Electronic Supplementary Material (ESI) for Green Chemistry.

Copper-Catalyzed Synthesis of α-Alkylidene Cyclic Carbonates from Propargylic Alcohols and CO_2

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[+] Crystallographic investigation

Supporting Information Content

1. General Information

CO_2 (N45) was supplied by AIR LIQUIDE Düsseldorf, Germany with a purity of 99.995%. The autoclave used for carboxylation reactions is a Berghof BR-500 reactor. Unless otherwise stated, all reactions were performed under an air atmosphere or inside an argon-filled glovebox/Schlenk techniques when needed.

Pure, colorless copper(I) chloride was employed for complex synthesis. Alternatively, oxidized CuCl was purified as follows: Greenish CuCl (7.5 g) was taken up in concentrated aqueous HCl (36.5 %v/v, *ca.* 2.5 mL) and distilled water was slowly added to the dark green paste under stirring at room temperature. After appearance of a colorless precipitate, solids were recovered by filtration and washed with absolute EtOH (2x50 mL) and anhydrous Et_2O (100 mL) and dried at 60 °C under vacuum (<1 mbar) for 6 hours. Pure CuCl is obtained as colorless powder (4.3 g, 57%) and stored under N_2 before used. All other chemicals were purchased from commercial suppliers (abcr, Acros, Alfa Aesar, Chempur, TCI chemicals and Sigma Aldrich) or from the Chemical store at the University of Heidelberg and used without further purification. Deuterated solvents were bought from Euriso-Top and Sigma Aldrich. Dry solvents (THF, Et_2O, DCM or CH_3CN) were dispensed from solvent purification system MB SPS-800. Dry acetone (extra dry with 4A MS) was purchased from Acros.

Flash column chromatography was accomplished using Silica gel 60 Å (0.063 - 0.200 mm / 70 - 200 mesh purchased from Sigma Aldrich). Thin Layer Chromatography (TLC) was carried out on precoated aluminum sheets (Macherey-Nagel ALUGRAM® Xtra SIL G/UV254). Detection was accomplished using UV-light (254 nm). Celite® (Diatomaceous earth, Fluka) was employed as needed.

NMR characterization data was collected at 296 K (unless otherwise stated) on Bruker Avance DRX 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) and Bruker Avance III 600 (600 MHz). ^{1}H NMR and ^{13}C NMR spectra are given relative to TMS (0.00 ppm) or to the residual protons in deuterated solvents (CD_2Cl_2: 5.22 ppm, 53.84 ppm; and $CDCl_3$: 7.26 ppm, 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shift δ are quoted in parts per million (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, td = triple doublet, br s = broad singlet) and coupling constant *J* in hertz (Hz), integration. ^{13}C NMR spectra were measured with 1H-decoupling. The multiplicities mentioned in these spectra [s (singlet, quaternary carbon), d (doublet, CH-group), t (triplet, CH_2-group), q (quartet, CH_3-group)] were determined with help of DEPT135, HSBC and HMQC experiments. The spectra were processed by using the software MestReNova 6.02.

Melting points were determined in a BÜCHI automated B-545 apparatus and are uncorrected. IR spectra (in cm^{-1}) were recorded on a Bruker Vector 22 Lumos FT-IR. High resolution mass spectra

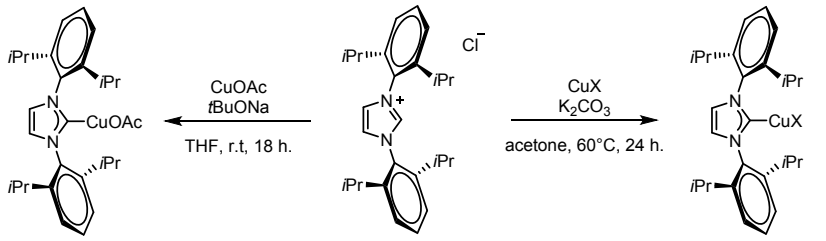
(HRMS) were recorded on a Bruker Apex-Qe hybrid 9.4 FT-ICR spectrometer (ESI^+, MALDI). Elemental analyses were carried out on an Elementar Vario MICRO cube equipment.

For the X-Ray diffraction analyses, the intensity data were collected at 200(2) K on Bruker Smart CCD or Bruker APEX-II diffractometers (MoKα radiation, λ=0.71073 Å). The structures were solved by direct methods with SHELXT-2018/2[13] and refined by full-matrix least-squares procedures using the SHELXL-2018/3software[14] with anisotropic thermal parameters for all the non-hydrogen atoms.

2. Synthesis of NHC metal complexes

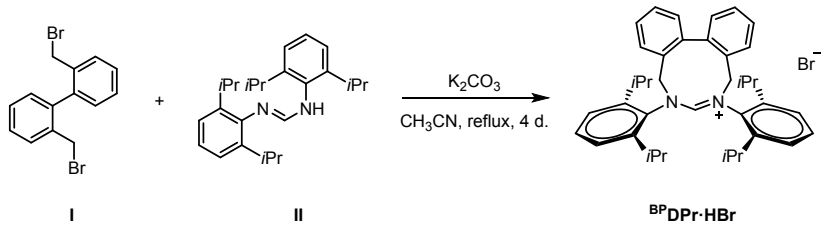
2.1 Synthesis of IPrCuX complexes (X = Cl, Br)

IPrCuOAc, IPrCuCl, IPrCuBr and IPrCuI were prepared according to reported procedures.[1] The identity of the products was confirmed by ^{13}C NMR spectroscopy.



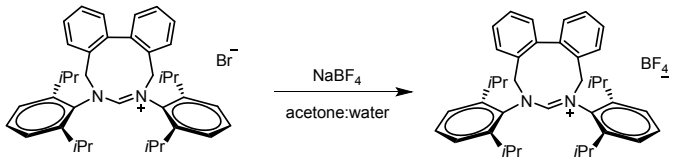
2.2 Synthesis of carbene precursors ^{BP}DPr·HX (X = Br, BF_4)

Compounds **I**, **II**, and amidinium salts ^{BP}DPr·HX (X= Br, BF_4) were synthesized according to previously reported protocols.[2] An improved gram scale synthesis of ^{BP}DPr·HBr ligand was made as follows:



I **II** **^{BP}DPr·HBr**

Procedure: In a round-bottomed flask, formamidine **II** (3.81 g, 10.5 mmol) was dissolved in acetonitrile (900 mL) under efficient stirring (*ca.* 700 rpm). Then, finely grinded K_2CO_3 (1.80 g, 13.1 mmol, 1.25 equiv.) was added to the solution and the resulting mixture was stirred at room temperature for 45 minutes followed by the addition of dibromide **I** (3.52 g, 10.4 mmol, 1.0 equiv.) in one portion. The flask was fitted to an oil bath provided with a condenser and the reaction mixture was refluxed for 4 days (90°C, oil bath temperature). The suspension was cooled down to room temperature, the solids were filtered off and solvent was removed under reduced pressure till dryness. The semi solid residue was taken up in DCM (200 mL), filtered through a short plug of celite and solvent was removed under reduced pressure till dryness. The oily residue was pulverized with a cold mixture diethyl ether/*n*-hexane (200 mL, 1:1 v/v) affording a colorless solid which was collected by filtration. Pure ^{BP}DPr·HBr was obtained in 82% yield (5.28 g) and its identity was confirmed by NMR spectroscopy.[2]

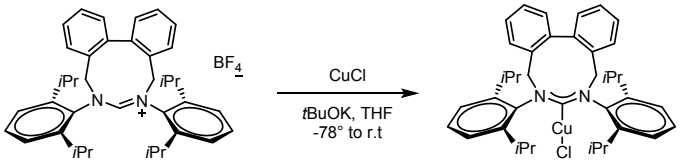


^{BP}DPr·HBr ^{BP}DPr·HBF$_4$

Anion exchange: Solutions of ^{BP}DPr·HBr (1.26 g, 2.0 mmol in 100 mL acetone) and $NaBF_4$ (1.10 g, 5.0 mmol in 75 mL distilled water) were mixed and stirred at room temperature for 1 hour followed by evaporation of acetone. Solid supernatant was extracted with DCM (2x50 mL), dried over anhydrous Na_2SO_4 and solvent was evaporated till a minimal amount. Addition of diethyl ether (100 mL) afforded ^{BP}DPr·HBF_4 as a colorless powder which was recovered by filtration (1.13 g, 89%). The identity of the product was confirmed by NMR spectroscopy.[2]

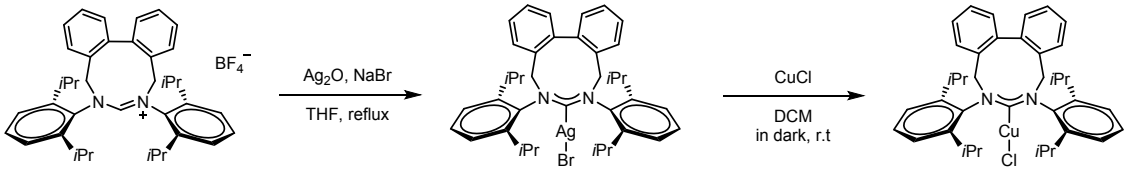
2.3 Synthesis and characterization data of ^{BP}DPrCuCl complex

Complexes ^{BP}DPrMBr (M = Ag, Cu) were synthesized according to our previously reported protocols.[3] Complex ^{BP}DPrCuCl was synthesized according to two procedures in moderate to good yields:



^{BP}DPr·HBF_4 ^{BP}DPrCuCl

Procedure 1. A 100 mL Schenk flask was charged with ^{BP}DPr·HBF_4 (315 mg, 0.5 mmol), CuCl (59 mg, 0.6 mmol) and anhydrous THF (40 mL) under a nitrogen atmosphere and the suspension was cooled to -78°C. A solution of *t*BuOK (1.0 mL, 12% w/v in dry THF, 1.0 mmol) was added dropwise to reaction mixture under efficient stirring (*ca.* 700 rpm) and temperature was maintained at -78°C during 4 hours after which, it was allowed to warm up to room temperature overnight. The solids were filtered off through a pad of celite followed by washing the pad with DCM (20 mL) and then the solvent was removed under reduced pressure till dryness. The oily to spongy residue was pulverized with cold *n*-hexane (*ca.* 4°C) and the solid was recrystallized with DCM:*n*-pentane mixture (1:5 v/v) to yield pure ^{BP}DPrCuCl as colorless solid (190 mg, 59%).



^{BP}DPr-HBF$_4$ ^{BP}DPrAgBr ^{BP}DPrCuCl

Procedure 2. A 50 mL Schlenk tube was charged with freshly purified CuCl (21 mg, 0.21 mmol, 1.05 equiv) and anhydrous DCM (10 mL). The mixture was stirred for 15 minutes at room temperature under nitrogen and ^{BP}DPrAgBr (146 mg, 0.2 mmol) was added to suspension. The mixture was stirred at room temperature for 24 hours in dark after which it was filtered through a pad of celite and solvent was removed in vacuo. Solid was recrystallized by slowly diffusing *n*-pentane into a saturated solution of complex in DCM to give ^{BP}DPrCuCl (103 mg, 81% yield) as colorless solid. The identity of the product was confirmed in ^{13}C NMR spectrum by disappearance of a doublet signal at δ = 230.9 ppm (dd, $J_C{}^{107}{}_{Ag}$ = 227.8 Hz, $J_C{}^{109}{}_{Ag}$ = 263.0 Hz, N*C*N) from ^{BP}DPrAgBr complex.

^{BP}DPrCuCl: Colorless solid. **m.p**: 233 °C (decomp). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (q, *J* = 7.3 Hz, 4H), 7.31–7.17 (m, 8H), 6.87 (d, *J* = 7.7 Hz, 2H), 5.12 (d, *J* = 14.8 Hz, 2H), 4.46 (d, *J* = 14.8 Hz, 2H), 2.98–2.89 (m, 2H), 2.89–2.80 (m, 2H), 1.31 (d, *J* = 6.7 Hz, 6H), 1.22 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.17 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 222.9 (s, 1C, N*C*N), 147.3 (s, 2C), 144.5 (s, 2C), 142.4 (s, 2C), 139.3 (s, 2C), 134.7 (s, 2C), 131.0 (d, 2C), 130.4 (d, 2C), 129.8 (d, 2C), 129.5 (d, 2C), 128.3 (d, 2C), 126.6 (d, 2C), 124.3 (d, 2C), 61.2 (t, 2C), 29.2 (d, 2C), 28.8 (d, 2C), 26.8 (q, 2C), 25.7 (q, 2C), 25.3 (q, 2C), 22.6 (q, 2C). **IR** (ATR): ν max (cm^{-1}) = 3060, 2659, 2869, 2828, 1588, 1469, 1440, 1429, 1389, 1367, 1345, 1324, 1296, 1282, 1228, 1203, 1178, 1122, 1099, 961, 933, 885, 864, 826, 801, 774, 766, 756, 739, 696, 666, 637. **HRMS** (DART+) calc. for $C_{39}H_{46}CuClN_2$: 640.2645, found: 640.2668. **Anal. Calcd**. for. $C_{39}H_{46}CuClN_2$: C 72.99%, H 7.22%, N 4.36%, Found: C 72.77%, H 7.29%, N 4.02%.

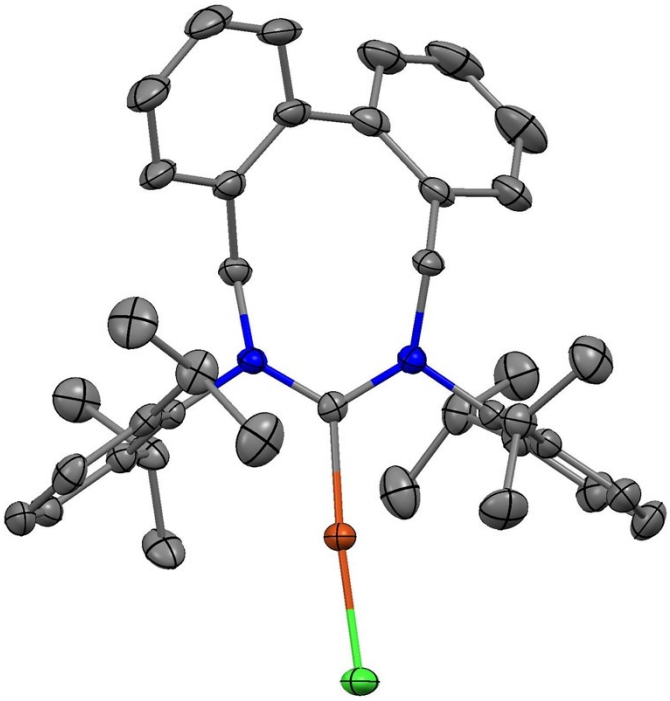
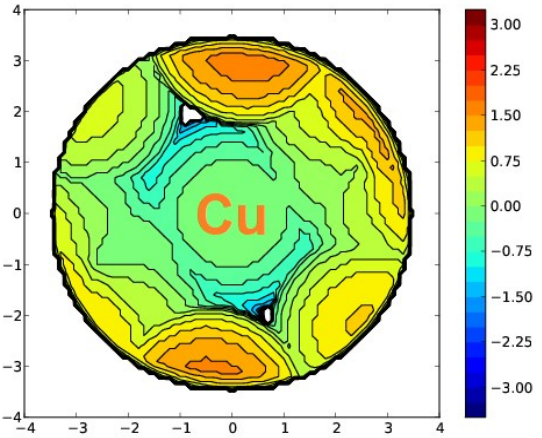


Figure S1. X-ray structure of **^{BP}DPrCuCl**. Ellipsoids are drawn at 45% thermal probability. Selected geometrical parameters (bond lengths in Å and angles in °): C_{NHC}–Cu 1.892(5), Cu–Cl 2.1267(16), C_{NHC}–Cu–Cl 174.96(17), ∠N–C–N 118.7(5) and torsion (C_{Ar}—N_2---N_5—$C_{Ar'}$) 27.8°.



V Free	V Buried	V Total	V Exact
75.5	104.0	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
42.1	**57.9**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	18.4	26.5	44.9	41.0	**59.0**
NW	21.4	23.4	44.9	47.7	**52.3**
NE	16.3	28.6	44.8	36.3	**63.7**
SE	19.4	25.5	44.9	43.2	**56.8**

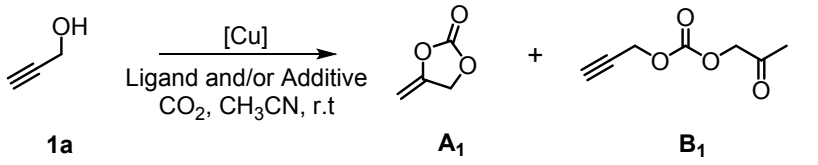
Figure S2. Left: Steric map of **^{BP}DPrCuCl** (distance from the center of the sphere in Å), Right: Table indicating the %V_{bur} values per quadrant and total, calculated with SambVca 2.0[4]

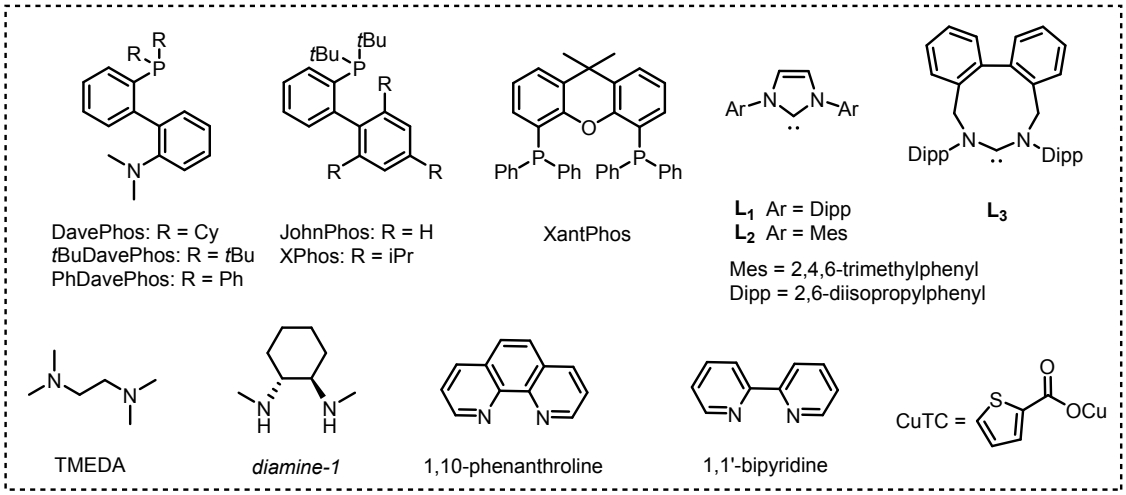
The V_{bur} value and steric distribution analysis of ^{BP}DPrCuCl complex (*vide supra*) reveals a highly hindered NHC-copper geometry as the four quadrants (SW, NW, NE, SE) exhibit a steric contribution higher than 52%.

3. Screening of the carboxylation conditions

General procedure: A 4.5 mL screw-cap Teflon coated vial provided with stirring bar was charged with **1a**, copper source, additive and anhydrous solvent at room temperature. The vial was sealed, a 0.5 mm ø cannula was coupled by the Teflon cap and vial was taken to an autoclave, pressurized with CO_2, and stirred at room temperature. To determine the % of product $\mathbf{A_1}$ in the mixture, at the end of the reaction $CDCl_3$ (1.0 mL) was added to the raw mixture and additionally stirred for 10 minutes. An 0.5 mL aliquot was directly analyzed by ^1H NMR.

Table S1. Screening of copper(I) sources, ligands and additives.[a]





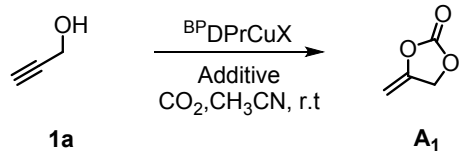
Entry	[Cu]	Ligand and/or Additive	$\mathbf{A_1}$ (%)[b]
1	CuTC	-	0
2	CuOAc	-	0
3	$Cu(CH_3CN)PF_6$	-	0
4	L_1CuCl	-	0
5	L_1CuBr	-	0
6	L_1CuI	-	0
7	L_2CuCl	-	0
8	L_3CuCl	-	trace
9	L_1CuOAc	-	trace
10	CuI	CsF	0
11	CuI	DavePhos / CsF	8
12	CuTC	*t*BuOLi	12

13	CuTC	XantPhos	7
14	CuTC	DavePhos	0
15	CuTC	JohnPhos	0
16	CuTC	P(2-furfuryl)$_3$	0
17	CuTC	1,10-phen / *t*BuOLi	0
18	CuTC	XantPhos / *t*BuOLi	20
19	CuOAc	CsF	0
22	Cu(CH$_3$CN)$_4$PF$_6$	PCy$_3$	0
23	Cu(CH$_3$CN)PF$_6$	bpy	0
24	Cu(CH$_3$CN)PF$_6$	DavePhos	0
25	CuCl	bpy	0
26	CuCl	1,10-phen	0
27	CuCl	TMEDA	0
28	CuCl	*diamine-1*	0
29	CuCl	AgOAc	0
30	CuCl	P(2-furfuryl)$_3$	0
31	CuCl	XantPhos	0
32	CuCl	DavePhos	0
33	CuCl	*t*BuDavePhos	0
34	CuCl	PhDavePhos	0
35	CuCl	XPhos	0
36	CuCl	JohnPhos	0
37	L$_1$CuCl	AgOAc	40
38	L$_3$CuCl	AgOAc	63
39	L$_1$CuCl	CsF	12
40	L$_3$CuCl	CsF	58

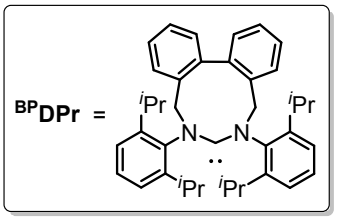
[a] Typical reaction conditions: **1a** (2 mmol), [Cu] (5 mol%) and ligand and/or additive (5 mol%) in anhydrous CH_3CN (2 mL) at room temperature under CO_2 (1 MPa) for 24 h.

[b] Determined by ^{1}H NMR analysis.

Table S2. Optimization of additives.[a]



1a **A_1**

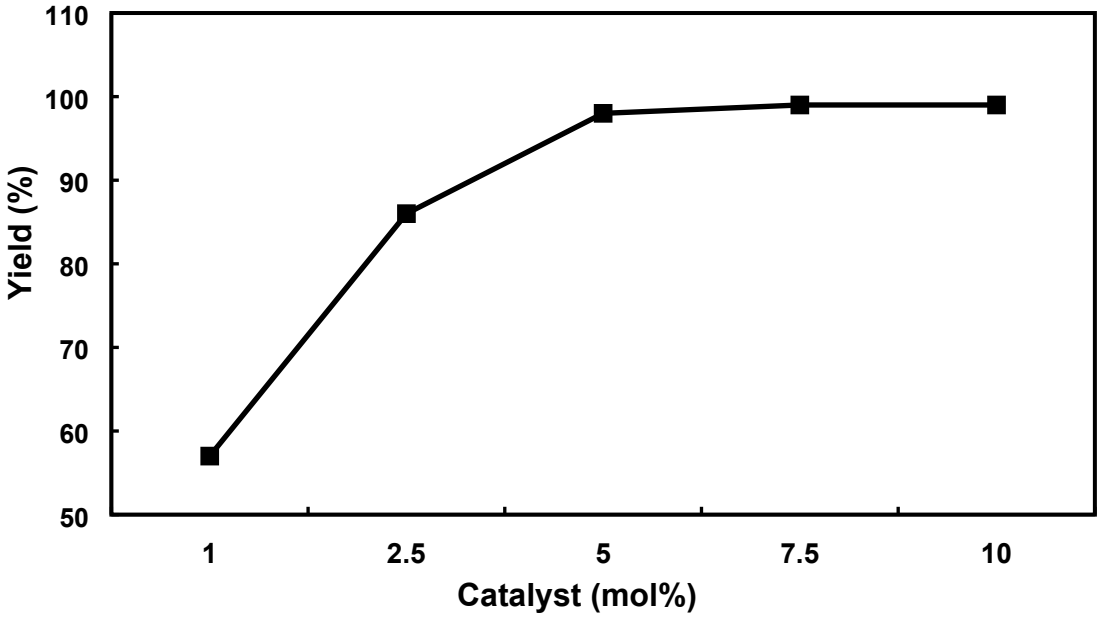


Entry	CuX	Additive	A_1(%)[b]
1	CuCl	*t*BuOK	2
2	CuBr	DBU	28
3	CuBr	$CsCO_3$	11
4	CuCl	NH_4OAc	22
5	CuCl	NaOAc	5
6	CuCl	KOAc	12
7	CuCl	CuOAc	27
8	CuCl	B_2pin_2	9
9	CuCl	CuTC	15
10	CuCl	CsF	94
11	CuCl	AgOAc	96
13	CuBr	CsF	57

[a] Typical reaction conditions: **1a** (1 mmol), LCu catalyst (10 mol%) and additive (10 mol%) in anhydrous CH_3CN (2 mL) at room temperature under CO_2 (1.5 MPa) for 24 h.

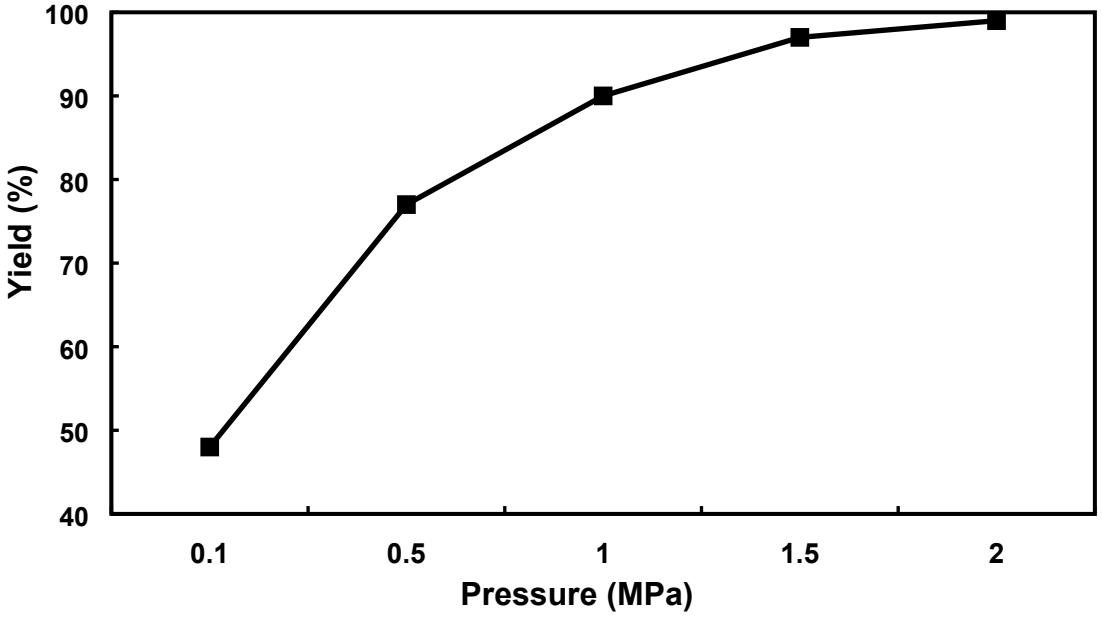
[b] Determined by ^1H NMR analysis.

Figure S3. Optimization of catalyst amount[a]



[a] Typical reaction conditions: **1a** (2 mmol) and (NHC)Cu catalyst (^{BP}DPrCuCl + CsF) at different dosages in anhydrous DCM (2 mL) at room temperature under CO_2 atmosphere (1.5 MPa) for 24 h. Yields were determined by ^{1}H NMR analysis.

Figure S4. Optimization of pressure[a]



[a] Typical reaction conditions: **1a** (2 mmol) and (NHC)Cu catalyst (5 mol%) in anhydrous DCM (2 mL) at room temperature under different pressures of CO_2 for 24 h. Yields were determined by ^{1}H NMR analysis.

Table S3. Solvent effect in the carboxylative cyclization of **1a**[a]

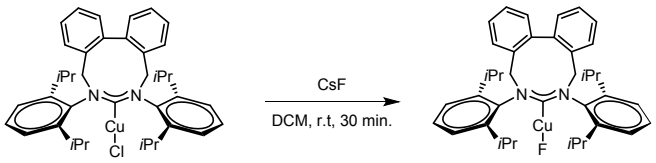
1a **A_1**

Entry	Solvent	**A_1** (%)[b]
1	**Dichloromethane**	**96**
2	Acetone	72
3	**Acetonitrile**	**97**
4	1,4-Dioxane	56
5	DMF	40
6	Toluene	N.R
7	Isopentyl acetate	<2
8	Butyl acetate	N.R
9	Glycerol	N.R
10	*p*-Cymene	12
11	γ-Valerolactone	20
12	Cyclohexanone	N.R

[a] Typical reaction conditions: **1a** (2 mmol), ^{BP}DPrCuCl (5 mol%) and CsF (5 mol%) in solvent (2 mL) were pressurized with CO_2 (2 MPa) and stirred for 24 hours at room temperature.

[b] Determined by ^{1}H NMR analysis.

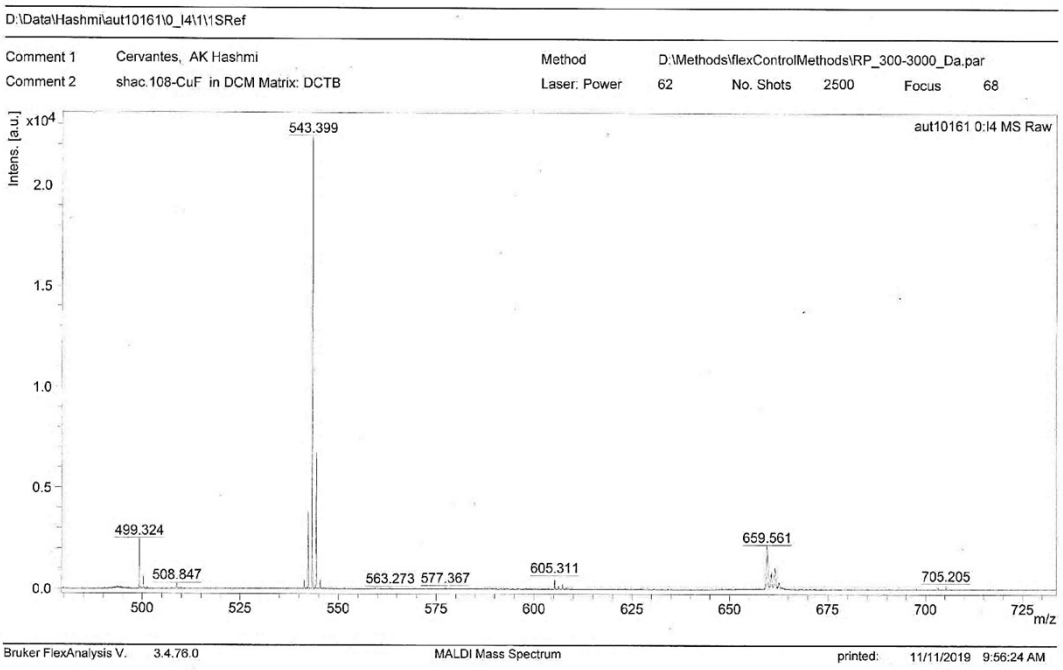
4. Detection of [^{BP}DPrCuF] in solution

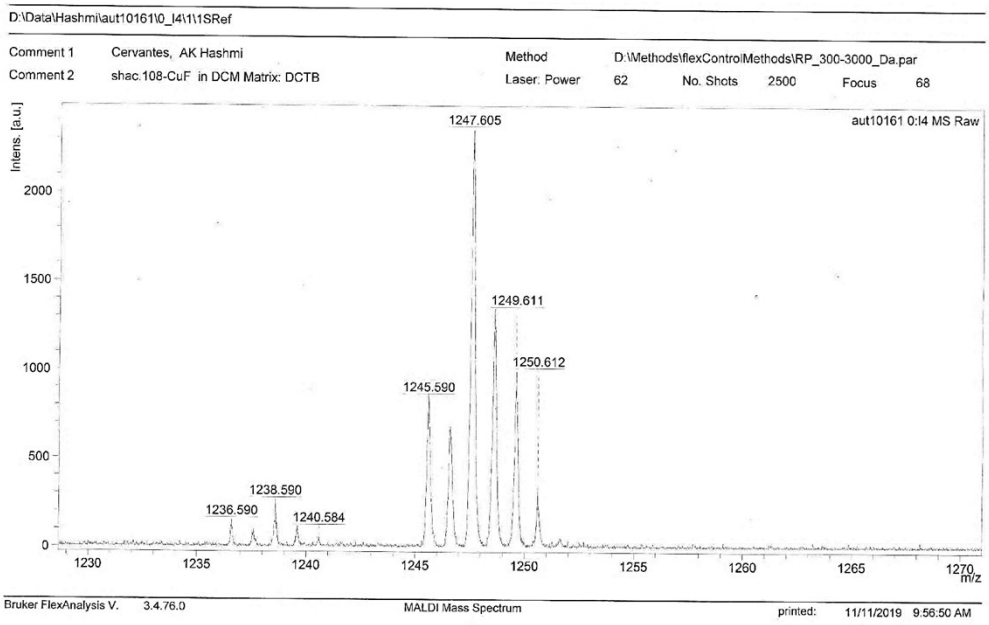


(NHC)CuCl **(NHC)CuF**

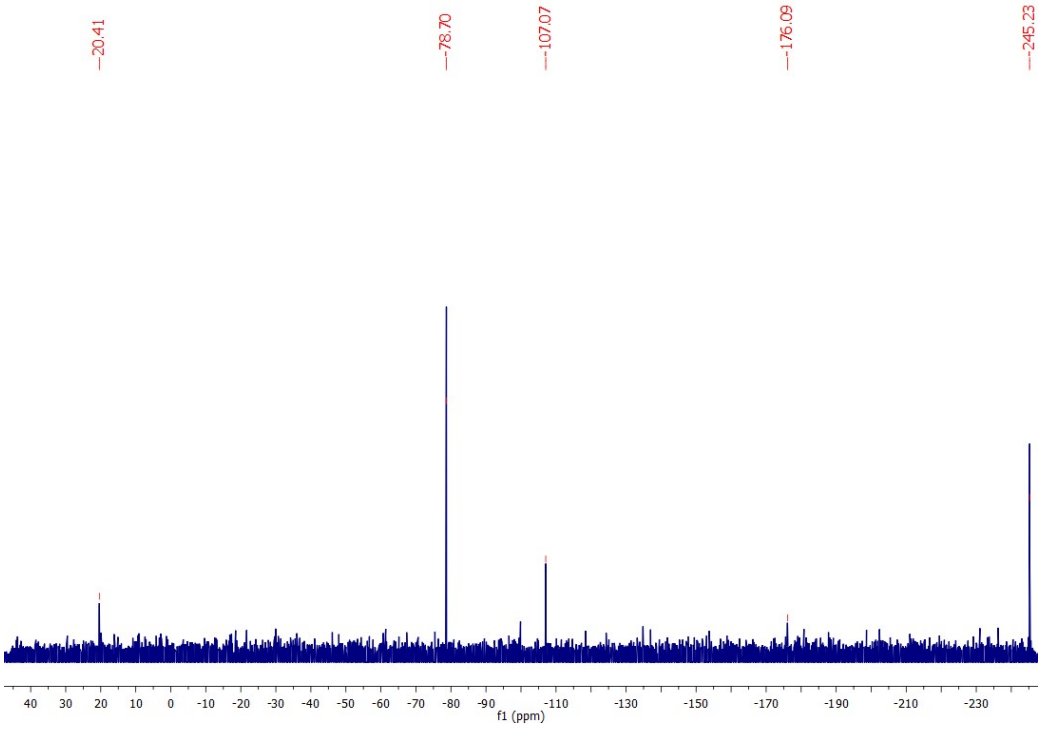
(MALDI+) m/z = 543.3746 $[(NHC)H]^+$
m/z = 605.2964 $[(NHC)Cu]^+$
m/z = 1247.5768 $[(NHC)Cu(\mu\text{-}F)]_2^+$

Experiment 1: A 4.5 mL screw-cap Teflon coated vial was charged with ^{BP}DPrCuCl complex (32 mg, 50 µmol), anhydrous CsF (8 mg, 55 µmol, 1.05 equiv) and anhydrous DCM (1.0 mL) under open-air conditions at room temperature. After stirring 30 minutes, the mixture was stand on the bench for 10 minutes and a 50 µL aliquot was taken from the clear solution, diluted with anhydrous DCM (0.9 mL) and immediately analyzed by mass spectrometry (MALDI+).





Experiment 2: An NMR tube was charged with ^{BP}DPrCuCl (32 mg, 50 µmol) and anhydrous CsF (7.5 mg, 50 µmol, 1 equiv) followed by 0.6 mL dried $CDCl_3$. The tube was vigorously shaken for 10 minutes in dark and the NMR experiments were measured at 296 K. ^{19}F NMR (471 MHz, $CDCl_3$) δ -245.2 ppm. Sample did not experience decomposition as revealed by ^{1}H NMR signals.



5. Recycling of the catalyst

Batch conditions[a]

1a **A_1**

Cycle	Conversion of **1a** (%)[b]
1	96
2	45
3	N.R

[a] Typical reaction conditions: **1a** (5 mmol), ^{BP}DPrCuCl (10 mol%) and CsF (10 mol%) in anhydrous CH_3CN (10 mL) were pressurized with CO_2 (2 MPa) and stirred for 24 hours at room temperature.

[b] Determined by ^{1}H NMR analysis.

General procedure: Product **A_1** was distilled out from reaction tube via Kugelrohr apparatus (0.6 mbar, 100°C) after a typical carboxylative cyclization experiment at the quantities indicated above. A new load of freshly distilled propargyl alcohol **1a** (280 mg, 5 mmol) was charged into the tube followed by solvent and the mixture was pressurized with CO_2 (2 MPa) under stirring. After the second run, yellowish to green precipitated appeared, presumably containing Cu(II) species formed by oxidation. This was again used for a third run nonetheless the catalyst was no longer effective.

Successive additions[a]

1a **A_1** **B_1**

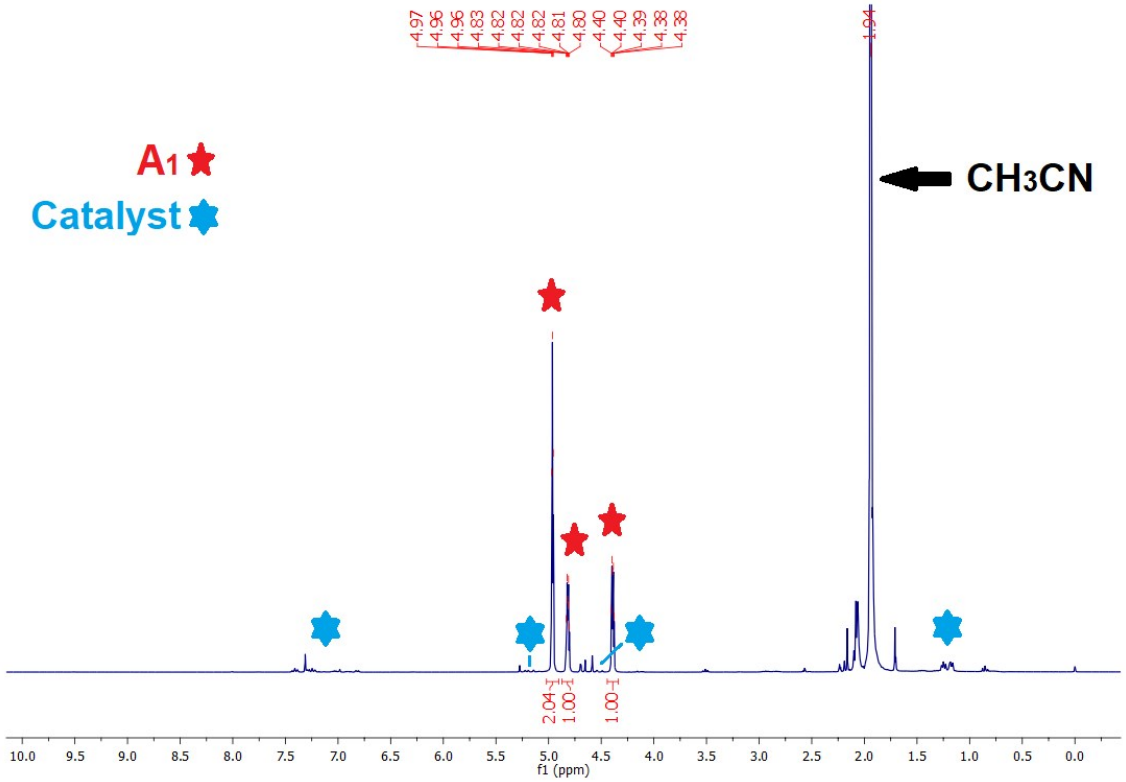
Addition	$\mathbf{A_1}$ (%)[b]	$\mathbf{B_1}$ (%)[b]
(fresh run)	98	n.d
1st	89	trace
2nd	71	trace
3rd	60	trace
4th	50	13

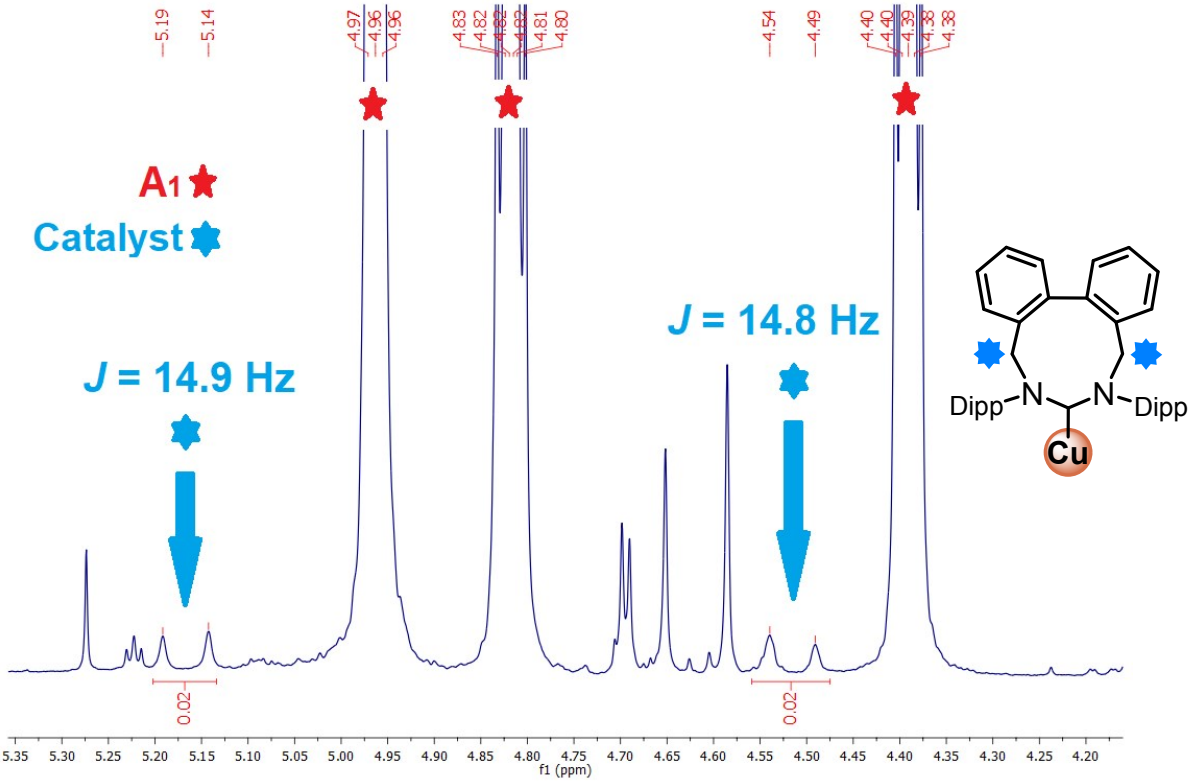
[a] Typical reaction conditions: **1a** (5 mmol), ^{BP}DPrCuCl (5 mol%) and CsF (5 mol%) in anhydrous CH_3CN (10 mL) were pressurized with CO_2 (*ca.* 2.3 MPa) and stirred for 24 hours at room temperature.

[b] Determined by ^{1}H NMR analysis using 1,3,5-tri*tert*butylbenzene as an internal standard.

General procedure: Freshly distilled propargyl alcohol **1a**, acetonitrile, and catalytic system were charged into reaction tube and the mixture was pressurized with CO_2 (*ca.* 2.3 MPa) under stirring. After 24 h the reactor was slowly depressurized, and a new load of fresh **1a** (5mmol) was introduced to reactor. This protocol was repeated four times until detecting a half product in the mixture. After each cycle, an aliquot of reaction mixture was taken, solubilized in 1 mL $CDCl_3$ and a standard was added. The yield was calculated by ^{1}H NMR after each cycle and turnover number was calculated by considering total mass of product $\mathbf{A_1}$ (74% yield, 18.4 mmol) and a total quantity of copper catalyst (0.71 mol%, 0.036 mmol), TON = 103.

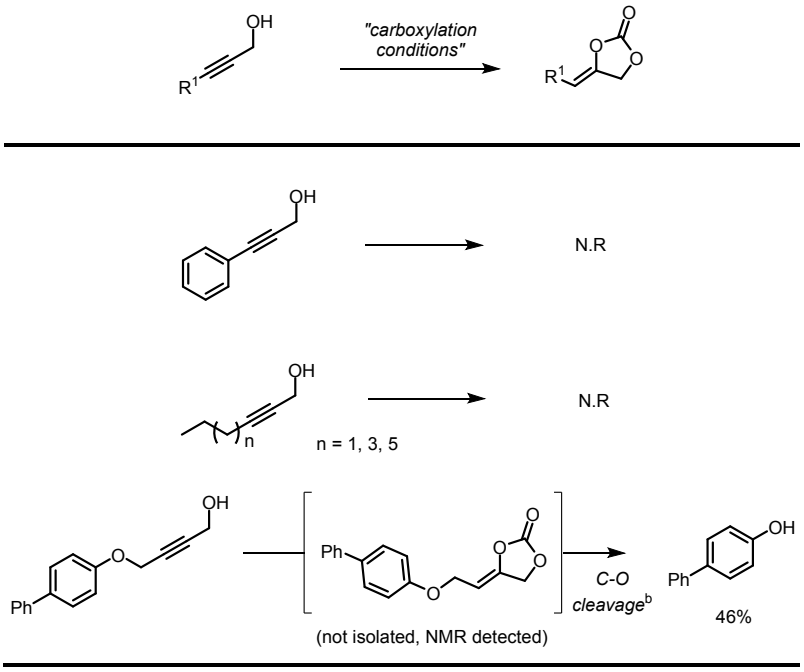
NMR spectrum of raw product $\mathbf{A_1}$ after the first add features trace of catalyst, which does not show decomposition as judged by integrating peaks of methylene groups within the NHC backbone in the copper complex (see below).


A1
Catalyst
CH3CN
f1 (ppm)


A1
Catalyst
J = 14.9 Hz
J = 14.8 Hz
Dipp
N
N
Dipp
Cu
f1 (ppm)

6. Limitations of the carboxylation protocol[a]

Figure S5. Attempts to synthesize cyclic carbonates from primary terminal aryl-, alkyl- and phenol-derived substrates.[a]

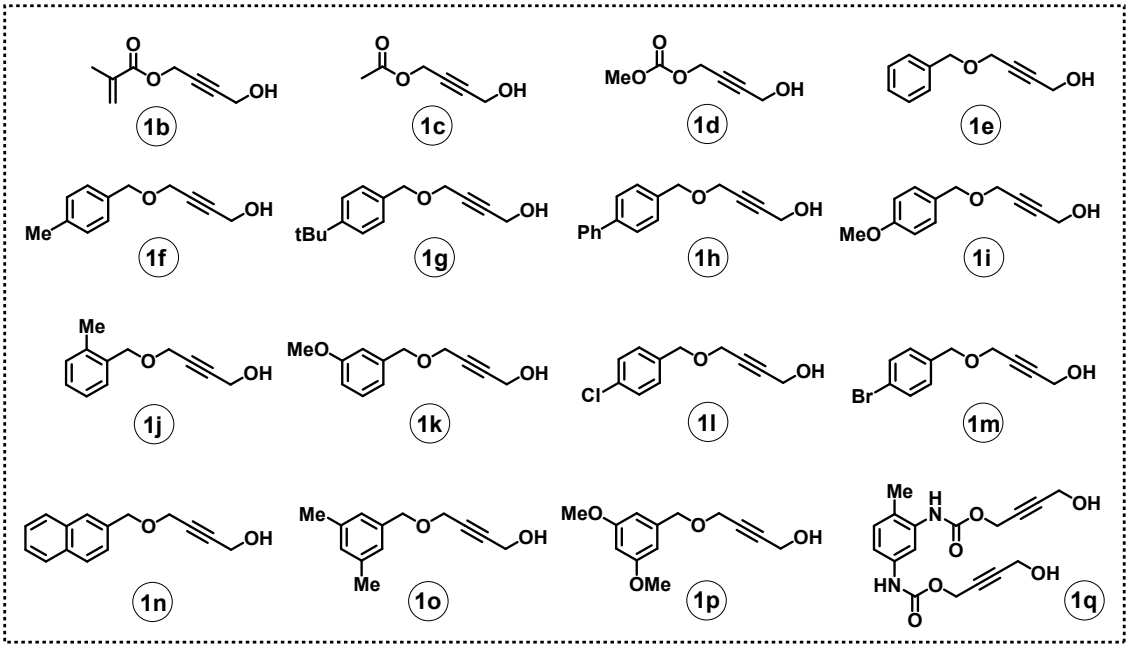


[a] Typical reaction conditions: Propargylic alcohol (2 mmol), ^{BP}DPrCuCl (5 mol%) and CsF (5 mol%) in solvent (5 mL) were pressurized with CO_2 (2 MPa) and stirred for 24 hours at room temperature.

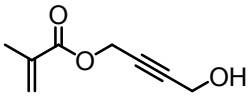
[b] Isolated yield after column chromatography.

7. Synthesis of Primary Propargylic Alcohols 1b–1q

Figure S6. Synthesized primary propargylic alcohols.



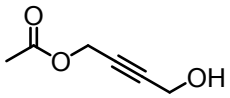
Compounds **1b–1d**, and **1q** were prepared according to literature procedures.



1b

4-Hydroxybut-2-yn-1-yl methacrylate (**1b**).[5]

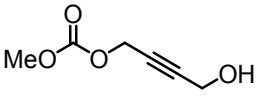
Freshly distilled Et_3N (12.9 mL, 93.4 mmol, 1.4 eq.) was added to a solution of 2-butyn-1,4-diol (5.7 g, 66.7 mmol, 1.0 eq.) in dry DCM/THF (30 mL/10 mL), and the resulting suspension was stirred at room temperature until dissolution was complete. Methacrylic anhydride (11 mL, 73.4 mmol, 1.1 eq.) was then added dropwise to the reaction mixture at 0 °C during 30 min. The reaction mixture was then warmed to room temperature and stirred overnight. Distilled water (150 mL) was added and the reaction mixture was extracted with DCM (3 × 60 mL). The collected organic layers were dried over anhydrous Na_2SO_4 and the solvents were evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, AcOEt/P.E 3:7) to give pure **1b** as a colorless oil (7.3 g, 71%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 6.10 (s, 1H), 5.56 (s, 1H), 4.73 (t, *J* = 1.8 Hz, 2H), 4.25 (t, *J* = 1.8 Hz, 2H), 2.06 (br s, 1H), 1.89 (dd, *J* = 1.4, 1.0 Hz, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 166.9, 135.7, 126.7, 85.2, 79.7, 52.6, 51.0, 18.3. Spectral data match that of literature.[5]



1c

4-Hydroxybut-2-yn-1-yl acetate (**1c**).[5]

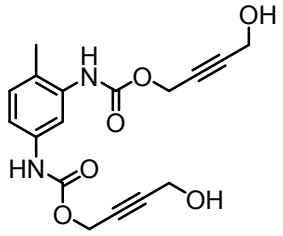
Freshly distilled Et_3N (11.5 mL, 81 mmol) was added to a solution of 2-butyn-1,4-diol (5.0 g, 58 mmol) in dry DCM/THF (25 mL/7 mL), and the resulting suspension was stirred at room temperature until dissolution was complete. Acetic anhydride (6 mL, 64 mmol) was then added dropwise to the reaction mixture at 0 °C during 30 min. The reaction mixture was then warmed to room temperature and stirred overnight. Water (120 mL) was added and the reaction mixture was extracted with DCM (3 × 50 mL). The collected organic layers were dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2, AcOEt/P.E 2:3) to give pure **1c** as a colorless oil (3.8 g, 51%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 4.65 (t, *J* = 1.8 Hz, 2H), 4.23 (t, *J* = 1.8 Hz, 2H), 2.86 (br s, 1H), 2.04 (s, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 170.6, 85.2, 79.4, 52.4, 50.7, 20.7. Spectral data match that of literature. [5]



1d

4-hydroxybut-2-yn-1-yl methyl carbonate (**1d**).[5]

To a cooled (0 °C) solution of 2-butyn-1,4-diol (15 g, 174 mmol, 3.0 eq.) in anhydrous DCM (350 mL) was successively added DIPEA (33 mL, 192 mmol, 3.3 eq.), DMAP (712 mg, 5.8 mmol, 0.1 eq.) and finally methyl chloroformate (4.5 mL, 58 mmol, 1.0 eq.) dropwise via a syringe. The reaction mixture was stirred at 0 °C for 2 hours followed by stirring overnight at room temperature. The reaction mixture was concentrated to half of its original volume followed by the addition of Et_2O (60 mL) and saturated $NaHCO_3$ (60 mL). The phases were separated, and the organic phase was washed three times with saturated $NaHCO_3$ before drying it over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude was purified by flash chromatography (SiO_2, AcOEt/P.E 2:3) to give **1d** as a colorless oil (6.8 g, 81%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 4.71 (t, *J* = 1.8 Hz, 2H), 4.23 (t, *J* = 1.8 Hz, 2H), 3.75 (s, 3H), 2.99 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 155.3, 86.0, 78.8, 55.7, 55.2, 50.6. Spectral data match that of literature.[5]

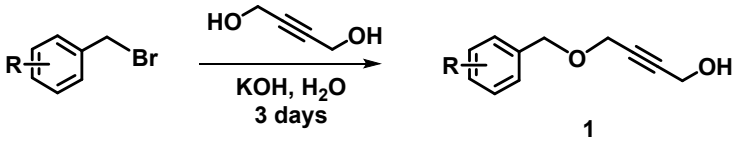


1q

Bis(4-hydroxybut-2-yn-1-yl) (4-methyl-1,3-phenylene)dicarbamate (**1q**).[5]

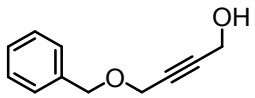
2,4-diisocyanato-1-methylbenzene (2.0 g, 11.6 mmol, 1.0 eq.) in anhydrous DMF (8.5 mL) was added dropwise (2 drop/sec) into an nitrogen purged 50 mL two-necked round-bottomed flask containing 2-butyn-1,4-diol (3 g, 35 mmol, 3.0 eq.) under stirring at 120 °C (oil bath). After the addition was complete, the reaction mixture was further stirred for 2 hours at 120 °C after which it was brought down to room temperature. Distilled water (200 mL) was then added to the reaction mixture and the product was let to crystallize in the fridge (*ca*. 4 °C) overnight. The crystals were filtered and recollected in a 500 mL round bottom flask containing 400 mL distilled water. The mixture was then refluxed at 110 °C, followed by hot filtration (<85°C). The oligomers were separated by filtration while the filtrate at the bottom was cooled down to obtain pure **1q** as a colorless solid (2.8 g, 71%). **^{1}H NMR** (301 MHz, CD_3CN) δ 7.87 (br s, 1H), 7.72 (br s, 1H), 7.28 (br s, 1H), 7.19–7.09 (m, 2H), 4.78 (t, *J* = 1.8 Hz, 2H), 4.76 (t, *J* = 1.8 Hz, 2H), 4.20 (br s, 4H), 3.32 (br s, 2H), 2.18 (s, 3H). **^{13}C NMR** (76 MHz, CD_3CN) δ 154.36, 153.82, 137.70, 137.06, 131.5, 118.2, 86.4, 86.4, 79.9, 79.9, 53.6, 53.4, 50.5, 17.3. Spectral data match that of literature.[5]

Compounds **1e–p** were prepared according to an adapted procedure reported for **1e**:[5]



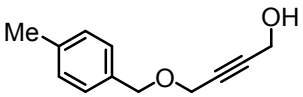
1

General Procedure: To a stirred solution of KOH (40 mmol, 2.0 equiv) in distilled water (40 mL), 2-butyn-1,4-diol (40 mmol, 2.0 equiv) was added at room temperature. After 20 minutes, the corresponding benzyl bromide (20 mmol, 1.0 equiv) was added drop by drop (4.0 M in THF for solid benzyl bromides) and the mixture was stirred for 3 days at room temperature. The reaction mixture was extracted with DCM (3x50 mL), the combined organic phases were washed with brine (2x100 mL) and water (80 mL) and dried over anhydrous Na_2SO_4. The organic fraction was concentrated under reduced pressure and the crude was purified by flash chromatography (SiO_2, AcOEt/P.E 8:2) to give the desired mono-benzylated alcohol as colorless oil or colorless solid.



