Supporting Information

Cu(I)-Catalyzed Enantioselective and Stereospecific Borylative annulation of Cyclic 1,3-Dione-Tethered 1,3-Enynes

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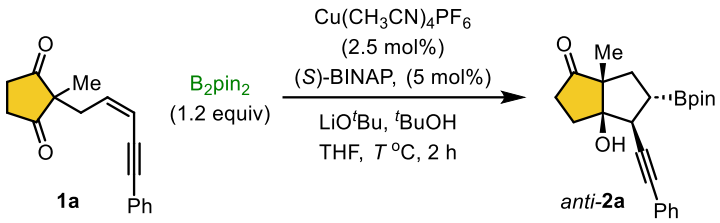
I. General details

***General information*:** Unless otherwise noted, all reagents, catalysts and ligands were purchased from commercial suppliers and were used without further purification. All reactions were performed under a nitrogen atmosphere and in flame-dried or oven-dried glassware with magnetic stirring. All solvents were dried before use following the standard procedures. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), iodine treatment, or using *p*-anisaldehyde stain or *β*-naphthol stain. Column chromatography was carried out using 100-200 mesh silica gel packed in glass columns. NMR spectra were recorded at 300, 400, 500, and 700 MHz (H) and 75, 101, 126, 176 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.16 ppm) as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS were recorded using ESI-TOF techniques. Enantiomeric ratio (*er*) values of products were determined by chiral HPLC analysis (Shimadzu LC-20AD) and diastereomer ratio (*dr*) values were determined by ^{1}H NMR analysis. All chiral compound's optical rotation was measured on a Horiba SEPA-300.

II. Additional screening for the reaction conditions:

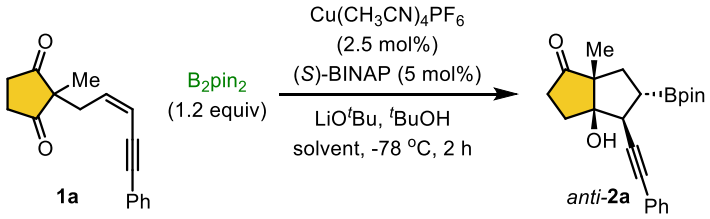
Table S1. Optimization of reaction temperature[a-d]



entry	*T* °C	yield (%)	*er*
1	rt	32	68:32
2	0	42	69:31
3	-20	27	71:29
4	-40	41	71:29
5	-78	54	96:04

[a]Reaction conditions: **1a** (50 mg, 0.2 mmol), $B_2(pin)_2$ (60 mg, 0.24 mmol), $Cu(CH_3CN)_4PF_6$ (1.9 mg, 2.5 mol %), BINAP (5.0 mol %), ^{t}BuOH (38 µL , 0.4 mmol,), LiO^tBu (36 µL, 0.4 mmol, 1.0 M THF solution), in THF solvent (3 mL, 0.1 M). [b]Isolated yields. [c]Enantiomeric ratio (*er*) was determined by HPLC analysis using a chiral stationary phase. [d]>20:1 *dr* was observed from ^{1}H NMR analysis

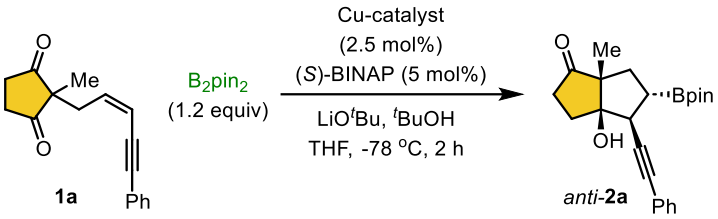
Table S2. Optimization of solvents[a]



entry	solvent	yield%	*er*
1	THF	54	96:04
2	Et_2O	-[b]	-
3	CH_2Cl_2	21	63:37
4	^{t}BuOH	<5	-
5	Toluene	25	69:31
6	DCE	-[b]	-
7	CH_3CN	-[b]	-

[a]Reaction conditions same as in Table S1. [b]Starting material recovered.

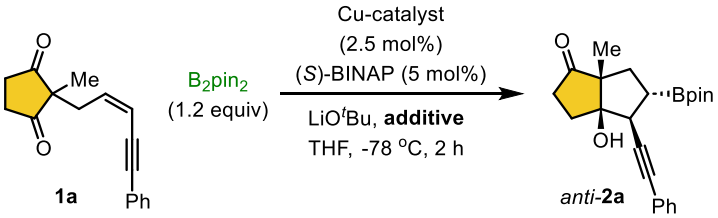
Table S3. Optimization of copper catalyst[a]



entry	Cu-catalyst	yield (%)	*er*
1	$Cu(CH_3CN)_4PF_6$	54	94:06
2	CuI	-[b]	-
3	CuBr	<5	-
4	$CuBr.Me_2S$	-[b]	-
5	CuCl	-[b]	-
6	$Cu(OTf)_2.H_2O$	<10	-
7	$CuSO_4$	-[b]	-
8	$Cu(OAc)_2.H_2O$	<10	-
9	$Cu(SO_3CF_3)_2$	<5	-

[a]Reaction conditions same as in Table S1. [b]Starting material recovered.

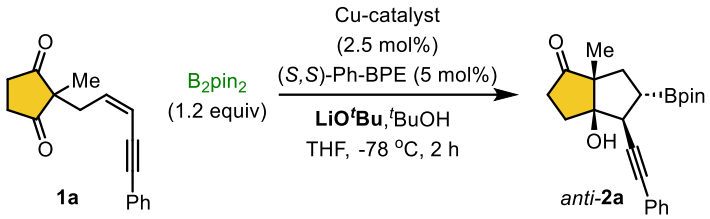
Table S4. Optimization of additive[a]



entry	additive	yield (%)	*er*
1	EtOH	46	81:19
2	MeOH	51	92:08
3	IPA	16	89:11
4	-	27	86:14
5	H_2O	36	90:10
6	CF_3CH_2OH	44	90:10
7	^{n}BuOH	26	90:10:
8	CCl_3CH_2OH	-[b]	-
9	HFIP	-[b]	-
10	^{t}BuOH	54	96:04

[a]Reaction conditions same as in Table S1. [b]Starting material recovered.

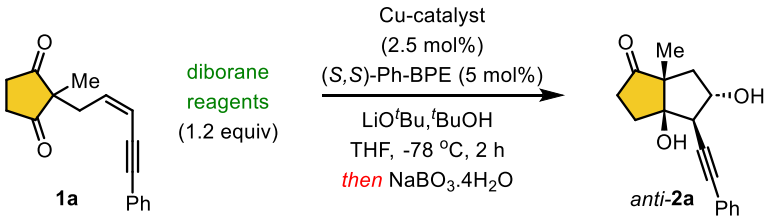
Table S5. Optimization of base loading[a]

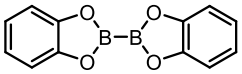
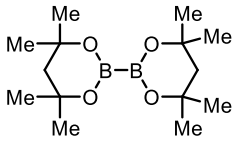
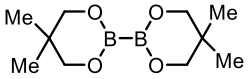


entry	LiO^tBu loading	yield (%)	*er*
1	0.5 equiv	41	>99
2	1.0 equiv	49	>99
3	1.5 equiv	76	>99
4	2.0 equiv	82	>99

[a]Reaction conditions same as in Table S1.

Table S6. Optimization of diborane reagents

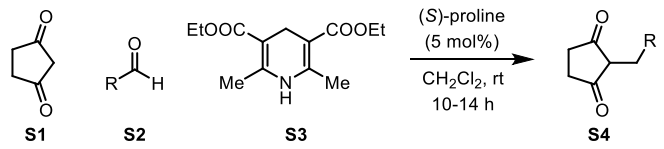


entry	diborane reagents	yield (%)	*er*
1		-[b]	-
2		-[b]	-
3		42[c]	98:02

[a]Reaction conditions same as in Table S1. [b]Starting material recovered. [c]Borylation product was highly unstable and decomposed while doing the column chromatography.

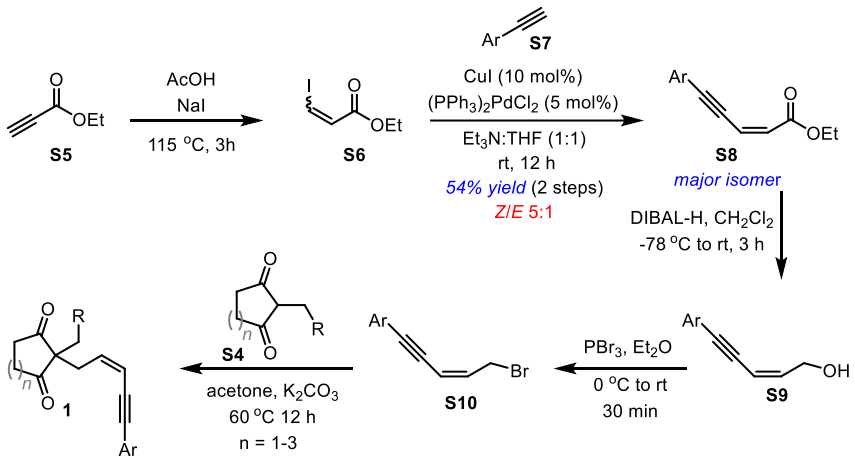
III. Experimental procedures and analytical data:

IIIa. Synthesis of 2-substituted 1,3-diketones using Ramachary protocol:[1]



General procedure: To a solution of 1,3-diketone **S1** (10 mmol, 1.0 equiv), aldehyde **S2** (20 mmol, 2 equiv), and Hantzsch ester **S3** (10 mmol, 1.0 equiv) in CH_2Cl_2 (0.3 M, 33 mL), was added (*S*)-proline (5 mol%) and the reaction mixture was stirred at room temperature for 10-14 h. After evaporation of the solvent, the crude reaction mixture was directly purified by using flash column chromatography (hexane/EtOAc) to afford 2-substituted 1,3-diketones **S4**.

IIIb. Synthesis of substrates 1a-1ad:[2,3]



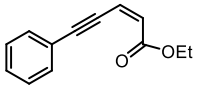
General procedure A:

We synthesized substrate **1** with commercially available feedstocks. Ethyl propiolate **S5** (6 g, 61 mmol) and NaI (14.68 g, 98 mol) were dissolved in the acetic acid (21 mL, 367 mmol) and the reaction mixture was stirred at 115 °C in a preheated oil-bath for 3 hours. After the completion of the reaction, the reaction mixture was cooled to room temperature and quickly transferred into a separating funnel, charged with 100 mL of H_2O and extracted with EtOAc (3 x 100 mL). The organic layer was washed with saturated $NaHCO_3$ (50 mL), saturated $Na_2S_2O_3$ (50 mL) and brine solution (50 mL), and dried over anhydrous Na_2SO_4 and concentrate. The crude residue **S6** was used in the next step without further purification.

The residue **S6** and aryl alkyne (73.2 mmol, 1.2 equiv) were added to a 250 mL round-bottom flask, followed by $PdCl_2(Ph_3P)_2$ (2.14 g, 5 mol%) and CuI (1.16 g, 10 mol%) into the 1:1 ratio of Et_3N

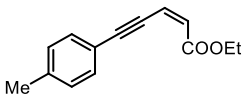
and THF (60 mL, 1.0 M). The reaction mixture was stirred overnight at room temperature. Upon completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl (100 mL) and extracted with EtOAc (3 x 100 mL). The organic layer was washed with H_2O (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The ^1H NMR analysis of the crude reaction mixture revealed a 5:1 ratio of *Z:E* isomers. Both isomers were separated by careful column chromatography (R_f = 0.25, 5% EtOAc in hexanes), affording both major and minor Z/E isomers of *α,β*-unsaturated esters **S8**, which are easily separated through simple column chromatography.

Ethyl (*Z*)-5-phenylpent-2-en-4-ynoate [(*Z*)-**S8a**]:



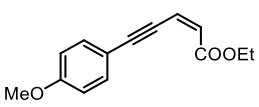
Prepared according to the general procedure as described above in (*Z*)-**S8a** (5.50 g, 45% yield) as brown liquid with 5:1 diastereoselectivity. It was purified by flash chromatography (5% EtOAc/hexanes; R_f = 0.5); ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 2H), 7.46 – 7.29 (m, 3H), 6.36 (d, *J* = 11.4 Hz, 1H), 6.13 (d, *J* = 11.4 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 132.2, 129.3, 128.5, 128.4, 123.0, 122.8, 101.3, 86.5, 60.6, 14.4; HRMS (ESI) calcd for $C_{13}H_{13}O_2$ $[M+H]^+$: 201.0915; found: 201.0894.

Ethyl (*Z*)-5-(*p*-tolyl)pent-2-en-4-ynoate [(*Z*)-**S8b**]:



Prepared according to the general procedure as described above in (*Z*)-**S8b** (2.79 g, 42% yield) as brown liquid with ~5:1 diastereoselectivity. It was purified by flash chromatography (5% EtOAc/hexanes; R_f = 0.5); ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.35 (d, *J* = 11.4 Hz, 1H), 6.10 (d, *J* = 11.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 139.7, 132.1, 129.3, 127.8, 123.1, 119.7, 101.8, 86.1, 60.5, 21.7, 14.4; HRMS (ESI) calcd for $C_{14}H_{15}O_2$ $[M+H]^+$: 215.1072; found: 215.1076.

Ethyl (*Z*)-5-(4-methoxyphenyl)pent-2-en-4-ynoate [(*Z*)-**S8c**]:



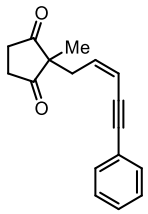
Prepared according to the general procedure as described above in (*Z*)-**S8c** (2.71 g, 38% yield) as brown liquid with ~5.5:1 diastereoselectivity. It was purified by flash chromatography (5% EtOAc/hexanes; R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.39 (m, 2H), 6.98 – 6.78 (m, 2H), 6.34 (d, *J* = 11.4 Hz, 1H), 6.08 (d, *J* = 11.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 160.6, 133.9, 127.2, 123.3, 114.9, 114.2, 102.0, 85.9, 60.5, 55.4, 14.5; HRMS (ESI) calcd for $C_{14}H_{15}O_3$ $[M+H]^+$: 231.1021; found: 231.1027.

The intermediate (*Z*)-**S8** (25 mmol) was dissolved in dry CH_2Cl_2 (15 mL, 0.6 M)) and cooled to -78 °C under an inert atmosphere. DIBAL-H (49 mL, 1.0 M solution in toluene) was then added dropwise *via* syringe over 30 minutes, and the reaction mixture was stirred at the same temperature for an additional 30 minutes. The reaction was then allowed to cool at room temperature and stirred for another 2 hours. After completion, the reaction mixture was quenched with saturated sodium potassium tartrate (50 mL), filtered through Celite, and extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude allyl alcohol **S9** was used directly in the next step without further purification.

The crude residue **S9** was dissolved in Et_2O (20 mL) and stirred at 0–5 °C using an ice bath. PBr_3 (0.95 mL, 10 mmol, 0.4 equiv) was added dropwise to the reaction mixture, which was stirred for 30 minutes at the same temperature. The reaction was quenched with saturated $NaHCO_3$ (30 mL), and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with water and brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting crude residue **S10** was used directly for the next step.

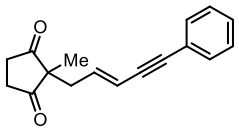
To a vigorously stirred suspension of 2-substituted 1,3-cyclopentanedione **S4** (4.0 mmol, 1.0 equiv) in acetone (6 mL, 1.0 M), K_2CO_3 (4.8 mmol, 1.2 equiv) was gradually added. After the initial frothing subsided, the crude residue of allyl bromide **S10** (1.3 g, 6 mmol, 1.5 equiv) was added, and the reaction mixture was stirred at 60 °C in a preheated oil bath for overnight. After completion, the reaction mixture was concentrated and diluted with water (10 mL). The aqueous phase was extracted with EtOAc (2 × 30 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/hexanes) to afford the desired products **1**.

(*Z*)-2-Methyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione [(*Z*)-1a]:



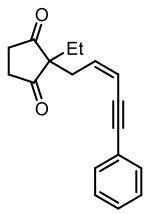
Prepared according to the general procedure A as described above in 35% yield (353mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.38 – 7.28 (m, 3H), 5.96 – 5.75 (m, 2H), 2.89 – 2.70 (m, 4H), 2.69 – 2.65 (m, 2H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.3, 135.4, 131.7, 128.5, 128.5, 123.2, 113.7, 95.2, 85.3, 56.6, 36.1, 35.3, 17.6; HRMS (ESI) calcd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.12231; found: 253.12185.

(*E*)-2-Methyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione [(*E*)-1a]:



Prepared according to the general procedure A as described above in 33% yield (333 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.33 – 7.26 (m, 3H), 5.97 (dt, *J* = 15.6, 7.7 Hz, 1H), 5.72 (d, *J* = 15.7 Hz, 1H), 2.85 – 2.61 (m, 4H), 2.45 (d, *J* = 7.7 Hz, 2H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.9, 136.5, 131.6, 128.4, 128.4, 123.2, 114.7, 89.7, 87.3, 56.8, 38.7, 35.4, 19.5; HRMS (ESI) calcd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.12231; found:253.12185.

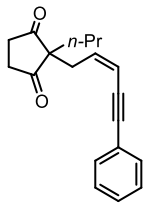
(*Z*)-2-Ethyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1b):



Prepared according to the general procedure as described above in 32% yield (340 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown solid; mp = 102–104°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.38 – 7.28 (m, 3H), 5.87 – 5.76 (m, 2H), 2.84 – 2.69 (m, 4H), 2.68 – 2.61 (m, 2H), 1.79 (q, *J* = 7.5 Hz, 2H), 0.79 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101

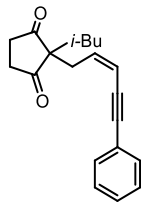
MHz, $CDCl_3$) δ 216.1, 135.6, 131.7, 128.5, 123.3, 113.4, 95.2, 85.3, 61.3, 36.3, 35.3, 27.2, 9.3; HRMS (ESI) calcd for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1373; found: 267.1379.

(*Z*)-2-(5-Phenylpent-2-en-4-yn-1-yl)-2-propylcyclopentane-1,3-dione (1c):



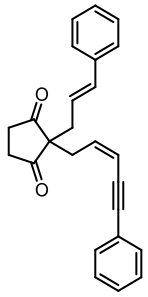
Prepared according to the general procedure A described above in 33% yield (370 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.28 – 7.22 (m, 3H), 5.78 – 5.69 (m, 2H), 2.70 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.68 – 2.60 (m, 3H), 2.60 – 2.55 (m, 2H), 1.66 – 1.60 (m, 2H), 1.11 – 1.00 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.1, 135.5, 131.6, 128.4, 123.2, 113.3, 95.1, 85.2, 60.8, 36.3, 36.1, 35.7, 18.2, 14.5; HRMS (ESI) calcd for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.15361; found: 281.15295.

(*Z*)-2-Isobutyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1d):



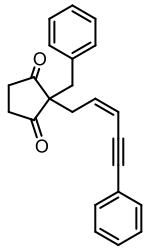
Prepared according to the general procedure A described above in 30% yield (353 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.35 – 7.29 (m, 3H), 5.86 – 5.77 (m, 2H), 2.87 – 2.69 (m, 4H), 2.63 (dd, *J* = 3.5, 2.7 Hz, 2H), 1.79 (s, 2H), 1.65 – 1.55 (m, 1H), 0.76 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.0, 135.1, 131.7, 128.5, 128.5, 123.2, 113.7, 95.3, 85.2, 60.4, 42.5, 37.8, 35.8, 25.2, 23.7; HRMS (ESI) calcd for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.16926; found: 295.16859.

2-Cinnamyl-2-((*Z*)-5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1e):



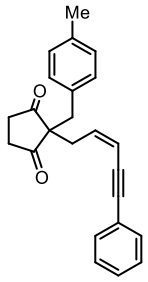
Prepared according to the general procedure A described above in 23% yield (326 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.25 – 7.21 (m, 3H), 7.17 (qd, *J* = 8.3, 4.3 Hz, 4H), 7.13 – 7.09 (m, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 5.90 (dt, *J* = 15.6, 7.7 Hz, 1H), 5.79 – 5.70 (m, 2H), 2.68 – 2.60 (m, 4H), 2.55 – 2.48 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.5, 136.7, 135.3, 134.9, 131.6, 128.6, 128.4, 128.4, 127.7, 126.3, 123.1, 122.7, 113.6, 95.3, 85.2, 60.9, 37.4, 36.2, 35.3; HRMS (ESI) calcd for $C_{25}H_{23}O_2$ $[M+H]^+$: 355.16926; found: 355.16842.

(*Z*)-2-Benzyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1f):



Prepared according to the general procedure A described above in 29% yield (380 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.39 – 7.31 (m, 3H), 7.25 – 7.15 (m, 3H), 7.05 (dd, *J* = 7.7, 1.8 Hz, 2H), 5.95 – 5.72 (m, 2H), 3.07 (s, 2H), 2.81 (d, *J* = 6.5 Hz, 2H), 2.51 (dd, *J* = 19.2, 6.9 Hz, 2H), 2.03 (dd, *J* = 19.2, 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.6, 135.7, 135.4, 131.7, 130.0, 128.7, 128.5, 128.5, 127.3, 123.3, 113.6, 95.4, 85.3, 62.4, 41.4, 36.6, 36.2; HRMS (ESI) calcd for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1541; found: 329.1543.

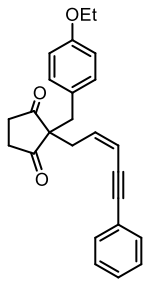
(*Z*)-2-(4-Methylbenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1g):



Prepared according to the general procedure A described above in 28% yield (383 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.39 – 7.31 (m, 3H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 5.90 – 5.82 (m, 1H), 5.80 (d, *J* = 10.8 Hz, 1H), 3.02 (s, 2H), 2.80 (d, *J* = 6.7 Hz, 2H), 2.50 (dd, *J* = 19.2, 6.9 Hz, 2H), 2.27 (s, 3H), 2.04 (dd, *J* = 19.1, 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

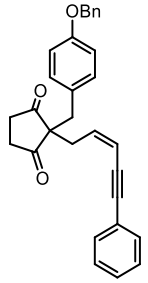
216.6, 136.8, 135.5, 132.5, 131.7, 129.7, 129.3, 128.4, 123.2, 113.4, 95.2, 85.3, 62.3, 41.0, 36.6, 36.0, 21.1; HRMS (ESI) calcd for $C_{24}H_{23}O_2$ $[M+H]^+$: 343.16926; found: 343.16873.

(*Z*)-2-(4-Ethoxybenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1h):



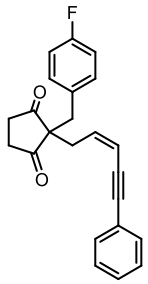
Prepared according to the general procedure A described above in 25% yield (372 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.37 – 7.30 (m, 3H), 6.97 – 6.93 (m, 2H), 6.75 – 6.71 (m, 2H), 5.84 (dt, *J* = 10.8, 7.1 Hz, 1H), 5.79 (d, *J* = 10.8 Hz, 1H), 3.95 (q, *J* = 7.0 Hz, 2H), 3.00 (s, 2H), 2.78 (d, *J* = 7.0 Hz, 2H), 2.49 (dd, *J* = 19.2, 6.9 Hz, 2H), 2.04 (dd, *J* = 19.2, 6.8 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.8, 158.0, 135.5, 131.6, 130.9, 128.4, 127.4, 123.2, 114.5, 113.4, 95.2, 85.3, 63.4, 62.4, 40.7, 36.6, 35.9, 14.9; HRMS (ESI) calcd for $C_{25}H_{25}O_3$ $[M+H]^+$: 373.17982; found: 373.17876.

(*Z*)-2-(4-(Benzyloxy)benzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1i):



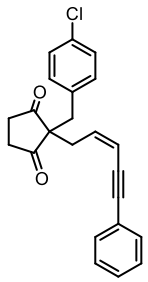
Prepared according to the general procedure A described above in 25% yield (434 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.44 – 7.28 (m, 8H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.94 – 5.64 (m, 2H), 5.00 (s, 2H), 3.02 (s, 2H), 2.79 (d, *J* = 6.7 Hz, 2H), 2.51 (dd, *J* = 19.2, 6.9 Hz, 2H), 2.05 (dd, *J* = 19.2, 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.8, 157.9, 136.9, 135.5, 131.7, 131.0, 128.7, 128.5 (2 peacks), 128.1, 127.9, 127.6, 123.3, 115.0, 113.5, 95.3, 85.3, 70.1, 62.5, 40.6, 36.6, 36.0; HRMS (ESI) calcd for $C_{30}H_{27}O_3$ $[M+H]^+$: 435.19547; found: 435.19437.

(*Z*)-2-(4-Fluorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1j):



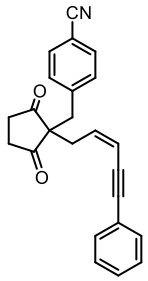
Prepared according to the general procedure described A above in 28% yield (388 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.36 – 7.31 (m, 3H), 7.05 – 6.99 (m, 2H), 6.92 – 6.85 (m, 2H), 5.90 – 5.72 (m, 2H), 3.03 (s, 2H), 2.80 – 2.76 (m, 2H), 2.55 (dd, *J* = 19.3, 6.8 Hz, 2H), 2.06 (dd, *J* = 19.3, 6.8 Hz, 2H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 216.2, 161.9 (d, J_{CF} = 246.0 Hz), 135.0 (d, J_{CF} = 4.3 Hz), 131.6, 131.5 (d, J_{CF} = 8.1 Hz), 131.5, 128.5, 128.4, 123.1, 115.4 (d, J_{CF} = 21.2 Hz), 113.7, 95.4, 85.1, 62.9, 39.7, 36.4, 36.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.21; HRMS (ESI) calcd for $C_{23}H_{20}O_2F$ $[M+H]^+$: 347.14418; found: 347.14343.

(*Z*)-2-(4-Chlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1k):



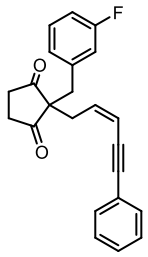
Prepared according to the general procedure A as described above in 28% yield (405 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.39 – 7.31 (m, 3H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 5.99 – 5.71 (m, 2H), 3.03 (s, 2H), 2.78 (d, *J* = 6.4 Hz, 2H), 2.58 (dd, *J* = 19.3, 6.9 Hz, 2H), 2.10 (dd, *J* = 19.3, 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.1, 134.9, 134.3, 133.2, 131.7, 131.5, 128.8, 128.6, 128.5, 123.2, 114.0, 95.5, 85.1, 62.3, 39.8, 36.5, 36.4; HRMS (ESI) calcd for $C_{23}H_{20}O_2Cl$ $[M+H]^+$: 363.11518; found: 363.11374.

(*Z*)-4-((2,5-Dioxo-1-(5-phenylpent-2-en-4-yn-1-yl)cyclopentyl)methyl)benzonitrile (1l):



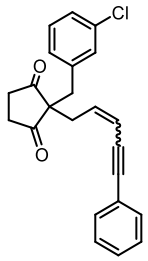
Prepared according to the general procedure A described above in 25% yield (353 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.7) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 4H), 7.37 – 7.32 (m, 3H), 7.19 (d, *J* = 8.3 Hz, 2H), 5.92 – 5.80 (m, 2H), 3.12 (s, 2H), 2.79 (d, *J* = 6.7 Hz, 2H), 2.66 (dd, *J* = 19.4, 6.8 Hz, 2H), 2.14 (dd, *J* = 19.4, 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.2, 141.6, 134.3, 132.3, 131.7, 131.1, 128.7, 128.6, 123.0, 118.7, 114.5, 111.3, 95.8, 85.0, 62.4, 39.4, 36.7, 36.3; HRMS (ESI) calcd for $C_{24}H_{20}O_2N$ $[M+H]^+$: 354.14886; found: 354.14808.

***Z*)-2-(3-Fluorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1m):**



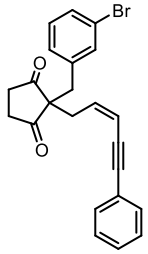
Prepared according to the general procedure A described above in 27% yield (374 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.38 – 7.31 (m, 3H), 7.17 (td, *J* = 7.9, 6.0 Hz, 1H), 6.88 (tdd, *J* = 8.5, 2.6, 0.8 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.80 – 6.75 (m, 1H), 5.88 – 5.76 (m, 2H), 3.05 (s, 2H), 2.78 (dd, *J* = 3.6, 2.8 Hz, 2H), 2.58 (dd, *J* = 19.3, 6.9 Hz, 2H), 2.11 (dd, *J* = 19.3, 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.9, 162.6 (d, J_{CF} = 246.7 Hz), 138.3 (d, J_{CF} = 7.3 Hz), 134.9, 131.7, 130.1 (d, J_{CF} = 8.2 Hz), 128.6, 128.5, 125.7 (d, J_{CF} = 2.2 Hz), 123.1,116.9 (d, J_{CF} = 21.3 Hz), 114.2 (d, J_{CF} = 20.9 Hz), 113.9, 95.5, 85.1, 62.2, 40.1, 36.5, 36.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.4; HRMS (ESI) calcd for $C_{23}H_{20}O_2F[M+H]^+$: 347.14418; found: 347.14360.

2-(3-Chlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1n):



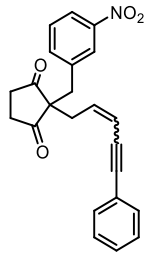
Prepared according to the general procedure A described above in 29% yield (420 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; Z/E ratio = 7:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.39 – 7.31 (m, 3H), 7.21 – 7.11 (m, 2H), 7.08 – 6.91 (m, 2H), 5.87 – 5.80 (m, 2H), 3.03 (s, 2H), 2.79 (dd, *J* = 5.1, 1.3 Hz, 2H), 2.66 – 2.52 (m, 2H), 2.19 – 2.07 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.8, 137.9, 134.9, 134.4, 131.7, 131.4, 130.0, 129.9, 128.5, 128.3, 127.5, 123.2, 114.0, 95.5, 85.1, 62.2, 39.9, 36.5, 36.4; HRMS (ESI) calcd for $C_{23}H_{20}O_2Cl$ $[M+H]^+$: 363.11463; found: 363.11368.

(*Z*)-2-(3-Bromobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1o):



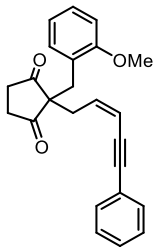
Prepared according to the general procedure A described above in 32% yield (520 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a brown semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.39 – 7.30 (m, 4H), 7.23 (t, *J* = 1.7 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 5.91 – 5.63 (m, 2H), 3.03 (s, 2H), 2.79 (dd, *J* = 4.9, 1.5 Hz, 2H), 2.60 (dd, *J* = 19.3, 6.9 Hz, 2H), 2.14 (dd, *J* = 19.3, 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.8, 138.2, 134.9, 132.9, 131.7, 130.5, 130.2, 128.8, 128.6, 128.5, 123.2, 122.6, 114.0, 95.6, 85.1, 62.2, 39.9, 36.5, 36.4; HRMS (ESI) calcd for $C_{23}H_{20}O_2Br$ $[M+H]^+$: 407.06466; found: 407.06412.

(*Z*)-2-(3-Nitrobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane -1,3-dione (1p):



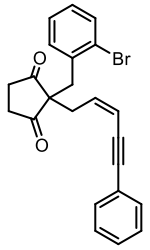
Prepared according to the general procedure A described above in 21% yield (313 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.8) to afford a brown liquid; Z/E ratio = 4:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 1H), 7.85 (t, *J* = 1.7 Hz, 0.8H), 7.82 (t, *J* = 1.7 Hz, 0.2H), 7.44 – 7.38 (m, 1.6H), 7.36 – 7.24 (m, 4.4H), 7.23 – 7.15 (m, 1H), 5.94 – 5.65 (m, 2H), 3.09 (s, 1.6H), 3.00 (s, 0.4H), 2.71 (d, *J* = 6.6 Hz, 1.6H), 2.62 (dd, *J* = 19.4, 6.8 Hz, 1.6H), 2.57 – 2.44 (m, 0.8H), 2.19 – 2.04 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$; major isomer peaks) δ 214.9, 148.2, 138.0, 136.4, 134.3, 131.6, 129.4, 128.6, 128.5, 124.9, 122.9, 122.2, 114.4, 95.7, 84.9, 62.2, 38.4, 36.6, 36.1; HRMS (ESI) calcd for $C_{23}H_{20}O_4N$ $[M+H]^+$: 374.13868; found: 374.13778.

(*Z*)-2-(2-Methoxybenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1q):



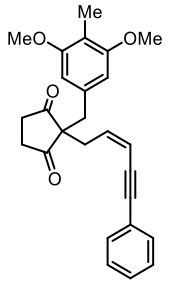
Prepared according to the general procedure A described above in 24% yield (344 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.6) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.36 – 7.30 (m, 3H), 7.24 – 7.18 (m, 1H), 7.07 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.86 (td, *J* = 7.5, 1.0 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 5.84 (dt, *J* = 10.7, 7.2 Hz, 1H), 5.79 – 5.74 (m, 1H), 3.73 (s, 3H), 3.06 (s, 2H), 2.81 (dd, *J* = 7.2, 0.8 Hz, 2H), 2.56 – 2.47 (m, 2H), 2.47 – 2.37 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.0, 157.3, 136.4, 132.1, 131.8, 128.3, 128.4, 128.4, 124.0, 123.5, 120.6, 113.1, 110.4, 95.1, 85.7, 60.9, 54.9, 36.3, 36.1, 34.9; HRMS (ESI) calcd for $C_{24}H_{23}O_3$ $[M+H]^+$: 359.16417; found: 359.16347.

(*Z*)-2-(2-Bromobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1r):



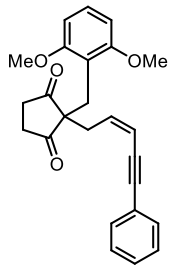
Prepared according to the general procedure A described above in 33% yield (537 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 3H), 7.36 – 7.31 (m, 3H), 7.19 (d, *J* = 7.6, 1.3 Hz, 1H), 7.11 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.06 (ddt, *J* = 7.3, 6.7, 1.2 Hz, 1H), 5.99 – 5.61 (m, 2H), 3.28 (s, 2H), 2.84 (d, *J* = 6.5 Hz, 2H), 2.67 – 2.54 (m, 2H), 2.54 – 2.41 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.9, 135.5, 135.4, 133.5, 131.7, 131.5, 128.9, 128.5, 128.4, 127.5, 125.6, 123.3, 113.8, 95.4, 85.4, 60.9, 39.7, 36.4, 35.4; HRMS (ESI) calcd for $C_{23}H_{20}O_2Br$ $[M+H]^+$: 407.06412; found: 407.06287.

(*Z*)-2-(3,5-Dimethoxy-4-methylbenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1s):



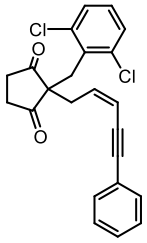
Prepared according to the general procedure A described above in 32% yield (515 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (ddd, *J* = 8.2, 3.7, 2.5 Hz, 2H), 7.37 – 7.29 (m, 3H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 8.5 Hz, 1H), 5.88 (dt, *J* = 10.8, 7.5 Hz, 1H), 5.80 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 3.58 (s, 3H), 3.01 (s, 2H), 2.78 (dd, *J* = 7.5, 0.9 Hz, 2H), 2.51 (dt, *J* = 9.5, 5.9 Hz, 2H), 2.40 (dt, *J* = 9.0, 5.7 Hz, 2H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.7, 158.2, 157.4, 136.2, 131.7, 129.1, 128.4 (2 peaks), 123.4, 120.9, 119.7, 113.2, 106.1, 95.1, 85.6, 60.7, 60.0, 55.6, 36.5, 36.3, 36.0, 9.3; HRMS (ESI) calcd for $C_{26}H_{27}O_4$ $[M+H]^+$: 403.19093; found: 403.18962.

(*Z*)-2-(2,6-Dimethoxybenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1t):



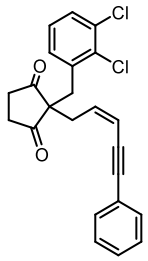
Prepared according to the general procedure A described above in 27% yield (419 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.7) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.25 – 7.16 (m, 3H), 6.65 – 6.57 (m, 2H), 6.54 (d, *J* = 2.3 Hz, 1H), 5.73 (dt, *J* = 10.8, 7.2 Hz, 1H), 5.66 (d, *J* = 10.8 Hz, 1H), 3.59 (s, 3H), 3.55 (s, 3H), 2.91 (s, 2H), 2.70 (d, *J* = 7.2 Hz, 2H), 2.47 – 2.38 (m, 2H), 2.38 – 2.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.6, 153.3, 151.4, 136.3, 131.6, 128.3, 128.3, 124.9, 123.3, 117.8, 113.1, 113.0, 111.3, 95.0, 85.5, 60.5, 55.6, 55.2, 36.1, 35.9, 34.8; HRMS (ESI) calcd for $C_{25}H_{25}O_4$ $[M+H]^+$: 389.17474; found: 389.17393.

(*Z*)-2-(2,6-Dichlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1u):



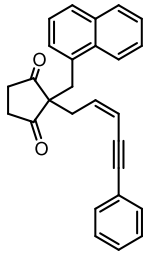
Prepared according to the general procedure A described above in 26% yield (412 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.27 – 7.23 (m, 3H), 7.20 (t, *J* = 8.4 Hz, 2H), 7.05 (dd, *J* = 8.4, 7.7 Hz, 1H), 5.76 – 5.68 (m, 2H), 3.32 (s, 2H), 2.90 (dd, *J* = 4.1, 2.1 Hz, 2H), 2.80 – 2.69 (m, 2H), 2.66 – 2.56 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.0, 136.5, 135.5, 133.2, 131.7, 128.9, 128.5, 128.4, 123.3, 114.0, 95.4, 85.4, 59.5, 36.5, 36.1, 34.9; HRMS (ESI) calcd for $C_{23}H_{19}O_2Cl_2$ $[M+H]^+$: 397.07566; found: 397.07464.

(*Z*)-2-(2,3-Dichlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1v):



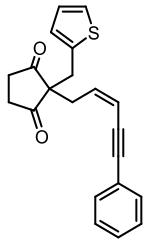
Prepared according to the general procedure A described above in 26% yield (413 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.34 (ddd, *J* = 6.5, 4.0, 2.8 Hz, 4H), 7.08 (t, *J* = 7.8 Hz, 1H), 7.03 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.91 – 5.76 (m, 2H), 3.29 (s, 2H), 2.83 (dd, *J* = 4.1, 2.0 Hz, 2H), 2.71 – 2.60 (m, 2H), 2.53 – 2.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.6, 136.2, 135.1, 133.8, 133.2, 131.7, 129.8, 129.6, 128.6, 128.5, 127.1, 123.2, 114.0, 95.6, 85.3, 60.7, 37.7, 36.3, 35.6; HRMS (ESI) calcd for $C_{23}H_{19}O_2Cl_2$ $[M+H]^+$: 397.07566; found: 397.07456.

(*Z*)-2-(Naphthalen-1-ylmethyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1w):



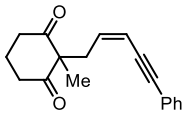
Prepared according to the general procedure A as described above in 29% yield (415 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.79 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.56 (dt, *J* = 4.4, 2.6 Hz, 2H), 7.51 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.41 – 7.31 (m, 4H), 7.23 (t, *J* = 6.4 Hz, 1H), 5.94 (dt, *J* = 10.7, 7.4 Hz, 1H), 5.86 (d, *J* = 10.8 Hz, 1H), 3.59 (s, 2H), 2.95 (d, *J* = 7.5 Hz, 2H), 2.53 – 2.32 (m, 2H), 1.99 – 1.72 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.6, 135.8, 133.9, 132.0, 131.8, 128.6, 128.5, 128.3, 126.3, 126.0, 125.3, 124.4, 123.4, 113.6, 95.4, 85.5, 62.0, 37.7, 36.7, 36.0; HRMS (ESI) calcd for $C_{27}H_{23}O_2$ $[M+H]^+$: 379.16926; found: 379.16841.

(*Z*)-2-(5-Phenylpent-2-en-4-yn-1-yl)-2-(thiophen-2-ylmethyl)cyclopentane-1,3-dione (1x):



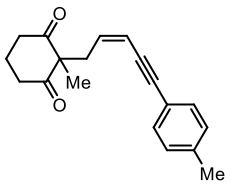
Prepared according to the general procedure A described above in 26% yield (347 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 7.38 – 7.31 (m, 3H), 7.08 (dd, *J* = 5.2, 1.1 Hz, 1H), 6.84 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.74 (d, *J* = 3.0 Hz, 1H), 5.95 – 5.75 (m, 2H), 3.30 (s, 2H), 2.76 (dd, *J* = 5.2, 1.3 Hz, 2H), 2.71 – 2.58 (m, 2H), 2.34 – 2.19 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.9, 137.3, 134.8, 131.7, 128.6, 128.5, 127.7, 127.1, 124.9, 123.1, 114.0, 95.6, 85.1, 62.2, 36.6, 36.1, 34.3; HRMS (ESI) calcd for $C_{21}H_{19}O_2S$ $[M+H]^+$: 335.11003; found: 335.10915.

(*Z*)-2-Methyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclohexane-1,3-dione (1y):



Prepared according to the general procedure A as described above in 29% yield (309 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 2H), 7.38 – 7.29 (m, 3H), 5.96 – 5.53 (m, 2H), 2.90 – 2.87 (m, 2H), 2.82 (ddd, *J* = 15.8, 9.9, 5.8 Hz, 2H), 2.63 (ddd, *J* = 16.0, 6.5, 5.2 Hz, 2H), 2.14 – 2.00 (m, 1H), 1.85 (ddq, *J* = 20.0, 10.1, 5.1 Hz, 1H), 1.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 136.5, 131.6, 128.5, 123.2, 113.0, 95.0, 85.7, 65.6, 37.9, 37.8, 18.0, 17.9; HRMS (ESI) calcd for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1385; found: 267.1405;

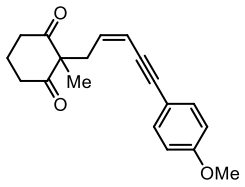
(*Z*)-2-Methyl-2-(5-(*p*-tolyl)pent-2-en-4-yn-1-yl)cyclohexane-1,3-dione (1z):



Prepared according to the general procedure A described above in 30% yield (336 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.90 – 5.67 (m, 2H), 2.88 (d, *J* = 6.5 Hz,

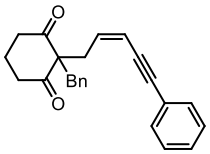
2H), 2.82 (td, *J* = 10.1, 5.1 Hz, 2H), 2.62 (ddd, *J* = 16.0, 6.3, 5.2 Hz, 2H), 2.35 (s, 3H), 2.15 – 1.98 (m, 1H), 1.83 (ddq, *J* = 19.1, 10.2, 5.1 Hz, 1H), 1.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 138.7, 135.9, 131.5, 129.3, 120.1, 113.1, 95.2, 85.0, 65.7, 37.9, 21.6, 17.9, 17.7; HRMS (ESI) calcd for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1541; found: 281.1542.

(Z)-2-(5-(4-Methoxyphenyl)pent-2-en-4-yn-1-yl)-2-methylcyclohexane-1,3-dione (1aa);



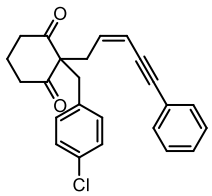
Prepared according to the general procedure A described above in 32% yield (379 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.6) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 6.88 – 6.82 (m, 2H), 5.94 – 5.60 (m, 2H), 3.81 (s, 3H), 2.87 (d, *J* = 6.5 Hz, 2H), 2.86 – 2.77 (m, 2H), 2.62 (ddd, *J* = 16.0, 6.3, 5.2 Hz, 2H), 2.12 – 2.01 (m, 1H), 1.83 (ddq, *J* = 19.1, 10.2, 5.1 Hz, 1H), 1.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 159.9, 135.5, 133.0, 115.3, 114.2, 113.2, 95.1, 84.5, 65.7, 55.4, 37.9, 17.9, 17.8; HRMS (ESI) calcd for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1490; found: 297.1492.

(Z)-2-Benzyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclohexane-1,3-dione (1ab):



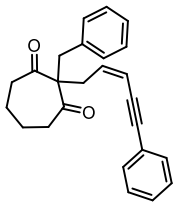
Prepared according to the general procedure A as described above in 29% yield (397 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liqued; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 2H), 7.39 – 7.29 (m, 3H), 7.25 – 7.14 (m, 3H), 7.04 (dt, *J* = 4.2, 2.3 Hz, 2H), 5.91 – 5.54 (m, 2H), 3.21 (s, 2H), 3.06 – 2.89 (m, 2H), 2.45 (ddd, *J* = 17.2, 8.6, 5.0 Hz, 2H), 2.14 (ddd, *J* = 17.1, 8.2, 4.9 Hz, 2H), 1.78 – 1.66 (m, 1H), 1.34 – 1.17 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 136.7, 136.5, 131.7, 130.2, 128.6, 128.5, 127.1, 123.4, 113.0, 95.0, 85.5, 68.8, 43.3, 40.7, 38.9, 15.9; HRMS (ESI) calcd for $C_{24}H_{26}NO_2$ $[M+NH_4]^+$: 360.1963; found: 360.1958.

(Z)-2-(4-Chlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclohexane-1,3-dione (1ac):



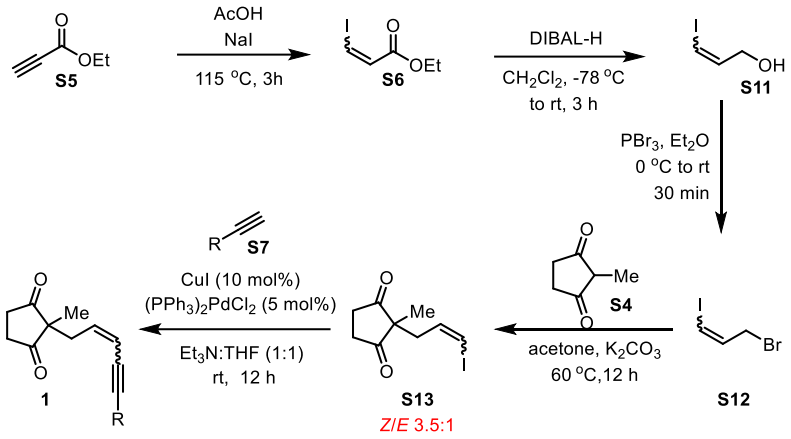
Prepared according to the general procedure A as described above in 27% yield (406 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H), 7.39 – 7.28 (m, 3H), 7.23 – 7.13 (m, 2H), 7.06 – 6.93 (m, 2H), 5.90 – 5.68 (m, 2H), 3.18 (s, 2H), 2.94 (d, *J* = 6.6 Hz, 2H), 2.50 (ddd, *J* = 17.2, 8.9, 5.0 Hz, 2H), 2.20 (ddd, *J* = 17.1, 7.9, 4.9 Hz, 2H), 1.79 (dtt, *J* = 18.0, 7.9, 5.0 Hz, 1H), 1.42 – 1.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.8, 136.0, 135.4, 133.0, 131.7, 128.7, 128.5, 128.5, 123.3, 113.4, 95.2, 85.3, 68.9, 41.4, 40.5, 39.1, 16.1; HRMS (ESI) calcd for $C_{24}H_{22}ClO_2$ $[M+H]^+$: 377.1308; found: 377.1320;

(Z)-2-Benzyl-2-(5-phenylpent-2-en-4-yn-1-yl)cycloheptane-1,3-dione (1ad):



Prepared according to the general procedure A as described above in 33% yield (470 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.36 – 7.28 (m, 3H), 7.25 – 7.15 (m, 3H), 7.05 (dd, *J* = 7.6, 1.7 Hz, 2H), 5.94 – 5.77 (m, 2H), 3.18 (s, 2H), 2.87 (d, *J* = 6.3 Hz, 2H), 2.47 (dt, *J* = 9.1, 4.2 Hz, 2H), 2.39 (dt, *J* = 11.9, 4.7 Hz, 2H), 1.90 – 1.79 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.4, 136.8, 136.0, 131.6, 130.3, 128.5, 128.5, 127.0, 123.3, 113.0, 95.1, 85.8, 70.1, 42.6, 37.7, 32.7, 28.1; HRMS (ESI) calcd for $C_{25}H_{25}O_2$ $[M+H]^+$: 357.1854; found: 357.1871.

IIIc. Synthesis of substrates 1ae-1as:[3,4]



General procedure B:

Ethyl propiolate **S5** (6 g, 61 mmol) and NaI (14.68 g, 98 mmol) were dissolved in acetic acid (21 mL, 367 mmol) and stirred at 115 °C using a preheated oil bath for 3 hours. Upon completion of the reaction, the reaction mixture was cooled to room temperature and quickly transferred to a separating funnel, charged with 100 mL of H_2O and extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with saturated $NaHCO_3$ (50 mL), saturated $Na_2S_2O_3$ (50 mL), and brine solution (50 mL), then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue **S6** was used directly in the next step.

Residue **S6** was dissolved in dry CH_2Cl_2 (50 mL) and stirred at -78 °C for 10 minutes under an inert atmosphere. Then, DIBAL-H (120 mL, 1.0 M solution in toluene) was added dropwise *via* syringe over 30 minutes, and the reaction mixture was stirred vigorously at the same temperature for an additional 30 minutes. The reaction was then gradually warmed to room temperature and stirred for another 2 hours. After completion of the reaction, the mixture was quenched with saturated sodium potassium tartrate (100 mL), filtered through Celite, and extracted with EtOAc (3 x 100 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to obtain crude allyl alcohol **S11**, which was used directly in the next step without further purification.

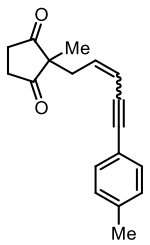
The residue **S11** was dissolved in Et_2O (50 mL) and stirred at 0–5 °C (ice bath). Then, PBr_3 (2.32 mL, 24.4 mmol, 0.4 equiv) was added dropwise to the reaction mixture, which was stirred for 30 minutes at the same temperature. The reaction was quenched with saturated $NaHCO_3$ (50 mL), and the aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced

pressure. The resulting crude residue **S12** was used directly in the next reaction without further purification

To a vigorously stirred suspension of 2-methyl-1,3-cyclopentanedione **S4** (4.48 g, 40.0 mmol) in acetone (60 mL, 1.0 M), K_2CO_3 (48 mmol, 1.2 equiv) was gradually added. After the frothing subsided, the crude residue of 3-bromo-1-iodoprop-1-ene **S12** was added, and the reaction mixture was stirred at 60 °C in a preheated oil bath for overnight. Upon completion, the reaction mixture was concentrated and diluted with water (50 mL). The aqueous phase was extracted with EtOAc (3 × 60 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (hexane/EtOAc) to afford **S13** as a light-yellow liquid in 45% yield (5.02 g) as a mixture of diastereomers. The ^{1}H NMR analysis of the crude product revealed a *Z:E* ratio of 3.5:1; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 – 6.39 (m, 0.5H), 6.32 (dtd, *J* = 8.9, 7.7, 1.2 Hz, 0.5H), 6.20 – 6.04 (m, 1H), 2.86 – 2.74 (m, 3H), 2.73 – 2.61 (m, 1H), 2.44 (dd, *J* = 7.1, 1.3 Hz, 1H), 2.32 (dd, *J* = 7.7, 1.0 Hz, 1H), 1.16 (d, *J* = 1.3 Hz, 1.5H), 1.11 (d, *J* = 1.2 Hz, 1.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.6, 215.1, 139.3, 134.5, 87.0, 80.2, 56.2, 55.7, 41.1, 39.7, 35.4, 35.2, 19.5, 18.1; HRMS (ESI for $C_9H_{12}IO_2$ $[M+H]^+$: calcd: 278.9882; found: 278.9846

The vinyl iodide **S13** (558 mg; 2 mmol, 1 equiv) was added to a 100 mL round-bottom flask, followed by $Pd(PPh_3)_2Cl_2$ (70 mg, 5 mol%), CuI (38 mg, 10 mol%), terminal alkyne **S7** (2.4 mmol, 1.2 equiv), into the 1:1 ratio of Et_3N/THF (8 mL, 0.25 M). The reaction mixture was stirred at room temperature for 12 hours, with progress monitored by TLC. Upon completion, the reaction was quenched with saturated NH_4Cl (20 mL) and extracted with EtOAc (2 x 30 mL). The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (EtOAc/hexanes) to afford the desired product **1** (**1aa**–**1am**).

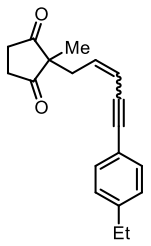
2-Methyl-2-(5-(*p*-tolyl)pent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1ae):



Prepared according to the general procedure B described above in 64% yield (346 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; Z/E ratio = ~6:1 (crude ^{1}H NMR analysis); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz, 1.7H), 7.29 (d, *J* = 8.2

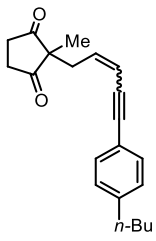
Hz, 0.3H), 7.15 – 7.12 (m, 1.7H), 7.10 (d, *J* = 7.9 Hz, 0.3H), 6.03 – 5.62 (m, 2H), 2.90 – 2.69 (m, 4H), 2.69 – 2.65 (m, 1.7H), 2.45 (dd, *J* = 7.7, 1.2 Hz, 0.3H), 2.35 (s, 2.6H), 2.33 (s, 0.4H), 1.18 (s, 2.6H), 1.15 (s, 0.4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.9, 215.3, 138.7, 138.6, 136.1, 134.9, 131.6, 129.3, 129.2, 120.1, 114.9, 113.8, 95.5, 90.0, 86.7, 84.7, 56.8, 56.7, 38.8, 36.1, 35.5, 35.3, 29.8, 21.7, 19.5, 17.4; HRMS (ESI) calcd for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1385; found: 267.1386.

2-(5-(4-Ethylphenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1af):



Prepared according to the general procedure B described above in 76% yield (426 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; Z/E ratio = 3:1 (crude ^{1}H NMR analysis); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 1.2H), 7.31 (d, *J* = 8.2 Hz, 0.4H), 7.16 (d, *J* = 8.2 Hz, 1.2H), 7.13 (d, *J* = 8.2 Hz, 0.8H), 6.02 – 5.65 (m, 2H), 2.84 (ddd, *J* = 10.4, 7.6, 4.6 Hz, 1.2H), 2.80 – 2.69 (m, 3H), 2.69 – 2.59 (m, 3H), 2.44 (dd, *J* = 7.7, 1.1 Hz, 0.8H), 1.22 (td, *J* = 7.6, 5.4 Hz, 3H), 1.18 (s, 1.8H), 1.14 (s, 1.2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.9, 215.3, 145.0, 144.8, 136.0, 134.9, 131.6, 128.1, 128.0, 120.4, 114.9, 113.8, 95.4, 90.0, 86.7, 84.7, 56.8, 56.7, 38.8, 36.1, 35.5, 35.2, 29.0, 28.9, 19.5, 17.4, 15.5, 15.4; HRMS (ESI) calcd for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1541; found: 281.1539.

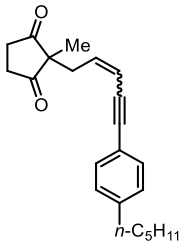
2-(5-(4-Butylphenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1ag):



Prepared according to the general procedure B described above in 70% yield (431 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; Z/E ratio ratio = 2:1 (crude ^{1}H NMR analysis); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 1.4H), 7.30 (d, *J* = 8.2 Hz, 0.6H), 7.14 (d, *J* = 8.2 Hz, 1.4H), 7.10 (d, *J* = 8.2 Hz, 0.6H), 6.00 – 5.68 (m, 2H), 2.92 – 2.70 (m, 4H), 2.67 (dd, *J* = 4.1, 2.2 Hz, 1.4H), 2.60 (dd, *J* = 15.4, 7.6 Hz, 2H), 2.45 (dd, *J* = 7.7, 1.1 Hz, 0.6H), 1.64 – 1.53 (m, 2H), 1.34 (ddd, *J* = 11.0, 9.1, 4.6 Hz, 2H), 1.18 (s, 2.1H), 1.15 (s, 0.9H), 0.95 –

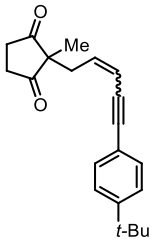
0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.0, 215.3, 143.7, 143.6, 136.0, 134.9, 131.6, 131.5, 128.6, 128.6, 120.3, 120.3, 115.0, 113.9, 95.5, 90.0, 86.7, 84.7, 56.9, 56.7, 38.8, 36.1, 35.7, 35.7, 35.5, 35.3, 33.5, 33.5, 29.8, 22.4, 19.5, 17.4, 14.1; HRMS (ESI) calcd for $C_{21}H_{25}O_2$ $[M+H]^+$: 309.18491; found: 309.18424.

2-Methyl-2-(5-(4-pentylphenyl)pent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1ah):



Prepared according to the general procedure B described above in 65% yield (419 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; Z/E ratio = 2.5:1 (crude ^{1}H NMR analysis); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 1.4H), 7.30 (d, *J* = 8.2 Hz, 0.6H), 7.14 (d, *J* = 8.3 Hz, 1.4H), 7.10 (d, *J* = 8.3 Hz, 0.6H), 6.00 – 5.66 (m, 2H), 2.89 – 2.69 (m, 4H), 2.67 (dd, *J* = 3.9, 2.5 Hz, 1.4H), 2.59 (dd, *J* = 16.4, 8.6 Hz, 2H), 2.44 (dd, *J* = 7.8, 1.2 Hz, 0.6H), 1.60 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.36 – 1.26 (m, 4H), 1.18 (s, 2.1H), 1.14 (s, 0.9H), 0.88 (td, *J* = 7.0, 4.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.0, 215.3, 143.8, 143.6, 136.0, 134.9, 131.5, 128.6, 128.6, 120.3, 114.9, 113.8, 95.5, 90.0, 86.7, 84.7, 56.8, 56.7, 38.8, 36.1, 36.0, 35.5, 35.2, 31.5, 31.1, 22.6, 19.5, 17.4, 14.1; HRMS (ESI) calcd for $C_{22}H_{27}O_2$ $[M+H]^+$: 323.2011; found: 323.2010.

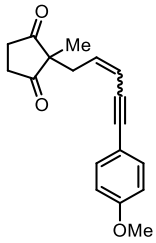
2-(5-(4-(*tert*-Butyl)phenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1ai):



Prepared according to the general procedure B described above in 68% yield (419 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; Z/E ratio = 3.5:1 (crude ^{1}H NMR analysis); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 1.6H), 7.35 (d, *J* = 8.5 Hz, 1.6H), 7.32 (d, *J* = 2.3 Hz, 0.8H), 6.02 – 5.66 (m, 2H), 2.89 – 2.70 (m, 4H), 2.67 (dd, *J* = 5.0, 1.3 Hz, 1.6H), 2.45 (dd, *J* = 7.8, 1.0 Hz, 0.4H), 1.31 (s, 7.2H), 1.30 (s, 1.8H), 1.18 (s, 2.4H), 1.15 (s, 0.6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.0, 215.3, 151.9, 151.7, 136.0, 135.0, 131.4, 125.5, 125.4, 120.2,

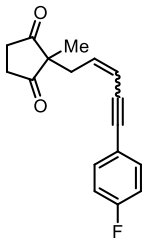
115.0, 113.9, 95.4, 89.9, 86.7, 84.7, 56.8, 56.7, 38.8, 36.1, 35.5, 35.3, 34.9, 31.3, 19.5, 17.4; HRMS (ESI) calcd for $C_{21}H_{25}O_2$ $[M+H]^+$: 309.1854; found: 309.1849.

2-(5-(4-Methoxyphenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1aj):



Prepared according to the general procedure B described above in 63% yield (355 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; Z/E ratio = 2:1 (crude ^{1}H NMR analysis); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 1.3H), 7.35 – 7.31 (m, 0.7H), 6.87 – 6.84 (m, 1.3H), 6.83 – 6.81 (m, 0.7H), 5.92 (dt, *J* = 15.6, 7.8 Hz, 0.35H), 5.85 – 5.75 (m, 1.3H), 5.71 (dd, *J* = 9.0, 7.8 Hz, 0.35H), 3.81 (s, 2H), 3.79 (s, 1H), 2.87 – 2.69 (m, 4H), 2.67 – 2.65 (m, 1.3H), 2.43 (dd, *J* = 7.8, 1.2 Hz, 0.7H), 1.17 (s, 2H), 1.14 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.0, 215.4, 159.9, 159.7, 135.6, 134.5, 133.1, 133.1, 115.3, 115.3, 115.0, 114.2, 114.1, 113.9, 95.3, 89.8, 86.1, 84.1, 56.9, 56.7, 55.4, 38.8, 36.2, 35.5, 35.3, 19.5, 17.4; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1334; found: 283.1335.

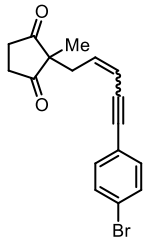
2-(5-(4-Fluorophenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1ak):



Prepared according to the general procedure B as described above in 68% yield (378 g). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a yellow semi-solid; Z/E ratio = 4:1 (crude ^{1}H NMR analysis); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 1.2H), 7.41 – 7.31 (m, 0.8H), 7.08 – 6.94 (m, 2H), 5.94 (ddd, *J* = 23.1, 15.5, 7.3 Hz, 0.4H), 5.86 – 5.80 (m, 1.2H), 5.70 (d, *J* = 15.8 Hz, 0.4H), 2.89 – 2.68 (m, 4H), 2.66 (d, *J* = 6.7 Hz, 1.2H), 2.44 (dd, *J* = 7.7, 1.1 Hz, 0.8H), 1.18 (s, 1.8H), 1.14 (s, 1.2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.4, 162.0 (d, J_{CF} = 249.8 Hz), 162.6 (d, J_{CF} = 249.6 Hz), 135.6, 133.57 (d, J_{CF} = 7.9 Hz), 133.49 (d, J_{CF} = 7.1 Hz), 119.3, 115.80 (d, J_{CF} = 22.1 Hz), 115.7 (d, J_{CF} = 22.1 Hz), 114.6, 113.5, 94.1, 88.6, 87.0, 85.0, 56.8, 56.6, 38.6, 36.0, 35.4,

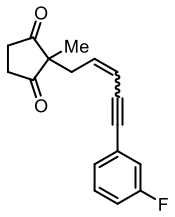
35.3, 19.6, 17.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.7, -110.9; HRMS (ESI) calcd for $C_{17}H_{16}O_2F$ $[M+H]^+$: 271.11288; found: 271.11232.

2-(5-(4-(*tert*-Butyl)phenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1al):



Prepared according to the general procedure B described above in 63% yield (417 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; Z/E ratio = 3:1 (crude ^{1}H NMR analysis); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 1.5H), 7.43 (d, *J* = 8.6 Hz, 0.5H), 7.35 – 7.30 (m, 1.5H), 7.25 (dt, *J* = 6.6, 2.0 Hz, 0.5H), 5.99 (dt, *J* = 15.6, 7.8 Hz, 0.25H), 5.87 (dt, *J* = 10.8, 7.4 Hz, 0.75H), 5.80 (d, *J* = 10.8 Hz, 0.75H), 5.70 (dt, *J* = 15.8, 1.2 Hz, 0.25H), 2.86 – 2.78 (m, 2H), 2.78 – 2.73 (m, 2H), 2.66 (dd, *J* = 7.4, 0.7 Hz, 1.5H), 2.45 (dd, *J* = 7.8, 1.3 Hz, 0.5H), 1.18 (s, 2.4H), 1.15 (s, 0.8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.8, 215.4, 137.2, 136.0, 133.1, 133.0, 131.8, 131.7, 122.8, 122.6, 122.2, 114.5, 113.4, 94.1, 88.6, 88.4, 86.4, 56.8, 56.5, 38.5, 36.0, 35.4, 35.3, 19.6, 17.9; HRMS (ESI) calcd for $C_{17}H_{16}BrO_2$ $[M+H]^+$: 331.0333; found: 331.0325.

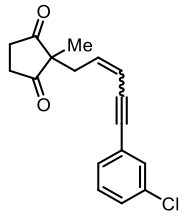
2-(5-(3-Fluorophenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1am):



Prepared according to the general procedure B described above in 72% yield (400 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; Z/E ratio = 2:1 (crude ^{1}H NMR analysis); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 1.7H), 7.19 – 7.15 (m, 0.9H), 7.12 – 6.97 (m, 1.4H), 6.01 (dt, *J* = 15.6, 7.8 Hz, 0.4H), 5.93 – 5.79 (m, 1.2H), 5.72 (dt, *J* = 15.8, 1.2 Hz, 0.4H), 2.87 – 2.69 (m, 4H), 2.67 (dd, *J* = 7.4, 0.8 Hz, 1.2H), 2.46 (dd, *J* = 7.8, 1.3 Hz, 0.8H), 1.19 (s, 1.8H), 1.16 (s, 1.2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.8, 215.3, 162.5 (d, J_{CF} = 246.5 Hz), 162.47 (d, J_{CF} = 246.6 Hz), 137.4, 136.3, 130.1 (d, J_{CF} = 8.4 Hz), 130.0 (d, J_{CF} = 7.8 Hz), 127.6 (d, J_{CF} = 3.0 Hz), 127.5 (d, J_{CF} = 3.0 Hz), 125.0 (d, J_{CF}= 9.5 Hz), 118.4 (d, J_{CF}= 22.7 Hz), 118.4 (d, J_{CF} = 22.7 Hz), 115.9 (d, J_{CF} = 21.2 Hz), 115.7 (d, J_{CF} = 21.3 Hz)., 114.4, 113.3, 93.9, 88.5, 88.2, 86.1, 56.8,

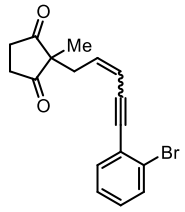
56.5, 38.5, 36.0, 35.4, 35.3, 19.6, 17.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.89, -113.01; HRMS (ESI) calcd for $C_{17}H_{16}O_2F$ $[M+H]^+$: 271.11288; found: 271.11225.

2-(5-(3-Chlorophenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1an):



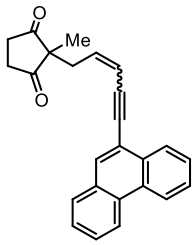
Prepared according to the general procedure B described above in 74% yield (423 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a brown liquid; Z/E ratio = 3:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 1.5 Hz, 0.6H), 7.32 (t, *J* = 1.6 Hz, 0.3H), 7.28 (dt, *J* = 7.2, 1.5 Hz, 0.7H), 7.25 – 7.14 (m, 2.4H), 5.93 (dt, *J* = 15.6, 7.8 Hz, 0.25H), 5.80 (ddd, *J* = 28.5, 16.0, 9.2 Hz, 1.5H), 5.69 – 5.59 (m, 0.25H), 2.80 – 2.63 (m, 4H), 2.60 (dd, *J* = 7.4, 0.8 Hz, 1.5H), 2.39 (dd, *J* = 7.8, 1.3 Hz, 0.5H), 1.11 (d, *J* = 2.1 Hz, 2.2H), 1.09 (s, 0.8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.8, 215.3, 137.5, 136.4, 134.3, 134.3, 131.4, 129.8, 129.7, 129.7, 128.8, 128.6, 124.9, 114.4, 113.2, 93.7, 88.4, 88.3, 86.4, 56.8, 56.5, 38.5, 36.0, 35.4, 35.3, 19.6, 18.0; HRMS (ESI) calcd for $C_{17}H_{16}O_2Cl$ $[M+H]^+$: 287.08333; found: 287.08270.

2-(5-(2-Bromophenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1ao):



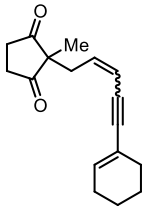
Prepared according to the general procedure B described above in 62% yield (410 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; Z/E ratio = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H), 7.49 (dd, *J* = 7.7, 1.6 Hz, 0.7H), 7.44 – 7.39 (m, 0.3H), 7.29 – 7.22 (m, 1H), 7.18 (d, *J* = 1.6 Hz, 1H), 6.05 (dt, *J* = 15.7, 7.8 Hz, 0.3H), 5.95 (dt, *J* = 10.7, 7.6 Hz, 0.7H), 5.87 (d, *J* = 10.7 Hz, 0.7H), 5.77 (d, *J* = 15.8 Hz, 0.3H), 2.88 (dt, *J* = 7.3, 6.1 Hz, 1.4H), 2.83 (dd, J = 8.8, 6.5 Hz, 0.3H), 2.80 – 2.70 (m, 3.7H), 2.47 (dd, *J* = 7.8, 1.0 Hz, 0.6H), 1.19 (s, 2.1H), 1.15 (s, 0.9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.8, 215.1, 137.6, 136.7, 133.6, 133.4, 132.5, 129.7, 129.5, 127.2, 127.1, 125.5, 125.4, 125.4, 125.3, 114.5, 113.4, 93.5, 91.7, 89.9, 88.2, 56.8, 56.6, 38.6, 36.0, 35.5, 35.2, 19.6, 17.0; HRMS (ESI) calcd for $C_{17}H_{16}BrO_2$ $[M+H]^+$: 331.0333; found: 331.0325.

2-Methyl-2-(5-(phenanthren-9-yl)pent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1ap):



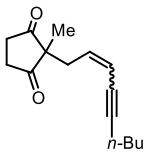
Prepared according to the general procedure B described above in 60% yield (422 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown liquid; Z/E ratio = 3.5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 – 8.63 (m, 2H), 8.51 – 8.46 (m, 0.8H), 8.39 – 8.33 (m,0.2H), 8.03 (s, 0.8H), 7.96 (s, 0.2H), 7.90 – 7.86 (m, 0.8H), 7.86 – 7.82 (m, 0.2H), 7.76 – 7.64 (m, 3H), 7.64 – 7.56 (m, 1H), 6.13 (dt, *J* = 15.6, 7.7 Hz, 0.2H), 6.02 (d, *J* = 10.7 Hz, 0.8H), 6.00 – 5.88 (m, 1H), 2.92 – 2.73 (m, 5.6H), 2.54 (dd, *J* = 7.7, 1.3 Hz, 0.2H), 1.25 (s, 2.4H), 1.20 (s, 0.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.9, 215.3, 136.9, 135.7, 132.2, 132.0, 131.3, 131.1, 130.5, 130.2, 128.8, 128.7, 127.7, 127.6, 127.3, 127.1, 122.9, 122.8, 119.7, 114.9, 113.8, 93.6, 91.8, 89.8, 88.1, 56.9, 56.6, 38.7, 36.2, 35.5, 35.3, 19.7, 17.7; HRMS (ESI) calcd for $C_{25}H_{21}O_2$ $[M+H]^+$: 353.1541; found: 353.1542.

2-(5-(Cyclohex-1-en-1-yl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1aq):



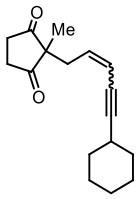
Prepared according to the general procedure described above in 68% yield (348 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown liquid; Z/E ratio = 6.5:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 – 6.09 (m, 0.85H), 6.07 (dd, *J* = 3.8, 2.0 Hz, 0.15H), 5.87 – 5.56 (m, 2H), 2.90 – 2.66 (m, 4H), 2.61 – 2.53 (m, 1.7H), 2.39 (dd, *J* = 7.7, 0.9 Hz, 0.3H), 2.19 – 2.06 (m, 4H), 1.69 – 1.50 (m, 4H), 1.13 (s, 2.55H), 1.11 (s, 0.45H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.0, 215.3, 135.6, 135.4, 135.2, 133.9, 120.8, 120.7, 115.1, 114.0, 97.3, 91.7, 84.7, 82.7, 56.8, 56.7, 38.8, 36.1, 35.4, 35.2, 29.2, 25.9, 22.4, 21.6, 19.4, 17.1; HRMS (ESI) calcd for $C_{17}H_{21}O_2$ $[M+H]^+$: 257.1541; found: 257.1547.

2-Methyl-2-(non-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1ar):



Prepared according to the general procedure B as described above in 62% yield (288 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a brown liquid; Z/E ratio = 4:1 (crude ^{1}H NMR analysis); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (dt, *J* = 15.5, 7.7 Hz, 0.2H), 5.69 – 5.54 (m, 1.6H), 5.47 (dtd, *J* = 14.4, 2.2, 1.1 Hz, 0.2H), 2.88 – 2.63 (m, 4H), 2.58 – 2.52 (m, 1.6H), 2.37 – 2.34 (m, 0.4H), 2.34 – 2.30 (m, 1.6H), 2.24 (td, *J* = 7.0, 2.0 Hz, 0.4H), 1.57 – 1.45 (m, 2H), 1.45 – 1.33 (m, 2H), 1.12 (s, 2.4H), 1.10 (s, 0.6H), 0.90 (dt, *J* = 12.8, 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.0, 215.4, 134.7, 133.6, 115.3, 114.1, 96.7, 90.9, 78.3, 76.4, 56.8, 56.6, 38.8, 36.0, 35.4, 35.2, 30.8, 22.1, 19.3, 19.3, 19.1, 17.1, 13.7; HRMS (ESI) calcd for $C_{15}H_{21}O_2$ $[M+H]^+$: 233.1541; found: 233.1553.

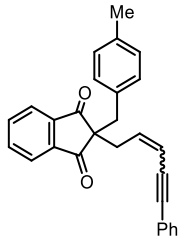
2-(5-Cyclohexylpent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1as):



Prepared according to the general procedure B as described above in 57% yield (295 Mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a brown liquid; Z/E ratio = 3:1 (crude ^{1}H NMR analysis); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (dt, *J* = 15.6, 7.8 Hz, 0.3H), 5.63 (tdd, *J* = 11.5, 6.3, 4.1 Hz, 1.5H), 5.52 – 5.45 (m, 0.2H), 2.90 – 2.64 (m, 4H), 2.56 (d, *J* = 7.0 Hz, 1.5H), 2.51 (ddd, *J* = 9.0, 6.6, 2.8 Hz, 0.8H), 2.44 – 2.38 (m, 0.2H), 2.35 (dd, *J* = 7.7, 1.1 Hz, 0.5H), 1.80 (dd, *J* = 17.0, 8.5 Hz, 2H), 1.69 (tdd, *J* = 10.0, 7.2, 3.5 Hz, 2.7H), 1.58 – 1.53 (m, 0.3H), 1.53 – 1.36 (m, 3H), 1.36 – 1.32 (m, 1H), 1.30 – 1.23 (m, 1H), 1.13 (s, 2.3H), 1.10 (s, 0.7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.0, 215.3, 134.5, 133.5, 115.3, 114.2, 100.7, 95.0, 78.2, 76.3, 56.8, 56.7, 38.8, 36.1, 35.4, 35.2, 32.7, 29.9, 29.8, 26.0, 25.0, 19.3, 17.1; HRMS (ESI) calcd for $C_{17}H_{23}O_2$ $[M+H]^+$: 259.1698; found: 259.1710.

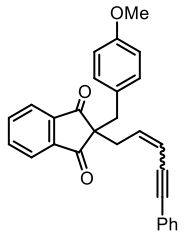
IIId. Synthesis of substrates 3a-3e: These substrates were prepared as a mixture of Z/E-isomers by using general procedure A.[2,3]

2-(4-Methylbenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3a):



Prepared according to the general procedure A described above in 34% yield (530 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a yellow semi-solid; Z/E ratio = 2.5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.61 (dd, *J* = 5.6, 2.9 Hz, 2H), 7.50 – 7.46 (m, 1.6H), 7.33 – 7.28 (m, 2.8H), 7.24 – 7.20 (m, 0.6H), 6.90 (d, *J* = 8.0 Hz, 1.6H), 6.86 (d, *J* = 8.1 Hz, 0.4H), 6.81 (d, *J* = 7.9 Hz, 2H), 5.96 (dt, *J* = 15.5, 7.7 Hz, 0.2H), 5.84 (dt, *J* = 10.7, 7.6 Hz, 0.8H), 5.75 (d, *J* = 15.7 Hz, 0.2H), 5.70 (d, *J* = 10.8 Hz, 0.8H), 3.22 (s, 1.6H), 3.12 (s, 0.4H), 2.98 (dd, *J* = 7.7, 0.9 Hz, 1.6H), 2.73 (dd, *J* = 7.7, 0.8 Hz, 0.4H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 202.9, 142.2, 142.1, 137.0, 136.2, 136.1, 135.9, 135.6, 135.5, 132.4, 132.0, 131.9, 131.5, 131.4, 129.8, 129.6, 128.7, 128.3, 128.2, 123.3, 122.8, 114.3, 113.1, 95.1, 89.3, 87.4, 85.4, 60.0, 59.7, 40.4, 39.5, 38.4, 35.8, 20.8; HRMS (ESI) calcd for $C_{28}H_{23}O_2$ $[M+H]^+$: 391.16926; found: 391.16843.

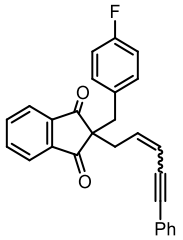
2-(4-Methoxybenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3b):



Prepared according to the general procedure A described above in 37% yield (600 mg). It was purified by flash chromatography (25% EtOAc/hexanes; R_f = 0.4) to afford a yellow semi-solid; Z/E ratio = 3:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 2H), 7.65 – 7.55 (m, 2H), 7.47 (dd, *J* = 4.6, 3.2 Hz, 1.6H), 7.33 – 7.24 (m, 2.8H), 7.20 (dd, *J* = 6.4, 3.5 Hz, 0.6H), 6.92 (d, *J* = 8.7 Hz, 1.6H), 6.88 (d, *J* = 8.6 Hz, 0.4H), 6.53 (dd, *J* = 8.9, 2.7 Hz, 2H), 5.95 (dt, *J* = 15.5, 7.7 Hz, 0.2H), 5.89 – 5.71 (m, 1H), 5.68 (d, *J* = 10.8 Hz, 0.8H), 3.54 (s, 3H), 3.19 (s, 1.6H), 3.10 (s, 0.4H), 2.96 (d, *J* = 7.7 Hz, 1.6H), 2.71 (d, *J* = 7.6 Hz, 0.4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.0, 202.9, 158.2, 158.1, 142.2, 142.0, 136.6, 135.9, 135.5, 135.4, 131.5, 131.3, 130.9, 130.7, 128.2, 128.1, 128.1, 127.4, 127.1, 123.2, 123.0, 122.7,

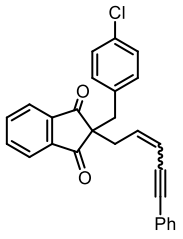
114.2, 113.3, 113.0, 95.1, 89.3, 87.4, 85.4, 60.0, 59.7, 54.8, 40.0, 39.0, 38.3, 35.7; HRMS (ESI) calcd for $C_{28}H_{23}O_3$ $[M+H]^+$: 407.16417; found: 407.16321.

2-(4-Fluorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3c):



Prepared according to the general procedure A described above in 33% yield (520 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a yellow liquid; Z/E ratio = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.64 – 7.54 (m, 2H), 7.39 (ddd, *J* = 6.6, 5.2, 3.9 Hz, 1.8H), 7.37 – 7.32 (m, 0.2H), 7.26 – 7.18 (m, 2.6H), 7.16 – 7.11 (m, 0.4H), 6.91 – 6.85 (m, 1.7H), 6.85 – 6.80 (m, 0.3H), 6.64 – 6.58 (m, 2H), 5.86 (dt, *J* = 15.5, 7.7 Hz, 0.1H), 5.74 (dt, *J* = 10.7, 7.6 Hz, 0.9H), 5.69 – 5.59 (m, 1H), 3.13 (s, 1.7H), 3.03 (s, 0.3H), 2.87 (dd, *J* = 7.6, 1.0 Hz, 1.8H), 2.63 (dd, *J* = 7.7, 1.1 Hz, 0.2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 161.6 (d, J_{CF} = 245.2 Hz), 142.1, 135.7, 131.6, 131.51 (d, J_{CF} = 8.1 Hz), 131.33 (d, J_{CF} = 1.9 Hz), 128.4, 128.3, 123.3, 123.0, 114.93 (d, J_{CF} = 21.2 Hz), 113.3, 95.3, 85.4, 59.7, 38.9, 35.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.7, -116.0; HRMS (ESI) calcd for $C_{27}H_{20}O_2F$ $[M+H]^+$: 395.14418; found: 395.14337.

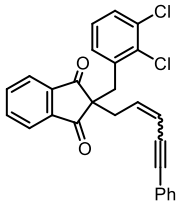
2-(4-Chlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3d):



Prepared according to the general procedure A described above in 35% yield (574 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a brown liquid; Z/E ratio = 3:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 2H), 7.67 – 7.60 (m, 2H), 7.49 – 7.45 (m, 1.5H), 7.34 – 7.26 (m, 2.75H), 7.23 – 7.18 (m, 0.75H), 7.00 – 6.86 (m, 4H), 5.96 (dt, *J* = 15.5, 7.7 Hz, 0.25H), 5.88 – 5.76 (m, 1H), 5.71 (d, *J* = 10.7 Hz, 0.75H), 3.21 (s, 1.5H), 3.11 (s, 0.5H), 2.96 (dd, *J* = 7.6, 0.8 Hz, 1.5H), 2.71 (dd, *J* = 7.7, 0.9 Hz, 0.5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.5, 202.4, 141.8, 136.2, 135.8, 135.7, 135.5, 134.0, 133.7, 132.6, 132.5, 131.5, 131.3, 131.3, 131.1, 128.3, 128.2, 128.1, 123.1,

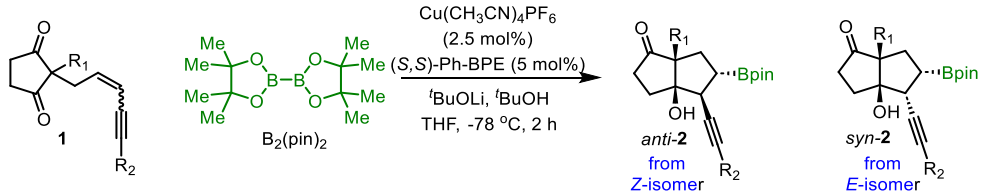
122.9, 114.4, 113.3, 95.2, 89.4, 87.3, 85.3, 59.7, 59.4, 39.6, 38.7, 38.5, 35.8; HRMS (ESI) calcd for $C_{27}H_{20}O_2Cl$ $[M+H]^+$: 411.11463; found: 411.11348.

2-(2,3-Dichlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3e):



Prepared according to the general procedure A described above in 32% yield (570 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a yellow liquid; Z/E ratio = 2.5:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 2H), 7.78 – 7.72 (m, 2H), 7.50 – 7.44 (m, 1.6H), 7.35 – 7.27 (m, 3H), 7.24 – 7.21 (m, 0.4H), 7.18 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.03 (dd, *J* = 7.8, 1.5 Hz, 0.8H), 6.99 (dd, *J* = 7.8, 1.8 Hz, 0.2H), 6.92 (dt, *J* = 11.0, 7.8 Hz, 1H), 5.96 – 5.84 (m, 0.2H), 5.84 – 5.76 (m, 1H), 5.71 (d, *J* = 10.7 Hz, 0.8H), 3.44 (s, 1.6H), 3.34 (s, 0.4H), 3.02 (dd, *J* = 7.5, 0.9 Hz, 1.6H), 2.79 (dd, *J* = 7.6, 0.8 Hz, 0.4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 141.8, 141.7, 136.3, 136.1, 135.9, 135.9, 135.7, 133.3, 133.1, 133.0, 131.6, 131.4, 130.1, 130.0, 129.4, 129.2, 128.3, 128.2, 126.7, 123.2, 114.8, 113.5, 95.3, 89.5, 87.4, 85.4, 58.8, 58.2, 38.4, 37.5, 37.2, 35.1; HRMS (ESI) calcd for $C_{27}H_{19}O_2Cl_2$ $[M+H]^+$: 445.07566; found: 445.07462.

IIIe. General procedure for enantioselective borylative cyclization:

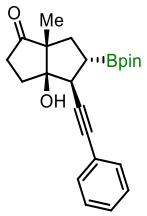


A solution of $Cu(CH_3CN)_4PF_6$ (2.8 mg, 2.5 mol%) and (*S*,*S*)-BPE (7.6 mg, 5 mol%) in dry THF (2.0 mL, 0.1 M) was stirred at room temperature under a nitrogen atmosphere for 10 minutes, then cooled to -78 °C. A solution of the substrate **1** (0.3 mmol) in dry THF (1.0 mL) was added *via* syringe, followed by the sequential addition of $B_2(pin)_2$ (91 mg, 0.36 mmol), ^{t}BuOH (57 µL, 0.6 mmol), and LiO^tBu (54 µL, 0.6 mmol, 1.0 M in THF) into the reaction mixture. The reaction mixture was stirred at -78 °C for 2 hours. Upon completion, the reaction was quenched by adding saturated NH_4Cl solution (5 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude

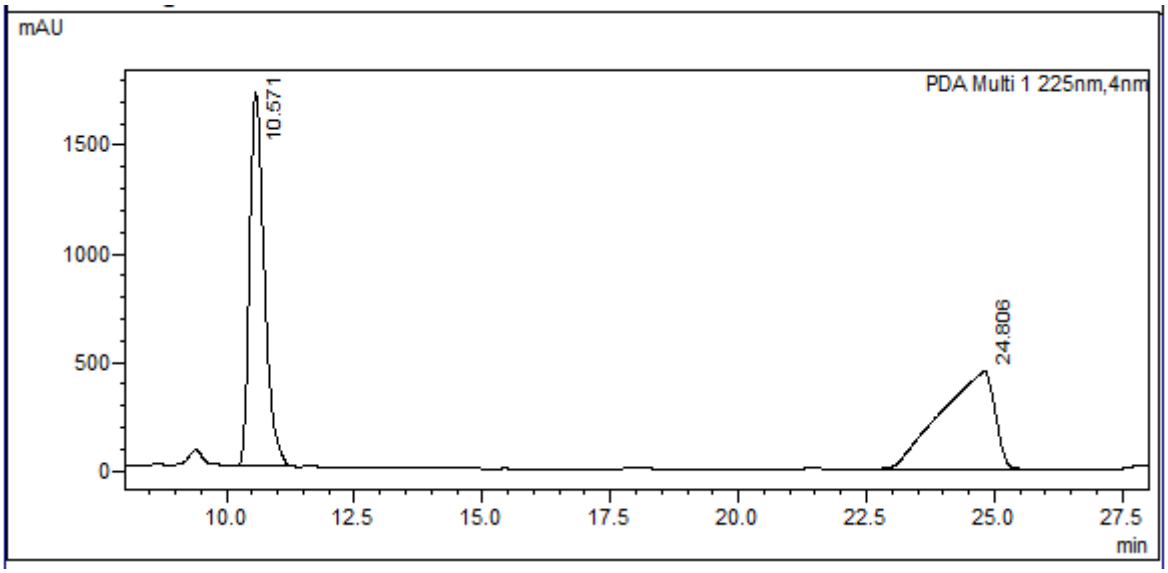
product was purified by column chromatography (EtOAc/hexanes) to afford the desired product **2** with high enantioselectivity and diastereoselectivity.

[*Note*: For the preparation of racemic products, the same reaction procedure was followed using (*rac*)-BINAP as the ligand].

(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (*anti*-2a):



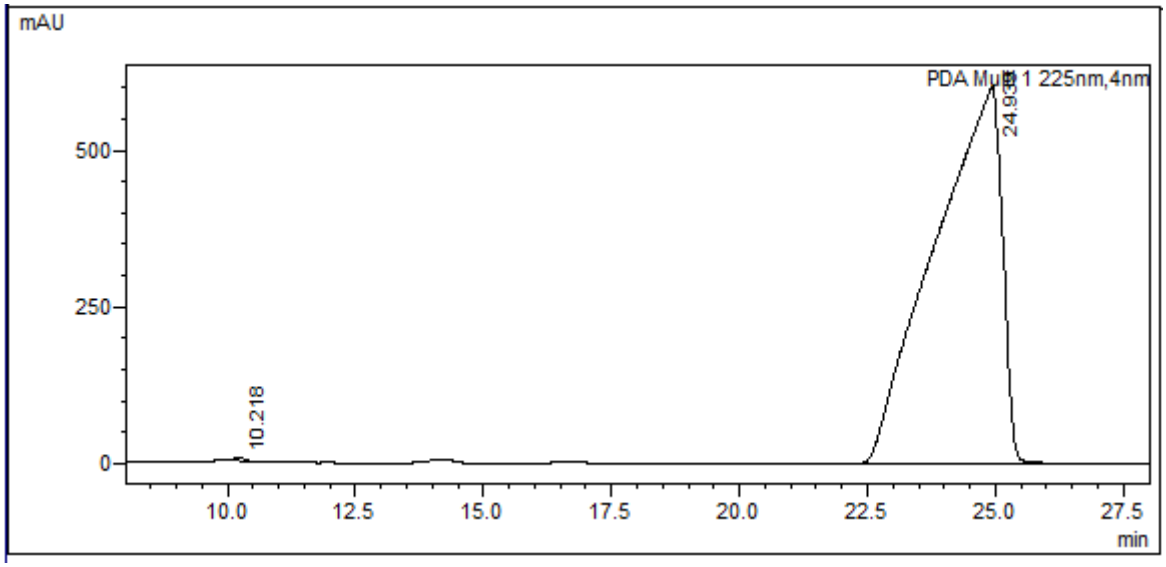
Prepared according to the general procedure as described above in 82% yield (93 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 102–104°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.33 – 7.28 (m, 3H), 2.86 (d, *J* = 10.5 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.42 (dd, *J* = 19.3, 9.3 Hz, 1H), 2.24 (ddd, *J* = 12.8, 8.9, 3.8 Hz, 1H), 2.00 (dt, *J* = 13.3, 9.9 Hz, 1H), 1.91 (qd, *J* = 9.7, 4.4 Hz, 2H), 1.85 – 1.78 (m, 1H), 1.24 (s, 12H), 1.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 221.2, 131.9, 128.4, 128.4, 123.0, 87.8, 87.3, 85.3, 83.8, 59.4, 44.9, 37.1, 35.8, 30.5, 24.9, 24.7, 17.0; HRMS (ESI) calcd for $C_{23}H_{30}O_4B$ $[M+H]^+$: 381.2232; found: 381.2223; $[\alpha]^{20}_D$ = -61.66° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 225 nm, Flow rate = 1 mL/min, Retention times: 24.939 min (major), 10.218 min (minor).



<Peak Table>

PDA Ch1 225nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.571	34512249	1722466	51.057	79.234
2	24.806	33082817	451430	48.943	20.766
Total		67595067	2173897	100.000	100.000

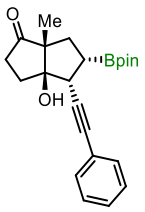


<Peak Table>

PDA Ch1 225nm

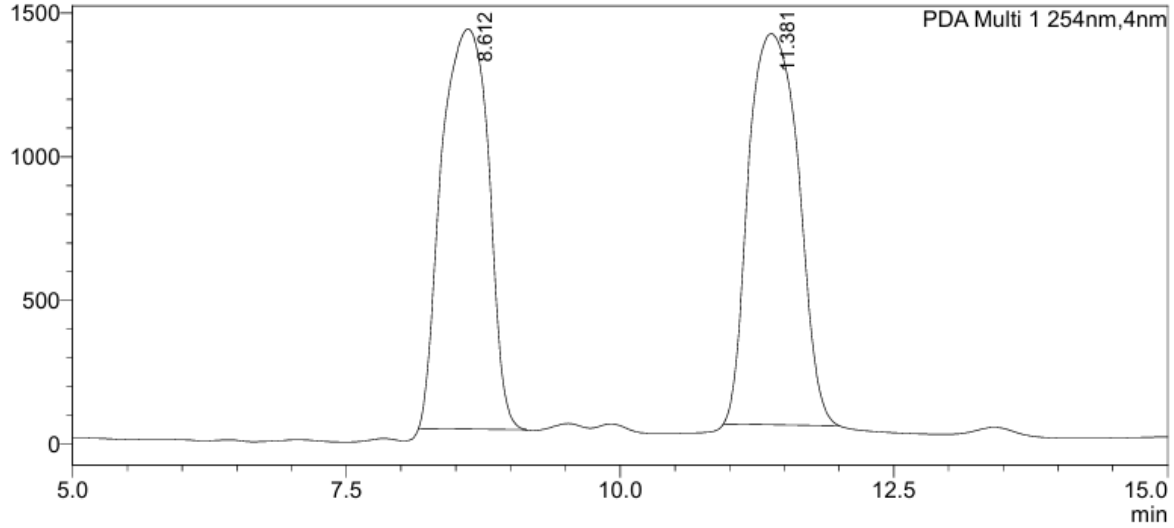
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.218	84460	4820	0.153	0.795
2	24.939	55186661	601846	99.847	99.205
Total		55271121	606666	100.000	100.000

(3a*R*,4*R*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (*syn*-2a):



Prepared according to the general procedure as described above in 47% yield (54 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.33 – 7.28 (m, 3H), 3.12 (d, *J* = 7.8 Hz, 1H), 2.57 (dt, *J* = 18.7, 8.4 Hz, 1H), 2.39 – 2.27 (m, 1H), 2.19 (dd, *J* = 13.9, 8.9 Hz, 1H), 2.12 (t, *J* = 8.5 Hz, 2H), 1.86 (dd, *J* = 13.9, 8.4 Hz, 1H), 1.68 (dd, *J* = 16.7, 8.4 Hz, 2H), 1.24 (s, 12H), 1.15 (s, 3H); ^{13}C NMR (101 MHz,

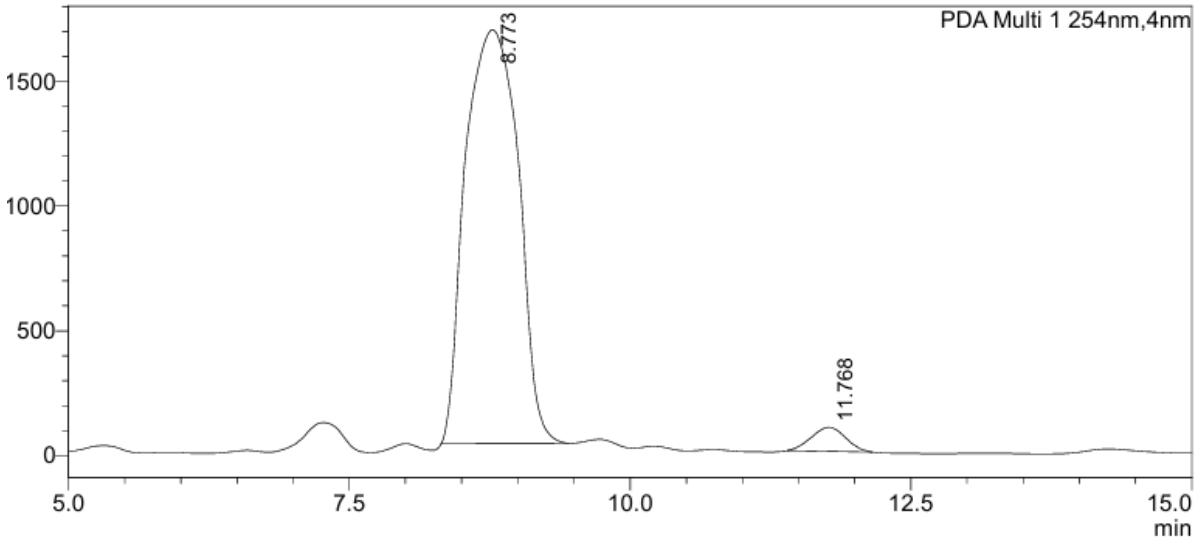
$CDCl_3$) δ 222.4, 131.8, 128.4, 128.3, 123.1, 88.0, 87.3, 86.0, 84.2, 58.9, 44.9, 36.8, 36.1, 31.1, 25.0, 24.9, 19.3; HRMS (ESI) calcd for $C_{23}H_{30}O_4B$ $[M+H]^+$: 381.2239; found: 381.2271; $[\alpha]^{20}_D$ = -66.10° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 92% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 94/06, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 8.773 min (major), 11.768 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.612	41631515	1392761	49.115	50.583
2	11.381	43131477	1360645	50.885	49.417
Total		84762993	2753406	100.000	100.000

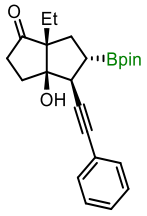


<Peak Table>

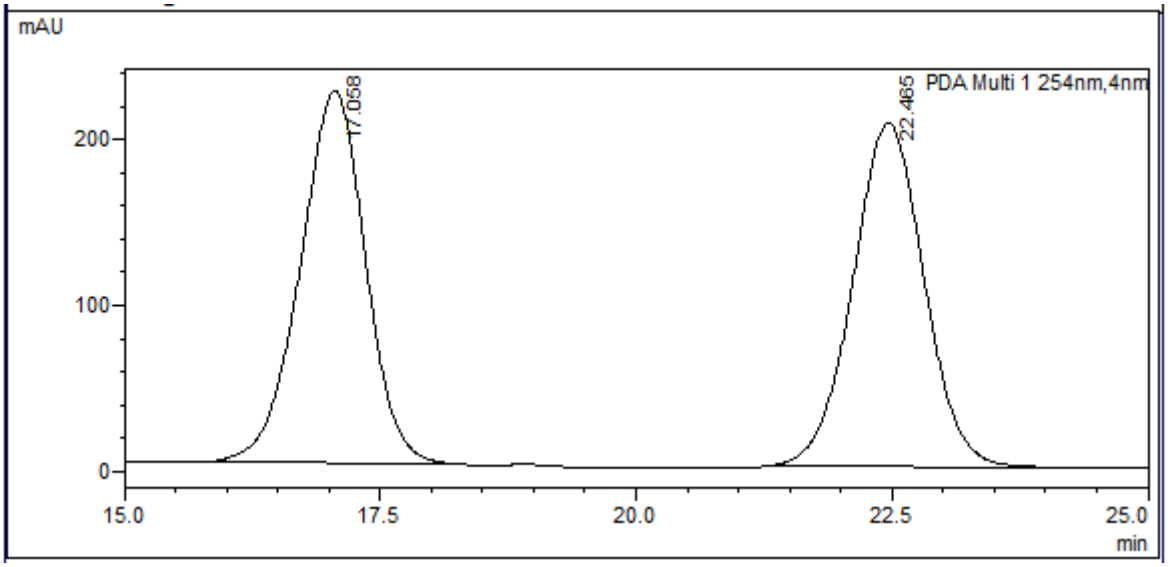
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.773	54364632	1656703	96.409	94.548
2	11.768	2024706	95528	3.591	5.452
Total		56389338	1752231	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-6a-Ethyl-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2b):



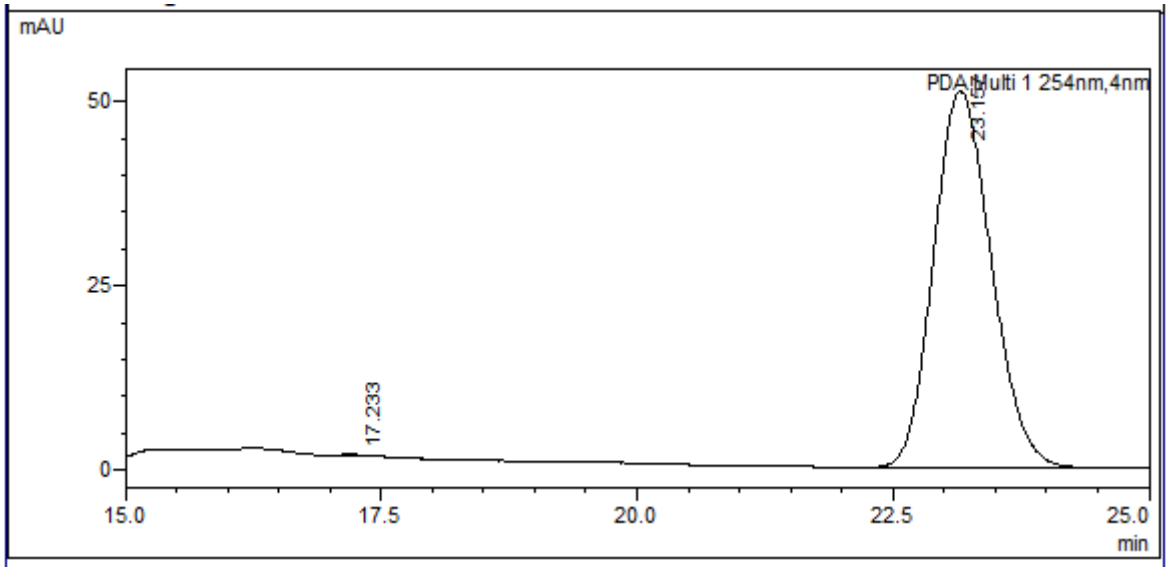
Prepared according to the general procedure as described above in 77% yield (91 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.35 – 7.28 (m, 3H), 2.73 (d, *J* = 11.3 Hz, 1H), 2.52 (ddd, *J* = 19.4, 10.7, 2.4 Hz, 1H), 2.46 – 2.35 (m, 2H), 2.33 – 2.24 (m, 1H), 2.09 – 1.92 (m, 1H), 1.91 – 1.82 (m, 2H), 1.75 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.66 (dd, *J* = 14.0, 7.3 Hz, 1H), 1.23 (s, 12H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.1, 131.9, 128.4, 128.4, 123.1, 88.1, 86.8, 85.0, 83.7, 63.1, 45.6, 36.4, 35.4, 30.3, 25.5, 24.9, 24.7, 9.5; HRMS (ESI) calcd for $C_{24}H_{32}O_4B$ $[M+H]^+$: 395.2388; found: 395.2377; $[\alpha]^{20}_D$ = -89.83° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 94/06, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 23.157 min (major), 17.233 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.058	10001846	224816	49.925	52.033
2	22.465	10032046	207252	50.075	47.967
Total		20033892	432068	100.000	100.000

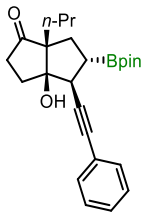


<Peak Table>

PDA Ch1 254nm

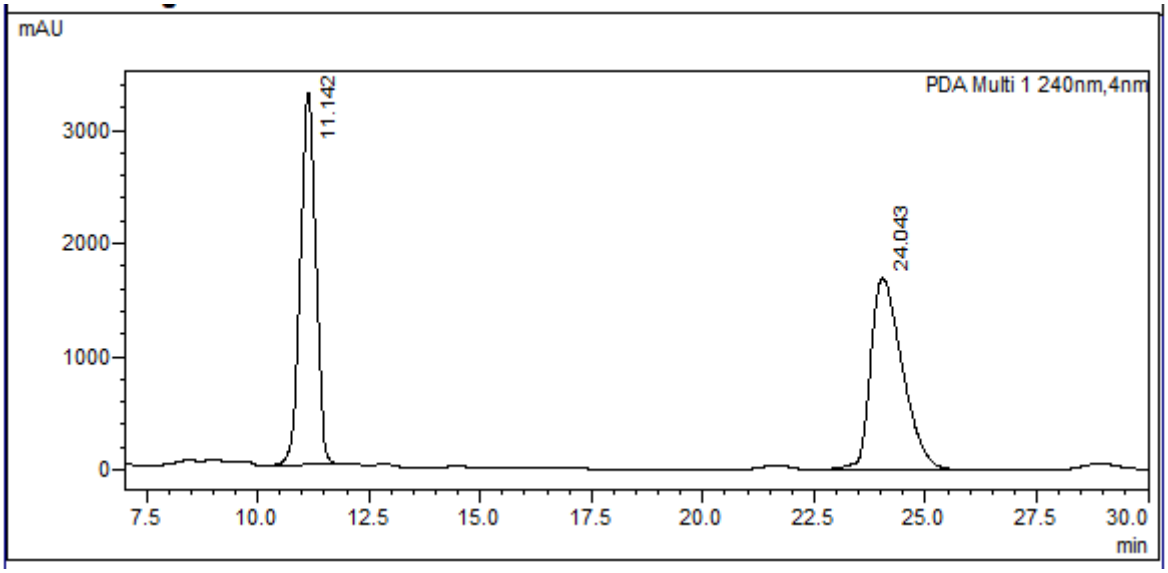
Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.233	444	53	0.022	0.104
2	23.157	2005068	51049	99.978	99.896
Total		2005511	51102	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-4-(phenylethynyl)-6a-propyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2c):



Prepared according to the general procedure as described above in 71% yield (87 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford a white solid; mp = 122–124°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.32 – 7.28 (m, 3H), 2.72 (d, *J* = 11.3 Hz, 1H), 2.52 (ddd, *J* = 19.5, 10.7, 2.2 Hz, 1H), 2.40 (dt, *J* = 19.5, 9.7 Hz, 1H), 2.31 – 2.24 (m, 1H), 2.02 (dt, *J* = 13.1, 10.5 Hz, 1H), 1.95 (dd, *J* = 5.6, 3.5 Hz, 1H), 1.93 – 1.82 (m, 3H), 1.61 (dtd, *J* = 25.7, 13.6, 4.5 Hz, 2H), 1.48 – 1.38 (m, 1H), 1.23 (s, 12H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.2, 131.9, 128.4, 128.3, 123.0, 88.1, 86.8, 85.0, 83.7, 62.9, 45.5, 36.3, 35.8, 35.0, 30.2, 24.9, 24.7,

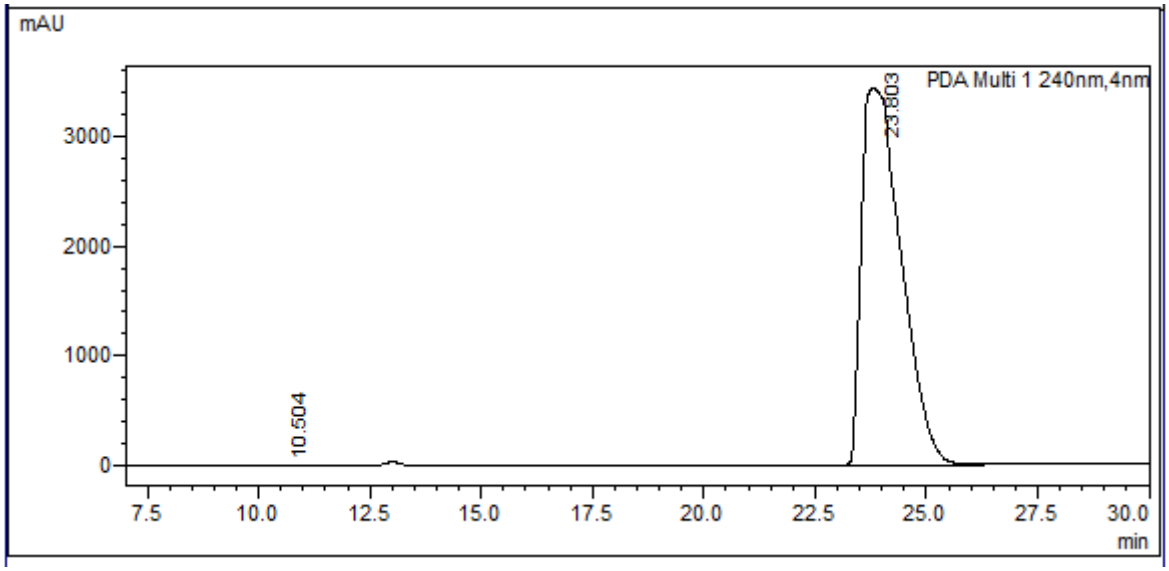
18.3, 14.9; HRMS (ESI) calcd for $C_{25}H_{34}O_4B$ $[M+H]^+$: 409.2545; found: 409.2334; $[\alpha]^{20}_D$ = -55.49° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 240 nm, Flow rate = 1 mL/min, Retention times: 23.803 min (major), 10.504 min (minor).



<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.142	79652340	3286759	48.748	66.039
2	24.043	83744698	1690237	51.252	33.961
Total		163397038	4976996	100.000	100.000

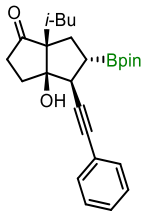


<Peak Table>

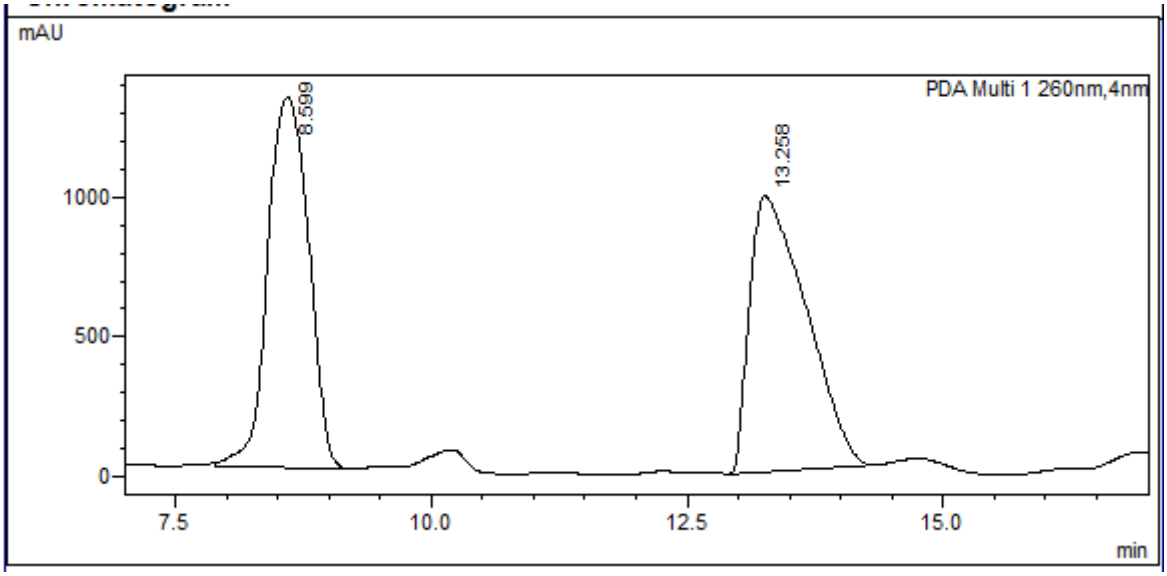
PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.504	642	26	0.000	0.001
2	23.803	214240015	3436088	100.000	99.999
Total		214240658	3436113	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-isobutyl-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2d):



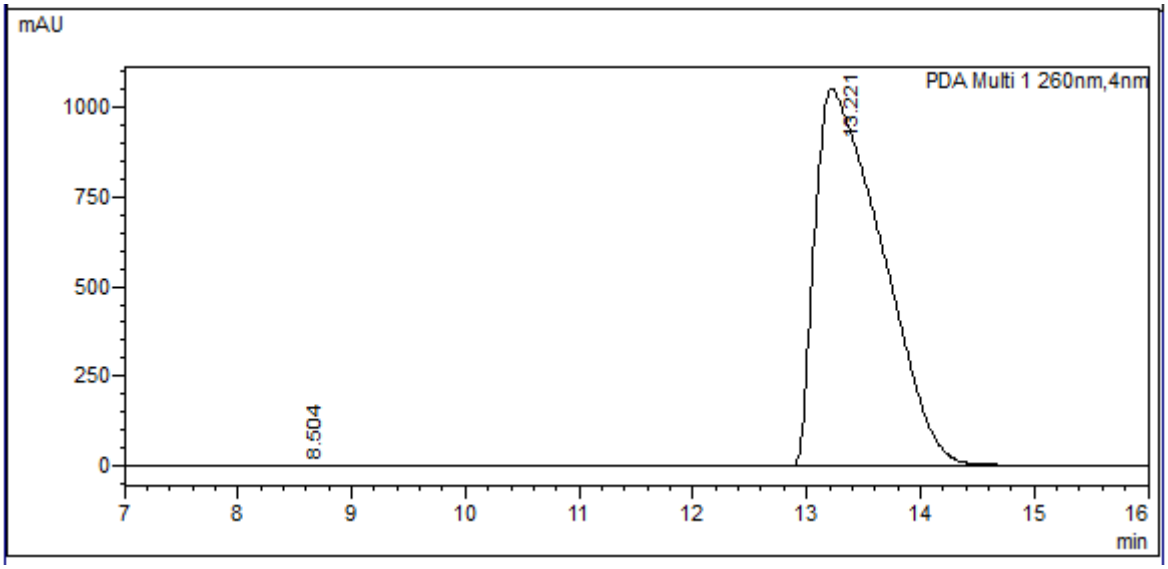
Prepared according to the general procedure as described above in 69% yield (87 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford a light white semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.33 – 7.27 (m, 3H), 2.64 (d, *J* = 11.9 Hz, 1H), 2.57 (ddd, *J* = 19.3, 11.1, 2.1 Hz, 1H), 2.43 – 2.32 (m, 1H), 2.25 (ddd, *J* = 11.8, 9.4, 2.2 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.88 (ddd, *J* = 22.0, 19.5, 10.0 Hz, 2H), 1.74 – 1.66 (m, 1H), 1.62 (d, *J* = 4.4 Hz, 1H), 1.55 (dd, *J* = 14.2, 7.9 Hz, 1H), 1.24 (s, 12H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.3, 131.9, 128.4, 128.3, 123.1, 88.6, 86.9, 84.9, 83.7, 62.9, 44.7, 41.3, 36.0, 35.6, 29.6, 25.2, 25.0, 24.9, 24.7, 24.0; HRMS (ESI) calcd for $C_{26}H_{36}O_4B$ $[M+H]^+$: 423.2701; found:423.2690; $[\alpha]^{20}_D$ = -109.16° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 260 nm, Flow rate = 1 mL/min, Retention times: 13.221 min (major), 8.504 min (minor).



<Peak Table>

PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.599	37101290	1327105	49.414	57.339
2	13.258	37980732	987366	50.586	42.661
Total		75082022	2314471	100.000	100.000

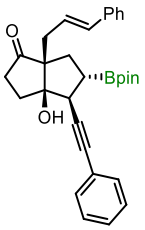


<Peak Table>

PDA Ch1 260nm

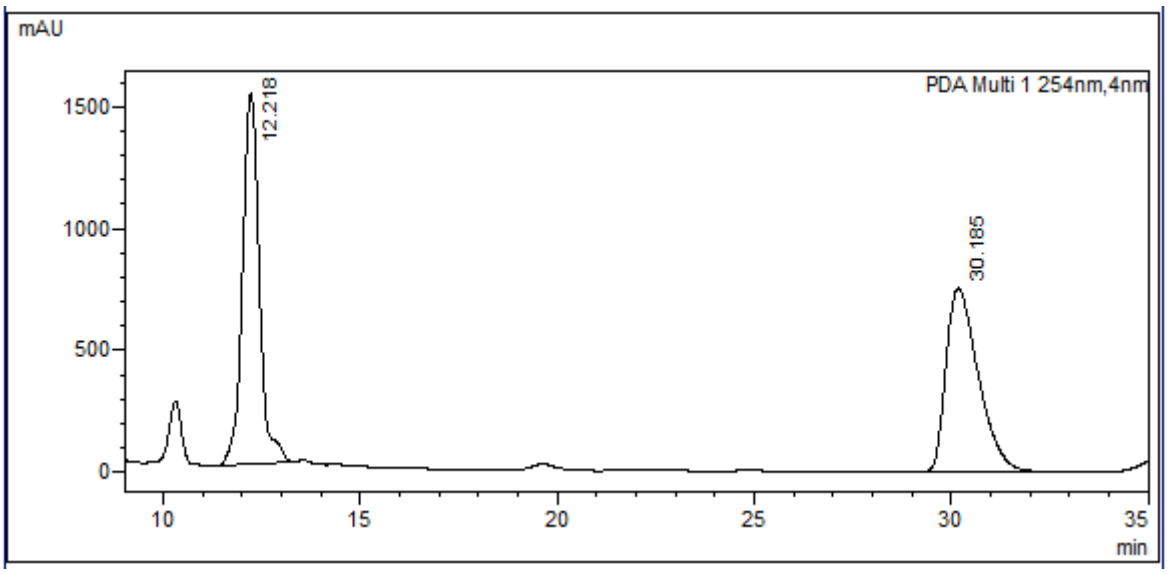
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.504	56011	1951	0.130	0.185
2	13.221	43114886	1051058	99.870	99.815
Total		43170897	1053009	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-Cinnamyl-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2e):



Prepared according to the general procedure as described above in 67% yield (97 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.27 – 7.20 (m, 6H), 7.14 – 7.06 (m, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.29 – 6.20 (m, 1H), 2.72 (dd, *J* = 7.4, 4.4 Hz, 1H), 2.50 (d, *J* = 7.6 Hz, 2H), 2.41 – 2.34 (m, 2H), 2.22 (ddd, *J* = 12.0, 7.9, 4.1 Hz, 1H), 1.96 (dt, *J* = 13.0, 10.2 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.16 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.2, 137.5, 133.2, 131.9, 128.6, 128.5, 128.4, 127.3, 126.3, 126.1, 123.0, 88.3, 86.7, 85.2, 83.7, 63.2, 45.8, 36.6, 36.5, 36.1, 30.7, 24.9, 24.7; HRMS (ESI) calcd

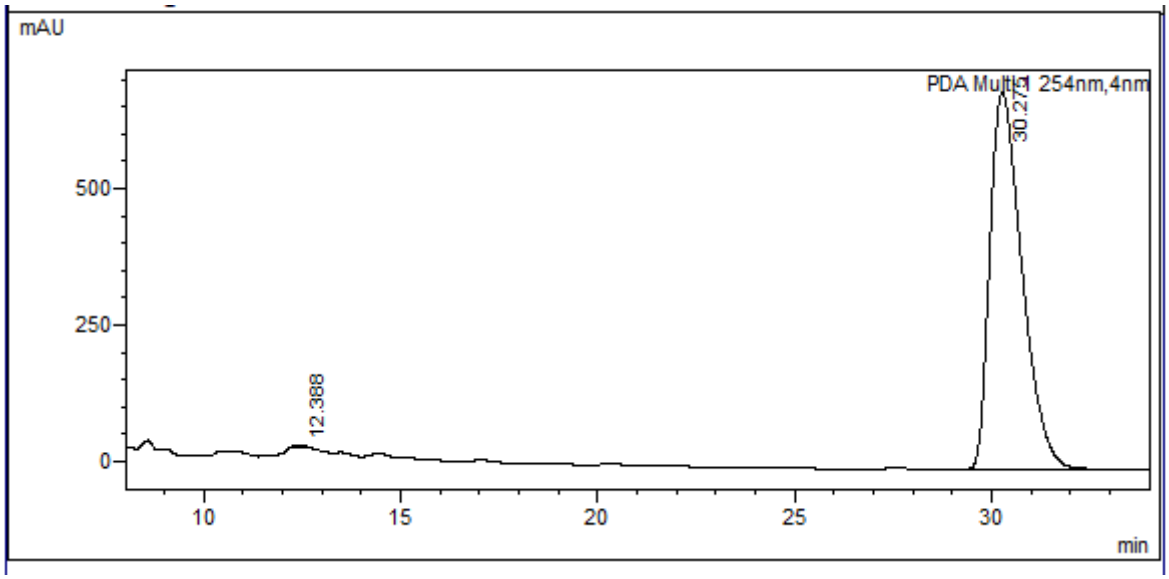
for $C_{31}H_{36}O_4B$ $[M+H]^+$: 483.2701; found: 483.2691; $[\alpha]^{20}_D$ = -32.86° (*c* 0.5, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 30.275 min (major), 12.388 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.218	45500816	1522359	51.551	66.921
2	30.185	42762422	752490	48.449	33.079
Total		88263238	2274849	100.000	100.000

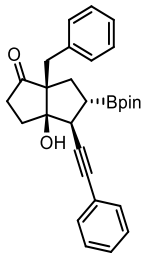


<Peak Table>

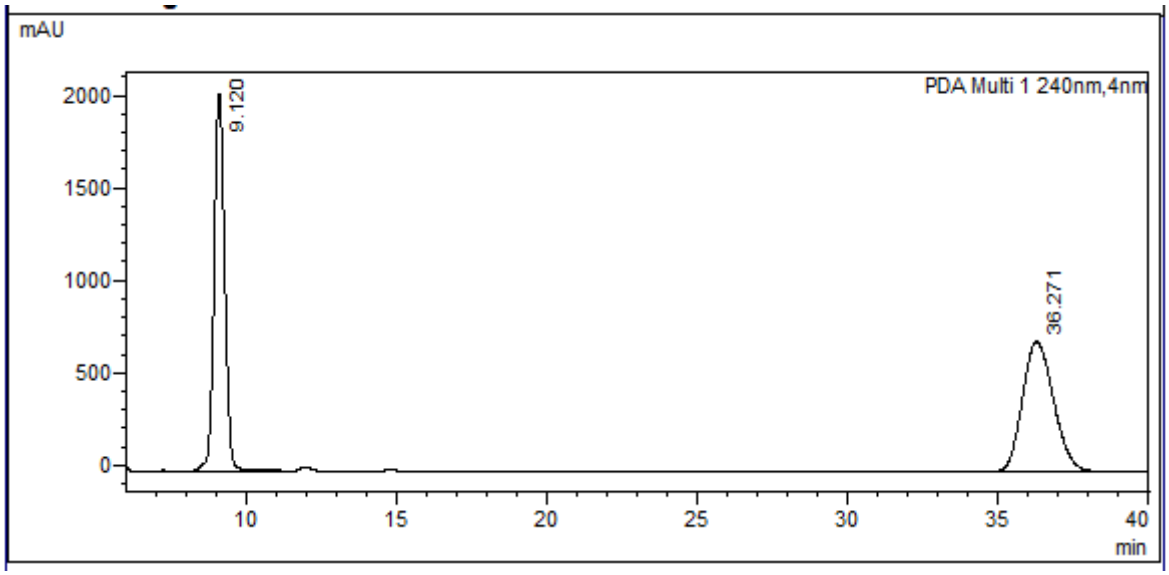
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.388	80045	4363	0.203	0.627
2	30.275	39330708	690991	99.797	99.373
Total		39410753	695353	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-Benzyl-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2f):



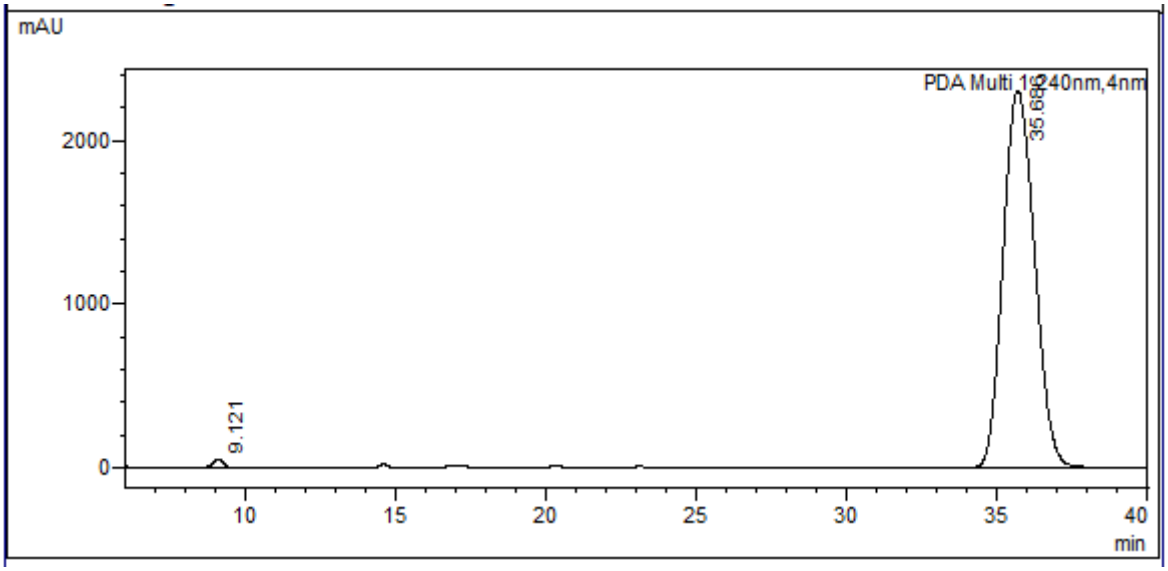
Prepared according to the general procedure as described above in 82% yield (112 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a white solid; mp = 159–161°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.23 (d, *J* = 2.0 Hz, 2H), 7.23 – 7.10 (m, 6H), 3.01 (d, *J* = 13.2 Hz, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.62 (d, *J* = 11.5 Hz, 1H), 2.42 (br.s, 1H), 2.20 (dt, *J* = 19.4, 9.7 Hz, 1H), 2.04 – 1.95 (m, 2H), 1.96 – 1.85 (m, 3H), 1.41 (dt, *J* = 13.1, 10.6 Hz, 1H), 1.16 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.2, 137.4, 131.9, 130.9, 128.4, 128.4, 128.0, 126.7, 123.0, 88.0, 86.7, 85.0, 83.7, 64.5, 46.1, 39.4, 37.0, 36.9, 29.9, 24.9, 24.7; HRMS (ESI) calcd for $C_{29}H_{34}BO_4$ $[M+H]^+$: 457.2259; found: 457.2557; $[\alpha]^{20}_D$ = -118.80° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 98% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 95/05, detected at 240 nm, Flow rate = 1 mL/min, Retention times: 35.686 min (major), 9.121 min (minor).



<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.120	50073119	2038476	49.780	74.363
2	36.271	50515583	702779	50.220	25.637
Total		100588702	2741254	100.000	100.000

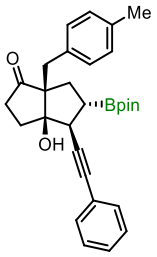


<Peak Table>

PDA Ch1 240nm

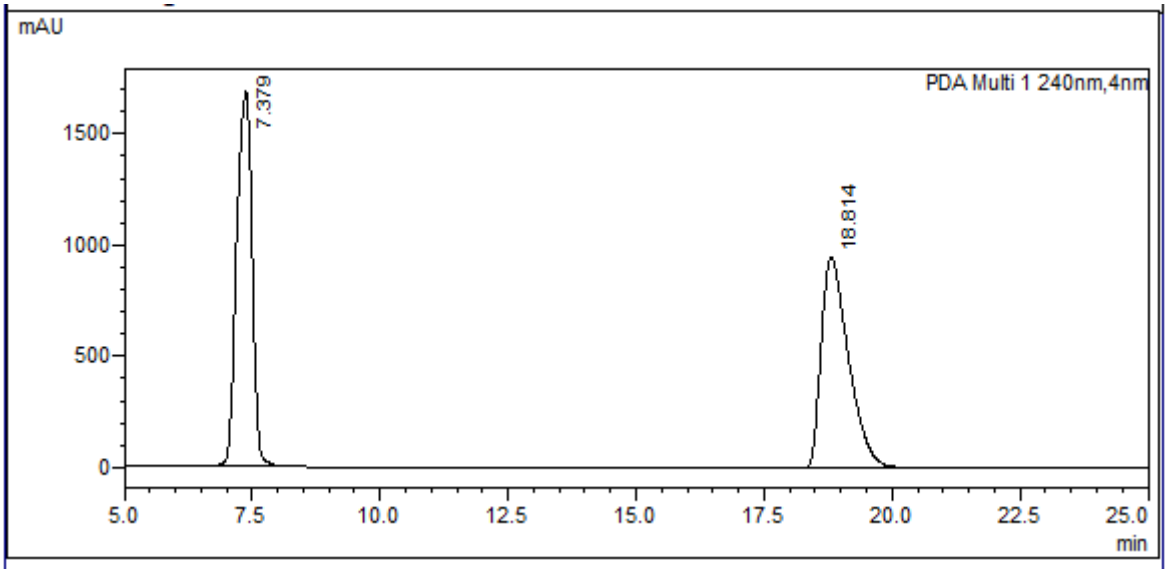
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.121	1101307	52268	0.652	2.220
2	35.686	167861117	2301825	99.348	97.780
Total		168962424	2354093	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-(4-methylbenzyl)-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2g):



Prepared according to the general procedure as described above in 78% yield (110 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 150–152°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.33 – 7.27 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 3.03 (d, *J* = 13.3 Hz, 1H), 2.94 (d, *J* = 13.3 Hz, 1H), 2.68 (d, *J* = 11.4 Hz, 1H), 2.29 (s, 3H), 2.33 – 2.21 (m, 1H), 2.12 – 2.05 (m, 2H), 2.05 – 1.90 (m, 3H), 1.59 – 1.46 (m, 1H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.2, 136.1, 134.2, 131.9, 130.7, 128.7, 128.4, 128.3, 123.1, 88.1, 86.8, 84.9, 83.7, 64.5, 46.0, 38.9, 36.9, 29.9, 24.9, 24.7, 21.2; HRMS (ESI) calcd for $C_{30}H_{36}O_4B$

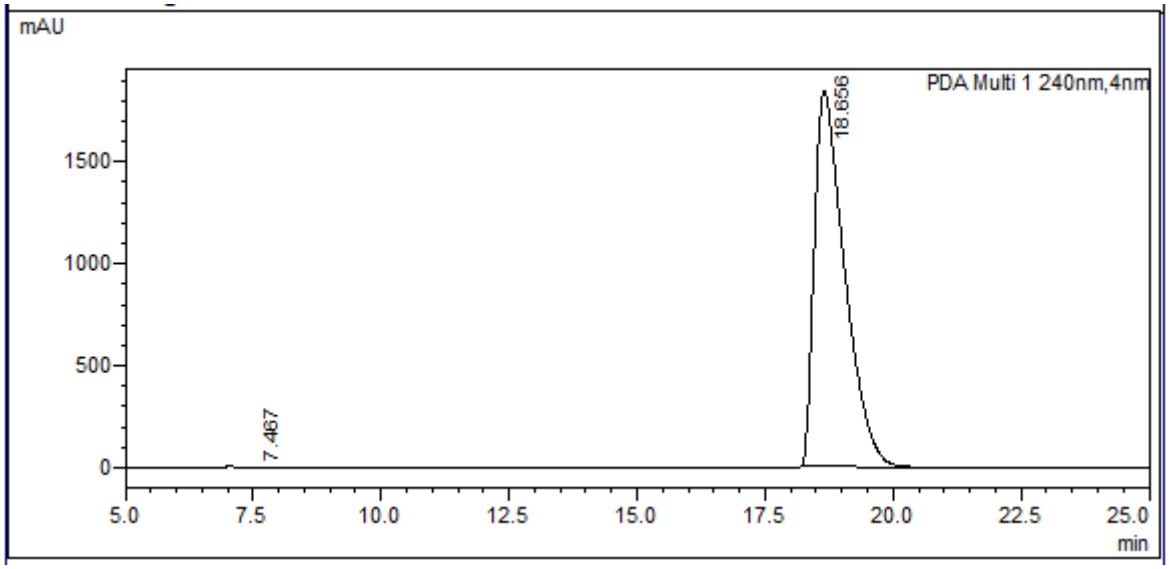
$[M+H]^+$: 471.2701; found: 471.2687; $[\alpha]^{20}_D$ = -169.00° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 240 nm, Flow rate = 1 mL/min, Retention times: 18.656 min (major), 7.467 min (minor).



<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.379	35441564	1688194	50.389	64.108
2	18.814	34893728	945150	49.611	35.892
Total		70335292	2633343	100.000	100.000

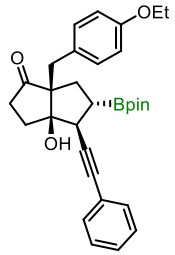


<Peak Table>

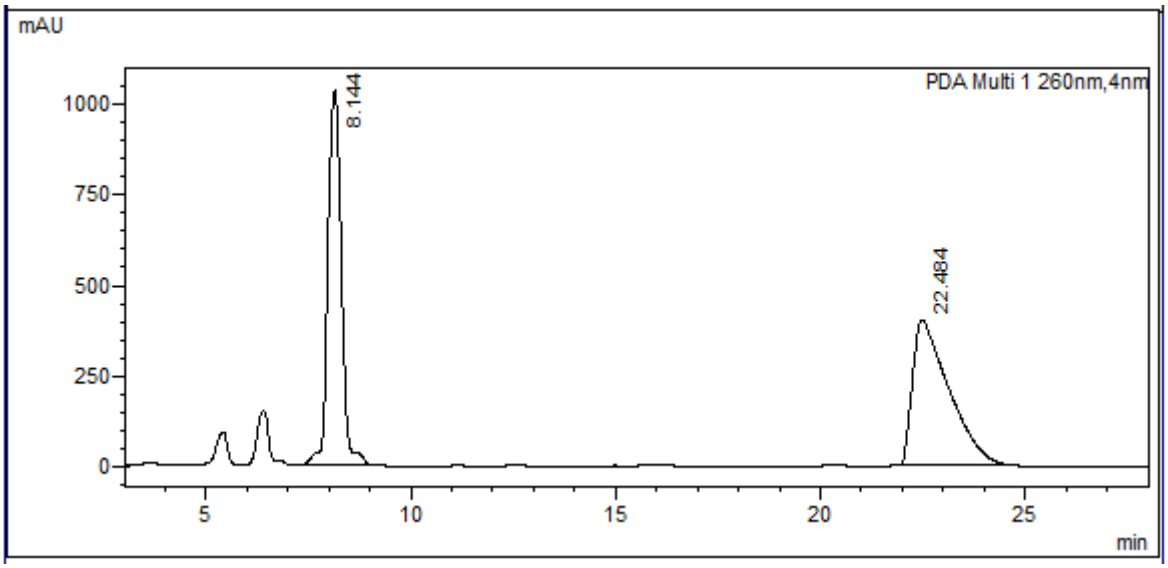
PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.467	2938	263	0.004	0.014
2	18.656	76075615	1841609	99.996	99.986
Total		76078552	1841872	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(4-Ethoxybenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2h):



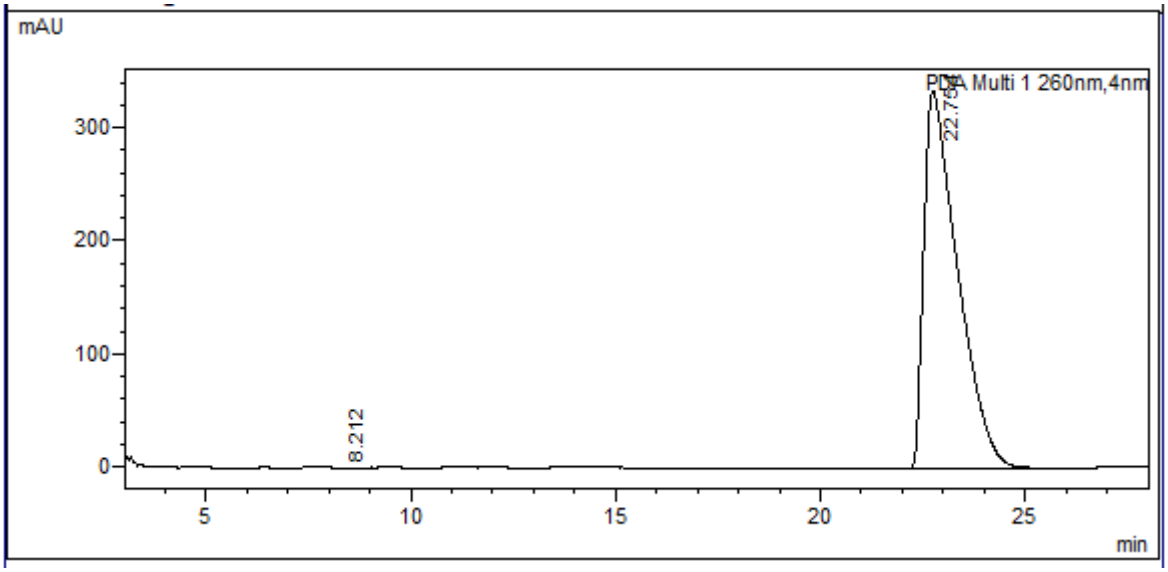
Prepared according to the general procedure as described above in 80% yield (120 gm). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 148–150°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.32 – 7.27 (m, 3H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 3.98 (q, *J* = 7.0 Hz, 2H), 3.04 (d, *J* = 13.4 Hz, 1H), 2.90 (d, *J* = 13.4 Hz, 1H), 2.68 (d, *J* = 11.0 Hz, 1H), 2.25 (dt, *J* = 19.5, 9.7 Hz, 1H), 2.10 – 1.99 (m, 2H), 1.99 – 1.90 (m, 3H), 1.49 (dt, *J* = 13.3, 10.7 Hz, 1H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.6, 157.7, 131.9, 131.9, 129.2, 128.4, 128.3, 123.0, 113.9, 88.1, 86.8, 84.9, 83.7, 64.6, 63.4, 46.2, 38.7, 37.1, 36.9, 29.9, 24.9, 24.7, 15.0; HRMS (ESI) calcd for $C_{31}H_{38}O_5B$ $[M+H]^+$: 501.2807; found: 501.2797; $[\alpha]^{20}_D$ = -96.83° (*c* 2.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 260 nm, Flow rate = 1 mL/min, Retention times: 22.754 min (major), 8.212 min (minor).



<Peak Table>

PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.144	23834256	1031048	49.103	71.988
2	22.484	24705122	401206	50.897	28.012
Total		48539378	1432254	100.000	100.000

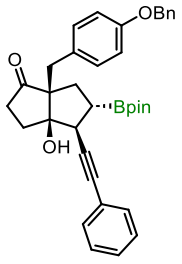


<Peak Table>

PDA Ch1 260nm

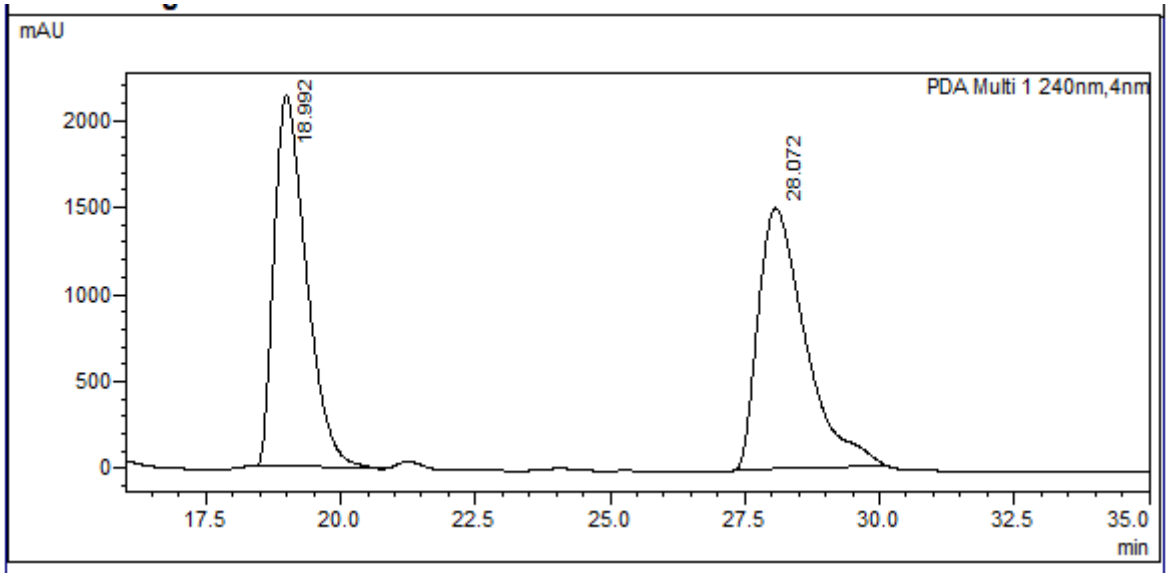
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.212	144	18	0.001	0.005
2	22.754	19158710	333717	99.999	99.995
Total		19158854	333735	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(4-(Benzyloxy)benzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2i):



Prepared according to the general procedure as described above in 65% yield (110 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a white solid; mp = 146–148°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 6H), 7.36 – 7.31 (m, 4H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.04 (s, 2H), 3.07 (d, *J* = 13.4 Hz, 1H), 2.94 (d, *J* = 13.4 Hz, 1H), 2.71 (d, *J* = 11.1 Hz, 1H), 2.29 (dt, *J* = 19.5, 9.7 Hz, 1H), 2.11 (dd, *J* = 12.9, 1.9 Hz, 1H), 2.07 – 2.03 (m, 1H), 2.03 – 1.93 (m, 3H), 1.59 – 1.48 (m, 1H), 1.26 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.6, 157.6, 137.2,

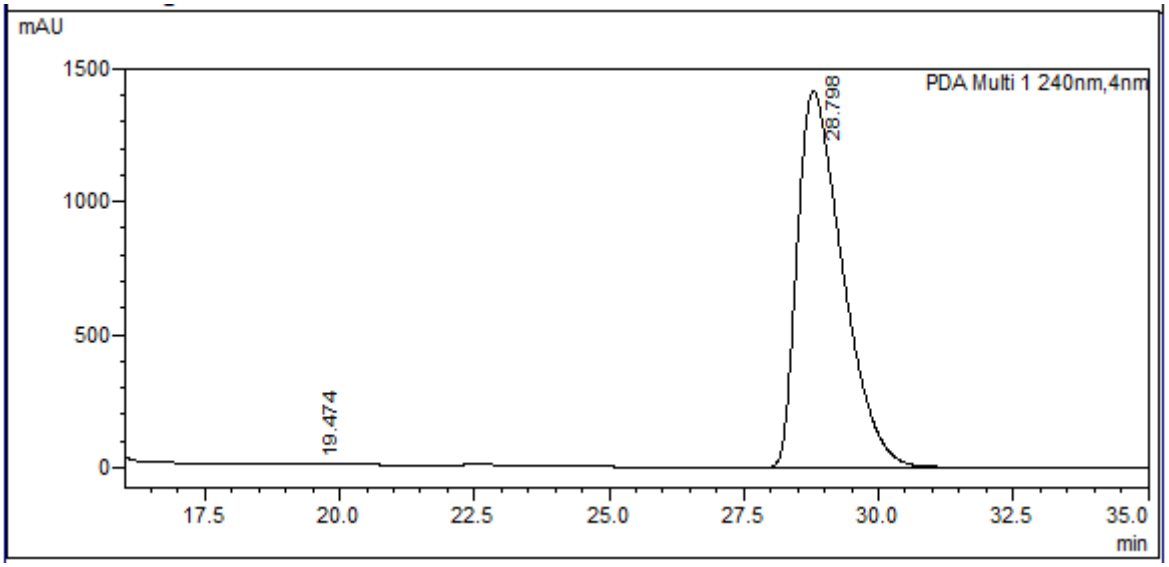
131.9, 129.7, 128.7, 128.4, 128.4, 128.0, 127.7, 123.0, 114.4, 88.1, 86.8, 85.0, 83.7, 70.1, 64.6, 46.2, 38.6, 37.0, 36.9, 29.9, 24.9, 24.7. HRMS (ESI) calcd for $C_{36}H_{40}O_5B$ $[M+H]^+$: 563.2963; found: 563.2949; $[\alpha]^{20}_D$ = -80.71° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 96:04, detected at 240 nm, Flow rate = 1 mL/min, Retention times: 28.798 min (major), 19.474 min (minor).



<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	18.992	89095295	2140079	49.322	58.766
2	28.072	91544612	1501615	50.678	41.234
Total		180639906	3641694	100.000	100.000

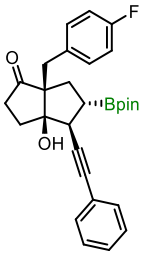


<Peak Table>

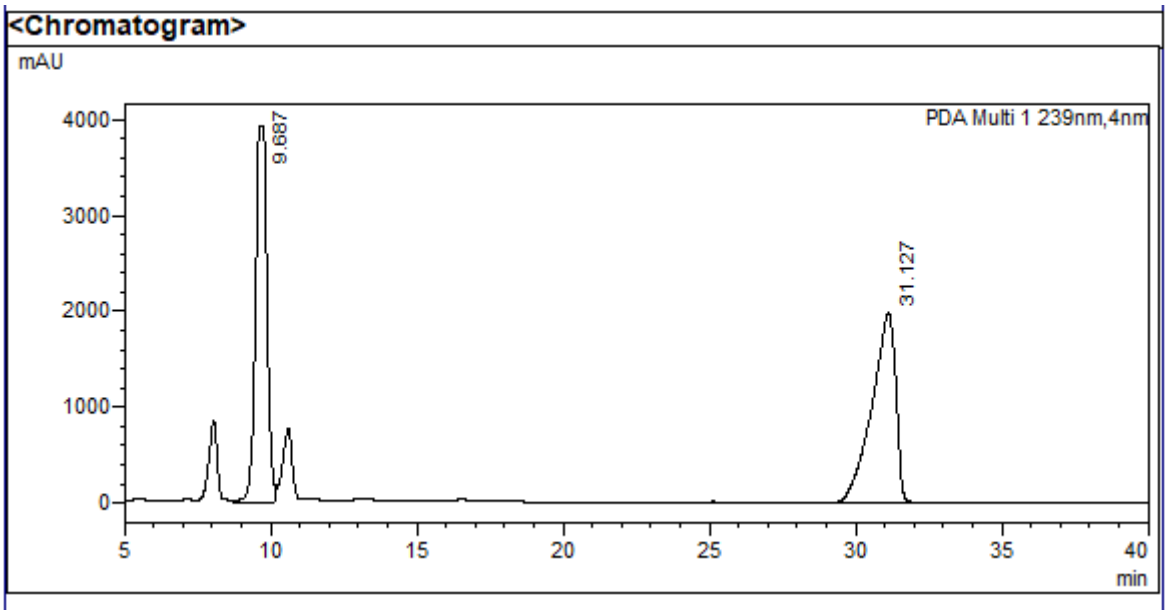
PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.474	8987	475	0.011	0.033
2	28.798	83138708	1417042	99.989	99.967
Total		83147695	1417517	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(4-Fluorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2j):



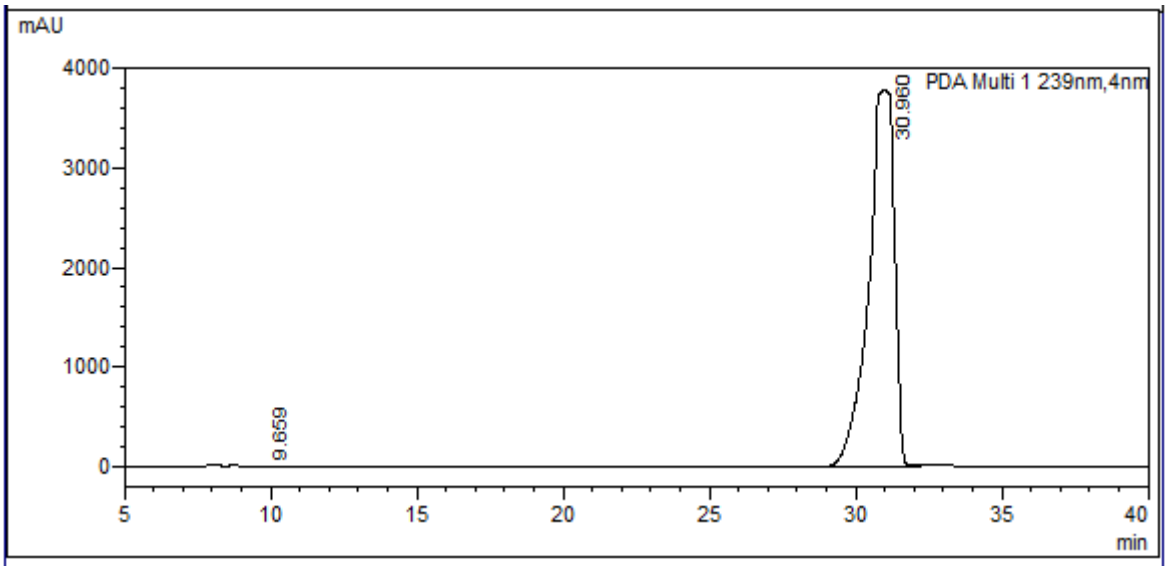
Prepared according to the general procedure as described above in 80% yield (114 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 172–174°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.26 – 7.20 (m, 3H), 7.19 – 7.13 (m, 2H), 6.86 – 6.80 (m, 2H), 2.99 (d, *J* = 13.4 Hz, 1H), 2.86 (d, *J* = 13.4 Hz, 1H), 2.63 (d, *J* = 11.3 Hz, 1H), 2.27 – 2.14 (m, 1H), 2.05 – 1.95 (m, 2H), 1.92 – 1.83 (m, 3H), 1.44 – 1.34 (m, 1H), 1.16 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.2, 161.8 (d, J_{CF} = 244.6 Hz), 133.1 (d$_{CF}$, *J* = 2.7 Hz), 132.4 (d, J_{CF} = 7.7 Hz), 131.9, 128.4, 122.9, 114.7 (d, J_{CF} = 21.0 Hz), 88.0, 86.6, 85.1, 83.7, 64.4, 46.2, 38.5, 37.2, 36.9, 29.9, 24.9, 24.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.5; HRMS (ESI) calcd for $C_{29}H_{33}O_4BF$ $[M+H]^+$: 475.2450; found: 475.2439; $[\alpha]^{20}_D$ = -51.22° (*c* 1.5, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 94/06, detected at 239 nm, Flow rate = 1 mL/min, Retention times: 30.960 min (major), 9.659 min (minor).



<Peak Table>

PDA Ch1 239nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.687	109440284	3932187	49.329	66.551
2	31.127	112418057	1976374	50.671	33.449
Total		221858341	5908561	100.000	100.000

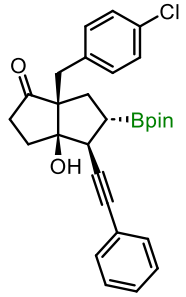


<Peak Table>

PDA Ch1 239nm

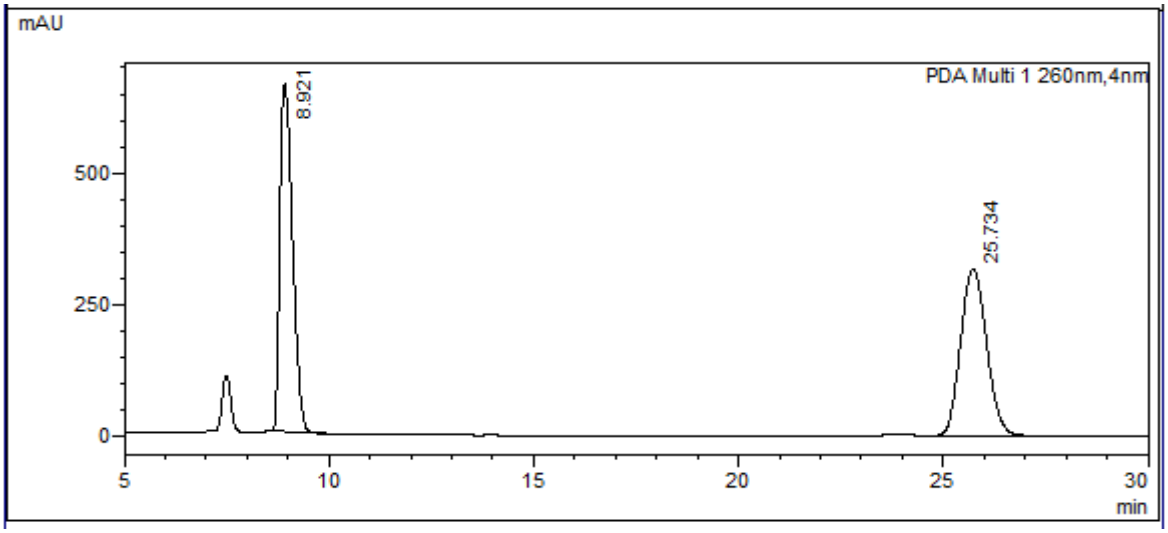
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.659	2829	27	0.001	0.001
2	30.960	232275050	3788949	99.999	99.999
Total		232277878	3788976	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(4-Chlorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2k):



Prepared according to the general procedure as described above in 82% yield (120 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 156–158°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.30 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.23 – 7.16 (m, 4H), 3.05 (d, *J* = 13.3 Hz, 1H), 2.92 (d, *J* = 13.3 Hz, 1H), 2.70 (d, *J* = 10.8 Hz, 1H), 2.50 (s, 1H), 2.29 (dt, *J* = 19.6, 9.8 Hz, 1H), 2.13 – 2.02 (m, 2H), 2.02 – 1.92 (m, 3H), 1.47 (dt, *J* = 13.5, 10.6 Hz, 1H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.1, 136.0, 132.5, 132.3, 131.9, 128.4, 128.1, 122.9,

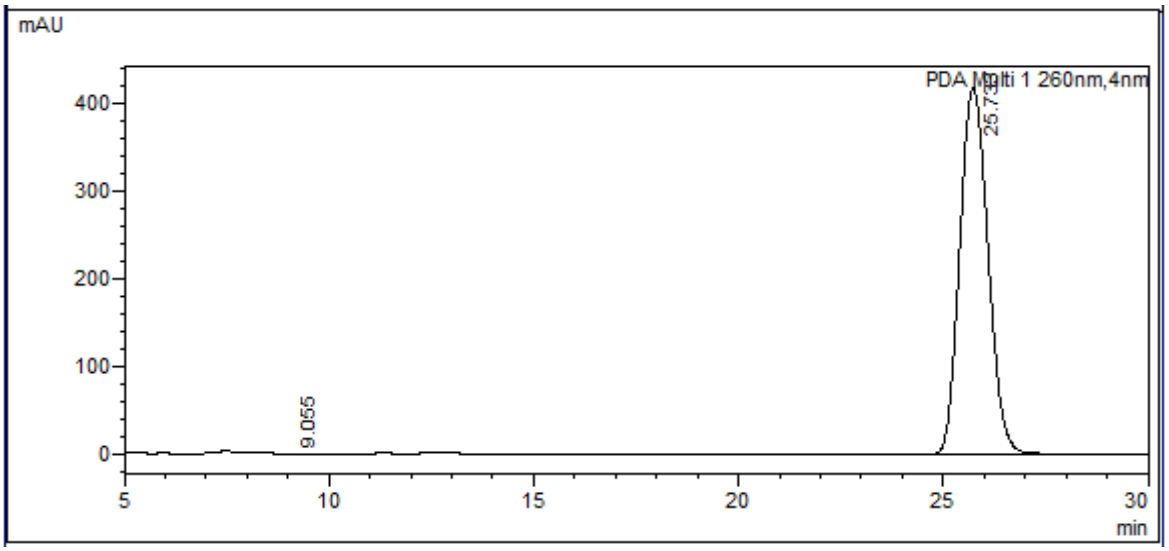
88.0, 86.5, 85.2, 83.7, 64.4, 46.2, 38.6, 37.2, 36.9, 30.0, 24.9, 24.7; HRMS (ESI) calcd for $C_{29}H_{33}O_4BCl$ $[M+H]^+$: 491.2155; found: 491.2145; $[\alpha]^{20}_D$ = -132.50° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 260 nm, Flow rate = 1 mL/min, Retention times: 25.733 min (major), 9.055 min (minor).



<Peak Table>

PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.921	14307175	661227	50.682	67.601
2	25.734	13921878	316904	49.318	32.399
Total		28229053	978131	100.000	100.000

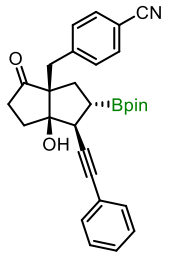


<Peak Table>

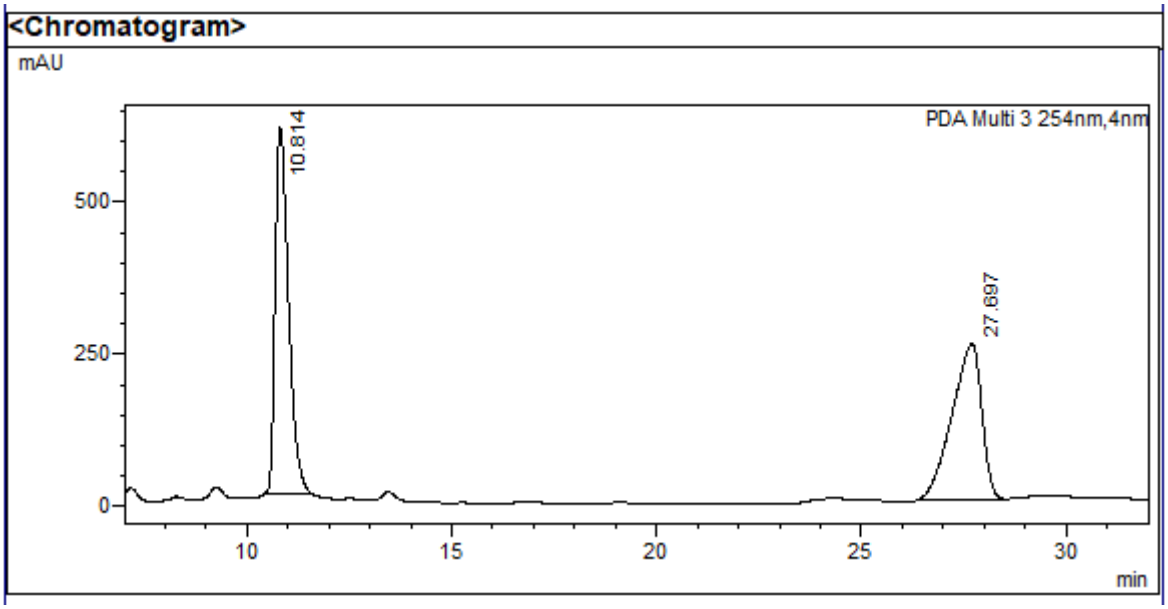
PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.055	484	52	0.002	0.013
2	25.733	20038903	417852	99.998	99.987
Total		20039386	417904	100.000	100.000

4-(((1*S*,2*S*,3a*S*,6a*R*)-6a-Hydroxy-4-oxo-1-(phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-3a(1*H*)-yl)methyl)benzonitrile (2l):



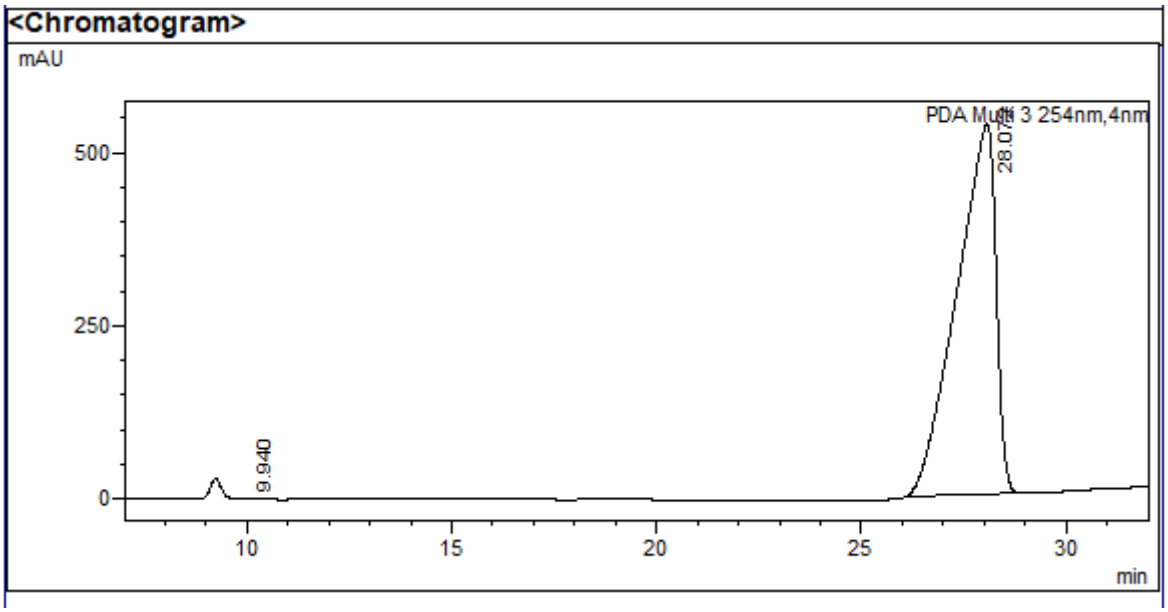
Prepared according to the general procedure as described above in 66% yield (95 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 166–168°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.36 (m, 4H), 7.34 – 7.27 (m, 3H), 3.11 (d, *J* = 13.1 Hz, 1H), 3.01 (d, *J* = 13.1 Hz, 1H), 2.73 (d, *J* = 10.8 Hz, 1H), 2.33 (dt, *J* = 19.8, 9.9 Hz, 1H), 2.16 – 2.06 (m, 2H), 2.06 – 1.98 (m, 1H), 1.97 – 1.89 (m, 2H), 1.43 (dt, *J* = 13.4, 10.5 Hz, 1H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.4, 143.3, 131.9, 131.8, 131.7, 128.5, 128.5, 122.8, 119.1, 110.5, 87.9, 86.2, 85.4, 83.8, 64.3, 46.2, 39.2, 37.3, 36.8, 30.1, 24.9, 24.7; HRMS (ESI) calcd for $C_{30}H_{33}O_4NB$ $[M+H]^+$: 482.2497; found: 482.2486; $[\alpha]^{20}_D$ = -137.88° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 88/12, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 28.072 min (major), 9.940 min (minor).



