Electronic Supplementary Information

Palladium-Catalyzed Direct γ-C(sp^3)-H Arylation of β-Alkoxy Cyclohexenones: Reaction Scope and Mechanistic Insights

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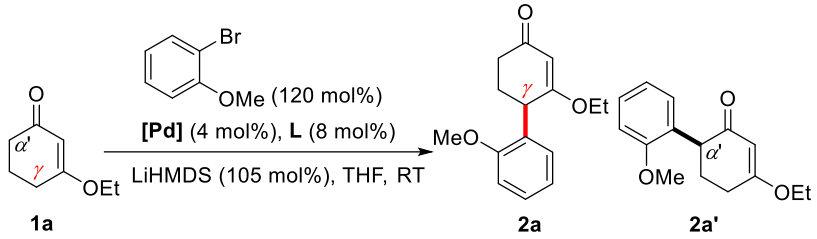
1. General Information

All reactions were conducted in oven-dried round-bottom flasks under argon atmosphere, except for the Pd-catalyzed γ-arylations of β-alkoxy cyclohexenones which were conducted in flame-dried round-bottom flasks. THF was freshly distilled with Na. All reagents were used from commercial sources without further purification, unless otherwise noted. The silica gel (200-300 meshes, Qingdao Marine Chemical Inc., Qingdao, China) was used for column chromatography. Thin layer chromatographies (TLC) were carried out on GF plates (0.25 mm layer thickness, Qingdao Marine Chemical Inc., Qingdao, China). Visualization of the developed chromatogram was performed by ultraviolet light (254 nm, if applicable) or by phosphomolybdic acid (50 g/L) in ethanol following heating as developing agents. Yields reported were for isolated, spectroscopically pure compounds, unless otherwise noted.

^{1}H and ^{13}C NMR spectras were recorded on AM-500 MHz and ADVANCE III 600 MHz spectrometers (Bruker, German) at ambient temperature. The residue solvent protons (^{1}H) or the solvent carbons (^{13}C) were used as internal standards. ^{1}H NMR data were presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant (Hz), integration). Chemical shifts (δ) were given in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.16)]. The following abbreviations are used in reporting NMR data: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, hept = heptet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet. HRMS (ESI) was taken on Agilent 6540 Q-TOF spectrometer. IR spectroscopy was scanned with KBr pellets on Affinity-1S spectrophotometer (Shimadzu, Kyoto, Japan). X-ray diffraction data were collected on a Bruker APEX DUO diffractometer equipped with an APEX II CCD using Cu Kα radiation (100 K).

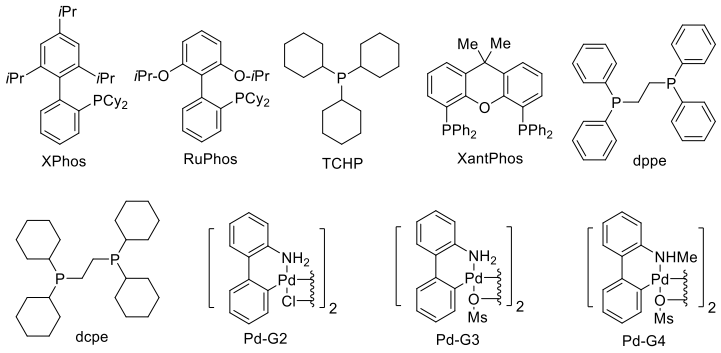
2. Additional Condition Optimization

Table S1. Screening of Pd sources and phosphine ligands [a]



Entry	[Pd]	L	Yield **2a**/**2a′** (%) [b]	Unreacted **1a** (%) [b]
1	$Pd(OAc)_2$	PPh_3	n.d [c]	NR [d]
2	$Pd(OAc)_2$	$P(tBu)_3 \cdot HBF_4$	n.d	NR
3	$Pd(OAc)_2$	$P(tBu)_3$	11/6	20
4	$Pd(OAc)_2$	BINAP	n.d	NR
5	$Pd(OAc)_2$	XPhos	7/29	21
6	$Pd(OAc)_2$	RuPhos	8/11	25
7	$Pd(OAc)_2$	TCHP	n.d	NR
8 [e]	$Pd(OAc)_2$	XantPhos	0/5	25
9 [e]	$Pd(OAc)_2$	dppe	n.d	NR
10 [e]	$Pd(OAc)_2$	dcpe	n.d	NR
11	$Pd(dba)_2$	$P(tBu)_3$	10/31	9
12	$Pd(TFA)_2$	$P(tBu)_3$	16/6	22
13	$PdCl_2$	$P(tBu)_3$	11/32	21
14	$Pd_2(dba)_3$	$P(tBu)_3$	13/26	18
15	$Pd(dppf)Cl_2$	$P(tBu)_3$	n.d	NR
16	$Pd(PPh_3)_2Cl_2$	$P(tBu)_3$	n.d	NR
17 [f]	Pd-G2	$P(tBu)_3$	61/5	23
18 [f]	Pd-G3	$P(tBu)_3$	50/2	26
19 [f]	Pd-G4	$P(tBu)_3$	71/1	22

[a] Unless otherwise noted, all of the reactions were performed in freshly distilled and degassed THF (1.5 mL) with **1a** (1.0 mmol) at RT for 0.5 h. [b] NMR yield based on **1a** (1,1,2,2-tetrachloroethane as internal standard); [c] n.d: not determined ; [d] NR: no reaction; [e] 5 mol% of ligands were used;[f] 3 mol% of [Pd]/$P(tBu)_3$ or [Pd] were used



General procedure for Table S1.

LiHMDS (1.05 mmol, 1.05 mL, 1.0 M in THF, 1.05 equiv) was added dropwise at 0 °C to a solution of **1a** (1.0 mmol, 1.0 equiv) in degassed THF (1.5 mL) in flame-dried two-necked flask (1#), which have been evacuated and refilled with argon. The resulting solution was stirring for 30 min at 0 °C. In the meantime, Pd catalysts (0.04 mmol, 0.04 equiv) was loaded in a two-necked flask (2#), and then evacuated and refilled with argon for three to five times. To this flask (2#), phosphine ligands (0.08 mmol, 0.08 equiv) in THF (0.75 mL) were added sequentially. After the Pd catalyst system solution was stirring for 10 ~ 15 min at room temperature, 2-methoxy bromobenzene (1.2 mmol, 1.2 equiv) was added to flask (2#) and stirred for additional 10 ~ 15 min. The cold enolate solution in flask (1#) was added dropwise into the flask (2#) by syringe at room temperature. After stirring for 0.5 h at room temperature, the reaction was quenched with water (1 mL). The resulting mixture was diluted with water (10 mL), extracted with EtOAc (15 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo. The NMR yields of each product in the crude mixture were determined using 1,1,2,2-tetrachloroethane (TCE) as the internal standard.

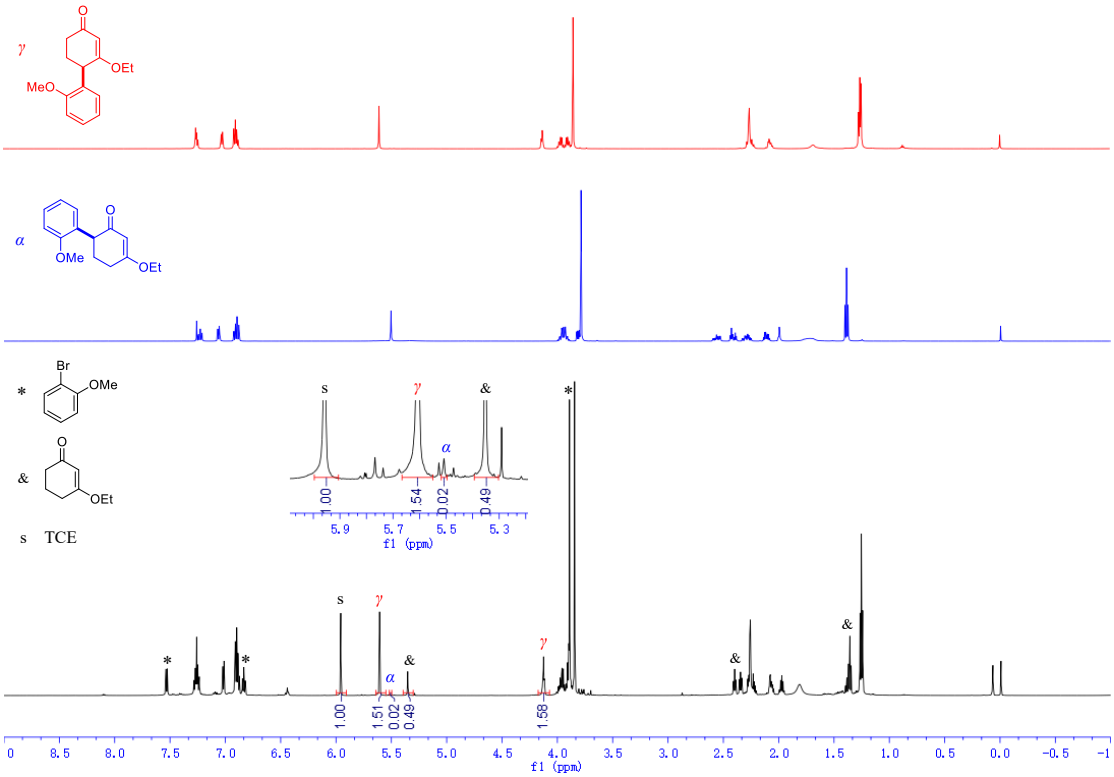
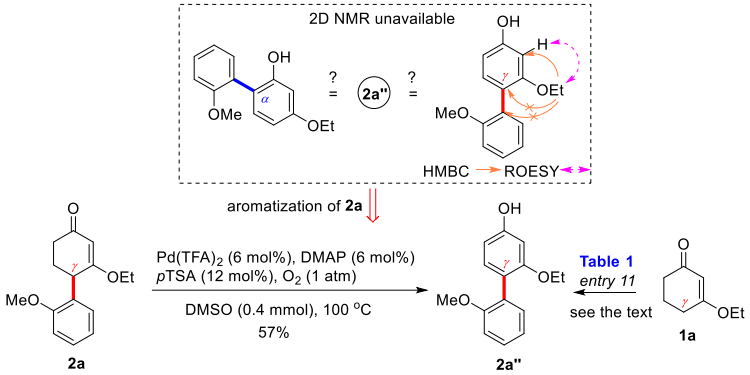


Figure S1. Crude NMR of the representative reaction (Table S1, entry 19).

Structure Determination of byproduct 2a″

Given that both **2a** and **2a′** could be aromatized, and the key correlations of **2a″** in 2D NMR are unavailable. Thus, the structure of **2a″** was confirmed by Pd-catalyzed aromatization of **2a** according to the literature.[1] To be detailed, **2a** (100 mg, 0.40 mmol), $Pd(TFA)_2$ (8 mg, 0.024 mmol), DMAP (3 mg, 0.024 mmol), and *p*TSA (9 mg, 0.048 mmol) in DMSO (1 mL) was degassed and refilled with O_2, the resulting reaction mixture was then heated at 100 °C for 72 h. After complete consumption of the starting materials, the reaction was cooled to room temperature, diluted with water (20 mL), and extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 5:1) to yield **2a″** (56 mg, 57%) as colorless oil. The NMR data of **2a″** obtained in scheme S1 were consistent with those obtained in Table 1, entry 11.



Scheme S1. Structure determination of **2a″** *via* Pd-catalyzed aromatization of **2a**.

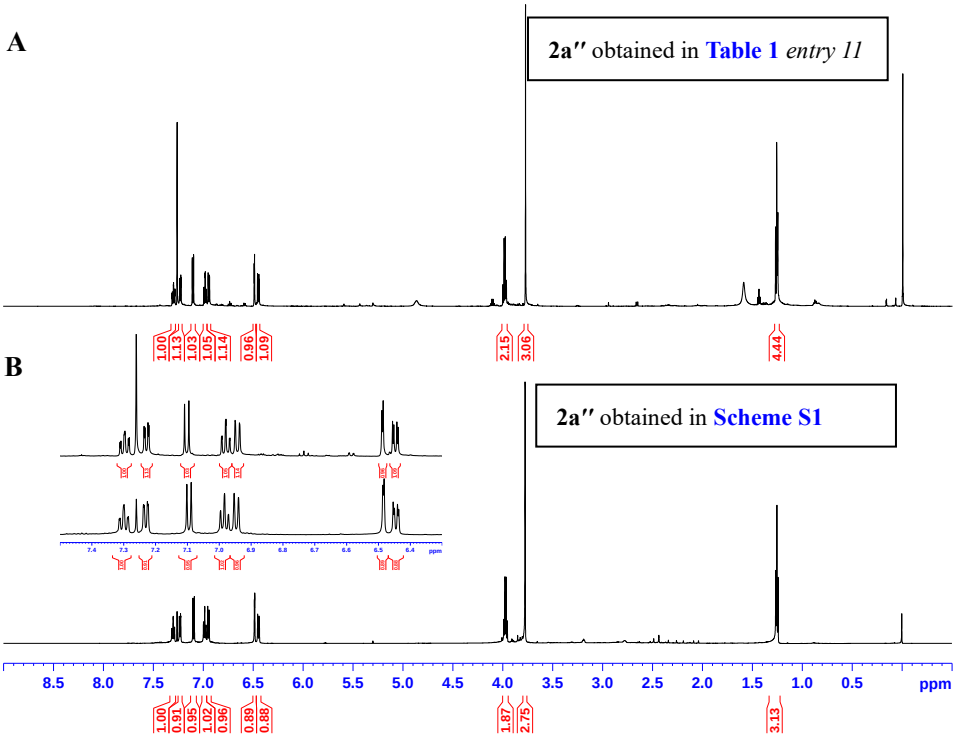


Figure S2. [1]H-NMR spectra of compound **2a″** (A) obtained in Table 1 entry 11; (B) obtained in Scheme S1.

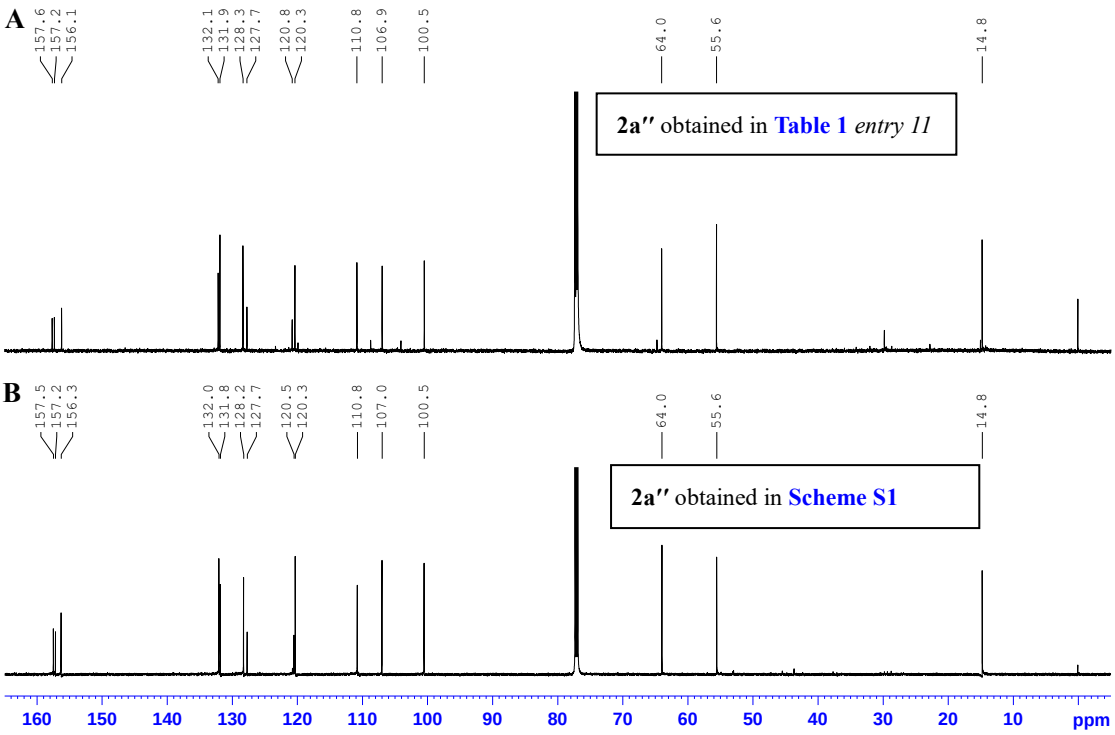
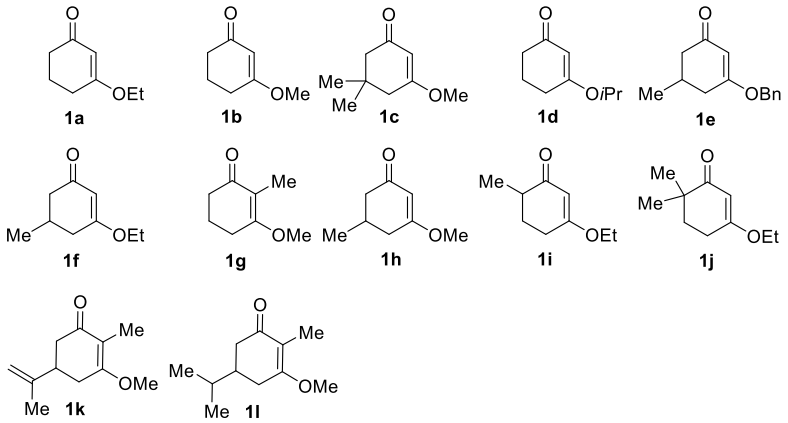


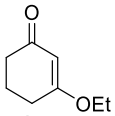
Figure S3. ^{13}C-NMR spectra of compound **2a″** (A) obtained in Table 1 entry 11; (B) obtained in Scheme S1.

3. Synthesis and Characterization of Substrates

General procedure for the preparation of *β*-alkoxy cyclohexenones (1a – 1l).

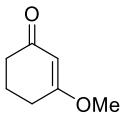


***β*-Alkoxy cyclohexenones (1a - 1h) were prepared according to the previous literature.**[2] To a solution of 1,3-cyclohexanedinones (1.0 equiv) in toluene (1.1 mmol/mL) was added the corresponding alcohols (6.7 equiv) and *p*-TSA monohydrate (0.018 equiv). The flask was equipped with a reflux condenser and placed in an oil bath. After stirring for 20 h at 110 °C, the reaction mixture was allowed to cool down to room temperature and the solvent was removed in vacuo to afford an oil. The crude products was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 4:1) to yield *β*-alkoxy cyclohexenones.



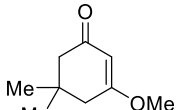
1a

3-ethoxycyclohex-2-en-1-one (1a): Orange oil. 97% yield (12.1 g). R_f = 0.40 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.33 (s, 1H), 3.88 (q, J = 7.1 Hz, 2H), 2.38 (t, J = 6.3 Hz, 2H), 2.32 (t, J = 6.5 Hz, 2H), 1.99 – 1.93 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.0, 178.1, 102.8, 64.3, 36.9, 29.2, 21.4, 14.2. The physical data and spectra is identical to those previously reported.[2]



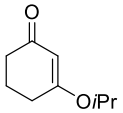
1b

3-methoxycyclohex-2-en-1-one (1b): Orange oil. 85% yield (428 mg). R_f = 0.35 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.34 (s, 1H), 3.66 (s, 3H), 2.38 (t, J = 6.3 Hz, 2H), 2.32 (dd, J = 7.2, 6.0 Hz, 2H), 1.98 – 1.93 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.9, 178.8, 102.4, 55.7, 36.8, 28.9, 21.3. **IR** (KBr, cm^{-1}): 2960, 2931, 1644, 1603, 1376, 1221, 1135, 1005, 853. **HR-ESI-MS** (m/z): calculated for $C_7H_{11}O_2$ $[M+H]^+$: 127.0754, found: 127.0753. The physical data and spectra is identical to those previously reported.[3]



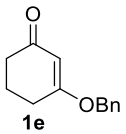
1c

3-methoxy-2,5,5-trimethylcyclohex-2-en-1-one (1c): Colorless oil. 85% yield (521 mg). R_f = 0.45 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.36 (s, 1H), 3.69 (s, 3H), 2.27 (s, 2H), 2.21 (s, 2H), 1.06 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.7, 177.1, 101.3, 55.8, 50.9, 42.8, 32.7, 28.4. **IR** (KBr, cm^{-1}): 2961, 2872, 1643, 1612, 1468, 1373, 1225, 1155, 1016, 824. **HR-ESI-MS** (m/z): calculated for $C_9H_{15}O_2$ $[M+H]^+$: 155.1067, found: 155.1062. The physical data and spectra is identical to those previously reported.[3]



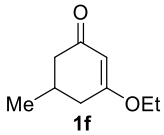
1d

3-isopropoxycyclohex-2-en-1-one (1d): Orange oil. 81% yield (499 mg). R_f = 0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.33 (s, 1H), 4.44 – 4.40 (m, 1H), 2.37 – 2.32 (m, 4H), 1.98 – 1.93 (m, 2H), 1.28 (d, J = 6.2 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.1, 177.0, 103.1, 71.0, 36.8, 29.7, 21.6, 21.3. **IR** (KBr, cm^{-1})**:** 2980, 2945, 1730, 1649, 1599, 1379, 1325, 1220, 1184, 1136, 1107, 941, 827. **HR-ESI-MS** (m/z): calculated for $C_9H_{15}O_2$ $[M+H]^+$: 155.1067, found: 155.1070. The physical data and spectra is identical to those previously reported.[3]



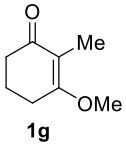
1e

3-(benzyloxy)cyclohex-2-en-1-one (1e): White amorphous powder. 74% yield (598 mg). R_f = 0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 5H), 5.48 (s, 1H), 4.89 (s, 2H), 2.47 (t, J = 6.3 Hz, 2H), 2.40 – 2.32 (m, 2H), 2.03 – 1.99 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.0, 177.7, 135.1, 128.9, 128.7, 128.0, 103.5, 70.6, 36.9, 29.2, 21.4. **IR** (KBr, cm^{-1}): 1643, 1632, 1452, 1179, 1051, 741. **HR-ESI-MS** (m/z): calculated for $C_{13}H_{15}O_2$ $[M+H]^+$: 203.1067, found: 203.1068. The physical data and spectra is identical to those previously reported.[3]



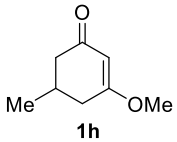
1f

3-ethoxy-5-methylcyclohex-2-en-1-one (1f): Orange oil. 81% yield (499 mg). R_f = 0.50 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.32 (s, 1H), 3.92 – 3.83 (m, 2H), 2.42 – 2.40 (m, 1H), 2.39 – 2.37 (m, 1H), 2.25 – 2.17 (m, 1H), 2.16 – 2.10 (m, 1H), 2.04 – 1.99 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.06 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.0, 177.5, 102.4, 64.4, 45.2, 37.4, 29.0, 21.0, 14.2. **IR** (KBr, cm^{-1}): 2981, 2954, 1651, 1602, 1379, 1213, 1138, 1029, 812. **HR-ESI-MS** (m/z): calculated for $C_9H_{15}O_2$ $[M+H]^+$: 155.1067, found: 155.1061. The physical data and spectra is identical to those previously reported.[4]



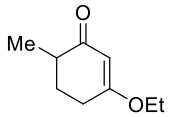
1g

3-methoxy-2-methylcyclohex-2-en-1-one (1g): Orange oil. 76% yield (426 mg). R_f = 0.50 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.79 (s, 3H), 2.54 (td, J = 6.2, 1.6 Hz, 2H), 2.33 – 2.30 (m, 2H), 1.98 – 1.94 (m, 2H), 1.66 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.0, 172.0, 114.9, 55.3, 36.3, 24.9, 20.9, 7.4. **IR** (KBr, cm^{-1}): 2951, 1730, 1713, 1612, 1381, 1359, 1246, 867. **HR-ESI-MS** (m/z): calculated for $C_8H_{13}O_2$ $[M+H]^+$: 141.0910, found: 141.0920. The physical data and spectra is identical to those previously reported.[5]



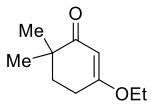
1h

3-methoxy-5-methylcyclohex-2-en-1-one (1h): Orange oil. 79% yield (442 mg). R_f = 0.55 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.34 (d, J = 1.0 Hz,1H), 3.67 (s, 3H), 2.42 – 2.40 (m, 1H), 2.39 – 2.37 (m, 1H), 2.25 – 2.17 (m, 1H), 2.16 – 2.10 (m, 1H), 2.05 – 1.99 (m, 1H), 1.06 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.9, 178.2, 102.0, 55.8, 45.2, 37.1, 29.0, 21.0. **IR** (KBr, cm^{-1}): 2963, 2933, 1649, 1606, 1379, 1220, 1138, 1006, 856. **HR-ESI-MS** (m/z): calculated for $C_8H_{13}O_2$ $[M+H]^+$: 141.0910, found: 141.0919. The physical data and spectra is identical to those previously reported.[6]



1i

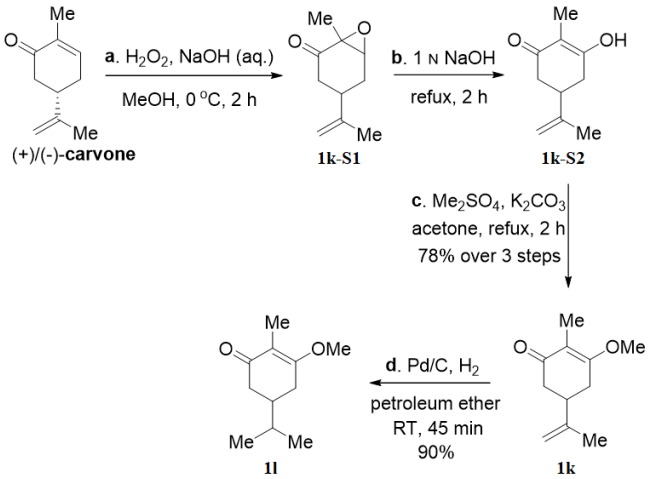
3-ethoxy-6-methylcyclohex-2-en-1-one (1i): Methylation of 3-ethoxycyclohex-2-en-1-one was carried out according to the previous literature.[2] To a solution of 3-ethoxycyclohex-2-en-1-one (575 mg, 4.11 mmol, 1.0 equiv) in THF (10 mL) was added lithium diisopropylamide (2.67 mL (2 N in THF), 5.34 mmol, 1.3 equiv) at -78 °C. After stirring for 0.5 h at -78 °C, methyl iodide (0.56 mL, 9.04 mmol, 2.2 equiv) was added dropwise. The reaction was allowed to warm up to room temperature and stirring for 21 h. The reaction was quenched with water (2 mL), diluted with 15 mL water, and the aqueous phase was extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 10:1) to give the methyl vinilogous ester. Orange oil. 74% yield (470 mg). R_f = 0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.30 (d, J = 1.2 Hz, 1H), 3.91 – 3.84 (m, 2H), 2.50 – 2.34 (m, 2H), 2.32 – 2.23 (m, 1H), 2.07 – 2.00 (m, 1H), 1.73 – 1.63 (m, 1H), 1.34 (t, J = 7.0 Hz, 3H), 1.14 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.1, 177.0, 102.2, 64.3, 40.3, 29.4, 28.6, 15.5, 14.3. The physical data and spectra is identical to those previously reported.[2]



1j

3-ethoxy-6,6-dimethylcyclohex-2-en-1-one (1j): Colorless oil. Prepared from the methylation of **1i** according to the previous literature (228 mg, 85% yield).[7] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.24 (s, 1H), 3.88 (q, J = 7.0 Hz, 2H), 2.42 (t, J = 6.4 Hz, 2H), 1.79 (t, J = 6.4 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H), 1.11 (s, 6H). The physical data and spectra is identical to those previously reported.[7]

Procedure for preparation of *β*-alkoxy cyclohexenones 1k and 1l from carvone.



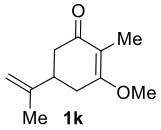
To a solution of (+)/(-)-carvone (2.0 g, 13.33 mmol, 1.0 equiv) in MeOH (25 mL) was added 30% H_2O_2 (3.0 mL, 26.66 mmol, 2.0 equiv) and 6 N NaOH (3 mL) dropwise at 0 °C. After stirring for 2 h, the reaction solution was diluted with water, extracted with EtOAc (30 mL × 3). The

combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated to give a crude residue containing **1k-S1** which was used in the next step (step **b**) without further purification.

The aforementioned crude **1k-S1** was suspended in 1N NaOH (30 mL), and heated to refux for 2 h. The reaction was quenched with 4 N HCl dropwise and adjusted to pH 2-3. The resulting aqueous solution was extracted with EtOAc (20 mL × 5). The combined organic layer were washed with brine, dried with Na_2SO_4, filtered and concentrated to give a crude residue containing **1k-S2** (racemic mixture) which was used in the next step (step **c**) without further purification.[3]

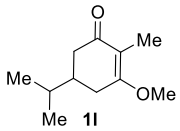
To a solution of the aforementioned crude **1k-S2** in acetone was added K_2CO_3 (3.68 g, 26.66 mmol, 2.0 equiv) and Me_2SO_4 (2.53 mL, 26.66 mmol, 2.0 equiv) sequentially. The resulting reaction mixture was heated to refux for 2 h. The mixture was filtered to remove the solid, diluted with water (20 mL), extracted with EtOAc (30 mL × 3). The combined organic layer was dried with Na_2SO_4, filtered and concentrated. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 8:1) to afford the product **1k**.

To a solution of **1k** (0.5 g, 2.78 mmol) in petroleum ether (20 mL) was added Pd/C (10% Pd on activated carbon, 50 mg). The resulting reaction mixture was connected to a H_2 balloon and stirred at 0 °C for 5 h. The mixture was passed through a pad of Celite®, washed with ethyl acetate (10 mL × 3). The combined organic layer was concentrated, and the residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 8:1) to afford the product **1l**.



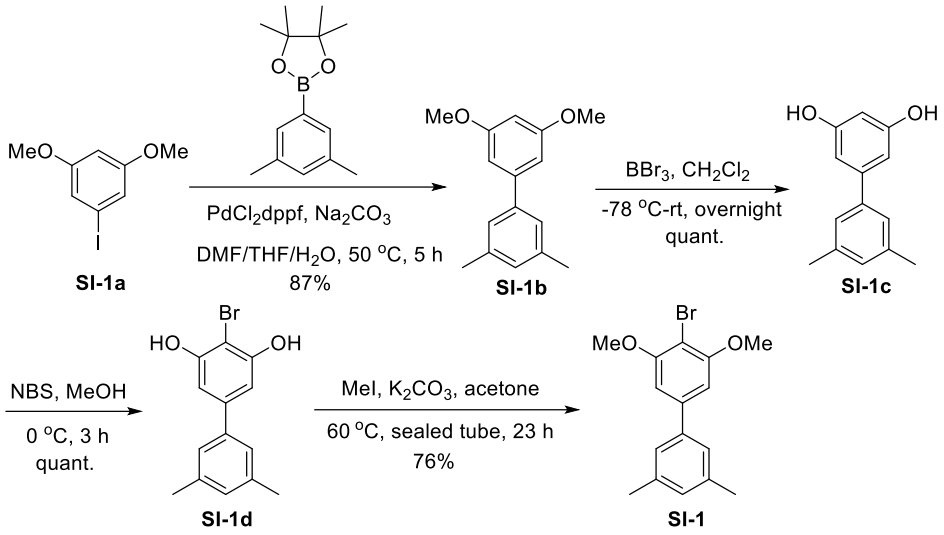
1k

3-methoxy-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one (1k): White amorphous powder. 78% yield (3 steps, 1.87 g). R_f = 0.45 (petroleum ether/EtOAc = 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.84 (s, 1H), 4.80 (s, 1H), 3.83 (s, 3H), 2.72 - 2.64 (m, 2H), 2.53 – 2.49 (m, 1H), 2.44 – 2.38 (m, 1H), 2.29 – 2.24 (m, 1H), 1.77 (s, 3H), 1.68 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.5, 171.2, 146.3, 114.6, 111.1, 55.4, 41.5, 40.4, 30.0, 20.6, 7.5. **IR** (KBr, cm^{-1}): 2932, 1713, 1643, 1612, 1454, 1383, 1233, 1123, 1047, 895. **HR-ESI-MS** (m/z): calculated for $C_{11}H_{17}O_2$ $[M+H]^+$: 181.1223, found: 181.1226.



1l

5-isopropyl-3-methoxy-2-methylcyclohex-2-en-1-one (1l): White amorphous powder. 90% yield (0.45 g). R_f = 0.45 (petroleum ether/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 2.62 (dd, J = 17.1, 4.5 Hz, 1H), 2.45 (dd, J = 16.0, 2.9 Hz, 1H), 2.25 – 2.13 (m, 1H), 2.02 (dd, J = 15.9, 13.5 Hz, 1H), 1.88 – 1.74 (m, 1H), 1.66 (s, 3H), 1.64 – 1.55 (m, 1H), 0.94 (d, J = 6.9 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.3, 171.8, 114.5, 55.2, 40.2, 39.7, 32.1, 28.8, 19.8, 19.5, 7.4. **IR** (KBr, cm^{-1}): 2936, 1715, 1648, 1611, 1375, 1230, 1125, 1047, 815. **HR-ESI-MS** (m/z): calculated for $C_{11}H_{19}O_2$ $[M+H]^+$: 183.1380, found: 183.1379.



Preparation of 4-bromo-3,5-dimethoxy-3',5'-dimethyl-1,1'-biphenyl (SI-1).

A mixture of 1-iodo-3,5-dimethoxybenzene **SI-1a (SI-1a** was prepared according to the previous literature[8]**)** (792 mg, 3 mmol, 1.0 equiv), pinacol borate (684 mg, 3 mol, 1.0 equiv), Na_2CO_3(760 mg, 7.17 mmol, 2.39 equiv), and $PdCl_2$dppf (66 mg, 0.09 mmol, 0.03 equiv) in degassed DMF/THF/H_2O (1:1:1, v/v) (27 mL) was heated at 50 °C for 6 h under an argon atmosphere. The product formed was extracted with EtOAc (20 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 100:1) to afford coupling product **SI-1b** in 87% yield (630 mg), which was used directly in the next step without characterization of the product **SI-1b**.[9]

To a solution of **SI-1b** (484 mg, 2 mmol, 1 equiv) in CH_2Cl_2 was added $BF_3{\cdot}Et_2O$ (1 N in CH_2Cl_2) (6 mL, 6 mmol, 3.0 equiv) at -78 °C, and then The reaction was allowed to warm to room temperature and stirred for overnight. The reaction was quenched with ice water (3 mL) at 0 °C. The mixture was diluted with water and extracted with EtOAc (20 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 3:1) to afford the product **SI-1c** in quantitative yield (428 mg), which was used directly in the next step without characterization of the product.

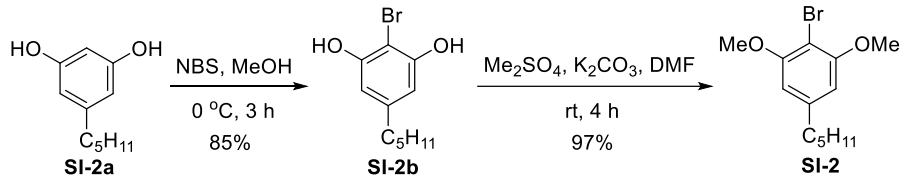
To a solution of **SI-1c** (428 mg, 2 mmol, 1 equiv) in methanol (25 mL) at 0 °C was added NBS (534 mg, 6 mmol, 3.0 equiv). After stirring for 3 h at 0 °C, a solution of Na_2SO_3 (252 mg, 6 mmol, 2.0 equiv) and NaOH (240 mg, 6 mmol, 2.0 equiv) in water (12 mL) was added, and it was reacted for 1h. 1 N HCl was added to tune the pH to 1.0. The crude mixture was extracted with EtOAc (20 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 10:1) to afford **SI-1d** in quantitative yield (586 mg), which was used directly in the next step without characterization of the product.[10]

To a solution of **SI-1d** (270 mg, 0.92 mmol, 1.0 equiv) in acetone (20 mL) in a sealed tube was added MeI (0.12 mL, 284 mg, 2 mmol, 2.2 equiv) and K_2CO_3 (ground powder, 317 mg, 2.3 mmol, 2.5 equiv). After stirring for 23 h at 60 °C, the unsolved solid was filtered through a pad of celite, washed with EtOAc (50 mL). The organic solution was washed with water (20 mL) and brine (20 mL) The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The

residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 100:1) to afford product **SI-1**.

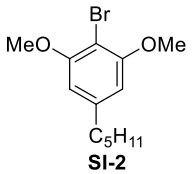
4-bromo-3,5-dimethoxy-3',5'-dimethyl-1,1'-biphenyl (SI-1): Colorless oil. 76% yield (224 mg). R_f = 0.55 (petroleum ether/EtOAc = 20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (s, 2H), 7.04 (s, 1H), 6.74 (s, 2H), 3.97 (s, 6H), 2.40 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.2, 142.4, 141.1, 138.6, 129.6, 125.1, 104.0, 100.0, 56.7, 21.5. **IR** (KBr, cm^{-1}): 2943, 1580, 1454, 1360, 1121, 831. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{18}O_2Br$ $[M+H]^+$: 321.0485, found: 321.0488.

Preparation of 2-bromo-1,3-dimethoxy-5-pentylbenzene (SI-2).



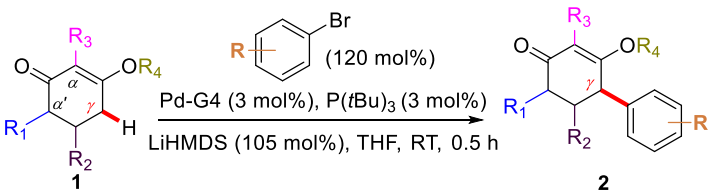
To a solution of 5-alkylbenzene-1,3-diol **SI-2a** (5.56 mmol, 1.0 equiv) in methanol (25 mL) at 0 °C was added NBS (16.68 mmol, 3.0 equiv).After stirring for 3 h at 0 °C, a solution of Na_2SO_3 (11.12 mmol, 2.0 equiv) and NaOH (0.44 g, 11.12 mmol, 2.0 equiv) in water (25 mL) was added, and it was reacted for 1h. 1 N HCl was added to tune the pH to 1.0. The crude mixture was extracted with EtOAc (20 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 6:1) to afford 2-bromo-5-alkylbenzene-1,3-diol (**SI-2b**), which was used directly in the next step without characterization of the product.

To a solution of **SI-2b** (4.71 mmol, 1.0 equiv) in DMF (10 mL) was added MeI (11.78 mmol, 2.5 equiv) and K_2CO_3 (ground powder, 14.13 mmol, 3.0 equiv). After stirring for 4 h at room temperature, the unsolved solid was dissolved with water (10 mL) and washed with EtOAc (50 mL). The organic solution was washed with water (20 mL) and brine (20 mL × 5) The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 60:1) to afford 2-bromo-1,3-dimethoxy-5-alkylbenzene **SI-2** as a colorless oil.



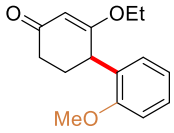
2-bromo-1,3-dimethoxy-5-pentylbenzene (SI-2): Colorless oil. 78% yield (2 steps, 1.35 g). R_f = 0.70 (petroleum ether/EtOAc = 15:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.40 (s, 2H), 3.88 (s, 6H), 2.57 (t, J = 7.8 Hz, 2H), 1.64 – 1.60 (m, 2H), 1.38-1.29 (m, 5H), 0.90 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.9, 144.0, 105.0, 97.8, 56.5, 36.6, 31.6, 31.3, 22.7, 14.2. **IR** (KBr, cm^{-1}): 2930, 2857, 1649, 1607, 1379, 1220, 1138, 1007, 856. **HR-ESI-MS** (m/z): calculated for $C_{13}H_{20}O_2Br$ $[M+H]^+$: 287.0641, found: 287.0643.

4. General Procedure for Pd-Catalyzed γ-Arylation of β-Alkoxy Cyclohexenones



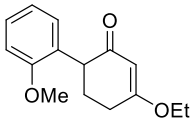
LiHMDS (1.05 mmol, 1.05 mL, 1.0 M in THF, 1.05 equiv) was added dropwise at 0 °C to a solution of **1** (1.0 mmol, 1.0 equiv) in degassed THF (1.5 mL) in flame-dried two-necked flask (1#), which have been evacuated and refilled with argon. The resulting solution was stirring for 45 min at 0 °C. In the meantime, Pd-G4 catalyst (0.03 mmol, 0.03 equiv) was loaded in a two-necked flask (2#), and then evacuated and refilled with argon for three to five times. To this flask (2#), P(*t*Bu)$_3$ (0.03 mmol, 0.03 equiv) in THF (0.75 mL) were added sequentially. After the Pd catalyst system solution was stirring for 10 ~ 15 min at room temperature, the corresponding bromobenzene (1.2 mmol, 1.2 equiv) was added to flask (2#) and stirred for additional 10 ~ 15 min. The cold enolate solution in flask (1#) was added dropwise into the flask (2#) by syringe at room temperature, and the resulting solution was immediately turned to deep red. After stirring for 0.5 h at room temperature, the reaction was quenched with water (1 mL). The resulting mixture was diluted with water (10 mL), extracted with EtOAc (15 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography to afford the desired product **2**.

5. Characterization of γ-Arylated Products and the Byproducts



2a

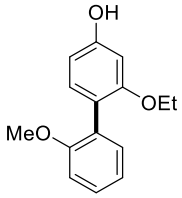
6-ethoxy-2'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2a): Colorless, viscous oil. 70% yield (172 mg). R_f = 0.38 (petroleum ether/EtOAc/DCM = 4:1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 1H), 7.02 (dd, J = 7.5, 1.7 Hz, 1H), 6.91 – 6.87 (m, 2H), 5.60 (s, 1H), 4.14 – 4.12 (m, 1H), 3.99 – 3.94 (m, 1H), 3.92 – 3.87 (m, 1H), 3.85 (s, 3H), 2.28 – 2.21 (m, 3H), 2.09-2.05 (m, 1H), 1.26 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.6, 178.3, 157.2, 128.3, 127.9, 127.6, 120.4, 110.8, 104.9, 64.5, 55.4, 39.1, 33.8, 27.8, 14.1. **IR** (KBr, cm^{-1}): 2980, 2941, 2835, 1658, 1604, 1492, 1379, 1244, 1188, 1109, 1028, 910, 814, 752. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found: 247.1333.



2a′

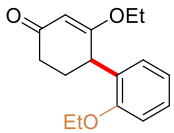
4-ethoxy-2'-methoxy-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one (2a′): (prepared following the procedure of **Table S1**, entry 11) Colorless, viscous oil. 31% yield (76 mg). R_f = 0.40 (petroleum ether/EtOAc/DCM = 4:1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (td, J = 7.8, 1.7 Hz, 1H), 7.06

(dd, J = 7.5, 1.7 Hz, 1H), 6.92 – 6.88 (m, 2H), 5.50 (s, 1H), 3.99-3.89 (m, 2H), 3.81 (dd, J = 11.1, 4.9 Hz, 1H), 3.79 (s, 3H), 2.60-2.53 (m, 1H), 2.41 (dt, J = 17.4, 4.6 Hz, 1H), 2.33-2.25 (m, 1H), 2.14 – 2.08 (m, 1H), 2.00-1.99 (m, 1H), 1.39 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.7, 177.3, 157.3, 129.5, 129.0, 128.2, 120.8, 111.1, 103.3, 64.4, 55.6, 47.4, 29.0, 28.1, 14.3. **IR** (KBr, cm^{-1}): 2940, 1614, 1495, 1379, 1244, 1188, 1109, 910, 814, 754. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found: 247.1325.



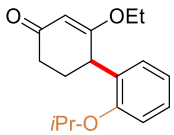
2a″

2-ethoxy-2'-methoxy-[1,1'-biphenyl]-4-ol (2a″): Colorless, viscous oil. 6% yield (14 mg) from **Table 1**, entry 11 or 57% yield from the Pd-catalyzed aromatization of **2a**, see **scheme S1**. R_f = 0.45 (petroleum ether/EtOAc/DCM = 4:1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 7.23 (dd, J = 7.5, 1.8 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 6.98 (td, J = 7.4, 1.1 Hz, 1H), 6.94 (dd, J = 8.2, 1.2 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 6.45 (dd, J = 8.1, 2.4 Hz, 1H), 4.85 (br s, 1H), 3.98 (q, J = 6.9 Hz, 2H), 3.77 (s, 3H), 1.27 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.6, 157.2, 156.1, 132.1, 131.8, 128.3, 127.7, 120.8, 120.3, 110.8, 106.9, 100.5, 64.0, 55.6, 14.8. **IR** (KBr, cm^{-1}): 2980, 2930, 1591, 1485, 1445, 1236, 1177, 1115, 758. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{15}O_3$ $[M-H]^-$: 243.1027, found: 243.1036.



2b

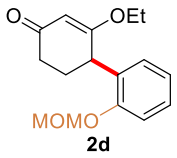
2',6-diethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2b): Colorless, viscous oil. 56% yield (146 mg). R_f = 0.30 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (td, J = 7.8, 1.7 Hz, 1H), 7.02 (dd, J = 7.6, 1.7 Hz, 1H), 6.89 – 6.86 (m, 2H), 5.60 (s, 1H), 4.13 (m, 1H), 4.06 (q, J = 7.0 Hz, 2H), 3.99-3.94 (m, 1H), 3.92– 3.87 (m, 1H), 2.28 – 2.21 (m, 3H), 2.13-2.09 (m, 1H), 1.42 (t, J = 7.0 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.7, 178.5, 156.6, 128.2, 128.0, 127.7, 120.2, 111.5, 104.8, 64.5, 63.6, 39.4, 33.9, 27.7, 15.0, 14.1. **IR** (KBr, cm^{-1}): 2980, 1659, 1601, 1452, 1248, 1223, 1043, 752. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485, found: 261.1487.



2c

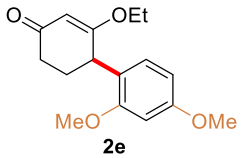
6-ethoxy-2'-isopropoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2c): Colorless, viscous oil. 51% yield (140 mg). R_f = 0.55 (petroleum ether/EtOAc/DCM = 3:1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 (td, J = 7.8, 1.7 Hz, 1H), 7.02 (dd, J = 7.5, 1.7 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 6.84 (td, J = 7.4, 1.1 Hz, 1H), 5.59 (s, 1H), 4.60 (hept, J = 6.1 Hz, 1H), 4.10 (t, J = 5.0 Hz, 1H), 3.98 – 3.92 (m,

1H), 3.91 – 3.88 (m, 1H), 2.31 – 2.19 (m, 3H), 2.13 – 2.07 (m, 1H), 1.35 – 1.33 (m, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.7, 178.6, 155.4, 128.4, 128.2, 128.1, 119.9, 112.6, 104.6, 69.8, 64.4, 39.5, 34.0, 27.7, 22.3, 22.2, 14.1. **IR** (KBr, cm^{-1}): 2978, 2934, 1651, 1605, 1487, 1452, 1375, 1288, 1242, 1219, 1182, 1163, 1117, 1032, 957, 843, 754. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{23}O_3$ $[M+H]^+$: 275.1642, found: 275.1639.



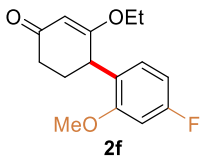
2d

6-ethoxy-2'-(methoxymethoxy)-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2d): Colorless, viscous oil. 53% yield (146 mg). R_f = 0.45 (DCM/acetone = 30:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 1H), 7.14 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.04 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.94 (td, *J* = 7.5, 1.2 Hz, 1H), 5.60 (s, 1H), 5.23 (dd, *J* = 6.6 Hz, 6.6 Hz, 2H), 4.16 – 4.14 (m, 1H), 3.99 – 3.93 (m, 1H), 3.92 – 3.87 (m, 1H), 3.49 (s, 3H), 2.32 – 2.24 (m, 3H), 2.11 – 2.07 (m, 1H), 1.26 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.4, 178.1, 155.0, 128.3, 128.1, 121.6, 114.3, 104.8, 94.5, 64.5, 56.3, 39.3, 33.9, 29.8, 28.0, 14.1. **IR** (KBr, cm^{-1}): 2982, 2951, 1657, 1601, 1491, 1452, 1375, 1346, 1220, 1153, 1078, 995, 922, 756. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1440.



2e

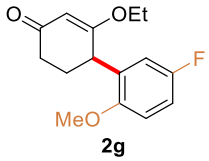
6-ethoxy-2',4'-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2e): Colorless, viscous oil. 72% yield (198 mg). R_f = 0.65 (DCM/acetone = 10:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.91 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.40 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.58 (s, 1H), 4.03 (t, *J* = 4.8 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.91 – 3.86 (m, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.30 – 2.17 (m, 3H), 2.05 – 3.01 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.7, 178.5, 160.0, 158.2, 128.3, 120.0, 104.8, 103.7, 99.0, 64.5, 55.48, 55.45, 38.6, 33.8, 28.0, 14.1. **IR** (KBr, cm^{-1}): 2994, 2932, 2882, 1657, 1599, 1503, 1445, 1373, 1260, 1159, 1115, 1047, 1026, 922, 837, 790. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1442.



2f

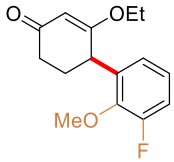
6-ethoxy-4'-fluoro-2'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2f): Colorless, viscous oil. 52% yield (138 mg). R_f = 0.45 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 8.4, 6.6 Hz, 1H), 6.63 (dd, *J* = 10.8, 2.5 Hz, 1H), 6.58 (td, *J* = 8.3, 2.4 Hz, 1H), 5.58 (s, 1H), 4.06 – 4.04 (t, *J* = 4.8 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.91 – 3.86 (m, 1H), 3.83 (s, 3H), 2.28 – 2.18 (m, 3H), 2.05 – 2.01 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.3, 177.9, 162.8 (d, $J_{C\text{-}F}$ = 245 Hz), 158.3 (d, $J_{C\text{-}F}$ = 9.0 Hz), 128.5, (d, $J_{C\text{-}F}$ = 10.5 Hz) 123.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 106.5 (d, $J_{C\text{-}F}$ = 21.0 Hz), 104.9, 99.4 (d, $J_{C\text{-}F}$ = 25.5 Hz), 64.5, 55.7, 38.7, 33.8,

27.8, 14.1; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.9. **IR** (KBr, cm^{-1}): 2940, 1661, 1603, 1503, 1416, 1279, 1223, 1159, 1103, 1032, 951, 843, 795. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{18}O_3F$ $[M+H]^+$: 265.1234, found: 265.1240.



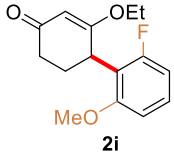
2g

6-ethoxy-5'-fluoro-2'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2g): Colorless, viscous oil. 52% yield (138 mg). R_f = 0.55 (petroleum ether/EtOAc/DCM = 4:1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.95 – 6.91 (m, 1H), 6.82 (dd, J = 8.9, 4.4 Hz, 1H), 6.75 (dd, J = 9.1, 3.1 Hz, 1H), 5.60 (s, 1H), 4.10 (t, J = 4.7 Hz, 1H), 3.99 – 3.88 (m, 2H), 3.83 (s, 3H), 2.28 – 2.21 (m, 3H), 2.08 – 2.04 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.1, 177.4, 156.9 (d, $J_{C\text{-}F}$ = 236 Hz), 153.4 (d, $J_{C\text{-}F}$ = 1.5 Hz), 129.5 (d, $J_{C\text{-}F}$ = 6.0 Hz), 115.0 (d, $J_{C\text{-}F}$ = 24.0 Hz), 114.0 (d, $J_{C\text{-}F}$ = 22.5 Hz), 111.5 (d, $J_{C\text{-}F}$ = 7.5 Hz), 105.0, 64.6, 56.0, 39.1, 33.8, 27.7, 14.1; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -123.8. **IR** (KBr, cm^{-1}): 2986, 2891, 1667, 1605, 1495, 1373, 1250, 1223, 1153, 1028,974, 939, 854, 812, 714. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{18}O_3F$ $[M+H]^+$: 265.1234, found: 265.1237.



2h

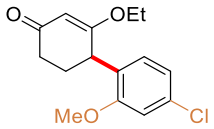
6-ethoxy-3'-fluoro-2'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2h): Colorless, viscous oil. 53% yield (140 mg). R_f = 0.55 (DCM/acetone = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.02 – 6.99 (m, 1H), 6.95 – 6.92 (m, 1H), 6.82 (dt, J = 7.7, 1.3 Hz, 1H), 5.57 (s, 1H), 4.11 (t, J = 5.5 Hz, 1H), 3.96 (d, J = 1.8 Hz, 3H), 3.95 – 3.85 (m, 2H), 2.34 – 2.30 (m, 2H), 2.29 – 2.23 (m, 1H), 2.06 – 2.01 (m, 1H), 1.24 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.9, 177.5, 155.7 (d, $J_{C\text{-}F}$ = 246 Hz), 145.7(d, $J_{C\text{-}F}$ = 10.5 Hz), 134.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 123.31 (d, $J_{C\text{-}F}$ = 3.0 Hz), 123.26 (d, $J_{C\text{-}F}$ = 7.5 Hz), 116.0 (d, $J_{C\text{-}F}$ = 19.5 Hz), 104.6, 64.6, 61.4 (d, $J_{C\text{-}F}$ = 7.5 Hz), 39.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 34.2, 28.7, 14.1; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -129.8. IR (KBr, cm^{-1}): 2986, 2947, 2837, 1643, 1605, 1485, 1346, 1275, 1221, 1072, 1026, 1003, 937, 821, 789, 750. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{18}O_3F$ $[M+H]^+$: 265.1234, found: 265.1240.



2i

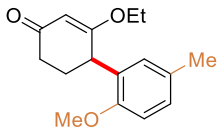
6-ethoxy-2'-fluoro-6'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2i): Colorless, viscous oil. 48% yield (126 mg). R_f = 0.40 (petroleum ether/acetone = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.20 – 7.16 (m, 1H), 6.67 (t, J = 8.2 Hz, 2H), 5.45 (s, 1H), 4.31 – 4.28 (m, 1H), 3.92 – 3.86 (m, 2H), 3.80 (s, 3H), 2.52 – 2.42 (m, 2H), 2.28 – 2.26 (m, 1H), 2.09 – 2.04 (m, 1H), 1.18 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.8, 178.7, 161.6 (d, $J_{C\text{-}F}$ = 243 Hz), 158.5 (d, $J_{C\text{-}F}$ =

7.5 Hz), 128.4 (d, $J_{C\text{-}F}$ = 10.5 Hz), 116.8 (d, $J_{C\text{-}F}$ = 15.0 Hz), 108.2 (d, $J_{C\text{-}F}$ = 22.5 Hz), 106.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 102.6, 64.5, 56.0, 37.0, 35.8, 27.9, 14.0; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.7，-117.6. **IR** (KBr, cm^{-1}): 2980, 2849, 1649, 1593, 1472, 1371, 1273, 1205, 1082, 988, 783. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{18}O_3F$ $[M+H]^+$: 265.1234, found: 265.1238.



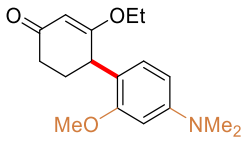
2j

4'-chloro-6-ethoxy-2'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2j): Colorless, viscous oil. 62% yield (174 mg). R_f = 0.60 (DCM/acetone = 30:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.20 (dd, J = 8.7, 2.6 Hz, 1H), 6.97 (d, J = 2.6 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 5.59 (s, 1H), 4.07 (t, J = 5.0 Hz, 1H), 3.98 – 3.88 (m, 2H), 3.83 (s, 3H), 2.28 – 2.19 (m, 3H), 2.07 – 2.02 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.1, 177.3, 155.9, 129.6, 128.0, 127.9, 125.5, 111.9, 105.0, 64.6, 55.8, 39.1, 33.8, 27.6, 14.1. **IR** (KBr, cm^{-1}): 2940, 1651, 1597, 1236, 1184, 1022, 833. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{18}ClO_3Cl$ $[M+H]^+$: 281.0939, found: 281.0944.



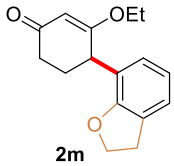
2k

6-ethoxy-2'-methoxy-5'-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2k): Colorless, viscous oil. 62% yield (162 mg). R_f = 0.50 (DCM/acetone = 30:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.03 (dd, J = 8.3, 2.1 Hz, 1H), 6.81 – 6.79 (m, 2H), 5.60 (s, 1H), 4.09 (t, J = 4.8 Hz, 1H), 3.99 – 3.88 (m, 2H), 3.81 (s, 3H), 2.31 – 2.19 (m, 6H), 2.08 – 2.02 (m, 1H), 1.26 (t, J = 7.1 Hz, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.7, 178.4, 155.1, 129.5, 128.55, 128.47, 127.4, 110.7, 104.8, 64.4, 55.5, 39.1, 33.8, 27.9, 20.7, 14.1. **IR** (KBr, cm^{-1}): 3055, 2839, 1649, 1601, 1495, 1454, 1373, 1233, 1109, 1030, 880, 804, 770, 714. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485, found: 261.1488.



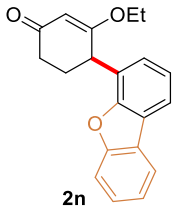
2l

4'-(dimethylamino)-6-ethoxy-2'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2l): Colorless, viscous oil. 51% yield (147 mg). R_f = 0.40 (petroleum ether /acetone = 30:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.86 (d, J = 8.4 Hz, 1H), 6.29 (d, J = 2.6 Hz, 1H), 6.23 (dd, J = 8.4, 2.5 Hz, 1H), 5.57 (s, 1H), 4.02 (t, J = 4.6 Hz, 1H), 3.98 – 3.86 (m, 2H), 3.84 (s, 3H), 2.95 (s, 6H), 2.33 – 2.28 (m, 1H), 2.24 – 2.16 (m, 2H), 2.04 – 2.00 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.9, 179.0, 158.0, 151.1, 128.2, 115.5, 104.6, 104.1, 96.3, 64.3, 55.2, 40.8, 38.3, 33.7, 28.1, 14.1. **IR** (KBr, cm^{-1}): 2949, 2803, 1649, 1603, 1516, 1445, 1358, 1240, 1111, 1031, 980, 816. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{24}O_3N$ $[M+H]^+$: 290.1751, found: 290.1757.



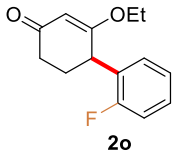
2m

4-(2,3-dihydrobenzofuran-7-yl)-3-ethoxycyclohex-2-en-1-one (2m): Colorless, viscous oil. 61% yield (157 mg). R_f = 0.45 (DCM/acetone = 30:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, J = 7.2 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.77 (t, J = 7.4 Hz, 1H), 5.58 (s, 1H), 4.58 (t, J = 8.8 Hz, 2H), 3.99 – 3.87 (m, 3H), 3.23 (t, J = 8.7 Hz, 2H), 2.31 – 2.21 (m, 3H), 2.14 – 2.09 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.2, 177.4, 158.1, 127.2, 126.2, 123.8, 121.4, 120.4, 104.7, 71.2, 64.5, 39.4, 33.8, 30.1, 27.8, 14.1. **IR** (KBr, cm^{-1}): 2916, 2849, 2359, 2340, 1660, 1605, 1375, 1219, 1163, 1033, 934, 758. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329, found: 259.1335.



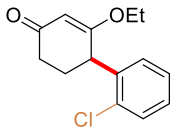
2n

4-(dibenzo[b,d]furan-4-yl)-3-ethoxycyclohex-2-en-1-one (2n): White amorphous powder. 76% yield (232 mg). R_f = 0.65 (DCM/acetone = 40:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 5.68 (s, 1H), 4.44 – 4.43 (m, 1H), 4.02 – 3.91 (m, 2H), 2.49 – 2.40 (m, 1H), 2.38 – 2.32 (m, 3H), 1.23 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.0, 176.9, 156.1, 154.4, 127.4, 125.6, 124.6, 124.4, 123.9, 123.0, 122.9, 120.9, 119.7, 111.8, 104.9, 64.7, 39.8, 34.1, 28.4, 14.1. **IR** (KBr, cm^{-1}): 2947, 2889, 1643, 1603, 1449, 1423, 1375, 1342, 1329, 1219, 1180, 1155, 1013, 935, 843, 760. **HR-ESI-MS** (m/z): calculated for $C_{20}H_{19}O_3$ $[M+H]^+$: 307.1329, found: 307.1332.



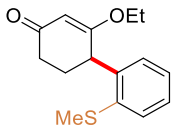
2o

6-ethoxy-2'-fluoro-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2o): Colorless, viscous oil. 40% yield (94 mg). R_f = 0.40 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 1H), 7.11 – 7.06 (m, 3H), 5.60 (s, 1H), 4.06 (t, J = 4.9 Hz, 1H), 3.98 – 3.87 (m, 2H), 2.33 – 2.30 (m, 3H), 2.12 – 2.07 (m, 1H), 1.26 (d, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.7, 176.7, 161.1 (d, $J_{C\text{-}F}$ = 245 Hz), 128.9 (d, $J_{C\text{-}F}$ =9.0 Hz), 128.8 (d, $J_{C\text{-}F}$ =4.5 Hz), 126.9 (d, $J_{C\text{-}F}$ =13.5 Hz), 124.1 (d, $J_{C\text{-}F}$ =3.0 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 104.9, 64.7, 38.8, 34.0, 28.5, 14.1; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.5. **IR** (KBr, cm^{-1}): 2936, 1659, 1605, 1491, 1454, 1375, 1346, 1217, 1109, 1032, 935, 826, 758. **HR-ESI-MS** (m/z): calculated for $C_{14}H_{16}O_2F$ $[M+H]^+$: 235.1129, found: 235.1132.



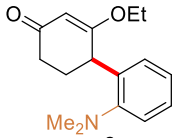
2p

2'-chloro-6-ethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2p): Colorless, viscous oil. 52% yield (130 mg). R_f = 0.45 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 1H), 7.22 – 7.20 (m, 2H), 7.13 – 7.11 (m, 1H), 5.63 (s, 1H), 4.21 (t, J = 4.9 Hz, 1H), 3.99 – 3.94 (m, 1H), 3.92 – 3.87 (m, 1H), 2.35 – 2.24 (m, 3H), 2.14 – 2.09 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.8, 176.8, 137.1, 134.3, 130.3, 128.5, 128.5, 126.9, 105.2, 64.7, 42.1, 33.5, 27.6, 14.1. **IR** (KBr, cm^{-1}): 2984, 2930, 1661, 1605, 1474, 1443, 1375, 1344, 1223, 1194, 1169, 1036, 937, 845, 750. **HR-ESI-MS** (m/z): calculated for $C_{14}H_{16}O_2Cl$ $[M+H]^+$: 251.0833, found: 251.0840.



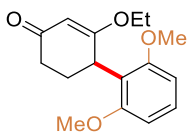
2q

6-ethoxy-2'-(methylthio)-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2q): Colorless, viscous oil. 58% yield (152 mg). R_f = 0.50 (DCM/acetone = 40:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.0, 1.4 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.11 (td, J = 7.4, 1.4 Hz, 1H), 7.06 (dd, J = 7.8, 1.7 Hz, 1H), 5.62 (s, 1H), 4.25 – 4.23 (m, 1H), 3.99 – 3.86 (m, 2H), 2.50 (s, 3H), 2.34 – 2.27 (m, 3H), 2.11 – 2.04 (m, 1H), 1.25 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.1, 177.4, 137.8, 137.6, 127.8, 127.2, 127.0, 125.3, 105.1, 64.6, 41.9, 33.6, 27.9, 16.6, 14.1. **IR** (KBr, cm^{-1}): 3062, 2922, 2864, 1659, 1605, 1469, 1435, 1375, 1346, 1227, 1188, 1166, 1028, 976, 935, 864, 748. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_2S$ $[M+H]^+$: 263.1100, found: 263.1110.



2r

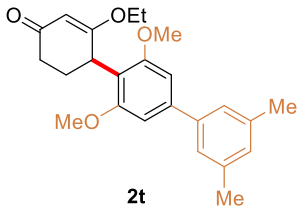
2'-(dimethylamino)-6-ethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2r): Colorless, viscous oil. 50% yield (130 mg). R_f = 0.40 (DCM/acetone = 30:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 – 7.23 (m, 2H), 7.08 – 7.03 (m, 2H), 5.59 (s, 1H), 4.48 (t, J = 5.9 Hz, 1H), 3.95 – 3.83 (m, 2H), 2.69 (s, 6H), 2.42 – 2.37 (m, 1H), 2.36 – 2.31 (m, 1H), 2.28 – 2.23 (m, 1H), 2.00 – 1.94 (m, 1H), 1.21 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.5, 179.3, 153.2, 136.4, 127.84, 127.79, 124.3, 121.1, 104.7, 64.4, 46.1, 39.2, 34.6, 29.8, 14.0. **IR** (KBr, cm^{-1}): 2984, 2783, 1667, 1601, 1487, 1452, 1346, 1217, 1163, 1032, 943, 843, 754. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{22}NO_2$ $[M+H]^+$: 260.1645, found: 260.1652.



2s

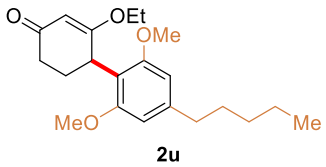
6-ethoxy-2',6'-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2s): Colorless bulk crystal

(recrystallized from petroleum ether/EtOAc), mp: 168.3 °C. 62% yield (172 mg). R_f = 0.40 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.18 (t, J = 8.3 Hz, 1H), 6.58 – 6.50 (m, 2H), 5.43 (s, 1H), 4.39 (dd, J = 11.2, 4.2 Hz, 1H), 3.92 – 3.69 (m, 8H), 2.47 – 2.45 (m, 2H), 2.34 – 2.27 (m, 1H), 1.98 – 1.93 (m, 1H), 1.16 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.6, 181.1, 158.4, 158.0, 128.1, 117.3, 104.0, 101.9, 64.2, 56.0, 55.3, 37.2, 35.9, 27.4, 14.0. **IR** (KBr, cm^{-1}): 2949, 2839, 1651, 1595, 1477, 1246, 1107, 1036, 864, 779, 731. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1438.



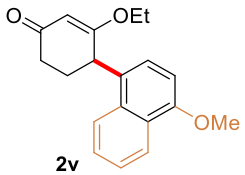
2t

6-ethoxy-2',6'-dimethoxy-3'',5''-dimethyl-2,3-dihydro-[1,1':4',1''-terphenyl]-4(1H)-one (2t): White amorphous powder. 58% yield (220 mg). R_f = 0.40 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.19 (s, 2H), 7.01 (s, 1H), 6.73 – 6.69 (m, 2H), 5.45 (s, 1H), 4.41 (dd, J = 11.2, 4.9 Hz, 1H), 3.94 – 3.77 (m, 8H), 2.49 – 2.47 (m, 2H), 2.39 (s, 6H), 2.35 – 2.28 (m, 1H), 2.01 – 1.98 (m, 1H), 1.19 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.5, 180.9, 158.5, 158.0, 141.8, 141.6, 138.4, 129.3, 127.2, 125.1, 116.2, 103.3, 103.2, 102.0, 64.3, 56.2, 55.4, 37.3, 35.9, 27.5, 21.6, 14.0. **IR** (KBr, cm^{-1}): 2972, 1641, 1591, 1456, 1217, 1113, 1045, 829. **HR-ESI-MS** (m/z): calculated for $C_{24}H_{29}O_4$ $[M+H]^+$: 381.2060, found: 381.2059.



2u

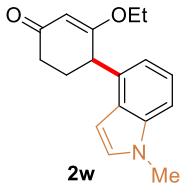
6-ethoxy-2',6'-dimethoxy-4'-pentyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2u): Colorless, viscous oil. 60% yield (208 mg). R_f = 0.40 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.36 (s, 2H), 5.41 (s, 1H), 4.35 – 4.32 (m, 1H), 3.93 – 3.66 (m, 8H), 2.59 – 2.55 (m, 2H), 2.46 – 2.43 (m, 2H), 2.33 – 2.24 (m, 1H), 1.98 – 1.92 (m, 1H), 1.66 – 1.60 (m, 2H), 1.38 – 1.32 (m, 4H), 1.17 (t, J = 7.0 Hz, 3H), 0.95 – 0.86 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.6, 181.2, 143.4, 114.5, 104.3, 102.0, 64.2, 37.3, 36.7, 35.9, 31.9, 31.2, 27.6, 22.7, 14.2, 14.0. **IR** (KBr, cm^{-1}): 2934, 2857, 1649, 1591, 1454, 1346, 1217, 1151, 1119, 1028, 985, 974, 822, 750. **HR-ESI-MS** (m/z): calculated for $C_{21}H_{31}O_4$ $[M+H]^+$: 347.2217, found: 347.2219.



2v

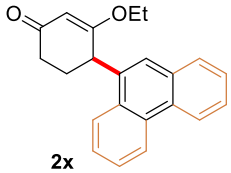
3-ethoxy-4-(4-methoxynaphthalen-1-yl)cyclohex-2-en-1-one (2v): White amorphous powder. 50% yield (148 mg). R_f = 0.60 (DCM/acetone = 40:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.35 (dd, J

= 8.5, 1.4 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.52 – 7.50 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.71 (s, 1H), 4.46 (dd, *J* = 5.5, 3.4 Hz, 1H), 4.04 – 3.98 (m, 4H), 3.96 – 3.91 (m, 1H), 2.47 – 2.40 (m, 1H), 2.32 – 2.23 (m, 2H), 2.21 – 2.17 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.4, 178.1, 155.0, 132.2, 127.0, 126.5, 126.4, 125.2, 124.5, 123.1, 122.8, 105.3, 103.0, 64.6, 55.6, 40.8, 33.4, 28.3, 14.1. **IR** (KBr, cm^{-1}): 2930, 1632, 1603, 1445, 1383, 1215, 1155, 1090, 1030, 820, 760. **HR-ESI-MS** (m/z): calculated for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1485, found: 297.1492.



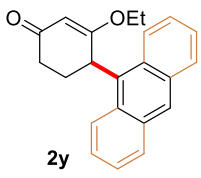
2w

3-ethoxy-4-(1-methyl-1H-indol-4-yl)cyclohex-2-en-1-one (2w): Colorless, viscous oil. 51% yield (138 mg). R_f = 0.60 (DCM/acetone = 30:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.3 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 3.1 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 3.1 Hz, 1H), 5.67 (s, 1H), 4.21 (t, *J* = 4.6 Hz, 1H), 4.02 – 3.91 (m, 2H), 3.81 (s, 3H), 2.44 – 2.31 (m, 2H), 2.28 – 2.24 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.5, 178.0, 137.0, 131.5, 128.9, 127.4, 121.5, 117.5, 108.5, 104.7, 98.8, 64.6, 42.7, 33.8, 33.2, 28.6, 14.1. **IR** (KBr, cm^{-1}): 3094, 2980, 2876, 1651, 1601, 1447, 1377, 1341, 1217, 1180, 1150, 1030, 847, 818, 743. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1489, found: 270.1491.



2x

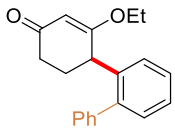
3-ethoxy-4-(phenanthren-9-yl)cyclohex-2-en-1-one (2x): White amorphous powder. 47% yield (148 mg). R_f = 0.70 (DCM/acetone = 40:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.79 – 8.78 (m, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.11 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.81 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.71 – 7.64 (m, 3H), 7.61 - 7.59 (m, 1H), 7.52 (s, 1H), 5.81 (s, 1H), 4.58 – 4.57 (m, 1H), 4.08 – 3.97 (m, 2H), 2.54 – 2.47 (m, 1H), 2.40 – 2.28 (m, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.3, 177.6, 132.7, 131.4, 131.2, 130.4, 130.1, 128.7, 127.0, 126.9, 126.6, 125.4, 123.8, 123.7, 122.6, 105.6, 64.8, 41.3, 33.4, 27.7, 14.1. **IR** (KBr, cm^{-1}): 3053, 2947, 1643, 1603, 1452, 1371, 1229, 1192, 1028, 872, 741, 723. **HR-ESI-MS** (m/z): calculated for $C_{22}H_{21}O_2$ $[M+H]^+$: 317.1536, found: 317.1544.



2y

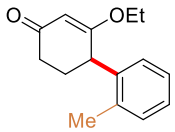
4-(anthracen-9-yl)-3-ethoxycyclohex-2-en-1-one (2y): White amorphous powder. 38% yield (120 mg). R_f = 0.60 (DCM/acetone = 40:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.32 (d, *J*

= 9.0 Hz, 1H), 8.13 (d, *J* = 8.9 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 5.71 (s, 1H), 5.35 – 5.32 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.90 – 3.81 (m, 2H), 2.76 – 2.67 (m, 3H), 2.34 – 2.31 (m, 1H), 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.2, 180.3, 132.1, 131.8, 131.7, 130.4, 129.9, 129.6, 129.6, 127.7, 126.6, 125.4, 125.1, 124.9, 124.8, 122.9, 103.3, 64.9, 40.7, 37.8, 29.4, 13.7. **IR** (KBr, cm^{-1}): 2986, 2963, 2851, 1651, 1603, 1454, 1221, 1175, 1022, 993, 932, 851, 773, 754. **HR-ESI-MS** (m/z): calculated for $C_{22}H_{21}O_2$ $[M+H]^+$: 317.1536, found: 317.1541.



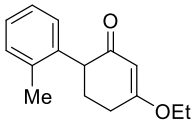
2z

6-ethoxy-2,3-dihydro-[1,1':2',1''-terphenyl]-4(1H)-one (2z): Colorless, viscous oil. 42% yield (122 mg). R_f = 0.45 (DCM/acetone = 40:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.40 – 7.37 (m, 1H), 7.35 – 7.34 (m, 2H), 7.32 – 7.30 (m, 2H), 7.27 – 7.25 (m, 1H), 7.20 – 7.19 (m, 1H), 5.56 (s, 1H), 4.01 (t, *J* = 6.0 Hz, 1H), 3.95 – 3.86 (m, 2H), 2.36 (ddd, *J* = 16.9, 9.0, 4.8 Hz, 1H), 2.19 (ddd, *J* = 16.9, 8.0, 4.8 Hz, 1H), 2.06 – 2.00 (m, 1H), 1.87 – 1.82 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.0, 178.4, 142.5, 141.3, 137.9, 130.7, 129.4, 128.5, 127.6, 127.3, 127.0, 126.8, 104.7, 64.6, 41.2, 34.2, 29.5, 14.1. **IR** (KBr, cm^{-1}): 2976, 2940, 2873, 1963, 1892, 1653, 1601, 1477, 1373, 1217, 1184, 1030, 937, 826, 756, 712. **HR-ESI-MS** (m/z): calculated for $C_{20}H_{21}O_2$ $[M+H]^+$: 293.1536, found: 293.1539.



2aa

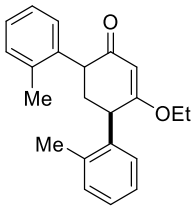
6-ethoxy-2'-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2aa): Colorless, viscous oil. 49% yield (112 mg). R_f = 0.45 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.18 (td, *J* = 7.4, 1.5 Hz, 1H), 7.14 (td, *J* = 7.5, 1.6 Hz, 1H), 7.06 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.63 (s, 1H), 3.99 – 3.94 (m, 2H), 3.92 – 3.87 (m, 1H), 2.39 (s, 3H), 2.36 – 2.24 (m, 3H), 1.99 – 1.93 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.1, 178.0, 137.6, 136.1, 131.2, 127.1, 126.7, 126.1, 105.0, 64.6, 41.5, 33.4, 28.0, 19.5, 14.1. **IR** (KBr, cm^{-1}): 2976, 2955, 1649, 1599, 1454, 1377, 1213, 1184, 1030, 841, 758. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1380, found: 231.1387.



2aa′

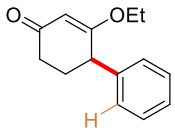
4-ethoxy-2'-methyl-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one (2aa′): Colorless, viscous oil. 10% yield (22 mg). R_f = 0.55 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 3H), 7.06 – 7.04 (m, 1H), 5.54 (s, 1H), 3.99 – 3.93 (m, 2H), 3.72 (t, *J* = 7.9 Hz, 1H), 2.61 – 2.55 (m, 1H), 2.47 (dt, *J* = 17.4, 4.7 Hz, 1H), 2.31 (s, 3H), 2.21 – 2.18 (m, 2H), 1.40 (t, *J* = 7.0

Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.6, 177.5, 138.7, 136.6, 130.7, 127.7, 126.9, 126.2, 103.6, 64.6, 49.1, 28.8, 28.6, 19.9, 14.3. **IR** (KBr, cm^{-1}): 2982, 2940, 2895, 1651, 1605, 1493, 1454, 1379, 1321, 1126, 1188, 1036, 910, 816, 752. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1380, found: 231.1383.



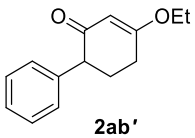
2aa″

6'-ethoxy-2,2''-dimethyl-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'(1'H)-one (2aa″): Colorless, viscous oil. 10% yield (32 mg). R_f = 0.65 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 4H), 7.16 – 7.09 (m, 3H), 7.04 (dd, J = 7.1, 1.7 Hz, 1H), 5.81 (s, 1H), 4.07 – 4.02 (m, 2H), 4.00 – 3.94 (m, 1H), 3.73 (dd, J = 12.8, 4.4 Hz, 1H), 2.64 (td, J = 13.1, 5.6 Hz, 1H), 2.36 (s, 3H), 2.05 (ddd, J = 13.2, 4.5, 2.6 Hz, 1H), 2.00 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.5, 176.9, 138.3, 136.9, 136.7, 136.2, 131.5, 130.6, 128.1, 127.4, 127.0, 126.24, 126.23, 126.1, 105.7, 64.9, 44.4, 41.7, 35.3, 19.6, 19.4, 14.2. **IR** (KBr, cm^{-1}): 2968, 2943, 1659, 1605, 1491, 1454, 1373, 1190, 1030, 920, 745. **HR-ESI-MS** (m/z): calculated for $C_{22}H_{25}O_2$ $[M+H]^+$: 321.1849, found: 321.1853.



2ab

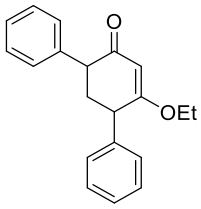
6-ethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ab): Colorless, viscous oil. 36% yield (78 mg). R_f = 0.40 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 7.2 Hz, 2H), 5.59 (s, 1H), 3.99 – 3.88 (m, 2H), 3.77 (t, J = 4.9 Hz, 1H), 2.42 – 2.25 (m, 3H), 2.06 – 2.02 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.9, 177.4, 139.8, 128.7, 127.8, 127.1, 104.5, 64.6, 44.8, 33.3, 30.3, 14.1. **IR** (KBr, cm^{-1}): 2945, 2870, 1649, 1601, 1452, 1379, 1335, 1225, 1192, 1028, 853, 762, 704. **HR-ESI-MS** (m/z): calculated for $C_{14}H_{17}O_2$ $[M+H]^+$: 217.1223, found: 217.1228.



2ab′

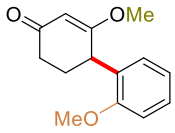
4-ethoxy-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one (2ab′): Colorless, viscous oil. 18% yield (40 mg). R_f = 0.50 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.8 Hz, 1H), 7.17 (d, J = 7.4 Hz, 2H), 5.51 (s, 1H), 3.98 – 3.91 (m, 2H), 3.53 (dd, J = 10.0, 5.1 Hz, 1H), 2.54 (ddd, J = 17.6, 9.2, 5.2 Hz, 1H), 2.45 (dt, J = 17.6, 5.2 Hz, 1H), 2.29 – 2.17 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.5, 177.5, 140.0, 128.7, 128.5, 127.0, 103.3, 64.6, 52.1, 29.6, 28.4, 14.3. **IR** (KBr, cm^{-1}): 2936, 1653, 1601, 1379, 1180,

1031, 847, 764. **HR-ESI-MS** (m/z): calculated for $C_{14}H_{17}O_2$ $[M+H]^+$: 217.1223, found: 217.1220. The physical data and spectra is identical to those previously reported.[11]



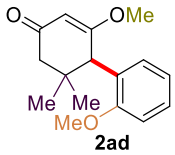
2ab″

6'-ethoxy-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'(1'H)-one (2ab″): Colorless, viscous oil. 18% yield (52 mg). R_f = 0.60 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.33 – 7.29 (m, 3H), 7.27 – 7.24 (m, 3H), 7.10 (dd, J = 8.2, 1.4 Hz, 2H), 5.76 (s, 1H), 4.07 – 3.96 (m, 2H), 3.88 (dd, J = 5.4, 3.5 Hz, 1H), 3.50 (dd, J = 12.2, 4.5 Hz, 1H), 2.74 – 2.69 (m, 1H), 2.32 – 2.28 (m, 1H), 1.33 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.4, 176.6, 139.9, 139.4, 128.9, 128.7, 128.6, 127.8, 127.3, 127.0, 104.9, 64.8, 48.1, 44.5, 38.5, 14.2. **IR** (KBr, cm^{-1}): 2934, 1655, 1601, 1371, 1192, 1024, 851, 764. **HR-ESI-MS** (m/z): calculated for $C_{20}H_{21}O_2$ $[M+H]^+$: 293.1536, found: 293.1536.