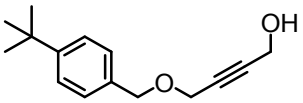
1e

4-(benzyloxy)but-2-yn-1-ol (**1e**). Colorless oil. Yield: 2.4 g (68%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.41–7.31 (m, 5H), 4.62 (s, 2H), 4.30 (t, *J* = 1.8 Hz, 2H), 4.23 (t, *J* = 1.8 Hz, 2H), 3.05 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 137.3, 128.5, 128.1, 127.9, 85.2, 81.3, 71.7, 57.4, 50.8. This is a known compound.[5]



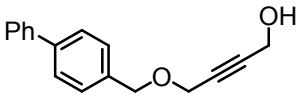
1f

4-((4-methylbenzyl)oxy)but-2-yn-1-ol (**1f**). Colorless oil. Yield: 2.1 g (56%).**^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 4.46 (s, 2H), 4.20 (t, *J* = 1.8 Hz, 2H), 4.09 (t, *J* = 1.8 Hz, 2H), 2.42 (s, 1H), 2.25 (s, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 137.74, 134.22, 129.2, 128.3, 84.9, 81.6, 71.6, 57.2, 50.9, 21.2. This is a known compound.[6]



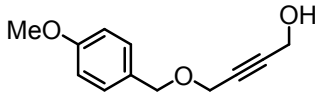
1g

4-((4-*tert*-butylbenzyl)oxy)but-2-yn-1-ol (**1g**). Colorless oil. Yield: 3.3 g (72%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 4.49 (s, 2H), 4.22 (t, *J* = 1.8 Hz, 2H), 4.12 (t, *J* = 1.8 Hz, 2H), 2.07 (s, 1H), 1.24 (s, 9H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 151.1 (s, 1C), 134.3 (s, 1C), 128.1 (d, 2C), 125.5 (d, 2C), 84.9 (s, 1C), 81.8 (s, 1C), 71.7 (t, 1C), 57.4 (t, 1C), 51.1 (t, 1C), 34.7 (s, 1C), 31.4 (q, 3C). **IR (ATR)** ν_{max} (cm^{-1}) = 3392 (O-H), 3028, 2961, 2866, 1514, 1461, 1411, 1123 (C-O), 1073 (C-O), 1017, 817, 673. **HR-MS** (ESI+) *m/z* calcd. for $C_{15}H_{20}NaO_2$ $[M+Na]^+$: 255.1366, found: 255.1358.



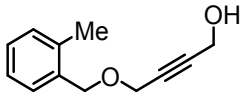
1h

4-([1,1'-biphenyl]-4-ylmethoxy)but-2-yn-1-ol (**1h**). Colorless solid. Yield: 1.3 g (26%).**^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.54–7.46 (m, 4H), 7.39–7.33 (m, 4H), 7.31–7.23 (m, 1H), 4.56 (s, 2H), 4.25 (t, *J* = 1.8 Hz, 2H), 4.17 (t, *J* = 1.8 Hz, 2H), 1.71 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 141.0 (s, 1C), 140.9 (s, 1C), 136.5 (s, 1C), 128.9 (d, 2C), 128.6 (d, 2C), 127.5 (d, 1C), 127.4 (d, 2C), 127.2 (d, 2C), 84.9 (s, 1C), 81.9 (s, 1C), 71.7 (t, 1C), 57.6 (t, 1C), 51.3 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 3343 (O-H), 3060, 2853, 1486, 1407, 1345, 1264, 1127 (C-O), 1089 (C-O), 1017, 754, 688. **HR-MS** (EI+) *m/z* calcd. for $C_{17}H_{16}O_2$ $[M]^+$: 252.11448, found: 252.11310.



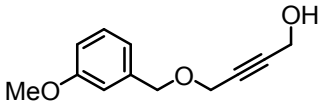
1i

4-((4-methoxybenzyl)oxy)but-2-yn-1-ol (**1i**). Colorless oil. Yield: 2.8 g (68%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.43 (s, 2H), 4.20 (s, 2H), 4.08 (s, 2H), 3.70 (s, 3H), 2.66 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 159.4 (s, 1C), 129.8 (d, 2C), 129.3 (s, 1C), 113.9 (d, 2C), 85.0 (s, 1C), 81.5 (s, 1C), 71.3 (t, 1C), 57.0 (t, 1C), 55.3 (q, 1C), 50.9 (t, 1C). This is a known compound.[7]



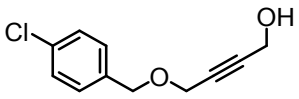
1j

4-((4-methylbenzyl)oxy)but-2-yn-1-ol (**1j**). Colorless oil. Yield: 1.7 g (43%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.26–7.23 (m, 1H), 7.15–7.07 (m, 3H), 4.52 (s, 2H), 4.24 (t, *J* = 1,9 Hz, 2H), 4.15 (t, *J* = 1,9 Hz, 2H), 2.29 (s, 3H), 1.54 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 137.0 (s, 1C), 135.3 (s, 1C), 130.3 (d, 1C), 129.04 (d, 1C), 128.1 (d, 1C), 125.8 (d, 1C), 70.2 (t, 1C) 57.5 (t, 1C), 51.2 (t, 1C), 18.8 (q, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 3375, 2861, 1441, 1349, 1121, 1070, 1012, 740. **HR-MS** (EI+) *m/z* calcd. for $C_{12}H_{14}O_2$ $[M]^+$: 190.09883, found: 190.09791.



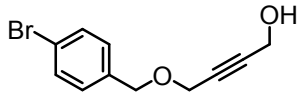
1k

4-((3-methoxybenzyl)oxy)but-2-yn-1-ol (**1k**). Colorless oil. Yield: 2.7 g (68%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.9 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.89 – 6.83 (m, 1H), 4.59 (s, 2H), 4.32 (t, *J* = 1.8 Hz, 2H), 4.22 (t, *J* = 1.8 Hz, 2H), 3.82 (s, 3H), 2.43 (br s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 159.8 (s, 1C), 138.9 (s, 1C), 129.5 (d, 1C), 120.4 (d, 1C), 113.7 (d, 1C), 113.4 (d, 1C), 85.1 (s, 1C), 81.5 (s, 1C), 71.6 (t, 1C), 57.5 (t, 1C), 55.3 (q, 1C), 51.0 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 3403, 3054, 2858, 1586, 1435, 1262, 1120, 1010, 740. **HR-MS** (EI+) *m/z* calcd. for $C_{12}H_{14}O_3$ $[M]^+$: 206.09375, found: 206.09326.



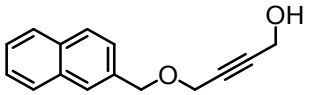
1l

4-((4-chlorobenzyl)oxy)but-2-yn-1-ol (**1l**). Colorless oil. Yield: 2.3 g (55%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.20 (q, *J* = 8.7 Hz, 4H), 4.45 (s, 2H), 4.20 (t, *J* = 1.8 Hz, 2H), 4.11 (t, *J* = 1.8 Hz, 2H), 2.65 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 135.8 (s, 1C), 133.7 (s, 1C), 129.4 (d, 2C), 128.6 (d, 2C), 85.2 (s, 1C), 81.2 (s, 1C), 70.9 (t, 1C), 57.5 (t, 1C), 50.8 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 3355, 2861, 1903, 1491, 1349, 1124, 1084, 1014, 806. **HR-MS** (EI+) *m/z* calcd. for $C_{13}H_{16}O_2$ $[M]^+$: 210.04421, found: 210.04357.



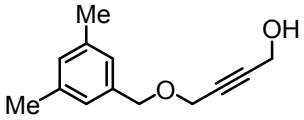
1m

4-((4-chlorobenzyl)oxy)but-2-yn-1-ol (**1m**). Colorless oil. Yield: 2.4 g (48%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.45 (s, 2H), 4.22 (t, *J* = 1.8 Hz, 2H), 4.12 (t, *J* = 1.8 Hz, 2H), 2.20 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 136.4 (s, 1C), 131.6 (d, 2C), 129.7 (d, 2C), 121.9 (s, 1C), 85.2 (s, 1C), 81.4 (s, 1C), 70.9 (t, 1C), 57.6 (t, 1C), 51.0 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 3361, 2859, 1902, 1487, 1347, 1123, 1069, 1009, 795. **HR-MS** (EI+) *m/z* calcd. for $C_{11}H_{11}O_2Br$ $[M]^+$: 253.99369, found: 253.99334.



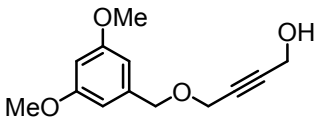
1n

4-(naphthalen-2-ylmethoxy)but-2-yn-1-ol (**1n**). Colorless oil (crystallizes upon several days at open-air conditions). Yield: 1.6 g (36%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.73–7.68 (m, 4H), 7.41–7.32 (m, 3H), 4.64 (s, 2H), 4.20 (t, *J* = 1.8 Hz, 2H), 4.13 (t, *J* = 1.8 Hz, 2H), 2.30 (br s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 134.8 (s, 1C), 133.3 (s, 1C), 133.1 (s, 1C), 128.3 (d, 1C), 127.9 (d, 1C), 127.8 (d, 1C), 126.9 (d, 1C), 126.2 (d, 1C), 126.1 (d, 1C), 125.9 (d, 1C), 85.1 (s, 1C), 81.6 (s, 1C), 71.9 (t, 1C), 57.5 (t, 1C), 51.0 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 3055 (O-H), 2852, 1691, 1599, 1332, 1173, 1122 (C-O), 1015 (C-O), 825, 751. **HR-MS** (EI+) *m/z* calcd. for $C_{15}H_{14}O_2$ $[M]^+$: 226.09883, found: 226.10038.



1o

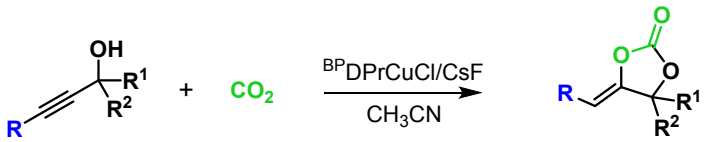
4-((3,5-dimethylbenzyl)oxy)but-2-yn-1-ol (**1o**). Colorless oil. Yield: 2.9 g (76%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.94 (s, 1H), 4.53 (s, 2H), 4.32 (t, *J* = 1.8 Hz, 2H), 4.21 (t, *J* = 1.8 Hz, 2H), 2.32 (s, 6H), 1.97 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 138.14 (s, 2C), 137.24 (s, 1C), 129.65 (d, 1C), 126.03 (d, 2C), 84.87 (s, 1C), 81.91 (s, 1C), 71.98 (t, 1C), 57.51 (t, 1C), 51.19 (t, 1C), 21.33 (q, 2C). **IR (ATR)** ν_{max} (cm^{-1}) = 3374 (O-H), 3014, 2917, 2861, 1607, 1444, 1349, 1122 (C-O), 1075, 1011 (C-O), 843, 712. **HR-MS** (EI+) *m/z* calcd. for $C_{13}H_{16}O_2$ $[M]^+$: 204.11448, found: 204.11515.



1p

4-((3,5-dimethoxybenzyl)oxy)but-2-yn-1-ol (**1p**). Colorless oil. Yield: 3.8 g (81%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 6.52 – 6.49 (m, 2H), 6.39 (t, *J* = 2.3 Hz, 1H), 4.53 (s, 2H), 4.31 (s, 2H), 4.20 (t, *J* = 1.7 Hz, 2H), 3.78 (s, 6H), 2.04 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 161.0 (s, 2C), 139.8 (s, 1C), 105.8 (d, 1C), 104.7 (d, 1C), 100.1 (d, 1C), 85.0 (s, 1C), 81.7 (s, 1C), 71.7 (t, 1C), 57.5 (q, 2C), 55.5 (t, 1C), 51.2 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 3421 (O-H), 2981, 2840, 1594, 1457, 1320, 1147 (C-O), 1051, 1012 (C-O), 832, 706. **HR-MS** (EI+) *m/z* calcd. for $C_{13}H_{16}O_4$ $[M]^+$: 236.10492, found: 236.10431.

8. Synthesis and characterization data of α-Alkylidene Cyclic Carbonates

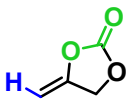


1a-p
2a-m

$A_{1\text{-}17}$ $R^1 = R^2 = H$
$C_{1\text{-}13}$ R^1 = H, alkyl, Ph; $R^2 \neq H$

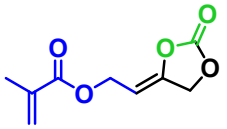
Procedure 1: A 20 mL scintillation vial provided with Teflon-coated stirring bar was charged with ^{BP}DPrCuCl (5 mol%), anhydrous CsF (5 mol%) and anhydrous CH_3CN (5 mL) at room temperature. After stirring for 15 minutes at same temperature, propargylic alcohol **1** (2 mmol) was added to mixture and the vial was introduced into an autoclave reactor and pressurized with CO_2 to *ca*. 2 MPa (~20 bar). The reaction mixture was stirred for 24 hours at room temperature after which overpressure was slowly released. Activated carbon was added to raw mixture, stirred additional 15 minutes, and filtered through a pad of celite. Filtrate was evaporated under reduced pressure till dryness and crude product was purified by flash chromatography (SiO_2, AcOEt/P.E, 2:8) to yield desired α-exovinylene cyclic carbonates **A_1**–**A_{17}**.

Procedure 2: A 10 mL scintillation vial provided with Teflon-coated stirring bar and a sealable Teflon cap was charged with ^{BP}DPrCuCl (2.5 mol%), anhydrous CsF (2.5 mol%) and anhydrous CH_3CN (5 mL) at room temperature. After stirring for 15 minutes at same temperature, propargylic alcohol **2** (2 mmol) was added to mixture under stirring and the vial was sealed. A CO_2-filled balloon was used to purge for 5 minutes via cannula and a new CO_2-filled balloon (*ca.* 1.5 L) was attached to reaction mixture. The reaction mixture was stirred for 24 hours at room temperature. Activated carbon was added to raw mixture, stirred additional 15 minutes, and filtered through a pad of celite. Filtrate was evaporated under reduced pressure till dryness and crude product was purified by flash chromatography (SiO_2, AcOEt/P.E, 5:95) to yield desired α-exovinylene cyclic carbonates **C_1**–**C_{13}**.



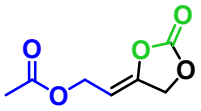
A_1

4-methylene-1,3-dioxolan-2-one (**A_1**). According to ***Procedure 1:*** Colorless oil. 188 mg (94%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 4.99 (t, *J* = 2.4 Hz, 2H), 4.86 (dt, *J* = 4.0, 2.6 Hz, 1H), 4.41 (dt, *J* = 4.2, 2.2 Hz, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 152.8, 148.9, 87.3, 67.6. Spectral data match that of literature.[5]



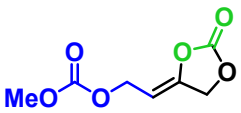
A_2

(Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl methacrylate (**A_2**). According to ***Procedure 1:*** Colorless solid. 348 mg (88%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 6.12 – 6.11 (m, 1H), 5.60 – 5.58 (m, 1H), 5.05 – 4.98 (m, 3H), 4.81 – 4.77 (m, 2H), 1.95 – 1.93 (m, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 167.2, 152.1, 145.4, 136.1, 126.2, 98.1, 67.4, 58.1, 18.4. Spectral data match that of literature.[5]



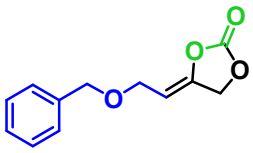
A_3

(Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl acetate (**A_3**). According to ***Procedure 1:*** Colorless oil. 296 mg (86%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 5.03 – 4.95 (m, 3H), 4.72 – 4.69 (m, 2H), 2.06 (s, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 170.9, 152.1, 145.5, 97.9, 67.4, 57.8, 20.9. Spectral data match that of literature.[5]



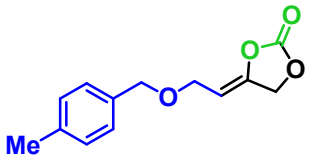
A_4

(Z)-methyl (2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl) carbonate (**A_4**). According to ***Procedure 1:*** Colorless oil. 293 mg (78%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 5.10 – 5.04 (m, 3H), 4.81 – 4.75 (m, 2H), 3.80 (s, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 156.0, 152.6, 146.7, 97.5, 68.1, 61.4, 55.4. Spectral data match that of literature.[5]



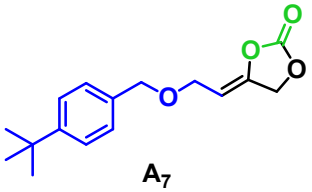
A_5

(Z)-4-(2-(benzyloxy)ethylidene)-1,3-dioxolan-2-one (**A_5**). According to ***Procedure 1:*** Colorless oil. 392 mg (89%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 5H), 4.99 – 4.93 (m, 3H), 4.52 (s, 2H), 4.23 – 4.18 (m, 2H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 152.4, 144.1, 137.9, 128.6, 127.9, 100.4, 72.9, 67.4, 63.5. Spectral data match that of literature.[5]



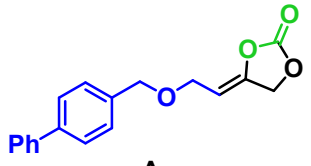
A_6

(Z)-4-(2-((4-methylbenzyl)oxy)ethylidene)-1,3-dioxolan-2-one (**A_6**). According to ***Procedure 1:*** Colorless oil. 445 mg (95%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.98 – 4.92 (m, 3H), 4.48 (s, 2H), 4.19 – 4.16 (m, 2H), 2.35 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.4 (s, 1C), 143.9 (s, 1C), 137.7 (s, 1C), 134.8 (s, 1C), 129.3 (d, 2C), 128.1 (d, 2C), 100.5 (d, 1C), 72.8 (t, 1C), 67.4 (t, 1C), 63.3 (t, 1C), 21.3 (q, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2958, 2930, 1840 (C=O), 1731, 1637, 1314, 1292, 1136 (C-O), 1052, 1011 (C-O), 944, 813, 651. **HR-MS** (EI+) *m/z* calcd. for $C_{13}H_{14}O_4$ $[M]^+$: 234.08866, found: 234.08771. **Anal. Calcd**. for. $C_{13}H_{14}O_4$: C 66.66%, H 6.02%, Found: C 67.59%, H 6.53%.



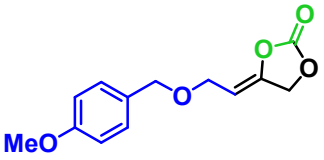
A_7

(Z)-4-(2-((4-*tert*-butylbenzyl)oxy)ethylidene)-1,3-dioxolan-2-one (**A_7**). According to ***Procedure 1:*** Colorless oil. 497 mg (90%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.01 – 4.94 (m, 3H), 4.52 (s, 2H), 4.24 – 4.20 (m, 2H), 1.36 (s, 9H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 152.3 (s, 1C), 150.7 (s, 1C), 143.9 (s, 1C), 134.8 (s, 1C), 127.7 (d, 2C), 125.3 (d, 2C), 100.2 (d, 1C), 72.4 (t, 1C), 67.3 (t, 1C), 63.2 (t, 1C), 34.5 (s, 1C), 31.3 (q, 3C). **IR (ATR)** ν_{max} (cm^{-1}) = 2961, 2867, 1832 (C=O), 1721, 1375, 1268, 1122, 1042, 815. **HR-MS** (EI+) *m/z* calcd. for $C_{16}H_{20}O_4$ $[M]^+$: 276.13561, found: 276.13665. **Anal. Calcd**. for. $C_{16}H_{20}O_4$: C 69.55%, H 7.30%, Found: C 69.41%, H 7.25%



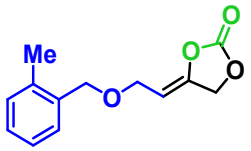
A_8

(Z)-4-(2-([1,1'-biphenyl]-4-ylmethoxy)ethylidene)-1,3-dioxolan-2-one (**A_8**). According to ***Procedure 1:*** Colorless solid. 545 mg (92%). **m.p.** 53 °C. **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 4H), 7.48 – 7.33 (m, 5H), 5.02 – 4.94 (m, 3H), 4.57 (s, 2H), 4.26 – 4.21 (m, 2H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 152.3 (s, 1C), 144.0 (s, 1C), 140.9 (s, 1C), 140.8 (s, 1C), 136.8 (s, 1C), 128.8 (d, 2C), 128.4 (d, 2C), 127.4 (d, 1C), 127.3 (d, 2C), 127.1 (d, 2C), 100.3 (d, 1C), 72.5 (t, 1C), 67.5 (t, 1C), 63.4 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2859, 1828 (C=O), 1726, 1486, 1377, 1115, 104, 1007, 958, 823, 757, 703. **HR-MS** (EI+) *m/z* calcd. for $C_{18}H_{16}O_4$ $[M]^+$: 296.10431, found: 296.10509. **Anal. Calcd**. for. $C_{18}H_{16}O_4$: C 72.96%, H 5.44%, found: C 72.93%, H 5.62%



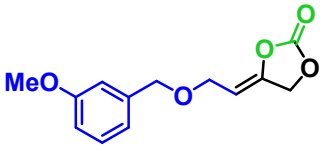
A_9

(Z)-4-(2-((4-methoxybenzyl)oxy)ethylidene)-1,3-dioxolan-2-one (**A_9**). According to ***Procedure 1:*** Colorless oil. 480 mg (96%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.92 – 4.86 (m, 3H), 4.40 (s, 2H), 4.13 – 4.09 (m, 2H), 3.75 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.2 (s, 1C), 152.3 (s, 1C), 143.7 (s, 1C), 129.8 (s, 1C), 129.4 (d, 2C), 113.7 (d, 2C), 100.1 (d, 1C), 72.1 (t, 1C), 67.3 (t, 1C), 62.9 (t, 1C), 55.1 (q, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2983, 2930, 1844 (C=O), 1739, 1637, 1454, 1371, 1183, 1123, 1016, 816, 652. **HR-MS** (EI+) *m/z* calcd. for $C_{13}H_{14}O_5$ $[M]^+$: 250.08357, found: 250.08300. **Anal. Calcd**. for. $C_{13}H_{14}O_5$: C 62.39%, H 5.64%, found: C 62.72%, H 5.35%.



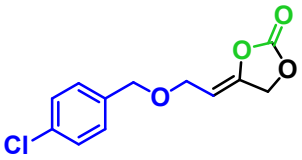
A_{10}

(Z)-4-(2-((2-methylbutylbenzyl)oxy)ethylidene)-1,3-dioxolan-2-one (**A_{10}**). According to ***Procedure 1:*** Colorless oil. 407 mg (90%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 4H), 5.02 – 4.95 (m, 3H), 4.55 (s, 2H), 4.30 – 4.21 (m, 2H), 2.38 (s, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 152.3 (s, 1C), 143.9 (s, 1C), 136.8 (s, 1C), 135.7 (s, 1C), 130.3 (d, 1C), 128.8 (d, 1C), 128.0 (d, 1C), 125.8 (d, 1C), 100.2 (d, 1C), 71.06 (t, 1C), 67.4 (t, 1C), 63.4 (t, 1C), 18.8 (q, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2863, 1826 (C=O), 1721, 1461, 1374, 1207, 1085, 1040, 743. **HR-MS** (EI+) *m/z* calcd. for $C_{13}H_{14}O_4$ $[M]^+$: 234.08866, found: 234.08838. **Anal. Calcd**. for. $C_{13}H_{14}O_4$: C 66.66%, H 6.02%, Found: C 67.04%, H 6.16%



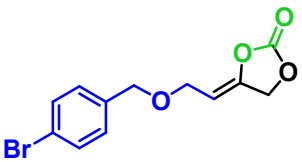
A_{11}

(Z)-4-(2-((2-methoxybenzyl)oxy)ethylidene)-1,3-dioxolan-2-one (**A_{11}**). According to ***Procedure 1:*** Colorless oil. 450 mg (90%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 1H), 6.86 – 6.82 (m, 2H), 6.79 – 6.74 (m, 1H), 4.94 – 4.86 (m, 3H), 4.43 (s, 2H), 4.14 – 4.10 (m, 2H), 3.74 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.8 (s, 1C), 152.3 (s, 1C), 144.1 (s, 1C), 139.4 (s, 1C), 129.5 (d, 1C), 119.9 (d, 1C), 113.4 (d, 1C), 113.1 (d, 1C), 100.1 (d, 1C), 72.5 (t, 1C), 67.4 (t, 1C), 63.3 (t, 1C), 55.2 (q, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2937, 1828 (C=O), 1722, 1686, 1456, 1376, 1264, 1123, 1040, 733, 693. **HR-MS** (EI+) *m/z* calcd. for $C_{13}H_{14}O_5$ $[M]^+$: 250.08357, found: 250.08202. **Anal. Calcd**. for. $C_{13}H_{14}O_5$: C 62.39%, H 5.64%, found: C 62.39%, H 5.75%.



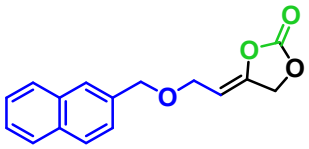
A_{12}

(Z)-4-(2-((4-chlorobenzyl)oxy)ethylidene)-1,3-dioxolan-2-one (**A_{12}**). According to ***Procedure 1:*** Colorless oil. 432 mg (85%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 4.99 – 4.92 (m, 3H), 4.47 (s, 2H), 4.18 (dt, *J* = 7.0, 1.5 Hz, 2H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 152.3 (s, 1C), 144.3 (s, 1C), 136.4 (s, 1C), 133.7 (s, 1C), 129.2 (d, 2C), 128.7 (d, 2C), 100.1 (d, 1C), 71.9 (t, 1C), 67.4 (t, 1C), 63.5 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2865, 1826 (C=O), 1720, 1598, 1491, 1375, 1266, 1082, 1042, 1014 (C-O), 806, 763, 669. **HR-MS** (EI+) *m/z* calcd. for $C_{12}H_{11}O_4Cl$ $[M]^+$: 254.03404, found: 234.03340. **Anal. Calcd**. for. $C_{12}H_{11}ClO_4$: C 56.60%, H 4.35%, found: C 56.48%, H 4.46%.



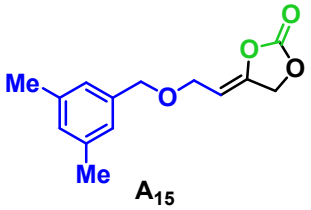
A_{13}

(Z)-4-(2-((4-bromobenzyl)oxy)ethylidene)-1,3-dioxolan-2-one (**A_{13}**). According to ***Procedure 1:*** Colorless oil. 484 mg (81%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.99 – 4.93 (m, 3H), 4.47 (s, 2H), 4.21 – 4.16 (m, 2H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 152.3 (s, 1C), 144.3 (s, 1C), 136.8 (s, 1C), 136.5 (s, 1C), 131.6 (d, 2C), 129.5 (d, 2C), 99.9 (d, 1C), 71.9 (t, 1C), 67.4 (t, 1C), 63.5 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2931, 2861, 1831 (C=O), 1734, 1487, 1377, 1249, 1068, 1010 (C-O), 962, 801. **HR-MS** (EI+) *m/z* calcd. for $C_{12}H_{10}BrO_4$ $[M]^+$: 296.97570, found: 296.97517.



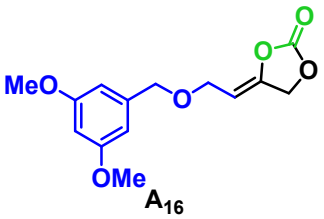
A_{14}

(Z)-4-(2-(naphthalen-2-ylmethoxy)ethylidene)-1,3-dioxolan-2-one (**A_{14}**). According to ***Procedure 1:*** Colorless oil. 453 mg (84%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 4H), 7.51 – 7.45 (m, 3H), 4.98 – 4.90 (m, 3H), 4.68 (s, 2H), 4.22 (dt, *J* = 7.0, 1.5 Hz, 2H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 152.3 (s, 1C), 144.1 (s, 1C), 135.4 (s, 1C), 133.3 (s, 1C), 133.1 (s, 1C), 128.3 (d, 1C), 127.9 (d, 1C), 127.7 (d, 1C), 126.7 (d, 1C), 126.2 (d, 1C), 126.0 (d, 1C), 125.8 (d, 1C), 100.2 (d, 1C), 72.8 (t, 1C), 67.36 (t, 1C), 63.41 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2860, 1813 (C=O), 1718, 1601, 1464, 1375, 1208, 1121, 815. **HR-MS** (EI+) *m/z* calcd. for $C_{16}H_{14}O_4$ $[M]^+$: 270.08866, found: 270.08804. **Anal. Calcd**. for. $C_{16}H_{14}O_4$: C 71.10%, H 5.22%, found: C 70.90%, H 5.08%



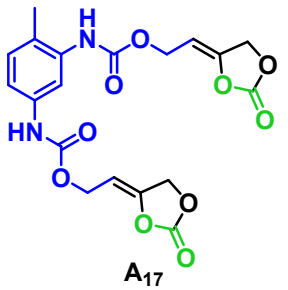
A_{15}

(Z)-4-(2-((3,5-dimethylbenzyl)oxy)ethylidene)-1,3-dioxolan-2-one (**A_{15}**). According to ***Procedure 1:*** Colorless oil. 436 mg (88%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 6.99 – 6.89 (m, 3H), 5.01 – 4.93 (m, 3H), 4.45 (s, 2H), 4.22 – 4.16 (m, 2H), 2.04 (s, 6H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 152.4 (s, 2C), 143.9 (s, 1C), 138.0 (d, 1C), 137.5 (s, 1C), 129.2 (s, 1C), 125.8 (d, 2C), 100.3 (d, 1C), 72.8 (t, 1C), 67.4 (t, 1C), 63.3 (t, 1C), 21.2 (q, 2C). **IR (ATR)** ν_{max} (cm^{-1}) = 2917, 2860, 1832 (C=O), 1724, 1607, 1462, 1376, 1262, 1120, 1078, 844, 711. **HR-MS** (EI+) *m/z* calcd. for $C_{14}H_{15}O_4$ $[M]^+$: 247.09649, found: 247.09560.



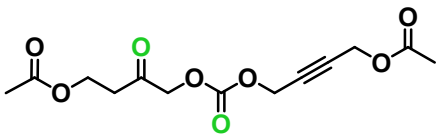
A_{16}

(Z)-4-(2-((3,5-dimethoxybenzyl)oxy)ethylidene)-1,3-dioxolan-2-one (**A_{16}**). According to ***Procedure 1:*** Colorless oil. 493 mg (88%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.48 (d, *J* = 2.3 Hz, 2H), 6.37 (t, *J* = 2.3 Hz, 1H), 4.97 – 4.90 (m, 3H), 4.43 (s, 2H), 4.18 – 4.14 (m, 2H), 3.77 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.9 (s, 2C), 152.3 (s, 1C), 144.1 (s, 1C), 140.2 (s, 1C), 105.5 (d, 2C), 100.1 (d, 1C), 99.9 (d, 1C), 72.6 (t, 1C), 67.4 (t, 1C), 63.3 (t, 1C), 55.3 (q, 2C). **IR (ATR)** ν_{max} (cm^{-1}) = 2939, 2841, 1827 (C=O), 1718, 1594, 1458, 1375, 1149, 1038, 833, 688. **HR-MS** (EI+) *m/z* calcd. for $C_{14}H_{16}O_6$ $[M]^+$: 280.09414, found: 280.09418. **Anal. Calcd**. for. $C_{14}H_{16}O_6$: C 60.00%, H 5.75%, found: C 60.03%, H 5.66%.



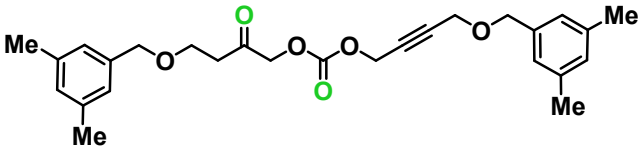
A_{17}

bis((Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl) (4-methyl-1,3-phenylene) dicarbamate (**A_{17}**). According to ***Procedure 1:*** Colorless solid. 738 mg (85%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.72 (s, 1H), 7.29 (s, 1H), 7.15 – 7.08 (m, 2H), 5.09 – 5.00 (m, 6H), 4.76 – 4.67 (m, 4H), 2.17 (s, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 154.0, 154.5, 153.7, 147.2, 137.9, 137.3, 131.5, 125.8, 118.4, 116.4, 114.5, 98.1, 98.1, 68.8, 59.131 58.9, 17.3. Spectral data match that of literature.[5]



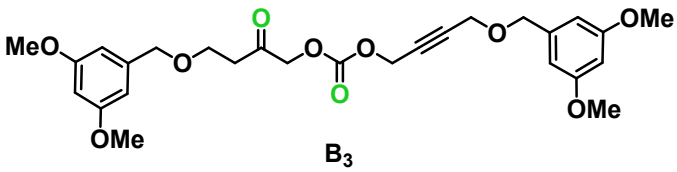
B_1

4-(((4-acetoxy-2-oxobutoxy)carbonyl)oxy)but-2-yn-1-yl acetate (**B_1**). According to ***Procedure 1*** the reaction of **1c** (2 mmol) and [Cu] cat. (5 mol%) under CO_2 (1 MPa) afforded **B_1** as a colorless oil. 93 mg (31%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.83 – 4.80 (m, 2H), 4.71 (s, 4H), 4.35 (t, *J* = 6.2 Hz, 2H), 2.78 (t, *J* = 6.2 Hz, 2H), 2.09 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 200.6 (s, 1C), 170.9 (s, 1C), 170.2 (s, 1C), 154.2 (s, 1C), 82.2 (s, 1C), 79.7 (s, 1C), 71.1 (t, 1C), 58.7 (t, 1C), 56.2 (t, 1C), 52.1 (t, 1C), 37.9 (t, 1C), 20.9 (q, 1C), 20.8 (q, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2941, 1736 (C=O), 1617, 1435, 1374, 1222, 1129, 1094, 1024, 964, 764, 733. **LR-MS** (EI+) *m/z* calcd. for $C_{13}H_{16}O_8$ $[M]^+$: 300.0845, found: 300.0839. **Anal. Calcd**. for. $C_{13}H_{16}O_8$: C 52.00%, H 5.37%, Found: C 52.16%, H 5.74%.



B_2

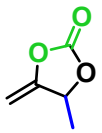
4-((3,5-dimethylbenzyl)oxy)-2-oxobutyl-(4-((3,5-dimethylbenzyl)oxy)but-2-yn-1-yl) carbonate (**B_2**). According to ***Procedure 1*** the reaction of **1o** (2 mmol) and [Cu] cat. (5 mol%) under CO_2 (1 MPa) afforded **B_2** as a colorless oil. 194 mg (43%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.93 (s, 4H), 4.84 (s, 2H), 4.75 (s, 2H), 4.52 (s, 2H), 4.43 (s, 2H), 4.21 (s, 2H), 3.75 (t, *J* = 6.1 Hz, 2H), 2.71 (t, *J* = 6.1 Hz, 2H), 2.31 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.9 (s, 1C), 154.3 (s, 1C), 138.1 (s, 4C), 137.7 (s, 1C), 137.2 (s, 1C), 129.7 (d, 1C), 129.6 (d, 1C), 126.1 (d, 2C), 125.8 (d, 2C), 84.2 (s, 1C), 79.6 (s, 1C), 73.6 (t, 1C), 71.9 (t, 1C), 71.5 (t, 1C), 64.9 (t, 1C), 57.4 (t, 1C), 56.3 (t, 1C), 39.6 (t, 1C), 21.4 (q, 4C). **IR (ATR)** ν_{max} (cm^{-1}) = 2924, 1762 (C=O), 1726 (C=O), 1426, 1269, 1109, 1093, 979, 939, 807, 774. **LR-MS** (EI+) *m/z* calcd. for $C_{27}H_{32}O_6$ $[M]^+$: 452.2199, found: 452.2208. **Anal. Calcd**. for. $C_{27}H_{32}O_6$: C 71.66%, H 7.13%, Found: C 71.25%, H 7.12%.



B_3

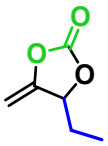
4-((3,5-dimethoxybenzyl)oxy)-2-oxobutyl-(4-((3,5-dimethoxybenzyl)oxy)but-2-yn-1-yl) carbonate (**B_3**). According to ***Procedure 1*** the reaction of **1p** (2 mmol) and [Cu] cat. (5 mol%) under CO_2 (1 MPa) afforded **B_3** as a colorless oil. 185 mg (36%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (d, J = 2.3 Hz, 2H), 6.46 (d, J = 2.3 Hz, 2H), 6.39 (dt, J = 4.4, 2.3 Hz, 2H), 4.83 (t, J = 1.8 Hz, 2H), 4.75 (s, 2H), 4.53 (s, 2H), 4.44 (s, 2H), 4.21 (t, J = 1.8 Hz, 2H), 3.79 (d, J = 0.6 Hz, 12H), 3.75 (t, J = 6.1 Hz,

2H), 2.71 (t, J = 6.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8 (s, 1C), 161.1 (s, 4C), 154.4 (s, 1C), 140.4 (s, 1C), 139.7 (s, 1C), 105.9 (d, 2C), 105.5 (d, 2C), 100.2 (d, 1C), 100.1 (d, 1C), 84.1 (s, 1C), 79.8 (s, 1C), 73.4 (t, 1C), 71.8 (t, 1C), 71.5 (t, 1C), 64.9 (t, 1C), 57.4 (t, 1C), 56.3 (t, 1C), 55.5 (q, 4C), 39.5 (t, 1C). **IR (ATR)** ν_{max} (cm^{-1}) = 2940, 2841, 1758 (C=O), 1737 (C=O), 1582, 1460, 1430, 1260, 1158, 1107, 837, 785, 689. **HR-MS** (EI+) *m/z* calcd. for $C_{27}H_{32}O_{10}$ $[M]^+$: 516.19900, found: 516.19907. **Anal. Calcd**. for. $C_{27}H_{32}O_{10}$: C 62.78%, H 6.24%, Found: C 62.94%, H 6.59%.



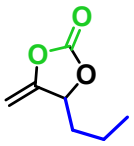
C_1

4-methyl-5-methylene-1,3-dioxolan-2-one (**C_1**). According to ***Procedure 1***. 214 mg (94%). According to ***Procedure 2***. 186 mg (81%). Colorless oil. **^{1}H NMR** (301 MHz, $CDCl_3$) δ 5.28–5.18 (m, 1H), 4.76 (dd, *J* = 4.0, 2.5 Hz, 1H), 4.32 (dd, *J* = 4.0, 2.0 Hz, 1H), 1.51 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 154.6, 151.9, 86.5, 76.3, 20.3. Spectral data match that of literature.[5]



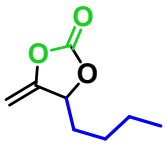
C_2

4-ethyl-5-methylene-1,3-dioxolan-2-one (**C_2**). According to ***Procedure 1***. Colorless oil. 230 mg (90%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 5.17 – 5.11 (m, 1H), 4.86 (dd, *J* = 3.9, 2.4 Hz, 1H), 4.34 (dd, *J* = 3.9, 2.0 Hz, 1H), 2.03 – 1.87 (m, 1H), 1.87 – 1.71 (m, 1H), 1.05 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 153.2, 152.3, 86.9, 80.8, 27.9, 8.0.Spectral data match that of literature.[12]



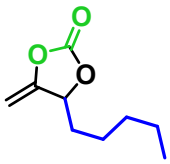
C_3

4-propyl-5-methylene-1,3-dioxolan-2-one (**C_3**). According to ***Procedure 1***. Colorless oil. 261 mg (92%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 5.14 – 5.07 (m, 1H), 4.79 (dd, *J* = 3.9, 2.4 Hz, 1H), 4.28 (dd, *J* = 3.9, 2.0 Hz, 1H), 1.81 – 1.64 (m, 2H), 1.53 – 1.34 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 153.5, 152.1, 86.6, 79.7, 36.7, 17.3, 13.4. Spectral data match that of literature.[10]



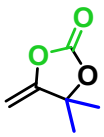
C_4

4-butyl-5-methylene-1,3-dioxolan-2-one (**C_4**). According to ***Procedure 1***. Colorless oil. 275 mg (88%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 5.17–5.10 (m, 1H), 4.79 (dd, *J* = 3.9, 2.4 Hz, 1H), 4.32 (dd, *J* = 3.9, 2.0 Hz, 1H), 1.89–1.65 (m, 2H), 1.49–1.25 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 153.5, 152.1, 86.6, 79.9, 34.4, 25.9, 22.1, 13.7. **IR (ATR)** ν_{max} (cm^{-1}) = 2959, 2873, 1829 (C=O), 1687, 1341, 1147, 1078, 1024, 849, 767. **HR-MS** (EI+) calcd. for $C_8H_{12}O_3$ $[M]^+$: 156.07810, found: 156.07926.



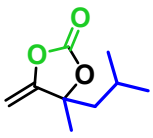
C_5

4-pentyl-5-methylene-1,3-dioxolan-2-one (**C_5**). According to ***Procedure 1***. Colorless oil. 279 mg (82%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 5.16–5.11 (m, 1H), 4.80 (dd, *J* = 3.9, 2.4 Hz, 1H), 4.32 (dd, *J* = 3.9, 2.0 Hz, 1H), 1.84–1.71 (m, 2H), 1.45–1.39 (m, 2H), 1.32–1.26 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 153.5, 152.162 86.7, 79.9, 34.7, 31.2, 23.6, 22.4, 13.9. Spectral data match that of literature.[10]



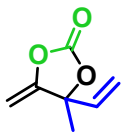
C_7

4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (**C_7**): According to ***Procedure 1***. 235 mg (92%). According to ***Procedure 2***. 217 mg (86%). Colorless oil. **^{1}H NMR** (301 MHz, $CDCl_3$) δ 4.76 (d, *J* = 3.9 Hz, 1H), 4.30 (d, *J* = 3.9 Hz, 1H), 1.61 (s, 6H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 158.8, 151.3, 85.3, 84.6, 27.6. Spectral data match that of literature.[8]



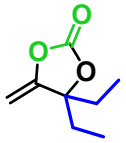
C_8

4-isobutyl-4-methyl-5-methylene-1,3-dioxolan-2-one (**C_8**). According to ***Procedure 2***. Colorless oil. 241 mg (71%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 4.76 (d, *J* = 3.9 Hz, 1H), 4.26 (d, *J* = 3.9 Hz, 1H), 1.86 – 1.72 (m, 2H), 1.69 – 1.61 (m, 1H), 1.55 (s, 3H), 0.94 (dd, *J* = 6.4, 2.0 Hz, 6H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 158.4, 151.5, 87.4, 85.7, 48.6, 27.1, 24.4, 24.0, 23.7. Spectral data match that of literature.[8]



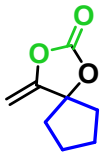
C_9

4-methyl-5-methylene-4-vinyl-1,3-dioxolan-2-one (**C_9**). According to ***Procedure 1***. 224 mg (80%). According to ***Procedure 2***. 193 mg (69%). Colorless oil. **^{1}H NMR** (301 MHz, $CDCl_3$) δ 6.06 – 5.89 (m, 1H), 5.48 (d, *J* = 17.1 Hz, 1H), 5.33 (d, *J* = 10.6 Hz, 1H), 4.87 (d, *J* = 3.9 Hz, 1H), 4.33 (d, *J* = 3.9 Hz, 1H), 1.69 (s, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 157.1, 151.9, 137.0, 117.5, 88.1, 86.7, 26.5. Spectral data match that of literature.[9]



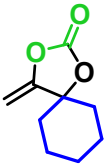
C_{10}

4,4-diethyl-5-methylene-1,3-dioxolan-2-one (**C_{10}**). According to ***Procedure 2***. Colorless oil. 243 mg (78%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 4.80 (d, *J* = 3.8 Hz, 1H), 4.18 (d, *J* = 3.8 Hz, 1H), 1.93 – 1.80 (m, 2H), 1.71 – 1.57 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 155.7, 151.9, 90.9, 85.8, 31.9, 7.1. Spectral data match that of literature.[8]



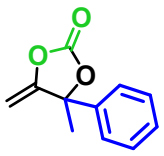
C_{11}

4-methylene-1,3-dioxaspiro[4.4]nonan-2-one (**C_{11}**). According to ***Procedure 2***. Colorless oil. 249 mg (81%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 4.70 (d, *J* = 4.0 Hz, 1H), 4.30 (d, *J* = 4.0 Hz, 1H), 2.19 – 2.09 (m, 2H), 1.91 – 1.74 (m, 6H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 157.7, 151.3, 94.2, 85.3, 40.5, 24.2. Spectral data match that of literature.[11]



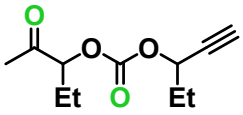
C_{12}

4-methylene-1,3-dioxaspiro[4.5]decan-2-one (**C_{12}**). According to ***Procedure 2***. Colorless oil. 281 mg (84%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 4.70 (d, *J* = 3.9 Hz, 1H), 4.26 (d, *J* = 3.9 Hz, 1H), 2.02 – 1.89 (m, 2H), 1.74 – 1.54 (m, 7H), 1.36 – 1.20 (m, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 158.7, 151.5, 86.4, 85.5, 36.5, 24.3, 21.6. Spectral data match that of literature.[8]



C_{13}

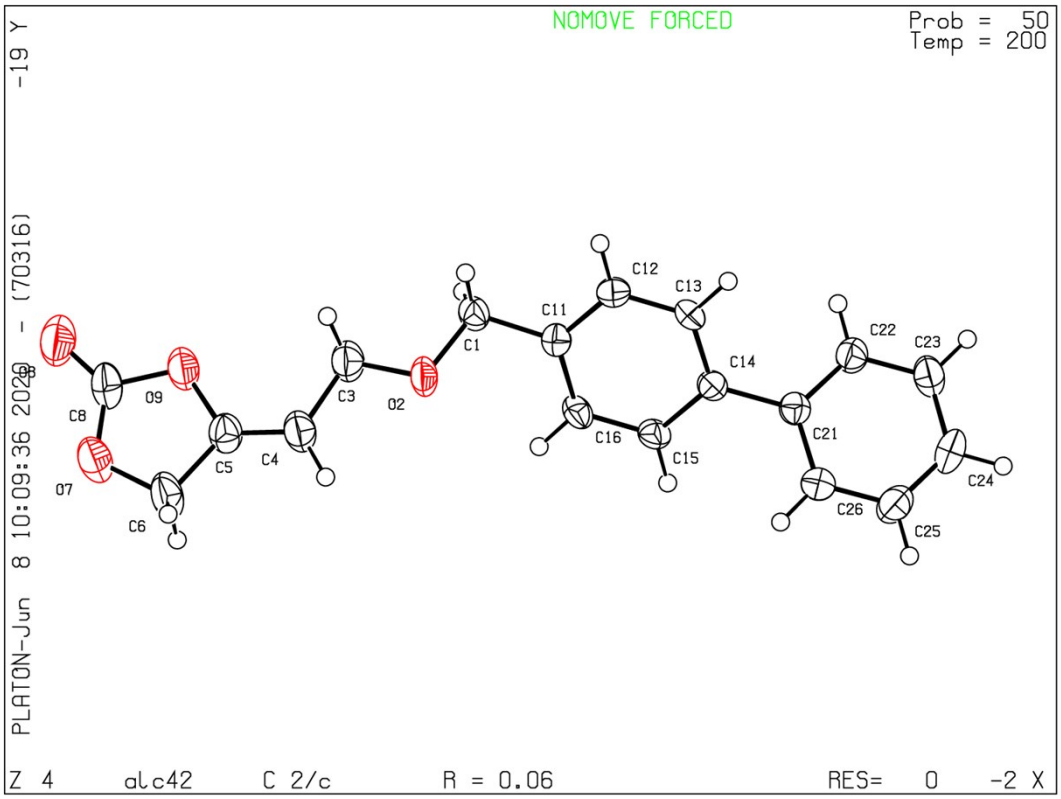
4-methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one (**C_{13}**). According to ***Procedure 2***. Yellowish oil. 346 mg (91%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.45 – 7.38 (m, 3H), 4.94 (d, *J* = 4.1 Hz, 1H), 4.51 (d, *J* = 4.1 Hz, 1H), 1.97 (s, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 157.4, 151.2, 139.3, 129.2, 128.9, 124.7, 88.2, 27.3. Spectral data match that of literature.[11]



D_1

2-oxopentan-3-yl pent-1-yn-3-yl carbonate (**D_1**). According to ***Procedure 1*** the reaction of 1-pentyn-3-ol (2 mmol) and [Cu] cat. (5 mol%) under CO_2 (1 MPa) afforded **D_1** as a colorless oil. 106 mg (50%). **^{1}H NMR** (301 MHz, $CDCl_3$) δ 5.18 – 5.11 (m, 1H), 4.85 (td, *J* = 7.6, 4.7 Hz, 1H), 2.52 (dd, *J* = 2.1, 0.8 Hz, 1H), 2.17 (d, *J* = 3.0 Hz, 3H), 1.92 – 1.74 (m, 4H), 1.07 – 0.95 (m, 6H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 205.1, 204.7, 154.1, 83.2, 82.9, 80.1, 79.9, 74.8, 74.7, 69.5, 69.4, 27.9, 27.8, 26.1, 25.9, 23.9, 23.8, 9.4, 9.3, 9.1, 9.0. **IR (ATR)** ν_{max} (cm^{-1}) = 3277 (≡C-H), 2964, 2876, 2123, 1752 (C=O), 1731 (C=O),1688, 1466, 1283, 1150, 1108, 1070, 1036, 953, 851, 787, 768, 651. **LR-MS** (EI+) *m/z* calcd. for $C_{11}H_{16}O_4$ $[M]^+$: 212.1049, found: 212.1032. **Anal. Calcd**. for. $C_{11}H_{16}O_4$: C 62.25%, H 7.60%, Found: C 62.02%, H 7.83%.

Figure S7. X-ray structure of $\mathbf{A_8}$ (PLATON representation). Ellipsoids are drawn at 50% thermal probability.



