Rhodium-catalyzed cycloisomerization of ester-tethered 1,6-diynes with cyclopropanol moiety leading to tetralone/exocyclic diene hybrid molecules

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Supporting Information

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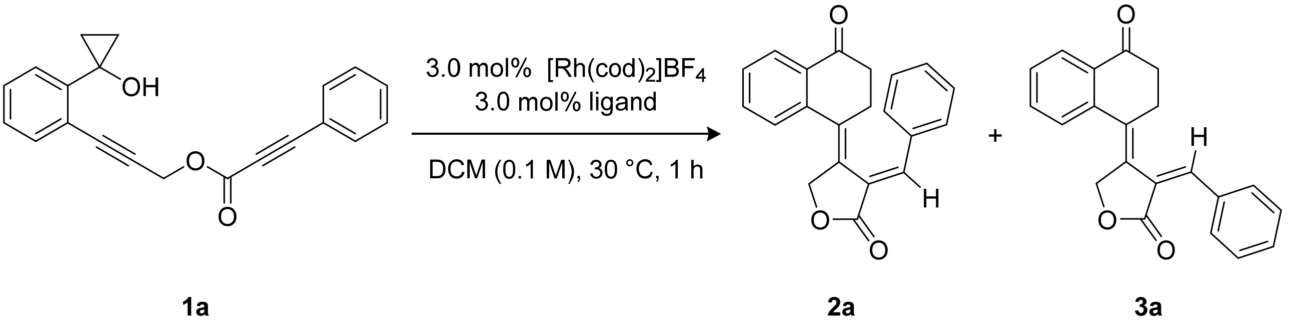
1. Optimization of Reaction Conditions

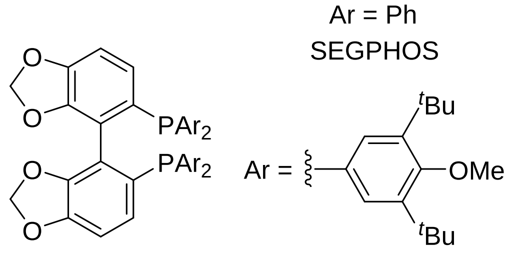
Despite of the high conversions, the isolated yields of **2a** were relatively low (entries 4–8 in Table S1) and any noticeable side products were not observed by ^{1}H NMR analyses of the crude materials. TLC analysis of the reaction showed tailing stains on the bottom of the TLC plate, which suggests that intermolecular side reactions may provide a complex mixture including oligomers.

Table S1 Screening of ligands[a]

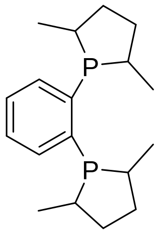


entry	ligand	conv. (%)	yield (%)[b]	ratio of **2a**:**3a**
1	PPh$_3$	8	-	-
2[c]	dppp	13	-	-
3	dppb	8	-	-
4	BINAP	>99	49 (47)	>99:1
5	Tol-BINAP	94	39	>99:1
6	H$_8$-BINAP	96	46	>99:1
7	SEGPHOS	98	47	>99:1
8	DTBM-SEGPHOS	75	11	>99:1
9	Me-Duphos	32	-	-
10	Ph-BPE	36	3	>99:1
11	Xantphos	42	2	>99:1

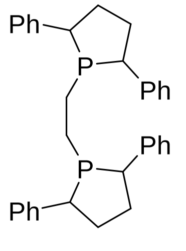
[a] Pre-activation of the rhodium catalyst was performed under H$_2$ atmosphere before addition of substrate **1a** to the reaction mixture.
[b] Isolated yield is shown in parenthesis. [c] 6.0 mol% PPh$_3$ was used.



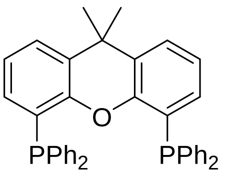
DTBM-SEGPHOS



Me-DuPhos

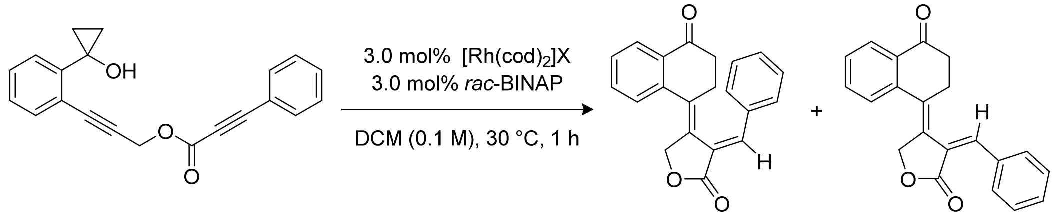


Ph-BPE



Xantphos

Table S2 Screening of counterions[a]

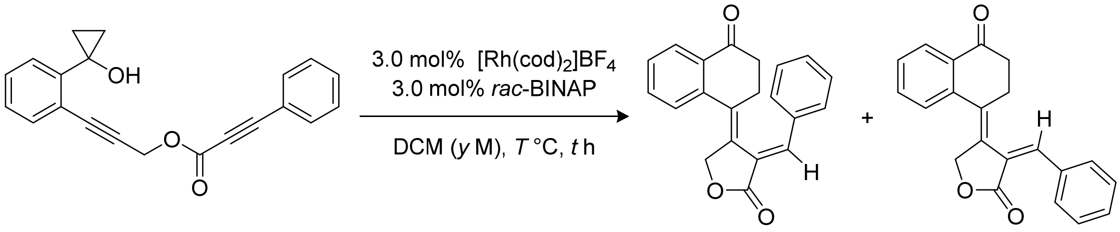


1a **2a** **3a**

entry	X	conv. (%)	NMR yield (%)[b]	ratio of **2a**:**3a**
1	BF_4	>99	49 (47)	>99:1
2	PF_6	92	40	>99:1
3[c]	BArF	66	14	>99:1
4	OTf	66	13	>99:1
5	ClO_4	92	47	>99:1

[a] Pre-activation of the rhodium catalyst was performed under H_2 atmosphere before addition of substrate **9a** to the reaction mixture. [b] Isolated yield is shown in parenthesis. [c] $BAr^F = B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4$

Table S3 Optimization of other conditions[a]



1a **2a** **3a**

entry	*y* (M)	*T* (°C)	*t* (h)	conv. (%)	yield (%)[b]	ratio of **2a**:**3a**
1	0.1	20	3	92	47	>99:1
2	0.05	20	3	91	62	>99:1
3	0.05	30	1	>99	70	>99:1
4	0.02	30	1	81	27	>99:1
5[c]	0.05	30	1	40	15	>99:1
6[d]	0.05	30	1	44	14	>99:1

[a] Pre-activation of the rhodium catalyst was performed under H_2 atmosphere before addition of substrate **1a** to the reaction mixture. [b] Isolated yield. [c] AcOH (5 mol%) was used as an additive. [d] *p*-TsOH (5 mol%) was used as an additive.

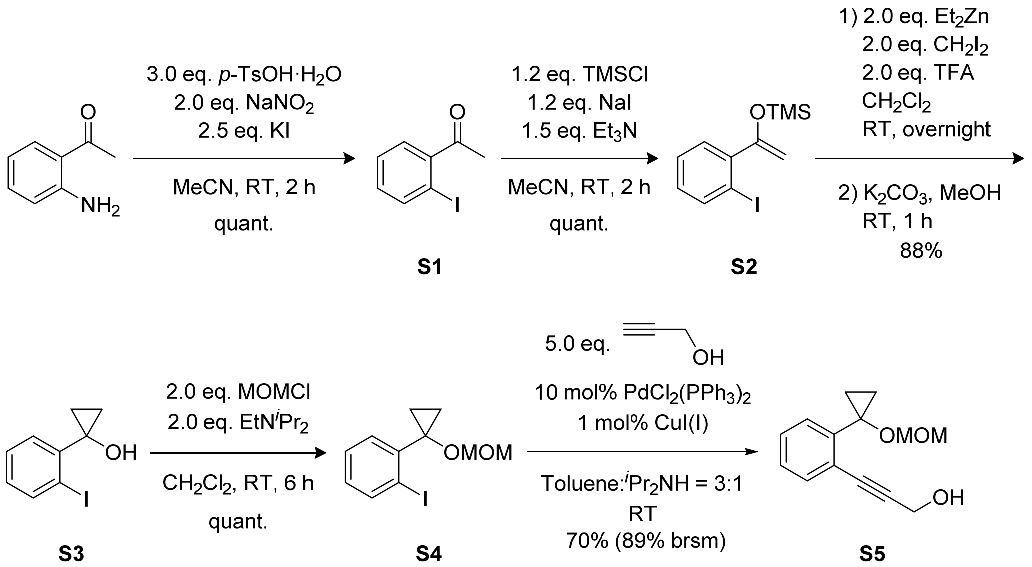
2. General information

General considerations: All air- and moisture-sensitive reactions were performed under an argon (Ar) atmosphere. Analytical thin layer chromatography was performed using 0.25 mm silica gel plate (Merck TLC Silica gel 60 F_{254}). Column chromatography was performed on silica gel (Cica silica gel 60N) with solvents specified below. Melting points were recorded on SRS OptiMelt MPA100. NMR spectra were recorded on JEOL ESC-400 spectrometer (^{1}H/400 MHz and ^{13}C/101 MHz) for samples in $CDCl_3$ solutions at 25 ˚C. ^{1}H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the signal at δ 0.00 ppm for internal tetramethylsilane. ^{13}C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ 77.0 ppm for $CDCl_3$. ^{19}F NMR spectra are reported in terms of chemical shift (δ, ppm) relative to the singlet at d −63.7 ppm for α,α,α-trifluorotoluene as an external standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. Infrared spectra were recorded on JASCO FT/IR-230 spectrometer. High-resolution mass spectra were recorded on JEOL JMS-T100LP mass spectrometer.

Reagents and Solvents: $[RhOH(cod)]_2$,[1] $[Cp^*RuCl_2]_2$,[2] $[Ir(cod)Cl]_2$,[3] $[Rh(cod)_2]BF_4$,[4] $[Rh(cod)_2]PF_6$,[4] $[Rh(cod)_2]BAr^F$,[5] $[Rh(cod)_2]OTf$[4] and $[Rh(cod)_2]ClO_4$,[4] $PdCl_2(PPh_3)_2$,[5] were prepared according to the report. *rac*-BINAP was purchased from Aldrich and used after recrystallization from toluene and EtOH. dry DCM was distilled from calcium hydride under Ar atmosphere and stored over 4 Å molecular sieves. Other solvents and reagents were purchased from chemical suppliers (Aldrich, Kanto Chemical, TCI, and Wako) and used as received.

3. Synthesis and Characterization of 1,6-Diynes 1

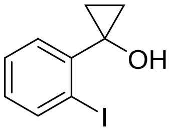
Synthesis of intermediate S5



Synthesis and characterization of S1 and S2

S1[6] and **S2**[7, 8] were prepared according to the previous reports.

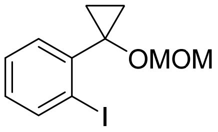
Synthesis and characterization of S3



S3

To a dried 500 mL two-necked flask was added degassed dry DCM (120 mL) and Et_2Zn (40 mL, 1.07 M in hexane) under Ar. The solution was cooled to –10 °C and a solution of TFA (3.30 mL, 43.0 mmol) in degassed dry DCM (20 mL) was then dripped into the reaction mixture for 1 h (*very slowly*). On stirring for additional 1 h, a solution of CH_2I_2 (3.70 mL, 43.0 mmol) in degassed dry DCM (20 mL) was added to the reaction mixture for 1 h (*very slowly*). After stirring at rt for 3 h, **S2** (6.85 g, 21.5 mmol) was added to the mixture. The reaction mixture was stirred at rt overnight. The reaction was quenched with saturated aqueous NH_4Cl and extracted with hexane. The organic layer was washed with sat. aq. $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. To a MeOH solution (50 mL) of the crude material in a 200 mL flask was added K_2CO_3 (2.97 mg, 21.5 mmol) at rt. After being stirred for 1 h, the reaction mixture was diluted with water and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by a silica gel column chromatography (Hexane/EtOAc = 40:1) to furnish **S3** (4.95 g, 88%) as a pale-yellow solid. **Analytical data for S3:** pale-yellow solid (mp 52.4–52.8 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.00 (dt, *J* = 7.8, 1.6 Hz, 1H), 2.99 (s, 1H), 1.29 (dd, *J* = 7.5, 5.3 Hz, 2H), 0.98 (dd, *J* = 7.5, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CHCl_3$) δ 143.9, 139.7, 131.0, 129.8, 128.4, 100.9, 61.0, 15.6; IR (neat) 3315 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_9H_9O_3I{\bullet}NH_4$ 278.0042, found 278.0050.

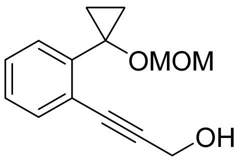
Synthesis and characterization of S4



S4

To a solution of **S3** (5.25 g, 20.2 mmol) and EtN^iPr_2 (7.0 mL, 40.4 mmol) in dry DCM (40 mL) was added MOMCl (3.0 mL, 40.4 mmol) at 0 °C, and the mixture was allowed to warm to rt. After being stirred at rt for 5 h, the reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 20:1) to furnish **S4** (5.96 g, quant.) as a yellow oil. **Analytical data for S4:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ7.91 (d, *J* = 7.4 Hz, 1H), 7.35–7.27 (m, 2H), 7.00 (dt, *J* = 7.4, 1.7 Hz, 1H), 4.61 (s, 2H), 3.17 (s, 3H), 1.34 (dd, *J* = 7.1, 5.7 Hz, 2H), 0.98 (dd, *J* = 7.1, 5.7 Hz, 2H); ^{13}C-NMR (101 MHz, $CHCl_3$) δ 141.9, 140.1, 132.2, 129.7, 127.6, 101.5, 95.2, 65.0, 55.8, 14.0; IR (neat) 1034 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{11}H_{13}IO_2{\bullet}NH_4$ 322.0304, found 322.0295.

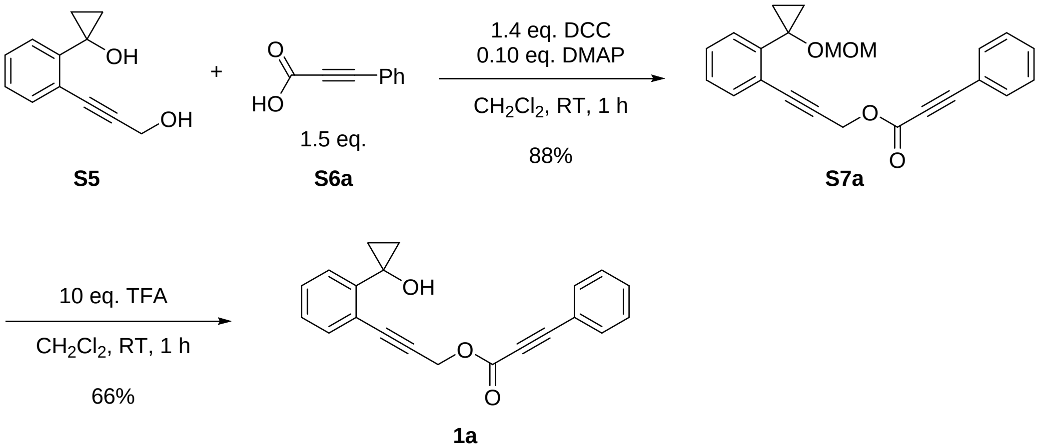
Synthesis and characterization of S5



S5

To a solution of **S4** (3.37 g, 11.1 mmol) in $^{i}Pr_2NH$ (6.0 mL) and toluene (19 mL) was added $PdCl_2(PPh_3)_2$ (772 mg, 1.11 mmol) and CuI (20.9 mg, 0.110 mmol). After degassed at –78 °C, the reaction mixture was warmed to room temperature. To the stirred solution was added a solution of propargyl alcohol (930 mg, 16.6 mmol) in $^{i}Pr_2NH$ (6.0 mL) and toluene (19 mL) over 1 h. Insoluble materials were filtered off through a pad of Celite®, and the filtrate was concentrated *in vacuo*. The obtained crude product was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to give **S5** (1.45 g, 70%) as a brown oil. **Analytical data for S5:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.33–7.24 (m, 2H), 4.70 (s, 2H), 4.51 (d, *J* = 5.5 Hz, 2H), 3.24 (s, 3H), 2.63 (t, *J* = 5.5 Hz, 1H), 1.29 (dd, *J* = 7.3, 5.5 Hz, 2H), 1.00 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CHCl_3$) δ 141.7, 132.3, 131.2, 128.4, 128.0, 124.4, 94.7, 92.5, 84.7, 61.2, 55.6, 51.7, 13.1; IR (neat) 3402, 1030 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{14}H_{16}O_3{\bullet}NH_4$ 250.1443, found 250.1418.

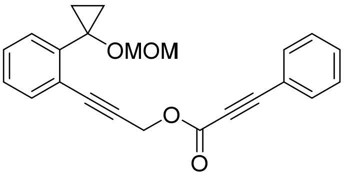
Representative procedure: synthesis of 1a–f and 1h–l.



Synthesis and characterization of S6b–d, S6f–h

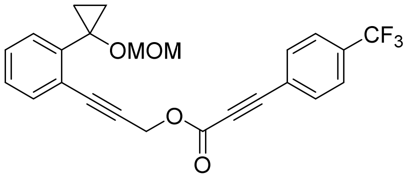
Compounds **S6b–d**[9], **S6e**[10], **S6f**[9], **S6i**[11], **S6j**[12] and **S6k**[13] were synthesized as reported.

Synthesis and characterization of S7a



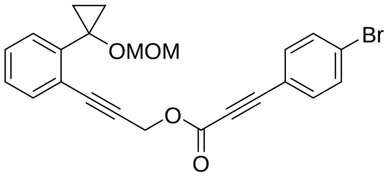
S7a

To a 50 mL flask was charged with **S5** (348 mg, 1.50 mmol), phenylpropiolic acid **S6a** (329 mg, 2.25 mmol) and DMAP (18.3 mg, 0.150 mmol). To the mixture was added a DCM (20 mL) solution of DCC (433 mg, 2.10 mmol) at 0 °C, and the resulting solution was stirred at room temperature for 1 h. After that, the reaction mixture was filtered through a pad of Celite® with EtOAc. The filtrate was washed with water, sat. aq. $NaHCO_3$ and brine. The solution was dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 20:1) to furnish **S7a** (476 mg, 88%) as an orange gum. **Analytical data for S7a:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.51–7.44 (m, 3H), 7.41–7.37 (m, 2H), 7.31–7.26 (m, 2H), 5.12 (s, 2H), 4.66 (s, 2H), 3.17 (s, 3H), 1.29 (dd, *J* = 7.2, 5.6 Hz, 2H), 1.00 (dd, *J* = 7.2, 5.6 Hz, 2H); ^{13}C-NMR (101 MHz, $CHCl_3$) δ 153.4, 142.2, 133.2, 131.0, 130.7, 128.7, 128.7, 127.9, 123.5, 119.5, 95.2, 87.3, 86.7, 86.1, 80.2, 61.5, 55.6, 54.4, 13.0; IR (neat) 2356, 2220, 1714, 1164 cm^{-1}; HRMS (DART) *m/z* [M+ NH_4]$^+$ calcd for $C_{23}H_{20}O_4$•NH_4 378.1705, found 378.1705



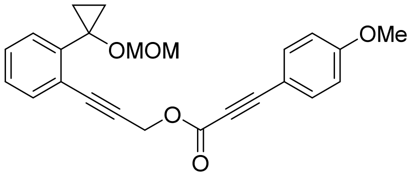
S7b

Analytical data for S7b: orange gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.50 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.45 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.32 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.26 (dt, *J* = 7.8, 1.3 Hz, 3H), 5.14 (s, 2H), 4.65 (s, 2H), 3.17 (s, 3H), 1.28 (dd, *J* = 7.3, 5.5 Hz, 2H), 1.00 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CHCl_3$) δ 153.0, 142.2, 133.3, 133.2, 130.7, 128.7, 127.9, 125.7, 125.7, 123.4, 123.3, 95.2, 86.3, 85.0, 81.7, 61.5, 55.6, 54.7, 13.0; ^{19}F-NMR (376 MHz, $CDCl_3$) δ –64.1; IR (neat) 2227, 1720, 1171 cm^{-1}; HRMS (DART) *m/z* [M+ NH_4]$^+$ calcd for $C_{24}H_{19}F_3O_4$•NH_4 446.1579, found 446.1584



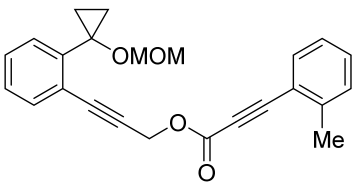
S7c

Analytical data for S7c: orange gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.50–7.44 (m, 4H), 7.33–7.29 (m, 1H), 7.28–7.24 (m, 1H), 5.12 (s, 2H), 4.65 (s, 2H), 3.16 (s, 3H), 1.28 (dd, *J* = 7.3, 5.5 Hz, 2H), 1.00 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.2, 142.2, 134.4, 133.2, 132.1, 130.7, 128.7, 127.9, 125.8, 123.5, 118.4, 95.2, 86.4, 86.2, 86.1, 81.1, 61.5, 55.6, 54.6, 13.0; IR (neat) 2343, 2222, 1716, 1162 cm^{-1}; HRMS (DART) *m/z* [M+ NH_4]$^+$ calcd for $C_{23}H_{19}BrO_4$•NH_4 456.0811, found 456.0838



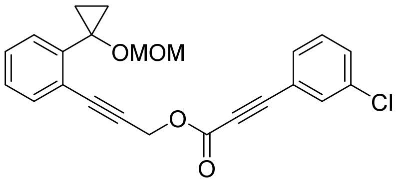
S7d

Analytical data for S7d: orange gum; ^{1}NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (m, 2H), 7.49 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.45 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.31 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.25 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.91–6.88 (m, 2H), 5.11 (s, 2H), 4.65 (s, 2H), 3.84 (s, 3H), 3.17 (s, 3H), 1.28 (dd, *J* = 7.1, 5.7 Hz, 2H), 1.00 (dd, *J* = 7.1, 5.7 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 161.8, 153.7, 142.2, 135.2, 133.2, 130.7, 128.6, 127.8, 123.6, 114.4, 111.3, 95.2, 88.3, 86.8, 86.0, 79.7, 61.5, 55.6, 55.5, 54.3, 13.0; IR (neat) 2211, 1710, 1155 cm^{-1}; HRMS (DART) *m/z* [M+ NH_4]$^+$ calcd for $C_{24}H_{22}O_5$•NH_4 408.1811, found 408.1815



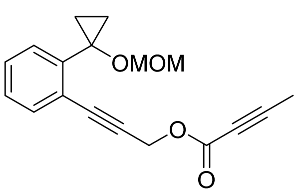
S7e

Analytical data for S7e: yellow gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57–7.55 (m, 1H), 7.50 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.37–7.24 (m, 4H), 7.19 (t, *J* = 7.6 Hz, 1H), 5.12 (s, 2H), 4.66 (s, 2H), 3.17 (s, 3H), 2.51 (s, 3H), 1.29 (dd, *J* = 7.1, 5.7 Hz, 2H), 1.00 (dd, *J* = 7.1, 5.7 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.4, 142.4, 142.3, 133.6, 133.1, 130.9, 130.7, 129.9, 128.6, 127.9, 126.0, 123.5, 119.3, 95.1, 86.9, 86.3, 86.0, 84.0, 61.4, 55.4, 54.3, 20.5, 13.0; IR (neat) 2216, 1714, 1173 cm^{-1}; HRMS (DART) *m/z* [M+ NH$_4$]$^+$ calcd for $C_{24}H_{22}O_4$•NH_4 392.1862, found 392.1889



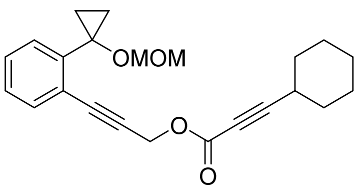
S7f

Analytical data for S7f: orange gum; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.59 (t, *J* = 1.8 Hz, 1H), 7.51–7.43 (m, 4H), 7.35–7.24 (m, 3H), 5.12 (s, 2H), 4.65 (s, 2H), 3.17 (s, 3H), 1.28 (dd, *J* = 7.3, 5.5 Hz, 2H), 1.00 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 152.9, 142.2, 134.6, 133.1, 132.7, 131.2, 130.7, 130.0, 128.7, 127.9, 123.4, 121.2, 95.1, 86.6, 86.2, 85.2, 81.0, 61.4, 55.5, 54.6, 13.0; IR (neat) 1718, 1172 cm^{-1}; HRMS (DART) *m/z* [M+ NH$_4$]$^+$ calcd for $C_{23}H_{19}O_4Cl$•NH_4 412.1316, found 412.1335



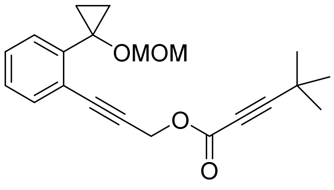
S7h

Analytical data for S7h: pale yellow gum; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.46 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.43 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.29 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.23 (dt, *J* = 7.2, 1.2 Hz, 1H), 5.02 (s, 2H), 4.63 (s, 2H), 3.15 (s, 3H), 2.00 (s, 3H), 1.25 (dd, *J* = 7.6, 5.3 Hz, 2H), 0.97 (dd, *J* = 7.6, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 153.1, 142.1, 133.1, 130.7, 128.6, 127.8, 123.5, 95.2, 86.7, 86.6, 85.9, 72.0, 61.4, 55.6, 54.2, 13.0, 4.0; IR (neat) 2310, 2238, 1716, 1243 cm^{-1}; HRMS (DART) *m/z* [M+ NH$_4$]$^+$ calcd for $C_{18}H_{18}O_4$•NH_4 316.1549, found 316.1539



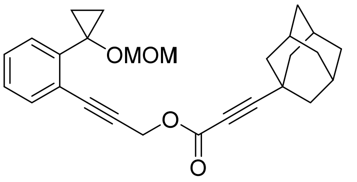
S7i

Analytical data for S7i: pale yellow gum; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.32–7.28 (m, 1H), 7.26–7.23 (m, 1H), 5.04 (s, 2H), 4.64 (s, 2H), 3.16 (s, 3H), 2.57–2.51 (m, 1H), 1.86–1.83 (m, 2H), 1.73–1.71 (m, 2H), 1.61-1.49 (m, 3H), 1.38–1.31 (m, 3H), 1.27 (dd, *J* = 7.3, 5.5 Hz, 2H), 0.99 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 153.4, 142.1, 133.1, 130.7, 128.6, 127.8, 123.6, 95.2, 94.3, 86.8, 85.8, 72.6, 61.4, 55.6, 54.1, 31.5, 29.0, 25.7, 24.7, 13.0; IR (neat) 2933, 2856, 2364, 2233, 1716, 1234 cm^{-1}; HRMS (DART) *m/z* [M+ NH$_4$]$^+$ calcd for $C_{23}H_{26}O_4$•NH_4 384.2174, found 384.2165



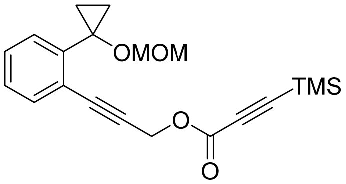
S7j

Analytical data for S7j: pale yellow gum; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.48 (d, *J* = 7.1 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.24 (t, *J* = 7.1 Hz, 1H), 5.04 (s, 2H), 4.64 (s, 2H), 3.17 (s, 3H), 1.30 (s, 9H), 1.26 (dd, *J* = 7.4, 5.4 Hz, 2H), 0.99 (dd, *J* = 7.4, 5.4 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 153.4, 142.1, 133.2, 130.7, 128.6, 127.8, 123.6, 97.8, 95.2, 86.8, 85.8, 71.3, 61.4, 55.6, 54.1, 30.0, 27.7, 13.0; IR (neat) 2971, 2225, 1716, 1211 cm^{-1}; HRMS (DART) *m/z* [M+ NH$_4$]$^+$ calcd for $C_{21}H_{24}O_4$•NH_4 358.2018, found 358.2031



S7k

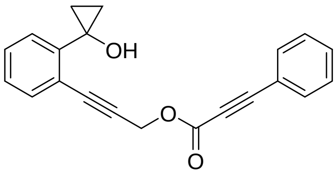
Analytical data for S7k: orange gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.30 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.24 (dt, *J* = 7.6, 1.2 Hz, 1H), 5.03 (s, 2H), 4.64 (s, 2H), 3.16 (s, 3H), 1.99 (br s, 3H), 1.93 (br s, 6H), 1.70 (br s, 6H), 1.27 (dd, J = 7.3, 5.5 Hz, 2H), 0.99 (dd, J = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.3, 142.1, 133.0, 130.7, 128.6, 127.8, 123.5, 96.9, 95.1, 86.9, 85.7, 71.7, 61.4, 55.4, 53.9, 41.5, 36.1, 29.7, 27.6, 12.9; IR (neat) 2908, 2852, 2227, 1716, 1240 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{27}H_{30}O_4$•NH_4 436.2488, found 436.2498



S7l

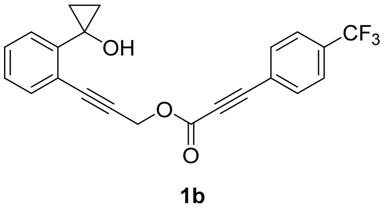
Analytical data for S7l: pale yellow gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.31 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.25 (dt, *J* = 7.4, 1.2 Hz, 1H), 5.05 (s, 2H), 4.64 (s, 2H), 3.16 (s, 3H), 1.27 (dd, *J* = 7.3, 5.5 Hz, 2H), 0.98 (dd, *J* = 7.3, 5.5 Hz, 2H), 0.26 (s, 9H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 152.4, 142.2, 133.2, 130.7, 128.7, 127.9, 123.5, 95.4, 95.2, 94.0, 86.4, 86.1, 61.4, 55.6, 54.4, 13.0, -0.8; IR (neat) 1718, 1209 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{20}H_{24}O_4Si$•NH_4 374.1788, found 374.1774

Synthesis and characterization of 1a



1a

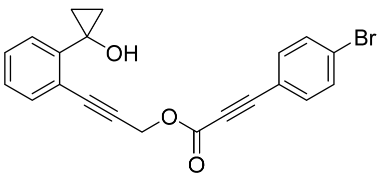
To a 50 mL flask was added **S7a** (360 mg, 1.00 mmol) followed by degassed DCM (10 mL). TFA (0.770 mL, 10.0 mmol) was slowly added to the solution. After being stirred at rt for 1 h under Ar atmosphere, the reaction mixture was diluted with water and extracted with EtOAc. The organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to furnish **1a** (209 mg, 66%) as an orange gum. **Analytical data for 1a:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.50–7.45 (m, 2H), 7.40–7.36 (m, 3H), 7.31 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.25 (dt, *J* = 7.6, 1.2 Hz, 1H), 5.09 (s, 2H), 3.35 (s, 1H), 1.23 (dd, *J* = 7.2, 5.2 Hz, 2H), 1.00 (dd, *J* = 7.2, 5.2 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.7, 145.0, 133.3, 133.0, 131.0, 129.3, 128.7, 128.2, 127.7, 122.2, 119.4, 87.9, 87.4, 86.1, 80.0, 56.9, 54.4, 14.4; IR (neat) 3533, 3403, 2220, 1712, 1166 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{21}H_{16}O_3$•NH_4 334.1443, found 334.1438



1b

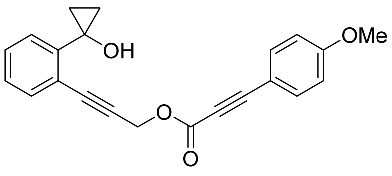
Analytical data for 1b: red gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 5.09 (s, 2H), 3.28 (br s, 1H), 1.23 (dd, *J* = 7.4, 5.4 Hz, 2H), 1.00 (dd, *J* = 7.4, 5.4 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.2, 145.0, 133.4, 133.0, 129.4, 128.2, 127.8, 125.7, 125.7, 125.6, 123.2, 122.1, 87.1, 86.3, 85.5, 81.5, 56.9, 54.6, 14.4; ^{19}F-NMR (376 MHz,

$CDCl_3$) δ –64.1; IR (neat) 3536, 3411, 2225, 1716, 1170 cm^{-1}; HRMS (DART) *m/z* [M+ NH_4]$^+$ calcd for $C_{22}H_{15}F_3O_3$•NH_4 402.1317, found 402.1299



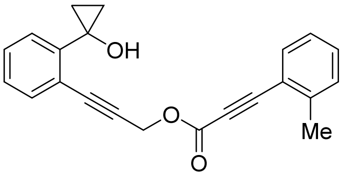
1c

Analytical data for 1c: orange gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 5.09 (s, 2H), 3.30 (br s, 1H), 1.22 (dd, *J* = 7.1, 5.3 Hz, 2H), 1.00 (dd, *J* = 7.1, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.4, 145.0, 134.5, 133.0, 132.2, 129.3, 128.2, 127.7, 125.9, 122.2, 118.3, 87.3, 86.6, 86.2, 80.9, 56.9, 54.5, 14.4; IR (neat) 3535, 3396, 2322, 2220, 1713, 1167 cm^{-1}; HRMS (DART) *m/z* [M+ NH_4]$^+$ calcd for $C_{21}H_{15}BrO_3$•NH_4 412.0548, found 412.0558



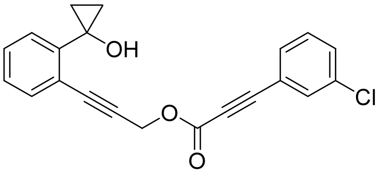
1d

Analytical data for 1d: orange gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2H), 7.49 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.37 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.31 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.25 (dt, *J* = 7.8, 1.4 Hz, 1H), 6.91–6.88 (m, 2H), 5.08 (s, 2H), 3.84 (s, 3H), 3.37 (s, 1H), 1.22 (dd, *J* = 7.1, 5.3 Hz, 2H), 0.99 (dd, *J* = 7.1, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 161.9, 153.9, 145.1, 135.3, 132.9, 129.2, 128.2, 127.7, 122.3, 114.4, 111.1, 88.9, 87.6, 86.0, 79.5, 56.9, 55.5, 54.2, 14.4; IR (neat) 3515, 1743 cm^{-1}; HRMS (DART) *m/z* [M+H]$^+$ calcd for $C_{22}H_{18}O_4$•H 347.1283, found 347.1276



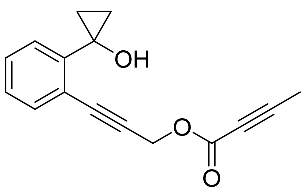
1e

Analytical data for 1e: yellow gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.49 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.38-7.29 (m, 3H), 7.27–7.23 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 5.09 (s, 2H), 3.30 (br s, 1H), 2.50 (s, 3H), 1.23 (dd, *J* = 7.3, 5.0 Hz, 2H), 1.00 (dd, *J* = 7.3, 5.0 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.8, 145.1, 142.6, 133.7, 132.9, 131.0, 129.9, 129.3, 128.2, 127.7, 125.9, 122.3, 119.2, 87.6, 87.0, 86.0, 83.7, 56.9, 54.3, 20.6, 14.4; IR (neat) 3535, 3405, 2213, 1711 cm^{-1}; HRMS (DART) *m/z* [M+ NH_4]$^+$ calcd for $C_{22}H_{18}O_3$•NH_4 348.1600, found 348.1600



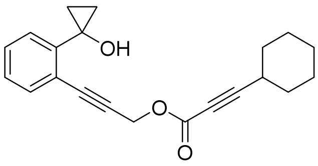
1f

Analytical data for 1f: orange gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 1.8 Hz, 1H), 7.50–7.44 (m, 3H), 7.39–7.30 (m, 2H), 7.26 (dt, *J* = 7.2, 1.2 Hz, 2H), 5.10 (s, 2H), 3.30 (s, 1H), 1.23 (dd, *J* = 7.1, 5.3 Hz, 2H), 1.00 (dd, *J* = 7.1, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.3, 145.0, 134.7, 133.0, 132.8, 131.3, 131.3, 130.0, 129.3, 128.3, 127.7, 122.2, 121.0, 87.2, 86.2, 85.8, 80.7, 56.9, 54.6, 14.4; IR (neat) 3535, 3408, 2224, 1714 cm^{-1}; HRMS (DART) *m/z* [M+ NH_4]$^+$ calcd for $C_{21}H_{15}O_3Cl$•NH_4 368.1054, found 368.1058



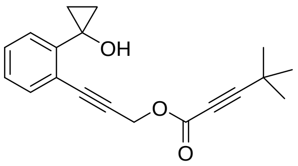
1h

Analytical data for 1h: pale yellow gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.31 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.24 (dt, *J* = 7.6, 1.2 Hz, 1H), 4.99 (s, 2H), 3.42 (br s, 1H), 2.01 (s, 3H), 1.19 (dd, *J* = 7.2, 4.8 Hz, 2H), 0.99 (dd, *J* = 7.2, 4.8 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.3, 145.0, 132.9, 129.2, 128.2, 127.7, 122.3, 87.5, 87.3, 85.9, 71.8, 56.9, 54.1, 14.4, 4.0; IR (neat) 3535, 3407, 2320, 2239, 1712, 1248 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{16}H_{14}O_3{\bullet}NH_4$ 272.1287, found 272.1259



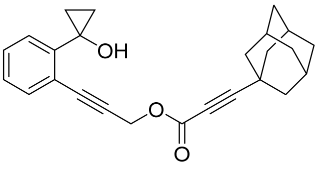
1i

Analytical data for 1i: pale yellow gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.31 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.23 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.00 (s, 2H), 3.34 (br s, 1H), 2.57–2.51 (m, 1H), 1.86-1.82 (m, 2H), 1.75–1.68 (m, 2H), 1.55–1.49 (m, 3H), 1.38–1.31 (m, 3H), 1.21 (dd, *J* = 7.3, 5.0 Hz, 2H), 0.98 (dd, *J* = 7.3, 5.0 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.6, 145.1, 132.9, 129.2, 128.2, 127.7, 122.3, 94.9, 87.6, 85.8, 72.5, 56.9, 54.1, 31.4, 29.0, 25.6, 24.7, 14.4; IR (neat) 3535, 3408, 2931, 2233, 1712, 1238 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{21}H_{22}O_3{\bullet}NH_4$ 340.1913, found 340.1911



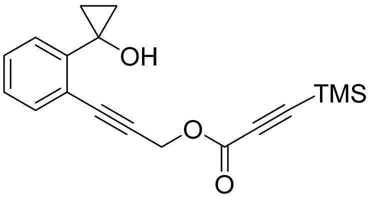
1j

Analytical data for 1j: light orange gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.33–7.29 (m, 1H), 7.25–7.22 (m, 1H), 5.00 (s, 2H), 3.35 (br s, 1H), 1.29 (s, 9H), 1.21 (dd, *J* = 7.1, 5.3 Hz, 2H), 0.98 (dd, *J* = 7.1, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.6, 145.1, 132.9, 129.2, 128.2, 127.7, 122.3, 98.4, 87.6, 85.8, 71.2, 56.9, 54.0, 29.9, 27.7, 14.4; IR (neat) 3539, 3415, 2972, 2225, 1712, 1213 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{19}H_{20}O_3{\bullet}NH_4$ 314.1756, found 314.1727



1k

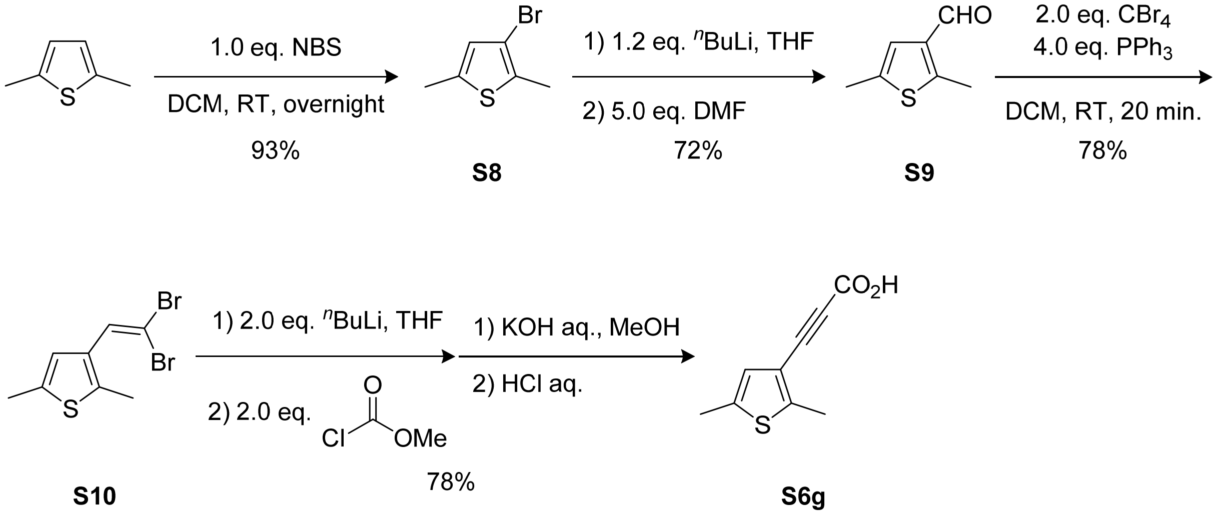
Analytical data for 1k: light orange gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 1H), 7.37–7.35 (m, 1H), 7.33-7.29 (m, 1H), 7.25–7.22 (m, 1H), 5.00 (s, 2H), 3.35 (br s, 1H), 1.99 (br s, 3H), 1.93 (br s, 6H), 1.70 (br s, 6H), 1.21 (dd, *J* = 7.1, 5.3 Hz, 2H), 0.98 (dd, *J* = 7.1, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.8, 145.1, 132.9, 129.2, 128.1, 127.7, 122.3, 97.9, 87.7, 85.8, 71.5, 56.9, 54.0, 41.5, 36.1, 29.8, 27.6, 14.4; IR (neat) 3535, 3409, 2908, 2225, 1712, 1242 cm^{-1}; HRMS (DART) *m/z* $[M- H_2O]^+$ calcd for $C_{25}H_{25}O_2$ 357.1855, found 357.1855



1l

Analytical data for 1l: pale yellow gum; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.37–7.35 (m, 1H), 7.33–7.29 (m, 1H), 7.25–7.23 (m, 1H), 5.02 (s, 2H), 3.27 (br s, 1H), 1.21 (dd, *J* = 7.1, 5.3 Hz, 2H), 0.98 (dd, *J* = 7.1, 5.3 Hz, 2H), 0.26 (s, 9H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 152.6, 145.0, 133.0, 129.3, 128.2, 127.7, 122.2, 96.0, 93.8, 87.3, 86.0, 56.9, 54.3, 14.4, -0.9; IR (neat) 3539, 3413, 2960, 1714, 1211 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{18}H_{20}O_3Si•NH_4$ 330.1525, found 330.1530

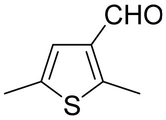
Synthesis of S6g



Synthesis and characterization of S8

A known compound **S8** was synthesized as reported[14].

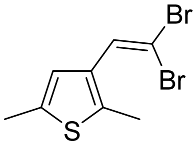
Synthesis and characterization of S9[15]



S9

A solution of **S8** (3.56 g, 18.6 mmol) in THF (40 mL) was cooled under Ar atmosphere to –78 °C. A solution of ⁿBuLi (14.0 mL, 1.60 M in hexane) was added and the mixture was stirred for 1 h. After addition of dry DMF (7.20 mL, 93.0 mmol), the mixture was warmed to rt and stirred for another 1 h. The reaction was quenched with water and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 20:1) to furnish **S9**[15] (1.87 g, 72%).

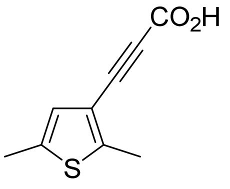
Synthesis and characterization of S10



S10

To a solution of PPh_3 (14.4 g, 54.9 mmol) in DCM (100 mL) was added CBr_4 (9.04 g, 27.3 mmol) and **S9** (1.87 g, 13.4 mmol) at 0 °C. The reaction mixture was stirred at rt for 20 min. The reaction was quenched with water. The aqueous phase was extracted with DCM. The combined organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane) to furnish **S10** (3.07 g, 78%). **Analytical data for S10:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.12 (s, 1H), 2.37 (s, 3H), 2.28 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 137.3, 135.6, 132.1, 131.1, 124.4, 88.3, 15.5, 13.8; IR (neat) 2916 cm^{-1}; HRMS (DART) *m/z* $[M+H]^+$ calcd for $C_8H_8Br_2S{\bullet}H$ 294.8792, found 294.8771

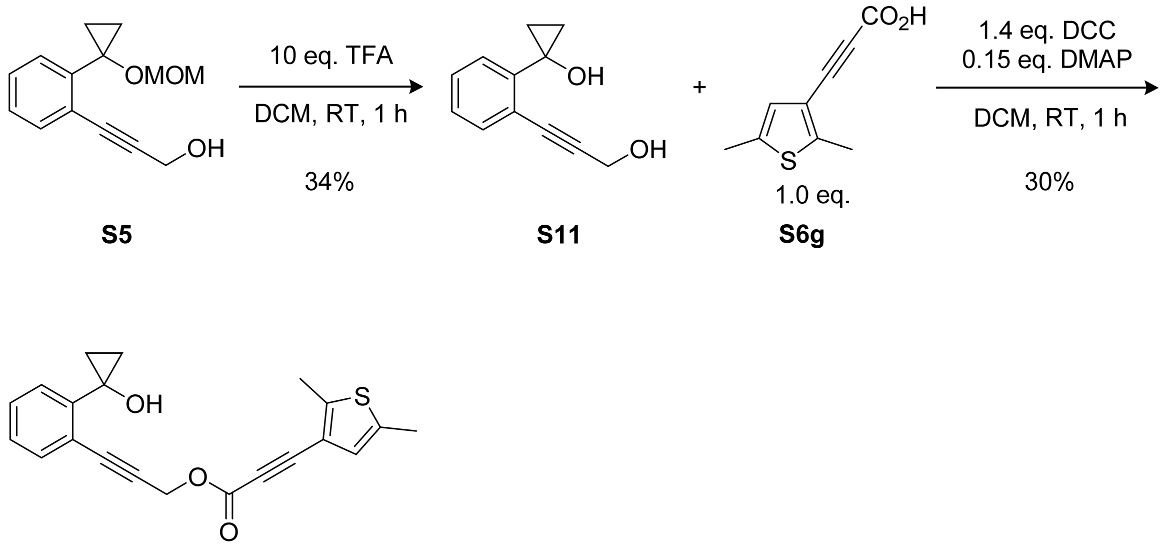
Synthesis and characterization of S6g



S6g

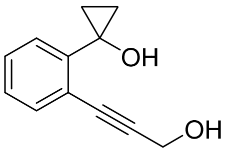
A solution of **S10** (3.07 g, 10.3 mmol) in THF (30 mL) was cooled under Ar atmosphere to 0 °C. A solution of ^{n}BuLi (12.8 mL, 1.60 M in hexane) was added and the mixture was stirred for 15 min. Methyl chloroformate (1.90 g, 20.6 mmol) was added to the mixture. After being stirred at 0 °C for 30 min, the reaction mixture was quenched with water and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. To a solution of the crude product in MeOH (40 mL) was added 20% aq. KOH (11.2 g, 200 mmol), and the solution was stirred at rt for 30 min. After that, 1 M aq. HCl was added slowly at 0 °C until the pH value was less than 1. This mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. **S6g** was obtained as a brown solid (1.44g, 78%). **Analytical data for S6g:** brown solid (mp 120.1–121.1 °C);^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 1H), 2.54 (s, 3H), 2.39 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.1, 149.4, 137.0, 127.3, 115.7, 85.2, 82.8, 15.2, 14.7; IR (neat) 2916, 1666 cm^{-1}; HRMS (DART) *m/z* $[M+H]^+$ calcd for $C_9H_8O_2S{\bullet}H$ 181.0239, found 181.0244

Synthesis and characterization of 1g



1g

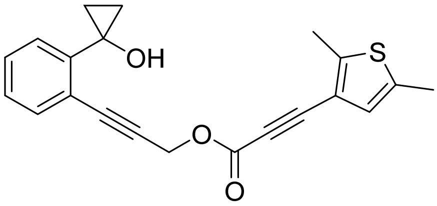
Synthesis and characterization of S11



S11

To a 50 mL flask was added **S5** (682 mg, 2.93 mmol) followed by degassed DCM (20 mL). TFA (2.20 mL, 29.3 mmol) was slowly added to the solution. After stirring at rt for 1 h under Ar atmosphere, the reaction mixture was diluted with water and extracted with EtOAc. The organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 5:1) to furnish **S11** (188 mg, 34%). **Analytical data for S11:** brown solid (mp 81.3–83.1 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.32–7.25 (m, 2H), 4.57 (d, *J* = 5.9 Hz, 2H), 3.19 (s, 1H), 1.83 (t, *J* = 5.9 Hz, 1H), 1.20 (t, *J* = 6.2 Hz, 2H), 1.01 (t, *J* = 6.2 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 144.0, 132.8, 128.6, 128.4, 127.8, 123.5, 92.8, 84.0, 57.1, 51.3, 14.1; IR (KBr) 3307 cm^{-1}; HRMS (DART) *m/z* $[M+H]^+$ calcd for $C_{12}H_{12}O_2$•H 189.0916, found 189.0903

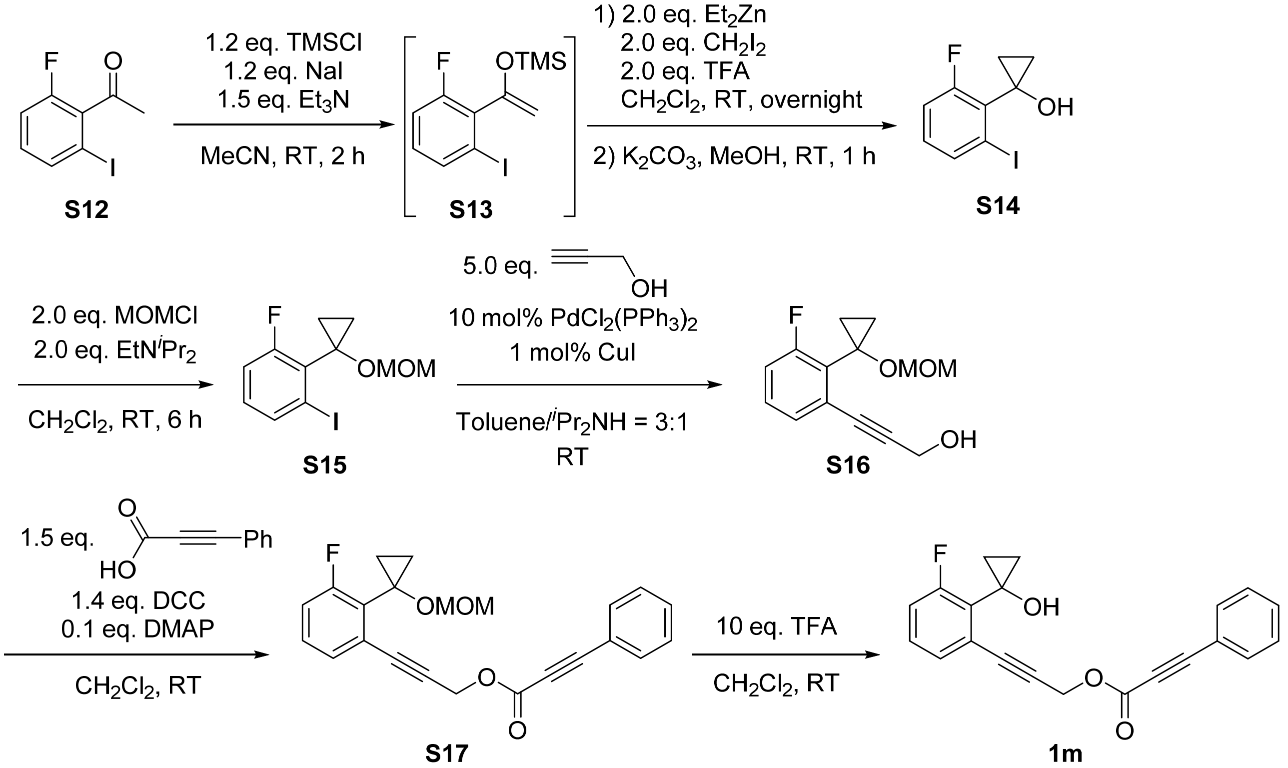
Synthesis and characterization of 1g



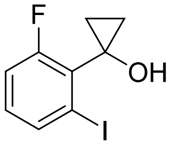
1g

To a 30 mL flask was charged with **S11** (157 mg, 0.840 mmol), **S6g** (151 mg, 0.840 mmol) and DMAP (15.4 mg, 0.130 mmol). To the mixture was added a DCM (8 mL) solution of DCC (193 mg, 0.935 mmol) at 0 °C, and the resulting solution was stirred at rt for 1 h. The reaction mixture was filtered through a pad of Celite® with EtOAc. The filtrate was washed with water, sat. aq. $NaHCO_3$ and brine. The solution was dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to furnish **1g** (89.4 mg, 30%). **Analytical data for 1g:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.36 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.31 (dt, *J* = 7.3, 1.4 Hz, 1H), 7.25 (dt, *J* = 7.3, 1.4 Hz, 1H), 6.70 (s, 1H), 5.06 (s, 2H), 3.39 (br s, 1H), 2.53 (s, 3H), 2.38 (s, 3H), 1.22 (dd, J = 7.1, 5.3 Hz, 2H), 0.99 (dd, J = 7.1, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 154.0, 148.9, 145.1, 136.9, 132.9, 129.2, 128.2, 127.7, 127.3, 122.3, 87.7, 85.9, 83.8, 82.4, 56.9, 54.2, 15.2, 14.7, 14.4; IR (neat) 3535, 3406, 2210, 1709 cm^{-1}; HRMS (DART) *m/z* $[M+H]^+$ calcd for $C_{21}H_{18}O_3S$•H 351.1055, found 351.1035

Synthesis of 1m



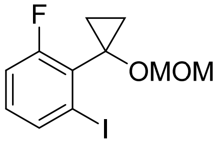
Synthesis and characterization of S14



S14

This compound was prepared in the same manner as described for **S3** using **S12**[16] instead of **S1** in 61% yield as a pale-yellow solid. **Analytical data for S14:** pale-yellow solid (mp 82.3–84.4 °C); ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.66 (d, J = 7.8 Hz, 1H), 7.08–7.03 (m, 1H), 6.99–6.94 (m, 1H), 2.83 (br s, 1H), 1.44–1.32 (m, 2H), 1.09–0.97 (m, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 161.1 (d, J = 256.1 Hz), 135.4 (d, J = 2.9 Hz), 131.3 (d, J = 13.5 Hz), 130.8 (d, J = 8.6 Hz), 116.4 (d, J = 23.1 Hz), 101.5, 55.3, 16.6 (d, J = 4.7 Hz, 2C); ^{19}F NMR (376 MHz, CDCl$_3$): δ –112.3; IR (KBr) 3402 cm^{-1}; HRMS (DART) *m/z* [M+NH$_4$]$^+$ calcd for $C_9H_8FIO{\bullet}NH_4$ 295.9948, found 295.9948.

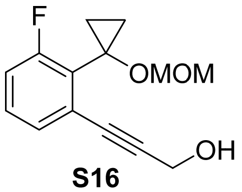
Synthesis and characterization of S15



S15

This compound was prepared in the same manner as described for **S4** using **S14** instead of **S3** in 91% yield as a yellow oil. **Analytical data for S15:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.70–7.68 (m, 1H), 7.06–7.01 (m, 1H), 6.98–6.93 (m, 1H), 4.74 (s, 2H), 3.12 (s, 3H), 1.44-1.42 (m, 2H), 1.05–1.02 (m, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 161.4 (d, J = 254.2 Hz), 135.7 (d, J = 3.8 Hz), 130.7 (d, J = 8.7 Hz), 130.2 (d, J = 13.5 Hz), 115.8 (d, J = 24.0 Hz), 102.2, 96.0, 59.4, 55.6, 15.5 (2C); ^{19}F NMR (376 MHz, CDCl$_3$) δ –110.6: IR (neat) 1562, 1440 cm^{-1}; HRMS (DART) *m/z* [M+NH$_4$]$^+$ calcd for $C_{11}H_{12}FIO_2{\bullet}NH_4$ 340.0210, found 340.0201.

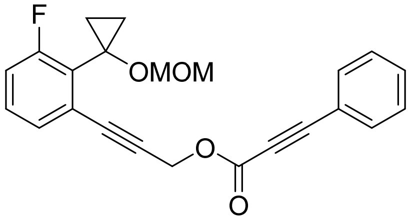
Synthesis and characterization of S16



S16

This compound was prepared in the same manner as described for **S5** using **S15** instead of **S4** in 59% yield as a brown oil. **Analytical data for S16:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.27–7.19 (m, 2H), 7.06–7.02 (m, 1H), 4.78 (s, 2H), 4.50 (d, *J* = 5.5 Hz, 2H), 3.29 (t, *J* = 5.5 Hz, 1H), 3.23 (s, 3H), 1.39–1.35 (m, 2H), 1.06–1.02 (m, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 162.3 (d, *J* = 251.4 Hz), 129.5 (d, *J* = 10.6 Hz), 128.9 (d, *J* = 14.4 Hz), 127.8 (d, *J* = 2.9 Hz), 126.3 (d, *J* = 4.7 Hz), 116.1 (d, *J* = 23.1 Hz), 95.0, 93.4, 83.7 (d, *J* = 3.8 Hz), 55.3, 55.2, 51.4, 13.7 (d, *J* = 2.8 Hz, 2C); ^{19}F NMR (376 MHz, CDCl$_3$) δ –114.1; IR (neat) 3417 cm^{-1}; HRMS (DART) *m/z* [M+NH$_4$]$^+$ calcd for $C_{14}H_{15}FO_3$•NH$_4$ 268.1349, found 268.1327.

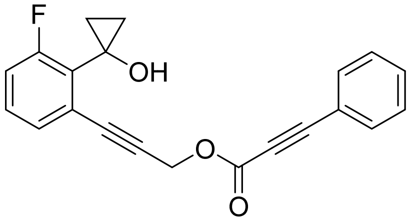
Synthesis and characterization of S17



S17

This compound was prepared in the same manner as described for **S7a** using **S16** instead of **S5** in 79% yield as an orange gum. **Analytical data for S17:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.62–7.59 (m, 2H), 7.49–7.45 (m, 1H), 7.41–7.37 (m, 2H), 7.29–7.21 (m, 2H), 7.08–7.03 (m, 1H), 5.11 (s, 2H), 4.76 (s, 2H), 3.13 (s, 3H), 1.38–1.34 (m, 2H), 1.06–1.03 (m, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 162.1 (d, *J* = 251.3 Hz), 153.2, 133.1 (2C), 130.9, 129.6 (d, *J* = 14.4 Hz), 129.4 (d, *J* = 9.6 Hz), 128.7 (d, *J* = 3.9 Hz), 128.6 (2C), 125.3 (d, *J* = 4.8 Hz), 119.3, 116.5 (d, *J* = 23.1 Hz, 2C), 95.7, 87.4, 87.3, 85.0 (d, *J* = 3.8 Hz), 79.9, 55.6, 55.3, 54.1, 13.8 (d, *J* = 2.8 Hz); ^{19}F NMR (376 MHz, CDCl$_3$) δ –114.6; IR (neat) 2222, 1715 cm^{-1}; HRMS (DART) *m/z* [M+NH$_4$]$^+$ calcd for $C_{23}H_{19}FO_4$•NH$_4$ 396.1611, found 396.1640.

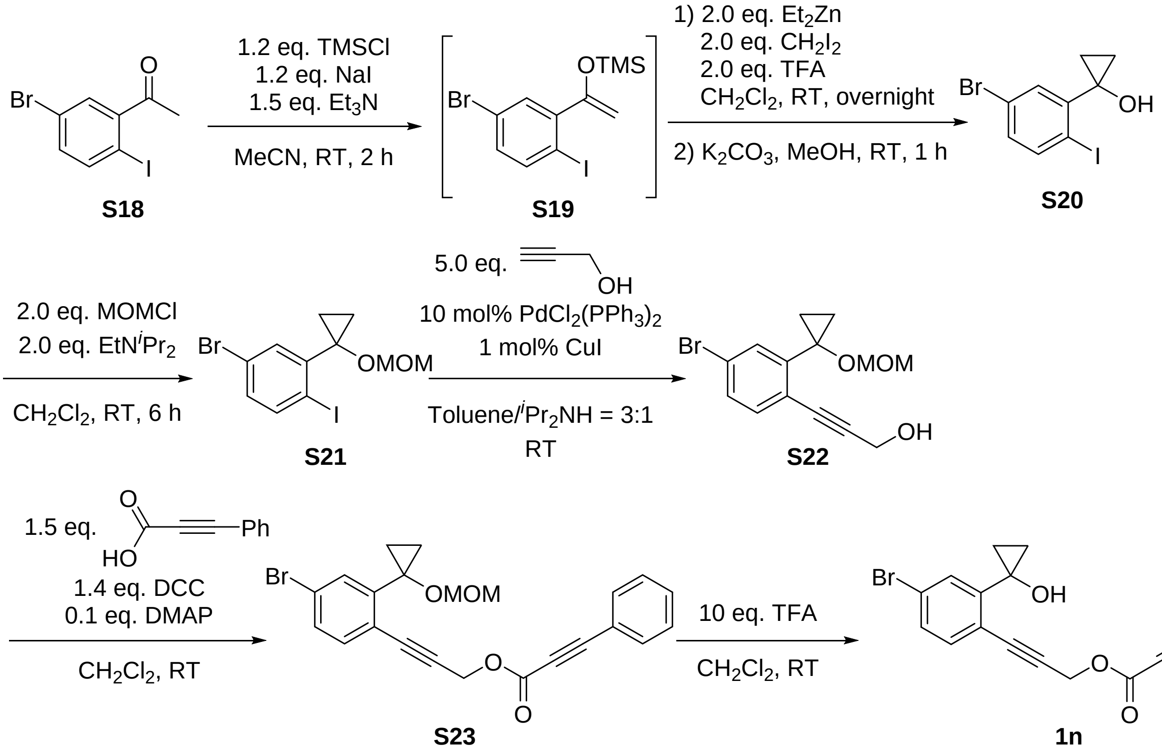
Synthesis and characterization of 1m



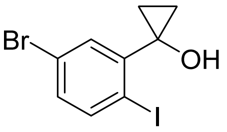
1m

This compound was prepared in the same manner as described for **1a** using **S17** instead of **S7a** in 69% yield as an orange gum. **Analytical data for 1m:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.61–7.59 (m, 2H), 7.49–7.45 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.28–7.19 (m, 2H), 7.08–7.03 (m, 1H), 5.09 (s, 2H), 2.99 (s, 1H), 1.30–1.27 (m, 2H), 1.07–1.03 (m, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 161.2 (d, *J* = 250.4 Hz), 153.4, 133.1 (2C), 131.3 (d, *J* = 14.4 Hz), 130.9, 129.3 (d, *J* = 9.6 Hz), 128.7 (d, *J* = 3.9 Hz), 128.6 (2C), 124.5 (d, *J* = 5.8 Hz), 119.2, 117.0 (d, *J* = 23.1 Hz), 87.80, 87.77, 84.8 (d, *J* = 4.8 Hz), 79.8, 54.1, 51.0 (d, *J* = 2.8 Hz), 15.1 (d, *J* = 3.8 Hz, 2C); ^{19}F NMR (376 MHz, CDCl$_3$) δ –115.8; IR (neat) 3399, 2221, 1713 cm^{-1}; HRMS (DART) *m/z* [M+NH$_4$]$^+$ calcd for C21H15FO3•NH$_4$ 352.1349, found 352.1361.

Synthesis of 1n



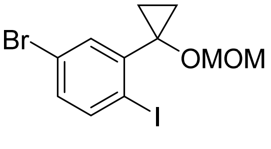
Synthesis and characterization of S20



S20

This compound was prepared in the same manner as described for **S3** using **S18**[16] instead of **S1** in 57% yield as a yellow solid. **Analytical data for S20:** yellow solid (mp 85.4–87.2 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 7.13 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.04 (s, 1H), 1.29 (dd, *J* = 7.3, 5.5 Hz, 2H), 0.97 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 145.7, 140.8, 133.9, 132.6, 122.4, 98.6, 60.5, 15.5 (2C); IR (KBr) 3195 cm^{-1}; HRMS (DART) *m/z* [M–OH]$^{+}$ calcd for $C_9H_7{}^{81}BrI$ 322.8755, found 322.8752.

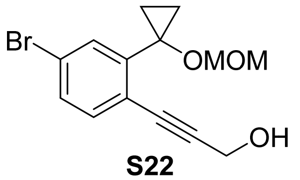
Synthesis and characterization of S21



S21

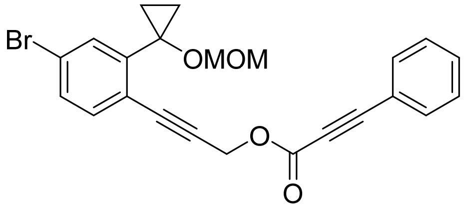
This compound was prepared in the same manner as described for **S4** using **S20** instead of **S3** in 88% yield as a yellow oil. **Analytical data for S21:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 2.7 Hz, 1H), 7.12 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.60 (s, 2H), 3.16 (s, 3H), 1.34 (dd, *J* = 7.6, 5.7 Hz, 2H), 0.96 (dd, *J* = 7.6, 5.7 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 144.0, 141.1, 134.8, 132.4, 121.7, 99.1, 95.2, 64.5, 55.7, 13.9 (2C); IR (neat) 2945, 1442 cm^{-1}; HRMS (DART) *m/z* [M+NH$_4$]$^{+}$ calcd for $C_{11}H_{12}BrIO_2{\bullet}NH_4$ 399.9409, found 399.9434.

Synthesis and characterization of S22


S22

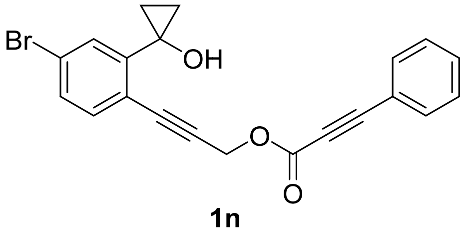
This compound was prepared in the same manner as described for **S5** using **S22** instead of **S4** in 45% yield as a brown oil. **Analytical data for S22:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.8 Hz, 1H), 7.39 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 4.68 (s, 2H), 4.49 (d, *J* = 4.6 Hz, 2H), 3.22 (s, 3H), 3.07 (t, *J* = 4.6 Hz, 1H), 1.29 (dd, *J* = 7.3, 6.0 Hz, 2H), 1.00 (dd, *J* = 7.3, 6.0 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 143.6, 133.9, 133.6, 131.1, 123.2, 122.1, 94.8, 93.5, 83.5, 60.9, 55.5, 51.5, 13.1 (2C); IR (neat) 3409 cm^{-1}; HRMS (FAB) *m/z* $[M+Na]^+$ calcd for $C_{14}H_{15}BrO_3$•Na 333.0102, found 333.0099

Synthesis and characterization of S23


S23

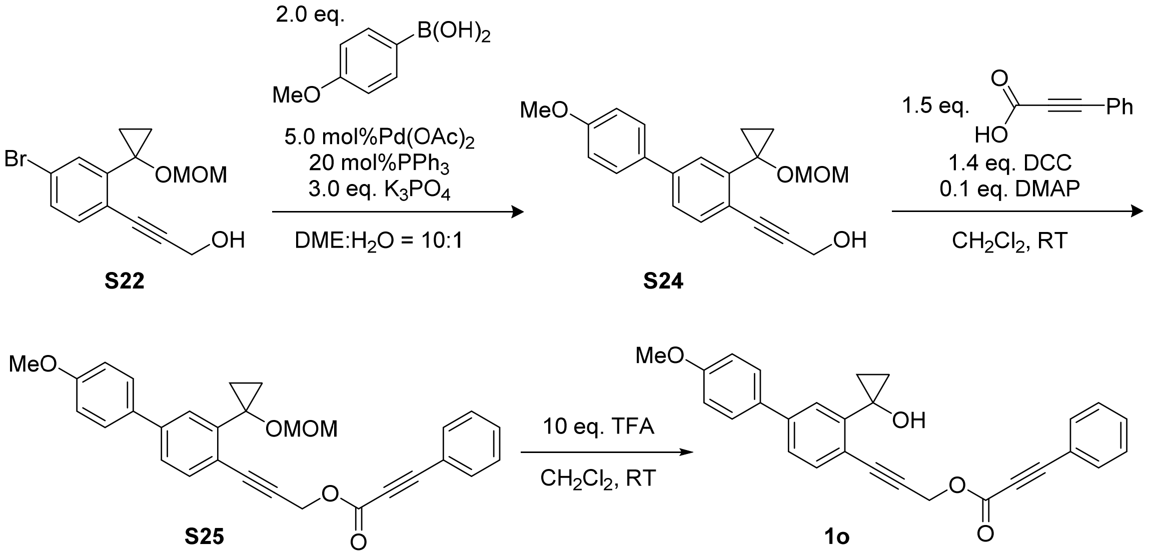
This compound was prepared in the same manner as described for **S7a** using **S22** instead of **S5** in 81% yield as an orange gum. **Analytical data for S23:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60–7.58 (m, 3H), 7.48–7.44 (m, 1H), 7.40–7.33 (m, 4H), 5.10 (s, 2H), 4.65 (s, 2H), 3.17 (s, 3H), 1.29 (dd, *J* = 7.3, 5.5 Hz, 2H), 0.99 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.1, 144.2, 134.2, 133.5, 133.0 (2C), 130.84, 130.79, 128.5 (2C), 122.5, 122.2, 119.2, 95.2, 87.6, 87.3, 84.9, 79.9, 61.0, 55.5, 54.1, 12.9 (2C); IR (neat) 2220, 1714 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{23}H_{19}BrO_4$•NH_4 456.0811, found 456.0819.

Synthesis and characterization of 1n

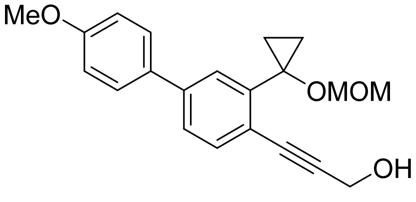

1n

This compound was prepared in the same manner as described for **1a** using **S23** instead of **S7a** in 69% yield as an orange gum. **Analytical data for 1n:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59–7.57 (m, 2H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.47–7.43 (m, 1H), 7.38–7.30 (m, 4H), 5.05 (s, 2H), 3.54 (br s, 1H), 1.27–1.16 (m, 2H), 1.04–0.96 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.4, 146.7, 134.1, 133.0 (2C), 131.4, 130.9, 130.6, 128.5 (2C), 123.1, 121.0, 119.0, 88.2, 87.8, 84.9, 79.7, 56.3, 54.1, 14.3 (2C); IR (neat) 3398, 2220, 1714 cm^{-1}; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{21}H_{15}BrO_3$•Na 417.0102, found 417.0090.

Synthesis of 1o



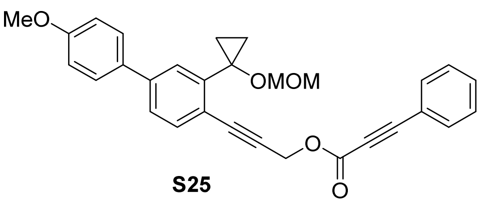
Synthesis and characterization of S24



S24

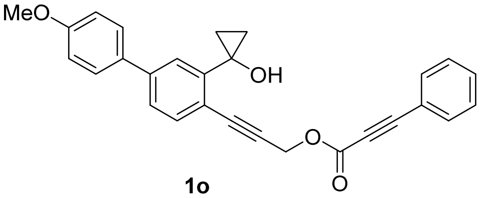
To a solution of **S22** (156 mg, 0.500 mmol) and 4-methoxyphenylbronic acid (152 mg, 1.00 mmol) in DME (3.0 mL) and H_2O (0.30 mL) was added $Pd(OAc)_2$ (5.61 mg, 0.0250 mmol), PPh_3 (26.2 mg, 0.100 mmol) and K_3PO_4 (318 mg, 1.50 mmol). Then the resulting solution was stirred at 60 °C for 4 h. After that, the reaction mixture was diluted with water and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 5:1) to furnish **S24** (120 mg, 72%) as a black gum. **Analytical data for S24:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.2 Hz, 1H), 7.52 (dd, *J* = 10.8, 2.0 Hz, 2H), 7.48-7.42 (m, 2H), 6.97 (dd, *J* = 10.8, 2.0 Hz, 2H), 4.73 (s, 2H), 4.53 (d, *J* = 3.6 Hz, 2H), 3.84 (s, 3H), 3.37 (br s, 1H), 3.25 (s, 3H), 1.33 (dd, *J* = 7.2, 5.6 Hz, 2H), 1.05 (dd, *J* = 7.2, 5.6 Hz, 2H); ^{13}C-NMR (101 MHz, $CHCl_3$) δ 159.6, 141.9, 140.7, 132.9, 132.5, 129.3, 128.2, 126.1, 122.6, 114.4, 94.8, 92.9, 84.5, 61.4, 55.6, 55.4, 51.7, 13.1 (2C); IR (neat) 3403 cm^{-1}; HRMS (ESI) *m/z* $[M+ NH_4]^+$ calcd for $C_{21}H_{22}O_4$•Na 361.1416, found 361.1387.

Synthesis and characterization of S25


S25

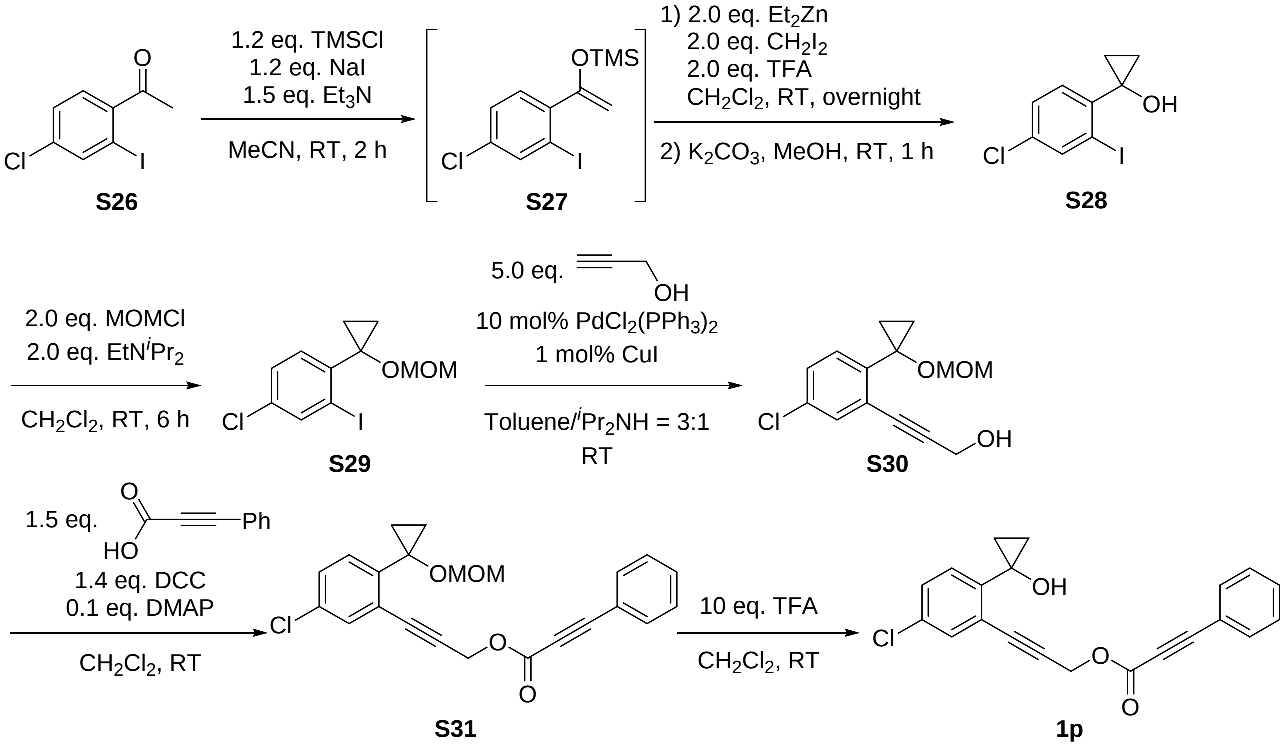
This compound was prepared in the same manner as described for **S7a** using **S24** instead of **S5** in 91% yield as an orange gum. **Analytical data for S25:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.66 (d, *J* = 1.6 Hz, 1H), 7.59 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.55-7.51 (m, 3H), 7.47-7.42 (m, 2H), 7.38-7.34 (m, 2H), 6.97 (dt, *J* = 9.6, 2.4 Hz, 2H), 5.14 (s, 2H), 4.70 (s, 2H), 3.83 (s, 3H), 3.20 (s, 3H), 1.33 (dd, *J* = 7.2, 5.6 Hz, 2H), 1.05 (dd, *J* = 7.2, 5.6 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 159.7, 153.4, 142.5, 141.0, 133.7, 133.2 (2C), 132.5, 131.0, 129.0, 128.7 (2C), 128.2 (2C), 125.9, 121.6, 119.5, 114.4 (2C), 95.2, 87.4, 87.0, 86.2, 80.2, 61.6, 55.7, 55.4, 54.5, 13.1 (2C); IR (neat) 2220, 1712 cm^{-1}; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for C$_{30}$H$_{26}$O$_5$•Na 489.1678, found 489.1692.

Synthesis and characterization of 1o

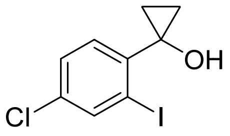

1o

This compound was prepared in the same manner as described for **1a** using **S25** instead of **S7a** in 66% yield as an orange gum. **Analytical data for 1o:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.60 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.56 (d, *J* = 1.6 Hz, 1H), 7.53-7.50 (m, 3H), 7.46-7.42 (m, 2H), 7.40-7.36 (m, 2H), 6.97 (dd, *J* = 6.8, 2.4 Hz, 2H), 5.10 (s, 2H), 3.84 (s, 3H), 3.43 (br s, 1H), 1.26 (dd, *J* = 7.2, 5.2 Hz, 2H), 1.04 (dd, *J* = 7.2, 5.2 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 159.7, 153.7, 145.4, 141.7, 133.4, 133.3 (2C), 132.6, 131.1, 128.7 (2C), 128.3 (2C), 126.5, 125.8, 120.3, 119.4, 114.4 (2C), 87.9, 87.7, 86.2, 80.0, 57.1, 55.5, 54.5, 14.5 (2C); IR (neat) 3427, 2221, 1712 cm^{-1}; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for C$_{28}$H$_{22}$O$_4$•Na 445.1416, found 445.1395.

Synthesis of 1p



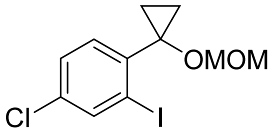
Synthesis and characterization of S28



S28

This compound was prepared in the same manner as described for **S3** using **S26**[17] instead of **S1** in 45% yield as a yellow solid. **Analytical data for S28:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 1.8 Hz, 1H), 7.27–7.22 (m, 2H), 3.15 (s, 1H), 1.25 (dd, J = 7.3, 5.5 Hz, 2H), 0.92 (dd, J = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 142.3, 138.7, 134.2, 131.4, 128.2, 100.7, 60.1, 15.5 (2C); IR (KBr) 3242 cm^{-1}; HRMS (DART) *m/z* $[M–OH]^+$ calcd for C_9H_7ClI 276.9281, found 276.9251.

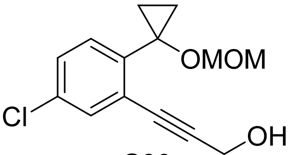
Synthesis and characterization of S29



S29

This compound was prepared in the same manner as described for **S4** using **S28** instead of **S3** in 98% yield as a yellow oil. **Analytical data for S29:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 1.8 Hz, 1H), 7.29–7.25 (m, 2H), 4.60 (s, 2H), 3.16 (s, 3H), 1.35–1.32 (m, 2H), 0.96–0.93 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 140.7, 139.2, 134.3, 132.6, 127.7, 101.3, 95.2, 64.4, 55.8, 14.0 (2C); IR (neat) 2947 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{11}H_{12}ClIO_2{\bullet}NH_4$ 355.9914, found 355.9929.

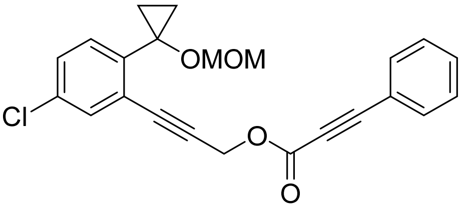
Synthesis and characterization of S30



S30

This compound was prepared in the same manner as described for **S5** using **S29** instead of **S4** in 45% yield as a brown oil. **Analytical data for S30:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.28–7.25 (m, 1H), 4.67 (s, 2H), 4.51 (d, *J* = 5.5 Hz, 2H), 3.21 (s, 3H), 2.97 (t, *J* = 5.5 Hz, 1H), 1.28 (dd, J = 7.3, 5.5 Hz, 2H), 0.97 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 140.2, 133.6, 132.3, 131.9, 128.4, 125.9, 94.7, 93.6, 83.2, 60.6, 55.5, 51.4, 13.1 (2C); IR (neat) 3411 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{14}H_{15}ClO_3$ •NH_4 284.1054, found 284.1025.

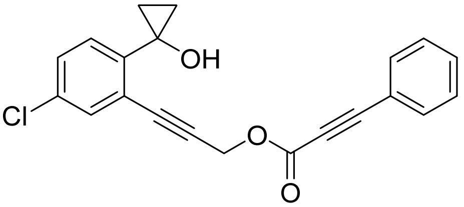
Synthesis and characterization of S31



S31

This compound was prepared in the same manner as described for **S7a** using **S30** instead of **S5** in 82% yield as an orange gum. **Analytical data for S31:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.49–7.45 (m, 2H), 7.41–7.36 (m, 3H), 7.28–7.26 (m, 1H), 5.11 (s, 2H), 4.64 (s, 2H), 3.15 (s, 3H), 1.28 (dd, *J* = 7.6, 5.7 Hz, 2H), 0.97 (dd, *J* = 7.6, 5.7 Hz, 2H; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.2, 140.8, 133.4, 133.1 (2C), 132.6, 131.8, 130.9, 128.7, 128.6 (2C), 125.0, 119.3, 95.2, 87.7, 87.4, 84.6, 80.0, 60.8, 55.5, 54.0, 13.0 (2C); IR (neat) 2220, 1716 cm^{-1}; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{23}H_{19}ClO_4$•Na 417.0870, found 417.0861.

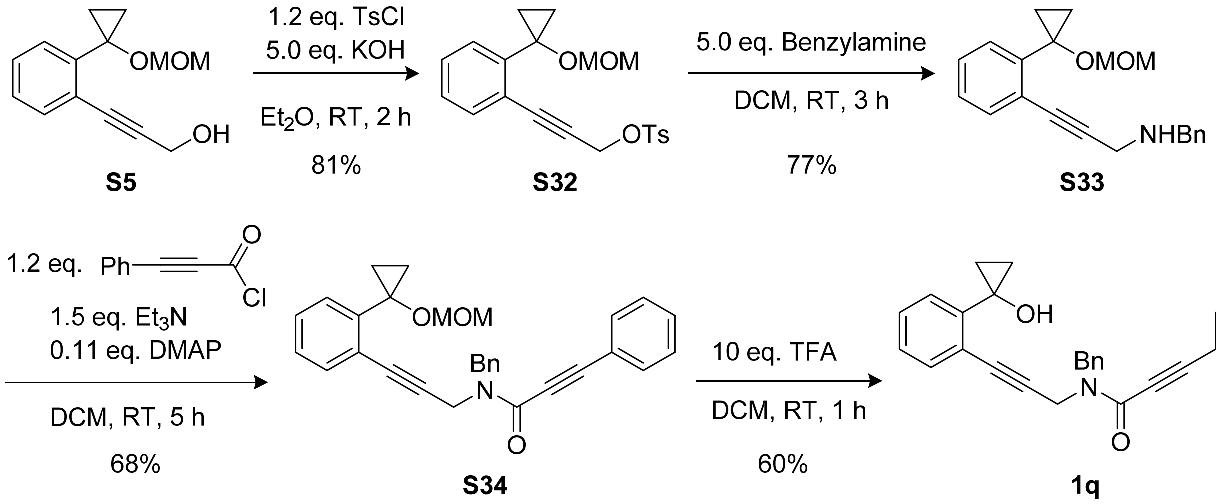
Synthesis and characterization of 1p



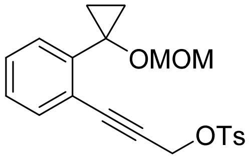
1p

This compound was prepared in the same manner as described for **1a** using **S31** instead of **S7a** in 65% yield as an orange gum. **Analytical data for 1p:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.49–7.45 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.31–7.25 (m, 2H), 5.07 (s, 2H), 3.34 (br s, 1H), 1.22 (dd, *J* = 7.6, 5.3 Hz, 2H), 0.96 (dd, *J* = 7.6, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.5, 143.4, 133.2, 133.1 (2C), 132.5, 131.0, 129.5, 129.2, 128.6 (2C), 123.8, 119.1, 88.4, 88.0, 84.6, 79.8, 56.2, 54.0, 14.4 (2C); IR (neat) 3403, 2220, 1712 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{21}H_{15}ClO_3$•NH_4 368.1054, found 368.1077.

Synthesis of 1q



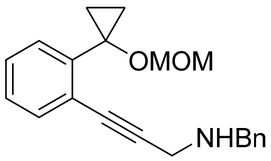
Synthesis and characterization of S32



S32

To a dry Et_2O solution (10 mL) of **S5** (1.16 g, 5.00 mmol) and *p*-toluenesulfonyl chloride (1.20 g, 6.00 mmol) was added KOH (1.43 g, 25 mmol) at 0 °C, and the resulting mixture was stirred at rt for 2 h. The reaction was quenched with water and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by a silica gel column chromatography (Hexane/EtOAc = 10:1) to furnish **S32** (1.57 g, 81%) as a yellow oil. **Analytical data for S32:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.30-7.20 (m, 3H), 5.01 (s, 2H), 4.58 (s, 2H), 3.12 (s, 3H), 2.41 (s, 3H), 1.20 (dd, *J* = 7.3, 5.5 Hz, 2H), 0.91 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 145.1, 142.1, 133.4, 133.2, 130.6, 129.9, 128.9, 128.2, 127.8, 123.0, 95.1, 87.7, 85.0, 61.4, 58.9, 55.6, 21.7, 12.9; IR (neat) 1367, 1176, 1032 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{21}H_{22}O_5S{\bullet}NH_4$ 404.1532, found 404.1521.

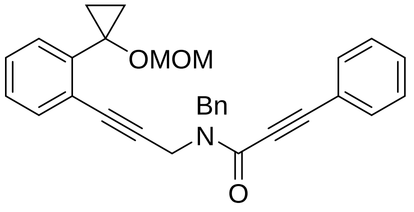
Synthesis and characterization of S33



S37

To a stirred solution of **S32** (1.14 g, 2.94 mmol) in DCM (15 mL) was added benzylamine (1.6 mL, 15.0 mmol) at 0 °C. The mixture was stirred at rt for 3 h, and the solvent was removed *in vacuo*. The reaction mixture was filtered through a pad of Celite® with EtOAc. The filtrate was dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to furnish **S33** (746 mg, 77%) as a yellow oil. **Analytical data for S33:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48–7.39 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28–7.25 (m, 3H), 4.66 (s, 2H), 4.01 (s, 2H), 3.73 (s, 2H), 3.17 (s, 3H), 1.27 (dd, *J* = 7.3, 5.5 Hz, 2H), 1.01 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 141.5, 139.9, 133.1, 130.7, 128.6, 128.5, 127.9, 127.8, 127.2, 124.9, 95.1, 92.5, 82.4, 61.6, 55.6, 52.5, 38.6, 13.0; IR (neat) 3319, 1153, 1032 cm^{-1}; HRMS (DART) *m/z* $[M+ H]^+$ calcd for $C_{21}H_{23}NO_2{\bullet}H$ 322.1807, found 322.1791

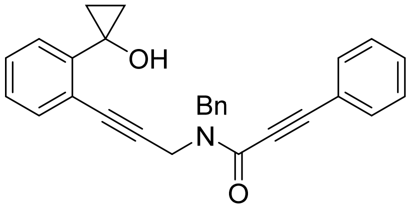
Synthesis and characterization of S34



S34

To a 30 mL flask was added **S33** (953 mg, 2.96 mmol) followed by dry DCM (5.0 mL), Et_3N (610 µL, 4.43 mmol), and DMAP (38.6 mg, 0.340 mmol). 3-Phenyl-2-propynoyl chloride[18] (583 mg, 3.54 mmol) was added slowly at 0 °C. After stirring for 5 h at rt, the reaction was quenched with water and extracted with DCM. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to furnish **S34** (930 mg, 68%) as an orange gum. **S34** was analyzed as a mixture of rotamers (major/minor = 3:2). **Analytical data for S34:** ^{1}H-NMR (400 MHz, $CDCl_3$) **major** δ 7.55–7.52 (m, 2H), 7.46–7.23 (m, 12H), 5.14 (s, 2H), 4.66 (s, 2H), 4.49 (s, 2H), 3.18 (s, 3H), 1.29-1.25 (m, 2H), 1.02-0.97 (m, 2H); **minor** δ 7.61–7.58 (m, 2H), 7.46–7.23 (m, 12H), 4.93 (s, 2H), 4.63 (s, 2H), 4.62 (s, 2H), 3.14 (s, 3H), 1.29-1.25 (m, 2H), 1.02-0.97 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) **major** δ 154.3, 142.0, 136.1, 133.1, 132.6, 130.48, 130.34, 128.8, 128.7, 128.2, 128.1, 127.9, 124.2, 120.38, 95.2, 91.0, 87.9, 83.1, 81.6, 61.6, 55.63, 51.4, 33.5, 12.9; **minor** δ 154.5, 142.2, 136.2, 133.0, 132.6, 130.50, 130.32, 129.0, 128.8, 128.4, 128.2, 127.9, 123.9, 120.43, 95.2, 91.3, 87.8, 83.8, 81.3, 61.6, 55.57, 46.7, 38.8, 12.9; IR (neat) 1631 cm^{-1}; HRMS (DART) *m/z* [M+ H]$^+$ calcd for $C_{30}H_{27}NO_3$•H 450.2069, found 450.2076.

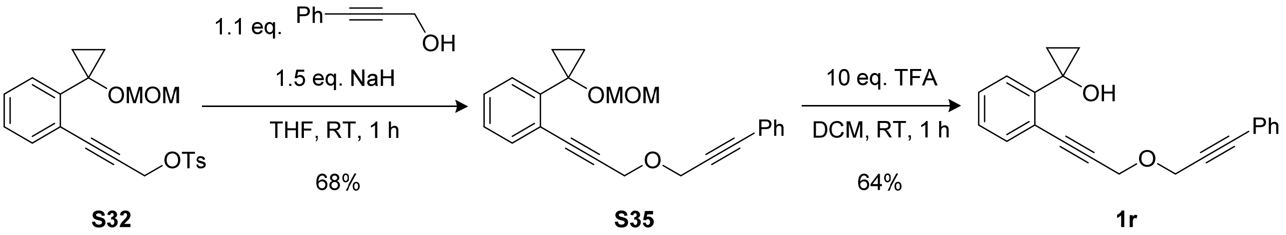
Synthesis and characterization of 1q



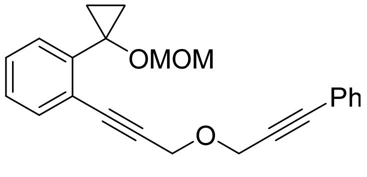
1q

To a 50 mL flask was added **S34** (439 mg, 0.97 mmol) followed by degassed DCM (12 mL). TFA (0.700 mL, 9.70 mmol) was added slowly, and the flask was flushed with Ar. After stirring at rt for 1 h, the reaction mixture was diluted with water and extracted with EtOAc. The organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to furnish **1q** (238 mg, 60%) as an orange gum. **1q** was analyzed as a mixture of rotamers (major/minor = 2:1). **Analytical data for 1q:** ^{1}H-NMR (400 MHz, $CDCl_3$) **major** δ 7.52–7.50 (m, 2H), 7.45–7.20 (m, 12H), 5.05 (s, 2H), 4.40 (s, 2H), 3.49 (br s, 1H), 1.21 (dd, *J* = 7.3, 5.0 Hz, 2H), 0.98 (dd, *J* = 7.3, 5.0 Hz, 2H); **minor** δ 7.59–7.56 (m, 2H), 7.45–7.20 (m, 12H), 4.87 (s, 2H), 4.62 (s, 2H), 2.92 (br s, 1H), 1.15 (dd, *J* = 7.3, 5.5 Hz, 2H), 0.97 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) **major** δ 154.6, 144.8, 135.6, 132.7, 132.5, 130.3, 128.9, 128.8, 128.5, 128.2, 128.0, 127.7, 127.5, 122.7, 120.0, 91.1, 88.6, 82.6, 81.1, 56.7, 52.5, 34.4, 14.2; **minor** δ 154.3, 144.3, 135.8, 133.0, 132.5, 130.3, 128.9, 128.6, 128.5, 128.2, 127.9, 127.7, 127.6, 122.4, 120.0, 91.5, 88.4, 83.4, 81.0, 57.0, 47.1, 38.6, 14.2; IR (neat) 3548, 2214, 1621 cm^{-1}; HRMS (DART) *m/z* [M+ H]$^+$ calcd for $C_{28}H_{23}NO_2$•H 406.1807, found 406.1805.

Synthesis of 1r



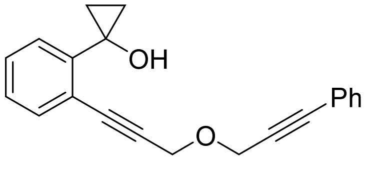
Synthesis and characterization of S35



S35

To a solution of 3-phenyl-2-propyn-1-ol (264 mg, 2.00 mmol) in dry THF (10 mL) was added NaH (60% dispersion in mineral oil, 121 mg, 3.00 mmol) at 0 °C under an Ar atmosphere. The reaction mixture was stirred at 0 °C for 1 h. To this reaction mixture was added a THF (5.0 mL) solution of **S32** (822 mg, 2.13 mmol), and the mixture was stirred for 1 h at rt. The reaction was quenched with water. The aqueous phase was extracted with EtOAc. The combined organic layer was washed with brine and dried over $MgSO_4$. After concentration *in vacuo*, the obtained crude product was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford **S35** (470 mg, 68%) as a yellow oil. **Analytical data for S35:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.50–7.42 (m, 4H), 7.33–7.23 (m, 5H), 4.65 (s, 2H), 4.63 (s, 2H), 4.62 (s, 2H), 3.17 (s, 3H), 1.29 (dd, J = 7.1, 5.7 Hz, 2H), 1.01 (dd, J = 7.1, 5.7 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 142.0, 133.1, 131.9, 130.5, 128.6, 128.4, 128.3, 127.9, 124.2, 122.7, 95.2, 89.2, 86.8, 85.7, 84.8, 61.6, 57.5, 57.2, 55.6, 12.9; IR (neat) 1230,1153 cm^{-1}; HRMS (DART) *m/z* [M– MOMOH]$^+$ calcd for $C_{21}H_{17}O$ 285.1279, found 285.1292

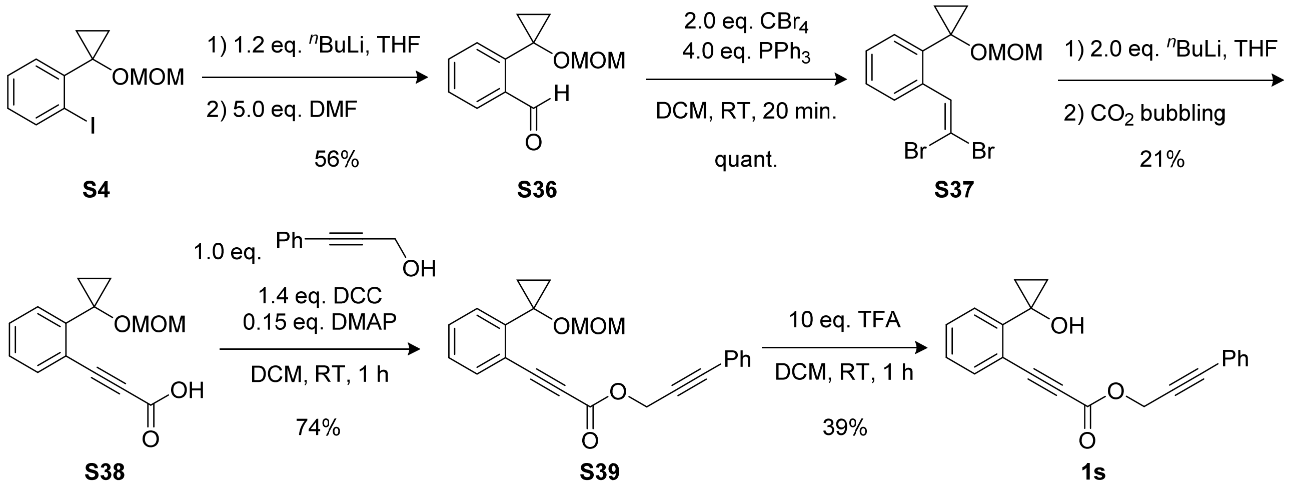
Synthesis and characterization of 1r



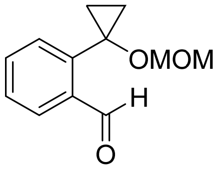
1r

To a 50 mL flask was added **S35** (468 mg, 1.35 mmol) followed by degassed DCM (13 mL). TFA (1.00 mL, 13.5 mmol) was slowly added to the solution. After stirring at rt for 1 h under Ar atmosphere, the reaction mixture was diluted with water and extracted with EtOAc. The organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to furnish **1r** (261 mg, 64%) as a yellow gum. **Analytical data for 1r:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.1, 1.1 Hz, 1H), 7.48–7.44 (m, 2H), 7.37–7.29 (m, 5H), 7.25 (dt, J = 7.4, 1.7 Hz, 1H), 4.63 (s, 2H), 4.59 (s, 2H), 3.18 (s, 1H), 1.22 (dd, J = 7.3, 5.0 Hz, 2H), 1.02 (dd, J = 7.3, 5.0 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 144.5, 133.1, 131.9, 128.9, 128.7, 128.4, 128.1, 127.8, 122.7, 122.5, 89.9, 87.2, 85.5, 84.2, 57.5, 57.4, 57.2, 14.4; IR (neat) 3413,1225 cm^{-1}; HRMS (DART) *m/z* [M– H_2O]$^+$ calcd for $C_{21}H_{17}O$ 285.1279, found 285.1289

Synthesis of 1s



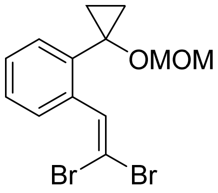
Synthesis and characterization of S36



S36

A solution of **S4** (2.97 g, 9.76 mmol) in THF (20 mL) was cooled under Ar atmosphere to –78 °C. A solution of ^{n}BuLi (7.46 mL, 1.60 M in hexane) was added and the mixture was stirred for 1 h. To the resulting mixture was added DMF (3.58 mL, 4.90 mmol) at –78 °C, and the mixture was stirred for 1 h. The reaction mixture was quenched by water and extracted with EtOAc. The organic layer was washed with brine, dried over MgSO$_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 20:1) to furnish **S36** (1.21 g, 56%) as an orange liquid. **Analytical data for S36:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 10.88 (s, 1H), 7.97 (dd, J = 7.5, 1.6 Hz, 1H), 7.55–7.51 (m, 1H), 7.46–7.42 (m, 2H), 4.60 (s, 2H), 3.11 (s, 3H), 1.36 (dd, J = 7.1, 5.3 Hz, 2H), 1.08 (dd, J = 7.1, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 193.0, 142.8, 135.3, 133.5, 129.3, 128.6, 127.8, 95.4, 59.7, 55.9, 12.8; IR (neat) 1693, 1032 cm^{-1}; HRMS (DART) *m/z* [M+NH$_4$]$^+$ calcd for $C_{12}H_{14}O_3{\bullet}NH_4$ 224.1287, found 224.1276

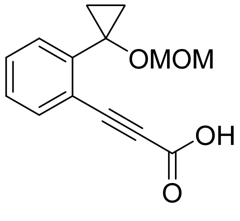
Synthesis and characterization of S37



S37

To a solution of PPh$_3$ (2.67 g, 10.2 mmol) in DCM (12 mL) was added CBr$_4$ (1.76 g, 5.08 mmol) and **S36** (559 mg, 2.54 mmol) at 0 °C. The reaction mixture was stirred at rt for 20 min. The reaction was quenched with water. The aqueous phase was extracted with DCM. The combined organic layer was washed with sat. aq. NaHCO$_3$ and brine, dried over MgSO$_4$ and concentrated to ca. 5 mL. The solution was poured slowly into hexane (40 mL). The resulting suspension was filtrated and the filtrate was concentrated. The resulting suspension was filtrated, concentrated, and purified by silica gel column chromatography (hexane was used as an eluent) to afford **S37** (827 mg, quant.) as a yellow liquid. **Analytical data for S37:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.98 (s, 1H), 7.64 (dd, J = 7.1, 2.1 Hz, 1H), 7.37–7.27 (m, 3H), 4.55 (s, 2H), 3.18 (s, 3H), 1.22 (dd, J = 7.1, 5.3 Hz, 2H), 0.91 (dd, J = 7.1, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 137.8, 136.9, 136.7, 129.7, 129.3, 128.1, 128.0, 95.0, 90.3, 60.8, 55.9, 12.4; IR (neat) 1032 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{13}H_{14}Br_2O_2$•NH_4 377.9704, found 377.9717

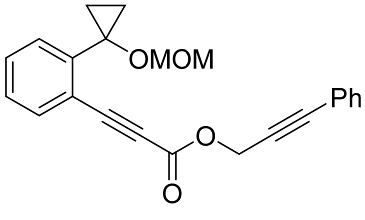
Synthesis and characterization of S38



S38

A solution of **S37** (635 mg, 2.00 mmol) in THF (19 mL) was cooled under Ar atmosphere to –78 °C. A solution of ^{n}BuLi (2.84 mL, 1.60 M in hexane) was added and the mixture was stirred for 1 h. The mixture was warmed to –40 °C and CO_2 gas bubbled into the solution for 1 h. The reaction mixture was quenched by the slow addition of 2.0 M aqueous HCl and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was recrystallized from toluene and hexane at rt, affording pure **S38** (105 mg, 21%) as a white powder (mp 81.9–83.0 °C). **Analytical data for S38:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.48 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.36 (dt, *J* = 7.6, 1.2 Hz, 1H), 4.77 (s, 2H), 3.34 (s, 3H), 1.36 (dd, *J* = 7.2, 6.0 Hz, 2H), 1.01 (dd, *J* = 7.2, 6.0 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 155.3, 143.5, 133.9, 131.3, 130.9, 128.5, 121.2, 94.8, 86.4, 84.9, 61.2, 55.7, 13.0; IR (KBr) 2943, 2210, 1678 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{14}H_{14}O_4$•NH_4 264.1236, found 264.1214

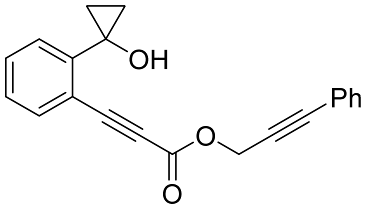
Synthesis and characterization of S39



S39

To a 20 mL flask was charged with **S38** (105 mg, 0.420 mmol), 3-phenyl-2-propyn-1-ol (55.5 mg, 0.420 mmol) and DMAP (5.13 mg, 0.042 mmol). To the mixture was added a DCM (4 mL) solution of DCC (122 mg, 0.590 mmol) at 0 °C, and the resulting solution was stirred at rt for 1 h. The reaction mixture was filtered through a pad of Celite® with EtOAc. The filtrate was washed with water, sat. aq. $NaHCO_3$ and brine. The solution was dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 20:1) to furnish **S39** (115 mg, 74%) as a light-yellow gum. **Analytical data for S39:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.3 Hz, 1H), 7.49–7.47 (m, 3H), 7.43–7.39 (m, 1H), 7.35–7.29 (m, 4H), 5.07 (s, 2H), 4.66 (s, 2H), 3.14 (s, 3H), 1.34 (dd, *J* = 7.1, 5.7 Hz, 2H), 1.03 (dd, *J* = 7.1, 5.7 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.5, 144.2, 134.3, 132.0, 130.6, 130.5, 129.0, 128.4, 128.0, 122.1, 121.0, 95.4, 87.2, 86.3, 84.3, 82.4, 61.4, 55.6, 54.2, 13.1; IR (neat) 2220, 1712, 1171 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{23}H_{20}O_4$•NH_4 378.1705, found 378.1717

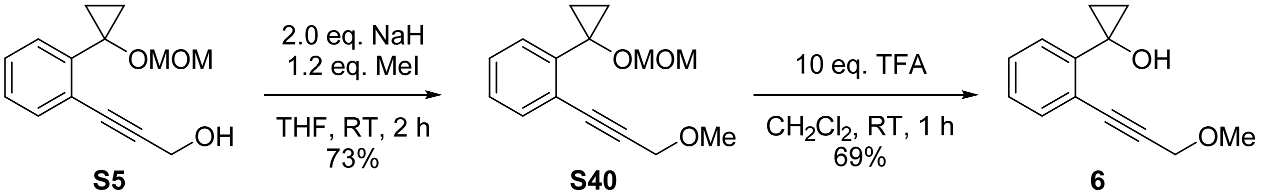
Synthesis and characterization of 1s



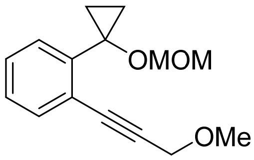
1s

To a 20 mL flask was added **S39** (115 mg, 0.31 mmol) followed by degassed DCM (4 mL). TFA (0.240 mL, 3.10 mmol) was slowly added to the solution. After stirring at rt for 1 h under Ar atmosphere, the reaction mixture was dilutedwith water and extracted with EtOAc. The organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to furnish **1s** (238 mg, 60%) as a light-yellow gum. **Analytical data for 1s:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.49–7.43 (m, 4H), 7.34–7.31 (m, 4H), 5.08 (s, 2H), 2.94 (s, 1H), 1.29 (dd, *J* = 7.3, 5.5 Hz, 2H), 1.05 (dd, *J* = 7.3, 5.5 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.3, 146.5, 134.4, 132.1, 131.2, 129.0, 128.8, 128.4, 128.0, 122.0, 119.8, 87.4, 86.1, 84.9, 82.1, 56.9, 54.4, 14.7; IR (neat) 3398, 2216, 1712, 1173 cm^{-1}; HRMS (DART) *m/z* $[M+ H]^+$ calcd for $C_{21}H_{16}O_3$•H 317.1178, found 317.1175

Synthesis of 6



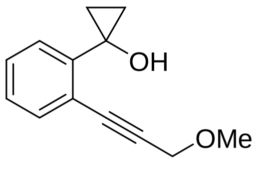
Synthesis and characterization of S40



S40

To a solution of **S5** (348 mg, 1.50 mmol) in dry THF (5 mL) was added NaH (60% dispersion in mineral oil, 122 mg, 3.00 mmol) at 0 °C under an Ar atmosphere. The reaction mixture was stirred at rt for 1 h. To this reaction mixture was added iodomethane (112 µL, 1.80 mmol) and the mixture was stirred at rt for 2 h. The reaction was quenched with water. The aqueous phase was extracted with EtOAc. The combined organic layer was washed with brine and dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to afford **S40** (268 mg, 73%) as a yellow oil. **Analytical data for S40:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.43 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.31–7.23 (m, 2H), 4.64 (s, 2H), 4.40 (s, 2H), 3.49 (s, 3H), 3.17 (s, 3H), 1.26 (dd, *J* = 7.2, 5.6 Hz, 2H), 1.00 (dd, *J* = 7.2, 5.6 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 141.8, 133.1, 130.6, 128.1, 127.8, 124.3, 95.1, 89.7, 85.1, 61.5, 60.6, 57.6, 55.5, 12.9; IR (neat) 1034 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{15}H_{18}O_3$•NH_4 264.1600, found 264.1600

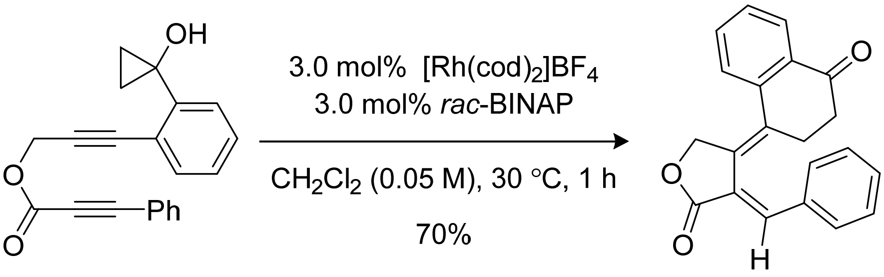
Synthesis and characterization of 6



6

To a 50 mL flask was added **S40** (268 mg, 1.10 mmol) followed by degassed DCM (10 mL). TFA (770 µL, 11.0 mmol) was slowly added to the solution. After being stirred at rt for 1 h under Ar atmosphere, the reaction was diluted with water and extracted with EtOAc. The organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to furnish **6** (154 mg, 69%) as a yellow liquid. **Analytical data for 6:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.35 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.29 (dt, *J* = 7.5, 1.6 Hz, 1H), 7.24 (dt, *J* = 7.5, 1.6 Hz, 1H), 4.39 (s, 2H), 3.47 (s, 3H), 1.19 (dd, *J* = 7.1, 5.3 Hz, 2H), 1.00 (dd, *J* = 7.1, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 144.4, 133.0, 128.8, 128.0, 127.7, 122.8, 90.5, 85.0, 60.6, 57.9, 57.1, 14.3; IR (neat) 3411, 1095 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{13}H_{14}O_2{\bullet}NH_4$ 2201338, found 220.1318

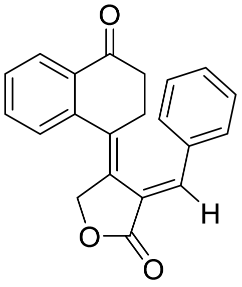
4. Representative Procedure for the Rhodium-Catalyzed Cycloisomerization of 1



1a **2a**

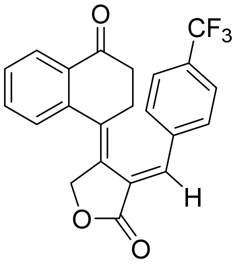
$[Rh(cod)_2]BF_4$ (1.21 mg, 0.00300 mmol) and *rac*-BINAP (1.88 mg, 0.00300 mmol) were dissolved in degassed DCM (1.0 mL) and the mixture was stirred at 30 °C for 10 min under Ar atmosphere. The reaction tube was evacuated and refilled with H_2 using a balloon, which was repeated 3 times. After stirring at 30 °C for 1 h under H_2 atmosphere, the reaction tube was evacuated and refilled with Ar using a balloon, which was repeated 3 times. To the resulting mixture was added a DCM (1.0 mL) solution of **1a** (31.6 mg, 0.100 mmol). After stirring at 30 °C for 1 h, the resulting solution was concentrated *in vacuo*. The crude was then purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to give **2a** (22.1 mg, 70%) as a yellow solid (mp 246.5–248.3 °C).