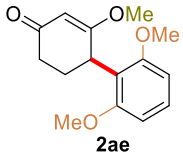
2ac

2',6-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ac): Colorless, viscous oil. 73% yield (170 mg). R_f = 0.50 (DCM/acetone = 40:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (t, J = 7.8 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 6.94 – 6.90 (m, 2H), 5.63 (s, 1H), 4.18 (t, J = 5.2 Hz, 1H), 3.86 (s, 3H), 3.69 (s, 3H), 2.34 – 2.22 (m, 3H), 2.12 – 2.06 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.3, 179.0, 157.2, 128.4, 128.0, 127.6, 120.5, 110.9, 104.4, 56.0, 55.5, 39.0, 34.1, 27.9. **IR** (KBr, cm^{-1}): 3065, 2914, 2839, 1643, 1612, 1454, 1373, 1335, 1225, 1169, 1105, 1026, 995, 866, 752. **HR-ESI-MS** (m/z): calculated for $C_{14}H_{17}O_3$ $[M+H]^+$: 233.1172, found: 233.1177.



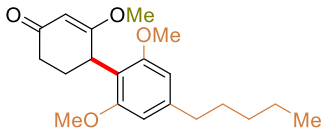
2ad

2',6-dimethoxy-2,2-dimethyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ad): Colorless, viscous oil. 42% yield (110 mg). R_f = 0.45 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 1H), 7.06 (dd, J = 7.7, 1.8 Hz, 1H), 6.93 – 6.88 (m, 2H), 5.61 (s, 1H), 4.10 (s, 1H), 3.86 (s, 3H), 3.63 (s, 3H), 2.42 (d, J = 17.0 Hz, 1H), 2.00 (d, J = 17.0 Hz, 1H), 1.22 (s, 3H), 0.73 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.0, 179.0, 158.0, 128.5, 127.5, 125.9, 120.5, 110.9, 103.1, 56.1, 55.5, 47.2, 47.0, 36.0, 29.2, 25.9. **IR** (KBr, cm^{-1}): 2965, 2839, 1643, 1605, 1492, 1443, 1360, 1242, 1224, 1156, 1028, 835, 758. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485, found: 261.1486.



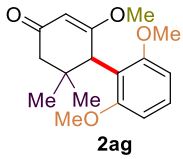
2ae

2',6,6'-trimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ae): Colorless, viscous oil. 66% yield (172 mg). R_f = 0.35 (petroleum ether/EtOAc = 3:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (t, J = 8.3 Hz, 1H), 6.57 – 6.55 (s, 2H), 5.44 (d, J = 1.7 Hz, 1H), 4.44 – 4.41 (m, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.60 (s, 3H), 2.48 – 2.45 (m, 2H), 2.36 – 2.28 (m, 1H), 1.99 – 1.94 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.3, 181.6, 158.5, 158.0, 128.2, 117.1, 104.4, 104.0, 101.7, 56.0, 55.9, 55.5, 37.4, 35.7, 27.4. **IR** (KBr, cm^{-1}): 2938, 2837, 1643, 1595, 1476, 1361, 1247, 1109, 999, 841, 779, 725. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_4$ $[M+H]^+$: 263.1278, found: 263.1281.



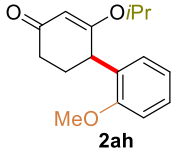
2af

2',6,6'-trimethoxy-4'-pentyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2af): Colorless, viscous oil. 63% yield (210 mg). R_f = 0.45 (petroleum ether/acetone = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.38 (s, 2H), 5.44 (d, J = 1.7 Hz, 1H), 4.36 (ddd, J = 11.2, 5.0, 1.8 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.60 (s, 3H), 2.58 – 2.56 (m, 2H), 2.47 – 2.44 (m, 2H), 2.33 – 2.26 (m, 1H), 1.97 – 1.93 (m, 1H), 1.65 – 1.60 (m, 2H), 1.36 – 1.33 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.4, 181.9, 158.2, 157.6, 143.6, 114.2, 104.5, 104.1, 101.7, 55.9, 55.5, 37.4, 36.7, 35.6, 31.9, 31.2, 27.5, 22.7, 14.2. **IR** (KBr, cm^{-1}): 2938, 2857, 1651, 1607, 1456, 1377, 1225, 1119, 1003, 829. **HR-ESI-MS** (m/z): calculated for $C_{20}H_{29}O_4$ $[M+H]^+$: 333.2060, found: 333.2060.



2ag

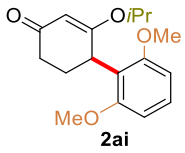
2',6,6'-trimethoxy-2,2-dimethyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ag): Colorless, viscous oil. 24% yield (70 mg). R_f = 0.40 (petroleum ether/EtOAc = 1.5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (t, J = 8.3 Hz, 1H), 6.59 (d, J = 8.3 Hz, 1H), 6.52 (d, J = 8.3 Hz, 1H), 5.49 (d, J = 1.4 Hz, 1H), 4.31 (d, J = 1.4 Hz, 1H), 3.83 (s, 3H), 3.64 (s, 3H), 3.59 (s, 3H), 2.49 (d, J = 15.8 Hz, 1H), 2.28 (d, J = 15.8 Hz, 1H), 1.07 (s, 3H), 0.80 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.5, 179.3, 159.1, 159.0, 128.4, 115.0, 104.5, 103.9, 101.3, 55.9, 55.2, 51.6, 45.2, 37.1, 30.0, 24.7. **IR** (KBr, cm^{-1}): 2967, 2839, 1643, 1593, 1470, 1362, 1223, 1098, 1030, 845, 779, 729. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{23}O_4$ $[M+H]^+$: 291.1591, found: 291.1590.



2ah

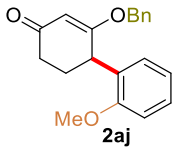
6-isopropoxy-2'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ah): Colorless, viscous oil.

34% yield (88 mg). R_f = 0.45 (petroleum ether/EtOAc/DCM = 4:1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 1H), 7.03 (dd, J = 7.6, 1.7 Hz, 1H), 6.91 – 6.87 (m, 2H), 5.60 (s, 1H), 4.51 – 4.43 (m, 1H), 4.08 – 4.07 (m, 1H), 3.84 (s, 3H), 2.27 – 2.19 (m, 3H), 2.08 – 2.03 (m, 1H), 1.25 (d, J = 6.1 Hz, 3H), 1.19 (d, J = 6.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.6, 177.3, 157.2, 128.2, 127.9, 127.8, 120.3, 110.7, 105.1, 71.1, 55.4, 39.4, 33.7, 27.7, 21.8, 21.0. **IR** (KBr, cm^{-1}): 2982, 2837, 1649, 1599, 1493, 1454, 1373, 1327, 1244, 1221, 1107, 1028, 951, 841, 754. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485, found: 261.1483.



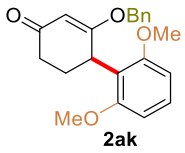
2ai

6-isopropoxy-2',6'-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ai): Colorless, viscous oil. 32% yield (92 mg). R_f = 0.35 (petroleum ether/EtOAc = 3:2). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 (t, J = 8.3 Hz, 1H), 6.56 – 6.49 (m, 2H), 5.41 (m, 1H), 4.40 – 4.35 (m, 2H), 3.82 (s, 3H), 3.68 (s, 3H), 2.46 – 2.44 (m, 2H), 2.35 – 2.28 (m, 1H), 1.96 – 1.92 (m, 1H), 1.15 (d, J = 6.1 Hz, 3H), 1.11 (d, J = 6.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.5, 180.1, 158.2, 158.0, 127.9, 117.4, 103.8, 103.7, 102.1, 70.9, 56.1, 55.0, 37.2, 36.2, 27.2, 21.7, 21.1. **IR** (KBr, cm^{-1}): 2972, 2837, 1643, 1593, 1472, 1368, 1327, 1244, 1221, 1109, 951, 829, 781. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{23}O_4$ $[M+H]^+$: 291.1591, found: 291.1594.



2aj

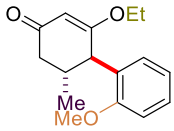
6-(benzyloxy)-2'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2aj): White amorphous powder. 76% yield (234 mg). R_f = 0.45 (DCM/acetone = 40:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 7.19 (dd, J = 7.4, 2.2 Hz, 2H), 7.04 (dd, J = 7.4, 1.7 Hz, 1H), 6.91 – 6.88 (m, 2H), 5.69 (s, 1H), 4.97 – 4.89 (m, 2H), 4.23 – 4.21 (m, 1H), 3.83 (s, 3H), 2.31 – 2.23 (m, 3H), 2.13 – 2.09 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.4, 177.9, 157.2, 135.2, 128.7, 128.43, 128.37, 128.1, 127.6, 127.5, 120.4, 110.8, 105.6, 70.5, 55.4, 39.2, 34.0, 27.8. **IR** (KBr, cm^{-1}): 2930, 1661, 1601, 1495, 1452, 1358, 1252, 1107, 972, 831, 750. **HR-ESI-MS** (m/z): calculated for $C_{20}H_{21}O_3$ $[M+H]^+$: 309.1485, found: 309.1487.



2ak

6-(benzyloxy)-2',6'-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ak): White amorphous powder. 74% yield (249 mg). R_f = 0.40 (petroleum ether/EtOAc = 1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 3H), 7.23 (t, J = 8.3 Hz, 1H), 7.09 (dd, J = 7.3, 2.2 Hz, 2H), 6.61 – 6.56 (m, 2H), 5.55 (d, J = 1.8 Hz, 1H), 4.90 (s, 2H), 4.55 – 4.52 (m, 1H), 3.85 (s, 3H), 3.69 (s, 3H), 2.52 – 2.50 (m, 2H), 2.44 – 2.37 (m, 1H), 2.05 – 2.00 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.4, 180.5, 158.4, 158.0, 135.8, 128.5, 128.2, 127.9, 126.9, 117.0, 104.0, 102.9, 70.1, 56.0, 55.4,

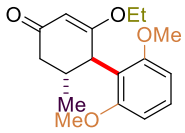
37.4, 35.9, 27.2. **IR** (KBr, cm^{-1}): 2949, 2837, 1659, 1601, 1454, 1350, 1244, 1105, 1034, 988, 920, 831, 743. **HR-ESI-MS** (m/z): calculated for $C_{21}H_{23}O_4$ $[M+H]^+$: 339.1591, found: 339.1592.



2al

dr = 6:1 (inseparable)

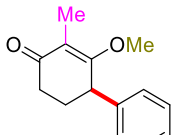
6-ethoxy-2'-methoxy-2-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2al): Colorless, viscous oil. 58% yield (150 mg). R_f = 0.50 (DCM/acetone = 30:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 7.01 (d, J = 7.2 Hz, 1H), 6.91 – 6.88 (m, 2H), 5.55 (s, 1H), 3.95 – 3.84 (m, 2H), 3.82 (s, 3H), 3.79 (d, J = 5.9 Hz, 1H), 2.45 (dd, J = 16.5, 4.7 Hz, 1H), 2.37 – 2.33 (m, 1H), 2.11 (dd, J = 16.5, 7.4 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H), 1.04 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.8, 177.4, 157.4, 128.4, 128.2, 128.1, 120.5, 110.8, 103.8, 64.5, 55.5, 47.1, 42.4, 34.2, 20.1, 14.0. **IR** (KBr, cm^{-1}): 2953, 1651, 1603, 1493, 1375, 1325, 1244, 1209, 1169, 1107, 1028, 930, 808, 746. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485, found: 261.1487.



2am

dr = 9:1 (inseparable)

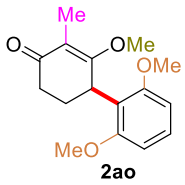
6-ethoxy-2',6'-dimethoxy-2-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2am): Colorless, viscous oil. 54% yield (156 mg). R_f = 0.35 (petroleum ether/acetone = 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.19 (t, J = 8.3 Hz, 1H), 6.54 (m, 2H), 5.41 (d, J = 1.8 Hz, 1H), 4.10 (dd, J = 10.5, 1.9 Hz, 1H), 3.88 – 3.79 (m, 5H), 3.67 (s, 3H), 2.61 – 2.55 (m, 1H), 2.47 (dd, J = 16.3, 4.0 Hz, 1H), 2.22 (dd, J = 16.3, 13.3 Hz, 1H), 1.13 (t, J = 7.0 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.1, 180.8, 159.0, 158.3, 128.1, 115.9, 104.1, 103.8, 101.7, 64.4, 56.1, 55.3, 46.0, 43.0, 33.3, 19.7, 13.9. **IR** (KBr, cm^{-1}): 3059, 2992, 2837, 1643, 1593, 1470, 1358, 1227, 1109, 1032, 939, 849, 777, 725. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{23}O_4$ $[M+H]^+$: 291.1591, found: 291.1596.



2an

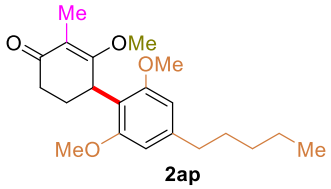
2',6-dimethoxy-5-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2an): Colorless, viscous oil. 59% yield (146 mg). R_f = 0.65 (petroleum ether/EtOAc/DCM = 3:1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.05 (dd, J = 7.4, 1.6 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 4.48 – 4.47 (m, 1H), 3.90 (s, 3H), 3.55 (s, 3H), 2.30 – 2.18 (m, 3H), 2.04 – 1.98 (m, 1H), 1.83 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.7, 171.9, 156.7, 128.8, 128.3, 125.8, 120.7, 117.1, 110.8, 55.5, 55.1, 33.7, 32.3, 27.1, 7.7. **IR** (KBr, cm^{-1}): 2949, 2836, 1643, 1612, 1454,

13348, 1240, 1128,1091, 1014, 934, 883, 847, 754. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found: 247.1330.



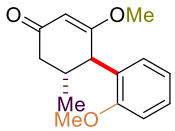
2ao

2',6,6'-trimethoxy-5-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ao): Colorless, viscous oil. 52% yield (144 mg). R_f = 0.45 (petroleum ether/EtOAc/DCM = 3:1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (t, J = 8.4 Hz, 1H), 6.56 (d, J = 8.3 Hz, 2H), 4.46 (m, 1H), 3.85 (br s, 3H), 3.68 (br s, 3H), 3.48 (s, 3H), 2.51 – 2.45 (m, 1H), 2.37 – 2.31 (m, 1H), 2.16 – 2.08 (m, 2H), 1.78 (d, J = 1.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.4, 175.0, 159.0, 157.7, 128.5, 117.2, 116.4, 105.1, 104.0, 56.4, 56.1, 35.6, 32.8, 28.0, 8.2. **IR** (KBr, cm^{-1}): 2949, 2845, 1634, 1614, 1472, 1350, 1242, 1105, 935, 885, 777. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1437.



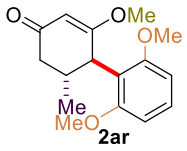
2ap

2',6,6'-trimethoxy-5-methyl-4'-pentyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ap): Colorless, viscous oil. 66% yield (228 mg). R_f = 0.45 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) **δ** 6.37 (s, 2H), 4.41 (m, 1H), 3.84 (s, 3H), 3.65 (s, 3H), 3.48 (s, 3H), 2.58 – 2.55 (m, 2H), 2.50 – 2.45 (m, 1H), 2.35 – 2.30 (m, 1H), 2.16 – 2.05 (m, 2H), 1.77 (d, J = 1.7 Hz, 3H), 1.63 – 1.59 (m, 2H), 1.37 – 1.31 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.5, 175.2, 158.8, 157.3, 143.9, 116.1, 114.2, 105.2, 104.1, 56.3, 56.0, 36.7, 35.5, 32.6, 31.8, 31.2, 28.1, 22.7, 14.2, 8.1. **IR** (KBr, cm^{-1}): 2932, 2857, 1643, 1612, 1468, 1346, 1236, 1119, 937, 826. **HR-ESI-MS** (m/z): calculated for $C_{21}H_{31}O_4$ $[M+H]^+$: 347.2217., found: 347.2220.



2aq

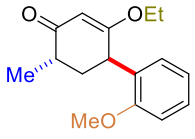
2',6-dimethoxy-2-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2aq): Colorless, viscous oil. 52% yield (128 mg). R_f = 0.60 (DCM/acetone = 30:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 1H), 7.02 (dd, J = 7.9, 1.7 Hz, 1H), 6.91 (t, J = 7.2 Hz, 2H), 5.57 (s, 1H), 3.824 (s, 3H), 3.816 (d, J = 8.0 Hz), 3.63 (s, 3H), 2.48 (dd, J = 16.4, 4.5 Hz, 1H), 2.39 – 2.33 (m, 1H), 2.14 (dd, J = 16.5, 8.4 Hz, 1H), 1.01 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.6, 178.5, 157.5, 128.6, 128.3, 127.9, 120.6, 110.9, 103.4, 56.1, 55.6, 47.0, 42.9, 34.4, 20.0. **IR** (KBr, cm^{-1}): 2961, 2839, 1661, 1605, 1495, 1358, 1217, 1165, 1026, 822, 758. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found: 247.1334.



2ar

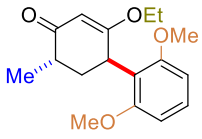
dr = 6:1 (inseparable)

2',6,6'-trimethoxy-2-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ar): Colorless, viscous oil. 63% yield (174 mg). R_f = 0.60 (petroleum ether/acetone = 30:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (t, J = 8.3 Hz, 1H), 6.58 (d, J = 8.1 Hz, 1H), 6.52 (d, J = 8.3 Hz, 1H), 5.44 (d, J = 1.5 Hz, 1H), 4.13 (dd, J = 10.5, 1.9 Hz, 1H), 3.88 (s, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 3.57 (s, 3H), 2.62 – 2.55 (m, 1H), 2.48 (dd, J = 16.3, 3.9 Hz, 1H), 2.26 – 2.16 (m, 1H), 0.82 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.9, 181.6, 158.9, 158.4, 128.3, 115.7, 104.4, 103.9, 101.4, 56.5, 56.0, 55.5, 46.0, 42.8, 33.4, 19.6. **IR** (KBr, cm^{-1}): 2934, 2841, 1649, 1587, 1472, 1242, 1219, 1126, 1107, 779, 729. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1440.



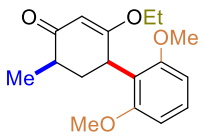
2as

6-ethoxy-2'-methoxy-3-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2as): Colorless, viscous oil. 59% yield (154 mg). R_f = 0.45 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (td, J = 7.8, 7.0, 2.1 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 5.62 (s, 1H), 4.14 (dd, J = 5.6, 2.9 Hz, 1H), 3.99 – 3.94 (dq, J = 10.0, 7.1 Hz, 1H), 3.92 – 3.87 (m, 1H), 3.86 (s, 3H), 2.27 – 2.20 (m, 1H), 2.08 – 2.01 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.05 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 202.7, 177.1, 157.2, 128.2, 127.6, 127.5, 120.3, 110.7, 104.8, 64.5, 55.4, 38.7, 35.9, 35.8, 15.0, 14.2. **IR** (KBr, cm^{-1}): 2932, 2870, 1649, 1606, 1490, 1454, 1373, 1244, 1190, 1037, 844, 754. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485, found: 261.1488.



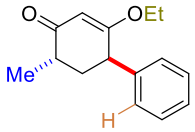
anti-**2at**

6-ethoxy-2',6'-dimethoxy-3-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (*anti*-2at): Colorless, viscous oil. 52% yield (150 mg). R_f = 0.35 (petroleum ether/EtOAc/CH_2Cl_2 = 4:1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.18 (t, J = 8.3 Hz, 1H), 6.53 (s, 2H), 5.35 (d, J = 1.5 Hz, 1H), 4.46 (ddd, J = 9.5, 5.5, 1.5 Hz, 1H), 3.93 – 3.67 (m, 8H), 2.51 – 2.46 (m, 1H), 2.36 – 3.32 (m, 1H), 1.78 (dt, J = 13.2, 5.1 Hz, 1H), 1.23 (d, J = 7.3 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 204.0, 179.6, 158.4, 158.1, 127.9, 117.2, 104.1, 100.6, 64.1, 56.0, 55.3, 39.4, 34.2, 32.1, 16.4, 14.0. **IR** (KBr, cm^{-1}): 2983, 2837, 1661, 1591, 1470, 1371, 1240, 1109, 1036, 841, 781, 731. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{23}O_4$ $[M+H]^+$: 291.1591, found: 291.1595.



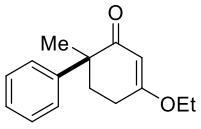
syn-**2at**

6-ethoxy-2',6'-dimethoxy-3-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (*syn*-2at): Colorless, viscous oil. 9% yield (26 mg). R_f = 0.45 (petroleum ether/EtOAc/CH_2Cl_2 = 4:1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.18 (t, J = 8.3 Hz, 1H), 6.57 (d, J = 8.3 Hz, 1H), 6.51 (d, J = 8.3 Hz, 1H), 5.41 (d, J = 1.9 Hz, 1H), 4.49 (ddd, J = 11.8, 4.7, 1.9 Hz, 1H), 3.90 – 3.83 (m, overlapped, 2H), 3.84 (s, 3H), 3.69 (s, 3H), 2.49 – 2.43 (m, 1H), 2.12 – 2.05 (m, 1H), 1.94 (dt, J = 12.7, 4.7 Hz, 1H), 1.17 – 1.14 (m, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 202.2, 180.1, 158.5, 157.9, 128.0, 117.4, 104.2, 103.9, 101.5, 64.2, 56.1, 55.4, 41.0, 36.5, 36.1, 15.2, 14.0. **IR** (KBr, cm^{-1}): 2981, 2834, 1660, 1593, 1468, 1374, 1243, 1105, 1037, 843, 778, 734. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{23}O_4$ $[M+H]^+$: 291.1591, found: 291.1595.



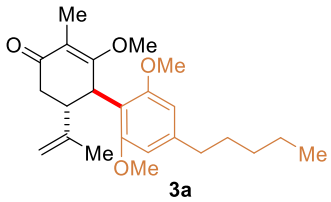
2au

6-ethoxy-3-methyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2au): Colorless, viscous oil. 39% yield (90 mg). R_f = 0.45 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (t, J = 7.2 Hz, 2H), 7.29 – 7.25 (t, J = 7.2 Hz, 1H), 7.21 (d, J = 7.2 Hz, 2H), 5.59 (s, 1H), 3.40 – 3.88 (m, 2H), 3.78 – 3.76 (m, 1H), 2.33 – 2.27 (m, 1H), 2.17 (td, J = 12.8, 5.5 Hz, 1H), 2.06 – 2.03 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 202.0, 176.3, 139.9, 128.8, 127.8, 127.1, 104.2, 64.6, 44.6, 38.5, 35.5, 15.2, 14.2. **IR** (KBr, cm^{-1}): 2984, 2872, 1661, 1612, 1454, 1371, 1186, 1040, 858, 754. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1380, found: 231.1385.



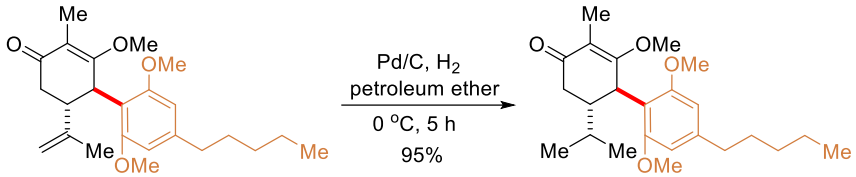
2au′

4-ethoxy-1-methyl-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one (2au′): Colorless, viscous oil. 10% yield (24 mg). R_f = 0.55 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 6H), 5.43 (s, 1H), 3.92 – 3.79 (m, 2H), 2.43 (dt, J = 13.7, 4.1 Hz, 1H), 2.29 – 2.26 (m, 2H), 2.07 (ddd, J = 13.7, 9.7, 6.5 Hz, 1H), 1.41 (s, 3H), 1.31 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 202.4, 176.7, 142.9, 128.6, 126.7, 126.3, 102.7, 64.4, 49.1, 34.8, 26.9, 26.7, 14.3. **IR** (KBr, cm^{-1}): 2981, 2880, 1659, 1611, 1453, 1370, 1183, 1041, 857, 752. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1380, found: 231.1385. The physical data and spectra is identical to those previously reported.[2]



3a

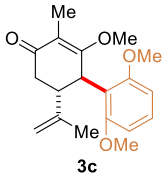
2',6,6'-trimethoxy-5-methyl-4'-pentyl-2-(prop-1-en-2-yl)-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (3a): White amorphous powder. 58% yield (224 mg). R_f = 0.40 (petroleum ether/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.34 (s, 2H), 4.55 (t, J = 1.7 Hz, 1H), 4.42 (dd, J = 8.4, 1.9 Hz, 1H), 4.40 (d, J = 1.7 Hz, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 3.44 (s, 3H), 3.11 – 3.06 (m, 1H), 2.56 – 2.49 (m, 4H), 1.77 (d, J = 1.8 Hz, 3H), 1.69 (s, 3H), 1.63 – 1.57 (m, 2H), 1.36 – 1.28 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.8, 174.8, 158.6, 158.0, 145.4, 143.8, 117.1, 113.6, 112.6, 105.2, 103.9, 57.0, 55.9, 55.8, 46.5, 41.3, 37.4, 36.6, 31.7, 31.1, 22.7, 19.4, 14.2, 8.3. **IR** (KBr, cm^{-1}): 2932, 2857, 1651, 1614, 1582, 1454, 1418, 1373, 1346, 1231, 1117, 1043, 891, 733. **HR-ESI-MS** (m/z): calculated for $C_{24}H_{35}O_4$ $[M+H]^+$: 387.2530, found: 387.2533.



3a **3b**

To a solution of **3a** (20 mg, 0.052 mmol) in petroleum ether (3 mL) was added Pd/C (10 wt%, 15 mg), and stirred for 5 h at 0 °C under H_2 atmosphere. The reaction mixture was filtered through a pad of Celite®, washed with EtOAc (20 mL), the resulting solution was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 10:1) to afford product **3b**.

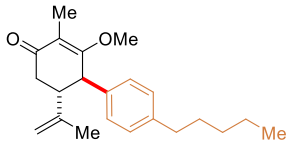
2-isopropyl-2',6,6'-trimethoxy-5-methyl-4'-pentyl-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (3b): White amorphous powder. 50% yield (194 mg) from **1k**, 95% yield (19 mg) from **3a**. R_f = 0.50 (petroleum ether/EtOAc = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.37 (s, 1H), 6.35 (s, 1H), 4.34 – 4.31 (m, 1H), 3.83 (s, 3H), 3.64 (s, 3H), 3.41 (s, 3H), 2.58 – 2.55 (m, 2H), 2.49 – 2.43 (m, 1H), 2.27 – 2.20 (m, 2H), 1.75 (d, J = 1.9 Hz, 3H), 1.65 – 1.59 (m, 2H), 1.56 – 1.50 (m, 1H), 1.37 – 1.31 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H), 0.84 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.7, 175.3, 158.8, 158.2, 143.9, 117.1, 113.7, 105.5, 103.7, 56.9, 55.9, 55.7, 44.4, 37.2, 36.8, 36.6, 31.8, 31.2, 28.4, 22.7, 21.6, 17.3, 14.2, 8.2. **IR** (KBr, cm^{-1}): 2934, 2857, 1651, 1616, 1576, 1456, 1418, 1231, 1121, 1045, 918, 826, 733. **HR-ESI-MS** (m/z): calculated for $C_{24}H_{37}O_4$ $[M+H]^+$: 389.2686., found: 389.2690.



3c

2',6,6'-trimethoxy-5-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (3c): White amorphous powder. 64% yield (202 mg). R_f = 0.40 (petroleum ether/EtOAc = 5:1). [purified by pre-HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 59%]. **^{1}H NMR** (500 MHz,

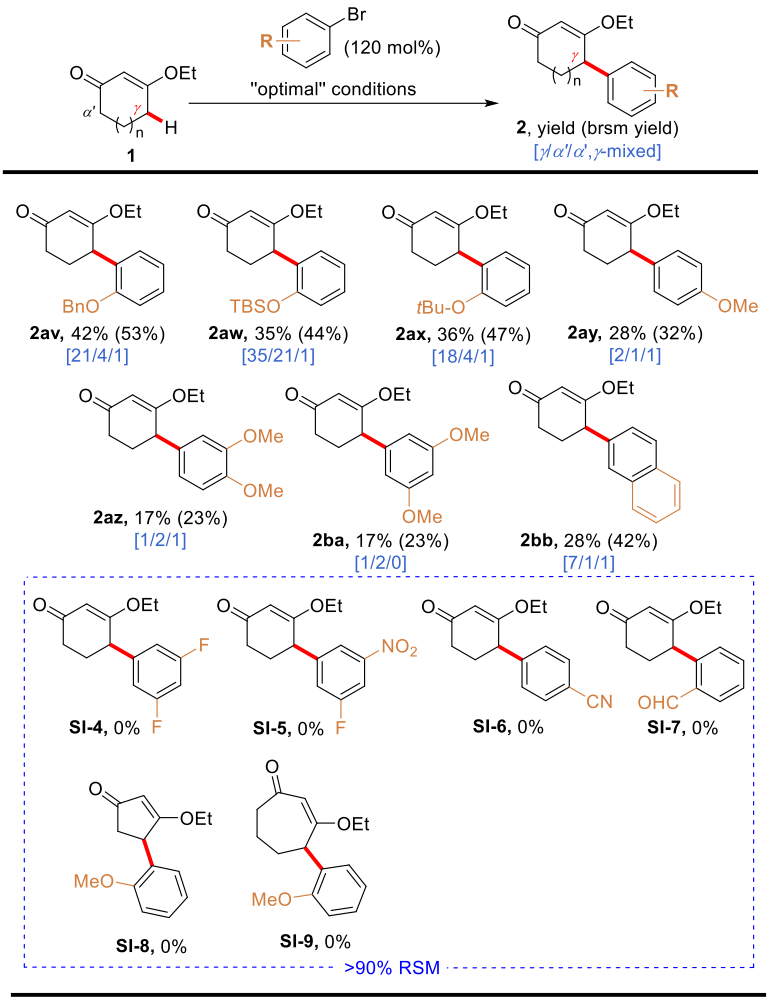
$CDCl_3$) δ 7.18 (t, J = 8.3 Hz, 1H), 6.53 (d, J = 8.4 Hz, 2H), 4.54 (t, J = 1.7 Hz, 1H), 4.49 (dd, J = 8.9, 2.0 Hz, 1H), 4.38 – 4.37 (m, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.43 (s, 3H), 3.17 – 3.12 (m, 1H), 2.57 – 2.45 (m, 2H), 1.77 (d, J = 1.9 Hz, 3H), 1.68 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.7, 174.8, 158.8, 158.3, 145.2, 128.5, 117.4, 116.4, 112.7, 105.1, 103.7, 57.2, 56.0, 55.8, 46.5, 41.5, 37.7, 19.1, 8.3. **IR** (KBr, cm^{-1}): 2941, 1620, 1468, 1344, 1240, 1105, 1036, 899, 721. **HR-ESI-MS** (m/z): calculated for $C_{19}H_{25}O_4$ $[M+H]^+$: 317.1747, found: 317.1743.



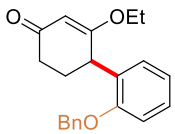
3d

6-methoxy-5-methyl-4'-pentyl-2-(prop-1-en-2-yl)-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (3d): White amorphous powder. 33% yield (108 mg). R_f = 0.65 (petroleum ether/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 4H), 4.87 (s, 1H), 4.71 (s, 1H), 4.11 (br s, 1H), 3.59 (s, 3H), 2.69 – 2.67 (m, 1H), 2.59 (t, J = 7.5 Hz, 2H), 2.51 (dd, J = 16.9, 5.6 Hz, 1H), 2.40 (dd, J = 16.9, 3.2 Hz, 1H), 1.83 (s, 3H), 1.81 (s, 3H), 1.63 – 1.57 (m, 2H), 1.36 – 1.29 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.0, 169.2, 145.6, 142.4, 136.3, 129.3, 127.7, 116.8, 112.6, 55.5, 48.1, 44.3, 36.4, 35.6, 31.7, 31.2, 22.7, 22.3, 14.2, 7.6. **IR** (KBr, cm^{-1}): 2930, 2857, 1651, 1624, 1510, 1456, 1375, 1352, 1256, 1225, 1163, 1125, 1098, 997, 897. **HR-ESI-MS** (m/z): calculated for $C_{22}H_{31}O_2$ $[M+H]^+$: 327.2319., found: 327.2321.

Table S2. Less effective examples [a]

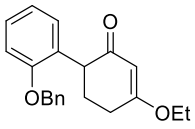


[a] Isolated yield and brsm yield in parenthesis were given. The *r.r.* values were determined by ^{1}H NMR analysis. [b] The regioselectivity was defined as [$\gamma/\alpha'/\alpha'$,γ-mixed].



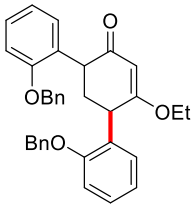
2av

2'-(benzyloxy)-6-ethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2av): Colorless, viscous oil. 42% yield (136 mg). R_f = 0.45 (petroleum ether/EtOAc/DCM = 5:1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 4H), 7.35 – 7.33 (m, 1H), 7.26 – 7.23 (m, 1H), 7.07 (dd, J = 7.6, 1.7 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.92 (td, J = 7.5, 1.0 Hz, 1H), 5.60 (s, 1H), 5.12 (s, 2H), 4.23 – 4.21 (m, 1H), 3.98 – 3.93 (m, 1H), 3.90 – 3.85 (m, 1H), 2.31 – 2.23 (m, 3H), 2.19-2.14 (m, 1H), 1.26 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.5, 178.2, 156.3, 137.1, 128.7, 128.3, 128.1, 128.0, 127.9, 127.2, 120.7, 112.0, 104.9, 70.0, 64.5, 39.2, 33.8, 27.8, 14.1. **IR** (KBr, cm^{-1}): 2972, 2949, 2820, 1643, 1593, 1492, 1452, 1375, 1358, 1223, 1022, 866, 760. **HR-ESI-MS** (m/z): calculated for $C_{21}H_{23}O_3$ $[M+H]^+$: 323.1647, found: 323.1643.



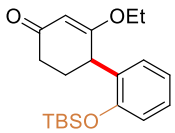
2av′

2'-(benzyloxy)-4-ethoxy-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one (2av′): Colorless, viscous oil. 8% yield (26 mg). R_f = 0.55 (petroleum ether/EtOAc/DCM = 5:1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.37 – 7.35 (m, 2H), 7.32 – 7.29 (m, 1H), 7.22 (td, J = 7.8, 1.8 Hz, 1H), 7.11 (dd, J = 7.5, 1.7 Hz, 1H), 6.95-6.93 (m, 2H), 5.47 (s, 1H), 5.06 (s, 2H), 3.92 – 3.87 (m, 2H), 3.82 (dd, J = 11.2, 5.0 Hz, 1H), 2.56 – 2.51 (m, 1H), 2.40 – 2.31 (m, 2H), 2.14 – 2.09 (m, 1H), 1.37 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.6, 177.2, 156.4, 137.4, 129.8, 129.5, 128.5, 128.2, 127.8, 127.4, 121.1, 112.4, 103.4, 70.3, 64.4, 48.0, 28.9, 28.1, 14.3. **IR** (KBr, cm^{-1}): 2976, 2870, 1660, 1611, 1452, 1305, 1232, 1186, 1024, 907, 856, 760, 732, 696. **HR-ESI-MS** (m/z): calculated for $C_{21}H_{23}O_3$ $[M+H]^+$: 323.1647, found: 323.1643.



2av″

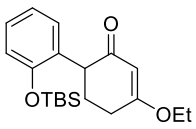
2,2''-bis(benzyloxy)-6'-ethoxy-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'(1'H)-one (2av″): Colorless, viscous oil. 2% yield (10 mg). R_f = 0.70 (petroleum ether/EtOAc/DCM = 5:1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 4H), 7.32 – 7.25 (m, 7H), 7.20 (td, J = 7.8, 1.8 Hz, 1H), 7.15 (dd, J = 7.5, 1.7 Hz, 1H), 7.03 (dd, J = 7.5, 1.7 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.95 – 6.88 (m, 3H), 5.72 (s, 1H), 5.07 (s, 2H), 4.97 (s, 2H), 4.28 (dd, J = 5.7, 2.5 Hz, 1H), 3.95-3.87 (m, 2H), 3.73 (dd, J = 12.7, 4.7 Hz, 1H), 2.74 (td, J = 13.0, 5.6 Hz, 1H), 2.23 (ddd, J = 13.3, 4.9, 2.6 Hz, 1H), 1.29 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.0, 176.6, 156.4, 137.3, 137.0, 130.5, 129.6, 128.7, 128.4, 128.3, 128.2, 128.0, 127.68, 127.66, 127.6, 127.3, 127.2, 121.1, 120.7, 112.3, 112.0, 105.6, 70.1, 69.9, 64.5, 39.0, 34.1, 14.2. **IR** (KBr, cm^{-1}): 3062, 3030, 2976, 2353, 1651, 1611, 1495, 1452, 1137, 1240, 1107, 1024, 914, 849, 750, 696. **HR-ESI-MS** (m/z): calculated for $C_{34}H_{33}O_4$ $[M+H]^+$: 505.2379, found: 505.2366.



2aw

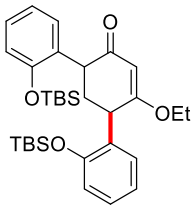
2'-((tert-butyldimethylsilyl)oxy)-6-ethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2aw): Colorless, viscous oil. 35% yield (122 mg). R_f = 0.30 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.15 (td, J = 7.7, 1.8 Hz, 1H), 7.01 (dd, J = 7.7, 1.8 Hz, 1H), 6.88 (td, J = 7.5, 1.2 Hz, 1H), 6.85 (dd, J = 8.1, 1.2 Hz, 1H), 5.61 (s, 1H), 4.13 – 4.11 (m, 1H), 3.98 – 3.93 (m, 1H), ,3.92 – 3.87 (m, 1H), 2.30 – 2.22 (m, 3H), 2.05 – 2.01 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.02 (s, 9H), 0.28 (s, 3H), 0.27 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.5, 178.3, 153.6, 129.9, 128.03, 127.98, 121.0, 118.7, 105.0, 64.5, 38.9, 33.5, 27.9, 25.9, 18.4, 14.1, -3.9, -4.1. **IR** (KBr,

cm^{-1}): 2953, 2930, 2857, 1655, 1599, 1489, 1452, 1258, 1211, 1184, 1088, 1049, 1022, 922, 837, 750. **HR-ESI-MS** (m/z): calculated for $C_{20}H_{31}O_3Si$ $[M+H]^+$: 347.2042, found: 347.2037.



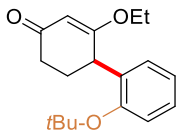
2aw′

2'-((tert-butyldimethylsilyl)oxy)-4-ethoxy-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one (2aw′): Colorless, viscous oil. 21% yield (72 mg). R_f = 0.45 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.11 (td, J = 7.8, 1.8 Hz, 1H), 7.04 (dd, J = 7.7, 1.8 Hz, 1H), 6.90 (td, J = 7.5, 1.2 Hz, 1H), 6.82 (dd, J = 8.1, 1.2 Hz, 1H), 5.51 (s, 1H), 3.97 – 3.92 (m, 2H), 3.89 (dd, J = 10.5, 5.1 Hz, 1H), 2.54 – 2.49 (m, 1H), 2.41 (dt, J = 17.5, 4.9 Hz, 1H), 2.23 – 2.17 (m, 1H), 2.16 – 2.11 (m, 1H), 1.39 (t, J = 7.0 Hz, 3H), 0.99 (s, 9H), 0.25 (s, 3H), 0.23 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.7, 177.3, 153.7, 130.9, 129.3, 127.8, 121.2, 118.4, 103.7, 64.4, 46.7, 28.7, 28.5, 26.0, 18.4, 14.3, -4.0, -4.1. **IR** (KBr, cm^{-1}): 2953, 2932, 2858, 1661, 1609, 1493, 1450, 1379, 1254, 1188, 1037, 918, 839, 781,756. **HR-ESI-MS** (m/z): calculated for $C_{20}H_{31}O_3Si$ $[M+H]^+$: 347.2042, found: 347.2038.



2aw″

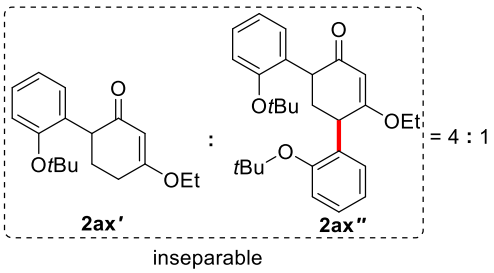
2,2''-bis((tert-butyldimethylsilyl)oxy)-6'-ethoxy-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'(1'H)-one (2aw″): Colorless oil. 1% yield (4 mg). R_f = 0.65 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.16 – 7.06 (m, 3H), 7.00 (dd, J = 7.7, 1.8 Hz, 1H), 6.91 – 6.87 (m, 2H), 6.83 (dd, J = 8.1, 1.2 Hz, 1H), 6.75 (dd, J = 8.2, 1.2 Hz, 1H), 5.77 (s, 1H), 4.19 (dd, J = 5.9, 2.8 Hz, 1H), 4.03 – 3.98 (m, 1H), 3.96 – 3.92 (m, 1H), 3.90 – 3.88 (m, 1H), 2.55 (td, J = 12.9, 5.7 Hz, 1H), 2.19 – 2.16 (m, 1H), 1.30 (t, J = 7.0 Hz, 3H), 0.96 (s, 9H), 0.80 (s, 9H), 0.24 (s, 3H), 0.23 (s, 3H), 0.11 (s, 3H), 0.07 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.1, 177.1, 153.8, 153.7, 131.1, 129.8, 129.4, 128.1, 127.8, 127.6, 121.22, 121.19, 118.8, 118.4, 105.9, 64.6, 38.8, 34.7, 25.91, 25.87, 18.3, 18.2, 14.2, -3.9, -4.0, -4.2, -4.3. **IR** (KBr, cm^{-1}): 2889, 2858, 2234, 1649, 1603, 1487, 1452, 1265, 1254, 1101, 937, 839, 781, 758. **HR-ESI-MS** (m/z): calculated for $C_{32}H_{49}O_4Si_2$ $[M+H]^+$: 553.3169, found: 553.3157.



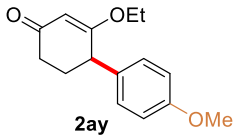
2ax

2'-(tert-butoxy)-6-ethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ax): Colorless, viscous oil. 36% yield (104 mg). R_f = 0.50 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 (td, J = 7.8, 1.8 Hz, 1H), 7.10 (dd, J = 8.2, 1.2 Hz, 1H), 7.04 (dd, J = 7.6, 1.8 Hz, 1H), 6.93

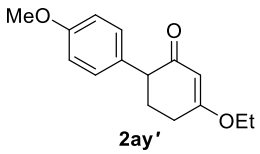
(td, J = 7.4, 1.2 Hz, 1H), 5.58 (s, 1H), 4.17 (t, J = 5.2 Hz, 1H), 3.97 – 3.92 (m, 1H), 3.90 – 3.85 (m, 1H), 2.34 – 2.20 (m, 3H), 2.06 – 2.01 (m, 1H), 1.46 (s, 9H), 1.23 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.5, 178.7, 154.3, 132.4, 128.1, 127.5, 121.8, 120.4, 104.7, 79.2, 64.4, 39.5, 34.0, 32.1, 29.5, 28.3, 22.8, 14.1. **IR** (KBr, cm^{-1}): 2916, 2847, 1661, 1605, 1481, 1375, 1242, 1219, 1163, 1034, 934, 758. **HR-ESI-MS** (m/z): calculated for $C_{18}H_{25}O_3$ $[M+H]^+$: 289.1804, found: 289.1803.



mixture of 2'-(tert-butoxy)-4-ethoxy-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one and 2,2''-di-tert-butoxy-6'-ethoxy-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'(1'H)-one (mixture of 2ax′and 2ax″): Colorless, viscous oil. 10% yield (32 mg). R_f = 0.60 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 1.53H), 7.11 – 7.01 (m, 2.87H), 6.98 – 6.93 (m, 1.89H), 5.76 (s, 0.25H), 5.50 (s, 1H), 4.23 (dd, J = 5.6, 2.6 Hz, 0.25H), 4.03 – 3.99 (m, 0.25H), 3.97 – 3.90 (m, 2.67H), 3.88 – 3.86 (m, 1.27H), 2.59 – 2.49 (m, 1.30H), 2.43 – 2.38 (dt, J = 17.5, 4.5 Hz, 1.05H), 2.28 – 2.21 (m, 1.08H), 2.14 – 2.06 (m, 1.31H), 1.414 (s, 2.25H), 1.408 (s, 9H), 1.39 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.0 Hz, 0.75H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.6, 200.0, 177.3, 177.1, 154.6, 154.3, 133.8, 133.6, 131.7, 129.7, 129.6, 127.6, 127.5, 127.3, 127.1, 122.3, 122.2, 121.6, 120.9, 120.4, 120.2, 105.8, 103.6, 79.2, 79.0, 78.8, 64.5, 64.4, 47.7, 42.9, 39.5, 35.3, 32.1, 29.42, 29.40, 29.2, 29.1, 28.8, 22.8, 14.4, 14.3, 14.2. **IR** (KBr, cm^{-1}): 2976, 2932, 1659, 1609, 1487, 1171, 1113, 1036, 899, 758. ***α′*-arylation TM**. **HR-ESI-MS** (m/z): calculated for $C_{18}H_{24}O_3Na$ $[M+Na]^+$: 311.1623, found: 311.1627. ***α′,γ*-diarylation TM**. HR-ESI-MS (m/z): calculated for $C_{28}H_{37}O_4$ $[M+H]^+$: 437.2692, found: 437.2691.

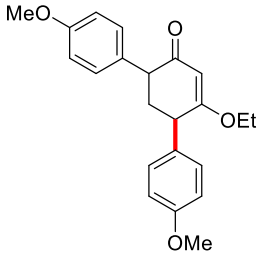


6-ethoxy-4'-methoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ay): Colorless, viscous oil. 28% yield (68 mg). R_f = 0.45 (petroleum ether/EtOAc = 3:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 55%, t_R = 15.2 min]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.11 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.56 (s, 1H), 3.98 – 3.87 (m, 2H), 3.80 (s, 3H), 3.71 (t, J = 4.5 Hz, 1H), 2.38 – 2.24 (m, 3H), 2.01 – 1.96 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.0, 177.8, 158.6, 131.7, 128.8, 114.1, 104.4, 64.6, 55.4, 44.0, 33.3, 30.4, 14.1. **IR** (KBr, cm^{-1}): 2940, 2845, 1635, 1604, 1443, 1384, 1212, 1151, 1087, 1031, 822, 755. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found: 247.1326.



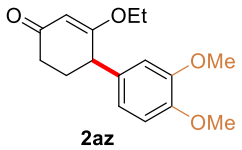
2ay′

4-ethoxy-4'-methoxy-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one (2ay′): Colorless, viscous oil. 13% yield (32 mg). R_f = 0.45 (petroleum ether/EtOAc = 3:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 55%, t_R = 17.1 min]. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.49 (s, 1H), 3.97 – 3.90 (m, 2H), 3.79 (s, 3H), 3.49 – 3.46 (dd, J = 10.2, 5.0 Hz, 1H), 2.56 -2.50 (m, 1H), 2.47 – 2.42 (dt, J = 17.5, 5.1 Hz, 1H), 2.26 – 2.15 (m, 2H), 1.38 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.8, 177.4, 158.5, 132.0, 129.4, 114.1, 103.2, 64.5, 55.4, 51.3, 29.6, 28.4, 14.3. **IR** (KBr, cm^{-1}): 2938, 1628, 1607, 1438, 1386, 1216, 1158, 1084, 1029, 824, 763. **HR-ESI-MS** (m/z): calculated for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found: 247.1327.



2ay″

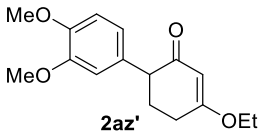
6'-ethoxy-4,4''-dimethoxy-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'(1'H)-one (2ay″): White amorphous powder. 12% yield (42 mg). R_f = 0.45 (petroleum ether/EtOAc = 3:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 55%, t_R = 19.6 min]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.15 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.71 (s, 1H), 4.04 - 3.92 (m, 2H), 3.82 (s, 3H), 3.81 – 3.80 (m, 1H), 3.77 (s, 3H), 3.44 (dd, J = 12.3, 4.5 Hz, 1H), 2.64 (td, J = 12.9, 5.3 Hz, 1H), 2.21 (dt, J = 13.2, 4.3 Hz, 1H), 1.32 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.8, 176.9, 158.7, 158.5, 132.0, 131.4, 129.7, 128.8, 114.2, 114.0, 104.7, 64.8, 55.4, 55.4, 47.2, 43.8, 38.7, 14.2. **IR** (KBr, cm^{-1}): 2952, 1634, 1612, 1429, 1378, 1221, 1163, 1077, 1033, 818, 756. **HR-ESI-MS** (m/z): calculated for $C_{22}H_{25}O_4$ $[M+H]^+$: 353.1747, found: 353.1749.



2az

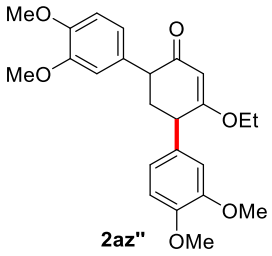
6-ethoxy-3',4'-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2az): Colorless, viscous oil. 17 % yield (46 mg). R_f = 0.30 (petroleum ether/EtOAc = 2:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 50%, t_R = 15.3 min]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.81 (d, J = 8.1 Hz, 1H), 6.73 – 6.70 (m, 2H), 5.56 (s, 1H), 3.99 – 3.87 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.71 – 3.69 (m, 1H), 2.37 – 2.26 (m, 3H), 2.05 – 1.98 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.9, 177.5, 149.1, 148.1, 132.2, 119.6, 111.19, 111.17, 104.4, 64.5, 56.0, 44.4, 33.4, 30.3, 14.1. **IR** (KBr, cm^{-1}): 2978, 2891, 1646, 1605, 1506, 1488, 1439, 1382,

1346, 1236, 1190, 1034, 933, 818. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1437.



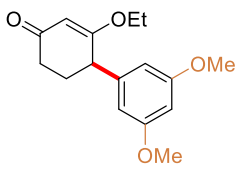
2az'

4-ethoxy-3',4'-dimethoxy-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one (2az′): Colorless, viscous oil. 31 % yield (86 mg). R_f = 0.30 (petroleum ether/EtOAc = 2:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 50%, t_R = 18.7 min]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.82 (d, J = 8.2 Hz, 1H), 6.71 (dd, J = 8.2, 2.1 Hz, 1H), 6.68 (d, J = 2.1 Hz, 1H), 5.48 (s, 1H), 3.96 – 3.89 (qt, J = 7.1, 3.2 Hz, 2H), 3.84 (s, 6H), 3.46 (dd, J = 10.2, 5.1 Hz, 1H), 2.54 (ddd, J = 17.5, 9.4, 5.3 Hz, 1H), 2.46 (dt, J = 17.5, 5.0 Hz, 1H), 2.27 – 2.17 (m, 2H), 1.37 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.6, 177.4, 148.9, 147.9, 132.5, 120.3, 111.7, 111.2, 103.1, 64.5, 55.9, 55.9, 51.7, 29.6, 28.5, 14.3. **IR** (KBr, cm^{-1}): 2984, 1639, 1611, 1512, 1490, 1433, 1376, 1353, 1240, 1184, 1028, 926, 821. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1436.



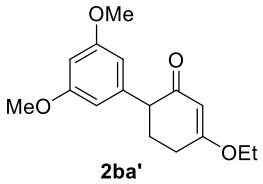
2az''

(1'R)-6'-ethoxy-3,3'',4,4''-tetramethoxy-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'(1'H)-one (2az″): Colorless, viscous oil. 16 % yield (66 mg). R_f = 0.30 (petroleum ether/EtOAc = 2:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 50%, t_R = 25.6 min]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.85 (d, J = 8.2 Hz, 1H), 6.79 (d, J = 8.3 Hz, 1H), 6.77 (dd, J = 8.3, 1.9 Hz, 1H), 6.75 (d, J = 1.9 Hz, 1H), 6.63 (dd, J = 8.2, 1.9 Hz, 1H), 6.59 (d, J = 1.9 Hz, 1H), 5.72 (s, 1H), 4.00 (ddd, J = 42.5, 10.0, 7.1 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 3.81 (s, 1H), 3.44 (dd, J = 12.4, 4.5 Hz, 1H), 2.66 (td, J = 13.0, 5.3 Hz, 1H), 2.25 (ddd, J = 13.2, 4.4, 3.4 Hz, 1H), 1.33 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.8, 176.8, 149.2, 148.9, 148.2, 148.0, 132.4, 131.7, 120.7, 119.5, 112.0, 111.2, 111.2, 104.8, 64.8, 56.02, 56.00, 55.96, 55.92, 47.8, 44.2, 38.7, 14.2. **IR** (KBr, cm^{-1}): 2985, 2981, 1642, 1616, 1517, 1485, 1430, 1375, 1351, 1242, 1181, 1032, 932, 818. **HR-ESI-MS** (m/z): calculated for $C_{24}H_{29}O_6$ $[M+H]^+$: 413.4859, found: 413.4858.



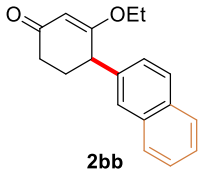
2ba

6-ethoxy-3',5'-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (2ba): Colorless, viscous oil. 17 % yield (46 mg). R_f = 0.35 (petroleum ether/EtOAc = 2:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 50%, t_R = 15.8 min]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.35 (d, J = 2.2 Hz, 1H), 6.33 (d, J = 2.3 Hz, 2H), 5.55 (s, 1H), 3.98 – 3.86 (m, 2H), 3.76 (s, 6H), 3.68 – 3.66 (m, 1H), 2.38 – 2.23 (m, 3H), 2.04 – 1.99 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.8, 177.0, 161.0, 142.1, 106.2, 104.5, 98.6, 64.6, 55.4, 44.9, 33.3, 30.1, 14.1. **IR** (KBr, cm^{-1}): 2932, 2882, 1657, 1599, 1503, 1445, 1373, 1260, 1159, 1115, 1047, 1026, 922, 837, 790. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1438.



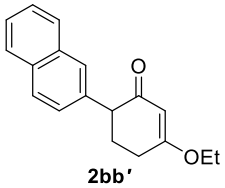
2ba'

4-ethoxy-3',5'-dimethoxy-5,6-dihydro-[1,1'-biphenyl]-2(1H)-one (2ba′): Colorless, viscous oil. 32 % yield (88 mg). R_f = 0.35 (petroleum ether/EtOAc = 2:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 50%, t_R = 18.1 min]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.36 (t, J = 2.3 Hz, 1H), 6.33 (d, J = 2.3 Hz, 2H), 5.49 (s, 1H), 3.97 – 3.90 (m, 2H), 3.77 (s, 6H), 3.46 (dd, J = 9.7, 5.1 Hz, 1H), 2.54 – 2.44 (m, 2H), 2.28 – 2.18 (m, 2H), 1.38 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.2, 177.6, 160.9, 142.3, 106.7, 103.2, 98.8, 64.6, 55.4, 52.3, 29.4, 28.3, 14.3. **IR** (KBr, cm^{-1}): 2943, 1649, 1587, 1507, 1448, 1388, 1252, 1161, 1118, 1055, 1031, 924, 844, 783. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1437.



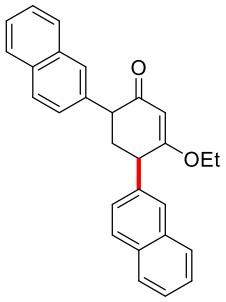
2bb

3-ethoxy-4-(naphthalen-2-yl)cyclohex-2-en-1-one (2bb): White amorphous powder. 28% yield (74 mg). R_f = 0.55 (petroleum ether/EtOAc = 4:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 60%, t_R = 20.3 min]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 2H), 7.80 – 7.778 (m, 1H), 7.62 (s, 1H), 7.50 – 7.45 (m, 2H), 7.33 (dd, J = 8.5, 1.9 Hz, 1H), 5.66 (s, 1H), 4.02 – 3.92 (m, 3H), 2.47 – 2.28 (m, 3H), 2.15 – 2.11 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.0, 177.4, 137.3, 133.4, 132.6, 128.6, 127.8, 127.7, 126.4, 126.3, 126.2, 126.0, 104.7, 64.7, 45.0, 33.4, 30.2, 14.1. **IR** (KBr, cm^{-1}): 3053, 2978, 2868, 1653, 1506, 1474, 1456, 1375, 1339, 1221, 1028, 750. **HR-ESI-MS** (m/z): calculated for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1385, found: 267.1384.



2bb'

3-ethoxy-6-(naphthalen-2-yl)cyclohex-2-en-1-one (2bb′): White amorphous powder. 4 % yield (11 mg). R_f = 0.55 (petroleum ether/EtOAc = 4:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 60%, t_R = 21.6 min]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 3H), 7.63 (s, 1H), 7.47 – 7.42 (m, 2H), 7.30 (dd, J = 8.5, 1.9 Hz, 1H), 5.56 (s, 1H), 4.01 – 3.93 (m, 2H), 3.71 (dd, J = 8.9, 6.1 Hz, 1H), 2.61 – 2.55 (m, 1H), 2.49 (dt, J = 17.6, 5.1 Hz, 1H), 2.38 – 2.31 (m, 2H), 1.40 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.6, 177.6, 137.5, 133.6, 132.6, 128.3, 127.8, 127.7, 127.1, 126.7, 126.1, 125.7, 103.3, 64.6, 52.2, 29.5, 28.4, 14.3. **IR** (KBr, cm^{-1}): 3051, 2976, 2864, 1655, 1503, 1472, 1453, 1377, 1336, 1223, 1024, 752. **HR-ESI-MS** (m/z): calculated for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1385, found: 267.1383.

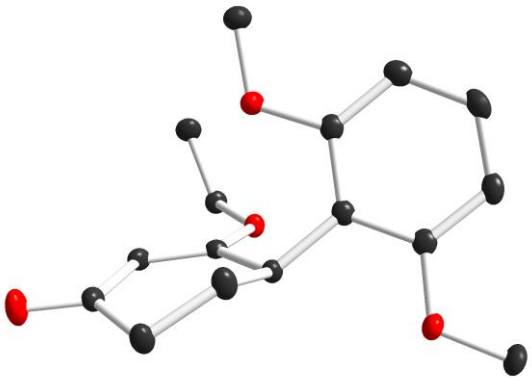


2bb″

3-ethoxy-4,6-di(naphthalen-2-yl)cyclohex-2-en-1-one (2bb″): White amorphous powder. 4 % yield (16 mg). R_f = 0.55 (petroleum ether/EtOAc = 4:1). [purified by HPLC (Eclipse XDB-C18) eluted with CH_3CN/H_2O = 60%, t_R = 26.3 min]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.82 (d, J = 7.3 Hz, 1H), 7.78 (d, J = 8.7 Hz, 2H), 7.71 – 7.69 (m, 2H), 7.54 – 7.49 (m, 3H), 7.42 – 7.39 (m, 3H), 7.23 (dd, J = 8.5, 1.8 Hz, 1H), 5.88 (s, 1H), 4.12 – 4.02 (m, 2H), 3.71 (dd, J = 12.2, 4.6 Hz, 1H), 2.87 (td, J = 12.8, 5.4 Hz, 1H), 2.43 (dt, J = 13.4, 4.1 Hz, 1H), 1.33 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.6, 176.8, 137.4, 136.9, 133.5, 133.5, 132.7, 132.6, 128.8, 128.3, 128.0, 127.8, 127.8, 127.7, 127.6, 126.8, 126.6, 126.4, 126.2, 126.1, 126.1, 125.8, 105.2, 65.0, 48.3, 44.8, 38.5, 14.2. **IR** (KBr, cm^{-1}): 3051, 2976, 2864, 1651, 1502, 1475, 1454, 1374, 1336, 1225, 1026, 755. **HR-ESI-MS** (m/z): calculated for $C_{28}H_{25}O_2$ $[M+H]^+$: 393.1849, found: 393.1851.

6. X-Ray Crystallography Data

X-ray data for 2s (CCDC 2118298)



Crystal data for **2s**: $C_{16}H_{20}O_4$, M = 276.32, a = 12.5182(6) Å, b = 15.0592(7) Å, c = 15.0679(8)

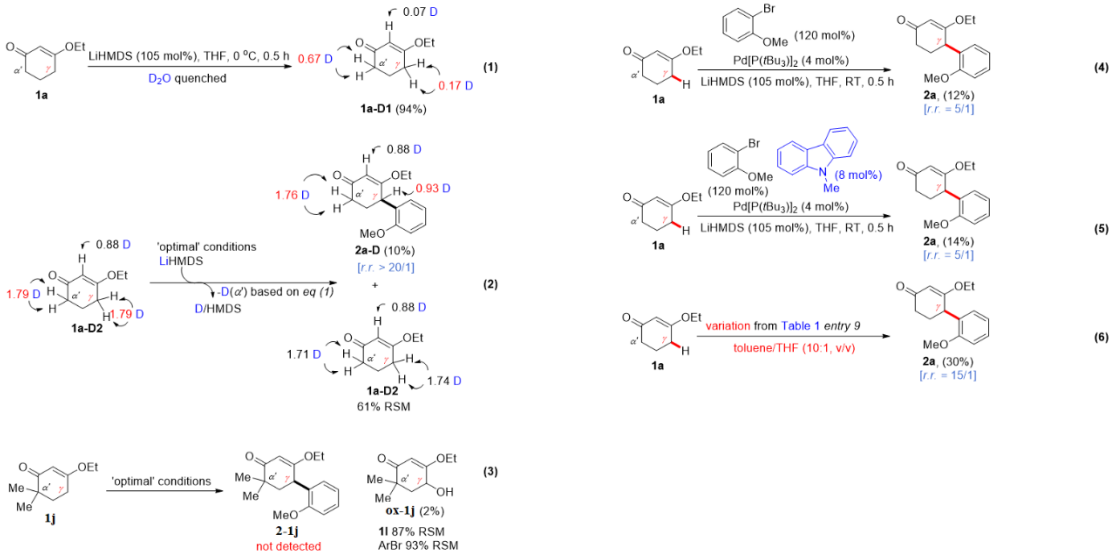
Å, α = 90°, β = 93.876(2)°, γ = 90°, V = 2834.0(2) Å^3, T = 100.(2) K, space group $P121/c1$, Z = 8, μ(Cu Kα) = 0.753 mm^{-1}, 61243 reflections measured, 5607 independent reflections (R_{int} = 0.0402). The final R_1 values were 0.0339 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0845 ($I > 2\sigma(I)$). The final R_1 values were 0.0347 (all data). The final $wR(F^2)$ values were 0.0850 (all data). The goodness of fit on F^2 was 1.039.

Crystal data and structure refinement for **2s_**0m.

Identification code	global	
Empirical formula	$C_{16}H_{20}O_4$	
Formula weight	276.32	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.5182(6) Å	= 90°.
	b = 15.0592(7) Å	= 3.876(2)°.
	c = 15.0679(8) Å	= 90°.
Volume	2834.0(2) Å^3	
Z	8	
Density (calculated)	1.295 Mg/m^3	
Absorption coefficient	0.753 mm^{-1}	
F(000)	1184	
Crystal size	0.320 x 0.320 x 0.240 mm^3	
Theta range for data collection	3.54 to 72.45°.	
Index ranges	-15<=h<=15, -18<=k<=18, -18<=l<=18	
Reflections collected	61243	
Independent reflections	5607 [R(int) = 0.0402]	
Completeness to theta = 72.45°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.84 and 0.70	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5607 / 0 / 367	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0845	
R indices (all data)	R1 = 0.0347, wR2 = 0.0850	
Largest diff. peak and hole	0.269 and -0.203 e.Å^{-3}	

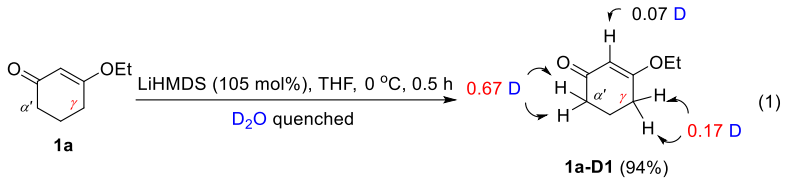
7. Mechanism Studies

Control experiments

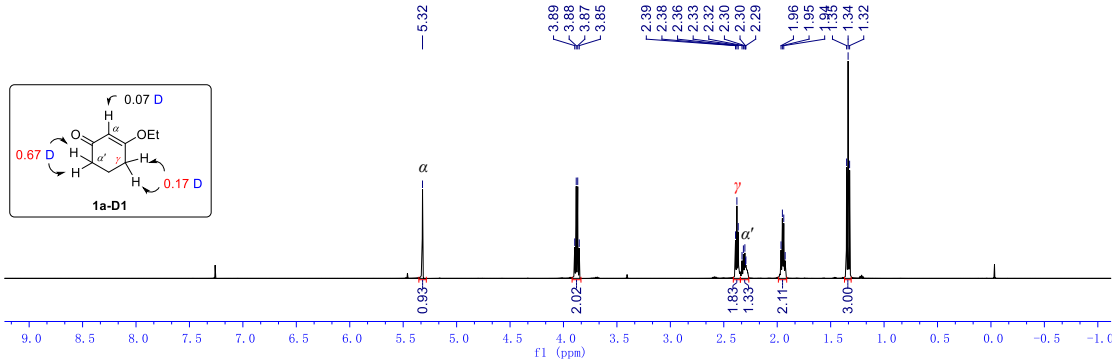


Scheme 4. Control experiments for mechanism study

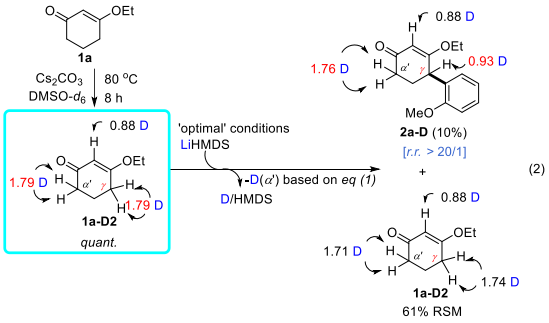
Deuteroxide quenching experiment (Scheme 4, eq 1)



LiHMDS (1.05 mL, 1.0 M in THF, 1.05 equiv) was added dropwise at 0 °C to a solution of **1a** (140 mg, 1.0 mmol, 1.0 equiv) in degassed THF (1.5 mL) in flame-dried two-necked flask, which have been evacuated and refilled with argon. The resulting solution was stirred for 0.5 h at 0 °C, and then deuteroxide (100 μL) was added. The reaction mixture was warmed to room temperature and stirred for additional 0.5 h. The crude mixture was portioned by EtOAc (10 mL) and water (10 mL), the aqueous layer was extracted with EtOAc (5 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to give **1a-D1** with NMR purity in 94% yields.

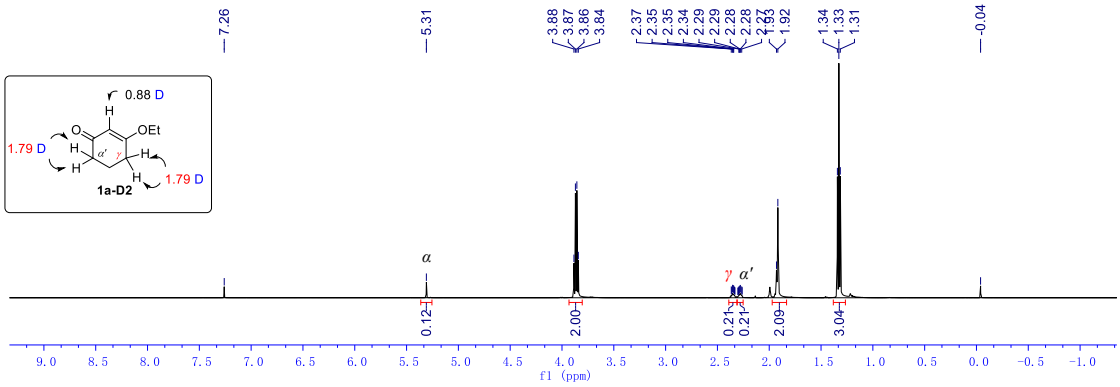


Deuterium labeling experiment (Scheme 4, eq 2)

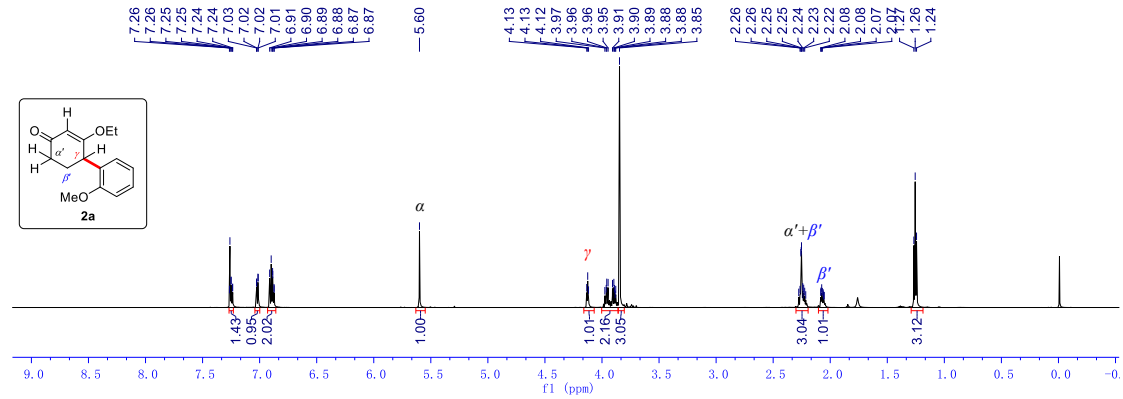


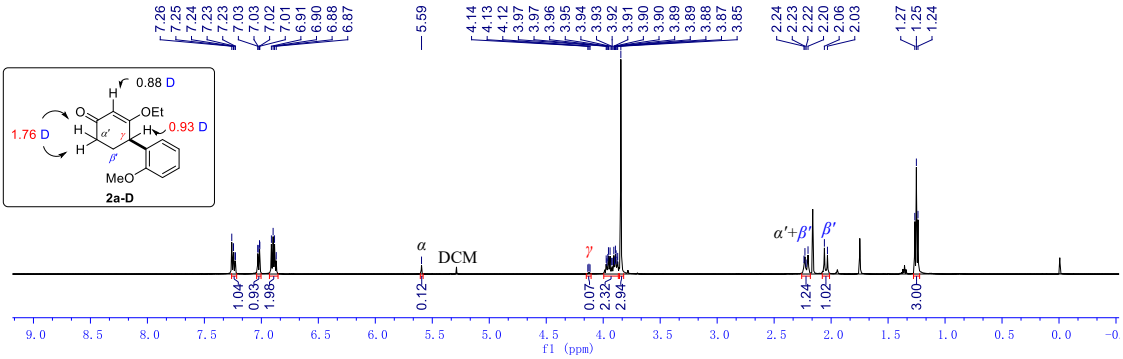
Synthesis of deuterated substrate **1a-D2**

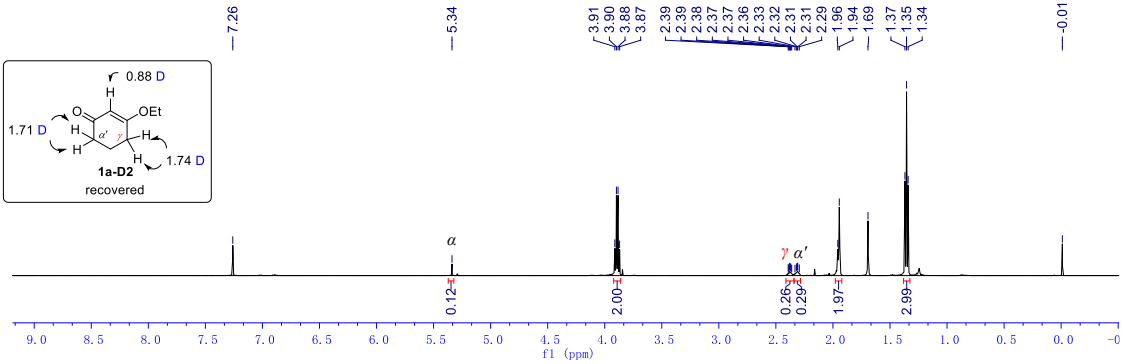
The deuterated substrate **1a-D2** was prepared according to the literature:[12] a reaction tube charged with **1a** (140 mg, 1.0 mmol), Cs_2CO_3 (0.98 g, 3.0 mmol), and DMSO-d_6 (2 mL) was sealed and heated at 80 °C for 8 h. The crude mixture was then cooled to room temperature and portioned by EtOAc (10 mL) and water (10 mL), the aqueous layer was extracted with EtOAc (5 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to give **1a-D2** with NMR purity in quantitative yields.



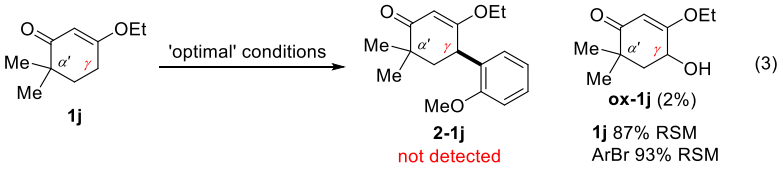
Following the 'optimal' conditions for Pd-catalyzed *γ*-arylation of *β*-alkoxy cyclohexenones except for prolonging the deprotonation time to 1 h due to the *α′*-KIE effect, **1a-D2** (1.0 mmol) was converted to *γ*-arylated product **2a-D** in 10% isolated yields and recovered 61% of the starting materials. The ^{1}H NMR spectra of **2a-D** showed 1.76 D (-0.03 D) of *α′*-site was retained and 0.86 D of *γ*-site was lost compared to substrate **1a-D2**. The deuterated ratio of the recovered **1a-D2** was also retained.



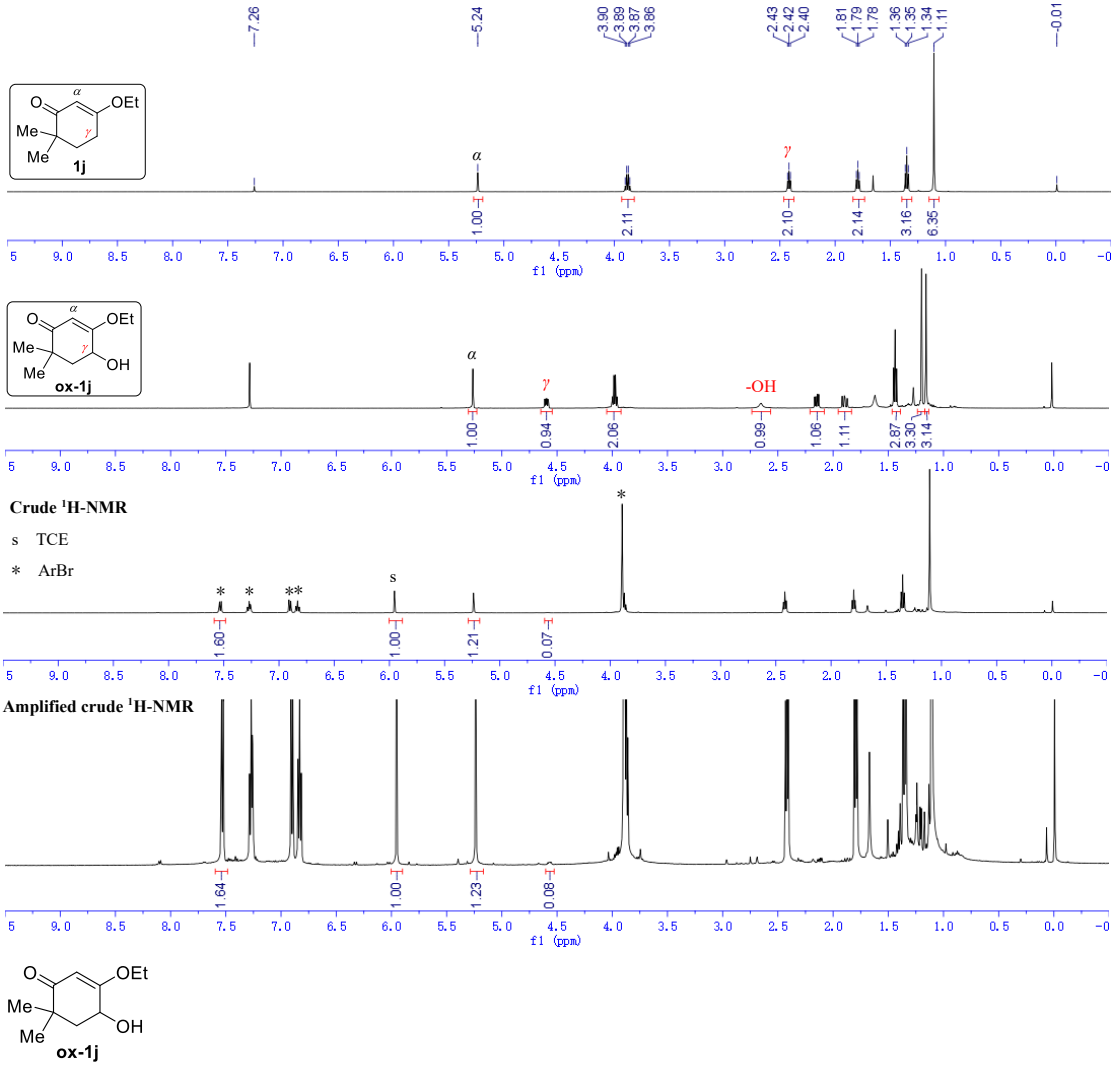




'Optimal' conditions using α'-site blocked substrate 1l (Scheme 4, eq 3)

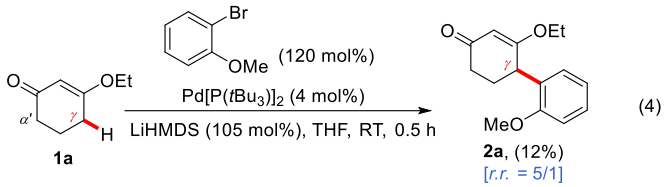


Following the 'optimal' conditions for Pd-catalyzed γ-arylation of β-alkoxy cyclohexenones except for replacing **1a** with α'-site blocked substrate **1j** (1.0 mmol). The crude NMR of reaction showed that no γ-arylated product **2-1j** was generated, instead 2% of γ-hydroxylated product **ox-1j** (spectroscopic data were listed bellow) was detected, and 87% of **1j** was recovered.