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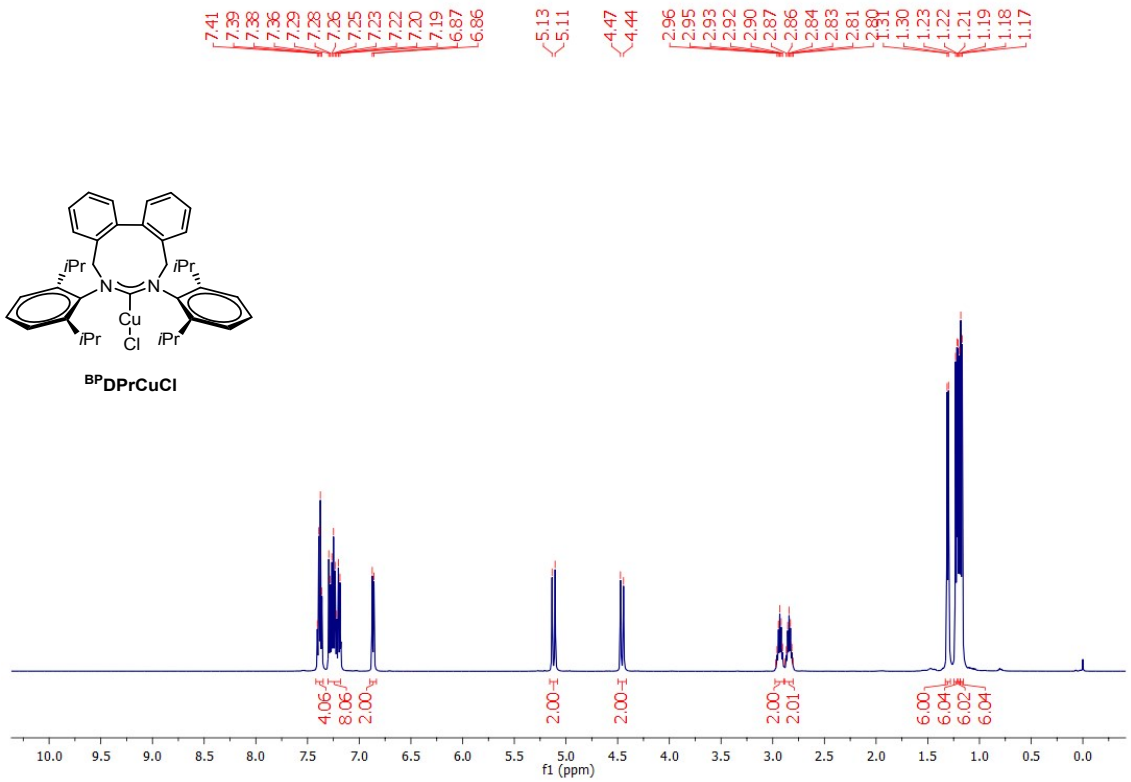
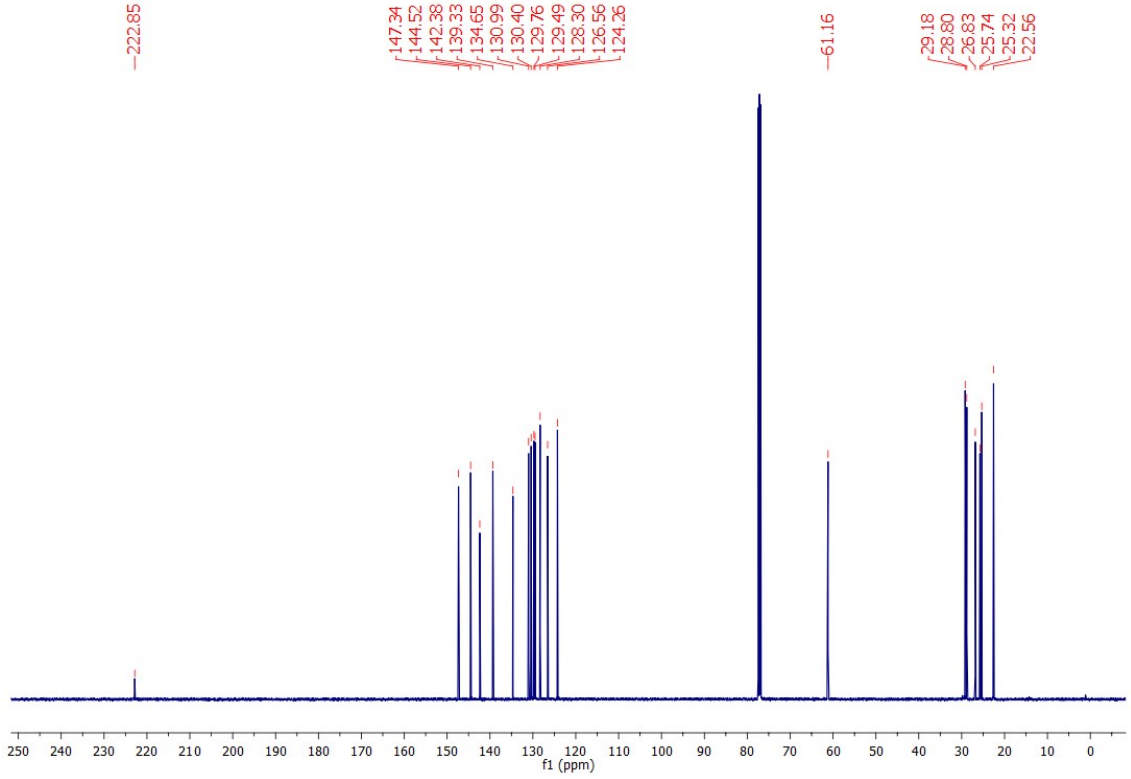
10. Copies of NMR spectra

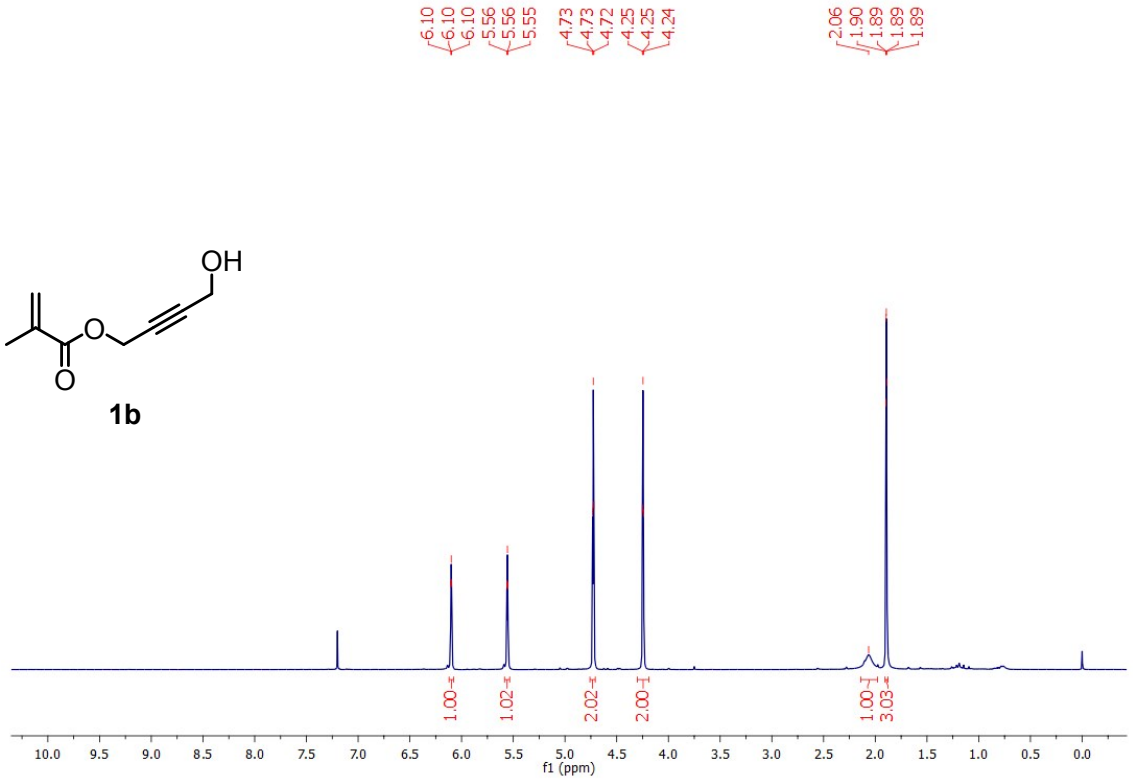
^{1}H NMR and ^{13}C NMR of ^{BP}DPrCuCl



^{BP}DPrCuCl



^{1}H NMR and **^{13}C NMR** of **1b**



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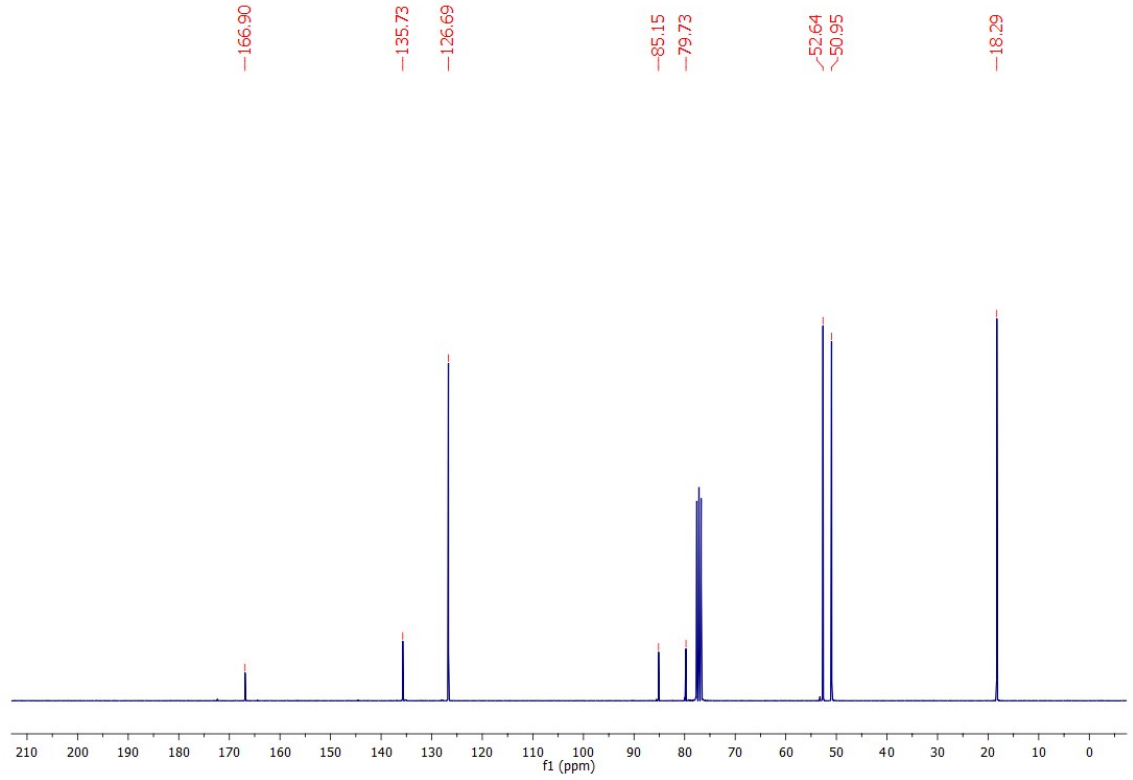

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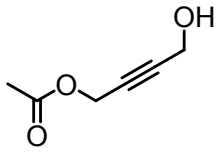

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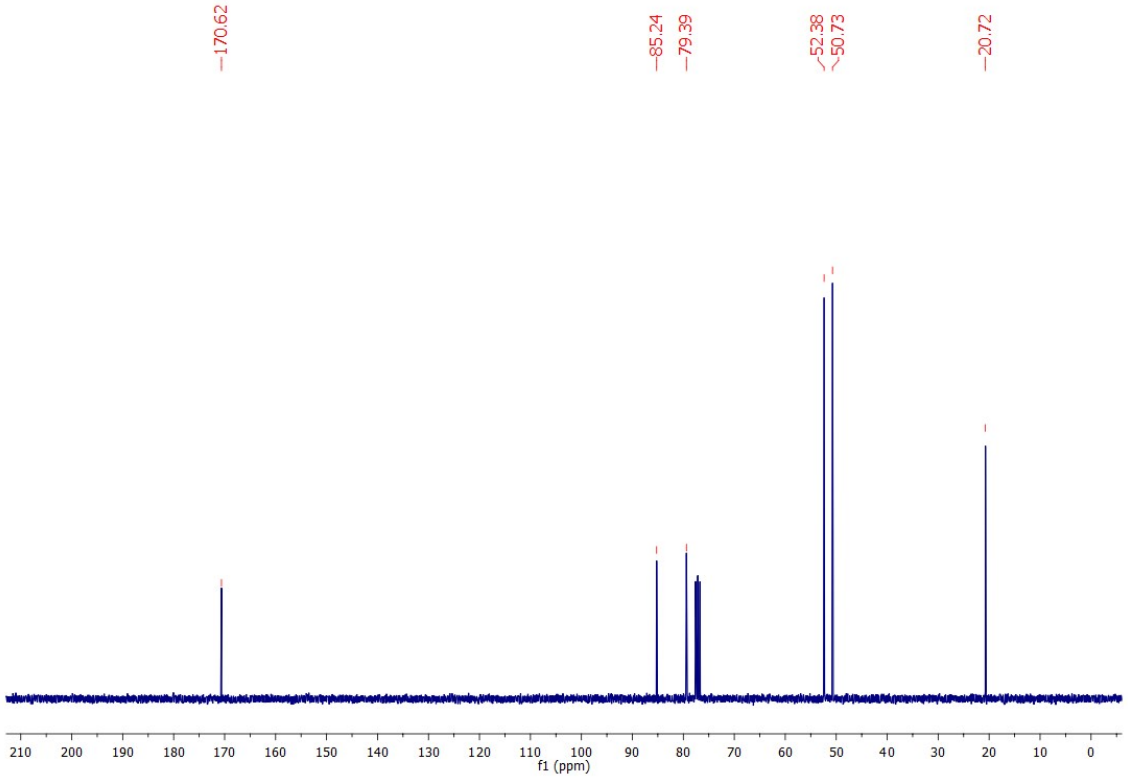

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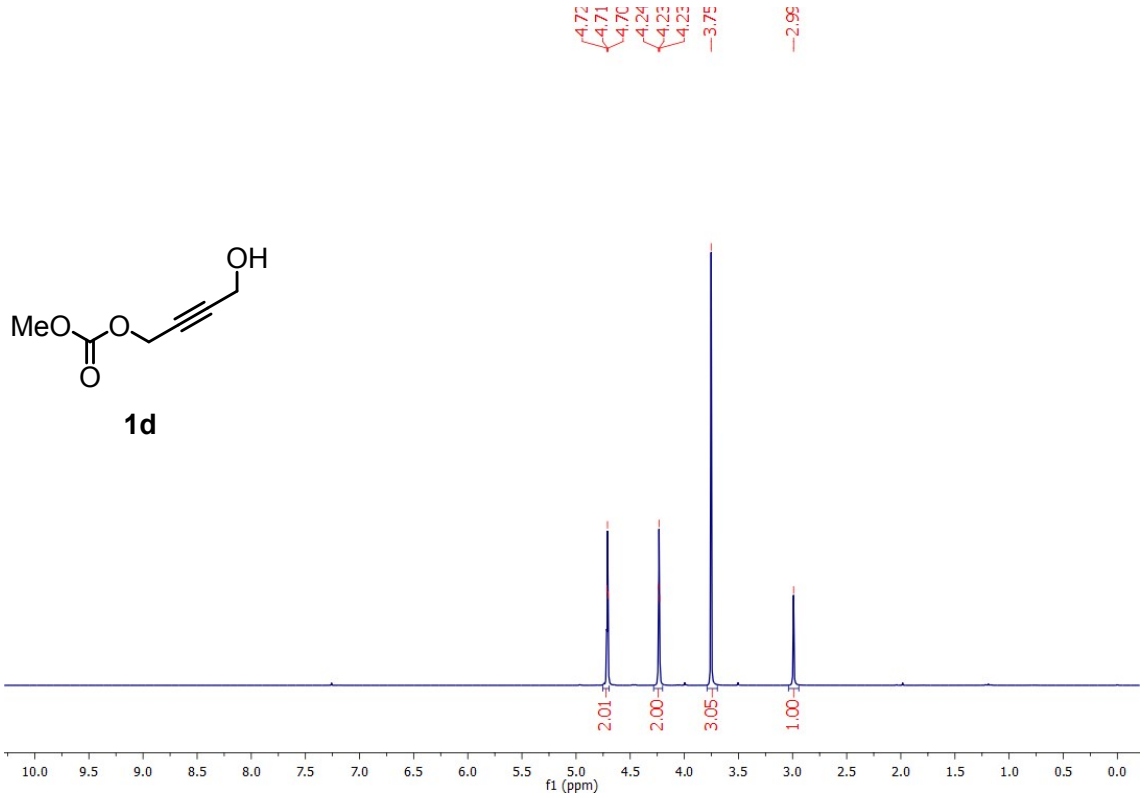

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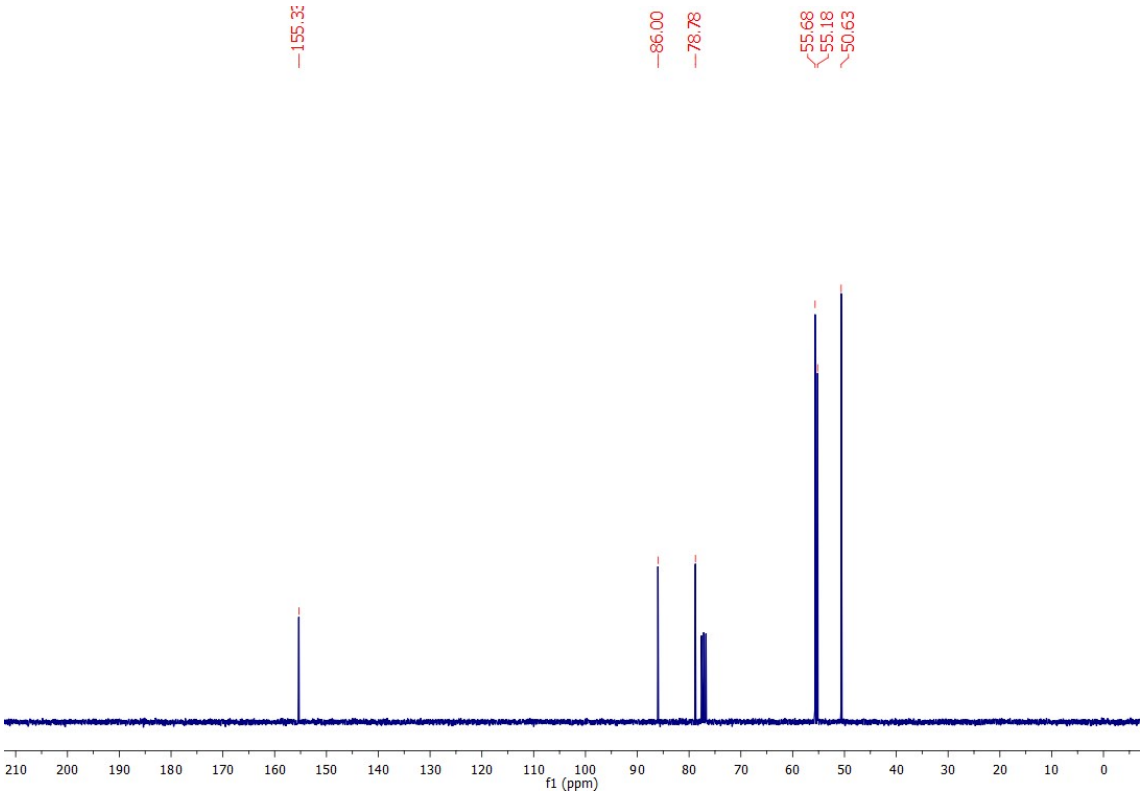

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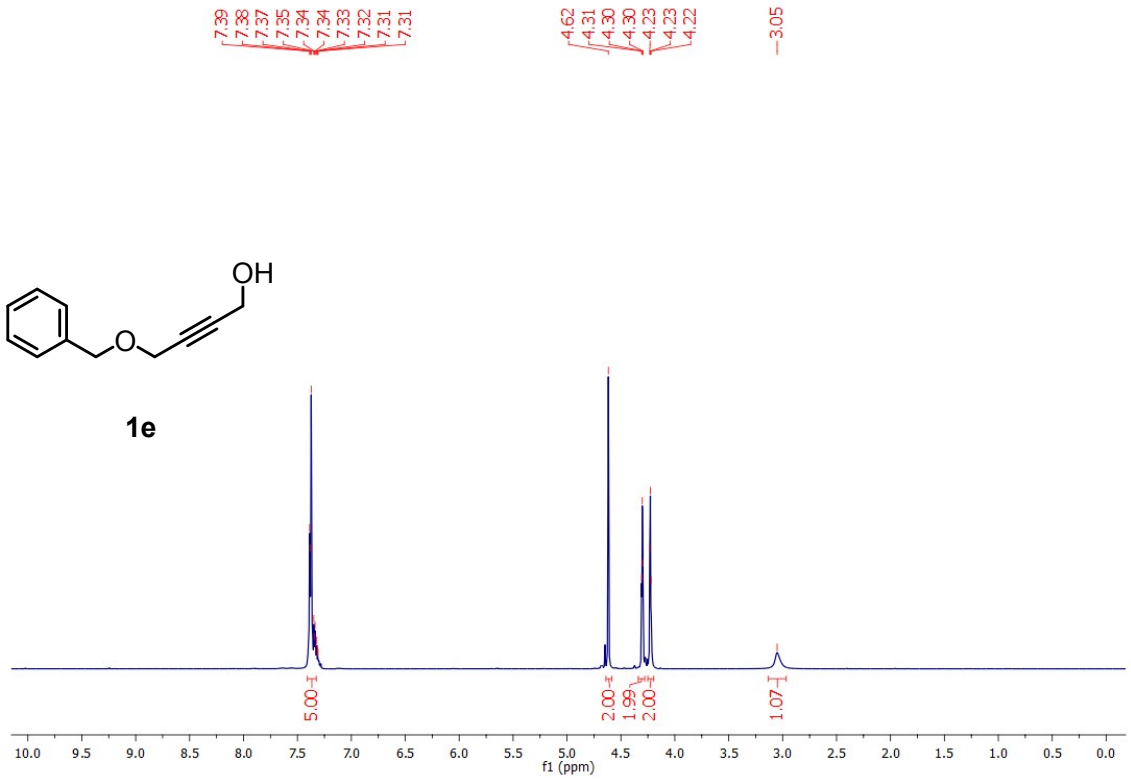

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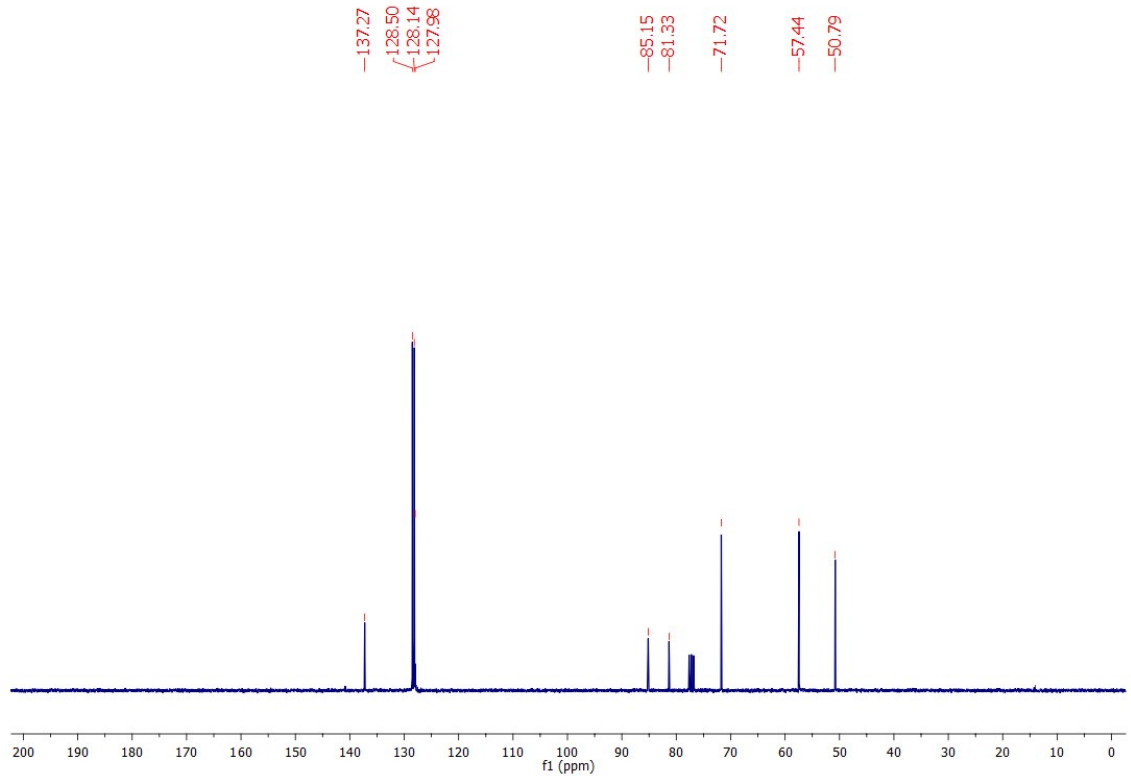

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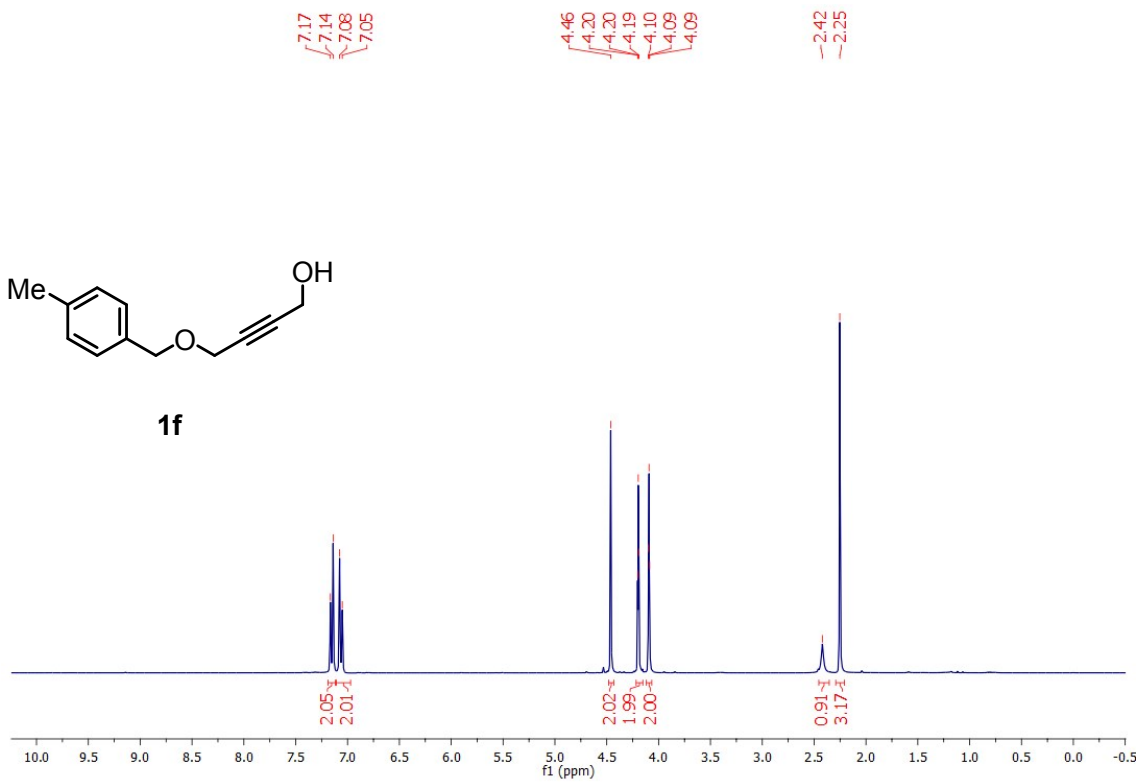

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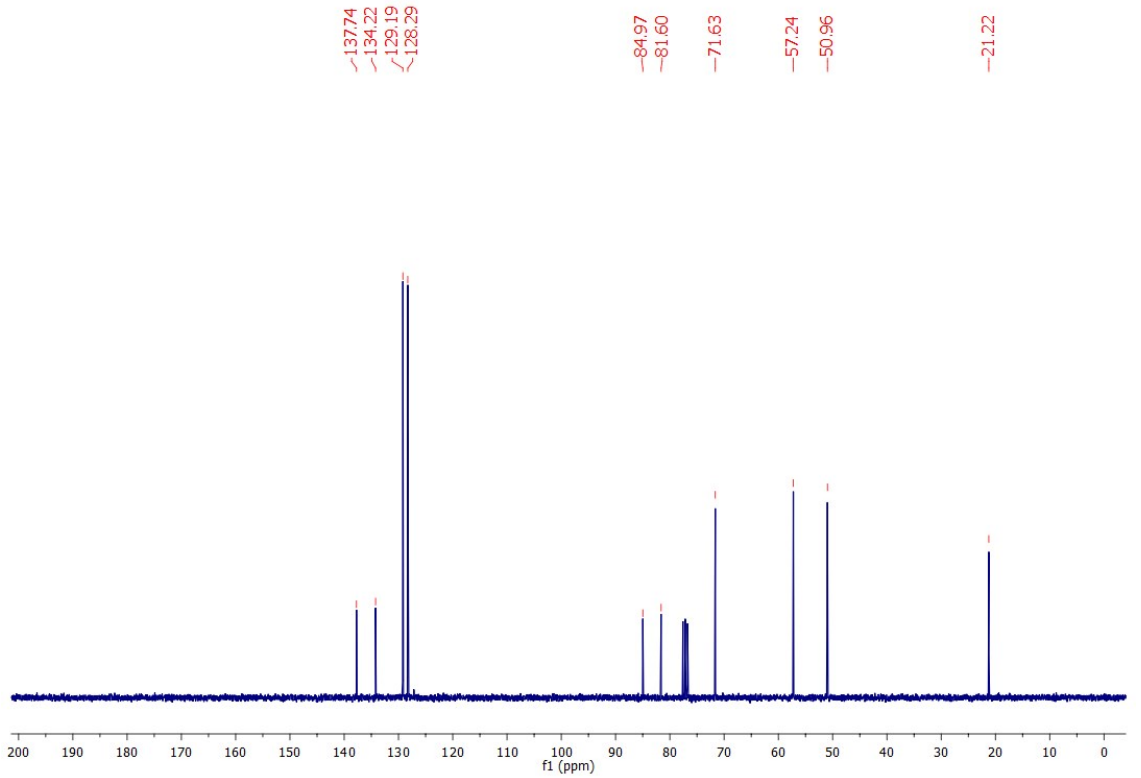

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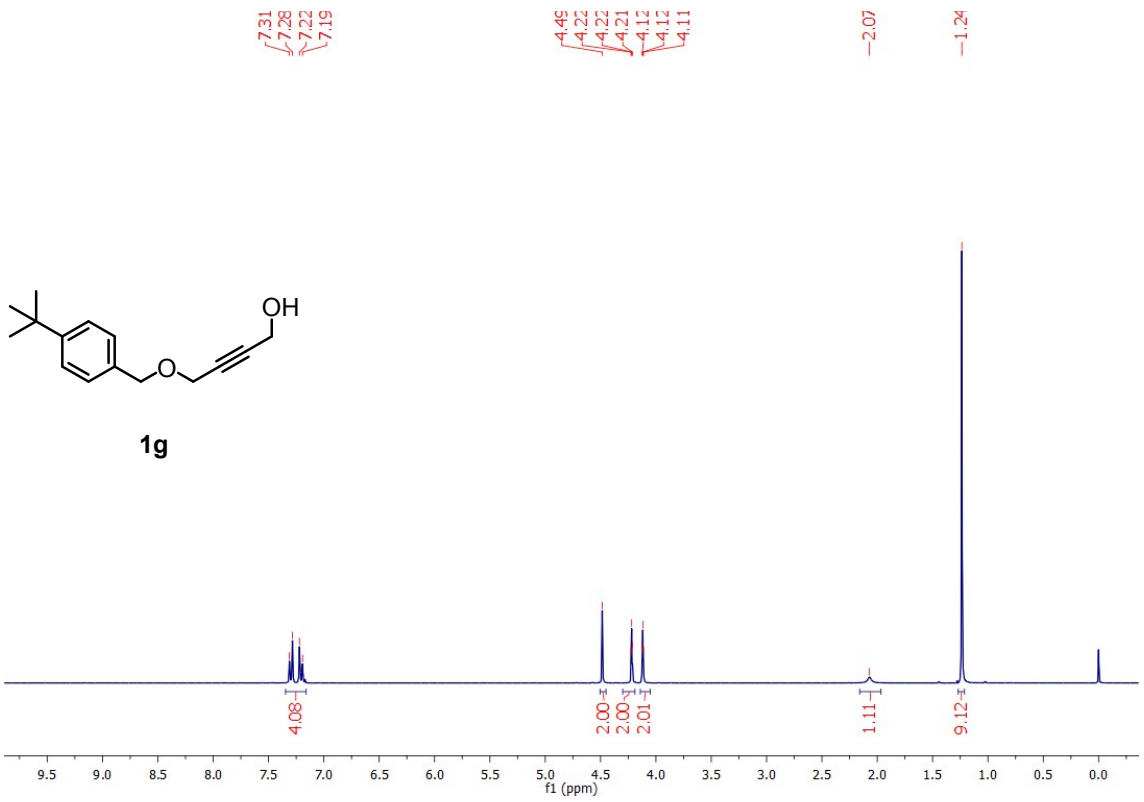

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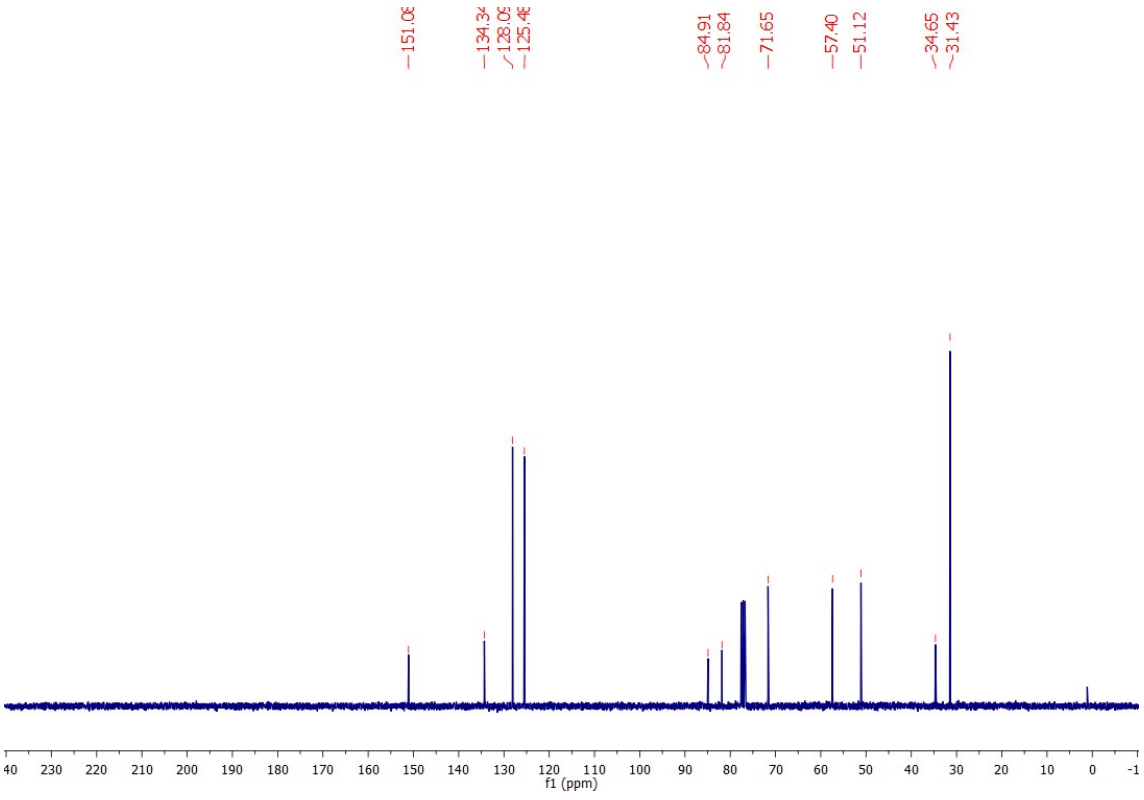

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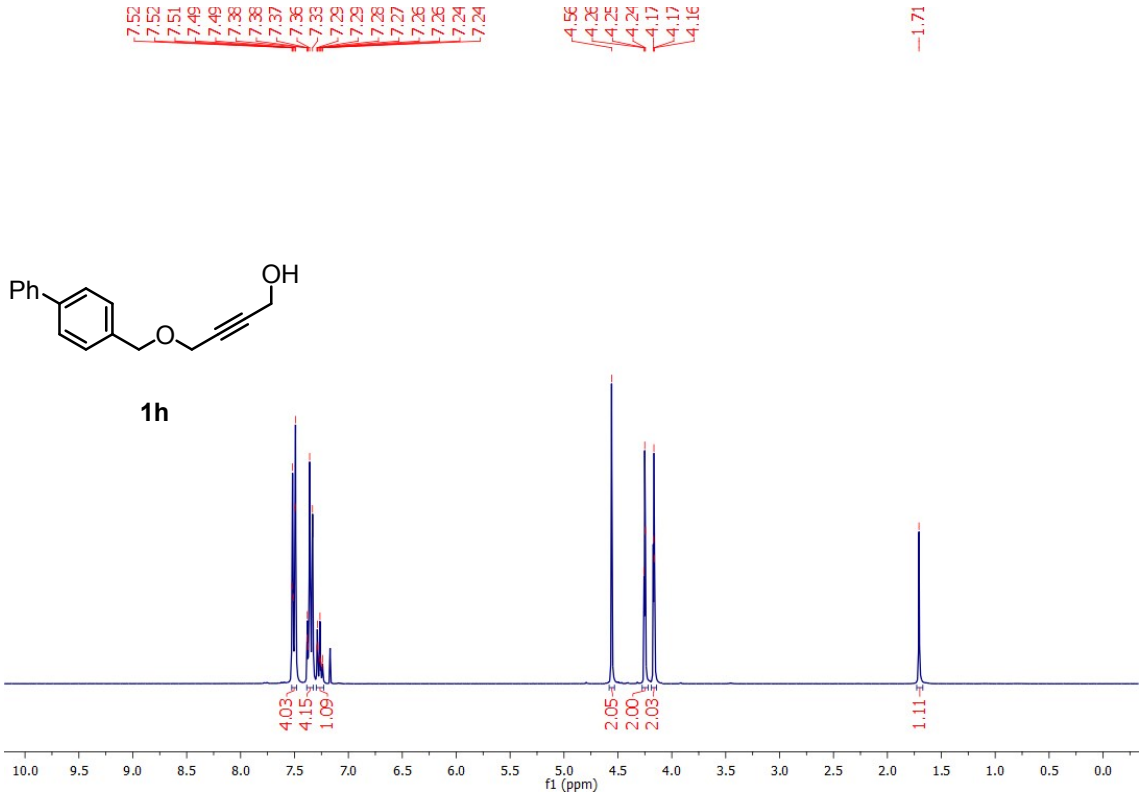

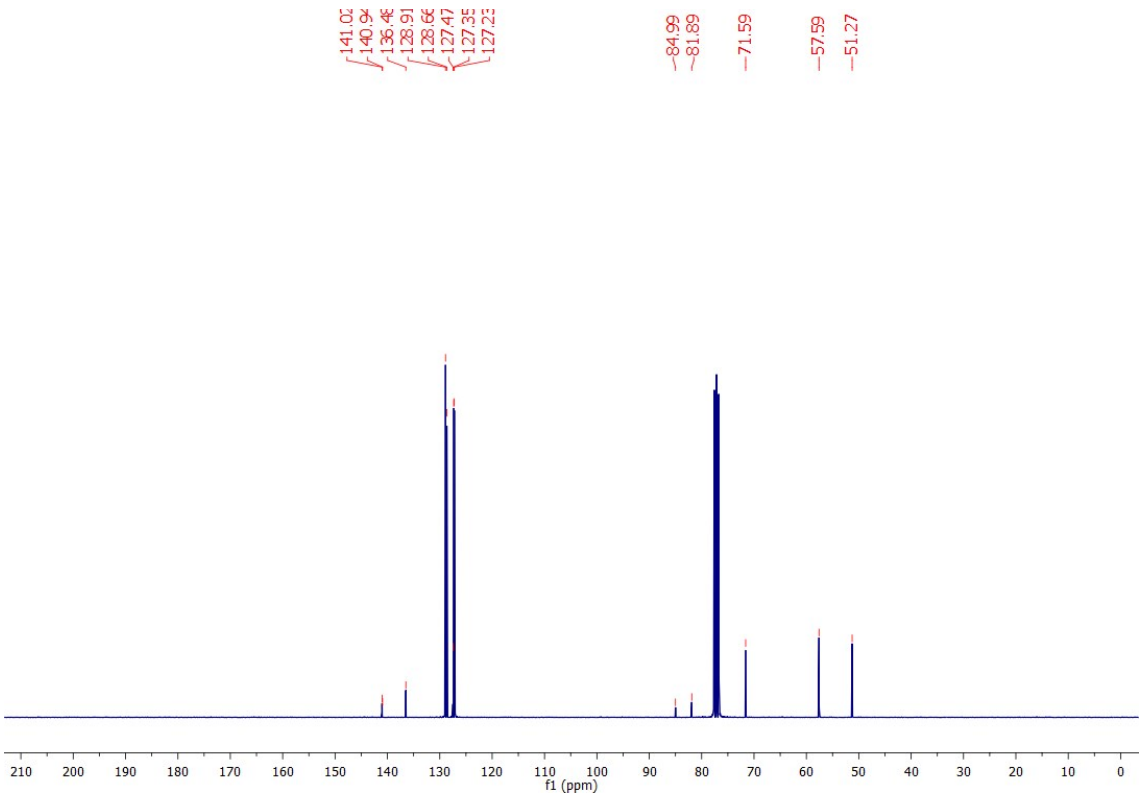

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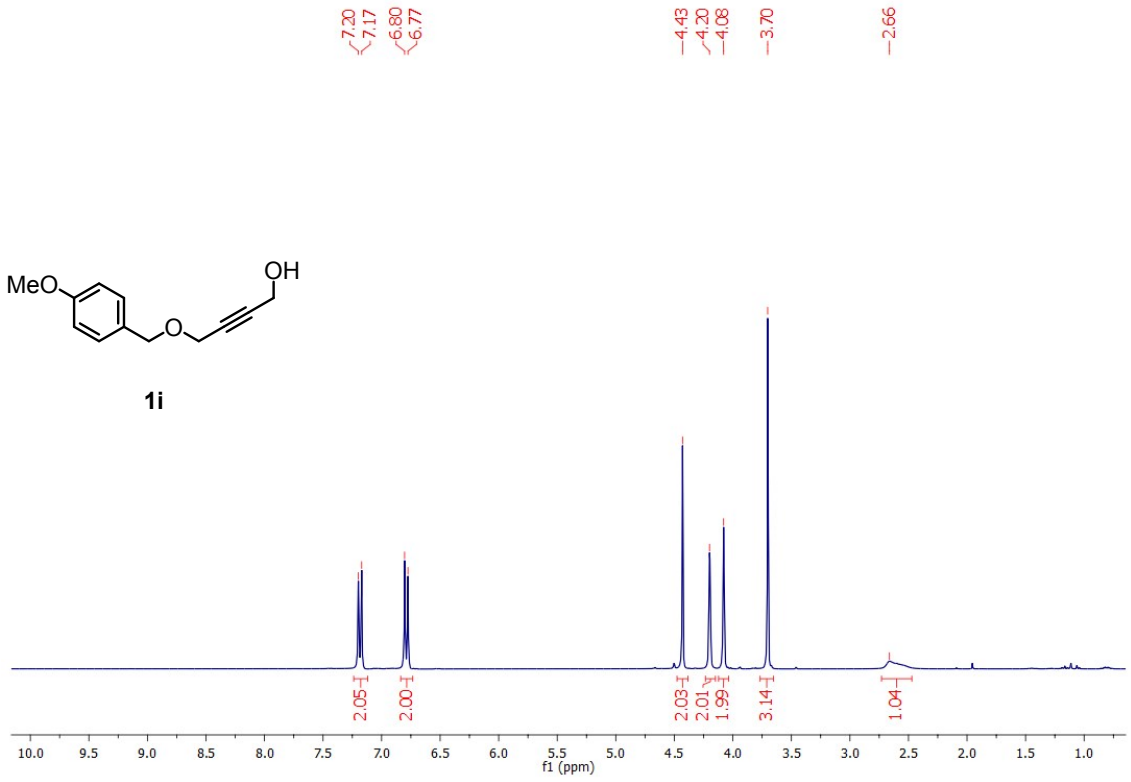

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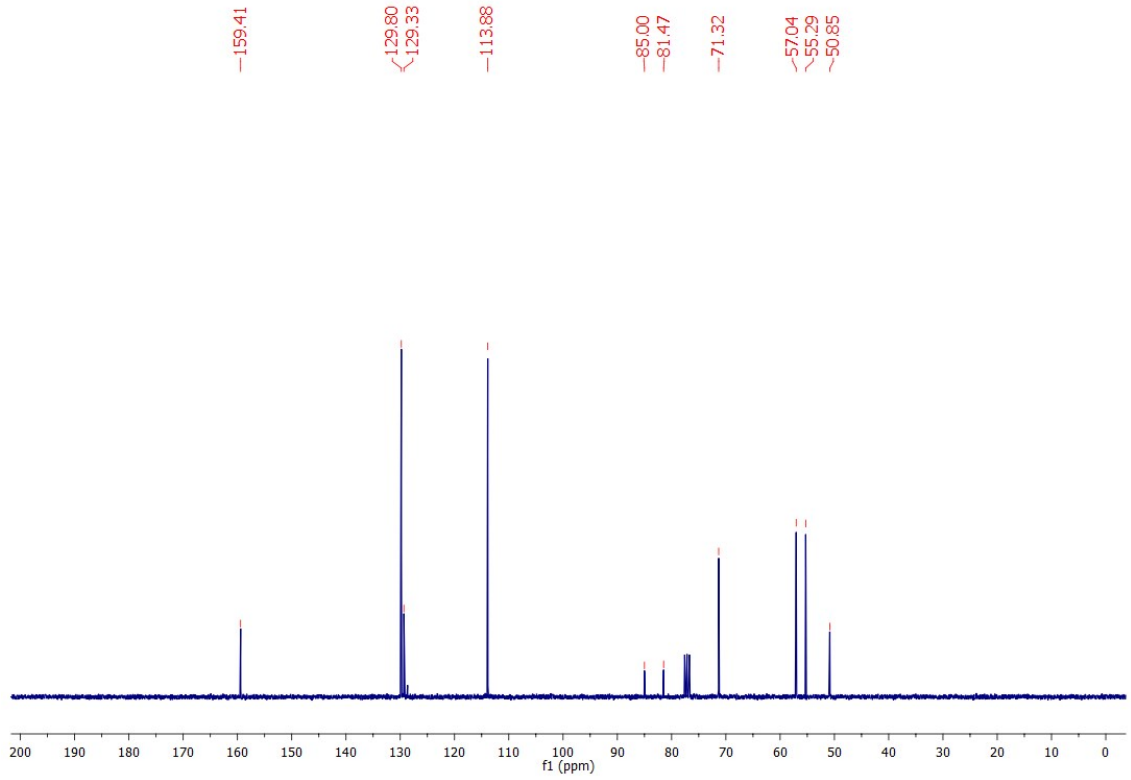

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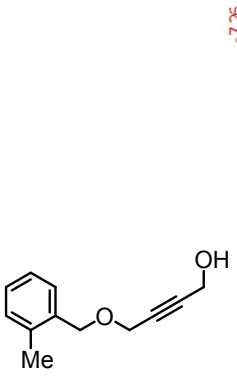

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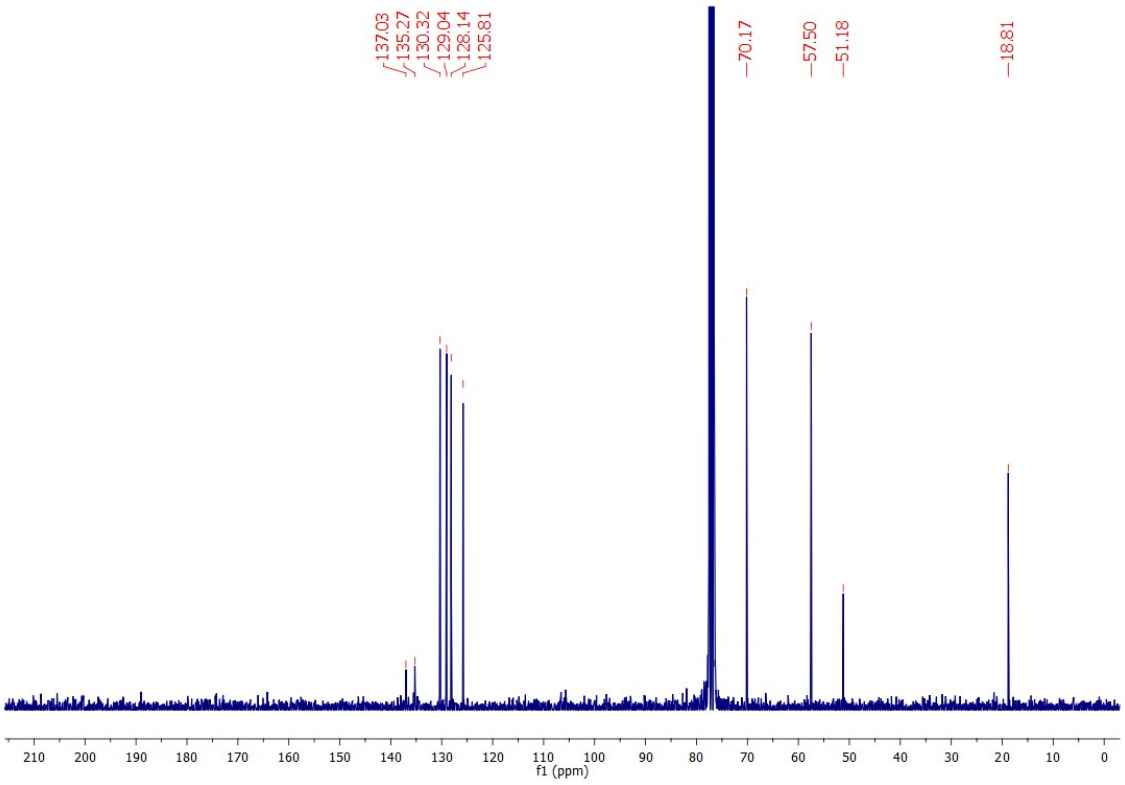

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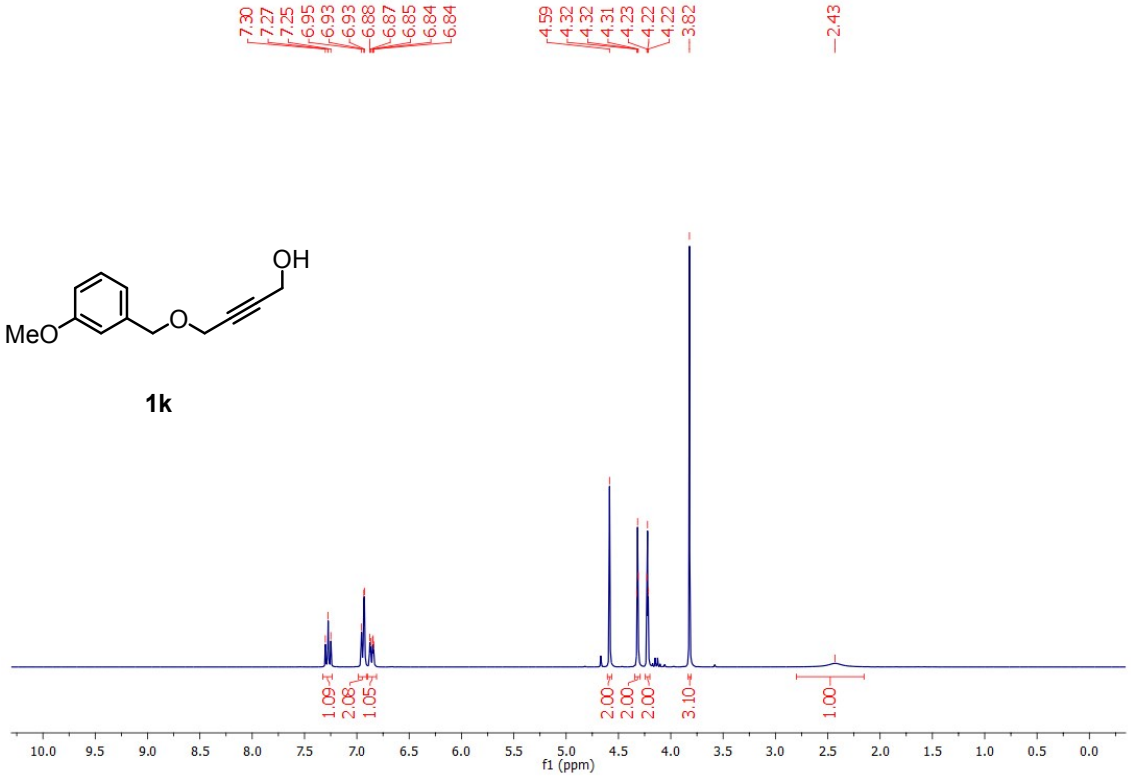

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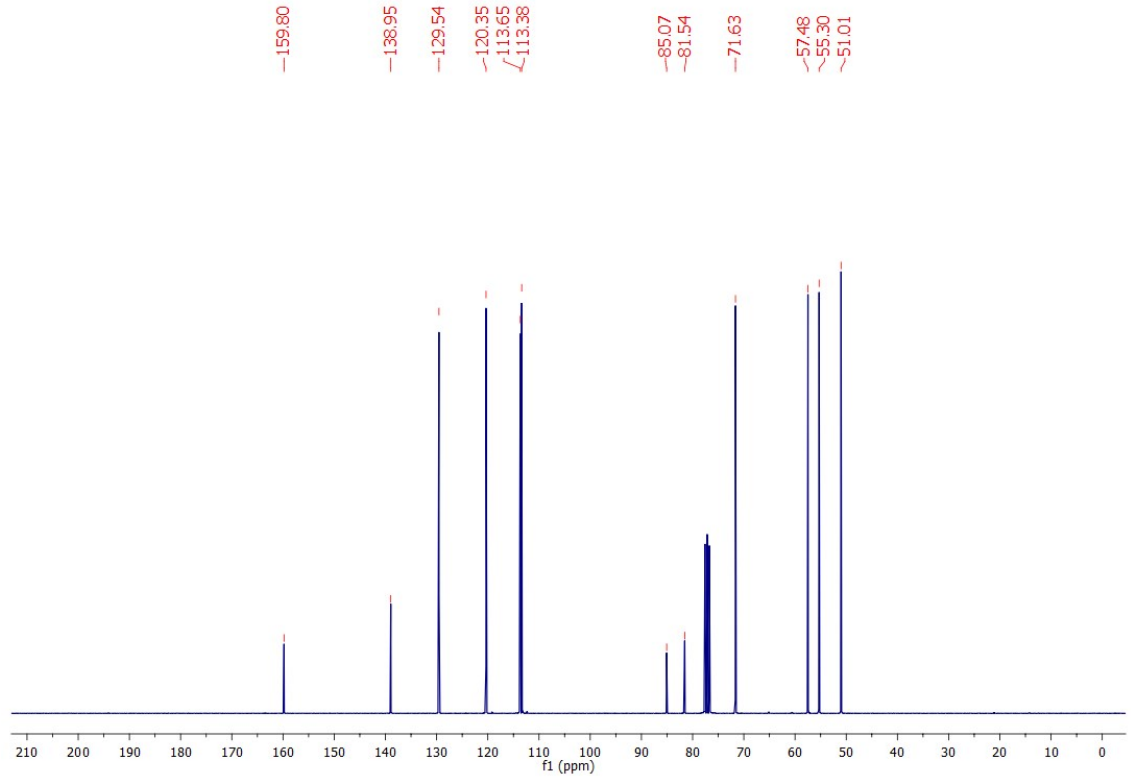

