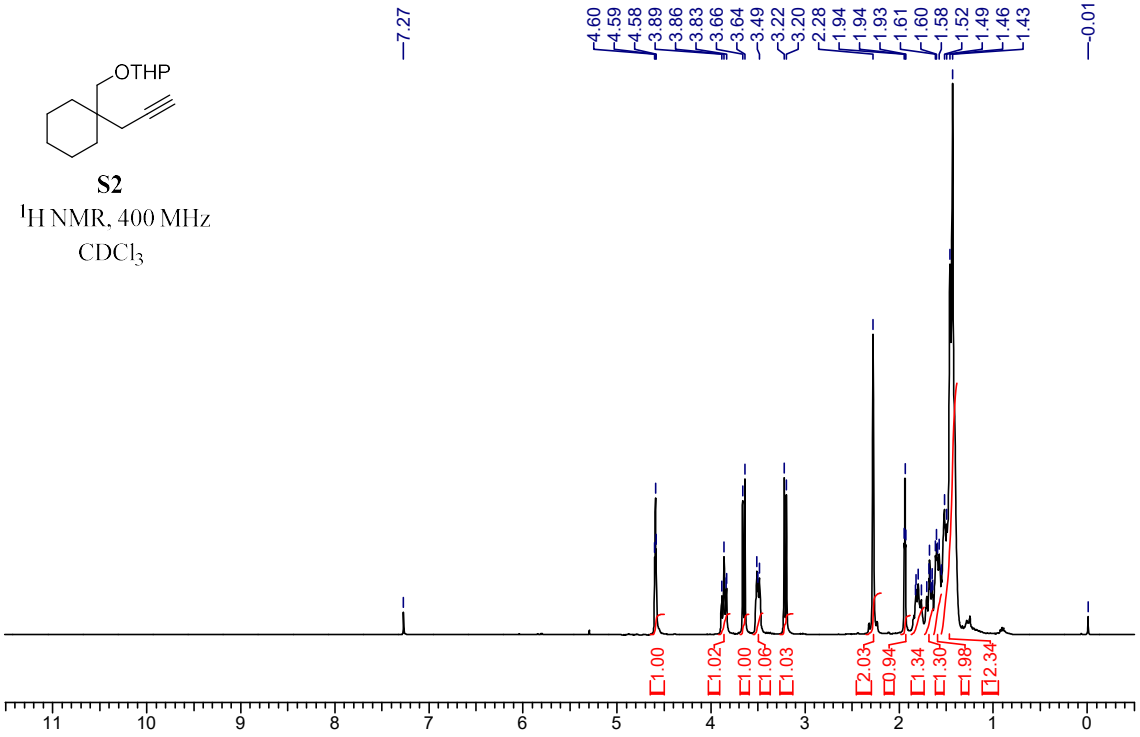


1a

^{13}C NMR, 101 MHz

$CDCl_3$

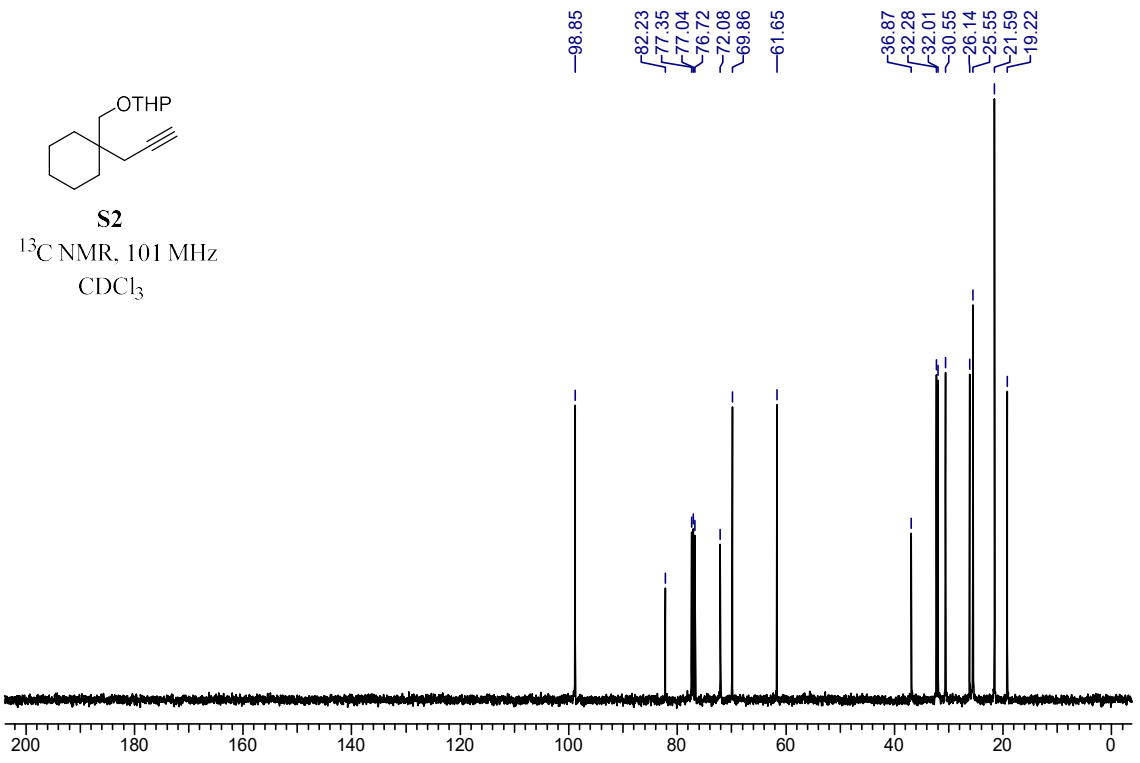
2-((1-(Prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S2):



S2

^{1}H NMR, 400 MHz

$CDCl_3$

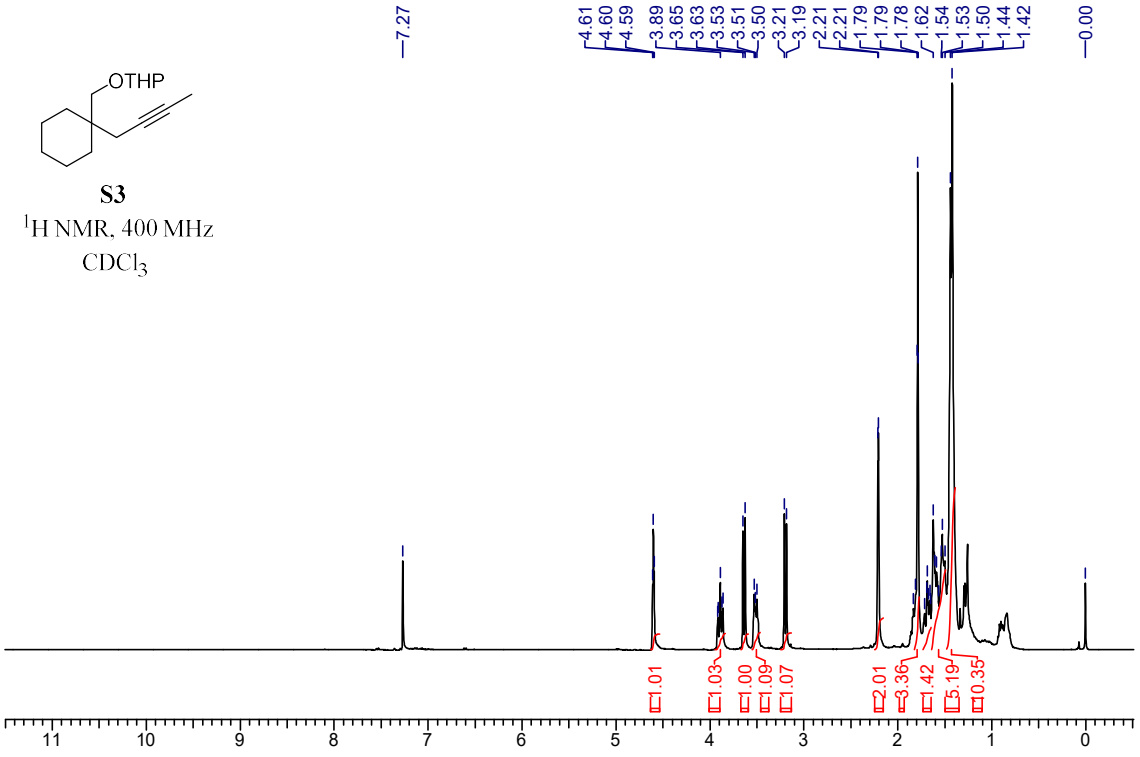


S2

^{13}C NMR, 101 MHz

$CDCl_3$

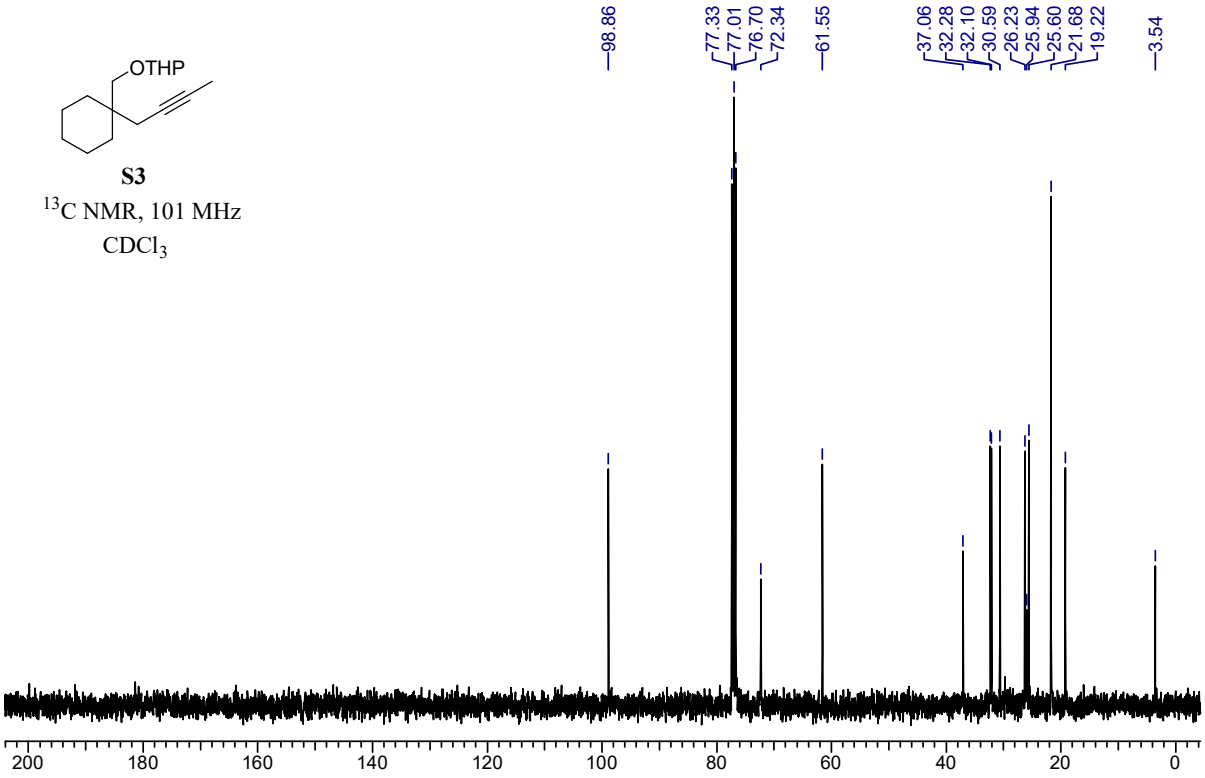
2-((1-(But-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S3):



S3

^{1}H NMR, 400 MHz

$CDCl_3$

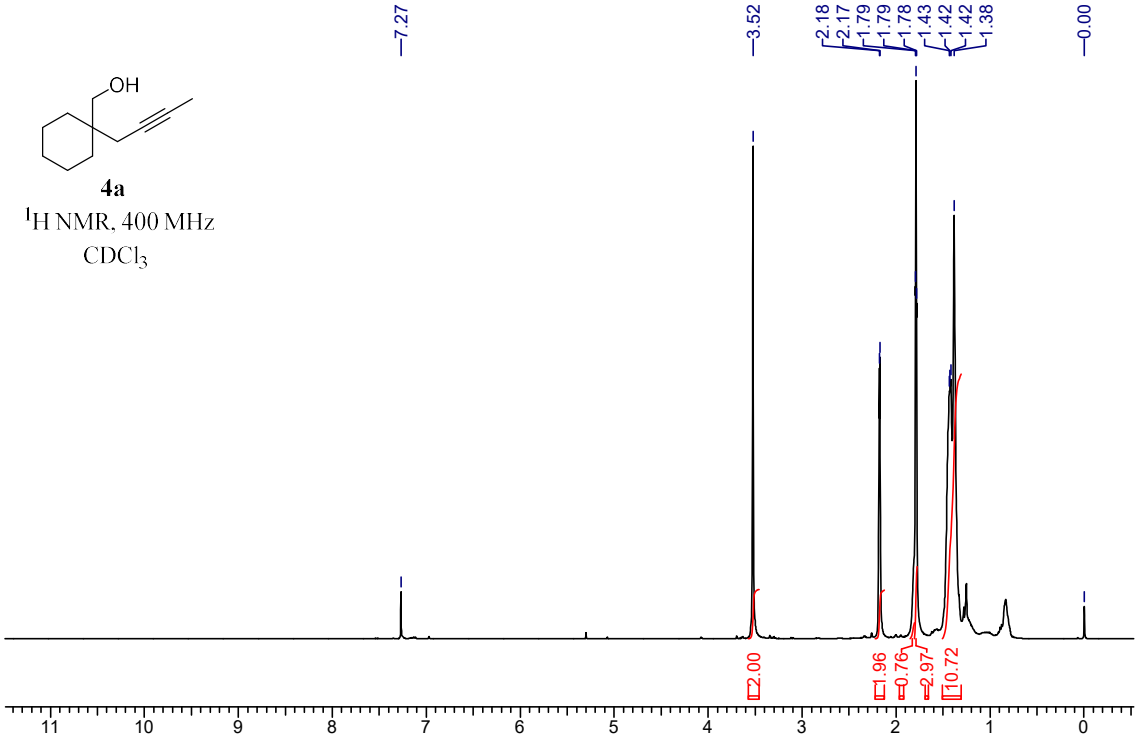


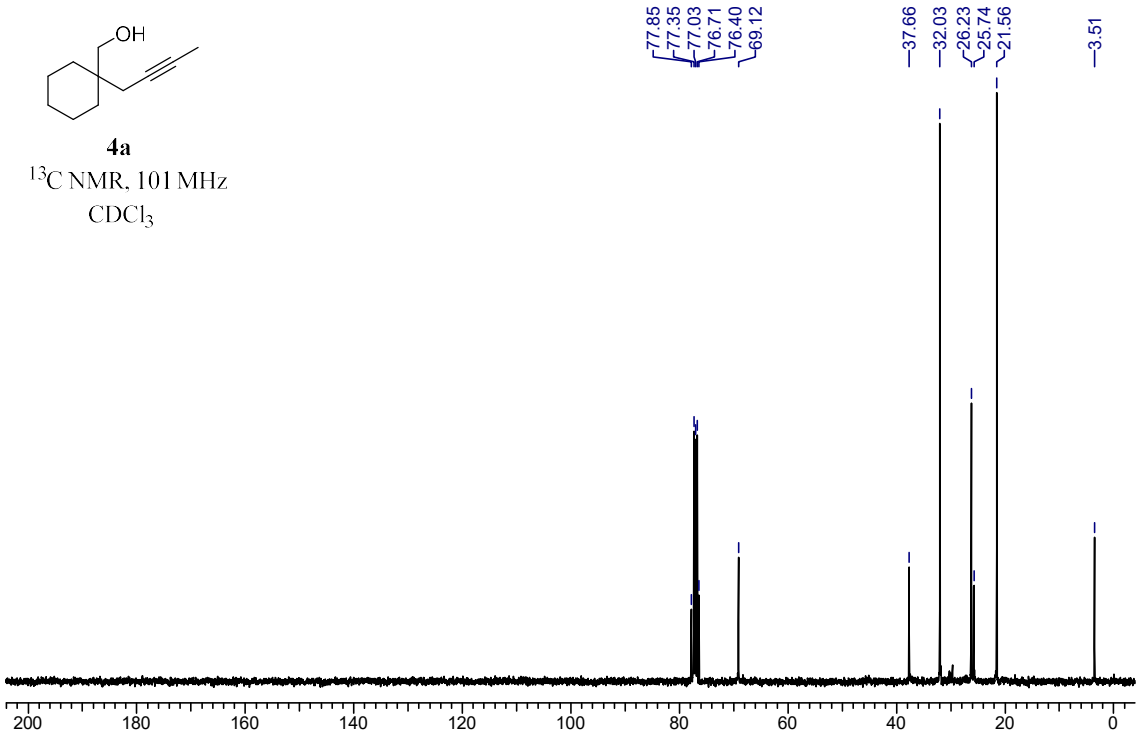
S3

^{13}C NMR, 101 MHz

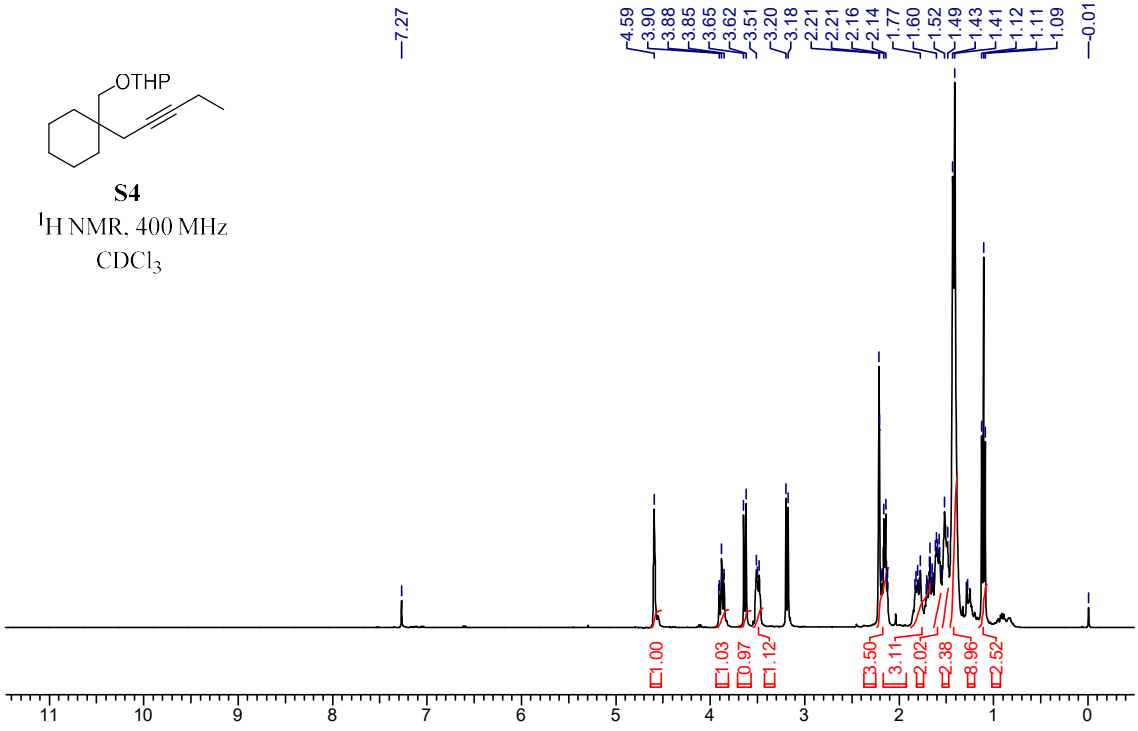
$CDCl_3$

(1-(But-2-yn-1-yl) cyclohexyl) methanol (4a):





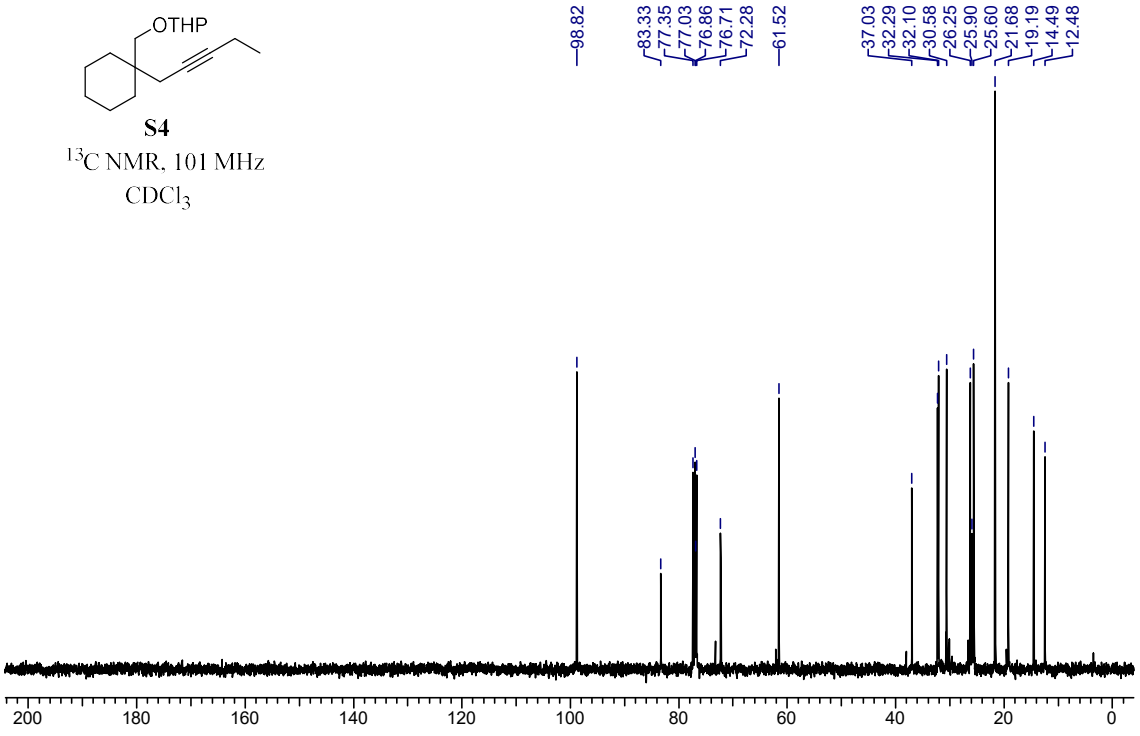
2-((1-(Pent-2-yn-1-yl)cyclohexyl)methoxy)tetrahydro-2H-pyran (S4):



S4

^{1}H NMR, 400 MHz

$CDCl_3$

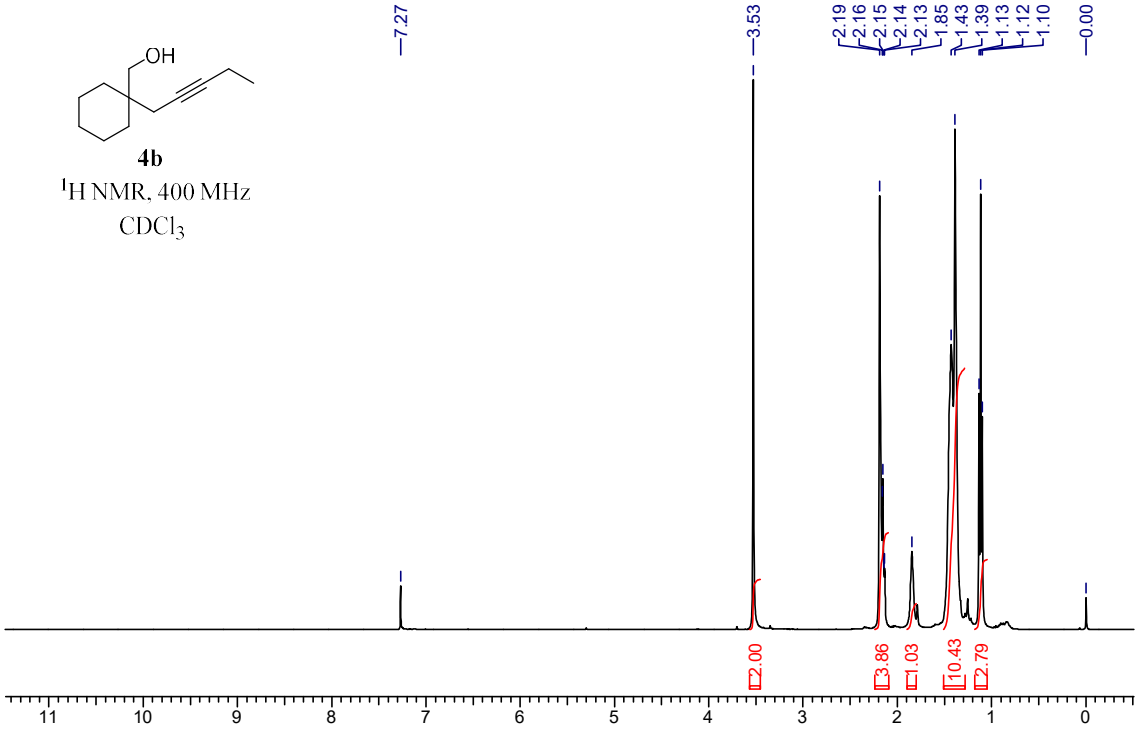


S4

^{13}C NMR, 101 MHz

$CDCl_3$

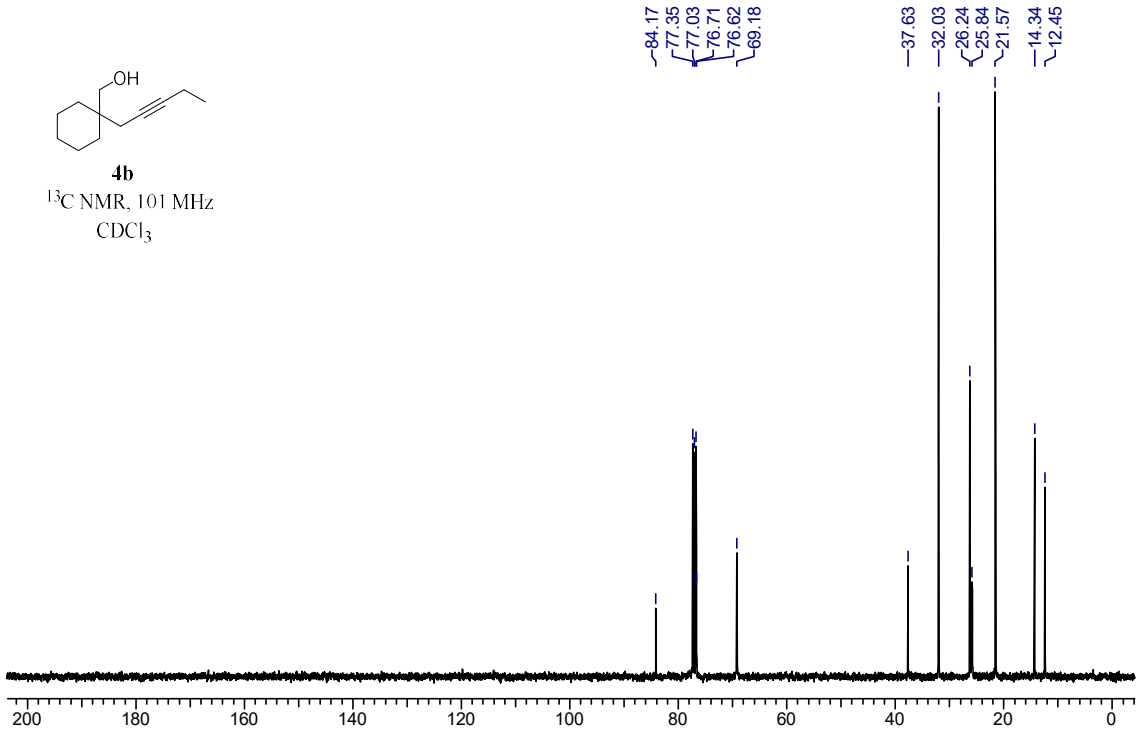
(1-(Pent-2-yn-1-yl) cyclohexyl) methanol (4b):



4b

^{1}H NMR, 400 MHz

$CDCl_3$

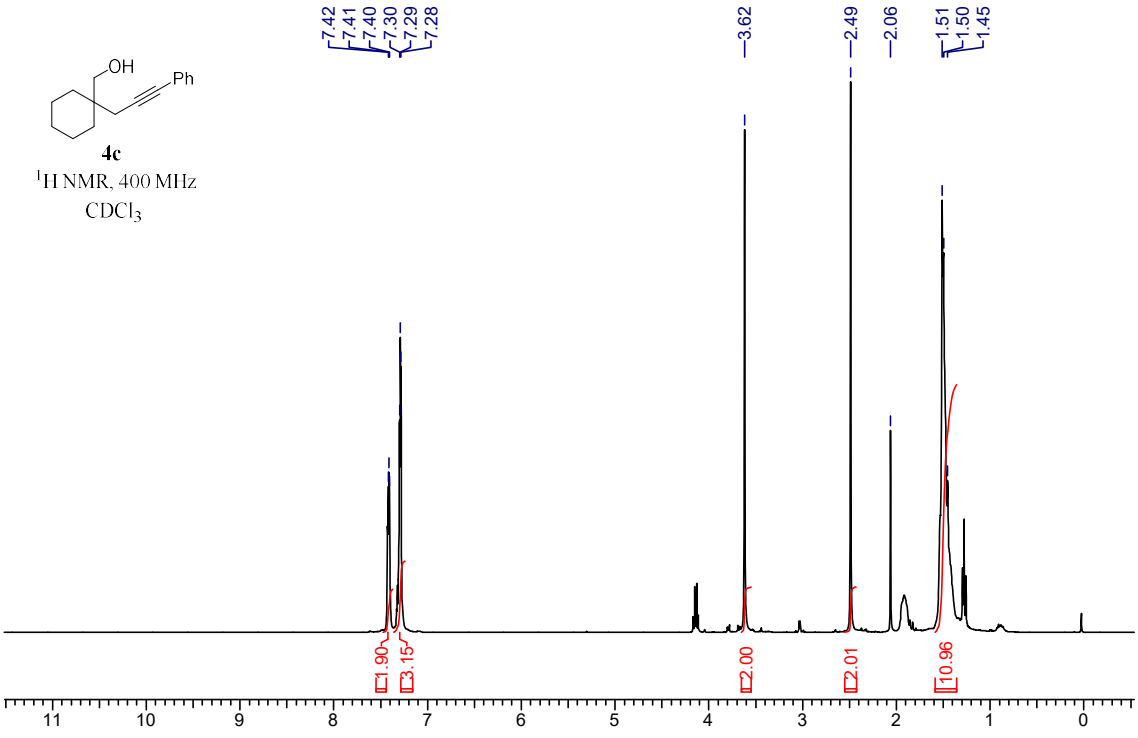


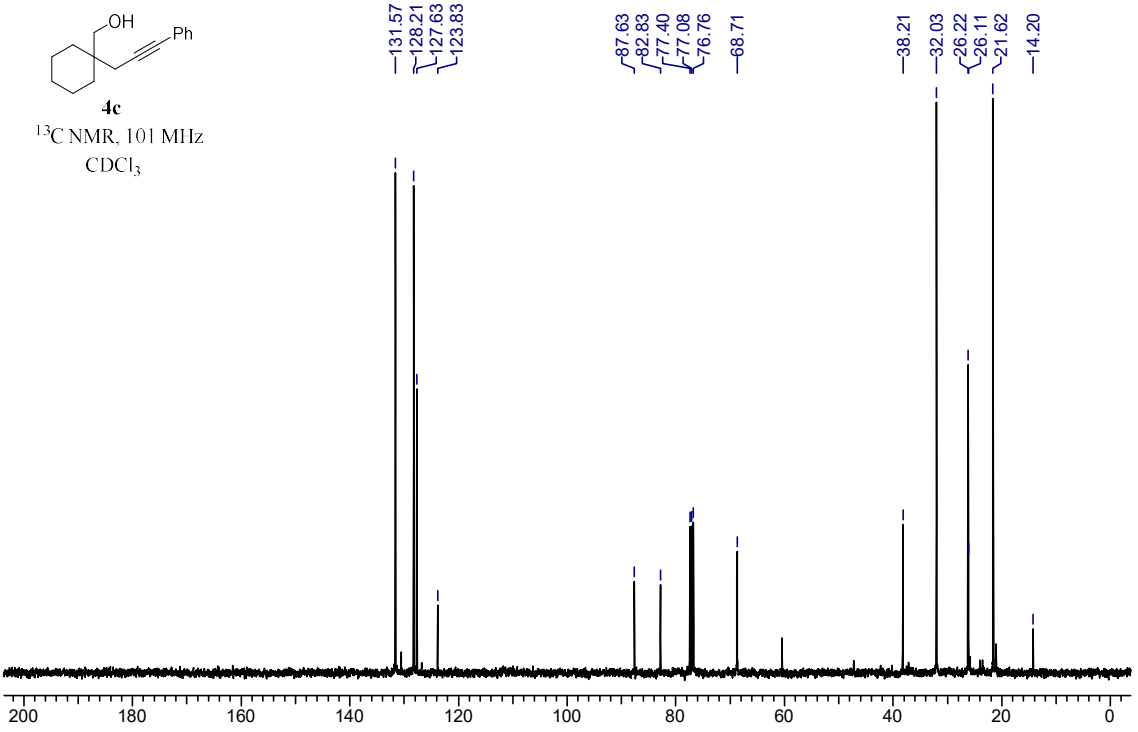
4b

^{13}C NMR, 101 MHz

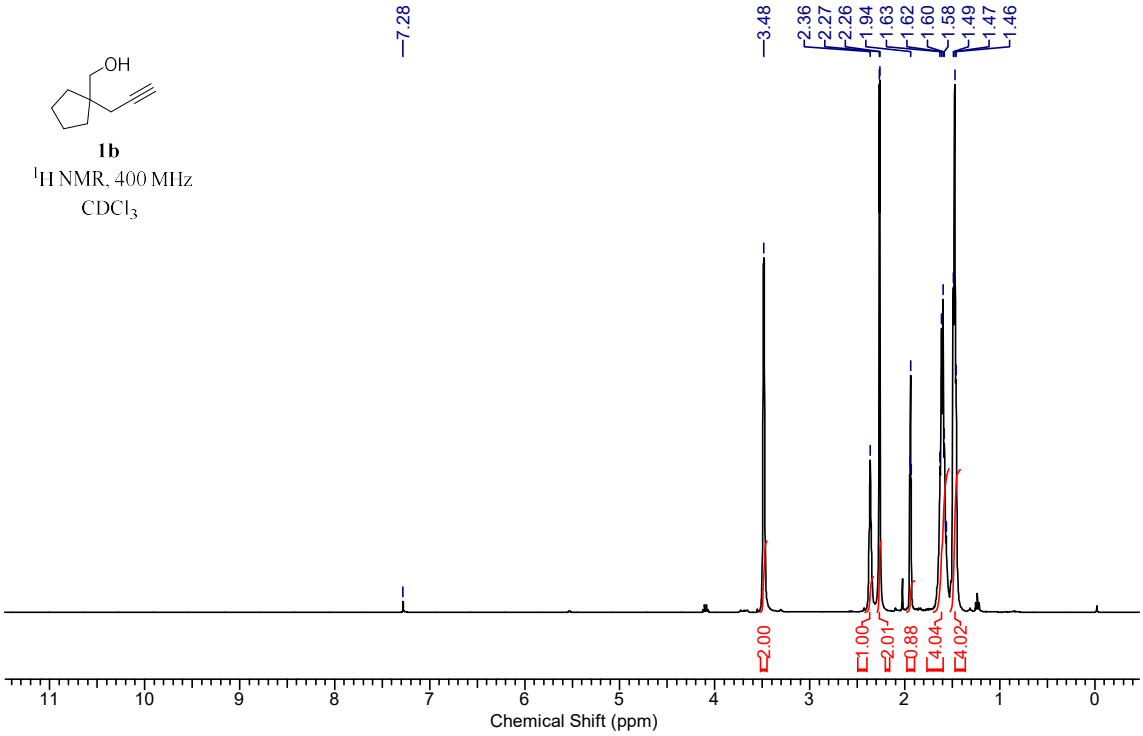
$CDCl_3$

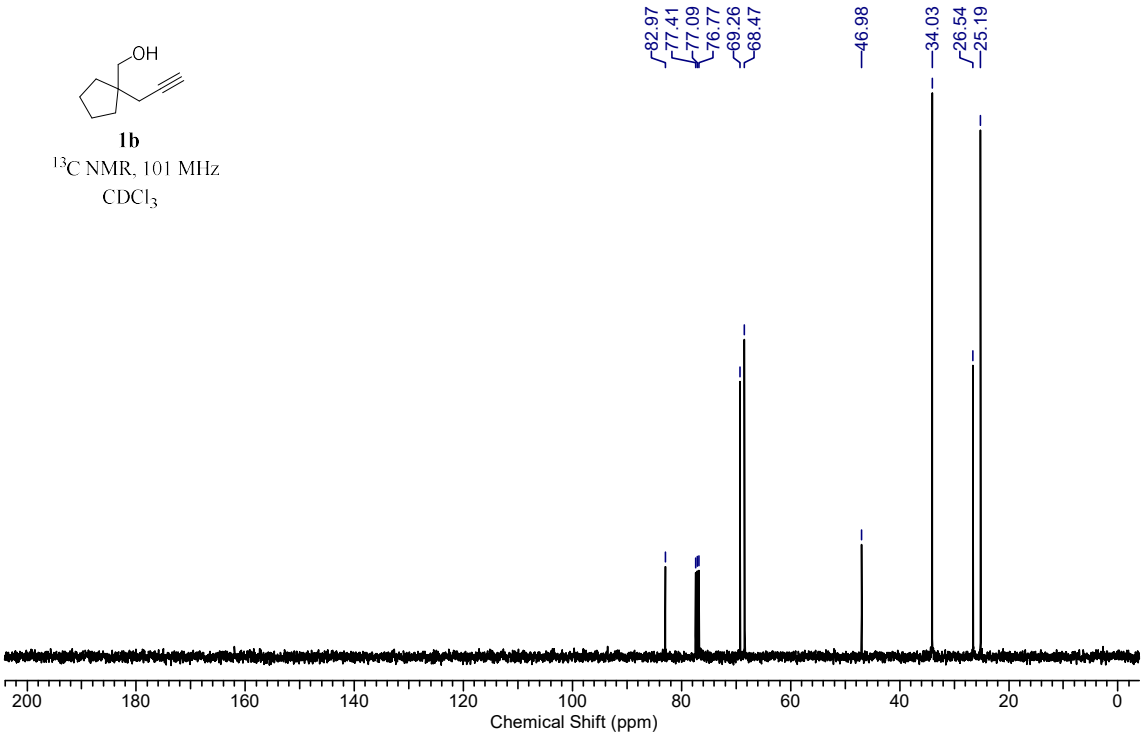
(1-(Phenylprop-2-yl)cyclohexyl)methanol (4c):



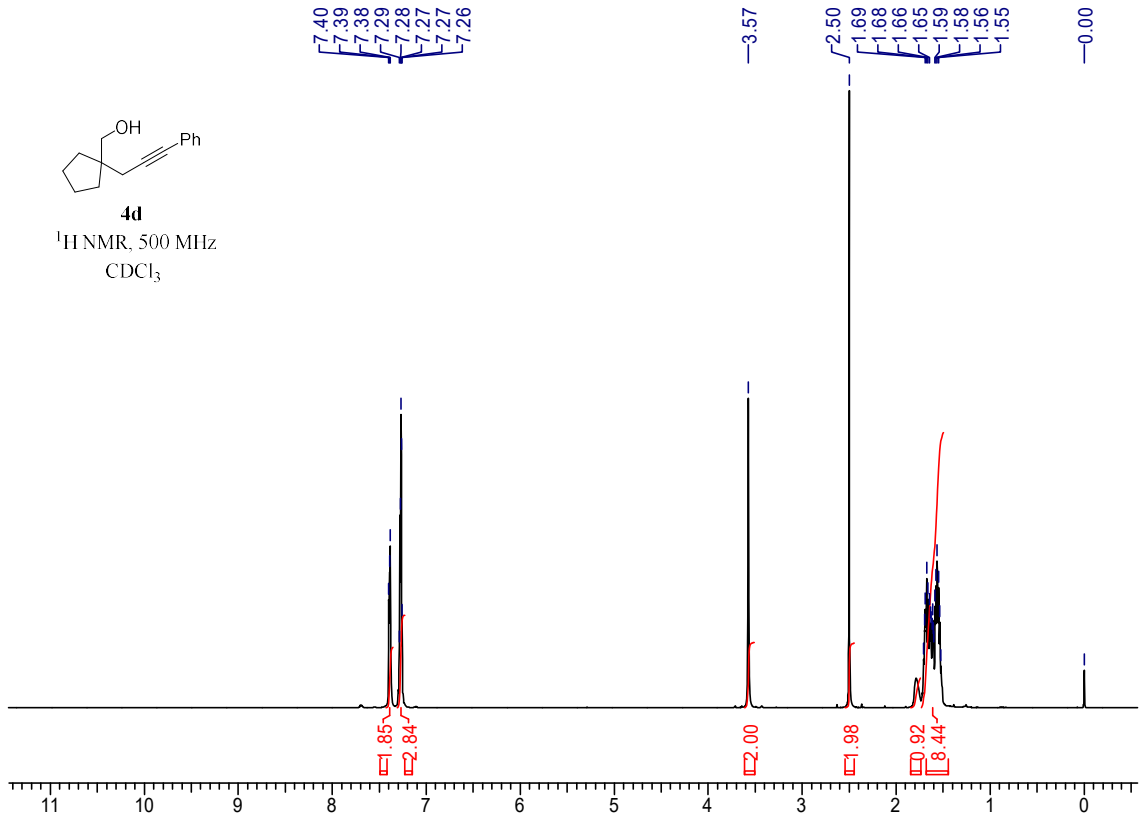


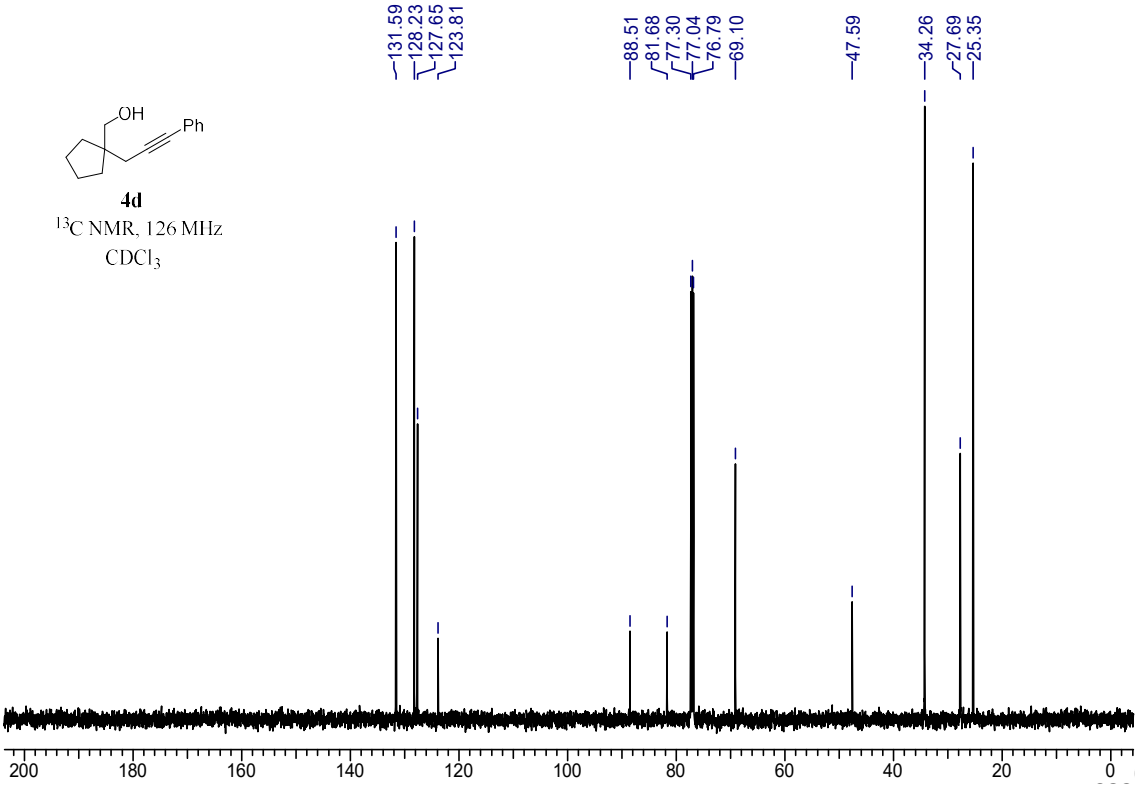
(1-(Prop-2-yn-1-yl) cyclopentyl) methanol (1b):



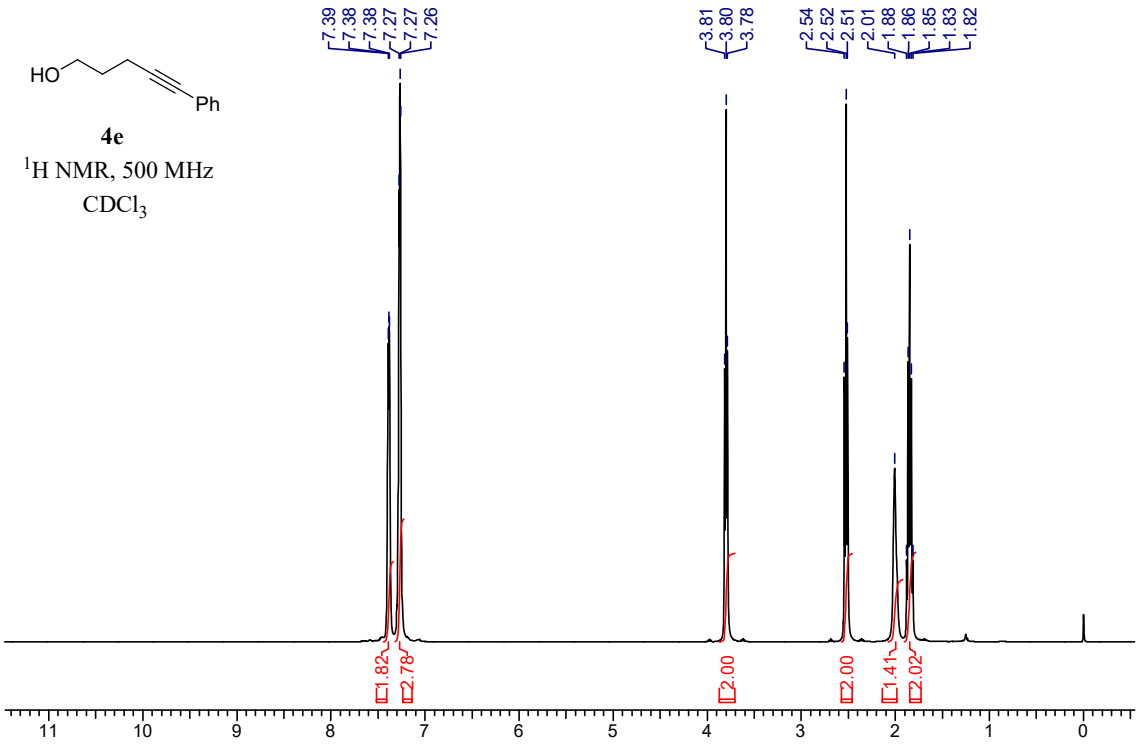


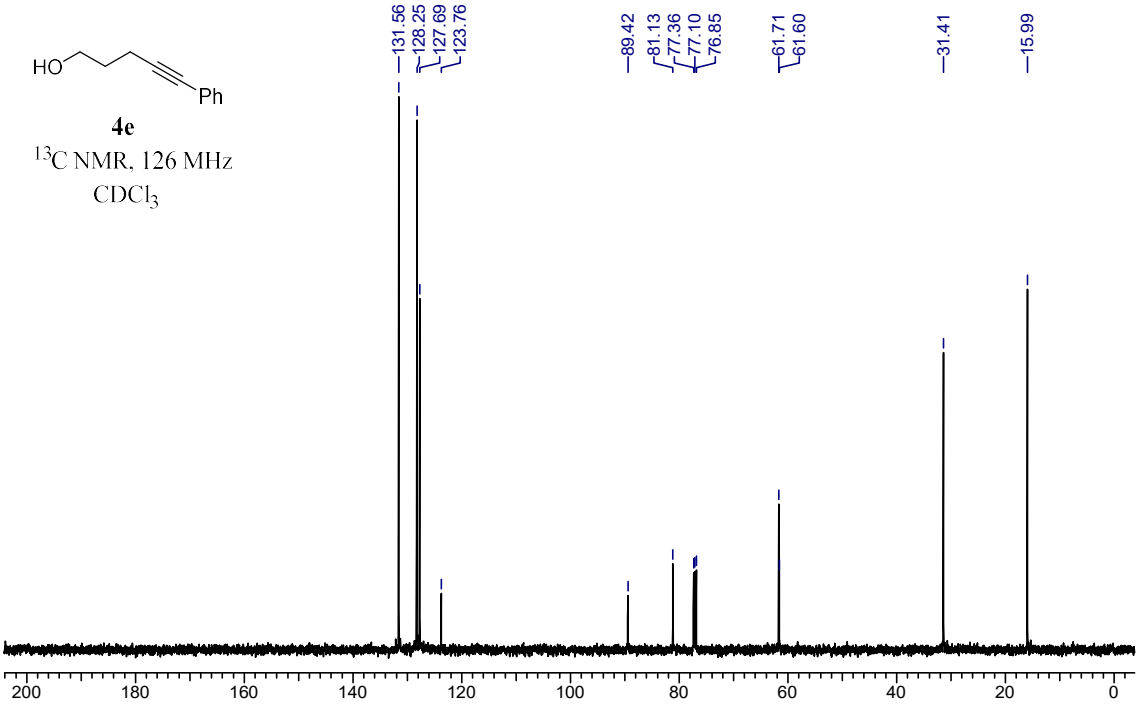
(1-(3-Phenylprop-2-yn-1-yl) cyclopentyl) methanol (4d):