5. Characterization of Exocyclic Dienes 2 and 3



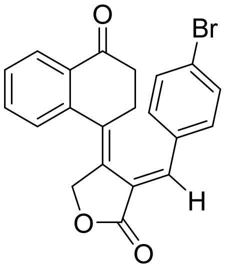
2a

Recrystallization from isopropanol at rt afforded pure **2a** as a yellow crystal. **Analytical data for 2a:**; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.12 (d, *J* = 7.8 Hz, 1H), 7.68 (s, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.55–7.50 (m, 3H), 7.41–7.36 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 1H), 5.23 (s, 2H), 2.60 (t, *J* = 6.9 Hz, 2H), 2.42 (t, *J* = 6.9 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 196.4, 171.0, 139.5, 137.5, 136.1, 134.9, 133.7, 132.2, 130.5, 130.0, 129.8, 128.9, 128.04, 127.96, 123.6, 70.5, 38.9, 32.7; IR (KBr) 1763, 1687 cm^{-1}; HRMS (DART) *m/z* [M+ NH$_4$]$^+$ calcd for $C_{21}H_{16}O_3$•NH$_4$ 334.1443, found 334.1414



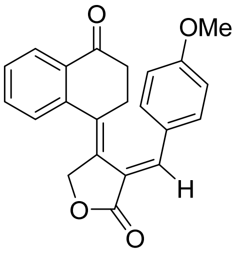
2b

According to the representative procedure, yellow solid (mp 168.6–169.8 °C) was obtained (68% yield). **Analytical data for 2b:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.68–7.65 (m, 6H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 5.22 (s, 2H), 2.62 (t, *J* = 6.9 Hz, 2H), 2.37 (t, *J* = 6.6 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 195.9, 170.4, 139.0, 138.2, 137.4, 135.1, 133.8, 132.3, 130.2, 129.9, 128.2, 128.1, 128.0, 125.9, 125.9, 125.9, 125.8, 70.5, 38.7, 32.7; ^{19}F-NMR (376 MHz, CDCl$_3$) δ –63.9; IR (KBr) 1766, 1689 cm^{-1}; HRMS (DART) *m/z* [M+ H]$^+$ calcd for $C_{22}H_{15}F_3O_3$•H 385.1052, found 385.1031



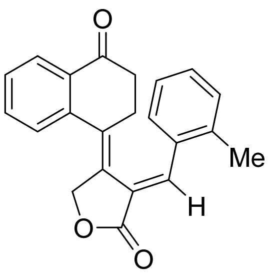
2c

According to the representative procedure, yellow solid (mp 163.0–164.5 °C) was obtained (61% yield). **Analytical data for 2c:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.14 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.65 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.60 (s, 1H), 7.55–7.51 (m, 3H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 7.3 Hz, 1H), 5.19 (s, 2H), 2.62 (t, *J* = 6.6 Hz, 2H), 2.41 (t, *J* = 6.6 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 196.1, 170.7, 139.2, 136.5, 135.9, 133.8, 133.8, 132.2, 131.3, 130.0, 128.6, 128.1, 128.0, 124.8, 124.2, 70.4, 38.8, 32.8; IR (KBr) 1761, 1689 cm^{-1}; HRMS (DART) *m/z* [M+H]$^+$ calcd for $C_{21}H_{15}BrO_3$•H 395.0283, found 395.0275



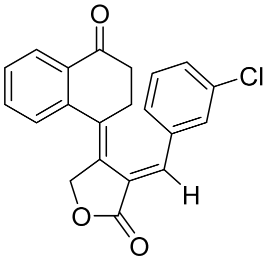
2d

According to the representative procedure, yellow solid (mp 179.3–180.9 °C) was obtained (46% yield). **Analytical data for 2d:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.13 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.65 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.63 (s, 1H), 7.53–7.49 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.17 (s, 2H), 3.84 (s, 3H), 2.62 (t, *J* = 6.6 Hz, 2H), 2.50 (t, *J* = 6.6 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 196.6, 171.4, 161.4, 139.7, 137.4, 135.1, 133.7, 132.2, 132.1, 129.6, 128.00, 127.96, 127.4, 121.0, 114.3, 70.4, 55.5, 39.0, 32.8; IR (KBr) 1745, 1675 cm^{-1}; HRMS (DART) *m/z* [M+H]$^+$ calcd for $C_{22}H_{18}O_4$•H 347.1283, found 347.1269



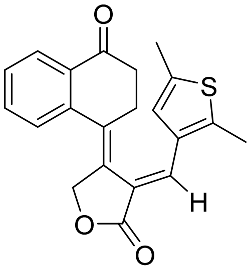
2e

The reaction was performed at 30 °C for 2 h. Yellow solid (mp 186.5–188.0 °C) was obtained (53% yield). Recrystallization from isopropanol at rt afforded pure **2e** as a yellow crystal. **Analytical data for 2e:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.85 (s, 1H), 7.63 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.52–7.47 (m, 2H), 7.29–7.25 (m, 2H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 5.21 (s, 2H), 2.57 (t, *J* = 6.9 Hz, 2H), 2.46 (s, 3H), 2.24 (t, *J* = 6.9 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.4, 171.0, 139.5, 138.6, 136.2, 135.5, 134.3, 133.7, 132.2, 131.1, 130.3, 129.7, 128.5, 128.0, 127.9, 127.6, 126.1, 124.4, 70.4, 38.8, 31.9, 20.2; IR (KBr) 1749, 1678 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{22}H_{18}O_3$•NH_4 348.1600, found 368.1598



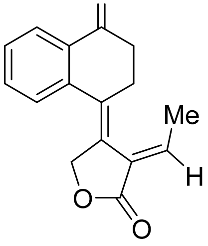
2f

According to the representative procedure, yellow solid (mp 175.2–176.5 °C) was obtained (85% yield). **Analytical data for 2f:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.66 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.60 (s, 1H), 7.54 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.50 (s, 1H), 7.44–7.41 (m, 1H), 7.34–7.33 (m, 2H), 7.22 (d, *J* = 6.9 Hz, 1H), 5.19 (s, 2H), 2.62 (t, *J* = 6.9 Hz, 2H), 2.41 (t, *J* = 6.6 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.1, 170.6, 139.2, 136.9, 136.7, 135.5, 134.9, 133.8, 132.3, 130.4, 130.1, 130.1, 129.6, 128.4, 128.1, 128.0, 127.9, 124.9, 70.5, 38.8, 32.7; IR (KBr) 1753, 1684 cm^{-1}; HRMS (DART) *m/z* $[M+ NH_4]^+$ calcd for $C_{21}H_{15}O_3Cl$•NH_4 368.1054, found 368.1074



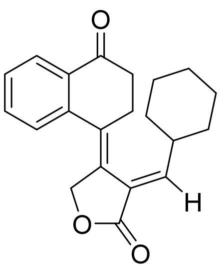
2g

According to the representative procedure, brown solid (mp 175.4–175.9 °C) was obtained (55% yield). **Analytical data for 2g:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.64 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.57 (s, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 5.12 (s, 2H), 2.64 (t, *J* = 6.2 Hz, 2H), 2.56 (t, *J* = 6.2 Hz, 2H), 2.53 (s, 3H), 2.33 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.7, 171.6, 144.8, 139.9, 136.4, 135.6, 133.7, 132.8, 132.2, 130.1, 129.8, 129.5, 127.9, 124.1, 120.8, 70.4, 39.2, 32.2, 15.3, 14.0; IR (KBr) 1757, 1681 cm^{-1}; HRMS (DART) *m/z* $[M+H]^+$ calcd for $C_{21}H_{18}O_3S$•H 351.1055, found 351.1051



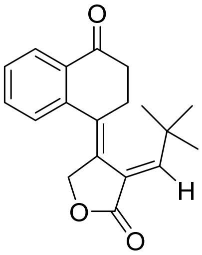
2h

According to the representative procedure, white solid (mp 173.8–174.9 °C) was obtained (62% yield). **Analytical data for 2h:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.61 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.93 (q, *J* = 7.5 Hz, 1H), 5.05 (s, 2H), 2.86 (t, *J* = 6.2 Hz, 2H), 2.77 (t, *J* = 6.2 Hz, 2H), 2.02 (d, *J* = 7.5 Hz, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.4, 170.2, 139.6, 137.3, 134.1, 133.7, 132.1, 129.6, 128.7, 128.0, 128.0, 127.9, 70.6, 39.4, 31.9, 18.3; IR (KBr) 1762, 1693 cm^{-1}; HRMS (DART) *m/z* $[M+NH_4]^+$ calcd for $C_{16}H_{14}O_3$•NH_4 272.1287, found 272.1268



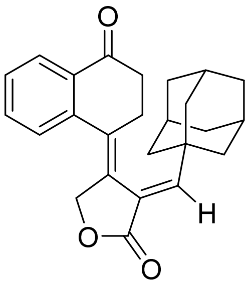
2i

According to the representative procedure, white solid (mp 151.6–153.0 °C) was obtained (66% yield). **Analytical data for 2i:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 7.8, 1.4 Hz, 1H), 7.59 (dt, J = 7.6, 1.3 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 6.63 (d, J = 11.4 Hz, 1H), 5.01 (s, 2H), 2.92 (t, J = 6.6 Hz, 2H), 2.77 (t, J = 6.6 Hz, 2H), 2.31-2.25 (m, 1H), 1.81-1.69 (m, 5H), 1.33-1.19 (m, 5H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.4, 170.8, 147.6, 139.6, 134.0, 133.7, 132.1, 129.5, 129.0, 128.1, 127.9, 124.0, 70.6, 40.7, 39.3, 31.8, 31.6, 25.7, 25.6; IR (KBr) 1766, 1687 cm^{-1}; HRMS (DART) m/z $[M+NH_4]^+$ calcd for $C_{21}H_{22}O_3$•NH_4 340.1913, found 340.1892



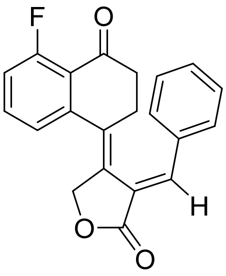
2j

The reaction was performed using $[Rh(cod)_2]BF_4$ (10 mol%) and *rac*-BINAP (10 mol%) at 60 °C in DCE and white solid (mp 166.7–167.3 °C) was obtained (56% yield). Recrystallization from isopropanol at rt afforded pure **2j** as a colorless crystal. **Analytical data for 2j:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.82 (s, 1H), 4.94 (s, 2H), 3.02 (t, J = 6.6 Hz, 2H), 2.77 (t, J = 6.6 Hz, 2H), 1.24 (s, 9H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.2, 170.7, 152.2, 139.7, 136.9, 133.7, 132.0, 129.7, 129.2, 128.1, 127.9, 122.7, 70.4, 39.5, 35.5, 33.1, 28.6; IR (KBr) 1765, 1684 cm^{-1}; HRMS (DART) m/z $[M+H]^+$ calcd for $C_{19}H_{20}O_3$•H 297.1491, found 297.1483



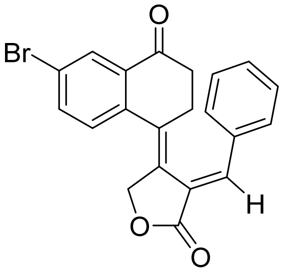
2k

The reaction was performed using $[Rh(cod)_2]BF_4$ (10 mol%) and *rac*-BINAP (10 mol%) at 60 °C in DCE and orange solid (mp 275.3–278.1 °C) was obtained (46% yield). **Analytical data for 2k:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 7.6, 1.4 Hz, 1H), 7.60 (dt, J = 7.6, 1.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.62 (s, 1H), 4.94 (s, 2H), 3.04 (t, J = 6.2 Hz, 2H), 2.78 (d, J = 6.2 Hz, 2H), 2.02 (br s, 3H), 1.82 (br s, 6H), 1.74 (br d, J = 12.4 Hz, 3H), 1.67 (br d, J = 12.4 Hz, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.3, 170.8, 151.8, 139.8, 136.8, 133.7, 132.0, 130.0, 129.6, 128.2, 127.8, 122.5, 70.4, 40.2, 39.5, 37.9, 36.4, 33.4, 27.9; IR (KBr) 3427, 2906, 1765, 1712 cm^{-1}; HRMS (DART) m/z $[M+NH_4]^+$ calcd for $C_{25}H_{26}O_3$•NH_4 392.2226, found 392.2206

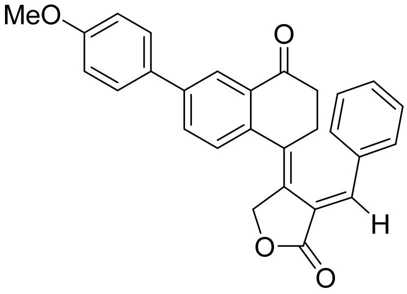


2m

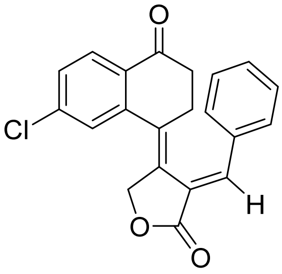
According to the representative procedure, pale-yellow solid (mp 194.4–195.8 °C) was obtained (62% yield). **Analytical data for 2m:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.63–7.58 (m, 1H), 7.55–7.52 (m, 2H), 7.41–7.38 (m, 3H), 7.20 (ddd, J = 11.0, 8.2, 0.9 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 5.15 (s, 2H), 2.58 (t, J = 6.9 Hz, 2H), 2.39 (t, J = 6.9 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 194.1, 170.6, 162.2 (d, J = 269.7 Hz), 141.6, 138.1, 135.4 (d, J = 2.9 Hz), 134.7, 134.6, 130.6, 129.9 (2C), 129.7, 128.8 (2C), 123.8 (d, J = 3.8 Hz), 123.3, 120.5 (d, J = 4.7 Hz), 118.3 (d, J = 23.1 Hz), 70.2, 39.7, 32.2; ^{19}F-NMR (376 MHz, $CDCl_3$) δ –110.8; IR (KBr) 1752, 1678 cm^{-1}; HRMS (DART) m/z $[M+NH_4]^+$ calcd for $C_{21}H_{15}FO_3$•NH_4 352.1349, found 352.1367


2n

According to the representative procedure, yellow solid (mp 199.8–201.2 °C) was obtained (40% yield). **Analytical data for 2n:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 2.3 Hz, 1H), 7.76 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.71 (s, 1H), 7.53–7.51 (m, 2H), 7.41–7.38 (m, 3H), 7.08 (d, *J* = 8.2 Hz, 1H), 5.16 (s, 2H), 2.59 (t, *J* = 6.9 Hz, 2H), 2.40 (t, *J* = 6.9 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 195.0, 170.6, 138.0, 136.4, 134.74, 134.69, 133.3, 130.9, 130.6, 129.9, 129.4, 128.8, 124.1, 123.3, 70.1, 38.6, 32.3; IR (KBr) 1759, 1680 cm^{-1}; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{21}H_{15}BrO_3$•Na 417.0102, found 417.0099.

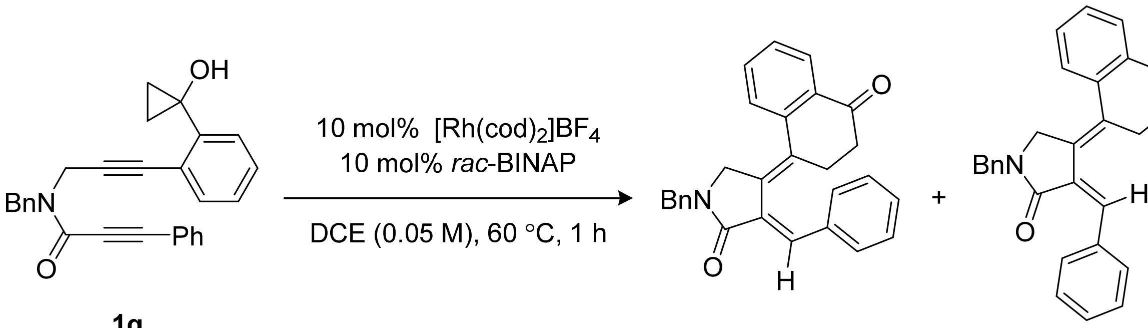

2o

According to the representative procedure, orange solid (mp 212.3–214.0 °C) was obtained (59% yield). **Analytical data for 2o:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 2.2 Hz, 1H), 7.84 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.69 (s, 1H), 7.63–7.61 (m, 2H), 7.56–7.54 (m, 2H), 7.39–7.38 (m, 3H), 7.28–7.26 (m, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 5.24 (s, 2H), 3.88 (s, 3H), 2.63 (t, *J* = 6.9 Hz, 2H), 2.43 (t, *J* = 6.9 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.5, 171.0, 160.0, 142.1, 137.4, 137.2, 135.7, 134.9, 132.4, 131.4, 131.3, 130.4, 129.9, 128.8, 128.6, 128.5, 128.1, 125.4, 123.6, 114.5, 70.4, 55.4, 38.9, 32.6; IR (KBr) 1765, 1681 cm^{-1}; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{28}H_{22}O_4$•Na 445.1416, found 445.1398


2p

According to the representative procedure, yellow solid (mp 188.0–189.5 °C) was obtained (72% yield). **Analytical data for 2p:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.72 (s, 1H), 7.54–7.52 (m, 2H), 7.47 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.41–7.39 (m, 3H), 7.19 (d, *J* = 1.8 Hz, 1H), 5.21 (s, 2H), 2.59 (t, *J* = 6.6 Hz, 2H), 2.40 (t, *J* = 6.6 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 195.2, 170.5, 140.7, 140.1, 138.3, 134.7, 134.6, 130.7, 130.4, 130.0, 129.9, 129.8, 129.5, 128.9, 127.6, 123.2, 77.3, 77.0, 76.7, 70.0, 38.6, 32.5; IR (KBr) 1763, 1689 cm^{-1}; HRMS (DART) *m/z* $[M+H]^+$ calcd for $C_{21}H_{15}ClO_3$•H 351.0788, found 351.0789

Rhodium-Catalyzed Cycloisomerization of 1q

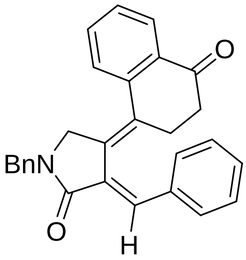


1q

2q 27%

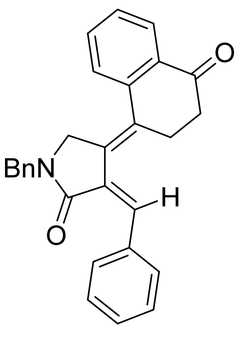
3q 19%

$[Rh(cod)_2]BF_4$ (4.07 mg, 0.0100 mmol) and *rac*-BINAP (6.23 mg, 0.0100 mmol) were dissolved in degassed DCE (1.0 mL) and the mixture was stirred at 30 °C for 10 min under Ar atmosphere. The reaction tube was evacuated and refilled with H_2 using a balloon, which was repeated 3 times. After stirring at 30 °C for 1 h under H_2 atmosphere, the reaction tube was evacuated and refilled with Ar using a balloon, which was repeated 3 times. To the resulting mixture was added a DCE (1.0 mL) solution of **1q** (40.6 mg, 0.100 mmol). After stirring at 60 °C for 1 h, the resulting solution was concentrated *in vacuo*. The crude product was then purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to give **2q** (11.0 mg, 27%) and **3q** (7.70 mg, 19%).



2q

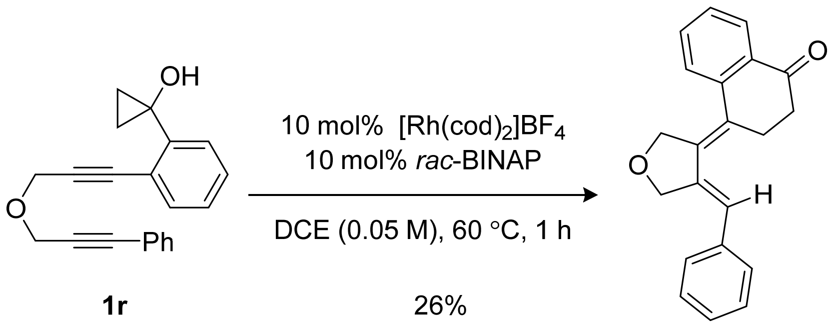
Analytical data for 2q: yellow solid (mp 169.9–170.9 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.58 (s, 1H), 7.56 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.37–7.28 (m, 9H), 4.67 (s, 2H), 4.22 (s, 2H), 2.55 (t, *J* = 6.6 Hz, 2H), 2.41 (t, *J* = 6.6 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 197.0, 168.6, 140.4, 136.2, 136.0, 134.6, 133.5, 132.6, 132.2, 130.0, 129.6, 129.3, 129.1, 129.0, 128.7, 128.3, 128.1, 127.9, 127.7, 51.5, 47.1, 39.0, 32.4; IR (KBr) 1691, 1619 cm^{-1}; HRMS (DART) *m/z* $[M+ H]^+$ calcd for $C_{28}H_{23}NO_2$•H 406.1807, found 406.1808



3q

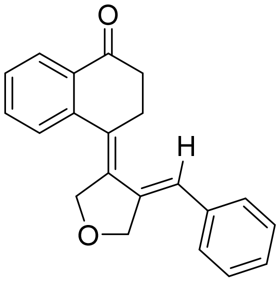
Analytical data for 3q: yellow solid (mp 175.6–179.4 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.02 (d, *J* = 6.8 Hz, 2H), 7.51 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.43–7.21 (m, 10H), 7.10 (s, 1H), 4.58 (s, 2H), 4.18 (s, 2H), 3.32 (t, *J* = 6.6 Hz, 2H), 2.74 (t, *J* = 6.6 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 197.0, 168.6, 140.4, 136.2, 136.0, 134.6, 133.5, 132.6, 132.2, 130.0, 129.6, 129.3, 129.1, 129.0, 128.7, 128.3, 128.1, 127.9, 127.7, 51.5, 47.1, 39.0, 32.4; IR (KBr) 1691, 1619 cm^{-1}; HRMS (DART) *m/z* $[M+ H]^+$ calcd for $C_{28}H_{23}NO_2$•H 406.1807, found 406.1793

Rhodium-Catalyzed Cycloisomerization of 1r



3r

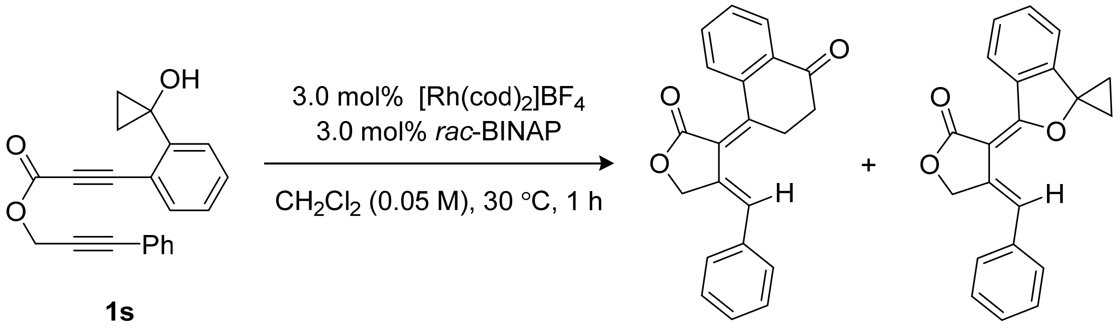
[Rh(cod)$_2$]BF$_4$ (4.07 mg, 0.0100 mmol) and *rac*-BINAP (6.23 mg, 0.0100 mmol) were dissolved in degassed DCE (1.0 mL) and the mixture was stirred at 30 °C for 10 min under Ar atmosphere. The reaction tube was evacuated and refilled with H$_2$ using a ballon, which was repeated 3 times. After stirring at 30 °C for 1 h under H$_2$ atmosphere, the reaction tube was evacuated and refilled with Ar using a balloon, which was repeated 3 times. To the resulting mixture was added a DCE (1.0 mL) solution of **1r** (30.2 mg, 0.100 mmol). After stirring at 60 °C for 1 h, the resulting solution was concentrated *in vacuo*. The crude product was then purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to give **3r** (7.86 mg, 26%).



3r

Analytical data for 3r: white solid (mp 119.0–122.4 °C); ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.10 (dd, J = 7.8, 1.6 Hz, 1H), 7.56 (dt, J = 7.8, 1.6 Hz, 1H), 7.44–7.39 (m, 3H), 7.32–7.24 (m, 3H), 7.08 (d, J = 7.8 Hz, 1H), 6.87 (t, J = 2.7 Hz, 1H), 4.82 (d, J = 2.7 Hz, 2H), 4.66 (s, 2H), 3.38 (t, J = 6.9 Hz, 2H), 2.80 (t, J = 6.9 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) 197.3, 142.2, 138.8, 137.7, 136.6, 133.4, 131.7, 130.3, 128.8, 128.4, 128.3, 127.8, 127.4, 127.0, 70.9, 70.0, 39.5, 30.3; IR (KBr) 1680 cm^{-1}; HRMS (DART) *m/z* [M+ H]$^+$ calcd for C$_{21}$H$_{18}$O$_2$ 303.1385, found 303.1397

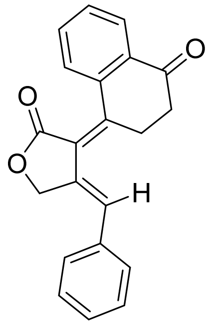
Rhodium-Catalyzed Cycloisomerization of 1s



1s

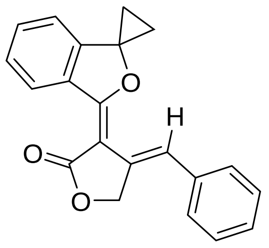
3s 30% **3s'** 30%

[Rh(cod)$_2$]BF$_4$ (1.21 mg, 0.00300 mmol) and *rac*-BINAP (1.88 mg, 0.00300 mmol) were dissolved in degassed DCM (1.0 mL) and the mixture was stirred at 30 °C for 10 min under Ar atmosphere. The reaction tube was evacuated and refilled with H_2 using a balloon, which was repeated 3 times. After stirring at 30 °C for 1 h under H_2 atmosphere, the reaction tube was evacuated and refilled with Ar using a balloon, which was repeated 3 times. To the resulting mixture was added a DCM (1.0 mL) solution of **1s** (31.6 mg, 0.100 mmol). After stirring at 30 °C for 1 h, the resulting solution was concentrated *in vacuo*. The crude product was then purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to give **3s** (9.16 mg, 30%) and **3s'** (9.23 mg, 30%).



3s

Recrystallization from hexane and EtOAc at rt afforded pure **3s** as a yellow crystal. **Analytical data for 3o:** yellow solid (mp 170.8–172.3 °C); ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.08-8.06 (m, 1H), 7.88-7.86 (m, 1H), 7.60-7.53 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.38-7.34 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 2.3 Hz, 1H), 5.20 (d, *J* = 2.3 Hz, 2H), 3.46 (t, *J* = 6.9 Hz, 2H), 2.84 (t, *J* = 6.9 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 196.0, 167.5, 150.2, 137.9, 135.3, 134.7, 132.3, 132.1, 131.9, 131.1, 129.2, 129.0, 128.8, 128.6, 126.5, 123.1, 68.9, 38.7, 33.7; IR (KBr) 1751, 1681 cm^{-1}; HRMS (DART) *m/z* [M+ H]$^+$ calcd for $C_{21}H_{16}O_3$•H 317.1178, found 317.1170

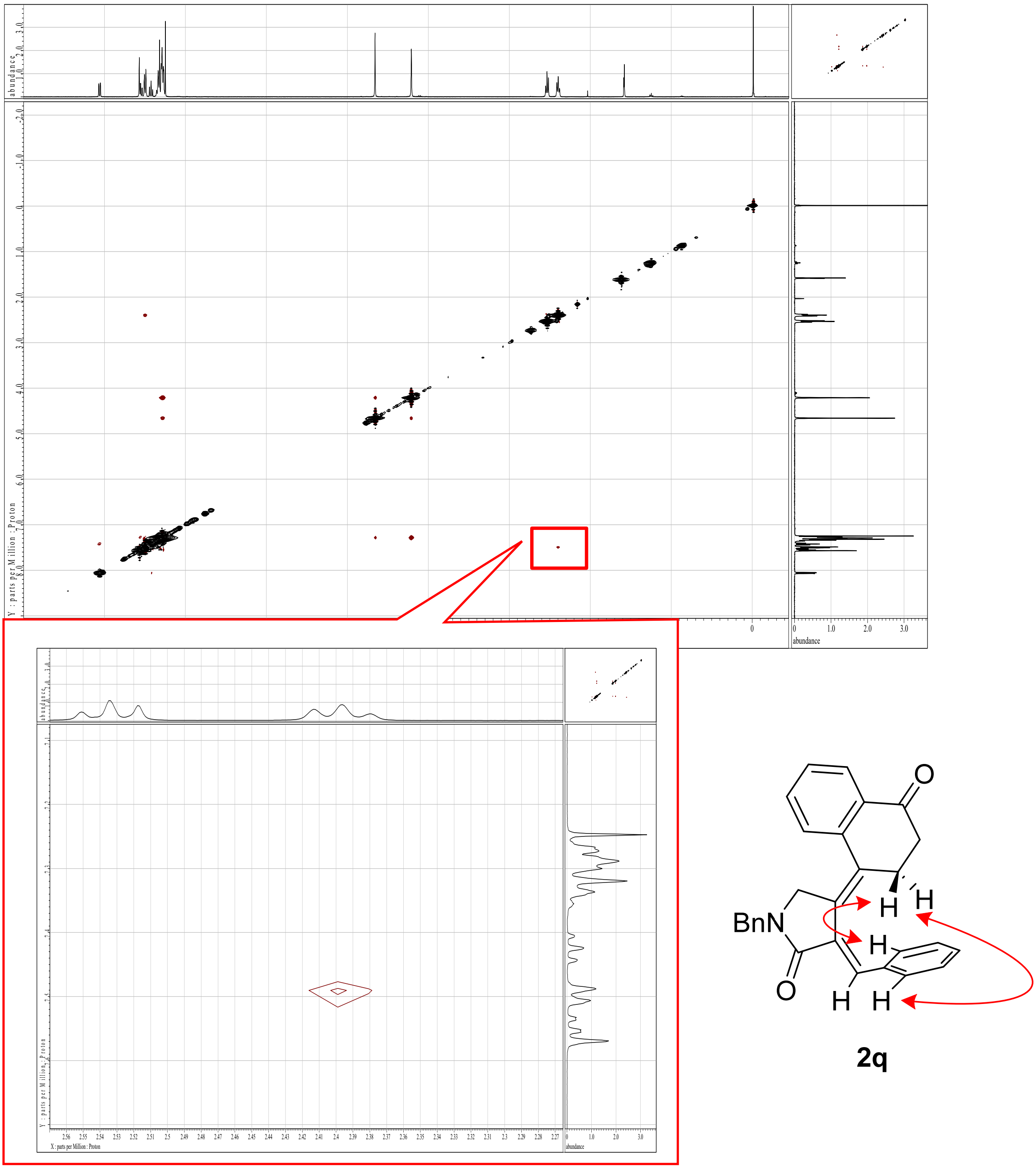


3s'

Analytical data for 3s': orange solid (mp 199.2–200.0 °C); ^{1}H-NMR (400 MHz, CDCl$_3$) δ 9.48 (dd, *J* = 7.1, 1.6 Hz, 1H), 7.54–7.47 (m, 2H), 7.40–7.36 (m, 2H), 7.30 (t, *J* = 2.3 Hz, 1H), 7.25–7.18 (m, 3H), 7.02–7.00 (m, 1H), 5.23 (d, *J* = 2.3 Hz, 2H), 1.89 (dd, *J* = 8.2, 6.0 Hz, 2H), 1.47 (dd, *J* = 8.2, 6.0 Hz, 2H); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 171.6, 166.8, 146.4, 137.7, 134.9, 131.9, 131.9, 129.0, 128.8, 128.4, 126.8, 121.7, 116.7, 100.5, 72.1, 69.9, 15.9; IR (KBr) 1732, 1570 cm^{-1}; HRMS (DART) *m/z* [M+ H]$^+$ calcd for $C_{21}H_{16}O_3$•H 317.1178, found 317.1167

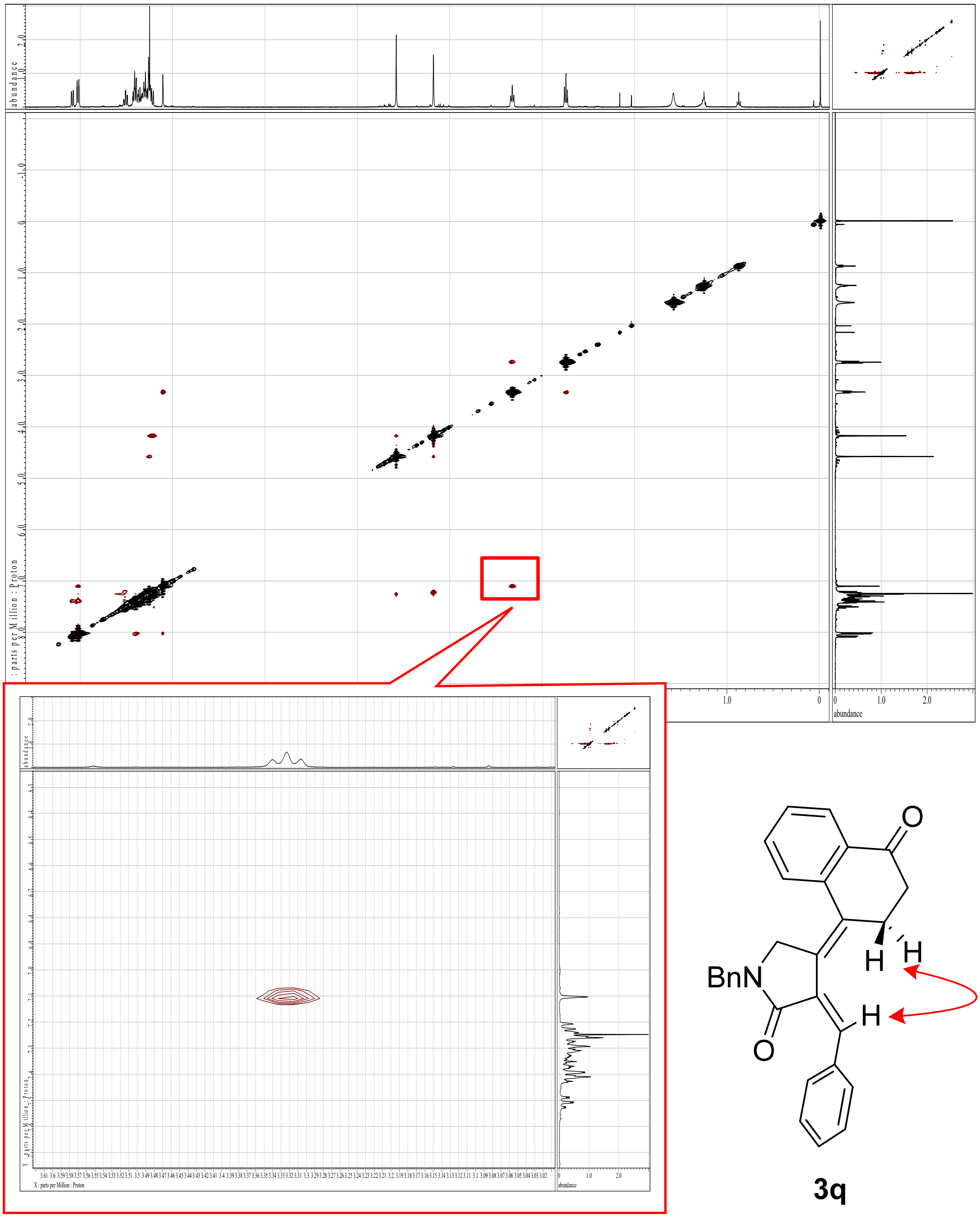
6. Determination of Structures of 2q, 3q, 3r, and 3s’

The structure of **2q** was assigned by NOESY experiments. The arrows shown below indicate the observed cross peaks.



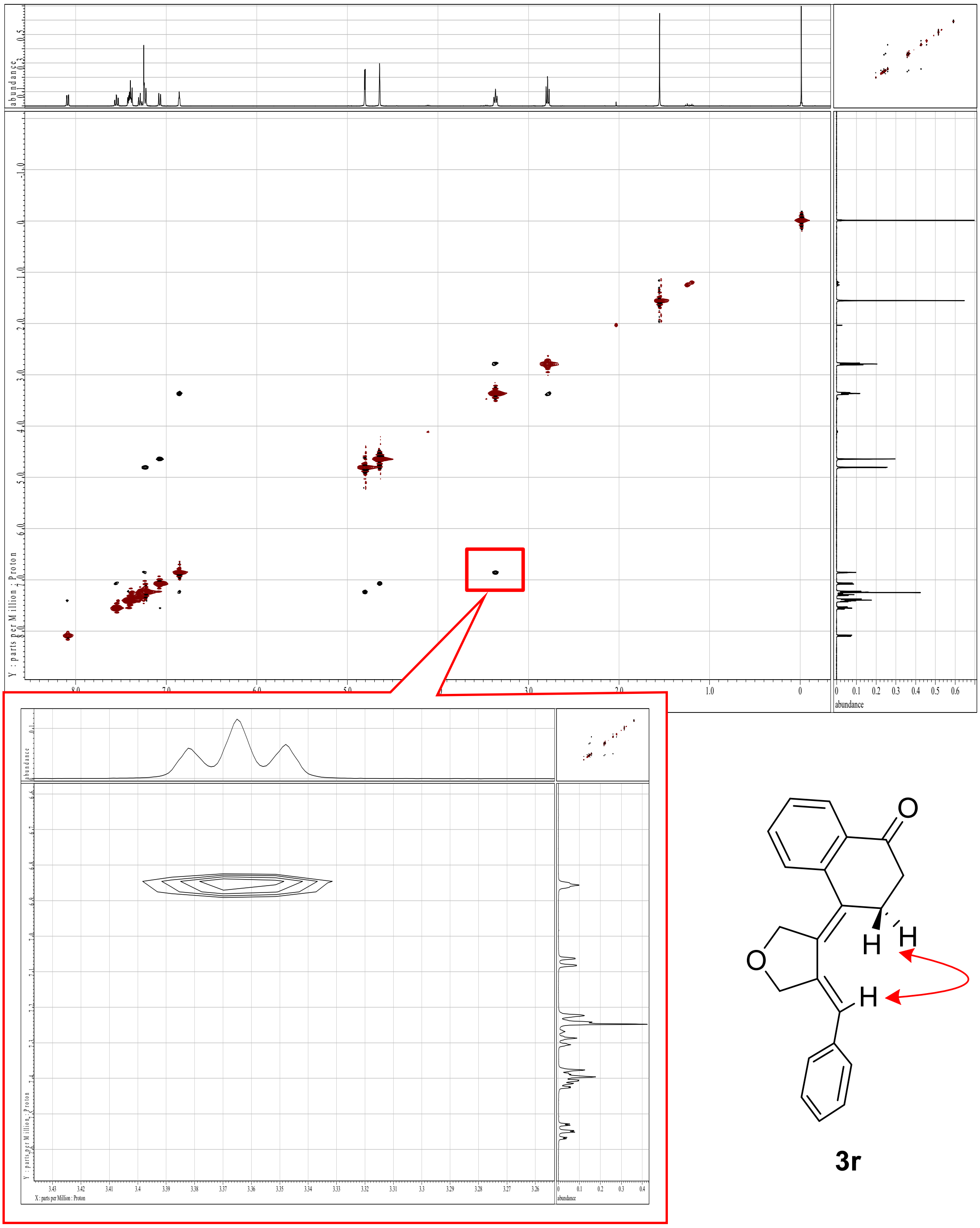
2q

The structure of **3q** was assigned by NOESY experiments. The arrow shown below indicate the observed cross peaks.



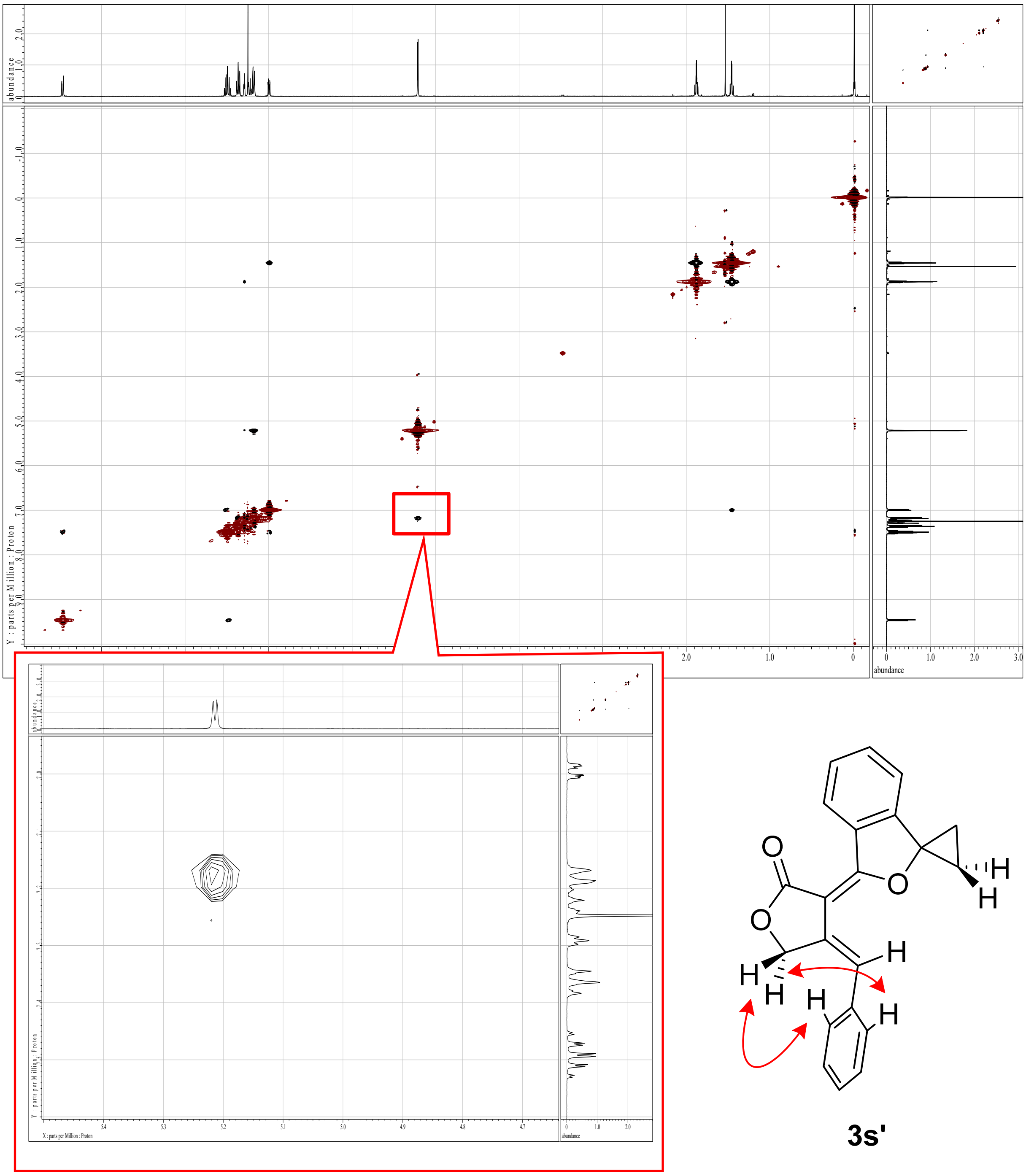
3q

The structure of **3r** was assigned by NOESY experiments. The arrow shown below indicate the observed cross peaks.



3r

The structure of **3s’** was assigned by NOESY experiments. The arrows shown below indicate the observed cross peaks.

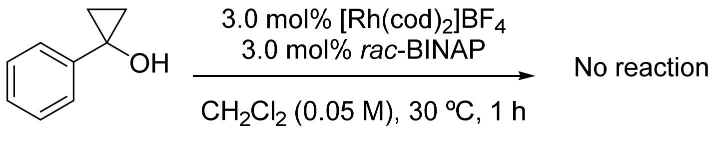


3s'

7. Control Experiments

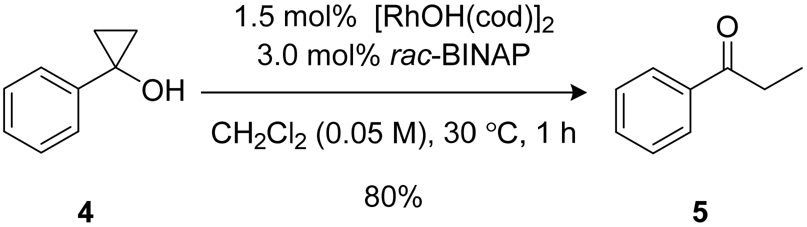
Ring-Opening Reaction of Phenylcyclopropanol 4

Phenylcyclopropanol **4** was prepared according to the previous report[19]. Characterization of **5** was identical to the previous reports[20].



4

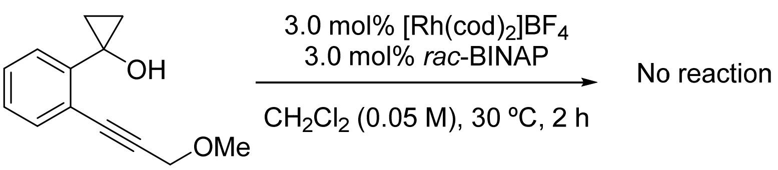
[Rh(cod)$_2$]BF$_4$ (1.21 mg, 0.00300 mmol) and *rac*-BINAP (1.88 mg, 0.00300 mmol) were dissolved in degassed DCM (1.0 mL) and the mixture was stirred at 30 °C for 10 min under Ar atmosphere. The reaction tube was evacuated and refilled with H_2 using a balloon, which was repeated 3 times. After stirring at 30 °C for 1 h under H_2 atmosphere, the reaction tube was evacuated and refilled with Ar using a balloon, which was repeated 3 times. To the resulting mixture was added a DCM (1.0 mL) solution of **4** (13.4 mg, 0.100 mmol). After stirring at 30 °C for 1 h, the resulting solution was concentrated *in vacuo*. The crude material was then purified by silica gel column chromatography (Hexane/EtOAc = 4:1) to recover starting material **4** (12.4 mg, RSM 92%).



4 **5**

[RhOH(cod)]$_2$ (1.21 mg, 0.00300 mmol), *rac*-BINAP (1.88 mg, 0.00300 mmol) and **4** (13.4 mg, 0.100 mmol) were dissolved in degassed DCM (2.0 mL). After stirring at 30 °C for 1 h, the resulting solution was concentrated *in vacuo*. The crude material was then purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to give **5** (10.6 mg, 80%).

Reaction of Alkyne substrate 6

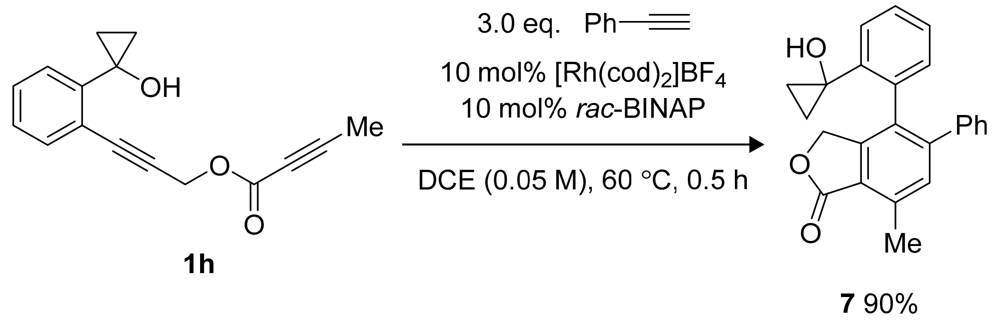


6

[Rh(cod)$_2$]BF$_4$ (1.21 mg, 0.00300 mmol) and *rac*-BINAP (1.88 mg, 0.00300 mmol) were dissolved in degassed DCM (1.0 mL) and the mixture was stirred at 30 °C for 10 min under Ar atmosphere. The reaction tube was evacuated and refilled with H_2 using a balloon, which was repeated 3 times. After stirring at 30 °C for 1 h under H_2 atmosphere, the reaction tube was evacuated and refilled with Ar using a balloon, which was repeated

3 times. To the resulting mixture was added a DCM (1.0 mL) solution of **6** (20.2 mg, 0.100 mmol). After stirring at 30 °C for 2 h, the resulting solution was concentrated. The crude was then purified by a silica gel column chromatography (Hexane/EtOAc = 10:1) to recover starting material **6**.

Rhodium-Catalyzed Cycloisomerization of 1h in the presence of Phenylacetylene

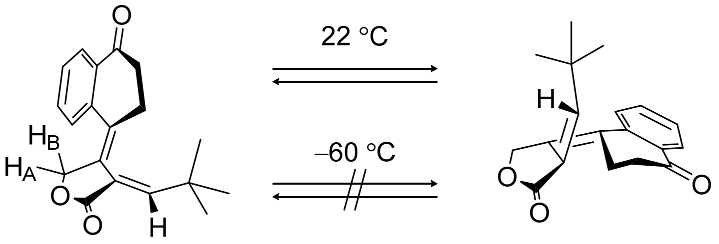


$[Rh(cod)_2]BF_4$ (4.07 mg, 0.0100 mmol) and *rac*-BINAP (6.23 mg, 0.0100 mmol) were dissolved in degassed DCE (1.0 mL) and the mixture was stirred at 30 °C for 10 min under Ar atmosphere. The reaction tube was evacuated and refilled with H_2 using a balloon, which was repeated 3 times. After stirring at 30 °C for 1 h under H_2 atmosphere, the reaction tube was evacuated and refilled with Ar using a balloon, which was repeated 3 times. To the resulting mixture was added a DCE (1.0 mL) solution of **1h** (31.6 mg, 0.100 mmol) and phenylacetylene (32.0 μL, 0.300 mmol). After stirring at 60 °C for 0.5 h, the resulting solution was concentrated *in vacuo*. The crude material was then purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to give **7** (32.2 mg, 90%). Recrystallization from hexane and EtOAc at rt afforded pure **7** as a colorless crystal.

Analytical data for 7: colorless crystal (mp 170.6–172.0 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.39-7.36 (m, 2H), 7.31-7.29 (m, 1H), 7.27-7.22 (m, 5H), 5.11 (d, *J* = 15.6 Hz, 1H), 4.74 (d, *J* = 15.6 Hz, 1H), 2.80 (s, 3H), 1.09 (s, 1H), 0.80-0.75 (m, 1H), 0.61-0.56 (m, 1H), 0.28-0.24 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 171.3, 147.4, 145.3, 139.5, 139.4, 135.2, 132.9, 132.3, 131.5, 130.8, 129.8, 128.7, 128.5, 128.1, 127.9, 122.5, 69.0, 56.3, 17.3, 15.1, 14.5; IR (KBr) 3464, 1720 cm^{-1}; HRMS (DART) *m/z* $[M+H]^+$ calcd for $C_{24}H_{20}O_3$•H 357.1491, found 357.1486

8. Variable-Temperature ^{1}H NMR Spectroscopy of 2j

Exocyclic dienes **2** have fluxional nature. Helical isomerization process (Figure S1) can be monitored by variable-temperature NMR study in CD_2Cl_2. The methylene protons (H_A and H_B) of **2j** are enantiotopic, appearing as a sharp singlet peak at 22 ºC (Figure S2). As the temperature decreases, the protons gradually appear as two doublets, and become diastereotopic below –60 ºC. This implies the two isomers are in rapid equilibrium at 22 ºC, but are distinguished each other below –60 ºC in the NMR time scale.



H_A, H_B: enantiotopic at 22 °C
diastereotopic at –60 °C

Figure S1 Helical isomerization of **2j**

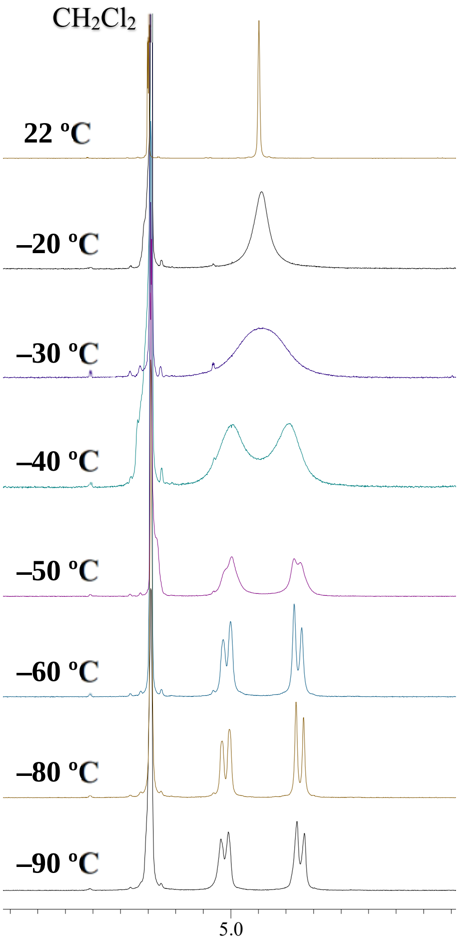


Figure S2 Variable-temperature ^{1}H NMR behavior of **2j** (only H_A and H_B shown)

9. X-Ray Diffraction Analysis of 2a

A single crystal of **2a** was mounted on a glass fiber, and diffraction data were collected in θ ranges specified in Table S4 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation ($\lambda = 1.54187$ Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S4. The supplementary crystallographic data for this paper (CCDC2007772) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

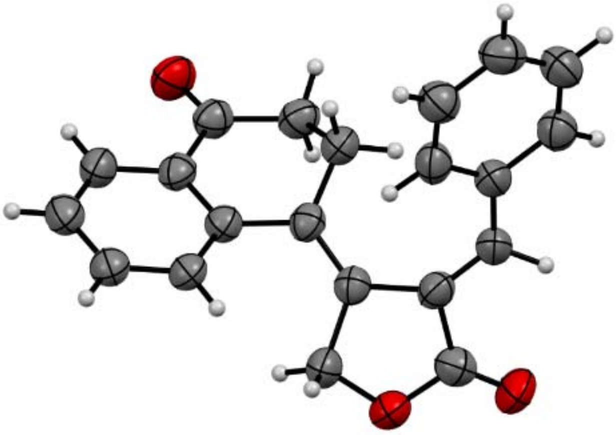


Figure S3 ORTEP plot of **2a**.

Table S4 Selected crystallographic data and collection parameters for **2a**.

formula	$C_{21}H_{16}O_3$	crystal size, mm	0.60 x 0.30 x 0.10
FW	316.36	maximum 2θ, deg	136.4
crystal system	orthorhombic	reflections collected	62519
space group	Pbca (#61)	independent reflections [*R*(int)]	5578 [*R*(int) = 0.1638]
a, Å	8.8744(6)	max. and min. transmission	0.929/0.601
b, Å	11.4021(7)	goodness-of-fit on F^2	1.069
c, Å	60.208(4)	R_1 [$I > 2\sigma(I)$]	0.1092
volume, Å^3	6092.2(7)	R, wR_2 (all data)	0.1600, 0.3326
Z	16	Weighting scheme	$R_1 = \Sigma \|\|Fo\| - \|Fc\|\| / \Sigma \|Fo\|$ $wR_2 = [\ \Sigma\ (w(Fo^2 - Fc^2)^2) / \Sigma\ w(Fo^2)^2\ ]^{1/2}$
D (calcd), Mg m^{-3}	1.380		
μ, cm^{-1}	7.395	largest diff. peak and hole, e Å^{-3}	0.61 and -0.61
F(000)	2656.00		

X-Ray Diffraction Analysis of 2e

A single crystal of **2e** was mounted on a glass fiber, and diffraction data were collected in θ ranges specified in Table S5 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation (λ = 1.54187 Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S5. The supplementary crystallographic data for this paper (CCDC2007776) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

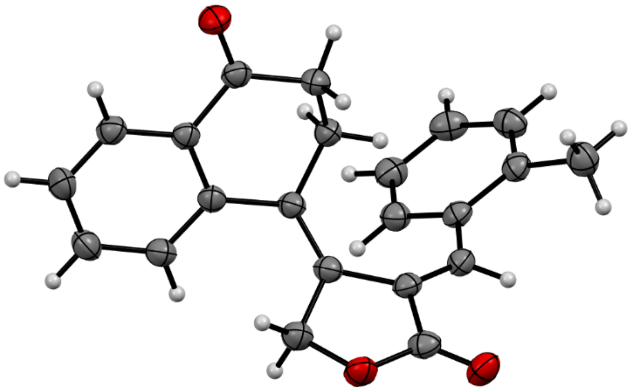


Figure S4 ORTEP plot of **2e**.

Table S5 Selected crystallographic data and collection parameters for **2e**.

formula	$C_{22}H_{18}O_3$	crystal size, mm	0.20 x 0.20 x 0.20
FW	330.38	maximum 2θ, deg	136.4
crystal system	monoclinic	reflections collected	17148
space group	$P2_1/c$ (#14)	independent reflections [R(int)]	3013 [R(int) = 0.1009]
a, Å	15.8736(5)	max. and min. transmission	0.406/0.868
b, Å	9.6592(3)	goodness-of-fit on F^2	1.268
c, Å	10.7426(3)	R_1 [$I > 2\sigma(I)$]	0.0773
volume, Å^3	1644.14(9)	R, wR_2 (all data)	0.1118, 0.3302
Z	4	Weighting scheme	$R_1 = \Sigma \|\|Fo\| - \|Fc\|\| / \Sigma \|Fo\|$ $wR_2 = [\Sigma (w(Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2}$
D (calcd), Mg m^{-3}	1.335		
μ, cm^{-1}	7.073	largest diff. peak and hole, e Å^{-3}	0.48 and -0.49
F(000)	696.00		

X-Ray Diffraction Analysis of 2j

A single crystal of **2j** was mounted on a glass fiber, and diffraction data were collected in θ ranges specified in Table S6 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation ($\lambda = 1.54187$ Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S6. The supplementary crystallographic data for this paper (CCDC2007773) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

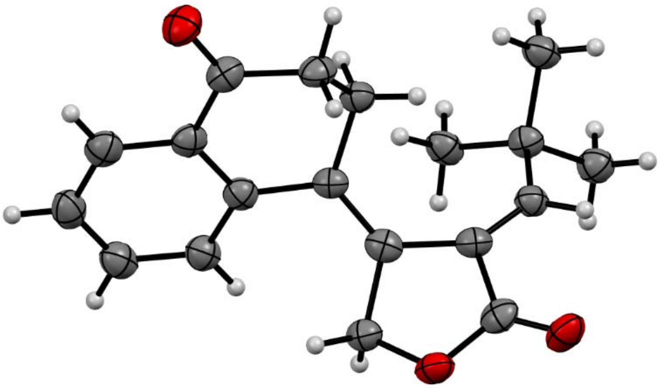


Figure S5 ORTEP plot of **2j**.

Table S6 Selected crystallographic data and collection parameters for **2j**.

formula	$C_{19}H_{20}O_3$	crystal size, mm	0.40 x 0.20 x 0.10
FW	296.37	maximum 2θ, deg	136.4
crystal system	monoclinic	reflections collected	8864
space group	$P2_1$ (#4)	independent reflections [*R*(int)]	2669 [*R*(int) = 0.0605]
a, Å	8.6683(12)	max. and min. transmission	0.934/0.694
b, Å	8.3860(10)	goodness-of-fit on F^2	1.174
c, Å	11.3586(14)	R_1 [$I > 2\sigma(I)$]	0.0386
β, deg	110.379(8)	R, wR_2 (all data)	0.0586, 0.1248
volume, $Å^3$	774.01(18)	Weighting scheme	$R_1 = \Sigma \|\|Fo\| - \|Fc\|\| / \Sigma \|Fo\|$
Z	2		$wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2}$
D (calcd), Mg m^{-3}	1.272	largest diff. peak and hole, e $Å^{-3}$	0.23 and -0.24
μ, cm^{-1}	6.818	flack parameter	-0.06(13)
F(000)	316.00		

X-Ray Diffraction Analysis of 3s

A single crystal of **3o** was mounted on a glass fiber, and diffraction data were collected in θ ranges specified in Table S7 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation (λ = 1.54187 Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S7. The supplementary crystallographic data for this paper (CCDC2007774) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

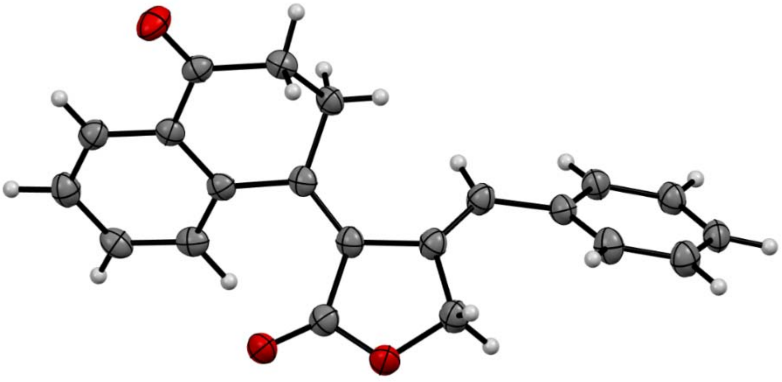


Figure S6 ORTEP plot of **3s**.

Table S7 Selected crystallographic data and collection parameters for **3s**.

formula	$C_{21}H_{16}O_3$	crystal size, mm	0.20 x 0.20 x 0.10
FW	316.36	maximum 2θ, deg	136.4
crystal system	monoclinic	reflections collected	8943
space group	$P2_1$ (#4)	independent reflections [*R*(int)]	2701 [*R*(int) = 0.0352]
a, Å	9.6092(3)	max. and min. transmission	0.929/0.734
b, Å	8.1201(3)	goodness-of-fit on F^2	1.076
c, Å	10.9799(4)	R_1 [$I > 2\sigma(I)$]	0.0317
β, deg	116.4260(18)	R, wR_2 (all data)	0.0333, 0.0822
volume, Å^3	767.22(4)	Weighting scheme	$R_1 = \Sigma \lvert\lvert Fo\rvert - \lvert Fc\rvert\rvert / \Sigma \lvert Fo\rvert$
Z	2		$wR_2 = [\Sigma (w(Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2}$
D (calcd), Mg m^{-3}	1.369	largest diff. peak and hole, e Å^{-3}	0.19 and -0.21
μ, cm^{-1}	7.340	flack parameter	0.05(8)
F(000)	332.00		

X-Ray Diffraction Analysis of 7

A single crystal of **7** was mounted on a glass fiber, and diffraction data were collected in θ ranges specified in Table S8 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation (λ = 1.54187 Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S8. The supplementary crystallographic data for this paper (CCDC2007775) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

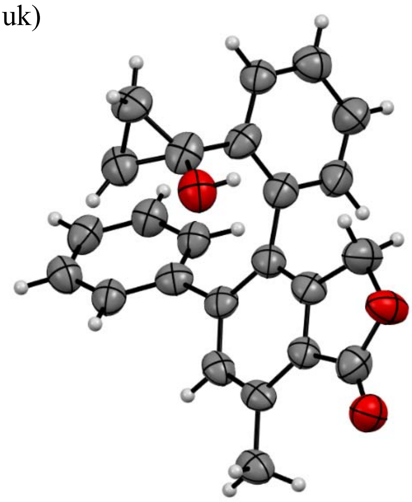


Figure S7 ORTEP plot of **7**.

Table S8 Selected crystallographic data and collection parameters for **7**.

formula	$C_{24}H_{20}O_3$	crystal size, mm	0.70 x 0.10 x 0.10
FW	356.42	maximum 2θ, deg	136.5
crystal system	monoclinic	reflections collected	19341
space group	$P2_1/n$ (#14)	independent reflections [R(int)]	3332 [R(int) = 0.1118]
a, Å	13.0170(6)	max. and min. transmission	0.934/0.433
b, Å	10.8103(5)	goodness-of-fit on F^2	0.881
c, Å	13.8173(6)	R_1 [$I > 2\sigma(I)$]	0.1038
β, deg	110.376(2)	R, wR_2 (all data)	0.1887, 0.3372
volume, Å^3	1822.68(15)	Weighting scheme	$R_1 = \Sigma \|\|Fo\| - \|Fc\|\| / \Sigma \|Fo\|$
Z	4		$wR_2 = [\Sigma (w(Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2}$
D (calcd), Mg m^{-3}	1.299	largest diff. peak and hole, e Å^{-3}	0.33 and -0.44
μ, cm^{-1}	6.777		
F(000)	752.00		

10. DFT Calculations

The Gaussian 16 program package was used for all calculations.[21] The geometries of the stationary points and transition states were fully optimized using the Becke's three-parameter hybrid density functional method (B3LYP),[22] with a [3*s*3*p*2*d*] contracted-valence basis set with the relativistic effective core potential of Hay and Wadt (LanL2DZ)[23] for Rh, and the 6-31G(d)[24] basis sets for other elements. The vibrational frequencies and the thermal correction to Gibbs free energy (TCGFE) including the zero-point energy were calculated at the same level of theory. The obtained structures were characterized by the number of imaginary frequencies (one or zero for the transition and ground states, respectively). The connectivity of each step was also confirmed using intrinsic reaction coordinate (IRC)[25] calculation from the transition states, followed by optimization of the resultant geometries. Single-point energies for geometries obtained using the above method were calculated at the same level of theory using a [6*s*5*p*3*d*] contracted-valence basis set with the Stuttgart-Dresden-Bonn energy-consistent pseudopotential (SDD)[26] for Rh, and the 6-311++G(d,p) basis sets[27] for other elements. The D3 version of Grimme's dispersion with Becke-Johnson damping[28] was used for empirical dispersion correction. To examine the solvent effect, the above single-point energy calculations were performed using the SMD model[29] with CH_2Cl_2 as the solvent. CYLview (Ver. 1.0b)[30] was used for the visualization of the optimized structures.

Table S9. Summary of theoretical calculations.

Model	TCGFE/au	SMD Energy/au	IF/cm^{-1}
A	0.834094	–3525.768839	
TS$_{AB}$	0.839935	–3525.770357	196.3824i
B	0.842284	–3525.820307	
TS$_{BC}$	0.843373	–3525.804259	139.3597i
C	0.846548	–3525.837278	
TS$_{CD}$	0.845812	–3525.804187	196.3342i
D	0.848022	–3525.838747	
TS$_{DE}$	0.847489	–3525.812232	414.6393i
E	0.841963	–3525.853145	
F	0.842689	–3525.864414	
G	0.845008	–3525.874465	
H	0.841103	–3525.893471	
TS$_{HI}$	0.839893	–3525.880753	713.8393i
I	0.846142	–3525.918818	
J	0.867360	–3602.346015	
TSJK	0.863551	–3602.300901	1196.9188i
K	0.866285	–3602.388430	

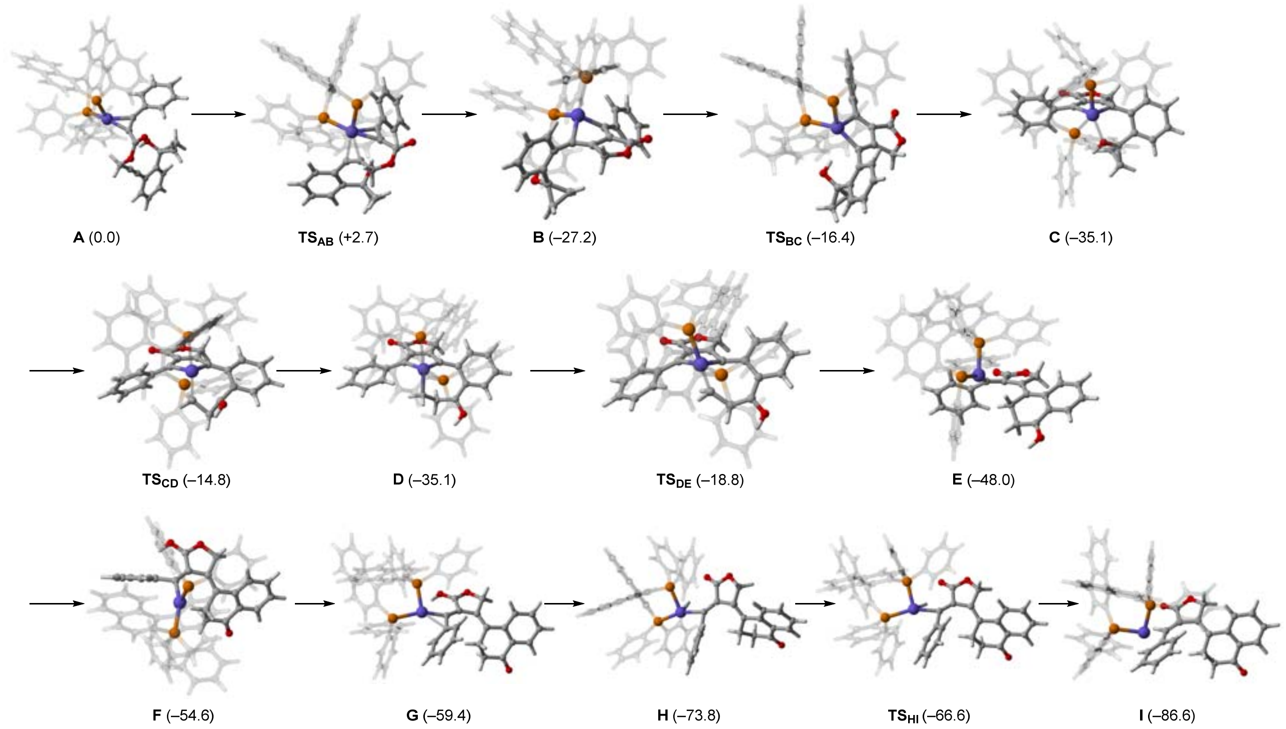
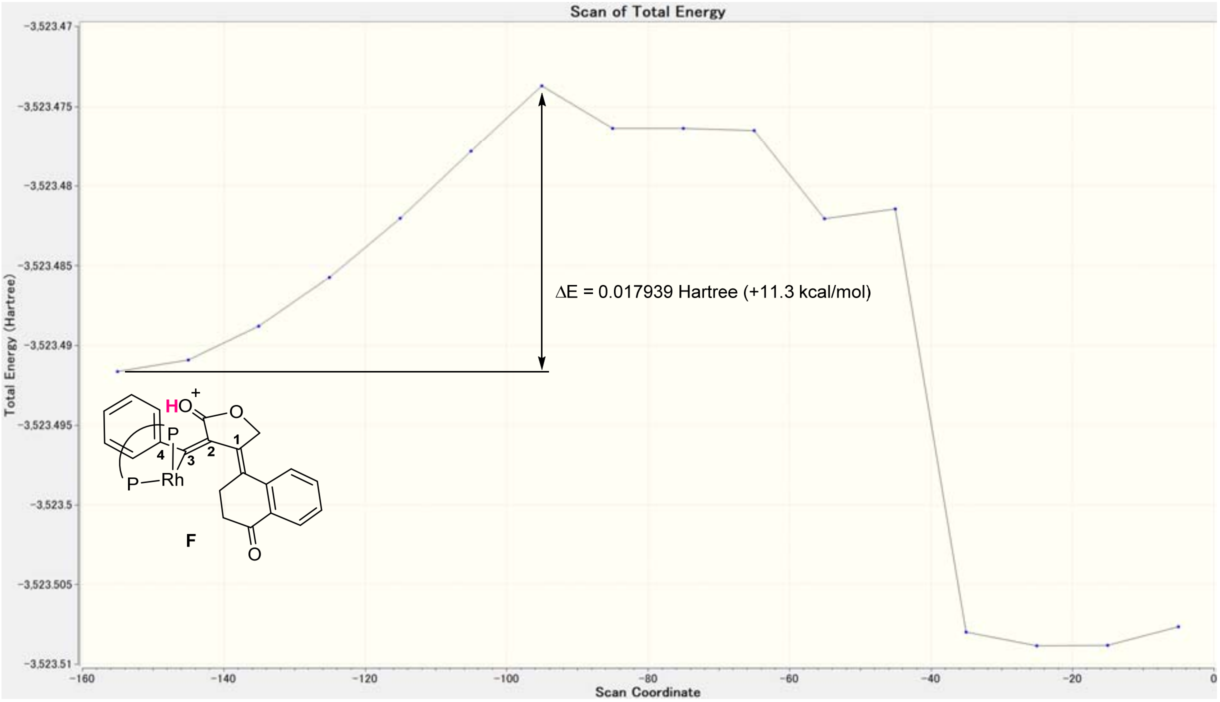
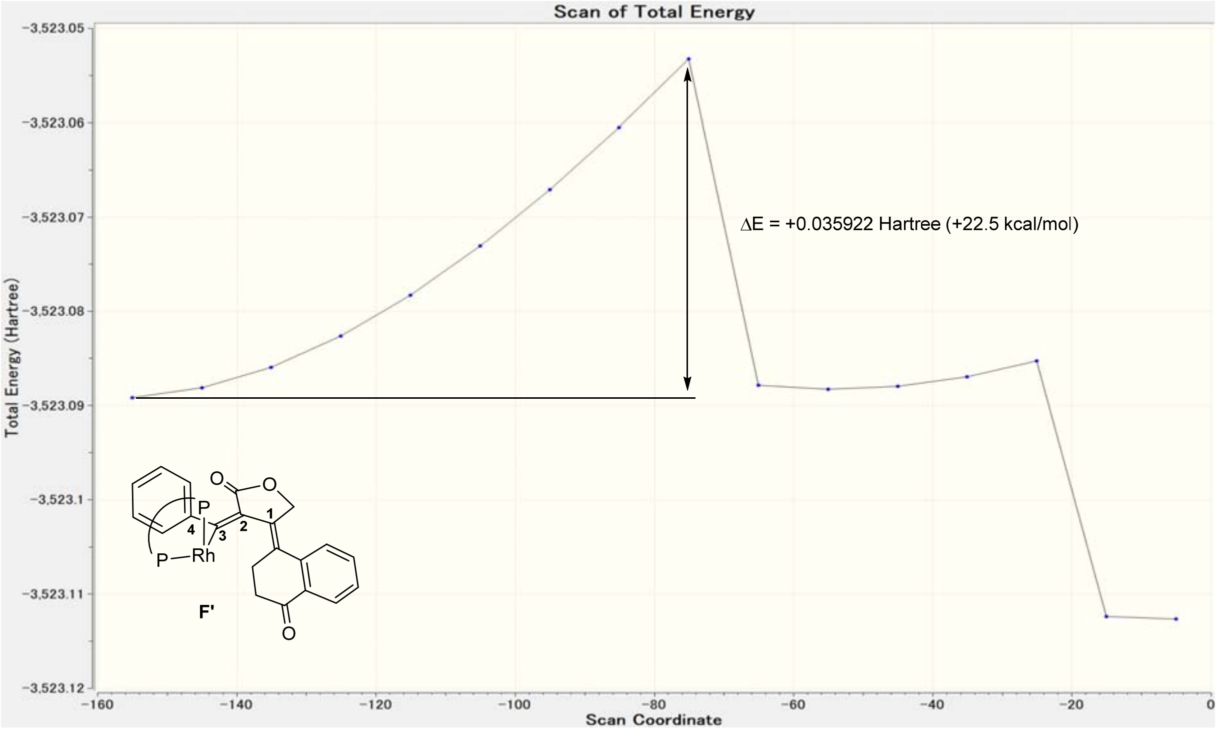


Figure S8. The overall process of the Rh-BINAP complex-catalyzed cycloisomerization reaction of **1a** with CYLview drawings.



∠C1-C2-C3-C4 (º)

Figure S9. Energy-scan profile for the bond-rotation step (the *E*/*Z* isomerization process; **F→G**).



∠C1-C2-C3-C4 (º)

Figure S10. Energy-scan profile for the bond-rotation step without protonation.

We conducted a DFT calculation for the protodemetalation of complex **F** without *E*/*Z* isomerization. However, this process seemed to be difficult due to the long distance between the rhodium center and proton on the lactone carbonyl group. Therefore, we conducted the calculation with a water molecule as a proton-transfer agent (Figure S11). The result elucidated that the water-assisted protodemetalation (**J**→**K**) proceeds via **TS$_{JK}$** with a barrier of 25.9 kcal/mol, indicating that this process is energetically unfavorable compared to the process (**F**→**I**) shown in Fig 1.

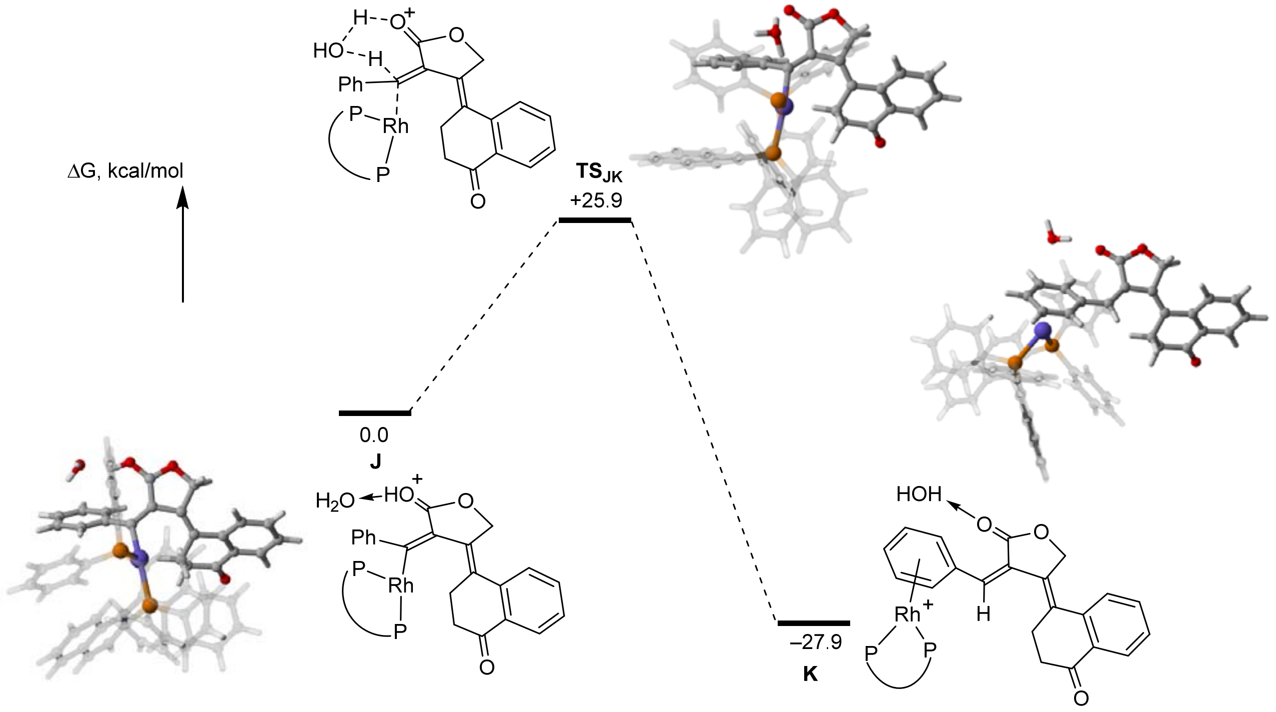


Figure S11. Gibbs free energy diagram for water-assisted protodemetalation without *E*/*Z* isomerization [SMD (CH_2Cl_2) B3LYP(GD3BJ)/6-311G++(d,p)-SDD//B3LYP/6-31G(d)-LanL2DZ].

To elucidate the effect of an amide tether moiety in the reaction of **1q**, we conducted energy-scan for the *E*/*Z*-isomerization of an amide-tethered 1,6-diyne substrate (Figure S12). Interestingly, the result suggests that the bond rotation proceeds via metallacyclopropene intermediate **M**. This intermediate **M** is generated from intermediate **L** with a barrier of 17.3 kcal/mol, which is 6 kcal/mol higher in energy compared to the case of ester-tethered 1,6-diyne substrate (11.3 kcal/mol). This result is consistent with the experimental result. Intermediate **M** successively evolves to **N** with a barrier of 15.0 kcal/mol.

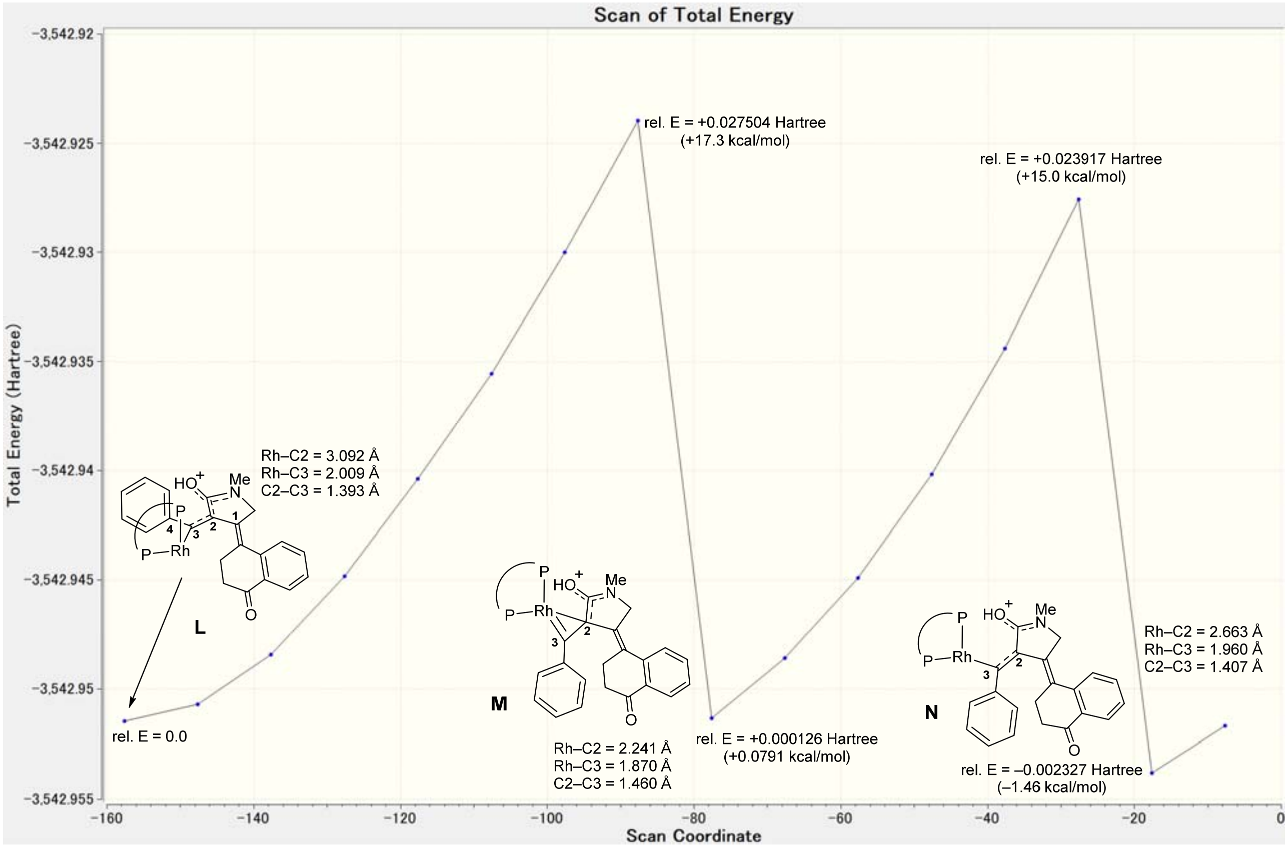


Figure S12. Energy-scan profile for the bond-rotation step in the reaction of an amide-tethered 1,6-diyne substrate.

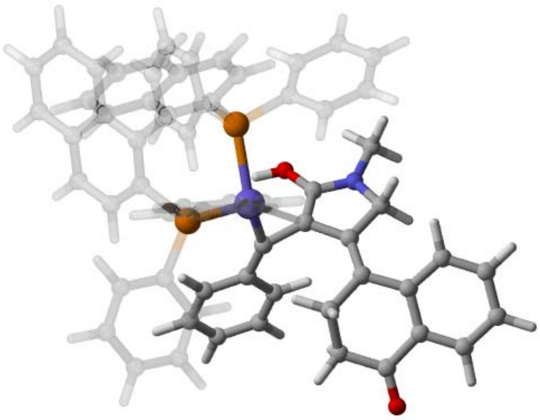


Figure S13. Structure of metallacyclopropene intermediate **M**.

11. References

(1) R. Usón, L. A. Oro, J. A. Cabeza, *Inorg. Synth.* **1985**, *23*, 126.

(2) A. Mercier, W. C. Yeo, J. Chou, P. D. Chaudhuri, G. Bernardinelli, E. P. Kündig, *Chem. Commun.* **2009**, 5227.

(3) D. Yang, Y. Long, J. Zhang, H. Zeng, S. Wang, C. Li, *Organometallics* **2010**, *29*, 3477.

(4) H. Qiu, Y. Inoue, S. Che, *Angew. Chem. Int. Ed.* **2009**, *48*, 3069-3072.

(5) H. S. Oskooie, M. M. Heravi, F. K. Behbahani, *Molecules* **2007**, *12*, 1438.

(6) L. Zheng, B. Zhou, H. Jin, T. Li, Y. Liu, *Org. Lett.* **2018**, *20*, 7053.

(7) P. Cazeau, F. Duboudin, F. Moulines, O. Babot, J. Dunogues, *Tetrahedron* **1987**, *43*, 2075.

(8) Z. Lou, S. Zhang, C. Chen, X. Pang, M.Li, L. Wen, *Adv. Synth. Catal.* **2014**, *356*, 153.

(9) Q. Feng, K. Yanga, Q. Song, *Chem. Commun.* **2015**, *51*, 15394.

(10) L. Yang, H. Li, Y. Du, K. Cheng, C. Qi, *Adv. Synth. Catal.* **2019**, *361*, 5030.

(11) A. Verma, R. J. Grams, B. P. Rastatter, W. L. Santo, *Tetrahedron*, **2019**, *75*, 2113.

(12) S. Gupta, Y. Lin, Y. Xia, D. J. Winka, D. Lee, *Chem. Sci.* **2019**, *10*, 2212.

(13) W. A. Chalifoux, M. J. Ferguson, R. McDonald, F. Melin, L. Echegoven, R. R. Tykwinski, *J. Phys. Org. Chem.* **2012**, *25*, 69.

(14) N. Ando, A. Fukazawa, T. Kushida, Y. Shiota, S. Itoyama, K. Yoshizawa, Y. Matsui, Y. Kuramoto, H. Ikeda, S. Yamaguchi, *Angew. Chem. Int. Ed.* 2017, *56*, 12210.

(15) P. Dallemagne, L. P. Khanh, A. Alsaïdi, O. Renault, I. Varlet, V. Collot, R. Bureau, S. Rault, *Bioorg. Med. Chem.* 2002, *10*, 2185.

(16) X. Hu, Y. Dong, G. Liu, *Mol. Divers.* 2015, *19*, 695.

(17) Z. Wu, D. Ma, B. Zhou, X. Ji, X. Ma, X. Wang, Y. Zhang, *Angew. Chem. Int. Ed.* 2017, *56*, 12288.

(18) J. Cao, K. Sun, S. Dong, T. Lu, Y. Dong, D. Du, *Org. Lett.* 2017, *19*, 6724.

(19) J. C. Lorenz, J. Long, Z. Yang, S. Xue, Y. Xie, Y. Shi, *J. Org. Chem.* 2004, *69*, 327.

(20) C. -B. Bo, Q. Bu, X. Li, G. Ma, D. Wei, C. Guo, B. Dai, N. Liu, *J. Org. Chem.* 2020, *85*, 4324.

(21) Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

(22) (a) W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **1996**, *100*, 12974-12980. (b) P. J. Stephen, F. J. Devlin, C. F. Chabalowski, M. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623-11627. (c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652. (d) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.

(23) (a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.

(24) (a) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257-2261. (b) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213-222. (c) M. M. Fracl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654-3665.

(25) (a) K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363-368. (b) C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.* **1989**, *90*, 2154-2161. (c) C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523-5527.

(26) D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, *77*, 123-141.

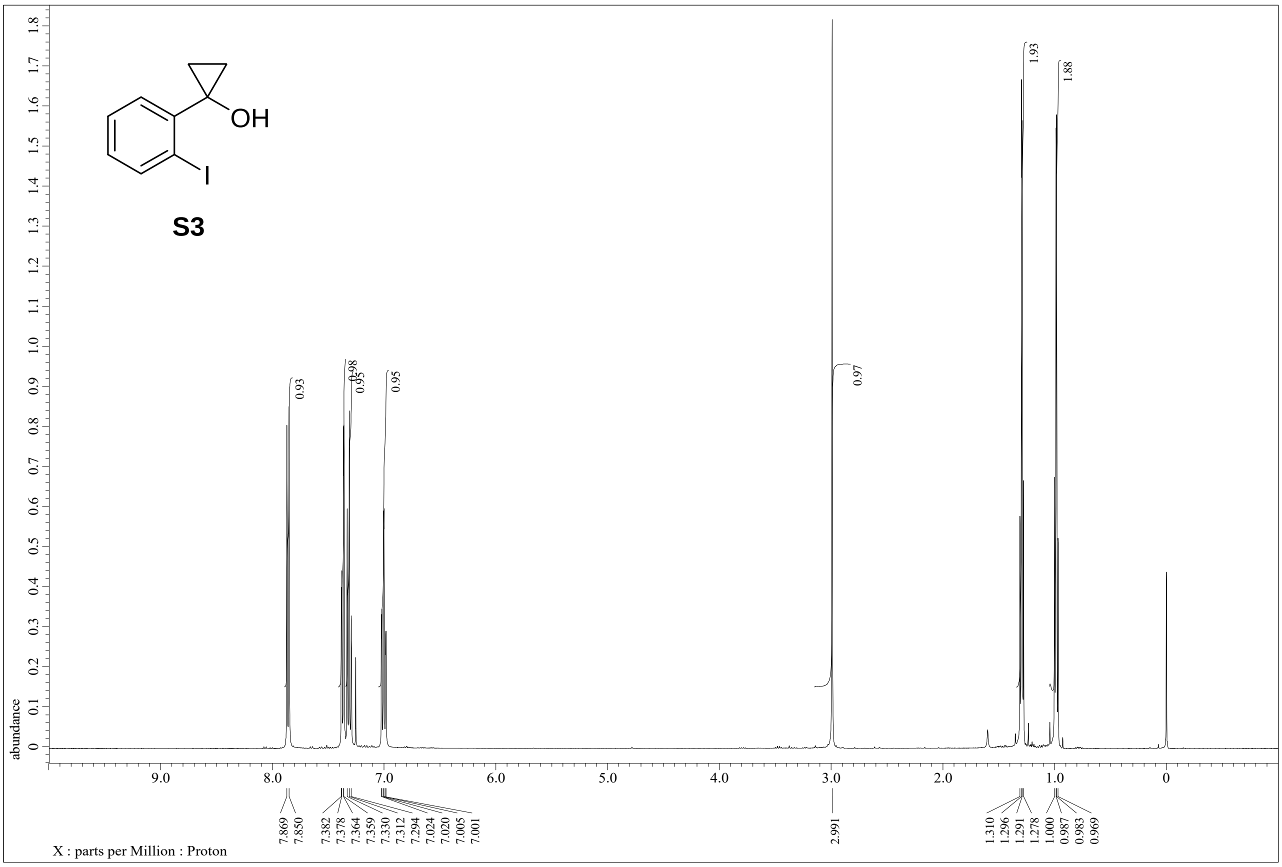
(27) (a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650-654. (b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639-5648. (c) M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265-3269. (d) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comp. Chem.* **1983**, *4*, 294-301.

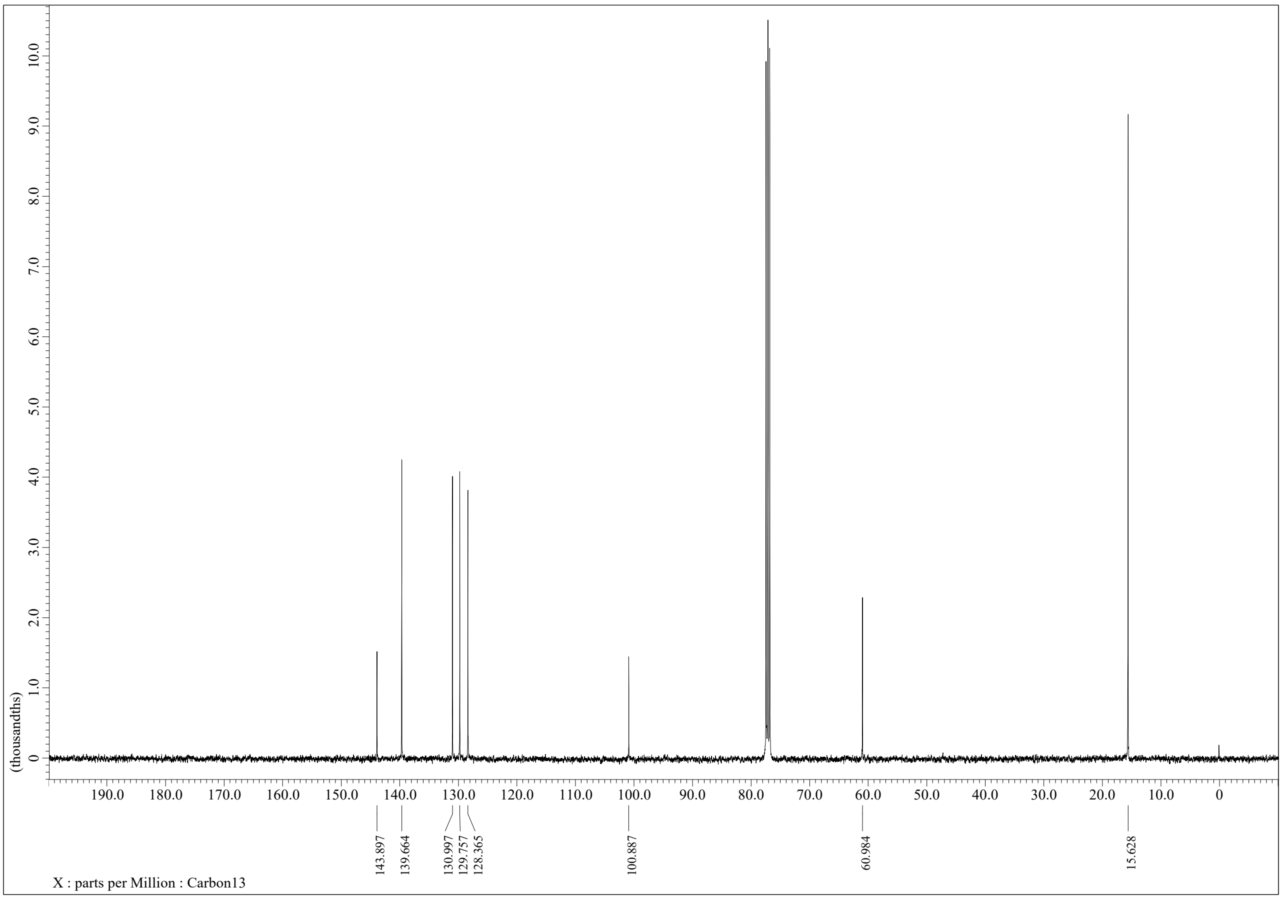
(28) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* **2011**, *32*, 1456-1465.

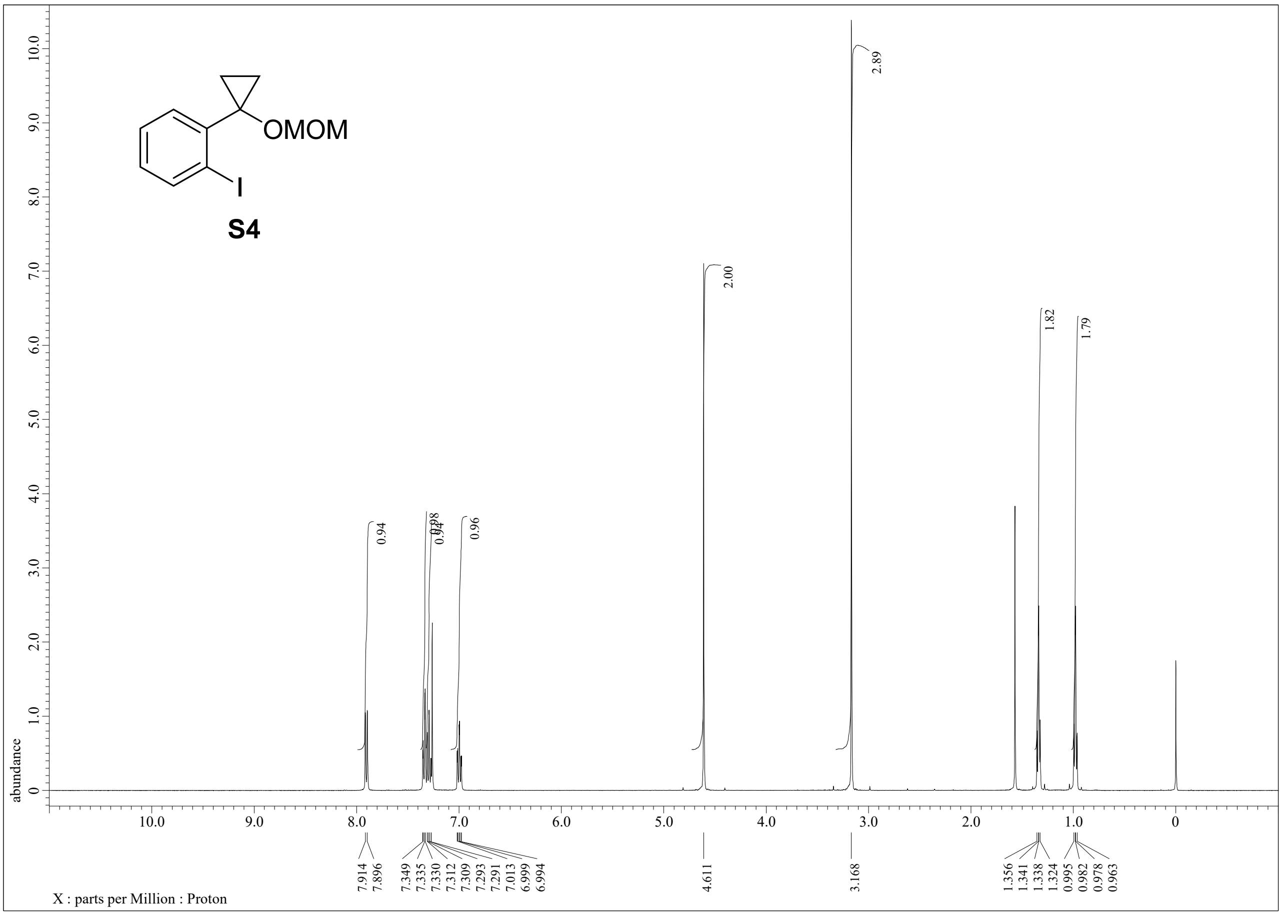
(29) V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

(30) CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).