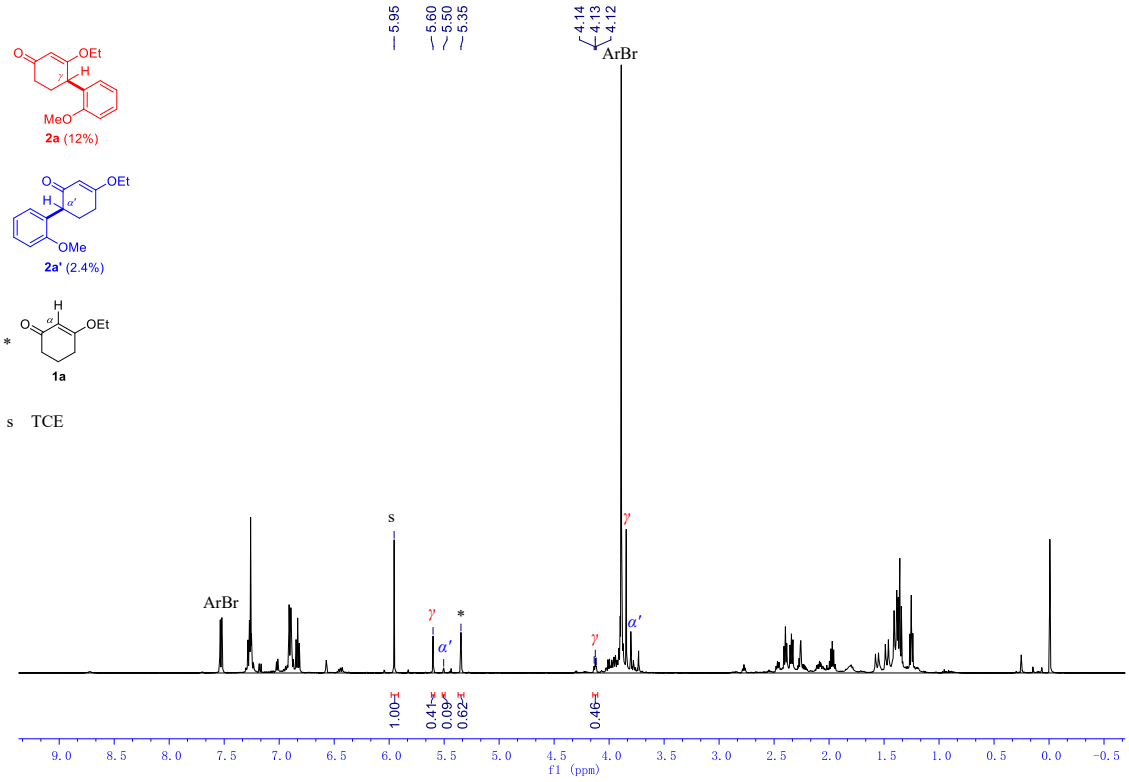
3-ethoxy-4-hydroxy-6,6-dimethylcyclohex-2-en-1-one (ox-1j): colorless oil, (2.4 mg, 2% yield). R_f = 0.20 (petroleum ether/EtOAc = 2:1). (purified by silica gel eluted with petroleum ether/EtOAc = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.24 (s, 1H), 4.57 (dd, J = 10.0, 5.5 Hz, 1H), 3.95 (q, J = 7.0 Hz, 2H), 2.63 (s, 1H), 2.12 (dd, J = 13.1, 5.5 Hz, 1H), 1.87 (dd, J = 13.0, 10.0 Hz, 1H), 1.41 (t, J = 7.0 Hz, 3H), 1.17 (s, 3H), 1.13 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.7, 173.7, 100.8, 65.6, 65.1, 43.4, 41.6, 25.9, 25.3, 14.2. **HR-ESI-MS** (m/z): calculated for $C_{10}H_{17}O_3$ $[M+H]^+$: 185.1172, found: 185.1170.

γ-Arylation of 1a catalyzed by biligated Pd(0) (Scheme 4, eq 4)

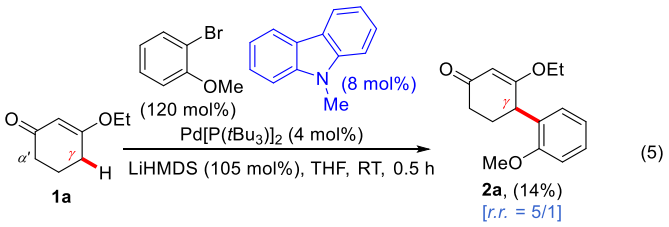


(4)

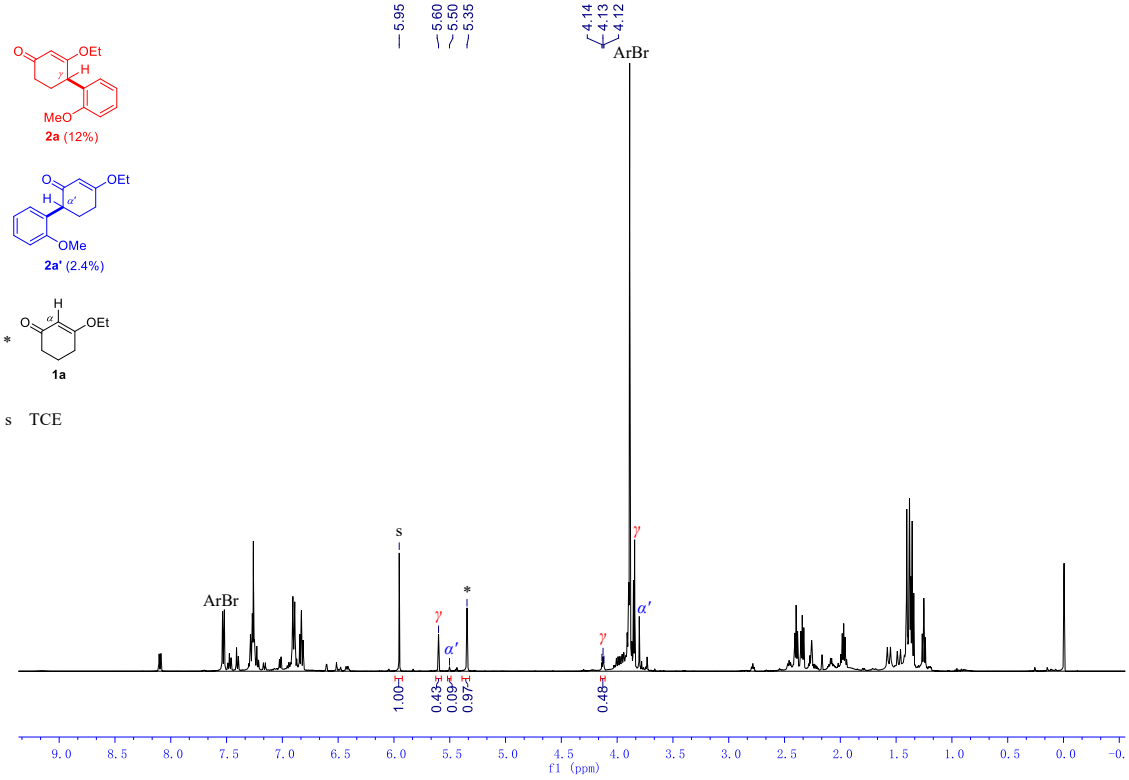
Following the 'optimal' conditions for Pd-catalyzed γ-arylation of β-alkoxy cyclohexenones except for replacing Pd-G4/P*t*Bu$_3$ with Pd[P(*t*Bu$_3$)]$_2$, **1a** (1.0 mmol) was converted to γ-arylated product **2a** in 12% NMR yields and recovered 17% of the starting materials.



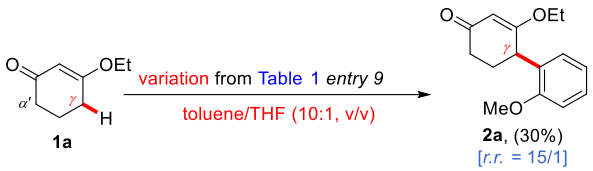
The influence of NMC to γ-Arylation (Scheme 4, eq 5)



Following the 'optimal' conditions for Pd-catalyzed γ-arylation of β-alkoxy cyclohexenones except for replacing Pd-G4/P*t*Bu$_3$ with Pd[P(*t*Bu$_3$)]$_2$ and adding of 8 mol% of NMC, **1a** (1.0 mmol) was converted to γ-arylated product **2a** in 14% NMR yields and recovered 30% of the starting materials.

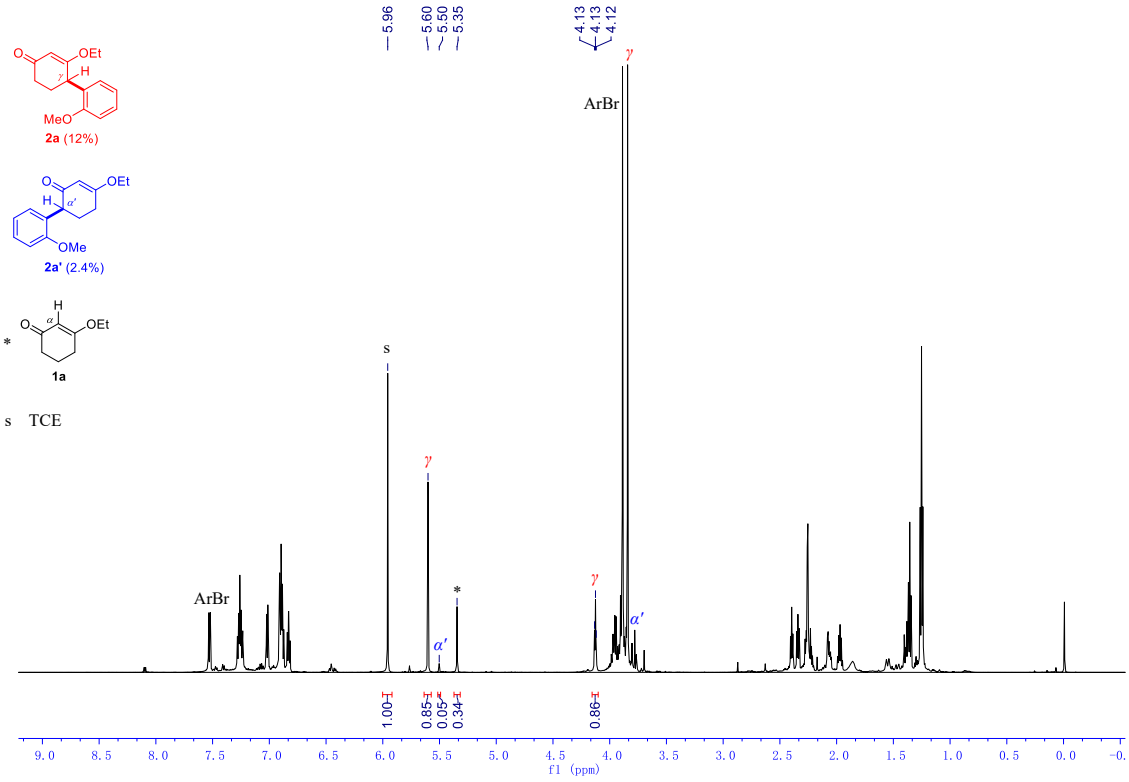


The influence of THF on γ-Arylation (Scheme 4, eq 6)



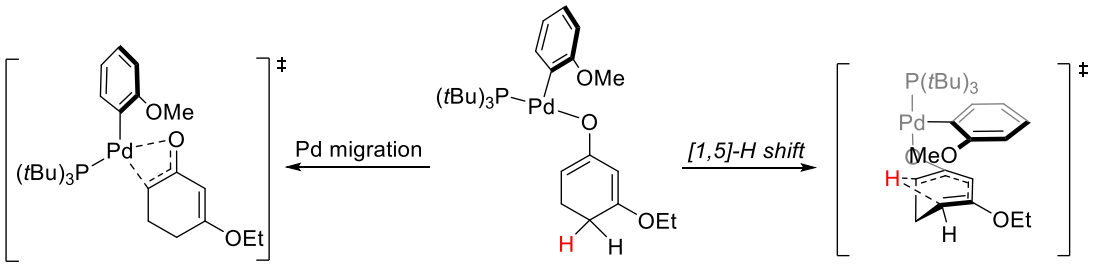
(6)

Following the conditions listed in Table 1 (entry 9) except for using toluene/THF (10:1, v/v) as the co-solvents, **1a** (1.0 mmol) was converted to γ-arylated product **2a** in 30% NMR yields and recovered 12% of the starting materials.

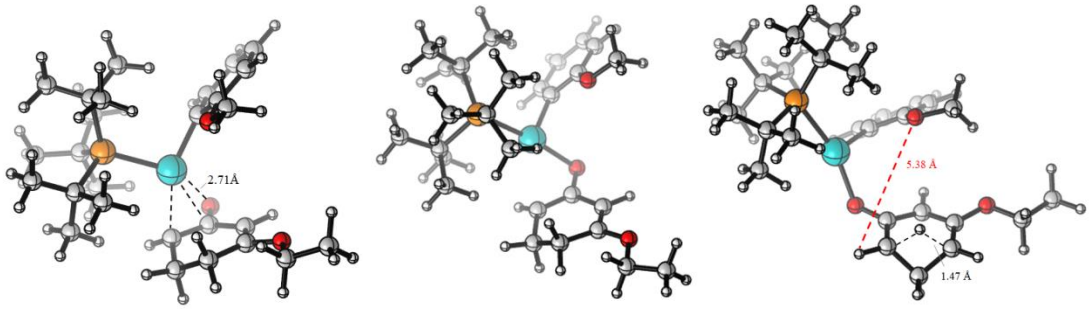


Computational Details.

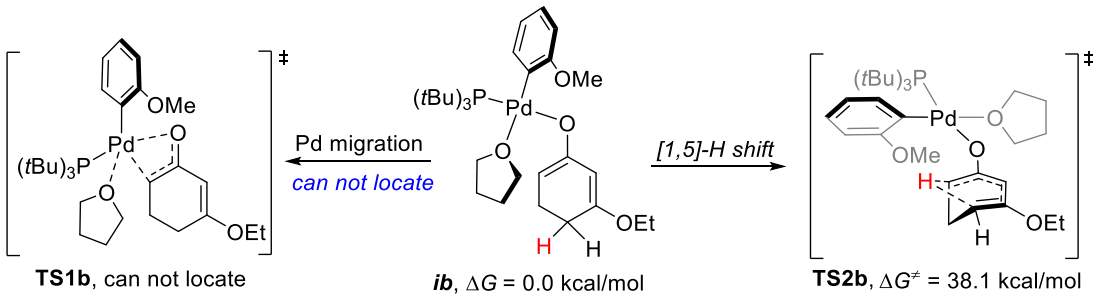
All DFT calculations were performed with Gaussian 09.[13] Geometry optimizations and frequency calculations were performed with or without SMD solvent model (tetrahydrofuran) using the B3LYP functional and combination of basis set LANL2DZ for Pd and 6-31G (d) for other atoms. Single point energies were calculated with the M062X functional and a mixed basis set SDD for Pd and 6-311+G (d, p) for other atoms.[14] The 3D structures were prepared using CYLView [15] and Multiwfn.[16]



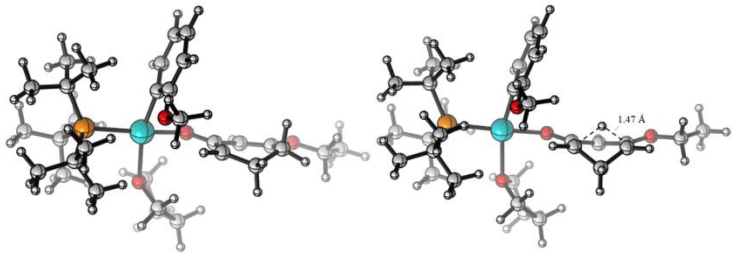
TS1a, $\Delta G^{\neq}$ = 11.4 kcal/mol ***ia***, ΔG = 0.0 kcal/mol **TS2a**, $\Delta G^{\neq}$ = 47.3 kcal/mol



TS1a, $\Delta G^{\neq}$ = 11.4 kcal/mol ***ia***, ΔG = 0.0 kcal/mol **TS2a**, $\Delta G^{\neq}$ = 47.3 kcal/mol



TS1b, can not locate ***ib***, ΔG = 0.0 kcal/mol **TS2b**, $\Delta G^{\neq}$ = 38.1 kcal/mol



ib, ΔG = 0.0 kcal/mol **TS2b**, $\Delta G^{\neq}$ = 38.1 kcal/mol

Kinetic data for the 'optimal' conditions

Table S3. Kinetic data for the 'optimal' conditions (0-30 min)

entry	time(min)	**2a** (mmol)	**1a** (mmol)
1	0	0	1.0
2	5	0.055	0.823
3	10	0.218	0.524
4	15	0.329	0.348
5	20	0.466	0.240
6	25	0.556	0.195
7	30	0.701	0.158

The corresponding concentration of each component (**2a** and **1a**) was determined by crude NMR analysis using 1,1,2,2-tetrachloroethane (TCE) as the internal standard.

Table S4. Kinetic data for the 'optimal' conditions (0-120 min)

entry	time(min)	**2a** (mmol)	**1a** (mmol)
1	0	0	1.0
2	15	0.394	0.420
3	30	0.719	0.162
4	45	0.716	0.150
5	60	0.716	0.161
6	75	0.712	0.156
7	90	0.720	0.136
8	105	0.718	0.161
9	120	0.727	0.158

The corresponding concentration of each component (**2a** and **1a**) was determined by crude NMR analysis using 1,1,2,2-tetrachloroethane (TCE) as the internal standard.

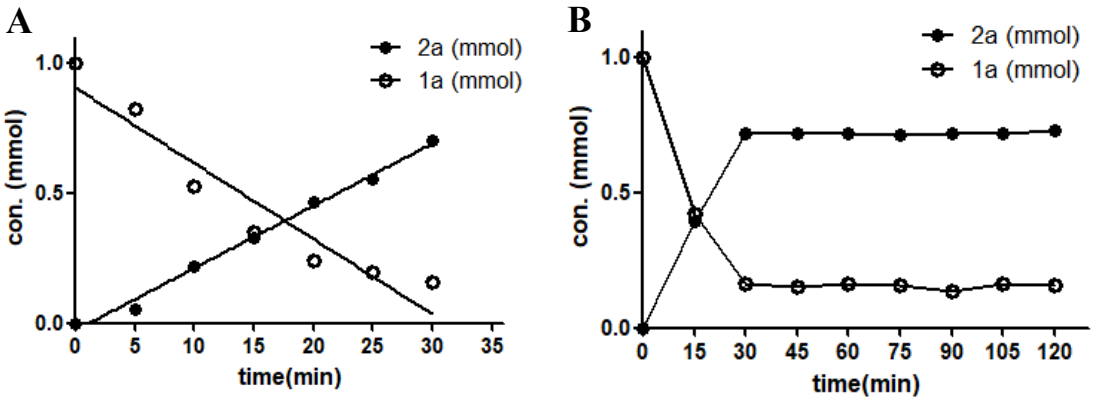
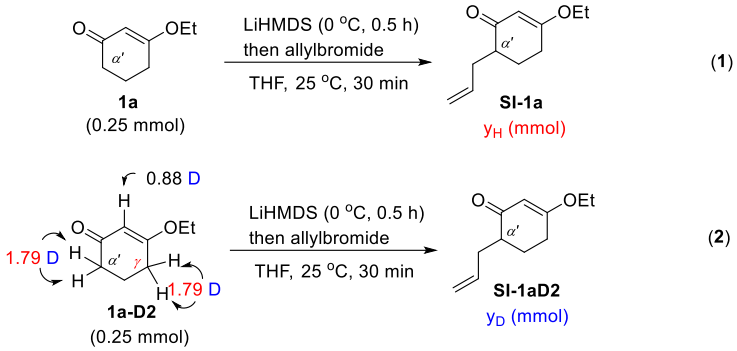


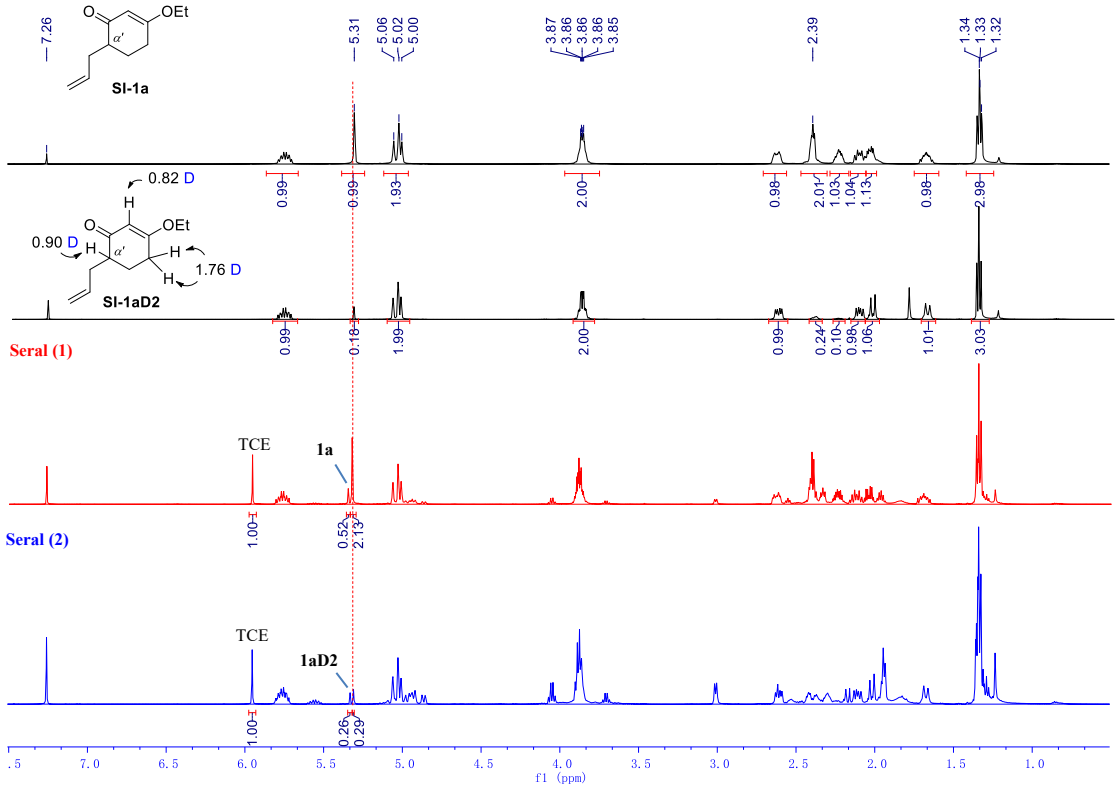
Figure S4. Kinetic profiles (concentration/mmol vs time/min) for the 'optimal' conditions: (**A**) 0 – 30 min; (**B**) 0 – 120 min.

Experimental data for KIE (25°C)

Determination of *α′*-KIE



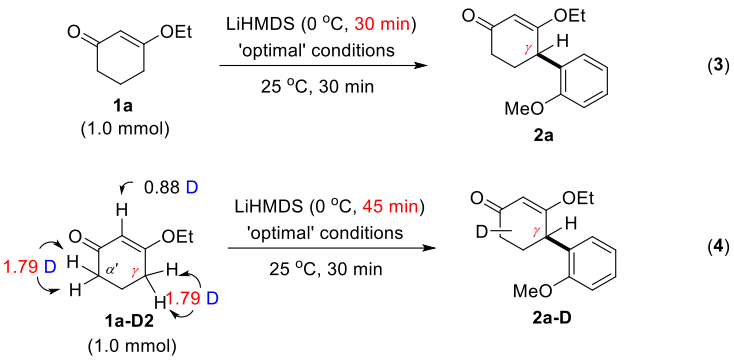
The *α′*-KIE value (k_H/k_D) was determined by two separate, side-by-side reactions serial (**1**) and (**2**).[17,18] The k_H/k_D value was determined by ^{1}H NMR of crude products from serial (**1**) and (**2**) using 1,1,2,2-tetrachloroethane (TCE) (2.0 mg, 0.01144 mmol) as internal standard based on three independent experiments.



No.	y_H (mmol)	y_D (mmol)	KIE (k_H/k_D)
1	0.122	0.092	1.32
2	0.126	0.086	1.46
3	0.124	0.090	1.37

The ***α′*-KIE** value was determined as **1.38 ± 0.07**

Determination of *γ*-KIE



Based on above results, the *γ*-KIE value (k_H/k_D) was determined by two separate, side-by-side reactions serial (**3**) and (**4**) under the 'optimal' conditions except for prolonging the deprotonation time to 45 min for serial (**4**) due to the *α'*-KIE effect. The ***γ*-KIE** value was determined as slope(serial-3)/slope(serial-4) based on following data, the final result is **6.38 ± 0.06**.

Table S5. Kinetic data for the serial (**3**) and (**4**) (0-30 min)

Serial (3)			**Serial (4)**		
entry	time(min)	**2a** (mmol)	entry	time(min)	**2a-D** (mmol)
1	0	0	1	0	0
2	5	0.055	2	5	0.0156
3	10	0.218	3	10	0.0358
4	15	0.329	4	15	0.063
5	20	0.466	5	20	0.0717
6	25	0.556	6	25	0.095
7	30	0.701	7	30	0.101

The corresponding concentration of **2a** and **2a-D** was determined by crude NMR analysis using 1,1,2,2-tetrachloroethane (TCE) as the internal standard.

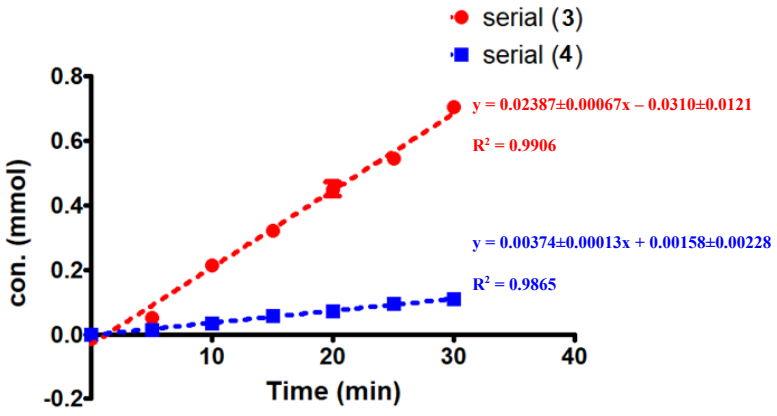
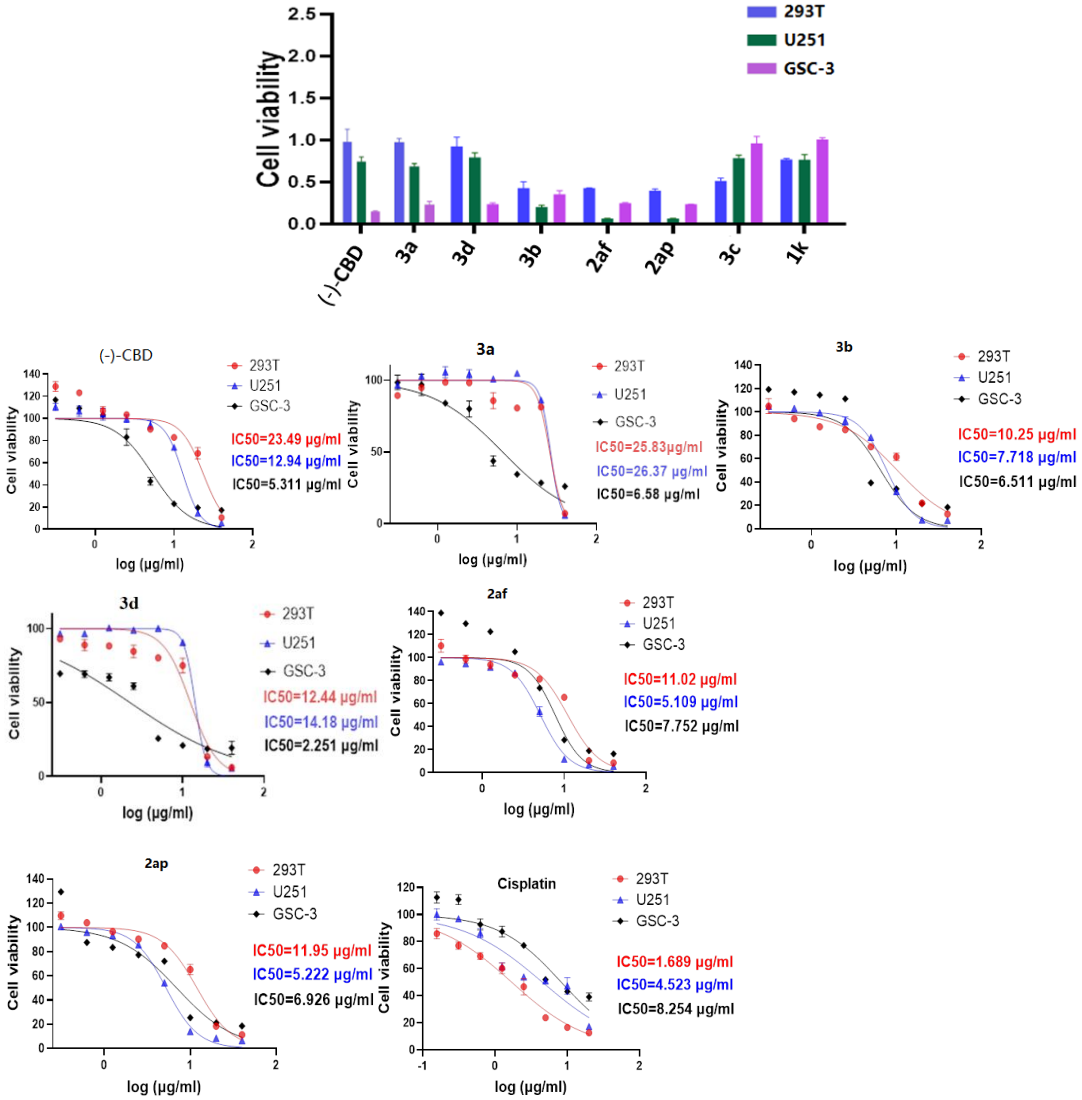


Figure S5. Plots of [**2a**] (red) and [**2a-D**] (blue) vs time (min) for serial (3) and (4). Results ± SEM are the average of two independent experiments.

8. Biological Assays.

The anti-proliferative effects of synthetic CBD analogues against GSC-3, U251, and 293T cells were measured by MTS method.[19] GSC-3 cells were established by Kunming Institute of Zoology from two human glioblastoma multiform samples. The glioma stem cells were cultured in serum-free medium DMEM supplemented with 1 × B27, bFGF and 50 ng/mL EGF and seeded in the pre-coated dishes with laminin and digested with TryplE express in a 37 °C, 5% CO_2 cell incubator for 5 min. The cells were suspended and seeded on the pre-coated dish with laminin. The cells were digested and seeded on 96-well-plate with 20,000 cells per well. The tested compounds were added in a serial gradient concentration (80, 40, 20, 10, 5, 2.5 μg/mL), then the treated cells were cultured in a cell incubator for 72 h. MTS reagent was diluted 1:10 with fresh medium and mixed thoroughly. The fresh medium was added after removing the old medium. Then, the cells were incubated for 1.5 h. Absorbance was measured by Hybrid Reader (BioTek synergy H1) at 490 nm. The cell viability was evaluated by percentage compared with DMSO control group. The half-maximal inhibitory concentration (IC_{50}) was measured and calculated by Graph Pad Prism 5 software.



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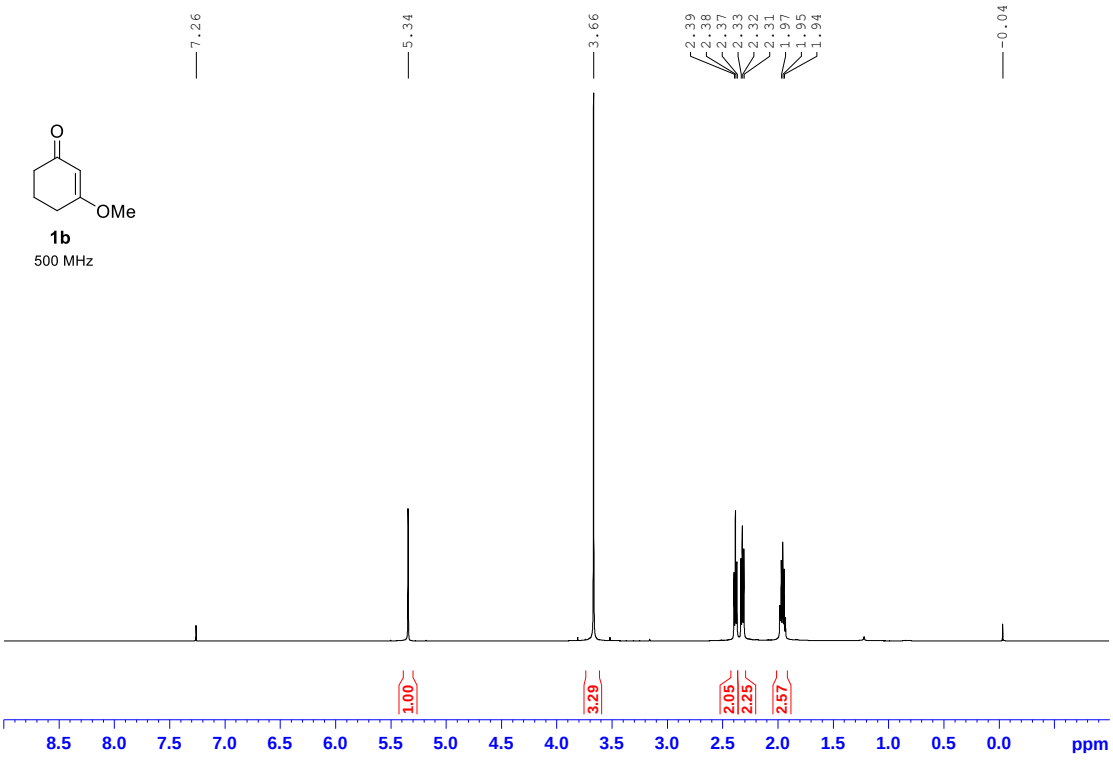
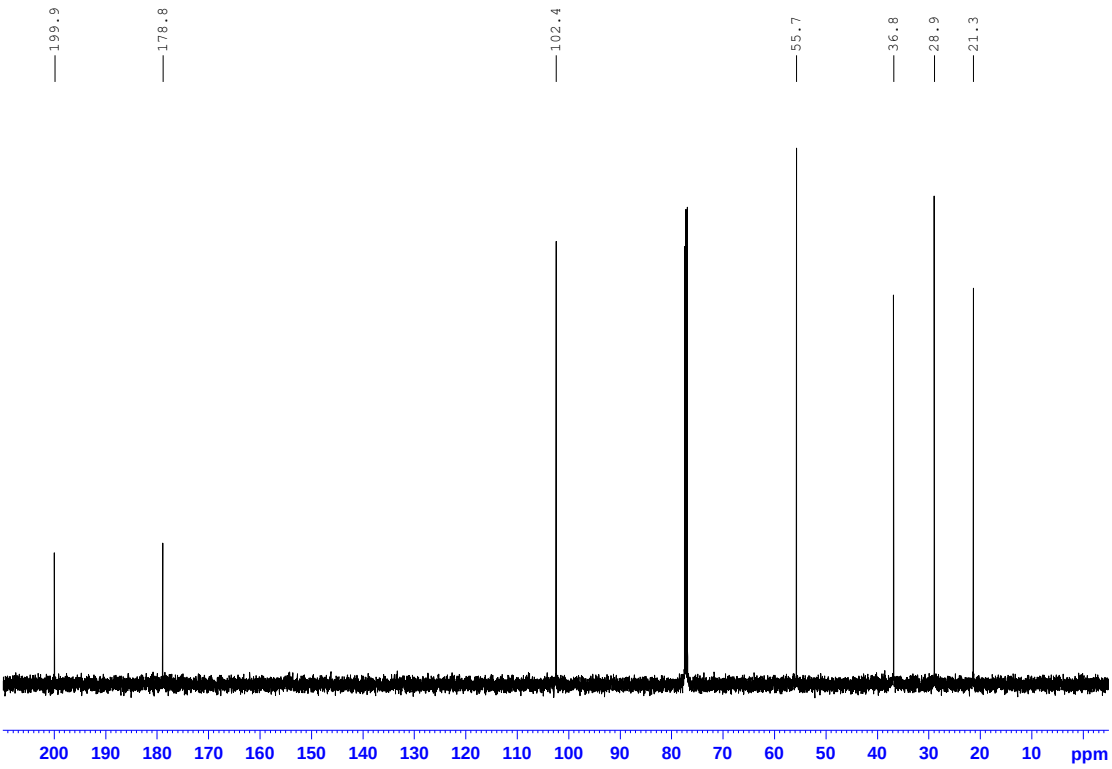
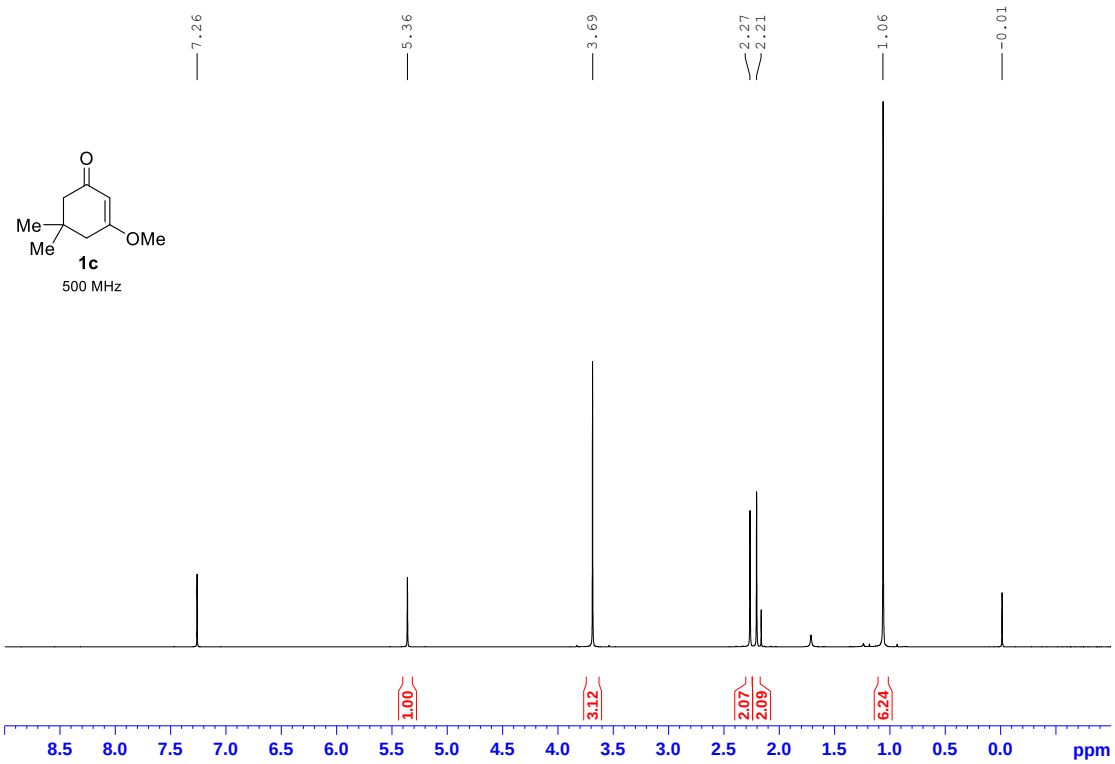
10. NMR spectra copies for synthetic compounds



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2.07
2.09
6.24
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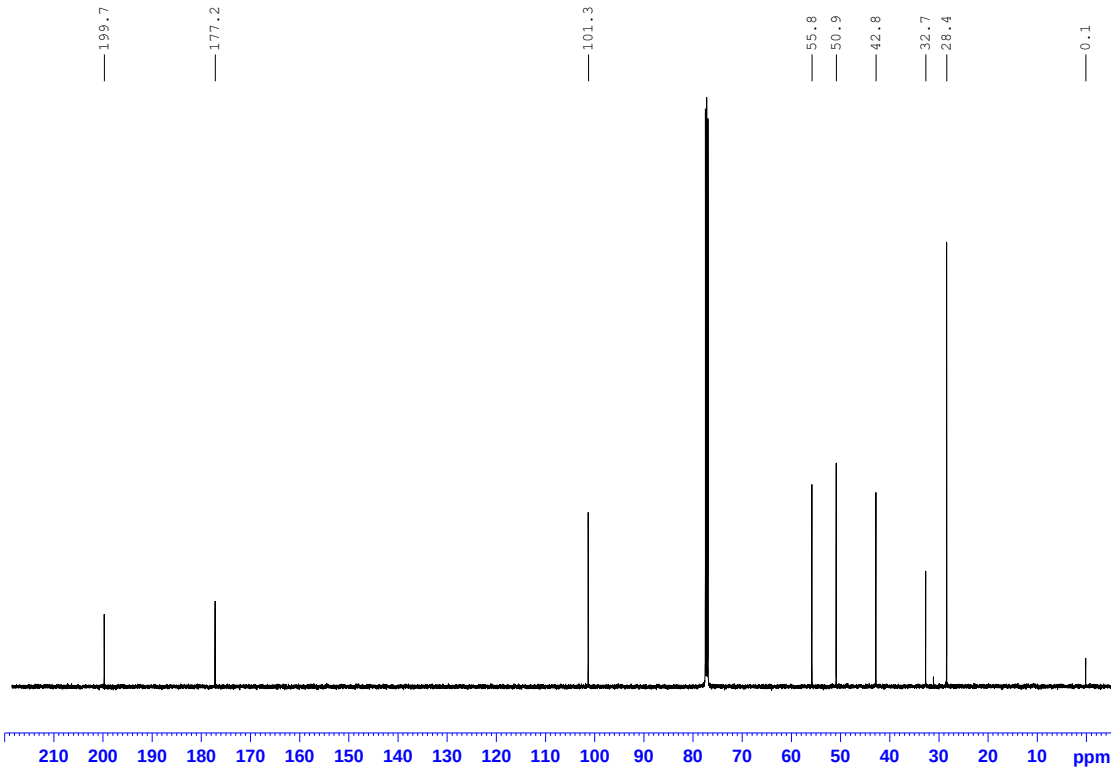
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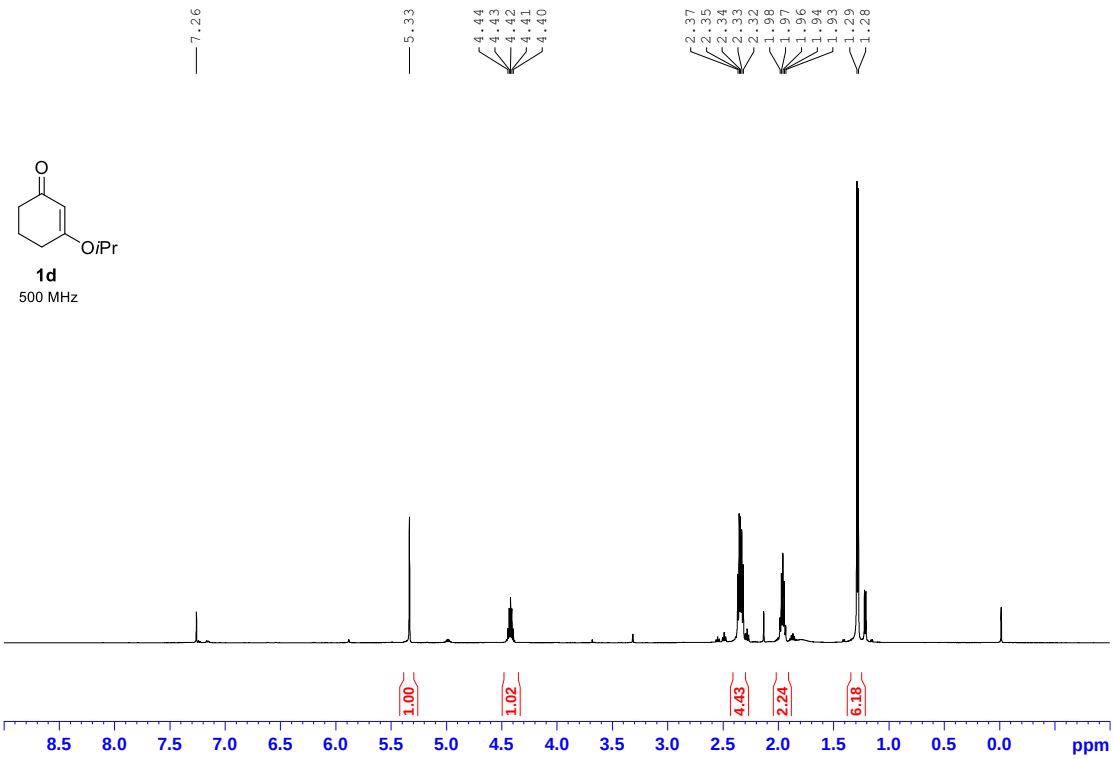
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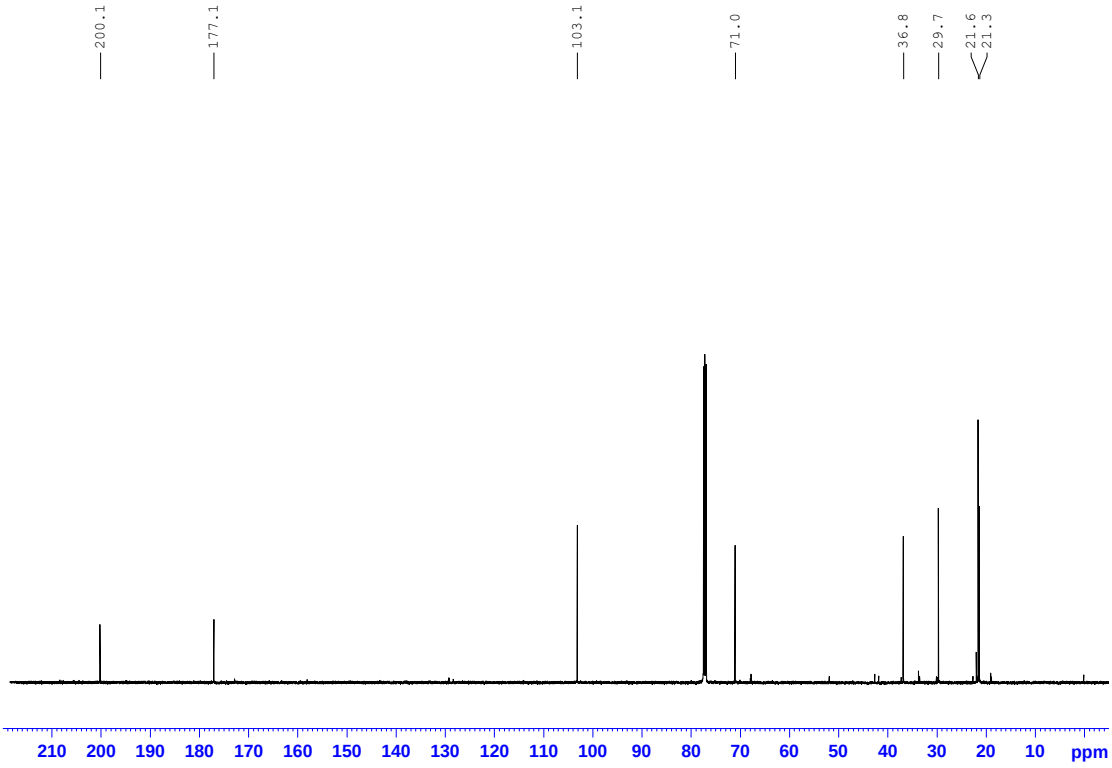
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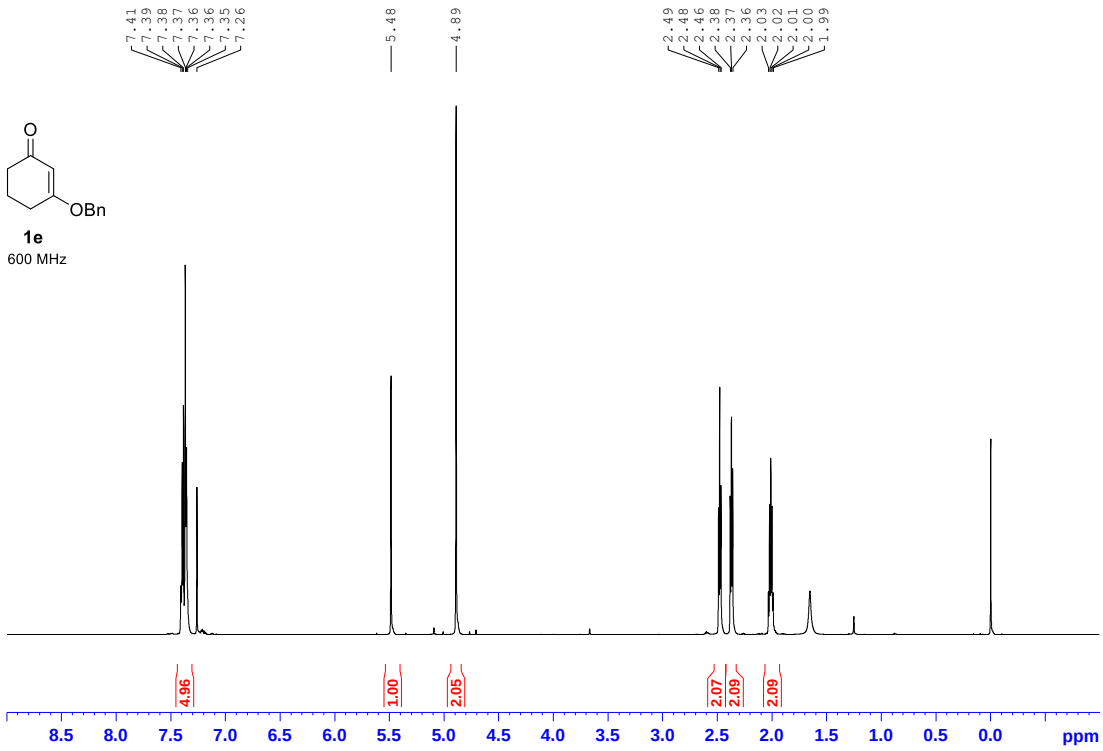
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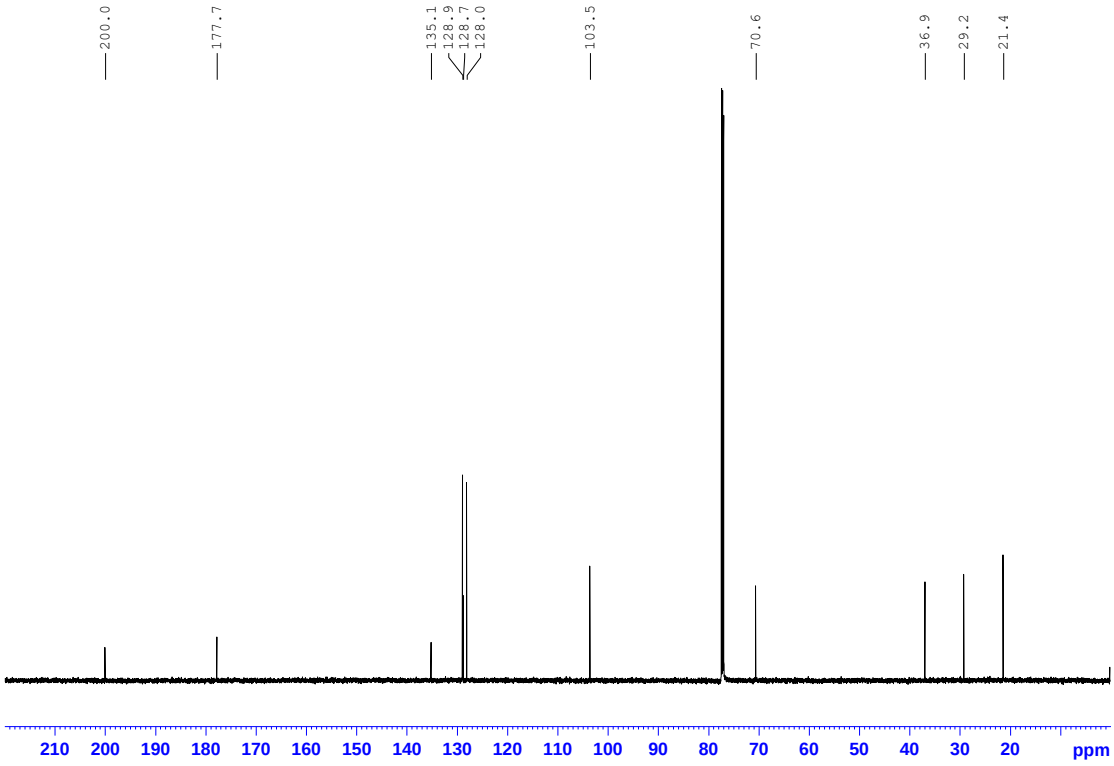
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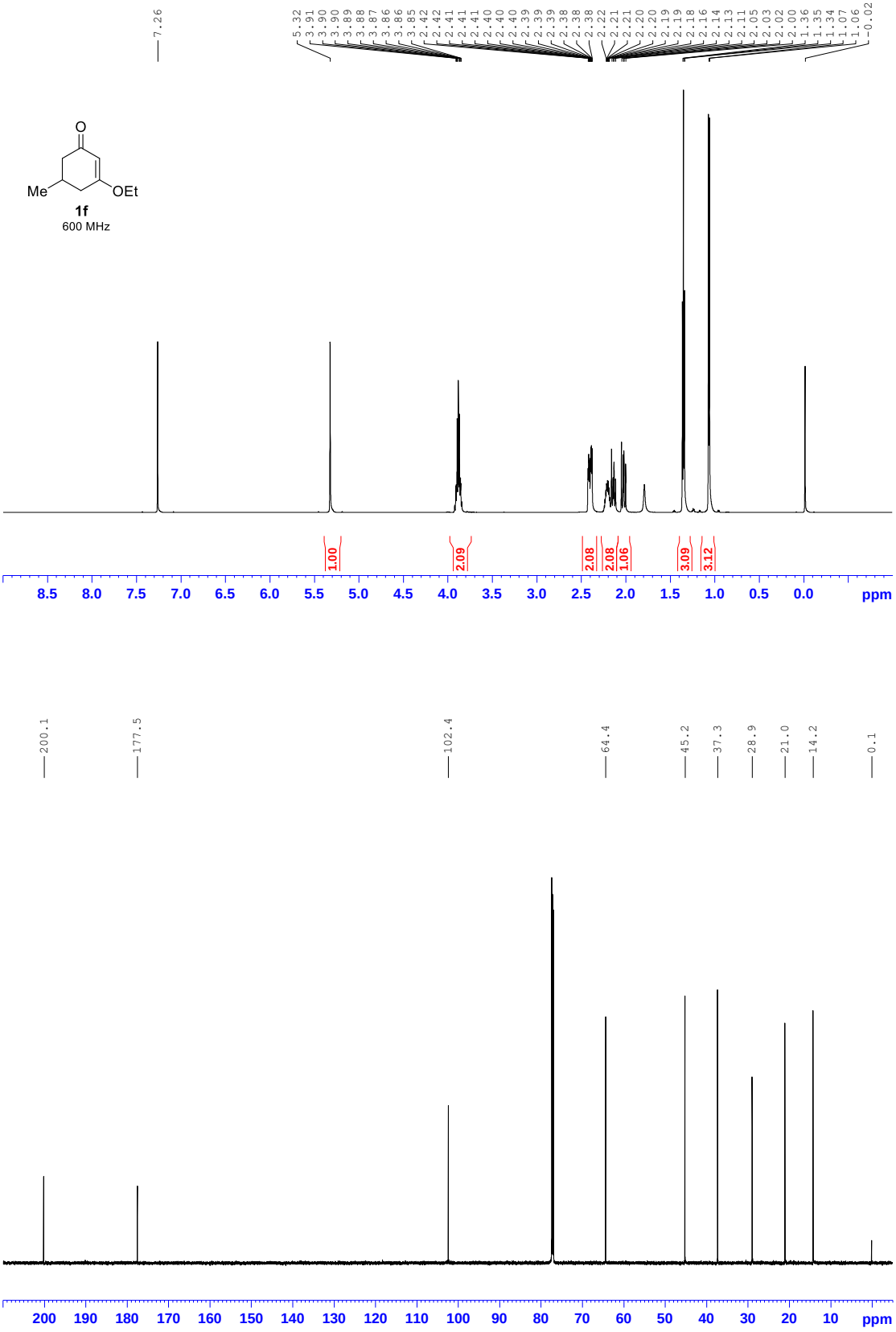
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2.13
2.11
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2.02
2.00
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1.06
0.02
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Me
OEt
1f
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1.00
2.09
2.08
2.08
1.06
3.09
3.12
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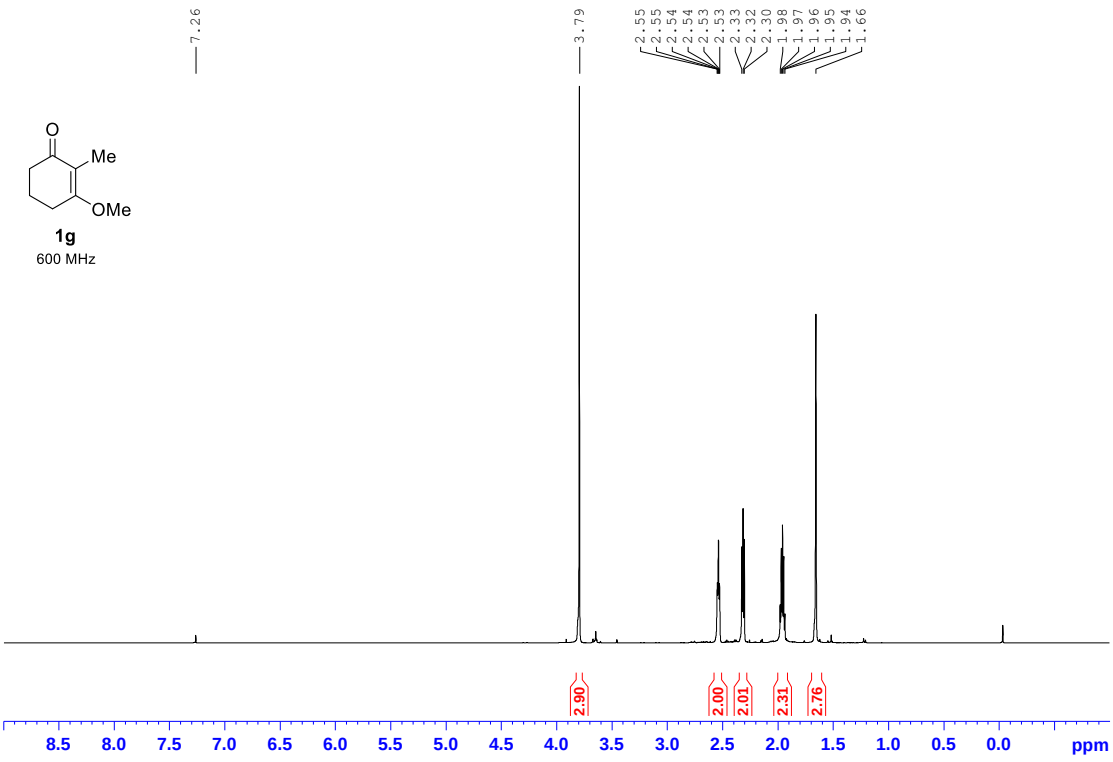
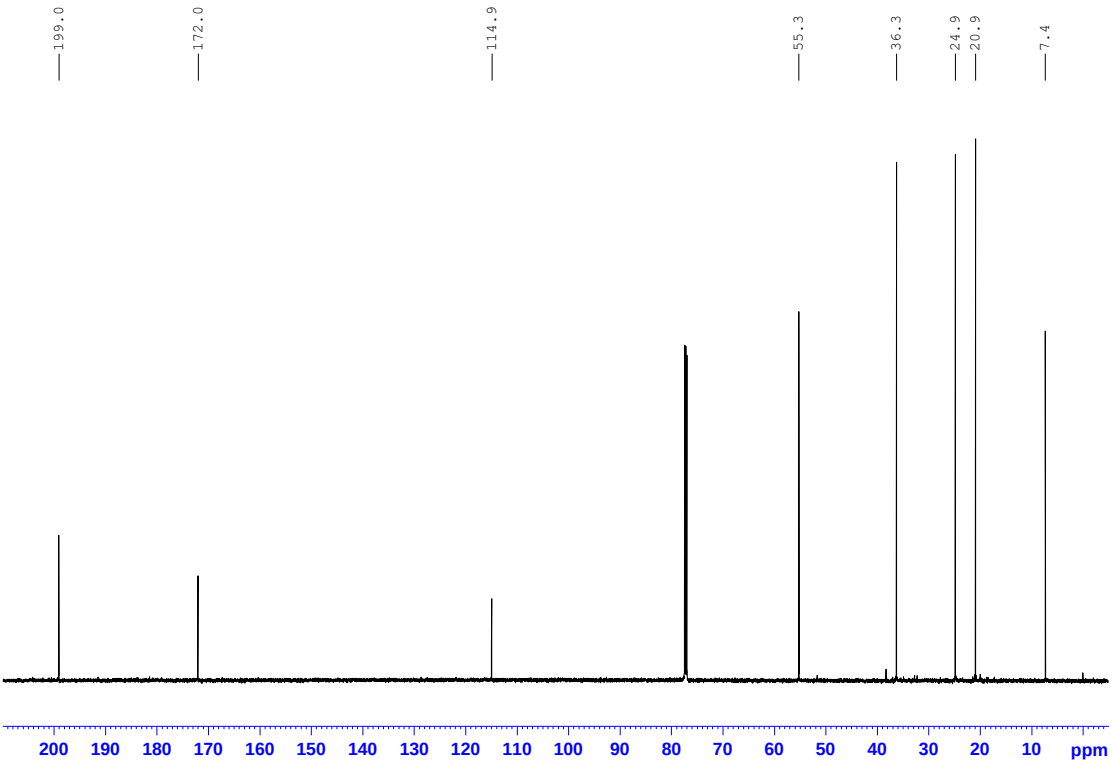
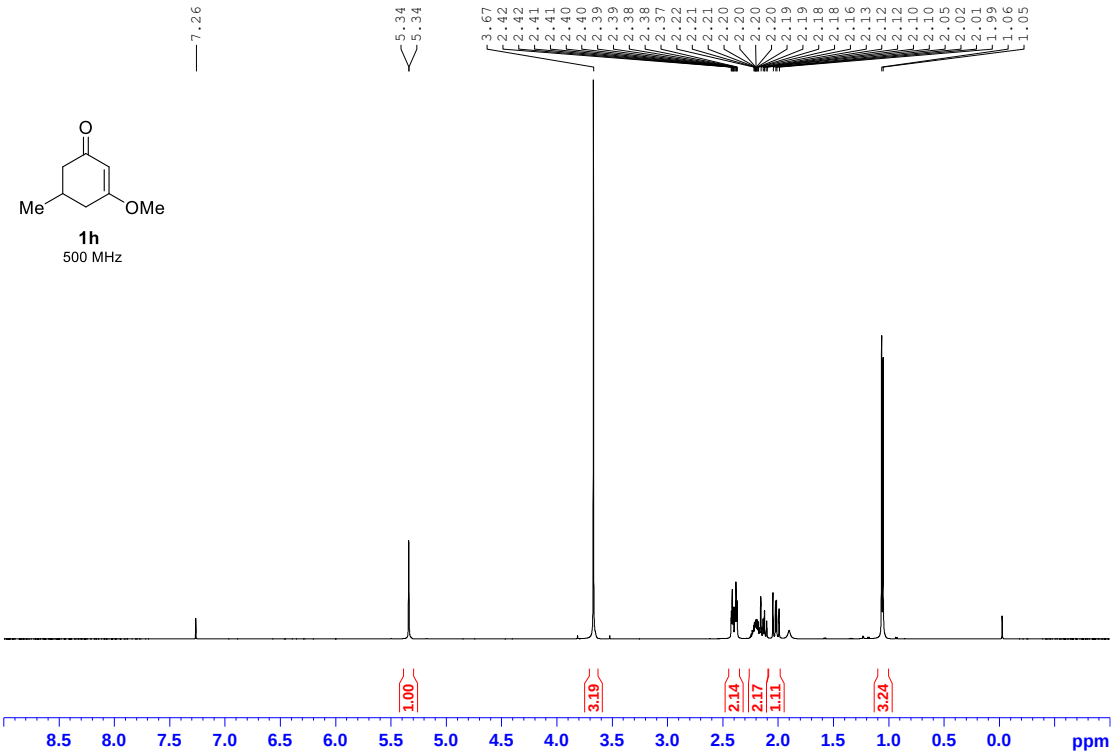
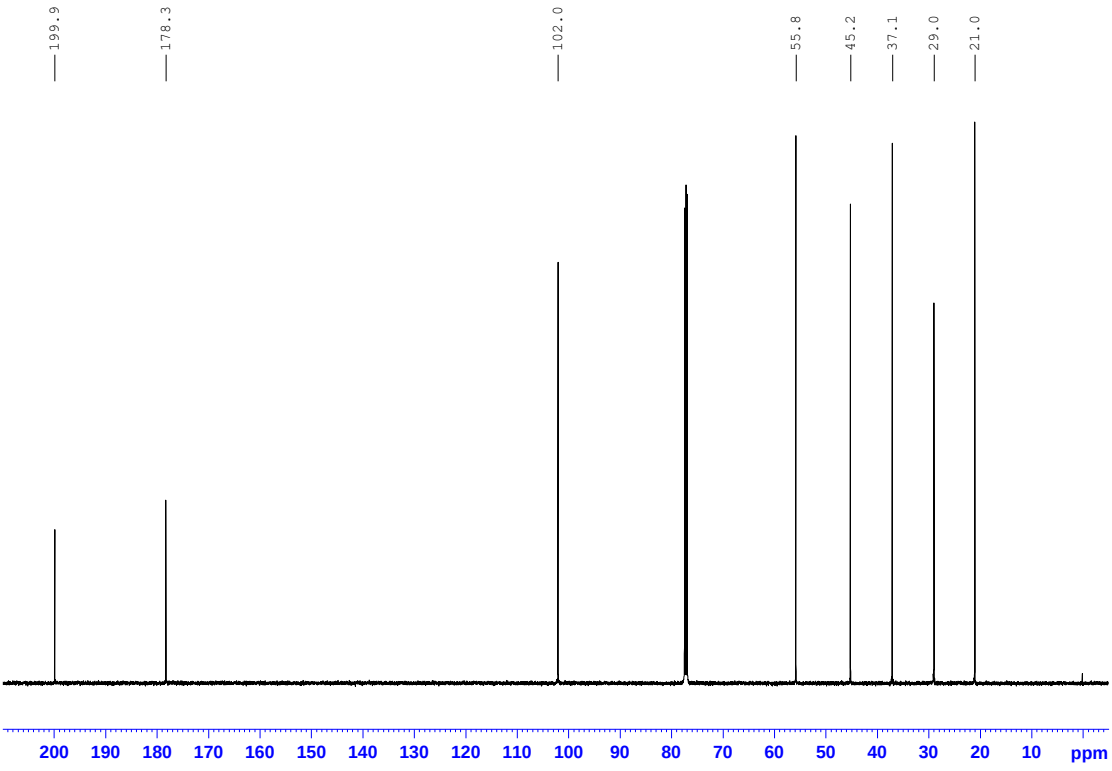
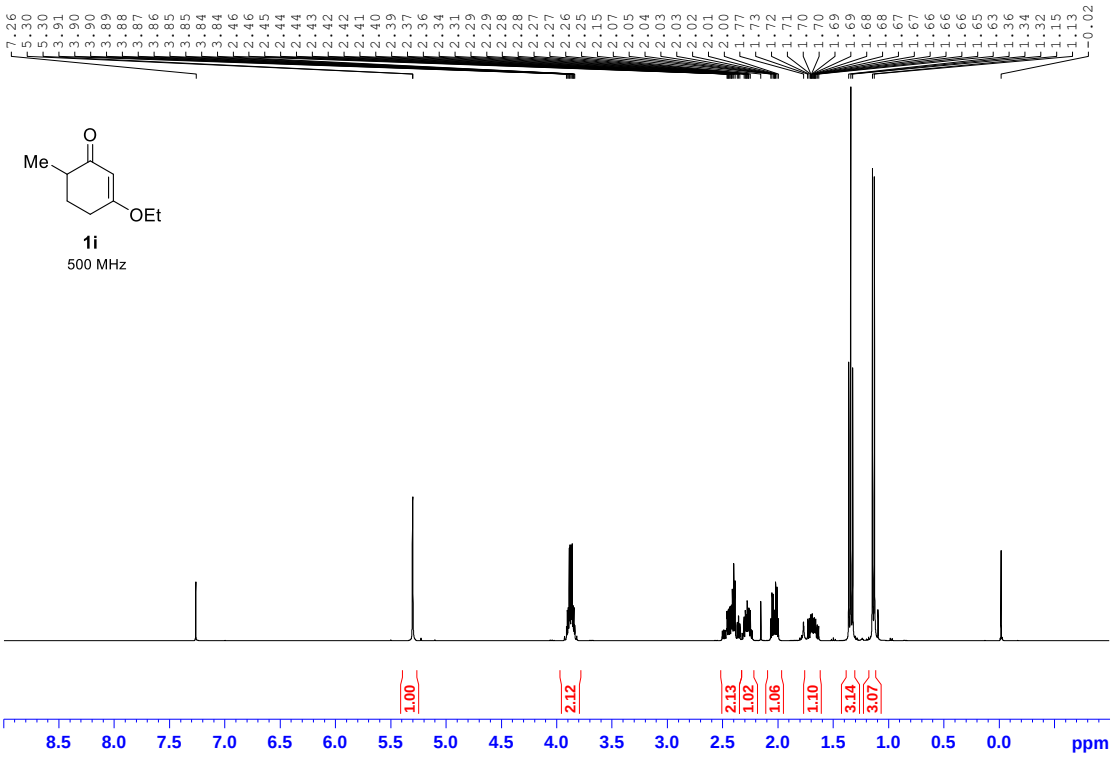
200.1
177.5
102.4
64.4
45.2
37.3
28.9
21.0
14.2
0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

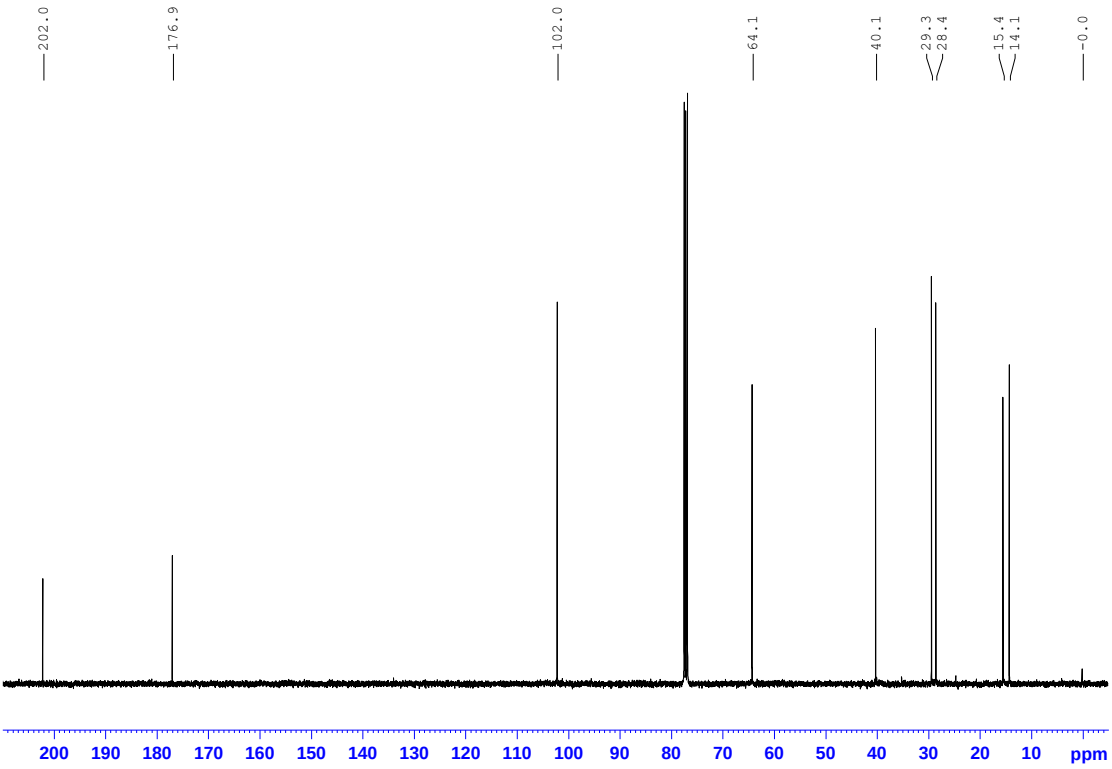

7.26
3.79
2.55
2.55
2.54
2.54
2.53
2.53
2.33
2.32
2.30
1.98
1.97
1.96
1.95
1.94
1.66
O
Me
OMe
1g
600 MHz
2.90
2.00
2.01
2.31
2.76
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

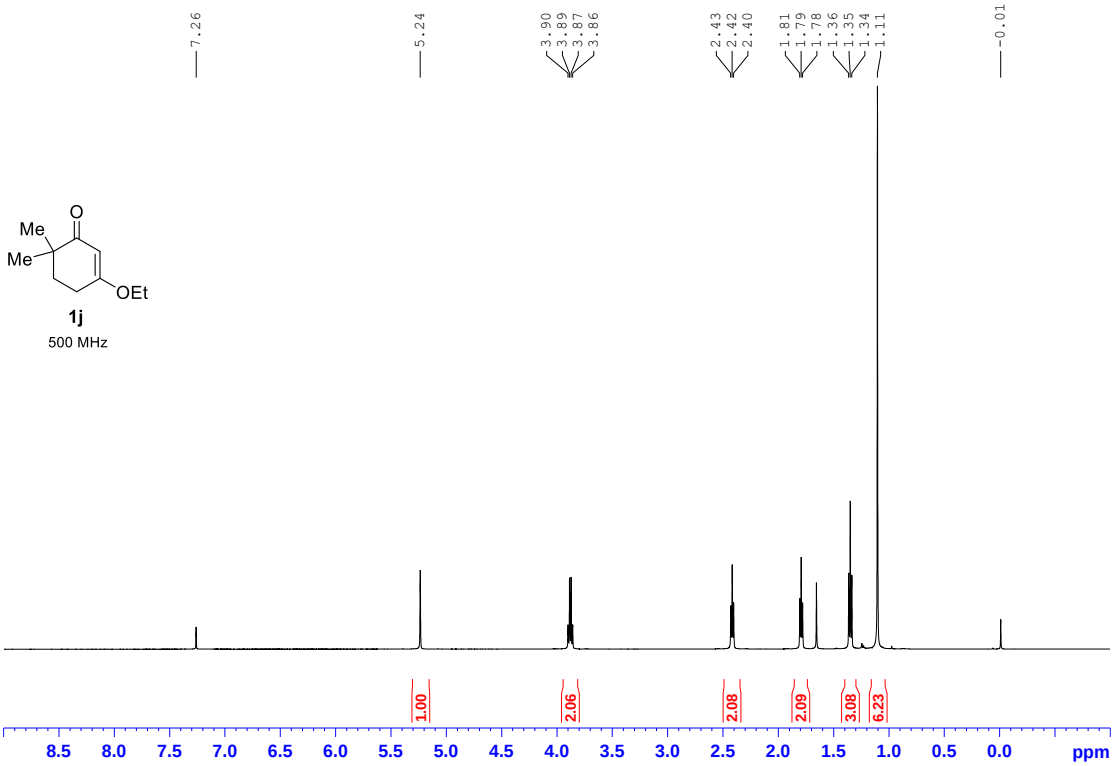

199.0
172.0
114.9
55.3
36.3
24.9
20.9
7.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

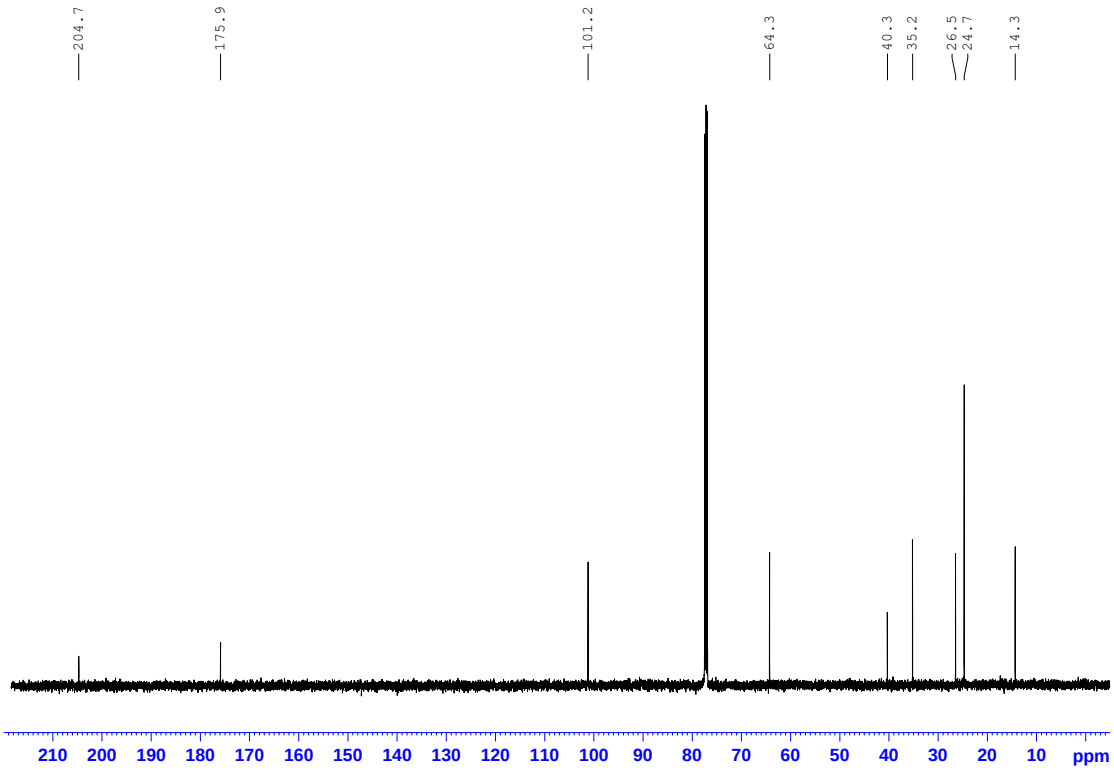

7.26
5.34
5.34
3.67
2.42
2.42
2.41
2.41
2.40
2.40
2.39
2.39
2.38
2.38
2.37
2.22
2.21
2.21
2.20
2.20
2.20
2.20
2.19
2.19
2.18
2.18
2.16
2.13
2.12
2.12
2.10
2.10
2.05
2.02
2.01
1.99
1.06
1.05
O
Me
OMe
1h
500 MHz
1.00
3.19
2.14
2.17
1.11
3.24
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

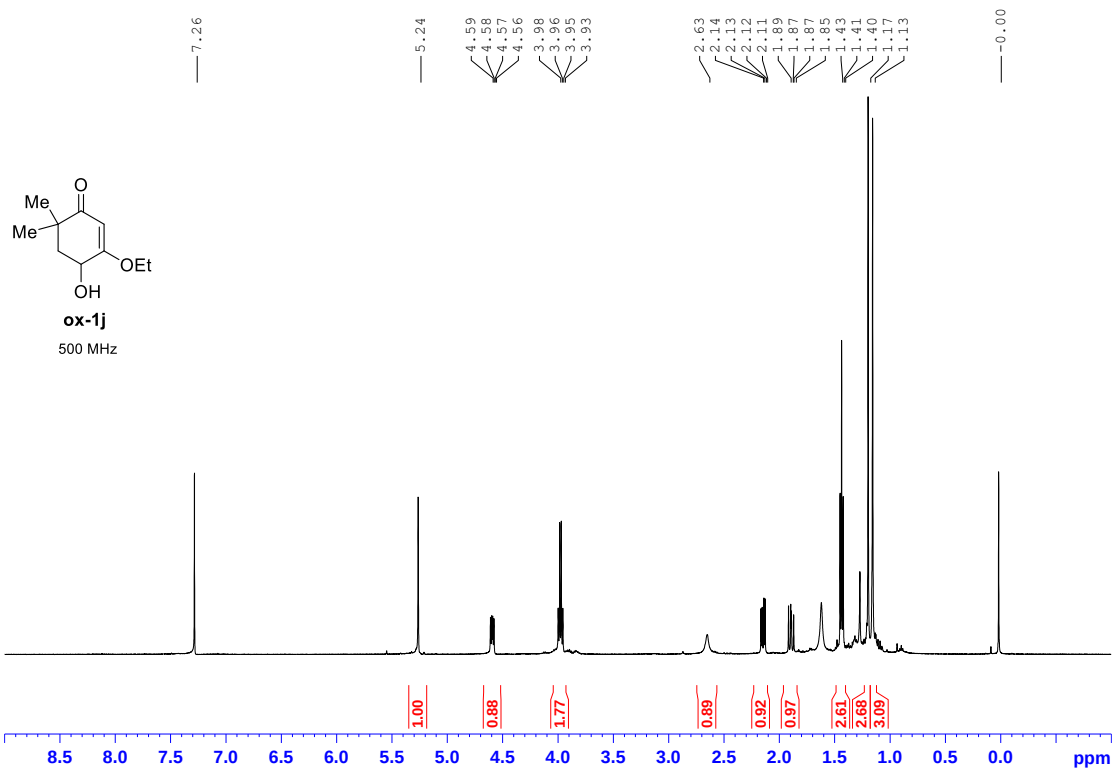

199.9
178.3
102.0
55.8
45.2
37.1
29.0
21.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