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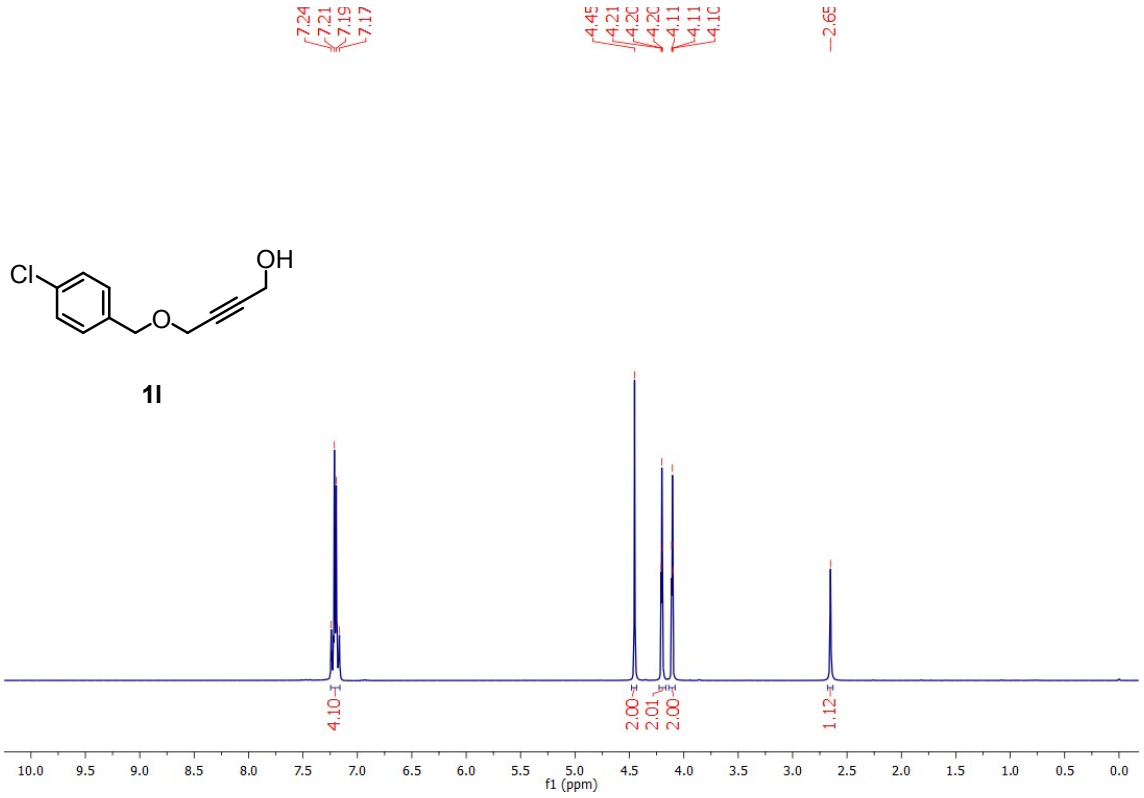

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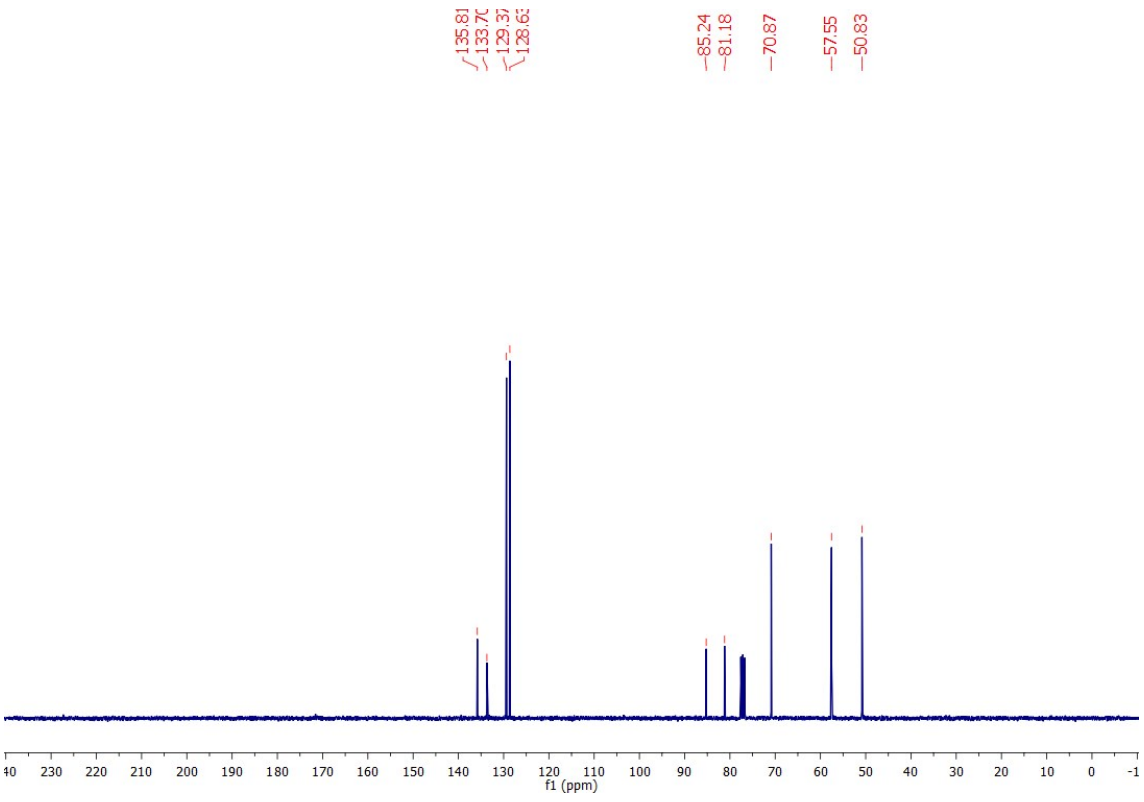

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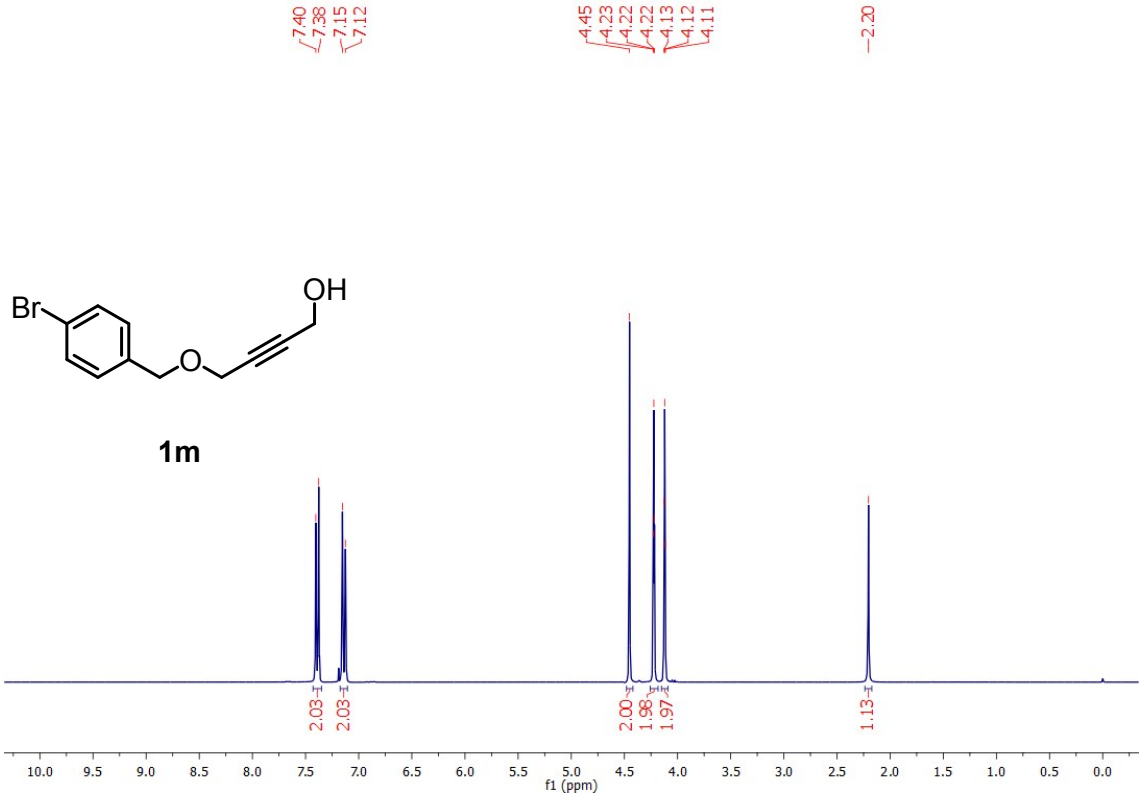

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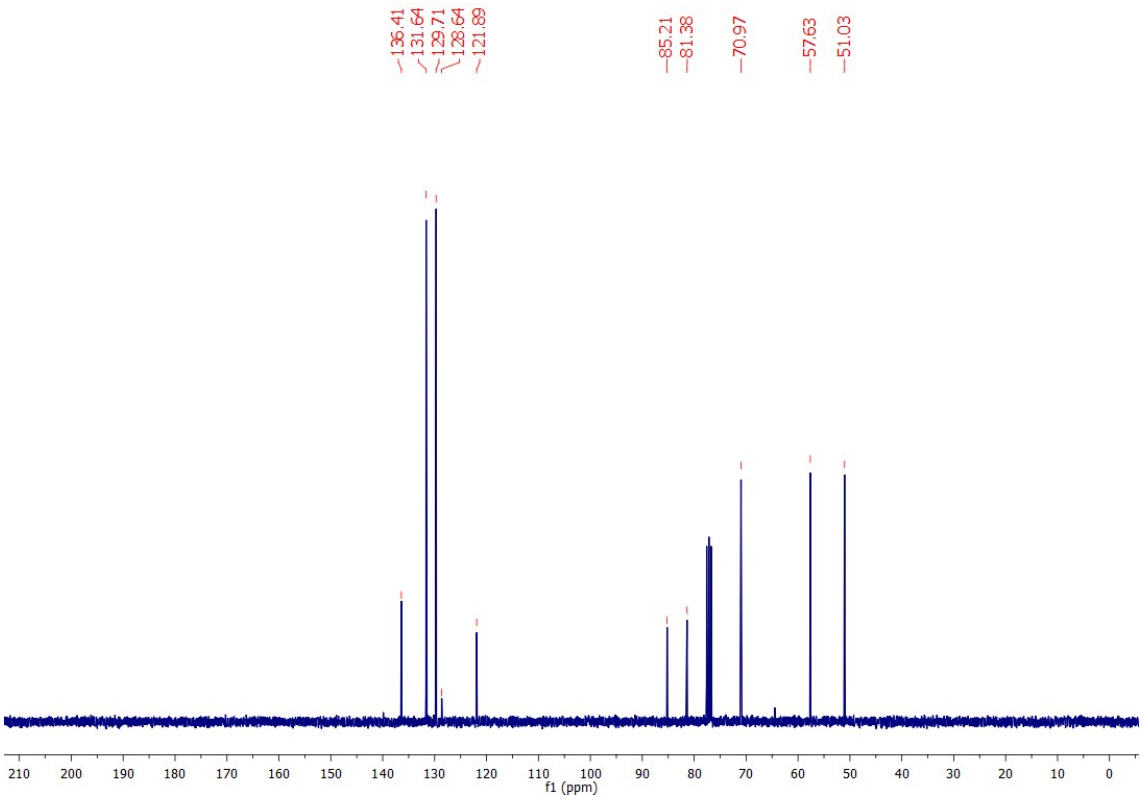

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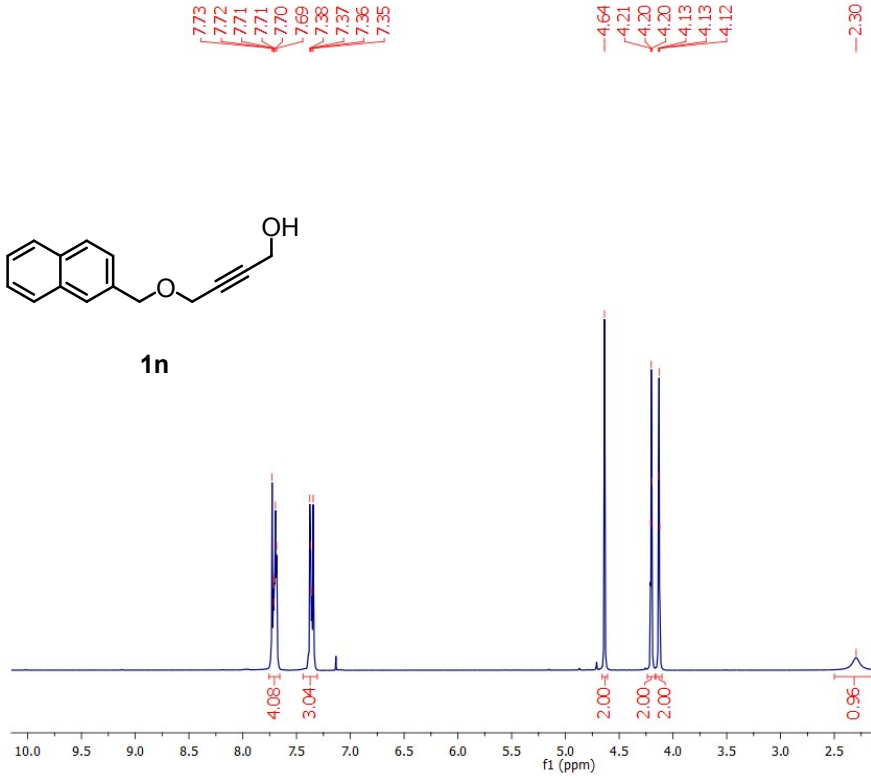

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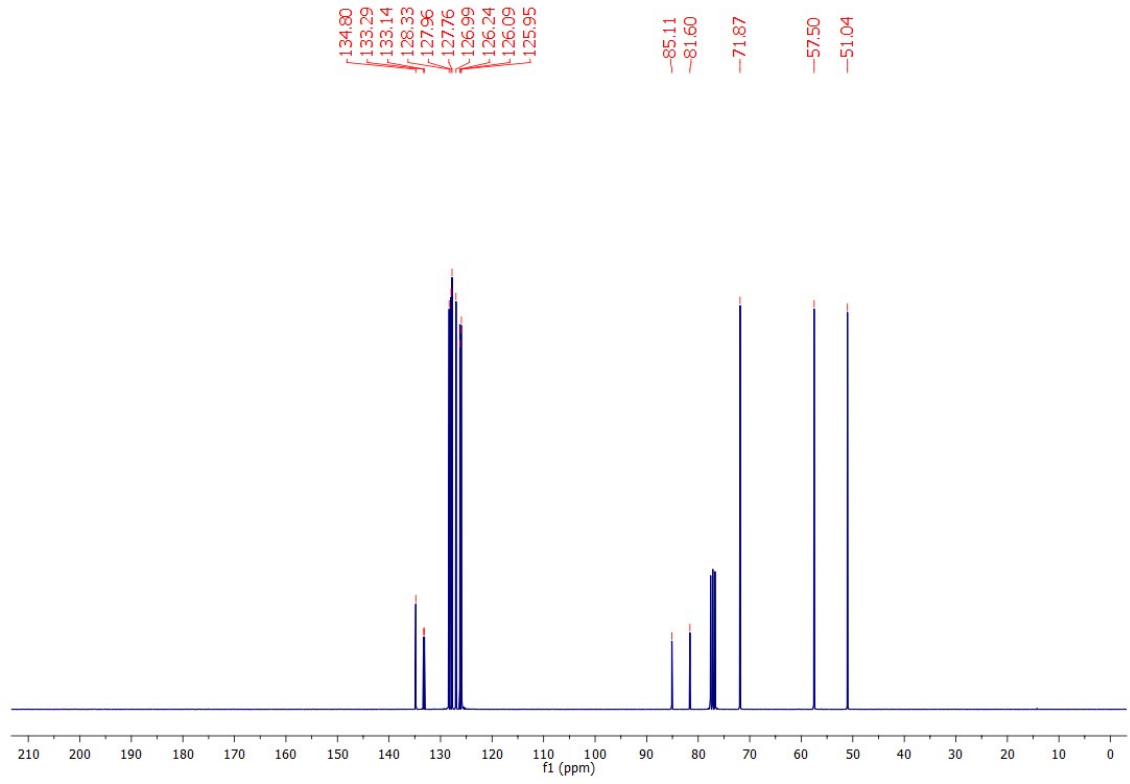
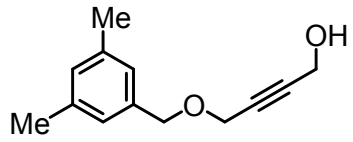


^{1}H NMR and **^{13}C NMR** of **1o**



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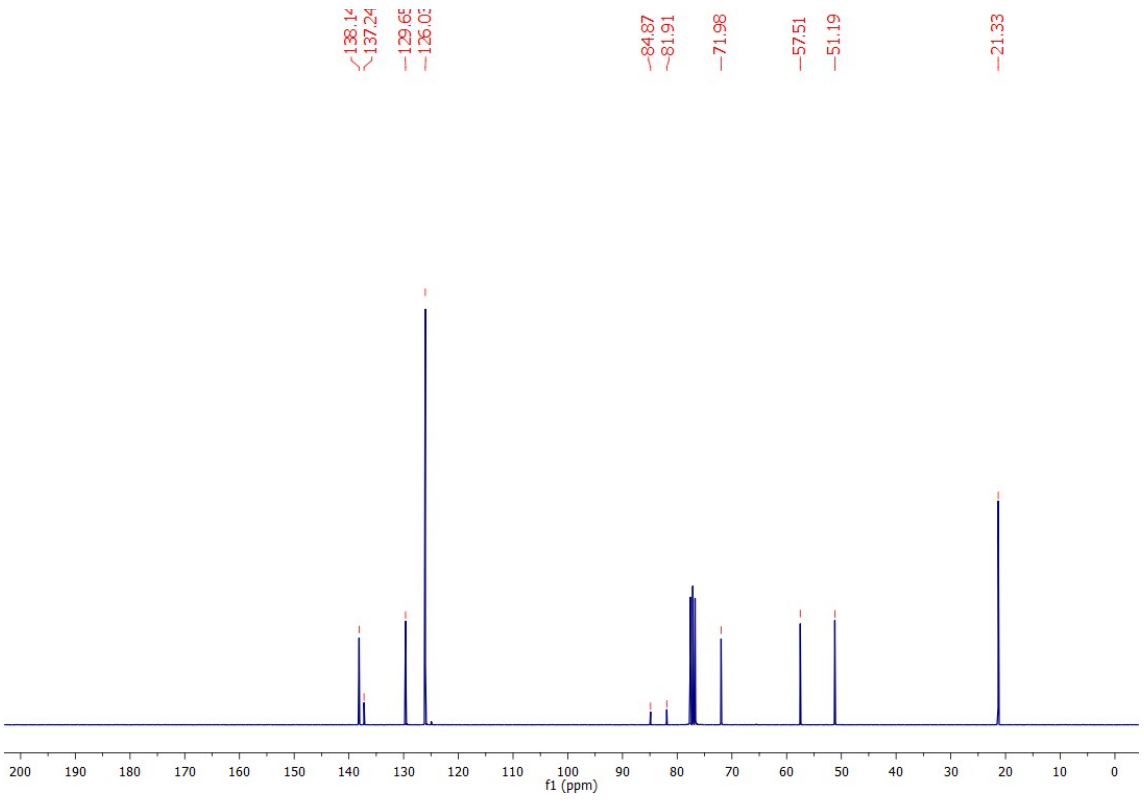

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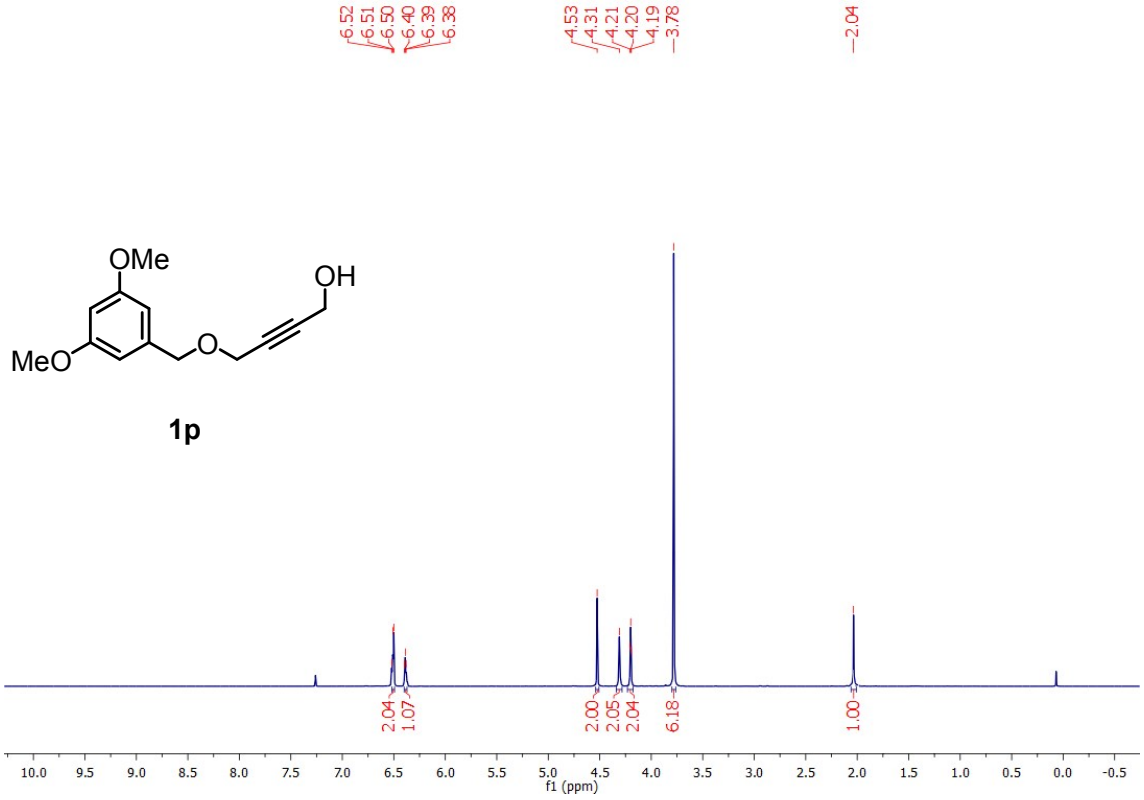

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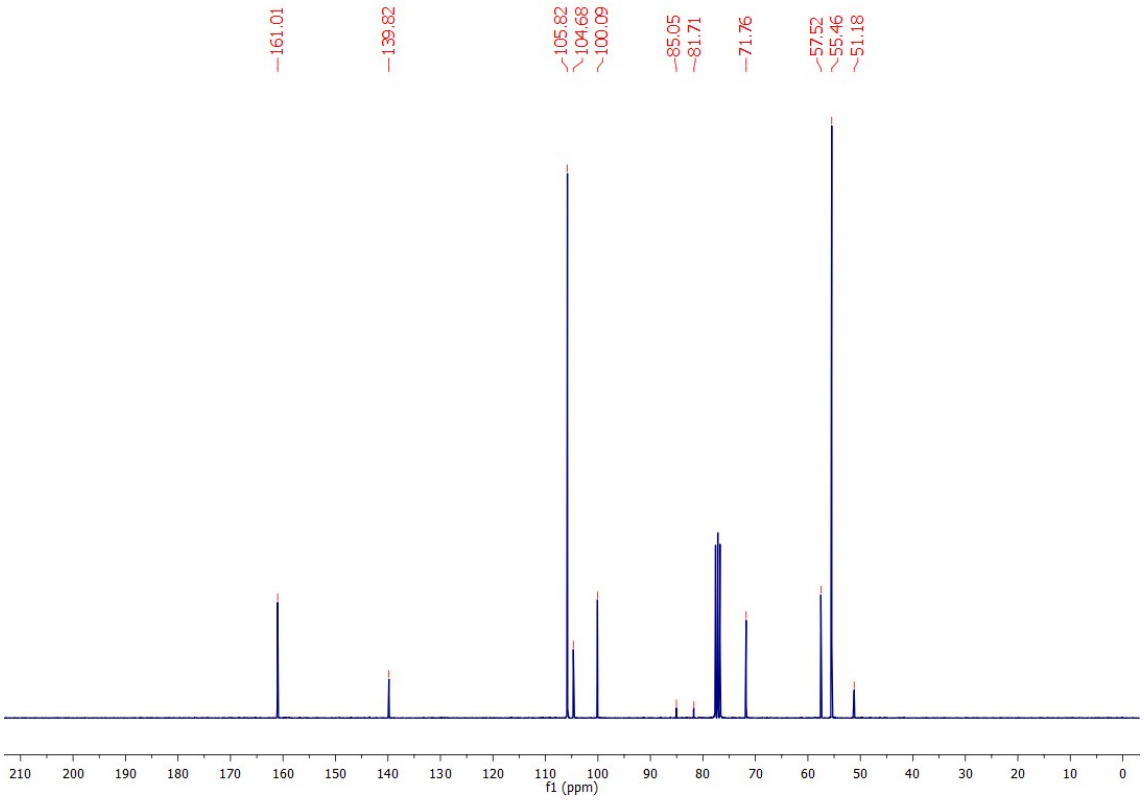

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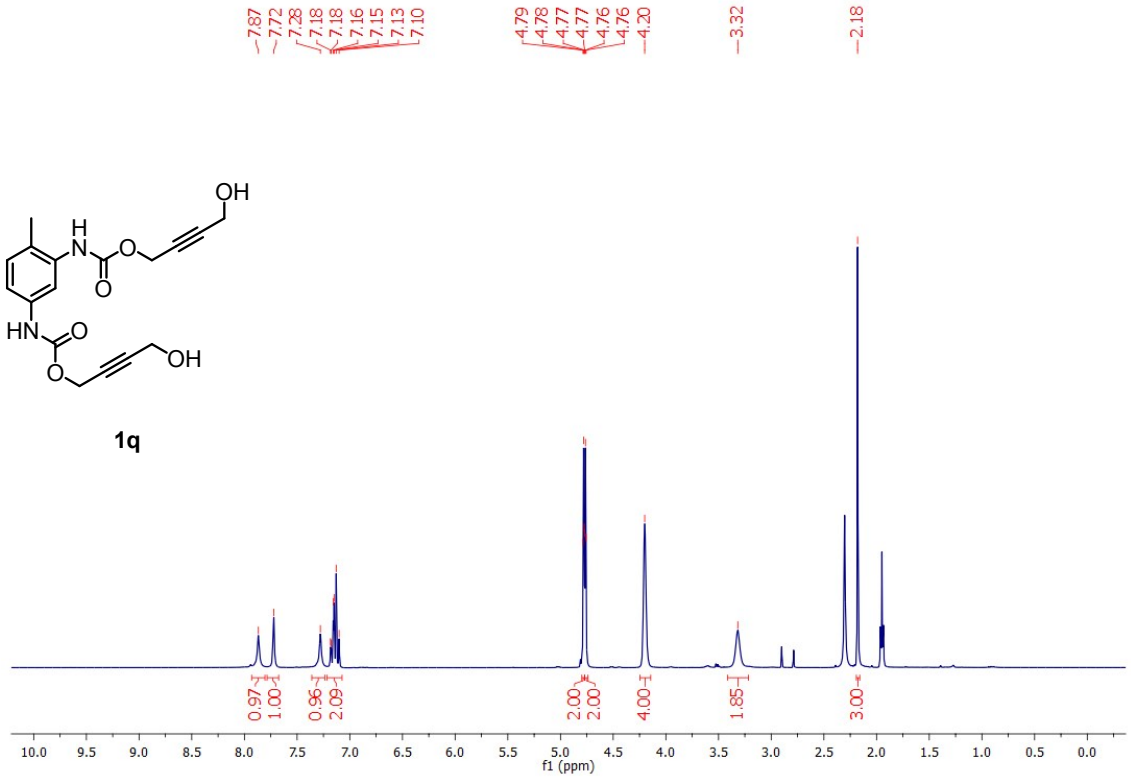

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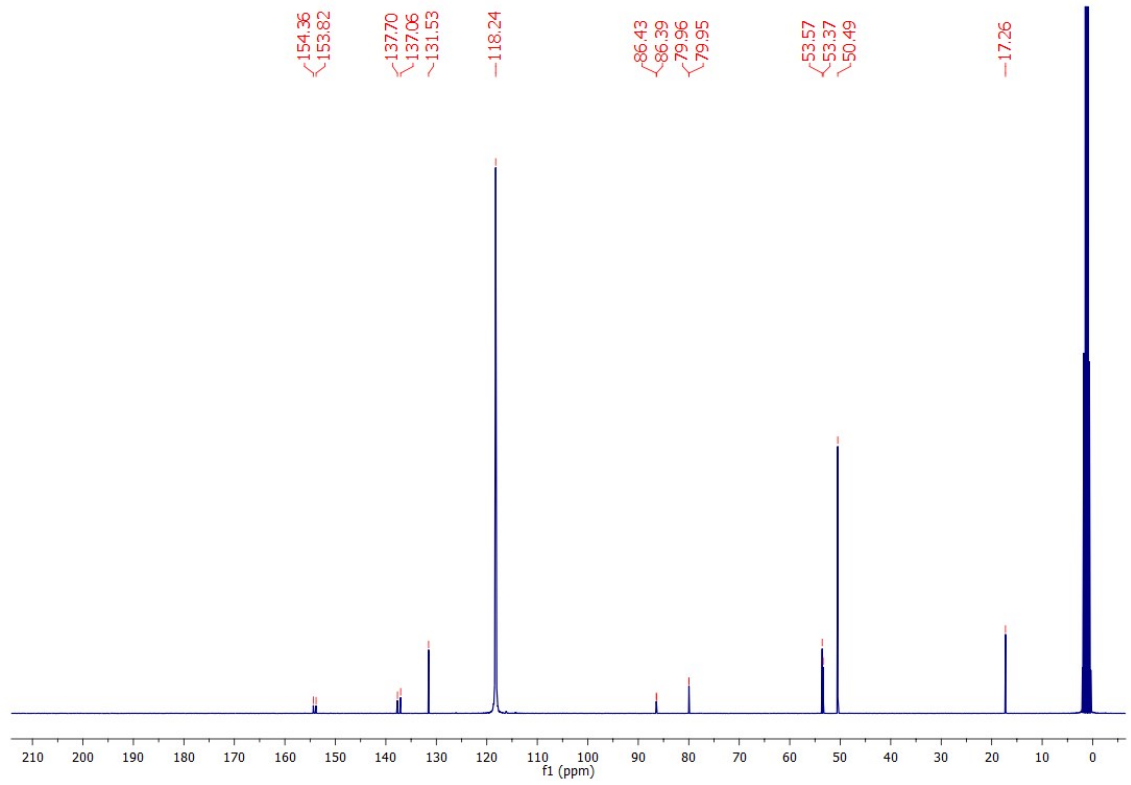
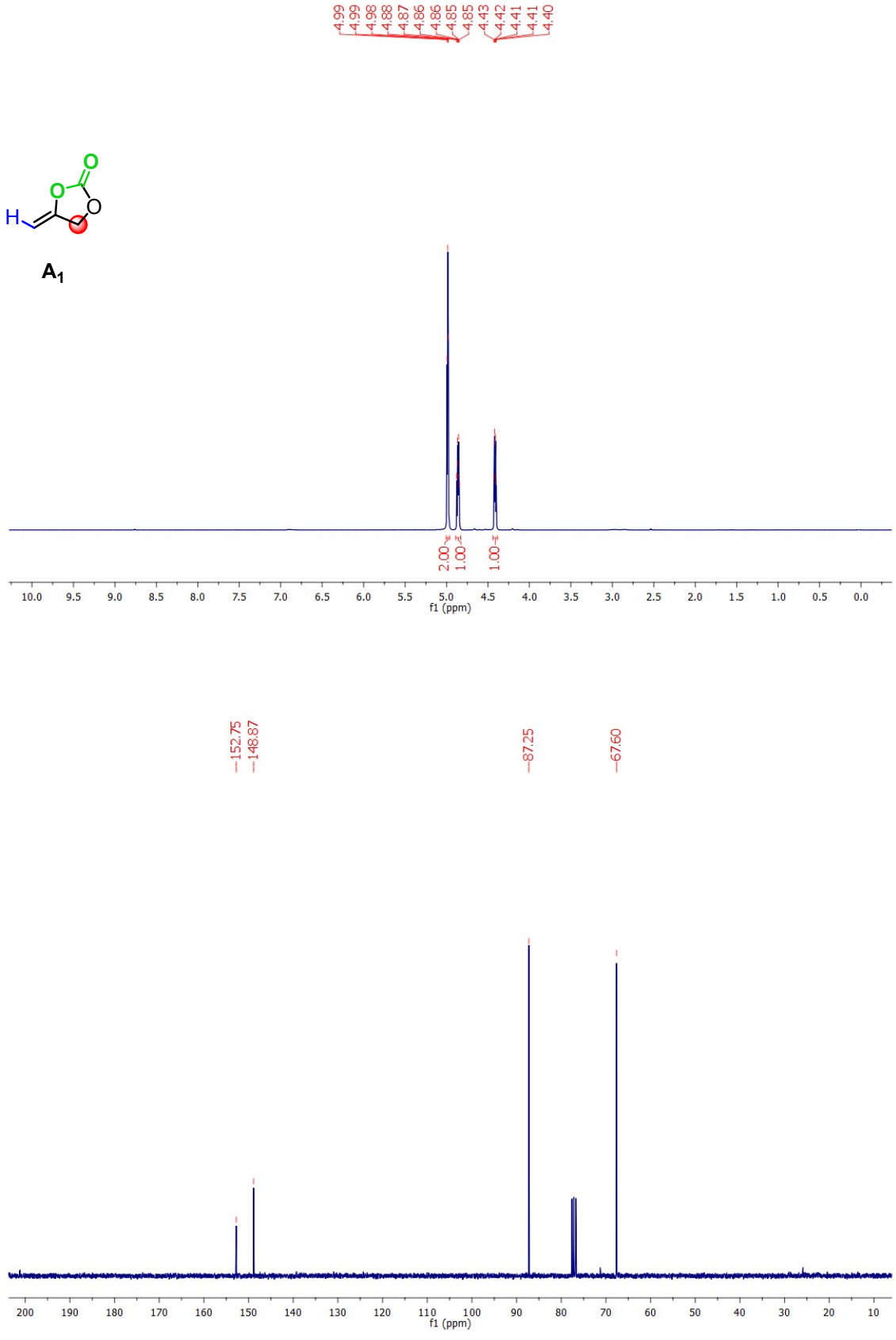
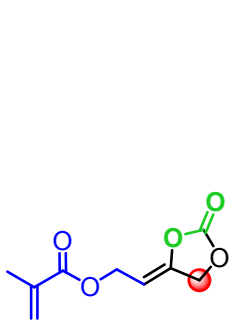


^{1}H NMR and **^{13}C NMR** of **A_1**

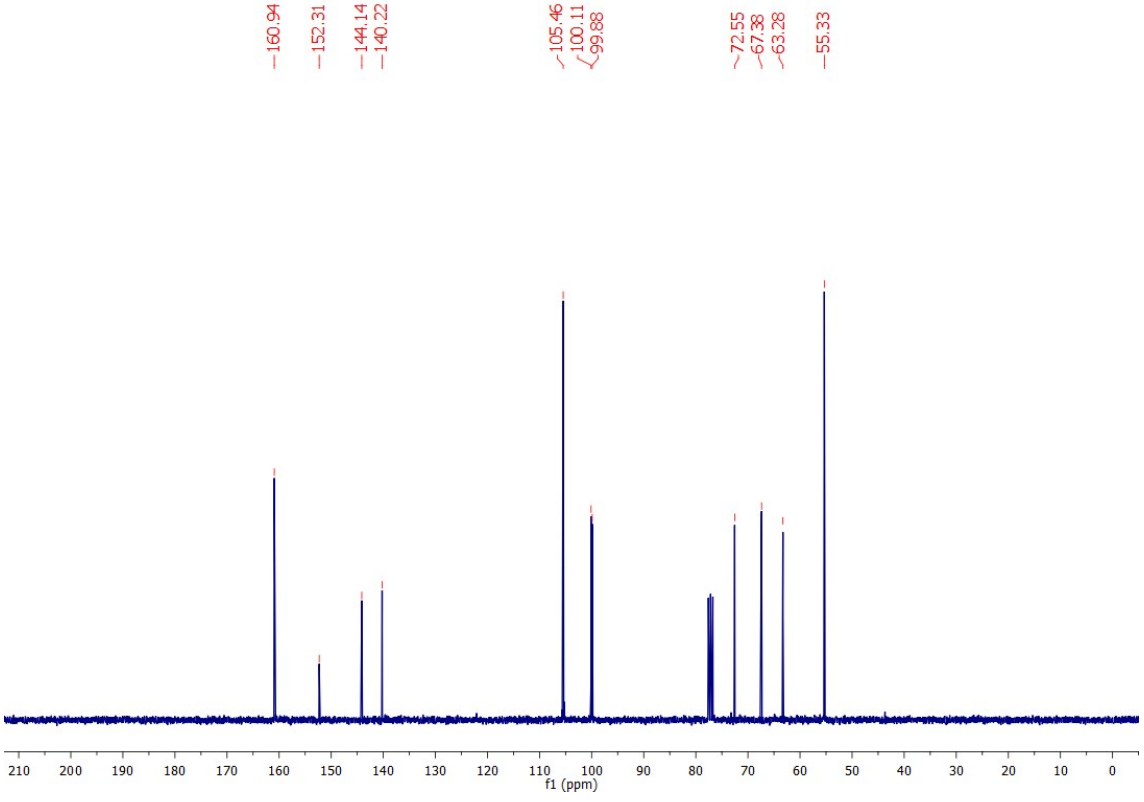


A_1

^{1}H NMR and **^{13}C NMR** of **A_2**



A_2



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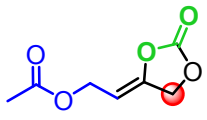

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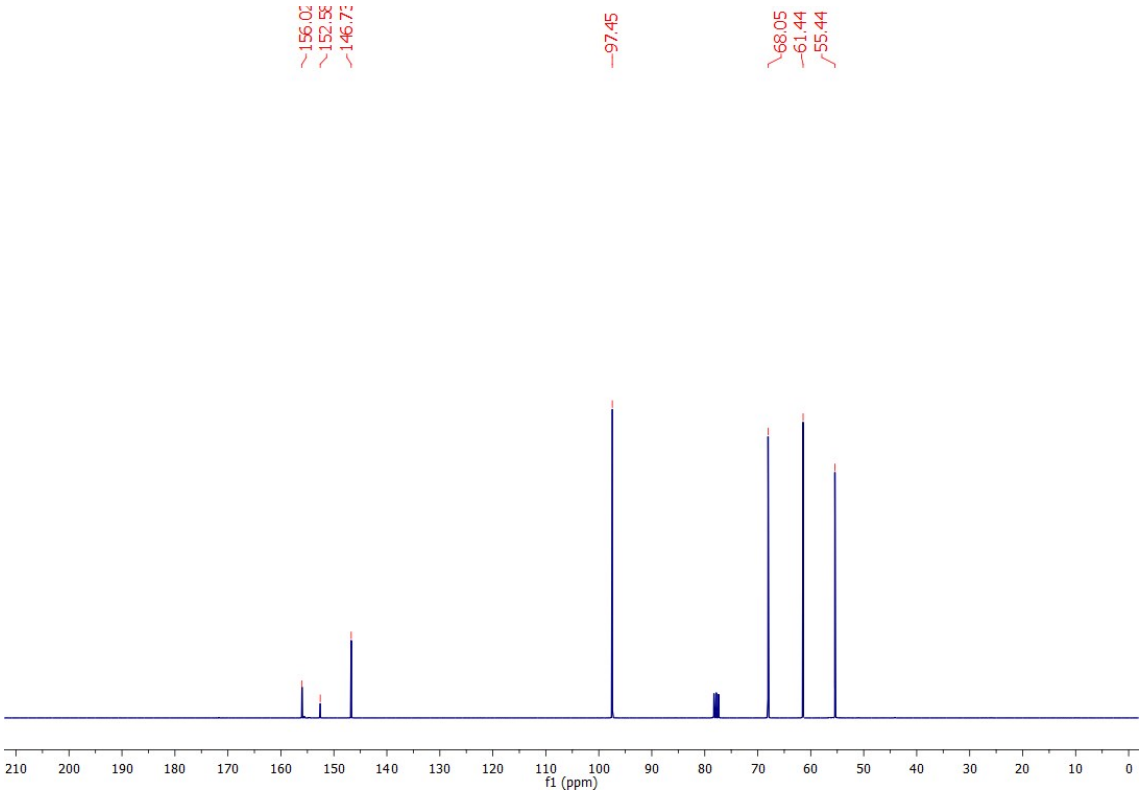
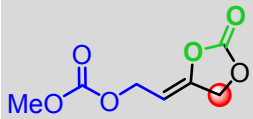
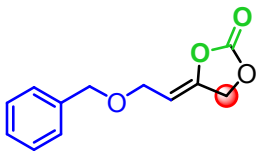