12. NMR Spectra



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6.0
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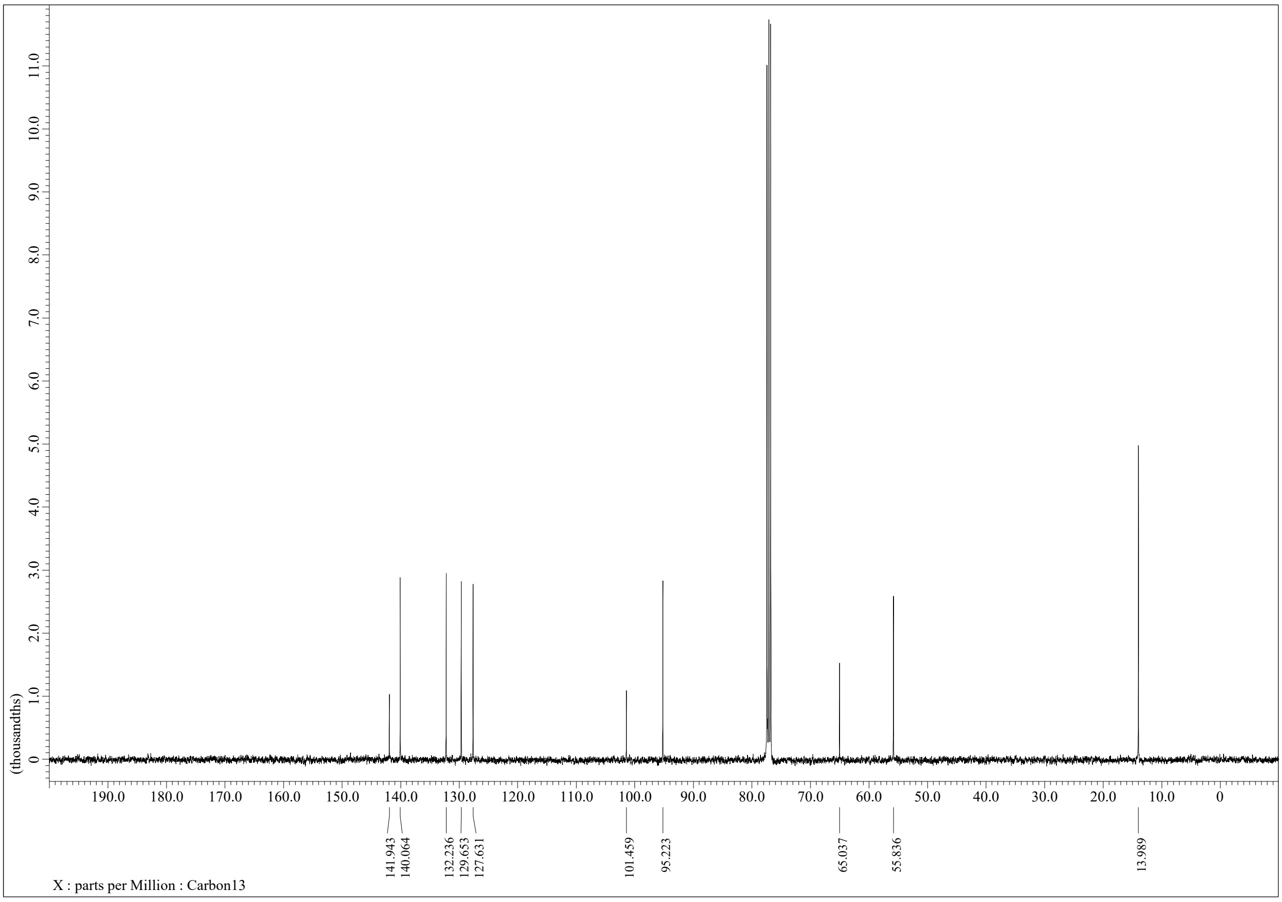
4.0
3.0
2.0
1.0
0
0.94
0.98
0.94
0.96
2.00
2.89
1.82
1.79
7.914
7.896
7.349
7.335
7.330
7.312
7.309
7.293
7.291
7.013
6.999
6.994
4.611
3.168
1.356
1.341
1.338
1.324
0.995
0.982
0.978
0.963
X : parts per Million : Proton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10.0
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8.0
7.0
6.0
5.0
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3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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140.064
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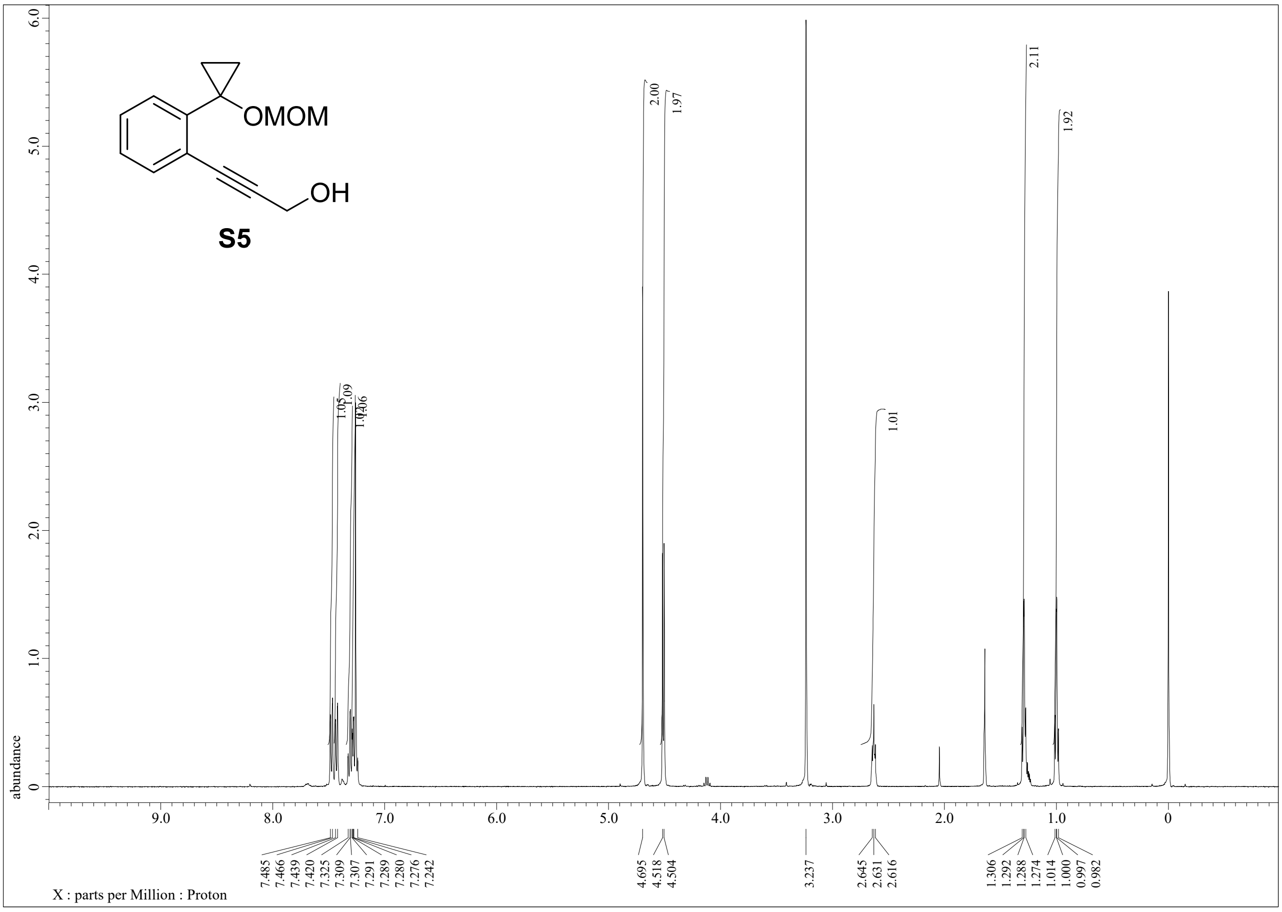
129.653
127.631
101.459
95.223
65.037
55.836
13.989
X : parts per Million : Carbon13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0
9.0
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton
1.05
1.09
1.02
1.06
2.00
1.97
1.01
2.11
1.92
7.485
7.466
7.439
7.420
7.325
7.309
7.307
7.291
7.289
7.280
7.276
7.242
4.695
4.518
4.504
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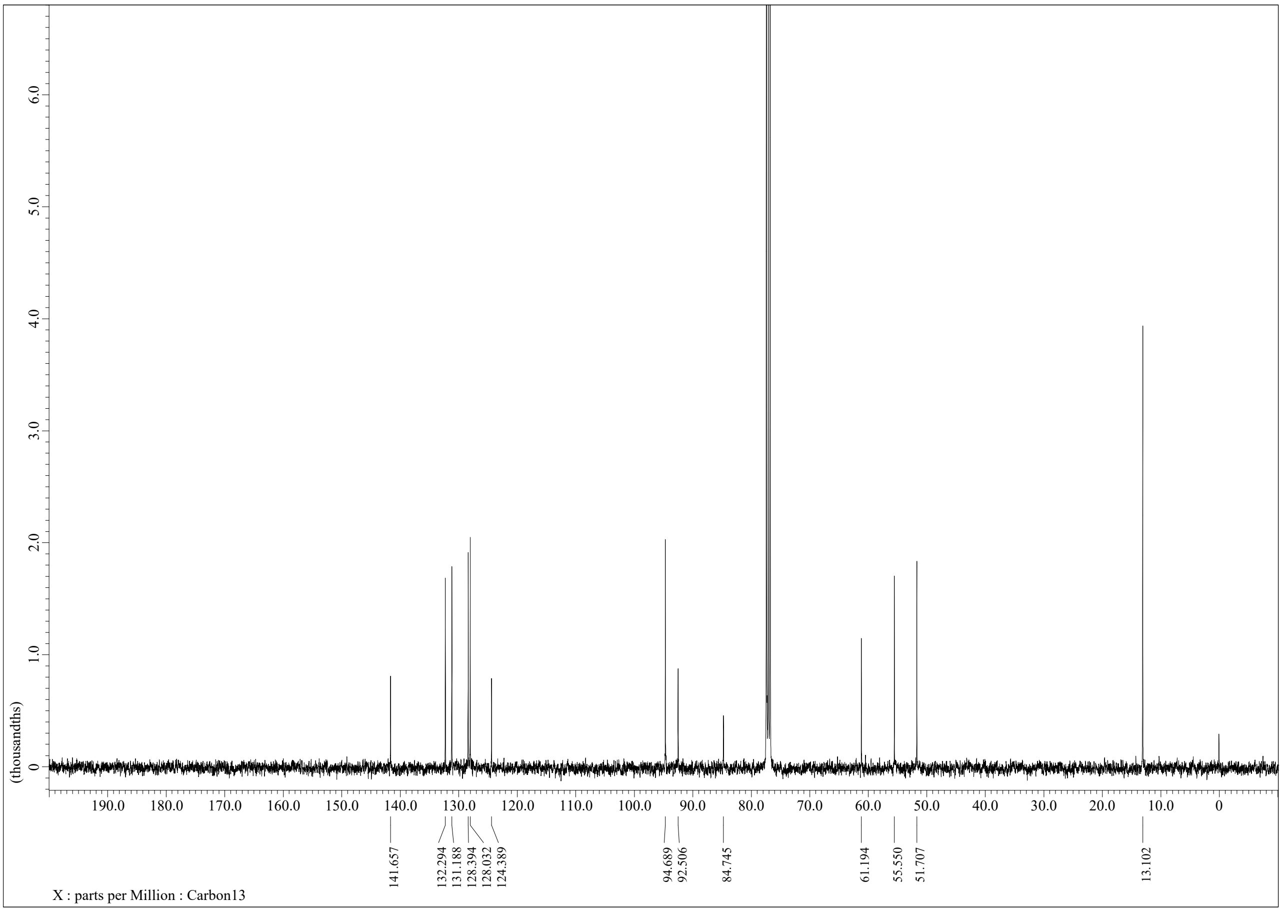
0.997
0.982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1.0
0
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180.0
170.0
160.0
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13
141.657
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128.394
128.032
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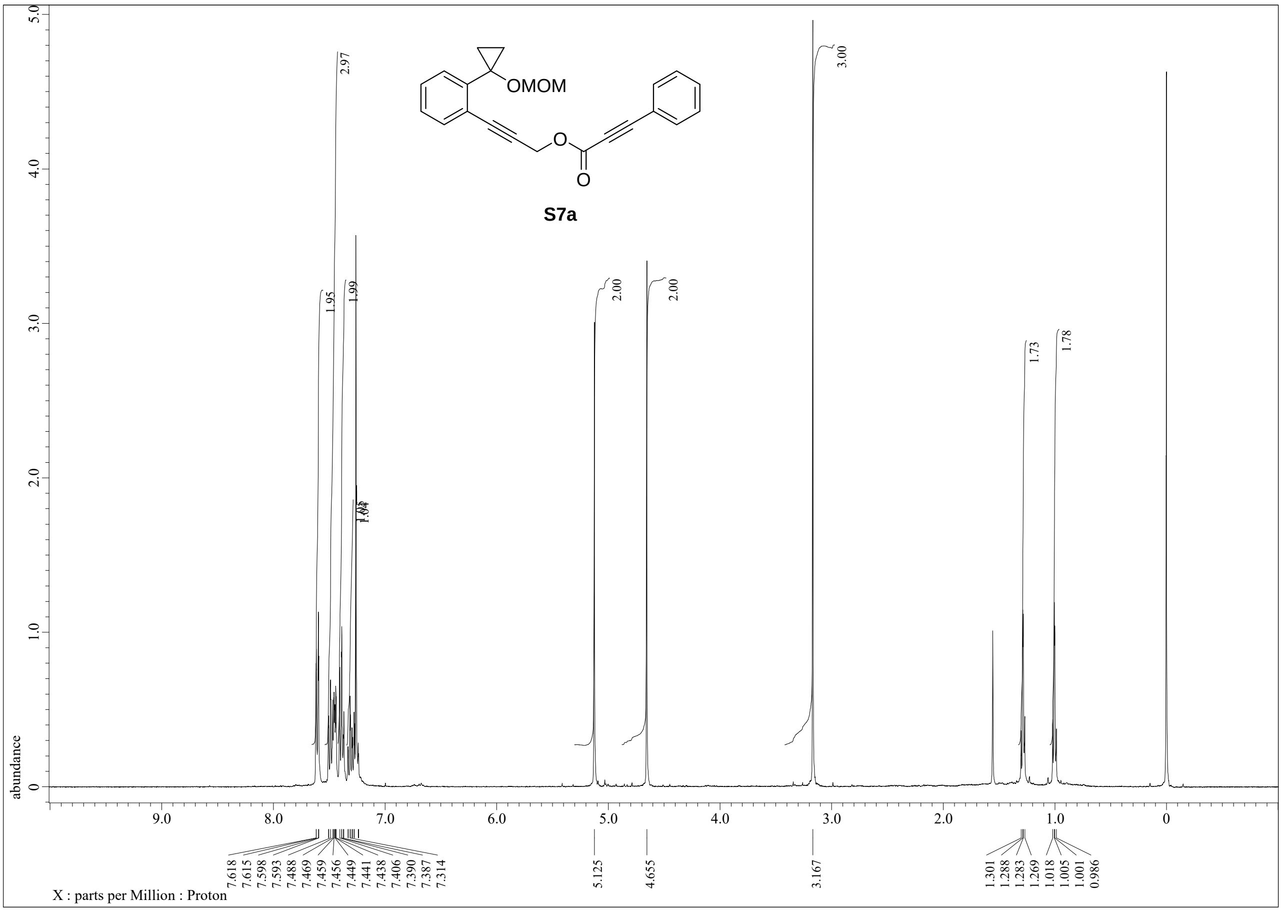
84.745
61.194
55.550
51.707
13.102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1.99
1.04
1.04
2.00
2.00
3.00
1.73
1.78
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.618
7.615
7.598
7.593
7.488
7.469
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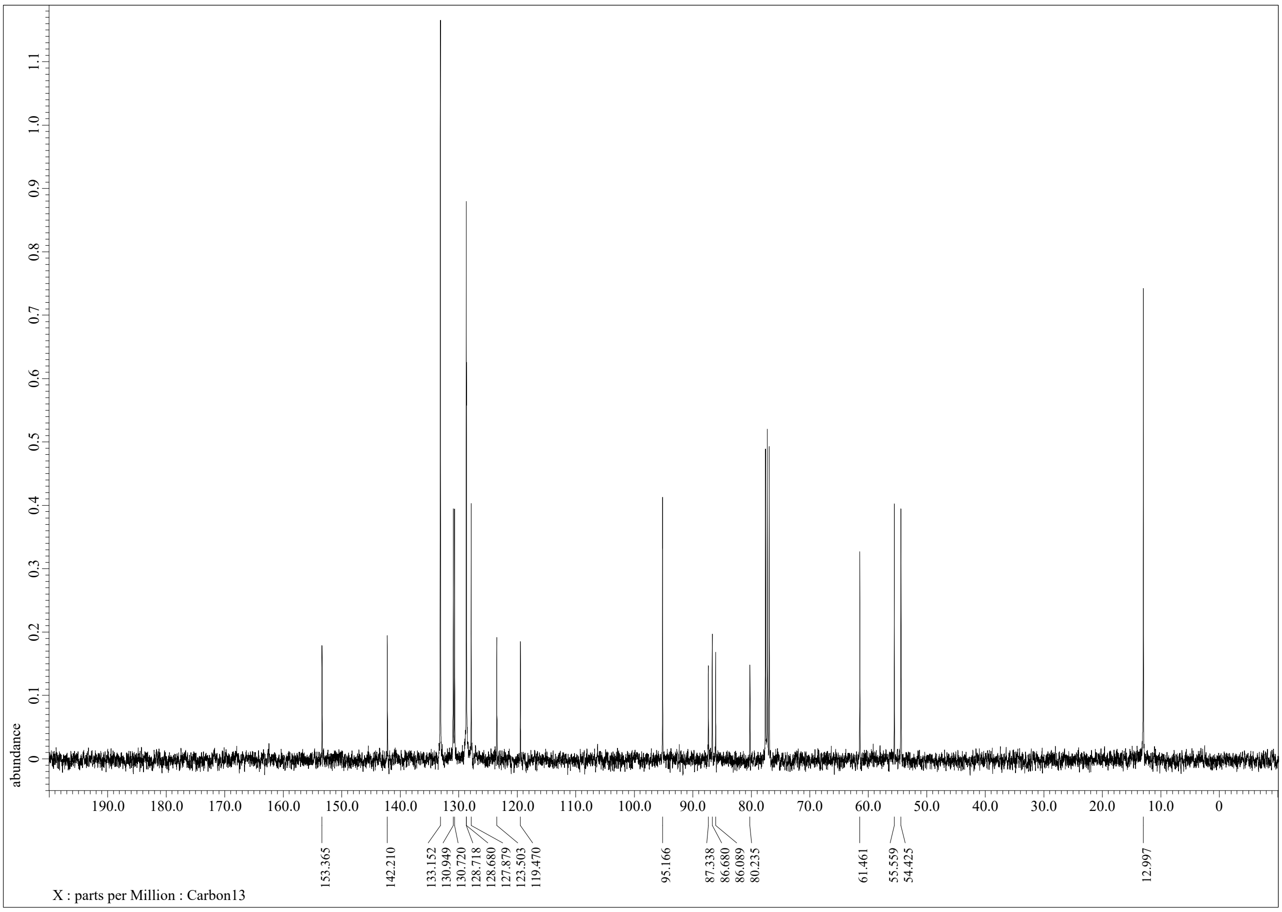
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0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.365
142.210
133.152
130.949
130.720
128.718
128.680
127.879
123.503
119.470
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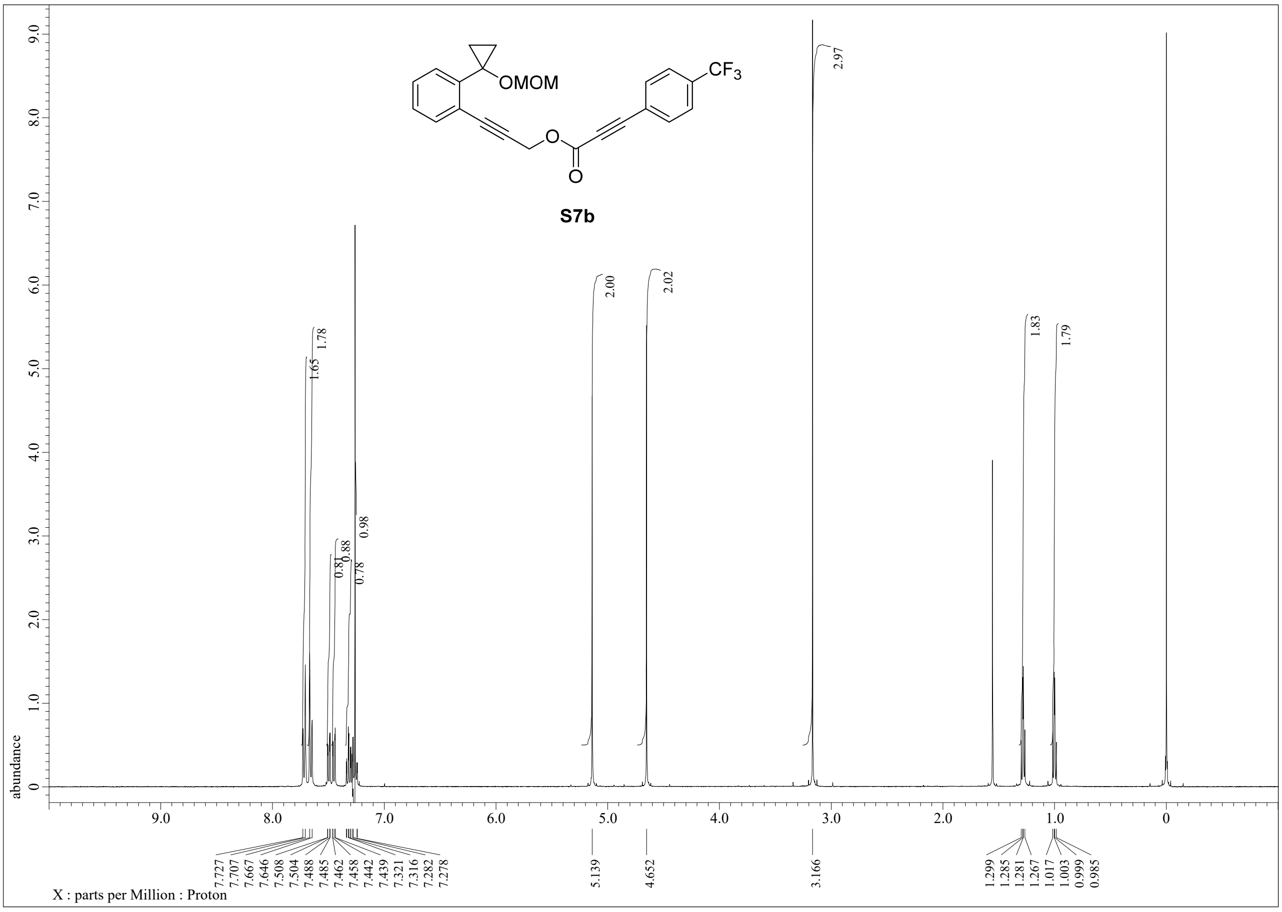
87.338
86.680
86.089
80.235
61.461
55.559
54.425
12.997
X : parts per Million : Carbon13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CF3
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O
S7b
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0.98
0.78
1.83
1.79
7.727
7.707
7.667
7.646
7.508
7.504
7.488
7.485
7.462
7.458
7.442
7.439
7.321
7.316
7.282
7.278
5.139
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1.003
0.999
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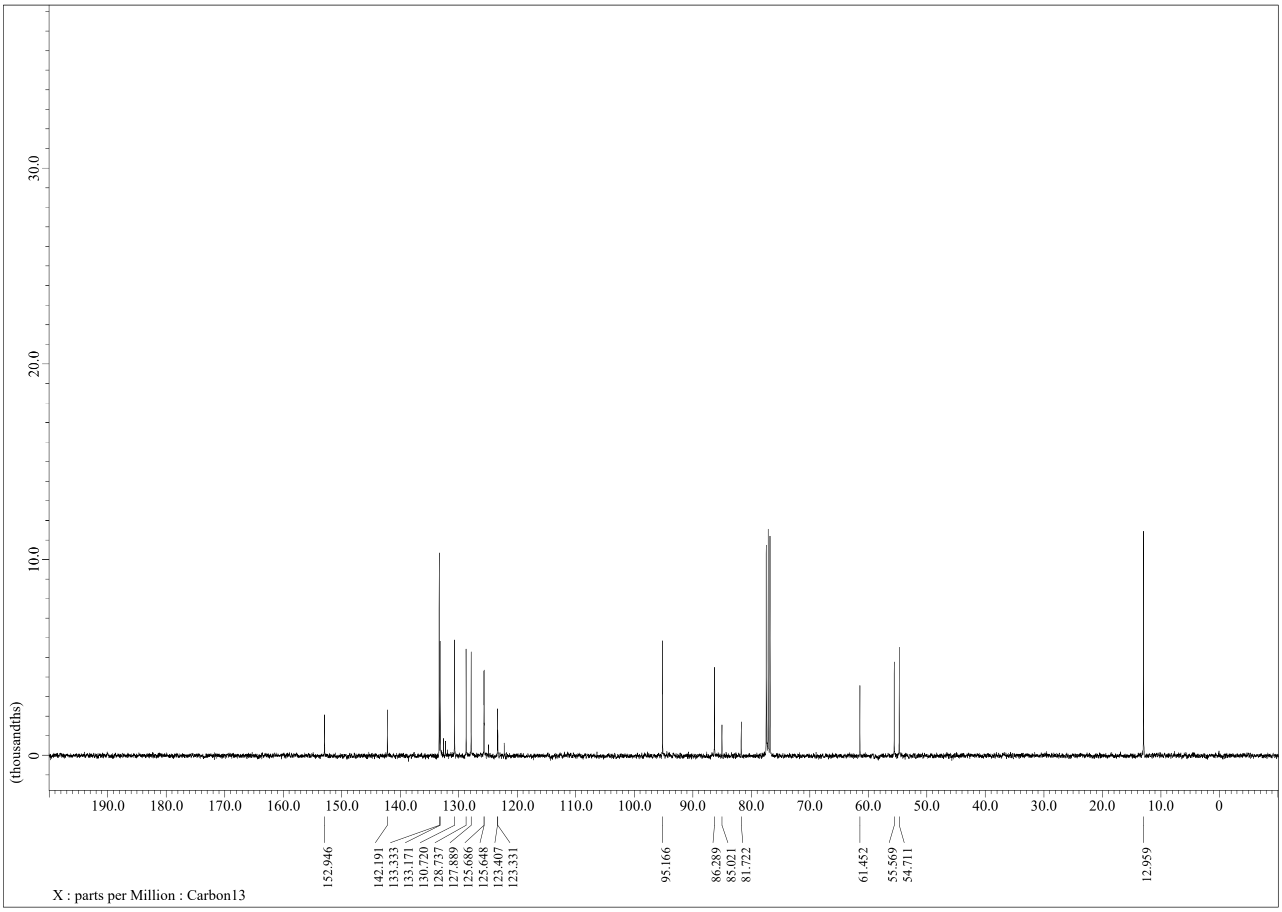
X : parts per Million : Proton


(thousandths)
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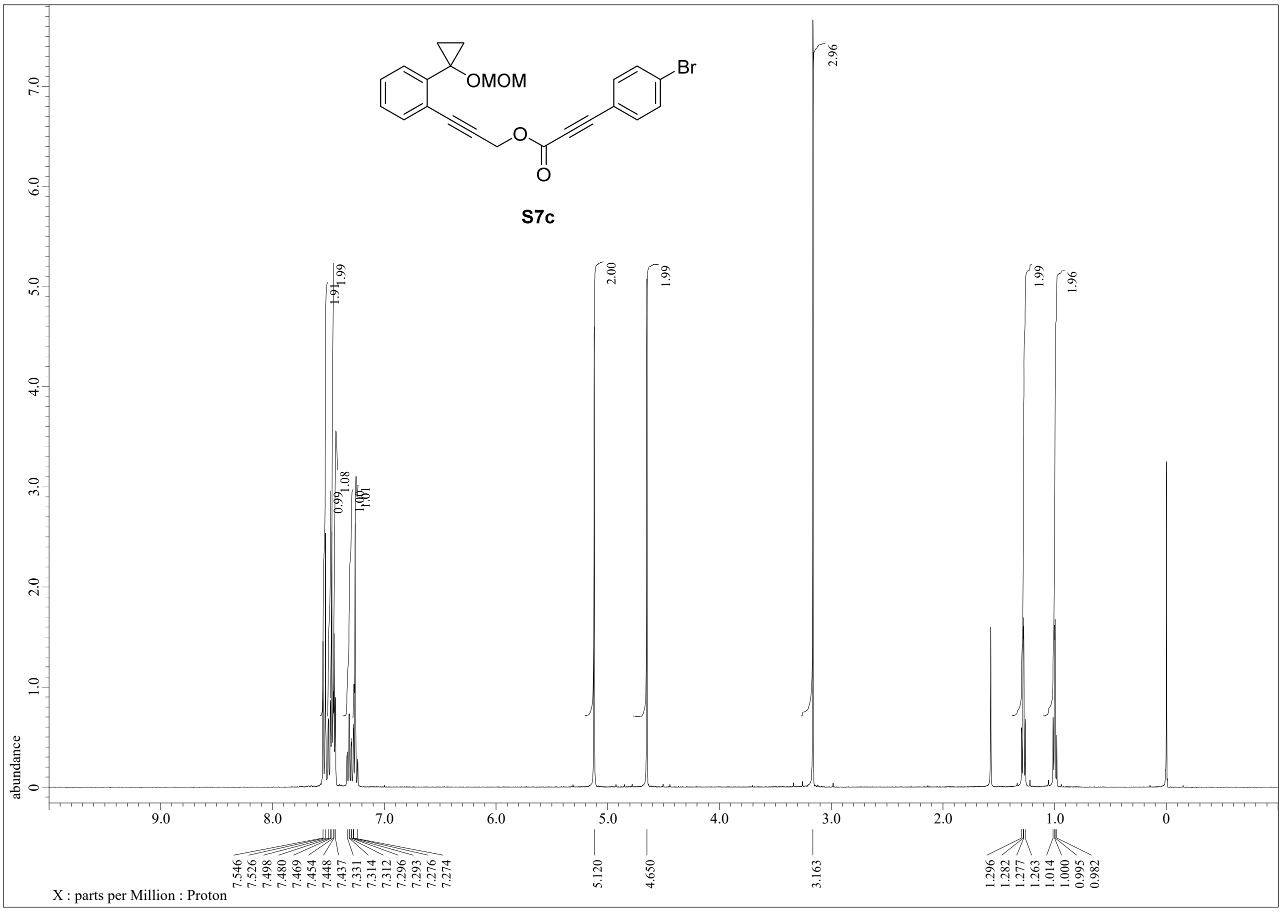
X : parts per Million : Carbon13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Br
O
O
S7c
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6.0
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1.99
0.99
1.08
1.00
1.01
2.00
1.99
2.96
1.99
1.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.546
7.526
7.498
7.480
7.469
7.454
7.448
7.437
7.331
7.314
7.312
7.296
7.293
7.276
7.274
5.120
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1.000
0.995
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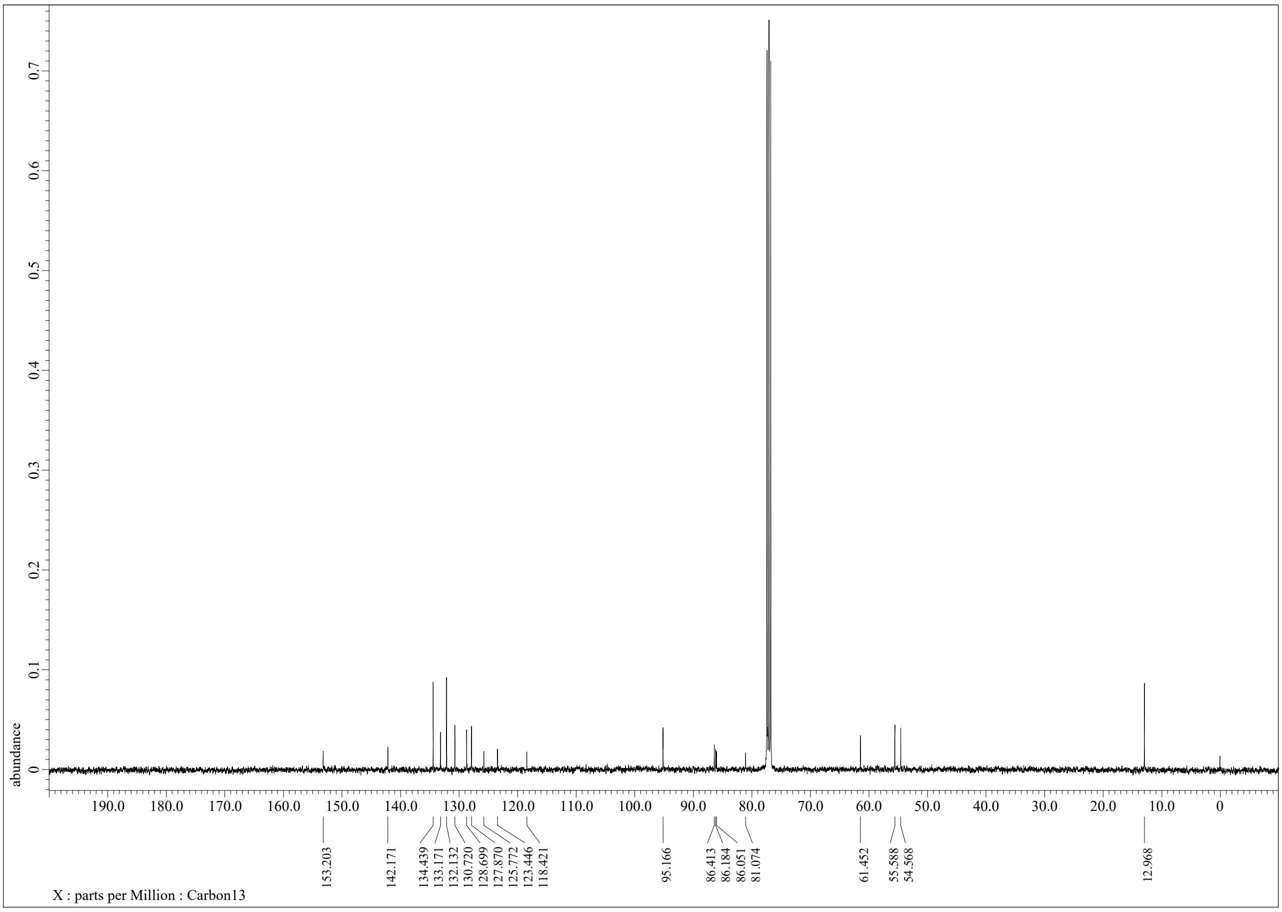
X : parts per Million : Proton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0.4
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0.6
0.7
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170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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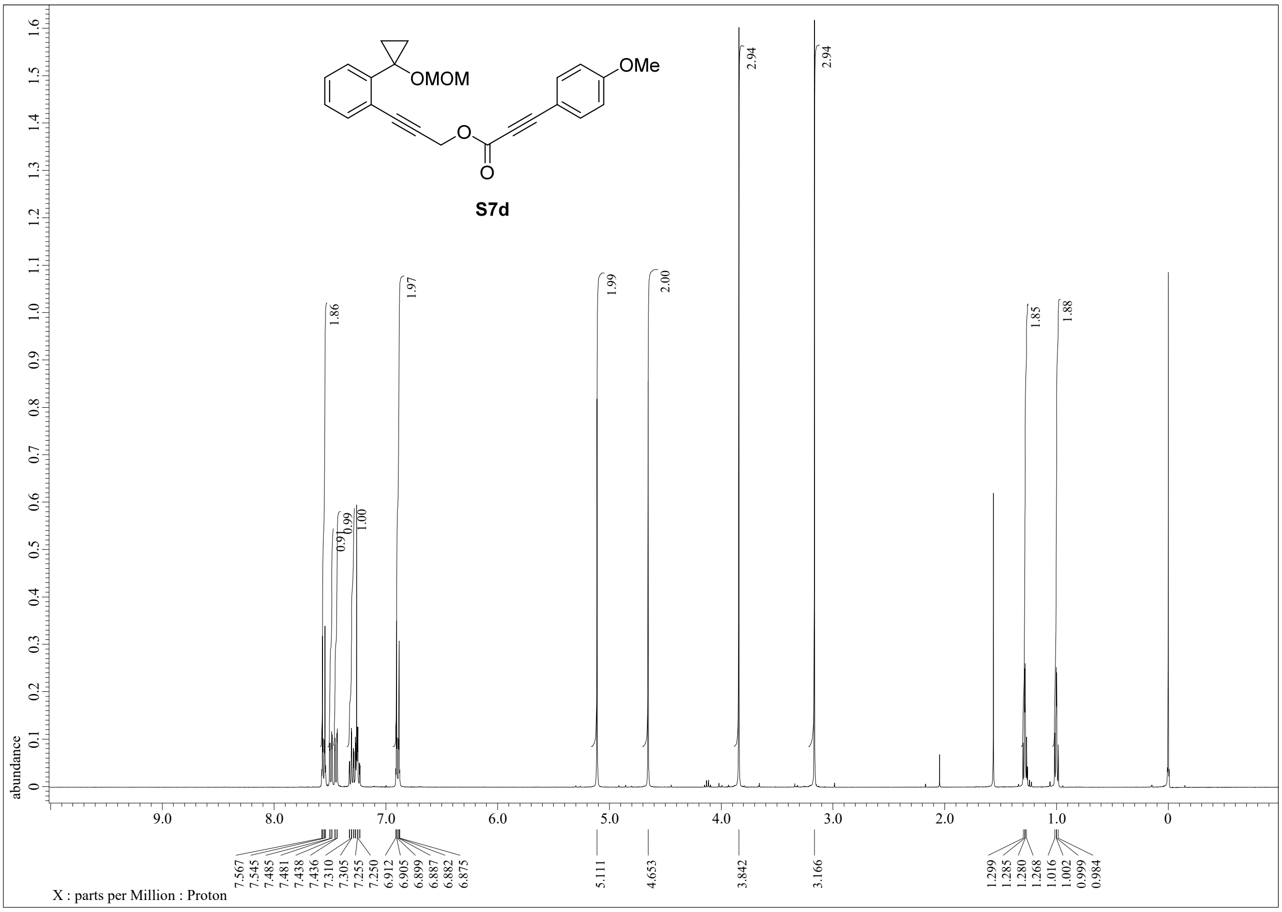
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1.88
abundance
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0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
9.0
8.0
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5.0
4.0
3.0
2.0
1.0
0
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7.545
7.485
7.481
7.438
7.436
7.310
7.305
7.255
7.250
6.912
6.905
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6.882
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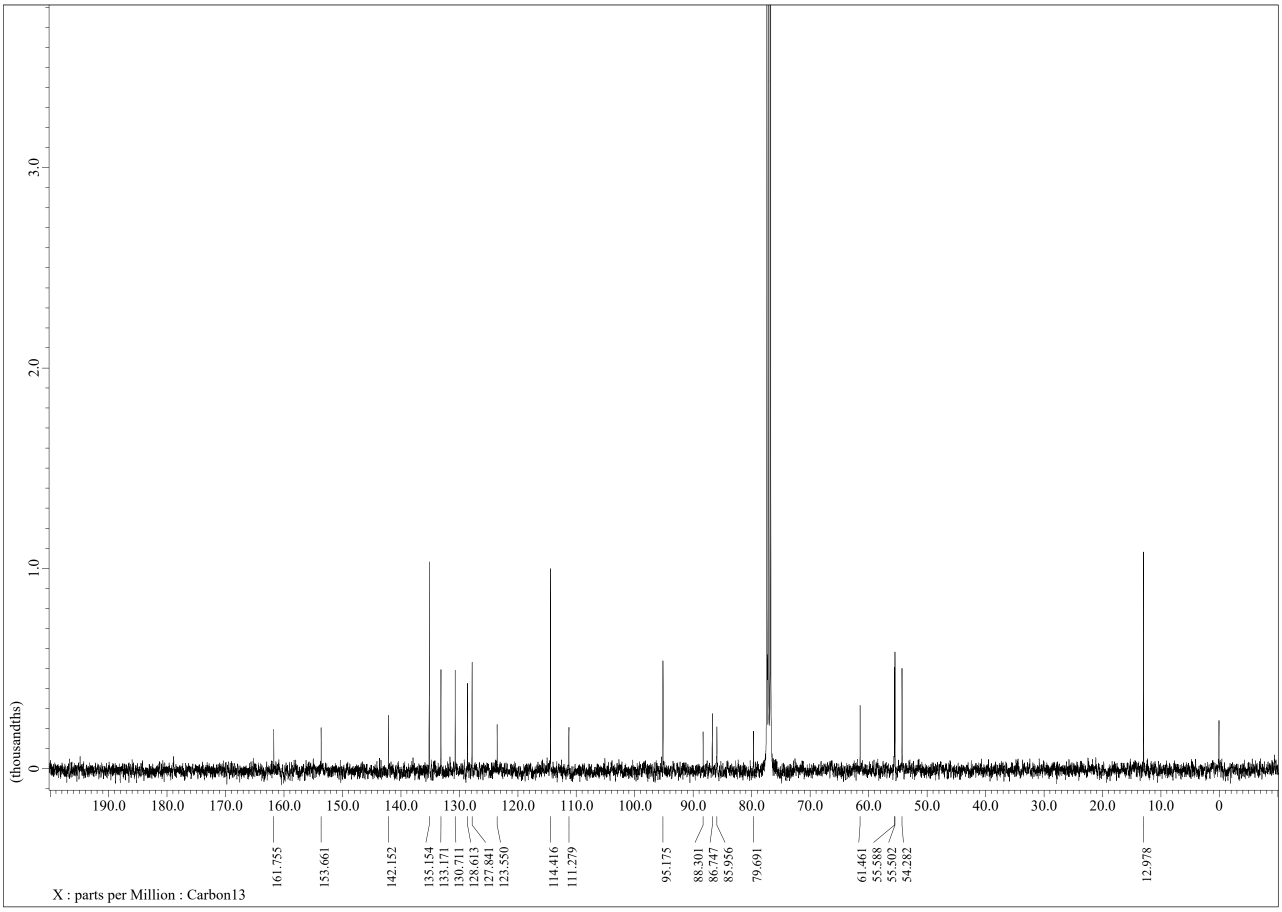
0.984
X : parts per Million : Proton

S7d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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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153.661
142.152
135.154
133.171
130.711
128.613
127.841
123.550
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111.279
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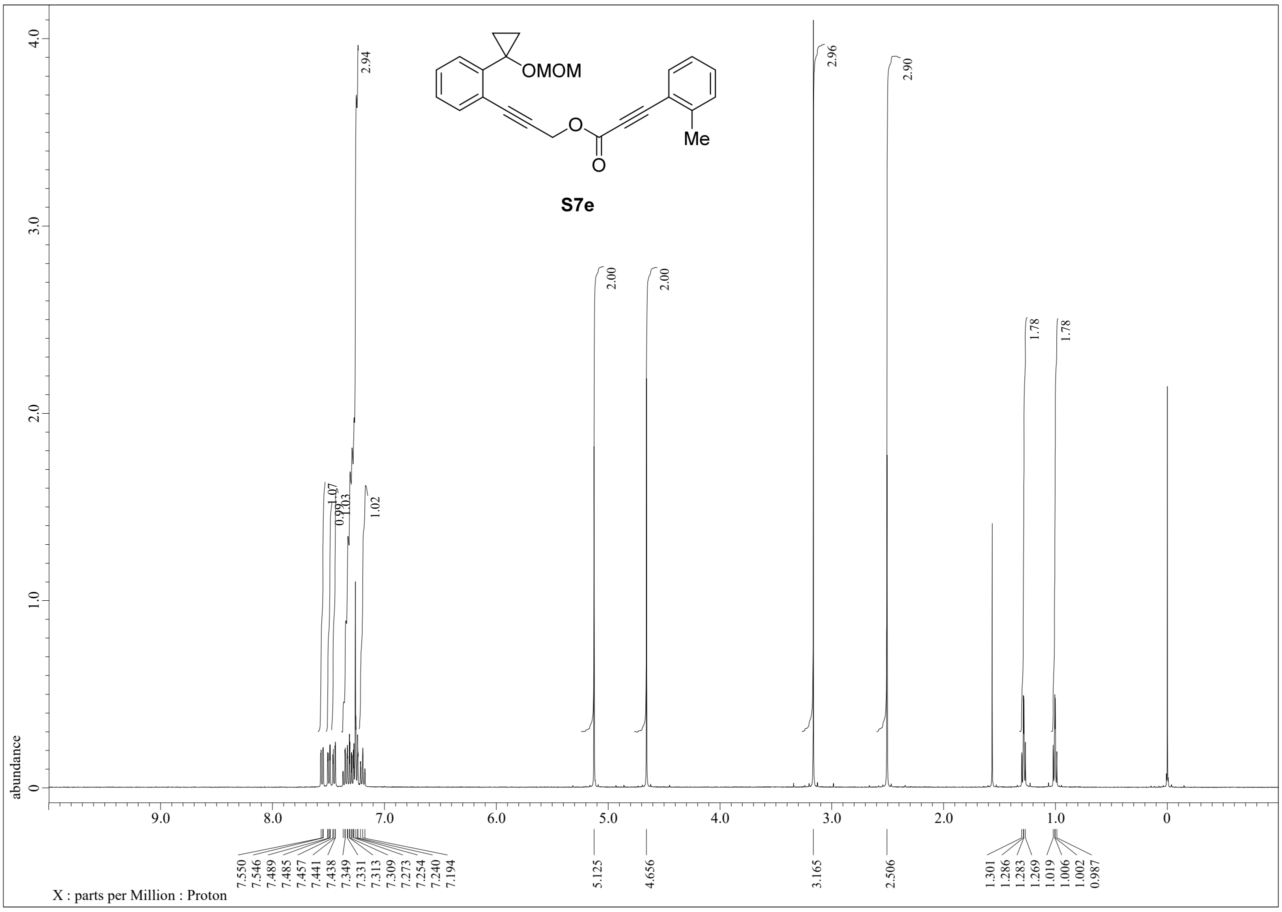
X : parts per Million : Carbon13



S7e

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O
O
Me
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0
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1.03
1.02
2.00
2.00
2.96
2.90
1.78
1.78
9.0
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6.0
5.0
4.0
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2.0
1.0
0
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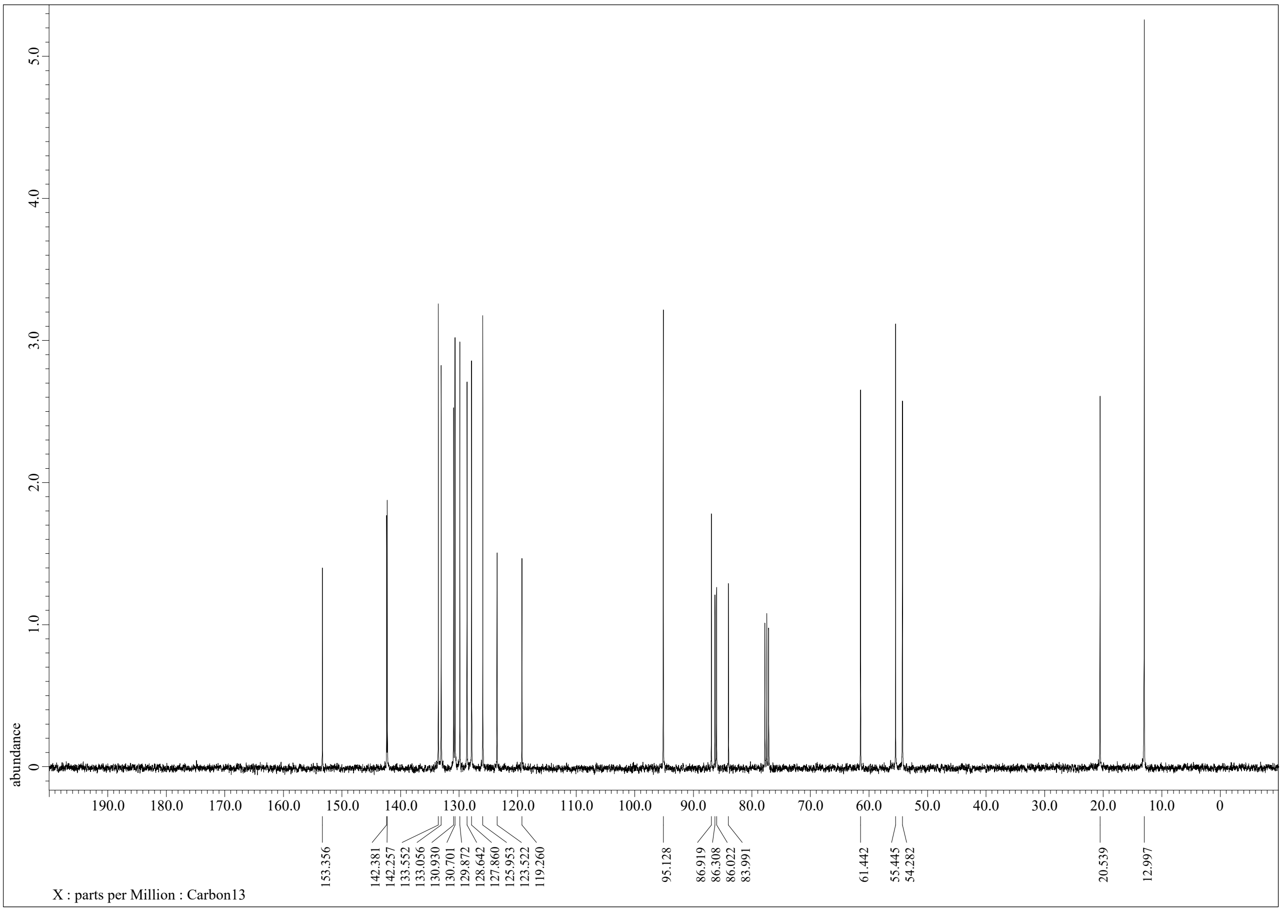
X : parts per Million : Proton



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130.0
120.0
110.0
100.0
90.0
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70.0
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130.701
129.872
128.642
127.860
125.953
123.522
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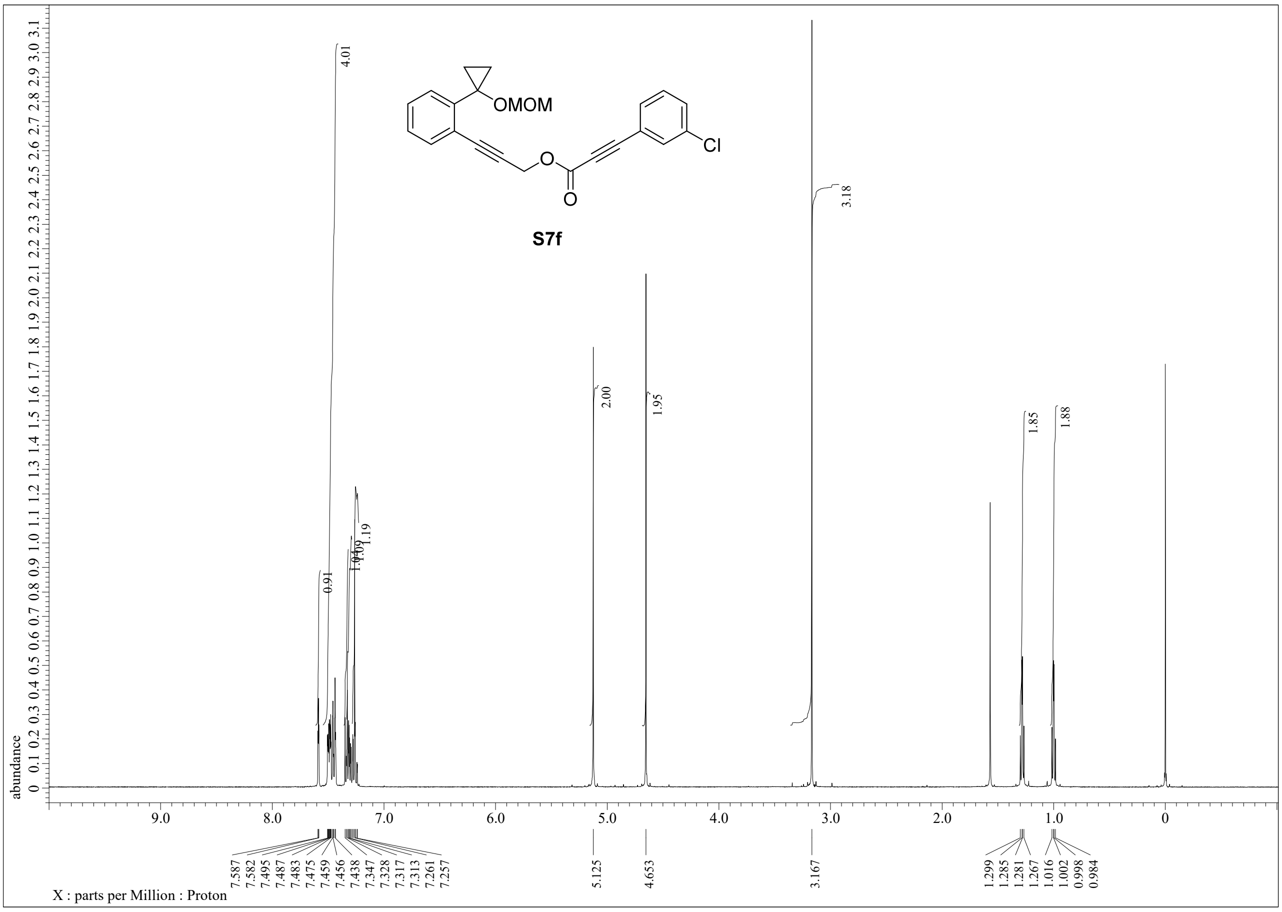
X : parts per Million : Carbon13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O
Cl
S7f
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9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
4.01
0.91
1.04
1.09
1.19
2.00
1.95
3.18
1.85
1.88
7.587
7.582
7.495
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7.438
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7.328
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7.313
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7.257
5.125
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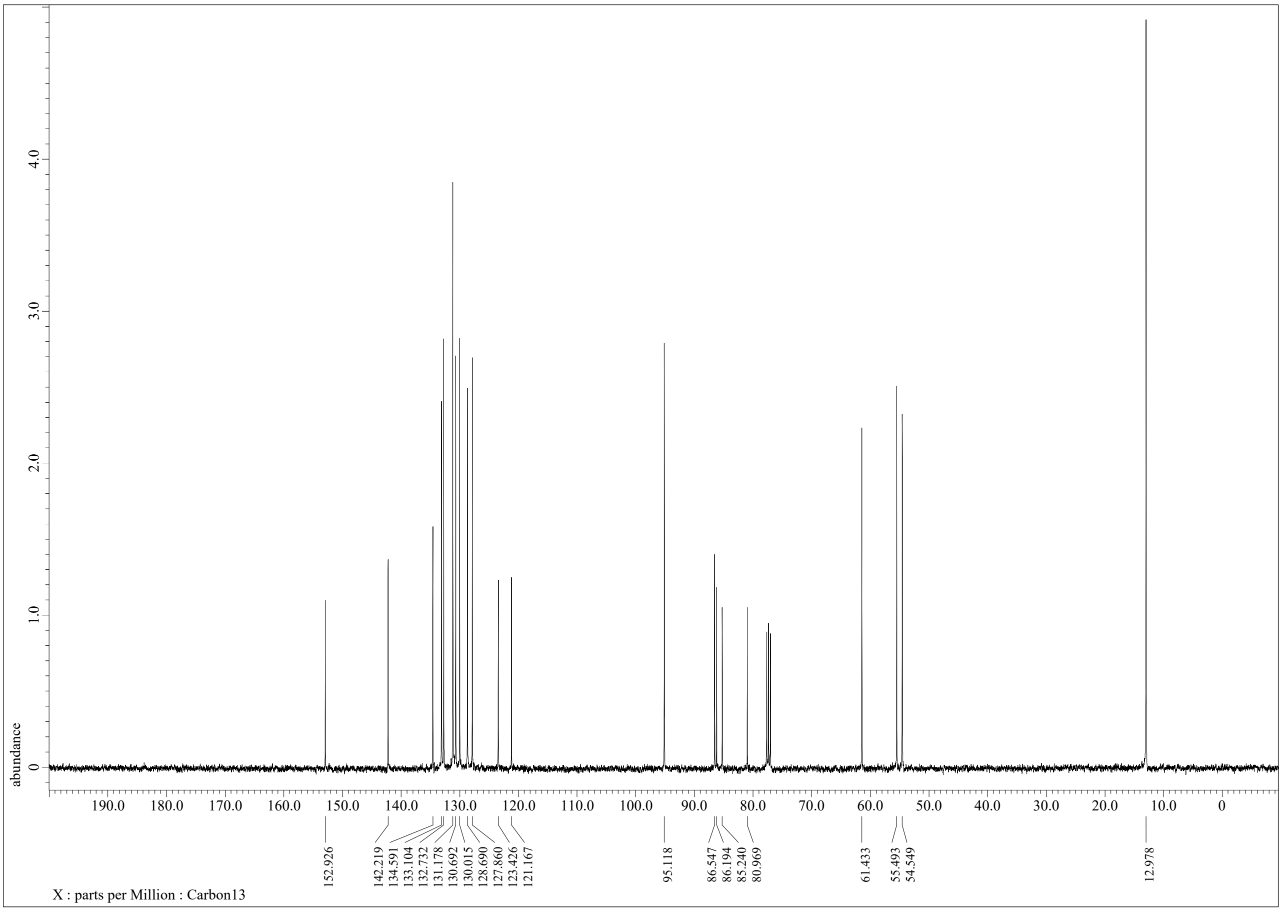
1.267
1.016
1.002
0.998
0.984
X : parts per Million : Proton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2.0
3.0
4.0
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152.926
142.219
134.591
133.104
132.732
131.178
130.692
130.015
128.690
127.860
123.426
121.167
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86.194
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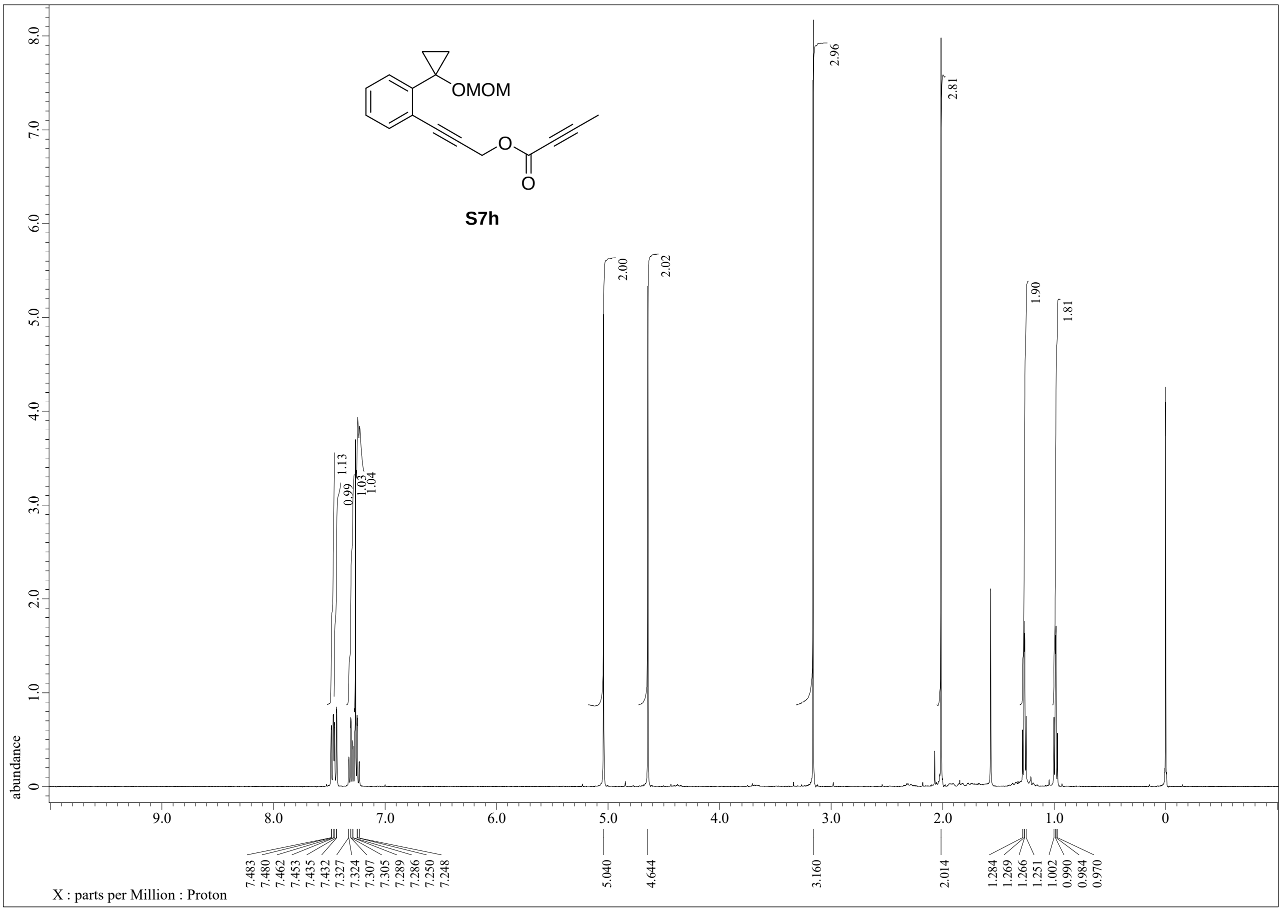
X : parts per Million : Carbon13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O
S7h
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0
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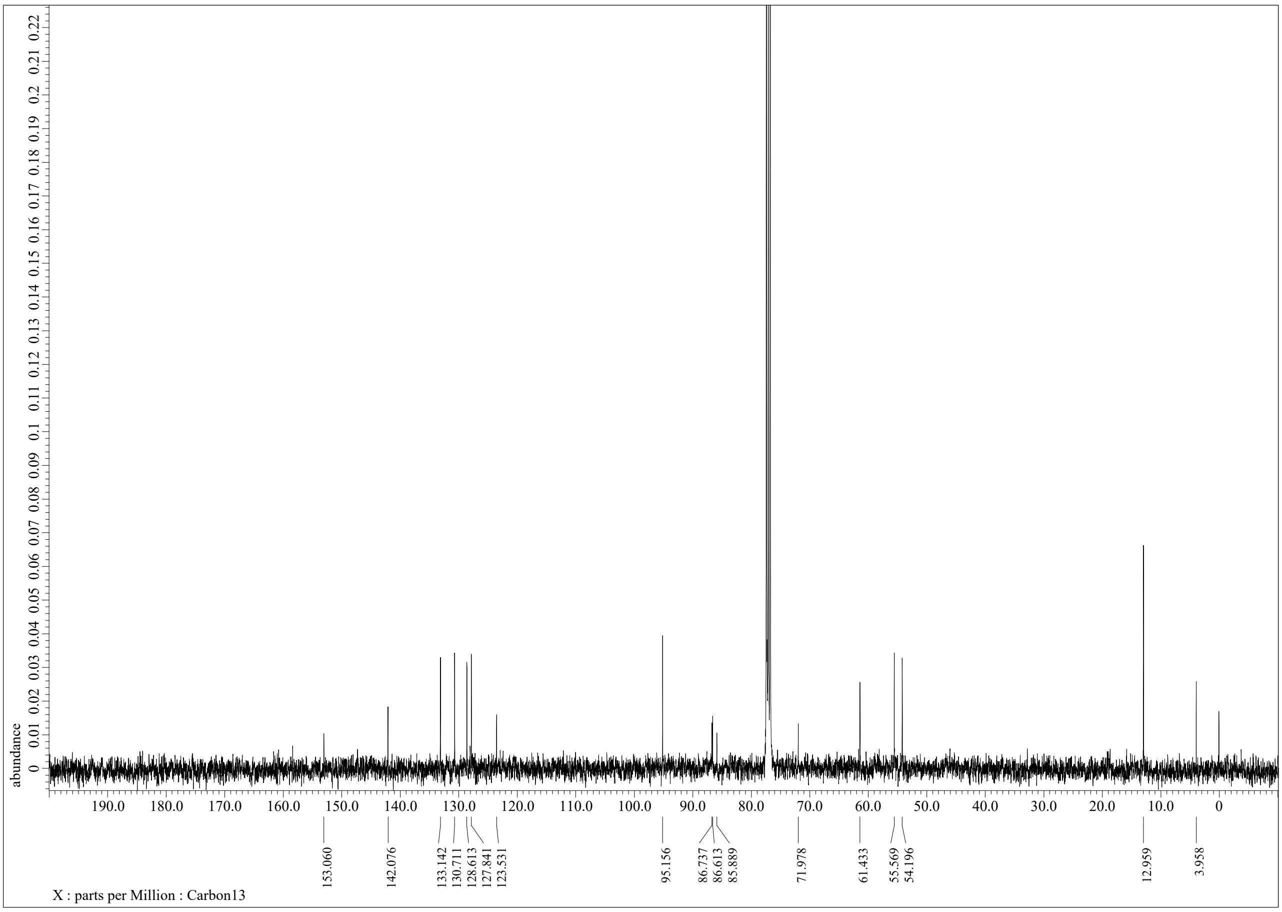
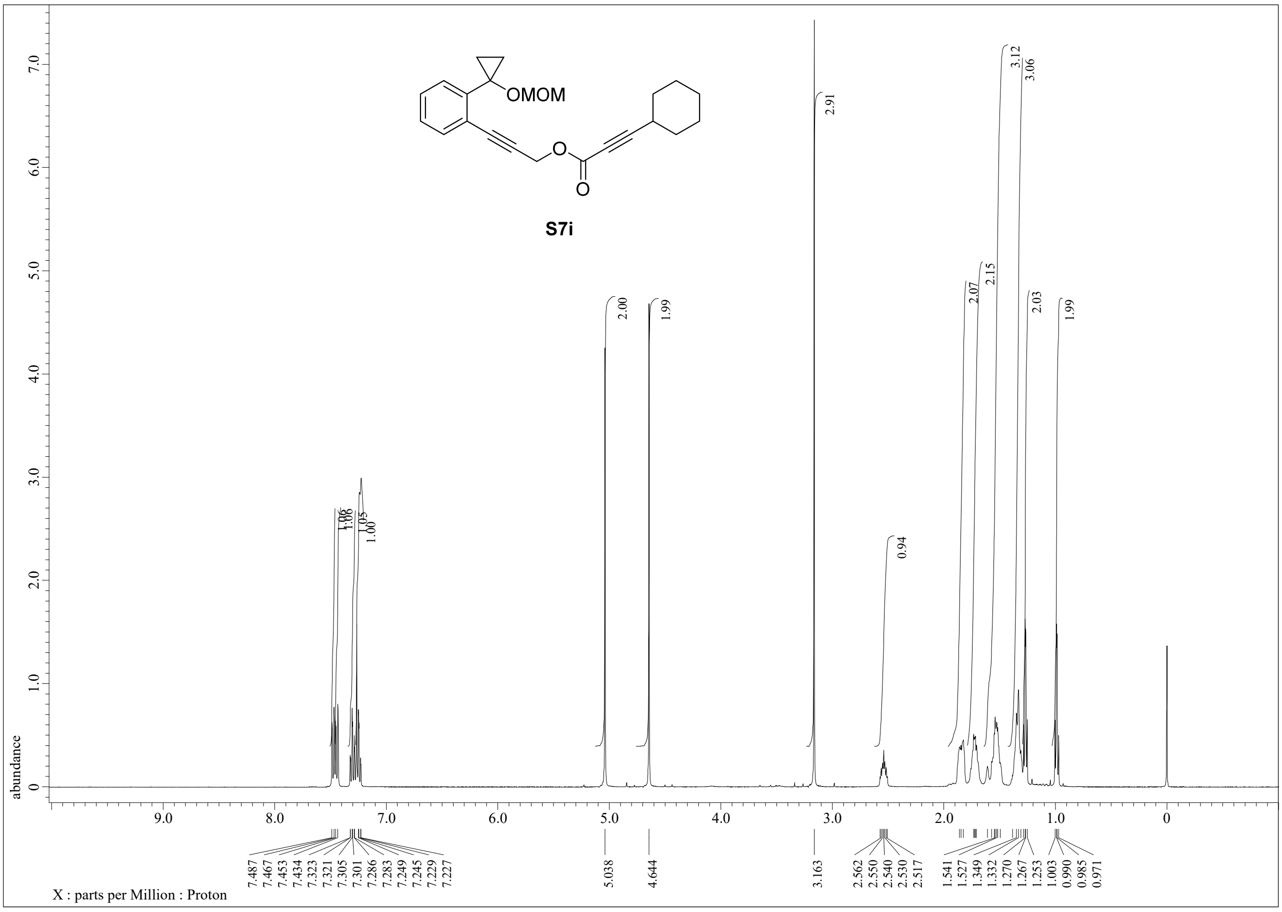
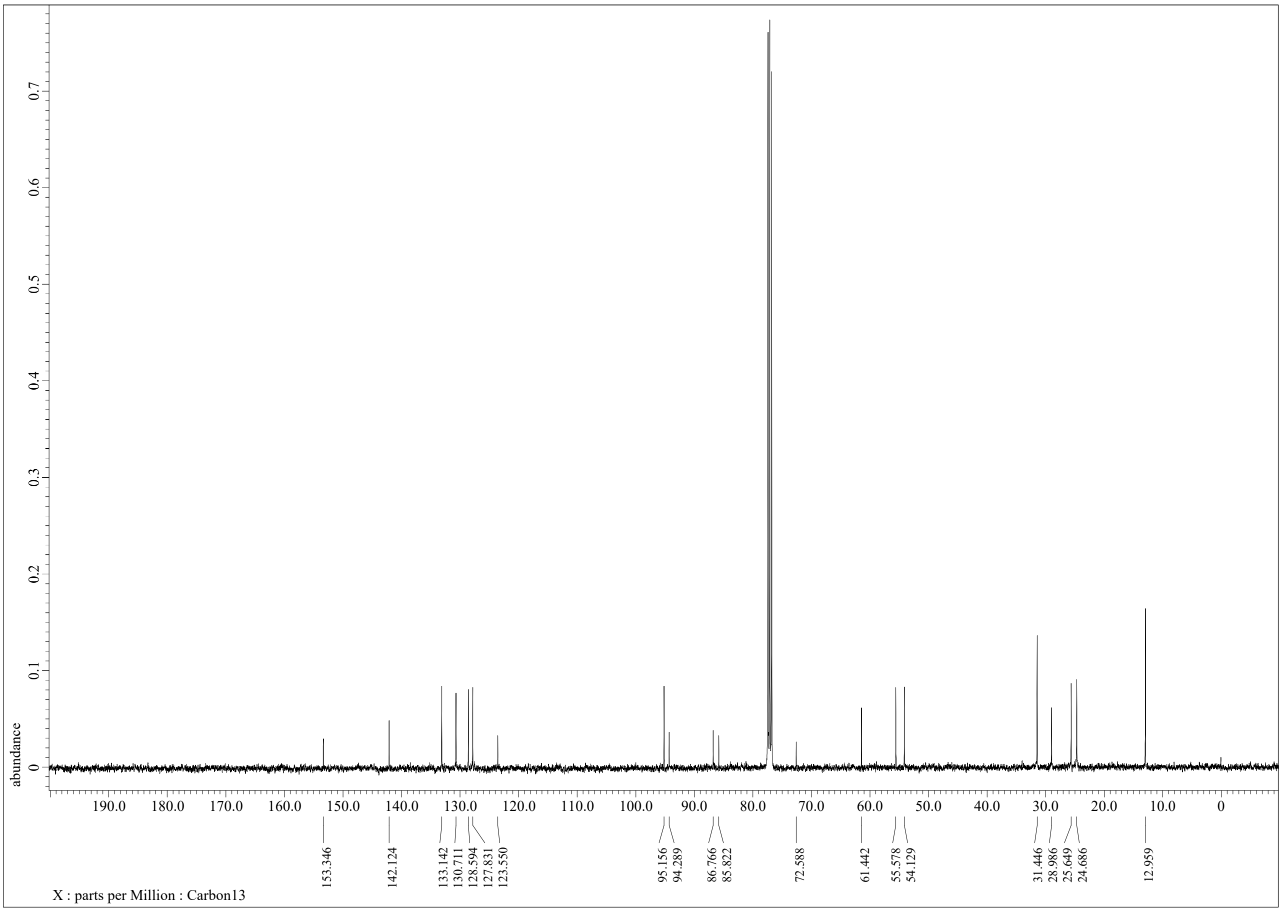
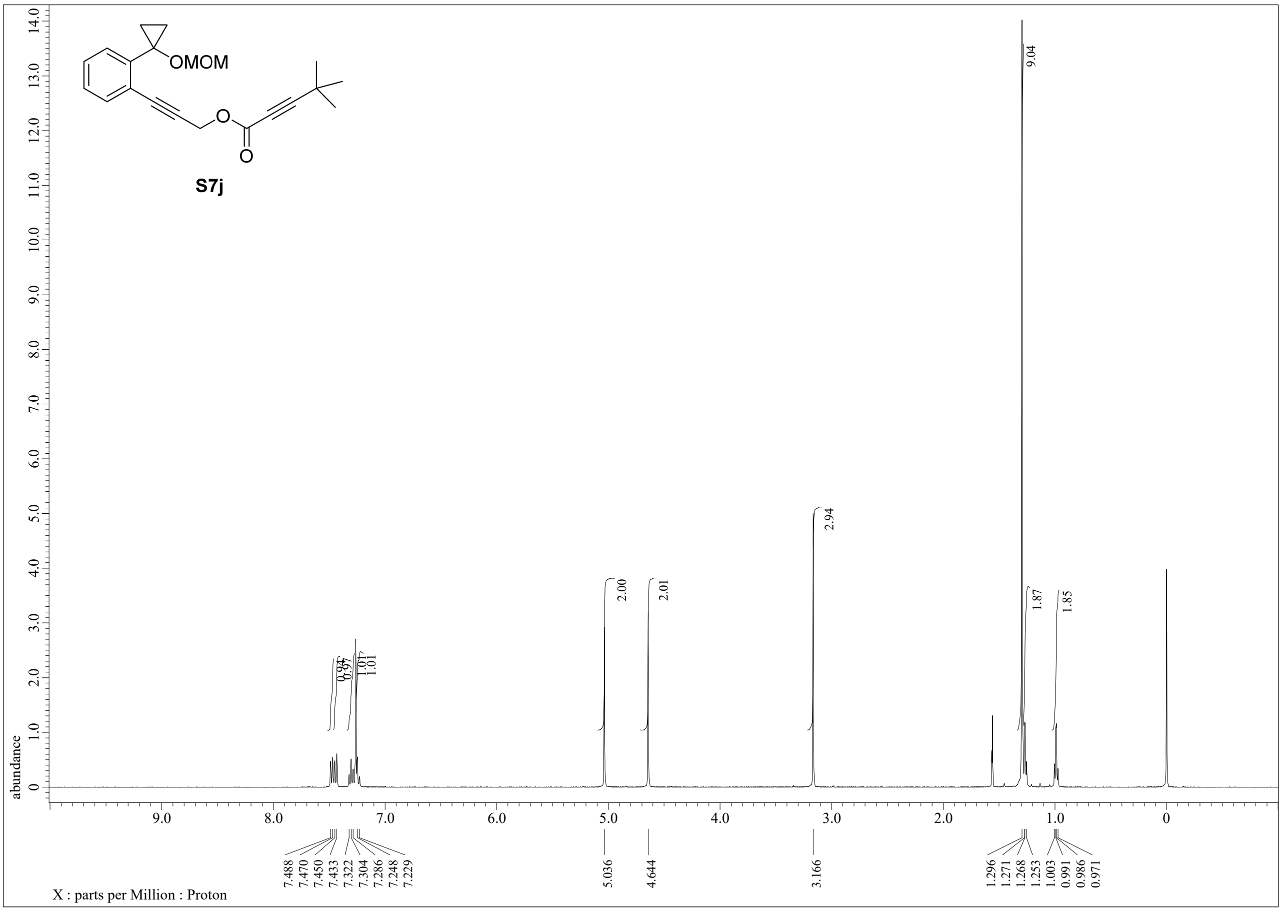
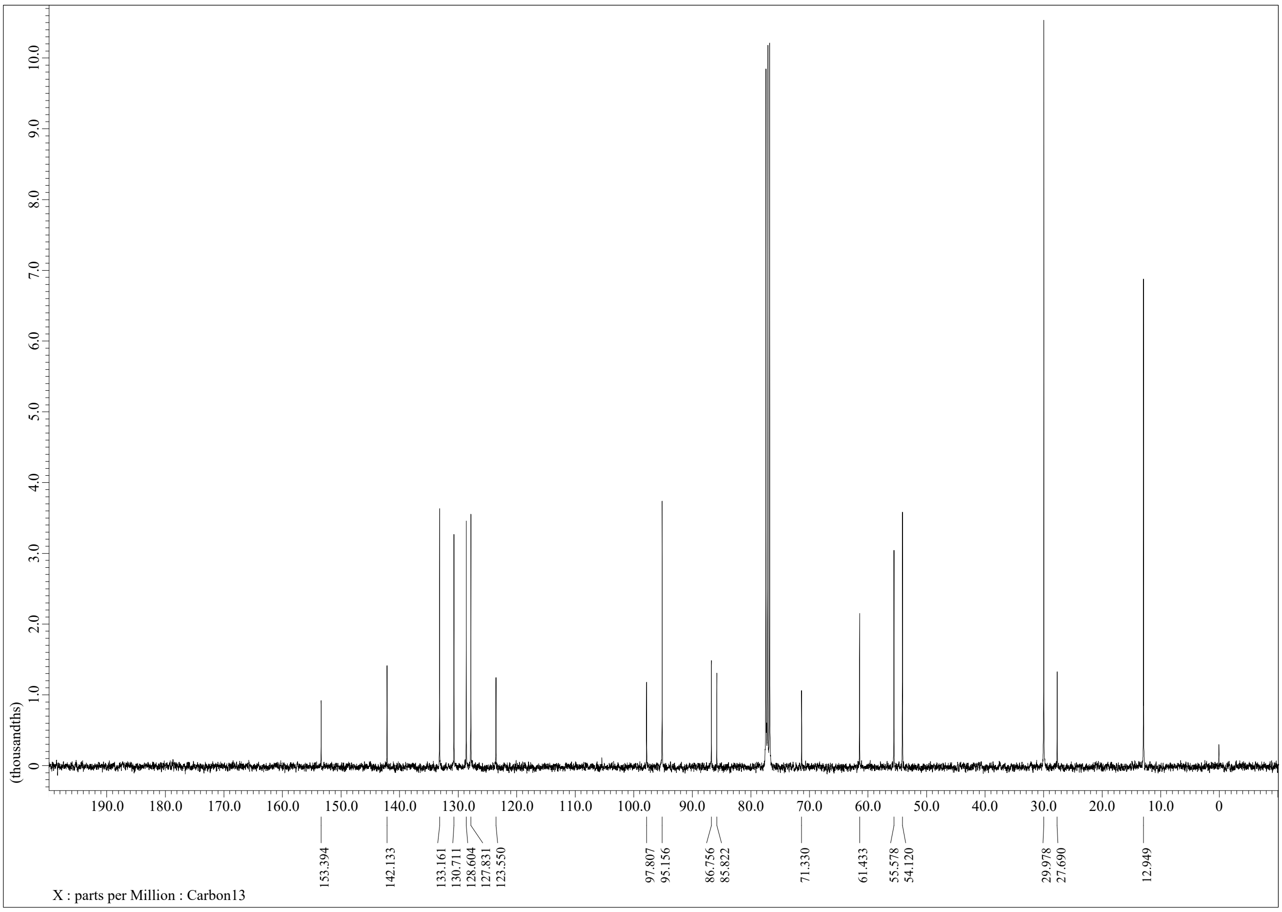
1.03
1.04
2.00
2.02
2.96
2.81
1.90
1.81
7.483
7.480
7.462
7.453
7.435
7.432
7.327
7.324
7.307
7.305
7.289
7.286
7.250
7.248
5.040
4.644
3.160
2.014
1.284
1.269
1.266
1.251
1.002
0.990
0.984
0.970
X : parts per Million : Proton

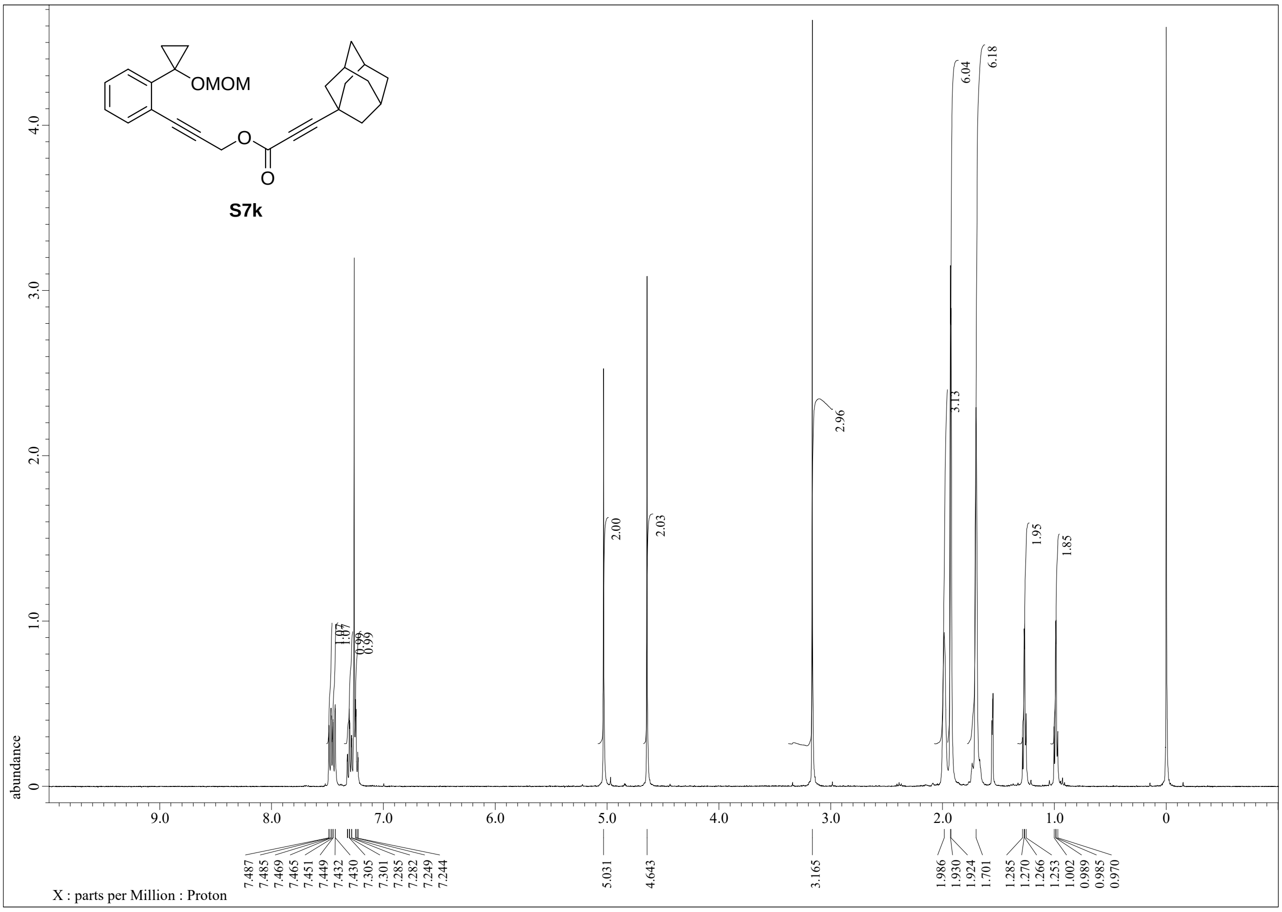

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
0.17
0.18
0.19
0.2
0.21
0.22
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.060
142.076
133.142
130.711
128.613
127.841
123.531
95.156
86.737
86.613
85.889
71.978
61.433
55.569
54.196
12.959
3.958
X : parts per Million : Carbon13

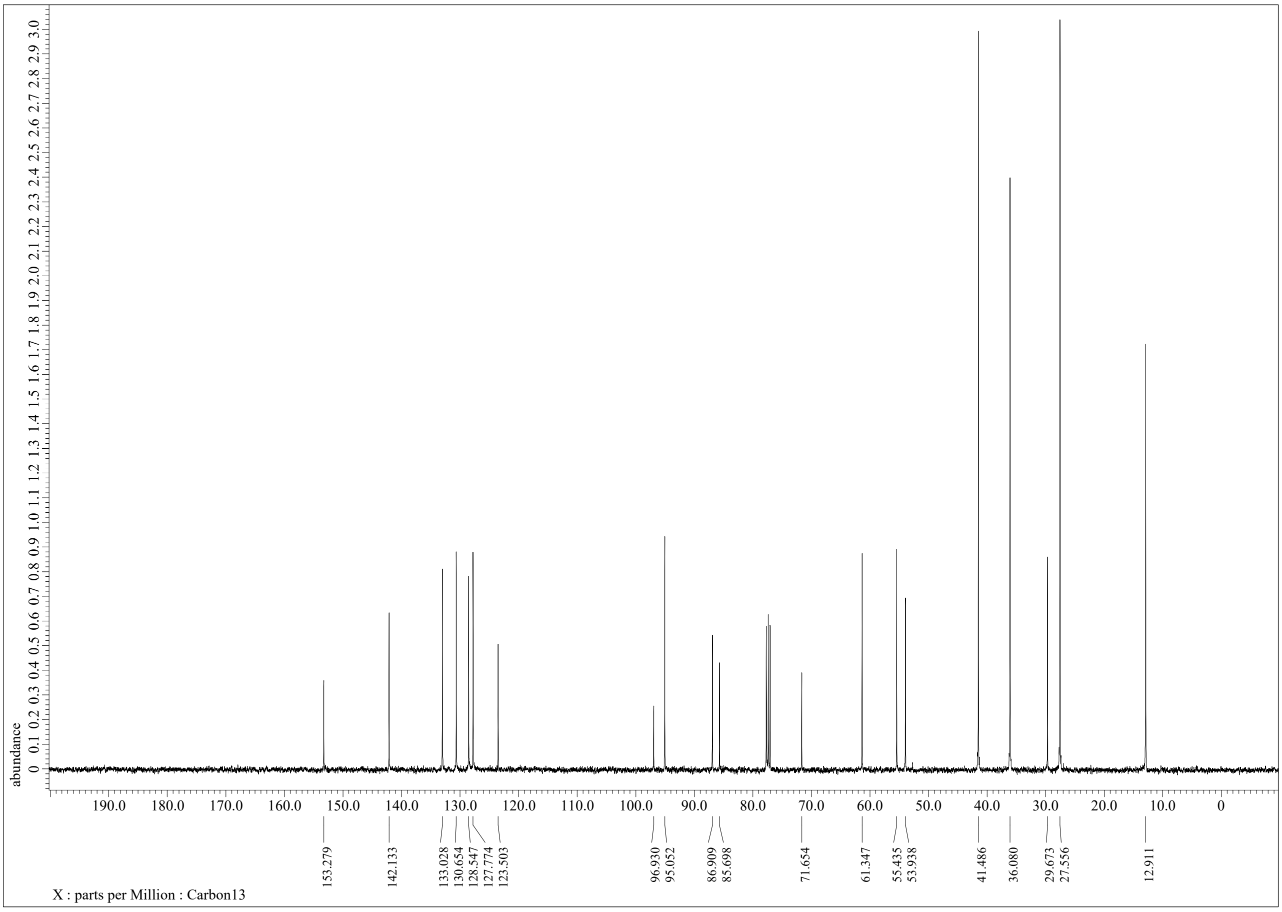

OMOM
O
O
S7i
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
1.06
1.08
1.05
1.00
2.00
1.99
2.91
0.94
2.07
2.15
3.12
3.06
2.03
1.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.487
7.467
7.453
7.434
7.323
7.321
7.305
7.301
7.286
7.283
7.249
7.245
7.229
7.227
5.038
4.644
3.163
2.562
2.550
2.540
2.530
2.517
1.541
1.527
1.349
1.332
1.270
1.267
1.253
1.003
0.990
0.985
0.971
X : parts per Million : Proton

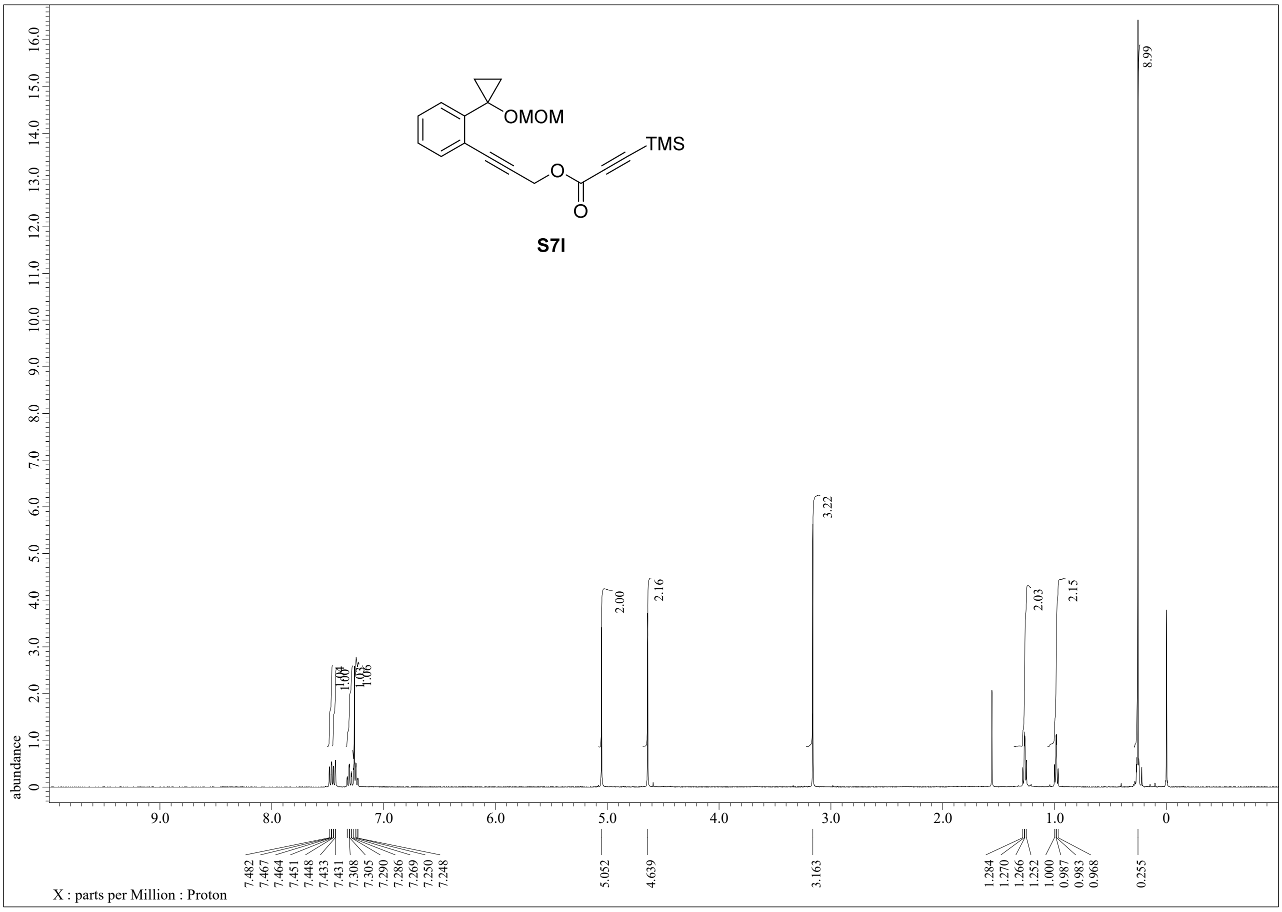

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.346
142.124
133.142
130.711
128.594
127.831
123.550
95.156
94.289
86.766
85.822
72.588
61.442
55.578
54.129
31.446
28.986
25.649
24.686
12.959
X : parts per Million : Carbon13

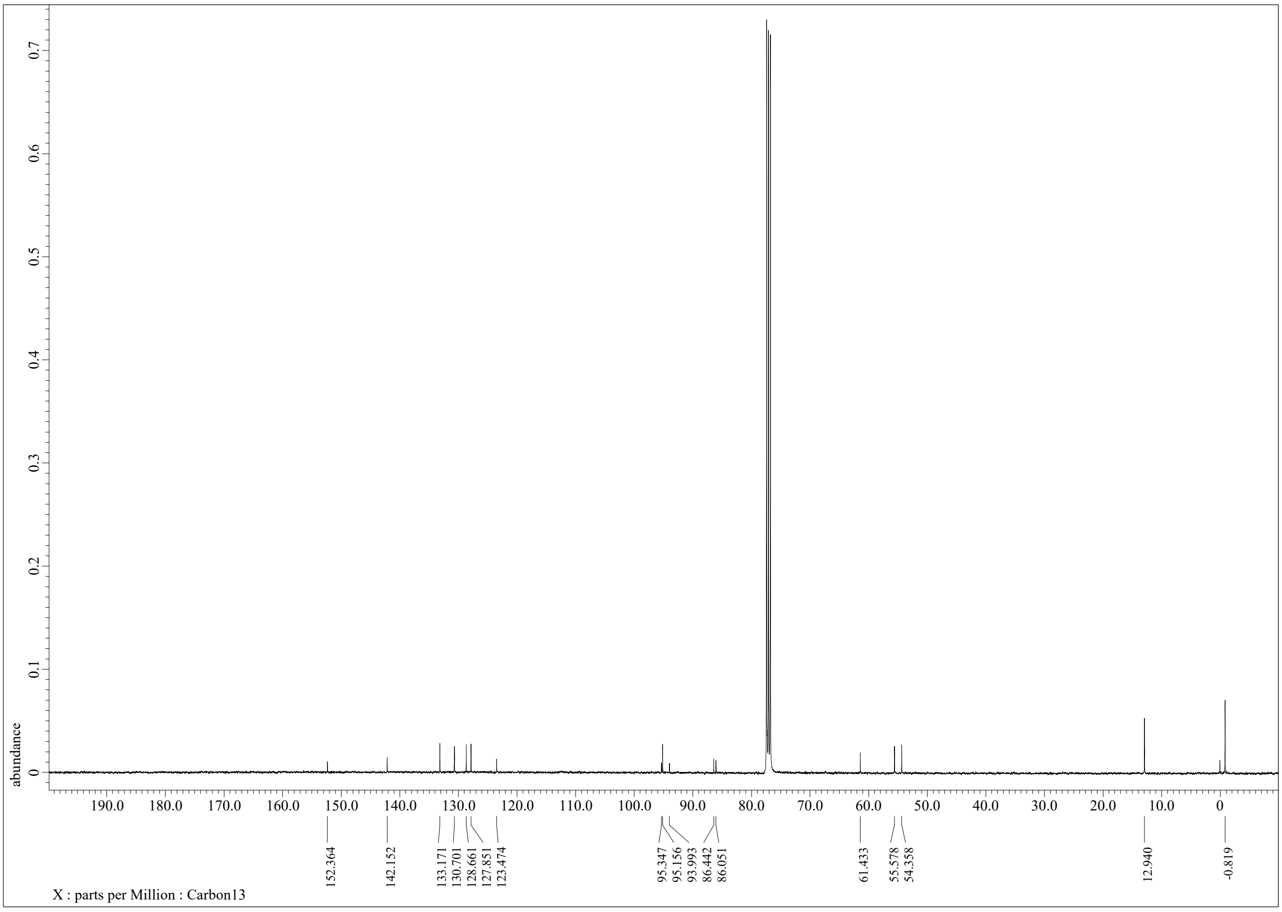

OMOM
O
O
O
S7j
abundance
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.04
2.94
2.00
2.01
1.87
1.85
0.94
0.97
1.01
1.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.488
7.470
7.450
7.433
7.322
7.304
7.286
7.248
7.229
5.036
4.644
3.166
1.296
1.271
1.268
1.253
1.003
0.991
0.986
0.971
X : parts per Million : Proton

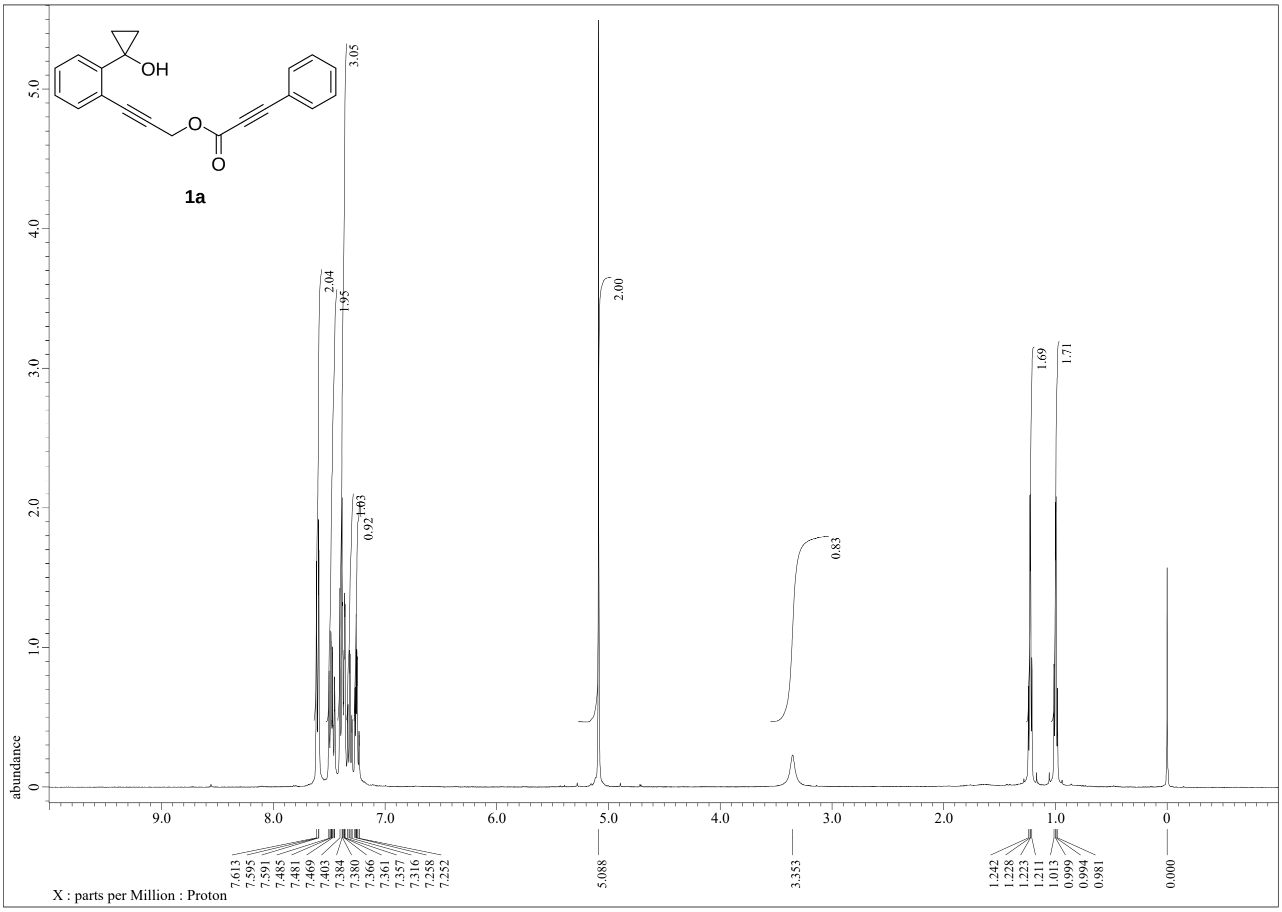

(thousandths)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.394
142.133
133.161
130.711
128.604
127.831
123.550
97.807
95.156
86.756
85.822
71.330
61.433
55.578
54.120
29.978
27.690
12.949
X : parts per Million : Carbon13

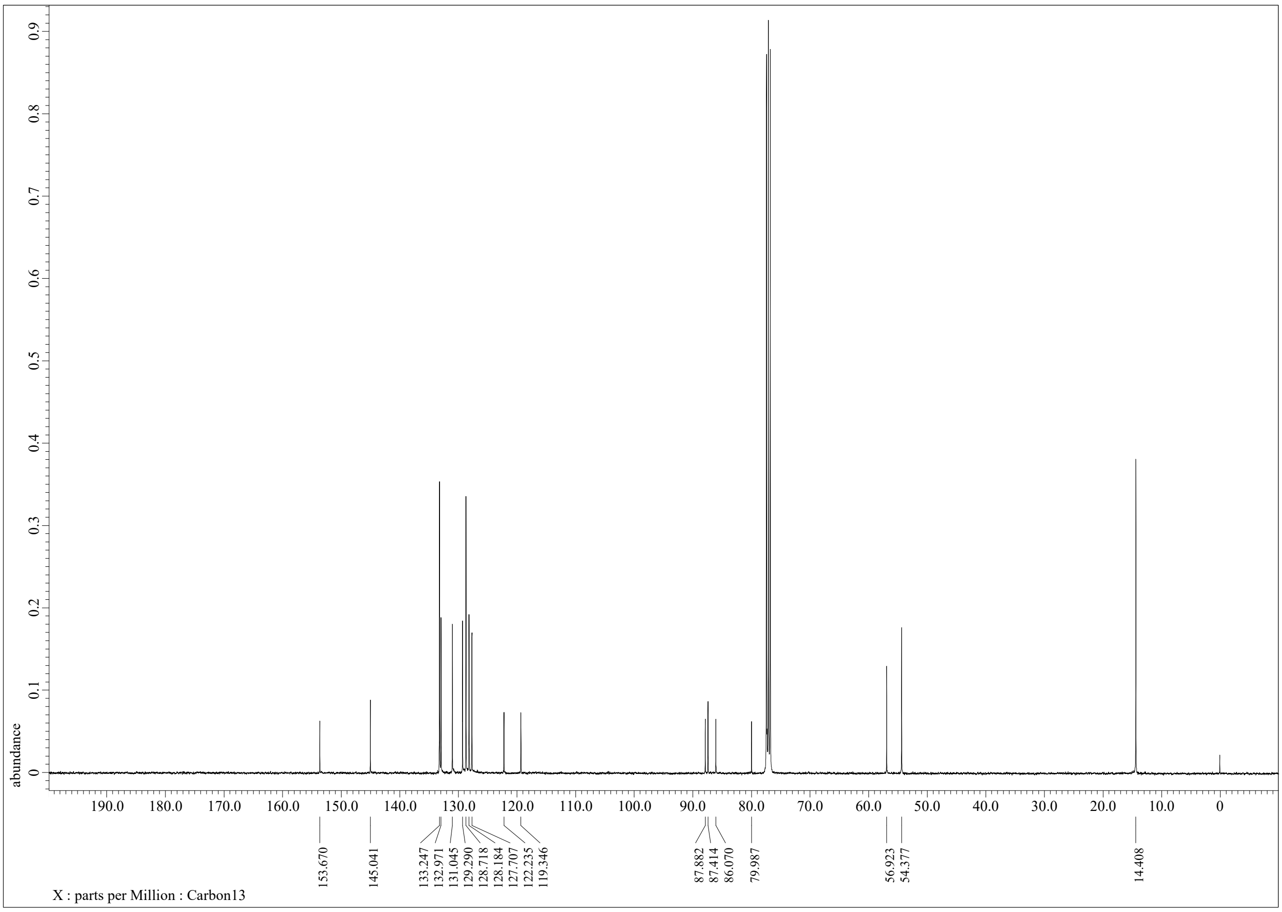

OMOM
O
O
S7k
abundance
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.07
1.07
0.99
0.99
2.00
2.03
2.96
3.13
6.04
6.18
1.95
1.85
7.487
7.485
7.469
7.465
7.451
7.449
7.432
7.430
7.305
7.301
7.285
7.282
7.249
7.244
5.031
4.643
3.165
1.986
1.930
1.924
1.701
1.285
1.270
1.266
1.253
1.002
0.989
0.985
0.970
X : parts per Million : Proton