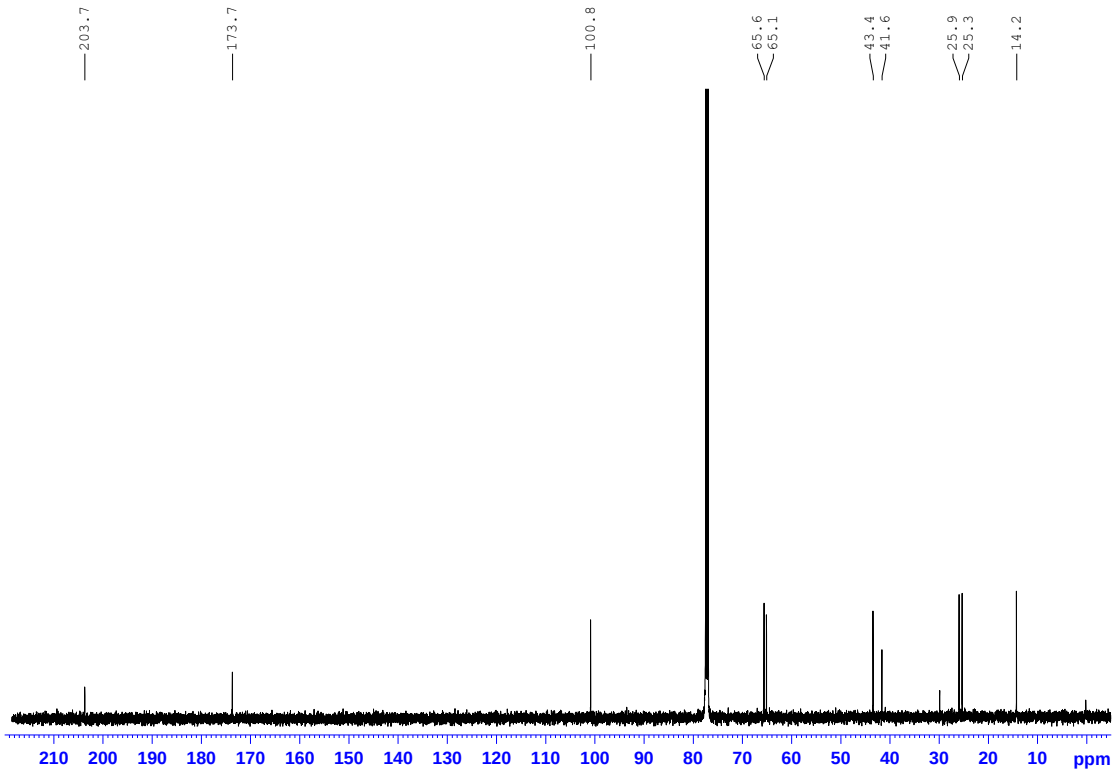

Me
O
OEt
1i
500 MHz
1.00
2.12
2.13
1.02
1.06
1.10
3.14
3.07
ppm

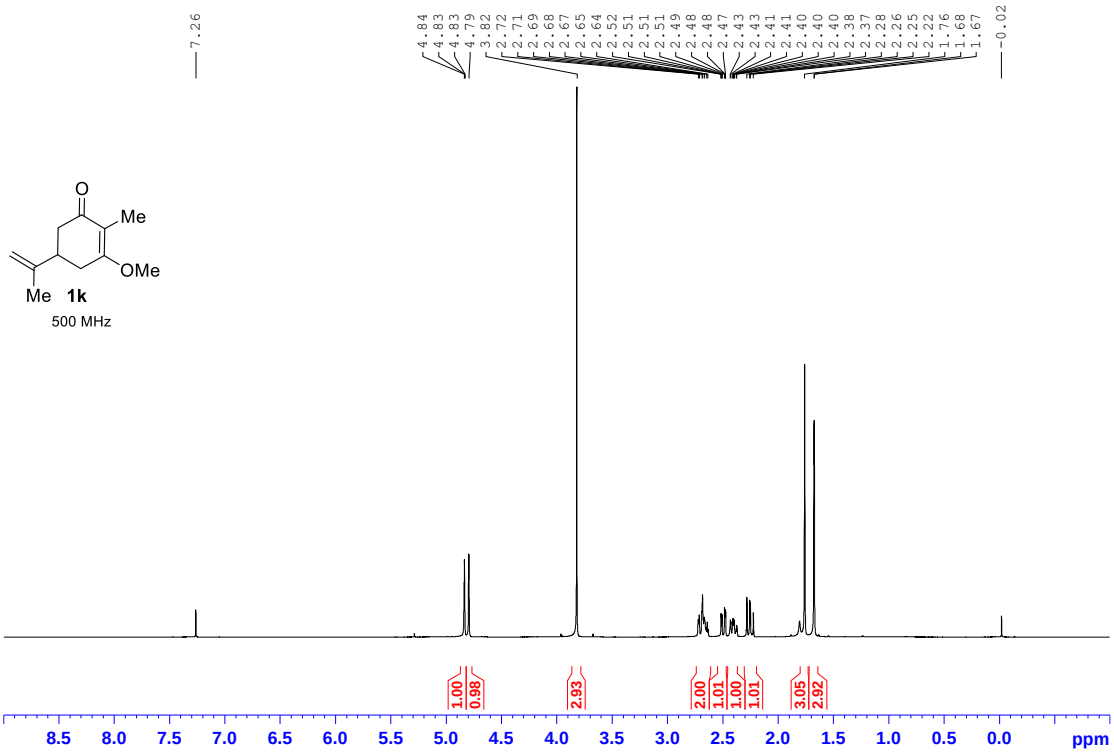

202.0
176.9
102.0
64.1
40.1
29.3
28.4
15.4
14.1
0.0
ppm

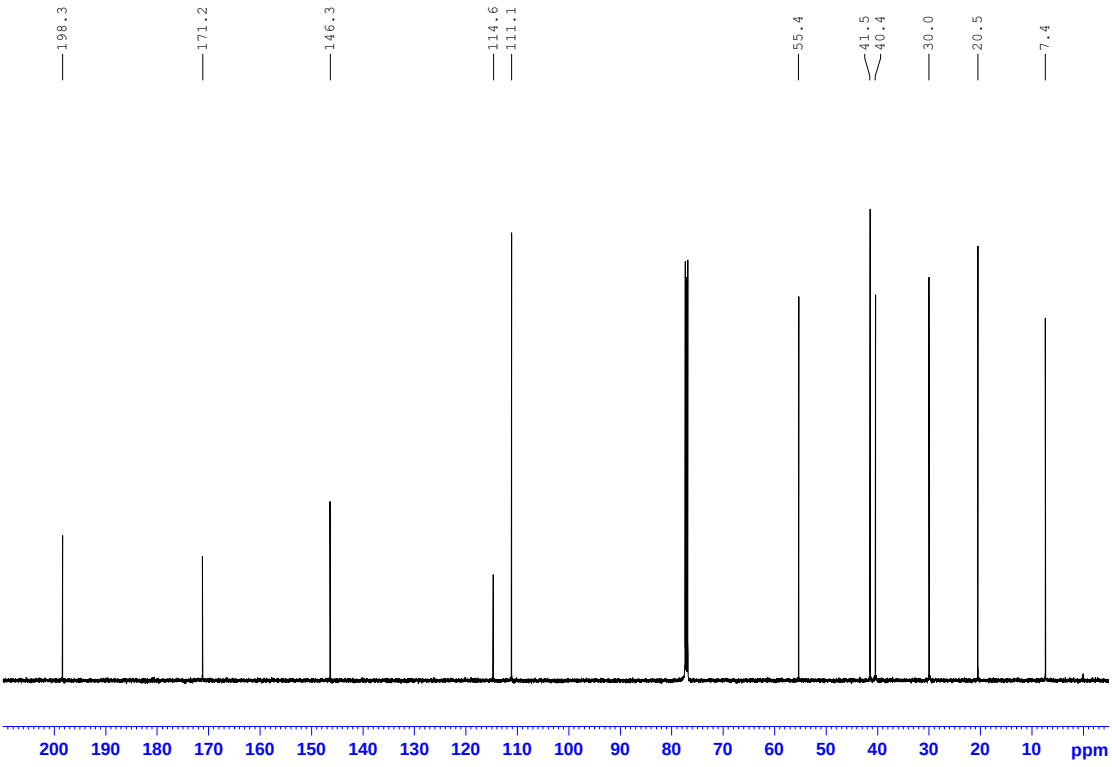

7.26
5.24
3.90
3.89
3.87
3.86
2.43
2.42
2.40
1.81
1.79
1.78
1.36
1.35
1.34
1.11
-0.01
O
Me
Me
OEt
1j
500 MHz
1.00
2.06
2.08
2.09
3.08
6.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

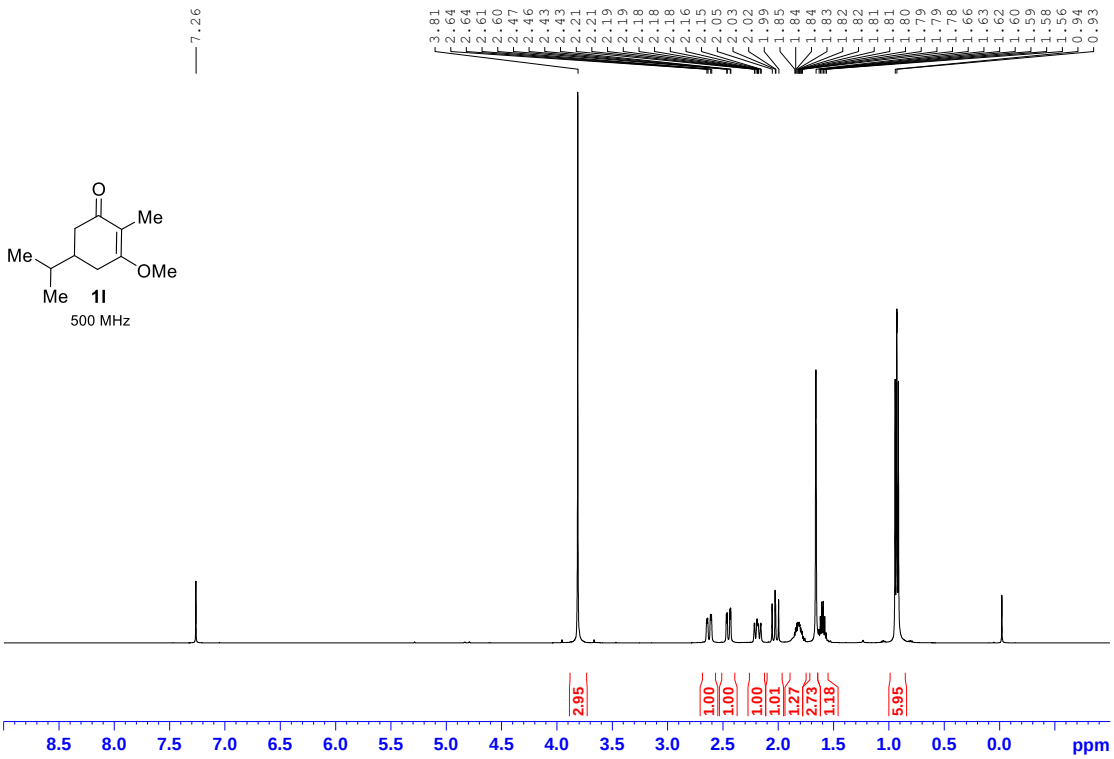

204.7
175.9
101.2
64.3
40.3
35.2
26.5
24.7
14.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

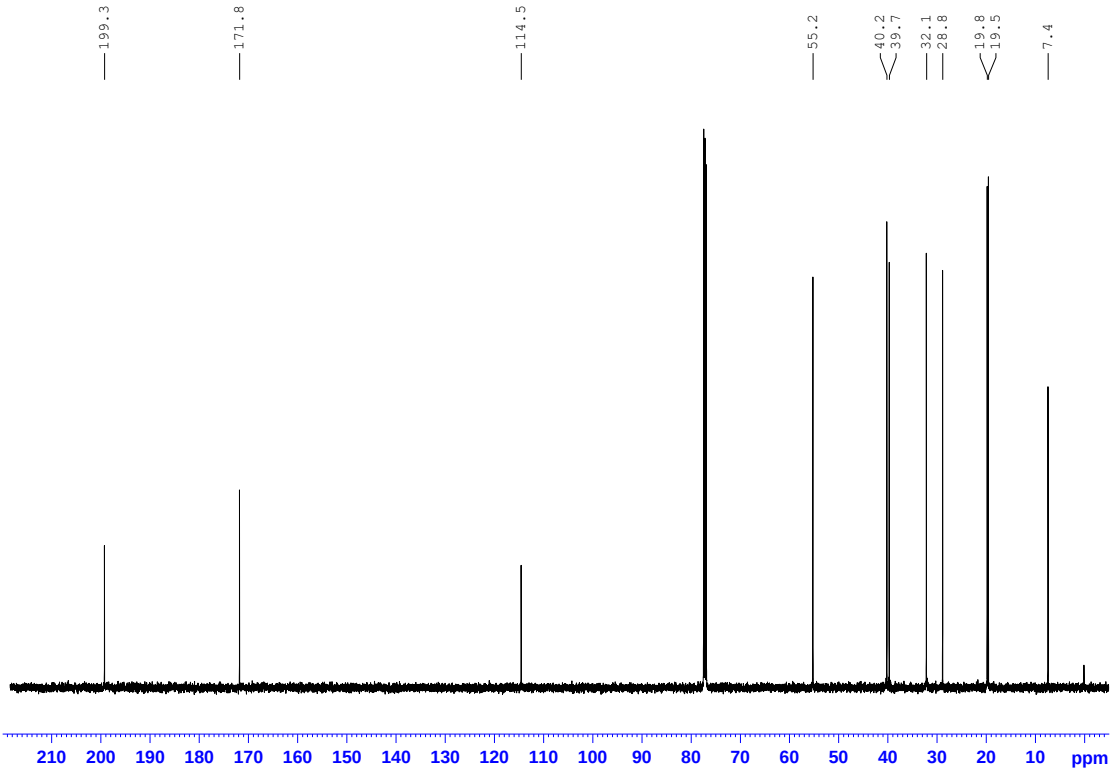

7.26
5.24
4.59
4.58
4.57
4.56
3.98
3.96
3.95
3.93
2.63
2.14
2.13
2.12
2.11
1.89
1.87
1.87
1.85
1.43
1.41
1.40
1.17
1.13
0.00
Me
Me
O
OEt
OH
ox-1j
500 MHz
1.00
0.88
1.77
0.89
0.92
0.97
2.61
2.68
3.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

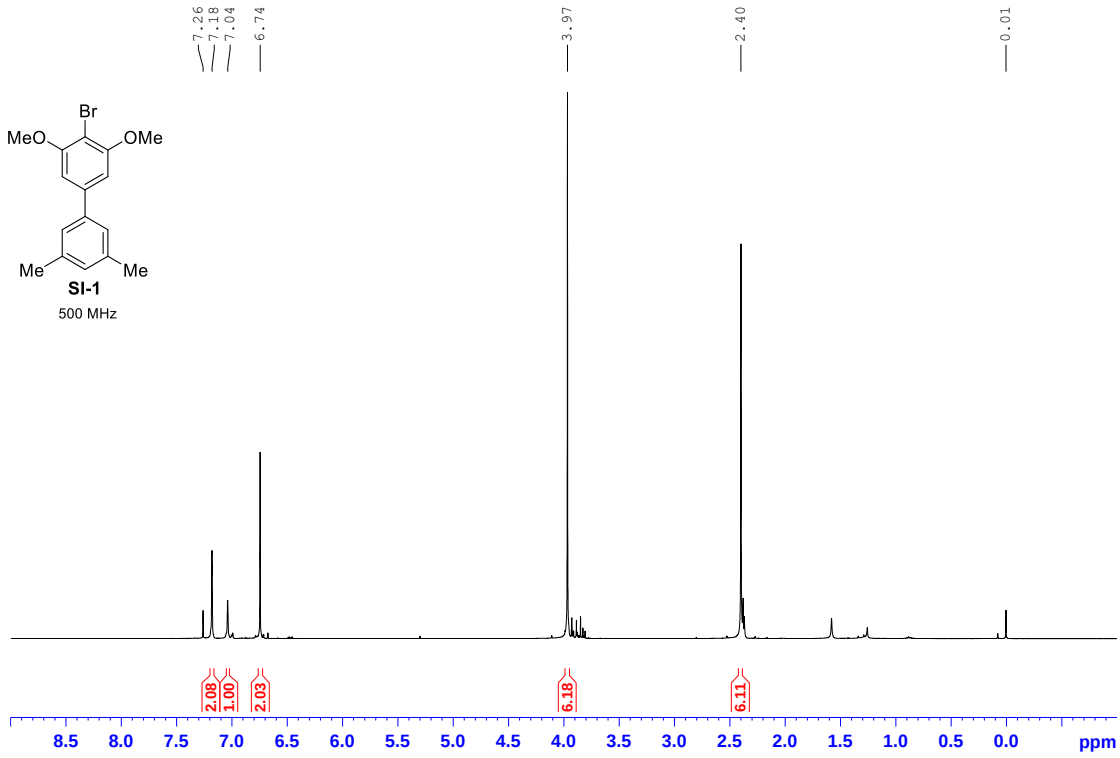

203.7
173.7
100.8
65.6
65.1
43.4
41.6
25.9
25.3
14.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

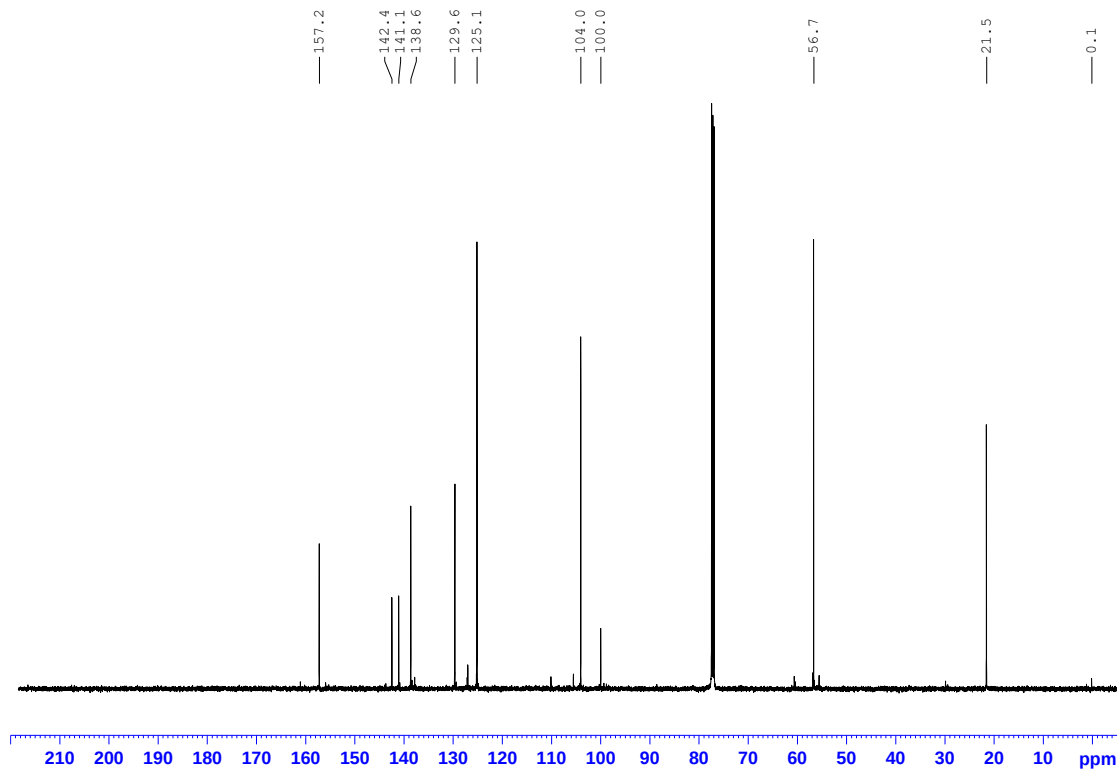

7.26
4.84
4.83
4.83
4.79
3.82
2.72
2.71
2.69
2.68
2.67
2.65
2.64
2.52
2.51
2.51
2.49
2.48
2.48
2.47
2.43
2.41
2.41
2.40
2.40
2.40
2.38
2.37
2.28
2.26
2.25
2.22
1.76
1.68
1.67
0.02
O
Me
OMe
Me
1k
500 MHz
1.00
0.98
2.93
2.00
1.01
1.00
1.01
3.05
2.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

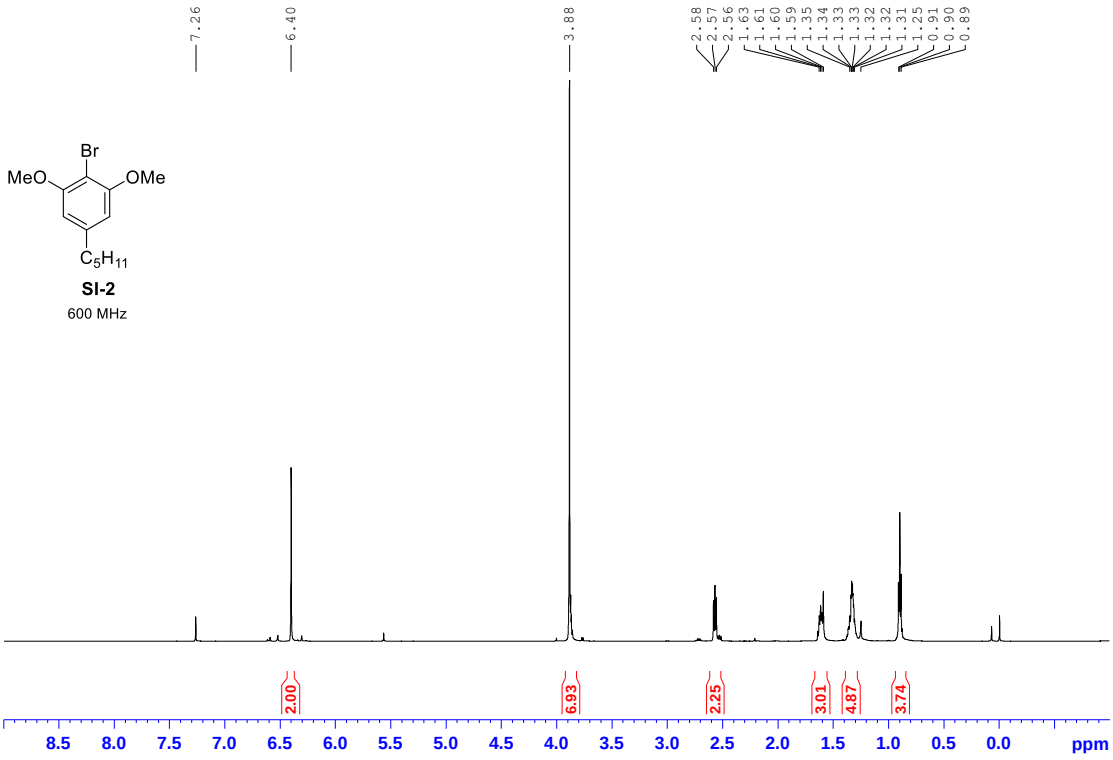

198.3
171.2
146.3
114.6
111.1
55.4
41.5
40.4
30.0
20.5
7.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

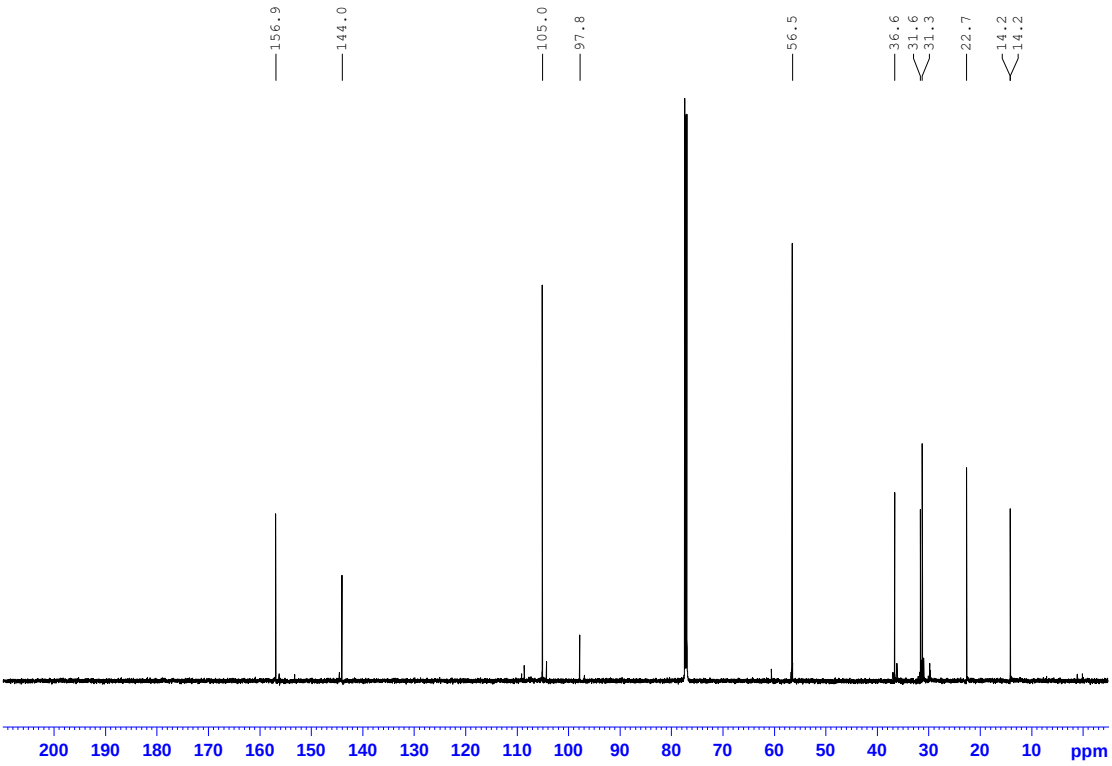

7.26
3.81
2.64
2.61
2.60
2.47
2.46
2.43
2.43
2.21
2.21
2.19
2.19
2.18
2.18
2.18
2.16
2.15
2.05
2.03
2.02
1.99
1.85
1.84
1.84
1.83
1.82
1.82
1.81
1.81
1.80
1.79
1.79
1.78
1.66
1.63
1.62
1.60
1.59
1.58
1.56
0.94
0.93
O
Me
Me
OMe
Me
1l
500 MHz
2.95
1.00
1.00
1.00
1.01
1.27
2.73
1.18
5.95
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

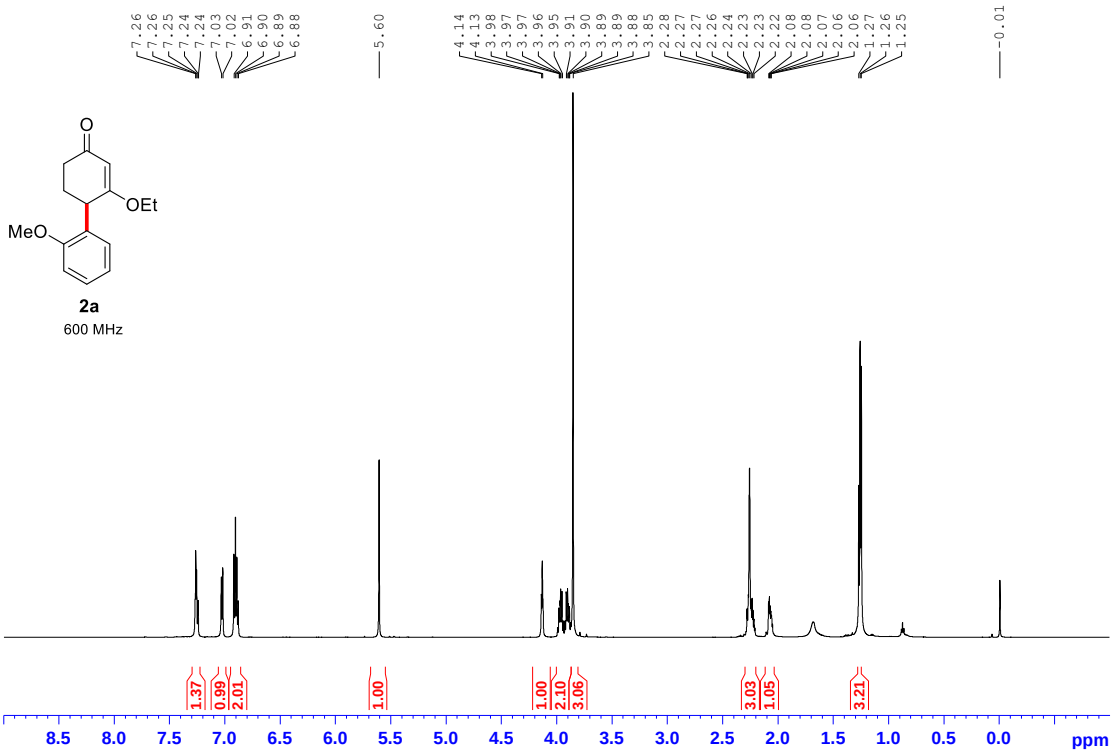

199.3
171.8
114.5
55.2
40.2
39.7
32.1
28.8
19.8
19.5
7.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

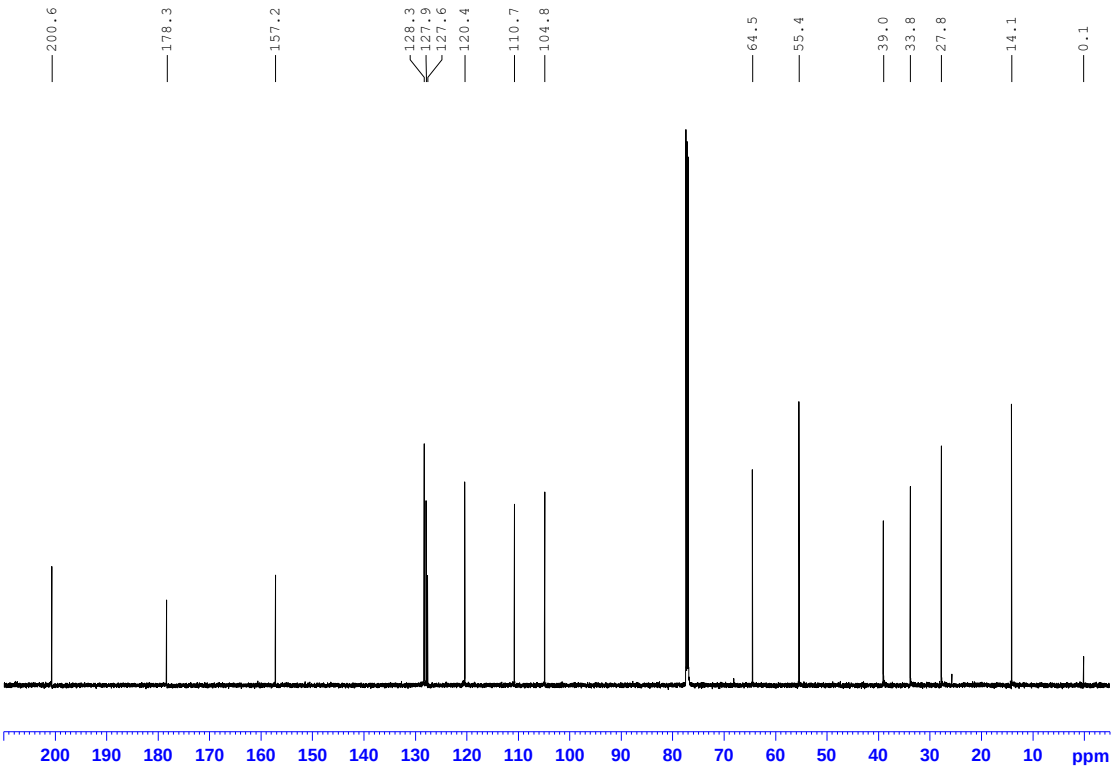

7.26
7.18
7.04
6.74
3.97
2.40
0.01
Br
MeO
OMe
Me
Me
SI-1
500 MHz
2.08
1.00
2.03
6.18
6.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

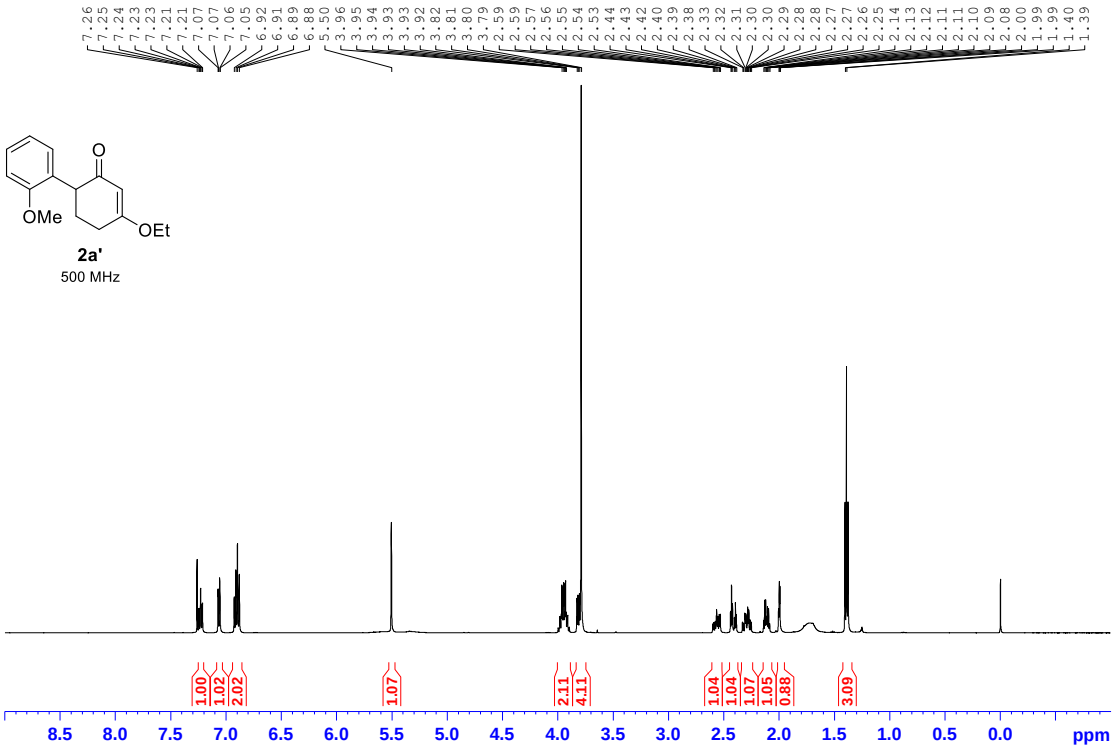

157.2
142.4
141.1
138.6
129.6
125.1
104.0
100.0
56.7
21.5
0.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

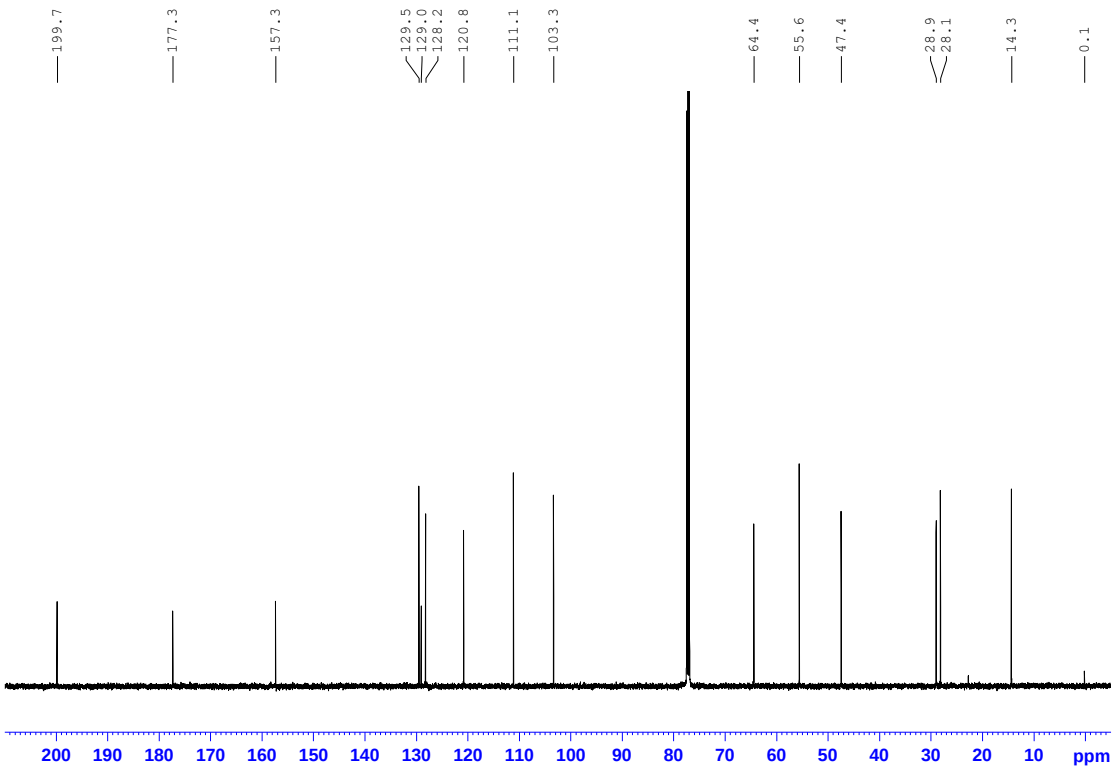

7.26
6.40
3.88
2.58
2.57
2.56
1.63
1.61
1.60
1.59
1.35
1.34
1.33
1.33
1.32
1.32
1.31
1.25
0.91
0.90
0.89
Br
MeO
OMe
C5H11
SI-2
600 MHz
2.00
6.93
2.25
3.01
4.87
3.74
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

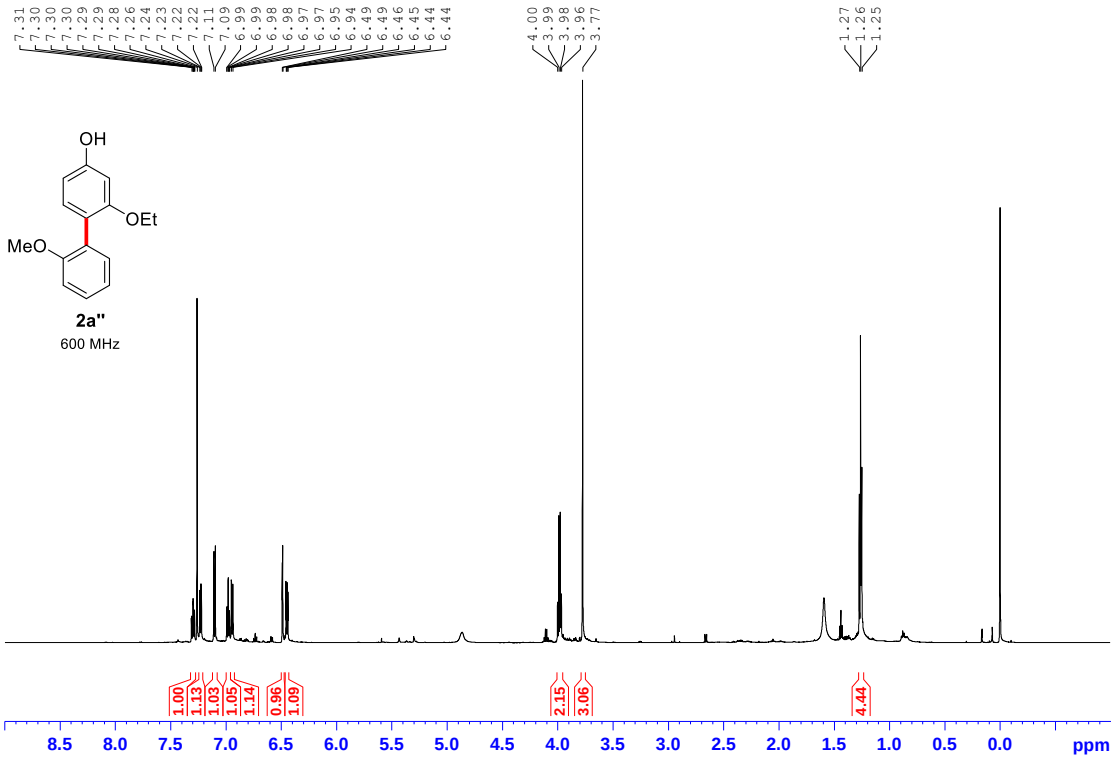

156.9
144.0
105.0
97.8
56.5
36.6
31.6
31.3
22.7
14.2
14.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

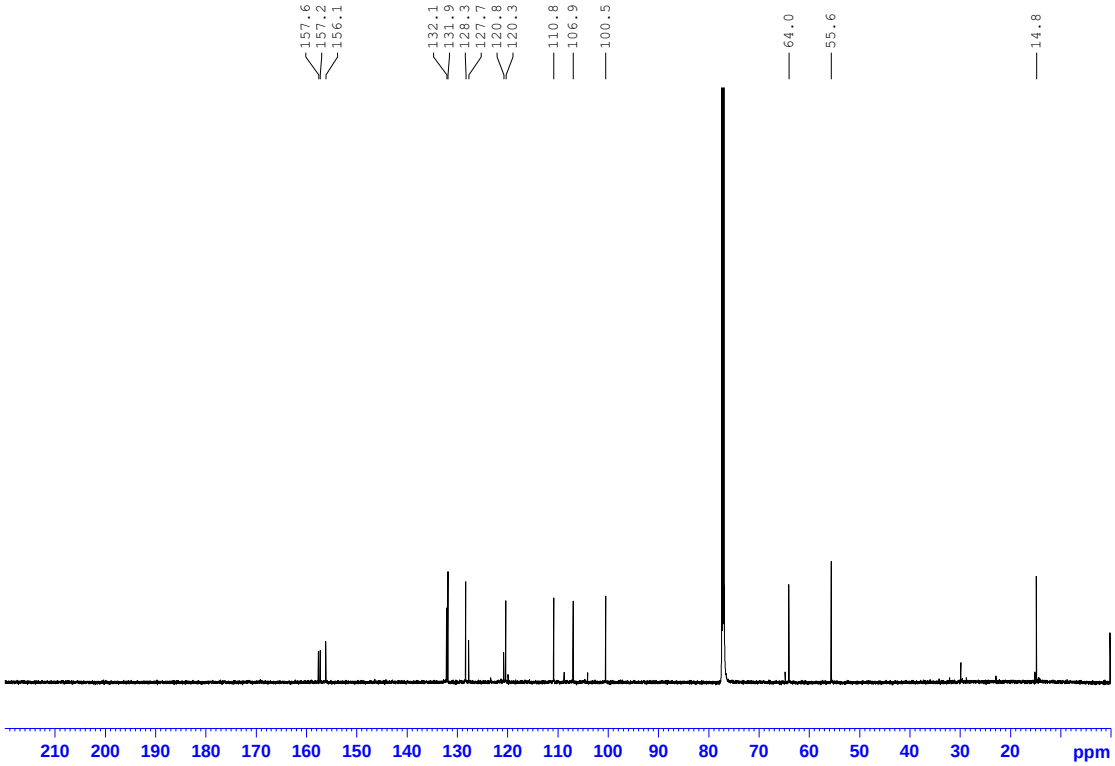

7.26
7.26
7.25
7.24
7.24
7.03
7.02
6.91
6.90
6.89
6.88
5.60
4.14
4.13
3.98
3.97
3.97
3.96
3.95
3.91
3.90
3.89
3.89
3.88
3.85
2.28
2.27
2.27
2.26
2.24
2.23
2.23
2.22
2.08
2.08
2.07
2.06
2.06
1.27
1.26
1.25
0.01
O
OEt
MeO
2a
600 MHz
1.37
0.99
2.01
1.00
1.00
2.10
3.06
3.03
1.05
3.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

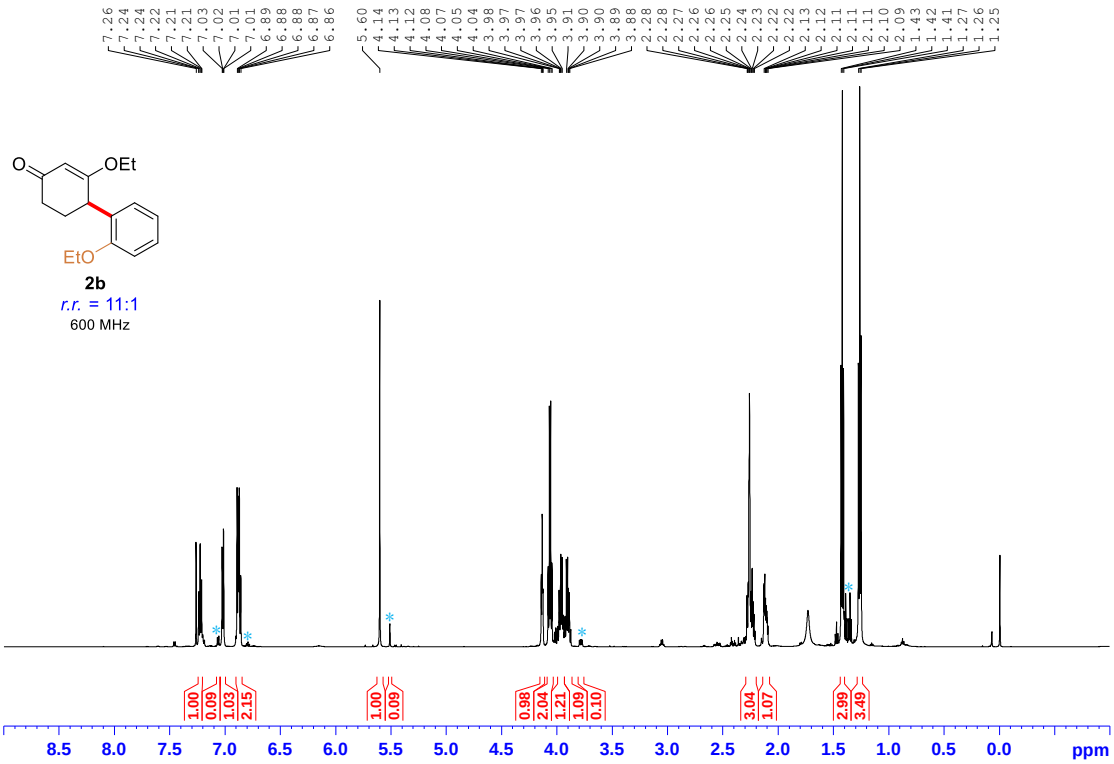

200.6
178.3
157.2
128.3
127.9
127.6
120.4
110.7
104.8
64.5
55.4
39.0
33.8
27.8
14.1
0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm


7.26 7.25 7.24 7.23 7.23 7.21 7.21 7.07 7.07 7.06 7.05 6.92 6.91 6.89 6.88 5.50 3.96 3.95 3.94 3.93 3.93 3.92 3.82 3.81 3.80 3.79 2.59 2.59 2.57 2.56 2.55 2.54 2.53 2.44 2.43 2.42 2.40 2.39 2.38 2.33 2.32 2.31 2.30 2.30 2.29 2.28 2.28 2.27 2.27 2.26 2.25 2.14 2.13 2.12 2.11 2.11 2.10 2.09 2.08 2.00 1.99 1.99 1.40 1.39
O
OMe
OEt
2a'
500 MHz
1.00 1.02 2.02 1.07 2.11 4.11 1.04 1.04 1.07 1.05 0.88 3.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

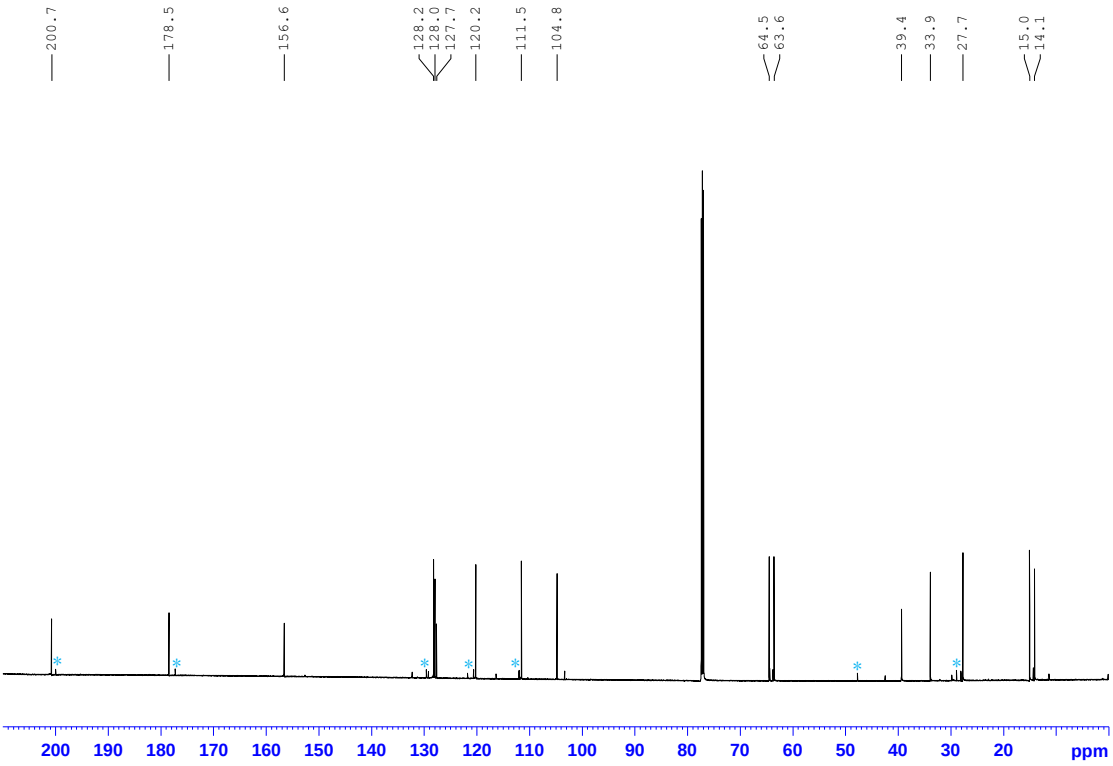

199.7 177.3 157.3 129.5 129.0 128.2 120.8 111.1 103.3 64.4 55.6 47.4 28.9 28.1 14.3 0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

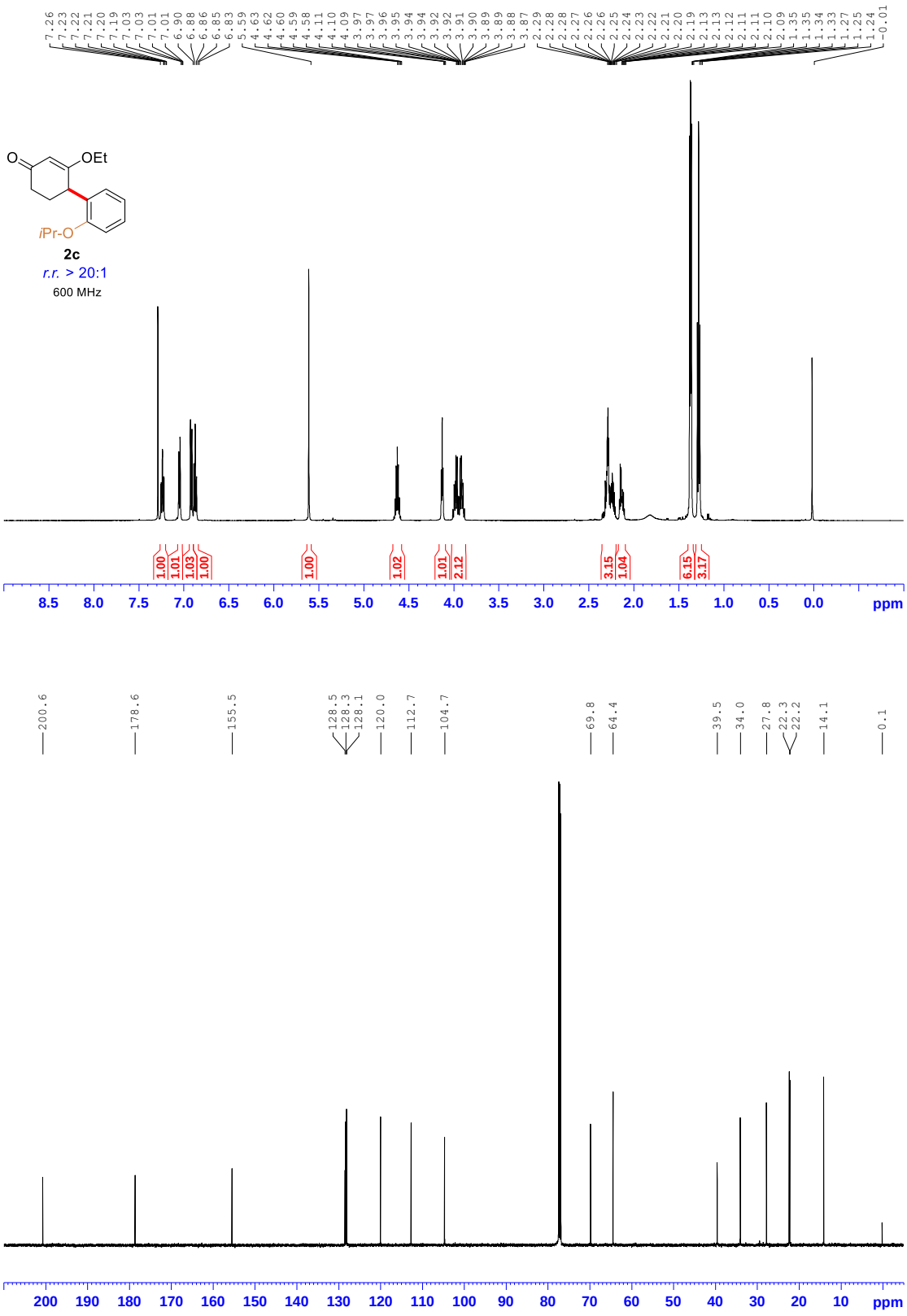

7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.26
7.24
7.23
7.22
7.22
7.11
7.09
6.99
6.99
6.98
6.98
6.97
6.97
6.95
6.94
6.49
6.49
6.46
6.45
6.44
6.44
4.00
3.99
3.98
3.96
3.77
1.27
1.26
1.25
OH
OEt
MeO
2a''
600 MHz
1.00
1.13
1.03
1.05
1.14
0.96
1.09
2.15
3.06
4.44
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

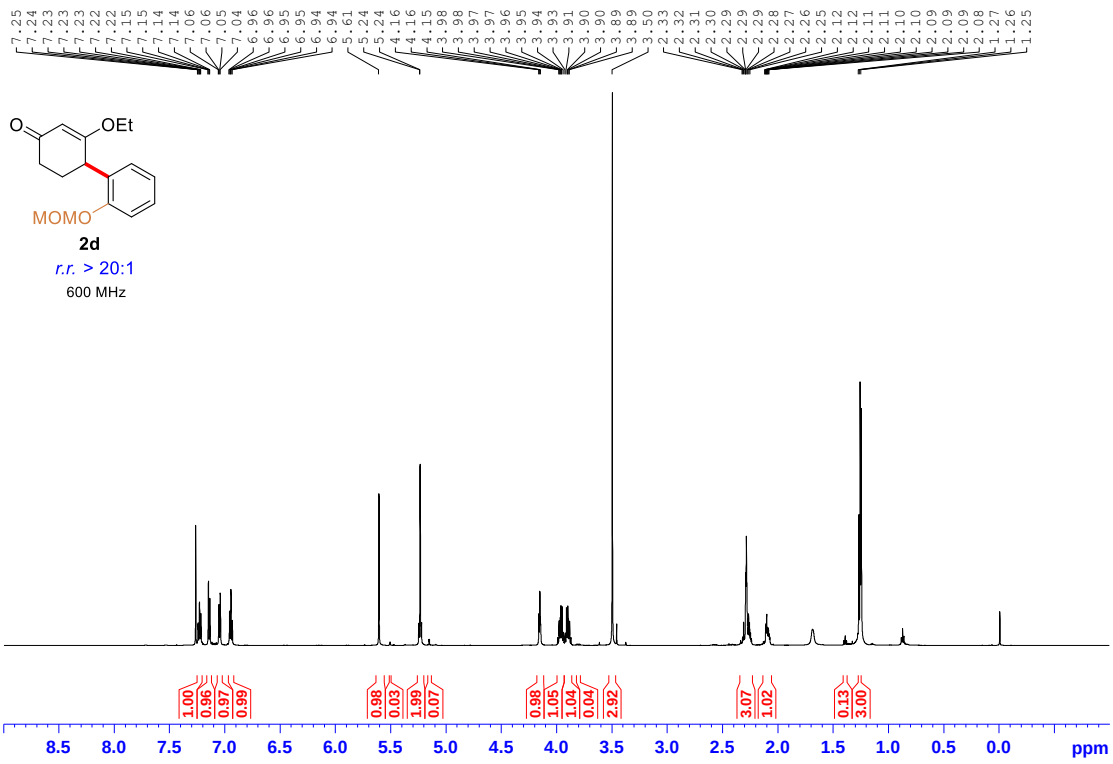

157.6
157.2
156.1
132.1
131.9
128.3
127.7
120.8
120.3
110.8
106.9
100.5
64.0
55.6
14.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

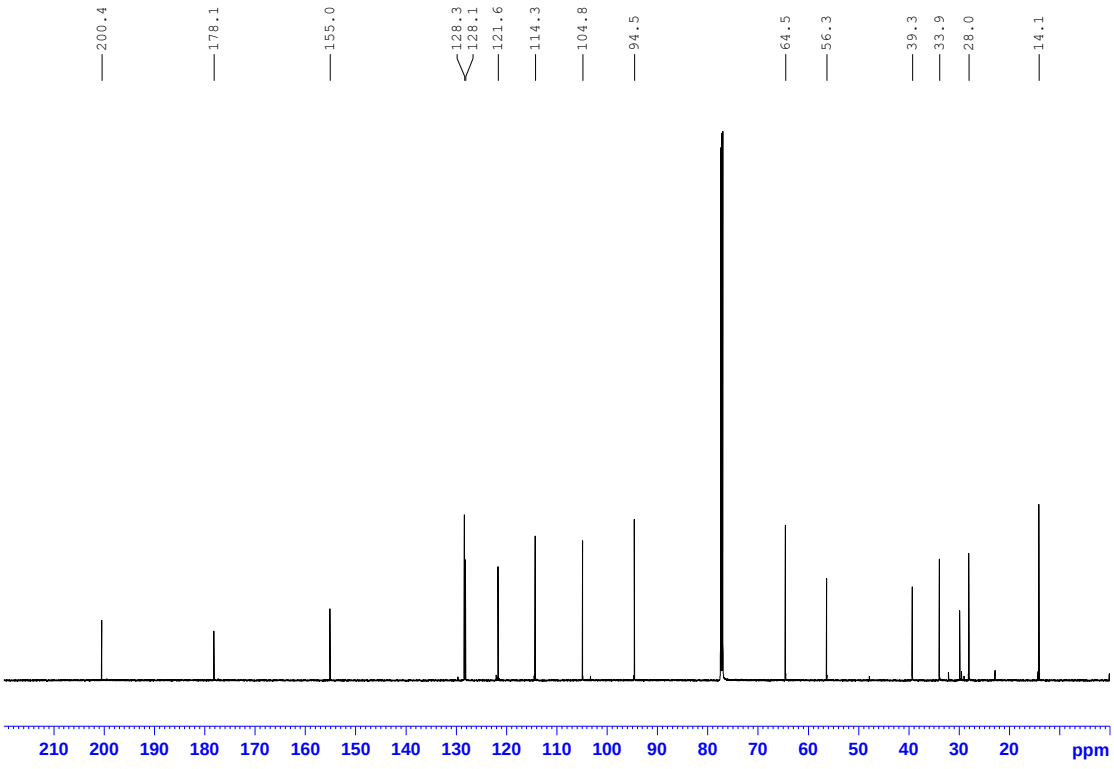


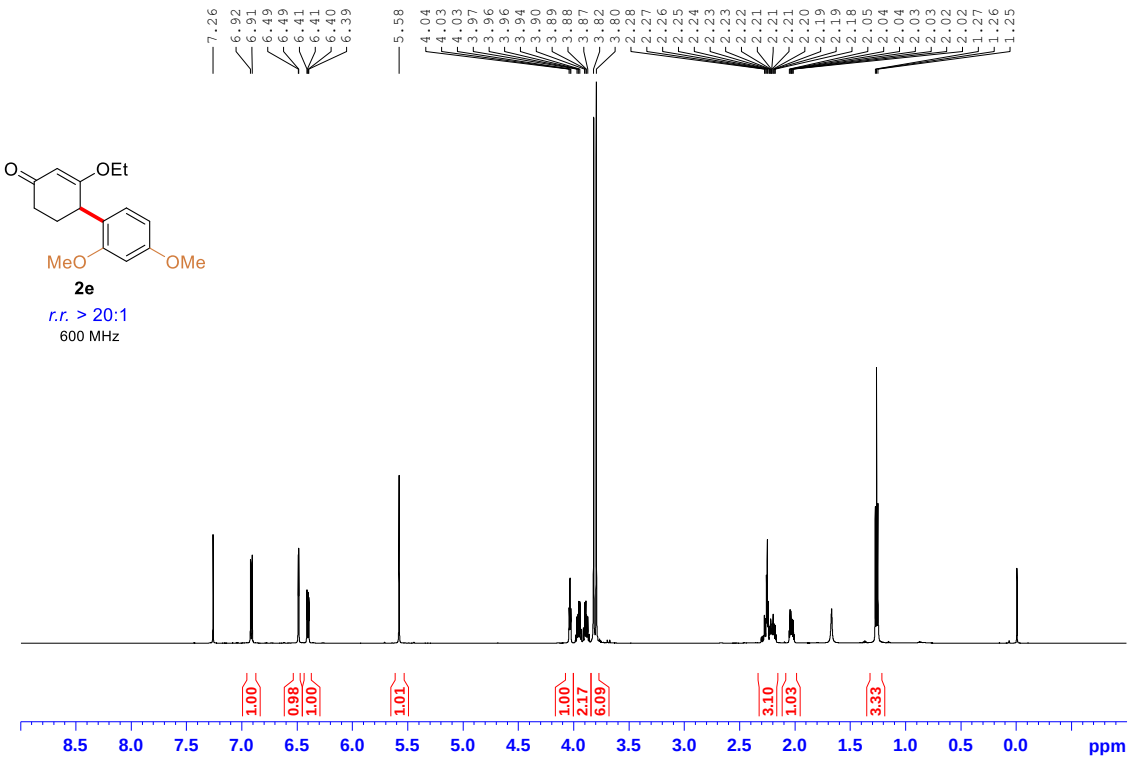
* is for α'-isomer

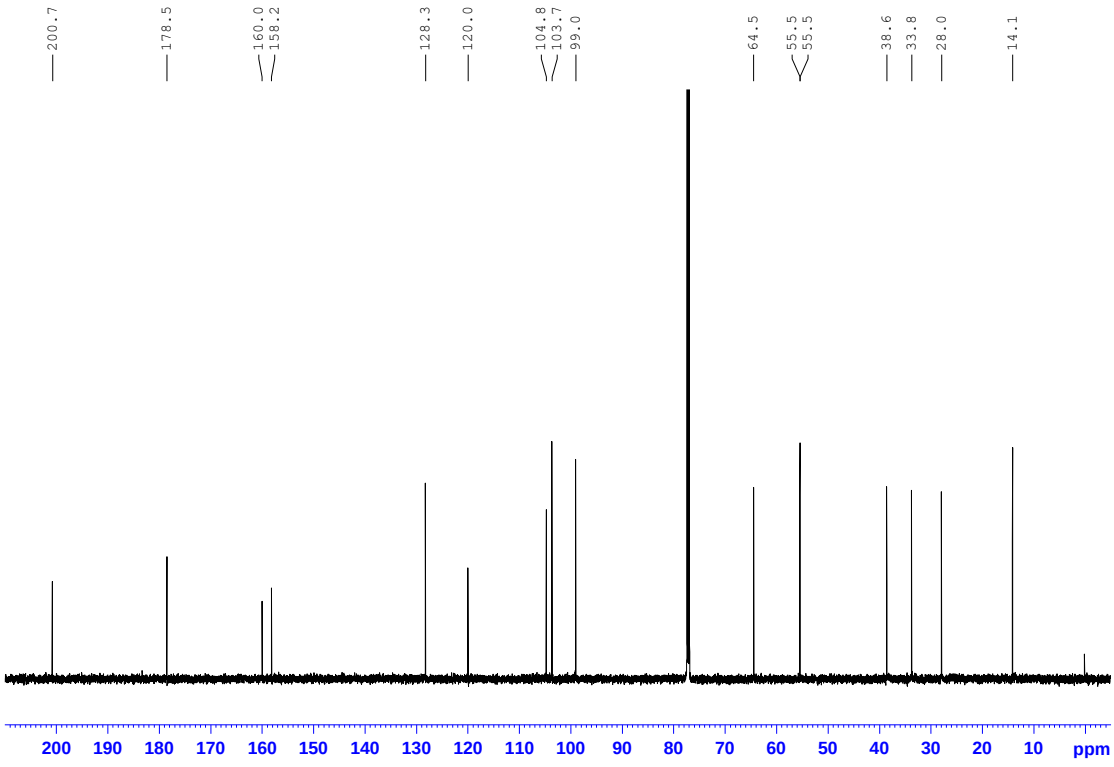


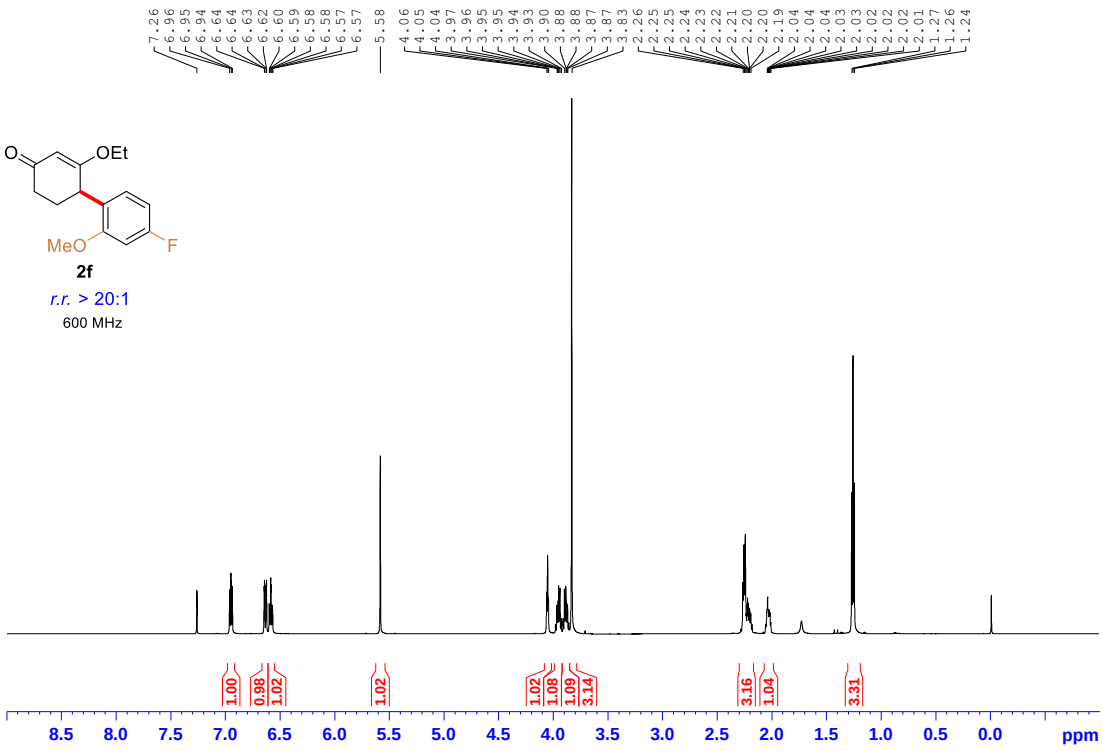

7.26 7.23 7.22 7.21 7.20 7.19 7.03 7.03 7.01 7.01 6.90 6.88 6.86 6.85 6.83 5.59 4.63 4.62 4.60 4.59 4.58 4.11 4.10 4.09 3.97 3.97 3.96 3.95 3.94 3.94 3.92 3.91 3.90 3.89 3.89 3.88 3.87 2.29 2.28 2.27 2.26 2.26 2.25 2.24 2.23 2.22 2.21 2.20 2.19 2.13 2.13 2.12 2.11 2.11 2.10 2.09 1.35 1.35 1.34 1.33 1.27 1.25 1.24 -0.01
O
OEt
iPr-O
2c
r.r. > 20:1
600 MHz
1.00 1.01 1.03 1.00 1.00 1.02 1.01 2.12 3.15 1.04 6.15 3.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
200.6 178.6 155.5 128.5 128.3 128.1 120.0 112.7 104.7 69.8 64.4 39.5 34.0 27.8 22.3 22.2 14.1 0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

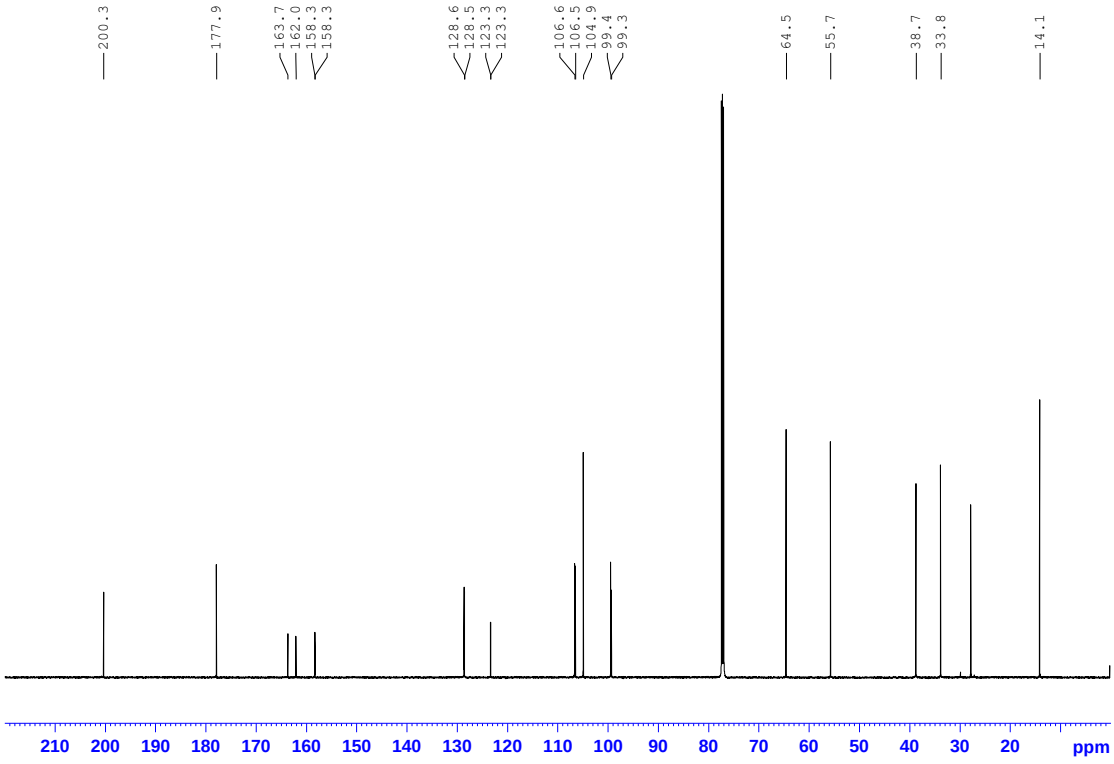

7.25 7.24 7.23 7.23 7.23 7.22 7.22 7.15 7.15 7.14 7.14 7.06 7.06 7.05 7.04 6.96 6.96 6.95 6.95 6.94 6.94
5.61 5.24 5.24 4.16 4.16 4.15 3.98 3.98 3.97 3.97 3.96 3.95 3.94 3.93 3.91 3.90 3.90 3.89 3.89 3.50
2.33 2.32 2.31 2.30 2.29 2.29 2.29 2.28 2.27 2.26 2.25 2.12 2.12 2.11 2.11 2.10 2.10 2.09 2.09 2.09 2.08 1.27 1.26 1.25
O
OEt
MOMO
2d
r.r. > 20:1
600 MHz
1.00 0.96 0.97 0.99 0.98 0.03 1.99 0.07 0.98 1.05 1.04 0.04 2.92 3.07 1.02 0.13 3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

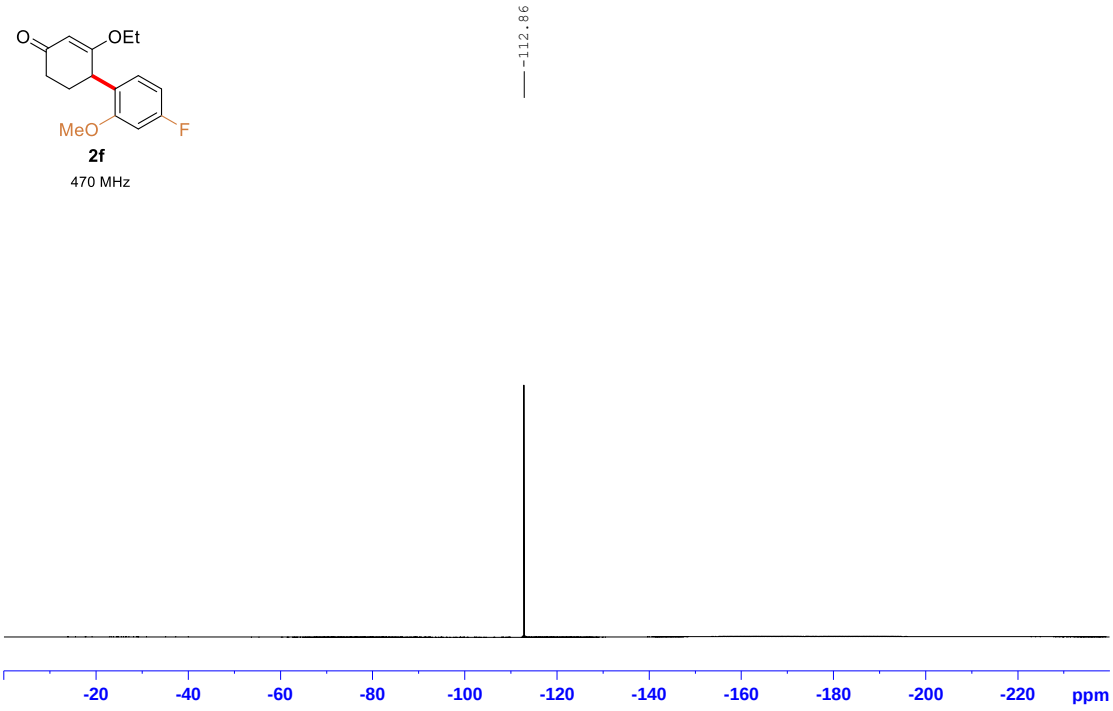

200.4 178.1 155.0 128.3 128.1 121.6 114.3 104.8 94.5 64.5 56.3 39.3 33.9 28.0 14.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

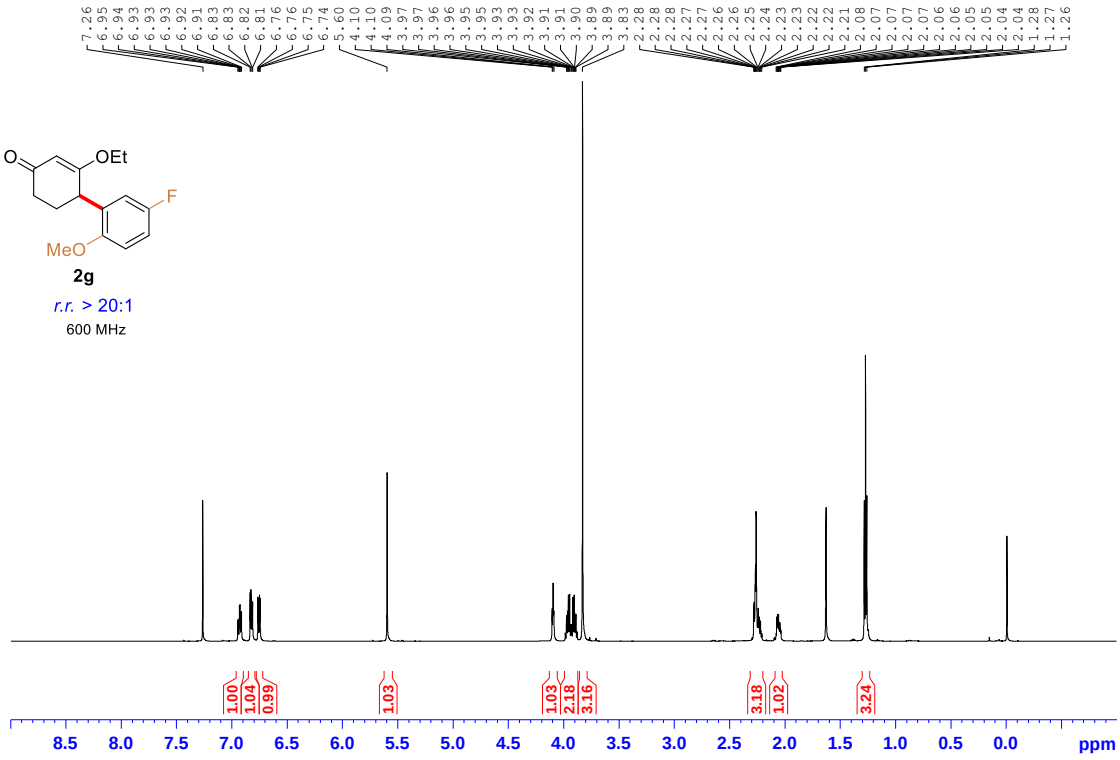

7.26
6.92
6.91
6.49
6.49
6.41
6.41
6.40
6.39
5.58
4.04
4.03
4.03
3.97
3.96
3.96
3.94
3.90
3.89
3.88
3.87
3.82
3.80
2.28
2.27
2.26
2.25
2.24
2.23
2.23
2.22
2.21
2.21
2.21
2.20
2.19
2.19
2.18
2.05
2.04
2.04
2.03
2.02
2.02
1.27
1.26
1.25
O
OEt
MeO
OMe
2e
r.r. > 20:1
600 MHz
1.00
0.98
1.00
1.01
1.00
2.17
6.09
3.10
1.03
3.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

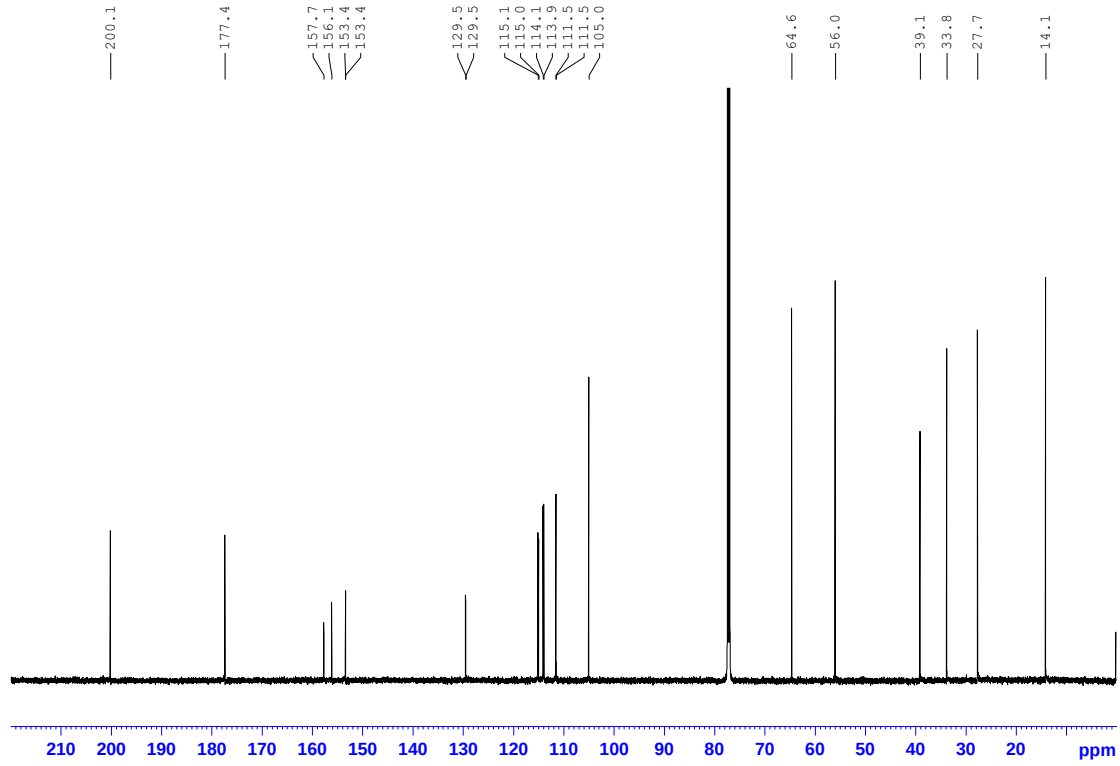

200.7
178.5
160.0
158.2
128.3
120.0
104.8
103.7
99.0
64.5
55.5
55.5
38.6
33.8
28.0
14.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