<Peak Table>

PDA Ch3 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.814	13616865	601929	51.298	70.257
2	27.697	12927784	254819	48.702	29.743
Total		26544649	856748	100.000	100.000

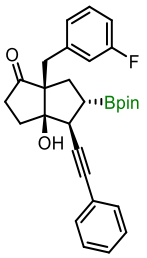


<Peak Table>

PDA Ch3 254nm

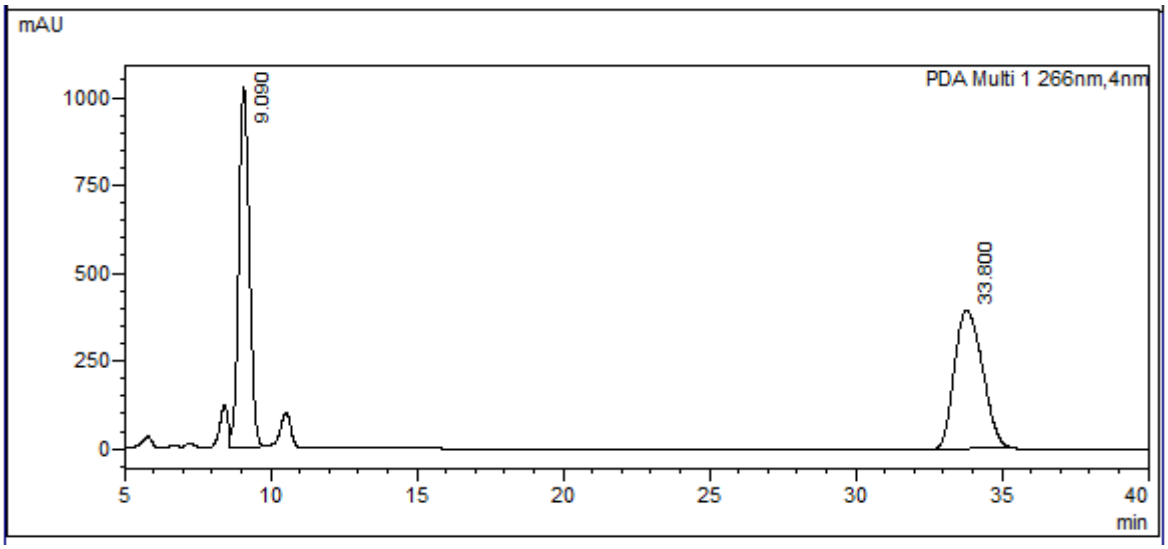
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.940	3852	253	0.011	0.047
2	28.072	35776791	536274	99.989	99.953
Total		35780643	536527	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(3-Fluorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2m):



Prepared according to the general procedure as described above in 79% yield (112 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford a white solid; mp = 188–190°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.33 – 7.28 (m, 3H), 7.17 (td, *J* = 7.9, 6.2 Hz, 1H), 7.05 (ddd, *J* = 10.2, 2.3, 1.7 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.88 (ddd, *J* = 8.4, 2.6, 1.3 Hz, 1H), 3.07 (d, *J* = 13.2 Hz, 1H), 2.96 (d, *J* = 13.2 Hz, 1H), 2.71 (d, *J* = 11.4 Hz, 1H), 2.29 (dt, *J* = 19.6, 9.8

Hz, 1H), 2.13 – 2.08 (m, 1H), 2.08 – 2.00 (m, 2H), 1.99 – 1.93 (m, 2H), 1.50 (dt, J = 13.4, 10.6 Hz, 1H), 1.23 (s, 12H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 222.0, 162.4 (d, J_{CF} = 245.0 Hz), 140.0 (d, J_{CF} = 7.3 Hz), 131.9, 129.3 (d, J_{CF} = 8.1 Hz), 128.4, 126.6, 122.9, 117.9 (d, J_{CF} = 21.3 Hz), 113.6 (d, J_{CF} = 21.0 Hz), 88.0, 86.5, 85.1, 83.7, 64.4, 46.2, 39.1, 37.3, 36.8, 29.9, 24.9, 24.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.78; HRMS (ESI) calcd for $C_{29}H_{33}O_4BF$ $[M+H]^+$: 475.2450; found: 475.2439; $[\alpha]^{20}_D$ = -164.83° (*c* 2.0, $CHCl_3$); HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 94/06, detected at 266 nm, Flow rate = 1 mL/min, Retention times: 33.103 min (major), 9.261 min (minor).

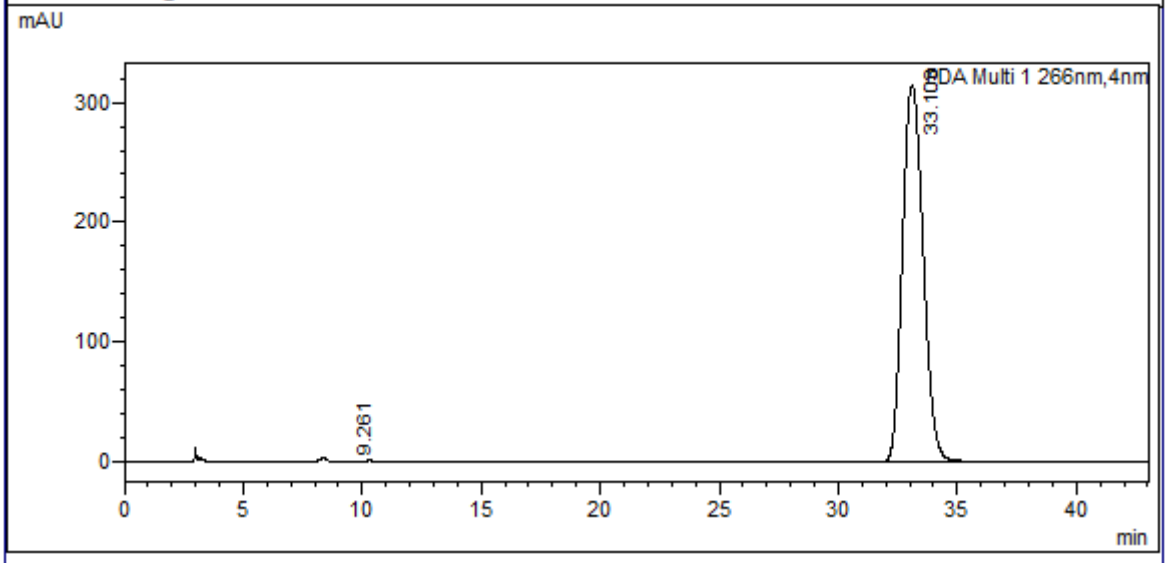


<Peak Table>

PDA Ch1 266nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.090	25818182	1026440	49.580	72.337
2	33.800	26255871	392526	50.420	27.663
Total		52074052	1418966	100.000	100.000

<Chromatogram>

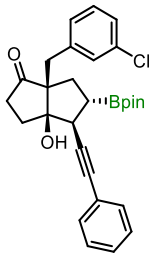


<Peak Table>

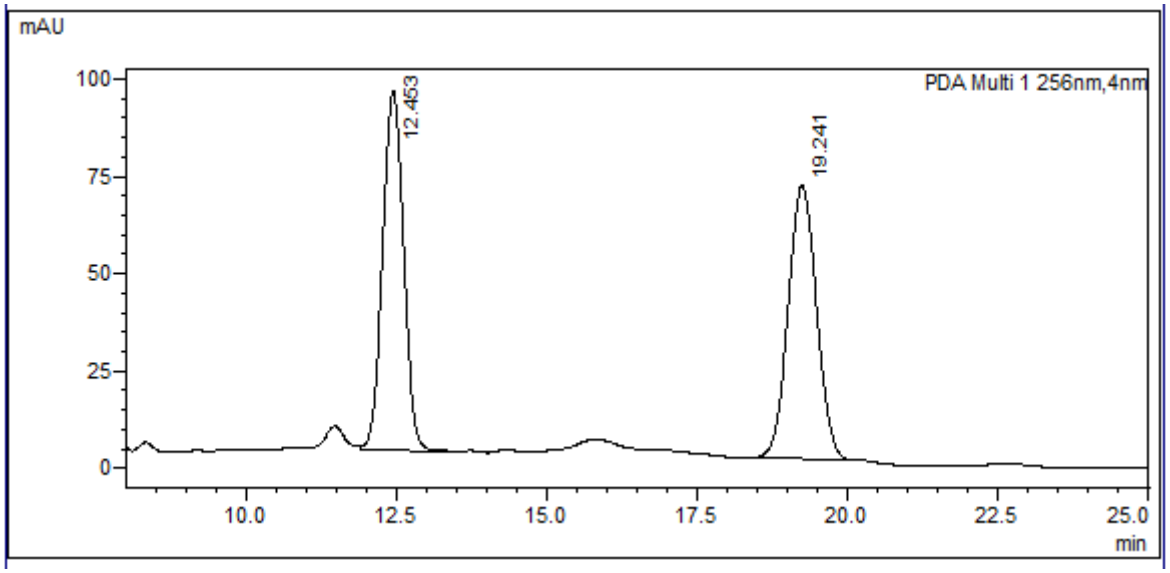
PDA Ch1 266nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.261	3320	185	0.017	0.059
2	33.103	19023849	314549	99.983	99.941
Total		19027170	314734	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(3-Chlorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2n):



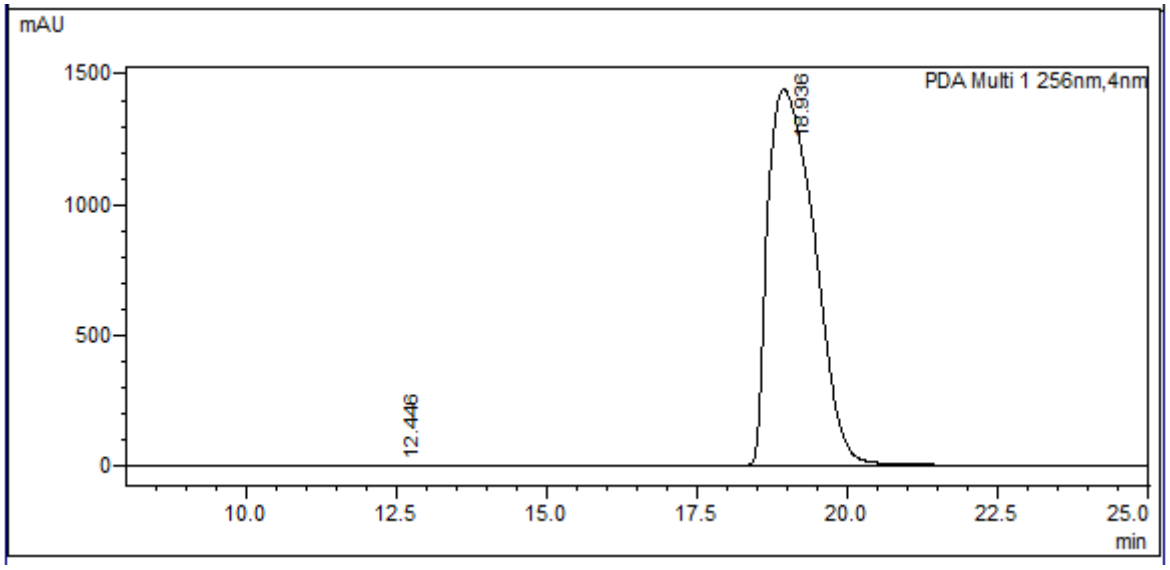
Prepared according to the general procedure as described above in 80% yield (118g). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 167–169°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (ddd, *J* = 4.7, 4.1, 2.2 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.22 – 7.17 (m, 1H), 7.17 – 7.14 (m, 1H), 7.13 – 7.09 (m, 1H), 3.05 (d, *J* = 13.2 Hz, 1H), 2.93 (dd, *J* = 13.3, 2.8 Hz, 1H), 2.70 (d, *J* = 11.1 Hz, 1H), 2.30 (ddd, *J* = 15.2, 12.1, 7.5 Hz, 1H), 2.09 (tdd, *J* = 11.3, 9.3, 1.9 Hz, 2H), 2.04 – 2.00 (m, 1H), 1.99 – 1.92 (m, 2H), 1.53 – 1.42 (m, 1H), 1.23 (s, 12H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 221.9, 139.5, 133.7, 132.3, 131.9, 131.1, 129.2, 129.1, 128.4, 126.9, 122.9, 87.9, 86.5, 85.1, 83.7, 64.3, 46.2, 38.9, 37.2, 36.8, 30.0, 24.9, 24.; HRMS (ESI) calcd for $C_{29}H_{33}O_4BCl$ $[M+H]^+$: 491.2155; found: 491.2143; $[\alpha]^{20}_D$ = -142.20° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 92/08, detected at 256 nm, Flow rate = 1 mL/min, Retention times: 18.936 min (major), 12.446 min (minor).



<Peak Table>

PDA Ch1 256nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.453	2260540	92473	49.387	56.799
2	19.241	2316669	70335	50.613	43.201
Total		4577209	162808	100.000	100.000

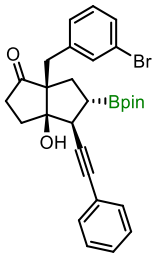


<Peak Table>

PDA Ch1 256nm

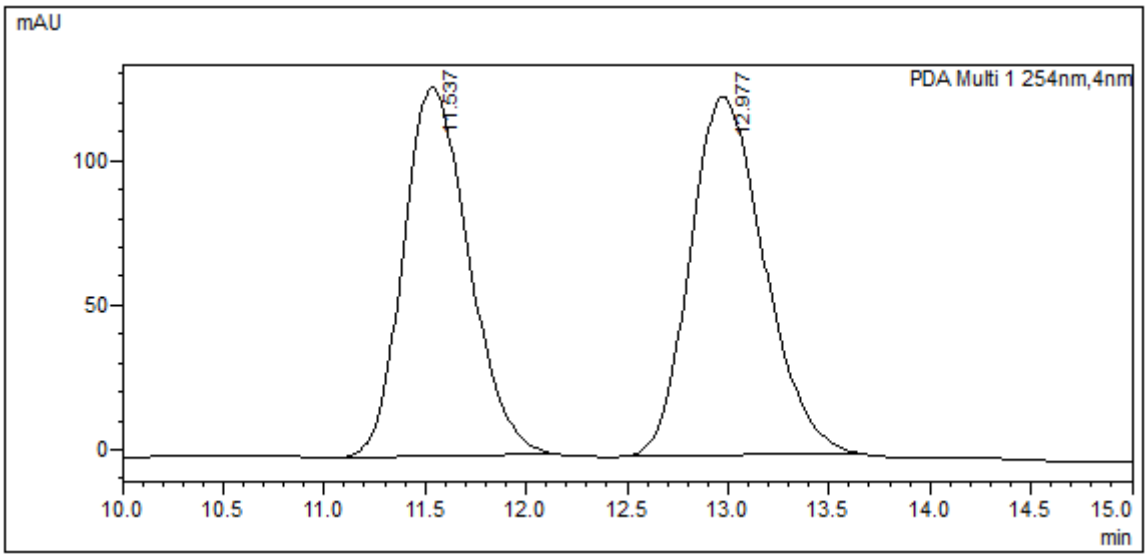
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.446	93	48	0.000	0.003
2	18.936	77622696	1440005	100.000	99.997
Total		77622789	1440053	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(3-Bromobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2o):



Prepared according to the general procedure as described above in 75% yield (120 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 170–172°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 1.6 Hz, 1H), 7.42 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.34 – 7.29 (m, 4H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.13 – 7.06 (m, 1H), 3.04 (d, *J* = 13.2 Hz, 1H), 2.92 (d, *J* = 13.2 Hz, 1H), 2.70 (d, *J* = 10.9 Hz, 1H), 2.53 (s, 1H), 2.30 (dt, *J* = 19.6, 9.8 Hz, 1H), 2.16 – 2.05 (m, 2H), 2.04

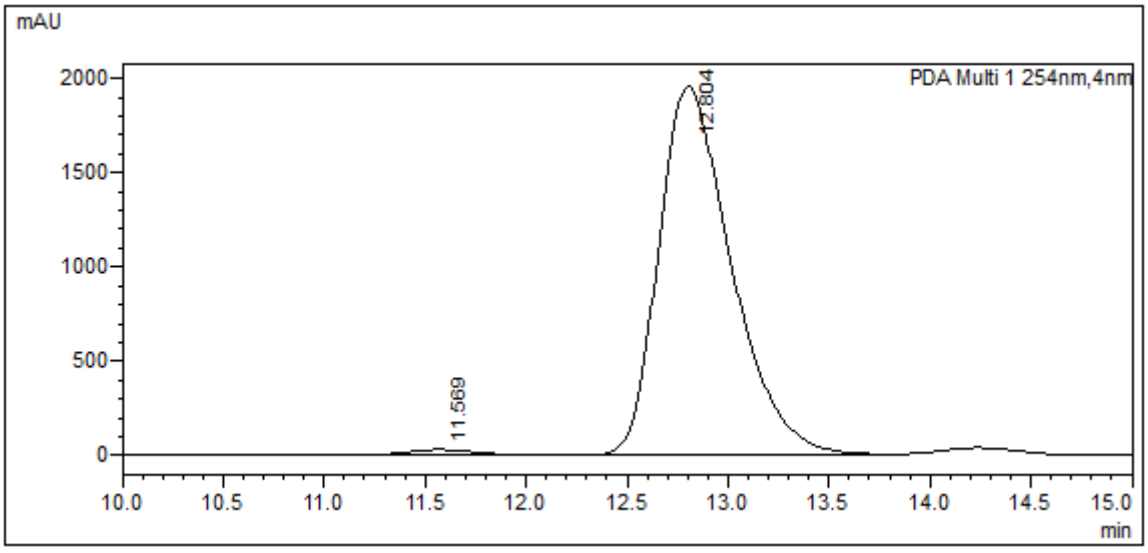
– 1.90 (m, 3H), 1.56 – 1.43 (m, 1H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.8, 139.9, 134.0, 131.9, 129.8, 129.5, 128.4, 122.9, 122.0, 88.0, 86.5, 85.2, 83.7, 64.4, 46.2, 38.9, 37.2, 36.8, 30.0, 24.9, 24.7; HRMS (ESI) calcd for $C_{29}H_{33}O_4BBr$ $[M+H]^+$: 535.1650; found: 535.1639; $[\alpha]^{20}_D$ = -137.75° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 98% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 12.804 min (major), 11.569 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.537	2873298	127699	49.750	51.501
2	12.977	2902197	120256	50.250	48.499
Total		5775495	247955	100.000	100.000

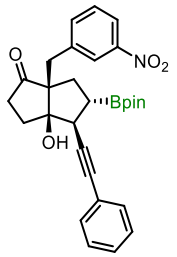


<Peak Table>

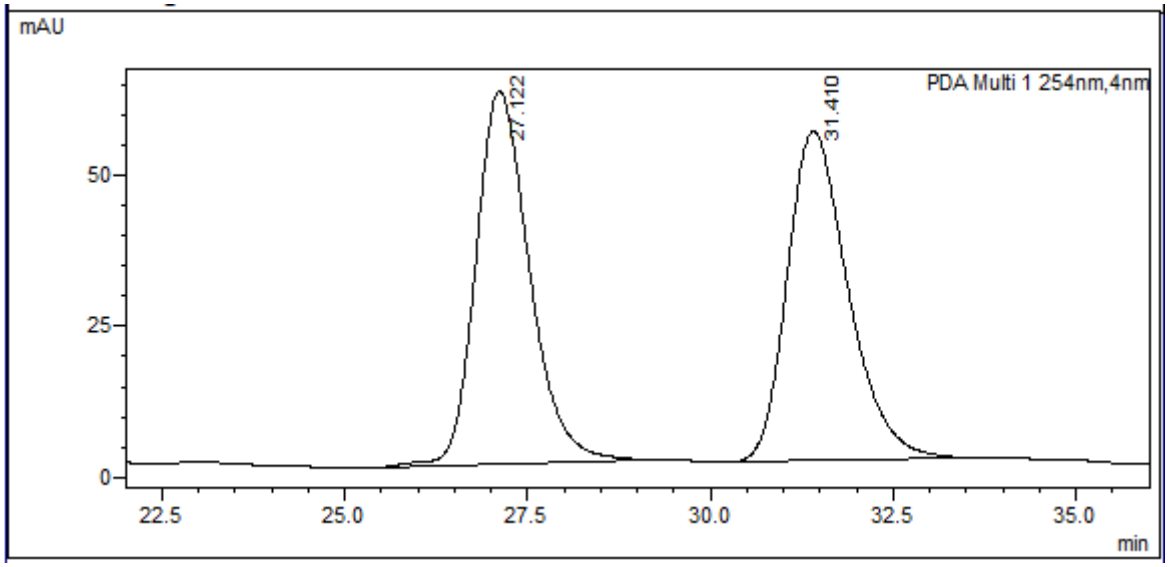
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.569	603047	27694	1.223	1.396
2	12.804	48692998	1955782	98.777	98.604
Total		49296045	1983476	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-(3-nitrobenzyl)-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2p):



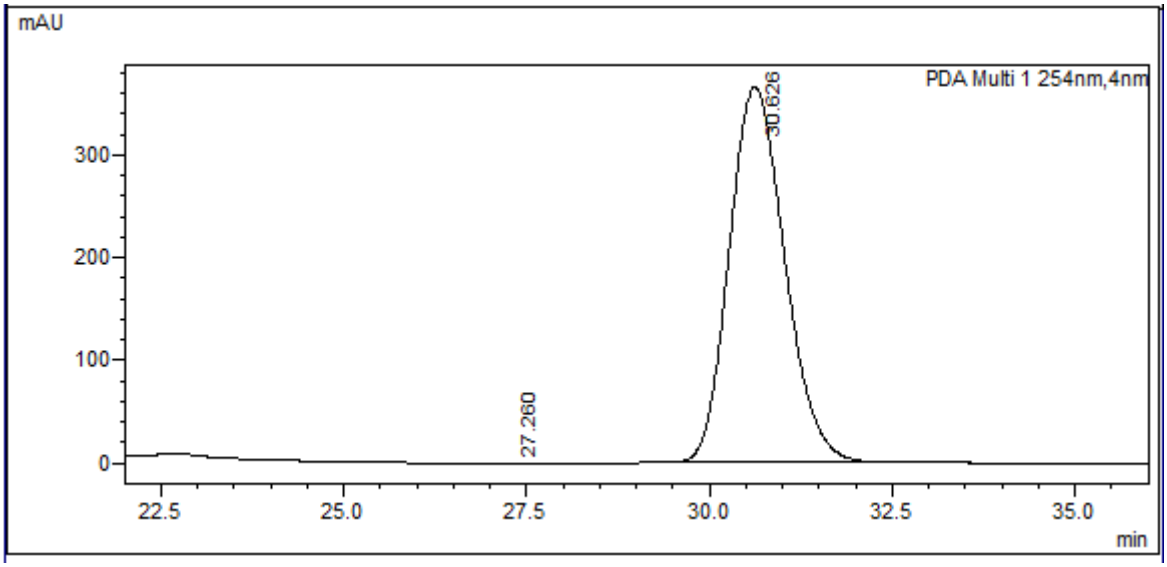
Prepared according to the general procedure as described above in 67% yield (101 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.6) to afford a brown solid; mp = 130–132°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (t, *J* = 1.9 Hz, 1H), 8.05 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.34 – 7.27 (m, 3H), 3.16 (d, *J* = 13.3 Hz, 1H), 3.06 (d, *J* = 13.3 Hz, 1H), 2.79 – 2.72 (m, 1H), 2.34 (dt, *J* = 19.8, 9.9 Hz, 2H), 2.19 – 2.03 (m, 3H), 2.00 – 1.94 (m, 1H), 1.44 (dt, *J* = 13.7, 10.6 Hz, 1H), 1.23 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.4, 148.0, 139.7, 137.1, 131.9, 128.8, 128.5, 128.5, 126.1, 122.8, 121.8, 87.9, 86.2, 85.4, 83.8, 64.1, 46.3, 38.7, 37.3, 30.2, 25.0, 24.9, 24.7; HRMS (ESI) calcd for $C_{29}H_{33}O_6BN$ $[M+H]^+$: 502.2395; found: 502.2382; $[\alpha]^{20}_D$ = -79.69° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 30.626 min (major), 27.260 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	27.122	3149836	61683	49.971	53.106
2	31.410	3153550	54468	50.029	46.894
Total		6303386	116151	100.000	100.000

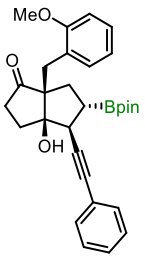


<Peak Table>

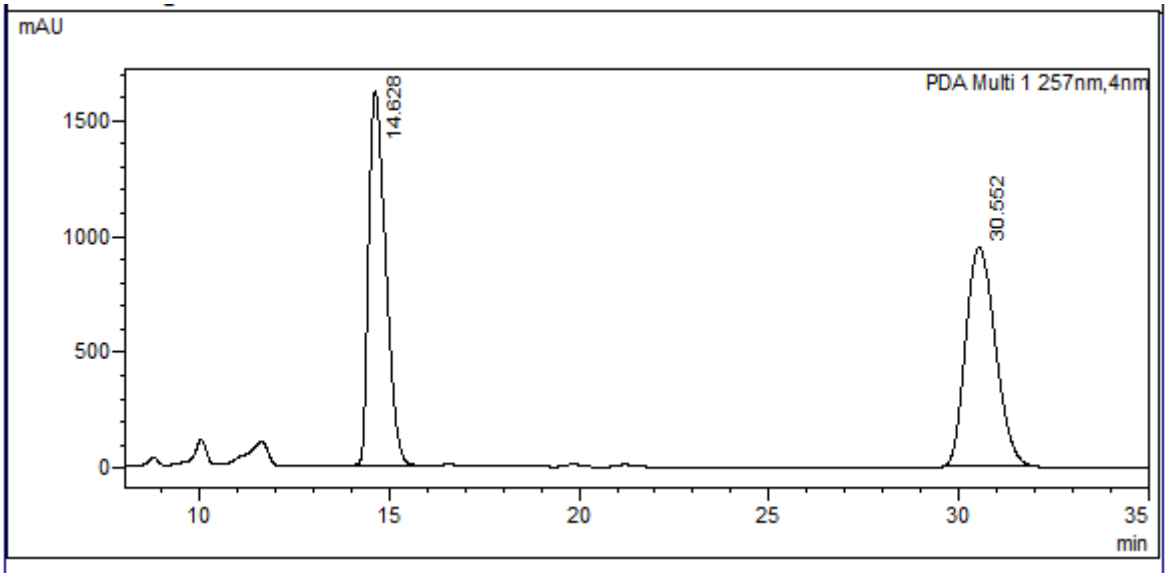
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	27.260	1518	65	0.008	0.018
2	30.626	19309222	365531	99.992	99.982
Total		19310740	365596	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-(2-methoxybenzyl)-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2q):



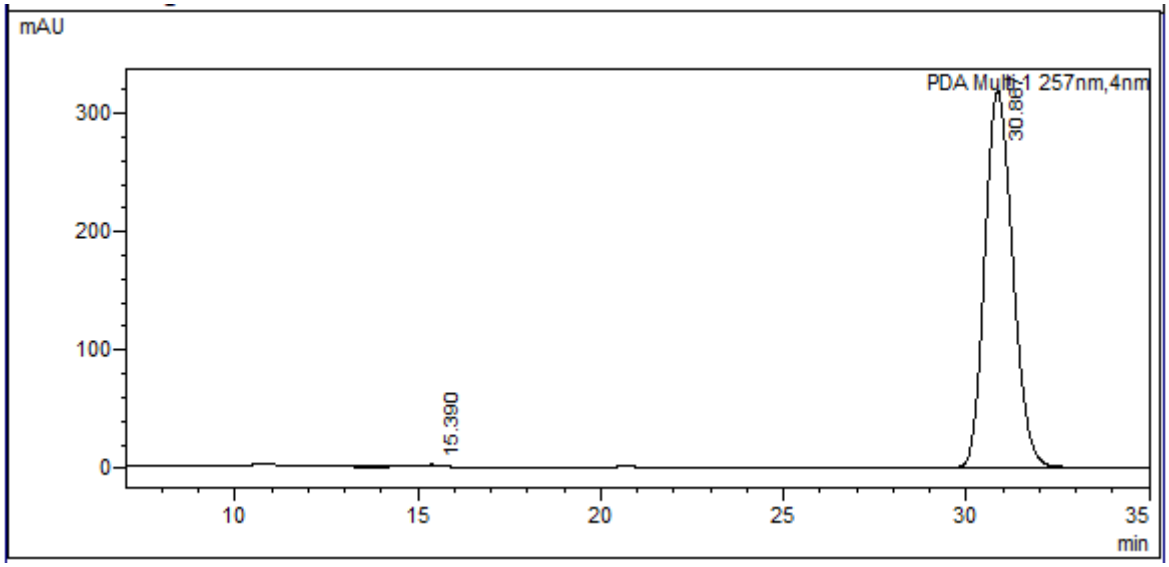
Prepared according to the general procedure as described above in 77% yield (112 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 193–195°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.29 – 7.26 (m, 3H), 7.22 (td, *J* = 8.1, 1.7 Hz, 1H), 7.09 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.89 (td, *J* = 7.4, 0.9 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 3H), 3.19 (d, *J* = 13.7 Hz, 1H), 2.79 (d, *J* = 13.7 Hz, 1H), 2.65 – 2.56 (m, 1H), 2.33 – 2.19 (m, 2H), 2.19 – 2.10 (m, 1H), 2.06 – 1.98 (m, 3H), 1.61 (dt, *J* = 11.7, 9.0 Hz, 1H), 1.22 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.6, 156.8, 132.2, 132.0, 128.4, 128.2, 127.9, 125.4, 123.6, 121.2, 110.8, 87.9, 87.7, 83.7, 83.6, 64.5, 55.6, 44.7, 36.3, 35.5, 32.4, 29.7, 24.9, 24.7; HRMS (ESI) calcd for $C_{30}H_{36}O_5B$ $[M+H]^+$: 487.2650; found: 487.2643; $[\alpha]^{20}_D$ = -98.19° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 257 nm, Flow rate = 1 mL/min, Retention times: 30.867 min (major), 15.390 min (minor).



<Peak Table>

PDA Ch1 257nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.628	49995762	1613567	49.339	63.096
2	30.552	51335769	943744	50.661	36.904
Total		101331531	2557311	100.000	100.000

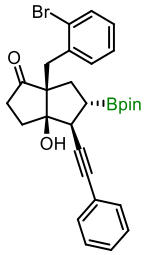


<Peak Table>

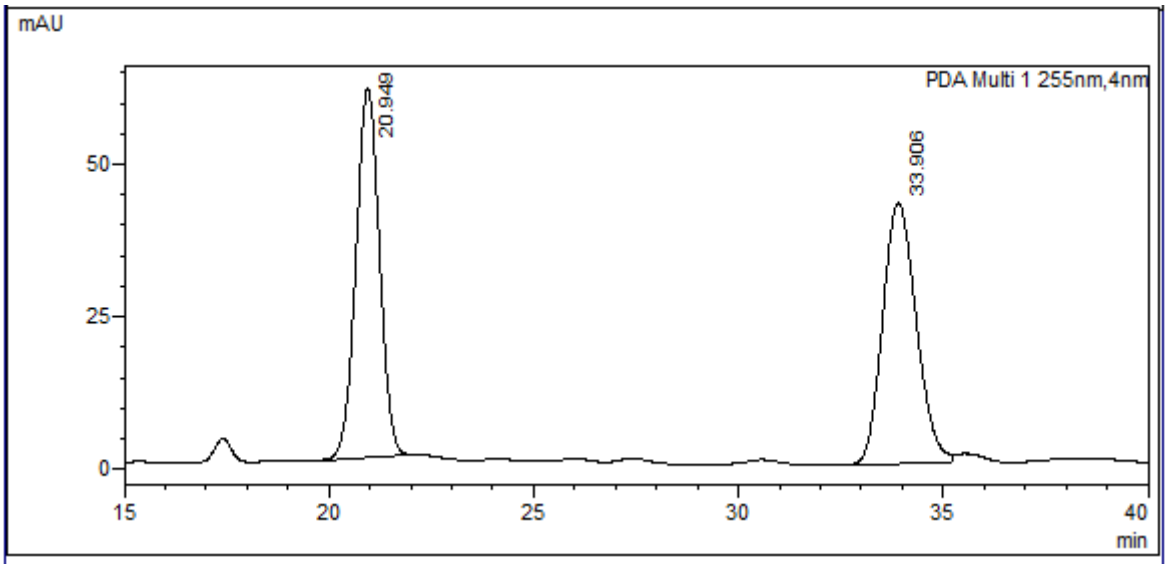
PDA Ch1 257nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.390	27065	1205	0.161	0.378
2	30.867	16833340	317594	99.839	99.622
Total		16860404	318799	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(2-Bromobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2r):



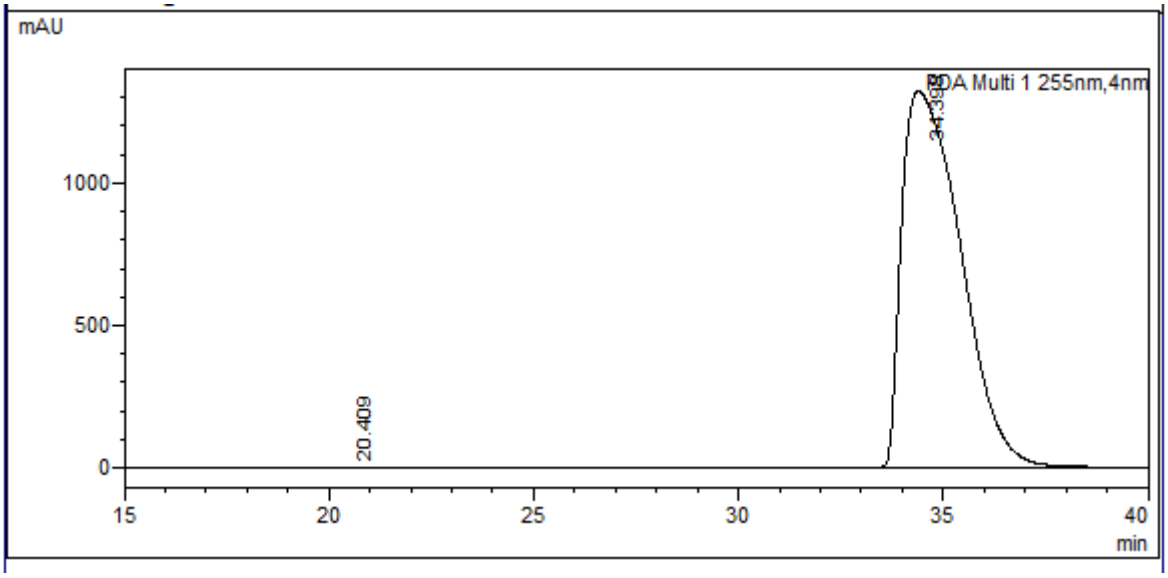
Prepared according to the general procedure as described above in 77% yield (124 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford a white solid; mp = 162–164°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.25 (ddd, *J* = 6.8, 6.2, 1.4 Hz, 4H), 7.14 (td, *J* = 7.5, 1.2 Hz, 1H), 6.99 (td, *J* = 7.9, 1.7 Hz, 1H), 3.18 (d, *J* = 14.3 Hz, 1H), 3.08 (d, *J* = 14.3 Hz, 1H), 2.72 – 2.60 (m, 2H), 2.31 (dt, *J* = 19.3, 9.5 Hz, 1H), 2.26 – 2.18 (m, 1H), 2.15 – 2.07 (m, 2H), 1.94 – 1.79 (m, 2H), 1.14 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.7, 137.0, 133.0, 132.0, 128.4, 128.4, 128.4, 127.2, 126.3, 123.0, 88.5, 86.8, 85.1, 83.7, 63.5, 44.6, 36.5, 36.3, 34.2, 29.5, 24.9, 24.7; HRMS (ESI) calcd for $C_{29}H_{33}O_4BBr$ $[M+H]^+$: 535.1650; found: 535.1641; $[\alpha]^{20}_D$ = -25.66° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 94/06, detected at 255 nm, Flow rate = 1 mL/min, Retention times: 34.398 min (major), 20.409 min (minor).



<Peak Table>

PDA Ch1 255nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.949	2407598	60412	49.479	58.555
2	33.906	2458261	42760	50.521	41.445
Total		4865858	103172	100.000	100.000

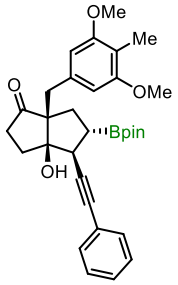


<Peak Table>

PDA Ch1 255nm

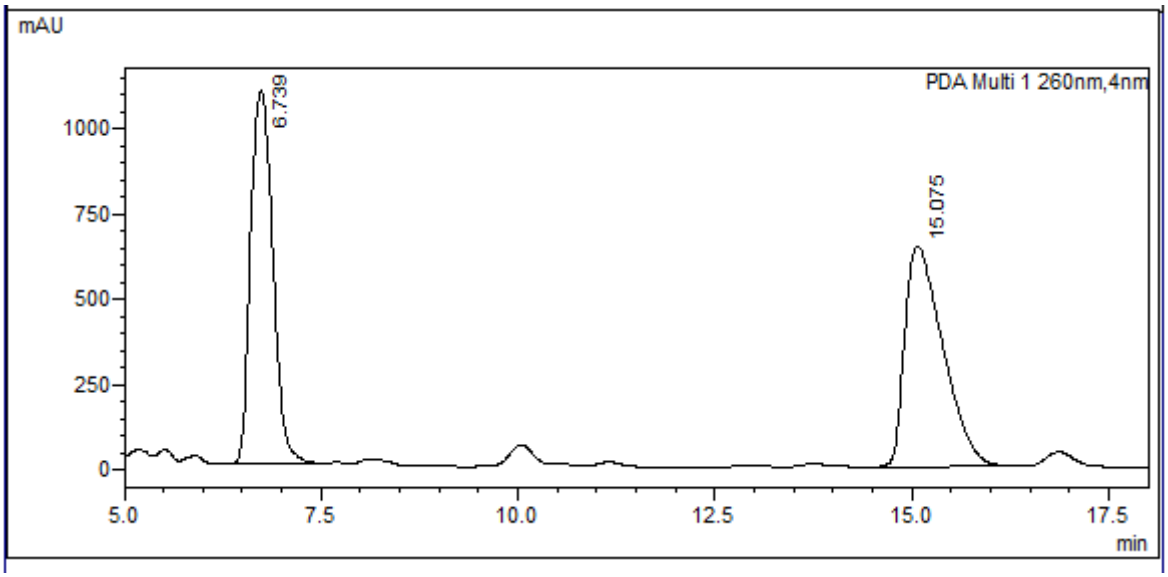
Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.409	84	17	0.000	0.001
2	34.398	132293547	1320916	100.000	99.999
Total		132293631	1320934	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(3,5-Dimethoxy-4-methylbenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2s):



Prepared according to the general procedure as described above in 65% yield (103 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a brown semi solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.25 – 7.20 (m, 3H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.99 (d, *J* = 13.7 Hz, 1H), 2.79 (d, *J* = 13.7 Hz, 1H), 2.57 (d, *J* = 12.2 Hz, 1H), 2.22 – 2.14 (m, 2H), 2.14 – 2.01 (m, 3H), 2.13 (s, 3H), 1.94 – 1.89 (m, 1H), 1.81 – 1.72 (m, 1H), 1.22 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 223.0, 158.0, 156.3, 132.0, 129.5, 128.1, 127.7, 123.9, 121.4, 119.7, 106.8, 88.9, 87.7, 83.5, 83.1, 75.1, 64.9, 61.2, 55.7, 44.9, 36.8, 36.7, 33.4, 30.0, 25.0, 24.9, 24.7, 9.4; HRMS (ESI) calcd for $C_{32}H_{40}O_6B$ $[M+H]^+$: 531.2912; found: 531.2902; $[\alpha]^{20}_D$ = -139.76° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6

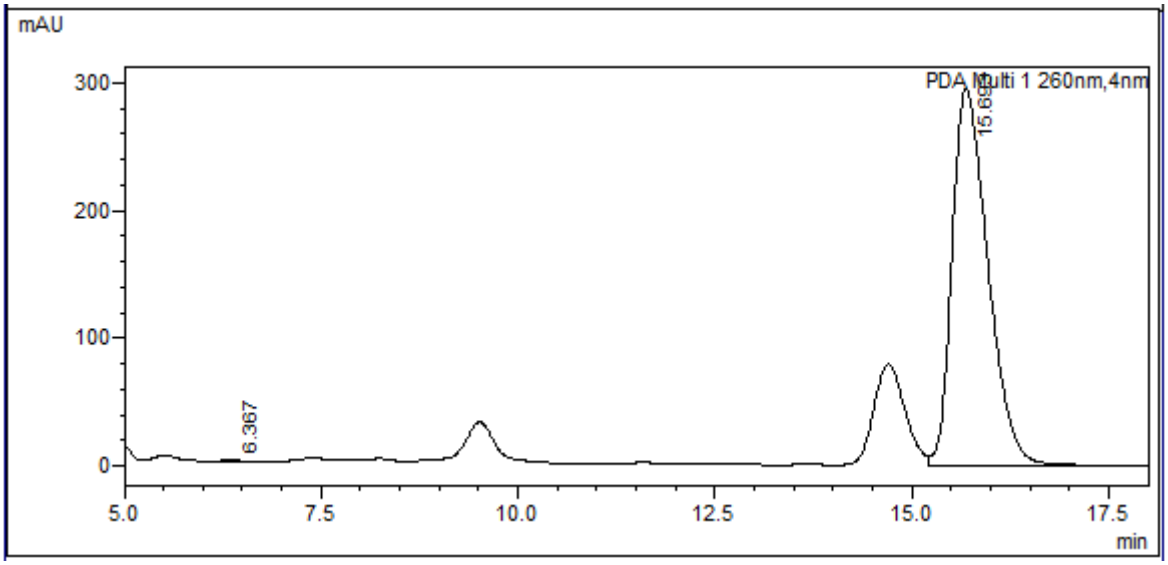
mm 5μ column; hexane/2-propanol = 90/10, detected at 260 nm, Flow rate = 1 mL/min, Retention times: 15.693 min (major), 6.367 min (minor).



<Peak Table>

PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.739	21574831	1096123	49.495	62.806
2	15.075	22015174	649132	50.505	37.194
Total		43590006	1745256	100.000	100.000

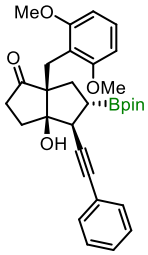


<Peak Table>

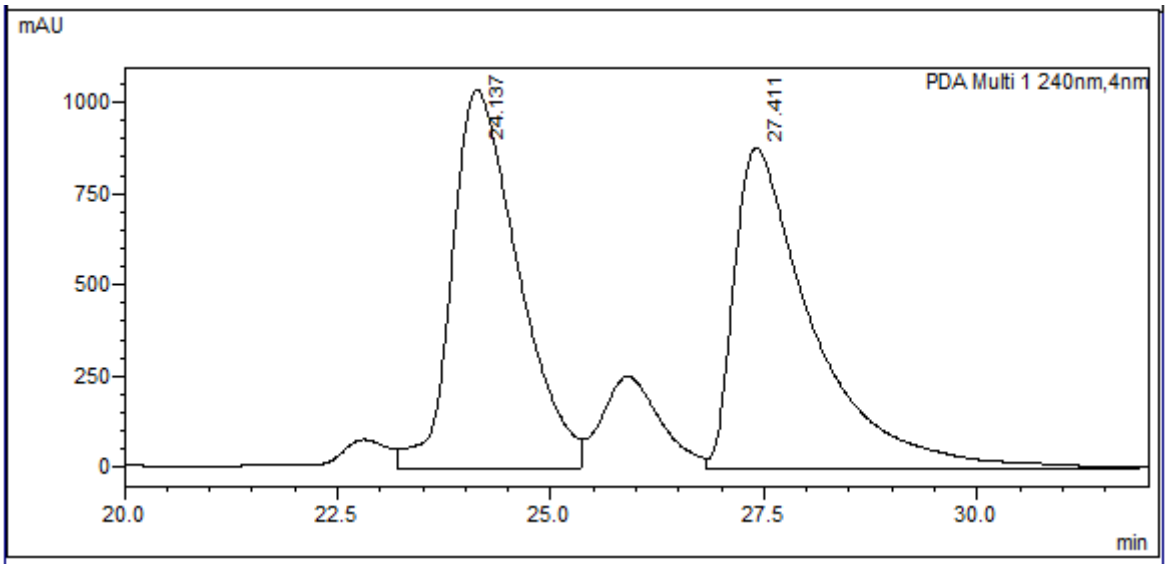
PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.367	5339	409	0.057	0.139
2	15.693	9351912	294532	99.943	99.861
Total		9357250	294941	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(2,6-Dimethoxybenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2t):



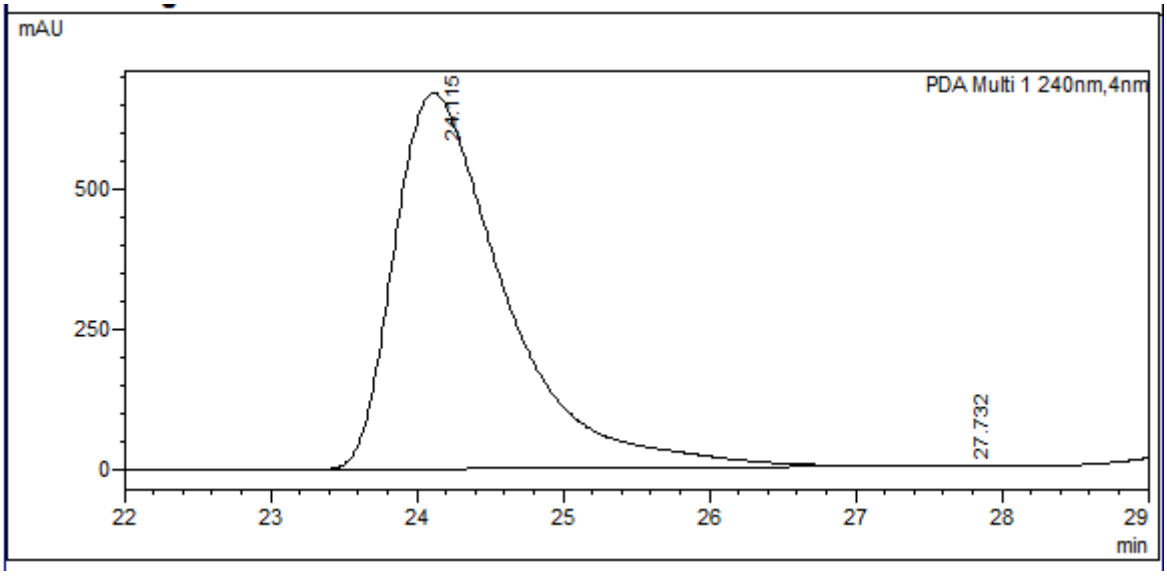
Prepared according to the general procedure as described above in 69% yield (107 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 210–212°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.31 – 7.27 (m, 3H), 6.77 (dt, *J* = 8.9, 5.9 Hz, 2H), 6.69 (d, *J* = 2.8 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.18 (d, *J* = 13.6 Hz, 1H), 2.76 (d, *J* = 13.6 Hz, 1H), 2.70 – 2.57 (m, 1H), 2.34 – 2.12 (m, 3H), 2.09 – 1.98 (m, 3H), 1.61 (ddd, *J* = 14.1, 10.0, 5.9 Hz, 1H), 1.24 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 153.8, 151.0, 132.0, 128.2, 127.9, 126.6, 123.7, 117.9, 113.0, 111.9, 87.9, 87.7, 83.7, 83.6, 64.5, 56.3, 55.8, 44.7, 36.4, 35.7, 32.7, 29.8, 24.9, 24.7; HRMS (ESI) calcd for $C_{31}H_{38}O_6B$ $[M+H]^+$: 517.2756; found: 517.2744; $[\alpha]^{20}_D$ = -140.51° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 93/07, detected at 240 nm, Flow rate = 1 mL/min, Retention times: 24.115 min (major), 27.732 min (minor).



<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	24.137	55898946	1035114	49.717	54.136
2	27.411	56535926	876954	50.283	45.864
Total		112434872	1912068	100.000	100.000

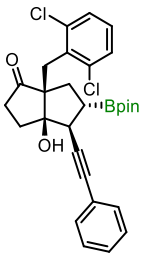


<Peak Table>

PDA Ch1 240nm

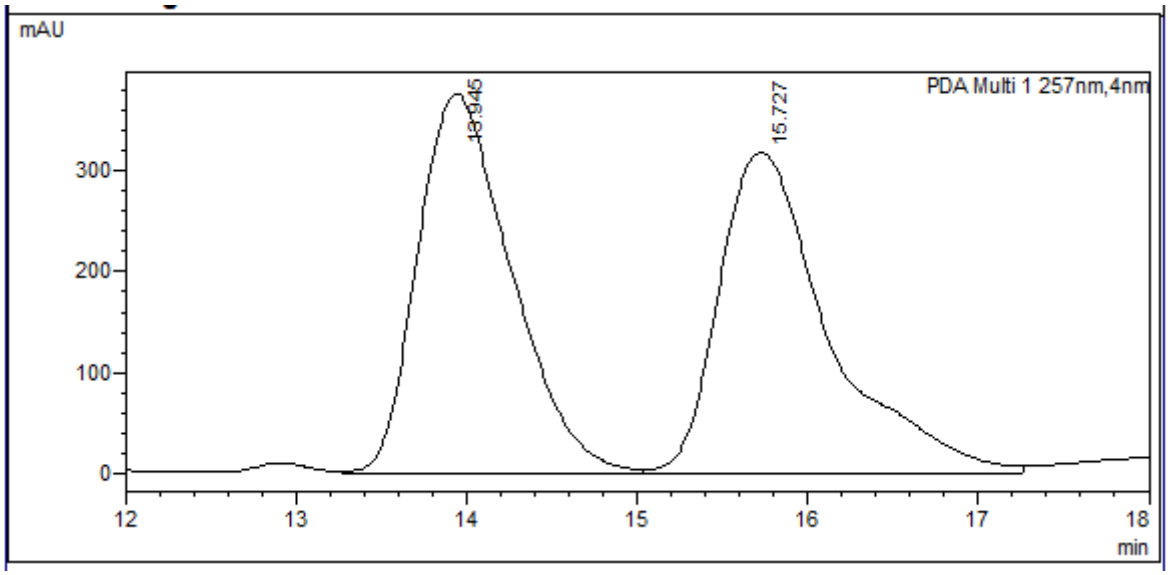
Peak#	Ret. Time	Area	Height	Area%	Height%
1	24.115	35692667	672599	100.000	99.998
2	27.732	36	12	0.000	0.002
Total		35692703	672611	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(2,6-Dichlorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2u):



Prepared according to the general procedure as described above in 78% yield (123 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a light white solid; mp = 172–174°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.30 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.25 (br.s, 2H), 7.07 (t, *J* = 8.0 Hz, 1H), 3.47 (d, *J* = 14.4 Hz, 1H), 3.31 (d, *J* = 14.4 Hz, 1H), 2.89 – 2.81 (m, 1H), 2.75 (d, *J* = 11.9 Hz, 1H), 2.65 (dd, *J* = 13.7, 10.2 Hz, 1H), 2.43 – 2.29 (m, 3H), 1.96 (dd, *J* = 21.8, 10.0 Hz, 1H), 1.80 (dd, *J* = 13.7, 9.8 Hz, 1H), 1.19 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.6, 136.7, 134.1, 132.0, 128.6, 128.5, 128.4, 128.3, 123.0, 89.0, 86.9, 85.3, 83.7, 63.8, 44.2, 36.3, 33.8, 32.0, 29.9, 24.8, 24.8; HRMS (ESI) calcd for $C_{29}H_{32}O_4BCl_2$ $[M+H]^+$: 525.1765; found:525.1752; $[\alpha]^{20}_D$ = -89.33° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*;

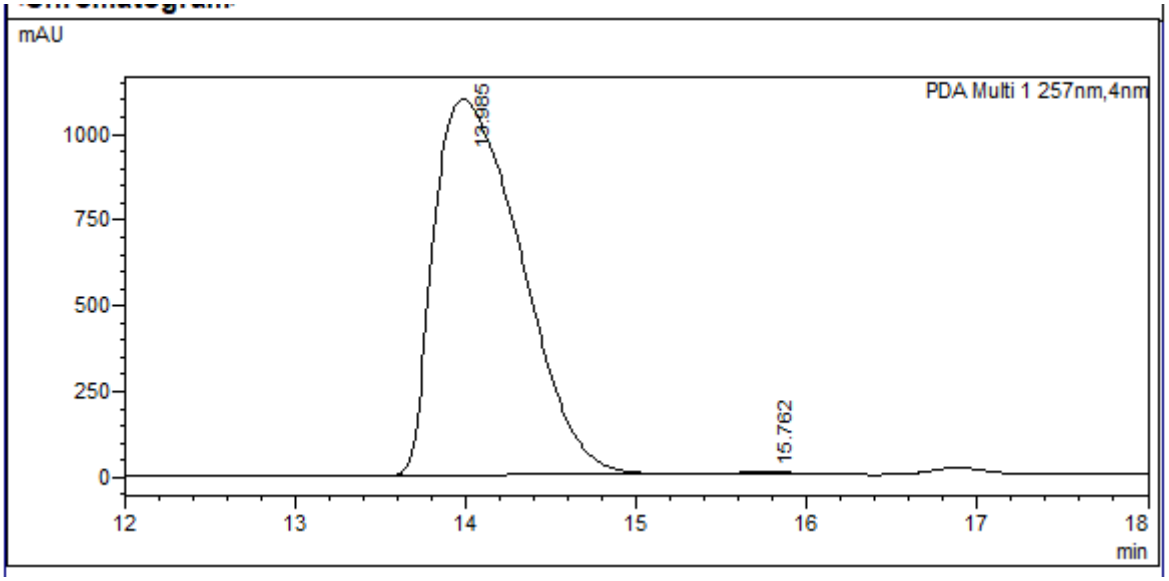
Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 257 nm, Flow rate = 1 mL/min, Retention times: 13.985 min (major), 15.762 min (minor).



<Peak Table>

PDA Ch1 257nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.945	14466637	377819	50.153	54.109
2	15.727	14378564	320433	49.847	45.891
Total		28845200	698251	100.000	100.000

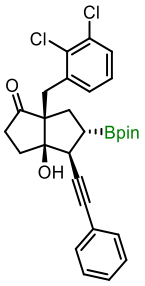


<Peak Table>

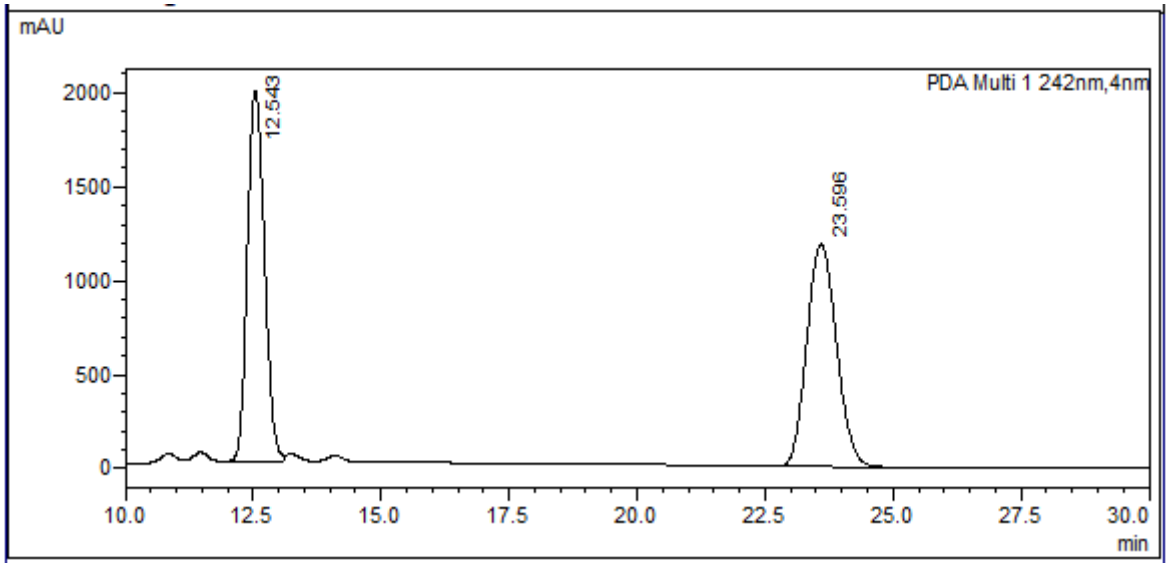
PDA Ch1 257nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.985	39008444	1096300	99.844	99.714
2	15.762	61025	3147	0.156	0.286
Total		39069469	1099447	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-6a-(2,3-Dichlorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2v):



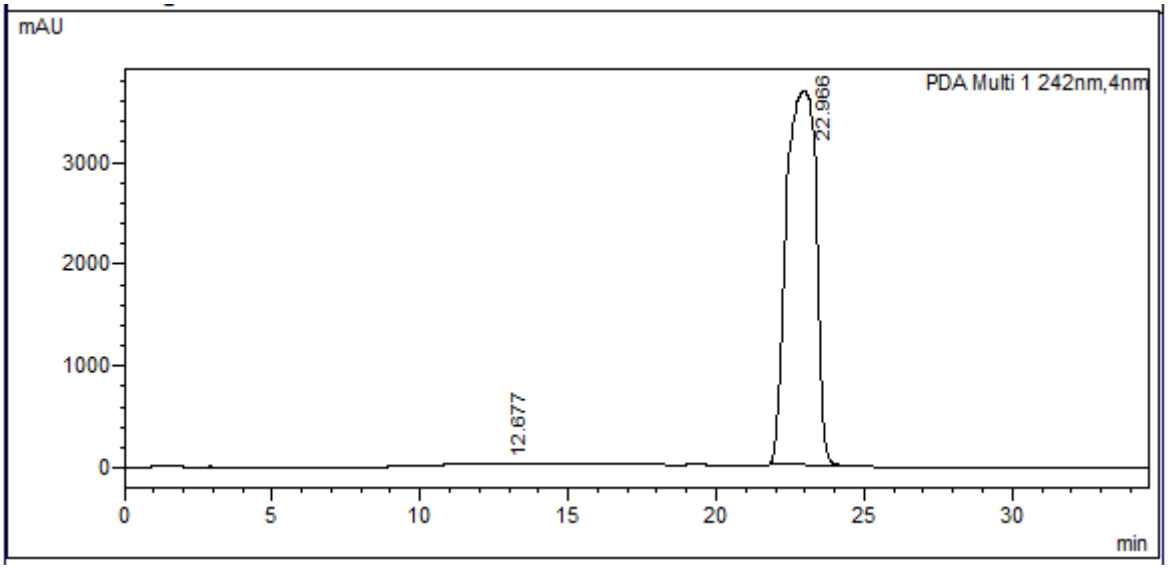
Prepared according to the general procedure as described above in 72% yield (113 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 178–180°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.27 – 7.22 (m, 4H), 7.17 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 3.20 (d, *J* = 14.2 Hz, 1H), 3.08 (d, *J* = 14.2 Hz, 1H), 2.66 (d, *J* = 11.7 Hz, 1H), 2.62 (ddd, *J* = 12.7, 10.8, 2.7 Hz, 1H), 2.32 (dt, *J* = 19.3, 9.5 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.13 – 2.03 (m, 2H), 1.92 – 1.77 (m, 2H), 1.14 (d, *J* = 1.5 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.4, 137.7, 133.5, 133.2, 131.9, 130.2, 129.0, 128.4, 126.8, 122.9, 88.4, 86.6, 85.1, 83.7, 63.3, 44.5, 36.0, 34.9, 34.1, 29.5, 24.8, 24.7; HRMS (ESI) calcd for $C_{29}H_{32}O_4BCl_2$ $[M+H]^+$: 525.1765; found: 525.1753; $[\alpha]^{20}_D$ = -63.90° (*c* 2.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 92/08, detected at 242 nm, Flow rate = 1 mL/min, Retention times: 22.966 min (major), 12.677 min (minor).



<Peak Table>

PDA Ch1 242nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.543	46388886	1973235	49.274	62.519
2	23.596	47755314	1182966	50.726	37.481
Total		94144199	3156202	100.000	100.000

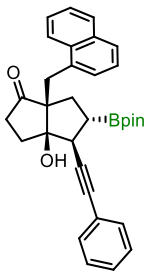


<Peak Table>

PDA Ch1 242nm

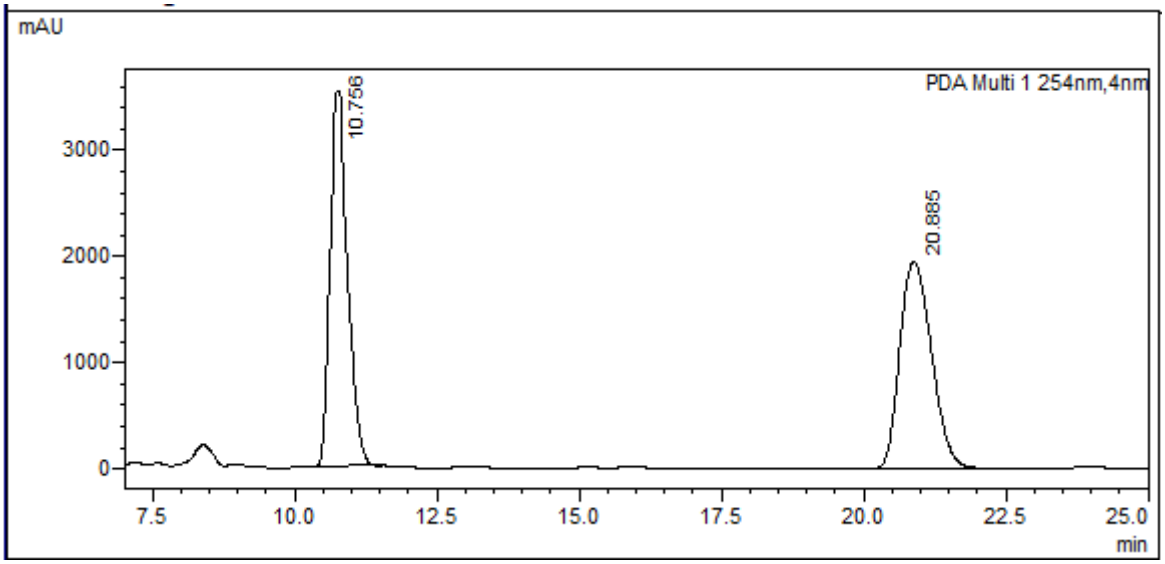
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.677	2670	13	0.001	0.000
2	22.966	255521832	3666338	99.999	100.000
Total		255524502	3666351	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-(naphthalen-1-ylmethyl)-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2w):



Prepared according to the general procedure as described above in 78% yield (118 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a white solid; mp = 186–188°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 6.6 Hz, 1H), 7.46 (ddd, *J* = 12.2, 8.0, 1.3 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.37 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.32 – 7.28 (m, 3H), 3.51 (dd, *J* = 34.6, 14.2 Hz, 2H), 2.68 (d, *J* = 12.1 Hz, 1H), 2.25

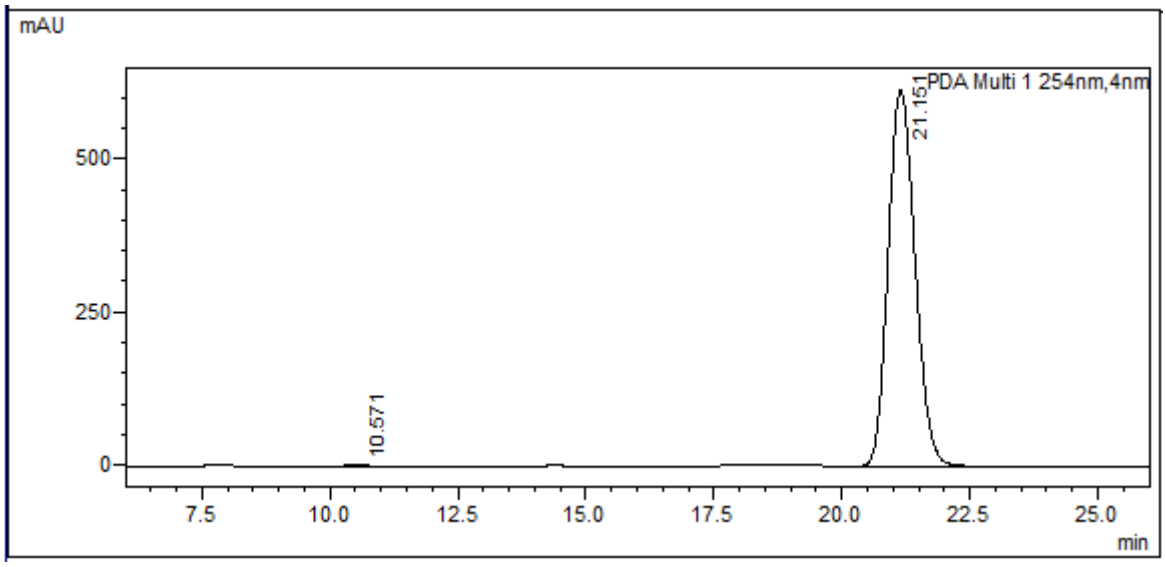
(dd, J = 19.4, 9.5 Hz, 1H), 2.16 – 2.01 (m, 4H), 1.99 – 1.89 (m, 1H), 1.72 (ddd, J = 14.2, 11.7, 9.5 Hz, 1H), 1.21 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.6, 133.9, 133.7, 132.8, 131.9, 129.1, 128.7, 128.4, 128.4, 127.6, 125.8, 125.5, 125.2, 124.8, 123.0, 88.0, 86.9, 85.0, 83.7, 64.3, 45.5, 36.5, 35.4, 33.5, 29.6, 24.9, 24.7; HRMS (ESI) calcd for $C_{33}H_{36}O_4B$ $[M+H]^+$: 507.2706; found: 507.2701; $[\alpha]^{20}_D$ = -79.66° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 94/06, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 21.151 min (major), 10.571 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.756	75683601	3534219	49.987	64.534
2	20.885	75722462	1942267	50.013	35.466
Total		151406063	5476486	100.000	100.000

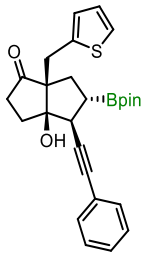


<Peak Table>

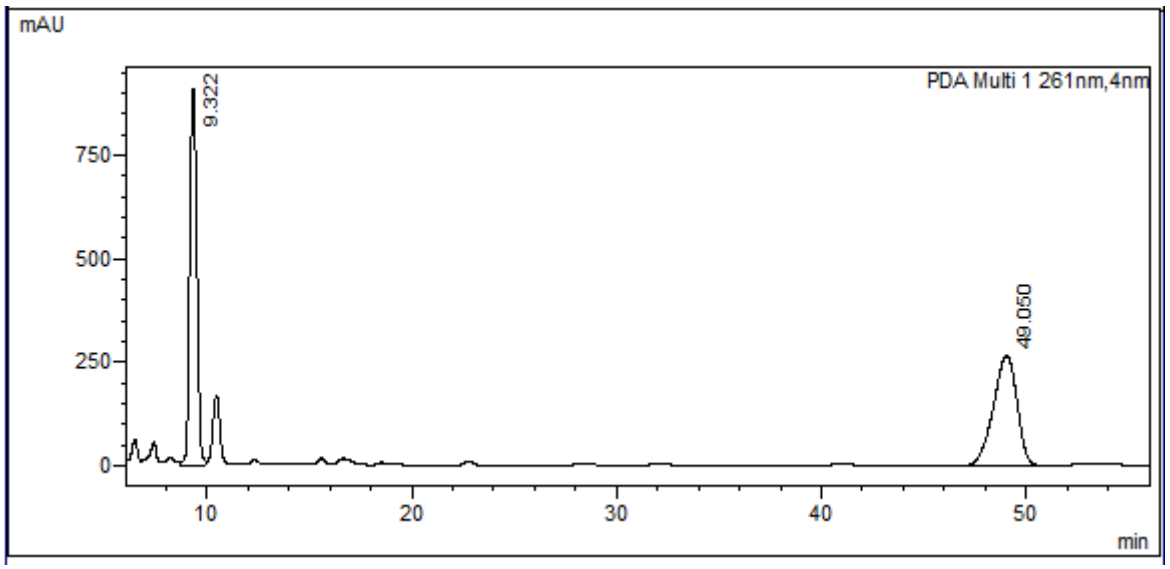
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.571	82139	2373	0.364	0.385
2	21.151	22487774	614426	99.636	99.615
Total		22569913	616799	100.000	100.000

(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6a-(thiophen-2-ylmethyl)hexahydropentalen-1(2*H*)-one (2x):



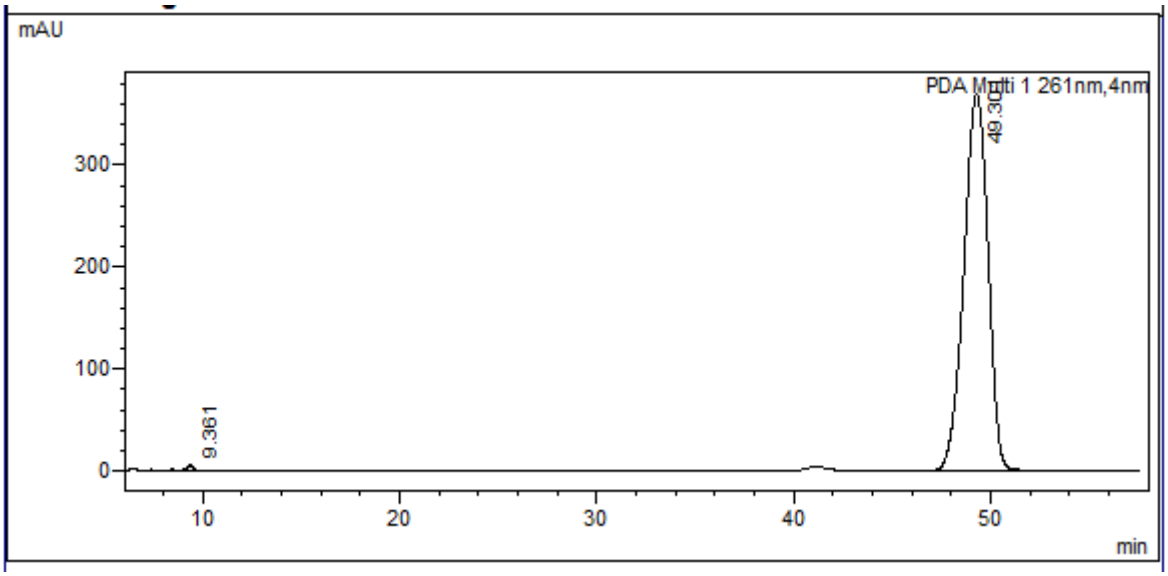
Prepared according to the general procedure as described above in 72% yield (100 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 146–148°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.30 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.11 (dd, *J* = 4.7, 1.6 Hz, 1H), 6.89 – 6.85 (m, 2H), 3.26 (q, *J* = 14.4 Hz, 2H), 2.76 (d, *J* = 11.1 Hz, 1H), 2.40 – 2.30 (m, 1H), 2.25 (dd, *J* = 10.3, 2.1 Hz, 1H), 2.23 – 2.12 (m, 2H), 1.98 (d, *J* = 8.4 Hz, 1H), 1.96 – 1.90 (m, 1H), 1.65 (dt, *J* = 13.0, 10.4 Hz, 1H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.9, 139.4, 131.9, 128.4, 128.4, 127.9, 126.6, 124.4, 123.0, 88.0, 86.6, 85.1, 83.7, 64.0, 46.3, 37.4, 37.0, 33.3, 30.4, 24.9, 24.7; HRMS (ESI) calcd for $C_{27}H_{32}O_4BS$ $[M+H]^+$: 463.2109; found: 463.2098; $[\alpha]^{20}_D$ = -112.25° (*c* 2.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 261 nm, Flow rate = 1 mL/min, Retention times: 49.301 min (major), 9.361 min (minor).



<Peak Table>

PDA Ch1 261nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.322	22003435	909692	50.740	77.326
2	49.050	21361372	266747	49.260	22.674
Total		43364807	1176438	100.000	100.000

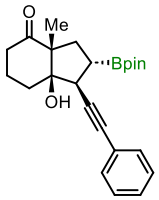


<Peak Table>

PDA Ch1 261nm

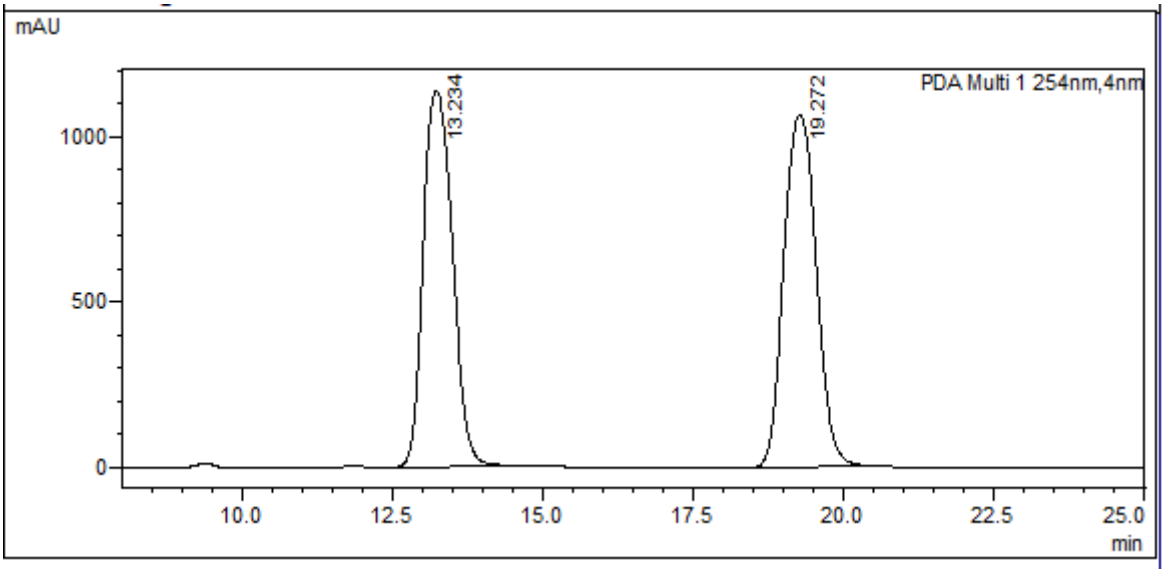
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.361	82991	4359	0.264	1.168
2	49.301	31409609	368966	99.736	98.832
Total		31492599	373325	100.000	100.000

(1*S*,2*S*,3a*R*,7a*R*)-7a-hydroxy-3a-methyl-1-(phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4*H*-inden-4-one (2y):



Prepared according to the general procedure as described above in 77% yield (91 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 133–135°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.31 – 7.26 (m, 3H), 2.89 (d, *J* = 10.0 Hz, 1H), 2.62 – 2.48 (m, 2H), 2.33 – 2.23 (m, 1H), 2.11 (br.s, 1H), 2.06 (dt, *J* = 14.3, 3.6 Hz, 1H), 2.01 – 1.87 (m, 2H), 1.82 – 1.70 (m, 2H), 1.64 (ddt, *J* = 13.4, 9.8, 4.7 Hz, 1H), 1.32 – 1.22 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.6, 131.9, 128.4, 128.2, 123.3, 88.3, 84.6, 83.8, 83.7, 60,5 41.1, 36.9, 32.8, 31.1, 25.0, 24.7, 20.2, 19.5; HRMS (ESI) calcd for $C_{24}H_{32}O_4B$ $[M+H]^+$: 395.2388; found: 395.2418;

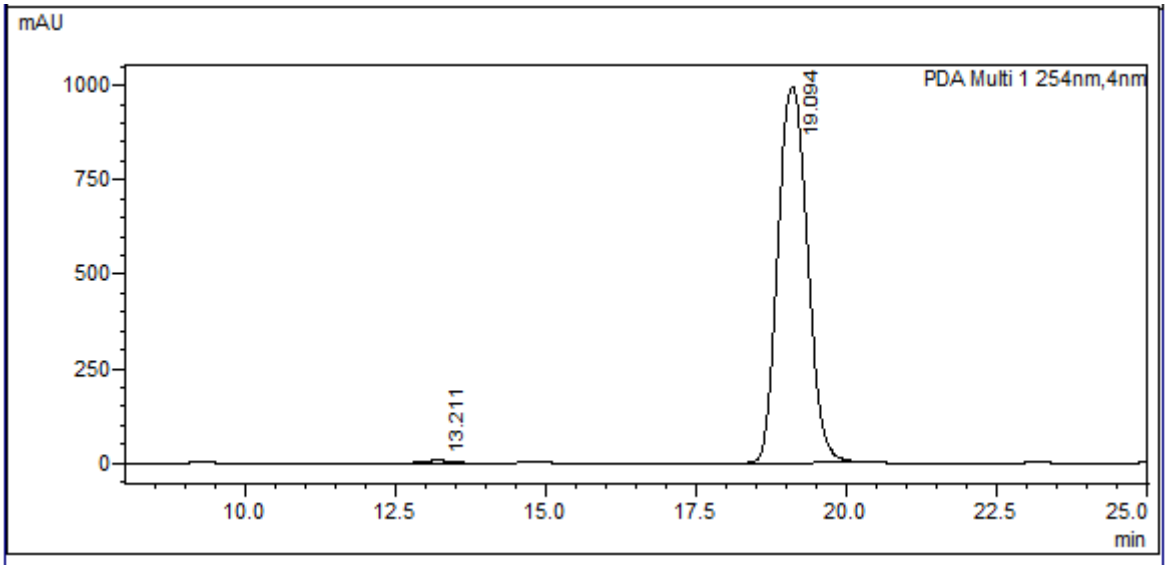
$[\alpha]^{25}_{D}$ = 57.80° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 99:01 *er*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 95/05, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 19.094 min (major), 13.211 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.234	38332124	1134162	48.939	51.629
2	19.272	39993579	1062581	51.061	48.371
Total		78325703	2196743	100.000	100.000

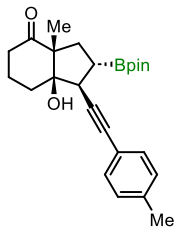


<Peak Table>

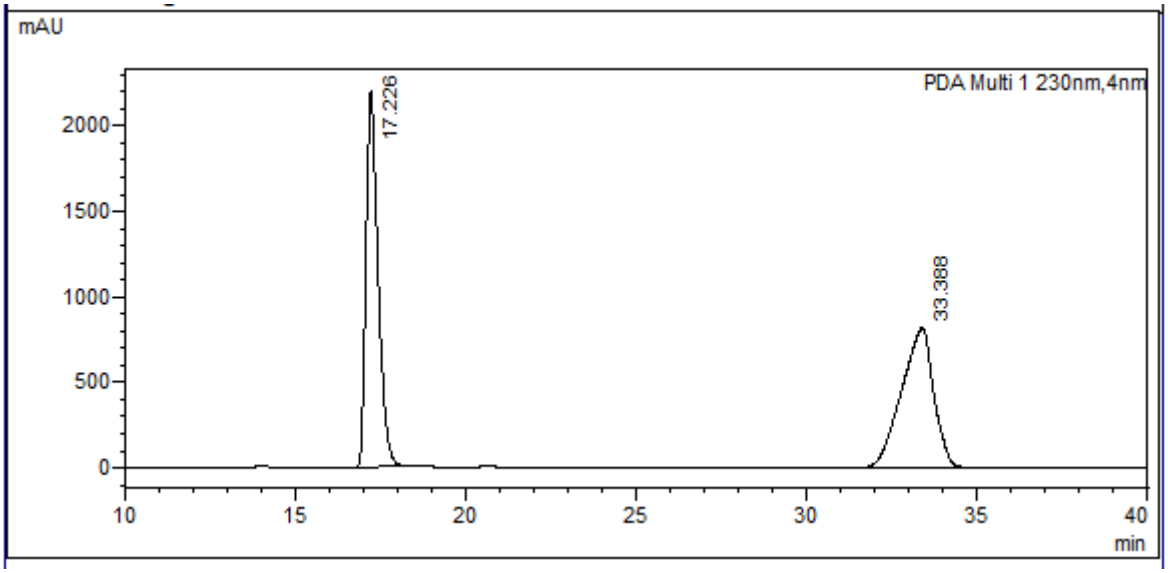
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.211	172741	6754	0.502	0.674
2	19.094	34254644	995169	99.498	99.326
Total		34427385	1001923	100.000	100.000

(1*S*,2*S*,3a*R*,7a*R*)-7a-Hydroxy-3a-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolylethynyl)octahydro-4*H*-inden-4-one (2z):



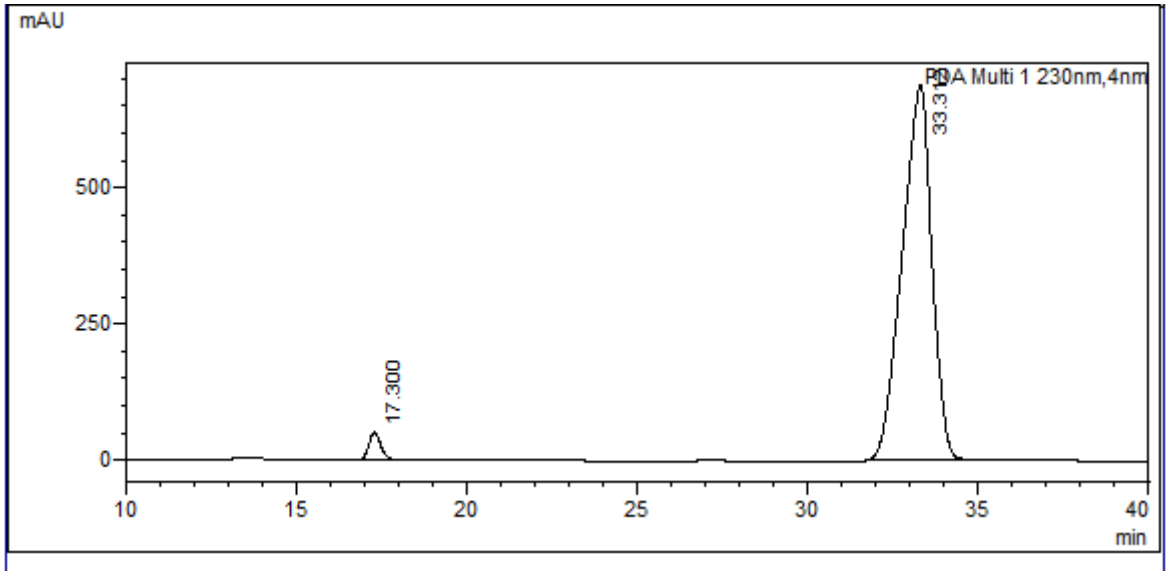
Prepared according to the general procedure as described above in 73% yield (89 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 172–174°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 8.1, 1.9 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 2.88 (d, *J* = 9.9 Hz, 1H), 2.55 (ddd, *J* = 18.9, 10.2, 5.4 Hz, 2H), 2.33 (s, 3H), 2.31 – 2.25 (m, 1H), 2.06 (dd, *J* = 14.5, 4.3 Hz, 1H), 2.00 – 1.88 (m, 2H), 1.76 (dt, *J* = 9.3, 8.5 Hz, 2H), 1.71 – 1.62 (m, 2H), 1.31 – 1.22 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.7, 138.3, 131.8, 129.1, 120.2, 87.5, 84.7, 83.7, 83.6, 60.5, 41.1, 36.9, 32.8, 31.1, 25.0, 24.7, 21.6, 20.2, 19.5; HRMS (ESI) calcd for $C_{25}H_{34}BO_4$ $[M+H]^+$: 409.2545; found: 409.2579; $[\alpha]^{25}_D$ = +52.80° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 97:3 *er*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 230 nm, Flow rate = 1 mL/min, Retention times: 33.312 min (major), 17.300 min (minor).



<Peak Table>

PDA Ch1 230nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.226	54135195	2199427	50.445	72.990
2	33.388	53179673	813902	49.555	27.010
Total		107314868	3013328	100.000	100.000

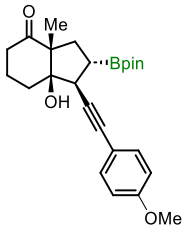


<Peak Table>

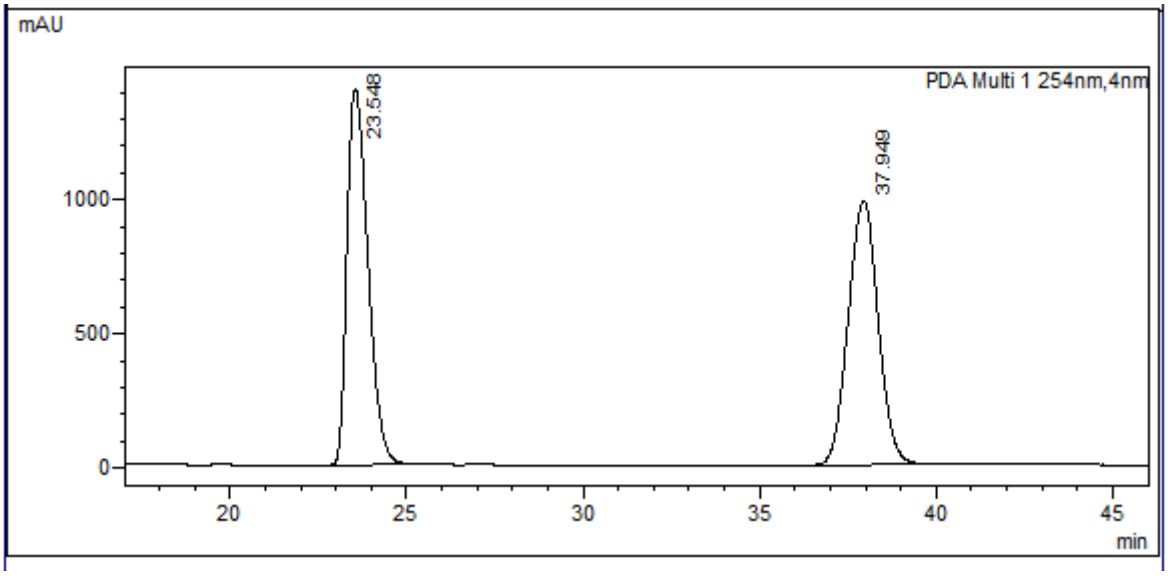
PDA Ch1 230nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.300	1215853	49769	2.859	6.753
2	33.312	41307032	687188	97.141	93.247
Total		42522885	736957	100.000	100.000

(1*S*,2*S*,3a*R*,7a*R*)-7a-Hydroxy-1-((4-methoxyphenyl)ethynyl)-3a-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (2aa):



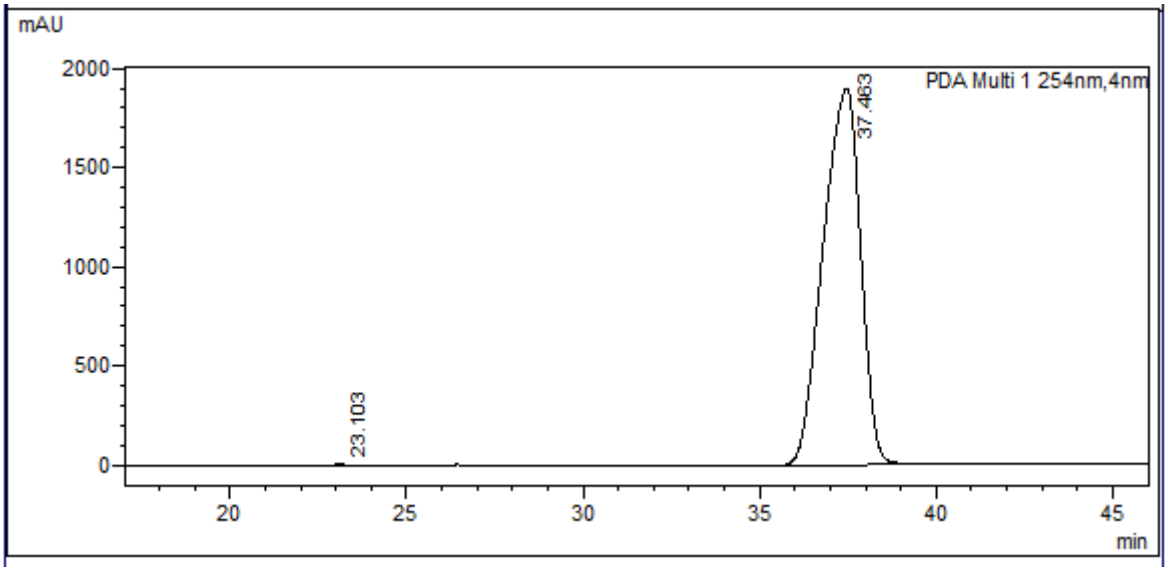
Prepared according to the general procedure as described above in 78% yield (99 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 154–156°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 8.9, 2.1 Hz, 2H), 6.81 (dt, *J* = 8.9, 2.1 Hz, 2H), 3.79 (s, 3H), 2.87 (d, *J* = 9.8 Hz, 1H), 2.61 – 2.46 (m, 2H), 2.34 – 2.17 (m, 2H), 2.11 – 1.93 (m, 2H), 1.89 (ddd, *J* = 11.1, 7.0, 4.3 Hz, 1H), 1.84 – 1.70 (m, 2H), 1.68 – 1.59 (m, 1H), 1.31 – 1.22 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.7, 159.5, 133.3, 115.4, 114.0, 86.7, 84.4, 83.7, 83.6, 60.5, 55.4, 41.1, 36.9, 32.8, 31.1, 25.0, 24.7, 20.2, 19.5; HRMS (ESI) calcd for $C_{25}H_{34}BO_5$ $[M+H]^+$: 425.2499; found: 425.2533; $[\alpha]^{25}_D$ = +65.80° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99.9:0.1 *er*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 92/08, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 37.463 min (major), 23.103 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	23.548	57874905	1398689	50.071	58.736
2	37.949	57709852	982618	49.929	41.264
Total		115584756	2381307	100.000	100.000

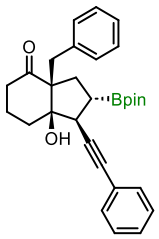


<Peak Table>

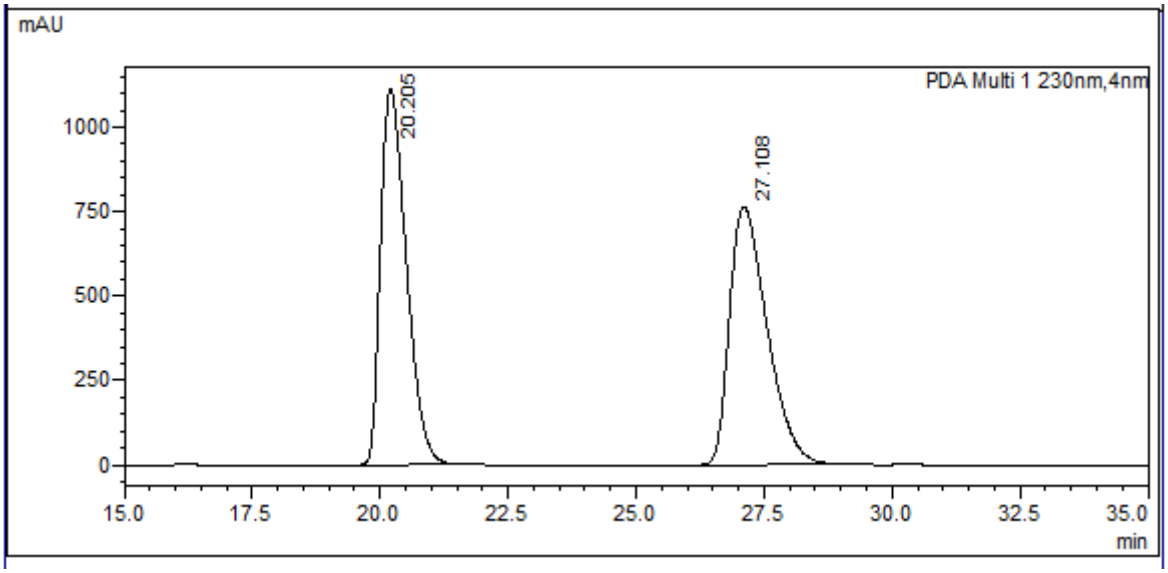
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	23.103	66905	2353	0.048	0.124
2	37.463	140399460	1895483	99.952	99.876
Total		140466365	1897837	100.000	100.000

(1*S*,2*S*,3a*S*,7a*R*)-3a-Benzyl-7a-hydroxy-1-(phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (2ab):



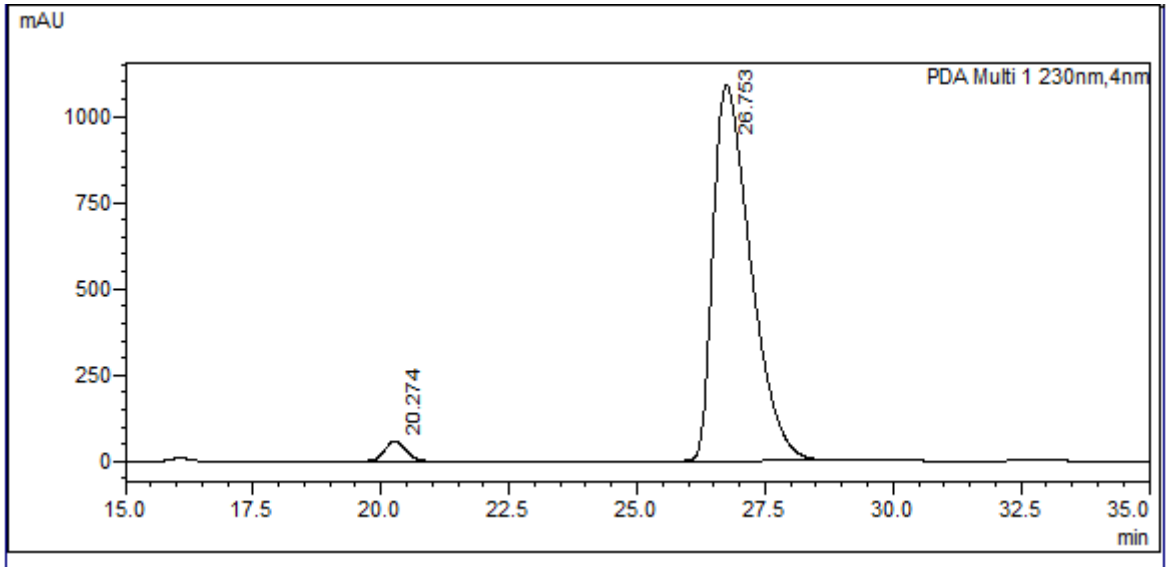
Prepared according to the general procedure as described above in 72% yield (102 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 175–177°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (ddd, *J* = 6.5, 5.1, 3.3 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.23 – 7.14 (m, 3H), 7.07 – 7.02 (m, 2H), 3.24 – 3.14 (m, 2H), 2.91 (d, *J* = 10.6 Hz, 1H), 2.70 (td, *J* = 13.9, 6.8 Hz, 1H), 2.40 – 2.29 (m, 2H), 2.12 (dd, *J* = 10.4, 4.0 Hz, 2H), 2.06 – 1.93 (m, 2H), 1.78 – 1.58 (m, 3H), 1.24 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.5, 137.6, 131.9, 129.6, 128.4, 128.3, 128.2, 126.6, 123.3, 88.1, 84.7, 84.7, 83.7, 65.8, 40.8, 39.5, 38.2, 30.8, 24.9, 24.8, 20.7; HRMS (ESI) calcd for $C_{30}H_{36}O_4B$ $[M+H]^+$: 471.2701; found: 471.2731; $[\alpha]^{25}_D$ = +74.60° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 97:3 *er*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 95/05, detected at 230 nm, Flow rate = 1 mL/min, Retention times: 26.753 min (major), 20.274 min (minor).



<Peak Table>

PDA Ch1 230nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.205	39038461	1112861	50.008	59.276
2	27.108	39025737	764549	49.992	40.724
Total		78064198	1877410	100.000	100.000

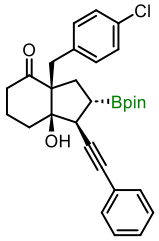


<Peak Table>

PDA Ch1 230nm

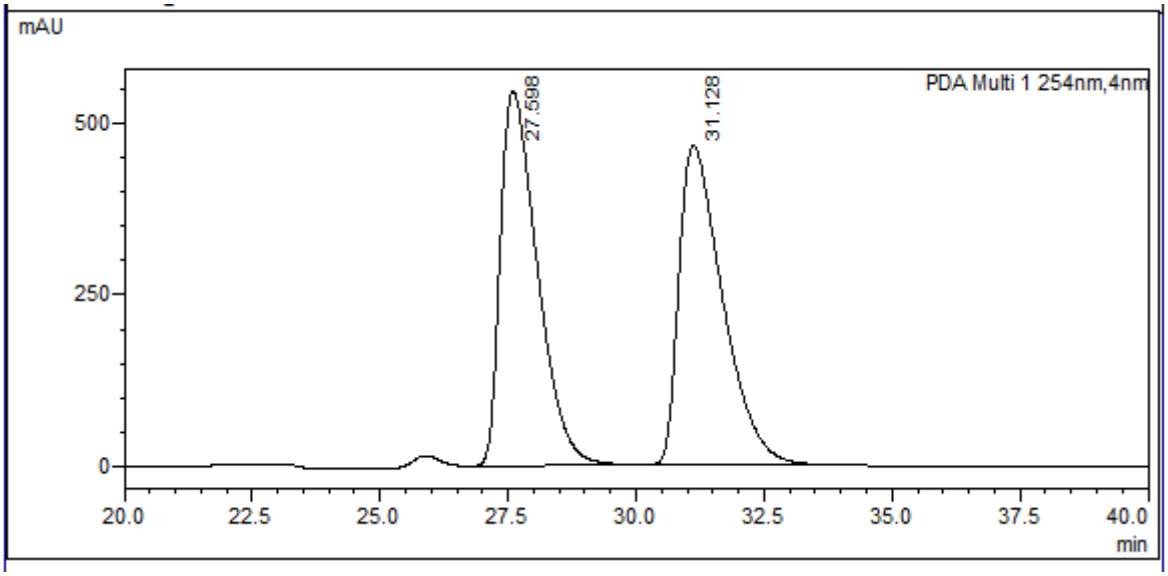
Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.274	1728066	58442	3.006	5.092
2	26.753	55764715	1089292	96.994	94.908
Total		57492781	1147733	100.000	100.000

(1*S*,2*S*,3a*S*,7a*R*)-3a-(4-Chlorobenzyl)-7a-hydroxy-1-(phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (2ac):



Prepared according to the general procedure as described above in 75% yield (113 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a white solid; mp = 193–195°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.33 – 7.28 (m, 3H), 7.17 (dt, *J* = 8.4, 1.7 Hz, 2H), 6.97 (dt, *J* = 8.4, 1.7 Hz, 2H), 3.15 (s, 2H), 2.91 (d, *J* = 10.6 Hz, 1H), 2.64 (td, *J* = 13.9, 6.8 Hz, 1H), 2.33 (dd, *J* = 12.6, 5.6 Hz, 3H), 2.18 – 2.03 (m, 2H), 2.03 – 1.91 (m, 2H), 1.81 – 1.62 (m, 2H), 1.25 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (126 MHz, CDCl3) δ 210.4, 136.1, 132.5, 131.9, 130.9, 128.5, 128.4, 128.3, 123.2, 87.9, 84.7, 84.6, 83.7, 65.6, 40.8, 38.8, 38.2, 30.9, 30.8, 24.9, 24.8, 20.6; HRMS (ESI)

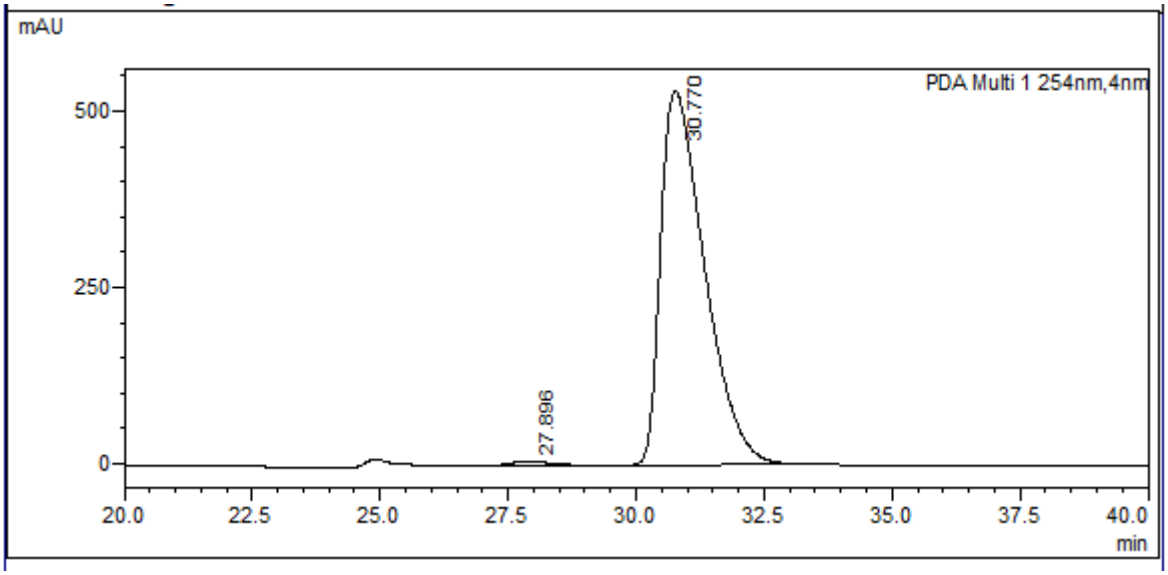
calcd for $C_{30}H_{35}O_4BCl$ $[M+H]^+$: 505.2316; found: 505.2345; $[\alpha]^{25}_D$ = +105.09° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 99:1 *er*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 96/4, detected at 225 nm, Flow rate = 1 mL/min, Retention times: 30.770 min (major), 27.896 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	27.598	27491301	547747	49.861	53.970
2	31.128	27645027	467172	50.139	46.030
Total		55136328	1014919	100.000	100.000

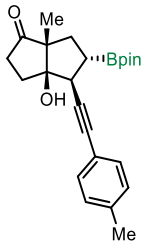


<Peak Table>

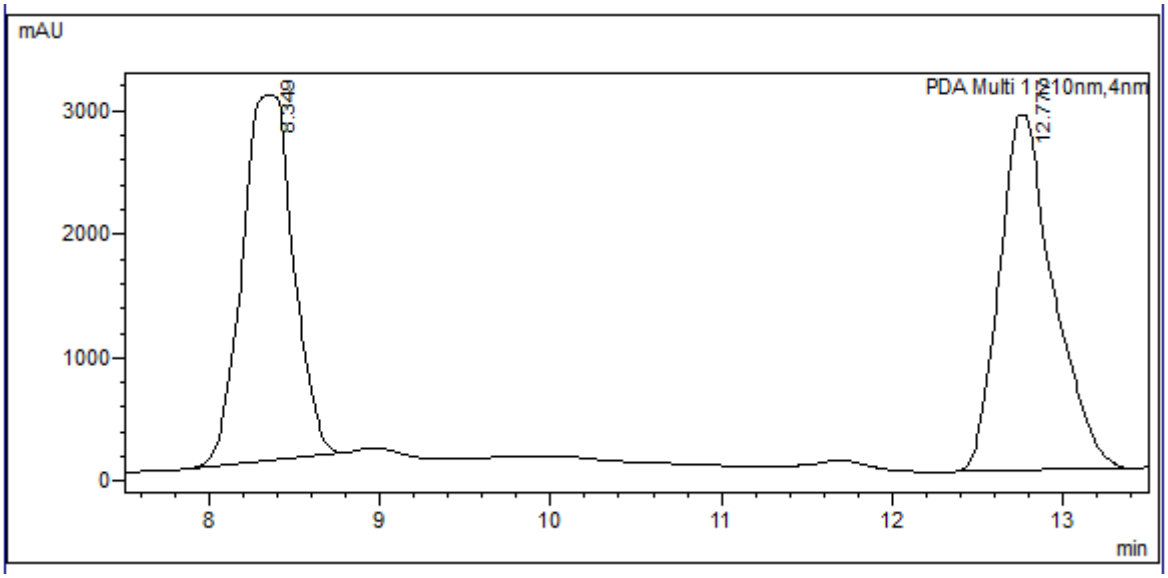
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	27.896	279635	5998	0.874	1.119
2	30.770	31703847	530131	99.126	98.881
Total		31983483	536128	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(p-tolylethynyl)hexahydropentalen-1(2*H*)-one (2ae):



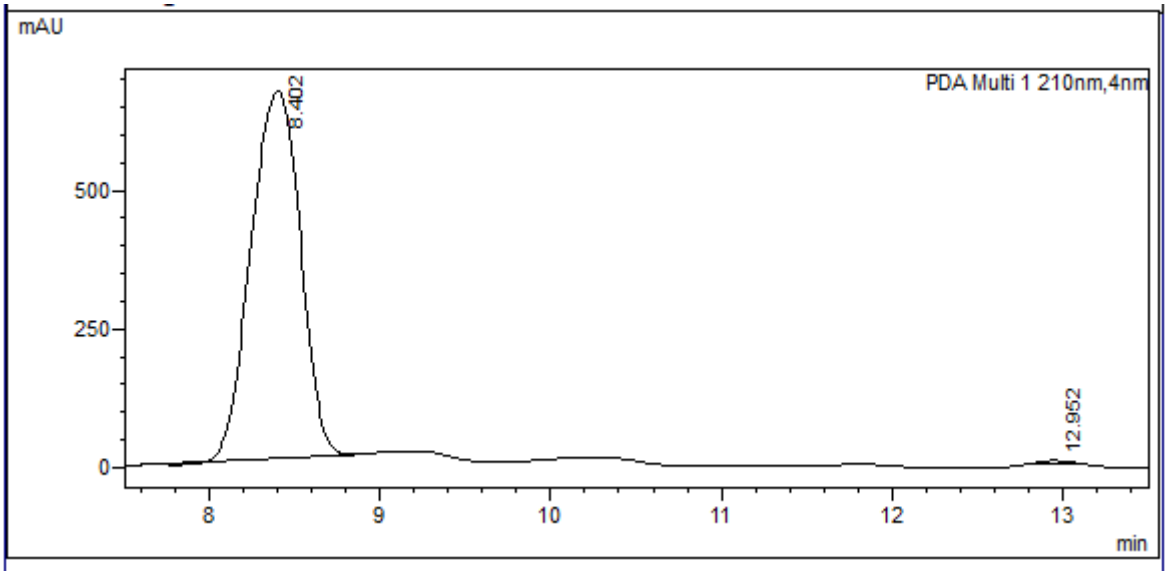
Prepared according to the general procedure as described above in 54% yield (64 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a white solid; mp = 149–151°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.85 (d, *J* = 10.2 Hz, 1H), 2.57 – 2.38 (m, 3H), 2.34 (s, 3H), 2.24 (ddd, *J* = 12.9, 9.0, 3.5 Hz, 1H), 1.99 (dt, *J* = 13.2, 9.9 Hz, 1H), 1.90 (qd, *J* = 10.2, 5.5 Hz, 1H), 1.80 (dd, *J* = 18.1, 14.4 Hz, 1H), 1.27 – 1.17 (m, 12H), 1.12 (d, *J* = 17.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.3, 138.5, 131.8, 129.2, 119.9, 87.8, 86.4, 85.4, 83.7, 59.3, 45.0, 37.1, 35.8, 30.5, 24.9, 24.7, 21.6, 17.0; HRMS (ESI) calcd for $C_{24}H_{32}BO_4$ $[M+H]^+$: 395.2393; found: 395.2399; $[\alpha]^{20}_D$ = -57.80° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 93/07, detected at 210 nm, Flow rate = 1 mL/min, Retention times: 8.402 min (major), 12.952 min (minor).



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.349	61801360	2957936	49.269	50.654
2	12.777	63635198	2881589	50.731	49.346
Total		125436558	5839526	100.000	100.000

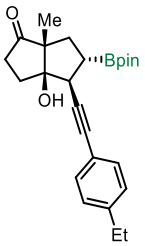


<Peak Table>

PDA Ch1 210nm

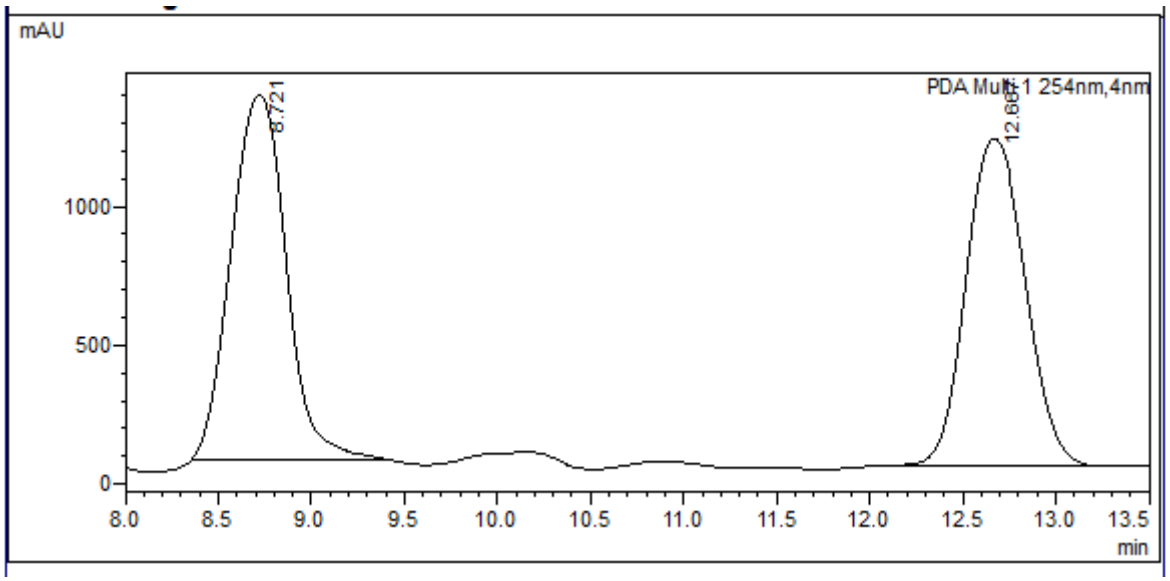
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.402	13320432	661835	99.579	99.223
2	12.952	56313	5183	0.421	0.777
Total		13376745	667018	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-4-((4-Ethylphenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2af):



Prepared according to the general procedure as described above in 45% yield (55 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 2.86 (d, *J* = 10.5 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.52 (ddd, *J* = 19.5, 10.2, 3.9 Hz, 1H), 2.50 – 2.37 (m, 1H), 2.23 (ddd, *J* = 12.8, 8.8, 3.8 Hz, 1H), 2.06 – 1.91 (m, 1H), 1.92 – 1.78 (m, 3H), 1.23 (s, 12H), 1.22 (t, *J* = 7.6 Hz, 3H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.3, 144.8, 131.9, 128.0, 120.1, 87.8, 86.4, 85.4, 83.7, 59.3,

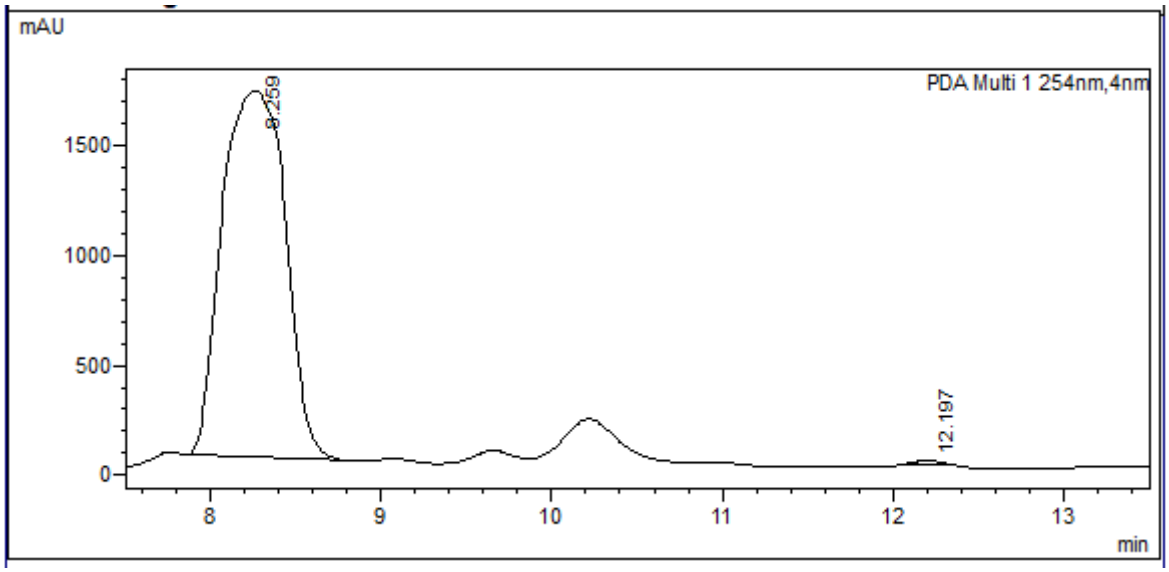
44.9, 37.1, 35.8, 30.4, 28.9, 24.9, 24.7, 17.0, 15.5; HRMS (ESI) calcd for $C_{25}H_{34}BO_4$ $[M+H]^+$: 409.2550; found: 409.2563; $[\alpha]^{20}_D$ = -9.50° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 93/07, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 8.259 min (major), 12.197 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.721	26732726	1310394	50.457	52.729
2	12.667	26248650	1174755	49.543	47.271
Total		52981376	2485149	100.000	100.000

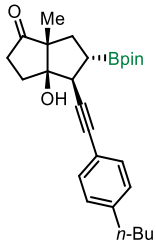


<Peak Table>

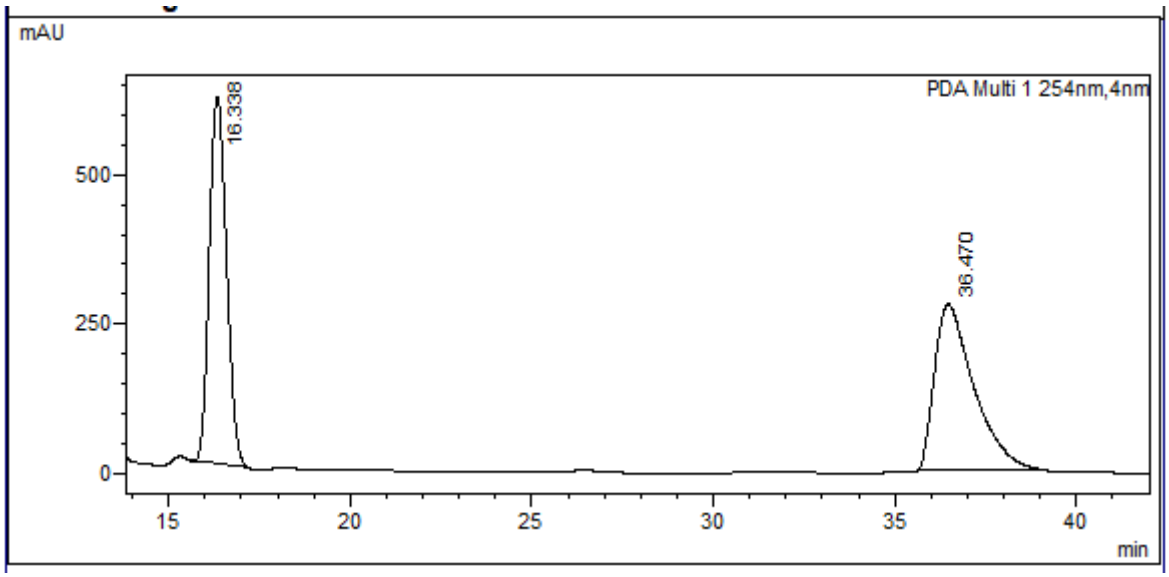
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.259	43018573	1663508	99.692	99.176
2	12.197	133107	13824	0.308	0.824
Total		43151681	1677331	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-4-((4-Butylphenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ag):



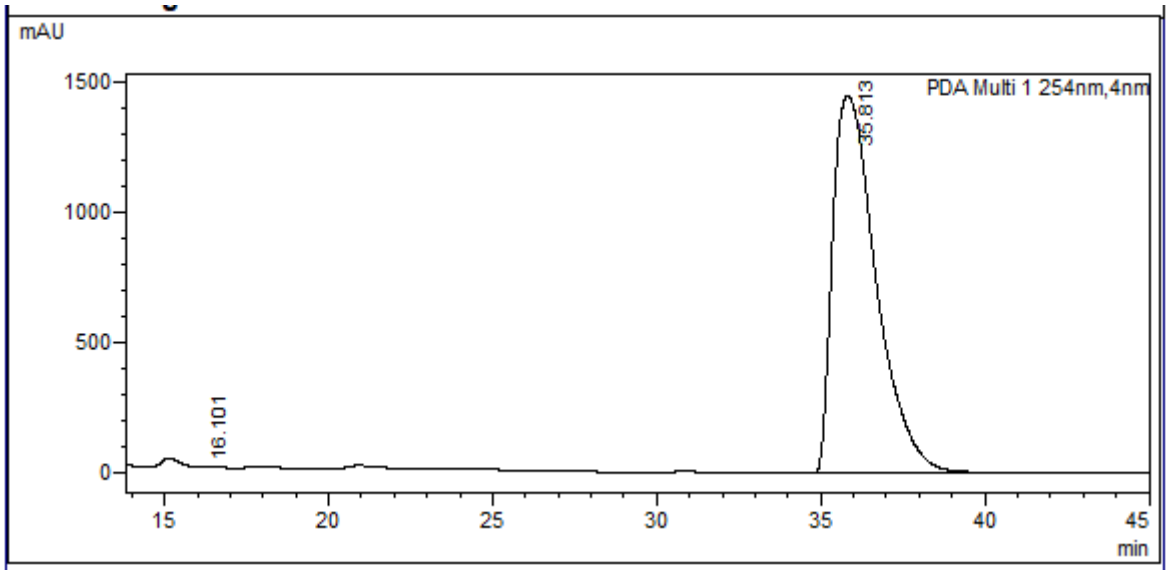
Prepared according to the general procedure as described above in 44% yield (58 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 2.86 (d, *J* = 10.5 Hz, 1H), 2.63 – 2.56 (m, 2H), 2.50 (dd, *J* = 10.2, 3.9 Hz, 1H), 2.42 (dd, *J* = 19.4, 9.2 Hz, 1H), 2.23 (ddd, *J* = 12.8, 8.8, 3.8 Hz, 1H), 2.05 – 1.97 (m, 1H), 1.96 – 1.85 (m, 2H), 1.84 – 1.78 (m, 1H), 1.58 (ddd, *J* = 15.4, 11.0, 7.5 Hz, 2H), 1.40 – 1.30 (m, 2H), 1.23 (s, 12H), 1.14 (s, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.3, 143.5, 131.8, 128.5, 120.1, 87.8, 86.4, 85.4, 83.7, 59.3, 45.0, 37.1, 35.8, 35.7, 33.5, 30.5, 24.9, 24.7, 22.4, 17.0, 14.1; HRMS (ESI) calcd for $C_{27}H_{38}O_4B$ $[M+H]^+$: 437.2863; found: 437.2847; $[\alpha]^{20}_D$ = -111.51° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 95/05, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 35.813 min (major), 16.101 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.338	20266532	614334	49.201	68.837
2	36.470	20924978	278107	50.799	31.163
Total		41191510	892442	100.000	100.000

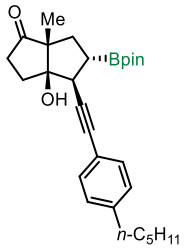


<Peak Table>

PDA Ch1 254nm

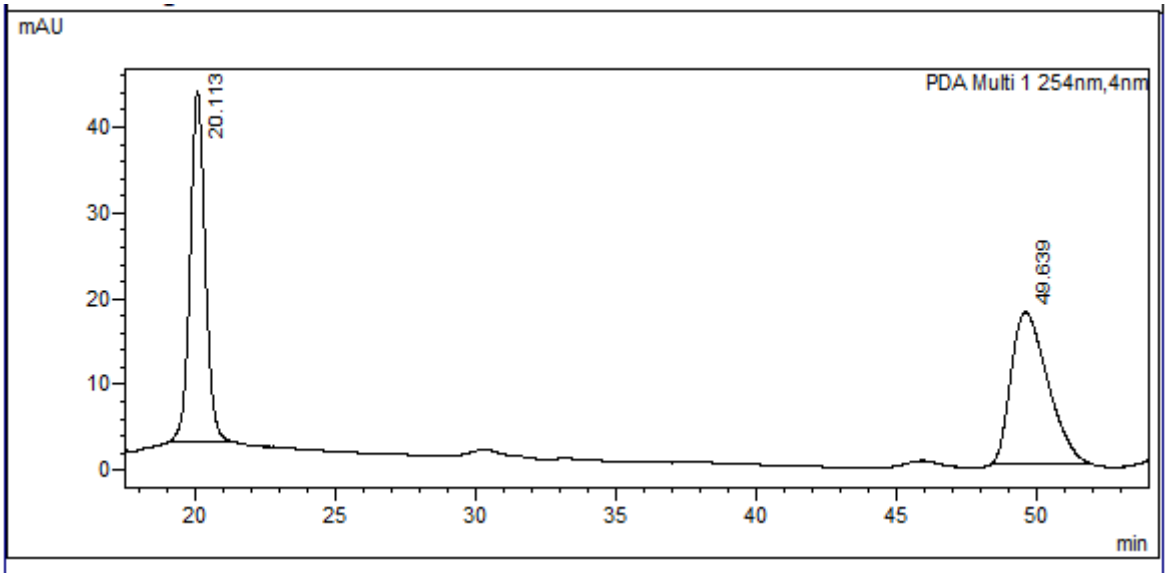
Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.101	4105	22	0.003	0.001
2	35.813	133074074	1442291	99.997	99.999
Total		133078178	1442312	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-4-((4-pentylphenyl)ethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ah):



Prepared according to the general procedure as described above in 47% yield (63 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 2.86 (d, *J* = 10.5 Hz, 1H), 2.63 – 2.56 (m, 2H), 2.54 – 2.37 (m, 2H), 2.26 – 2.18 (m, 1H), 2.05 – 1.95 (m, 2H), 1.92 – 1.77 (m, 4H), 1.59 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.31 (dd, *J* = 6.6, 3.5 Hz, 2H), 1.23 (s, 12H), 1.14 (s, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.3, 143.6, 131.8, 128.6, 120.1, 87.8, 86.4, 85.4, 83.7, 59.4,

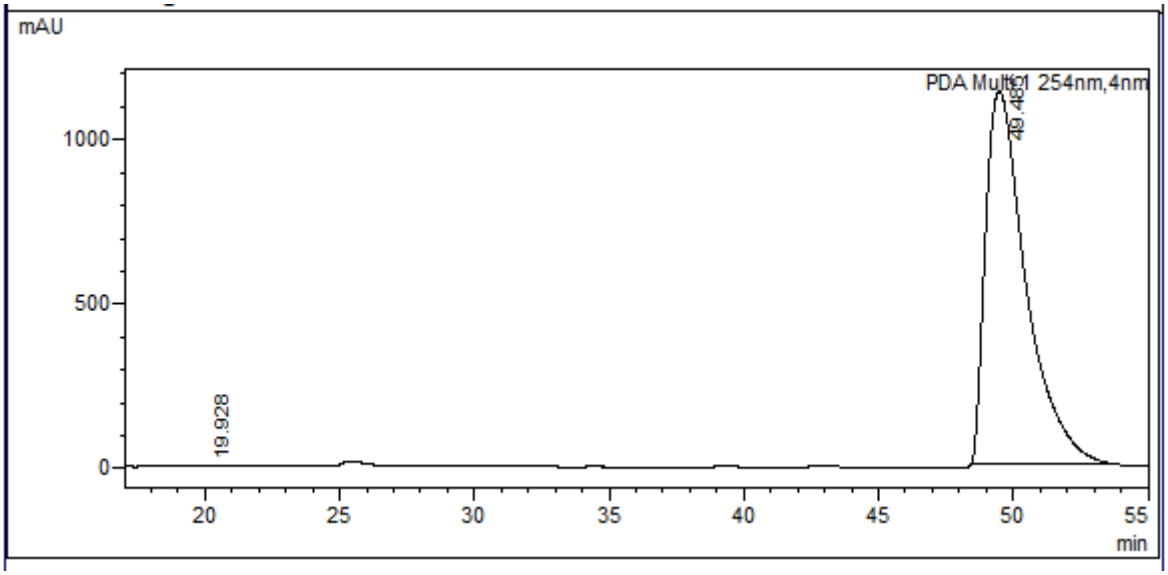
45.0, 37.1, 36.0, 35.9, 31.6, 31.1, 30.5, 29.8, 24.9, 24.7, 22.6, 17.0, 14.1; HRMS (ESI) calcd for $C_{28}H_{40}BO_4$ $[M+H]^+$: 451.3019; found: 451.2986; $[\alpha]^{20}_D$ = -44.50° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 96/04, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 49.485 min (major), 19.928 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.113	1538356	40945	48.984	69.889
2	49.639	1602202	17641	51.016	30.111
Total		3140558	58585	100.000	100.000

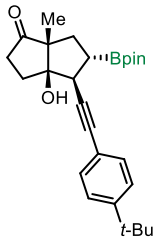


<Peak Table>

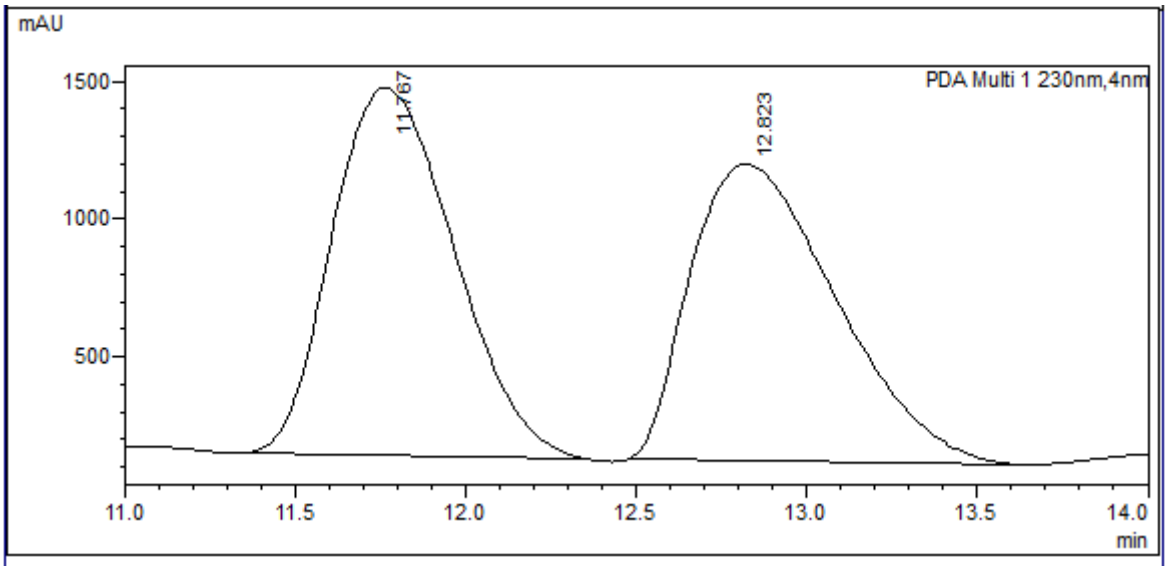
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.928	42421	2115	0.036	0.186
2	49.485	119097243	1135962	99.964	99.814
Total		119139663	1138077	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-4-((4-(*tert*-Butyl)phenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ai):



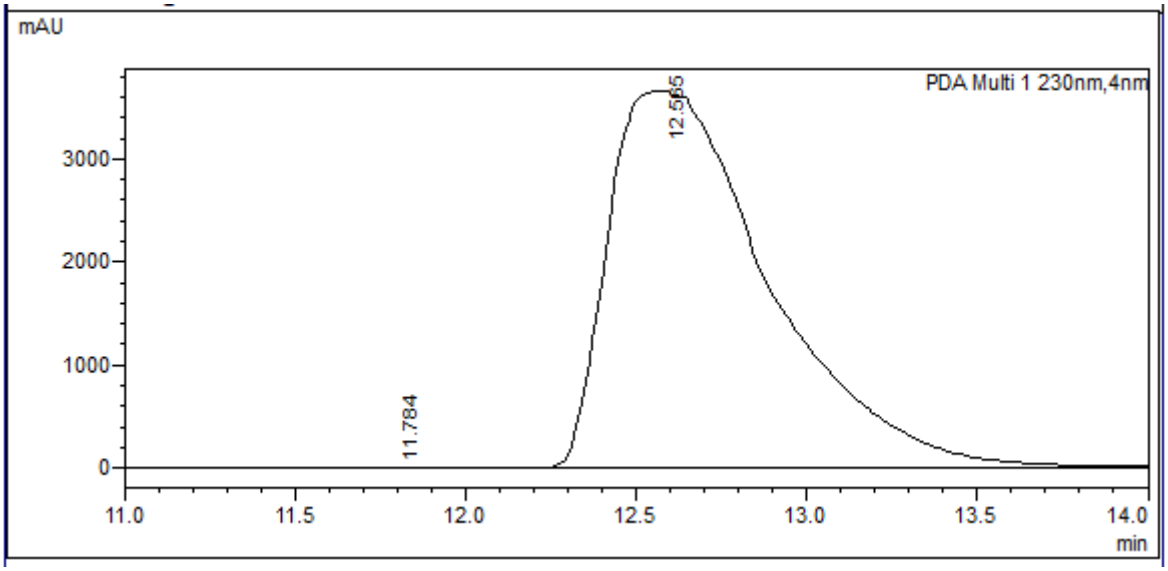
Prepared according to the general procedure as described above in 51% yield (67 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a white solid; mp = 140–142°C; ^{1}H ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.20 (m, 4H), 2.86 (d, *J* = 10.3 Hz, 1H), 2.60 – 2.35 (m, 2H), 2.23 (ddd, *J* = 12.8, 8.5, 4.1 Hz, 1H), 2.08 – 1.91 (m, 2H), 1.91 – 1.77 (m, 2H), 1.30 (s, 9H), 1.23 (s, 12H), 1.14 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.3, 151.7, 131.6, 125.4, 120.0, 87.8, 86.5, 85.3, 83.7, 59.3, 45.0, 37.1, 35.8, 34.9, 31.3, 30.5, 24.9, 24.7, 17.0; HRMS (ESI) calcd for $C_{27}H_{38}BO_4$ $[M+H]^+$: 437.2863; found: 437.2870; $[\alpha]^{20}_D$ = -49.40° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 93/07, detected at 230 nm, Flow rate = 1 mL/min, Retention times: 12.565 min (major), 11.784 min (minor).



<Peak Table>

PDA Ch1 230nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.767	33305774	1335579	51.077	55.363
2	12.823	31900634	1076806	48.923	44.637
Total		65206407	2412384	100.000	100.000

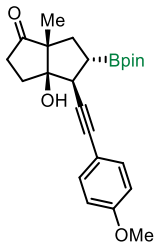


<Peak Table>

PDA Ch1 230nm

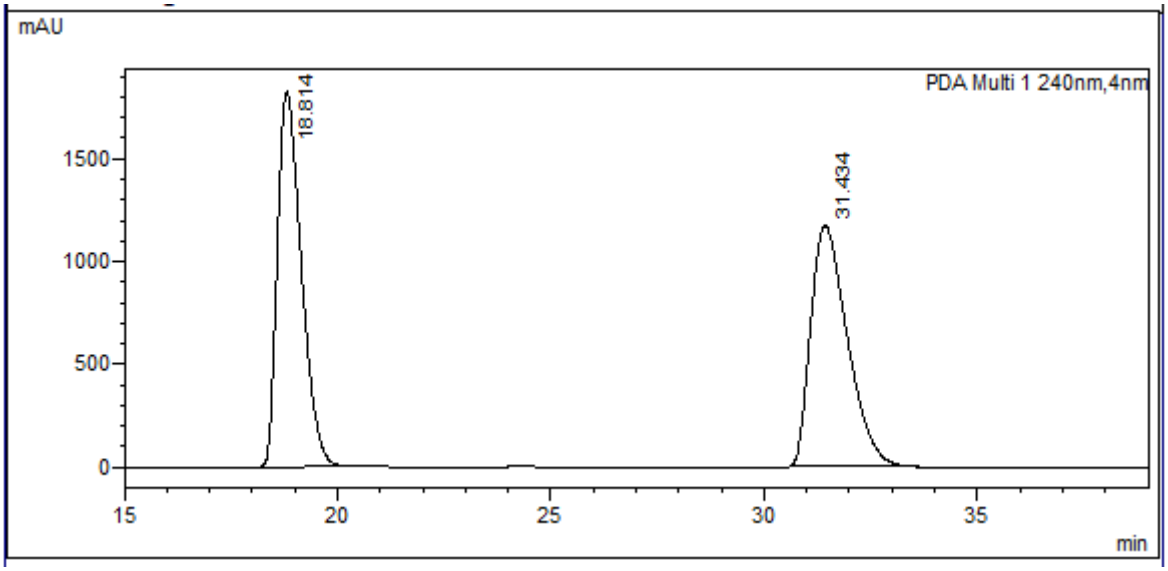
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.784	17243	1050	0.014	0.029
2	12.565	119837232	3654945	99.986	99.971
Total		119854474	3655995	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-4-((4-methoxyphenyl)ethynyl)-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2aj):



Prepared according to the general procedure as described above in 36% yield (44 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 121–123°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.85 (d, *J* = 10.5 Hz, 1H), 2.52 (ddd, *J* = 19.3, 10.0, 3.6 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.23 (ddd, *J* = 12.9, 9.0, 3.6 Hz, 1H), 1.99 (dt, *J* = 13.2, 9.9 Hz, 1H), 1.94 – 1.86 (m, 2H), 1.84 – 1.76 (m, 1H), 1.23 (s, 12H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.3, 159.7, 133.3, 115.1, 114.0, 87.8, 85.6, 85.2, 83.7, 59.3, 55.4, 45.0, 37.1, 35.8, 30.5, 24.9, 24.7, 17.0; HRMS (ESI) calcd for $C_{24}H_{32}BO_5$ $[M+H]^+$:

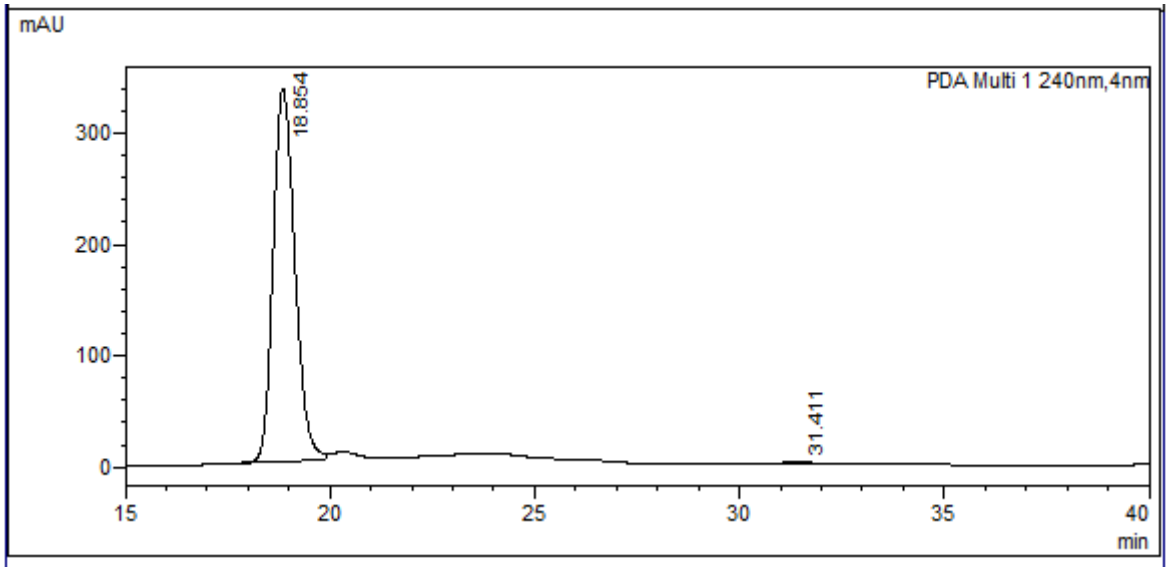
411.2342; found: 411.2351; $[\alpha]^{20}_{D}$ = -47.00° (*c* 1.0, $CHCl_3$); HPLC analysis of the product: 98% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 97/03, detected at 240 nm, Flow rate = 1 mL/min, Retention times: 18.854 min (major), 31.411 min (minor).



<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Height	Area	Height%	Area%
1	18.814	1827484	70977125	60.995	50.425
2	31.434	1168621	69780267	39.005	49.575
Total		2996105	140757392	100.000	100.000

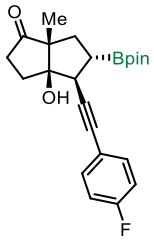


<Peak Table>

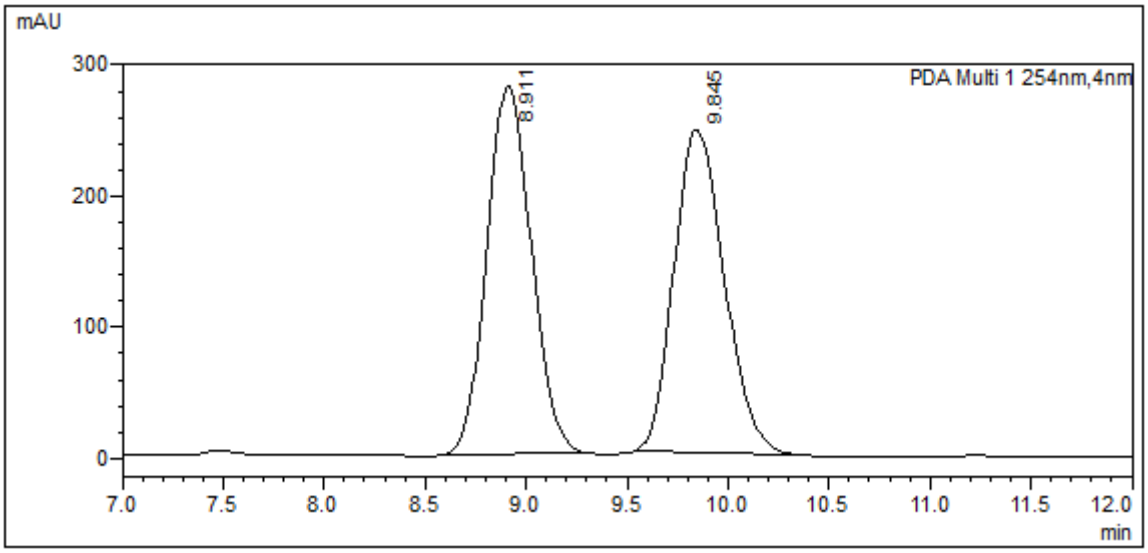
PDA Ch1 240nm

Peak#	Ret. Time	Height	Area	Height%	Area%
1	18.854	334780	12420015	99.349	99.192
2	31.411	2194	101171	0.651	0.808
Total		336974	12521185	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-4-((4-Fluorophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ak):



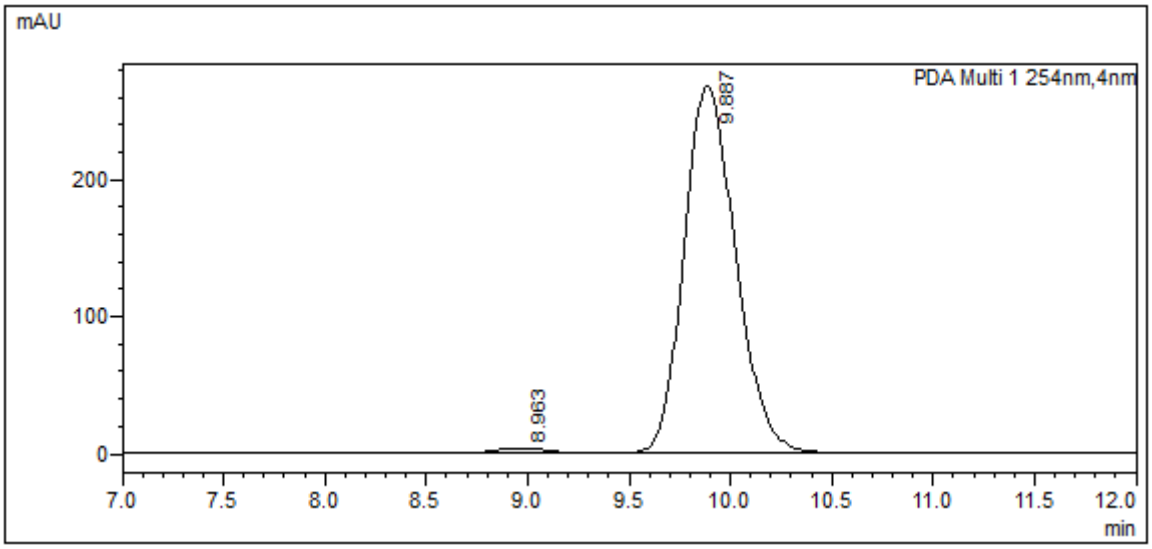
Prepared according to the general procedure as described above in 48% yield (57 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.34 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 2.83 (d, *J* = 10.6 Hz, 1H), 2.52 – 2.46 (m, 1H), 2.42 (dd, *J* = 19.3, 9.3 Hz, 1H), 2.23 (ddd, *J* = 12.8, 8.9, 3.7 Hz, 1H), 2.04 – 1.97 (m, 1H), 1.96 – 1.85 (m, 2H), 1.81 (dt, *J* = 7.2, 3.1 Hz, 1H), 1.23 (s, 12H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.1, 162.5 (d, J_{CF} = 249.3 Hz), 133.7 (d, J_{CF} = 8.3 Hz), 119.0 (d, J_{CF} = 3.2 Hz), 115.7 (d, J_{CF} = 22.1 Hz), 87.9, 87.0, 84.1, 83.8, 59.4, 44.8, 37.1, 35.8, 30.4, 24.9, 24.7, 17.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.0; HRMS (ESI) calcd for $C_{23}H_{29}O_4BF$ $[M+H]^+$: 399.2137; found: 399.2128; $[\alpha]^{20}_D$ = -140.21° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 98% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 93/07, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 9.887 min (major), 8.963 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.911	4299105	280499	50.191	53.229
2	9.845	4266407	246471	49.809	46.771
Total		8565512	526970	100.000	100.000

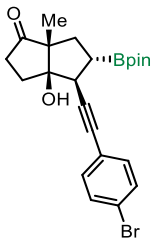


<Peak Table>

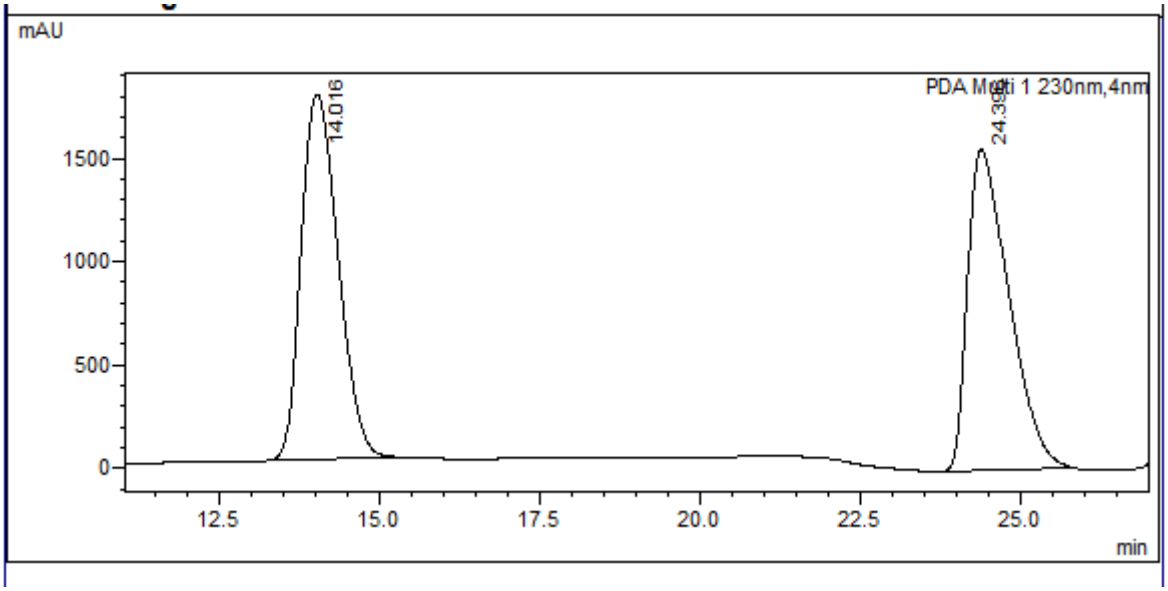
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.963	47603	3319	0.996	1.225
2	9.887	4730235	267543	99.004	98.775
Total		4777837	270862	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-4-((4-Bromophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2al):



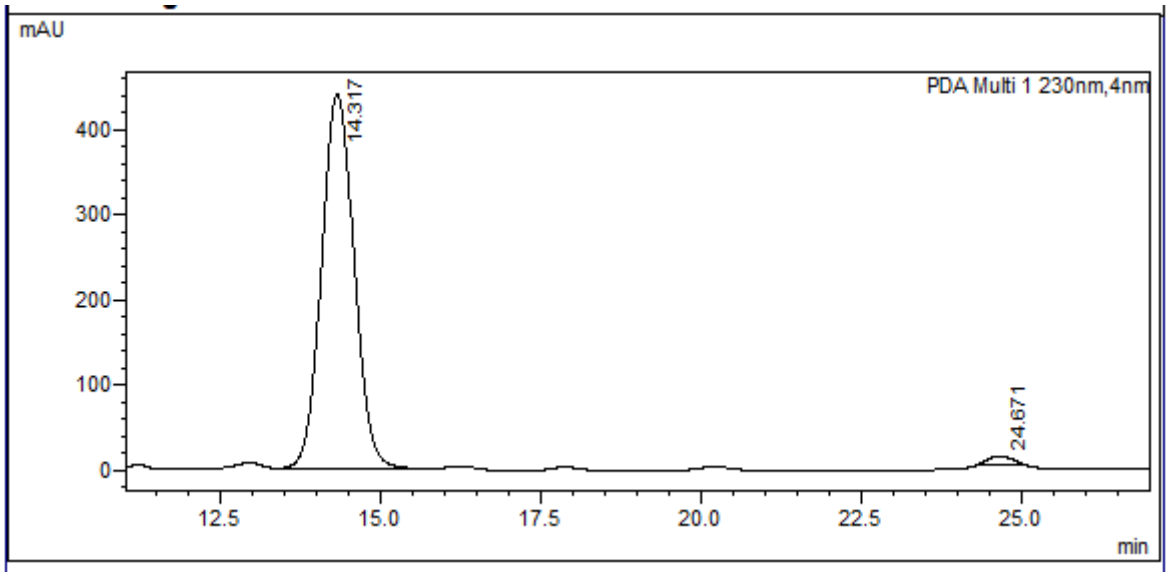
Prepared according to the general procedure as described above in 53% yield (73 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a brown solid; mp 126–128°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 2.83 (d, *J* = 10.5 Hz, 1H), 2.60 – 2.42 (m, 2H), 2.36 (t, *J* = 10.1 Hz, 1H), 2.23 (ddd, *J* = 17.0, 8.5, 4.3 Hz, 1H), 2.07 – 1.95 (m, 1H), 1.94 – 1.86 (m, 1H), 1.86 – 1.76 (m, 1H), 1.23 (s, 12H), 1.13 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.0, 133.3, 131.7, 122.6, 122.0, 88.6, 87.9, 84.1, 83.8, 59.4, 44.9, 37.1, 35.8, 30.4, 24.9, 24.7, 17.0; HRMS (ESI) calcd for $C_{23}H_{29}BBrO_4$ $[M+H]^+$: 459.1342; found: 459.1364; $[\alpha]^{20}_D$ = -72.20° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 98% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 97/03, detected at 230 nm, Flow rate = 1 mL/min, Retention times: 14.317 min (major), 24.671 min (minor).



<Peak Table>

PDA Ch1 230nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.016	71083165	1762885	50.343	53.130
2	24.396	70114045	1555177	49.657	46.870
Total		141197210	3318062	100.000	100.000

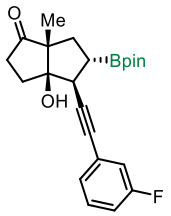


<Peak Table>

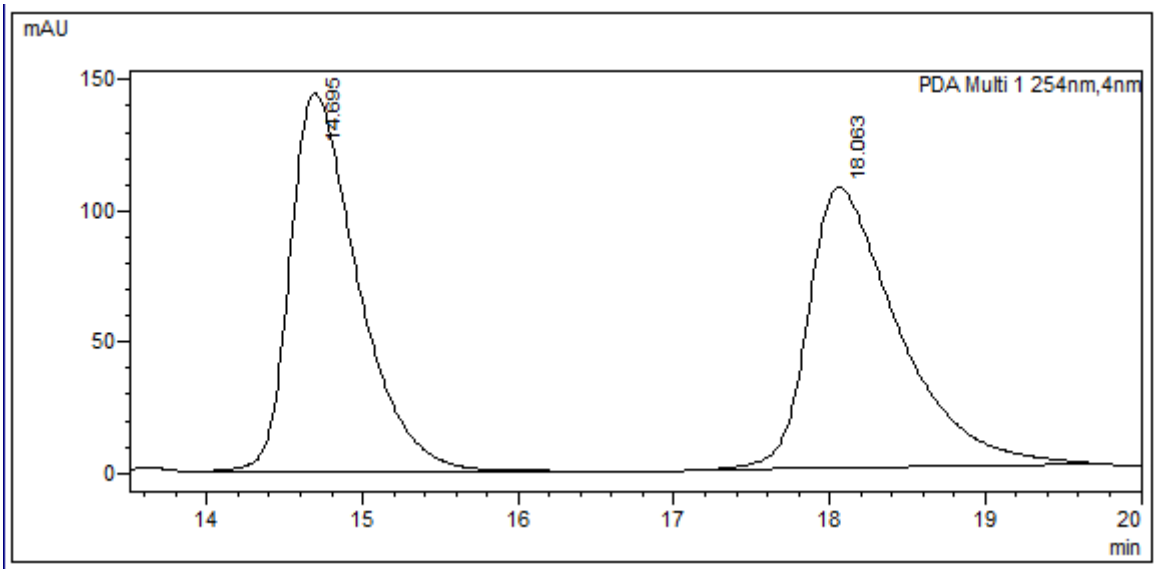
PDA Ch1 230nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.317	15519517	438896	98.556	97.994
2	24.671	227444	8983	1.444	2.006
Total		15746960	447879	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-4-((3-Fluorophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2am):



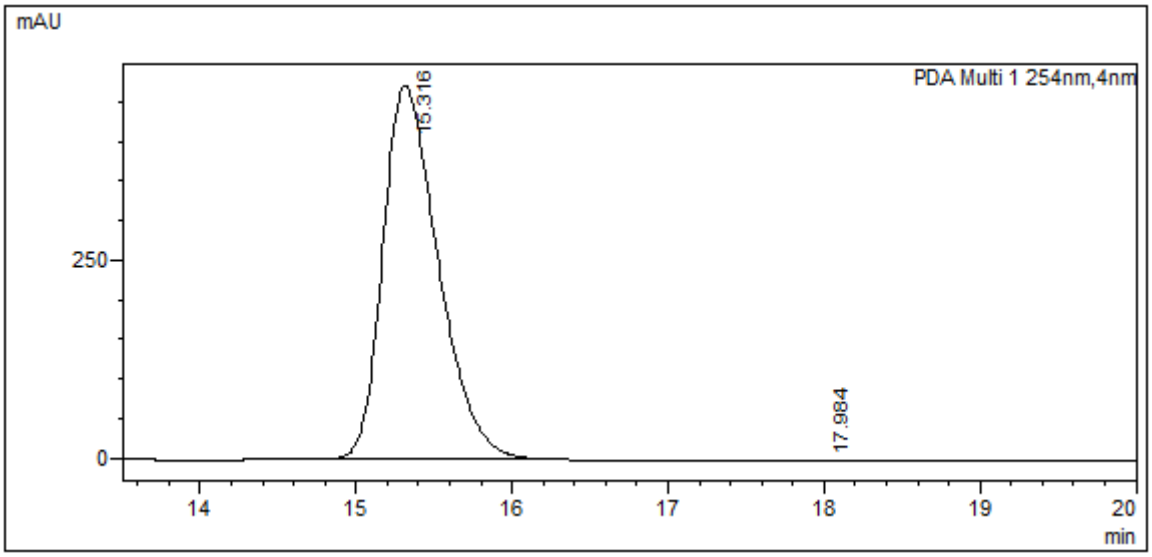
Prepared according to the general procedure as described above in 49% yield (59 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 7.19 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.10 (ddd, *J* = 9.4, 2.5, 1.4 Hz, 1H), 7.02 (tdd, *J* = 8.5, 2.6, 1.1 Hz, 1H), 2.85 (d, *J* = 10.7 Hz, 1H), 2.54 (ddd, *J* = 19.4, 10.1, 3.7 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.34 (s, 1H), 2.24 (ddd, *J* = 12.8, 8.9, 3.7 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.94 – 1.86 (m, 2H), 1.82 (dt, *J* = 7.3, 3.1 Hz, 1H), 1.24 (s, 12H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 162.5 (d, J_{CF} = 246.6 Hz), 130.0 (d, J_{CF} = 8.7 Hz), 127.8 (d, J_{CF} = 2.3 Hz), 124.9 (d, J_{CF} = 9.5 Hz), 118.7 (d, J_{CF} = 22.7 Hz), 115.7 (d, J_{CF} = 21.0 Hz), 88.5, 87.9, 84.0, 83.8, 59.4, 44.8, 37.1, 35.8, 30.4, 24.9, 24.7, 17.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.9; HRMS (ESI) calcd for $C_{23}H_{29}O_4BF$ $[M+H]^+$: 399.2137; found: 399.2125; $[\alpha]^{20}_D$ = -105.50° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 97/03, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 15.316 min (major), 17.984 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.695	4420731	144588	50.285	57.466
2	18.063	4370622	107017	49.715	42.534
Total		8791353	251605	100.000	100.000

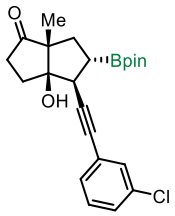


<Peak Table>

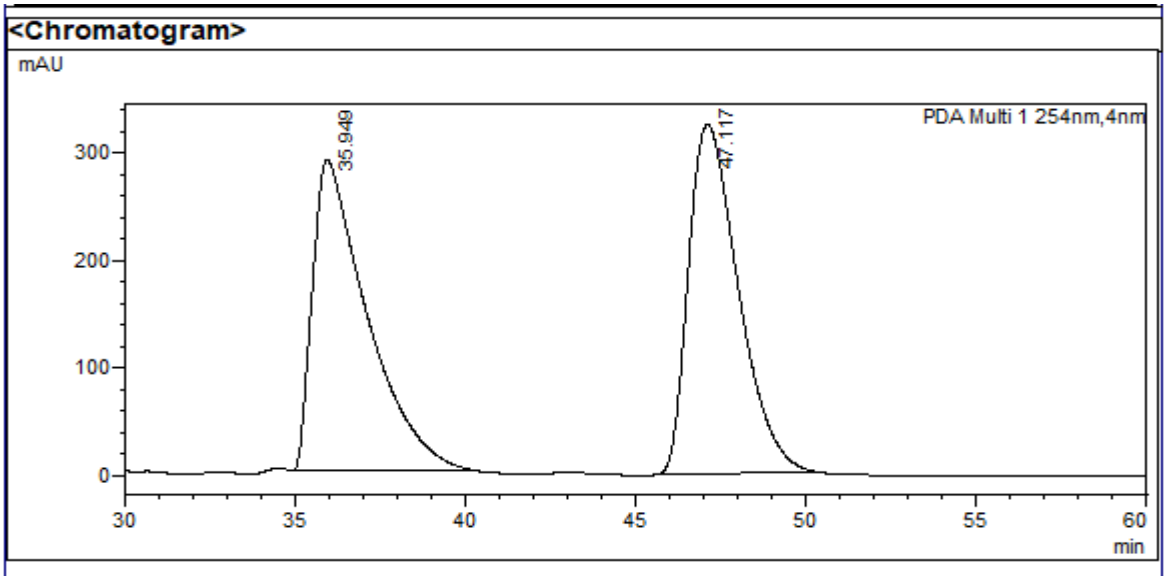
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.316	11668212	471236	99.680	99.840
2	17.984	37460	755	0.320	0.160
Total		11705672	471991	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-4-((3-Chlorophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2an):



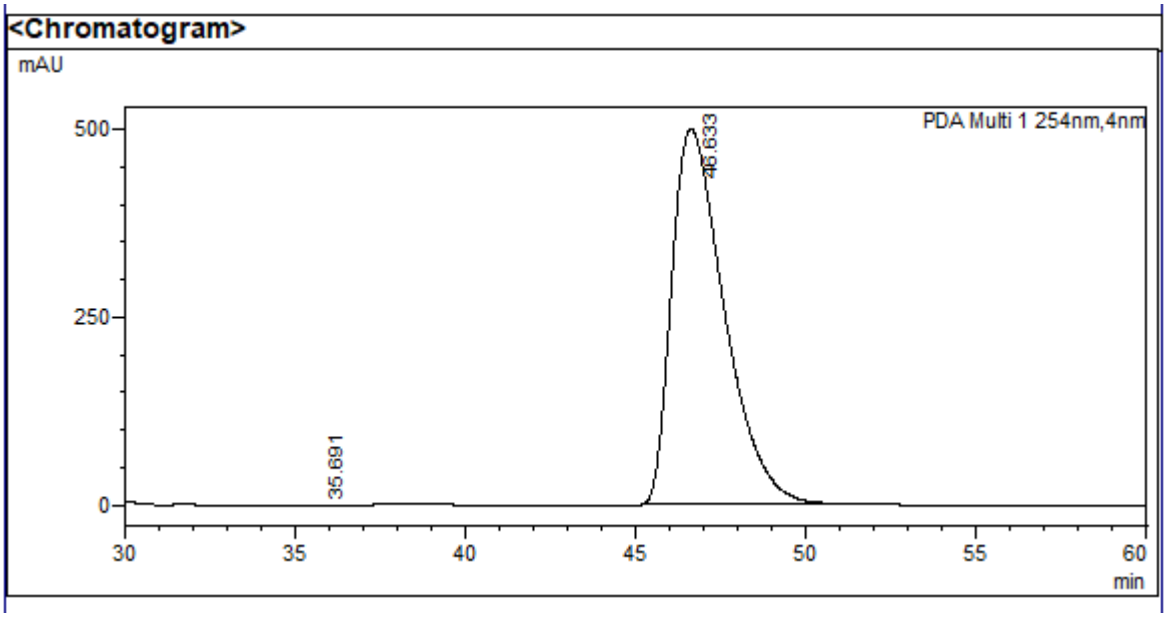
Prepared according to the general procedure as described above in 51% yield (63 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 158–160°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 1.6 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 2.84 (d, *J* = 10.7 Hz, 1H), 2.53 (ddd, *J* = 19.4, 10.1, 3.6 Hz, 1H), 2.42 (dd, *J* = 19.4, 9.3 Hz, 1H), 2.35 (br.s, 1H), 2.23 (ddd, *J* = 12.8, 8.9, 3.7 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.93 – 1.86 (m, 2H), 1.81 (dt, *J* = 7.5, 3.4 Hz, 1H), 1.23 (s, 12H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 134.2, 131.8, 130.0, 129.7, 128.6, 124.7, 88.8, 87.9, 83.8, 59.4, 44.8, 37.1, 35.8, 30.4, 24.9, 24.7, 17.0; HRMS (ESI) calcd for $C_{23}H_{29}O_4BCl$ $[M+H]^+$: 415.1842; found: 415.1831; $[\alpha]^{20}_D$ = -92.71° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 98/02, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 46.633 min (major), 35.691 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	35.949	32188347	289709	49.215	47.072
2	47.117	33214908	325754	50.785	52.928
Total		65403255	615463	100.000	100.000

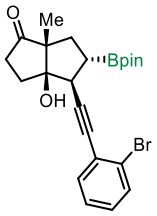


<Peak Table>

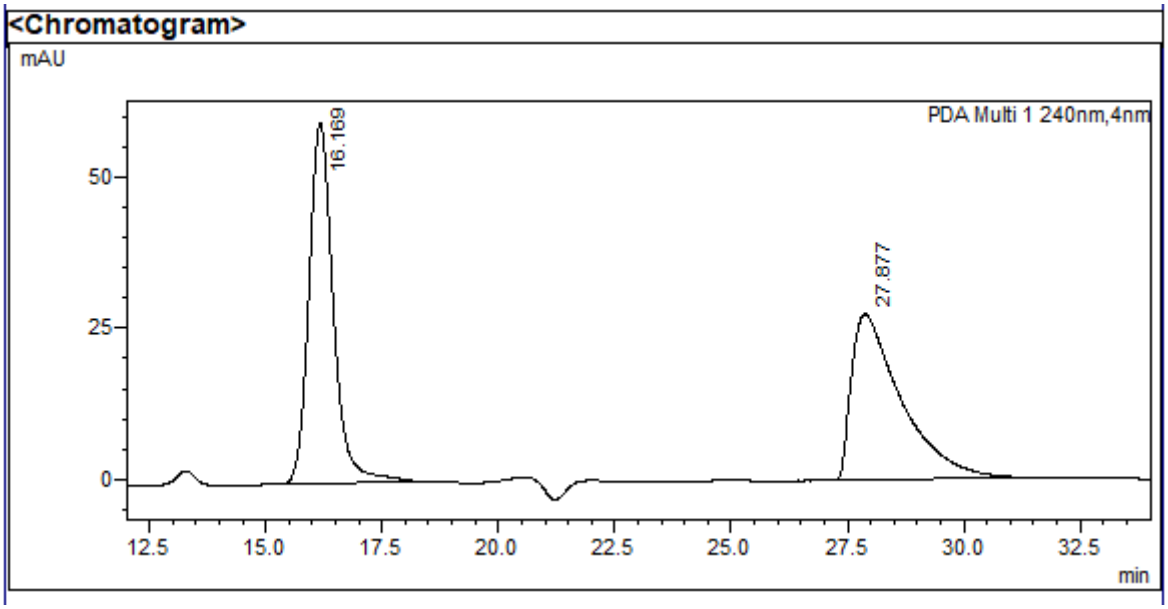
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	35.691	141	33	0.000	0.007
2	46.633	53193460	497831	100.000	99.993
Total		53193600	497864	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-4-((2-Bromophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ao):



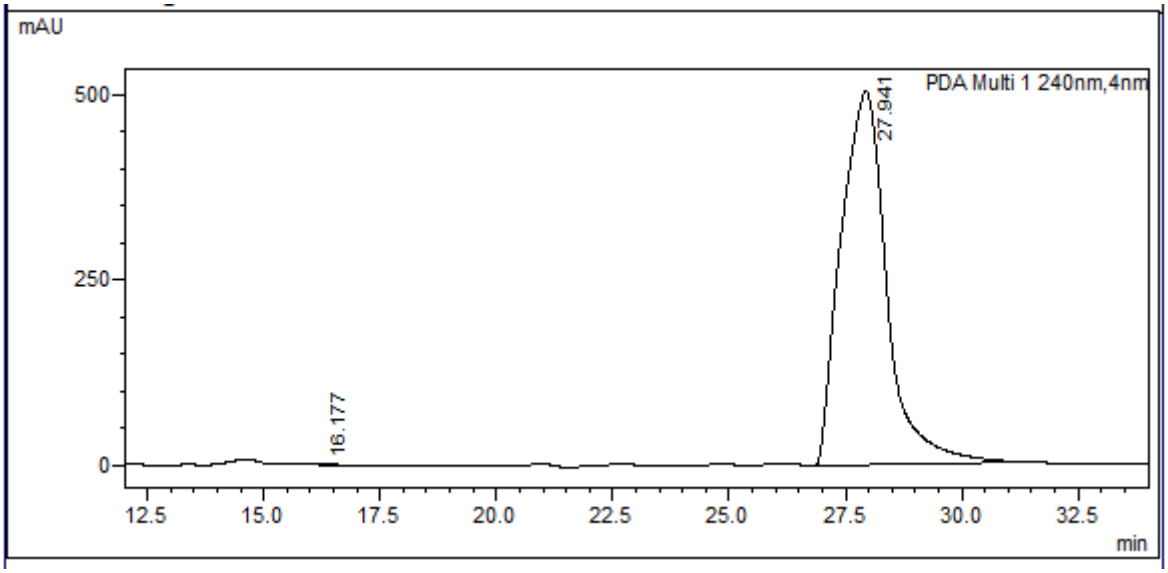
Prepared according to the general procedure as described above in 54% yield (74 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a brown semi solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.29 – 7.21 (m, 1H), 7.16 (td, *J* = 7.7, 1.8 Hz, 1H), 2.90 (d, *J* = 10.6 Hz, 1H), 2.76 (s, 1H), 2.48 (ddd, *J* = 26.1, 14.7, 7.2 Hz, 2H), 2.28 (ddd, *J* = 12.9, 8.6, 4.0 Hz, 1H), 2.12 – 1.97 (m, 2H), 1.98 – 1.81 (m, 2H), 1.25 (s, 12H), 1.16 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.1, 133.4, 132.4, 129.5, 127.2, 125.9, 125.2, 92.8, 88.3, 83.8, 83.7, 59.4, 44.9, 37.1, 35.9, 30.5, 24.9, 24.8, 17.0; HRMS (ESI) calcd for $C_{23}H_{29}BBrO_4$ $[M+H]^+$: 459.1363; found: 458.1359; $[\alpha]^{20}_D$ = -24.60° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 96/04, detected at 240 nm, Flow rate = 1 mL/min, Retention times: 27.941 min (major), 16.177 min (minor).