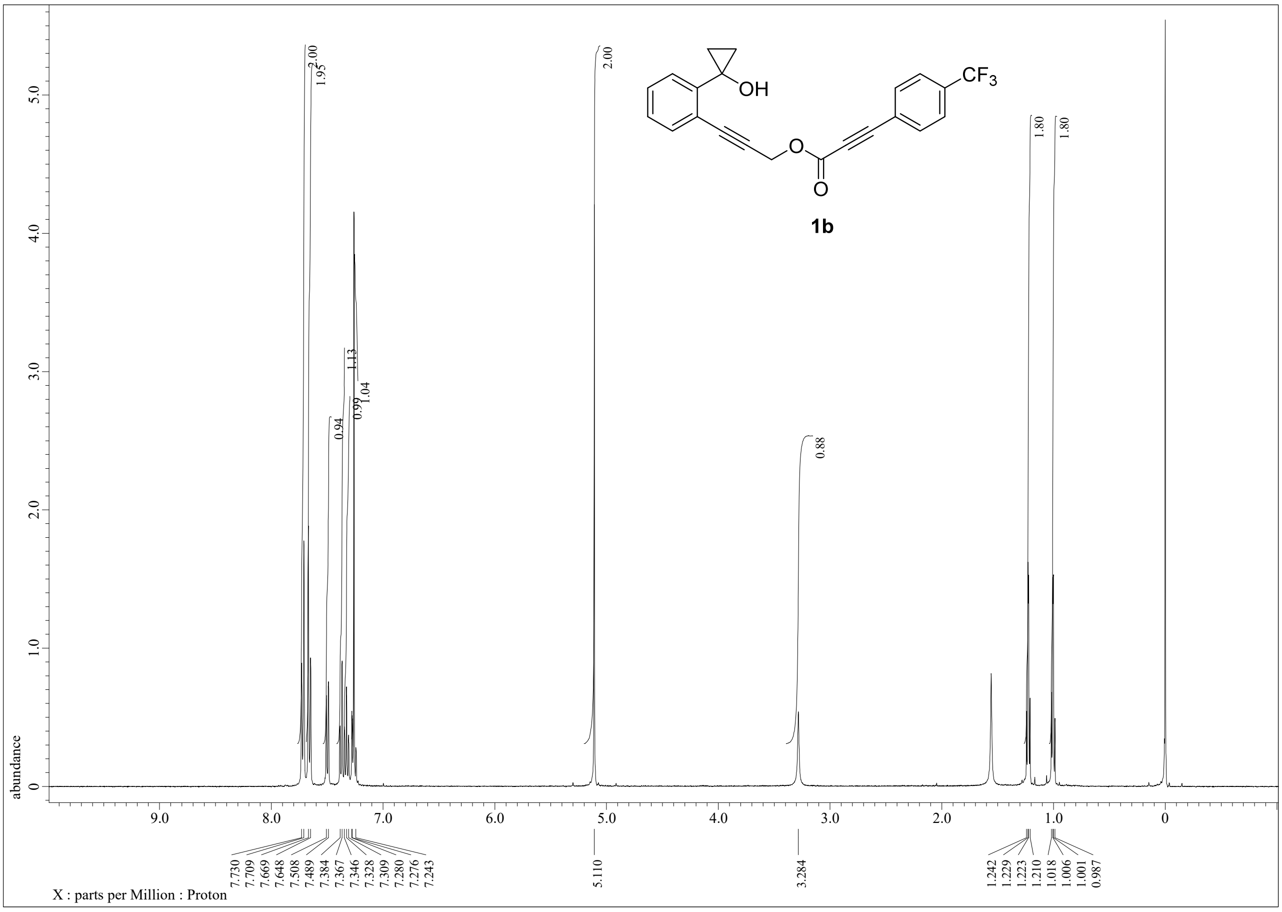

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.279
142.133
133.028
130.654
128.547
127.774
123.503
96.930
95.052
86.909
85.698
71.654
61.347
55.435
53.938
41.486
36.080
29.673
27.556
12.911
X : parts per Million : Carbon13

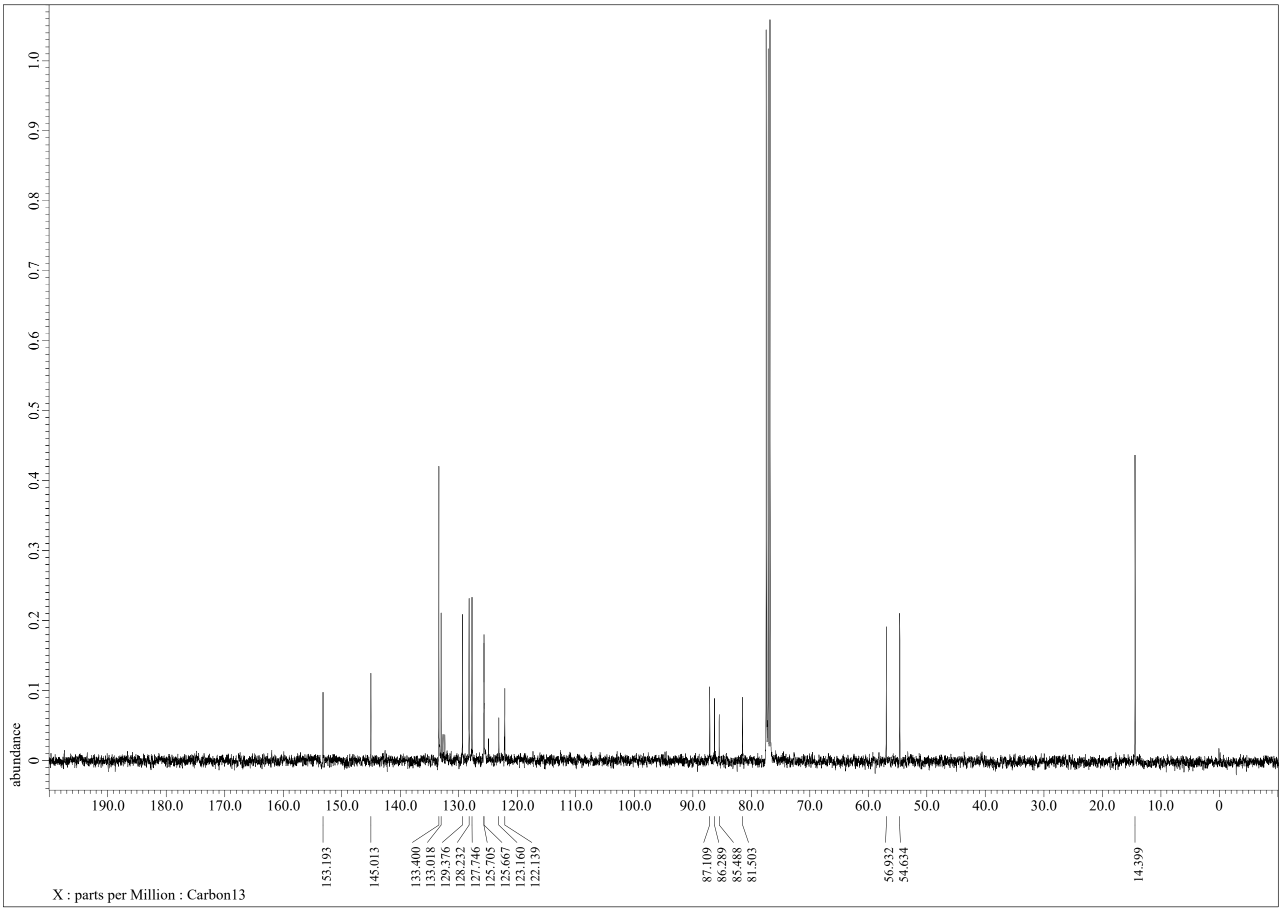

OMOM
TMS
O
O
S7l
abundance
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.04
1.00
1.03
1.06
2.00
2.16
3.22
2.03
2.15
8.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.482
7.467
7.464
7.451
7.448
7.433
7.431
7.308
7.305
7.290
7.286
7.269
7.250
7.248
5.052
4.639
3.163
1.284
1.270
1.266
1.252
1.000
0.987
0.983
0.968
0.255
X : parts per Million : Proton

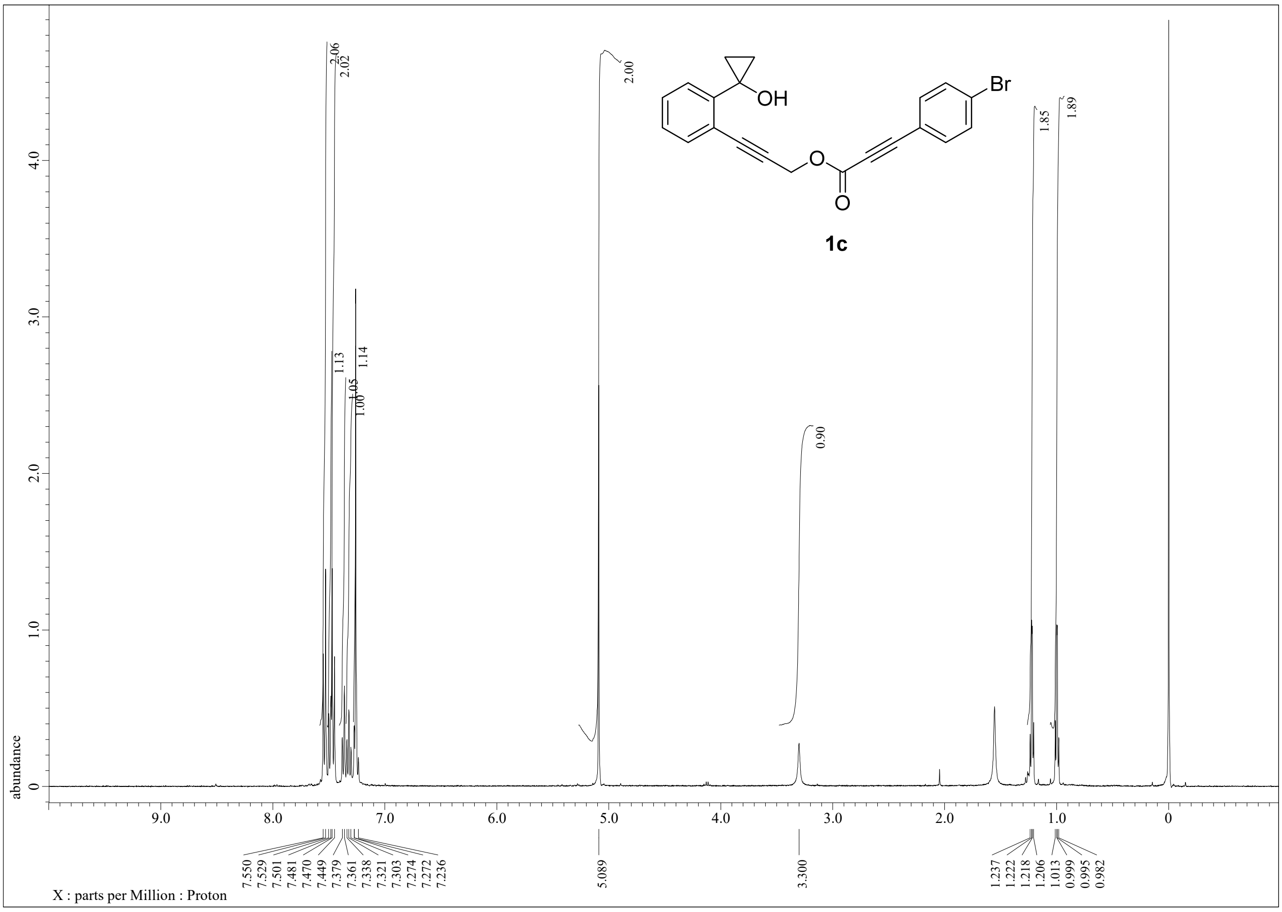

abundance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
152.364
142.152
133.171
130.701
128.661
127.851
123.474
95.347
95.156
93.993
86.442
86.051
61.433
55.578
54.358
12.940
-0.819
X : parts per Million : Carbon13

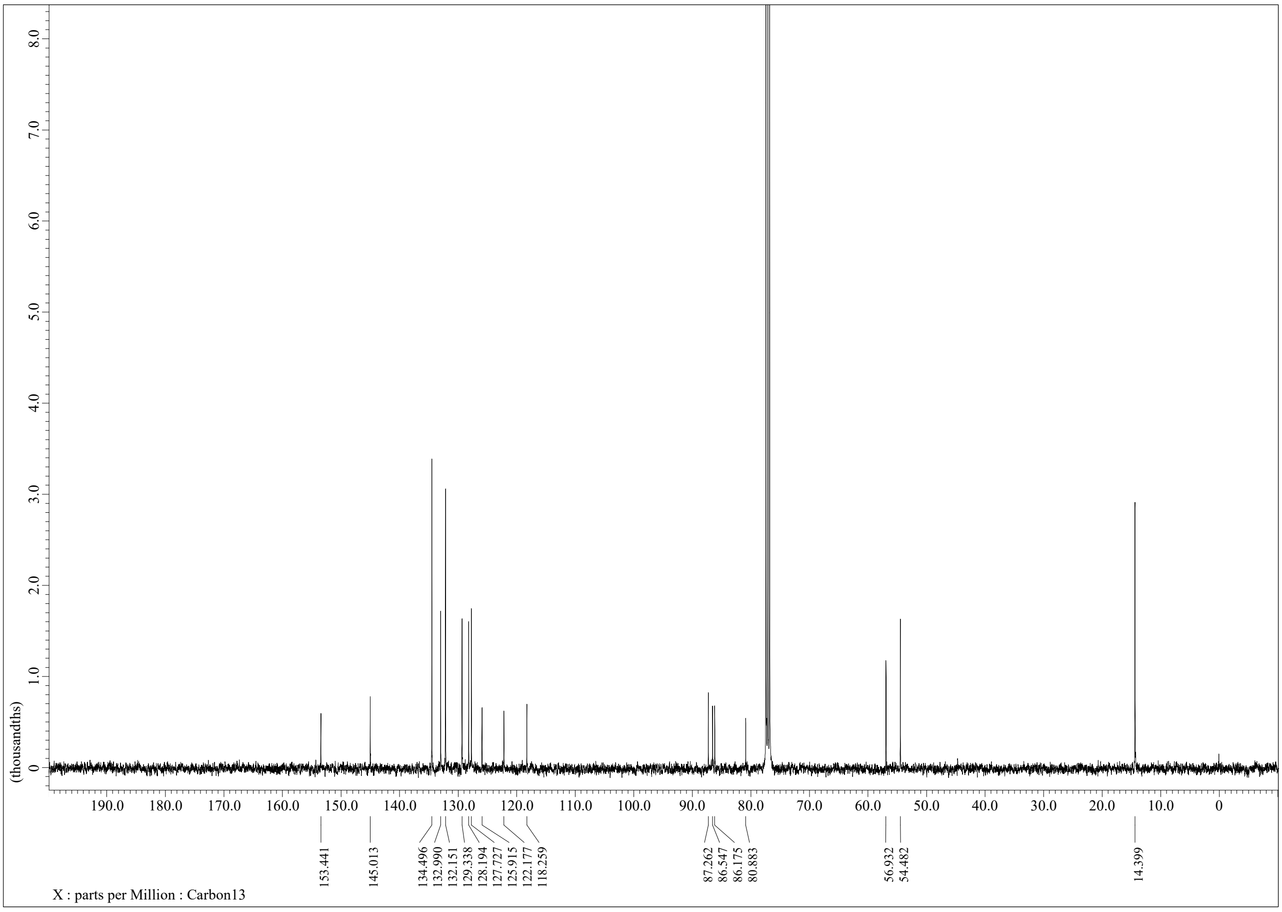

OH
O
O
1a
5.0
4.0
3.0
2.0
1.0
0
abundance
3.05
2.04
1.95
1.03
0.92
2.00
0.83
1.69
1.71
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.613
7.595
7.591
7.485
7.481
7.469
7.403
7.384
7.380
7.366
7.361
7.357
7.316
7.258
7.252
5.088
3.353
1.242
1.228
1.223
1.211
1.013
0.999
0.994
0.981
0.000
X : parts per Million : Proton

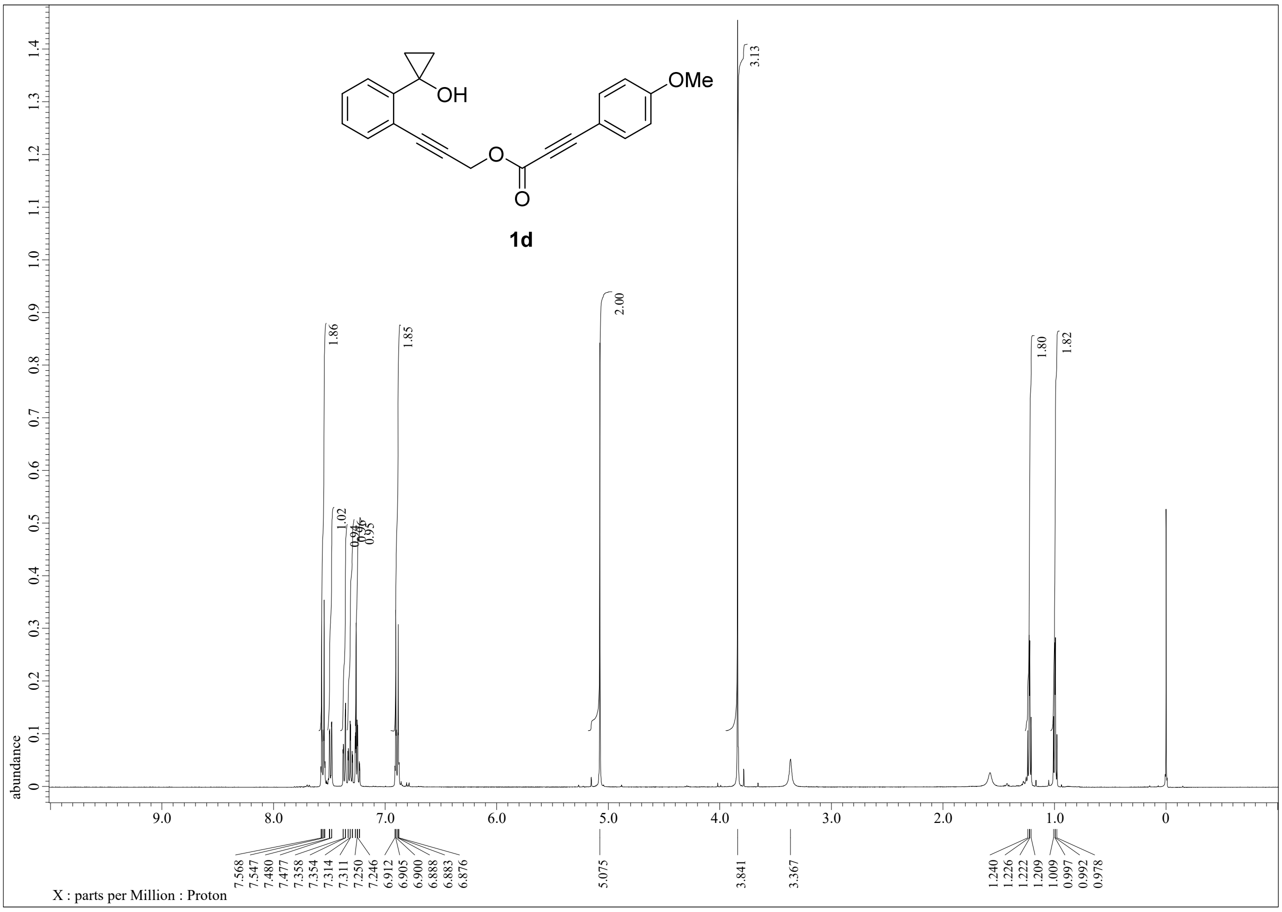

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.670
145.041
133.247
132.971
131.045
129.290
128.718
128.184
127.707
122.235
119.346
87.882
87.414
86.070
79.987
56.923
54.377
14.408
X : parts per Million : Carbon13


OH
CF3
O
O
1b
2.00
1.95
0.94
1.13
0.99
1.04
2.00
0.88
1.80
1.80
abundance
0
1.0
2.0
3.0
4.0
5.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.730
7.709
7.669
7.648
7.508
7.489
7.384
7.367
7.346
7.328
7.309
7.280
7.276
7.243
5.110
3.284
1.242
1.229
1.223
1.210
1.018
1.006
1.001
0.987
X : parts per Million : Proton

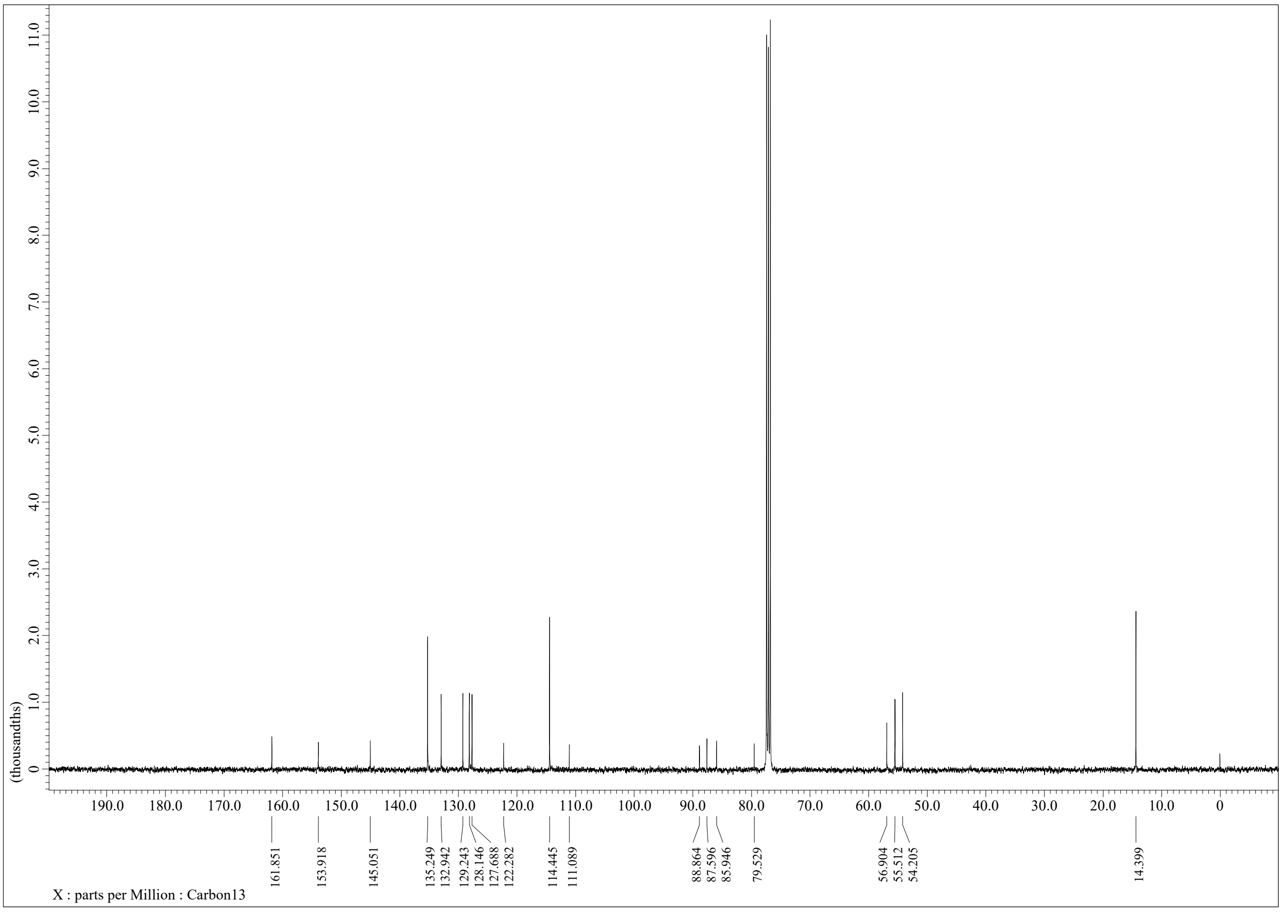

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.193
145.013
133.400
133.018
129.376
128.232
127.746
125.705
125.667
123.160
122.139
87.109
86.289
85.488
81.503
56.932
54.634
14.399
X : parts per Million : Carbon13

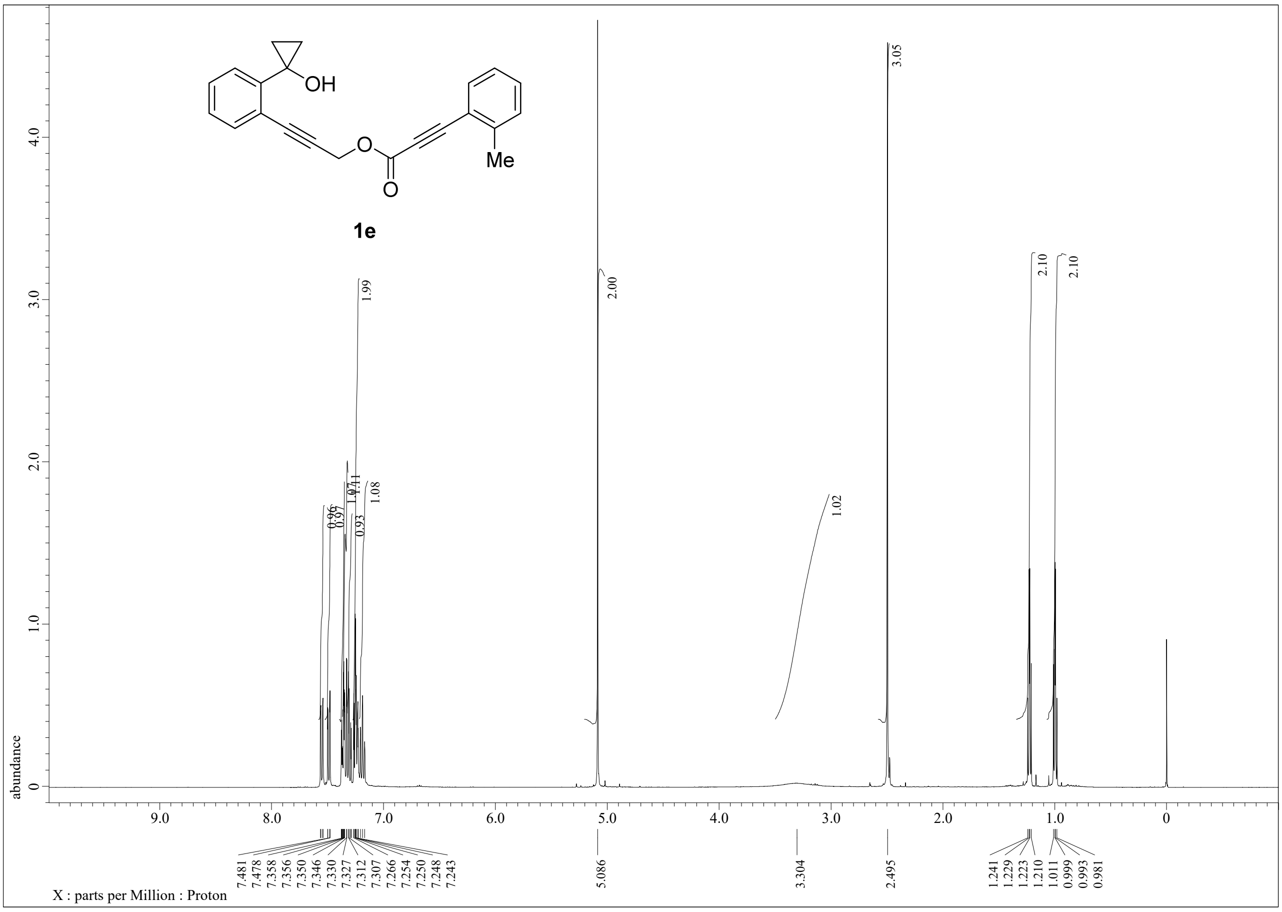

OH
Br
O
O
1c
abundance
0
1.0
2.0
3.0
4.0
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
2.06
2.02
1.13
1.05
1.00
1.14
2.00
0.90
1.85
1.89
7.550 7.529 7.501 7.481 7.470 7.449 7.379 7.361 7.338 7.321 7.303 7.274 7.272 7.236
5.089
3.300
1.237 1.222 1.218 1.206 1.013 0.999 0.995 0.982
X : parts per Million : Proton

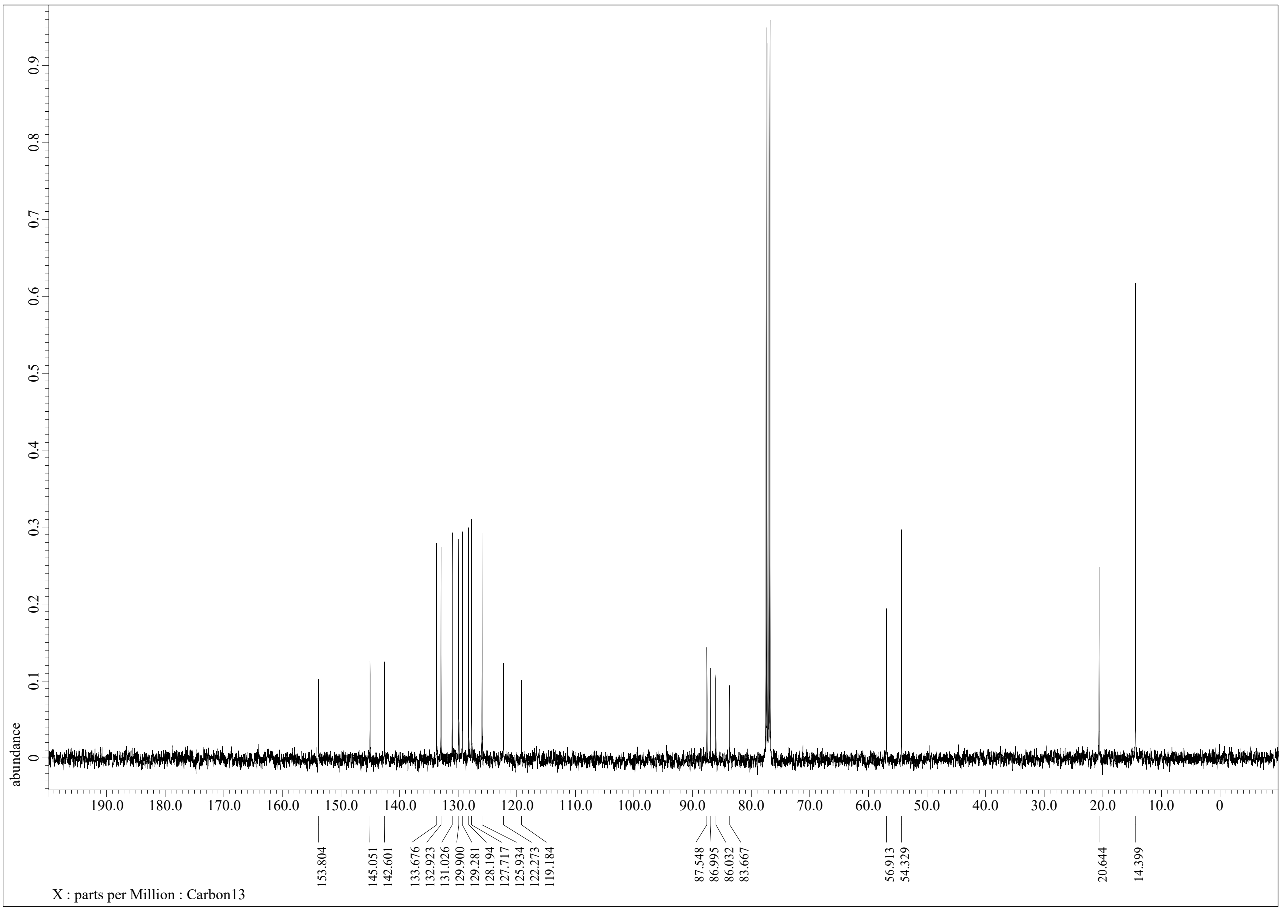

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
153.441
145.013
134.496 132.990 132.151 129.338 128.194 127.727 125.915 122.177 118.259
87.262 86.547 86.175 80.883
56.932 54.482
14.399
X : parts per Million : Carbon13

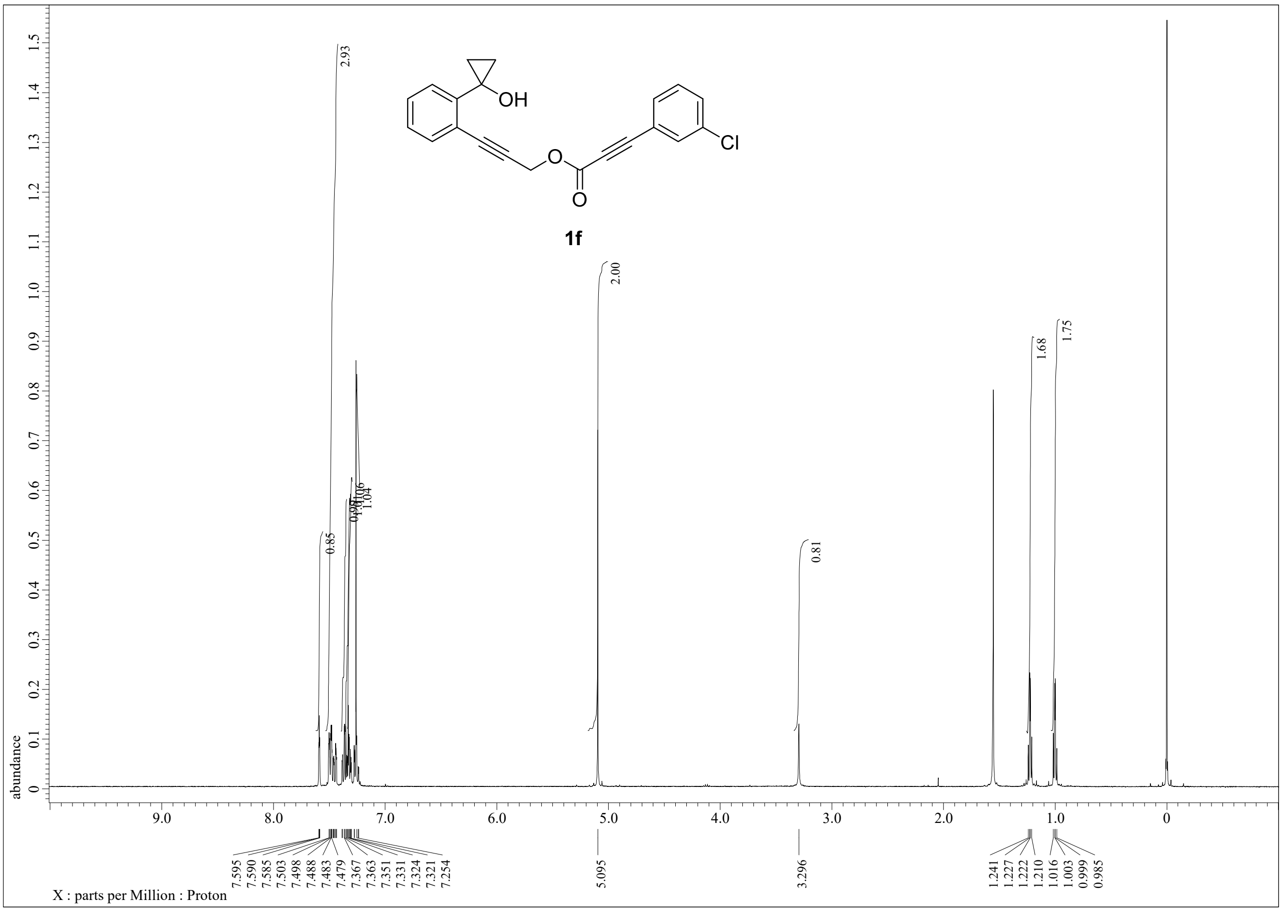

OH
OMe
O
O
abundance
1.86
1.85
1.02
0.94
0.96
0.95
2.00
3.13
1.80
1.82
7.568
7.547
7.480
7.477
7.358
7.354
7.314
7.311
7.250
7.246
6.912
6.905
6.900
6.888
6.883
6.876
5.075
3.841
3.367
1.240
1.226
1.222
1.209
1.009
0.997
0.992
0.978
X : parts per Million : Proton

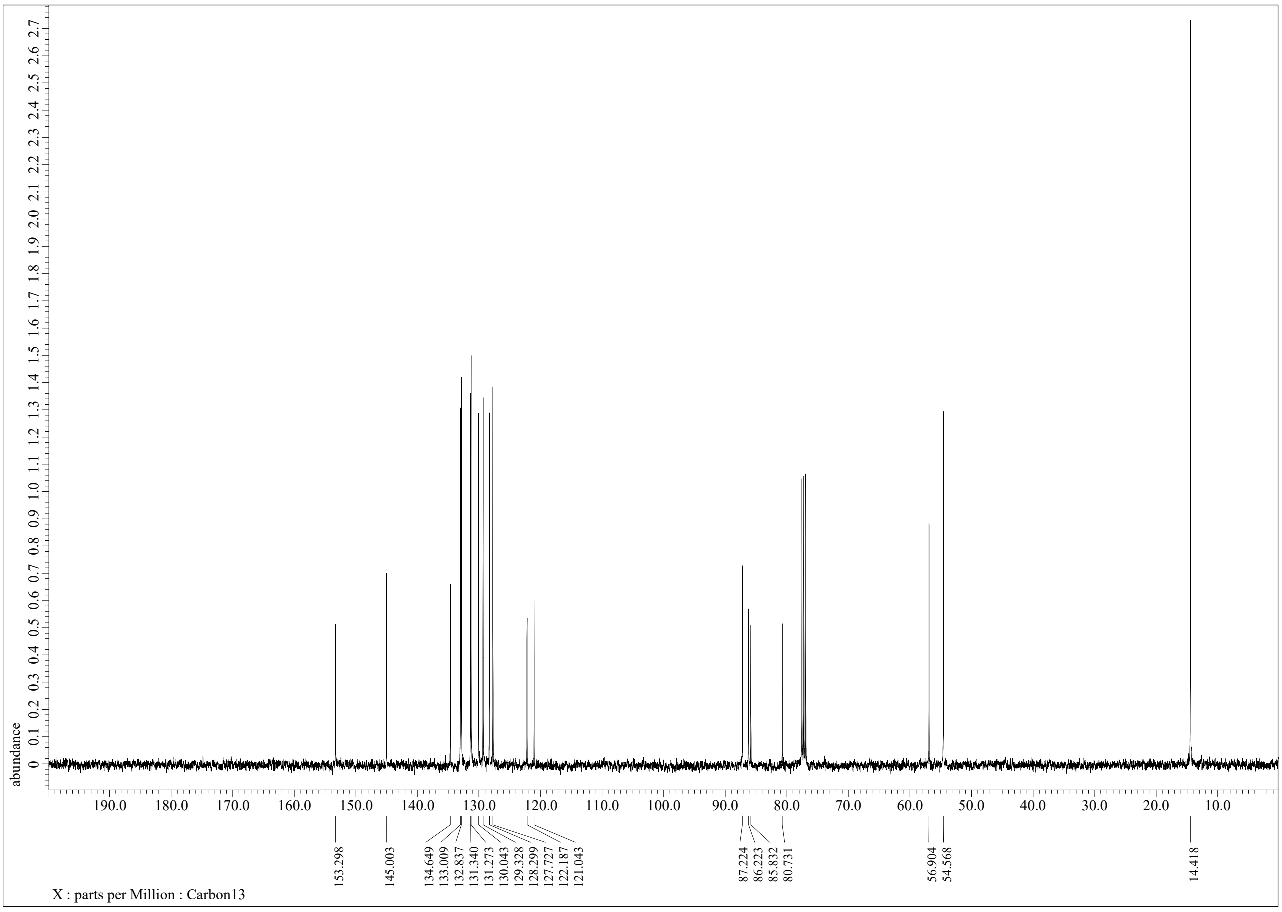
1d

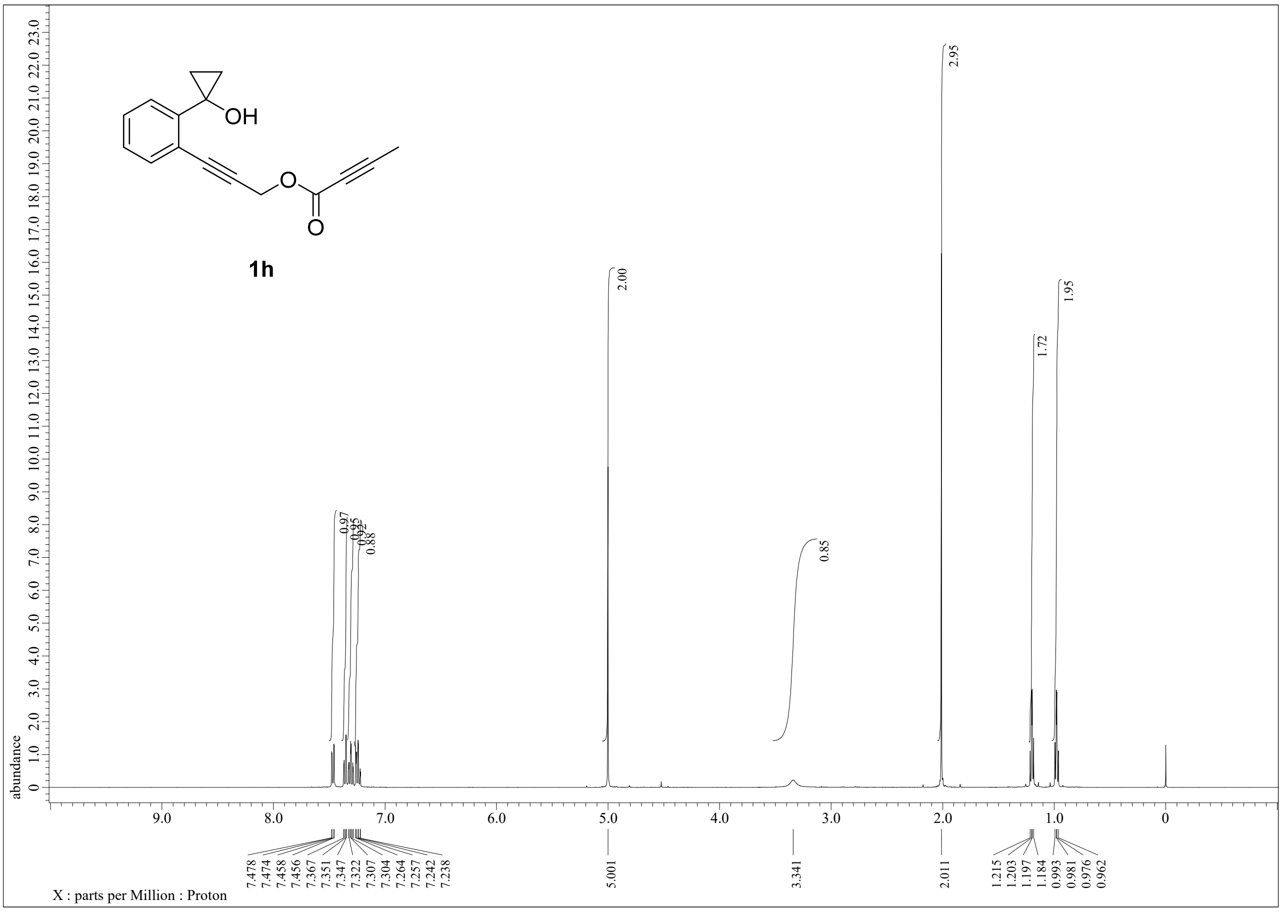

(thousandths)
161.851
153.918
145.051
135.249
132.942
129.243
128.146
127.688
122.282
114.445
111.089
88.864
87.596
85.946
79.529
56.904
55.512
54.205
14.399
X : parts per Million : Carbon13

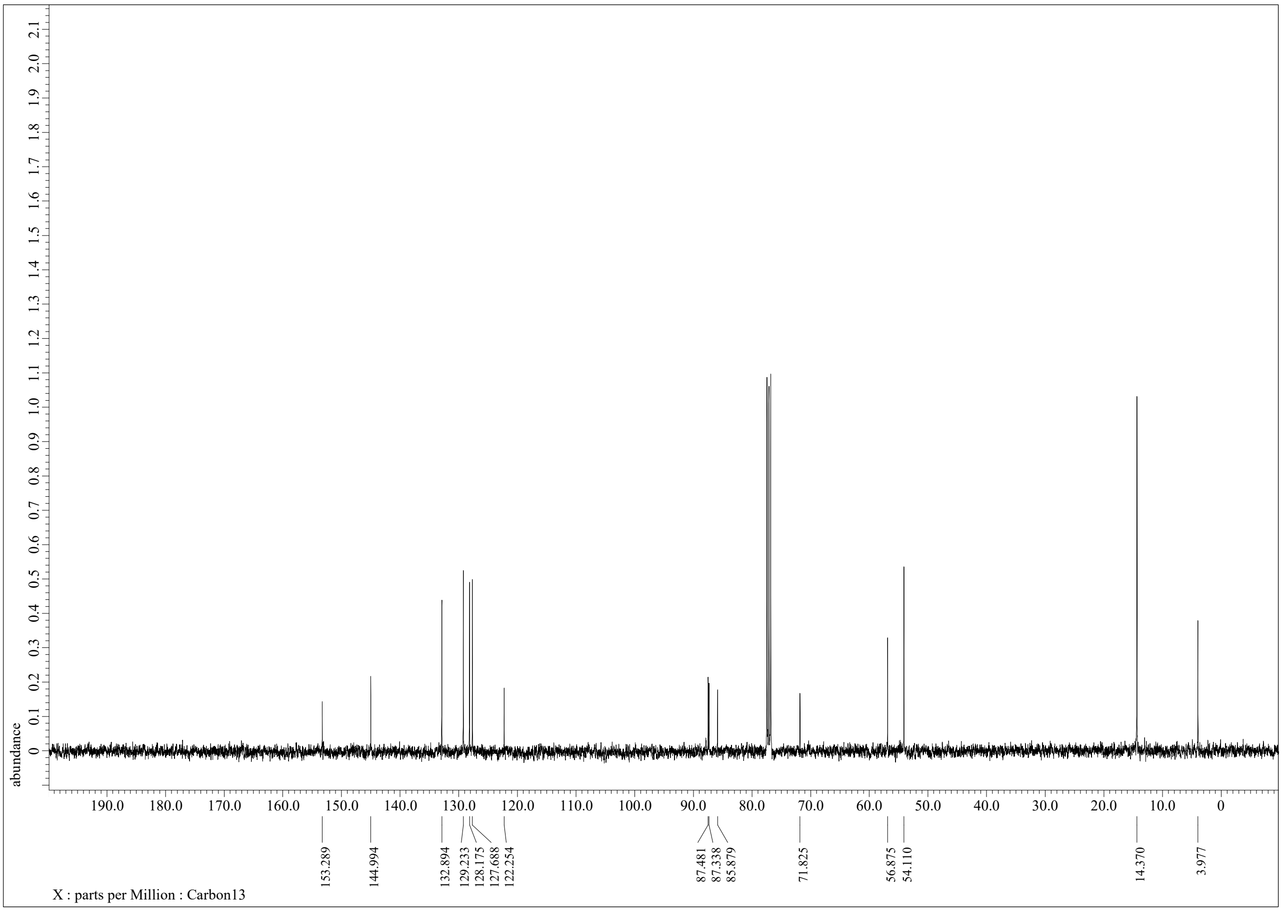

OH
Me
O
O
1e
abundance
0
1.0
2.0
3.0
4.0
0.96
0.97
1.07
1.11
0.93
1.08
1.99
2.00
1.02
3.05
2.10
2.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.481
7.478
7.358
7.356
7.350
7.346
7.330
7.327
7.312
7.307
7.266
7.254
7.250
7.248
7.243
5.086
3.304
2.495
1.241
1.229
1.223
1.210
1.011
0.999
0.993
0.981
X : parts per Million : Proton

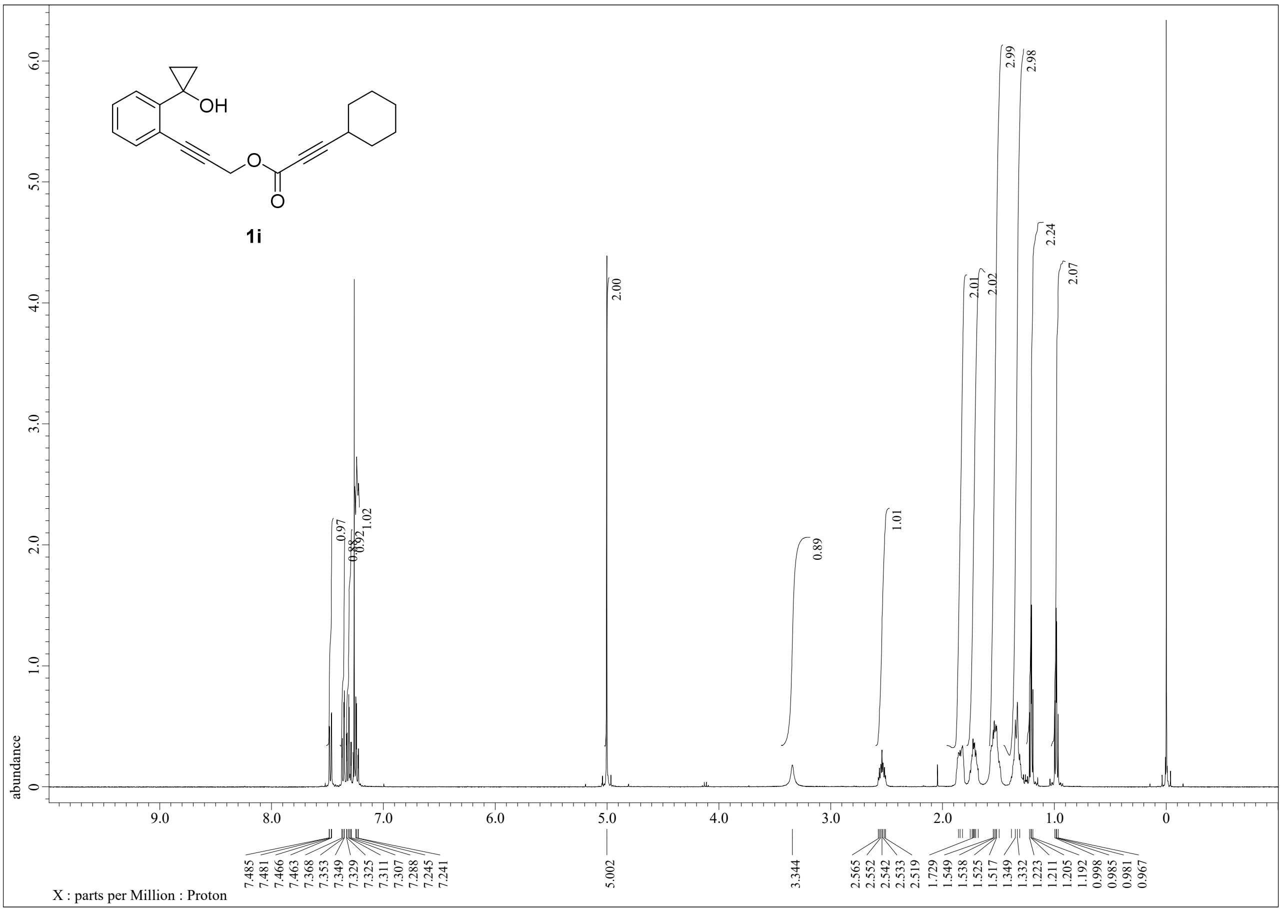

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.804
145.051
142.601
133.676
132.923
131.026
129.900
129.281
128.194
127.717
125.934
122.273
119.184
87.548
86.995
86.032
83.667
56.913
54.329
20.644
14.399
X : parts per Million : Carbon13

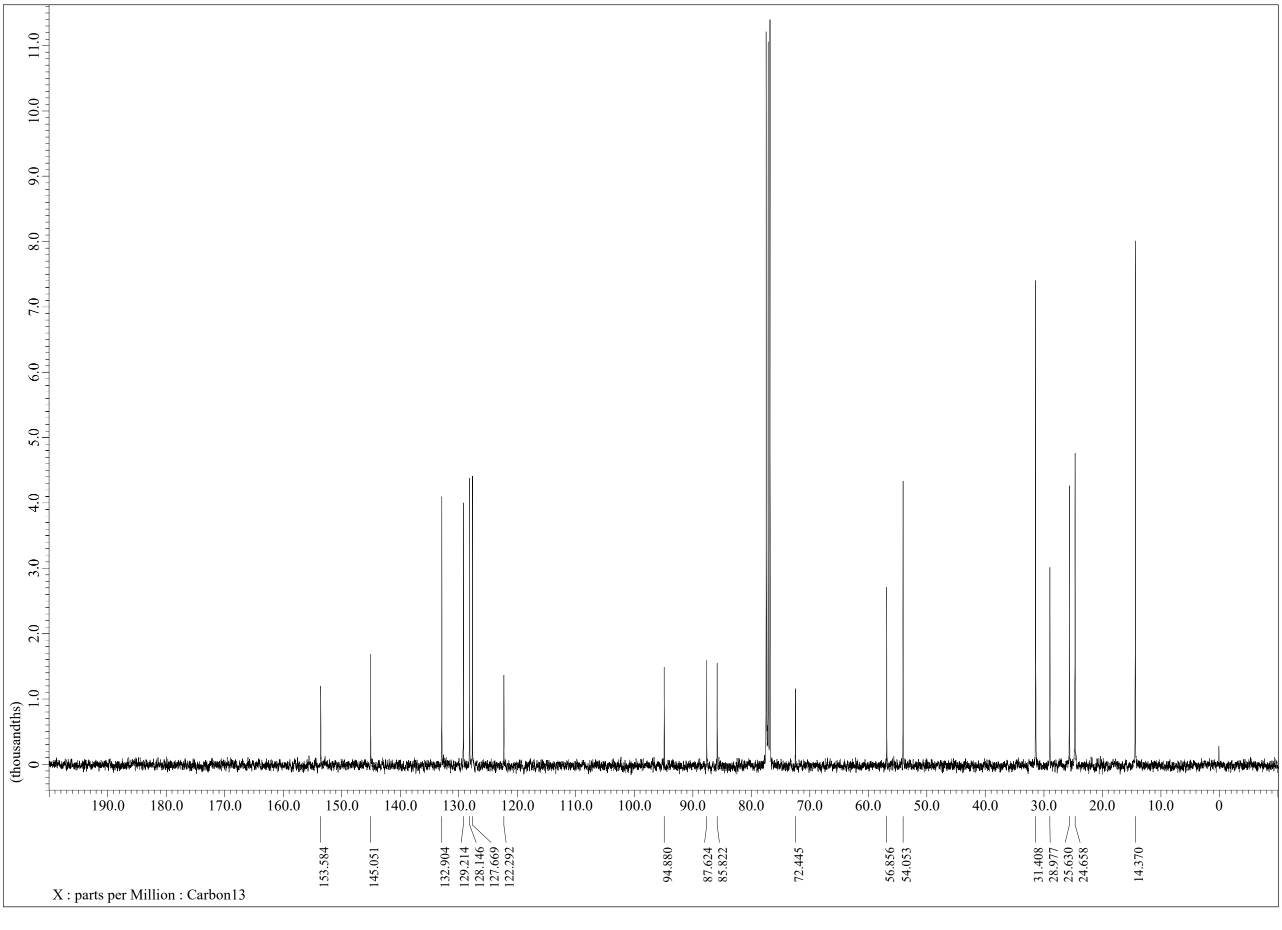

OH
Cl
O
O
1f
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
2.93
0.85
0.98
1.01
1.06
1.04
2.00
0.81
1.68
1.75
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.595
7.590
7.585
7.503
7.498
7.488
7.483
7.479
7.367
7.363
7.351
7.331
7.324
7.321
7.254
5.095
3.296
1.241
1.227
1.222
1.210
1.016
1.003
0.999
0.985
X : parts per Million : Proton

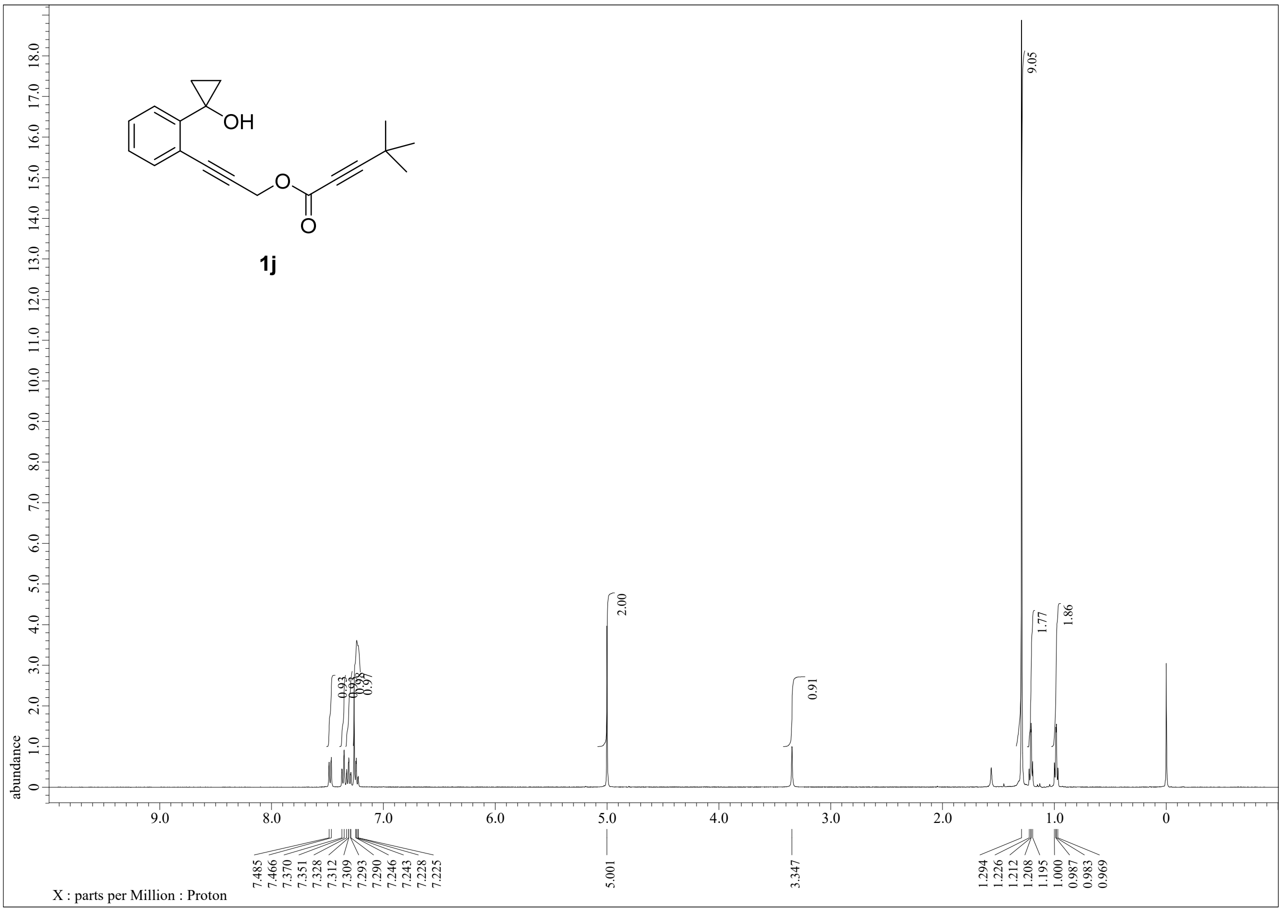

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
153.298
145.003
134.649
133.009
132.837
131.340
131.273
130.043
129.328
128.299
127.727
122.187
121.043
87.224
86.223
85.832
80.731
56.904
54.568
14.418
X : parts per Million : Carbon13

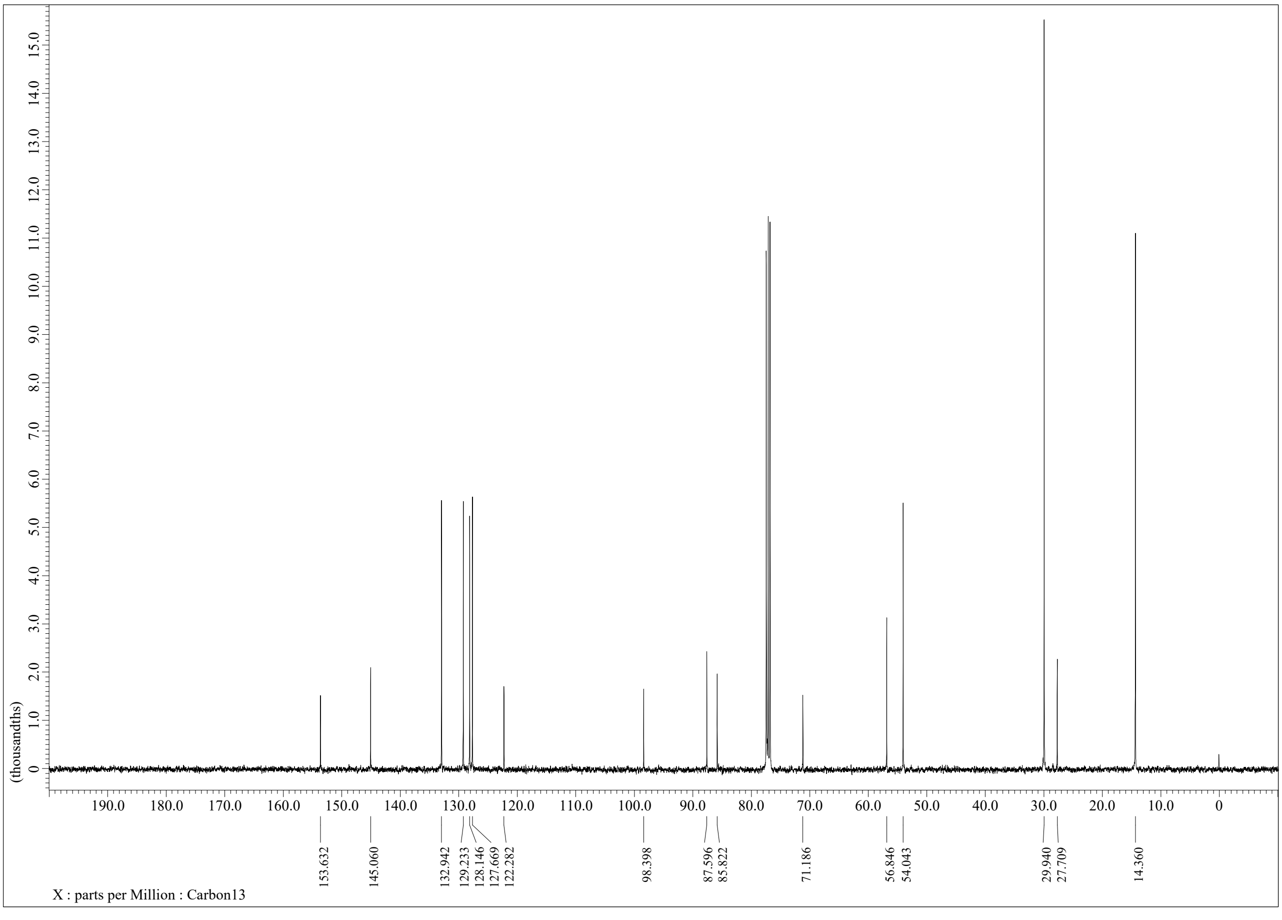

OH
O
O
1h
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
0.97
0.95
0.92
0.88
2.00
0.85
2.95
1.72
1.95
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.478
7.474
7.458
7.456
7.367
7.351
7.347
7.322
7.307
7.304
7.264
7.257
7.242
7.238
5.001
3.341
2.011
1.215
1.203
1.197
1.184
0.993
0.981
0.976
0.962
X : parts per Million : Proton

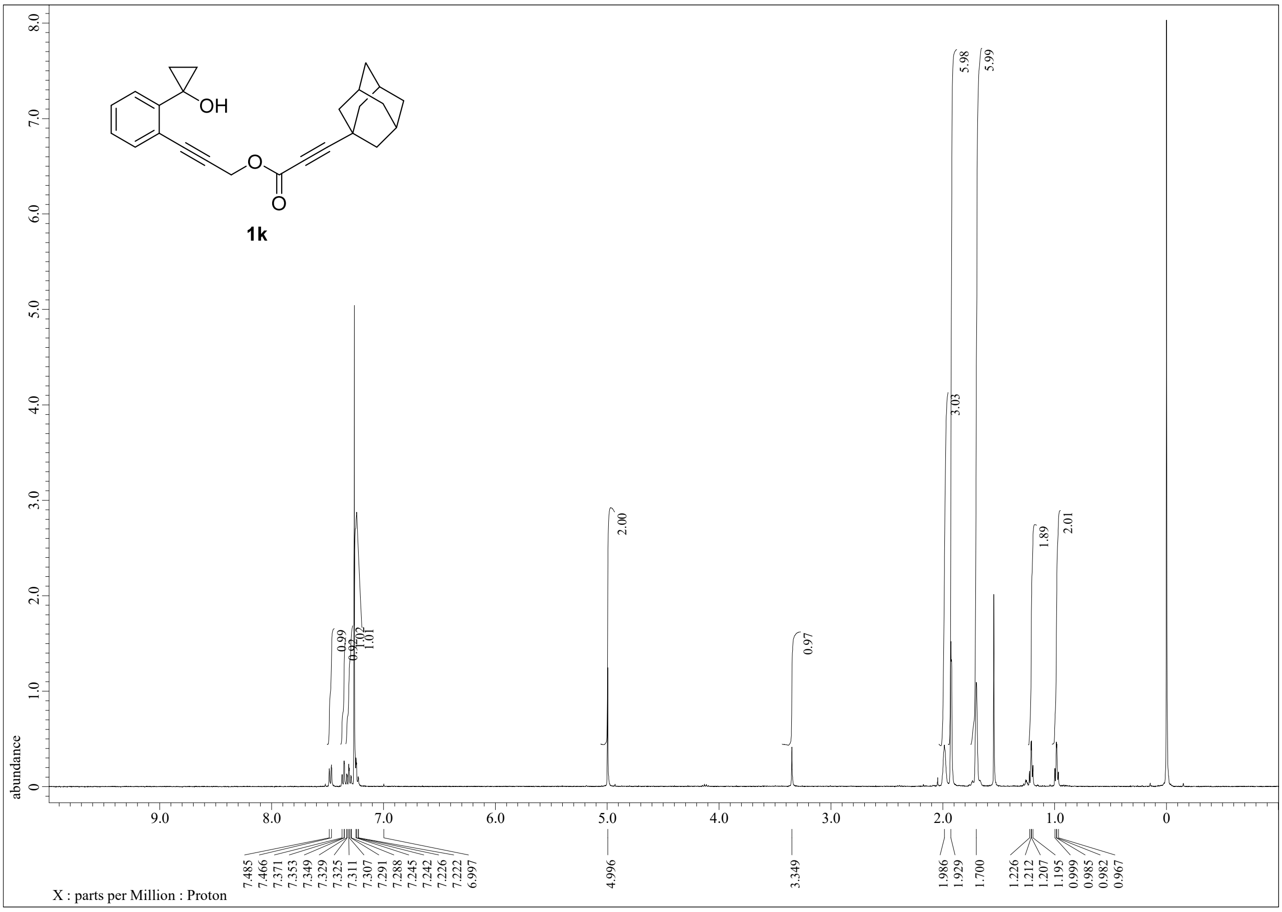

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.289
144.994
132.894
129.233
128.175
127.688
122.254
87.481
87.338
85.879
71.825
56.875
54.110
14.370
3.977
X : parts per Million : Carbon13

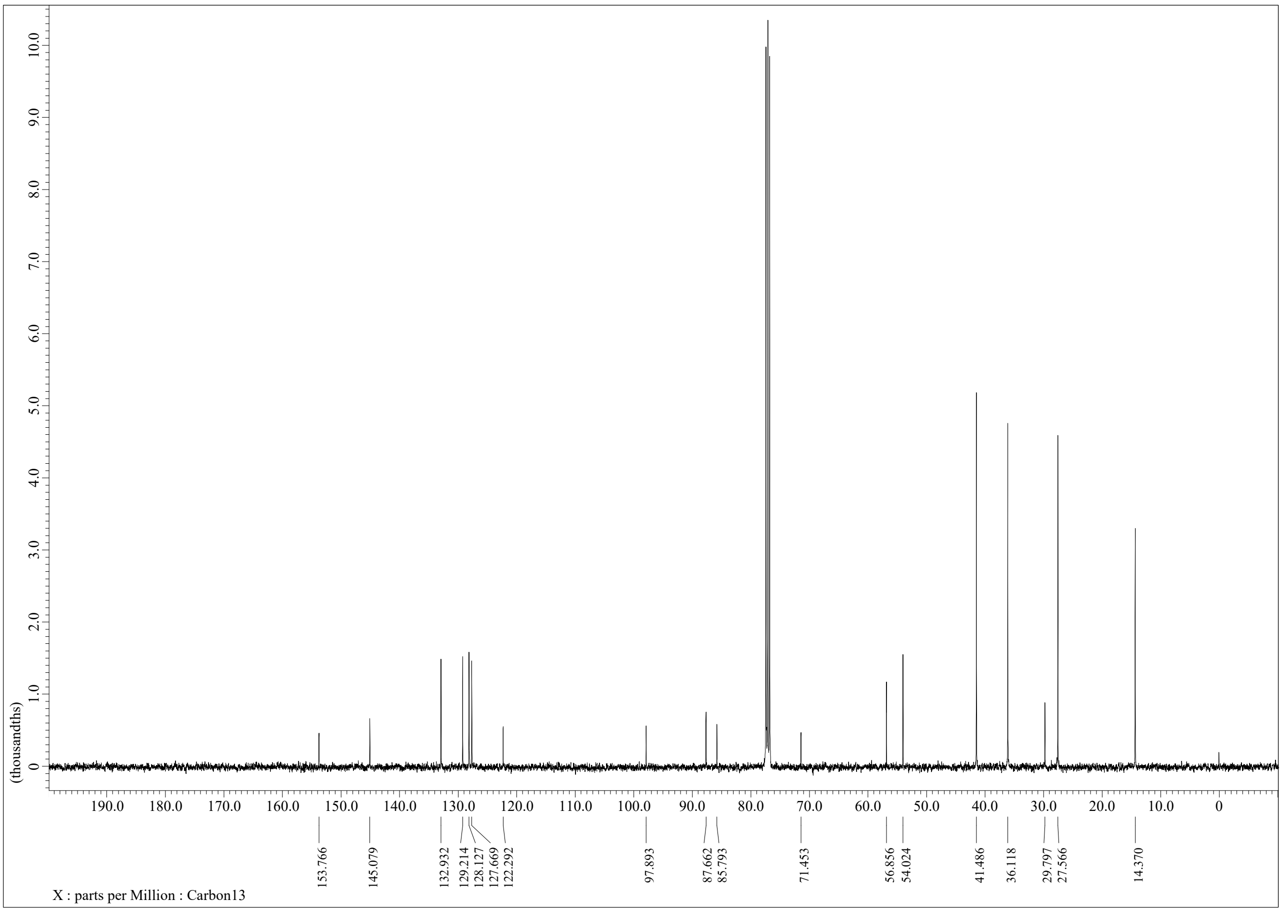

OH
O
O
1i
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
0.97
0.88
0.92
1.02
2.00
0.89
1.01
2.01
2.02
2.99
2.98
2.24
2.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.485
7.481
7.466
7.463
7.368
7.353
7.349
7.329
7.325
7.311
7.307
7.288
7.245
7.241
5.002
3.344
2.565
2.552
2.542
2.533
2.519
1.729
1.549
1.538
1.525
1.517
1.349
1.332
1.223
1.211
1.205
1.192
0.998
0.985
0.981
0.967
X : parts per Million : Proton

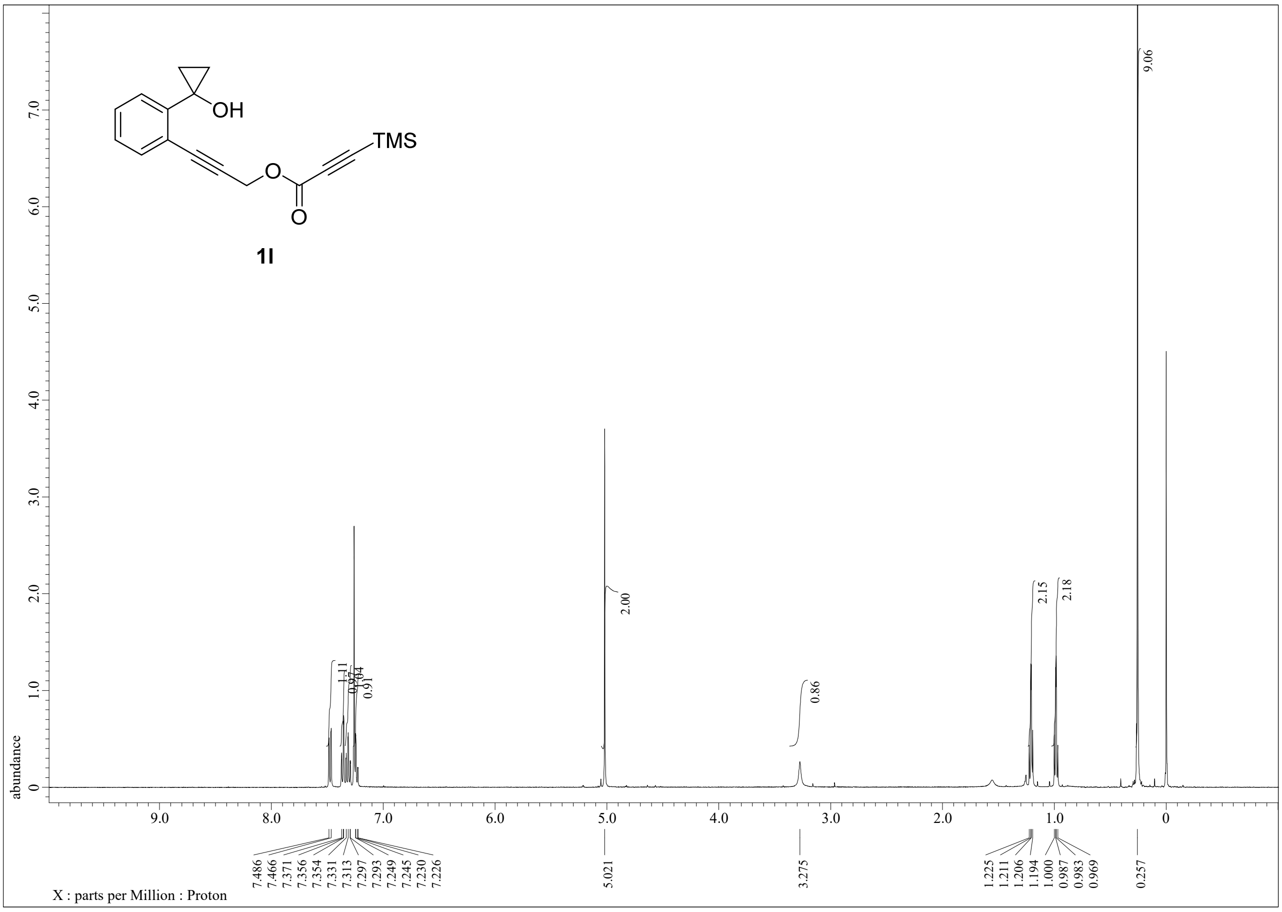

(thousandths)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.584
145.051
132.904
129.214
128.146
127.669
122.292
94.880
87.624
85.822
72.445
56.856
54.053
31.408
28.977
25.630
24.658
14.370
X : parts per Million : Carbon13

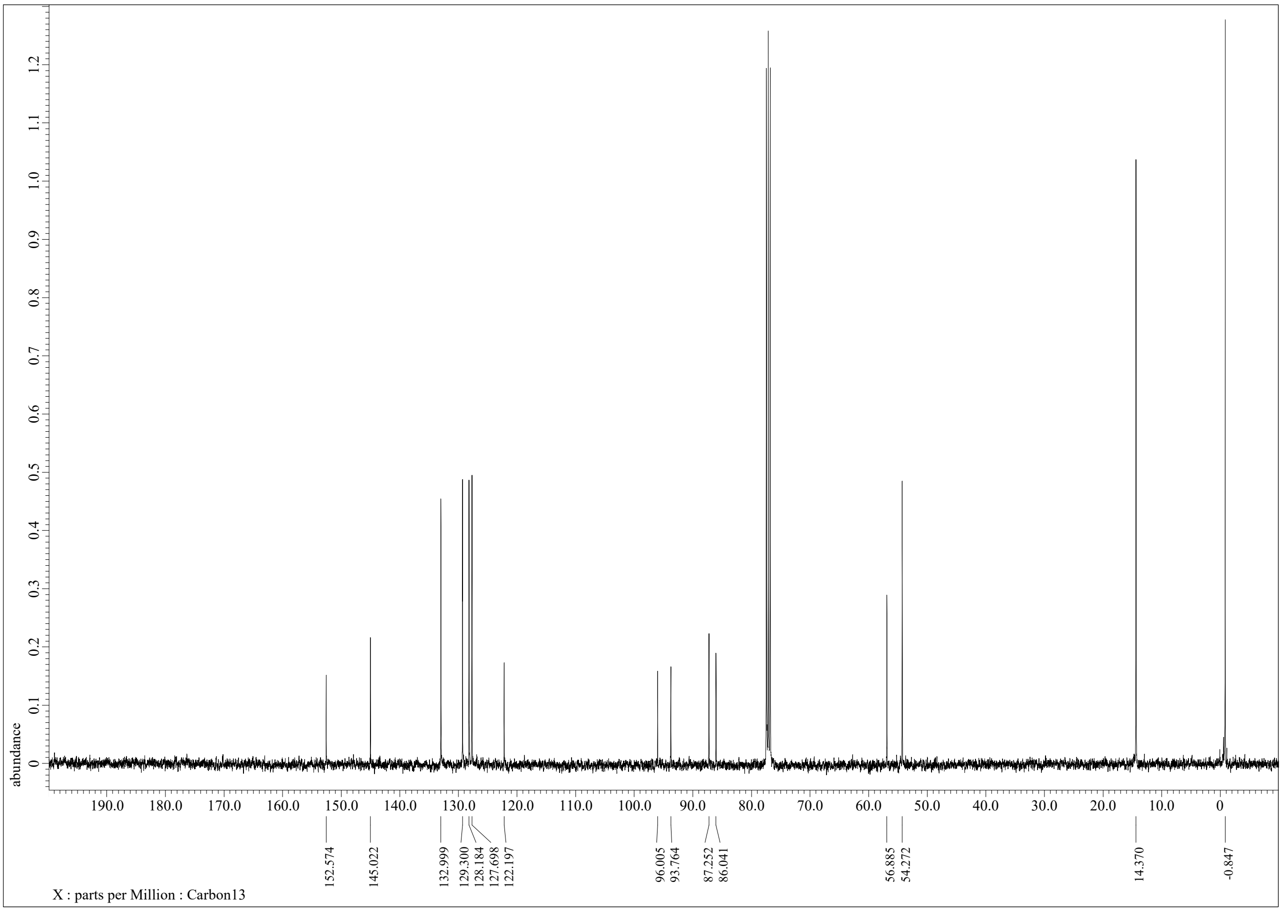

OH
O
O
1j
abundance
9.05
2.00
1.77
1.86
0.91
0.93
0.93
0.98
0.97
7.485
7.466
7.370
7.351
7.328
7.312
7.309
7.293
7.290
7.246
7.243
7.228
7.225
5.001
3.347
1.294
1.226
1.212
1.208
1.195
1.000
0.987
0.983
0.969
X : parts per Million : Proton

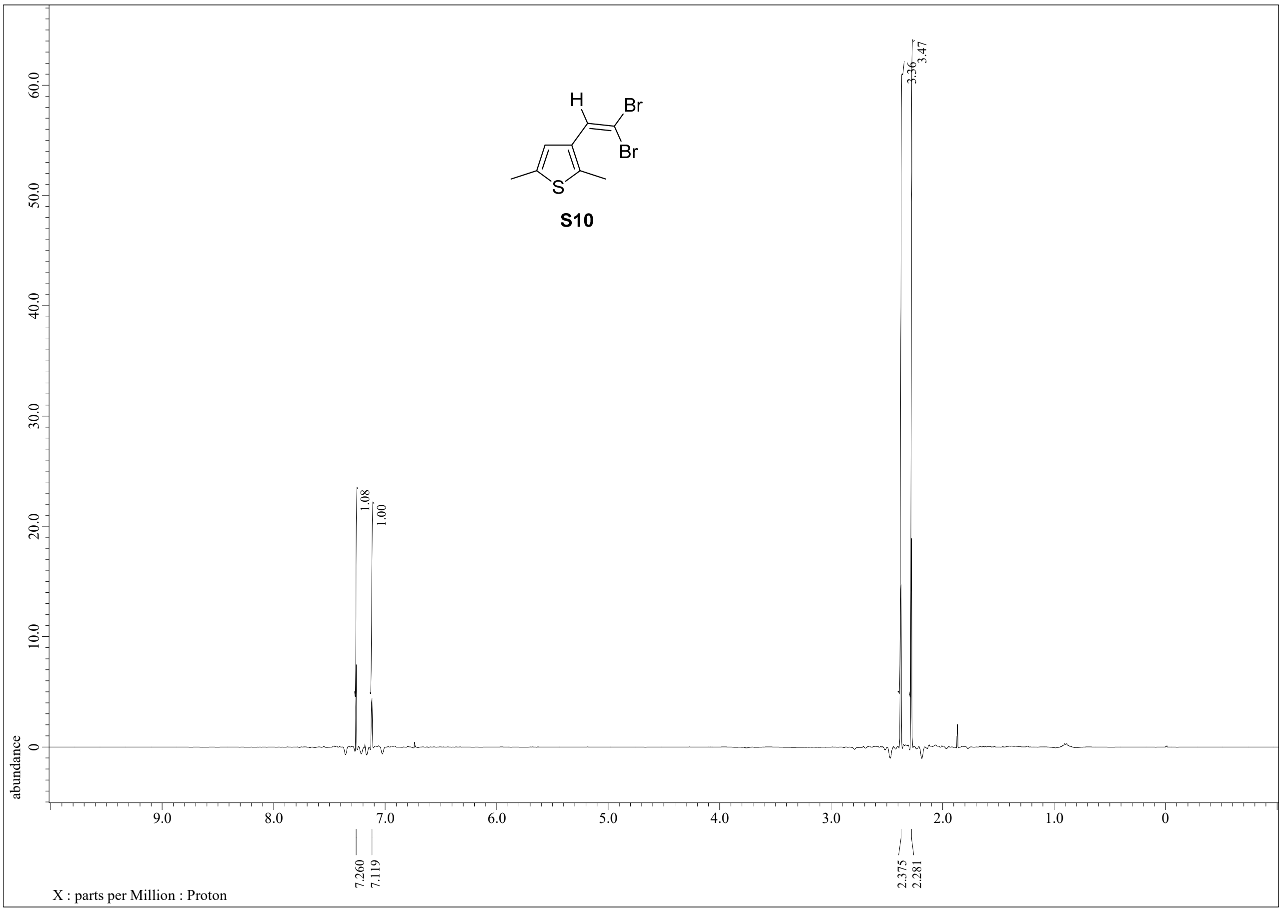

(thousandths)
153.632
145.060
132.942
129.233
128.146
127.669
122.282
98.398
87.596
85.822
71.186
56.846
54.043
29.940
27.709
14.360
X : parts per Million : Carbon13


OH
O
O
1k
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.99
0.92
1.02
1.01
2.00
0.97
3.03
5.98
5.99
1.89
2.01
7.485
7.466
7.371
7.353
7.349
7.329
7.325
7.311
7.307
7.291
7.288
7.245
7.242
7.226
7.222
6.997
4.996
3.349
1.986
1.929
1.700
1.226
1.212
1.207
1.195
0.999
0.985
0.982
0.967
X : parts per Million : Proton

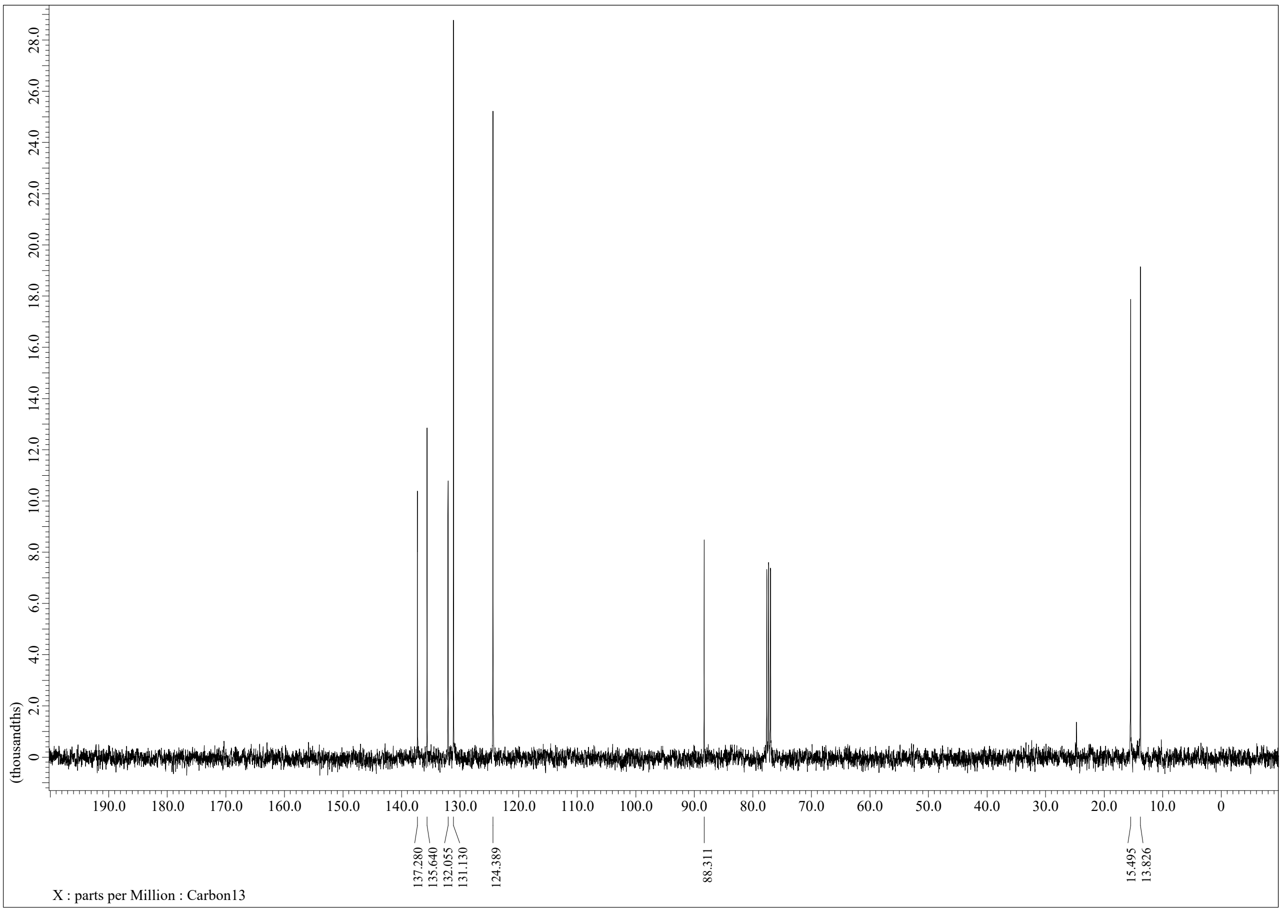

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.766
145.079
132.932
129.214
128.127
127.669
122.292
97.893
87.662
85.793
71.453
56.856
54.024
41.486
36.118
29.797
27.566
14.370
X : parts per Million : Carbon13


OH
O
O
TMS
1l
9.06
2.00
1.11
0.97
1.04
0.91
0.86
2.15
2.18
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.486
7.466
7.371
7.356
7.354
7.331
7.313
7.297
7.293
7.249
7.245
7.230
7.226
5.021
3.275
1.225
1.211
1.206
1.194
1.000
0.987
0.983
0.969
0.257
X : parts per Million : Proton

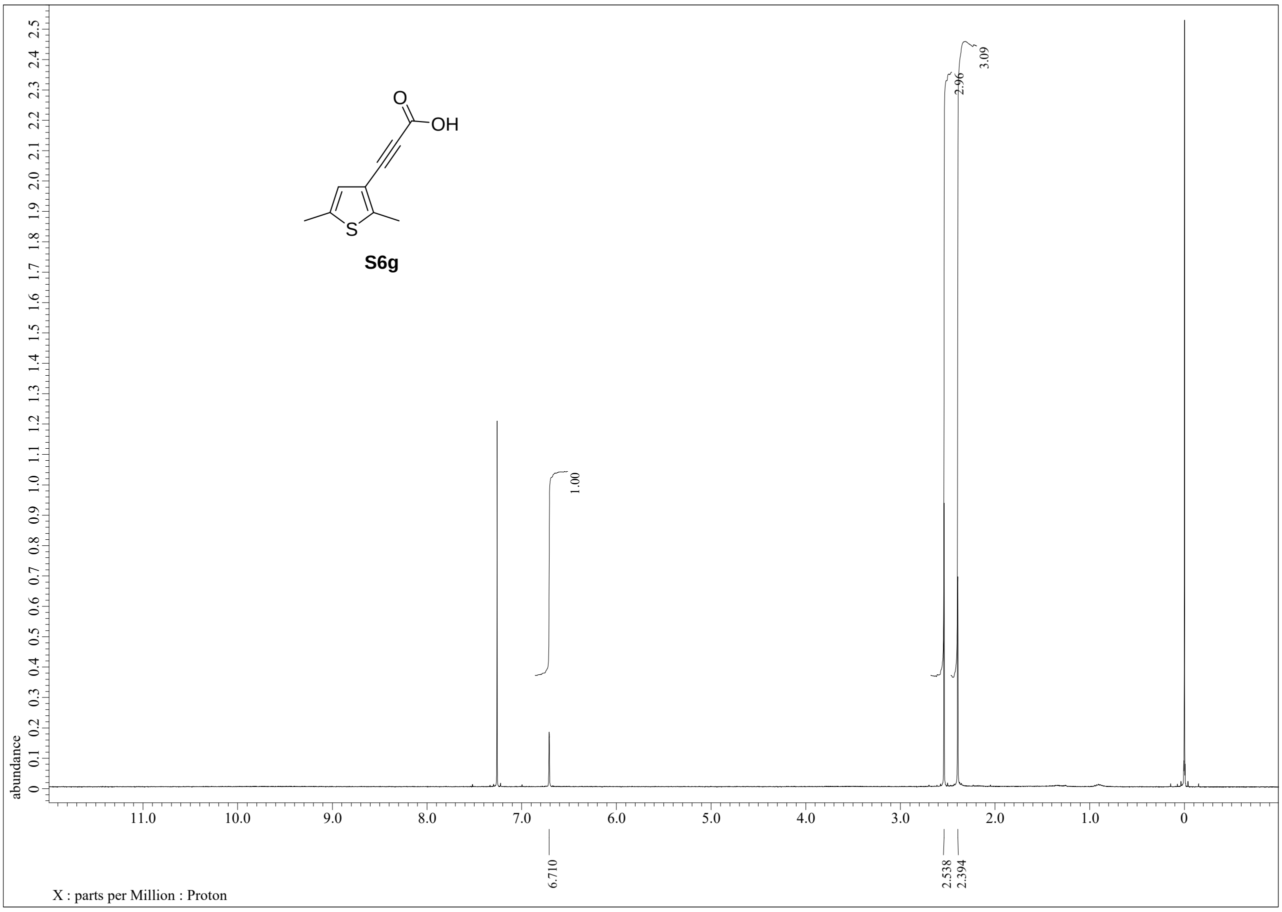

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
152.574
145.022
132.999
129.300
128.184
127.698
122.197
96.005
93.764
87.252
86.041
56.885
54.272
14.370
-0.847
X : parts per Million : Carbon13

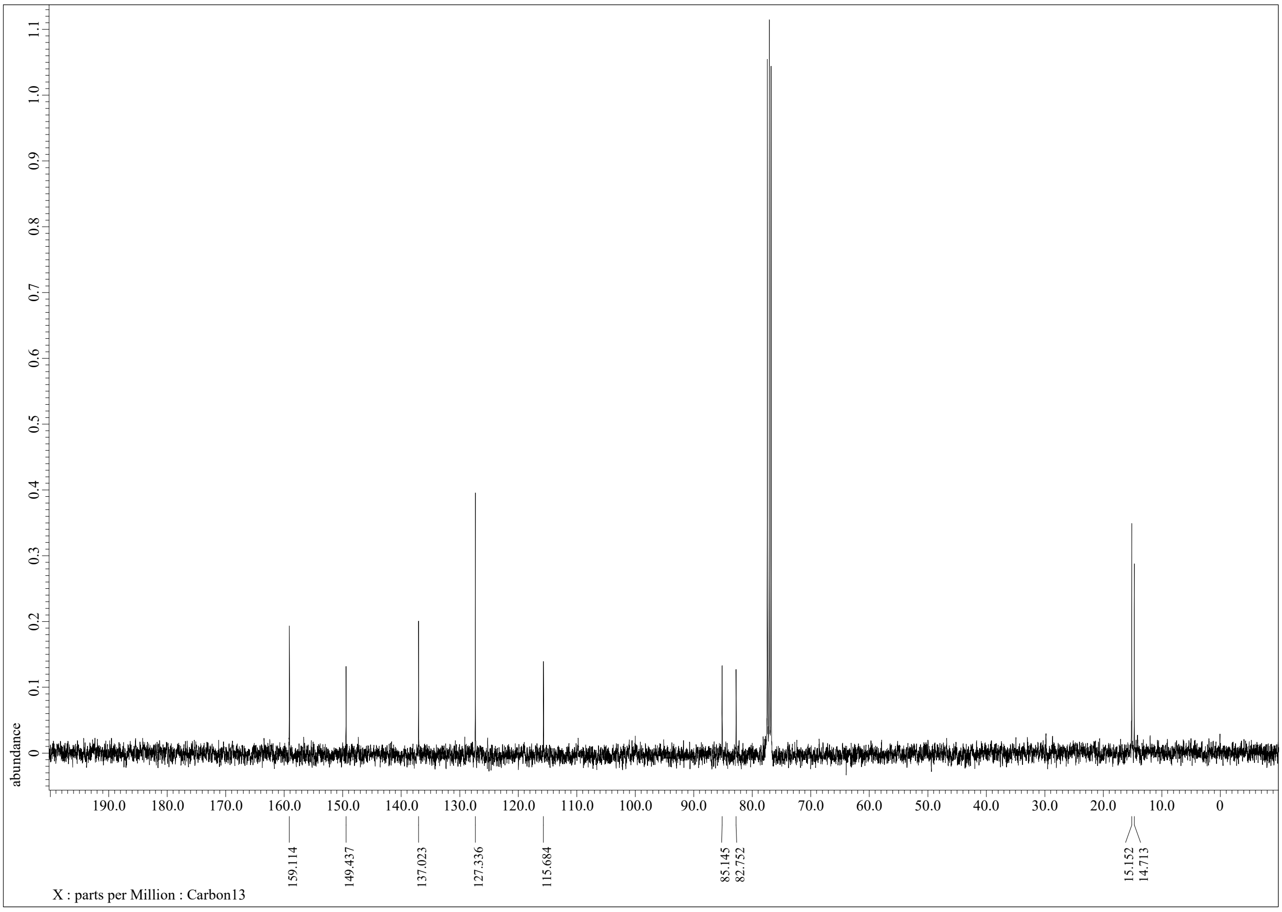


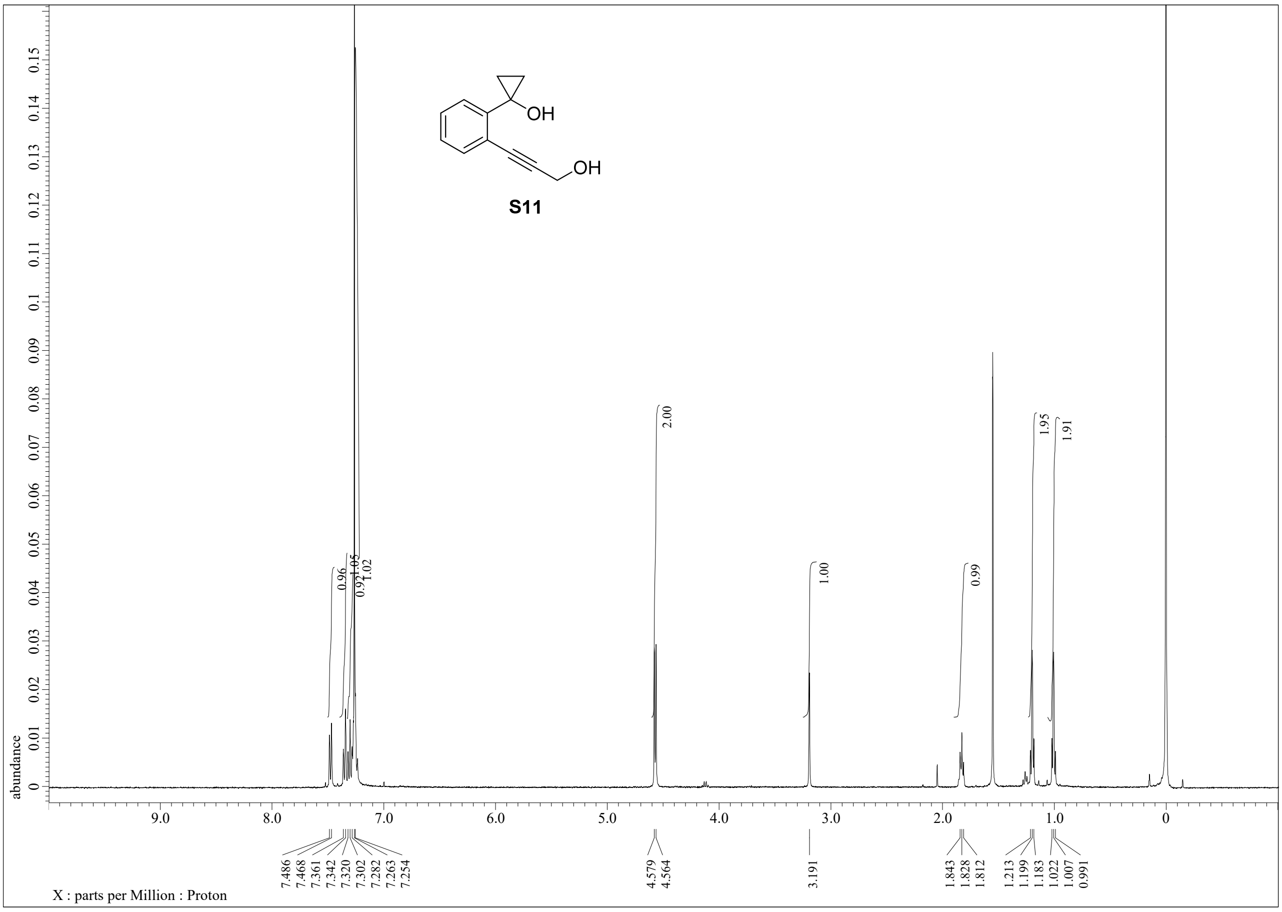
H
Br
Br
S
S10
3.36
3.47
1.08
1.00
abundance
0
10.0
20.0
30.0
40.0
50.0
60.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
7.119
2.375
2.281
X : parts per Million : Proton

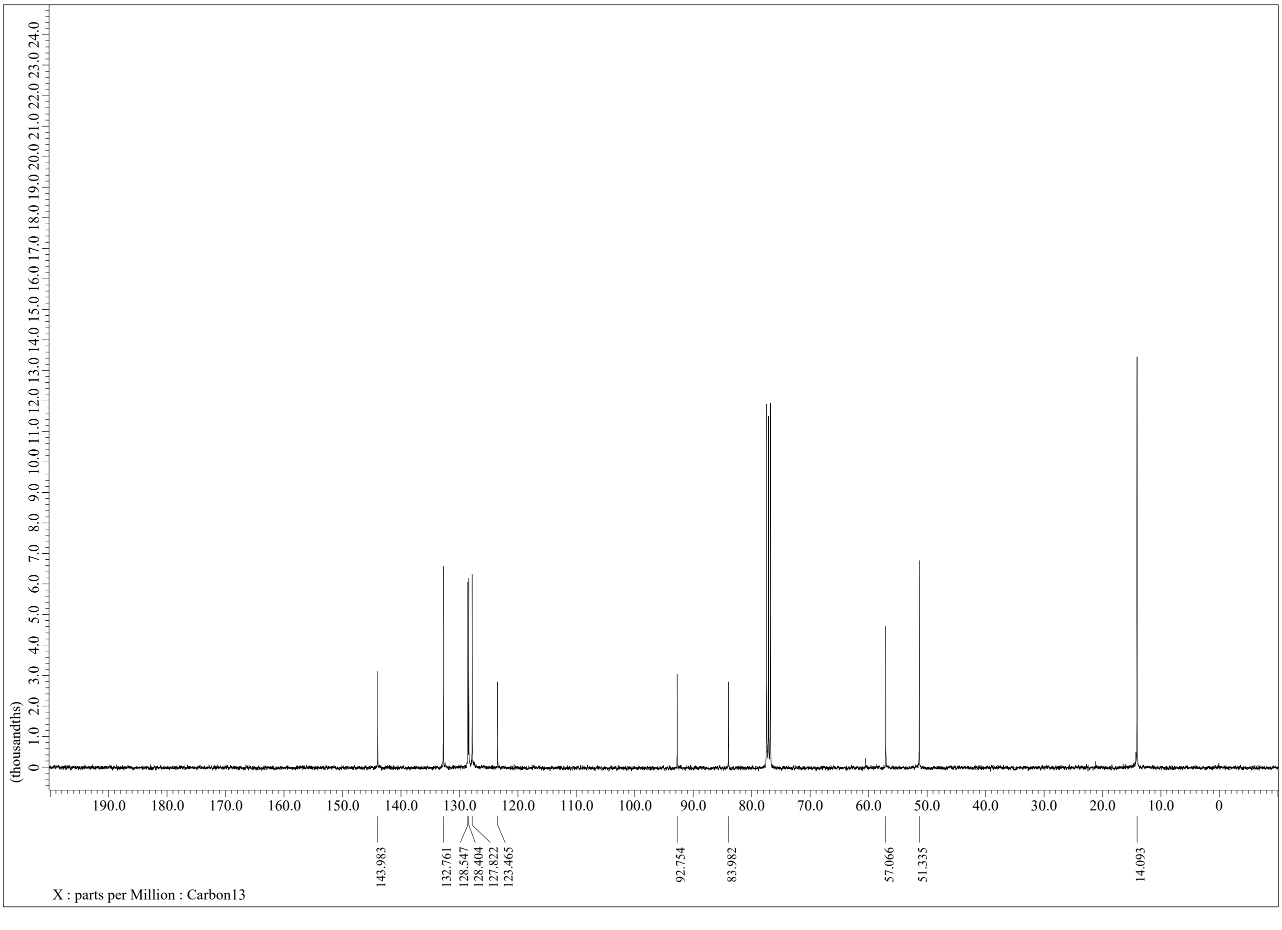


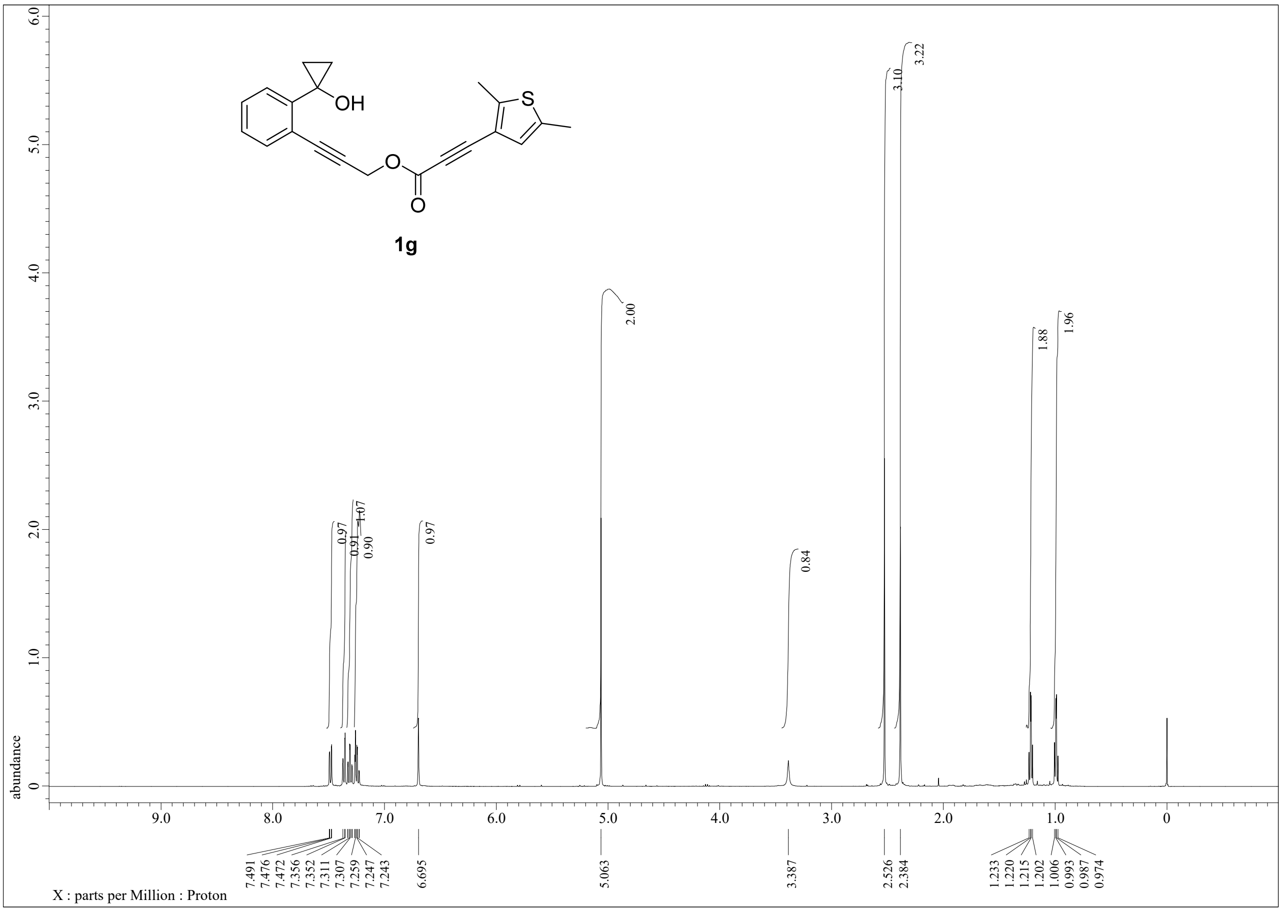
(thousandths)
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
28.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
137.280
135.640
132.055
131.130
124.389
88.311
15.495
13.826
X : parts per Million : Carbon13