^{1}H NMR and **^{13}C NMR** of **A_4**

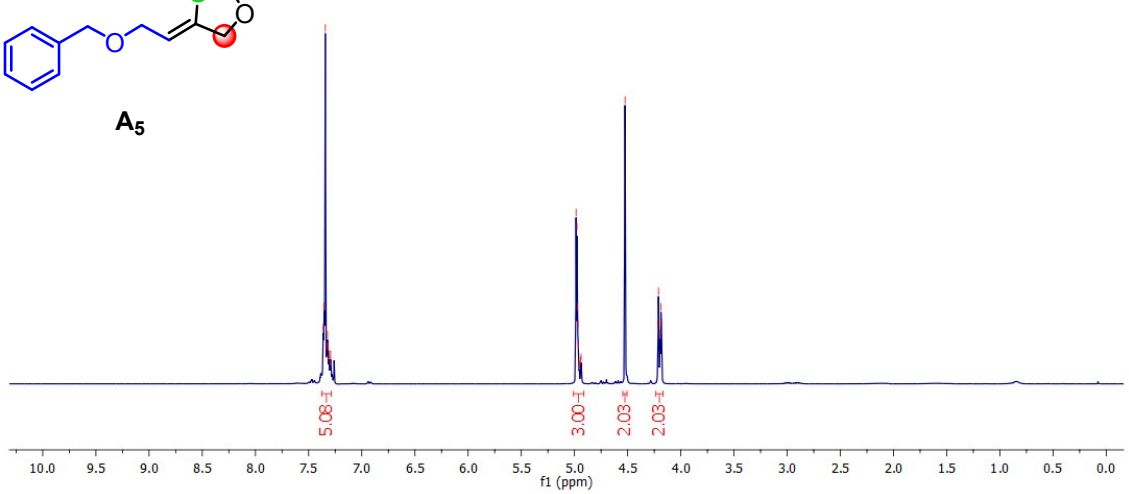


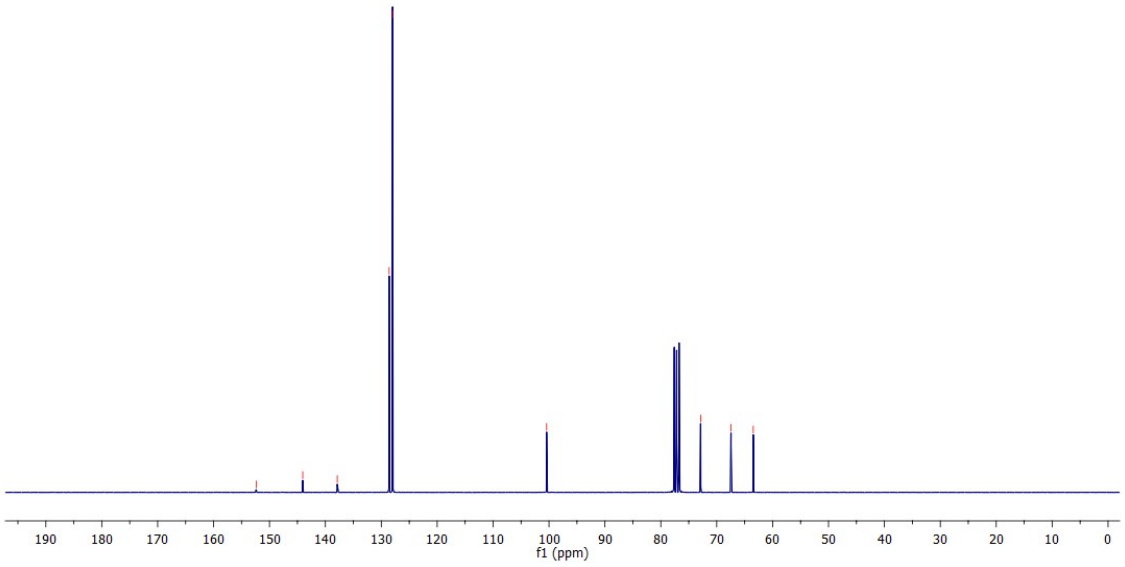
A_4

^{1}H NMR and **^{13}C NMR** of **A_5**

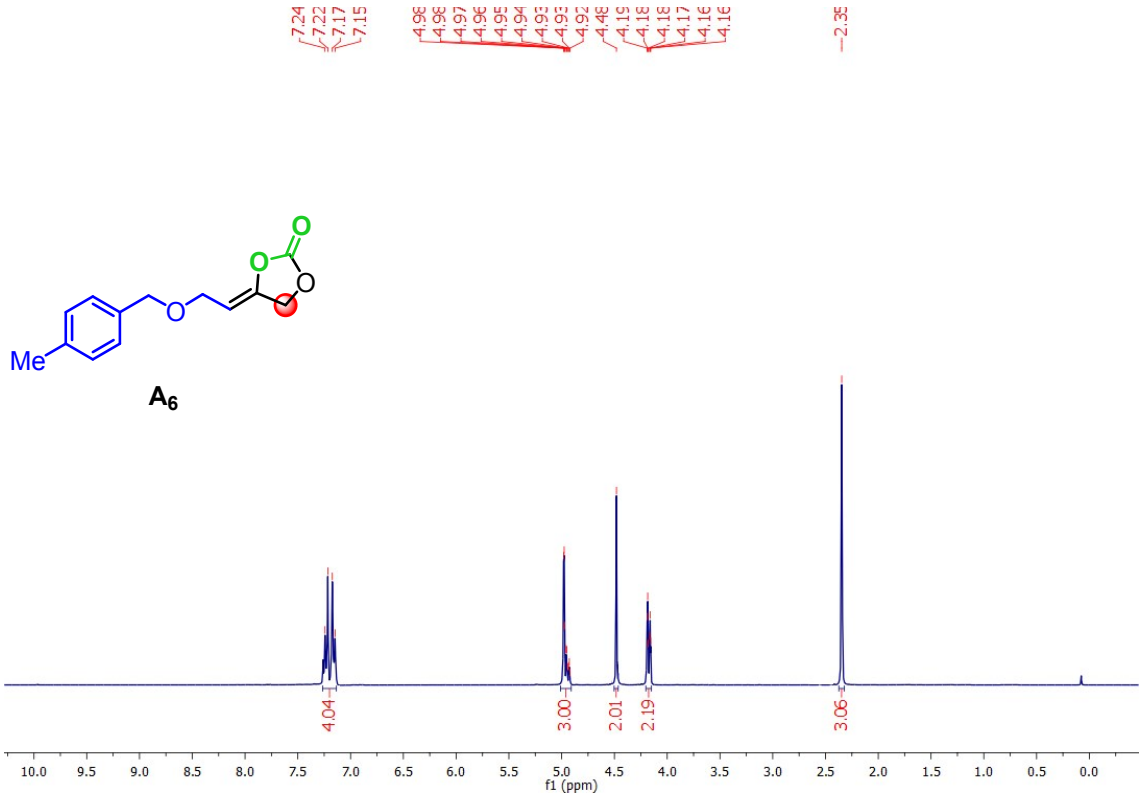


A_5

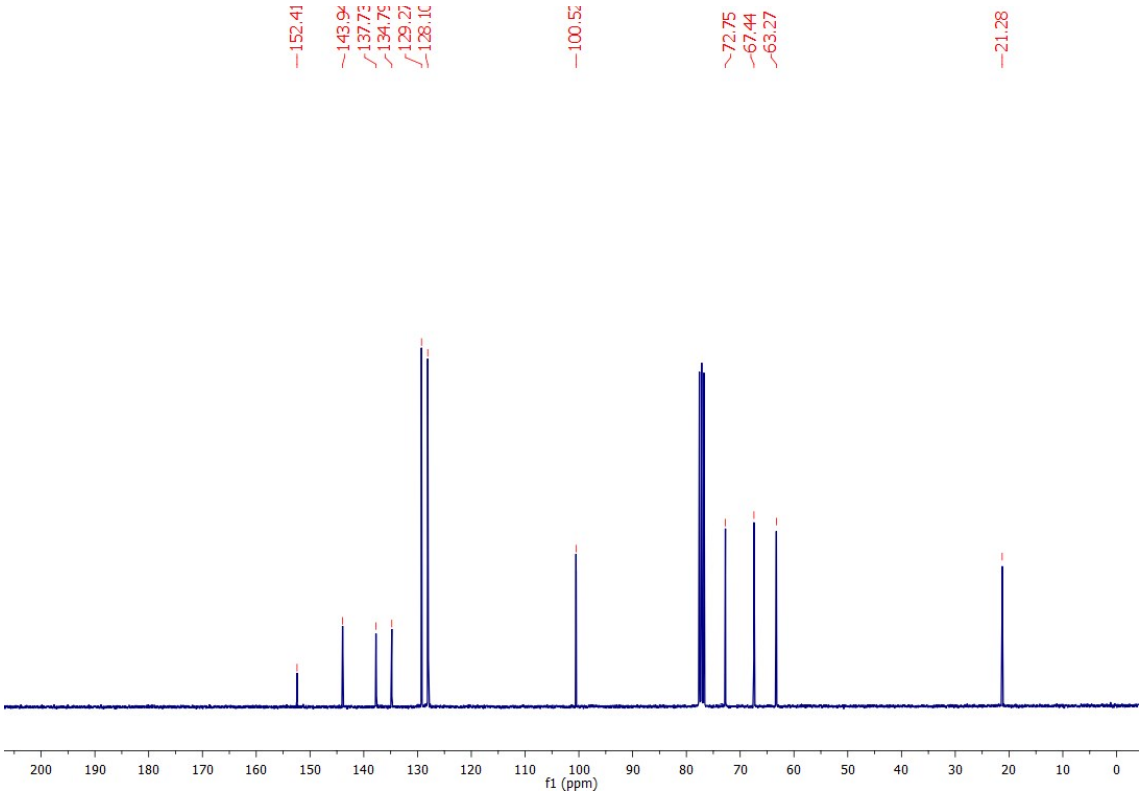




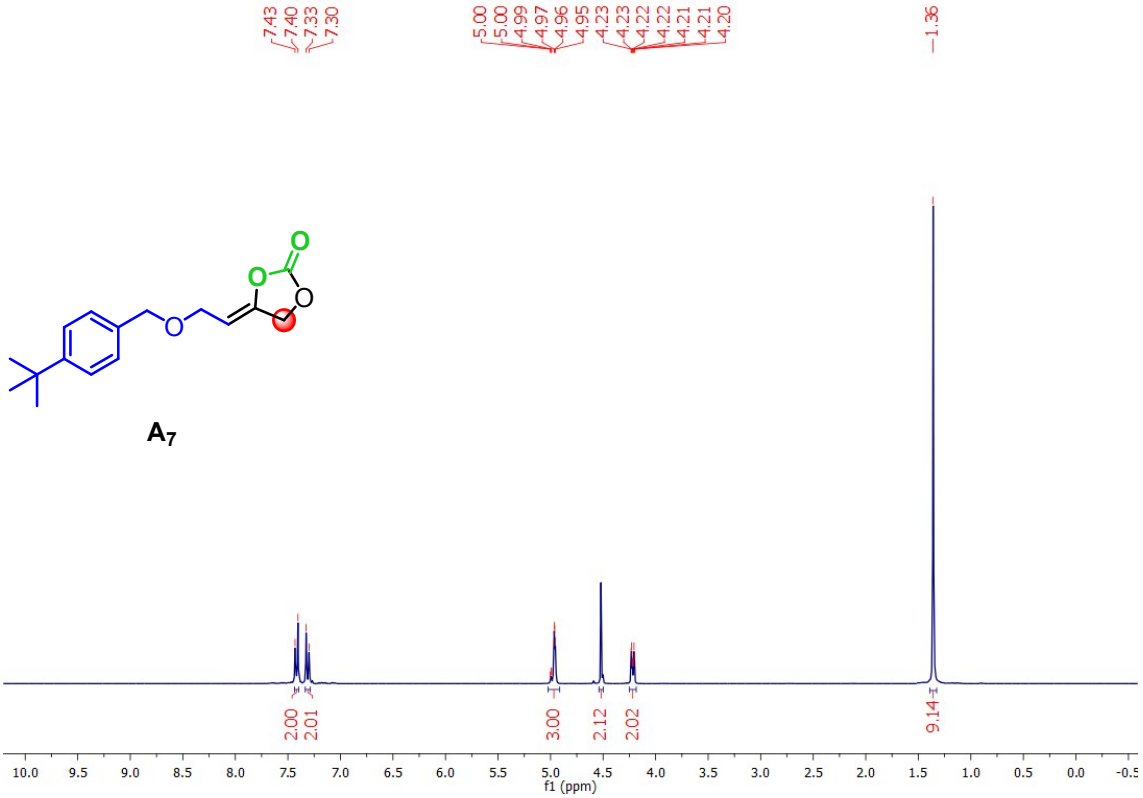
^{1}H NMR and **^{13}C NMR** of **A_6**



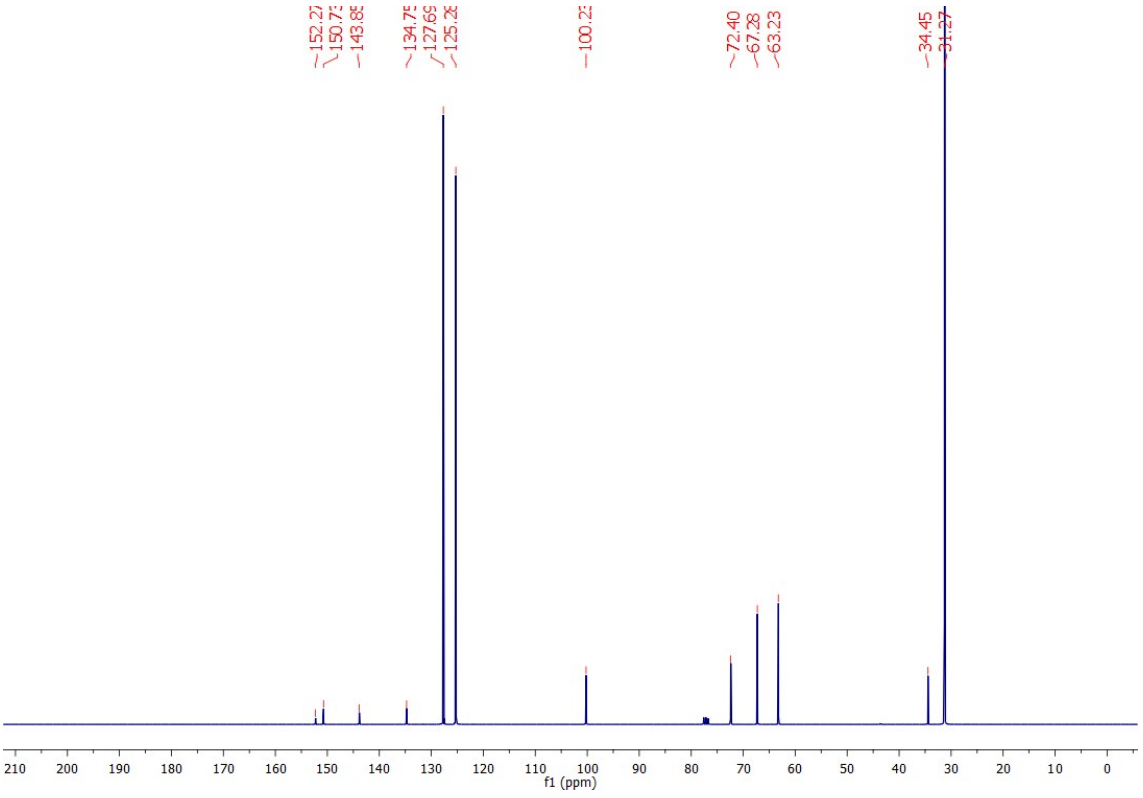
A_6



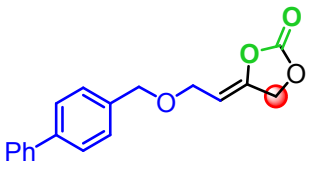
^{1}H NMR and **^{13}C NMR** of **A_7**



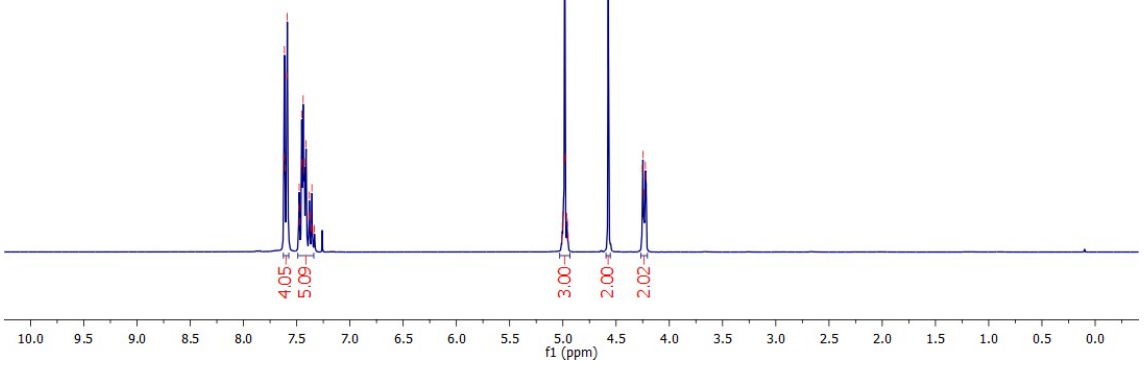
A_7

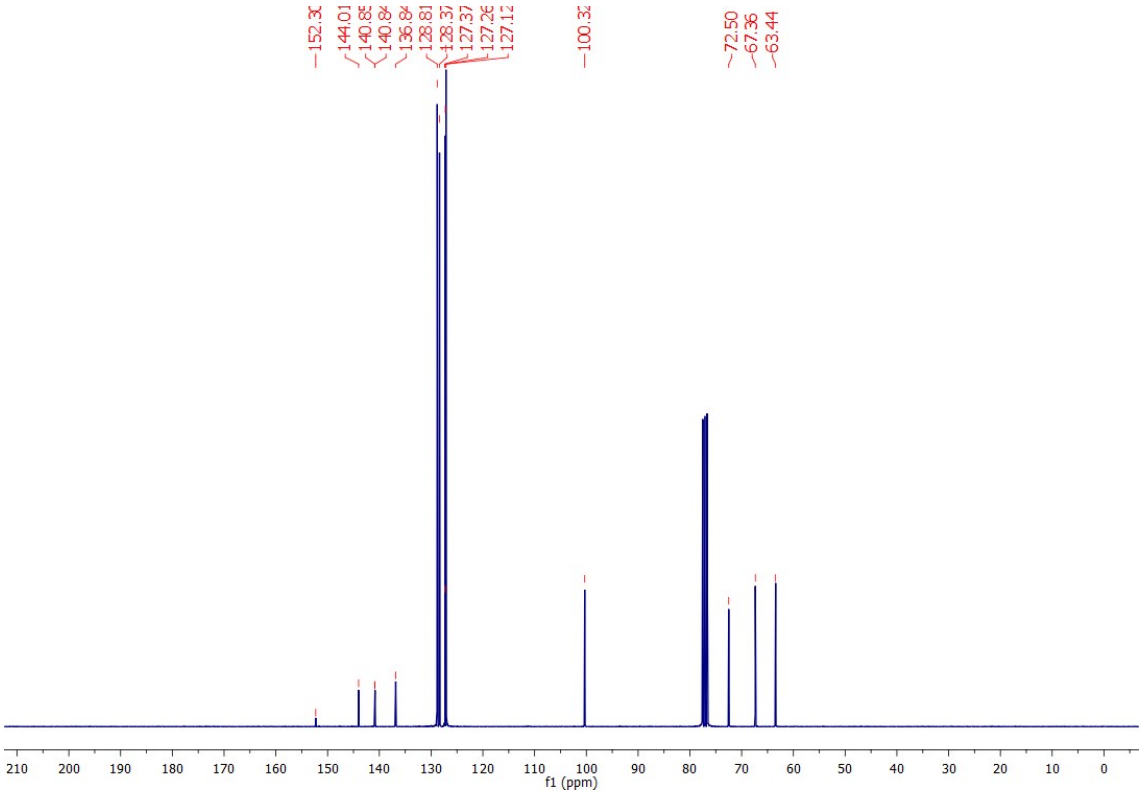


^{1}H NMR and **^{13}C NMR** of **A_8**

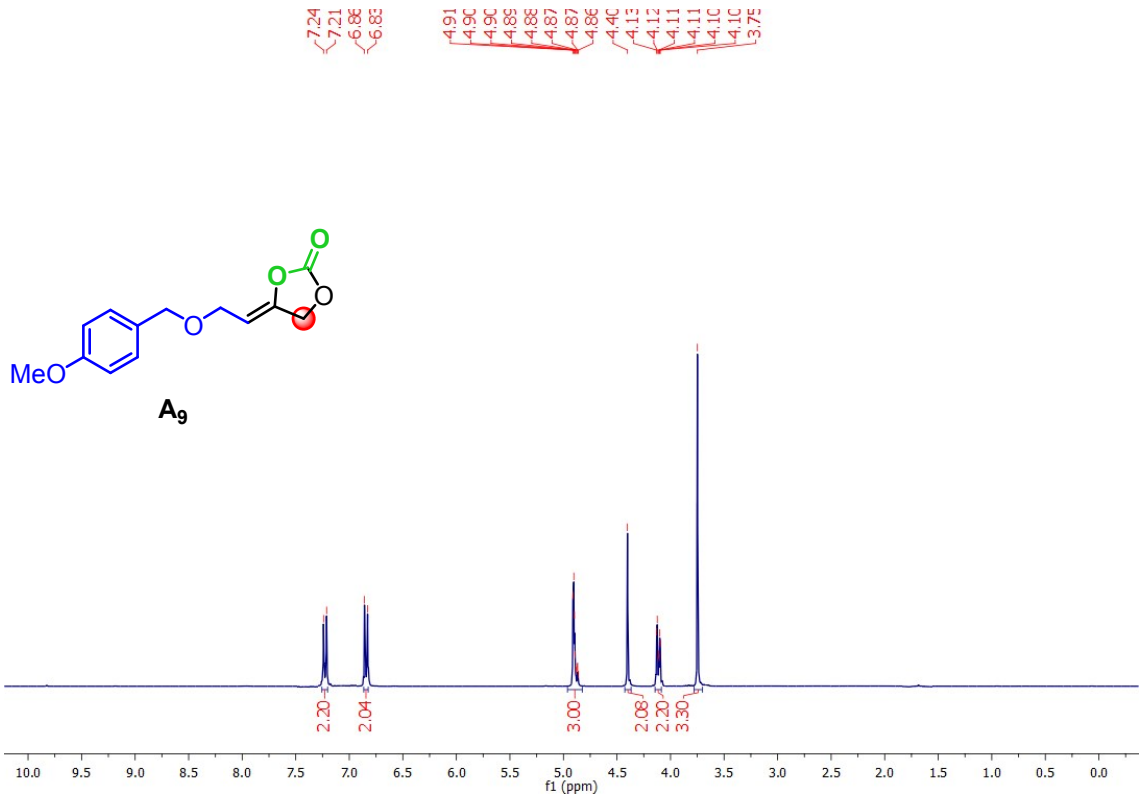


A_8

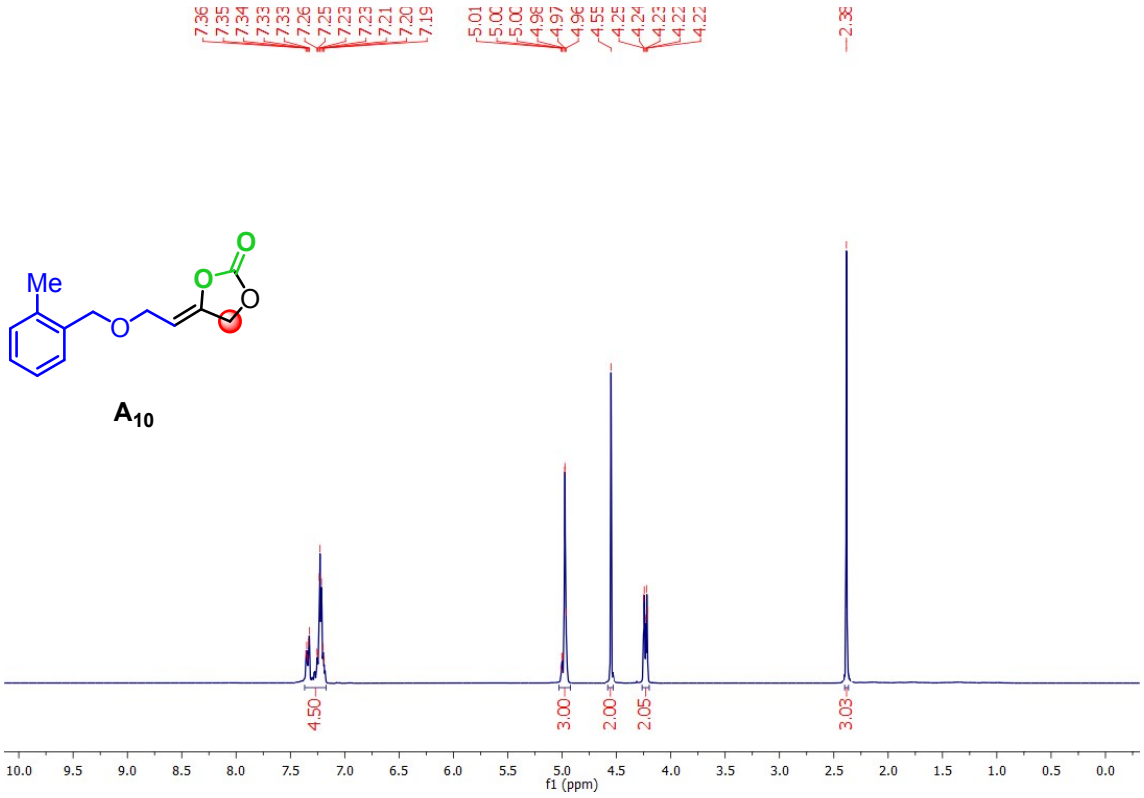




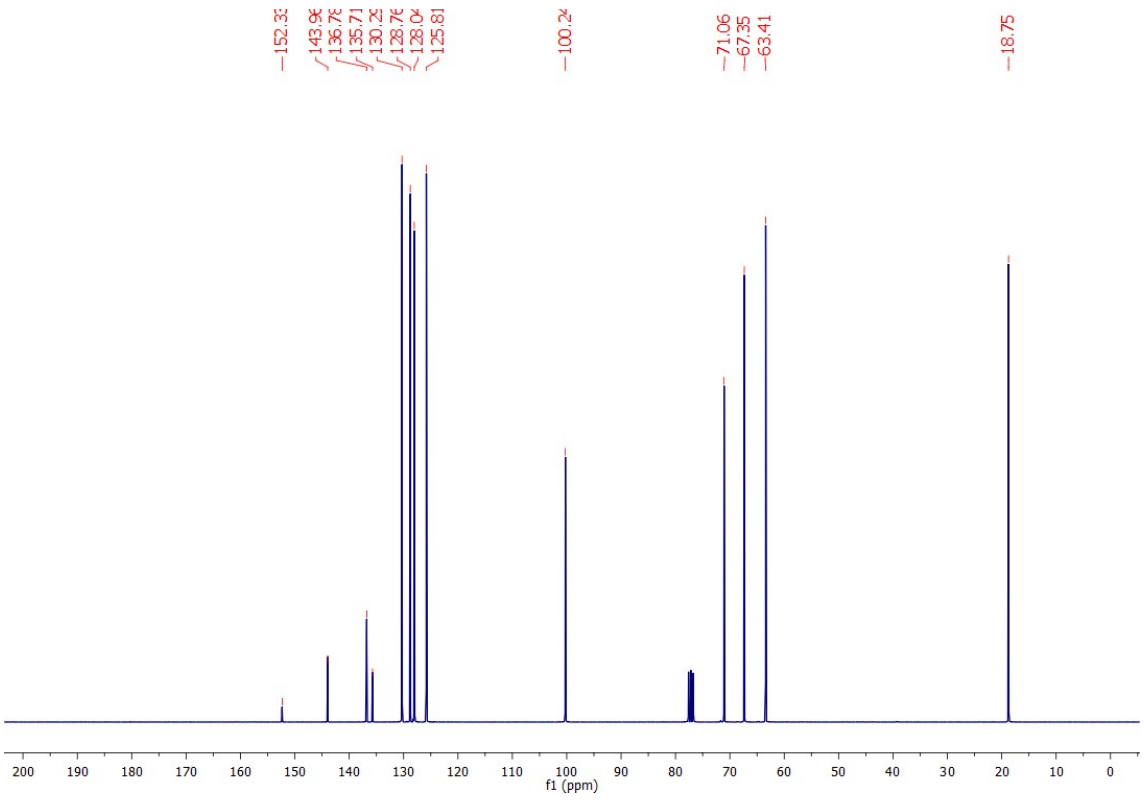
^{1}H NMR and **^{13}C NMR** of **A_9**



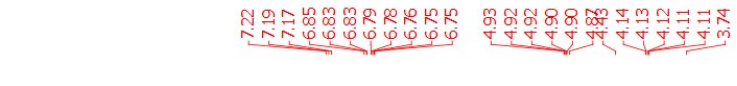
^{1}H NMR and **^{13}C NMR** of **A_{10}**

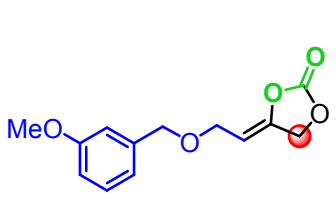


A_{10}

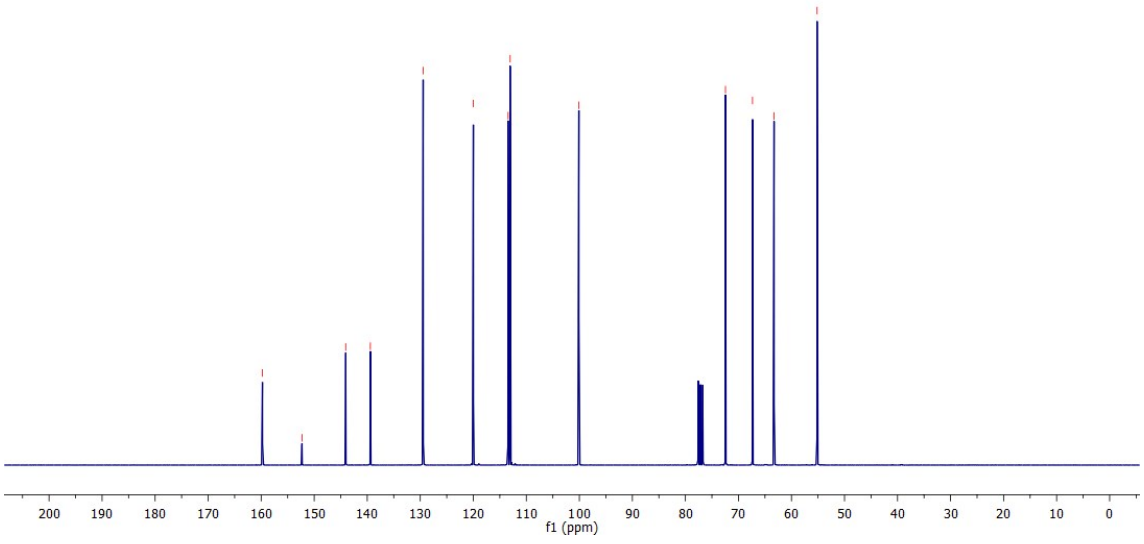


^{1}H NMR and **^{13}C NMR** of **A_{11}**

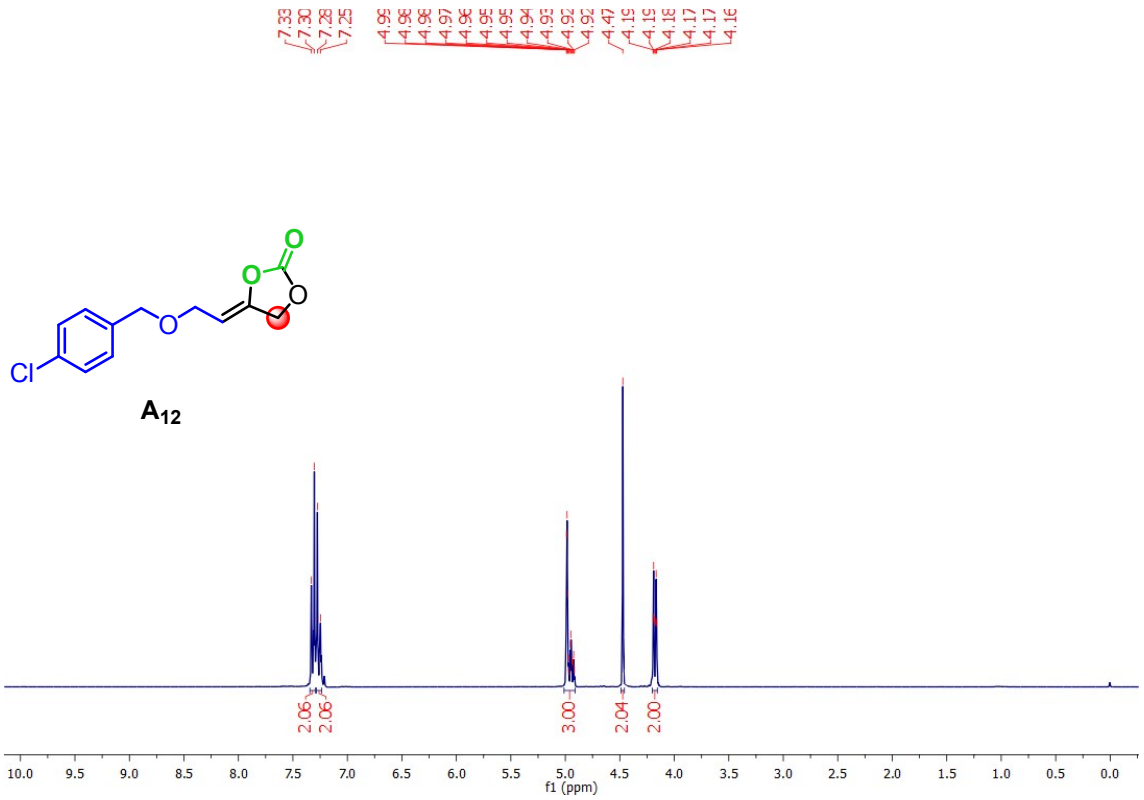




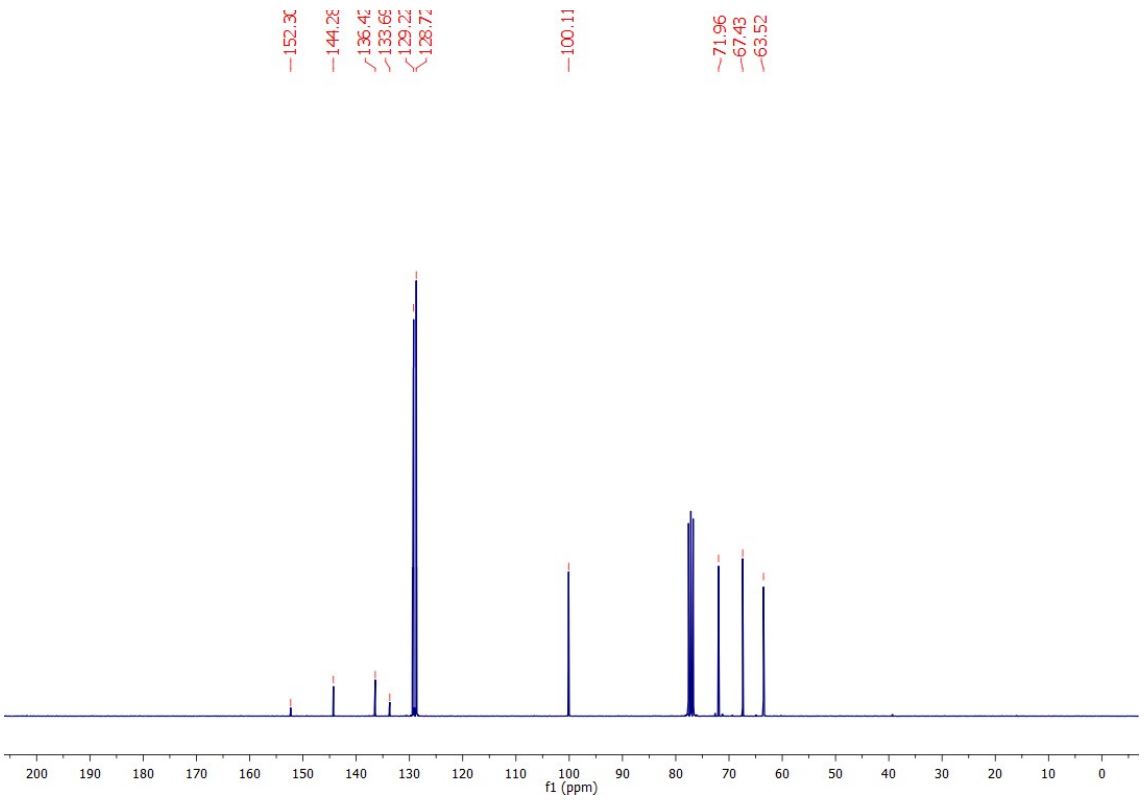
A_{11}



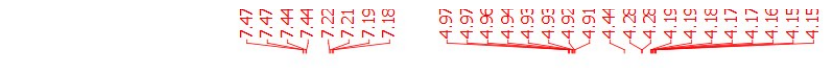
^{1}H NMR and **^{13}C NMR** of **A_{12}**

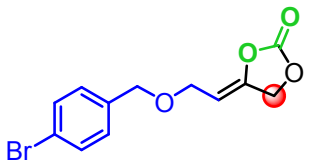


A_{12}

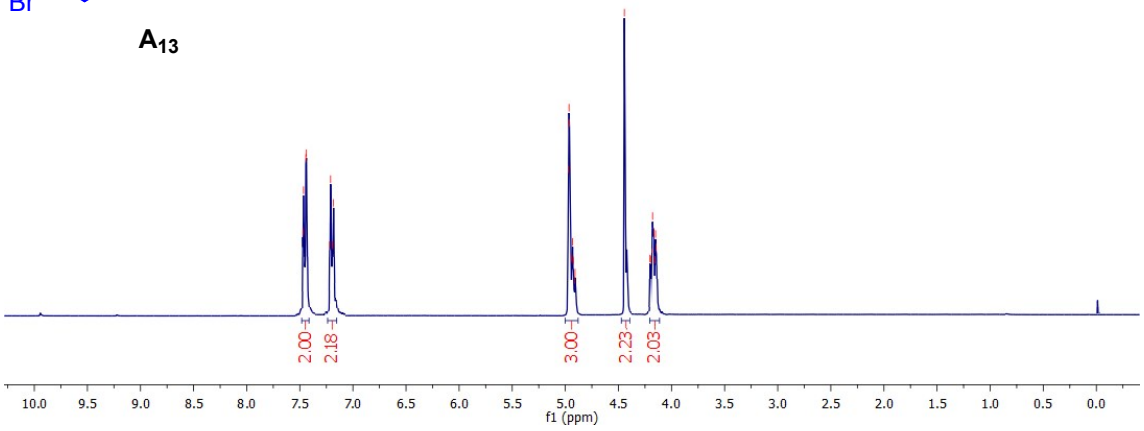


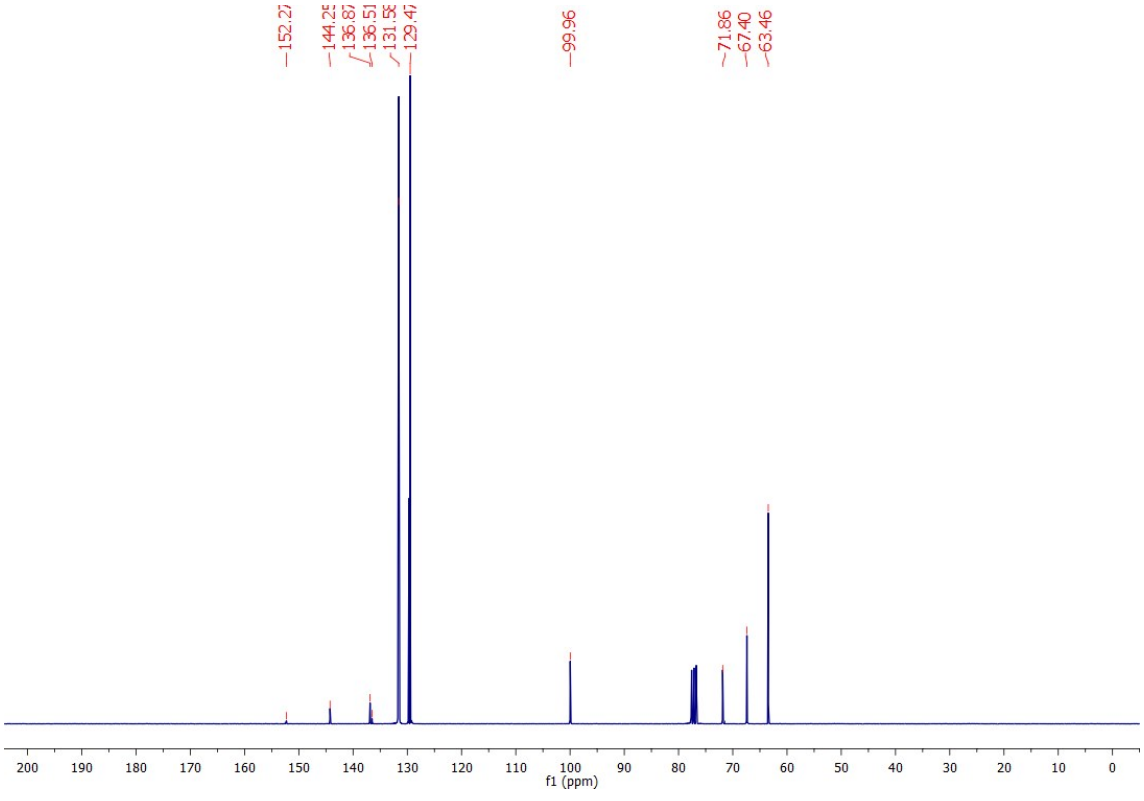
^{1}H NMR and **^{13}C NMR** of **A_{13}**



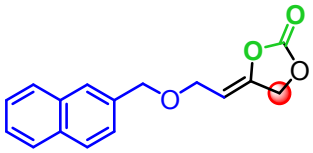


A_{13}

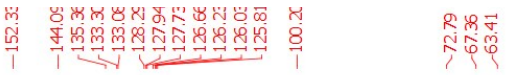


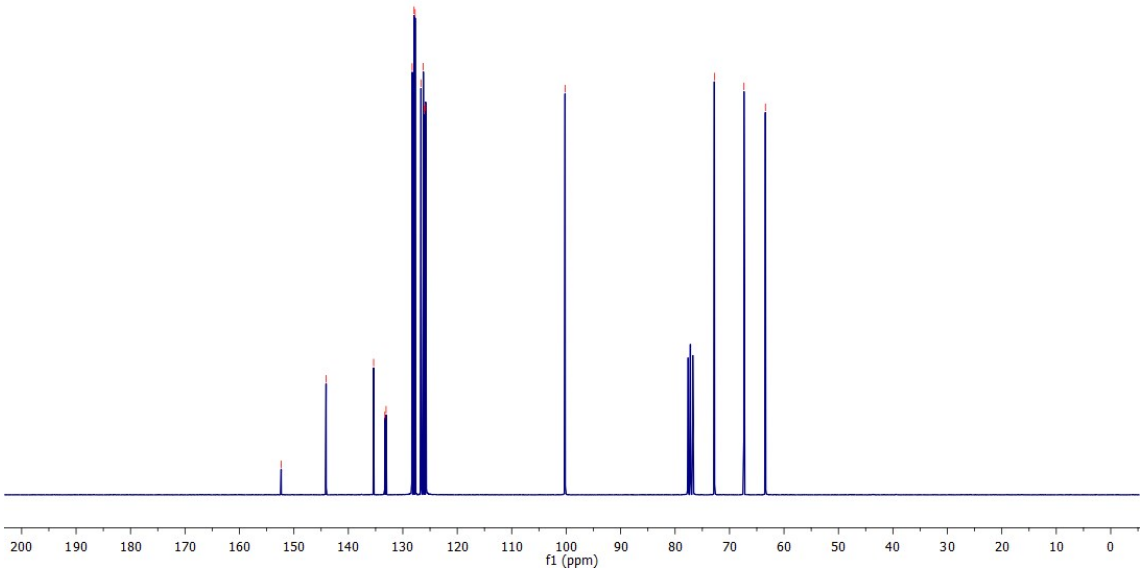


^{1}H NMR and **^{13}C NMR** of **A_{14}**

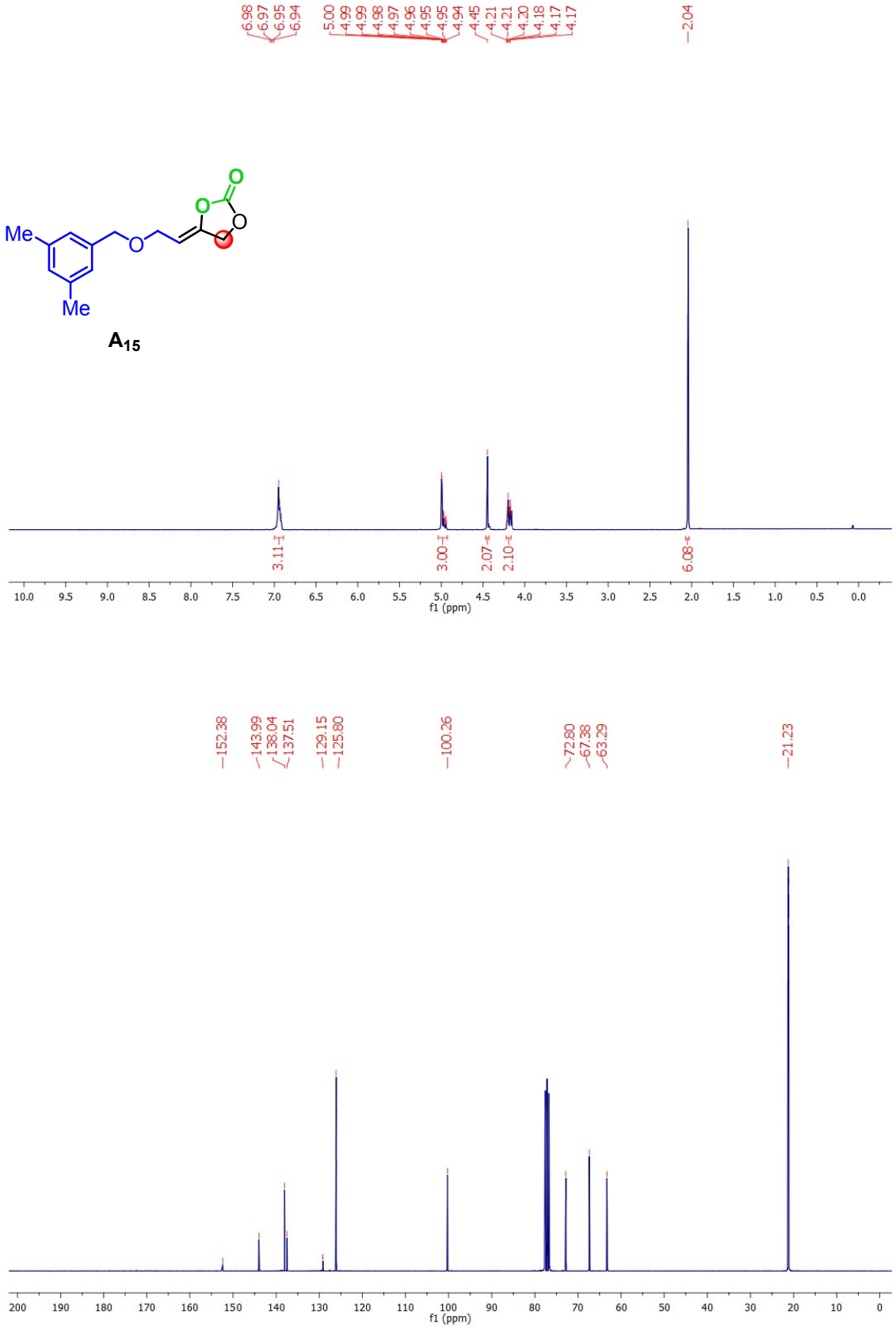


A_{14}



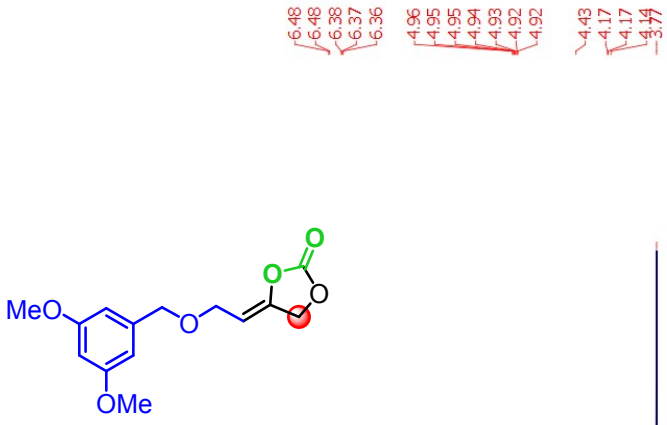


^{1}H NMR and **^{13}C NMR** of **A_{15}**



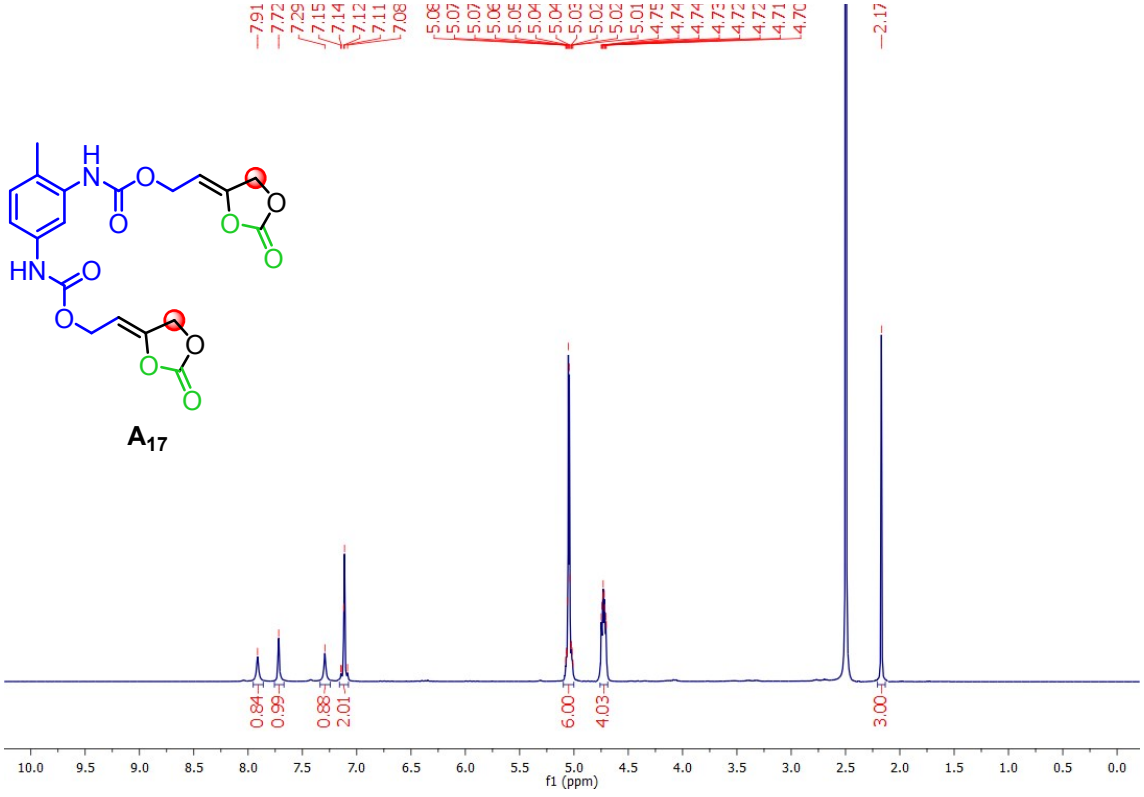
A_{15}

^{1}H NMR and **^{13}C NMR** of **A_{16}**

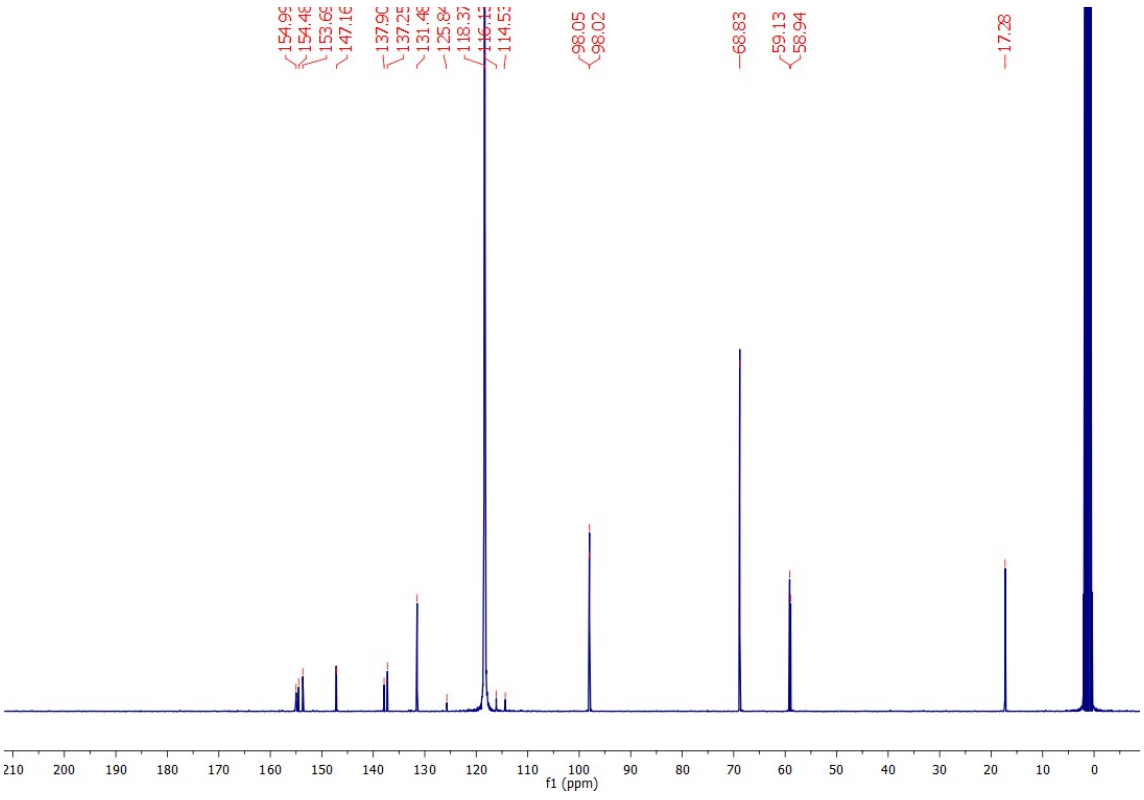


A_{16}

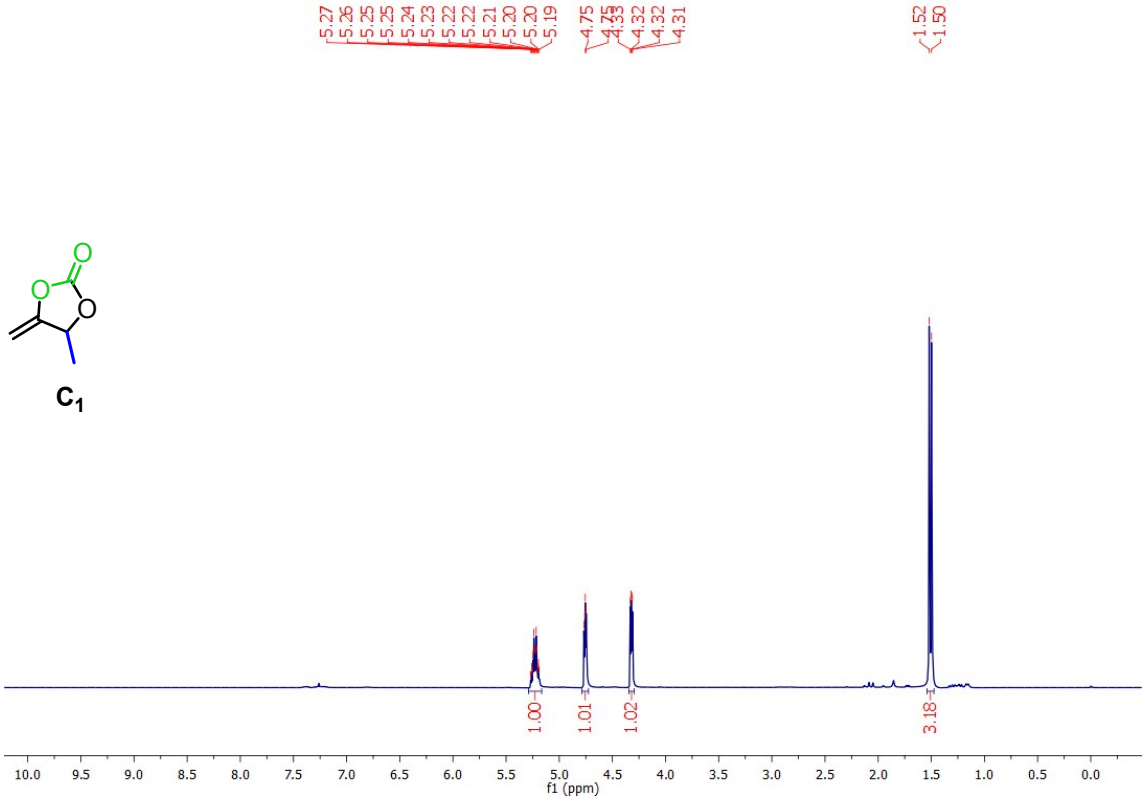
^{1}H NMR and **^{13}C NMR** of **A_{17}**