<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.169	2172481	59726	51.620	68.524
2	27.877	2036085	27434	48.380	31.476
Total		4208566	87160	100.000	100.000

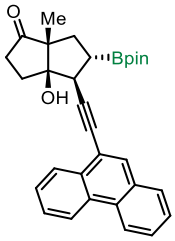


<Peak Table>

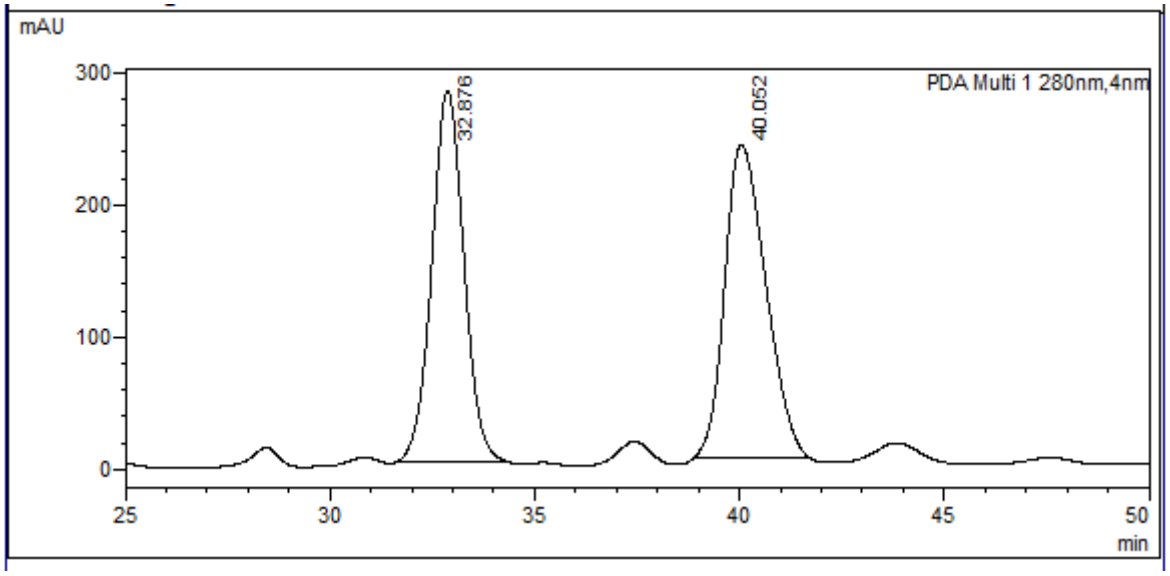
PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.177	30601	1019	0.089	0.202
2	27.941	34420929	502478	99.911	99.798
Total		34451531	503497	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-4-(phenanthren-9-ylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ap):



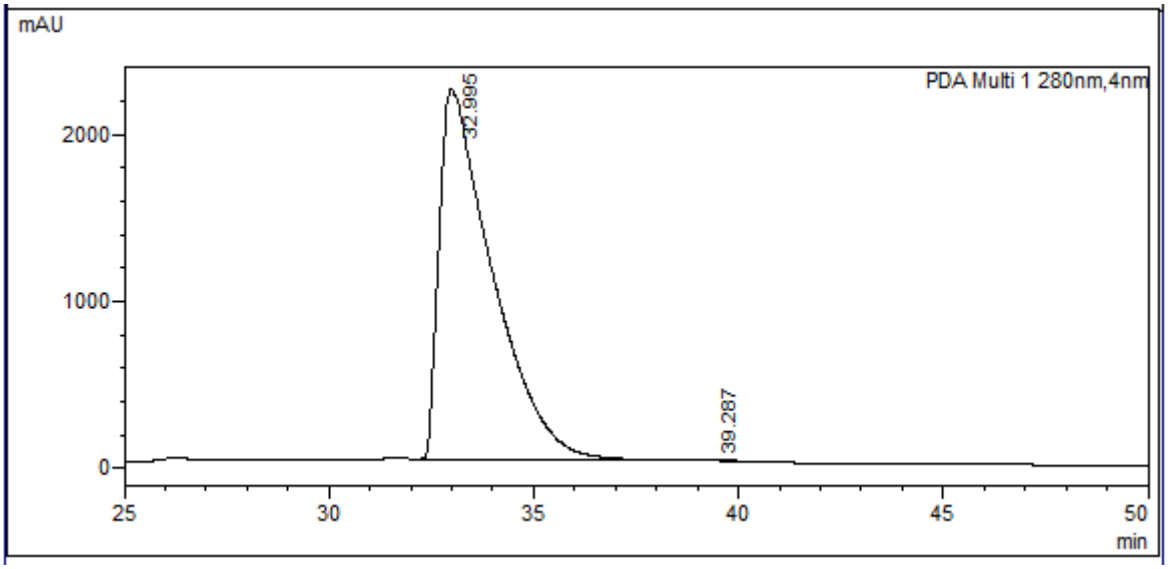
Prepared according to the general procedure as described above in 43% yield (62 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.62 (m, 2H), 8.48 – 8.41 (m, 1H), 7.98 (s, 1H), 7.84 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.73 – 7.64 (m, 3H), 7.63 – 7.57 (m, 1H), 3.03 (d, *J* = 11.3 Hz, 1H), 2.64 – 2.45 (m, 2H), 2.38 (ddd, *J* = 12.3, 8.7, 3.5 Hz, 1H), 2.15 – 2.03 (m, 2H), 1.99 (d, *J* = 10.6 Hz, 1H), 1.88 (dd, *J* = 13.0, 9.1 Hz, 1H), 1.27 (s, 6H), 1.26 (s, 6H), 1.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.3, 132.1, 131.4, 131.2, 130.4, 130.2, 128.6, 127.6, 127.2, 127.2, 127.1, 127.0, 122.9, 122.8, 119.4, 91.9, 88.1, 83.8, 83.3, 59.4, 45.3, 37.2, 35.9, 30.5, 25.0, 24.8, 17.2; HRMS (ESI) calcd for $C_{31}H_{34}BO_4$ $[M+H]^+$: 481.2550; found: 481.2581; $[\alpha]^{20}_D$ = +7.50° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 96/04, detected at 280 nm, Flow rate = 1 mL/min, Retention times: 32.995 min (major), 39.287 min (minor).



<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	32.876	15278820	280269	48.217	54.241
2	40.052	16409120	236442	51.783	45.759
Total		31687940	516711	100.000	100.000

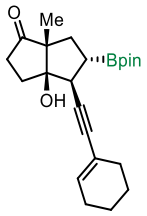


<Peak Table>

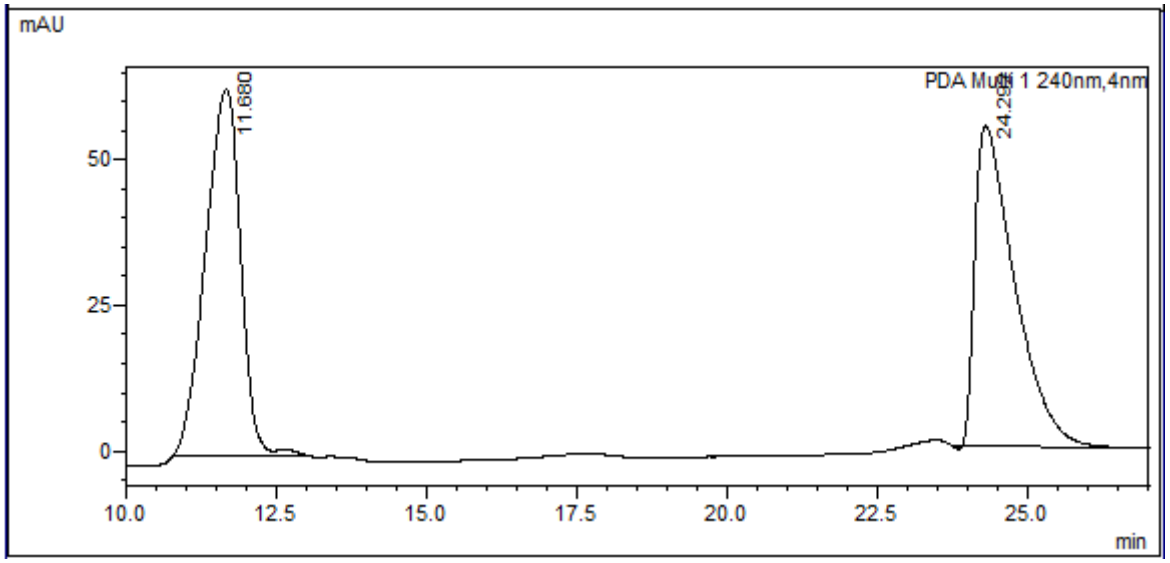
PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	32.995	198639784	2213056	99.787	99.672
2	39.287	423534	7288	0.213	0.328
Total		199063317	2220344	100.000	100.000

(3a*R*,4*S*,5*S*,6a*R*)-4-(Cyclohex-1-en-1-ylethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2aq):



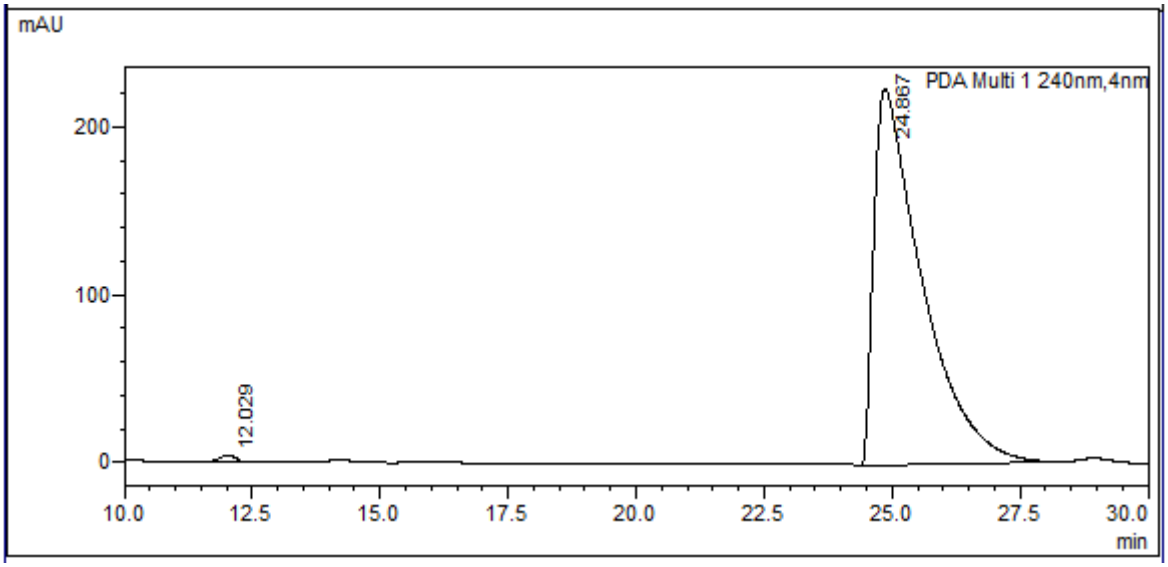
Prepared according to the general procedure as described above in 58% yield (67 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 – 6.04 (m, 1H), 2.75 (d, *J* = 10.3 Hz, 1H), 2.54 – 2.33 (m, 2H), 2.16 (ddd, *J* = 12.9, 8.9, 3.8 Hz, 1H), 2.12 – 2.04 (m, 3H), 1.99 – 1.86 (m, 2H), 1.87 – 1.72 (m, 3H), 1.66 – 1.54 (m, 4H), 1.22 (s, 12H), 1.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.5, 134.9, 120.4, 87.5, 87.3, 84.1, 83.7, 59.2, 44.9, 37.1, 35.8, 30.4, 29.6, 25.7, 24.9, 24.7, 22.4, 21.6, 17.0; HRMS (ESI) calcd for $C_{23}H_{34}BO_4$ $[M+H]^+$: 385.2504; found: 385.2513; $[\alpha]^{20}_D$ = -15.50° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 97.5/2.5, detected at 240 nm, Flow rate = 1 mL/min, Retention times: 24.867 min (major), 12.029 min (minor).



<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.680	2556403	62943	50.188	53.364
2	24.292	2537275	55009	49.812	46.636
Total		5093678	117952	100.000	100.000

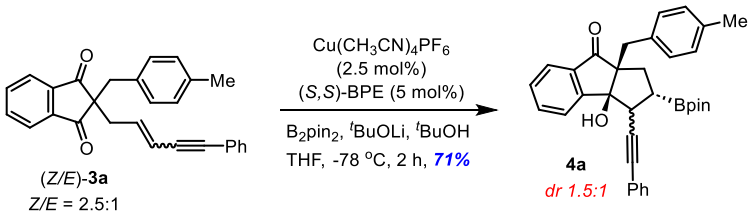


<Peak Table>

PDA Ch1 240nm

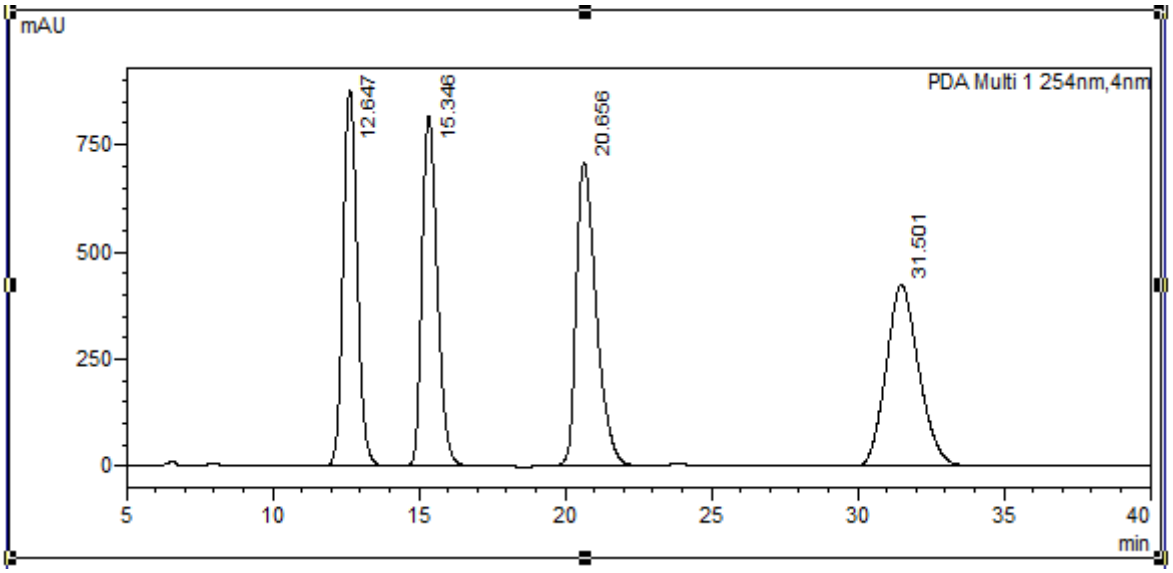
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.029	68301	3527	0.464	1.550
2	24.867	14643494	224060	99.536	98.450
Total		14711795	227586	100.000	100.000

(2*S*,3a*S*,8a*S*)-3a-Hydroxy-8a-(4-methylbenzyl)-3-(phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (4a):



Prepared according to the general procedure as described above in 71% yield (110 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford inseparable mixture of diastereomers as a white solid in 71% yield (110 mg; combined yield); mp = 177–179°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 1.4H), 7.64 – 7.56 (m, 1.6H), 7.50 – 7.38 (m, 2.6H), 7.38 – 7.27 (m, 3.4H), 7.17 (d, *J* = 8.0 Hz, 0.4H), 7.07 (d, *J* = 8.0 Hz, 1.6H), 6.95 (d, *J* = 7.9 Hz, 2H), 3.46 (d, *J* = 6.1 Hz, 0.4H), 3.18 – 3.00 (m, 2H), 2.99 – 2.92 (m, 0.6H), 2.45 – 2.28 (m, 0.4H), 2.22 (s, 3H), 2.20 – 2.06 (m, 2.6H), 1.17 (s, 2.4H), 1.15 (s, 4.8H), 1.12 (s, 4.8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 207.6, 155.0, 135.8, 135.3, 134.7, 134.3, 131.9, 131.0, 130.8, 129.6, 129.4, 128.7, 128.6, 128.5, 128.3, 125.0, 123.7, 123.5, 122.9, 122.8, 87.9, 87.1, 86.7, 86.3, 86.1, 83.8, 83.7, 66.9, 64.1, 48.9, 47.4, 39.5, 38.4, 36.1, 34.7, 25.1, 24.8, 24.7, 21.1; HRMS (ESI) calcd for $C_{34}H_{36}O_4B$ [M+H]+: 519.26858; found: 519.27012; $[\alpha]^{20}D$ = -142.19° (c 1.0, $CHCl_3$); Chiral HPLC analysis of the product: **4a/4a'**: >99 *ee* (for both isomers); Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 93/07, detected at

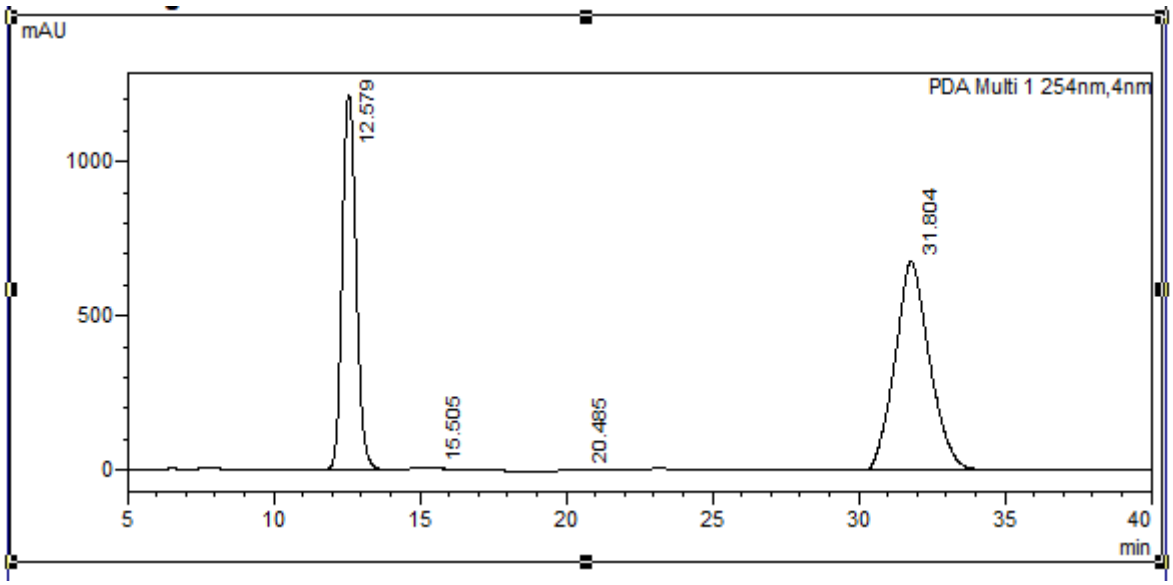
254 nm, Flow rate = 1 mL/min, Retention times: 12.579 min (major), 31.804 min (major), 15.505 min (minor), 20.485 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.647	29392173	875726	23.560	31.099
2	15.346	29419411	811858	23.581	28.831
3	20.656	33479116	705759	26.836	25.063
4	31.501	32465620	422602	26.023	15.007
Total		124756321	2815945	100.000	100.000

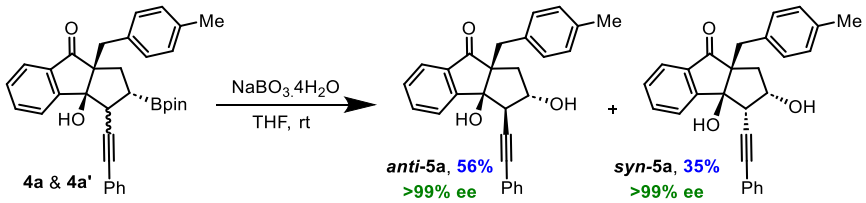


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.579	40166689	1212147	42.035	64.067
2	15.505	120275	4586	0.126	0.242
3	20.485	25168	789	0.026	0.042
4	31.804	55242187	674469	57.812	35.649
Total		95554320	1891990	100.000	100.000

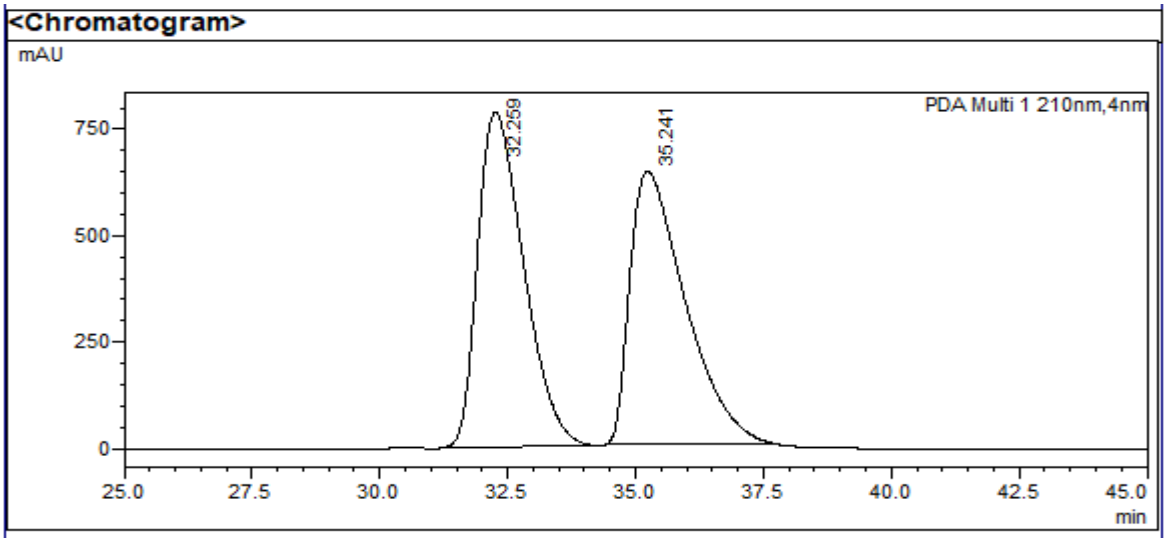
Synthesis of *anti*-5a/*syn*-5a:[5]



To a solution of **4a** (78 mg, 0.15 mmol, 1 equiv) in H_2O (3 mL) was added $NaBO_3 \cdot H_2O$ (75 mg, 0.75 mmol) in one portion. the resulting mixture was stirred vigorously at room temperature for 0.5 h under open air. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL), extracted with EtOAc (3 × 15 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. It was purified by flash chromatography (30% EtOAc/hexanes; *Rf* = 0.6) to afford a white solid of **5a** in 56% yield and **5a'** in 35 % yield [Note: Other analytical data of *anti*-**5a** and *syn*-**5a** matched from one-pot synthesis (see the next section)].

(2*S*,3*R*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methylbenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*anti*-5a): $[\alpha]^{20}D$ = -155.93° (c 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 93/07, detected at 210 nm, Flow rate = 1 mL/min, Retention times: 31.955 min (major).

<Chromatogram>

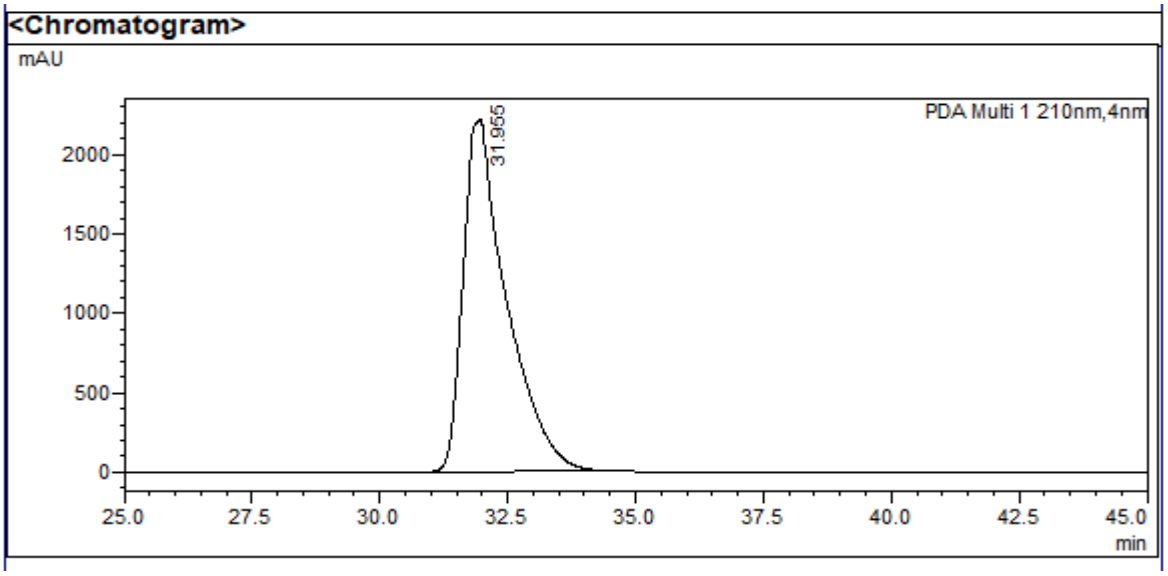


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	32.259	49184626	785252	50.639	55.112
2	35.241	47942746	639585	49.361	44.888
Total		97127372	1424837	100.000	100.000

<Chromatogram>

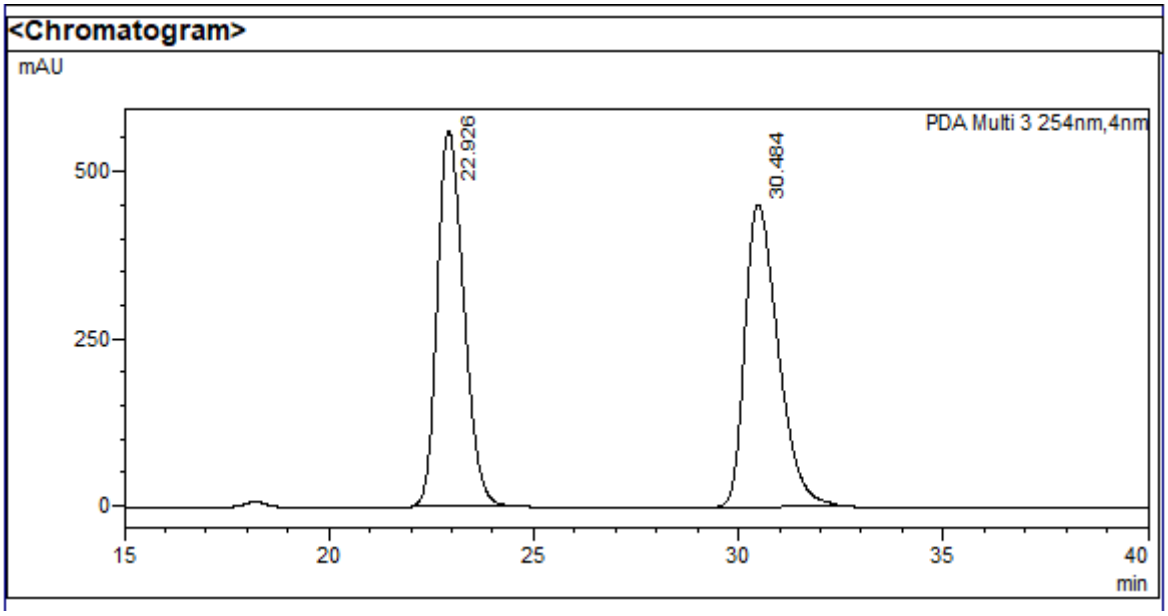


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	31.955	129953081	2216179	100.000	100.000
Total		129953081	2216179	100.000	100.000

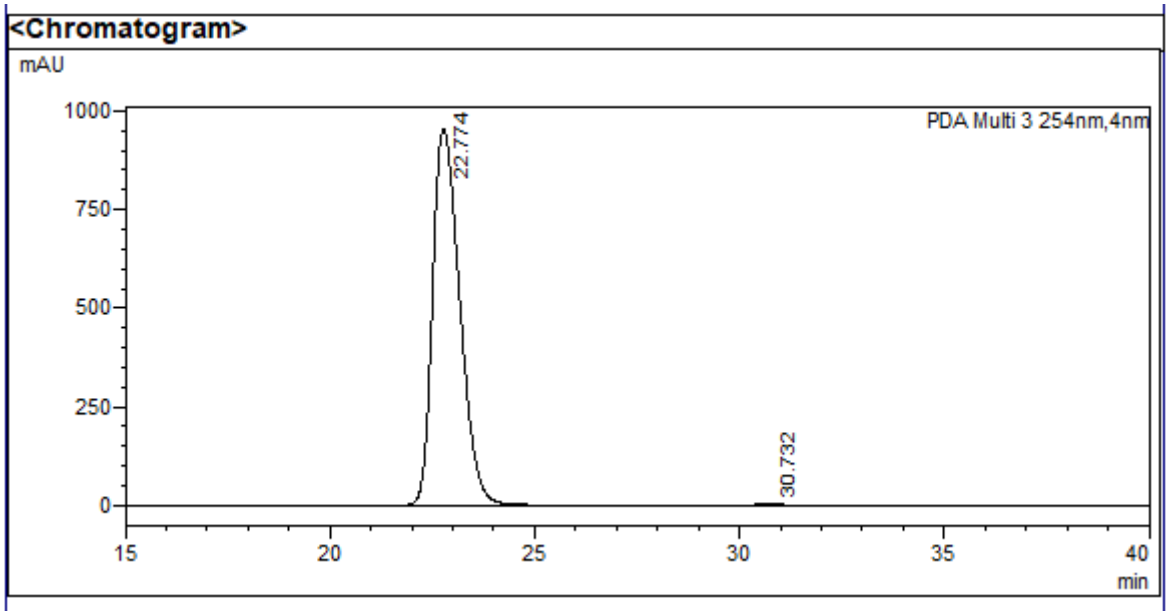
(2S,3*S*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methylbenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*syn*-5a): $[\alpha]^{20}D$ = -167.01° (c 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 93/07, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 22.774 min (minor), 30.732 min (minor).



<Peak Table>

PDA Ch3 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	22.926	25240645	561006	49.622	55.384
2	30.484	25624892	451933	50.378	44.616
Total		50865537	1012939	100.000	100.000

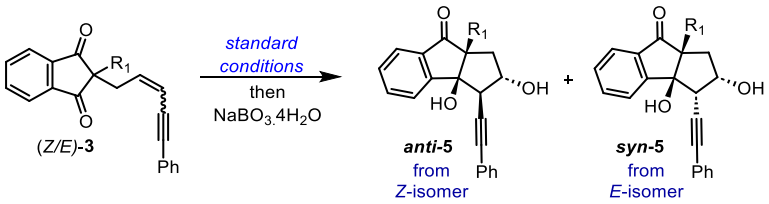


<Peak Table>

PDA Ch3 254nm

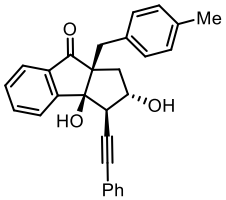
Peak#	Ret. Time	Area	Height	Area%	Height%
1	22.774	44109620	955047	99.644	99.653
2	30.732	157689	3328	0.356	0.347
Total		44267309	958376	100.000	100.000

IIIf. General procedure for one-pot borylative cyclization/oxidation:[5]



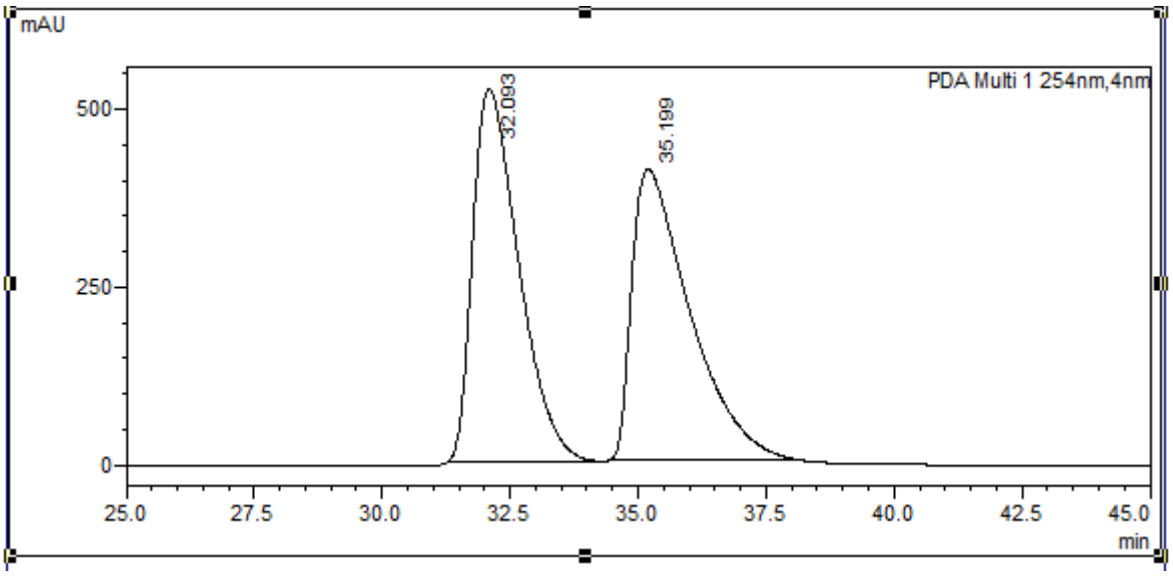
A solution of $Cu(CH_3CN)_4PF_6$ (2.8 mg, 2.5 mol %) and (*S,S*)-BPE (7.6 mg, 5 mol%), in dry THF (3 mL, 0.1 M) was stirred for 20 min at room temperature under nitrogen atmosphere at -78 °C temperature in precooled julabo instrument bath. A solution of **3** (0.3 mmol) in dry THF (1.0 mL) was added *via* syringe into the reaction mixture then $B_2(pin)_2$ (91 mg, 0.36 mmol) and *t*-BuOH (57 µl, 0.6 mmol) was added sequentially followed by addition of LiO^tBu (54 µl, 0.6 mmol, 1 M in THF) and resulting mixture was stirred at -78 °C for 2 h. Then $NaBO_3 \cdot H_2O$ (150 mg, 1.5 mmol) in H_2O (2 mL) was added in one portion and the resulting mixture was stirred vigorously at room temperature for 0.5 h under open air. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL), extracted with EtOAc (3 × 15 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resultant crude product was purified by column chromatography (hexanes/EtOAc) to obtain the desired products *anti*-**5** *& syn*-**5**.

(2*S*,3*R*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methylbenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*anti*-5a):



Prepared according to the general procedure as described above in 54% yield (66 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 177–179°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.59 (m, 3H), 7.43 (td, *J* = 7.3, 1.3 Hz, 1H), 7.37 – 7.30 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 4.44 (q, *J* = 4.5 Hz, 1H), 3.29 (br.s, 1H), 3.14 (dd, *J* = 4.3, 0.8 Hz, 1H), 3.04 (dd, *J* = 38.1, 13.9 Hz, 2H), 2.51 (dd, *J* = 13.9, 5.0 Hz, 1H), 2.22 (s, 3H), 2.22 (dd, *J* = 14.3, 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 156.2, 136.0, 135.5, 135.2, 134.2, 132.0, 131.0, 129.5, 128.9, 128.8, 128.5, 124.1, 123.6, 122.1, 89.0, 85.6, 83.9, 76.8, 63.2, 53.5, 41.9,

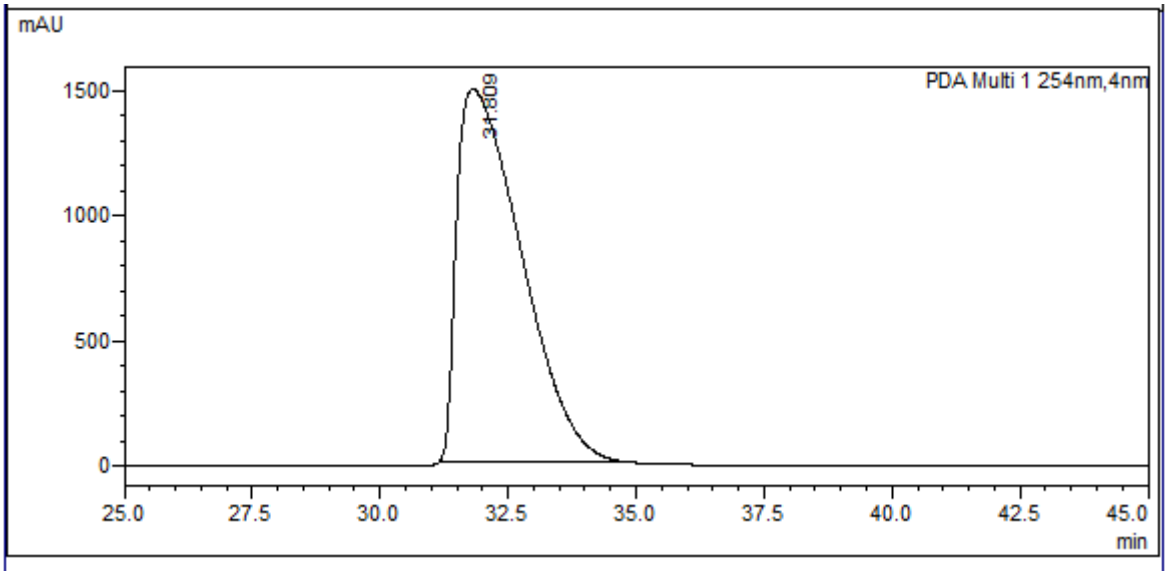
38.7, 21.1; HRMS (ESI) calcd for $C_{28}H_{25}O_3$ $[M+H]^+$: 409.1803; found: 409.1809; $[\alpha]^{20}_D$ = -157.53° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 93/07, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 31.809 min (major), - min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	32.093	32656543	522631	50.344	56.147
2	35.199	32210260	408193	49.656	43.853
Total		64866803	930824	100.000	100.000

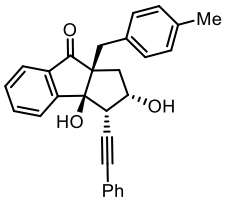


<Peak Table>

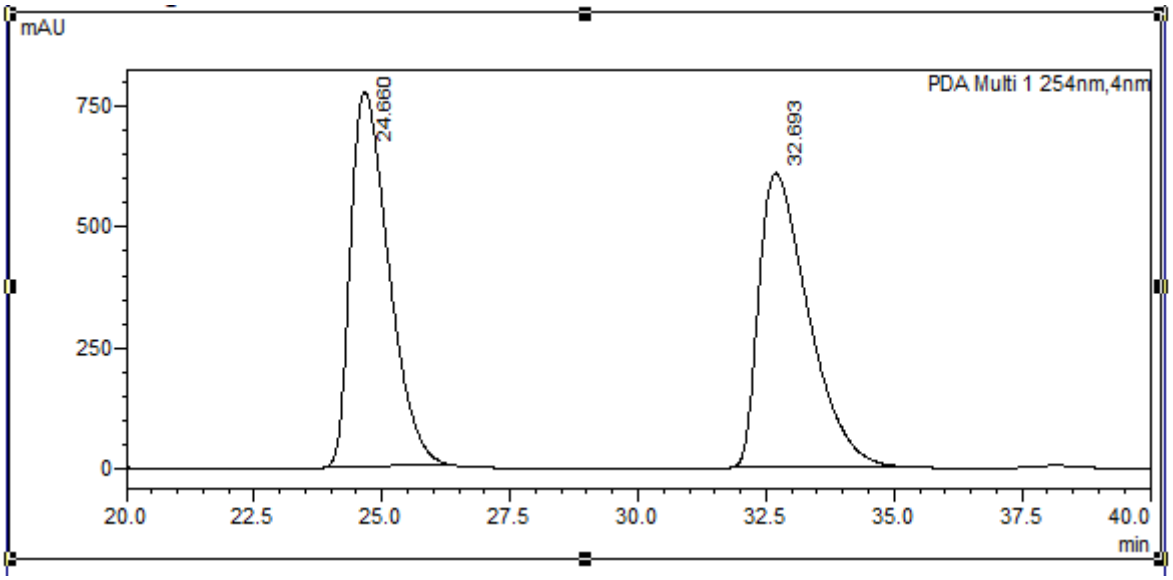
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	31.809	130048768	1488330	100.000	100.000
Total		130048768	1488330	100.000	100.000

(2S,3*S*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methylbenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*syn*-5a):



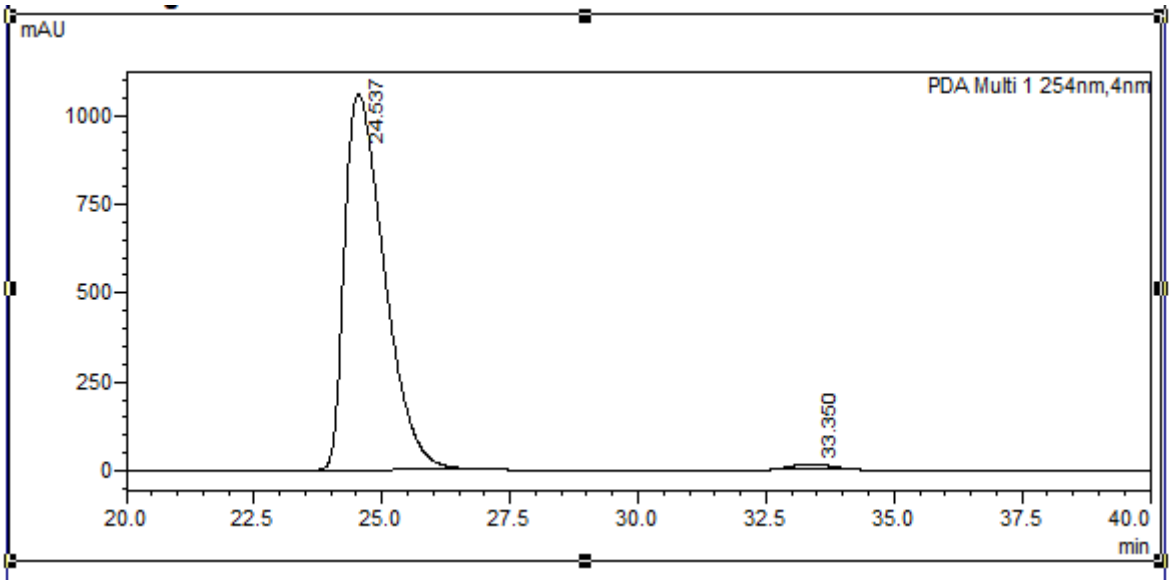
Prepared according to the general procedure as described above in 23% yield (28 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 164–165°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.48 – 7.40 (m, 3H), 7.38 – 7.31 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 4.35 – 4.19 (m, 1H), 3.11 (q, *J* = 13.8 Hz, 2H), 2.91 (d, *J* = 4.0 Hz, 1H), 2.38 (dd, *J* = 14.4, 5.0 Hz, 1H), 2.26 (dd, *J* = 14.6, 3.9 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.2, 154.1, 136.0, 135.6, 134.4, 133.9, 132.1, 130.8, 129.7, 128.8, 128.7, 128.5, 124.4, 123.7, 122.5, 88.6, 87.1, 82.7, 76.0, 65.7, 52.3, 40.0, 40.0, 21.1; HRMS (ESI) calcd for $C_{28}H_{25}O_3$ $[M+H]^+$: 409.1803; found: 409.1807; $[\alpha]^{20}_D$ = -167.90° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 98% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 93/07, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 24.537 min (major), 33.350 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	24.660	40478049	774755	49.917	56.093
2	32.693	40612309	606444	50.083	43.907
Total		81090358	1381199	100.000	100.000

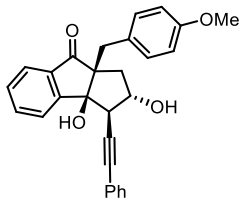


<Peak Table>

PDA Ch1 254nm

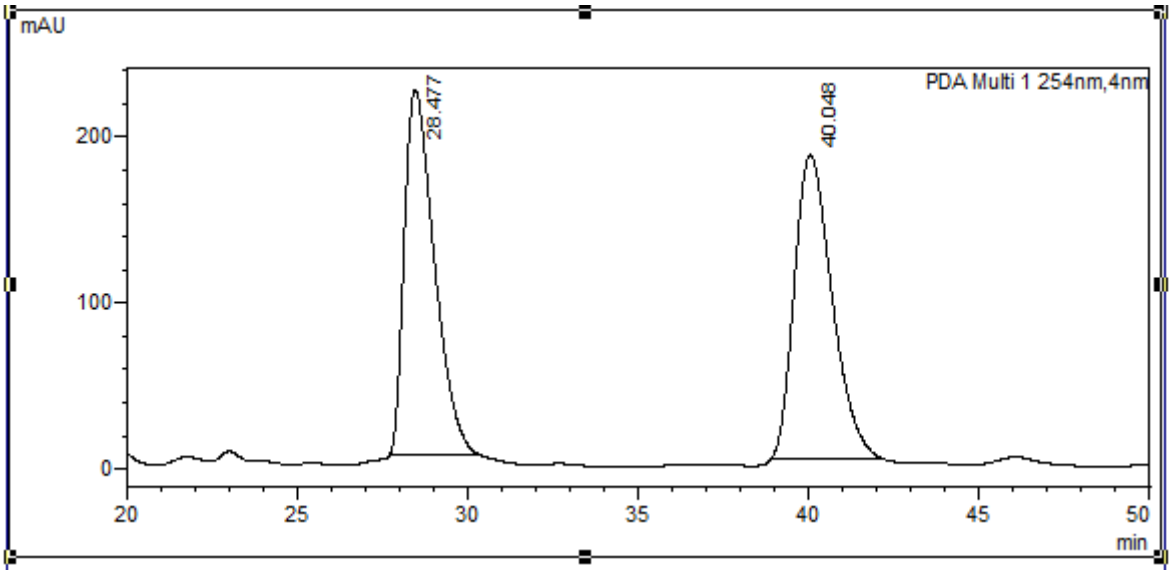
Peak#	Ret. Time	Area	Height	Area%	Height%
1	24.537	57106641	1056001	98.552	98.530
2	33.350	838814	15759	1.448	1.470
Total		57945455	1071760	100.000	100.000

(2*S*,3*R*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methoxybenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*anti*-5b):



Prepared according to the general procedure as described above in 61% yield (78 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a brown solid; mp = 159–161°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 3H), 7.46 – 7.29 (m, 6H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 4.44 (q, *J* = 4.6 Hz, 1H), 3.68 (s, 3H), 3.32 (br.s, 1H), 3.13 (d, *J* = 4.4 Hz, 1H), 3.03 (dd, *J* = 30.8, 14.0 Hz, 2H), 2.49 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.20 (ddd, J = 13.9, 4.3, 0.7 Hz, 1H);

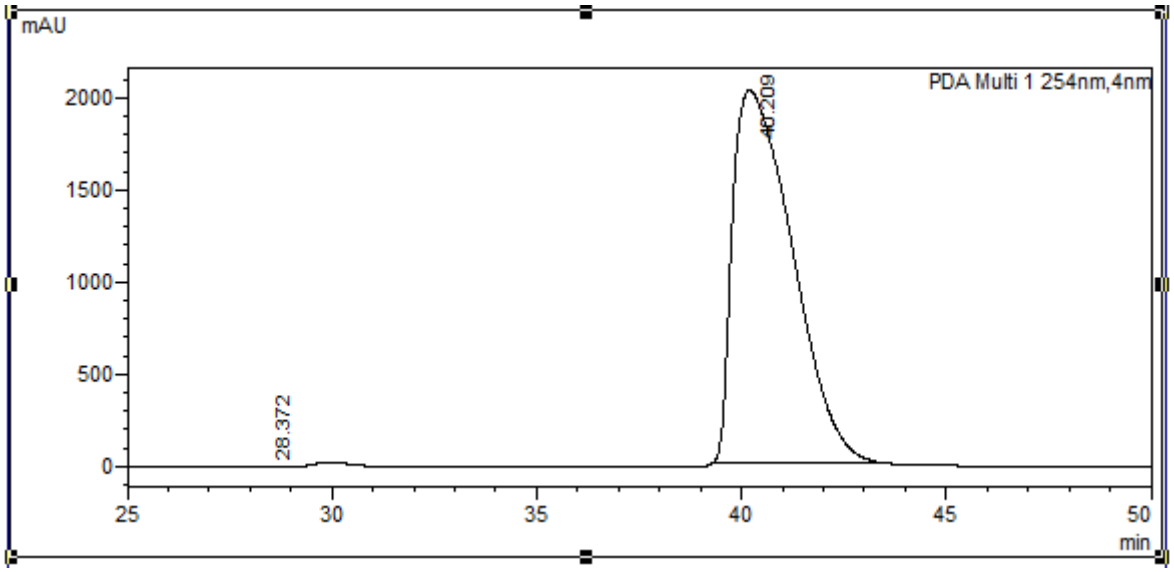
^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 158.2, 156.2, 135.5, 135.2, 132.1, 132.0, 129.5, 129.2, 128.9, 128.5, 124.0, 123.5, 122.1, 113.4, 89.0, 85.5, 84.0, 76.8, 63.3, 55.2, 53.6, 41.9, 38.3; HRMS (ESI) calcd for $C_{28}H_{25}O_4$ $[M+H]^+$: 425.1752; found: 425.1757; $[\alpha]^{20}_D$ = -211.50° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 88/12, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 40.209 min (major), 28.372 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	28.477	13488786	219917	48.911	54.581
2	40.048	14089313	183002	51.089	45.419
Total		27578099	402919	100.000	100.000

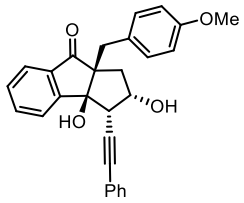


<Peak Table>

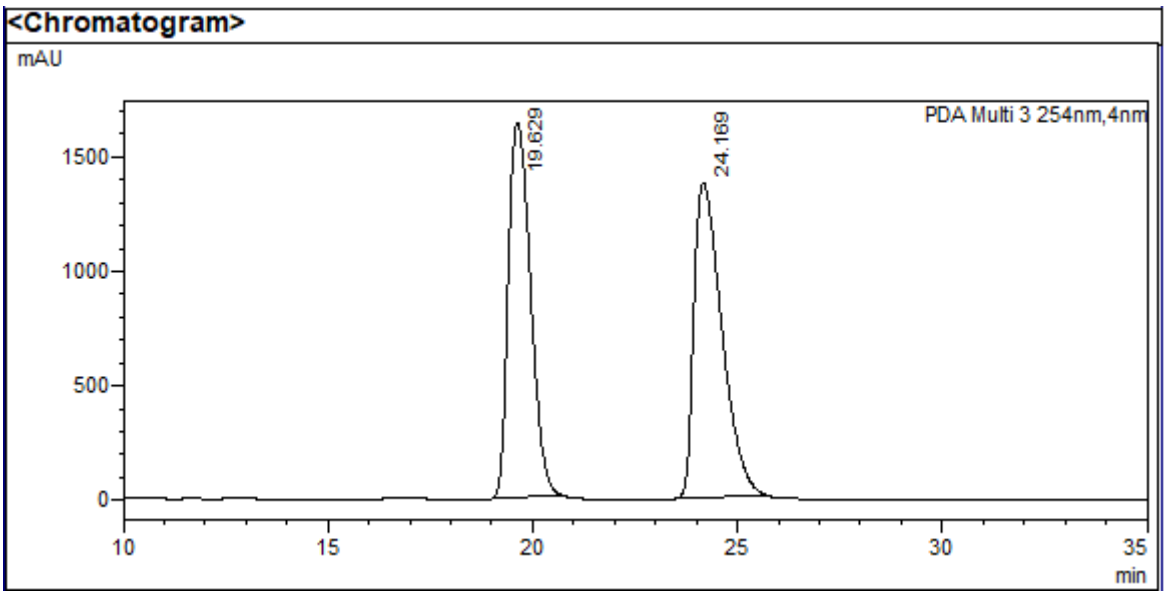
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	28.372	46	9	0.000	0.000
2	40.209	206152981	2025313	100.000	100.000
Total		206153027	2025322	100.000	100.000

(2*S*,3*S*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methoxybenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*syn*-5b):



Prepared according to the general procedure as described above in 17% yield (22 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a brown solid; mp = 173–175°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.49 – 7.41 (m, 3H), 7.41 – 7.31 (m, 3H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.29 (dd, *J* = 8.7, 3.9 Hz, 1H), 3.76 (br.s, 1H), 3.69 (s, 3H) 3.17 – 3.05 (m, 2H), 2.90 (d, *J* = 4.0 Hz, 1H), 2.40 (dd, *J* = 14.4, 5.0 Hz, 1H), 2.24 (dd, *J* = 14.5, 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.4, 158.2, 154.2, 135.6, 134.4, 132.1, 131.9, 129.7, 129.0, 128.8, 128.5, 124.3, 123.6, 122.5, 113.4, 88.6, 87.0, 82.7, 76.1, 65.8, 55.2, 52.4, 40.2, 39.7; HRMS (ESI) calcd for $C_{28}H_{25}O_4$ $[M+H]^+$: 425.1752; found: 425.1757; $[\alpha]^{20}_D$ = -199.60° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 94% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 88/12, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 18.920 min (major), 23.928 min (minor).

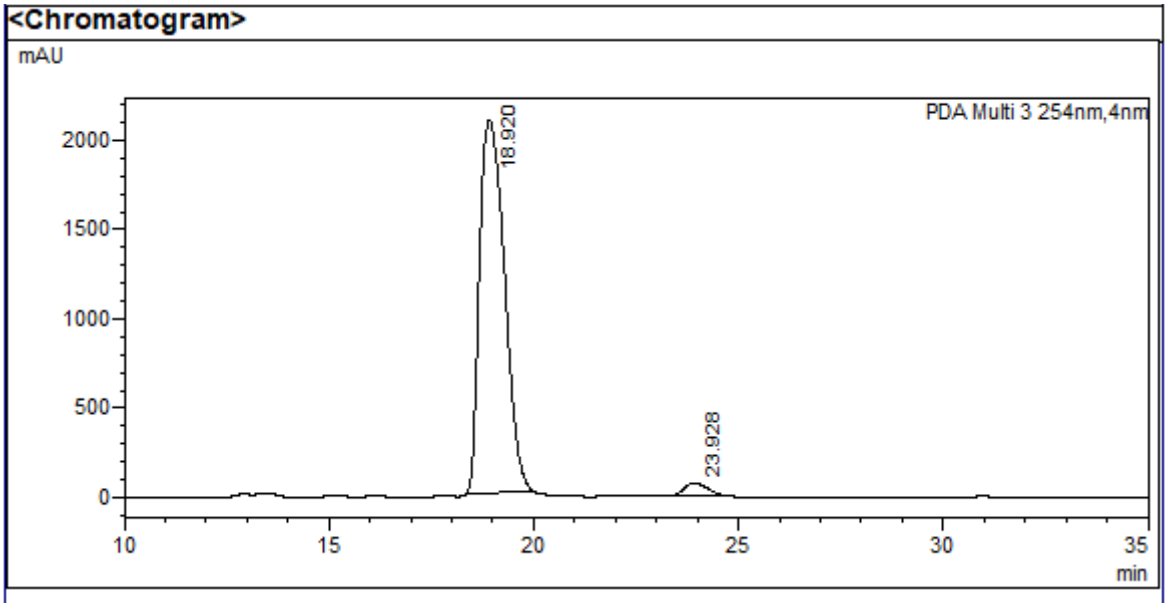


<Peak Table>

PDA Ch3 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.629	61917437	1635352	48.662	54.388
2	24.169	65322732	1371487	51.338	45.612
Total		127240169	3006839	100.000	100.000

<Chromatogram>

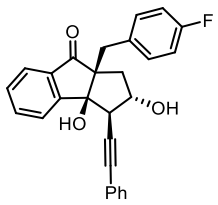


<Peak Table>

PDA Ch3 254nm

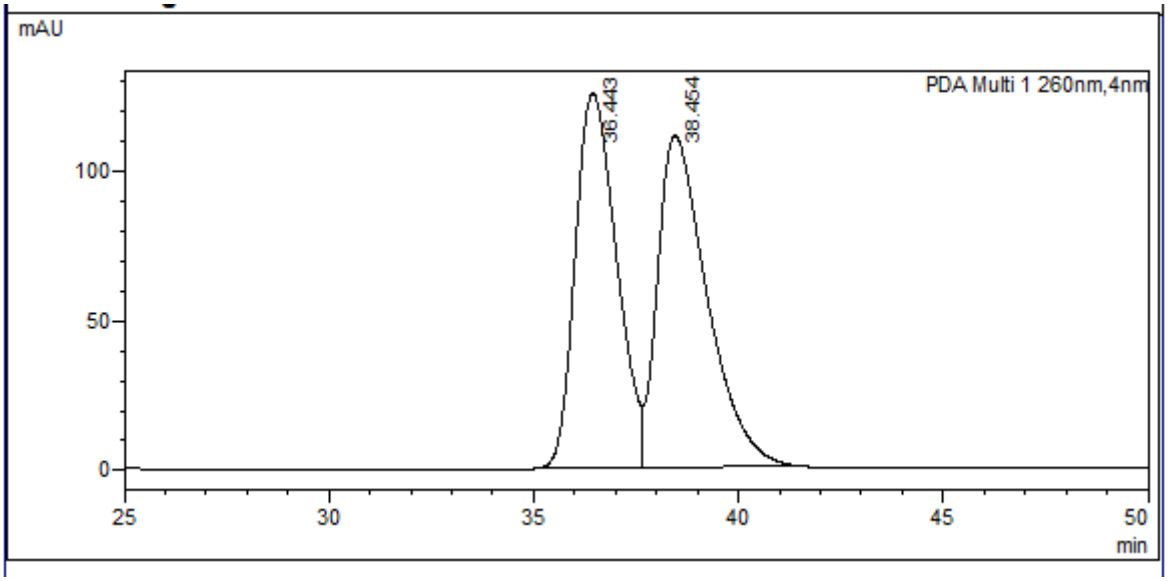
Peak#	Ret. Time	Area	Height	Area%	Height%
1	18.920	88494897	2089158	97.217	96.802
2	23.928	2533045	69012	2.783	3.198
Total		91027942	2158170	100.000	100.000

(2*S*,3*R*,3a*S*,8a*R*)-8a-(4-Fluorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*anti*-5c):



Prepared according to the general procedure as described above in 57% yield (70 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a brown solid; mp = 124–126°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.57 (m, 3H), 7.46 – 7.32 (m, 6H), 7.23 – 7.15 (m, 2H), 6.86 – 6.76 (m, 2H), 4.48 (q, *J* = 4.8 Hz, 1H), 3.12 (d, *J* = 4.2 Hz, 1H), 3.07 (q, *J* = 17.1 Hz, 2H), 2.45 (dd, *J* = 13.9, 5.2 Hz, 1H), 2.24 (dd, *J* = 13.8, 4.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 161.7 (d,

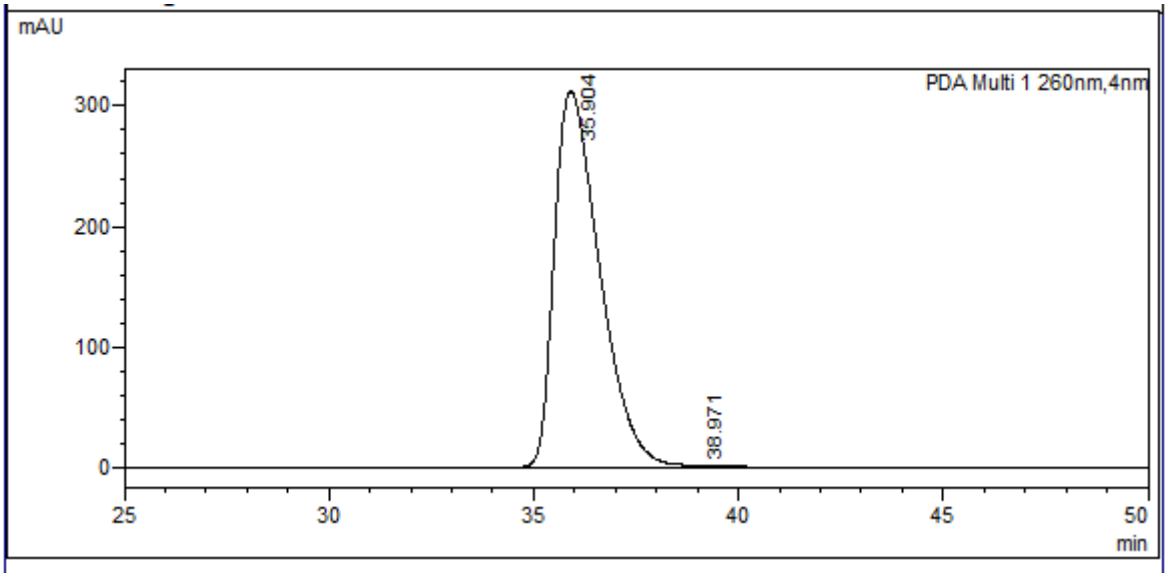
J_{CF} = 244.5 Hz), 156.0, 135.6, 135.1, 132.9 (d, J_{CF} = 2.9 Hz), 132.6 (d, J_{CF} = 7.8 Hz), 132.0, 129.5, 129.1, 128.6, 123.9, 123.5, 121.9, 114.7 (d, J_{CF} = 21.0 Hz), 89.3, 85.1, 83.8, 77.0, 63.3, 53.9, 42.1, 38.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.8; HRMS (ESI) calcd for $C_{27}H_{22}FO_3$ $[M+H]^+$: 413.1552; found: 413.1562; $[\alpha]^{20}_D$ = -183.39° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5μ column; hexane/2-propanol = 93/07, detected at 260 nm, Flow rate = 1 mL/min, Retention times: 35.904 min (major), 38.971 min (minor).



<Peak Table>

PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	36.443	8763445	124898	48.508	53.048
2	38.454	9302447	110546	51.492	46.952
Total		18065892	235444	100.000	100.000

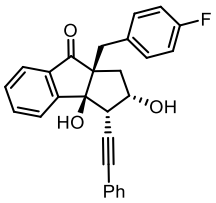


<Peak Table>

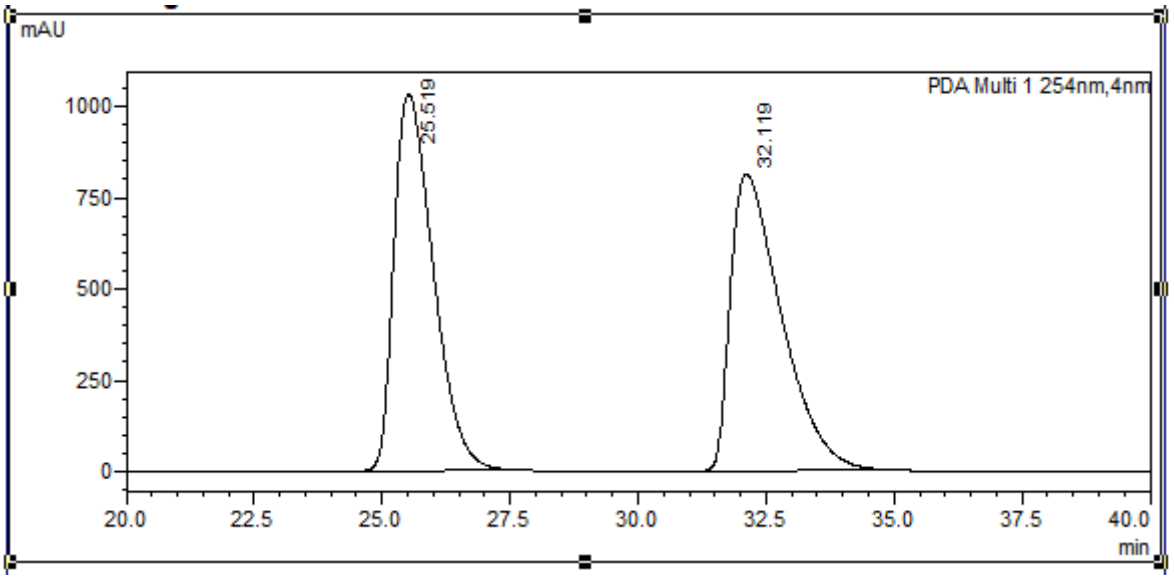
PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	35.904	24094184	312362	99.676	99.447
2	38.971	78258	1737	0.324	0.553
Total		24172443	314099	100.000	100.000

(2*S*,3*S*,3a*S*,8a*R*)-8a-(4-Fluorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*syn*-5c):



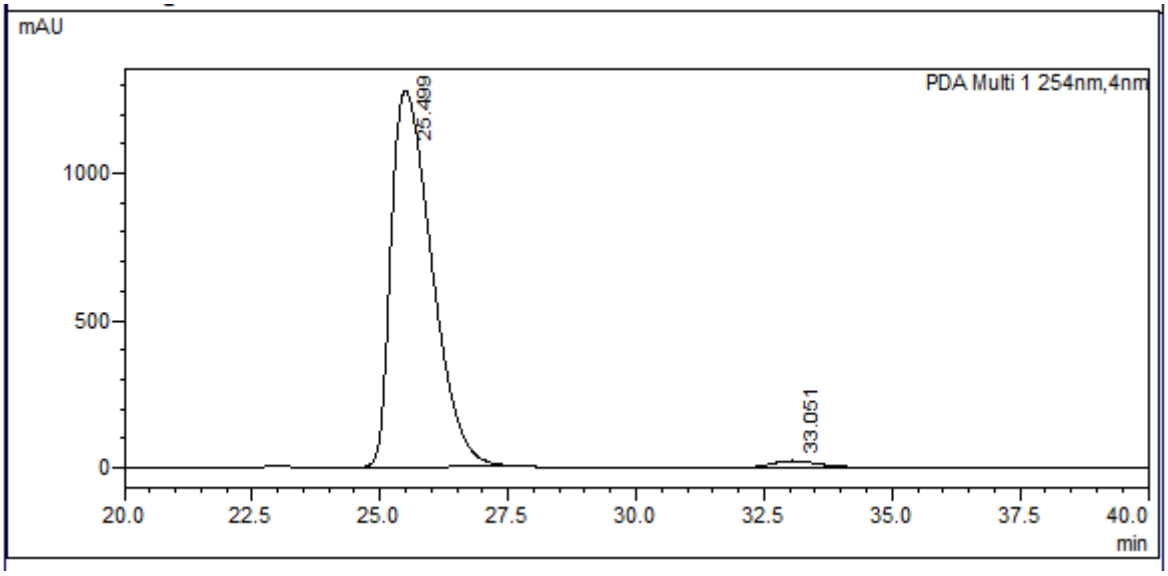
Prepared according to the general procedure as described above in 23% yield (28 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.6) to afford a brown solid; mp = 128–130°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 7.7, 0.8 Hz, 1H), 7.63 (td, *J* = 7.5, 1.2 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.50 – 7.44 (m, 2H), 7.43 – 7.30 (m, 4H), 7.17 – 7.09 (m, 2H), 6.83 – 6.73 (m, 2H), 4.38 – 4.31 (m, 1H), 3.26 – 3.05 (m, 2H), 2.84 (d, *J* = 3.8 Hz, 1H), 2.44 (dd, *J* = 14.6, 5.0 Hz, 1H), 2.19 (dd, *J* = 14.6, 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 161.6 (d, J_{CF}= 244.3 Hz), 154.1, 135.6, 134.3, 132.6 (d, J_{CF} = 3.0 Hz), 132.4 (d, J_{CF} = 7.8 Hz), 132.1, 129.7, 128.9, 128.6, 124.2, 123.5, 122.4, 114.6 (d, J_{CF} = 21.1 Hz), 88.5, 87.0, 82.7, 76.6, 66.1, 52.6, 40.4, 40.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.8; HRMS (ESI) calcd for $C_{27}H_{22}FO_3$ $[M+H]^+$: 413.1552; found: 413.1557; $[\alpha]^{20}_D$ = -225.00° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 96% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 93/07, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 25.499 min (major), 33.051 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	25.519	55304512	1031240	49.628	55.947
2	32.119	56133380	812004	50.372	44.053
Total		111437891	1843244	100.000	100.000

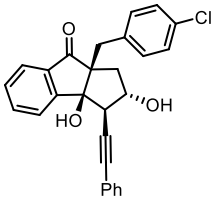


<Peak Table>

PDA Ch1 254nm

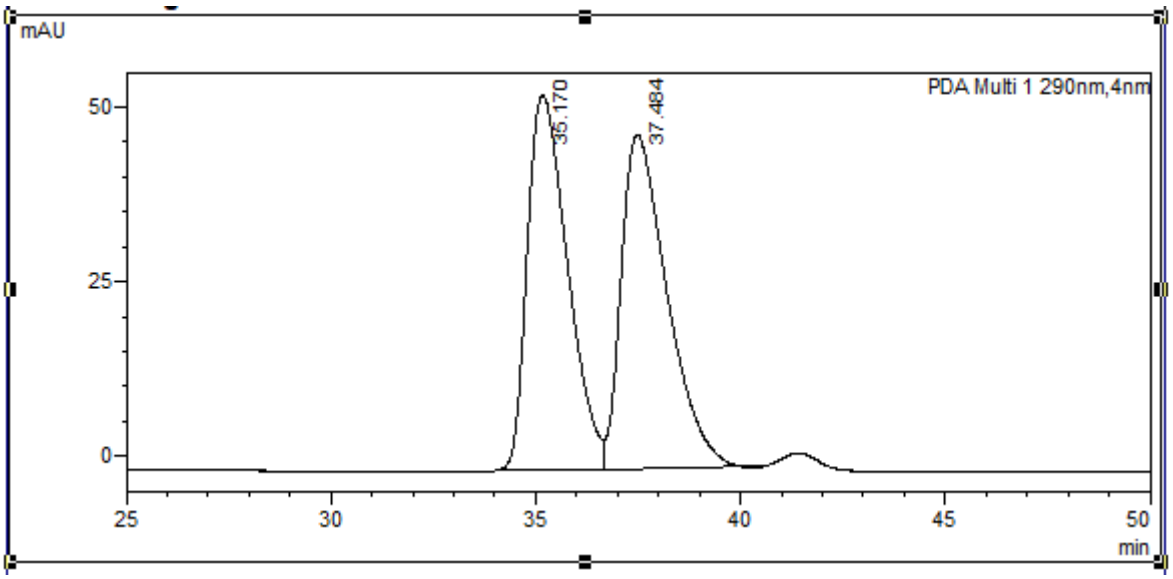
Peak#	Ret. Time	Area	Height	Area%	Height%
1	25.499	70749741	1275234	98.195	98.312
2	33.051	1300545	21897	1.805	1.688
Total		72050286	1297131	100.000	100.000

(2*S*,3*R*,3a*S*,8a*R*)-8a-(4-Chlorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*anti*-5d):



Prepared according to the general procedure as described above in 54% yield (69 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a brown solid; mp = 142-143°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.60 (m, 3H), 7.45 – 7.36 (m, 6H), 7.20 – 7.08 (m, 4H), 4.46 (q, *J* = 4.5 Hz, 1H), 3.37 (br.s, 1H), 3.15 (dd, *J* = 4.3, 0.7 Hz, 1H), 3.05 (q, *J* = 13.8 Hz, 2H), 2.44 (dd, *J* = 13.9, 5.0 Hz, 1H), 2.23 (ddd, *J* = 13.9, 4.3, 0.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 156.1, 135.8, 135.6, 135.1, 132.5, 132.4, 132.0, 129.6, 129.1, 128.6, 128.0, 124.0, 123.6, 121.9, 89.4, 85.2,

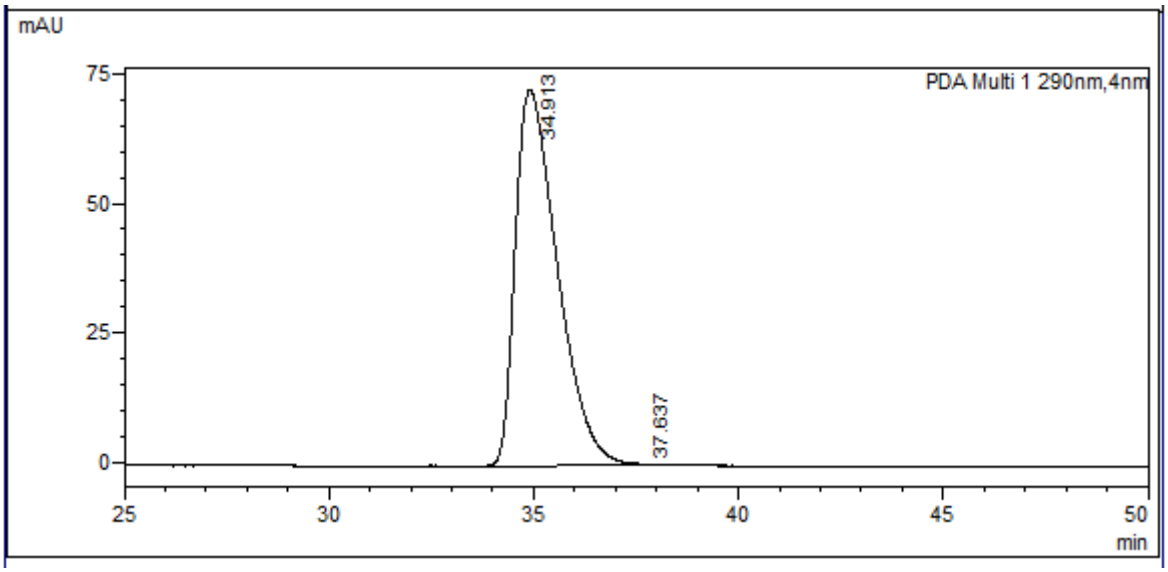
83.7, 76.8, 63.2, 53.7, 42.1, 38.6; HRMS (ESI) calcd for $C_{27}H_{22}ClO_3$ $[M+H]^+$: 429.1257; found: 429.1264; $[\alpha]^{20}_D$ = -124.19° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 93/07, detected at 290 nm, Flow rate = 1 mL/min, Retention times: 34.913 min (major), 37.637 min (minor).



<Peak Table>

PDA Ch1 290nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	35.170	3658492	53560	49.602	52.918
2	37.484	3717184	47653	50.398	47.082
Total		7375676	101213	100.000	100.000

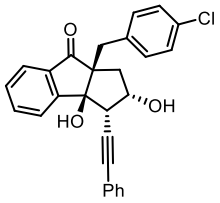


<Peak Table>

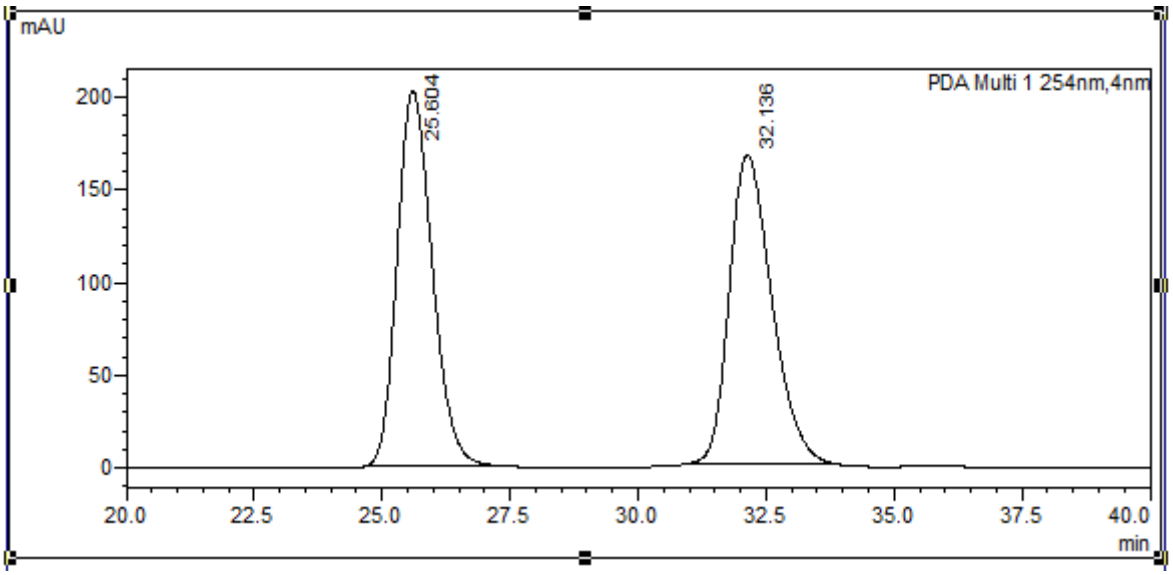
PDA Ch1 290nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	34.913	5189152	72621	99.968	99.999
2	37.637	1683	1	0.032	0.001
Total		5190836	72622	100.000	100.000

(2*S*,3*S*,3a*S*,8a*R*)-8a-(4-Chlorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*syn*-5d):



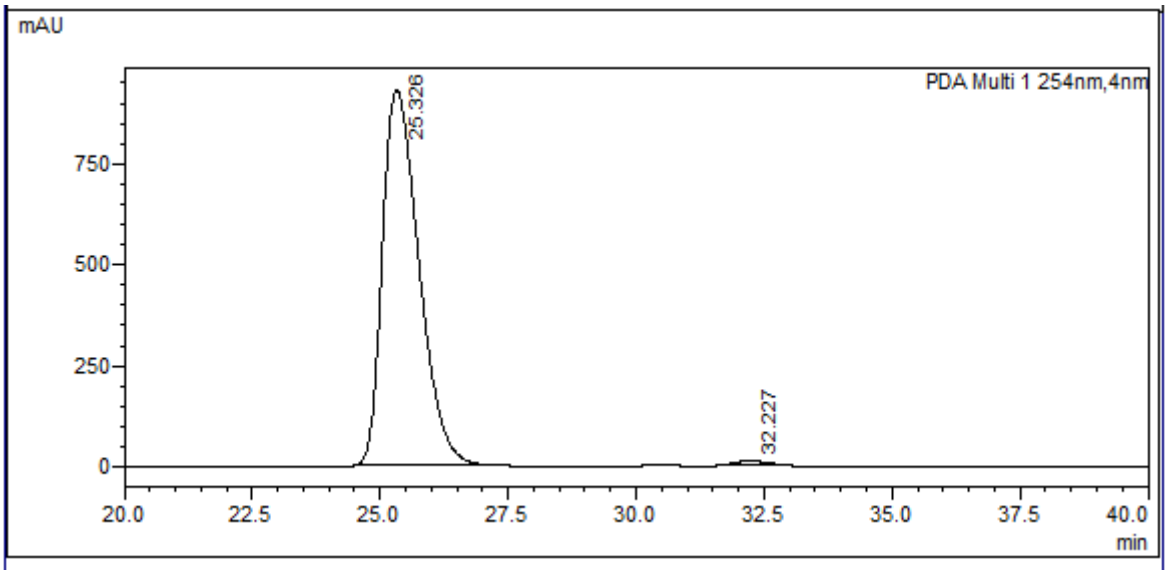
Prepared according to the general procedure as described above in 23% yield (30 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a brown solid; mp = 150–152°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.64 (td, *J* = 7.5, 1.1 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.41 (dt, J = 7.3, 0.9 Hz, 1H), 7.38 – 7.34 (m, 3H), 7.15 – 7.05 (m, 4H), 4.32 (dd, *J* = 8.5, 3.6 Hz, 1H), 3.83 (br.s, 1H), 3.65 (br.s, 1H), 3.18 – 3.09 (m, 2H), 2.88 (d, *J* = 3.9 Hz, 1H), 2.43 (dd, *J* = 14.5, 5.0 Hz, 1H), 2.20 (dd, *J* = 14.6, 3.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 154.1, 135.8, 135.5, 134.2, 132.4, 132.3, 132.1, 129.8, 128.9, 128.6, 128.0, 124.3, 123.6, 122.4, 88.7, 86.9, 82.6, 76.3, 65.9, 52.5, 40.4, 40.0; HRMS (ESI) calcd for $C_{27}H_{22}ClO_3$ $[M+H]^+$: 429.1257; found: 429.1250; $[\alpha]^{20}_D$ = -126.89° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 98% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 93/07, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 25.326 min (major), 32.227 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	25.604	9608967	202143	49.821	54.772
2	32.136	9678169	166920	50.179	45.228
Total		19287136	369062	100.000	100.000

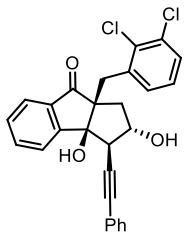


<Peak Table>

PDA Ch1 254nm

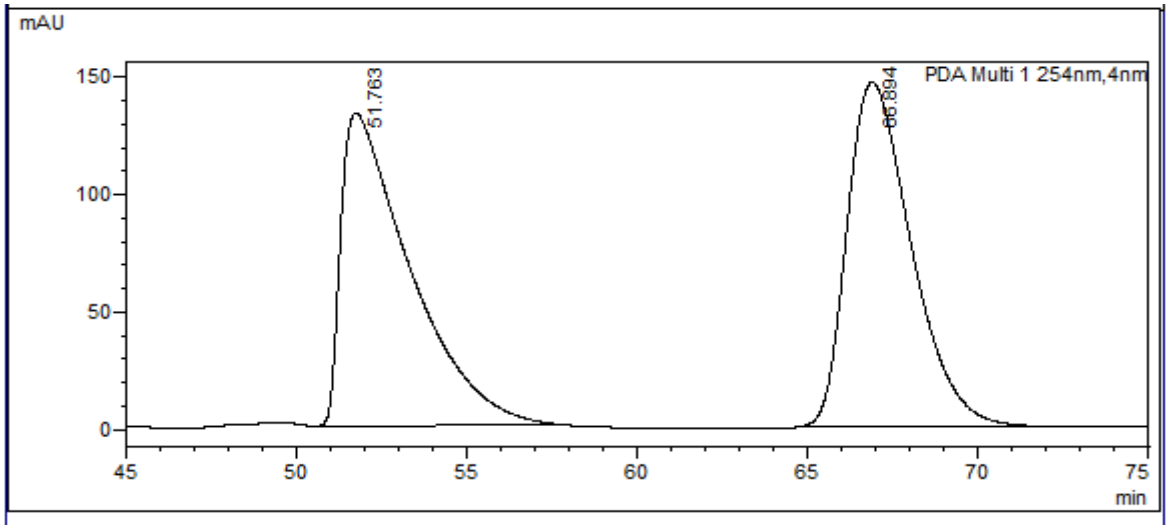
Peak#	Ret. Time	Area	Height	Area%	Height%
1	25.326	46234682	928946	98.980	98.858
2	32.227	476280	10731	1.020	1.142
Total		46710962	939676	100.000	100.000

(2*S*,3*R*,3a*S*,8a*R*)-8a-(2,3-Dichlorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*anti*-5e):



Prepared according to the general procedure as described above in 56% yield (77 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.57 (m, 3H), 7.44 – 7.37 (m, 3H), 7.34 – 7.26 (m, 3H), 7.23 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.17 (dd, *J* = 7.3, 1.5 Hz, 1H)), 6.97 (t, *J* = 7.9 Hz, 1H), 4.41 (q, *J* = 4.3 Hz, 1H), 3.46 (br.s, 1H), 3.28 (d, *J* = 14.3 Hz, 1H), 3.13 (d, *J* = 3.7 Hz, 1H), 3.07 (d, *J* = 14.3 Hz, 1H), 2.41 (dd, *J* = 14.0, 4.9 Hz, 1H), 2.10 (ddd, *J* = 14.0, 4.1, 0.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 155.6, 138.1, 135.6, 135.1, 133.8, 133.1, 132.0, 130.6, 129.7, 129.1, 129.0, 128.6, 126.7, 124.3, 123.9, 122.0, 89.4,

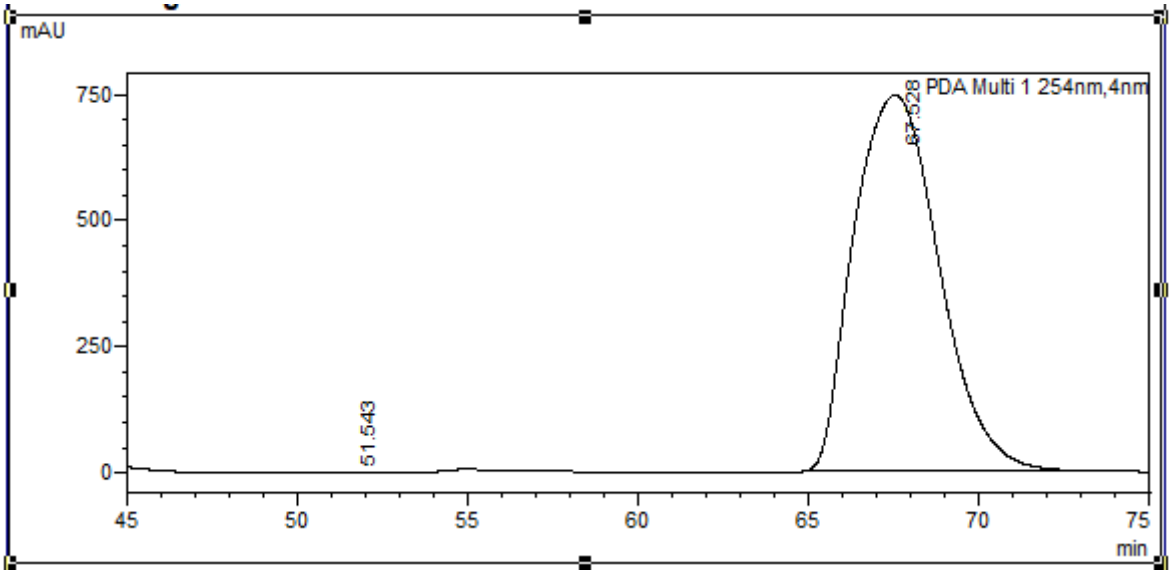
85.4, 83.9, 77.0, 62.6, 53.2, 41.6, 36.5; HRMS (ESI) calcd for $C_{27}H_{21}Cl_2O_3$ $[M+H]^+$: 463.0867; found: 463.0878; $[\alpha]^{20}_D$ = -155.60° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: 99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 93/07, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 67.528 min (major), 51.543 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	51.763	18728997	133242	49.580	47.646
2	66.894	19046292	146408	50.420	52.354
Total		37775289	279650	100.000	100.000



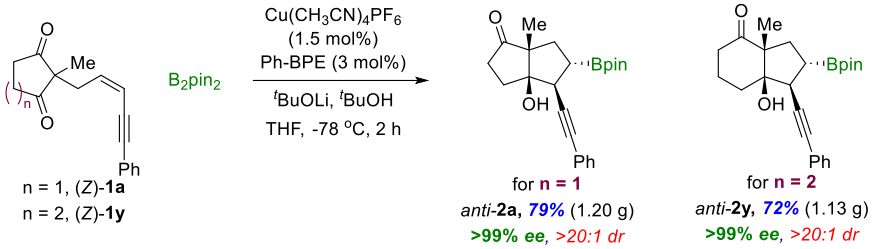
<Peak Table>

PDA Ch1 254nm

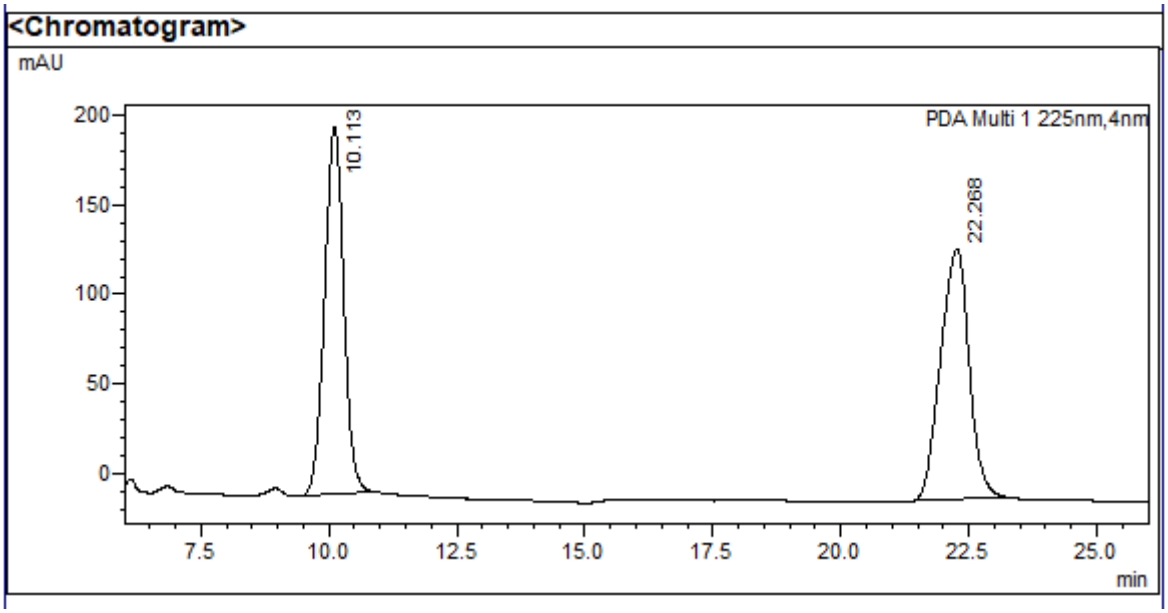
Peak#	Ret. Time	Area	Height	Area%	Height%
1	51.543	787	13	0.001	0.002
2	67.528	129502511	744954	99.999	99.998
Total		129503298	744966	100.000	100.000

IIIg. Large-scale reaction and further transformations

Gram scale reaction on 1a and 1y:



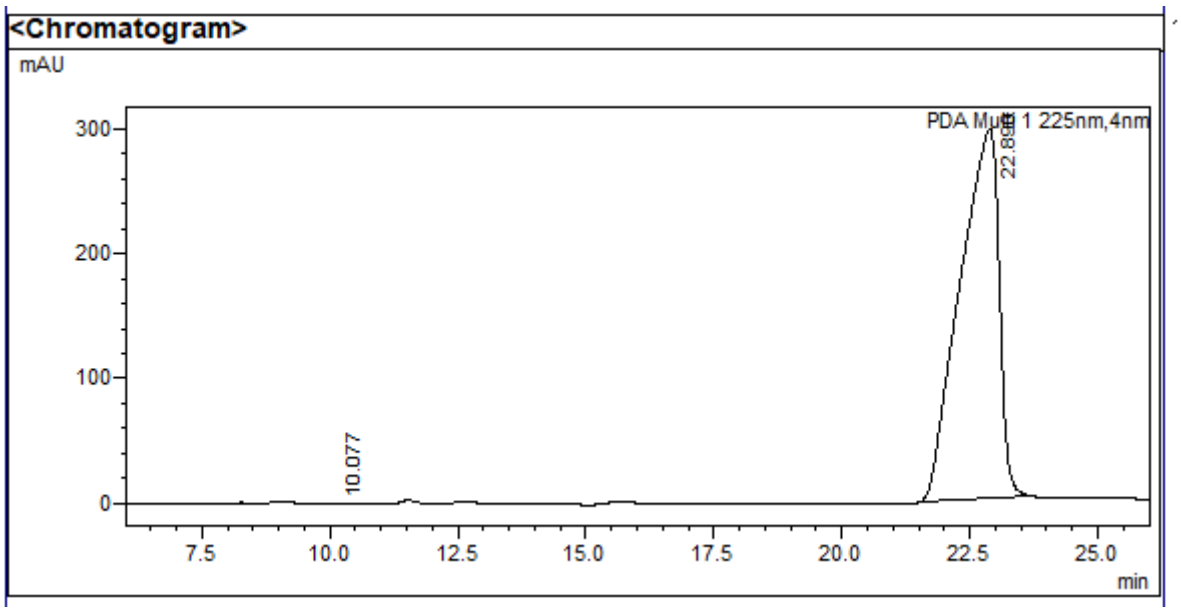
A solution of $Cu(CH_3CN)_4PF_6$ (22.0 mg, 1.5 mol %) and (*S,S*)-BPE (61 mg, 3 mol%) in dry THF (6 mL, 0.2 M) was stirred for 20 min at room temperature under nitrogen atmosphere. Then maintained at -78 °C. A solution of **1a** (4.0 mmol) in dry THF (1.0 mL) was added via syringe, $B_2(pin)_2$ (1.22 g, 4.8 mmol) and *t*-BuOH (0.76 ml, 8.0 mmol) was added sequentially followed by addition of LiO^tBu (0.72 ml, 8.0 mmol, 1 M in THF) the resulting mixture was stirred at -78 °C for 2 h. The reaction mixture was diluted with saturated NH_4Cl solution (20 mL) and extracted with EtOAc (2 x 30 mL). The combined organic solvent was washed with brine (10 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated under in *vacuo*. The crude reaction mixture was purified by column chromatography (EtOAc/hexanes) to give the desired product **2a** in 79% yield (1.2 g) with >99% enantioselectivity and high diastereoselectivity. $[\alpha]^{20}_D$ = -63.04° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 93/07, detected at 225 nm, Flow rate = 1 mL/min, Retention times: 22.890 min (major), 10.077 min (minor).



<Peak Table>

PDA Ch1 225nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.113	5322877	203929	49.773	59.531
2	22.268	5371525	138631	50.227	40.469
Total		10694402	342561	100.000	100.000



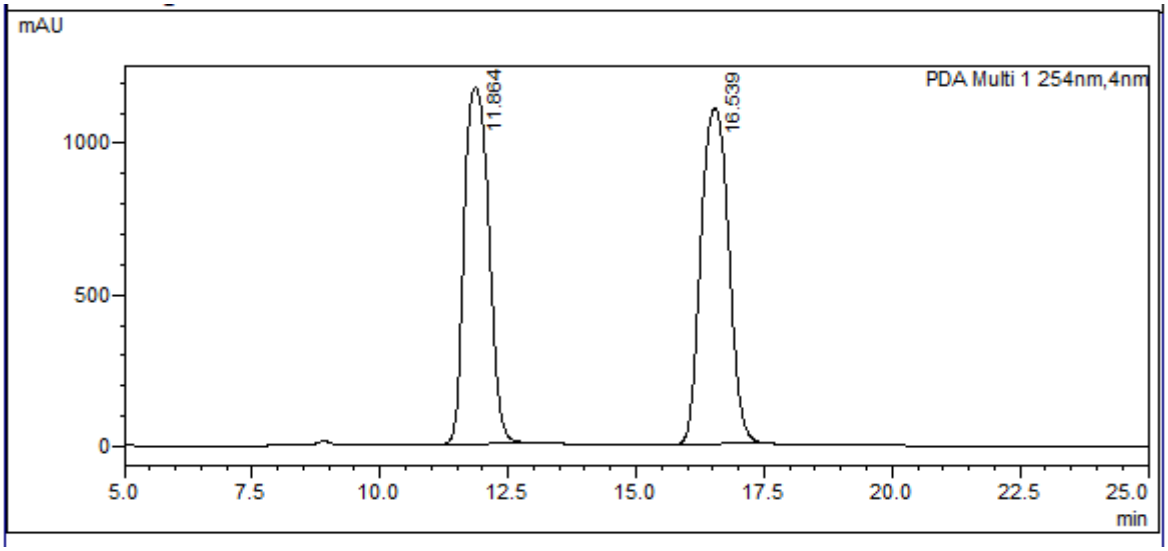
<Peak Table>

PDA Ch1 225nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.077	466	64	0.003	0.022
2	22.890	15744453	296182	99.997	99.978
Total		15744919	296246	100.000	100.000

Gram scale reaction of 1y:

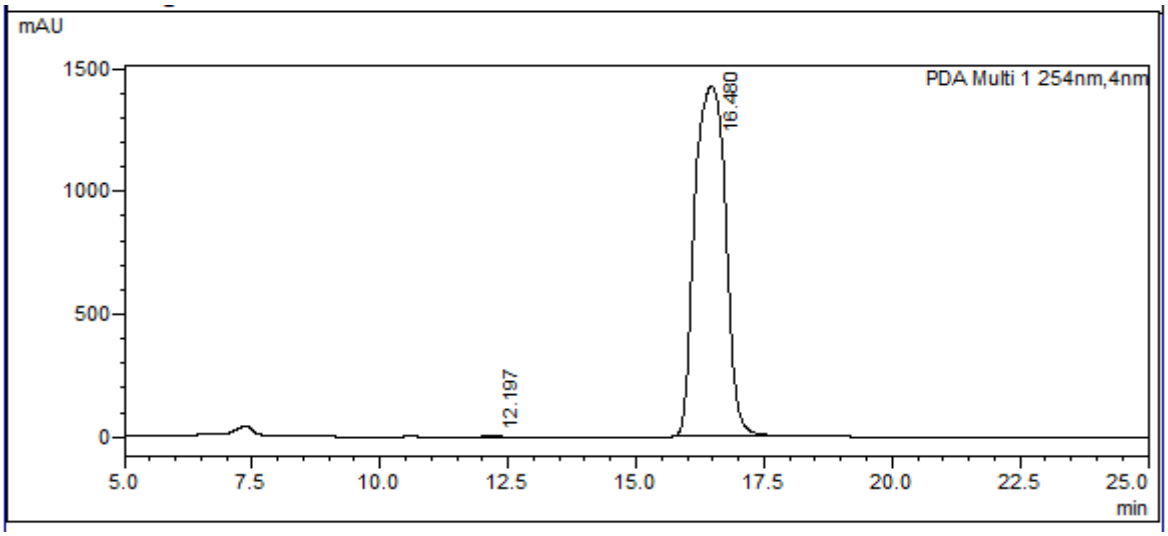
Under similar reaction conditions cyclohexadione substrate **1y** (4.0 mmol) gave the desired product **2y** in 72% yield (1.13 g) with >99% enantioselectivity and high diastereoselectivity. $[\alpha]^{25}_{D}$ = +58.87° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 95/05, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 16.480 min (major), 12.197 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.864	39535322	1179877	48.523	51.573
2	16.539	41941618	1107908	51.477	48.427
Total		81476940	2287785	100.000	100.000

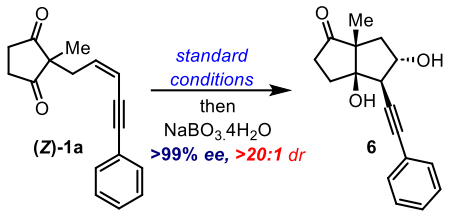


<Peak Table>

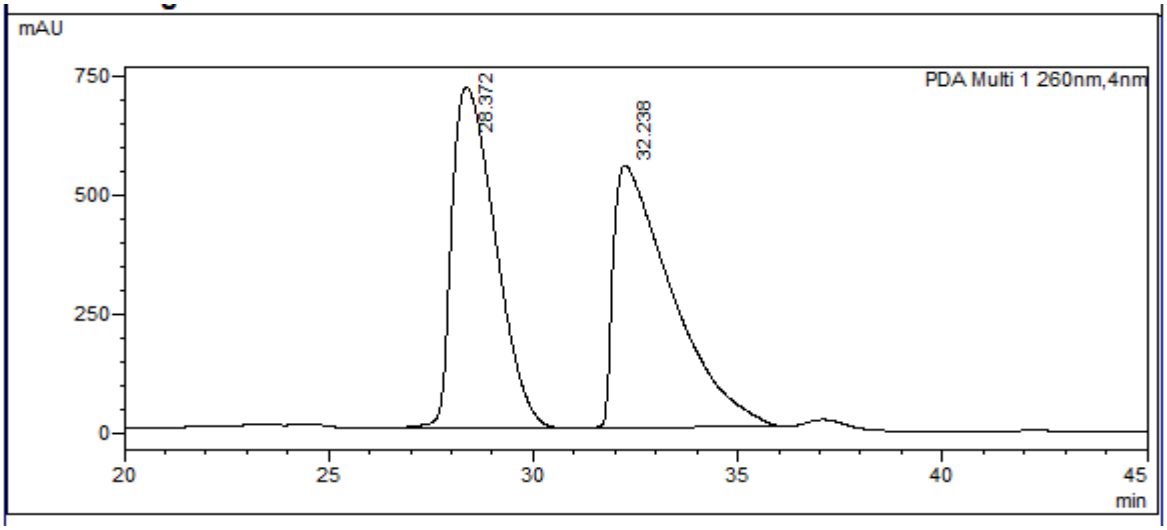
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.197	100764	3014	0.169	0.211
2	16.480	59635201	1423526	99.831	99.789
Total		59735966	1426540	100.000	100.000

One-pot borylative cyclization/oxidation of (*Z*)-1a:[5]



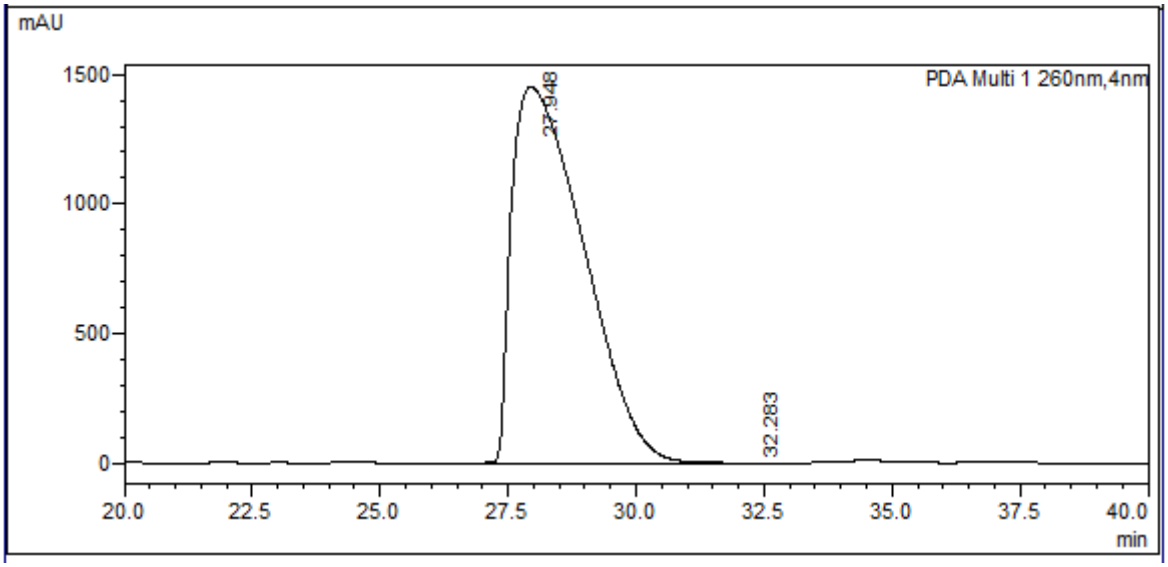
A solution of $Cu(CH_3CN)_4PF_6$ (2.8 mg, 2.5 mol %) and (*S,S*)-BPE (7.6 mg, 5 mol%) in dry THF 2 mL, 0.1 M) was stirred for 20 min at room temperature under nitrogen atmosphere and then maintained at -78 ºC. A solution of **1a** (0.3 mmol) in dry THF (1.0 mL) was added *via* syringe, $B_2(pin)_2$ (91 mg, 0.36 mmol) and *t*-BuOH (57 µl, 0.6 mmol, 1 M in THF) were added sequentially followed by the addition of LiO^{t}Bu (54 µl, 0.6 mmol, 1 M in THF) the resulting mixture was stirred at -78 ºC for 2 h. then $NaBO_3 \cdot H_2O$ (150 mg, 1.5 mmol) in H_2O (2 mL) was added in one portion and the resulting mixture was stirred vigorously at room temperature for 0.5 h under open air. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL), extracted with EtOAc (3 × 15 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. It was purified by flash chromatography (30% EtOAc/hexanes; *Rf* = 0.6) to afford a brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.36 – 7.27 (m, 3H), 4.48 (q, *J* = 6.8 Hz, 1H), 2.83 (d, *J* = 7.2 Hz, 1H), 2.70 – 2.38 (m, 4H), 2.30 (ddd, *J* = 13.1, 9.1, 3.9 Hz, 1H), 2.11 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.07 – 1.96 (m, 2H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 132.0, 128.7, 128.5, 122.4, 86.6, 86.0, 85.4, 76.4, 57.0, 51.5, 43.2, 33.5, 31.2, 17.8; HRMS (ESI) calcd for $C_{17}H_{19}O_3$ [M+H]+: 271.1330; found: 271.1327; Chiral HPLC analysis of the product: >99% *ee*; Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 94/06, detected at 260 nm, Flow rate = 1 mL/min, Retention times: 27.948 min (major), 32.283 min (minor).



<Peak Table>

PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	28.372	52578502	713598	49.149	56.519
2	32.238	54398287	548992	50.851	43.481
Total		106976790	1262590	100.000	100.000

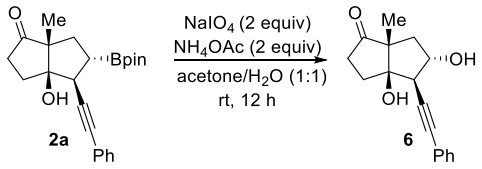


<Peak Table>

PDA Ch1 260nm

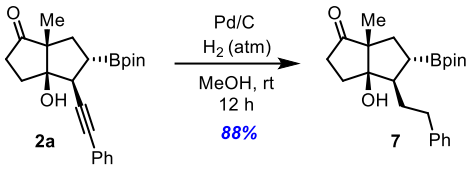
Peak#	Ret. Time	Area	Height	Area%	Height%
1	27.948	141599932	1446967	99.990	99.997
2	32.283	14348	37	0.010	0.003
Total		141614279	1447004	100.000	100.000

Oxidation of 2a:[6]



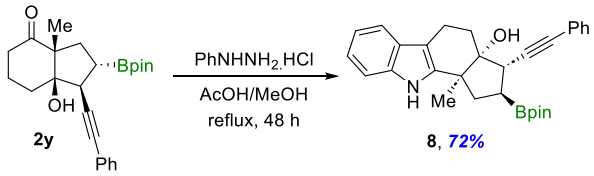
To a solution of **2a** (70 mg, 0.18 mmol, 1 equiv) in acetone/H_2O (1:1, v/v), $NaIO_4$ (79 mg, 0.36 mmol, 2 equiv) and NH_4OAc (28 mg, 0.36 mmol, 2 equiv) were added. The reaction mixture was stirred at room temperature for 12 h. After filtration, the filtrate was extracted with Et_2O (2 × 20 mL). The organic layers were combined and dried over anhydrous Na_2SO_4, and filtered and concentrated. Then the resulting crude product was purified by column chromatography on silica gel (30% EtOAc/hexanes; *Rf* = 0.6) to afford a brown liquid (41 mg, 84% yield) [For experimental data see the **6**].

Reduction of 2a:[7]



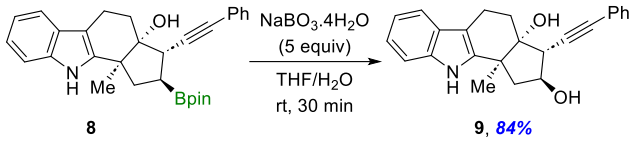
To a round-bottom flask were charged **2a** (70 mg, 0.18 mmol), MeOH (2.5 mL) and Pd/C (7.0 mg, 100 wt %). The flask was evacuated and backfilled with H_2. The reaction mixture was allowed to stir at room temperature overnight, then filtered through a short plug of celite, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography (30% EtOAc/hexanes; $R_f = 0.5$) to afford **7** as a white semi-solid in 88% yield (62 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.16 – 7.07 (m, 3H), 2.69 – 2.49 (m, 2H), 2.42 – 2.16 (m, 2H), 2.00 (ddd, J = 12.6, 8.7, 3.8 Hz, 1H), 1.88 – 1.71 (m, 4H), 1.69 – 1.50 (m, 3H), 1.33 (dd, J = 21.0, 10.1 Hz, 1H), 1.16 (s, 12H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.7, 142.8, 128.5, 128.5, 126.0, 89.1, 83.5, 60.4, 50.0, 36.8, 35.5, 35.1, 32.3, 30.7, 24.9, 16.7; HRMS (ESI) calcd for $C_{23}H_{34}BO_4$ 385.2550; found: 385.2556.

Synthesis of compound 8:[8]



A solution of **2y** (197 mg, 0.5 mmol, 1 equiv), phenylhydrazine hydrochloride (145 mg, 1.0 mmol, 2 equiv), and acetic acid (1.0 mL) in 2.5 mL (0.2 M) of methanol was refluxed for 24 h in preheated oil bath. The solvent was then evaporated to a smaller volume, diluted with water (5 mL) and extracted with CH_2Cl_2 (10 mL x 3). The organic phase was dried under reduced pressure and the residue was purified by flash column chromatography (30% EtOAc/hexanes; $R_f = 0.5$) to give the indole **8** obtained in 72% yield (163 mg) as a brown solid with exclusive diastereoselectivity; mp = 239–241°C; $[\alpha]^{25}_D$ = -102.49° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.50 – 7.40 (m, 3H), 7.35 – 7.27 (m, 4H), 7.09 (dt, J = 22.4, 7.2 Hz, 2H), 3.30 (d, J = 9.6 Hz, 1H), 2.95 – 2.84 (m, 1H), 2.80 – 2.60 (m, 1H), 2.36 (t, J = 11.9 Hz, 2H), 2.18 – 1.99 (m, 3H), 1.90 (td, J = 10.4, 6.0 Hz, 1H), 1.43 (s, 3H), 1.03 (s, 6H), 0.90 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 136.8, 131.9, 128.4, 128.1, 127.4, 123.5, 121.4, 119.3, 118.3, 110.7, 107.6, 89.4, 84.9, 83.4, 82.8, 46.8, 40.5, 39.0, 29.7, 24.7, 24.5, 23.3, 18.7; HRMS (ESI) calcd for $C_{30}H_{35}O_3BN$ $[M+H]^+$: 468.2741; found: 468.2719.

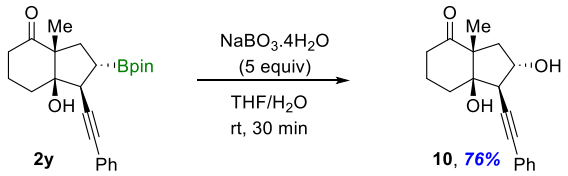
Synthesis of compound 9:



8 **9**, *84%*

To a solution of **8** (70 mg, 0.15 mmol, 1 equiv) in THF/H_2O (1:2 ratio, 3 mL) was added $NaBO_3 \cdot 4H_2O$ (75 mg, 0.75 mmol) in one portion. the resulting mixture was stirred vigorously at room temperature for 30 minutes under open air. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL), extracted with EtOAc (3 × 15 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. It was purified by flash chromatography (40% EtOAc/hexanes; *Rf* = 0.5) to afford a brown semi solid of **9** in 84% yield (43 mg); $[\alpha]^{25}_D$ = -169.39° (*c* 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.51 – 7.43 (m, 3H), 7.35 – 7.28 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.62 (td, *J* = 8.3, 4.6 Hz, 1H), 3.15 (d, *J* = 7.6 Hz, 1H), 2.92 (dd, *J* = 16.2, 5.9 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.55 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.18 (brs, 1H), 2.11 – 1.98 (m, 3H), 1.84 (brs, 1H), 1.39 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 140.9, 136.9, 132.0, 128.5, 127.1, 122.9, 121.8, 119.5, 118.4, 110.9, 107.0, 107.0, 87.0, 85.9, 83.1, 48.5, 45.6, 45.0, 29.6, 23.6, 18.8; HRMS (ESI) calcd for $C_{24}H_{24}O_2N$ $[M+H]^+$: 358.1807; found: 358.1825;

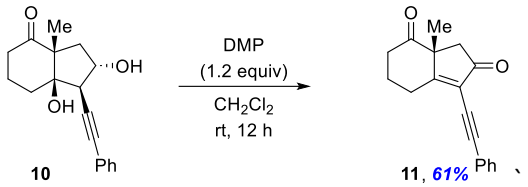
Synthesis of compound 10:



2y **10**, *76%*

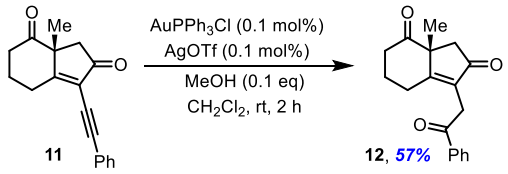
To a solution of **2y** (276 mg, 0.7 mmol, 1 equiv) in THF/H_2O (1:2 ratio, 4 mL) was added $NaBO_3 \cdot 4H_2O$ (349 mg, 3.5 mmol) in one portion. the resulting mixture was stirred vigorously at room temperature for 30 minutes under open air. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL), extracted with EtOAc (3 × 15 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. It was purified by flash chromatography (40% EtOAc/hexanes; *Rf* = 0.5) to afford a brown semi solid of **10** in 76% yield (151 mg) with *dr* ratio of 6:1 (crude ^{1}H NMR analysis); $[\alpha]^{25}_D$ = -230.19° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD) δ 7.49 – 7.39 (m, 2H), 7.34 – 7.23 (m, 3H), 4.42 (ddd, *J* = 9.4, 8.4, 4.4 Hz, 1H), 3.32 (dt, *J* = 3.3, 1.6 Hz, 1H), 2.72 – 2.60 (m, 3H), 2.34 – 2.25 (m, 1H), 2.20 – 2.12 (m, 1H), 2.03 – 1.94 (m, 2H), 1.91 (dd, *J* = 14.0, 9.5 Hz, 1H), 1.71 – 1.53 (m, 2H), 1.21 (s, 3H); ^{13}C NMR (101 MHz, CD_3OD) δ 214.7, 132.8, 129.3, 128.9, 125.1, 88.2, 85.0, 84.7, 76.0, 60.7, 49.4, 40.5, 37.8, 30.9, 20.9, 20.5; HRMS (ESI) calcd for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1490; found: 285.1475.

Synthesis of 11:



To a stirred solution of alcohol **10** (128 mg, 0.45 mmol, 1 equiv) in CH_2Cl_2 (4 mL) was added Dess Martin periodinane (229 mg, 1.2 equiv) in one portion at 0 °C and stirred the reaction mixture room-temperature for 12 h under nitrogen atmosphere. The reaction mixture was diluted with hexanes (10 mL) and filtered through Celite, washed with hexanes (10 mL) and then concentrated in *vacuo*. The crude product was purified by column chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford colorless liquid **11** in 61% yield (72 mg); $[\alpha]^{25}_D$ = -230.49° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.38 – 7.29 (m, 3H), 3.34 – 3.19 (m, 2H), 2.88 – 2.70 (m, 2H), 2.52 – 2.45 (m, 1H), 2.37 – 2.28 (m, 1H), 2.25 (d, *J* = 19.1 Hz, 1H), 1.80 (qt, *J* = 13.4, 4.5 Hz, 1H), 1.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.0, 202.0, 181.6, 132.0, 129.0, 128.5, 123.3, 122.5, 97.9, 79.0, 57.9, 43.5, 37.3, 26.3, 26.1, 24.5; HRMS (ESI) calcd for $C_{18}H_{17}O_2$ $[M+H]^+$: 265.1228; found: 265.1231.

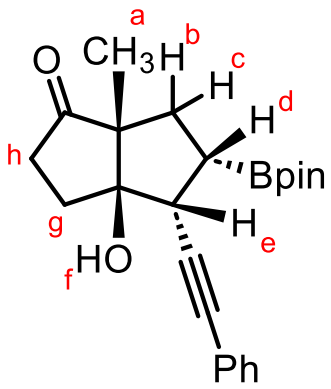
Synthesis of 12:[9]



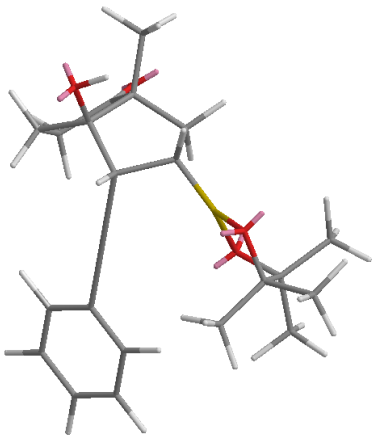
A solution of $AuPPh_3Cl$ (10.0 mg, 0.10 mol %) and AgOTf (5 mg, 0.10 mol%) in dry CH_2Cl_2 (2.5 mL, 0.2 M) was added compound **11** (53 mg, 0.2 mmol, 1 equiv) and MeOH (0.1 equiv), sequentially under inert atmosphere. The reaction was stirred at room temperature for 2 h. Then, the reaction mixture concentrated in *vacuo* and the crude product was directly purified by column chromatography (40% EtOAc/hexanes; R_f = 0.4) to afford product **12** in 57% yield (32 mg) as a colorless liquid; $[\alpha]^{25}_D$ = -30.50° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.92 (m, 2H), 7.57 (tt, *J* = 7.3, 1.6 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.86 (s, 2H), 3.22 (d, *J* = 19.0 Hz, 1H), 2.88 – 2.73 (m, 2H), 2.71 – 2.60 (m, 1H), 2.49 – 2.40 (m, 1H), 2.28 – 2.14 (m, 2H), 1.83 – 1.68 (m, 1H), 1.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.0, 205.1, 195.7, 177.6, 136.4, 133.6, 131.5, 128.8, 128.5, 57.8, 43.2, 37.4, 32.9, 26.3, 25.0, 24.6; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1334; found: 283.1340.

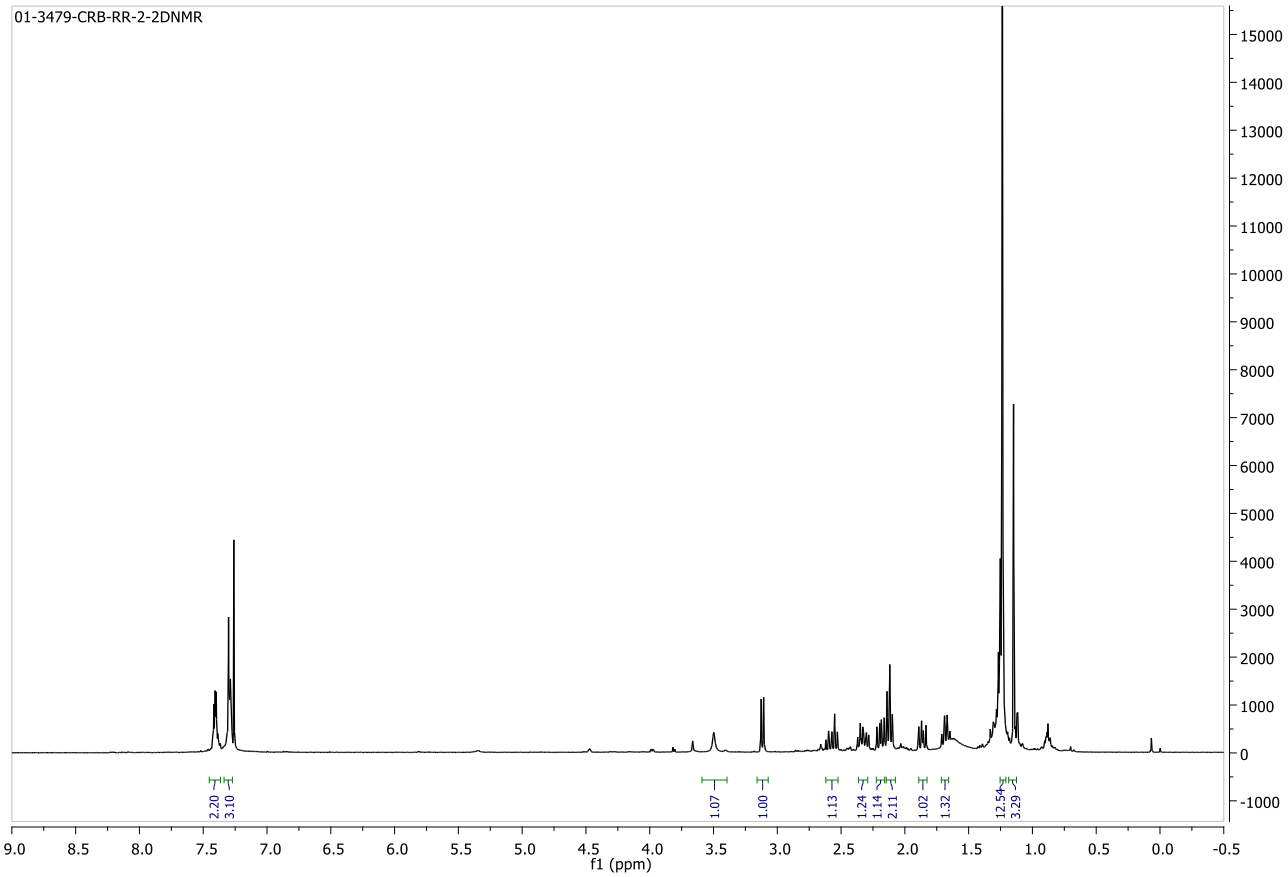
VI. 2D-NMR Analysis of Compound *syn*-2a.

The structure and relative stereochemistry of compound **2a** were elucidated by using 1D and 2D NMR experiments.

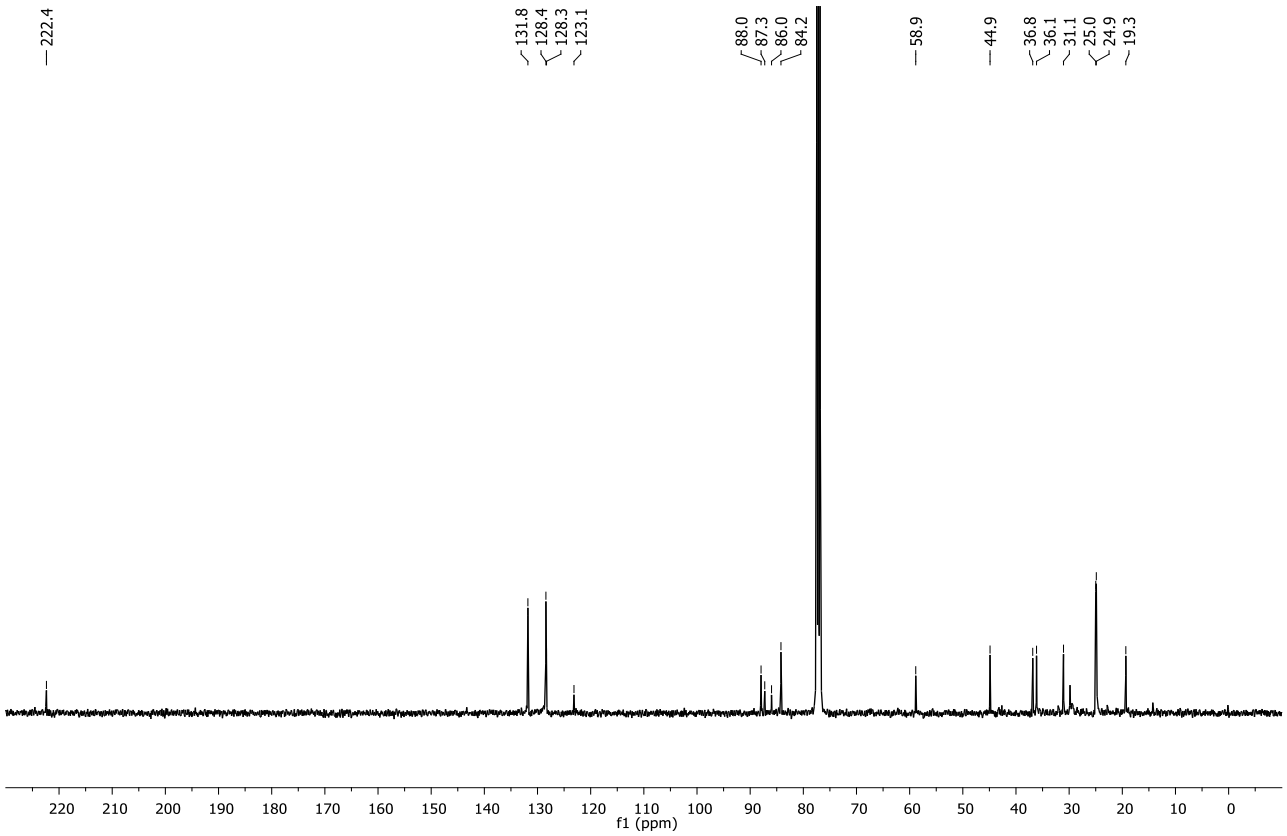


Compound *syn*-2a

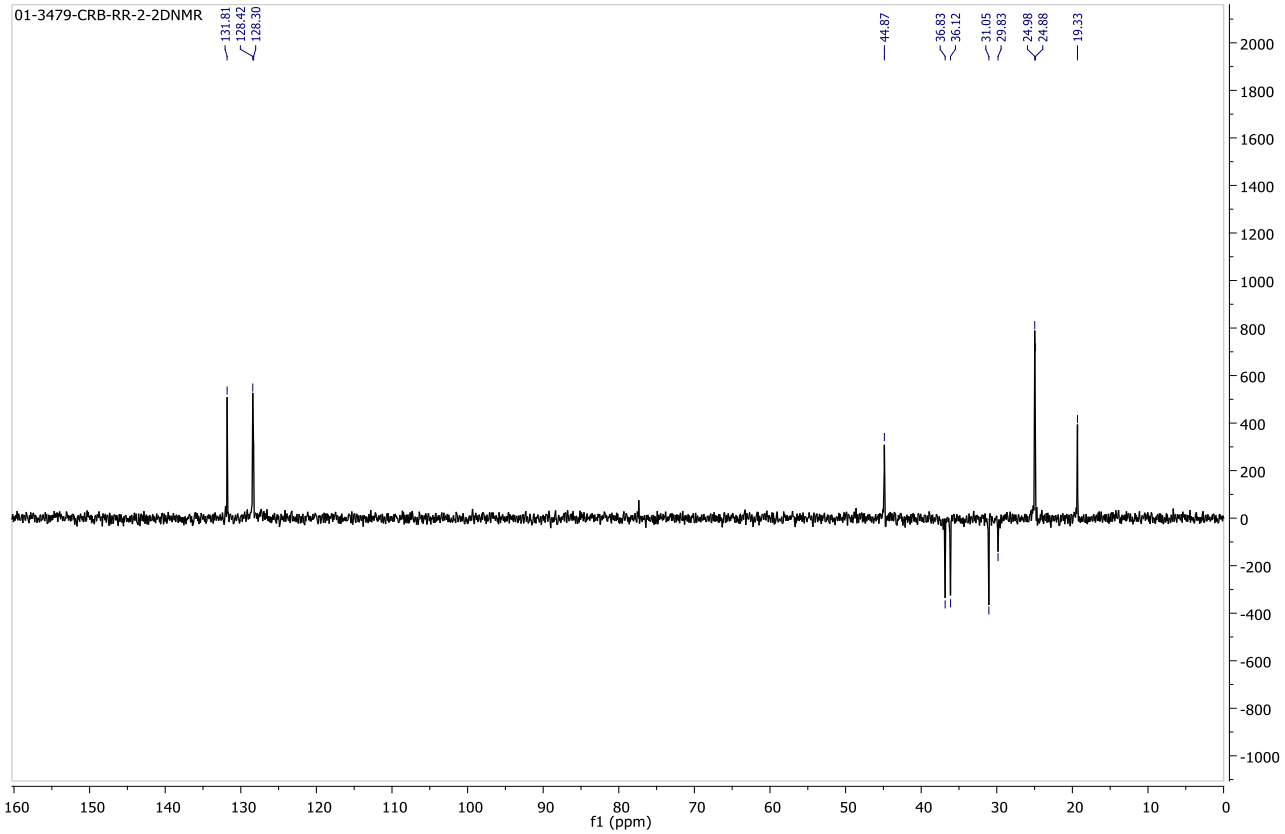




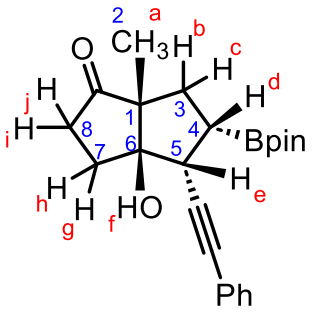
^{13}C NMR spectrum of **2a** recorded in $CDCl_3$ on 400 MHz at 25 °C



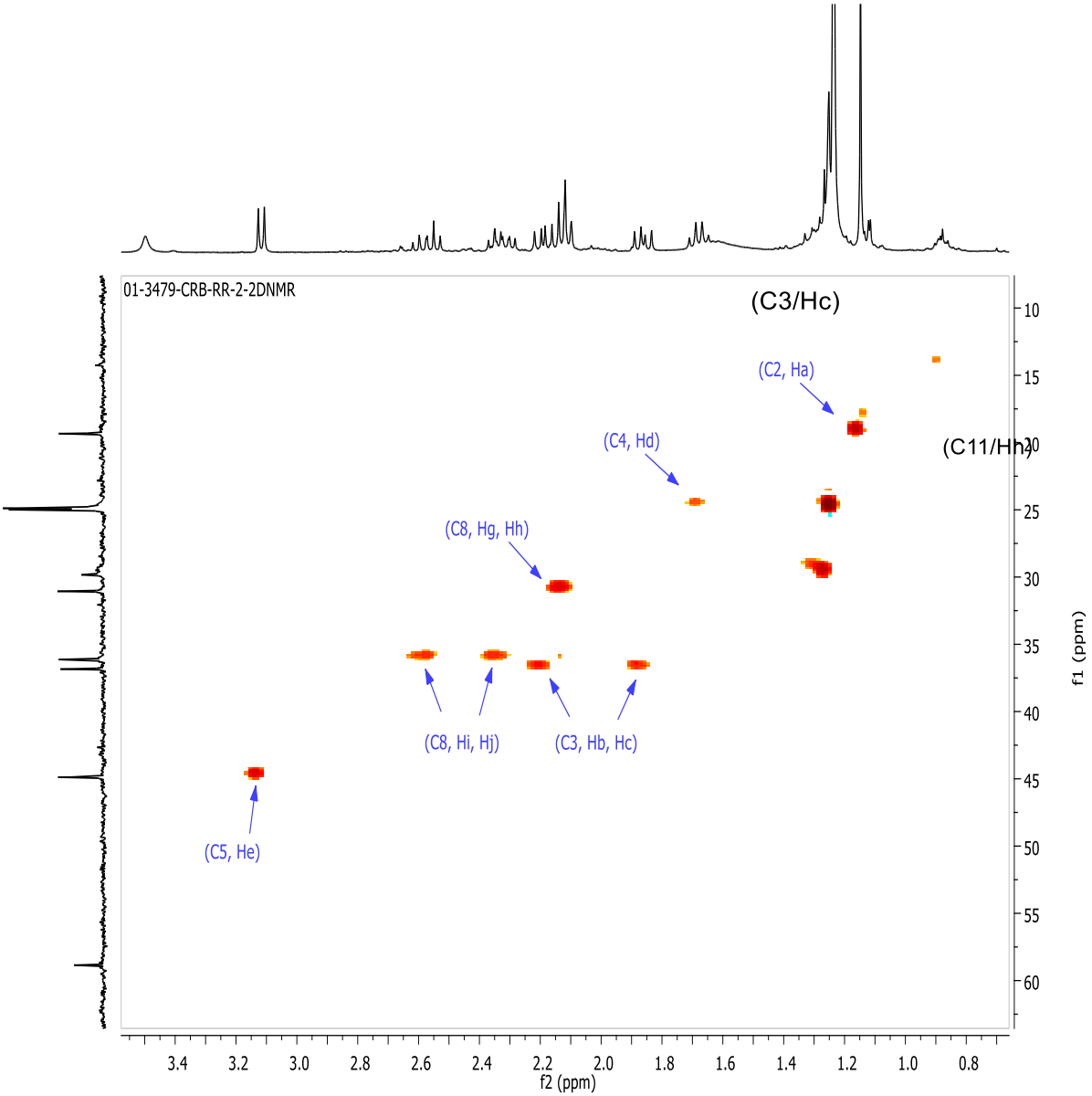
^{13}C NMR spectrum of **2a** recorded in $CDCl_3$ on 400 MHz at 25 °C



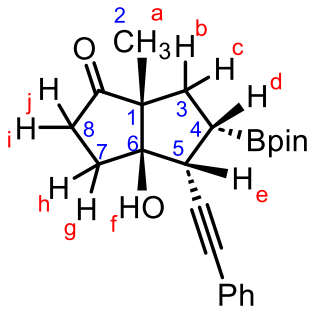
DEPT ^{13}C NMR spectrum of **2a** recorded in $CDCl_3$ on 400 MHz at 25 °C



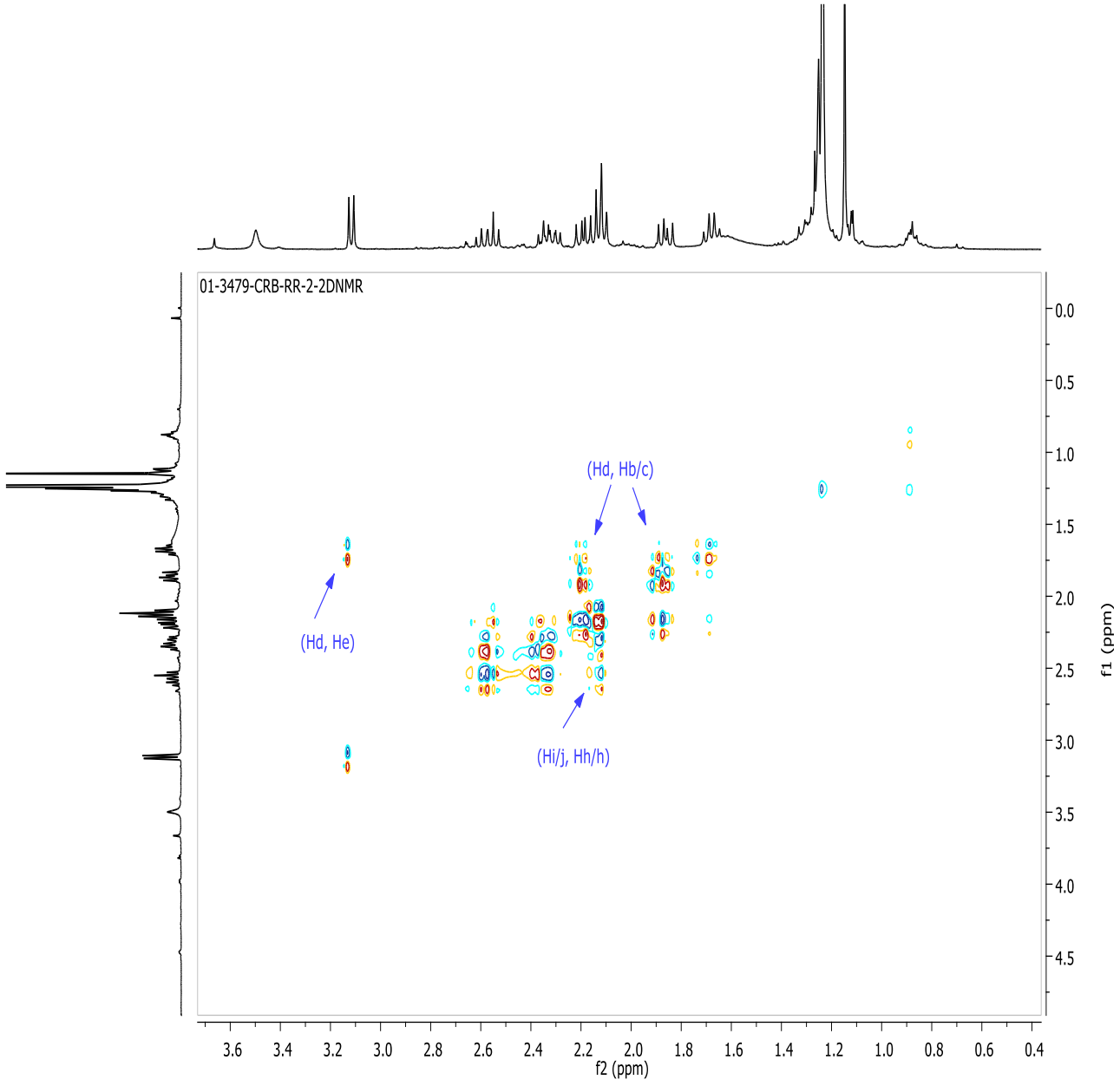
Compound *syn*-2a



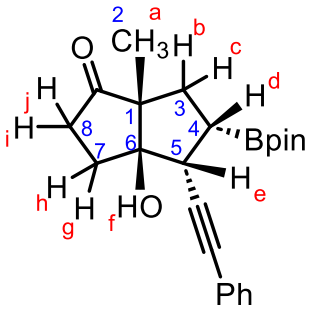
^{1}H-^{13}C 2D-HSQC spectrum of **2a** recorded in $CDCl_3$ on 400 MHz at 25 °C.



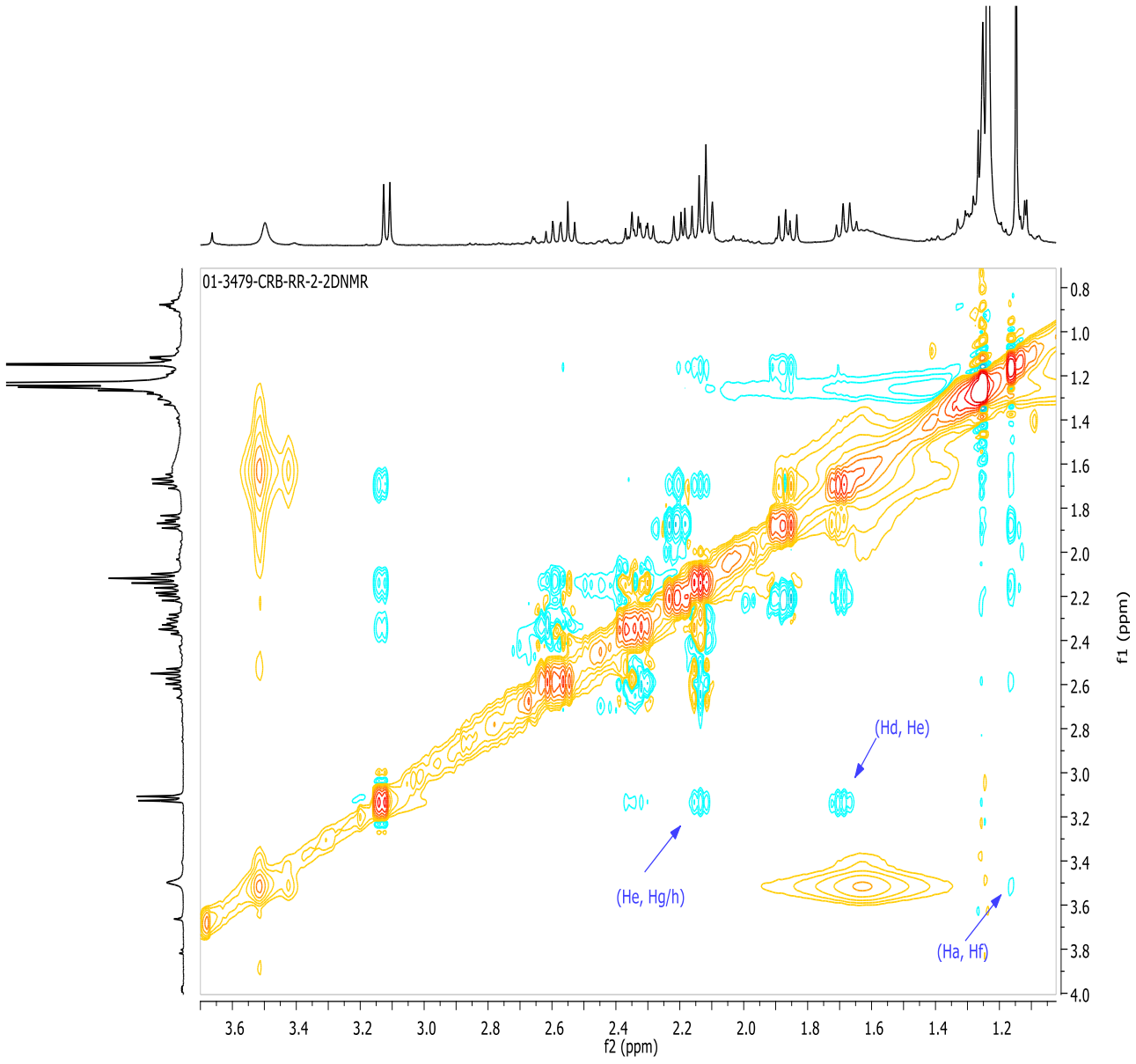
Compound *syn*-2a



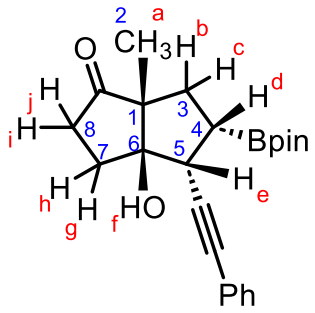
^{1}H-^{1}H 2D-COSY spectrum of **2a** recorded in $CDCl_3$ on 400 MHz at 25 °C.



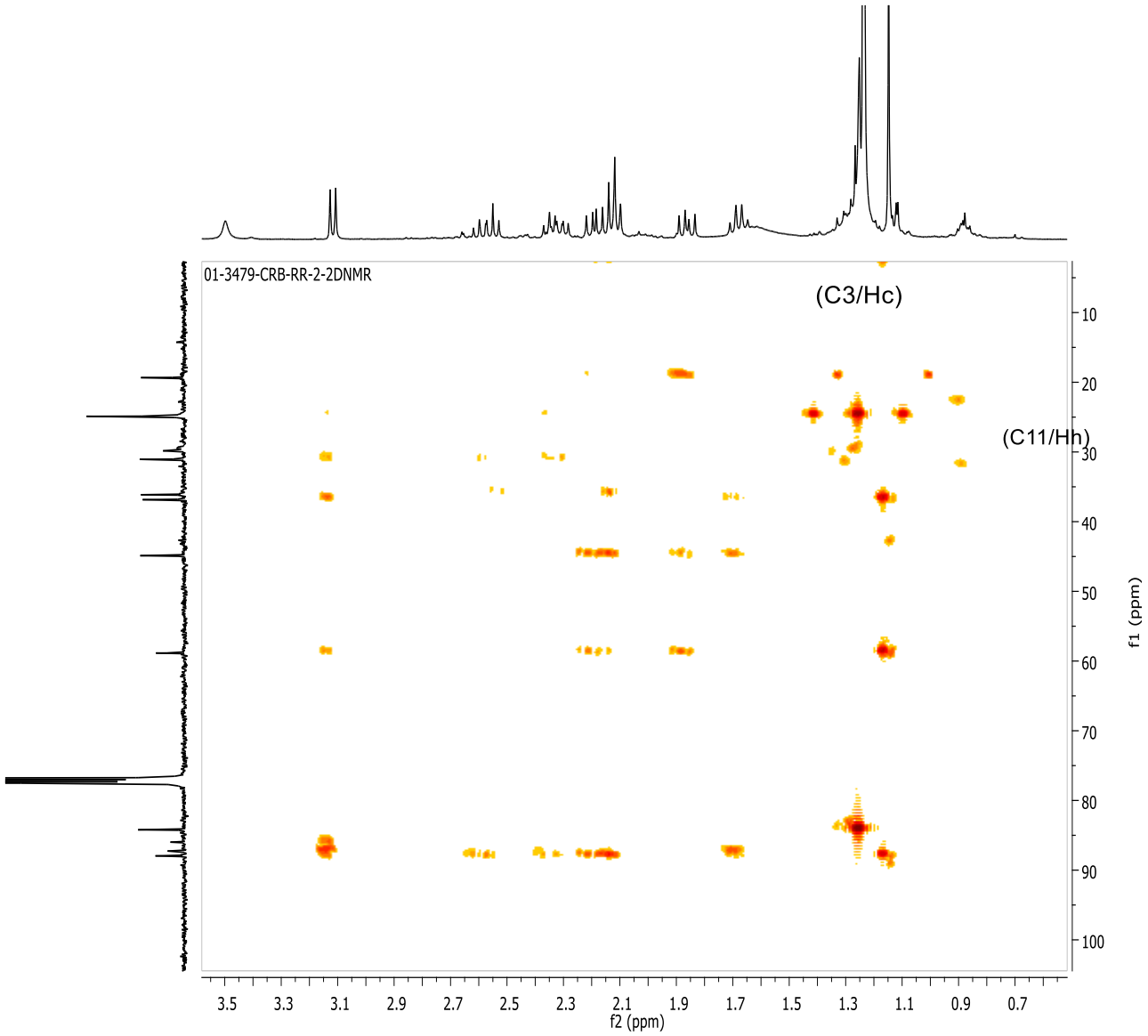
Compound *syn*-2a



^{1}H-^{1}H 2D-NOESY spectrum of **2a** recorded in $CDCl_3$ on 400 MHz at 25 °C



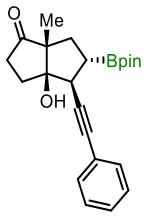
Compound *syn*-2a



^{1}H-^{13}C 2D-HMBC spectrum of **2a** recorded in $CDCl_3$ on 400 MHz at 25 °C.

V. X-Ray crystallographic data

X-ray crystallographic data for compound *anti*-2a: (*relative stereochemistry*)



The purified compound *anti*-**2a** was dissolved in a mixed solvent of isopropanol/ dichloromethane (1:3), and placed in a dark cabinet for slowly evaporation. Colorless crystals were collected after few days for X-ray analysis.

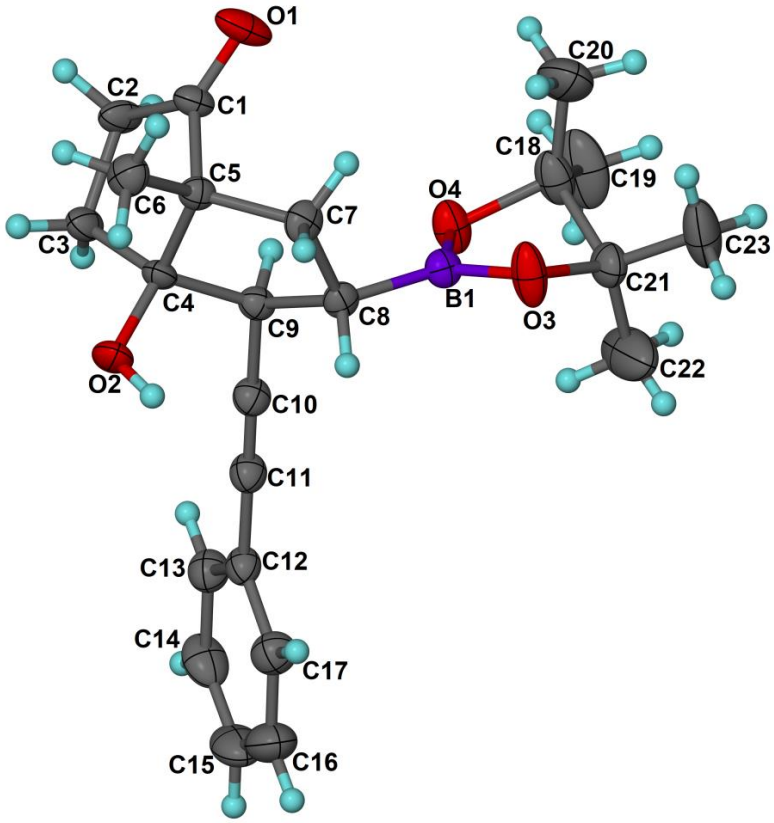
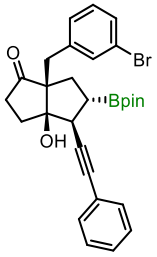


Figure caption: ORTEP diagram of KB1056 compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius. The tetramethyl dioxoborolan ring is disordered over two sites with the site occupancy of 0.632(6) for the major component and 0.368(6) for the minor component of the disordered atoms; only the major component of the disordered tetramethyl dioxoborolan ring atoms is shown for clarity purpose.

X-ray crystallographic data for compound *anti*-2o: (*absolute stereochemistry*)



The purified compound *anti*-**2o** was dissolved in a mixed solvent of isopropanol/dichloromethane (1:3), and placed in a dark cabinet for slowly evaporation. Colorless crystals were collected after few days for X-ray analysis.

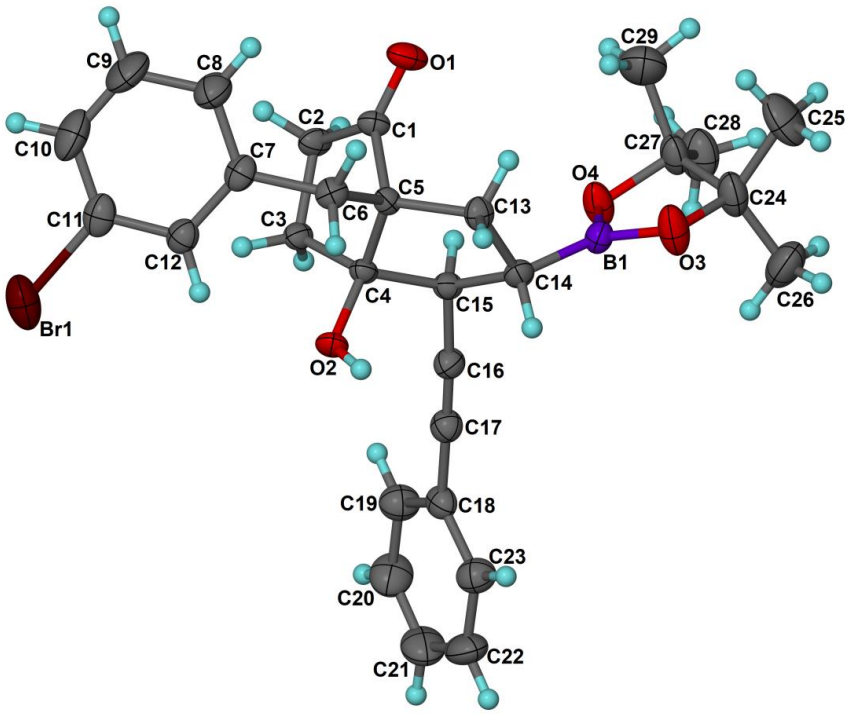


Figure caption: ORTEP diagram of KB1112 compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius. Only major component of the disordered atoms are shown for clarity purpose. The tetramethyl dioxoborolan ring is disordered over two sites with the site occupancy of 0.753(7) for the major component and 0.247(7) for the minor component of the disordered atoms; only the major component of the disordered tetramethyl dioxoborolan ring atoms is shown for clarity purpose.

Crystal data for KB1056 (2a) : $C_{23}H_{29}BO_4$, $M = 380.27$, Orthorhombic, Space group $P2_12_12_1$ (No.19), $a = 6.6993(11)$Å, $b = 14.819(2)$Å, $c = 21.974(3)$Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 2181.5(6)$Å^3, $Z = 4$, $D_c = 1.158$ g/cm^3, $F_{000} = 816$, Bruker D8 QUEST PHOTON III C7 HPAD detector, Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 294(2)$K, $2\theta_{max} = 55°$, $\mu = 0.077$ mm^{-1}, 19760 reflections collected, 4996

unique (R_{int} = 0.0598), 331 parameters, *R1* = 0.0522, *wR2* = 0.1022, *R* indices based on 3485 reflections with I > 2σ(I) (refinement on F^2), Final *GooF* = 1.033, largest difference hole and peak = -0.123 and 0.164 e.Å^{-3}. The **CCDC deposition number 2443592** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Crystal data for KB1112 (2o) : $C_{29}H_{32}BBrO_4$, *M* = 535.26, Orthorhombic, Space group $P2_12_12_1$ (No.19), *a* = 6.661(2)Å, *b* = 19.722(5)Å, *c* = 20.481(5)Å, *α* = 90°, *β* = 90°, *γ* = 90°, *V* = 2690.4(13)Å^3, *Z* = 4, D_c = 1.321 g/cm^3, F_{000} = 1112, Bruker D8 QUEST PHOTON III C7 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, *T* = 294(2)K, $2\theta_{max}$ = 55°, μ = 1.560 mm^{-1}, 32534 reflections collected, 6169 unique (R_{int} = 0.0829), 401 parameters, *R1* = 0.0462, *wR2* = 0.1034, *R* indices based on 3313 reflections with I > 2σ(I) (refinement on F^2), Final *GooF* = 1.020, largest difference hole and peak = -0.360 and 0.466 e.Å^{-3}. The **CCDC deposition number 2443593** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Data collection and Structure solution details:

X-ray data for the compound were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON-III C7 HPAD detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[10] The structure was solved using intrinsic phasing method and further refined with the SHELXL program and expanded using Fourier techniques.[11-13] Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms]. In KB1056, tetramethyl dioxoborolan ring is disordered over two sites with site occupancy factors of 0.632(6) for the major component (atoms O3/O4/C18/C19/C20/C21/C22/C23) and 0.368(6) for the minor component (atoms O3D/O4D/C18D/C19D/C20D/C21D/C22D/C23D).[12] Similarly, in KB1112, the tetramethyl dioxoborolan ring is disordered over two sites with site occupancy factors of 0.753(7) for the major component (atoms O3/O4/C24/C25/C26/C27/C28/C29) and 0.247(7) for the minor component (atoms O3D/O4D/C24D/C25D/C26D/C27D/C28D/C29D).[12] For modeling the structural disorder, PART, FVAR, DELU, SIMU and DFIX instructions were utilized as appropriate and the site occupancies for the major and minor components were refined. The absolute configuration of the compound KB1112 (C4, R; C5, S; C14, S; C15, S) was assigned based on the refinement of Flack parameter (0.046(9)).[14] **CCDC deposition numbers 2443592-2443593** contain the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

VI. References

1. D. B. Ramachary and M. Kishora, *Org. Biomol. Chem*., 2008, **6**, 4176.

2. B-H. Yuan, Z-C. Zhang, W-J. Liu and X-W. Sun, *Tetrahedron Lett.*, 2016, **57**, 2147–2151.

3. V. B. Patil, G. R. Ramudu and R. Chegondi, *Org. Lett.*, 2024, **26**, 6353−6358.

4. D. Brasseur, l. Marek and J-F. Normant, *Tetrahedron*, 1996, **52**, 7235-7250.

5. S. B. Jadhav, S. R. Dash, S. Maurya, J. B. Nanubolu, K. Vanka, R. Chegondi. *Nat. Commun.,* 2022, **13**, 854.

6. L. Ling, Y. He, X. Zhang, M. Luo, Xi. Zeng. *Angew. Chem. Int. Ed.,* 2019, **58**, 6554–6558.

7. X. Z. Zhao, D. Hymel, T. R. B. Jr. *Bioorg. Med. Chem. Lett*., 2016, **26**, 5009–5012.

8. D. L. Hughes, Org. Prep. Proceed. Int., 1993, **25**, 609.

9. R. Dorel, A. M. Echavarren, *Chem. Rev.,* 2015, **115**, 9028–9072.

10. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

11. G. M. Sheldrick, *Acta Crystallogr.,* 2015, **C71**: 3-8.

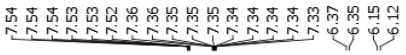
12. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, ShelXle: a Qt graphical user interface for SHELXL, *J. Appl. Cryst.*, 2011, **44**, 1281-1284.

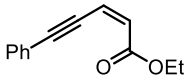
13. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.