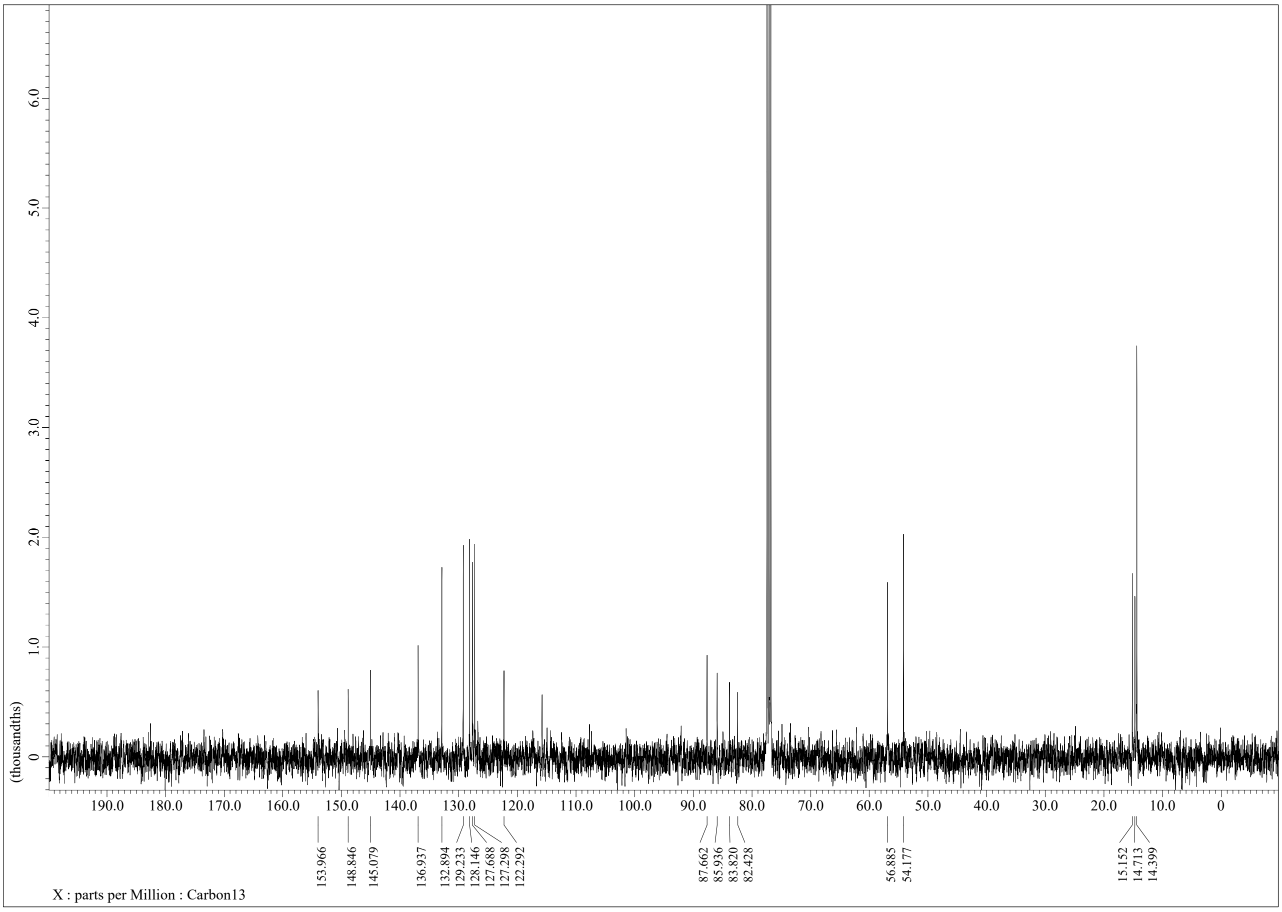

O
OH
S
S6g
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
1.00
2.96
3.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
6.710
2.538
2.394
X : parts per Million : Proton

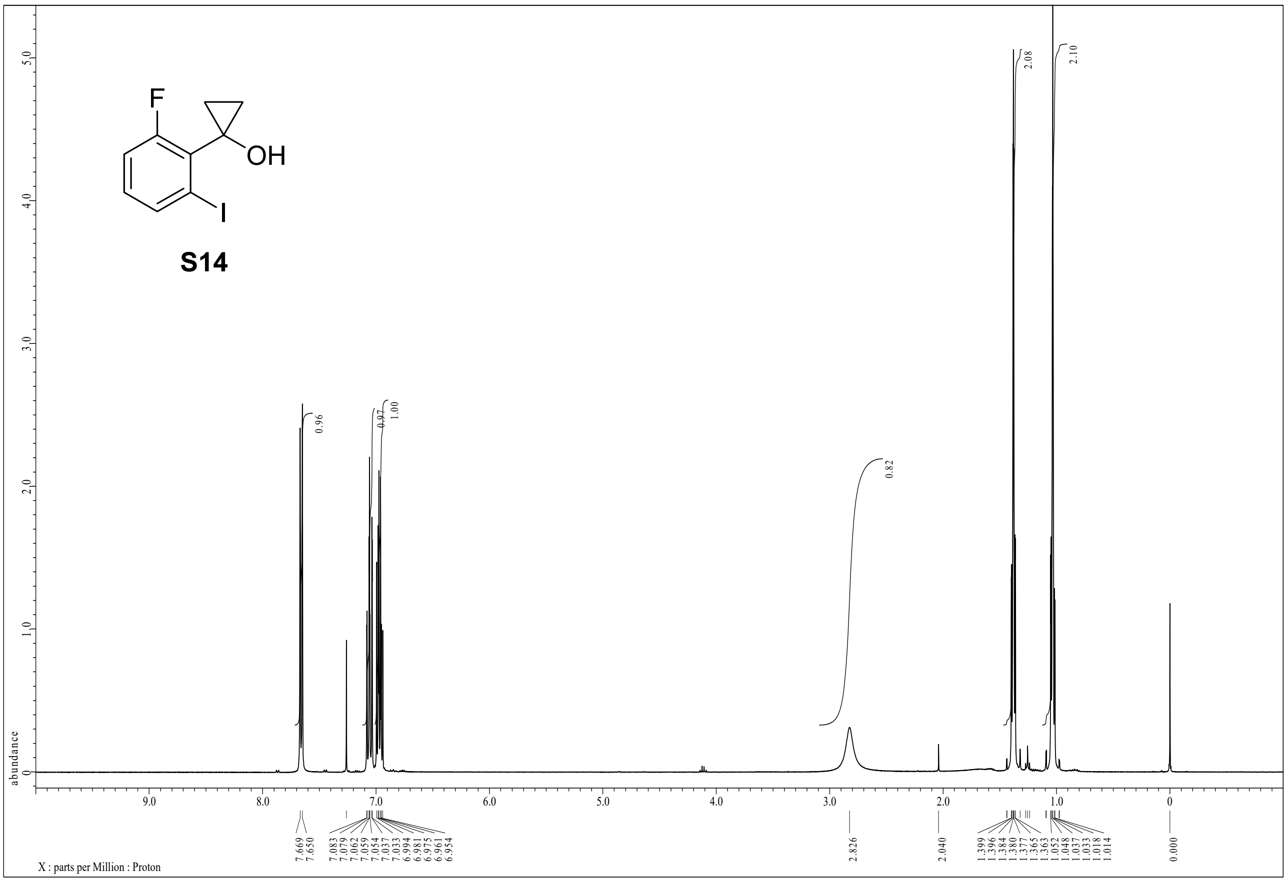

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.114
149.437
137.023
127.336
115.684
85.145
82.752
15.152
14.713
X : parts per Million : Carbon13

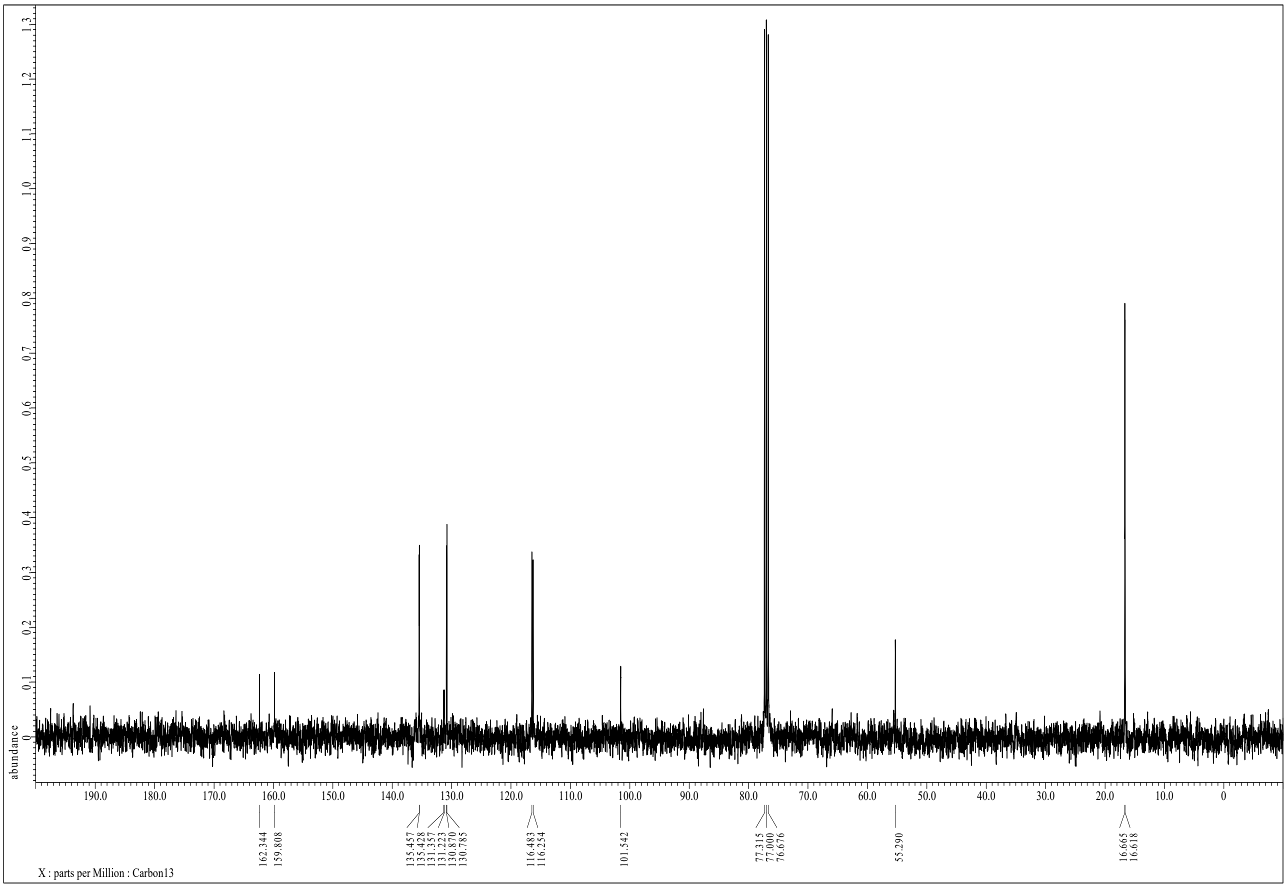

S11
OH
OH
abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
0.96
1.05
0.93
1.02
2.00
1.00
0.99
1.95
1.91
7.486 7.468 7.361 7.342 7.320 7.302 7.282 7.263 7.254
4.579 4.564
3.191
1.843 1.828 1.812
1.213 1.199 1.183 1.022 1.007 0.991
X : parts per Million : Proton

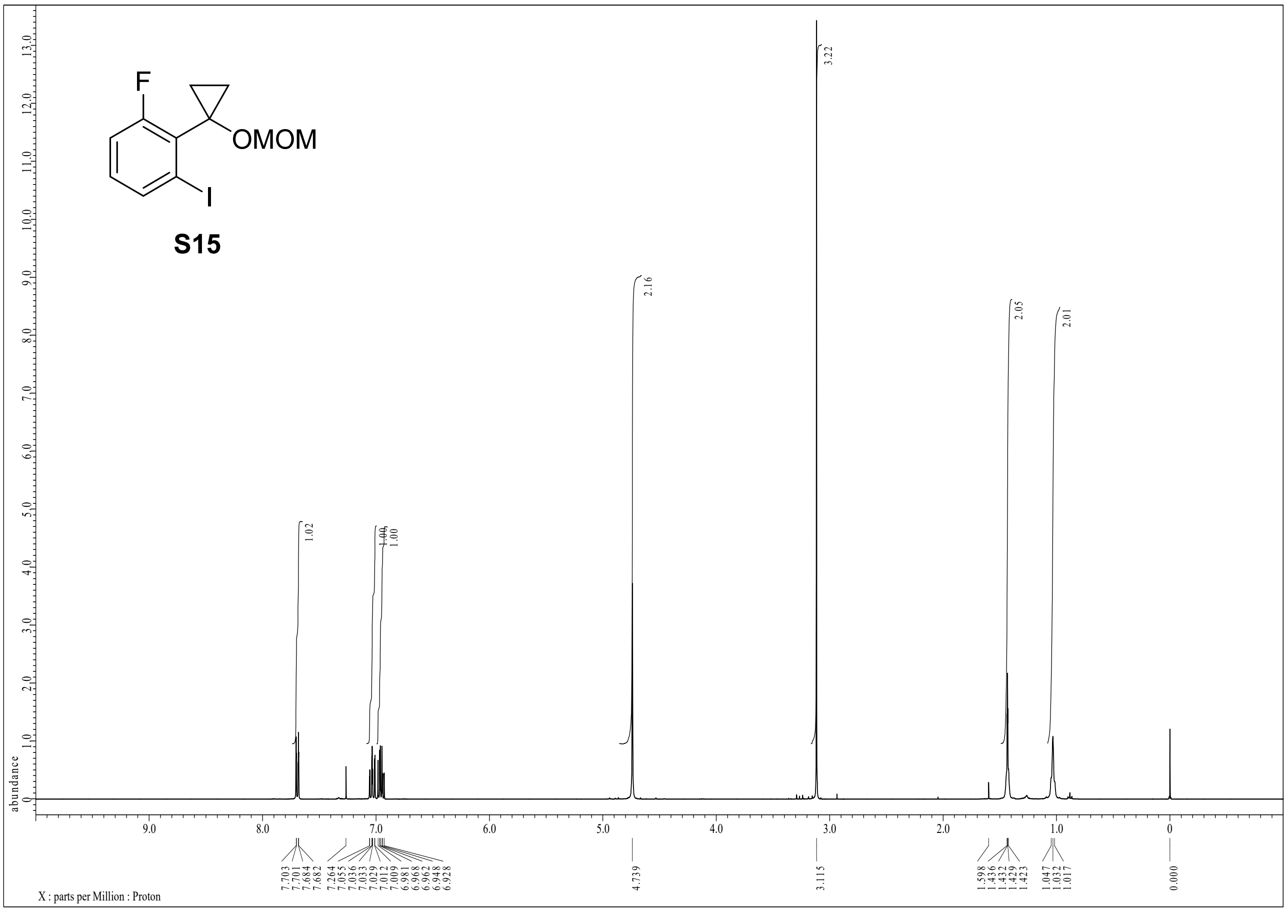

(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
143.983
132.761 128.547 128.404 127.822 123.465
92.754
83.982
57.066
51.335
14.093
X : parts per Million : Carbon13

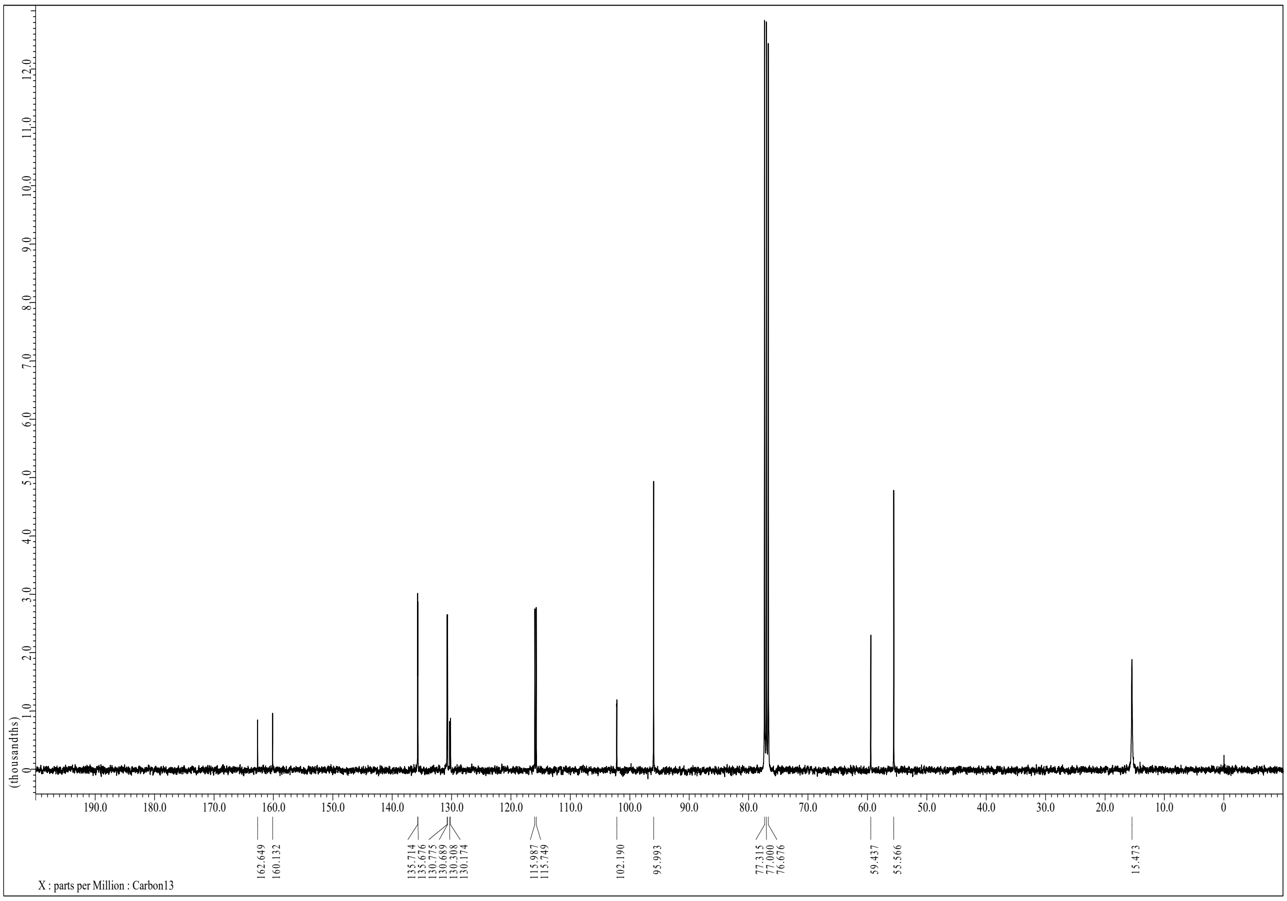

OH
S
O
O
1g
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
0.97
0.91
1.07
0.90
0.97
2.00
0.84
3.10
3.22
1.88
1.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.491
7.476
7.472
7.356
7.352
7.311
7.307
7.259
7.247
7.243
6.695
5.063
3.387
2.526
2.384
1.233
1.220
1.215
1.202
1.006
0.993
0.987
0.974
X : parts per Million : Proton

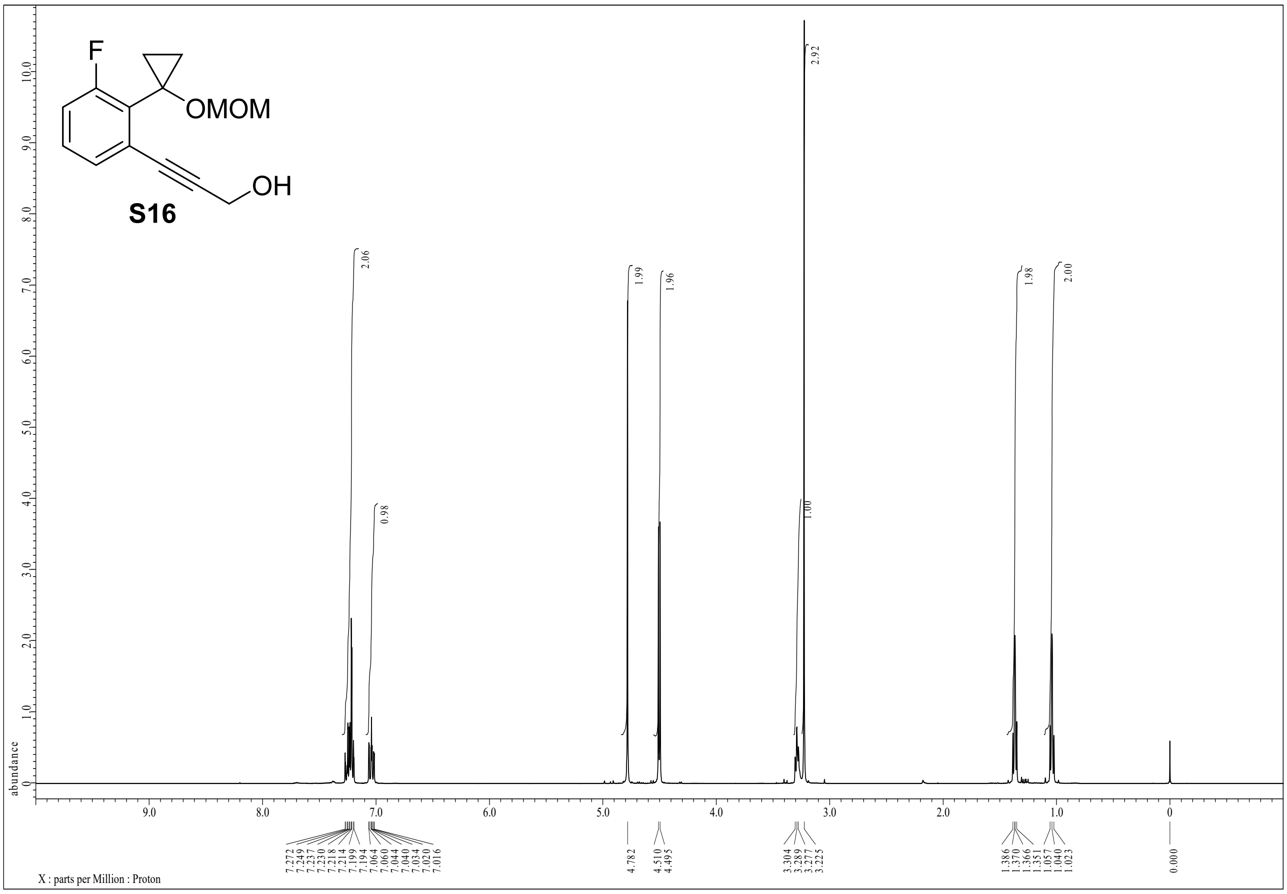

(thousandths)
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.966
148.846
145.079
136.937
132.894
129.233
128.146
127.688
127.298
122.292
87.662
85.936
83.820
82.428
56.885
54.177
15.152
14.713
14.399
X : parts per Million : Carbon13

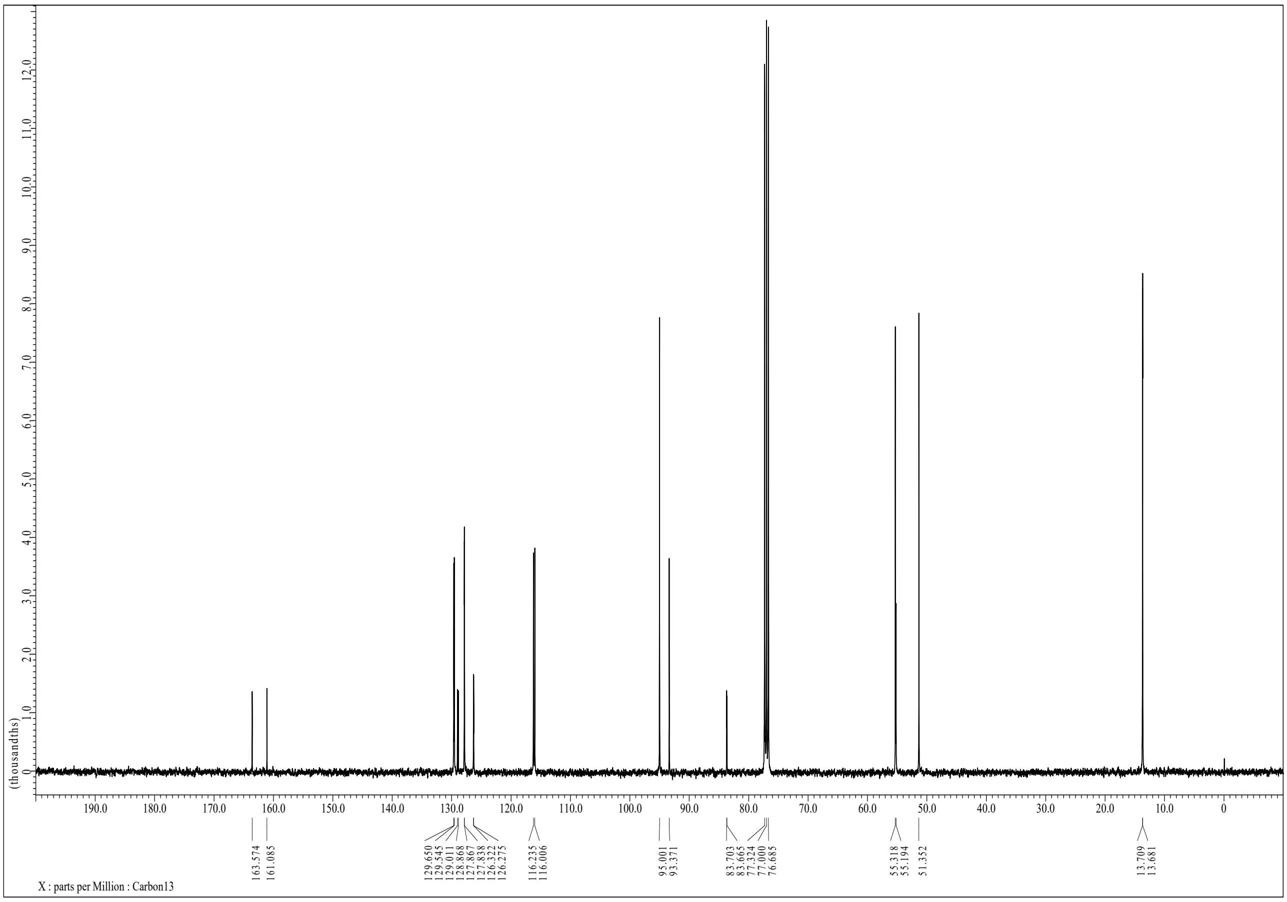

F
OH
I
S14
abundance
5.0
4.0
3.0
2.0
1.0
0
0.96
0.97
1.00
0.82
2.08
2.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.669
7.650
7.083
7.079
7.062
7.059
7.054
7.037
7.033
6.994
6.981
6.975
6.961
6.954
2.826
2.040
1.399
1.396
1.384
1.380
1.377
1.365
1.363
1.052
1.048
1.037
1.033
1.018
1.014
0.000
X : parts per Million : Proton

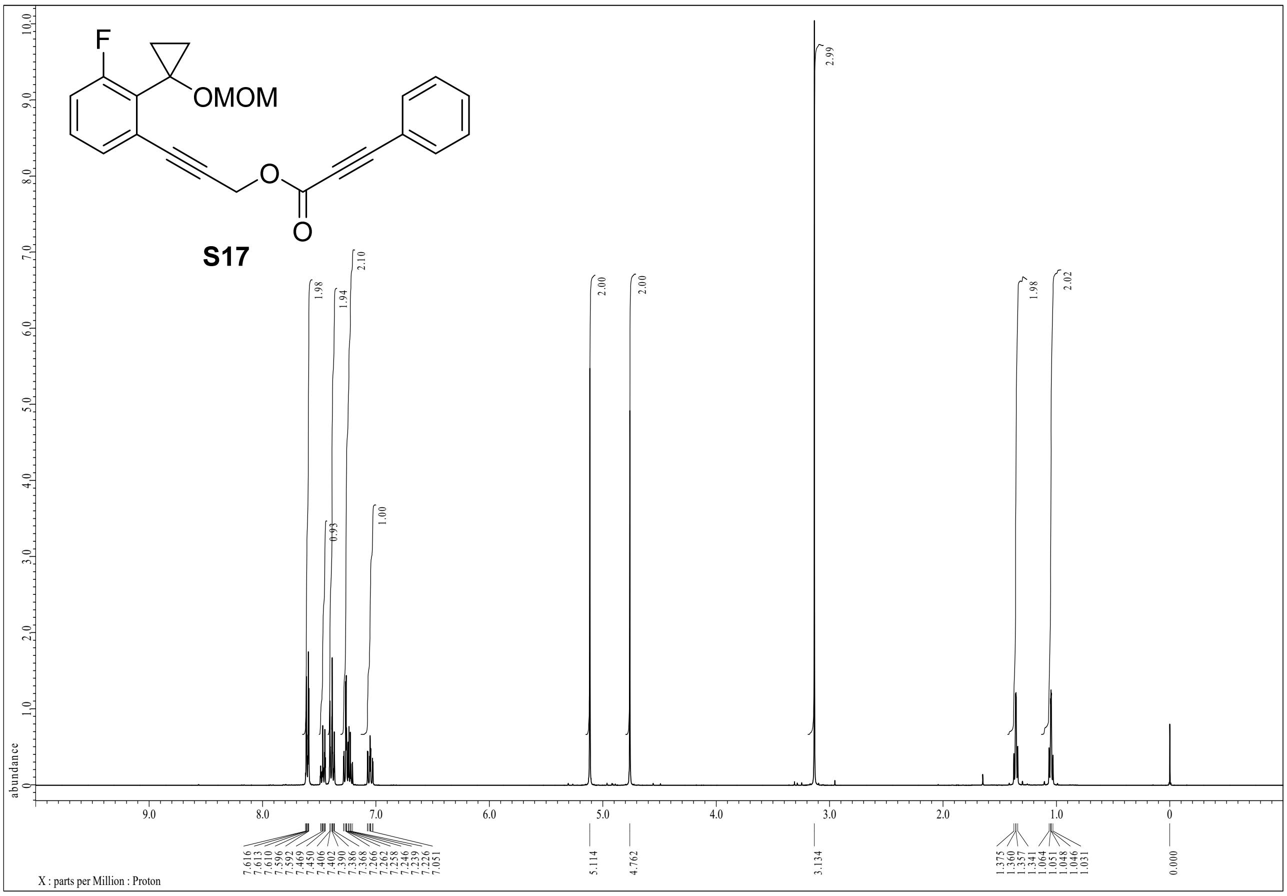

abundance
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.344
159.808
135.457
135.428
131.357
131.225
130.870
130.785
116.483
116.254
101.542
77.315
77.000
76.676
55.290
16.665
16.618
X : parts per Million : Carbon13

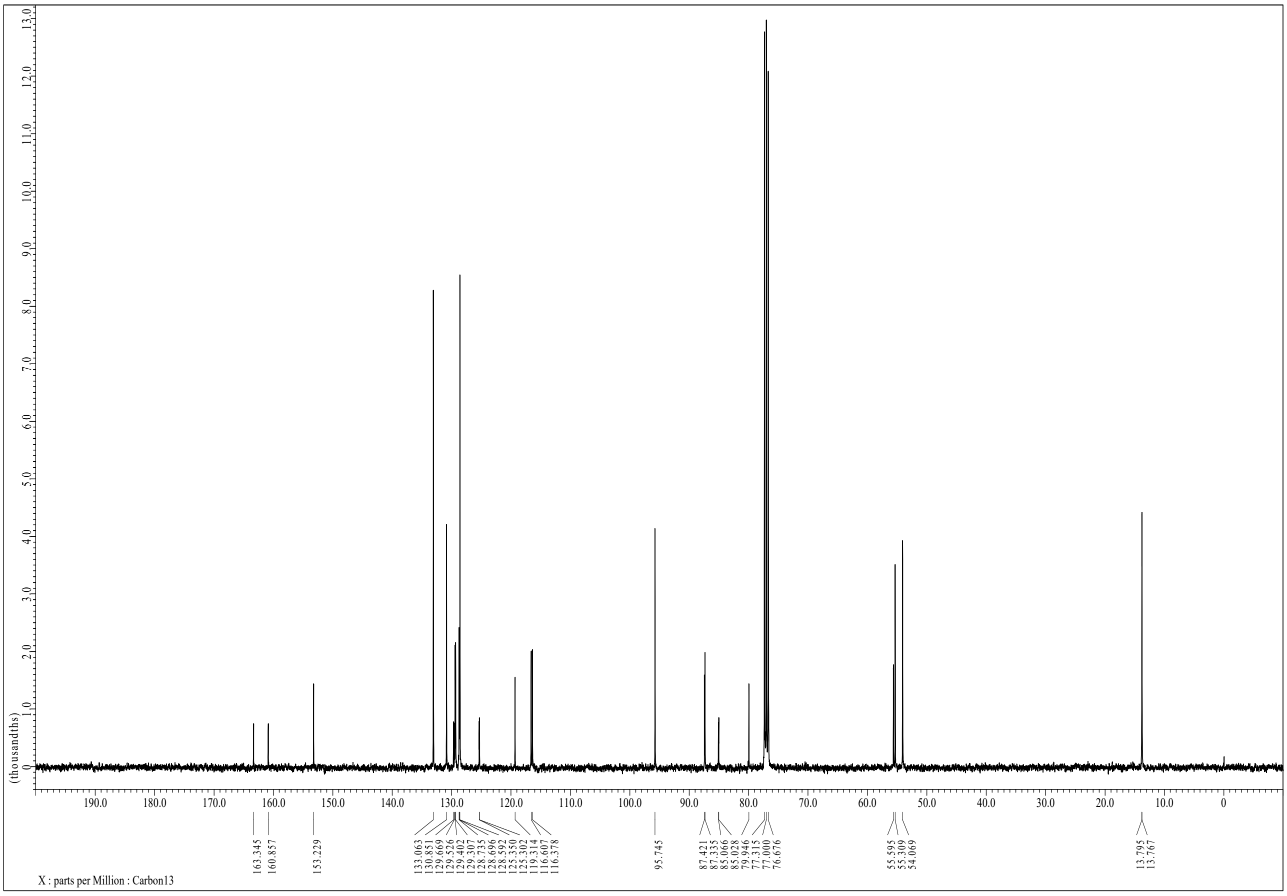

F
OMOM
I
S15
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
1.02
1.00
1.00
2.16
3.22
2.05
2.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.703
7.701
7.684
7.682
7.264
7.055
7.036
7.033
7.029
7.012
7.009
6.981
6.968
6.962
6.948
6.928
4.739
3.115
1.598
1.436
1.432
1.429
1.423
1.047
1.032
1.017
0.000
X : parts per Million : Proton


(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.649
160.132
135.714
135.676
130.775
130.689
130.308
130.174
115.987
115.749
102.190
95.993
77.315
77.000
76.676
59.437
55.566
15.473
X : parts per Million : Carbon13


F
OMOM
OH
S16
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.06
0.98
1.99
1.96
2.92
1.00
1.98
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.272
7.249
7.237
7.230
7.218
7.214
7.199
7.194
7.064
7.060
7.044
7.040
7.034
7.020
7.016
4.782
4.510
4.495
3.304
3.289
3.277
3.225
1.386
1.370
1.366
1.351
1.057
1.040
1.023
0.000
X : parts per Million : Proton


(thousandths)
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
163.574
161.085
129.650
129.545
129.011
128.868
127.867
127.838
126.322
126.275
116.235
116.006
95.001
93.371
83.703
83.665
77.324
77.000
76.685
55.318
55.194
51.352
13.709
13.681
X : parts per Million : Carbon13


F
OMOM
O
O
S17
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.98
0.93
1.94
2.10
1.00
2.00
2.00
2.99
1.98
2.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.616
7.613
7.610
7.596
7.592
7.469
7.450
7.406
7.402
7.390
7.386
7.368
7.266
7.262
7.258
7.246
7.239
7.226
7.051
5.114
4.762
3.134
1.375
1.360
1.357
1.341
1.064
1.051
1.048
1.046
1.031
0.000
X : parts per Million : Proton


(thousandths)
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
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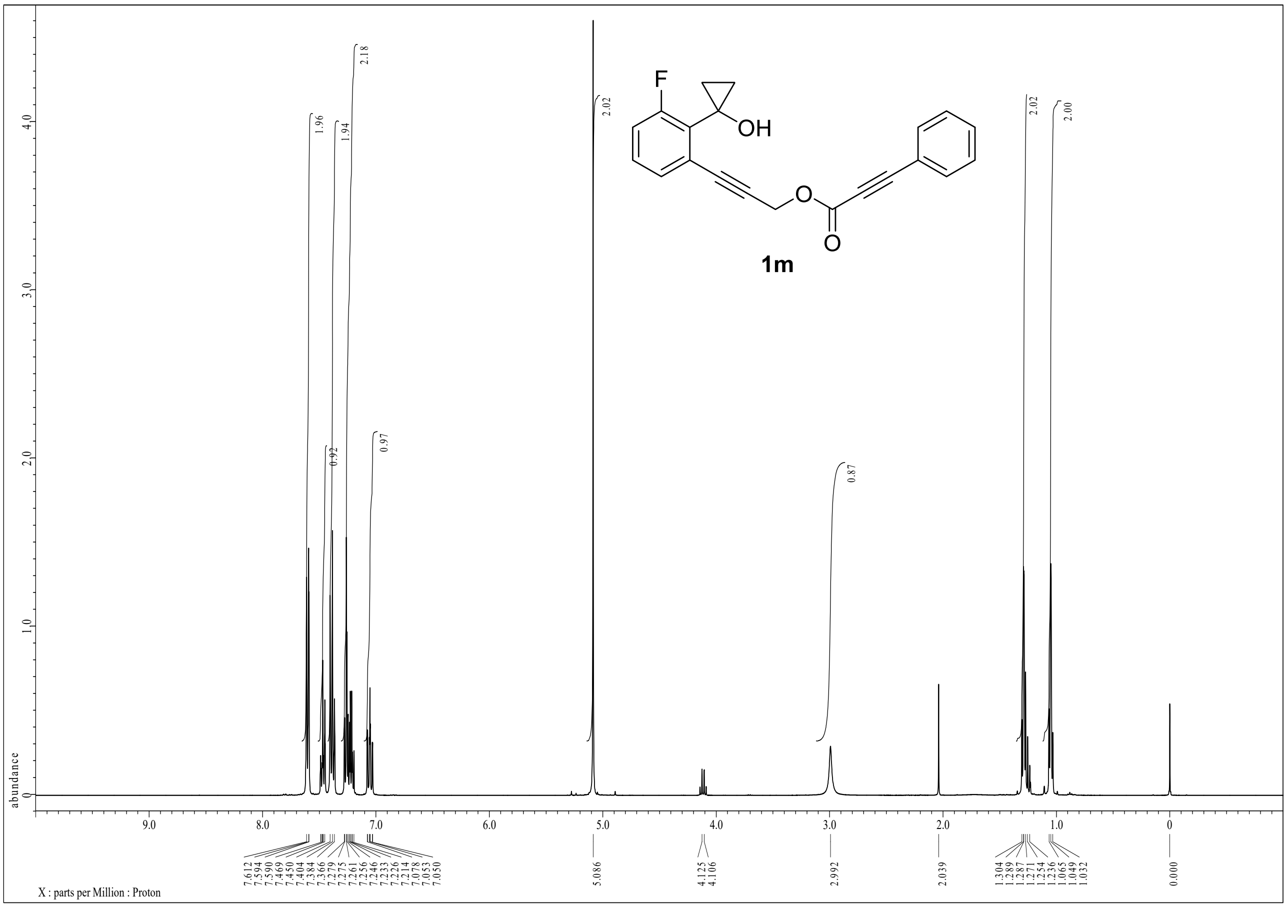
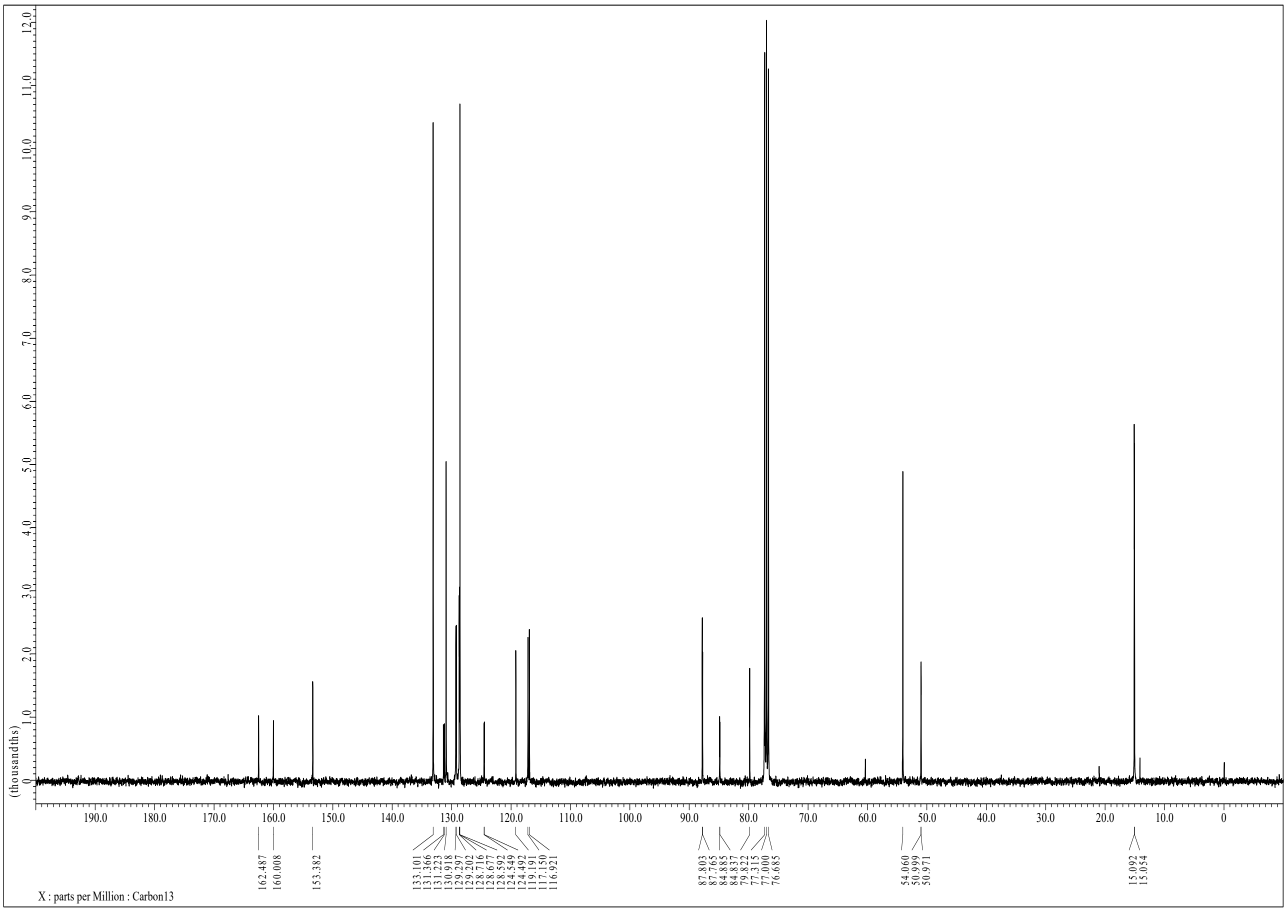
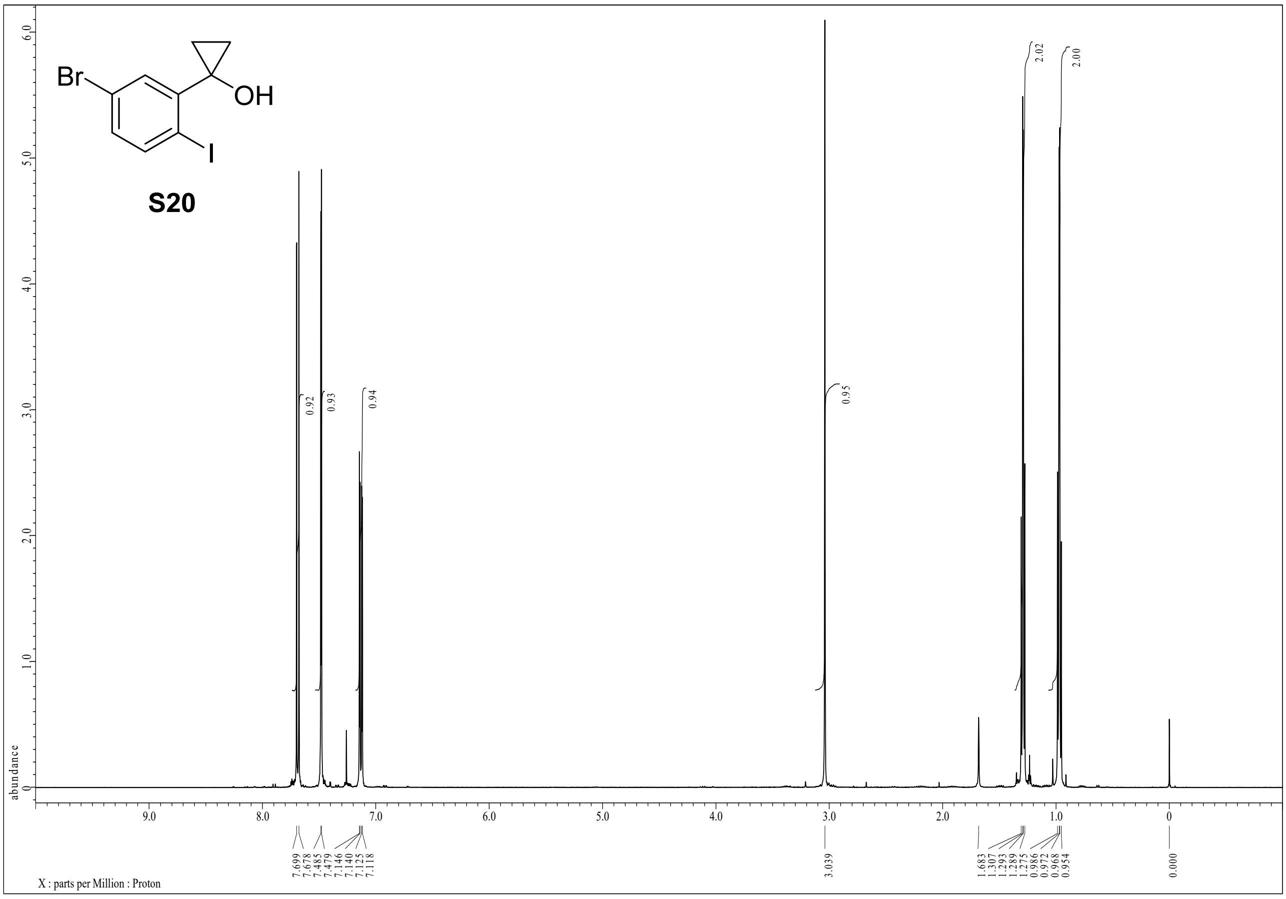
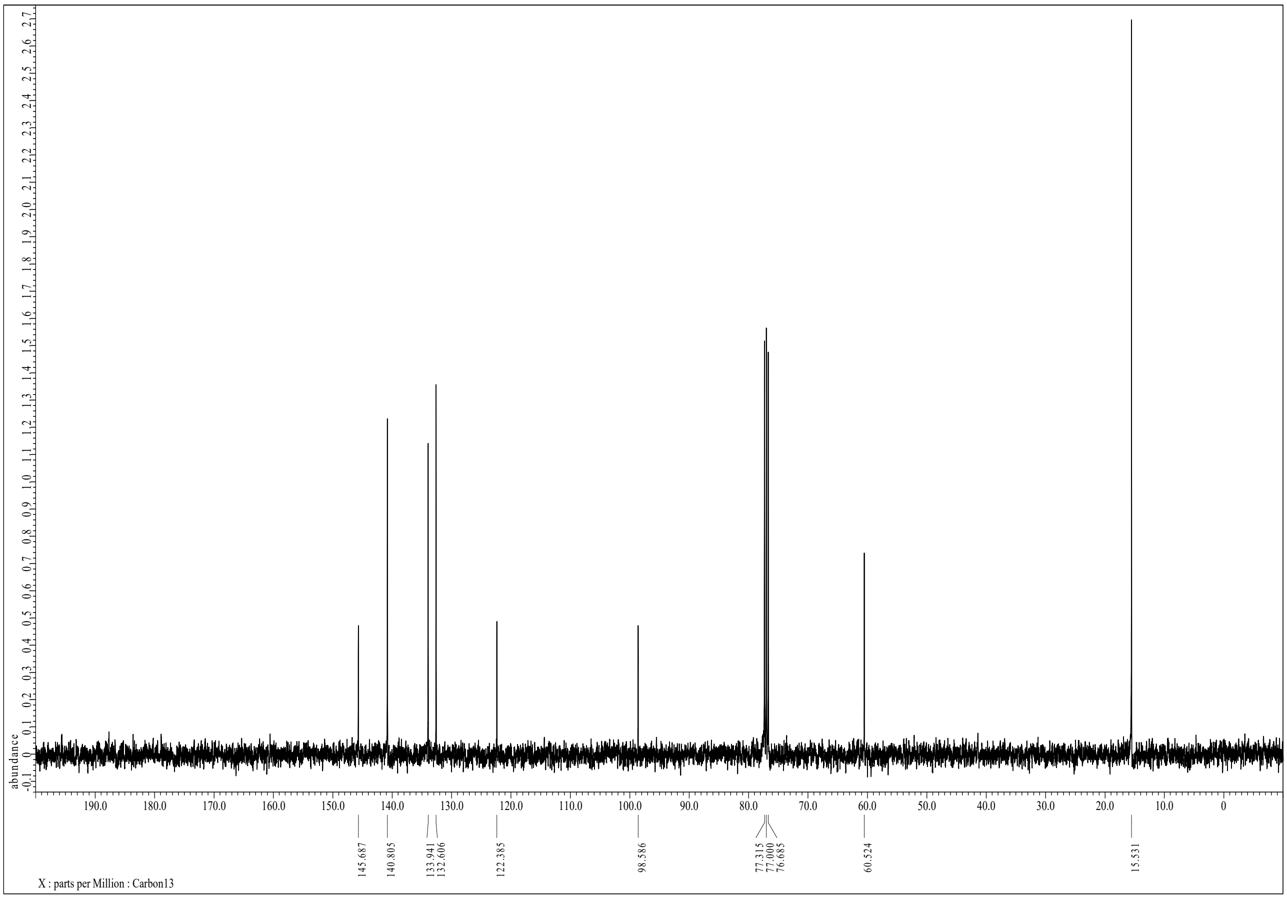
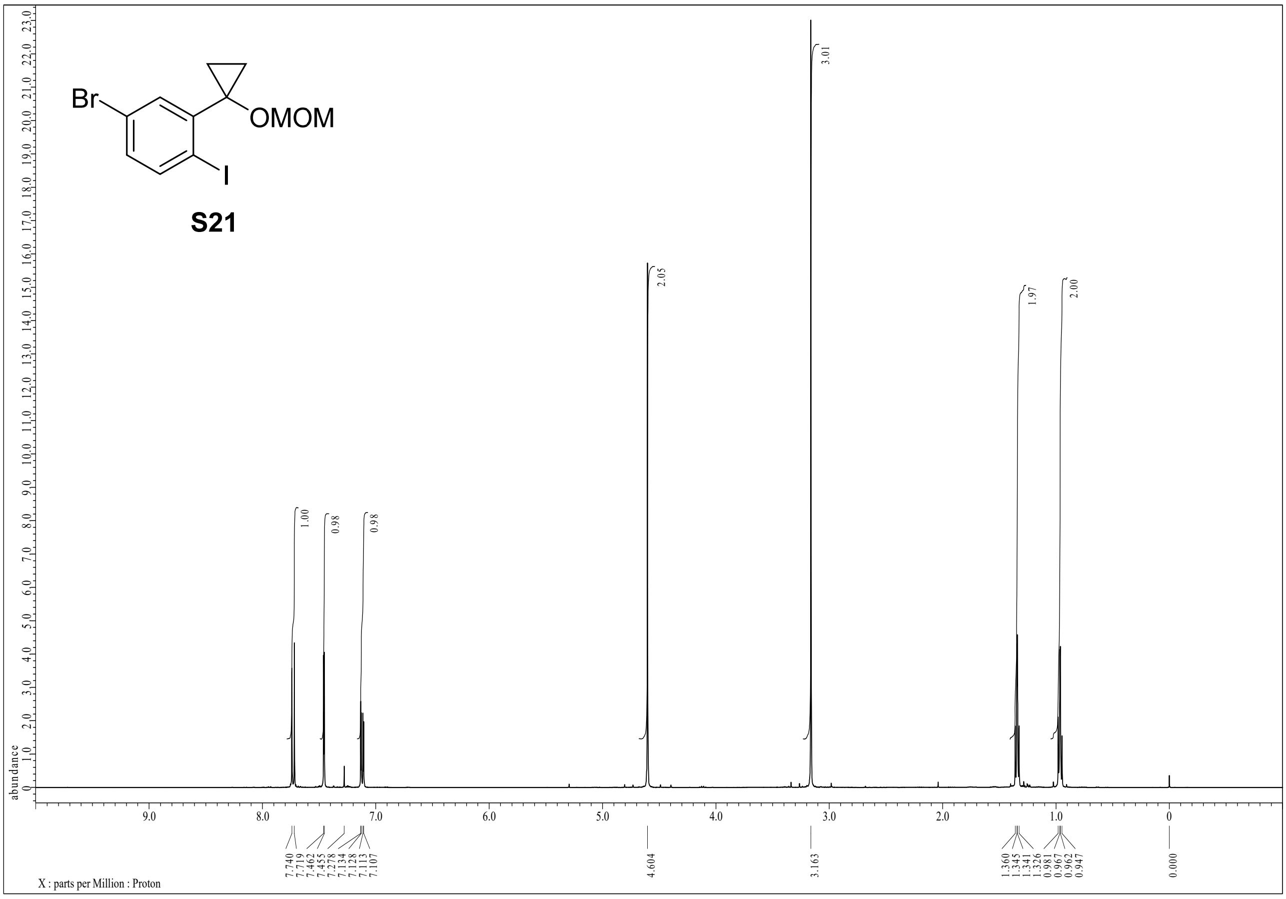
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
163.345
160.857
153.229
133.063
130.851
129.669
129.526
129.402
129.307
128.735
128.696
128.592
125.350
125.302
119.314
116.607
116.378
95.745
87.421
87.335
85.066
85.028
79.946
77.315
77.000
76.676
55.595
55.309
54.069
13.795
13.767
X : parts per Million : Carbon13

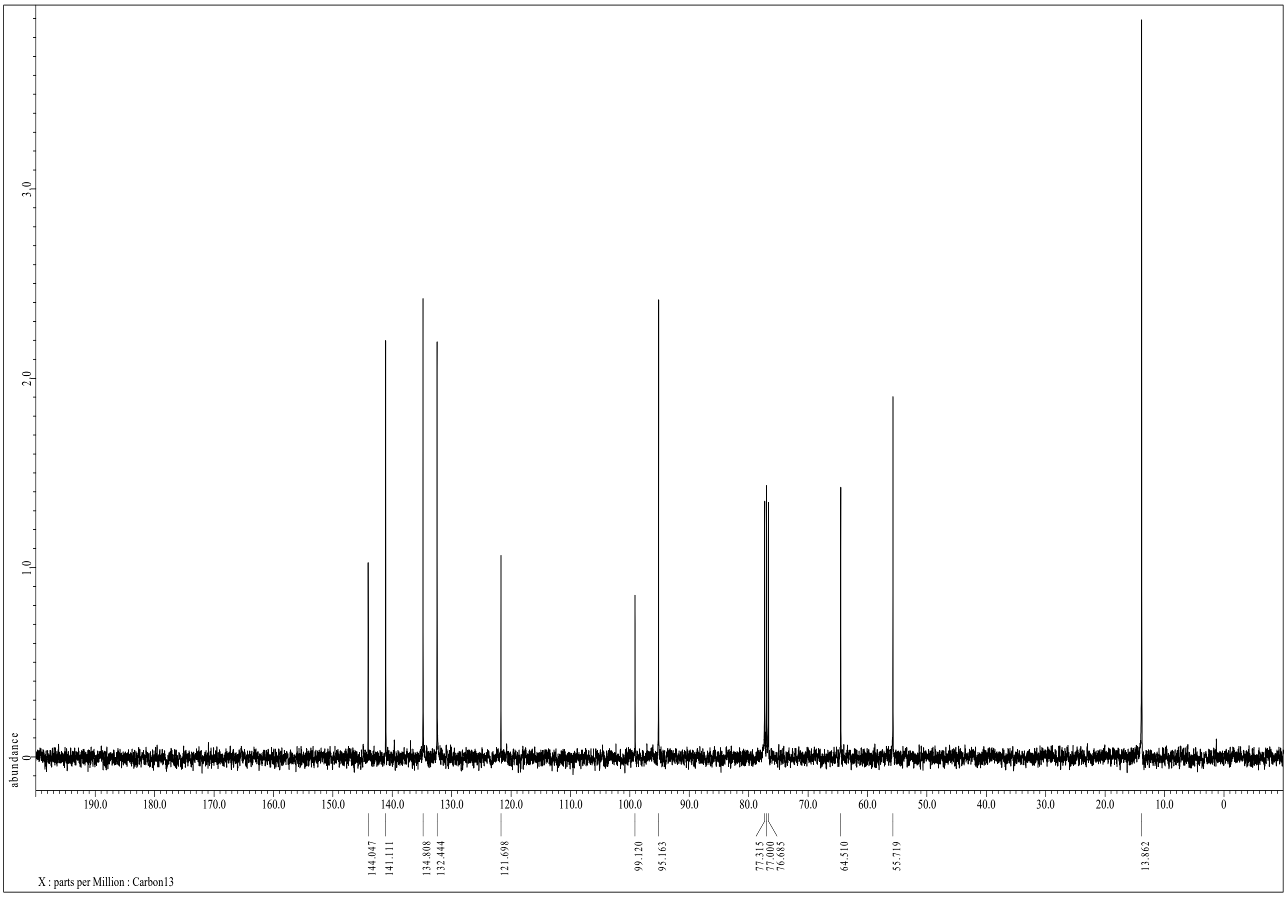

F
OH
O
O
1m
abundance
0
1.0
2.0
3.0
4.0
1.96
0.92
1.94
2.18
0.97
2.02
0.87
2.02
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.612
7.594
7.590
7.469
7.450
7.404
7.384
7.366
7.275
7.261
7.256
7.246
7.233
7.226
7.214
7.078
7.053
7.050
5.086
4.125
4.106
2.992
2.039
1.304
1.289
1.287
1.271
1.254
1.236
1.065
1.049
1.032
0.000
X : parts per Million : Proton

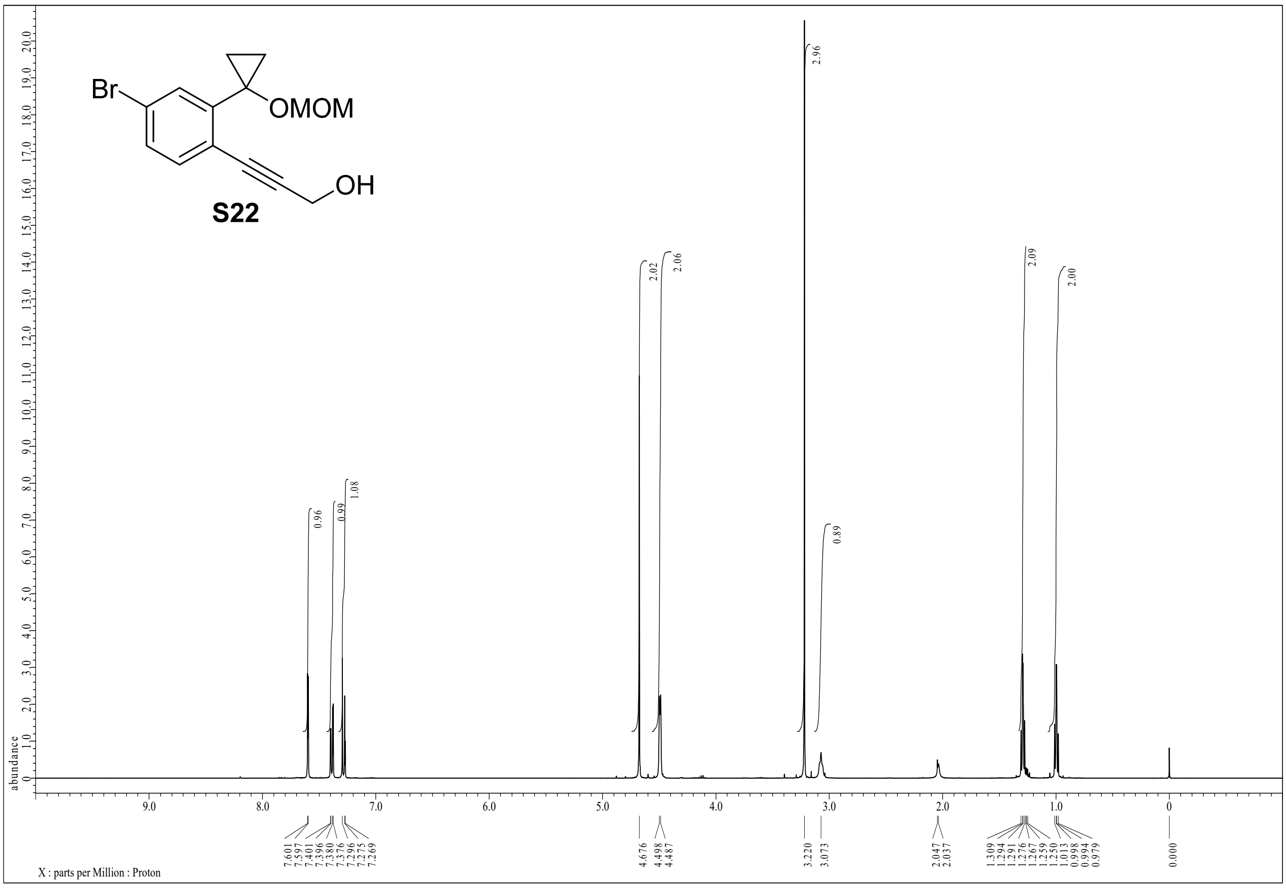

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.487
160.008
153.382
133.101
131.366
131.223
130.918
129.297
129.202
128.716
128.677
128.592
124.549
124.492
119.191
117.150
116.921
87.803
87.765
84.885
84.837
79.822
77.315
77.000
76.685
54.060
50.999
50.971
15.092
15.054
X : parts per Million : Carbon13

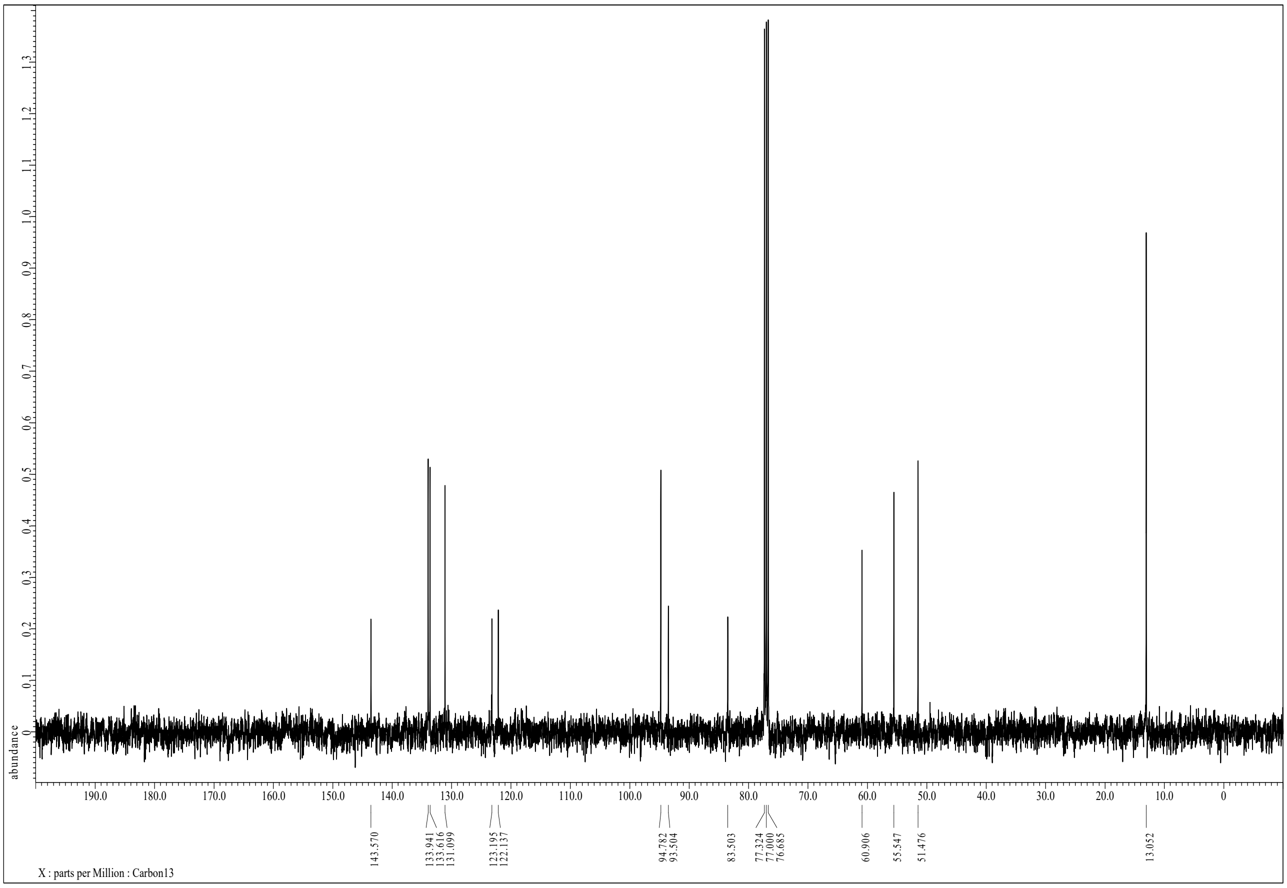

Br
OH
I
S20
abundance
0.92
0.93
0.94
0.95
2.02
2.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.699 7.678 7.485 7.479 7.146 7.140 7.125 7.118
3.039
1.683 1.307 1.293 1.289 1.275 0.986 0.972 0.968 0.954
0.000
X : parts per Million : Proton

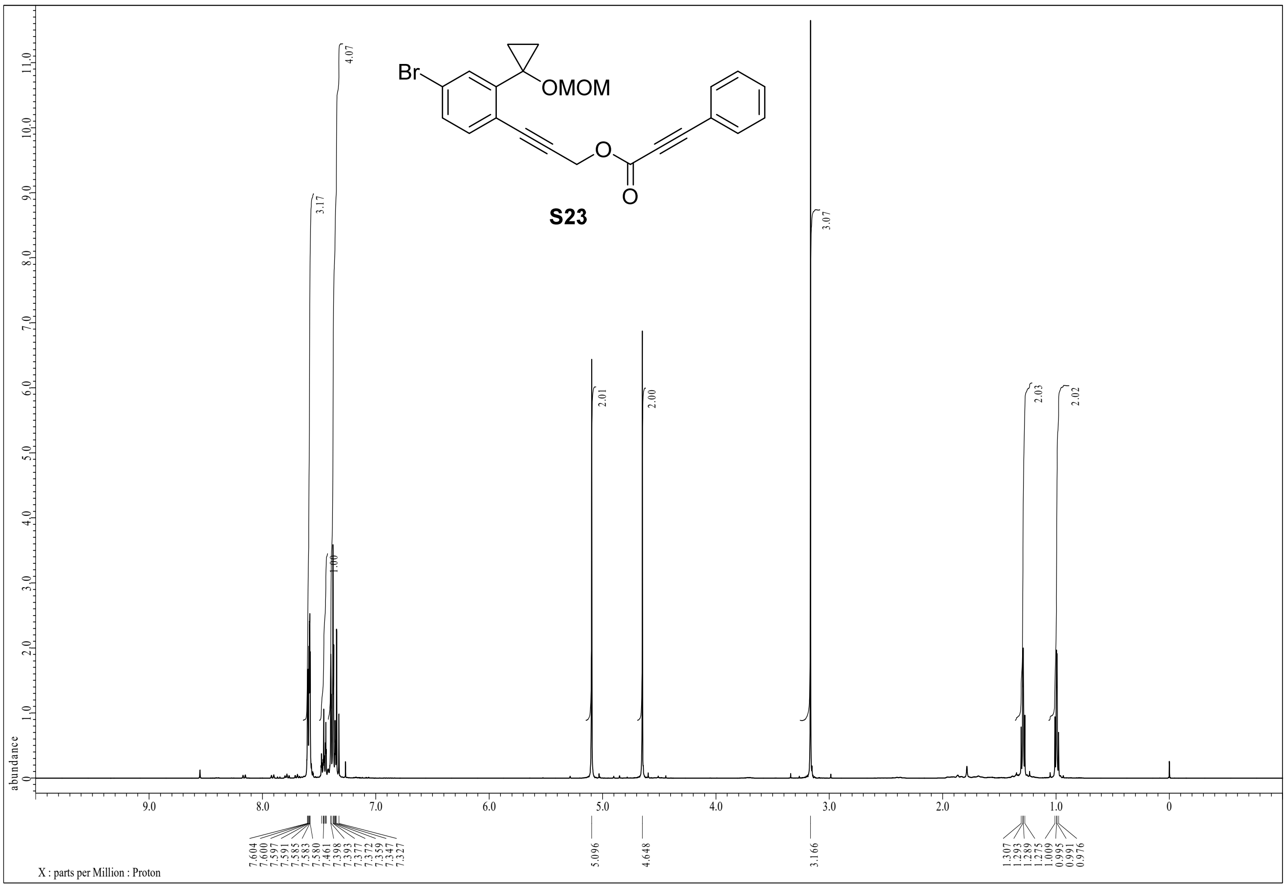

abundance
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
145.687
140.805
133.941 132.606
122.385
98.586
77.315 77.000 76.685
60.524
15.531
X : parts per Million : Carbon13

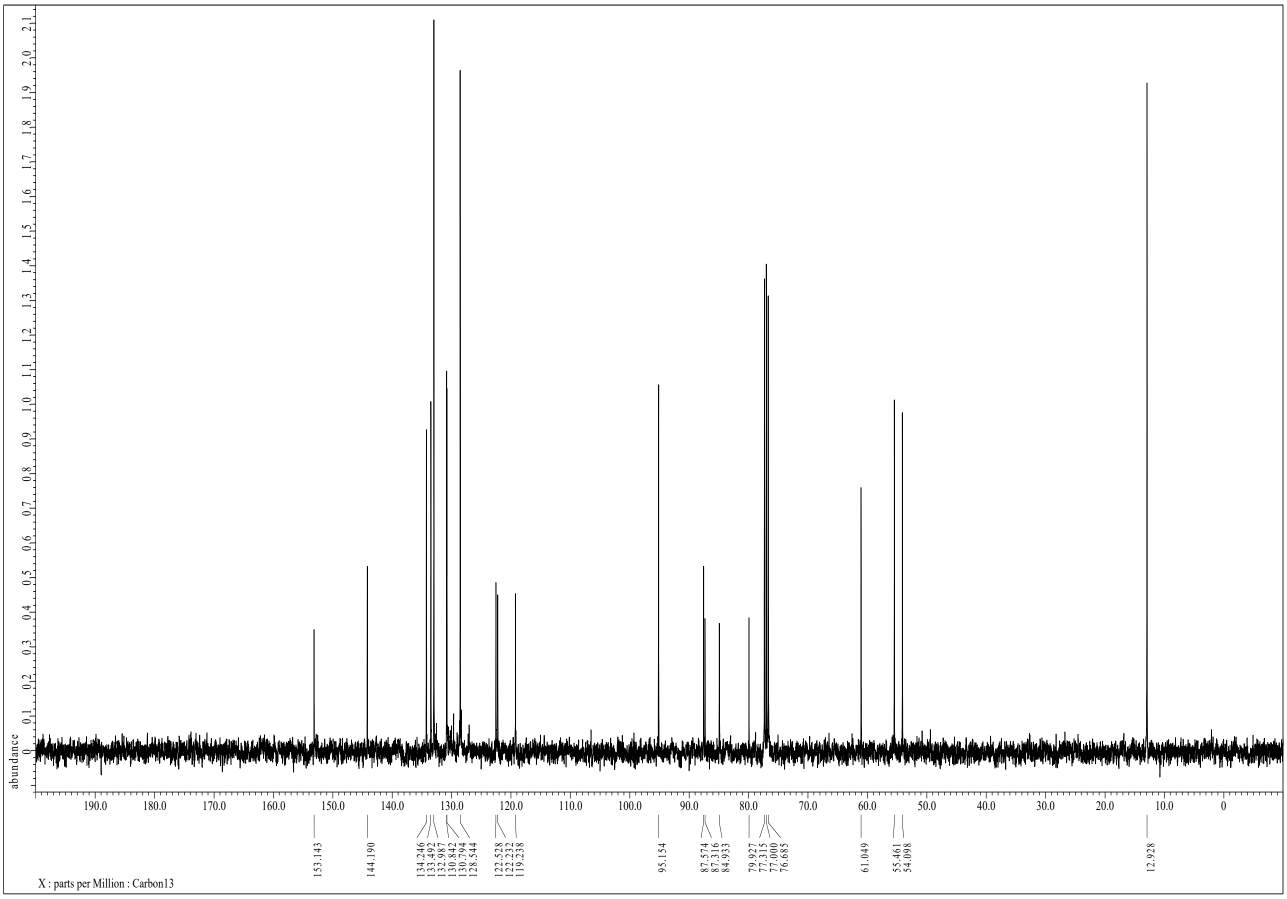

Br
OMOM
I
S21
abundance
1.00
0.98
0.98
2.05
3.01
1.97
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.740
7.719
7.462
7.455
7.278
7.134
7.128
7.113
7.107
4.604
3.163
1.360
1.345
1.341
1.326
0.981
0.967
0.962
0.947
0.000
X : parts per Million : Proton

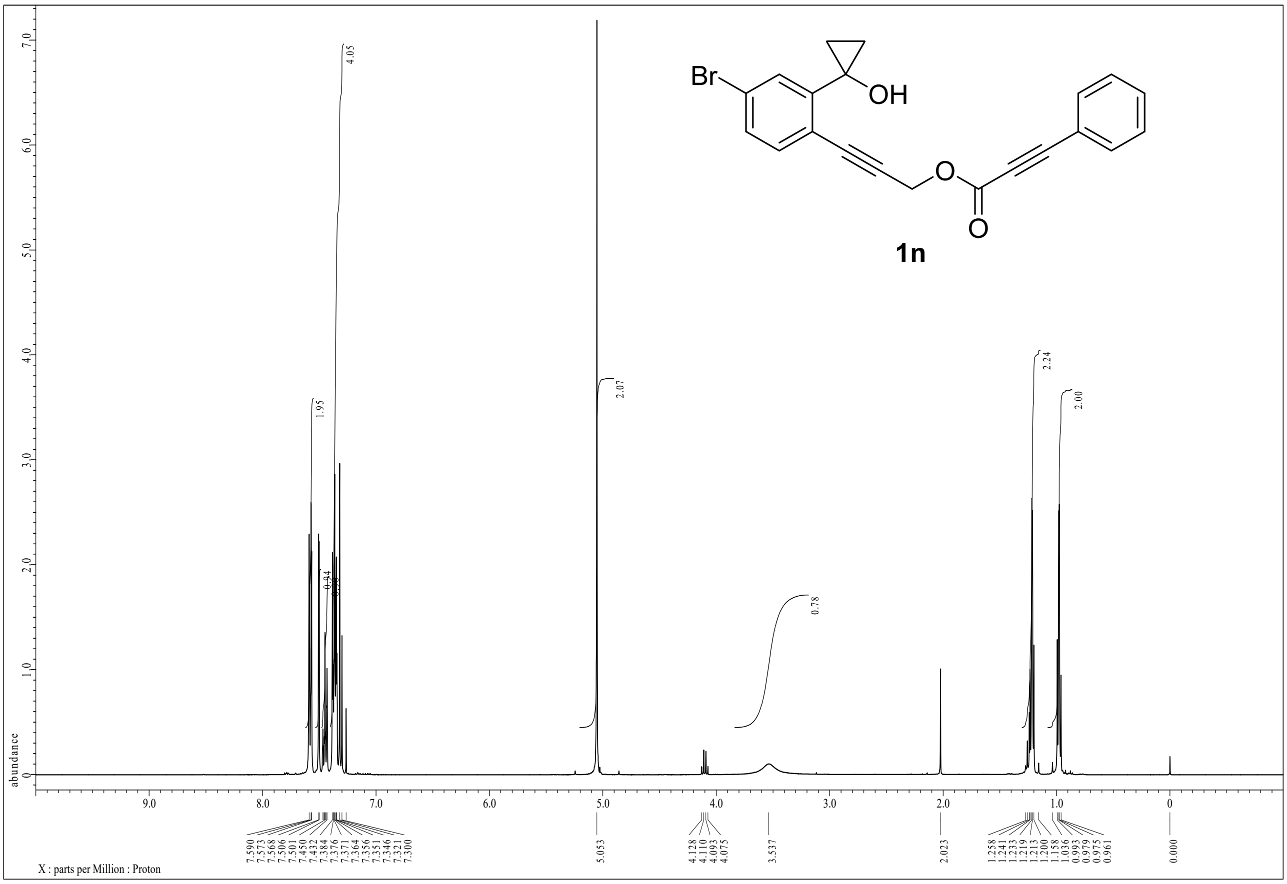

abundance
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
144.047
141.111
134.808
132.444
121.698
99.120
95.163
77.315
77.000
76.685
64.510
55.719
13.862
X : parts per Million : Carbon13

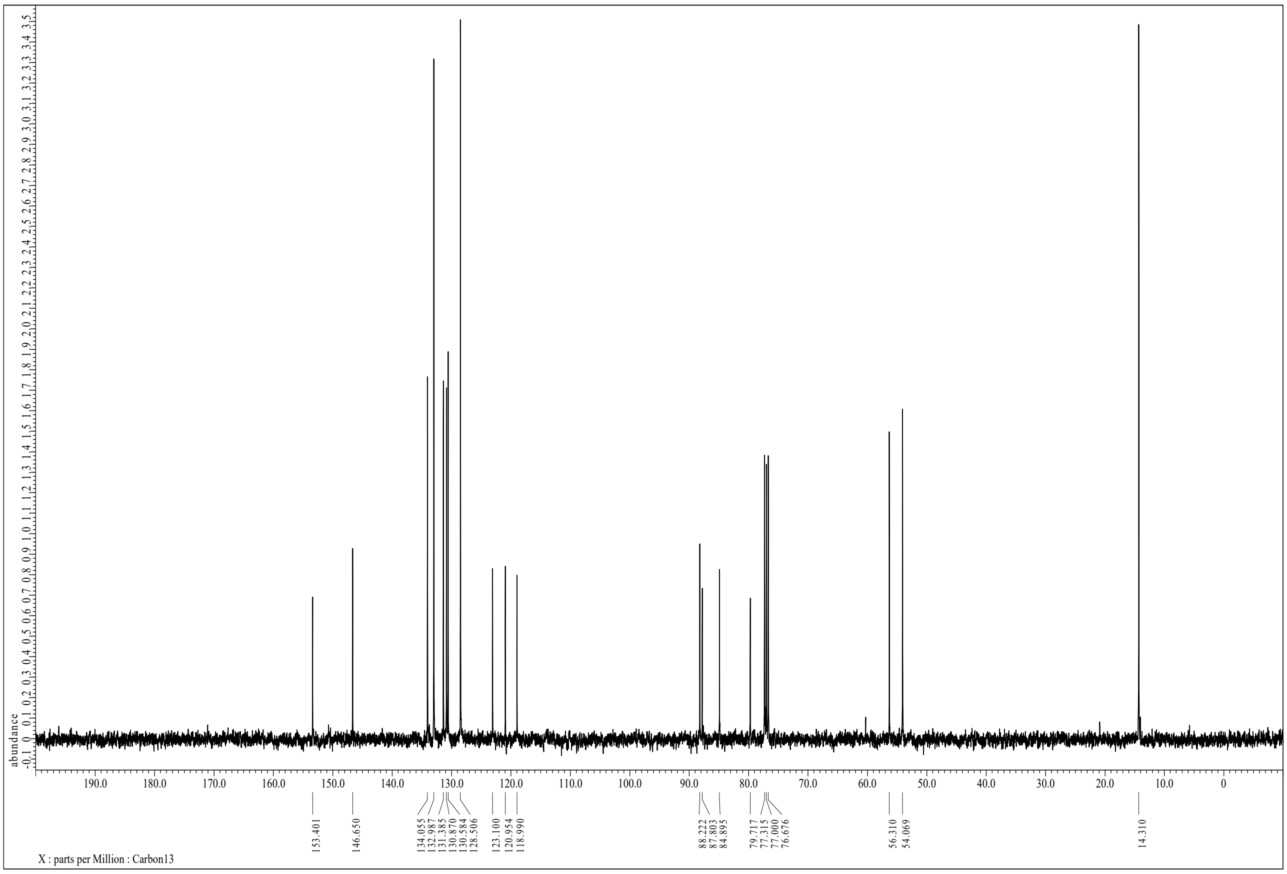

Br
OMOM
OH
S22
abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
0.96
0.99
1.08
2.02
2.06
2.96
0.89
2.09
2.00
7.601 7.597 7.401 7.396 7.380 7.376 7.296 7.275 7.269
4.676 4.498 4.487
3.220 3.073
2.047 2.037
1.309 1.294 1.291 1.276 1.267 1.259 1.250 1.013 0.998 0.994 0.979
0.000
X : parts per Million : Proton

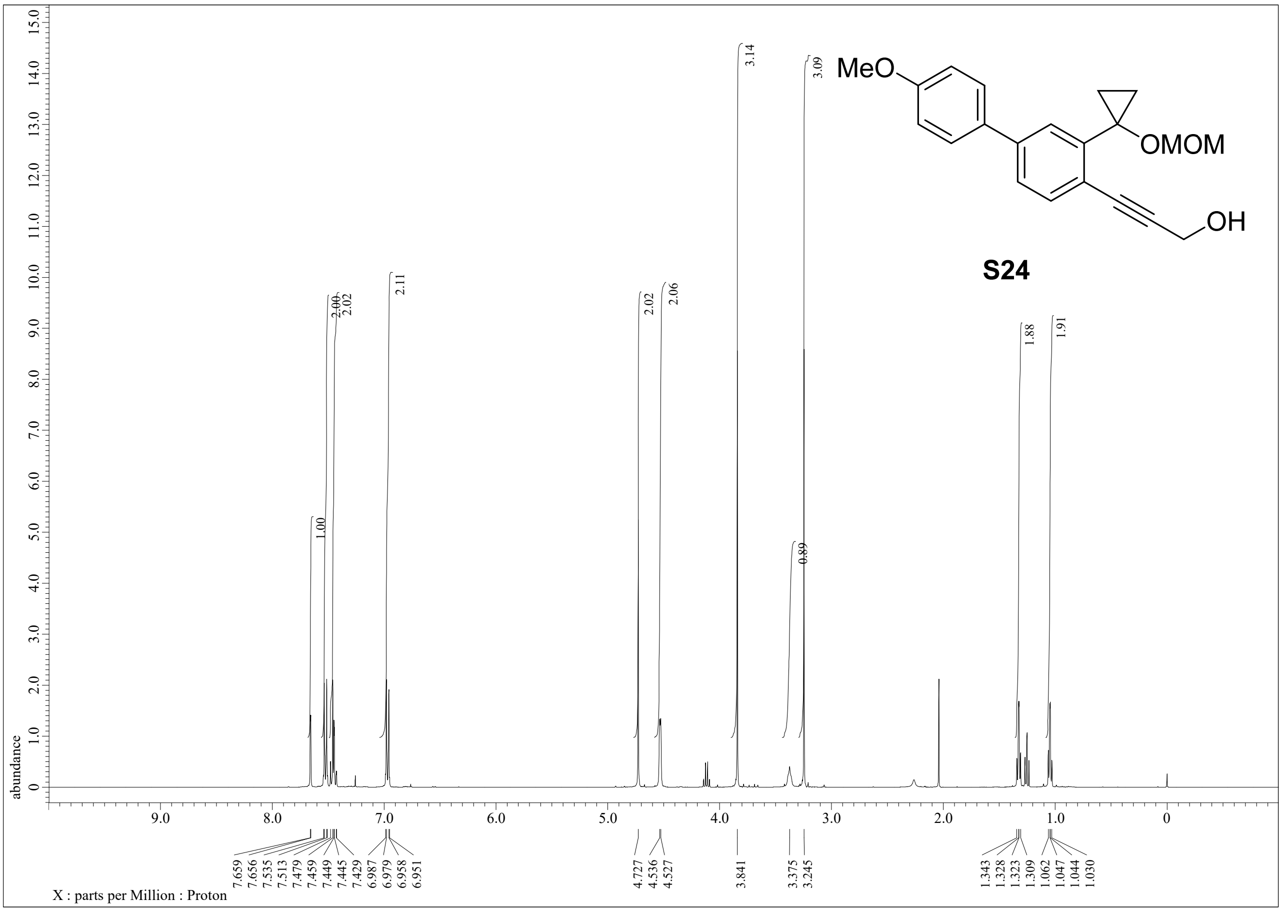

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
143.570
133.941 133.616 131.099
123.195 122.137
94.782 93.504
83.503
77.324 77.000 76.685
60.906
55.547
51.476
13.052
X : parts per Million : Carbon13

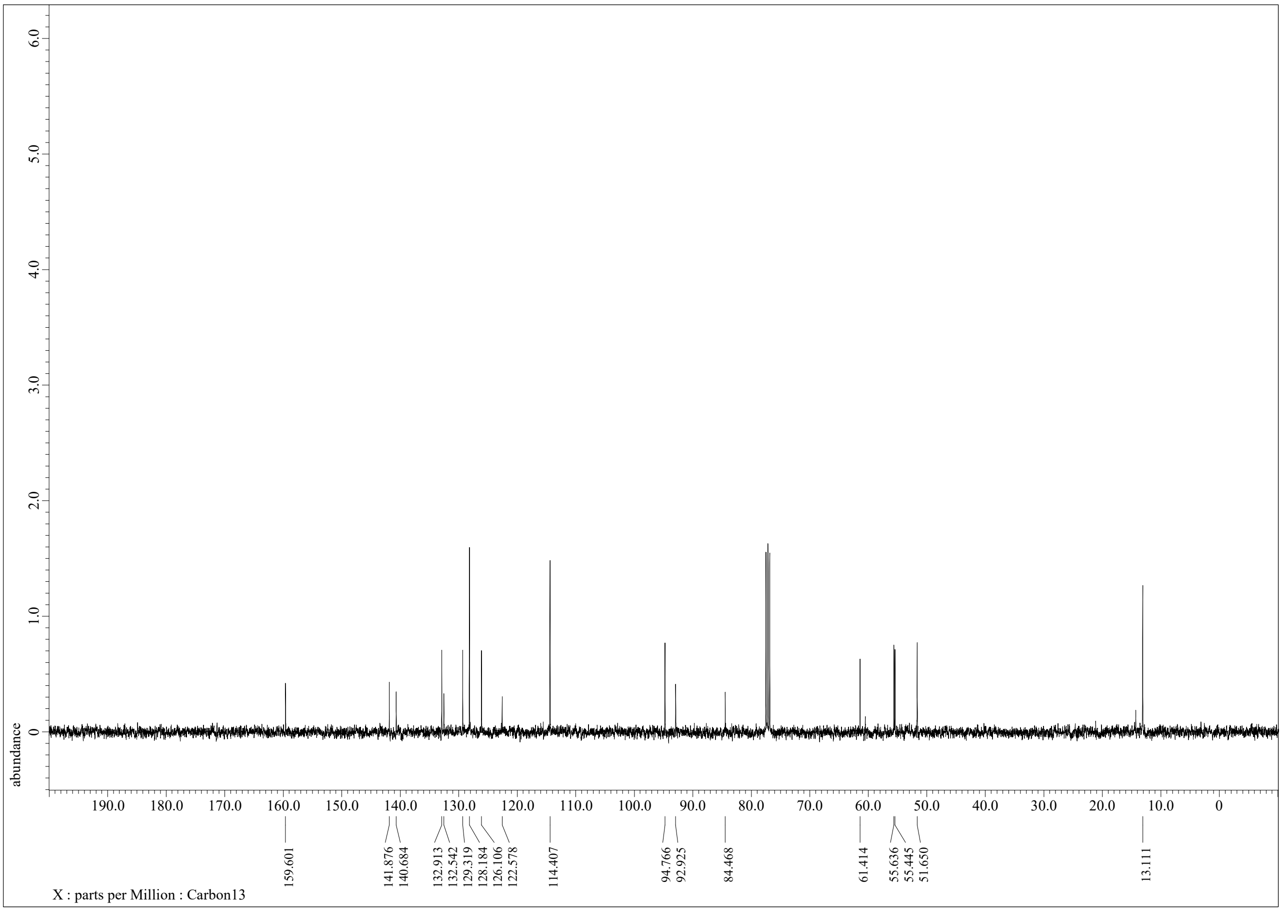

Br
OMOM
O
O
S23
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.17
4.07
1.00
2.01
2.00
3.07
2.03
2.02
7.604
7.600
7.597
7.591
7.585
7.583
7.580
7.461
7.398
7.393
7.377
7.372
7.359
7.347
7.327
5.096
4.648
3.166
1.307
1.293
1.289
1.275
1.009
0.995
0.991
0.976
X : parts per Million : Proton

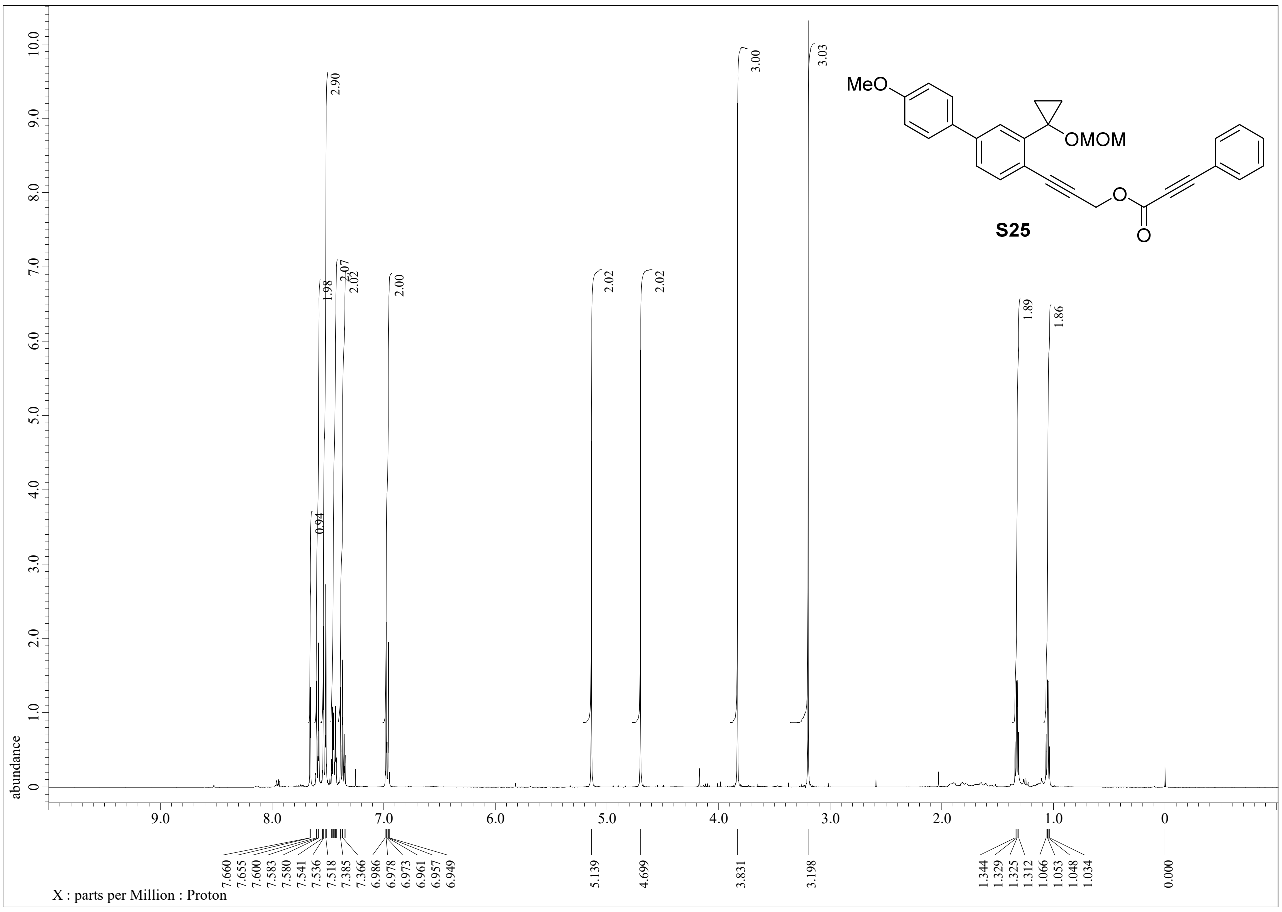

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.143
144.190
134.246
133.492
132.987
130.842
130.794
128.544
122.528
122.232
119.238
95.154
87.574
87.316
84.933
79.927
77.315
77.000
76.685
61.049
55.461
54.098
12.928
X : parts per Million : Carbon13

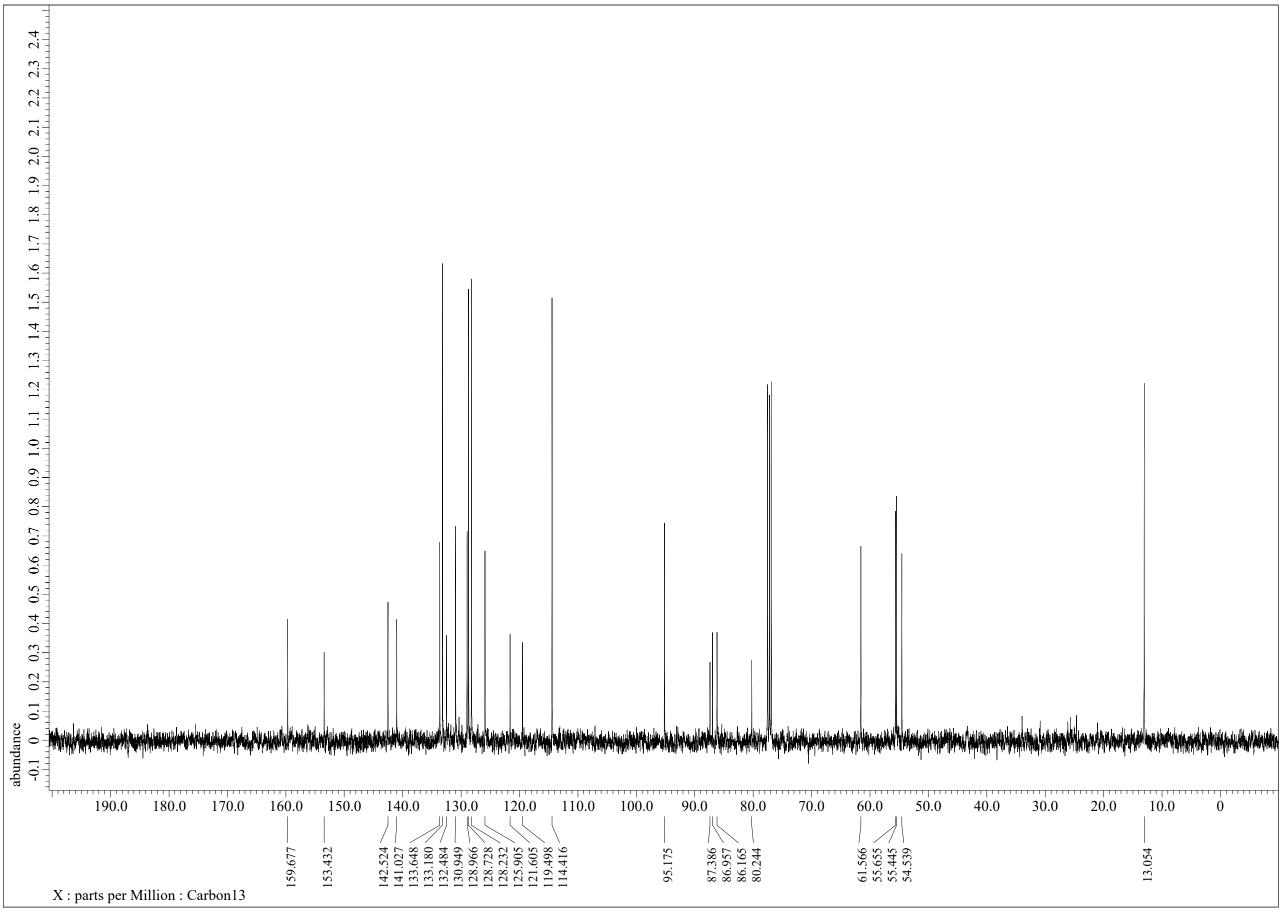

Br
OH
O
O
1n
abundance
1.95
4.05
0.94
2.07
0.78
2.24
2.00
7.590
7.573
7.568
7.506
7.501
7.450
7.432
7.384
7.376
7.371
7.364
7.356
7.351
7.346
7.321
7.300
5.053
4.128
4.110
4.093
4.075
3.537
2.023
1.258
1.241
1.233
1.219
1.213
1.200
1.158
1.036
0.993
0.979
0.975
0.961
0.000
X : parts per Million : Proton

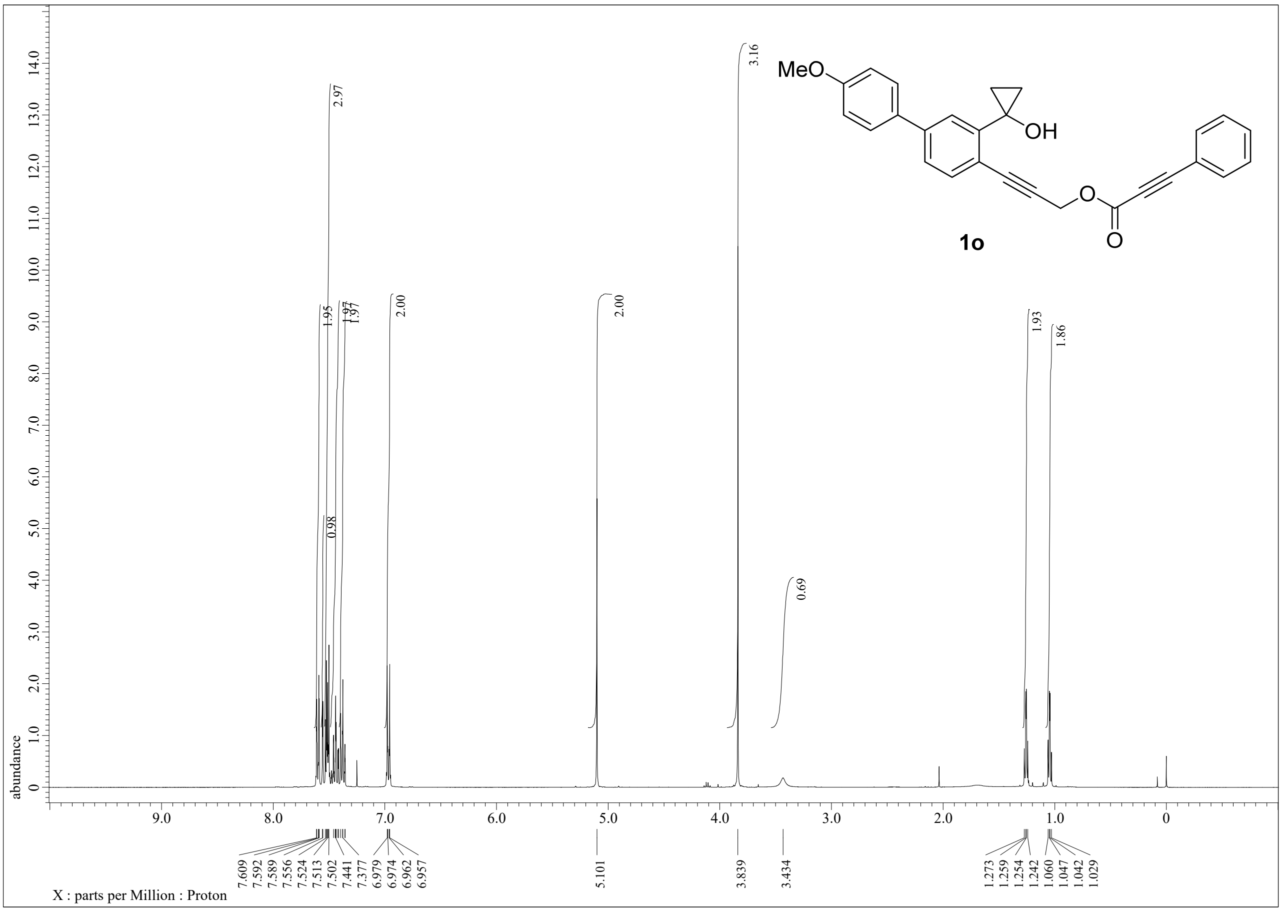

abundance
153.401
146.650
134.055
132.987
131.385
130.870
130.584
128.506
123.100
120.954
118.990
88.222
87.803
84.895
79.717
77.315
77.000
76.676
56.310
54.069
14.310
X : parts per Million : Carbon13