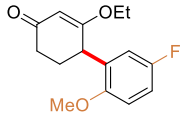

7.26
6.96
6.95
6.94
6.64
6.64
6.63
6.62
6.60
6.59
6.58
6.58
6.57
6.57
5.58
4.06
4.05
4.04
3.97
3.96
3.95
3.95
3.94
3.93
3.90
3.88
3.88
3.87
3.87
3.83
2.26
2.25
2.25
2.24
2.23
2.22
2.21
2.20
2.20
2.19
2.04
2.04
2.04
2.03
2.02
2.02
2.02
2.01
1.27
1.26
1.24
O
OEt
MeO
F
2f
r.r. > 20:1
600 MHz
1.00
0.98
1.02
1.02
1.02
1.08
1.09
3.14
3.16
1.04
3.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


200.3
177.9
163.7
162.0
158.3
158.3
128.6
128.5
123.3
123.3
106.6
106.5
104.9
99.4
99.3
64.5
55.7
38.7
33.8
14.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


O
OEt
MeO
F
2f
470 MHz
-112.86
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm

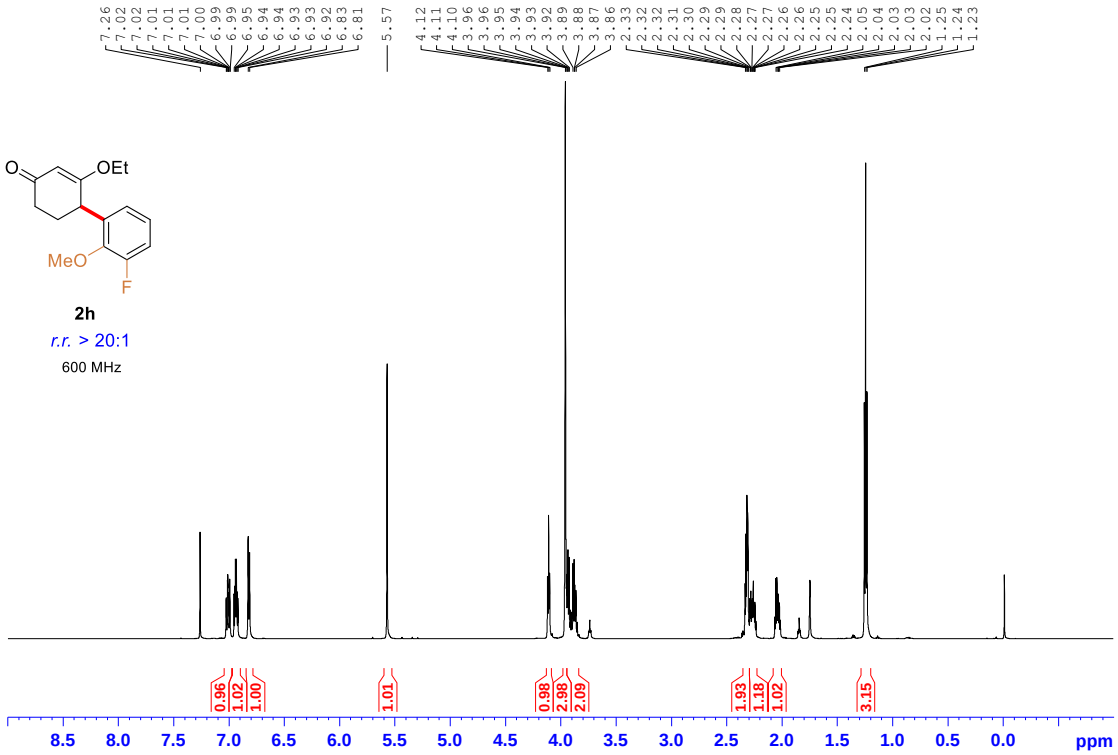

7.26 6.95 6.94 6.93 6.93 6.93 6.92 6.91 6.83 6.83 6.82 6.81 6.76 6.76 6.75 6.74 5.60 4.10 4.10 4.09 3.97 3.97 3.96 3.96 3.95 3.95 3.93 3.93 3.92 3.91 3.91 3.90 3.89 3.89 3.83 2.28 2.28 2.27 2.27 2.26 2.26 2.25 2.24 2.23 2.23 2.22 2.22 2.21 2.08 2.07 2.07 2.07 2.06 2.06 2.05 2.05 2.04 2.04 1.28 1.27 1.26
O
OEt
F
MeO
2g
r.r. > 20:1
600 MHz
1.00 1.04 0.99 1.03 1.03 2.18 3.16 3.18 1.02 3.24
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

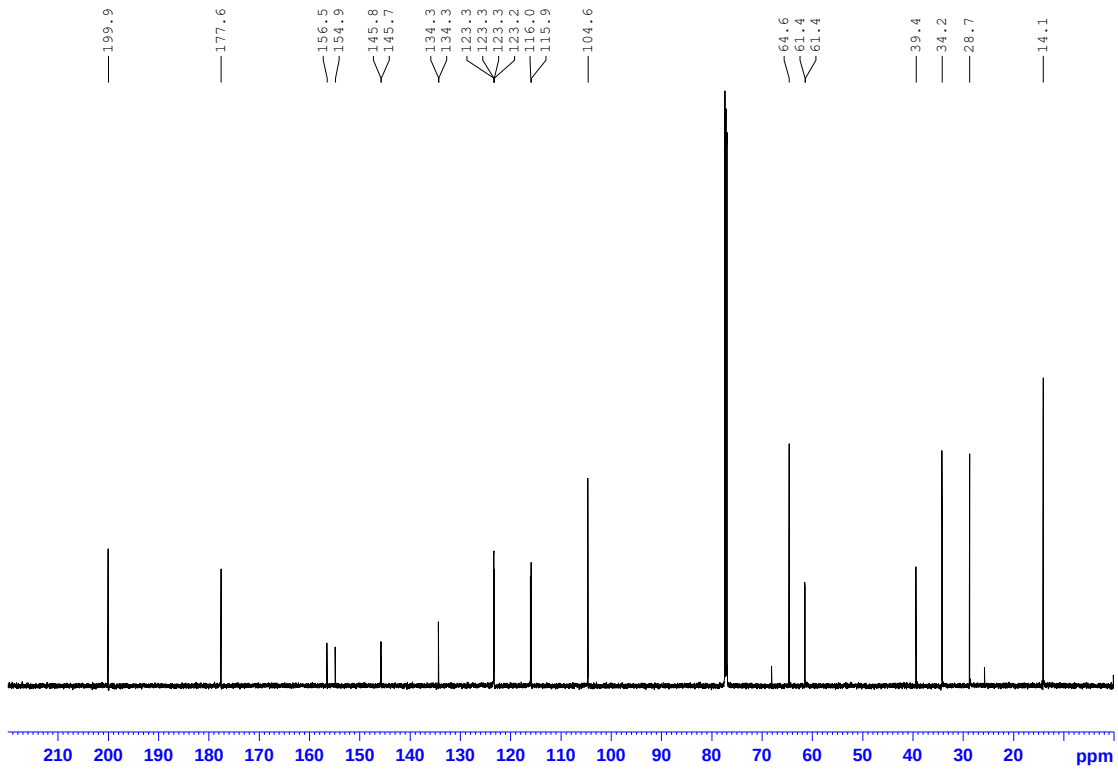

200.1 177.4 157.7 156.1 153.4 153.4 129.5 129.5 115.1 115.0 114.1 113.9 111.5 111.5 105.0 64.6 56.0 39.1 33.8 27.7 14.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

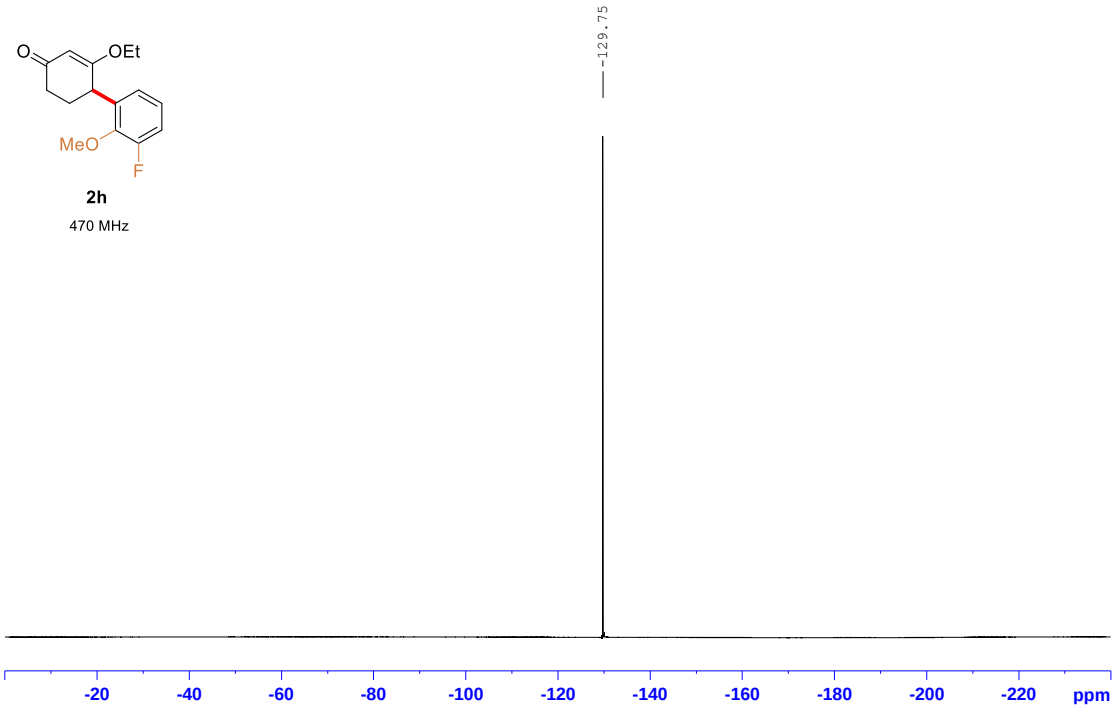


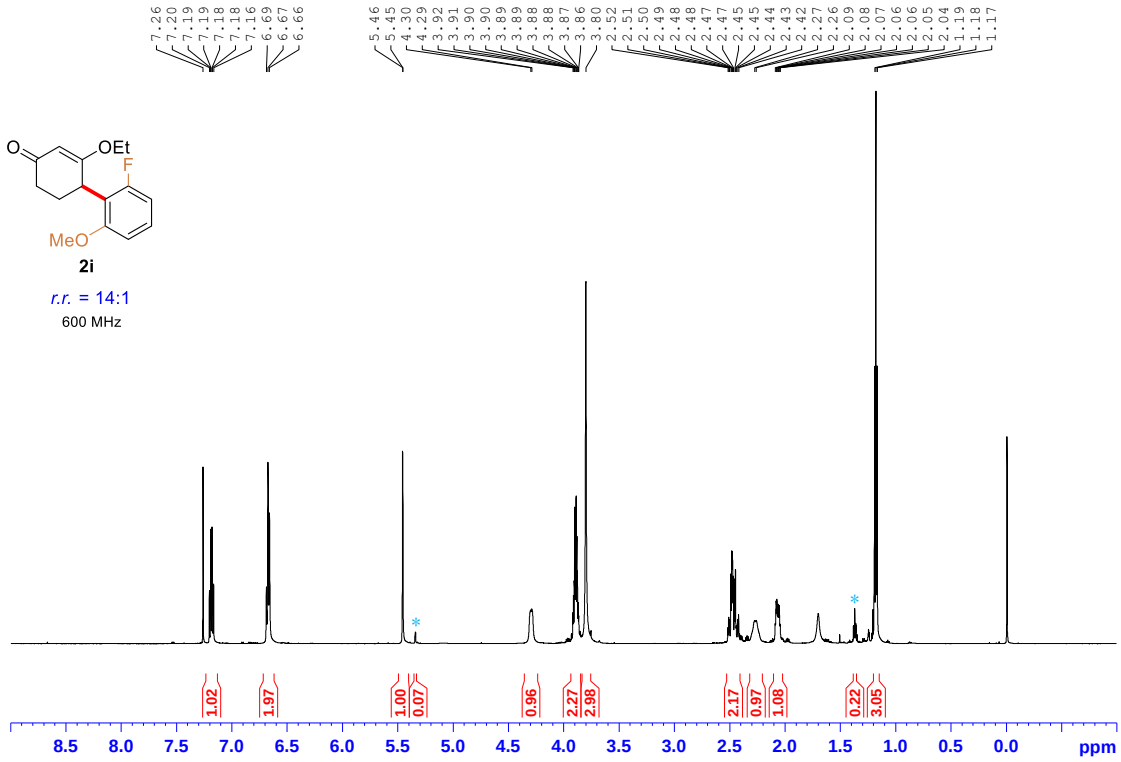
2g

470 MHz

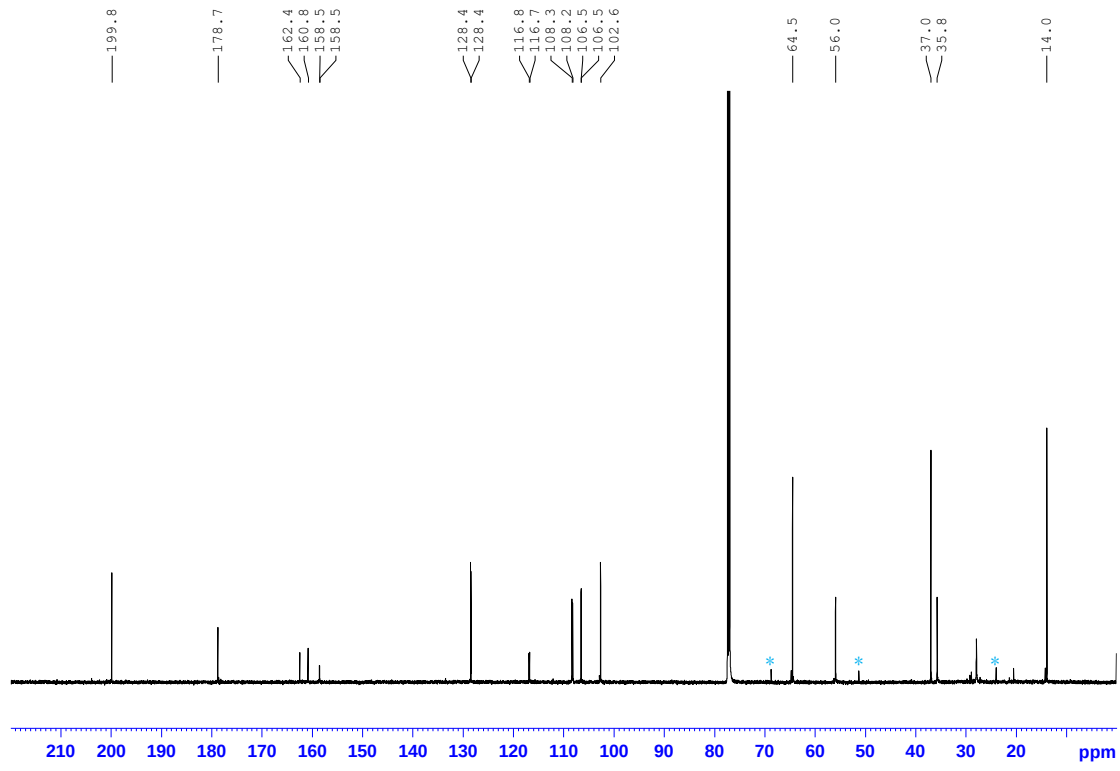

7.26 7.02 7.02 7.01 7.01 7.01 7.00 6.99 6.99 6.95 6.94 6.94 6.93 6.93 6.92 6.83 6.81
5.57
4.12 4.11 4.10 3.96 3.96 3.95 3.94 3.93 3.92 3.89 3.88 3.87 3.86
2.33 2.32 2.32 2.31 2.30 2.29 2.29 2.28 2.27 2.27 2.26 2.26 2.25 2.25 2.24 2.05 2.04 2.03 2.03 2.02 1.25 1.24 1.23
O
OEt
MeO
F
2h
r.r. > 20:1
600 MHz
0.96 1.02 1.00 1.01 0.98 2.98 2.09 1.93 1.18 1.02 3.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

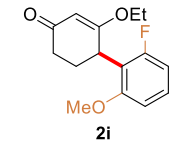

199.9
177.6
156.5 154.9 145.8 145.7 134.3 134.3 123.3 123.3 123.3 123.2 116.0 115.9
104.6
64.6 61.4 61.4
39.4 34.2 28.7
14.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


O
OEt
MeO
F
2h
470 MHz
-129.75
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm



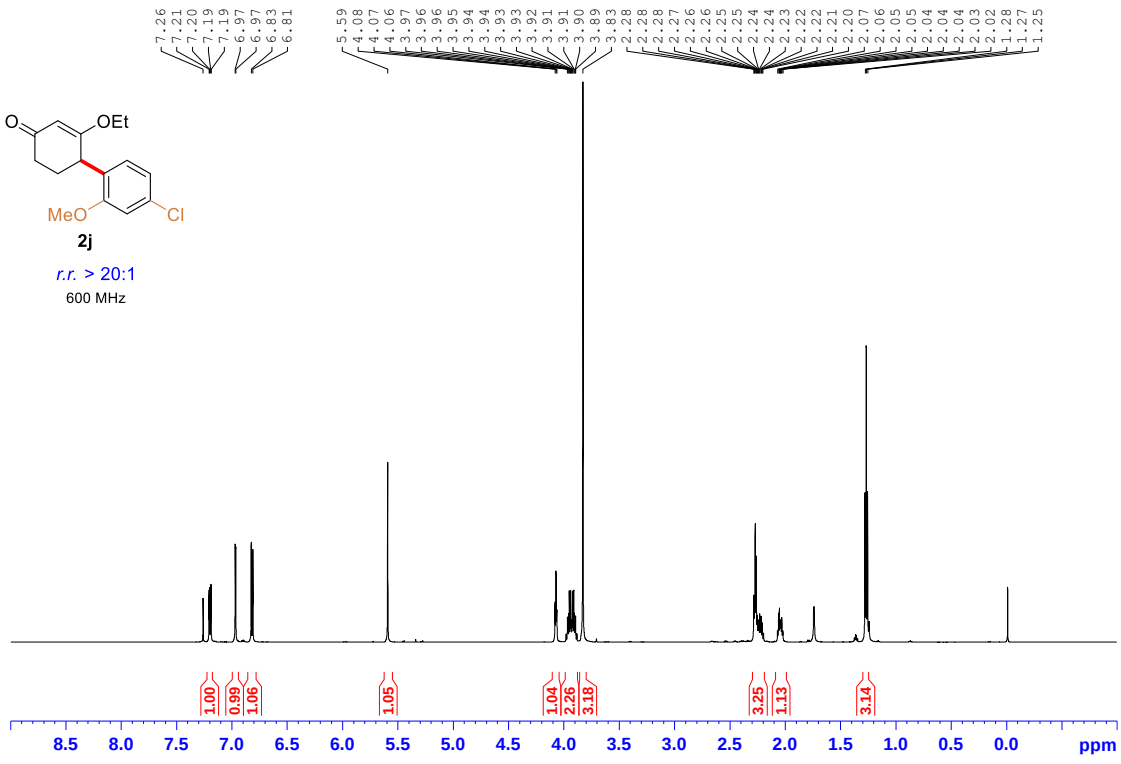
* is for α'-isomer

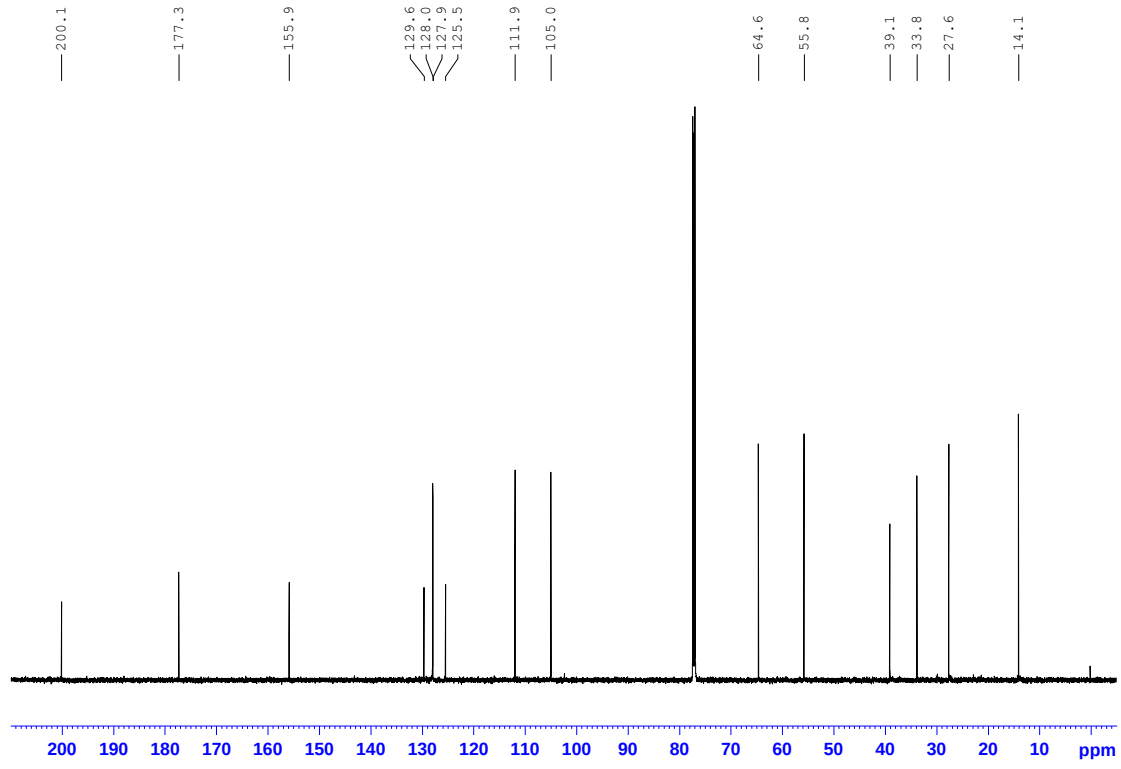


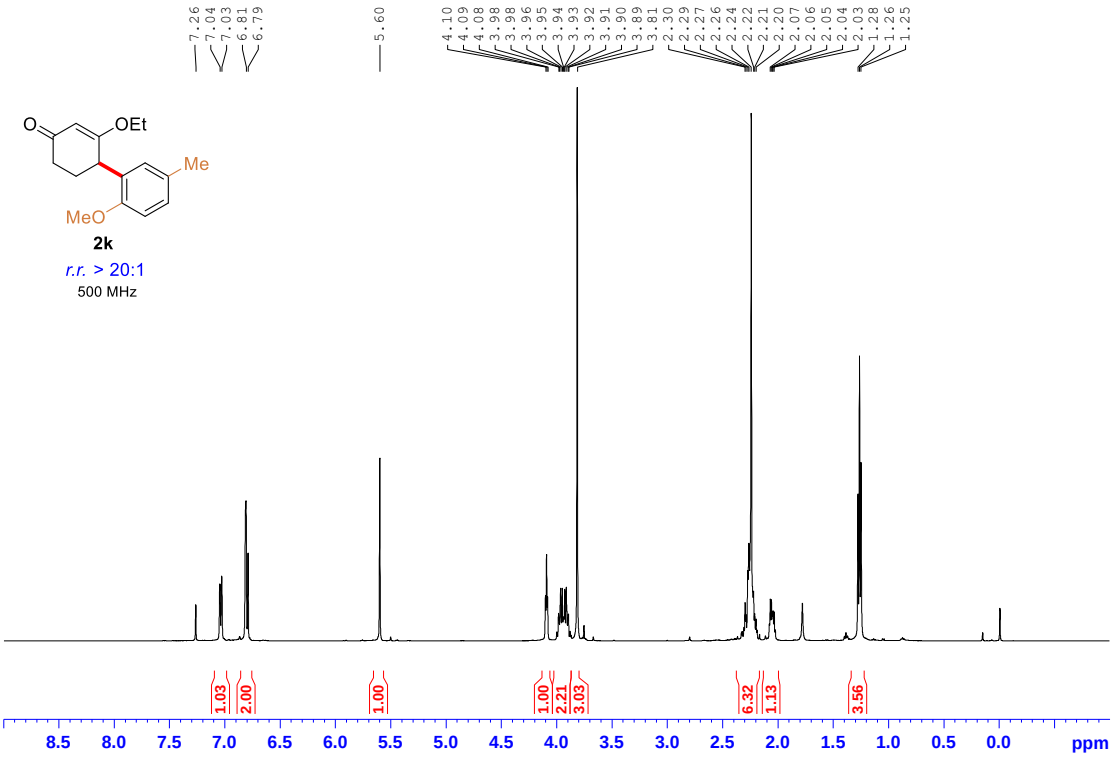


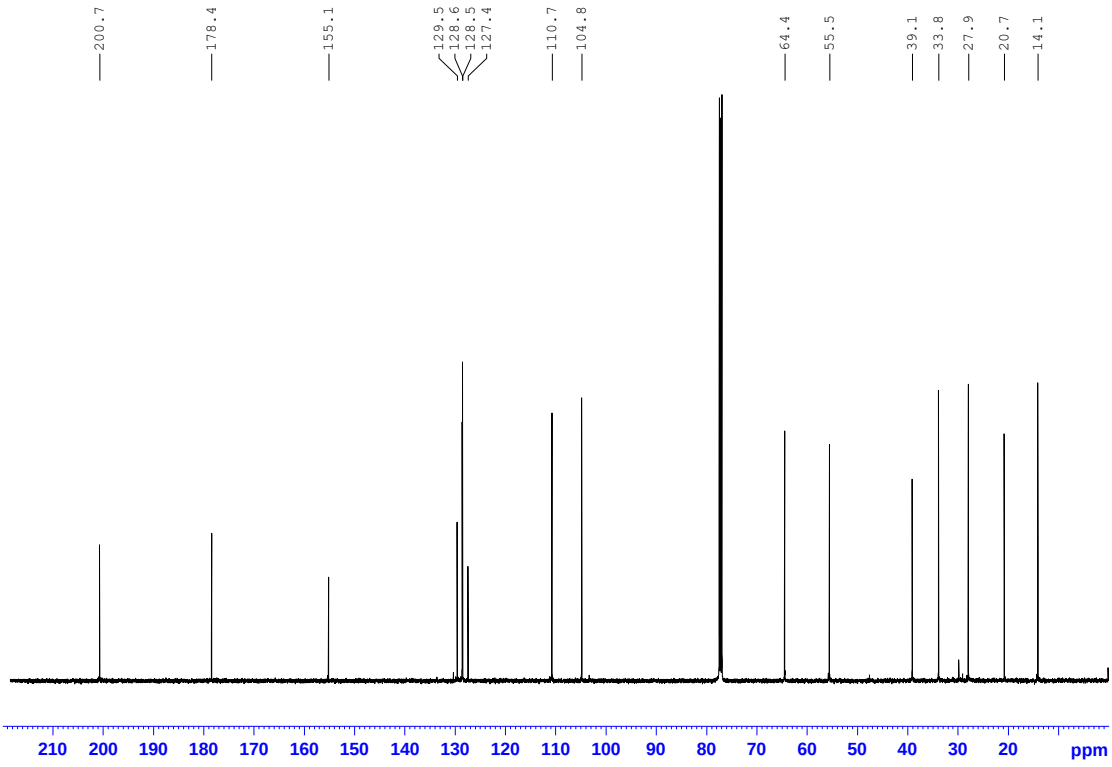
2i

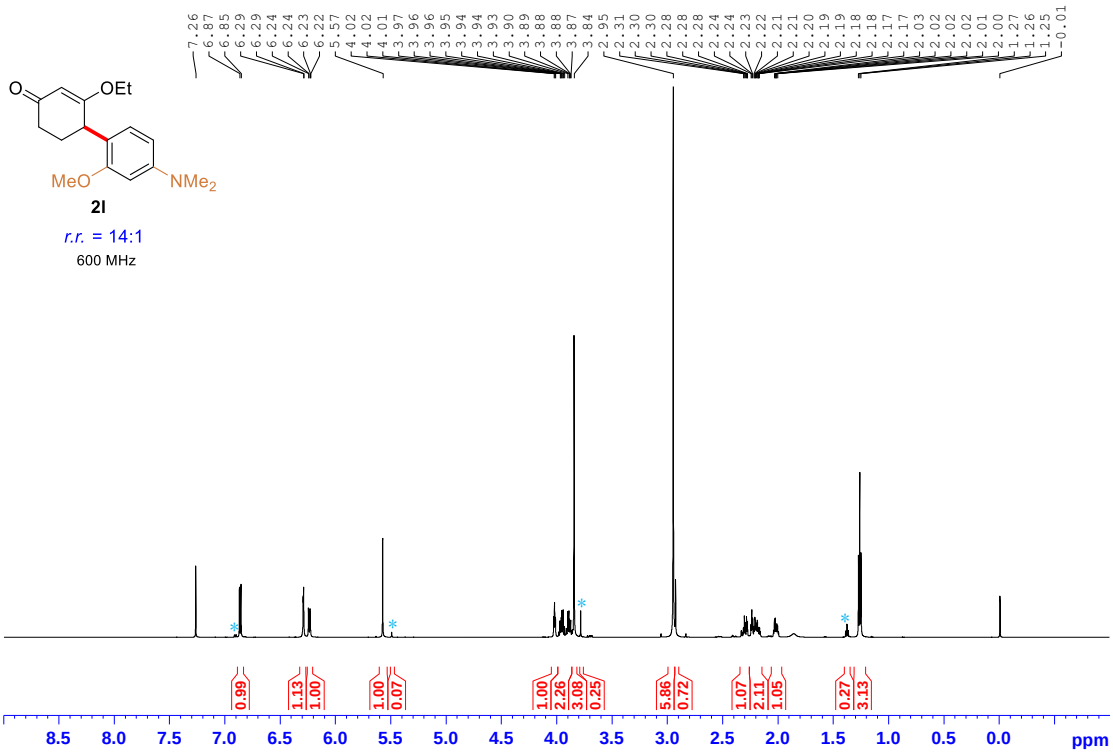
470 MHz


7.26
7.21
7.20
7.19
7.19
6.97
6.97
6.83
6.81
5.59
4.08
4.07
4.06
3.97
3.96
3.95
3.94
3.94
3.93
3.93
3.92
3.91
3.91
3.90
3.89
3.83
2.28
2.28
2.27
2.26
2.26
2.25
2.25
2.24
2.24
2.23
2.22
2.22
2.21
2.20
2.07
2.06
2.05
2.05
2.04
2.04
2.04
2.03
2.02
1.28
1.27
1.25
O
OEt
MeO
Cl
2j
r.r. > 20:1
600 MHz
1.00
0.99
1.06
1.05
1.04
2.26
3.18
3.25
1.13
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

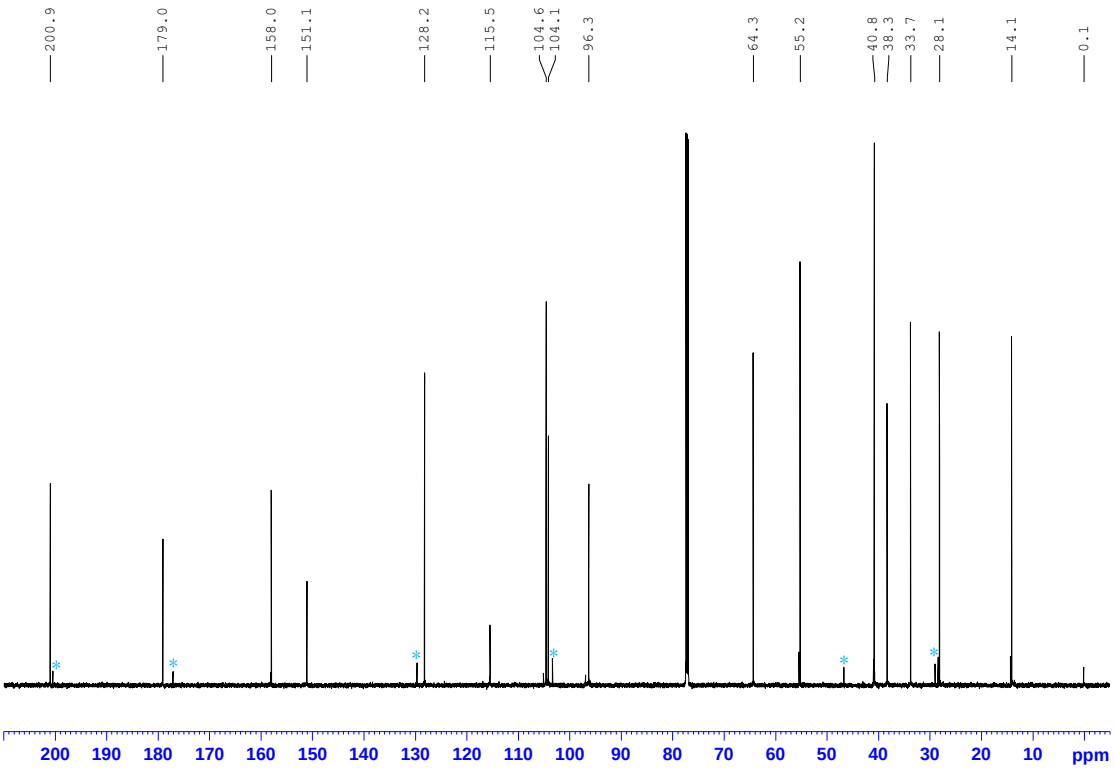

200.1
177.3
155.9
129.6
128.0
127.9
125.5
111.9
105.0
64.6
55.8
39.1
33.8
27.6
14.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

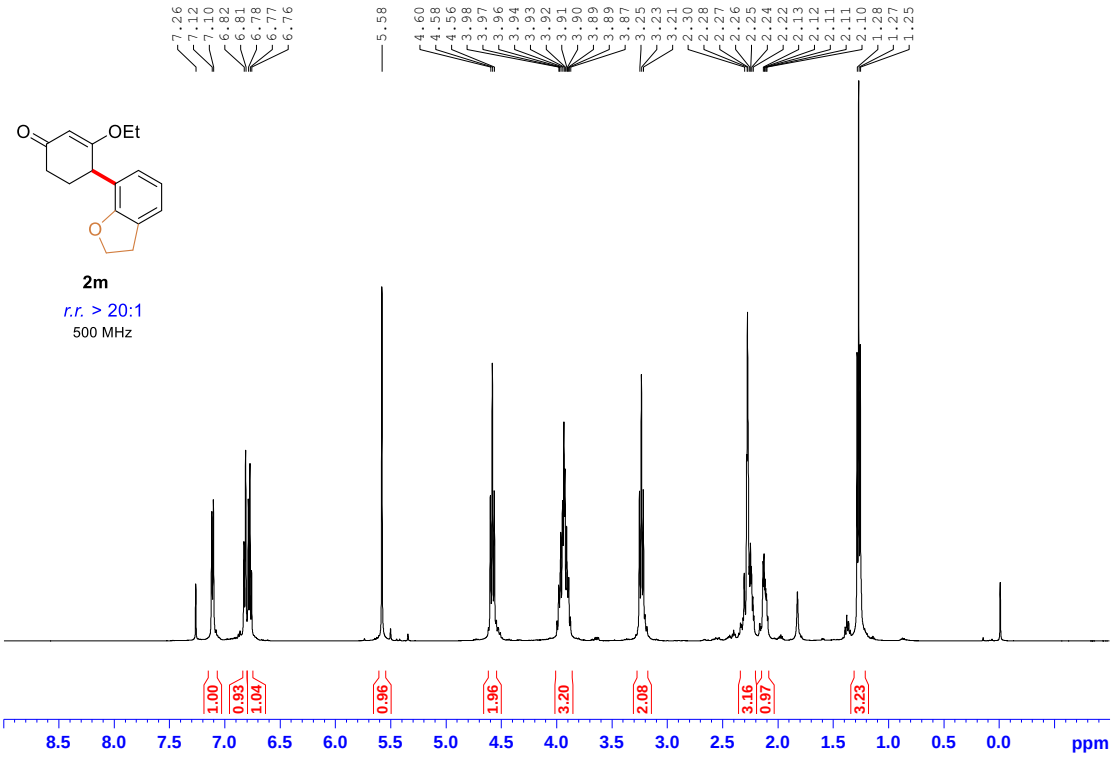

7.26
7.04
7.03
6.81
6.79
5.60
4.10
4.09
4.08
3.98
3.96
3.95
3.94
3.93
3.92
3.91
3.90
3.89
3.81
2.30
2.29
2.27
2.26
2.24
2.22
2.21
2.20
2.07
2.06
2.05
2.04
2.03
1.28
1.26
1.25
O
OEt
Me
MeO
2k
r.r. > 20:1
500 MHz
1.03
2.00
1.00
1.00
2.21
3.03
6.32
1.13
3.56
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

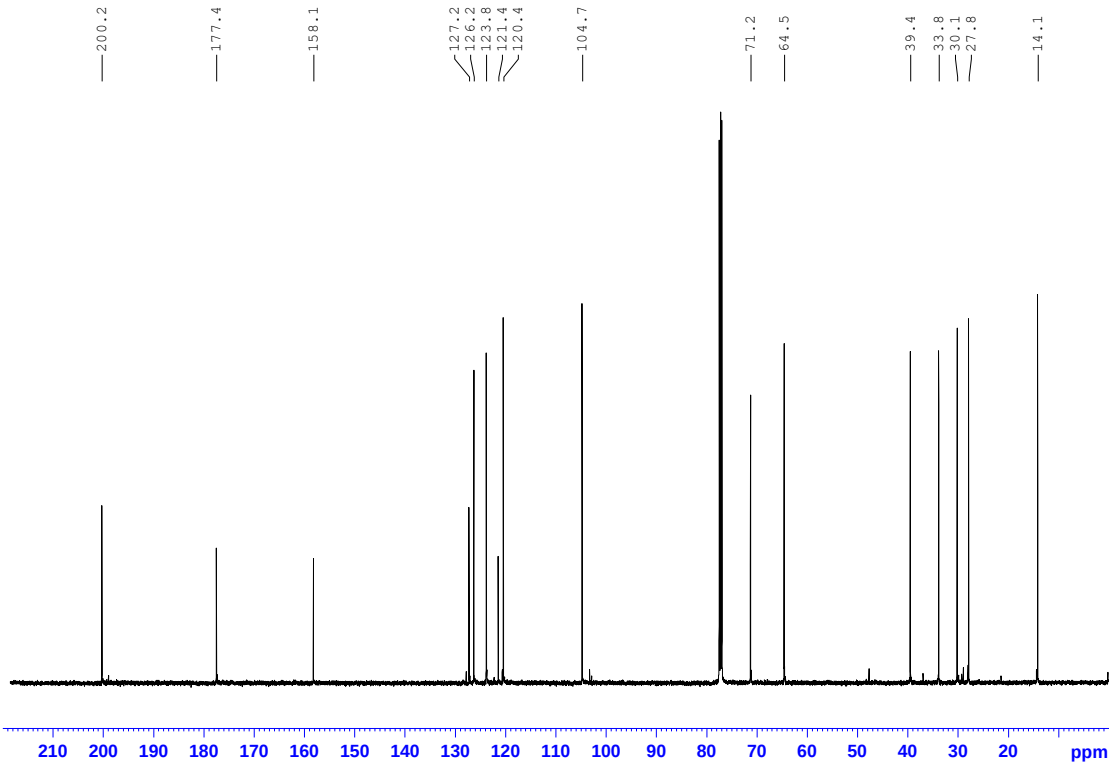

200.7
178.4
155.1
129.5
128.6
128.5
127.4
110.7
104.8
64.4
55.5
39.1
33.8
27.9
20.7
14.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

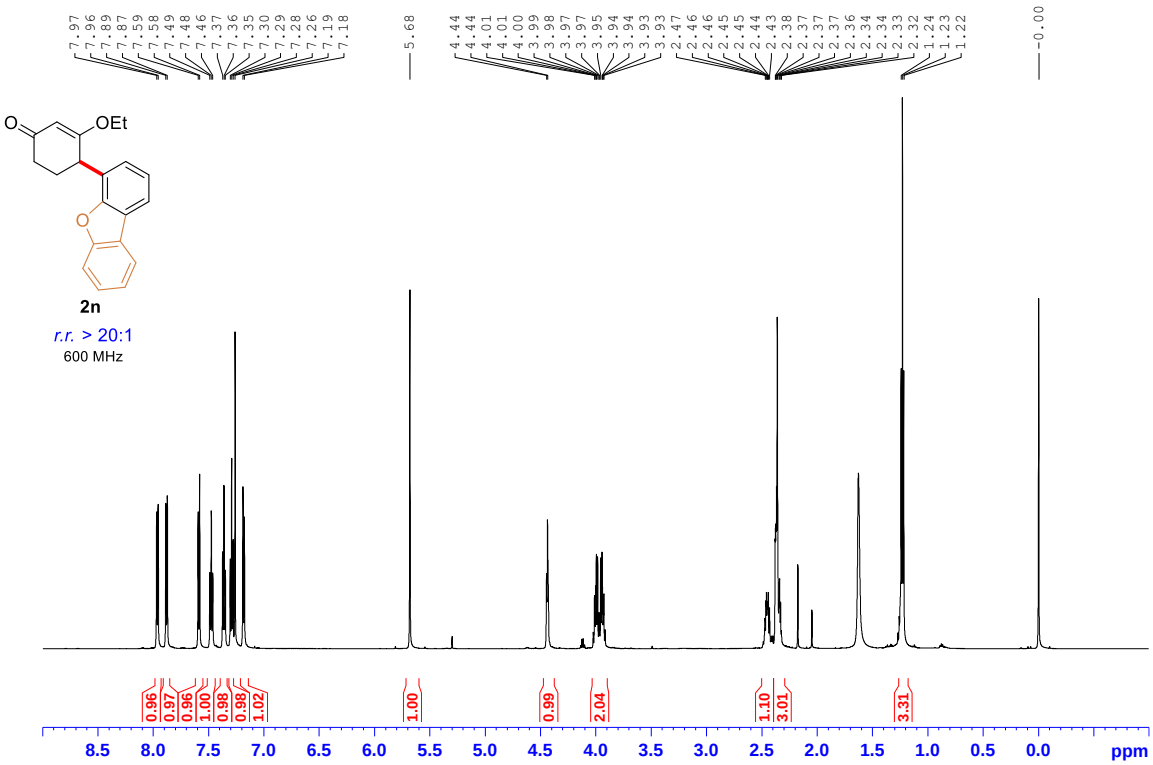


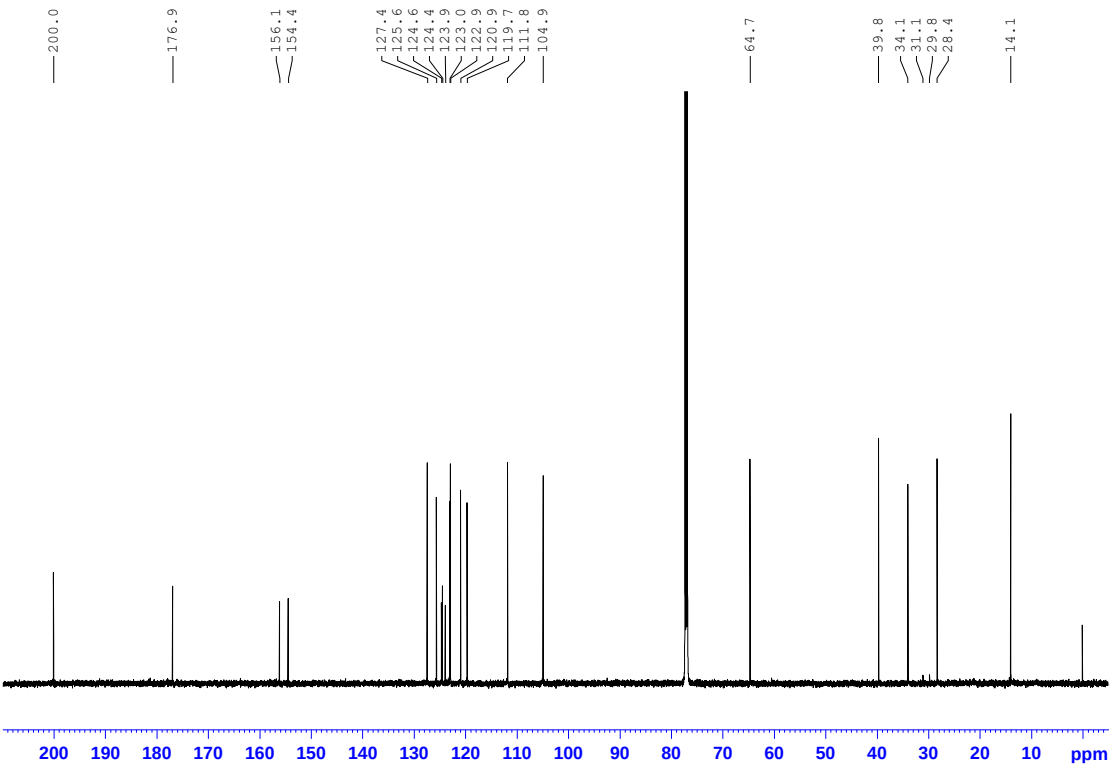
* is for α'-isomer

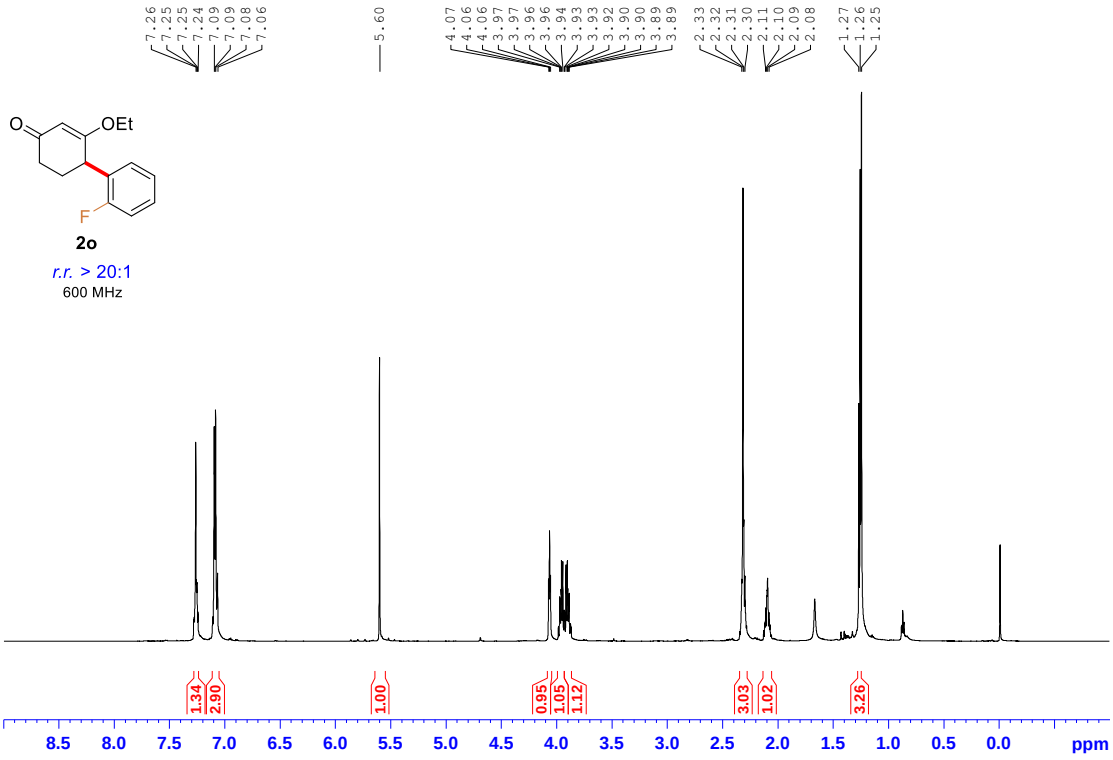


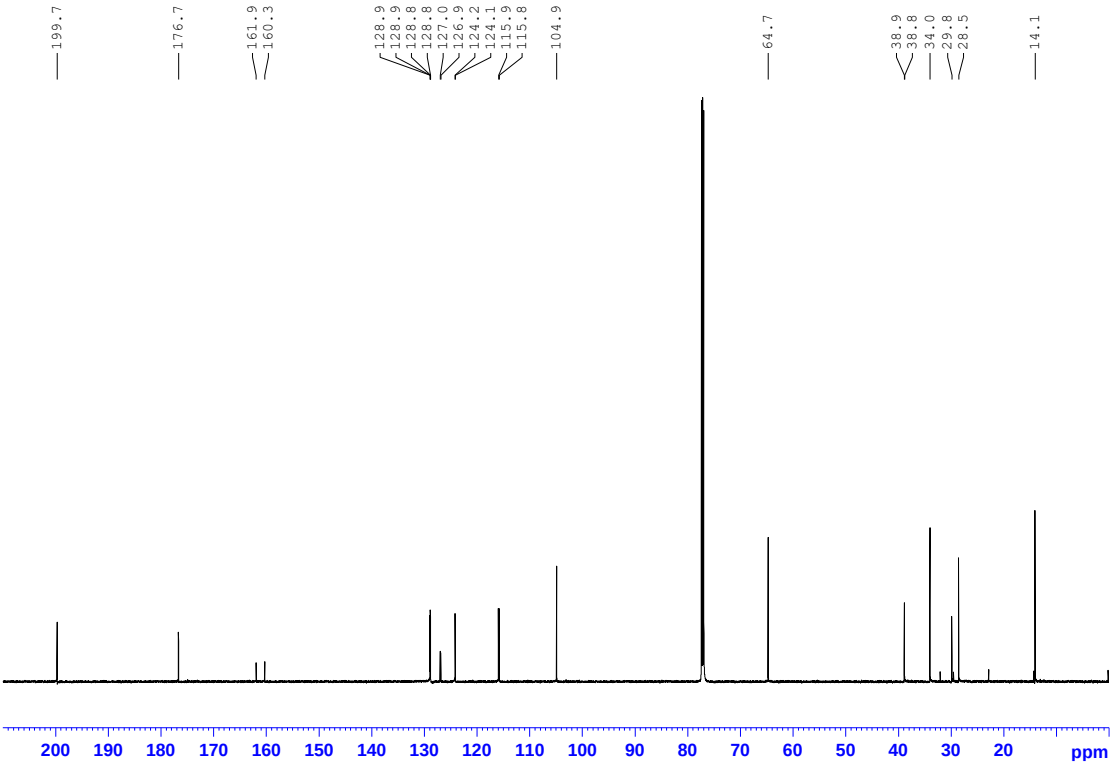

7.26
7.12
7.10
6.82
6.81
6.78
6.77
6.76
5.58
4.60
4.58
4.56
3.98
3.97
3.96
3.94
3.93
3.92
3.91
3.90
3.89
3.89
3.87
3.25
3.23
3.21
2.30
2.28
2.27
2.26
2.25
2.24
2.22
2.13
2.12
2.11
2.11
2.10
1.28
1.27
1.25
O
OEt
O
2m
r.r. > 20:1
500 MHz
1.00
0.93
1.04
0.96
1.96
3.20
2.08
3.16
0.97
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

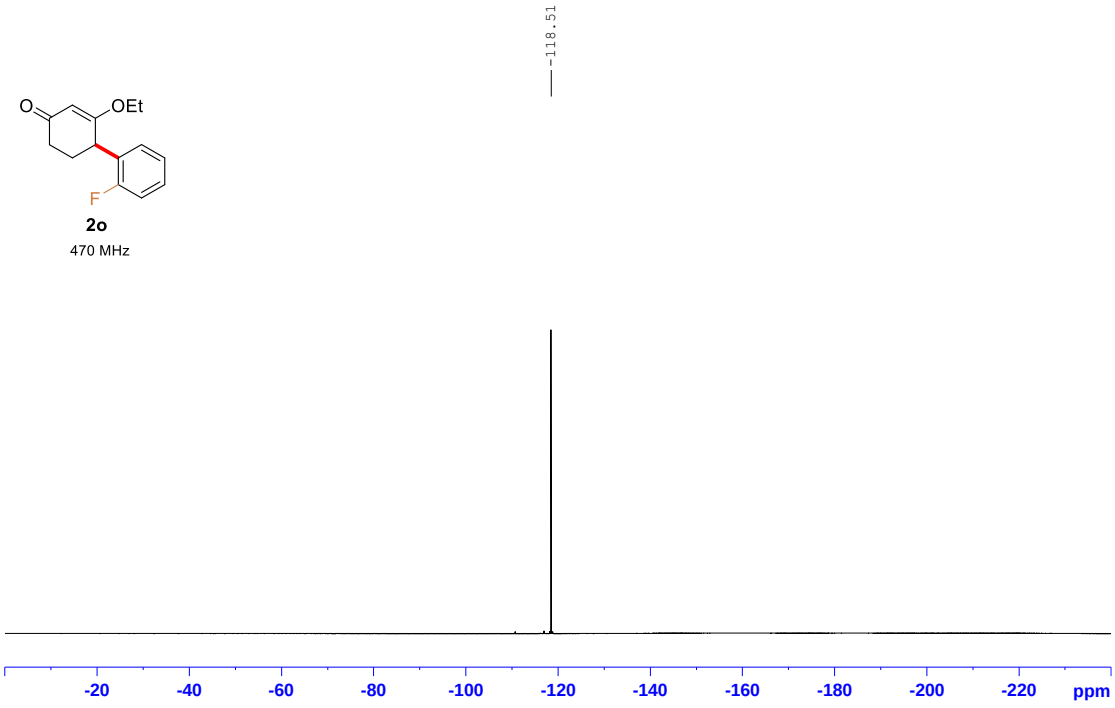

200.2
177.4
158.1
127.2
126.2
123.8
121.4
120.4
104.7
71.2
64.5
39.4
33.8
30.1
27.8
14.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

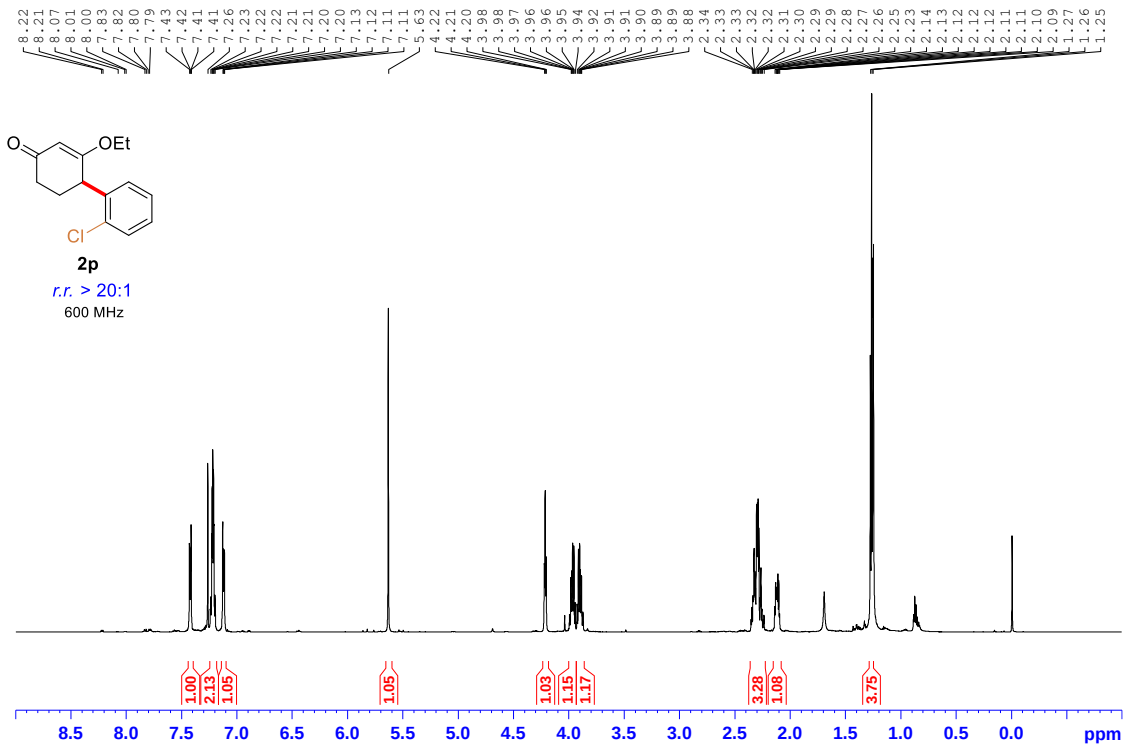

7.97
7.96
7.89
7.87
7.59
7.58
7.49
7.48
7.46
7.37
7.36
7.35
7.30
7.29
7.28
7.26
7.19
7.18
5.68
4.44
4.44
4.01
4.00
3.99
3.98
3.97
3.97
3.95
3.94
3.94
3.93
3.93
2.47
2.46
2.46
2.45
2.45
2.44
2.43
2.38
2.37
2.37
2.37
2.36
2.34
2.34
2.33
2.32
1.24
1.23
1.22
0.00
O
OEt
O
2n
r.r. > 20:1
600 MHz
0.96
0.97
0.96
1.00
0.98
0.98
1.02
1.00
0.99
2.04
1.10
3.01
3.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

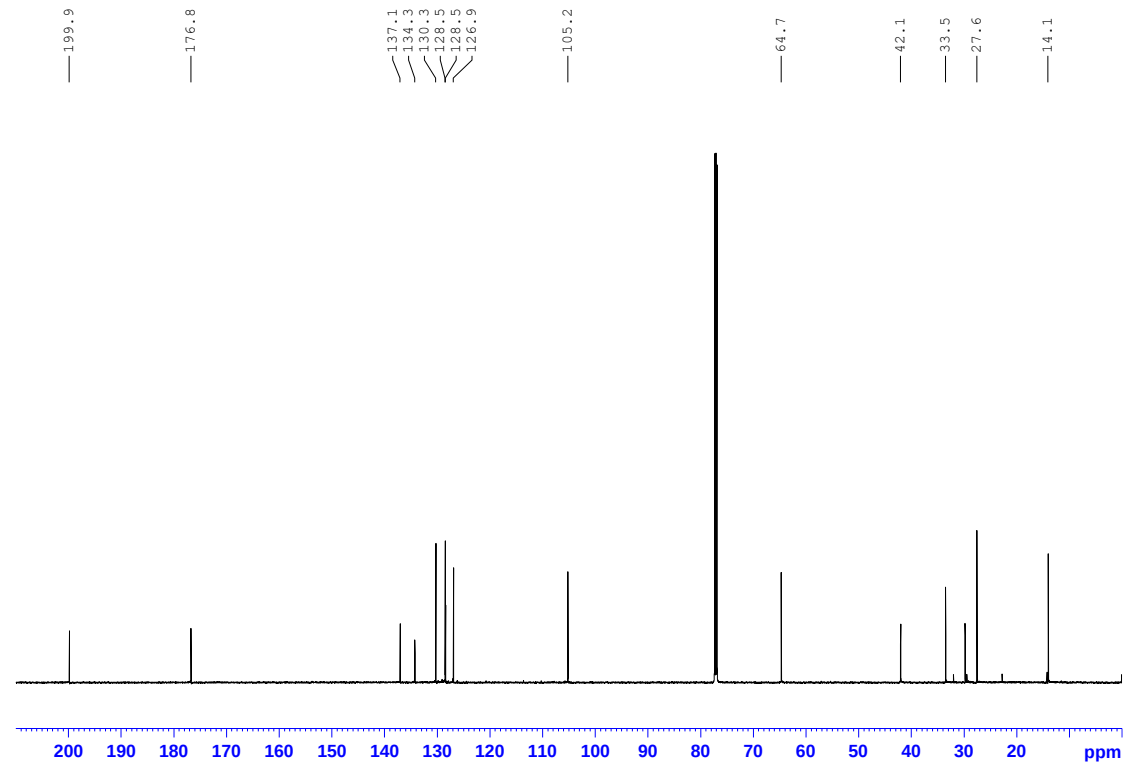

200.0
176.9
156.1
154.4
127.4
125.6
124.6
124.4
123.9
123.0
122.9
120.9
119.7
111.8
104.9
64.7
39.8
34.1
31.1
29.8
28.4
14.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

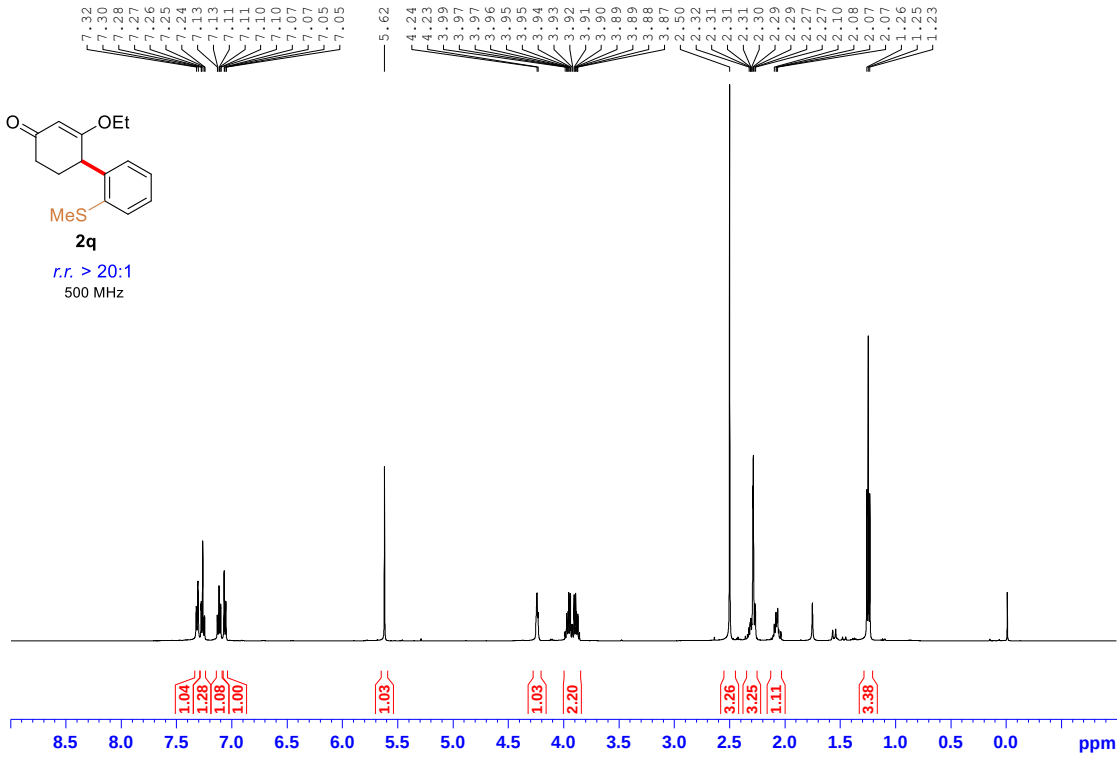

7.26
7.25
7.25
7.24
7.09
7.09
7.08
7.06
5.60
4.07
4.06
4.06
3.97
3.97
3.96
3.96
3.94
3.93
3.93
3.92
3.90
3.90
3.89
3.89
2.33
2.32
2.31
2.30
2.11
2.10
2.09
2.08
1.27
1.26
1.25
O
OEt
F
2o
r.r. > 20:1
600 MHz
1.34
2.90
1.00
0.95
1.05
1.12
3.03
1.02
3.26
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

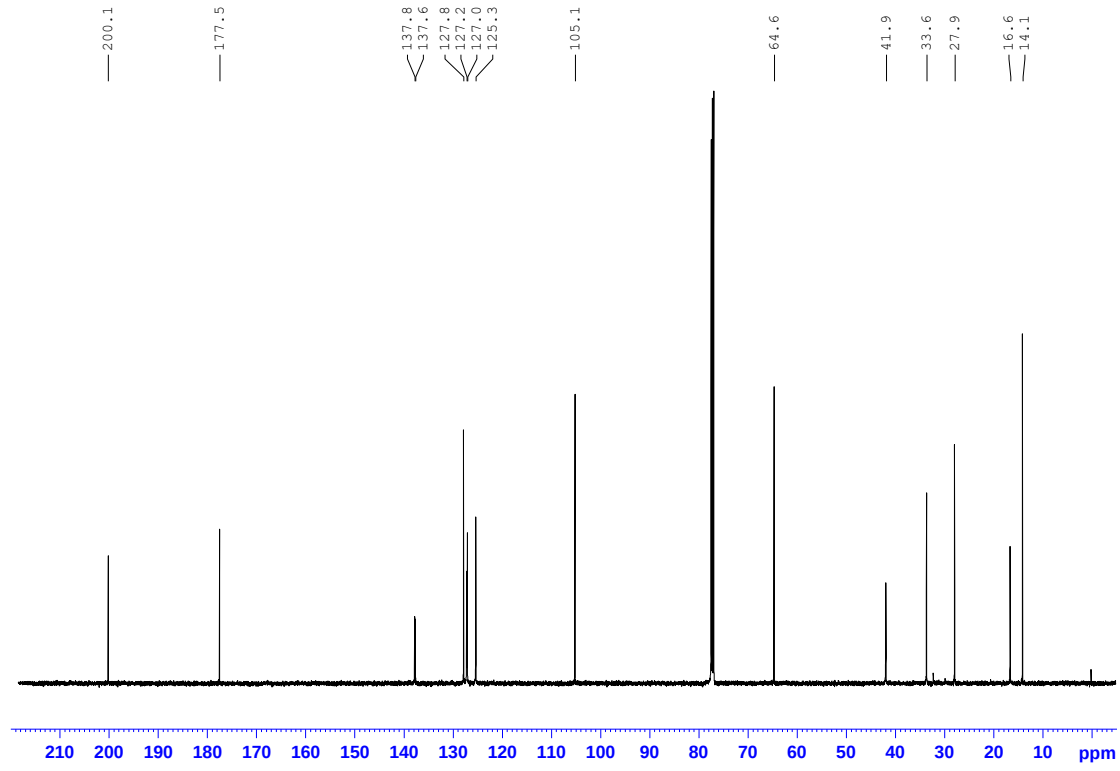

199.7
176.7
161.9
160.3
128.9
128.9
128.8
128.8
127.0
126.9
124.2
124.1
115.9
115.8
104.9
64.7
38.9
38.8
34.0
29.8
28.5
14.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

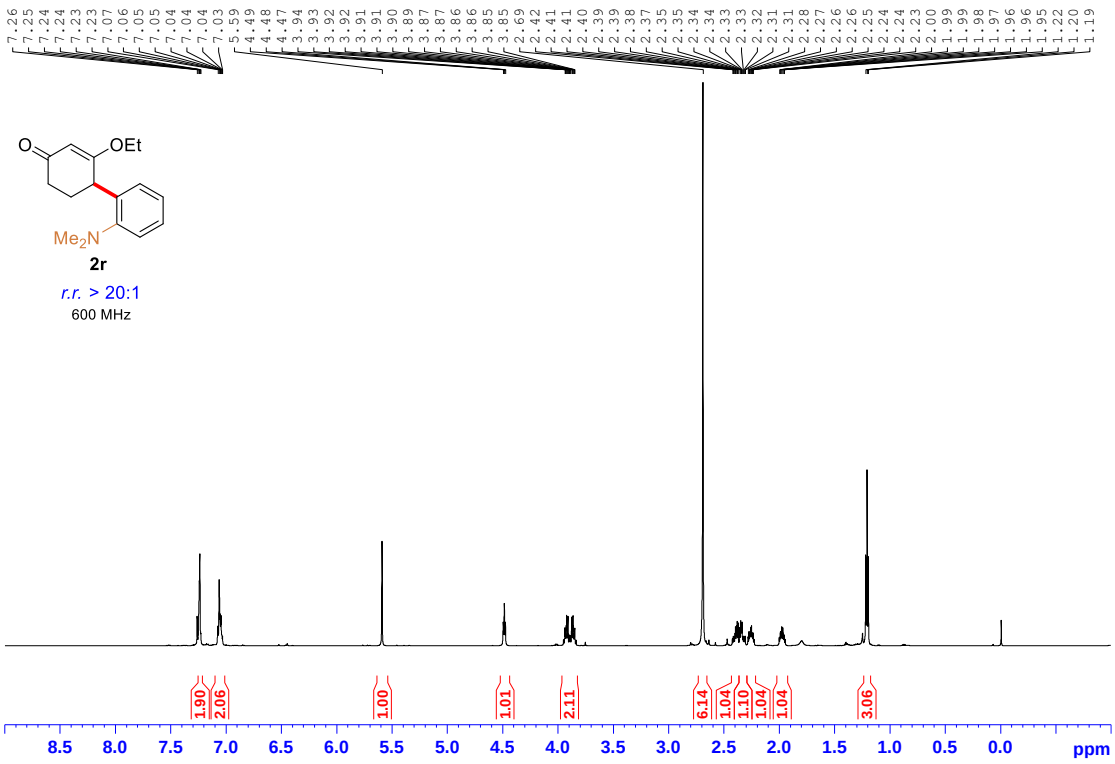

-118.51
O
OEt
F
2o
470 MHz
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm

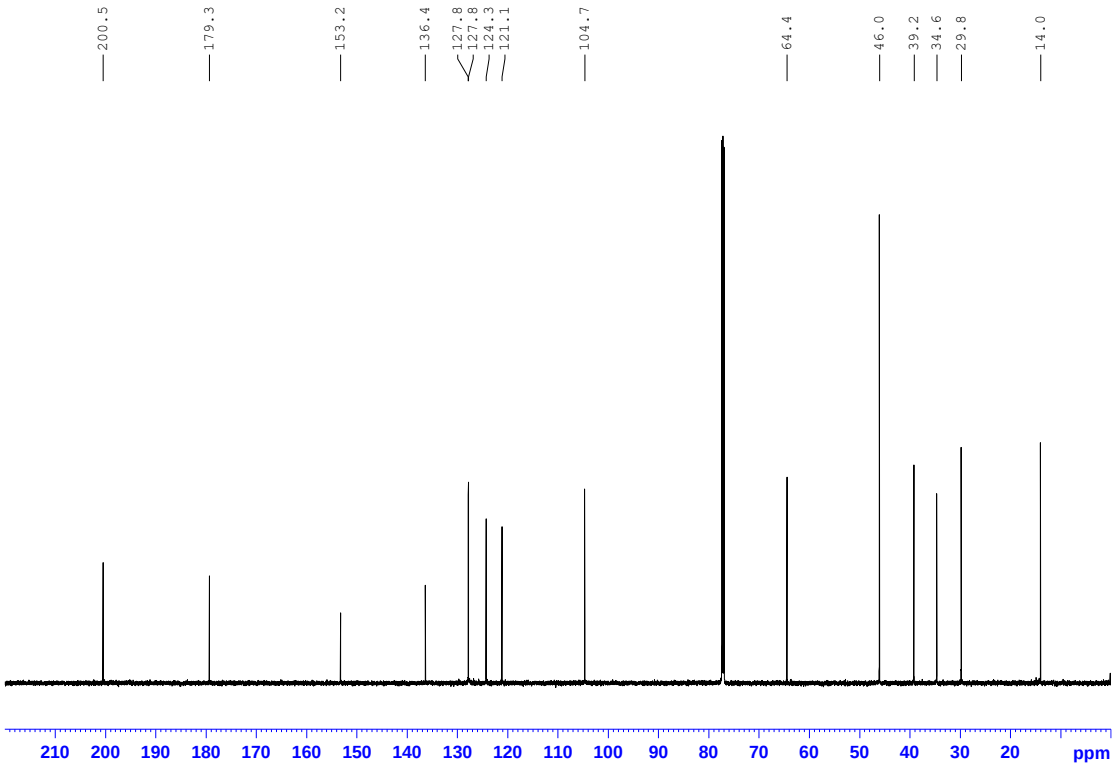

8.22 8.21 8.07 8.01 8.00 7.83 7.82 7.80 7.79 7.43 7.42 7.41 7.41 7.26 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.13 7.12 7.11 7.11 5.63 4.22 4.21 4.20 3.98 3.98 3.97 3.96 3.96 3.95 3.94 3.92 3.91 3.91 3.90 3.89 3.89 3.88 2.34 2.33 2.33 2.32 2.32 2.31 2.30 2.29 2.29 2.28 2.27 2.26 2.25 2.23 2.14 2.13 2.12 2.12 2.12 2.11 2.11 2.10 2.09 1.27 1.26 1.25
O
OEt
Cl
2p
r.r. > 20:1
600 MHz
1.00 2.13 1.05 1.05 1.03 1.15 1.17 3.28 1.08 3.75
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

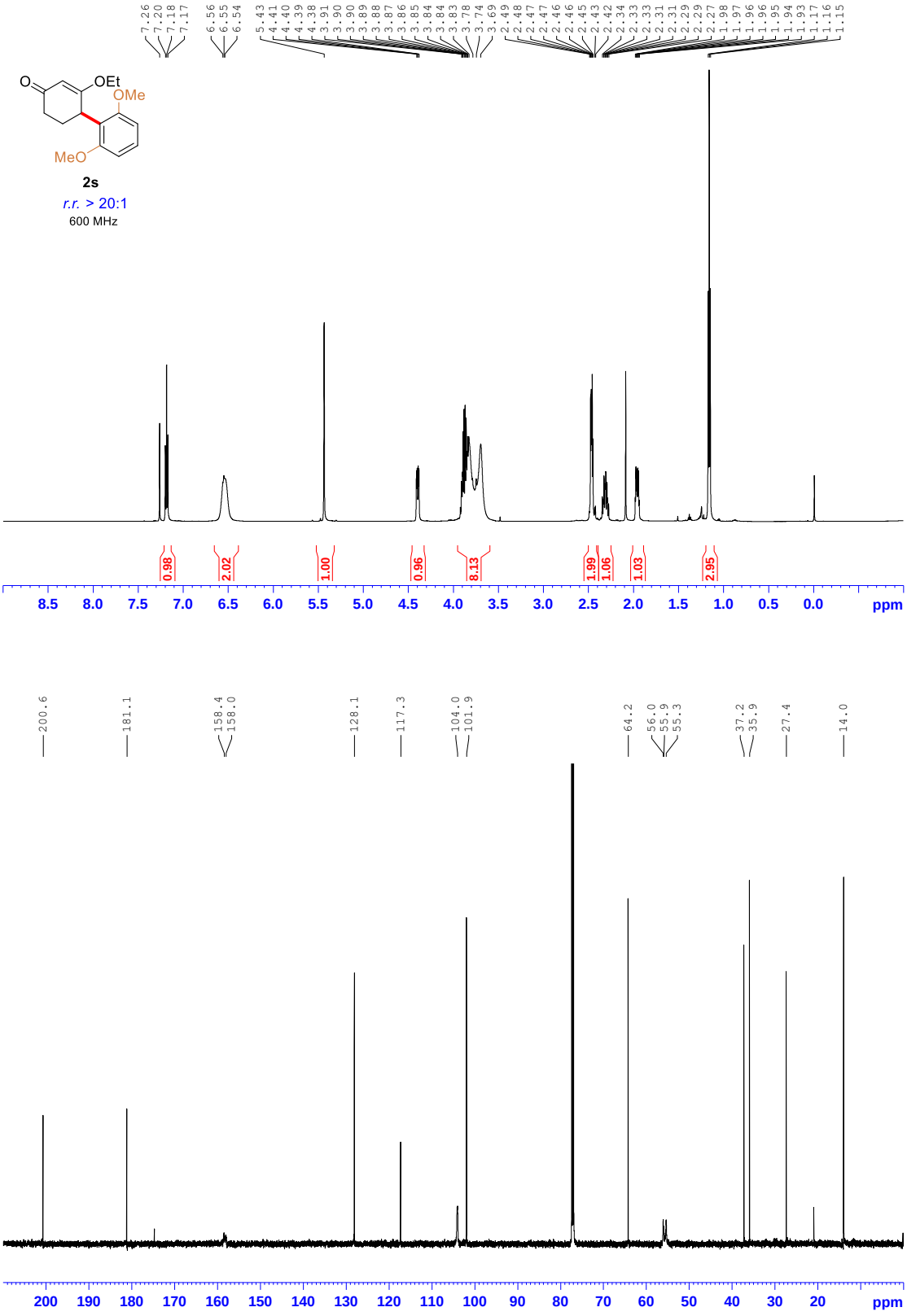

199.9 176.8 137.1 134.3 130.3 128.5 128.5 126.9 105.2 64.7 42.1 33.5 27.6 14.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

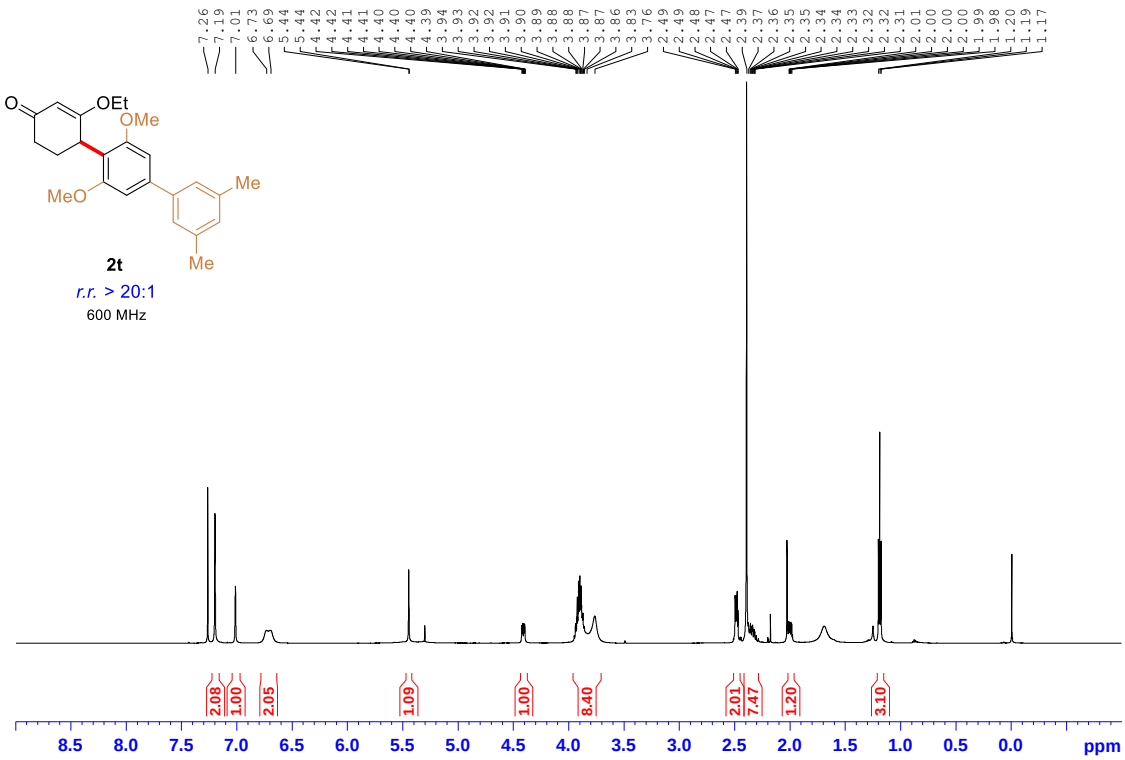

7.32
7.30
7.28
7.27
7.26
7.25
7.24
7.13
7.11
7.11
7.10
7.10
7.07
7.07
7.05
7.05
5.62
4.24
4.23
3.99
3.97
3.96
3.95
3.95
3.94
3.93
3.92
3.91
3.90
3.89
3.89
3.88
3.87
2.50
2.32
2.31
2.31
2.30
2.29
2.29
2.27
2.27
2.10
2.08
2.07
2.07
1.26
1.25
1.23
O
OEt
MeS
2q
r.r. > 20:1
500 MHz
1.04
1.28
1.08
1.00
1.03
1.03
2.20
3.26
3.25
1.11
3.38
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