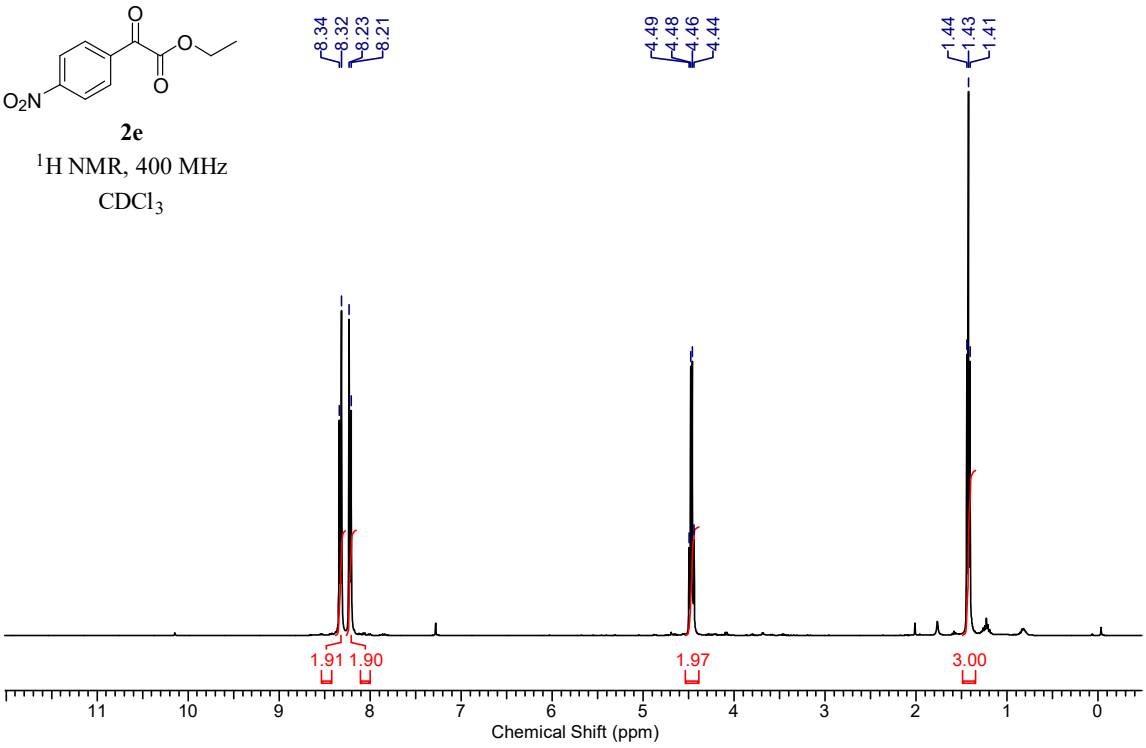


5-Phenylpent-4-yn-1-ol (4e):





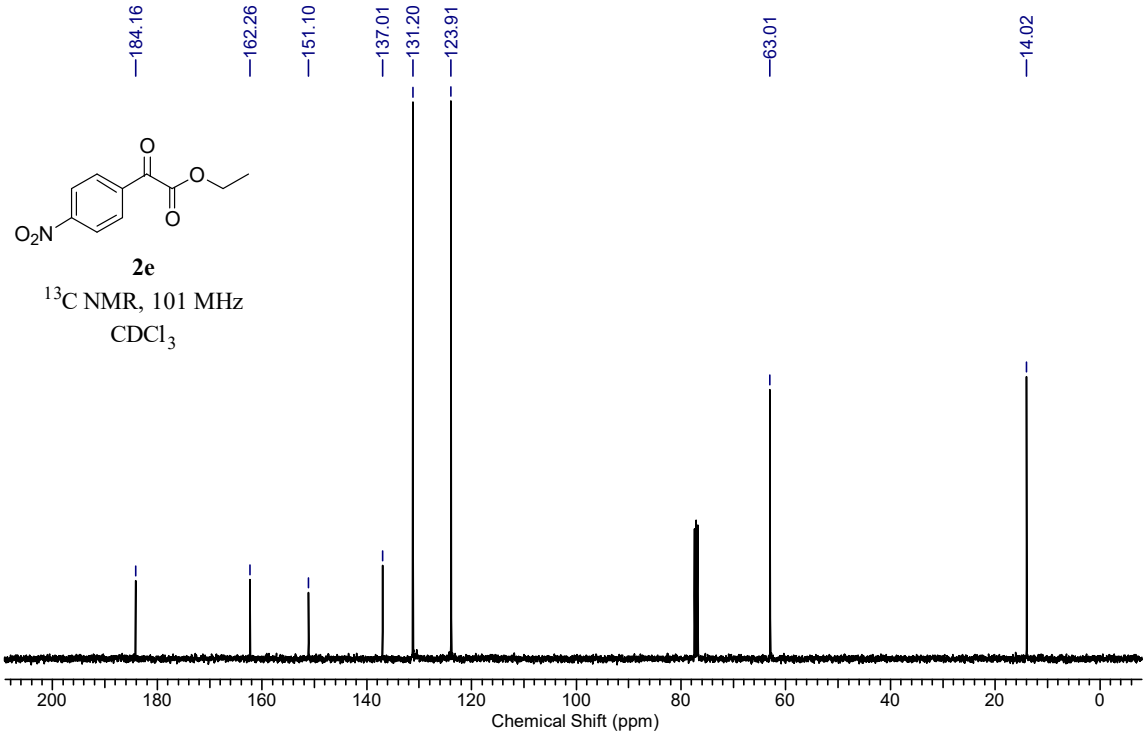
Ethyl 2-(4-nitrophenyl)-2-oxoacetate (2e):



2e

^{1}H NMR, 400 MHz

$CDCl_3$

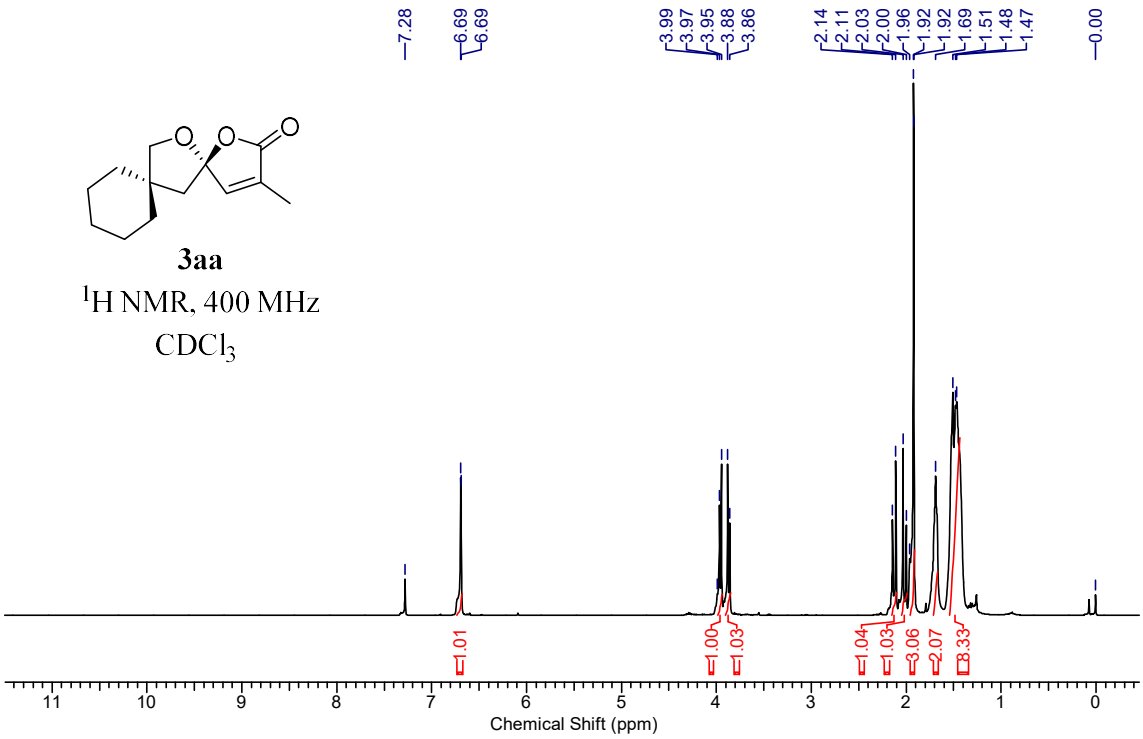


2e

^{13}C NMR, 101 MHz

$CDCl_3$

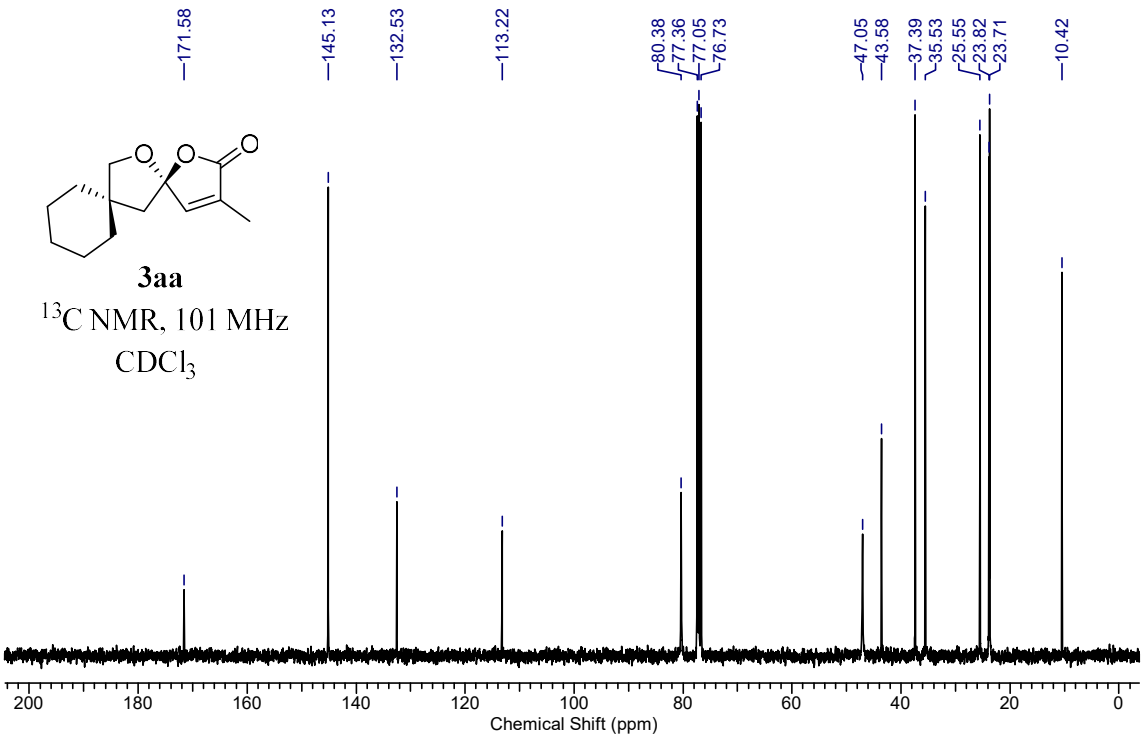
3-Methyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (3aa):



3aa

^{1}H NMR, 400 MHz

$CDCl_3$

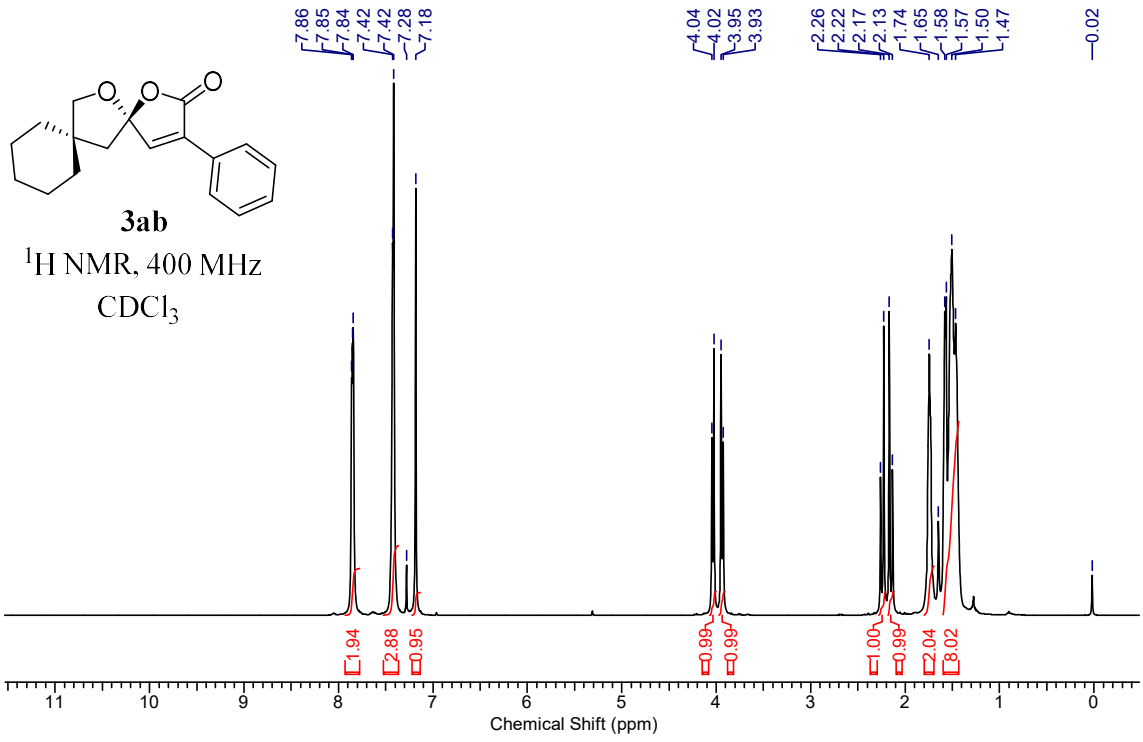


3aa

^{13}C NMR, 101 MHz

$CDCl_3$

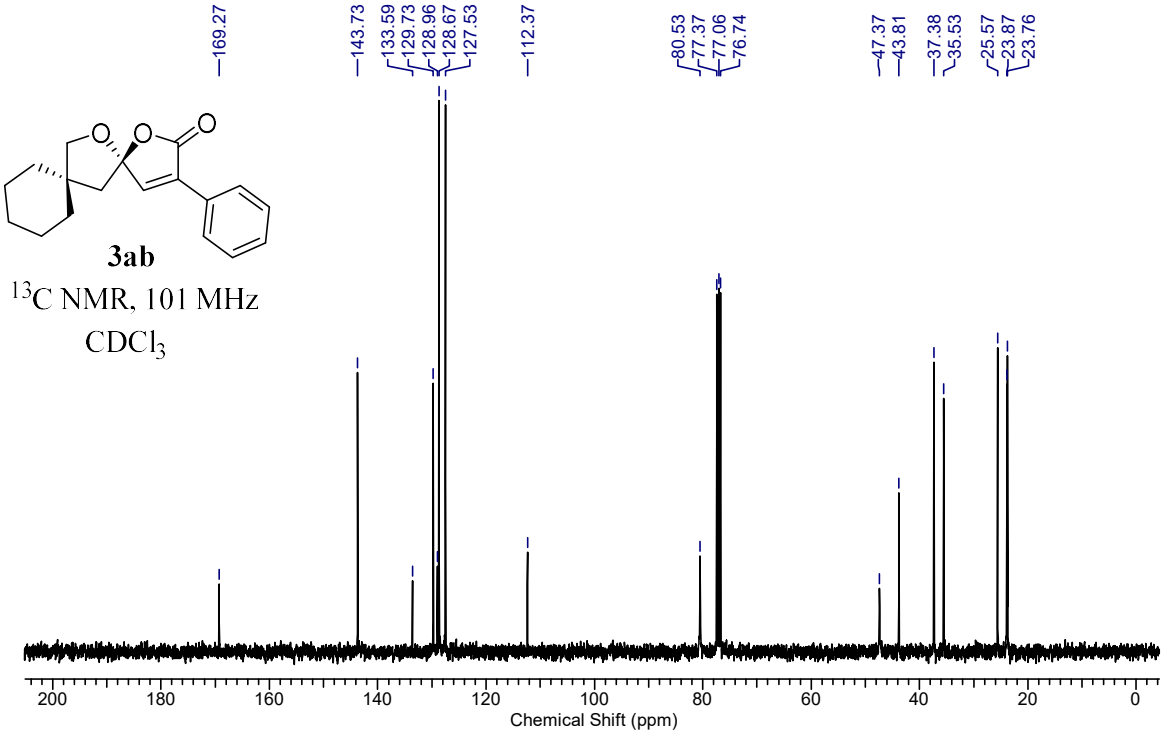
3-Phenyl-1, 14-dioxadispiro [4.4.5^{7}.2^{5}] tetradec-3-en-one (3ab):



3ab

^{1}H NMR, 400 MHz

$CDCl_3$

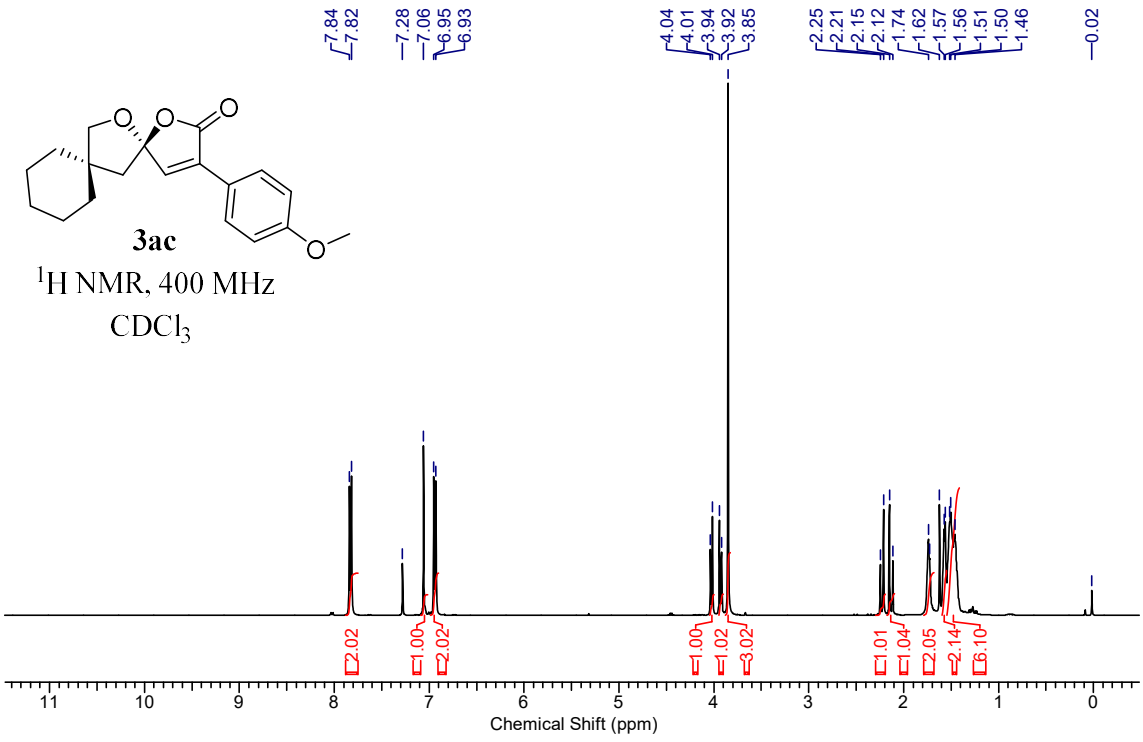


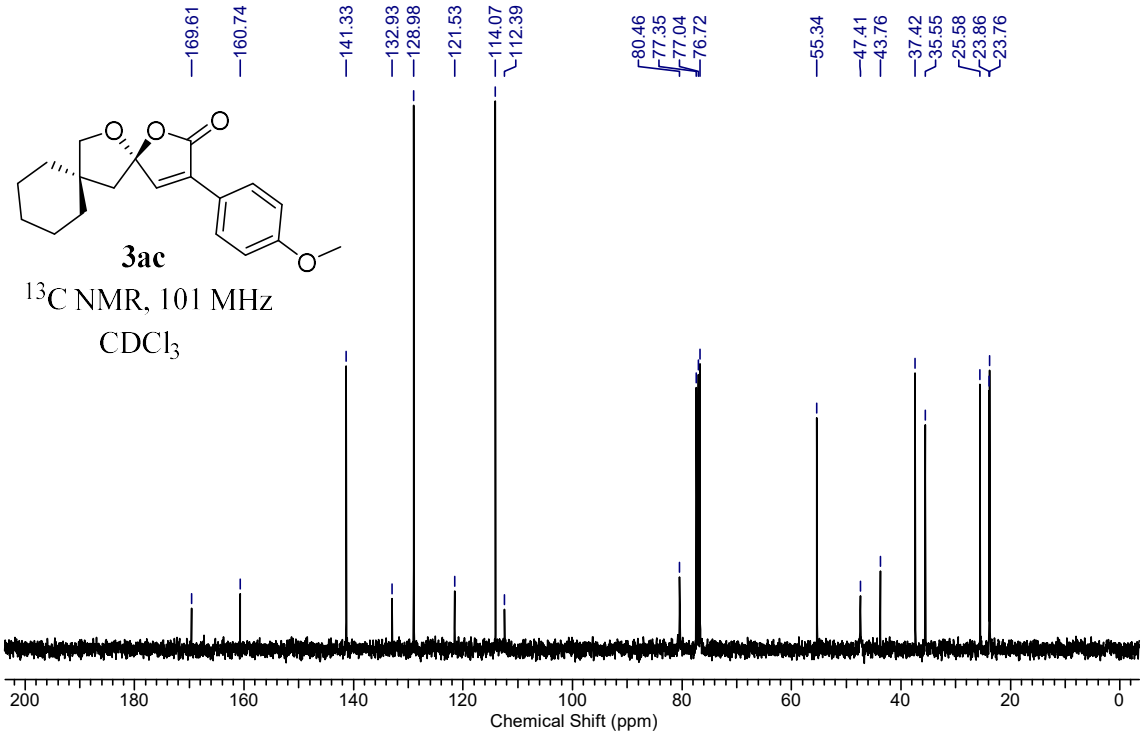
3ab

^{13}C NMR, 101 MHz

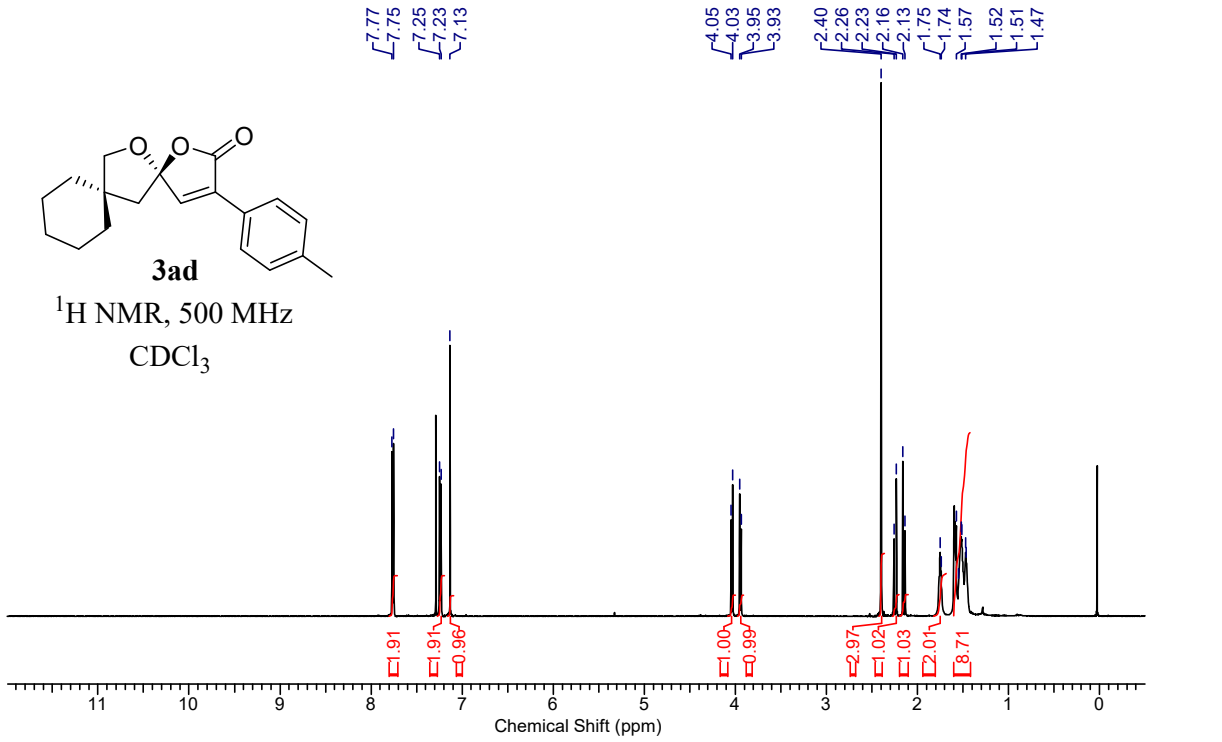
$CDCl_3$

3-(4-Methoxyphenyl)-1,14-dioxadispiro[4.1.5^{7}.2^{5}]tetradec-3-en-2-one(3ac):





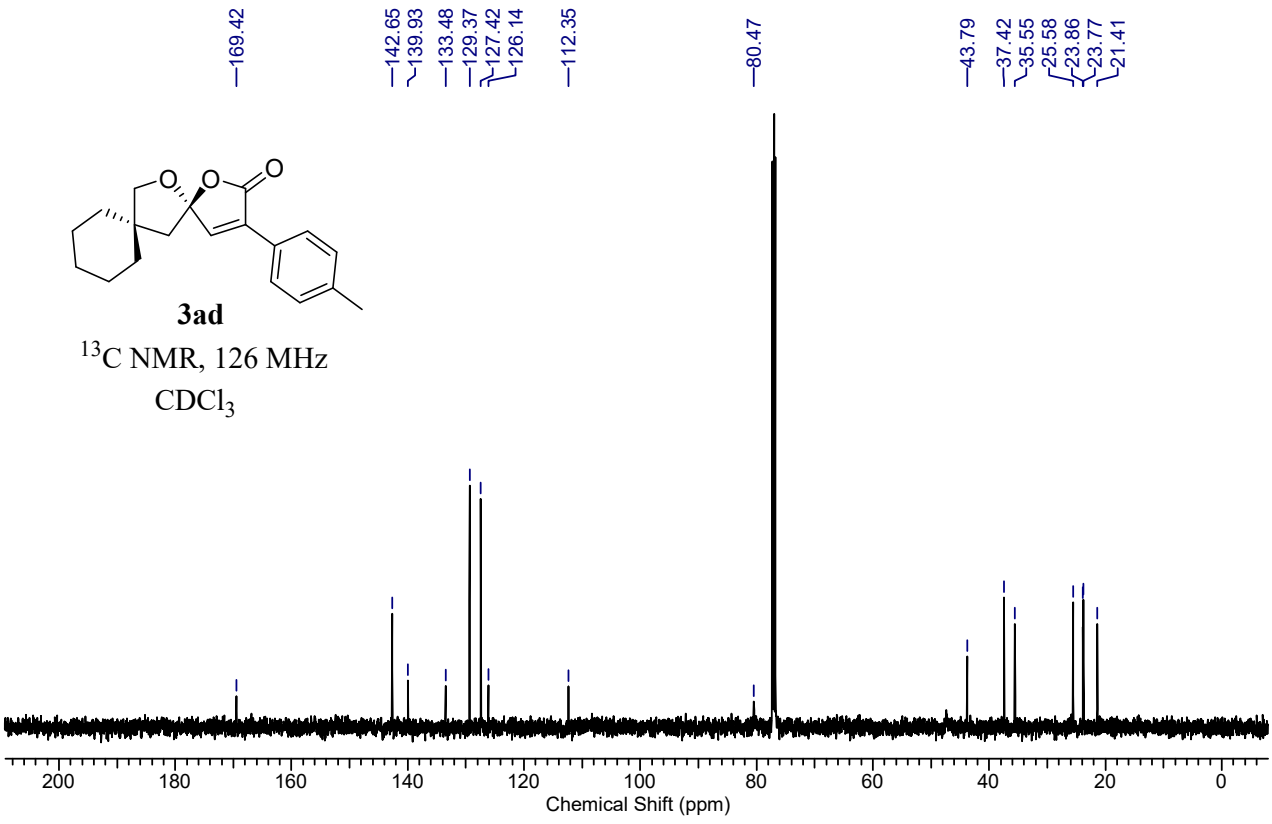
3-(p-Tolyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (3ad):



3ad

^{1}H NMR, 500 MHz

$CDCl_3$

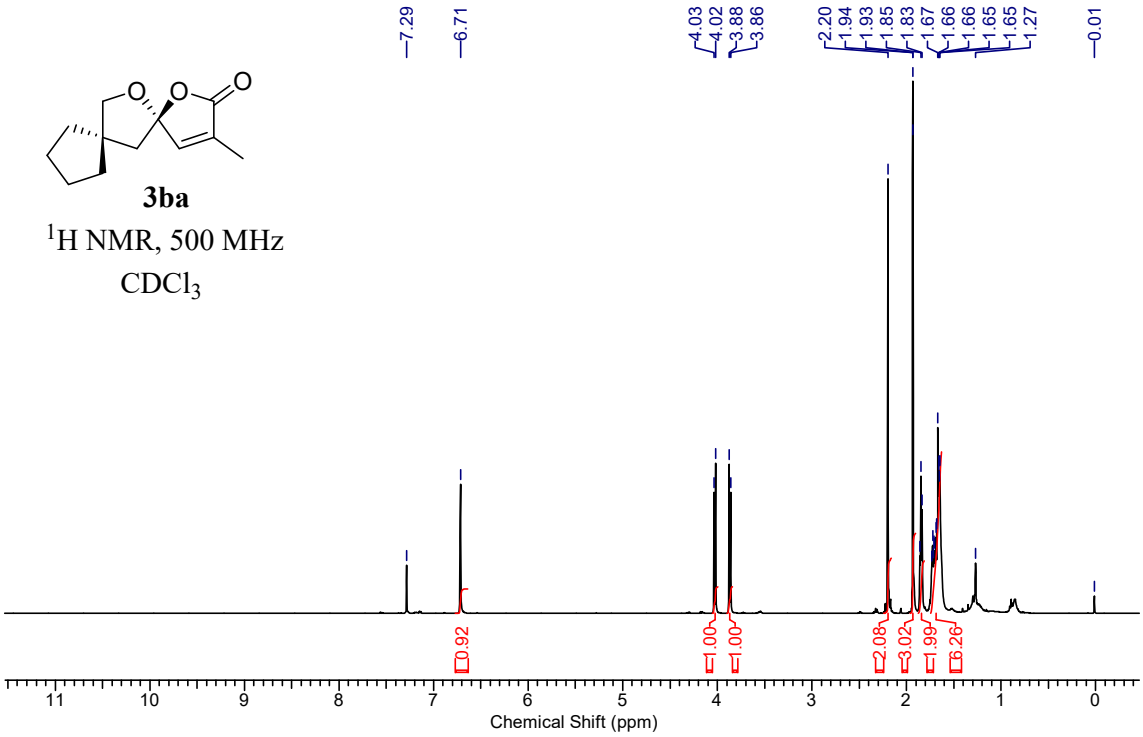


3ad

^{13}C NMR, 126 MHz

$CDCl_3$

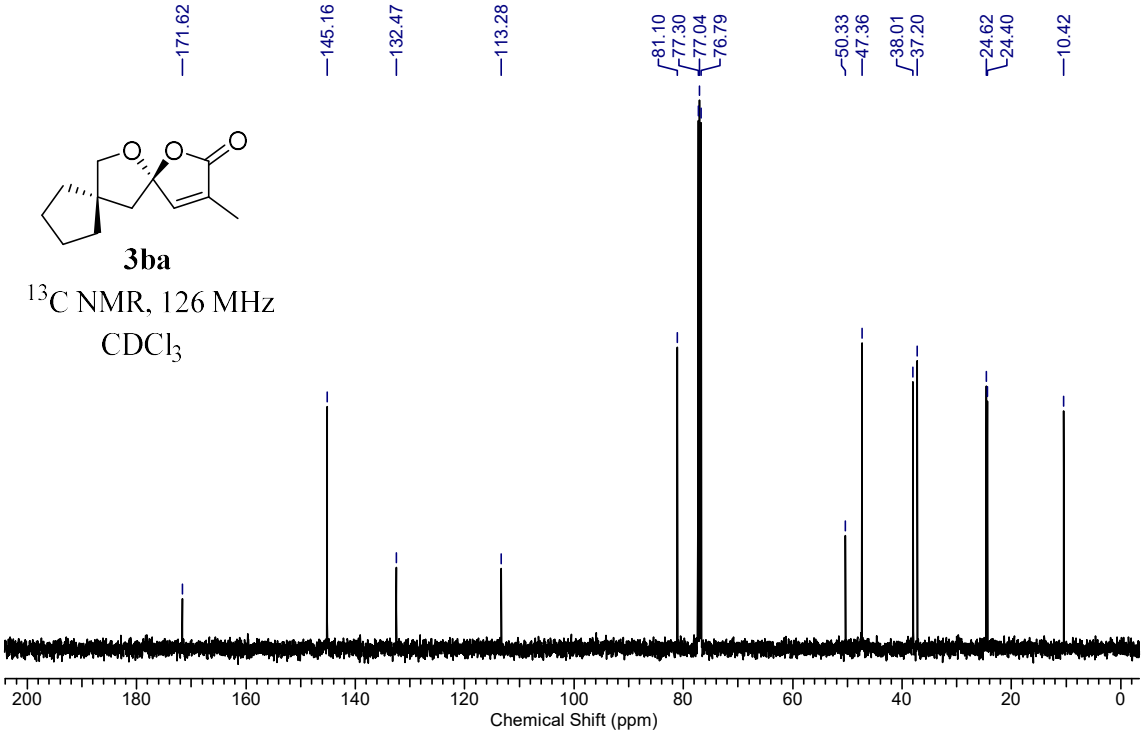
3-Methyl-1,13-dioxadispiro[4.1.4^{7}.2^{5}]tridec-3-en-2-one (3ba):



3ba

^{1}H NMR, 500 MHz

$CDCl_3$

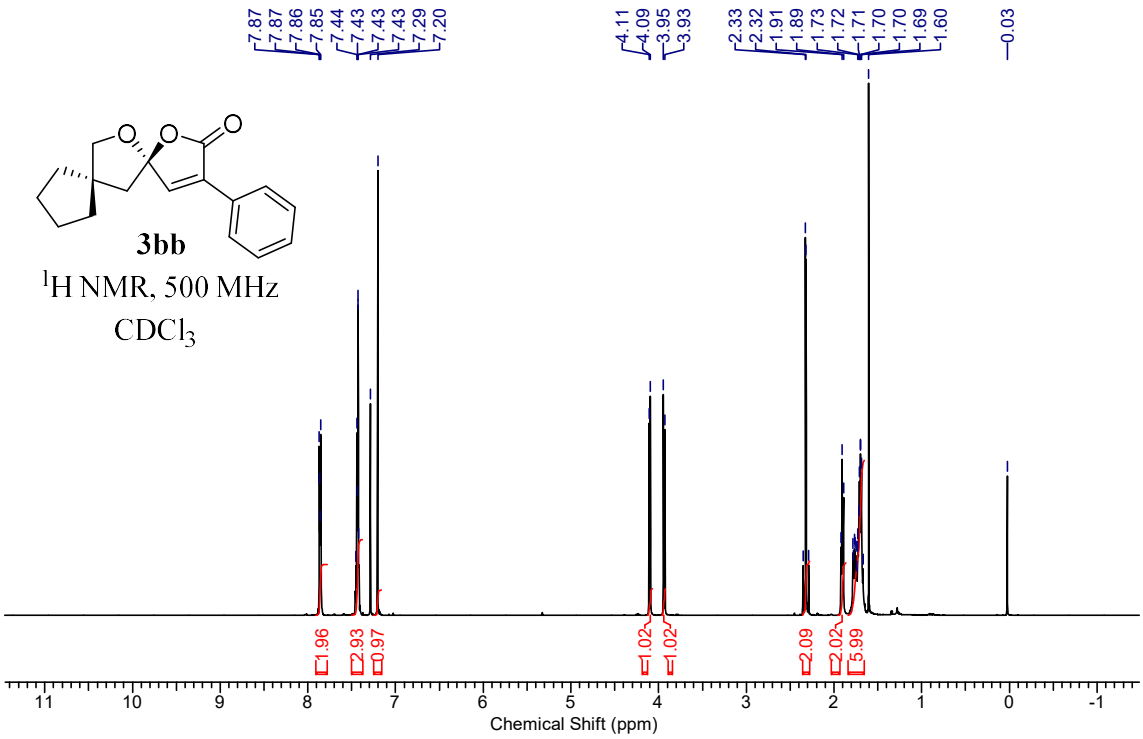


3ba

^{13}C NMR, 126 MHz

$CDCl_3$

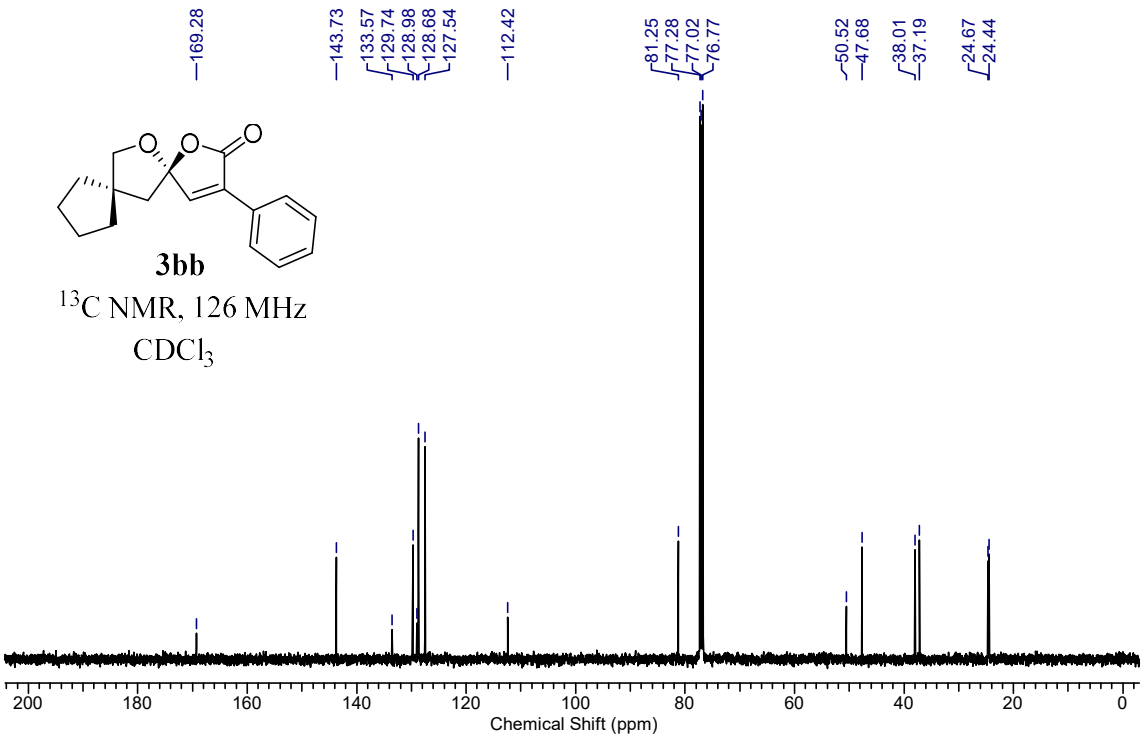
3-Phenyl-1,13-dioxadispiro[4.1.4^{7}.2^{5}]tridec-3-en-one(3bb):



3bb

^{1}H NMR, 500 MHz

$CDCl_3$

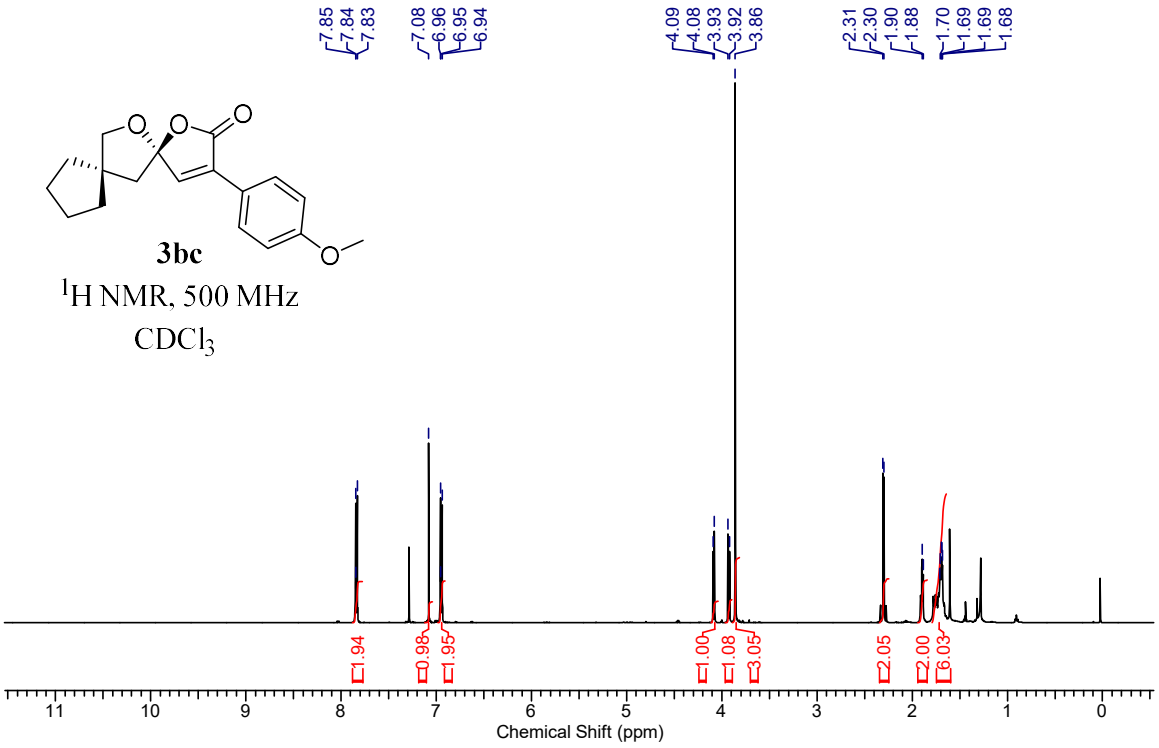


3bb

^{13}C NMR, 126 MHz

$CDCl_3$

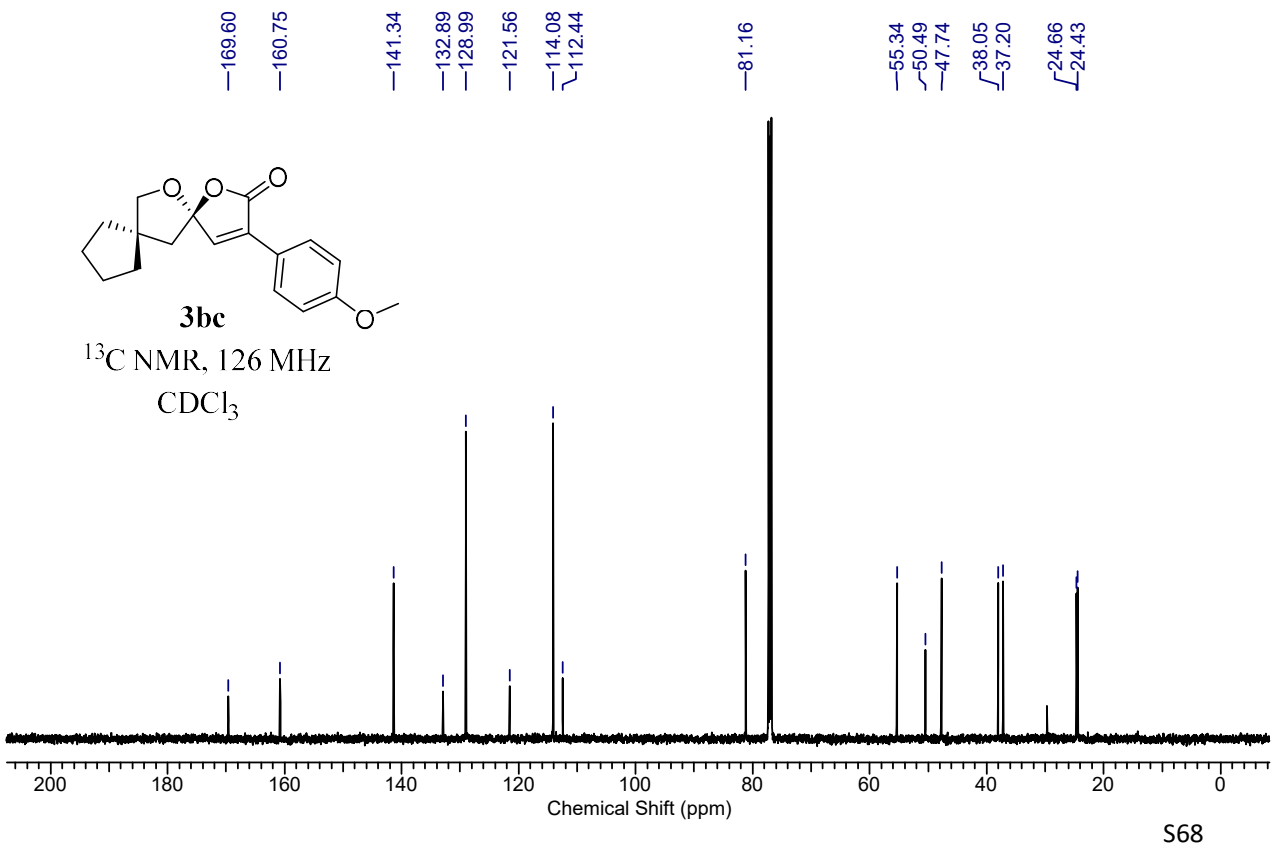
3-(4-Methoxyphenyl)-1,13-dioxadispiro[4.1.4^{7}.2^{5}]tridec-3-en-2-one (3bc):