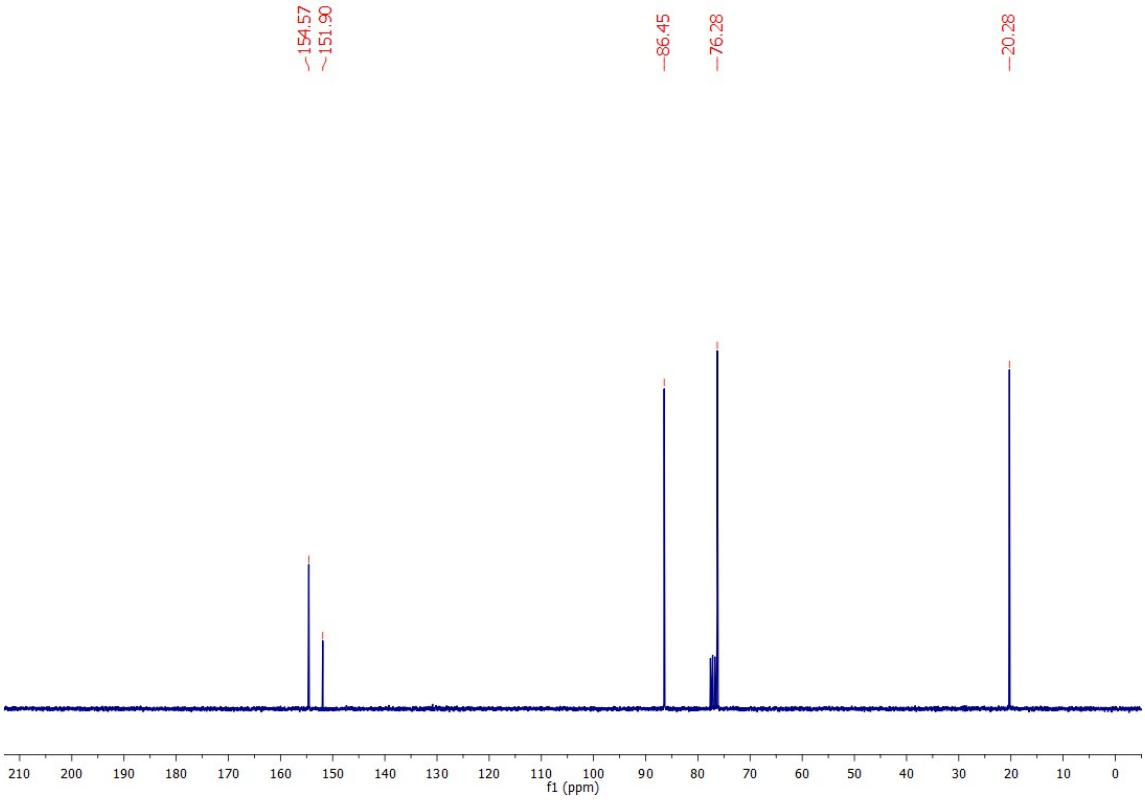
A_{17}



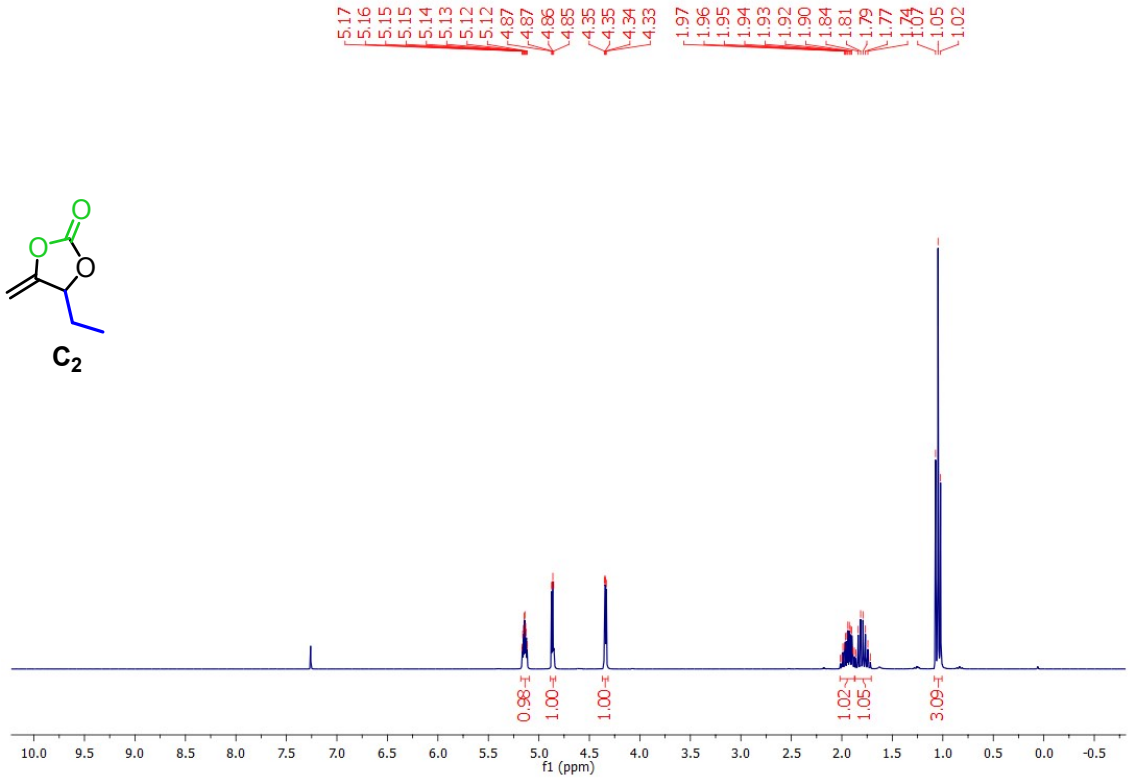
^{1}H NMR and **^{13}C NMR** of **C_1**

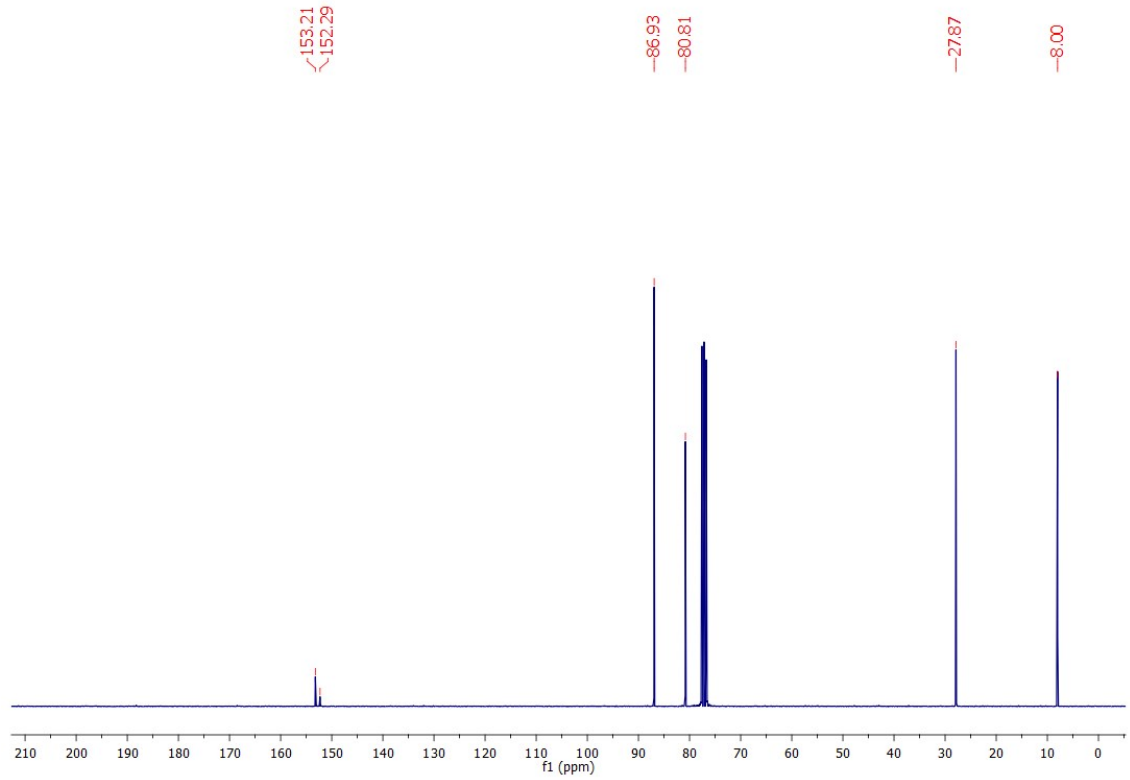


C_1

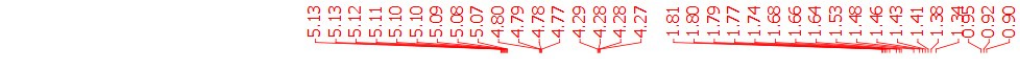


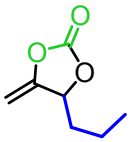
^{1}H NMR and **^{13}C NMR** of **C_2**



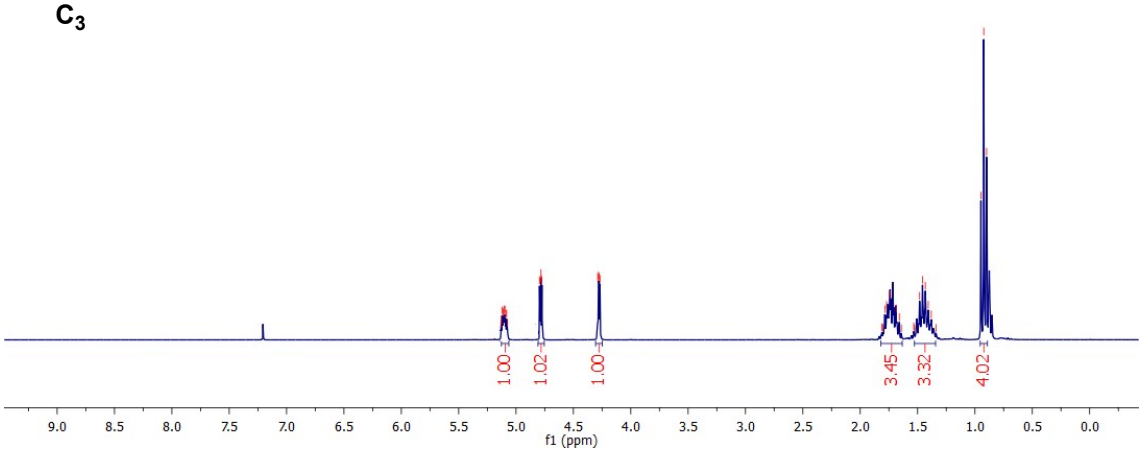


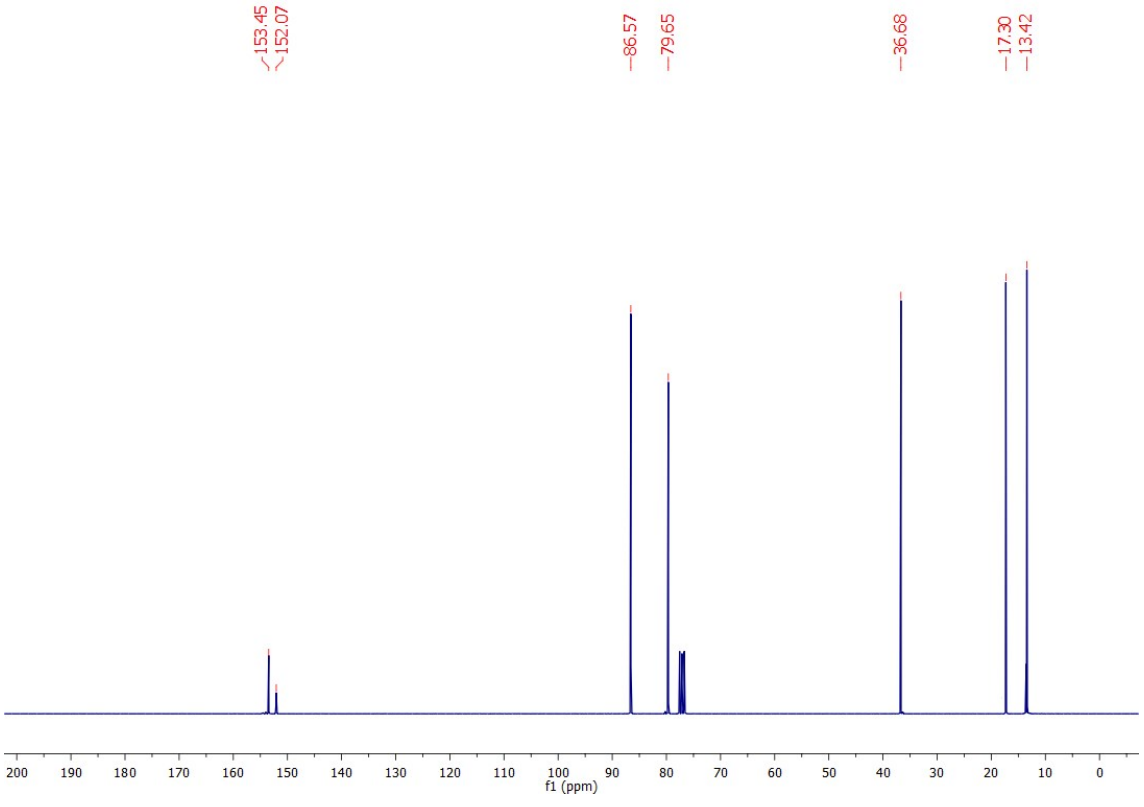
^{1}H NMR and **^{13}C NMR** of **C_3**



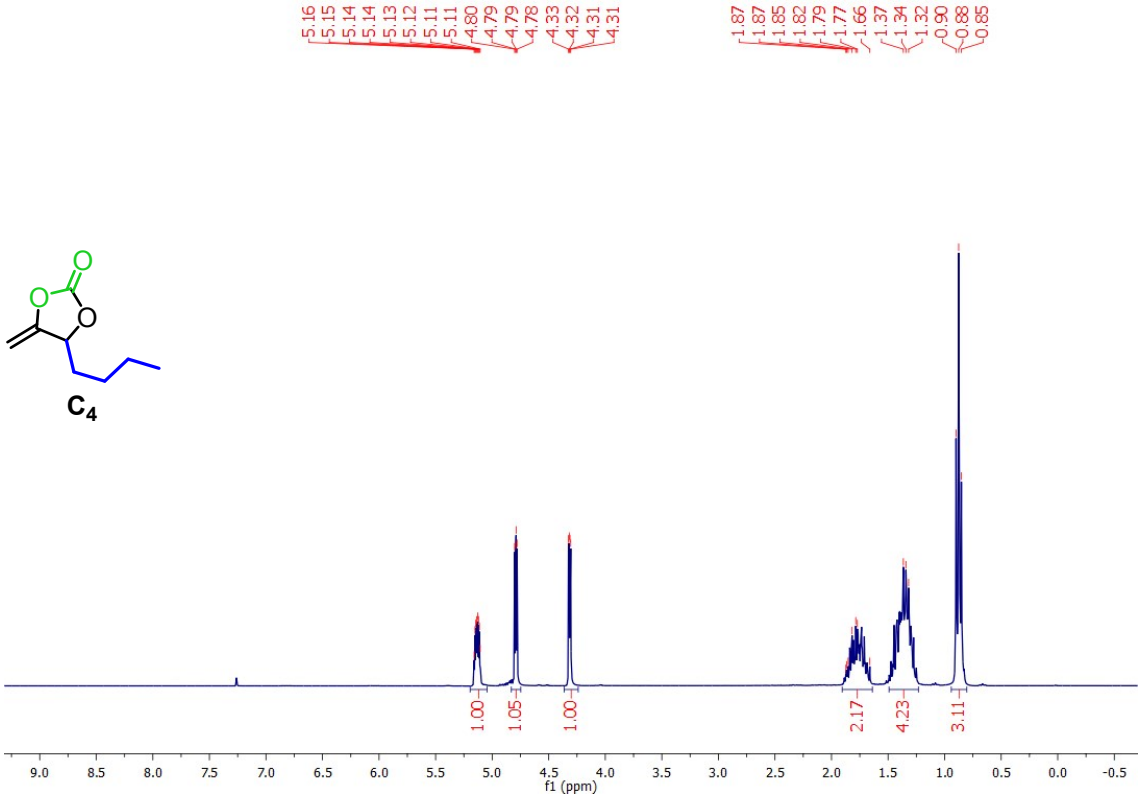


C_3

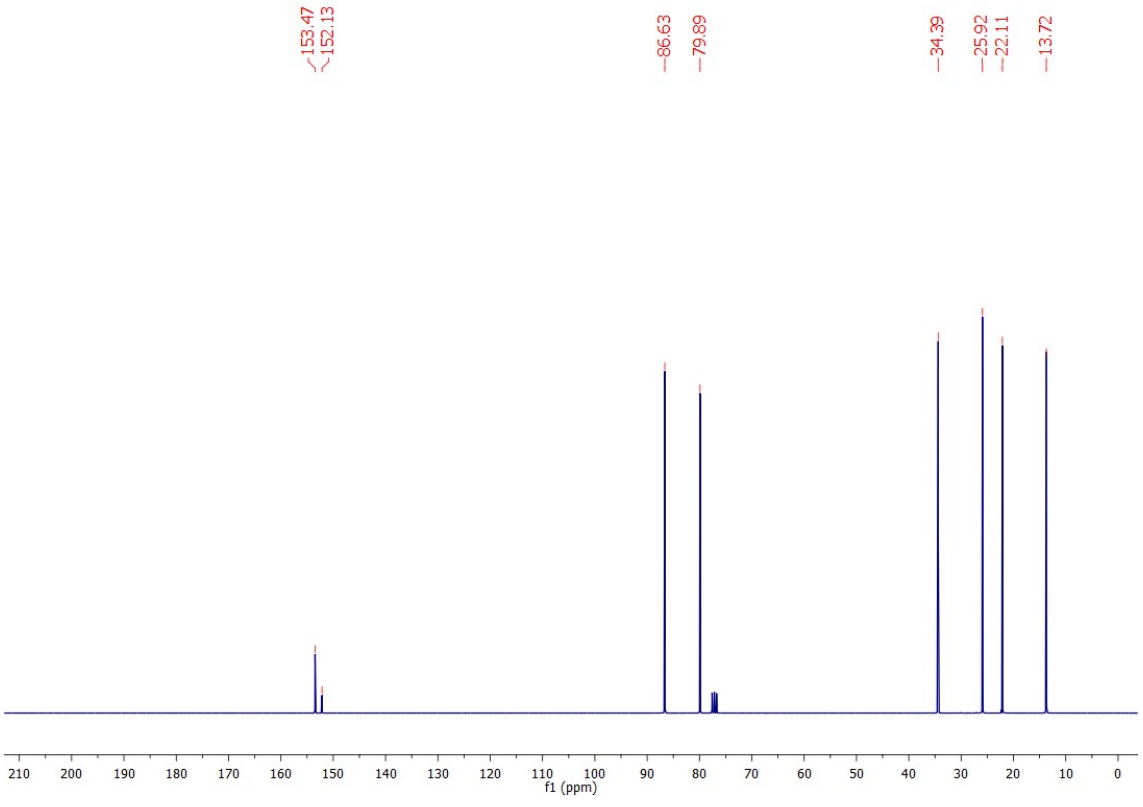




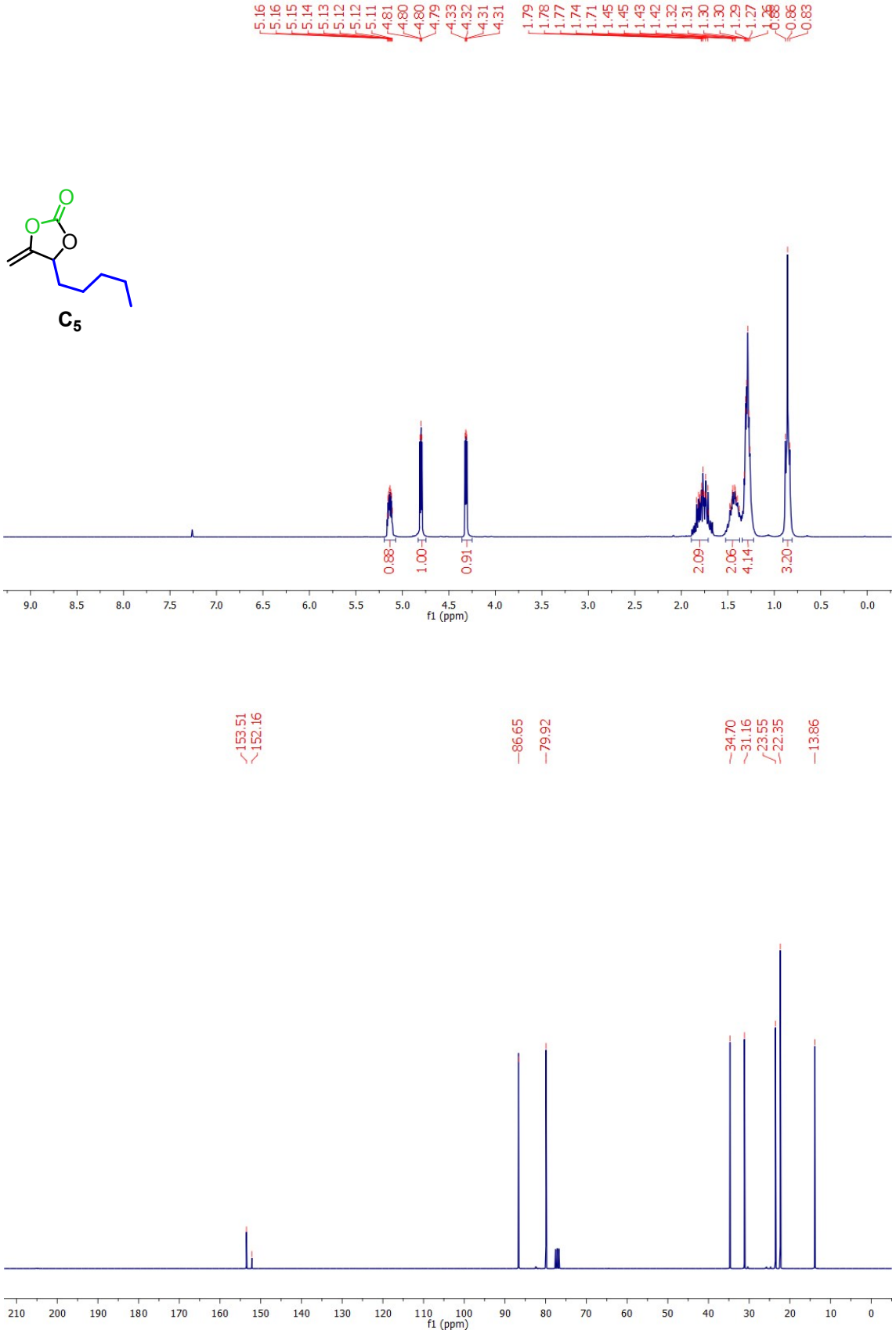
^{1}H NMR and **^{13}C NMR** of **C_4**



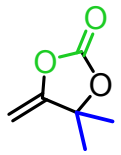
C_4



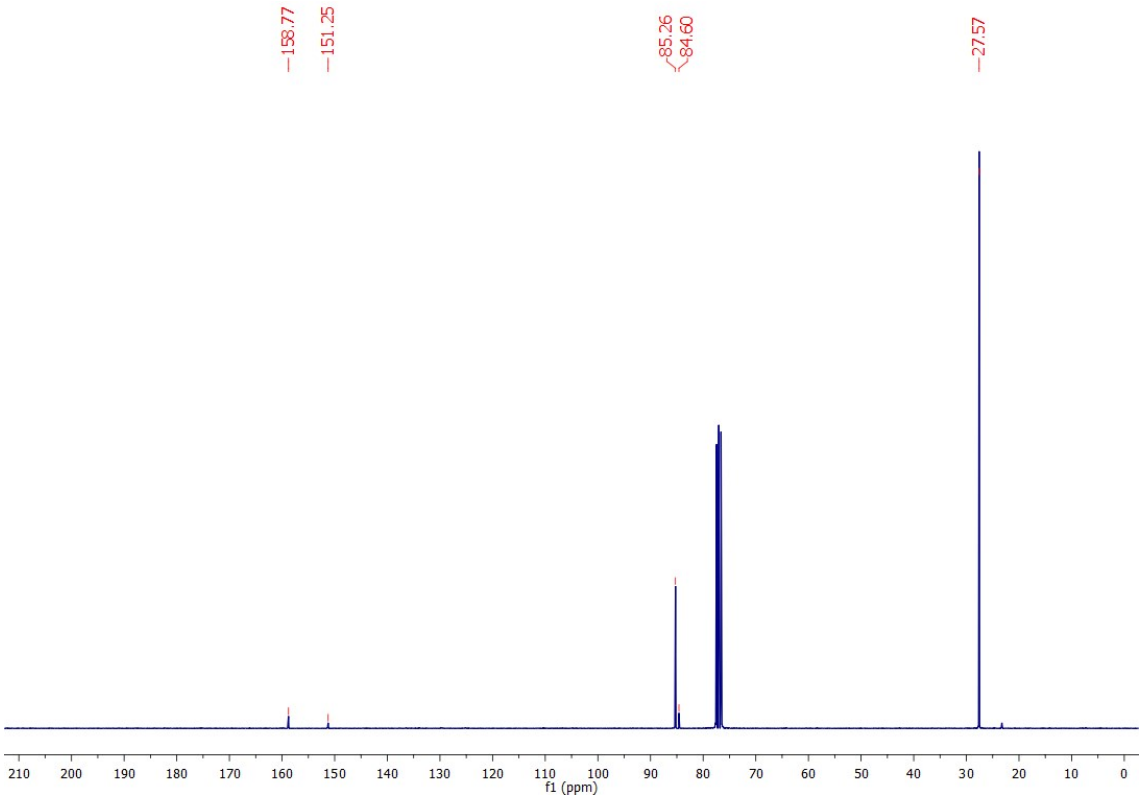
^{1}H NMR and **^{13}C NMR** of **C_5**



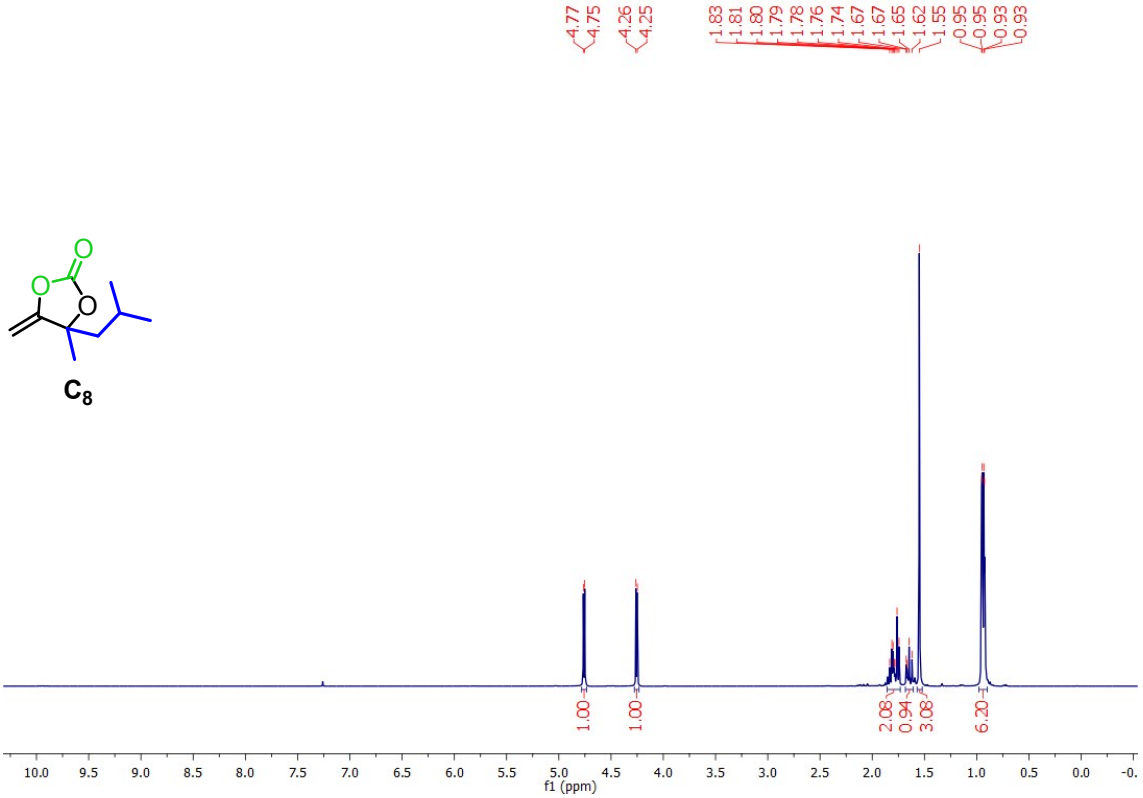
^{1}H NMR and **^{13}C NMR** of **C_7**

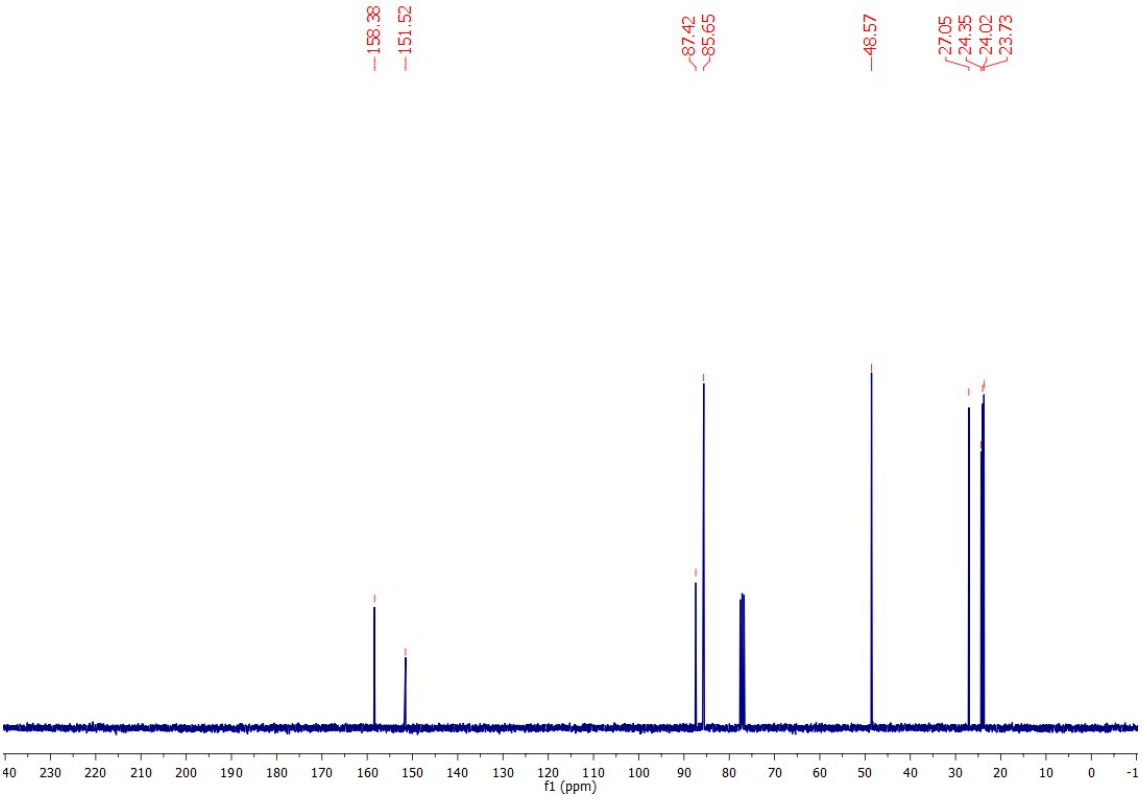


C_7

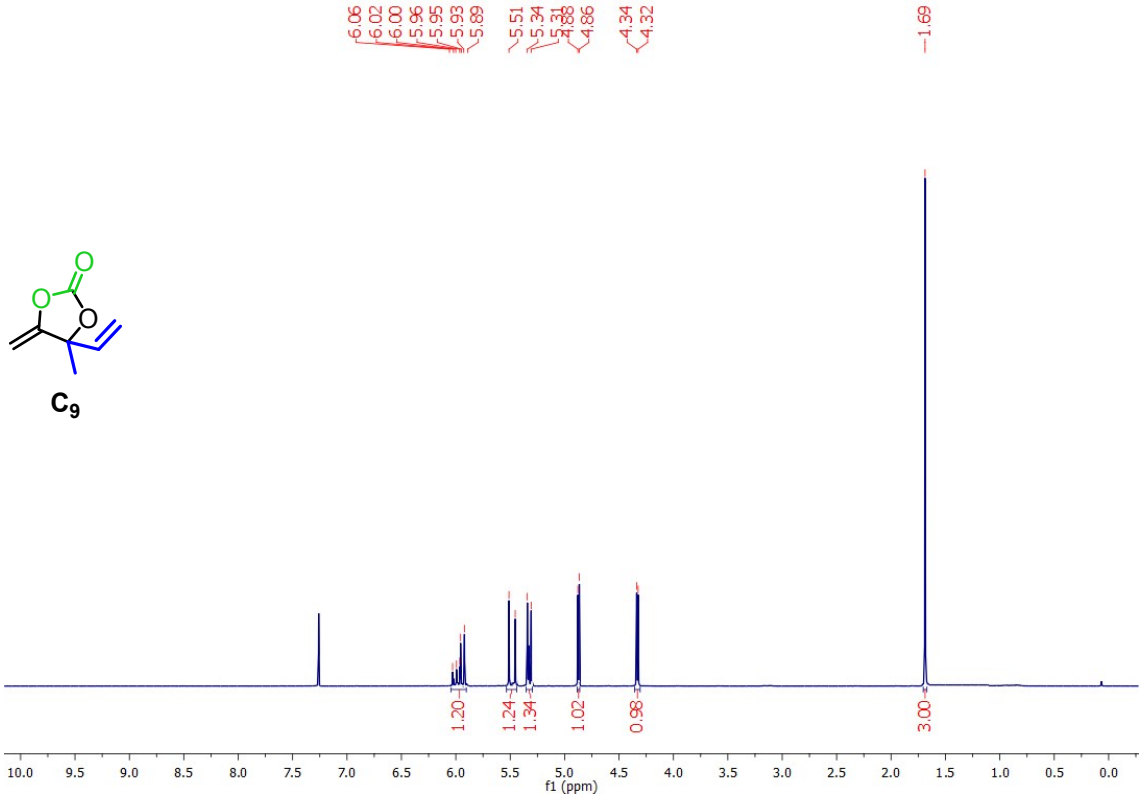


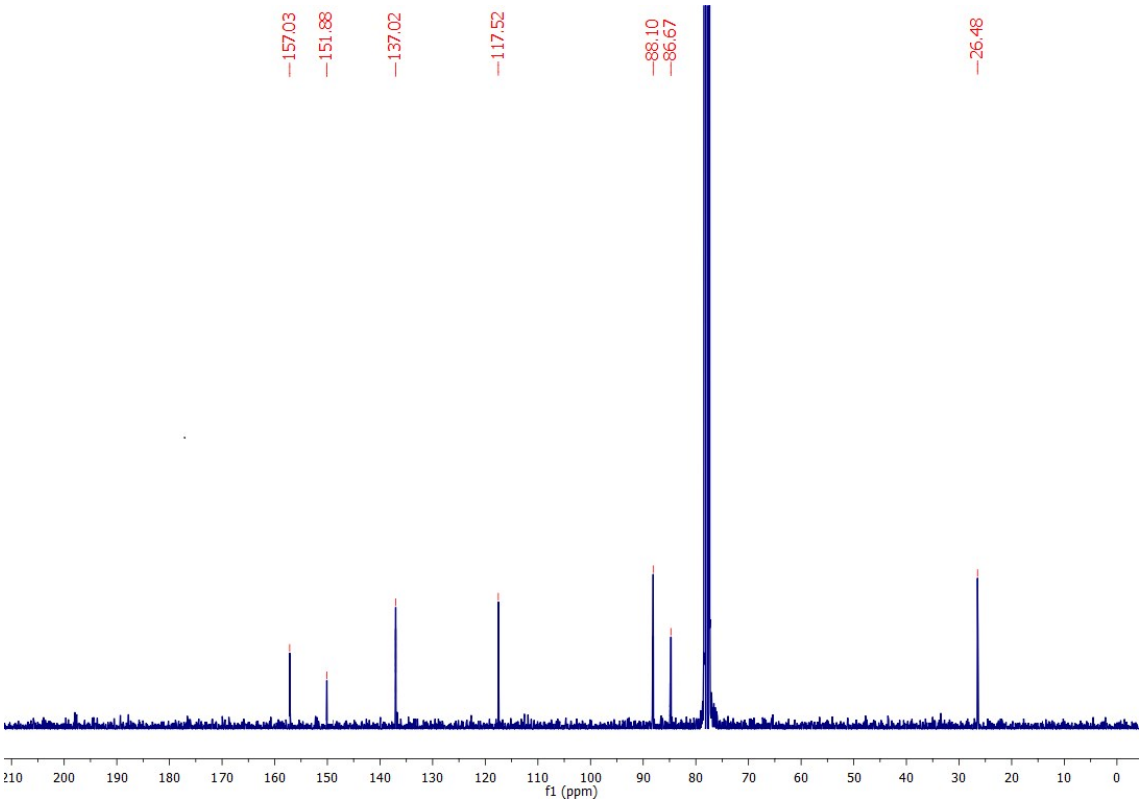
^{1}H NMR and **^{13}C NMR** of **C_8**



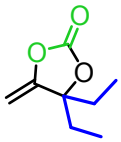


^{1}H NMR and **^{13}C NMR** of **C_9**

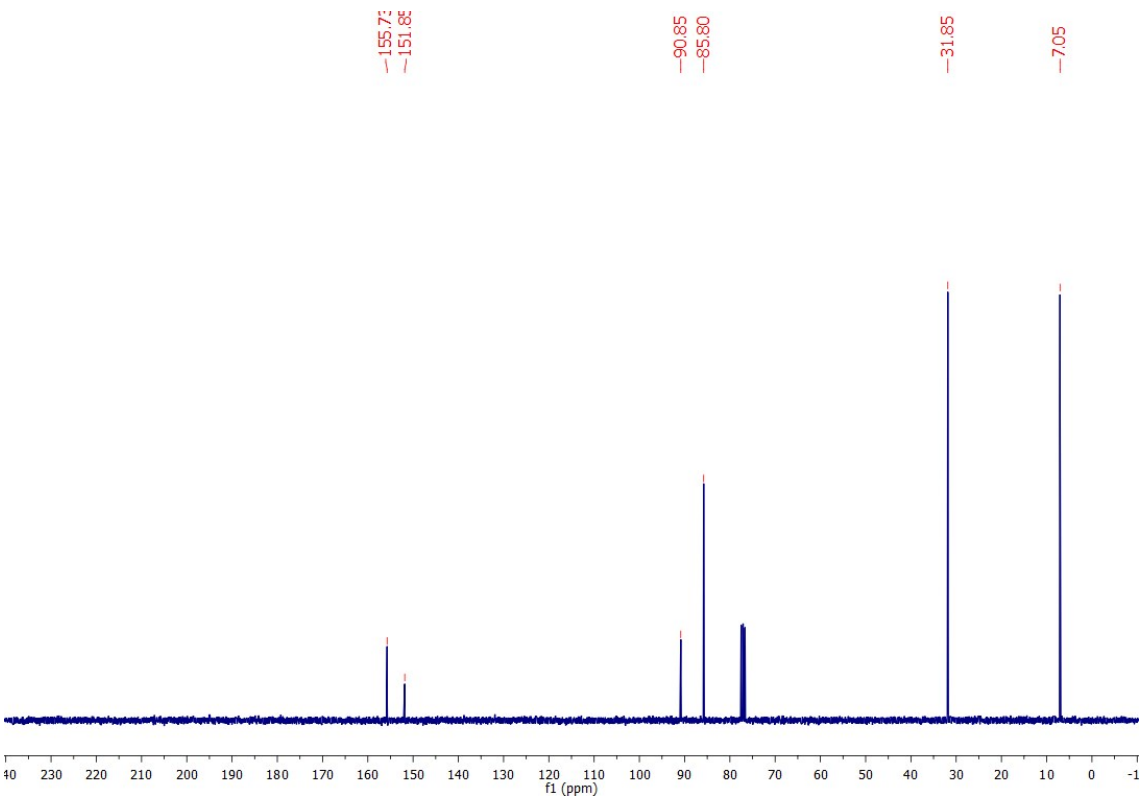




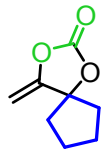
^{1}H NMR and **^{13}C NMR** of **C_{10}**



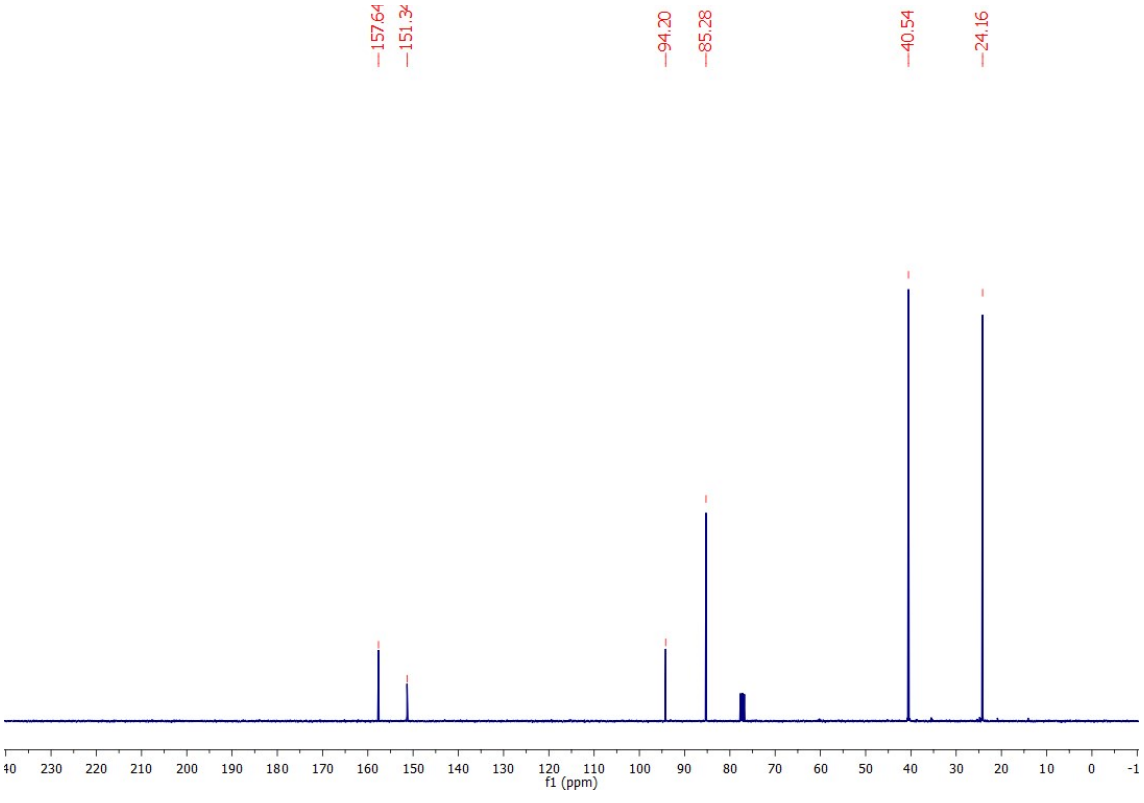
C_{10}



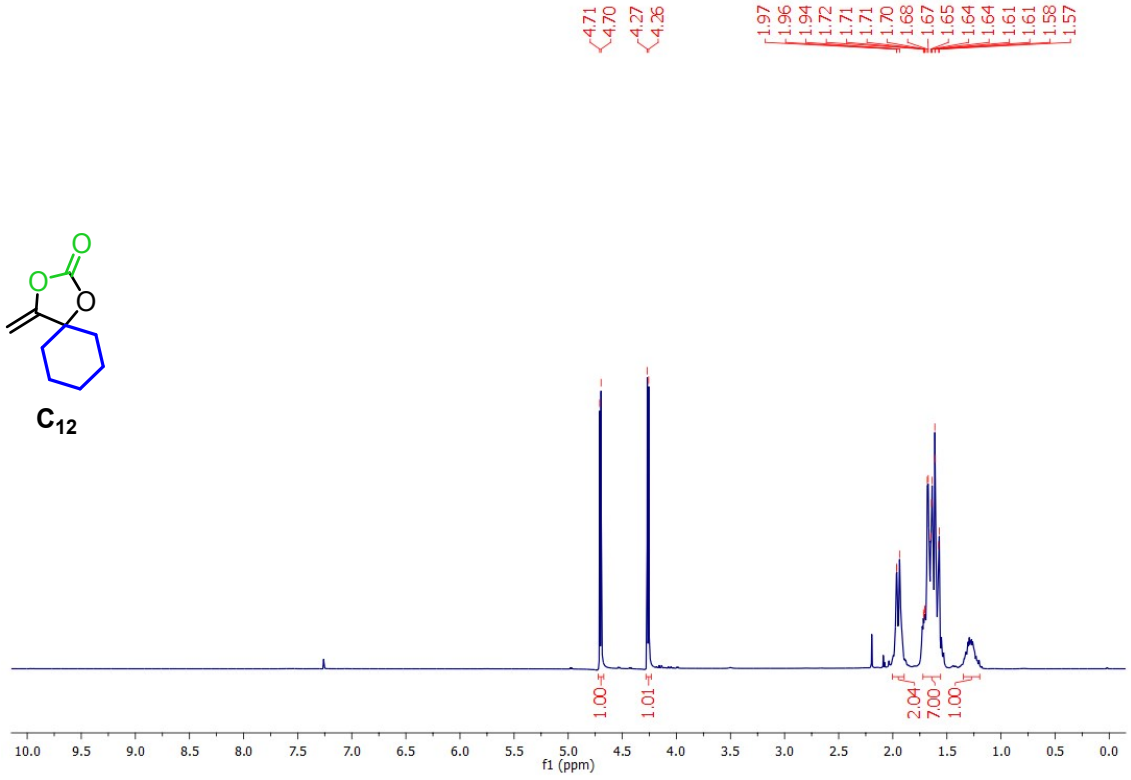
^{1}H NMR and **^{13}C NMR** of **C_{11}**



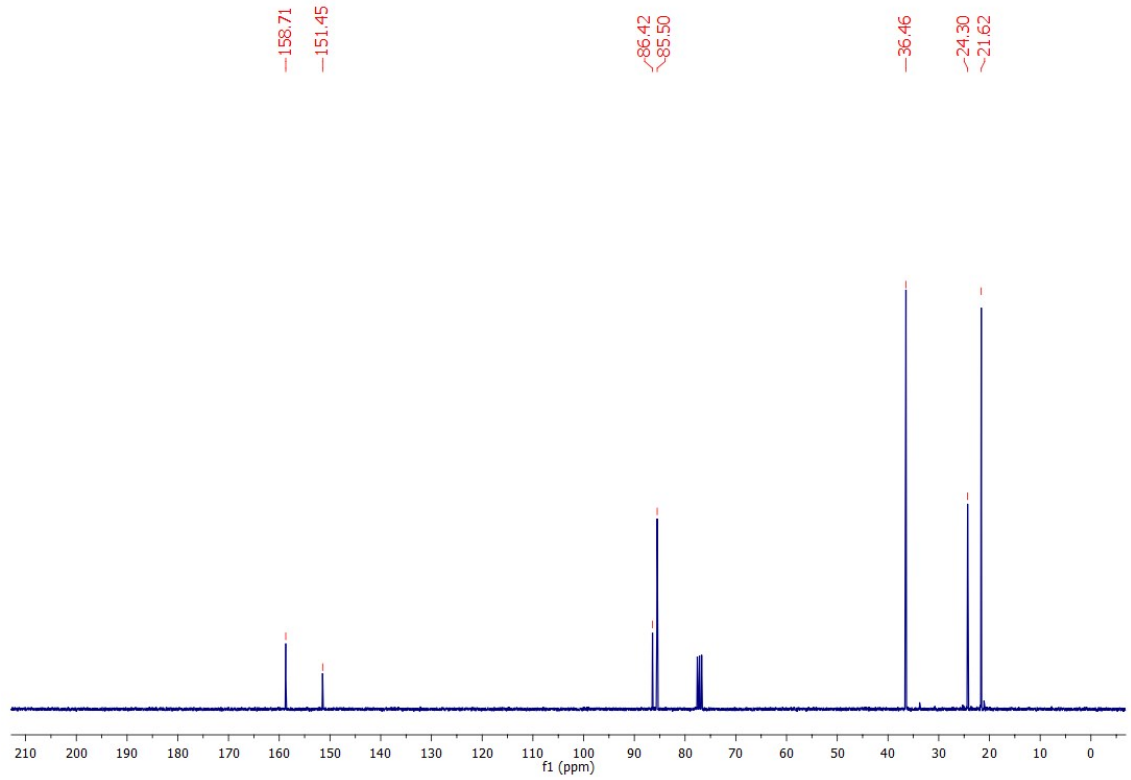
C_{11}



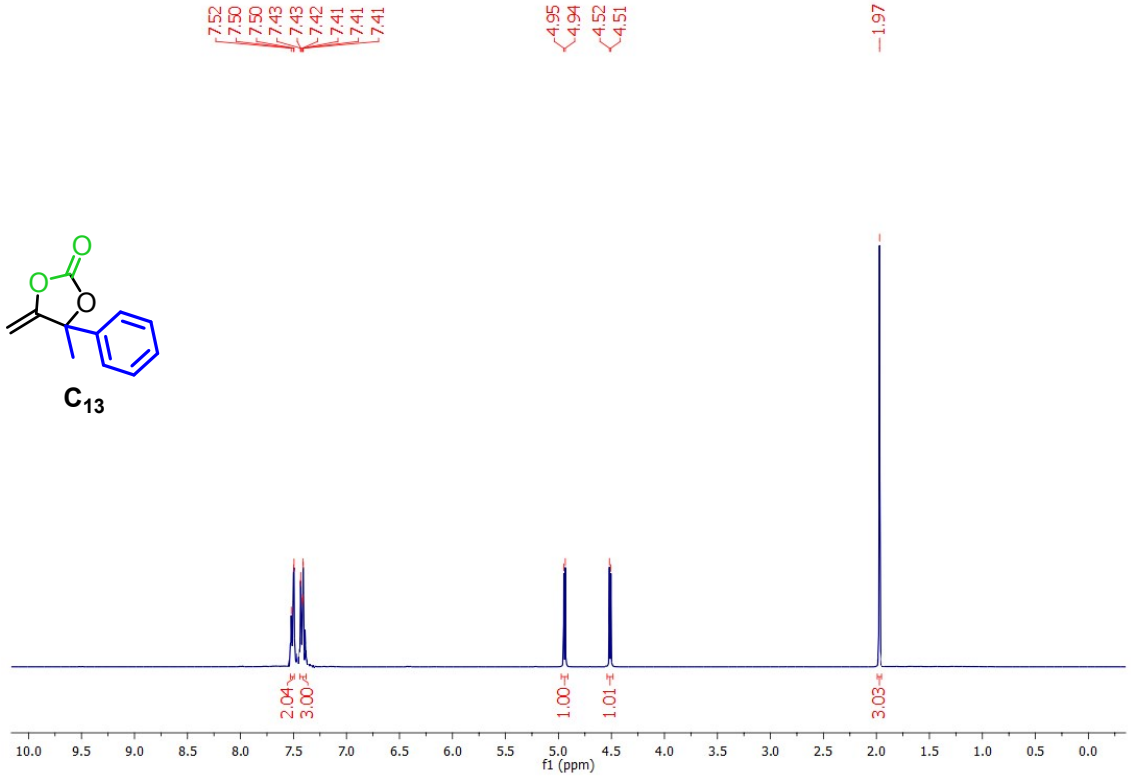
^{1}H NMR and **^{13}C NMR** of **C_{12}**



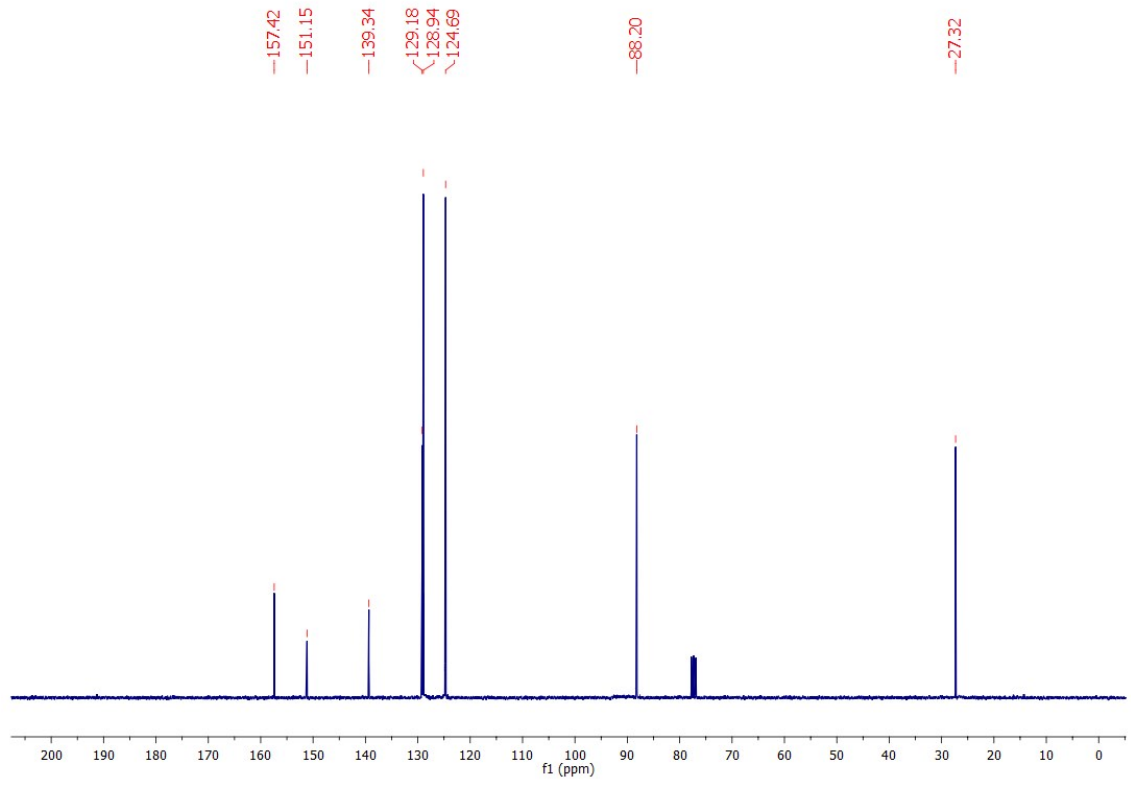
C_{12}



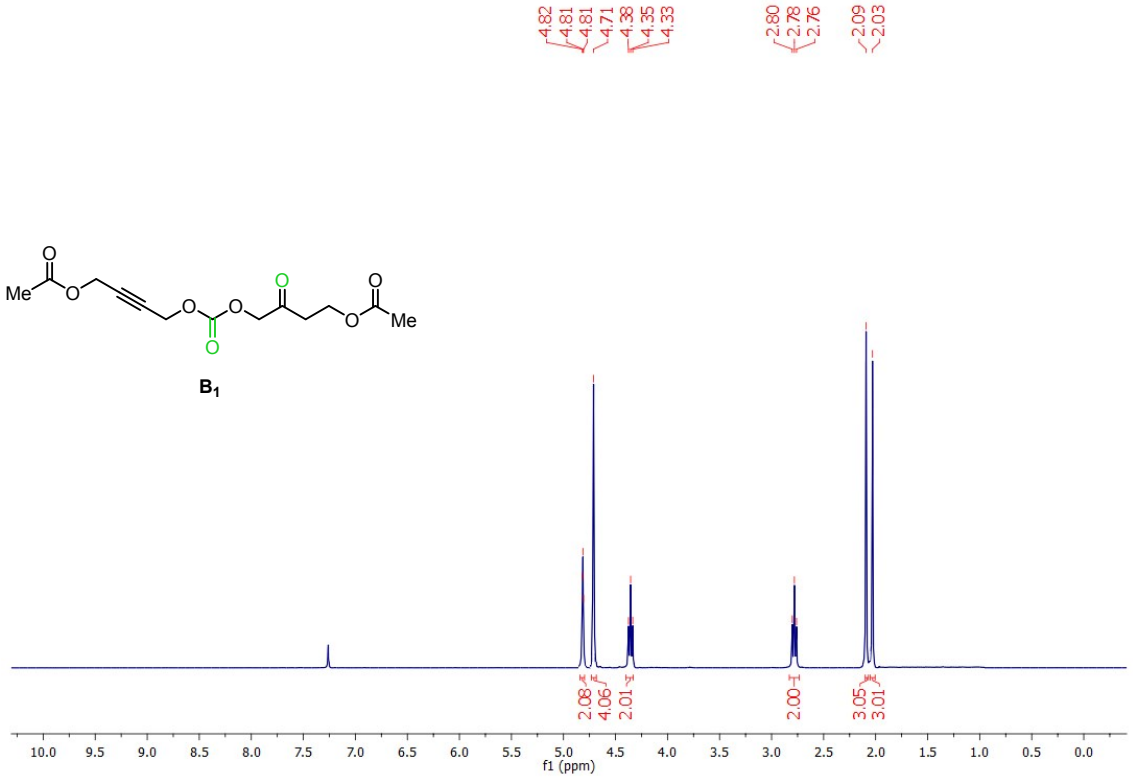
^{1}H NMR and **^{13}C NMR** of **C_{13}**