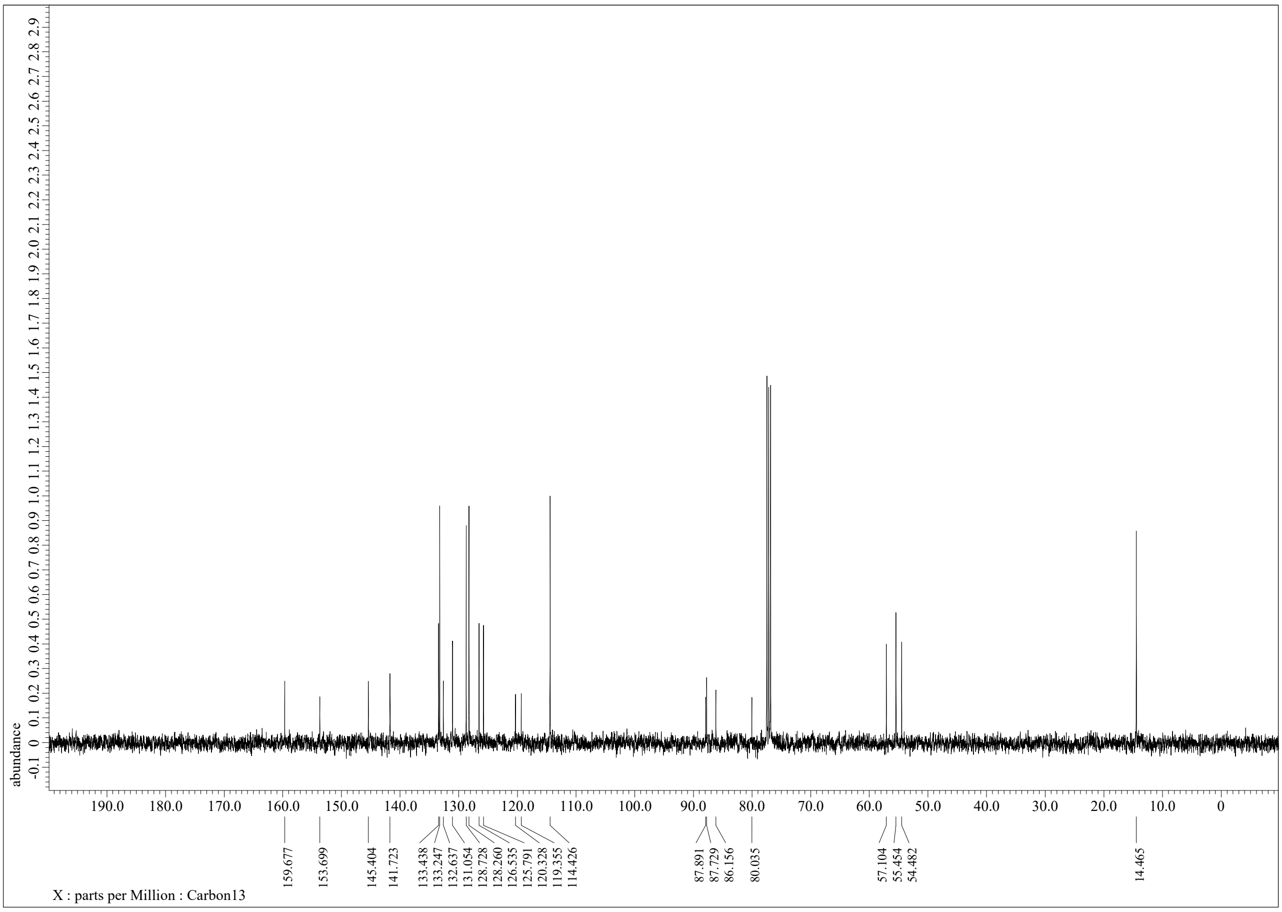

MeO
OMOM
OH
S24
abundance
1.00
2.00
2.02
2.11
2.02
2.06
3.14
0.89
3.09
1.88
1.91
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.659
7.656
7.535
7.513
7.479
7.459
7.449
7.445
7.429
6.987
6.979
6.958
6.951
4.727
4.536
4.527
3.841
3.375
3.245
1.343
1.328
1.323
1.309
1.062
1.047
1.044
1.030
X : parts per Million : Proton

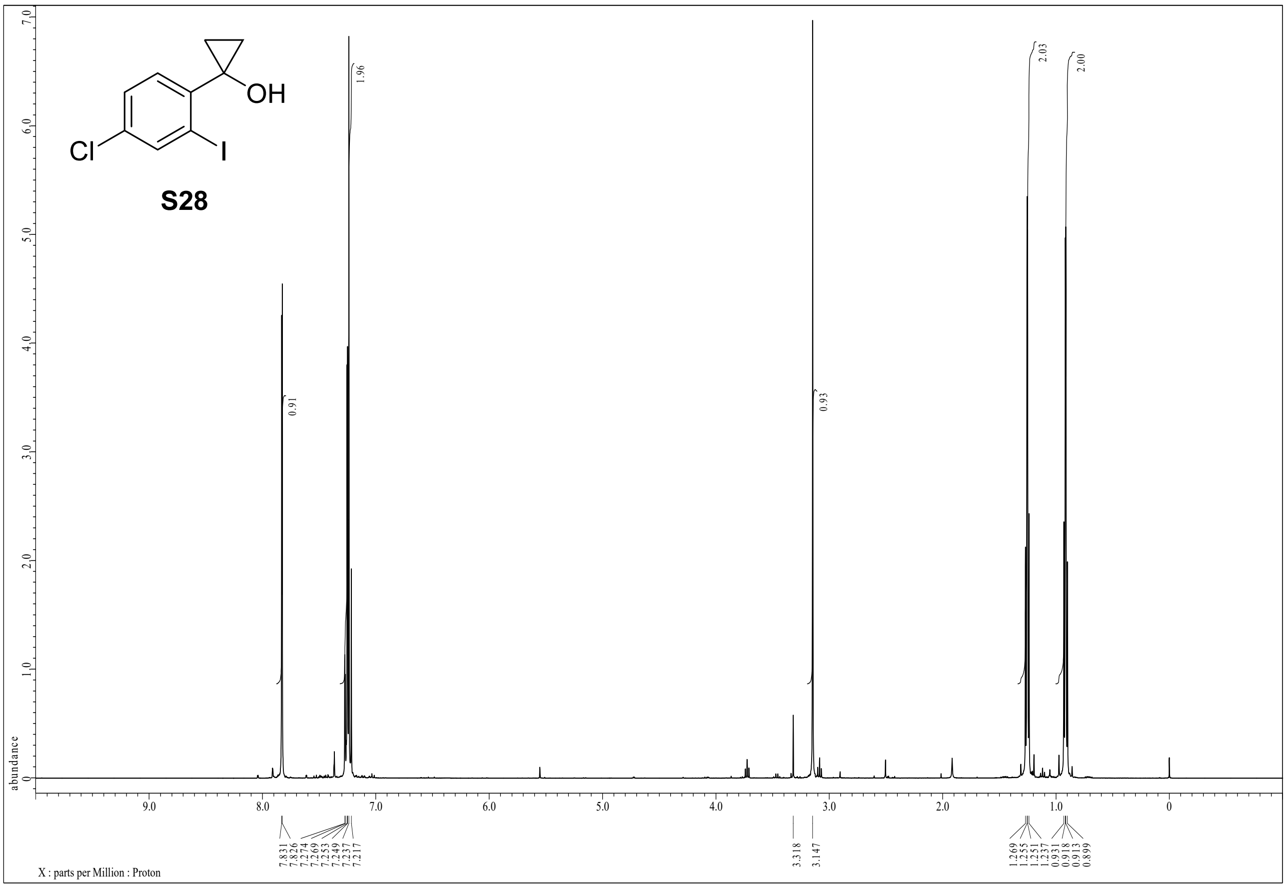

abundance
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
159.601
141.876
140.684
132.913
132.542
129.319
128.184
126.106
122.578
114.407
94.766
92.925
84.468
61.414
55.636
55.445
51.650
13.111
X : parts per Million : Carbon13

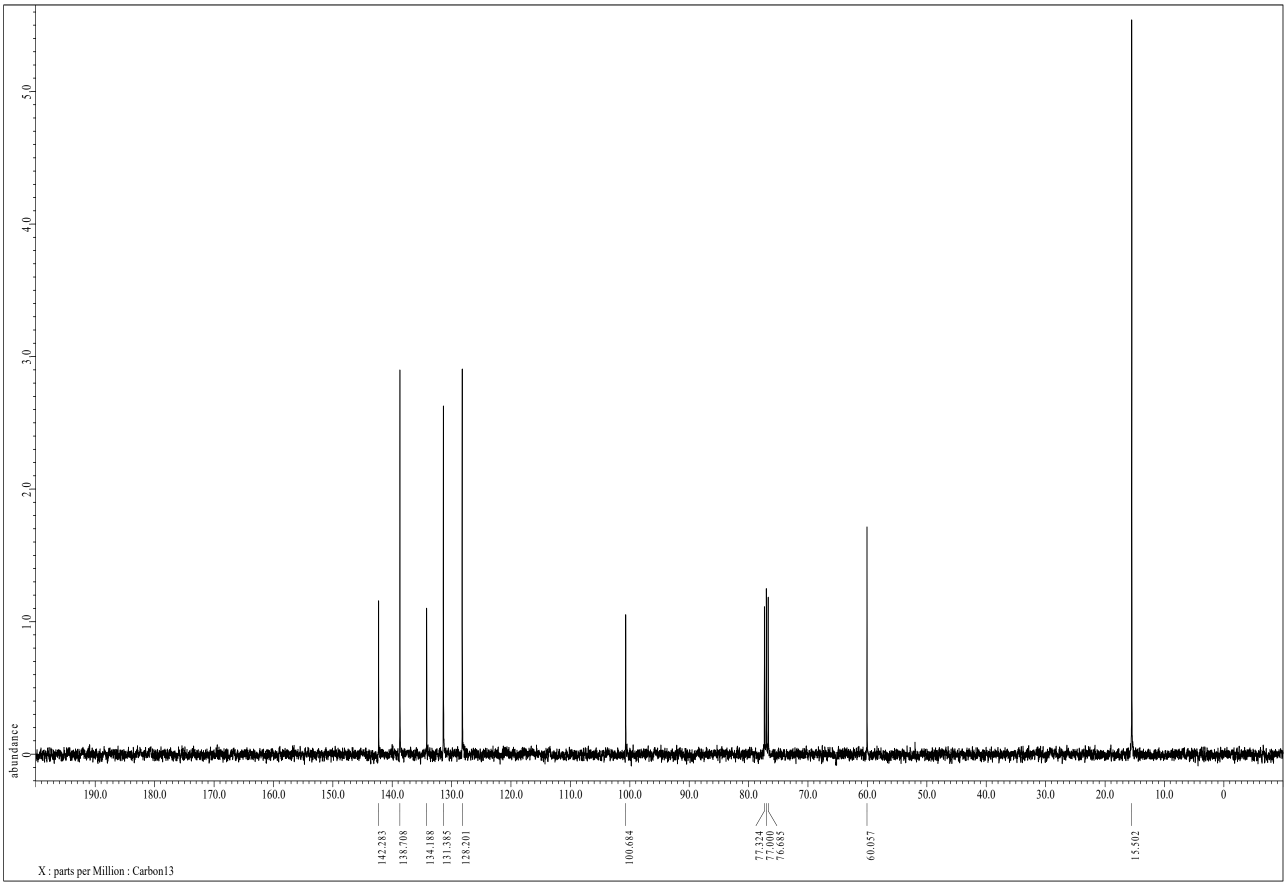

MeO
OMOM
O
O
S25
abundance
X : parts per Million : Proton
0.94
1.98
2.90
2.07
2.02
2.00
2.02
2.02
3.00
3.03
1.89
1.86
7.660
7.655
7.600
7.583
7.580
7.541
7.536
7.518
7.385
7.366
6.986
6.978
6.973
6.961
6.957
6.949
5.139
4.699
3.831
3.198
1.344
1.329
1.325
1.312
1.066
1.053
1.048
1.034
0.000

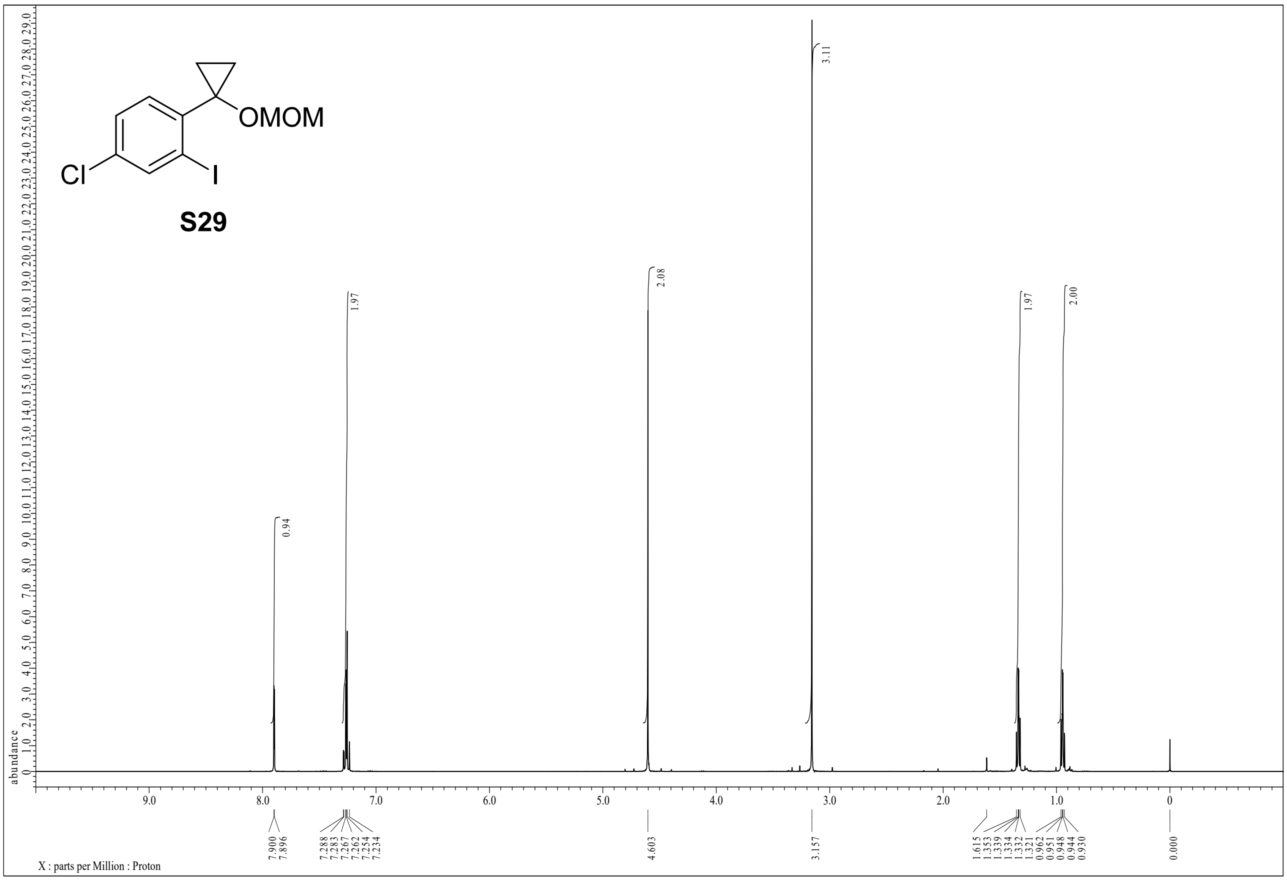

abundance
X : parts per Million : Carbon13
159.677
153.432
142.524
141.027
133.648
133.180
132.484
130.949
128.966
128.728
128.232
125.905
121.605
119.498
114.416
95.175
87.386
86.957
86.165
80.244
61.566
55.655
55.445
54.539
13.054

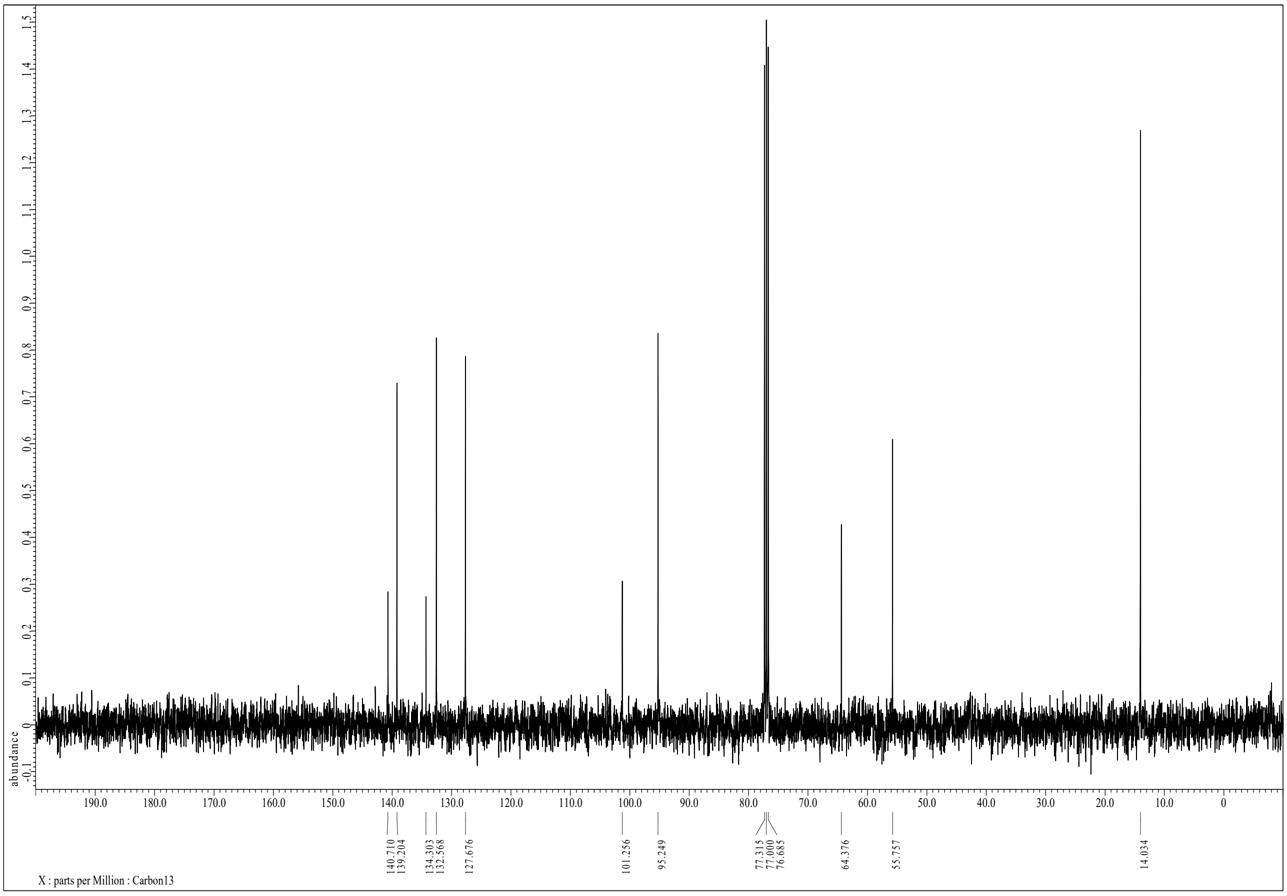

MeO
OH
O
O
1o
1.95
2.97
0.98
1.97
1.97
2.00
2.00
3.16
0.69
1.93
1.86
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.609
7.592
7.589
7.556
7.524
7.513
7.502
7.441
7.377
6.979
6.974
6.962
6.957
5.101
3.839
3.434
1.273
1.259
1.254
1.242
1.060
1.047
1.042
1.029
X : parts per Million : Proton

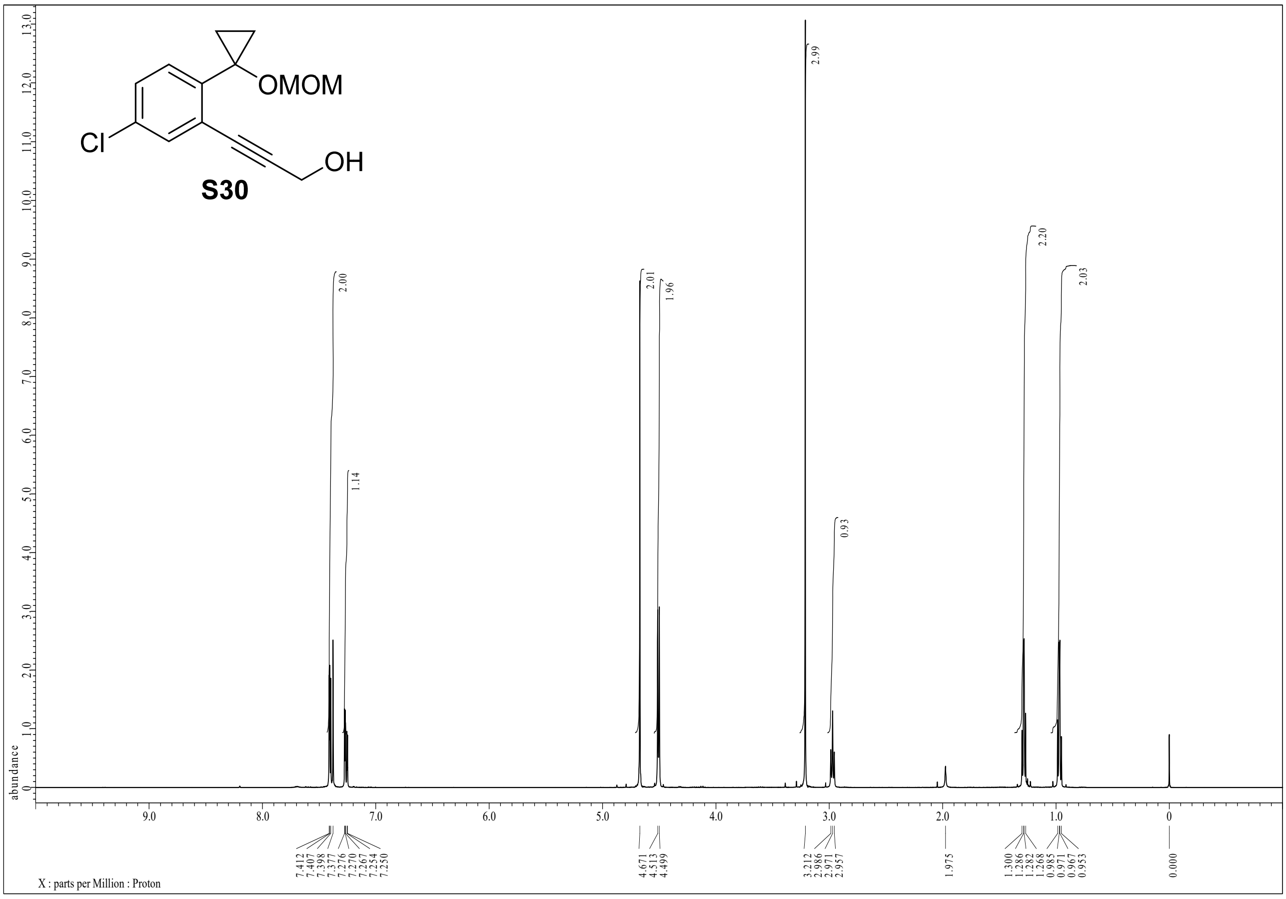

abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.677
153.699
145.404
141.723
133.438
133.247
132.637
131.054
128.728
128.260
126.535
125.791
120.328
119.355
114.426
87.891
87.729
86.156
80.035
57.104
55.454
54.482
14.465
X : parts per Million : Carbon13

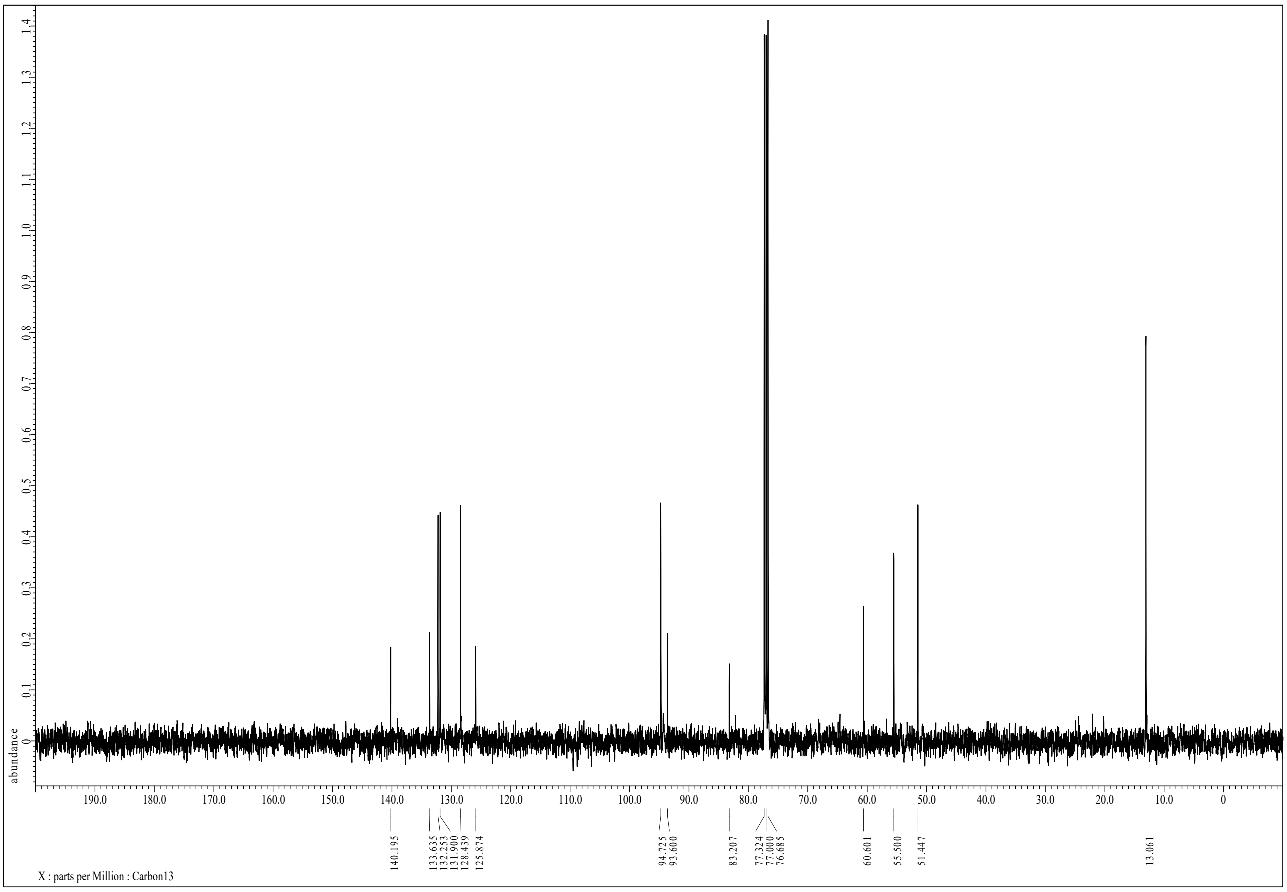

OH
Cl
I
S28
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
0.91
1.96
0.93
2.03
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.831
7.826
7.274
7.269
7.253
7.249
7.237
7.217
3.318
3.147
1.269
1.255
1.251
1.237
0.931
0.918
0.913
0.899
X : parts per Million : Proton

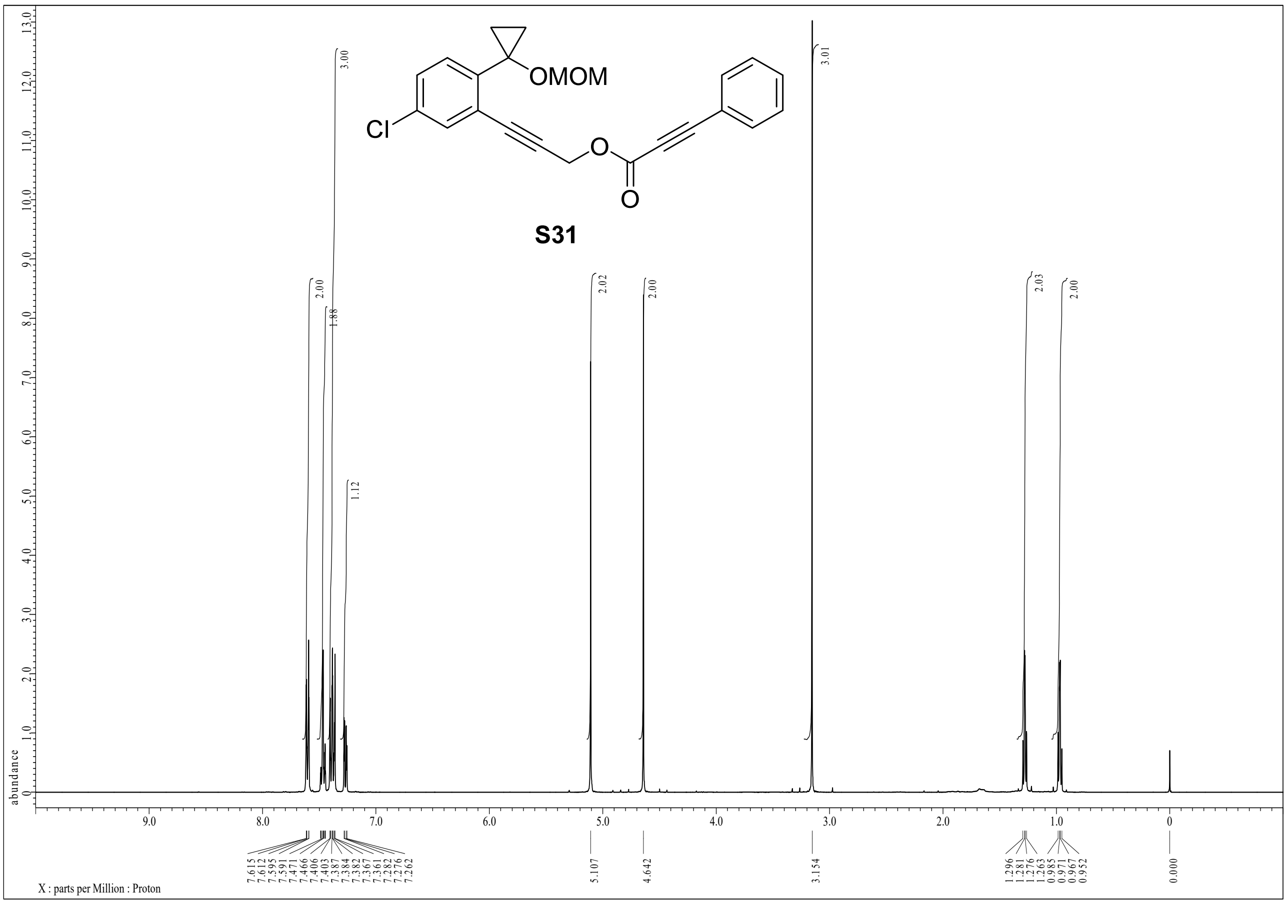

abundance
0
1.0
2.0
3.0
4.0
5.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.283
138.708
134.188
131.385
128.201
100.684
77.324
77.000
76.685
60.057
15.502
X : parts per Million : Carbon13

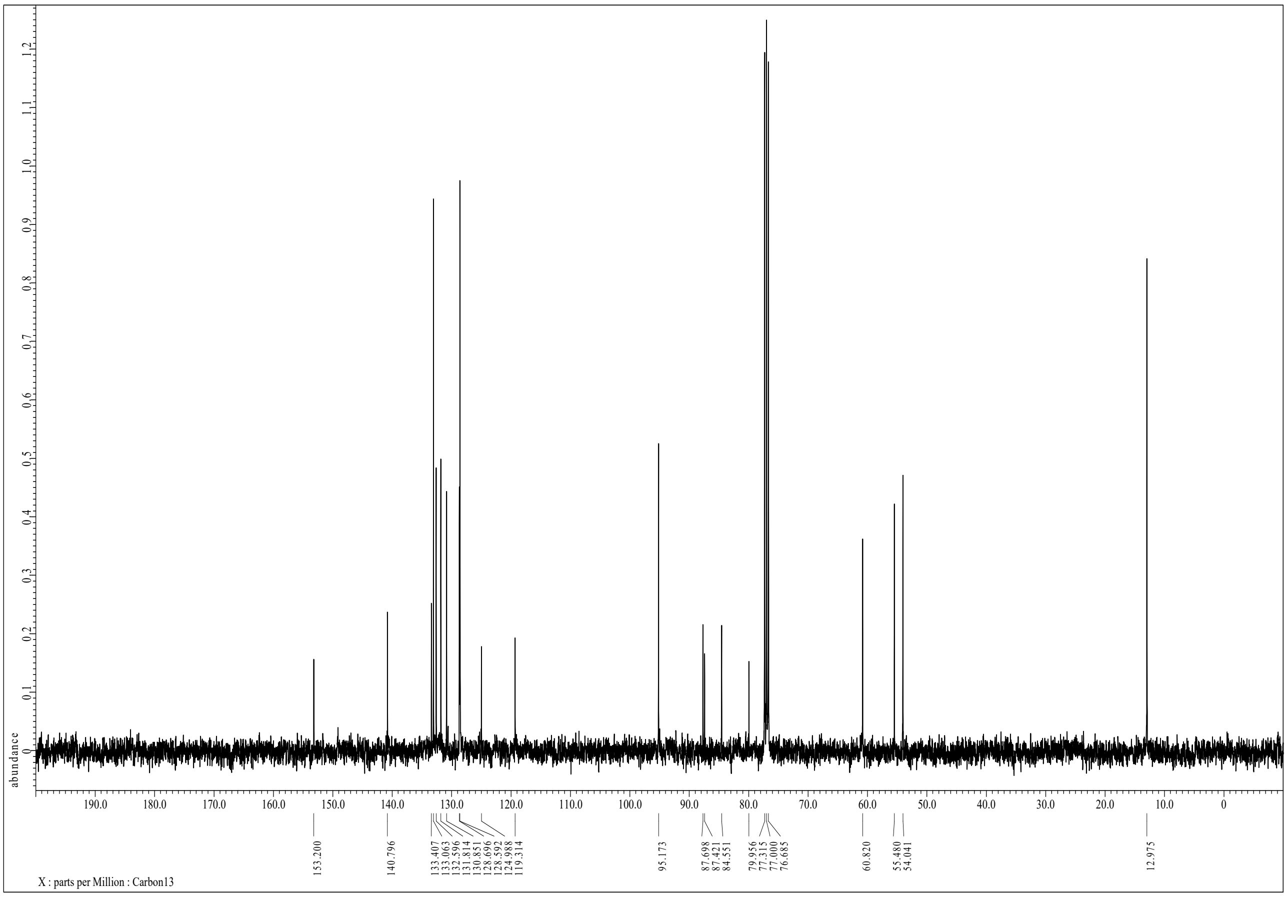

OMOM
Cl
I
S29
abundance
0.94
1.97
2.08
3.11
1.97
2.00
7.900
7.896
7.288
7.283
7.267
7.262
7.254
7.234
4.603
3.157
1.615
1.353
1.339
1.334
1.332
1.321
0.962
0.951
0.948
0.944
0.930
0.000
X : parts per Million : Proton

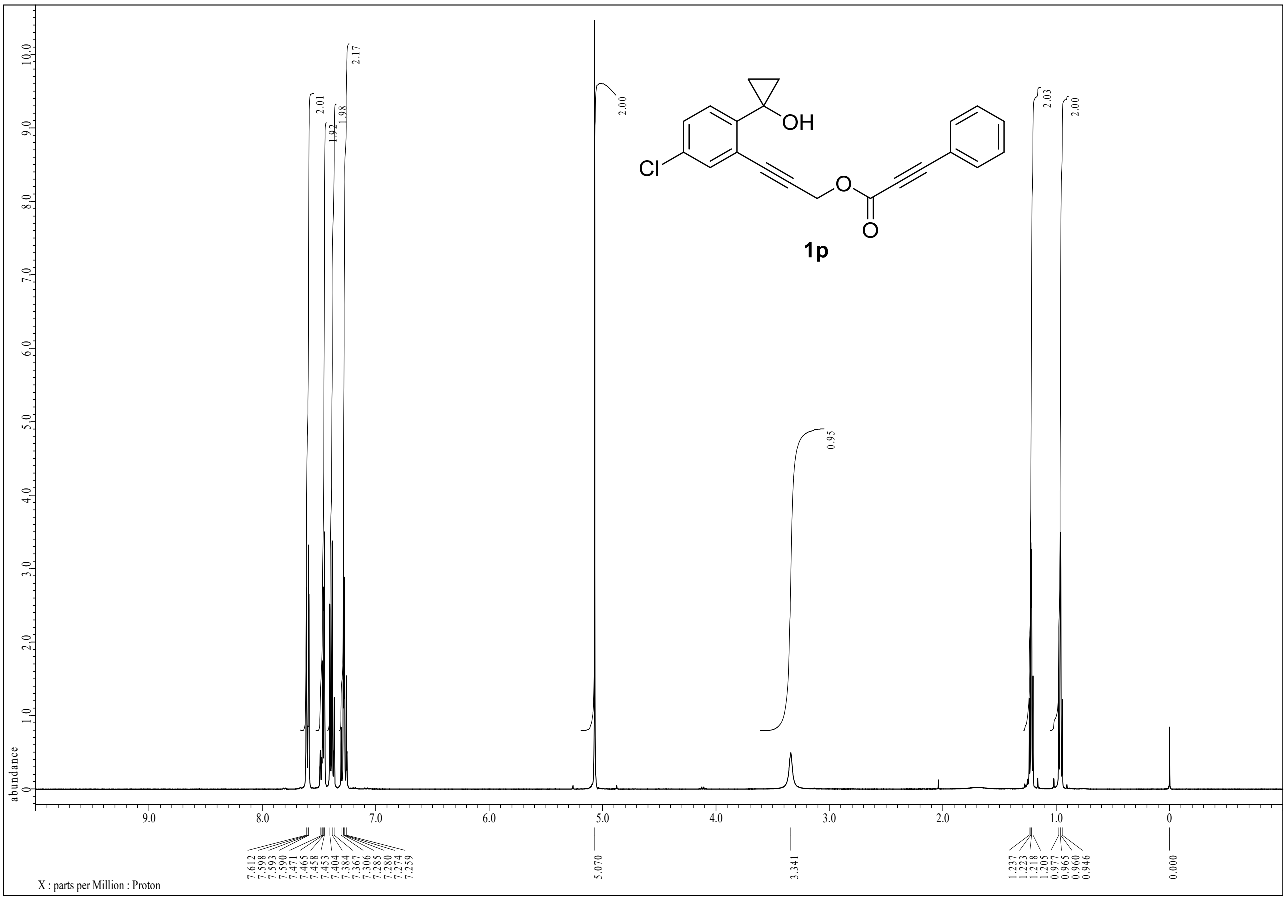

abundance
140.710
139.204
134.303
132.568
127.676
101.256
95.249
77.315
77.000
76.685
64.376
55.757
14.034
X : parts per Million : Carbon13

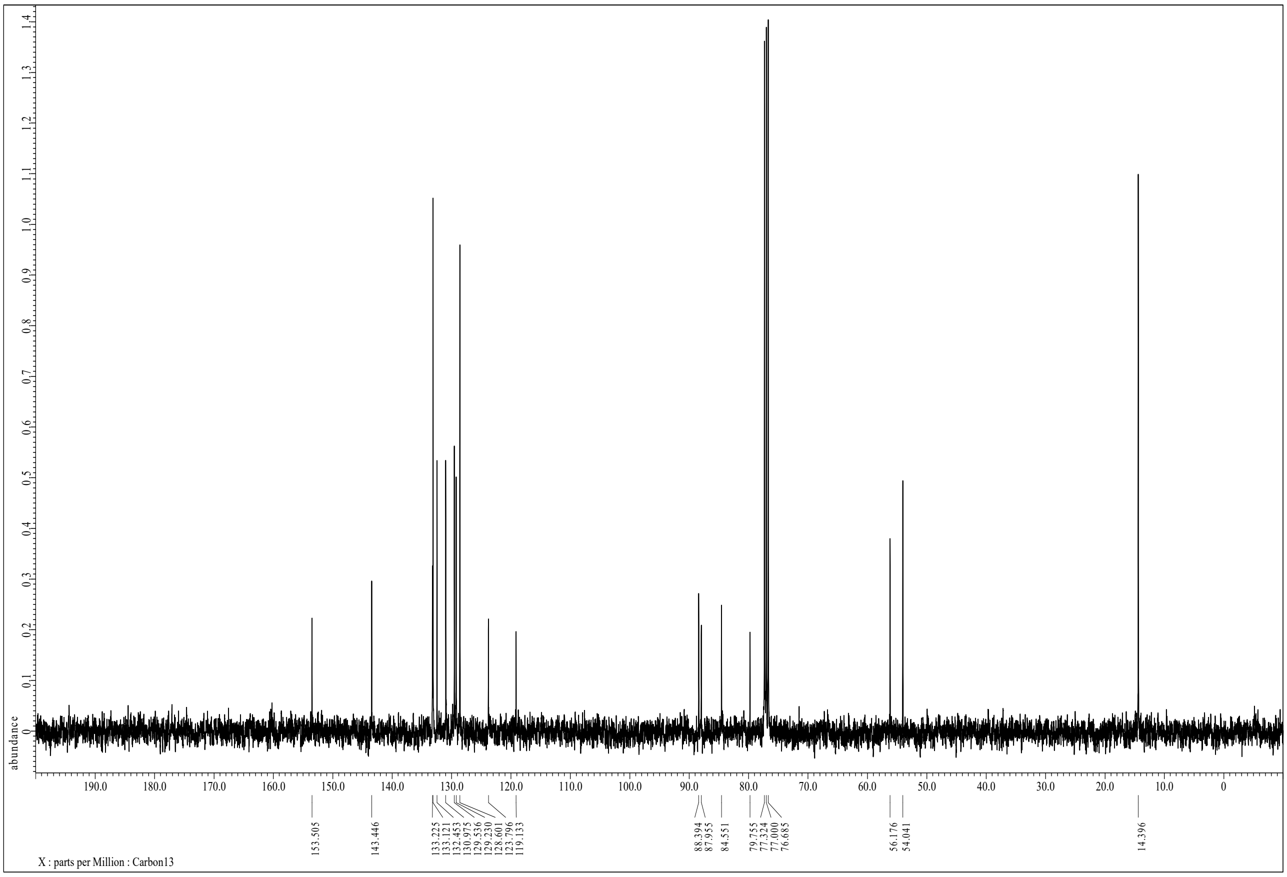

OMOM
Cl
OH
S30
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
2.00
1.14
2.01
1.96
2.99
0.93
2.20
2.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.412
7.407
7.398
7.377
7.276
7.270
7.267
7.254
7.250
4.671
4.513
4.499
3.212
2.986
2.971
2.957
1.975
1.300
1.286
1.282
1.268
0.985
0.971
0.967
0.953
0.000
X : parts per Million : Proton

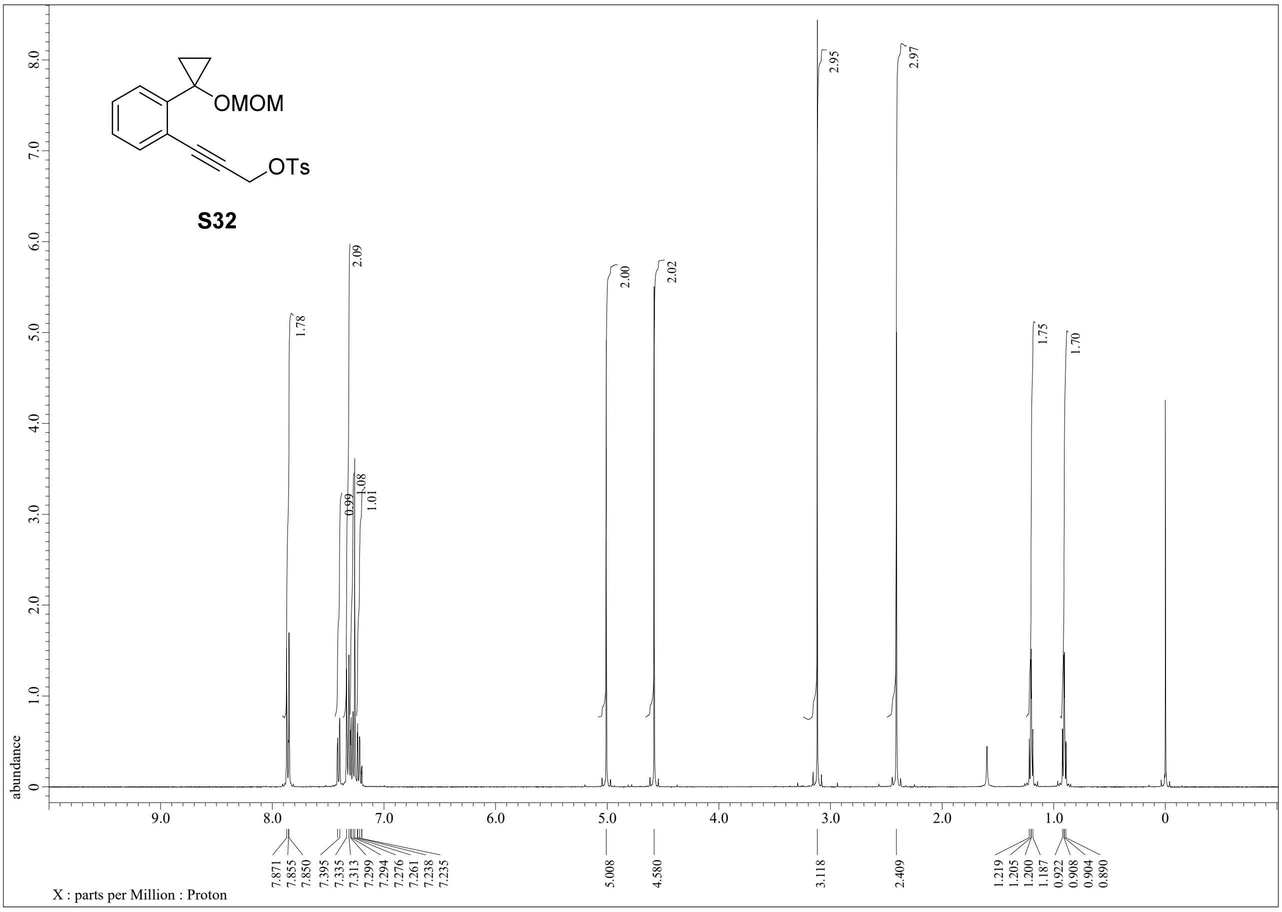

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
140.195
133.635
132.253
131.900
128.439
125.874
94.725
93.600
83.207
77.324
77.000
76.685
60.601
55.500
51.447
13.061
X : parts per Million : Carbon13


OMOM
Cl
O
O
S31
abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0
2.00
1.88
3.00
1.12
2.02
2.00
3.01
2.03
2.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.615
7.612
7.595
7.591
7.471
7.466
7.406
7.403
7.387
7.384
7.382
7.367
7.361
7.282
7.276
7.262
5.107
4.642
3.154
1.296
1.281
1.276
1.263
0.985
0.971
0.967
0.952
0.000
X : parts per Million : Proton


abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
153.200
140.796
133.407
133.063
132.596
131.814
130.851
128.696
128.592
124.988
119.314
95.173
87.698
87.421
84.551
79.956
77.315
77.000
76.685
60.820
55.480
54.041
12.975
X : parts per Million : Carbon13

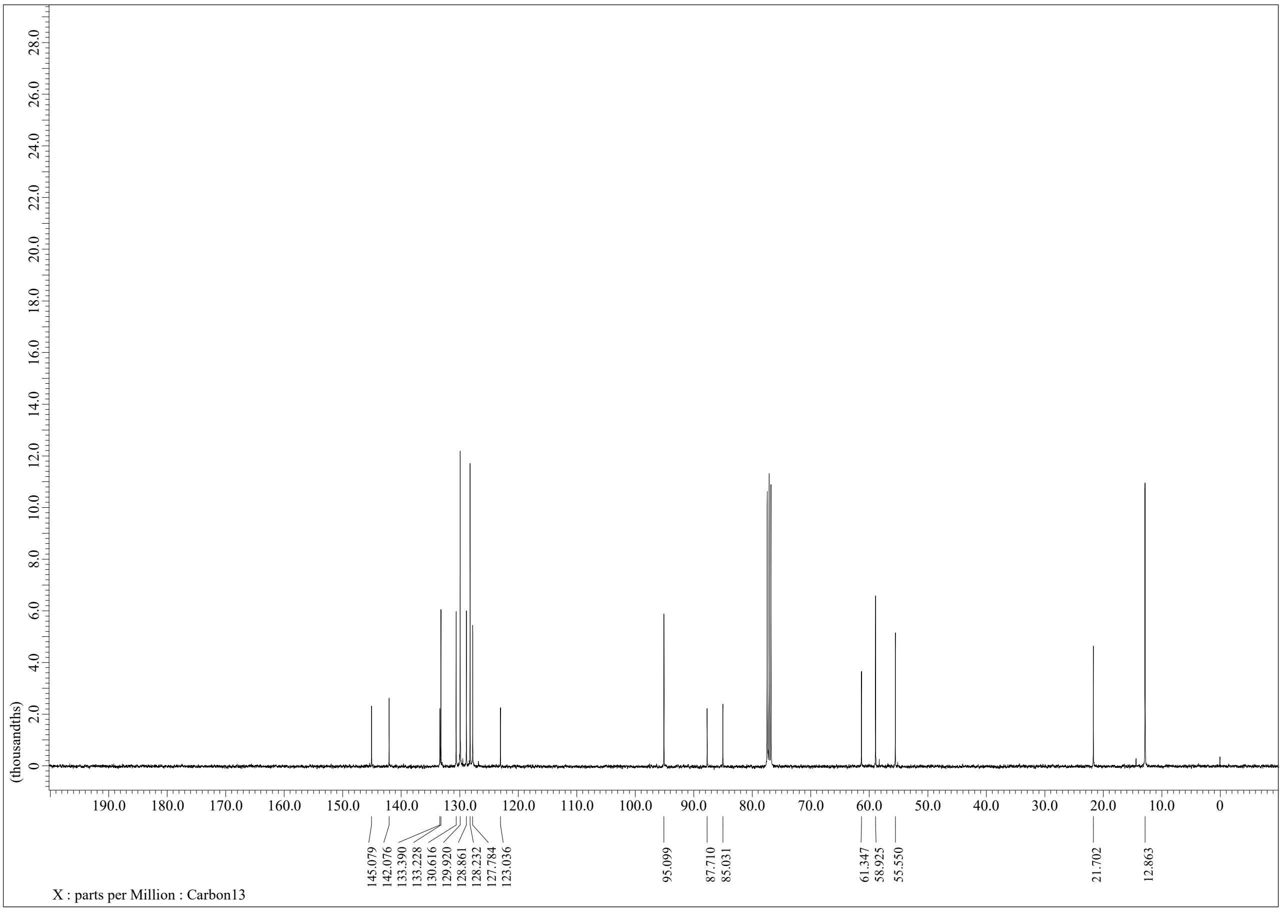

abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
OH
Cl
O
O
1p
2.01
1.92
1.98
2.17
2.00
0.95
2.03
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.612
7.598
7.593
7.590
7.471
7.465
7.458
7.453
7.404
7.384
7.367
7.306
7.285
7.280
7.274
7.259
5.070
3.341
1.237
1.223
1.218
1.205
0.977
0.965
0.960
0.946
0.000
X : parts per Million : Proton


abundance
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.505
143.446
133.225
133.121
132.453
130.975
129.536
129.230
128.601
123.796
119.133
88.394
87.955
84.551
79.755
77.324
77.000
76.685
56.176
54.041
14.396
X : parts per Million : Carbon13

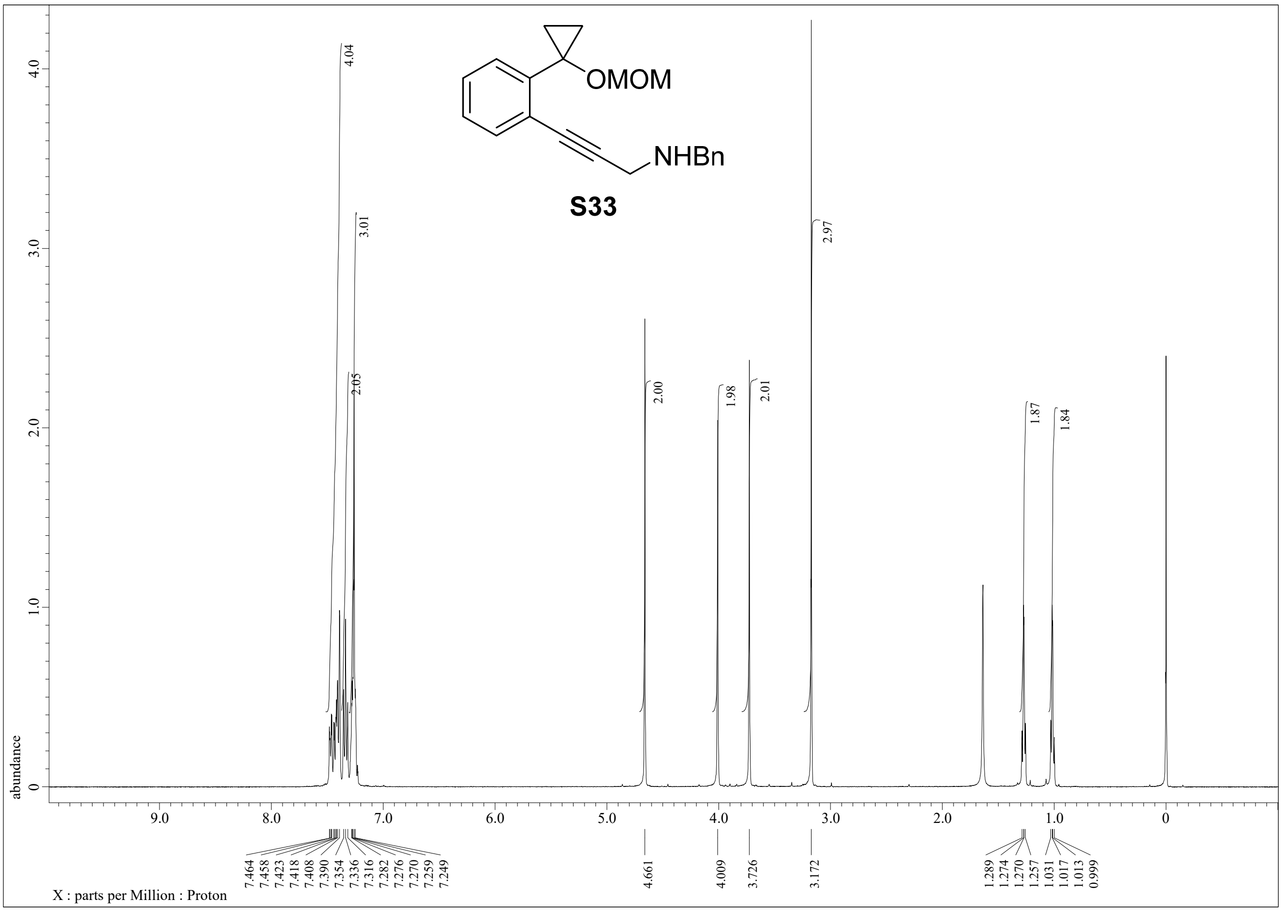


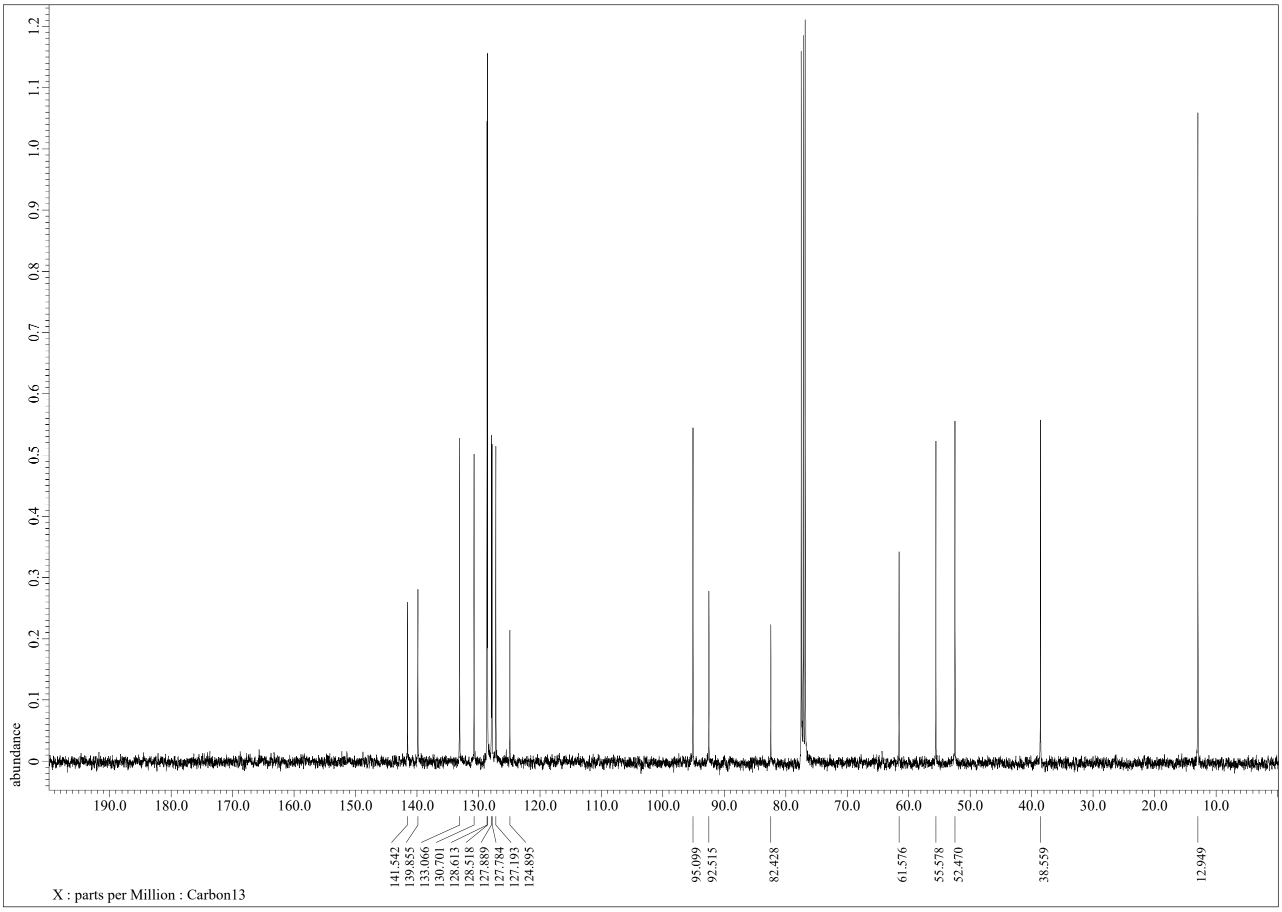
S32

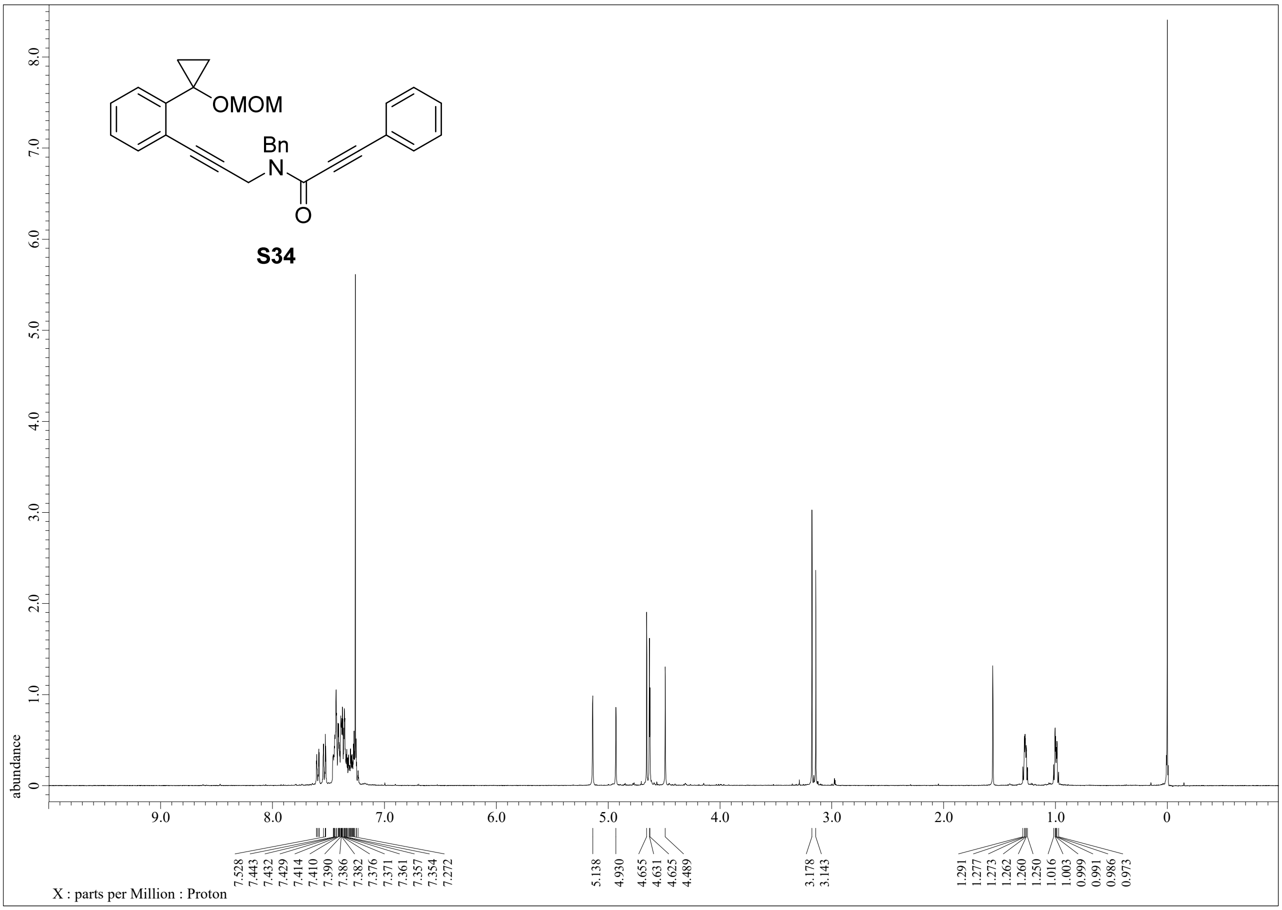
OMOM
OTs
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
1.78
2.09
0.99
1.08
1.01
2.00
2.02
2.95
2.97
1.75
1.70
7.871
7.855
7.850
7.395
7.335
7.313
7.299
7.294
7.276
7.261
7.238
7.235
5.008
4.580
3.118
2.409
1.219
1.205
1.200
1.187
0.922
0.908
0.904
0.890
X : parts per Million : Proton

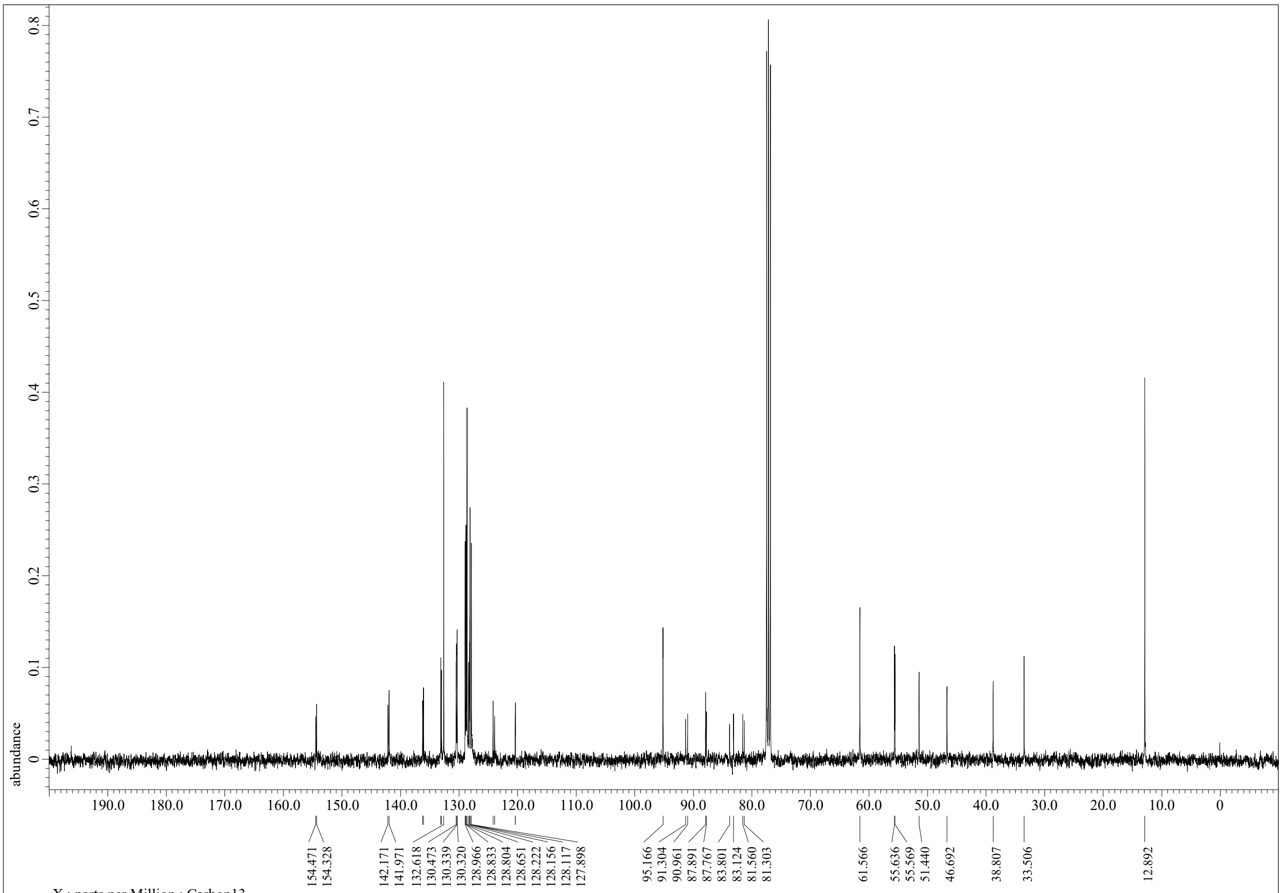


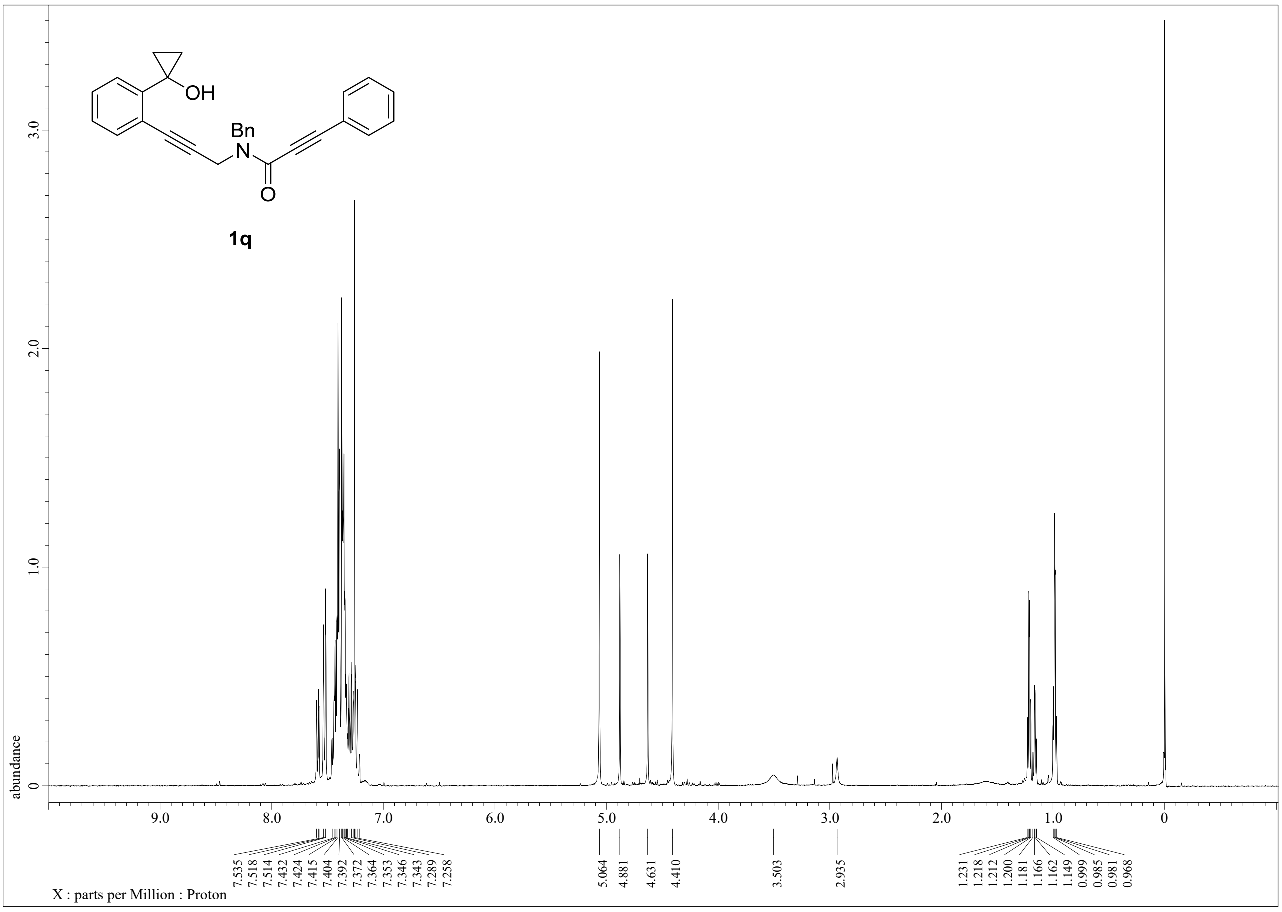
(thousandths)
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
28.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
145.079
142.076
133.390
133.228
130.616
129.920
128.861
128.232
127.784
123.036
95.099
87.710
85.031
61.347
58.925
55.550
21.702
12.863
X : parts per Million : Carbon13

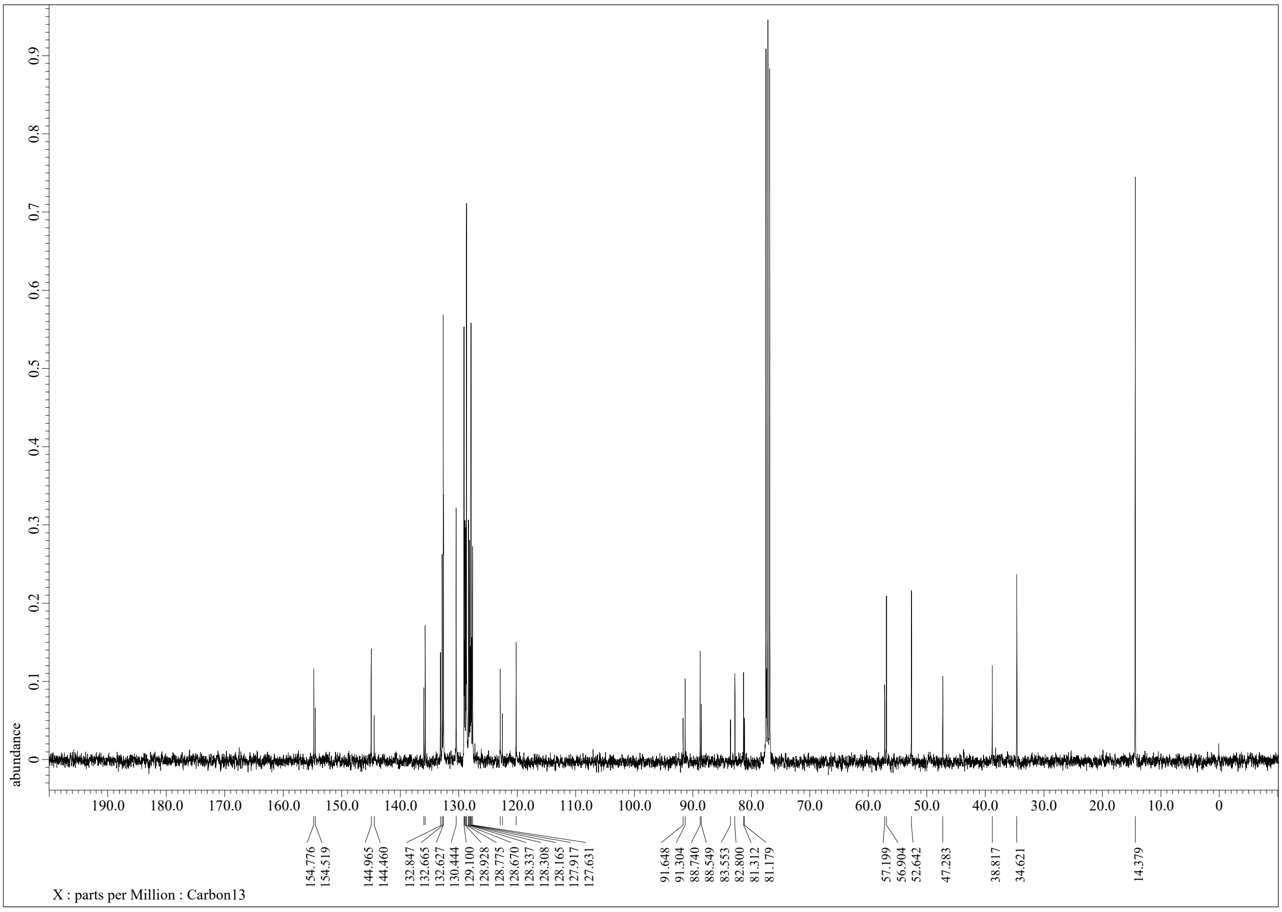

OMOM
NHBn
S33
4.04
3.01
2.05
2.00
1.98
2.01
2.97
1.87
1.84
abundance
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.464
7.458
7.423
7.418
7.408
7.390
7.354
7.336
7.316
7.282
7.276
7.270
7.259
7.249
4.661
4.009
3.726
3.172
1.289
1.274
1.270
1.257
1.031
1.017
1.013
0.999
X : parts per Million : Proton

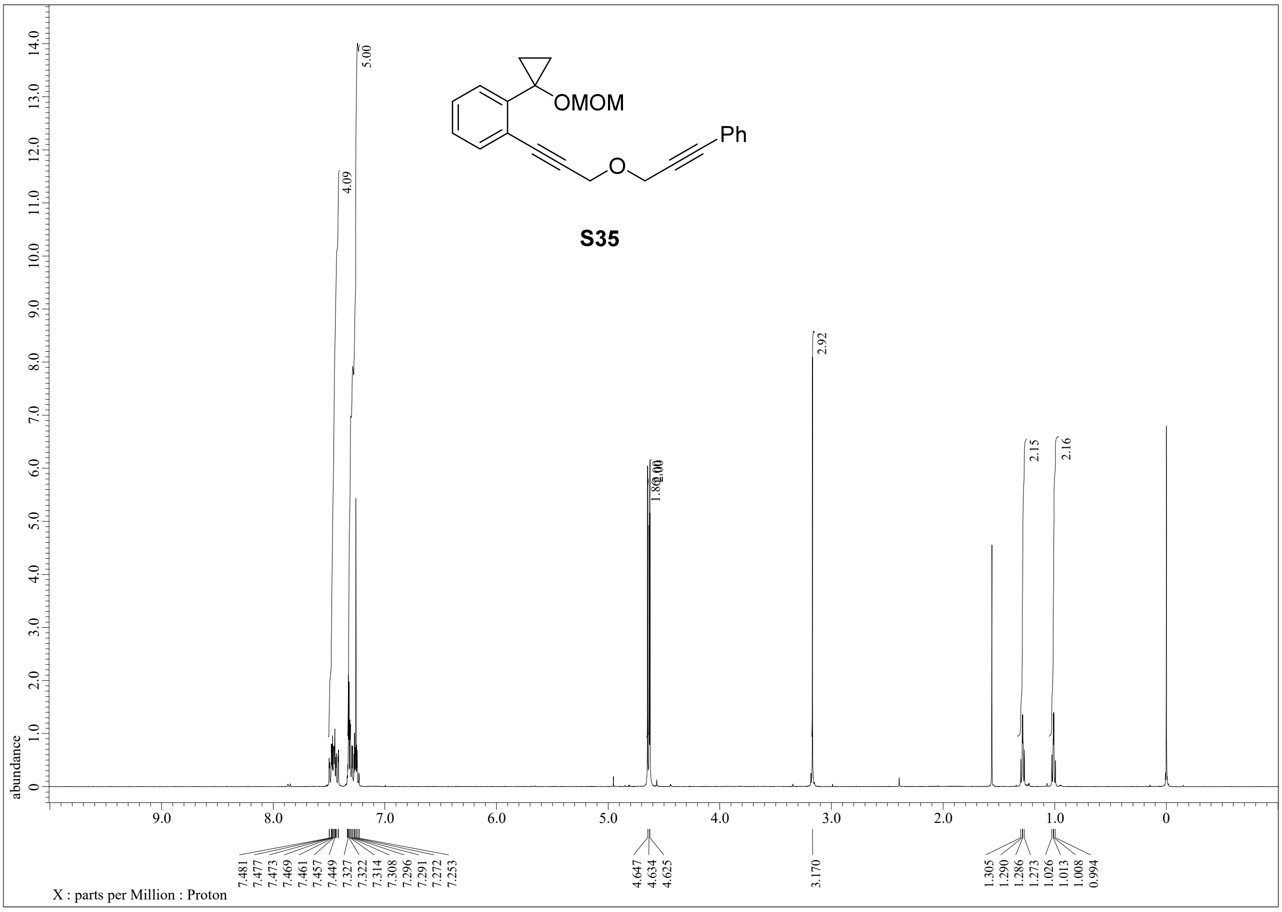

abundance
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
141.542
139.855
133.066
130.701
128.613
128.518
127.889
127.784
127.193
124.895
95.099
92.515
82.428
61.576
55.578
52.470
38.559
12.949
X : parts per Million : Carbon13

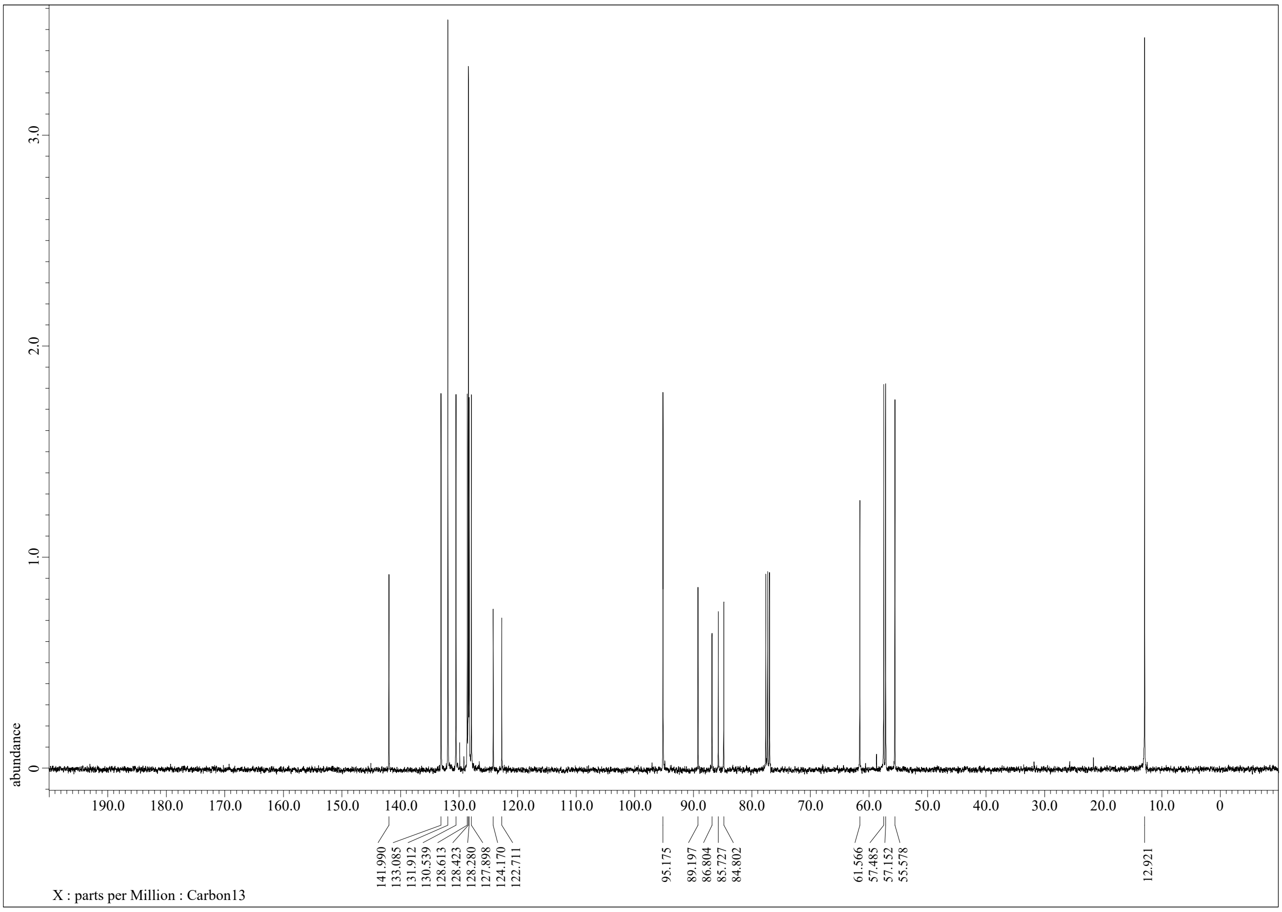

S34
OMOM
Bn
N
O
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.528
7.443
7.432
7.429
7.414
7.410
7.390
7.386
7.382
7.376
7.371
7.361
7.357
7.354
7.272
5.138
4.930
4.655
4.631
4.625
4.489
3.178
3.143
1.291
1.277
1.273
1.262
1.260
1.250
1.016
1.003
0.999
0.991
0.986
0.973
X : parts per Million : Proton

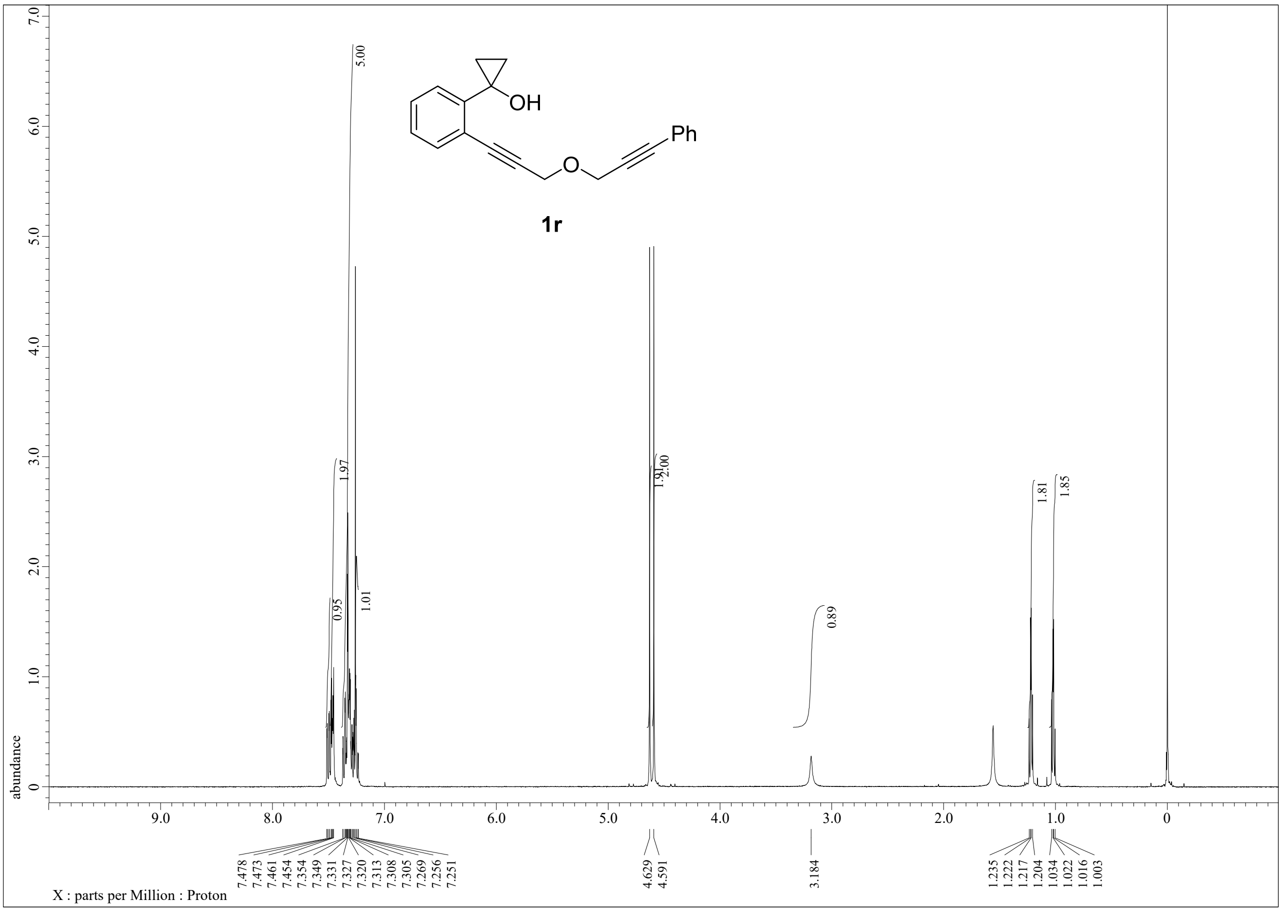

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
154.471
154.328
142.171
141.971
132.618
130.473
130.339
130.320
128.966
128.833
128.804
128.651
128.222
128.156
128.117
127.898
95.166
91.304
90.961
87.891
87.767
83.801
83.124
81.560
81.303
61.566
55.636
55.569
51.440
46.692
38.807
33.506
12.892
X : parts per Million : Carbon13

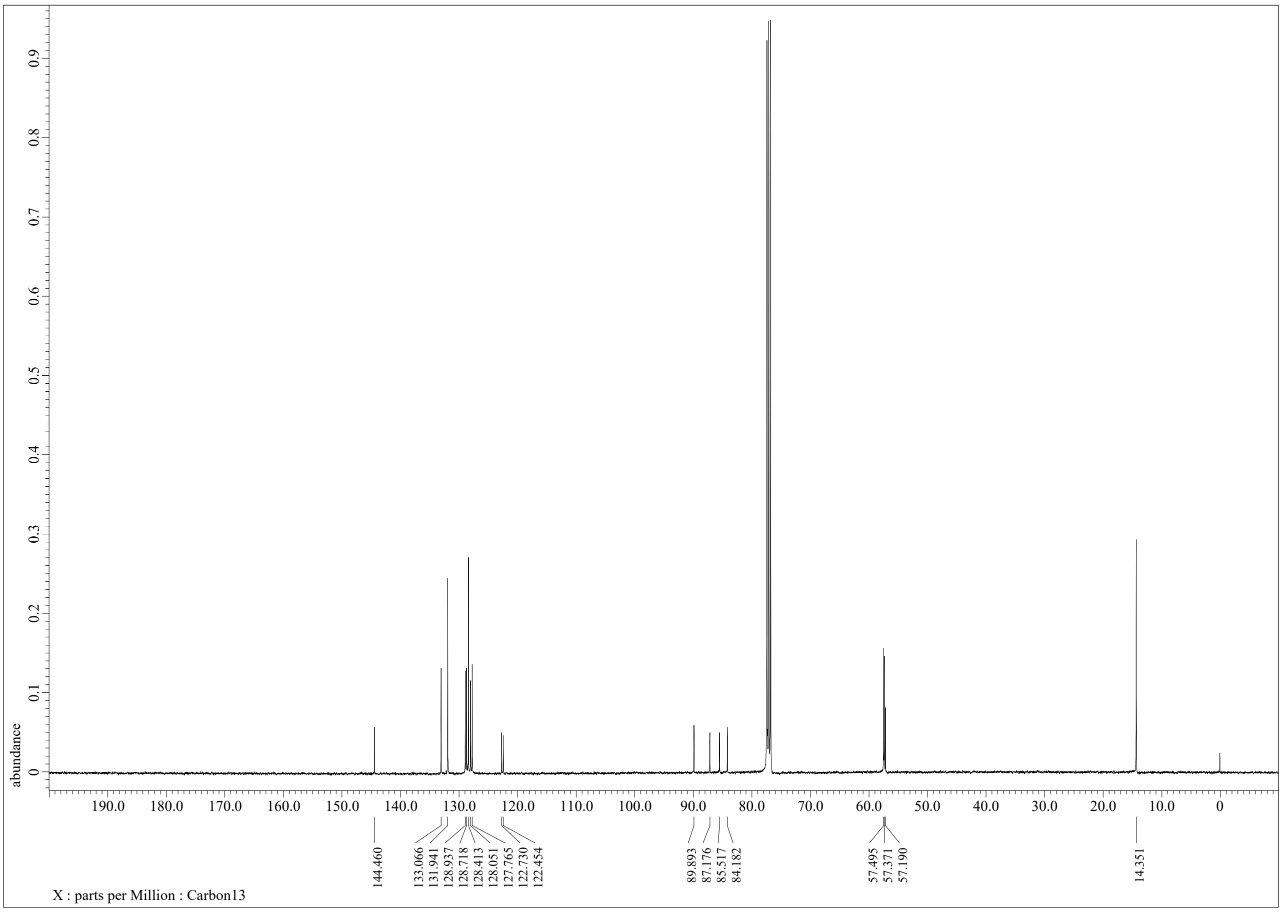

OH
Bn
N
O
1q
abundance
0
1.0
2.0
3.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.535
7.518
7.514
7.432
7.424
7.415
7.404
7.392
7.372
7.364
7.353
7.346
7.343
7.289
7.258
5.064
4.881
4.631
4.410
3.503
2.935
1.231
1.218
1.212
1.200
1.181
1.166
1.162
1.149
0.999
0.985
0.981
0.968
X : parts per Million : Proton

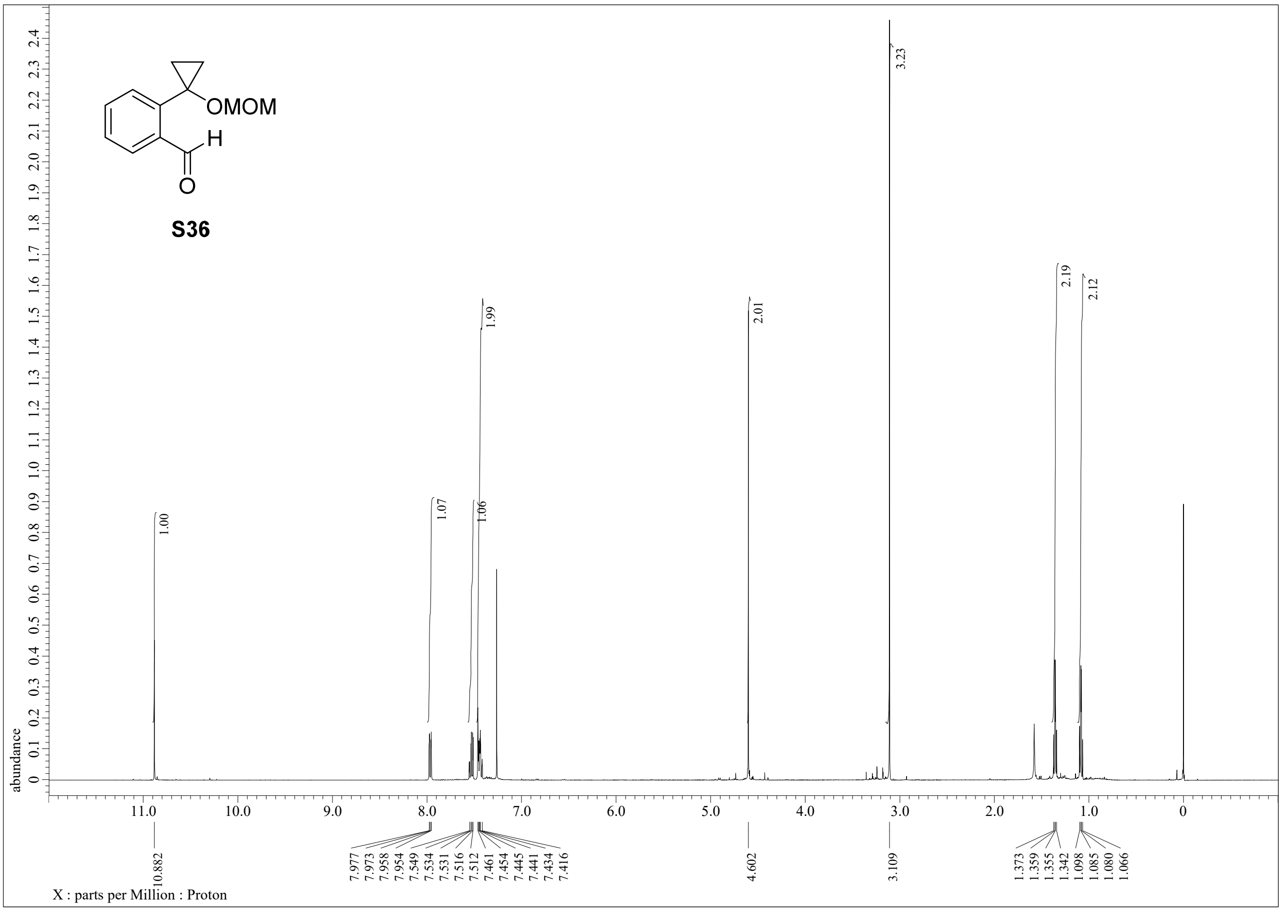

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
154.776
154.519
144.965
144.460
132.847
132.665
132.627
130.444
129.100
128.928
128.775
128.670
128.337
128.308
128.165
127.917
127.631
91.648
91.304
88.740
88.549
83.553
82.800
81.312
81.179
57.199
56.904
52.642
47.283
38.817
34.621
14.379
X : parts per Million : Carbon13

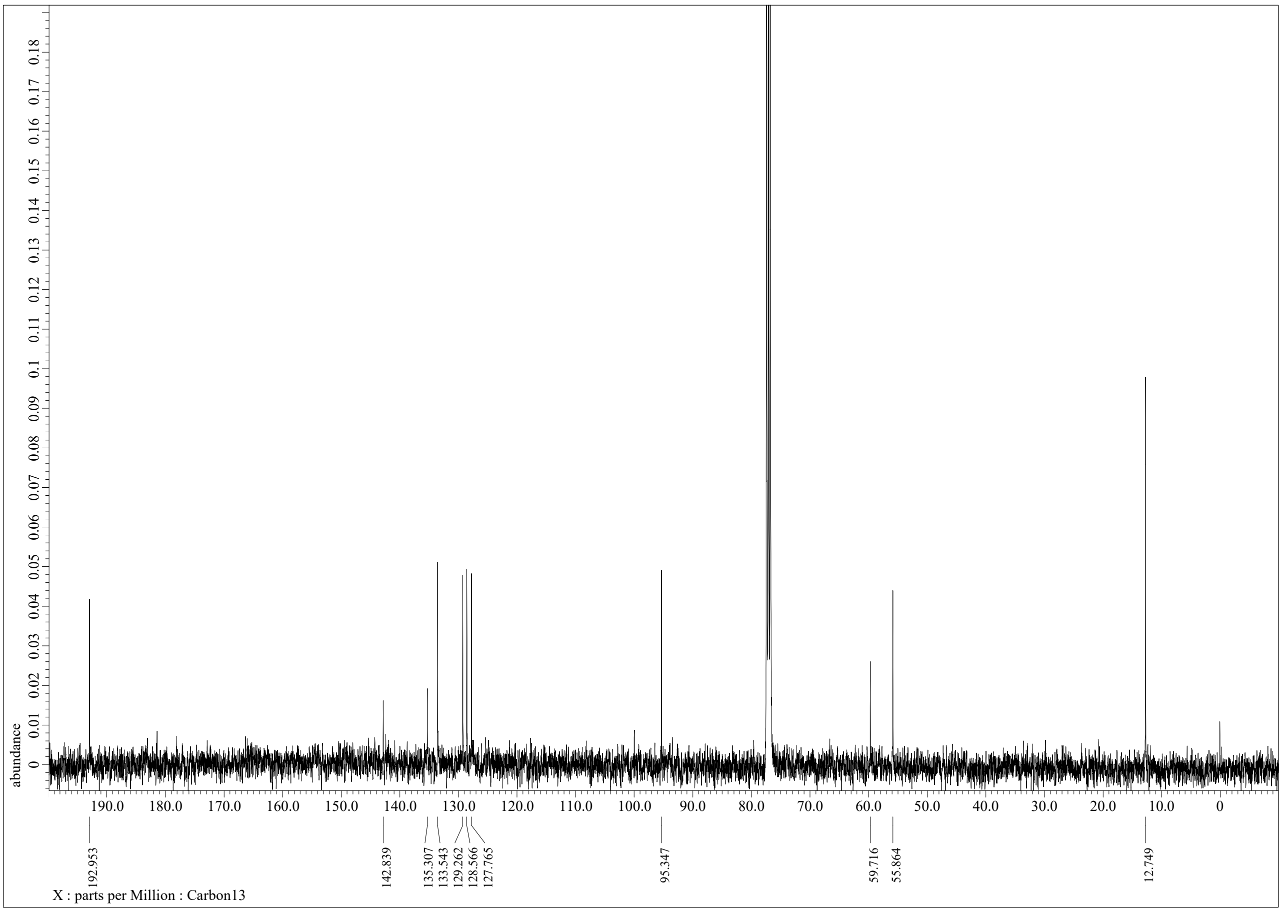

OMOM
O
Ph
S35
abundance
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.00
4.09
1.80
2.00
2.00
2.92
2.15
2.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.481
7.477
7.473
7.469
7.461
7.457
7.449
7.327
7.322
7.314
7.308
7.296
7.291
7.272
7.253
4.647
4.634
4.625
3.170
1.305
1.290
1.286
1.273
1.026
1.013
1.008
0.994
X : parts per Million : Proton

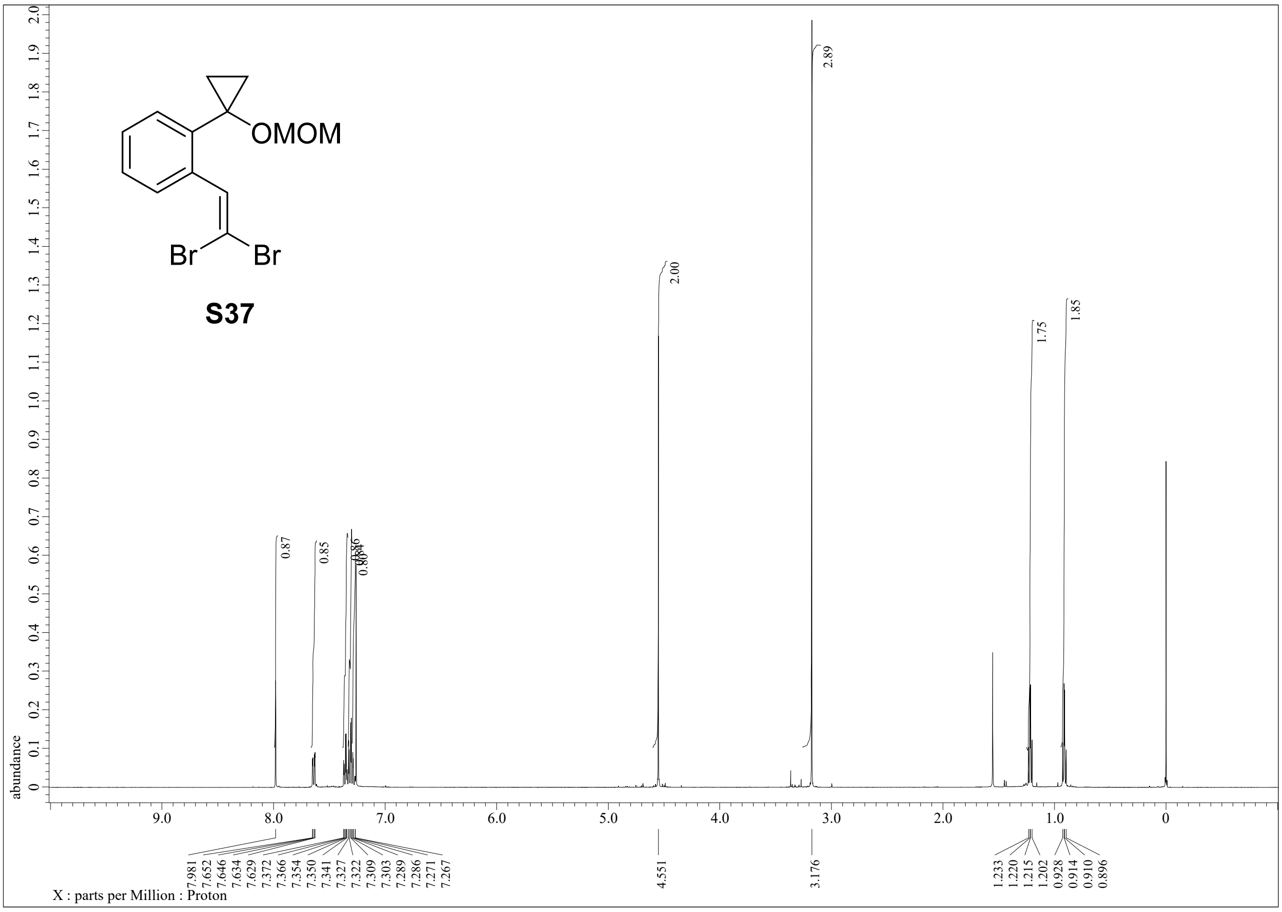

abundance
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.990
133.085
131.912
130.539
128.613
128.423
128.280
127.898
124.170
122.711
95.175
89.197
86.804
85.727
84.802
61.566
57.485
57.152
55.578
12.921
X : parts per Million : Carbon13