3bc

^{1}H NMR, 500 MHz

$CDCl_3$

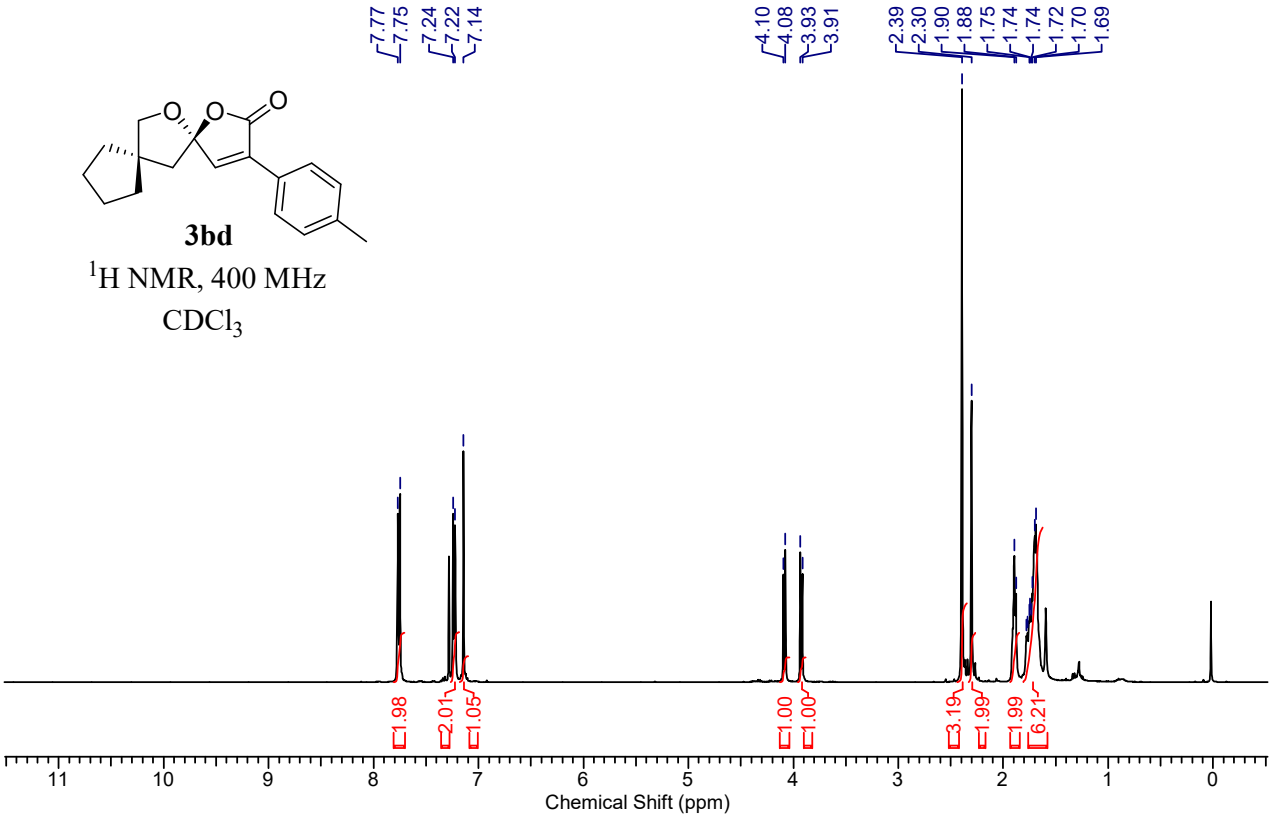


3bc

^{13}C NMR, 126 MHz

$CDCl_3$

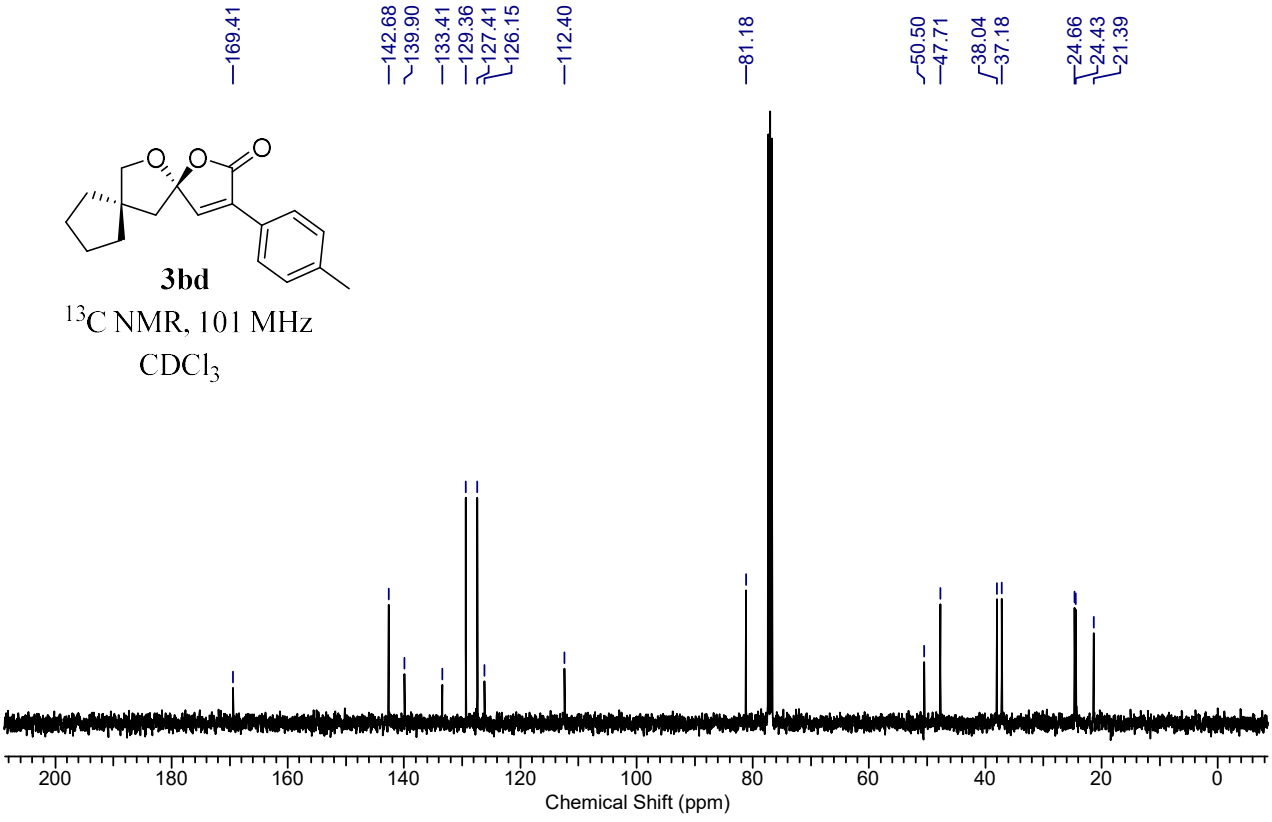
3-(p-Tolyl)-1,13-dioxadispiro[4.1.4^{7}.2^{5}]tridec-3-en-2-one (3bd):



3bd

^{1}H NMR, 400 MHz

$CDCl_3$

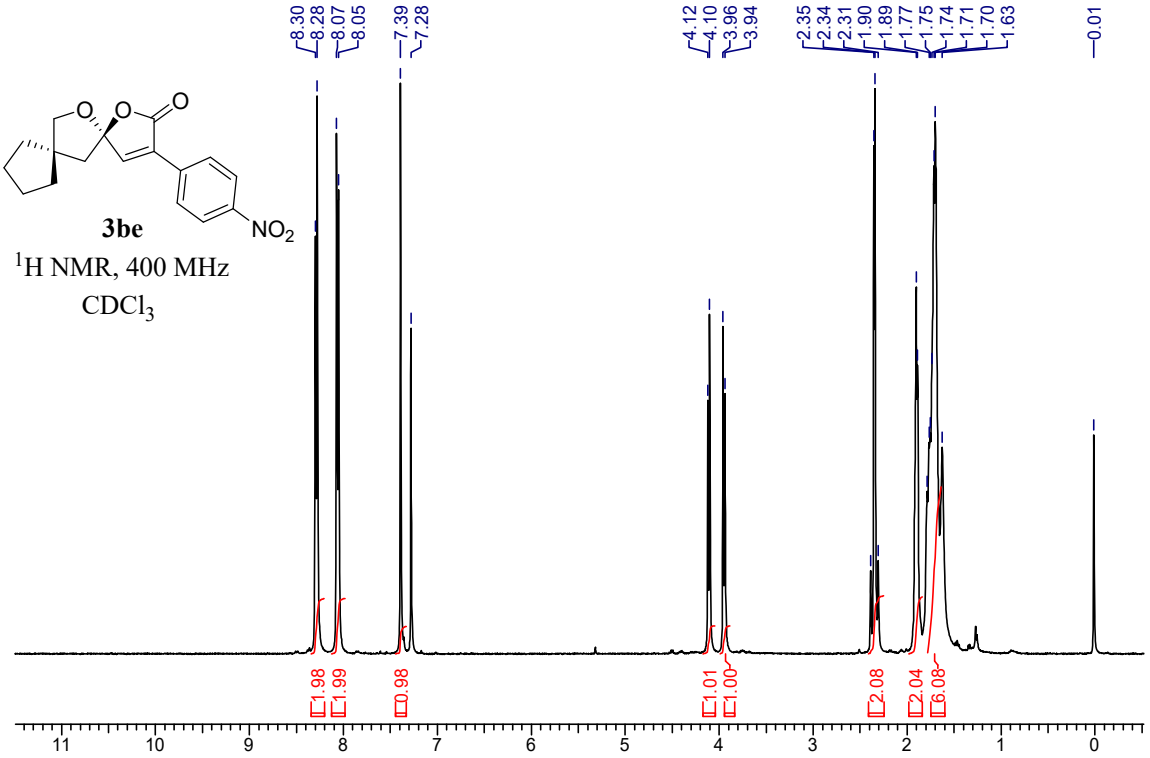


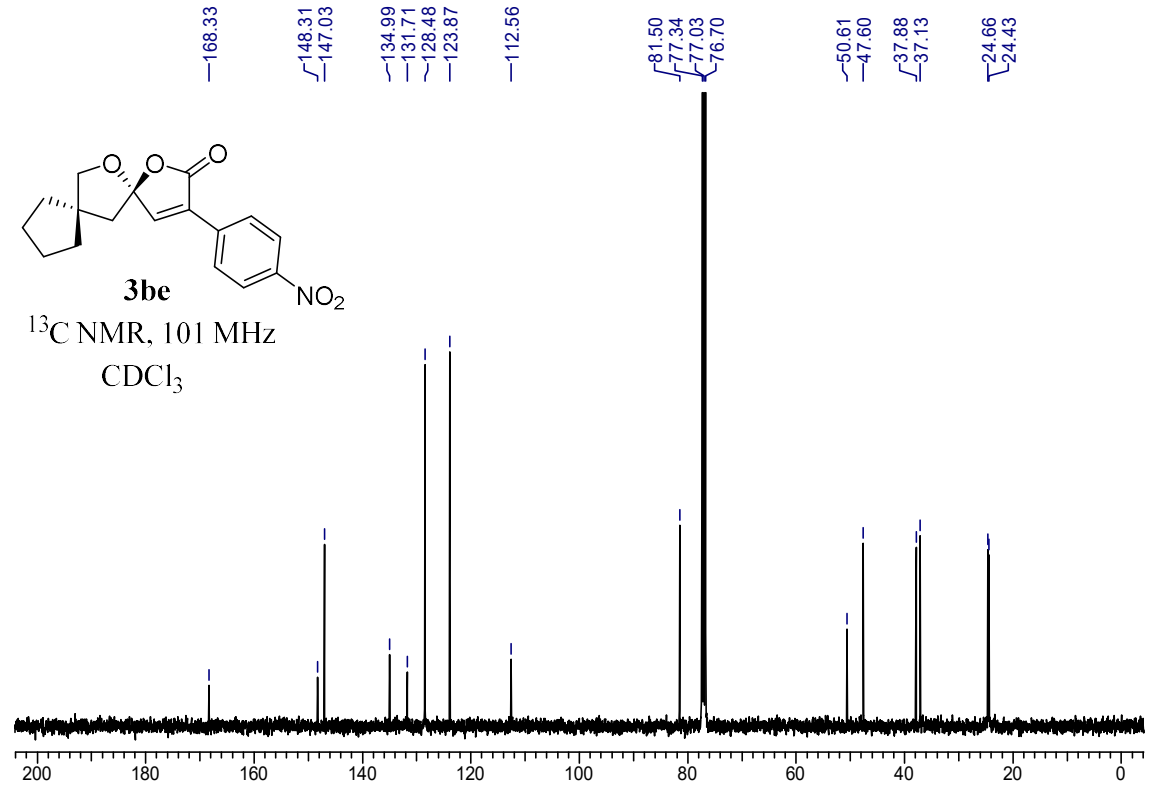
3bd

^{13}C NMR, 101 MHz

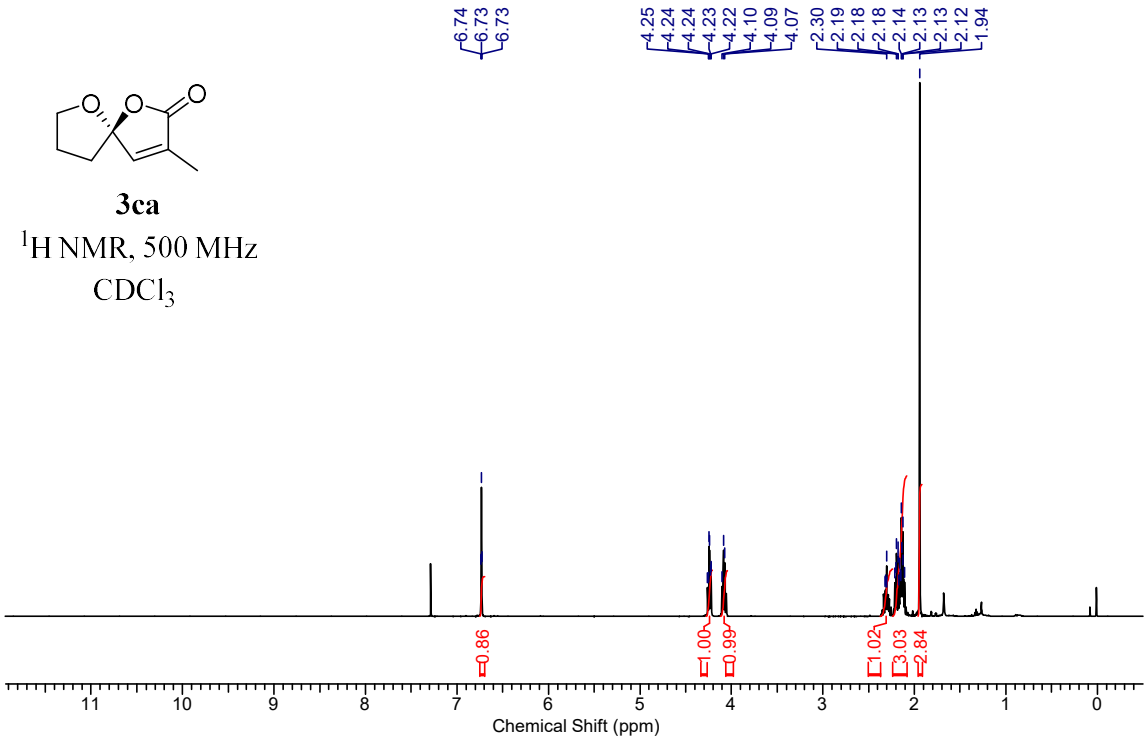
$CDCl_3$

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





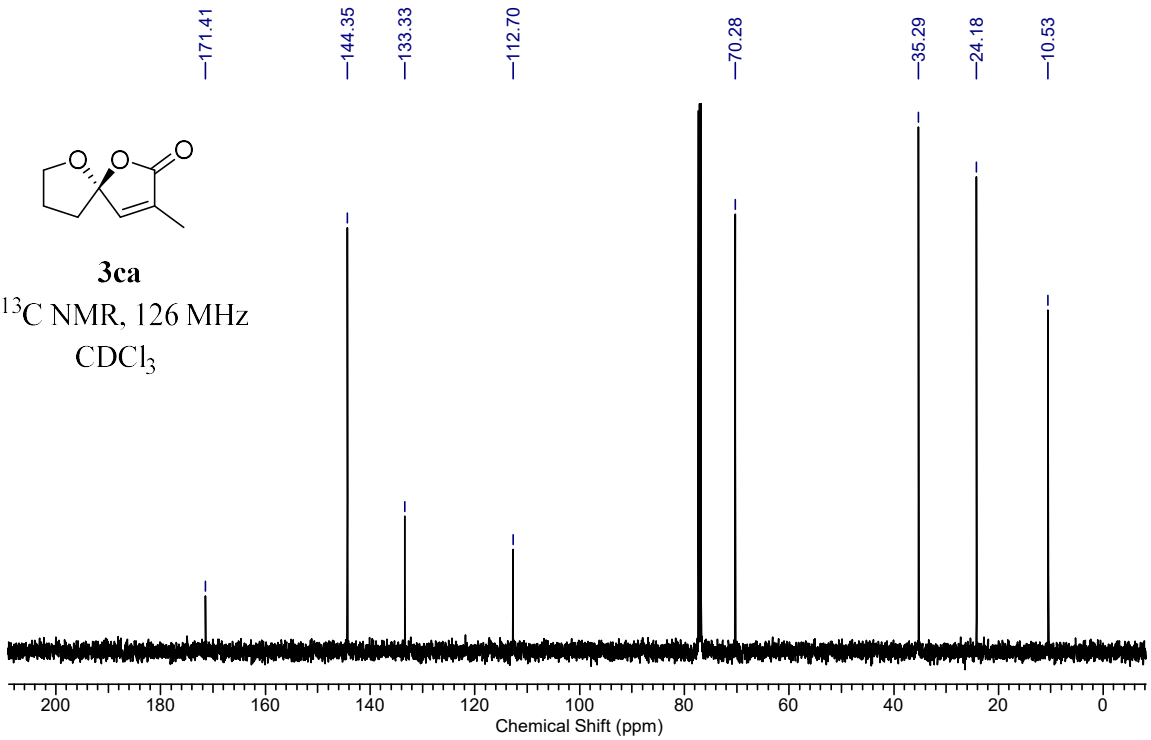
3-Methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ca):



3ca

^{1}H NMR, 500 MHz

$CDCl_3$

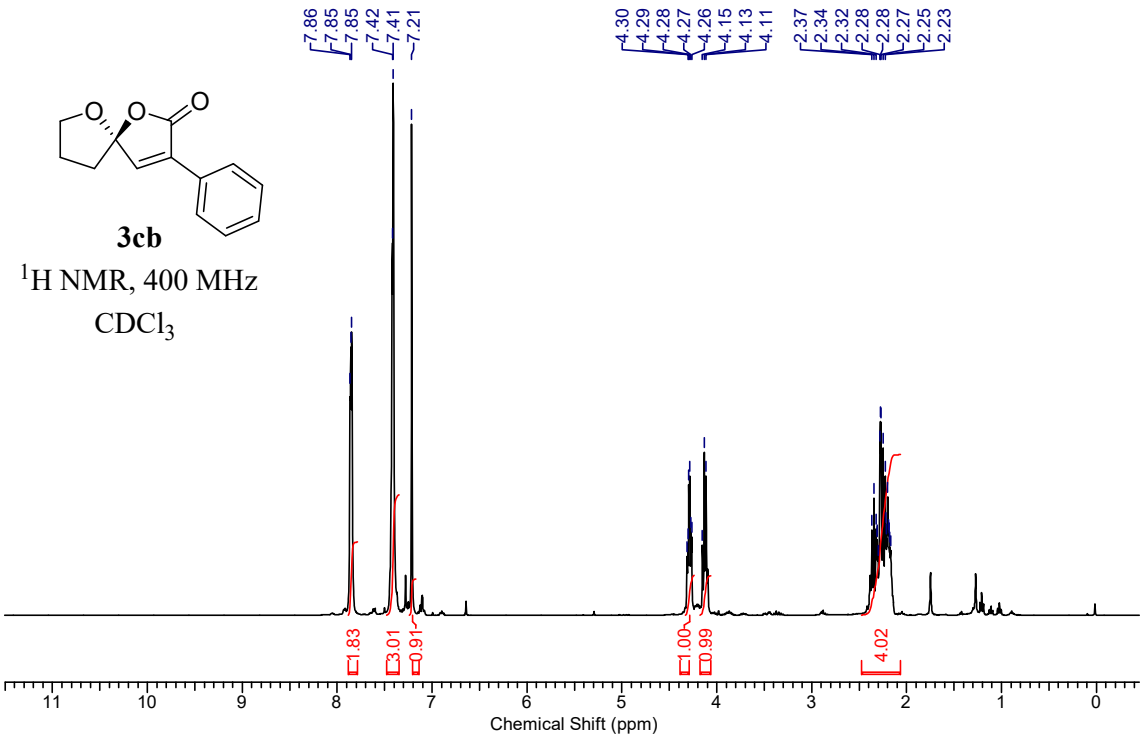


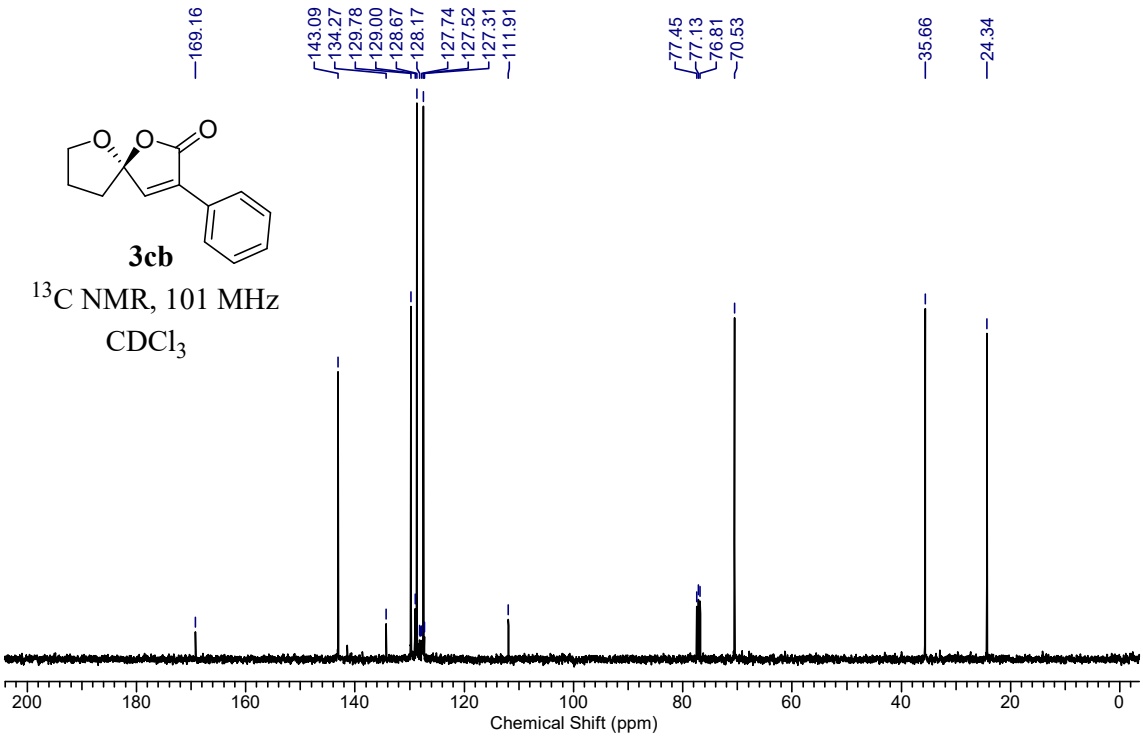
3ca

^{13}C NMR, 126 MHz

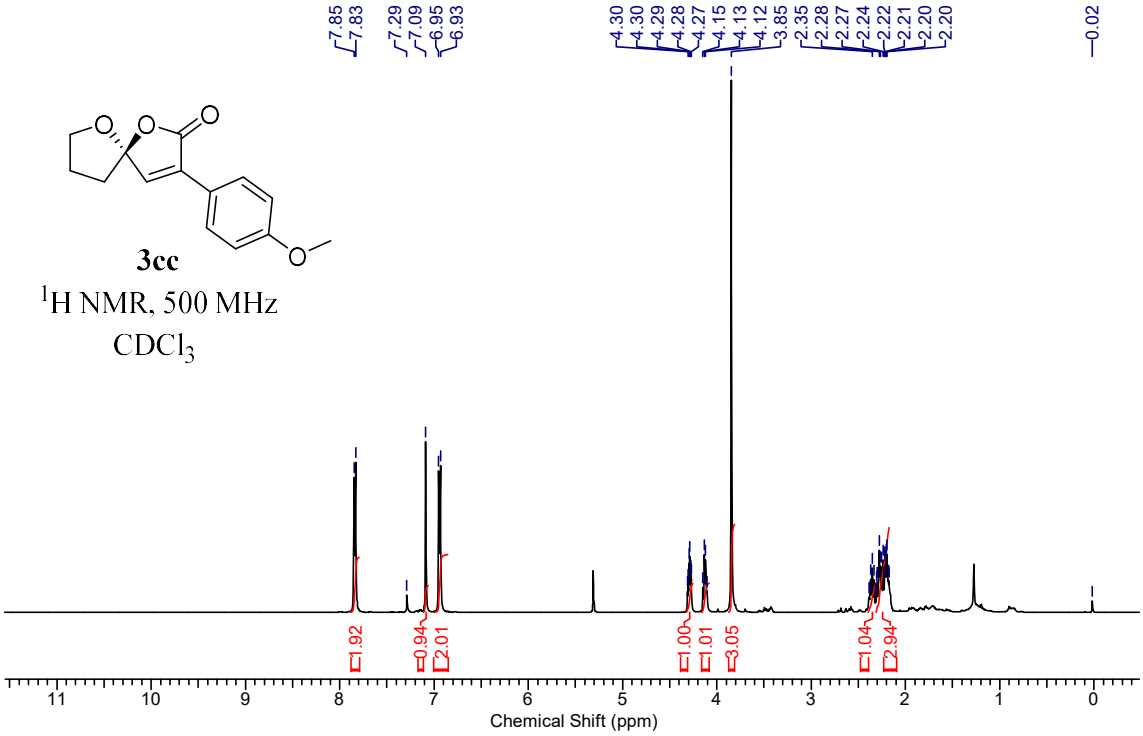
$CDCl_3$

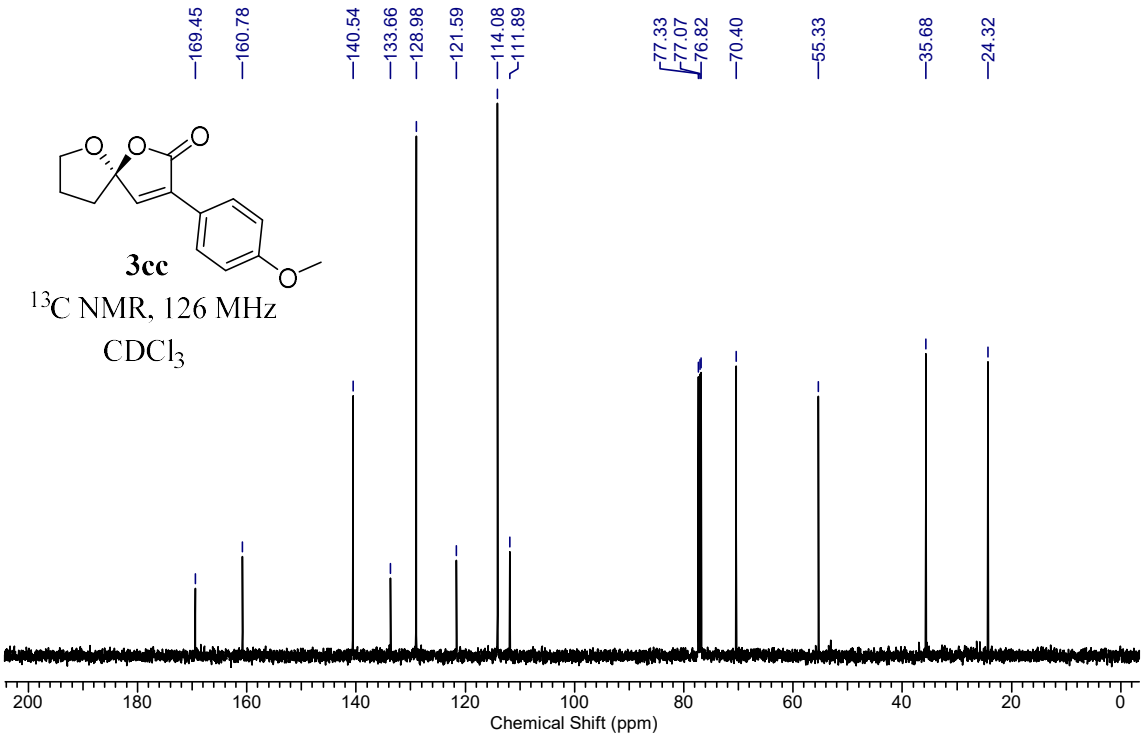
3-Phenyl-1,6-dioxaspiro[4,4]non-3-en-2-one (3cb):



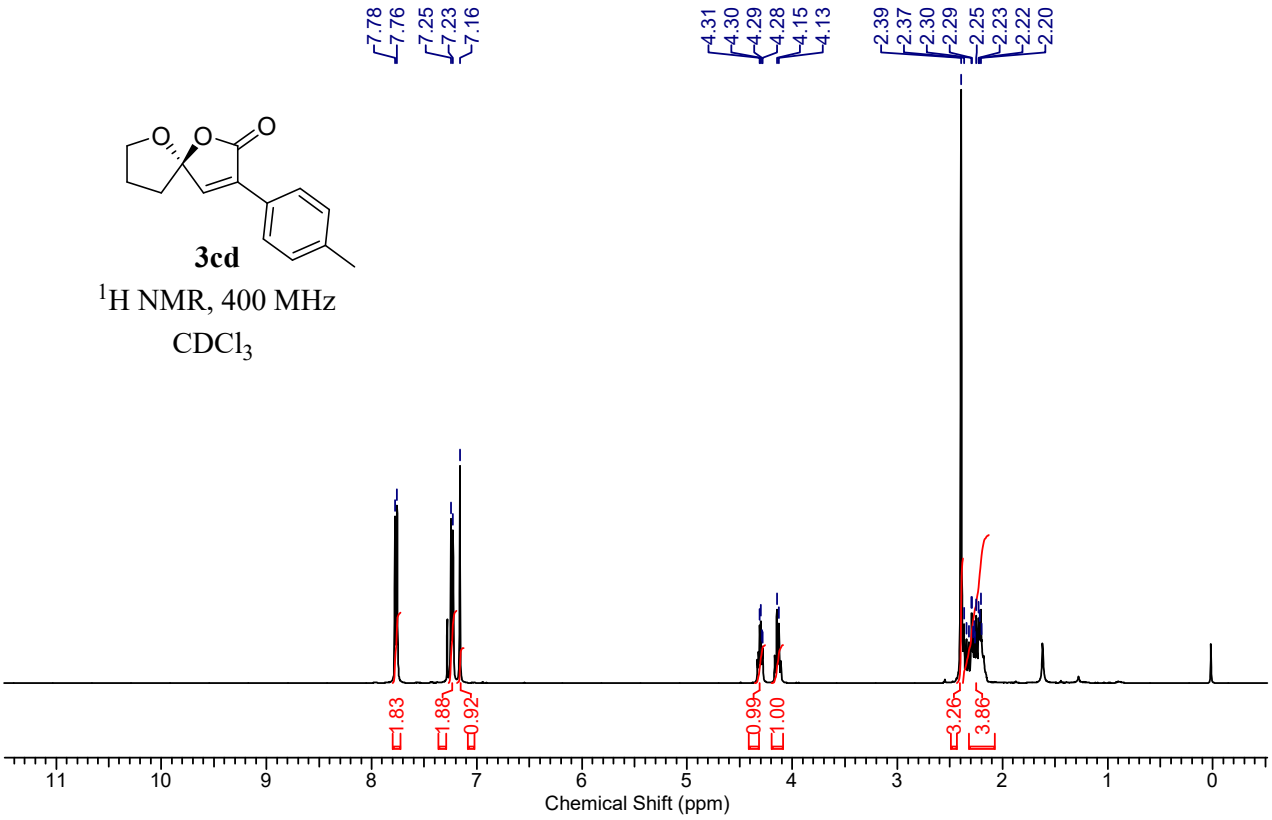


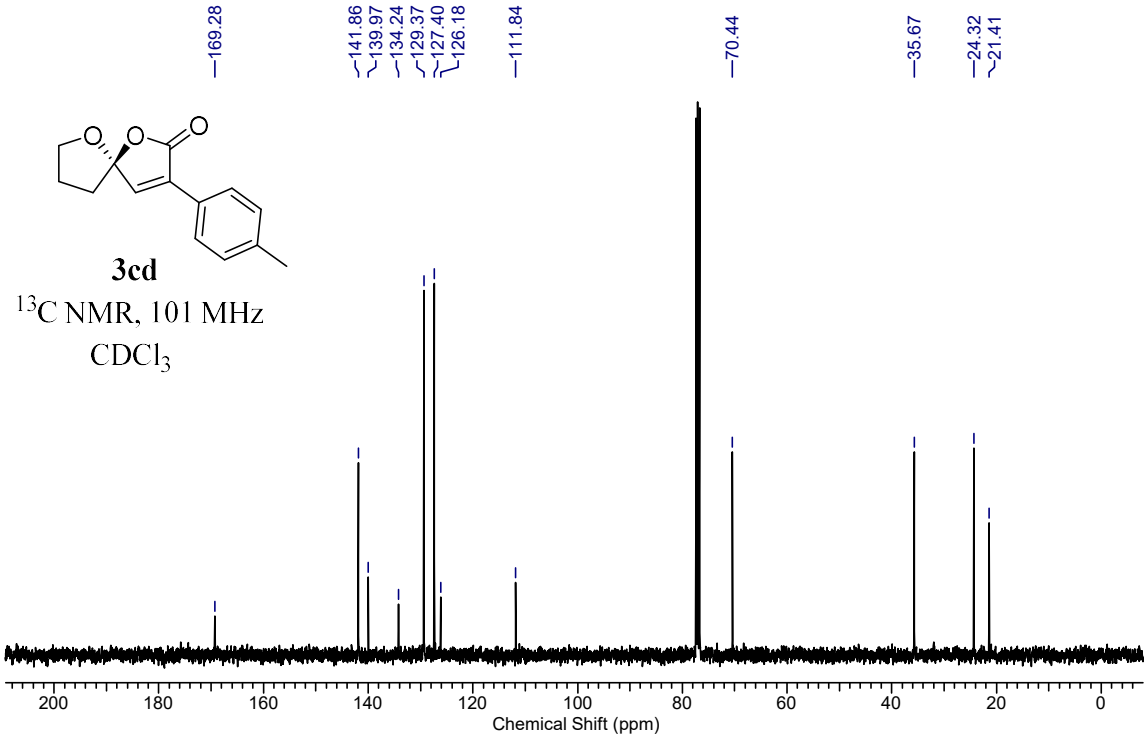
3-(4-Methoxyphenyl)-1,6-dioxaspiro[4,4]non-3-en-2-one(3cc):



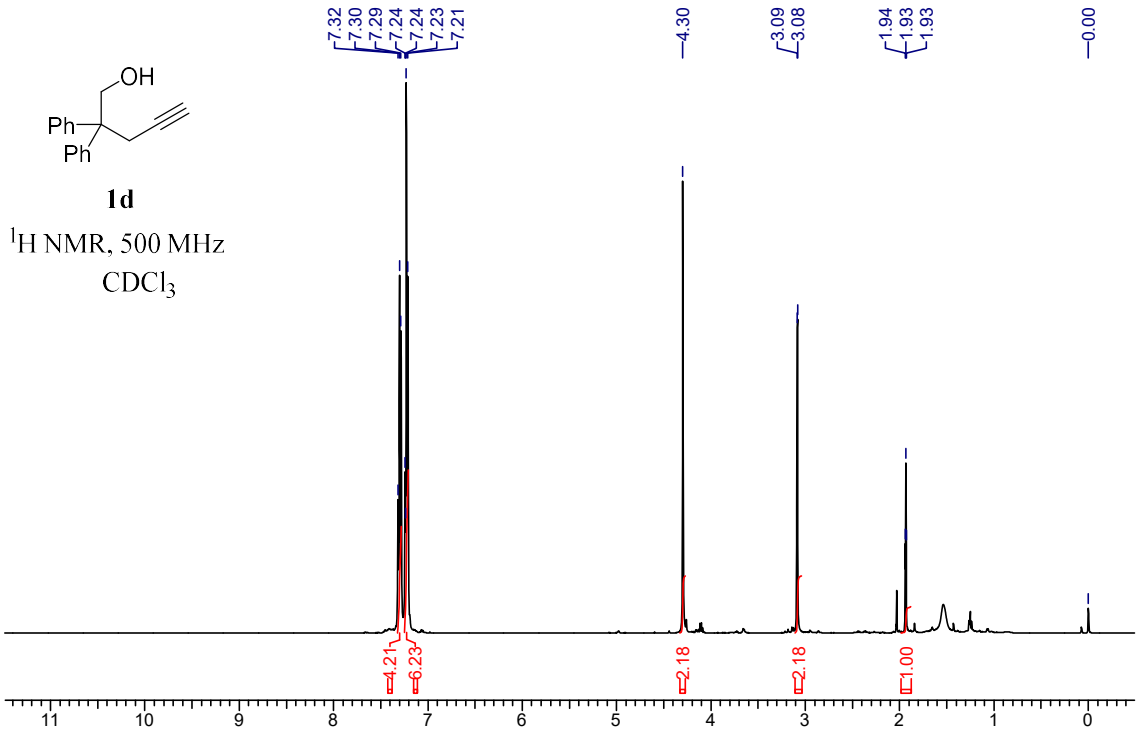


3-(p-Tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one (3cd):





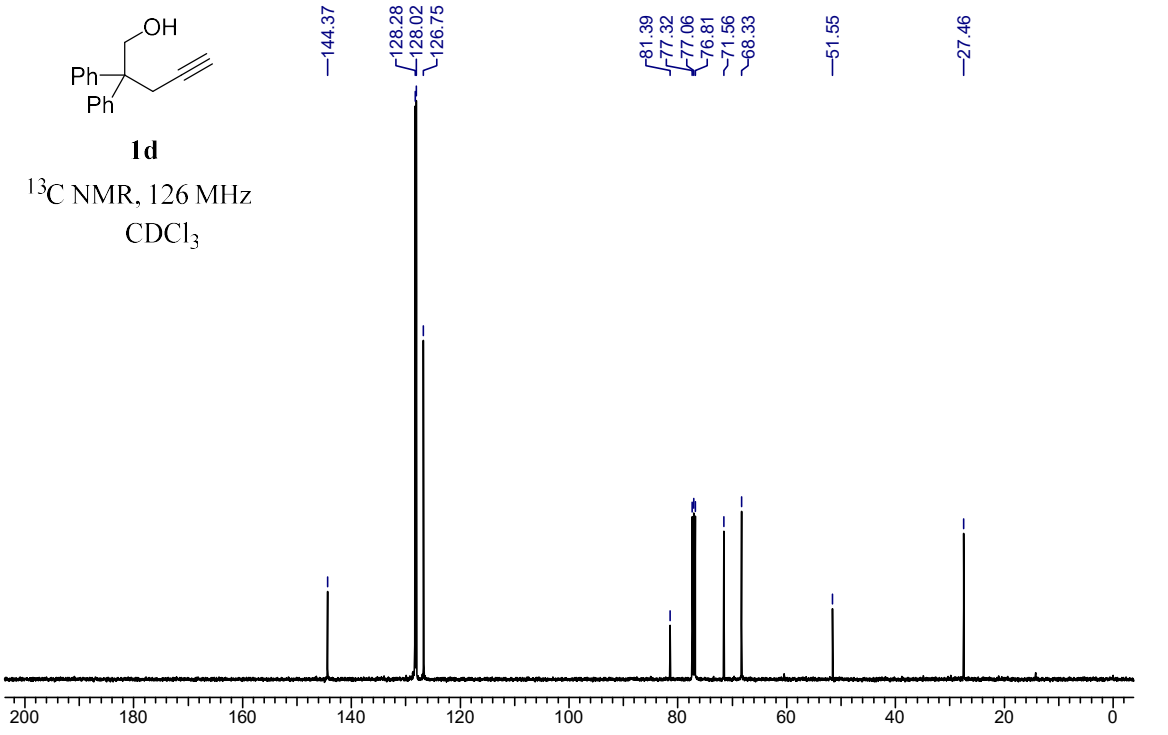
2, 2-diphenylpent-4-yn-1-ol (1d):



1d

^{1}H NMR, 500 MHz

$CDCl_3$

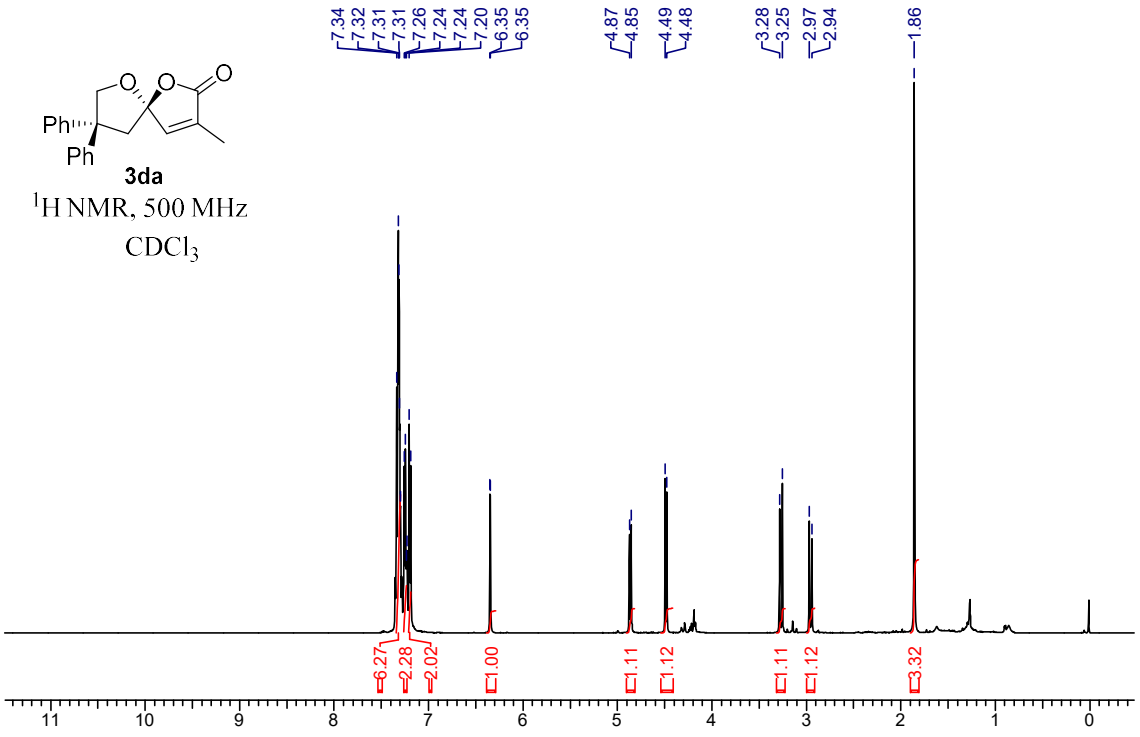


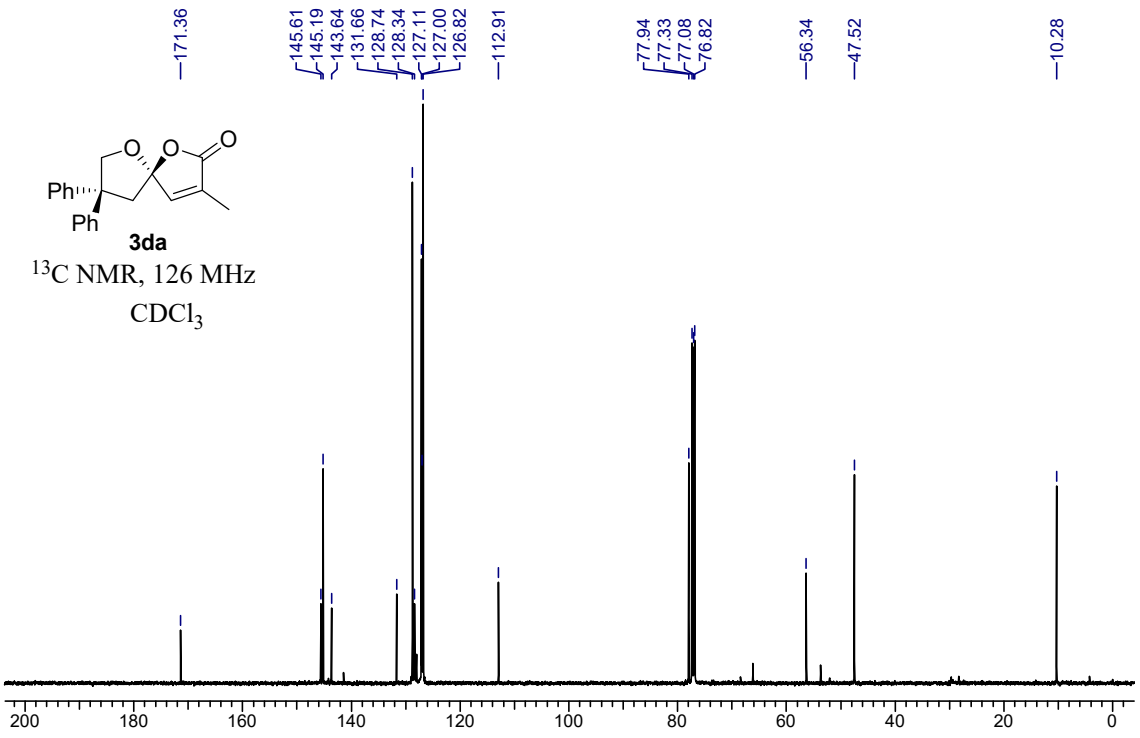
1d

^{13}C NMR, 126 MHz

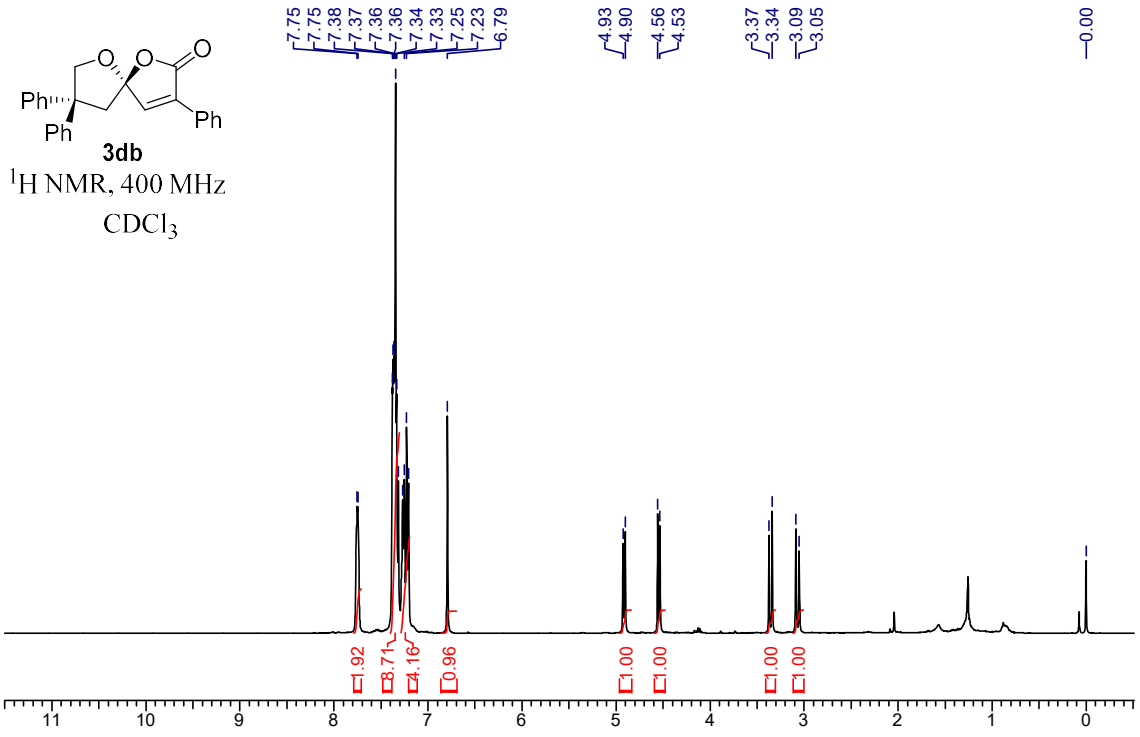
$CDCl_3$

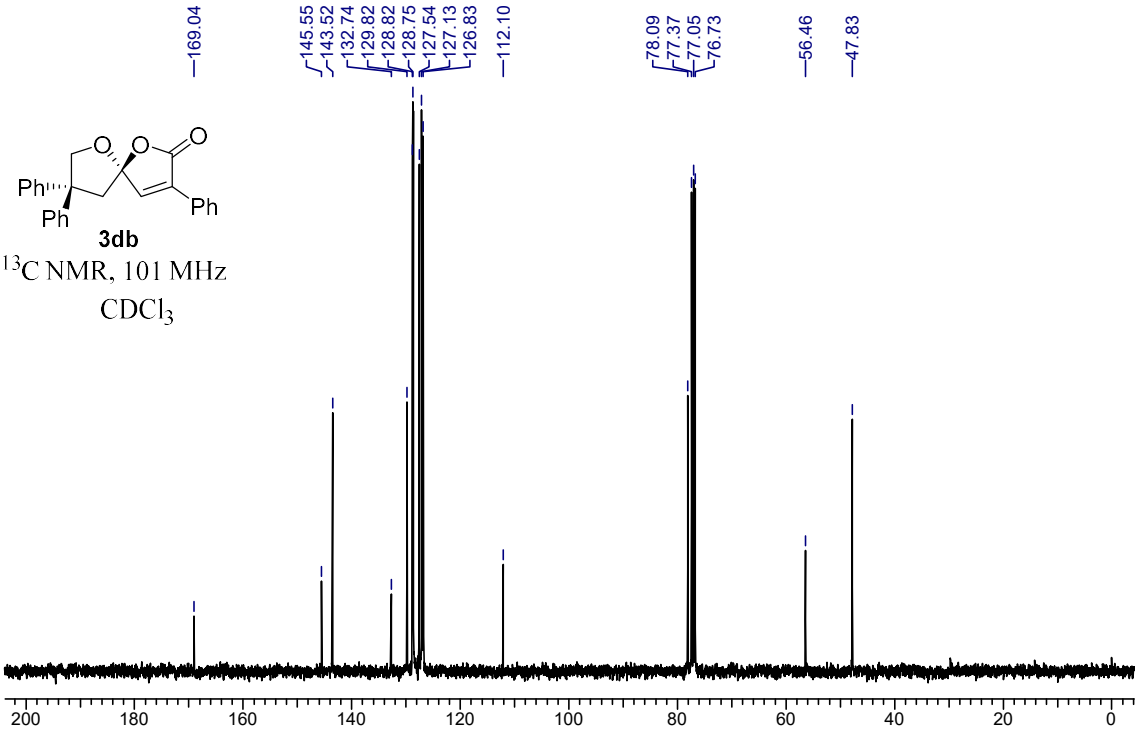
3-methyl-8, 8-diphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3da):