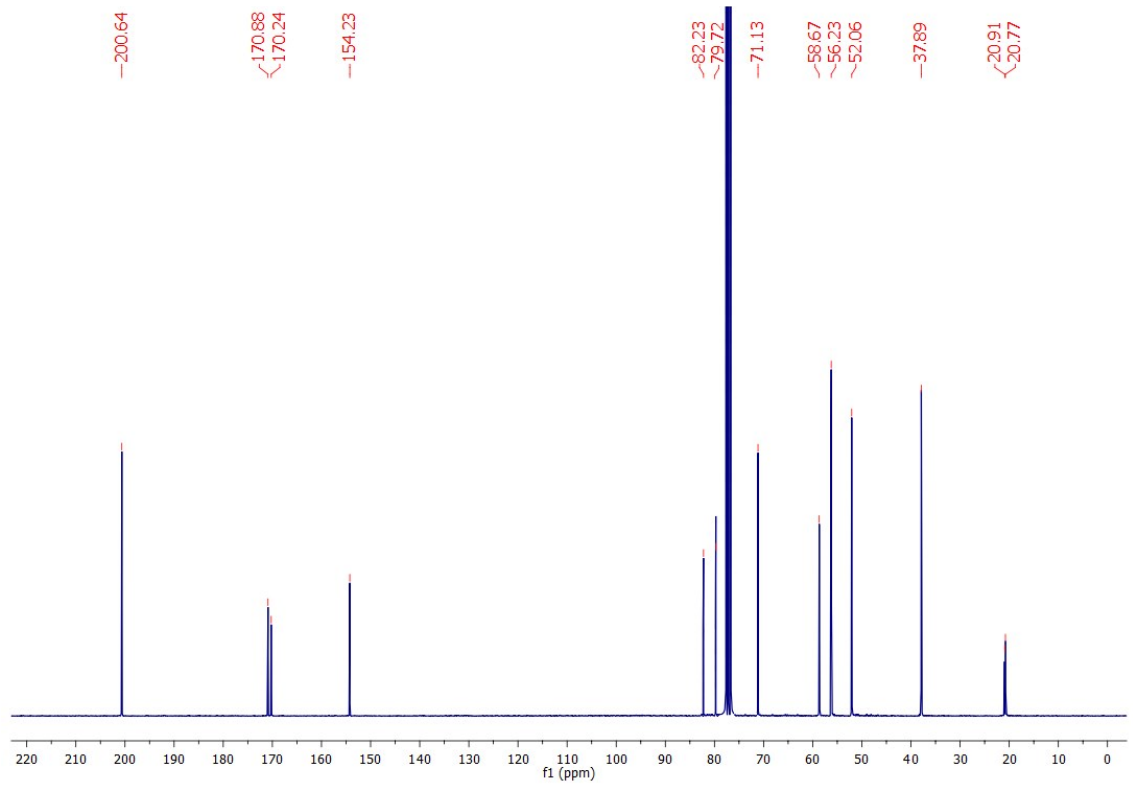
C_{13}



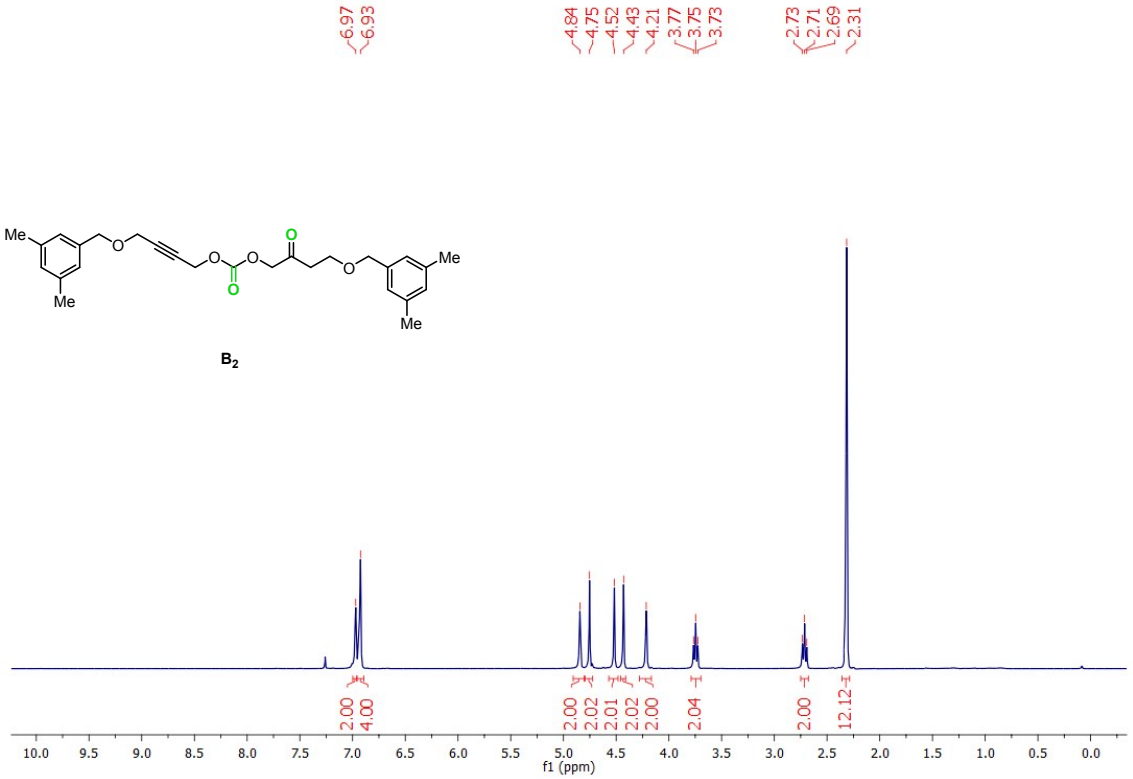
^{1}H NMR and **^{13}C NMR** of **B_1**



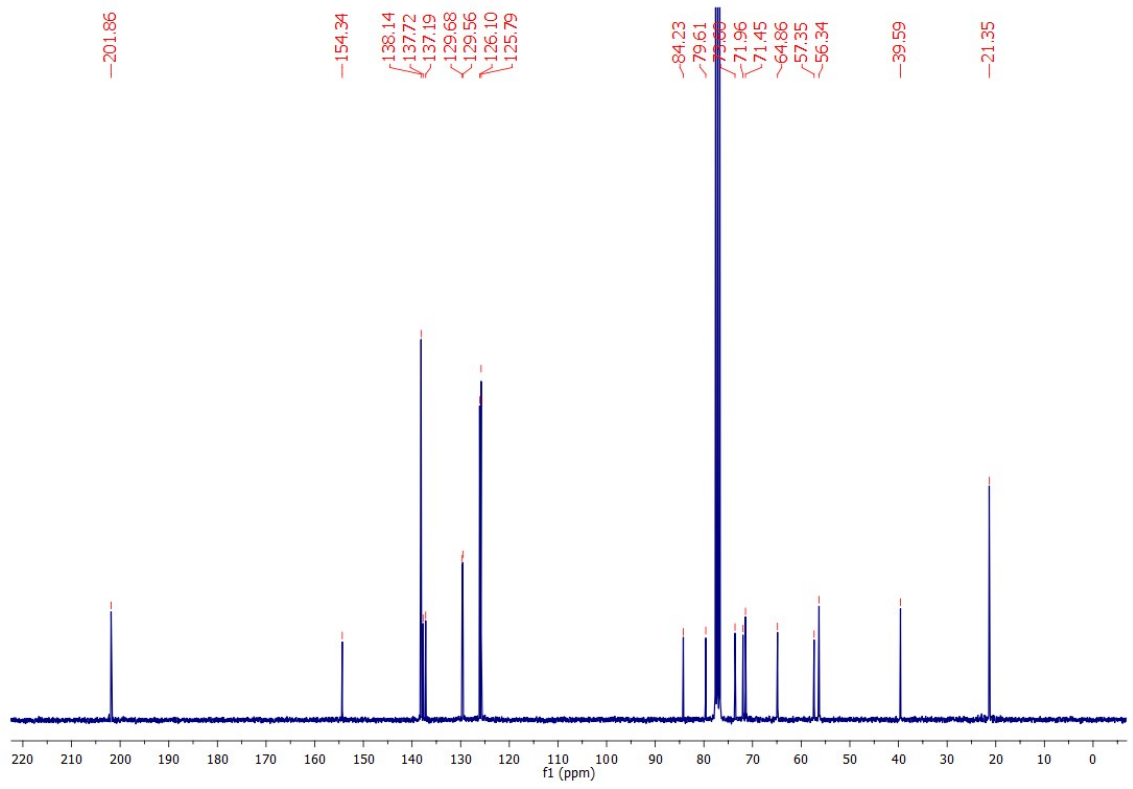
B_1



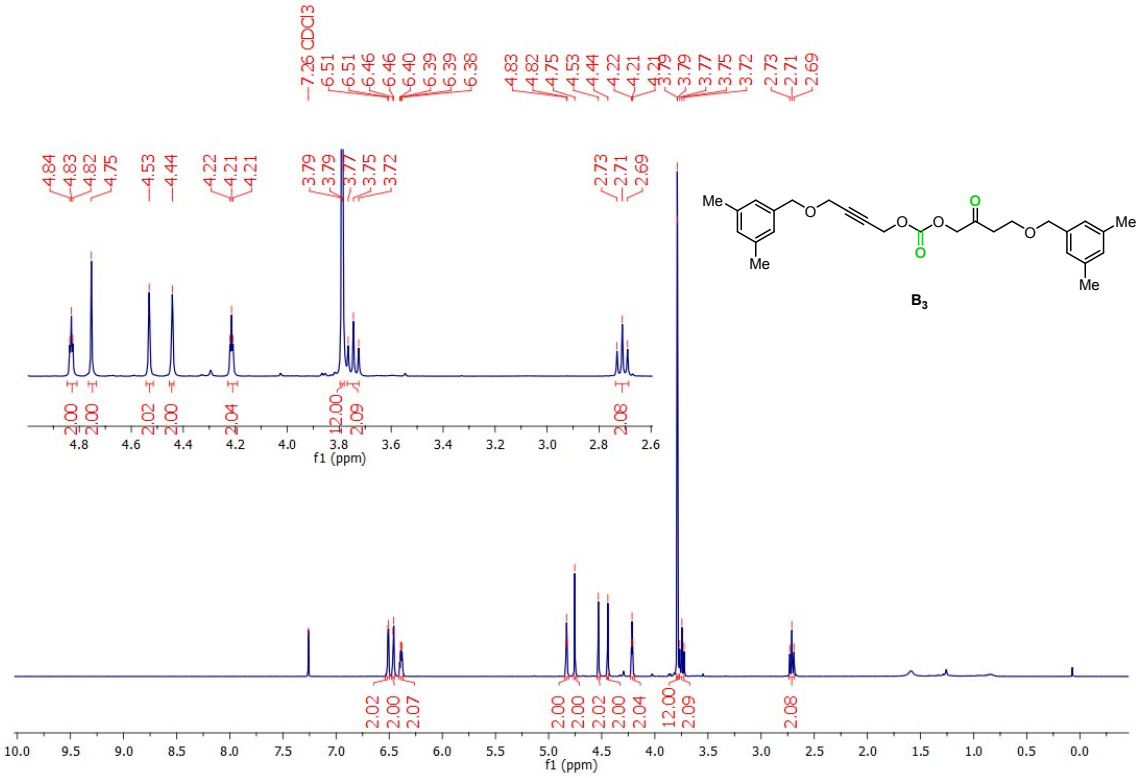
^{1}H NMR and **^{13}C NMR** of **B_2**

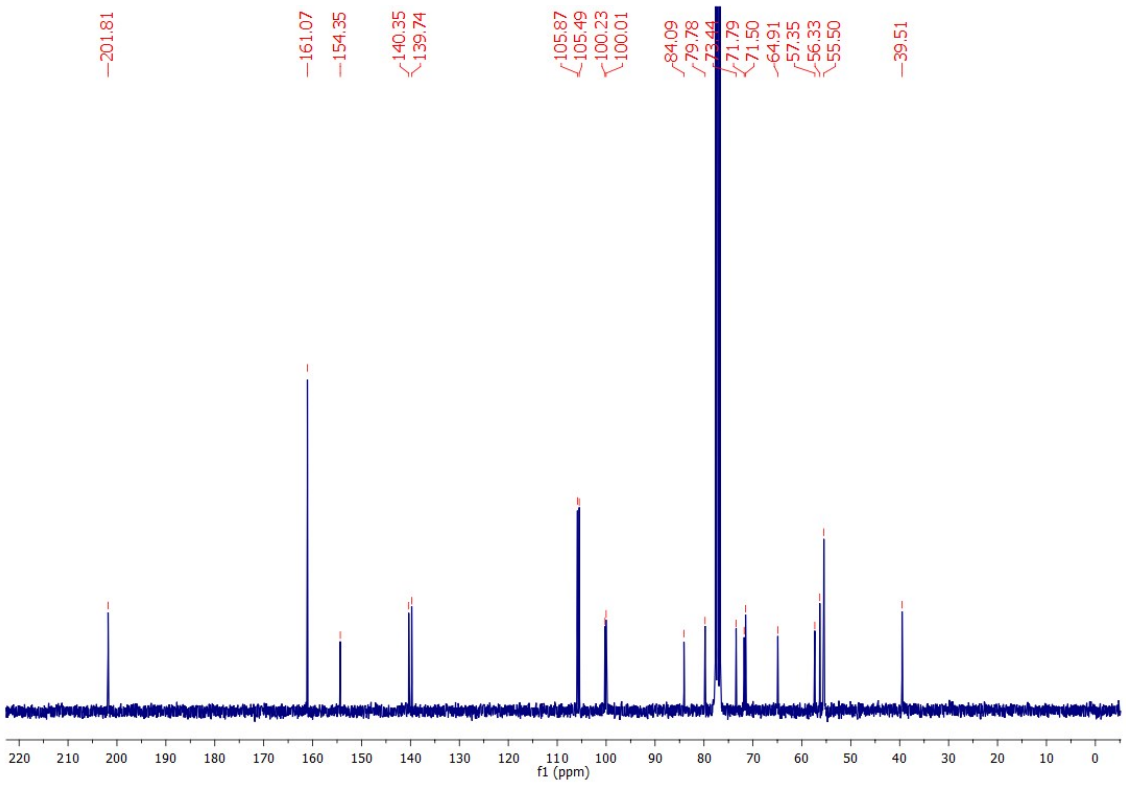


B_2

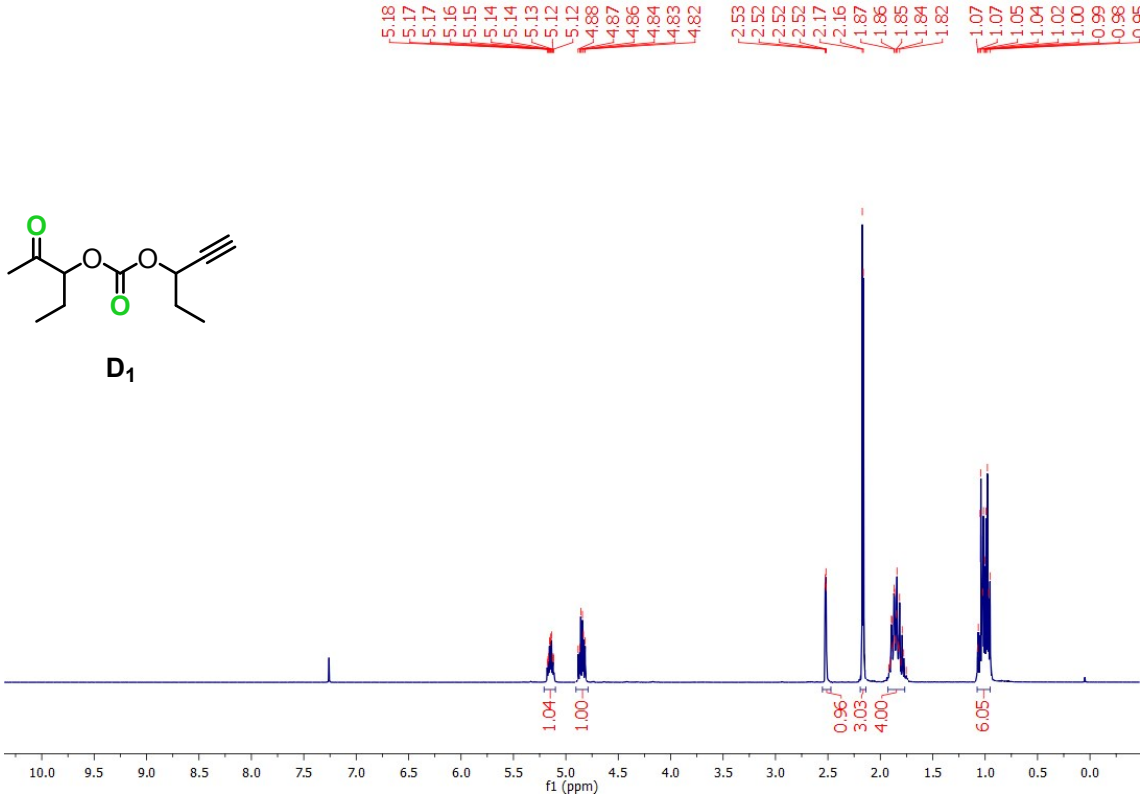


^{1}H NMR and **^{13}C NMR** of **B_3**

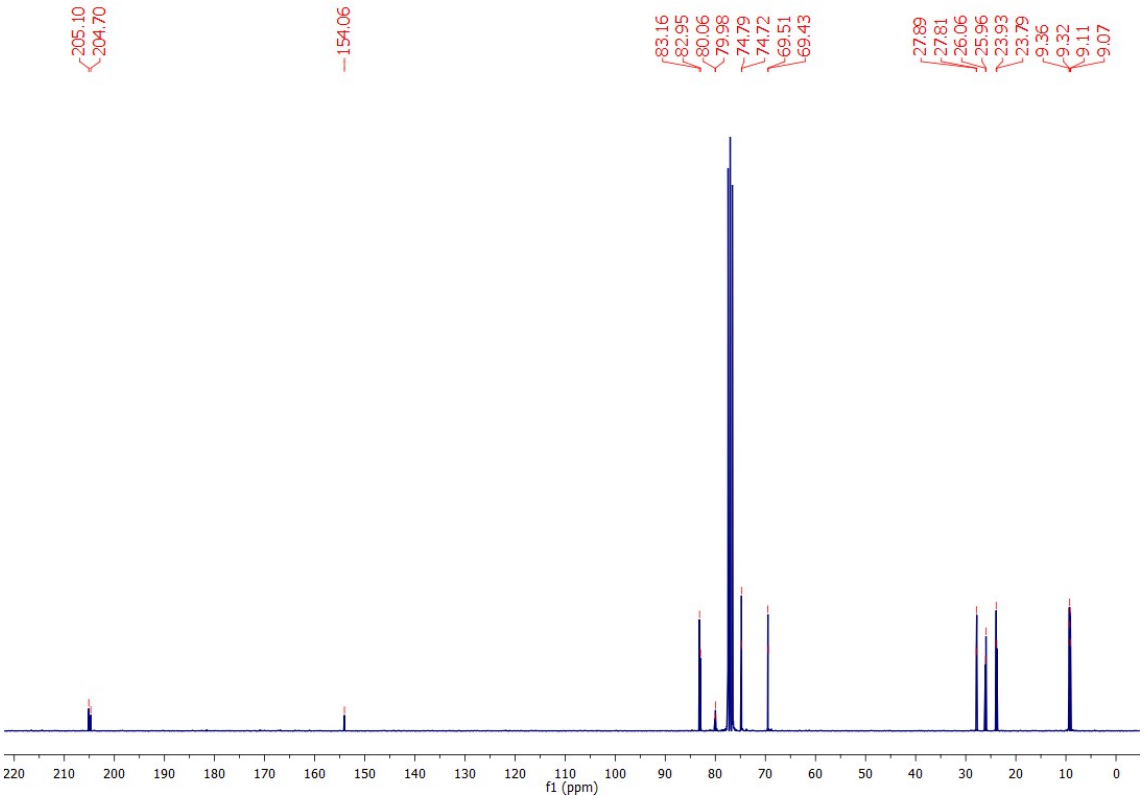




^{1}H NMR and **^{13}C NMR** of **D_1**



D_1



11. Computational details

Gaussian 16[1] was used to fully optimize all the structures reported in this paper at the B3LYP level of theory.[2] For all the calculations, solvent effects were considered using the SMD solvation model with acetonitrile as the solvent.[3] The SDD basis set[4] *with effective core potential (ECP*) was chosen to describe copper. The [6-31G(d)] basis set was used for other atoms.[5] This basis set combination will be referred to as BS1. We also employed the D3 empirical dispersion correction for all the calculations. Frequency calculations were carried out at the same level of theory as those for the structural optimization. Transition structures were located using the Berny algorithm. Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structures and minima.[6] To further refine the energies obtained from the SMD/B3LYP-D3/SDD,6-31G(d) calculations, we carried out single-point energy calculations using the B3LYP-D3 functional method[7] with SMD solvation model in acetonitrile along with a larger basis set (BS2) for all the optimized structures. BS2 utilizes the def2-TZVP basis set[8] on all atoms. Tight convergence criterion and ultrafine integral grid were exploited to increase the accuracy of the single point calculations In this work, the free energy for each species in solution was calculated using the following formula:

$$G = E(BS2) + G(BS1) - E(BS1) + \Delta G^{1atm \rightarrow 1M} \quad (1)$$

where $\Delta G^{1atm \rightarrow 1M}$ = 1.89 kcal/mol is the free-energy change for compression of 1 mol of an ideal gas from 1 atm to the 1 M solution phase standard state.

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Table S1 Cartesian coordinates and total energies for all of the calculated structures.

^{BP}DPrCuF

E (B3LYP-D3-SMD/BS1) = -1920.76953970 au

H (B3LYP-D3-SMD/BS1) = -1919.961551 au

G (B3LYP-D3-SMD/BS1) = -1920.076690 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3364.63884193 au

C	-2.10379600	-4.25595100	-0.97816400
C	-0.73869300	-4.47205500	-0.78105900
C	-0.04835700	-3.63868300	0.09243900
C	-0.66869700	-2.58203400	0.77579700
C	-2.06466400	-2.41646600	0.65308200
C	-2.74830000	-3.25823900	-0.25434900
H	-2.66955100	-4.87090700	-1.67268000
H	-0.21904400	-5.27503500	-1.29610300
H	1.00529100	-3.80909800	0.27150700
H	-3.81302300	-3.10954700	-0.40056000
C	-2.92991100	-1.51615400	1.48047900
C	-4.08158300	-2.13581300	2.01847300
C	-2.75109400	-0.13598800	1.72810800
C	-5.04411600	-1.43964800	2.74206800
H	-4.21071000	-3.20361700	1.87209800
C	-3.74902700	0.55658900	2.43916200
C	-4.88475400	-0.06934700	2.94366000
H	-5.90842600	-1.96502800	3.13898700
H	-3.61988700	1.62316500	2.60658600
H	-5.62841400	0.50560100	3.48857600
C	-1.52897100	0.71627500	1.43045400
H	-1.85412200	1.74794800	1.54198000
H	-0.78394500	0.58100200	2.21463600
C	0.24105600	-1.69585300	1.59973900
H	-0.28746300	-1.21203900	2.41786600
H	1.02336100	-2.30433200	2.05440500
N	-0.82778500	0.66470900	0.12902900
C	0.47319900	0.29076900	-0.01595900
N	0.98199000	-0.69943400	0.74717000
Cu	1.58018800	1.28139800	-1.18285400
C	2.43796100	-0.78549300	0.78440600

C	3.16687700	-1.48724000	-0.20349900
C	3.08841600	-0.11534100	1.84500700
C	4.56479300	-1.51588900	-0.08251800
C	4.48498300	-0.18135700	1.92146300
C	5.22120800	-0.88132000	0.96839400
H	5.14721900	-2.04240600	-0.83298900
H	5.00137700	0.33734800	2.72374800
H	6.30517000	-0.92312800	1.03831400
C	-1.34268400	1.57767000	-0.88121700
C	-1.23522500	2.97812200	-0.69799200
C	-1.93387700	1.03032900	-2.03901300
C	-1.78757100	3.81234700	-1.67851000
C	-2.45185400	1.90947500	-3.00055600
C	-2.39570800	3.28854800	-2.81783600
H	-1.72485100	4.88960100	-1.55349600
H	-2.90104800	1.50696600	-3.90350800
H	-2.81308100	3.95598500	-3.56755800
C	2.32528500	0.76344100	2.82982700
H	1.26035900	0.54230100	2.73722000
C	2.53543600	-2.17490000	-1.40959500
H	1.44978500	-2.11187600	-1.30820700
C	-1.94187400	-0.46838400	-2.29909800
H	-1.73173700	-0.96869500	-1.35457300
C	-0.50292100	3.61952500	0.47930100
H	-0.05661100	2.82742600	1.08531700
C	2.71054000	0.51062300	4.29551600
H	2.07992600	1.11669500	4.95714200
H	2.57296000	-0.54329200	4.56525900
H	3.75370300	0.77938000	4.49778300
C	2.51618500	2.24346700	2.44364300
H	3.56338400	2.54591600	2.56950300
H	2.24095700	2.40998600	1.39552500
H	1.89408700	2.89217600	3.07274700
C	2.93884100	-3.66128900	-1.49567400
H	3.98952500	-3.76557800	-1.79073400
H	2.81473900	-4.18565900	-0.54279500
H	2.33035800	-4.17312100	-2.25061500
C	2.91883200	-1.47813700	-2.72983500
H	2.61319200	-0.42738700	-2.73414900
H	4.00230200	-1.51718700	-2.89538300
H	2.42894300	-1.97864700	-3.57415100
C	-1.45803000	4.43380900	1.37258700
H	-2.29696500	3.82932700	1.73708600
H	-0.91969700	4.82772100	2.24316200
H	-1.87657600	5.28497200	0.82227100
C	0.66178700	4.50788200	0.00074000
H	0.29950100	5.37682000	-0.56099500
H	1.22627800	4.87986200	0.86442400

H	1.34873300	3.94706200	-0.64218400
C	-3.29744400	-0.98752100	-2.80098200
H	-4.10306900	-0.72964900	-2.10307800
H	-3.55643200	-0.57981500	-3.78511700
H	-3.26635100	-2.07875400	-2.89350800
C	-0.80600600	-0.84138600	-3.27120900
H	-0.74816300	-1.93006400	-3.39476500
H	-0.96945600	-0.39132200	-4.25896500
H	0.15925600	-0.48600100	-2.89333600
F	2.64465500	2.33235100	-2.22011200

1a

E (B3LYP-D3-SMD/BS1) = -191.857771917 au

H (B3LYP-D3-SMD/BS1) = -191.791279 au

G (B3LYP-D3-SMD/BS1) = -191.823595 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -191.955708239 au

C	0.61398900	0.57175300	0.00003600
H	0.79272900	1.20315700	-0.88483700
H	0.79263800	1.20318600	0.88491600
C	-0.78501700	0.13811100	-0.00001900
C	-1.94206900	-0.21110400	-0.00002900
H	-2.96726400	-0.51697100	-0.00004600
O	1.46058700	-0.57929000	0.00010500
H	2.37577600	-0.24761500	-0.00079900

MeCN

E (B3LYP-D3-SMD/BS1) = -132.760986376 au

H (B3LYP-D3-SMD/BS1) = -132.710945 au

G (B3LYP-D3-SMD/BS1) = -132.739455 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -132.718131753 au

N	-1.43914500	0.00014900	0.00019800
C	-0.27825300	-0.00031700	-0.00043300
C	1.18014300	0.00007500	0.00007100
H	1.55450400	-0.83286400	-0.60387100
H	1.55422700	0.93987600	-0.41901100
H	1.55394800	-0.10660200	1.02366800

TS_1

E (B3LYP-D3-SMD/BS1) = -2112.63349850 au

H (B3LYP-D3-SMD/BS1) = -2111.760291 au

G (B3LYP-D3-SMD/BS1) = -2111.886601 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3556.59699073 au

Cu	1.86030500	0.41081900	0.00431900
C	3.68532700	1.83875400	-1.92404800
H	2.80279500	2.24514700	-2.43196700
H	3.92386600	0.88148700	-2.40897900
C	4.81704900	2.76118300	-2.08761600
C	5.74954800	3.52087200	-2.21546700

H	6.57545700	4.19158300	-2.32816100
O	3.36045000	1.65540500	-0.54874100
F	4.13606700	-0.21314200	0.60710800
H	3.94166400	0.86316400	-0.06779900
C	-3.45173200	-1.74356400	-3.26520300
C	-2.50792300	-2.74448800	-3.02683100
C	-1.96374000	-2.86194400	-1.75234900
C	-2.31987700	-2.00587000	-0.69998500
C	-3.34042600	-1.05423200	-0.90842600
C	-3.86868000	-0.93336800	-2.21400000
H	-3.87835500	-1.60657800	-4.25507600
H	-2.19959500	-3.42247300	-3.81760600
H	-1.24469700	-3.64479400	-1.54755500
H	-4.61821900	-0.17214300	-2.40328600
C	-4.02294700	-0.24299900	0.14954000
C	-5.43588400	-0.27386500	0.09431400
C	-3.42198500	0.56472300	1.14138100
C	-6.24045100	0.47195000	0.94900600
H	-5.91091000	-0.92148900	-0.63590800
C	-4.25263700	1.33076900	1.98129900
C	-5.64109900	1.29765900	1.89933200
H	-7.32209500	0.40726900	0.86872000
H	-3.78720000	1.96820100	2.72934000
H	-6.24201100	1.90512500	2.57046100
C	-1.95308700	0.64227600	1.52653800
H	-1.85331200	1.55011400	2.11703500
H	-1.70874300	-0.16282100	2.21984200
C	-1.55169600	-2.17913900	0.59191000
H	-2.11551100	-1.83312300	1.45445600
H	-1.35016500	-3.23792400	0.75695900
N	-0.87205500	0.71433100	0.51873900
C	0.09872300	-0.22878100	0.36169400
N	-0.19062800	-1.53502100	0.52141900
C	0.95008400	-2.43476000	0.66068000
C	1.64164100	-2.94112900	-0.46345600
C	1.34218600	-2.76424400	1.97877500
C	2.72236300	-3.80543000	-0.22689300
C	2.42496400	-3.63309900	2.15671500
C	3.10921200	-4.15725800	1.06218800
H	3.27317500	-4.20275100	-1.07436800
H	2.74752700	-3.88914800	3.16111700
H	3.94895900	-4.83043100	1.21465900
C	-0.50911500	2.06441200	0.10931900
C	0.06726600	2.95835600	1.04467600
C	-0.72537500	2.44268300	-1.23225300
C	0.36844500	4.25639800	0.61372900
C	-0.38609400	3.74756100	-1.61782900
C	0.14122100	4.65438400	-0.70244400

H	0.80814700	4.95826000	1.31670600
H	-0.53317500	4.05274600	-2.64961200
H	0.38918100	5.66523700	-1.01610200
C	0.69105900	-2.10991000	3.19268300
H	-0.28541700	-1.72347500	2.89450200
C	1.32307500	-2.57620600	-1.90998100
H	0.41867800	-1.96365700	-1.91751100
C	-1.22474900	1.45517800	-2.27621100
H	-1.60804000	0.58085700	-1.75106300
C	0.44888100	2.55430000	2.46744400
H	0.21183100	1.49742500	2.60610400
C	0.44917700	-3.07679000	4.36164200
H	-0.11036200	-2.56644900	5.15472000
H	-0.13186200	-3.95031700	4.04279400
H	1.38694800	-3.43433100	4.80196400
C	1.54463000	-0.90424700	3.63292700
H	2.52446800	-1.23806500	3.99715800
H	1.71461100	-0.22052300	2.79417800
H	1.04878200	-0.34929900	4.43905400
C	1.08181200	-3.82594200	-2.78128900
H	2.02018200	-4.36182900	-2.96588300
H	0.38739100	-4.53367900	-2.31782100
H	0.67225100	-3.53114300	-3.75465800
C	2.45360700	-1.74262100	-2.54219200
H	2.63776700	-0.82872500	-1.97248200
H	3.39126800	-2.30979700	-2.57935800
H	2.18696100	-1.45422800	-3.56619200
C	-0.32682100	3.36217200	3.52408400
H	-1.41165300	3.26901800	3.39479400
H	-0.07335000	3.01005200	4.53136700
H	-0.07473500	4.42779600	3.46722400
C	1.96668500	2.69125700	2.69471800
H	2.28936000	3.73714100	2.63281800
H	2.23354400	2.31379200	3.68925100
H	2.52974300	2.11967400	1.94933300
C	-2.37077300	2.01725500	-3.13094300
H	-3.20965200	2.34128000	-2.50348300
H	-2.04971800	2.87204500	-3.73765800
H	-2.73898400	1.24524700	-3.81554600
C	-0.05334500	0.97826200	-3.15619200
H	-0.38952800	0.20119200	-3.85406600
H	0.36510900	1.80741800	-3.74094500
H	0.74823700	0.56093100	-2.53778400

2

E (B3LYP-D3-SMD/BS1) = -2112.63752831 au

H (B3LYP-D3-SMD/BS1) = -2111.764472 au

G (B3LYP-D3-SMD/BS1) = -2111.891027 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3556.60528495 au

Cu	1.78535900	0.50389300	-0.13193100
C	3.57628300	1.82453500	-1.88888300
H	2.69776400	2.40640200	-2.20445500
H	3.65553000	0.97847400	-2.59158800
C	4.77512800	2.66779000	-2.02991700
C	5.76022500	3.36240500	-2.13681900
H	6.63250500	3.97444800	-2.23152500
O	3.41147900	1.38644200	-0.55283800
F	4.71267700	-0.43334900	0.25237400
H	4.22248700	0.40195900	-0.14745000
C	-3.53084700	-2.11263200	-2.99205700
C	-2.54596500	-3.06010100	-2.70611700
C	-1.95466000	-3.05210100	-1.44738400
C	-2.30327000	-2.12141500	-0.45783600
C	-3.36291500	-1.22359900	-0.70639900
C	-3.93948600	-1.23037200	-1.99703900
H	-3.99528800	-2.07286000	-3.97352100
H	-2.24145200	-3.79235200	-3.44845200
H	-1.20084700	-3.79023600	-1.20507200
H	-4.72123200	-0.51205900	-2.22083700
C	-4.03816400	-0.34855200	0.30465700
C	-5.44972100	-0.43598000	0.30916000
C	-3.43415300	0.56538200	1.19723000
C	-6.25121500	0.35250300	1.12782700
H	-5.92503700	-1.16211300	-0.34287600
C	-4.26270100	1.37272000	1.99957300
C	-5.65079900	1.28101000	1.97729000
H	-7.33159200	0.24098900	1.09763400
H	-3.79543200	2.09073500	2.66941700
H	-6.25051800	1.92308600	2.61649800
C	-1.95661900	0.72865900	1.51423800
H	-1.86764100	1.68841900	2.01751700
H	-1.65597700	-0.00166200	2.26645600
C	-1.47696100	-2.15666400	0.80926700
H	-2.01456600	-1.75765700	1.66585800
H	-1.22584800	-3.18914900	1.05336700
N	-0.91901900	0.74691500	0.46019700
C	0.07597700	-0.17401300	0.34122400
N	-0.14899600	-1.47104200	0.61906700
C	1.03586800	-2.30732800	0.78599500
C	1.69584100	-2.89639500	-0.31721700
C	1.50397400	-2.48637800	2.10774600
C	2.81429700	-3.70167500	-0.05074300
C	2.62195800	-3.30267900	2.31651700
C	3.26959600	-3.91588800	1.24652900
H	3.34180800	-4.16058600	-0.88176700
H	3.00167800	-3.44295400	3.32393300

H	4.13730300	-4.54651600	1.42241600
C	-0.60791600	2.06649400	-0.07436700
C	-0.01994100	3.05037200	0.75891800
C	-0.88277200	2.32211700	-1.43380700
C	0.22794000	4.31369500	0.20767200
C	-0.59428600	3.59713500	-1.94188100
C	-0.05995700	4.59184400	-1.12757500
H	0.67178200	5.08516900	0.83052000
H	-0.78711600	3.80796200	-2.98953300
H	0.14701900	5.57819100	-1.53490900
C	0.90219800	-1.72143500	3.28150300
H	-0.07867700	-1.34550300	2.98446100
C	1.31118000	-2.66769700	-1.77546900
H	0.38990300	-2.08110000	-1.79825000
C	-1.38774400	1.23512400	-2.37071900
H	-1.72531200	0.39817600	-1.76011300
C	0.42244600	2.77875000	2.19582900
H	0.24693900	1.72390300	2.41986000
C	0.68990200	-2.58382400	4.53495000
H	0.17759300	-1.99756800	5.30725700
H	0.07541100	-3.46417600	4.31191100
H	1.63799900	-2.93044800	4.96173400
C	1.78657400	-0.49572100	3.58588300
H	2.77401000	-0.81126600	3.94572100
H	1.93606400	0.10993200	2.68453600
H	1.32561800	0.13557500	4.35559500
C	1.07369900	-3.99310200	-2.52776200
H	2.01931600	-4.51948000	-2.70229000
H	0.41718700	-4.67588200	-1.97963500
H	0.62081600	-3.79348600	-3.50607900
C	2.39528000	-1.86357100	-2.52023400
H	2.59772400	-0.91138400	-2.02318800
H	3.33678800	-2.42353200	-2.56898500
H	2.07195200	-1.65118800	-3.54652500
C	-0.36858500	3.62651700	3.20943400
H	-1.45018300	3.47056400	3.12073700
H	-0.07132700	3.36891100	4.23322600
H	-0.17337500	4.69536200	3.06104000
C	1.93613200	3.01338300	2.36980700
H	2.19586100	4.07024800	2.23717100
H	2.24674600	2.71601000	3.37872500
H	2.51376000	2.42906600	1.64528100
C	-2.58052100	1.68916900	-3.22578600
H	-3.40751700	2.03816400	-2.59592000
H	-2.30964800	2.50045900	-3.91165100
H	-2.94611900	0.85200300	-3.83068200
C	-0.23202900	0.71963400	-3.24990000
H	-0.56712100	-0.12106400	-3.87016400

H	0.14252500	1.50934900	-3.91370800
H	0.60290200	0.37654200	-2.62923900

3

E (B3LYP-D3-SMD/BS1) = -2012.16756709 au

H (B3LYP-D3-SMD/BS1) = -2011.307281 au

G (B3LYP-D3-SMD/BS1) = -2011.432487 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3456.07224605 au

C	-3.36172900	-3.22962700	-1.99691900
C	-2.18935100	-3.89893900	-1.63977800
C	-1.48334000	-3.46356400	-0.52355800
C	-1.89947700	-2.37123600	0.25142200
C	-3.12775400	-1.74690800	-0.05040300
C	-3.82406200	-2.18814600	-1.19897600
H	-3.92492600	-3.52671200	-2.87736200
H	-1.82966400	-4.74489600	-2.21866300
H	-0.58228500	-3.98287200	-0.22341000
H	-4.74532600	-1.68506800	-1.47390800
C	-3.84083200	-0.73936900	0.79786700
C	-5.20537200	-1.02688100	1.03268500
C	-3.32143000	0.46255400	1.33022200
C	-6.04691700	-0.16909900	1.73293700
H	-5.60686600	-1.96523000	0.66304600
C	-4.19467600	1.32936900	2.01429600
C	-5.53869900	1.03437500	2.22035100
H	-7.08714600	-0.44023200	1.89109600
H	-3.79730100	2.26391000	2.40314200
H	-6.17491700	1.73349400	2.75608300
C	-1.87170600	0.91935200	1.37737800
H	-1.90577700	1.98140800	1.60914200
H	-1.37180200	0.46938800	2.23567000
C	-0.96161800	-1.94435900	1.35970400
H	-1.47899500	-1.41698300	2.15747200
H	-0.50880700	-2.82641300	1.81353000
N	-0.96503000	0.80511200	0.21397200
C	0.16454800	0.04585100	0.19564000
N	0.19750200	-1.14710700	0.82645000
Cu	1.74948200	0.74073200	-0.57813700
C	1.52500100	-1.71997500	1.03472700
C	2.19159600	-2.45164500	0.02317000
C	2.12960000	-1.48384600	2.29091100
C	3.46742100	-2.95738900	0.31896700
C	3.40204200	-2.01557000	2.53363700
C	4.06731200	-2.75393000	1.55808100
H	4.00025600	-3.51678600	-0.44430800
H	3.88489500	-1.83207900	3.48875300
H	5.05590200	-3.15903900	1.75840800
C	-0.95440400	1.96439300	-0.66735400

C	-0.45421800	3.20622700	-0.20470000
C	-1.43333600	1.80845200	-1.98454800
C	-0.50246100	4.29962700	-1.07913800
C	-1.44211800	2.92982800	-2.82621900
C	-0.99569400	4.16953200	-2.37617500
H	-0.13182700	5.26346300	-0.74176500
H	-1.79815500	2.82743600	-3.84696100
H	-1.01928700	5.03135600	-3.03837100
C	1.48988100	-0.57153200	3.33157900
H	0.43507500	-0.44715900	3.08083600
C	1.64061500	-2.68794800	-1.37974600
H	0.63082800	-2.27345400	-1.42374400
C	-1.85156400	0.44973100	-2.52532900
H	-1.99712200	-0.21388300	-1.67390800
C	0.17907100	3.39811000	1.17200500
H	0.21805400	2.42872400	1.67428900
C	1.54561900	-1.13614300	4.75942500
H	0.99712000	-0.47600000	5.44205500
H	1.09055600	-2.13249600	4.81041600
H	2.57331600	-1.21283700	5.13237600
C	2.14621500	0.82117100	3.25167100
H	3.20111600	0.76926600	3.54911200
H	2.10400000	1.21198300	2.22841400
H	1.63696000	1.53099600	3.91532900
C	1.57485600	-4.19100700	-1.72229100
H	2.57982800	-4.60127400	-1.87564200
H	1.09894600	-4.78211600	-0.93371600
H	1.01067400	-4.34072400	-2.65043600
C	2.48819200	-1.97512700	-2.45345200
H	2.56322900	-0.89892400	-2.26697300
H	3.50469800	-2.38507500	-2.48579000
H	2.03566800	-2.11943300	-3.44234400
C	-0.64161000	4.36301000	2.04870300
H	-1.68076900	4.03248200	2.16277100
H	-0.19766300	4.43754600	3.04885700
H	-0.65863100	5.36890000	1.61226500
C	1.63543100	3.89057400	1.05876300
H	1.68362600	4.90018400	0.63376400
H	2.09439600	3.92588000	2.05454700
H	2.23366000	3.22370300	0.42695100
C	-3.17388200	0.48941200	-3.30561200
H	-3.98232400	0.90572600	-2.69259400
H	-3.09586500	1.08993400	-4.21955500
H	-3.46164800	-0.52573500	-3.60089100
C	-0.71618200	-0.14961500	-3.37745400
H	-0.97139300	-1.16779700	-3.69679200
H	-0.53483700	0.45668600	-4.27436900
H	0.21666700	-0.19238200	-2.80396700

C	4.49228700	0.85567200	-0.72596600
H	4.50116300	-0.23710100	-0.90480100
H	4.61666600	0.96954600	0.36949500
C	5.70470400	1.41203300	-1.36736800
C	6.68885300	1.87500900	-1.90104400
H	7.55820100	2.28486400	-2.37037800
O	3.33133500	1.47425400	-1.19785400

HF
E (B3LYP-D3-SMD/BS1) = -100.426566351 au
H (B3LYP-D3-SMD/BS1) = -100.414430 au
G (B3LYP-D3-SMD/BS1) = -100.434179 au
E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -100.499484504 au

H	0.00000000	0.00000000	-0.84701900
F	0.00000000	0.00000000	0.09411300

HCl
E (B3LYP-D3-SMD/BS1) = -460.798104804 au
H (B3LYP-D3-SMD/BS1) = -460.788207 au
G (B3LYP-D3-SMD/BS1) = -460.809413 au
E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -460.840407791 au

Cl	0.00000000	0.00000000	0.07198700
H	0.00000000	0.00000000	-1.22377700

F^-
E (B3LYP-D3-SMD/BS1) = -99.9002530106 au
H (B3LYP-D3-SMD/BS1) = -99.897893 au
G (B3LYP-D3-SMD/BS1) = -99.914412 au
E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -100.020979501 au

F	0.00000000	0.00000000	0.00000000

E (B3LYP-D3-SMD/BS1) = -460.357358878 au
H (B3LYP-D3-SMD/BS1) = -460.354998 au
G (B3LYP-D3-SMD/BS1) = -460.372382 au
E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -460.396980269 au

Cl	0.00000000	0.00000000	0.00000000

^{BP}DprCuF.HF
E (B3LYP-D3-SMD/BS1) = -2021.23269445 au
H (B3LYP-D3-SMD/BS1) = -2020.410729 au
G (B3LYP-D3-SMD/BS1) = -2020.530335 au
E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3465.16349491 au

C	-2.75589800	-3.88525000	-1.28939400
C	-1.44056600	-4.29429100	-1.06055800
C	-0.68553300	-3.61949500	-0.10722500
C	-1.19274800	-2.53638800	0.62511800
C	-2.54599300	-2.17364400	0.46177300
C	-3.29506500	-2.85690200	-0.52322000

H	-3.36636500	-4.37409800	-2.04368600
H	-1.00892900	-5.12465900	-1.61216000
H	0.32795900	-3.93935600	0.09751600
H	-4.32329700	-2.55688900	-0.69664400
C	-3.31321300	-1.21373700	1.31744900
C	-4.55734400	-1.70059700	1.78092800
C	-2.95751900	0.11095700	1.65840900
C	-5.44099600	-0.92488100	2.52368100
H	-4.82480800	-2.72907600	1.55956400
C	-3.87595400	0.88834700	2.38919500
C	-5.10261900	0.39452100	2.82188200
H	-6.38270500	-1.34910400	2.86099700
H	-3.60944000	1.91473800	2.63019900
H	-5.77916500	1.03125200	3.38524500
C	-1.62584500	0.81259600	1.44330000
H	-1.82872100	1.87270900	1.57761600
H	-0.93899500	0.56191400	2.25282400
C	-0.21749200	-1.83558900	1.54528200
H	-0.72095200	-1.32127100	2.36043800
H	0.44395500	-2.57129200	2.00367300
N	-0.87498200	0.71831100	0.17176300
C	0.36753600	0.17199300	0.06265900
N	0.70133700	-0.91327100	0.78820000
Cu	1.62060700	1.05591400	-1.04070300
C	2.12704300	-1.21676700	0.87132600
C	2.79782100	-1.93479400	-0.14565600
C	2.81169200	-0.73990800	2.01284800
C	4.16908300	-2.17995000	0.02837500
C	4.17721400	-1.02018500	2.13911800
C	4.85359900	-1.74027300	1.15695500
H	4.70754200	-2.72405100	-0.74200600
H	4.72143200	-0.65394000	3.00409700
H	5.91491400	-1.94829500	1.26616700
C	-1.20313600	1.74174900	-0.81232400
C	-0.90833500	3.10217700	-0.54934400
C	-1.79618800	1.33960600	-2.02730500
C	-1.27813200	4.05212200	-1.50980900
C	-2.13010200	2.32872300	-2.96342000
C	-1.88974600	3.67527800	-2.70394900
H	-1.06697500	5.10149000	-1.32456000
H	-2.57843600	2.03830500	-3.90871600
H	-2.16463800	4.42985000	-3.43656600
C	2.13148900	0.16940900	3.03074700
H	1.05065700	0.04226100	2.94282200
C	2.14156600	-2.42720200	-1.43169800
H	1.07413800	-2.20108900	-1.37857600
C	-1.98923600	-0.12862300	-2.37423800
H	-1.90615500	-0.70044500	-1.45085400

C	-0.15262900	3.57351900	0.69113000
H	0.12564400	2.69804800	1.28115400
C	2.49969500	-0.14750000	4.48794100
H	1.90374200	0.47645500	5.16472300
H	2.30041000	-1.19835600	4.72936200
H	3.55542000	0.05618500	4.70019800
C	2.44929800	1.63644300	2.67900400
H	3.51944100	1.84087400	2.80903200
H	2.19134500	1.84919100	1.63552300
H	1.88664400	2.32328100	3.32344400
C	2.31745200	-3.94918200	-1.61504400
H	3.35577800	-4.19462500	-1.86685800
H	2.05919900	-4.51417800	-0.71411500
H	1.68397200	-4.30488400	-2.43624100
C	2.71066300	-1.71479000	-2.67526600
H	2.59509200	-0.62838600	-2.61399900
H	3.77825900	-1.93269200	-2.79885100
H	2.18872700	-2.05969100	-3.57624800
C	-1.01473400	4.49424600	1.57467600
H	-1.95389100	4.01435800	1.87405000
H	-0.46725100	4.76660900	2.48515000
H	-1.26846600	5.42039100	1.04522400
C	1.16316700	4.28017500	0.31022800
H	0.97336800	5.21785000	-0.22529000
H	1.73428800	4.52041400	1.21527800
H	1.78580300	3.64424100	-0.32862900
C	-3.36678800	-0.43324500	-2.98080200
H	-4.17411400	-0.09977700	-2.31778400
H	-3.50480700	0.05013900	-3.95502900
H	-3.47587000	-1.51308000	-3.13004200
C	-0.85258500	-0.59997500	-3.30164000
H	-0.92896500	-1.67844300	-3.48787400
H	-0.89062100	-0.07977900	-4.26749100
H	0.12268100	-0.39663000	-2.84606100
F	2.76571000	2.08409700	-2.11347300
F	4.64523000	1.56645100	-0.71914100
H	3.90906200	1.81965300	-1.33863400

CO_2

E (B3LYP-D3-SMD/BS1) = -188.577768095 au

H (B3LYP-D3-SMD/BS1) = -188.562657 au

G (B3LYP-D3-SMD/BS1) = -188.586978 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -188.669945568 au

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16959500
O	0.00000000	0.00000000	-1.16959500

TS_3

E (B3LYP-D3-SMD/BS1) = -2200.76238794 au
H (B3LYP-D3-SMD/BS1) = -2199.886610 au
G (B3LYP-D3-SMD/BS1) = -2200.019432 au
E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3644.75245446 au

C	-3.63471400	-2.40726400	-2.81691800
C	-2.50462400	-3.21136600	-2.65467200
C	-1.80708600	-3.15339600	-1.45288700
C	-2.18950100	-2.30872100	-0.39966200
C	-3.37774000	-1.55919900	-0.52418100
C	-4.06633100	-1.61555500	-1.75796400
H	-4.18951300	-2.40994200	-3.75110900
H	-2.17180200	-3.87441400	-3.44827300
H	-0.94534400	-3.79103200	-1.30622100
H	-4.95433800	-1.00516300	-1.88616800
C	-4.05715800	-0.78645600	0.56383400
C	-5.44064300	-1.04473500	0.69799600
C	-3.48625400	0.19401600	1.40671500
C	-6.25158700	-0.35755900	1.59515200
H	-5.88348200	-1.82284400	0.08404400
C	-4.32793000	0.89761200	2.28865700
C	-5.69127900	0.63942400	2.39284200
H	-7.30887100	-0.59838500	1.66399700
H	-3.88997300	1.66836700	2.91844400
H	-6.30234100	1.20665000	3.08953300
C	-2.01500400	0.52441400	1.59472500
H	-1.98743600	1.48008300	2.11422600
H	-1.56924400	-0.18096900	2.29673400
C	-1.27203300	-2.27906300	0.80472900
H	-1.79584600	-1.98030400	1.71102000
H	-0.88216400	-3.28105000	0.98744100
N	-1.08224600	0.67603200	0.45535200
C	0.00310300	-0.11812000	0.26047300
N	-0.05173700	-1.43337700	0.56057100
Cu	1.64286700	0.65175700	-0.31534300
C	1.24295800	-2.09164300	0.70456300
C	1.95920600	-2.57402900	-0.41645300
C	1.76865100	-2.18768300	2.01242800
C	3.21496900	-3.15549800	-0.18546000
C	3.02277900	-2.78693200	2.18671800
C	3.74440700	-3.26799500	1.09781900
H	3.78687100	-3.52460500	-1.03185300
H	3.44386100	-2.85785100	3.18554200
H	4.72021100	-3.72308500	1.24664700
C	-0.97123600	2.03306500	-0.06321500
C	-0.37395000	3.04613700	0.72494700
C	-1.45922500	2.29505800	-1.35996600
C	-0.32797000	4.34302900	0.19636300
C	-1.37824400	3.60687100	-1.84672200

C	-0.82928600	4.62642400	-1.07260000
H	0.11795500	5.13935300	0.78555200
H	-1.74245400	3.83063800	-2.84467300
H	-0.78131500	5.64034400	-1.46176500
C	1.05223700	-1.60659600	3.22663400
H	0.08297400	-1.22420900	2.90466600
C	1.46000400	-2.48689200	-1.85515300
H	0.46657200	-2.03347100	-1.84202900
C	-1.98774700	1.17399200	-2.24077700
H	-2.27970200	0.35655500	-1.58323000
C	0.25443500	2.78717400	2.09328900
H	0.21875700	1.71339400	2.29481800
C	0.78509900	-2.66870100	4.30625300
H	0.21967500	-2.22885500	5.13686200
H	0.20266500	-3.50584000	3.90336300
H	1.71885700	-3.07214900	4.71548300
C	1.83498900	-0.40961500	3.79711700
H	2.80693400	-0.72460200	4.19519100
H	2.01703700	0.34326400	3.02312500
H	1.27104300	0.06211600	4.61151200
C	1.35668600	-3.88835800	-2.49167500
H	2.35319400	-4.30309900	-2.68400000
H	0.82640700	-4.60015700	-1.85021600
H	0.82880300	-3.83085800	-3.45106800
C	2.35889600	-1.60065400	-2.73935000
H	2.44250500	-0.58458900	-2.34370900
H	3.37003000	-2.01658400	-2.82079300
H	1.93879600	-1.53748600	-3.75097900
C	-0.50758100	3.51463800	3.21721600
H	-1.56949400	3.24344700	3.23757400
H	-0.07439100	3.26297100	4.19292200
H	-0.44430200	4.60215600	3.09094500
C	1.74302000	3.18633900	2.11693000
H	1.86992900	4.26816400	1.99162700
H	2.18930800	2.90619900	3.07882000
H	2.30309200	2.68159200	1.32256000
C	-3.22589700	1.56595500	-3.05924500
H	-4.02178500	1.95654700	-2.41367100
H	-2.99833600	2.32494700	-3.81695900
H	-3.61561600	0.68565100	-3.58272400
C	-0.86705200	0.63651400	-3.15275600
H	-1.22456000	-0.22496300	-3.73039500
H	-0.52927600	1.40803700	-3.85627300
H	-0.00146000	0.31809300	-2.56116400
C	4.44978600	0.60060800	-0.47223300
H	5.32647500	0.98275700	-1.01715800
H	4.33617400	-0.45550000	-0.76956400
C	4.73174600	0.64022200	0.97409900

C	4.92151300	0.67356600	2.16963300
H	5.09697300	0.70374400	3.22386800
O	3.31817600	1.36979700	-0.81098100
C	3.35535000	2.09550000	-2.73836000
O	4.37927100	1.67231500	-3.16586400
O	2.33306500	2.69791800	-2.76594300

4

E (B3LYP-D3-SMD/BS1) = -2200.76685905 au

H (B3LYP-D3-SMD/BS1) = -2199.889004 au

G (B3LYP-D3-SMD/BS1) = -2200.020527 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3644.75667579 au

C	-3.74208700	-2.46371600	-2.67585100
C	-2.61399300	-3.27144600	-2.51708700
C	-1.88305100	-3.17873300	-1.33763900
C	-2.23007500	-2.29558900	-0.30357400
C	-3.41591000	-1.54145600	-0.42081900
C	-4.13878700	-1.63358900	-1.63287000
H	-4.32209900	-2.49292700	-3.59412900
H	-2.30807200	-3.96348300	-3.29660300
H	-1.02307700	-3.81918800	-1.19300100
H	-5.02554700	-1.02051300	-1.75715900
C	-4.05921800	-0.72600000	0.65817800
C	-5.44008000	-0.96848100	0.83956800
C	-3.45872700	0.28039300	1.44858300
C	-6.22129700	-0.24270800	1.73272900
H	-5.90489500	-1.76462600	0.26641100
C	-4.27086800	1.02220600	2.32681800
C	-5.63259200	0.77859200	2.47737800
H	-7.27789700	-0.47261100	1.83910800
H	-3.81072700	1.81181100	2.91603000
H	-6.22041000	1.37571700	3.16904300
C	-1.98059100	0.60429600	1.58539200
H	-1.92929300	1.57780200	2.06930600
H	-1.52205000	-0.08072200	2.29886800
C	-1.28135900	-2.23315400	0.87499200
H	-1.77876100	-1.89995200	1.78415200
H	-0.89321600	-3.23124300	1.08101300
N	-1.07793800	0.70784600	0.41595100
C	-0.00835700	-0.10397100	0.21791400
N	-0.06128700	-1.40560800	0.57124200
Cu	1.61239500	0.62642600	-0.46406100
C	1.23237600	-2.06567200	0.71652200
C	1.92558800	-2.59280100	-0.39864300
C	1.78033500	-2.11864300	2.01775100
C	3.18378700	-3.16999400	-0.16988600
C	3.03511600	-2.71707500	2.19054600
C	3.73647400	-3.23762700	1.10667500

H	3.73776800	-3.57416700	-1.01213200
H	3.47177900	-2.75750000	3.18436700
H	4.71330900	-3.69082700	1.25419300
C	-0.96346800	2.04860600	-0.14387600
C	-0.31066000	3.06631000	0.59116100
C	-1.50591700	2.28753300	-1.42293800
C	-0.25557100	4.34677800	0.02422000
C	-1.41057900	3.58163600	-1.95159400
C	-0.80067000	4.60661700	-1.23156400
H	0.23254200	5.14806000	0.57174800
H	-1.81551600	3.78870200	-2.93724800
H	-0.74289900	5.60746100	-1.65193900
C	1.08218800	-1.50807400	3.22824100
H	0.12280000	-1.10281700	2.90521800
C	1.39321300	-2.56965900	-1.82770400
H	0.40339000	-2.10860100	-1.81305500
C	-2.12011500	1.15727700	-2.23300600
H	-2.44392800	0.39576600	-1.52521600
C	0.36305700	2.82846600	1.94126900
H	0.31173400	1.76143800	2.17355100
C	0.78956900	-2.56013600	4.31154100
H	0.23980100	-2.10374300	5.14372500
H	0.18311500	-3.38185700	3.91243800
H	1.71447800	-2.98790200	4.71635400
C	1.89291200	-0.32875000	3.79562800
H	2.85764200	-0.66358300	4.19476400
H	2.09056100	0.41983600	3.02146700
H	1.33971000	0.15607000	4.60961000
C	1.26485000	-4.00089400	-2.38980700
H	2.25353000	-4.43088400	-2.58901100
H	0.74988400	-4.67552200	-1.69772800
H	0.70974700	-3.98853600	-3.33531900
C	2.27459100	-1.73770300	-2.77952600
H	2.34994500	-0.69451700	-2.46049400
H	3.28985400	-2.14632900	-2.84305100
H	1.84379900	-1.74839700	-3.78840800
C	-0.34162100	3.60128800	3.07217000
H	-1.40761400	3.35403400	3.13648900
H	0.12079400	3.36443300	4.03810500
H	-0.25952600	4.68357500	2.91543400
C	1.85911100	3.19549000	1.89933300
H	2.00461600	4.26960600	1.73543100
H	2.33580200	2.93398000	2.85164600
H	2.37962900	2.65587100	1.10102800
C	-3.35297900	1.57789300	-3.04485500
H	-4.10307700	2.06271900	-2.40851500
H	-3.09781700	2.26796600	-3.85770100
H	-3.81356200	0.69283500	-3.49845600

C	-1.05960400	0.50301300	-3.14014100
H	-1.48801100	-0.35637400	-3.67026800
H	-0.68699300	1.21773000	-3.88502900
H	-0.20339200	0.15195000	-2.55358600
C	4.56916900	0.45122300	-0.56735700
H	5.43031900	0.84174600	-1.11798000
H	4.42872500	-0.60081000	-0.84478000
C	4.76583400	0.56852200	0.87611300
C	4.91100100	0.65420900	2.07349800
H	5.04585600	0.73181300	3.13145900
O	3.41391900	1.20587600	-0.96997300
C	3.47175700	1.93907300	-2.31794600
O	4.57868200	1.94577000	-2.84271900
O	2.34937800	2.37377600	-2.57980300

5

E (B3LYP-D3-SMD/BS1) = -2200.77672375 au

H (B3LYP-D3-SMD/BS1) = -2199.898007 au

G (B3LYP-D3-SMD/BS1) = -2200.028721 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3644.76432516 au

C	-1.30720900	2.98262300	-3.35669100
C	-0.13288700	2.28936800	-3.65603900
C	-0.02056200	0.95900700	-3.26916100
C	-1.03947600	0.28305700	-2.57993800
C	-2.24654300	0.96214200	-2.31772900
C	-2.34398800	2.31678200	-2.71336200
H	-1.42220300	4.02758500	-3.63129100
H	0.67957800	2.77100400	-4.19187100
H	0.87309200	0.40947300	-3.52505500
H	-3.25448100	2.86007600	-2.48508500
C	-3.48321500	0.37908200	-1.71041200
C	-4.68964900	0.68120900	-2.37970800
C	-3.56377900	-0.34846800	-0.50088700
C	-5.93685700	0.32307000	-1.87746200
H	-4.63805700	1.20635300	-3.32852800
C	-4.83427100	-0.67408300	0.00787900
C	-6.01297900	-0.34724200	-0.65719900
H	-6.83673900	0.57320500	-2.43265400
H	-4.89426600	-1.21173800	0.95097100
H	-6.97374600	-0.61945000	-0.22907800
C	-2.41960800	-0.97652500	0.27416400
H	-2.82540900	-1.27313100	1.24112800
H	-2.14216800	-1.90932100	-0.21185900
C	-0.74870500	-1.15558100	-2.19396500
H	-1.65986500	-1.72990800	-2.03217500
H	-0.21927800	-1.64347100	-3.01388000
N	-1.17137600	-0.23981400	0.59032600
C	0.06389700	-0.60178700	0.15978900