14. Flack, H. D. *Acta Cryst.* 1983, **A39**, 876-881.

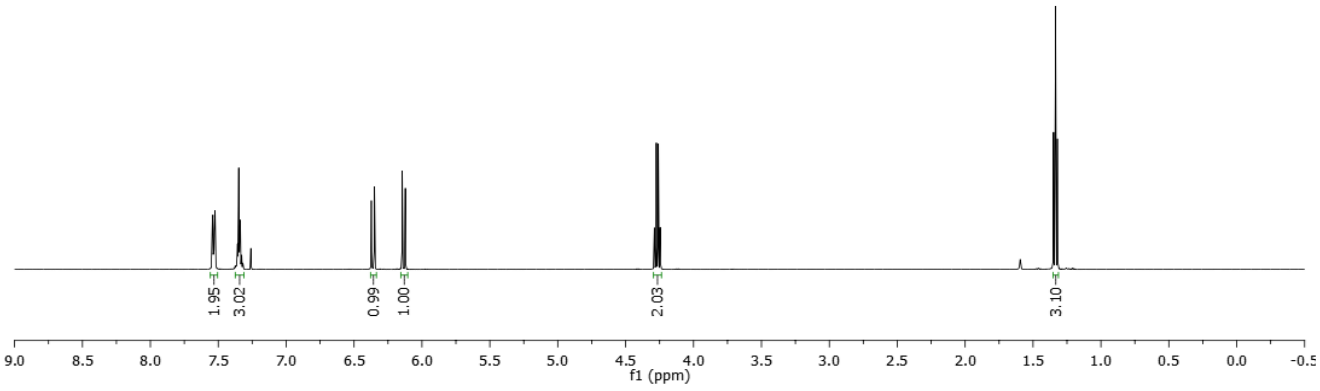
VII. ^{1}H NMR & ^{13}C NMR spectra

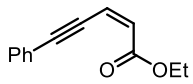
Ethyl-5-phenylpent-2-en-4-ynoate [(Z)-S8a]:



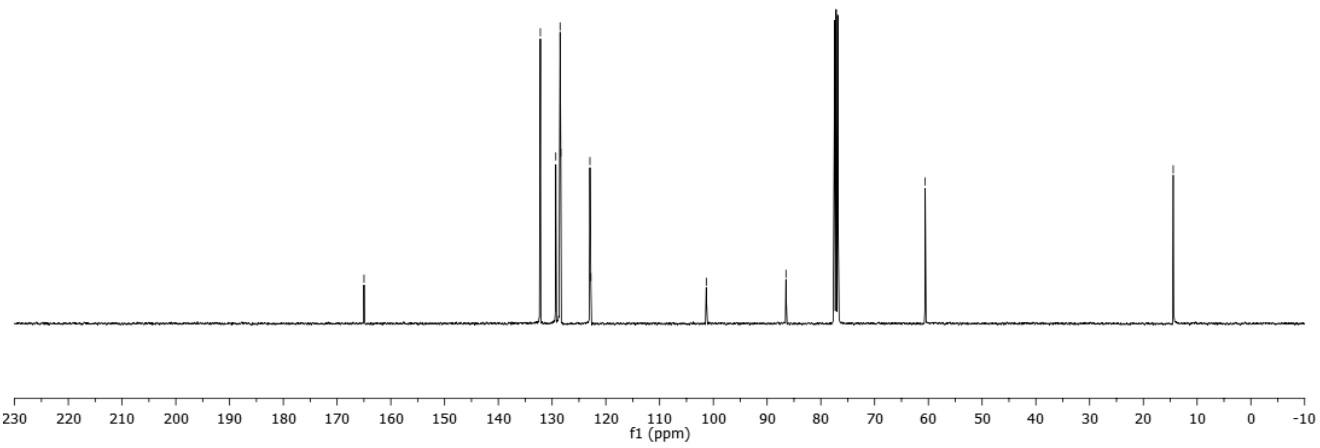


^{1}H NMR (500 MHz, $CDCl_3$)

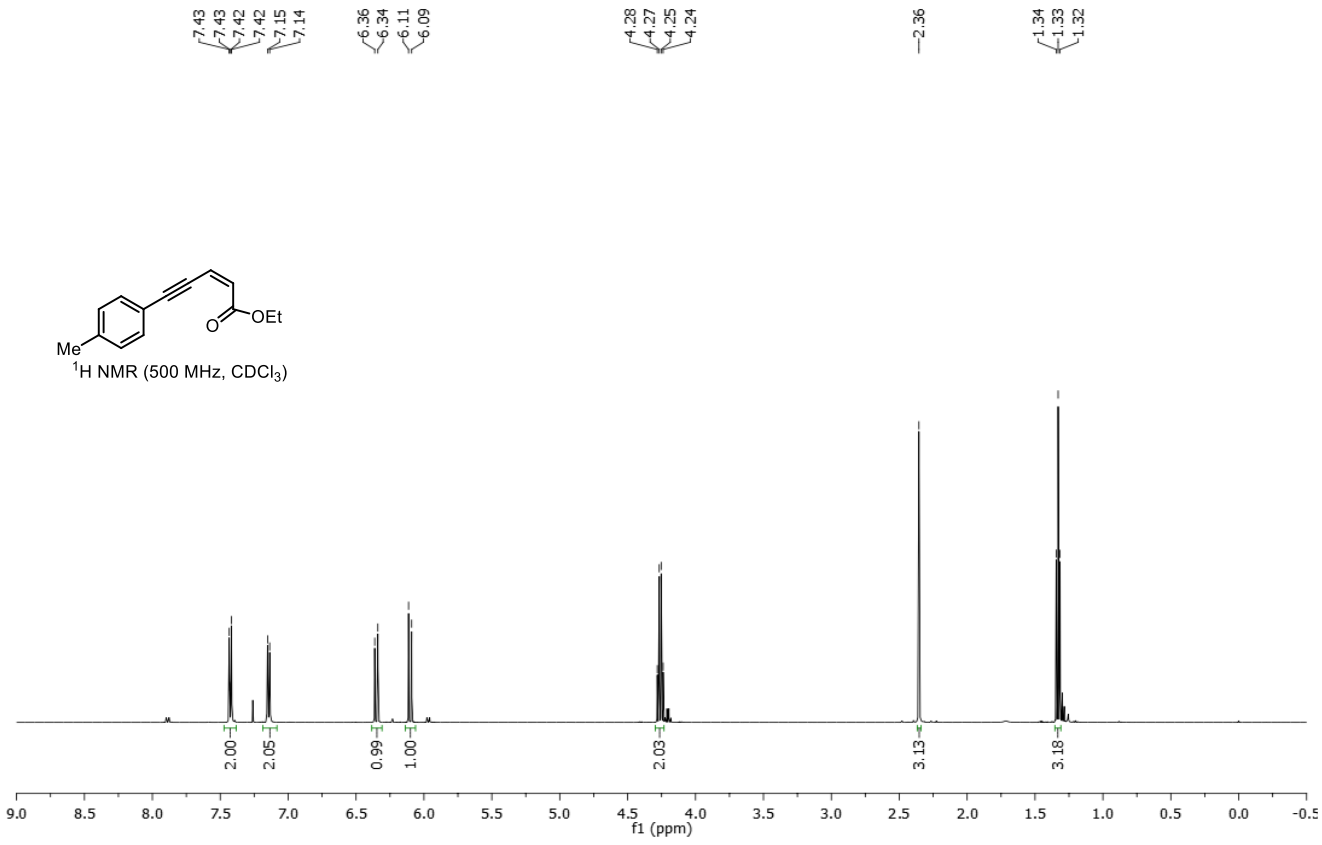


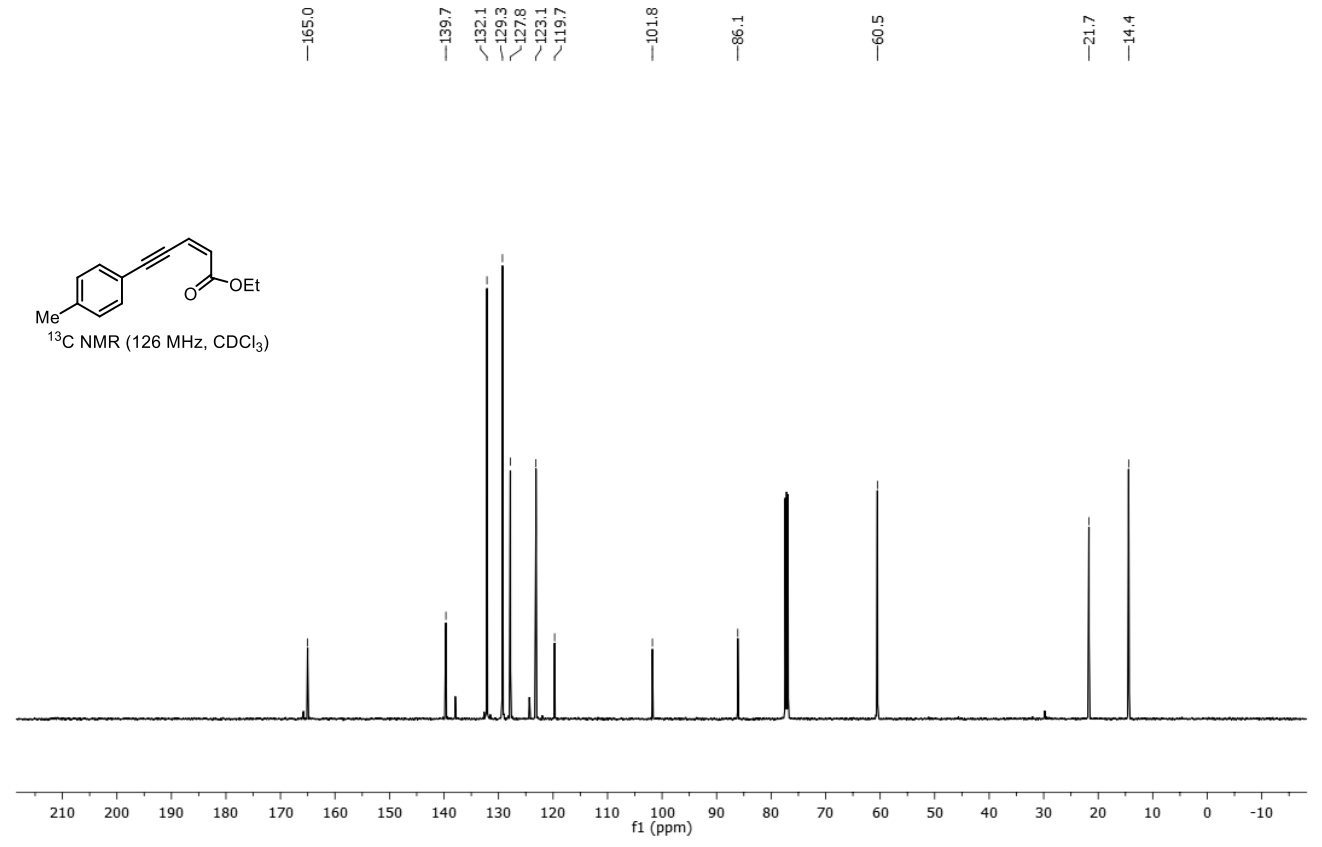


^{13}C NMR (101 MHz, $CDCl_3$)

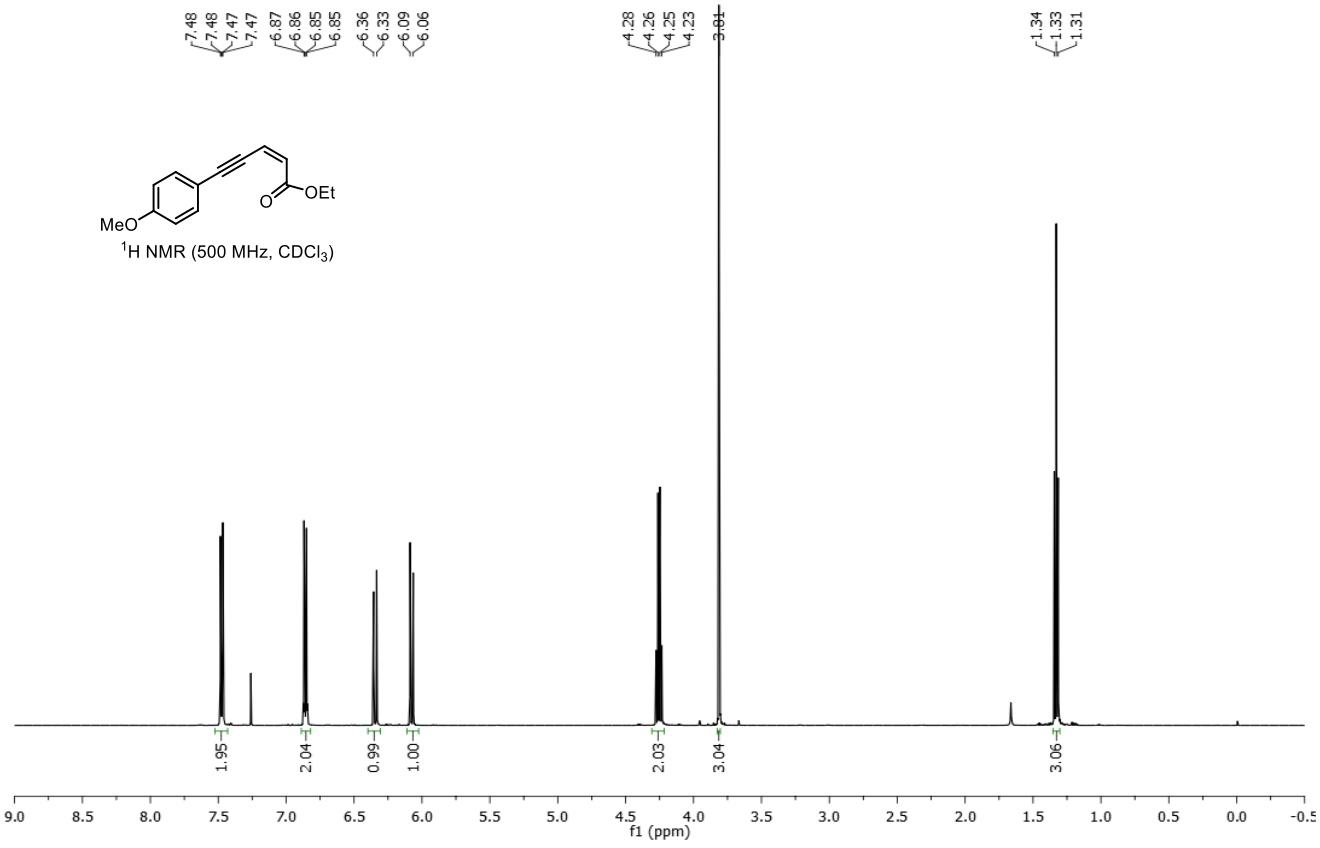


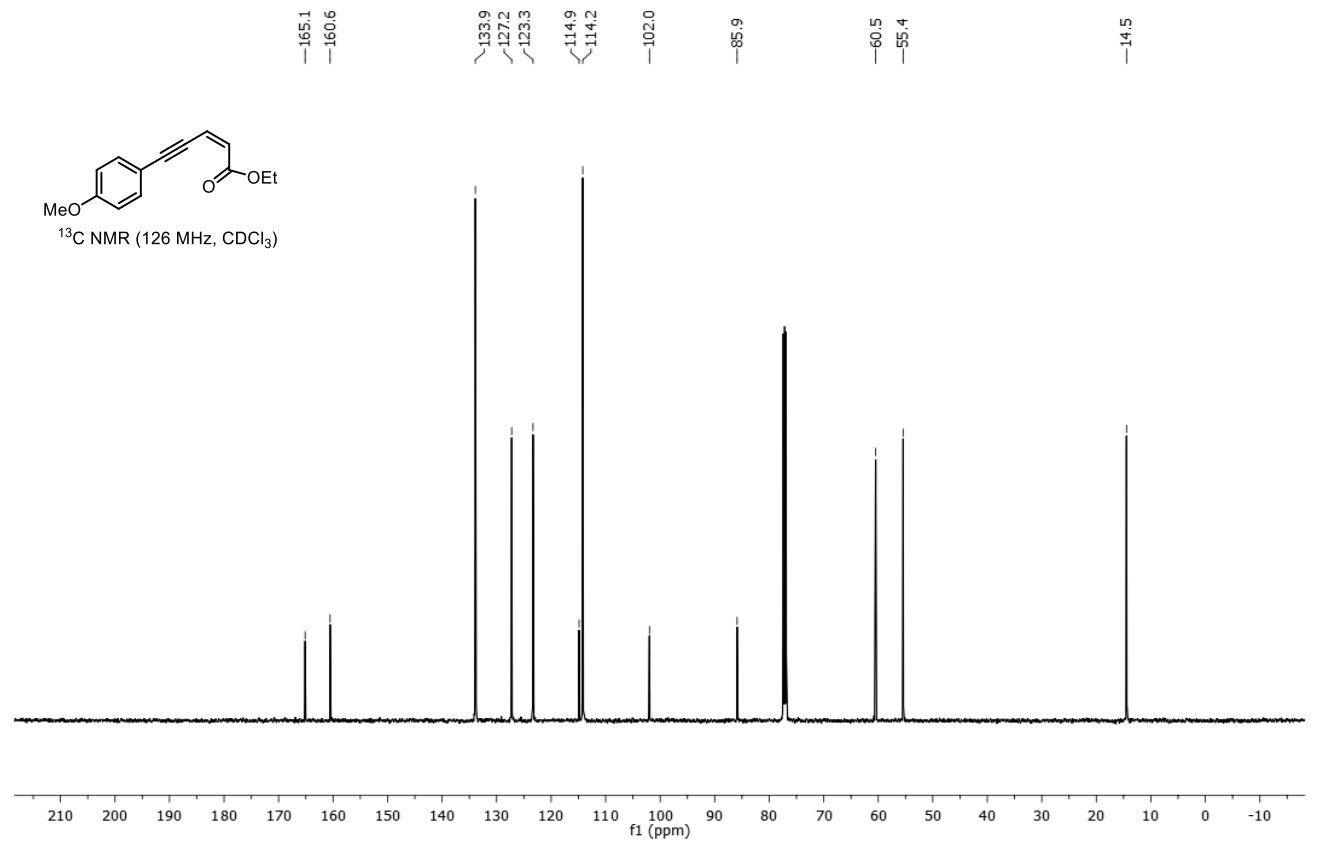
Ethyl (*Z*)-5-(*p*-tolyl)pent-2-en-4-ynoate [(*Z*)-**S8b**]:



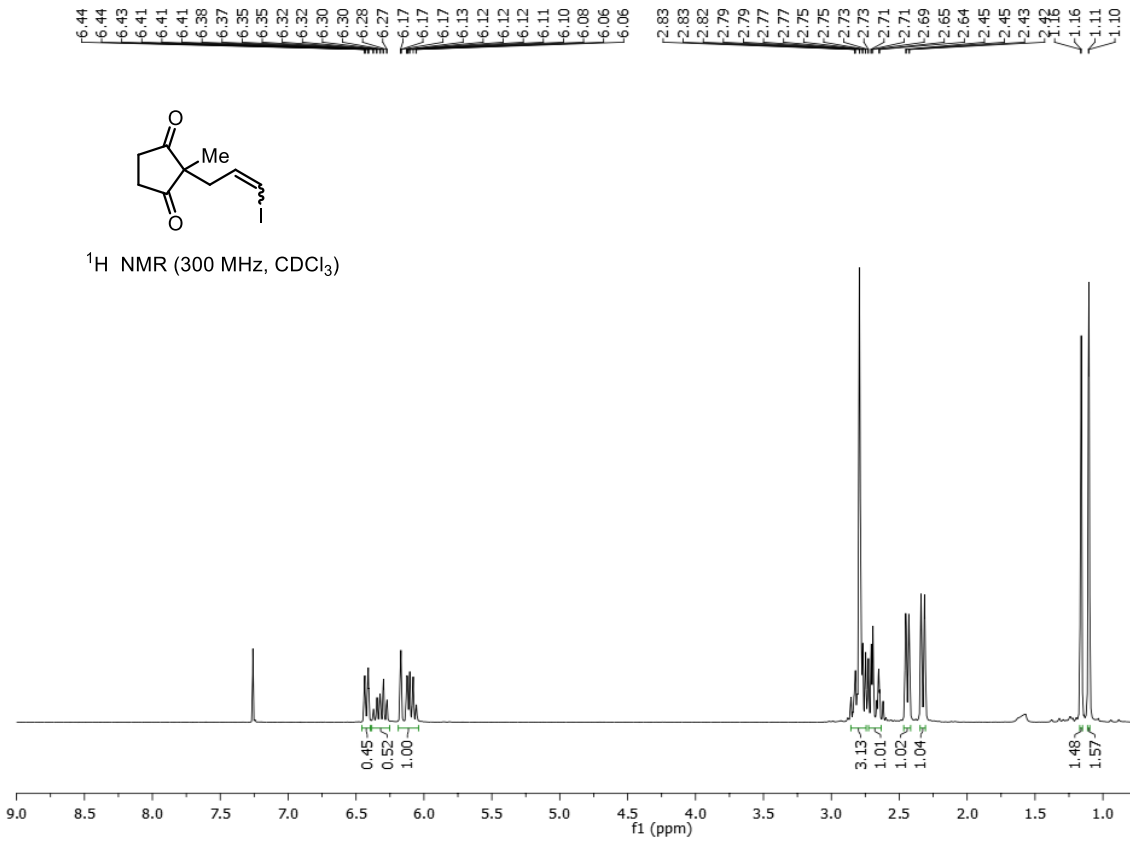


Ethyl (*Z*)-5-(4-methoxyphenyl)pent-2-en-4-ynoate [(*Z*)-**S8c**]:

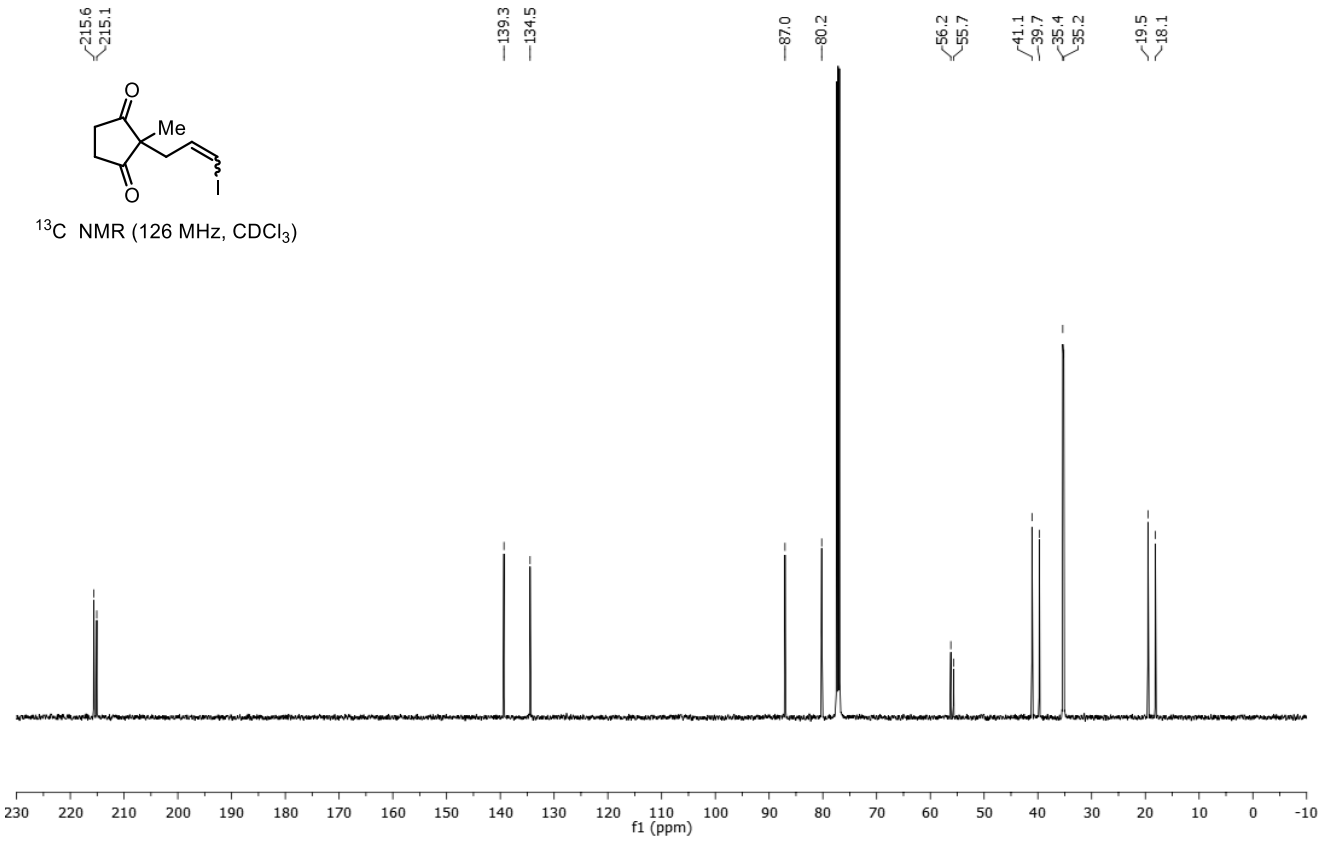




2-(3-Iodoallyl)-2-methylcyclopentane-1,3-dione (S13):

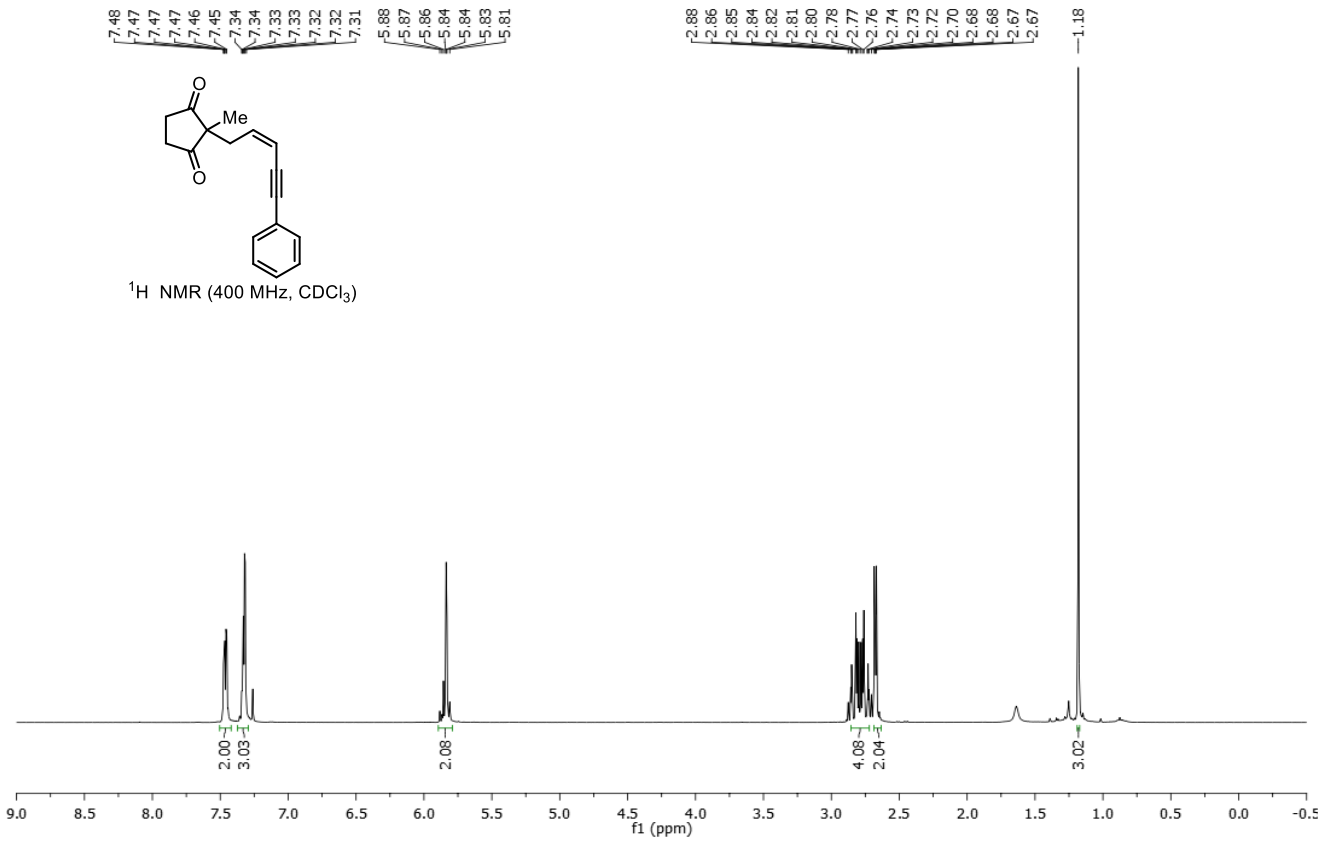


^{1}H NMR (300 MHz, $CDCl_3$)

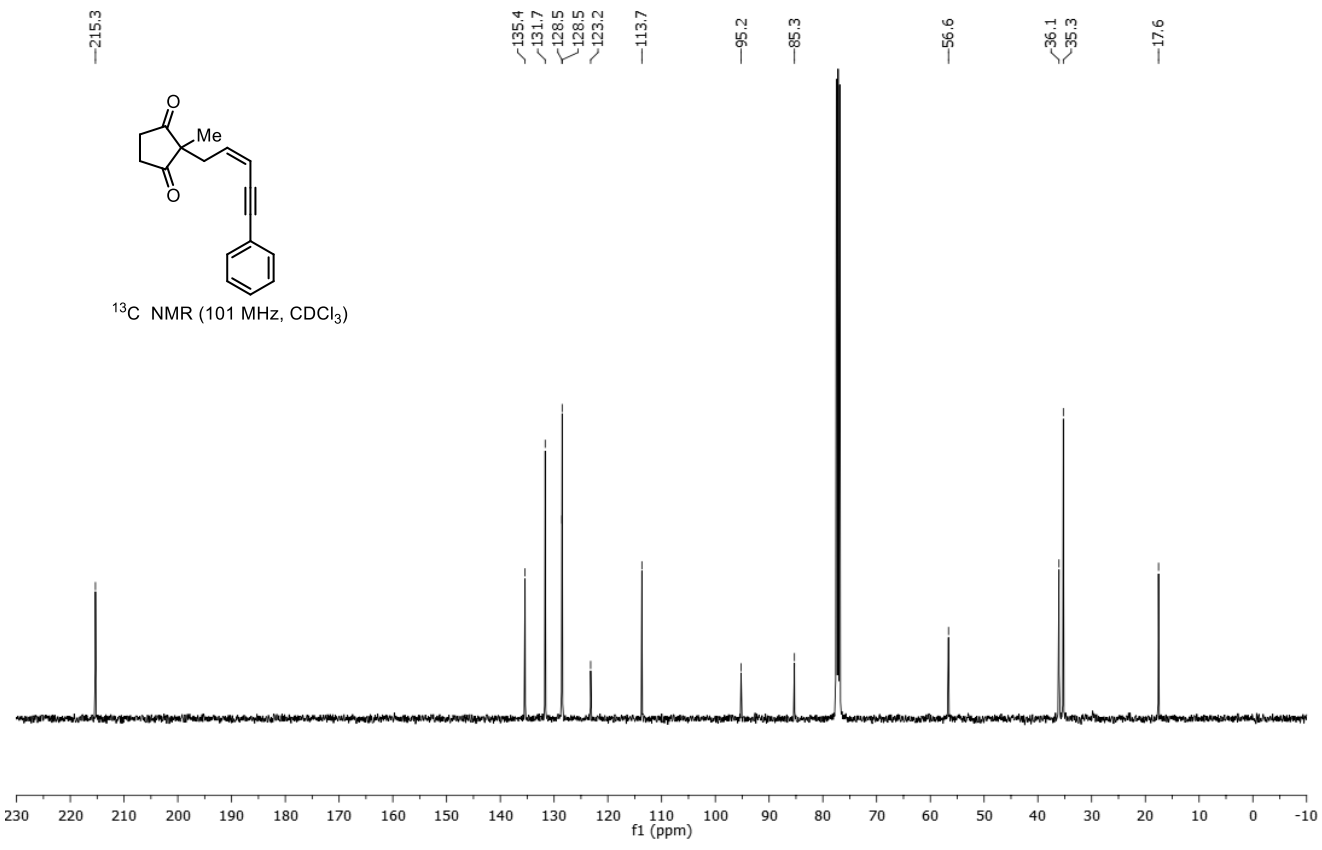


^{13}C NMR (126 MHz, $CDCl_3$)

(*Z*)-2-Methyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1a):

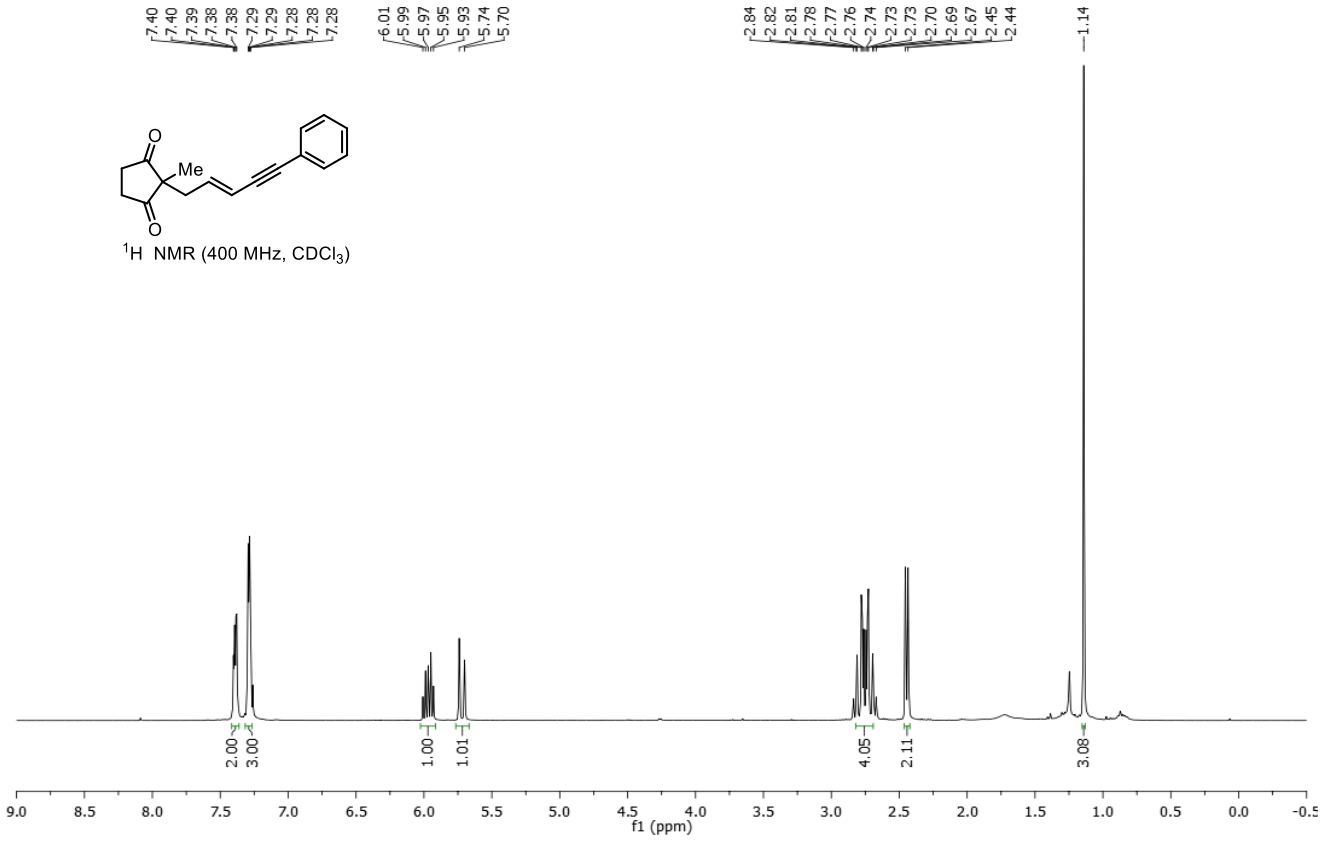


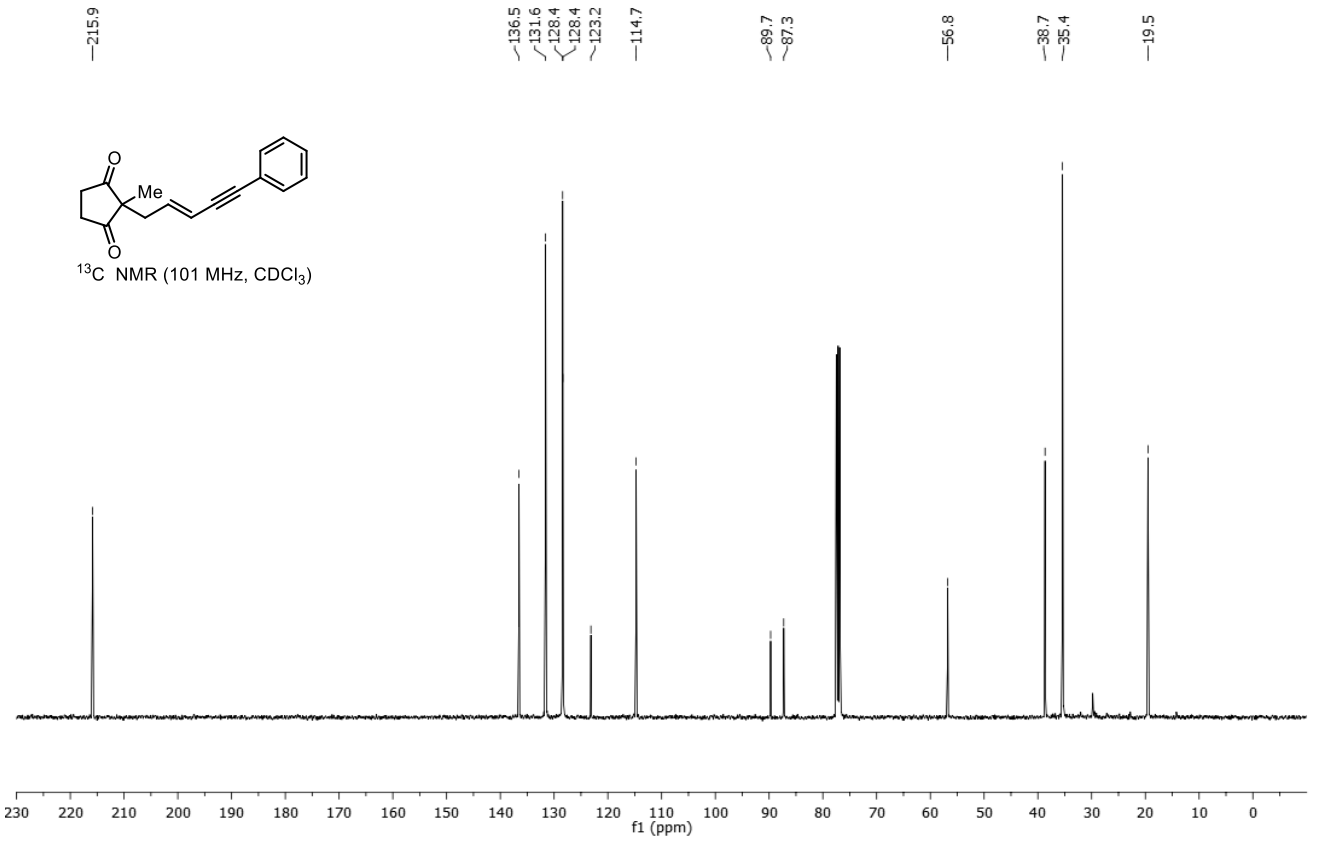
^{1}H NMR (400 MHz, $CDCl_3$)



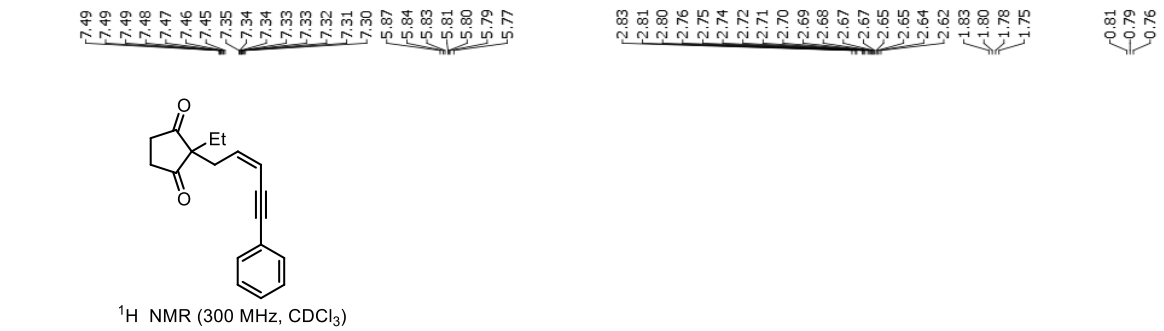
^{13}C NMR (101 MHz, $CDCl_3$)

(*E*)-2-Methyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione [(*E*)-(1a)]:

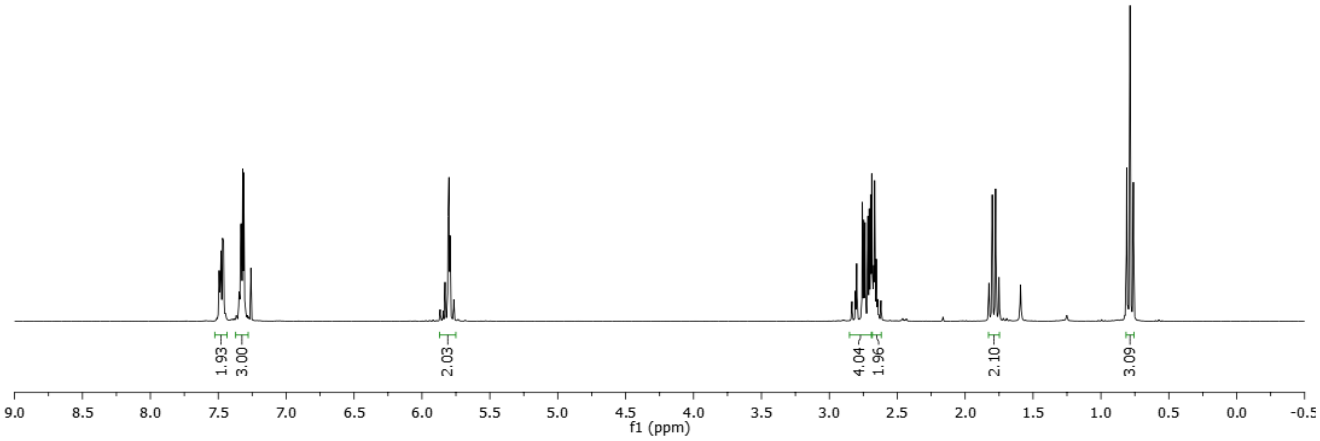


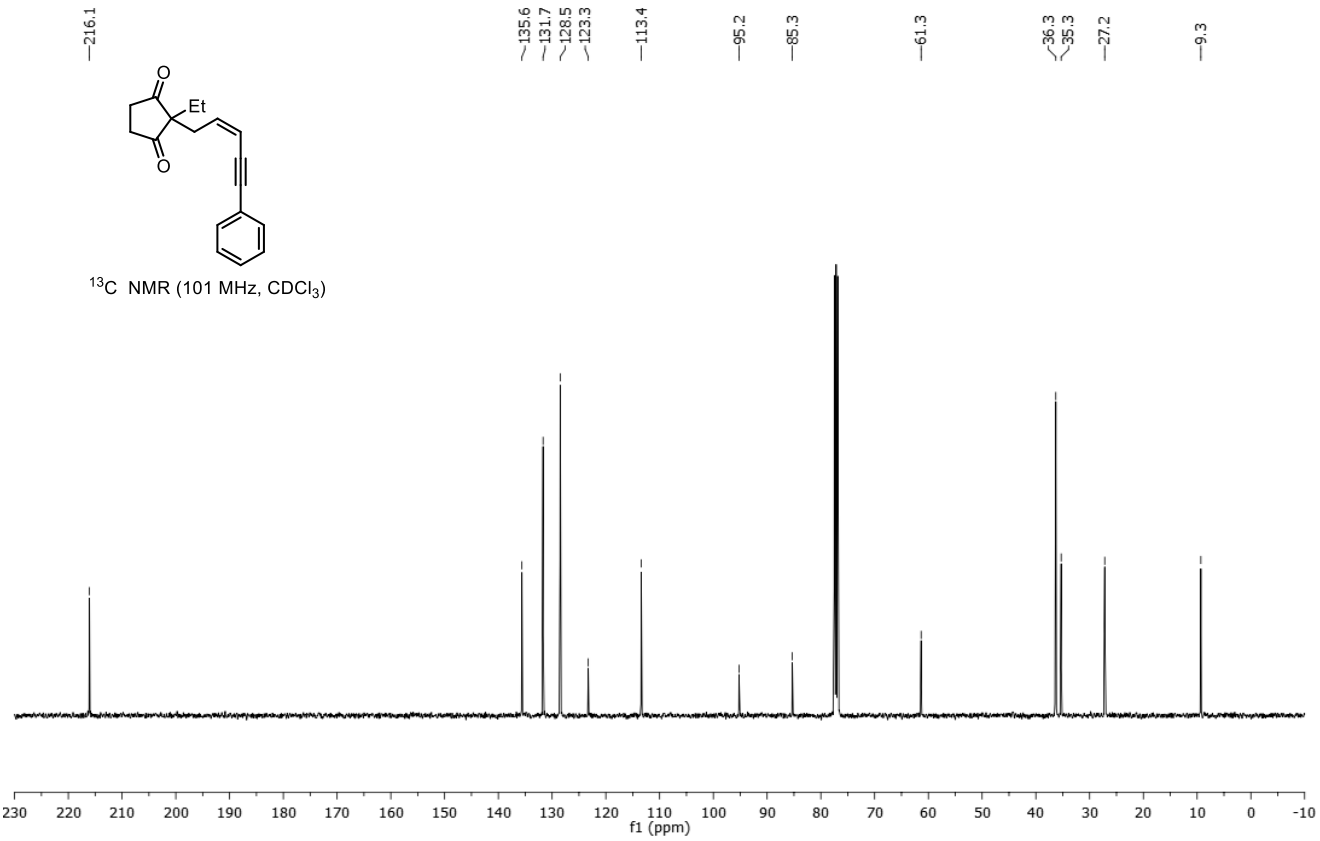


(*Z*)-2-Ethyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1b):



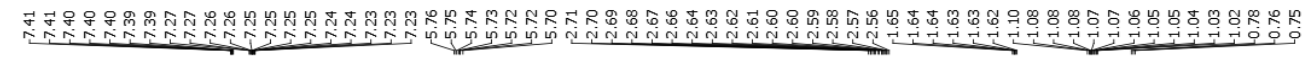
^{1}H NMR (300 MHz, $CDCl_3$)

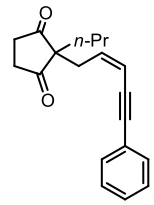




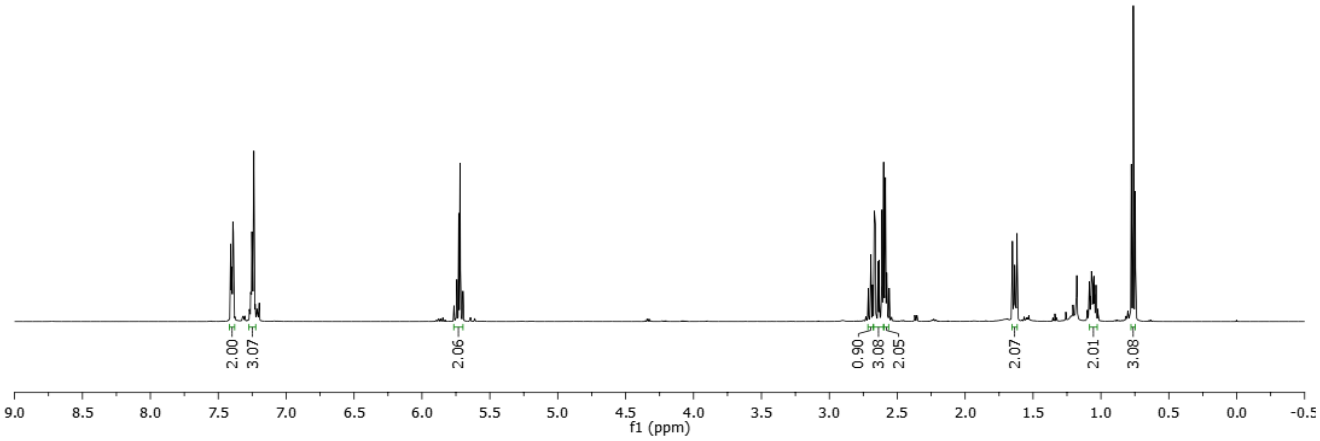
^{13}C NMR (101 MHz, $CDCl_3$)

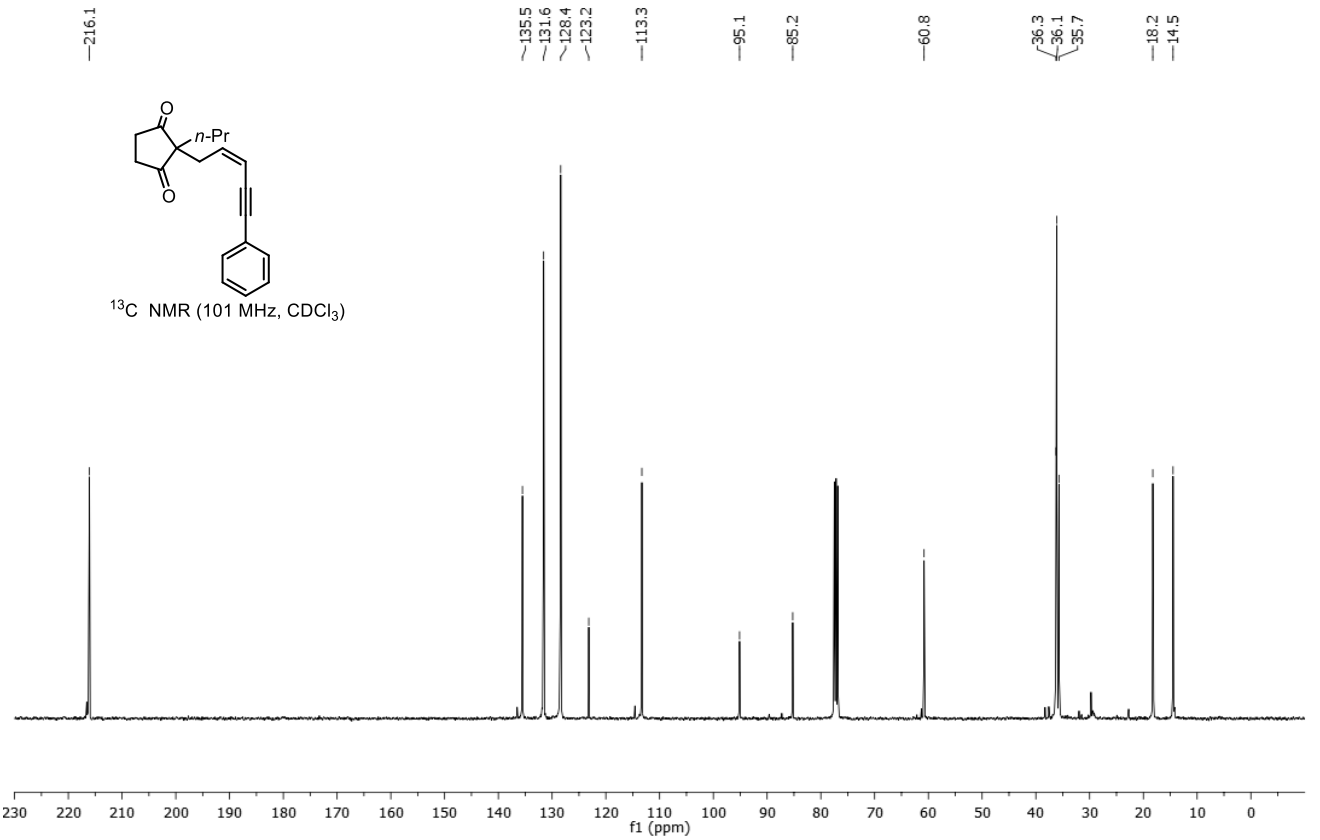
(*Z*)-2-(5-Phenylpent-2-en-4-yn-1-yl)-2-propylcyclopentane-1,3-dione (1c):





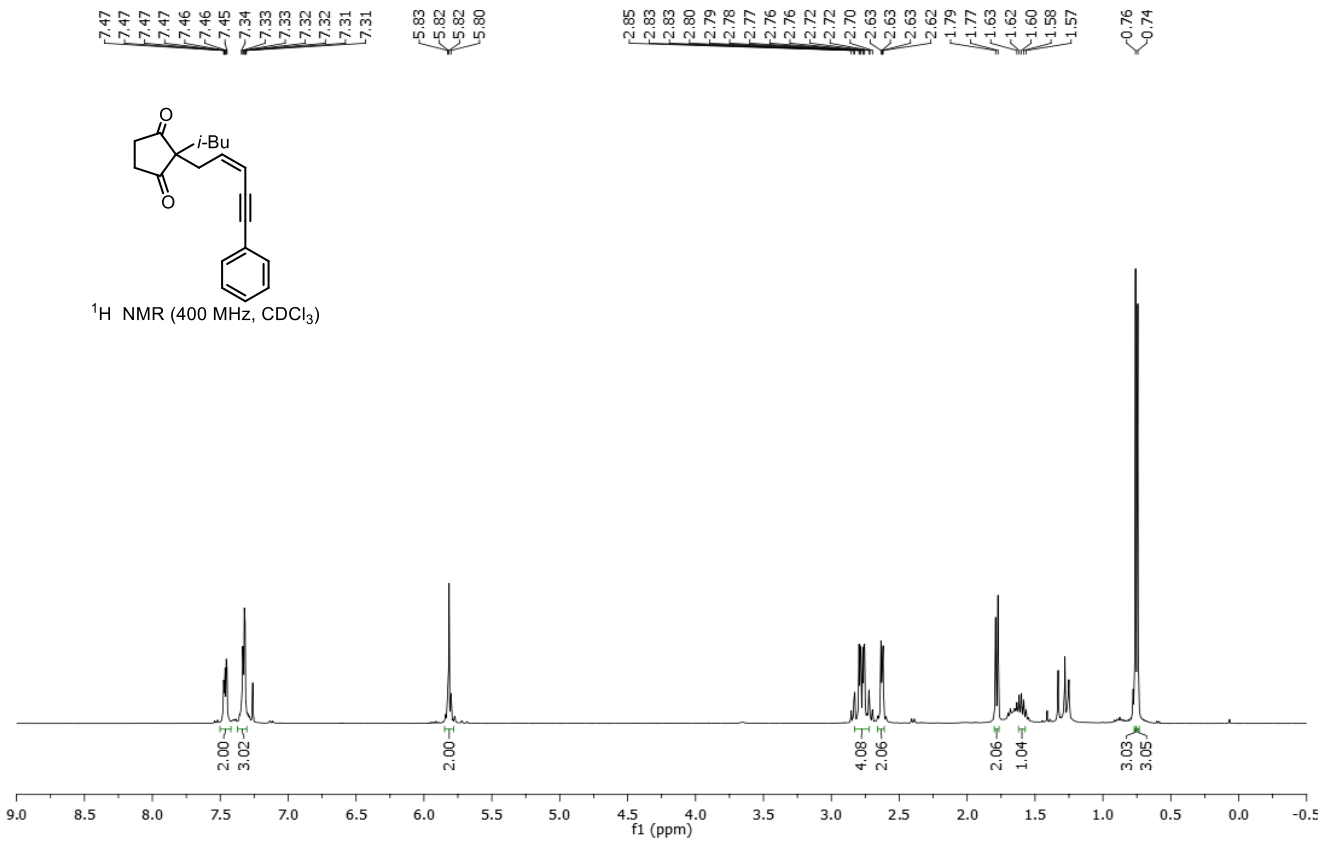
^{1}H NMR (500 MHz, $CDCl_3$)

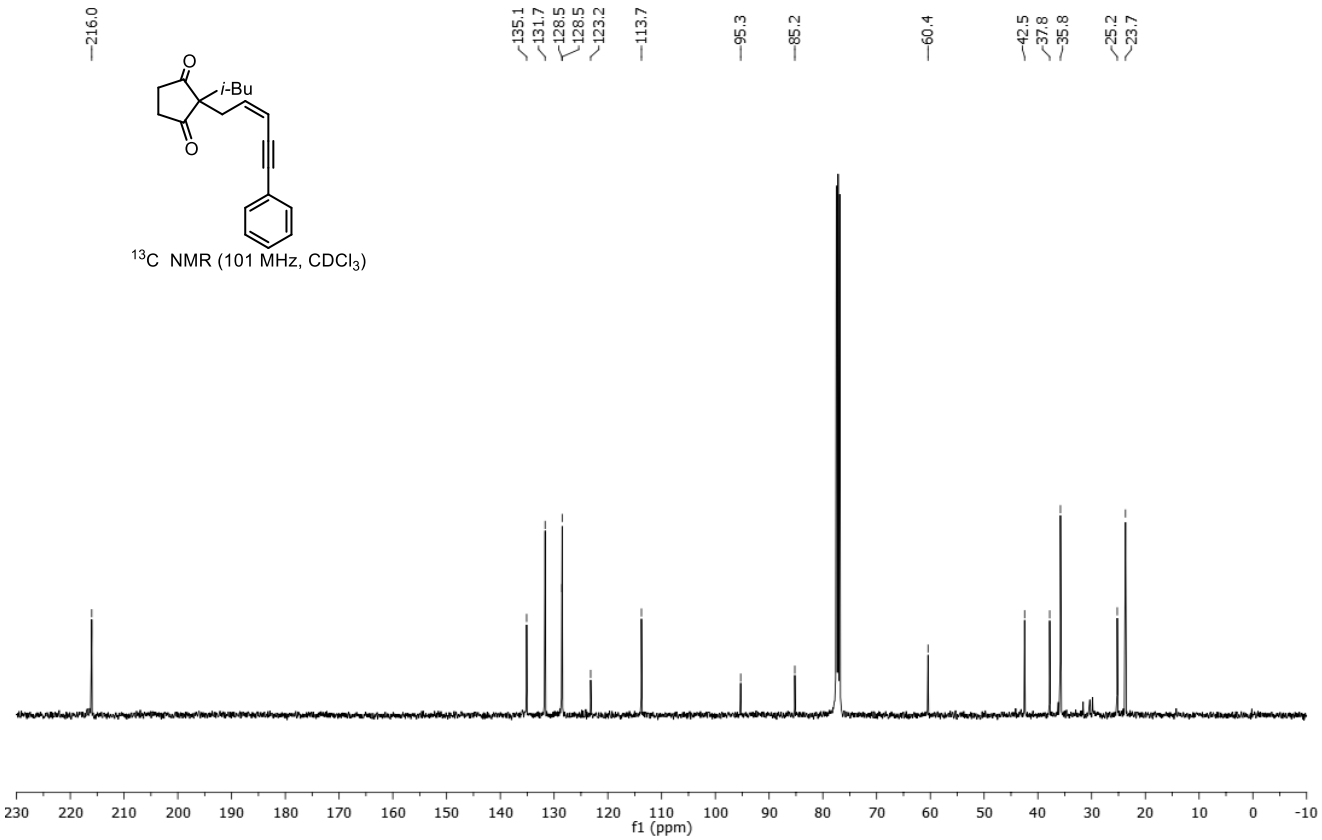




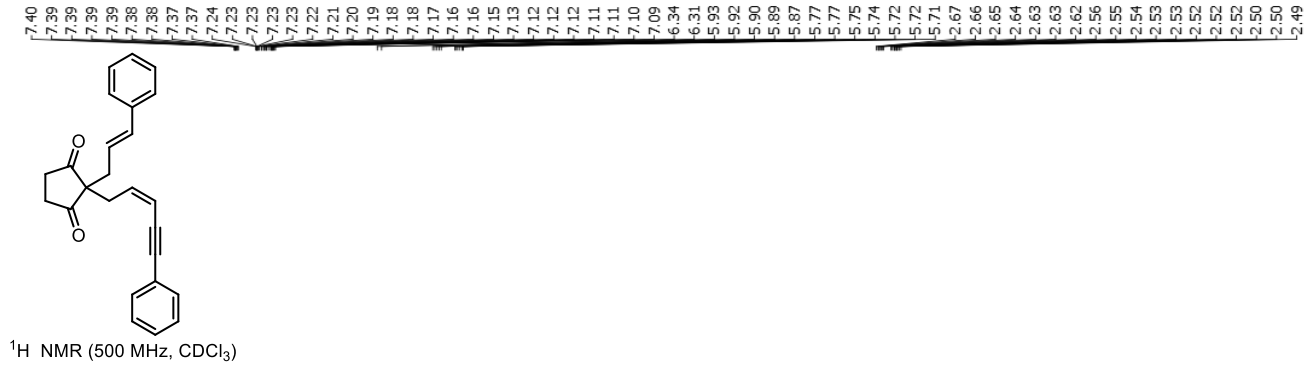
^{13}C NMR (101 MHz, $CDCl_3$)

(*Z*)-2-Isobutyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1d):

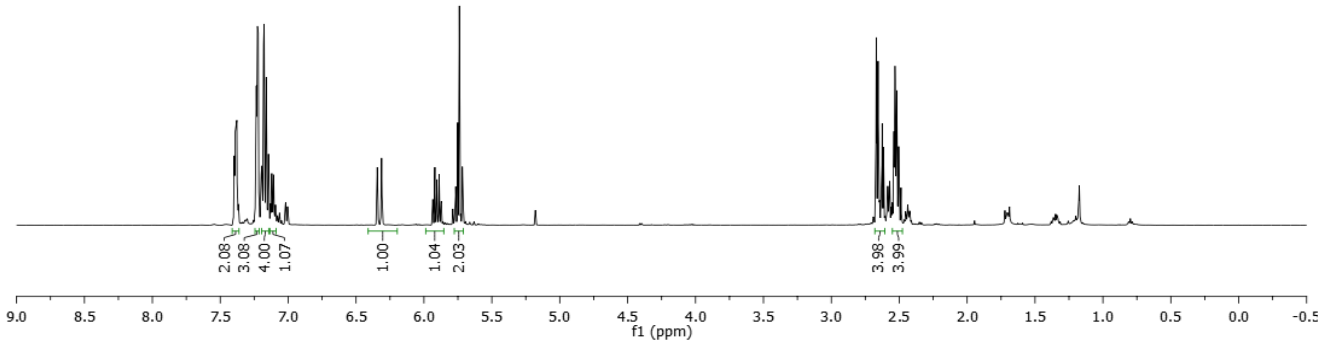


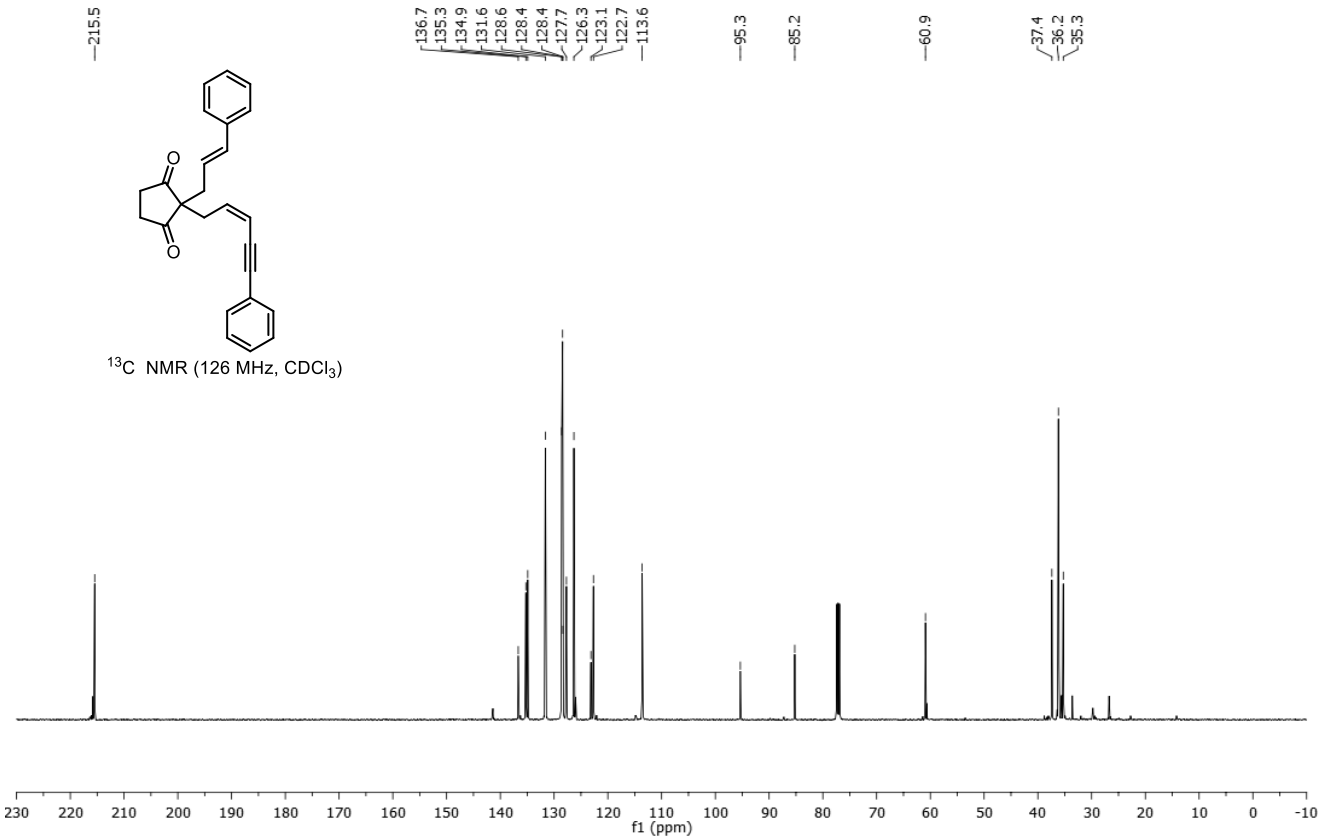


2-Cinnamyl-2-((Z)-5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1e):



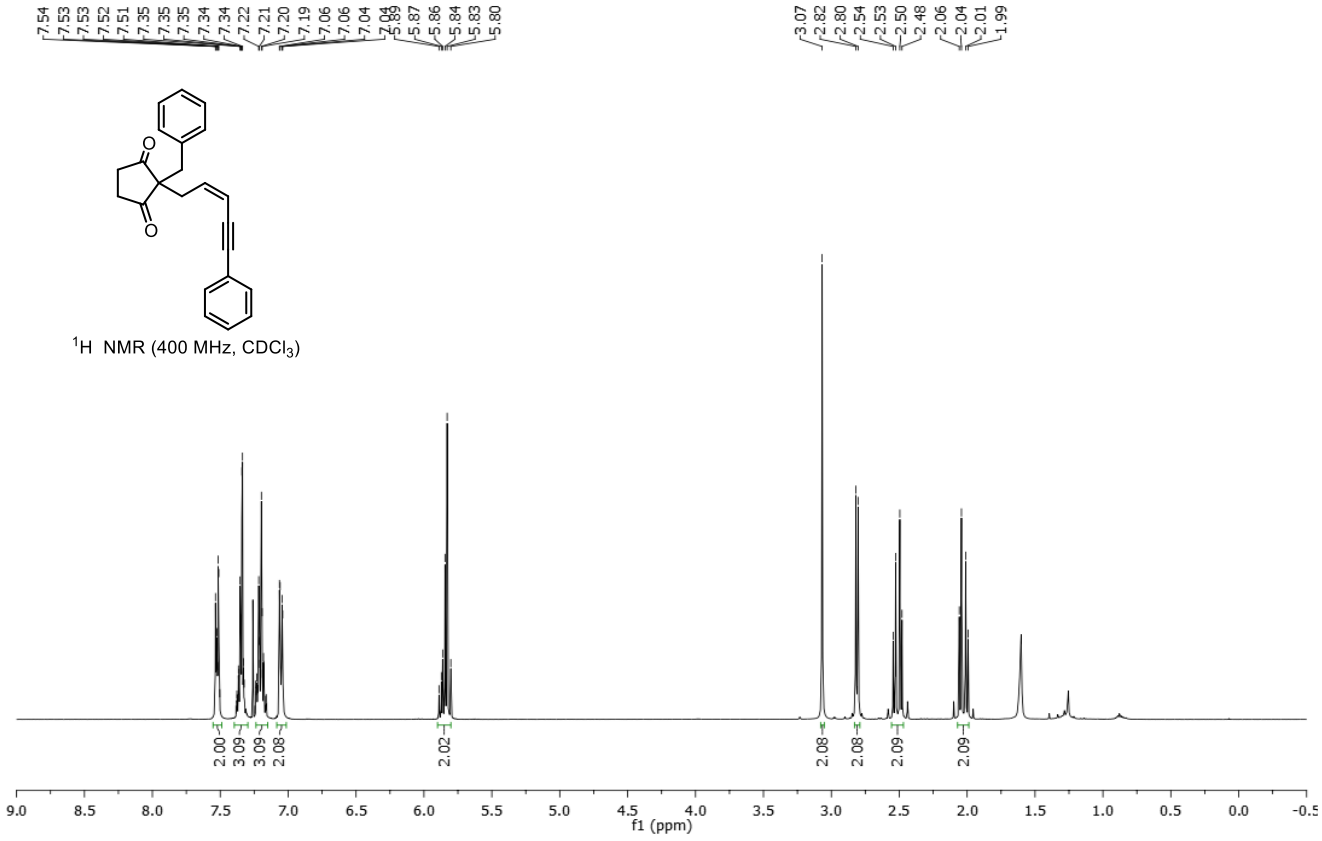
^{1}H NMR (500 MHz, $CDCl_3$)

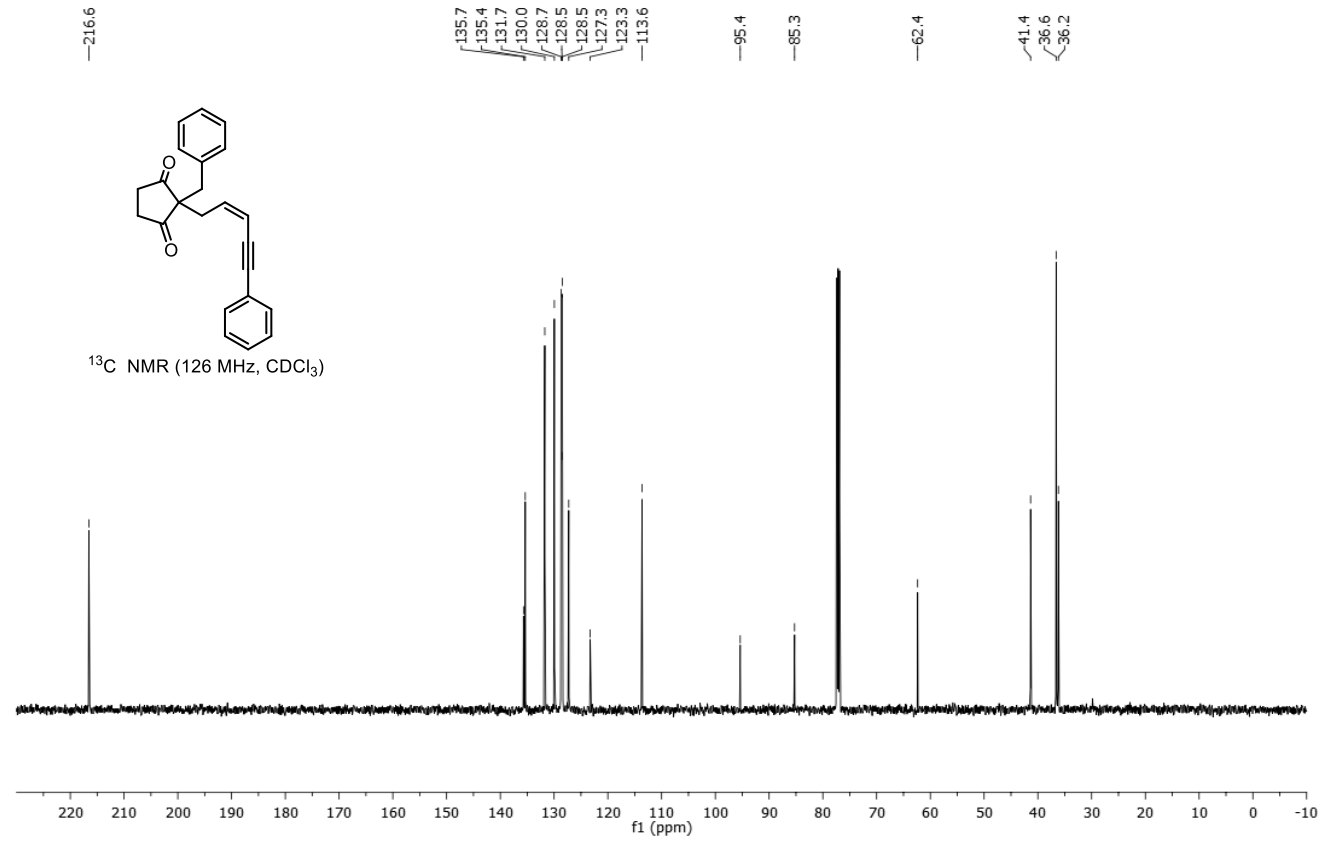




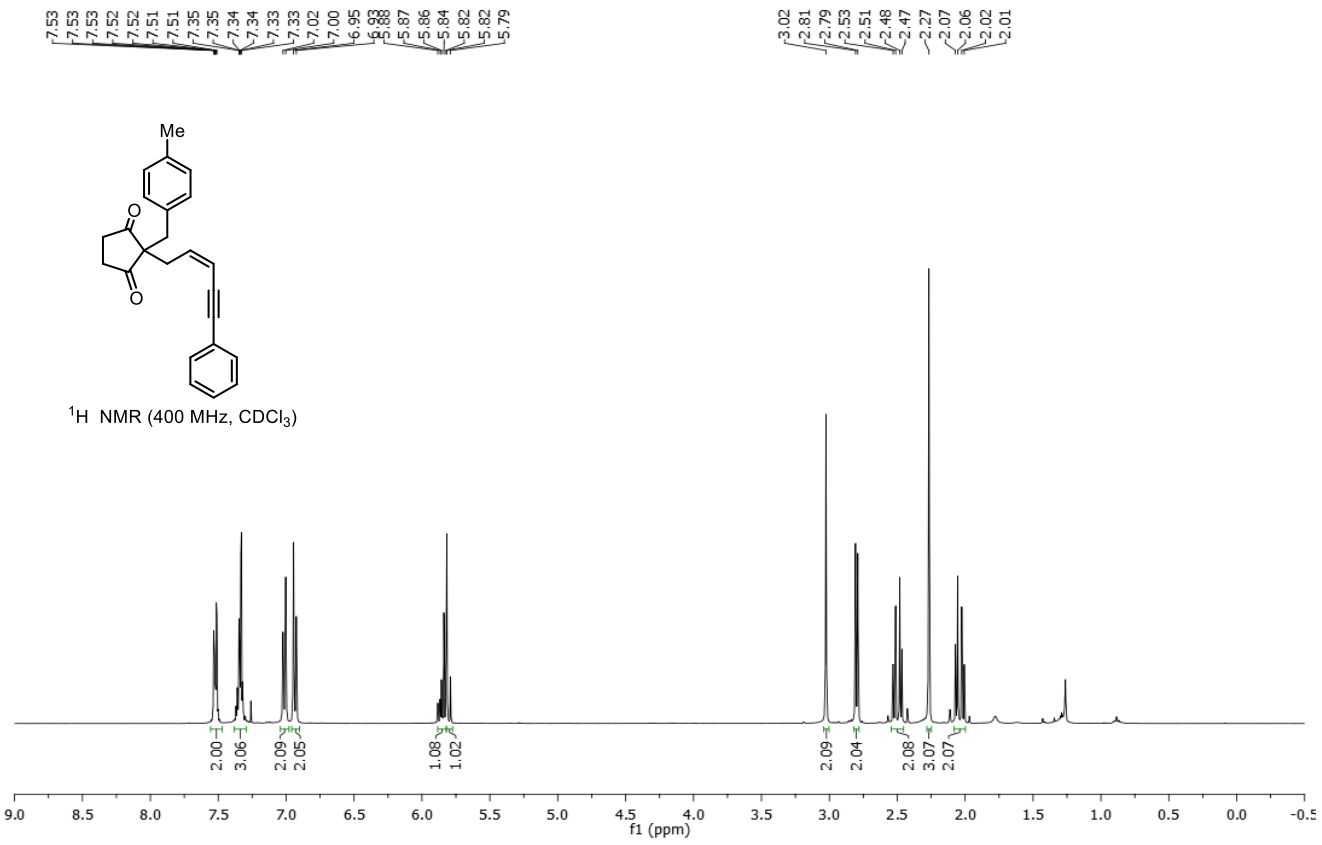
^{13}C NMR (126 MHz, $CDCl_3$)

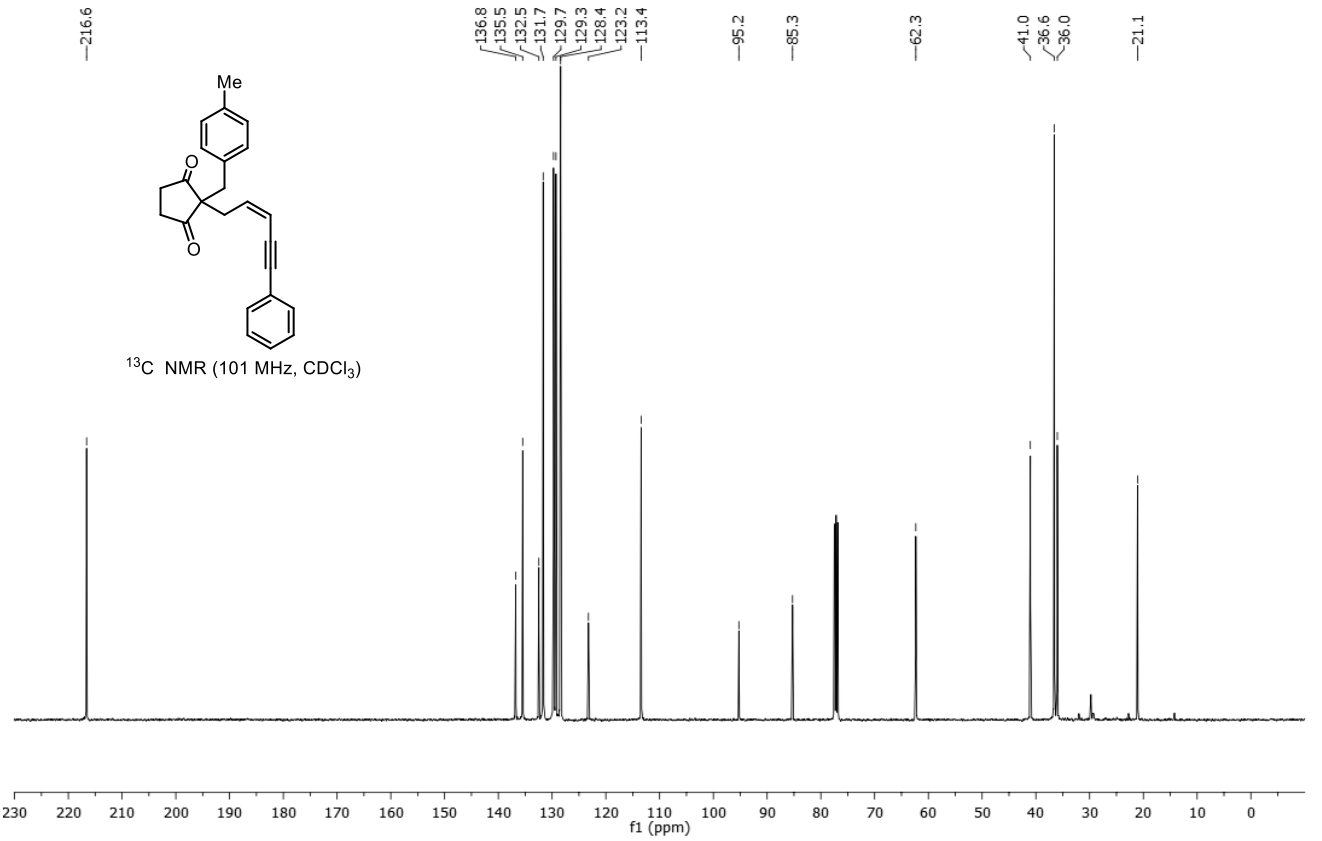
(*Z*)-2-Benzyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1f):



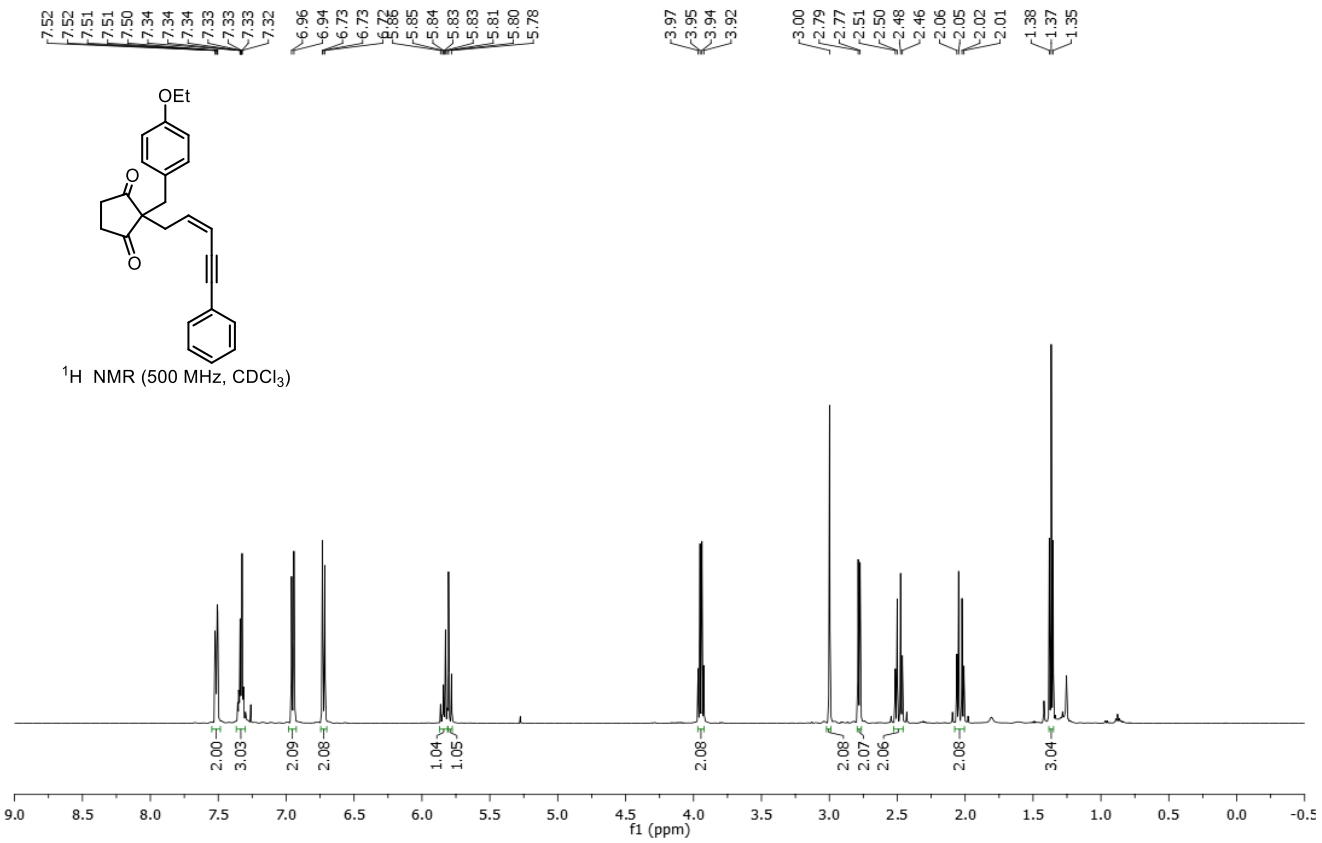


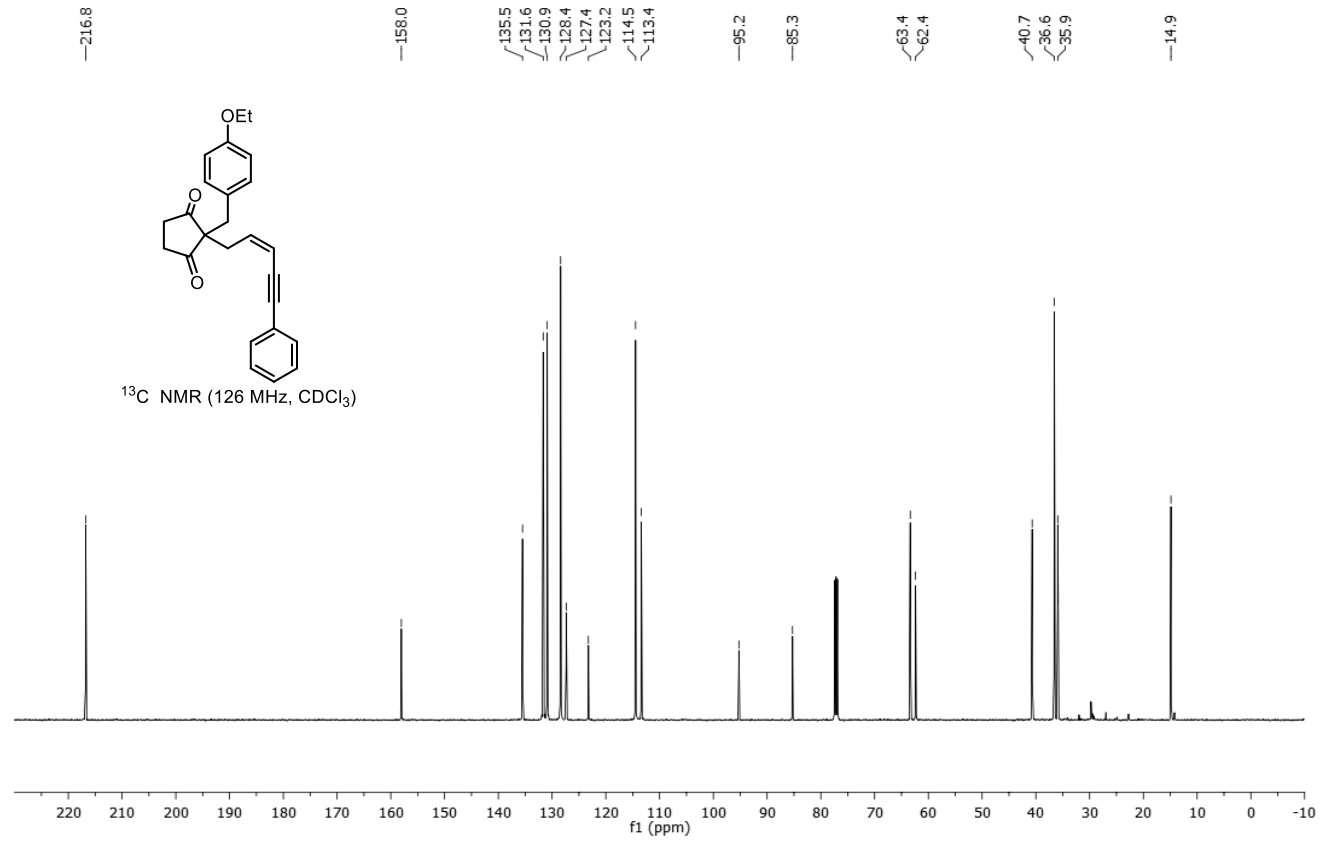
(*Z*)-2-(4-Methylbenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1g):



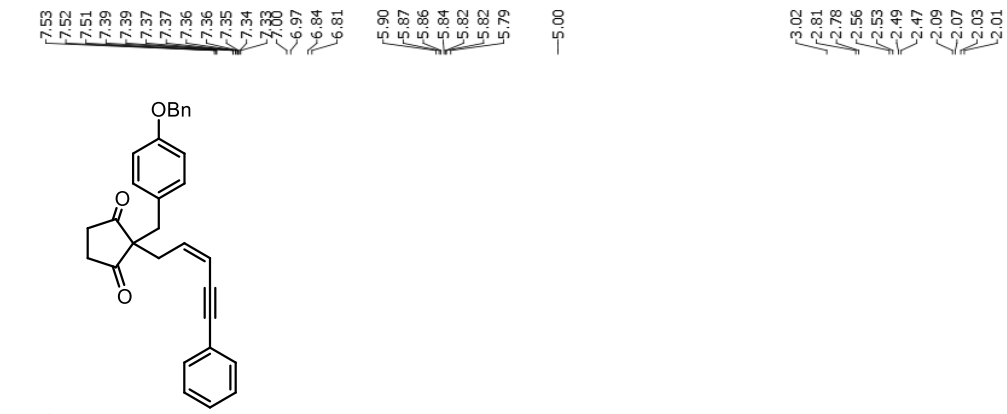


(*Z*)-2-(4-Ethoxybenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1h):

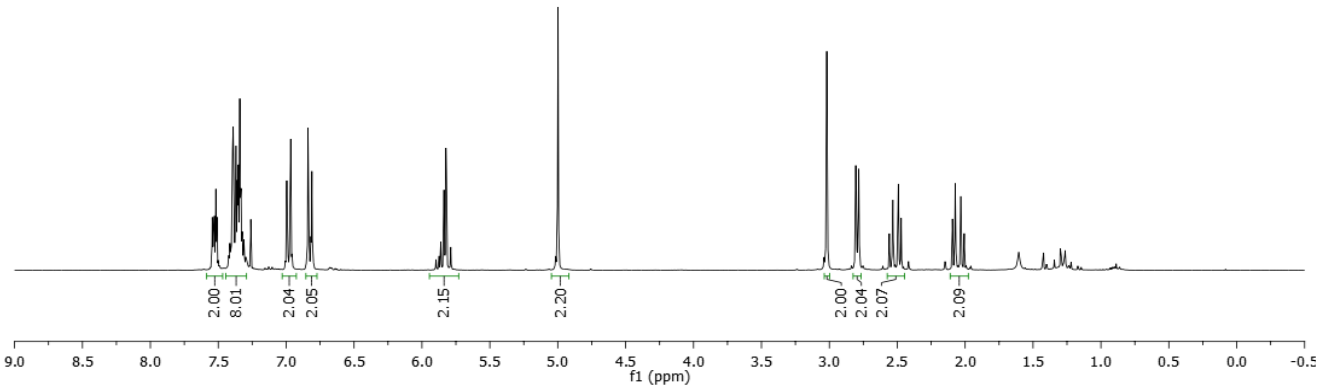


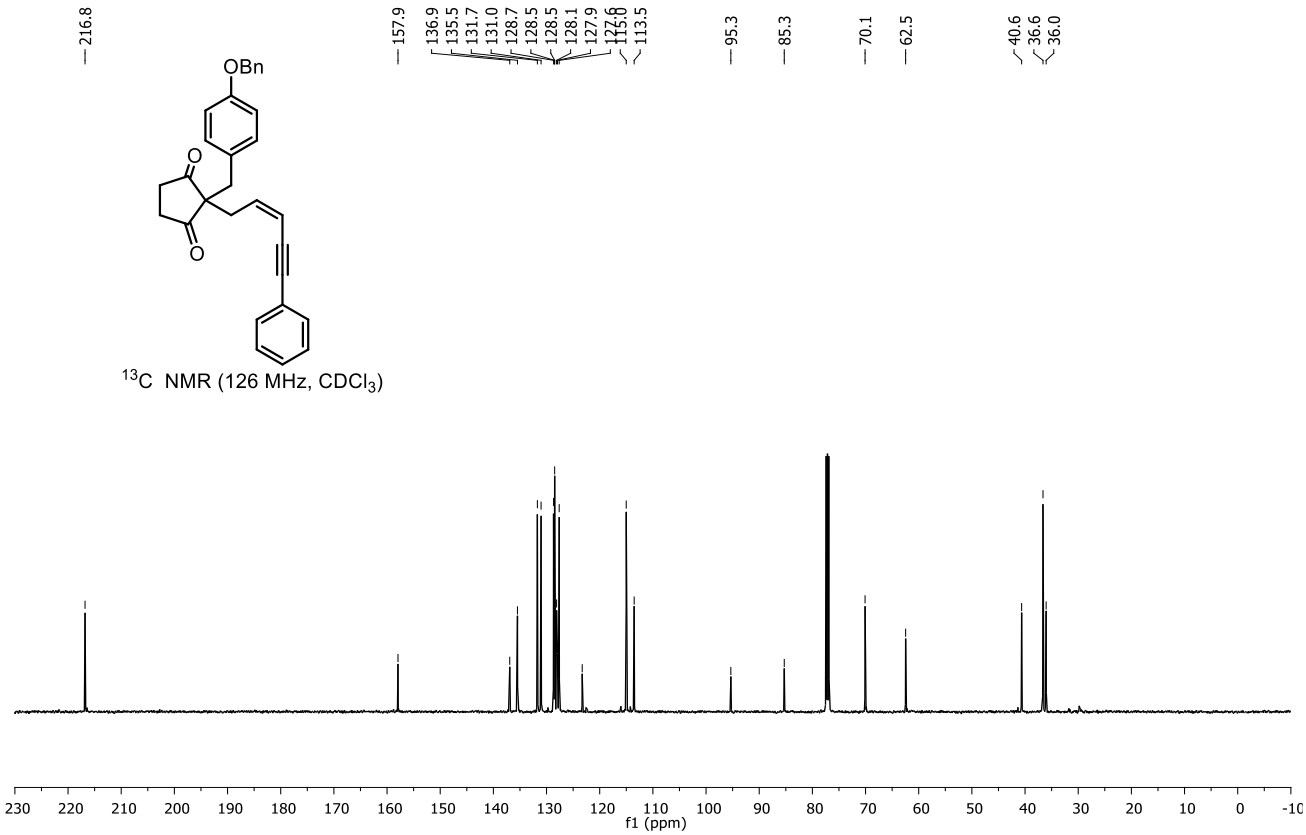


(*Z*)-2-(4-(Benzyloxy)benzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1i):



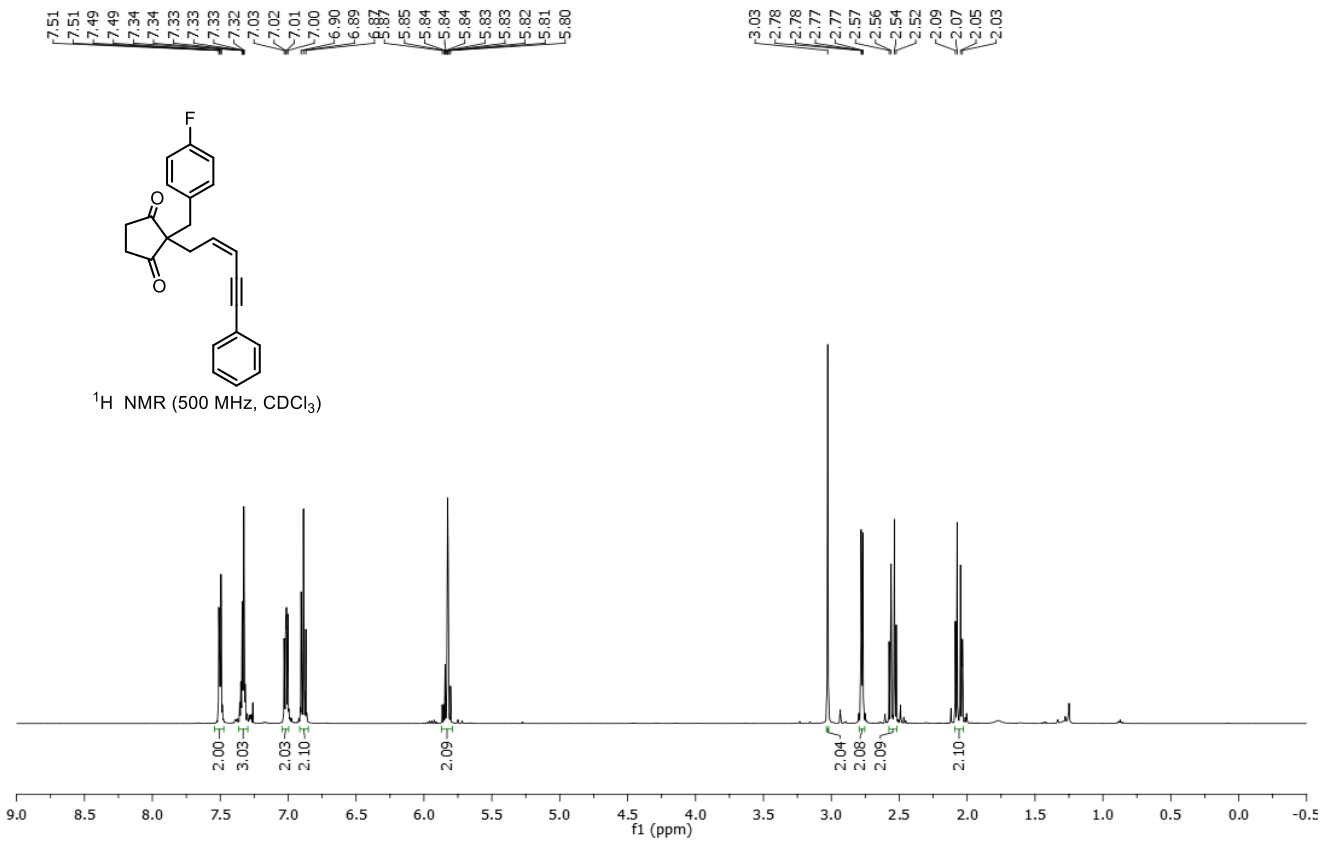
^{1}H NMR (300 MHz, $CDCl_3$)

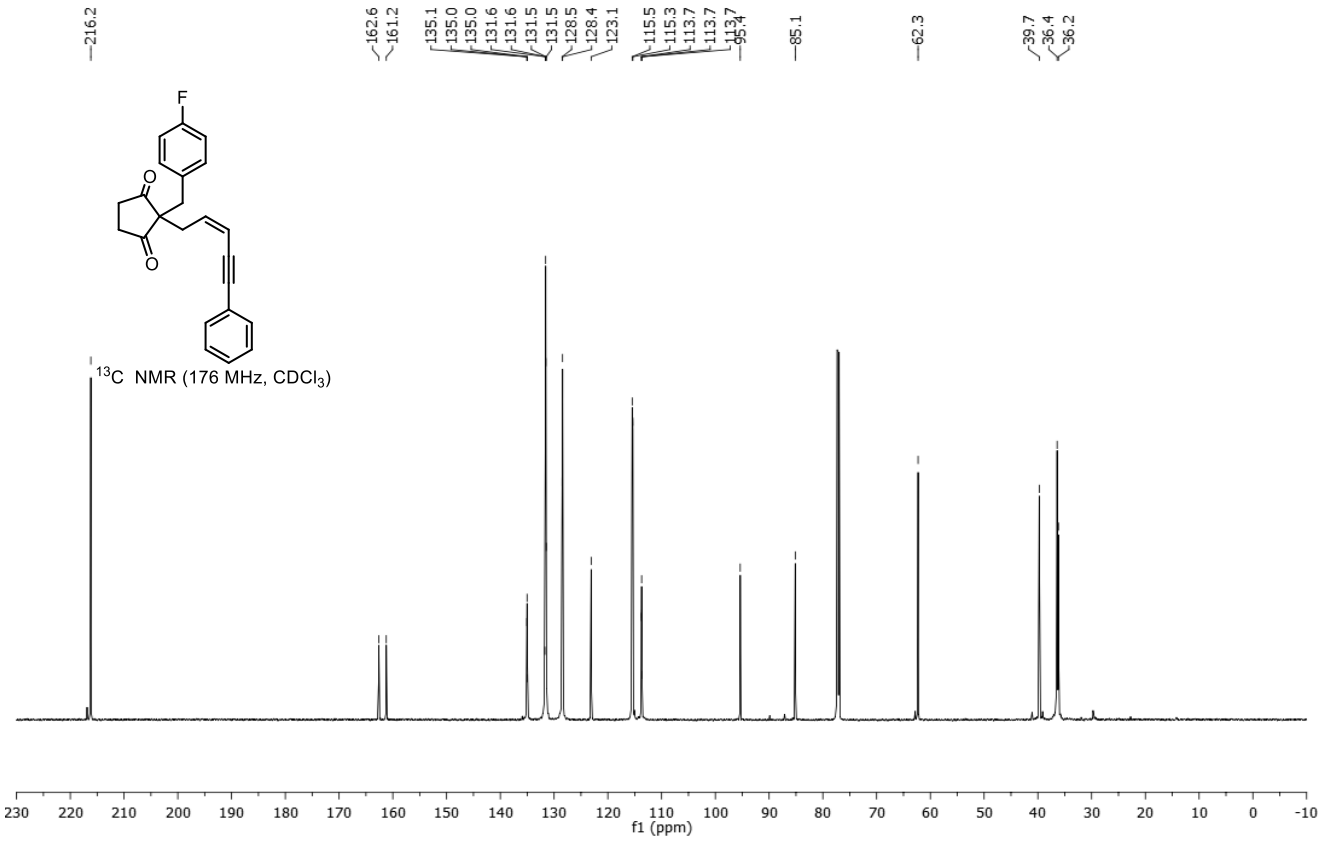


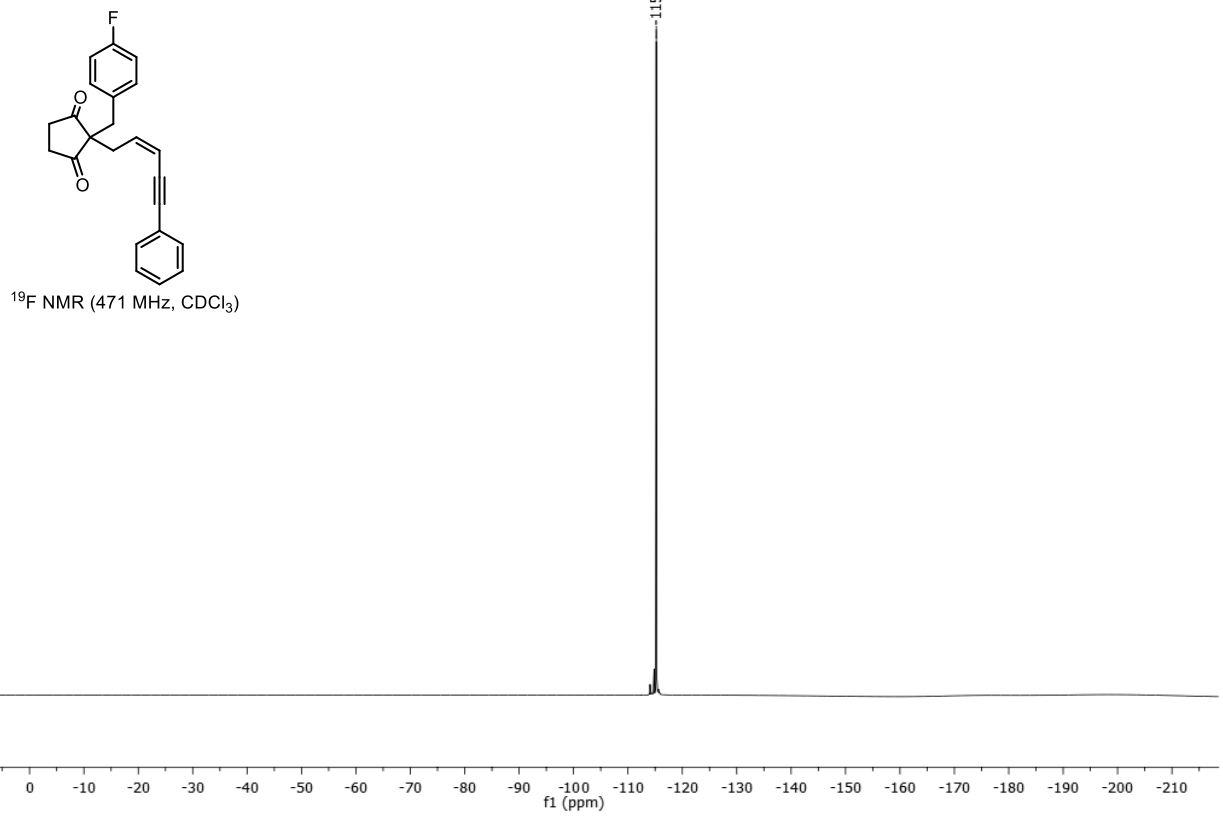


^{13}C NMR (126 MHz, $CDCl_3$)

(*Z*)-(4-Fluorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1j):

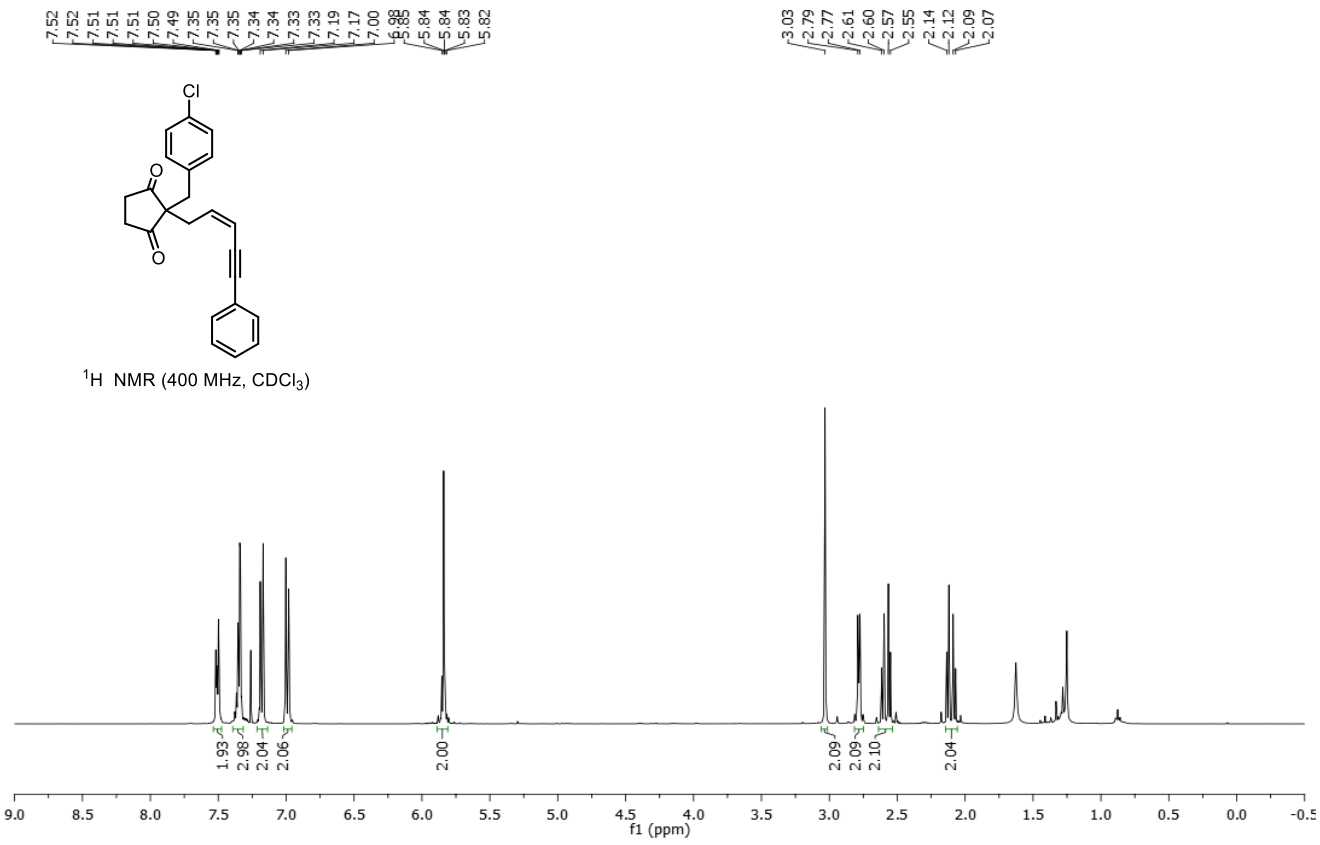


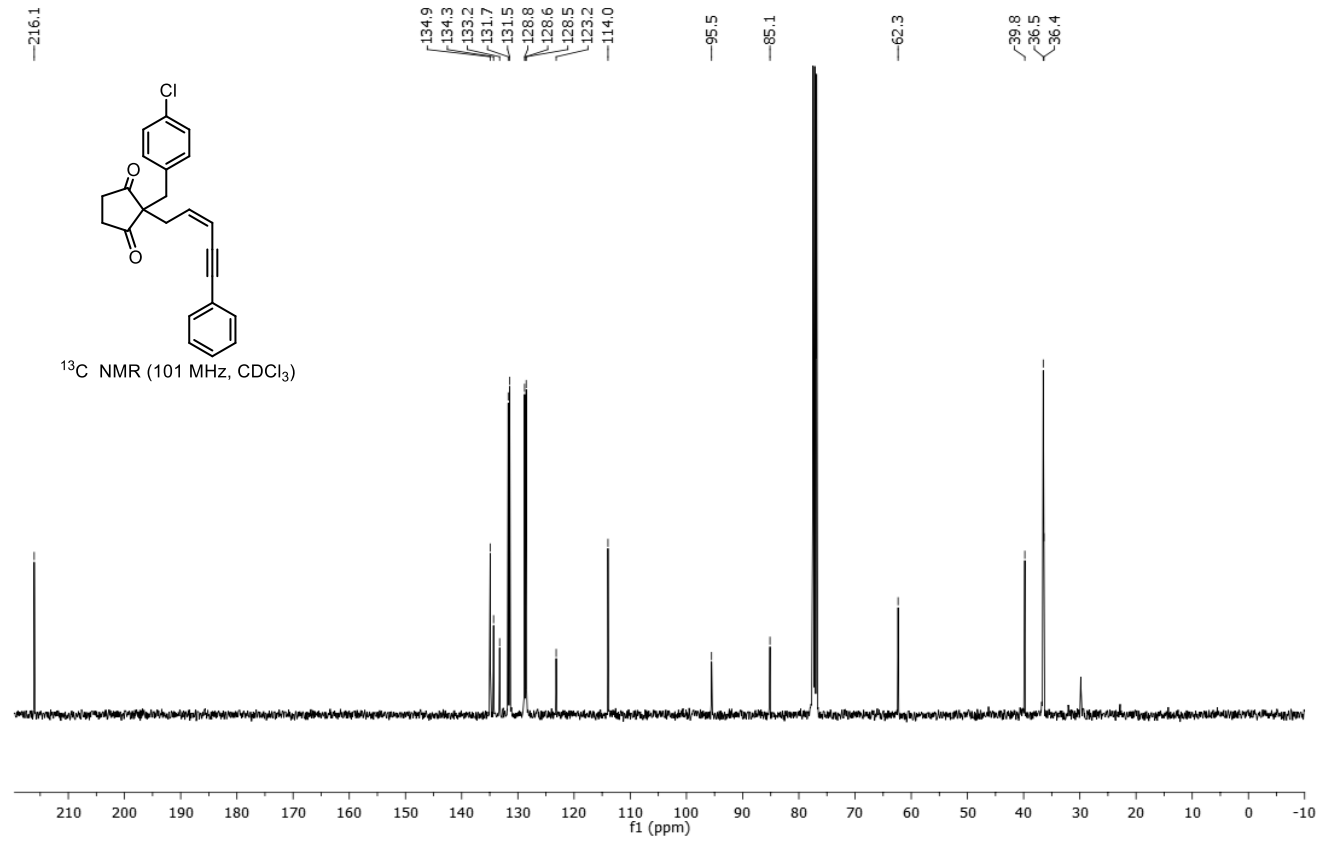




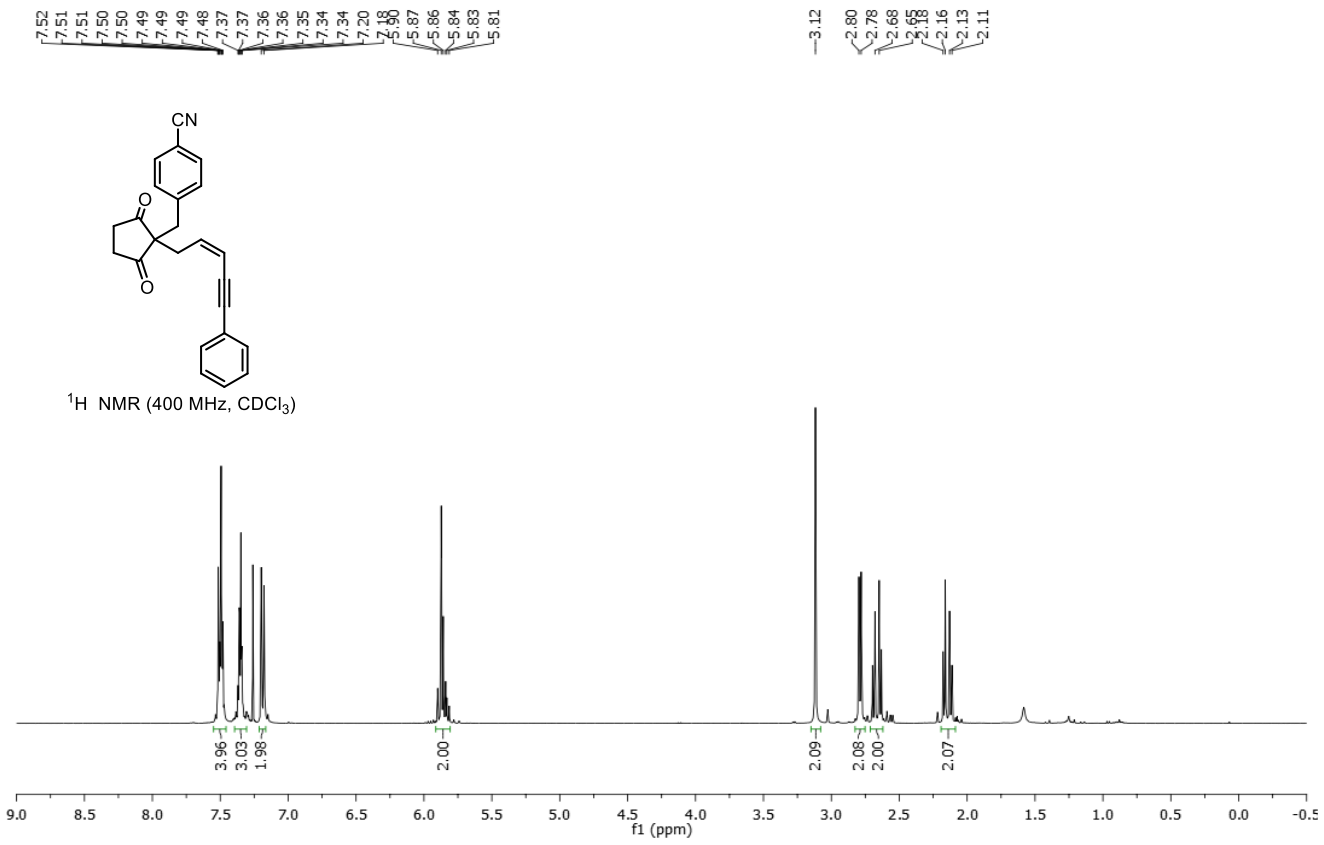
^{19}F NMR (471 MHz, $CDCl_3$)

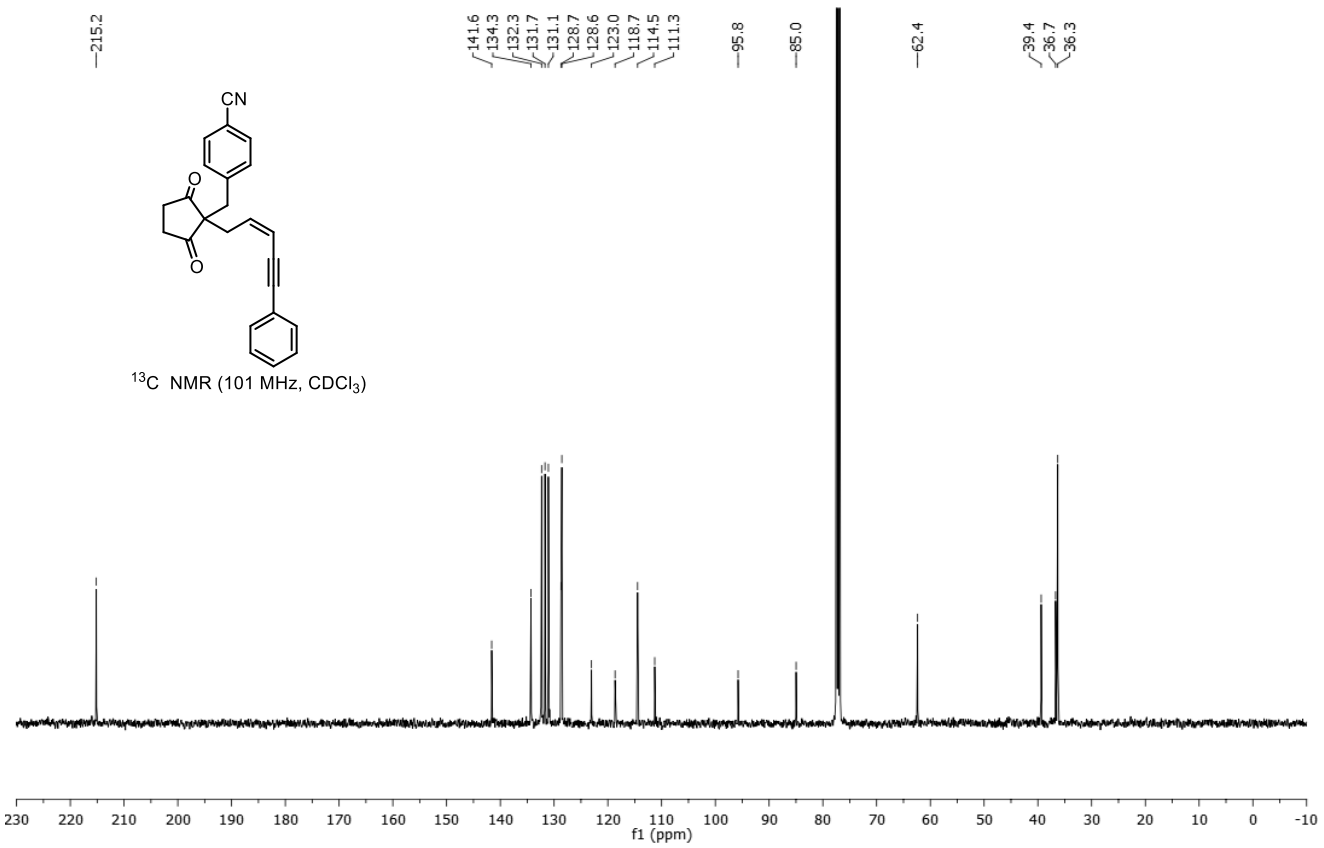
(*Z*)-2-(4-Chlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1k):



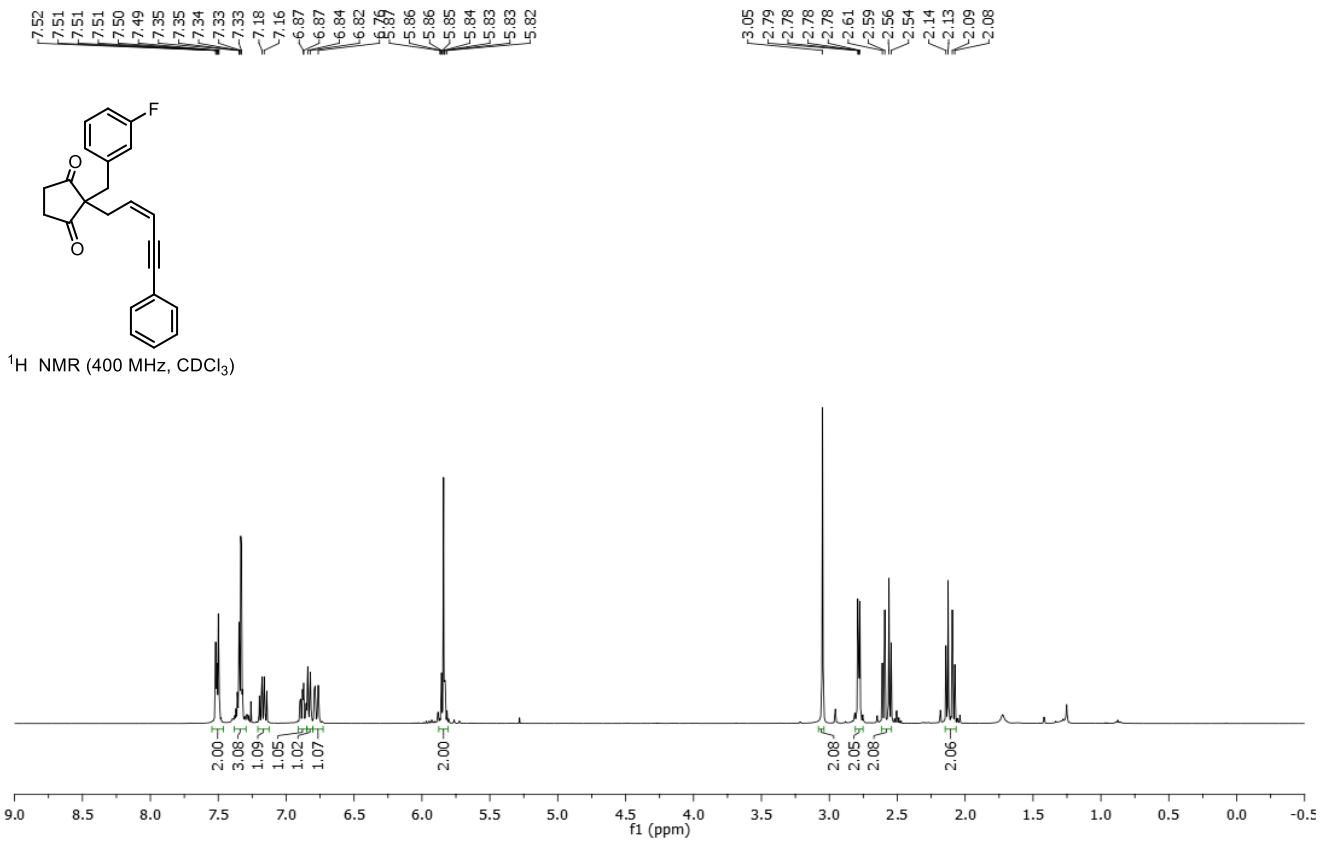


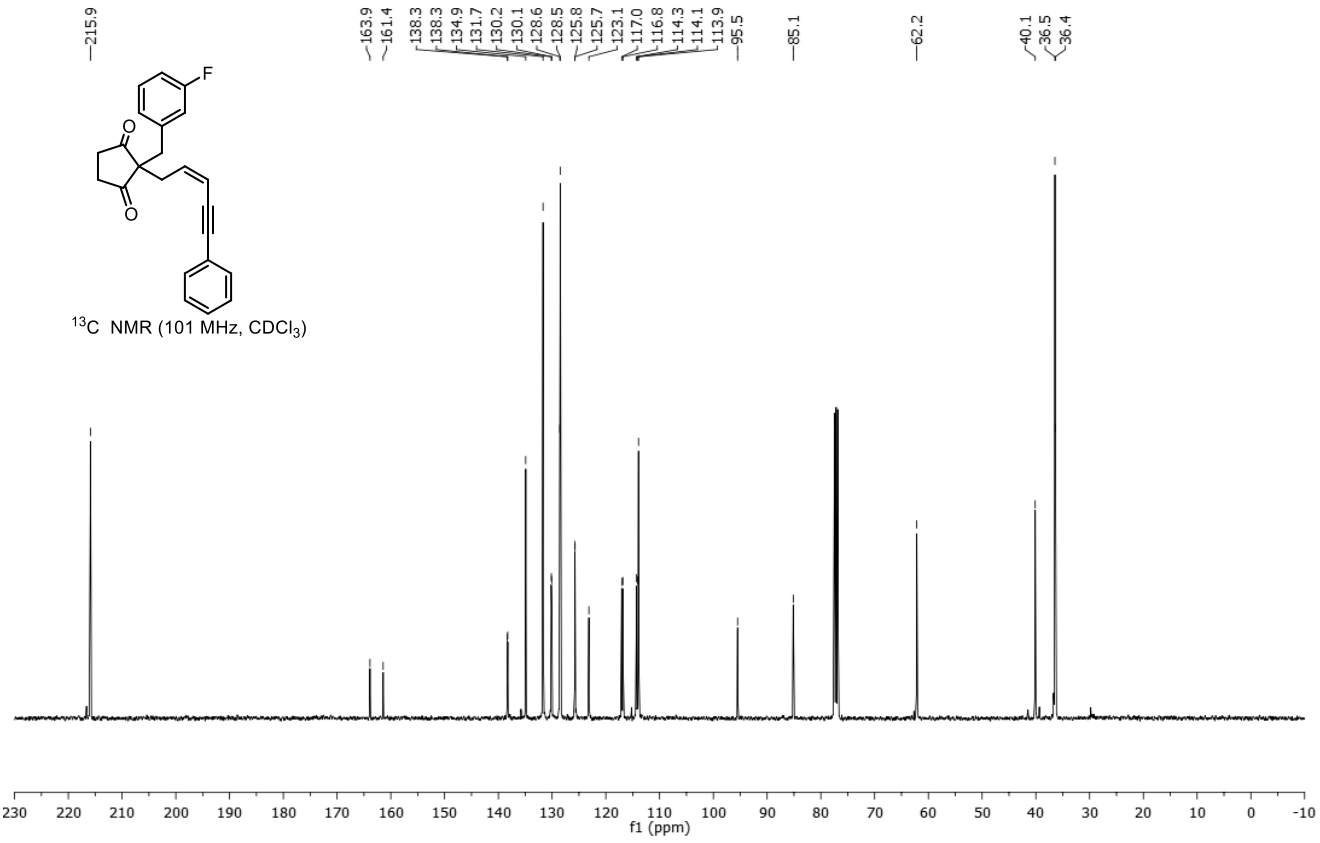
(*Z*)-4-((2,5-Dioxo-1-(5-phenylpent-2-en-4-yn-1-yl)cyclopentyl)methyl)benzonitrile (1l):

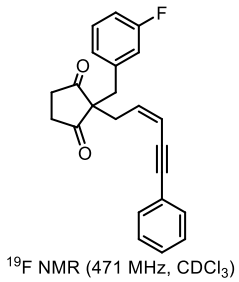




(*Z*)2-(3-Fluorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1m):

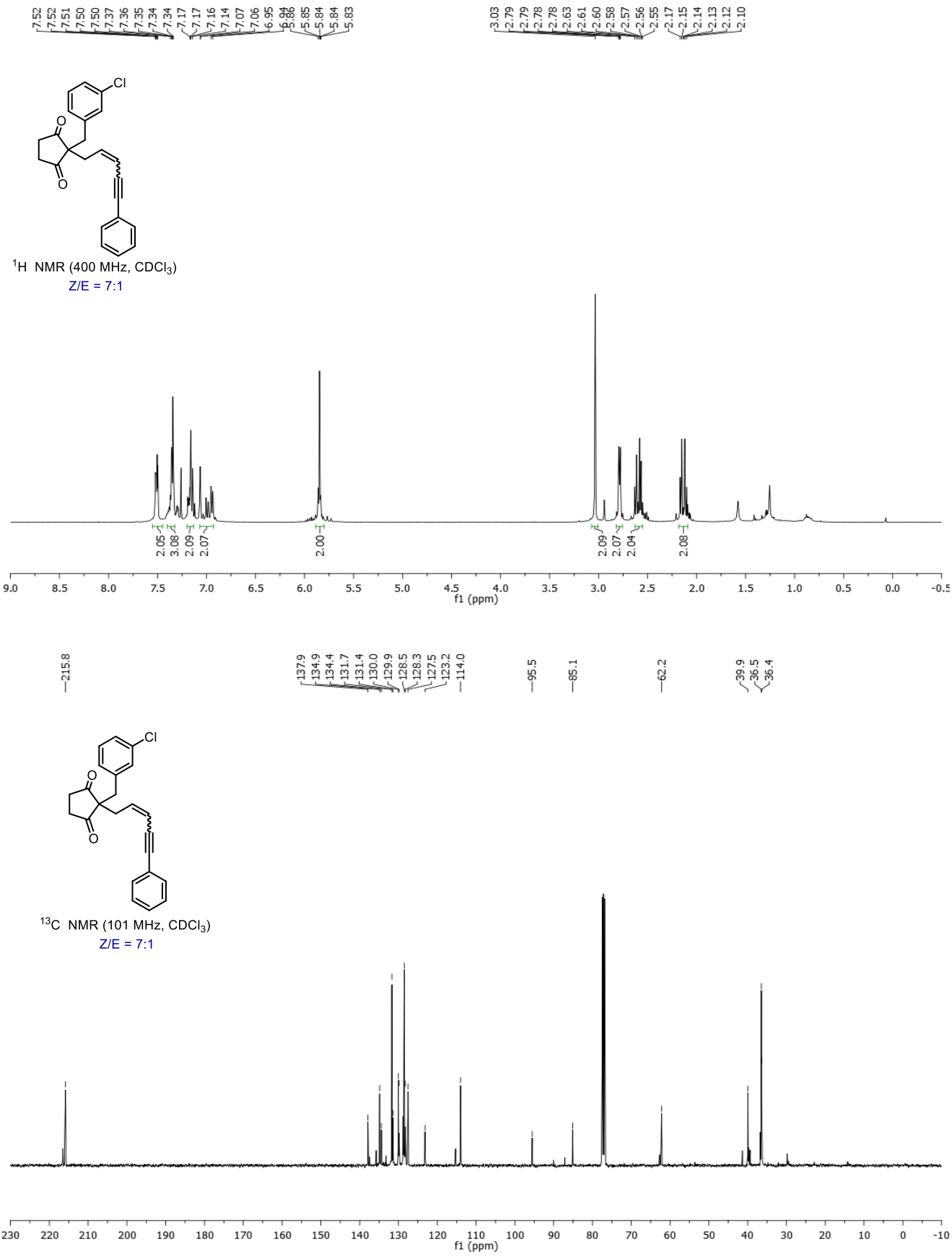




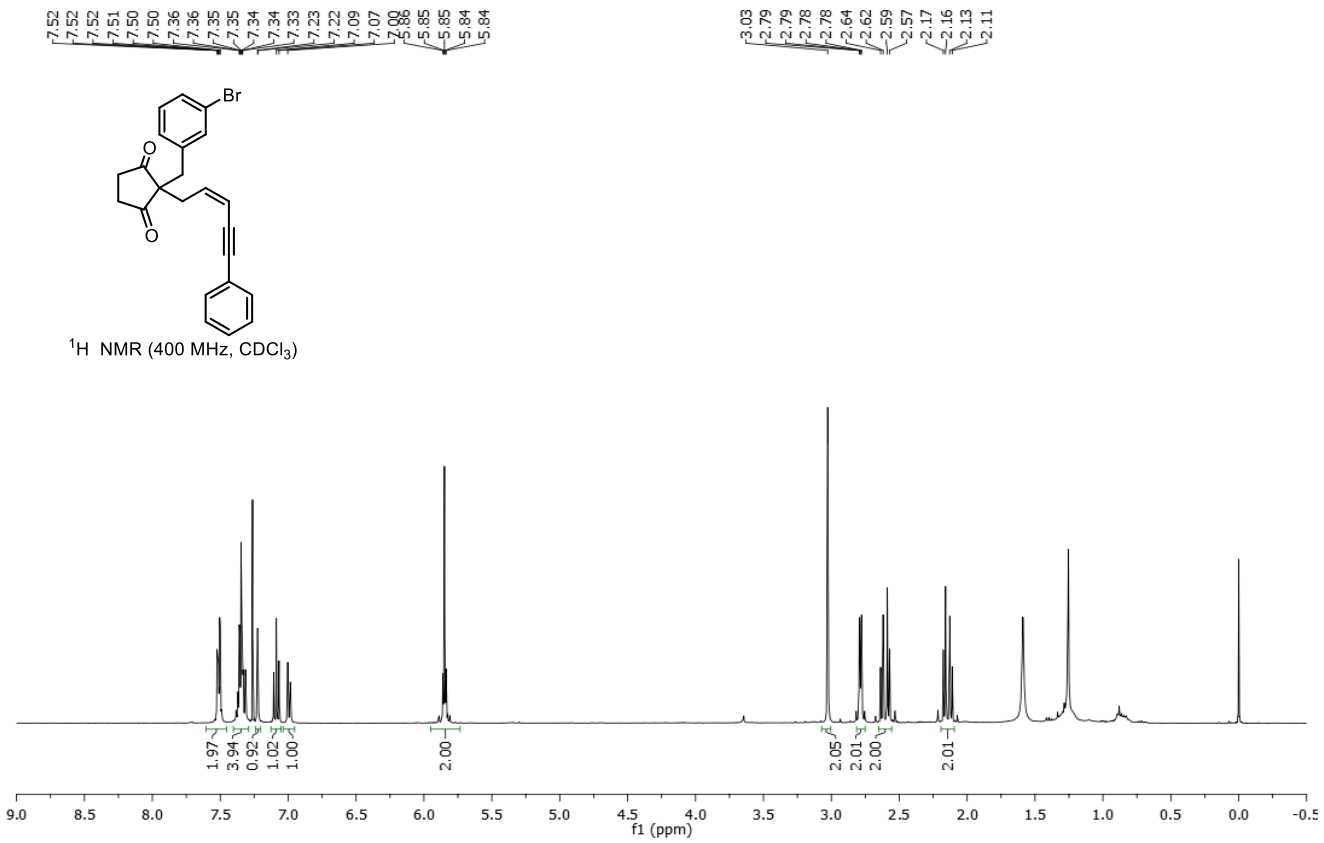


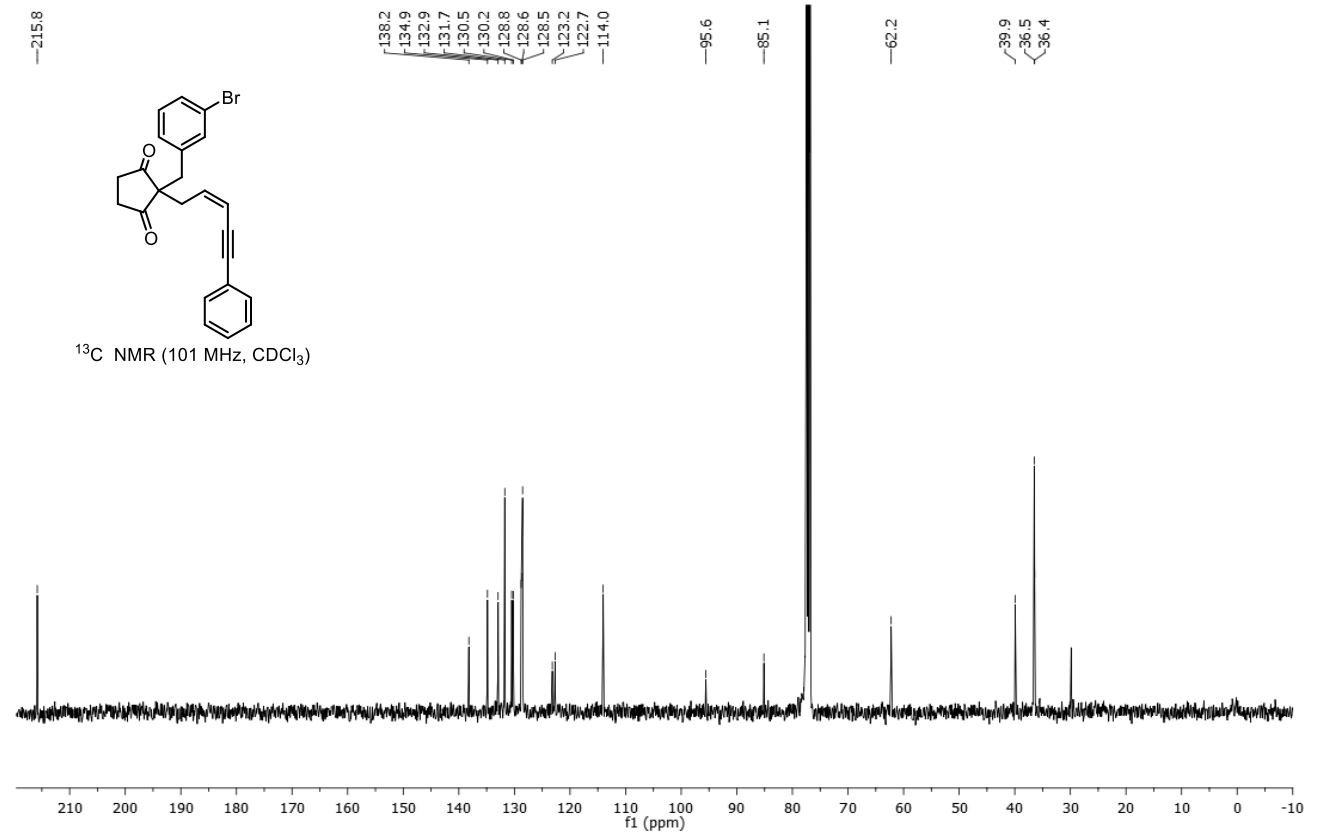
^{19}F NMR (471 MHz, $CDCl_3$)

2-(3-Chlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1n):

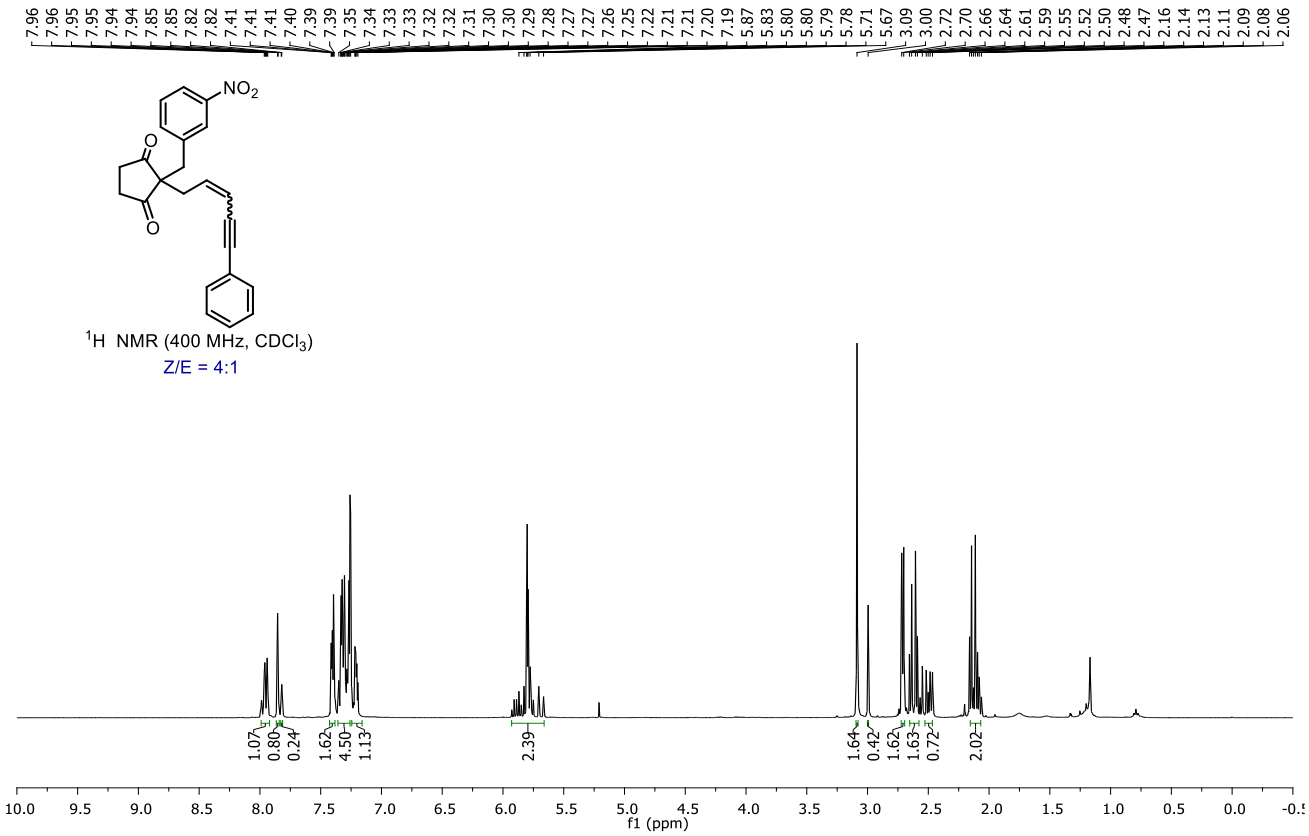


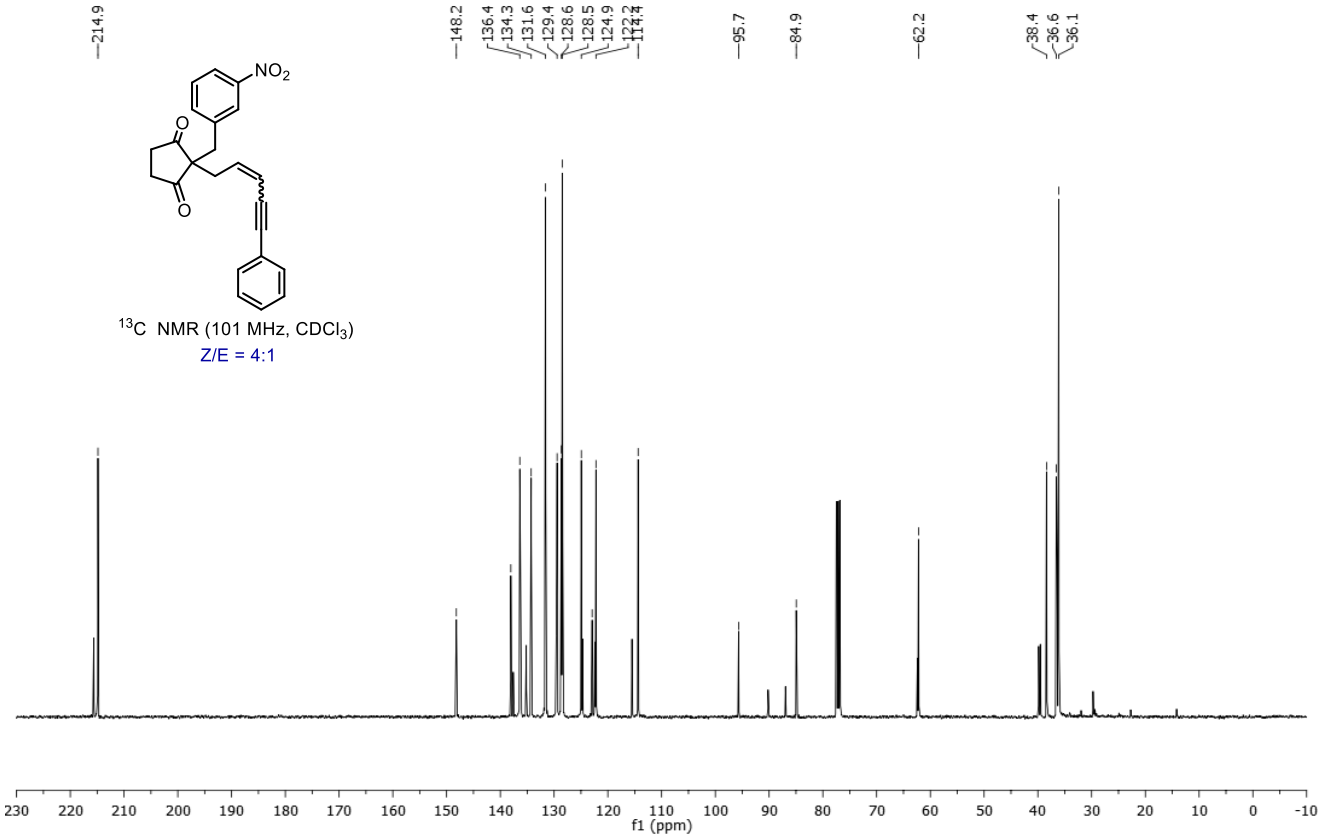
2-(3-Bromobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1o):



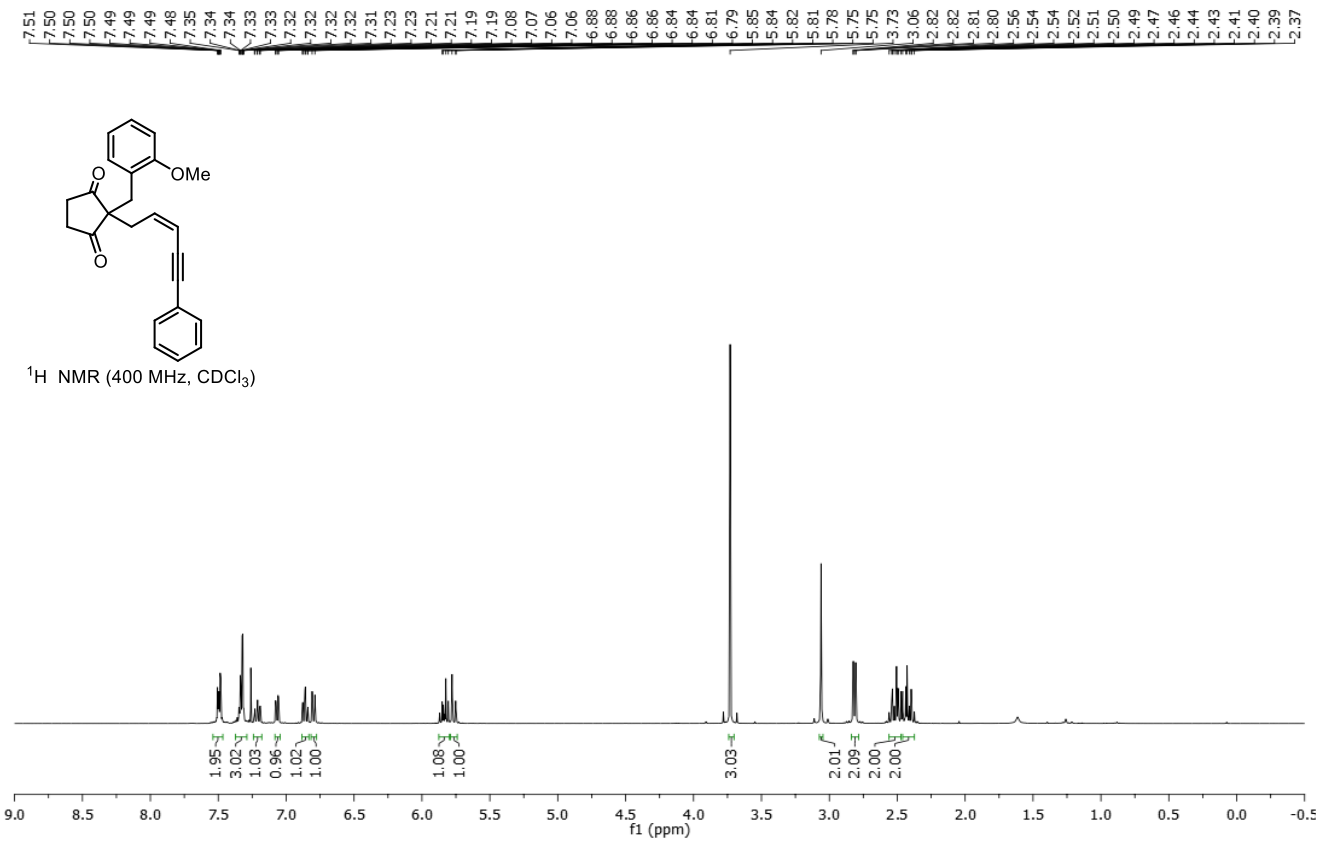


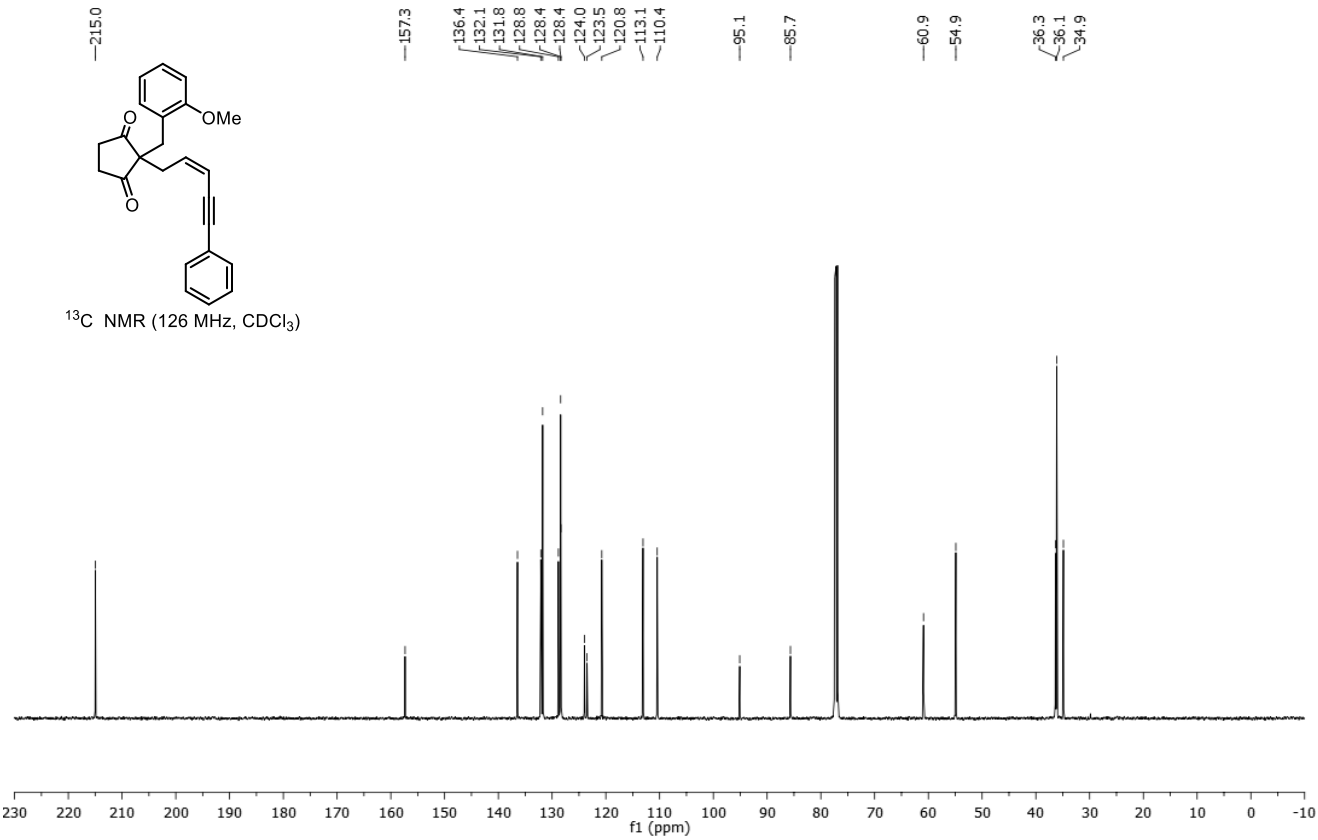
2-(3-Nitrobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1p):



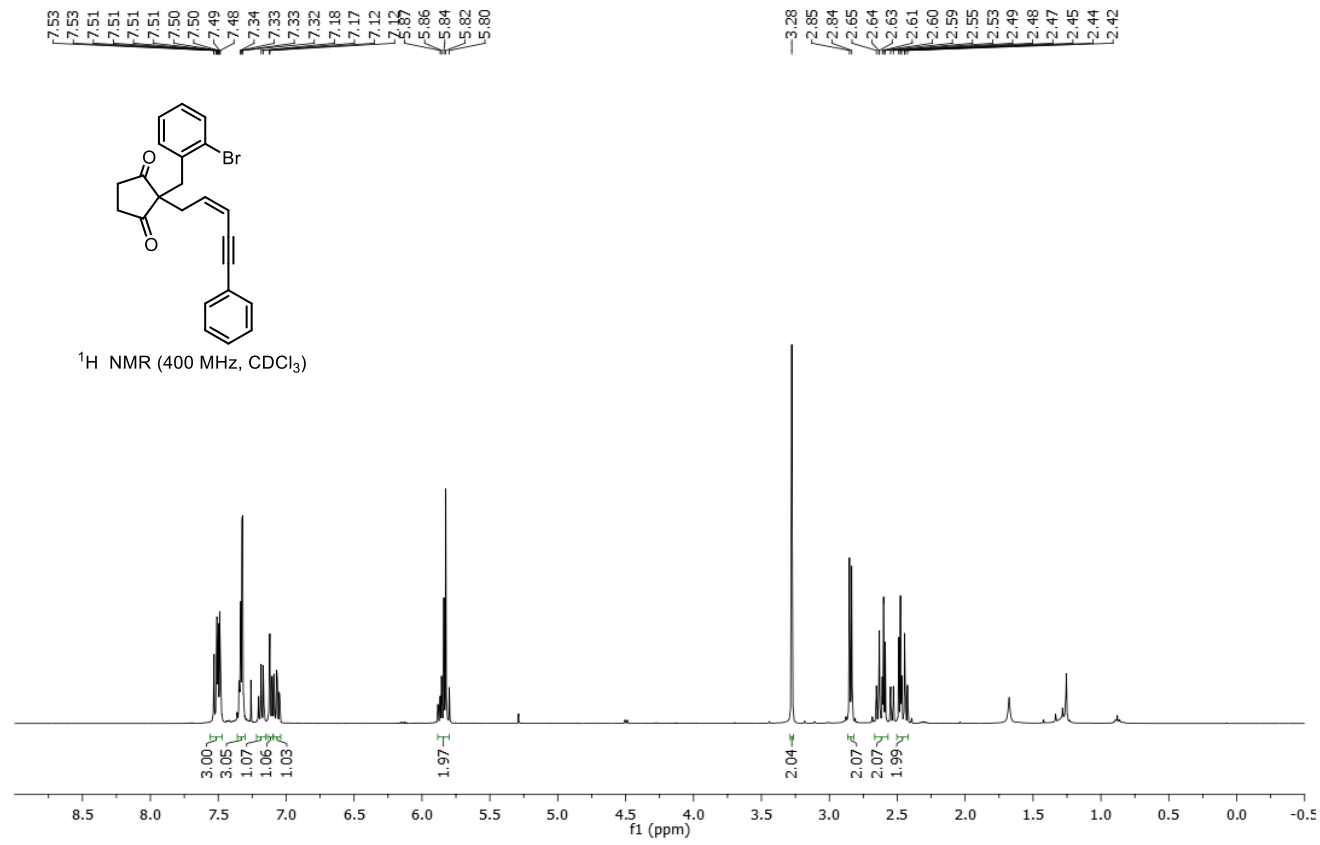


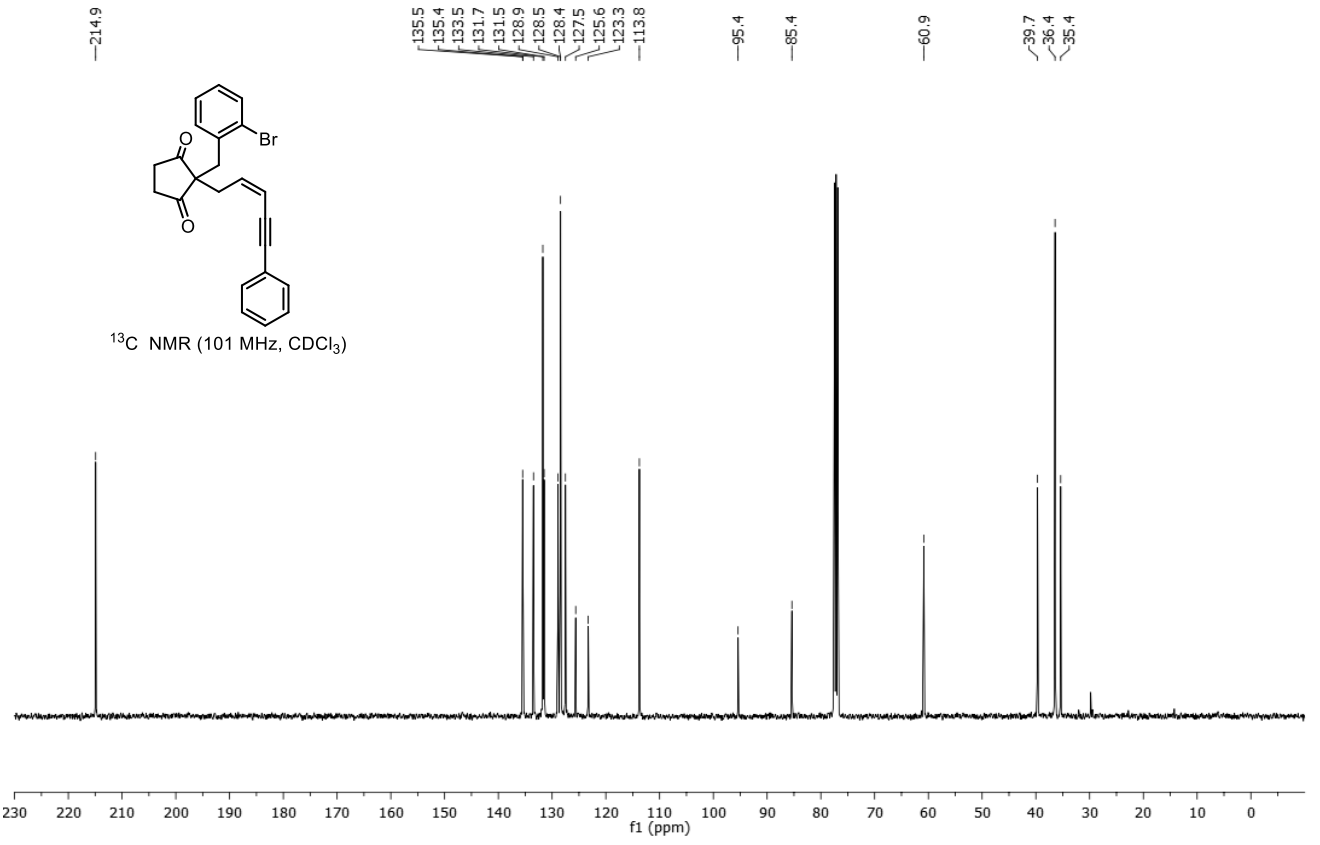
(*Z*)-2-(2-Methoxybenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1q):



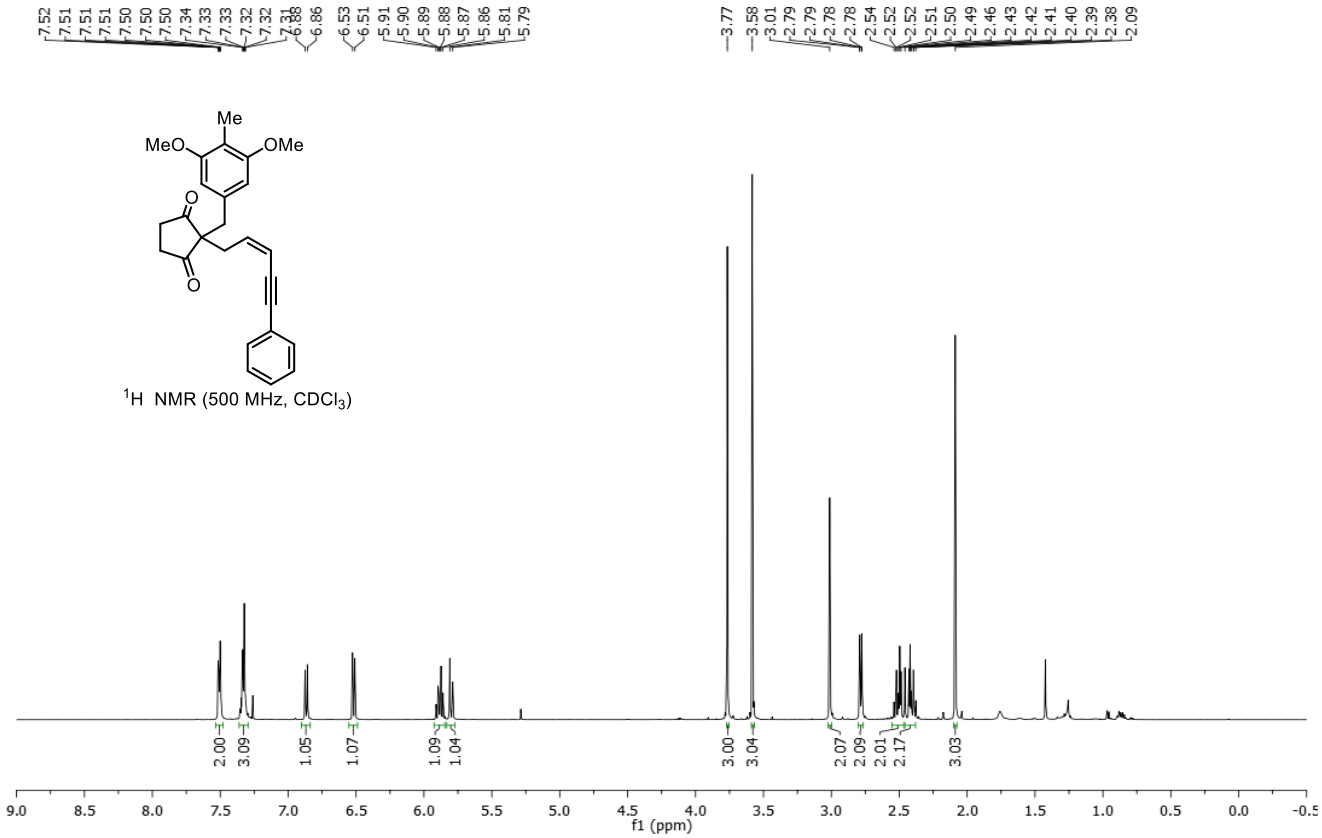


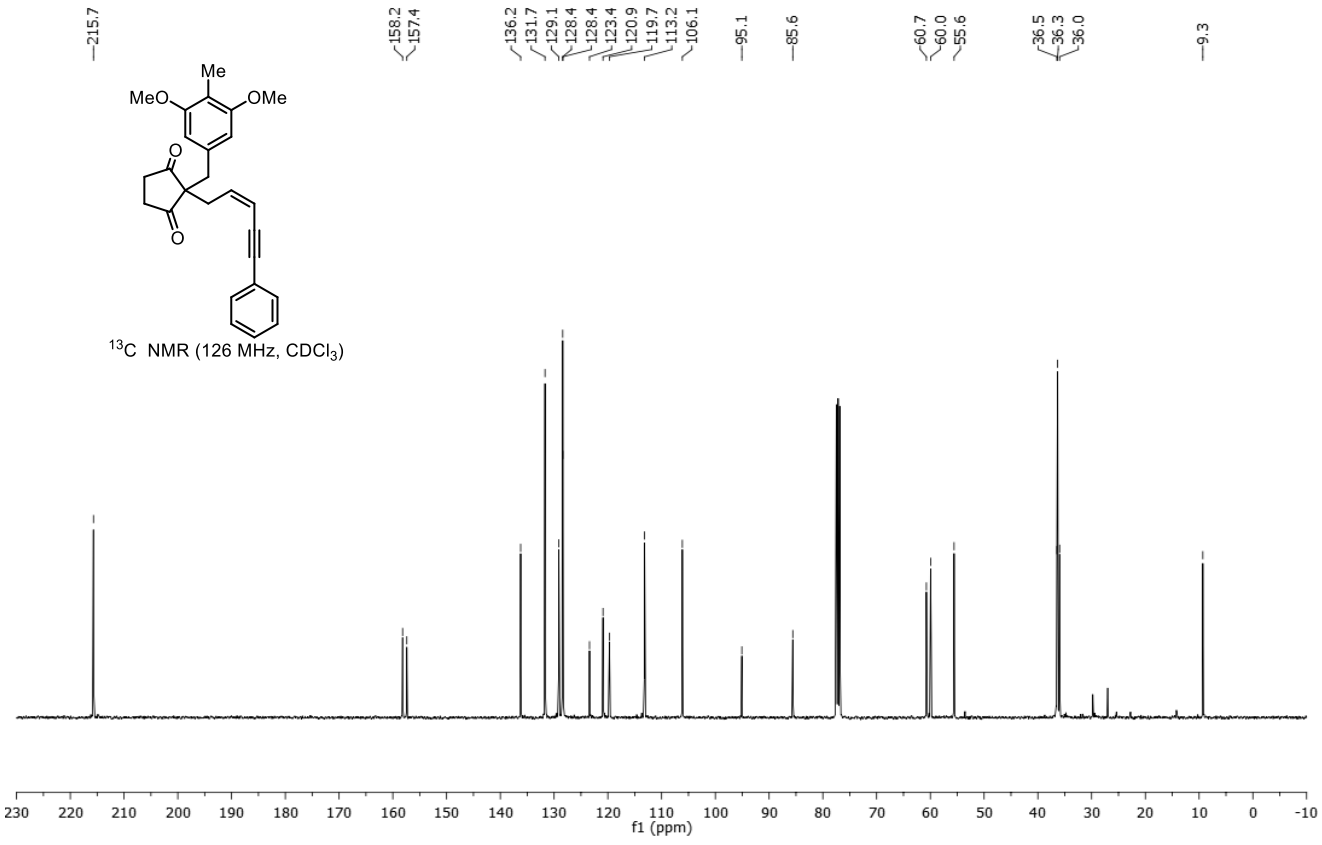
(*Z*)-2-(2-Bromobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1r):