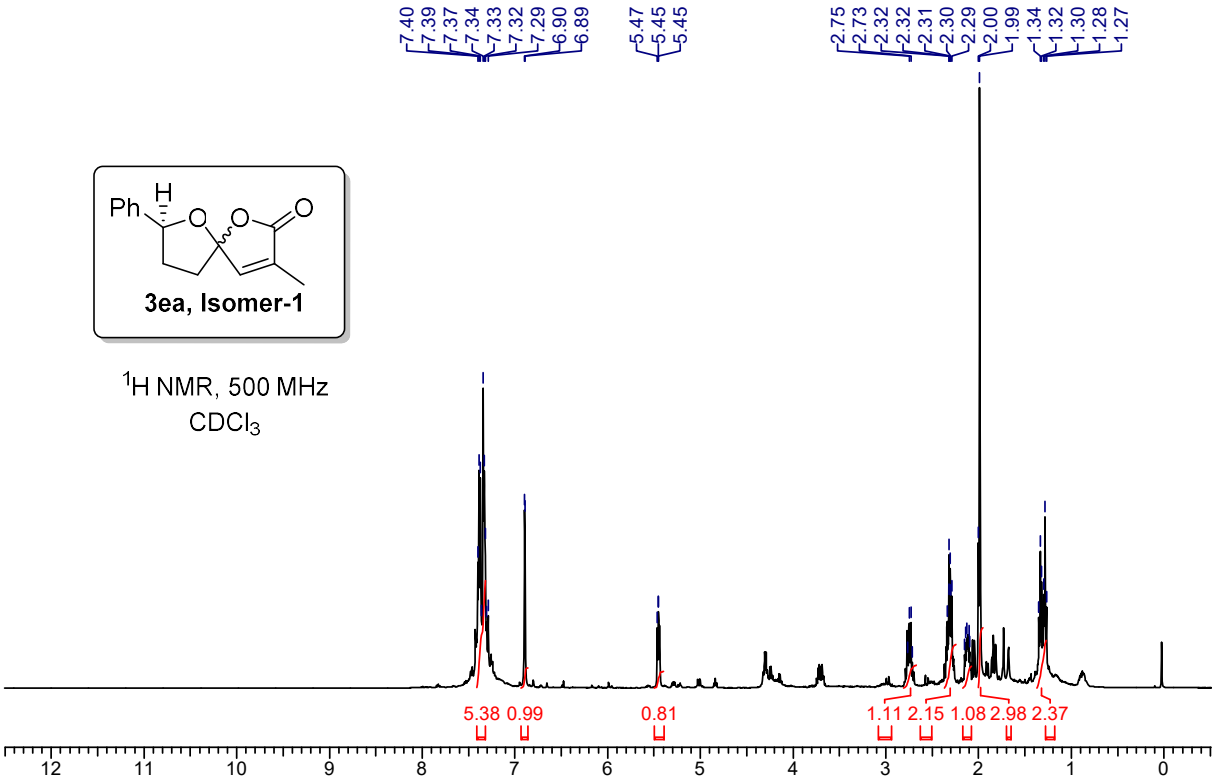


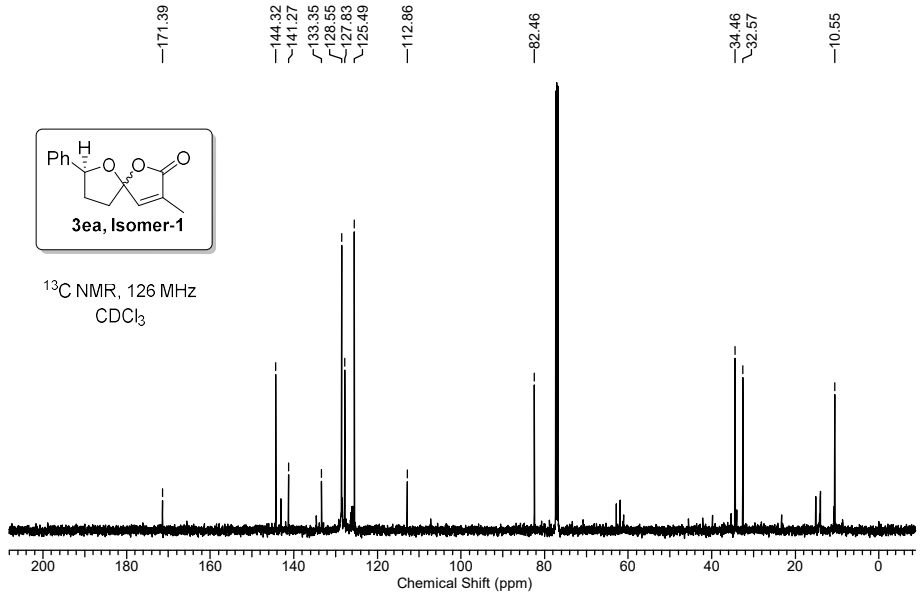
3, 8, 8-triphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3db):



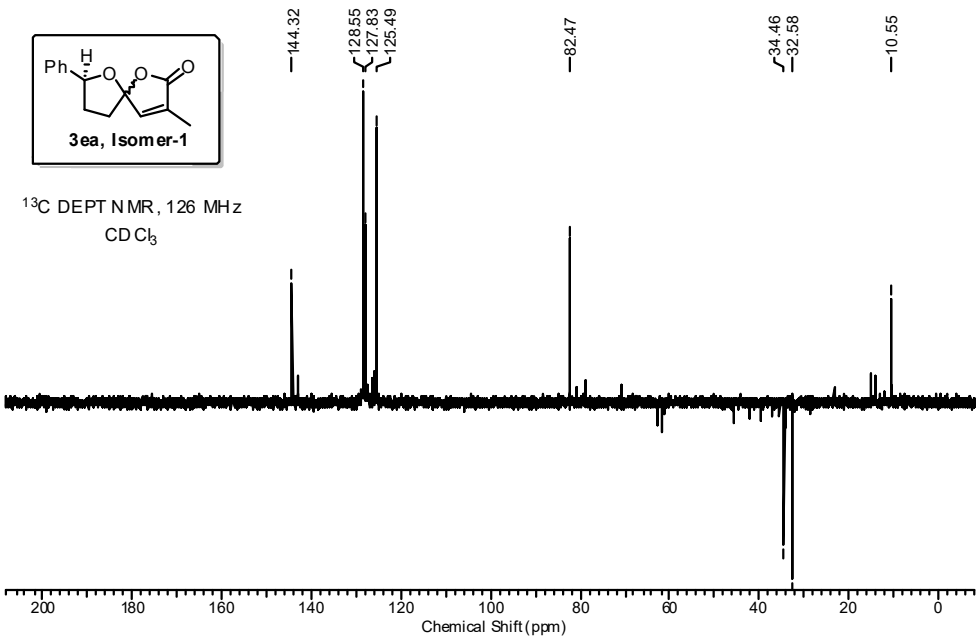


3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):

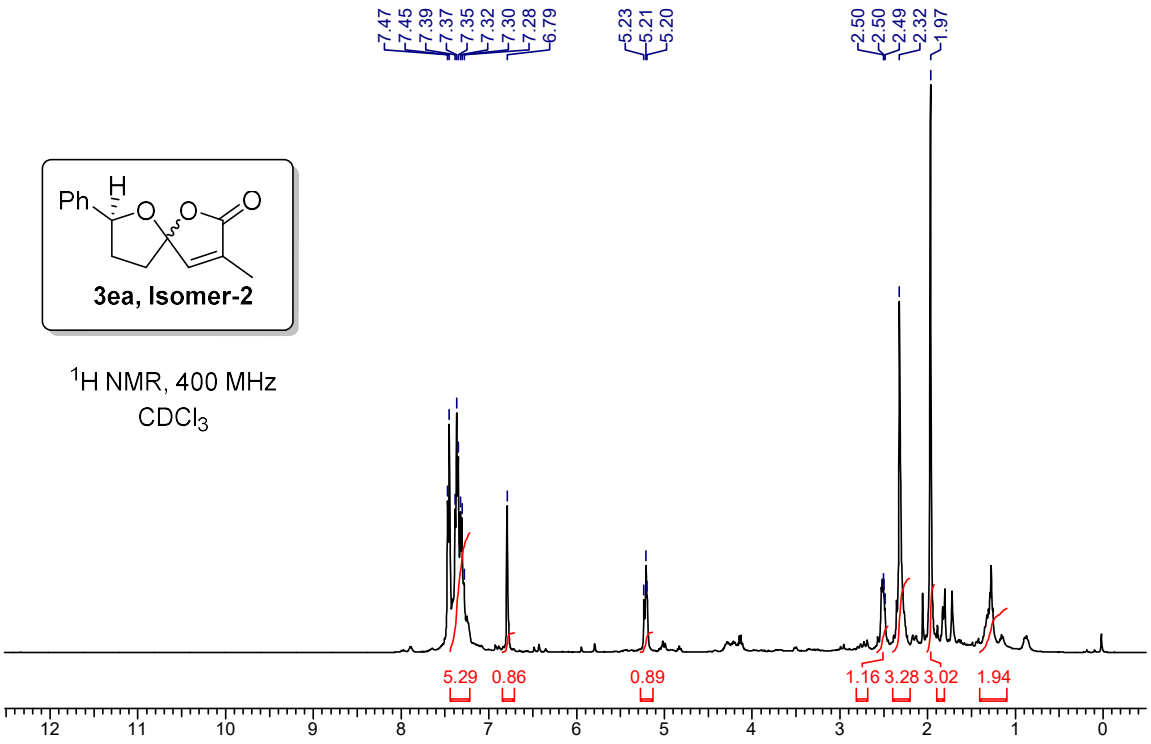




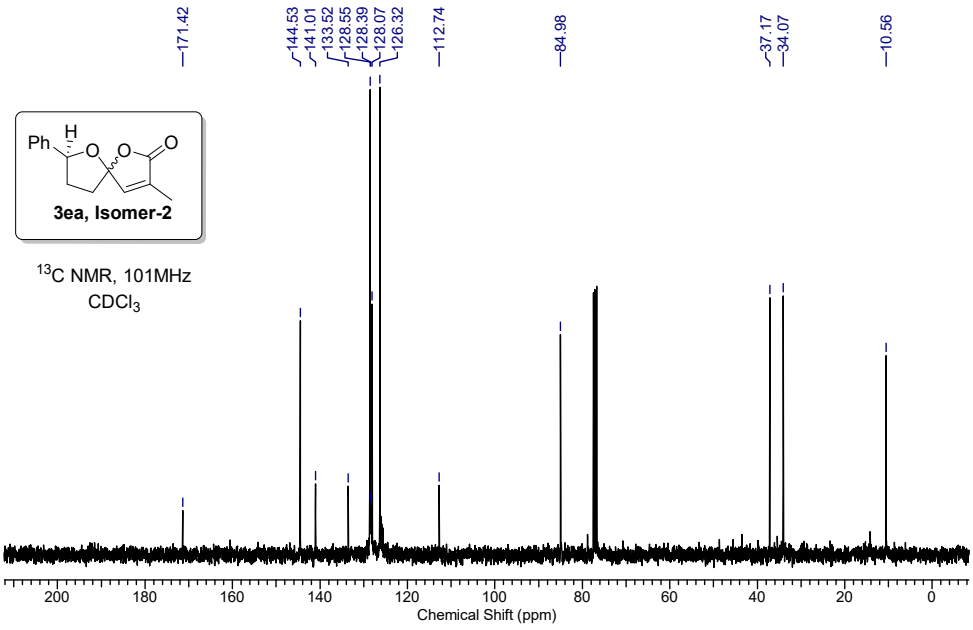
3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):

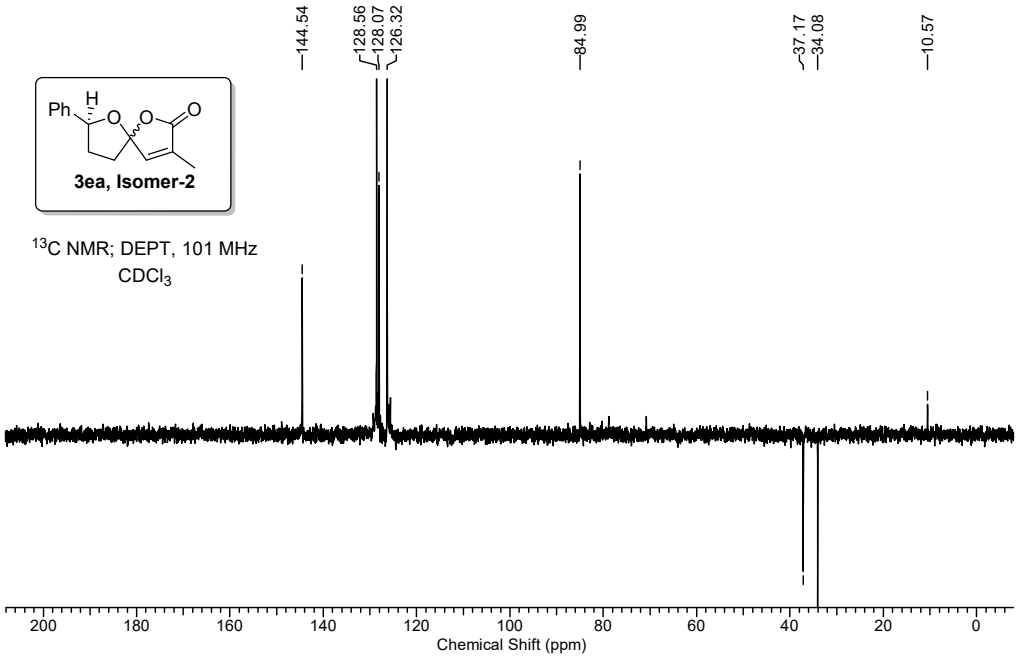


3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):

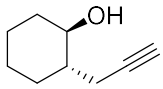


3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):





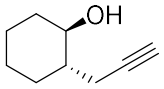
2-(prop-2-yn-1-yl)cyclohexan-1-ol (1f):



1f

^{1}H NMR-500 MHz

$CDCl_3$

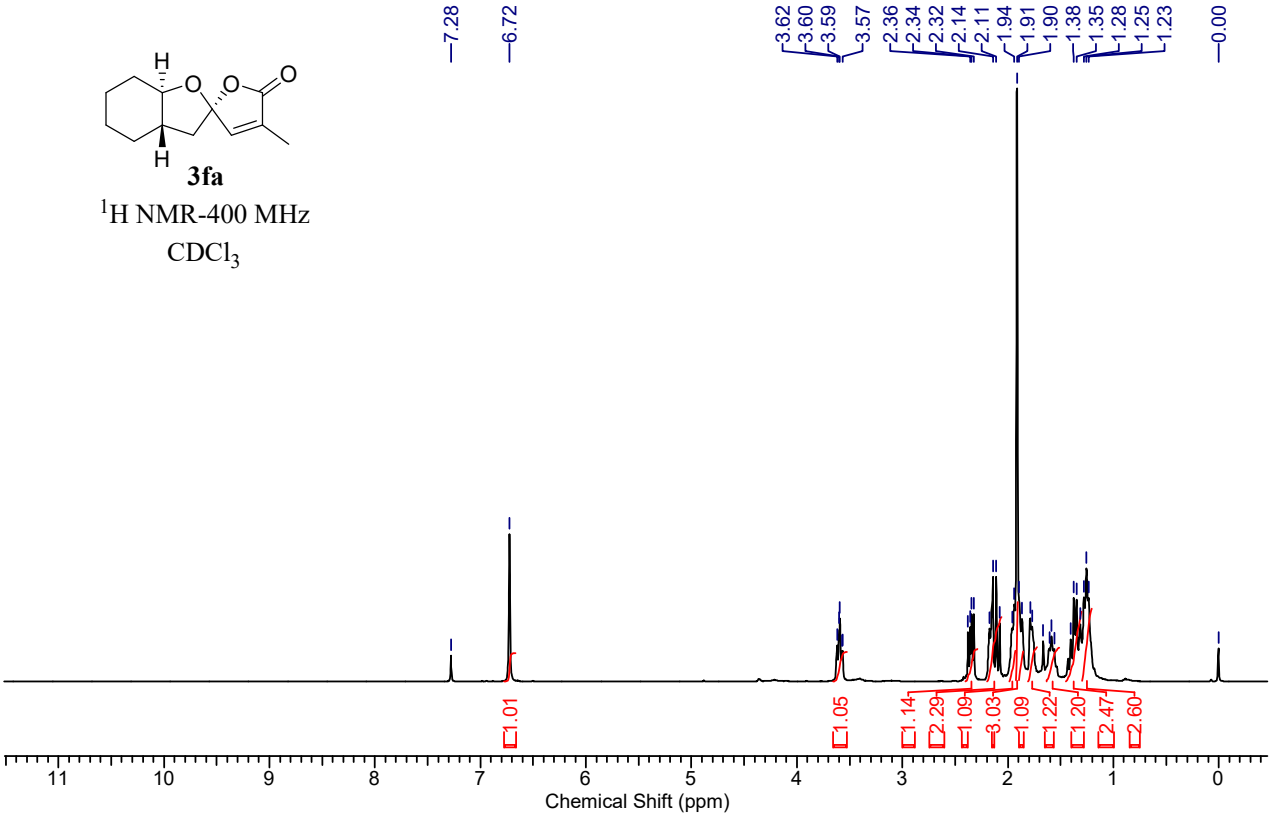


1f

^{13}C NMR-126 MHz

$CDCl_3$

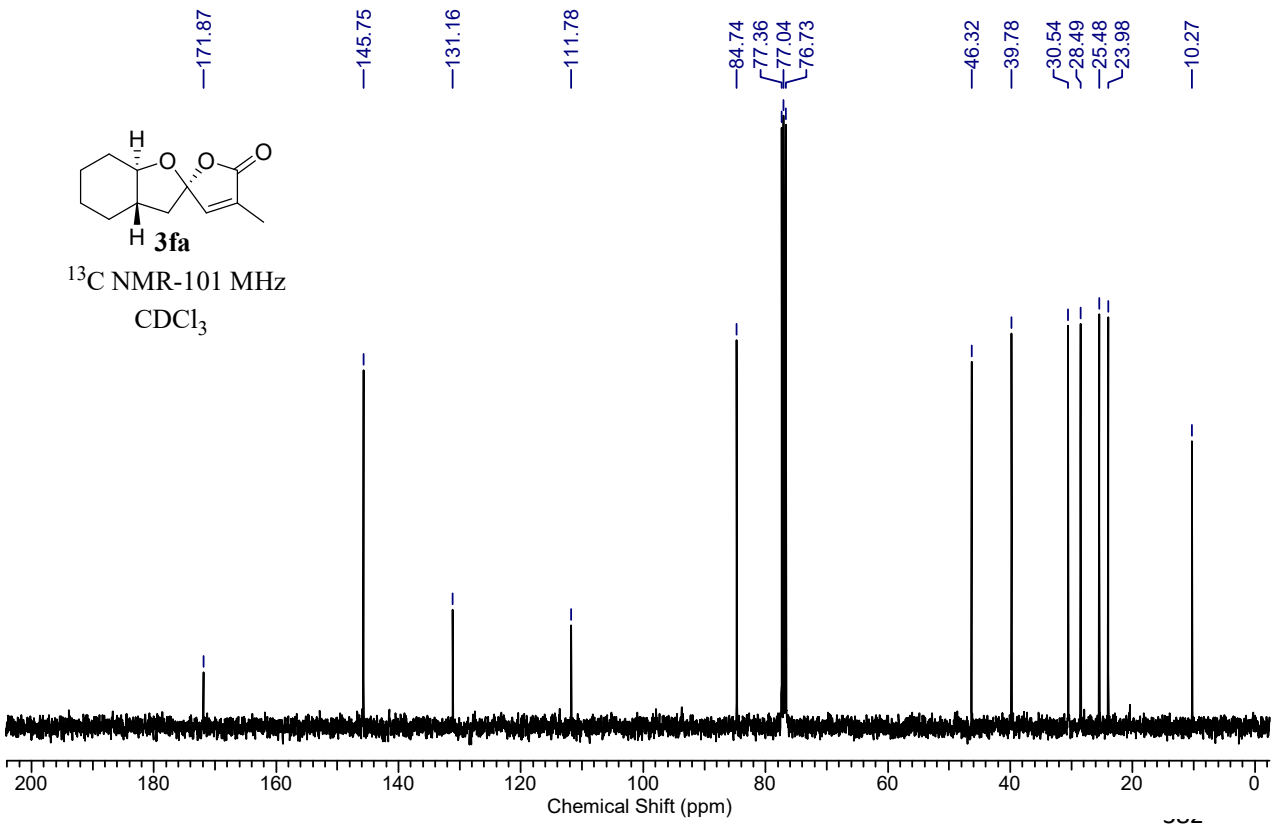
4'-methyl-3a,4,5,6,7,7a-hexahydro-3*H*,5'*H*-spiro[benzofuran-2,2'-furan]-5'-one (3fa)



3fa

^{1}H NMR-400 MHz

$CDCl_3$

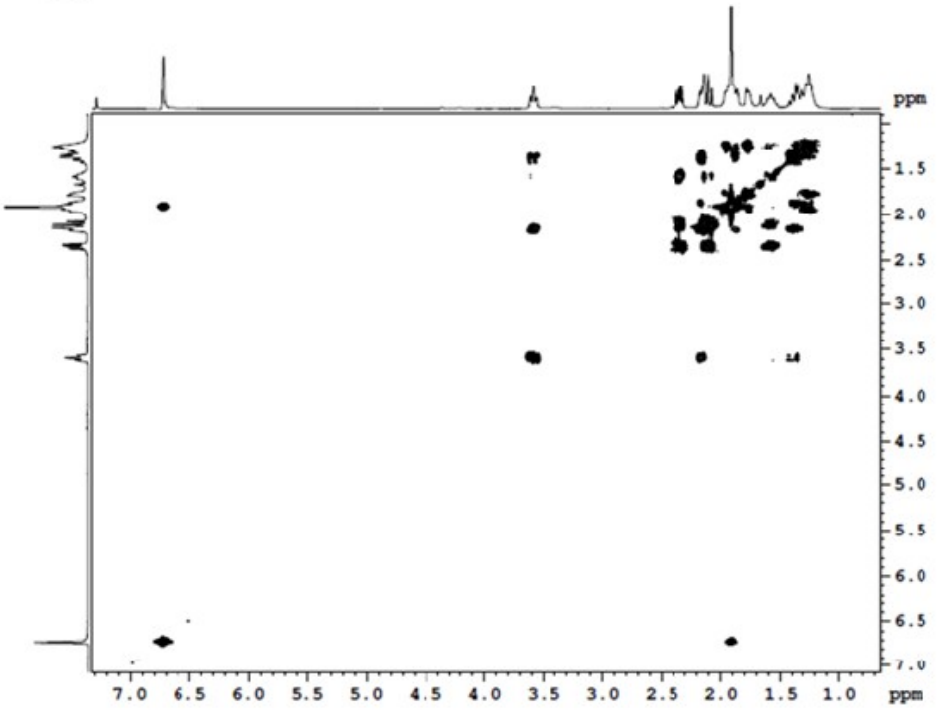


3fa

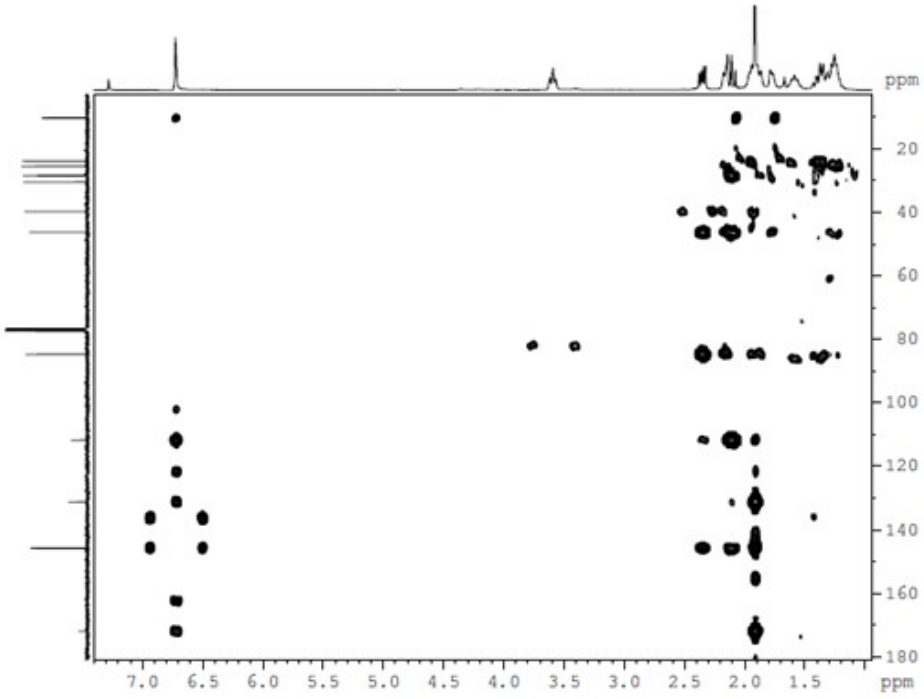
^{13}C NMR-101 MHz

$CDCl_3$

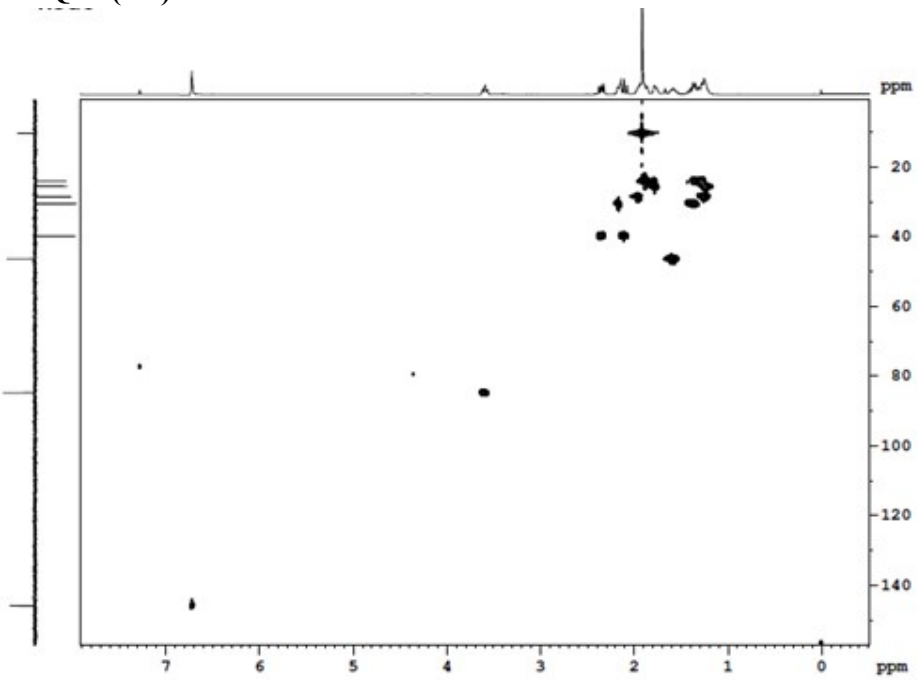
COSY: (3fa)



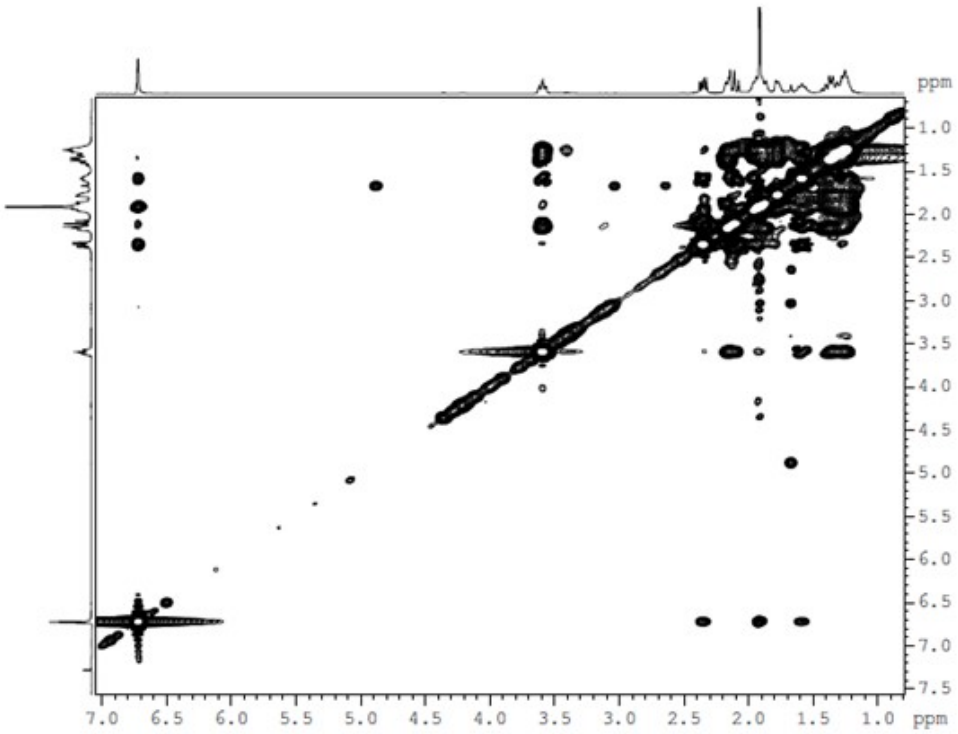
HMBC: (3fa)



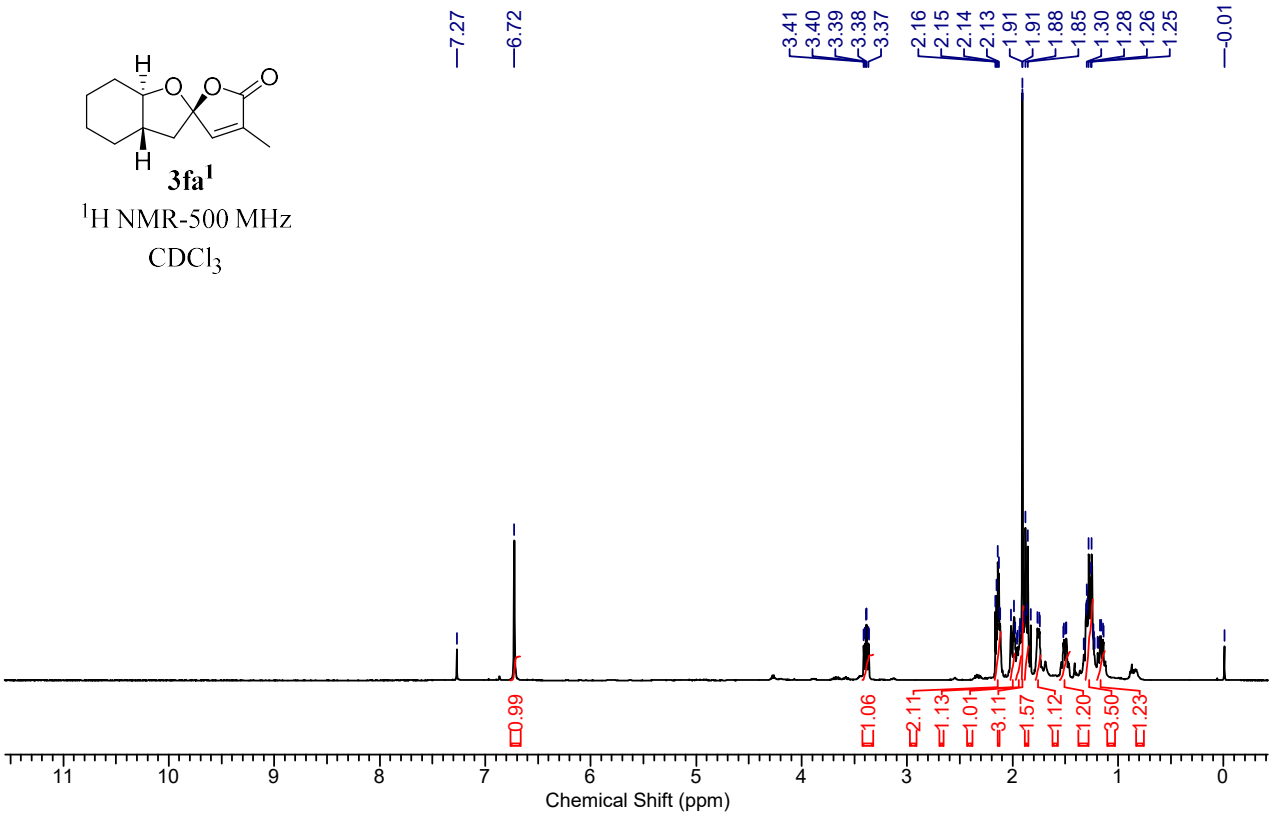
HSQC: (3fa)



NOESY: (3fa)



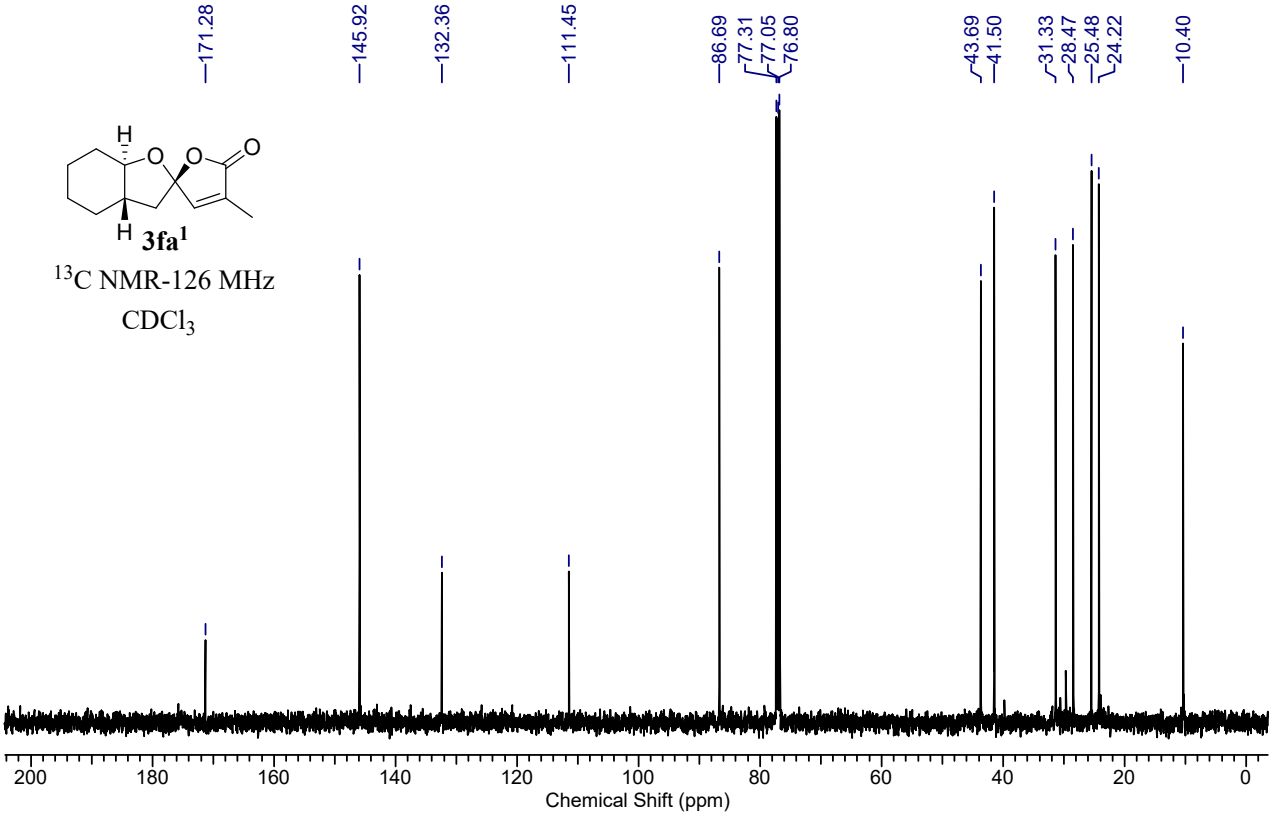
4'-methyl-3a,4,5,6,7,7a-hexahydro-3*H*,5'*H*-spiro[benzofuran-2,2'-furan]-5'-one (3fa[1])



3fa[1]

^{1}H NMR-500 MHz

$CDCl_3$

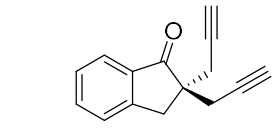


3fa[1]

^{13}C NMR-126 MHz

$CDCl_3$

2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1*H*-inden-1-one (S9)

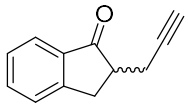


S9

^{1}H NMR-200 MHz

$CDCl_3$

2-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-inden-1-one (S10)

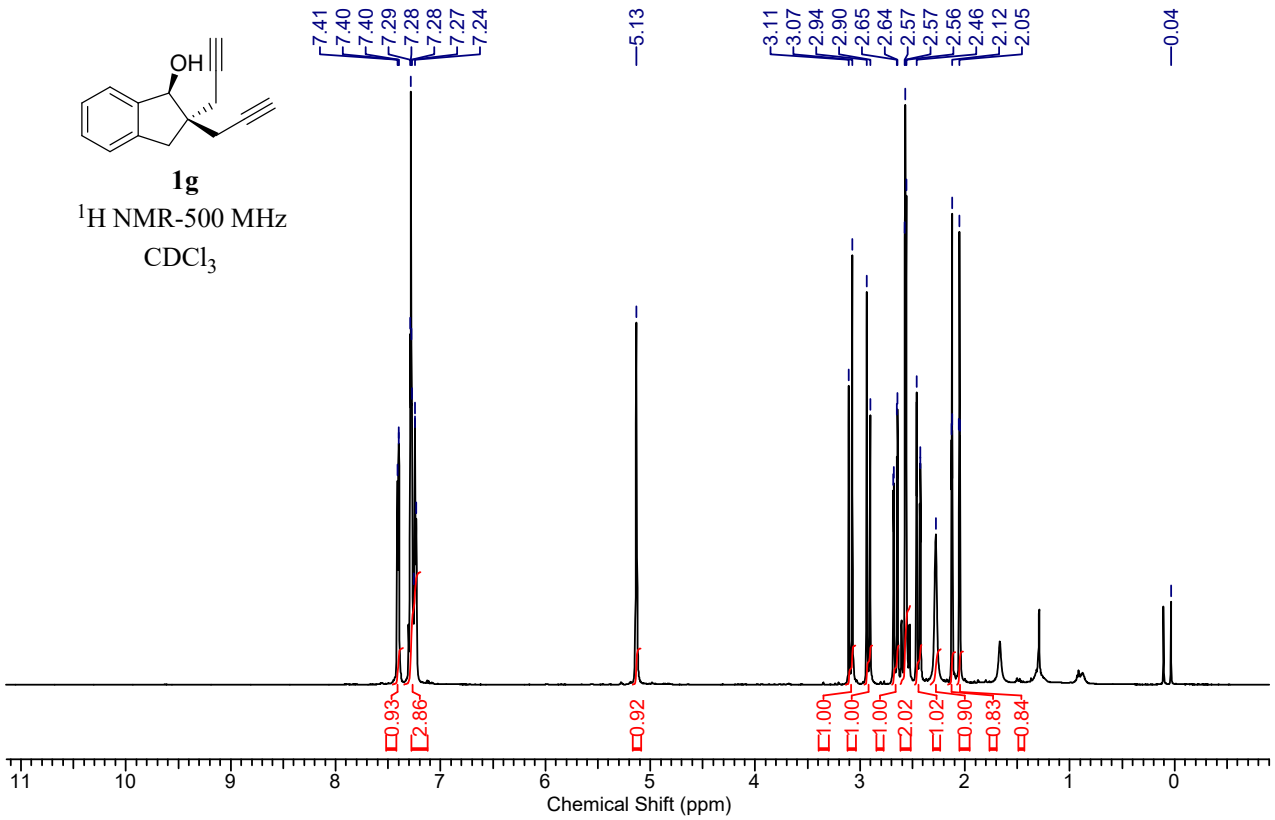


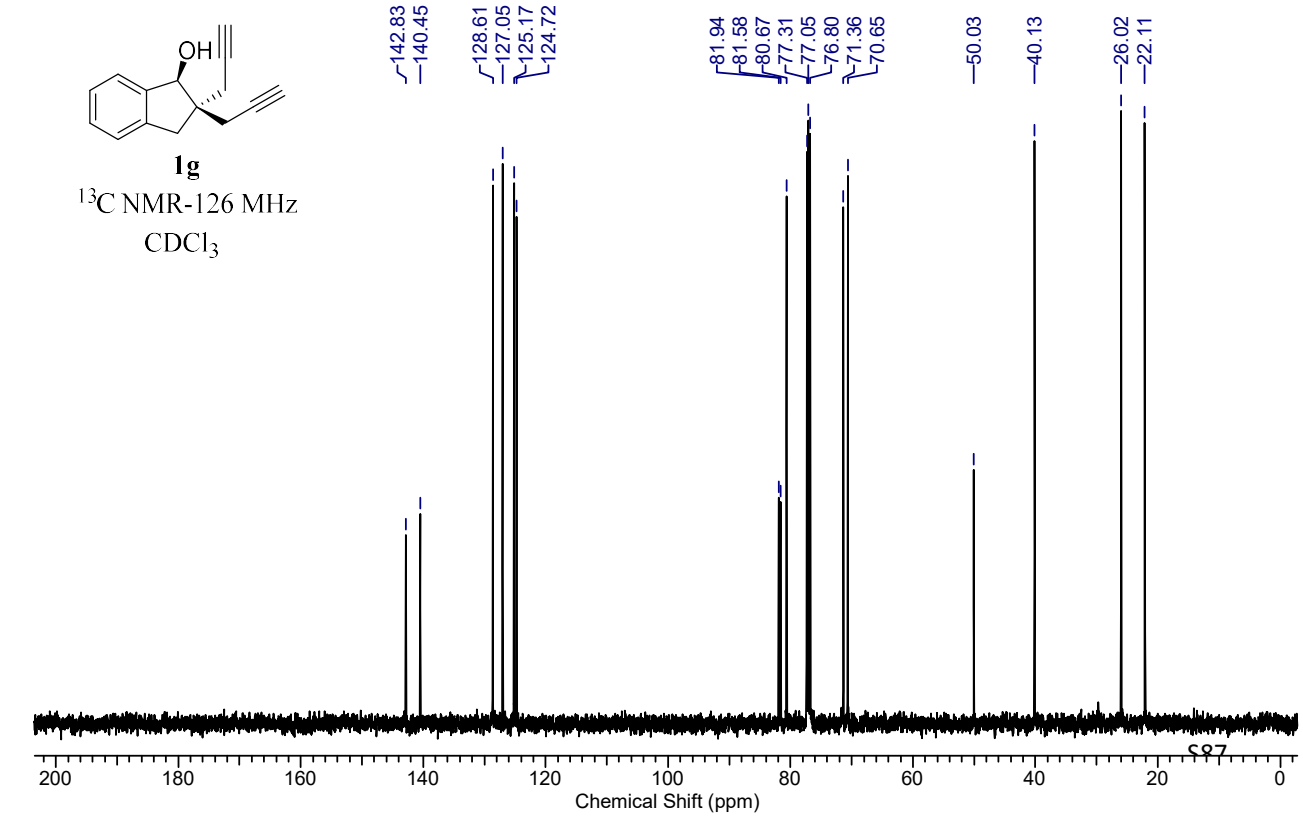
S10

^{1}H NMR-500 MHz

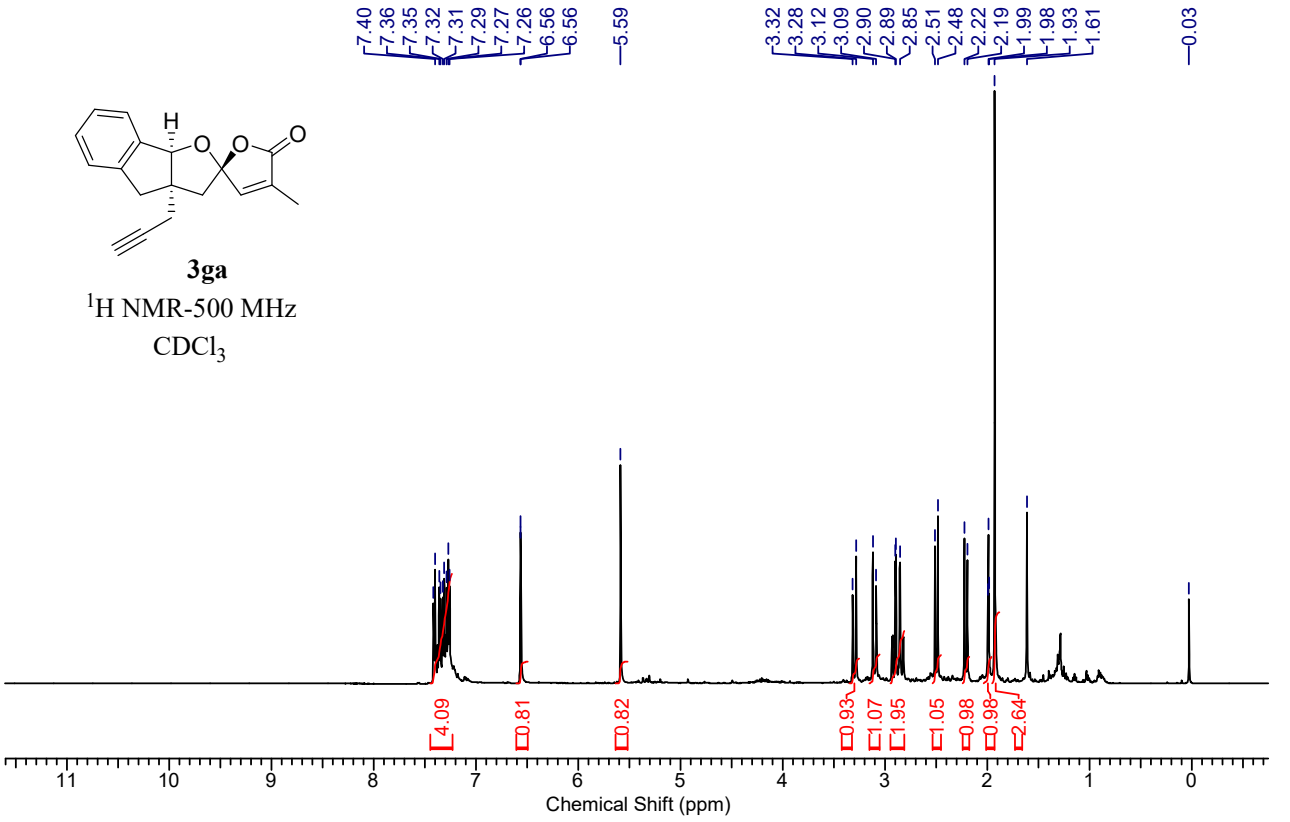
$CDCl_3$

2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1*H*-inden-1-ol (1g)