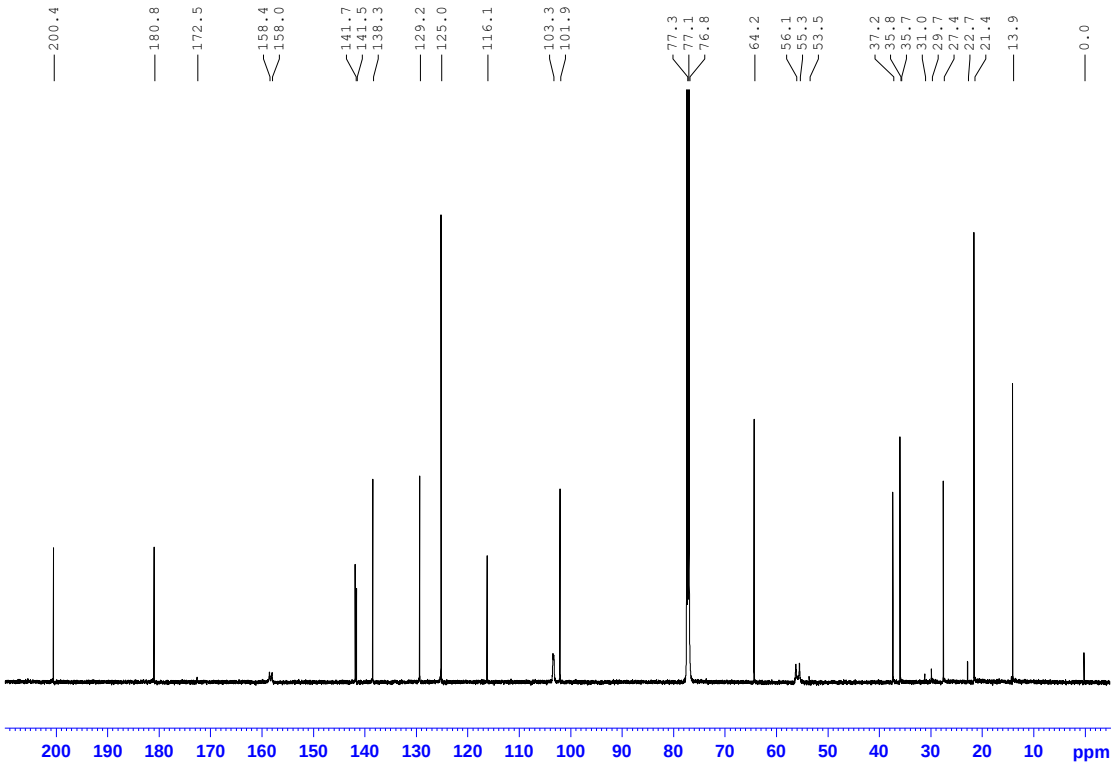

200.1
177.5
137.8
137.6
127.8
127.2
127.0
125.3
105.1
64.6
41.9
33.6
27.9
16.6
14.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

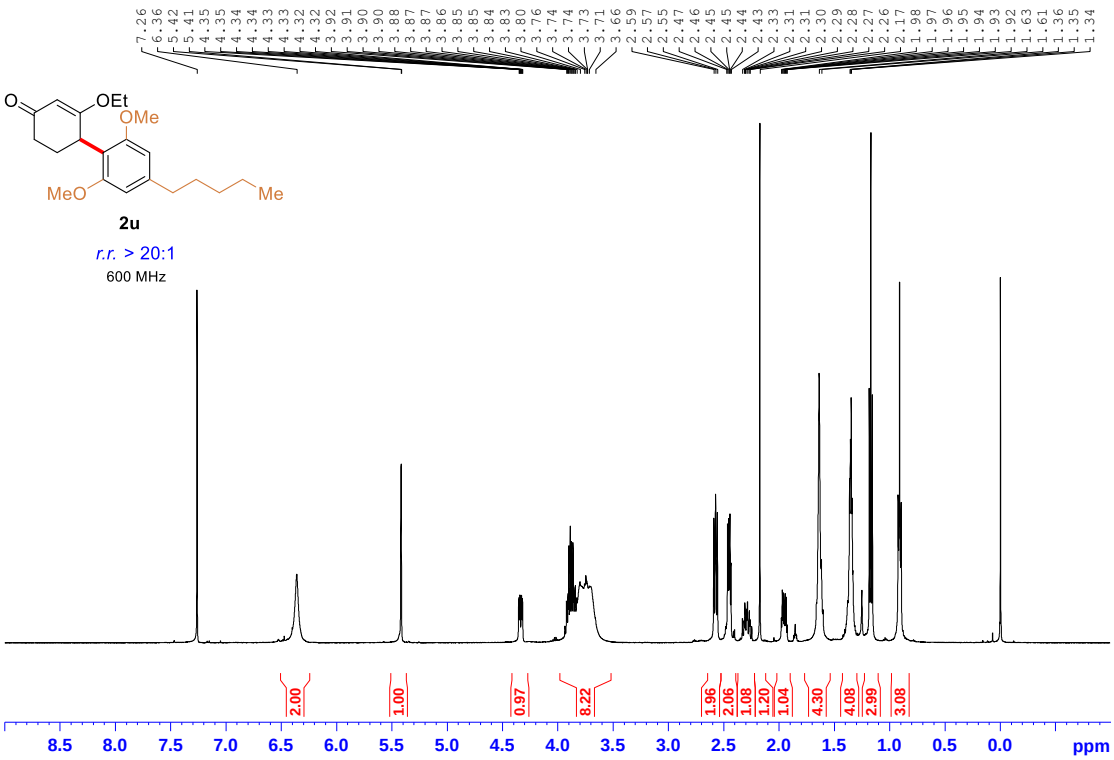

7.26 7.25 7.24 7.24 7.23 7.23 7.07 7.06 7.05 7.05 7.04 7.04 7.04 7.03 5.59 4.49 4.48 4.47 3.94 3.93 3.92 3.92 3.91 3.91 3.90 3.89 3.87 3.87 3.86 3.86 3.85 3.85 2.69 2.42 2.41 2.41 2.40 2.39 2.39 2.38 2.37 2.35 2.35 2.34 2.34 2.33 2.33 2.32 2.31 2.31 2.28 2.27 2.26 2.26 2.25 2.24 2.24 2.23 2.00 1.99 1.99 1.98 1.97 1.96 1.96 1.95 1.22 1.20 1.19
O
OEt
Me2N
2r
r.r. > 20:1
600 MHz
1.90 2.06 1.00 1.01 2.11 6.14 1.04 1.10 1.04 1.04 3.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

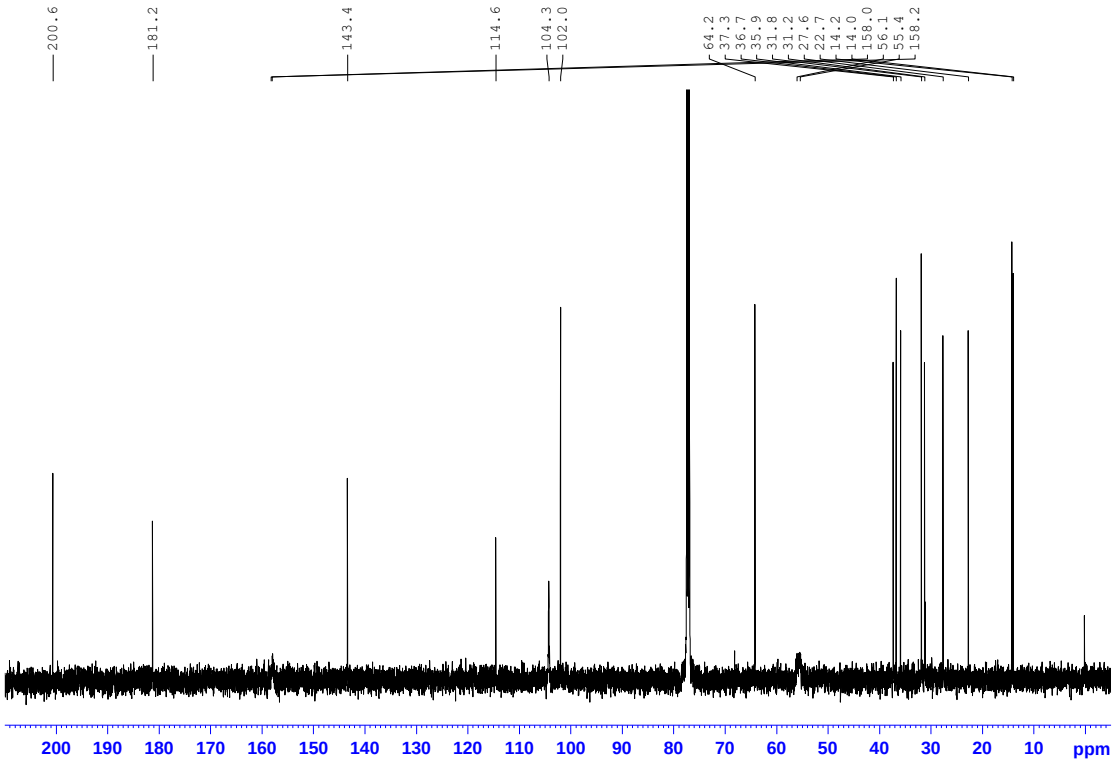

200.5 179.3 153.2 136.4 127.8 127.8 124.3 121.1 104.7 64.4 46.0 39.2 34.6 29.8 14.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

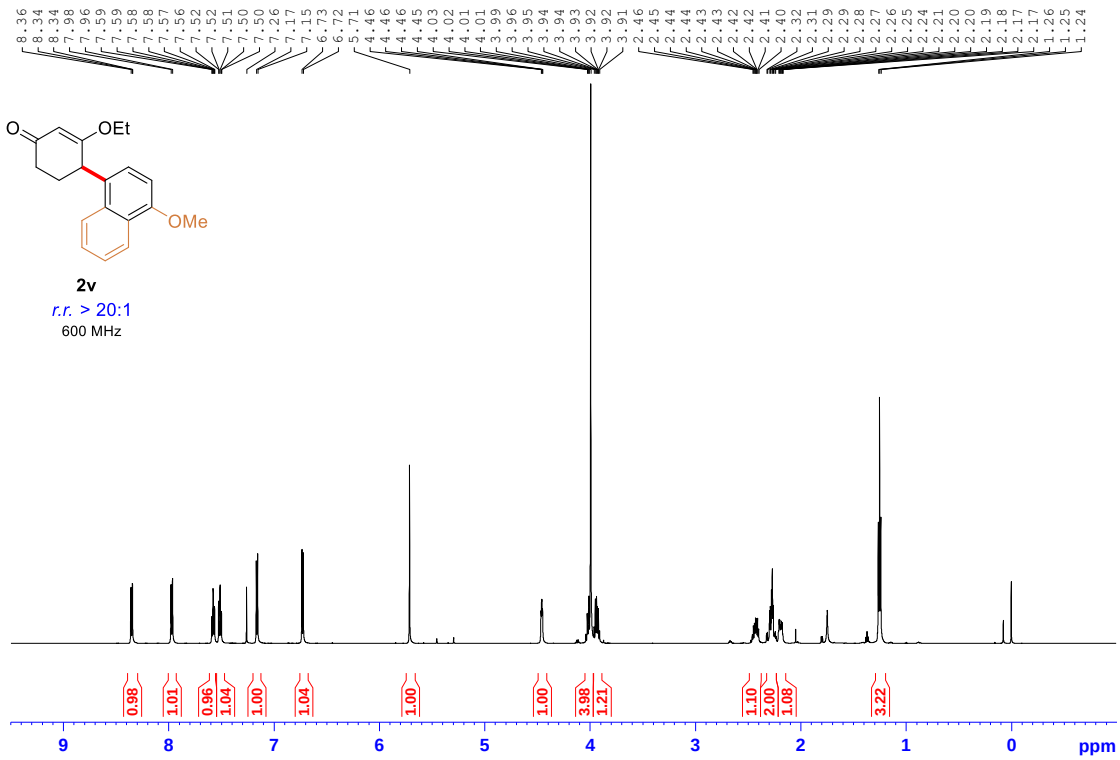

7.26
7.20
7.18
7.17
6.56
6.55
6.54
5.43
4.41
4.40
4.39
4.38
3.91
3.90
3.89
3.88
3.87
3.86
3.85
3.84
3.84
3.83
3.78
3.74
3.69
2.49
2.48
2.47
2.47
2.46
2.46
2.45
2.43
2.42
2.34
2.33
2.33
2.31
2.31
2.29
2.29
2.27
1.98
1.97
1.96
1.96
1.95
1.94
1.93
1.17
1.16
1.15
O
OEt
OMe
MeO
2s
r.r. > 20:1
600 MHz
0.98
2.02
1.00
0.96
8.13
1.99
1.06
1.03
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
200.6
181.1
158.4
158.0
128.1
117.3
104.0
101.9
64.2
56.0
55.9
55.3
37.2
35.9
27.4
14.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

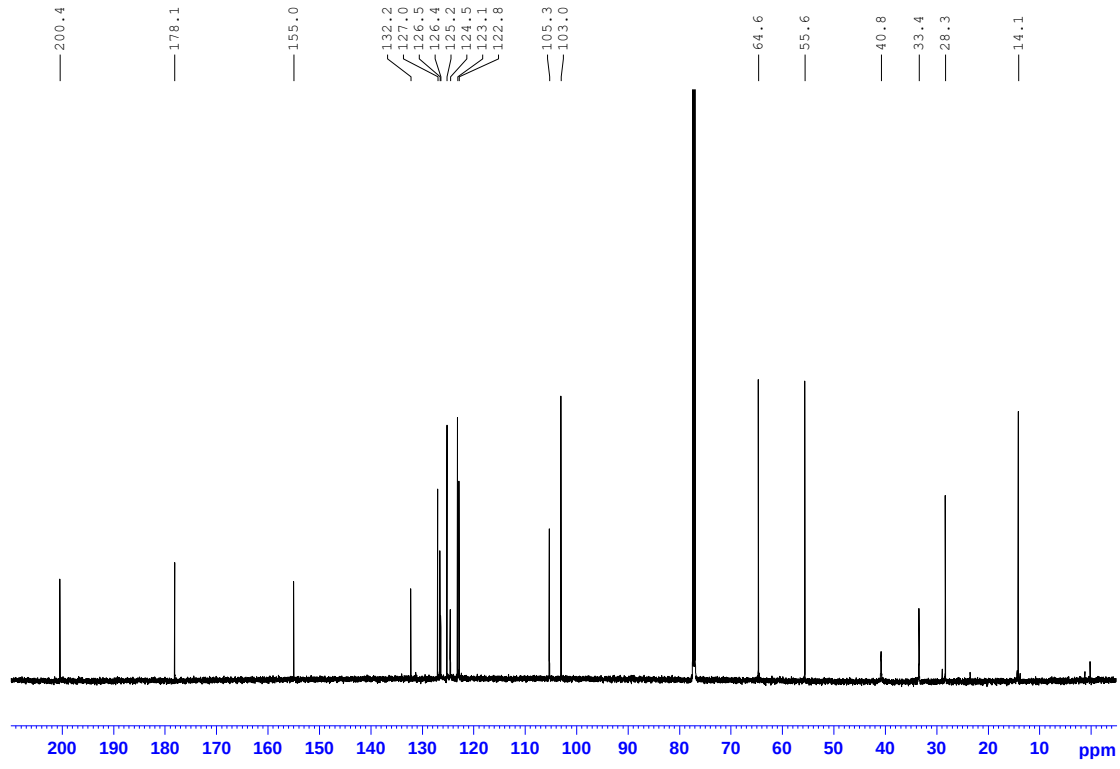

O
OEt
OMe
MeO
Me
Me
2t
r.r. > 20:1
600 MHz
7.26 7.19 7.01 6.73 6.69 5.44 4.42 4.41 4.40 4.39 3.94 3.93 3.92 3.91 3.90 3.89 3.88 3.87 3.86 3.83 3.76 2.49 2.48 2.47 2.39 2.37 2.36 2.35 2.34 2.33 2.32 2.31 2.01 2.00 2.00 1.99 1.98 1.20 1.19 1.17
2.08 1.00 2.05 1.09 1.00 8.40 2.01 7.47 1.20 3.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

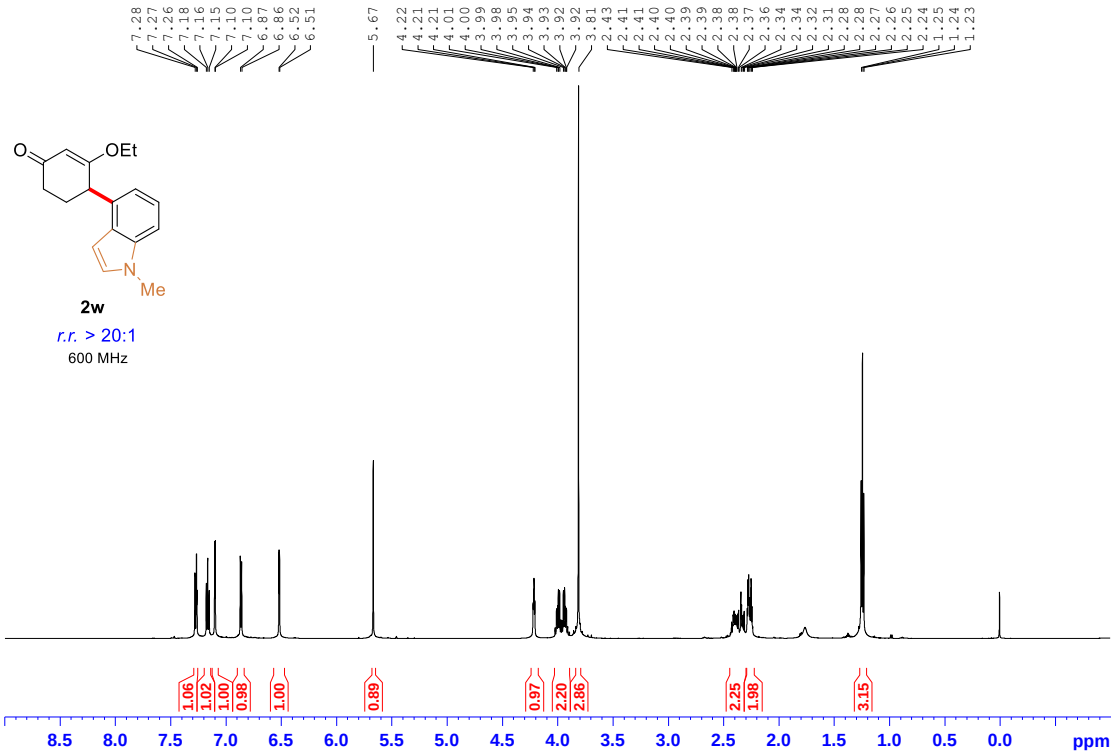

200.4 180.8 172.5 158.4 158.0 141.7 141.5 138.3 129.2 125.0 116.1 103.3 101.9 77.3 77.1 76.8 64.2 56.1 55.3 53.5 37.2 35.8 35.7 31.0 29.7 27.4 22.7 21.4 13.9 0.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

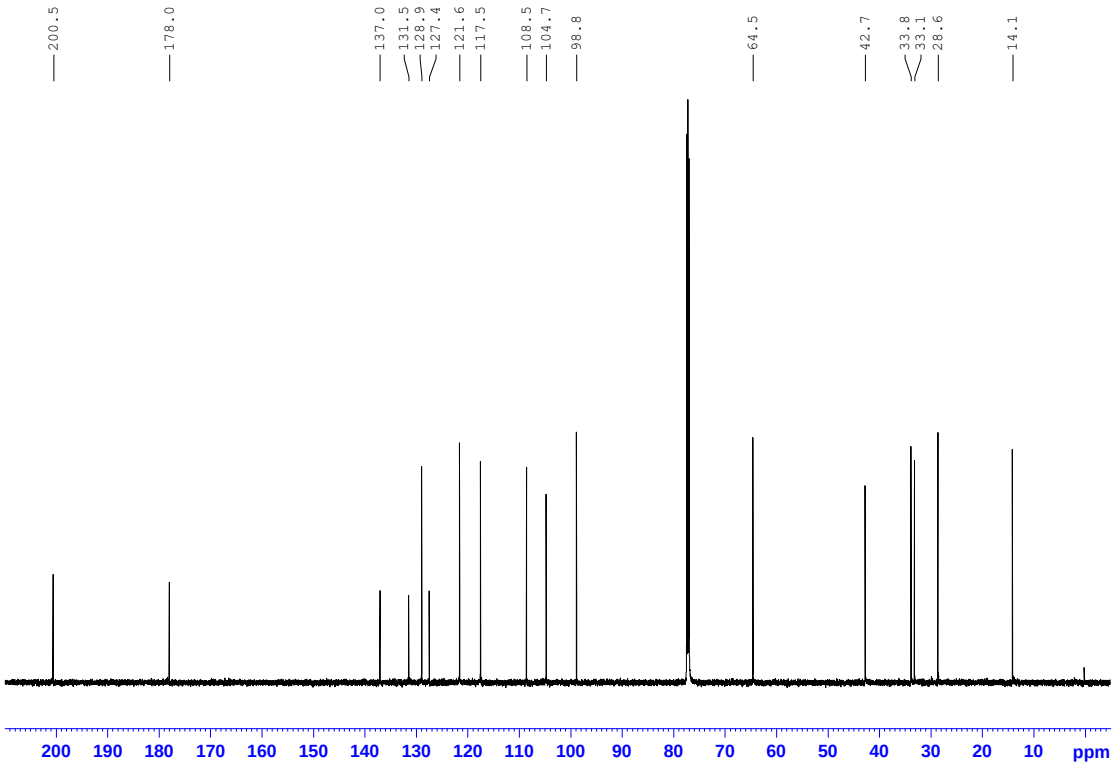

7.26 6.36 5.42 5.41 4.35 4.34 4.34 4.33 4.33 4.32 4.32 3.92 3.91 3.90 3.90 3.88 3.87 3.87 3.86 3.85 3.85 3.84 3.83 3.80 3.76 3.74 3.74 3.73 3.71 3.66 2.59 2.57 2.55 2.47 2.46 2.45 2.45 2.44 2.43 2.33 2.31 2.30 2.29 2.28 2.27 2.26 2.17 1.98 1.97 1.96 1.95 1.94 1.93 1.92 1.63 1.61 1.36 1.35 1.34
O
OEt
OMe
MeO
Me
2u
r.r. > 20:1
600 MHz
2.00 1.00 0.97 8.22 1.96 2.06 1.08 1.20 1.04 4.30 4.08 2.99 3.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

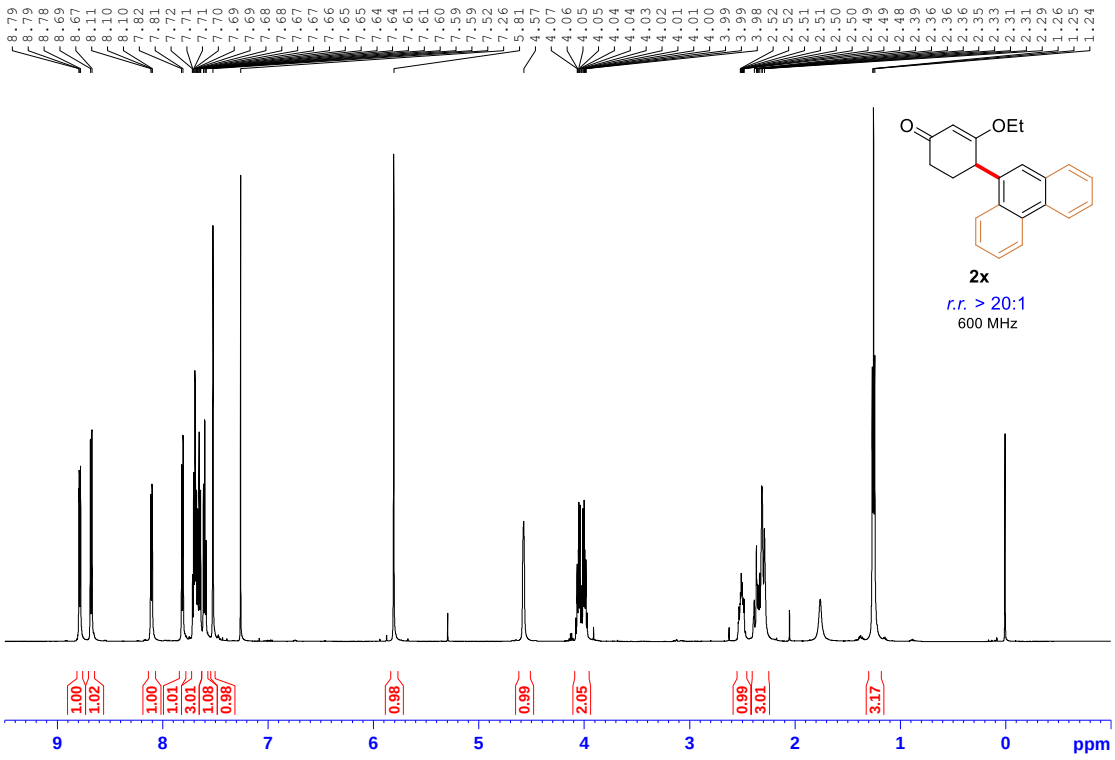

200.6 181.2 143.4 114.6 104.3 102.0 64.2 37.3 36.7 35.9 31.8 31.2 27.6 22.7 14.2 14.0 158.0 56.1 55.4 158.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

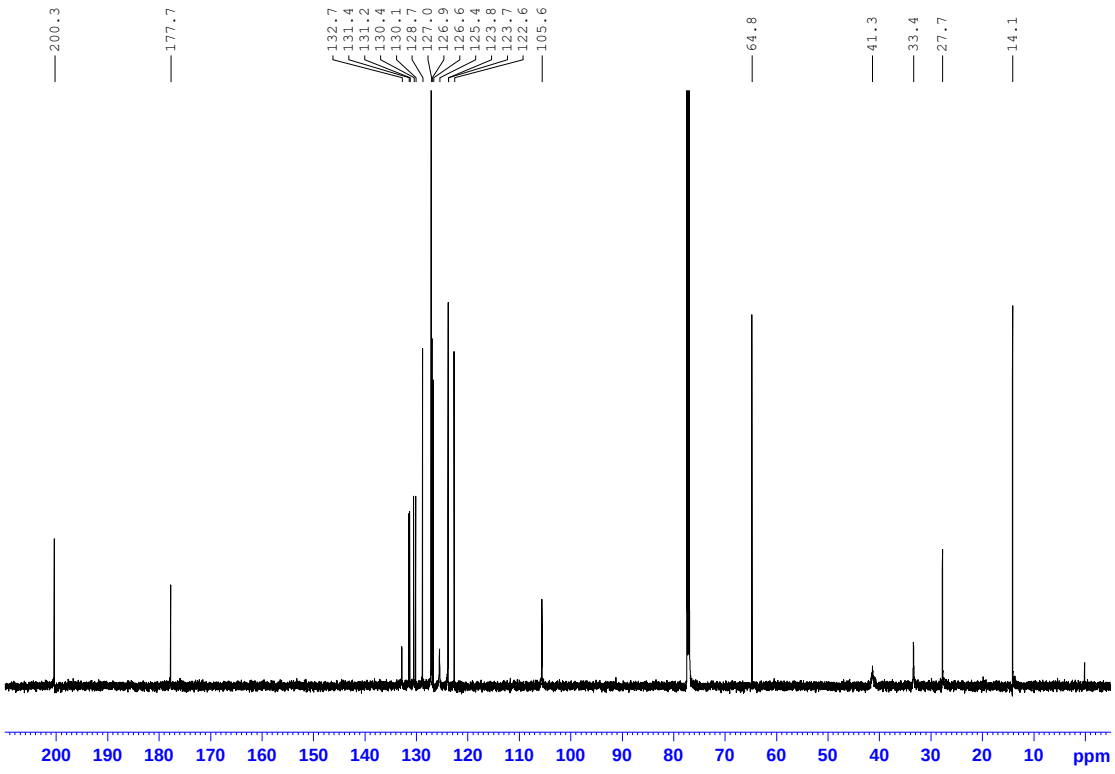

8.36 8.34 8.34 7.98 7.96 7.59 7.58 7.58 7.57 7.56 7.52 7.52 7.51 7.50 7.50 7.26 7.17 7.15 6.73 6.72 5.71 4.46 4.46 4.45 4.03 4.02 4.01 4.01 3.99 3.96 3.95 3.94 3.94 3.93 3.92 3.92 3.91 2.46 2.45 2.44 2.44 2.43 2.43 2.42 2.42 2.41 2.40 2.32 2.31 2.29 2.29 2.28 2.27 2.26 2.25 2.24 2.21 2.20 2.20 2.19 2.18 2.17 2.17 1.26 1.25 1.24
O
OEt
OMe
2v
r.r. > 20:1
600 MHz
0.98 1.01 0.96 1.04 1.00 1.04 1.00 1.00 3.98 1.21 1.10 2.00 1.08 3.22
9 8 7 6 5 4 3 2 1 0 ppm

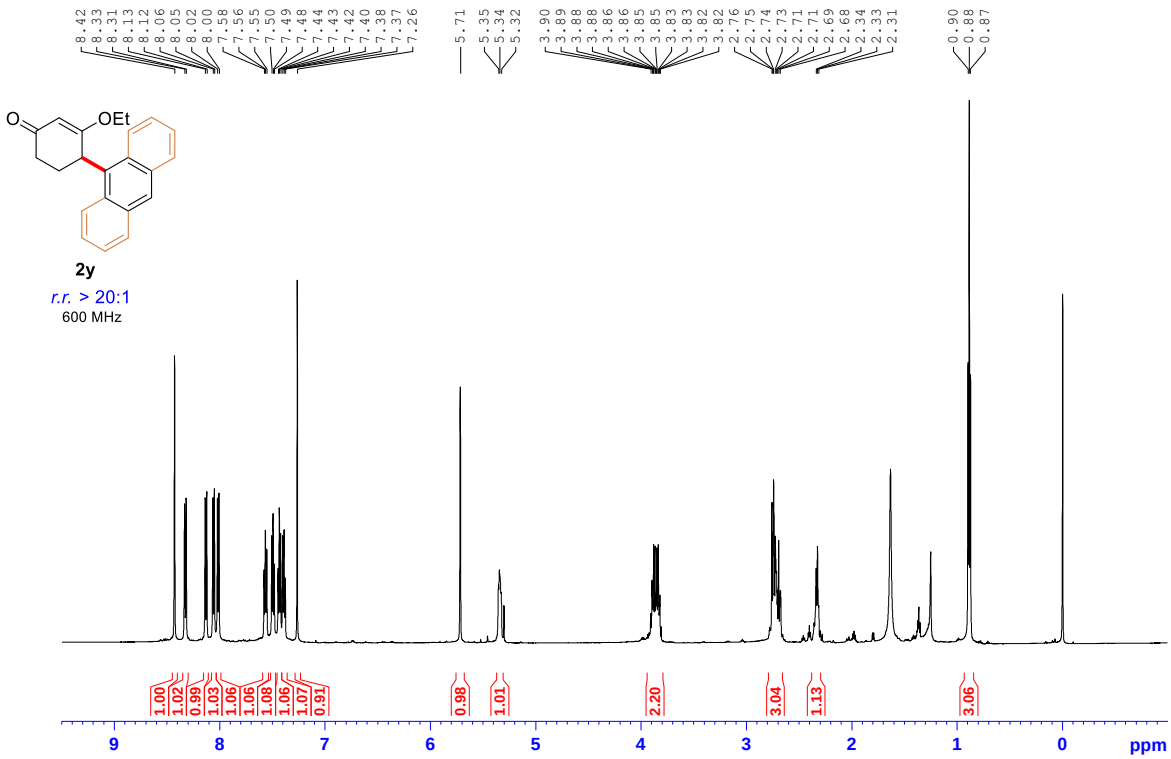

200.4 178.1 155.0 132.2 127.0 126.5 126.4 125.2 124.5 123.1 122.8 105.3 103.0 64.6 55.6 40.8 33.4 28.3 14.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

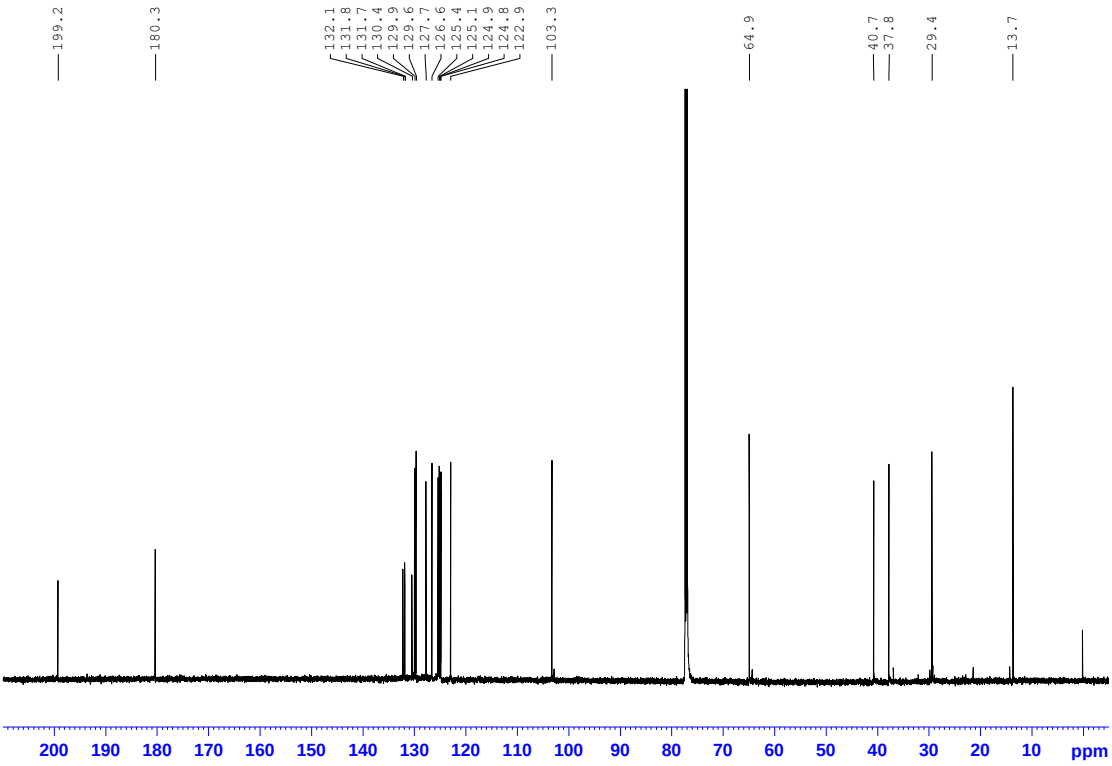

7.28
7.27
7.26
7.18
7.16
7.15
7.10
6.87
6.86
6.52
6.51
5.67
4.22
4.21
4.21
4.01
4.00
3.99
3.98
3.95
3.94
3.93
3.92
3.81
2.43
2.41
2.41
2.40
2.40
2.39
2.39
2.38
2.38
2.37
2.36
2.34
2.34
2.32
2.31
2.28
2.28
2.27
2.26
2.25
2.24
1.25
1.24
1.23
O
OEt
N
Me
2w
r.r. > 20:1
600 MHz
1.06
1.02
1.00
0.98
1.00
0.89
0.97
2.20
2.86
2.25
1.98
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

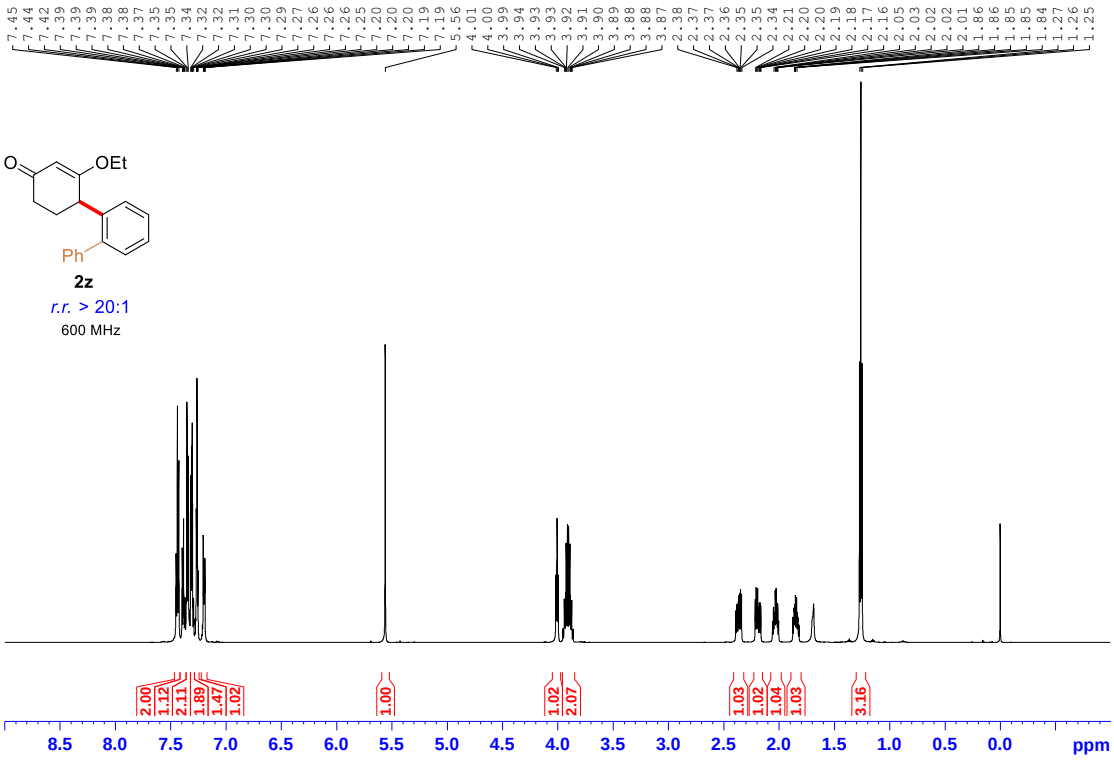

200.5
178.0
137.0
131.5
128.9
127.4
121.6
117.5
108.5
104.7
98.8
64.5
42.7
33.8
33.1
28.6
14.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.79 8.79 8.78 8.69 8.67 8.11 8.10 8.10 7.82 7.81 7.72 7.71 7.71 7.70 7.69 7.69 7.68 7.68 7.67 7.67 7.66 7.65 7.64 7.64 7.61 7.61 7.60 7.59 7.59 7.52 7.26 5.81 4.57 4.07 4.06 4.05 4.05 4.04 4.04 4.03 4.02 4.01 4.01 4.00 3.99 3.99 3.98 2.52 2.52 2.51 2.51 2.50 2.50 2.49 2.49 2.48 2.39 2.36 2.36 2.35 2.33 2.31 2.29 1.26 1.25 1.24
O
OEt
2x
r.r. > 20:1
600 MHz
1.00 1.02 1.00 1.01 3.01 1.08 0.98 0.98 0.99 2.05 0.99 3.01 3.17
9 8 7 6 5 4 3 2 1 0 ppm


200.3 177.7 132.7 131.4 131.2 130.4 130.1 128.7 127.0 126.9 126.6 125.4 123.8 123.7 122.6 105.6 64.8 41.3 33.4 27.7 14.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.42
8.33
8.31
8.13
8.12
8.06
8.05
8.02
8.00
7.58
7.56
7.55
7.50
7.49
7.48
7.44
7.43
7.42
7.40
7.38
7.37
7.26
5.71
5.35
5.34
5.32
3.90
3.89
3.88
3.88
3.86
3.86
3.85
3.85
3.83
3.83
3.82
3.82
2.76
2.75
2.74
2.73
2.71
2.71
2.69
2.68
2.34
2.33
2.31
0.90
0.88
0.87
O
OEt
2y
r.r. > 20:1
600 MHz
1.00
1.02
0.99
1.03
1.06
1.06
1.08
1.06
1.07
0.91
0.98
1.01
2.20
3.04
1.13
3.06
9
8
7
6
5
4
3
2
1
0
ppm


199.2
180.3
132.1
131.8
131.7
130.4
129.9
129.6
127.7
126.6
125.4
125.1
124.9
124.8
122.9
103.3
64.9
40.7
37.8
29.4
13.7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
OEt
Ph
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1.02
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1.03
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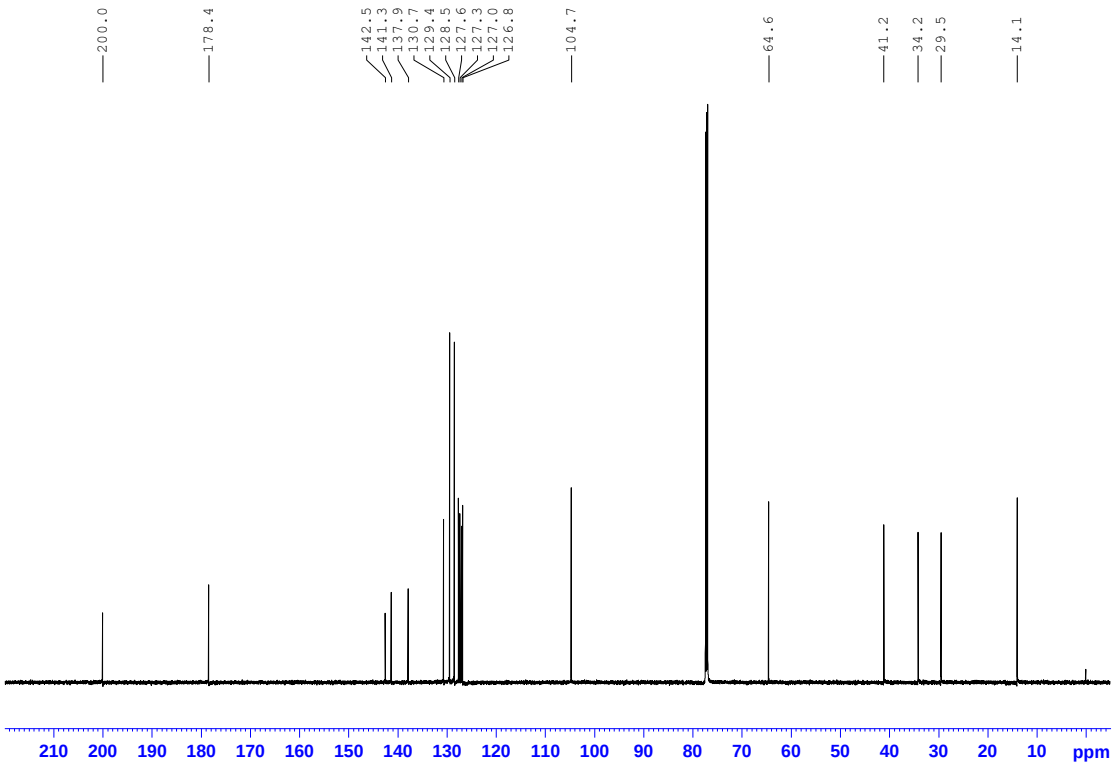
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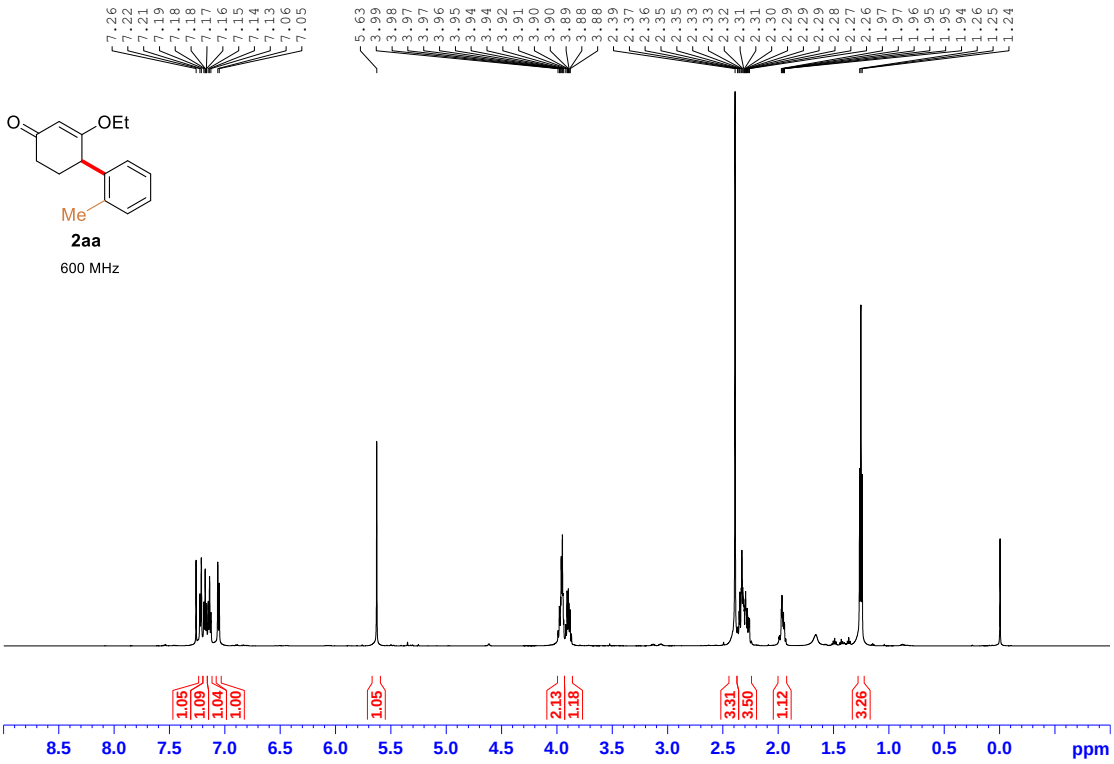
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1.95
1.95
1.94
1.26
1.25
1.24
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OEt
Me
2aa
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1.04
1.00
1.05
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3.31
3.50
1.12
3.26
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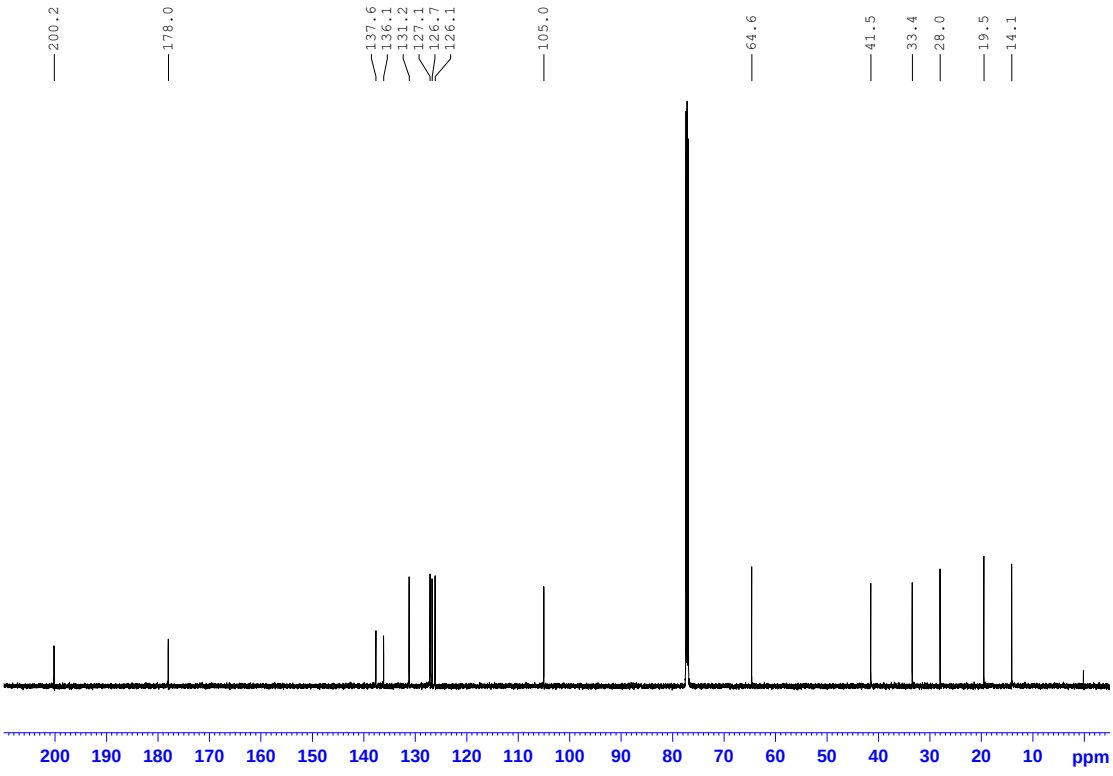
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14.1
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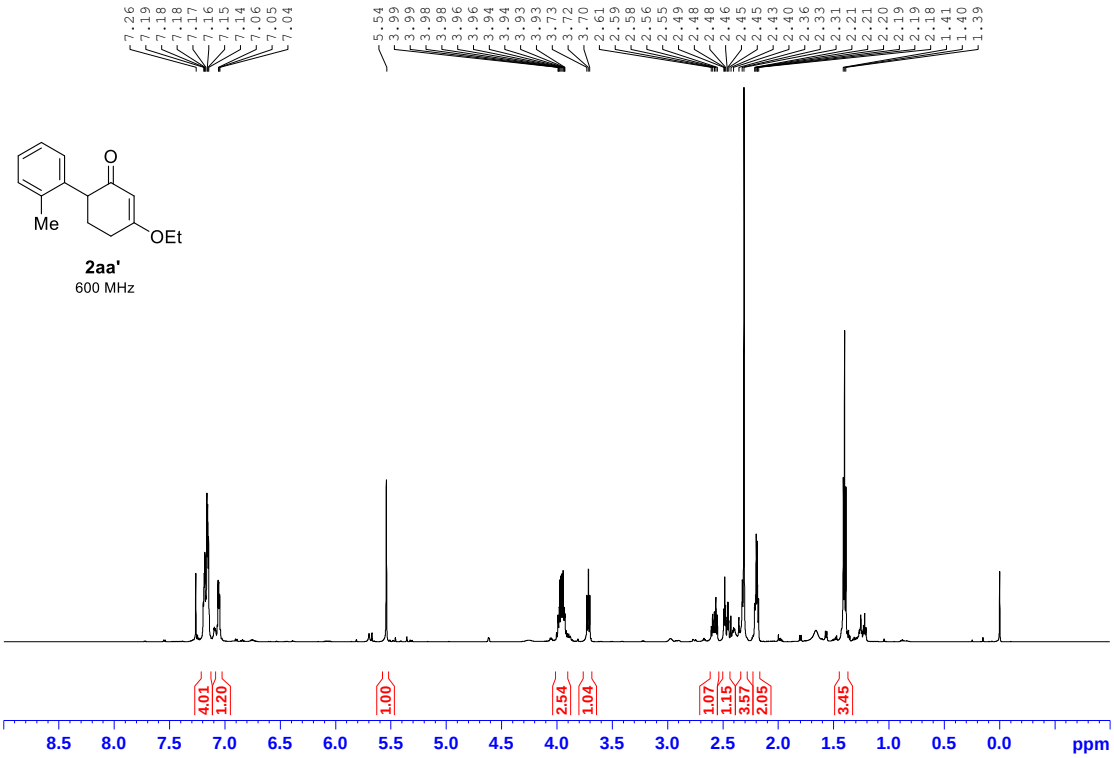
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2.48
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2.45
2.45
2.43
2.40
2.36
2.33
2.31
2.21
2.21
2.20
2.19
2.18
1.41
1.40
1.39
O
Me
OEt
2aa'
600 MHz
4.01
1.20
1.00
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1.07
1.15
3.57
2.05
3.45
8.5
8.0
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7.0
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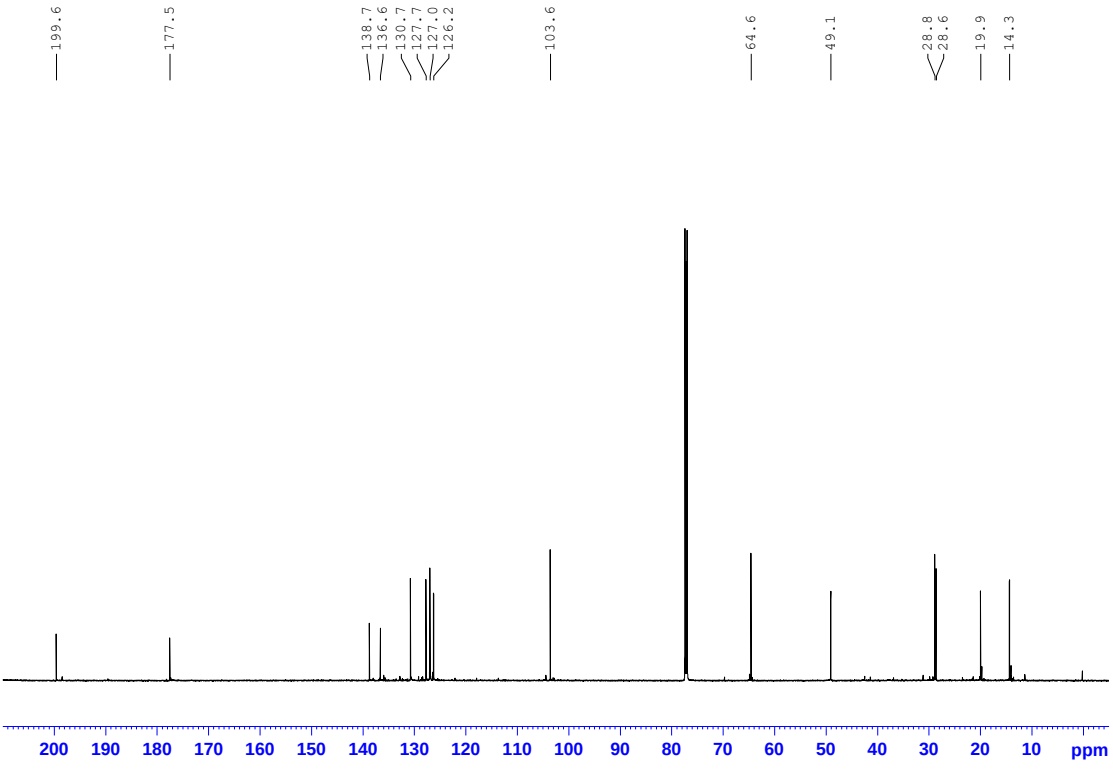
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28.8
28.6
19.9
14.3
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30
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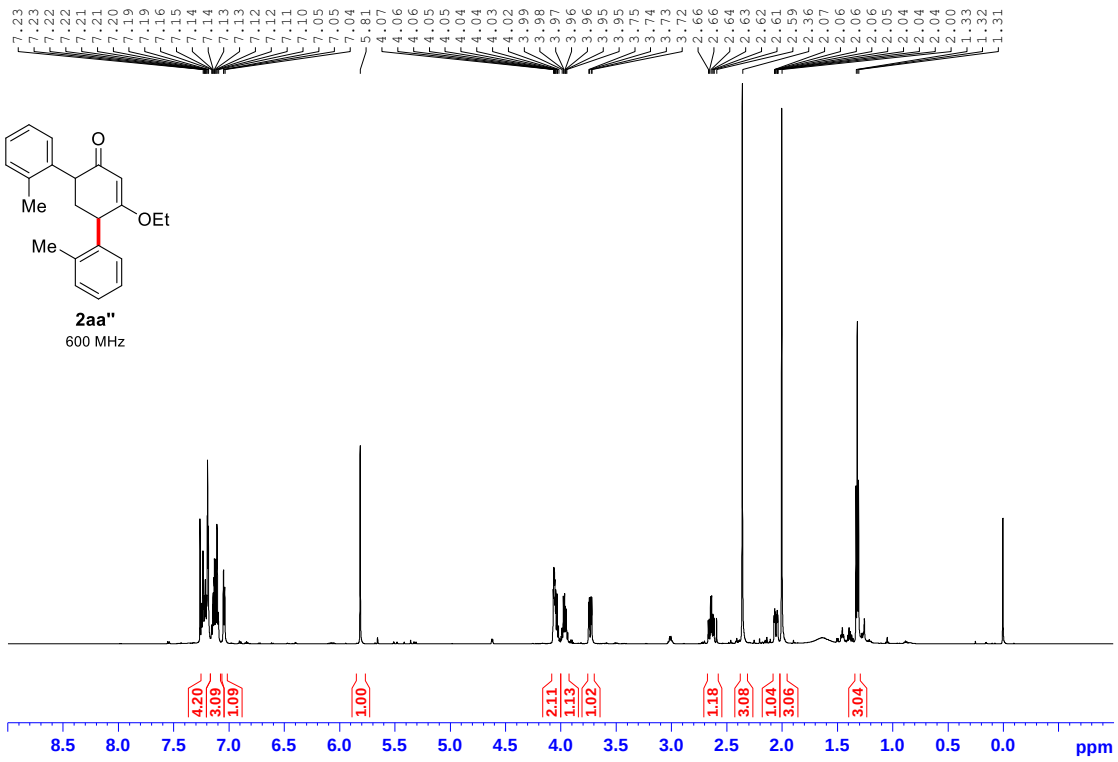
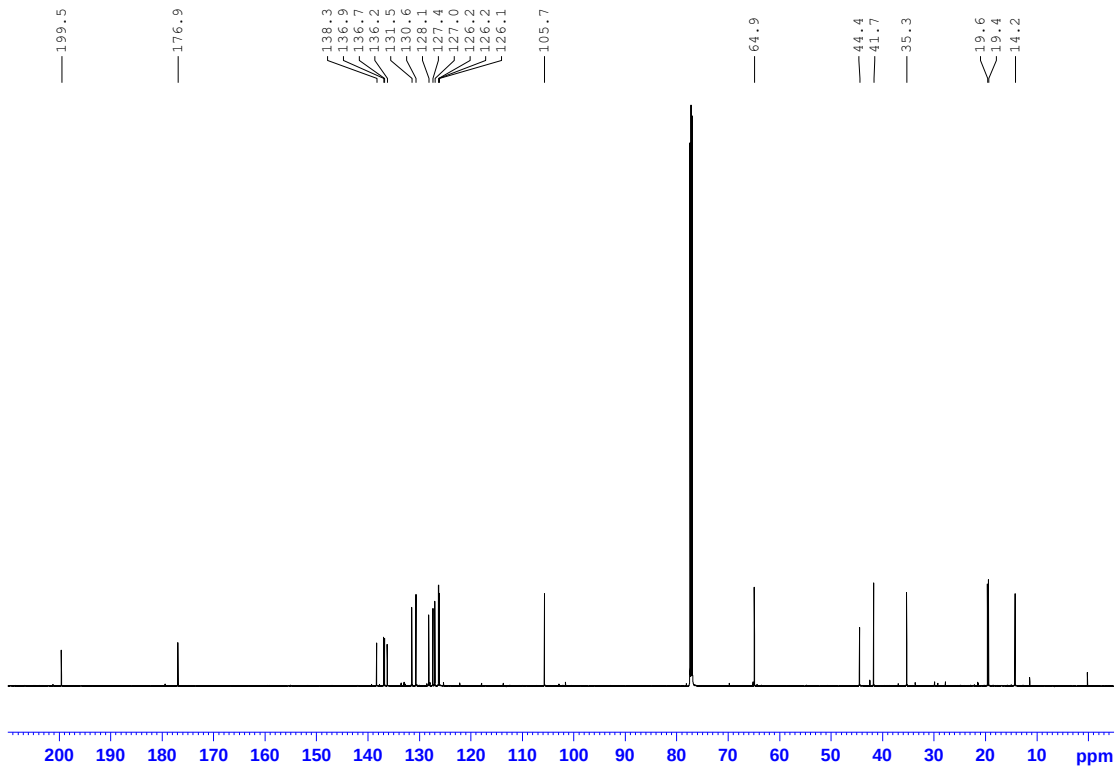
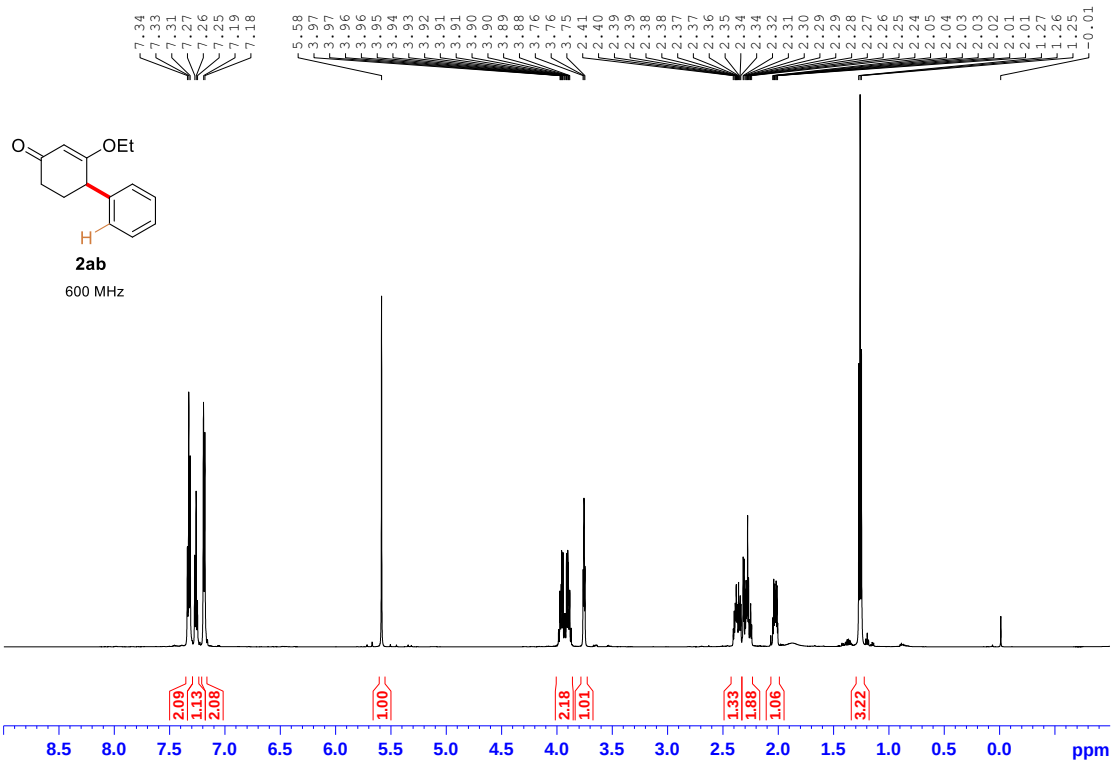
10
ppm


7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.19 7.19 7.16 7.15 7.14 7.14 7.13 7.13 7.12 7.12 7.11 7.10 7.05 7.05 7.04 5.81 4.07 4.06 4.06 4.05 4.05 4.04 4.04 4.03 4.02 3.99 3.98 3.97 3.96 3.96 3.95 3.95 3.75 3.74 3.73 3.72 2.66 2.66 2.64 2.63 2.62 2.61 2.59 2.36 2.07 2.06 2.06 2.05 2.04 2.04 2.00 1.33 1.32 1.31
O
Me
OEt
Me
2aa"
600 MHz
4.20 3.09 1.09 1.00 2.11 1.13 1.02 1.18 3.08 1.04 3.06 3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