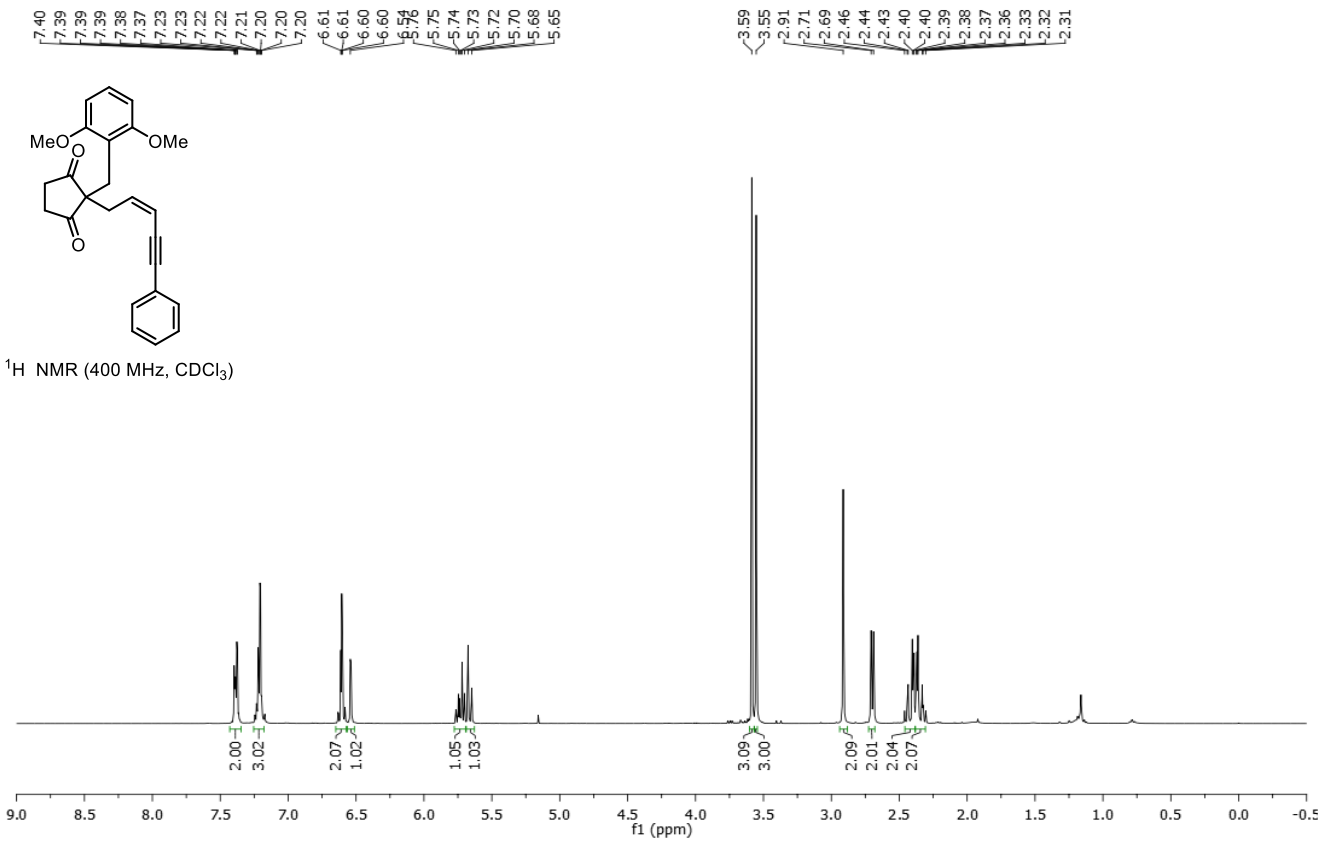


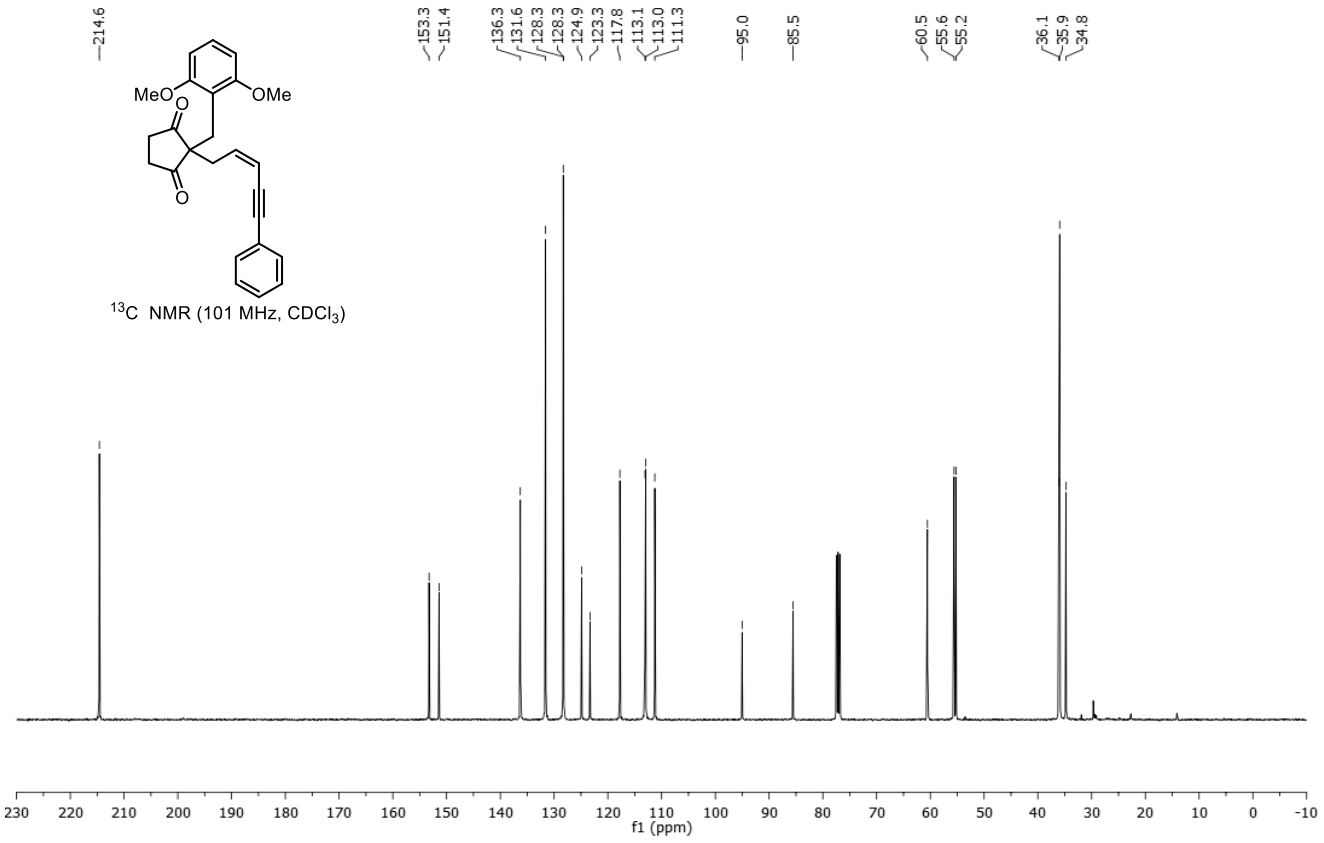
(*Z*)-2-(3,5-Dimethoxy-4-methylbenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1s):



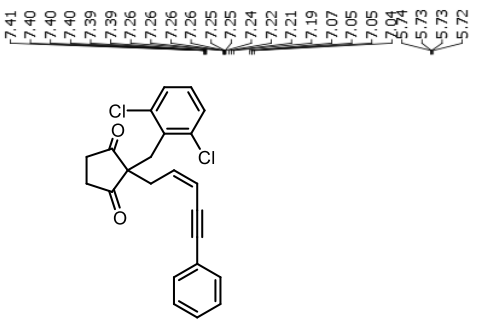


(*Z*)-2-(2,6-Dimethoxybenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1t):

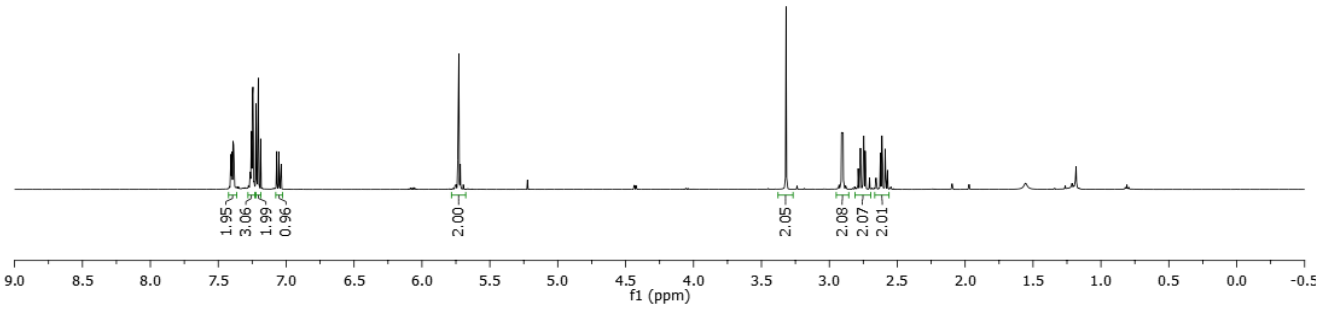


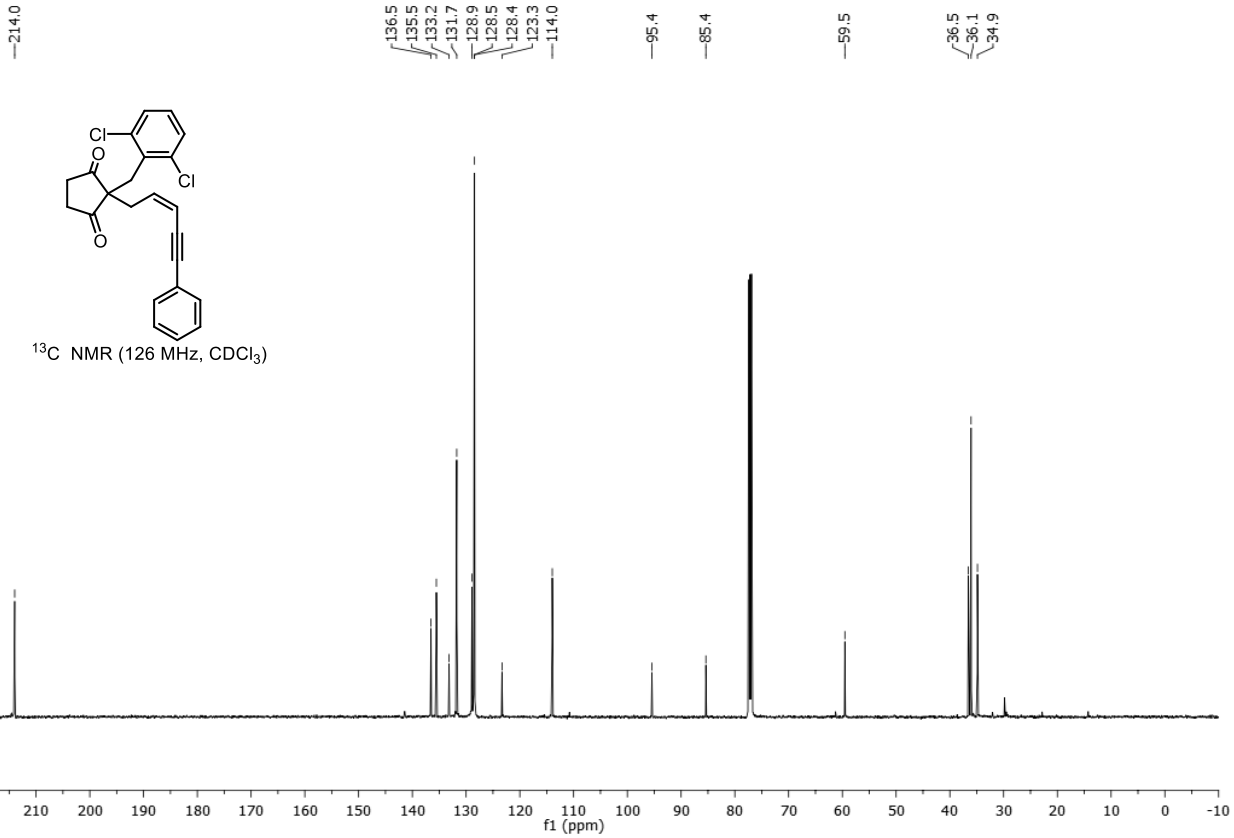


(*Z*)2-(2,5-Dichlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1u):



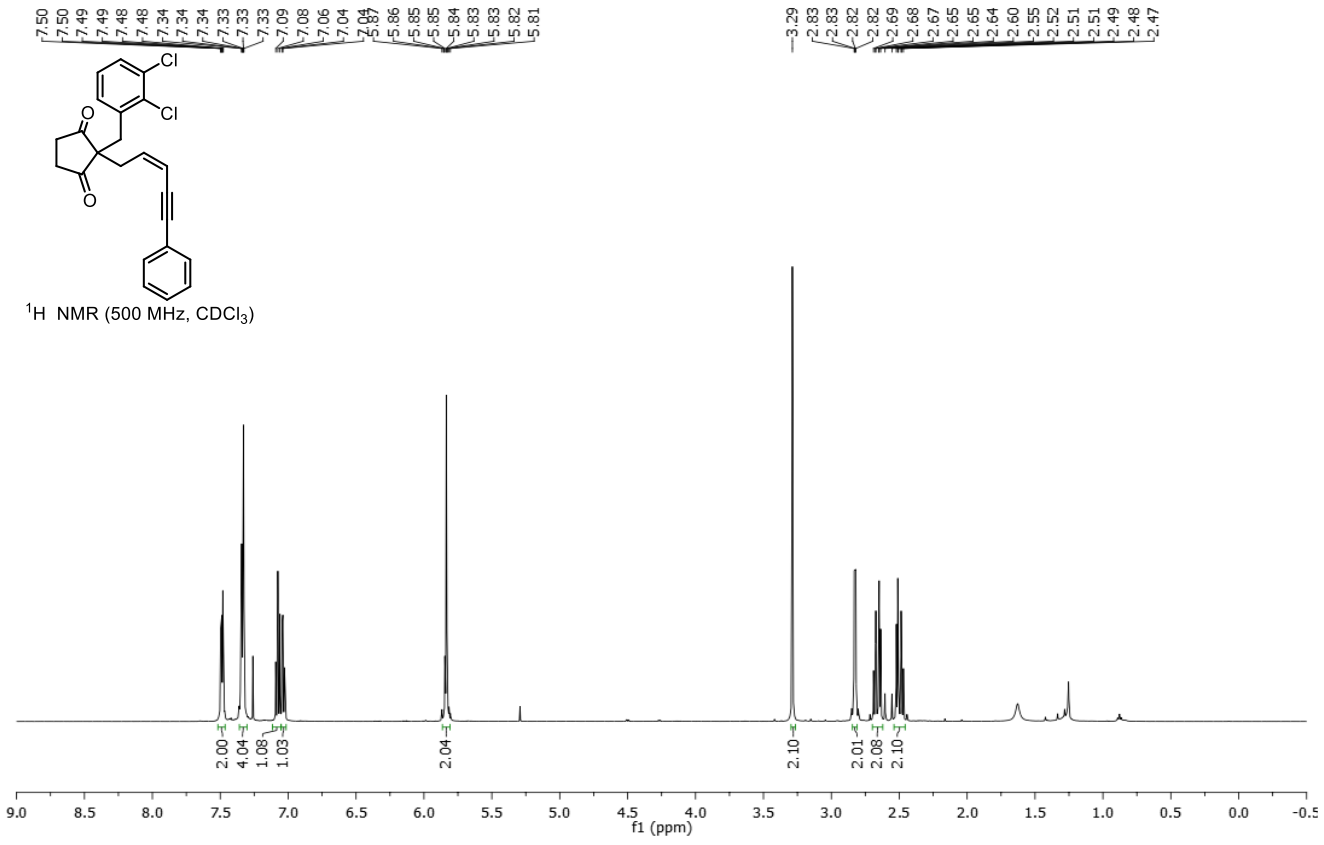
^{1}H NMR (500 MHz, $CDCl_3$)

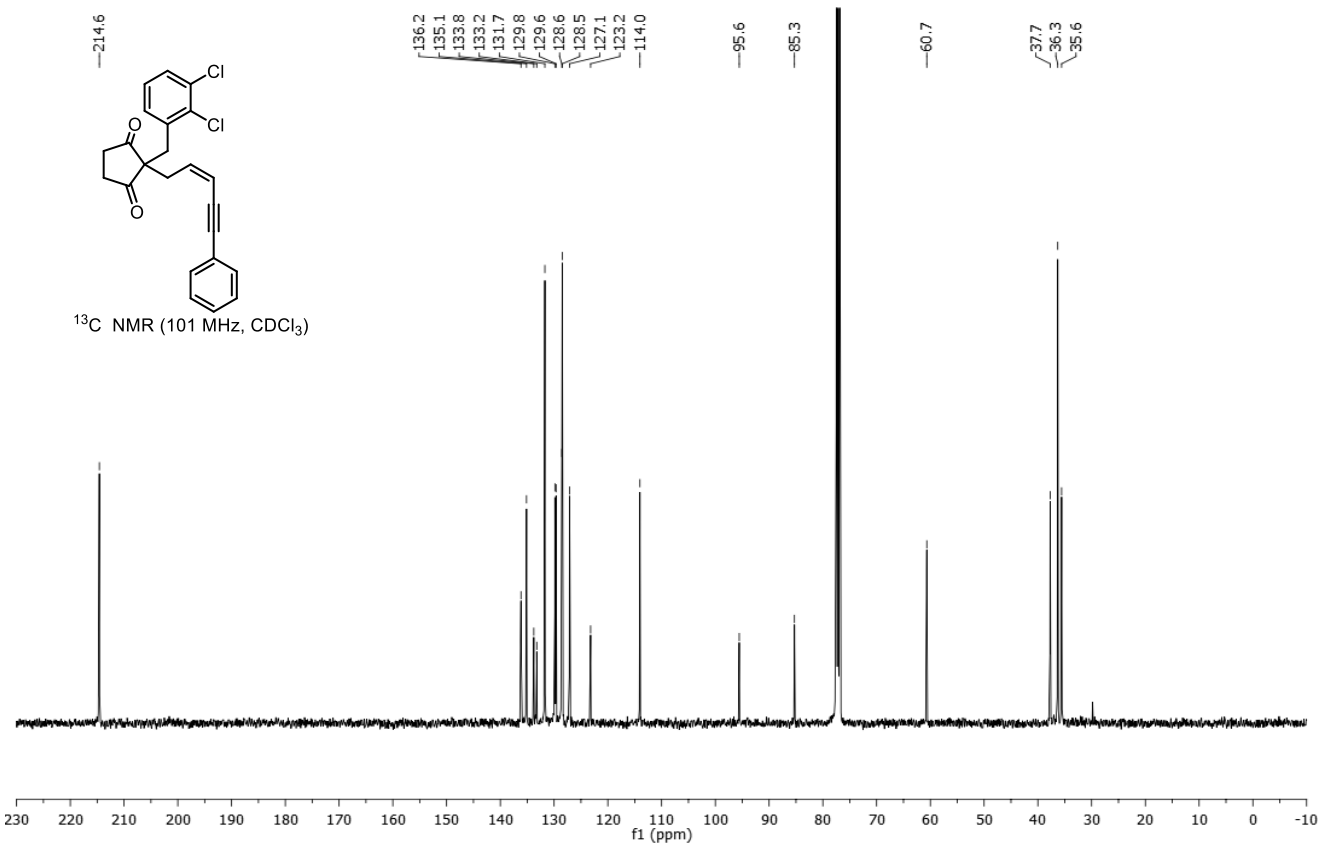




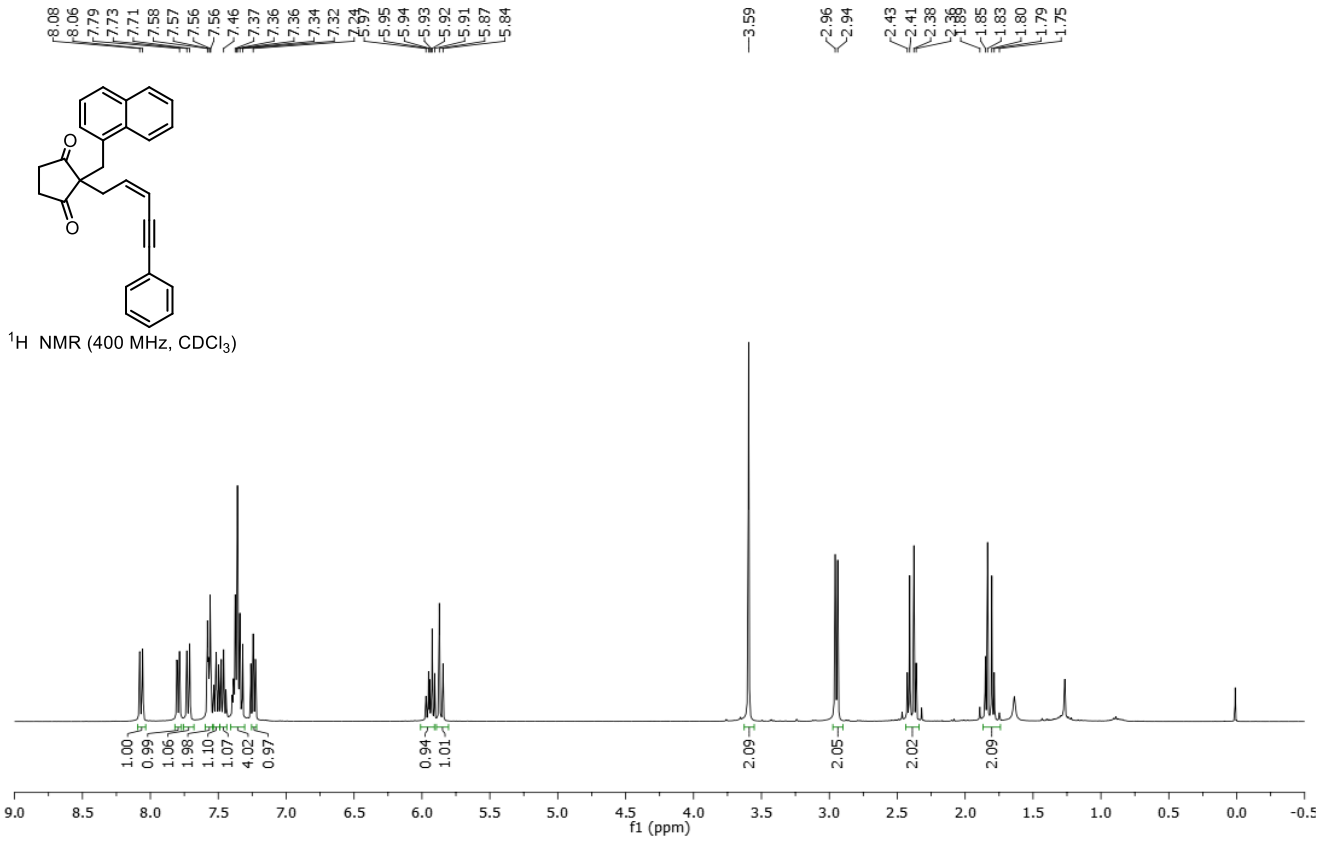
^{13}C NMR (126 MHz, $CDCl_3$)

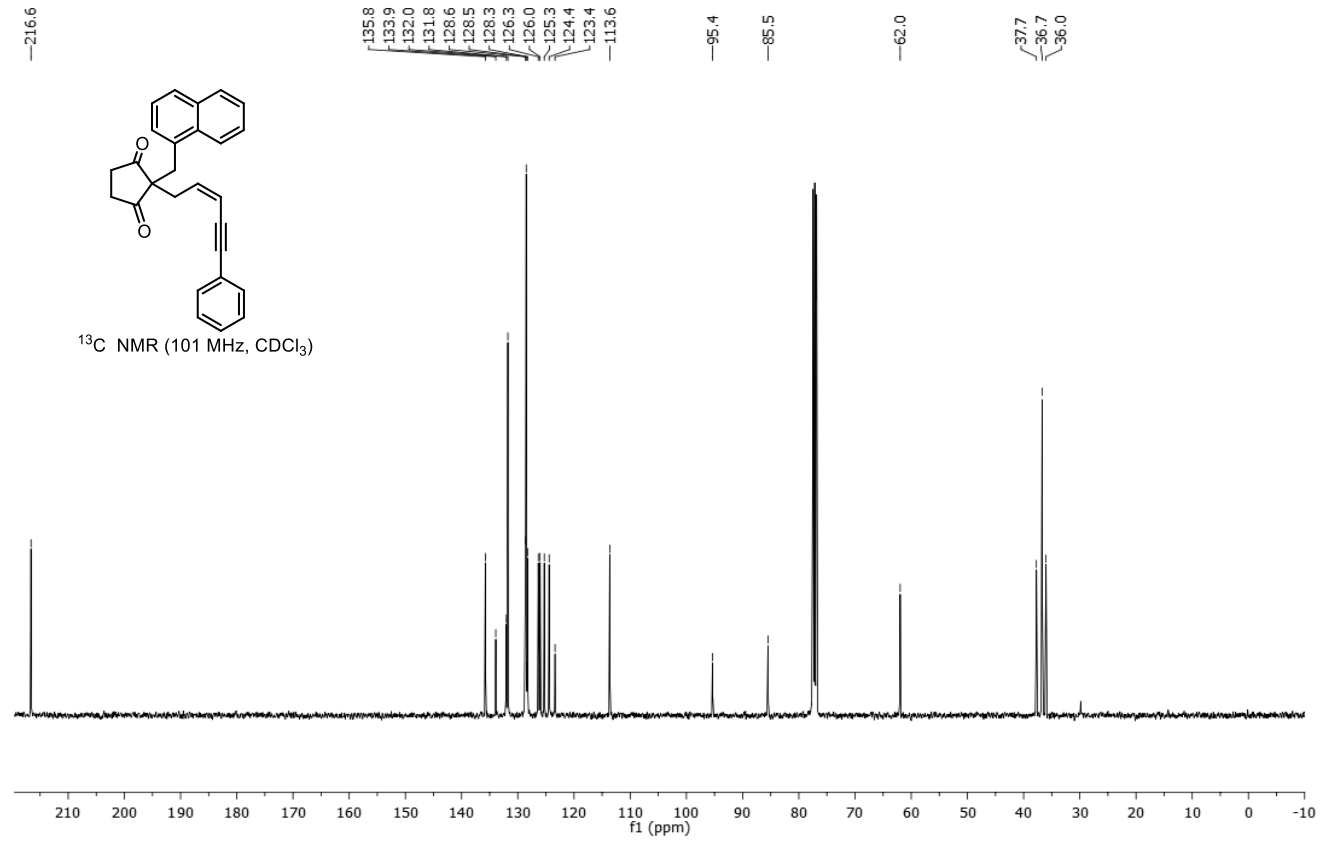
(*Z*)-2-(2,3-Dichlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1v):



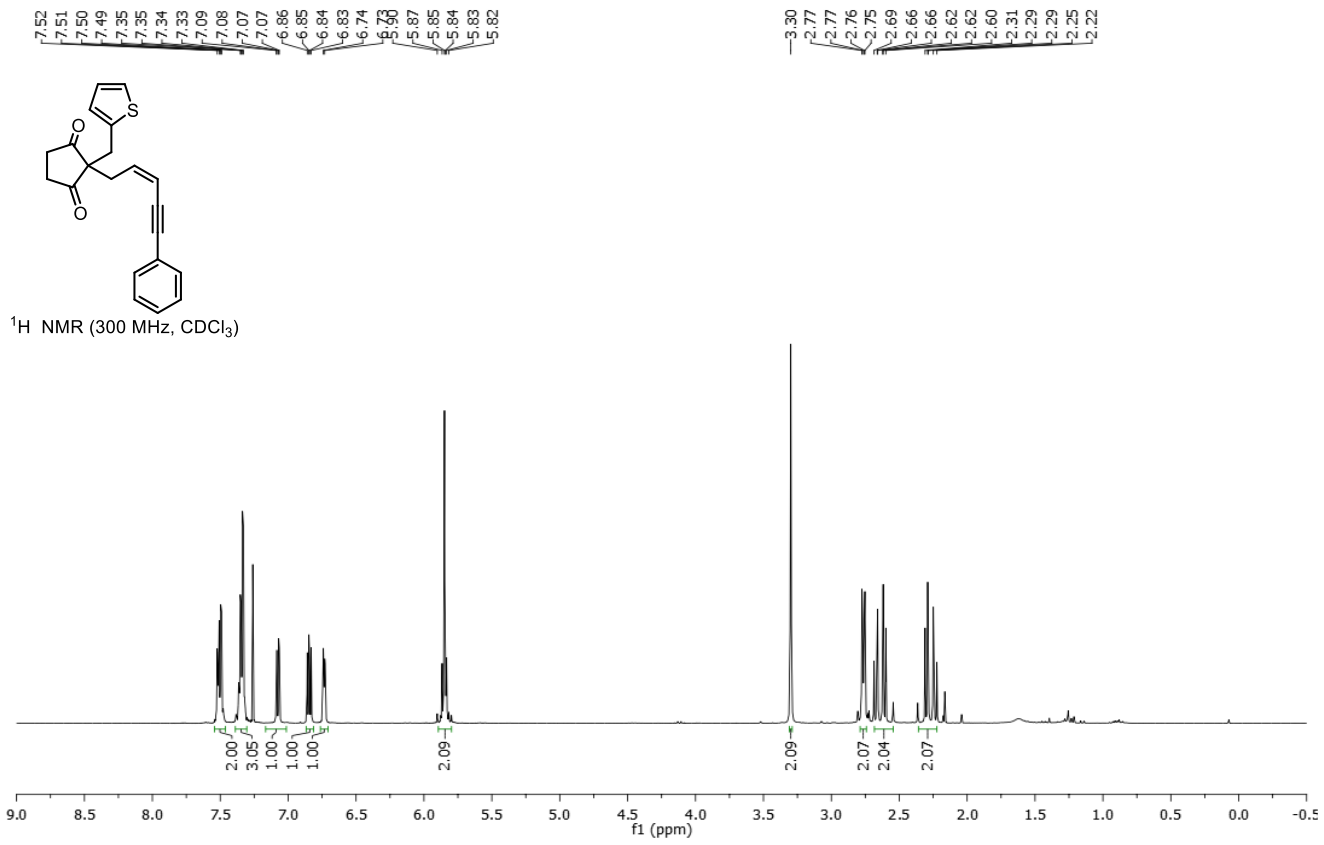


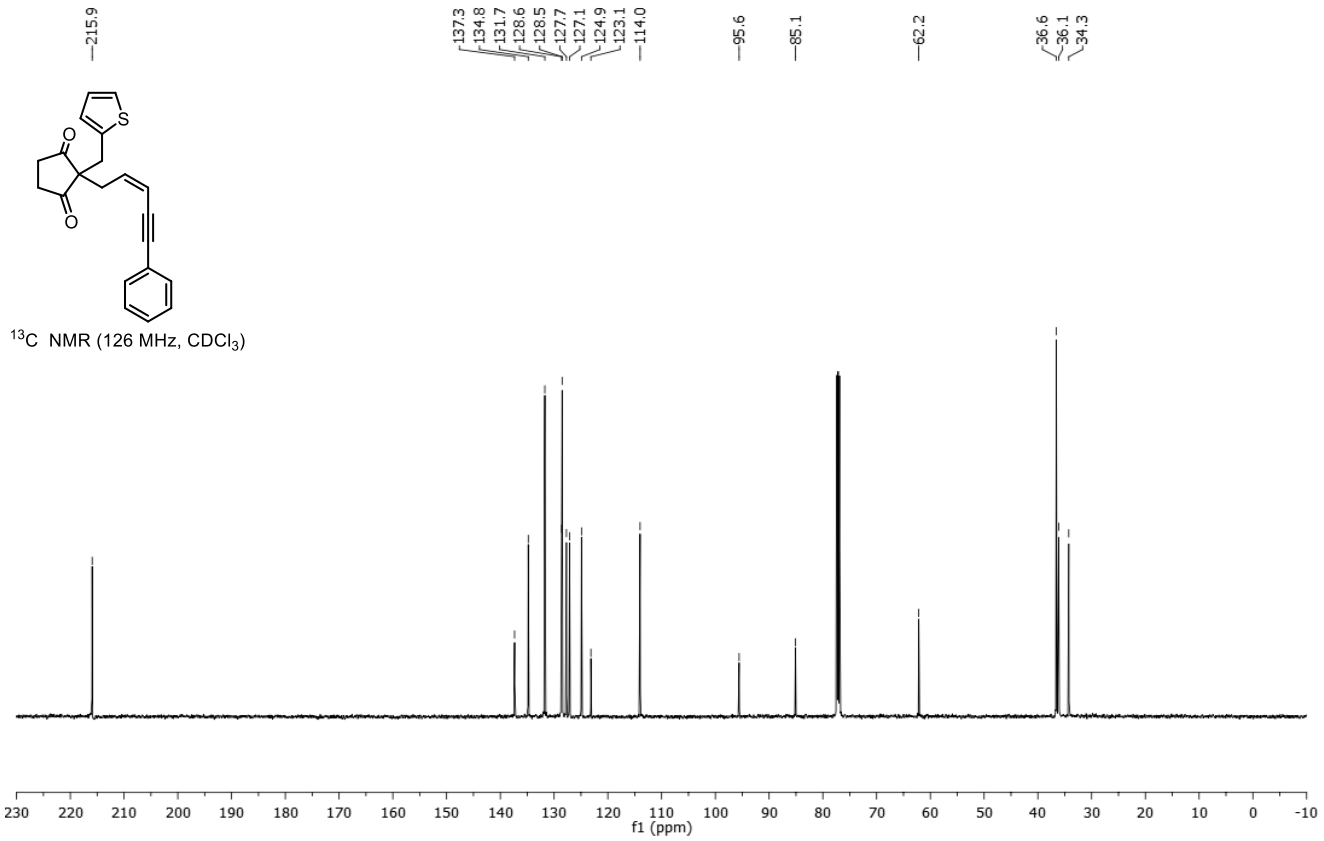
(*Z*)2-(Naphthalen-1-ylmethyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1w):



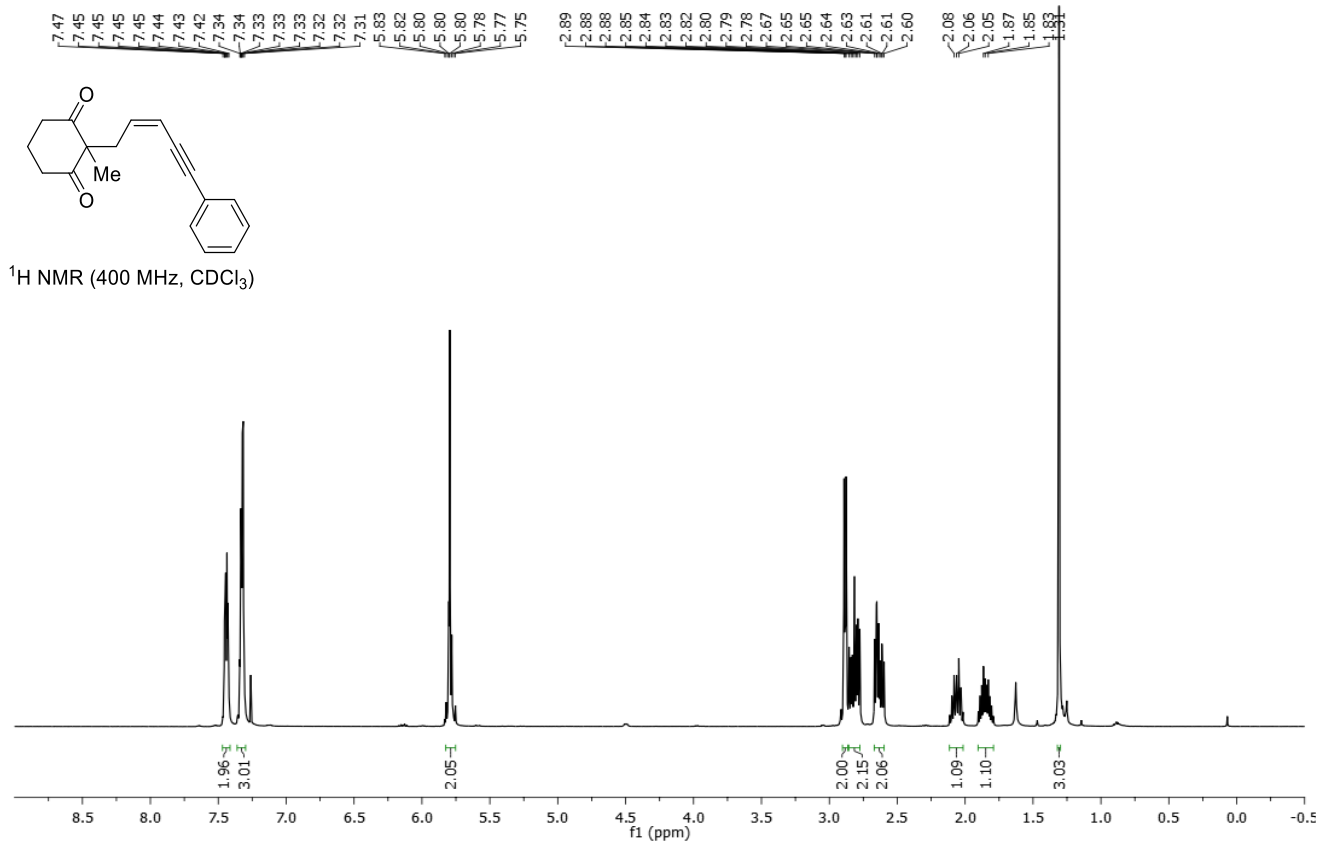


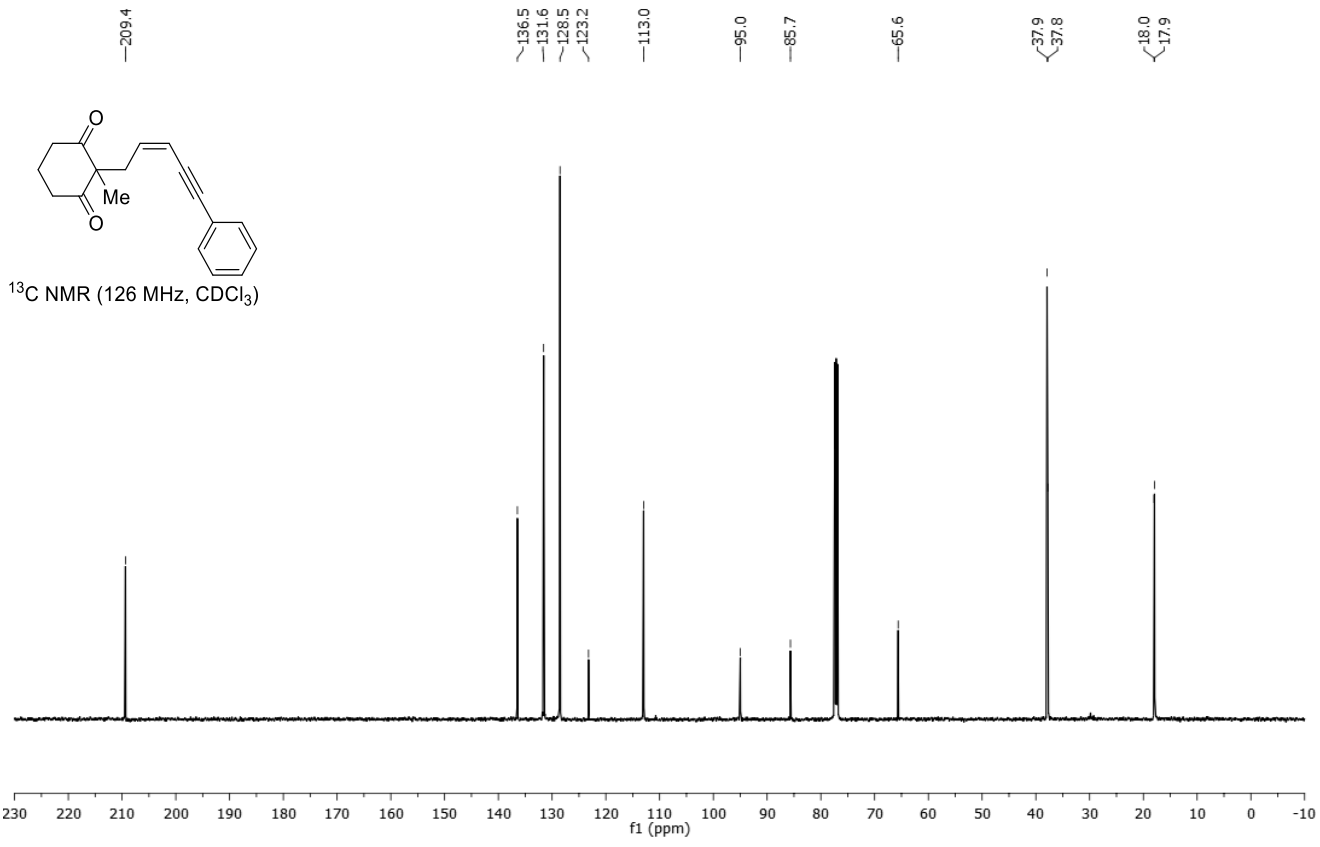
(*Z*)-2-(5-Phenylpent-2-en-4-yn-1-yl)-2-(thiophen-2-ylmethyl)cyclopentane-1,3-dione (1x):



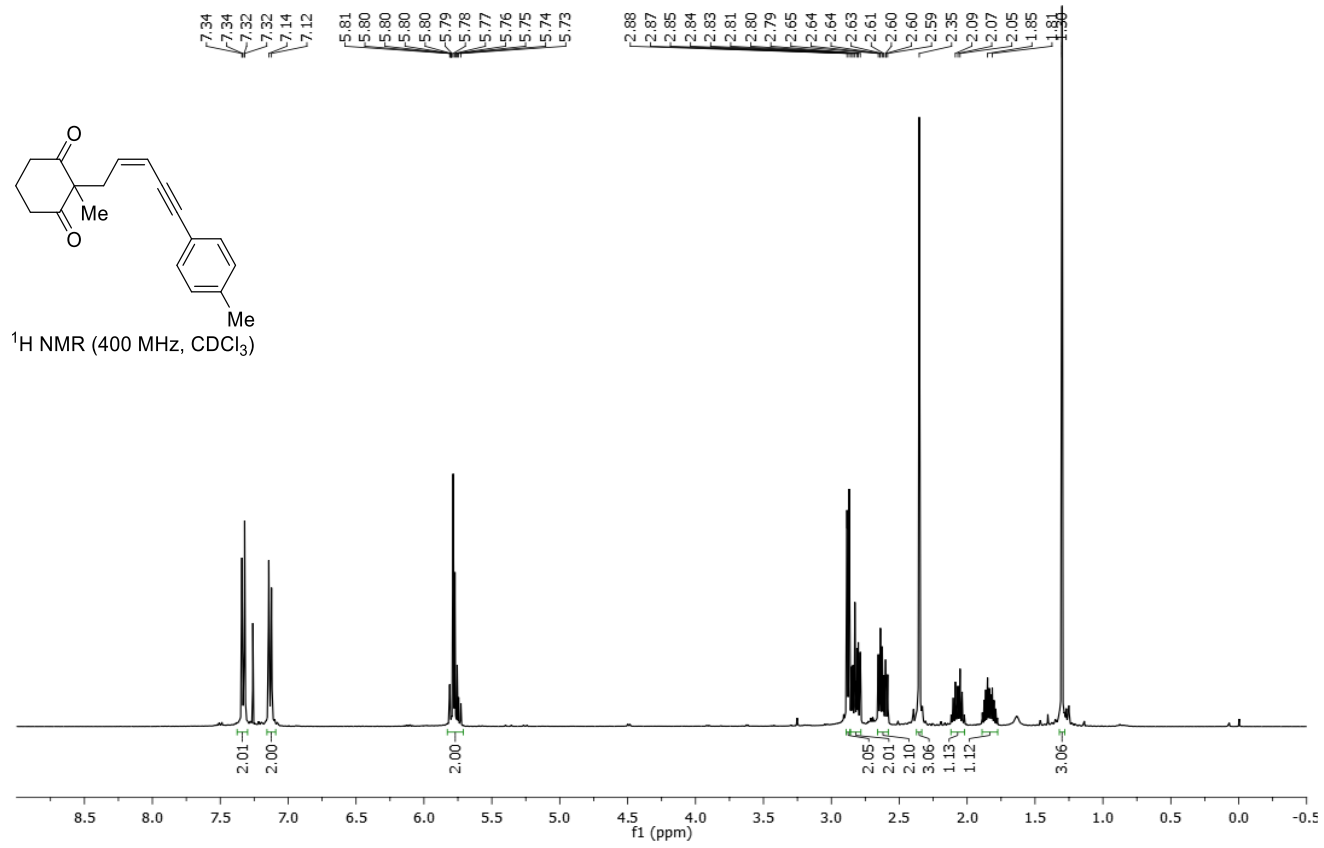


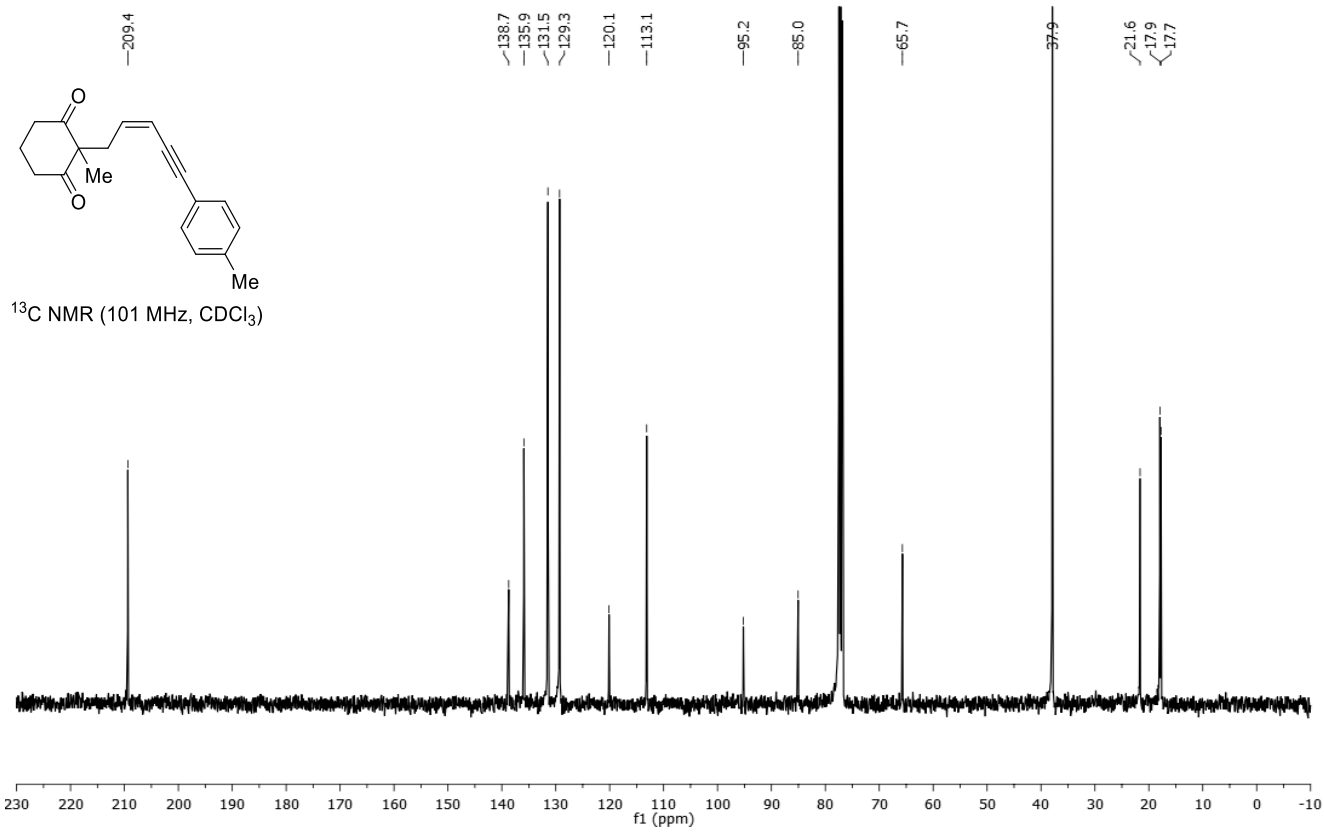
(Z)-2-Methyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclohexane-1,3-dione (1y):



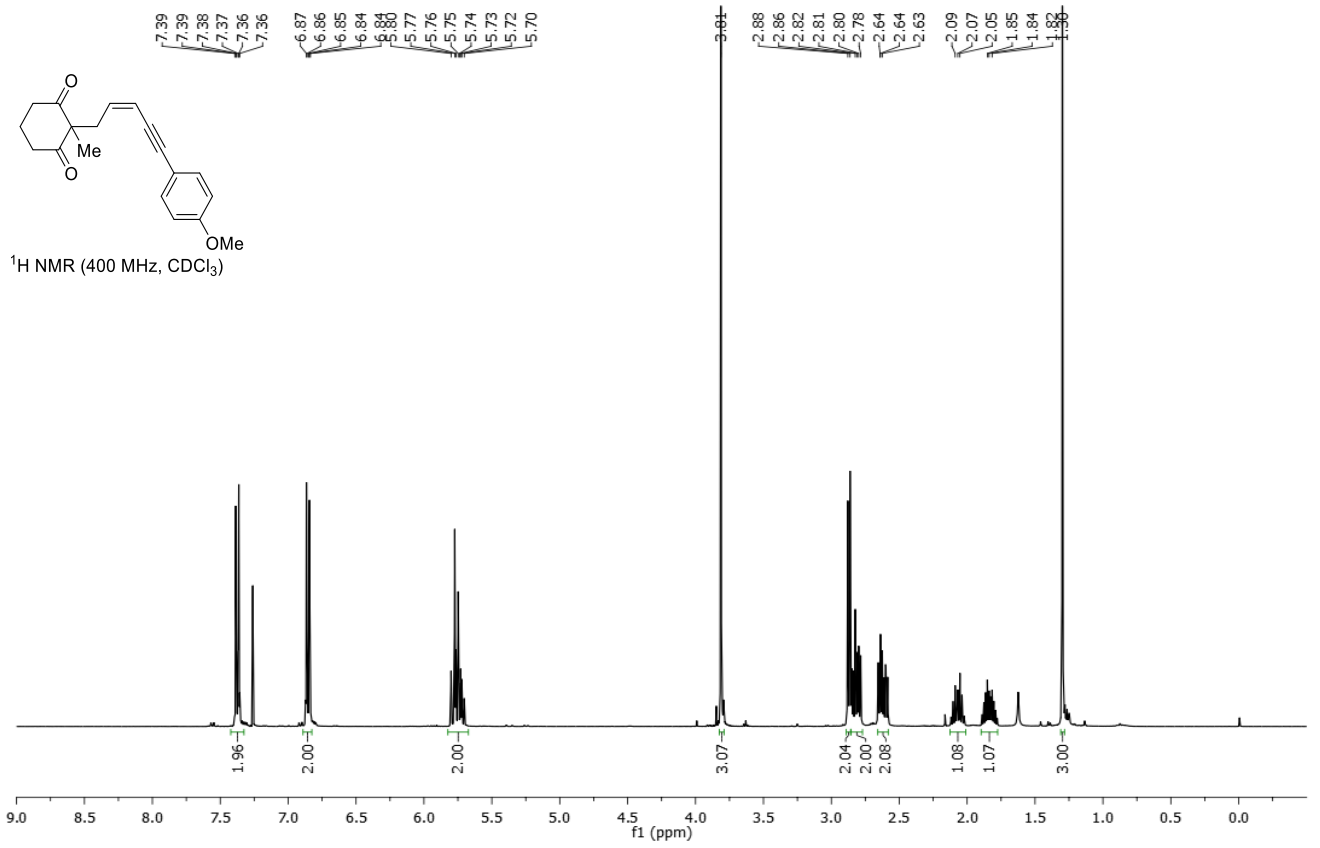


(Z)-2-Methyl-2-(5-(p-tolyl)pent-2-en-4-yn-1-yl)cyclohexane-1,3-dione (1z):

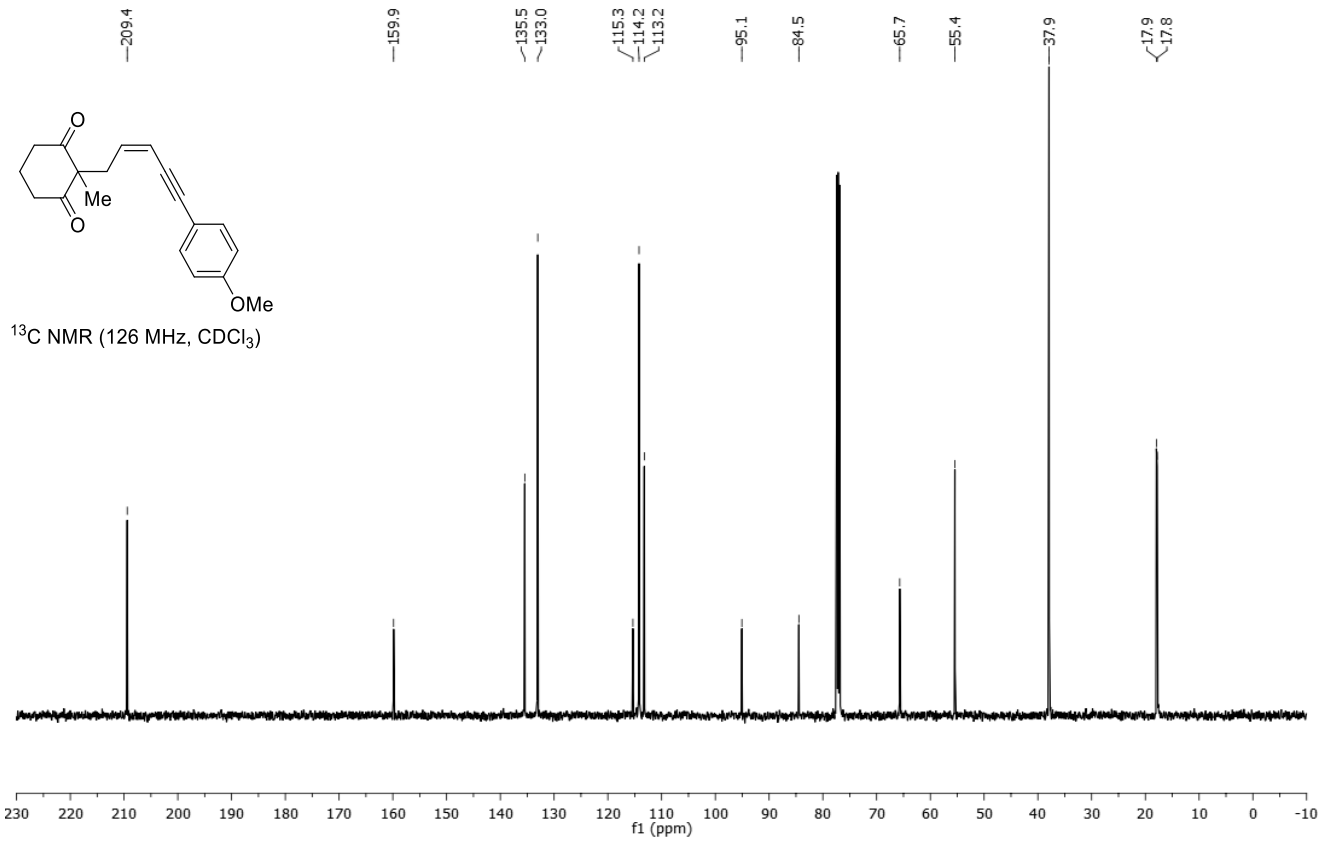




(Z)-2-(5-(4-Methoxyphenyl)pent-2-en-4-yn-1-yl)-2-methylcyclohexane-1,3-dione (1aa):

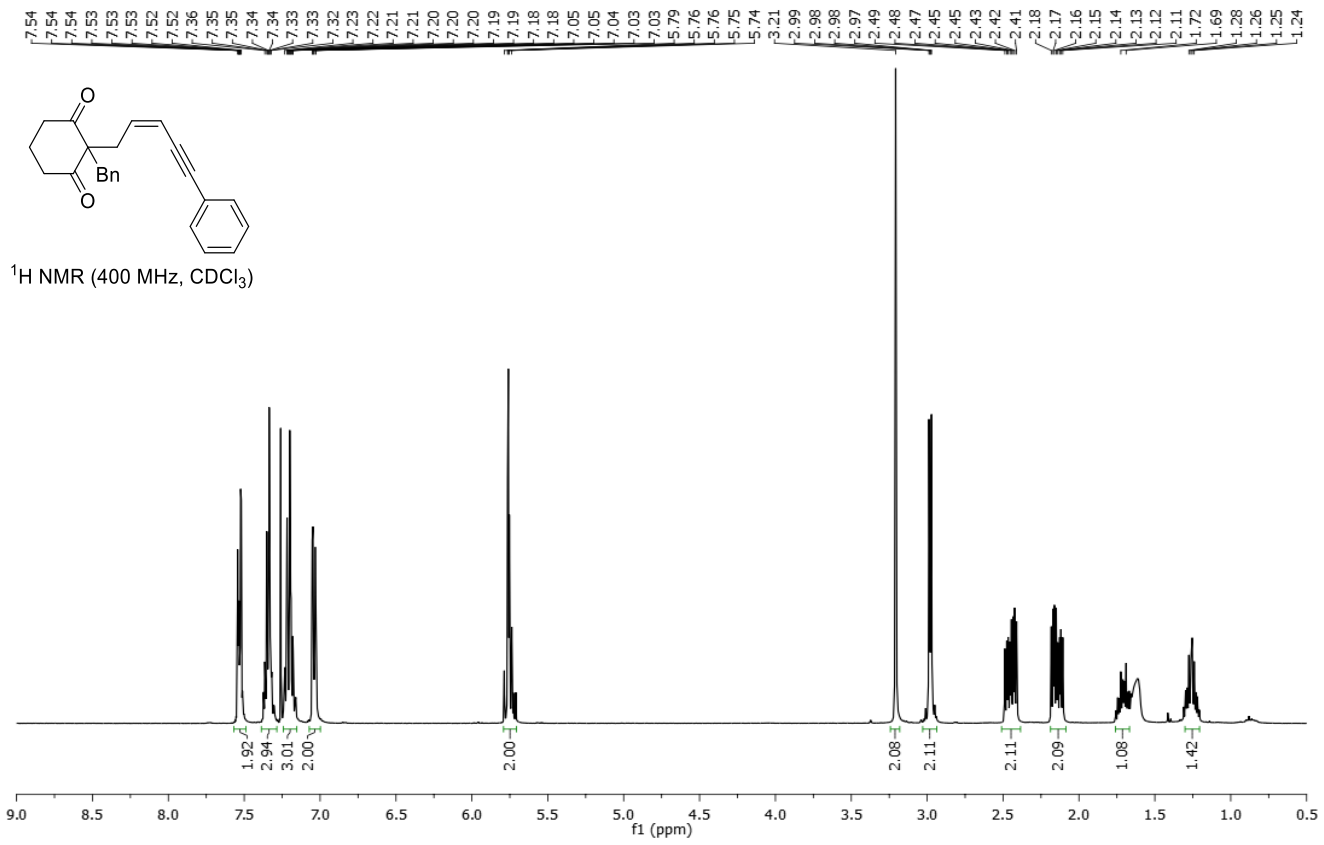


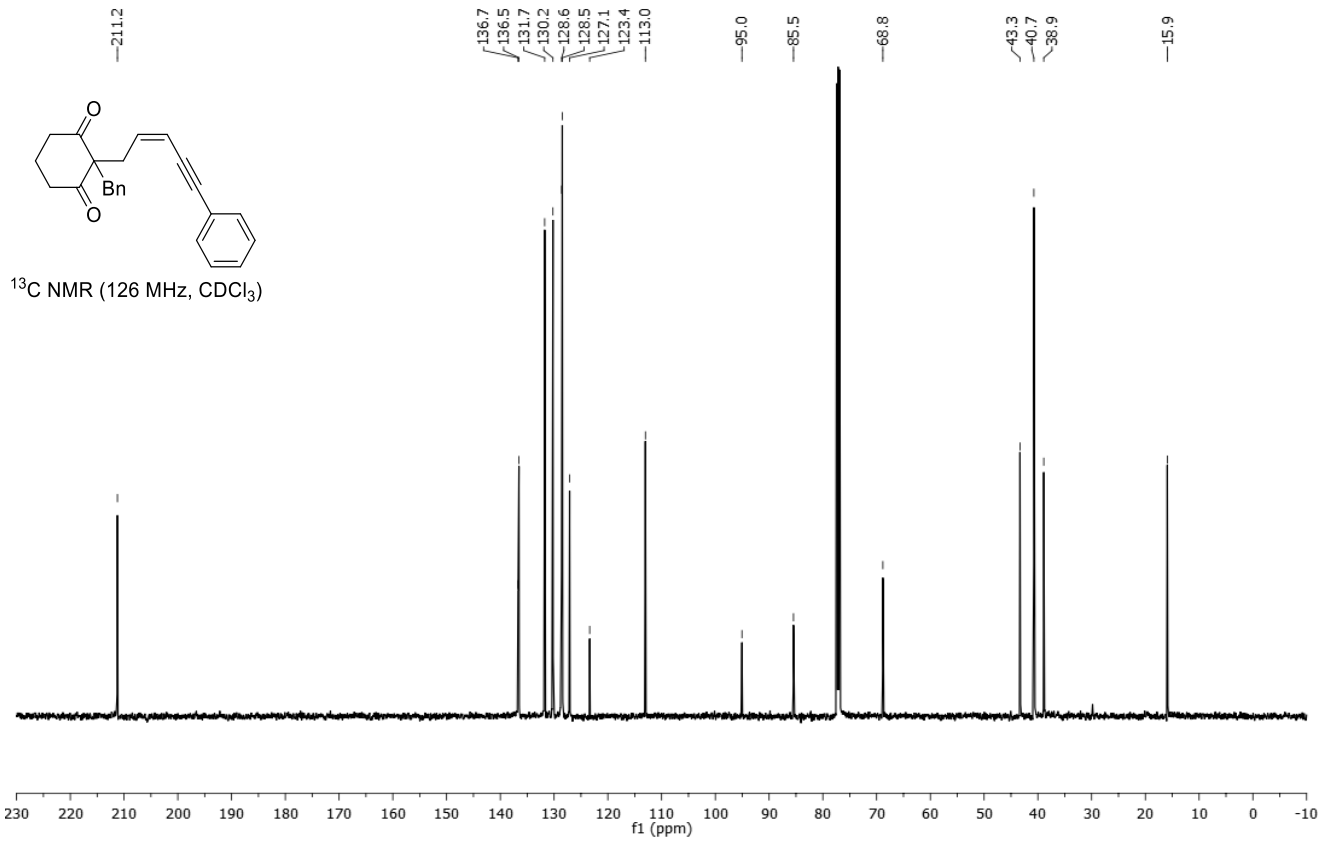
^{1}H NMR (400 MHz, $CDCl_3$)



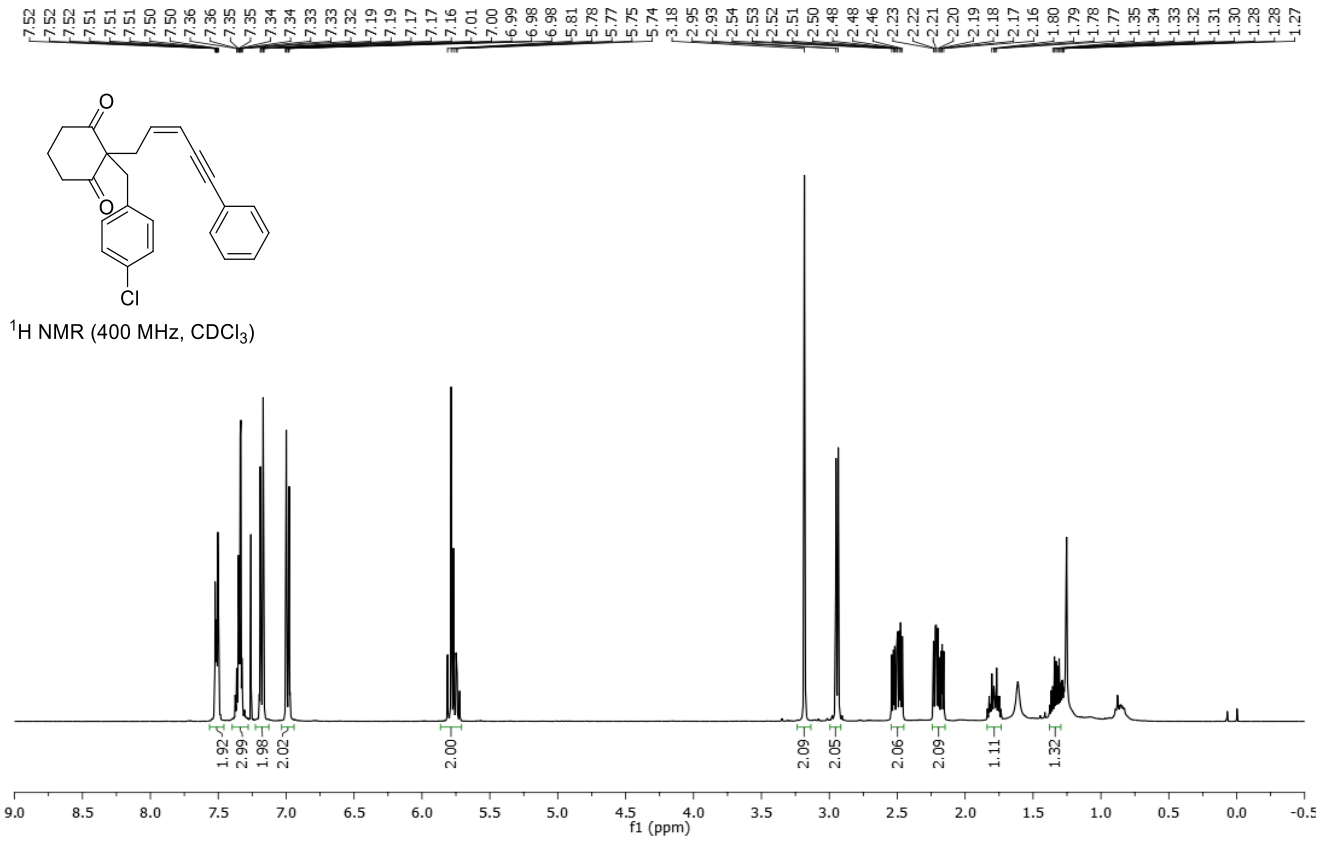
^{13}C NMR (126 MHz, $CDCl_3$)

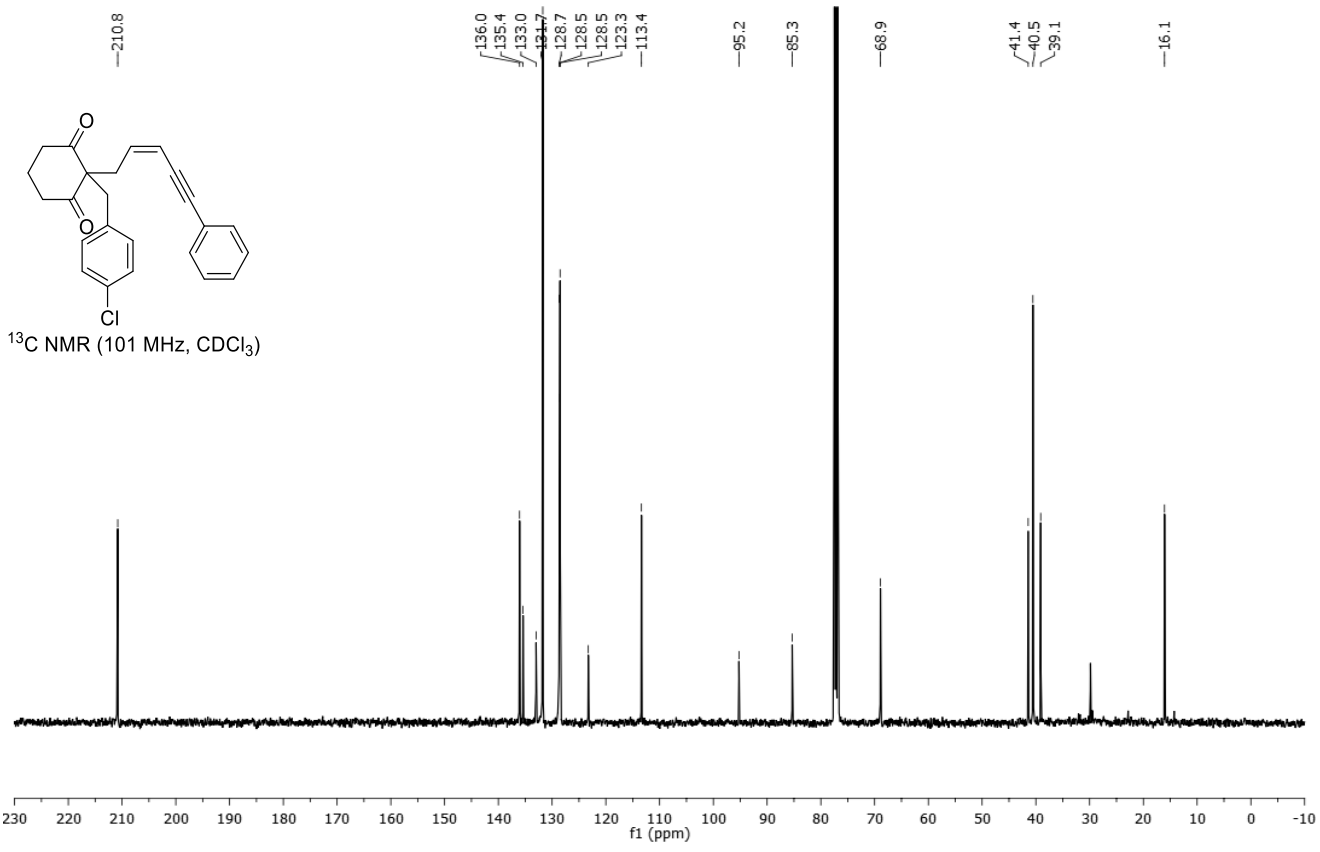
((Z)-2-Benzyl-2-(5-phenylpent-2-en-4-yn-1-yl)cyclohexane-1,3-dione (1ab):



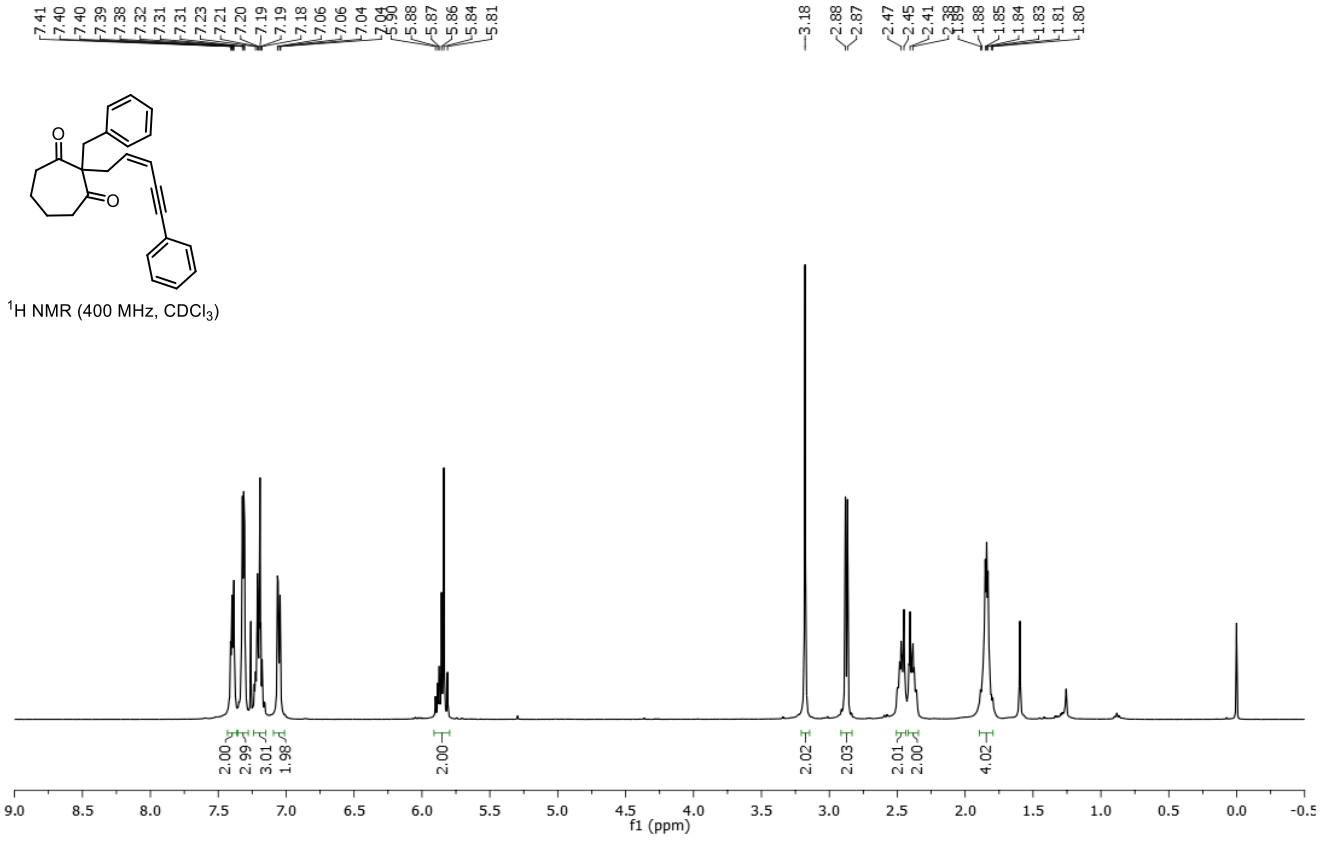


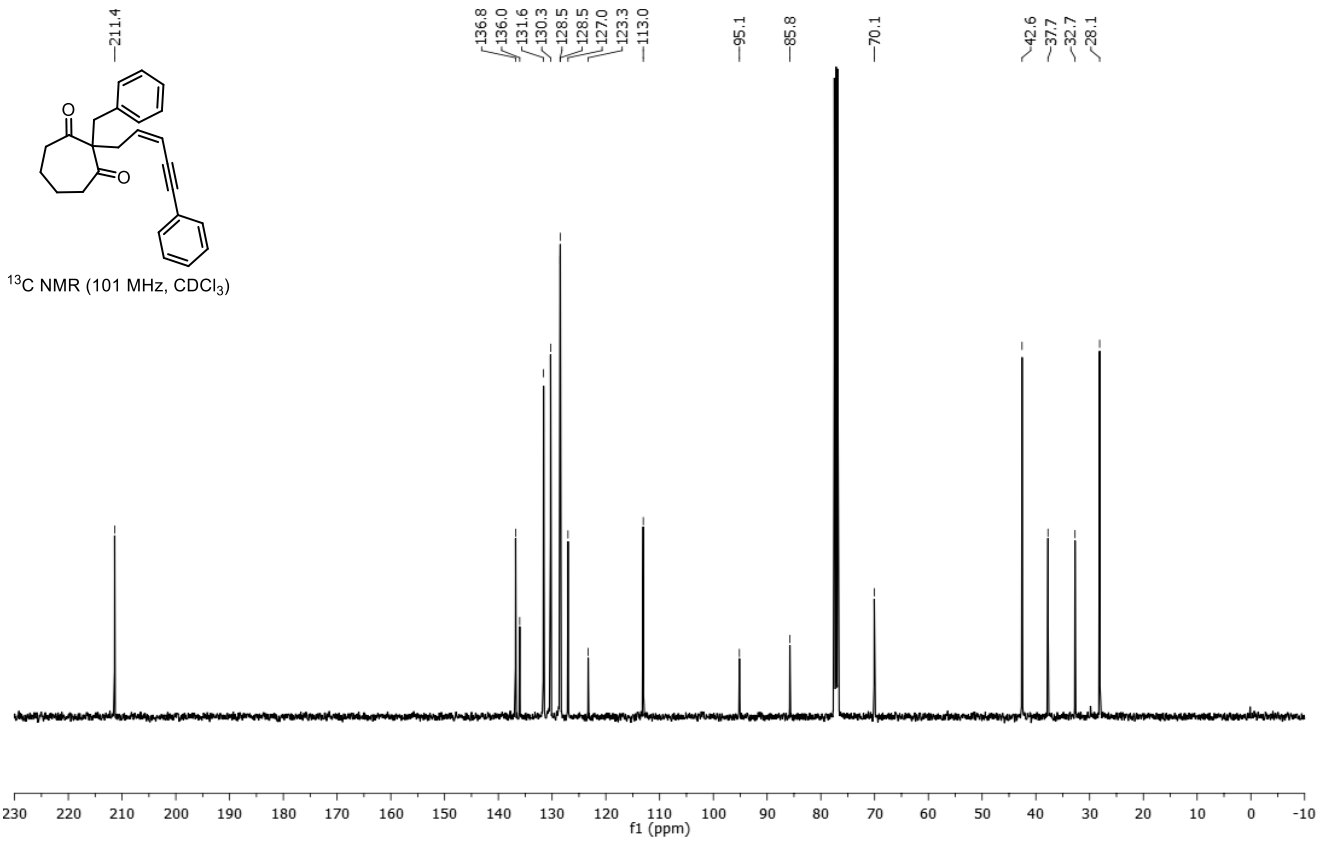
(*Z*)-2-(4-Chlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)cyclohexane-1,3-dione (1ac):



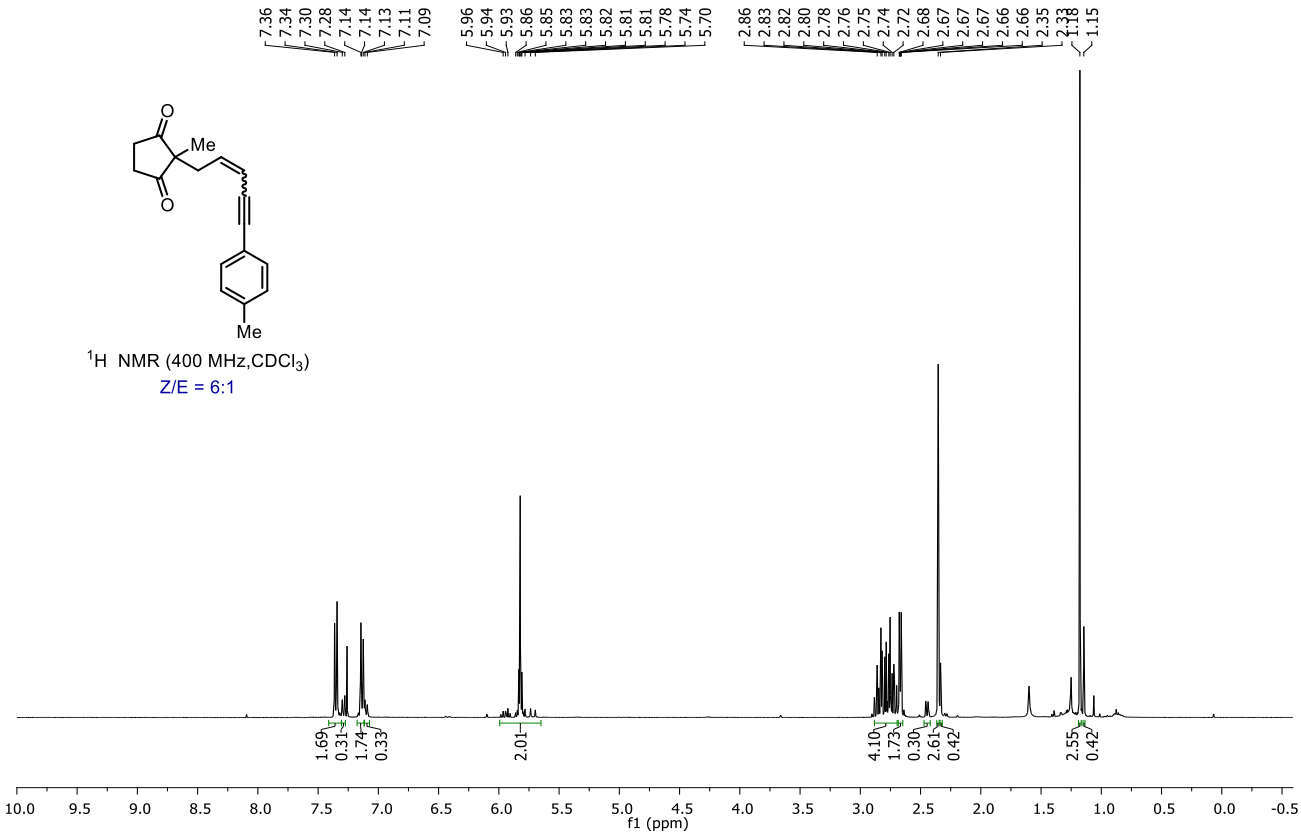


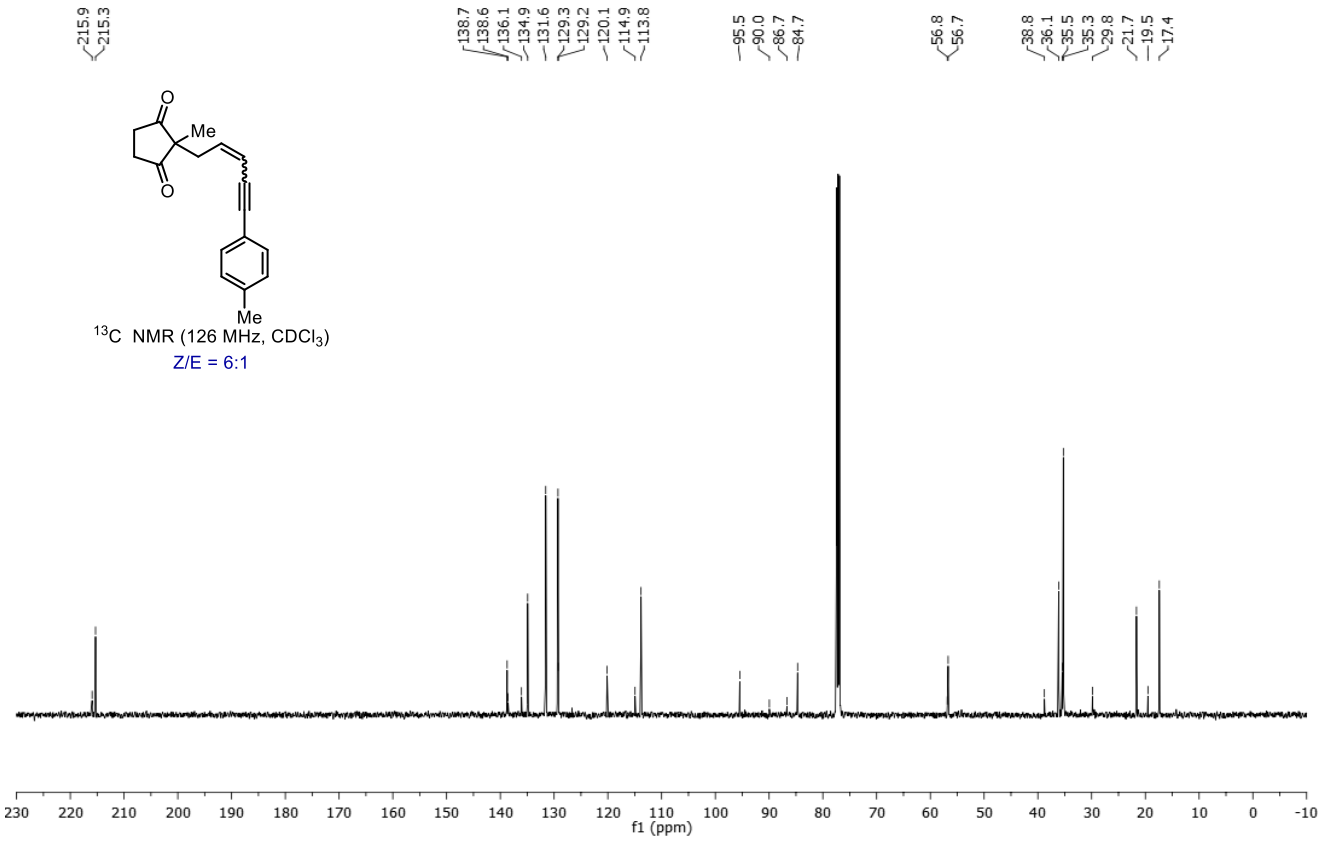
(*Z*)-2-Benzyl-2-(5-phenylpent-2-en-4-yn-1-yl)cycloheptane-1,3-dione (1ad):



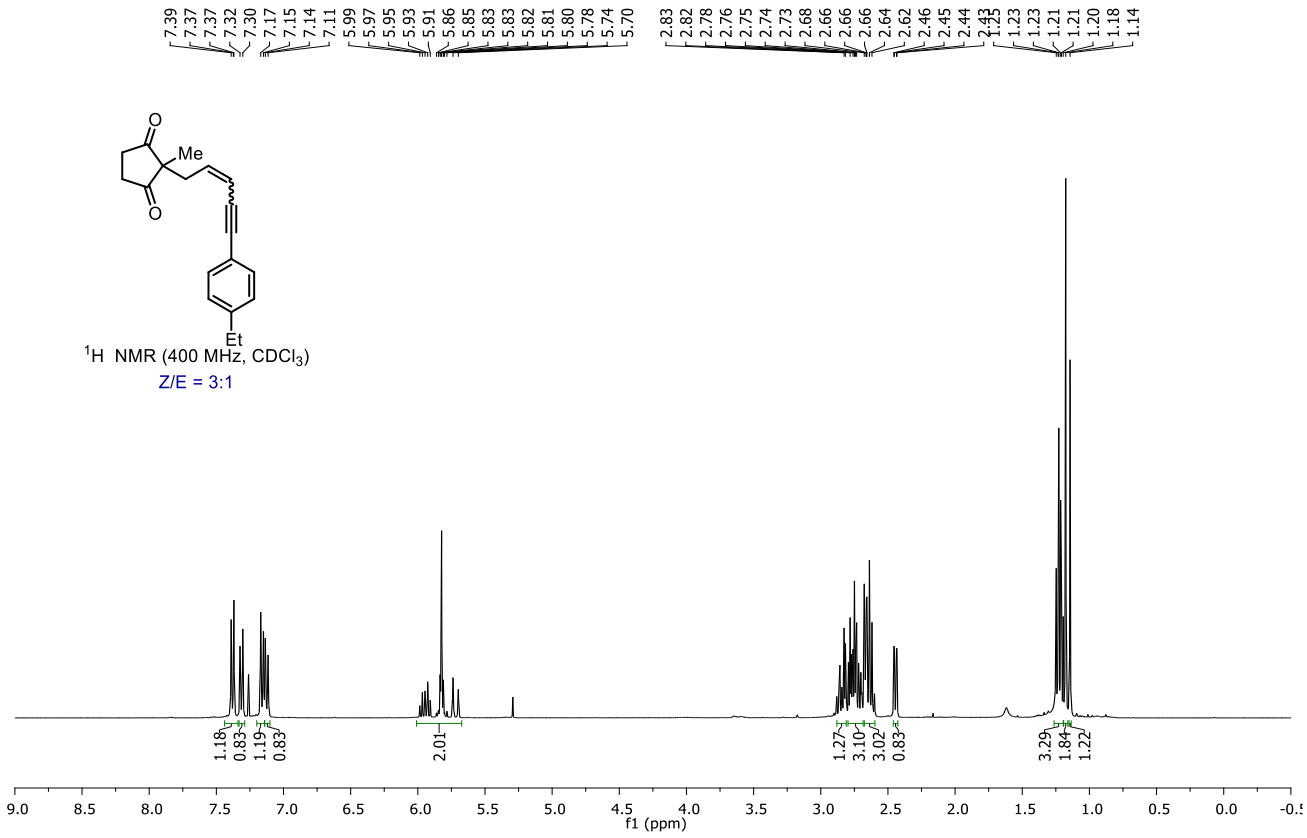


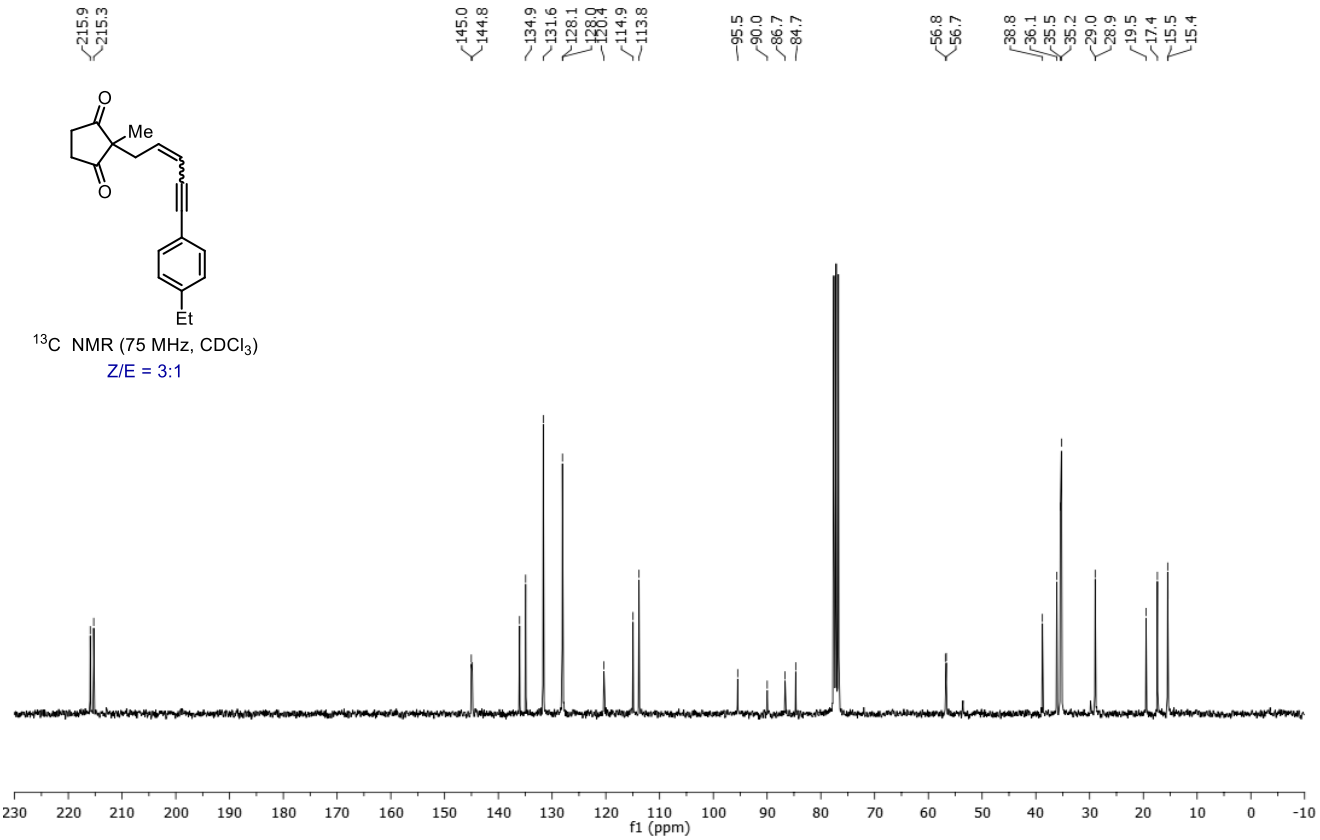
2-Methyl-2-(5-(p-tolyl)pent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1ae):



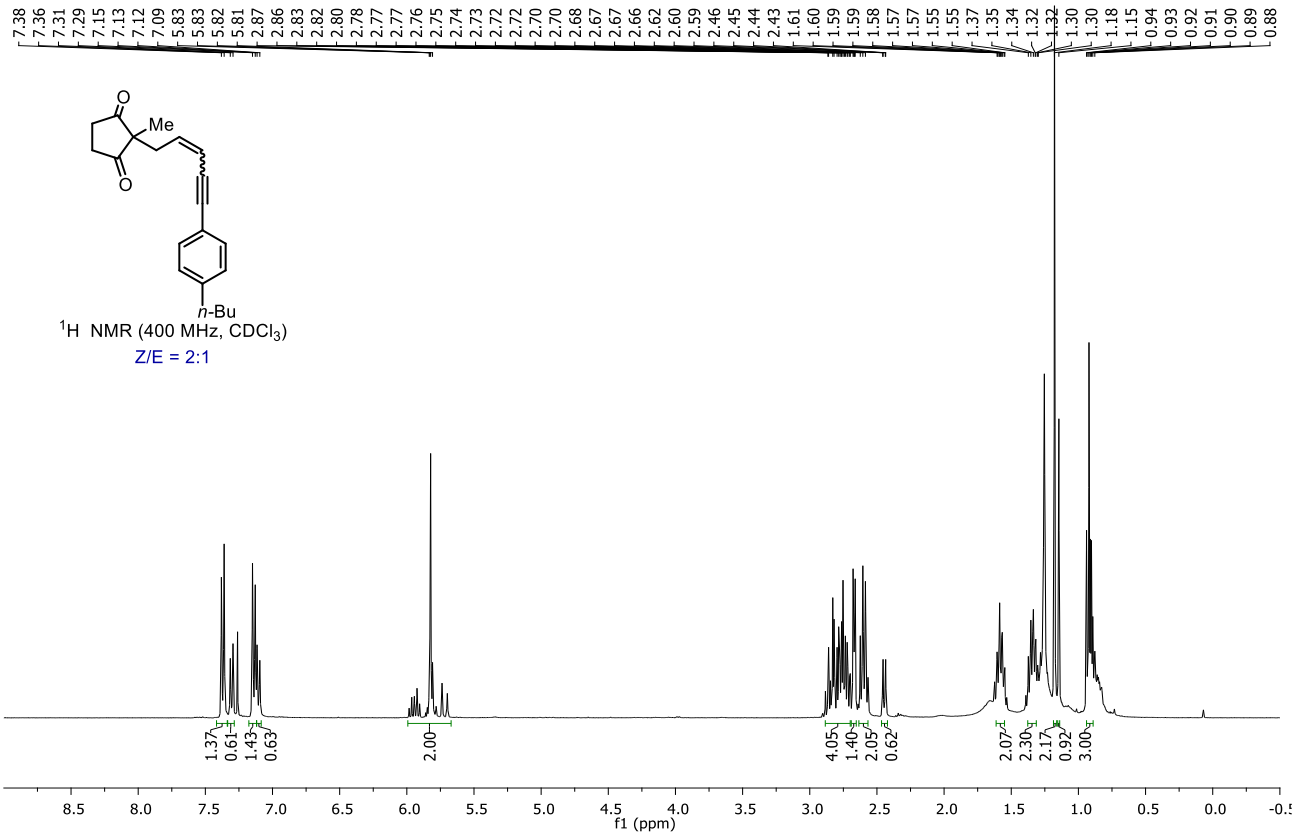


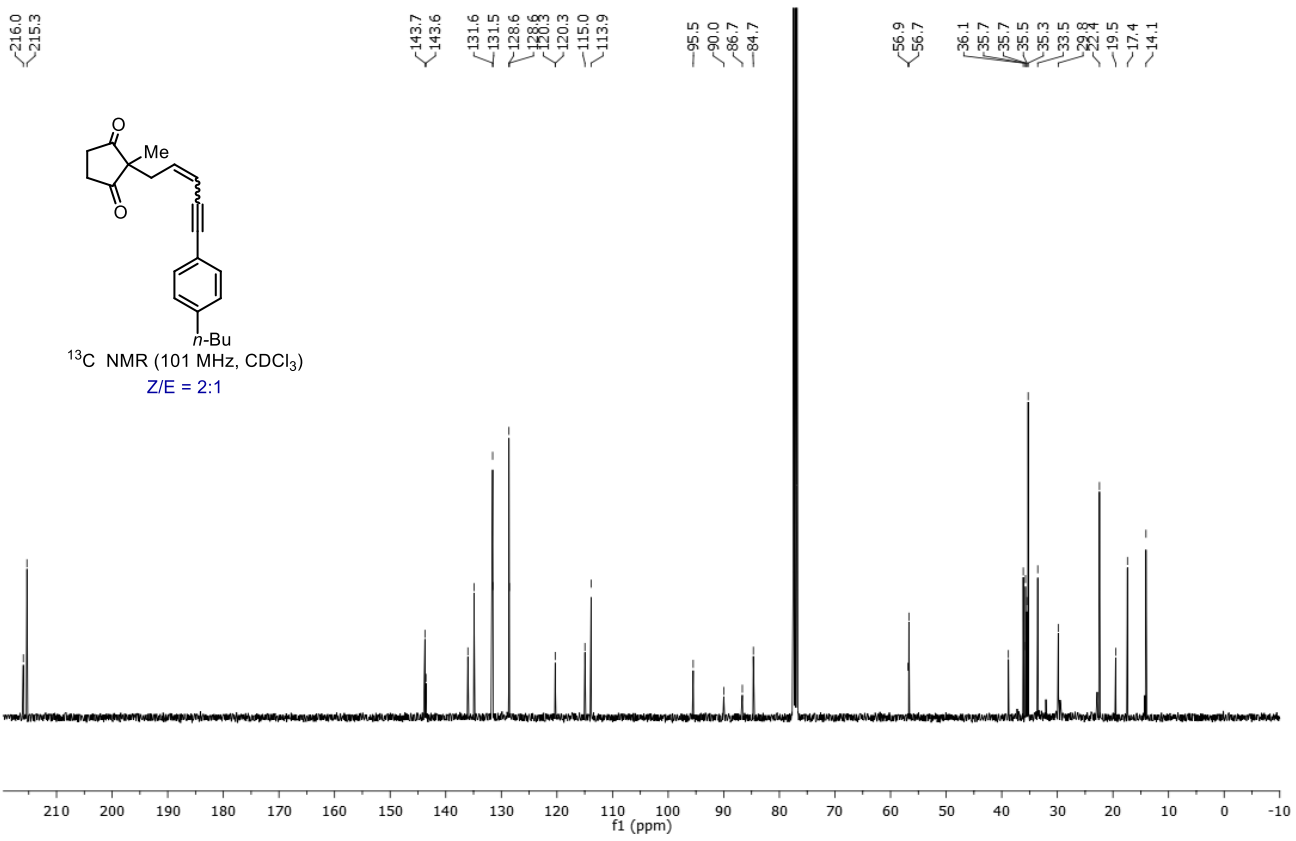
2-(5-(4-Ethylphenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1af):



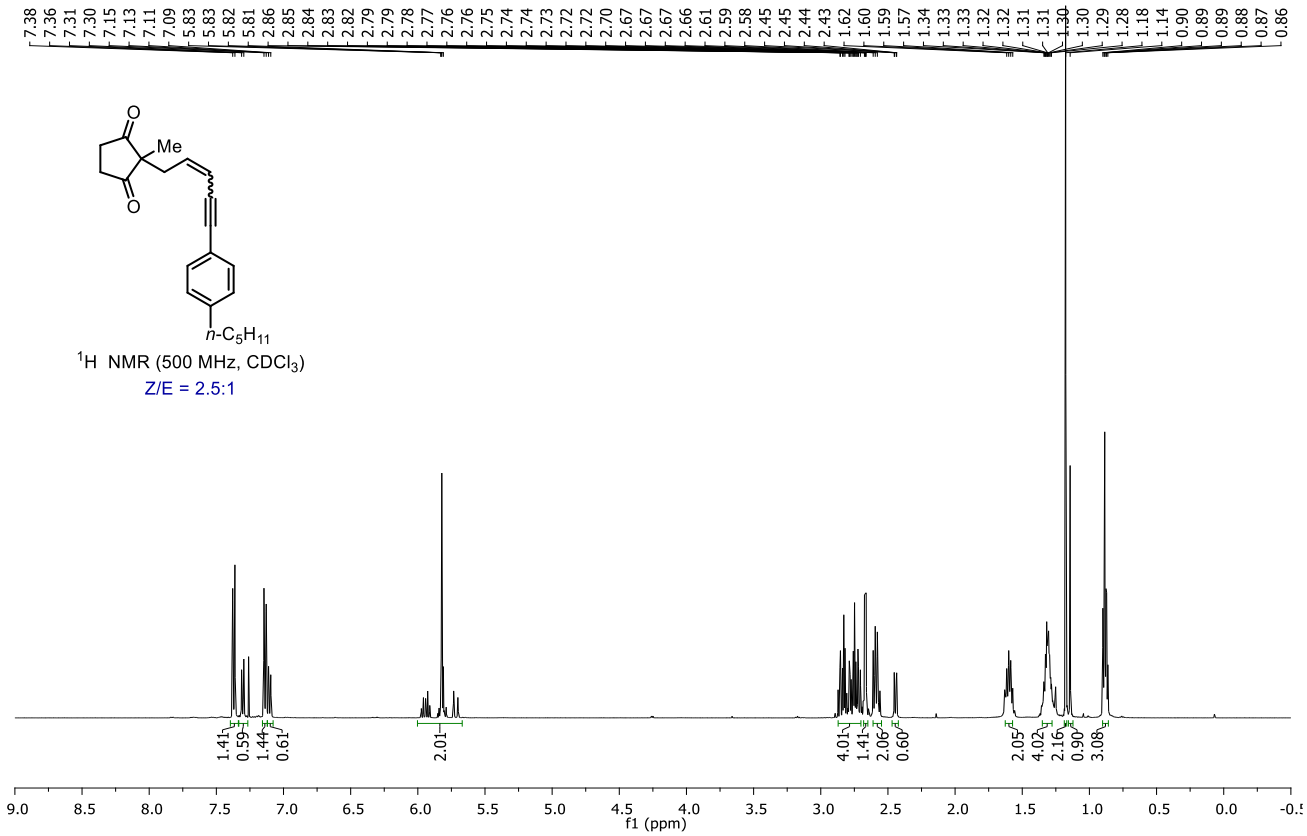


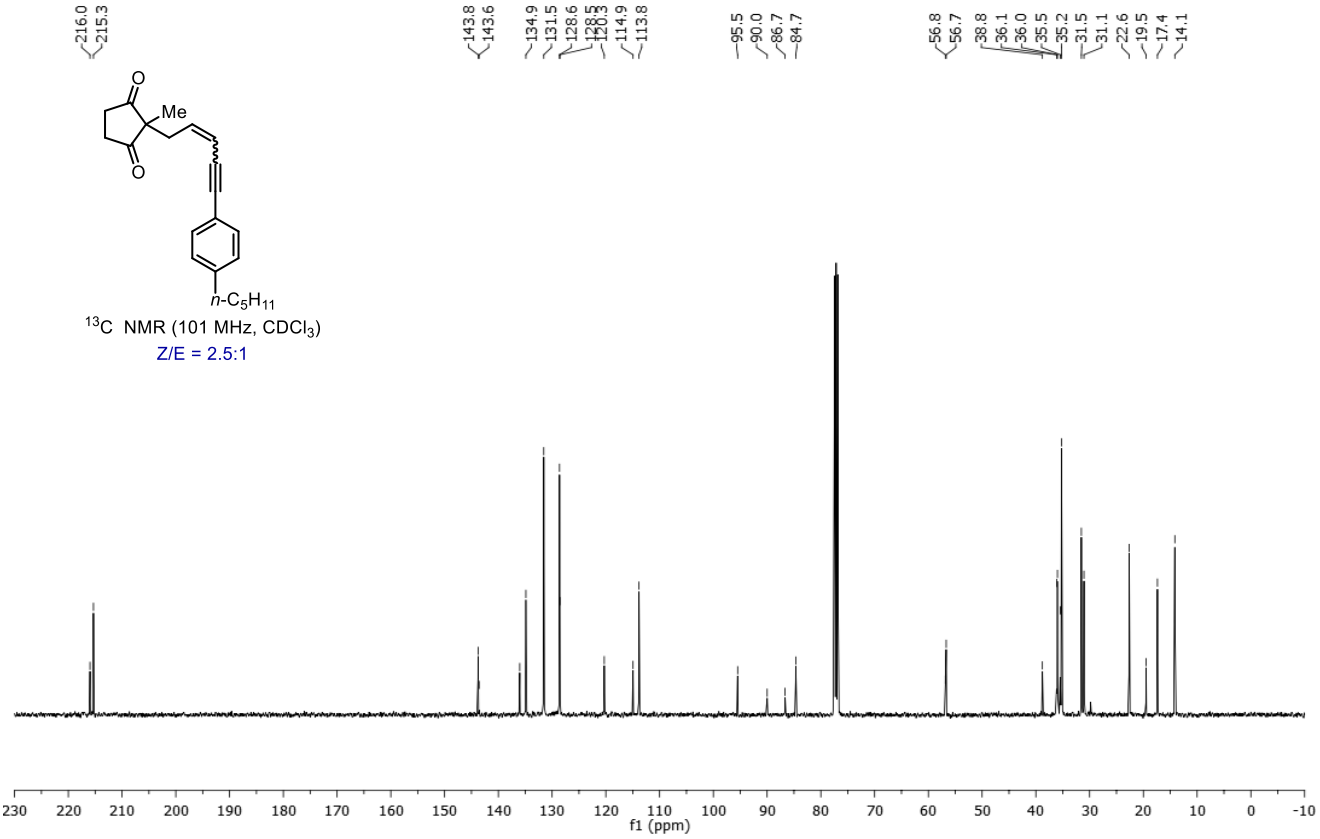
2-(5-(4-Butylphenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1ag):



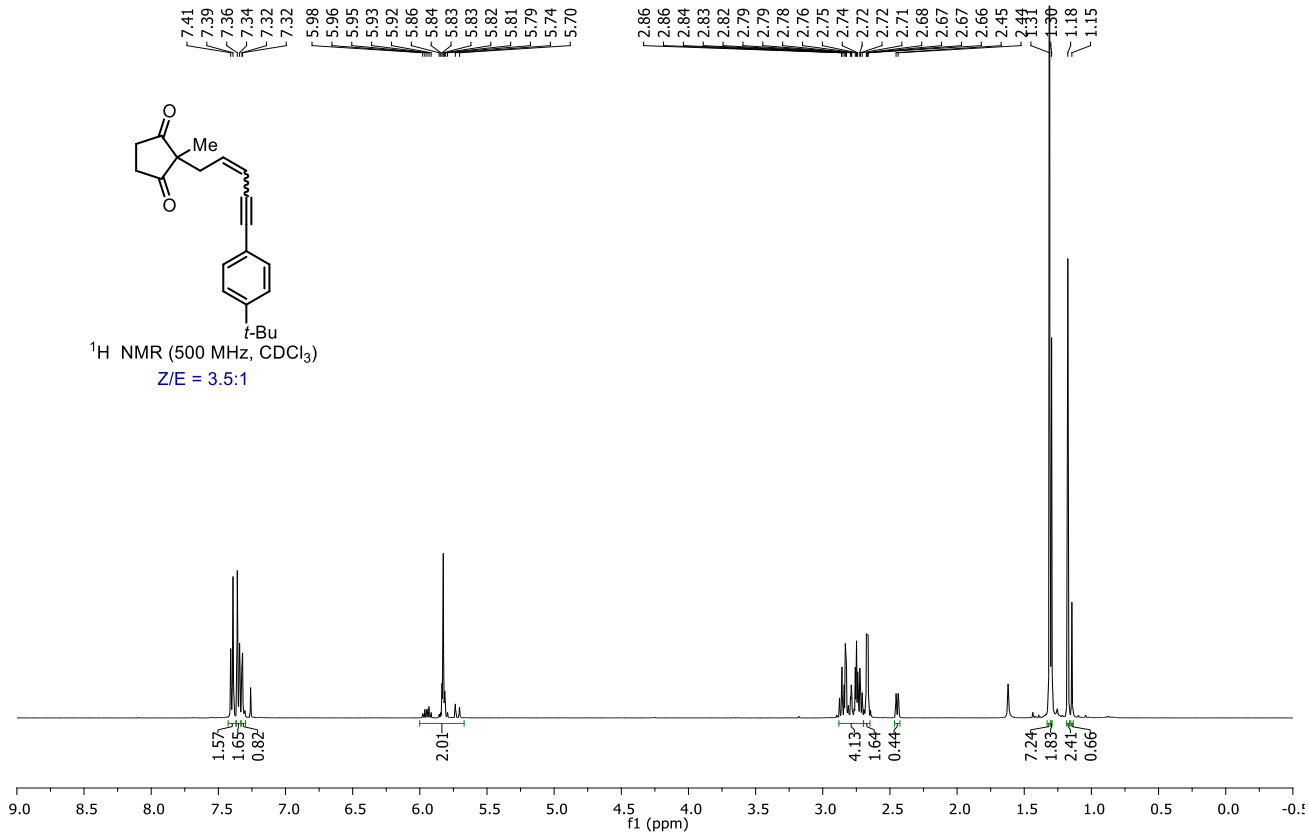


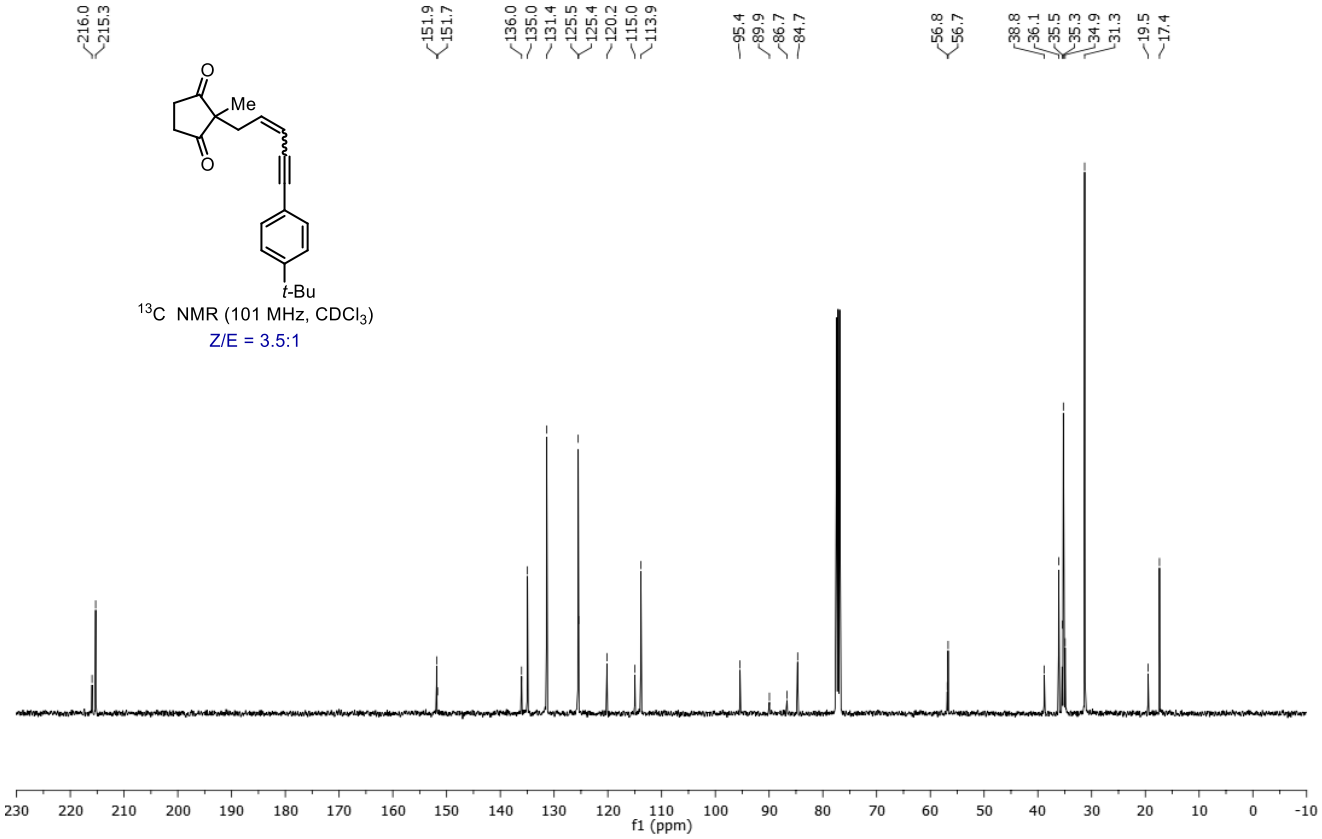
2-Methyl-2-(5-(4-pentylphenyl)pent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1ah):



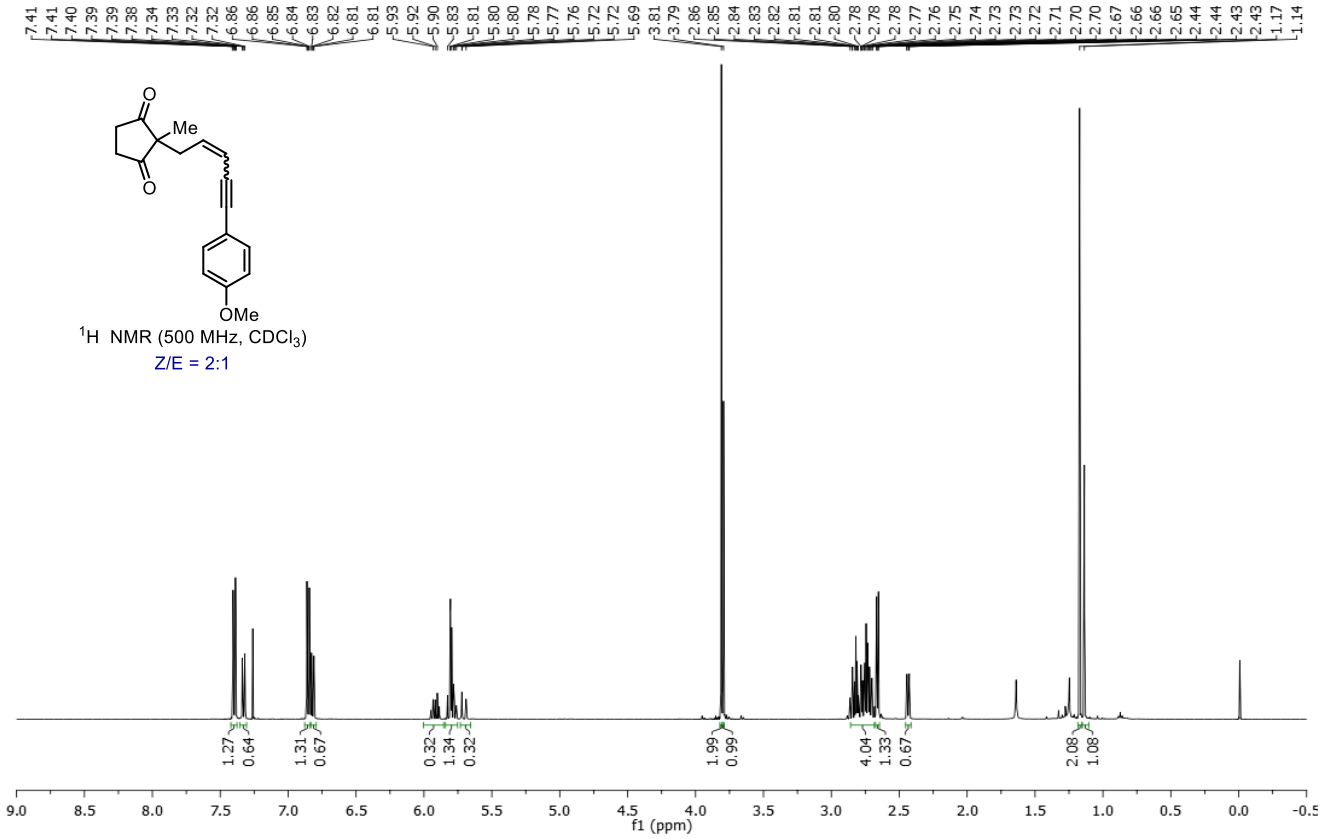


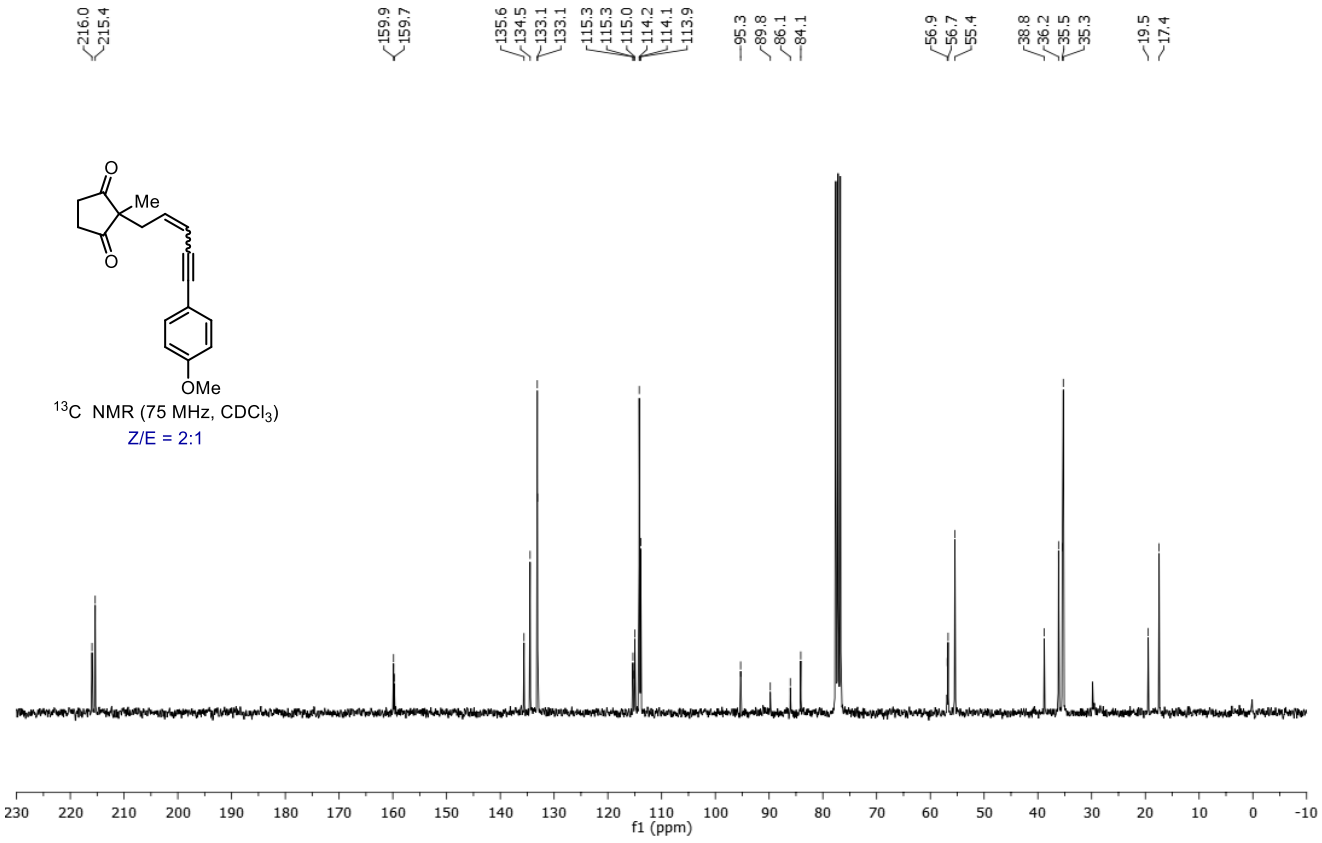
2-(5-(4-(tert-Butyl)phenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1ai):



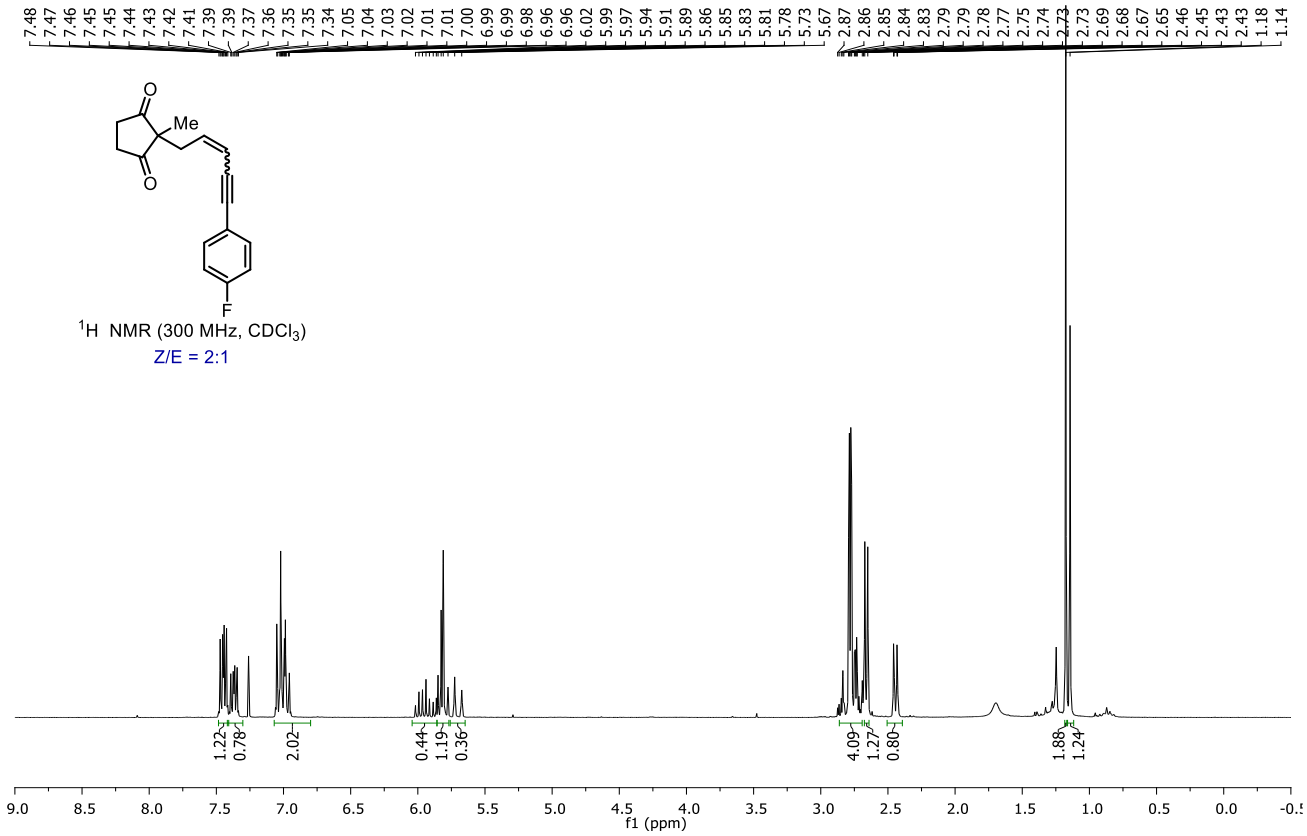


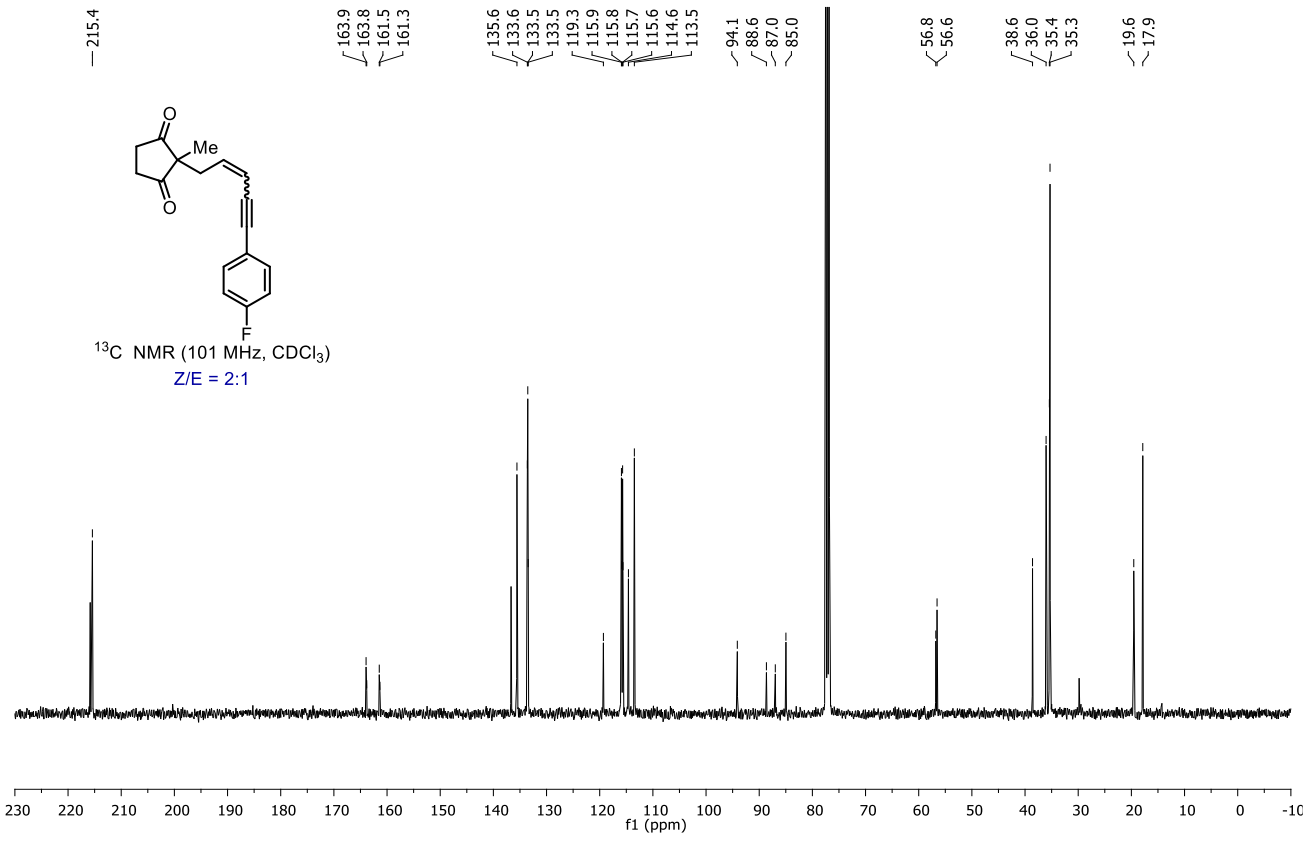
2-(5-(4-Methoxyphenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1aj):



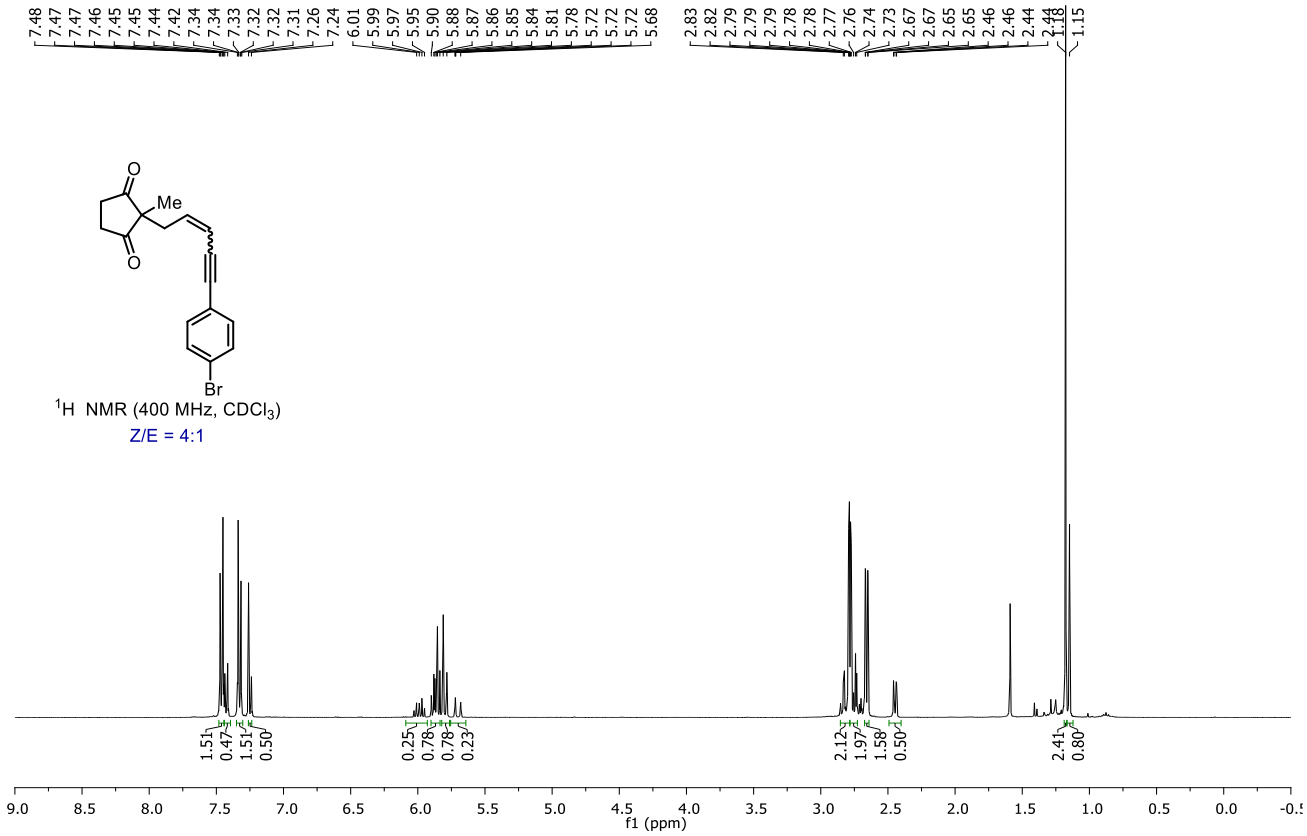


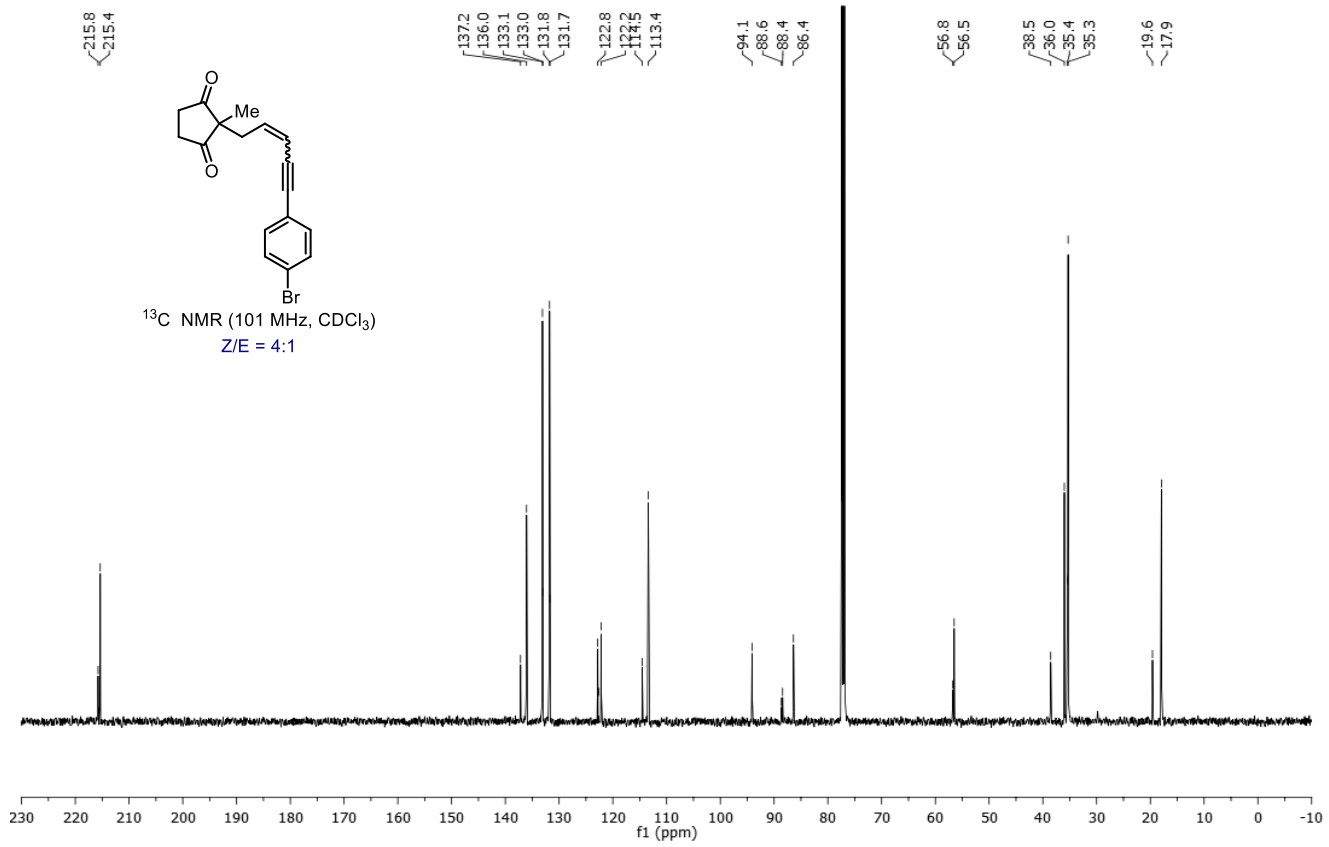
2-(5-(4-Fluorophenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1ak):



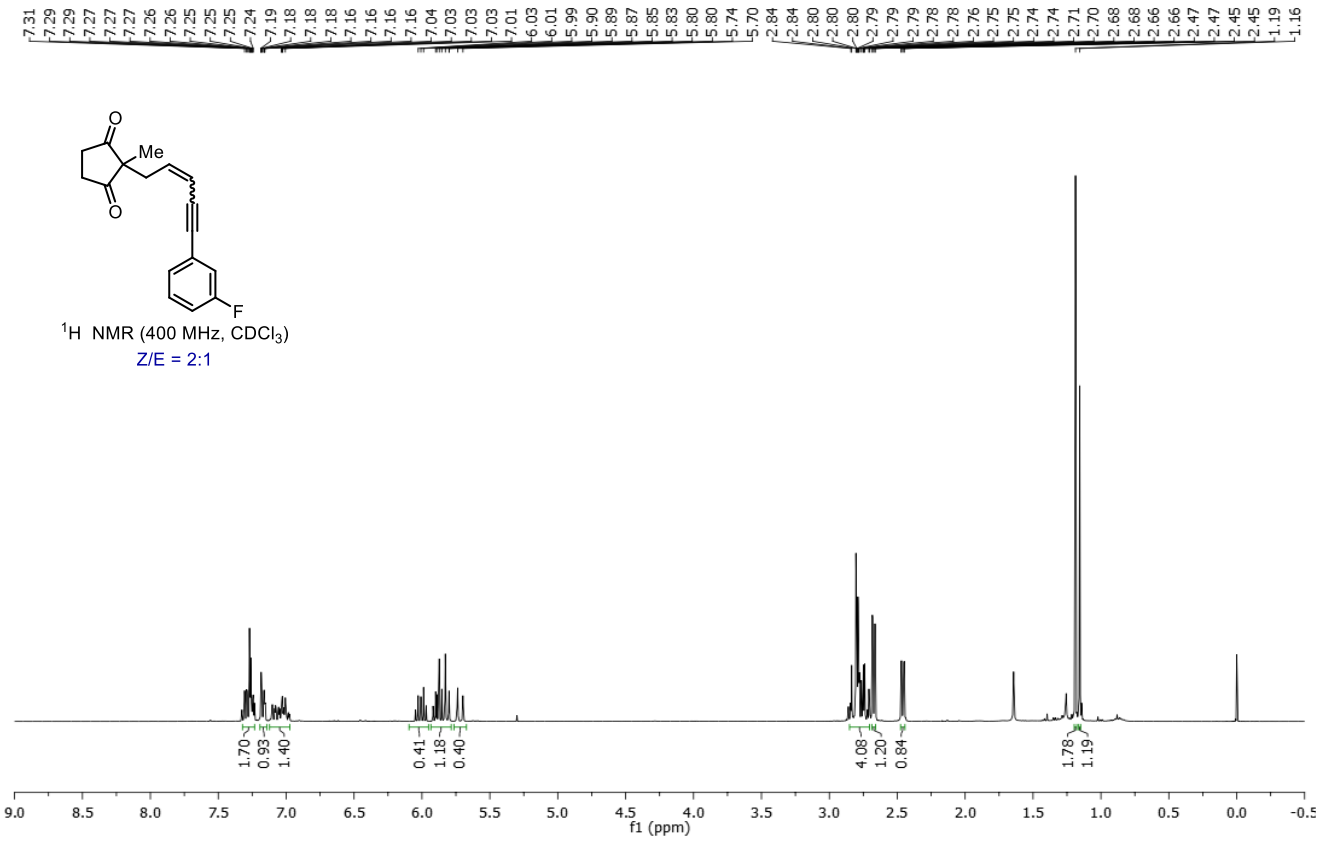


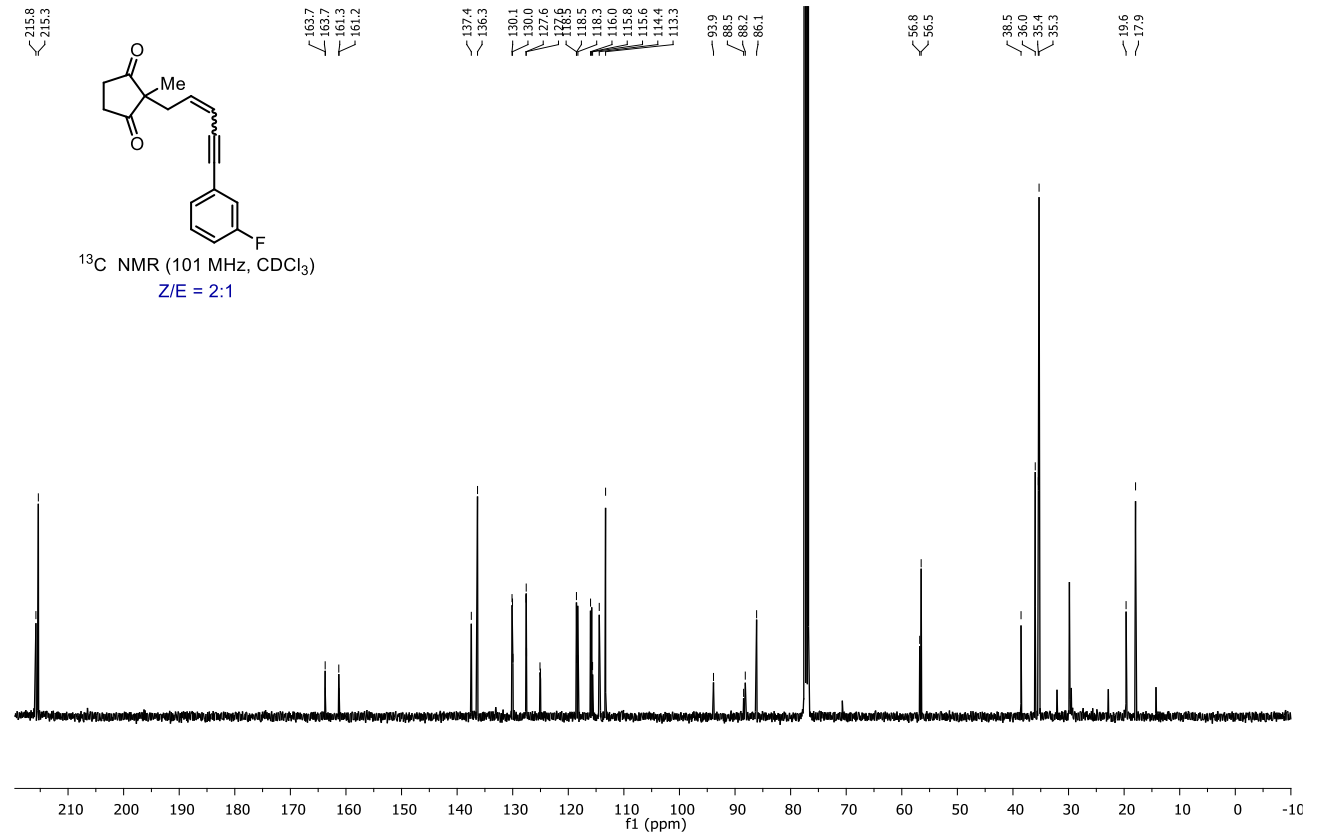
2-(5-(4-(*tert*-Butyl)phenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1al):

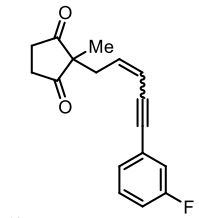




2-(5-(3-Fluorophenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1am):



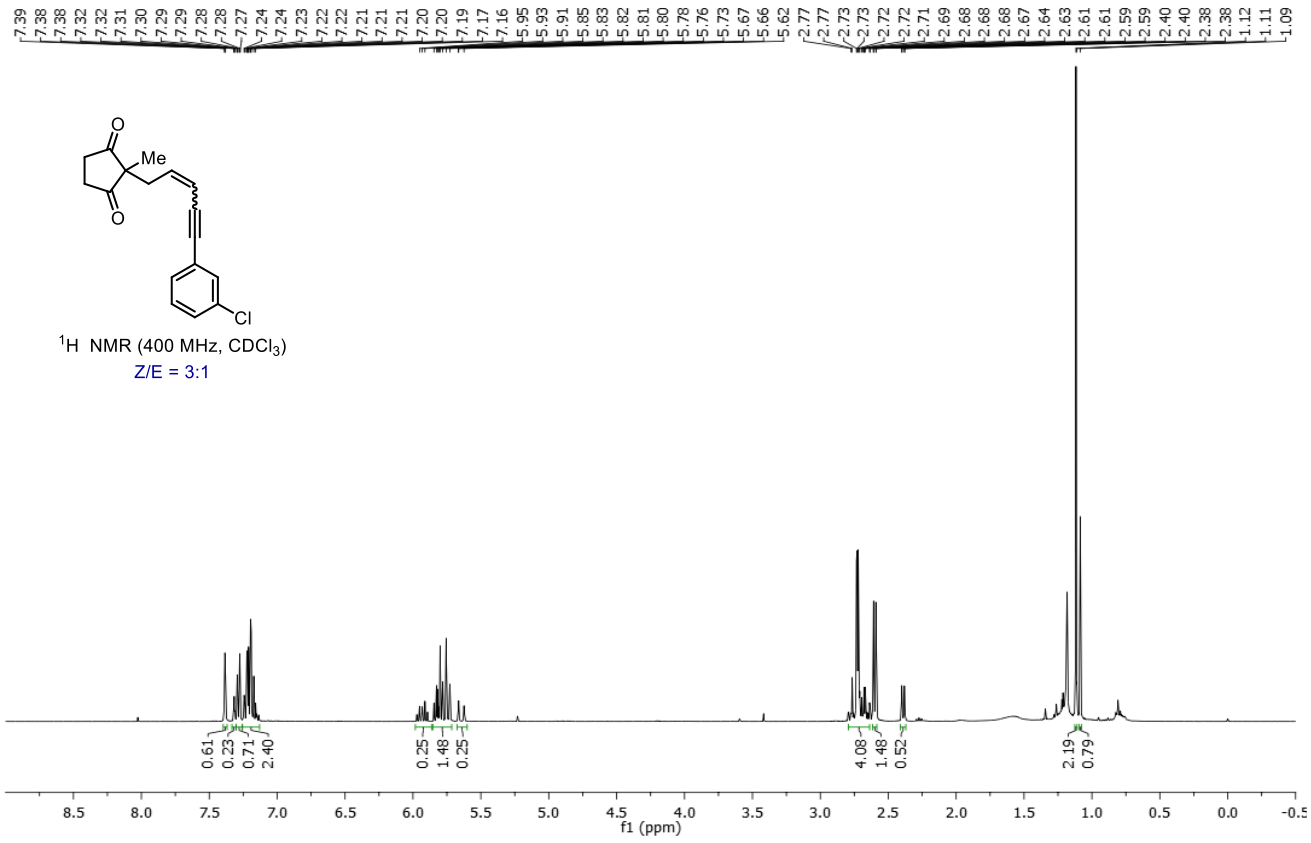


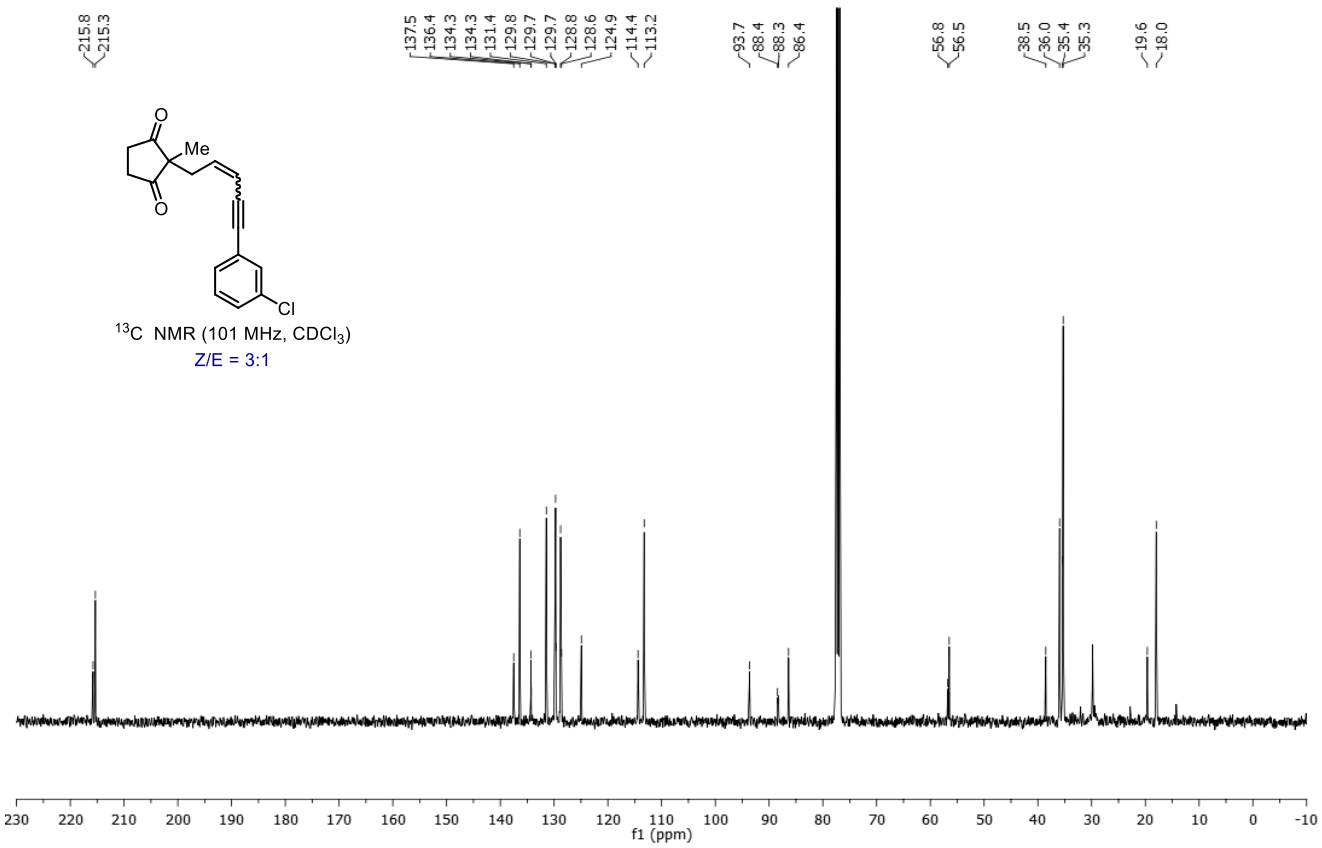


^{19}F NMR (376 MHz, $CDCl_3$)

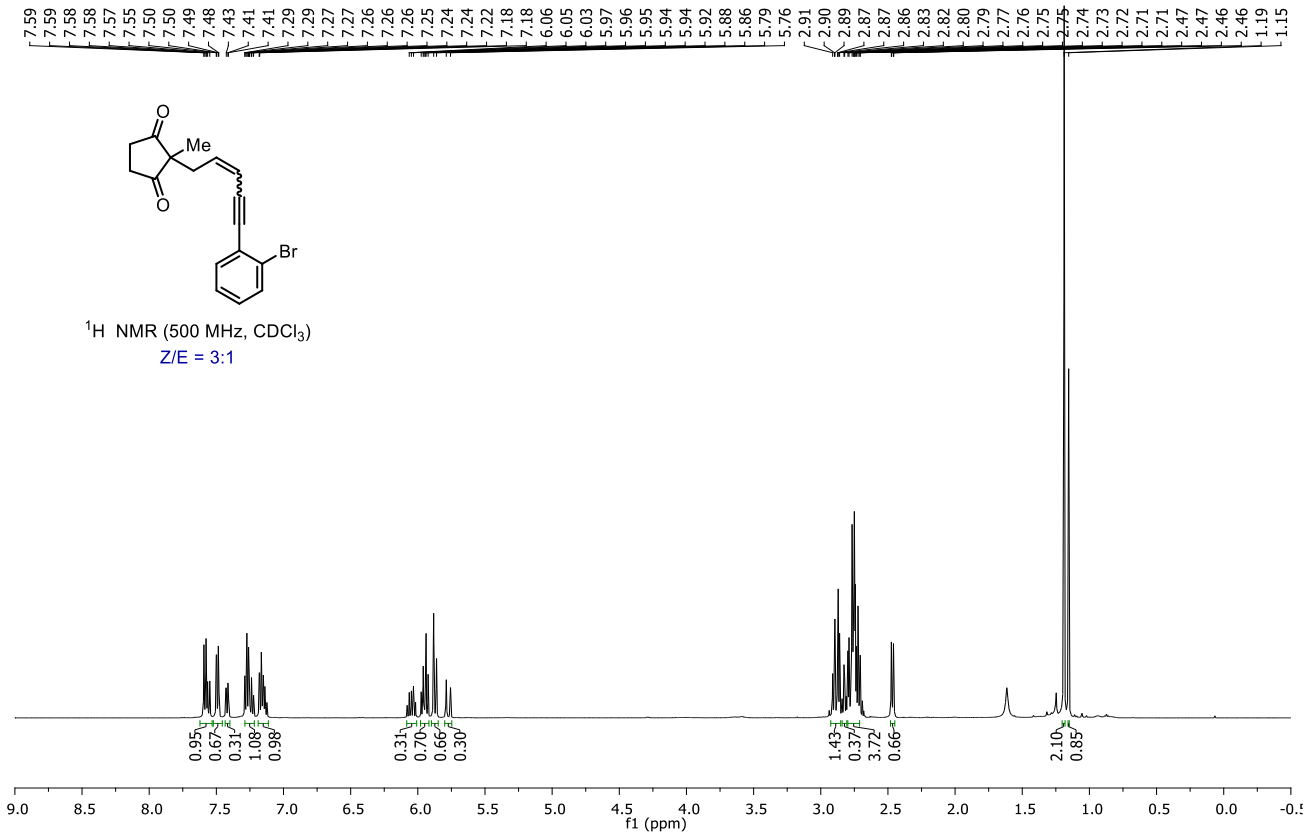
Z/E = 2:1

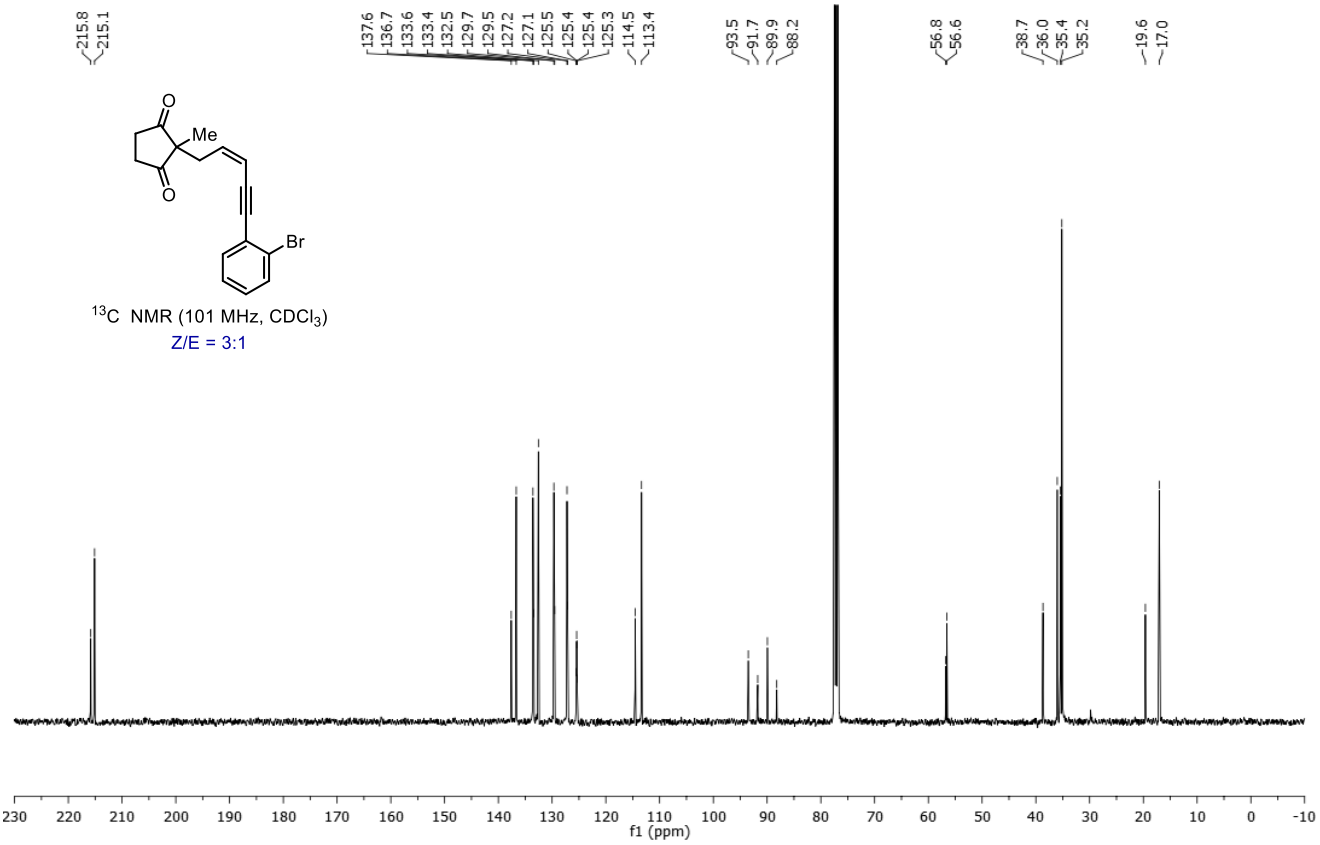
2-(5-(3-Chlorophenyl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1an):



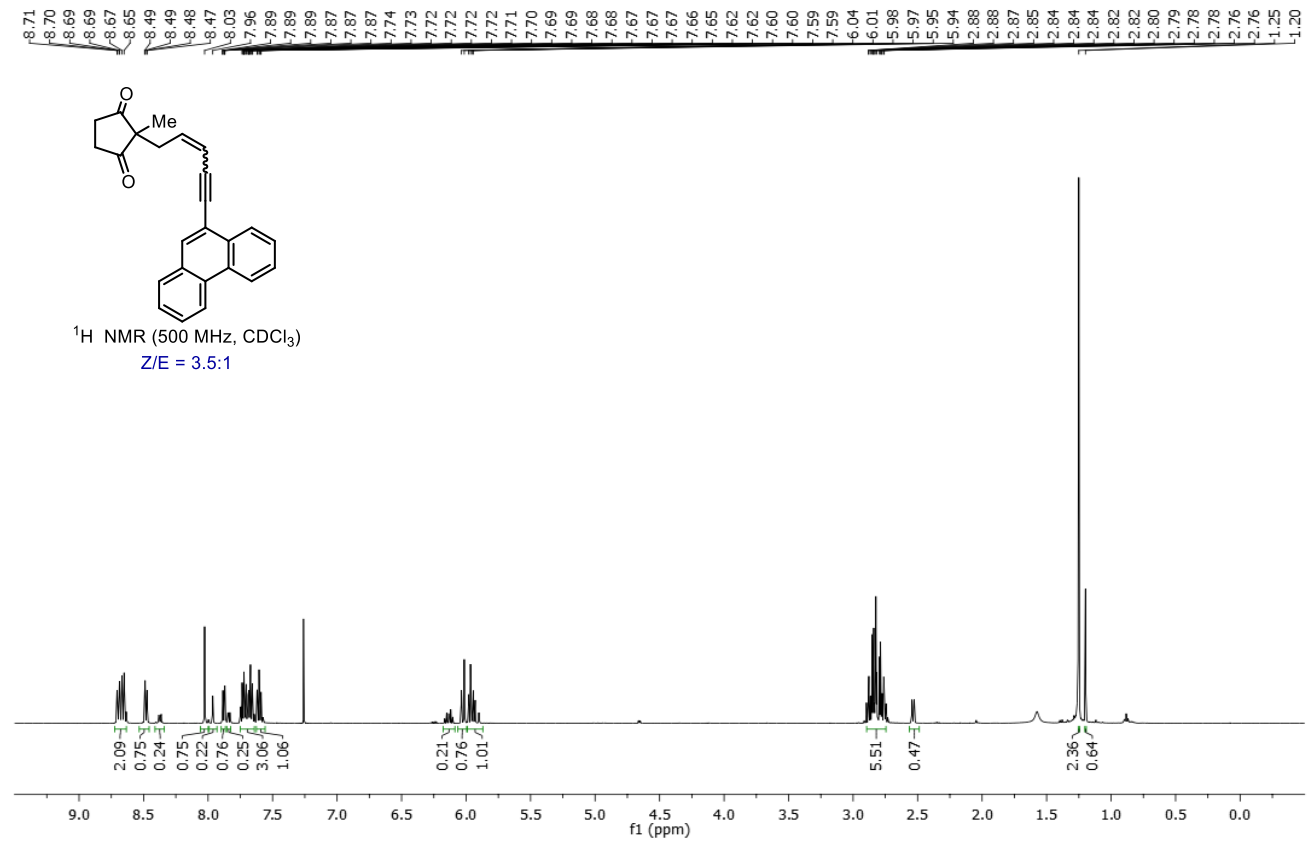


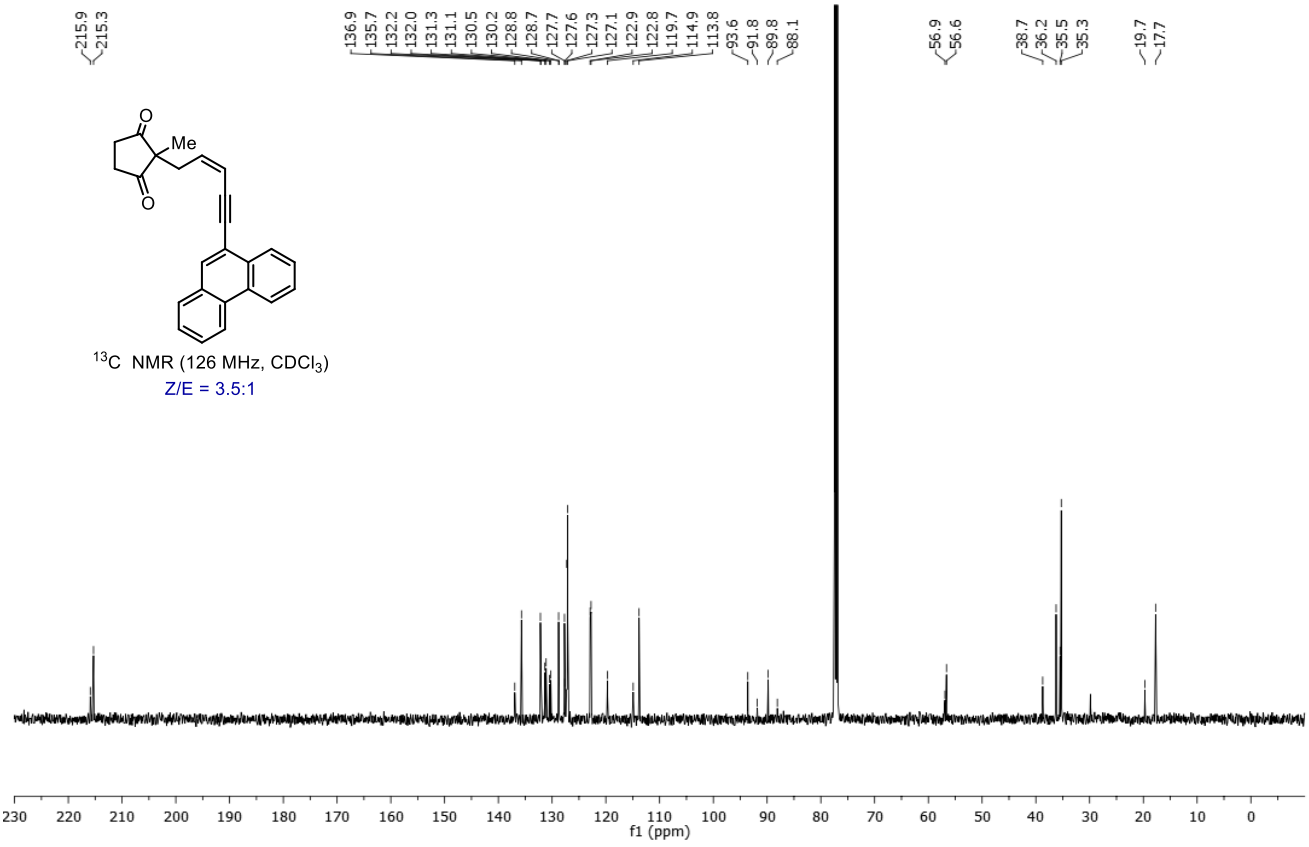
2-Methyl-2-(5-(p-tolyl)pent-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1ao):