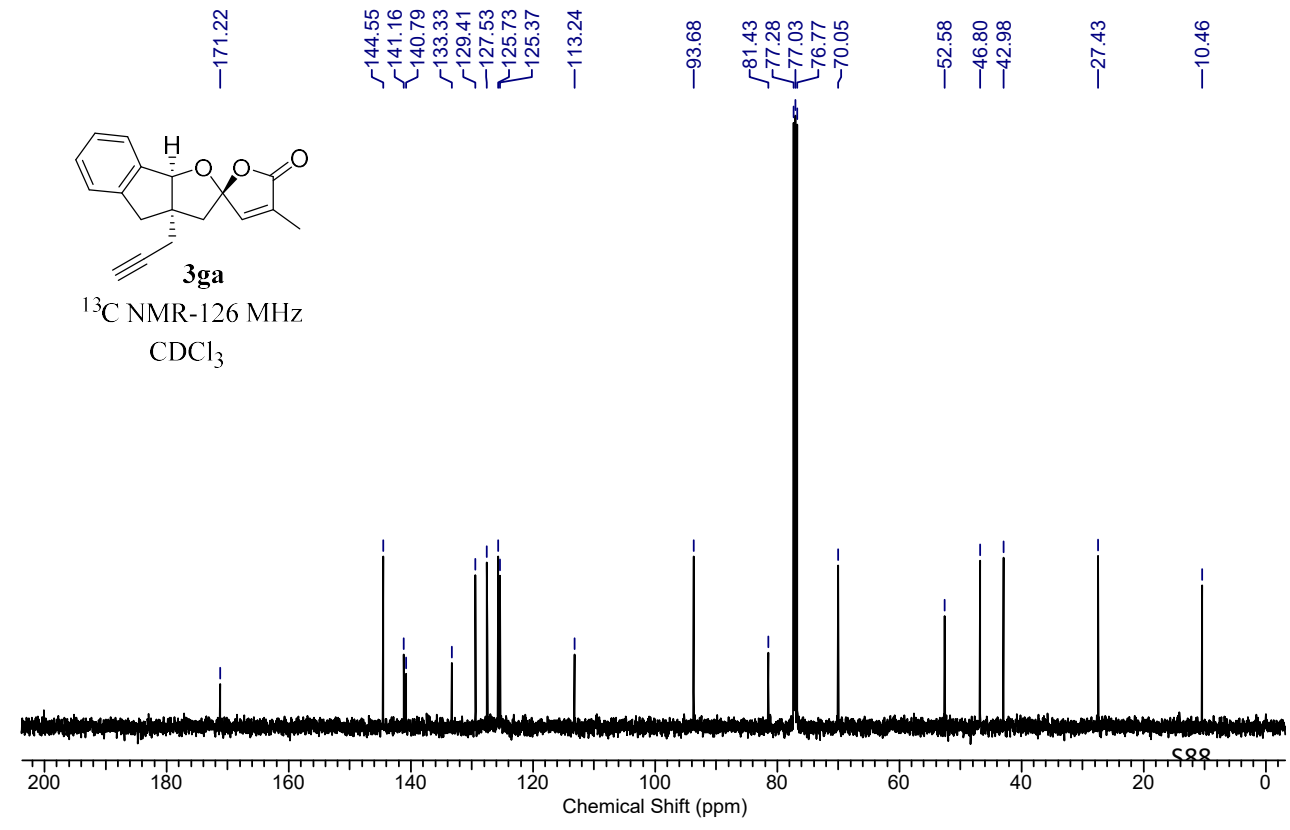
4-methyl-3a'-(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5*H*-spiro[furan-2,2'-indeno[1,2-*b*]furan]-5-one (3ga)



3ga

^{1}H NMR-500 MHz

$CDCl_3$

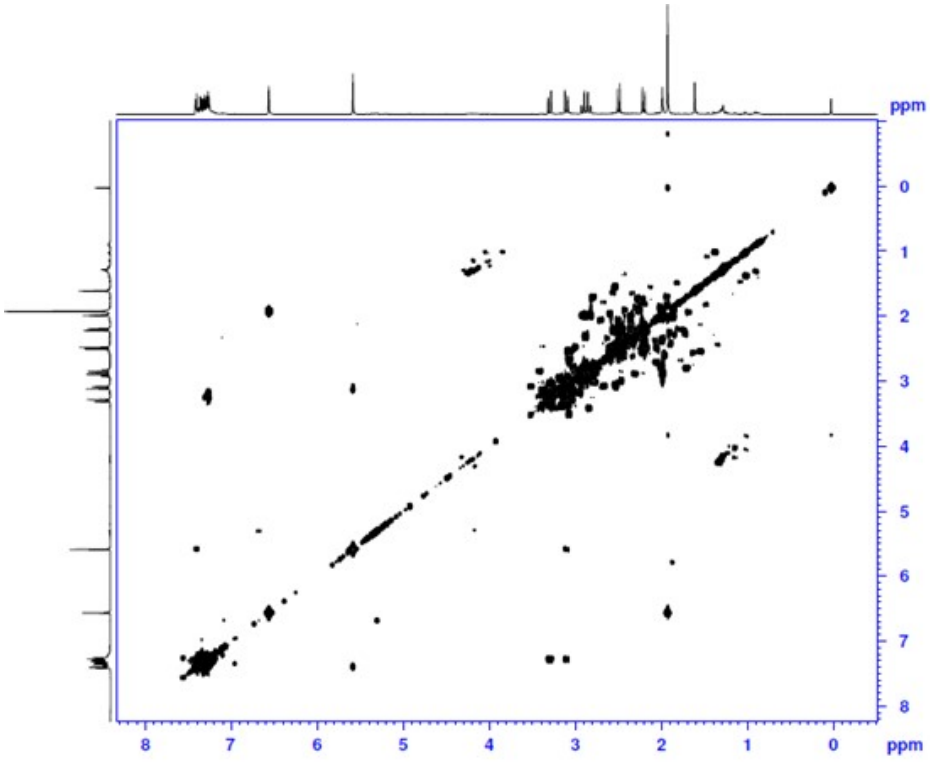


3ga

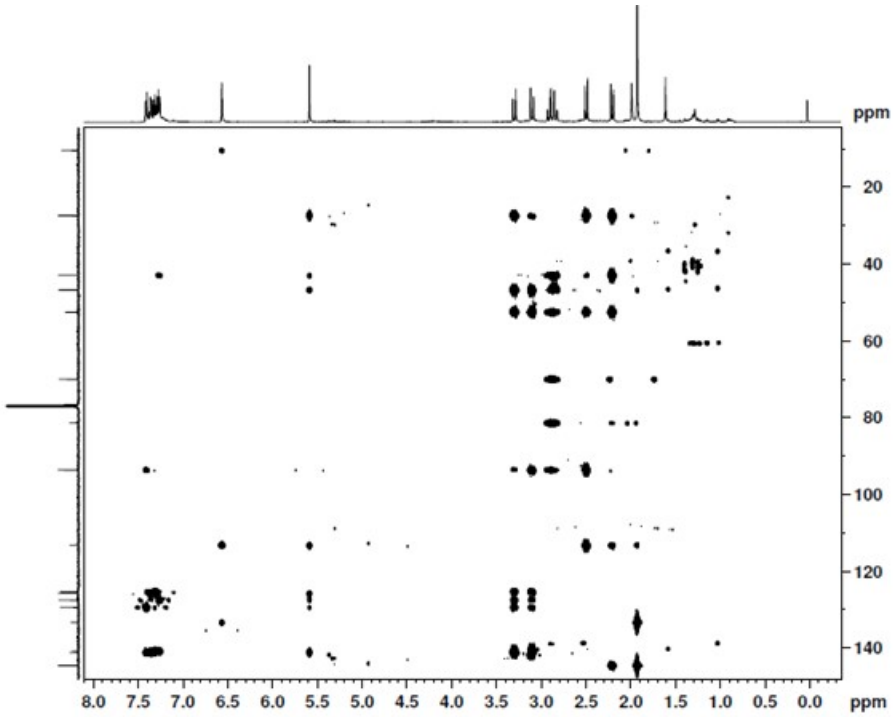
^{13}C NMR-126 MHz

$CDCl_3$

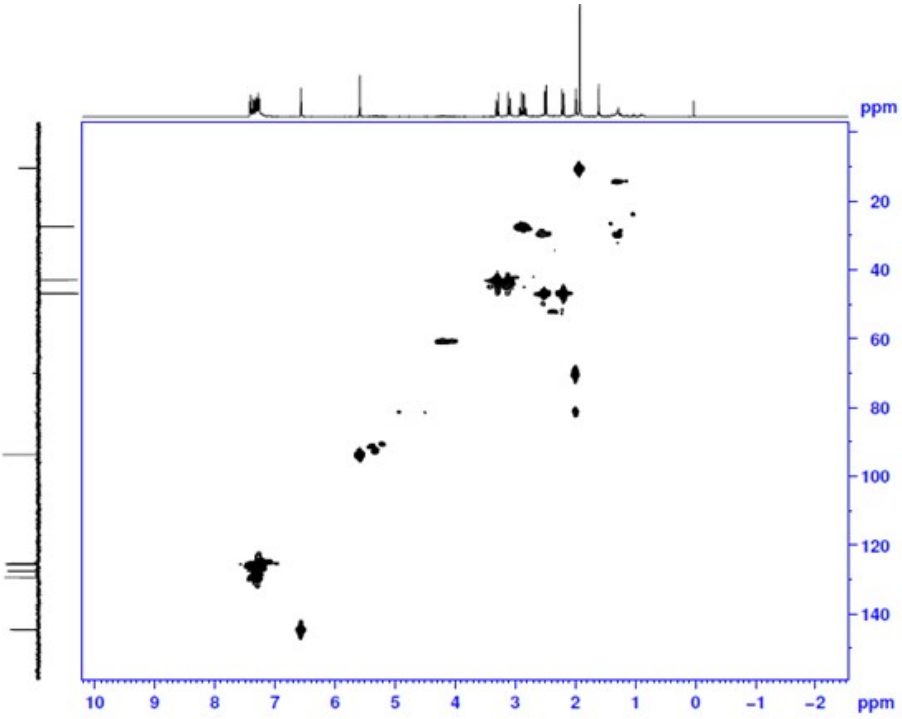
COSY: (3ga)



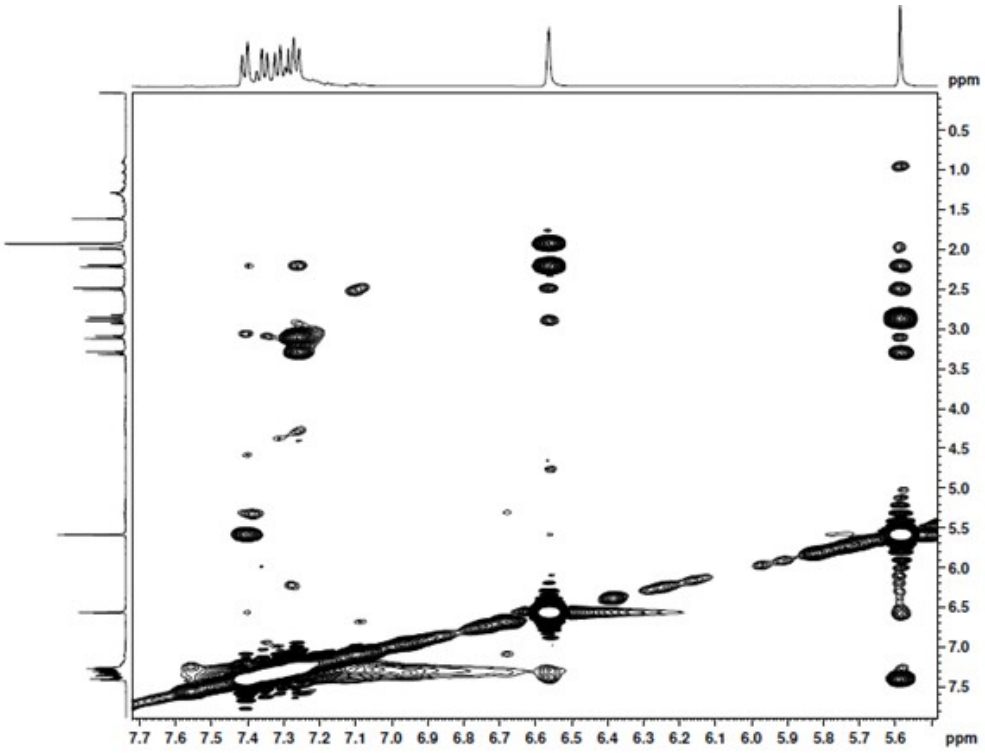
HMBC: (3ga)



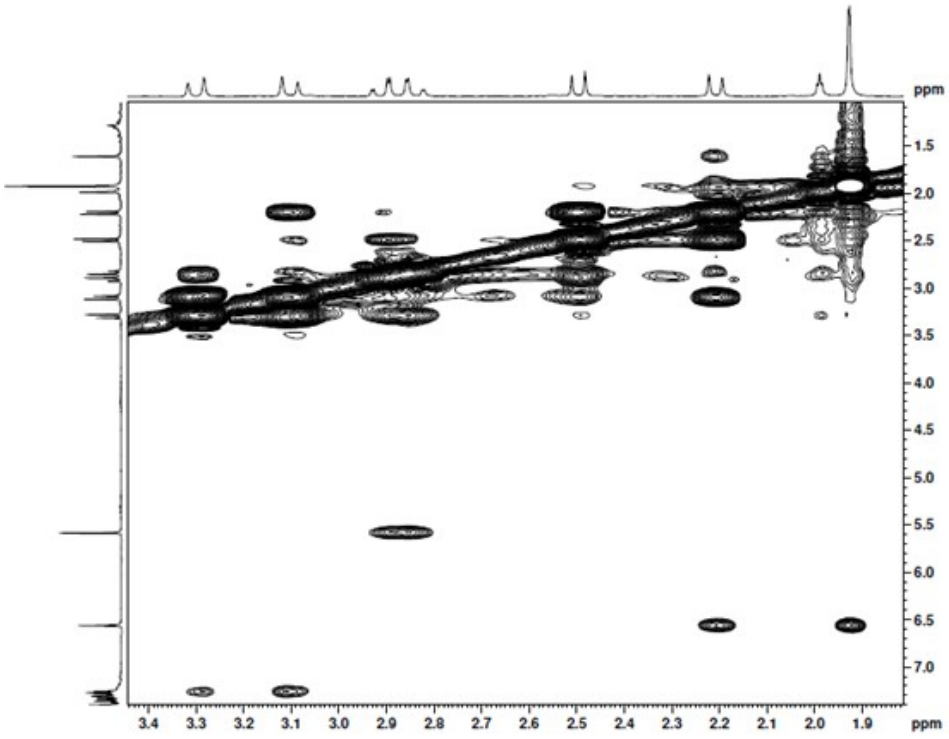
HSQC: (3ga)



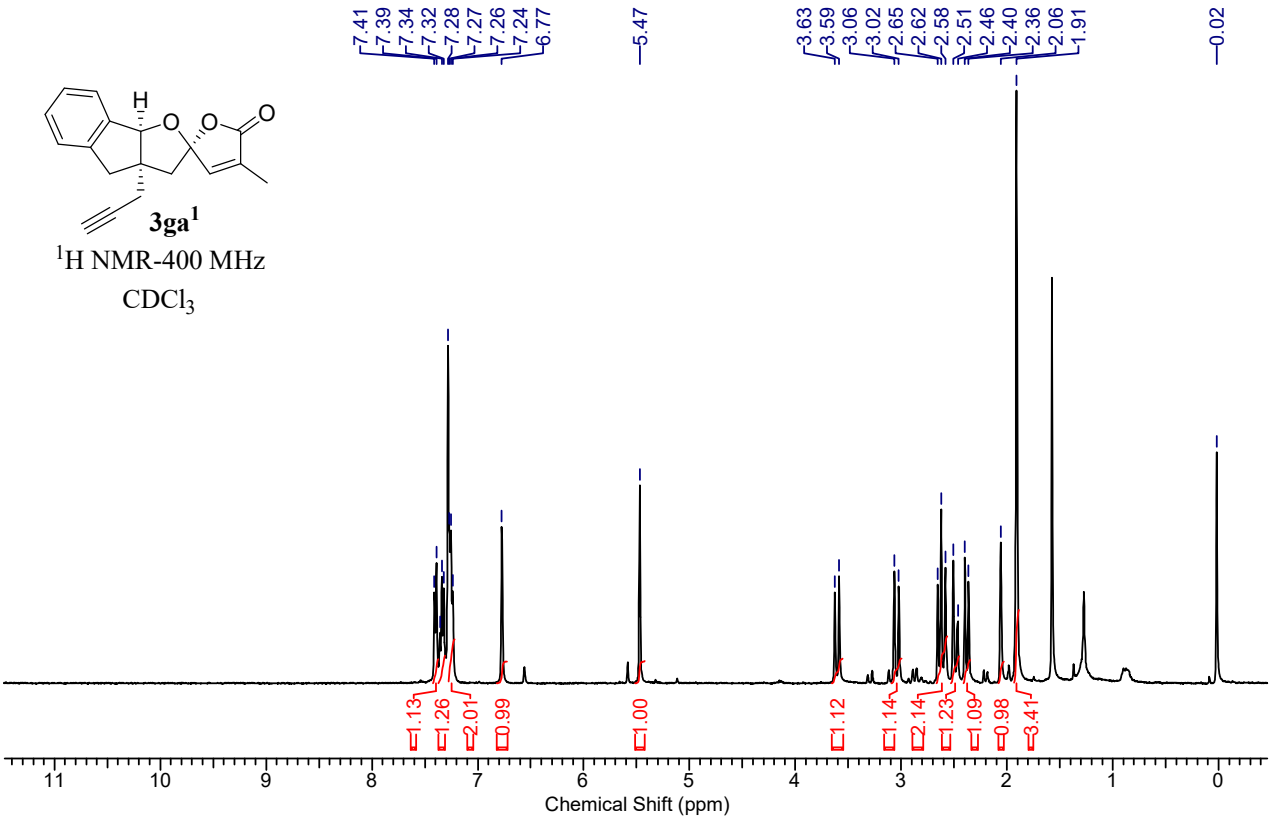
NOESY: (3ga)



NOESY: (3ga)


ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
ppm

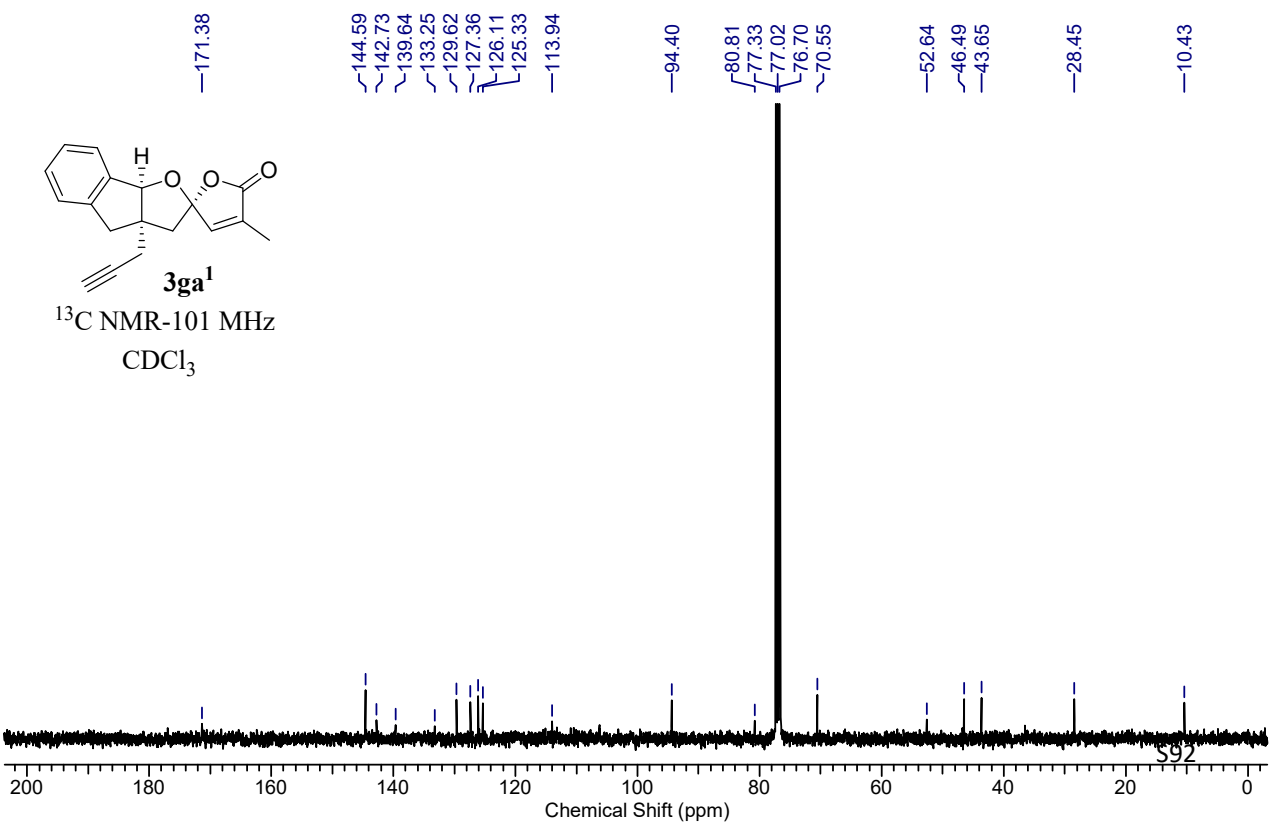
4-methyl-3a'-(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5*H*-spiro[furan-2,2'-indeno[1,2-*b*]furan]-5-one (3ga[1])



3ga[1]

^{1}H NMR-400 MHz

$CDCl_3$

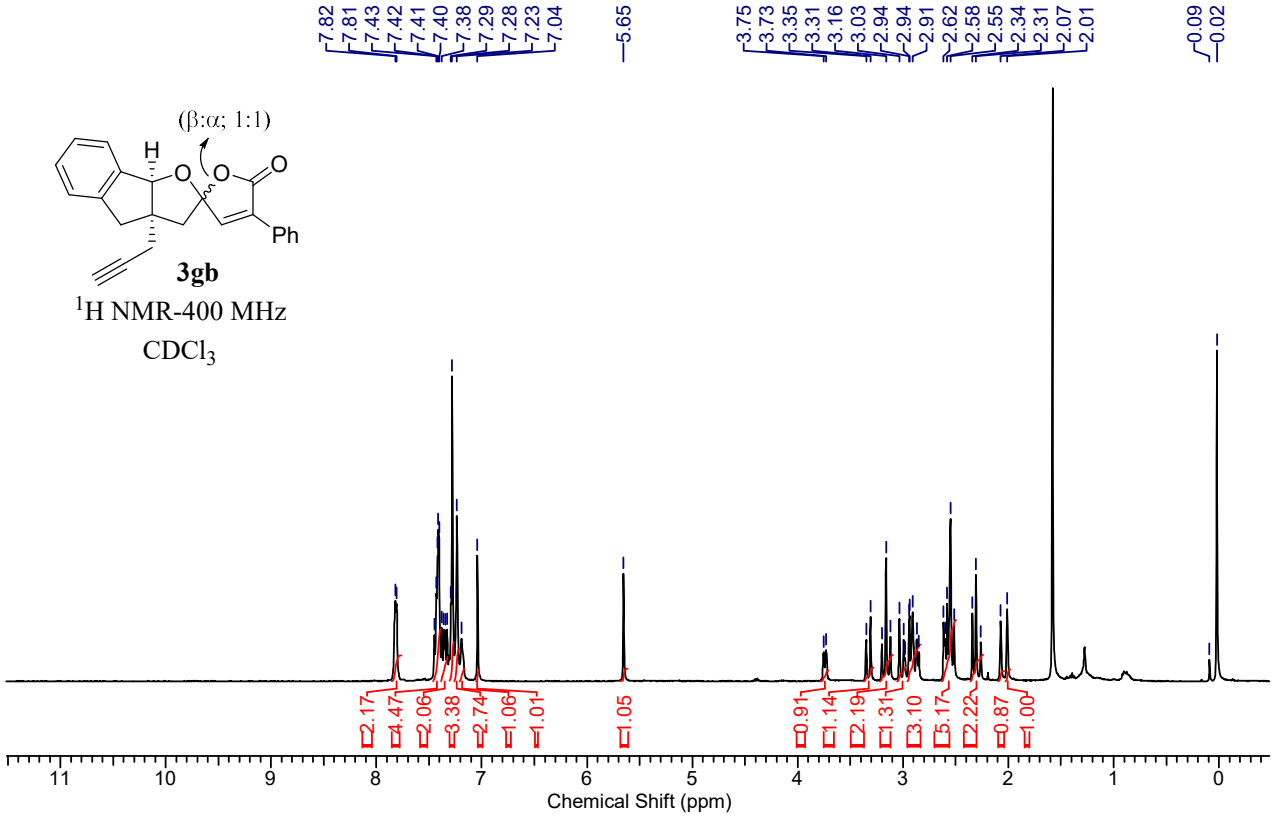


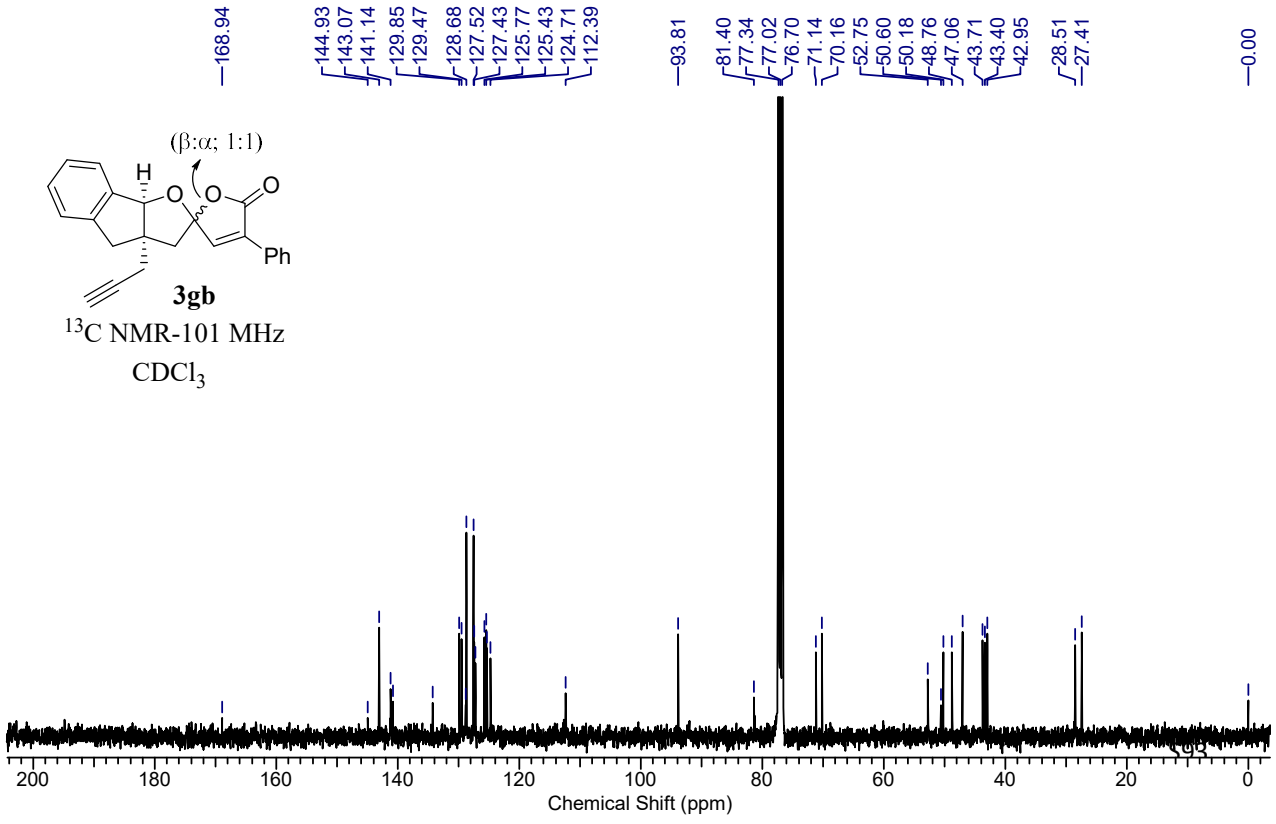
3ga[1]

^{13}C NMR-101 MHz

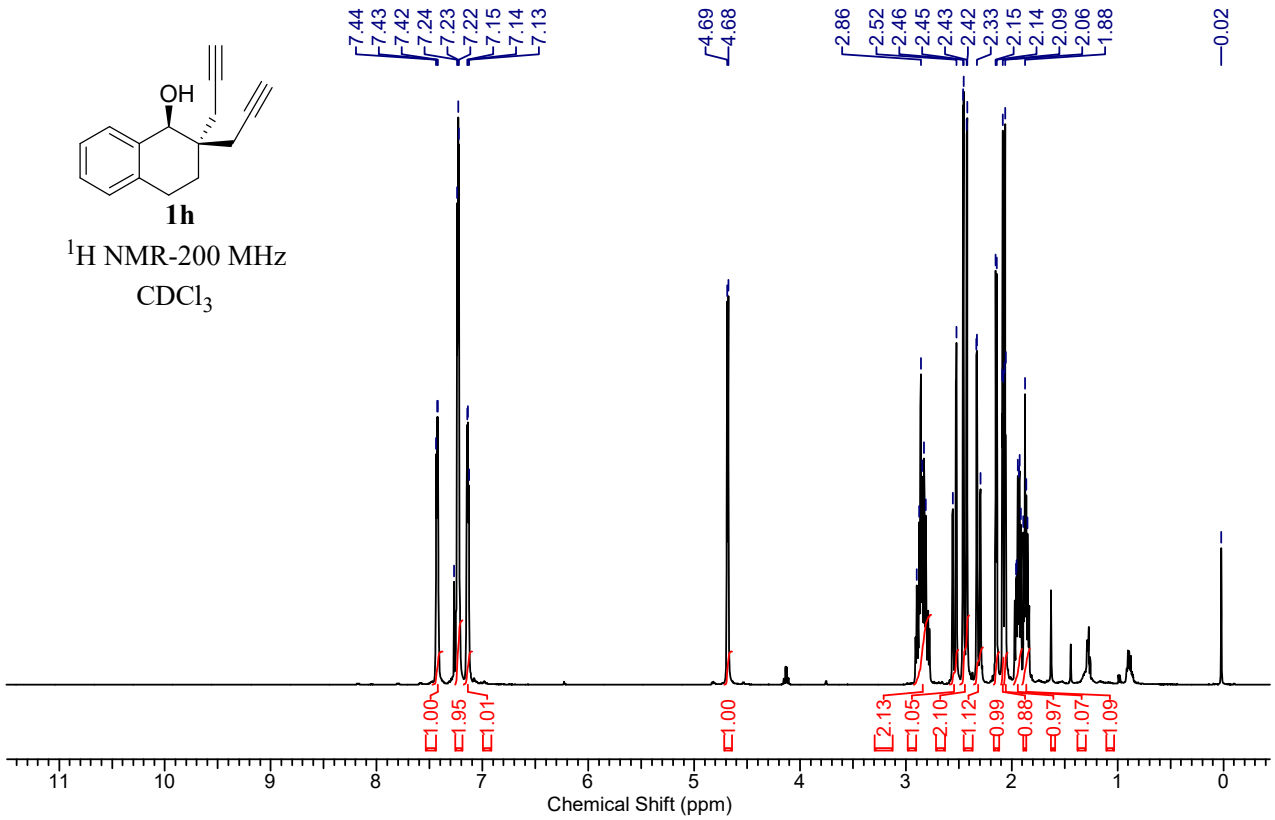
$CDCl_3$

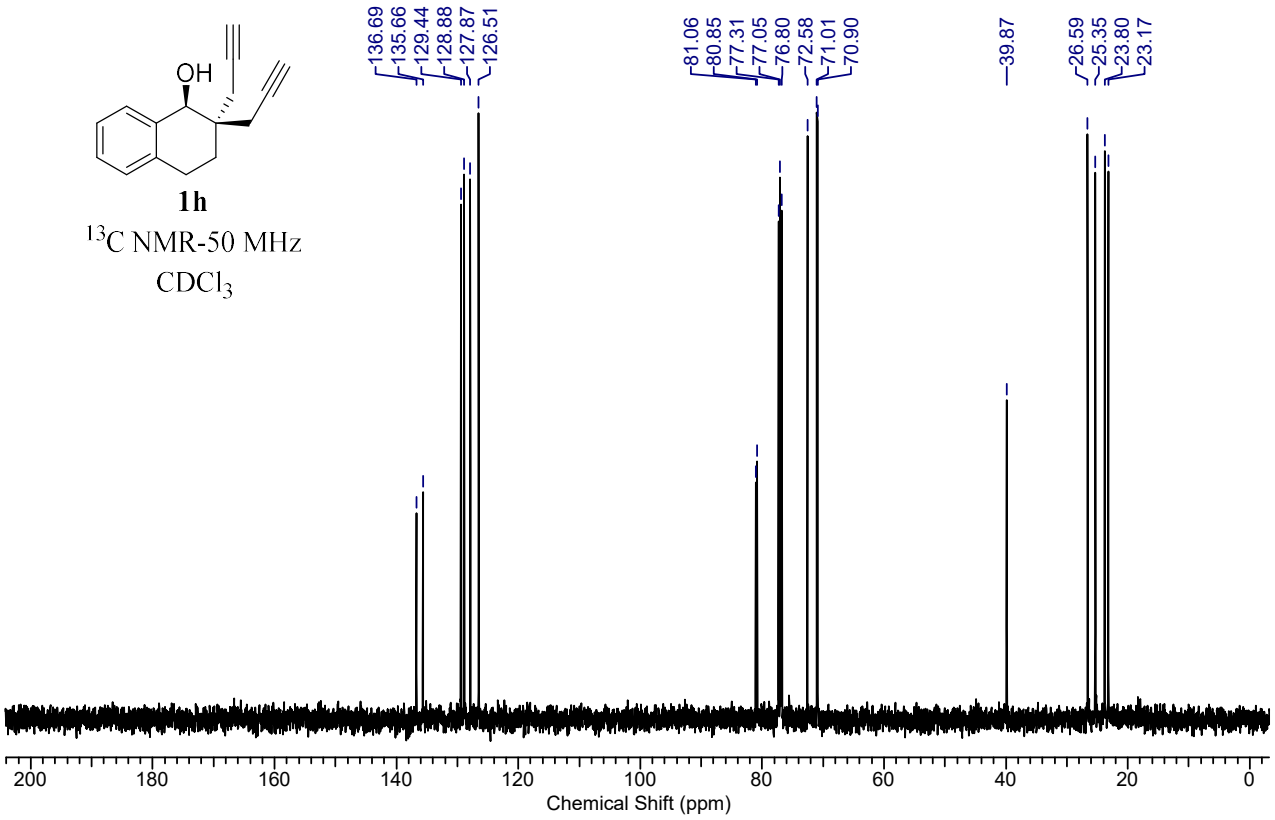
4-phenyl-3a'-(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5*H*-spiro[furan-2,2'-indeno[1,2-*b*]furan]-5-one (3gb)



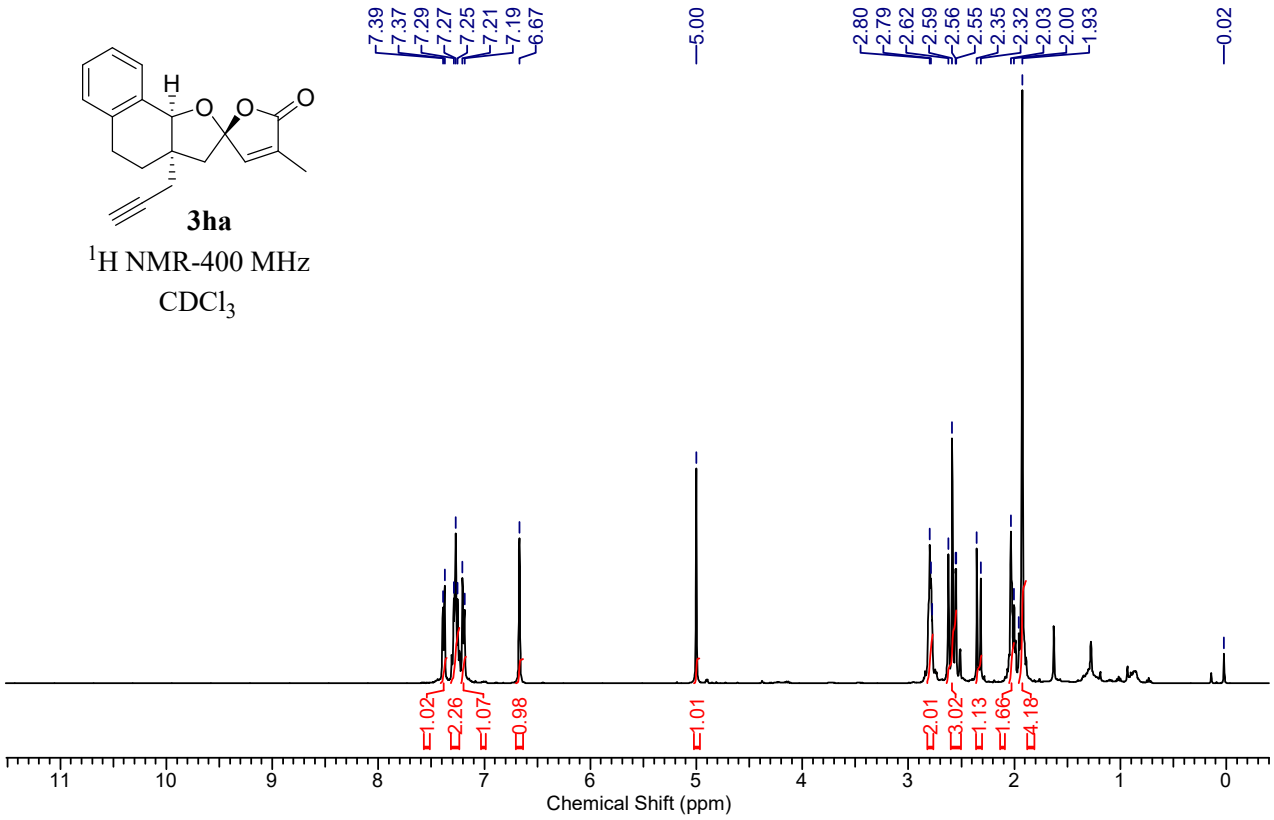


2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (1h)





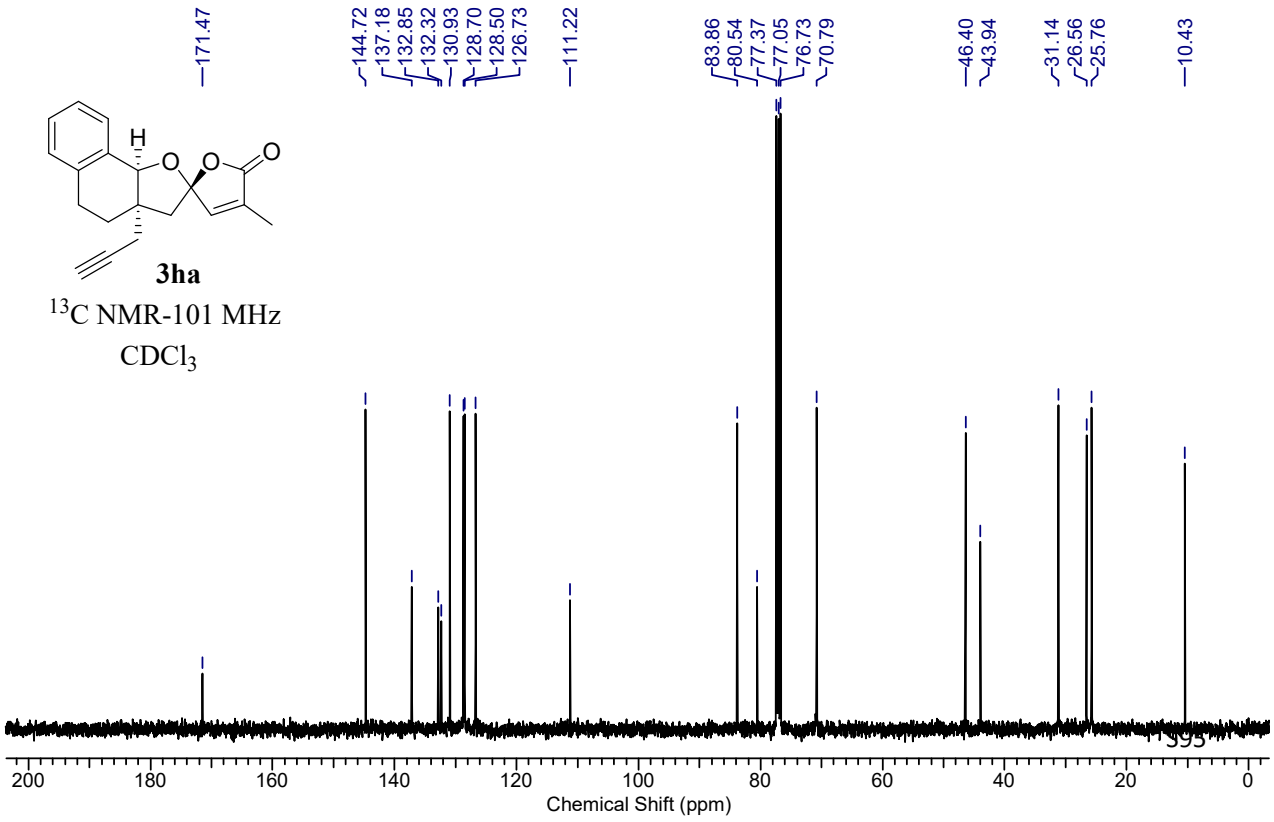
4-methyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'*H*,5*H*-spiro[furan-2,2'-naphtho[1,2-*b*]furan]-5-one (3ha)



3ha

^{1}H NMR-400 MHz

$CDCl_3$

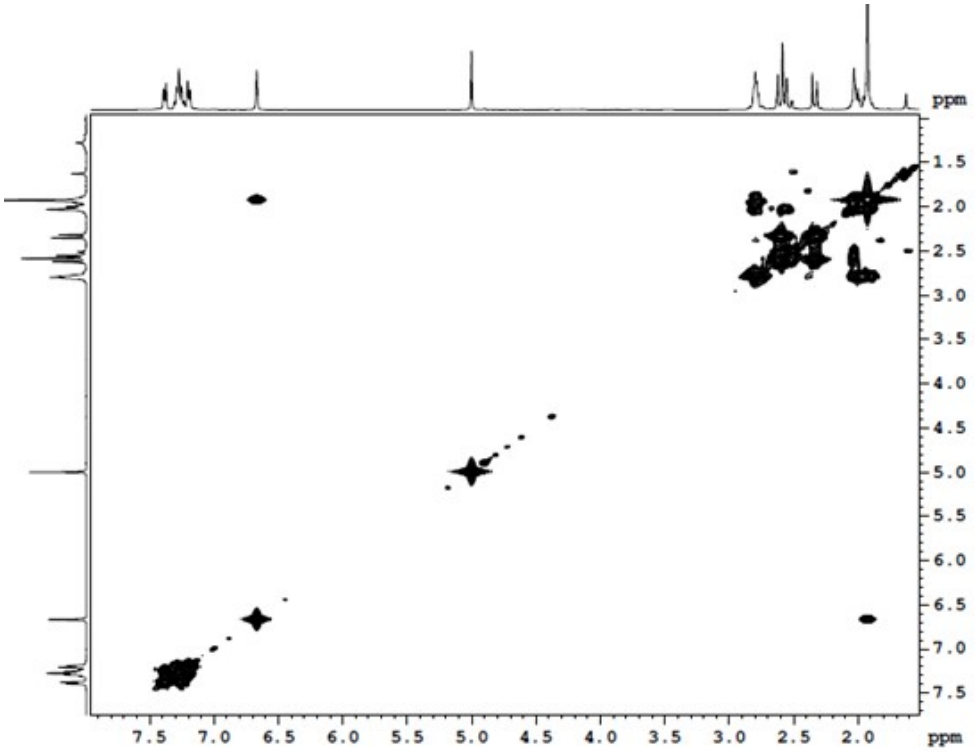


3ha

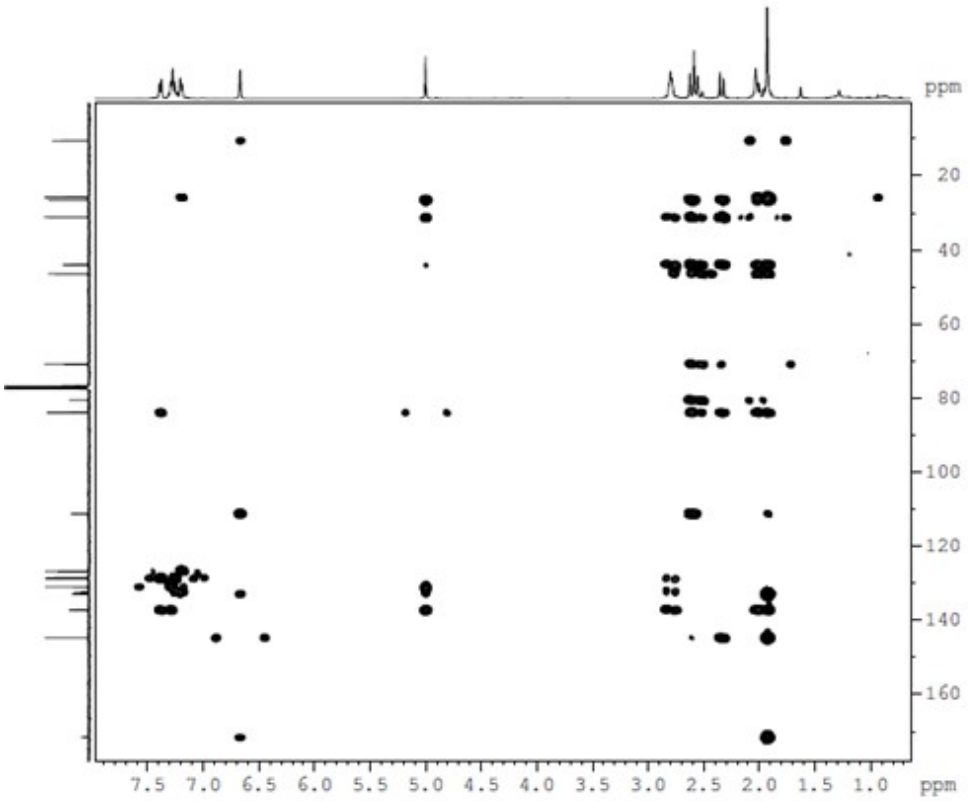
^{13}C NMR-101 MHz

$CDCl_3$

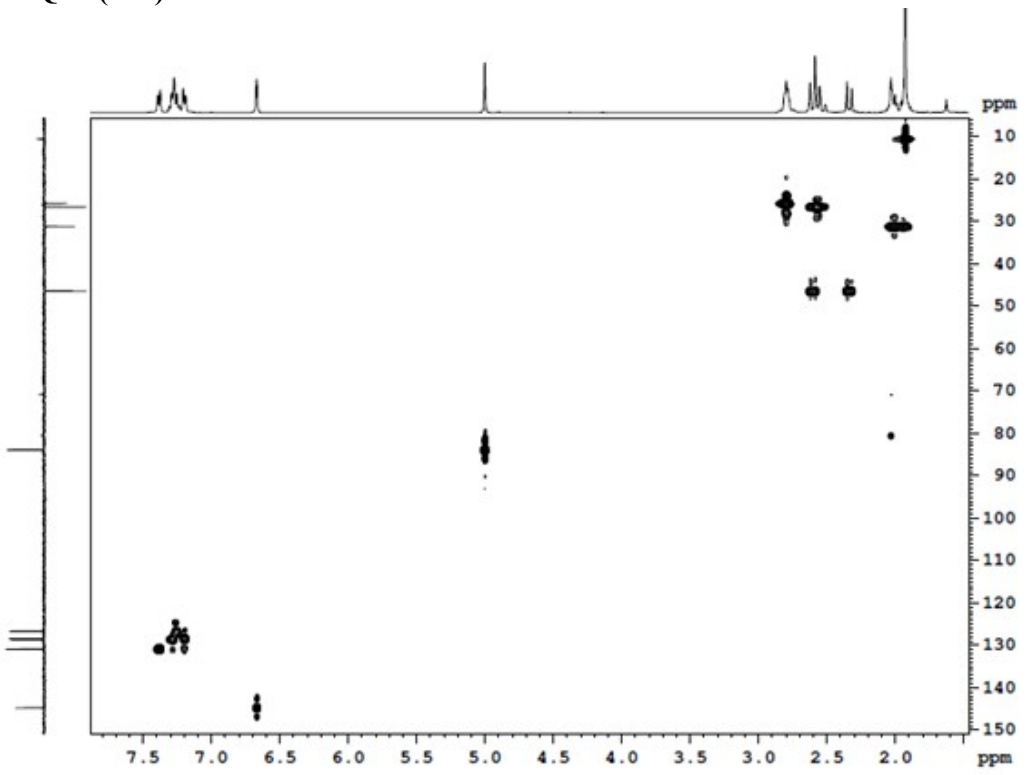
COSY: (3ha)