199.5 176.9 138.3 136.9 136.7 136.2 131.5 130.6 128.1 127.4 127.0 126.2 126.2 126.1 105.7 64.9 44.4 41.7 35.3 19.6 19.4 14.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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3.90
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2.25
2.24
2.05
2.04
2.03
2.03
2.02
2.01
2.01
1.27
1.26
1.25
0.01
O
OEt
H
2ab
600 MHz
2.09
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1.88
1.06
3.22
8.5
8.0
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7.0
6.5
6.0
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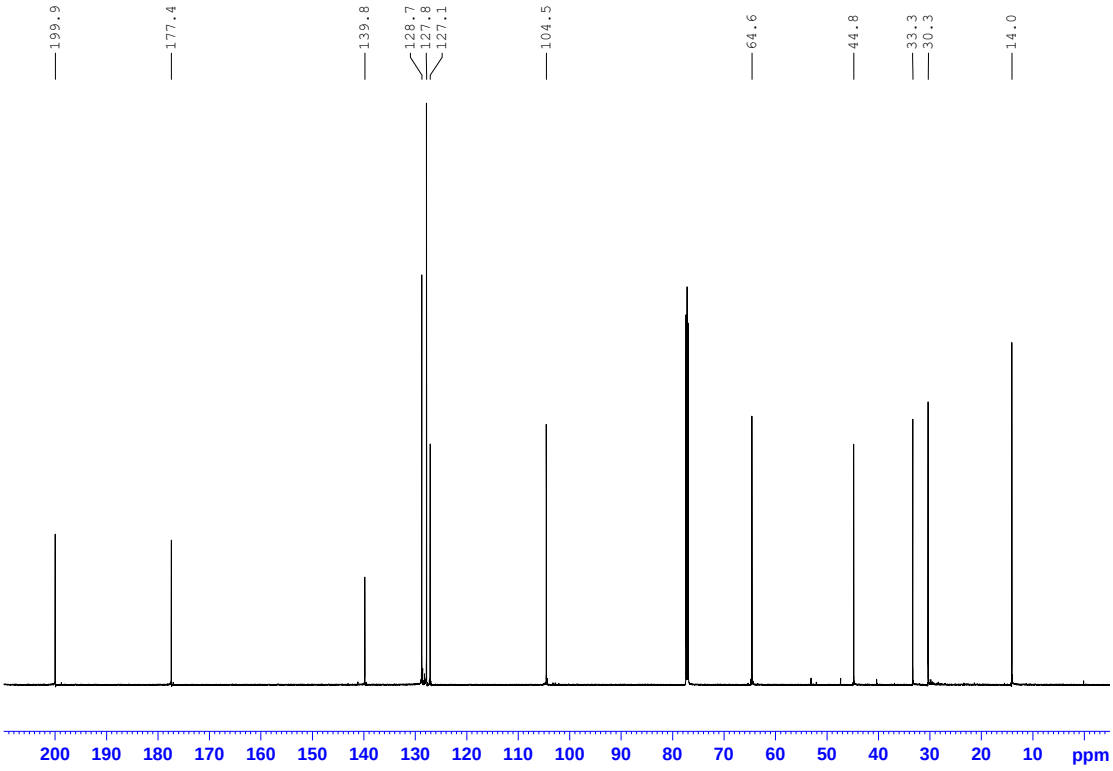
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64.6
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33.3
30.3
14.0
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180
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150
140
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120
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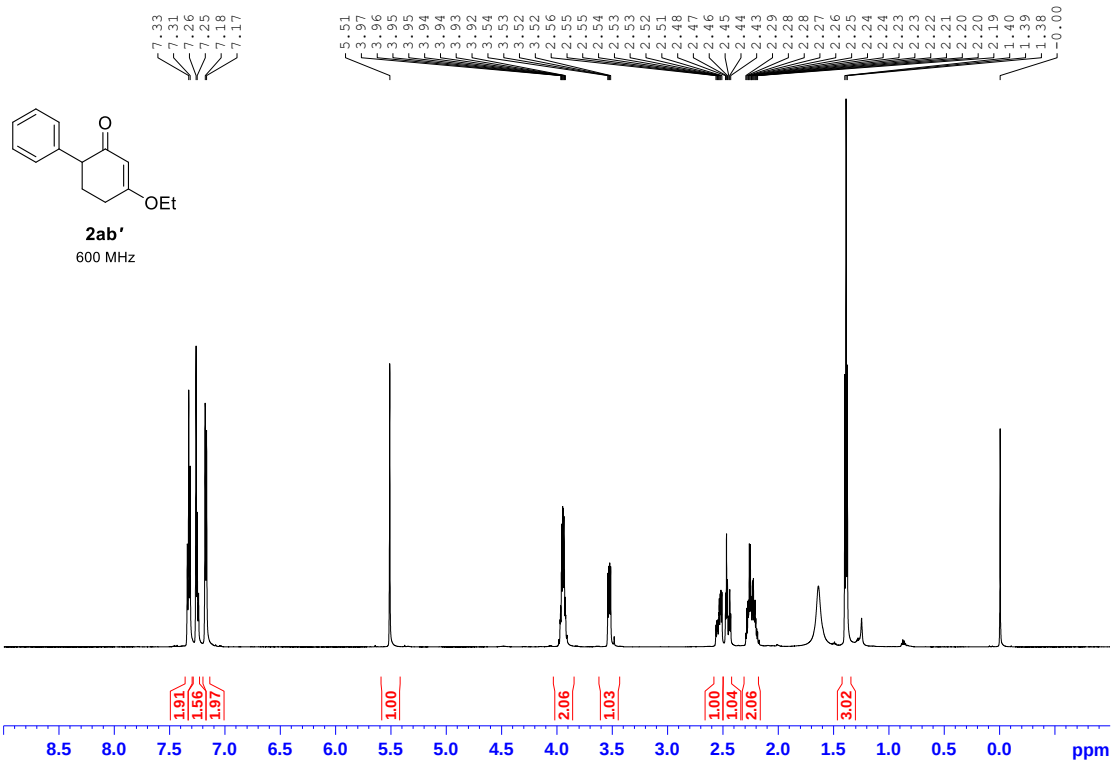
10
ppm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3.94
3.93
3.92
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3.52
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2.51
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2.47
2.46
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2.25
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2.24
2.23
2.23
2.22
2.21
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2.20
2.19
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1.39
1.38
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OEt
2ab′
600 MHz
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1.56
1.97
1.00
2.06
1.03
1.00
1.04
2.06
3.02
8.5
8.0
7.5
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6.5
6.0
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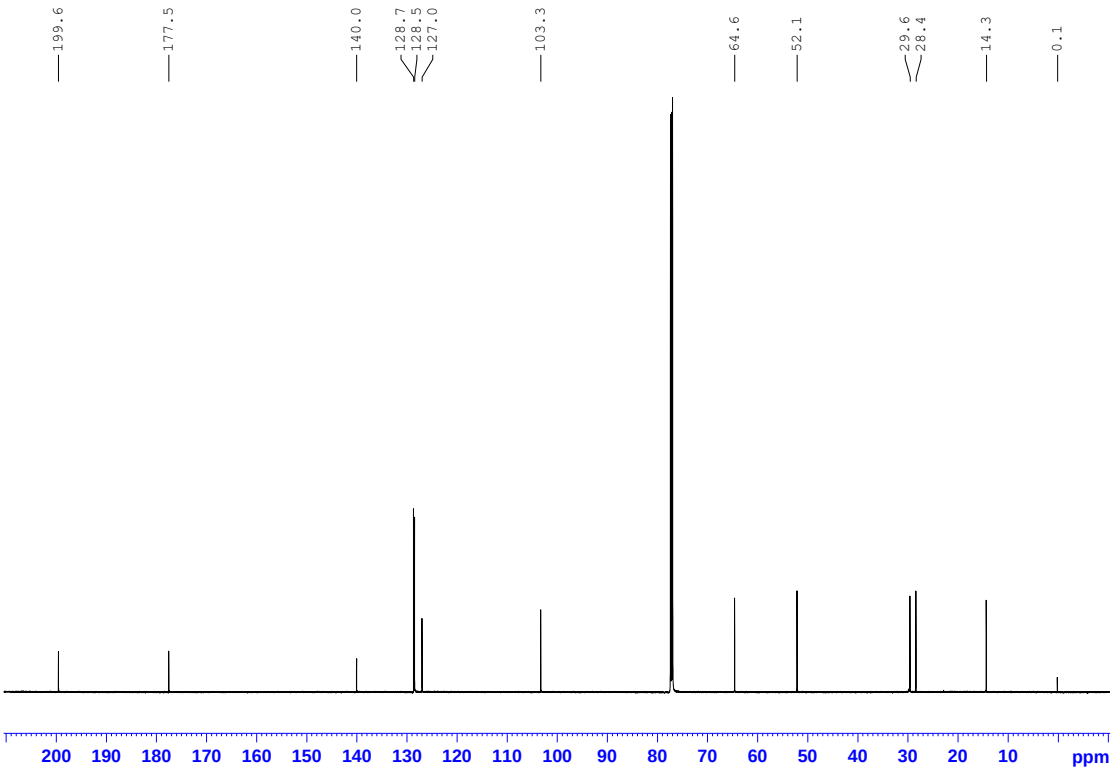
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64.6
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29.6
28.4
14.3
0.1
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180
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120
110
100
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30
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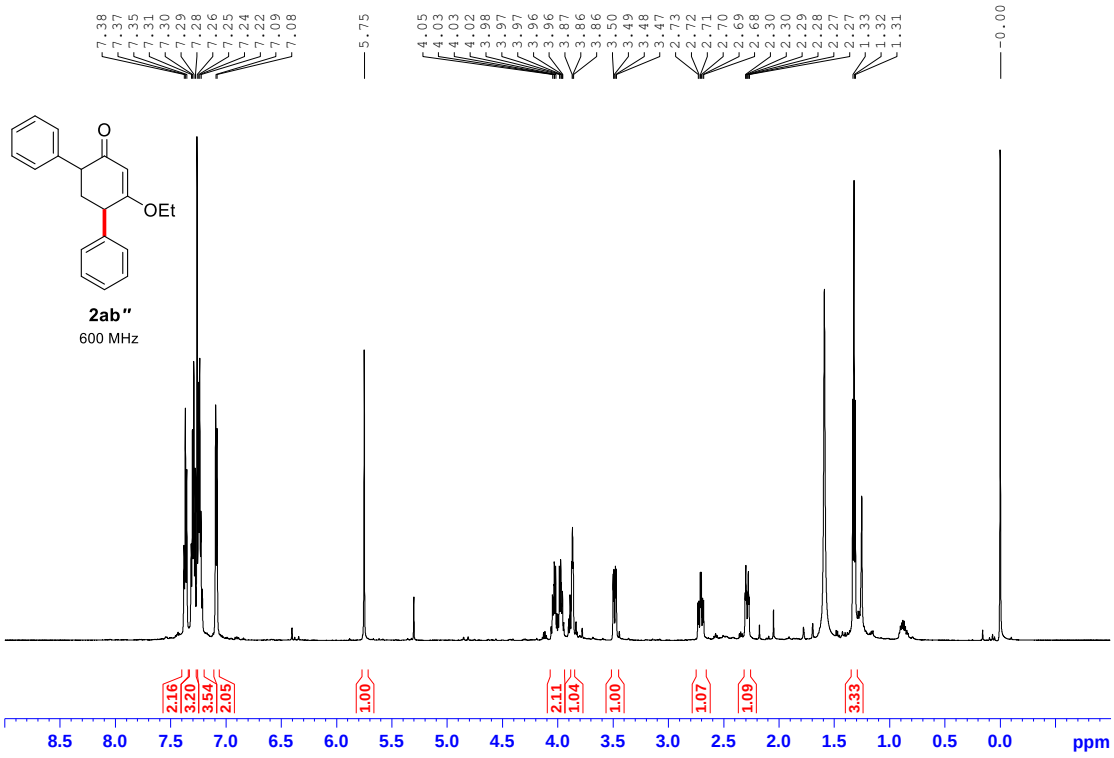
10
ppm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4.02
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3.97
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3.48
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2.70
2.69
2.68
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2.30
2.29
2.28
2.27
2.27
1.33
1.32
1.31
0.00
O
OEt
2ab"
600 MHz
2.16
3.20
3.54
2.05
1.00
2.11
1.04
1.00
1.07
1.09
3.33
8.5
8.0
7.5
7.0
6.5
6.0
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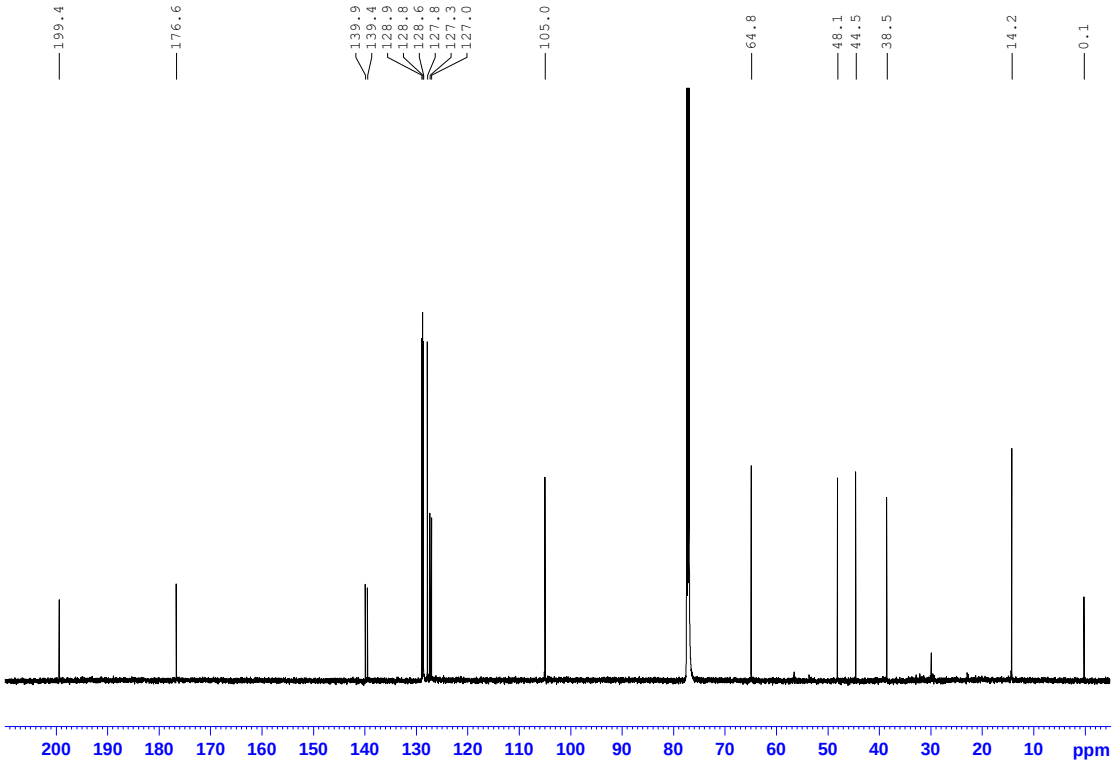
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127.8
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127.0
105.0
64.8
48.1
44.5
38.5
14.2
0.1
200
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180
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150
140
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120
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100
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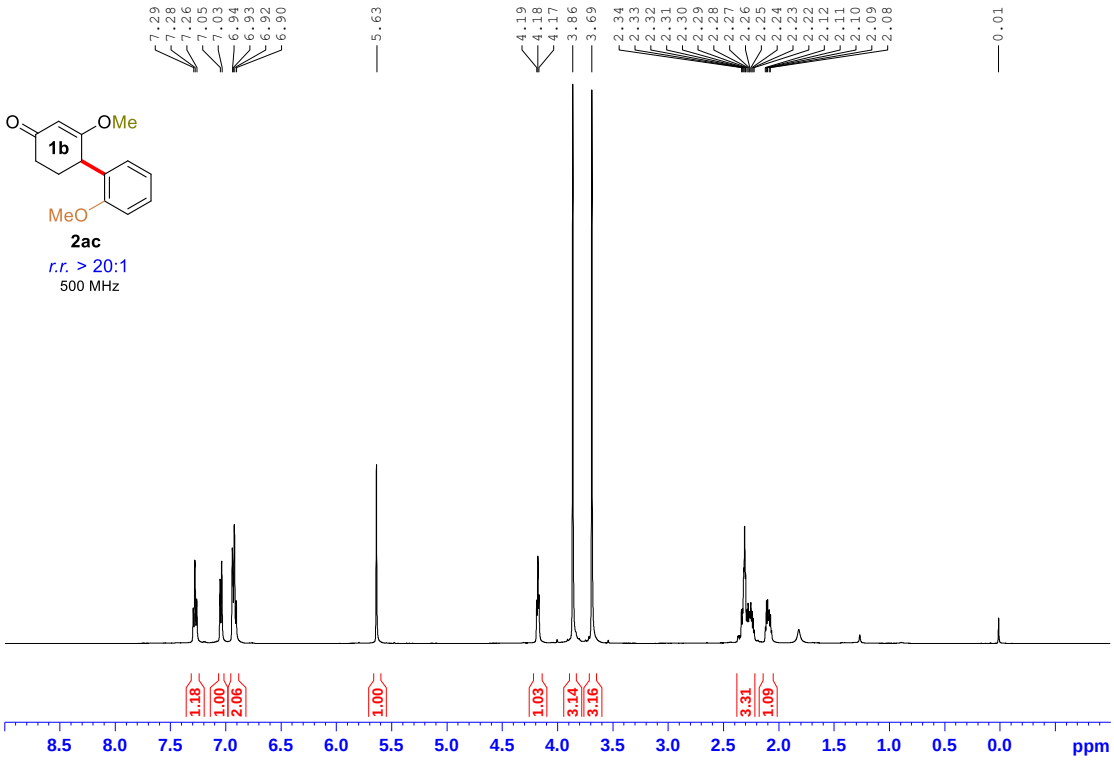
10
ppm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4.17
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3.69
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2.33
2.32
2.31
2.30
2.29
2.28
2.27
2.26
2.25
2.24
2.23
2.22
2.12
2.11
2.10
2.09
2.08
0.01
O
OMe
1b
MeO
2ac
r.r. > 20:1
500 MHz
1.18
1.00
2.06
1.00
1.03
3.14
3.16
3.31
1.09
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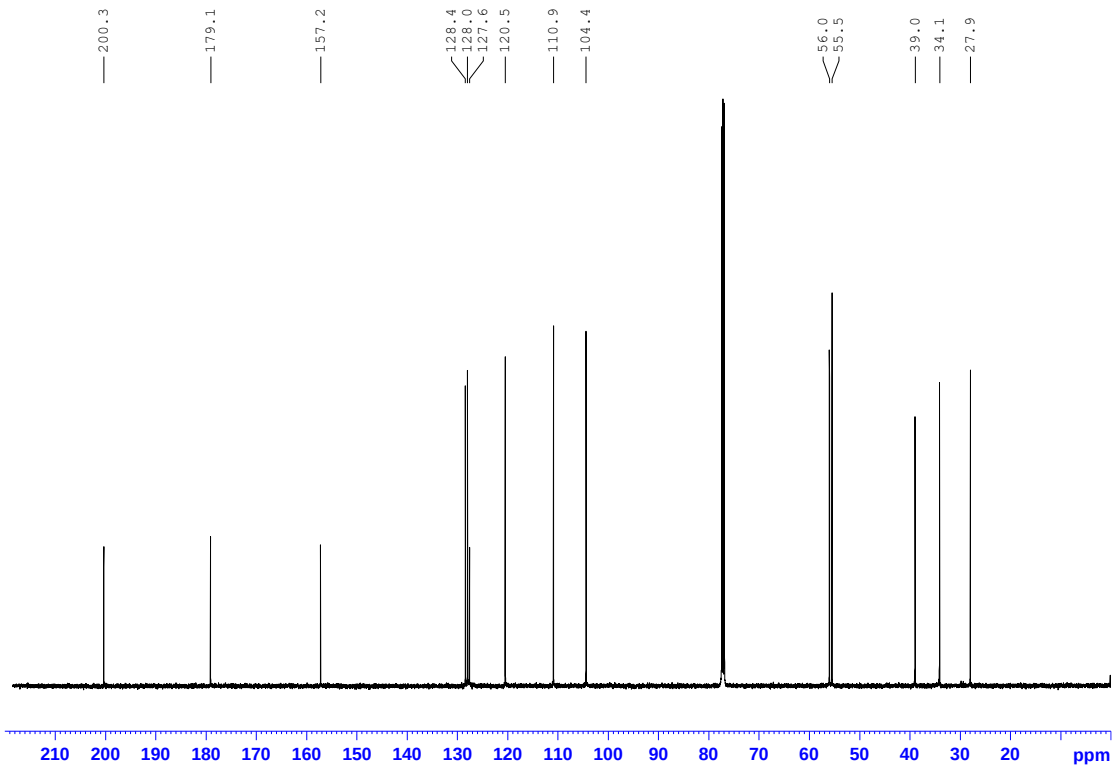
ppm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127.6
120.5
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55.5
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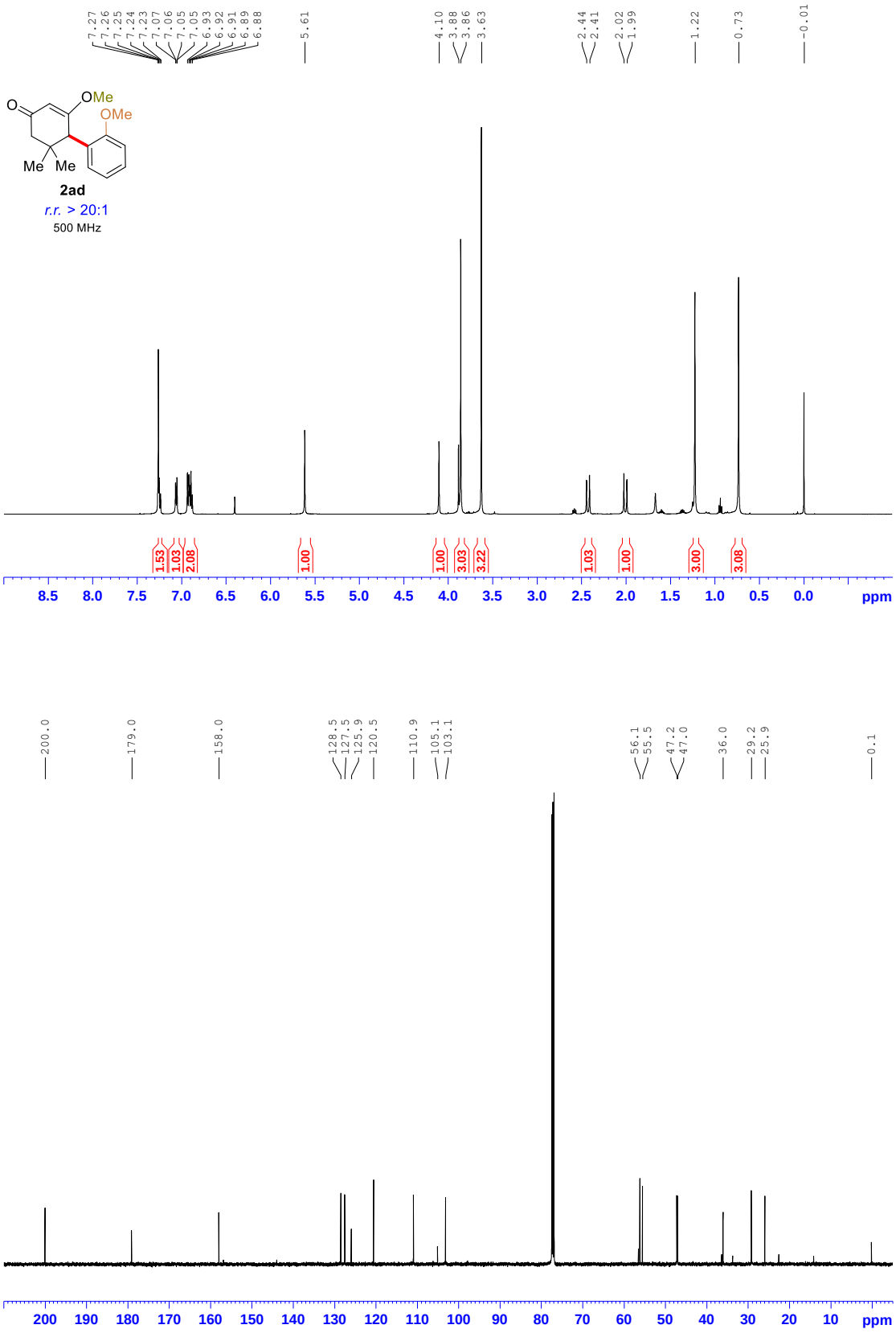
34.1
27.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm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7.06
7.05
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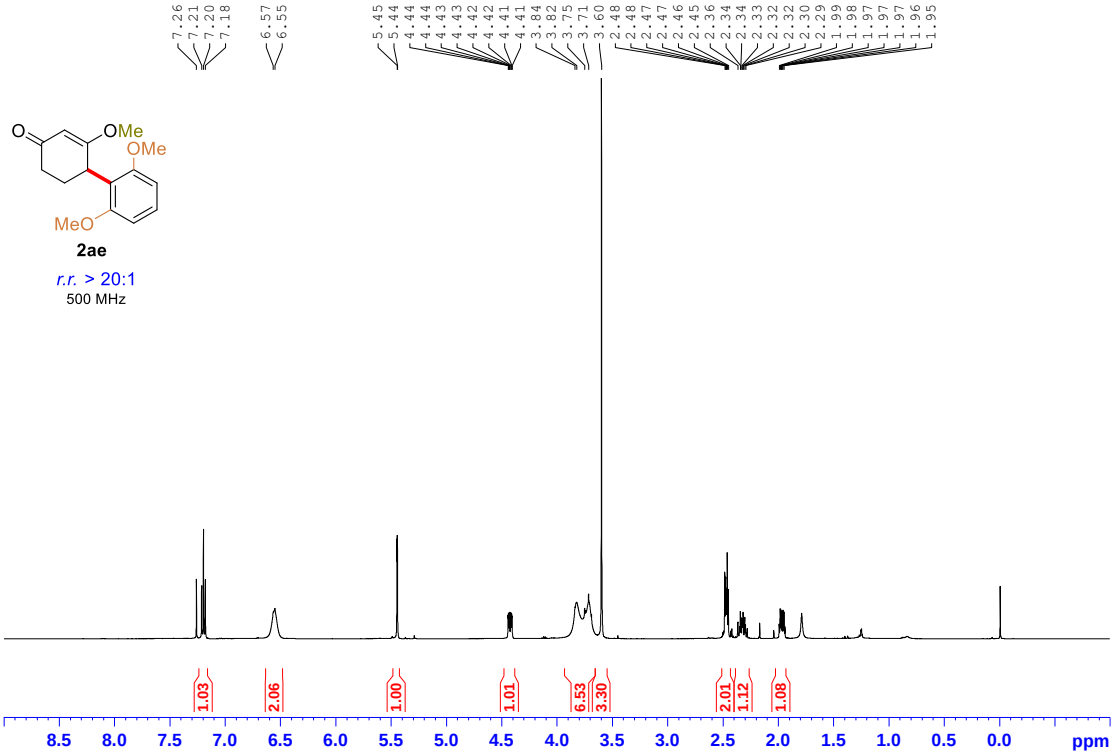
6.92
6.91
6.89
6.88
5.61
4.10
3.88
3.86
3.63
2.44
2.41
2.02
1.99
1.22
0.73
0.01
OMe
OMe
O
Me
Me
2ad
r.r. > 20:1
500 MHz
1.53
1.03
2.08
1.00
1.00
3.03
3.22
1.03
1.00
3.00
3.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
200.0
179.0
158.0
128.5
127.5
125.9
120.5
110.9
105.1
103.1
56.1
55.5
47.2
47.0
36.0
29.2
25.9
0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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4.42
4.41
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2.45
2.36
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2.30
2.29
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1.98
1.97
1.97
1.97
1.96
1.95
O
OMe
OMe
MeO
2ae
r.r. > 20:1
500 MHz
1.03
2.06
1.00
1.01
6.53
3.30
2.01
1.12
1.08
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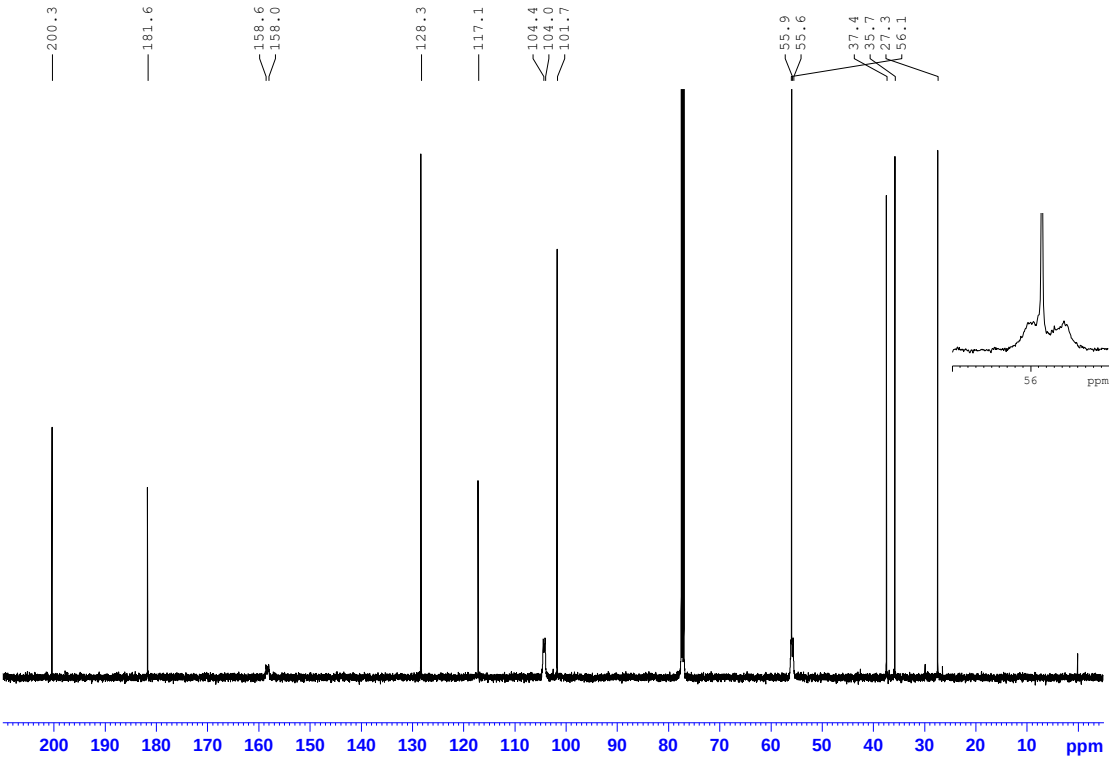
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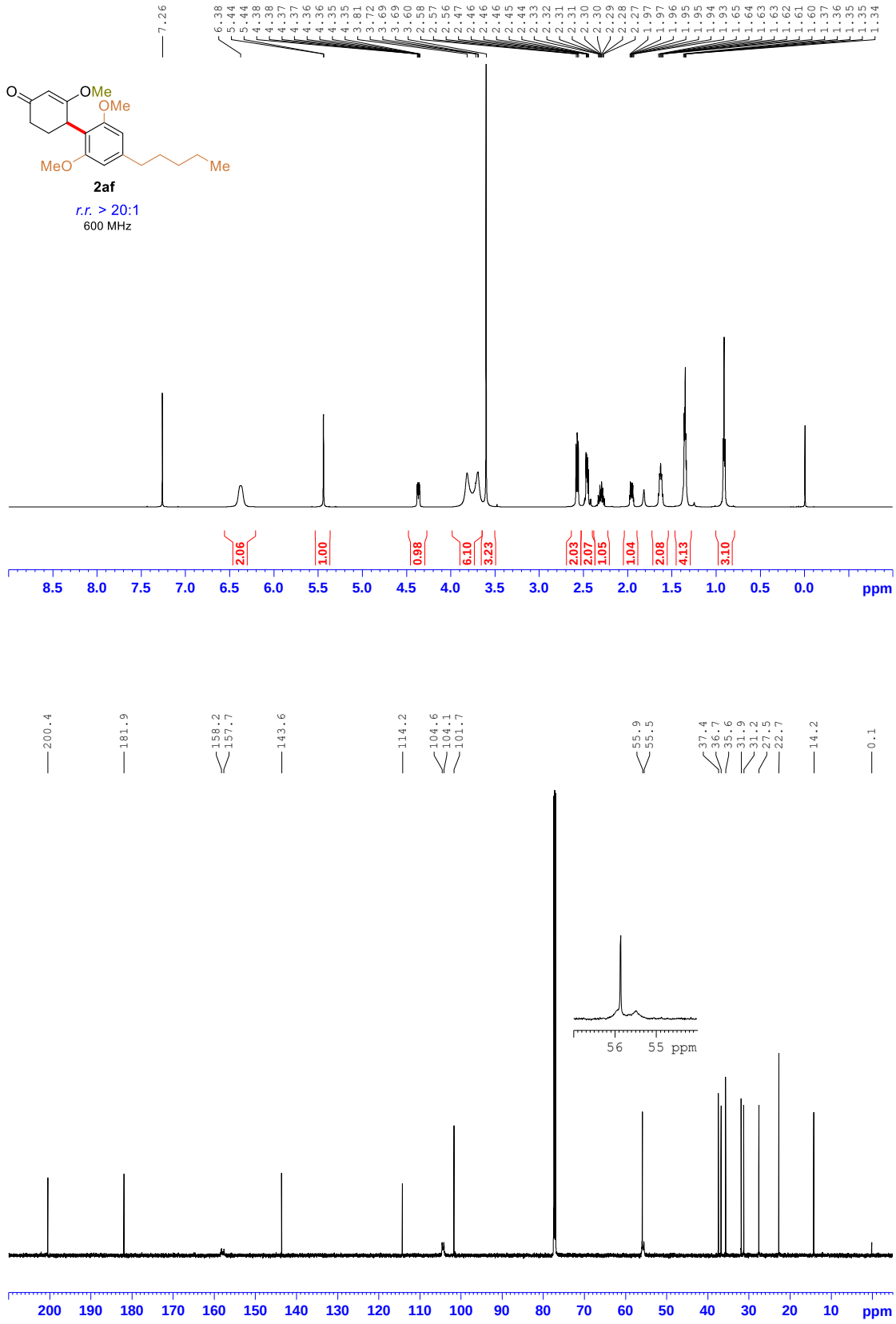
158.6
158.0
128.3
117.1
104.4
104.0
101.7
55.9
55.6
37.4
35.7
27.3
56.1
56
ppm
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm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2.57
2.56
2.47
2.46
2.45
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2.33
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2.31
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2.29
2.28
2.27
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1.96
1.95
1.94
1.93
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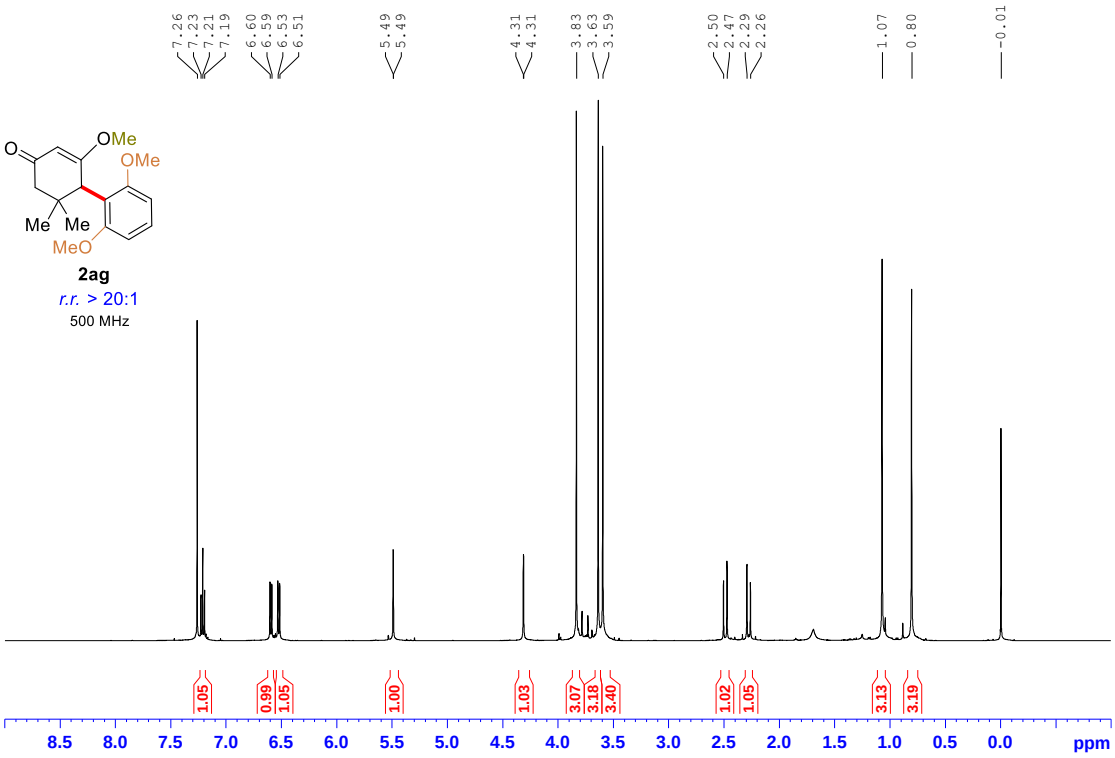
1.64
1.63
1.62
1.61
1.60
1.37
1.36
1.35
1.34
O
OMe
OMe
MeO
Me
2af
r.r. > 20:1
600 MHz
2.06
1.00
0.98
6.10
3.23
2.03
2.07
1.05
1.04
2.08
4.13
3.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
200.4
181.9
158.2
157.7
143.6
114.2
104.6
104.1
101.7
55.9
55.5
37.4
36.7
35.6
31.9
31.2
27.5
22.7
14.2
0.1
56 55 ppm
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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4.31
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3.63
3.59
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2.47
2.29
2.26
1.07
0.80
0.01
OMe
OMe
Me
Me
MeO
2ag
r.r. > 20:1
500 MHz
1.05
0.99
1.05
1.00
1.03
3.07
3.18
3.40
1.02
1.05
3.13
3.19
8.5
8.0
7.5
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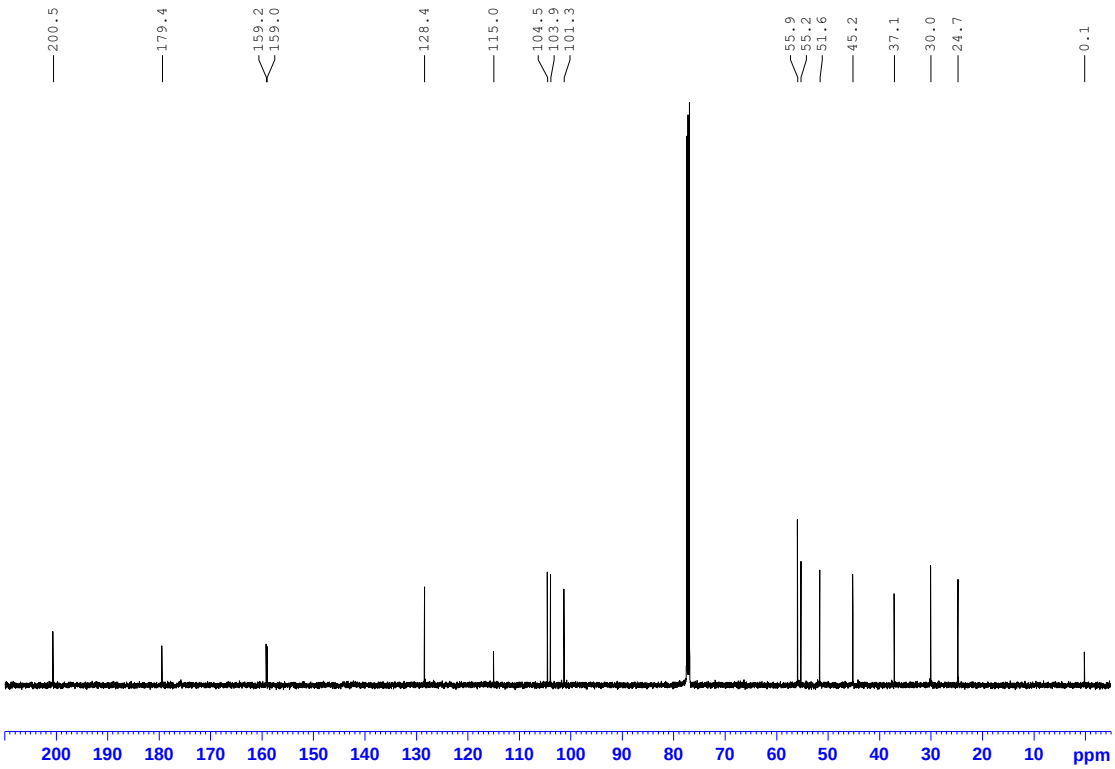
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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179.4
159.2
159.0
128.4
115.0
104.5
103.9
101.3
55.9
55.2
51.6
45.2
37.1
30.0
24.7
0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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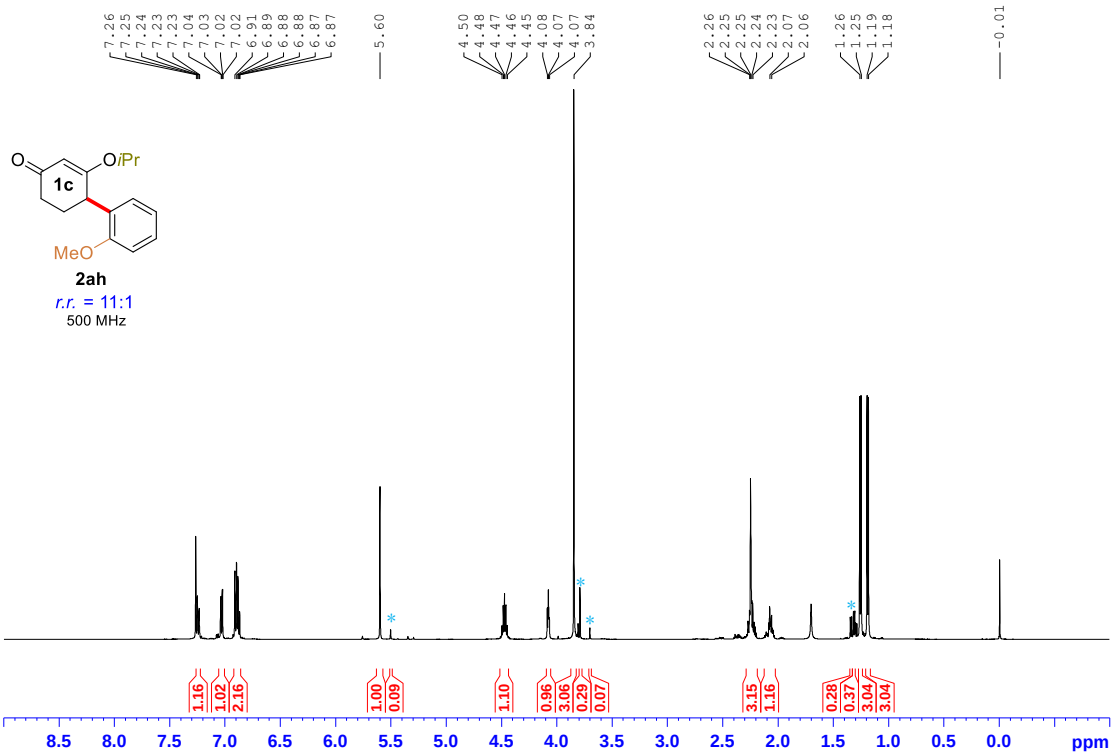
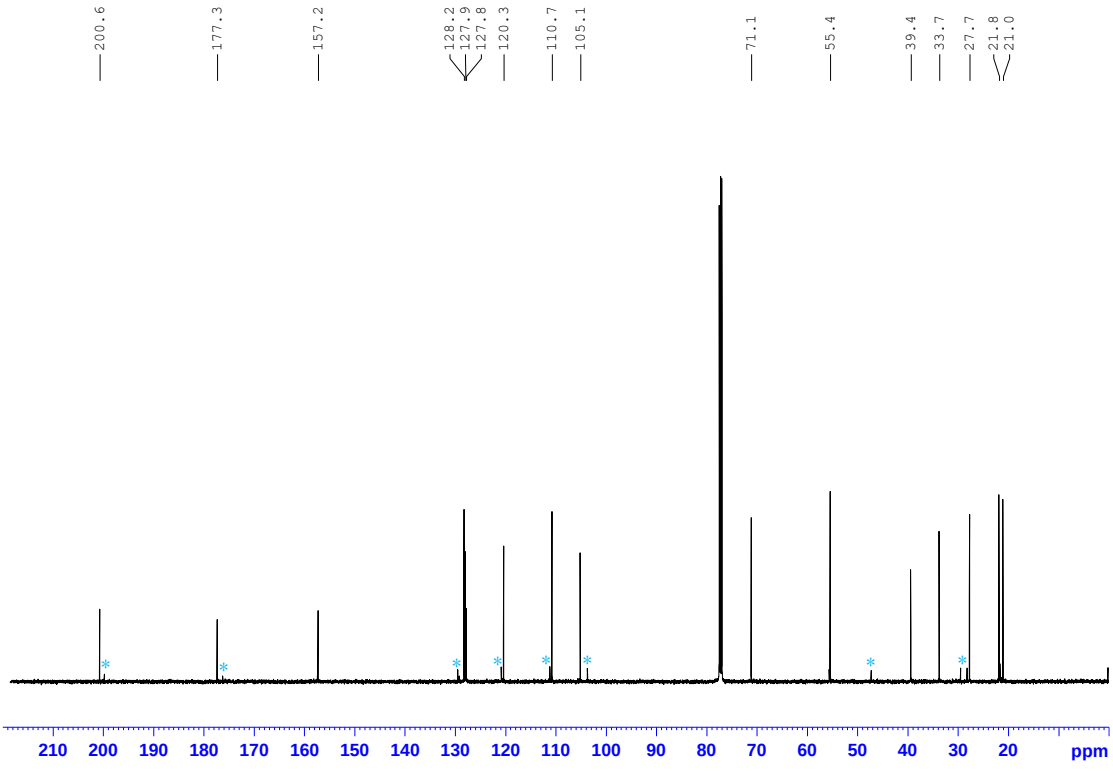
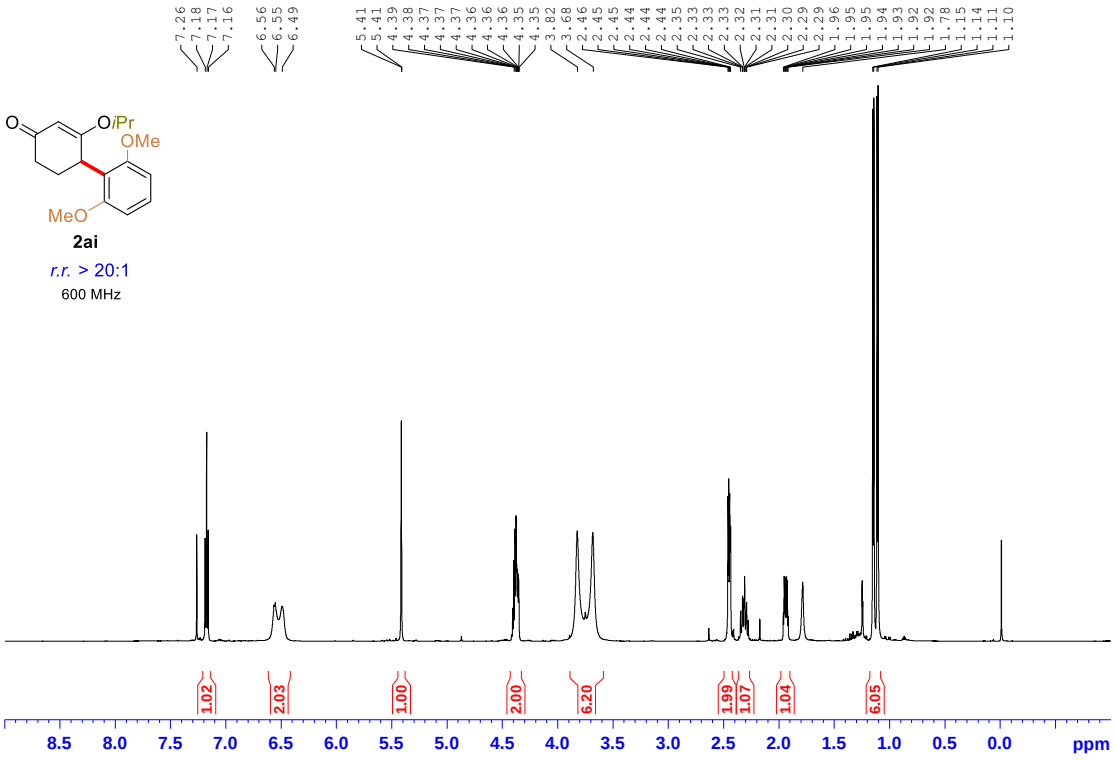
50
40
30
20
10
ppm



* is for α′-isomer

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6.55
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5.41
5.41
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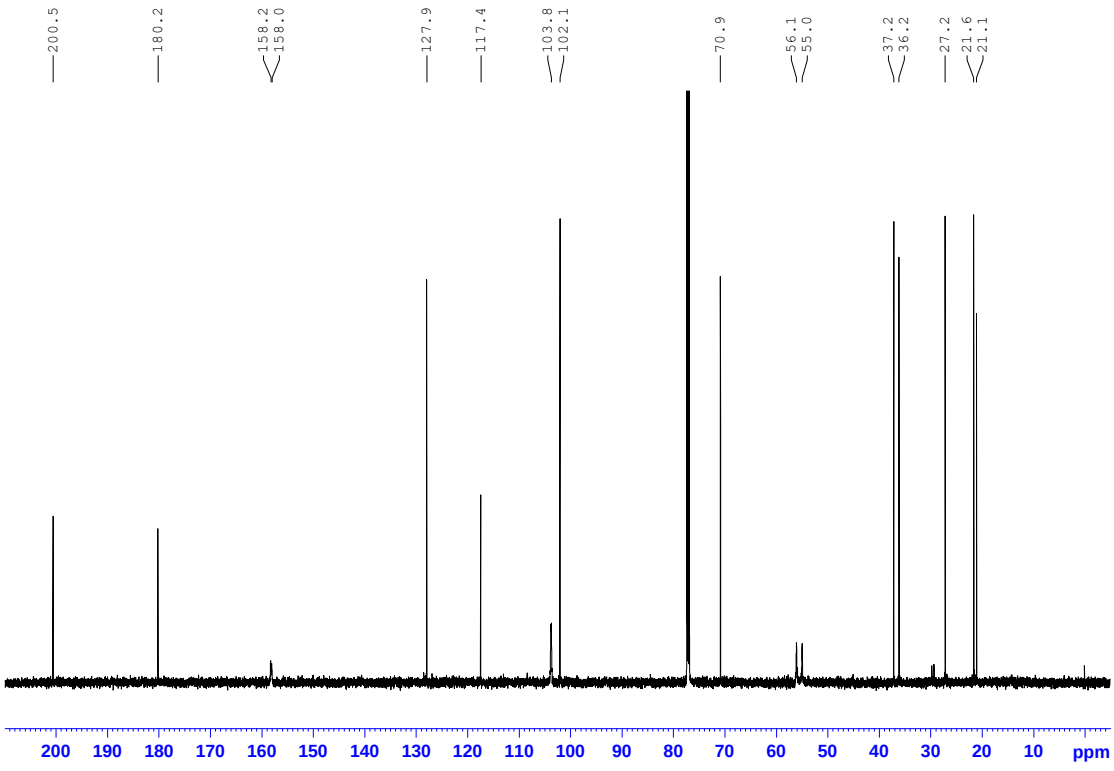
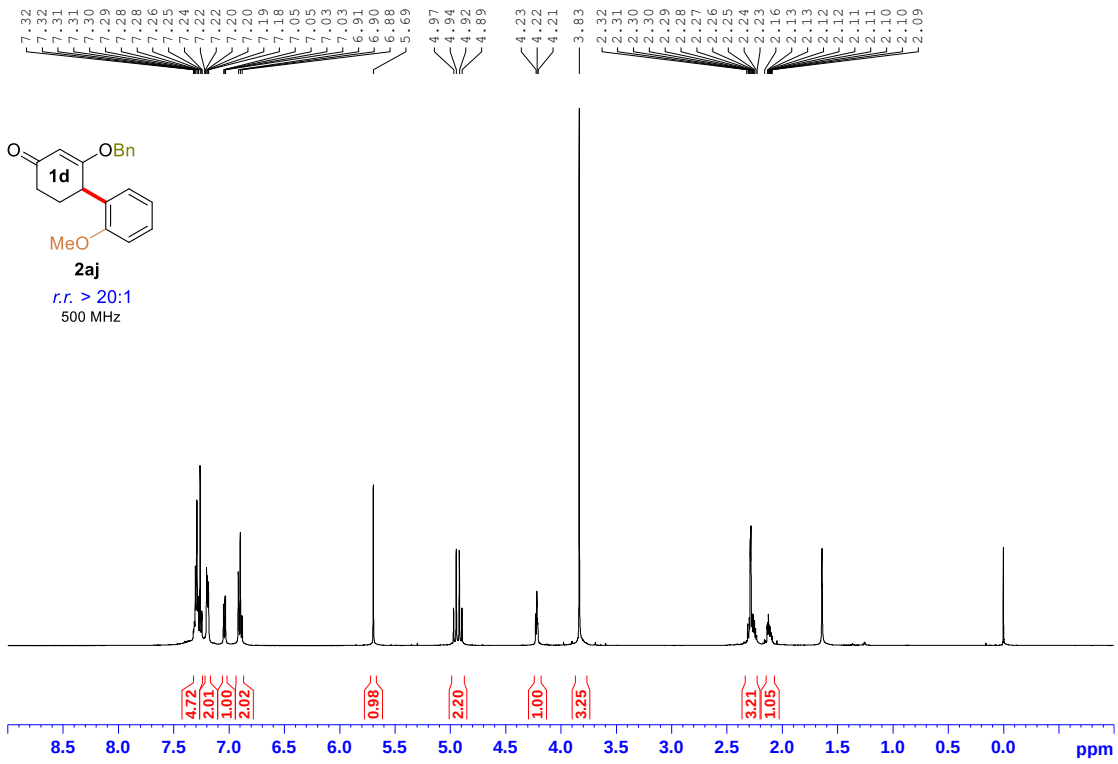
4.38
4.37
4.37
4.37
4.36
4.36
4.36
4.35
4.35
3.82
3.68
2.46
2.45
2.45
2.44
2.44
2.44
2.35
2.33
2.33
2.33
2.32
2.31
2.31
2.30
2.29
2.29
1.96
1.95
1.95
1.94
1.93
1.92
1.92
1.78
1.15
1.14
1.11
1.10
O
OiPr
OMe
MeO
2ai
r.r. > 20:1
600 MHz
1.02
2.03
1.00
2.00
6.20
1.99
1.07
1.04
6.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


200.5
180.2
158.2
158.0
127.9
117.4
103.8
102.1
70.9
56.1
55.0
37.2
36.2
27.2
21.6
21.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.32
7.32
7.31
7.31
7.30
7.29
7.28
7.28
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7.25
7.24
7.22
7.22
7.20
7.20
7.19
7.18
7.05
7.05
7.03
7.03
6.91
6.90
6.88
5.69
4.97
4.94
4.92
4.89
4.23
4.22
4.21
3.83
2.32
2.31
2.30
2.30
2.29
2.28
2.27
2.26
2.25
2.24
2.23
2.16
2.13
2.13
2.12
2.12
2.11
2.11
2.10
2.10
2.09
O
OBn
1d
MeO
2aj
r.r. > 20:1
500 MHz
4.72
2.01
1.00
2.02
0.98
2.20
1.00
3.25
3.21
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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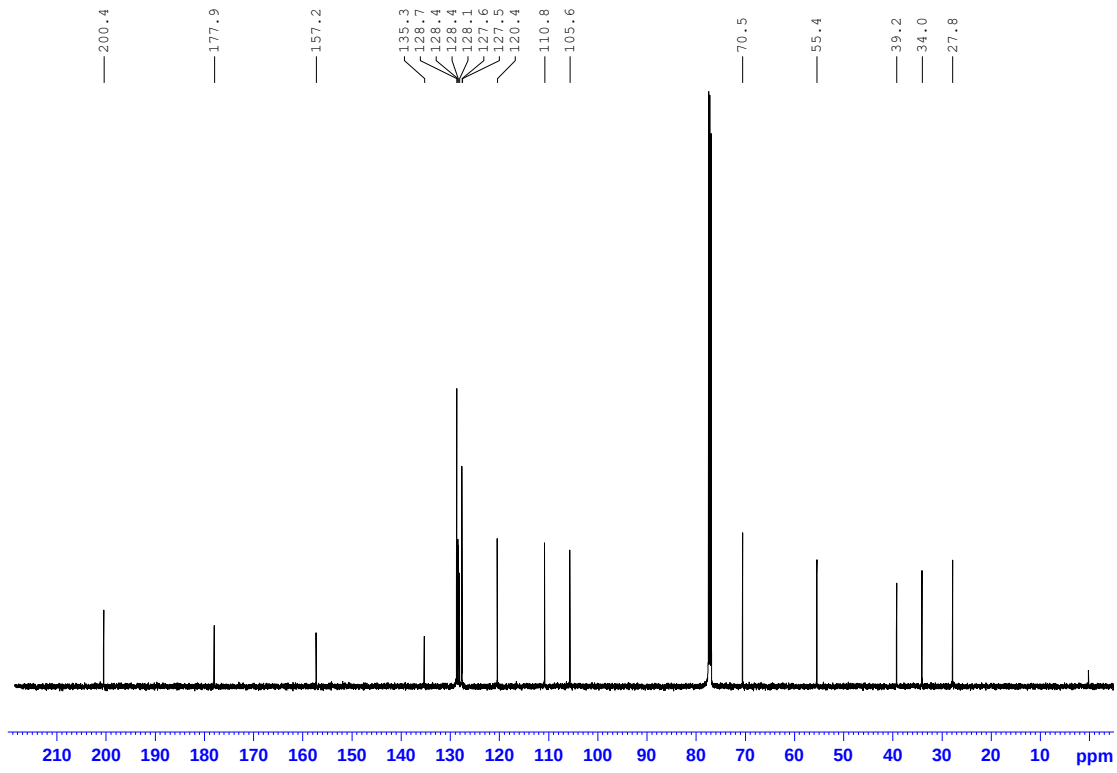
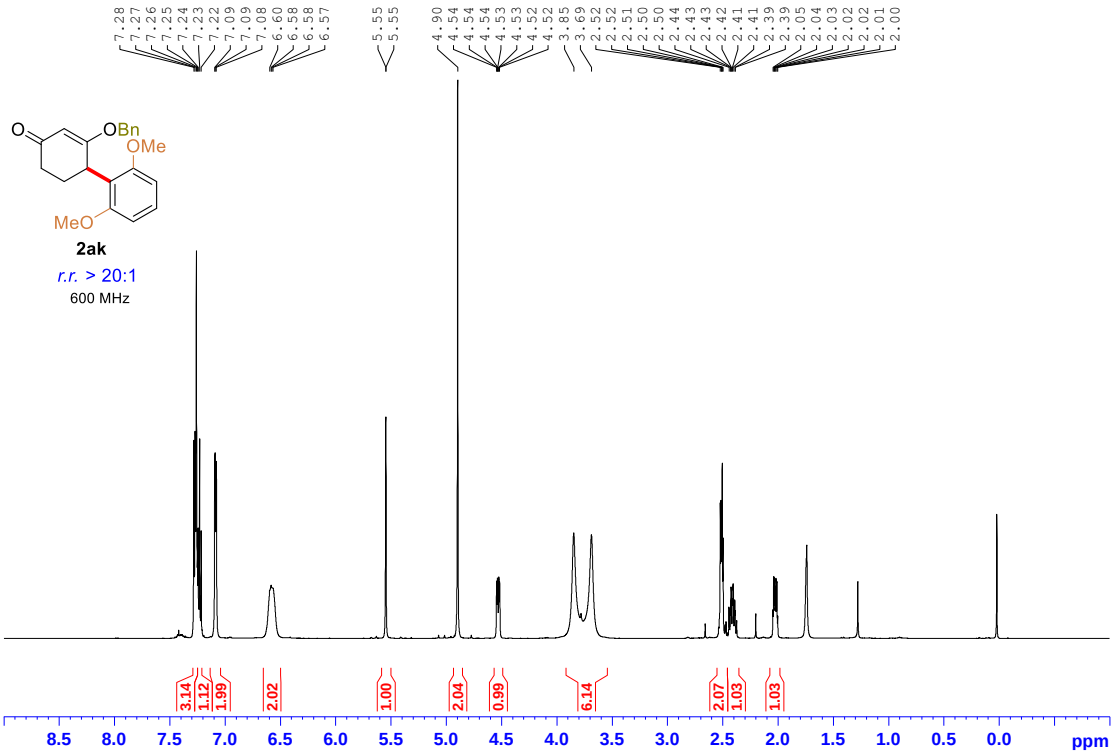
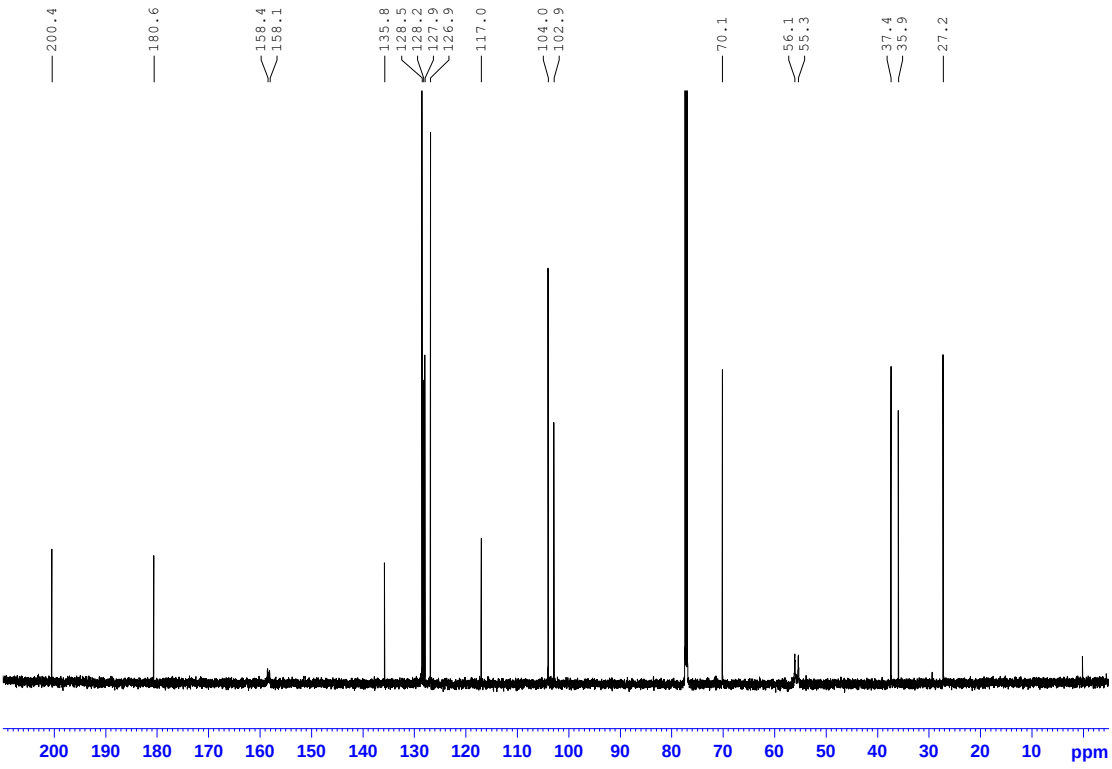
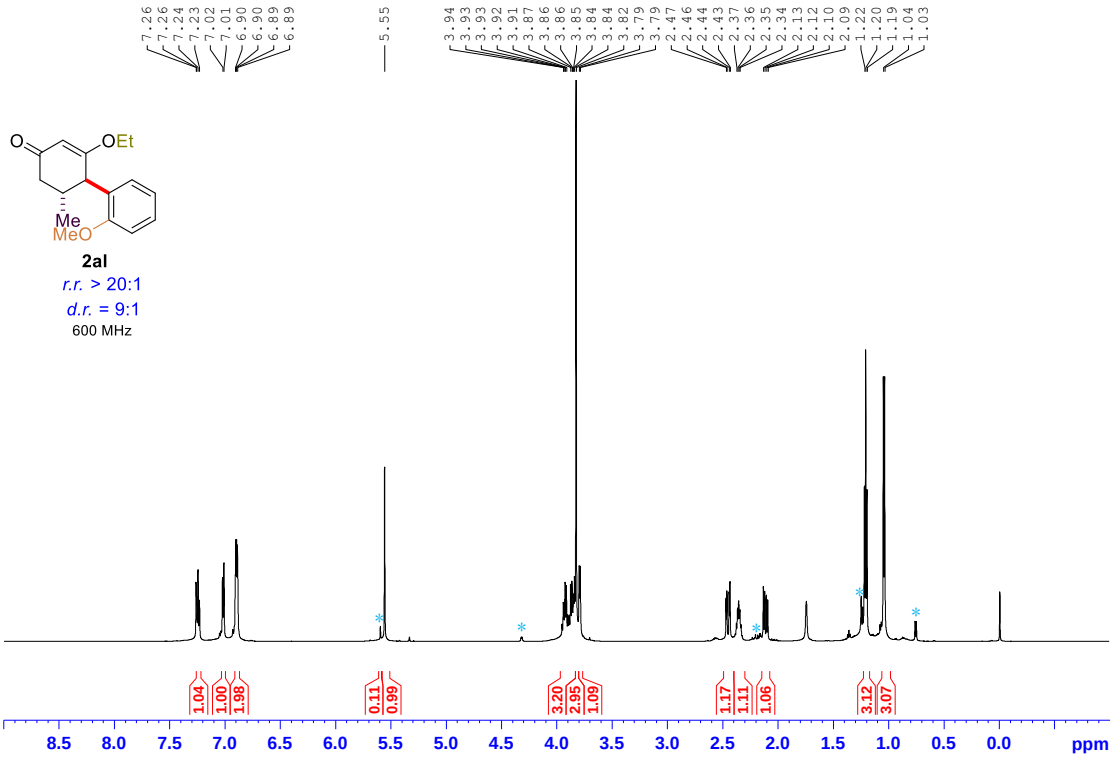
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

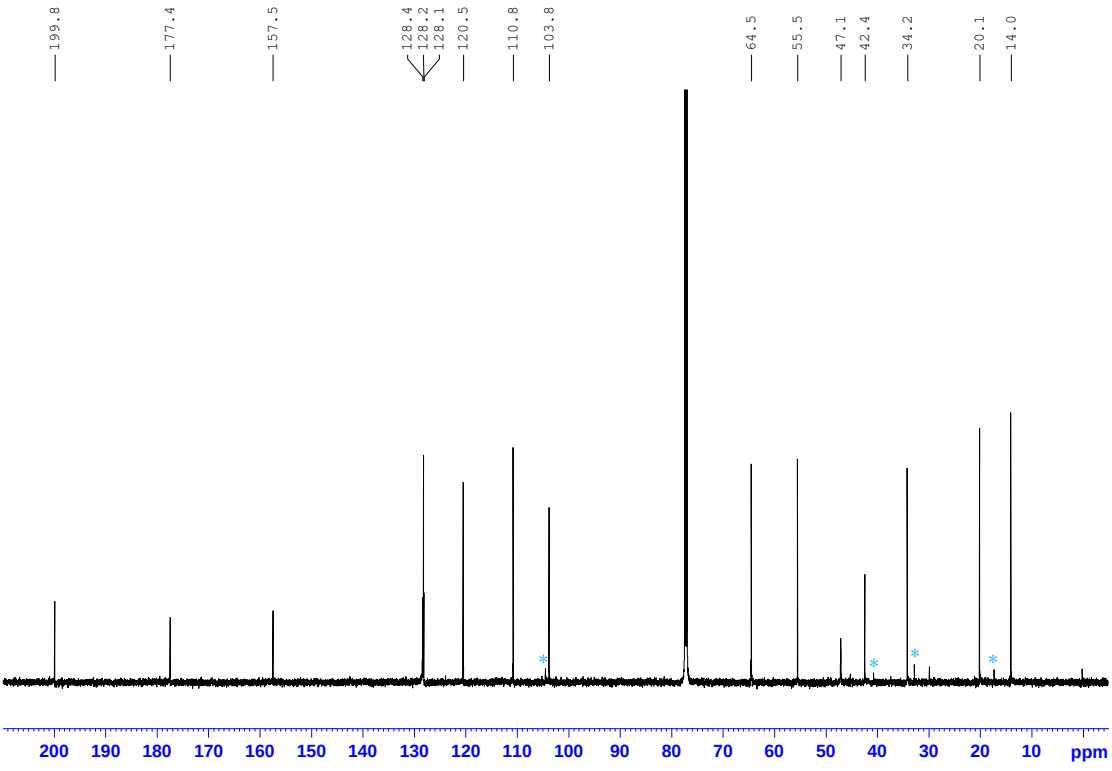

200.4
177.9
157.2
135.3
128.7
128.4
128.4
128.1
127.6
127.5
120.4
110.8
105.6
70.5
55.4
39.2
34.0
27.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

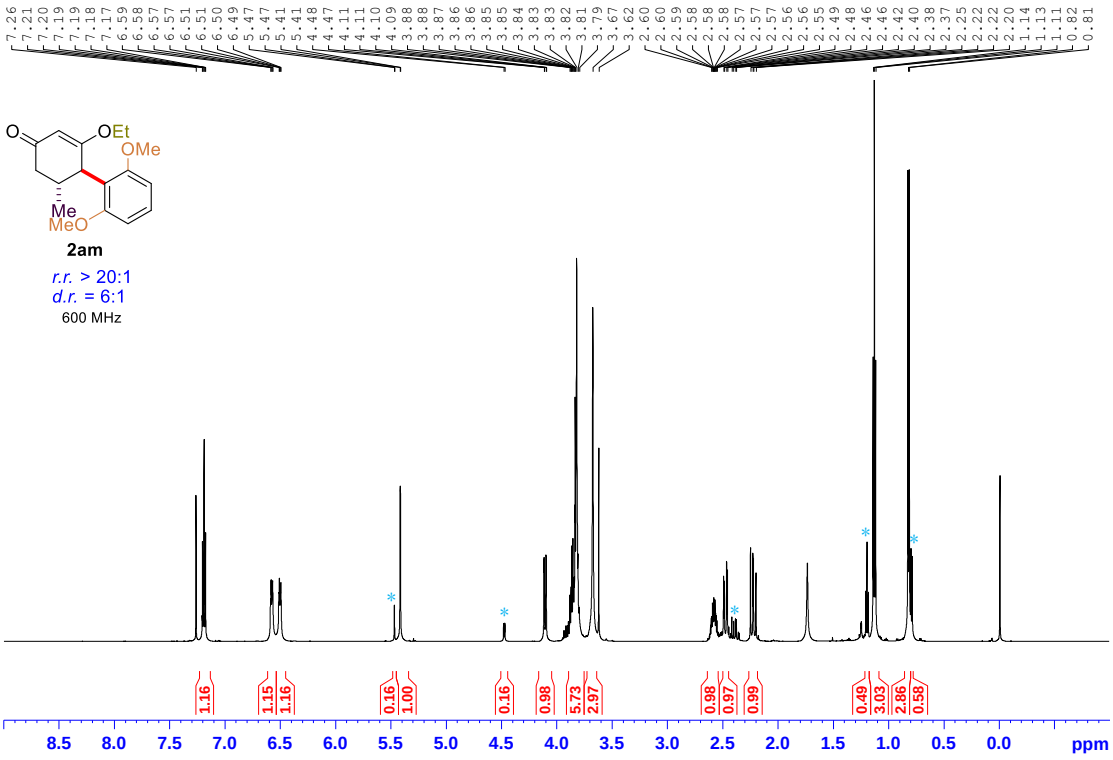

7.28 7.27 7.26 7.25 7.24 7.23 7.22 7.09 7.09 7.08 6.60 6.58 6.58 6.57
5.55 5.55
4.90 4.54 4.54 4.54 4.53 4.53 4.52 4.52
3.85 3.69
2.52 2.52 2.51 2.50 2.50 2.44 2.43 2.43 2.42 2.41 2.41 2.39 2.39 2.05 2.04 2.03 2.02 2.02 2.01 2.00
O
OBn
OMe
MeO
2ak
r.r. > 20:1
600 MHz
3.14 1.12 1.99 2.02 1.00 2.04 0.99 6.14 2.07 1.03 1.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


200.4
180.6
158.4 158.1
135.8 128.5 128.2 127.9 126.9
117.0
104.0 102.9
70.1
56.1 55.3
37.4 35.9
27.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

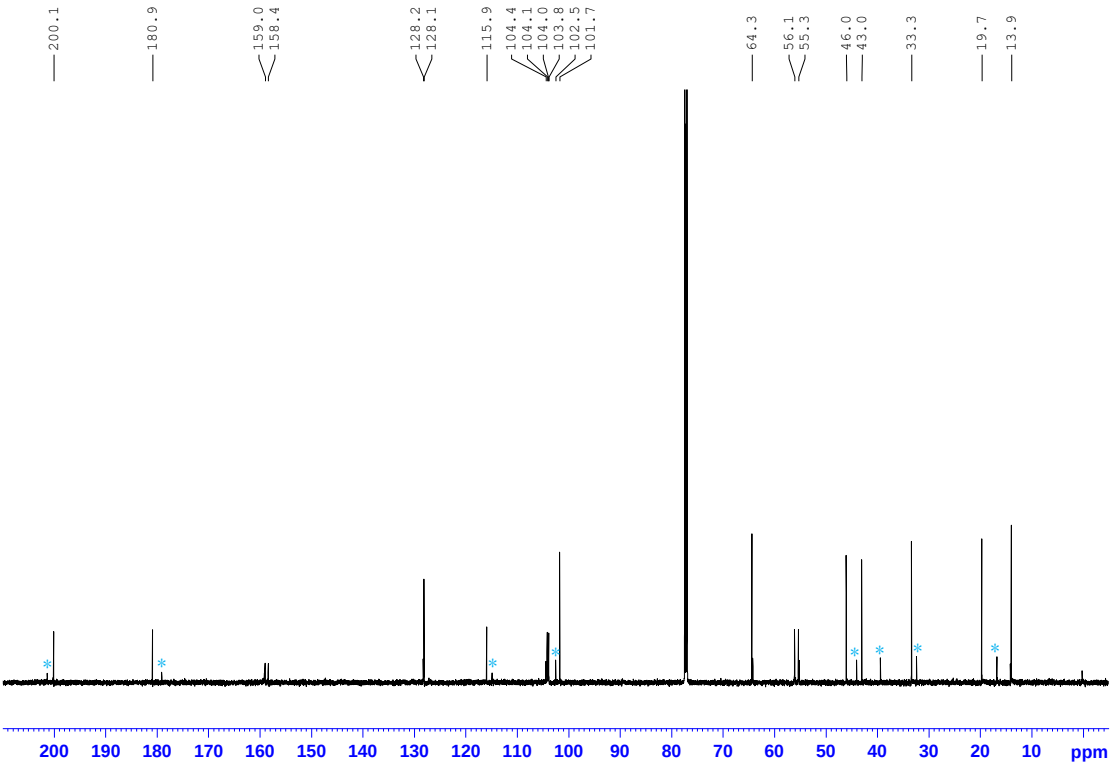


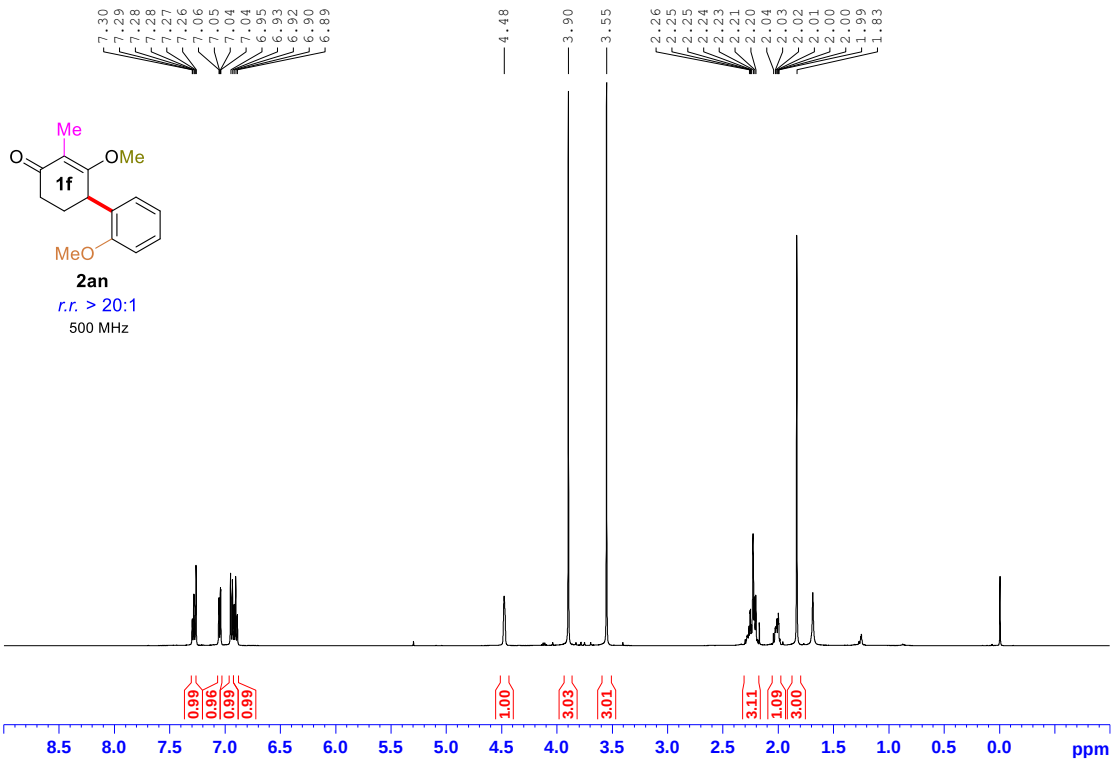
* is for *syn*-isomer

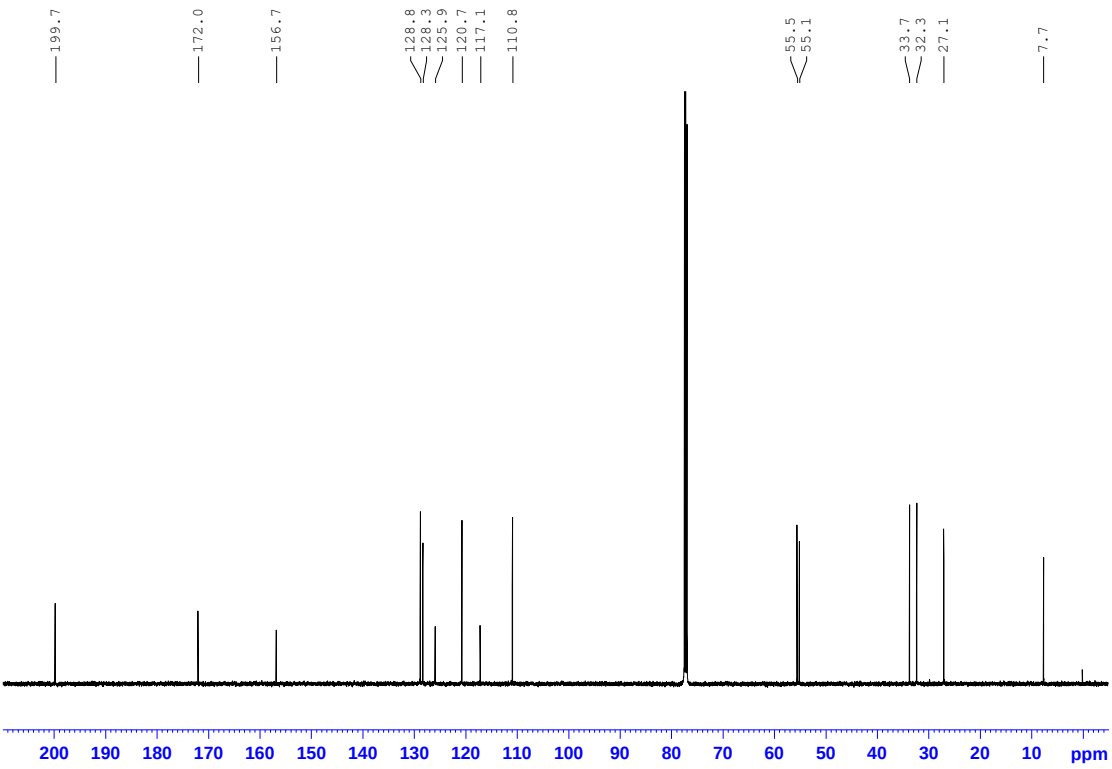


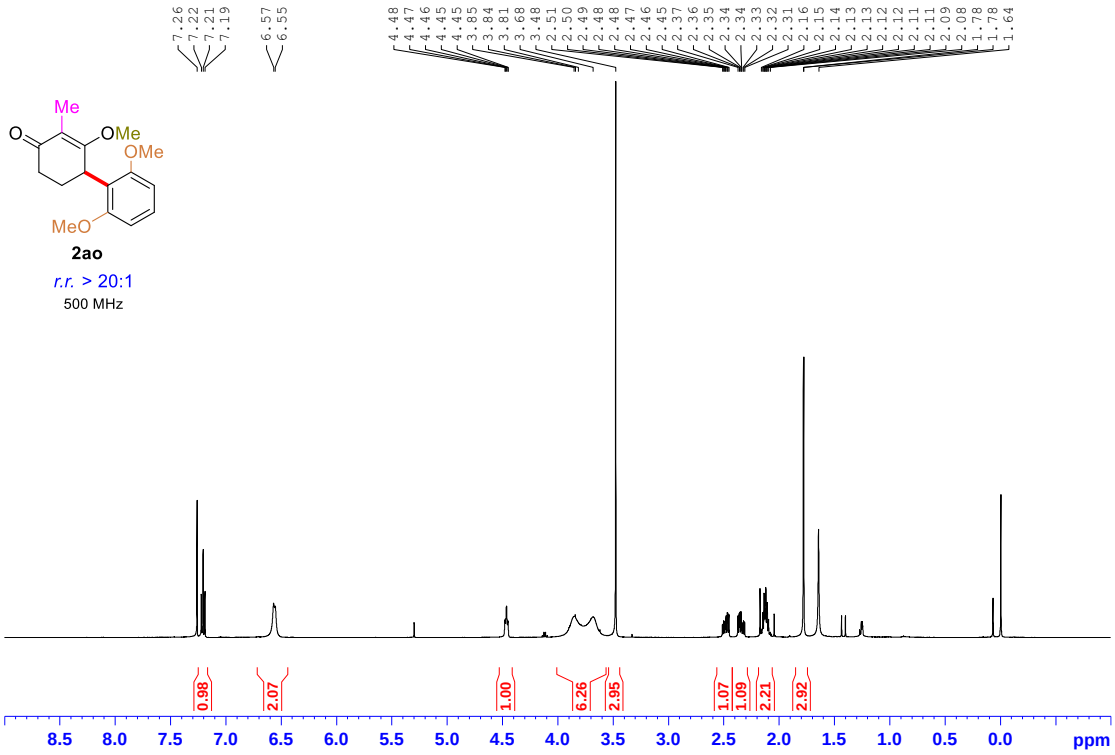


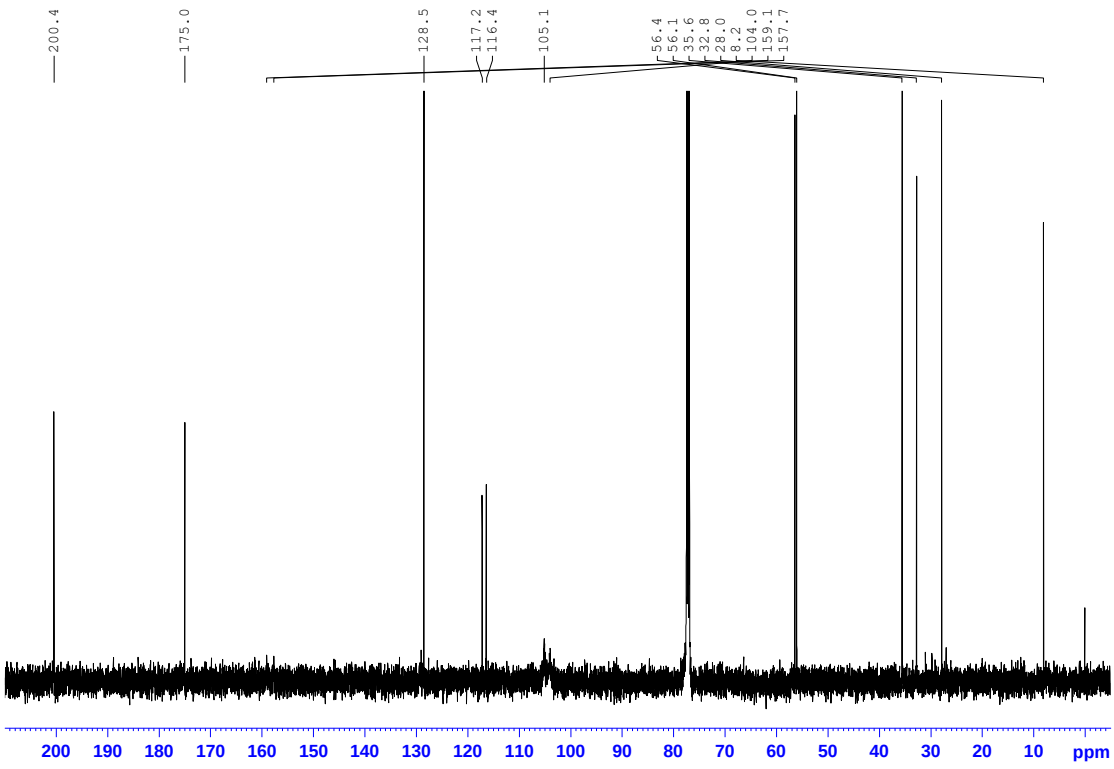
* is for *syn*-isomer

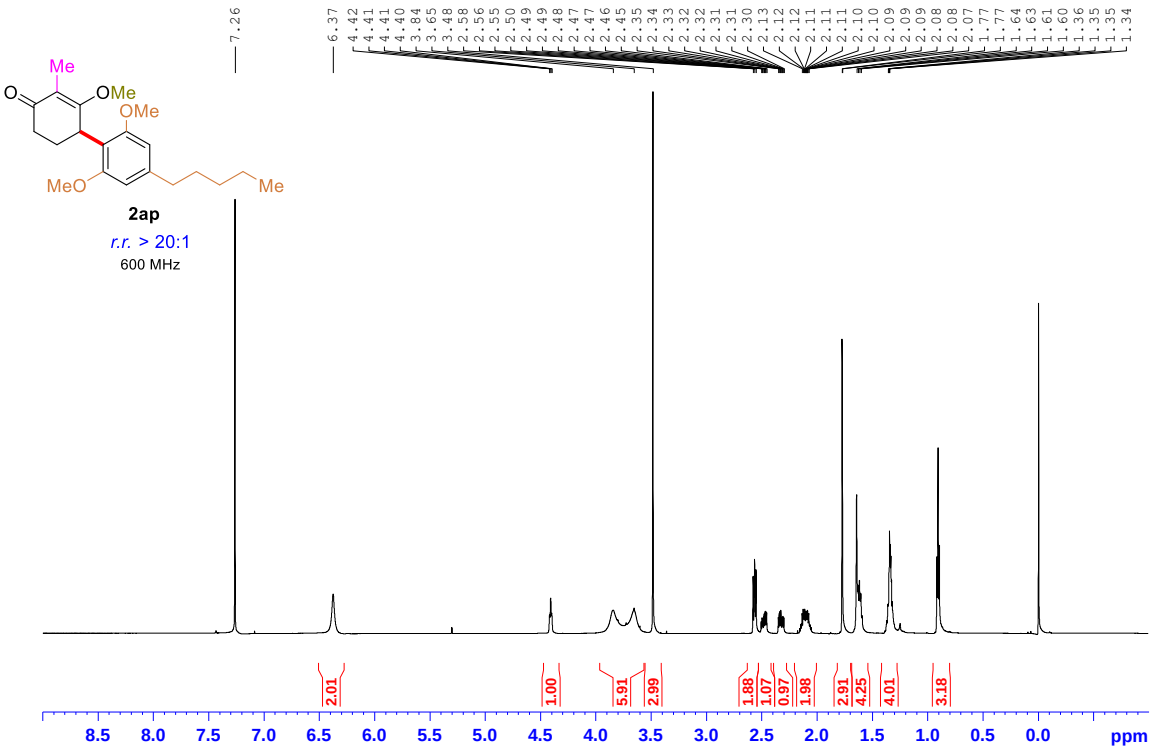


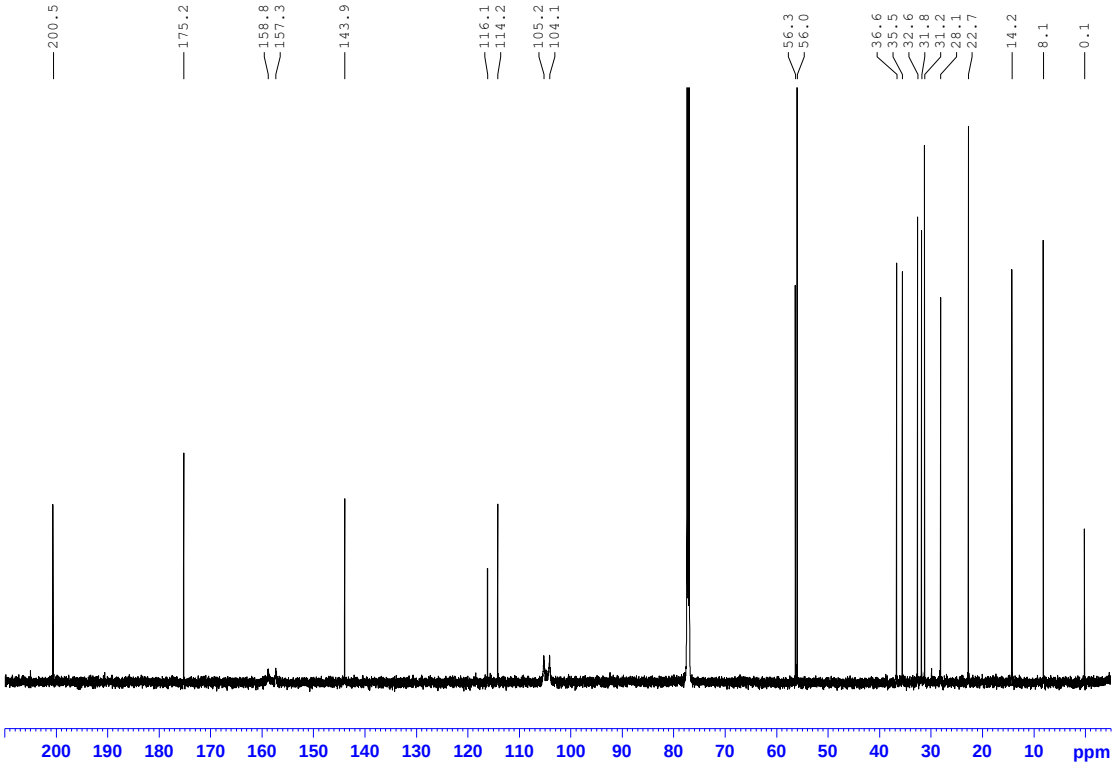

7.30
7.29
7.28
7.28
7.27
7.26
7.06
7.05
7.04
7.04
6.95
6.93
6.92
6.90
6.89
4.48
3.90
3.55
2.26
2.25
2.25
2.24
2.23
2.21
2.20
2.04
2.03
2.02
2.01
2.00
2.00
1.99
1.83
Me
O
OMe
1f
MeO
2an
r.r. > 20:1
500 MHz
0.99
0.96
0.99
0.99
1.00
3.03
3.01
3.11
1.09
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

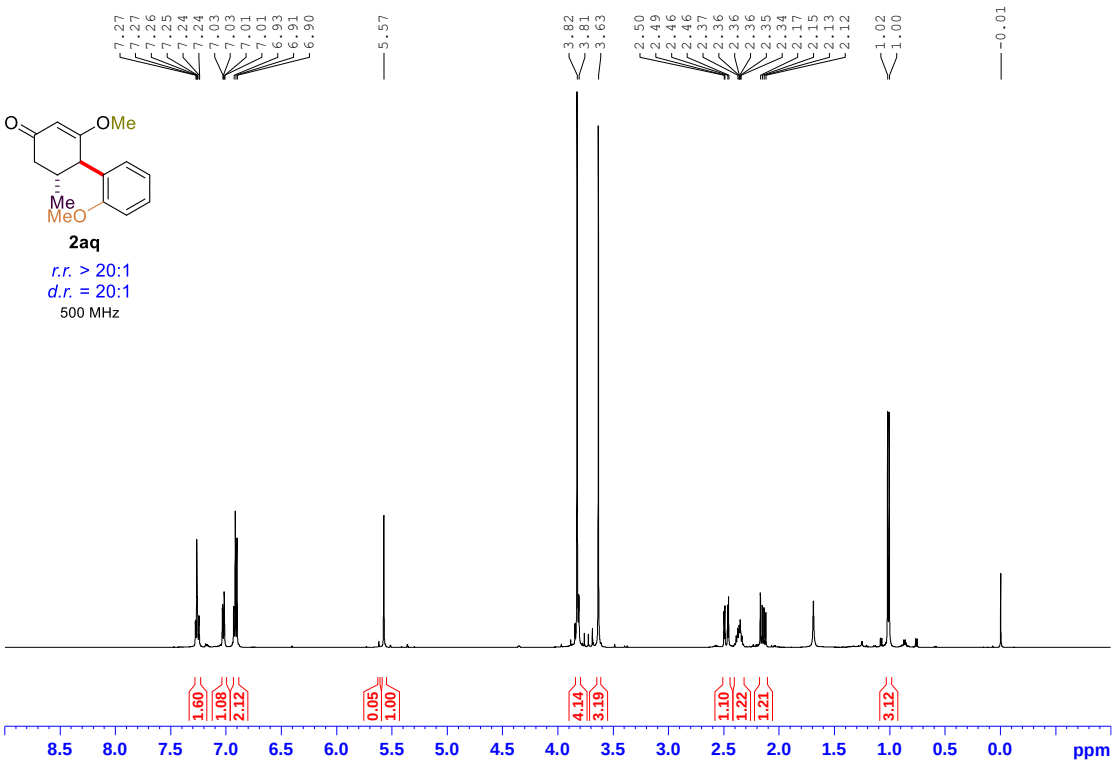

199.7
172.0
156.7
128.8
128.3
125.9
120.7
117.1
110.8
55.5
55.1
33.7
32.3
27.1
7.7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

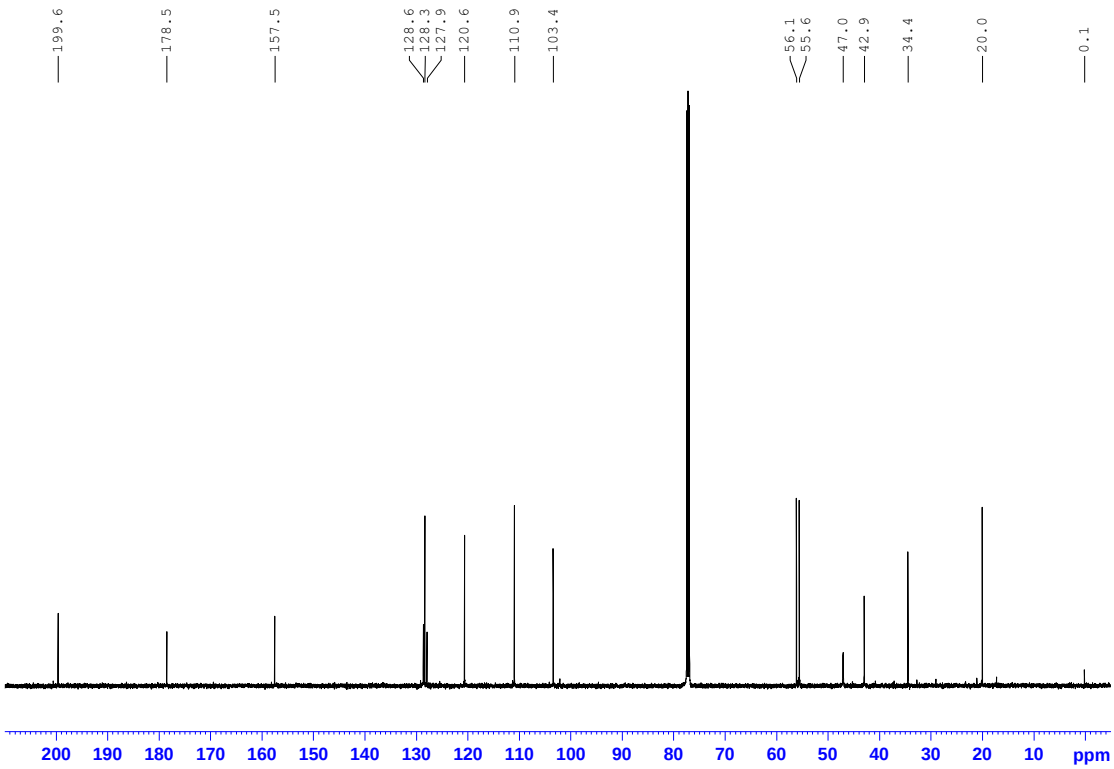

Me
O
OMe
OMe
MeO
2ao
r.r. > 20:1
500 MHz
7.26
7.22
7.21
7.19
6.57
6.55
4.48
4.47
4.46
4.45
4.45
3.85
3.84
3.81
3.68
3.48
2.51
2.50
2.49
2.48
2.48
2.47
2.46
2.45
2.37
2.36
2.35
2.34
2.34
2.33
2.32
2.31
2.16
2.15
2.14
2.13
2.13
2.12
2.12
2.11
2.11
2.09
2.08
1.78
1.78
1.64
0.98
2.07
1.00
6.26
2.95
1.07
1.09
2.21
2.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