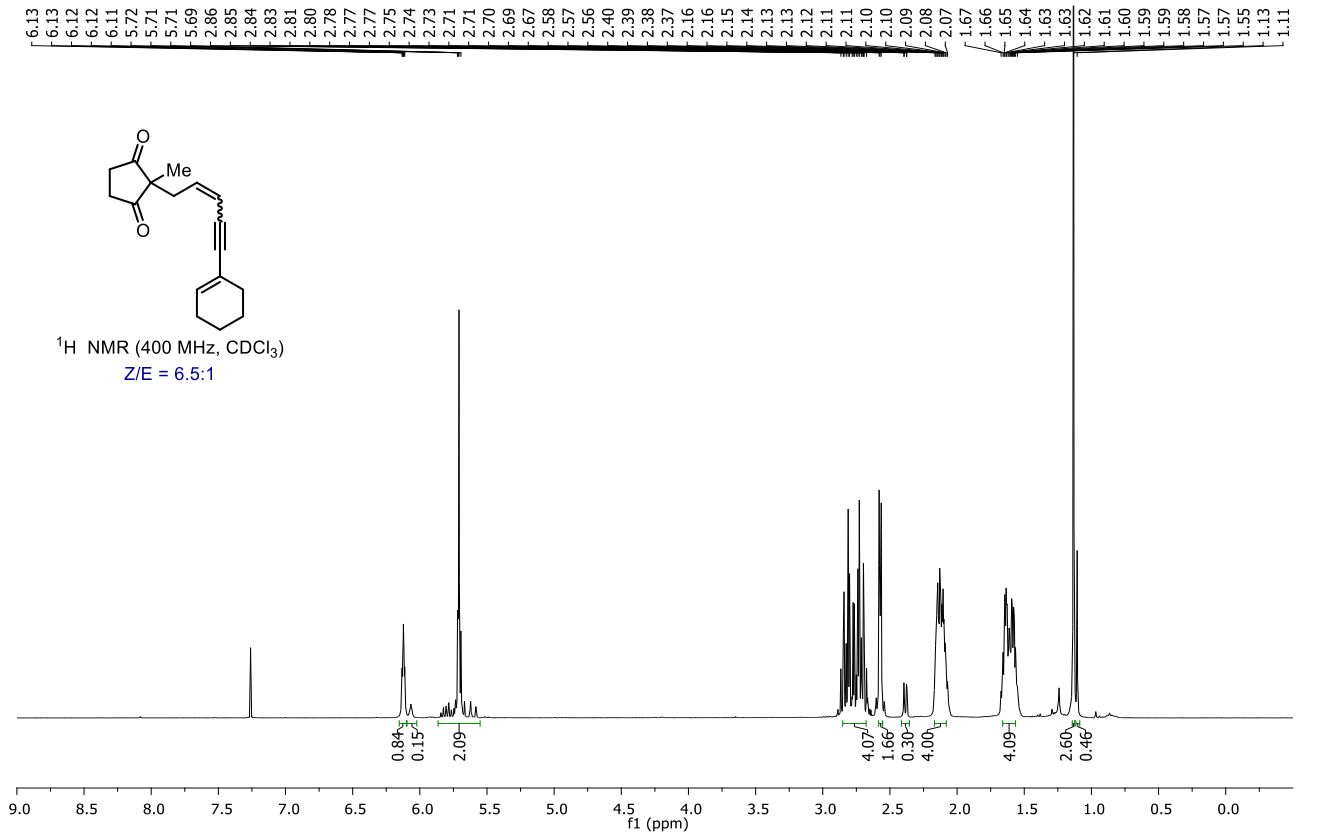


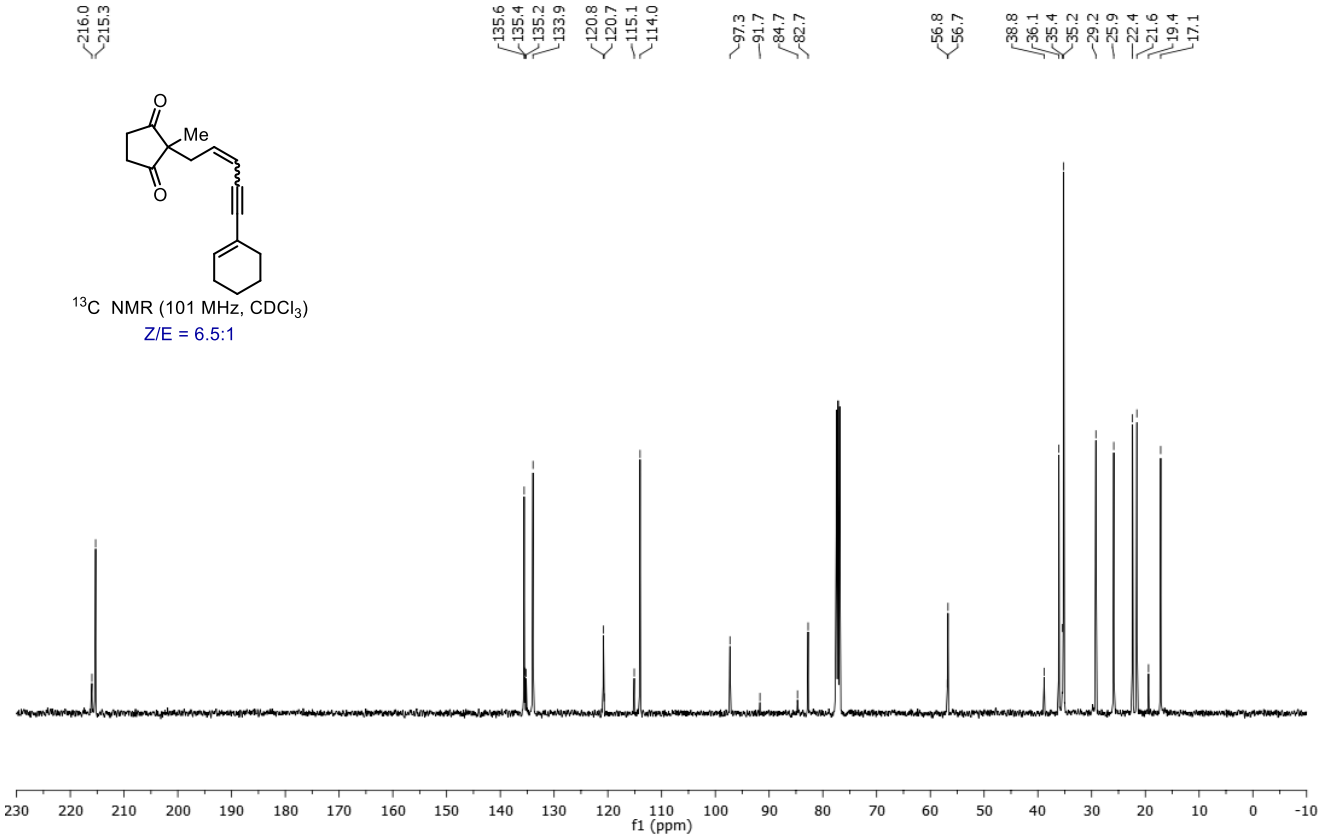
2-(5-(3a1H-Phenalen-2-yl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1ap):



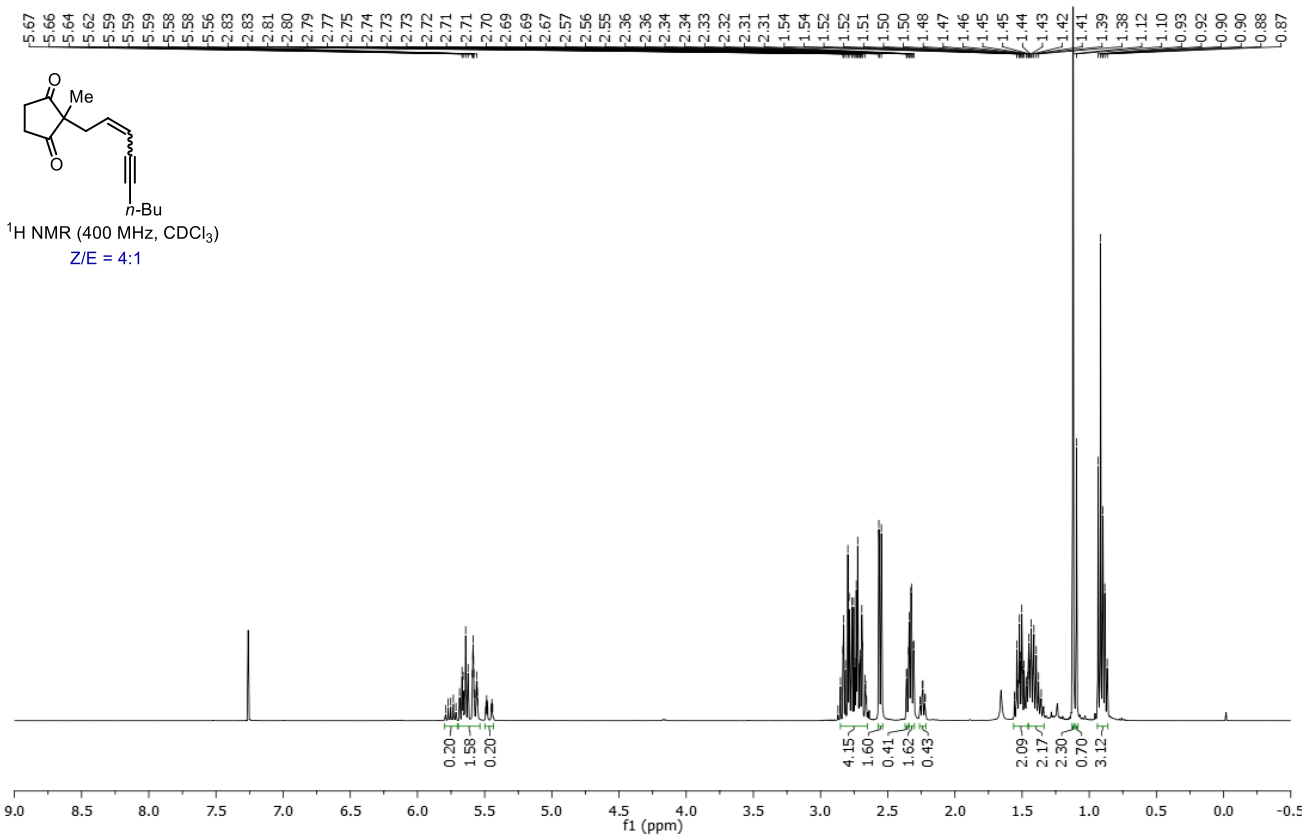


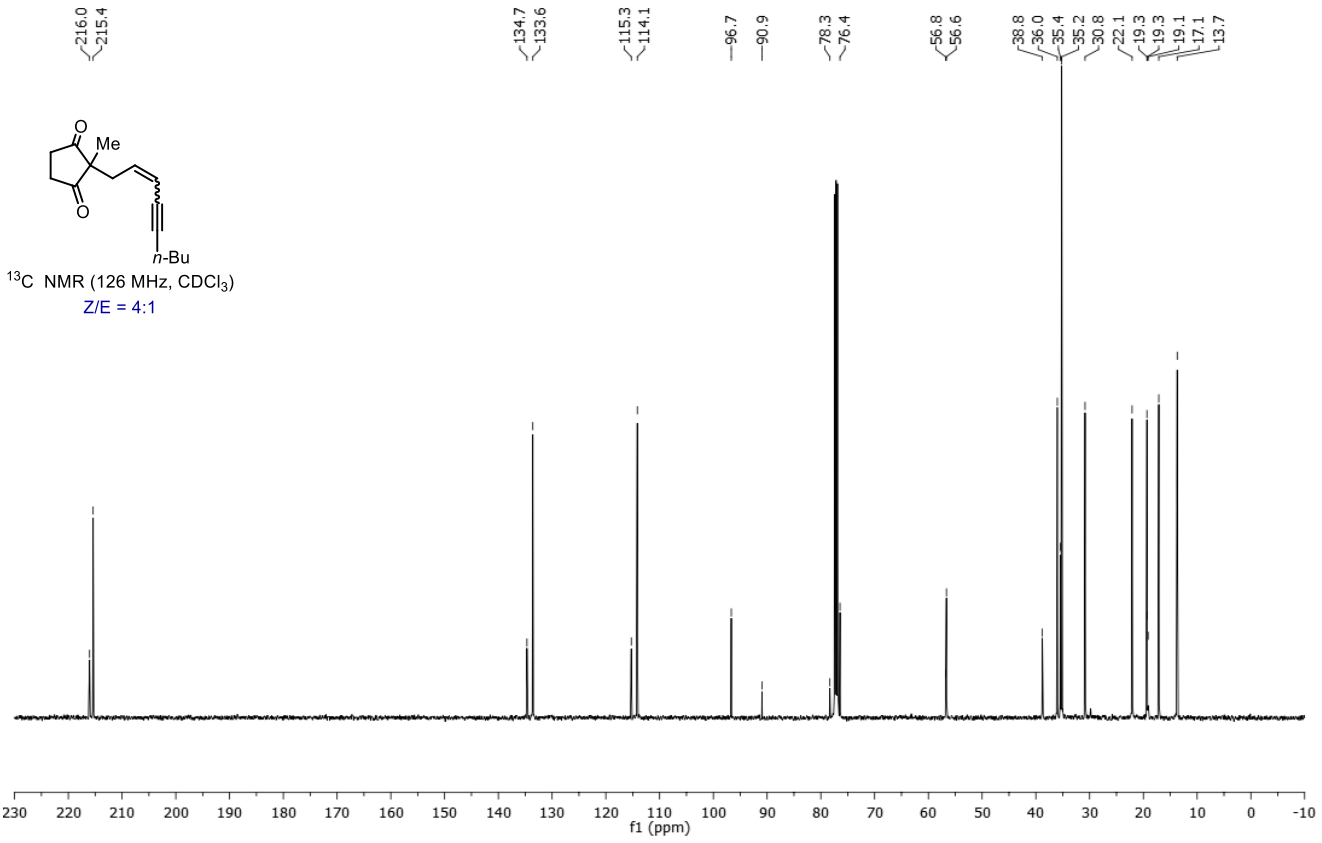
2-(5-(Cyclohex-1-en-1-yl)pent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1aq):



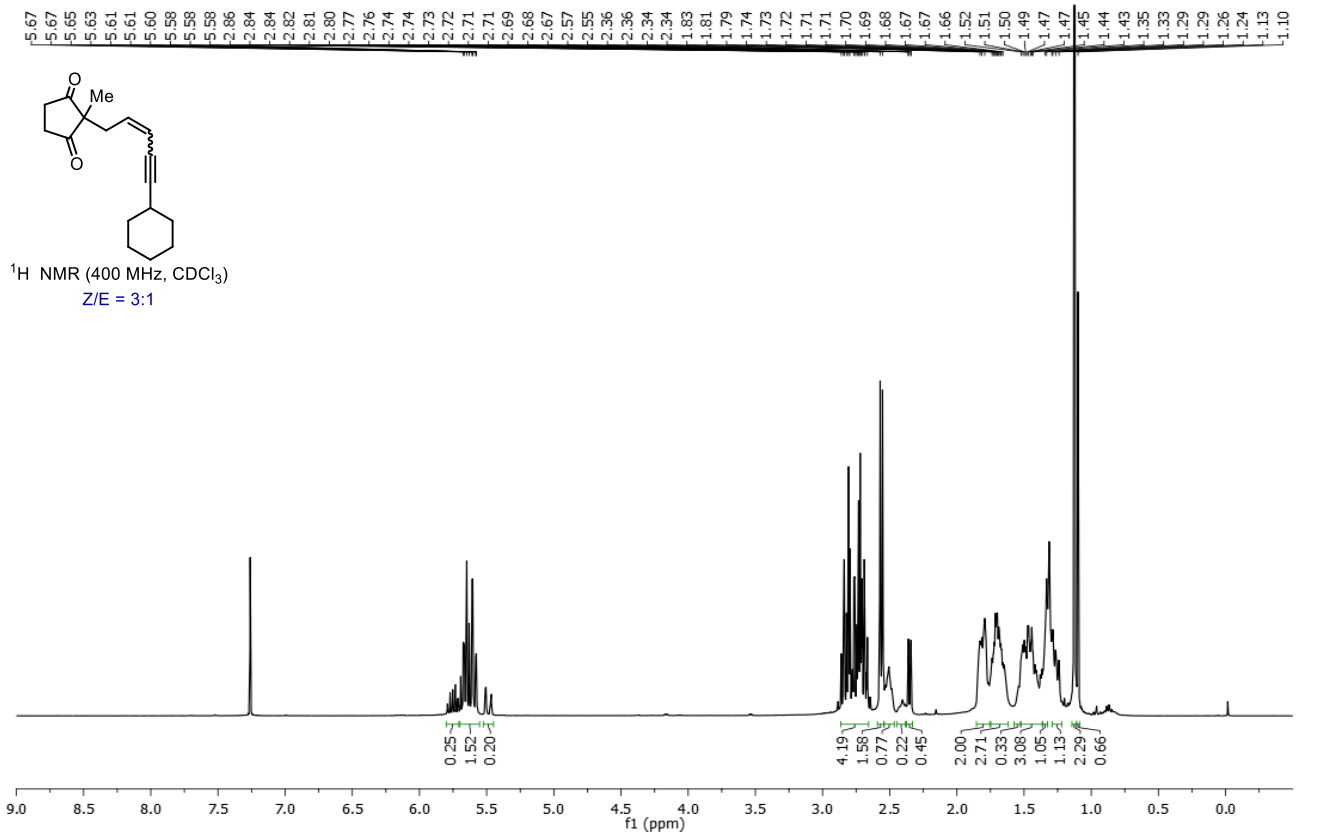


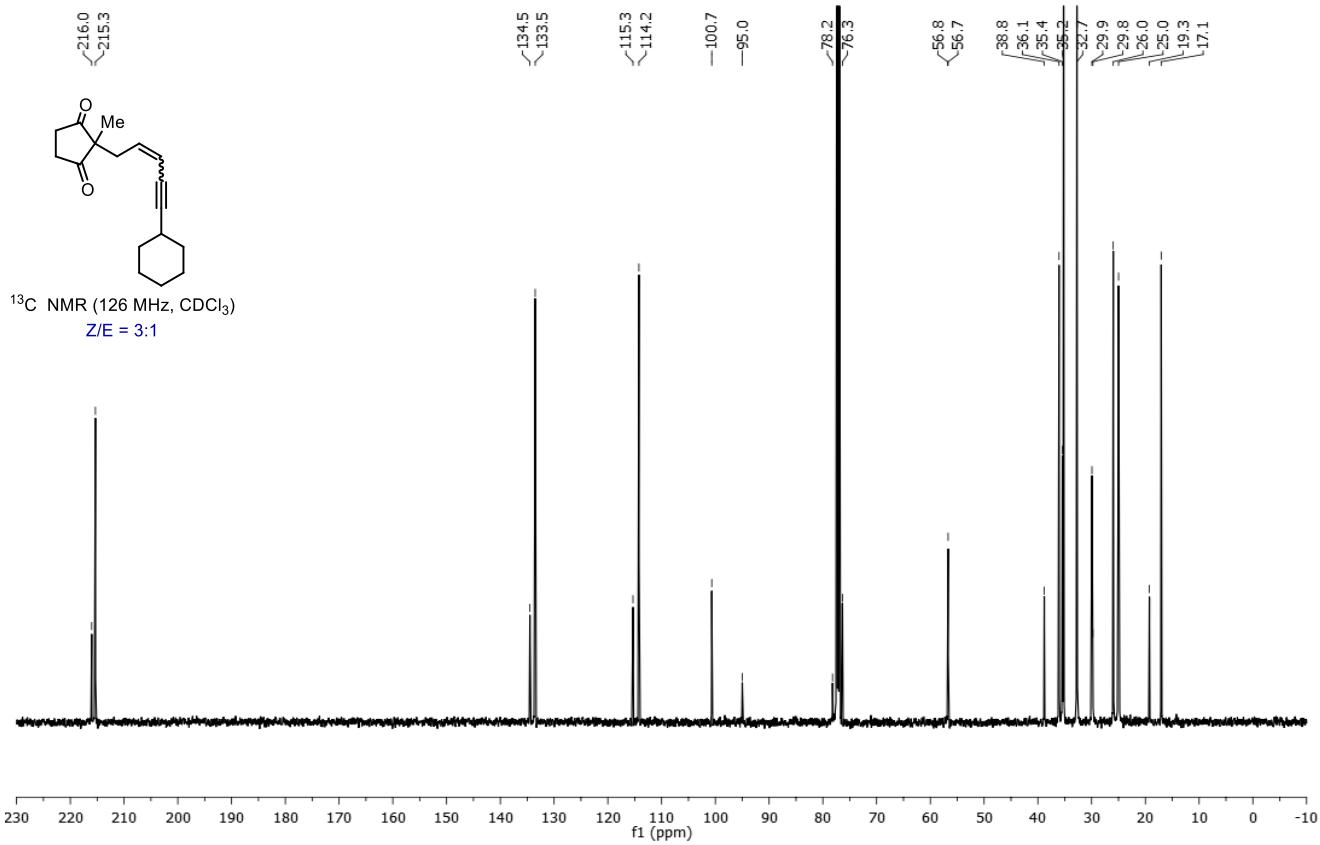
2-Methyl-2-(non-2-en-4-yn-1-yl)cyclopentane-1,3-dione (1ar):



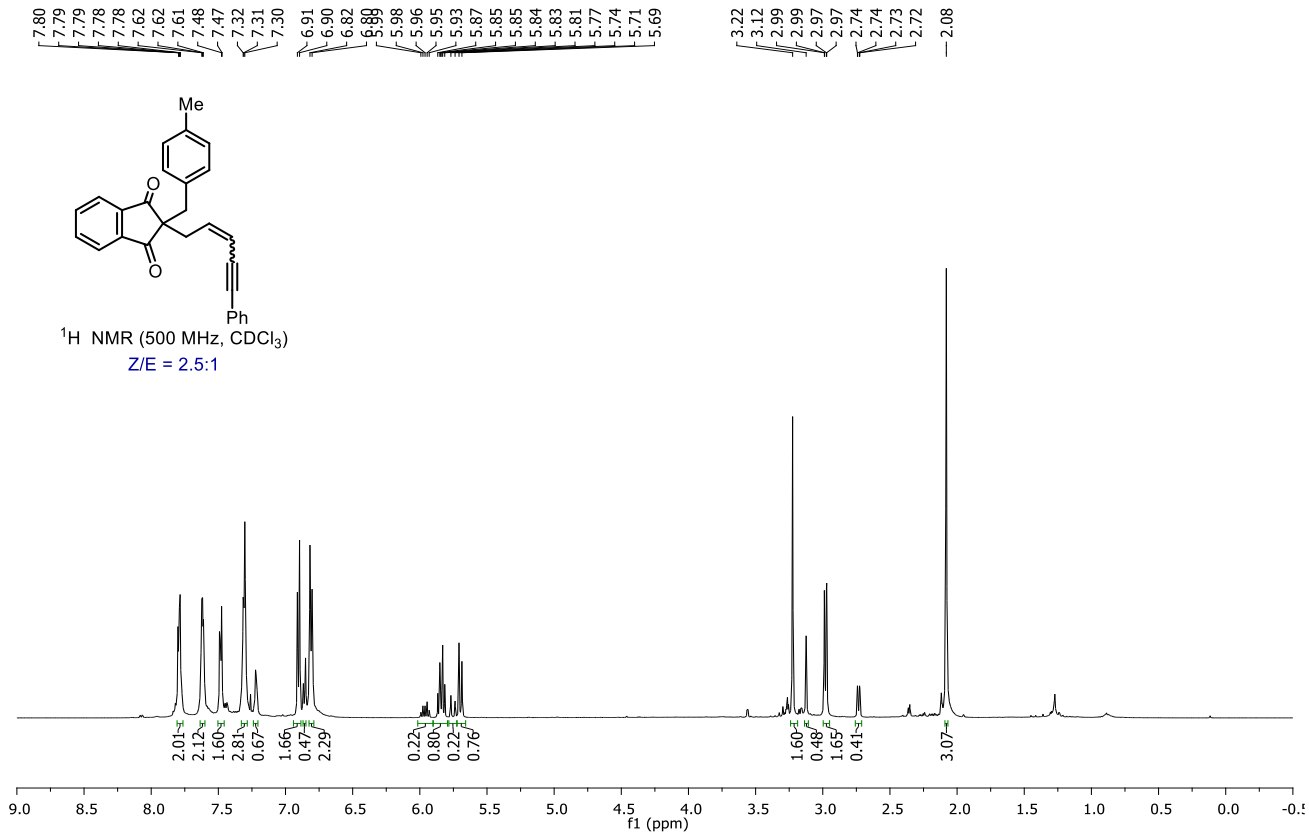


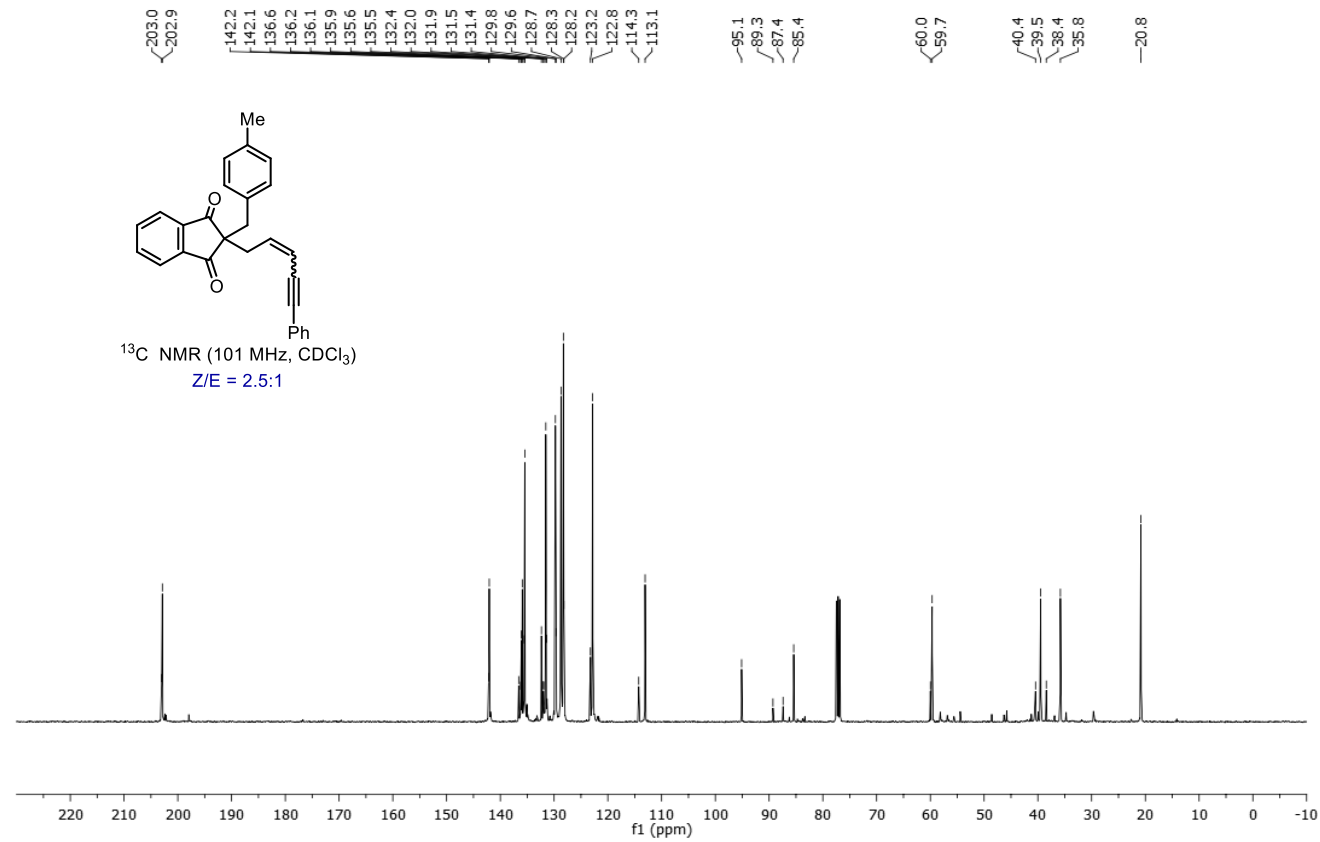
2-(5-Cyclohexylpent-2-en-4-yn-1-yl)-2-methylcyclopentane-1,3-dione (1as):



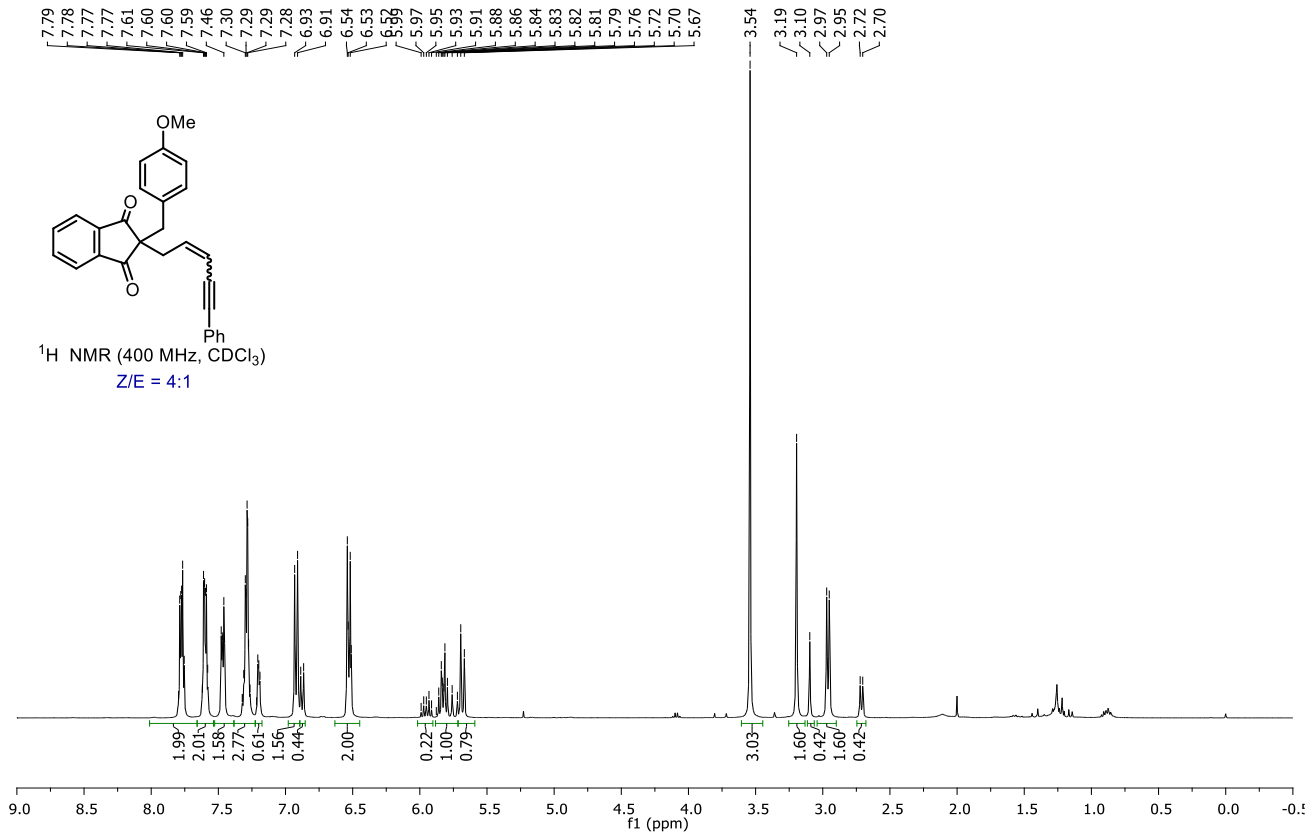


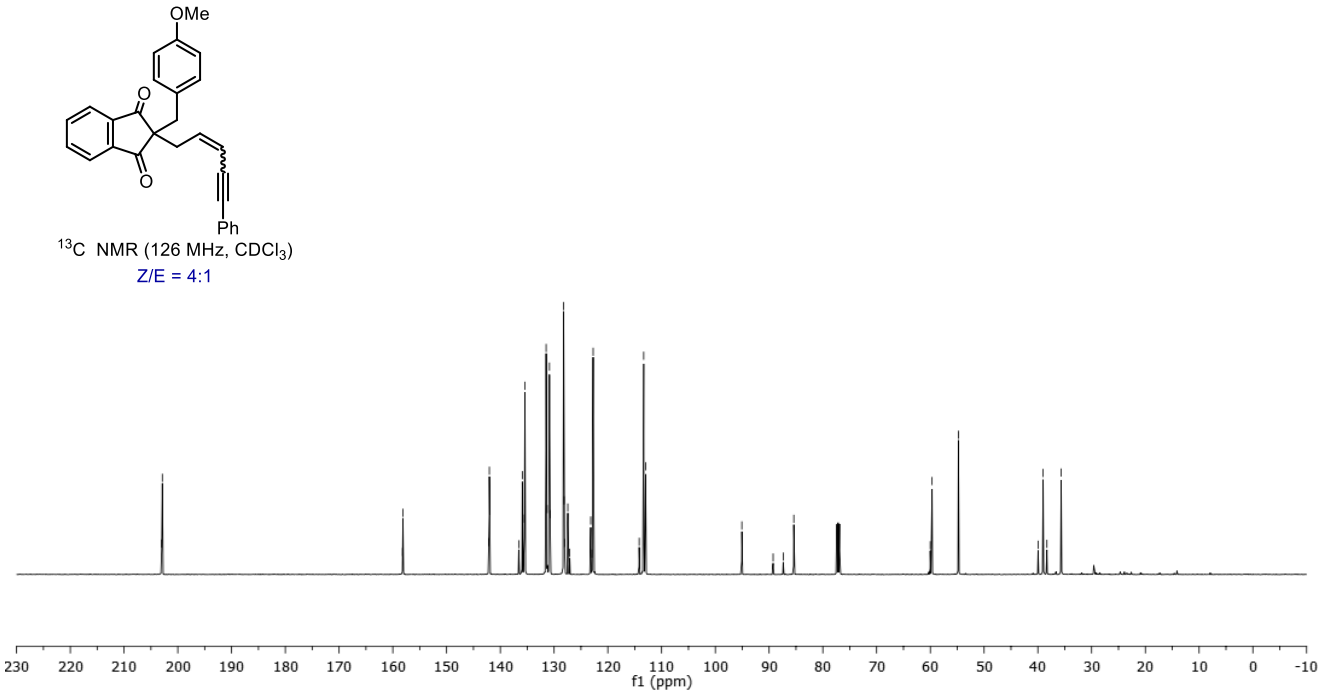
2-(4-Methylbenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3a):



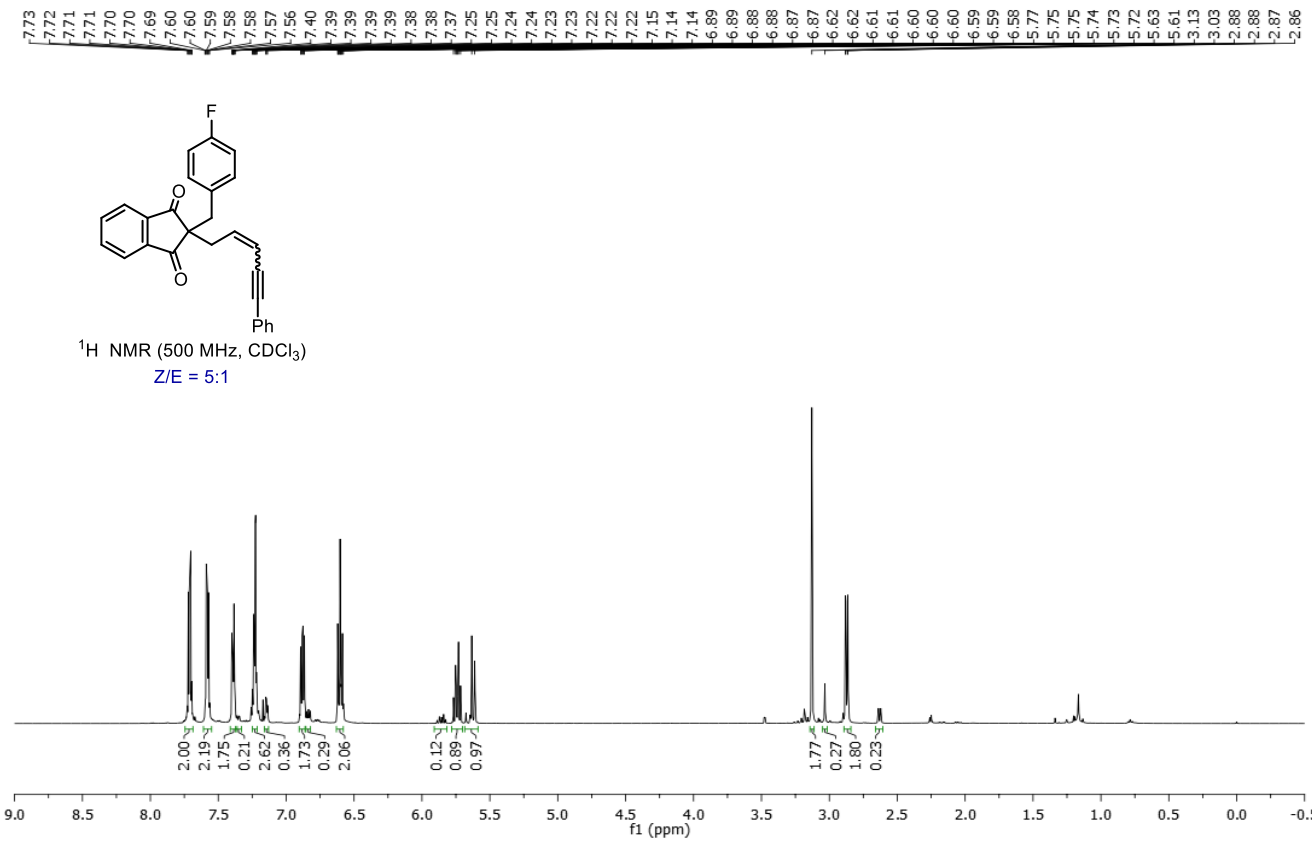


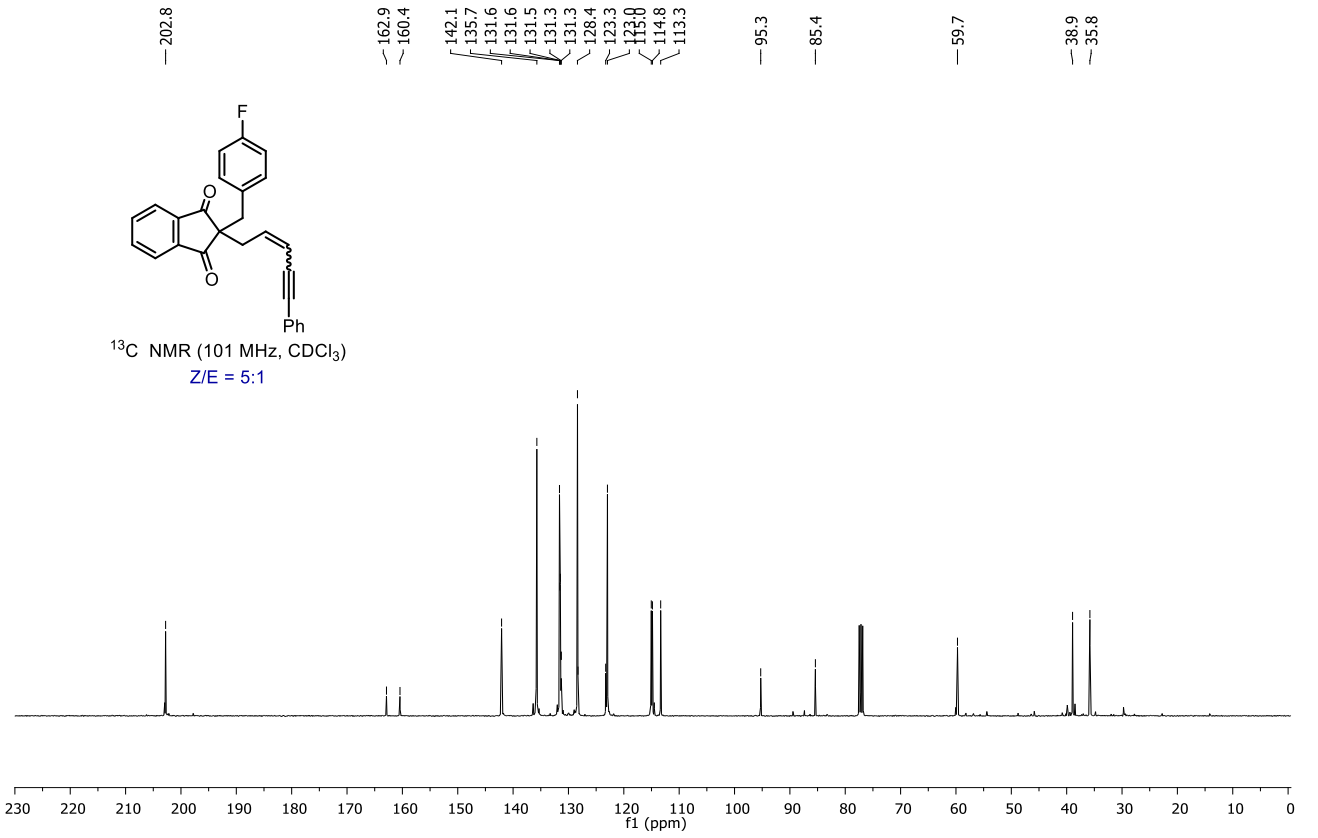
2-(4-Methoxybenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3b):

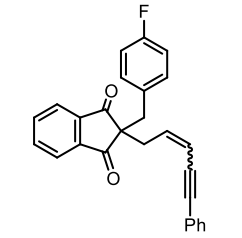




2-(4-Fluorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3c):



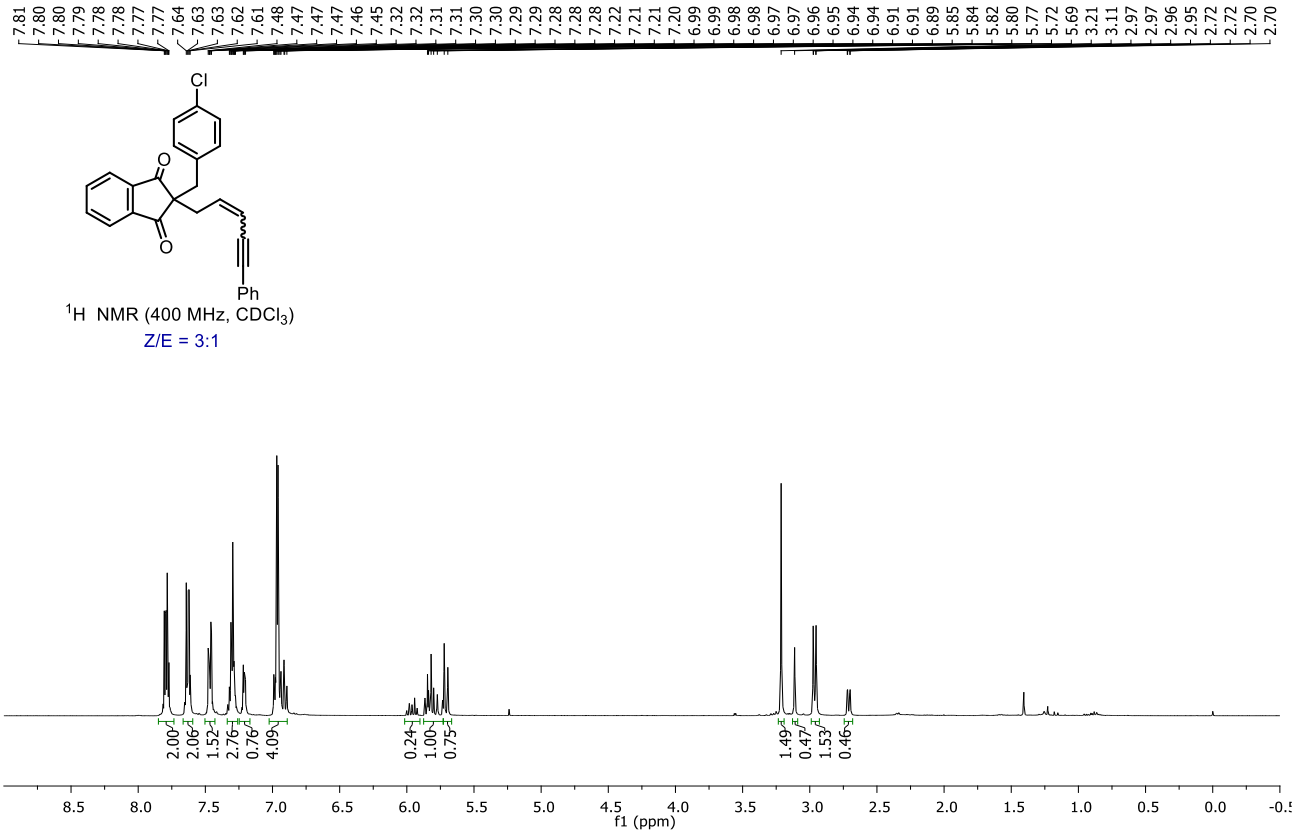


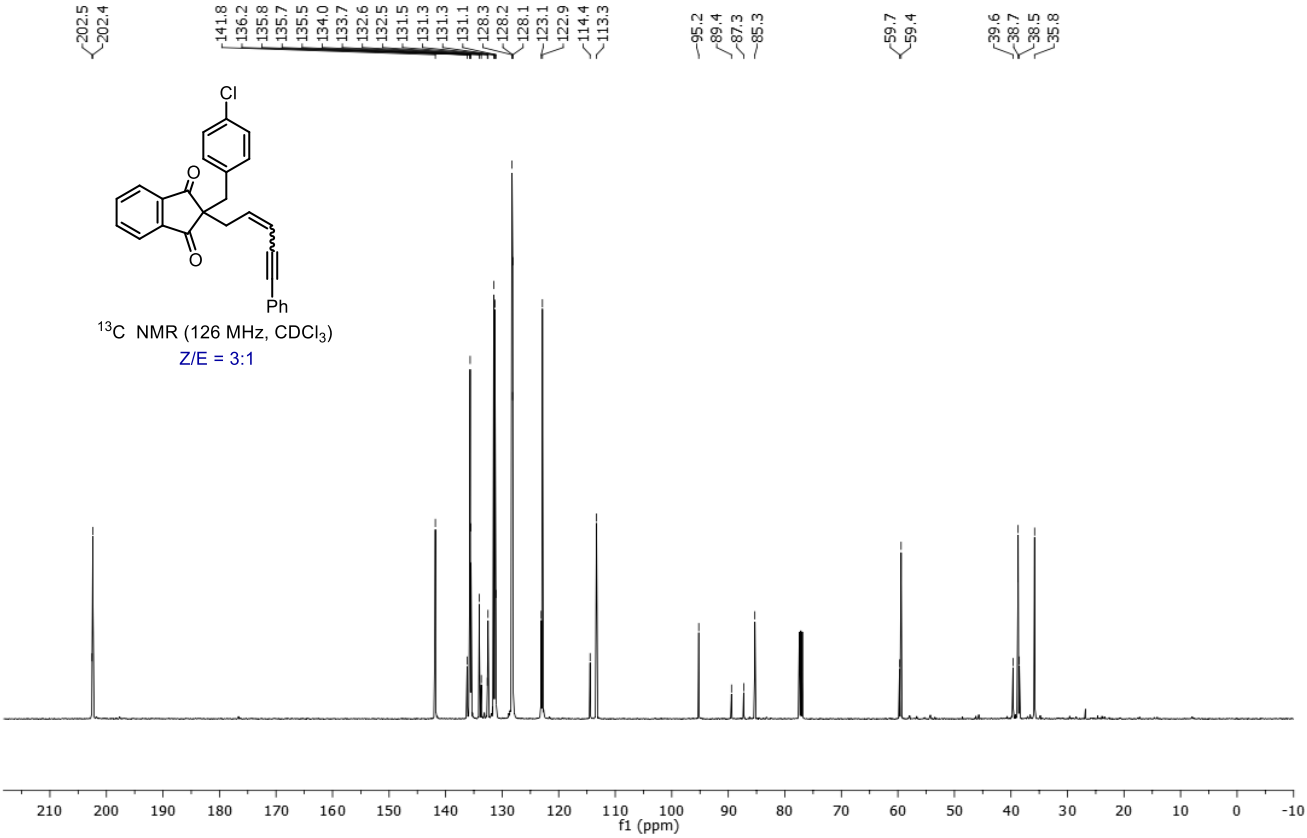


^{19}F NMR (471 MHz, $CDCl_3$)

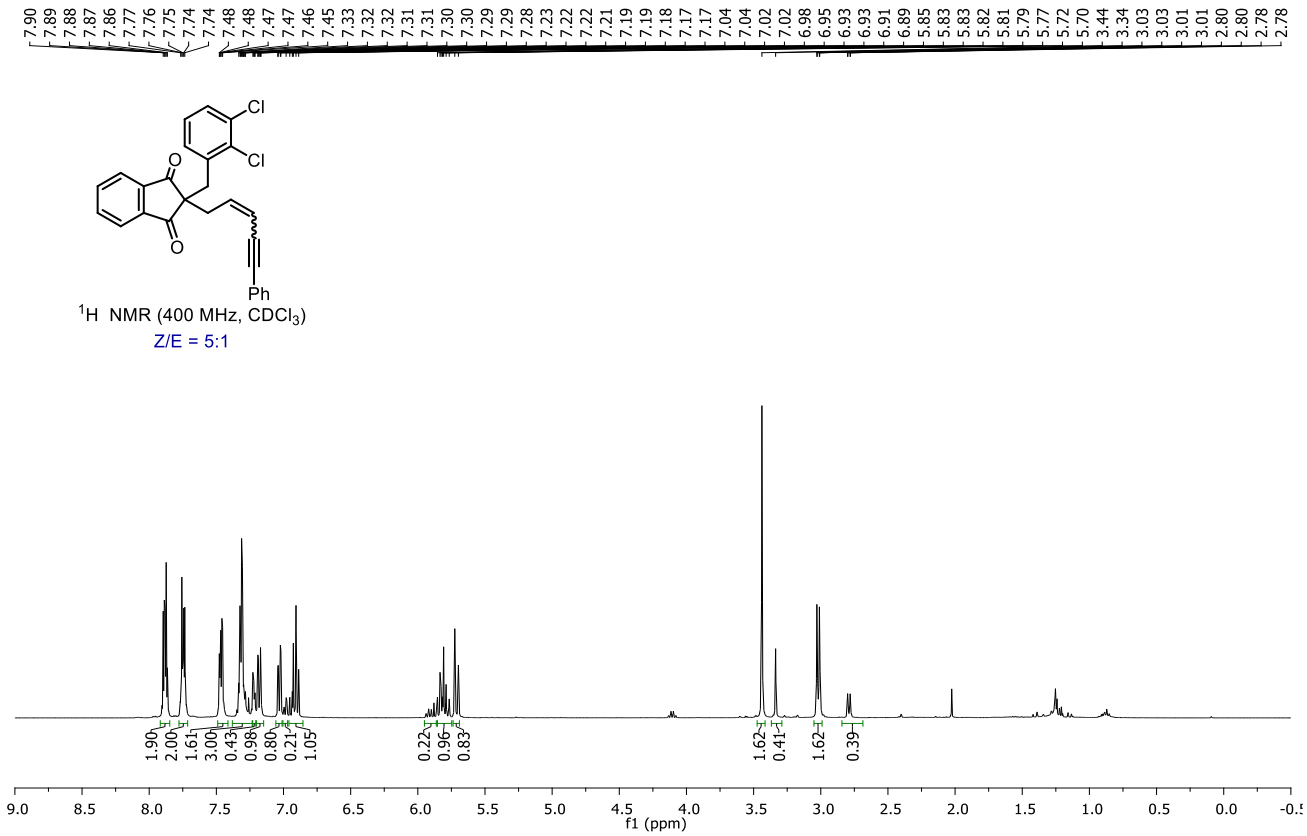
Z/E = 5:1

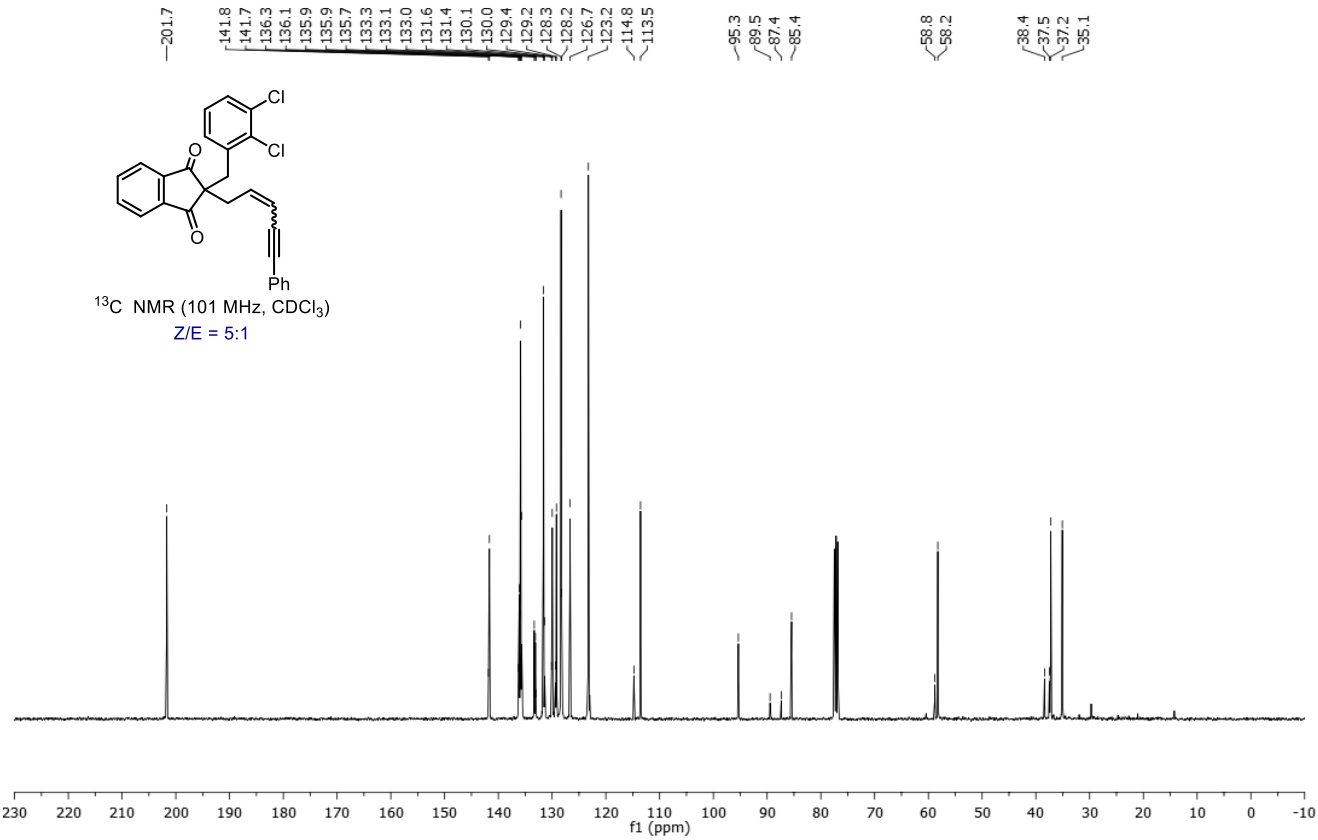
2-(4-Chlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3d):



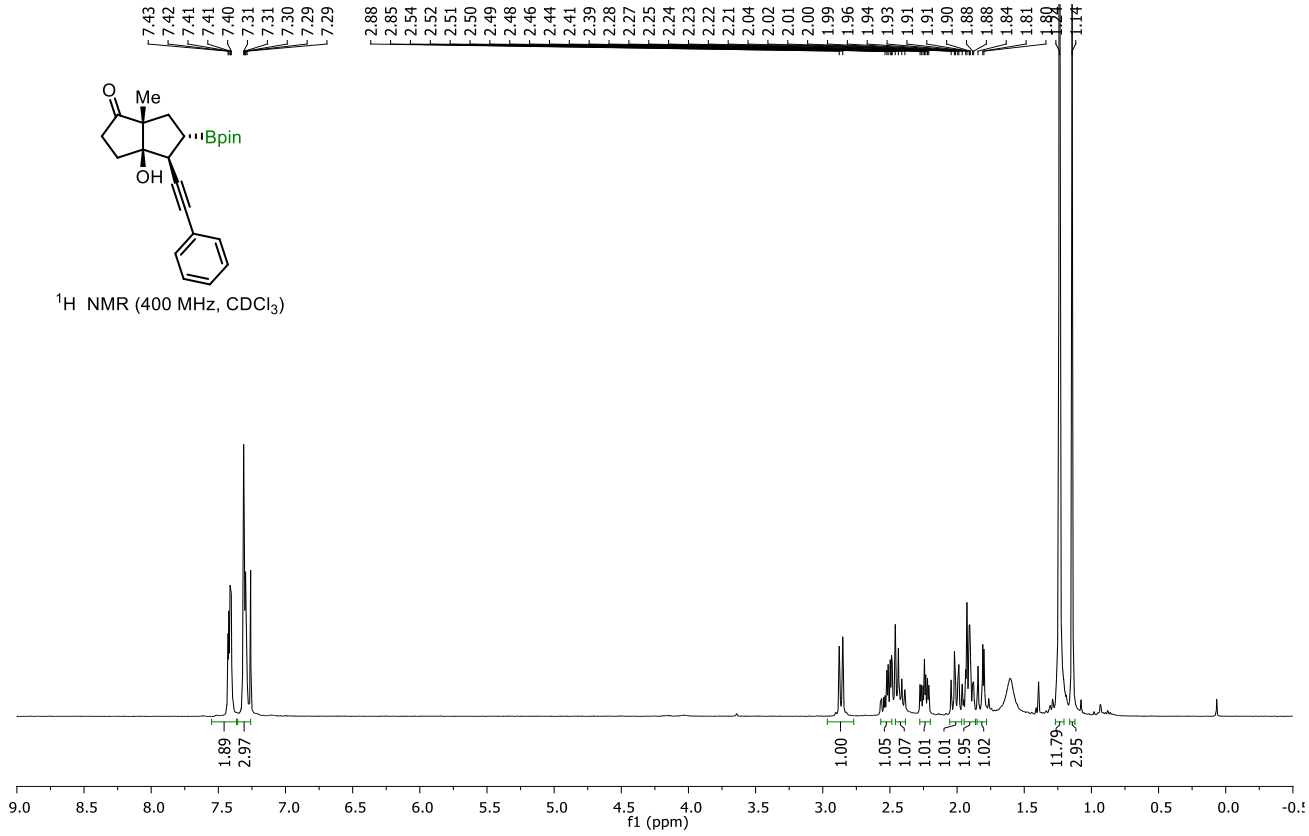


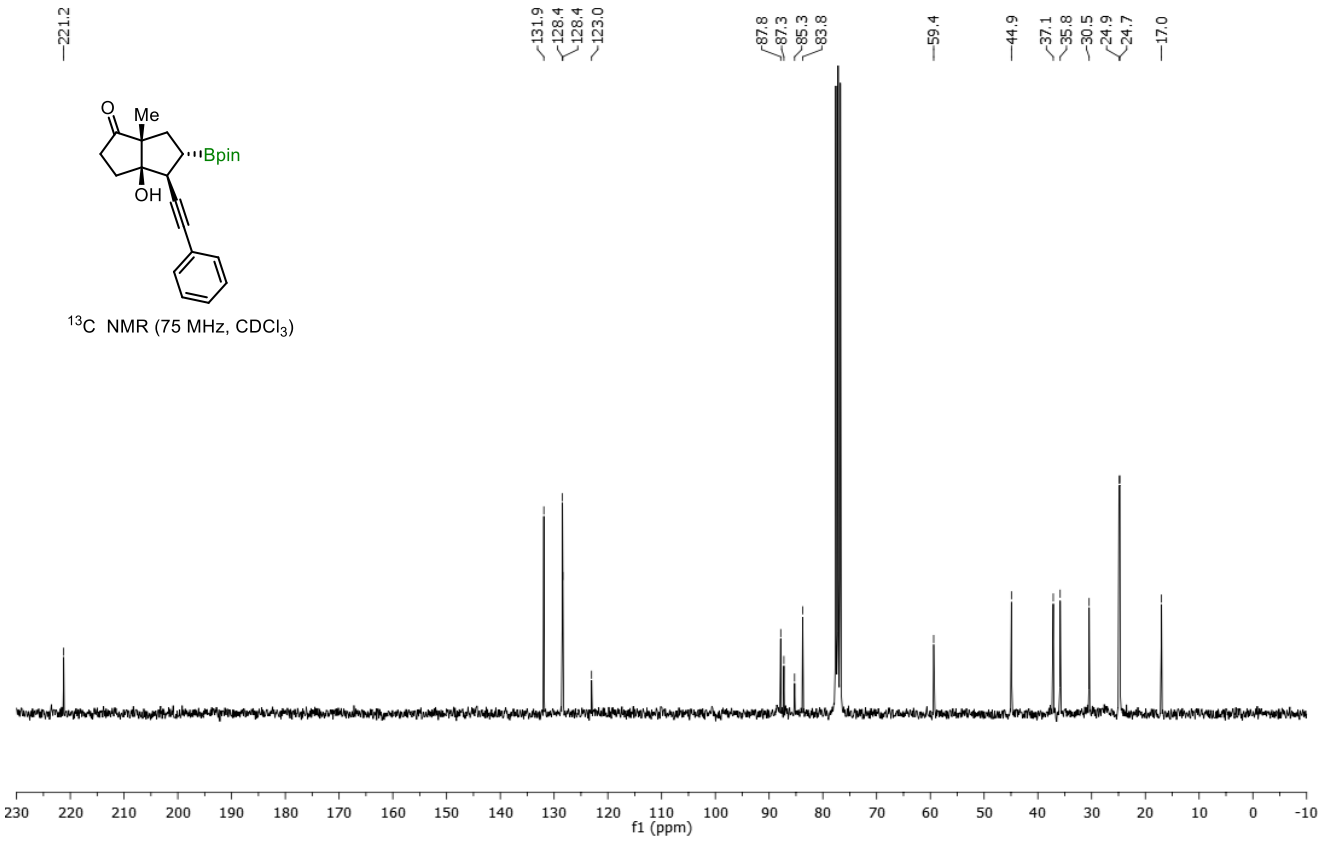
2-(2,3-Dichlorobenzyl)-2-(5-phenylpent-2-en-4-yn-1-yl)-1H-indene-1,3(2H)-dione (3e):



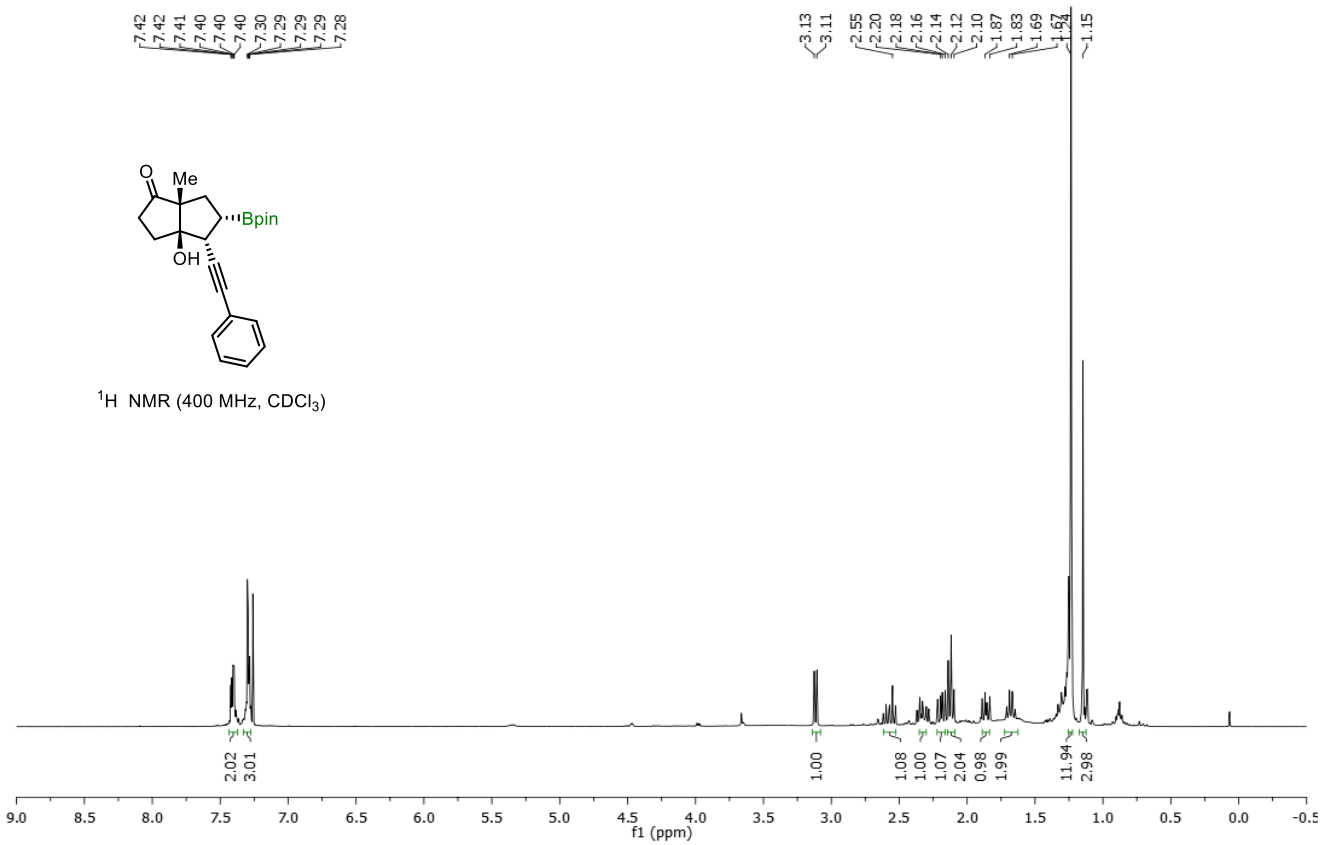


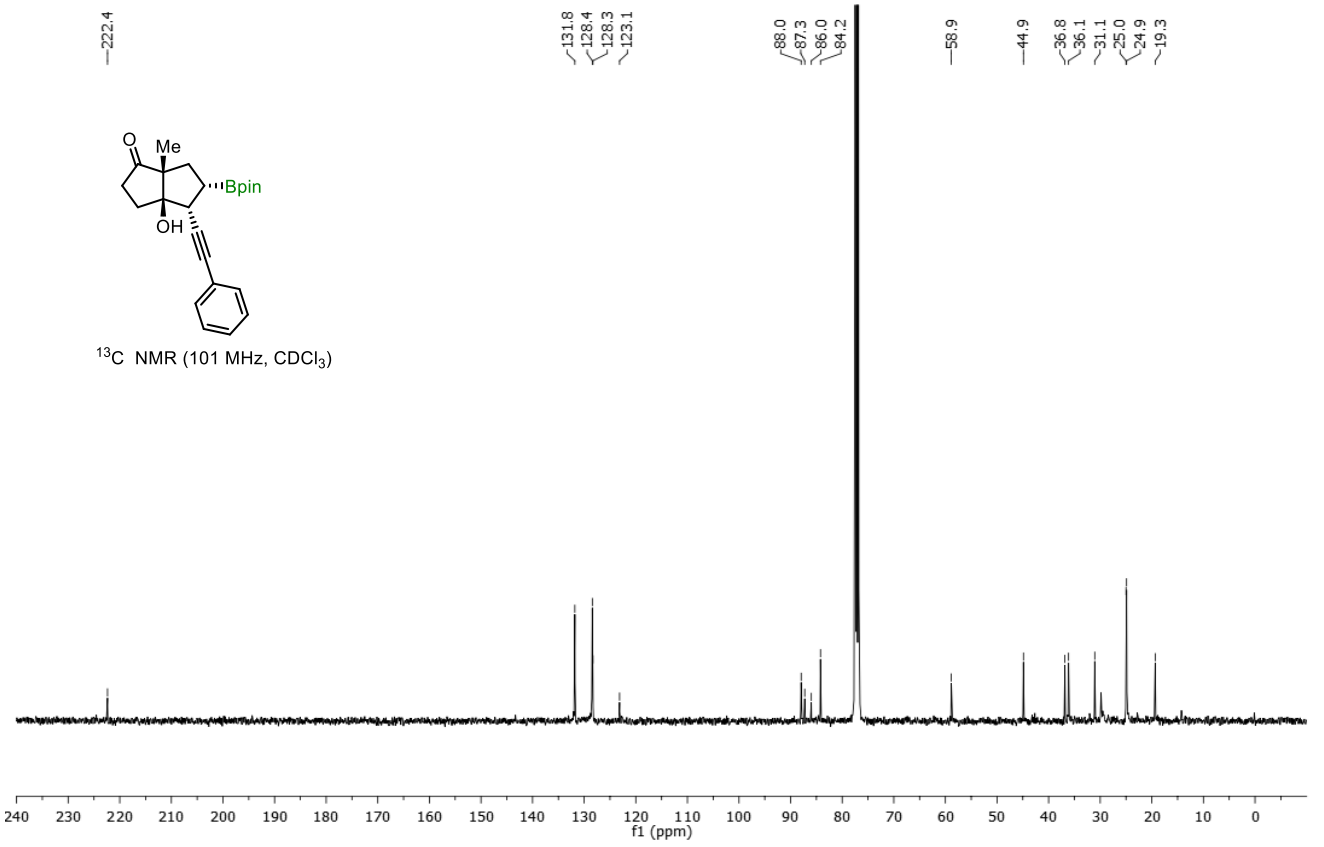
(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (anti-2a):



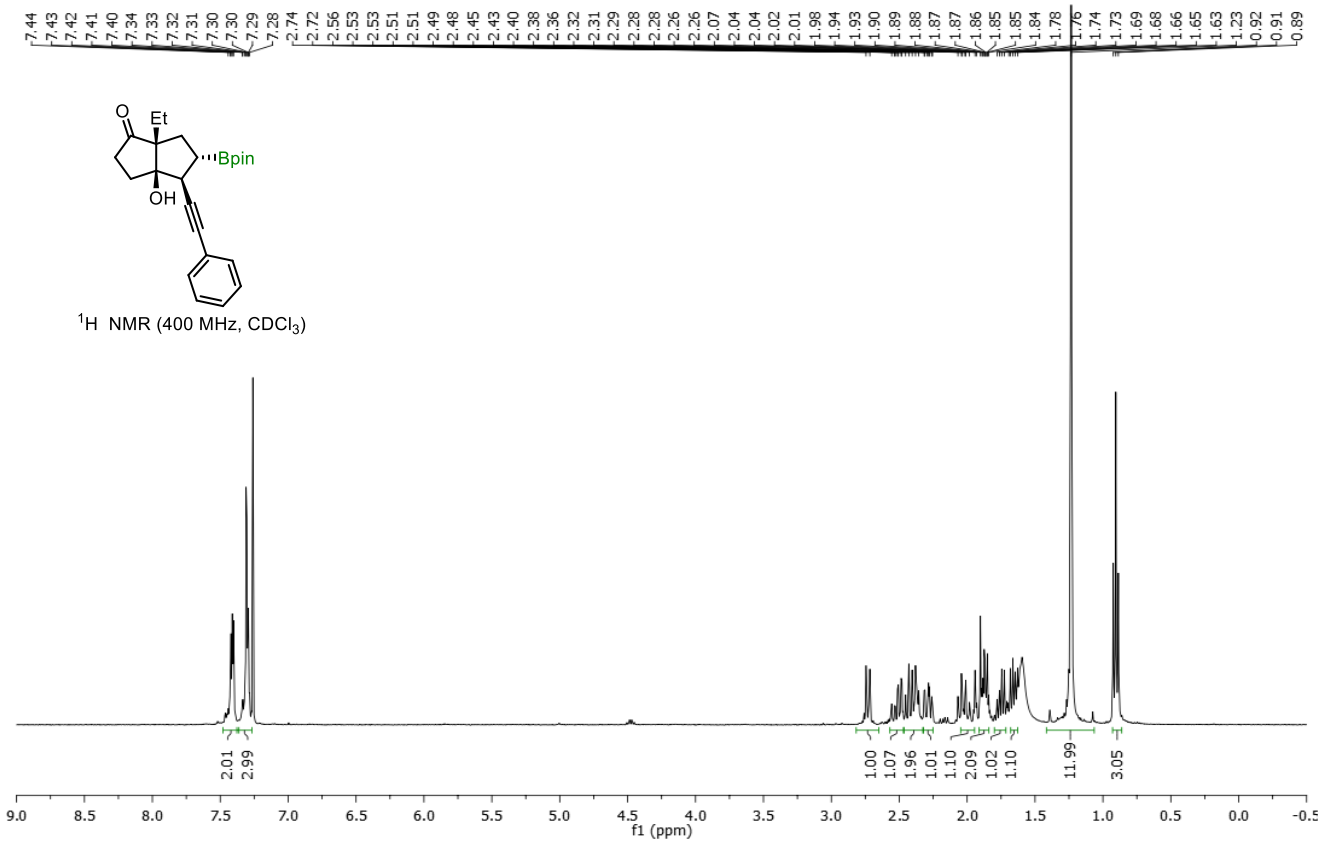


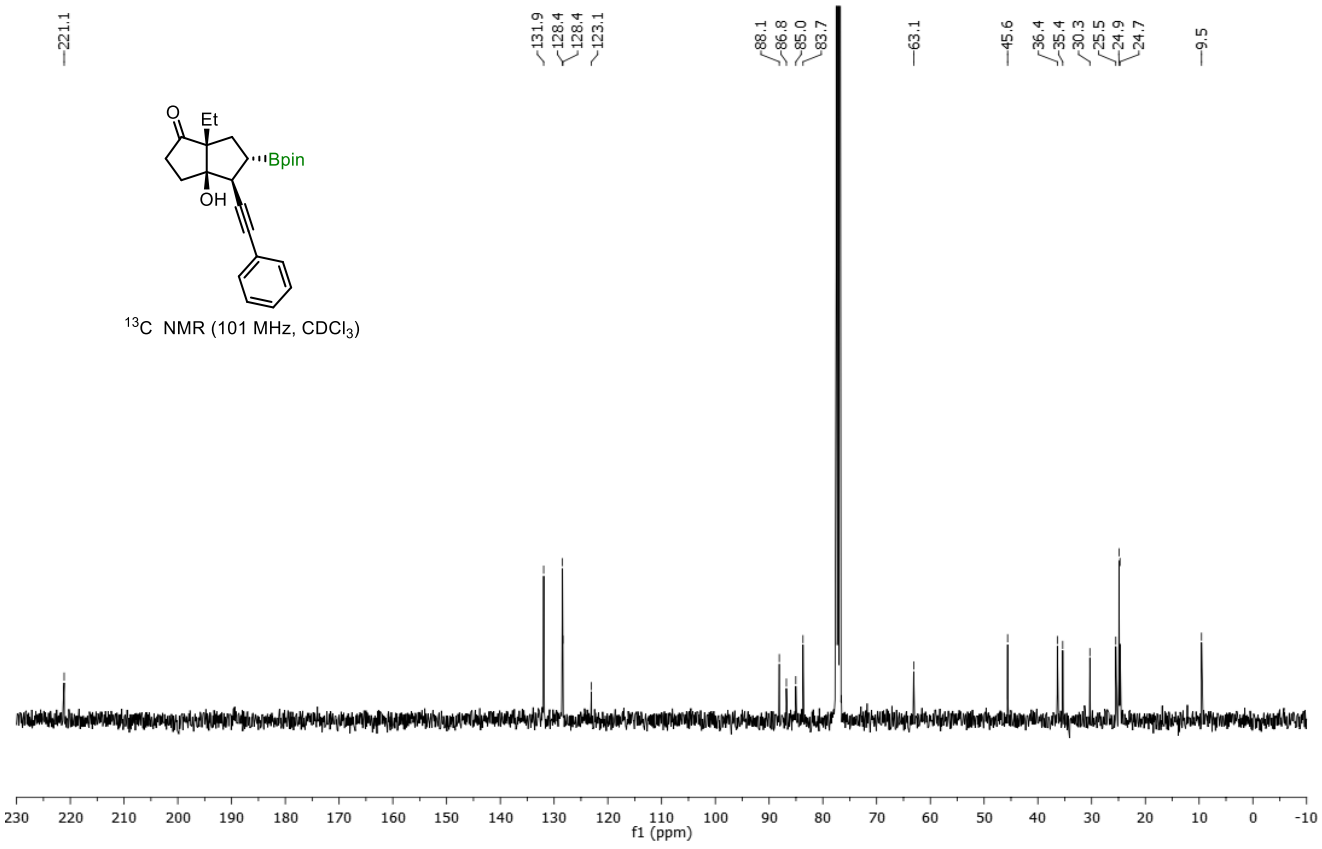
(3a*R*,4*R*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (syn-2a):



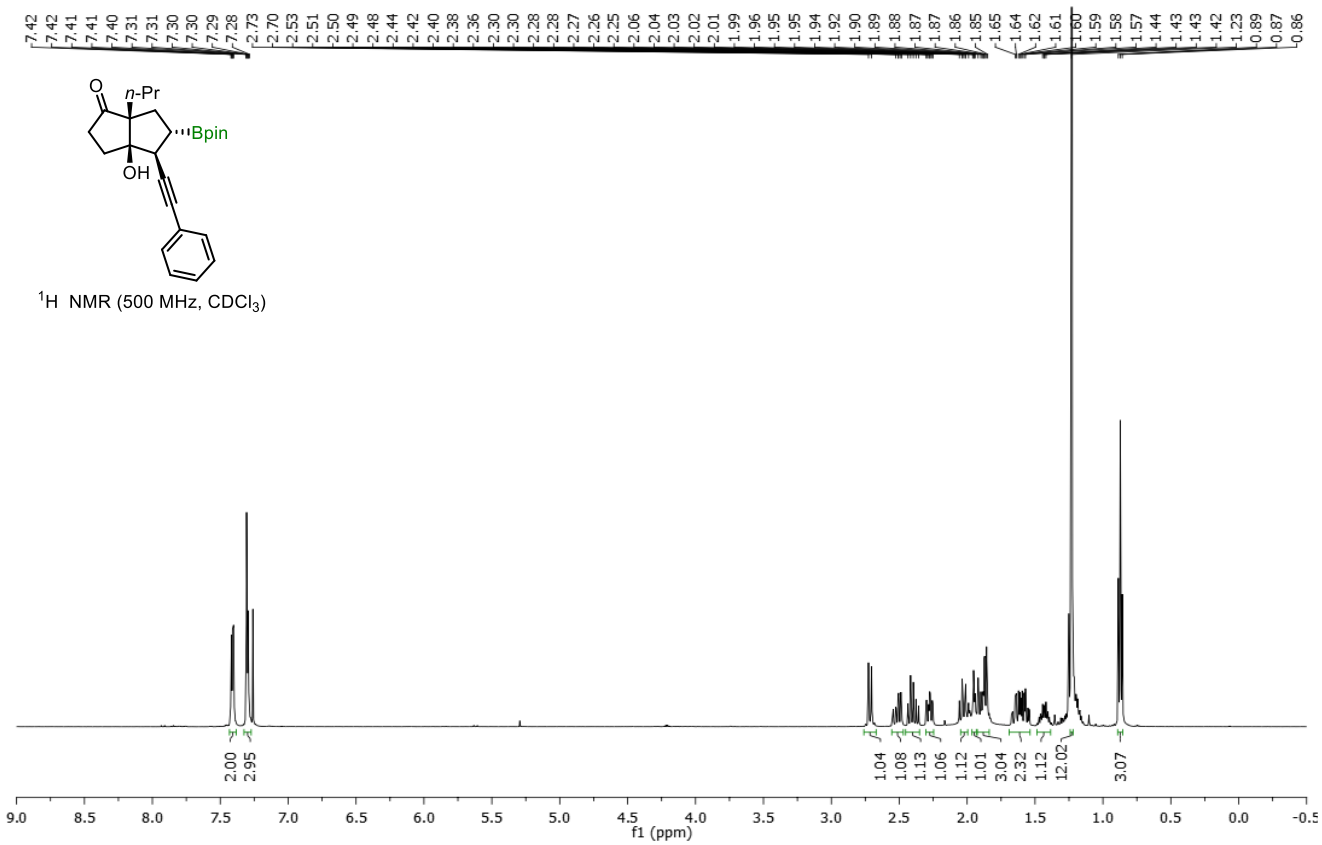


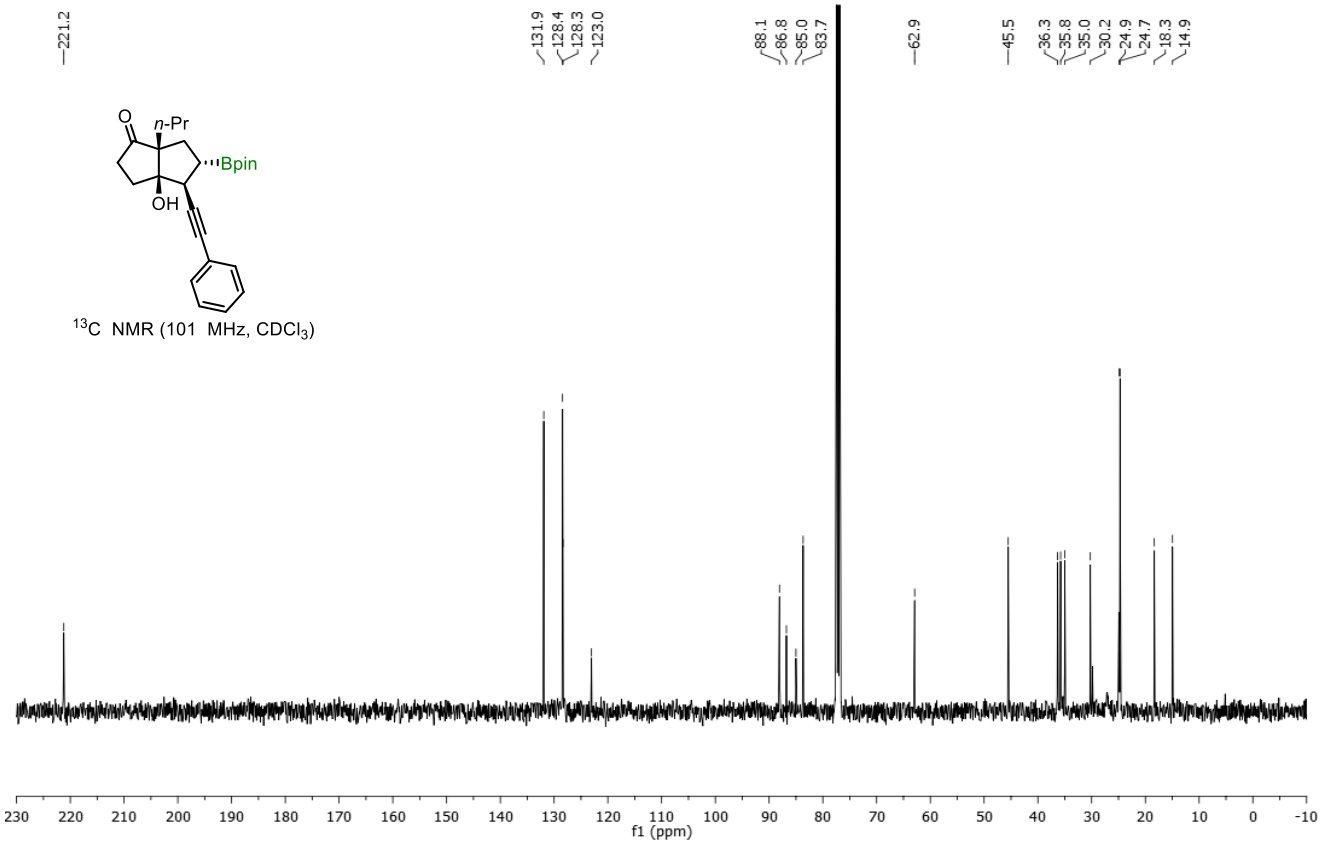
(3a*R*,4*S*,5*S*,6a*R*)-6a-Ethyl-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one ; (2b)



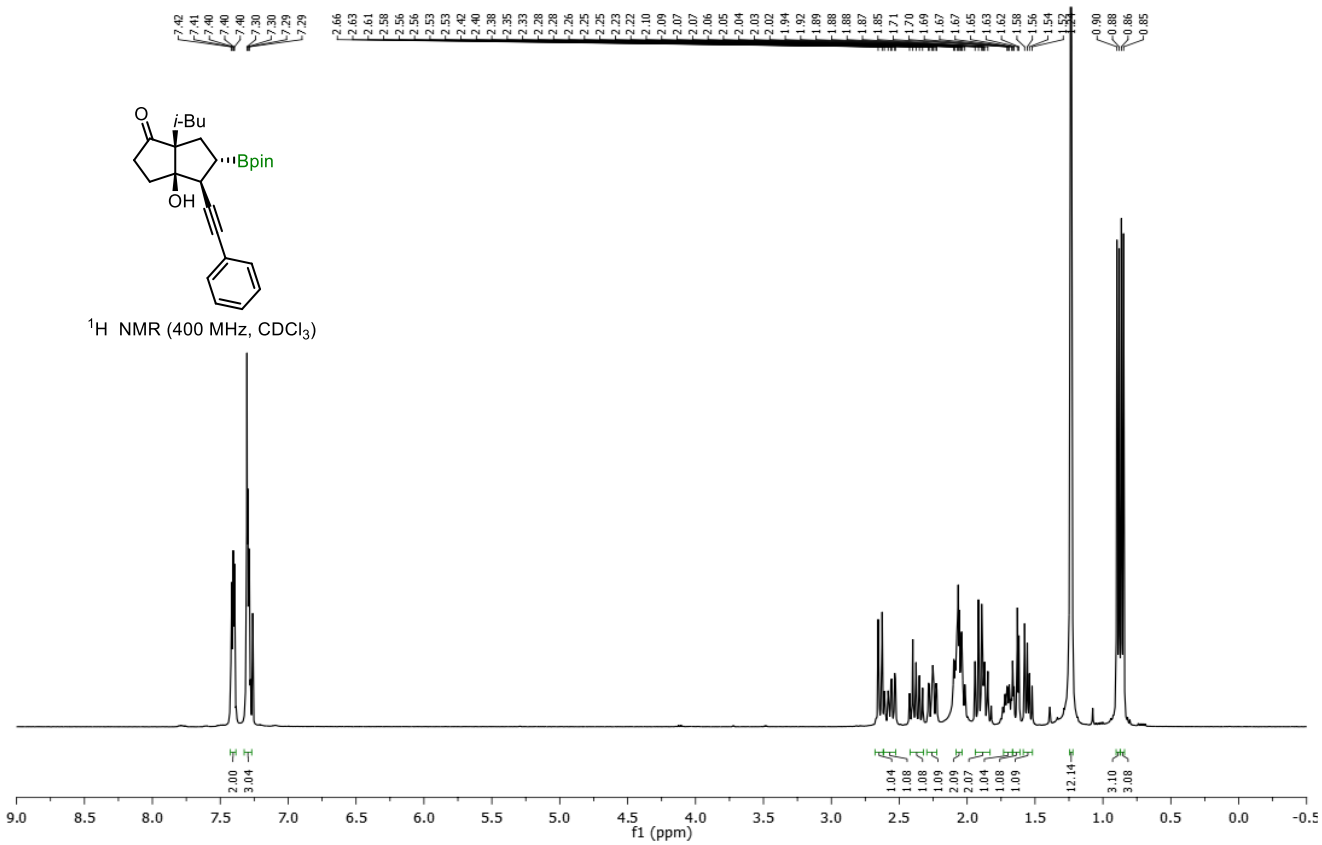


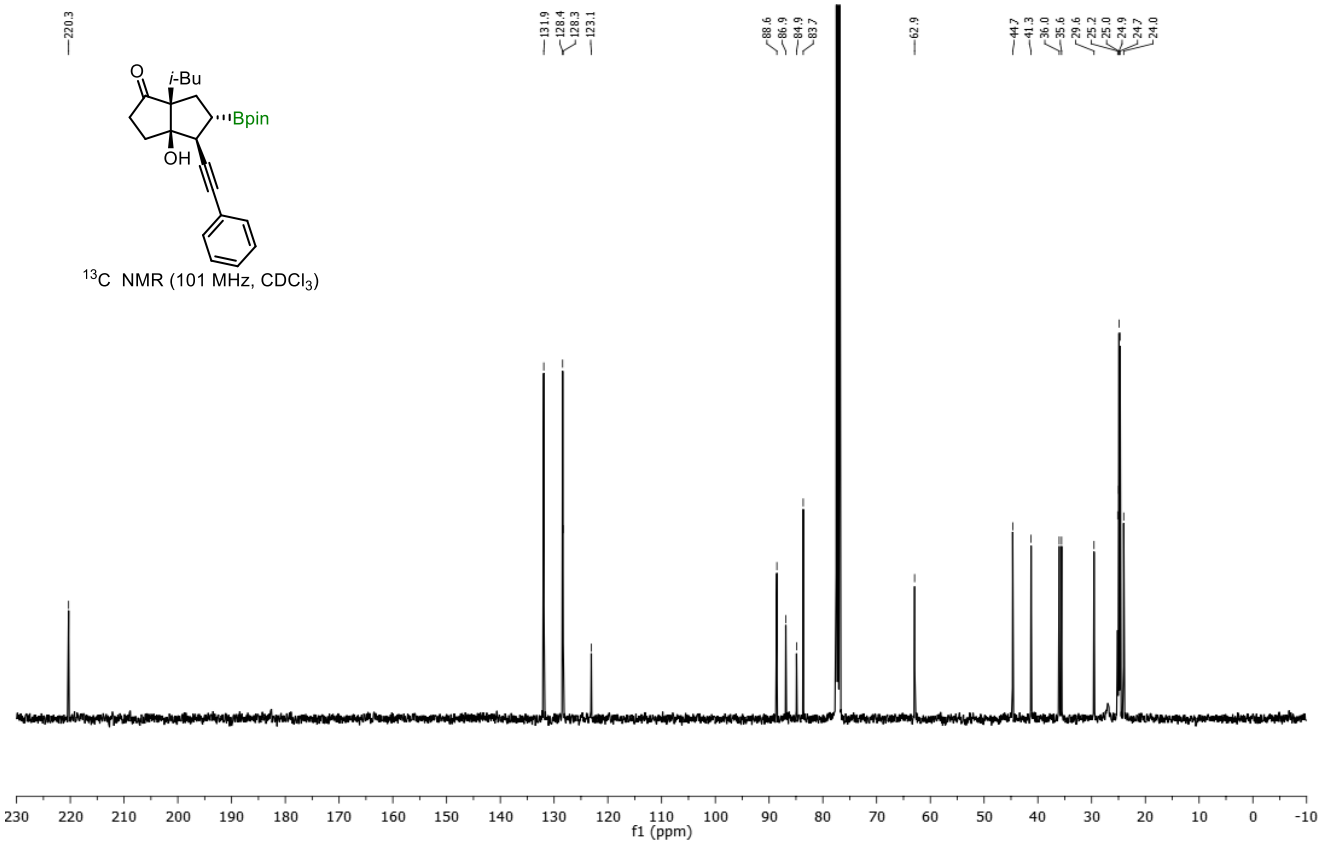
(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-4-(phenylethynyl)-6a-propyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2c):



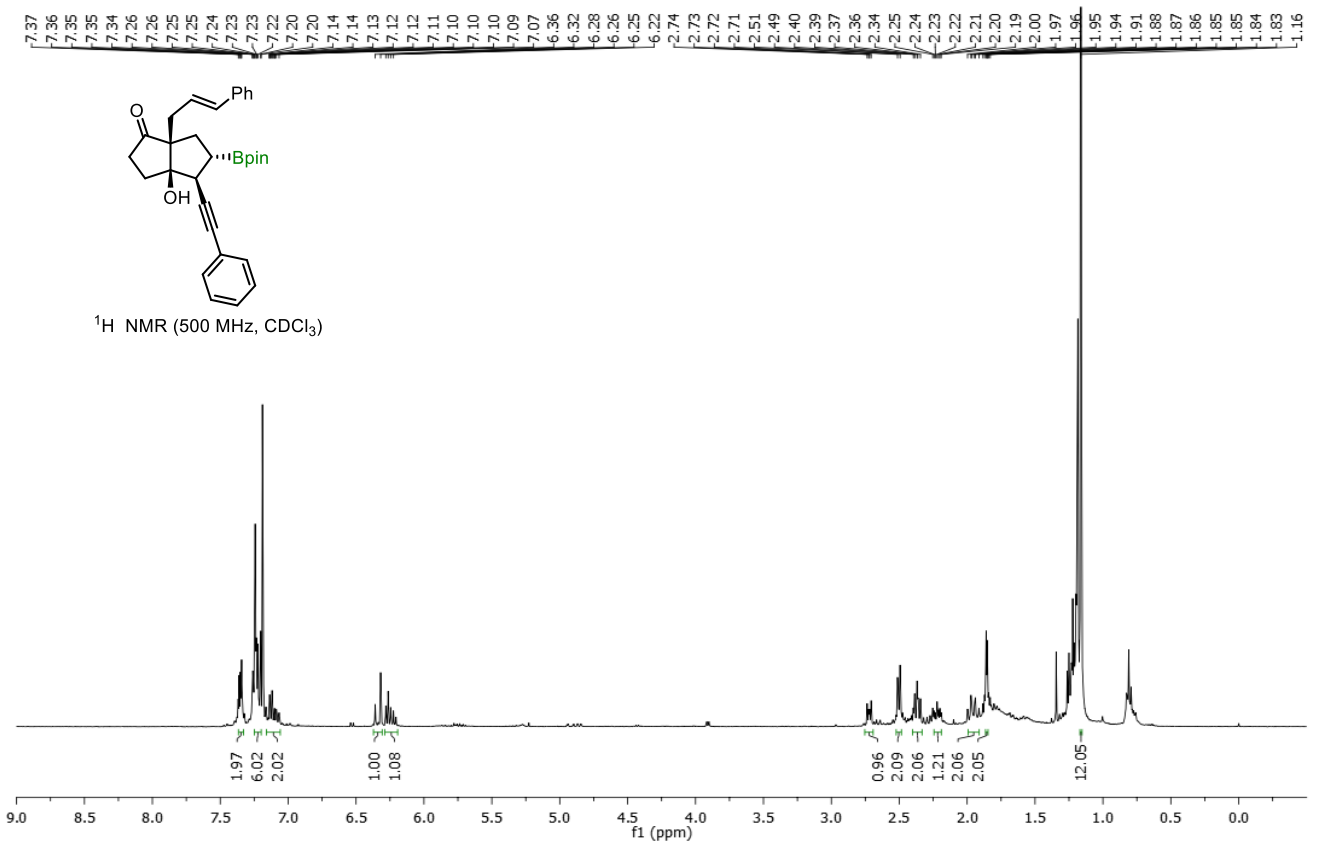


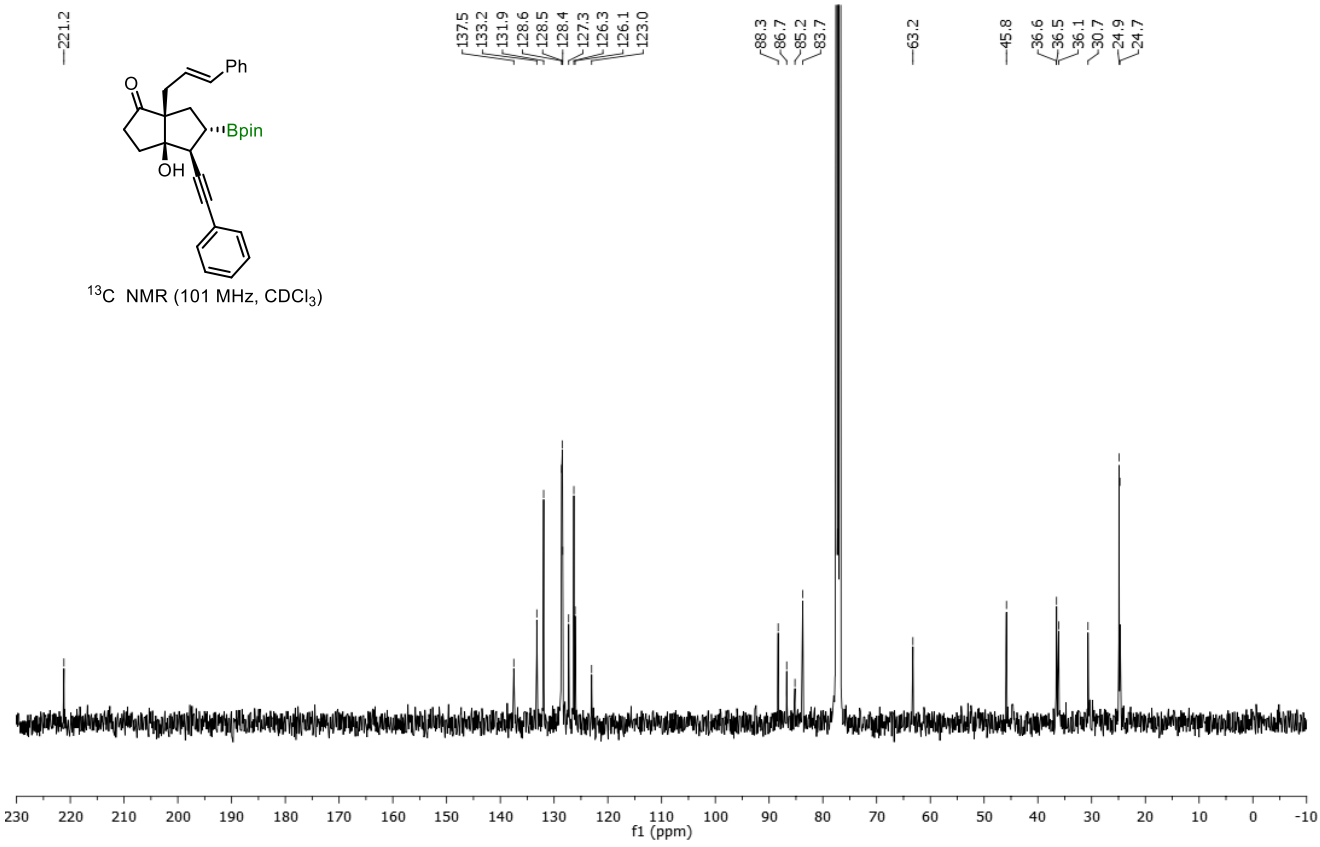
(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-isobutyl-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2d):



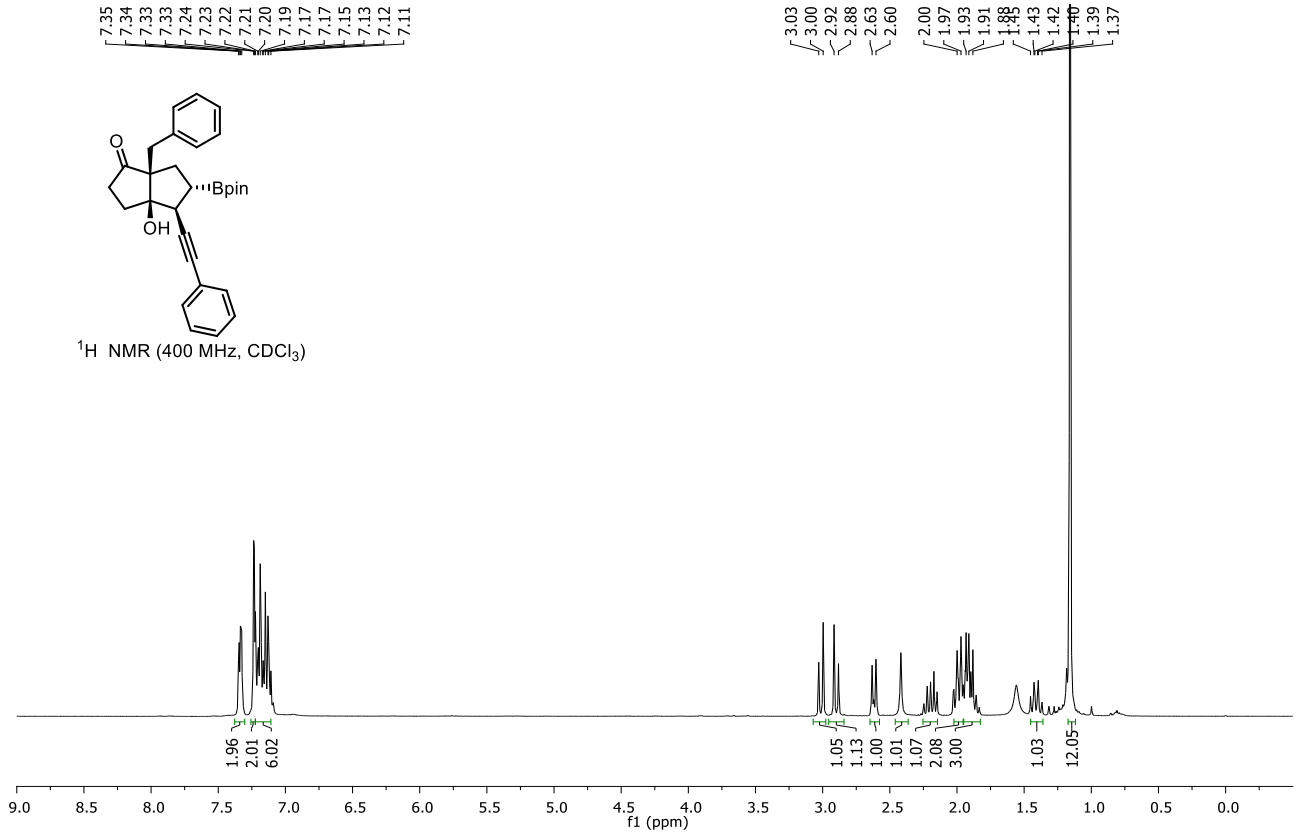


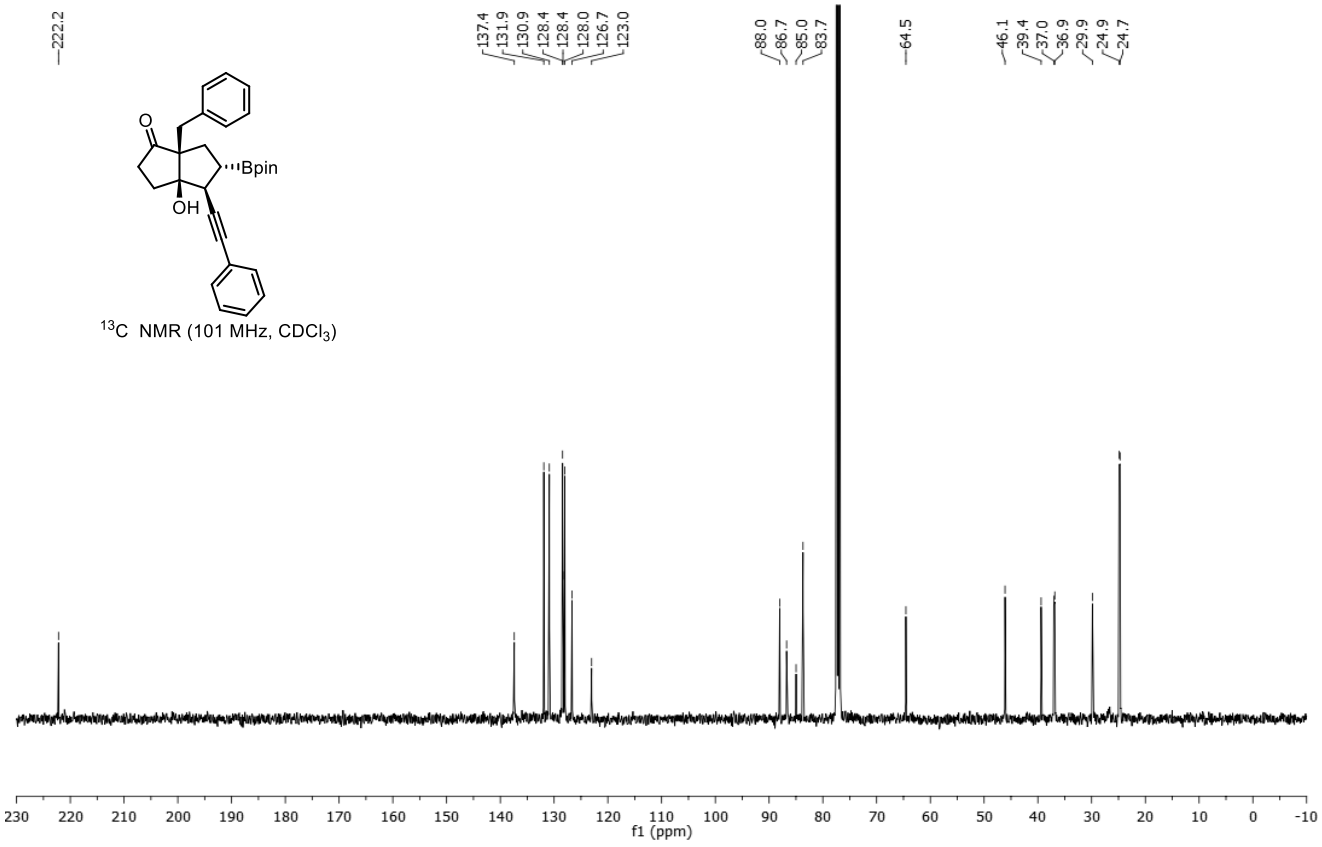
(3a*R*,4*S*,5*S*,6a*S*)-6a-Cinnamyl-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2e):



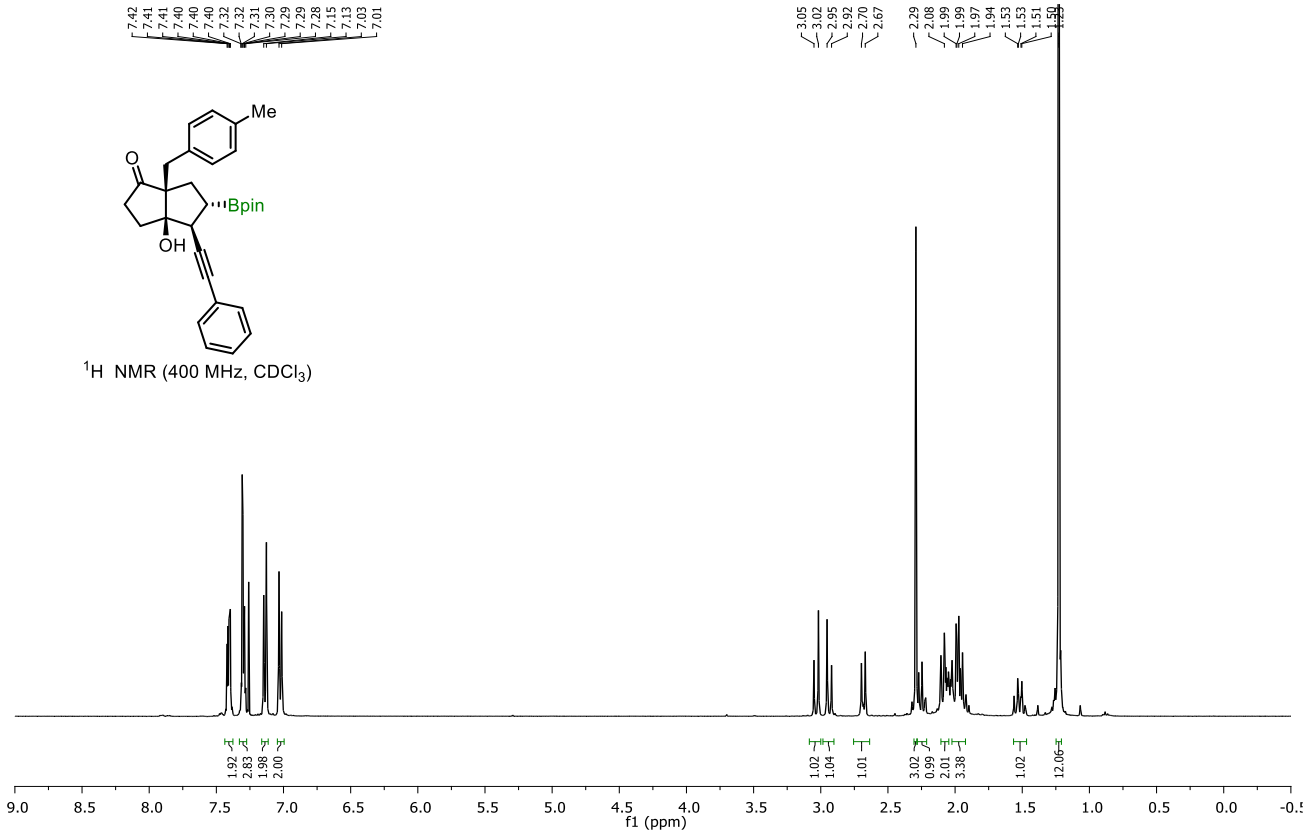


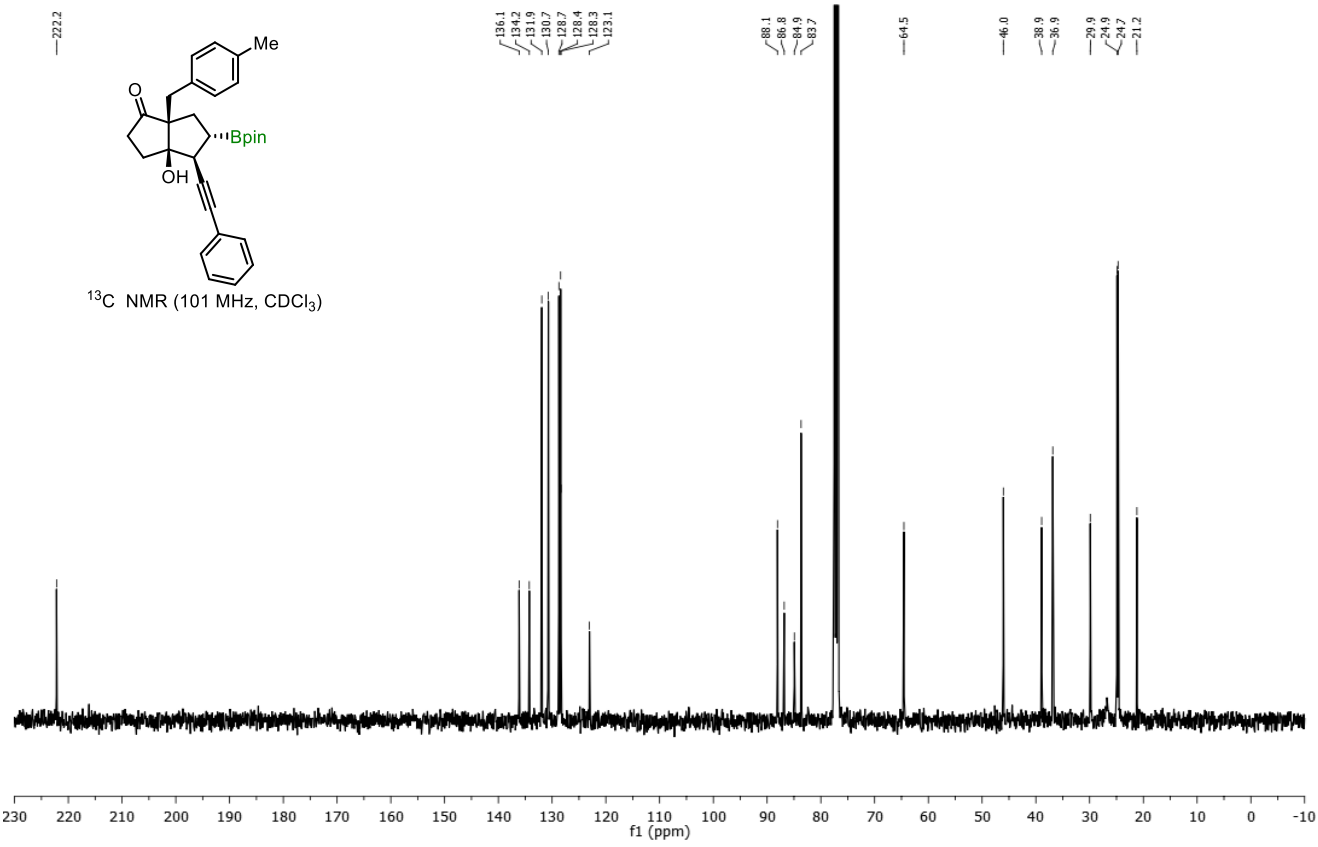
(3a*R*,4*S*,5*S*,6a*S*)-6a-Benzyl-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2f):



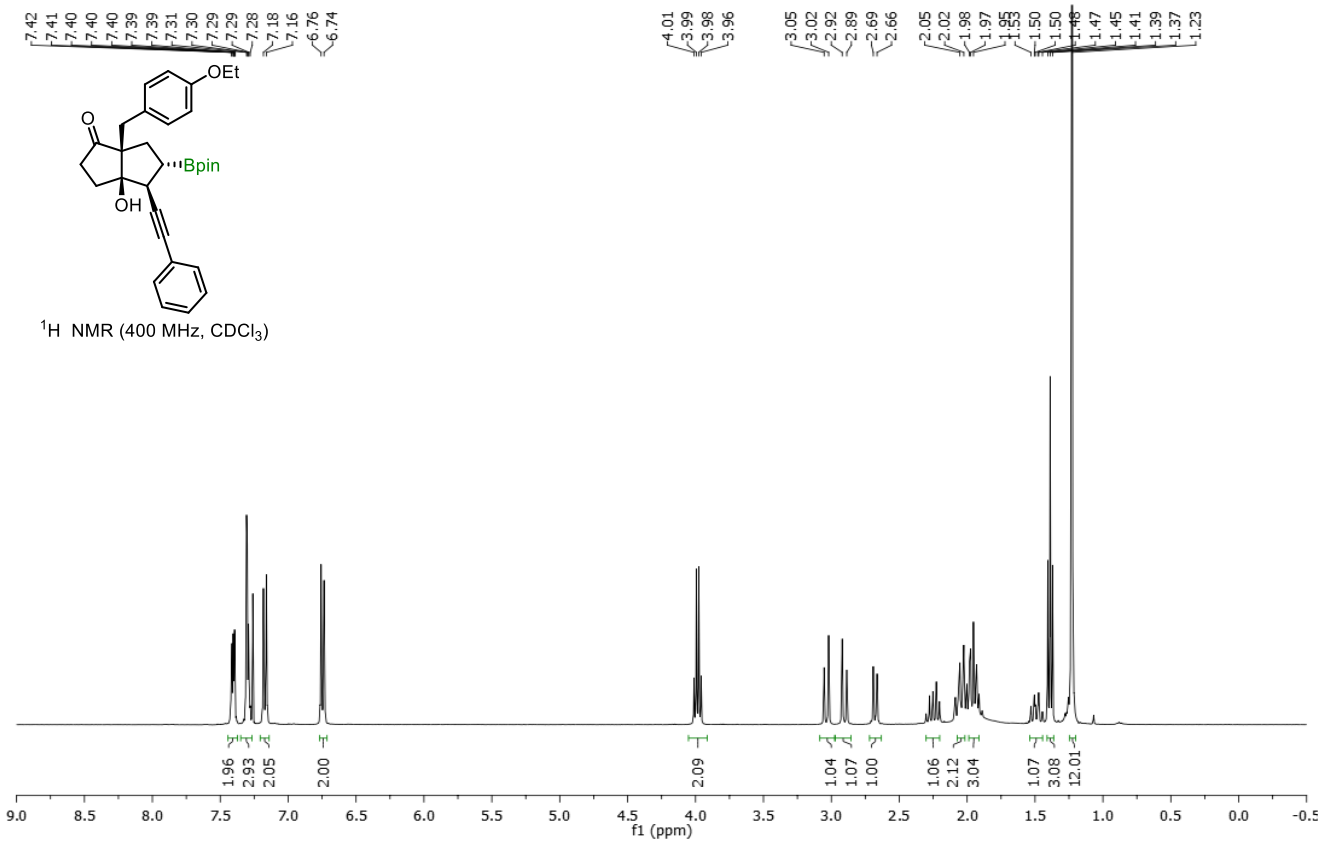


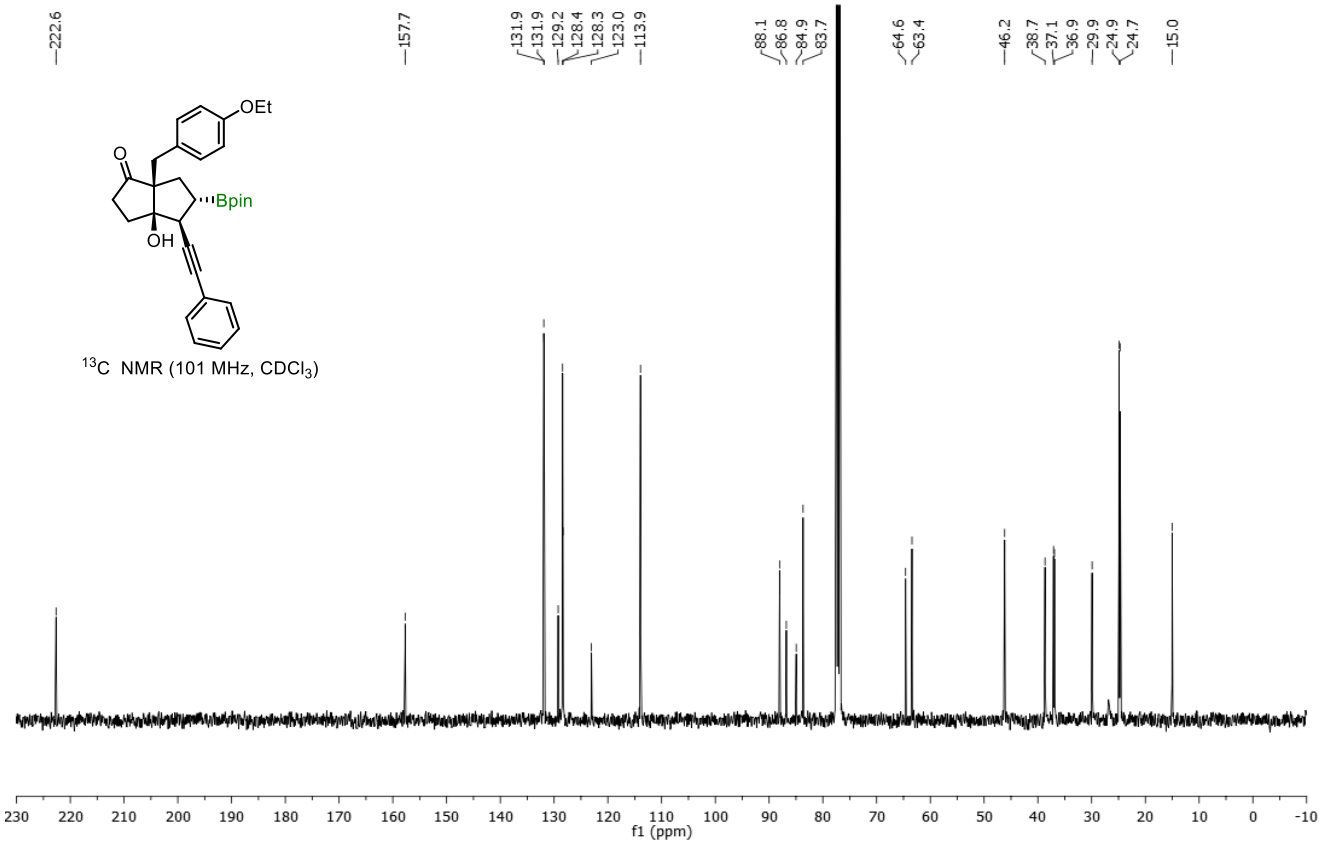
(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-(4-methylbenzyl)-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one(2g):



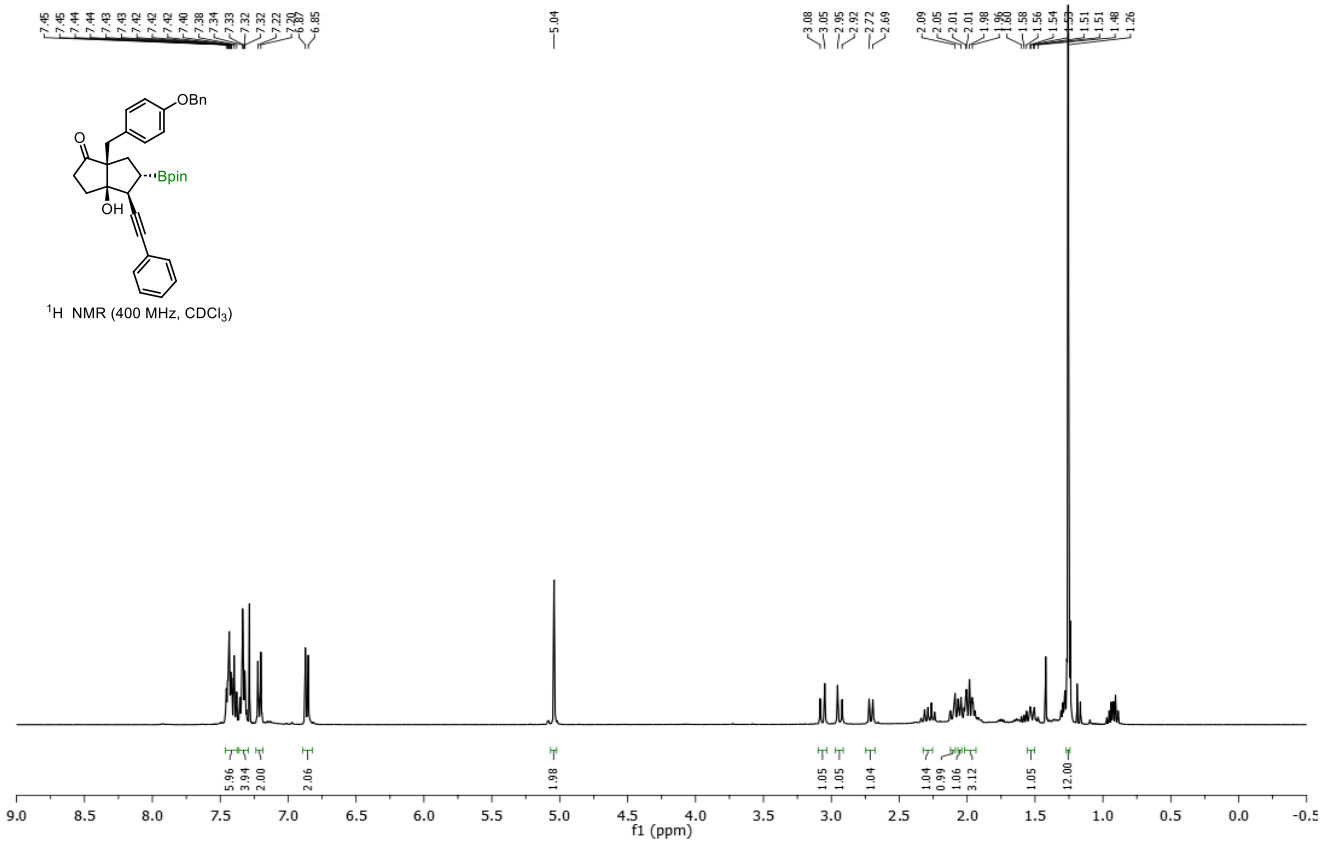


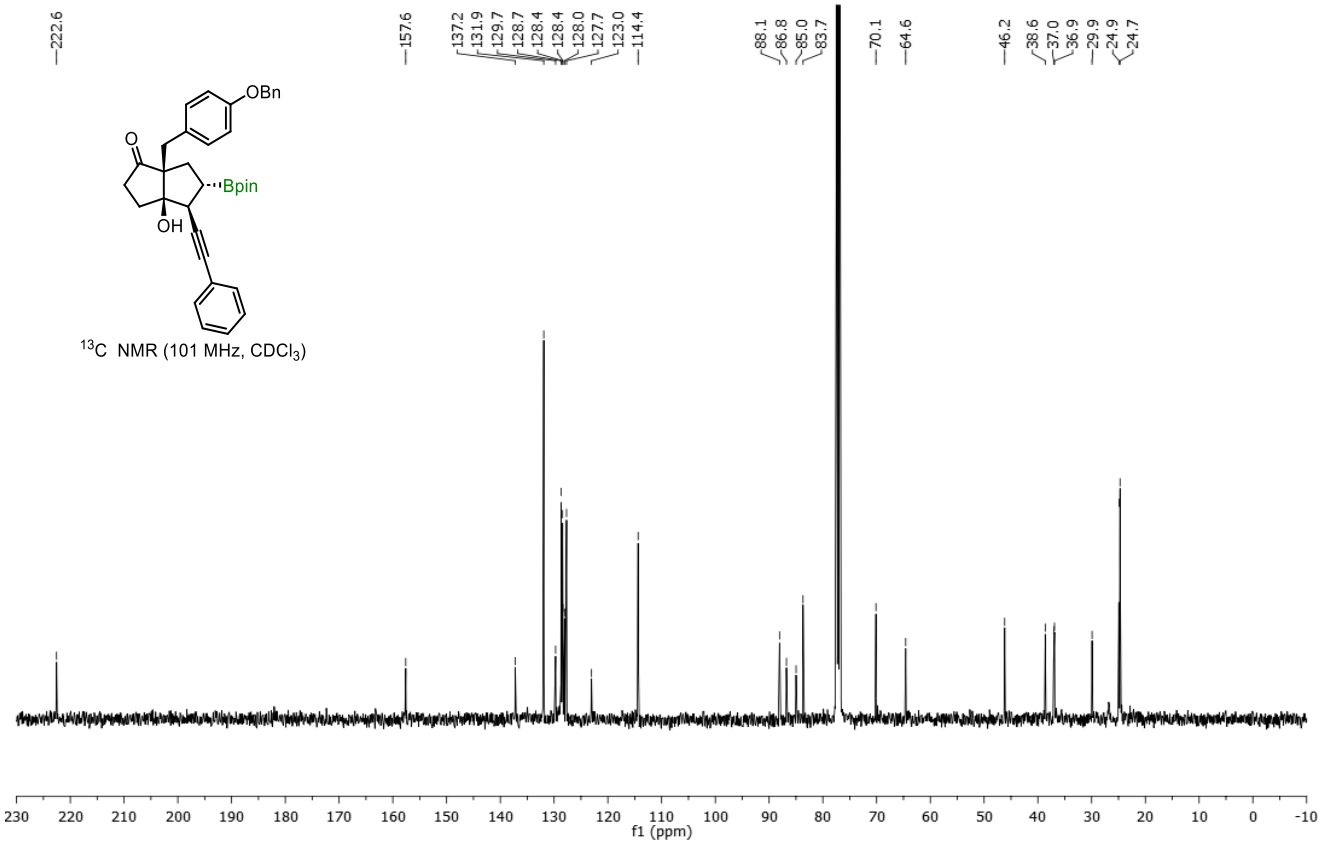
(3a*R*,4*S*,5*S*,6a*S*)-6a-(4-Ethoxybenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2h):



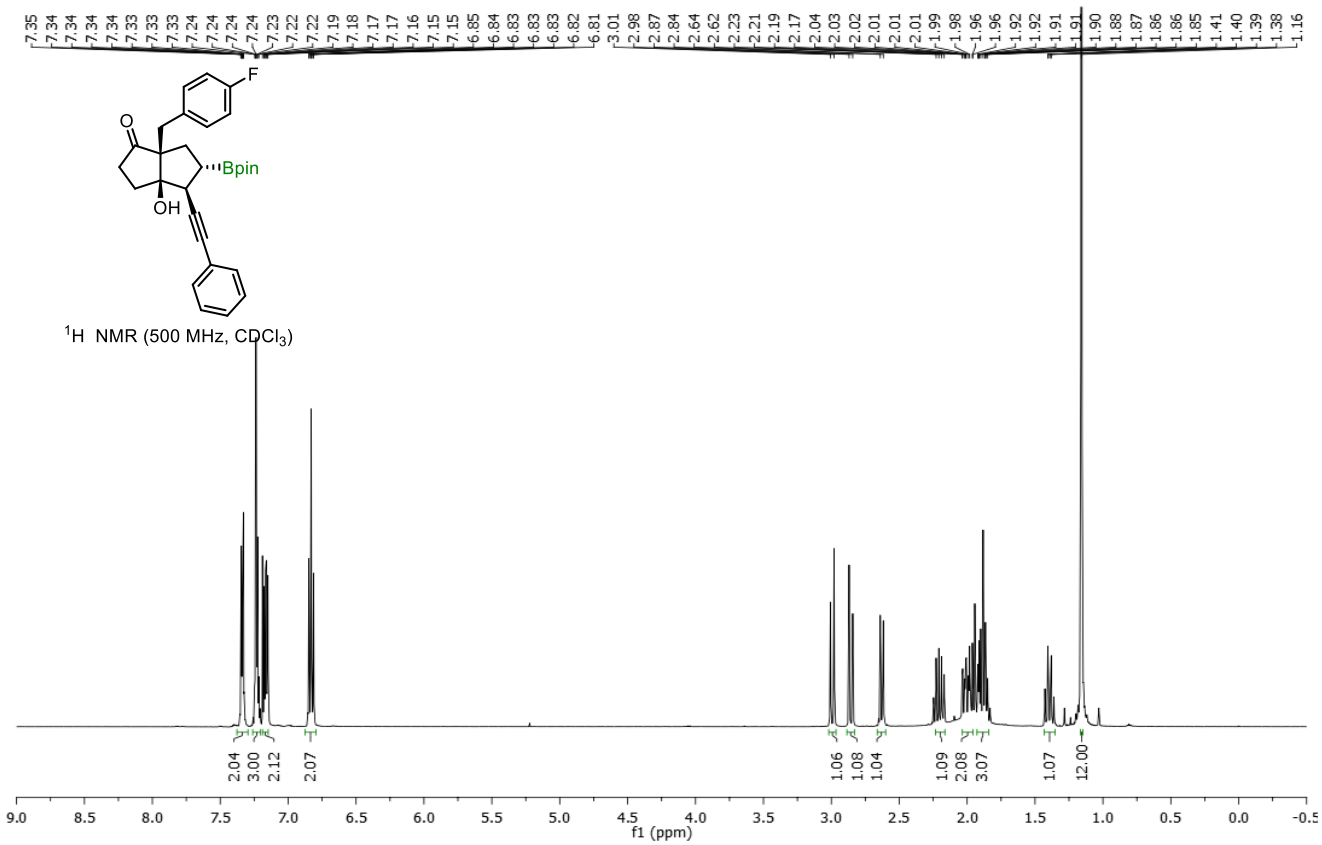


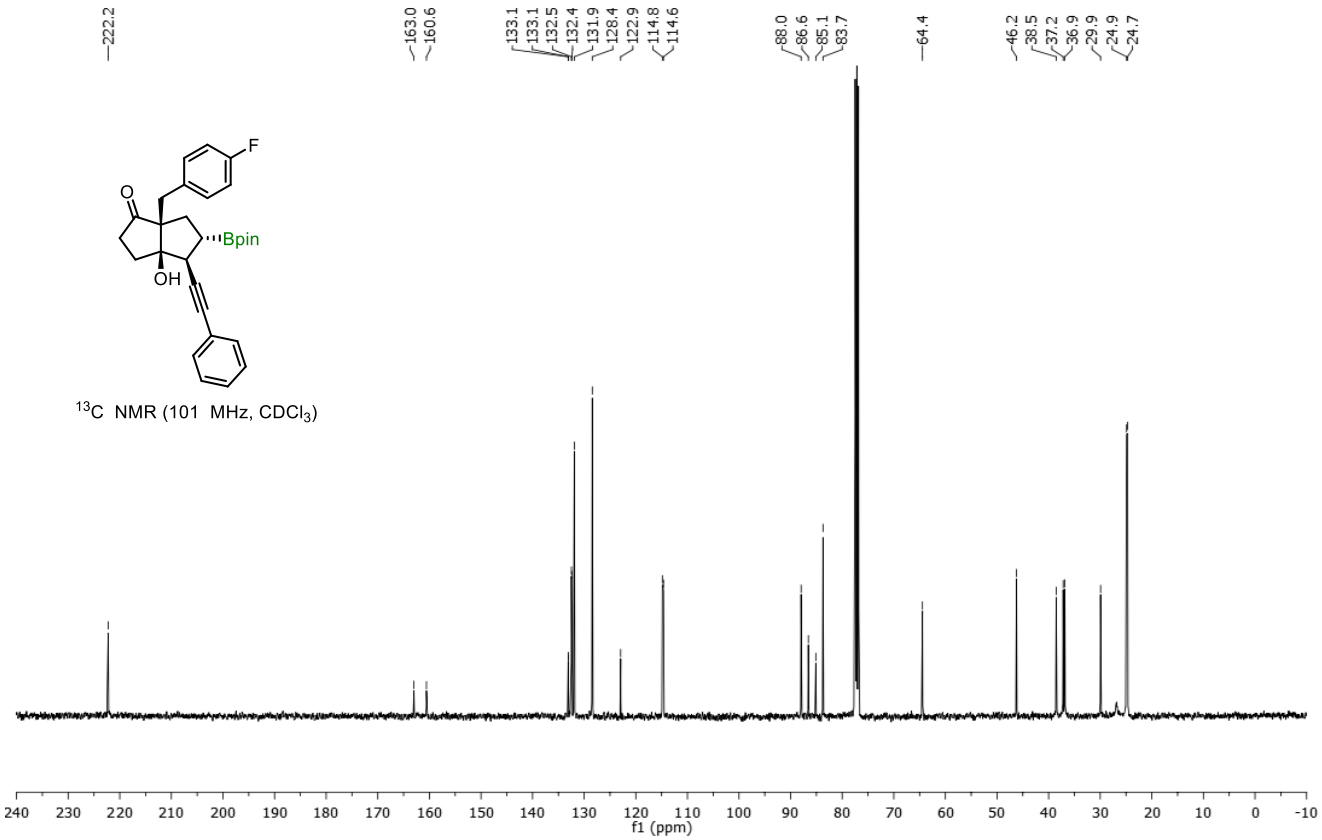
(3a*R*,4*S*,5*S*,6a*S*)-6a-(4-(Benzyloxy)benzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2i):

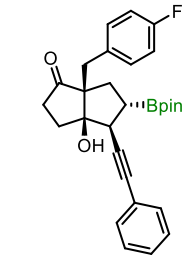




(3a*R*,4*S*,5*S*,6a*S*)-6a-(4-Fluorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2j):

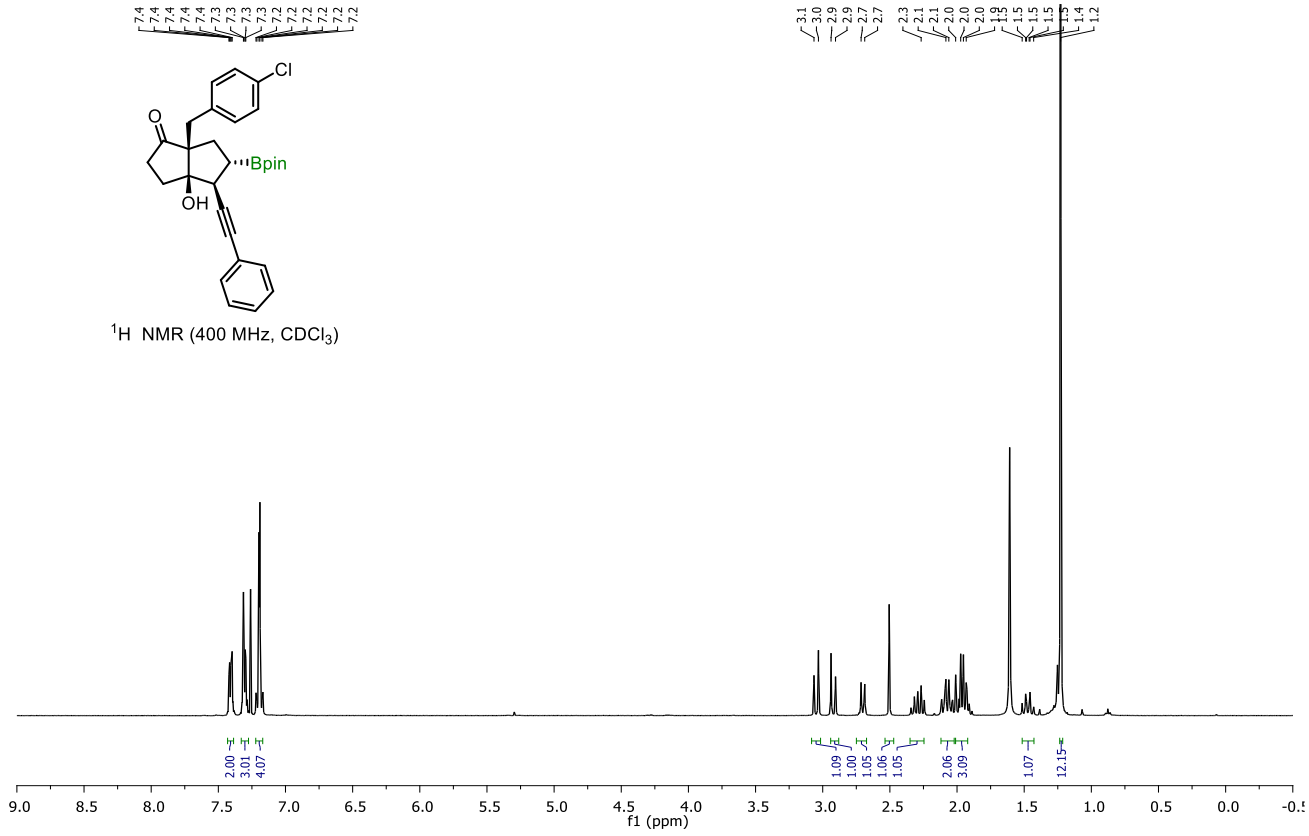


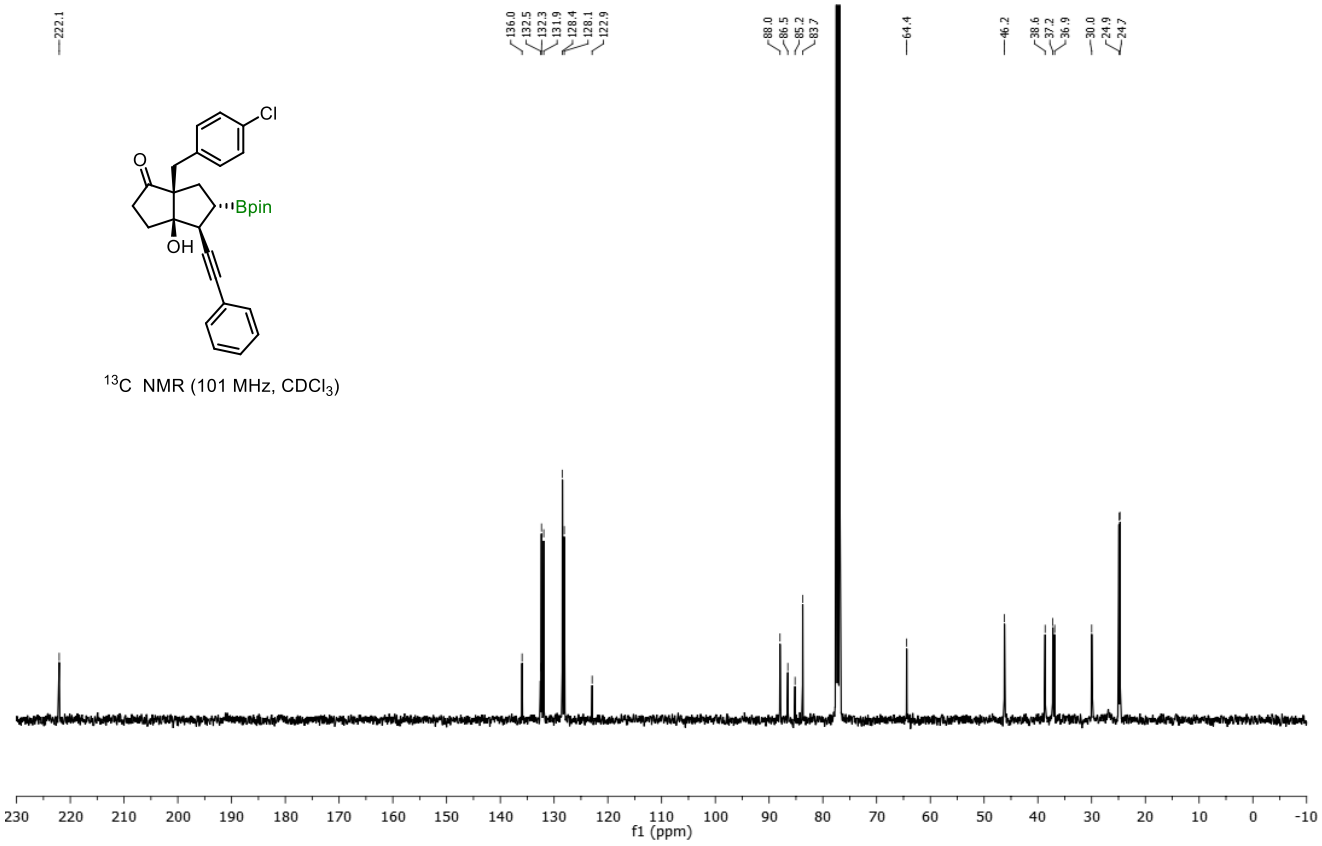




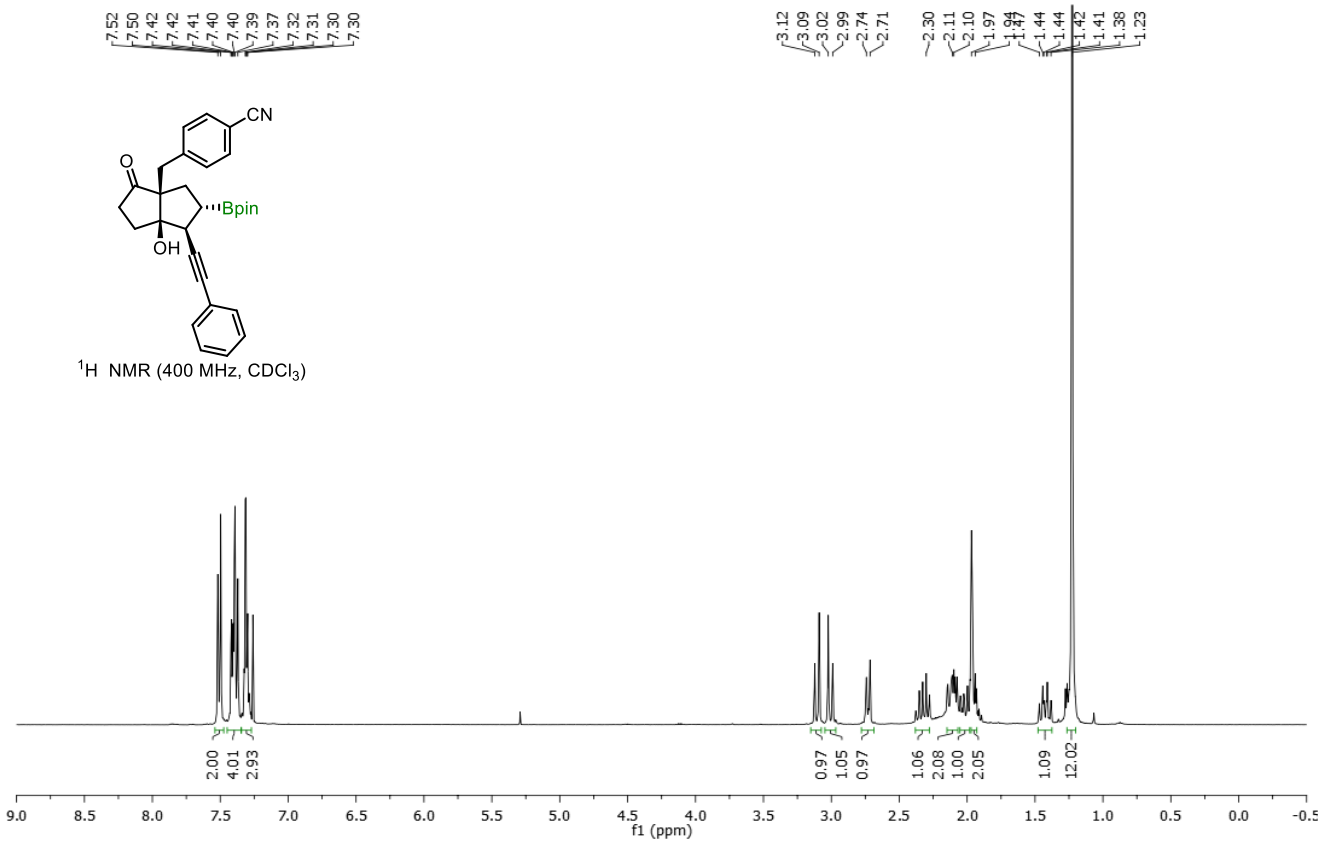
^{19}F NMR (376 MHz, $CDCl_3$)

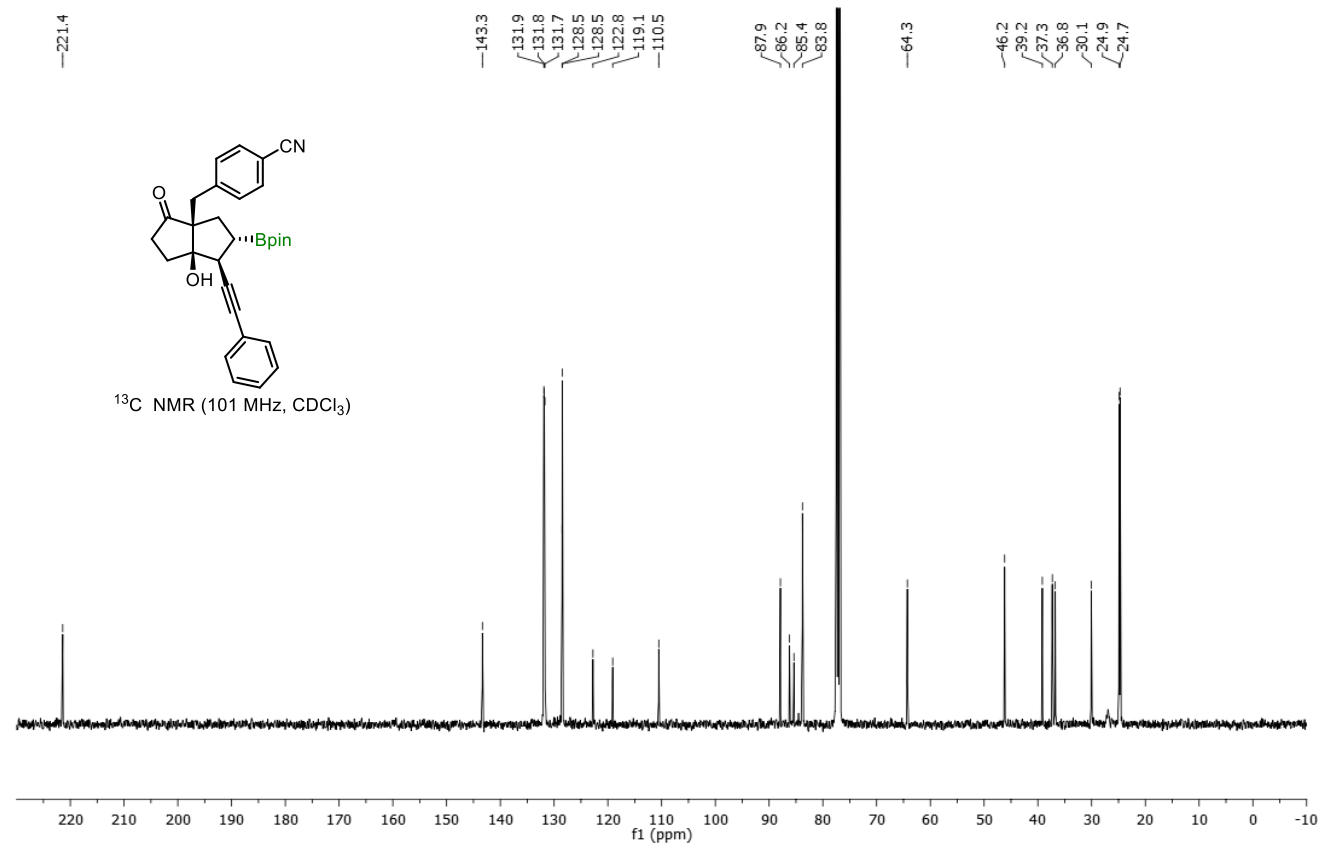
(3a*R*,4*S*,5*S*,6a*S*)-6a-(4-Chlorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2k):



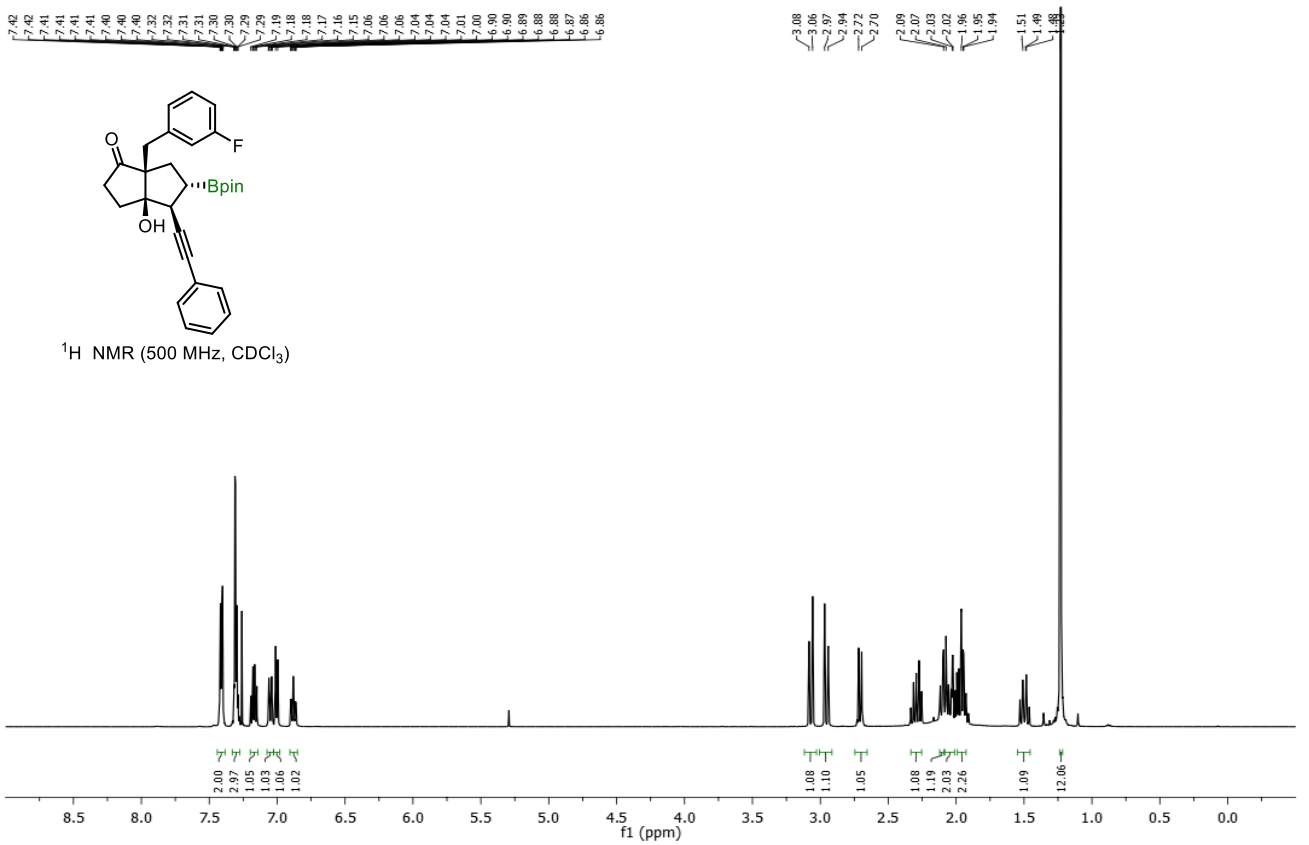


4-(((1*S*,2*S*,3a*S*,6a*R*)-6a-Hydroxy-4-oxo-1-(phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-3a(1*H*)-yl)methyl)benzonitrile (2l):

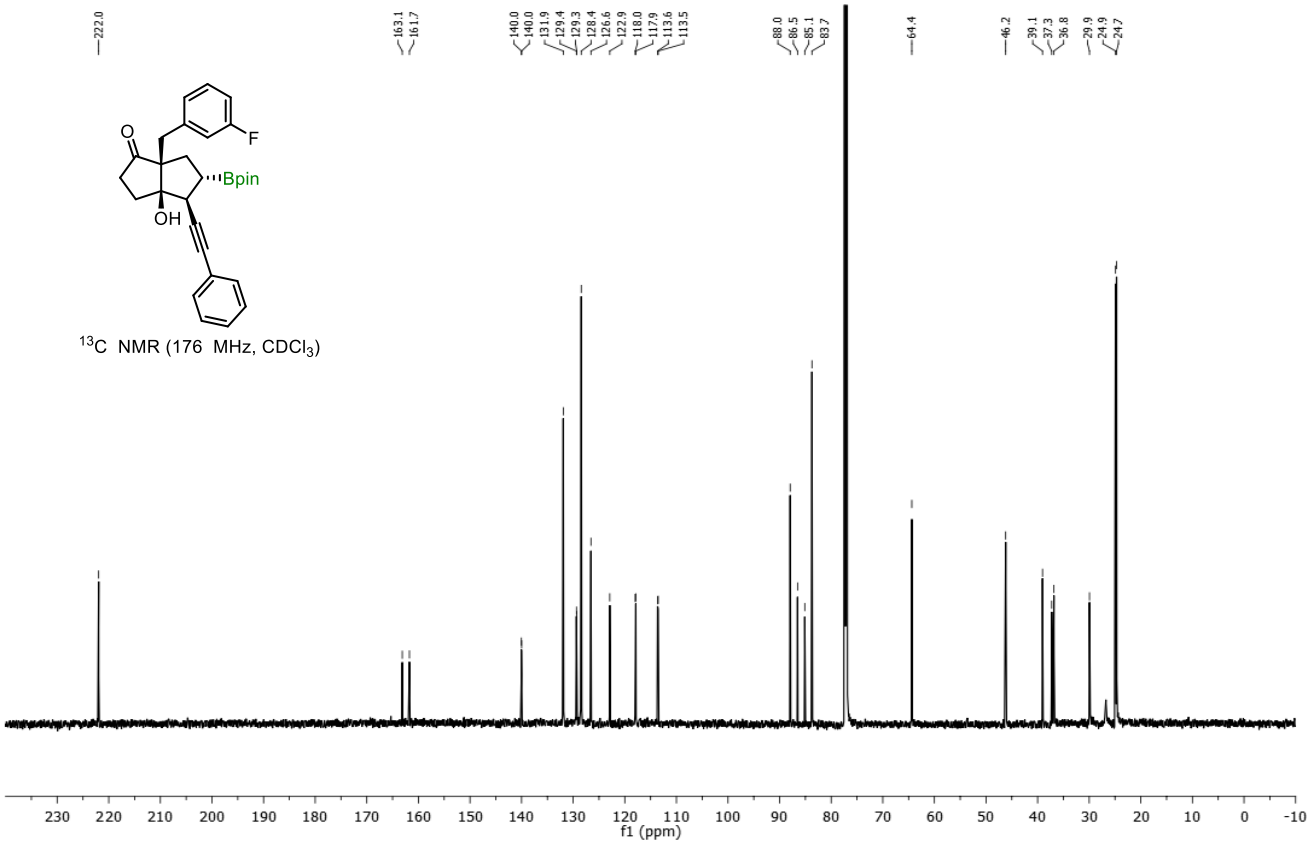




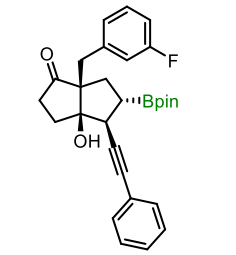
(3a*R*,4*S*,5*S*,6a*S*)-6a-(3-Fluorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2m):



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

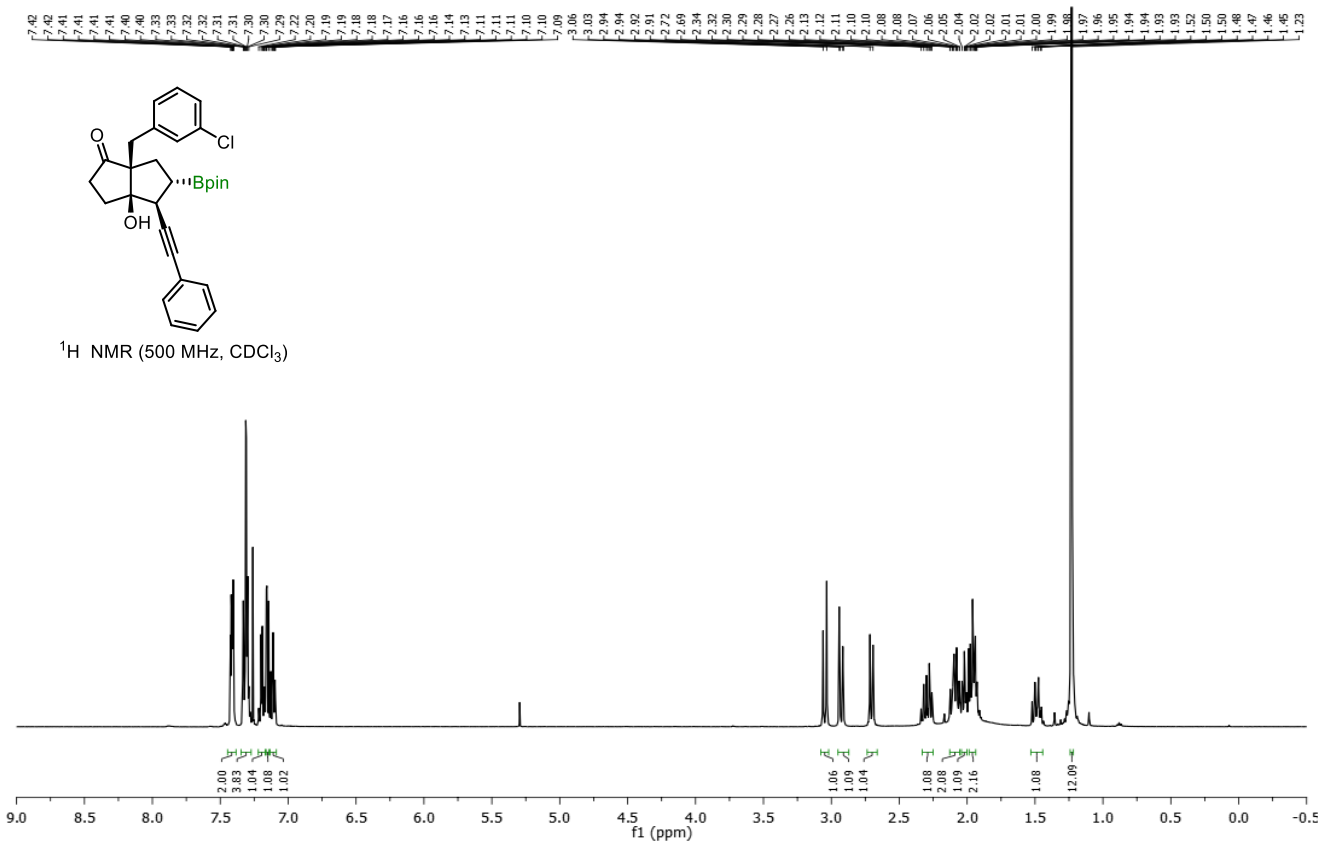


^{13}C NMR (176 MHz, $CDCl_3$)