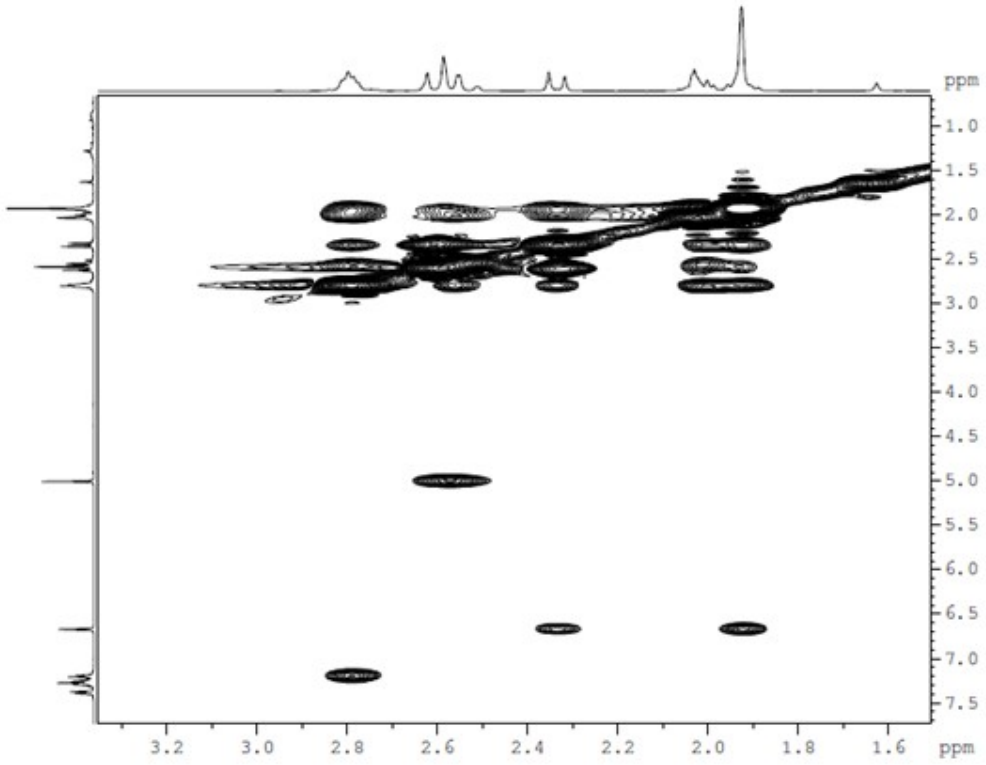
HMBC: (3ha)



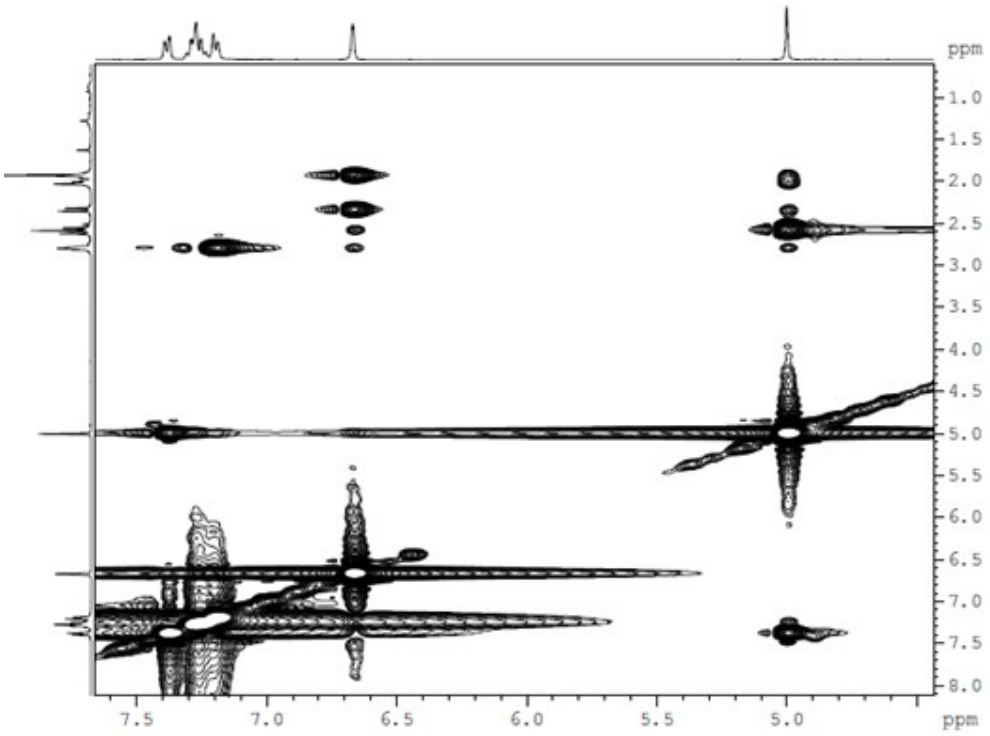
HSQC: (3ha)



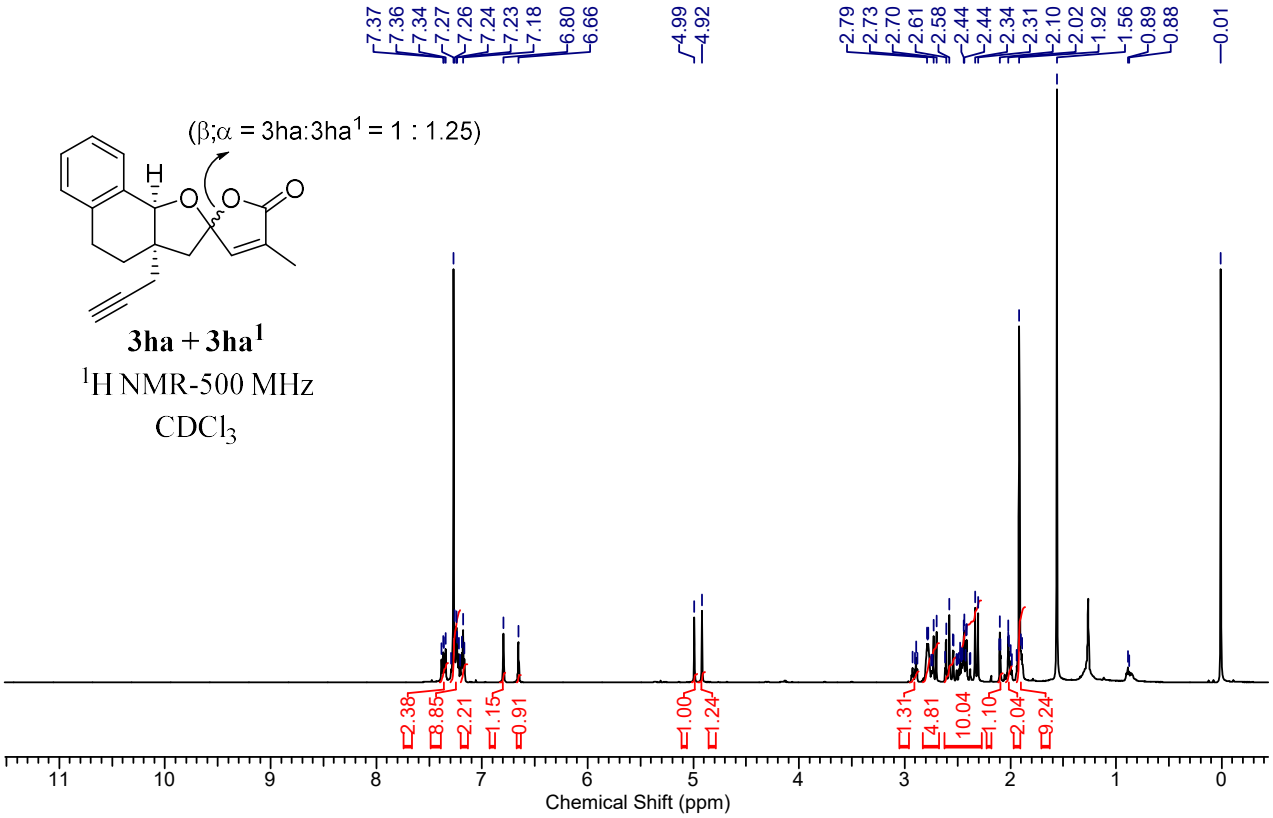
NOESY: (3ha)

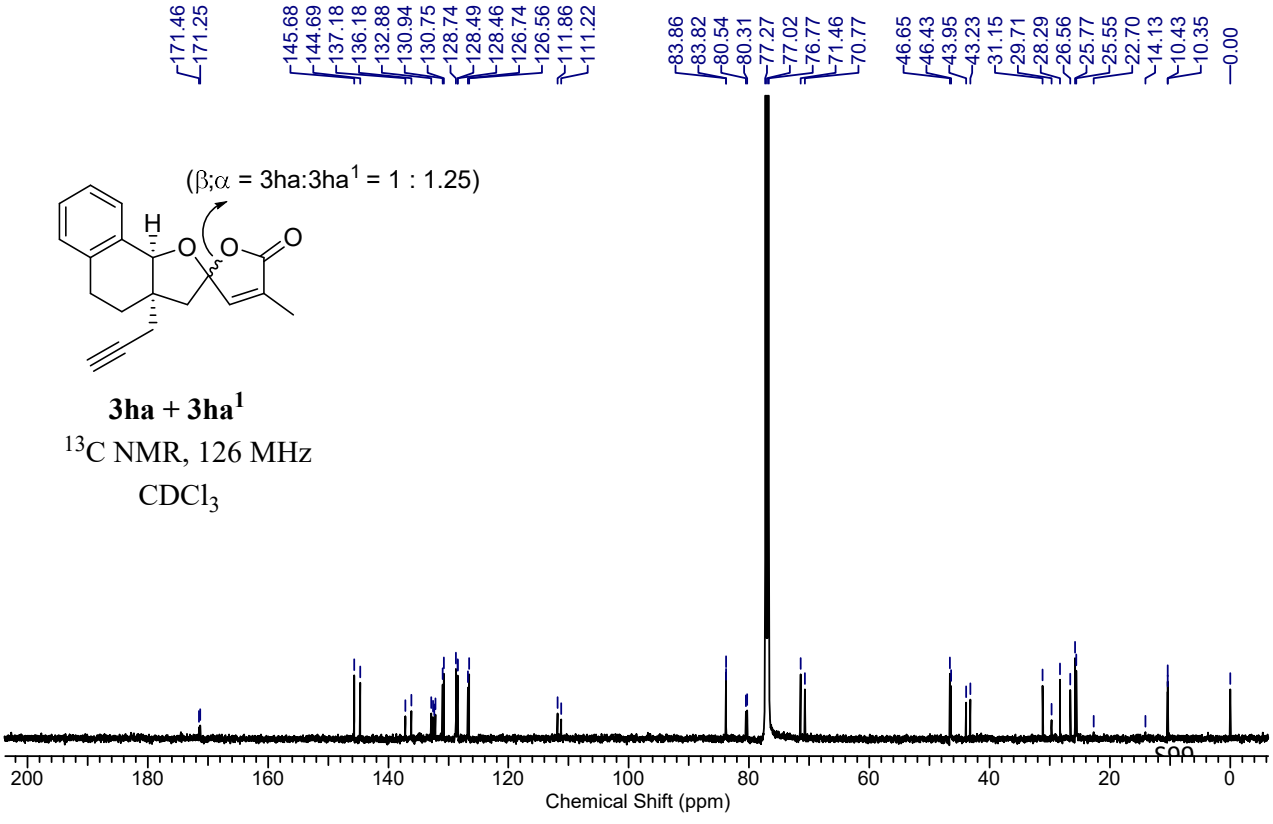


NOESY: (3ha)

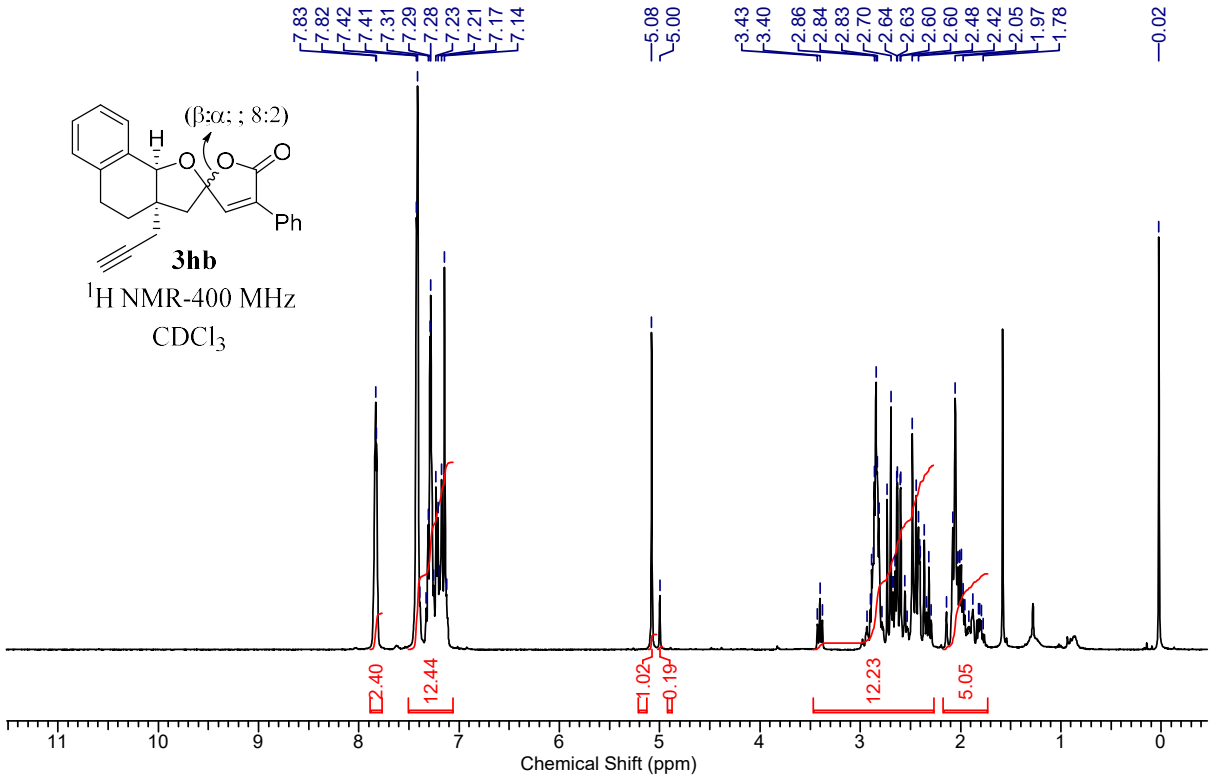


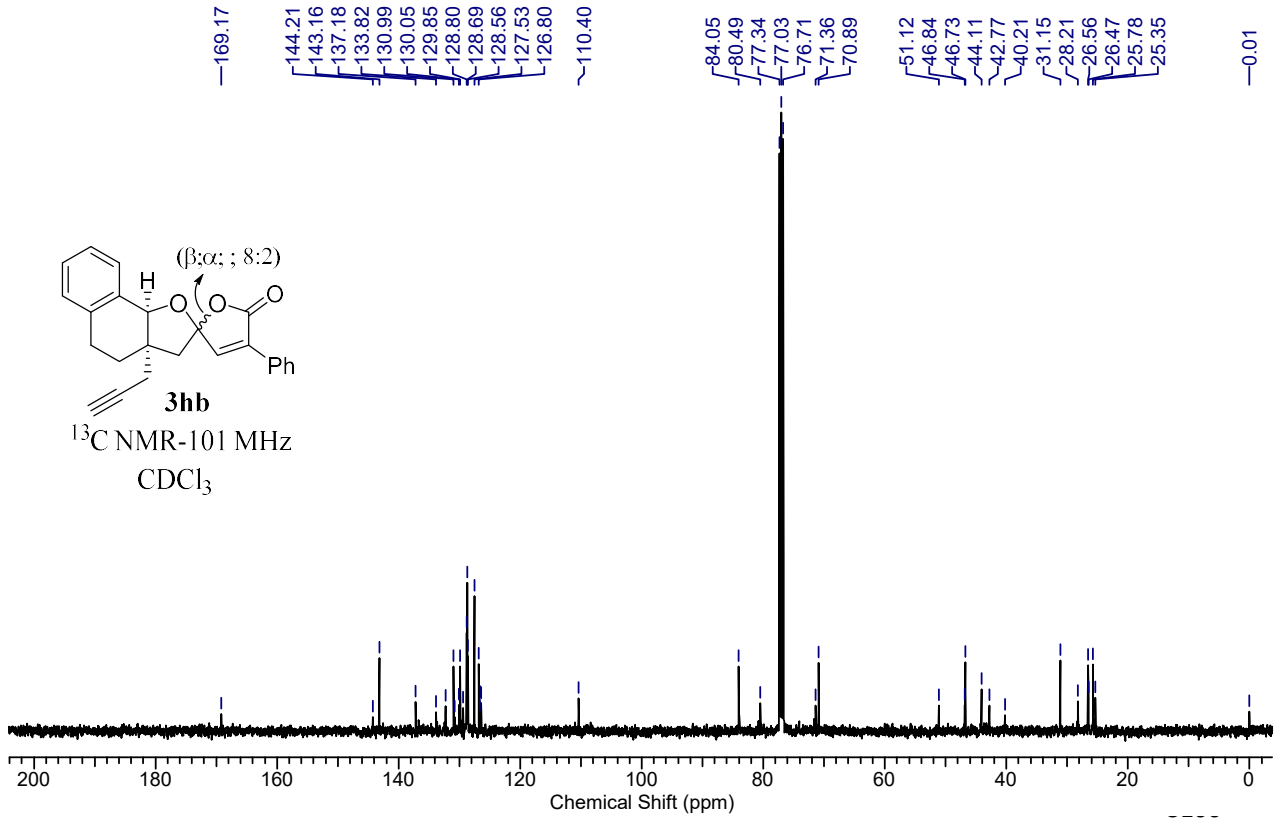
4-methyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'*H*,5*H*-spiro[furan-2,2'-naphtho[1,2-*b*]furan]-5-one (3ha[1])



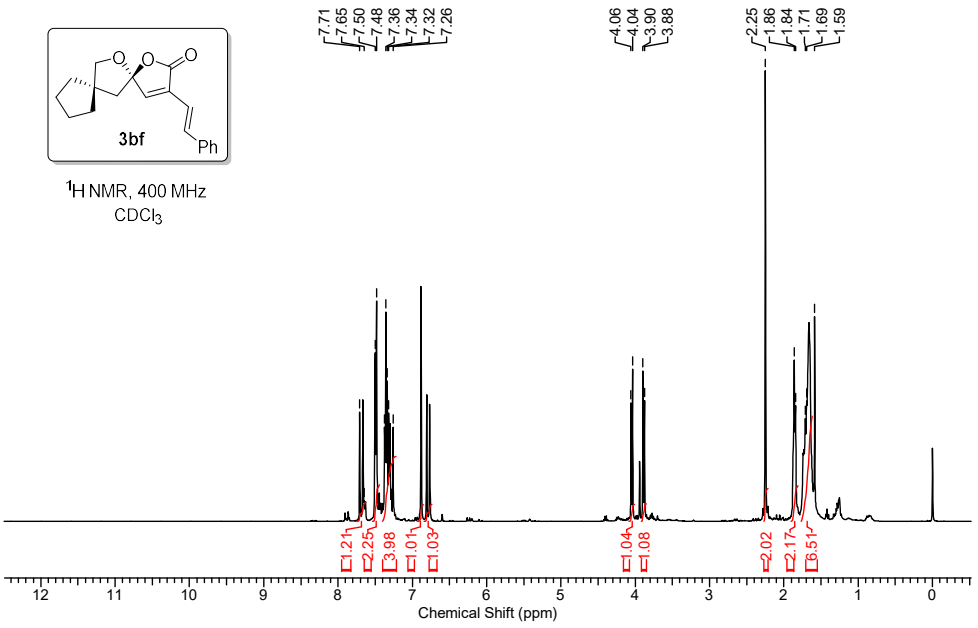


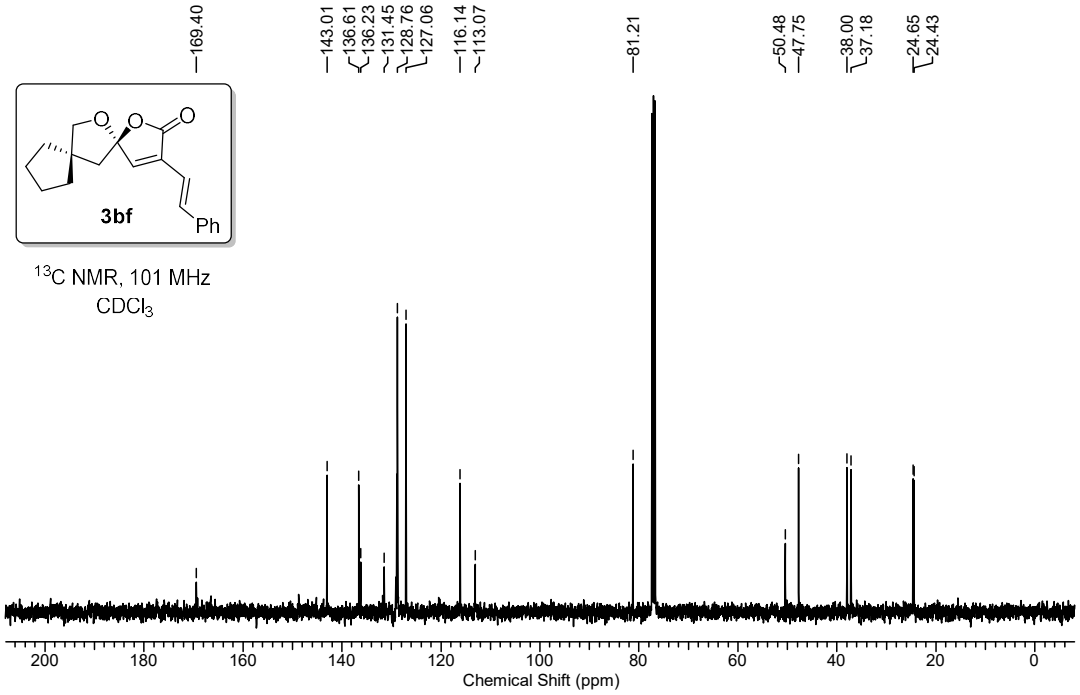
4-phenyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'*H*,5*H*-spiro[furan-2,2'-naphtho[1,2-*b*]furan]-5-one (3hb)



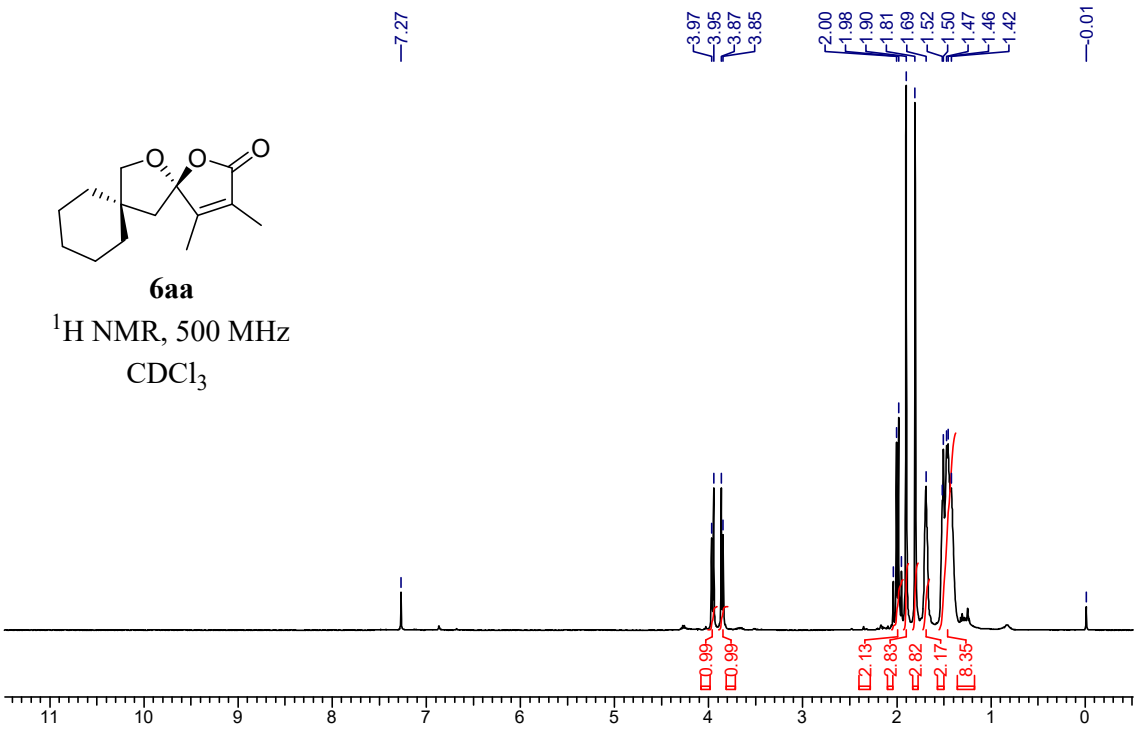


(*E*)-3-styryl-1,13-dioxadispiro[4.1.4^{7}.2^{5}]tridec-3-en-2-one (3bf)





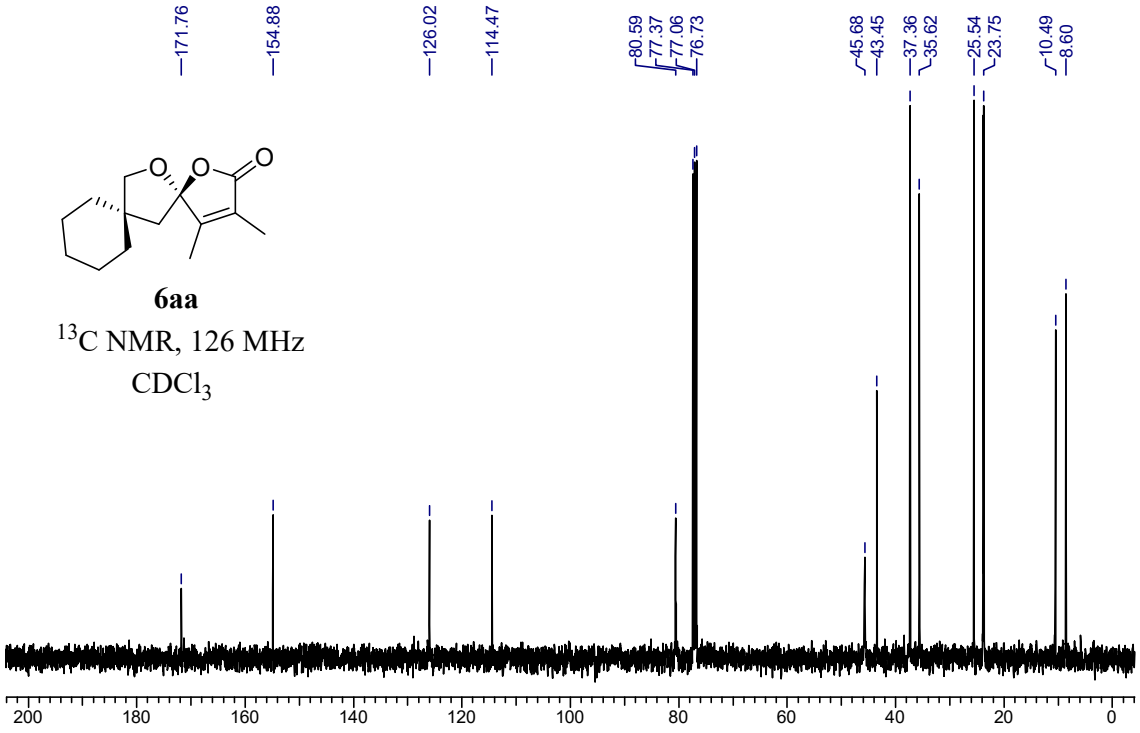
3, 4-Dimethyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6aa):



6aa

^{1}H NMR, 500 MHz

$CDCl_3$

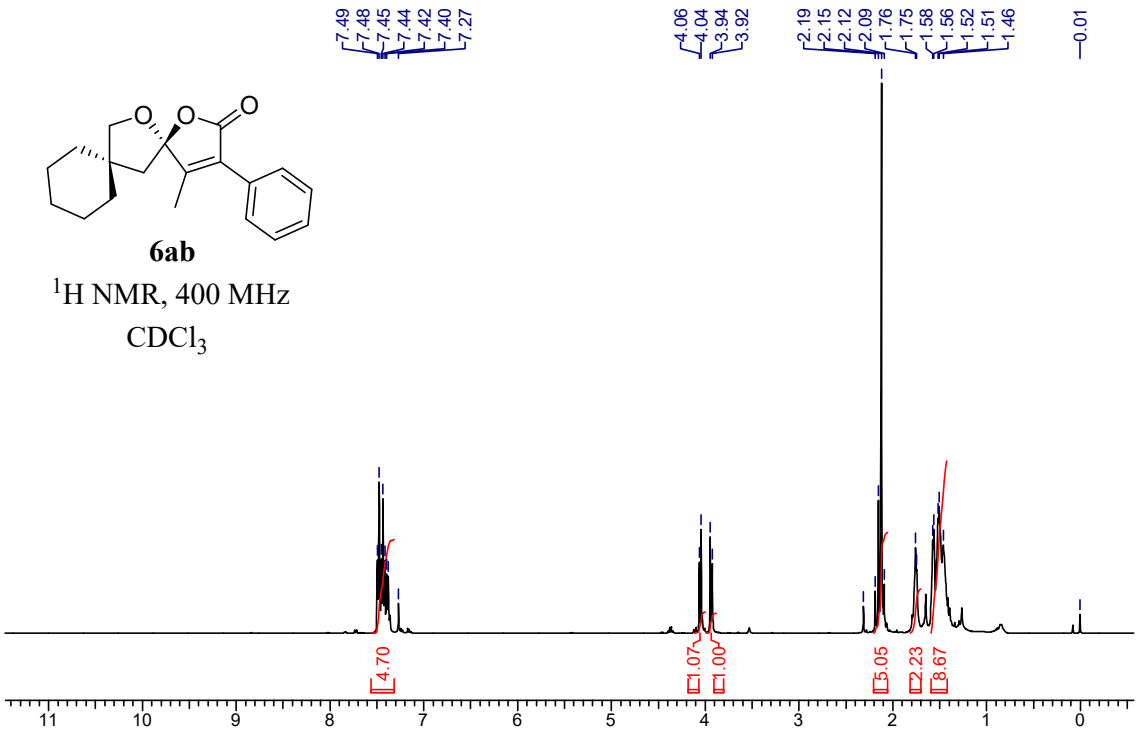


6aa

^{13}C NMR, 126 MHz

$CDCl_3$

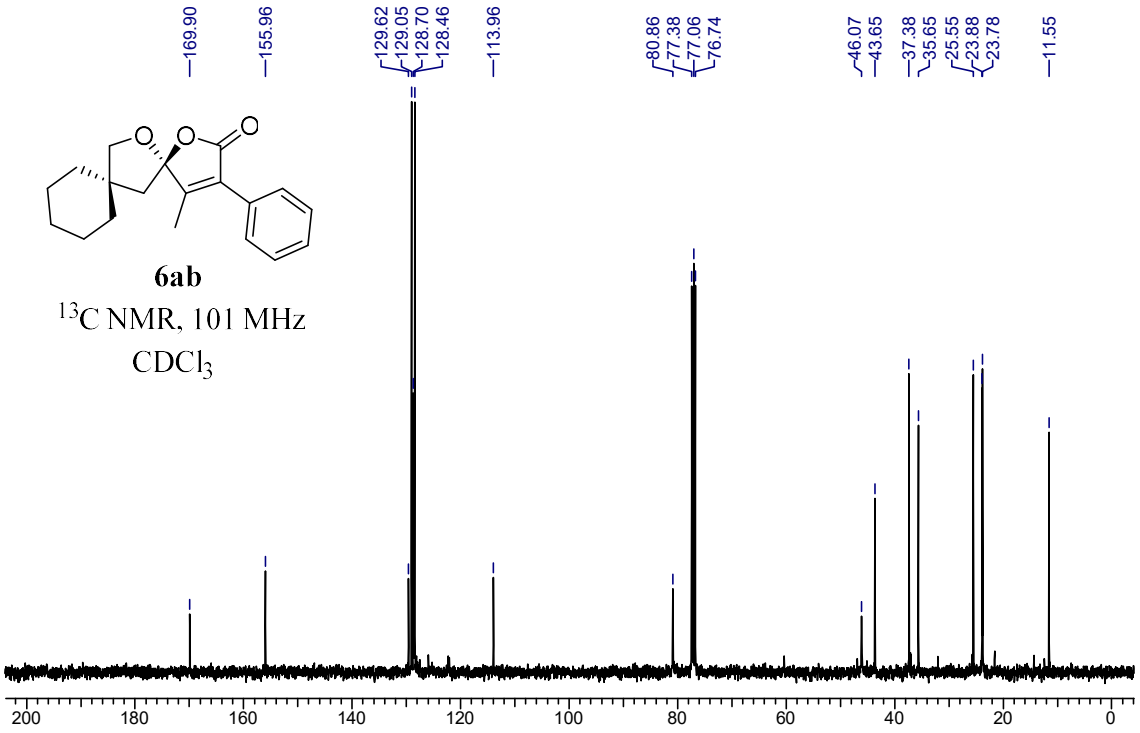
4-Methyl-3-phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6ab):



6ab

^{1}H NMR, 400 MHz

$CDCl_3$

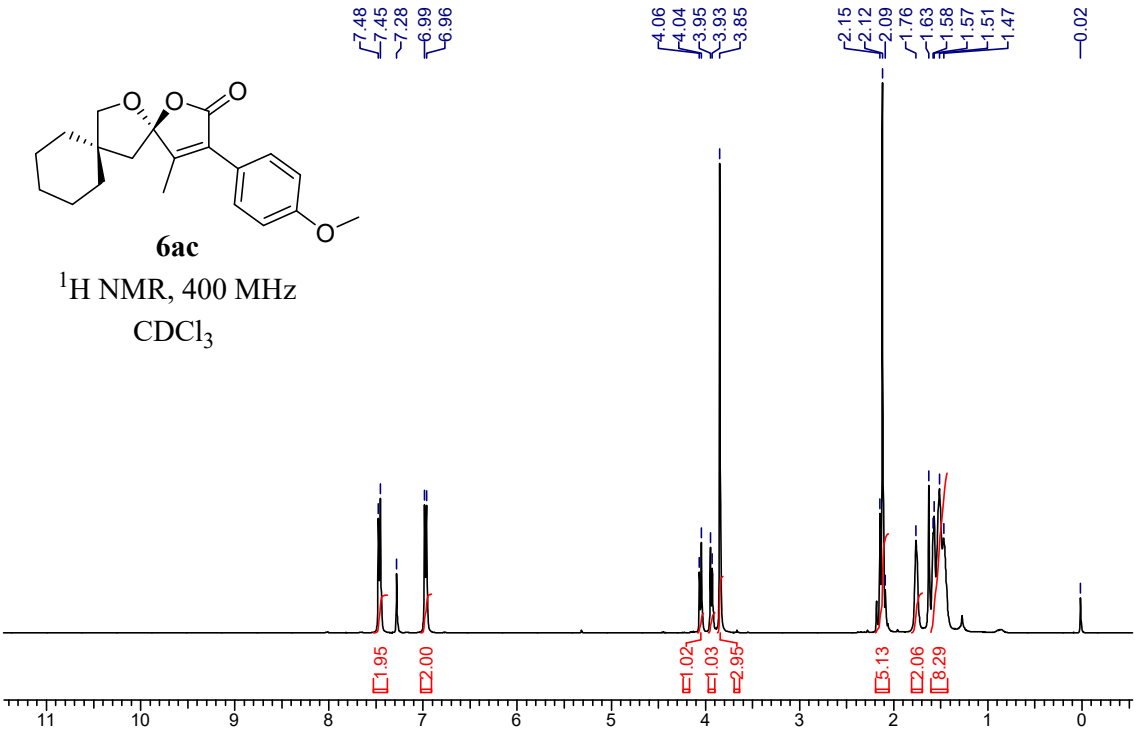


6ab

^{13}C NMR, 101 MHz

$CDCl_3$

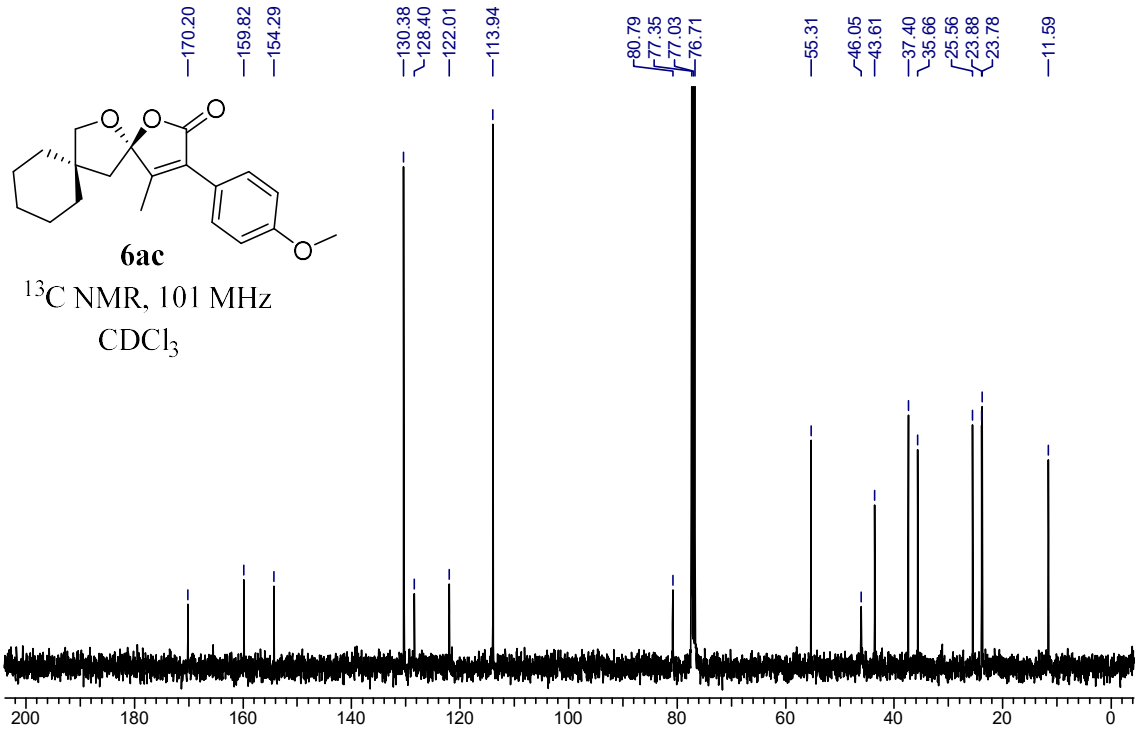
3-(4-Methoxyphenyl)-4-methyl-1, 14 dioxadispiro [4.1.5^7.2^5] tetradec -3-en-2-one (6ac):



6ac

^{1}H NMR, 400 MHz

$CDCl_3$

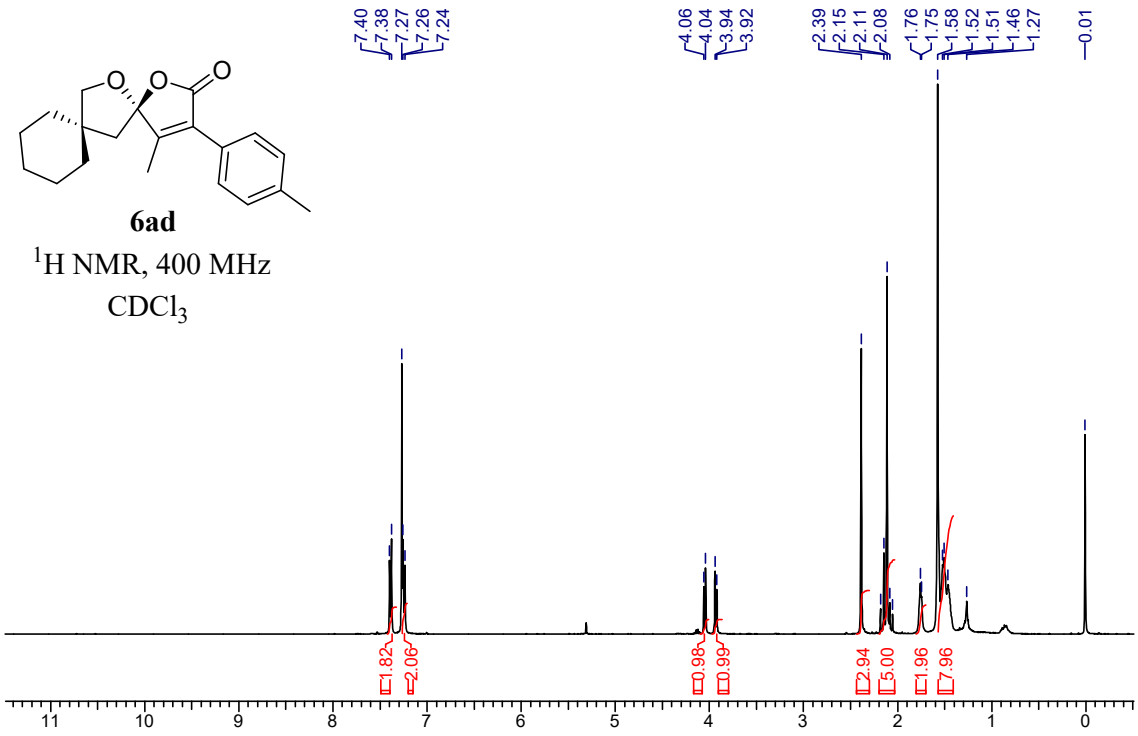


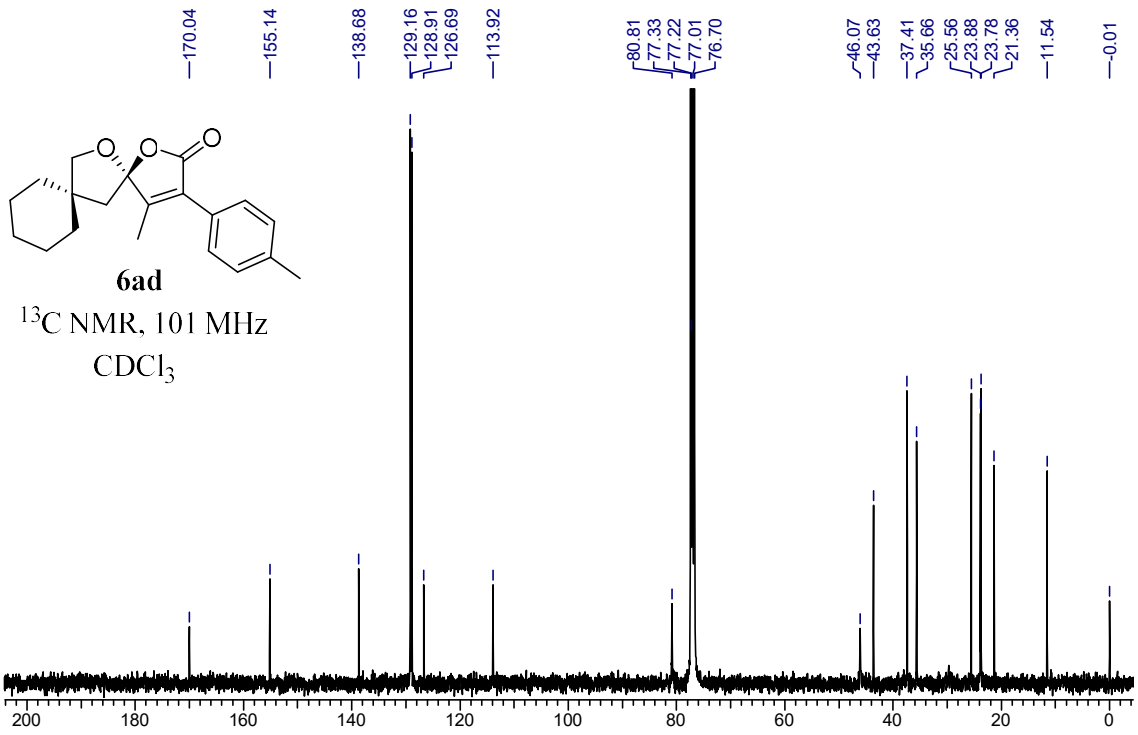
6ac

^{13}C NMR, 101 MHz

$CDCl_3$

4-Methyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5^{7}.2^{5}] tetradec-3-en-2-one (6ad):





6ad

^{1}H NMR, 400 MHz

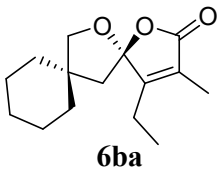
$CDCl_3$

6ad

^{13}C NMR, 101 MHz

$CDCl_3$

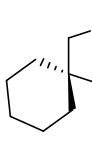
4-Ethyl-3-methyl-1, 14-dioxadispiro [4.1.5^{7}.2^{5}] tetradec-3-en-2-one (6ba):



6ba

^{1}H NMR, 400 MHz

$CDCl_3$

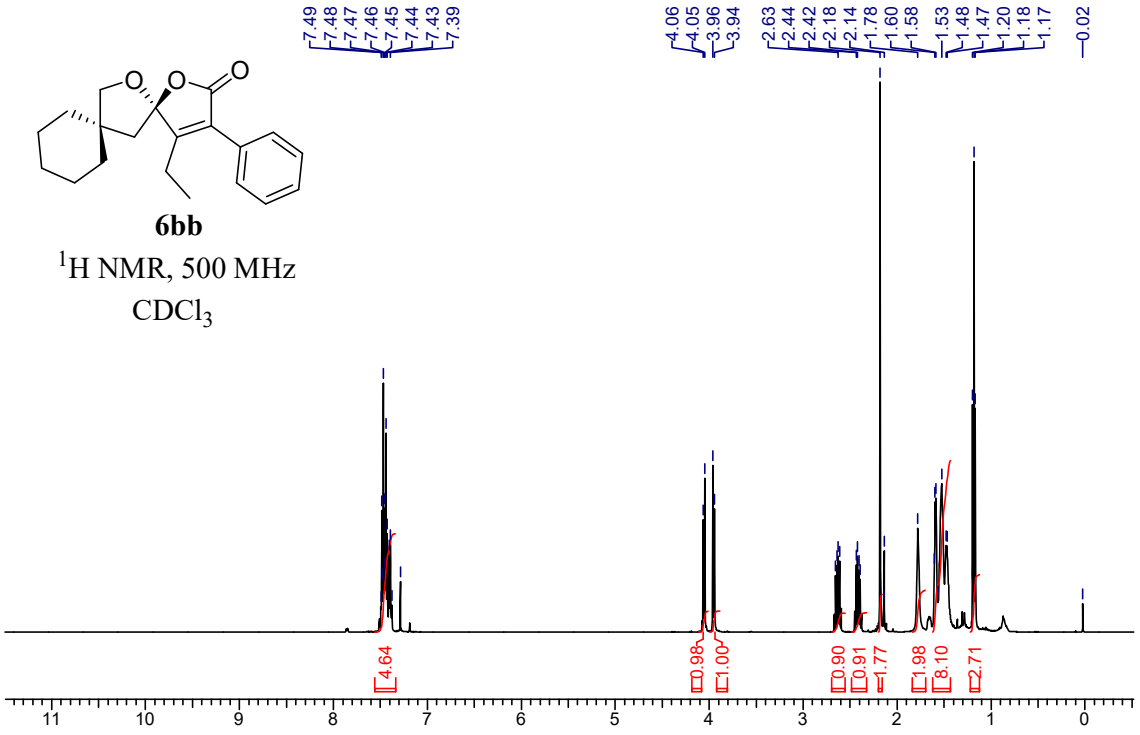


6ba

^{13}C NMR, 101 MHz

$CDCl_3$

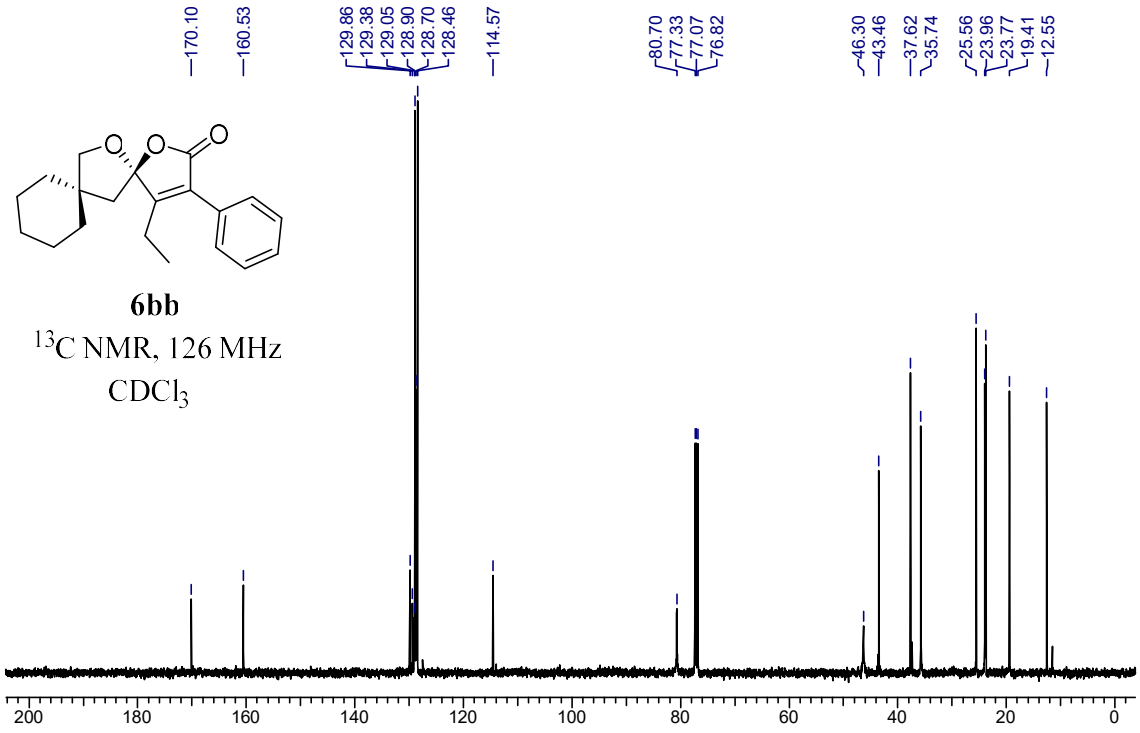
4-Ethyl-3-phenyl-1, 14-dioxadispiro [4.1.5^{7}.2^{5}] tetradec-3-en-2-one (6bb):