N	0.19923300	-1.23872900	-1.03065500
Cu	1.54676600	-0.03599800	1.21044800
C	1.33314900	-2.14525000	-1.18962000
C	2.60001700	-1.70671300	-1.64358400
C	1.09808500	-3.51449900	-0.90806300
C	3.59855000	-2.67312000	-1.84256200
C	2.12733200	-4.43684200	-1.13614900
C	3.36996300	-4.02456700	-1.60674100
H	4.57490000	-2.35395000	-2.19461900
H	1.94898100	-5.49016900	-0.94130500
H	4.15915000	-4.75133500	-1.78132700
C	-1.22058400	0.43745100	1.88158300
C	-1.10148200	-0.33537300	3.06396200
C	-1.40926000	1.83056400	1.92505200
C	-1.17046300	0.33420500	4.29140900
C	-1.46727200	2.45328500	3.18109800
C	-1.35026200	1.71585700	4.35511400
H	-1.07895500	-0.23591300	5.21145200
H	-1.60775200	3.52934600	3.23199400
H	-1.40074200	2.21364400	5.32014600
C	-0.23633100	-4.03200300	-0.38538900
H	-0.83007100	-3.17400000	-0.07498500
C	2.96648800	-0.25331200	-1.91567800
H	2.11061800	0.37231600	-1.64896400
C	-1.53676400	2.67085500	0.66603900
H	-1.44455000	2.00104100	-0.18806900
C	-0.88694400	-1.84820800	3.06307500
H	-0.81369600	-2.19557600	2.02985900
C	-1.01748100	-4.76437400	-1.49134200
H	-1.99929100	-5.08364900	-1.12046400
H	-1.17470500	-4.11912800	-2.36286500
H	-0.47425200	-5.65718200	-1.82519000
C	-0.07682800	-4.92055800	0.86023200
H	0.42514200	-5.86714000	0.62922200
H	0.50134000	-4.41025100	1.63819400
H	-1.06399500	-5.16238100	1.27238500
C	3.31018700	-0.02992300	-3.40315500
H	4.26380500	-0.50893400	-3.65522300
H	2.55284000	-0.44498300	-4.07663300
H	3.40734700	1.04269000	-3.61134000
C	4.16355000	0.19775500	-1.05478200
H	3.98628700	0.01150500	0.00740700
H	5.07964800	-0.32918300	-1.34643000
H	4.33483700	1.27085600	-1.18863400
C	-2.06866700	-2.58568300	3.72003500
H	-3.02046700	-2.33630700	3.23663400
H	-1.92409800	-3.67033200	3.64637100
H	-2.15432900	-2.32922100	4.78273200

C	0.43713600	-2.22989600	3.75027000
H	0.44932600	-1.92044800	4.80172700
H	0.58054000	-3.31632900	3.71862800
H	1.28857000	-1.75824500	3.24523900
C	-2.91595300	3.34750800	0.58441800
H	-3.72227700	2.60499600	0.59466900
H	-3.07388400	4.03294600	1.42607000
H	-2.99982900	3.92900500	-0.34056600
C	-0.40092800	3.70293100	0.55967900
H	-0.45068200	4.22074500	-0.40591100
H	-0.46869800	4.45884400	1.35225900
H	0.57606400	3.21592700	0.63591000
C	3.45536300	3.61522200	0.40993800
H	4.54685900	3.53301700	0.44209300
H	3.16866100	4.46226700	1.04632400
C	2.99335700	3.82380000	-0.96132200
C	2.61773000	3.99975900	-2.09675500
H	2.28926900	4.16268700	-3.10105400
O	2.85985900	2.40687200	0.90448700
C	3.51950400	1.78507800	1.96248300
O	4.50600000	2.30571500	2.47442000
O	2.96267400	0.67069800	2.27756800

6

E (B3LYP-D3-SMD/BS1) = -2200.77253157 au

H (B3LYP-D3-SMD/BS1) = -2199.894342 au

G (B3LYP-D3-SMD/BS1) = -2200.020902 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3644.76005866 au

Cu	-1.74475800	-0.50864800	-0.79415800
C	-4.42154000	-1.30321800	-1.94206100
H	-4.66100500	-0.23823400	-2.04827000
H	-5.00395100	-1.86516800	-2.67951800
C	-2.98134500	-1.49493000	-2.19970300
C	-1.81716900	-1.71907400	-2.52577600
H	-0.90627800	-2.06572100	-2.97255800
O	-4.83143500	-1.79161500	-0.66683600
C	-4.37874000	-1.08529300	0.46965500
O	-3.49720100	-0.18549100	0.27430700
O	-4.90650300	-1.43410800	1.52459100
C	4.19611300	2.58337500	-1.91980500
C	3.07913700	3.41490800	-1.81393400
C	2.17839600	3.19781700	-0.77698300
C	2.34256300	2.16686600	0.16020800
C	3.50556600	1.37190700	0.10430900
C	4.40560600	1.59585200	-0.96310100
H	4.90911800	2.71107900	-2.72967400
H	2.91316600	4.22136500	-2.52263800
H	1.32465500	3.85280900	-0.66548800

H	5.27987200	0.95899000	-1.04896600
C	3.93857900	0.36654100	1.12467700
C	5.29113500	0.46681500	1.52376000
C	3.16718300	-0.68599300	1.66934600
C	5.88882800	-0.43845800	2.39420900
H	5.88236000	1.29495100	1.14555100
C	3.79776200	-1.60756900	2.52666200
C	5.13627300	-1.50147000	2.89197600
H	6.93108200	-0.31326100	2.67463100
H	3.20960000	-2.43045600	2.92564600
H	5.57954300	-2.23586500	3.55884600
C	1.66571200	-0.90410500	1.56225800
H	1.49271500	-1.92307200	1.89756600
H	1.15332300	-0.28627000	2.29924600
C	1.23635600	2.01054000	1.18038300
H	1.57783500	1.51834900	2.08750500
H	0.88790400	2.99850900	1.48151800
N	0.92664500	-0.78904000	0.28313300
C	-0.08400300	0.10262400	0.07427300
N	0.01566600	1.33971400	0.60221900
C	-1.20524800	2.13370400	0.67752300
C	-1.67291600	2.88237200	-0.42599700
C	-1.88324300	2.14369600	1.91651800
C	-2.82447800	3.66365400	-0.24197300
C	-3.00858200	2.96404700	2.05510300
C	-3.47896200	3.72196800	0.98570000
H	-3.20638500	4.24340400	-1.07739600
H	-3.53000100	2.99568300	3.00764600
H	-4.35800600	4.35037500	1.10539700
C	0.87850400	-2.02298600	-0.48738200
C	0.15880200	-3.14038800	-0.00107500
C	1.55555400	-2.06368700	-1.72445300
C	0.17298500	-4.31392400	-0.76728100
C	1.52167900	-3.25546800	-2.46230100
C	0.84814000	-4.37729800	-1.98395600
H	-0.36698800	-5.18589400	-0.40986100
H	2.02790600	-3.30591900	-3.42123700
H	0.84015200	-5.29671900	-2.56381000
C	-1.43699800	1.28807200	3.09679200
H	-0.65701400	0.60939700	2.74601300
C	-1.01540200	2.88485600	-1.80238600
H	-0.08876200	2.30994900	-1.73855200
C	2.24459400	-0.83088400	-2.28970100
H	2.44752500	-0.16391000	-1.45376200
C	-0.67631300	-3.11485600	1.27854100
H	-0.70625800	-2.08676900	1.65224000
C	-0.82989700	2.15365900	4.21554500
H	-0.47585100	1.52210500	5.03991000

H	0.01831600	2.74416900	3.85039100
H	-1.57629700	2.84881000	4.61982400
C	-2.58117300	0.40812200	3.63265800
H	-3.35760100	1.01187900	4.11900900
H	-3.05419500	-0.16417200	2.82762800
H	-2.19129500	-0.29039600	4.38431300
C	-0.67610900	4.31506300	-2.27226200
H	-1.58453000	4.86222300	-2.55012400
H	-0.16759900	4.90127300	-1.50010800
H	-0.02888100	4.27734200	-3.15655800
C	-1.90720000	2.21494300	-2.86532400
H	-2.13908900	1.17839200	-2.60676700
H	-2.85470600	2.75530700	-2.97994200
H	-1.39811600	2.21425800	-3.83737300
C	-0.08016000	-4.02060100	2.37388900
H	0.95241900	-3.75255500	2.62476300
H	-0.68016100	-3.95205900	3.28938700
H	-0.08054000	-5.06775100	2.04795800
C	-2.13536400	-3.52832500	1.00428700
H	-2.21571300	-4.60366400	0.80579200
H	-2.76514400	-3.29468600	1.86905100
H	-2.54459100	-2.99701900	0.14228800
C	3.58800500	-1.13809200	-2.96686100
H	4.25629000	-1.68866600	-2.29387100
H	3.46495600	-1.72781800	-3.88287800
H	4.08350400	-0.20119300	-3.24408900
C	1.30431200	-0.07362700	-3.24783500
H	1.78144600	0.84971300	-3.59852400
H	1.05899700	-0.68723200	-4.12447700
H	0.36755800	0.19298500	-2.74777700

7

E (B3LYP-D3-SMD/BS1) = -2200.75806366 au

H (B3LYP-D3-SMD/BS1) = -2199.880617 au

G (B3LYP-D3-SMD/BS1) = -2200.005776 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3644.75198950 au

Cu	1.87170700	0.39416700	0.16099200
C	4.56855900	1.42440200	-1.23866000
H	5.24681200	2.22412700	-0.91643000
H	5.16064500	0.63533200	-1.71676700
C	3.96491000	0.84080800	-0.01451500
C	3.73530200	0.28995700	1.06031800
H	3.72443600	-0.17228300	2.02874600
O	3.65554800	1.88300700	-2.21025400
C	2.96174400	3.11830700	-1.87961100
O	2.27989000	3.53483300	-2.82663800
O	3.16846600	3.55550000	-0.72942800
C	-3.21229000	-1.72180000	-3.53633500
C	-2.21240000	-2.68093700	-3.36567200

C	-1.70413100	-2.89844400	-2.08968900
C	-2.15083100	-2.18558100	-0.96599000
C	-3.23774800	-1.29681700	-1.11349900
C	-3.72393300	-1.06587300	-2.42181800
H	-3.61103100	-1.50270000	-4.52300400
H	-1.83174700	-3.24909100	-4.20968300
H	-0.94253400	-3.65313500	-1.94266800
H	-4.51866300	-0.33998800	-2.55954200
C	-4.02789300	-0.65782000	-0.01182500
C	-5.43009800	-0.78127300	-0.14623600
C	-3.53855900	0.08388700	1.08739100
C	-6.32780800	-0.17992900	0.72993800
H	-5.82128000	-1.38402000	-0.95971600
C	-4.46166300	0.70823300	1.94694100
C	-5.83858200	0.59034300	1.78380700
H	-7.39647300	-0.31168900	0.58438500
H	-4.07989300	1.29883400	2.77625300
H	-6.51470700	1.08817300	2.47333900
C	-2.10194400	0.20201500	1.56181200
H	-2.09373200	1.00635300	2.29358600
H	-1.82415300	-0.68521000	2.12850800
C	-1.40311500	-2.44062700	0.32656400
H	-2.02555100	-2.27525100	1.20276300
H	-1.08810400	-3.48375200	0.36256500
N	-0.99023300	0.51274900	0.63362100
C	0.05270300	-0.31552900	0.39666200
N	-0.11582900	-1.65538200	0.40003000
C	1.11178200	-2.43587400	0.53793000
C	1.91152700	-2.76435400	-0.58132500
C	1.49526800	-2.79758100	1.84892800
C	3.10707900	-3.46034600	-0.34635200
C	2.69503300	-3.49853300	2.02556200
C	3.49927300	-3.82796600	0.93762600
H	3.74149400	-3.71539100	-1.19005800
H	3.01010700	-3.77118400	3.02847500
H	4.43110500	-4.36645200	1.09001200
C	-0.76198700	1.93627200	0.42881700
C	-0.30003400	2.73660900	1.49988100
C	-1.03892700	2.48494000	-0.84101800
C	-0.18080300	4.11556700	1.28264400
C	-0.88163300	3.86687200	-1.01133500
C	-0.47589500	4.67990700	0.04403100
H	0.16200300	4.75177000	2.09371300
H	-1.07826300	4.31176300	-1.98100900
H	-0.37200600	5.75179400	-0.10380400
C	0.70046600	-2.37150700	3.07806100
H	-0.25311900	-1.95711800	2.74743900
C	1.56438700	-2.40234300	-2.02100400

H	0.59231200	-1.90565300	-2.02081400
C	-1.44510700	1.59893400	-2.00886600
H	-1.92947400	0.71684600	-1.59057100
C	0.10426300	2.16936000	2.85801600
H	0.00760000	1.08169100	2.82367300
C	0.37914100	-3.54590700	4.01621700
H	-0.25078400	-3.20123200	4.84513700
H	-0.16004500	-4.33978100	3.48581000
H	1.28614500	-3.98296100	4.44969500
C	1.44980200	-1.24691600	3.81687100
H	2.40559900	-1.60846800	4.21590600
H	1.65918700	-0.41330300	3.13924100
H	0.85175500	-0.86750400	4.65455800
C	1.47346800	-3.66636200	-2.90136600
H	2.46971700	-4.08445200	-3.08775900
H	0.87030700	-4.45476900	-2.43912000
H	1.02967300	-3.41870700	-3.87282800
C	2.57794300	-1.42813300	-2.64900400
H	2.61573700	-0.47101300	-2.12379000
H	3.58923400	-1.85252600	-2.65223900
H	2.29716900	-1.22047200	-3.68918700
C	-0.79485400	2.69507500	3.99282900
H	-1.85592800	2.49598900	3.80209900
H	-0.52475400	2.21640400	4.94193600
H	-0.67640500	3.77806300	4.11667100
C	1.58224900	2.46989000	3.16817900
H	1.75880000	3.54646600	3.27408400
H	1.87591400	1.98624700	4.10771600
H	2.23478600	2.09492700	2.37339300
C	-2.44973700	2.25810700	-2.96435100
H	-3.32095800	2.64778400	-2.42414400
H	-2.00182400	3.08341100	-3.53024300
H	-2.80407800	1.51751700	-3.69038300
C	-0.19714200	1.11374300	-2.77293200
H	-0.48833800	0.47741200	-3.61843300
H	0.39803500	1.95675200	-3.14182700
H	0.45027400	0.52468600	-2.11517600

TS_6

E (B3LYP-D3-SMD/BS1) = -2200.74327093 au

H (B3LYP-D3-SMD/BS1) = - -2199.866570 au

G (B3LYP-D3-SMD/BS1) = -2199.994200 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3644.73109953 au

C	3.10925700	1.64991300	-3.66250600
C	2.14957400	2.63157100	-3.40664800
C	1.73135300	2.83315500	-2.09590300
C	2.23292700	2.08332400	-1.02093400
C	3.27769700	1.16522100	-1.25731000

C	3.67171500	0.95164600	-2.59908100
H	3.43706100	1.44433200	-4.67779600
H	1.73010100	3.22739700	-4.21224700
H	0.99690100	3.59938200	-1.88112700
H	4.43364800	0.20671400	-2.80450700
C	4.11214000	0.47586300	-0.21956600
C	5.50664500	0.56097300	-0.43870300
C	3.66862200	-0.27865300	0.89155900
C	6.43854600	-0.08741400	0.36512300
H	5.86466200	1.17153000	-1.26165400
C	4.62511700	-0.95026100	1.67614200
C	5.99220400	-0.86860400	1.42992000
H	7.49964100	0.01648000	0.15557200
H	4.27807200	-1.54988100	2.51435200
H	6.69411600	-1.40289700	2.06425300
C	2.26178500	-0.37083000	1.45781600
H	2.27594500	-1.20322800	2.15773500
H	2.05530900	0.50163300	2.07732200
C	1.58386900	2.32622900	0.32407900
H	2.25153600	2.09743900	1.15053100
H	1.32415900	3.38098800	0.41844100
N	1.07919900	-0.60948800	0.59976200
C	0.04808600	0.26455500	0.46359300
N	0.27191900	1.59519500	0.45342600
Cu	-1.79473100	-0.35133100	0.51045400
C	-0.91298000	2.43221900	0.62765500
C	-1.75005400	2.77199400	-0.46132800
C	-1.20777300	2.85459900	1.94376200
C	-2.88522700	3.55166500	-0.19058600
C	-2.35004000	3.63625800	2.15612500
C	-3.18491700	3.98613900	1.09746800
H	-3.54807300	3.81617100	-1.00925600
H	-2.59787300	3.95641400	3.16388100
H	-4.07094500	4.58975900	1.27693100
C	0.75773200	-2.01605800	0.39575100
C	0.26882200	-2.79713700	1.46950200
C	0.95017000	-2.56429400	-0.89025500
C	-0.00721500	-4.14931300	1.22311900
C	0.64962800	-3.91865000	-1.08600300
C	0.18000700	-4.70825600	-0.03881800
H	-0.37820400	-4.77005800	2.03365700
H	0.78161800	-4.35968300	-2.06890800
H	-0.04277100	-5.75900800	-0.20652800
C	-0.38769100	2.39238000	3.14284400
H	0.54009500	1.94921800	2.77701100
C	-1.52117100	2.31388600	-1.89776600
H	-0.56162300	1.79574000	-1.93904400
C	1.40831900	-1.69404500	-2.04971600

H	1.98429600	-0.87320200	-1.62344000
C	0.01794300	-2.24202500	2.86971900
H	0.17731500	-1.16096800	2.84921600
C	0.00297800	3.54109900	4.08572300
H	0.64872000	3.16342500	4.88765400
H	0.54968800	4.32564300	3.54908500
H	-0.87368700	4.00020800	4.55694100
C	-1.15567800	1.28528100	3.89078800
H	-2.07997400	1.68107000	4.33005900
H	-1.42874100	0.47438800	3.20628600
H	-0.54410400	0.86567500	4.69912000
C	-1.47581000	3.50605200	-2.87522500
H	-2.47301100	3.94054200	-3.01166600
H	-0.81483500	4.30696400	-2.52845500
H	-1.12298300	3.17167500	-3.85794900
C	-2.60424800	1.32330200	-2.36672100
H	-2.64047300	0.43281300	-1.73594700
H	-3.59709600	1.78946200	-2.35126700
H	-2.39828800	0.99788800	-3.39339100
C	0.98675700	-2.85406000	3.90041700
H	2.03595400	-2.70965900	3.61749700
H	0.83398500	-2.39391700	4.88423800
H	0.81548600	-3.93247500	4.00196400
C	-1.43770100	-2.46424100	3.32066900
H	-1.66466000	-3.53018800	3.43792800
H	-1.60841600	-1.97694400	4.28826600
H	-2.14313300	-2.04255000	2.59653900
C	2.32213800	-2.41837000	-3.04762000
H	3.16934200	-2.89721000	-2.54183000
H	1.78644900	-3.18663800	-3.61767400
H	2.72169100	-1.69568200	-3.76854600
C	0.19518600	-1.06827800	-2.76407300
H	0.52992200	-0.39526000	-3.56375400
H	-0.46102800	-1.83188700	-3.19668000
H	-0.41014300	-0.49074100	-2.06056300
C	-5.29680000	-1.87027400	-0.68245100
H	-5.42597800	-2.90676300	-0.34207400
H	-6.25599100	-1.34697600	-0.58777500
C	-4.30093700	-1.18090500	0.15523300
C	-3.73015500	-0.43829100	0.98941000
H	-4.07221200	0.24885400	1.75401900
O	-4.92222900	-1.83967000	-2.05374200
C	-3.54815700	-2.12279700	-2.20921900
O	-3.14203100	-2.24324500	-3.36158600
O	-2.93174700	-2.20392700	-1.09439800

TS_7

E (B3LYP-D3-SMD/BS1) = -2200.74743232 au

H (B3LYP-D3-SMD/BS1) = -2199.870227 au
G (B3LYP-D3-SMD/BS1) = -2199.996685 au
E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3644.73924792 au

Cu	-1.36828500	1.28049800	0.29245600
C	-4.04770200	0.73655500	-1.73943300
H	-4.74426400	1.42690200	-2.23718800
H	-3.10216900	0.75133100	-2.28719600
C	-3.82854400	1.20763300	-0.36336500
C	-3.27034800	1.78334200	0.60395900
H	-3.56241000	2.11193500	1.59097500
O	-4.54904000	-0.58744500	-1.76387700
C	-5.51723400	-0.80182200	-0.74589700
O	-6.02831100	-1.92196600	-0.73569500
O	-5.70465700	0.20479800	0.00344100
C	2.29075200	-1.97427700	-3.94541100
C	2.41788900	-0.58744400	-4.05018600
C	2.63918600	0.15493800	-2.89549000
C	2.73284500	-0.43522000	-1.62560300
C	2.69817800	-1.84117500	-1.52495800
C	2.45024800	-2.58136400	-2.70437700
H	2.09095300	-2.58225600	-4.82345300
H	2.34624900	-0.09077700	-5.01370200
H	2.76328100	1.22707500	-2.96743400
H	2.36962400	-3.66130000	-2.63242200
C	3.01769900	-2.64990700	-0.30580300
C	3.94031600	-3.69987100	-0.51744000
C	2.46111800	-2.51322600	0.98577800
C	4.29298400	-4.60439500	0.47858500
H	4.40253000	-3.79294700	-1.49525400
C	2.80949500	-3.45403400	1.97308800
C	3.70887600	-4.48972300	1.73952300
H	5.01256400	-5.39042700	0.26679400
H	2.36238200	-3.35988900	2.95977800
H	3.94999200	-5.19181000	2.53284400
C	1.60319300	-1.37831400	1.52066000
H	1.15920200	-1.75109600	2.44171700
H	2.24330600	-0.55377000	1.83626500
C	2.86320700	0.51325600	-0.45177200
H	3.34871600	0.04691700	0.40333300
H	3.48508000	1.36207000	-0.73802800
N	0.47386600	-0.80375800	0.75526500
C	0.41404100	0.47643400	0.30459700
N	1.53491800	1.11989700	-0.08201200
C	1.46043300	2.57679700	-0.08720100
C	0.93000400	3.29478600	-1.18438000
C	1.92560600	3.24116600	1.07050100
C	0.87968800	4.69370400	-1.08616500
C	1.86755000	4.64039400	1.10867800

C	1.34548900	5.36530000	0.04098800
H	0.47003300	5.26501400	-1.91409400
H	2.22681800	5.16298800	1.99068800
H	1.30059700	6.45038900	0.08646800
C	-0.82868800	-1.40111700	1.03040100
C	-1.46052100	-1.16244400	2.27417100
C	-1.45699500	-2.13566900	0.00556100
C	-2.75596600	-1.66712600	2.45147200
C	-2.76778500	-2.58122700	0.21876800
C	-3.41419500	-2.34882900	1.42979200
H	-3.26639500	-1.49552500	3.39500400
H	-3.30351300	-3.08349700	-0.57875500
H	-4.44025600	-2.67881100	1.56138200
C	2.46875500	2.49439800	2.28355500
H	2.38542700	1.42388900	2.09235500
C	0.41099300	2.64577400	-2.46215700
H	0.54108100	1.56502800	-2.37073200
C	-0.76197100	-2.37439000	-1.32485000
H	0.30395000	-2.22381700	-1.16130700
C	-0.81594000	-0.36958500	3.41133600
H	0.13685700	0.03819800	3.06376500
C	3.95796000	2.80350300	2.51550500
H	4.33995100	2.22118700	3.36291800
H	4.55693000	2.55315600	1.63196800
H	4.11357000	3.86569400	2.73970200
C	1.63310400	2.78661600	3.54262700
H	1.71957000	3.83572800	3.84940700
H	0.57329200	2.57090800	3.36934500
H	1.97602300	2.16356400	4.37780200
C	1.19789700	3.13828800	-3.69455800
H	0.95166100	4.18234700	-3.92094700
H	2.28155200	3.08466800	-3.54690500
H	0.94024100	2.53647600	-4.57420200
C	-1.08886700	2.91552900	-2.68645700
H	-1.68907700	2.58942100	-1.83232200
H	-1.28119800	3.98375700	-2.84328500
H	-1.43761500	2.37690600	-3.57603100
C	-0.53305900	-1.28028100	4.62158700
H	0.07895400	-2.14677700	4.34481100
H	-0.00157800	-0.72266500	5.40224200
H	-1.46823100	-1.65727200	5.05290900
C	-1.66732600	0.83998600	3.83668800
H	-2.66577700	0.53889300	4.17316900
H	-1.17927600	1.36791200	4.66444800
H	-1.78296400	1.54372200	3.00626000
C	-0.94328500	-3.80593900	-1.85054200
H	-0.62856000	-4.54618700	-1.10512000
H	-1.98454400	-4.01676700	-2.12122200

H	-0.33298600	-3.94932200	-2.75016100
C	-1.21153800	-1.34110300	-2.37319500
H	-0.66370900	-1.48344300	-3.31253800
H	-2.28446000	-1.43656100	-2.57249200
H	-1.02180700	-0.32118300	-2.01799200

8

E (B3LYP-D3-SMD/BS1) = -2200.78347729 au

H (B3LYP-D3-SMD/BS1) = -2199.903641 au

G (B3LYP-D3-SMD/BS1) = -2200.032470 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3644.76738234 au

Cu	-1.66664100	0.46606800	0.40276700
C	-3.88801600	-1.30643500	-1.38844800
H	-3.46300500	-0.79061200	-2.25544000
H	-3.19056200	-2.07805400	-1.05319900
C	-4.30970100	-0.36370600	-0.28532500
C	-3.58736600	0.42424900	0.50478000
H	-4.18301100	1.01288600	1.21312400
O	-5.12413900	-1.94294100	-1.79816000
C	-6.15769000	-1.40611900	-1.11861300
O	-7.31038200	-1.72626500	-1.27548800
O	-5.73744400	-0.47050800	-0.24162300
C	3.56336700	0.24321500	-3.76328500
C	3.07027100	1.53501500	-3.56950800
C	2.79169900	1.95750600	-2.27419100
C	2.97986700	1.13259100	-1.15533400
C	3.57312800	-0.13533900	-1.33354100
C	3.82675900	-0.55984100	-2.65837700
H	3.76493100	-0.13068300	-4.76338000
H	2.90270900	2.20224900	-4.41019400
H	2.42241500	2.96129200	-2.10636000
H	4.23154300	-1.55382800	-2.81738700
C	4.09045700	-1.03509500	-0.25263100
C	5.40212600	-1.51786800	-0.46957900
C	3.41059800	-1.48149800	0.90382200
C	6.02321500	-2.42534800	0.38203600
H	5.95253600	-1.15077400	-1.33006300
C	4.04584600	-2.41983300	1.73930100
C	5.33039200	-2.89614100	1.49645800
H	7.03552600	-2.75959700	0.17202100
H	3.51061500	-2.77929100	2.61485000
H	5.78112800	-3.61897600	2.17089600
C	2.08664100	-0.98626500	1.46271900
H	1.78823400	-1.72197200	2.20535800
H	2.24228900	-0.07105600	2.03408700
C	2.50366800	1.68814000	0.16908200
H	3.04278800	1.26270400	1.01174400
H	2.68282300	2.76325800	0.19779100

N	0.89380700	-0.78812500	0.61132700
C	0.28260700	0.40953900	0.40618800
N	1.01184800	1.54120800	0.32913400
C	0.25441100	2.78310600	0.45035500
C	-0.39546300	3.37292200	-0.65893800
C	0.17520200	3.35386800	1.74131300
C	-1.10999800	4.56083700	-0.43747100
C	-0.54708300	4.54216000	1.90461100
C	-1.18298900	5.14714400	0.82271100
H	-1.62251900	5.02961100	-1.27234400
H	-0.62878700	4.98766400	2.89145900
H	-1.74174300	6.06888600	0.96348300
C	0.04702400	-1.96322800	0.46311900
C	-0.65428500	-2.48312900	1.57844800
C	-0.06342800	-2.55035100	-0.81447100
C	-1.43720200	-3.62875200	1.38523100
C	-0.87342700	-3.68589300	-0.95801400
C	-1.54718600	-4.22987300	0.13243200
H	-1.97907100	-4.04785300	2.22821700
H	-0.98227200	-4.14302700	-1.93692500
H	-2.16607400	-5.11449000	0.00576100
C	0.75386700	2.65272200	2.96584100
H	1.45631700	1.88842700	2.62799900
C	-0.40176300	2.78561400	-2.06701000
H	0.25085800	1.90985300	-2.07292600
C	0.60563500	-1.93640800	-2.03455900
H	1.35514900	-1.23048400	-1.67897300
C	-0.62823000	-1.83929500	2.96343000
H	-0.06652600	-0.90426500	2.89982200
C	1.53192900	3.59382700	3.89849500
H	1.99336100	3.01665500	4.70879700
H	2.32867100	4.11880700	3.35812600
H	0.88222900	4.34599500	4.36046600
C	-0.37965400	1.92752100	3.71776700
H	-1.09609200	2.65008800	4.12856000
H	-0.92599800	1.25715300	3.04396700
H	0.02223500	1.33337000	4.54785400
C	0.11774800	3.79712600	-3.10984300
H	-0.61521900	4.59431700	-3.28055700
H	1.05315400	4.27492400	-2.80238900
H	0.28882900	3.29379300	-4.06872400
C	-1.80941700	2.32021800	-2.48891800
H	-2.21376600	1.57863500	-1.79319800
H	-2.50802400	3.16524900	-2.52429500
H	-1.77195800	1.87037400	-3.48871600
C	0.05888700	-2.75085400	3.99844800
H	1.07344500	-3.03184900	3.69260800
H	0.12494900	-2.24200700	4.96777000

H	-0.51260900	-3.67581300	4.14132500
C	-2.04217400	-1.46561900	3.44603200
H	-2.66062500	-2.35610700	3.60871200
H	-1.98074800	-0.92269200	4.39704500
H	-2.54852200	-0.82562700	2.71585800
C	1.33051800	-2.96958000	-2.90983300
H	2.06933000	-3.53267600	-2.32697400
H	0.63626500	-3.68665900	-3.36324800
H	1.85850000	-2.46101100	-3.72423700
C	-0.42174400	-1.13144100	-2.85224200
H	0.07165100	-0.61061600	-3.68238900
H	-1.19519500	-1.78837400	-3.26978000
H	-0.91572700	-0.38407600	-2.22224400

TS_8

E (B3LYP-D3-SMD/BS1) = -2301.23071685 au

H (B3LYP-D3-SMD/BS1) = -2300.340720 au

G (B3LYP-D3-SMD/BS1) = -2300.472023 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3745.27215238 au

Cu	-1.46701400	0.56344600	-0.54909400
C	-4.18750700	-1.34348200	-1.49832700
H	-4.36275700	-1.34555900	-2.57792400
H	-3.26457300	-1.87761200	-1.27212300
C	-4.23039400	0.04796500	-0.91736500
C	-3.36271100	1.05245400	-1.08336400
H	-3.65239800	2.02014800	-0.66513500
O	-5.29526800	-2.01290400	-0.84865000
C	-5.98712500	-1.12831200	-0.11253400
O	-6.97594500	-1.37316000	0.52351300
O	-5.40992500	0.11157900	-0.17451500
F	-2.13632900	0.34845900	-3.20679600
H	-2.64184000	0.78233400	-2.24263300
C	4.94557800	0.99113400	-2.12934200
C	4.40561000	2.23243300	-1.78923000
C	3.61682000	2.32769000	-0.64791000
C	3.33674800	1.22373800	0.17088700
C	3.97322500	-0.00675800	-0.10169700
C	4.74765900	-0.09387700	-1.28163700
H	5.54098100	0.87122700	-3.03031100
H	4.59017800	3.11061200	-2.40137200
H	3.19982900	3.28567200	-0.36478700
H	5.20138300	-1.04542300	-1.53590100
C	4.04480000	-1.19646800	0.80814500
C	5.34792600	-1.71910200	0.98287700
C	2.98129700	-1.86437400	1.45778300
C	5.60998200	-2.86499700	1.72630900
H	6.18162400	-1.19251100	0.52970200
C	3.26297300	-3.03683100	2.18447000

C	4.55058600	-3.54476700	2.32510900
H	6.63158900	-3.21968800	1.83160000
H	2.43801400	-3.56039500	2.66156700
H	4.72029500	-4.45289500	2.89691100
C	1.53497800	-1.41846300	1.58610600
H	0.99393900	-2.28771900	1.95124300
H	1.43660700	-0.68236300	2.38315300
C	2.34038400	1.45939600	1.28532900
H	2.50474200	0.79624700	2.13027400
H	2.44918000	2.47644000	1.66289200
N	0.75715800	-0.93589700	0.42448500
C	0.26186400	0.31917200	0.28081600
N	0.91956100	1.38574400	0.78415100
C	0.12885900	2.61037700	0.89010400
C	-0.02692000	3.49700800	-0.20118100
C	-0.51060500	2.84860700	2.12880100
C	-0.84947400	4.61967000	-0.01525200
C	-1.31283300	3.98837800	2.26129700
C	-1.48537200	4.86982100	1.19674700
H	-0.99030500	5.31021700	-0.84153200
H	-1.82403800	4.17628000	3.20057400
H	-2.11563200	5.74807700	1.31095300
C	0.05974200	-1.97747700	-0.31483500
C	-1.00687200	-2.68222000	0.29644300
C	0.46306500	-2.25227500	-1.63721600
C	-1.63428400	-3.69224700	-0.44422500
C	-0.21287700	-3.25991700	-2.34169400
C	-1.24609100	-3.98130800	-1.75197200
H	-2.45249500	-4.24752600	0.00541000
H	0.08084600	-3.47938300	-3.36426200
H	-1.75473000	-4.76329500	-2.30983400
C	-0.44812900	1.84557500	3.27527600
H	0.37977000	1.15756800	3.09351100
C	0.63701800	3.32124600	-1.56293800
H	1.27841500	2.43870000	-1.51855700
C	1.58746000	-1.49155200	-2.32546700
H	1.98364500	-0.76148700	-1.61920600
C	-1.51801300	-2.38676900	1.70612600
H	-0.96310200	-1.53727800	2.10987500
C	-0.19438500	2.49400400	4.64478700
H	-0.07734900	1.71526400	5.40805900
H	0.71934700	3.10010400	4.63410000
H	-1.02507300	3.13680100	4.95742500
C	-1.74297400	1.01148300	3.27522100
H	-2.60914700	1.63923200	3.51983700
H	-1.91290100	0.57557000	2.28526100
H	-1.68778100	0.19945000	4.01041400
C	1.50625300	4.54890300	-1.91259200

H	0.87778700	5.40614600	-2.18116300
H	2.14654600	4.86229600	-1.08190800
H	2.14648800	4.32405700	-2.77359900
C	-0.37875500	3.10117000	-2.69940200
H	-0.94918000	2.17763700	-2.58818200
H	-1.08770300	3.93625100	-2.76152800
H	0.15249800	3.04627800	-3.65867300
C	-1.30343600	-3.59055200	2.64353800
H	-0.25515000	-3.91098400	2.66502900
H	-1.60115900	-3.33145500	3.66668400
H	-1.90714300	-4.44832200	2.32418300
C	-2.99923600	-1.96857400	1.70453900
H	-3.64467500	-2.74886100	1.28740100
H	-3.33298900	-1.76606000	2.72901500
H	-3.13558900	-1.05407000	1.12109600
C	2.74022000	-2.43419000	-2.71319600
H	3.16069500	-2.93069600	-1.83090400
H	2.40335500	-3.20983700	-3.41155200
H	3.54313700	-1.87068900	-3.20103100
C	1.07475200	-0.71503900	-3.55252400
H	1.86488900	-0.05688000	-3.93543200
H	0.78655700	-1.39812800	-4.36197200
H	0.19896800	-0.10663900	-3.30589900

A_1

E (B3LYP-D3-SMD/BS1) = -380.495958381 au

H (B3LYP-D3-SMD/BS1) = -380.410142 au

G (B3LYP-D3-SMD/BS1) = -380.446701 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -380.665328511 au

C	0.59630100	1.28181800	0.00015800
H	0.88285400	1.84156900	0.89462400
H	0.88327400	1.84199500	-0.89388600
C	1.10777300	-0.13750500	0.00003300
C	2.34334100	-0.61709000	-0.00014100
H	2.53467100	-1.68487700	-0.00017400
O	-0.84034400	1.10986300	-0.00018700
C	-1.14642400	-0.19877000	-0.00002700
O	-2.25766400	-0.65329700	-0.00006900
O	-0.01351300	-0.96109000	0.00022000
H	3.18541700	0.06679000	-0.00040800

^{BP}DPrCuCl

E (B3LYP-D3-SMD/BS1) = -2281.15296551 au

H (B3LYP-D3-SMD/BS1) = -2280.345505 au

G (B3LYP-D3-SMD/BS1) = -2280.461859 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -3725.00571689 au

C	-2.50062500	-3.96893400	-1.45613100
C	-1.19298100	-4.36069900	-1.16356500

C	-0.50020900	-3.68550900	-0.16455900
C	-1.06135000	-2.61993900	0.55481700
C	-2.41500500	-2.28639700	0.33548900
C	-3.09752800	-2.96512200	-0.70050900
H	-3.06229900	-4.45453300	-2.24940500
H	-0.71862400	-5.17581200	-1.70263300
H	0.50787600	-3.98952100	0.08596800
H	-4.12170300	-2.68287500	-0.92047000
C	-3.25529600	-1.37409100	1.17621000
C	-4.50827000	-1.91130100	1.55270400
C	-2.96184000	-0.05131100	1.57948700
C	-5.45837500	-1.18514600	2.26302900
H	-4.73022300	-2.94033300	1.28837100
C	-3.94627000	0.67634800	2.27443000
C	-5.18117800	0.13446000	2.61701900
H	-6.40383600	-1.64830700	2.53172600
H	-3.72584700	1.70191100	2.56046000
H	-5.91005700	0.73382100	3.15552600
C	-1.63887700	0.68825100	1.47228100
H	-1.86957600	1.73219600	1.66999100
H	-0.98136500	0.39610400	2.29088100
C	-0.13630900	-1.90614600	1.51682100
H	-0.67696700	-1.43601600	2.33411900
H	0.54375100	-2.62797900	1.96967500
N	-0.83724400	0.69446500	0.22914400
C	0.41642900	0.18103100	0.12035000
N	0.76448800	-0.92625700	0.80748100
Cu	1.70055000	1.13661600	-0.94550400
Cl	3.13708500	2.31269900	-2.11222600
C	2.19754200	-1.18569900	0.90945600
C	2.90534000	-1.87063500	-0.10545800
C	2.85148600	-0.69485300	2.06278500
C	4.28400000	-2.06094200	0.07828600
C	4.22722600	-0.91729800	2.19726900
C	4.94138600	-1.59908600	1.21459300
H	4.85018500	-2.57839900	-0.69058700
H	4.74789100	-0.53583400	3.07041700
H	6.00970200	-1.76291700	1.33060000
C	-1.17563600	1.75162600	-0.71322100
C	-0.94236300	3.10644400	-0.37404900
C	-1.71709500	1.38682300	-1.96350400
C	-1.31027800	4.08748900	-1.30379100
C	-2.04800900	2.40676000	-2.86680100
C	-1.86002200	3.74664900	-2.53823900
H	-1.14713700	5.13383300	-1.06166100
H	-2.45404100	2.14590500	-3.83956800
H	-2.13163400	4.52546600	-3.24627300
C	2.12683800	0.16017000	3.09695000

H	1.05113600	0.03110300	2.96311800
C	2.27800300	-2.38651900	-1.39645500
H	1.20130800	-2.20933100	-1.34655600
C	-1.87672900	-0.06951000	-2.37296700
H	-1.78213600	-0.67791200	-1.47431200
C	-0.26810500	3.54500200	0.92443700
H	0.02866600	2.65328000	1.48099700
C	2.44554200	-0.23325700	4.54756300
H	1.83257500	0.35992000	5.23677300
H	2.23143800	-1.29348200	4.72758700
H	3.49574200	-0.05081900	4.80222800
C	2.44280000	1.64567100	2.83489400
H	3.50682700	1.85147700	3.00664000
H	2.21134600	1.91411400	1.79789100
H	1.85641600	2.29174200	3.49986600
C	2.52498500	-3.89829000	-1.58303700
H	3.57257700	-4.09323500	-1.84058900
H	2.29900300	-4.47614500	-0.68148200
H	1.90509800	-4.28269600	-2.40156200
C	2.81489400	-1.64369100	-2.63517000
H	2.64254100	-0.56560000	-2.57008800
H	3.89337600	-1.80491500	-2.75308700
H	2.31713000	-2.01573800	-3.53918800
C	-1.21845900	4.37339500	1.80978300
H	-2.14682400	3.83542500	2.03499400
H	-0.73077200	4.62152300	2.76026500
H	-1.49130200	5.31376100	1.31613500
C	1.02547900	4.33365900	0.64794900
H	0.81698900	5.28210900	0.13917400
H	1.53239100	4.56404300	1.59288000
H	1.71213200	3.75463900	0.02131700
C	-3.25163700	-0.37275400	-2.98753600
H	-4.06141800	-0.08853400	-2.30488000
H	-3.40456800	0.15538600	-3.93594700
H	-3.33997200	-1.44607300	-3.18909800
C	-0.73703100	-0.48437400	-3.32249200
H	-0.80111500	-1.55487000	-3.55433400
H	-0.78559700	0.07536200	-4.26544000
H	0.23897500	-0.29007900	-2.86405000

5a

E (B3LYP-D3-SMD/BS1) = -576.761215225 au

H (B3LYP-D3-SMD/BS1) = -576.542610 au

G (B3LYP-D3-SMD/BS1) = -576.600598 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -577.012109827 au

C	4.82157800	-0.69780200	0.68280100
H	5.57894700	-0.00663200	1.08669400
H	4.56825200	-1.39984300	1.49342000

C	3.62545600	0.06368600	0.32344000
C	2.63451100	0.69473400	0.03279600
O	5.31040600	-1.38866900	-0.46980300
H	6.09365400	-1.88847000	-0.17933900
C	1.44613700	1.46987500	-0.31729600
H	1.40987600	2.38969000	0.29102100
H	1.50963500	1.79082800	-1.37103200
C	-0.90976400	1.40137500	-0.43897000
H	-0.97972600	2.31424800	0.17341900
H	-0.87495600	1.71092300	-1.49533800
O	0.28017400	0.67974600	-0.10259800
C	-2.09142400	0.50097200	-0.18817500
C	-2.69003500	0.45145200	1.07795200
C	-2.57650400	-0.33474100	-1.20282300
C	-3.75866800	-0.41337600	1.32545400
H	-2.31663100	1.09614100	1.87046000
C	-3.64526900	-1.20103000	-0.95981500
H	-2.11483300	-0.30269200	-2.18713800
C	-4.23835400	-1.24156400	0.30578900
H	-4.21749400	-0.43991600	2.31047700
H	-4.01560800	-1.84140700	-1.75623400
H	-5.07173400	-1.91297800	0.49588200

$TS_{6'}$

E (B3LYP-D3-SMD/BS1) = -2585.656861 au

H (B3LYP-D3-SMD/BS1) = -2584.627485 au

G (B3LYP-D3-SMD/BS1) = -2584.775805 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -2584.775805 au

C	-5.24193100	0.43268900	-2.72402000
C	-4.13783300	0.43458600	-3.57925200
C	-3.03811200	-0.35271000	-3.25564900
C	-2.99190600	-1.14032000	-2.09593800
C	-4.13477300	-1.21302300	-1.27299000
C	-5.23871200	-0.39469300	-1.60594800
H	-6.10828500	1.05380600	-2.93424100
H	-4.13232900	1.03649800	-4.48355600
H	-2.18556400	-0.38034000	-3.92157800
H	-6.10637200	-0.40078700	-0.95431800
C	-4.34502500	-2.16264100	-0.13434500
C	-5.57869500	-2.85307500	-0.16073300
C	-3.48524400	-2.39357400	0.96388600
C	-5.98198700	-3.71519000	0.85335000
H	-6.23036800	-2.71432100	-1.01767400
C	-3.92241200	-3.24991700	1.99238300
C	-5.14812900	-3.90721600	1.95424400
H	-6.93795600	-4.22657500	0.78162300
H	-3.26903000	-3.40869200	2.84707100
H	-5.44240700	-4.56055000	2.77098800

C	-2.04851500	-1.93032200	1.14902900
H	-1.82905200	-2.07066900	2.20501900
H	-1.37100400	-2.61338500	0.63512400
C	-1.69174800	-1.86530400	-1.82621600
H	-1.83998700	-2.74388100	-1.20261800
H	-1.27109100	-2.21972000	-2.76778600
N	-1.60824000	-0.55032300	0.84290300
C	-0.68899100	-0.24130900	-0.10902200
N	-0.63923400	-0.94623700	-1.25993100
Cu	0.67481500	1.08102800	0.27762900
C	0.57853700	-0.80089300	-2.05444800
C	0.78778000	0.31323200	-2.90115700
C	1.54997800	-1.82233400	-1.92592400
C	2.00151300	0.37755900	-3.60467700
C	2.73507600	-1.71417200	-2.66309500
C	2.96387300	-0.62148100	-3.49672000
H	2.18831700	1.22910000	-4.25240000
H	3.49799800	-2.47876300	-2.56460100
H	3.89370100	-0.54646200	-4.05465100
C	-1.70047700	0.38421000	1.95746400
C	-0.86246000	0.22732300	3.08847300
C	-2.62482300	1.44550200	1.86547700
C	-0.99767300	1.14720600	4.13683300
C	-2.71181700	2.34540300	2.93671900
C	-1.91291500	2.19563800	4.06745500
H	-0.36893700	1.04257900	5.01656200
H	-3.40875900	3.17593600	2.88058600
H	-1.99754200	2.89923100	4.89184700
C	1.38109800	-2.97332300	-0.93800200
H	0.31583800	-3.11080700	-0.74318300
C	-0.21531300	1.44535400	-3.10411600
H	-1.11533800	1.20893400	-2.53277300
C	-3.45720200	1.66109300	0.61162300
H	-3.48171500	0.71476100	0.07367900
C	0.18884000	-0.87328700	3.21261700
H	0.21513600	-1.43288300	2.27626000
C	1.91648200	-4.31644800	-1.45790900
H	1.65242600	-5.11524600	-0.75472600
H	1.48956700	-4.56776400	-2.43600500
H	3.00835000	-4.31364900	-1.55137500
C	2.05008700	-2.60044900	0.39870900
H	3.13425400	-2.51046800	0.27433300
H	1.67141500	-1.64227400	0.76651100
H	1.85391100	-3.36550700	1.16024200
C	-0.59865000	1.58604400	-4.59275500
H	0.22986800	2.01263000	-5.17023700
H	-0.85558100	0.62649100	-5.05290600
H	-1.45812600	2.25861700	-4.69801100

C	0.31148300	2.80358500	-2.60123500
H	0.53911000	2.78964800	-1.53341800
H	1.22293900	3.09571400	-3.13709700
H	-0.44254400	3.58183000	-2.76950600
C	-0.15388500	-1.85649900	4.34814500
H	-1.15078300	-2.29540300	4.22398100
H	0.57674600	-2.67408200	4.37507700
H	-0.13149000	-1.35205500	5.32153100
C	1.60355500	-0.29916900	3.41747600
H	1.69670700	0.20678000	4.38559500
H	2.34456800	-1.10754100	3.38727600
H	1.85398500	0.42150400	2.63217500
C	-4.91171400	2.05581700	0.90538900
H	-5.39572400	1.32753900	1.56745800
H	-4.98587000	3.04418200	1.37388100
H	-5.48021200	2.09258800	-0.03070500
C	-2.77751500	2.68675600	-0.31524700
H	-3.33491100	2.77712700	-1.25615200
H	-2.72323800	3.67614500	0.15383000
H	-1.75231700	2.38258100	-0.54747900
C	2.80391200	4.41734300	1.03573900
H	2.78276000	4.62901800	2.11351300
H	3.81618000	4.60760900	0.65894400
C	2.45883700	3.01204500	0.77097500
C	2.53787200	1.80239400	0.44594700
O	1.91040000	5.28738500	0.34672300
C	0.58857100	4.81238800	0.42713500
O	-0.28535600	5.52576000	-0.05577500
O	0.50542100	3.67292200	1.00384300
C	3.52739400	0.77779500	0.04461000
H	3.33925900	0.50608800	-1.00428500
H	3.36804800	-0.12835700	0.63714800
C	5.80992600	0.37487700	-0.43164300
H	5.63269700	0.35421200	-1.51868800
H	6.78700500	0.84241500	-0.26218200
O	4.87147900	1.24173700	0.20372700
C	5.80044600	-1.04331400	0.11070200
C	5.89808600	-2.14010500	-0.75300400
C	5.67331300	-1.27289500	1.48825000
C	5.88235300	-3.44592000	-0.25114900
H	5.98042200	-1.97227500	-1.82435900
C	5.64337800	-2.57448900	1.99153600
H	5.57745700	-0.42302700	2.15922800
C	5.75027800	-3.66613600	1.12224300
H	5.96002600	-4.28794800	-0.93420100
H	5.53500100	-2.73832800	3.06075100
H	5.72470300	-4.67992600	1.51300200

$TS_{7'}$

E (B3LYP-D3-SMD/BS1) = -2585.662856 au

H (B3LYP-D3-SMD/BS1) = -2585.662856 au

G (B3LYP-D3-SMD/BS1) = -2584.782155 au

E (B3LYP-D3-SMD/BS2//B3LYP-D3-SMD/BS1) = -4029.805261 au

Cu	0.73581400	0.76462800	-0.18253900
C	0.69761400	3.66758500	-1.40678200
H	0.56068500	3.53498600	-2.48987000
H	-0.23445900	3.38990900	-0.90781400
C	1.78480400	2.78603600	-0.94509500
C	2.40612700	1.82807200	-0.43564300
O	0.96188400	5.02432100	-1.09417500
C	2.31184500	5.39108200	-1.37228500
O	2.55475800	6.59259000	-1.25323400
O	3.05929400	4.41977900	-1.69064200
C	-4.68057400	-1.73891900	-3.18282500
C	-3.50985400	-2.44134100	-3.47568300
C	-2.64988100	-2.77183300	-2.43406700
C	-2.91040700	-2.41990400	-1.10136200
C	-4.13876600	-1.80177800	-0.78480800
C	-4.99007100	-1.44935400	-1.85790600
H	-5.36111200	-1.43829100	-3.97467700
H	-3.26754500	-2.72476500	-4.49593000
H	-1.74464900	-3.32770400	-2.64322800
H	-5.91286200	-0.92256000	-1.63832600
C	-4.70352400	-1.59282300	0.58804000
C	-6.04296200	-2.02085300	0.74045900
C	-4.07933400	-0.98527200	1.70230100
C	-6.76528100	-1.83931500	1.91509100
H	-6.52206200	-2.52687900	-0.09165400
C	-4.83494300	-0.78763000	2.87359400
C	-6.15820300	-1.20001700	2.99490100
H	-7.79071300	-2.19256400	1.98015000
H	-4.35850000	-0.29991600	3.72056400
H	-6.70109600	-1.02724500	3.92004600
C	-2.61656900	-0.60734900	1.86840300
H	-2.57466300	0.03671000	2.74406600
H	-2.03330900	-1.48510200	2.14710300
C	-1.81538100	-2.72831400	-0.10417300
H	-2.20214500	-2.85969300	0.90299400
H	-1.32638700	-3.66490200	-0.37384900
N	-1.86423500	0.11774000	0.82042300
C	-0.78995600	-0.38640900	0.16214900
N	-0.71892300	-1.69463700	-0.14830700
C	0.60376400	-2.16715300	-0.54952100
C	1.08381800	-2.00807700	-1.87123400
C	1.40039400	-2.75391700	0.45976400
C	2.38636000	-2.45372700	-2.14714400

C	2.68476500	-3.19631500	0.12364200
C	3.17944000	-3.04626000	-1.16940000
H	2.78251300	-2.33079300	-3.15089700
H	3.31836800	-3.63260800	0.88761800
H	4.18675600	-3.37598400	-1.40682200
C	-1.93081400	1.56989100	0.91588700
C	-1.29508900	2.24313600	1.98684000
C	-2.63445400	2.27254700	-0.08455900
C	-1.40676200	3.63912800	2.04040200
C	-2.71372700	3.66876600	0.01423300
C	-2.11177400	4.34845100	1.07024800
H	-0.92934000	4.17712200	2.85423200
H	-3.24068800	4.22951600	-0.75150500
H	-2.18109100	5.43135200	1.13165400
C	0.94857700	-2.80593100	1.91532700
H	-0.13056800	-2.64433600	1.95246700
C	0.29071900	-1.37184100	-3.00848700
H	-0.70791300	-1.13397500	-2.63586100
C	-3.22052600	1.55375200	-1.28911700
H	-3.31615800	0.50131800	-1.02574500
C	-0.48938700	1.52877700	3.06978000
H	-0.43636200	0.46676800	2.81878300
C	1.22305600	-4.15797800	2.59163600
H	0.80121400	-4.15988700	3.60388900
H	0.76750100	-4.98300700	2.03116300
H	2.29622500	-4.36108200	2.68348700
C	1.61019100	-1.64886200	2.68863600
H	2.69703500	-1.78523500	2.73348700
H	1.41844800	-0.69080100	2.19456700
H	1.22535700	-1.59598800	3.71477000
C	0.15432500	-2.33468800	-4.20695300
H	1.11055300	-2.44133900	-4.73243000
H	-0.16554400	-3.33711200	-3.90636100
H	-0.57641300	-1.94186100	-4.92365600
C	0.92897200	-0.05956700	-3.50306300
H	1.00780000	0.68075900	-2.70299600
H	1.93649700	-0.23549900	-3.89902900
H	0.32078600	0.37251600	-4.30725500
C	-1.16398200	1.66413300	4.44888600
H	-2.20025600	1.30682000	4.43683200
H	-0.61293100	1.08376000	5.19875600
H	-1.17688300	2.71088700	4.77534900
C	0.96275800	2.03642700	3.14056500
H	1.00578200	3.09490400	3.42275600
H	1.51909600	1.46651800	3.89477800
H	1.47805400	1.91603900	2.18263100
C	-4.61714200	2.05408400	-1.68363300
H	-5.31199700	1.99934800	-0.83701200

H	-4.59979300	3.08911800	-2.04441800
H	-5.01740400	1.43108800	-2.49137300
C	-2.24280200	1.63335400	-2.47714200
H	-2.61453700	1.03842500	-3.32057400
H	-2.11747600	2.66976000	-2.81507100
H	-1.25767300	1.24867600	-2.19396900
C	3.77234500	1.30327400	-0.19457700
H	3.96833000	0.47482900	-0.89082900
H	4.50676100	2.09901600	-0.39533000
C	5.21832100	0.59321100	1.57331900
H	5.87168600	1.42834800	1.27792600
H	5.17269100	0.56368000	2.66583800
O	3.87401600	0.86829500	1.15856000
C	5.76260100	-0.71421700	1.03936800
C	6.40522100	-0.77325800	-0.20620000
C	5.61380000	-1.89619800	1.77849700
C	6.87910700	-1.98854100	-0.70713700
H	6.54268100	0.14023300	-0.78002300
C	6.09427100	-3.11201600	1.28629000
H	5.12406000	-1.86041500	2.74883000
C	6.72497000	-3.16120600	0.03917900
H	7.37475800	-2.01913400	-1.67394800
H	5.97699500	-4.01860900	1.87433100
H	7.09976200	-4.10598000	-0.34571900