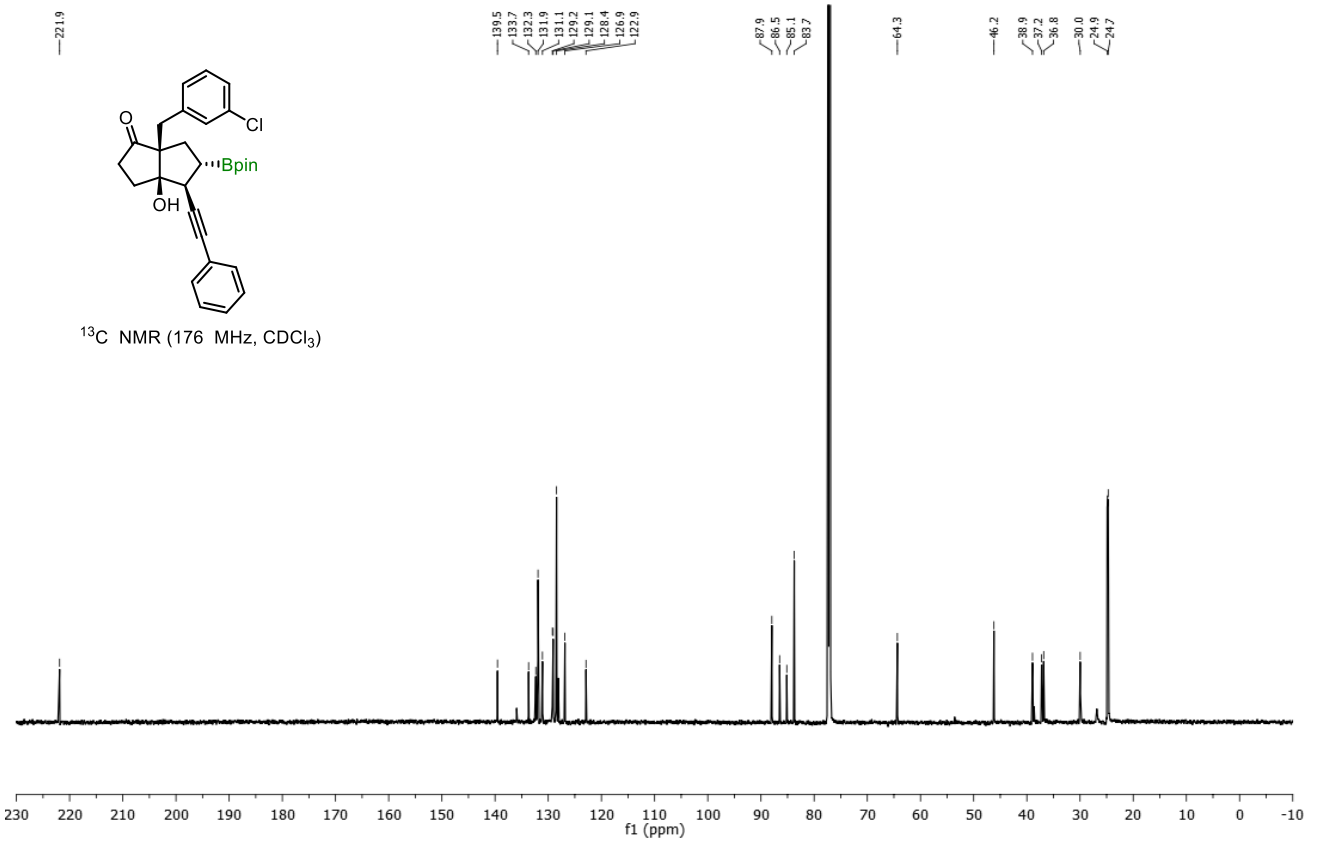


^{19}F NMR (377 MHz, $CDCl_3$)

(3a*R*,4*S*,5*S*,6a*S*)-6a-(3-Chlorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2n):

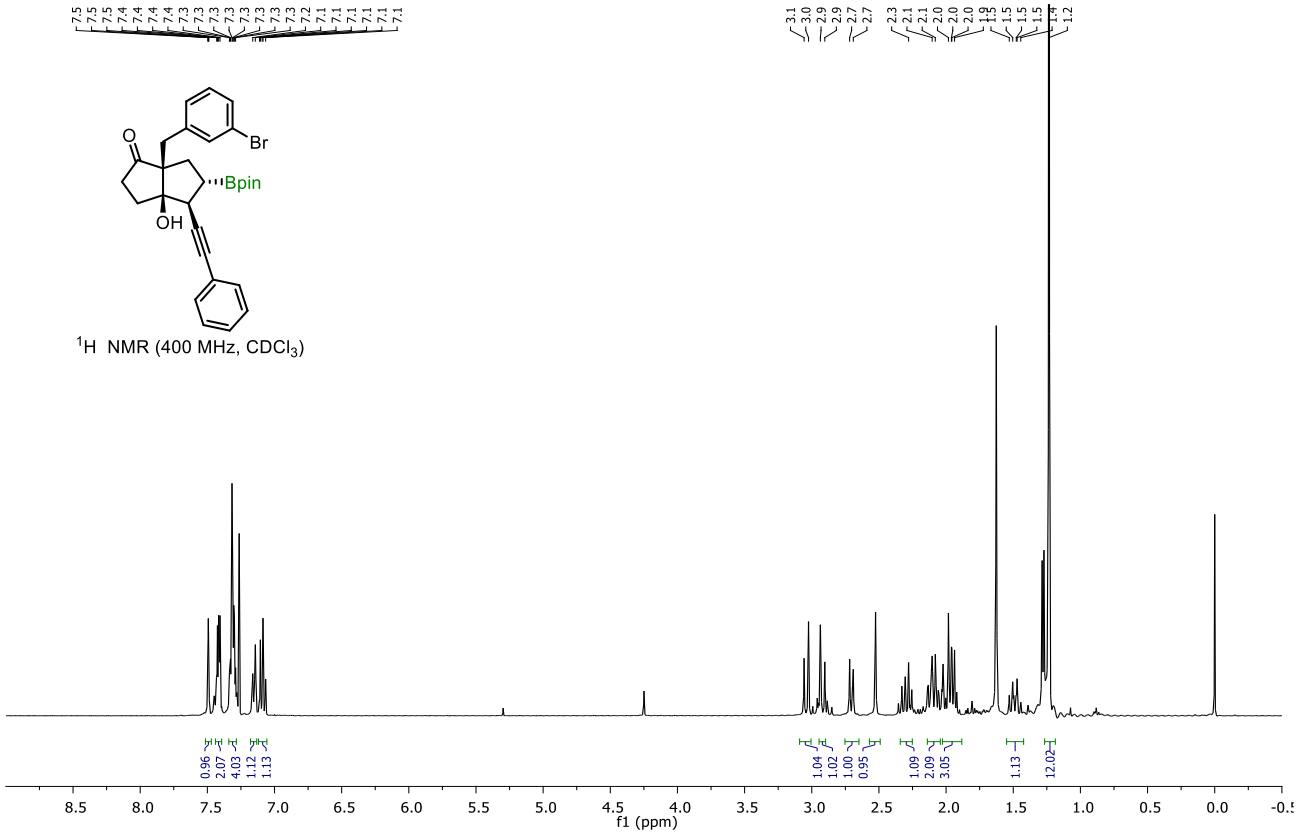


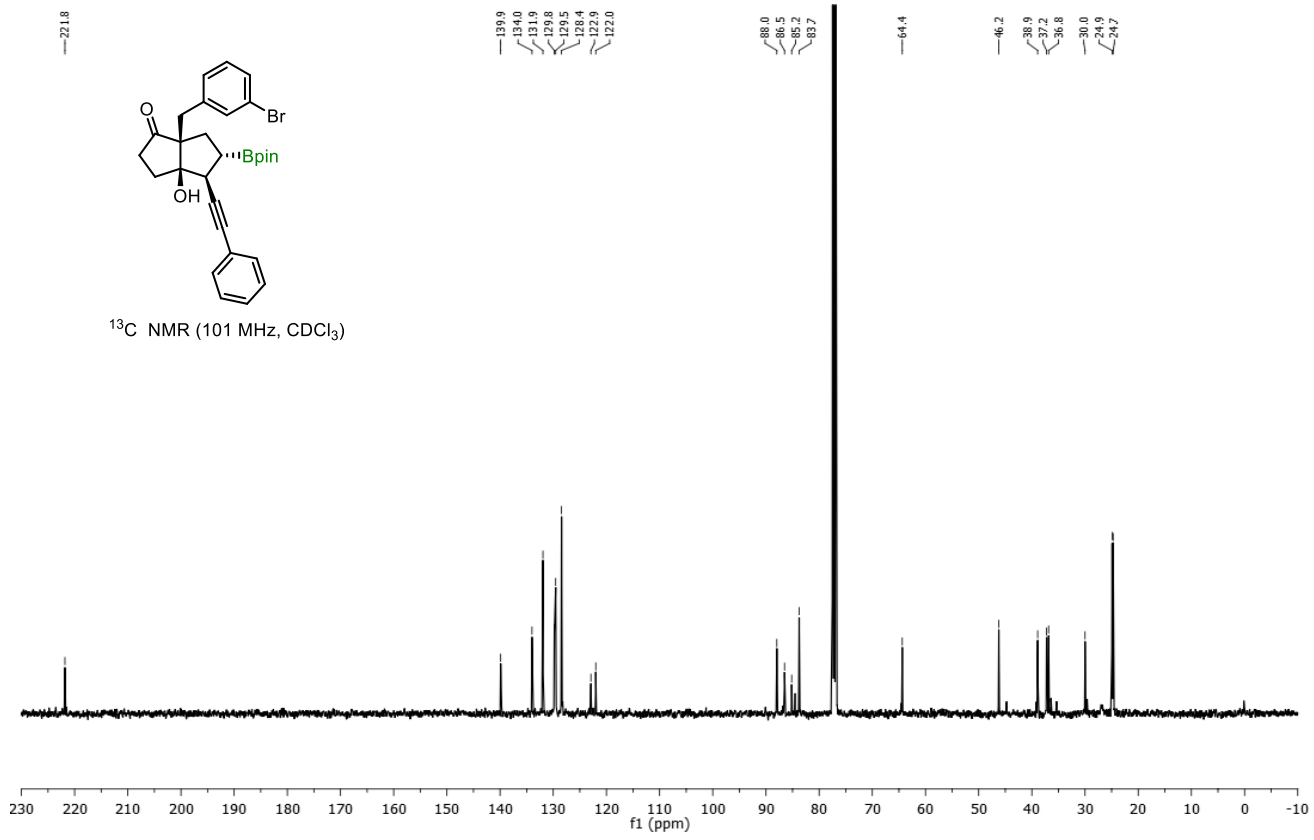
^{1}H NMR (500 MHz, $CDCl_3$)



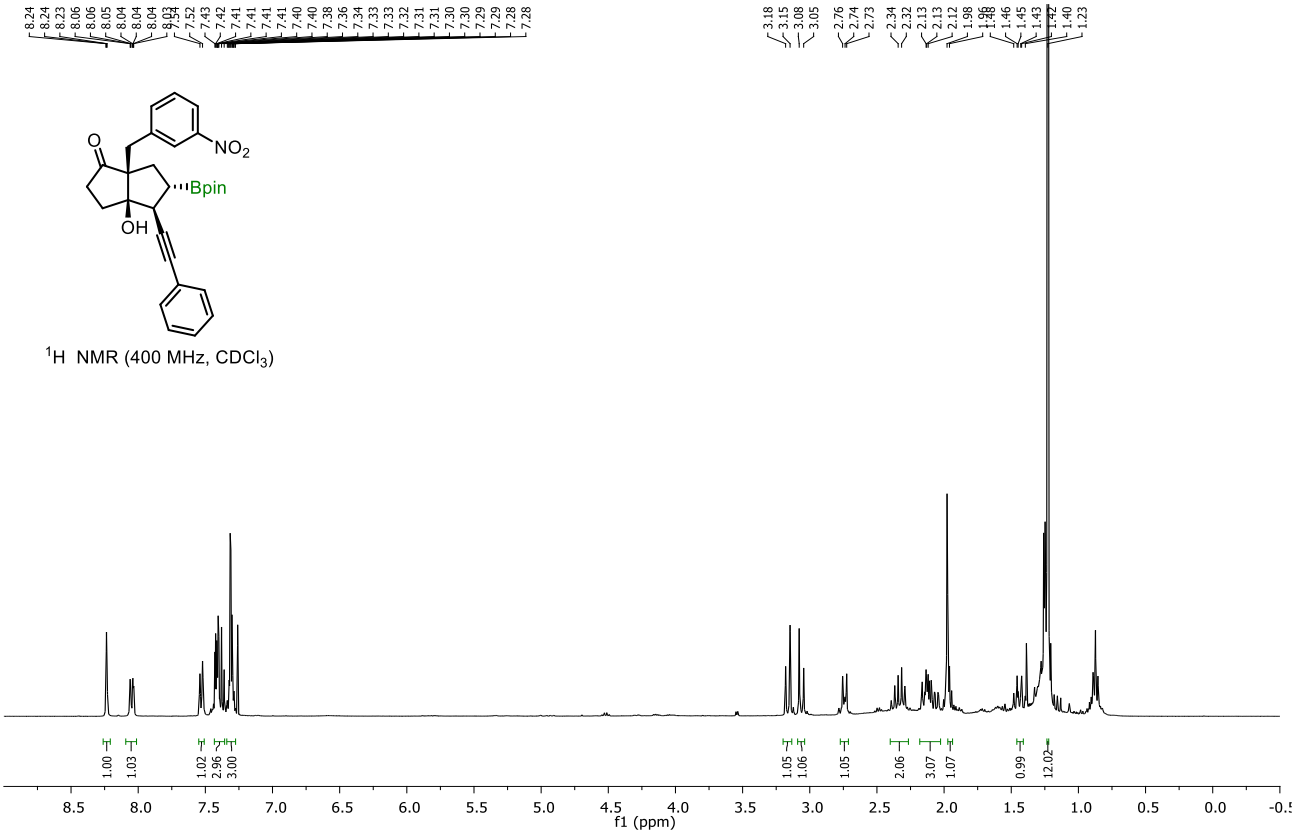
^{13}C NMR (176 MHz, $CDCl_3$)

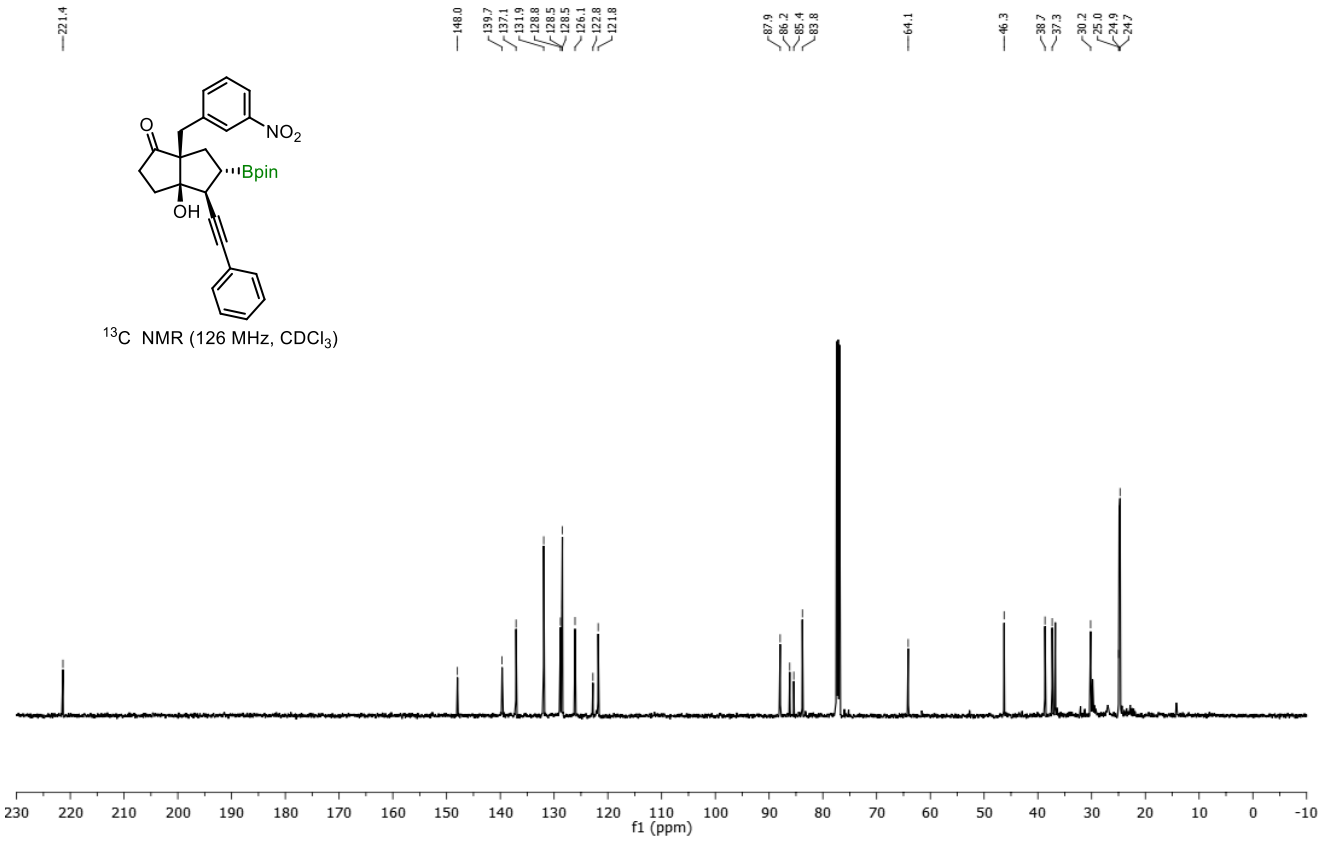
(3a*R*,4*S*,5*S*,6a*S*)-6a-(3-Bromobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2o):



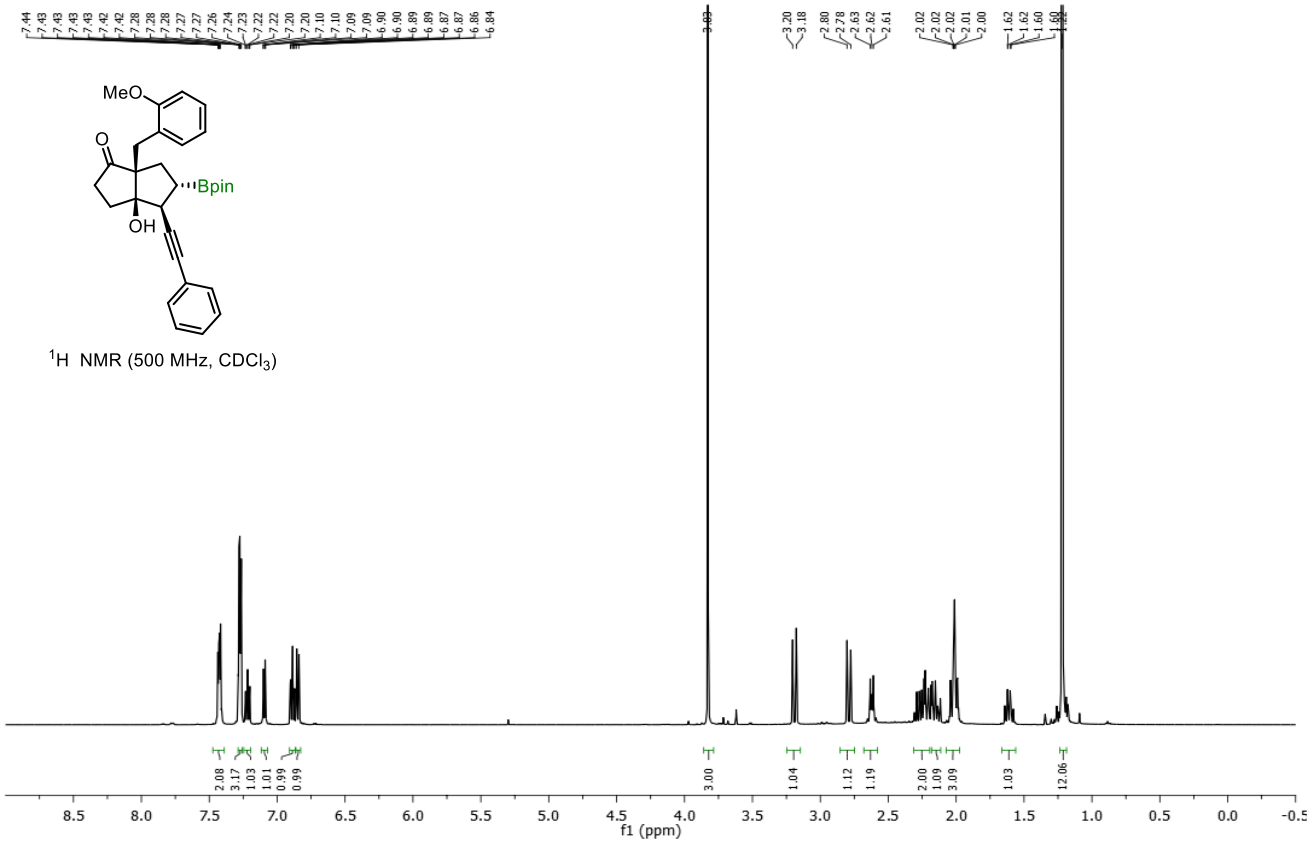


(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-(3-nitrobenzyl)-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2p):

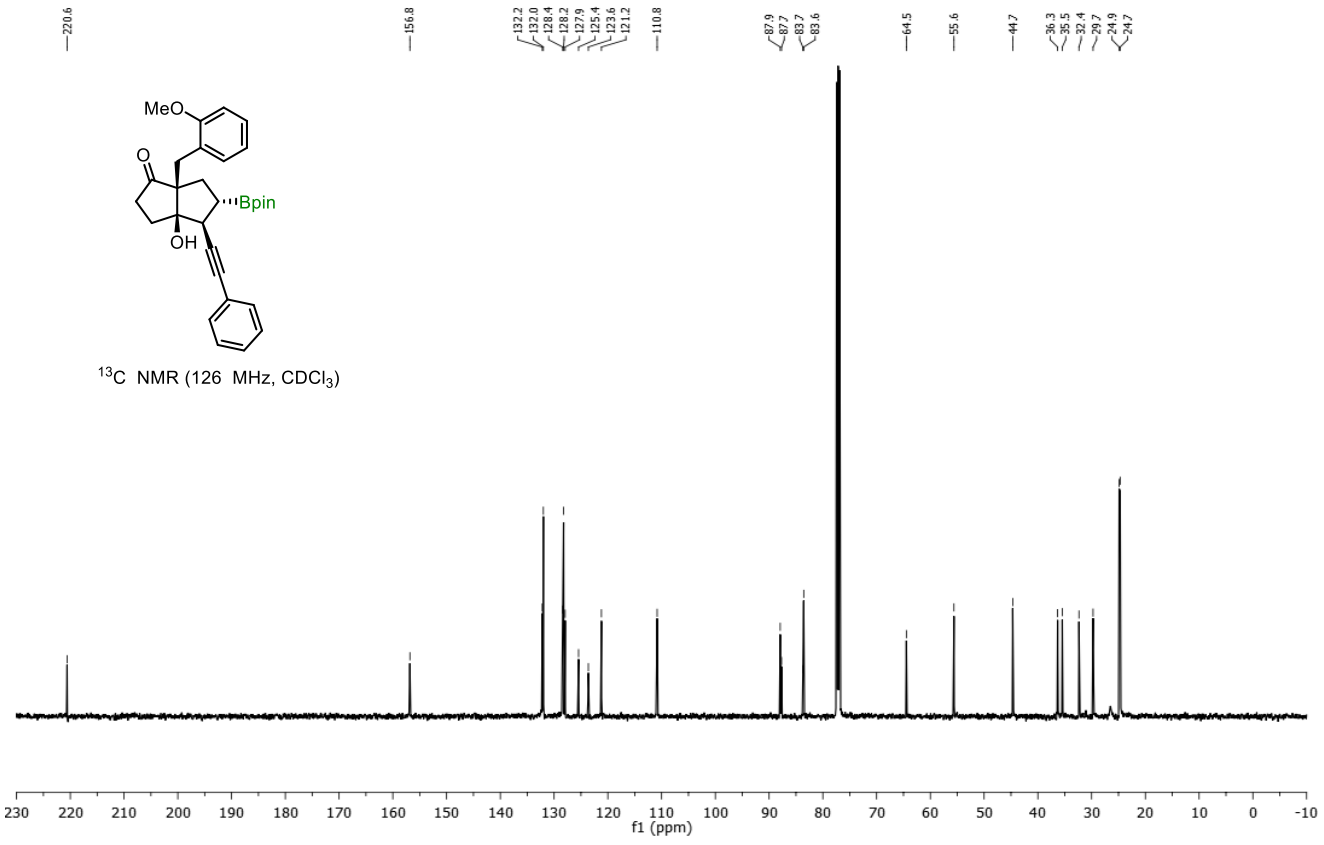




(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-(2-methoxybenzyl)-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2q):

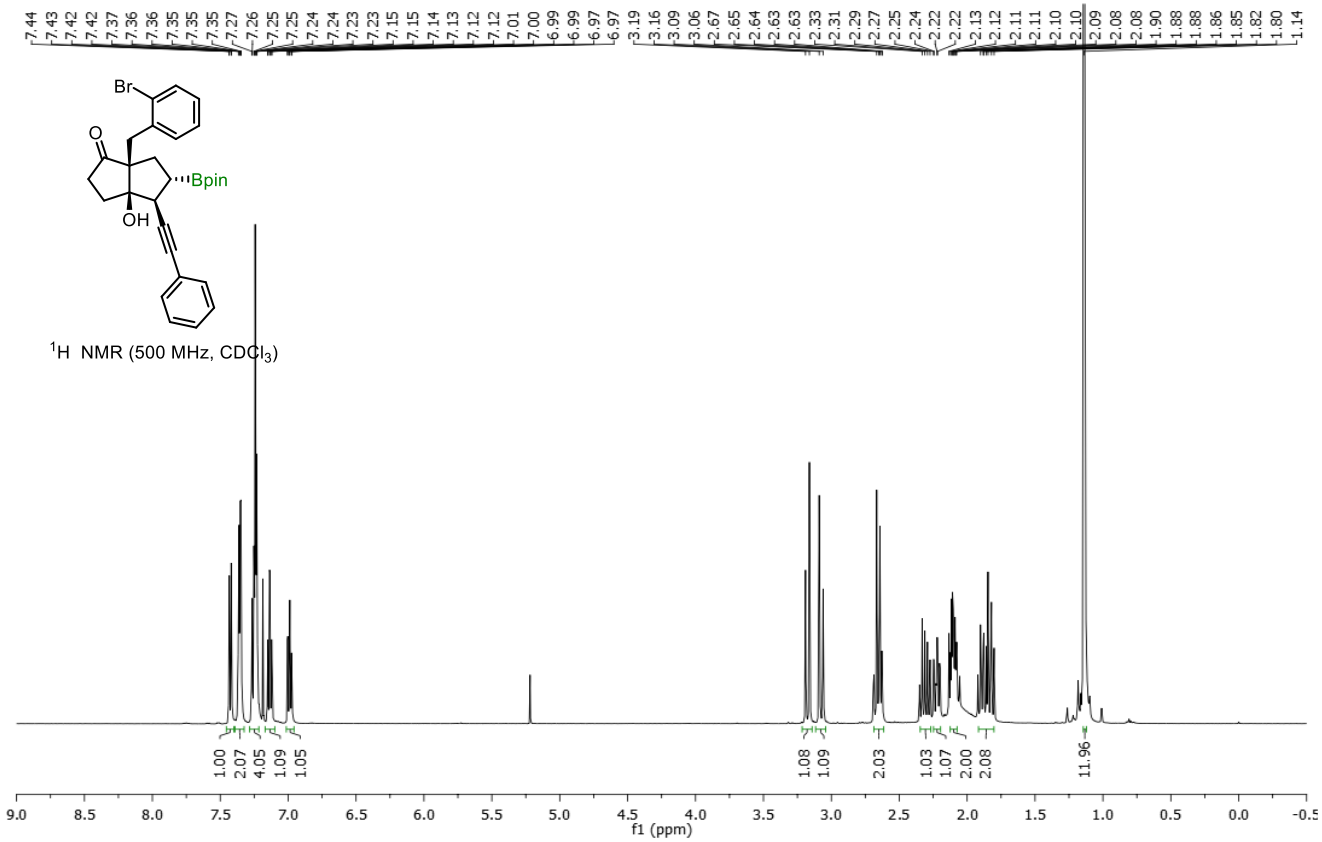


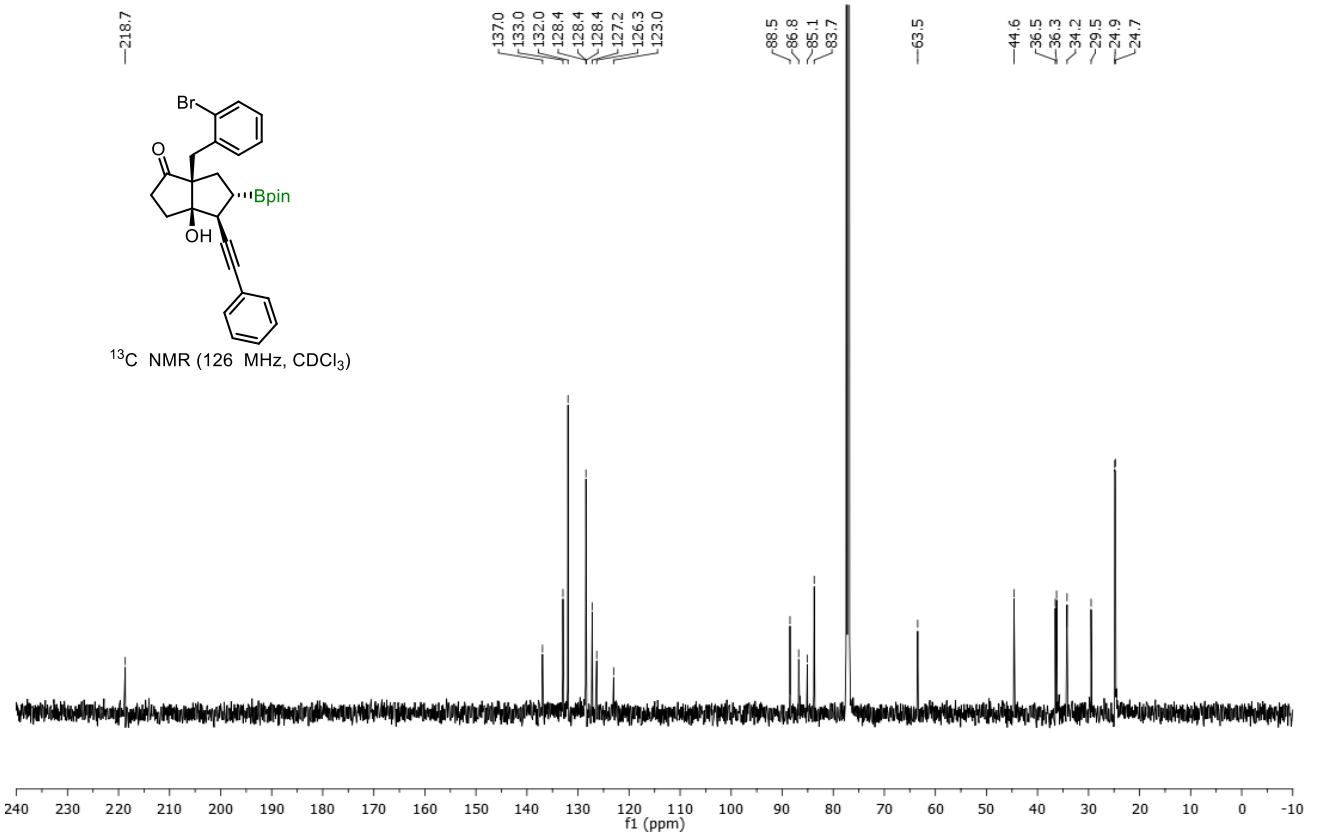
^{1}H NMR (500 MHz, $CDCl_3$)



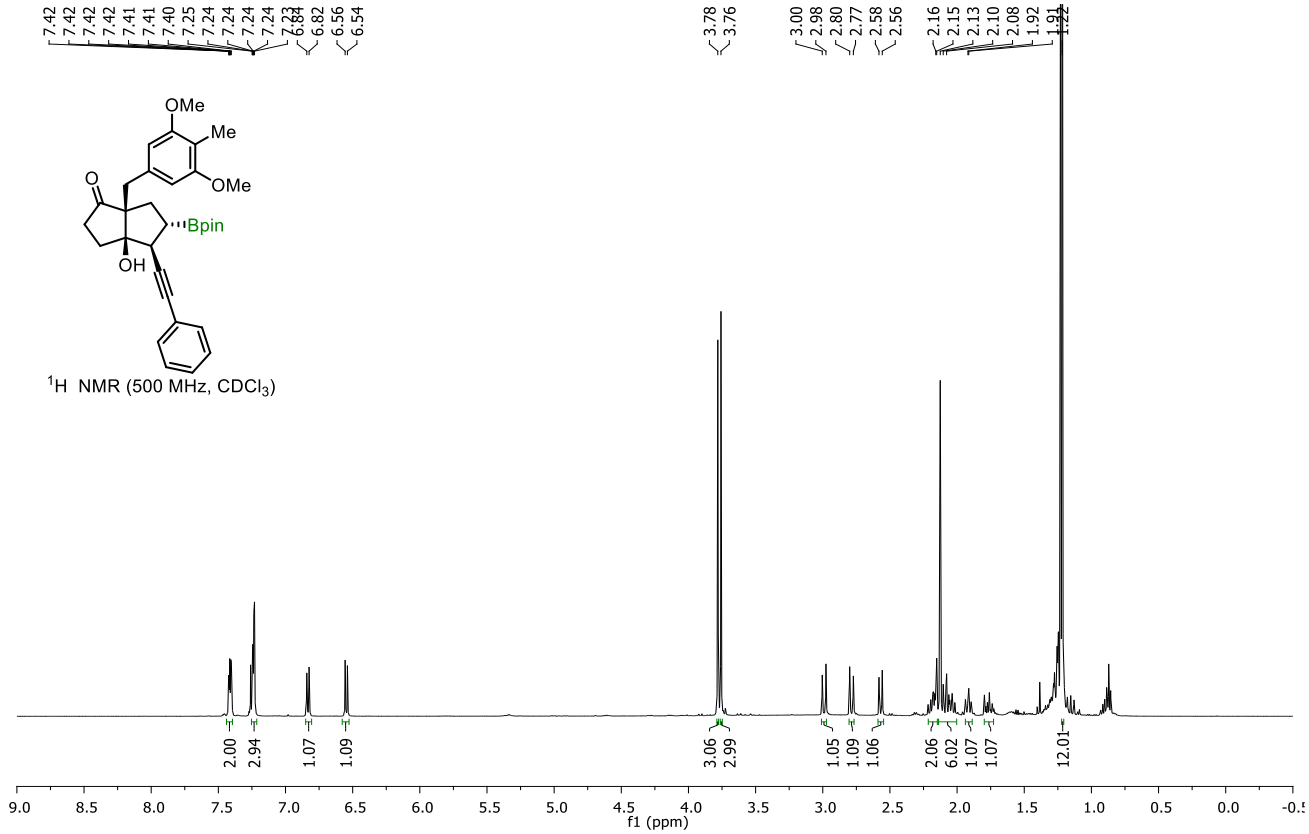
^{13}C NMR (126 MHz, $CDCl_3$)

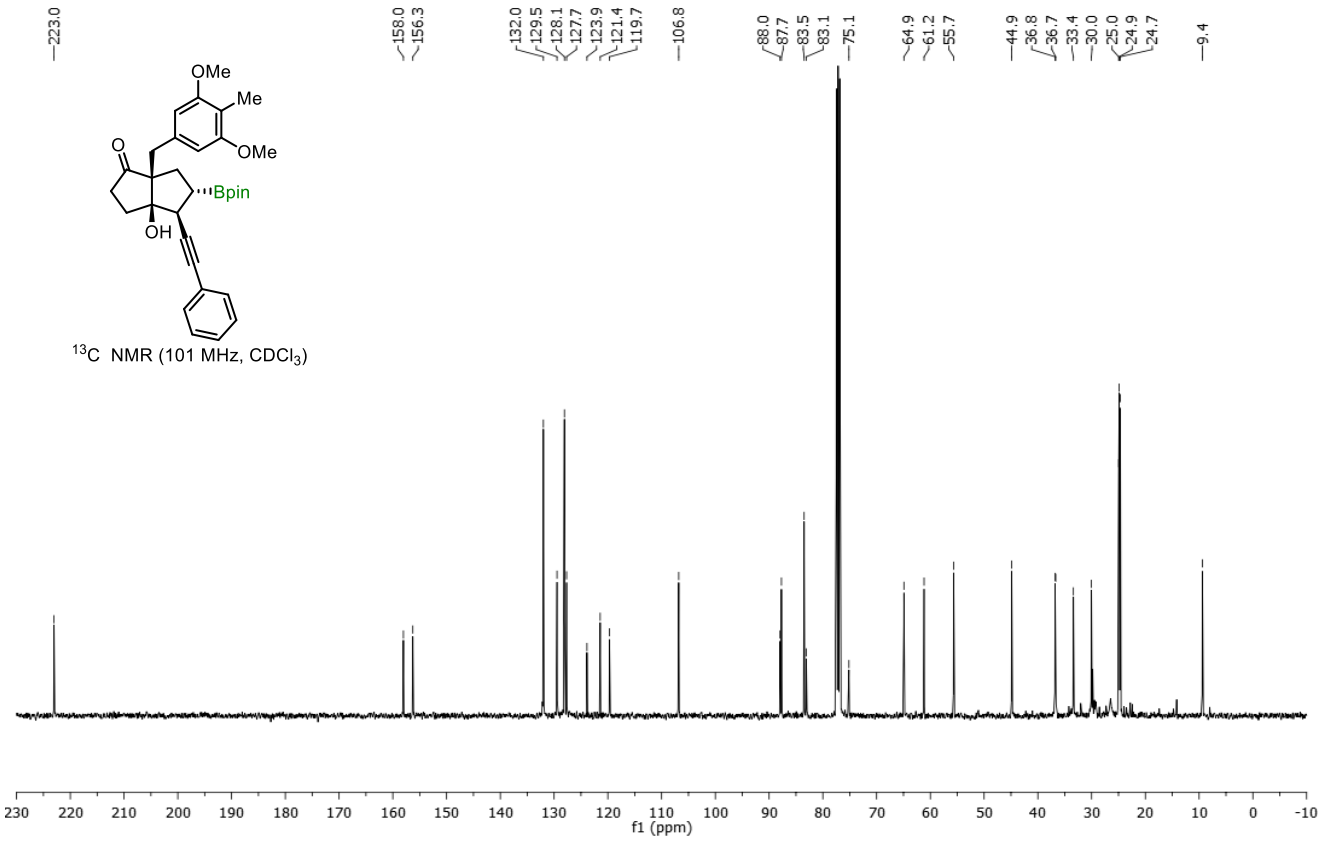
(3a*R*,4*S*,5*S*,6a*S*)-6a-(2-Bromobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2r):



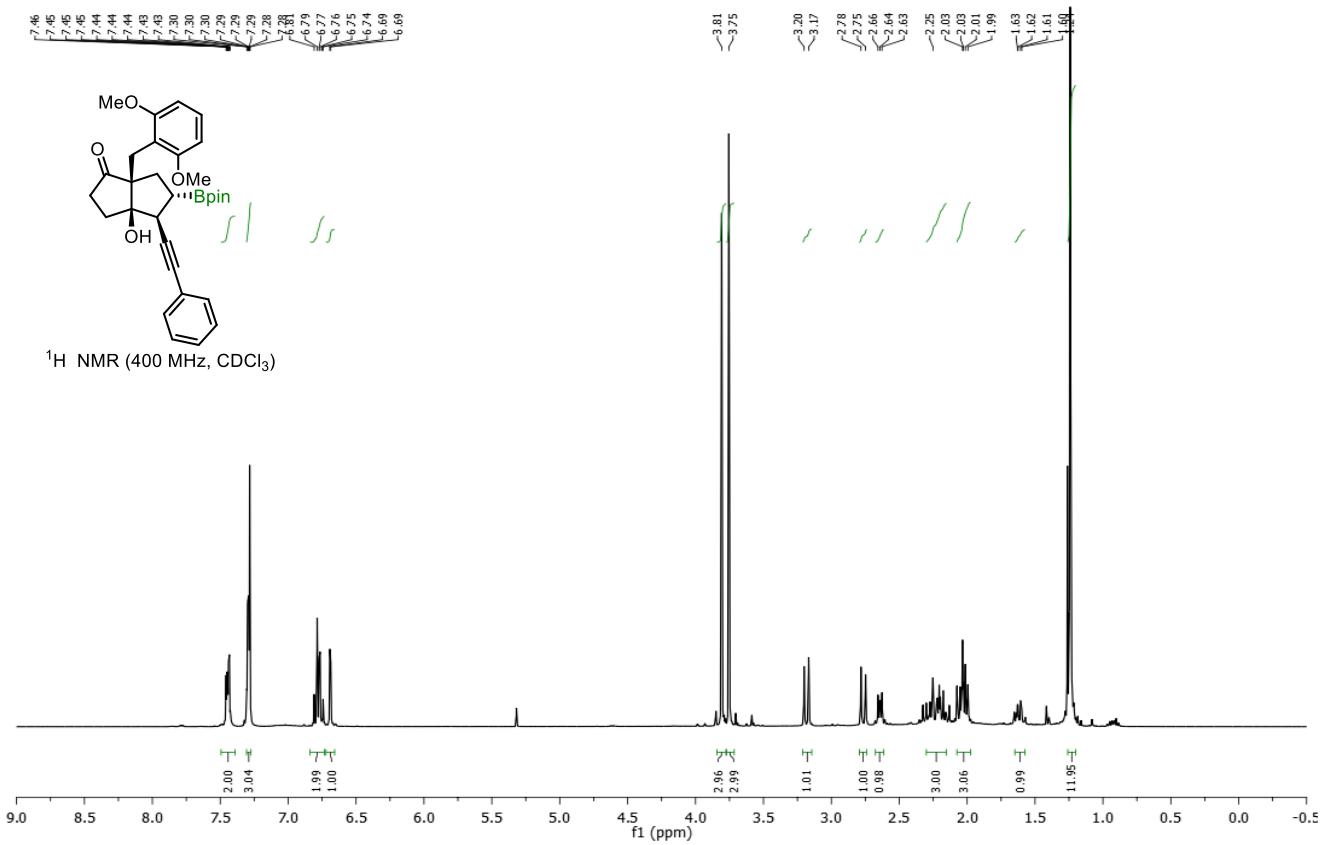


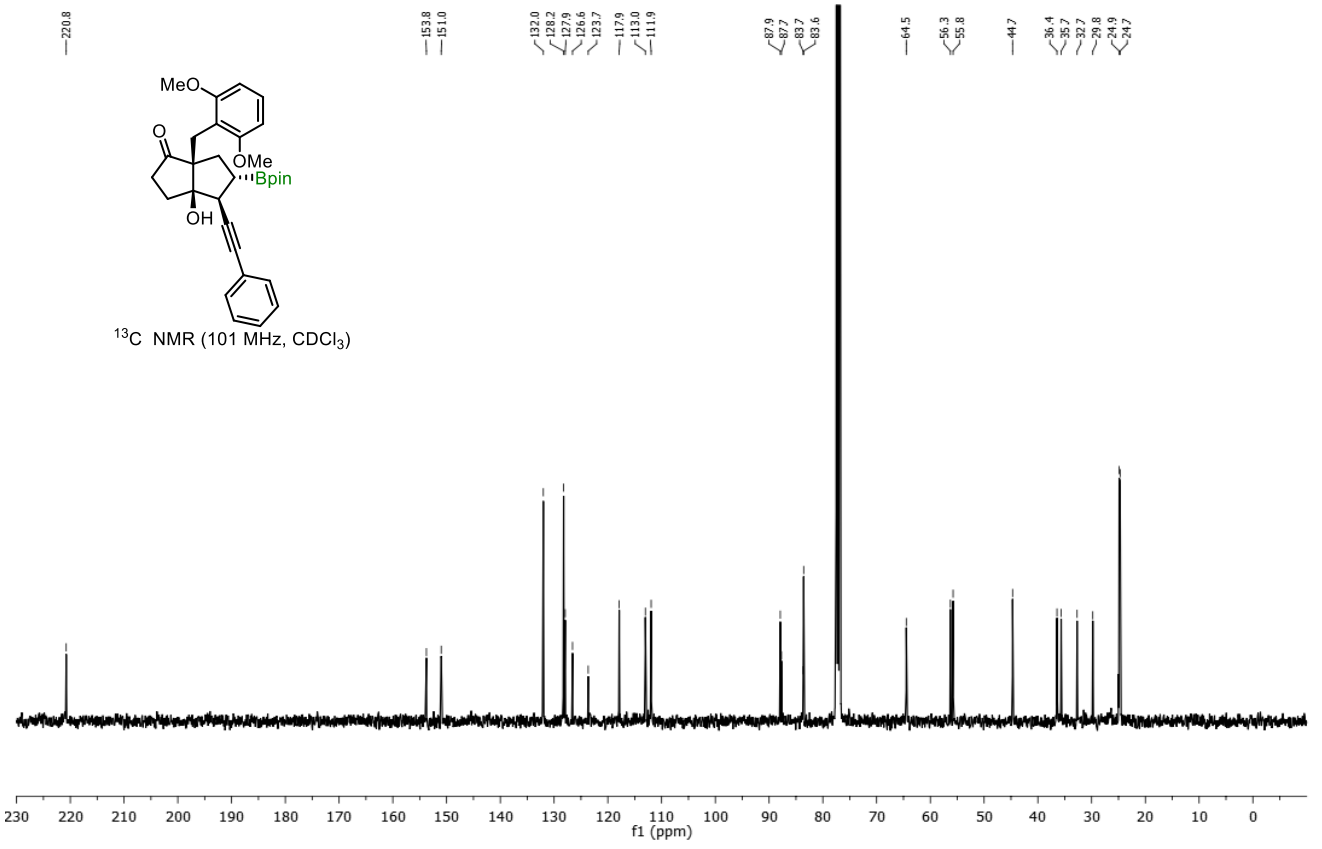
(3a*R*,4*S*,5*S*,6a*S*)-6a-(3,5-Dimethoxy-4-methylbenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2s):



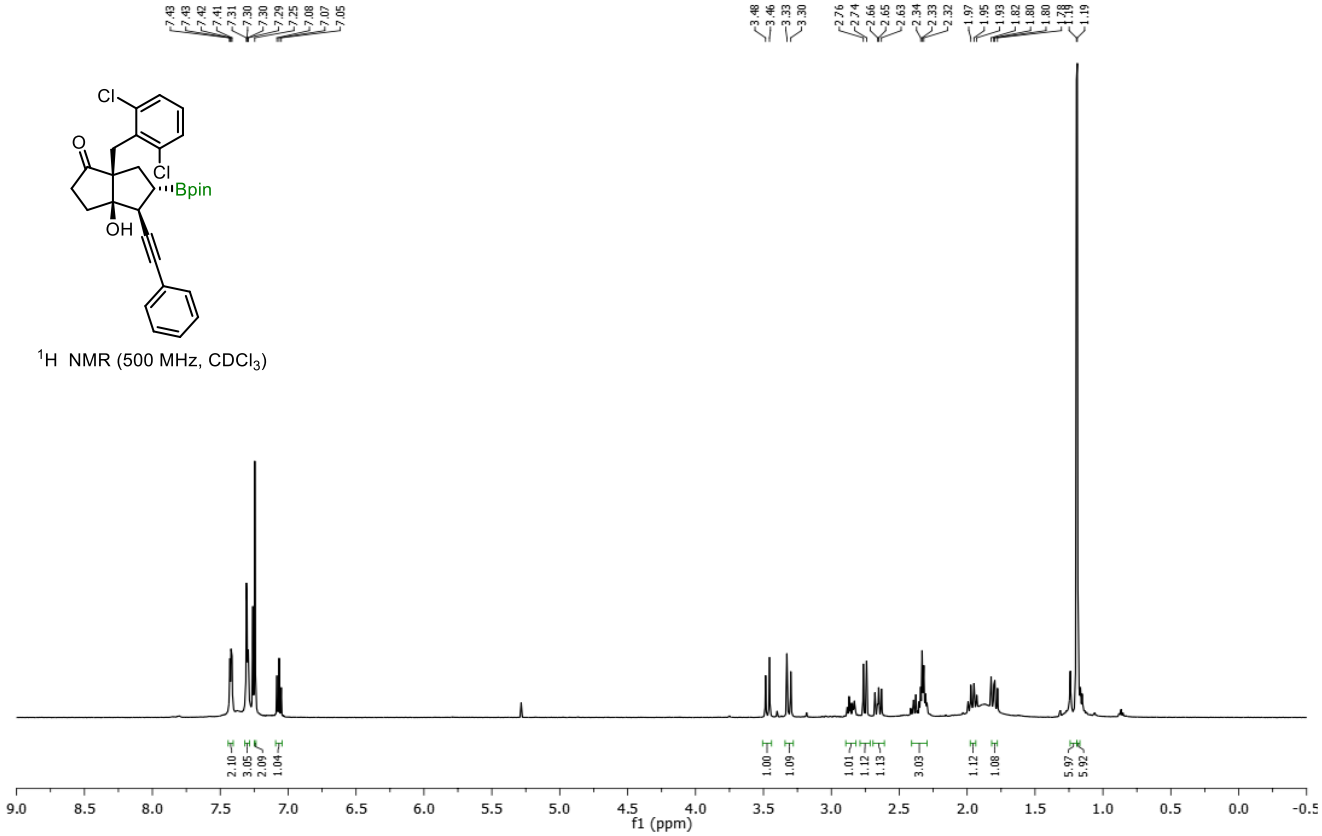


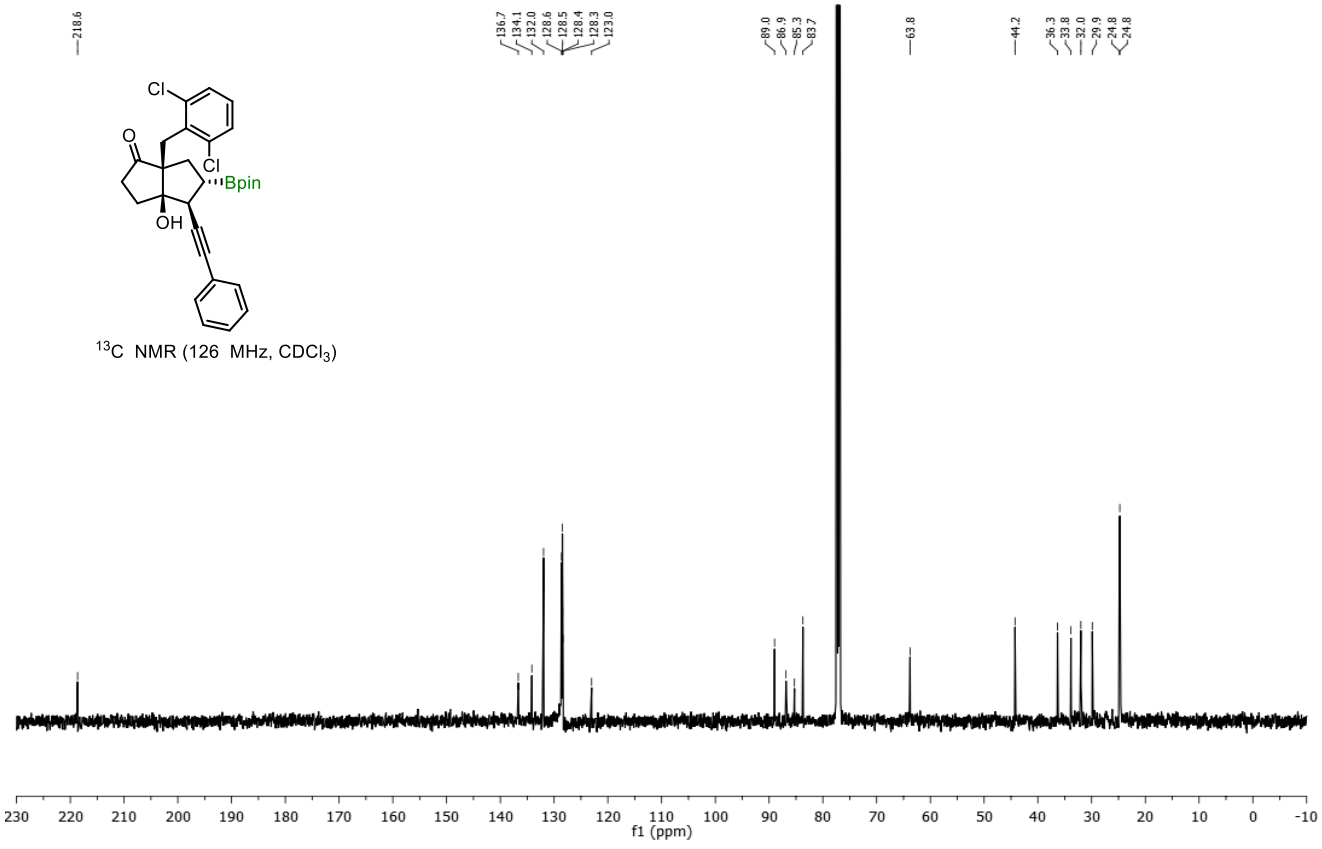
(3a*R*,4*S*,5*S*,6a*S*)-6a-(2,6-Dimethoxybenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2t):



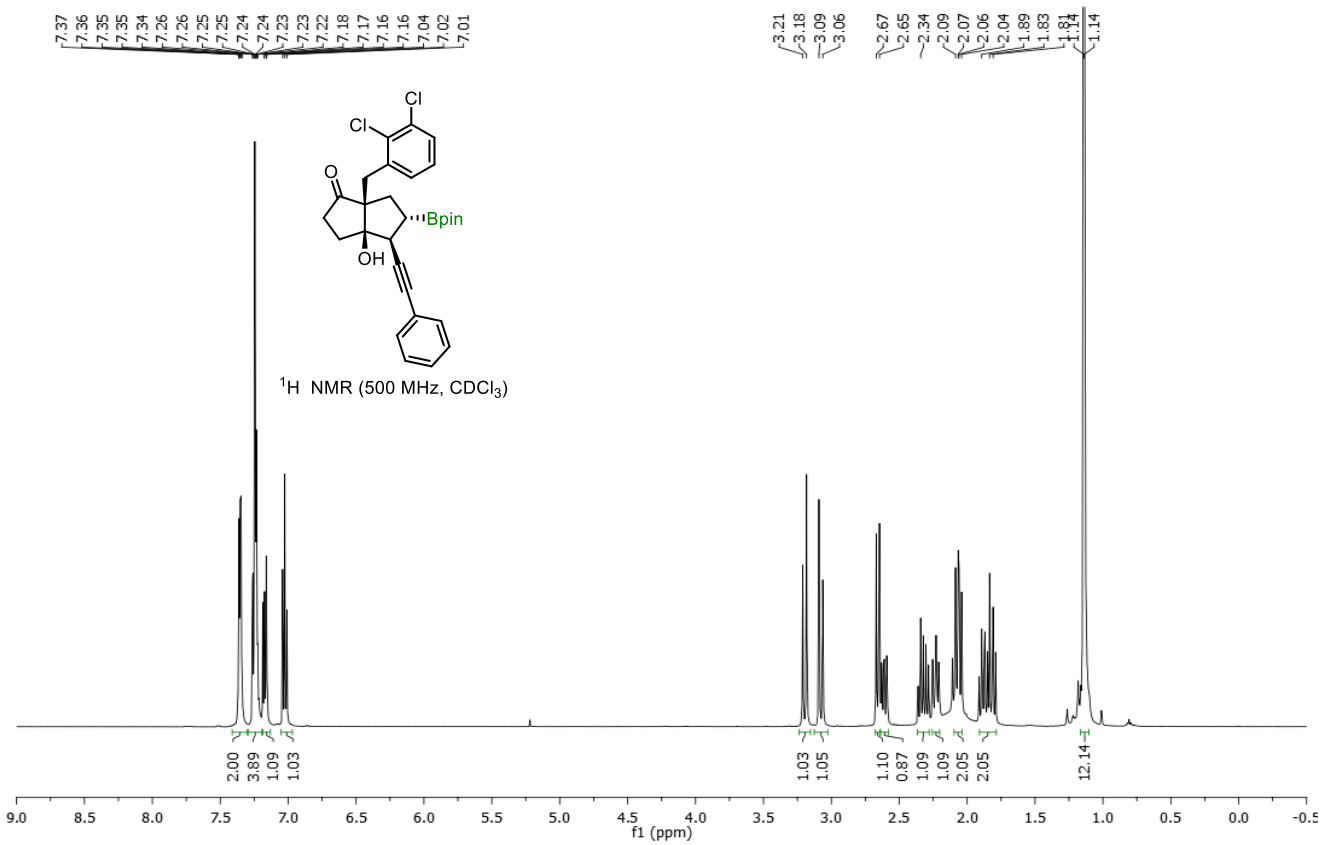


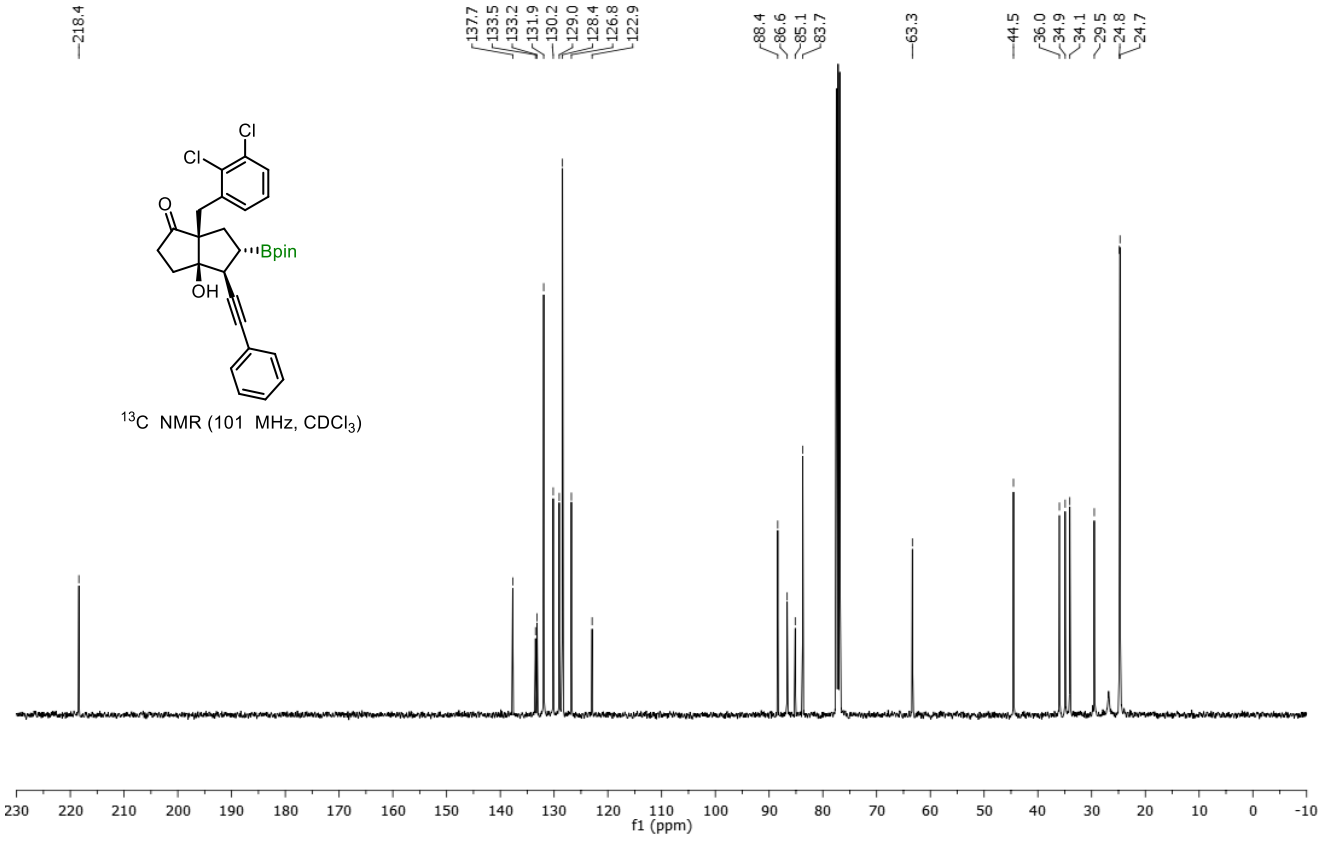
(3a*R*,4*S*,5*S*,6a*S*)-6a-(2,6-Dichlorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2u):



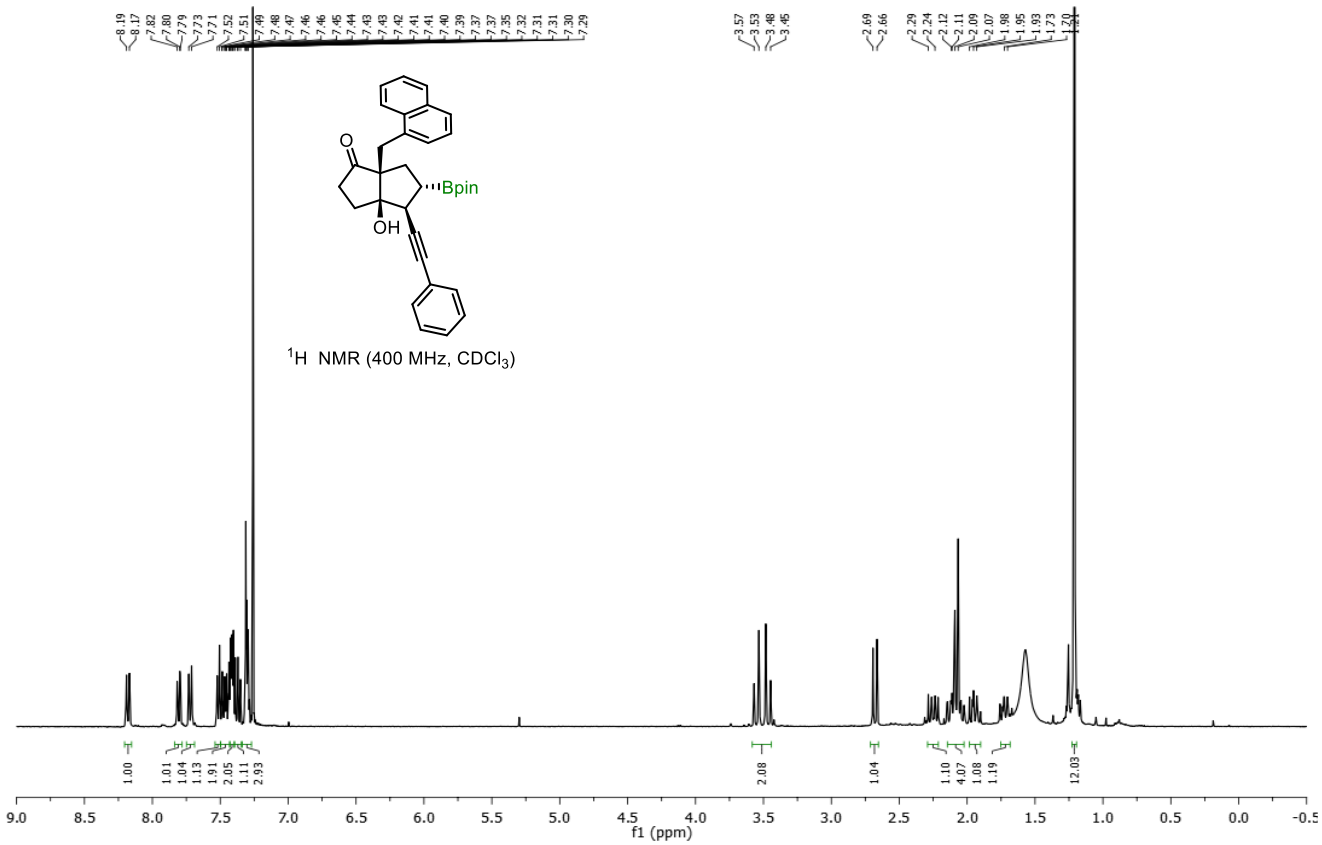


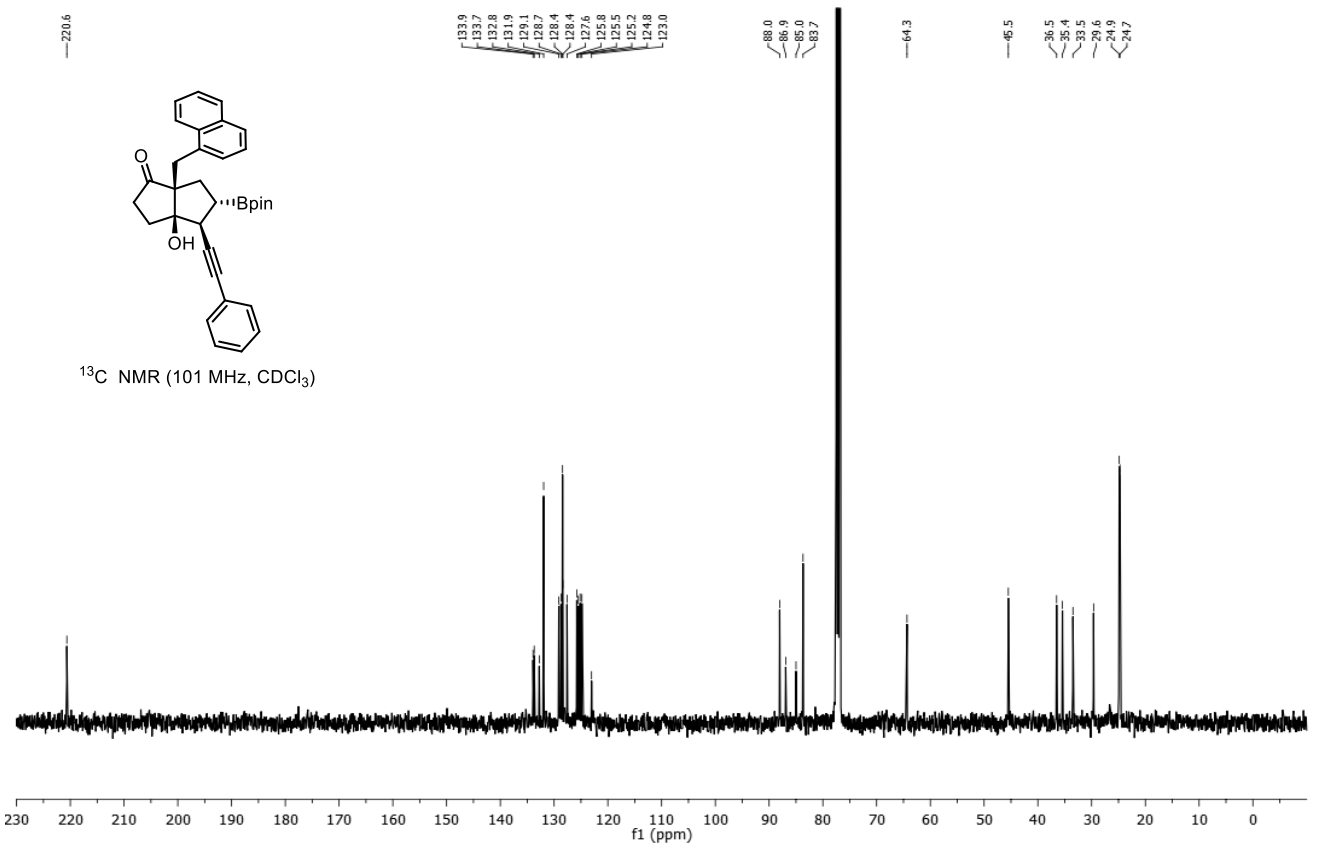
(3a*R*,4*S*,5*S*,6a*S*)-6a-(2,3-Dichlorobenzyl)-3a-hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2v):



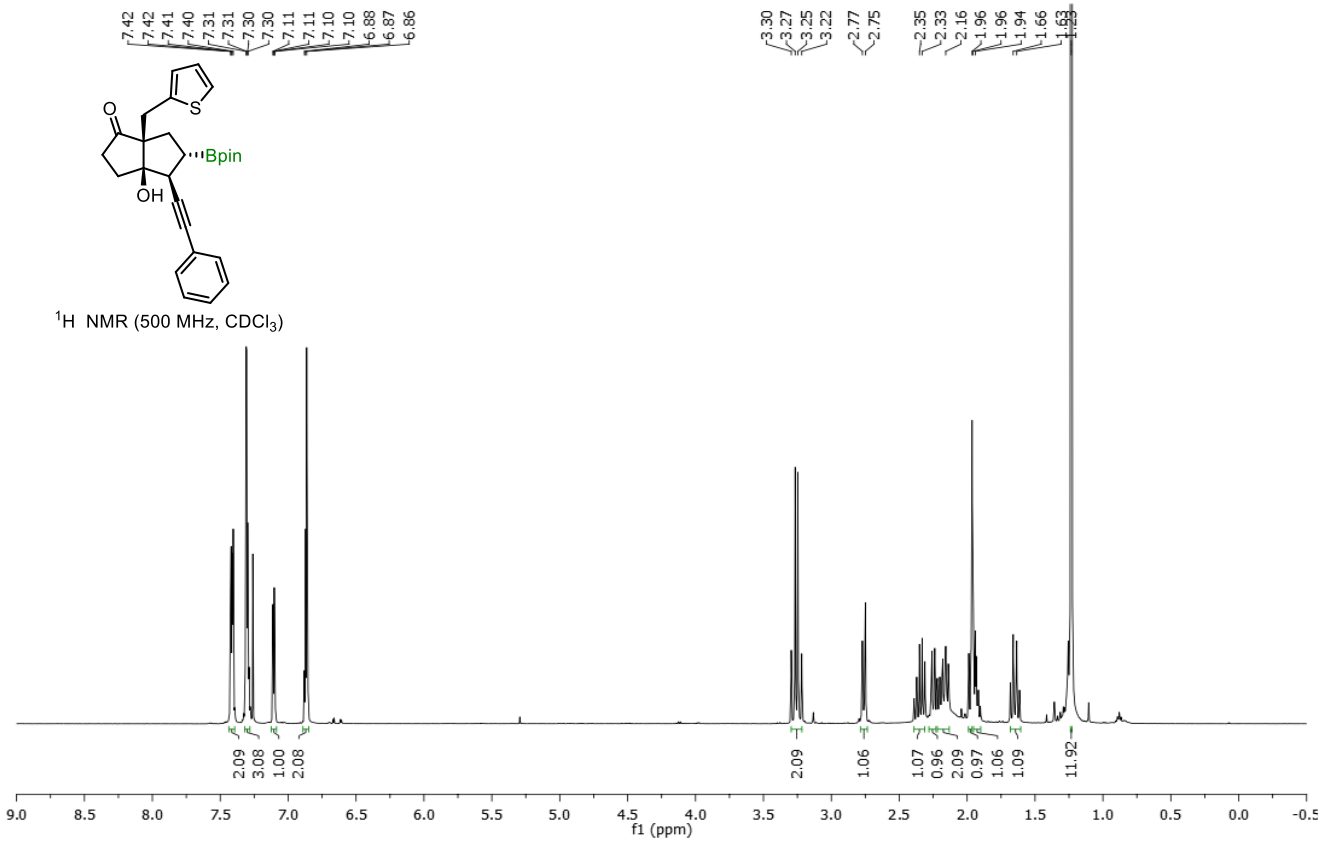


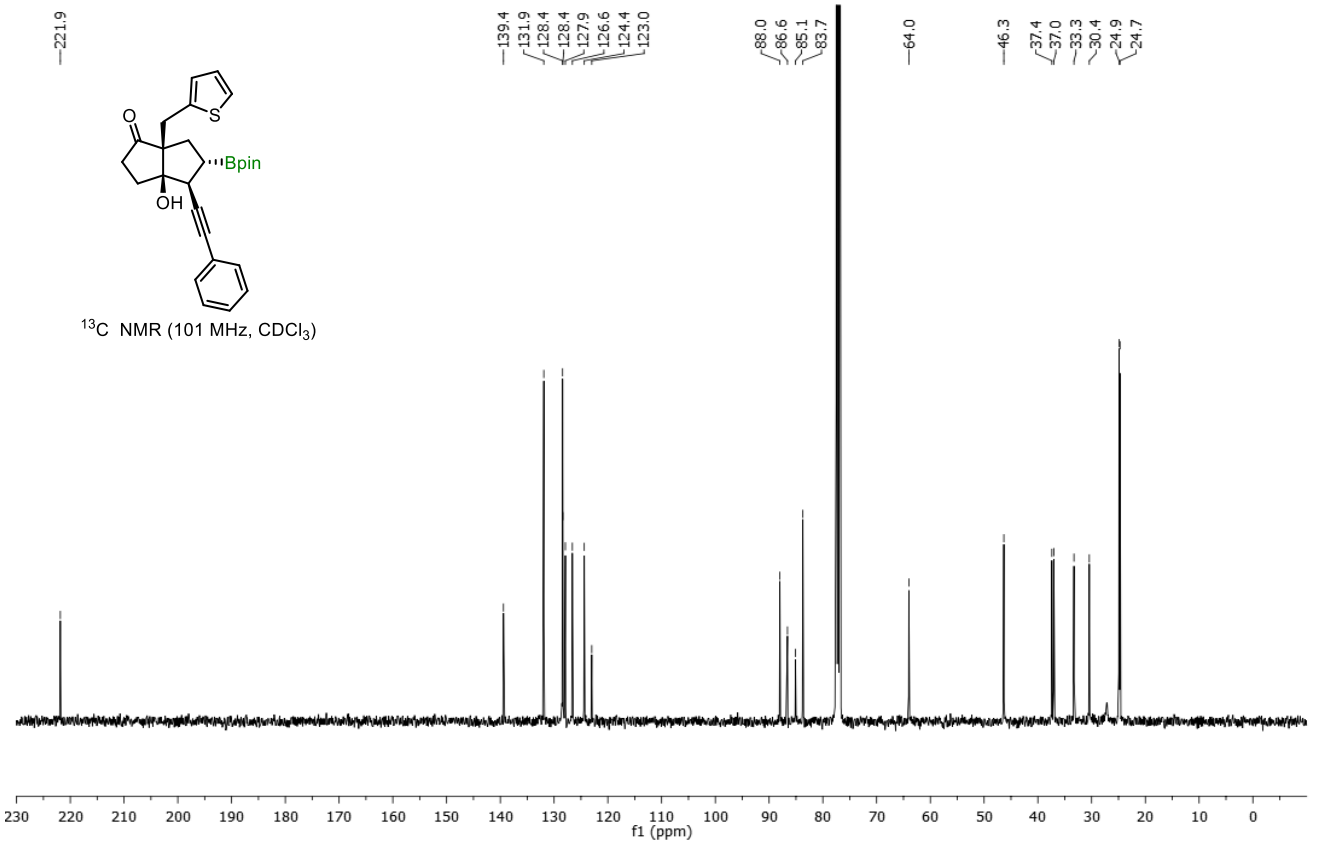
(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-6a-(naphthalen-1-ylmethyl)-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2w):



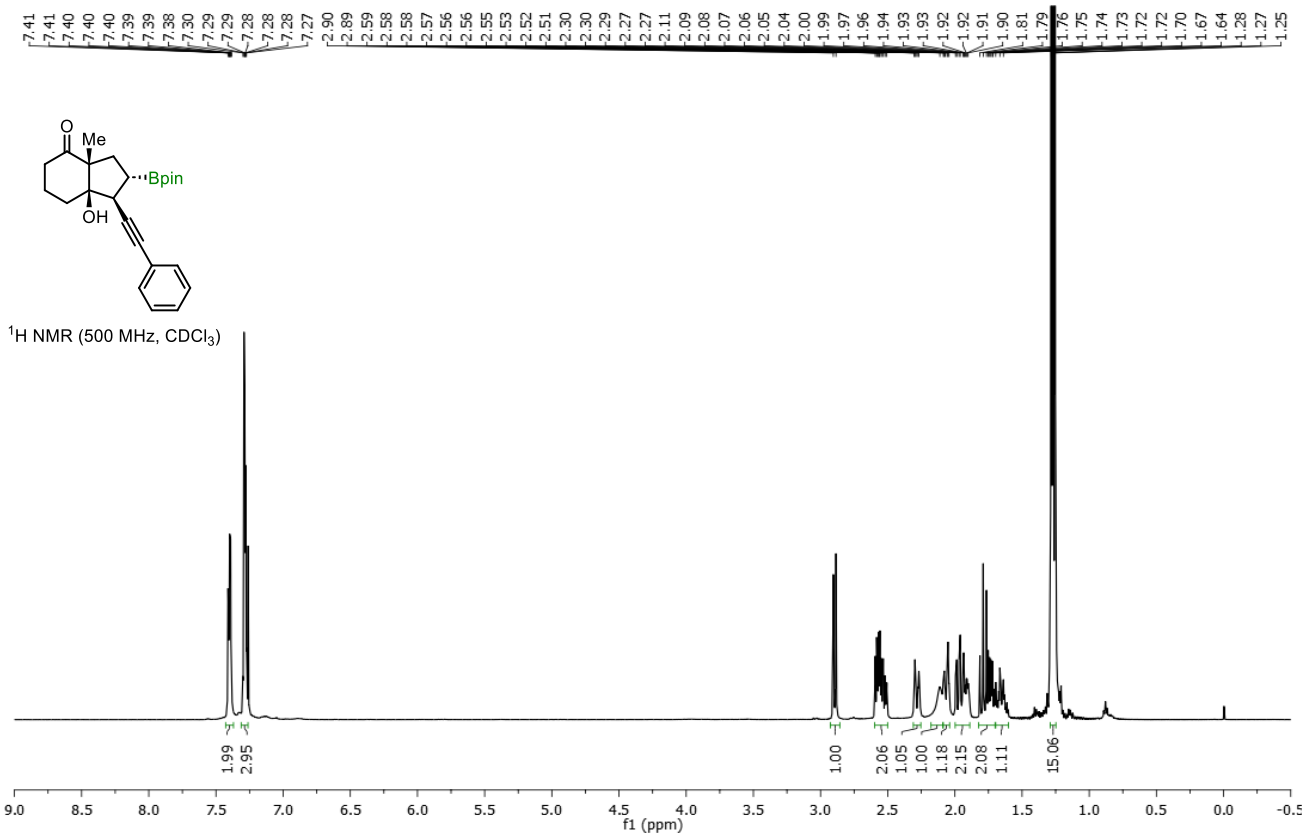


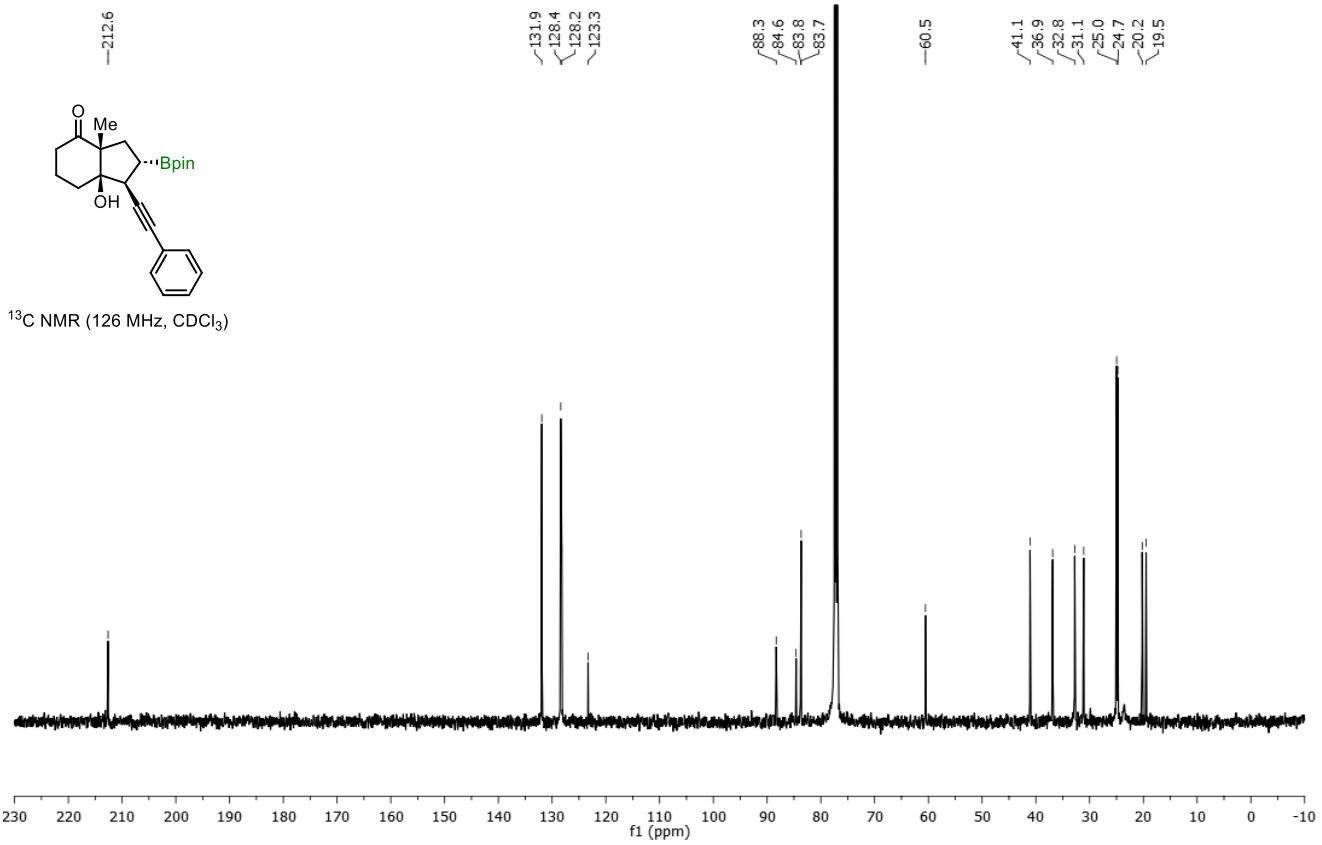
(3a*R*,4*S*,5*S*,6a*S*)-3a-Hydroxy-4-(phenylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6a-(thiophen-2-ylmethyl)hexahydropentalen-1(2*H*)-one (2x):



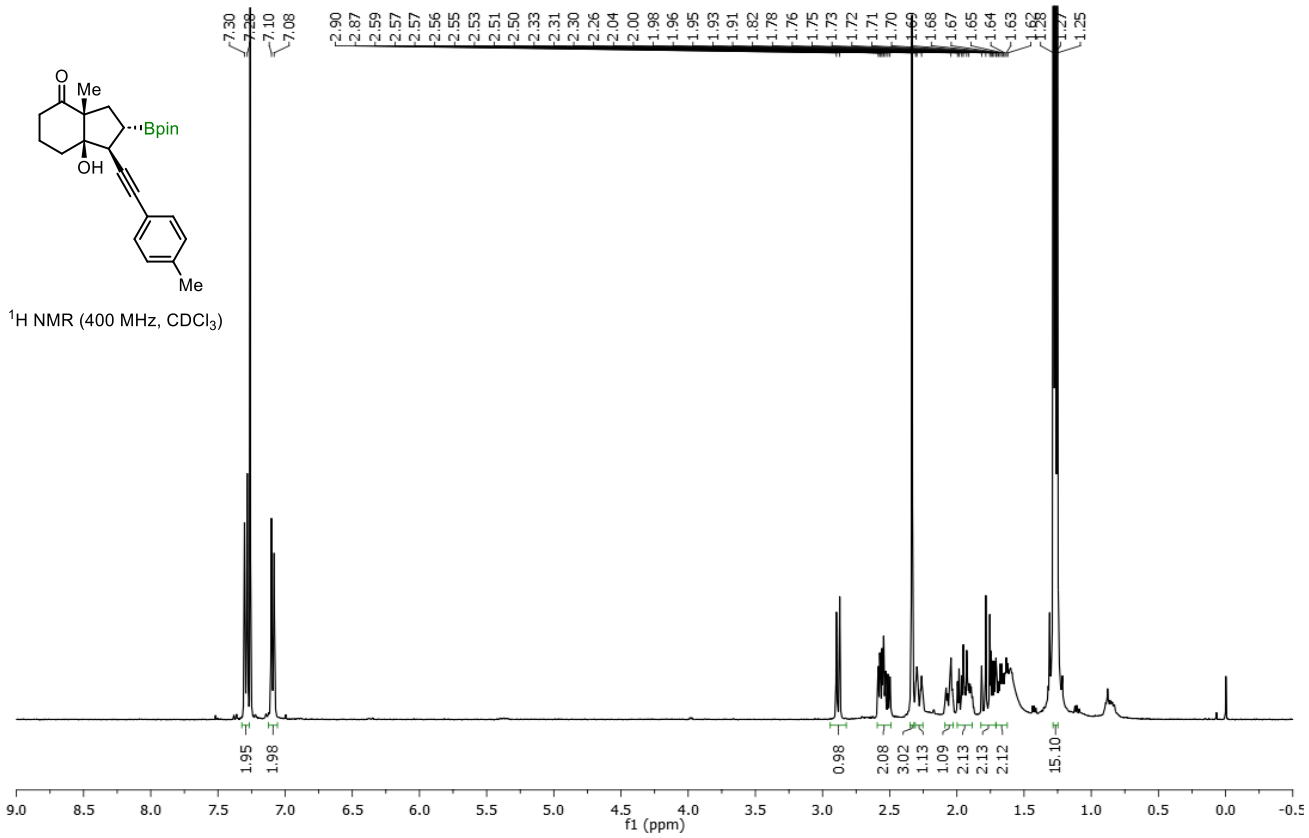


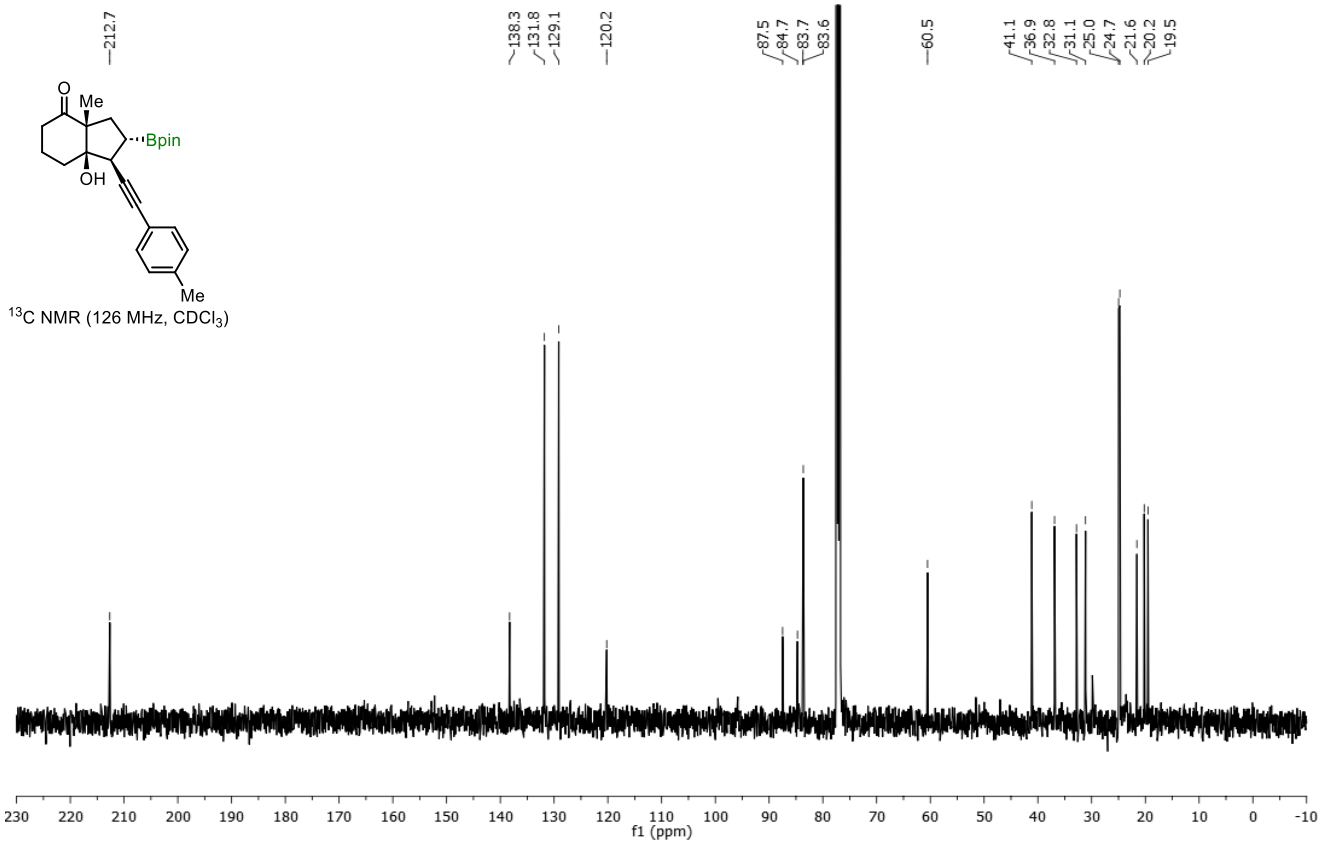
(1*S*,2*S*,3a*R*,7a*R*)-7a-Hydroxy-3a-methyl-1-(phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4*H*-inden-4-one (2y):



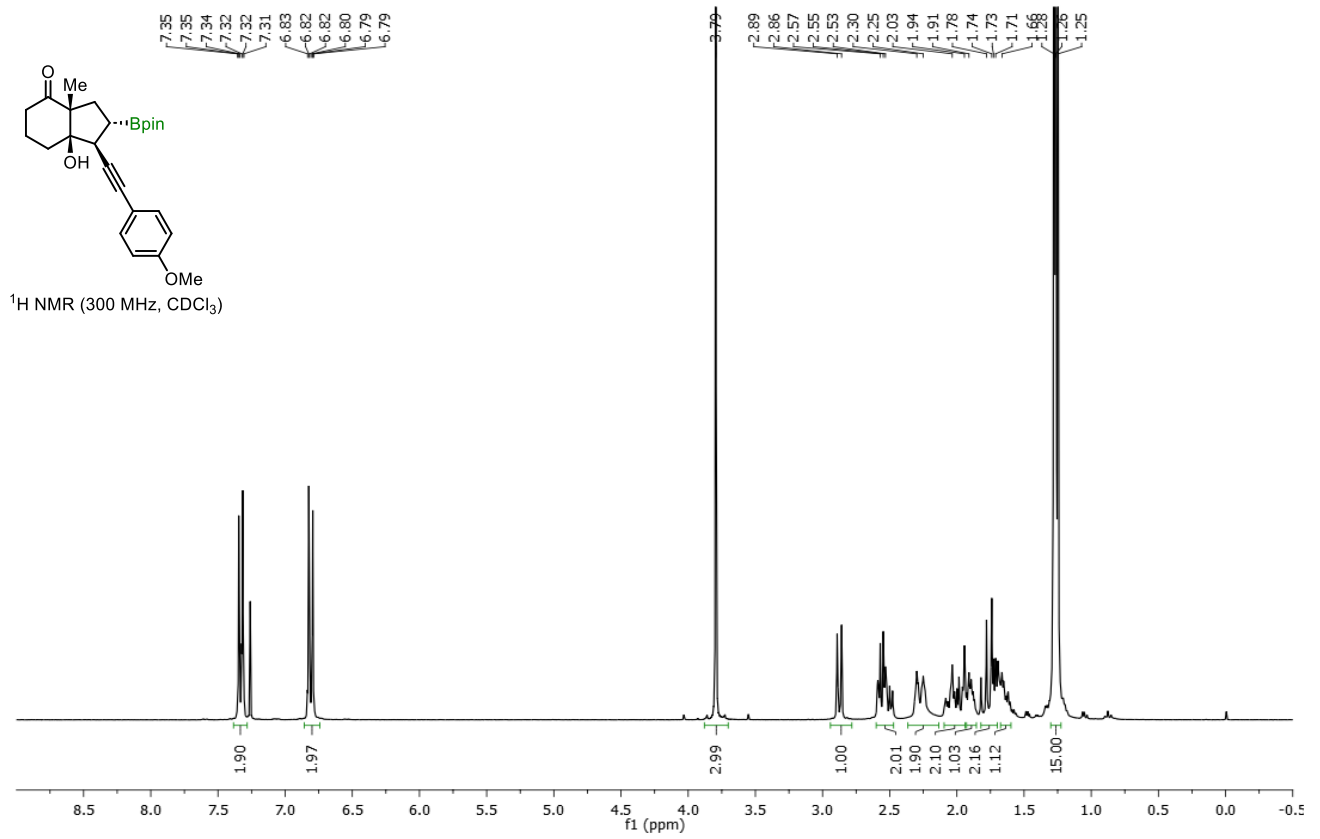


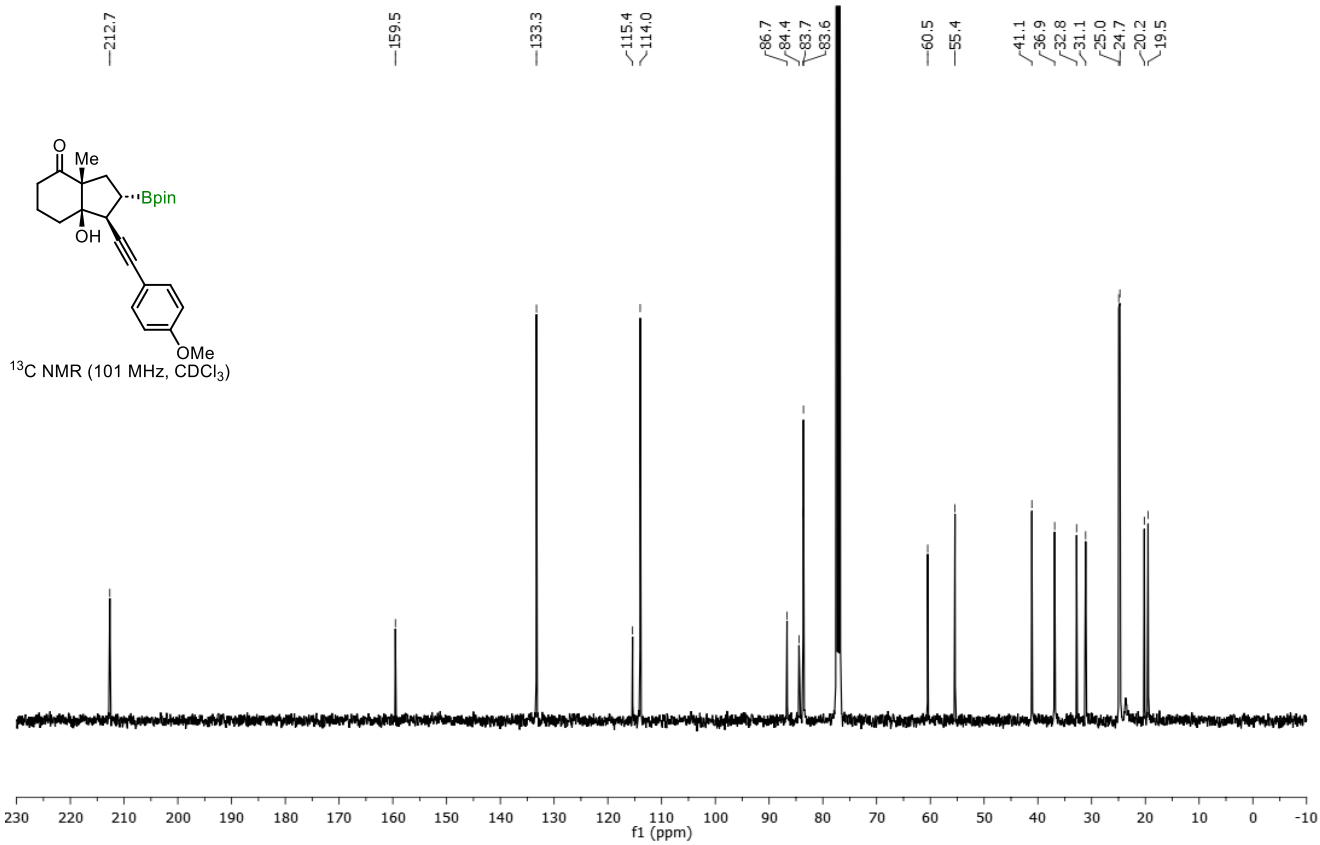
(1*S*,2*S*,3a*R*,7a*R*)-7a-Hydroxy-3a-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolylethynyl)octahydro-4*H*-inden-4-one (2z):



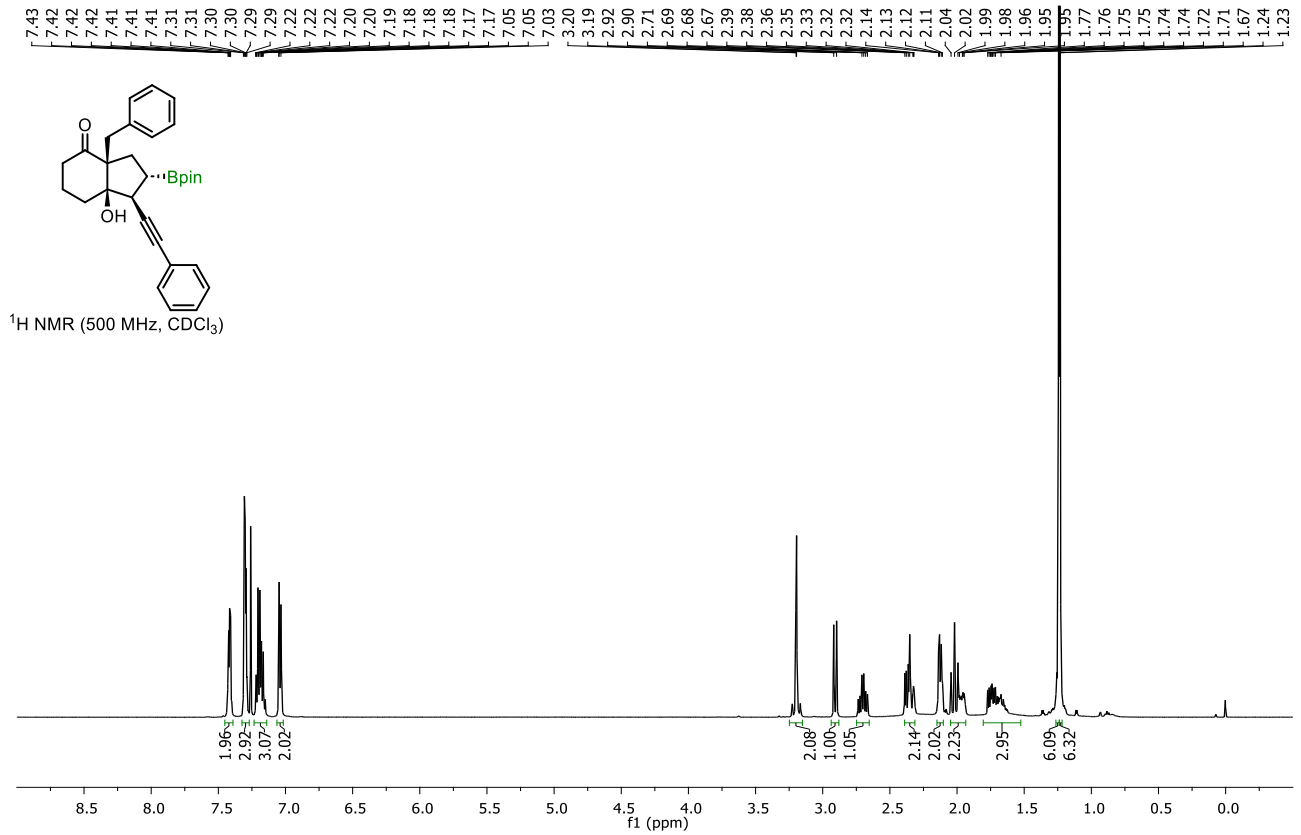


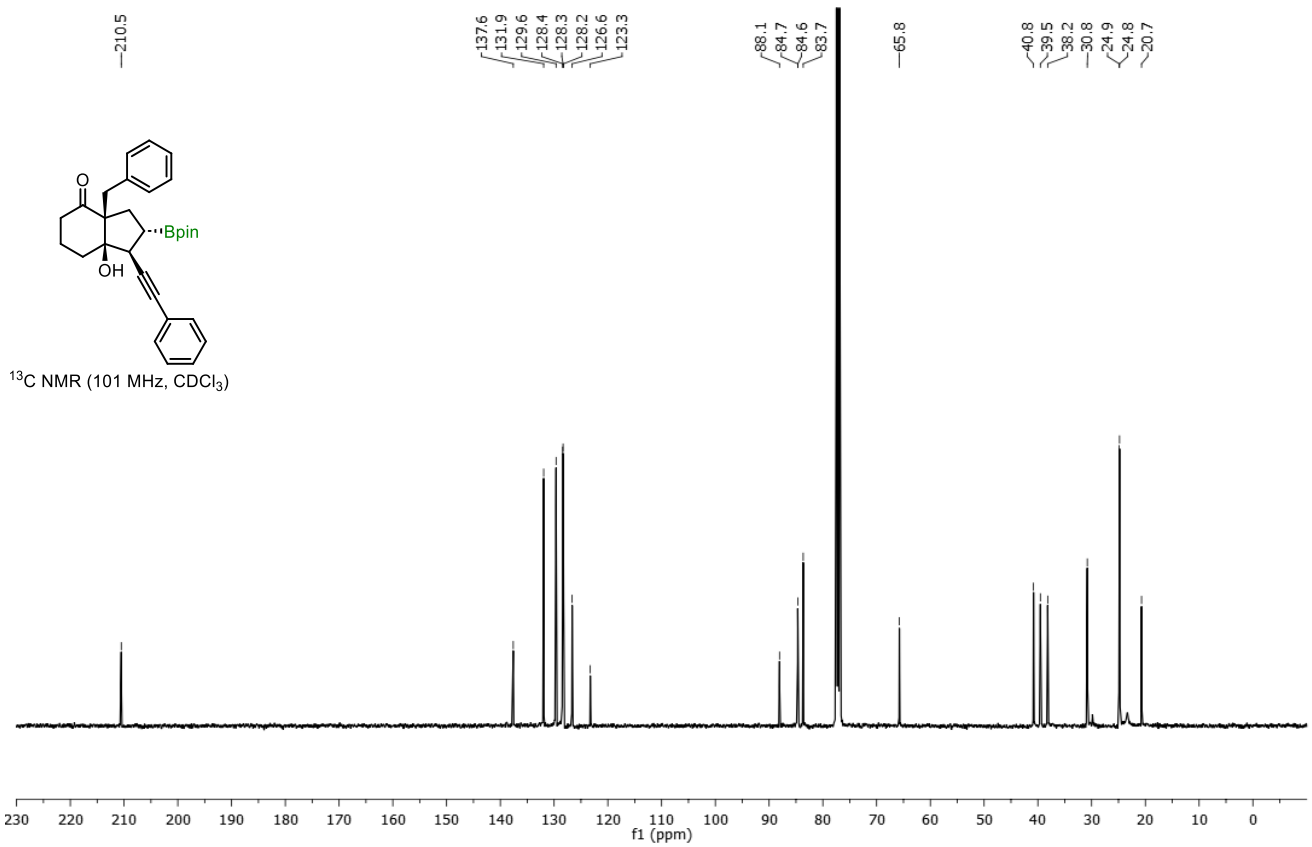
(1*S*,2*S*,3a*R*,7a*R*)-7a-Hydroxy-1-((4-methoxyphenyl)ethynyl)-3a-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4*H*-inden-4-one (2aa)



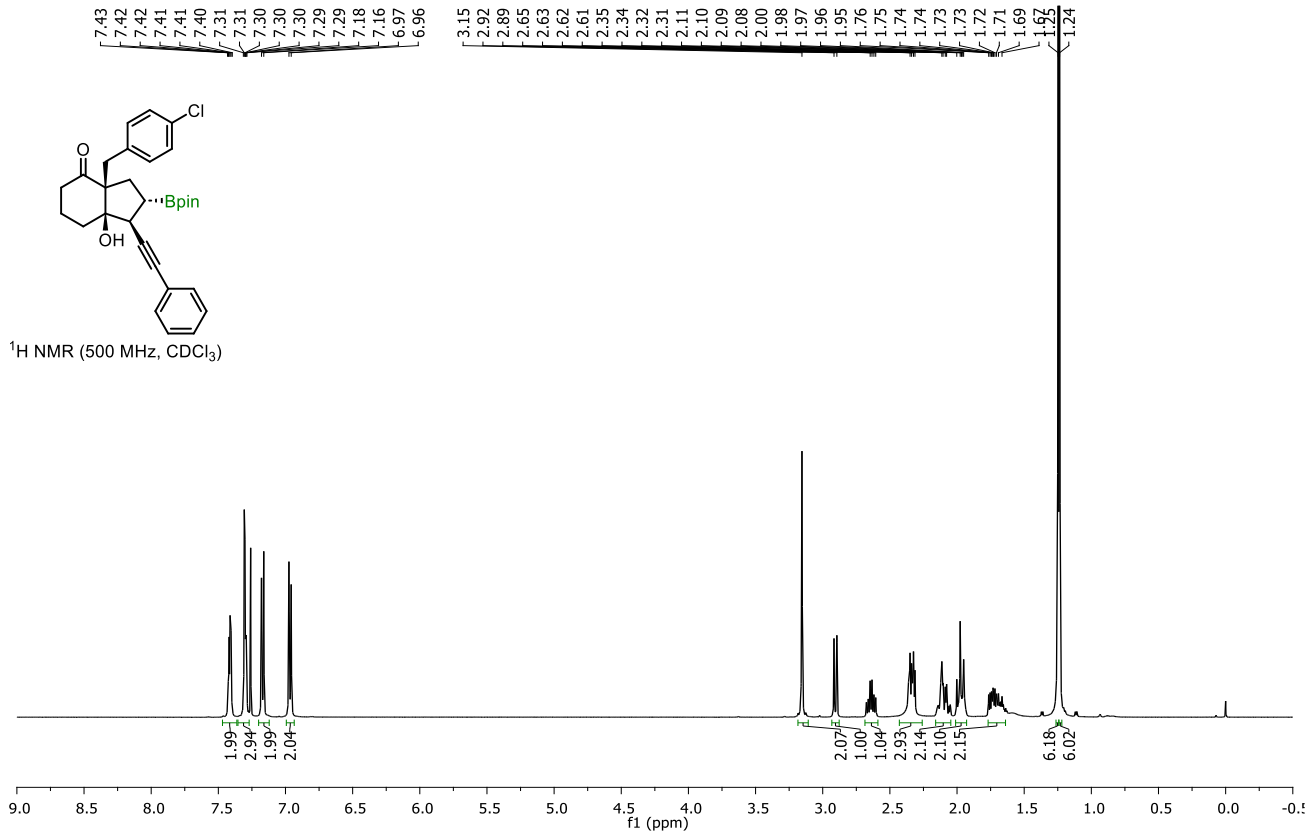


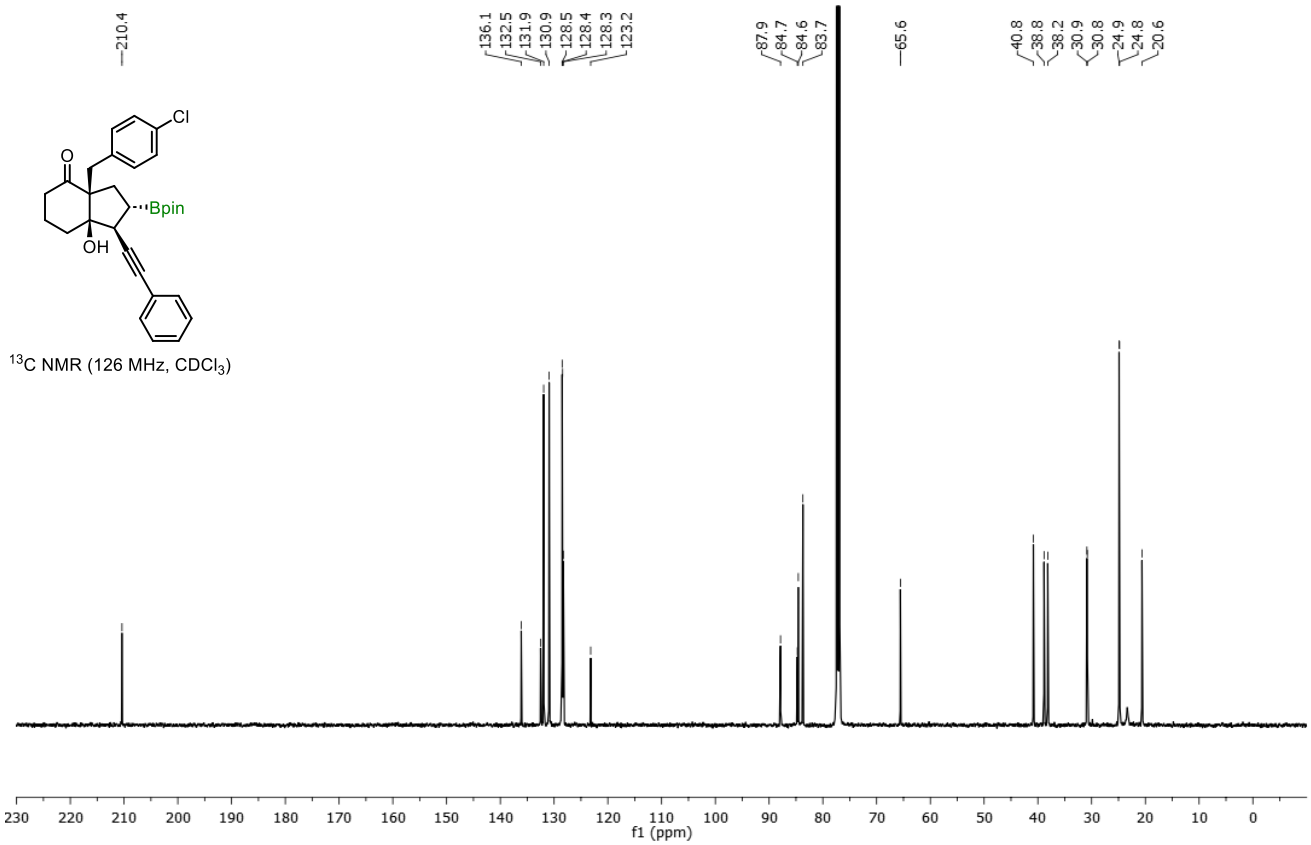
(1*S*,2*S*,3a*S*,7a*R*)-3a-Benzyl-7a-hydroxy-1-(phenyletynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4*H*-inden-4-one (2ab):



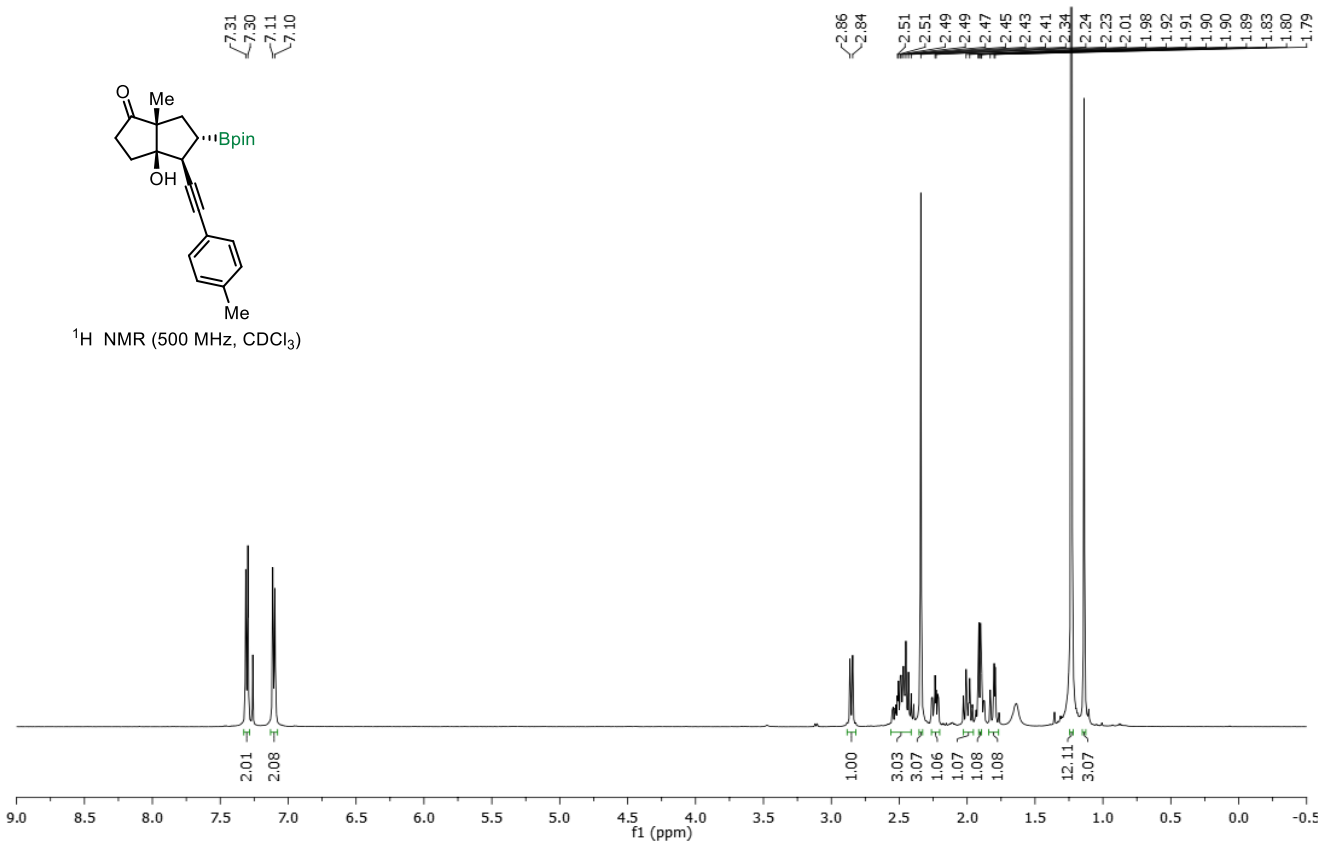


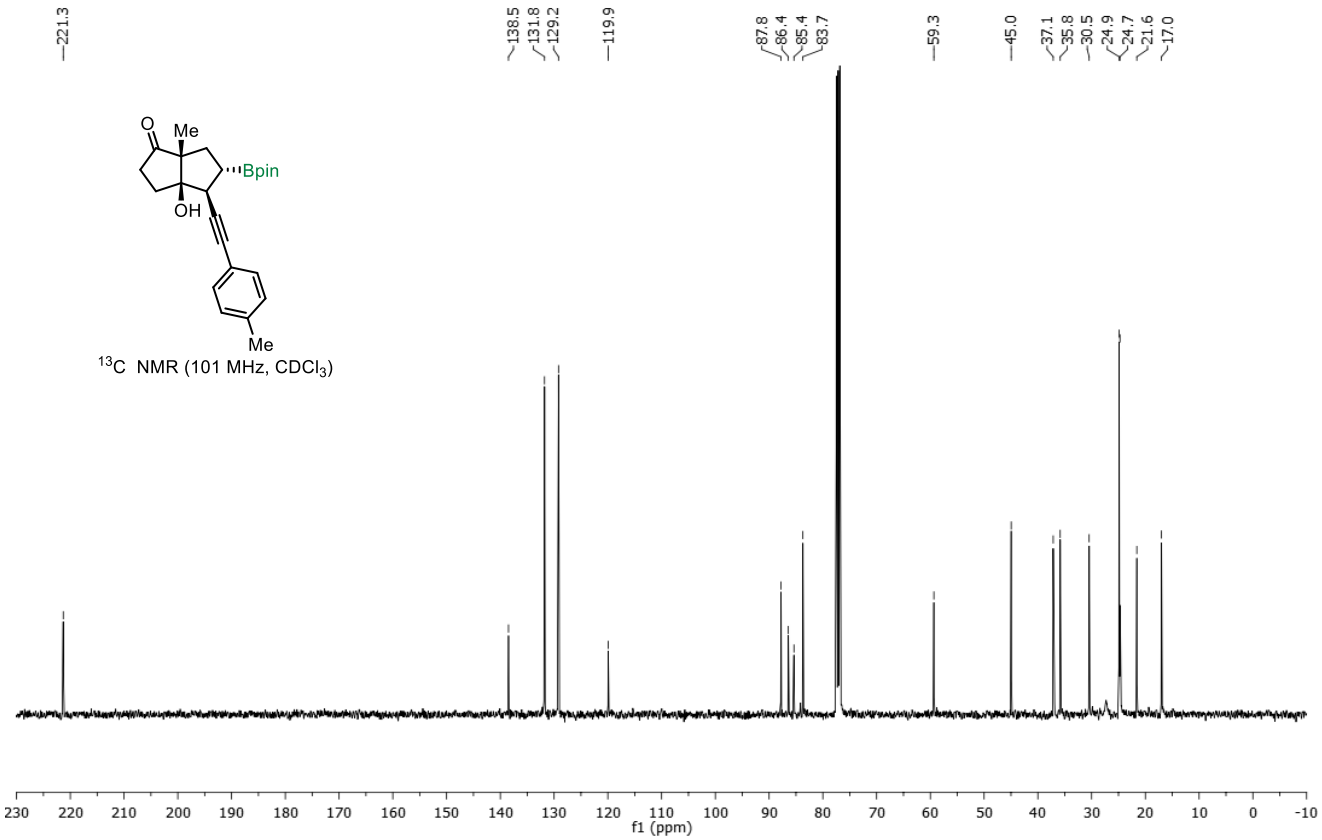
(1*S*,2*S*,3a*S*,7a*R*)-3a-(4-Chlorobenzyl)-7a-hydroxy-1-(phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4*H*-inden-4-one (2ac):



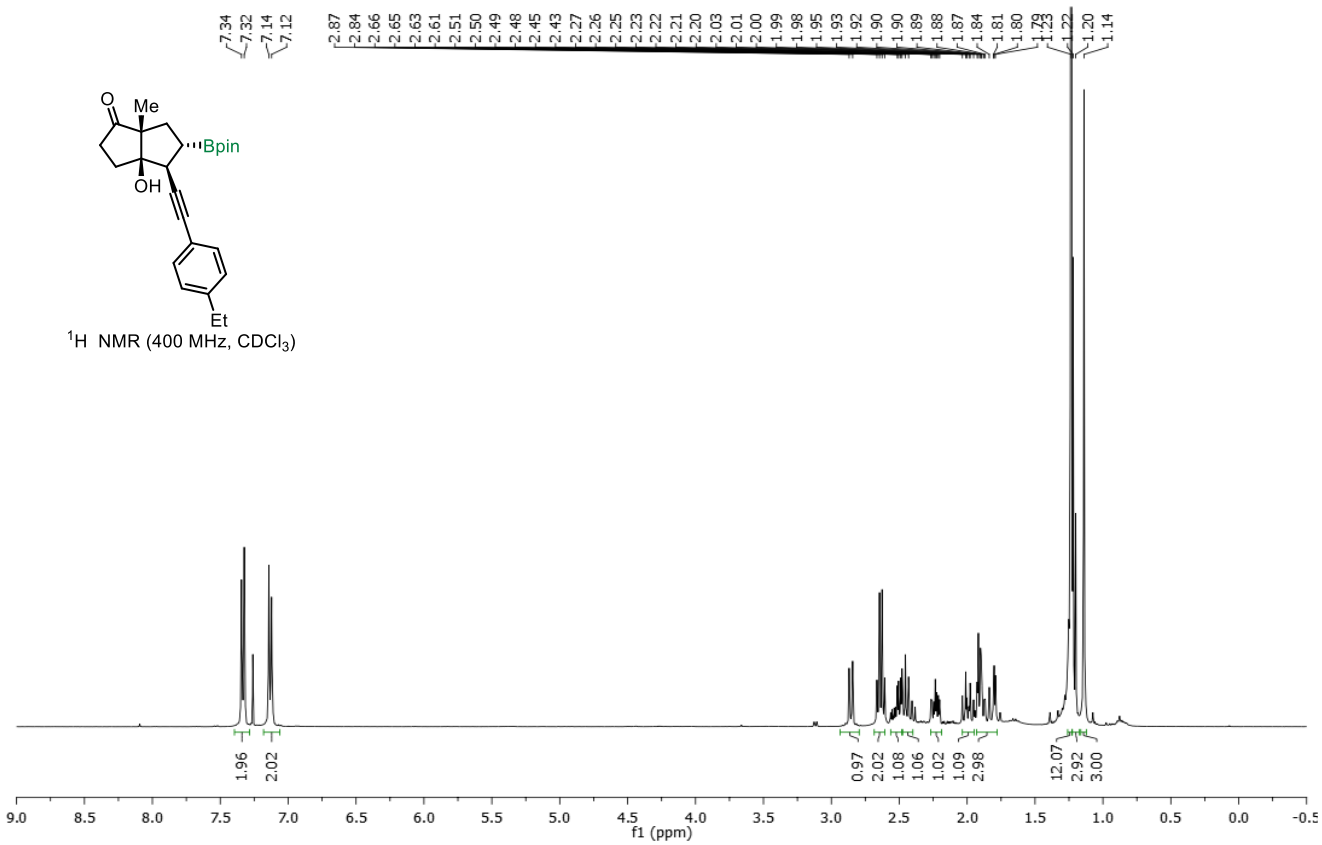


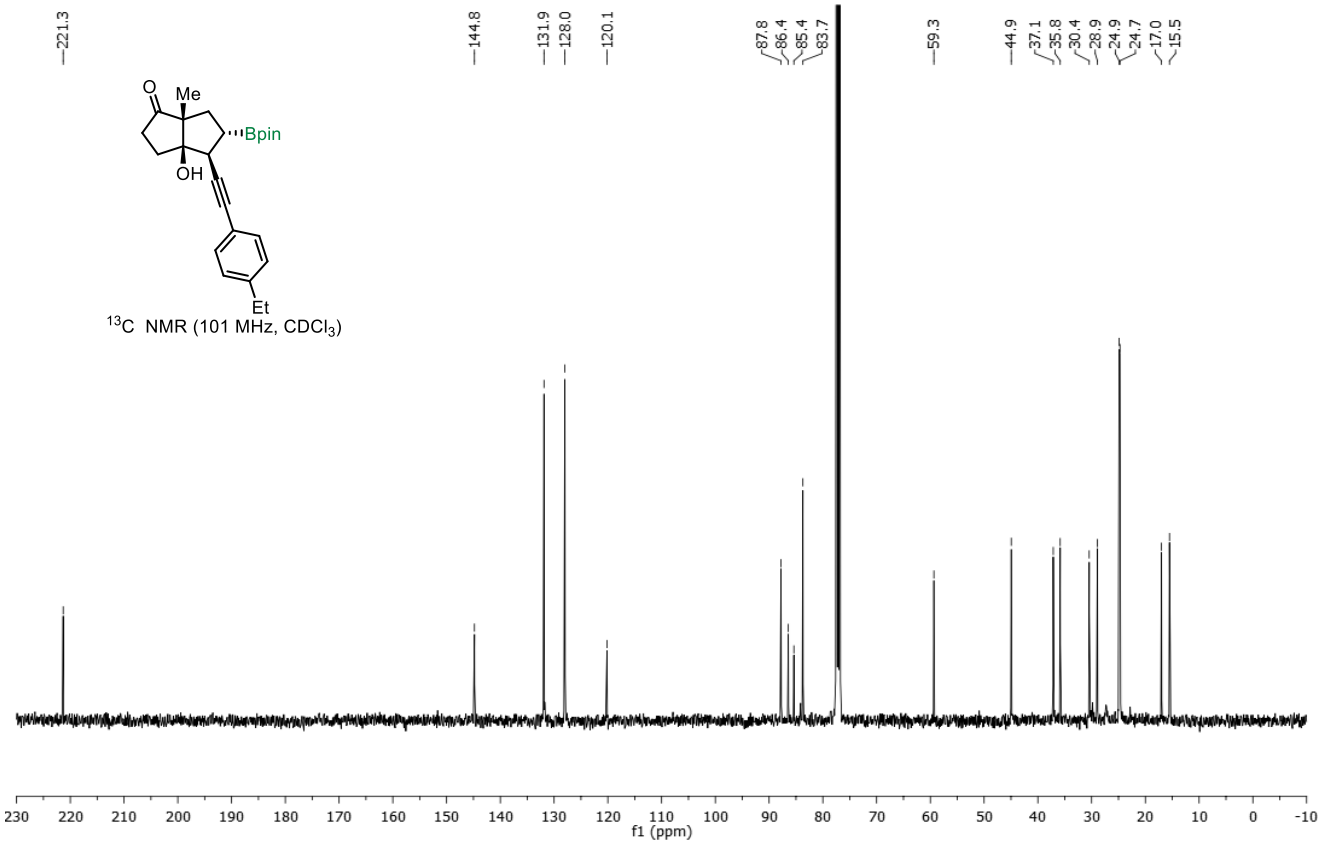
(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(p-tolylethynyl)hexahydropentalen-1(2*H*)-one (2ae):



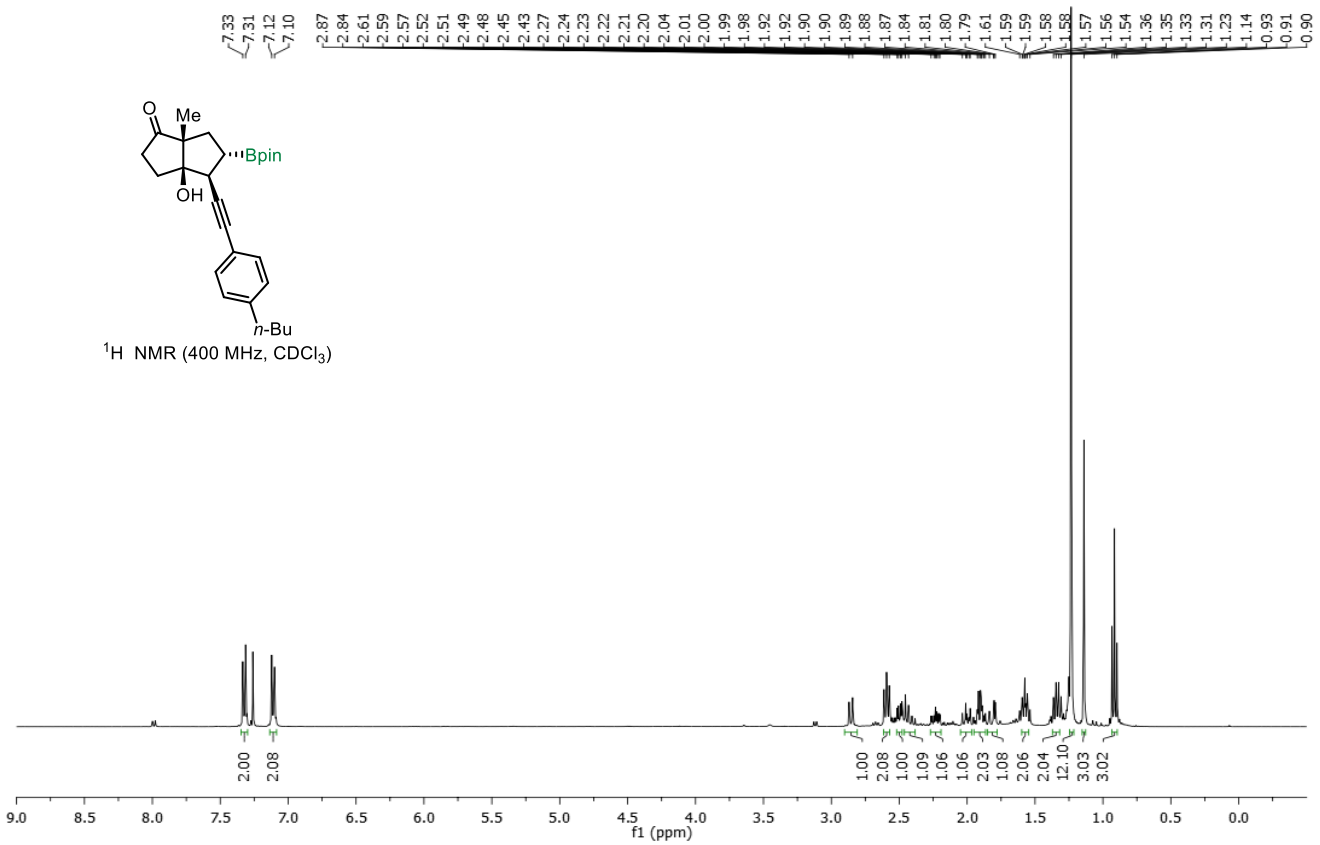


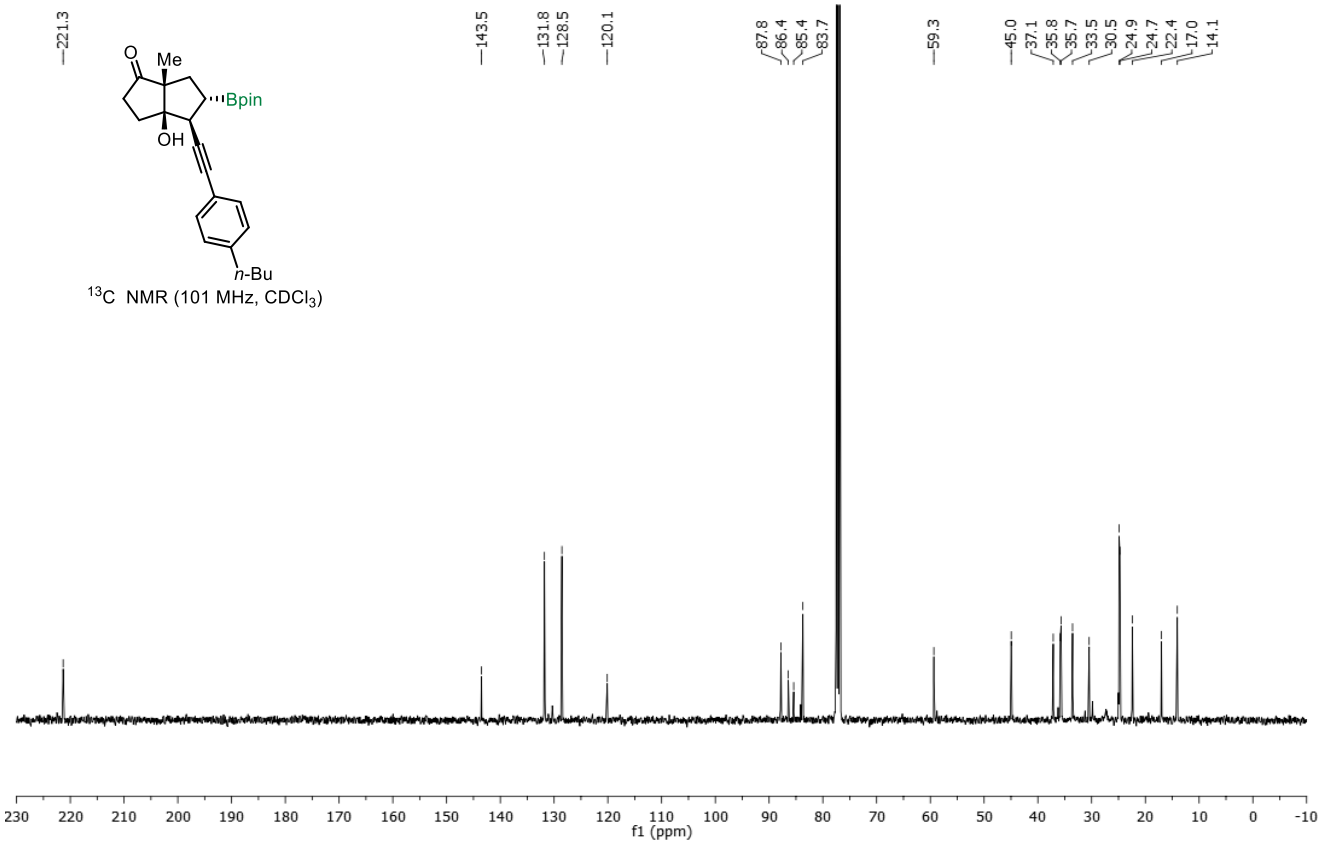
(3a*R*,4*S*,5*S*,6a*R*)-4-((4-Ethylphenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2af):



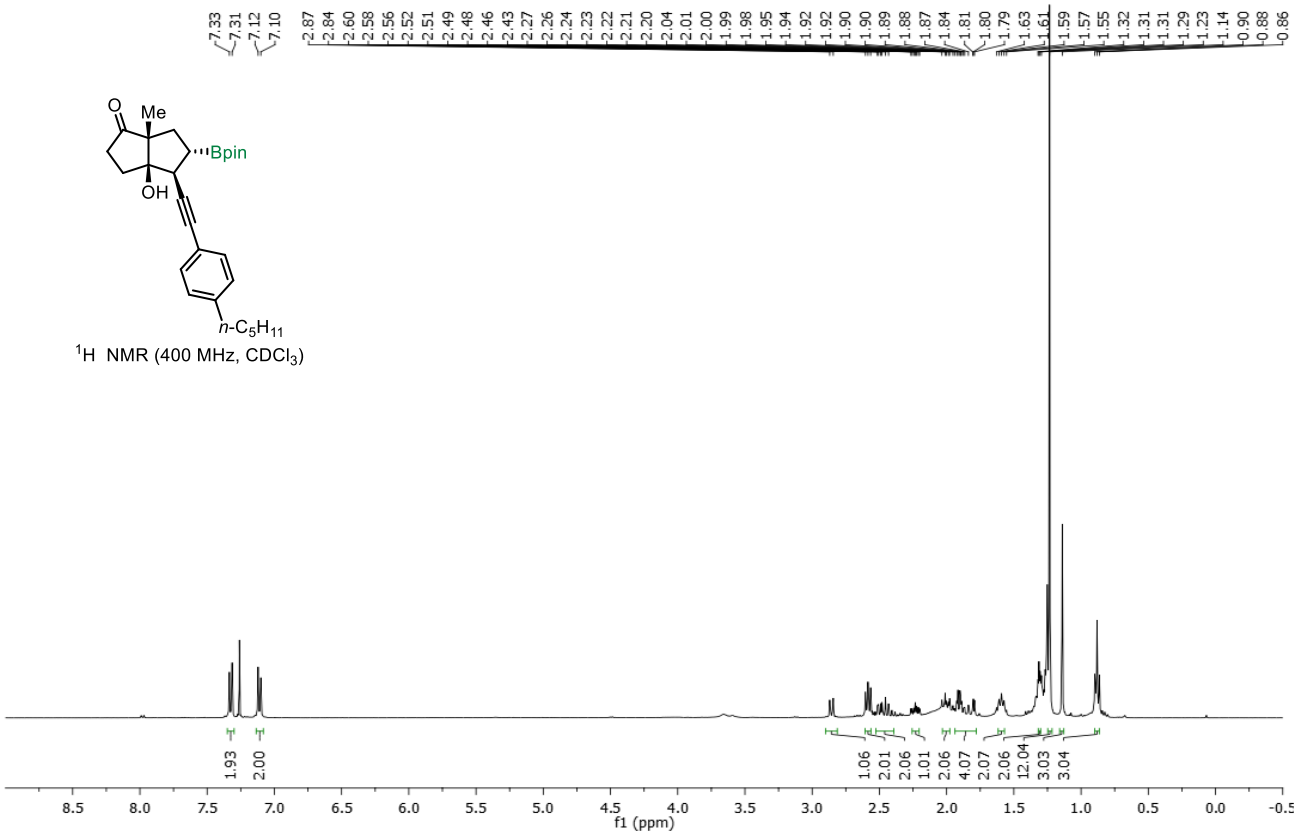


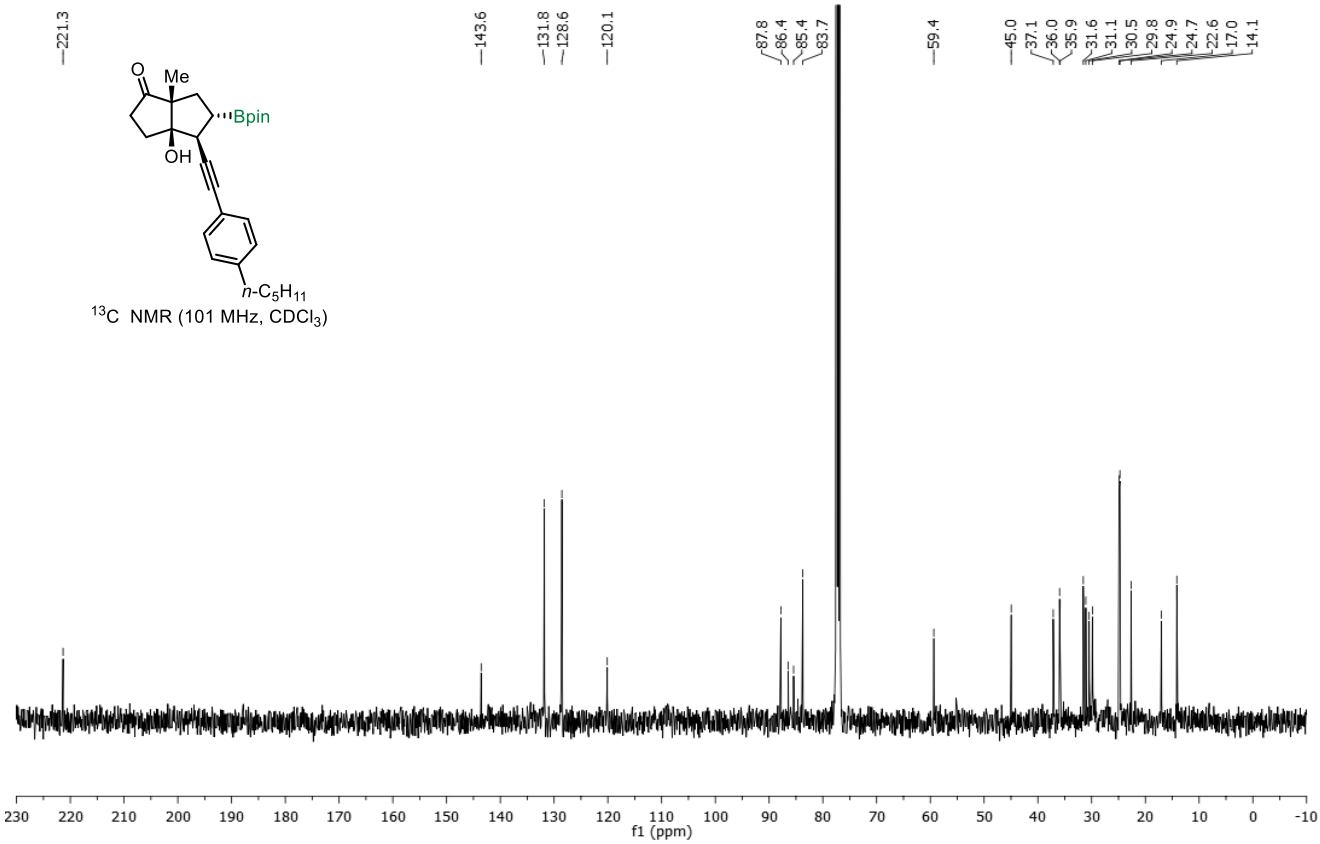
(3a*R*,4*S*,5*S*,6a*R*)-4-((4-Butylphenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ag):



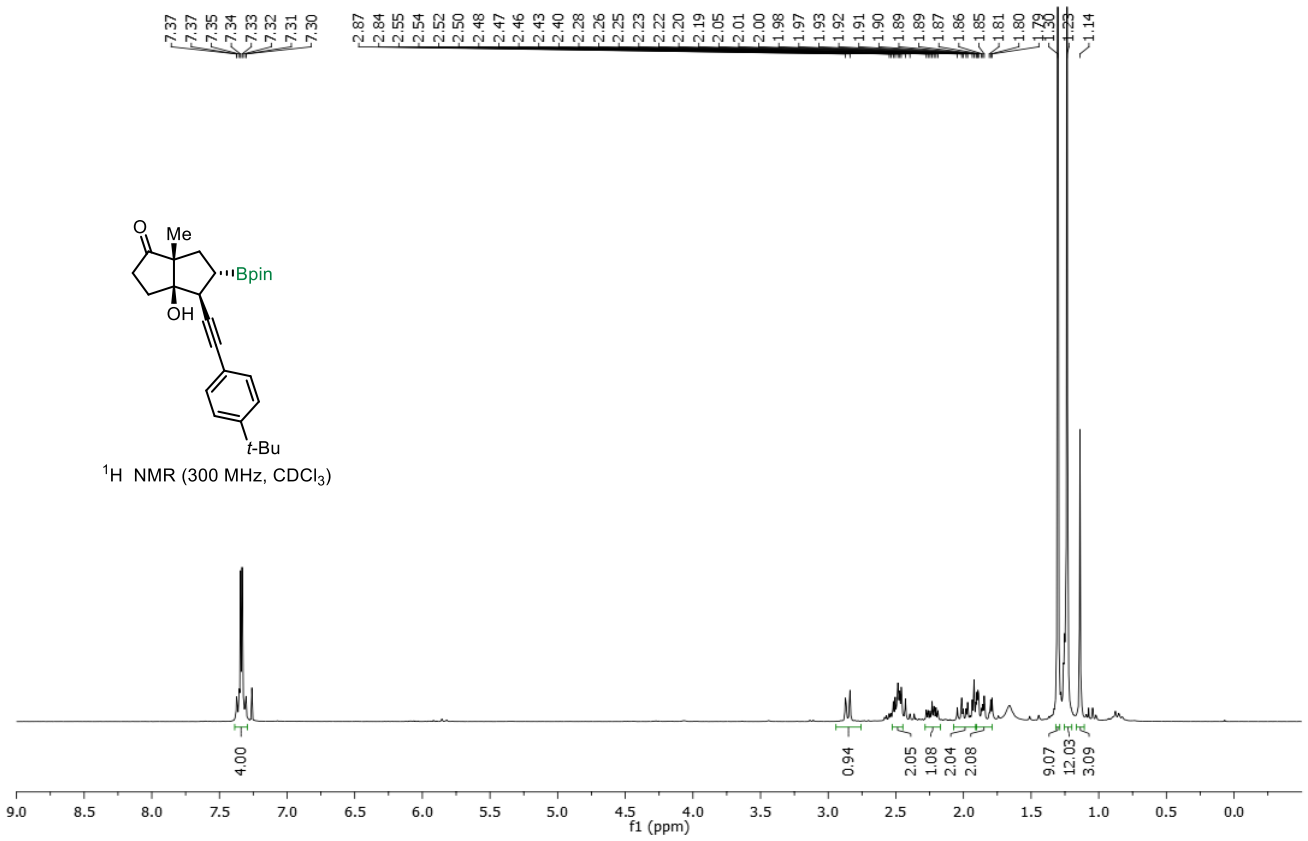


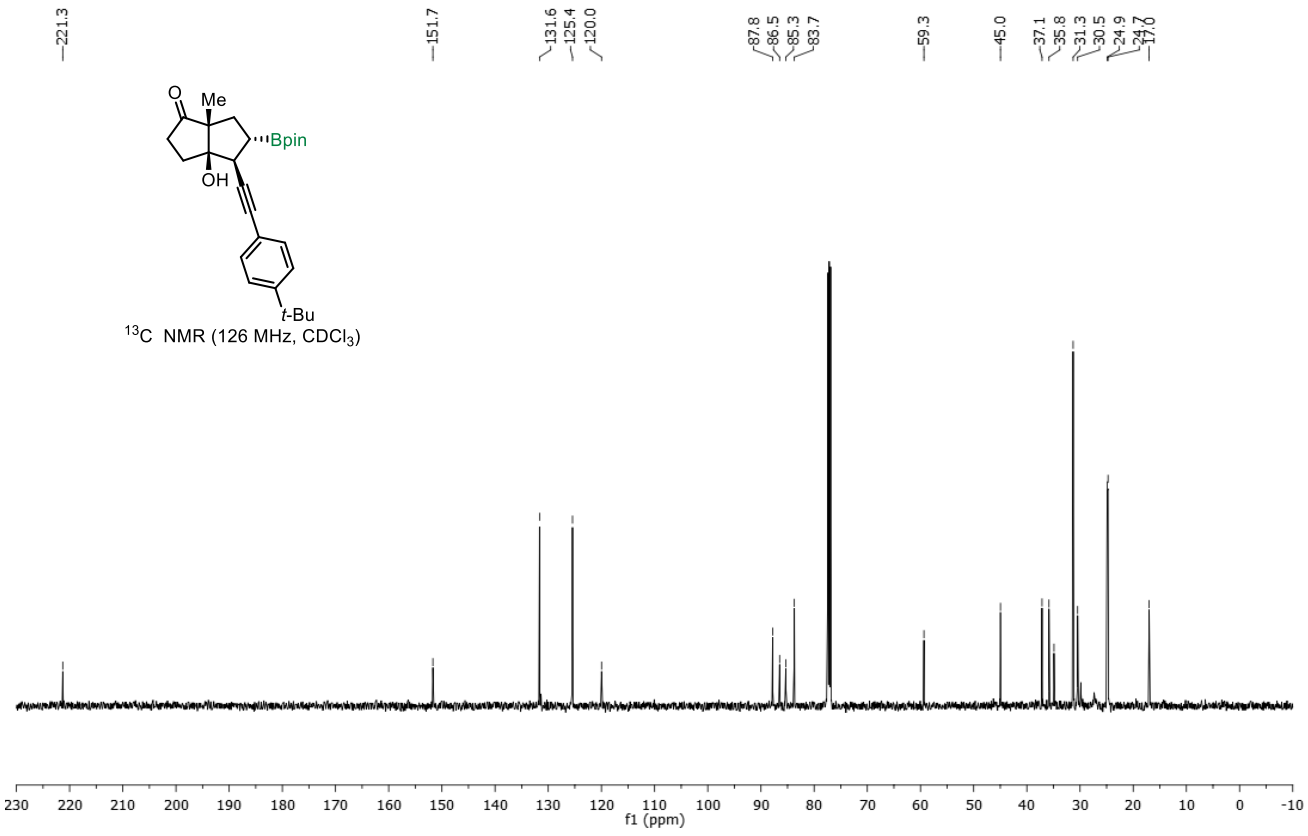
(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-4-((4-pentylphenyl)ethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ah):



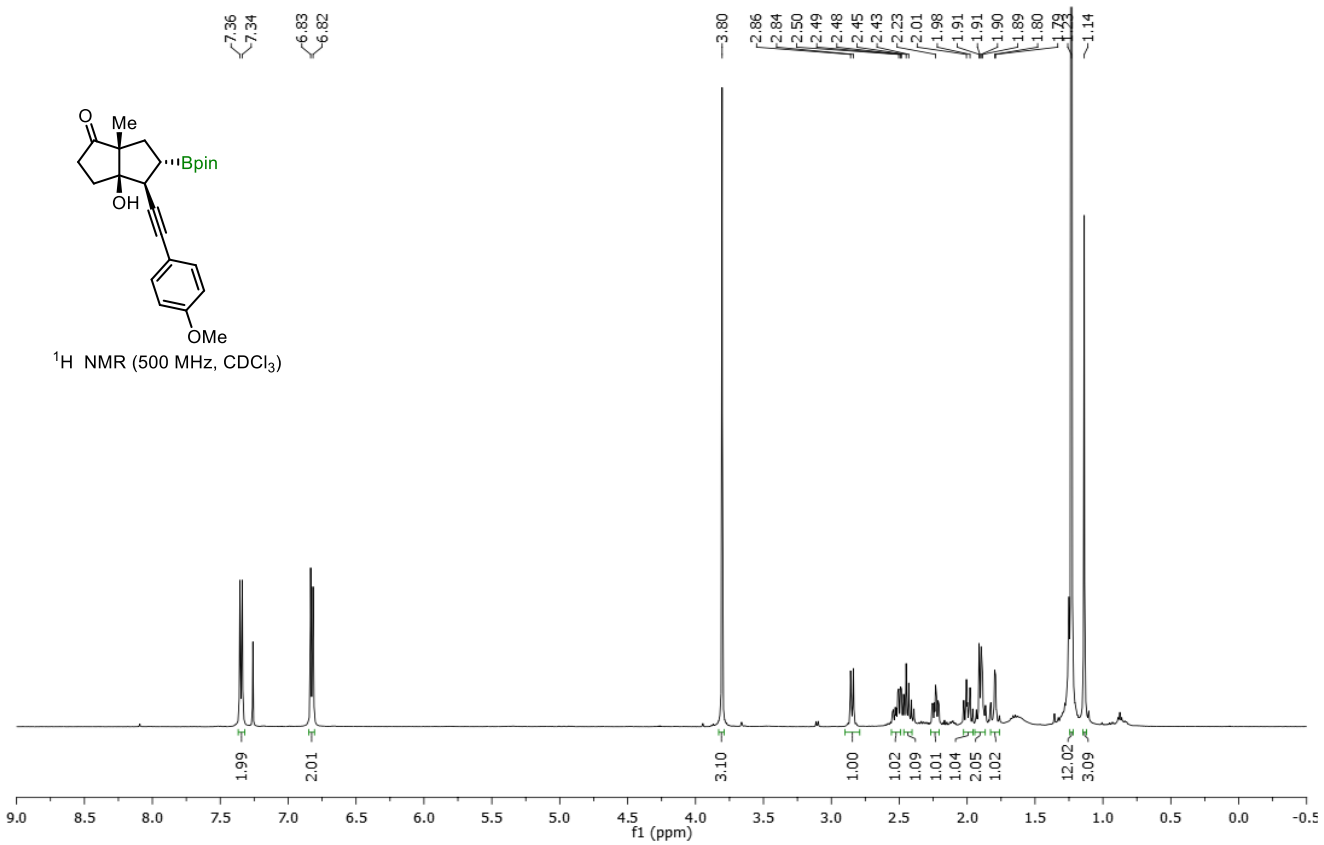


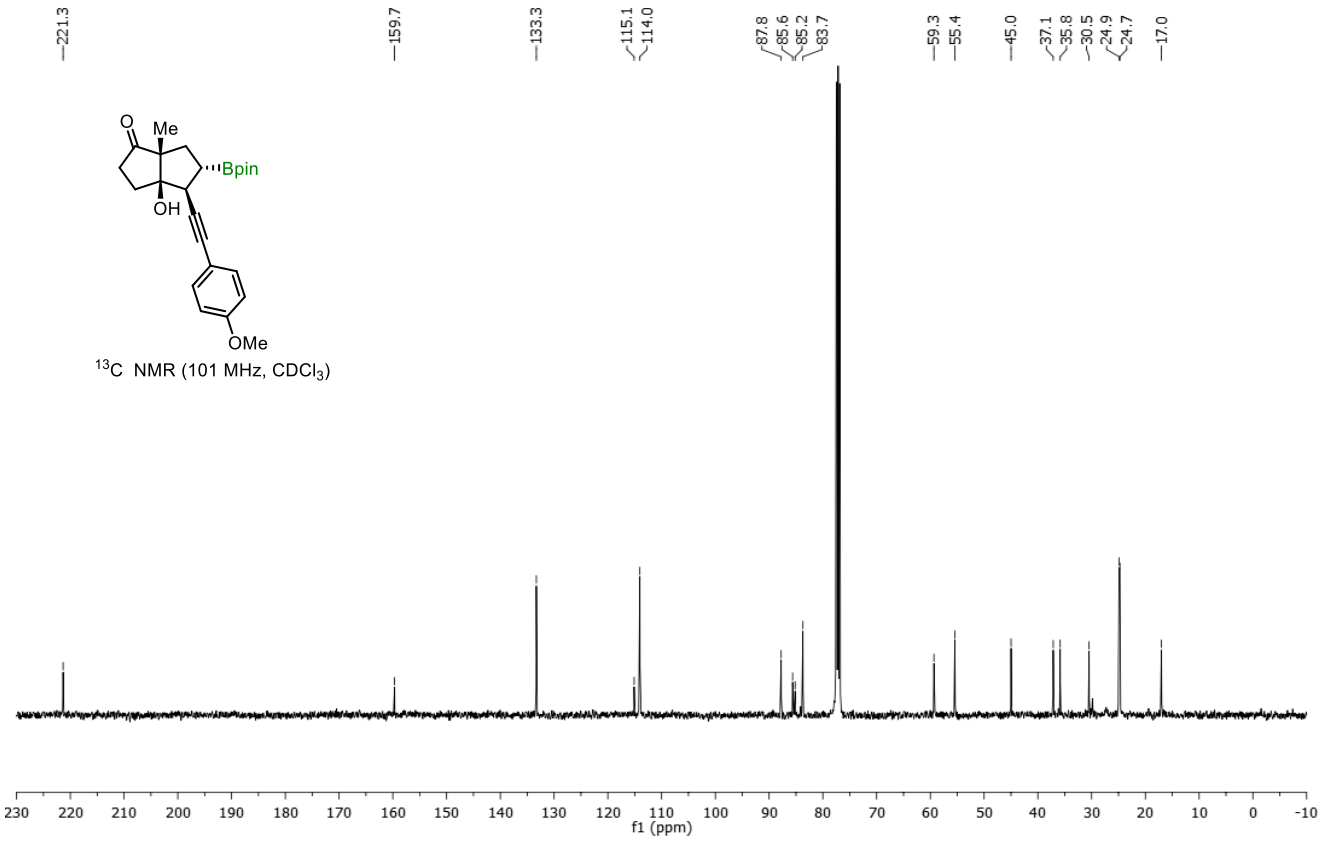
(3a*R*,4*S*,5*S*,6a*R*)-4-((4-(tert-Butyl)phenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ai):



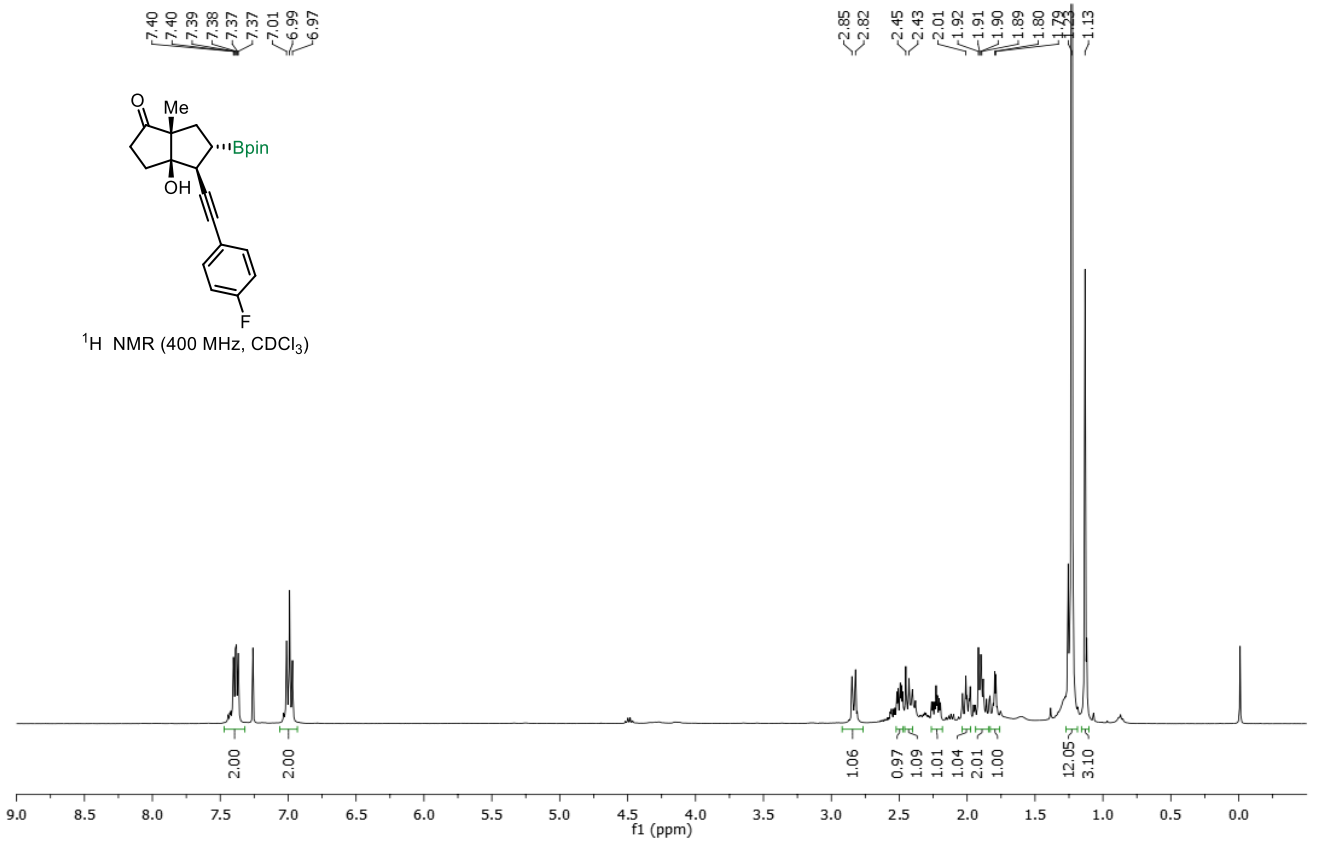


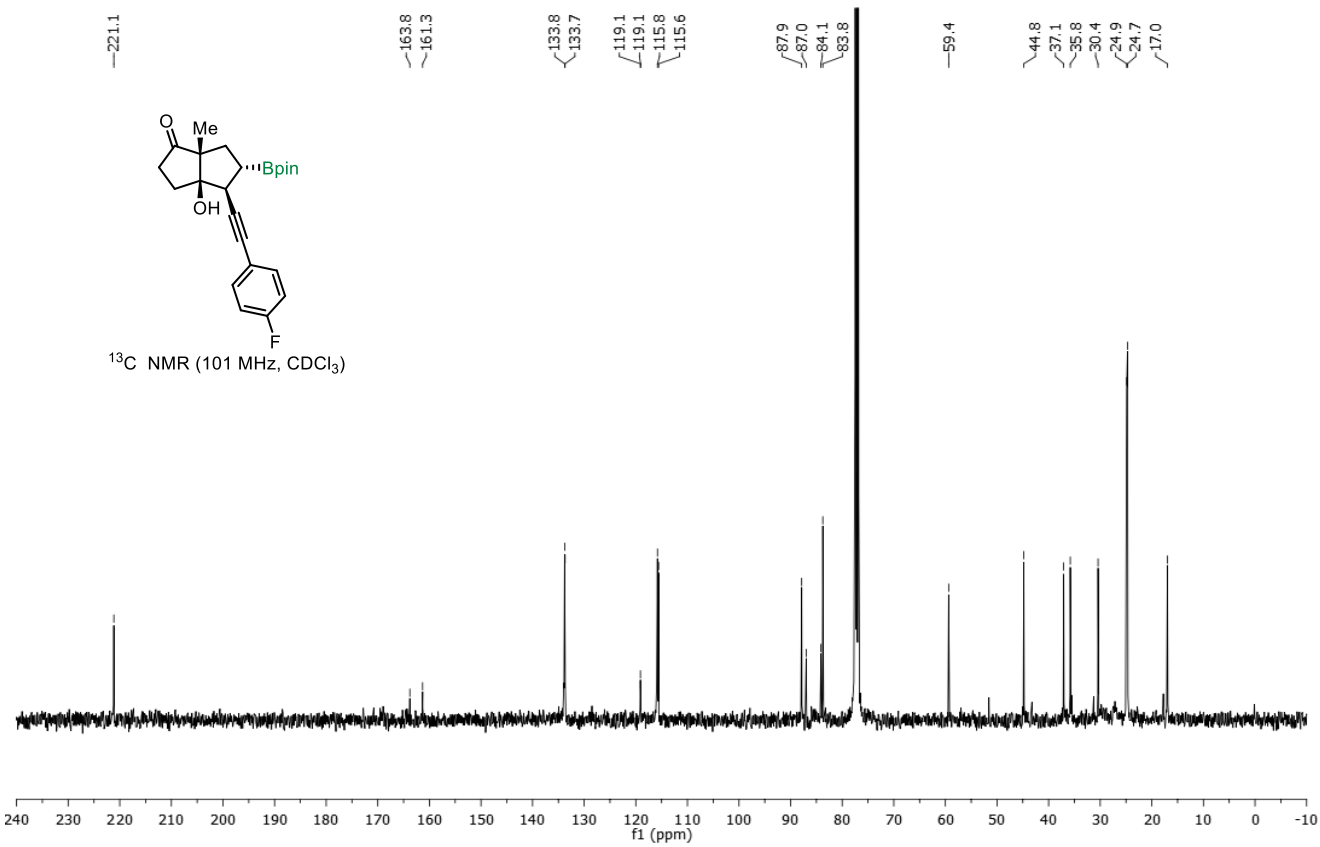
(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-4-((4-methoxyphenyl)ethynyl)-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2aj):

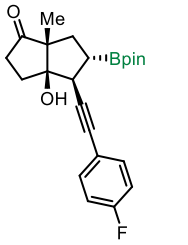




(3a*R*,4*S*,5*S*,6a*R*)-4-((4-Fluorophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ak):