6bb

^{1}H NMR, 500 MHz

$CDCl_3$

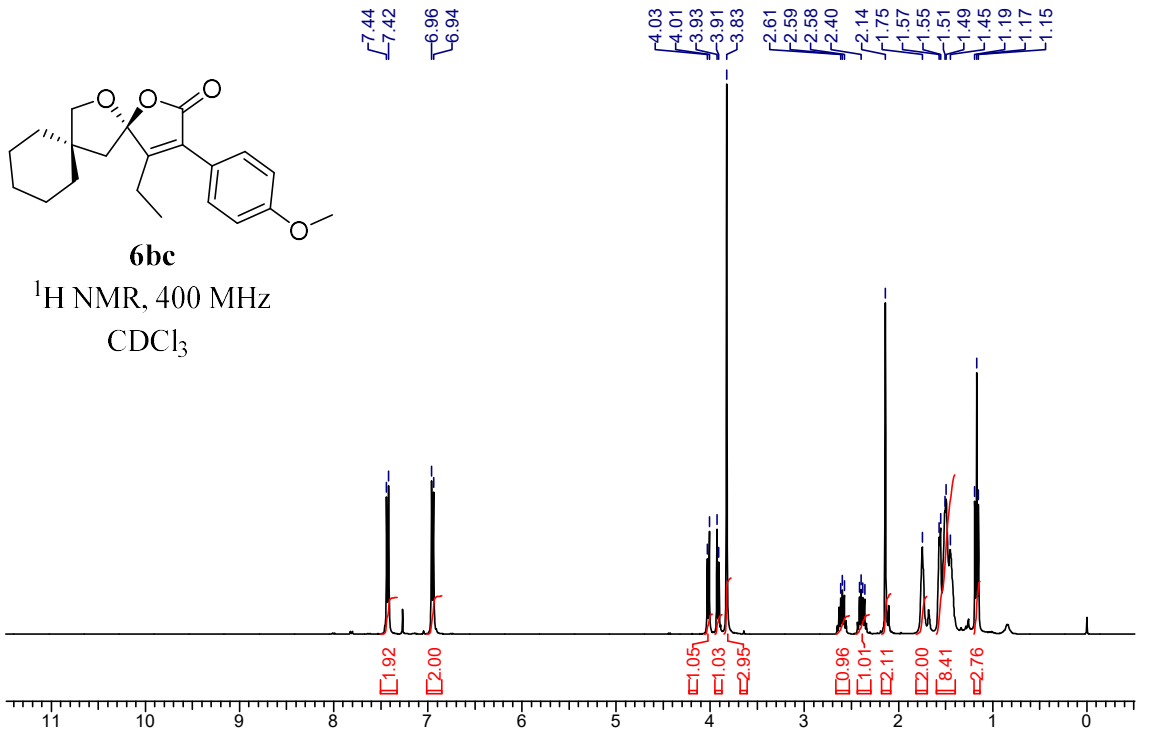


6bb

^{13}C NMR, 126 MHz

$CDCl_3$

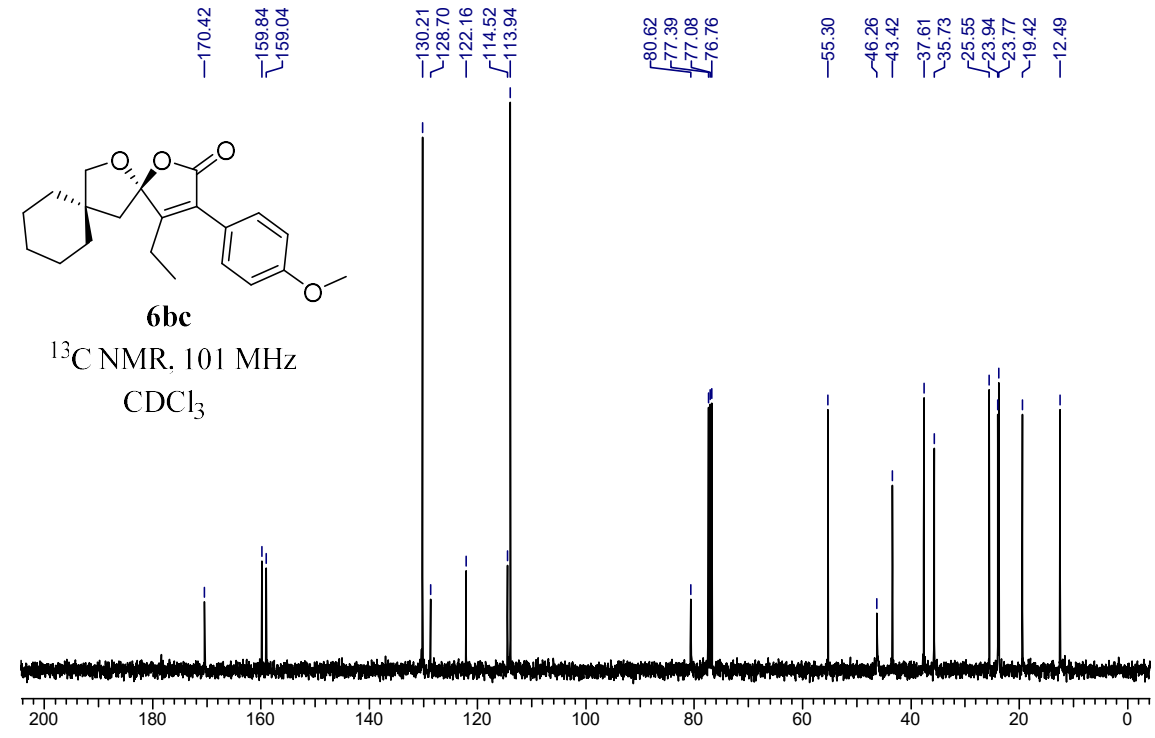
4-Ethyl-3-(4-methoxyphenyl)-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6bc):



6bc

^{1}H NMR, 400 MHz

$CDCl_3$

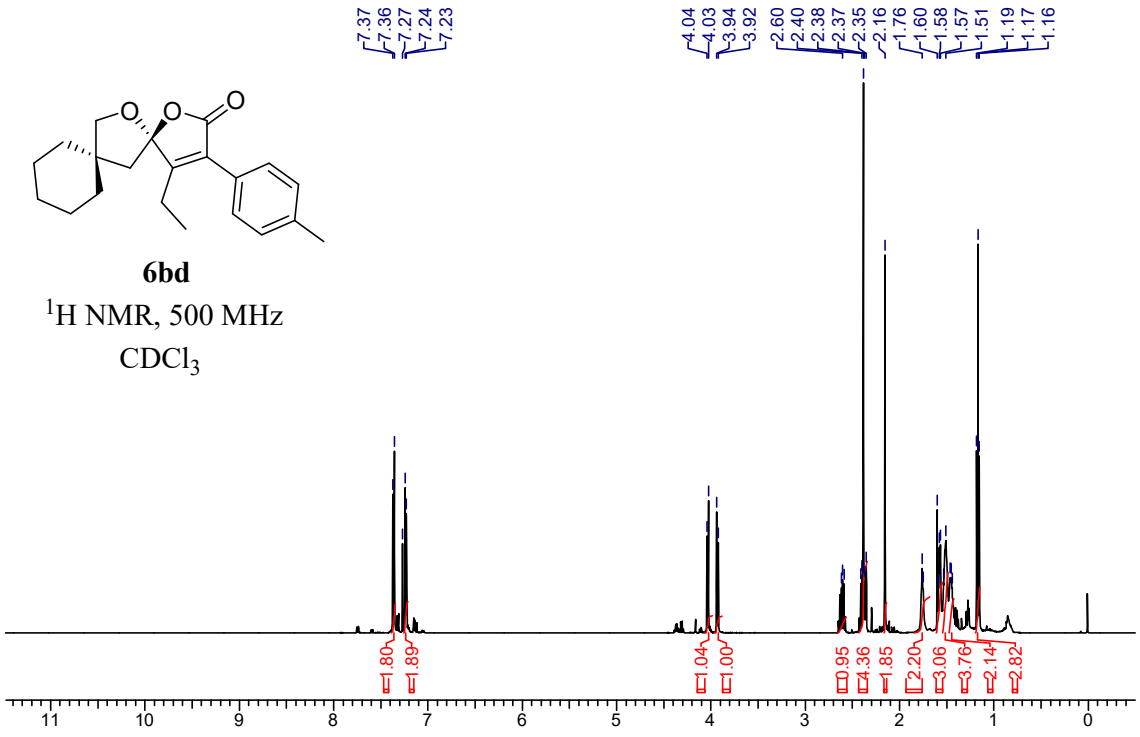


6bc

^{13}C NMR, 101 MHz

$CDCl_3$

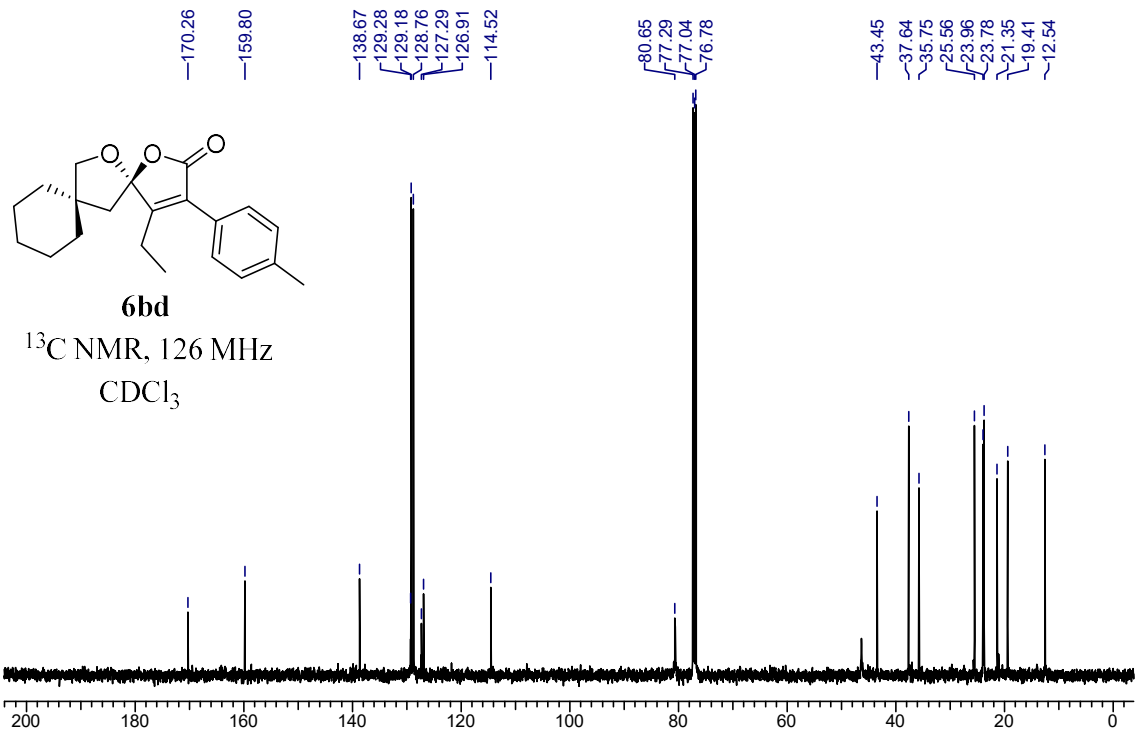
4-Ethyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5^{7}.2^{5}] tetradec-3-en-2-one (6bd):



6bd

^{1}H NMR, 500 MHz

$CDCl_3$

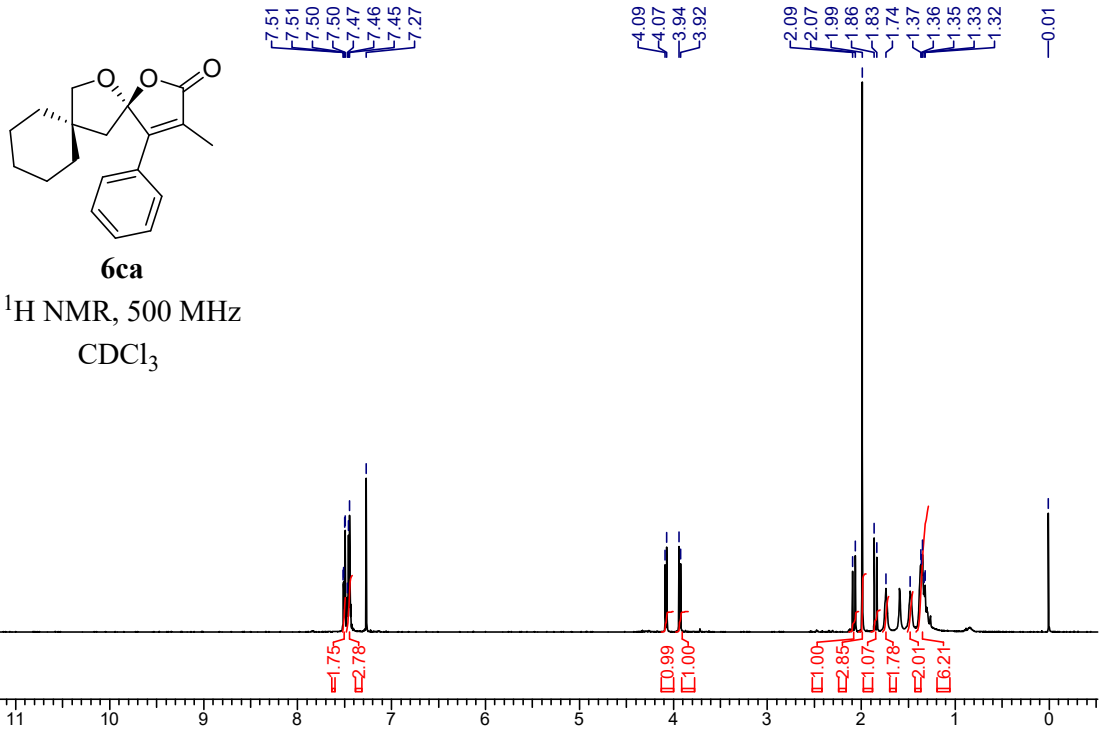


6bd

^{13}C NMR, 126 MHz

$CDCl_3$

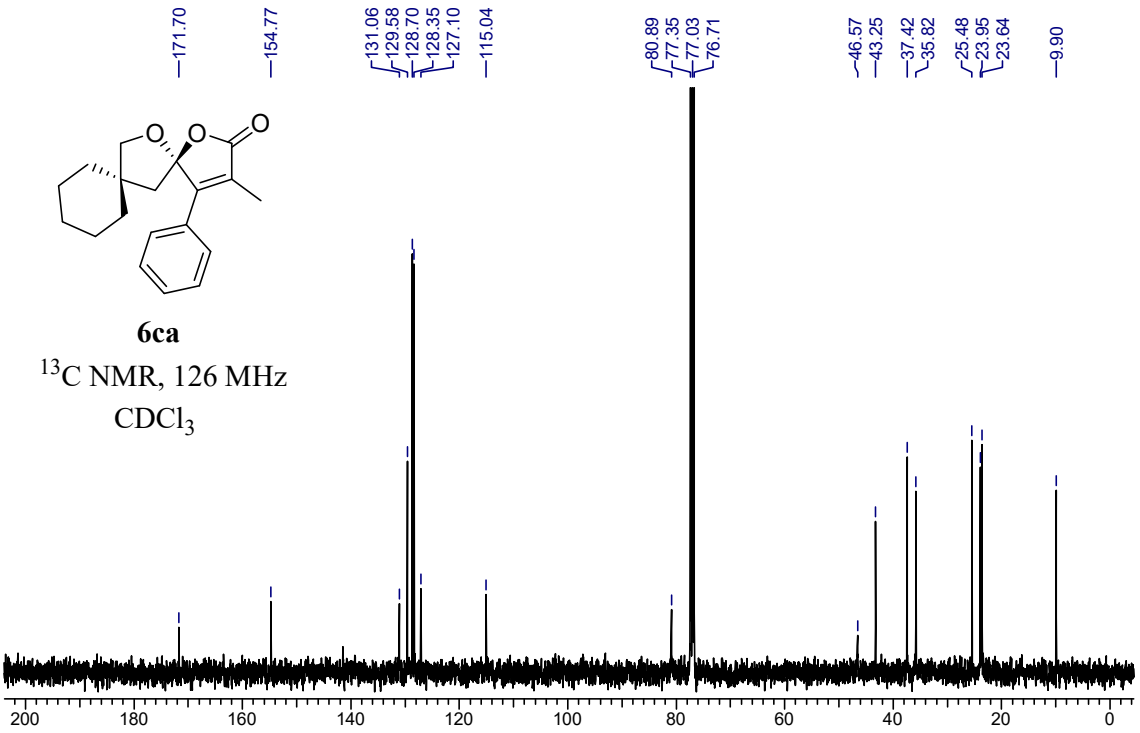
3-Methyl-4-phenyl-1,14-dioxadispiro[4.1.5^{7}.2^{5}]tetradec-3-en-2-one (6ca):



6ca

^{1}H NMR, 500 MHz

$CDCl_3$

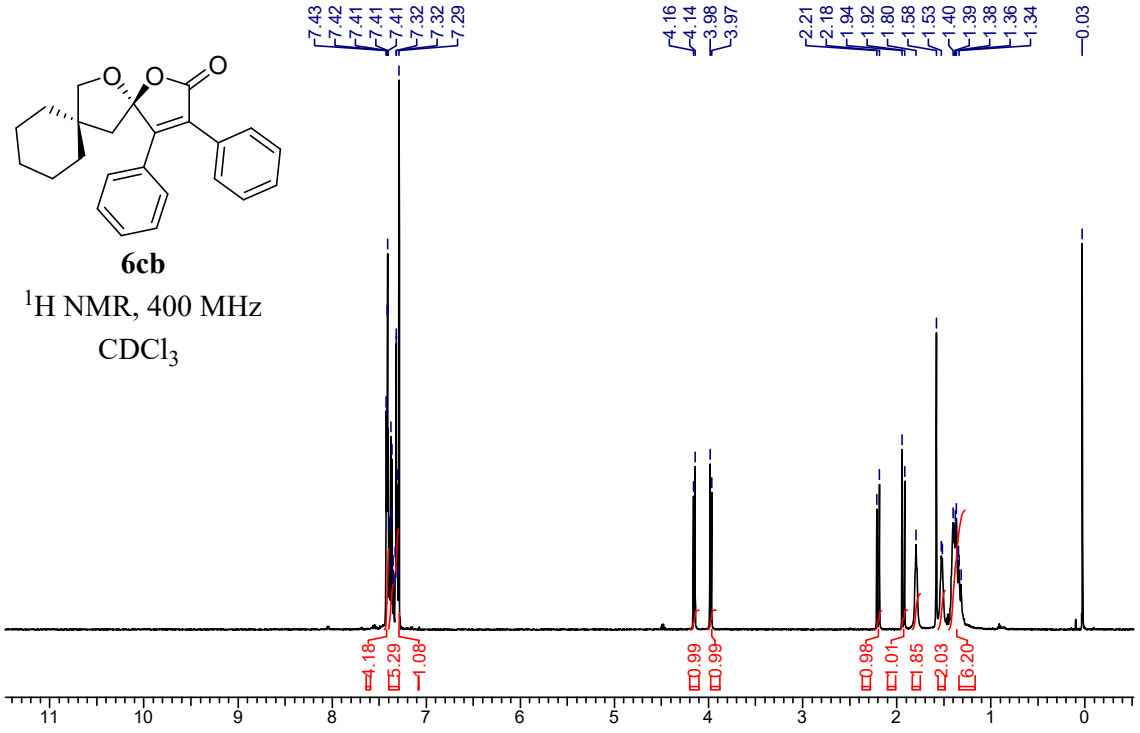


6ca

^{13}C NMR, 126 MHz

$CDCl_3$

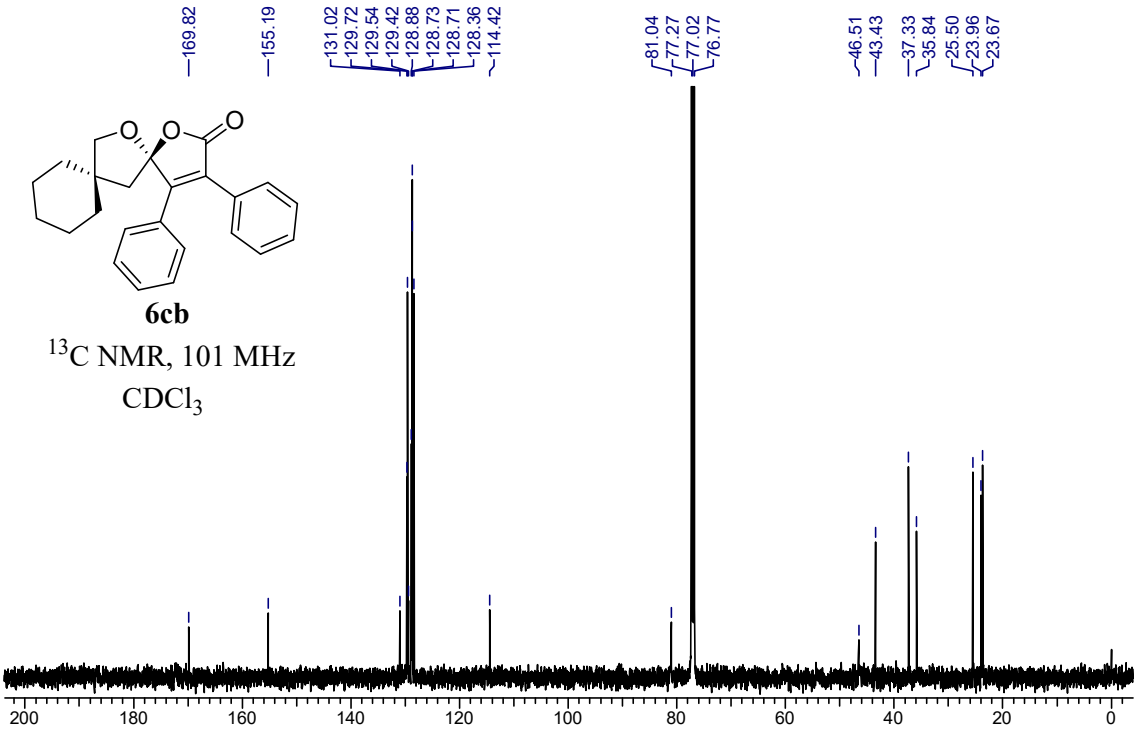
3,4-Diphenyl-1,14-dioxadispiro[4.1.5^{7}.2^{5}]tetradec-3-en-2-one (6cb):



6cb

^{1}H NMR, 400 MHz

$CDCl_3$

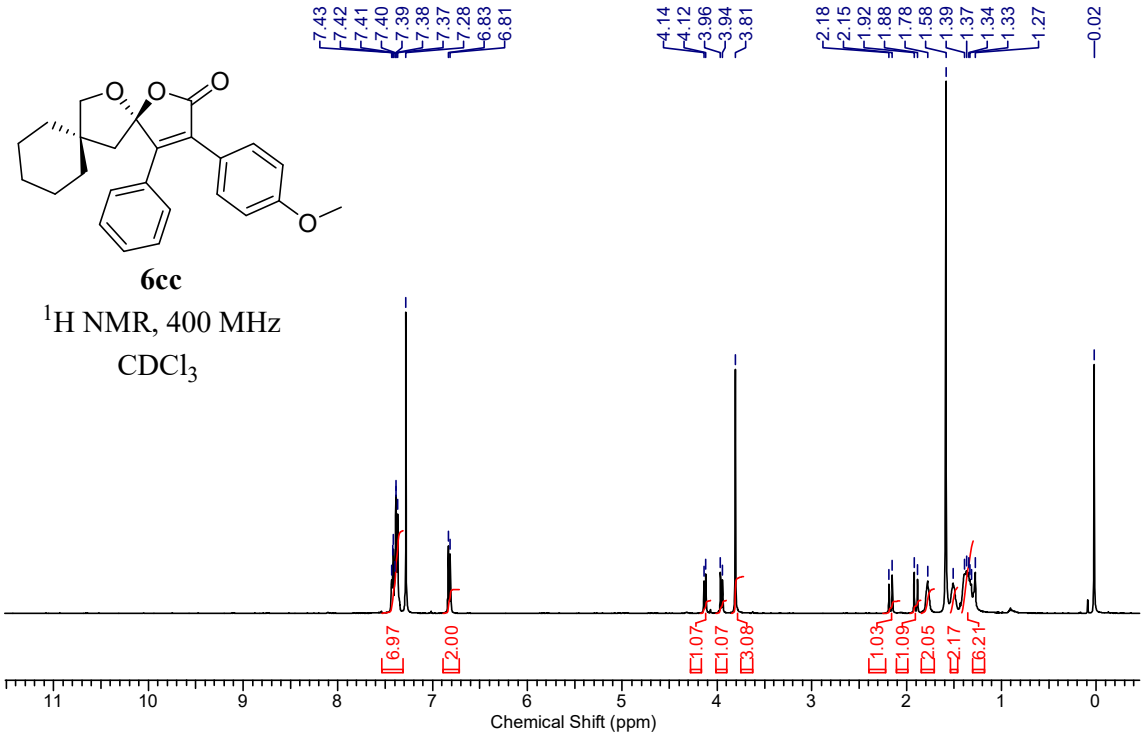


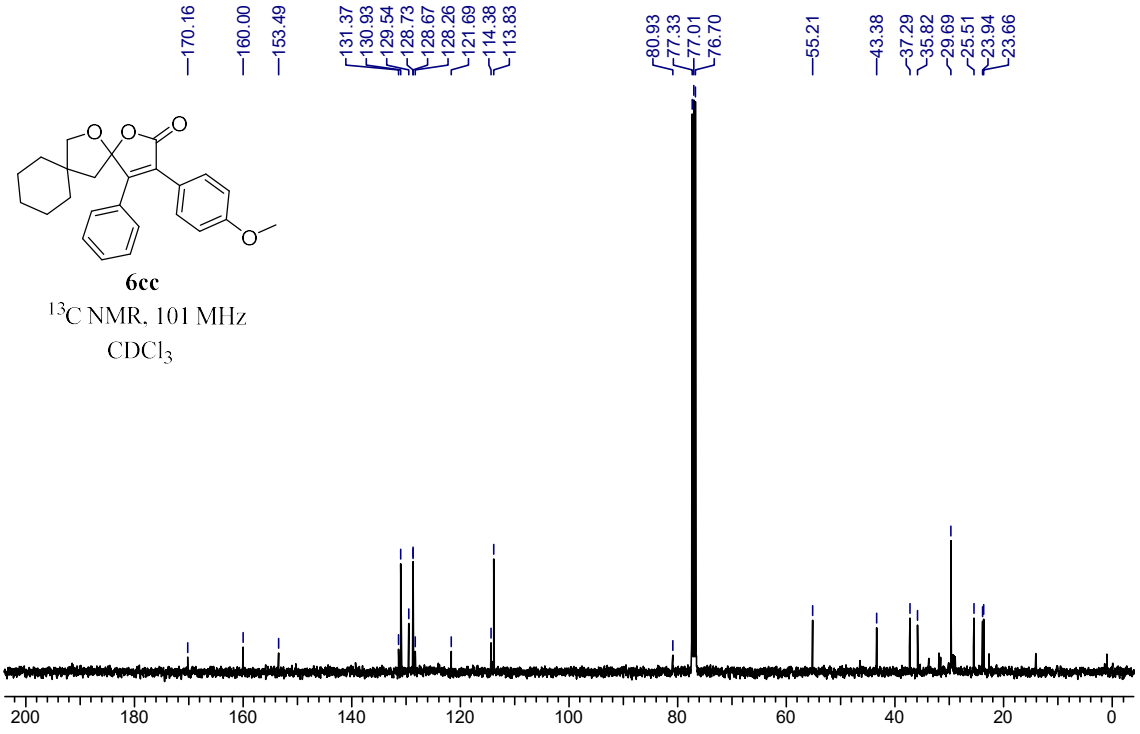
6cb

^{13}C NMR, 101 MHz

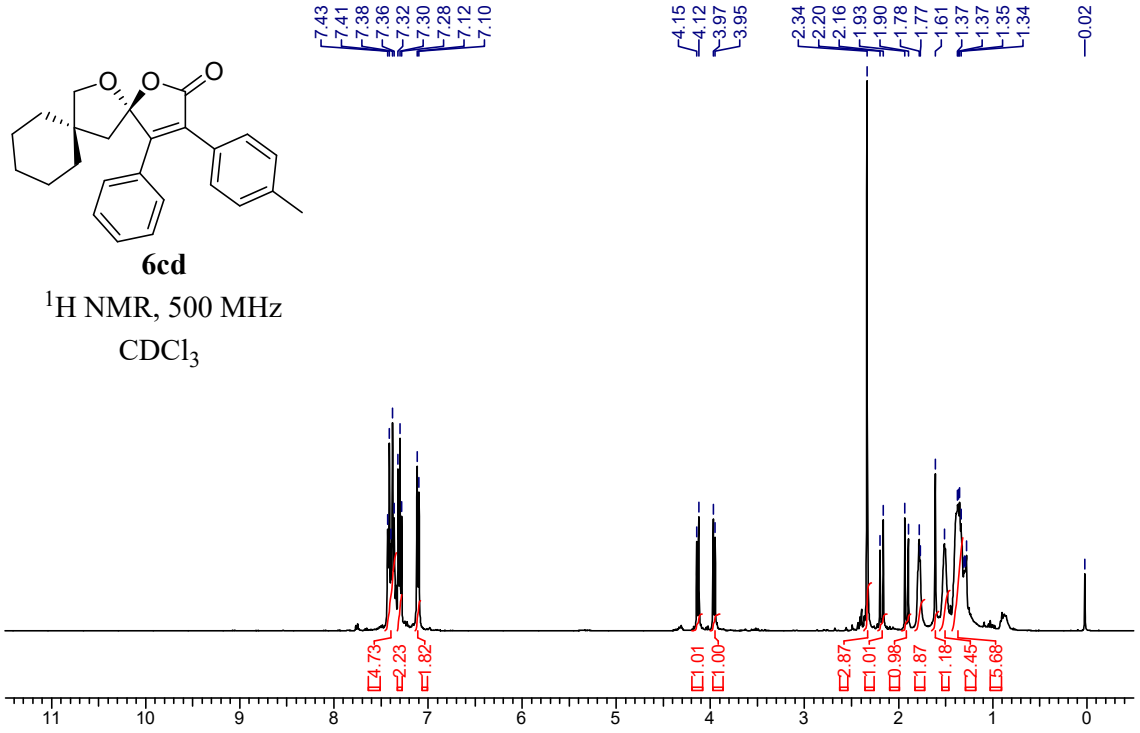
$CDCl_3$

3-(4-Methoxyphenyl)-4-phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6cc):





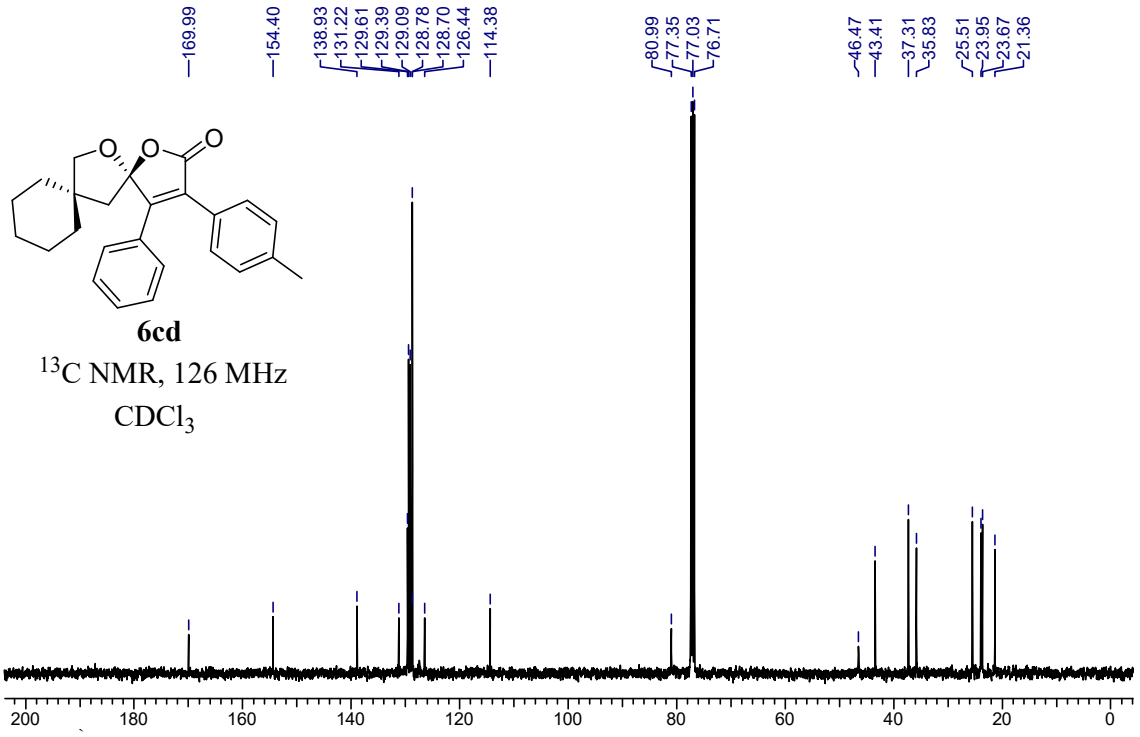
4-Phenyl-3-(p-tolyl)-1,14-dioxadispiro[4.1.5^{7}.2^{5}]tetradec-3-en-2-one (6cd):



6cd

^{1}H NMR, 500 MHz

$CDCl_3$

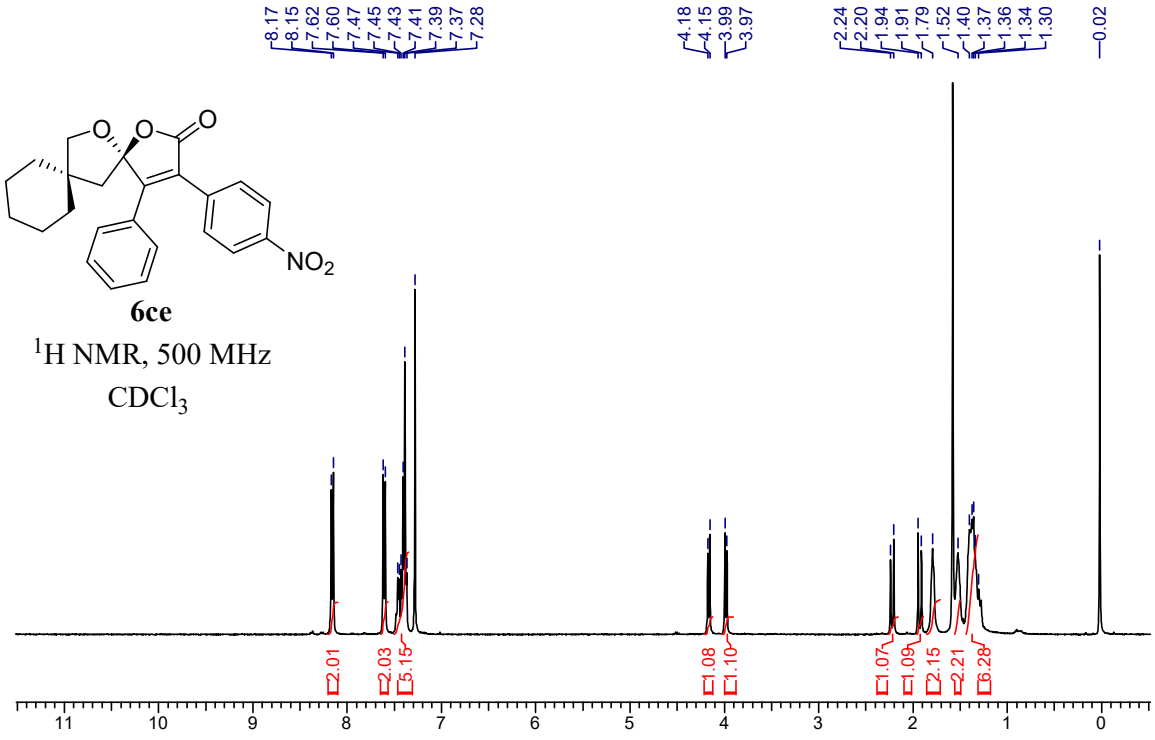


6cd

^{13}C NMR, 126 MHz

$CDCl_3$

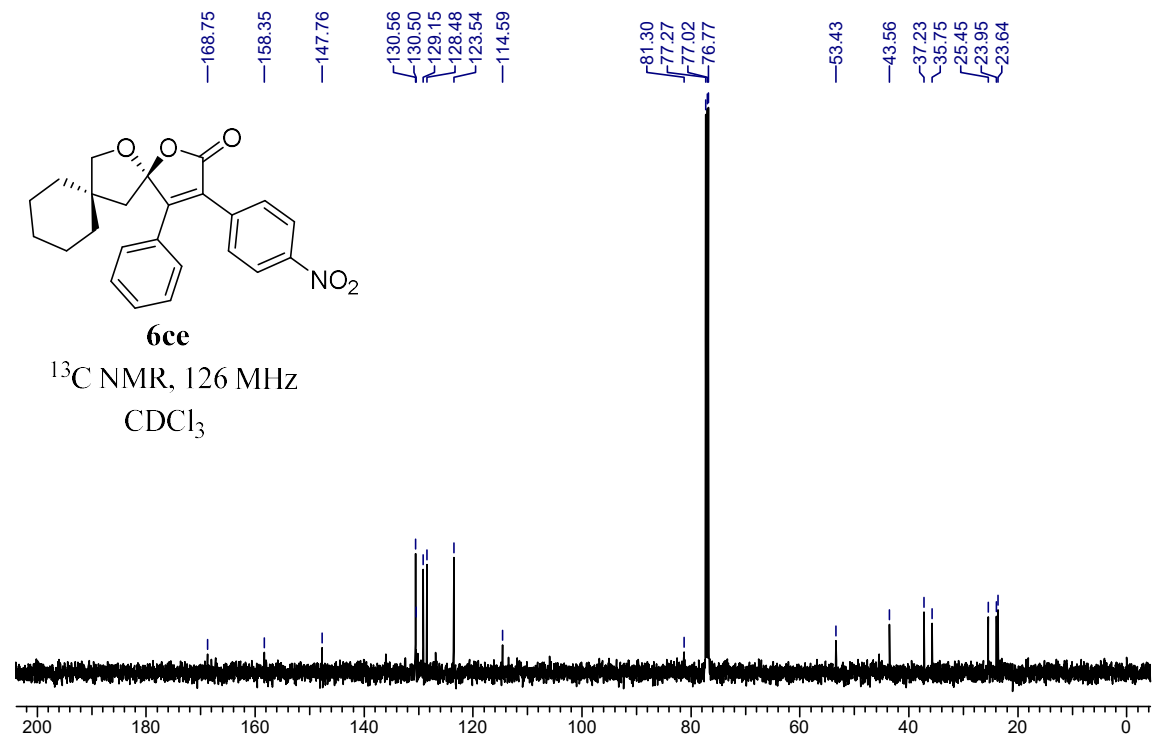
3-(4-Nitrophenyl)-4-phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6ce):



6ce

^{1}H NMR, 500 MHz

$CDCl_3$

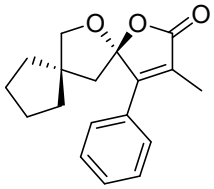


6ce

^{13}C NMR, 126 MHz

$CDCl_3$

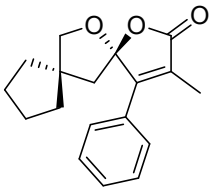
3-Methyl-4-phenyl-1, 13-dioxadispiro [4.1.4^{7}.2^{5}] tridec-3-en-2-one (6da):



6da

^{1}H NMR, 500 MHz

$CDCl_3$

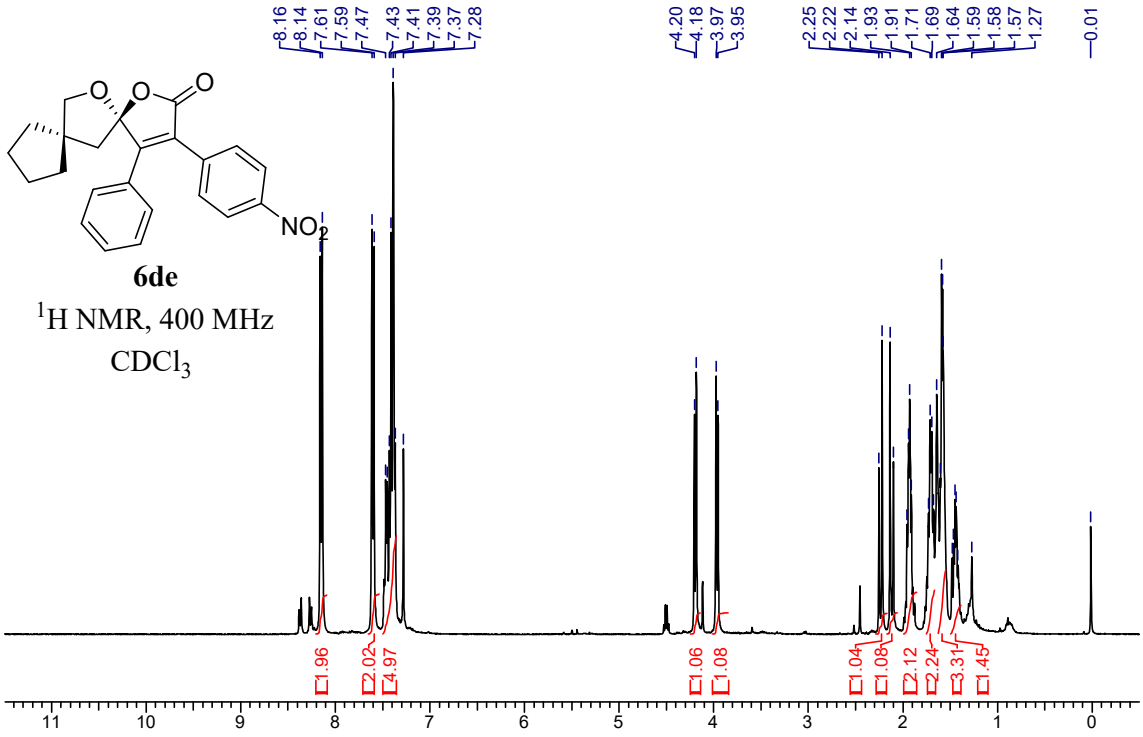


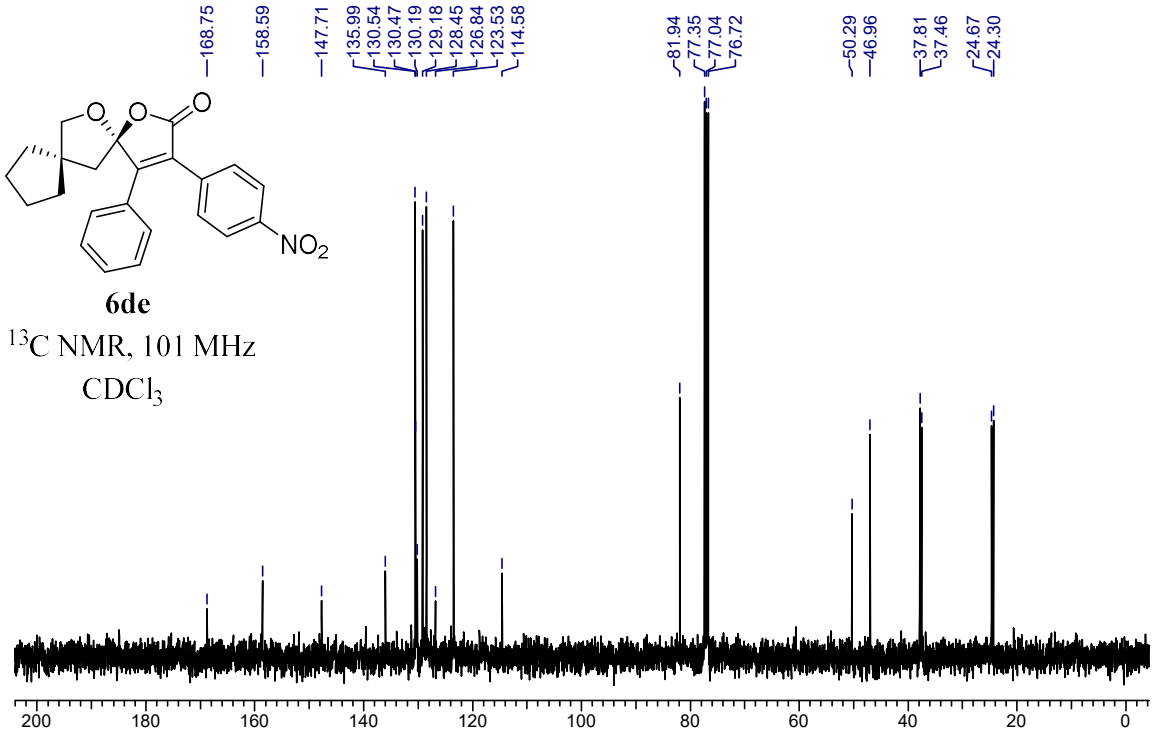
6da

^{13}C NMR, 126 MHz

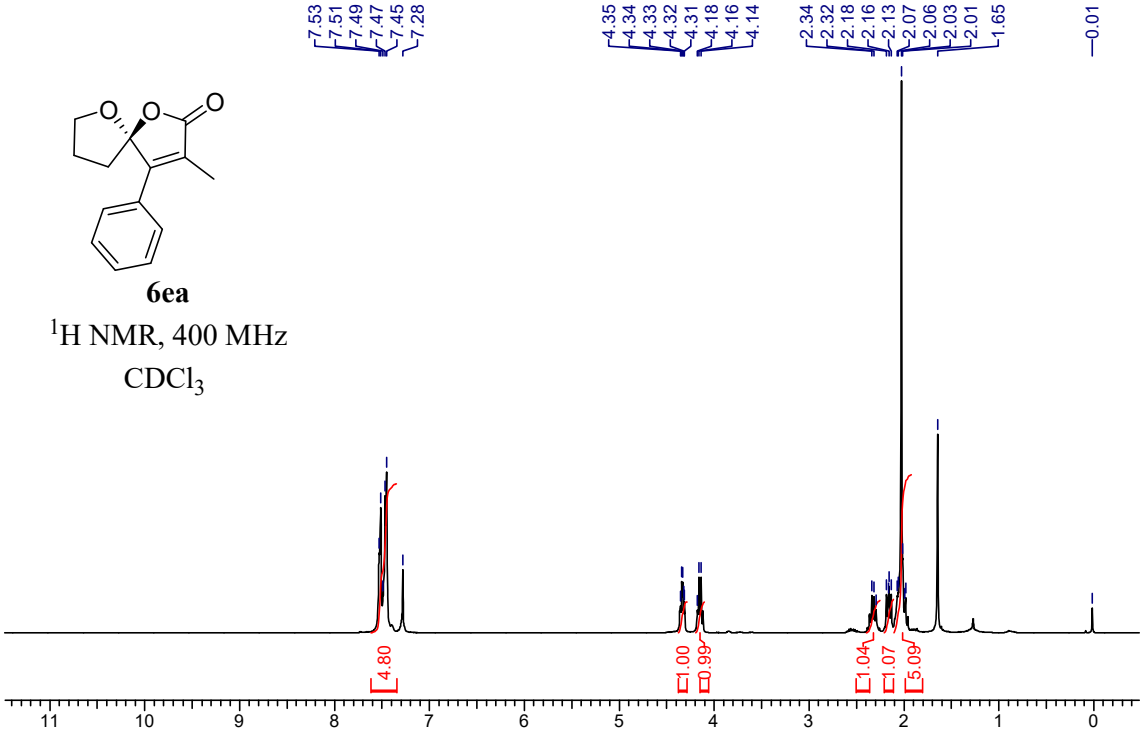
$CDCl_3$

3-(4-Nitrophenyl)-4-phenyl-1, 13-dioxadispiro [4.1.4^7.2^5] tridec-3-en-2-one (6de):