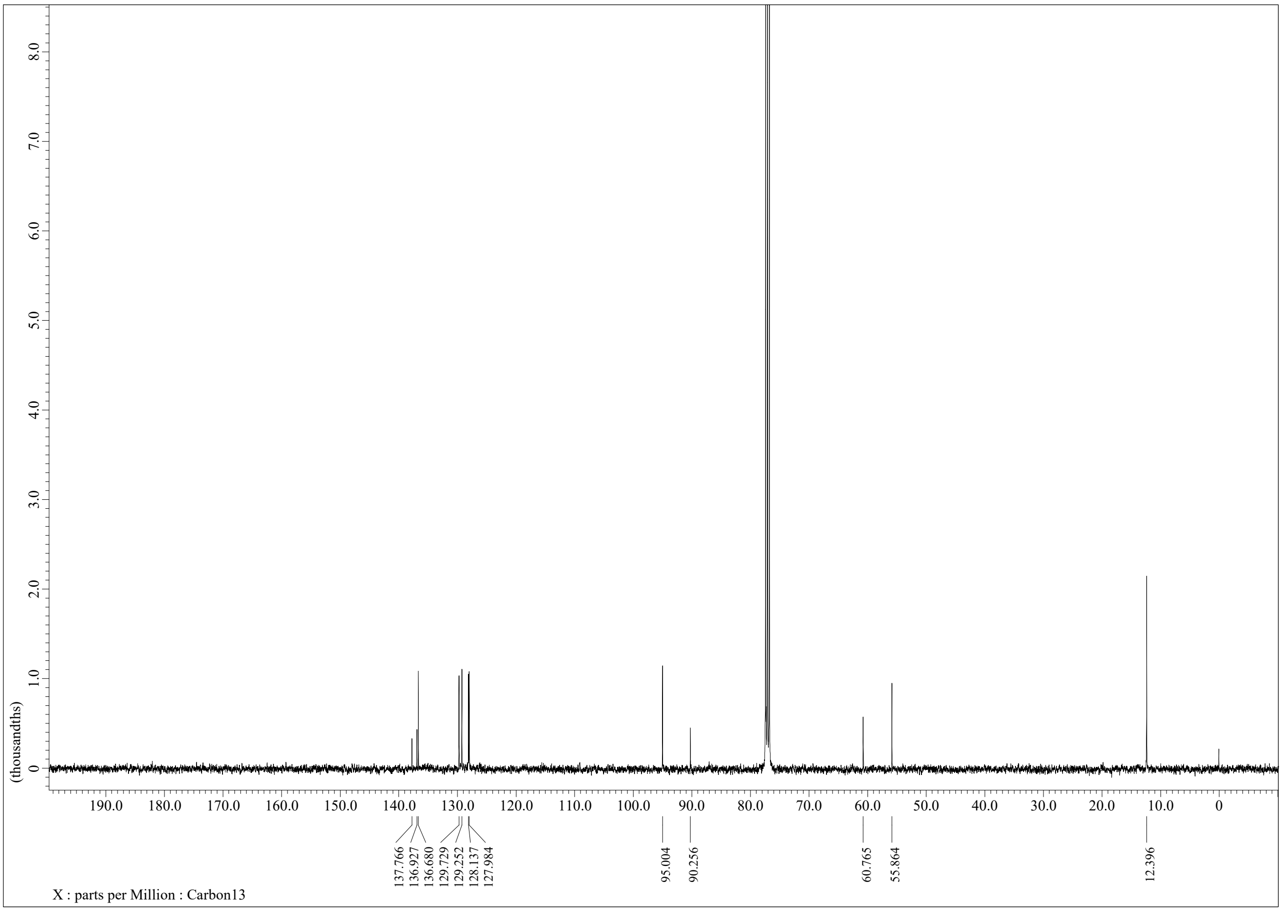

OH
O
Ph
1r
abundance
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.00
1.97
0.95
1.01
1.91
2.00
0.89
1.81
1.85
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.478
7.473
7.461
7.454
7.354
7.349
7.331
7.327
7.320
7.313
7.308
7.305
7.269
7.256
7.251
4.629
4.591
3.184
1.235
1.222
1.217
1.204
1.034
1.022
1.016
1.003
X : parts per Million : Proton

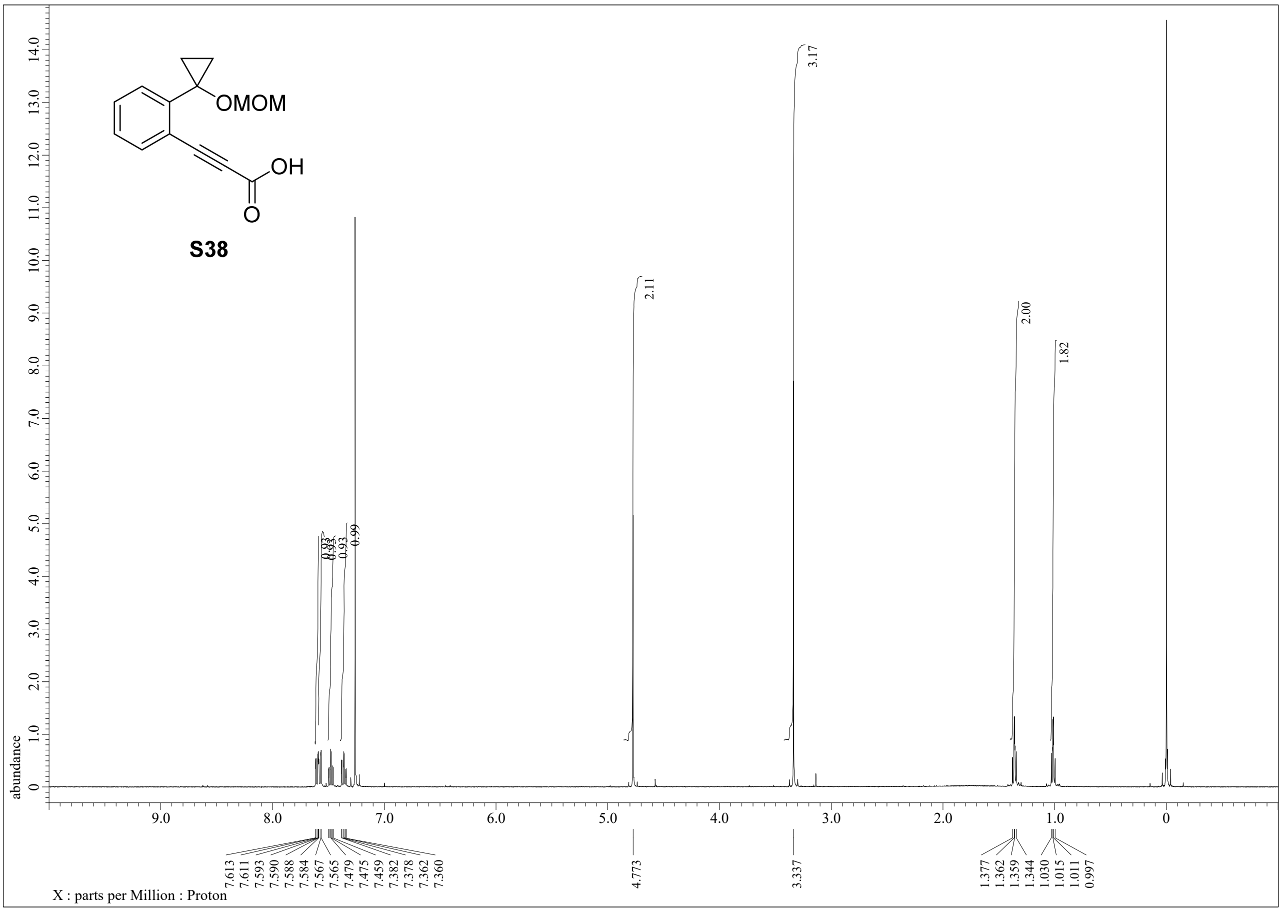

abundance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
144.460
133.066
131.941
128.937
128.718
128.413
128.051
127.765
122.730
122.454
89.893
87.176
85.517
84.182
57.495
57.371
57.190
14.351
X : parts per Million : Carbon13

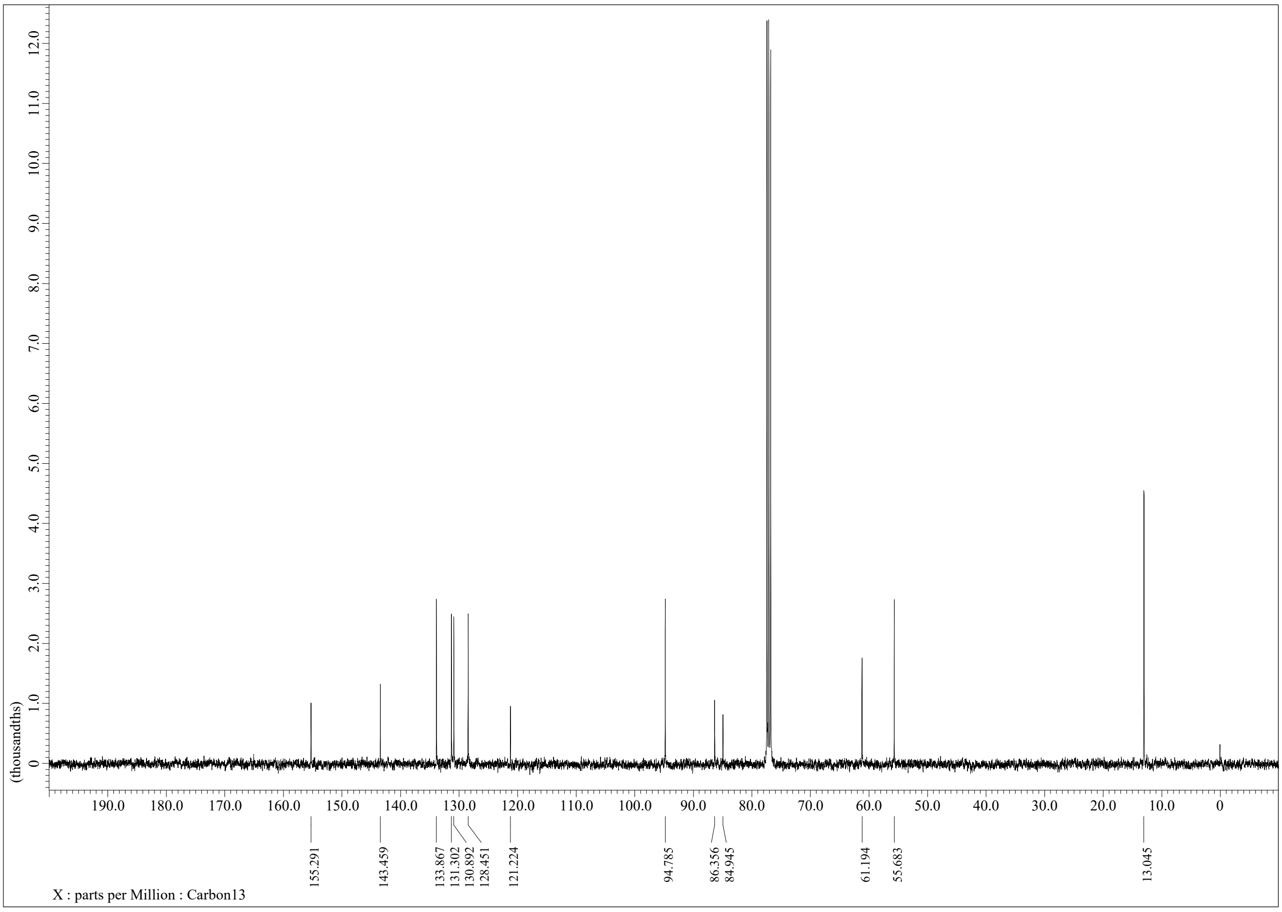

OMOM
H
O
S36
abundance
1.00
1.07
1.06
1.99
2.01
3.23
2.19
2.12
10.882
7.977
7.973
7.958
7.954
7.549
7.534
7.531
7.516
7.512
7.461
7.454
7.445
7.441
7.434
7.416
4.602
3.109
1.373
1.359
1.355
1.342
1.098
1.085
1.080
1.066
X : parts per Million : Proton

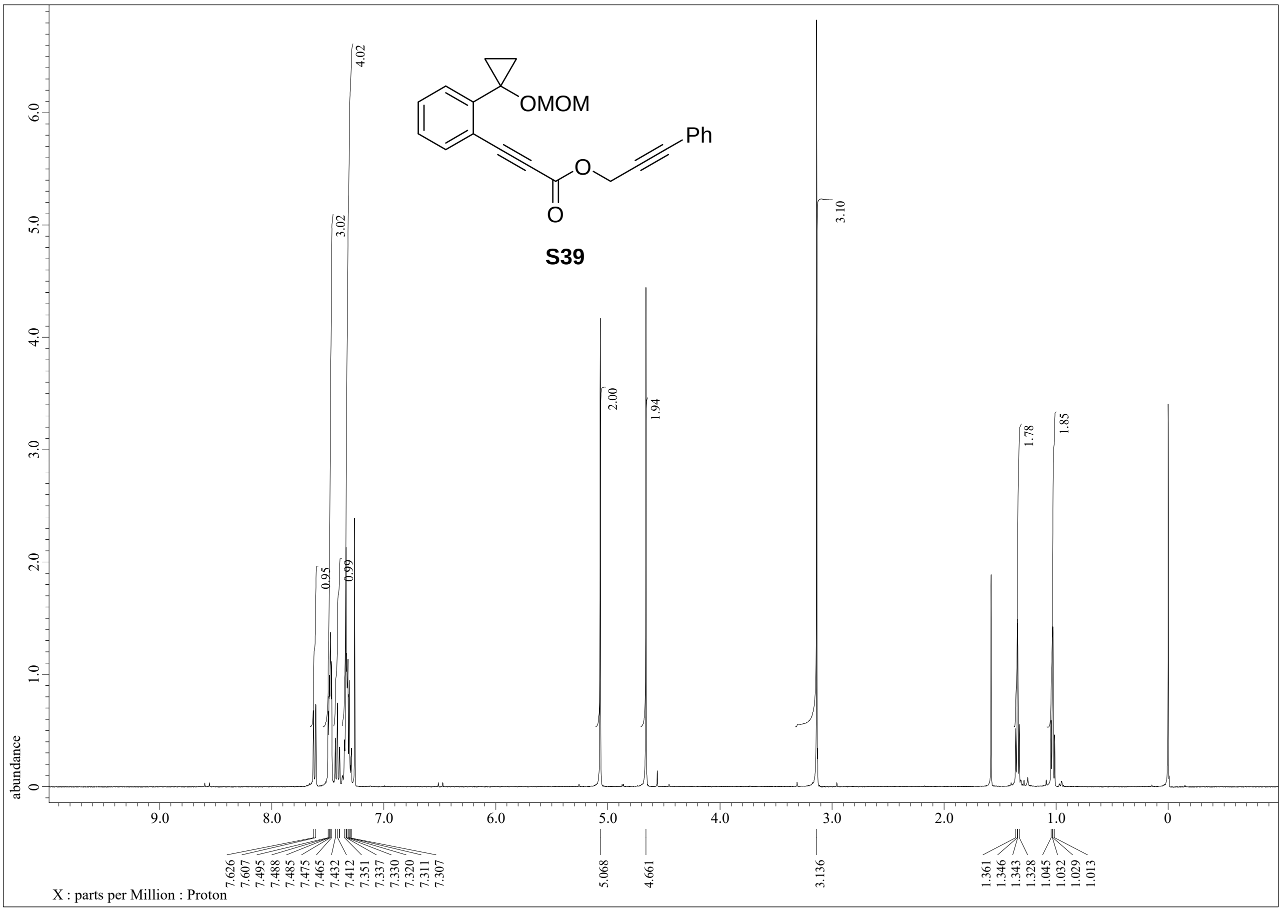

abundance
192.953
142.839
135.307
133.543
129.262
128.566
127.765
95.347
59.716
55.864
12.749
X : parts per Million : Carbon13

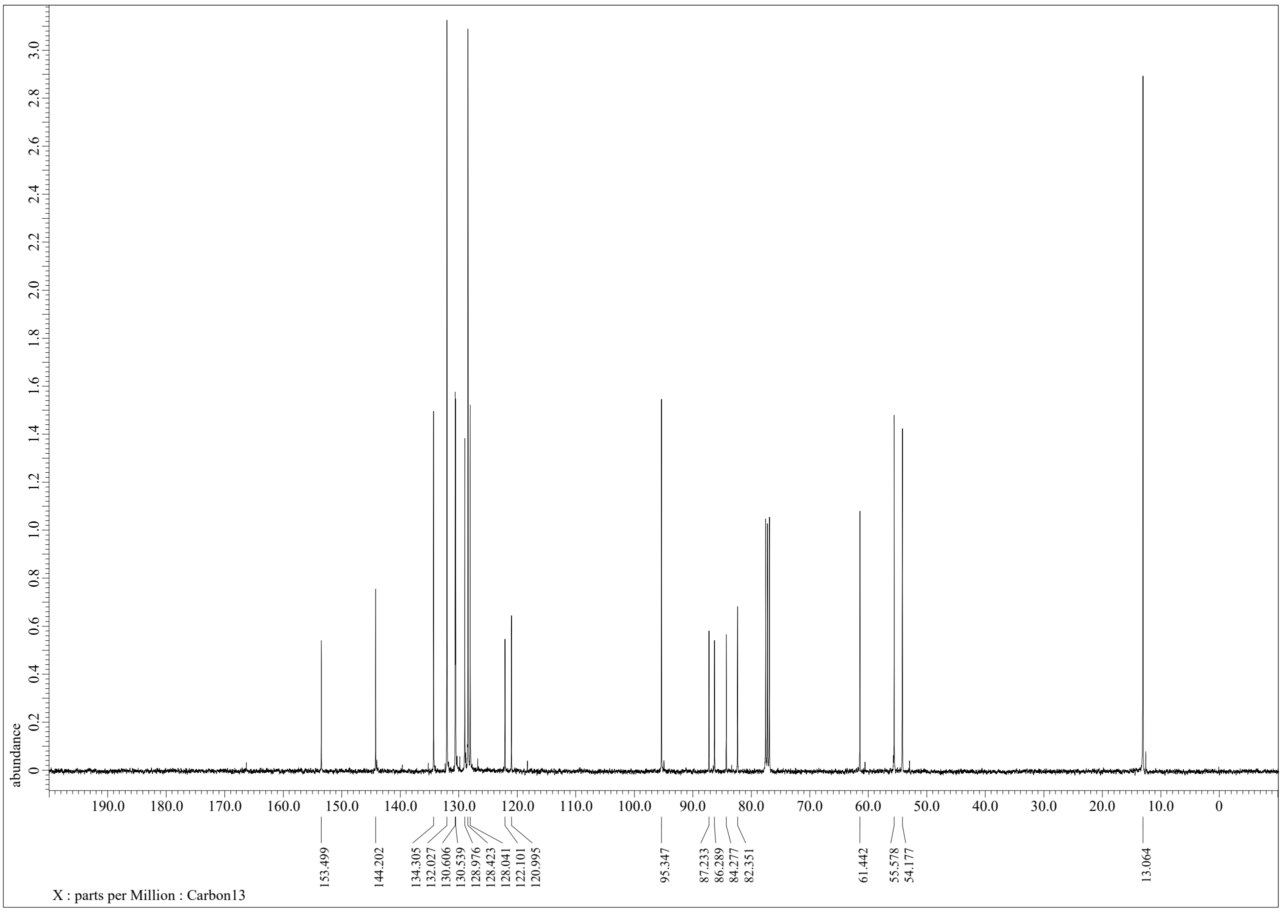

OMOM
Br
Br
S37
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
0.87
0.85
0.86
0.94
0.80
2.00
2.89
1.75
1.85
7.981 7.652 7.646 7.634 7.629 7.372 7.366 7.354 7.350 7.341 7.327 7.322 7.309 7.303 7.289 7.286 7.271 7.267
4.551
3.176
1.233 1.220 1.215 1.202 0.928 0.914 0.910 0.896
X : parts per Million : Proton

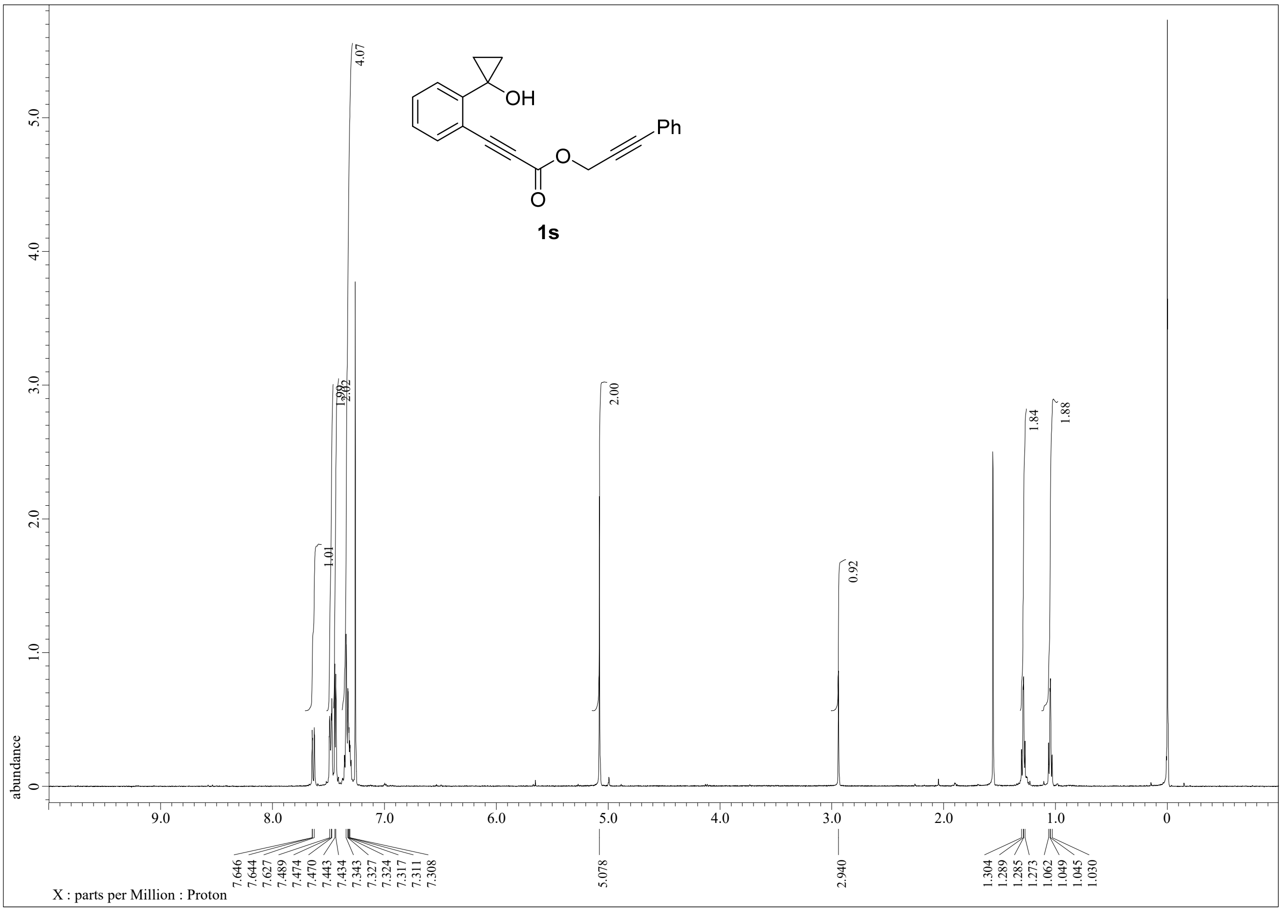

(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
137.766 136.927 136.680 129.729 129.252 128.137 127.984
95.004
90.256
60.765
55.864
12.396
X : parts per Million : Carbon13

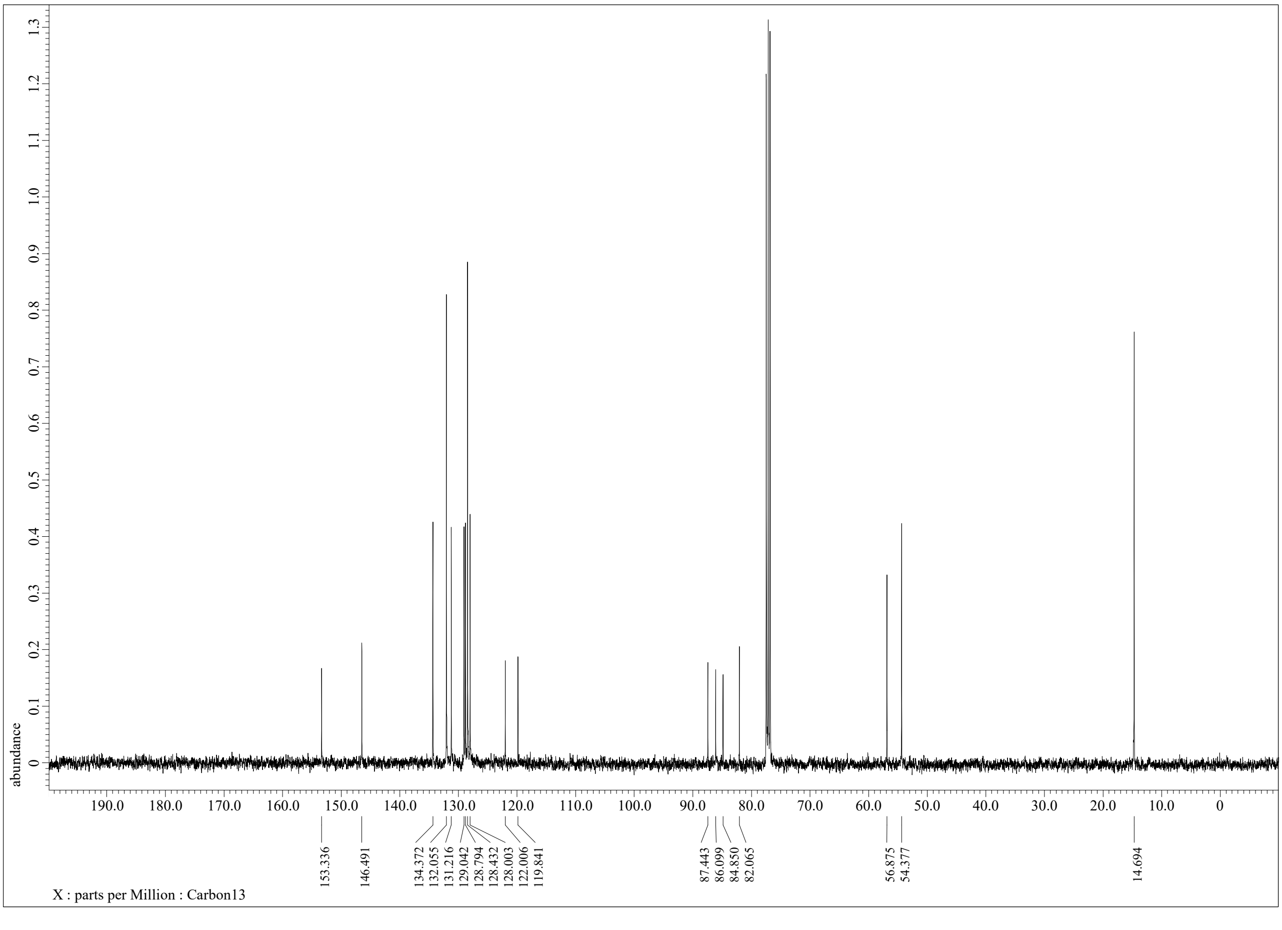

OMOM
OH
O
S38
abundance
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.93
0.93
0.93
0.99
2.11
3.17
2.00
1.82
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.613
7.611
7.593
7.590
7.588
7.584
7.567
7.565
7.479
7.475
7.459
7.382
7.378
7.362
7.360
4.773
3.337
1.377
1.362
1.359
1.344
1.030
1.015
1.011
0.997
X : parts per Million : Proton

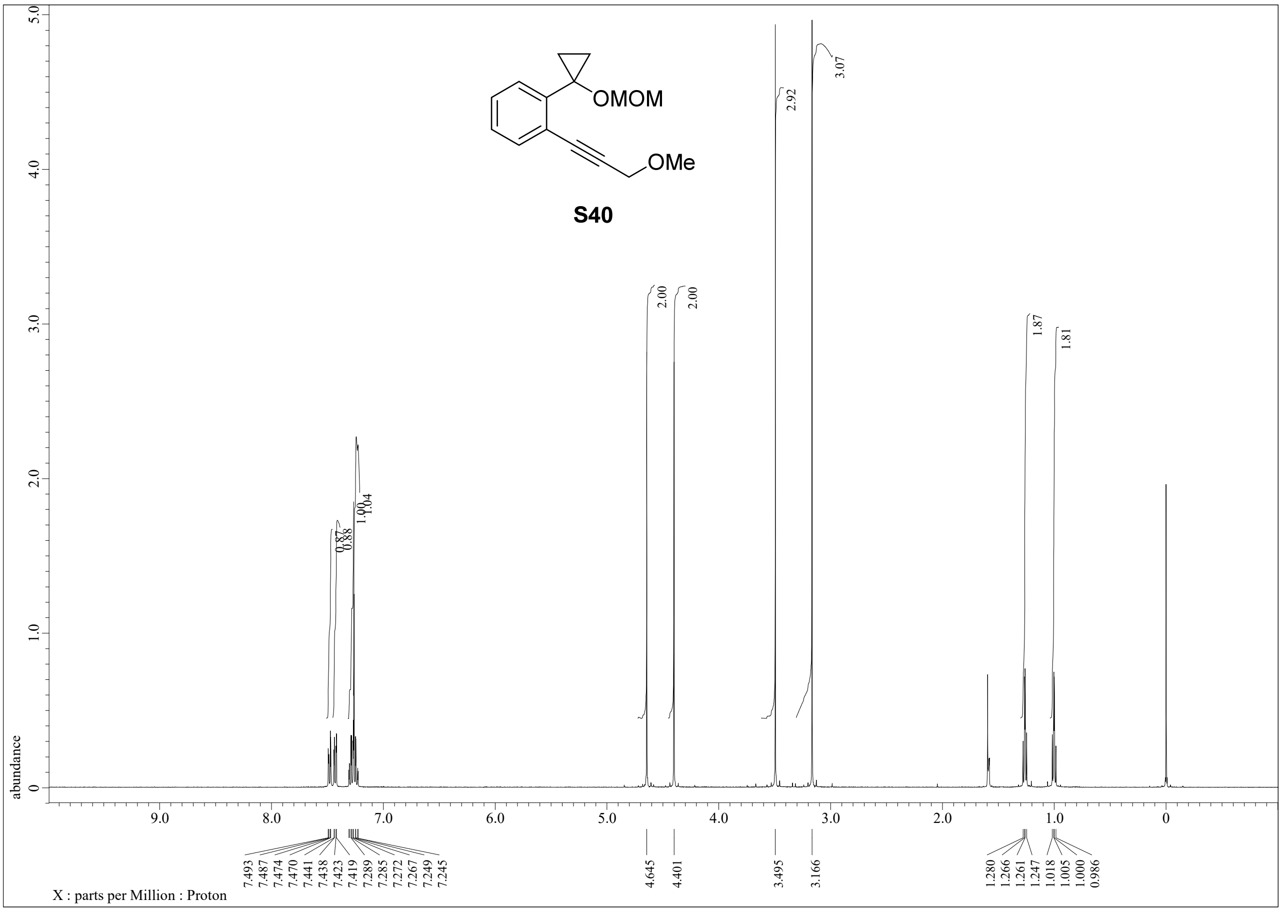

(thousandths)
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
155.291
143.459
133.867
131.302
130.892
128.451
121.224
94.785
86.356
84.945
61.194
55.683
13.045
X : parts per Million : Carbon13


OMOM
Ph
O
O
S39
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
0.95
3.02
4.02
0.99
2.00
1.94
3.10
1.78
1.85
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.626
7.607
7.495
7.488
7.485
7.475
7.465
7.432
7.412
7.351
7.337
7.330
7.320
7.311
7.307
5.068
4.661
3.136
1.361
1.346
1.343
1.328
1.045
1.032
1.029
1.013
X : parts per Million : Proton


abundance
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.499
144.202
134.305
132.027
130.606
130.539
128.976
128.423
128.041
122.101
120.995
95.347
87.233
86.289
84.277
82.351
61.442
55.578
54.177
13.064
X : parts per Million : Carbon13

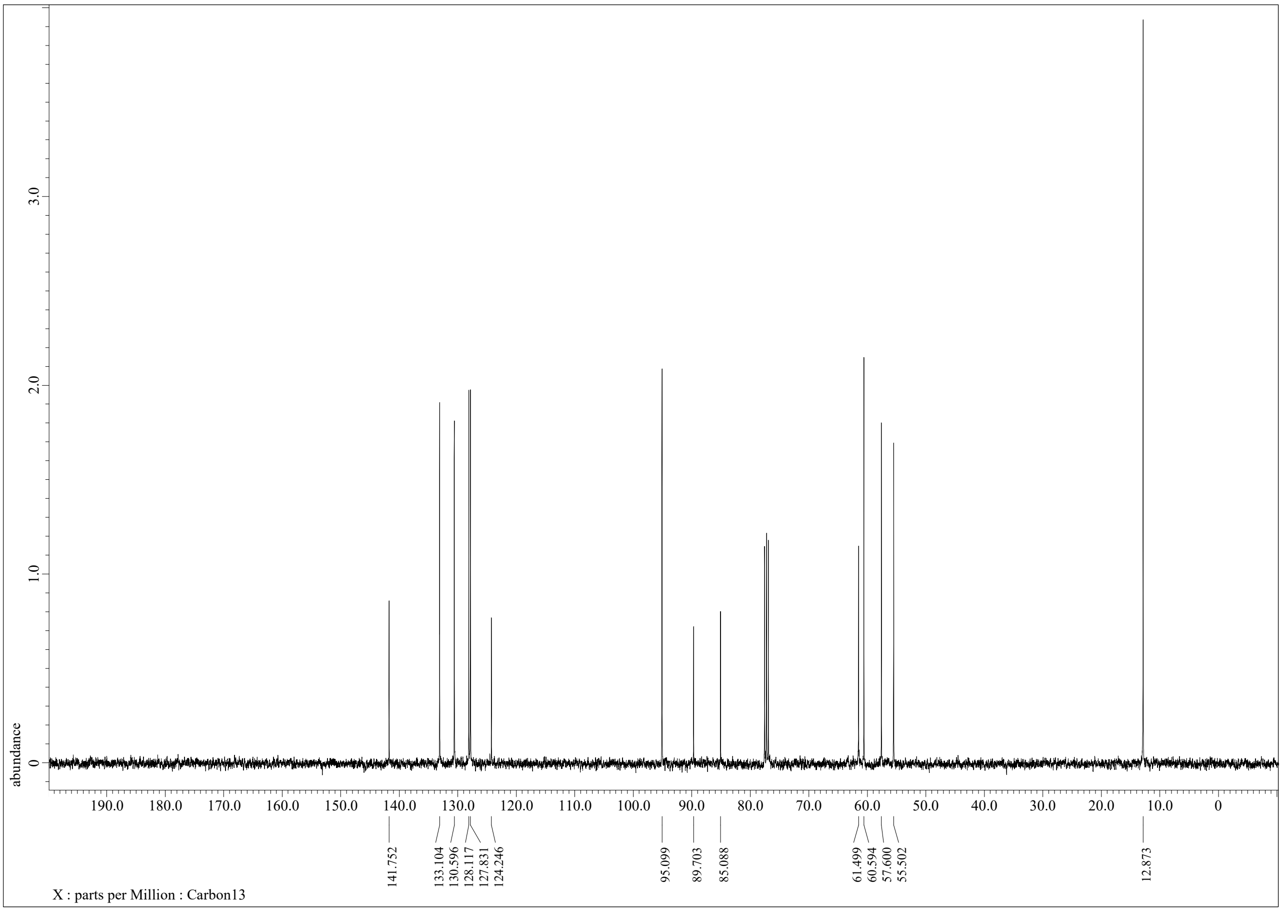

OH
O
O
Ph
1s
abundance
0
1.0
2.0
3.0
4.0
5.0
1.01
1.99
2.02
4.07
2.00
0.92
1.84
1.88
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.646
7.644
7.627
7.489
7.474
7.470
7.443
7.434
7.343
7.327
7.324
7.317
7.311
7.308
5.078
2.940
1.304
1.289
1.285
1.273
1.062
1.049
1.045
1.030
X : parts per Million : Proton


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.336
146.491
134.372
132.055
131.216
129.042
128.794
128.432
128.003
122.006
119.841
87.443
86.099
84.850
82.065
56.875
54.377
14.694
X : parts per Million : Carbon13

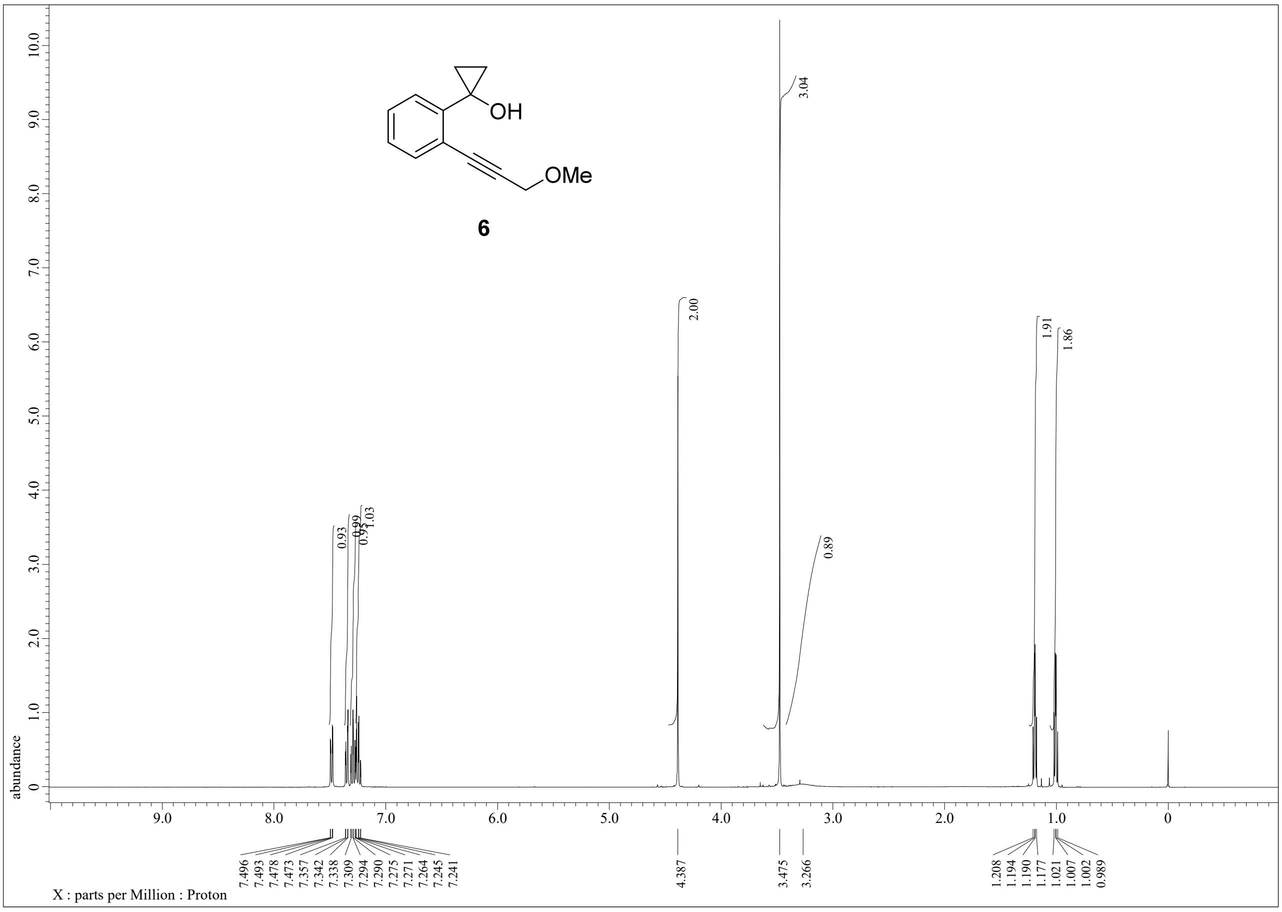


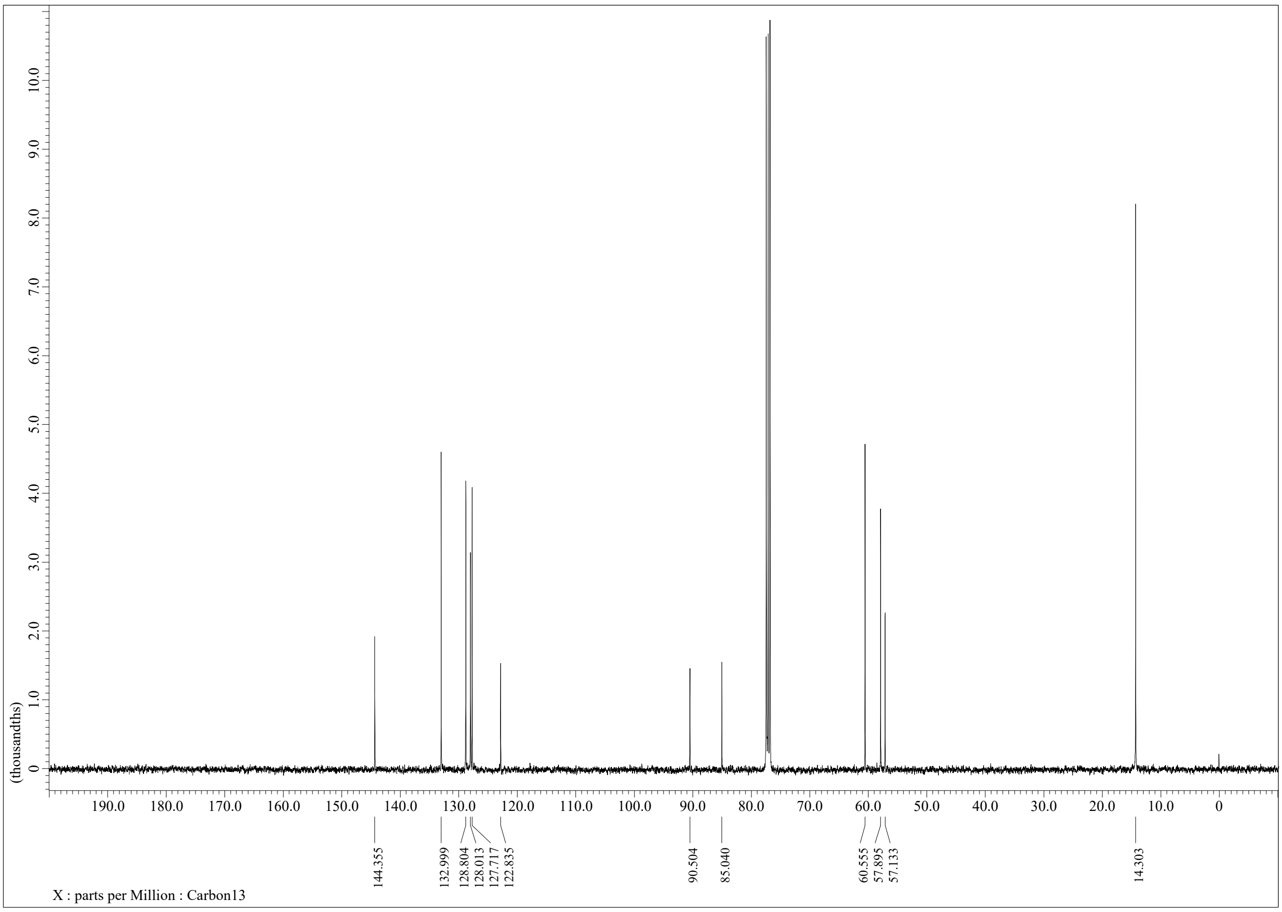
S40

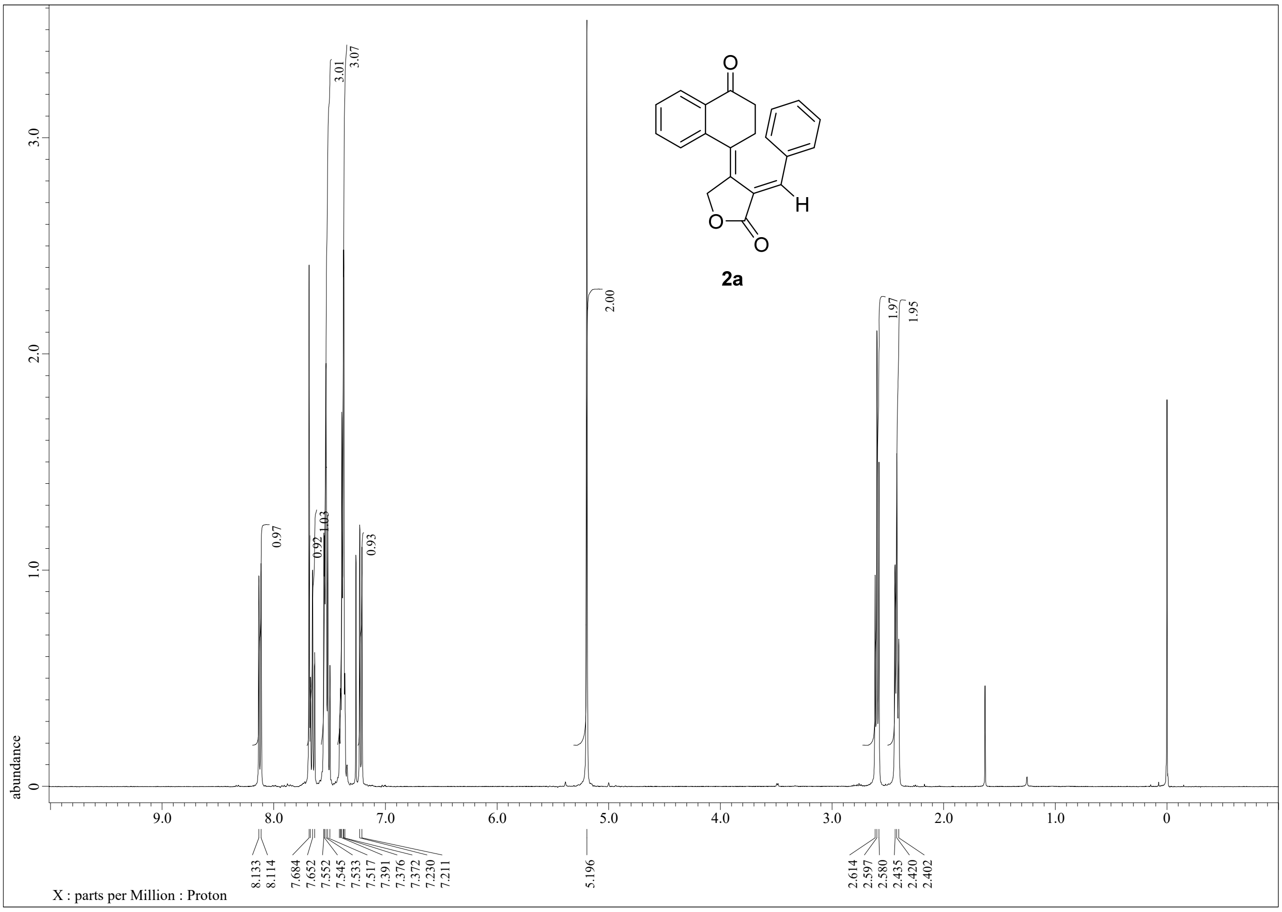
OMOM
OMe
abundance
0
1.0
2.0
3.0
4.0
5.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.87
0.88
1.00
1.04
2.00
2.00
2.92
3.07
1.87
1.81
7.493
7.487
7.474
7.470
7.441
7.438
7.423
7.419
7.289
7.285
7.272
7.267
7.249
7.245
4.645
4.401
3.495
3.166
1.280
1.266
1.261
1.247
1.018
1.005
1.000
0.986
X : parts per Million : Proton

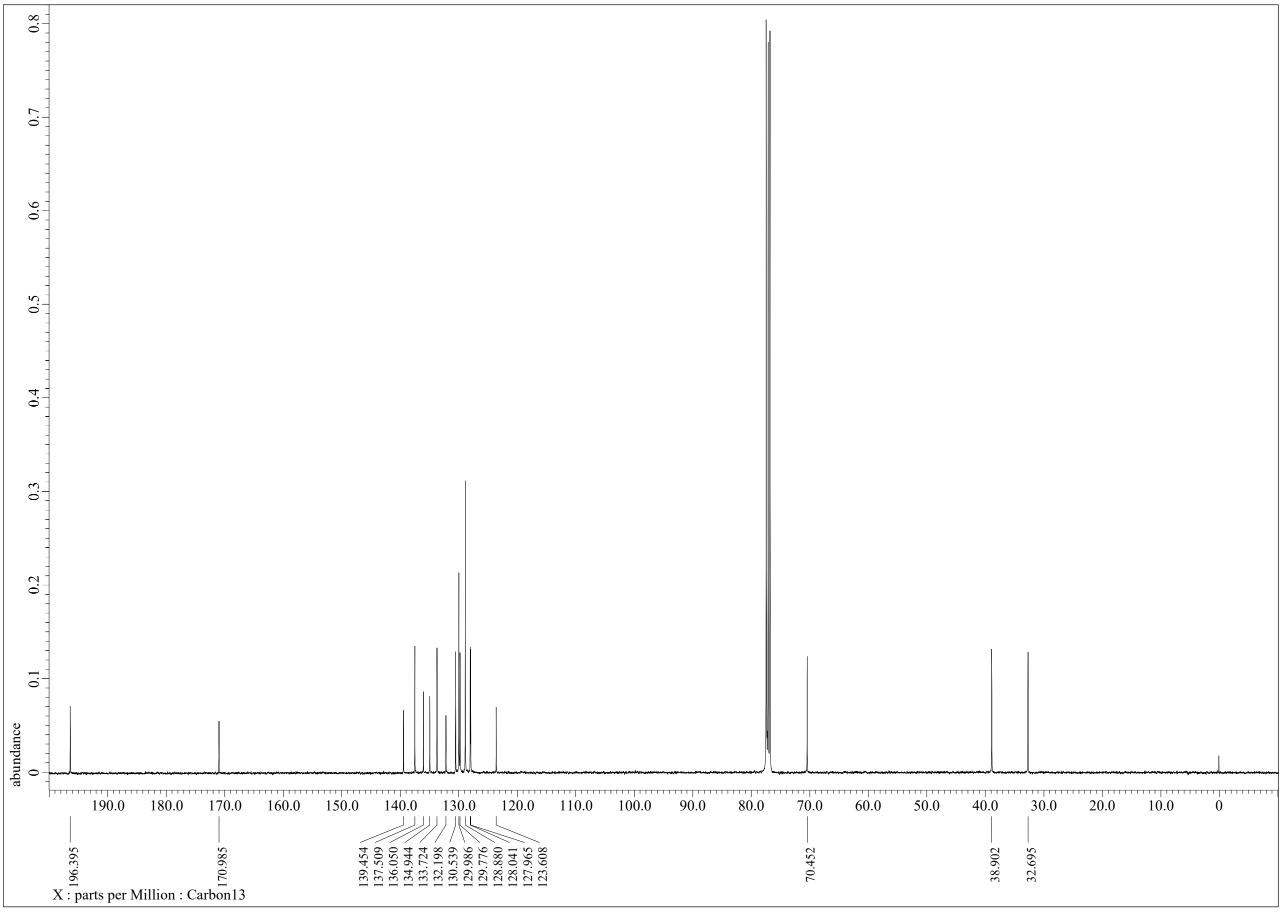


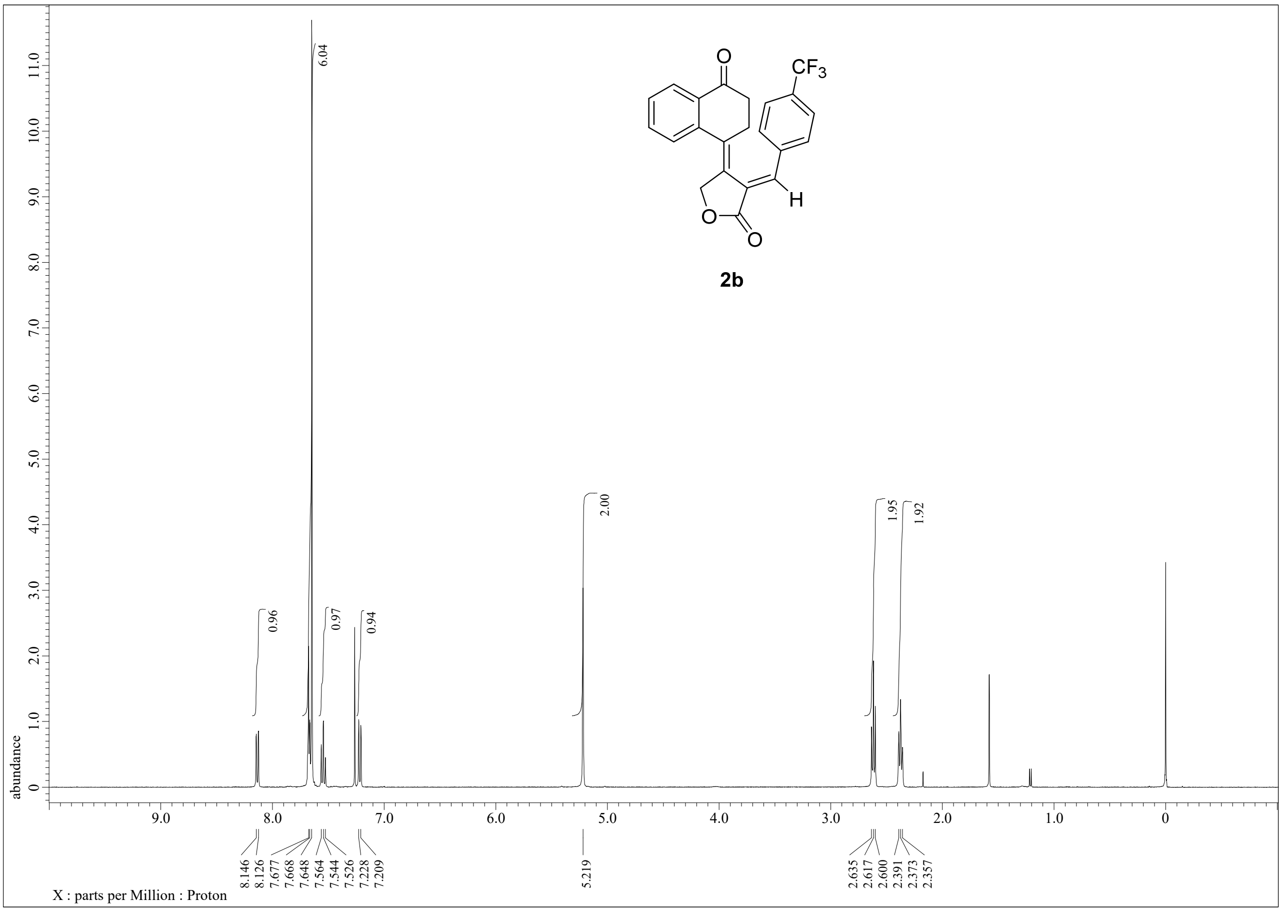
abundance
0
1.0
2.0
3.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.752
133.104
130.596
128.117
127.831
124.246
95.099
89.703
85.088
61.499
60.594
57.600
55.502
12.873
X : parts per Million : Carbon13

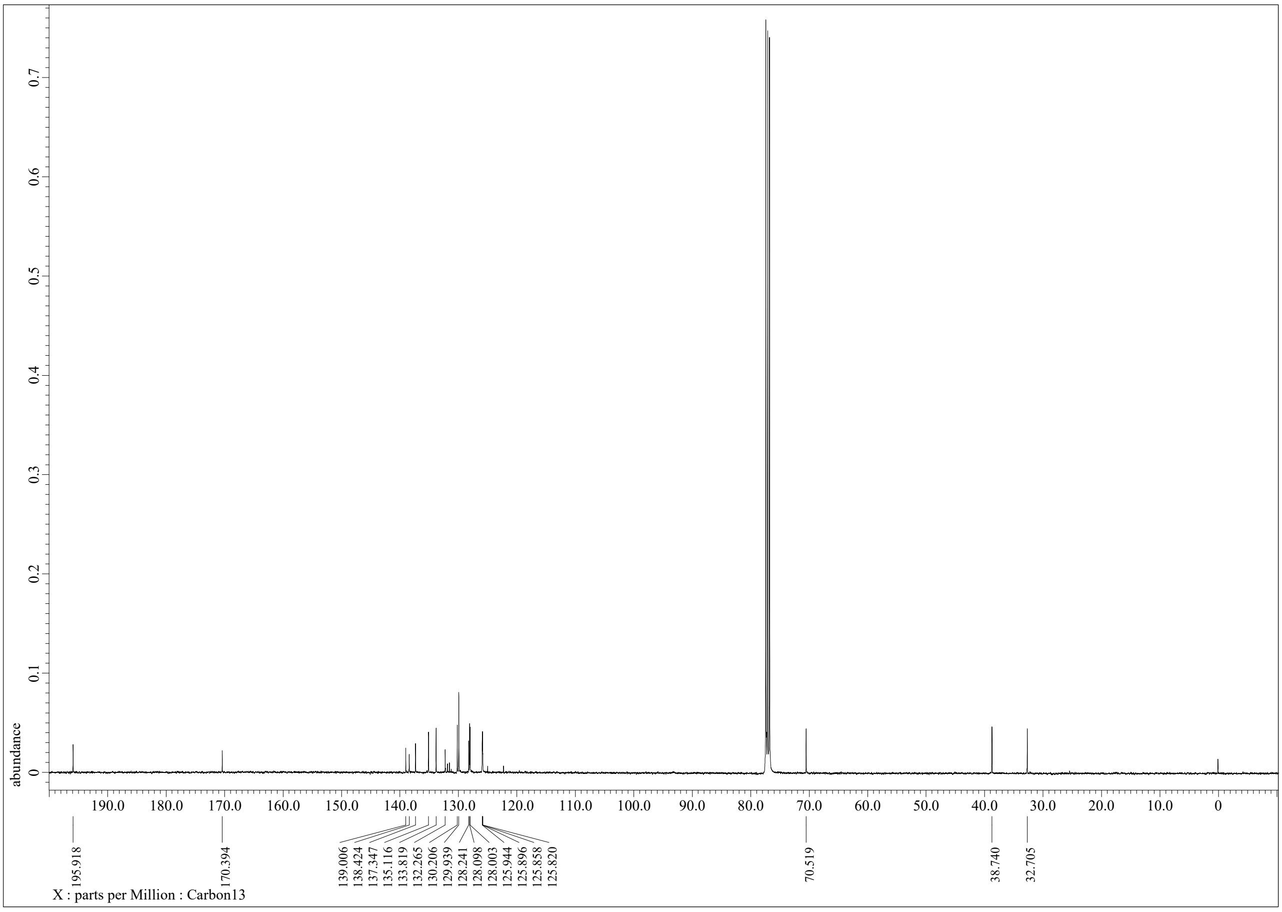

OH
OMe
6
abundance
3.04
2.00
0.93
0.99
0.95
1.03
0.89
1.91
1.86
7.496
7.493
7.478
7.473
7.357
7.342
7.338
7.309
7.294
7.290
7.275
7.271
7.264
7.245
7.241
4.387
3.475
3.266
1.208
1.194
1.190
1.177
1.021
1.007
1.002
0.989
X : parts per Million : Proton

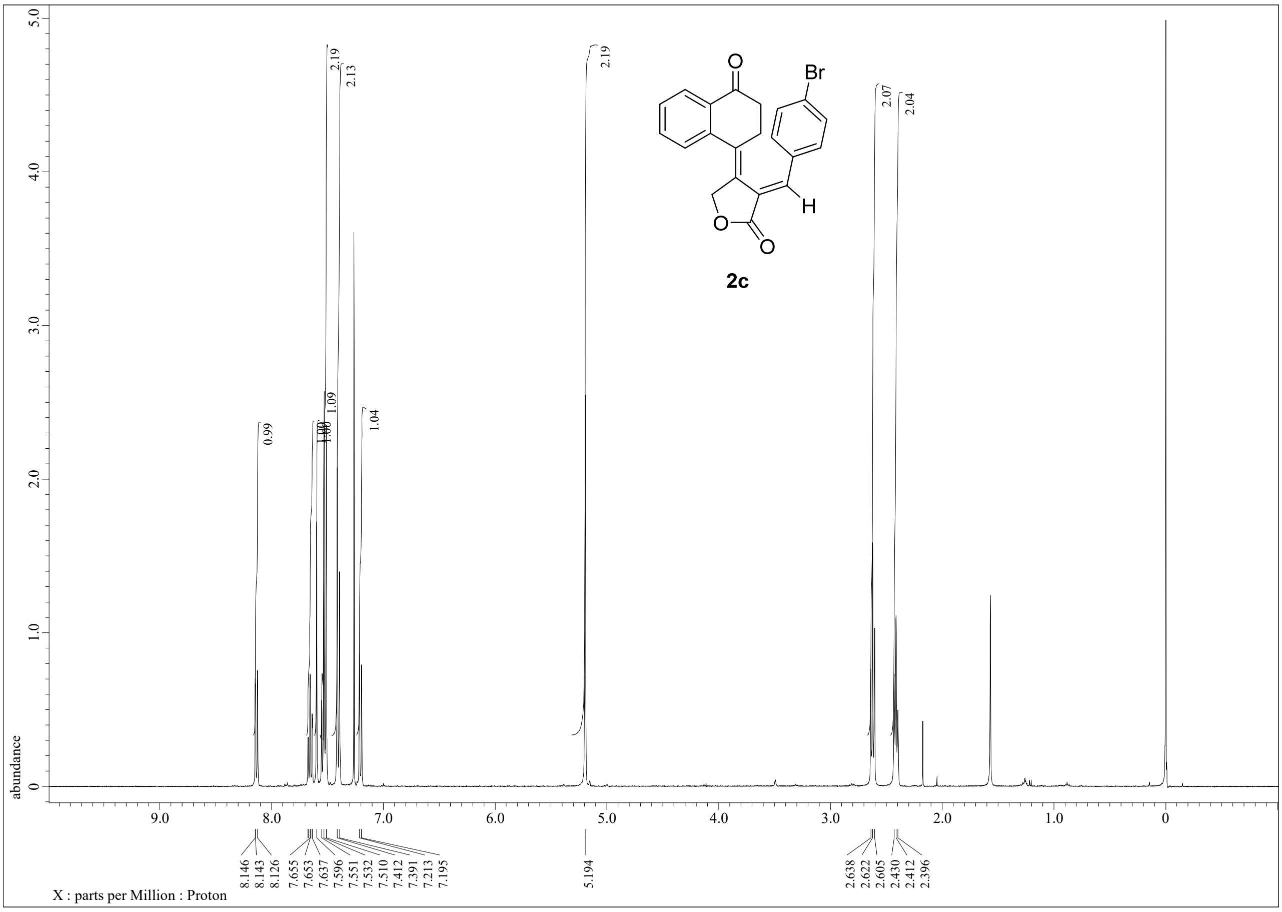

(thousandths)
144.355
132.999
128.804
128.013
127.717
122.835
90.504
85.040
60.555
57.895
57.133
14.303
X : parts per Million : Carbon13


2a
O
O
O
H
abundance
0
1.0
2.0
3.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.97
0.92
1.03
3.01
3.07
0.93
2.00
1.97
1.95
8.133
8.114
7.684
7.652
7.552
7.545
7.533
7.517
7.391
7.376
7.372
7.230
7.211
5.196
2.614
2.597
2.580
2.435
2.420
2.402
X : parts per Million : Proton

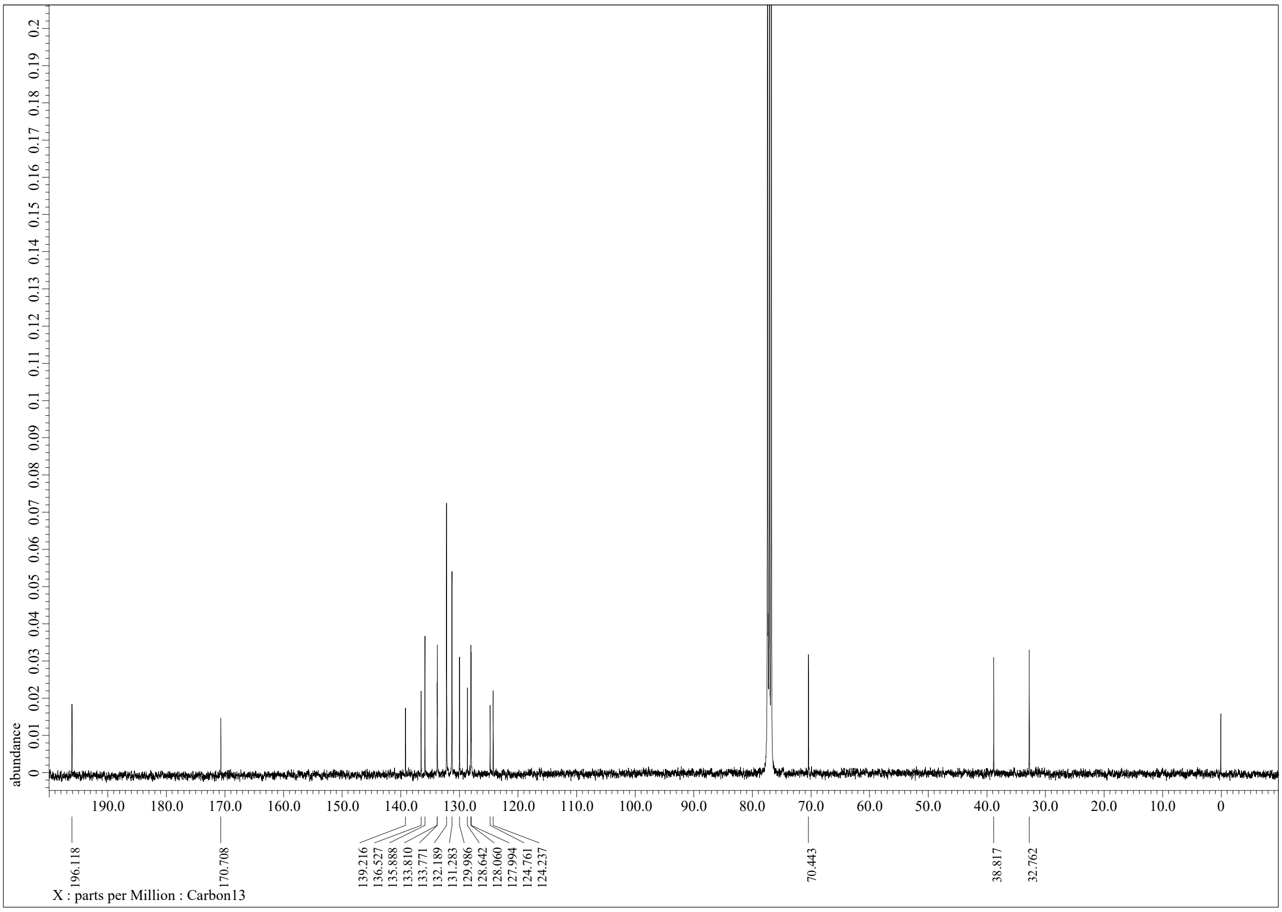

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.395
170.985
139.454
137.509
136.050
134.944
133.724
132.198
130.539
129.986
129.776
128.880
128.041
127.965
123.608
70.452
38.902
32.695
X : parts per Million : Carbon13

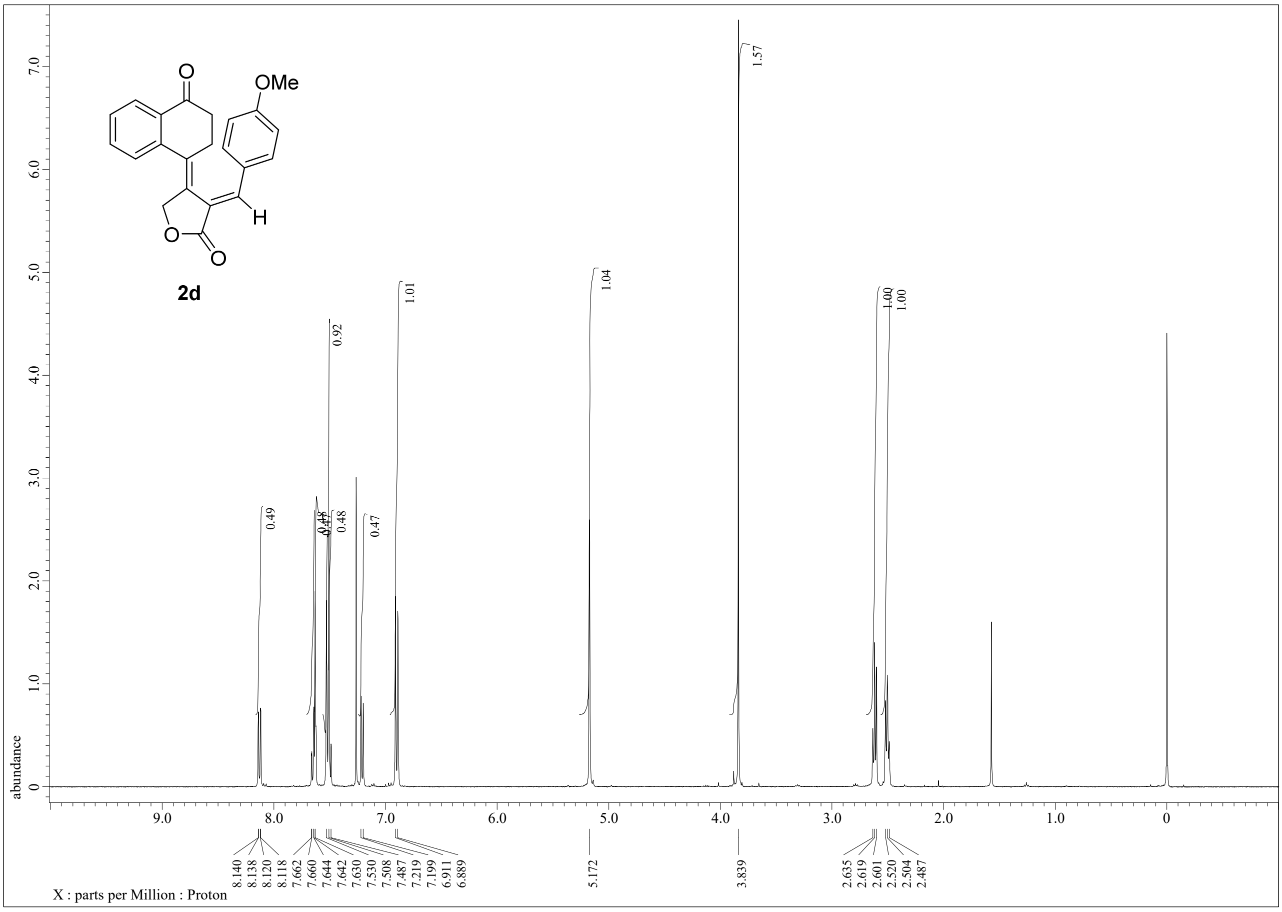

CF3
O
O
O
H
2b
abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0
0.96
6.04
0.97
0.94
2.00
1.95
1.92
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
8.146
8.126
7.677
7.668
7.648
7.564
7.544
7.526
7.228
7.209
5.219
2.635
2.617
2.600
2.391
2.373
2.357
X : parts per Million : Proton

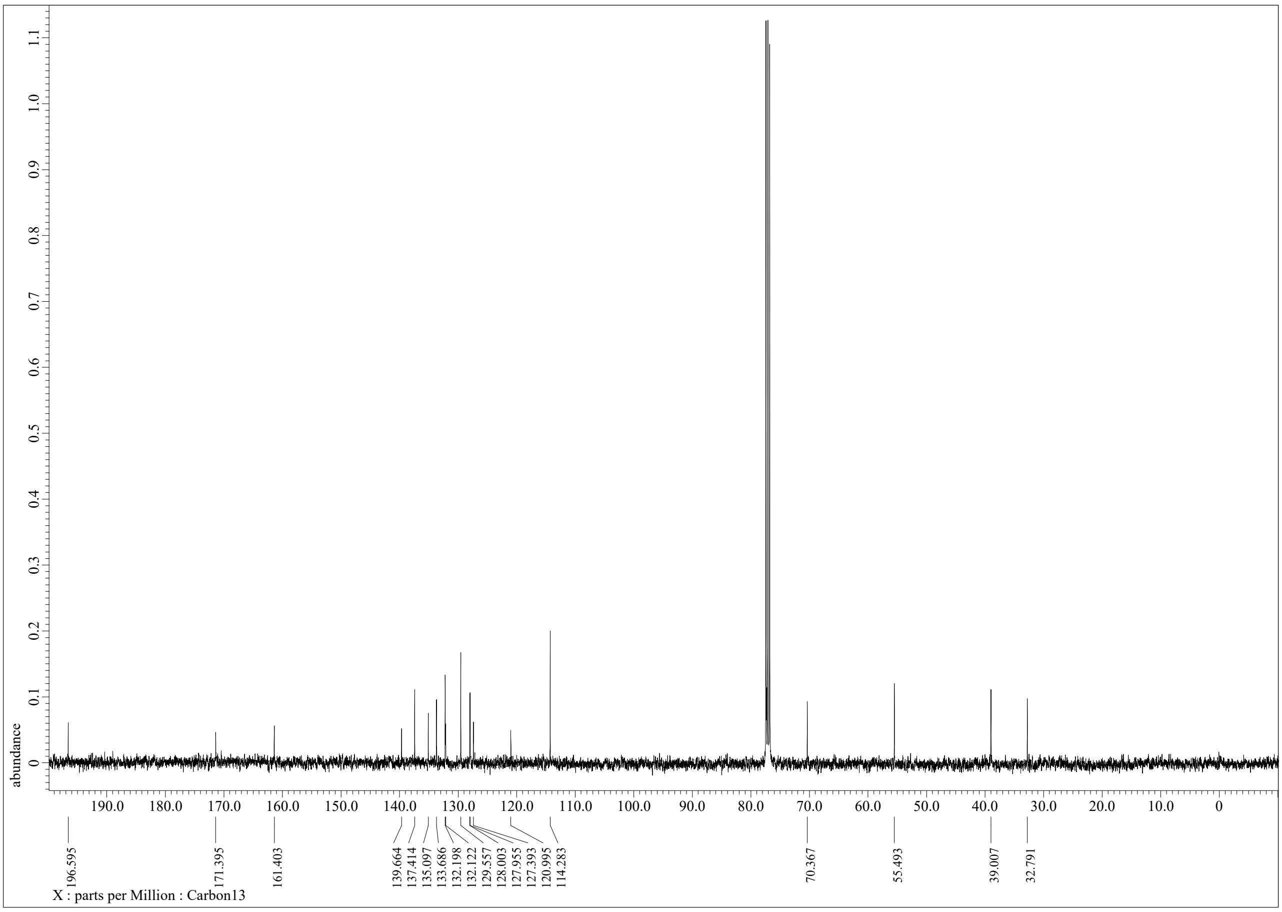

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
195.918
170.394
139.006
138.424
137.347
135.116
133.819
132.265
130.206
129.939
128.241
128.098
128.003
125.944
125.896
125.858
125.820
70.519
38.740
32.705
X : parts per Million : Carbon13

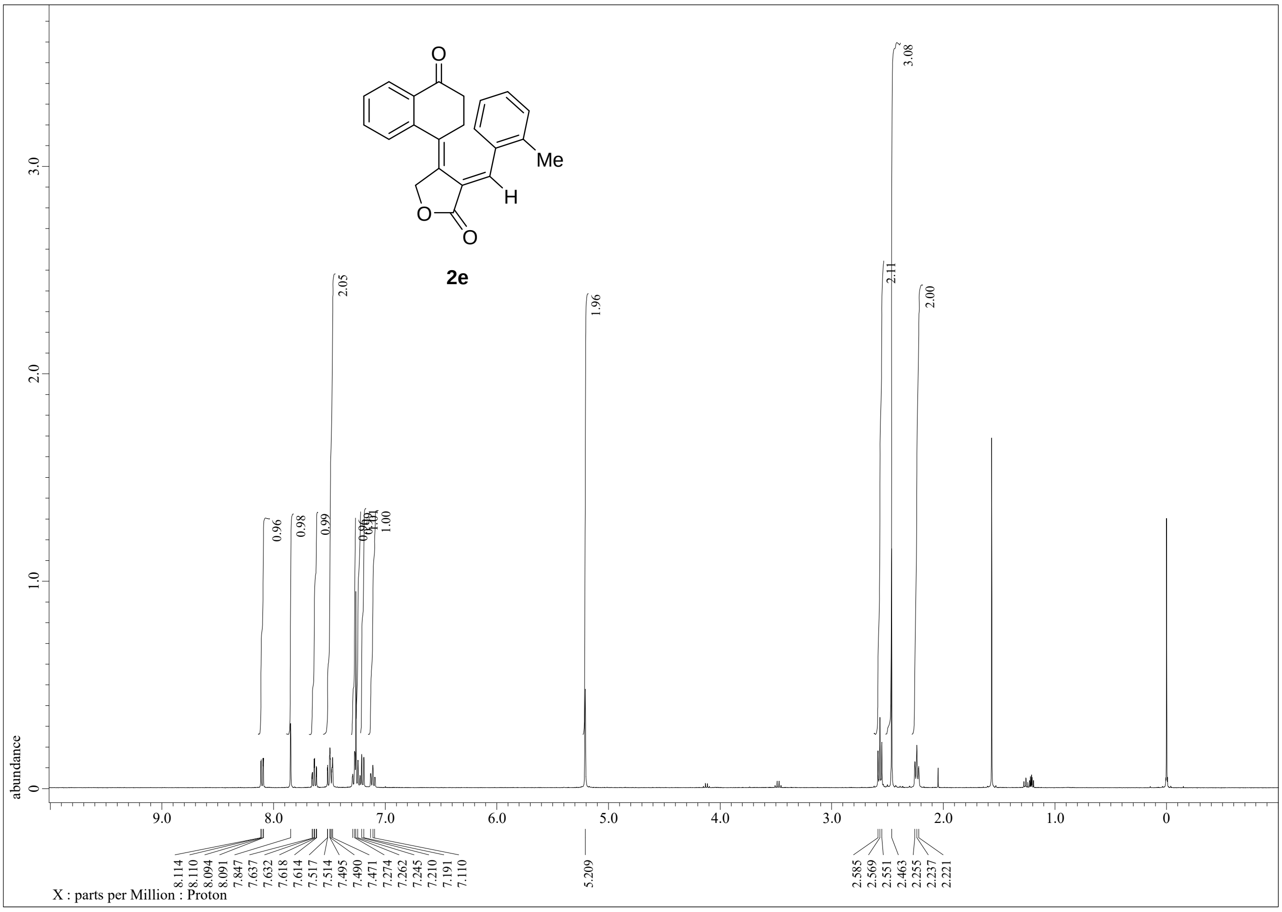

2.19
2.13
2.19
2.07
2.04
0.99
1.00
1.00
1.09
1.04
Br
O
O
O
H
abundance
0
1.0
2.0
3.0
4.0
5.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.146
8.143
8.126
7.655
7.653
7.637
7.596
7.551
7.532
7.510
7.412
7.391
7.213
7.195
5.194
2.638
2.622
2.605
2.430
2.412
2.396
X : parts per Million : Proton

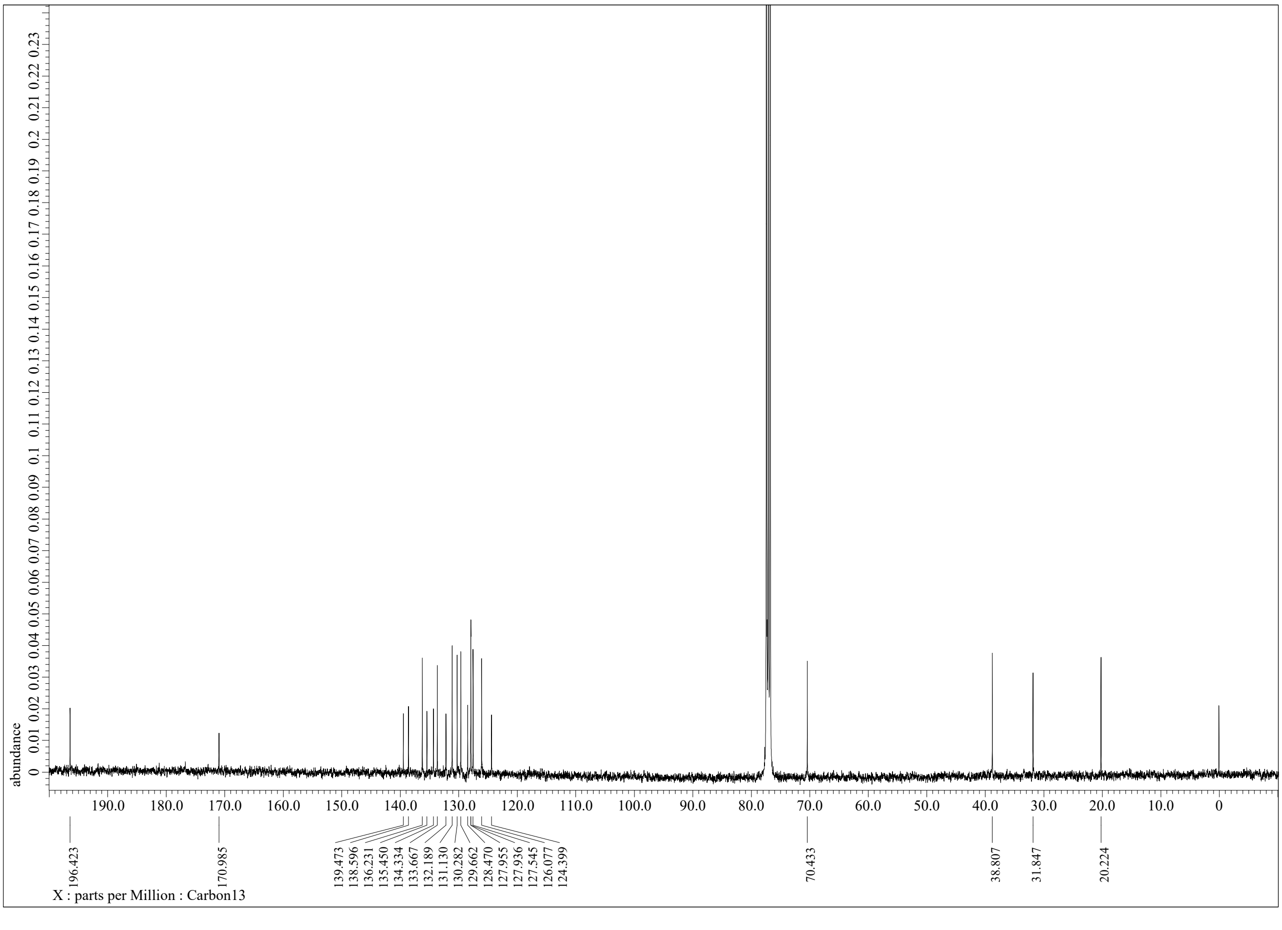
2c

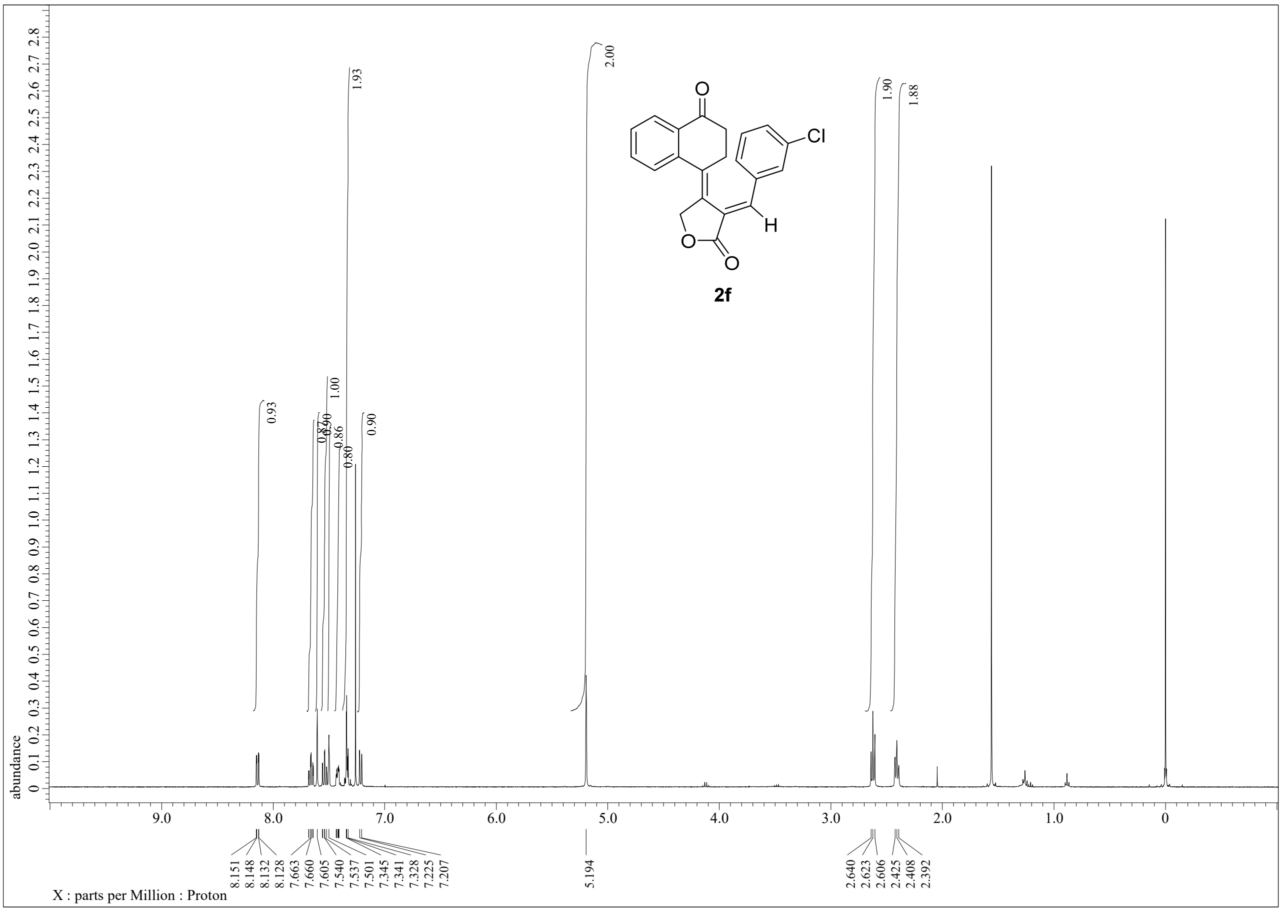

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
0.17
0.18
0.19
0.2
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.118
170.708
139.216
136.527
135.888
133.810
133.771
132.189
131.283
129.986
128.642
128.060
127.994
124.761
124.237
70.443
38.817
32.762
X : parts per Million : Carbon13

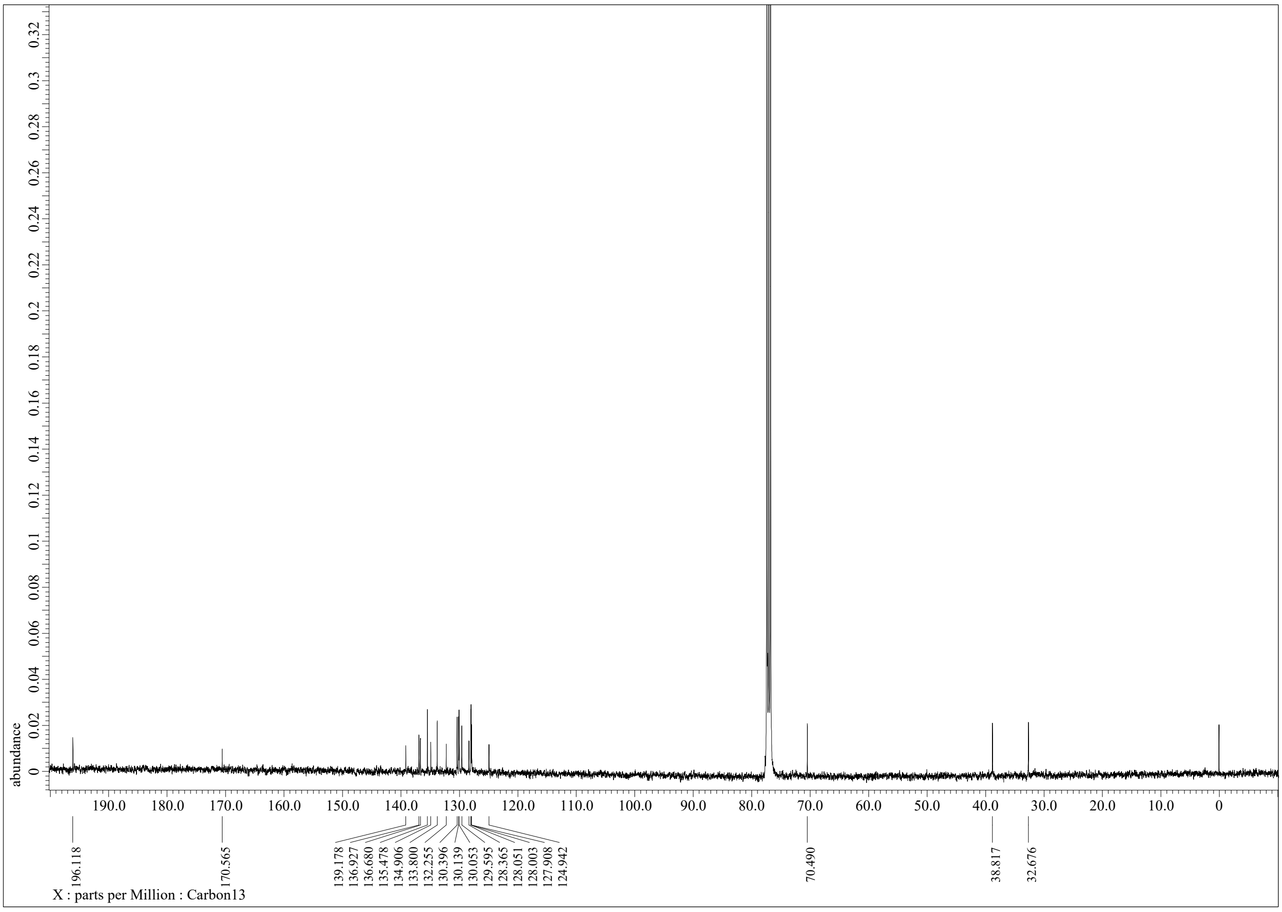

OMe
H
O
O
O
2d
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
0.49
0.46
0.47
0.92
0.48
0.47
1.01
1.04
1.57
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.140
8.138
8.120
8.118
7.662
7.660
7.644
7.642
7.630
7.530
7.508
7.487
7.219
7.199
6.911
6.889
5.172
3.839
2.635
2.619
2.601
2.520
2.504
2.487
X : parts per Million : Proton

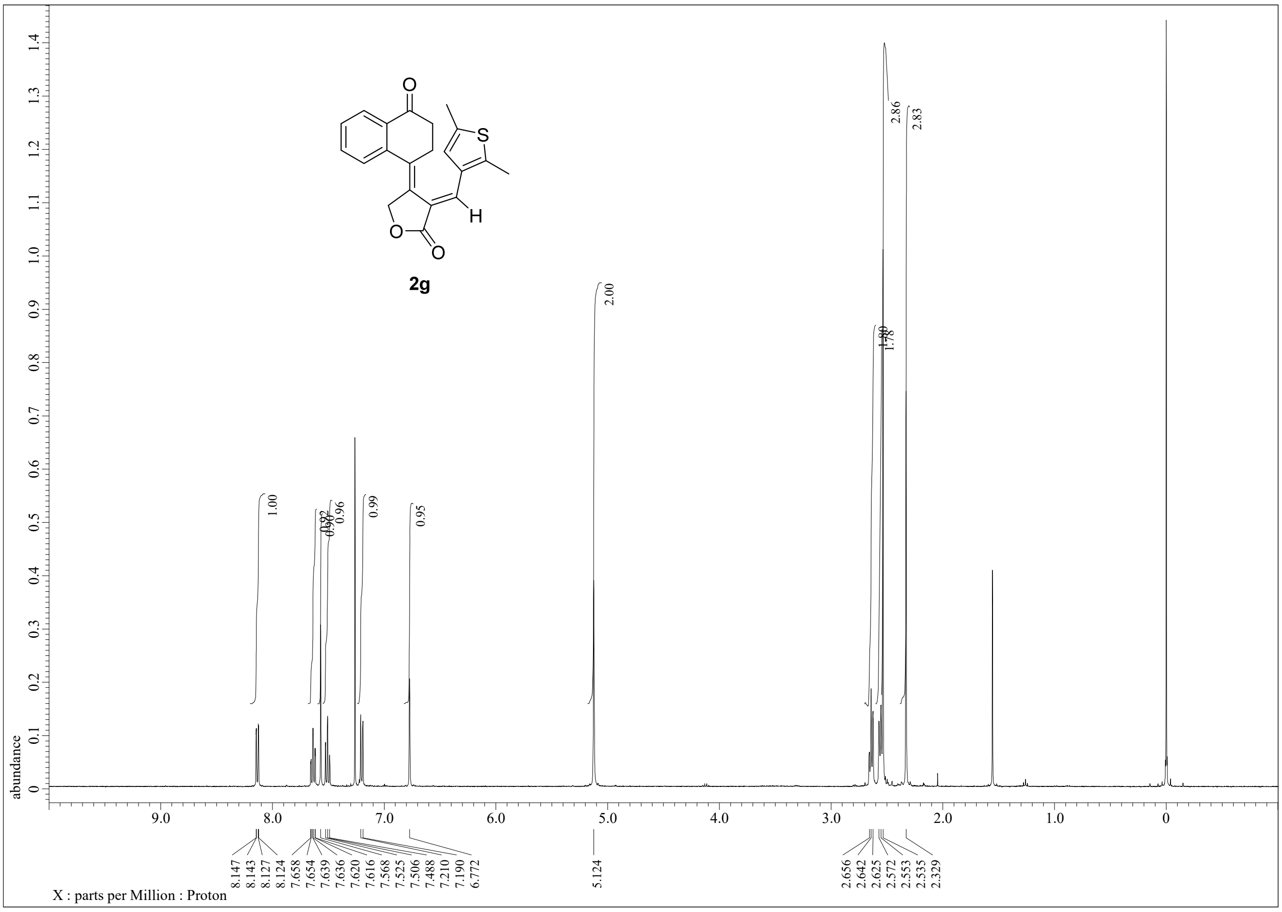

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.595
171.395
161.403
139.664
137.414
135.097
133.686
132.198
132.122
129.557
128.003
127.955
127.393
120.995
114.283
70.367
55.493
39.007
32.791
X : parts per Million : Carbon13

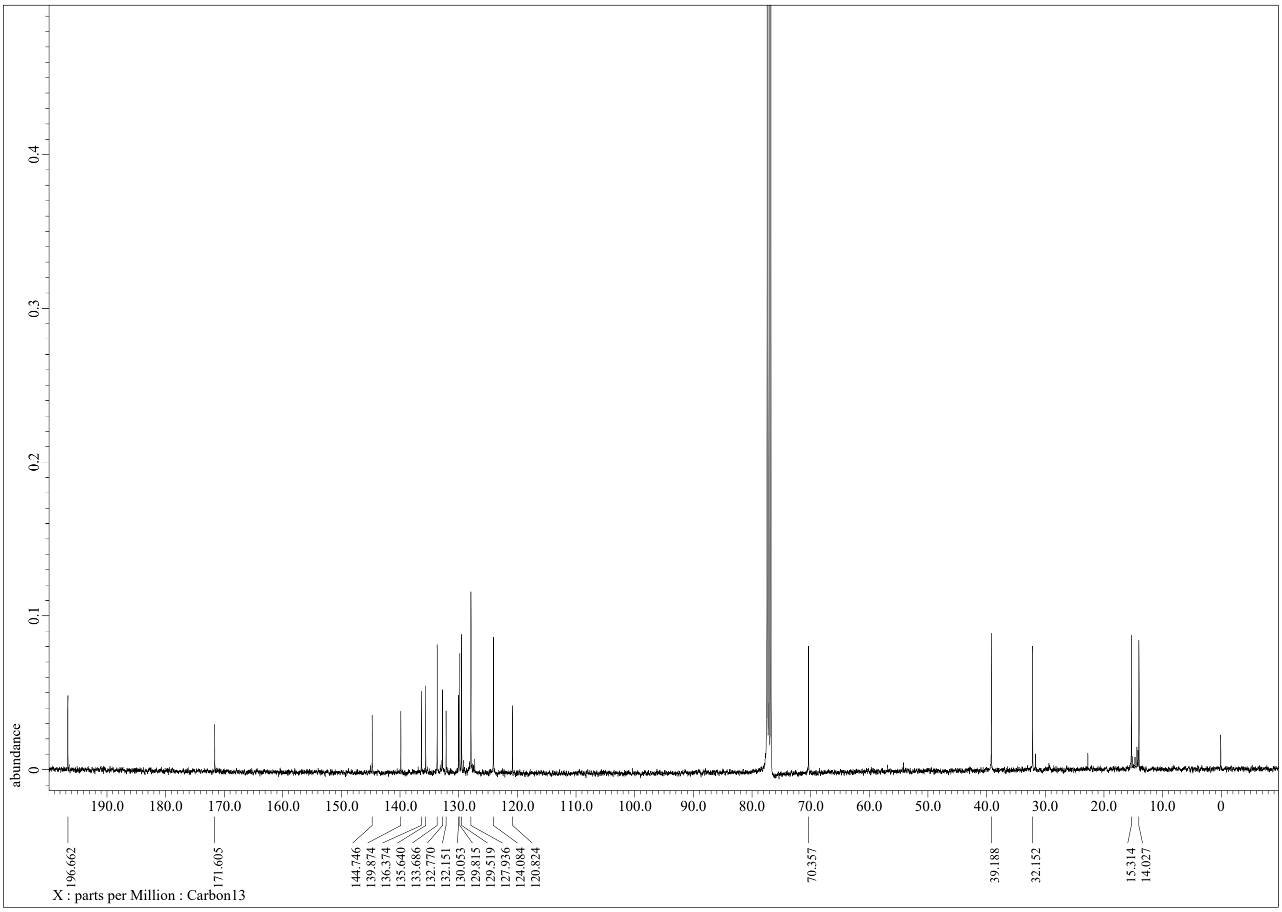

2e
O
Me
H
O
O
3.0
2.0
1.0
0
abundance
0.96
0.98
0.99
2.05
0.96
0.99
1.01
1.00
1.96
2.11
3.08
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.114
8.110
8.094
8.091
7.847
7.637
7.632
7.618
7.614
7.517
7.514
7.495
7.490
7.471
7.274
7.262
7.245
7.210
7.191
7.110
5.209
2.585
2.569
2.551
2.463
2.255
2.237
2.221
X : parts per Million : Proton


abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
0.17
0.18
0.19
0.2
0.21
0.22
0.23
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.423
170.985
139.473
138.596
136.231
135.450
134.334
133.667
132.189
131.130
130.282
129.662
128.470
127.955
127.936
127.545
126.077
124.399
70.433
38.807
31.847
20.224
X : parts per Million : Carbon13


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
0.93
0.87
0.90
1.00
0.86
0.80
1.93
0.90
2.00
1.90
1.88
O
Cl
H
O
O
2f
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.151
8.148
8.132
8.128
7.663
7.660
7.605
7.540
7.537
7.501
7.345
7.341
7.328
7.225
7.207
5.194
2.640
2.623
2.606
2.425
2.408
2.392
X : parts per Million : Proton


abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
0.26
0.28
0.3
0.32
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.118
170.565
139.178
136.927
136.680
135.478
134.906
133.800
132.255
130.396
130.139
130.053
129.595
128.365
128.051
128.003
127.908
124.942
70.490
38.817
32.676
X : parts per Million : Carbon13