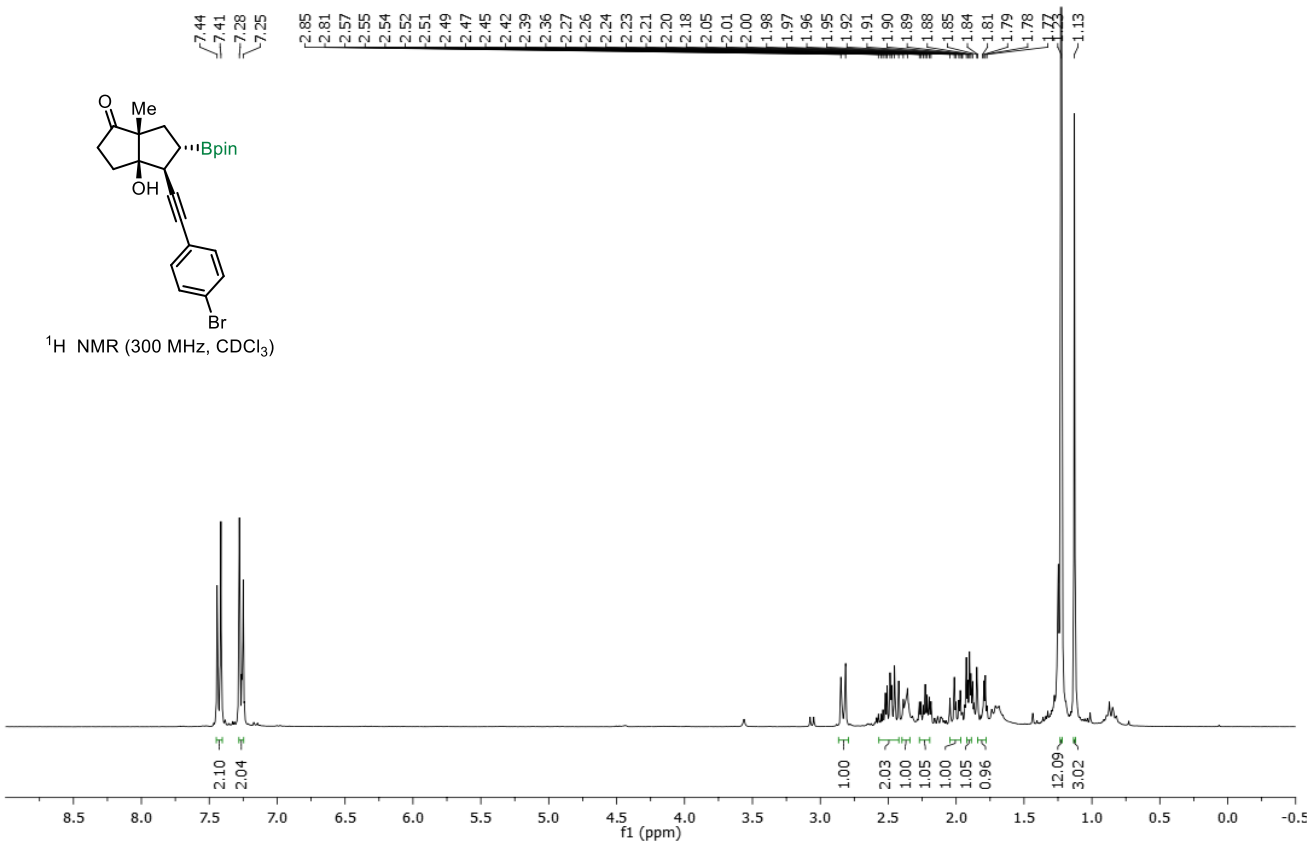


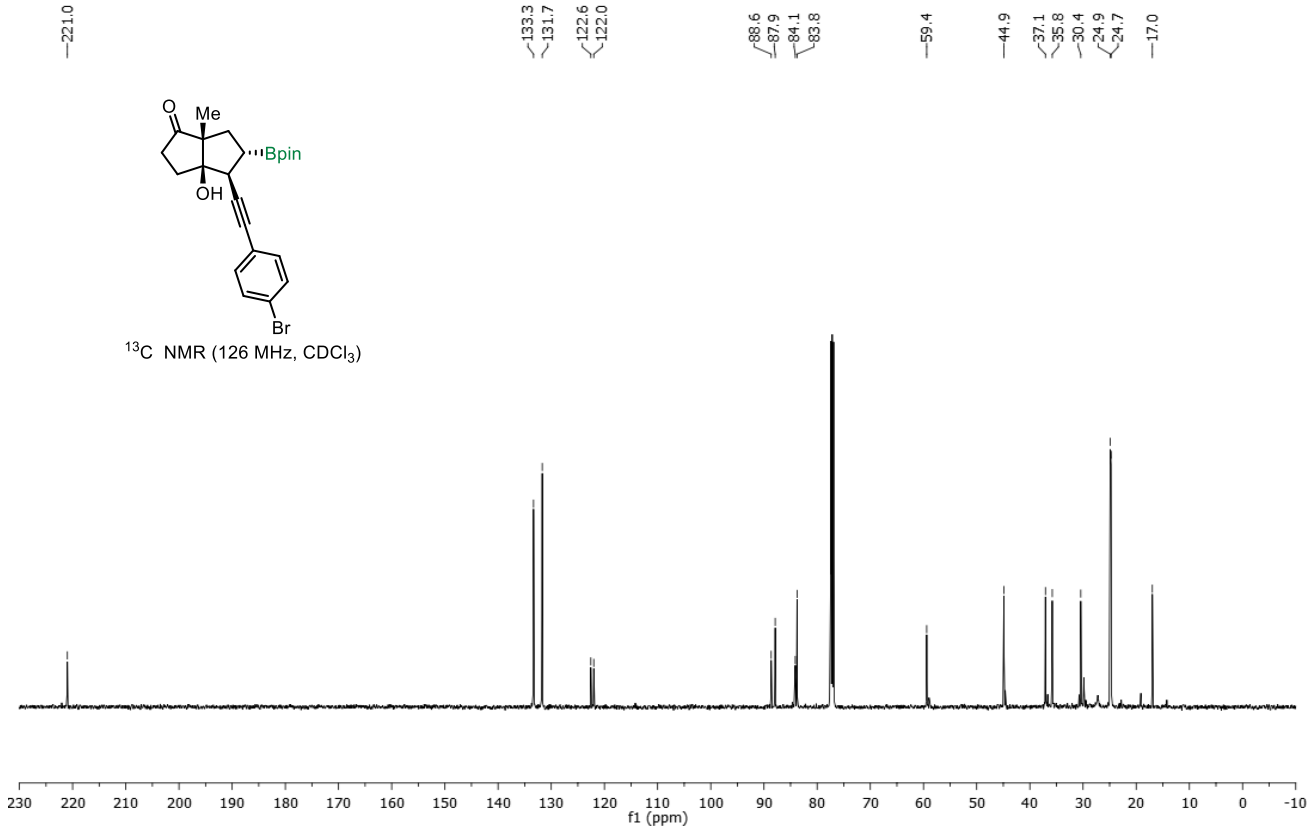




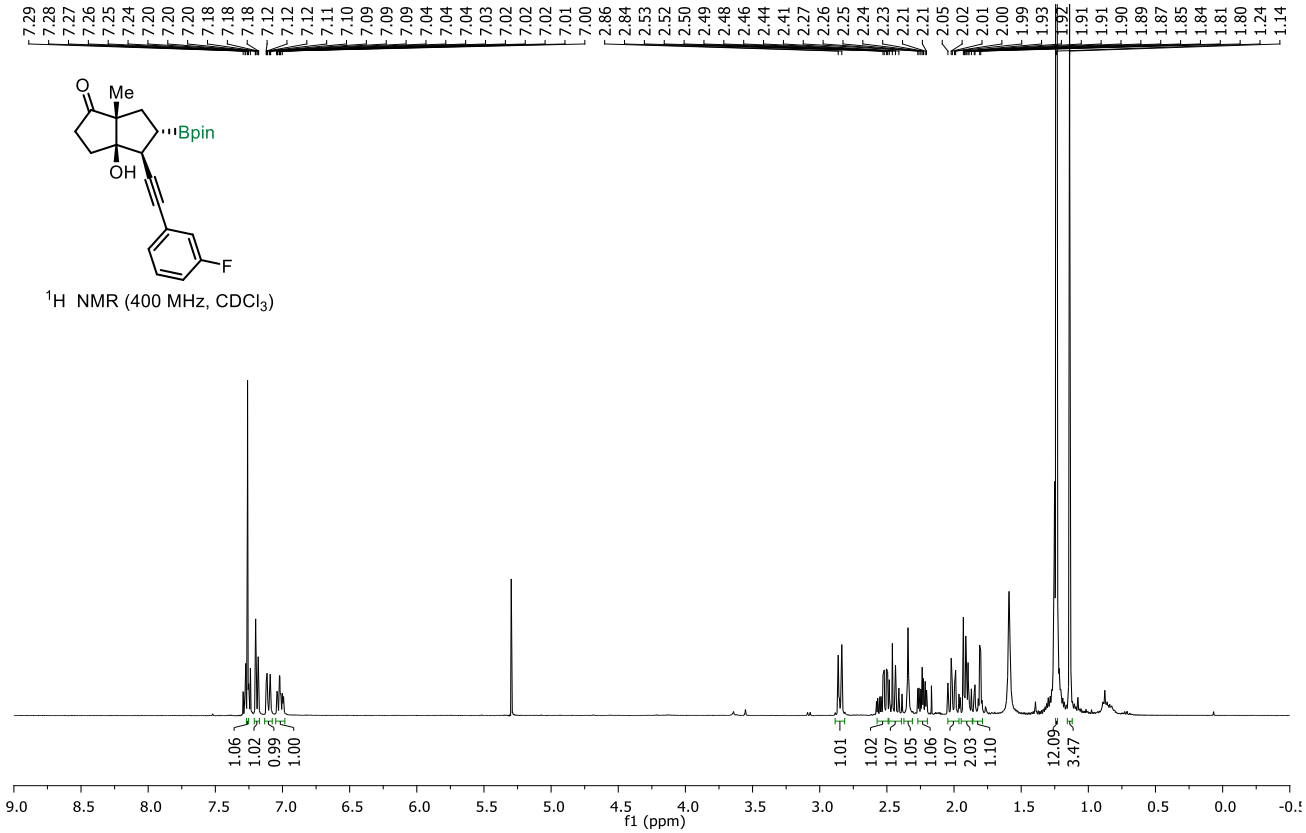
^{19}F NMR (376 MHz, $CDCl_3$)

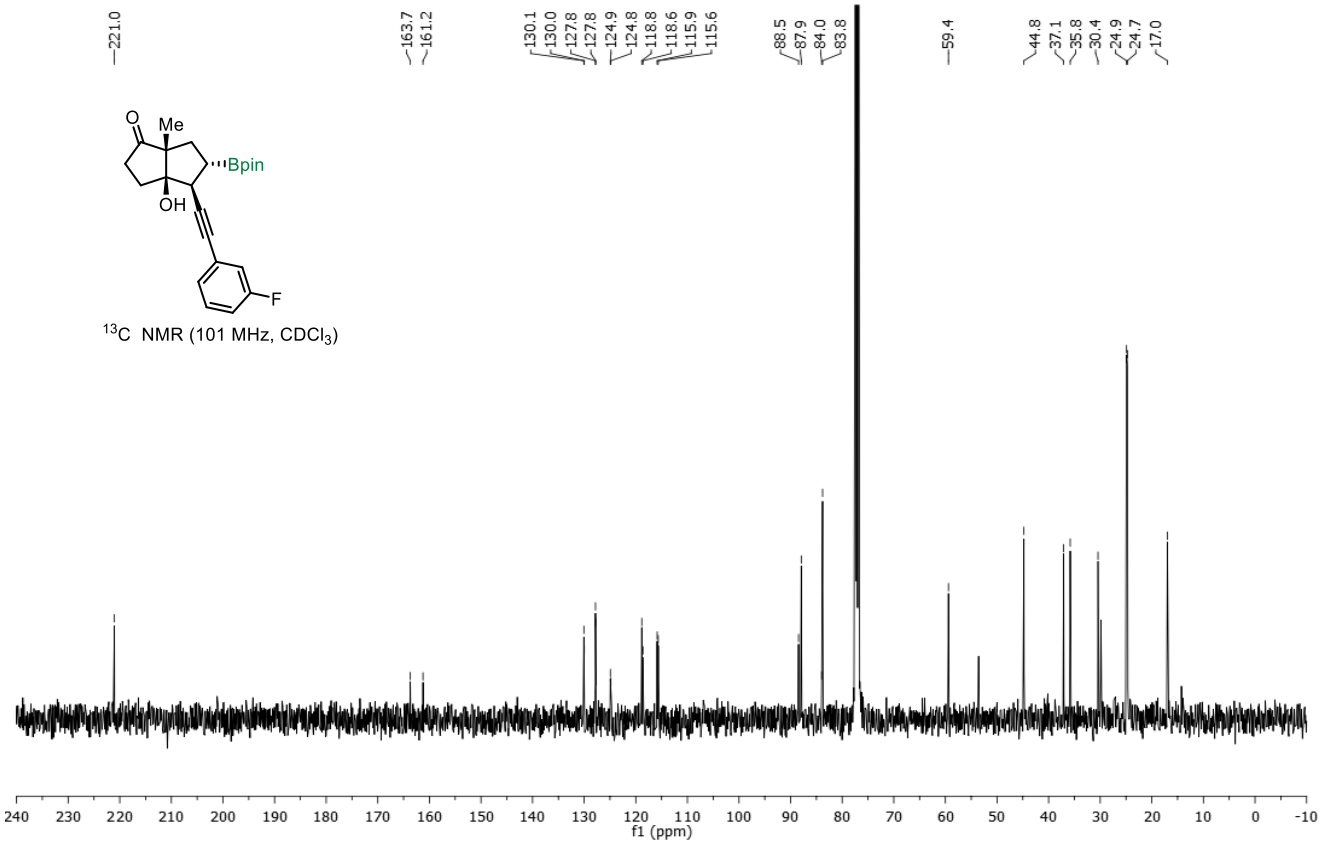
(3a*R*,4*S*,5*S*,6a*R*)-4-((4-Bromophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2al):

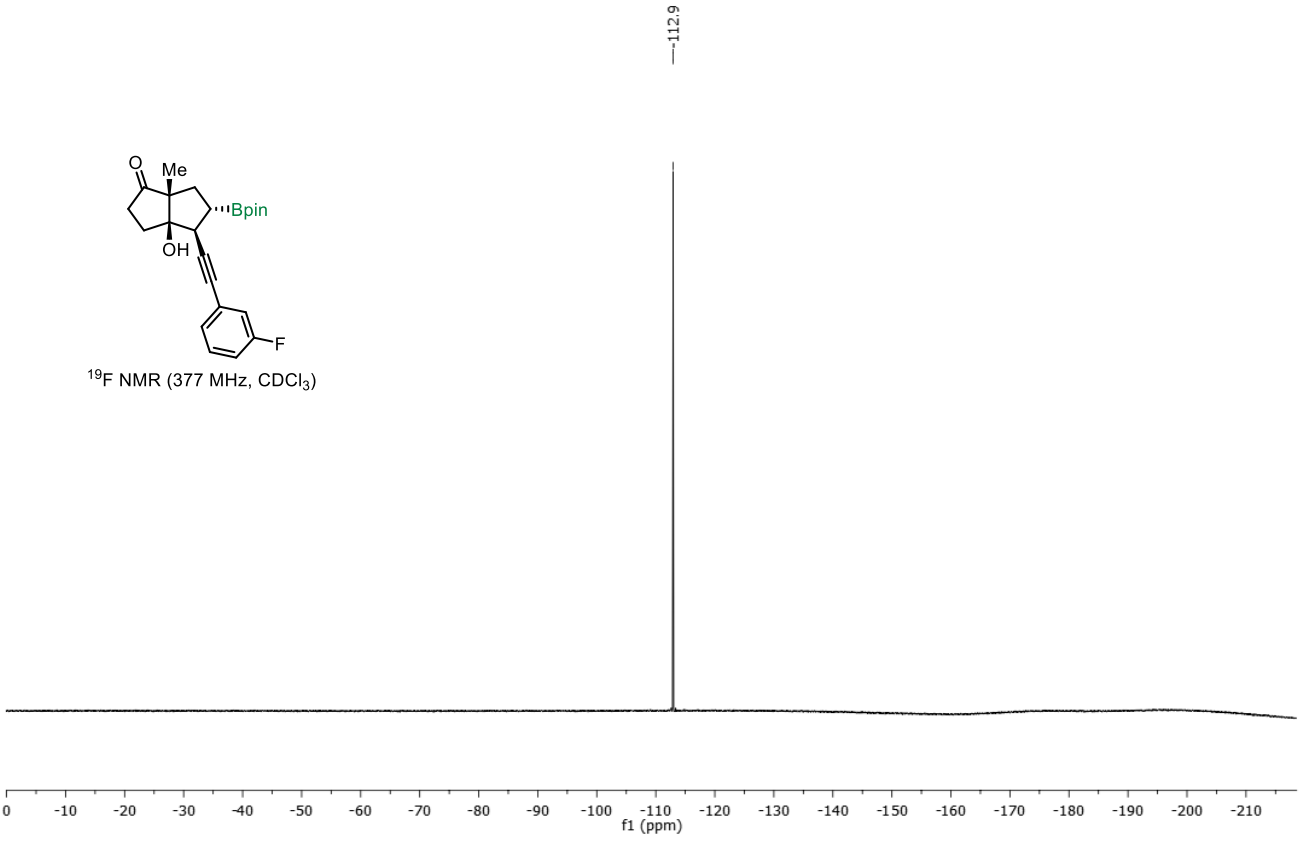




(3a*R*,4*S*,5*S*,6a*R*)-4-((3-Fluorophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2am):

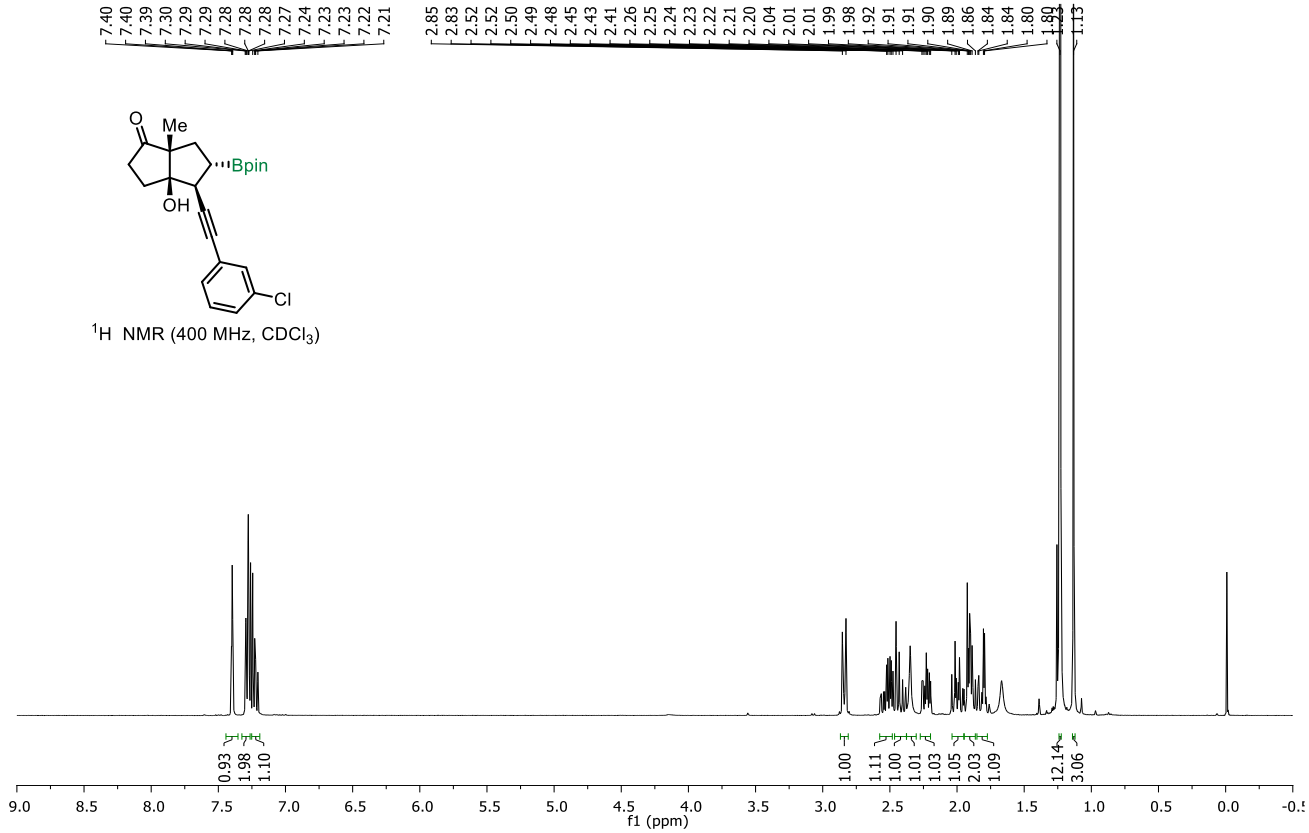


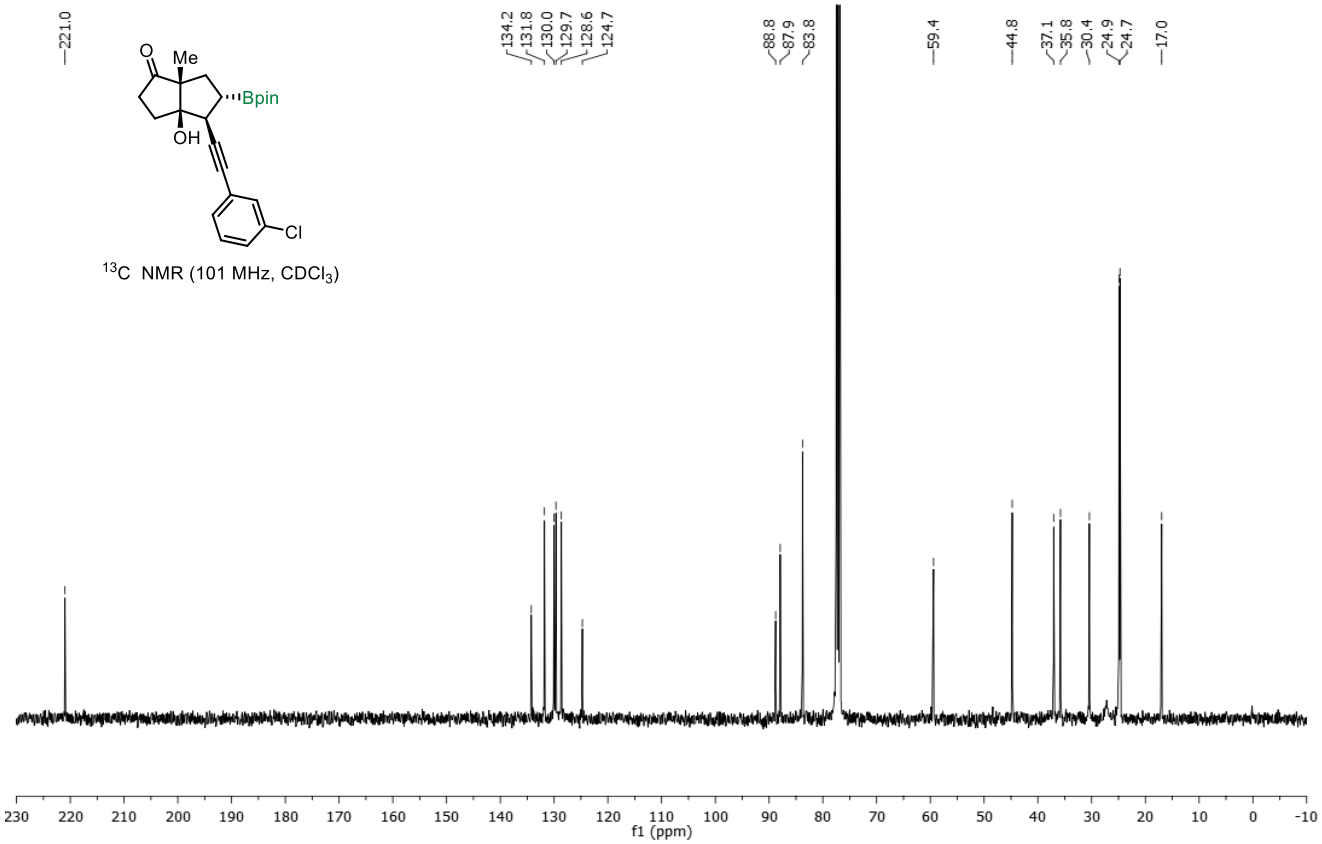




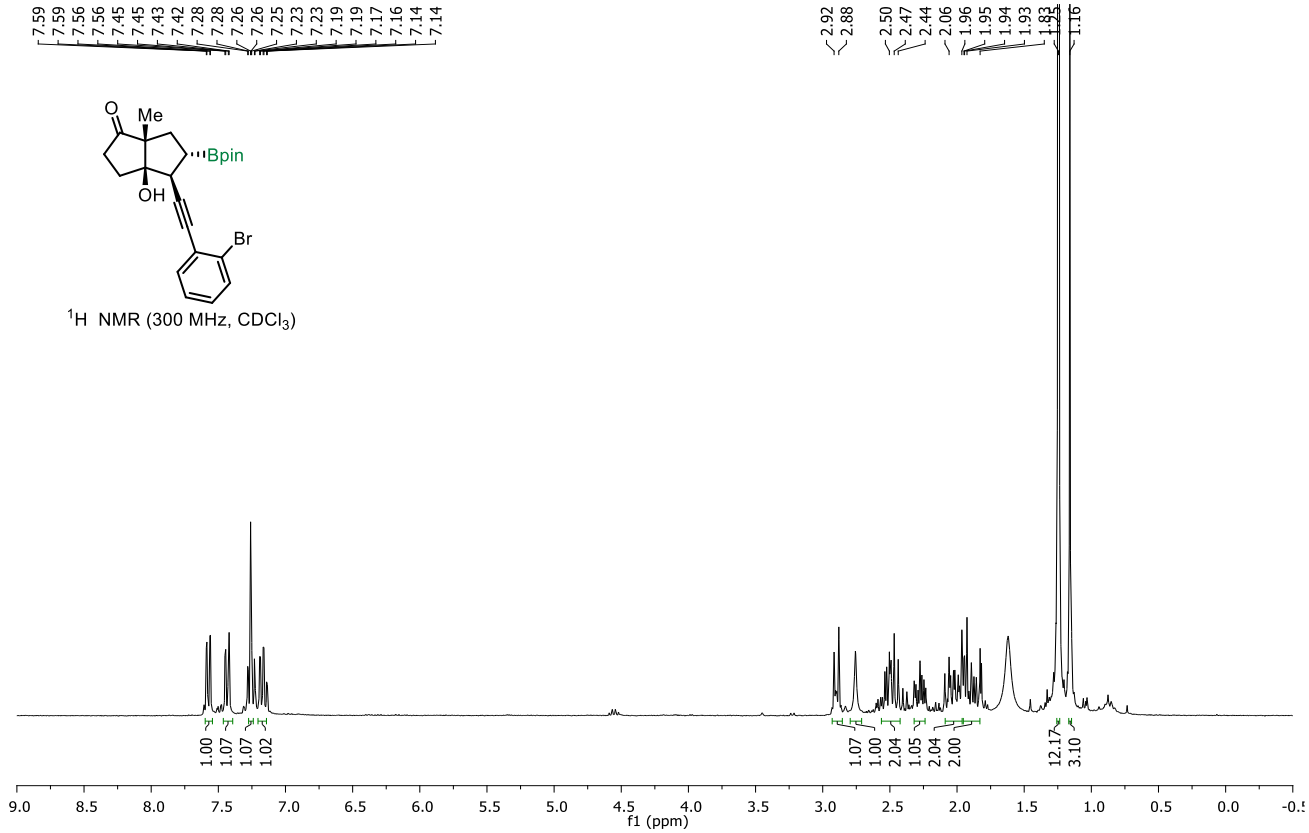
^{19}F NMR (377 MHz, $CDCl_3$)

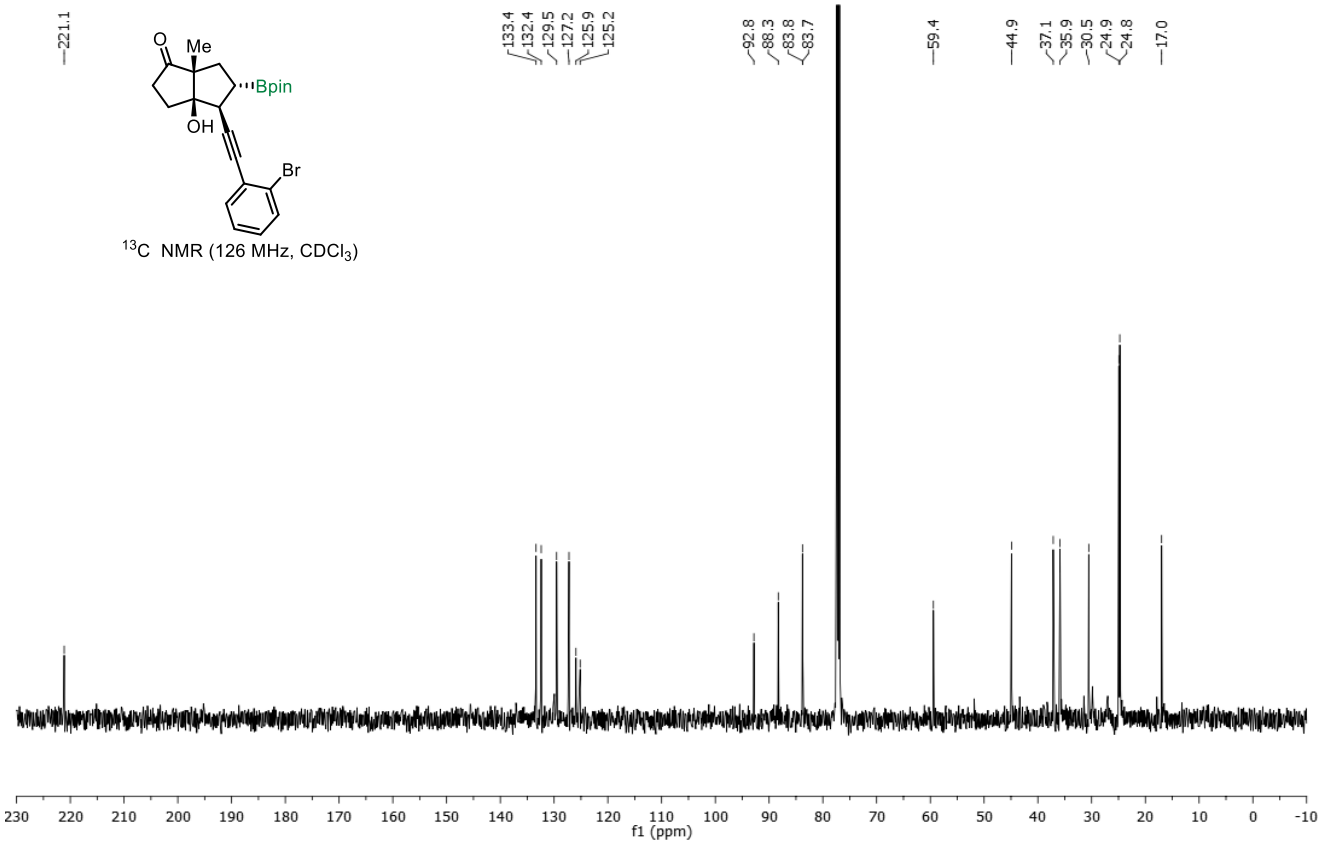
(3a*R*,4*S*,5*S*,6a*R*)-4-((3-Chlorophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2an):



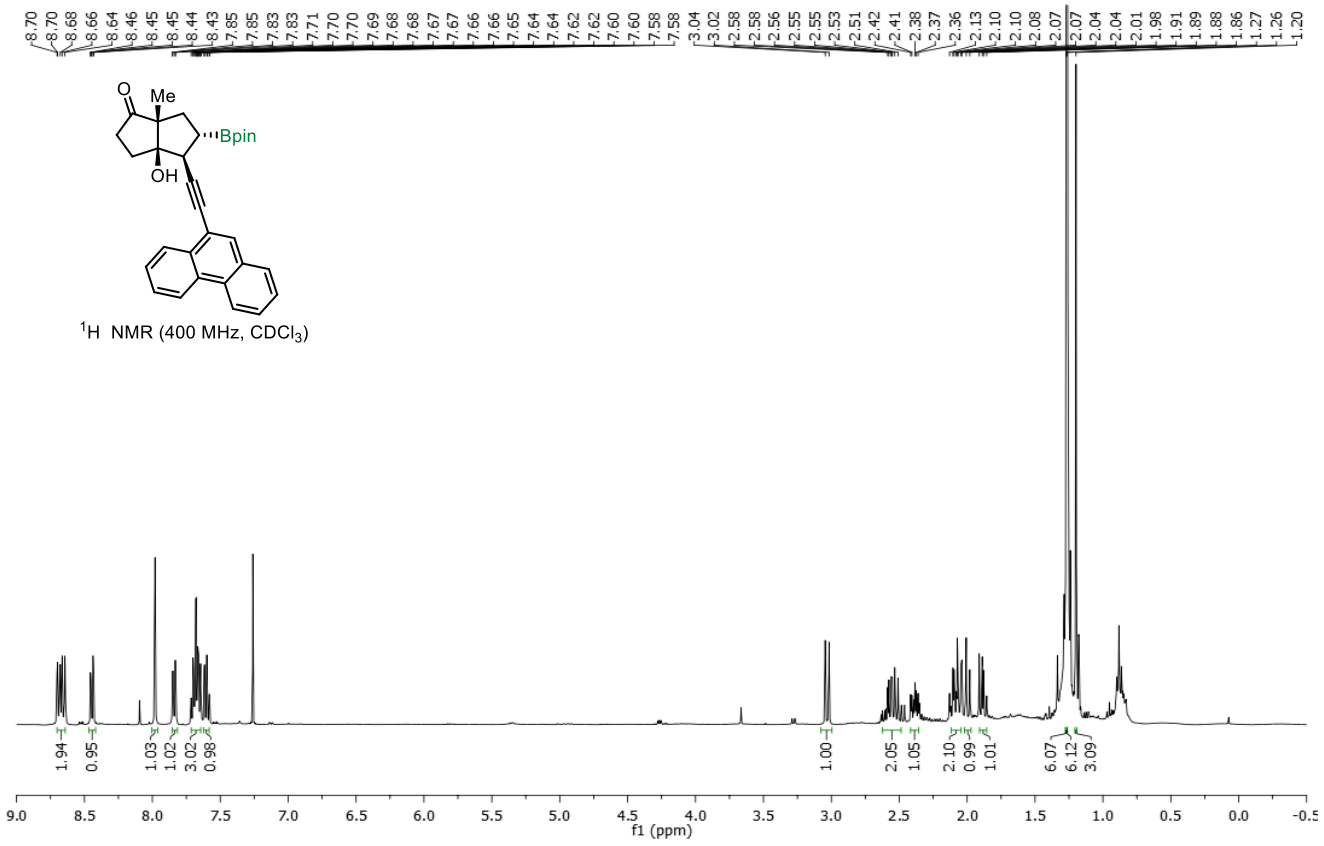


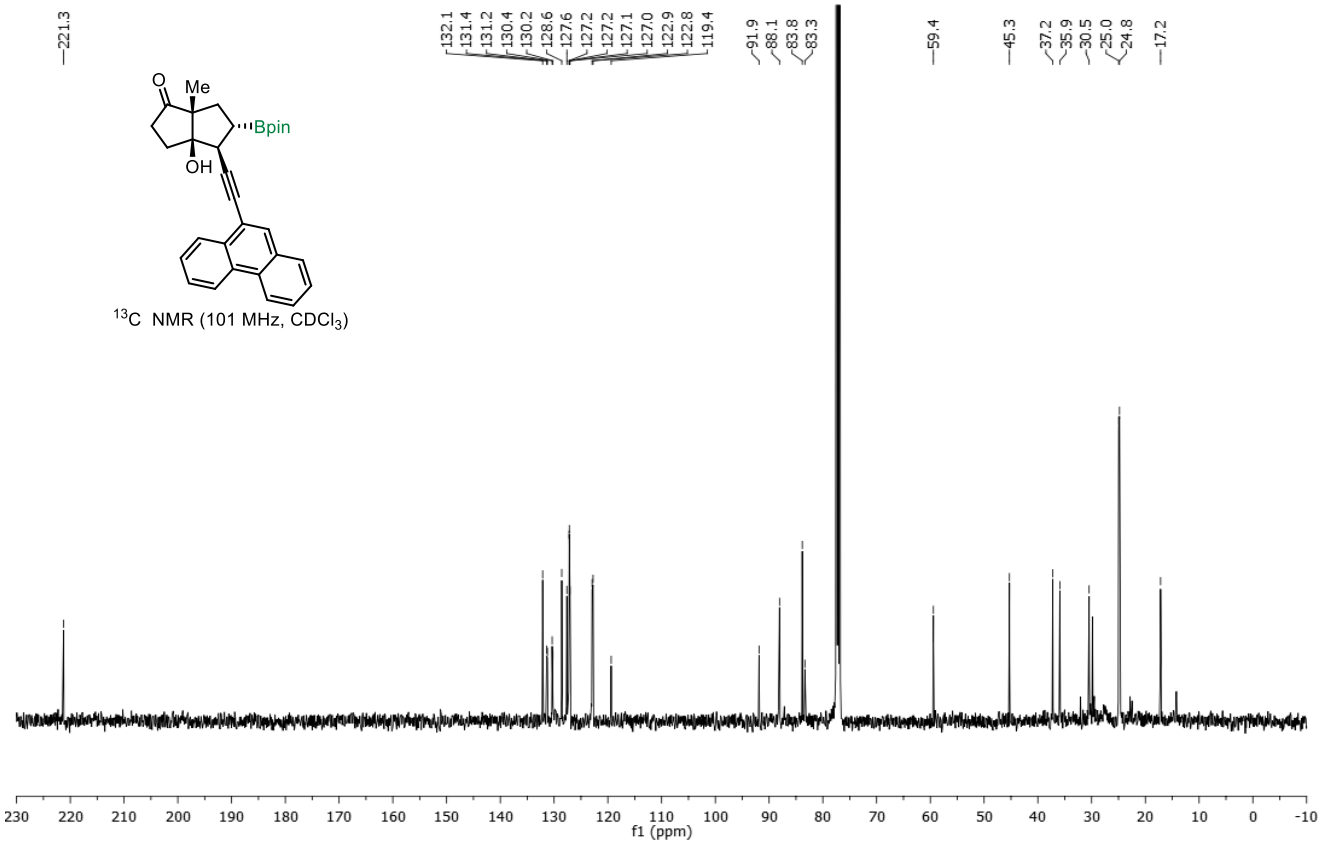
(3a*R*,4*S*,5*S*,6a*R*)-4-((2-Bromophenyl)ethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ao):



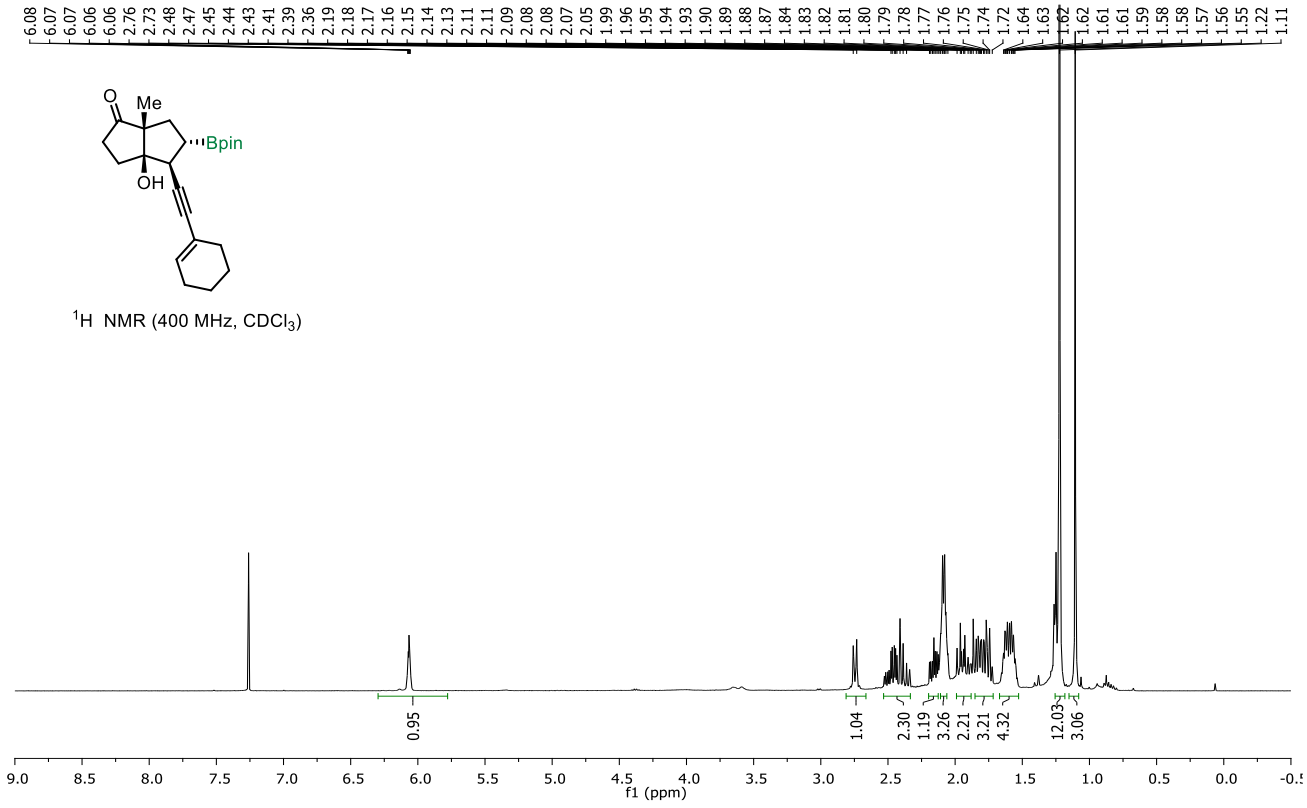


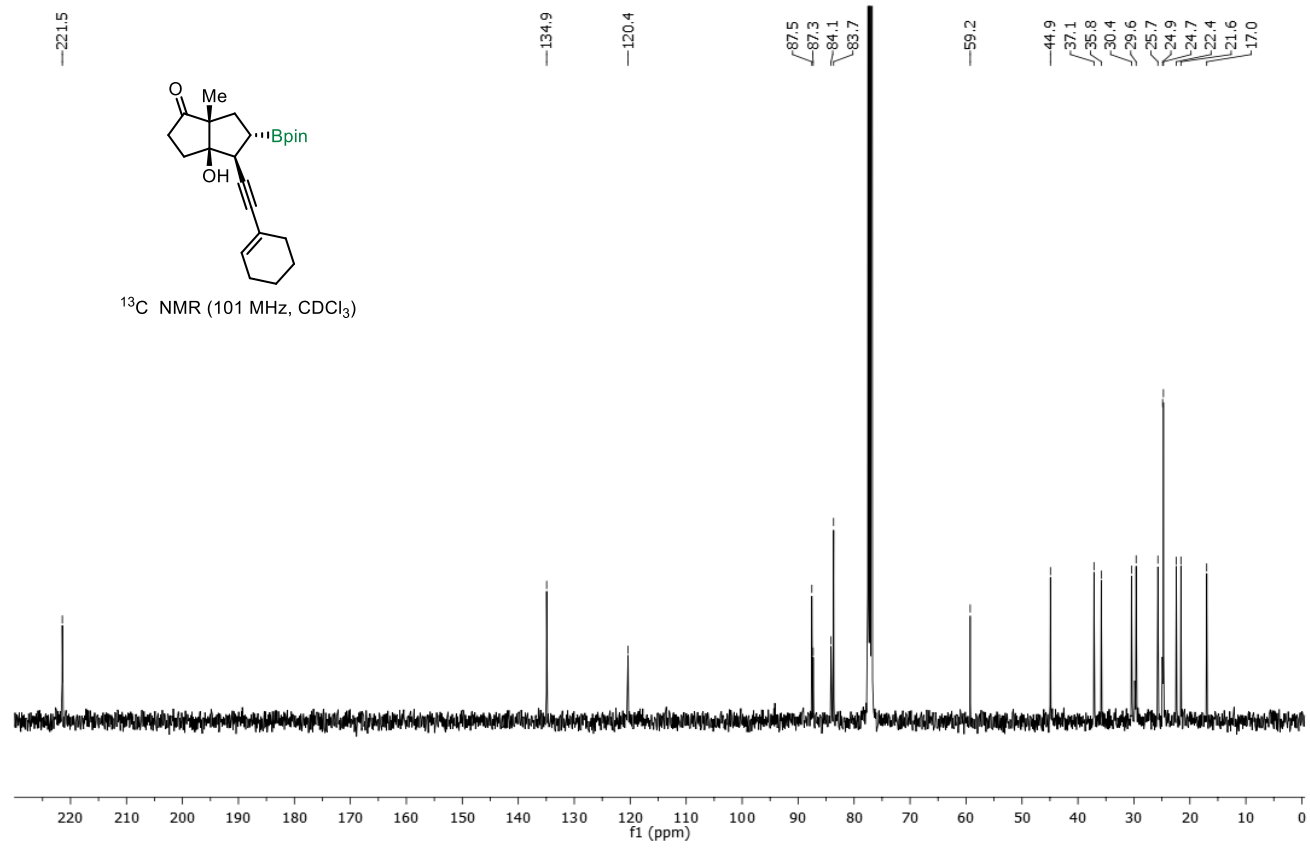
(3a*R*,4*S*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-4-(phenanthren-9-ylethynyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2ap):



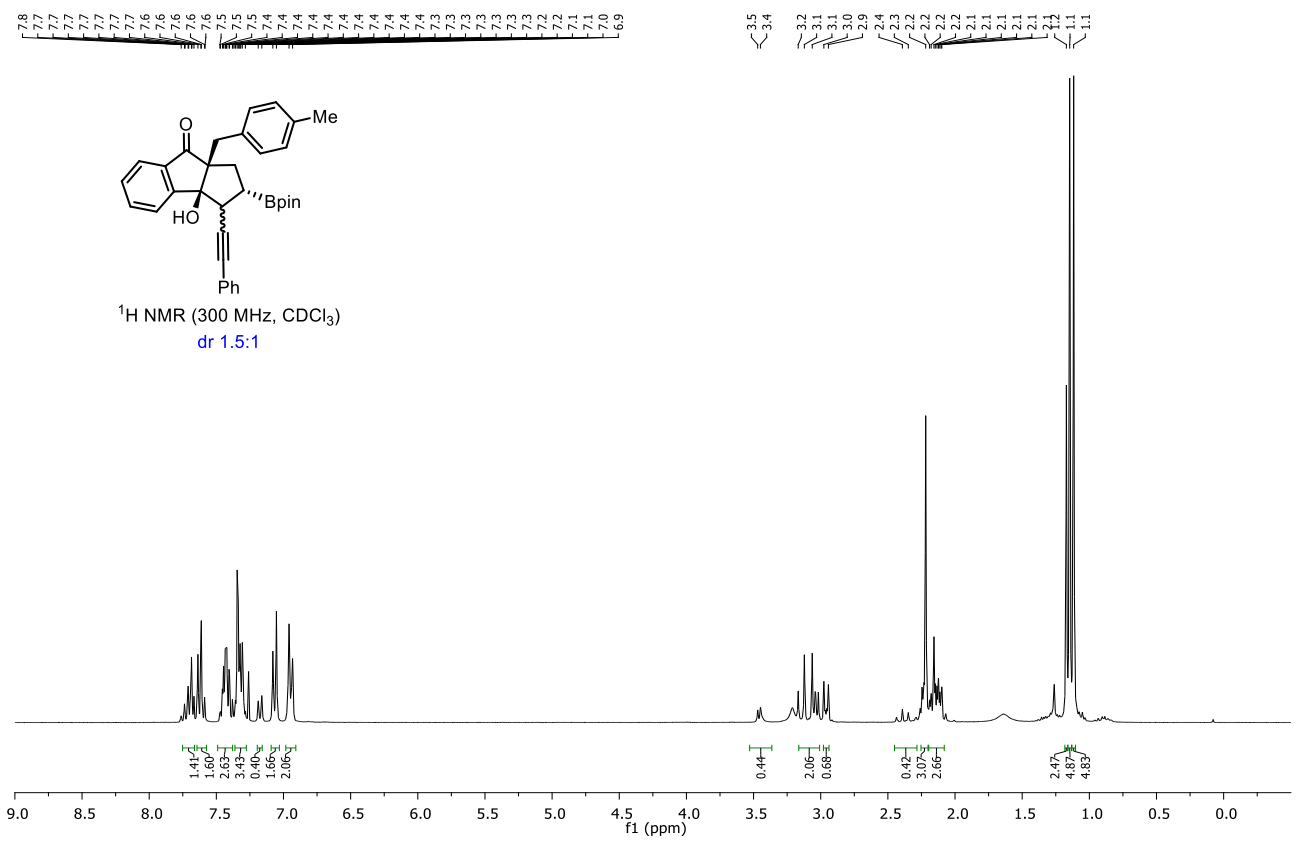


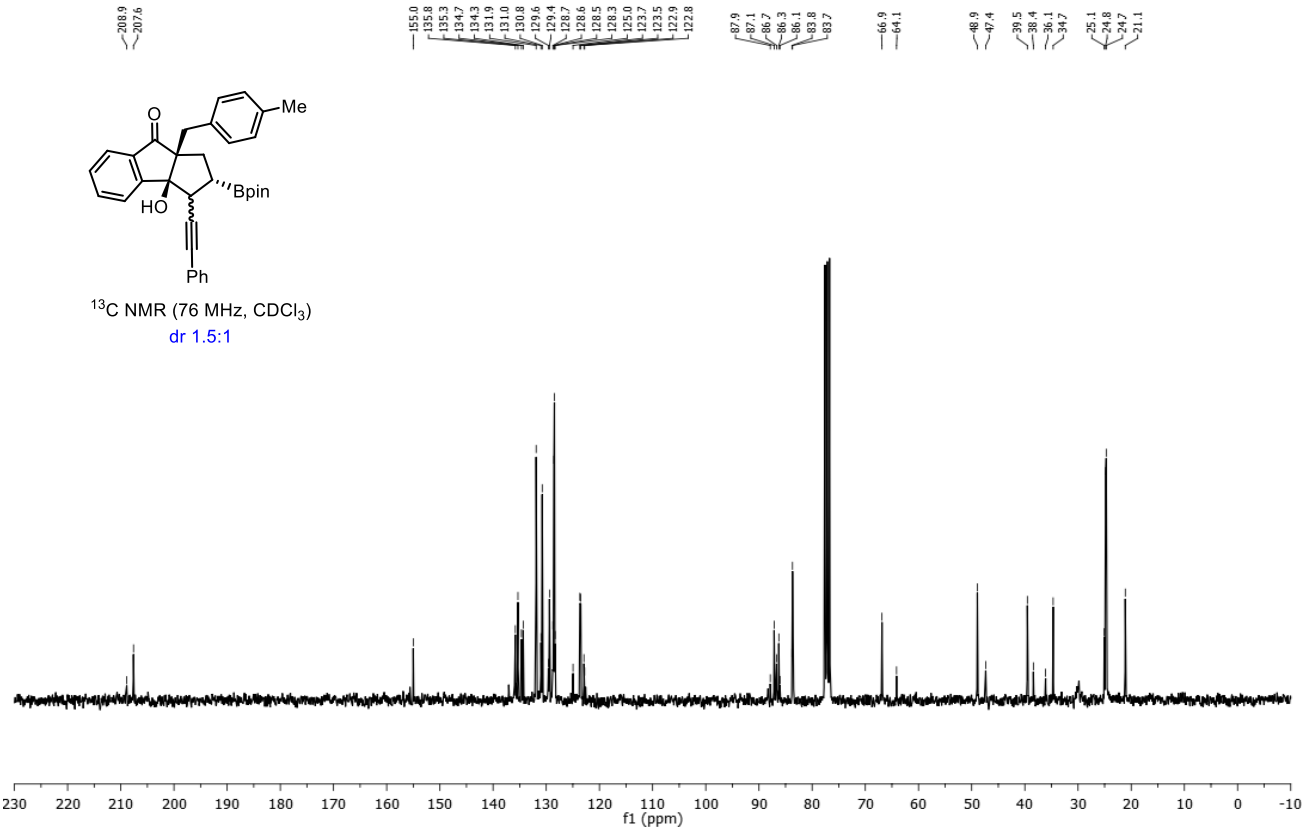
(3a*R*,4*S*,5*S*,6a*R*)-4-(Cyclohex-1-en-1-ylethynyl)-3a-hydroxy-6a-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (2aq):



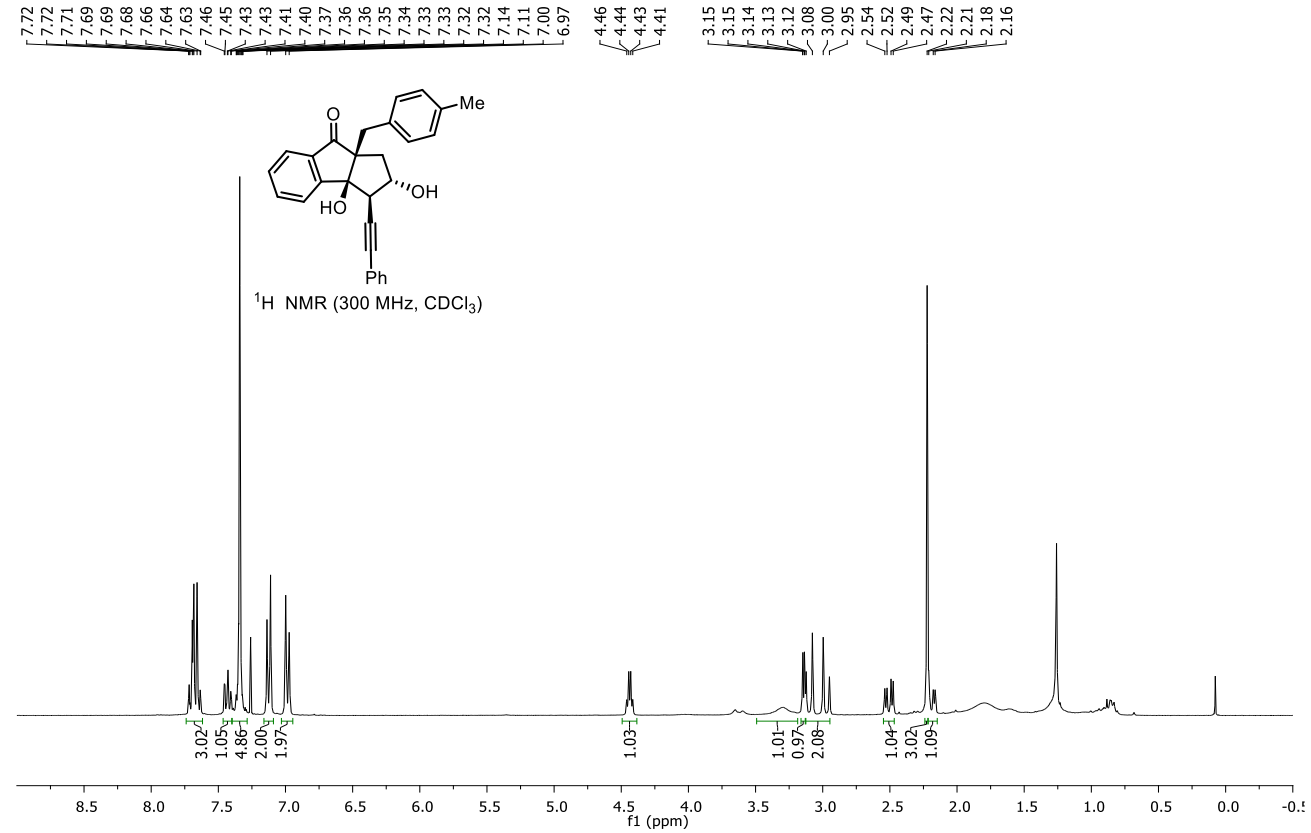


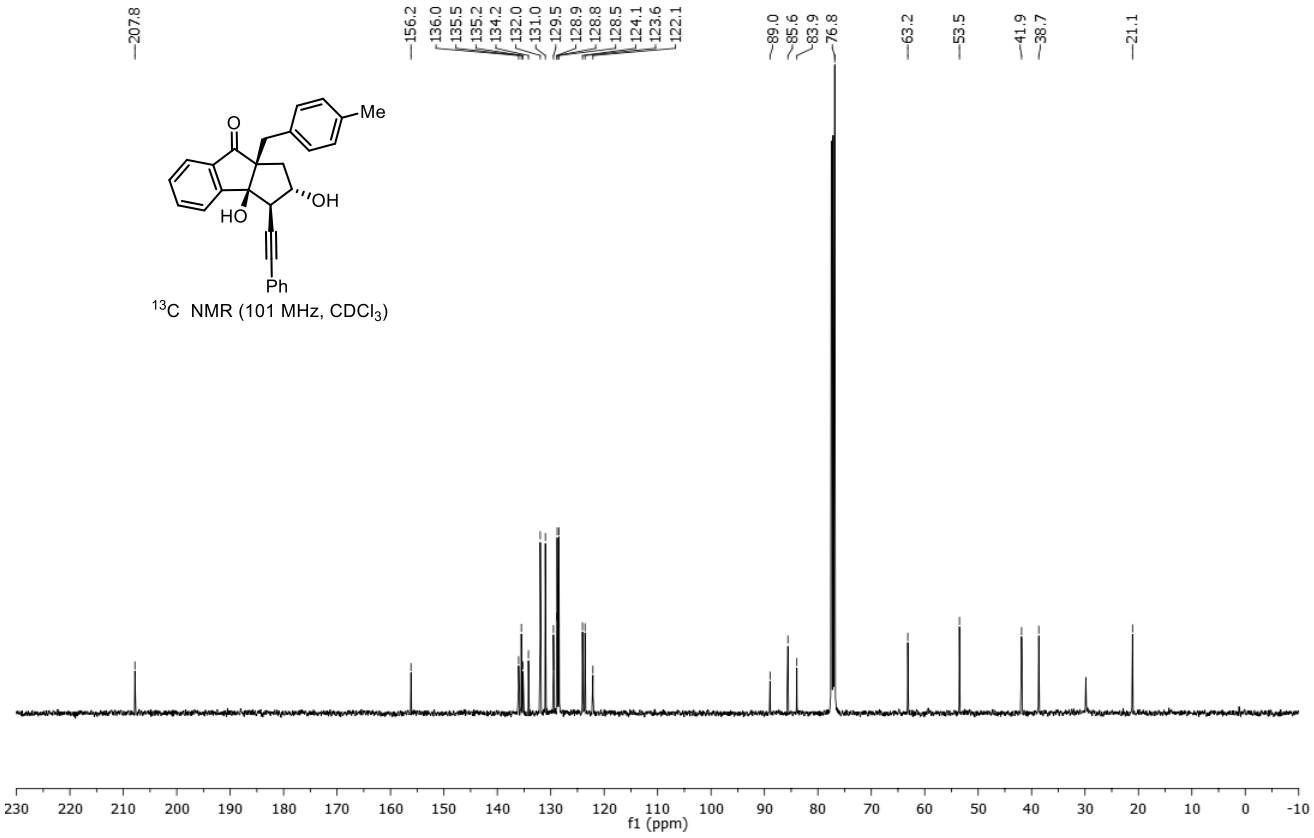
(2*S*,3aS,8aS)-3a-Hydroxy-8a-(4-methylbenzyl)-3-(phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (4a/4a'):



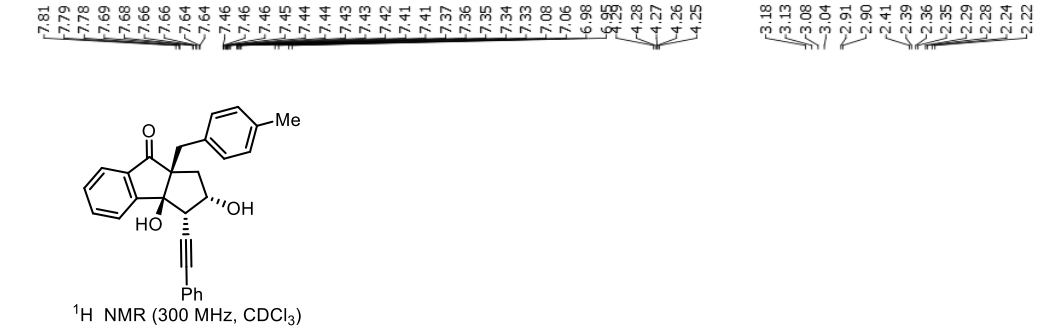


(2*S*,3*R*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methylbenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (anti-5a):

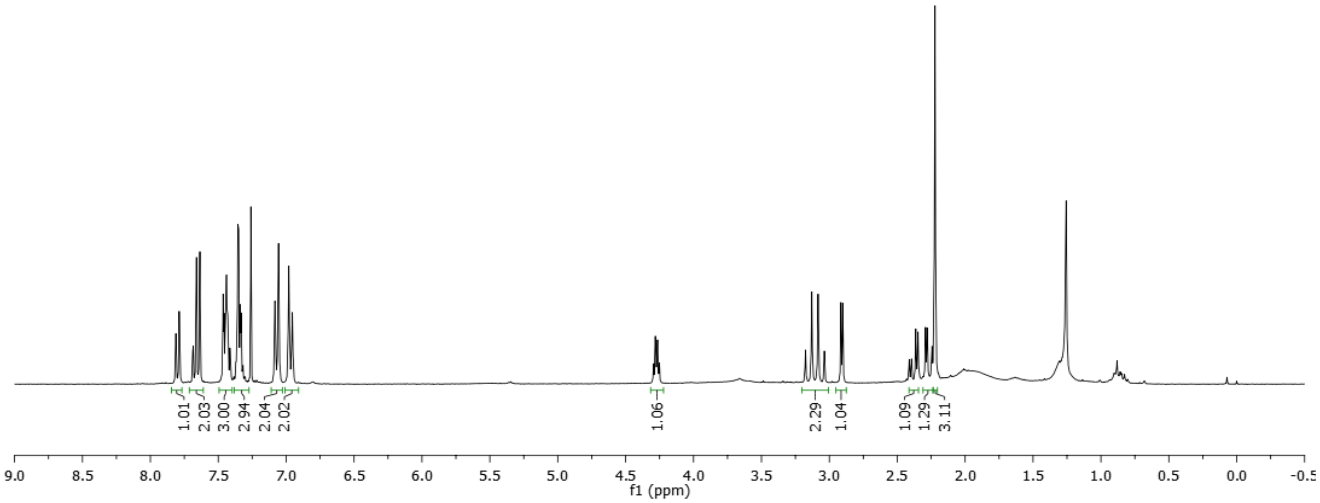


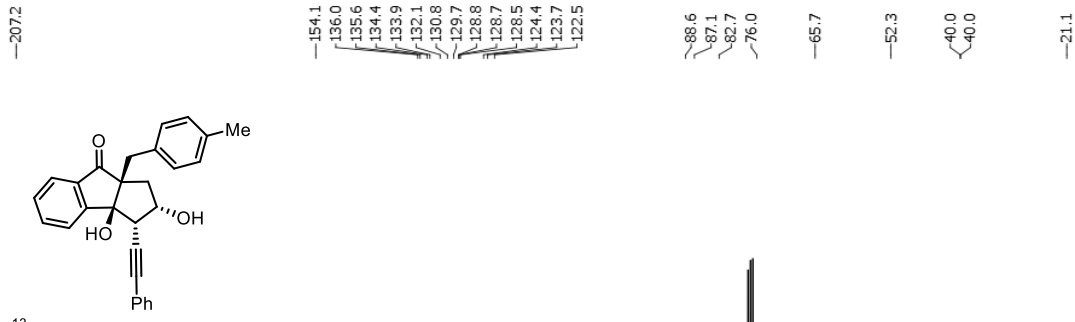


(2*S*,3*S*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methylbenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (syn-5a):

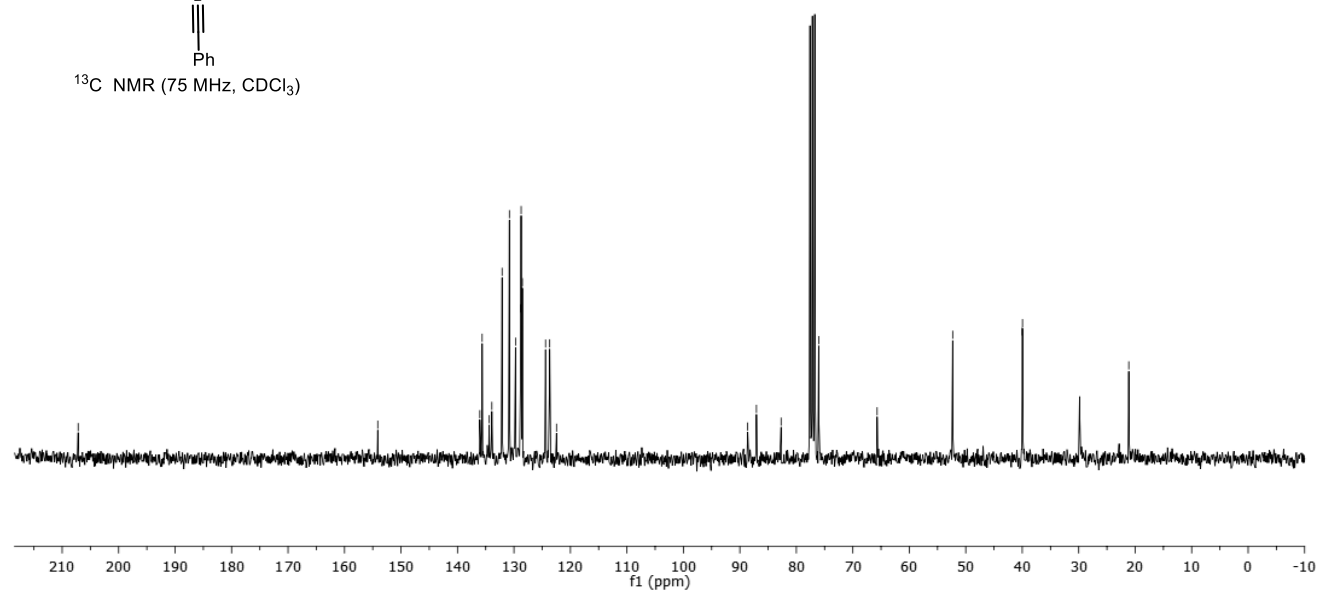


^{1}H NMR (300 MHz, $CDCl_3$)

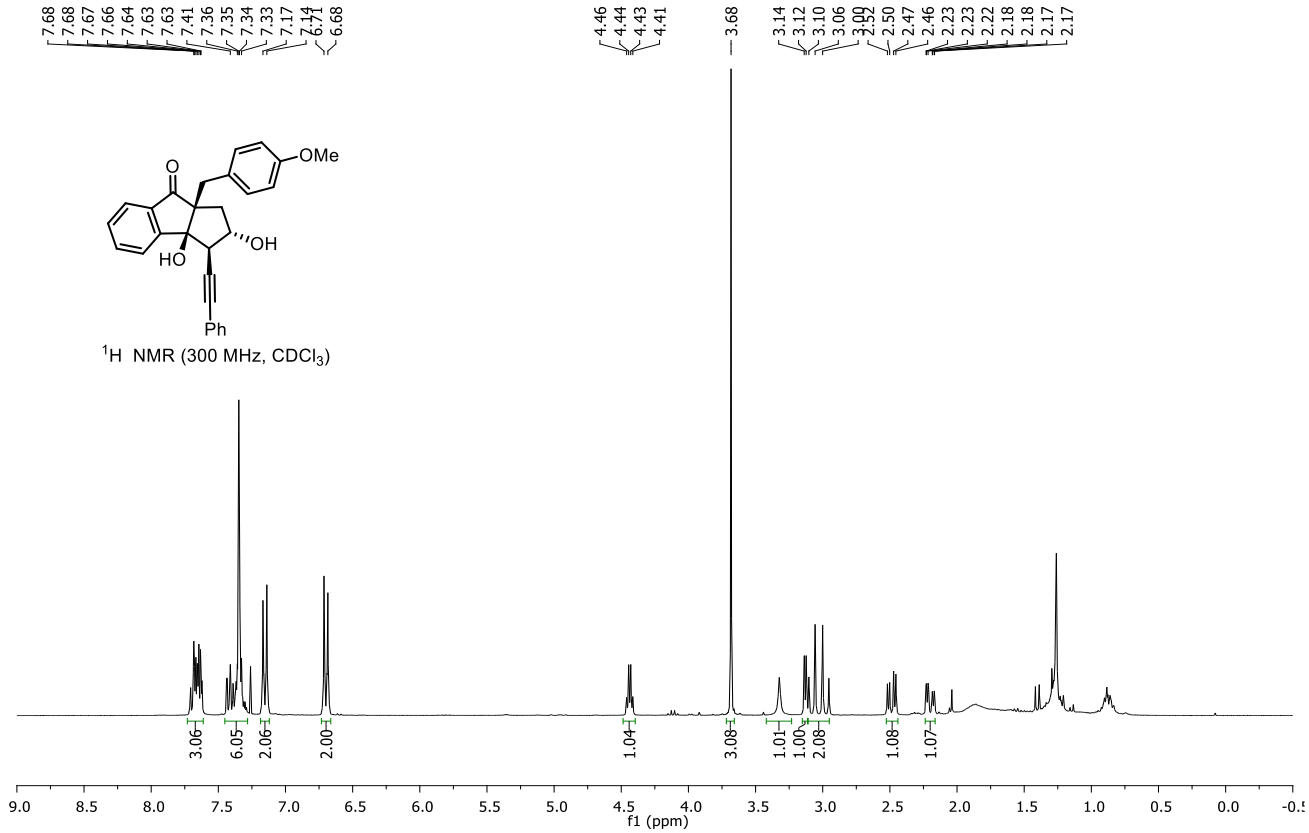


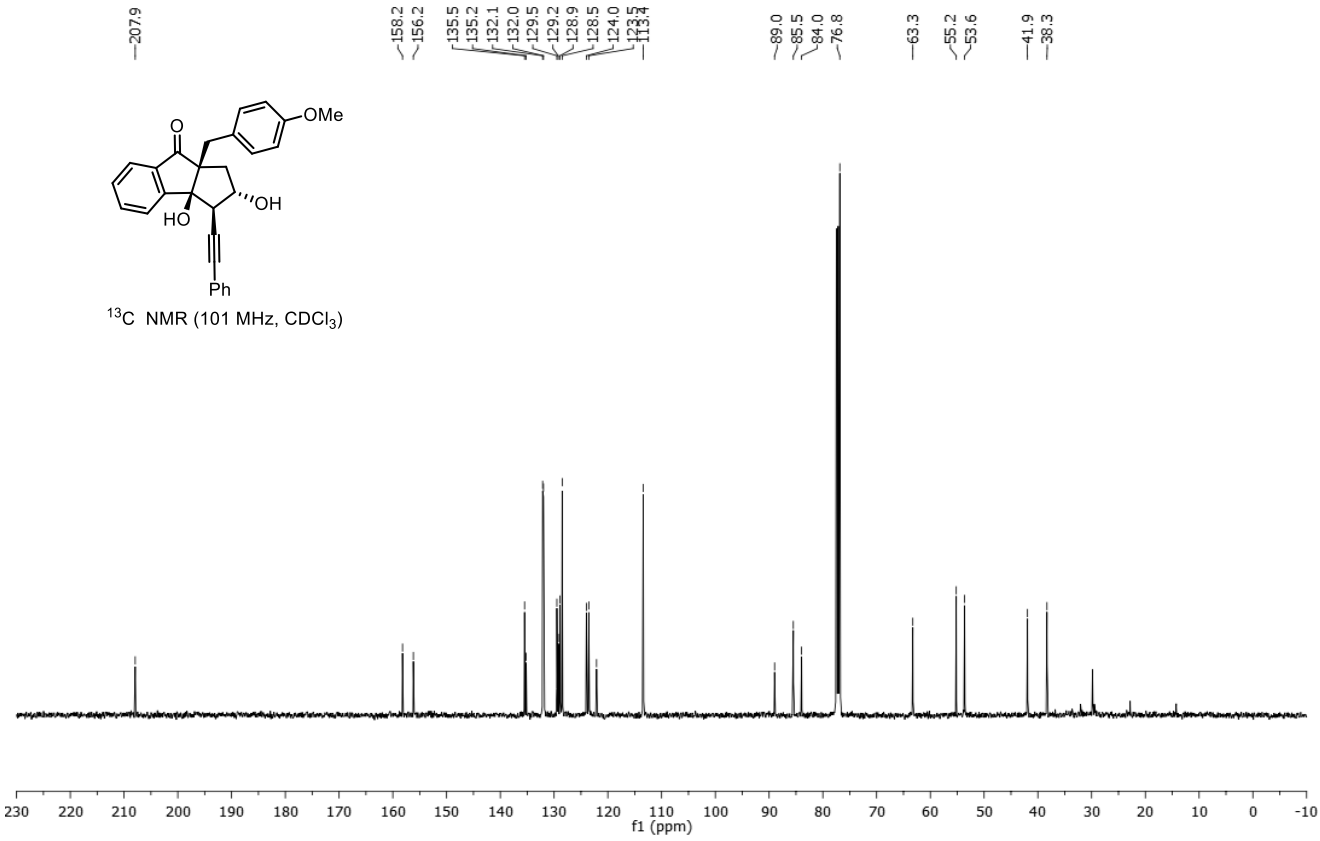


^{13}C NMR (75 MHz, $CDCl_3$)

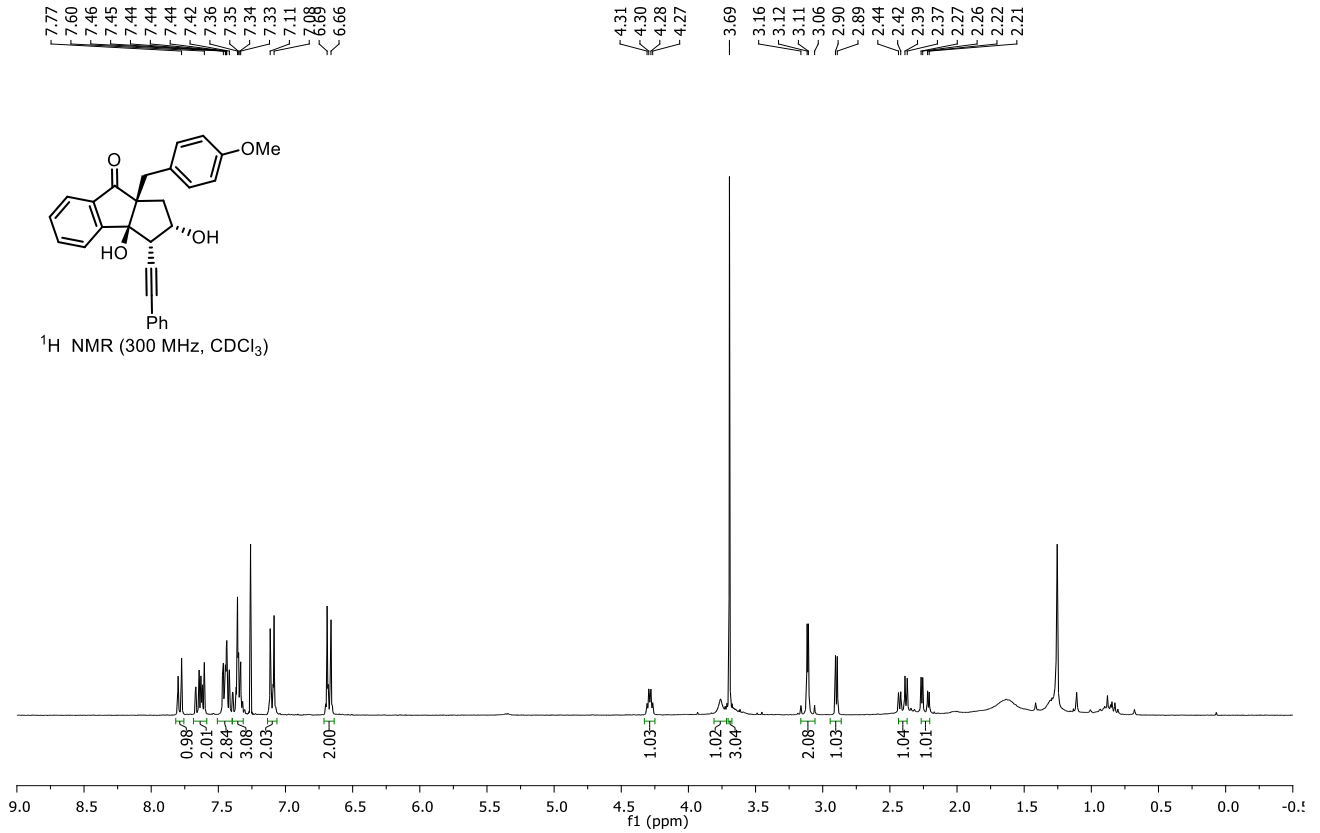


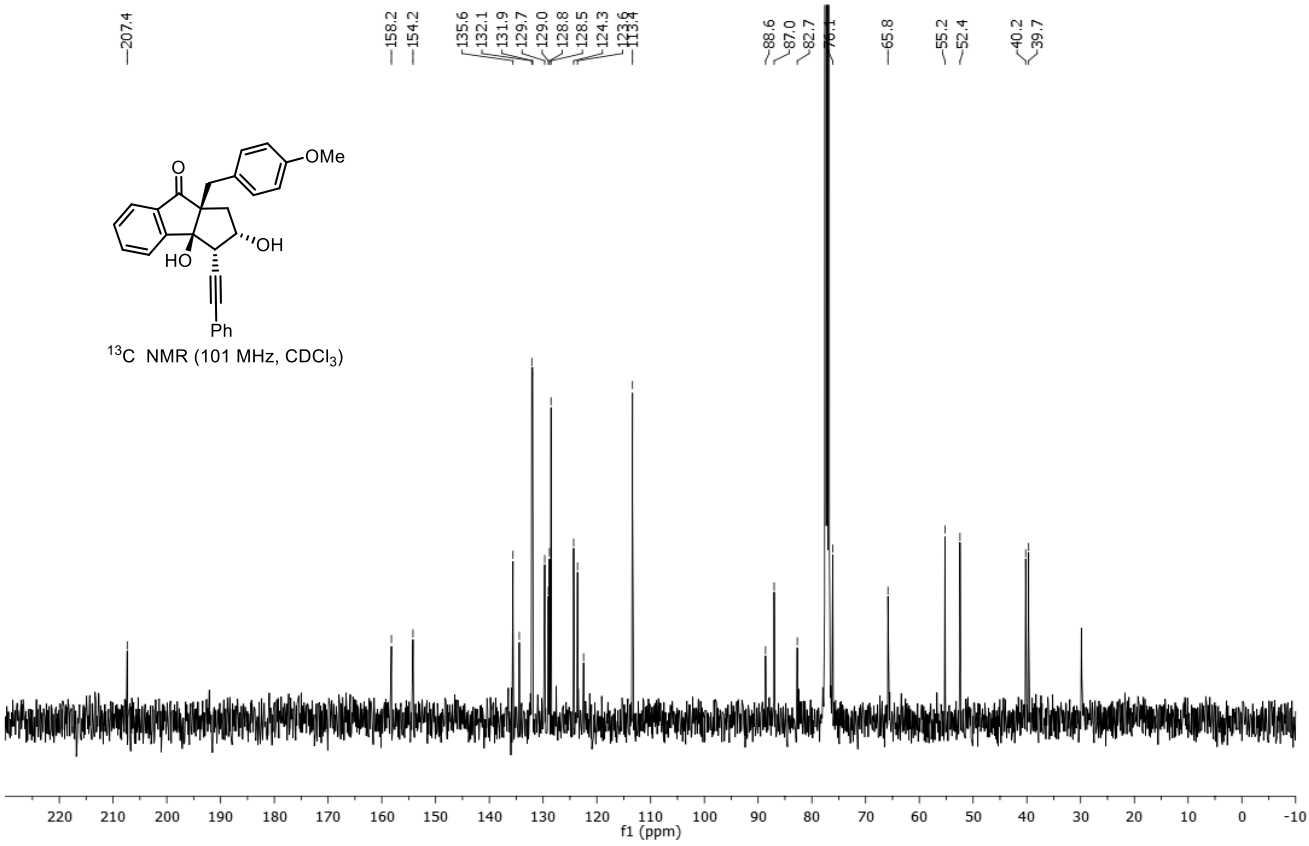
(2*S*,3*R*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methoxybenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*anti*-5b):





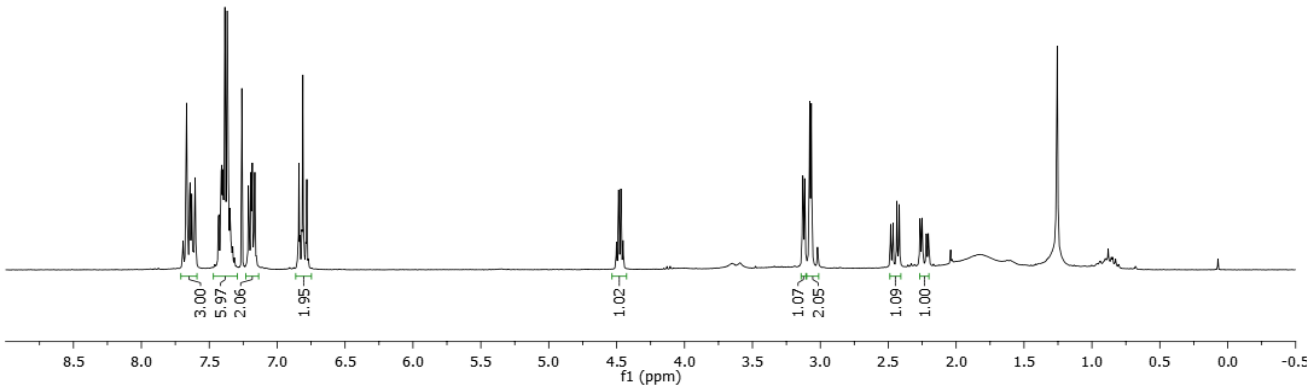
(2*S*,3*S*,3a*S*,8a*R*)-2,3a-Dihydroxy-8a-(4-methoxybenzyl)-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*syn*-5b):

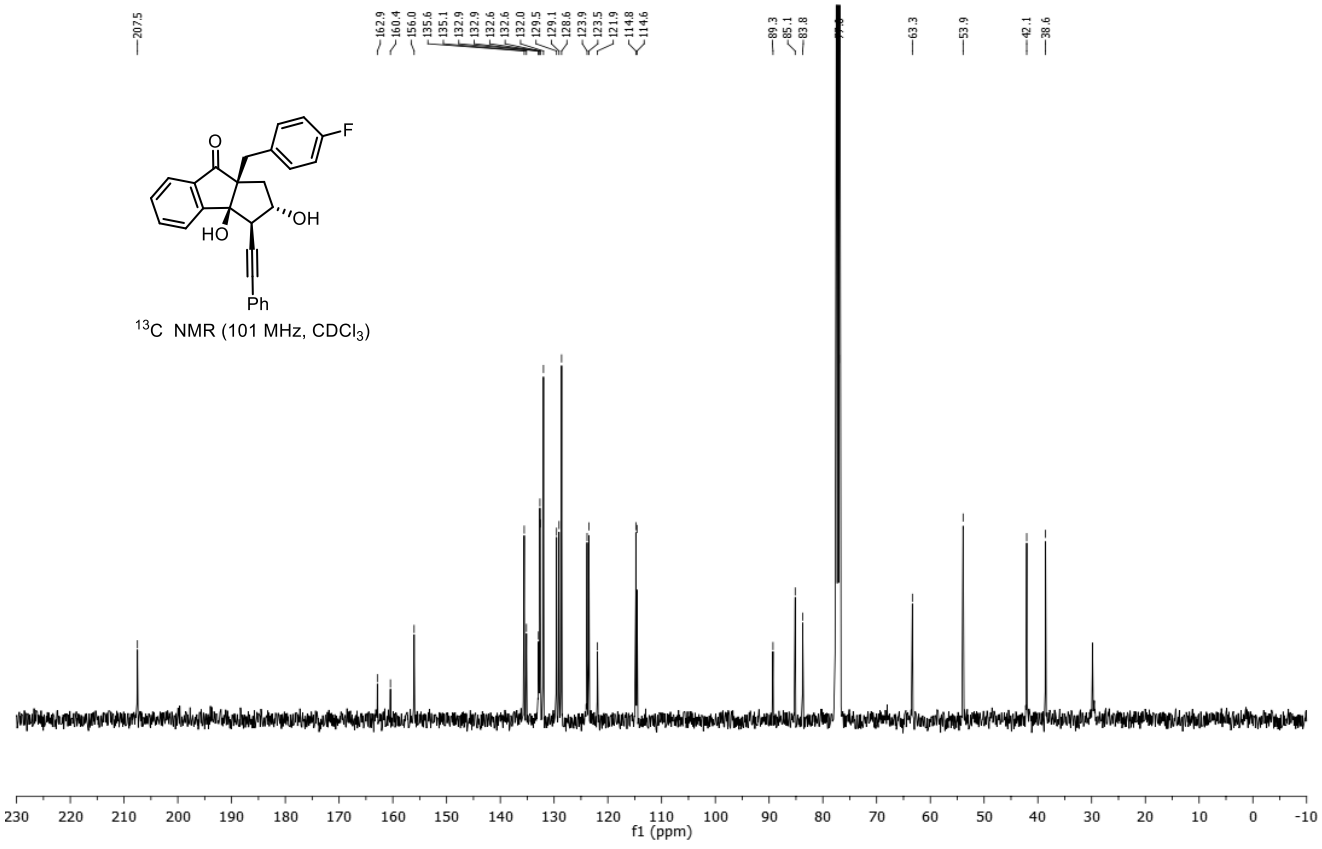




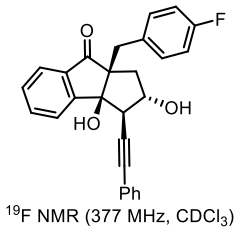
(2*S*,3*R*,3a*S*,8a*R*)-8a-(4-Fluorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (anti-5c):

^{1}H NMR (300 MHz, $CDCl_3$)



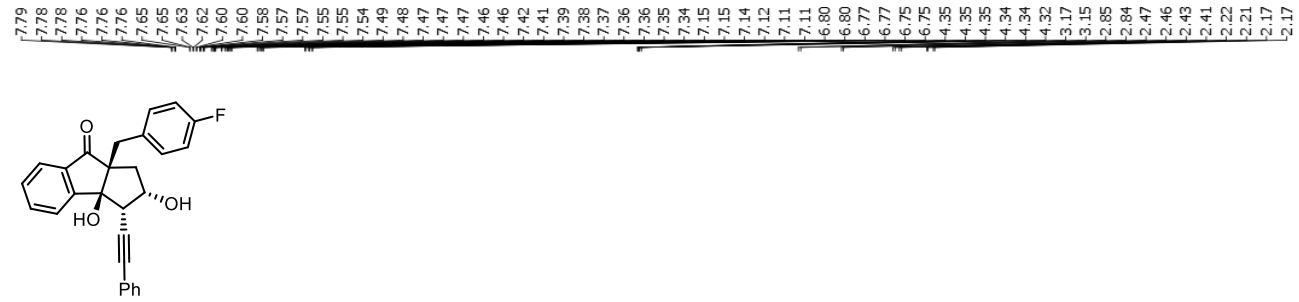


^{13}C NMR (101 MHz, $CDCl_3$)

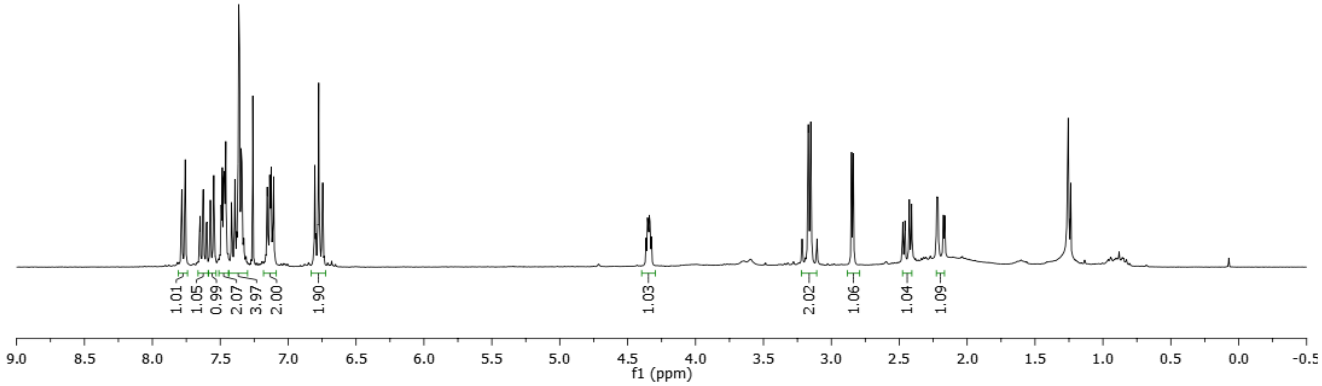


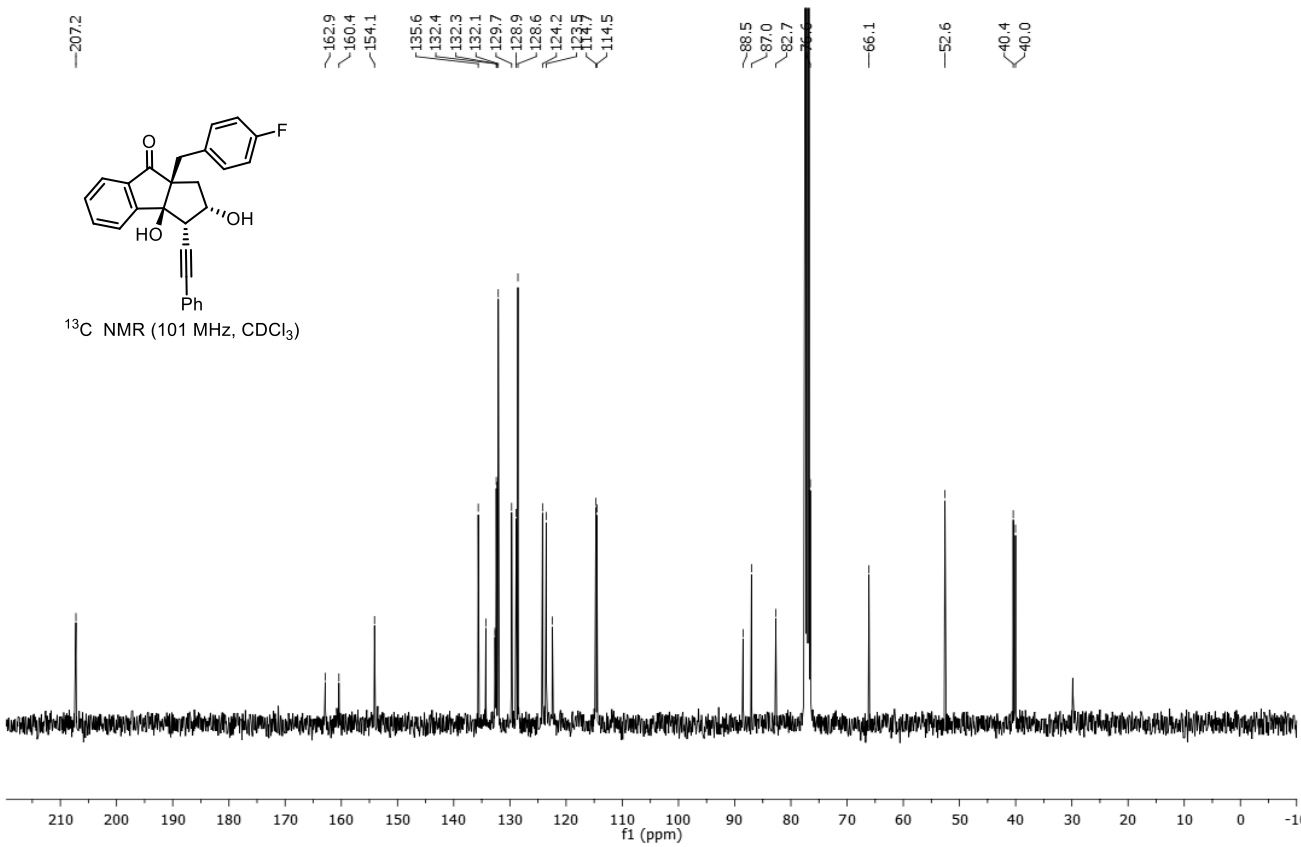
^{19}F NMR (377 MHz, $CDCl_3$)

(2*S*,3*S*,3a*S*,8a*R*)-8a-(4-Fluorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (syn-5c):

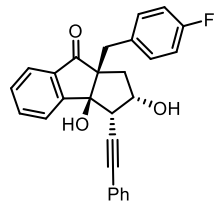


^{1}H NMR (300 MHz, $CDCl_3$)



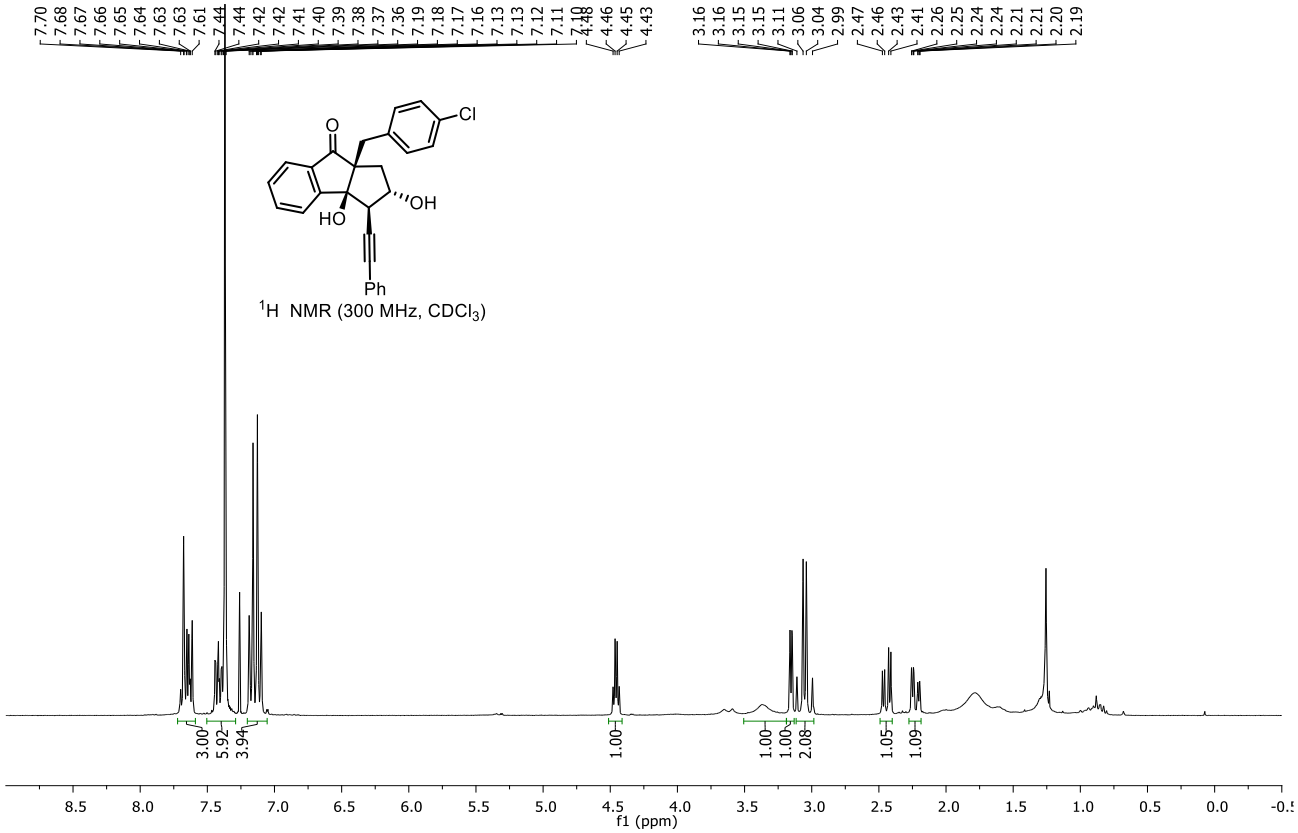


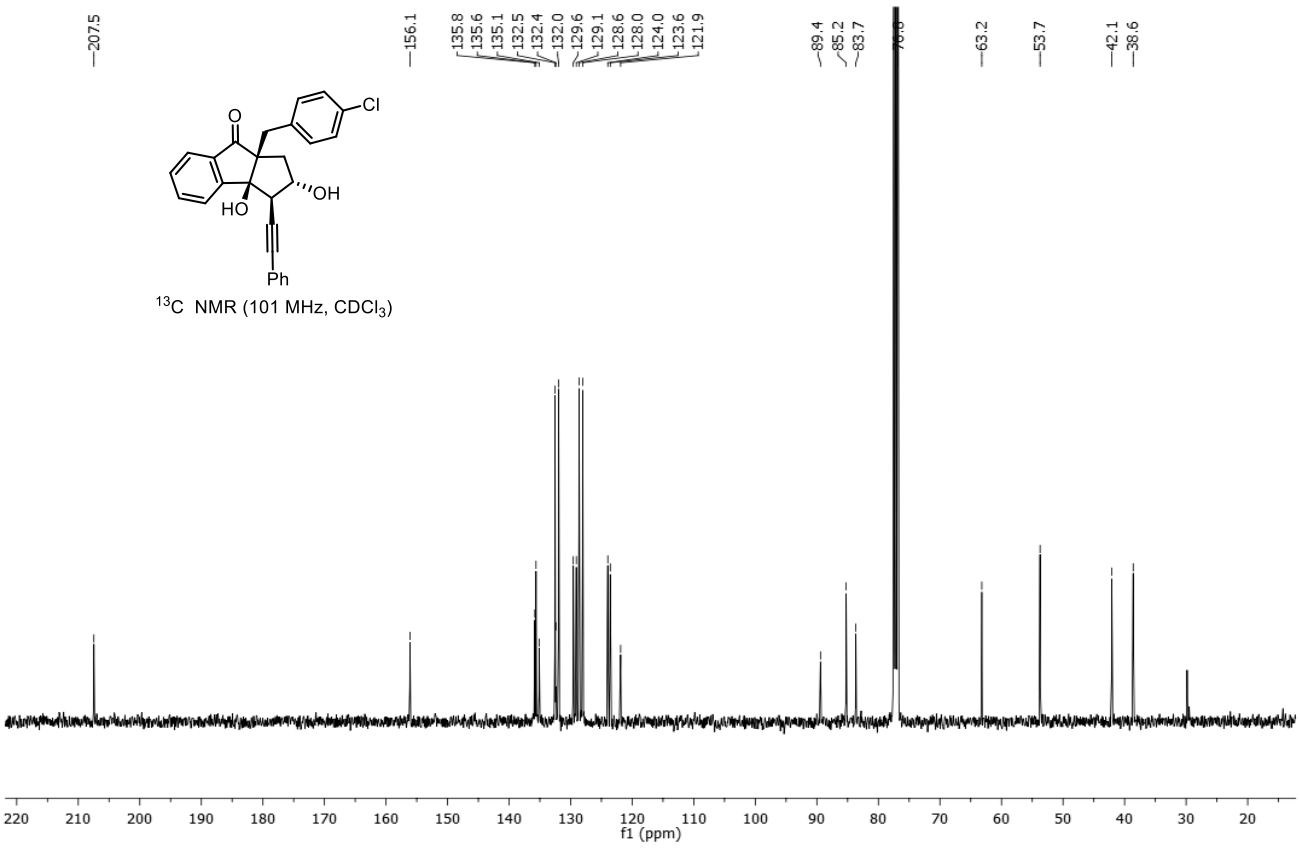
^{13}C NMR (101 MHz, $CDCl_3$)



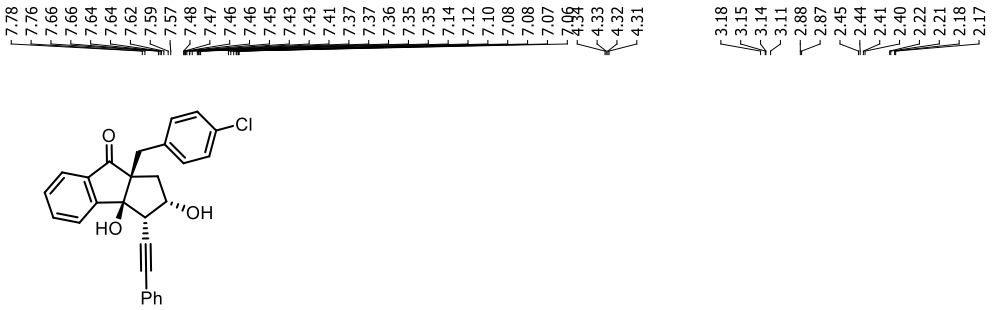
^{19}F NMR (377 MHz, $CDCl_3$)

(2*S*,3*R*,3a*S*,8a*R*)-8a-(4-Chlorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*anti*-5d):

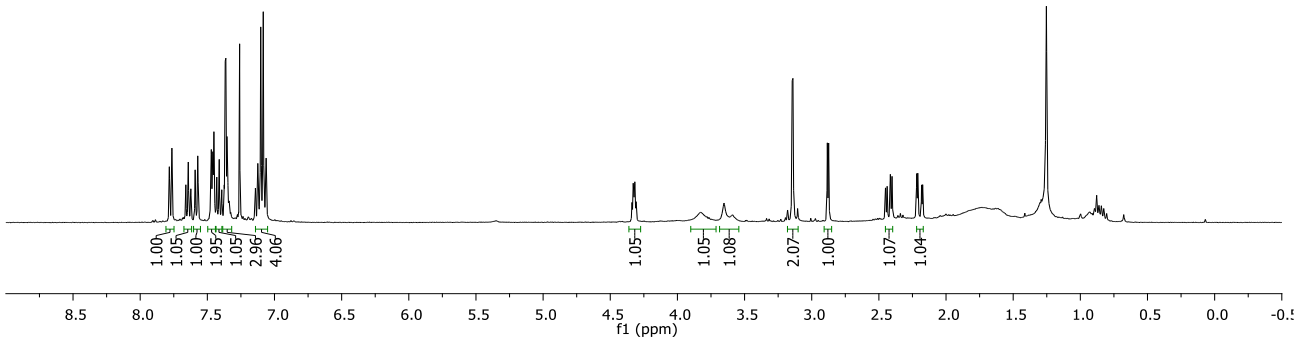


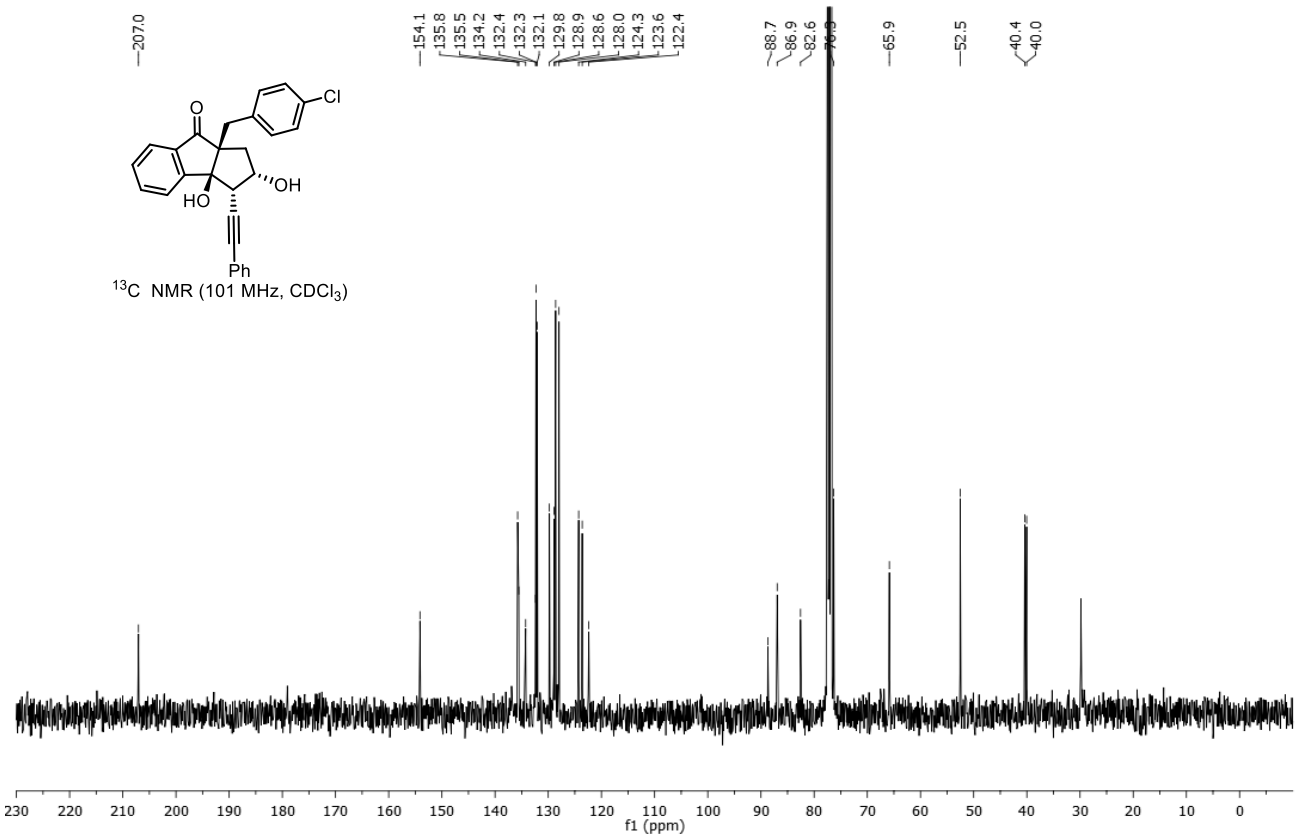


(2*S*,3*S*,3a*S*,8a*R*)-8a-(4-Chlorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*syn*-5d):



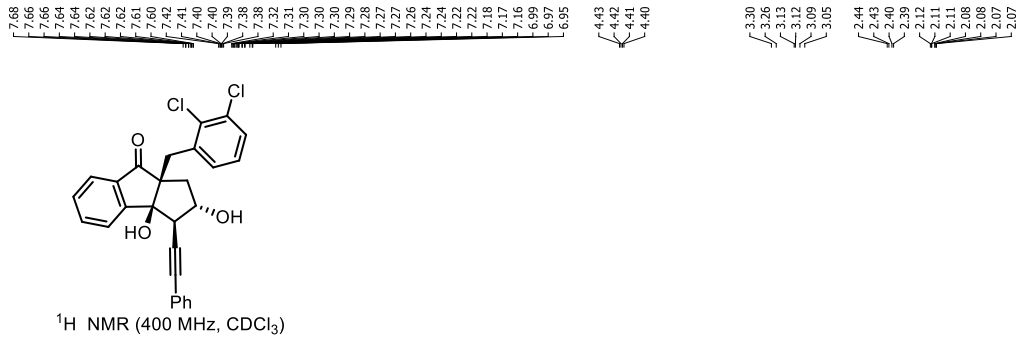
^{1}H NMR (300 MHz, $CDCl_3$)



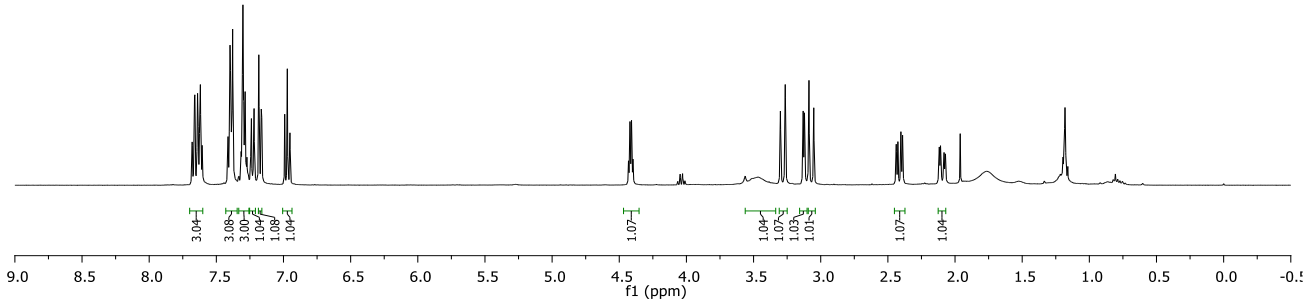


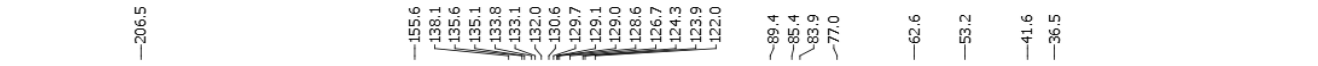
^{13}C NMR (101 MHz, $CDCl_3$)

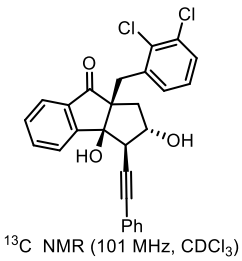
(2*S*,3*R*,3a*S*,8a*R*)-8a-(2,3-Dichlorobenzyl)-2,3a-dihydroxy-3-(phenylethynyl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one (*anti*-5e):



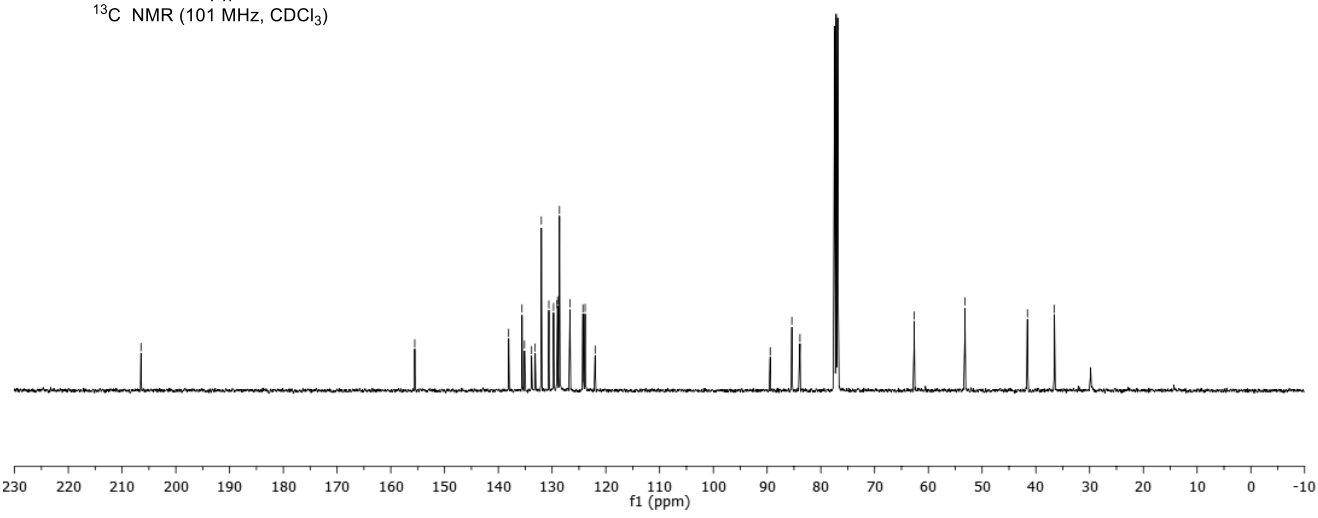
^{1}H NMR (400 MHz, $CDCl_3$)



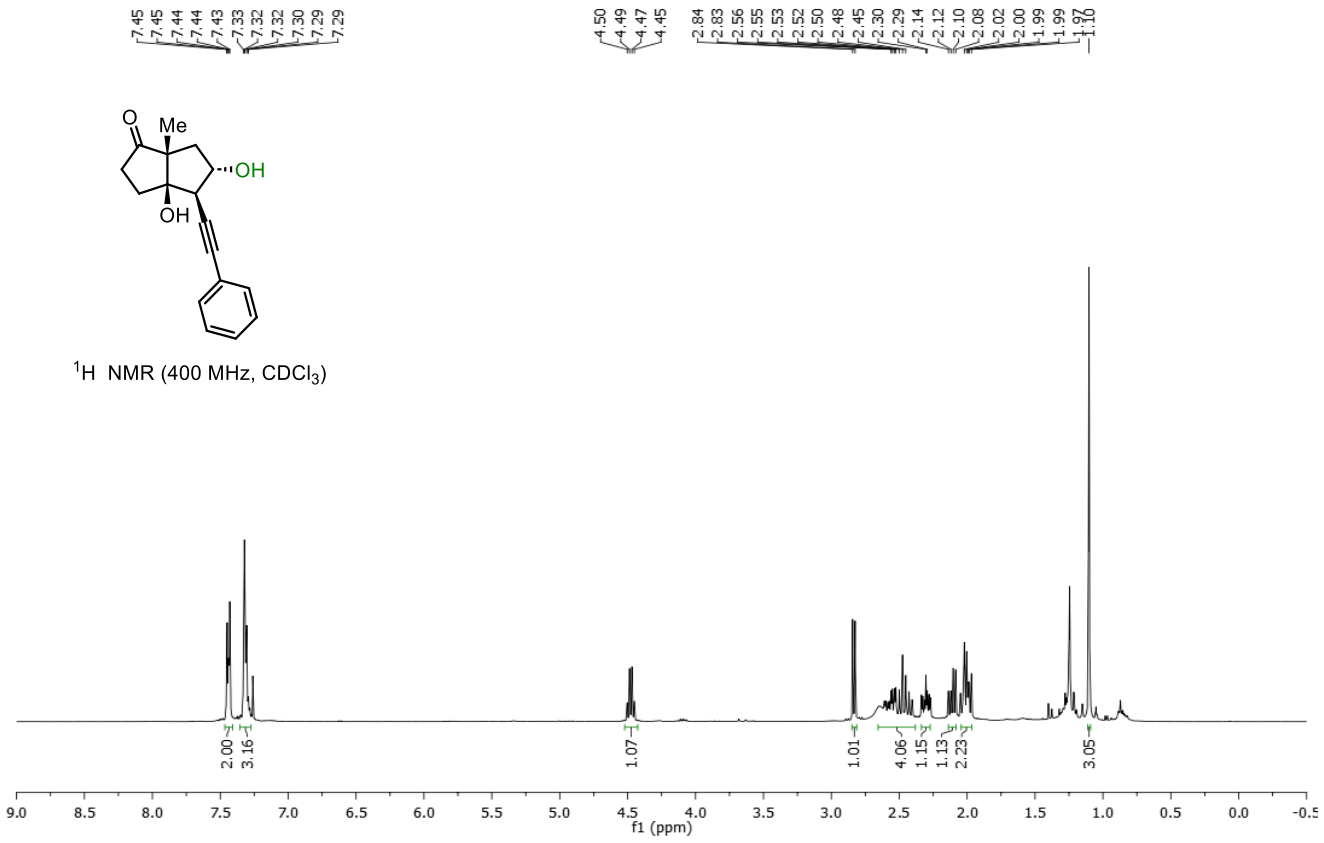




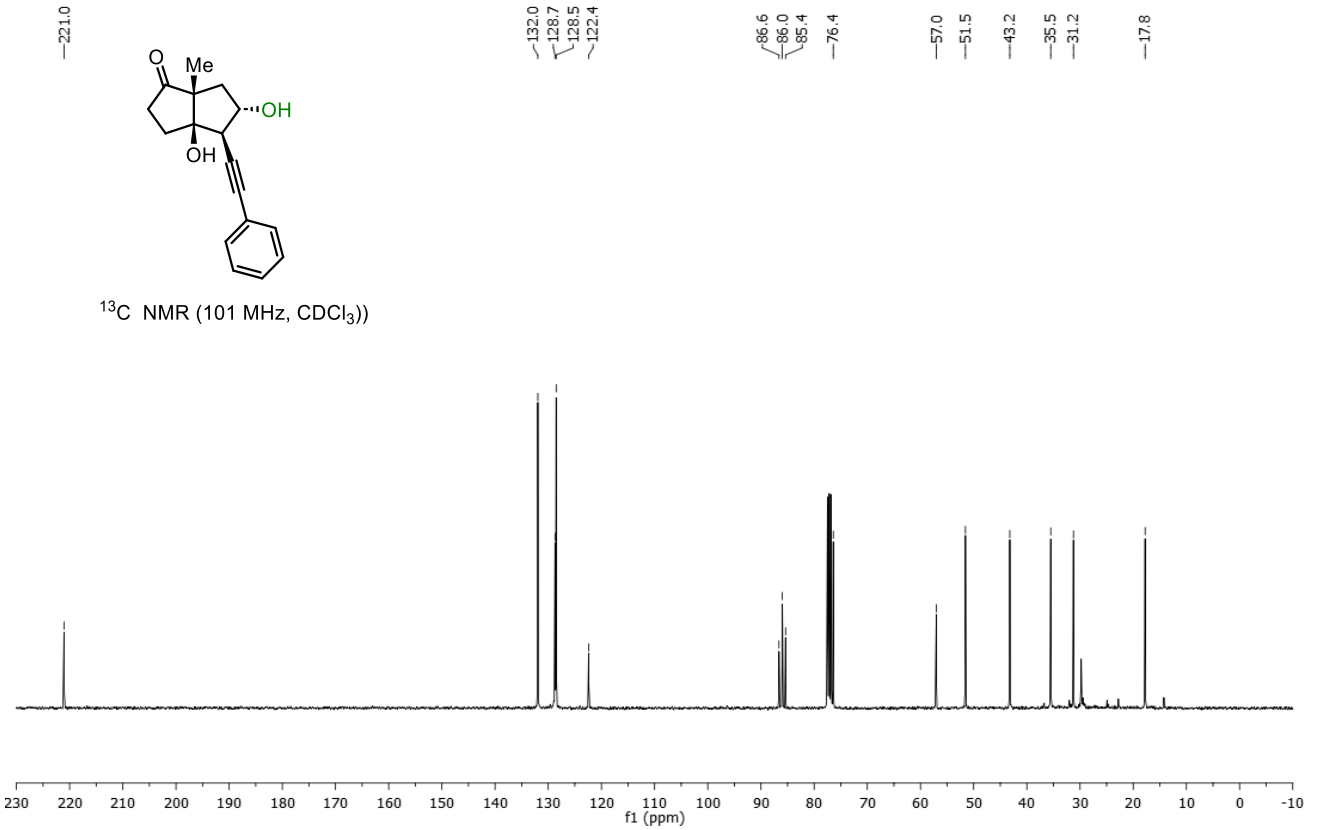
^{13}C NMR (101 MHz, $CDCl_3$)



(3a*R*,4*R*,5*S*,6a*R*)-3a,5-Dihydroxy-6a-methyl-4-(phenylethynyl)hexahydropentalen-1(2*H*)-one (6):

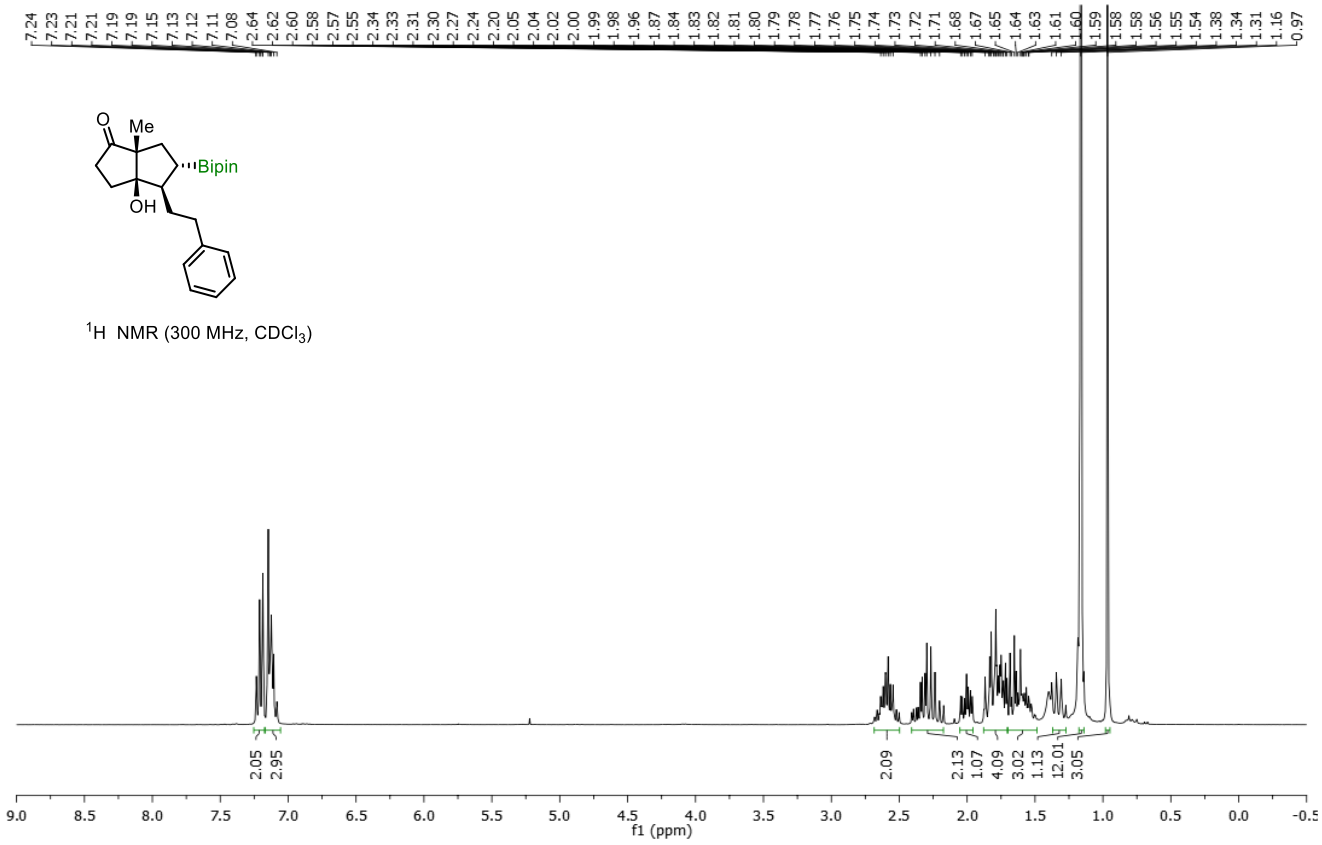


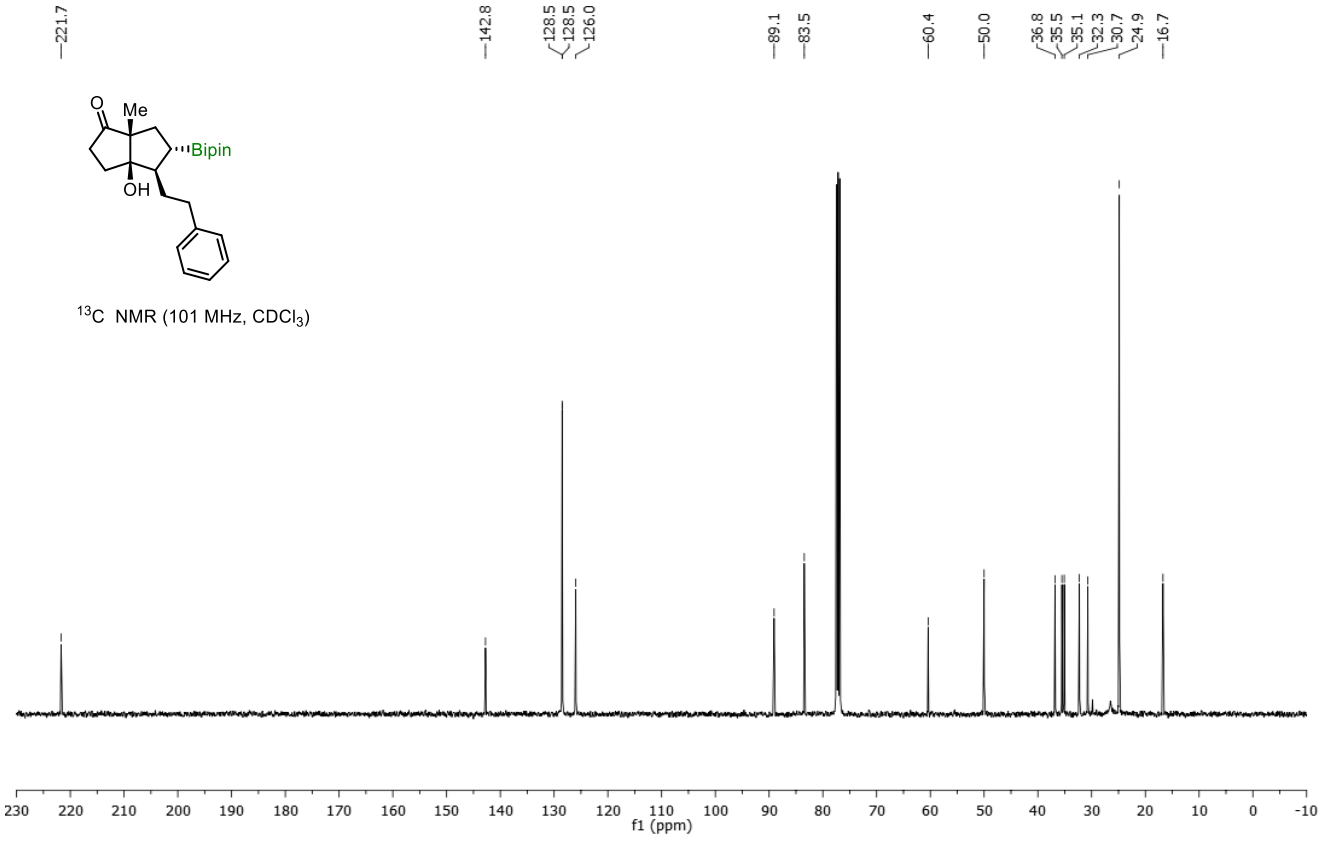
^{1}H NMR (400 MHz, $CDCl_3$)



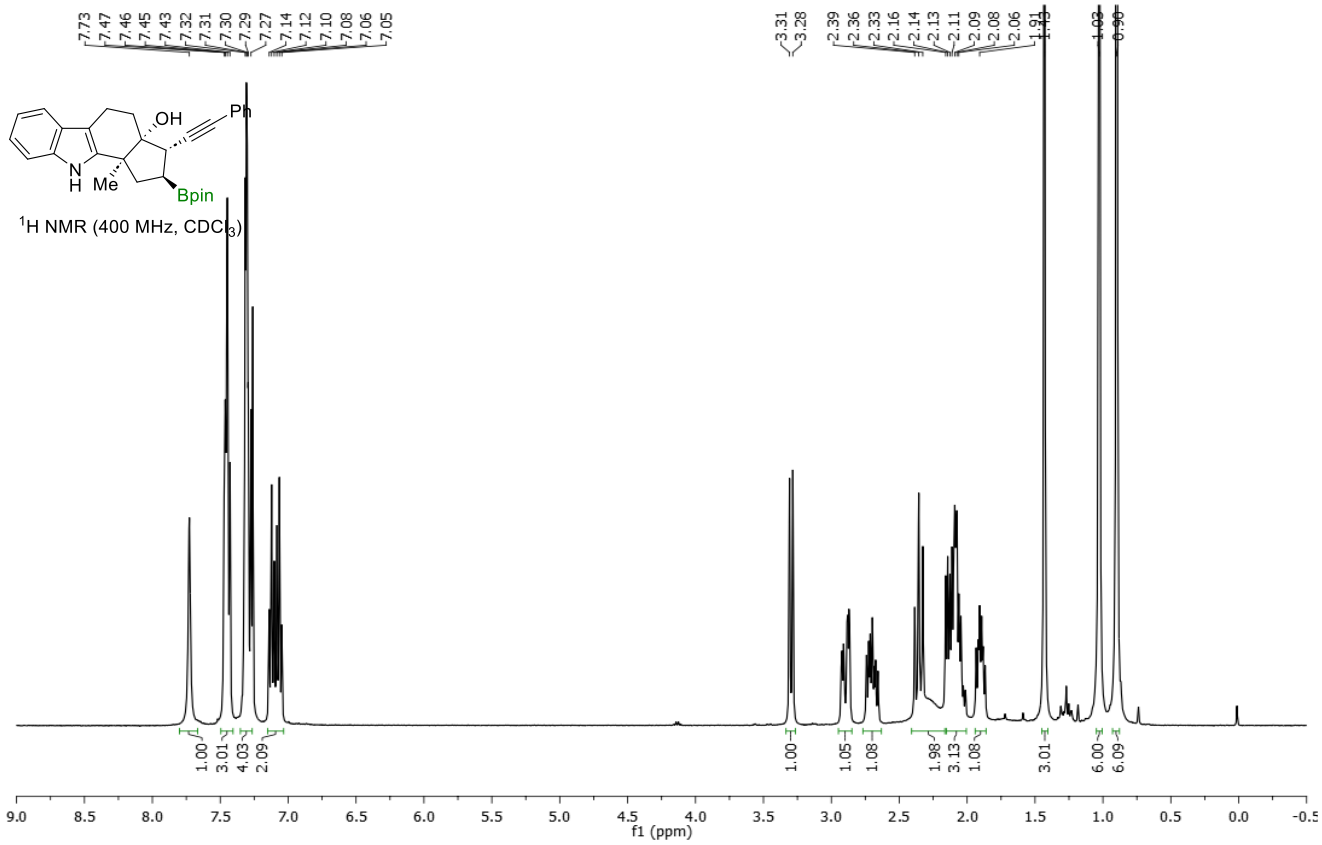
^{13}C NMR (101 MHz, $CDCl_3$))

(3a*R*,4*R*,5*S*,6a*R*)-3a-Hydroxy-6a-methyl-4-phenethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2*H*)-one (7):

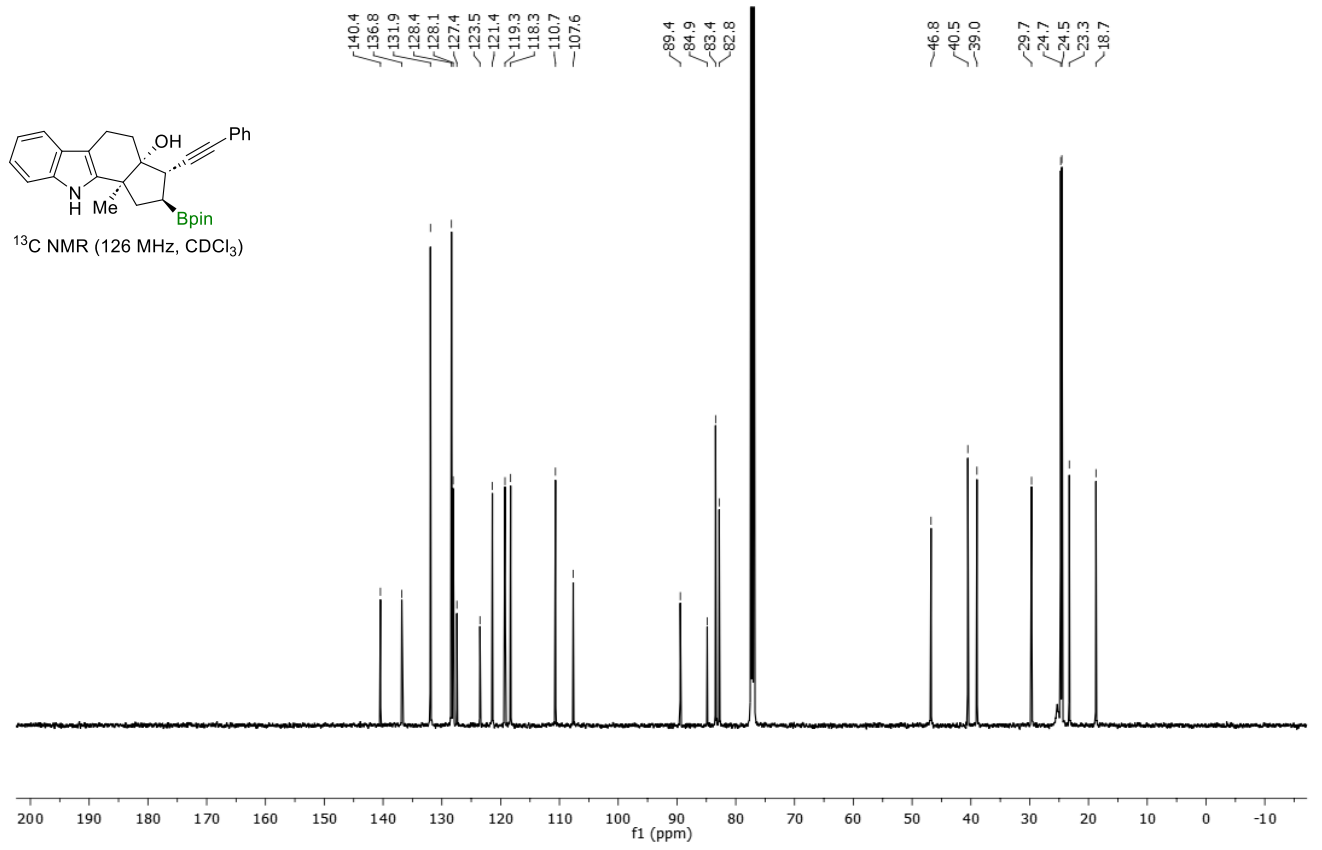




Compound 8:

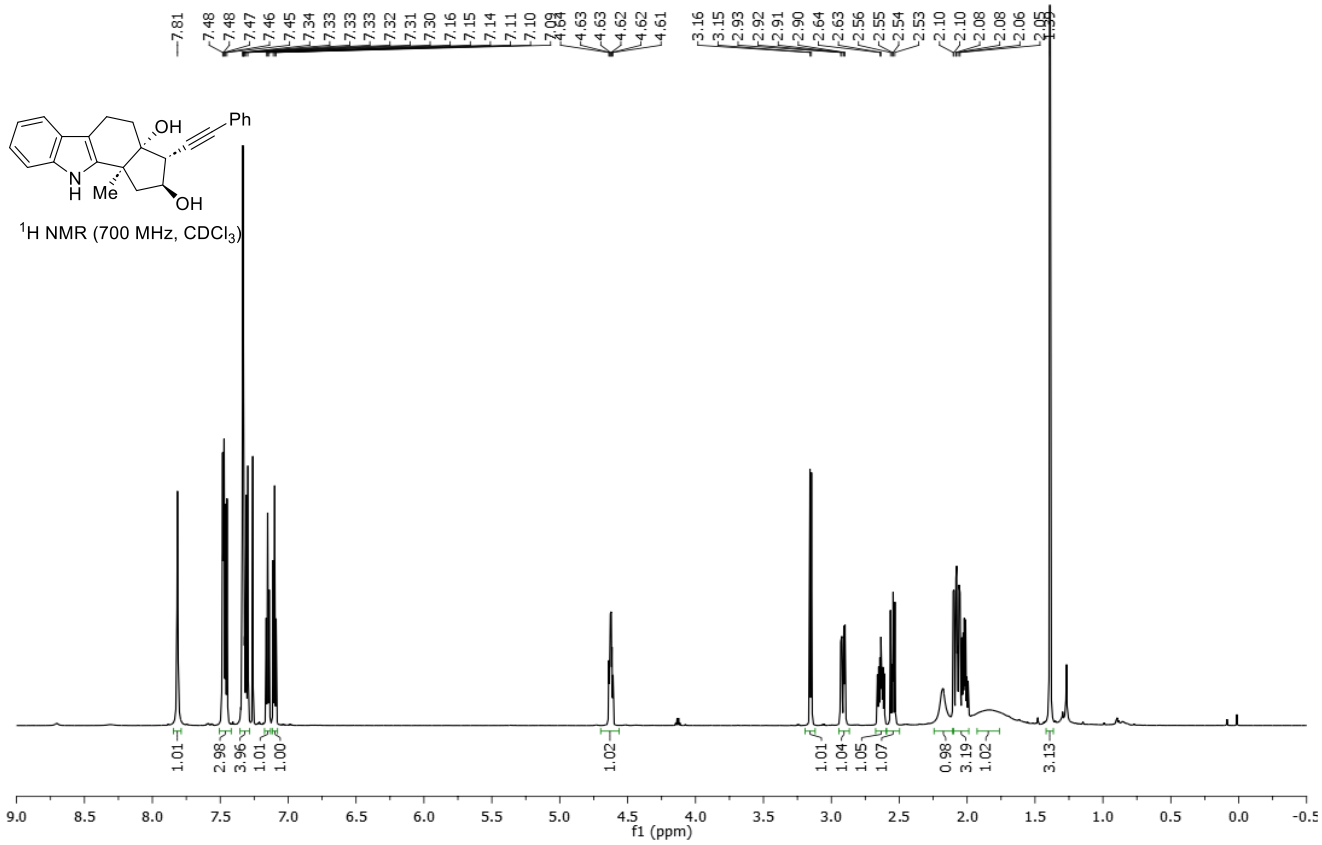


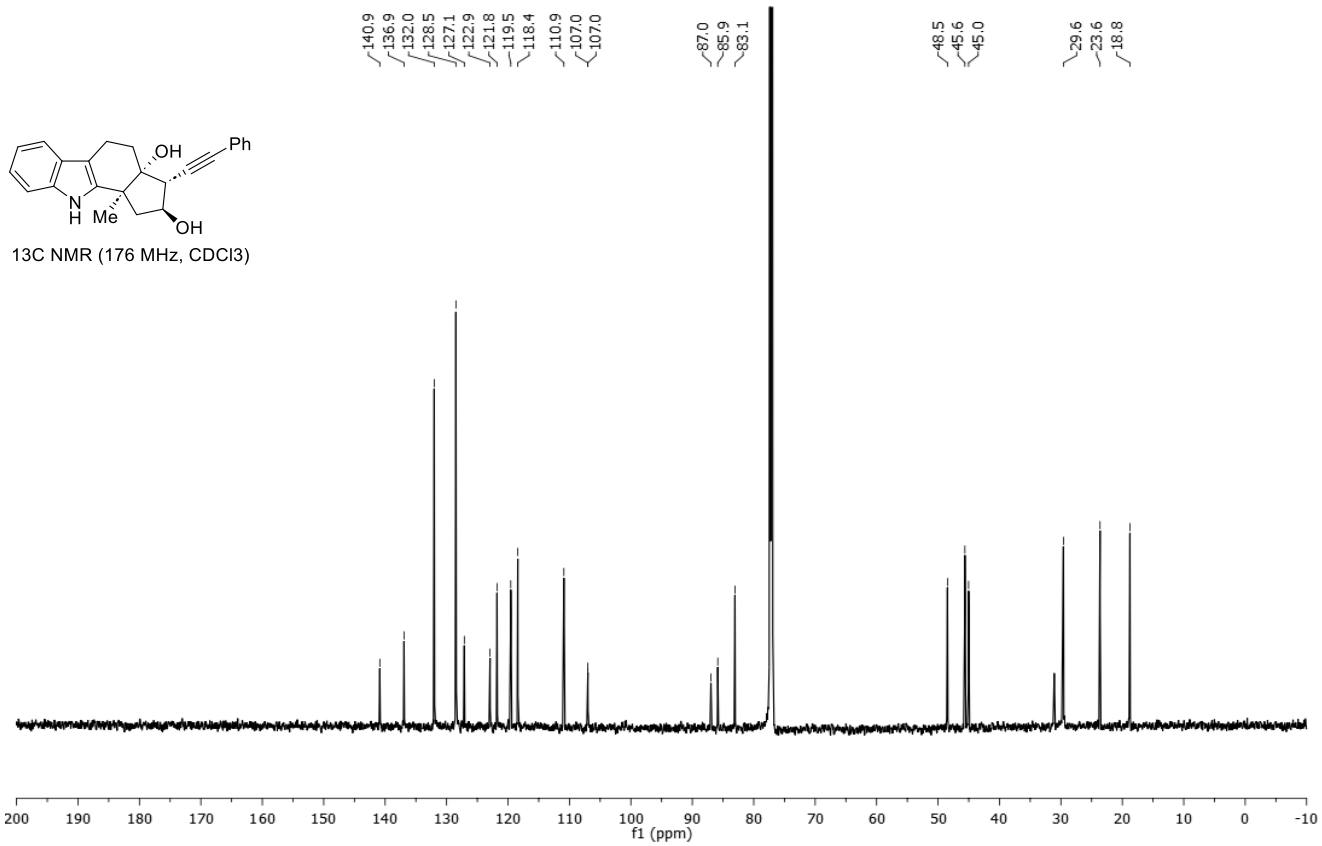
^{1}H NMR (400 MHz, $CDCl_3$)



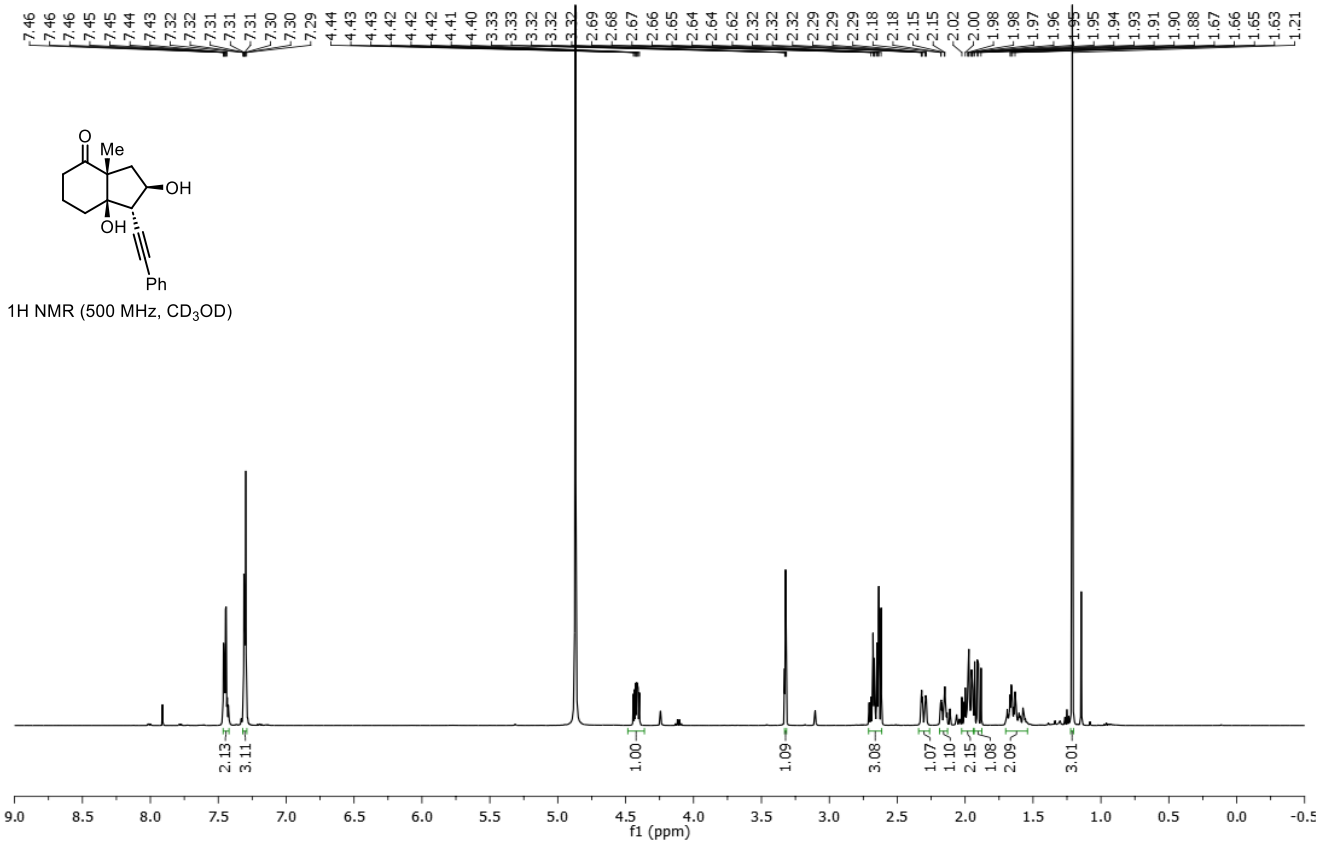
^{13}C NMR (126 MHz, $CDCl_3$)

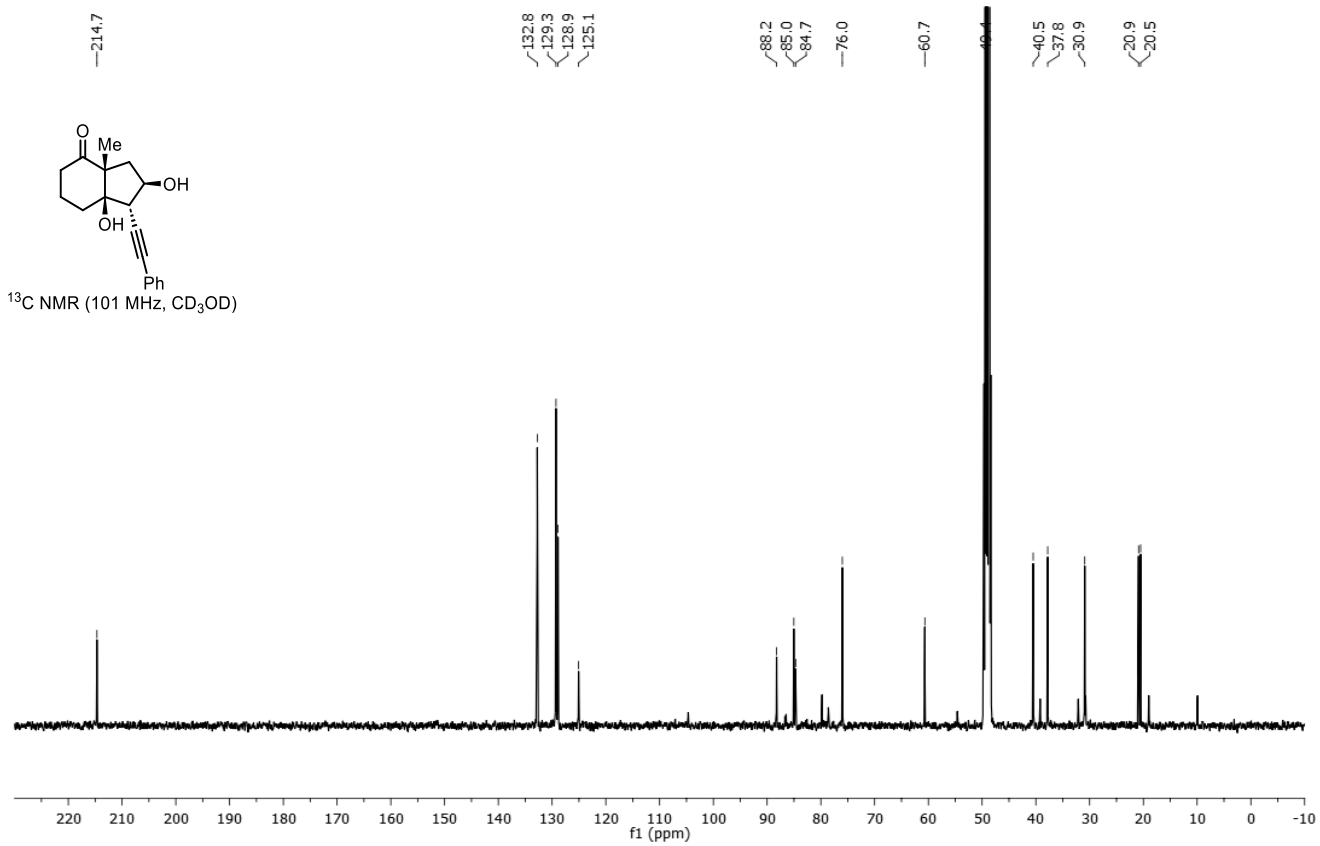
Compound 9:


OH
Ph
N
H
Me
OH
1H NMR (700 MHz, CDCl3)
f1 (ppm)

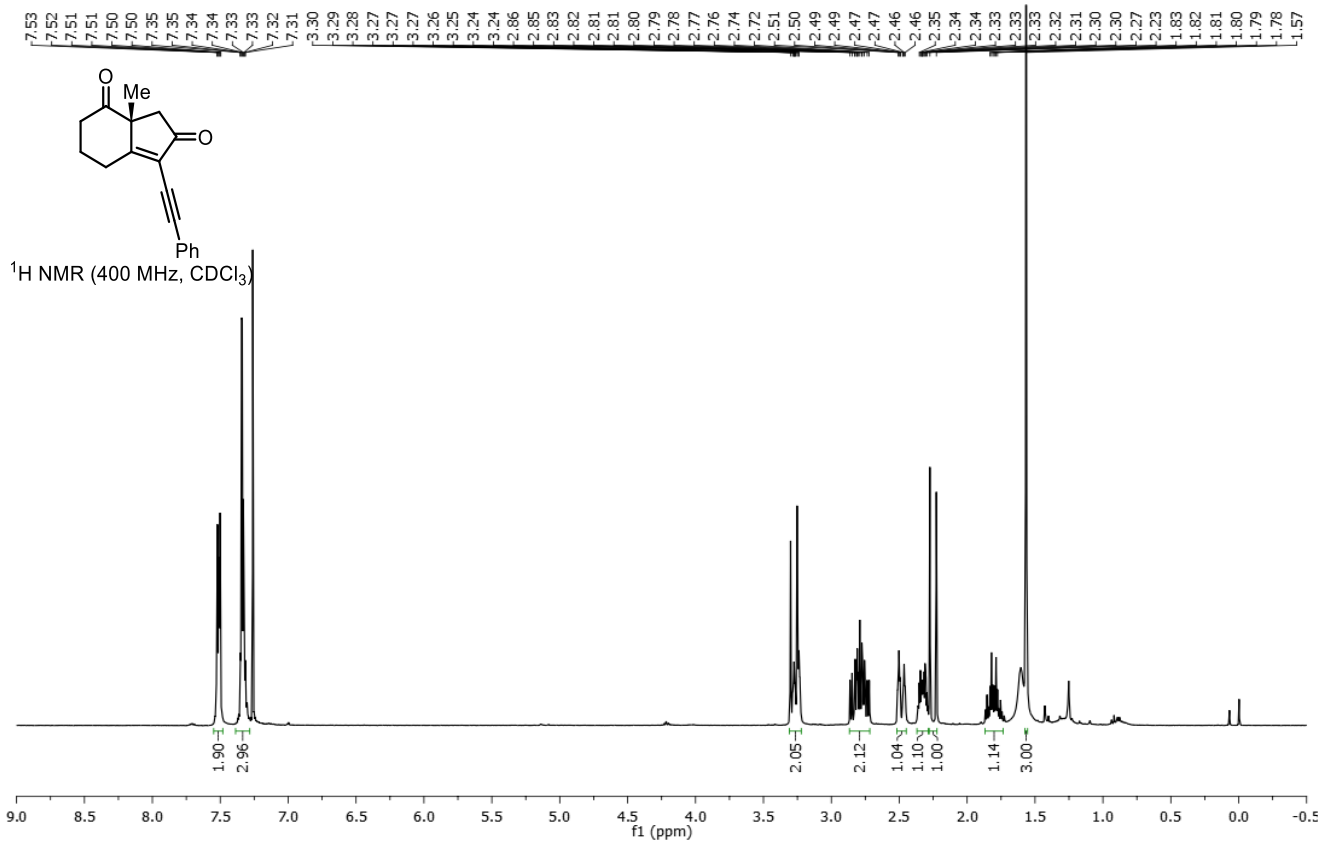

OH
Ph
N
H
Me
OH
13C NMR (176 MHz, CDCl3)
f1 (ppm)

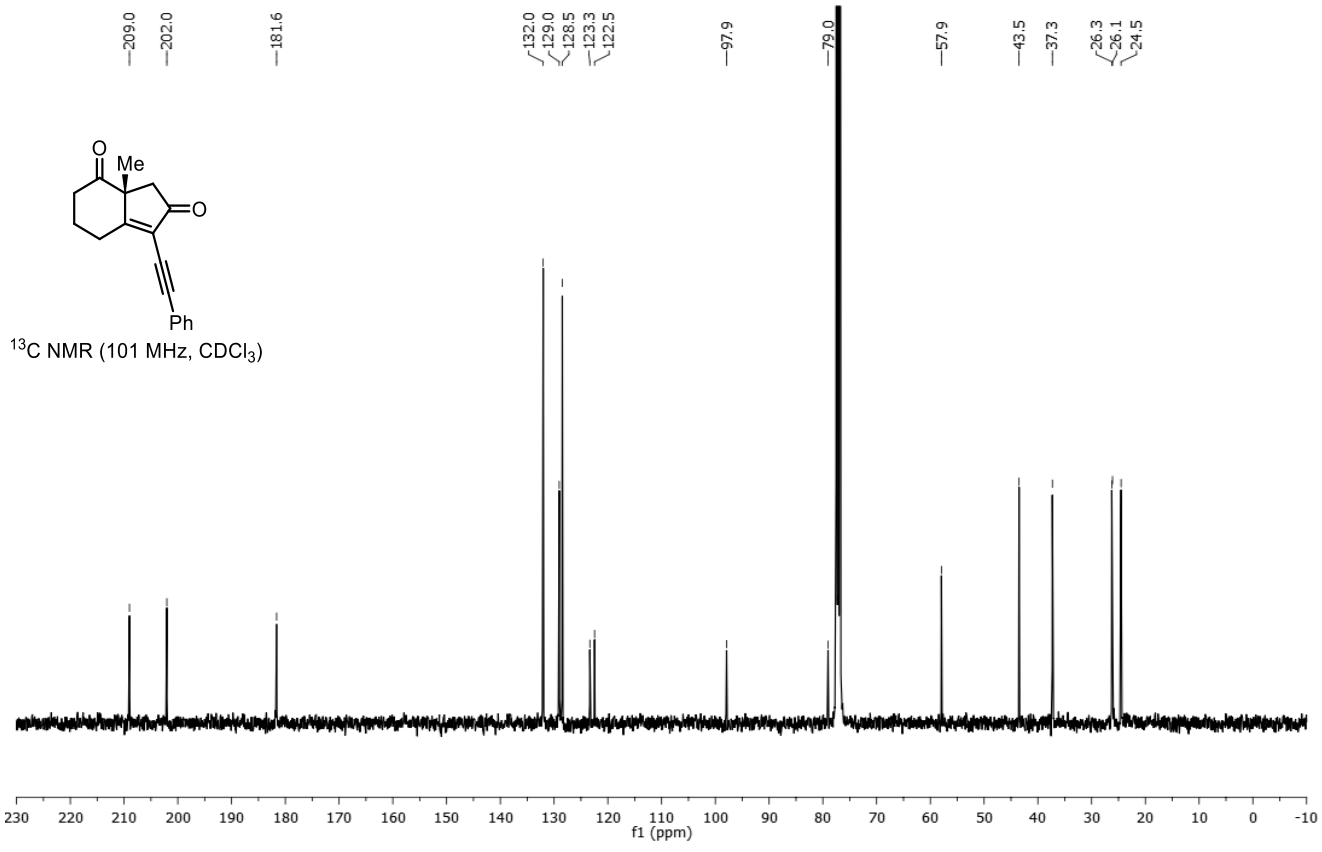
Compound 10:


O
Me
OH
OH
Ph
1H NMR (500 MHz, CD3OD)
f1 (ppm)

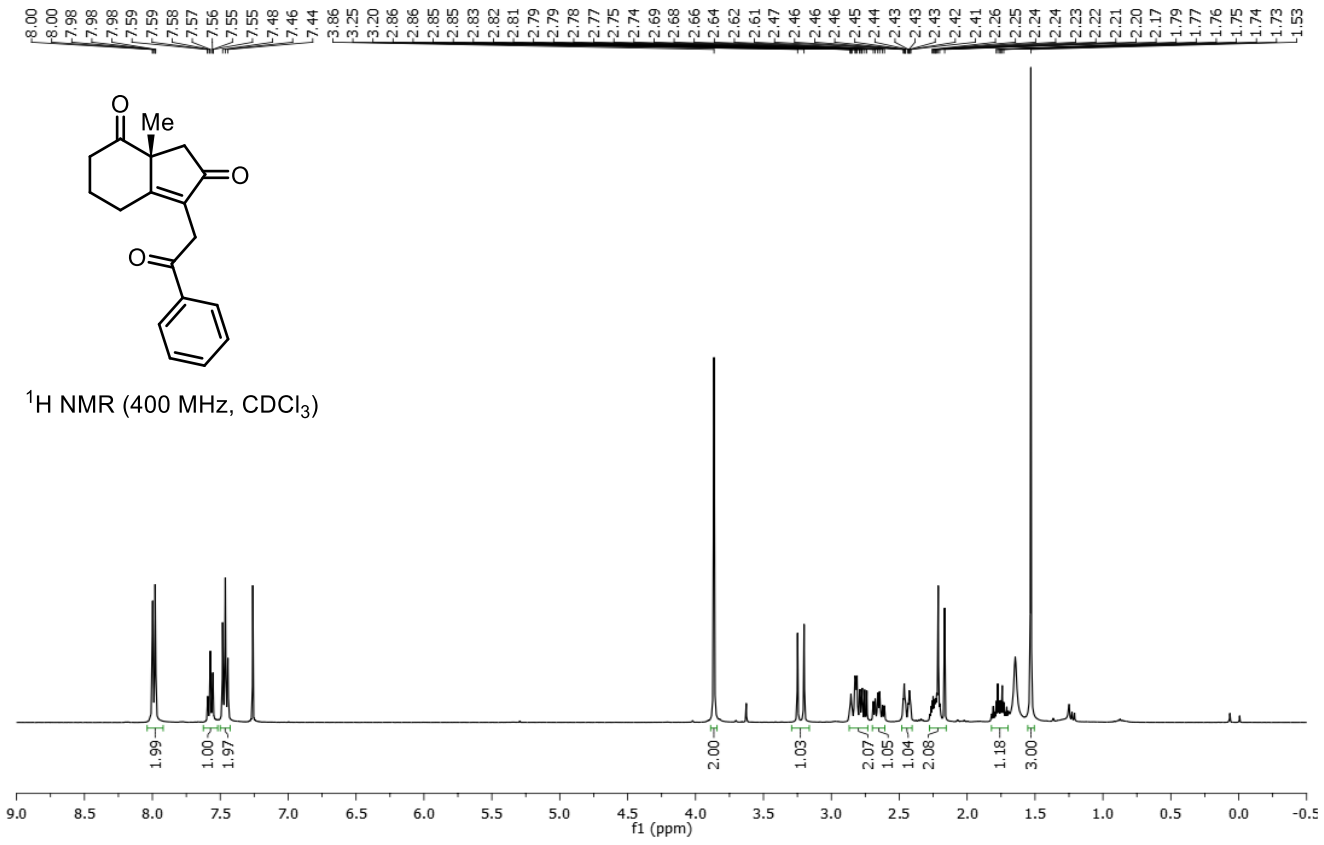

O
Me
OH
OH
Ph
13C NMR (101 MHz, CD3OD)
f1 (ppm)

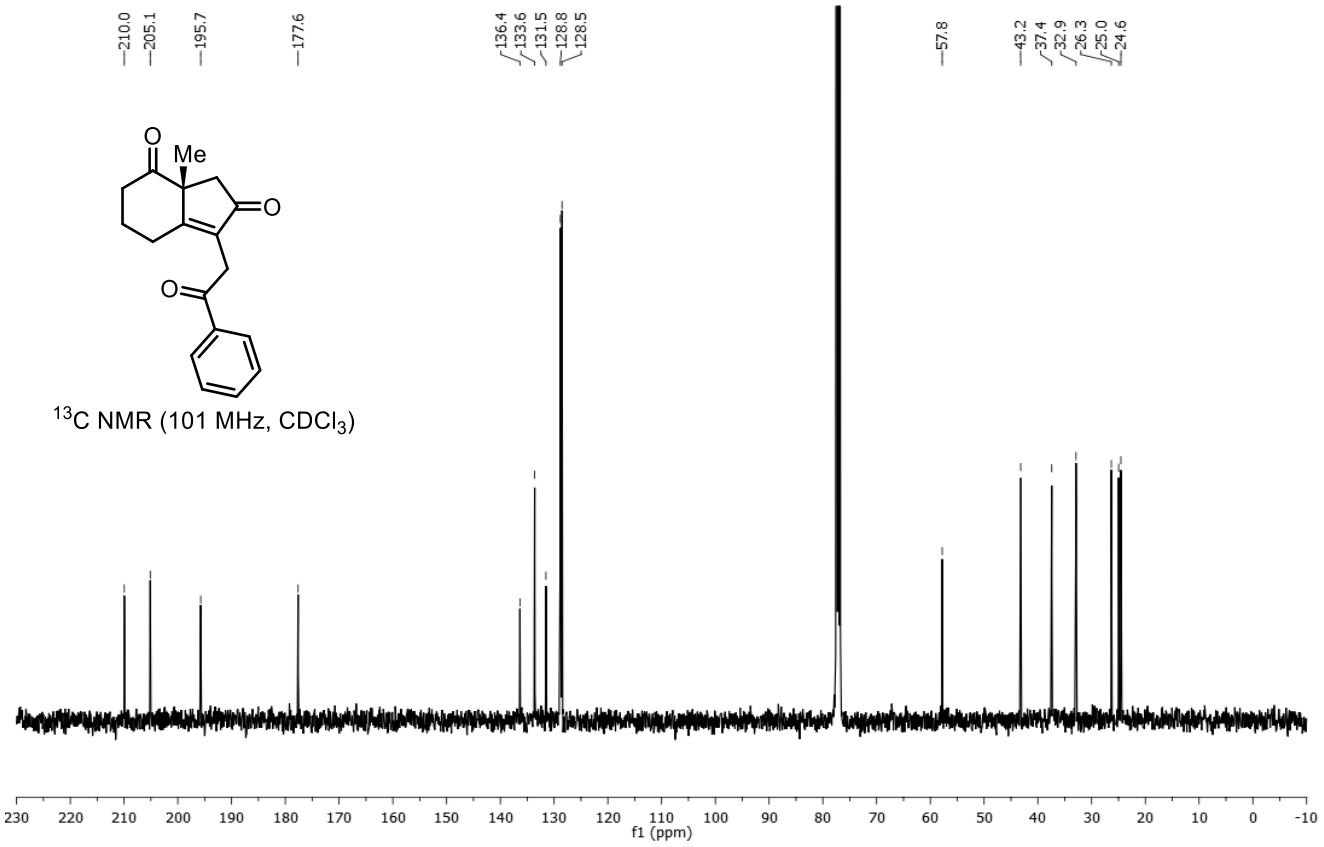
Compound 11:


Me
O
O
Ph
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Me
O
O
Ph
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound(12):


Me
O
O
O
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Me
O
O
O
13C NMR (101 MHz, CDCl3)
f1 (ppm)