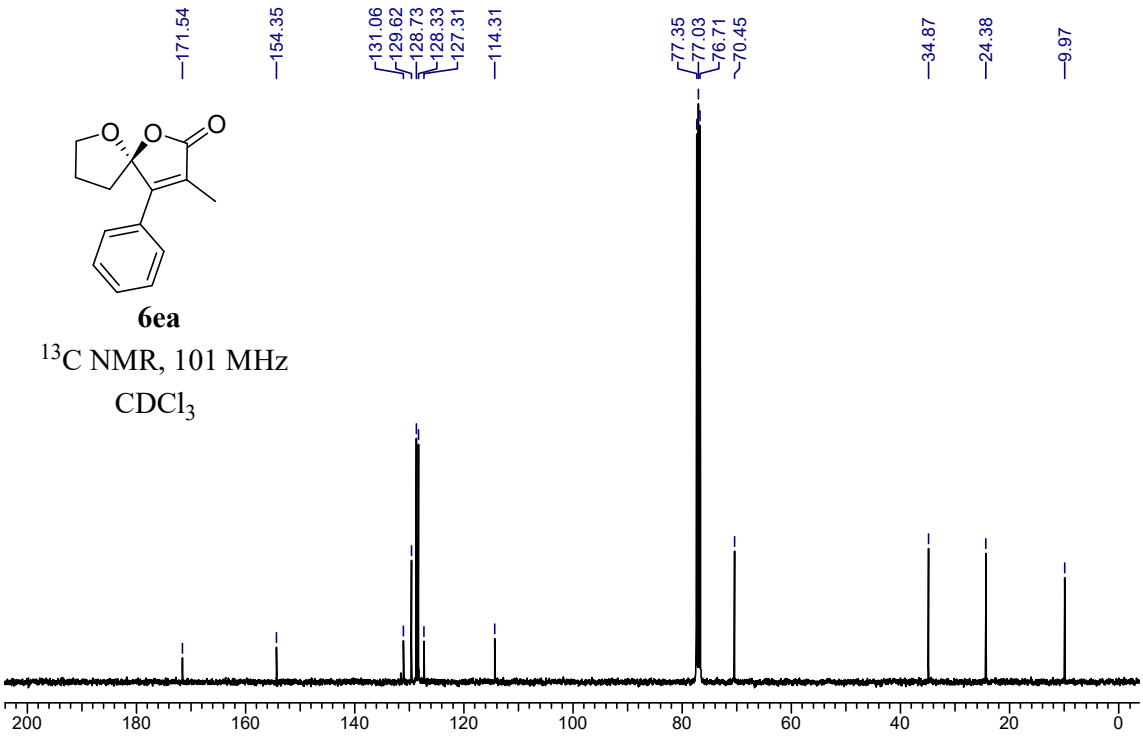
3-Methyl-4-phenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (6ea):



6ea

^{1}H NMR, 400 MHz

$CDCl_3$

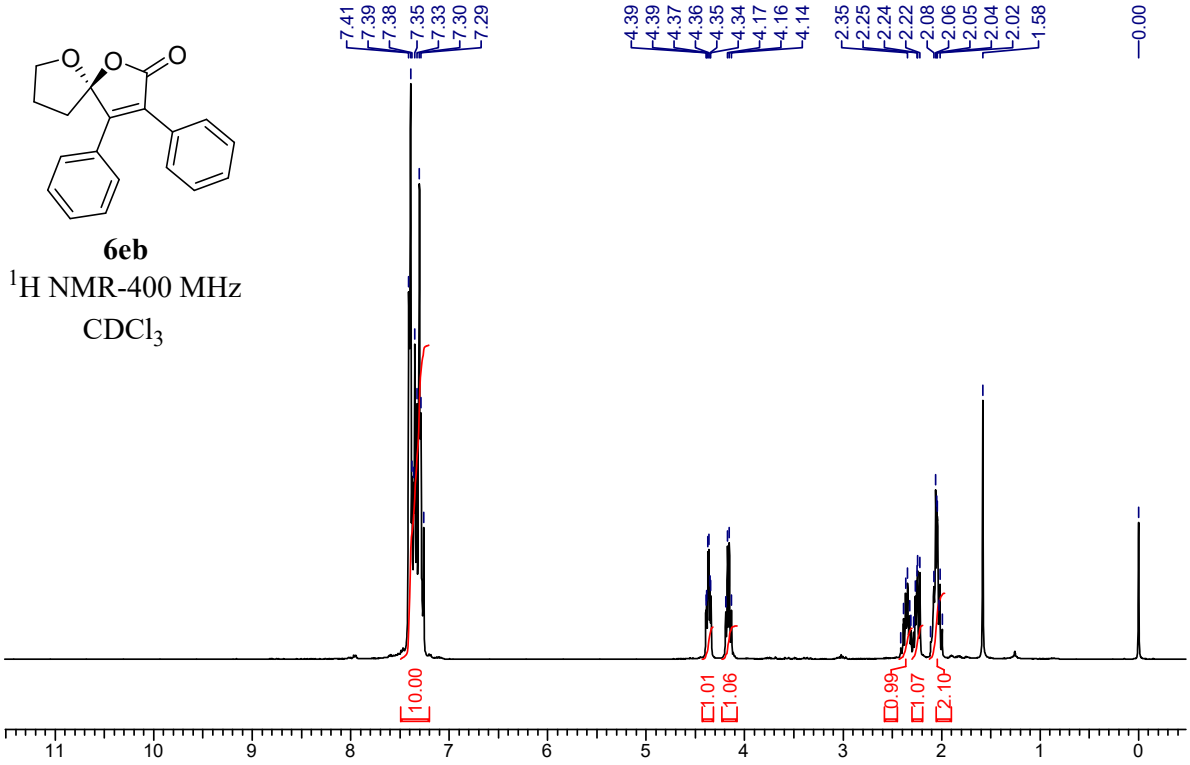


6ea

^{13}C NMR, 101 MHz

$CDCl_3$

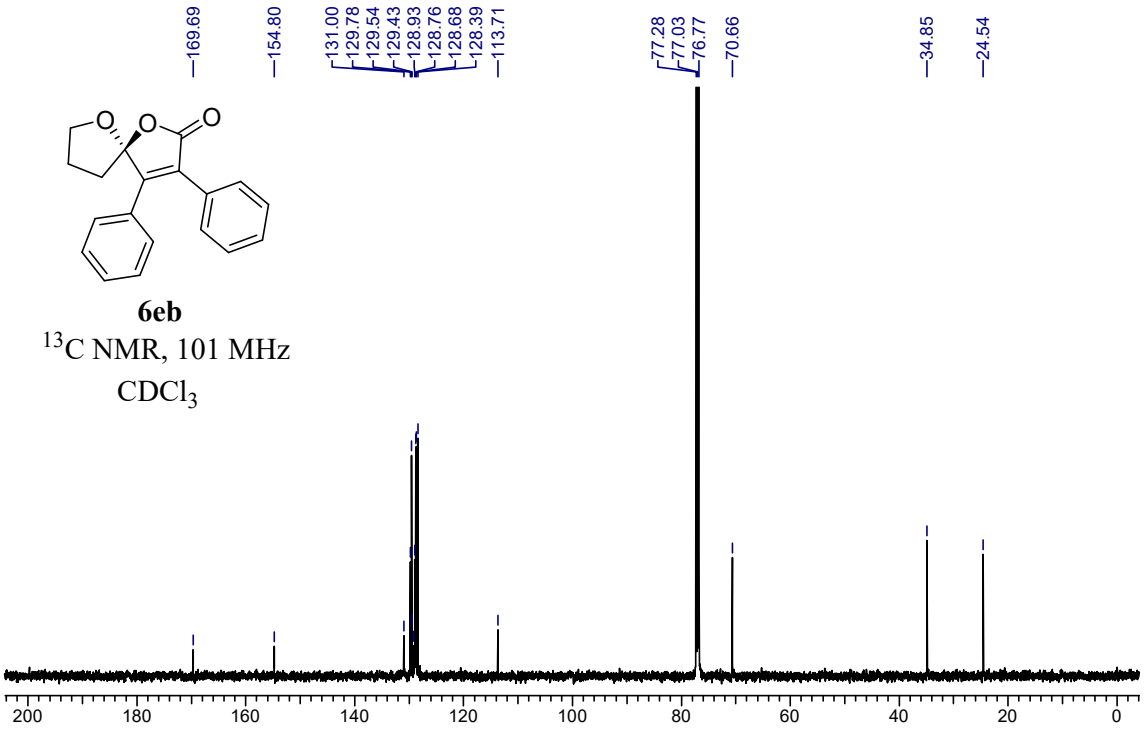
3,4-Diphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6eb)



6eb

^{1}H NMR-400 MHz

$CDCl_3$

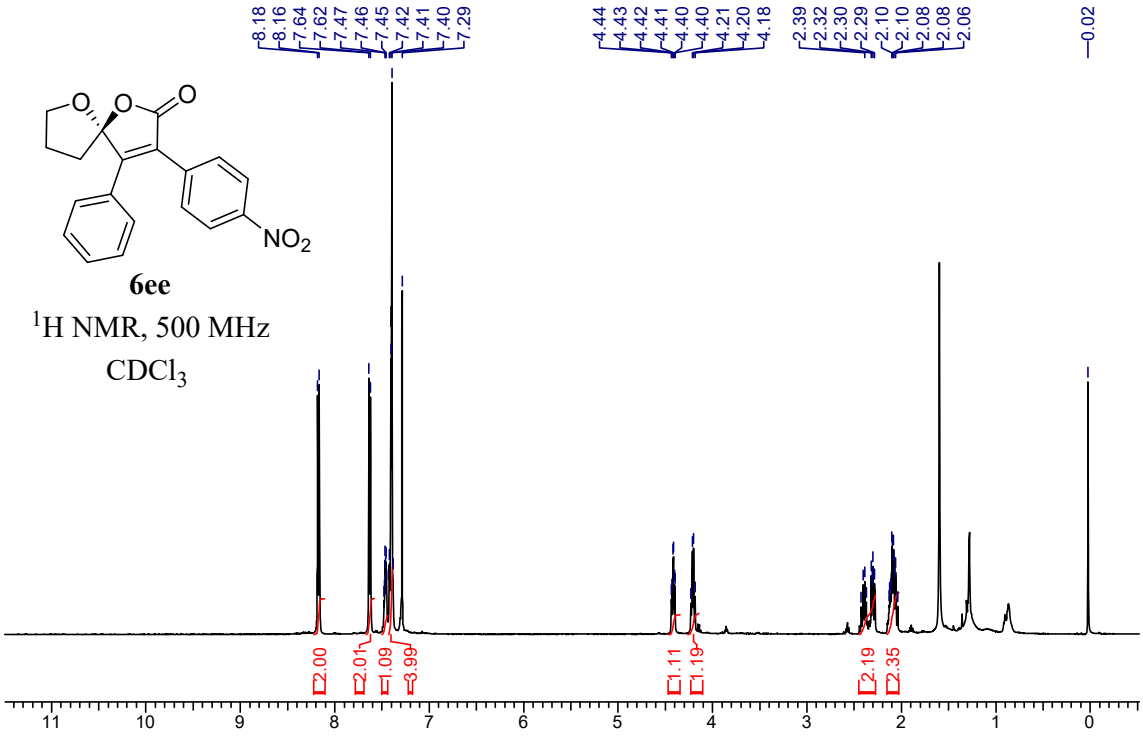


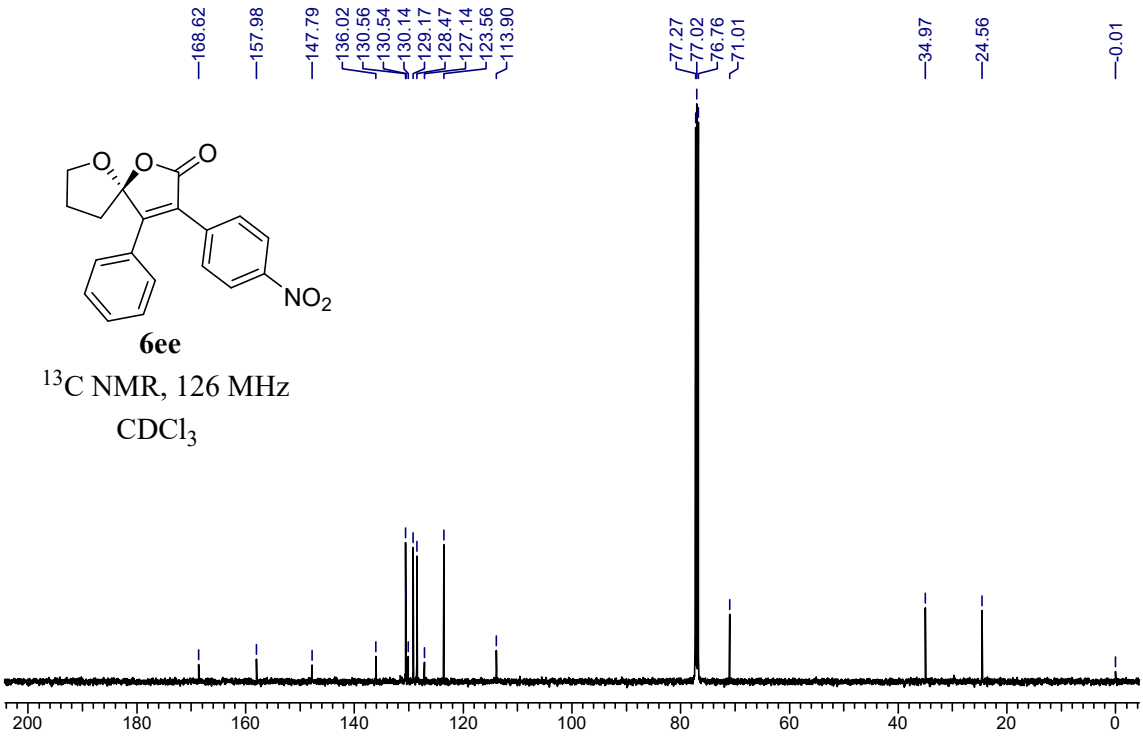
6eb

^{13}C NMR, 101 MHz

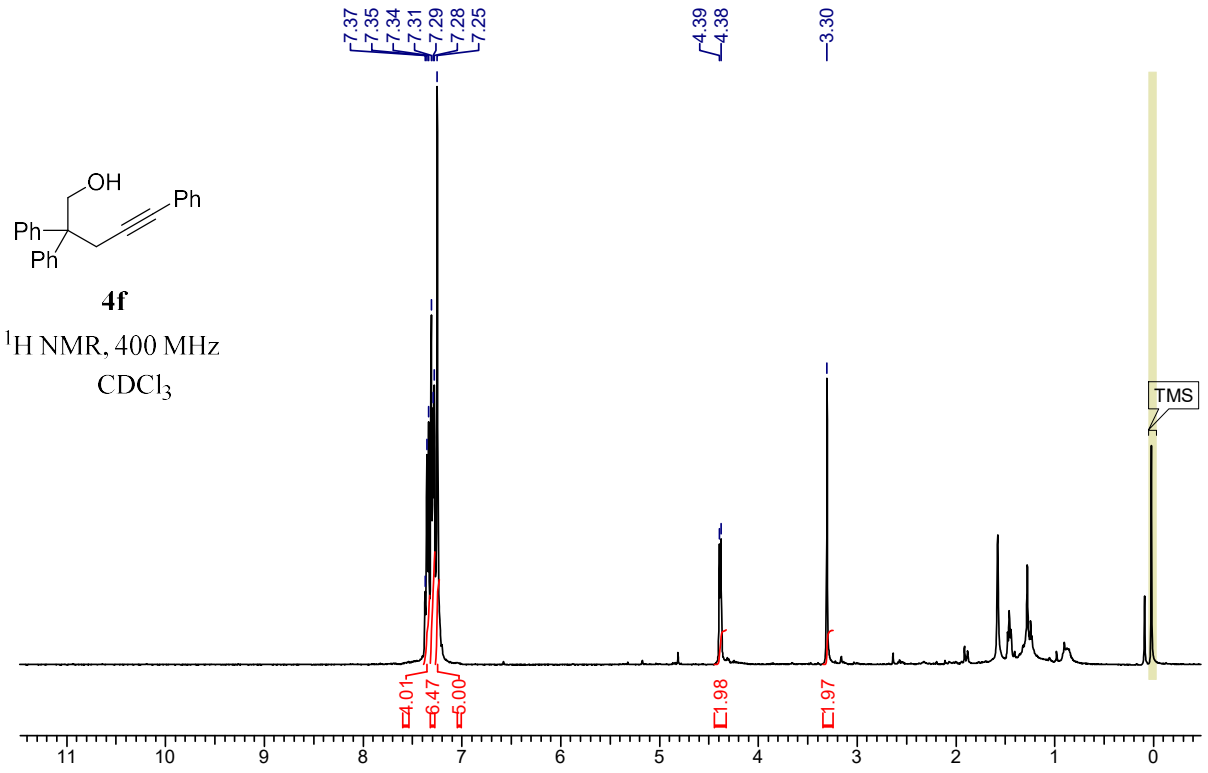
$CDCl_3$

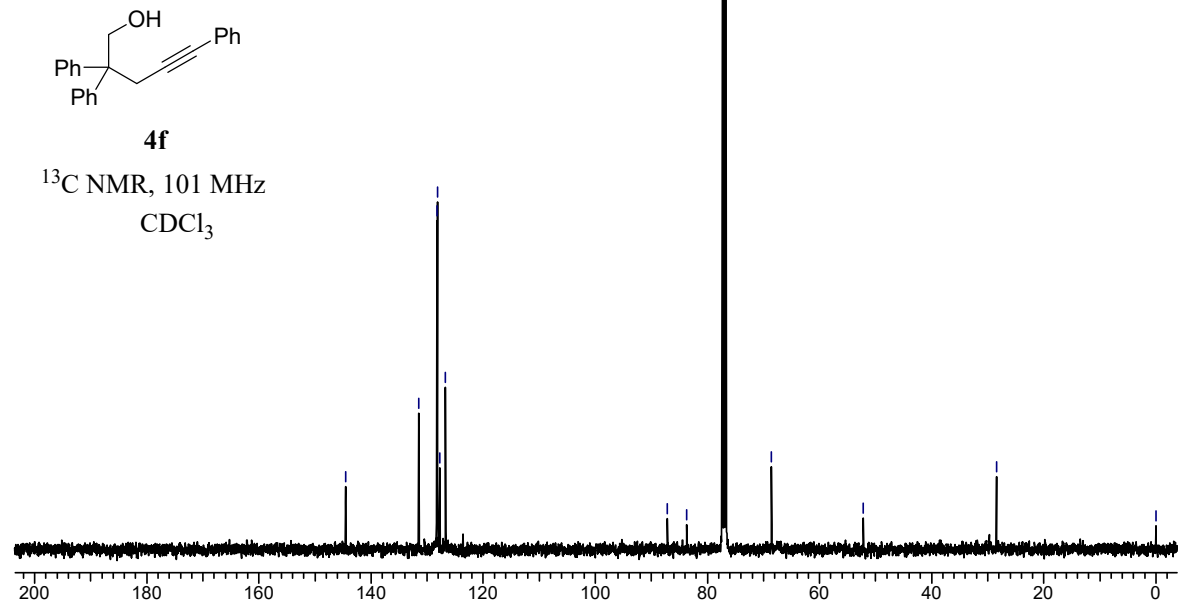
3-(4-Nitrophenyl)-4-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6ee):





2, 2, 5-triphenylpent-4-yn-1-ol (4f):





4f

^{1}H NMR, 400 MHz

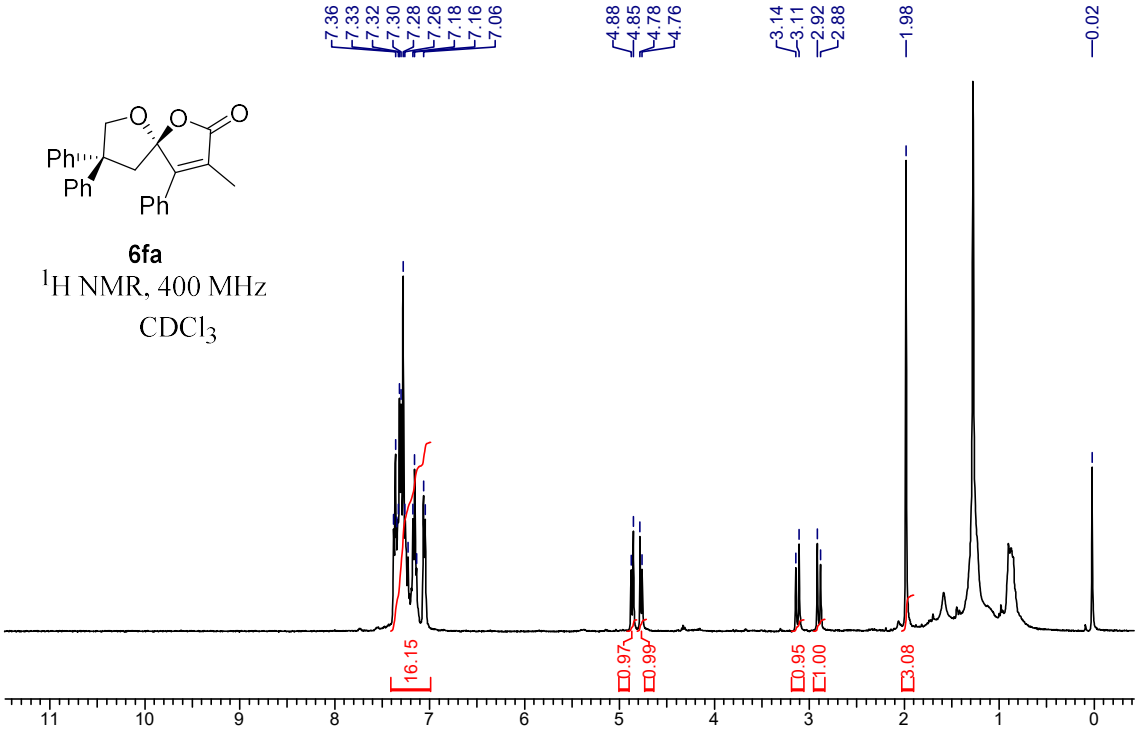
$CDCl_3$

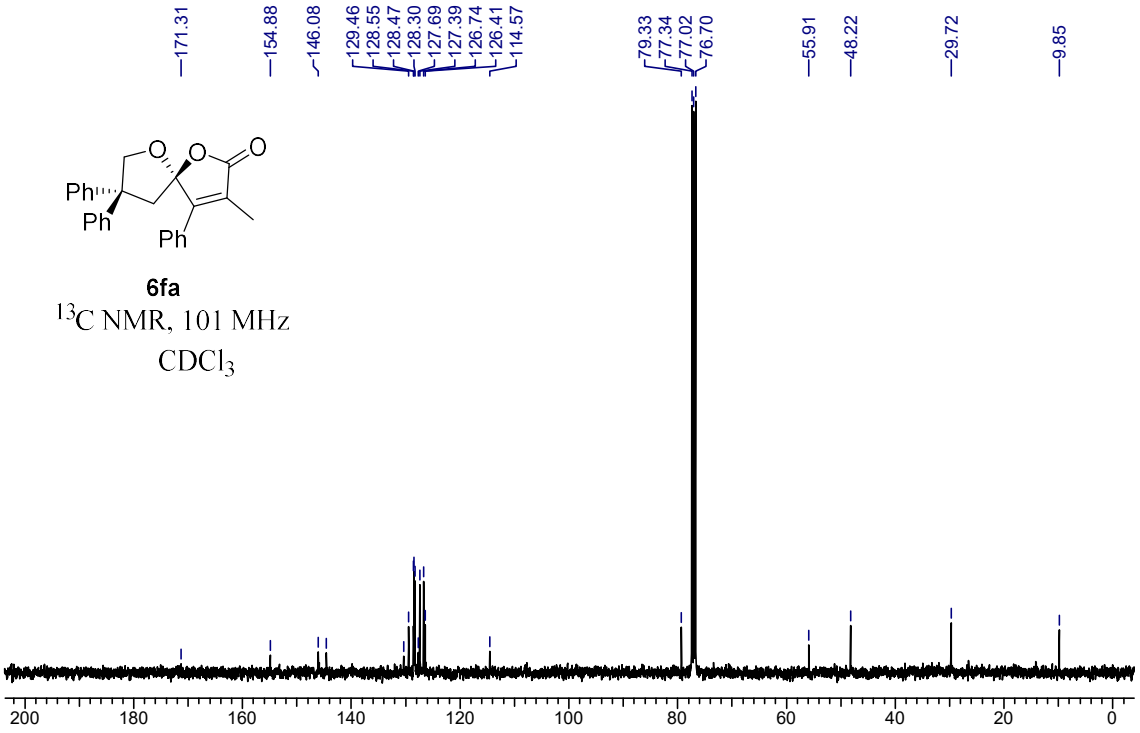
4f

^{13}C NMR, 101 MHz

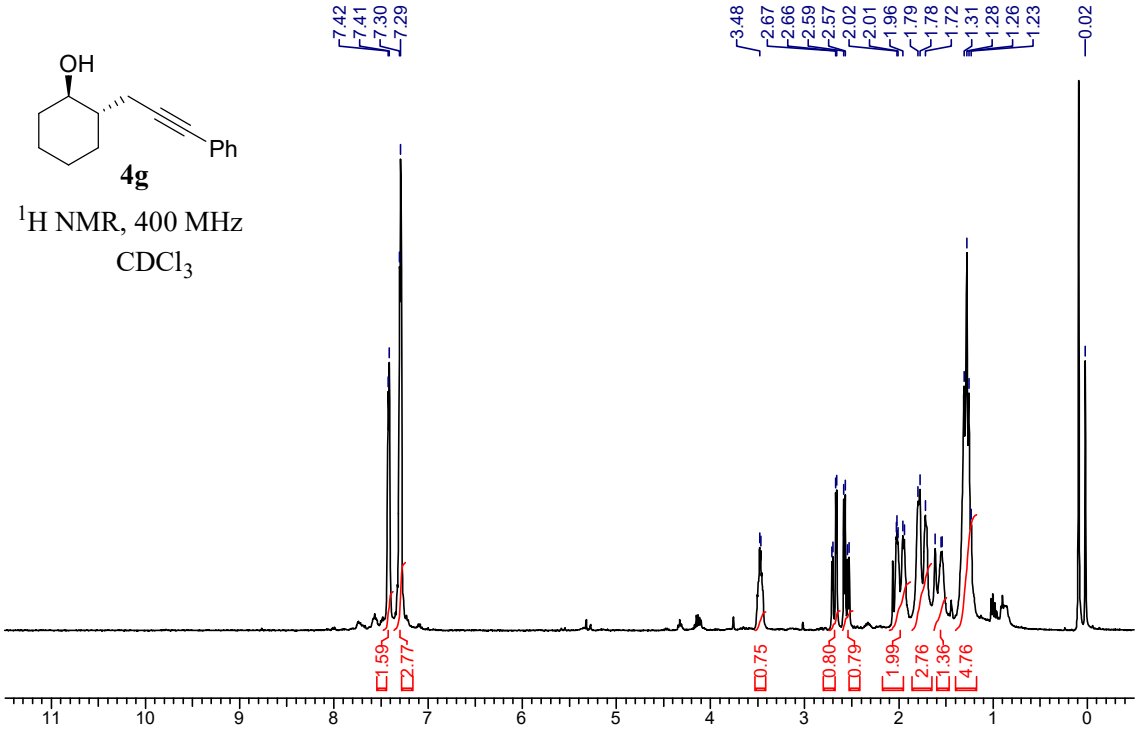
$CDCl_3$

3-methyl-4, 8, 8-triphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (6fa):

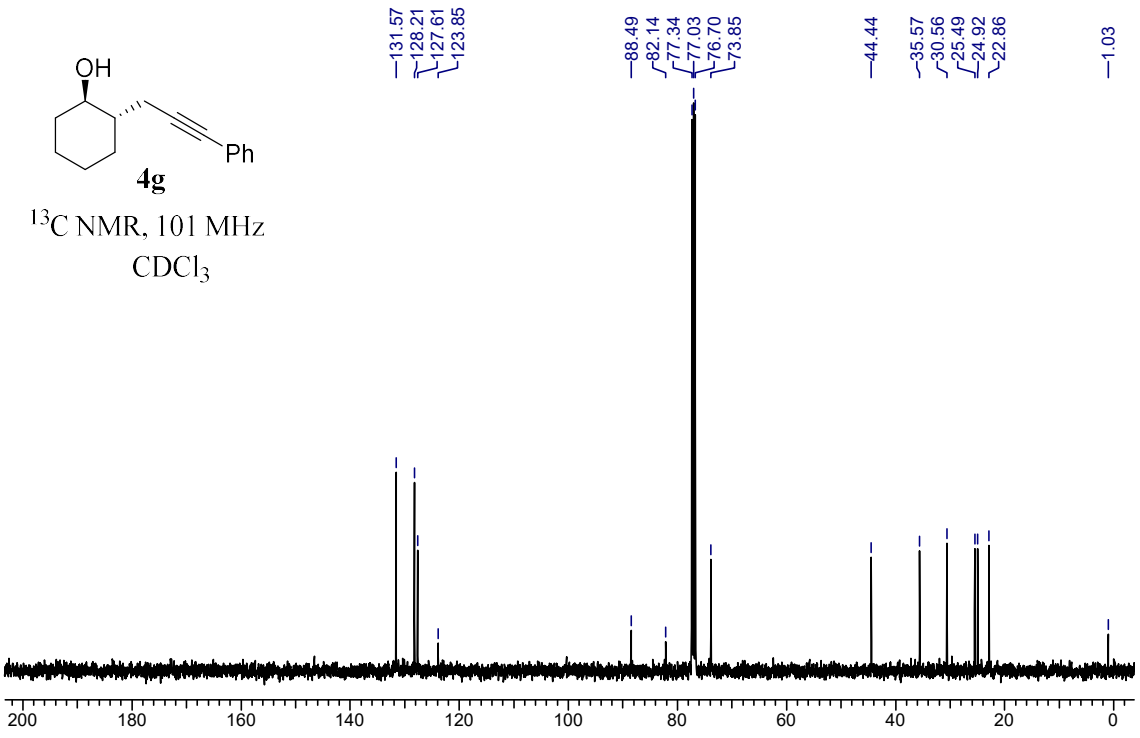




2-(3-phenylprop-2-yn-1-yl) cyclohexan-1-ol (4g):

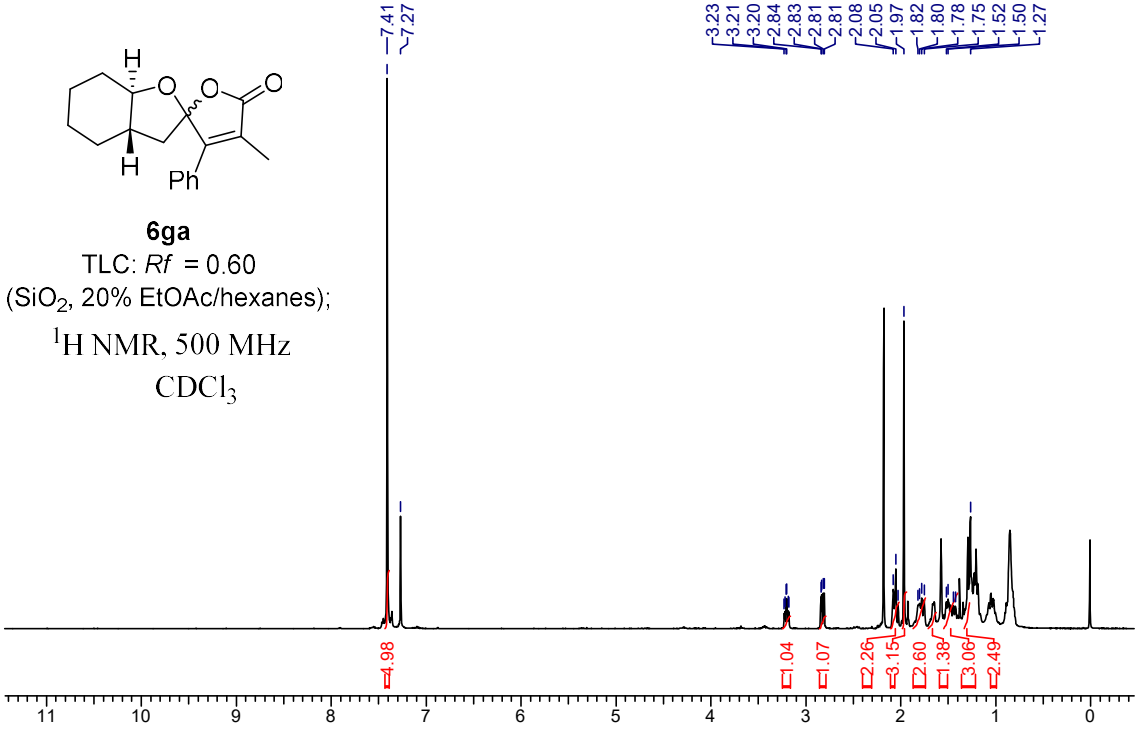


^{1}H NMR, 400 MHz
$CDCl_3$



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

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

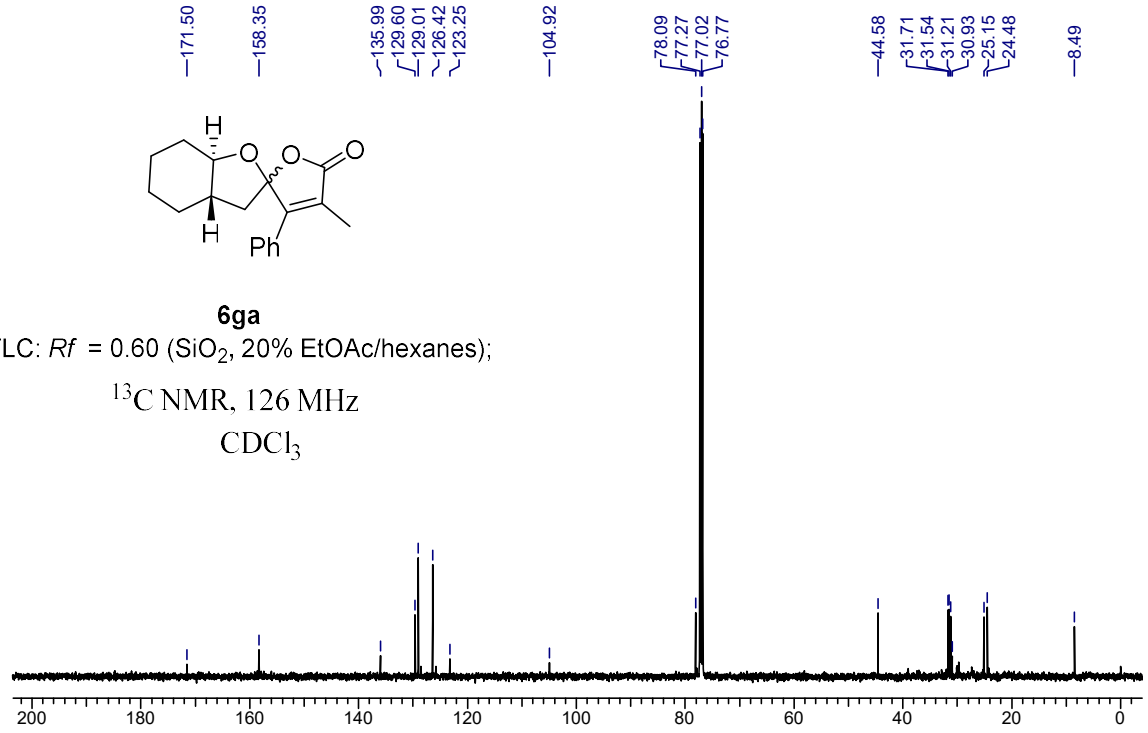


6ga

TLC: *Rf* = 0.60 (SiO_2, 20% EtOAc/hexanes);

^{1}H NMR, 500 MHz

$CDCl_3$



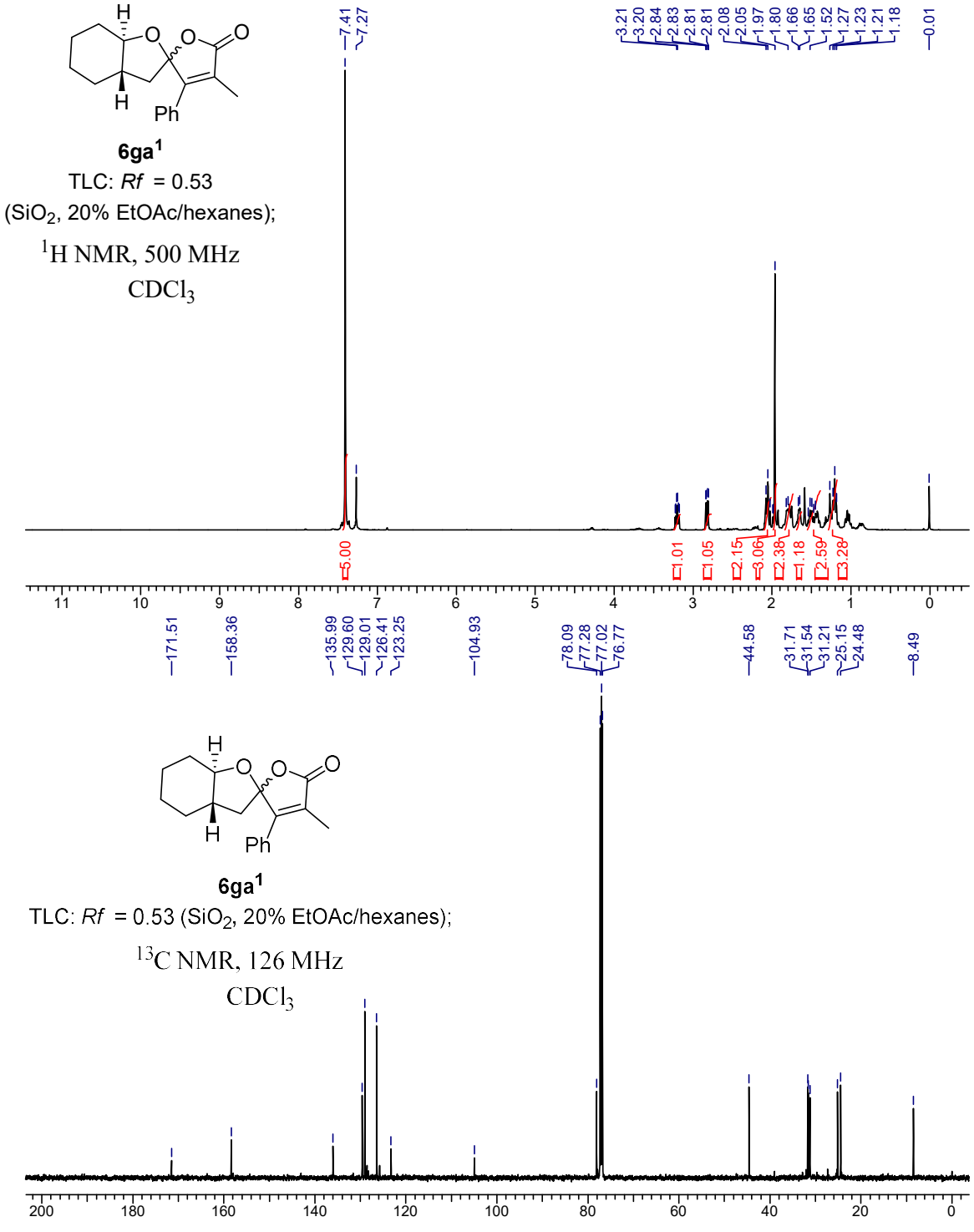
6ga

TLC: *Rf* = 0.60 (SiO_2, 20% EtOAc/hexanes);

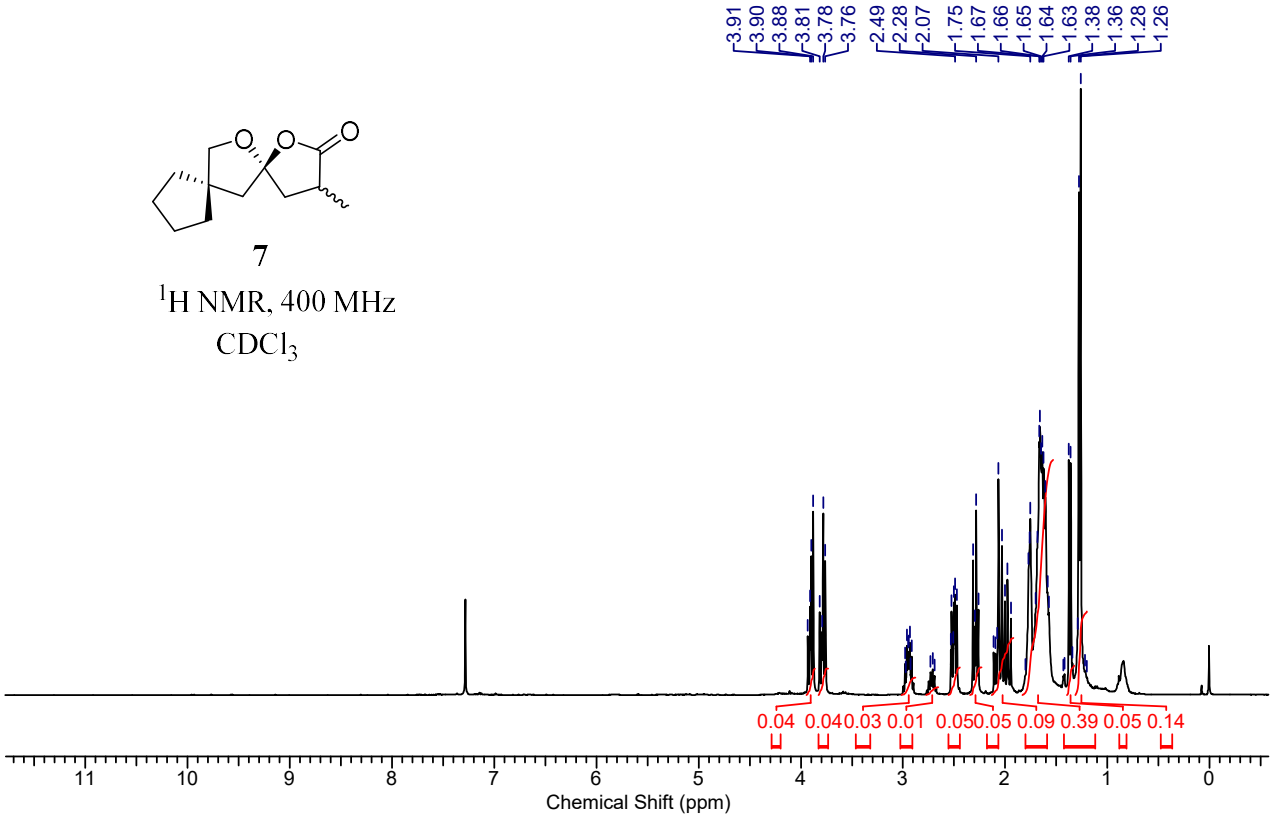
^{13}C NMR, 126 MHz

$CDCl_3$

4'-methyl-3'-phenyl-3a, 4, 5, 6, 7, 7a-hexahydro-3*H*, 5'*H*-spiro [benzofuran-2, 2'-furan]-5'-one (6ga[1]):



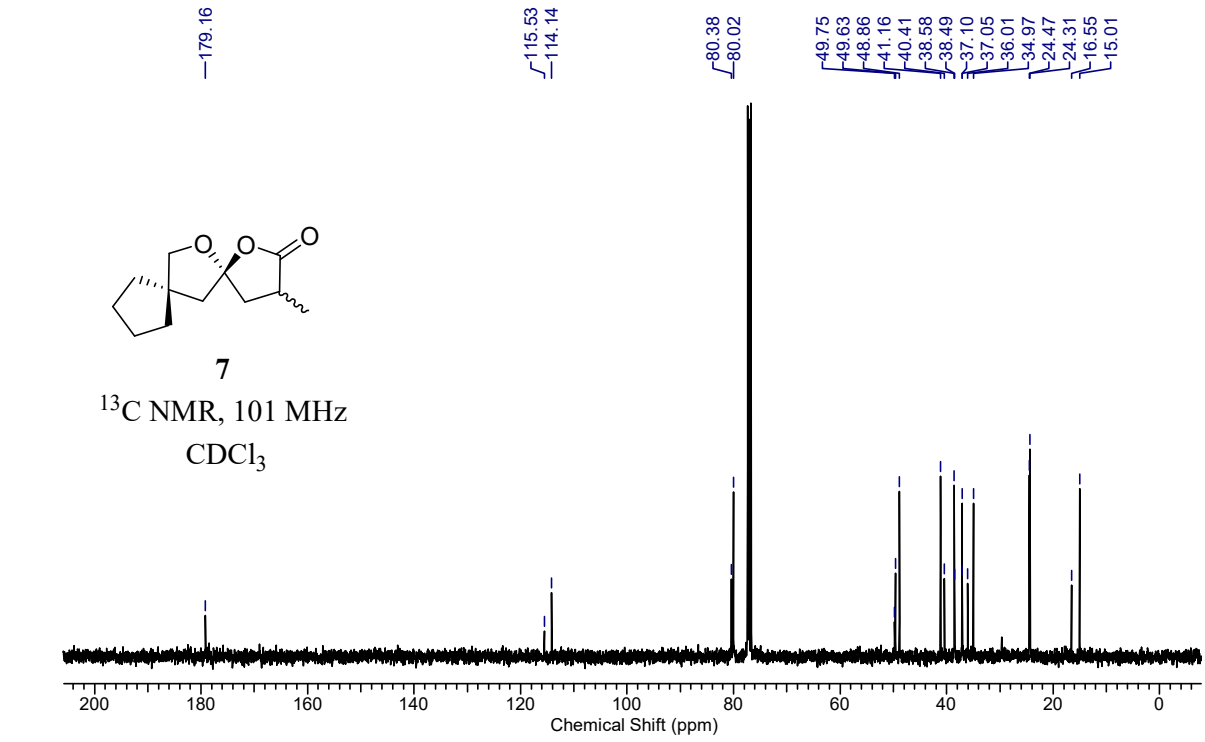
3-Methyl-1, 13-dioxadispiro [4.1.4^{7}.2^{5}] tridecan-2-one (7):



7

^{1}H NMR, 400 MHz

$CDCl_3$

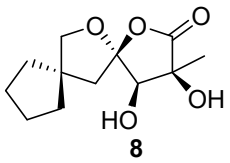


7

^{13}C NMR, 101 MHz

$CDCl_3$

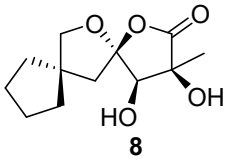
3, 4-Dihydroxy-3-methyl-1, 13-dioxadispiro [4.1.4^{7}.2^{5}] tridecan-2-one (8):



8

^{1}H NMR, 400 MHz

$CDCl_3$



8

^{13}C NMR, 101 MHz

$CDCl_3$