O
S
H
O
O
2g
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.00
0.92
0.90
0.96
0.99
0.95
2.00
1.80
1.78
2.86
2.83
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.147
8.143
8.127
8.124
7.658
7.654
7.639
7.636
7.620
7.616
7.568
7.525
7.506
7.488
7.210
7.190
6.772
5.124
2.656
2.642
2.625
2.572
2.553
2.535
2.329
X : parts per Million : Proton


abundance
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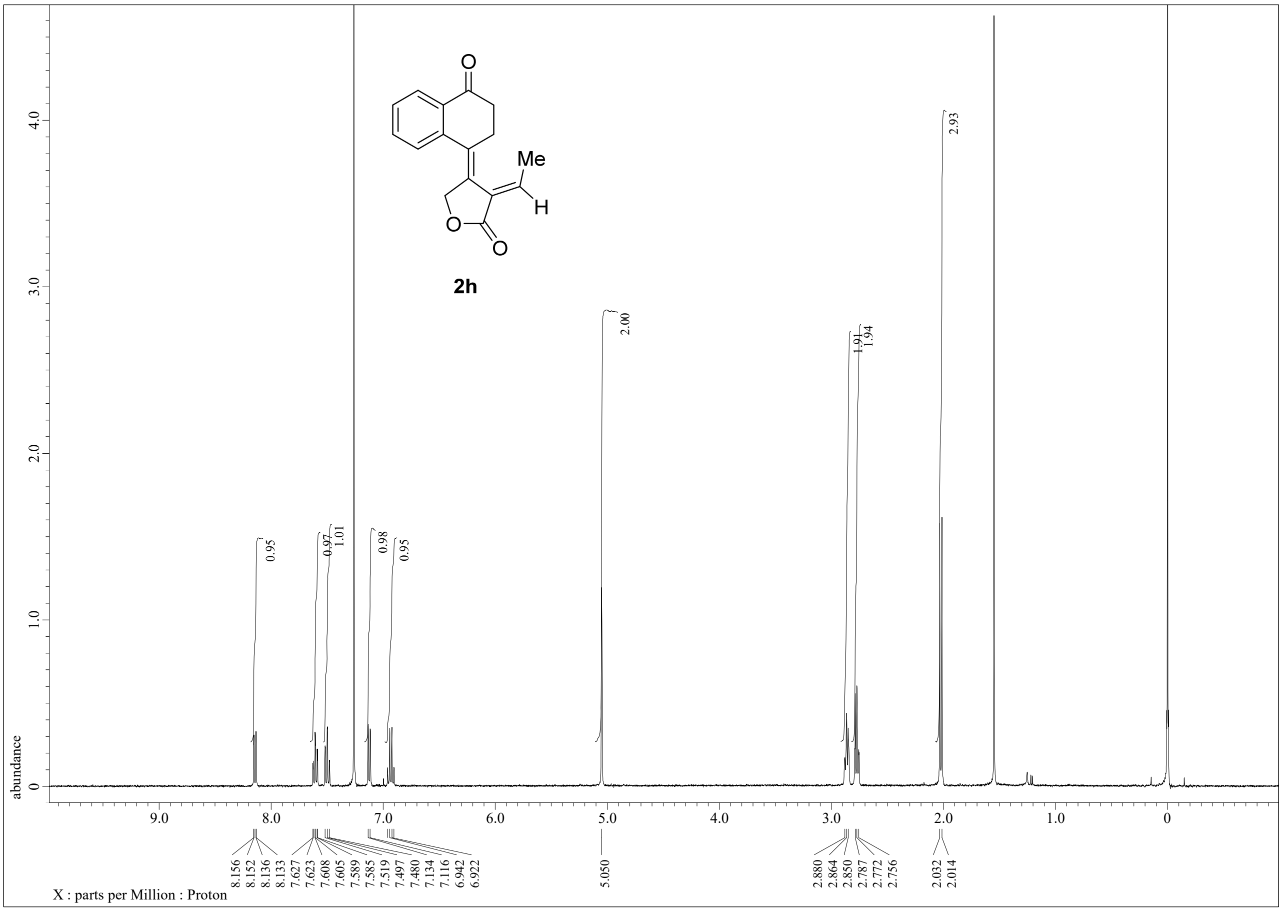
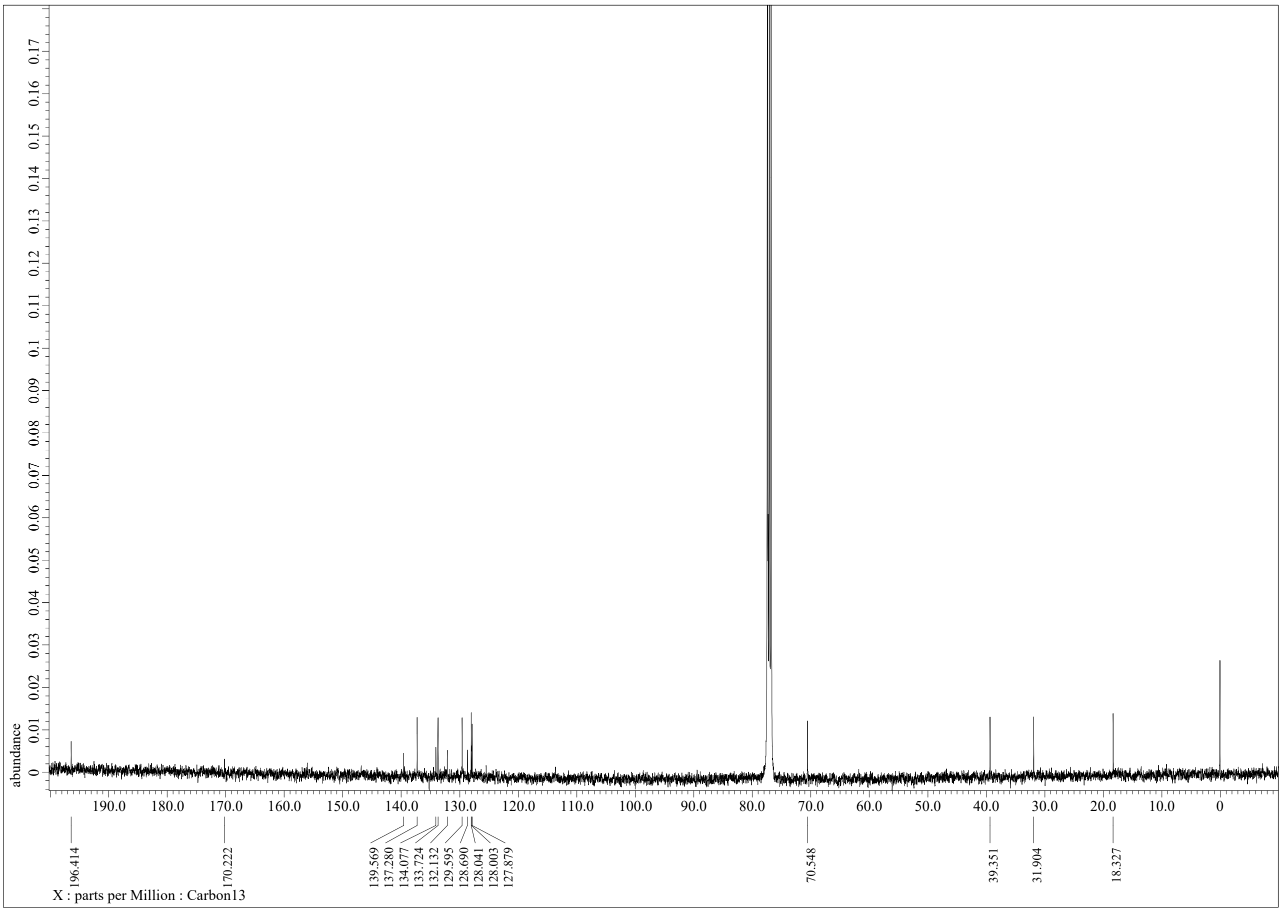
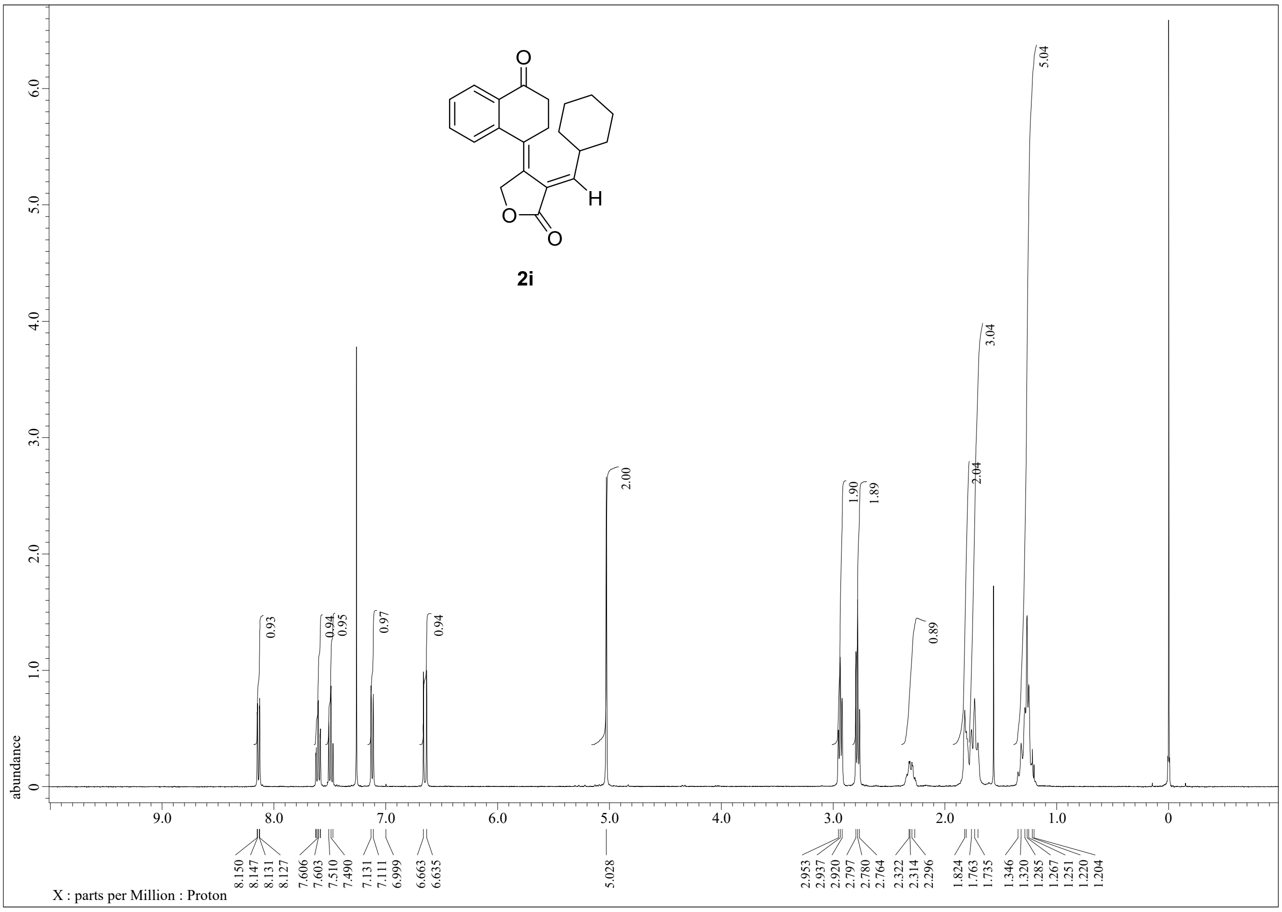
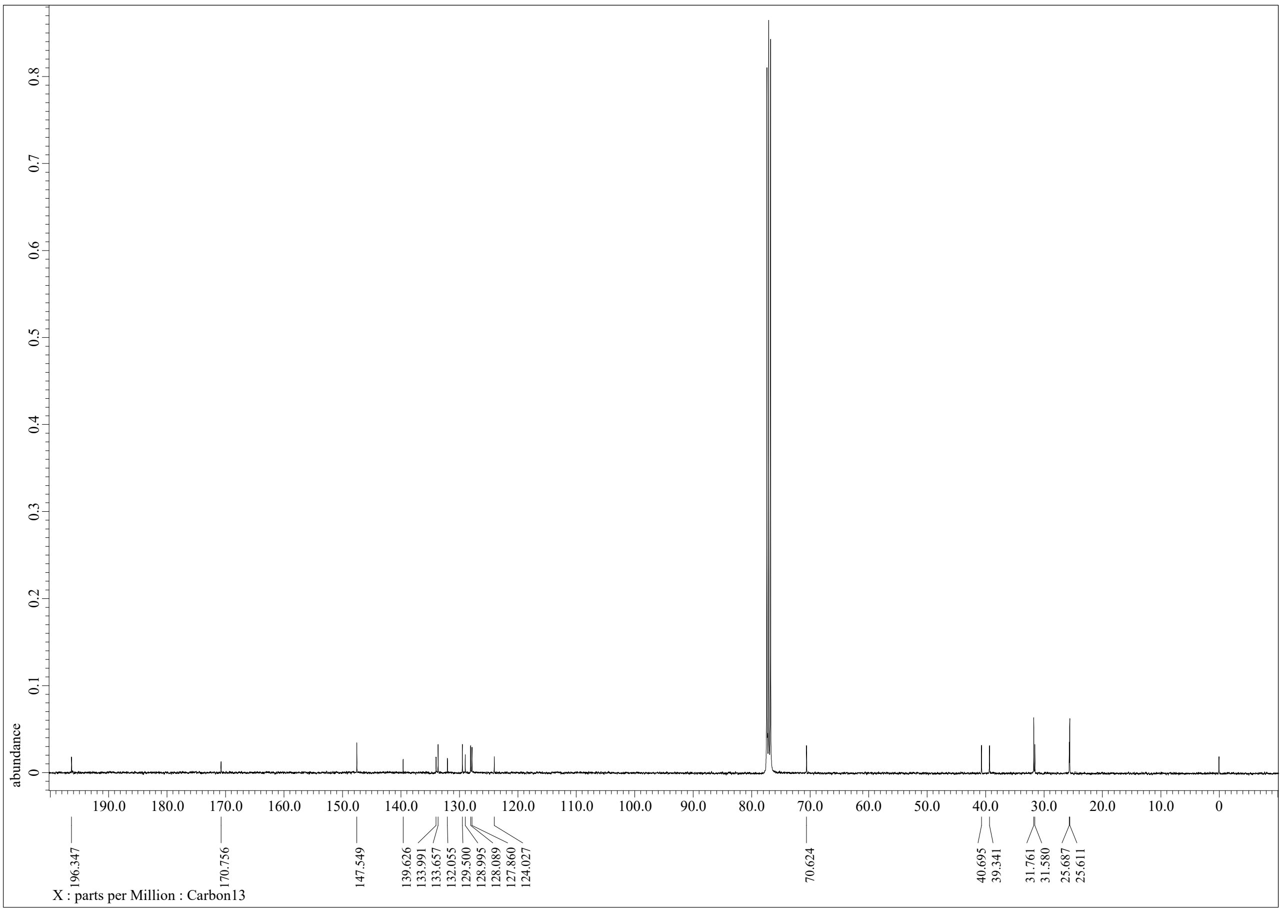
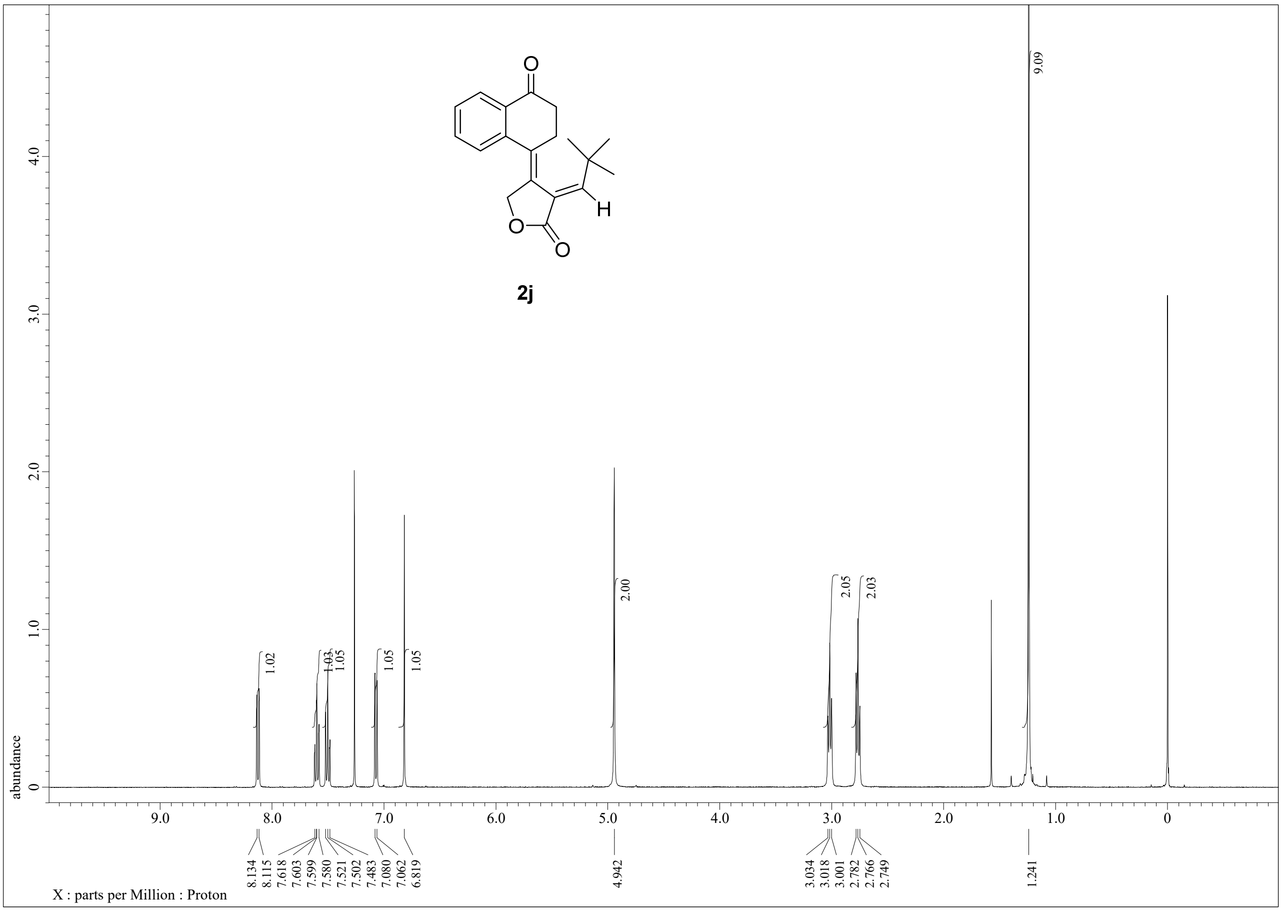
0.1
0.2
0.3
0.4
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.662
171.605
144.746
139.874
136.374
135.640
133.686
132.770
132.151
130.053
129.815
129.519
127.936
124.084
120.824
70.357
39.188
32.152
15.314
14.027
X : parts per Million : Carbon13

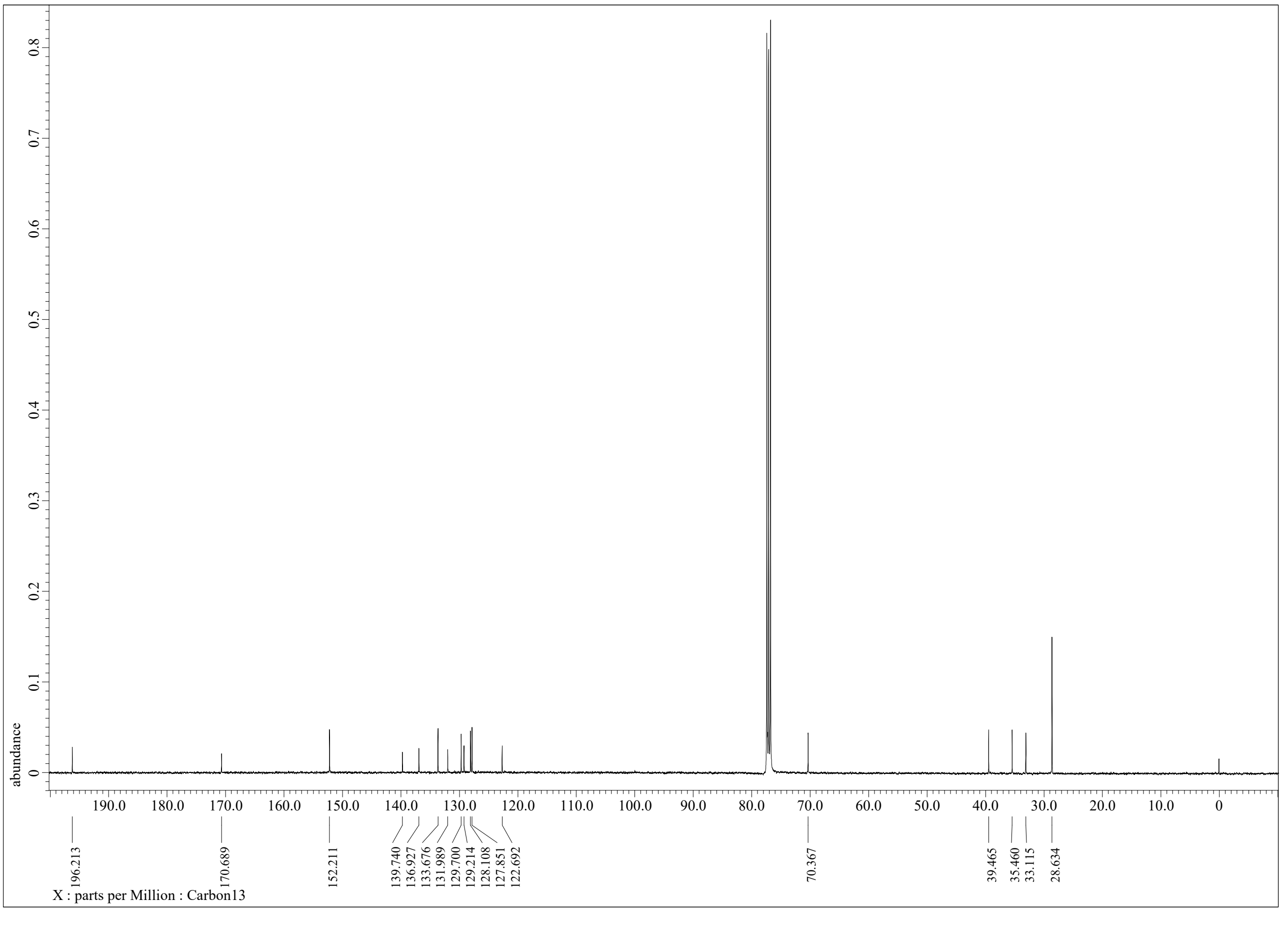

O
Me
H
O
O
2h
0.95
0.97
1.01
0.98
0.95
2.00
1.91
1.94
2.93
abundance
0
1.0
2.0
3.0
4.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.156
8.152
8.136
8.133
7.627
7.623
7.608
7.605
7.589
7.585
7.519
7.497
7.480
7.134
7.116
6.942
6.922
5.050
2.880
2.864
2.850
2.787
2.772
2.756
2.032
2.014
X : parts per Million : Proton

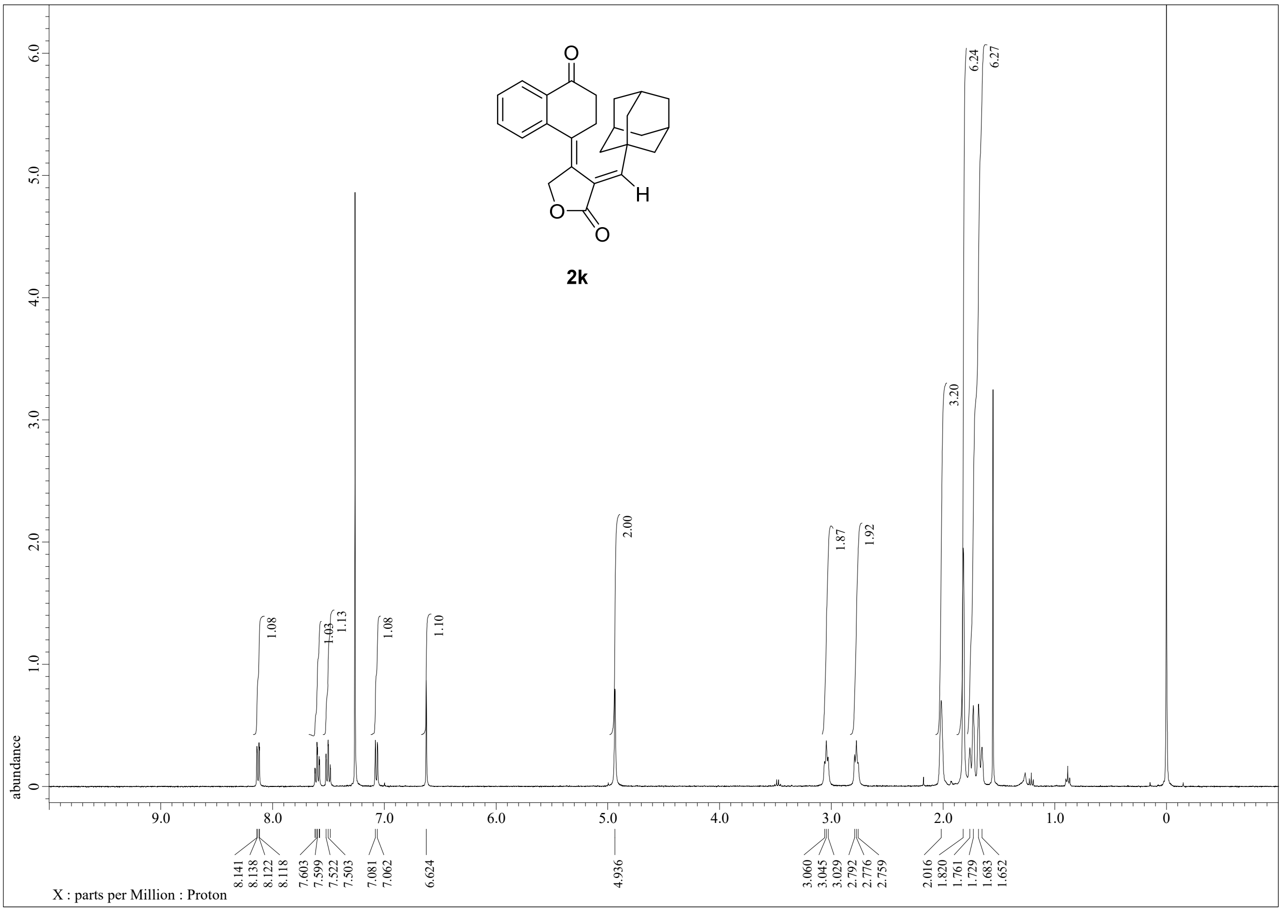

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
0.17
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.414
170.222
139.569
137.280
134.077
133.724
132.132
129.595
128.690
128.041
128.003
127.879
70.548
39.351
31.904
18.327
X : parts per Million : Carbon13

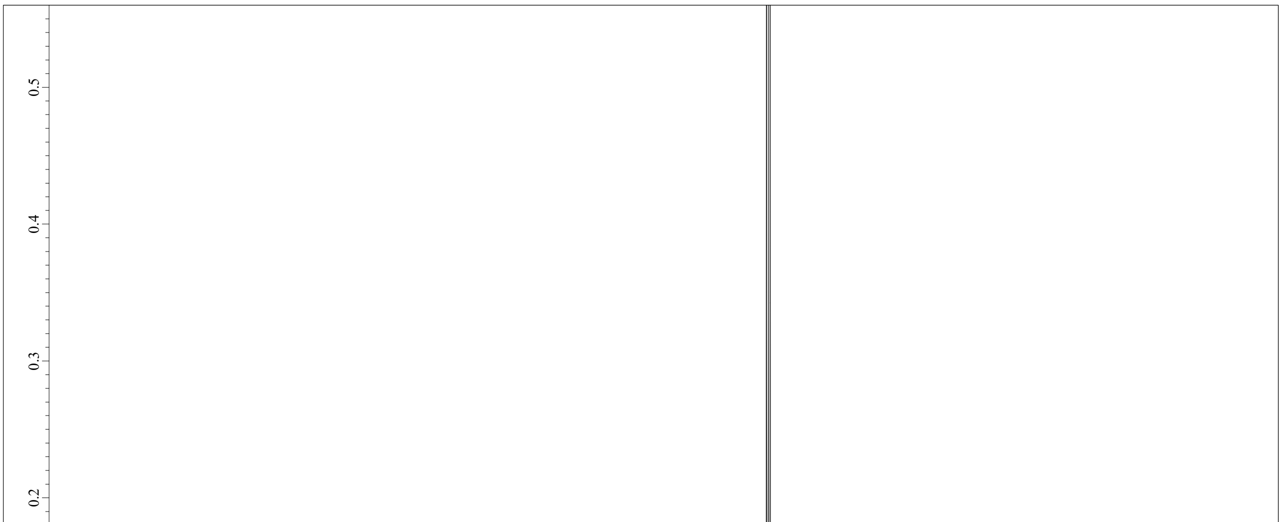

O
O
O
H
2i
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
0.93
0.94
0.95
0.97
0.94
2.00
1.90
1.89
2.04
0.89
3.04
5.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.150
8.147
8.131
8.127
7.606
7.603
7.510
7.490
7.131
7.111
6.999
6.663
6.635
5.028
2.953
2.937
2.920
2.797
2.780
2.764
2.322
2.314
2.296
1.824
1.763
1.735
1.346
1.320
1.285
1.267
1.251
1.220
1.204
X : parts per Million : Proton

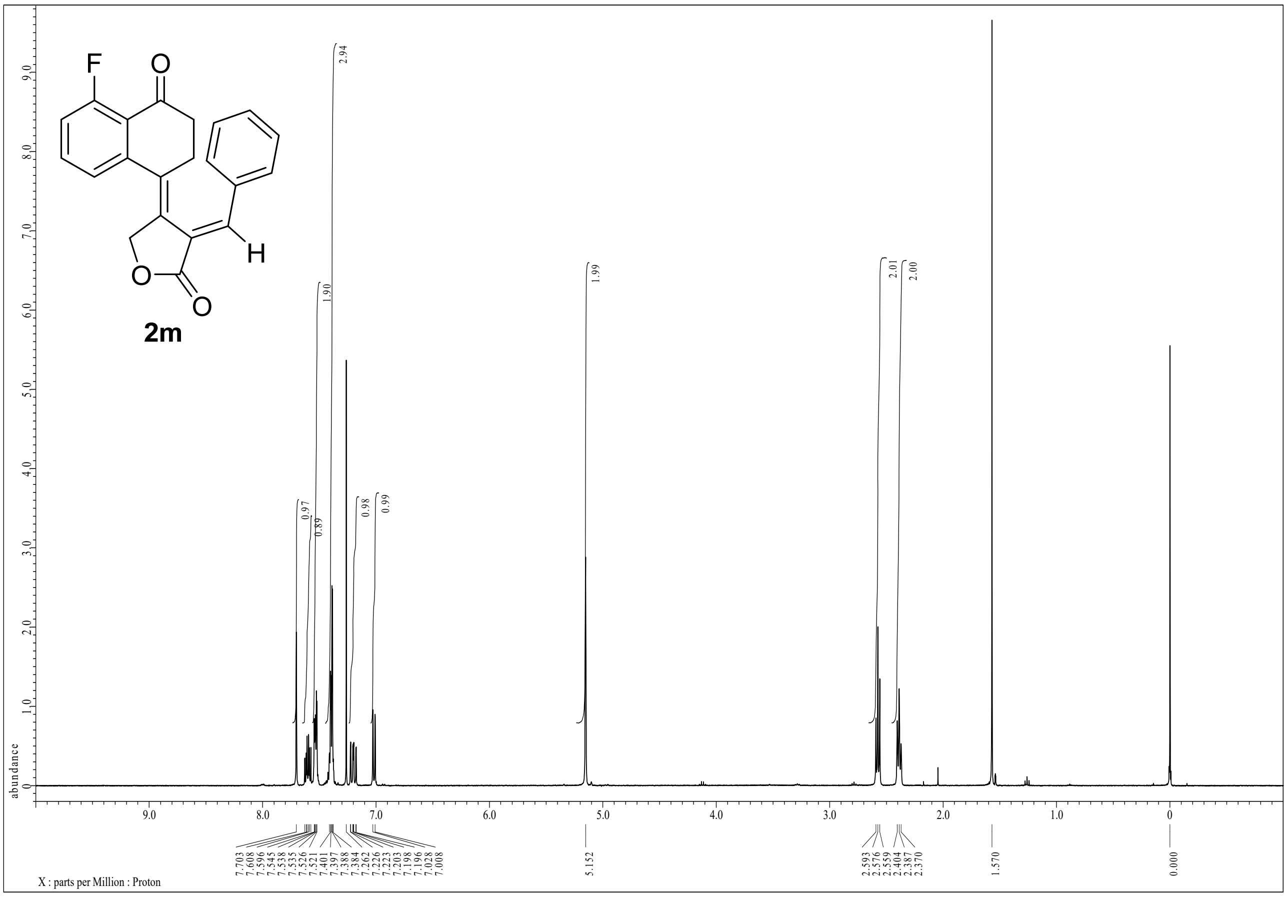

abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.347
170.756
147.549
139.626
133.991
133.657
132.055
129.500
128.995
128.089
127.860
124.027
70.624
40.695
39.341
31.761
31.580
25.687
25.611
X : parts per Million : Carbon13


2j
O
O
O
H
9.09
1.02
1.03
1.05
1.05
1.05
2.00
2.05
2.03
abundance
0
1.0
2.0
3.0
4.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.134
8.115
7.618
7.603
7.599
7.580
7.521
7.502
7.483
7.080
7.062
6.819
4.942
3.034
3.018
3.001
2.782
2.766
2.749
1.241
X : parts per Million : Proton


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.213
170.689
152.211
139.740
136.927
133.676
131.989
129.700
129.214
128.108
127.851
122.692
70.367
39.465
35.460
33.115
28.634
X : parts per Million : Carbon13

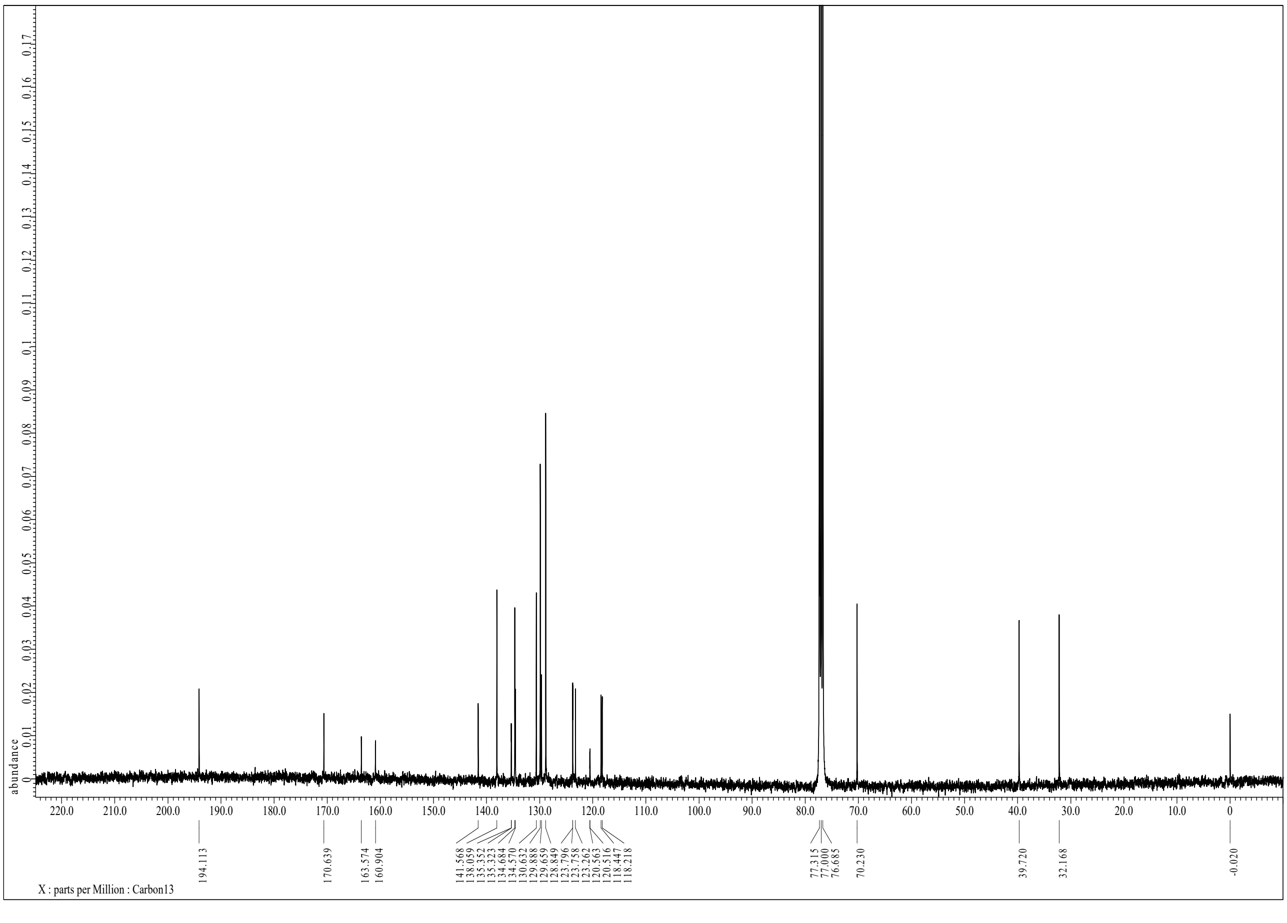

2k
O
O
O
H
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
1.08
1.03
1.13
1.08
1.10
2.00
1.87
1.92
3.20
6.24
6.27
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.141
8.138
8.122
8.118
7.603
7.599
7.522
7.503
7.081
7.062
6.624
4.936
3.060
3.045
3.029
2.792
2.776
2.759
2.016
1.820
1.761
1.729
1.683
1.652
X : parts per Million : Proton


0.5
0.4
0.3
0.2
0.1
0
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.271
170.832
151.792
139.826
136.794
133.657
131.989
129.967
129.643
128.194
127.841
122.454
70.386
40.190
39.513
37.863
36.385
33.420
27.909
X : parts per Million : Carbon13

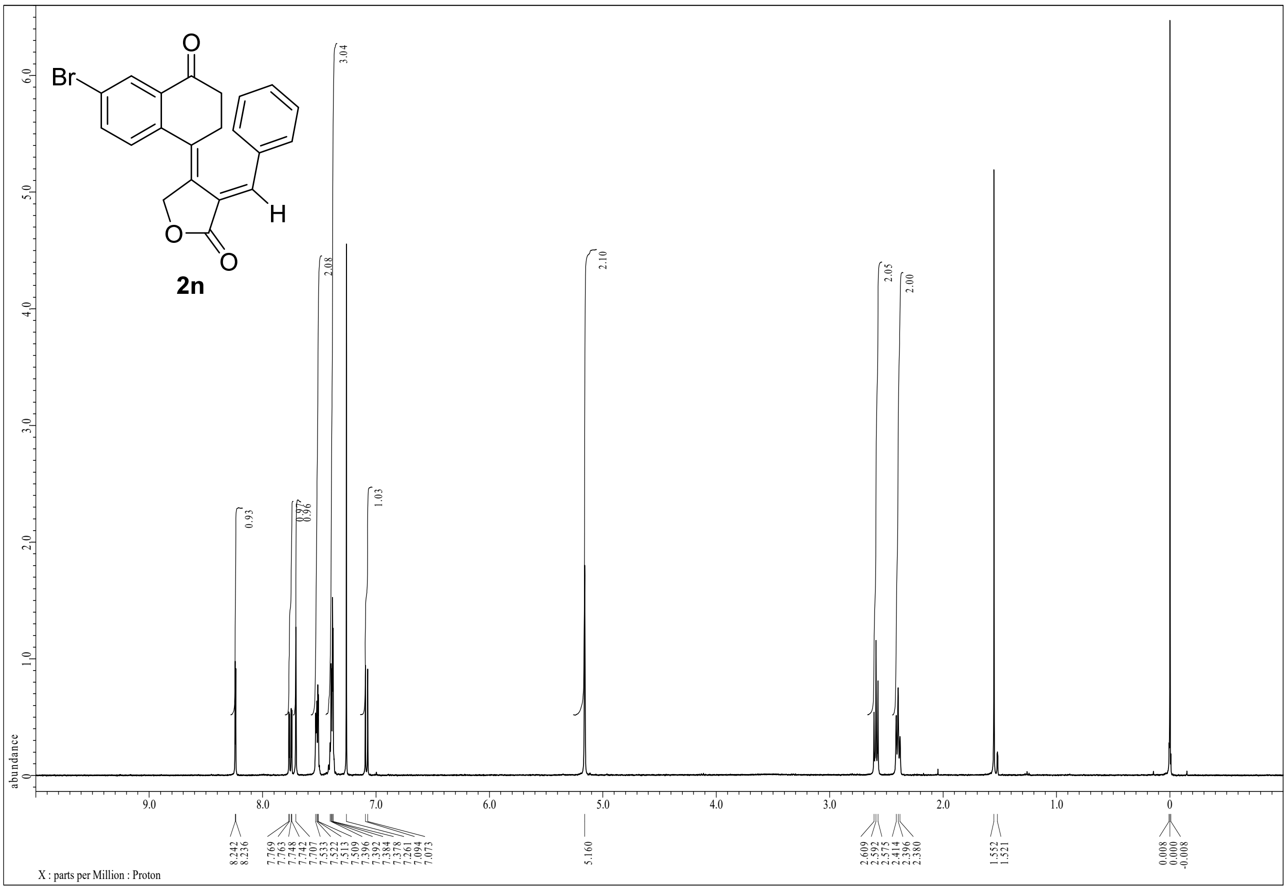


2m

F
O
O
O
H
abundance
0.97
0.89
1.90
2.94
0.98
0.99
1.99
2.01
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.703
7.608
7.596
7.545
7.538
7.535
7.526
7.521
7.401
7.397
7.388
7.384
7.262
7.226
7.223
7.203
7.198
7.196
7.028
7.008
5.152
2.593
2.576
2.559
2.404
2.387
2.370
1.570
0.000
X : parts per Million : Proton

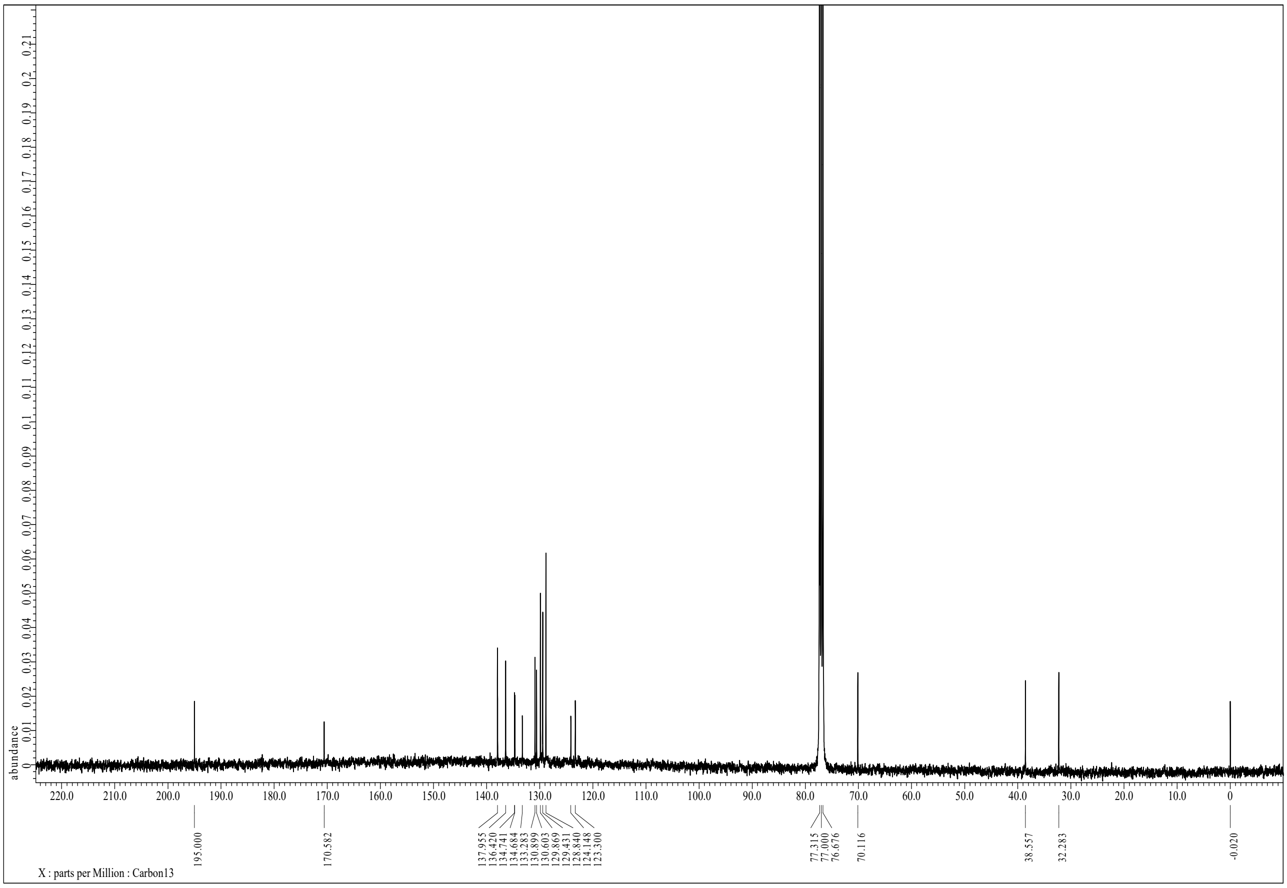


abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
0.17
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
194.113
170.639
163.574
160.904
141.568
138.059
135.352
135.323
134.684
134.570
130.632
129.888
129.659
128.849
123.796
123.758
123.262
120.563
120.516
118.447
118.218
77.315
77.000
76.685
70.230
39.720
32.168
-0.020
X : parts per Million : Carbon13

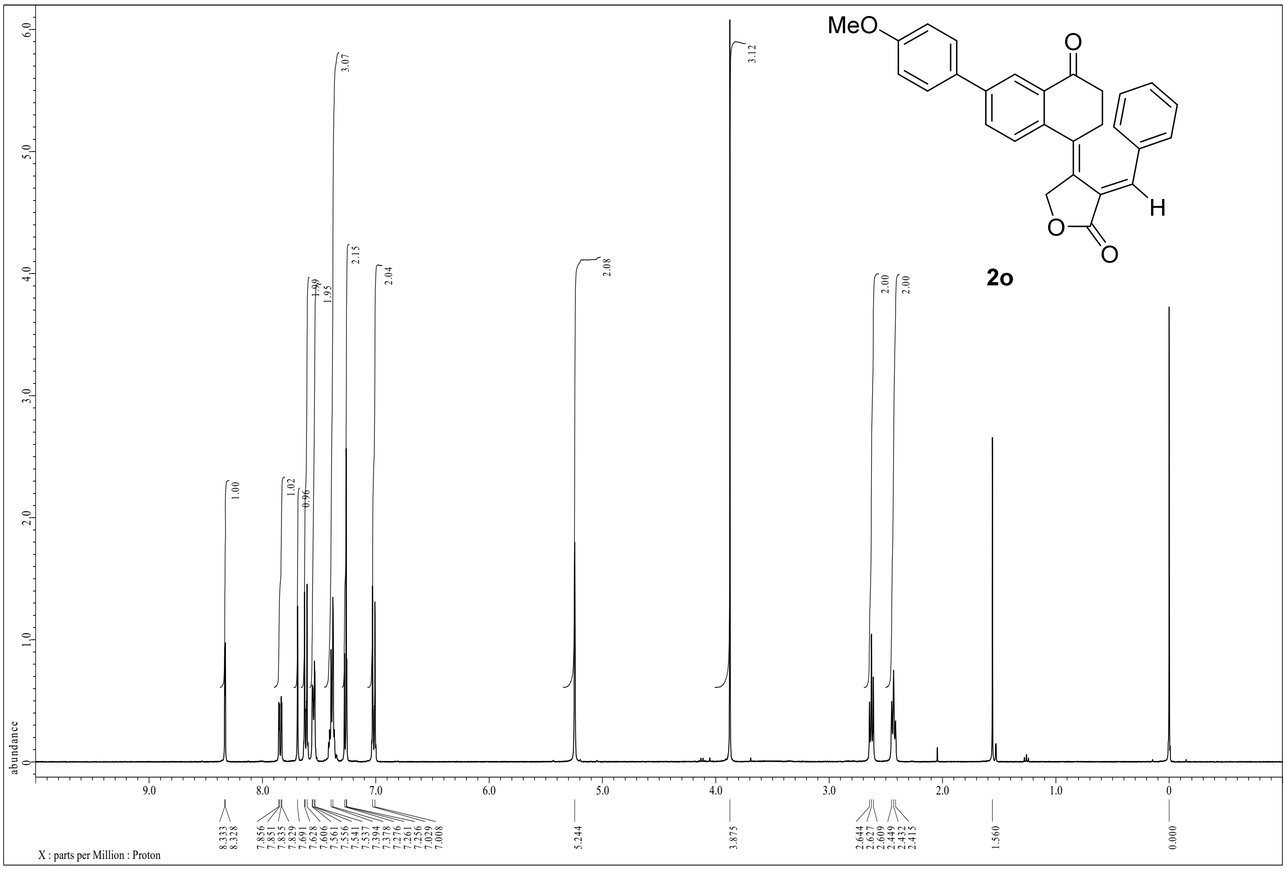


2n

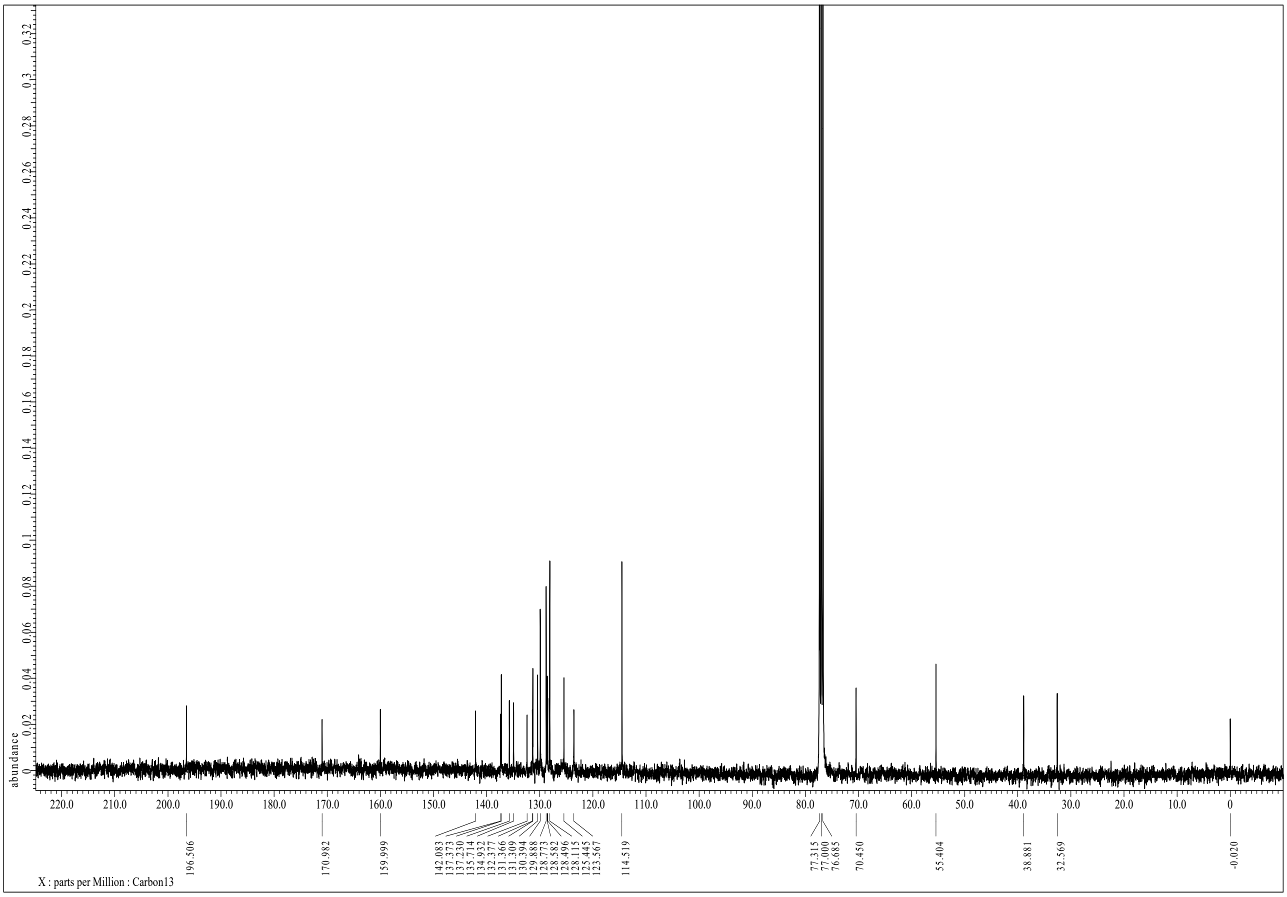
Br
O
O
O
H
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
0.93
0.97
0.96
2.08
3.04
1.03
2.10
2.05
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.242
8.236
7.769
7.763
7.748
7.742
7.707
7.533
7.522
7.513
7.509
7.396
7.392
7.384
7.378
7.261
7.094
7.073
5.160
2.609
2.592
2.575
2.414
2.396
2.380
1.552
1.521
0.008
0.000
-0.008
X : parts per Million : Proton



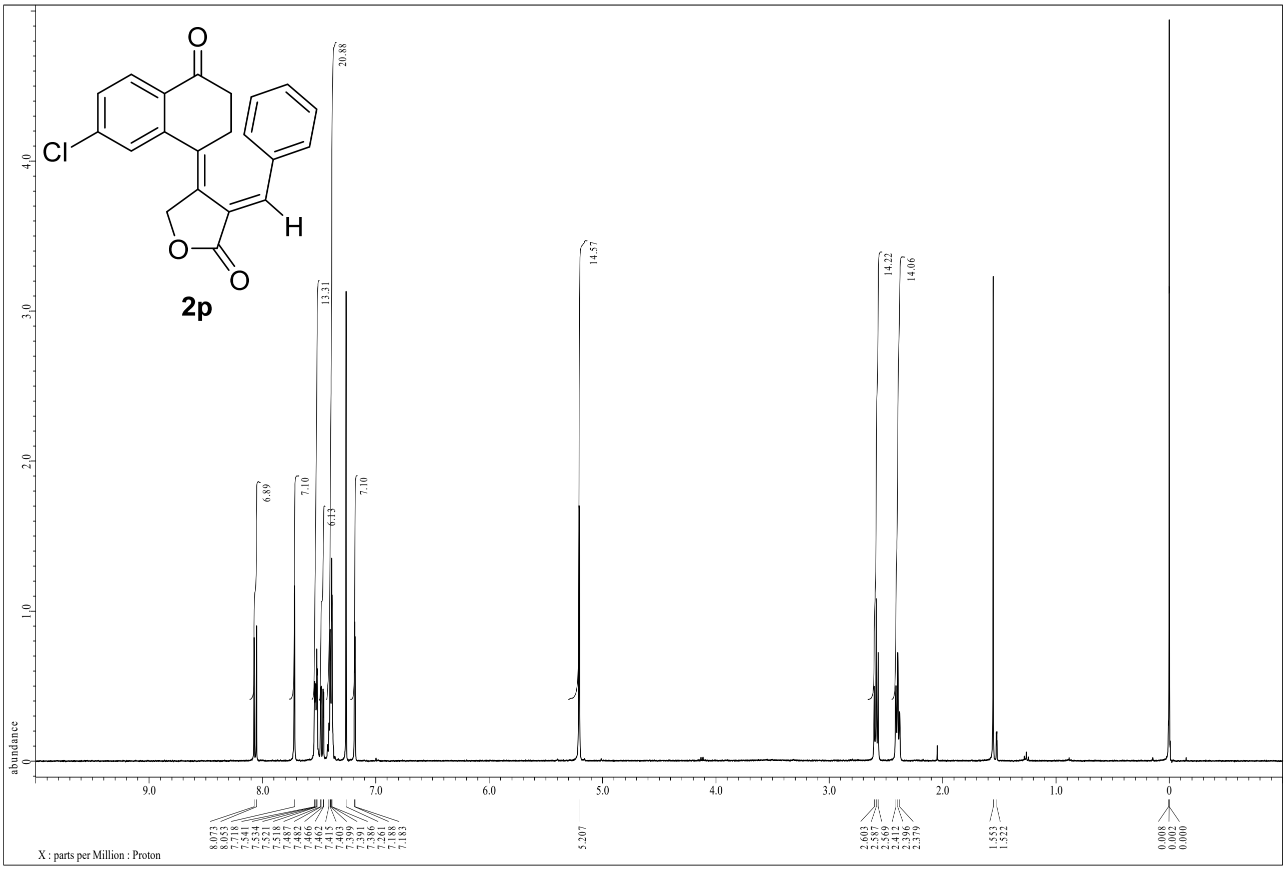
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
0.17
0.18
0.19
0.2
0.21
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
195.000
170.582
137.955
136.420
134.741
134.684
133.283
130.899
130.603
129.869
129.431
128.840
124.148
123.300
77.315
77.000
76.676
70.116
38.557
32.283
-0.020
X : parts per Million : Carbon13

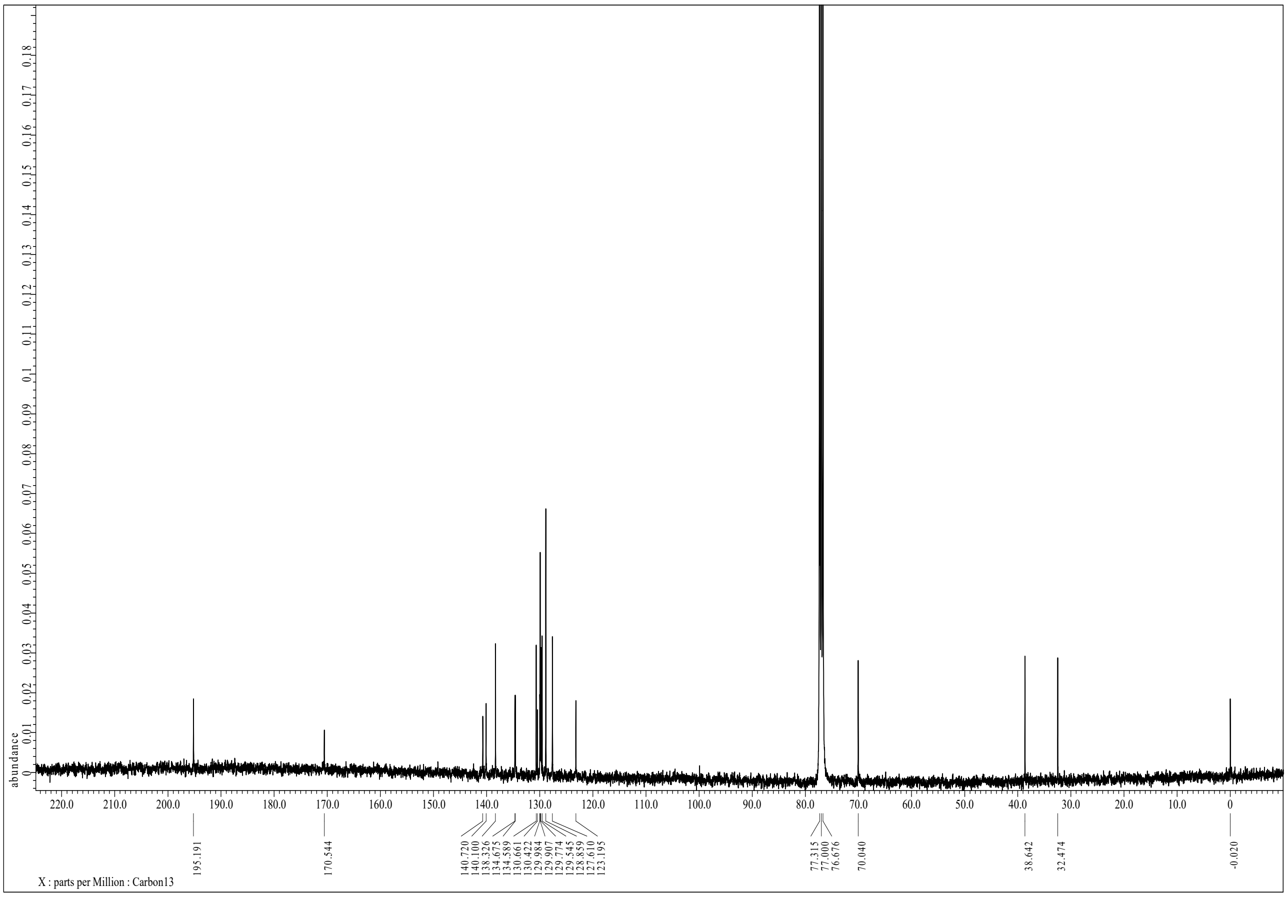


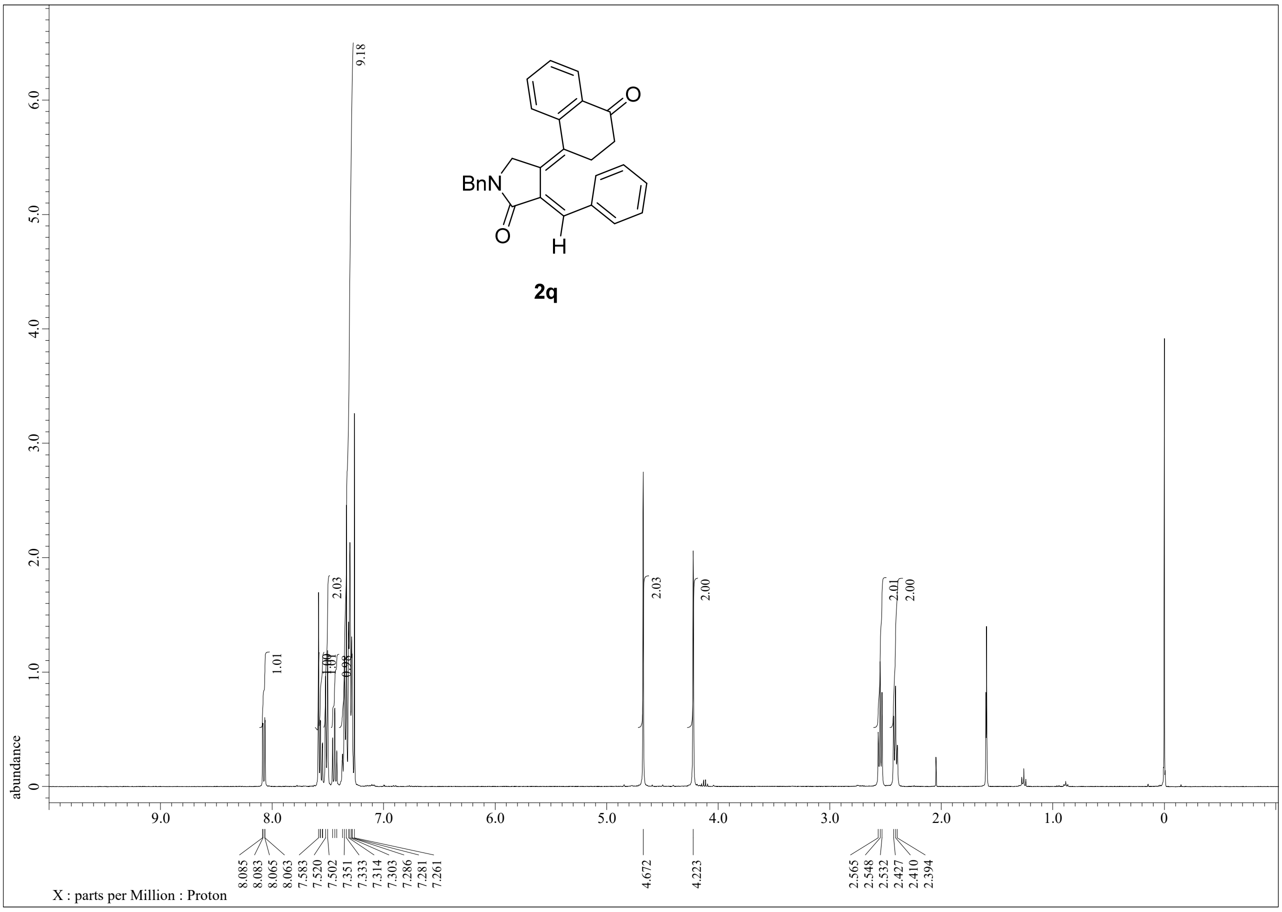
MeO
O
H
O
O
2o
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
1.00
1.02
0.96
1.99
1.95
3.07
2.15
2.04
2.08
3.12
2.00
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.333
8.328
7.856
7.851
7.835
7.829
7.691
7.628
7.606
7.561
7.556
7.541
7.537
7.394
7.378
7.276
7.261
7.256
7.029
7.008
5.244
3.875
2.644
2.627
2.609
2.449
2.432
2.415
1.560
0.000
X : parts per Million : Proton

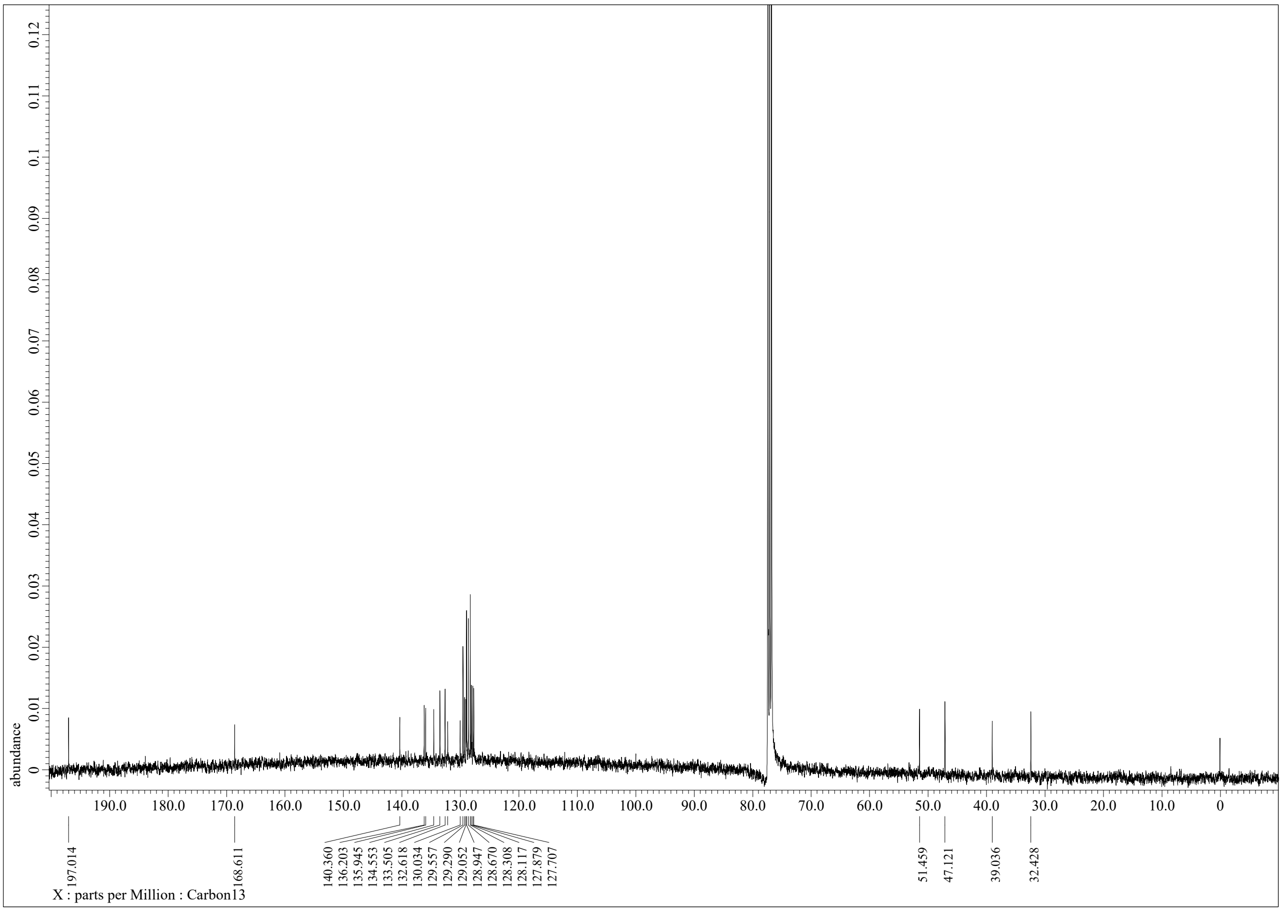


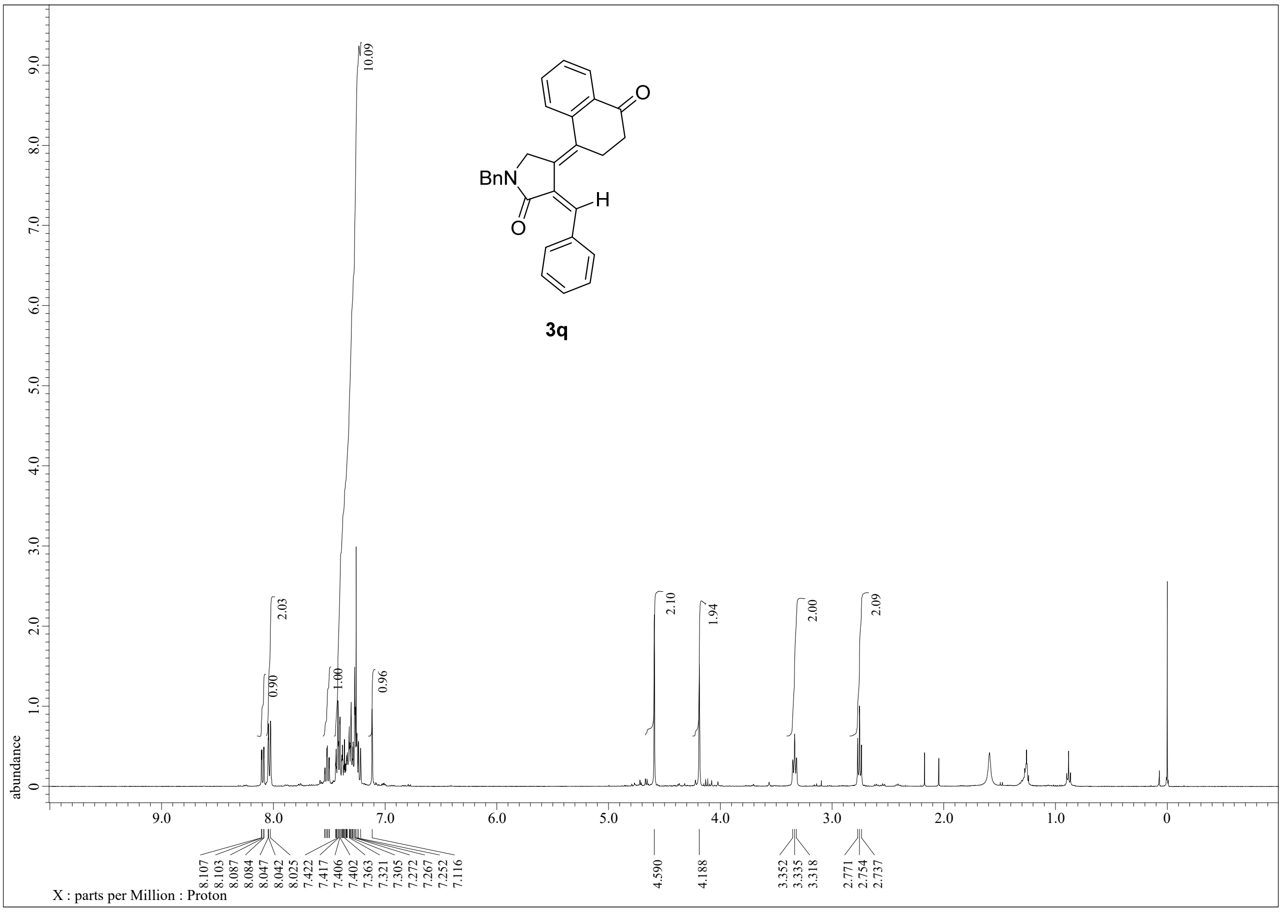
abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
0.26
0.28
0.3
0.32
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.506
170.982
159.999
142.083
137.373
137.230
135.714
134.932
132.377
131.366
131.309
130.394
129.888
128.773
128.582
128.496
128.115
125.445
123.567
114.519
77.315
77.000
76.685
70.450
55.404
38.881
32.569
-0.020
X : parts per Million : Carbon13

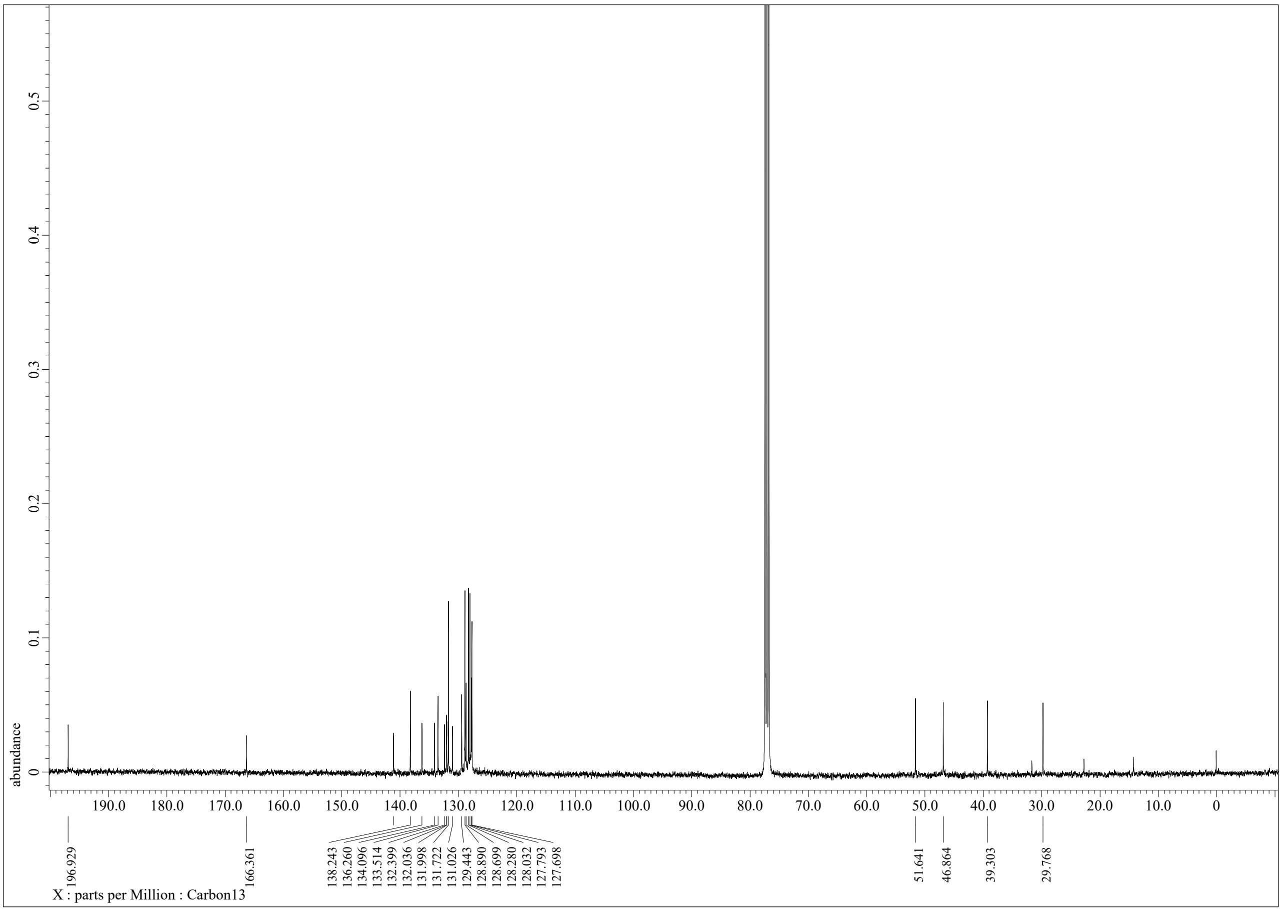

O
Cl
H
O
O
2p
20.88
13.31
14.57
14.22
14.06
6.89
7.10
6.13
7.10
abundance
0
1.0
2.0
3.0
4.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.073
8.053
7.718
7.541
7.534
7.521
7.518
7.487
7.482
7.466
7.462
7.415
7.403
7.399
7.391
7.386
7.261
7.188
7.183
5.207
2.603
2.587
2.569
2.412
2.396
2.379
1.553
1.522
0.008
0.002
0.000
X : parts per Million : Proton

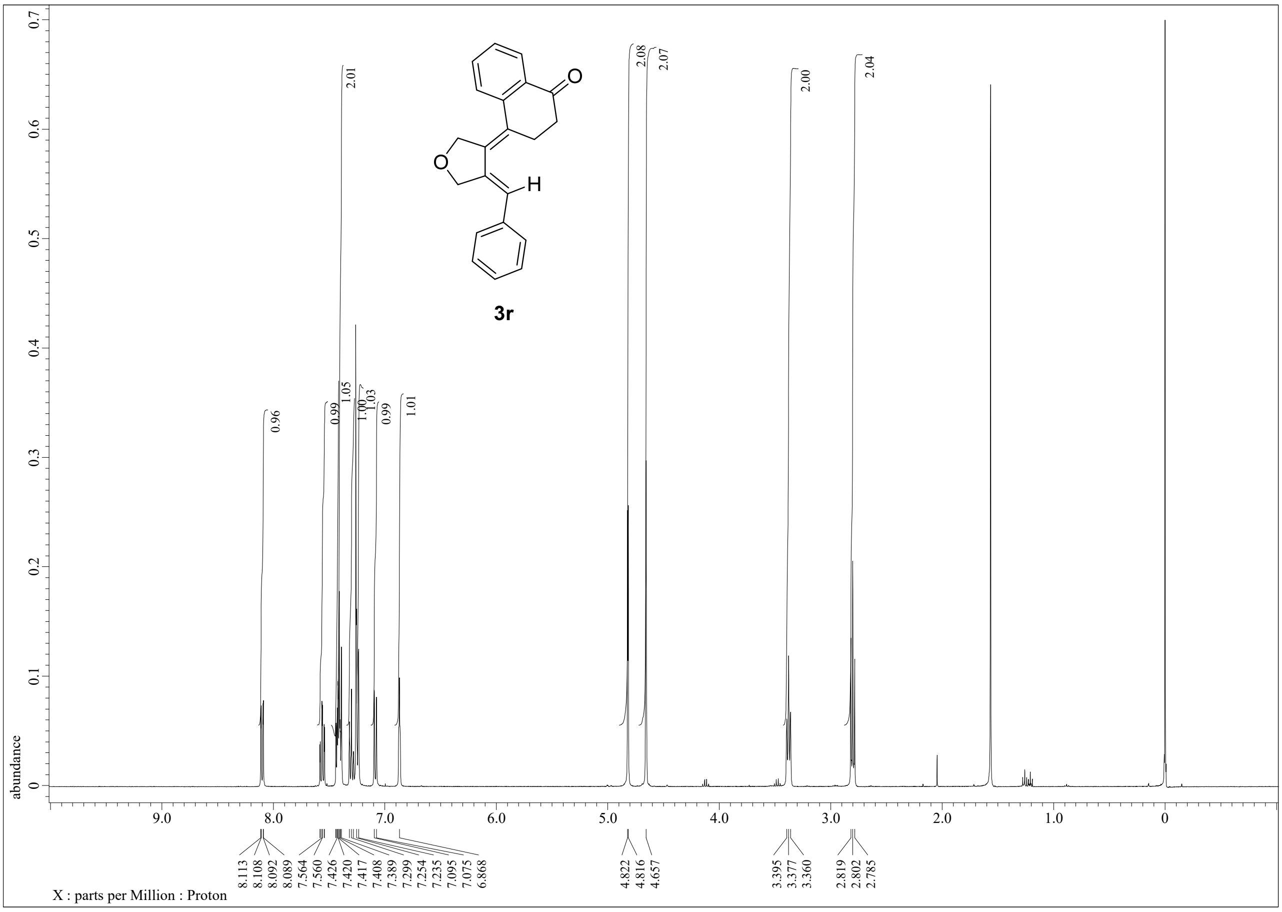

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
0.17
0.18
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
195.191
170.544
140.720
140.100
138.326
134.675
134.589
130.661
130.422
129.984
129.907
129.774
129.545
128.859
127.610
123.195
77.315
77.000
76.676
70.040
38.642
32.474
-0.020
X : parts per Million : Carbon13

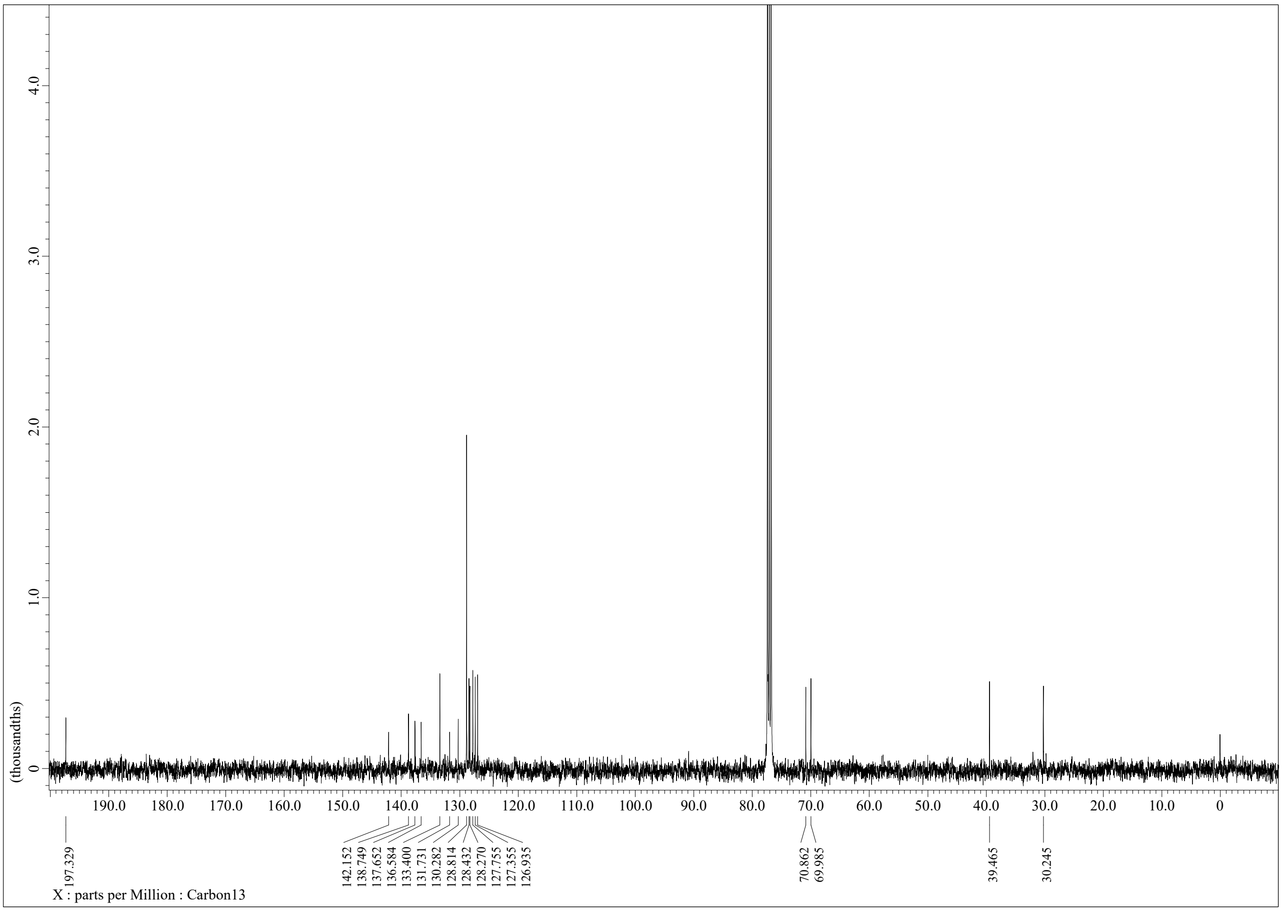

BnN
O
O
H
2q
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
9.18
1.01
1.00
1.01
2.03
0.98
2.03
2.00
2.01
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.085
8.083
8.065
8.063
7.583
7.520
7.502
7.351
7.333
7.314
7.303
7.286
7.281
7.261
4.672
4.223
2.565
2.548
2.532
2.427
2.410
2.394
X : parts per Million : Proton

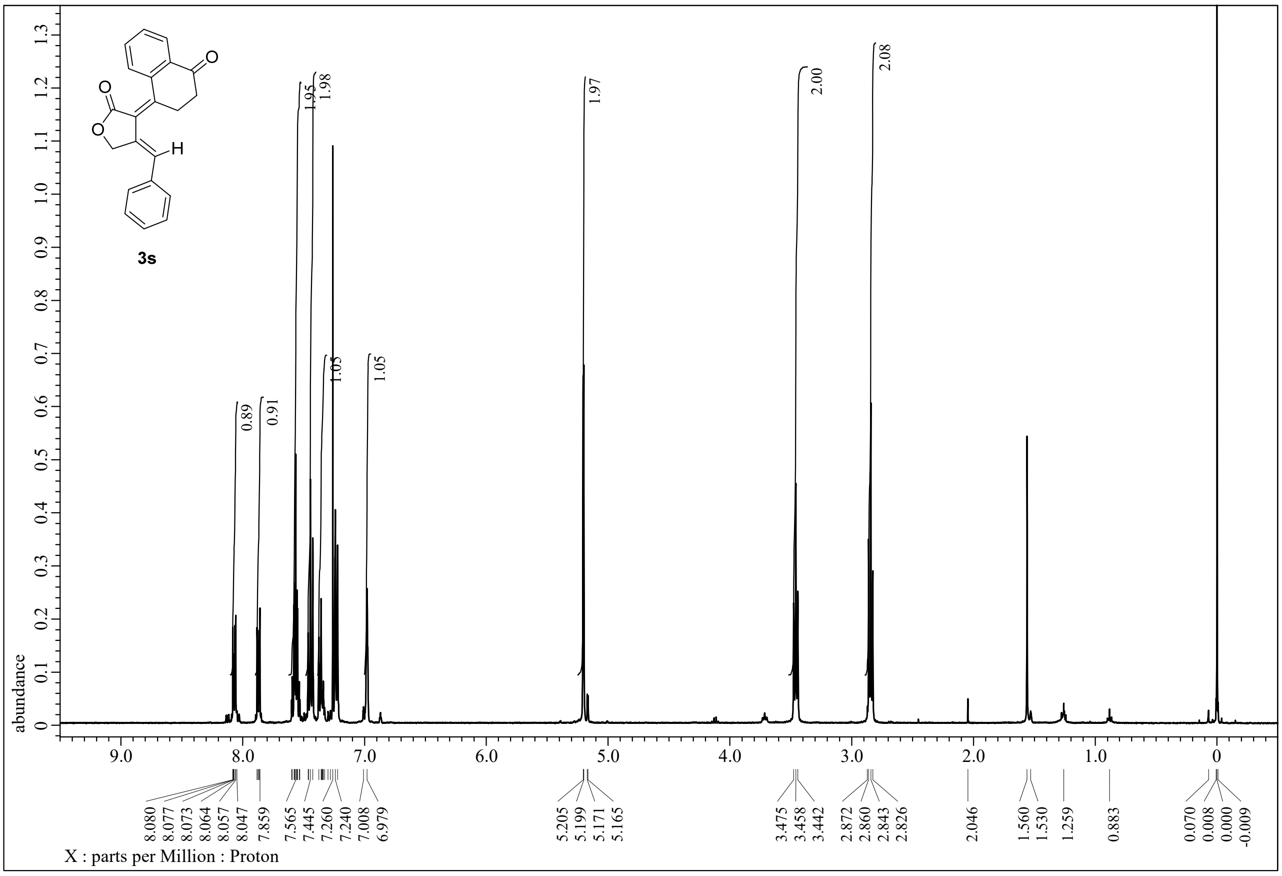

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
197.014
168.611
140.360
136.203
135.945
134.553
133.505
132.618
130.034
129.557
129.290
129.052
128.947
128.670
128.308
128.117
127.879
127.707
51.459
47.121
39.036
32.428
X : parts per Million : Carbon13

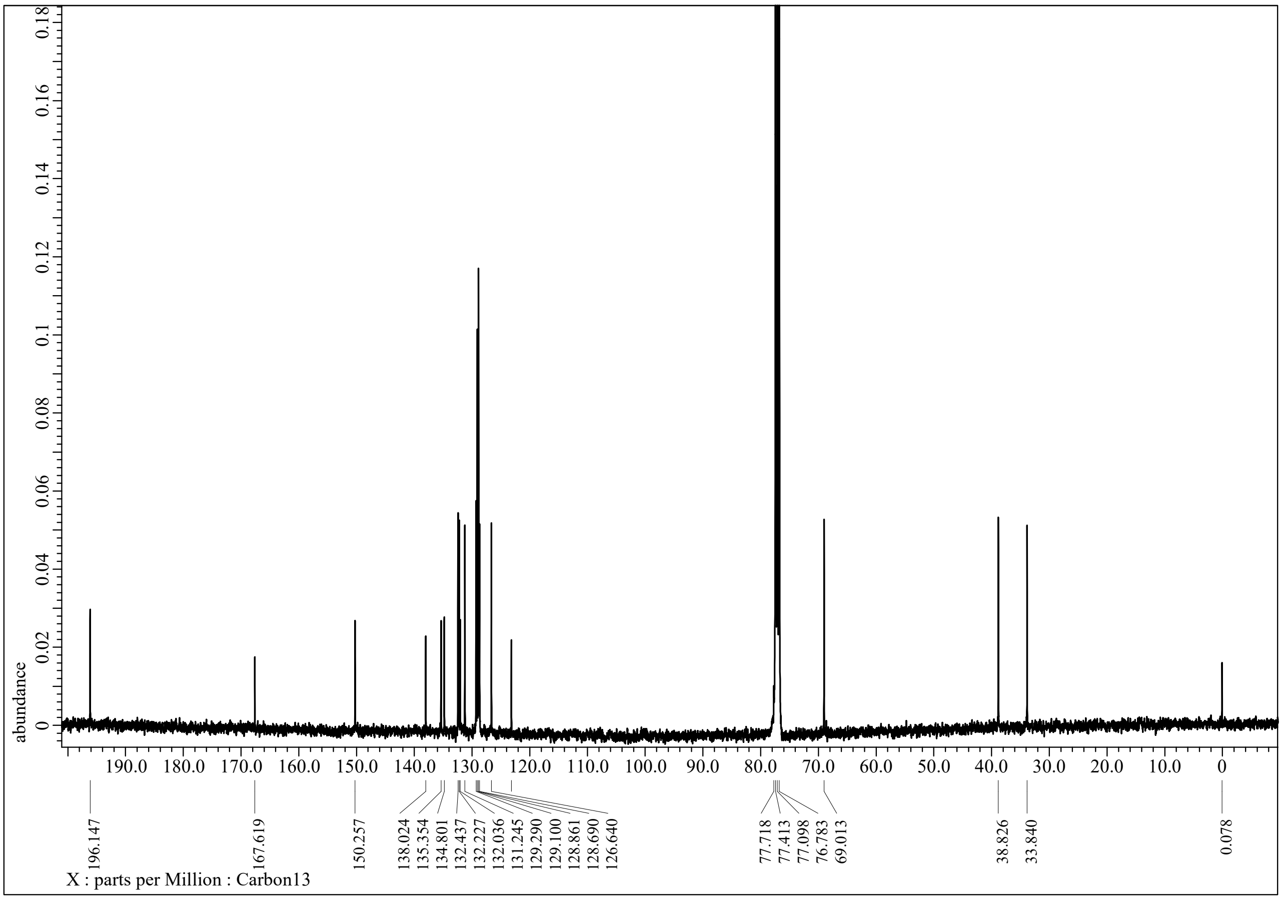

BnN
O
O
H
3q
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.09
2.03
0.90
1.00
0.96
2.10
1.94
2.00
2.09
8.107
8.103
8.087
8.084
8.047
8.042
8.025
7.422
7.417
7.406
7.402
7.363
7.321
7.305
7.272
7.267
7.252
7.116
4.590
4.188
3.352
3.335
3.318
2.771
2.754
2.737
X : parts per Million : Proton

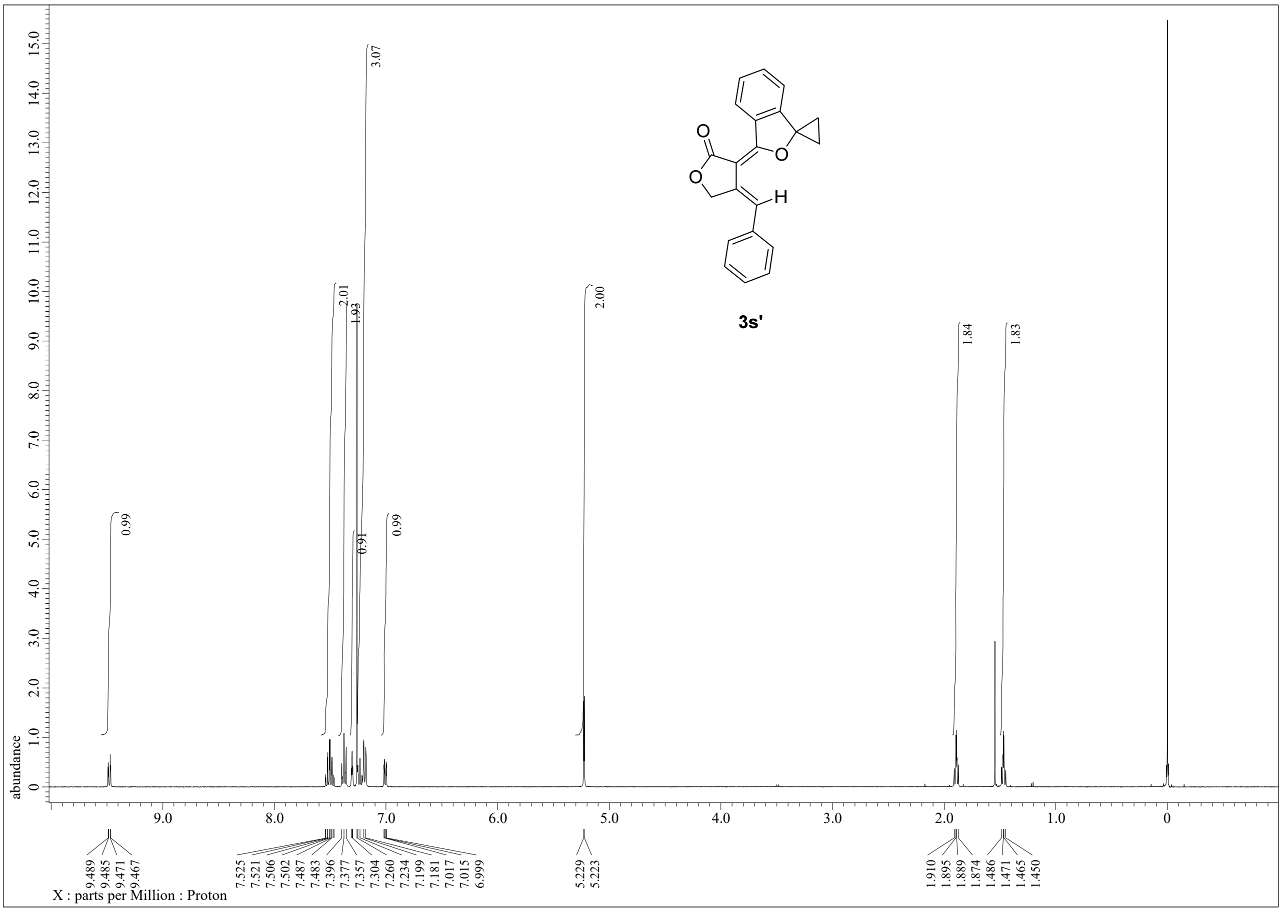

abundance
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.929
166.361
138.243
136.260
134.096
133.514
132.399
132.036
131.998
131.722
131.026
129.443
128.890
128.699
128.280
128.032
127.793
127.698
51.641
46.864
39.303
29.768
X : parts per Million : Carbon13


O
O
H
3r
abundance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.96
0.99
2.01
1.05
1.00
1.03
0.99
1.01
2.08
2.07
2.00
2.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.113
8.108
8.092
8.089
7.564
7.560
7.426
7.420
7.417
7.408
7.389
7.299
7.254
7.235
7.095
7.075
6.868
4.822
4.816
4.657
3.395
3.377
3.360
2.819
2.802
2.785
X : parts per Million : Proton

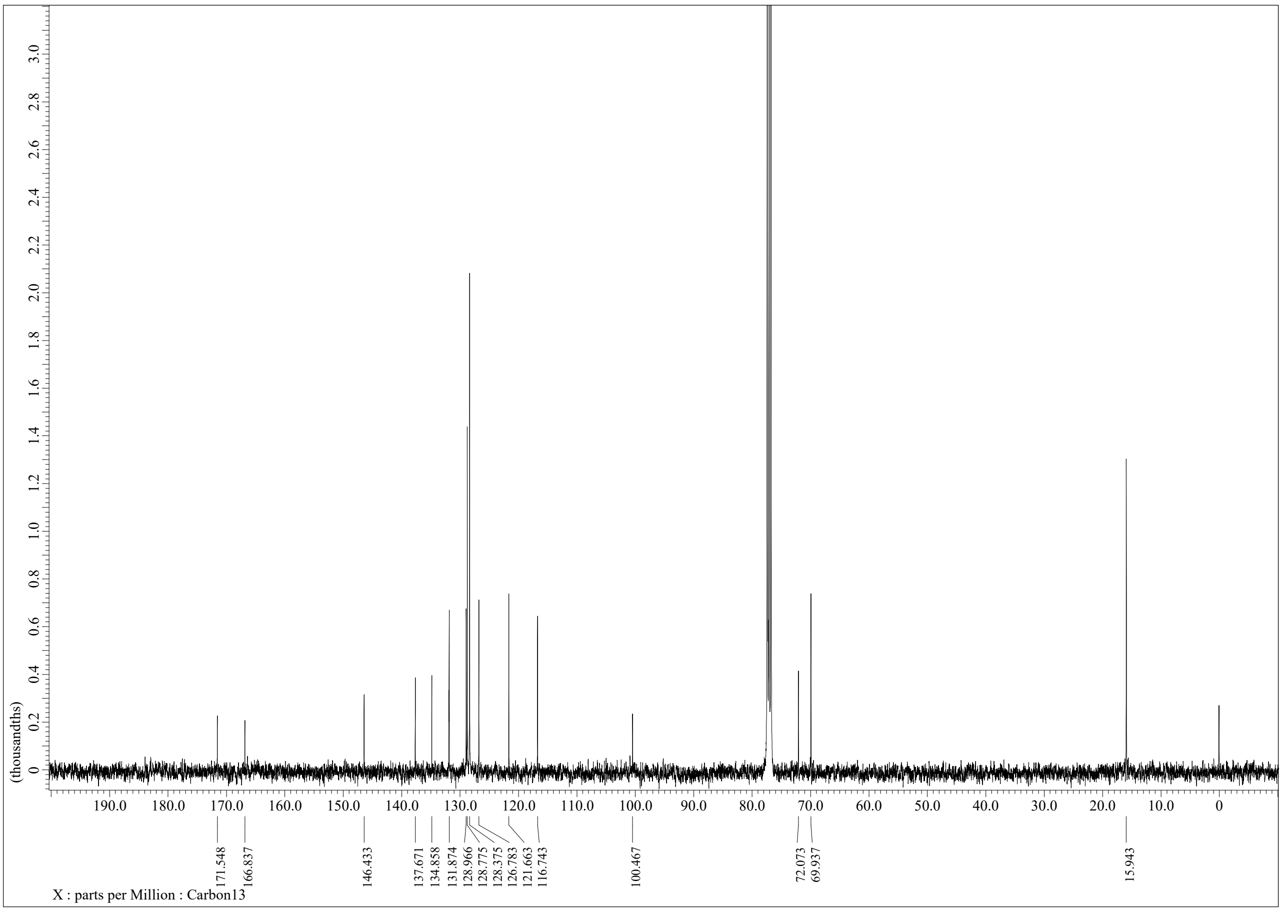

(thousandths)
4.0
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
197.329
142.152
138.749
137.652
136.584
133.400
131.731
130.282
128.814
128.432
128.270
127.755
127.355
126.935
70.862
69.985
39.465
30.245
X : parts per Million : Carbon13

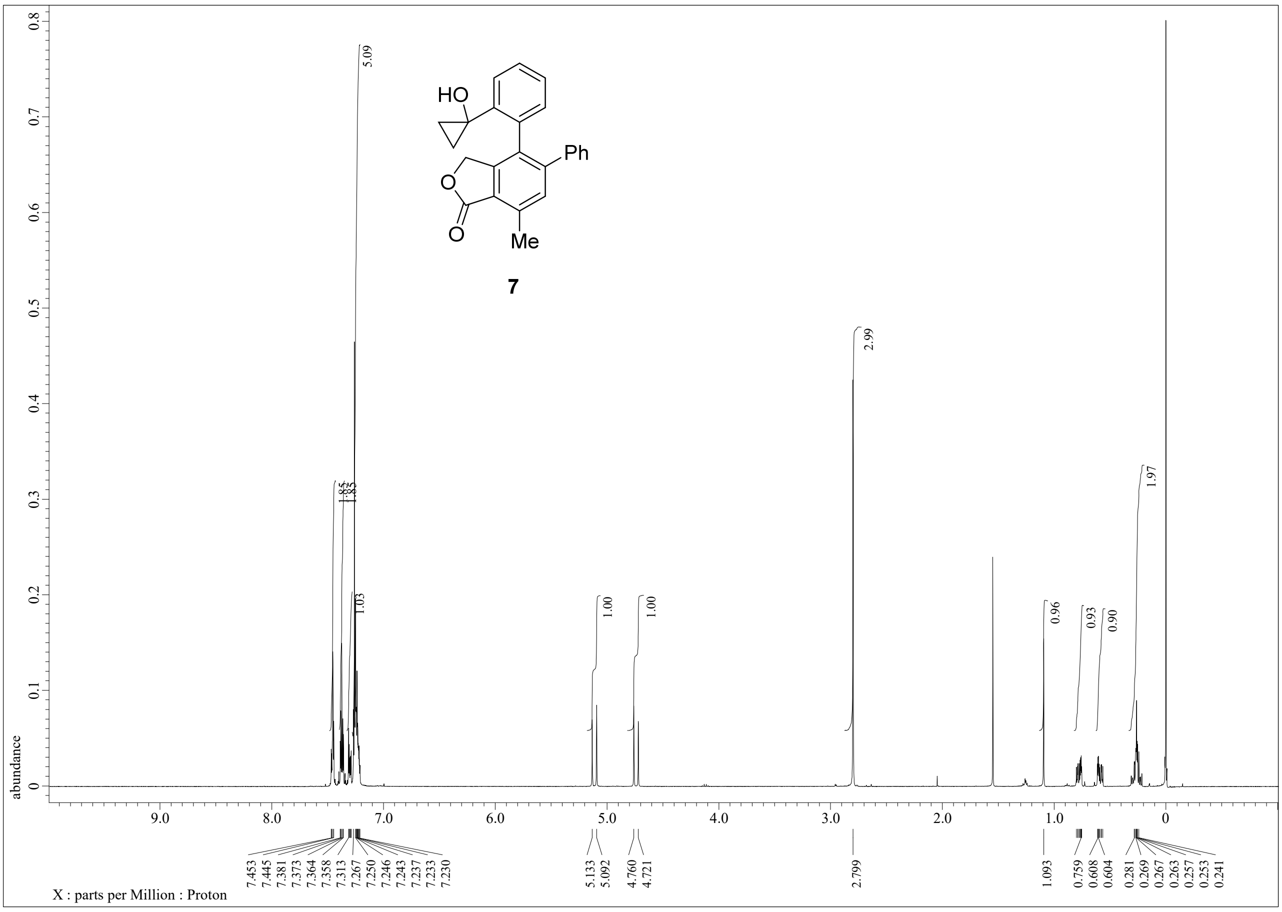

3s
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3
0.89
0.91
1.95
1.98
1.05
1.05
1.97
2.00
2.08
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
8.080
8.077
8.073
8.064
8.057
8.047
7.859
7.565
7.445
7.260
7.240
7.008
6.979
5.205
5.199
5.171
5.165
3.475
3.458
3.442
2.872
2.860
2.843
2.826
2.046
1.560
1.530
1.259
0.883
0.070
0.008
0.000
-0.009
X : parts per Million : Proton


abundance
0 0.02 0.04 0.06 0.08 0.1 0.12 0.14 0.16 0.18
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
196.147
167.619
150.257
138.024
135.354
134.801
132.437
132.227
132.036
131.245
129.290
129.100
128.861
128.690
126.640
77.718
77.413
77.098
76.783
69.013
38.826
33.840
0.078
X : parts per Million : Carbon13

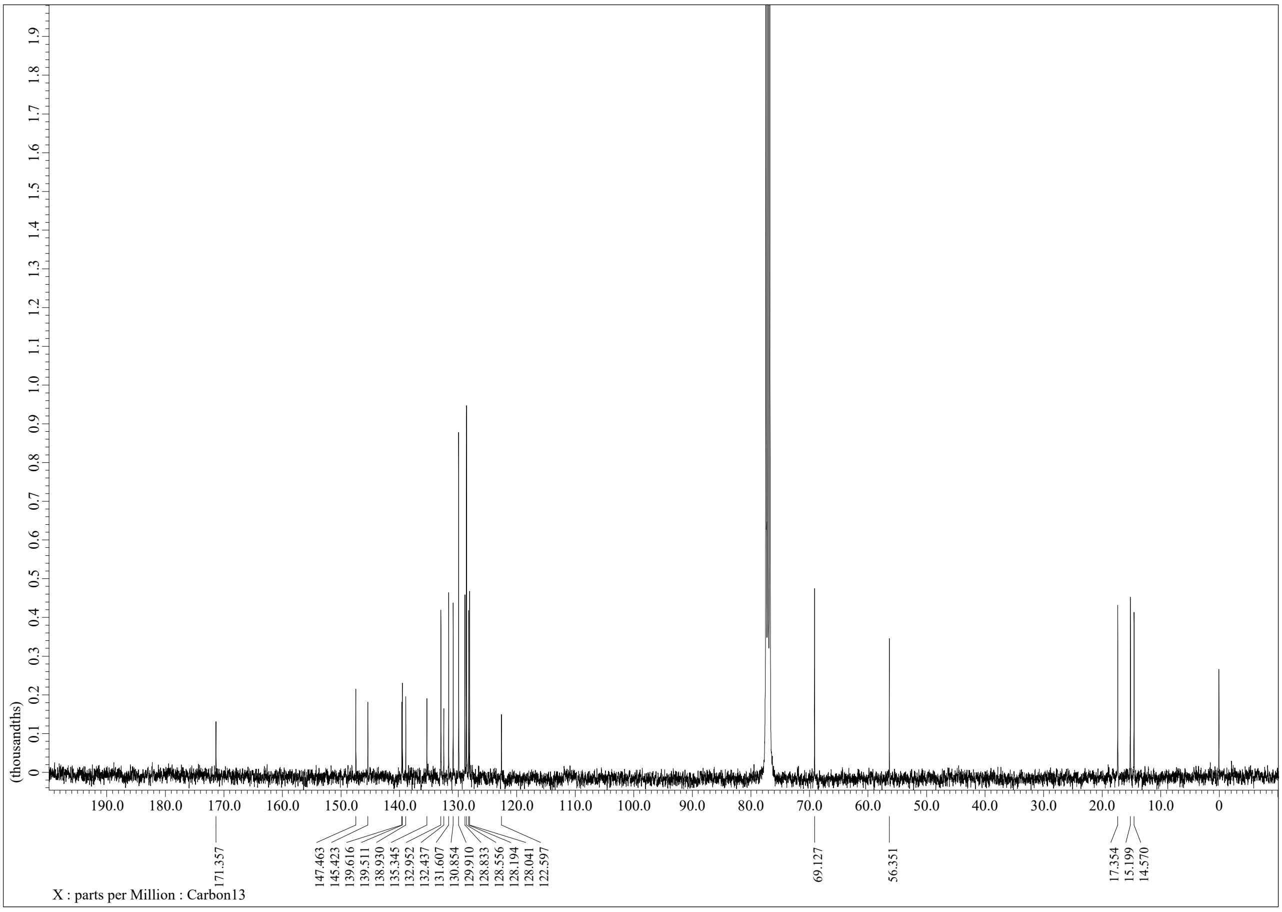

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
0.99
2.01
1.93
3.07
0.91
0.99
2.00
1.84
1.83
O
O
O
H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.489
9.485
9.471
9.467
7.525
7.521
7.506
7.502
7.487
7.483
7.396
7.377
7.357
7.304
7.260
7.234
7.199
7.181
7.017
7.015
6.999
5.229
5.223
1.910
1.895
1.889
1.874
1.486
1.471
1.465
1.450
X : parts per Million : Proton

3s'


(thousandths)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.548
166.837
146.433
137.671
134.858
131.874
128.966
128.775
128.375
126.783
121.663
116.743
100.467
72.073
69.937
15.943
X : parts per Million : Carbon13


HO
Ph
O
O
Me
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
5.09
1.85
1.85
1.03
1.00
1.00
2.99
0.96
0.93
0.90
1.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.453
7.445
7.381
7.373
7.364
7.358
7.313
7.267
7.250
7.246
7.243
7.237
7.233
7.230
5.133
5.092
4.760
4.721
2.799
1.093
0.759
0.608
0.604
0.281
0.269
0.267
0.263
0.257
0.253
0.241
X : parts per Million : Proton

7


(thousandths)
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.357
147.463
145.423
139.616
139.511
138.930
135.345
132.952
132.437
131.607
130.854
129.910
128.833
128.556
128.194
128.041
122.597
69.127
56.351
17.354
15.199
14.570
X : parts per Million : Carbon13