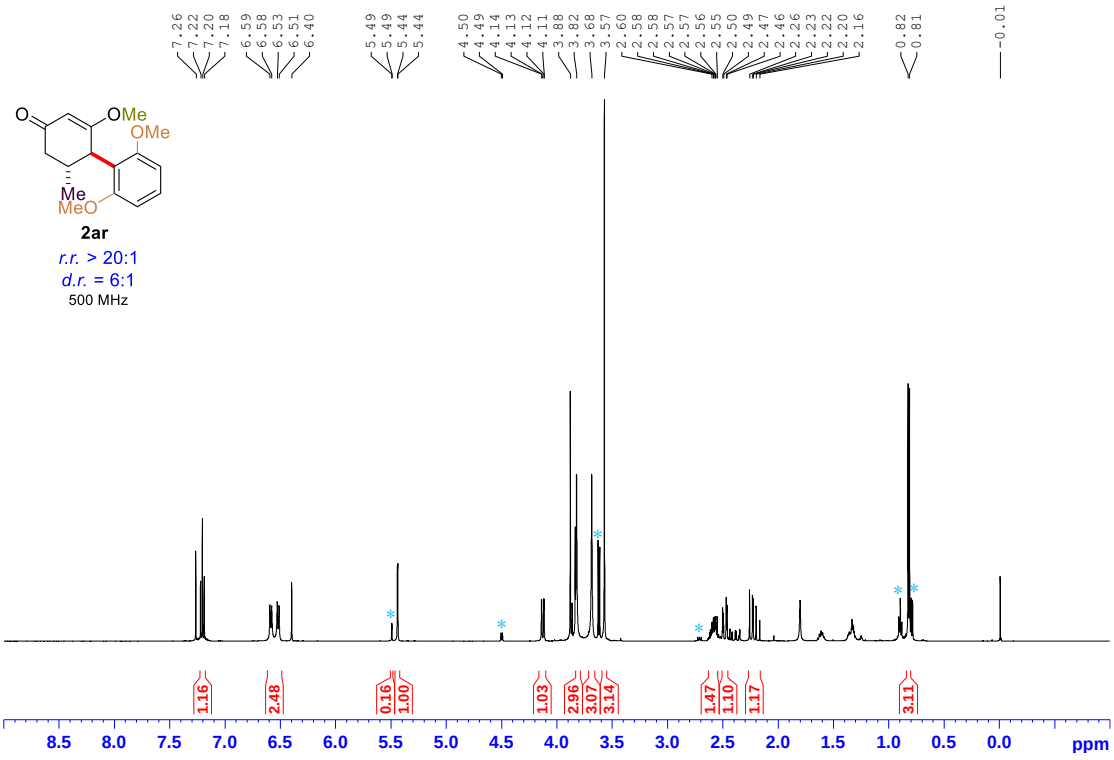

200.4
175.0
128.5
117.2
116.4
105.1
56.4
56.1
35.6
32.8
28.0
8.2
104.0
159.1
157.7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Me
O
OMe
OMe
MeO
Me
2ap
r.r. > 20:1
600 MHz
7.26
6.37
4.42
4.41
4.41
4.40
3.84
3.65
3.48
2.58
2.56
2.55
2.50
2.49
2.48
2.47
2.47
2.46
2.45
2.35
2.34
2.33
2.32
2.32
2.31
2.31
2.30
2.13
2.12
2.12
2.11
2.11
2.11
2.10
2.10
2.09
2.09
2.09
2.08
2.08
2.07
1.77
1.77
1.64
1.63
1.61
1.60
1.36
1.35
1.35
1.34
2.01
1.00
5.91
2.99
1.88
1.07
0.97
1.98
2.91
4.25
4.01
3.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

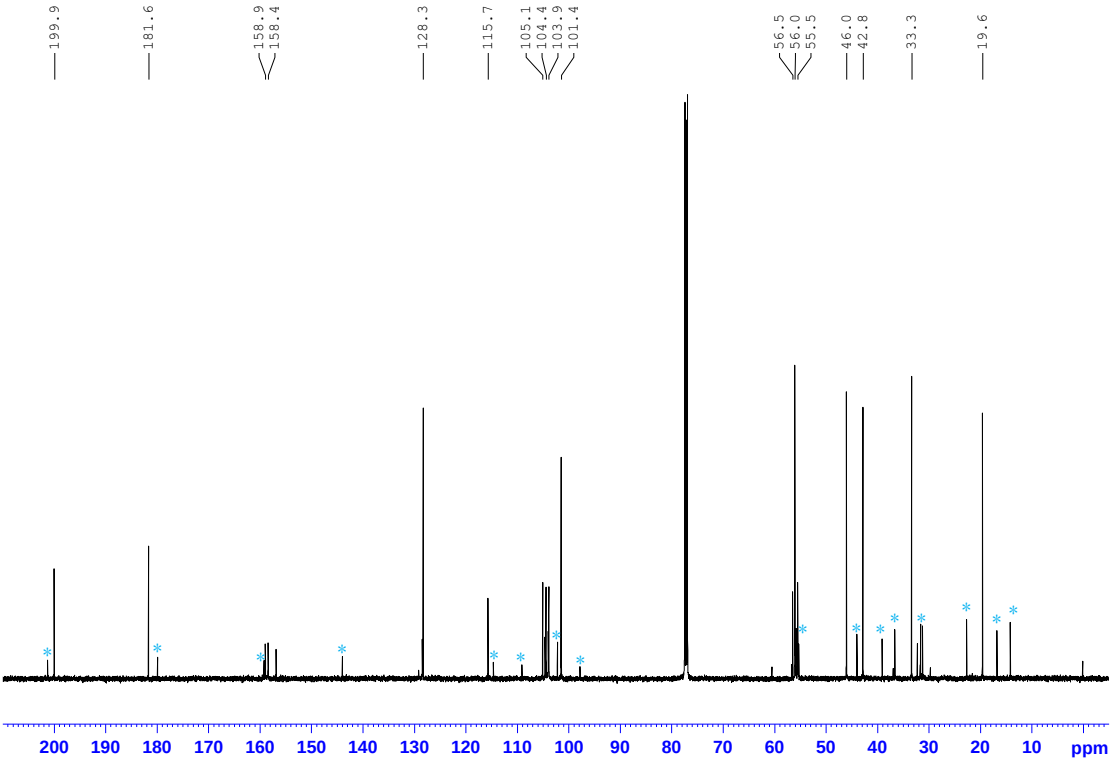

200.5
175.2
158.8
157.3
143.9
116.1
114.2
105.2
104.1
56.3
56.0
36.6
35.5
32.6
31.8
31.2
28.1
22.7
14.2
8.1
0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

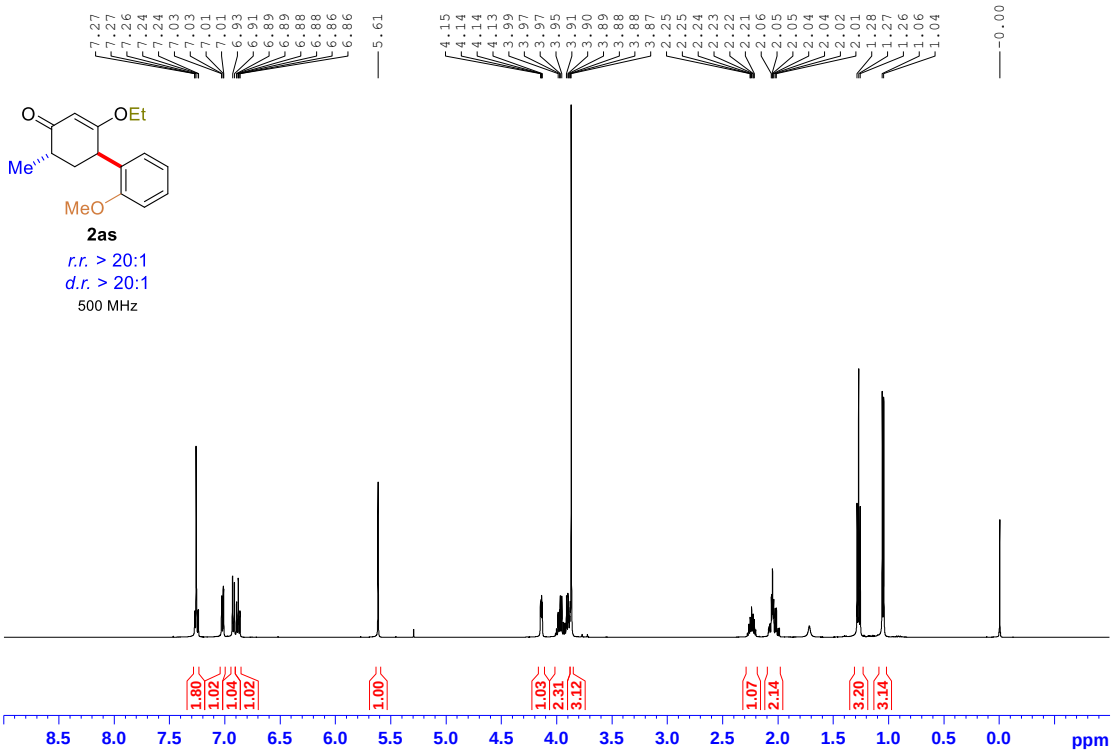

7.27
7.27
7.26
7.25
7.24
7.24
7.03
7.03
7.01
7.01
6.93
6.91
6.90
5.57
3.82
3.81
3.63
2.50
2.49
2.46
2.46
2.37
2.36
2.36
2.36
2.35
2.34
2.17
2.15
2.13
2.12
1.02
1.00
-0.01
O
OMe
Me
MeO
2aq
r.r. > 20:1
d.r. = 20:1
500 MHz
1.60
1.08
2.12
0.05
1.00
4.14
3.19
1.10
1.22
1.21
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

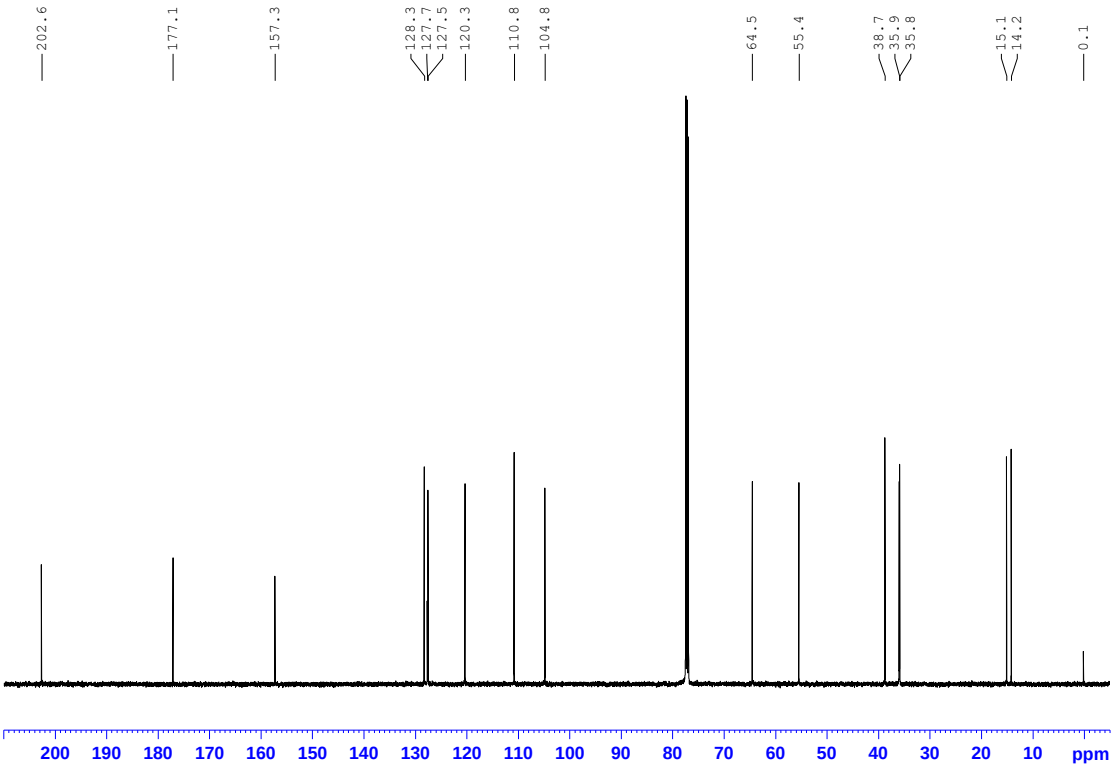

199.6
178.5
157.5
128.6
128.3
127.9
120.6
110.9
103.4
56.1
55.6
47.0
42.9
34.4
20.0
0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

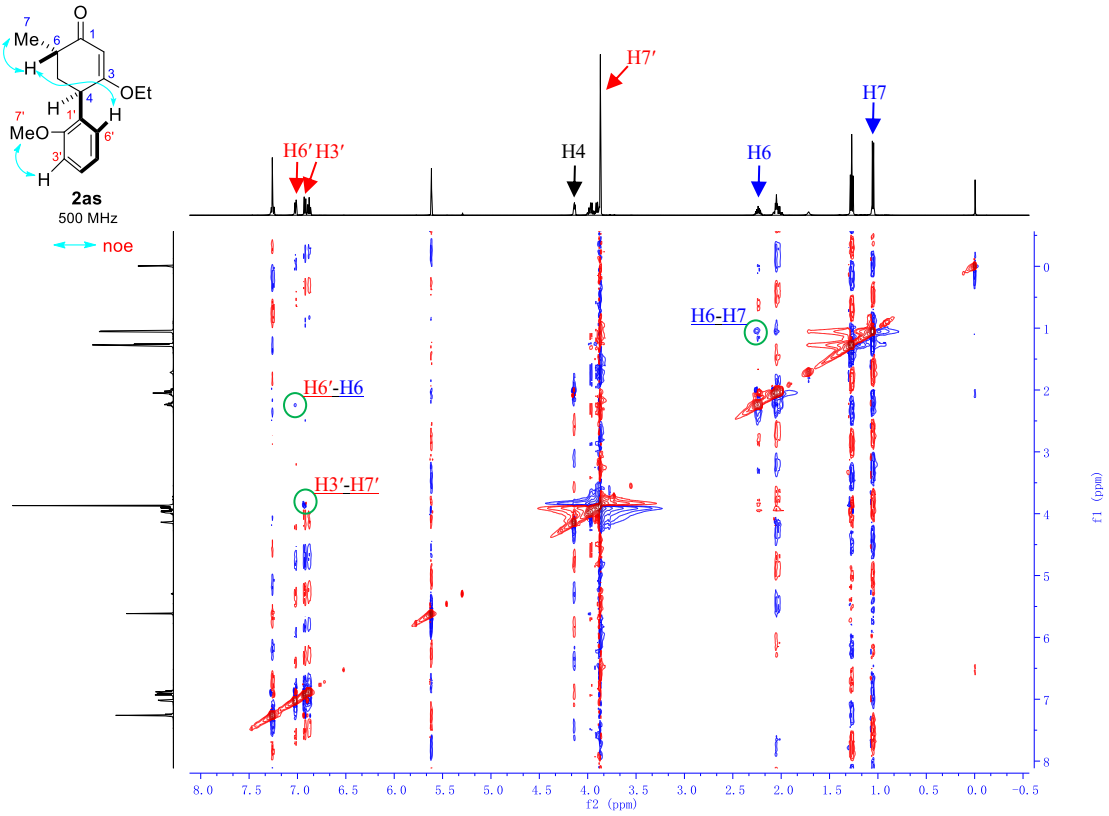


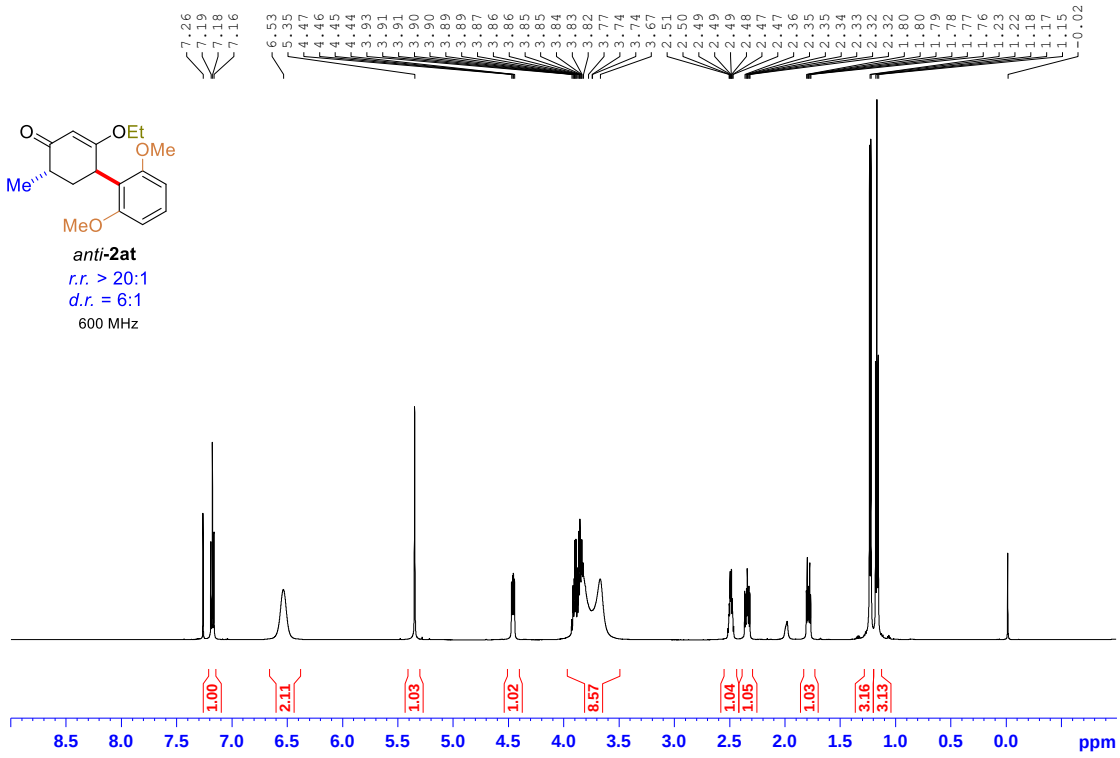
* is for *syn*-isomer

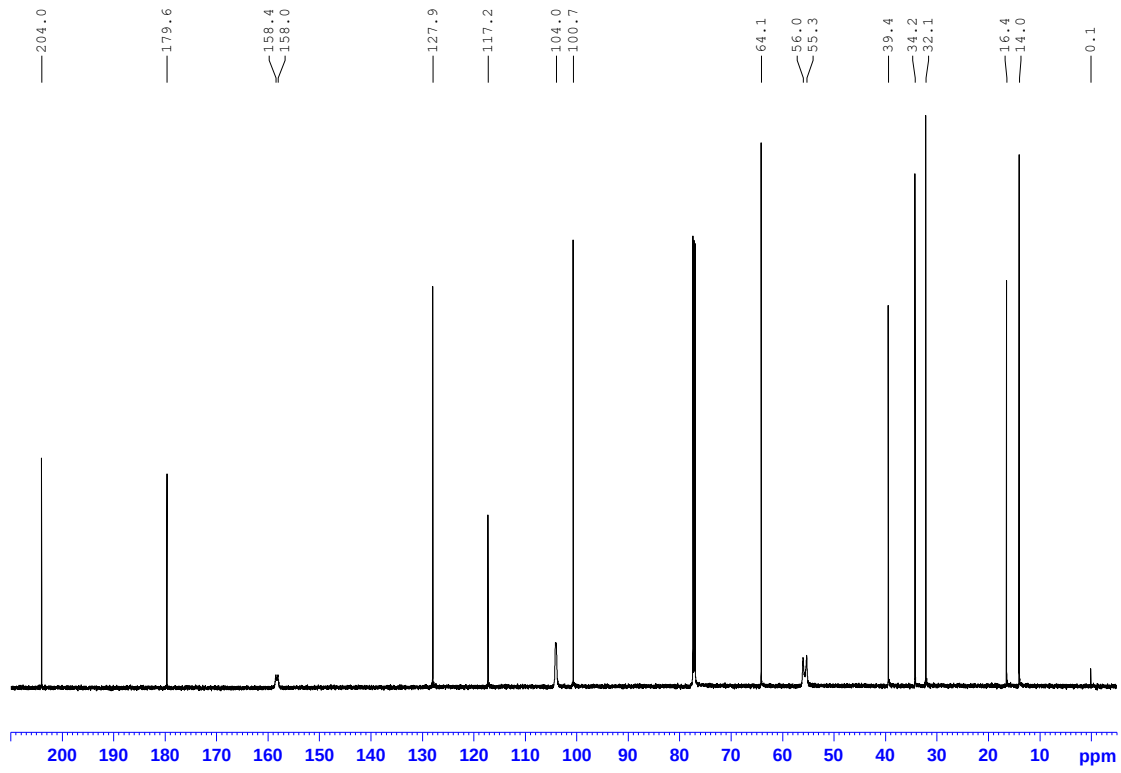


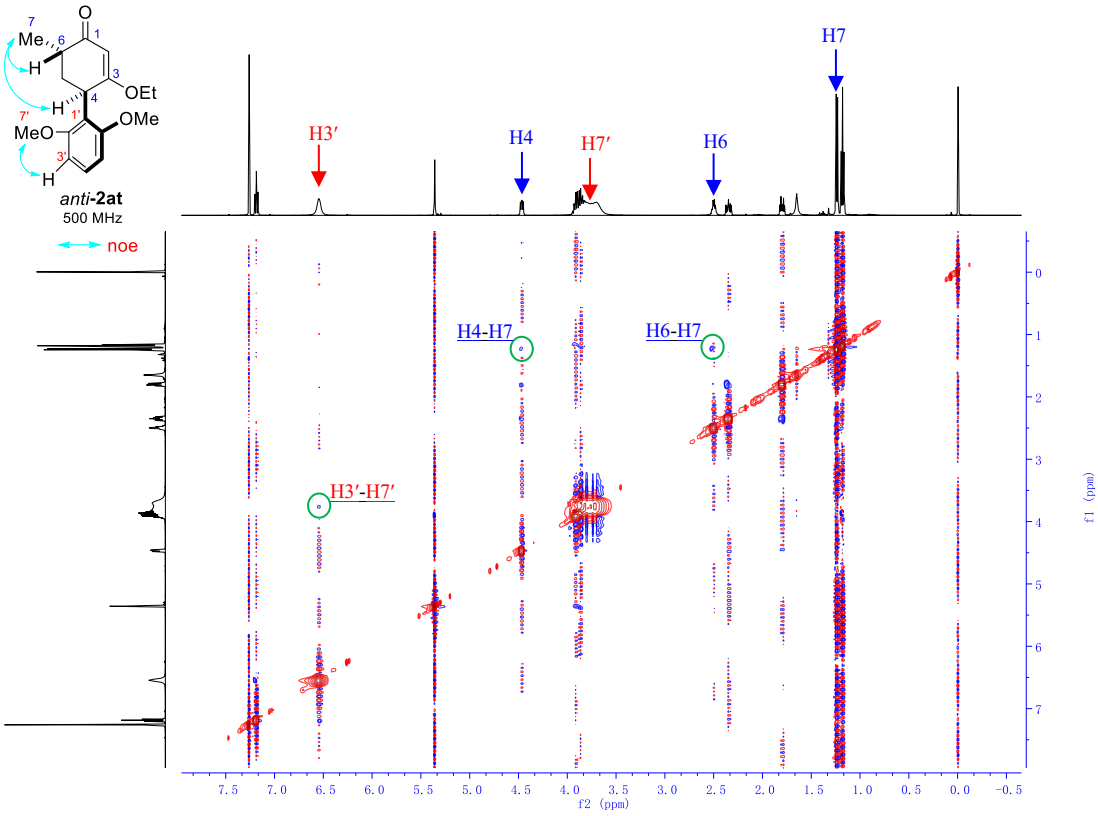

7.27
7.27
7.26
7.24
7.24
7.03
7.03
7.01
7.01
6.93
6.91
6.89
6.89
6.88
6.88
6.86
6.86
5.61
4.15
4.14
4.14
4.13
3.99
3.97
3.97
3.95
3.91
3.90
3.89
3.88
3.88
3.87
2.25
2.25
2.24
2.23
2.22
2.21
2.06
2.05
2.05
2.04
2.04
2.02
2.01
1.28
1.27
1.26
1.06
1.04
0.00
O
OEt
Me
MeO
2as
r.r. > 20:1
d.r. > 20:1
500 MHz
1.80
1.02
1.04
1.02
1.00
1.03
2.31
3.12
1.07
2.14
3.20
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

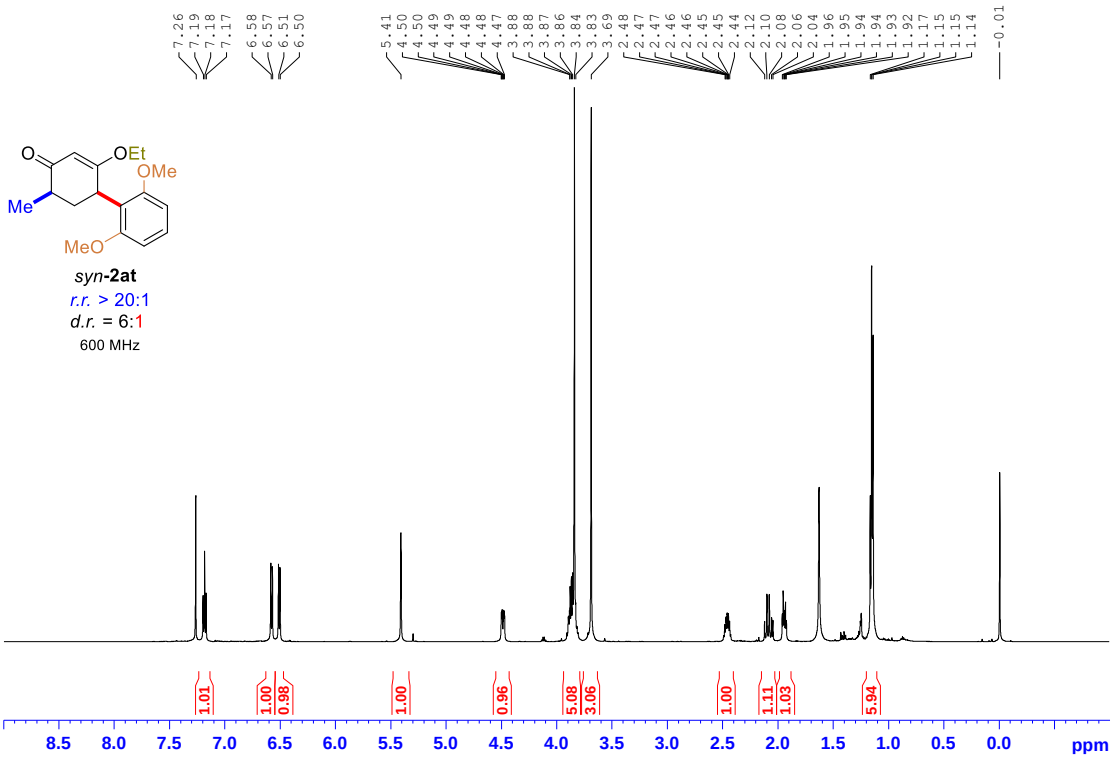

202.6
177.1
157.3
128.3
127.7
127.5
120.3
110.8
104.8
64.5
55.4
38.7
35.9
35.8
15.1
14.2
0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

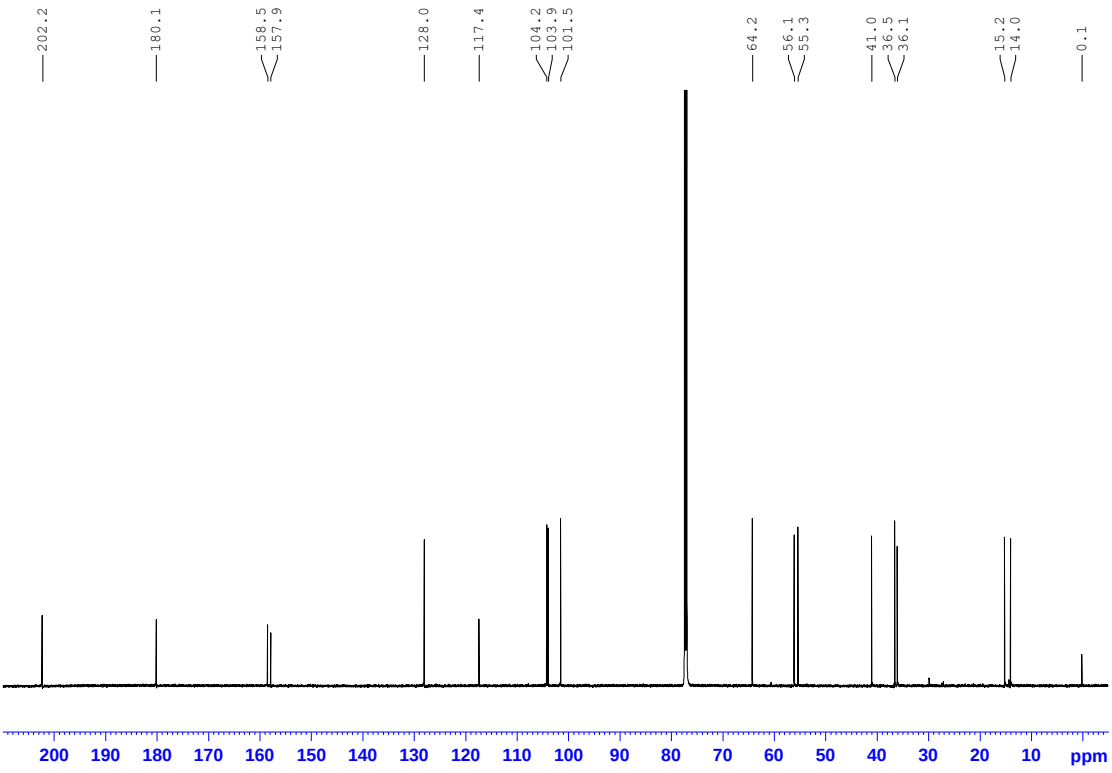

2as
500 MHz
noe
H6′H3′
H4
H7′
H6
H7
H6′-H6
H3′-H7′
H6-H7
f2 (ppm)
f1 (ppm)

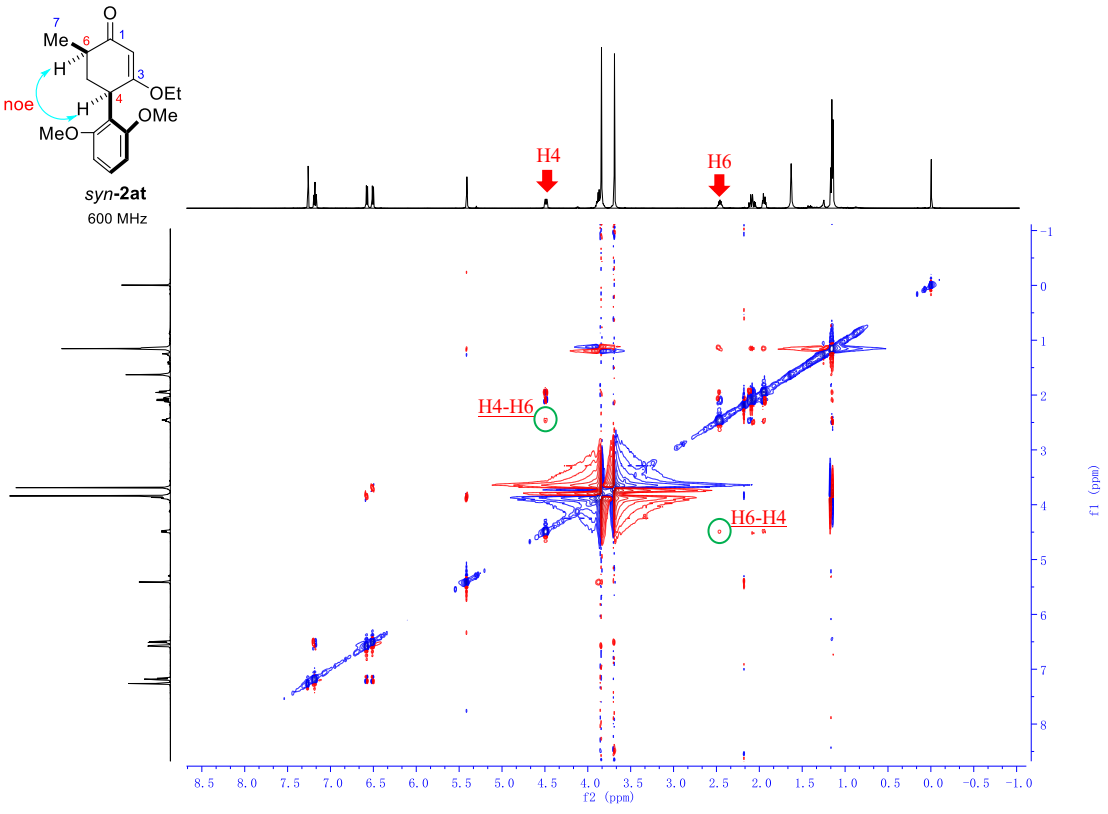

7.26
7.19
7.18
7.16
6.53
5.35
4.47
4.46
4.45
4.44
3.93
3.91
3.90
3.90
3.89
3.89
3.87
3.86
3.86
3.85
3.85
3.84
3.83
3.82
3.77
3.74
3.74
3.67
2.51
2.50
2.49
2.49
2.49
2.48
2.47
2.47
2.36
2.35
2.35
2.34
2.33
2.32
2.32
1.80
1.80
1.79
1.78
1.77
1.76
1.23
1.22
1.18
1.17
1.15
0.02
O
OEt
OMe
Me
MeO
anti-2at
r.r. > 20:1
d.r. = 6:1
600 MHz
1.00
2.11
1.03
1.02
8.57
1.04
1.05
1.03
3.16
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

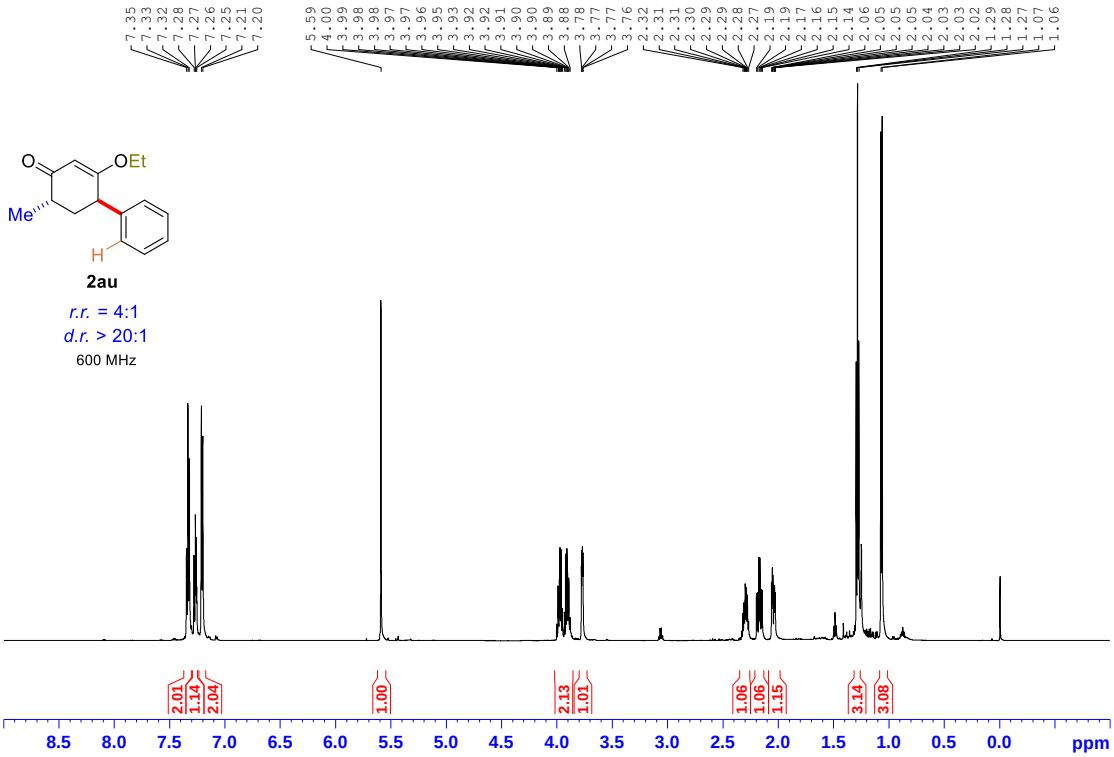

204.0
179.6
158.4
158.0
127.9
117.2
104.0
100.7
64.1
56.0
55.3
39.4
34.2
32.1
16.4
14.0
0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

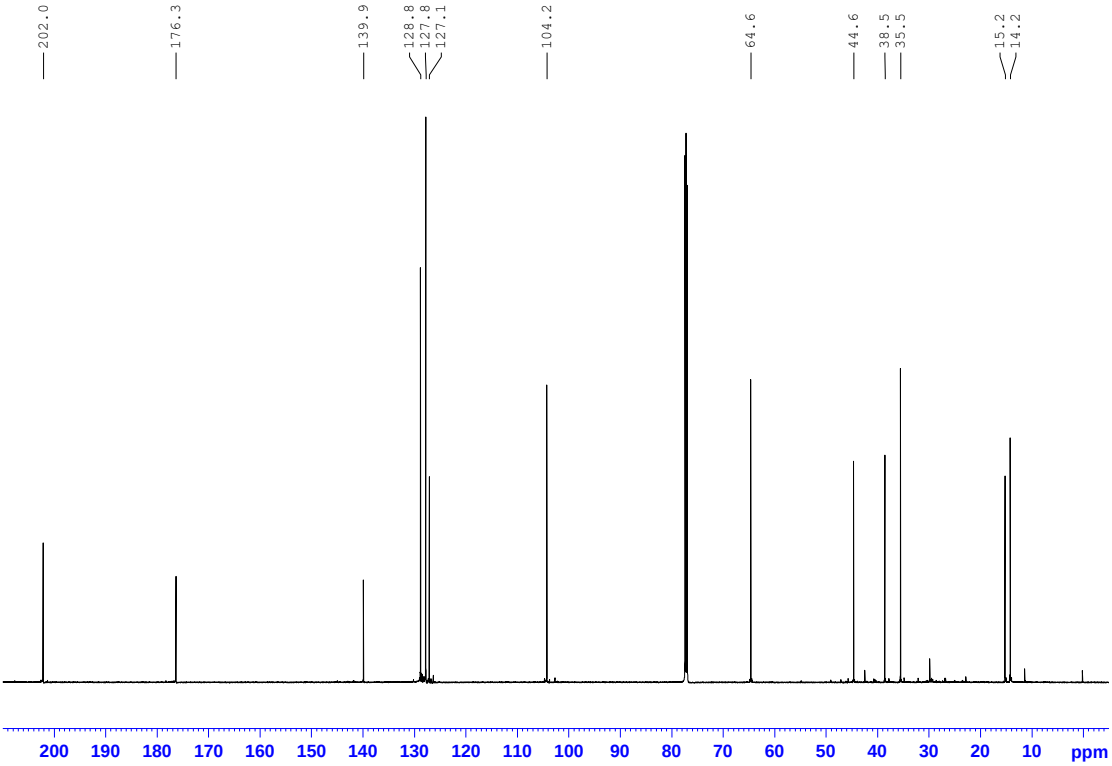

anti-2at
500 MHz
noe
H3′
H4
H7′
H6
H7
H4-H7
H6-H7
H3′-H7′
f2 (ppm)
f1 (ppm)

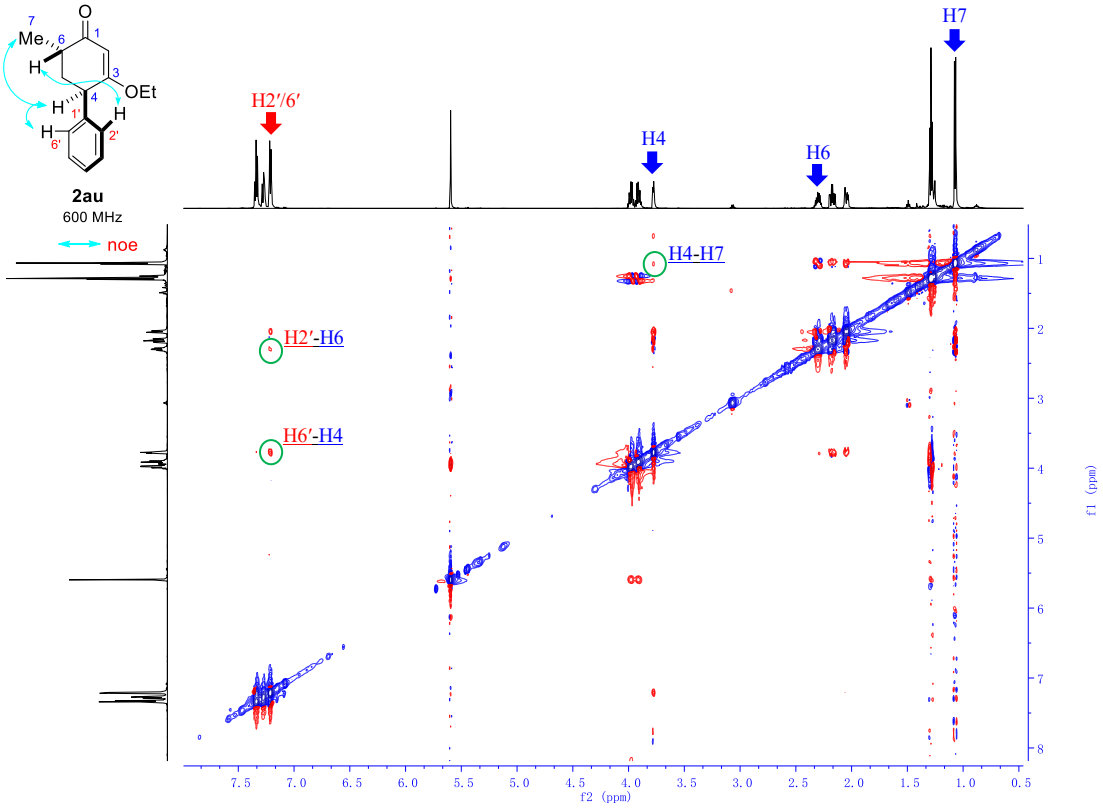

7.26
7.19
7.18
7.17
6.58
6.57
6.51
6.50
5.41
4.50
4.50
4.49
4.49
4.48
4.48
4.47
3.88
3.88
3.87
3.86
3.84
3.83
3.69
2.48
2.47
2.47
2.46
2.45
2.45
2.44
2.12
2.10
2.08
2.06
2.04
1.96
1.95
1.94
1.94
1.93
1.92
1.17
1.15
1.15
1.14
-0.01
O
OEt
OMe
Me
MeO
syn-2at
r.r. > 20:1
d.r. = 6:1
600 MHz
1.01
1.00
0.98
1.00
0.96
5.08
3.06
1.00
1.11
1.03
5.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

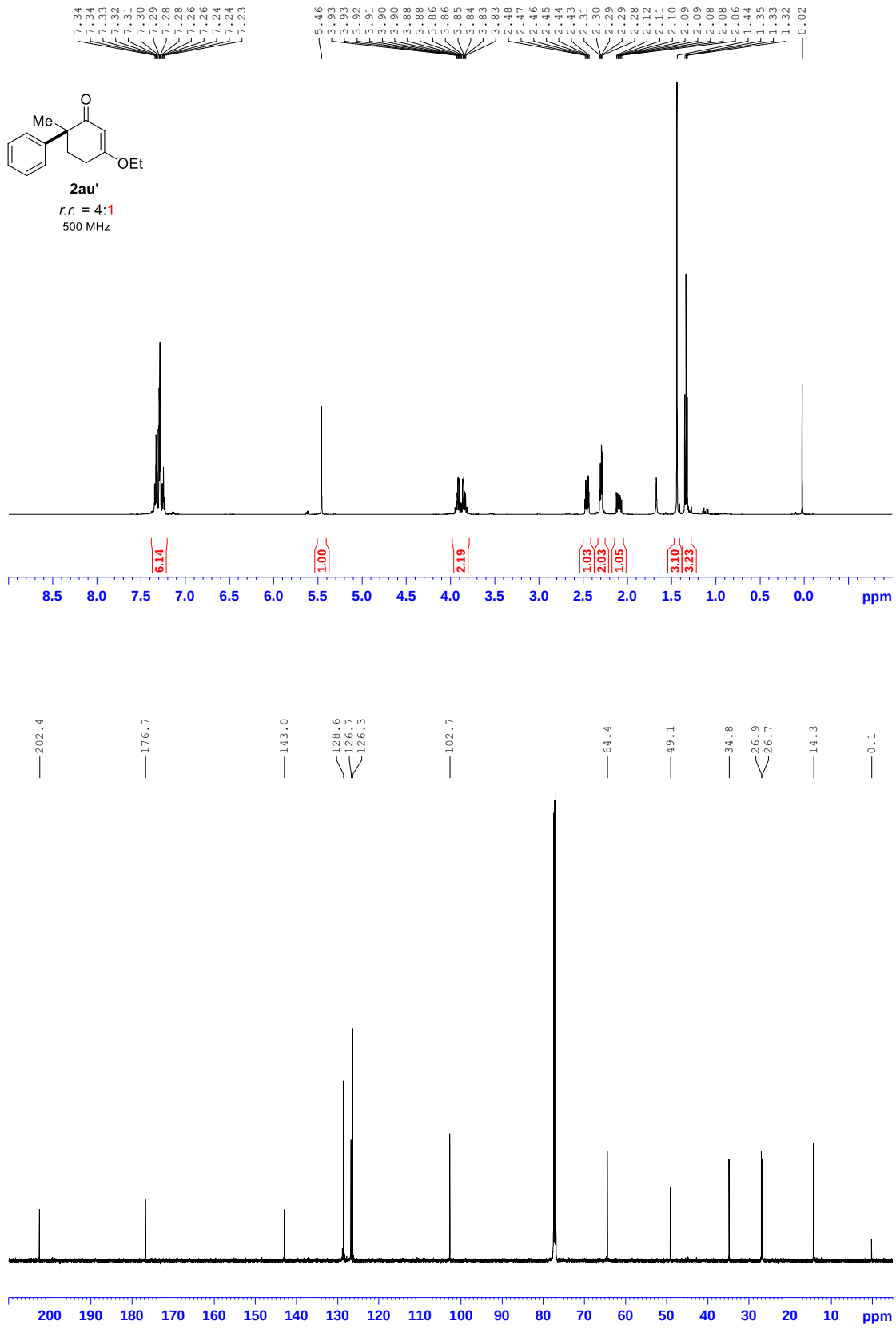

202.2
180.1
158.5
157.9
128.0
117.4
104.2
103.9
101.5
64.2
56.1
55.3
41.0
36.5
36.1
15.2
14.0
0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

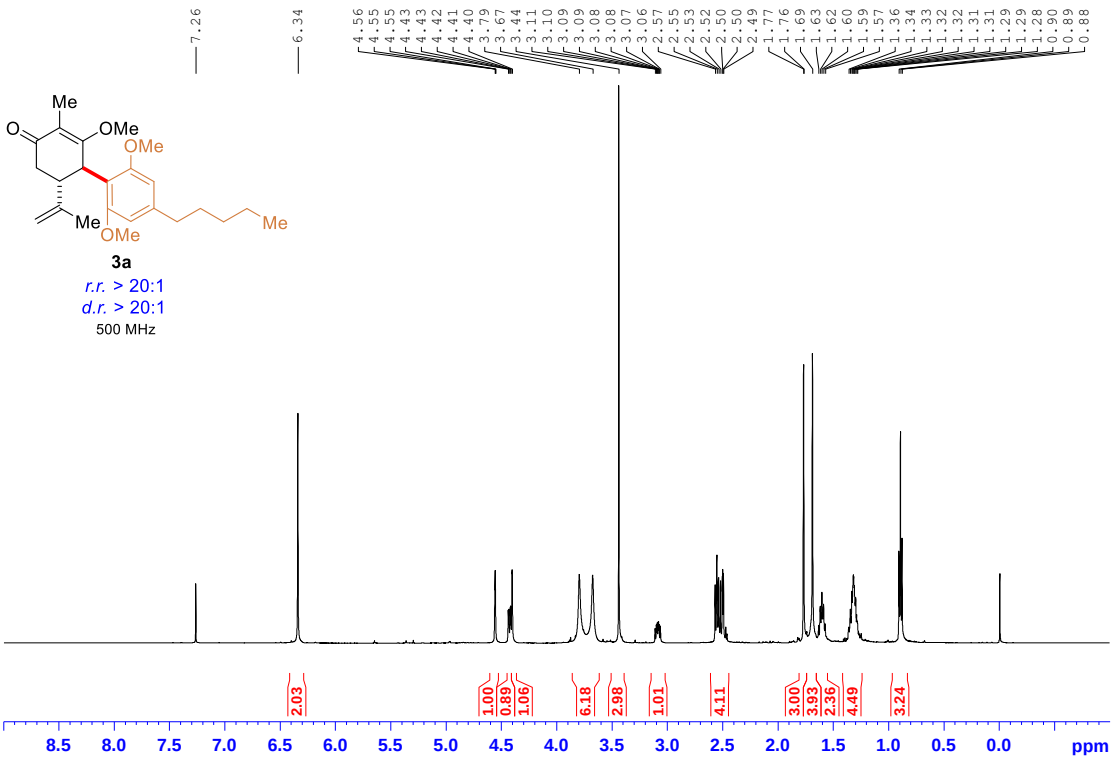

noe
Me
H
H
MeO
OEt
OMe
syn-2at
600 MHz
H4
H6
H4-H6
H6-H4
f2 (ppm)
f1 (ppm)

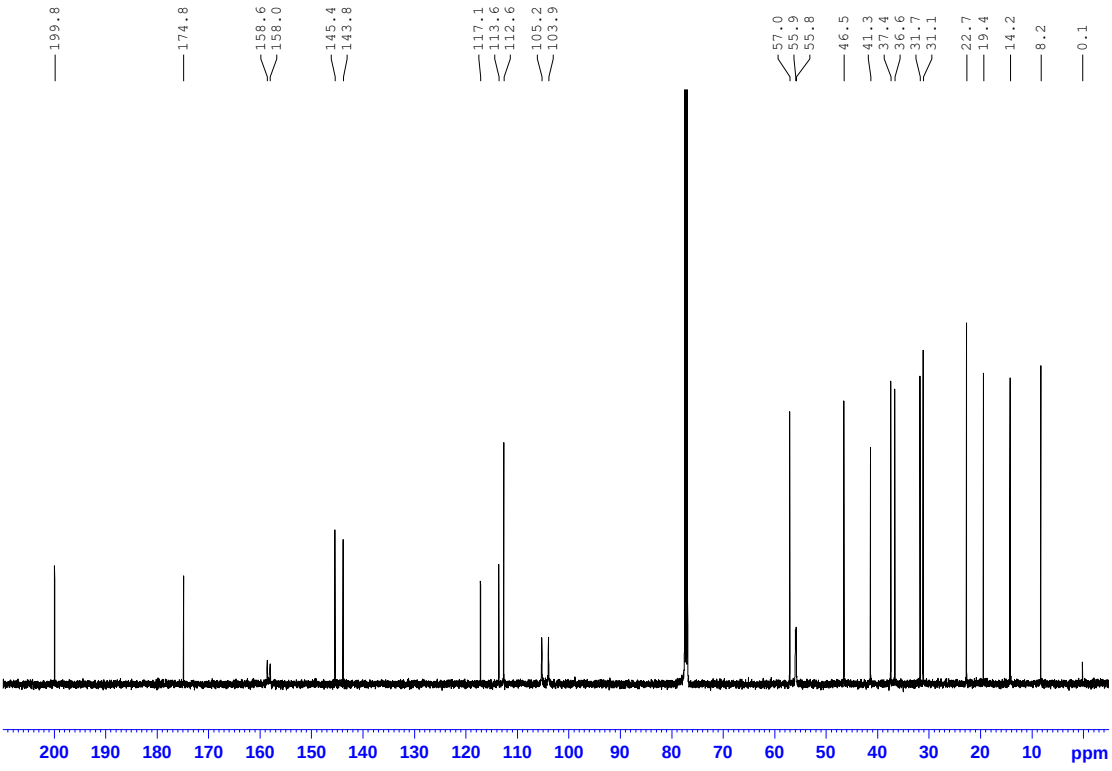

O
OEt
Me
H
2au
r.r. = 4:1
d.r. > 20:1
600 MHz
ppm

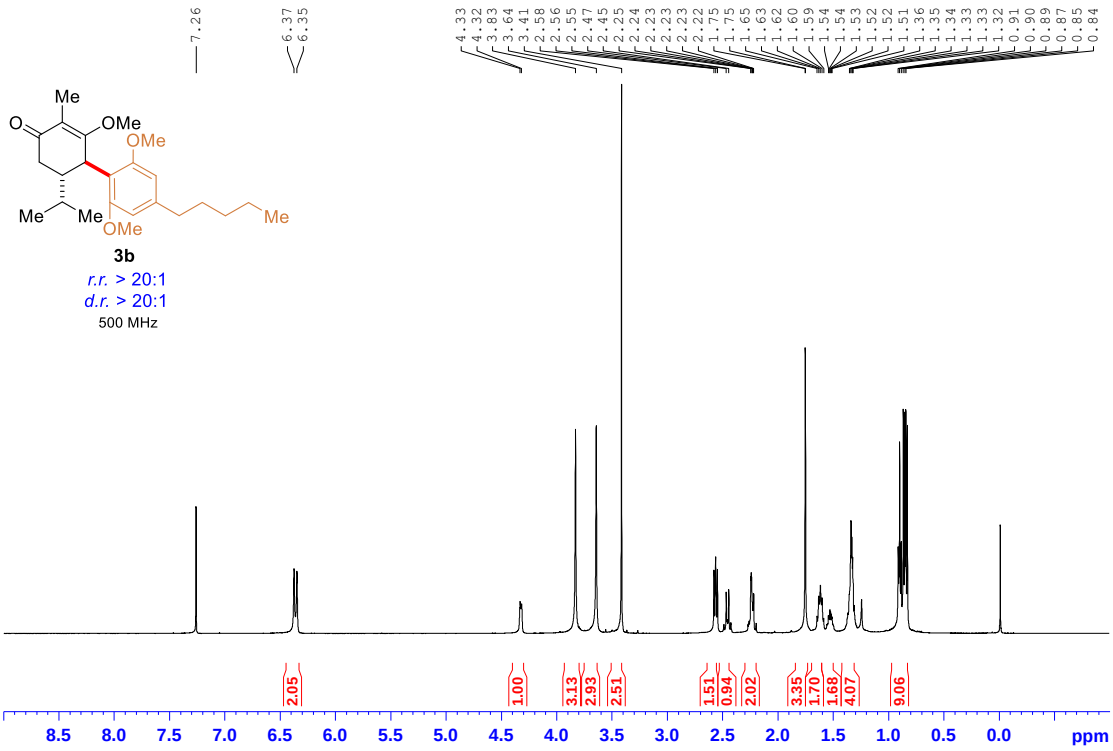

ppm

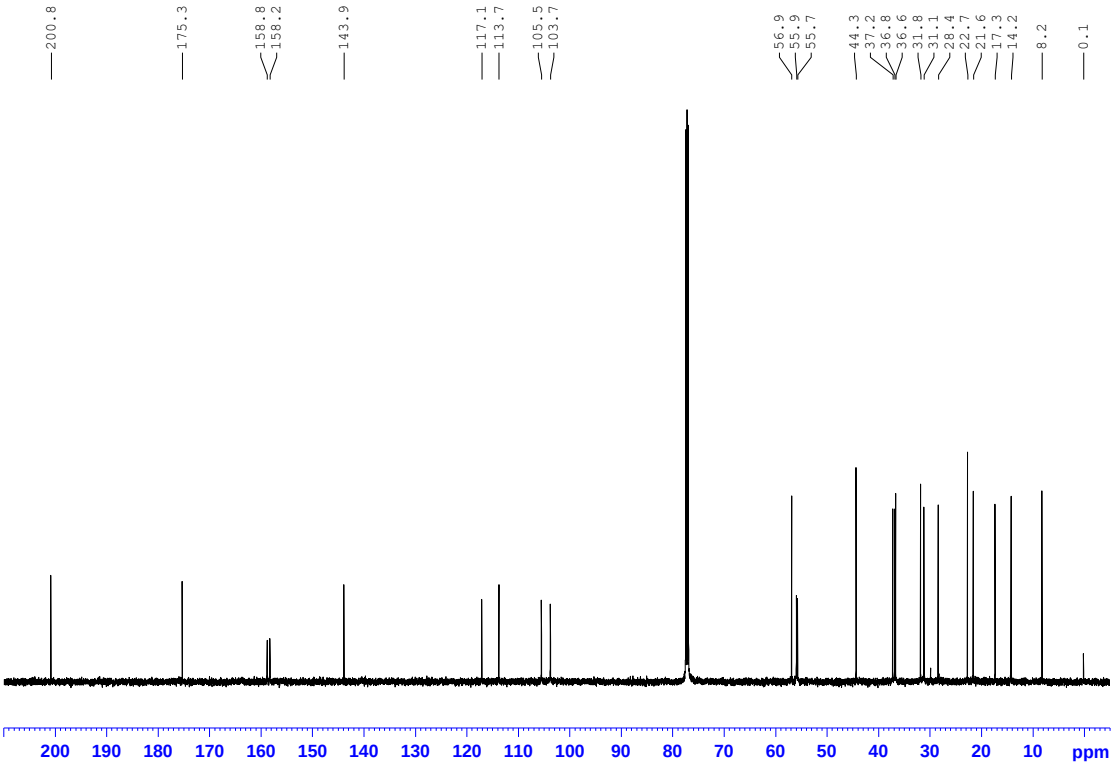

O
7
Me
6
1
H
3
OEt
4
H
1'
H
2'
6'
2au
600 MHz
noe
H2′/6′
H4
H6
H7
H4-H7
H2′-H6
H6′-H4
f1 (ppm)
f2 (ppm)

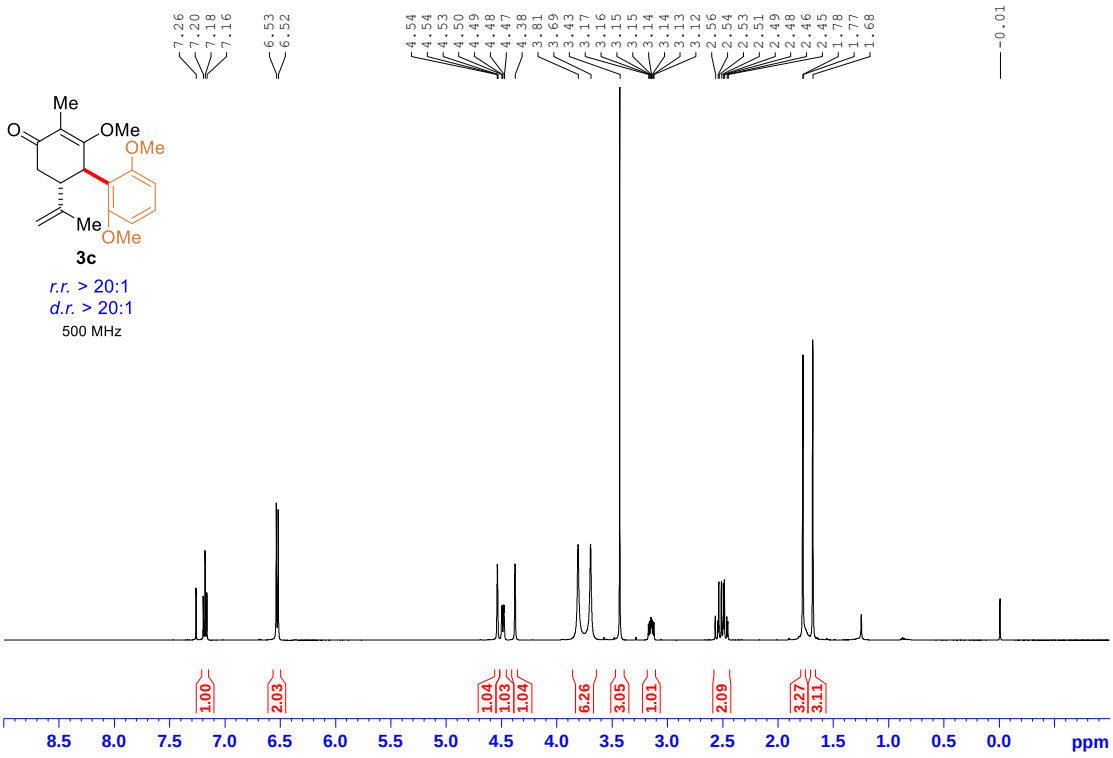

7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.26
7.26
7.24
7.24
7.23
5.46
3.93
3.93
3.92
3.91
3.90
3.90
3.88
3.88
3.86
3.86
3.85
3.84
3.83
3.83
2.48
2.47
2.46
2.45
2.44
2.43
2.31
2.30
2.29
2.29
2.28
2.12
2.11
2.10
2.09
2.09
2.08
2.08
2.06
1.44
1.35
1.33
1.32
0.02
Me
O
OEt
2au'
r.r. = 4:1
500 MHz
6.14
1.00
2.19
1.03
2.03
1.05
3.10
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
202.4
176.7
143.0
128.6
126.7
126.3
102.7
64.4
49.1
34.8
26.9
26.7
14.3
0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

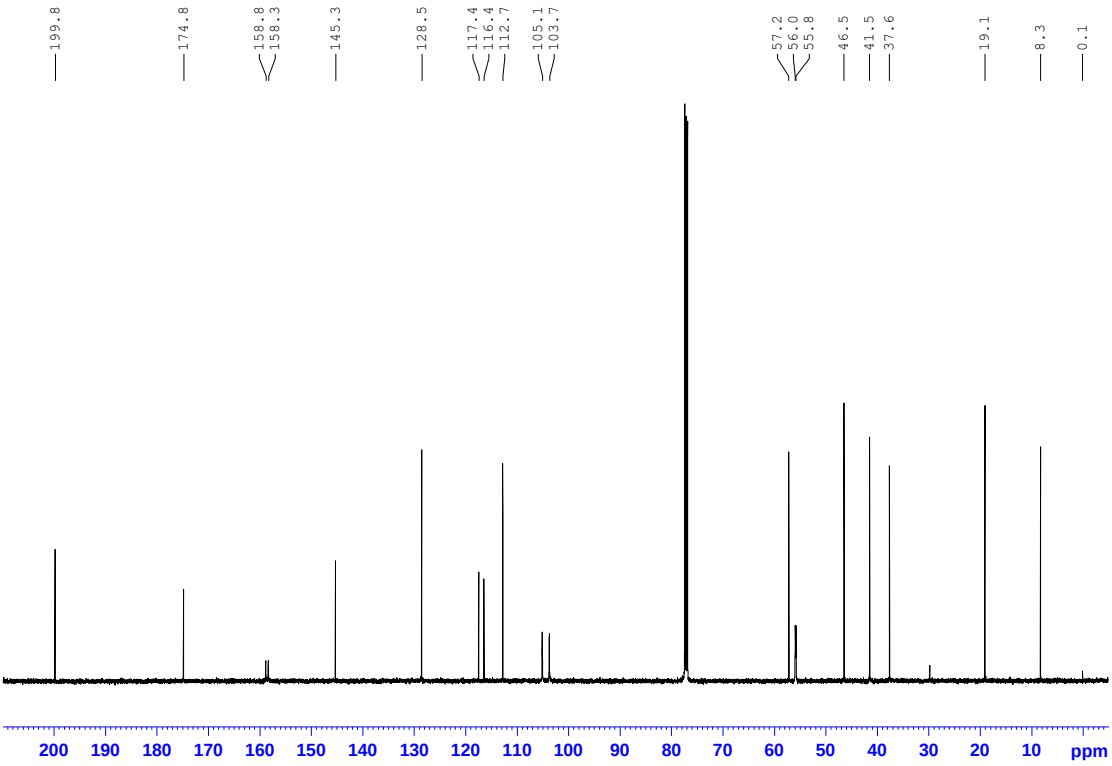

7.26
6.34
4.56 4.55 4.55 4.43 4.43 4.42 4.41 4.40 3.79 3.67 3.44 3.11 3.10 3.09 3.09 3.08 3.08 3.07 3.06 2.57 2.55 2.53 2.52 2.50 2.50 2.49 1.77 1.76 1.69 1.63 1.62 1.60 1.59 1.57 1.36 1.34 1.33 1.32 1.32 1.31 1.31 1.29 1.29 1.28 0.90 0.89 0.88
Me
O
OMe
OMe
Me
OMe
Me
3a
r.r. > 20:1
d.r. > 20:1
500 MHz
2.03
1.00
0.89
1.06
6.18
2.98
1.01
4.11
3.00
3.93
2.36
4.49
3.24
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

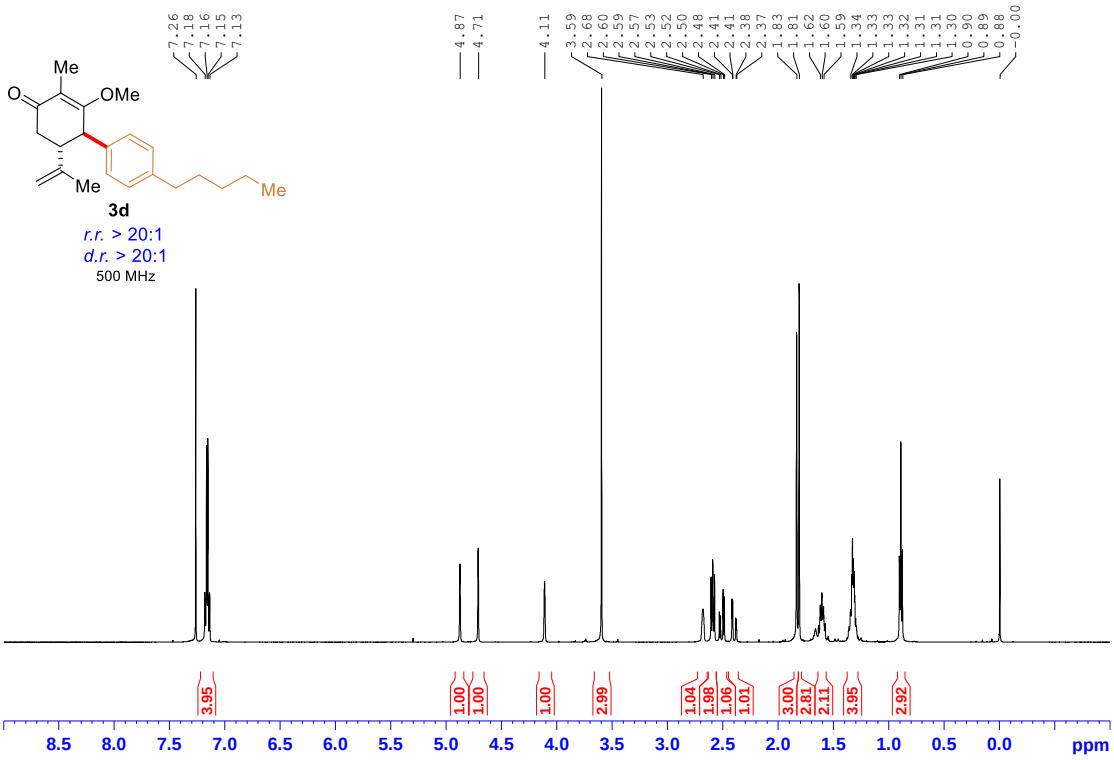

199.8
174.8
158.6
158.0
145.4
143.8
117.1
113.6
112.6
105.2
103.9
57.0
55.9
55.8
46.5
41.3
37.4
36.6
31.7
31.1
22.7
19.4
14.2
8.2
0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

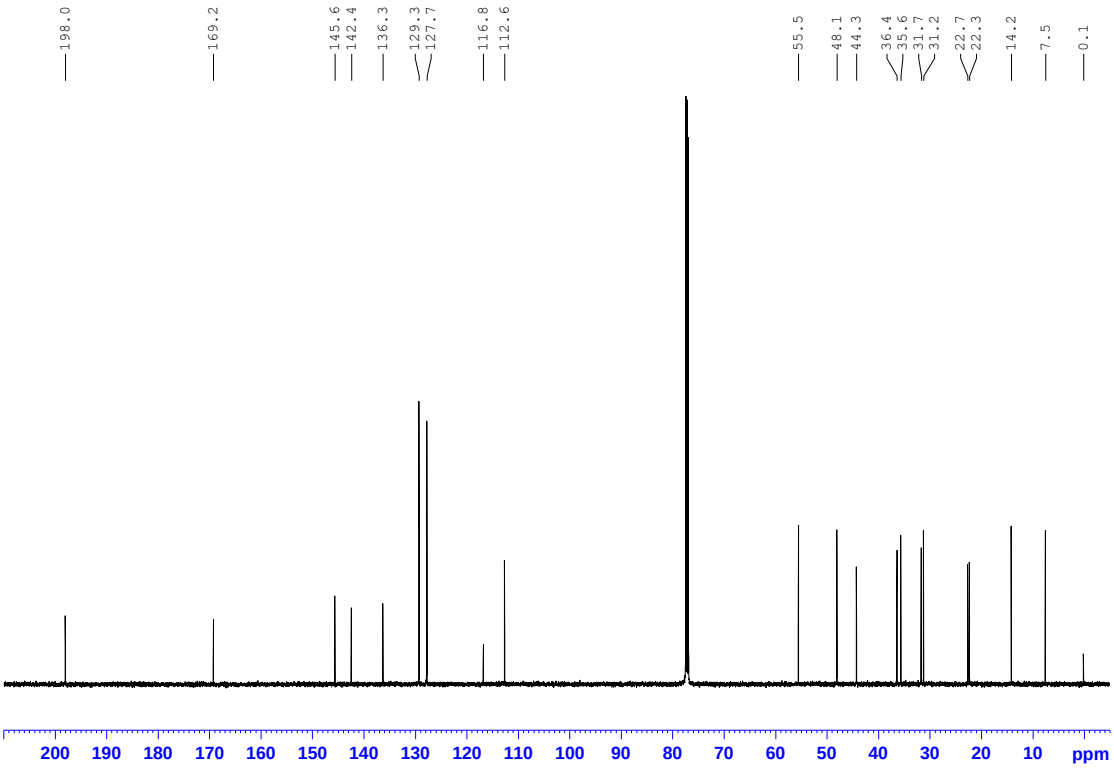

Me
O
OMe
OMe
Me
Me
OMe
Me
3b
r.r. > 20:1
d.r. > 20:1
500 MHz
7.26
6.37
6.35
4.33
4.32
3.83
3.64
3.41
2.58
2.56
2.55
2.47
2.45
2.25
2.24
2.23
2.23
2.23
2.22
1.75
1.75
1.65
1.63
1.62
1.60
1.59
1.54
1.54
1.53
1.52
1.52
1.51
1.36
1.35
1.34
1.33
1.33
1.32
0.91
0.90
0.89
0.87
0.85
0.84
2.05
1.00
3.13
2.93
2.51
1.51
0.94
2.02
3.35
1.70
1.68
4.07
9.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

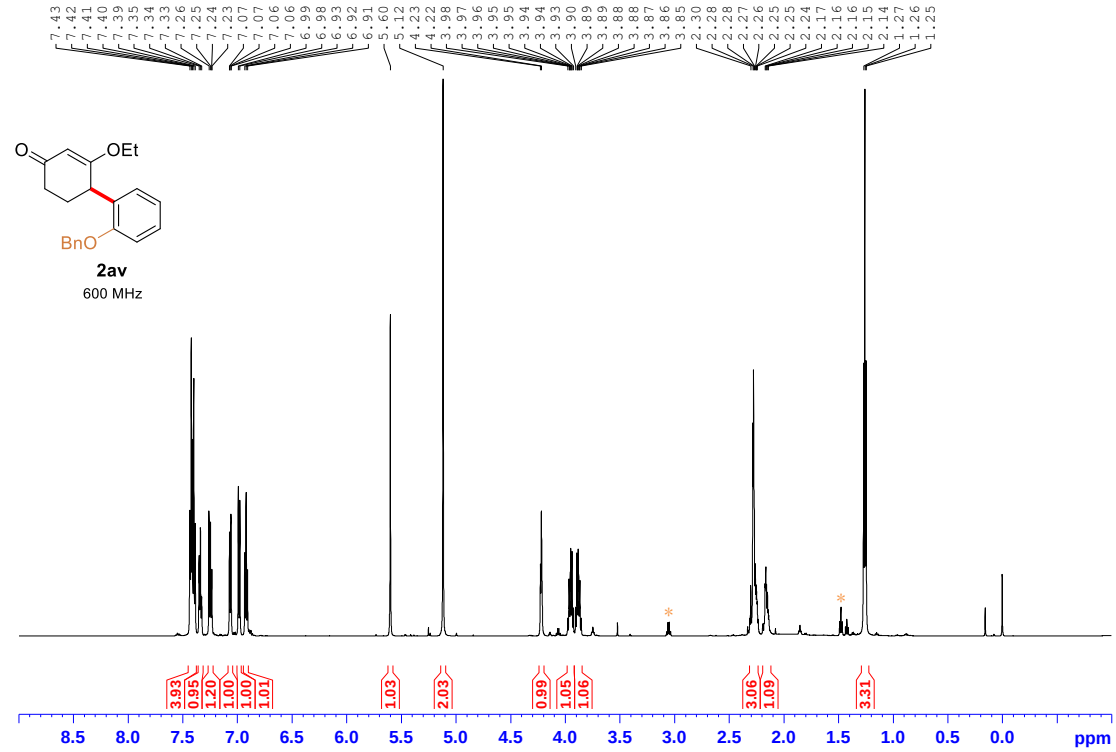

200.8
175.3
158.8
158.2
143.9
117.1
113.7
105.5
103.7
56.9
55.9
55.7
44.3
37.2
36.8
36.6
31.8
31.1
28.4
22.7
21.6
17.3
14.2
8.2
0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm


7.26
7.20
7.18
7.16
6.53
6.52
4.54
4.54
4.53
4.50
4.49
4.48
4.47
4.38
3.81
3.69
3.43
3.17
3.16
3.15
3.15
3.14
3.14
3.13
3.12
2.56
2.54
2.53
2.51
2.49
2.48
2.46
2.45
1.78
1.77
1.68
0.01
Me
O
OMe
OMe
Me
OMe
3c
r.r. > 20:1
d.r. > 20:1
500 MHz
1.00
2.03
1.04
1.03
1.04
6.26
3.05
1.01
2.09
3.27
3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

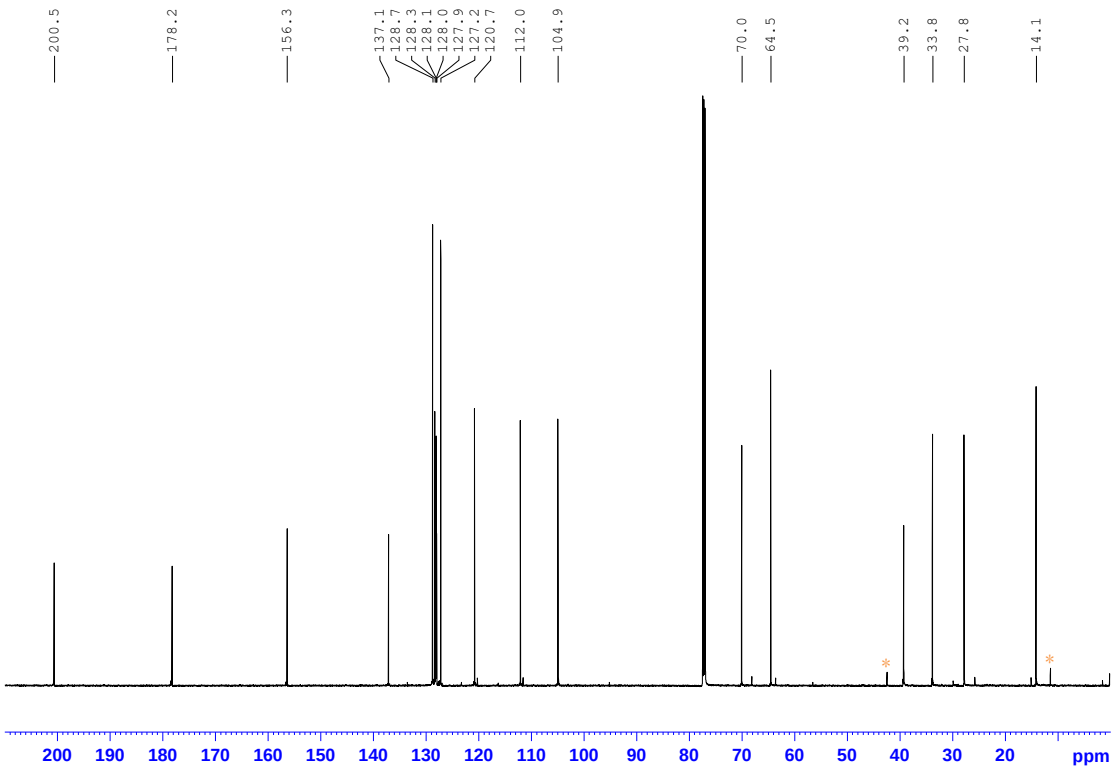

199.8
174.8
158.8
158.3
145.3
128.5
117.4
116.4
112.7
105.1
103.7
57.2
56.0
55.8
46.5
41.5
37.6
19.1
8.3
0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

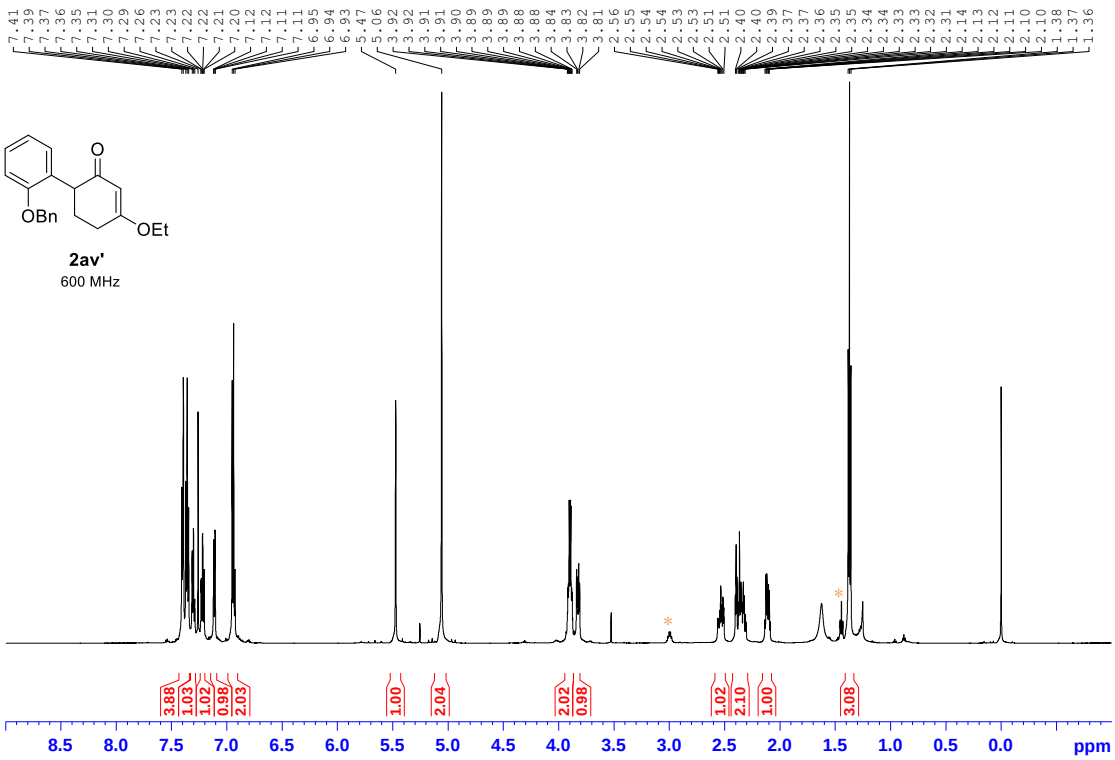

Me
O
OMe
Me
Me
3d
r.r. > 20:1
d.r. > 20:1
500 MHz
7.26
7.18
7.16
7.15
7.13
4.87
4.71
4.11
3.59
2.68
2.60
2.59
2.57
2.53
2.52
2.50
2.48
2.41
2.41
2.38
2.37
1.83
1.81
1.62
1.60
1.59
1.34
1.33
1.33
1.32
1.31
1.31
1.30
0.90
0.89
0.88
0.00
3.95
1.00
1.00
1.00
2.99
1.04
1.98
1.06
1.01
3.00
2.81
2.11
3.95
2.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


198.0
169.2
145.6
142.4
136.3
129.3
127.7
116.8
112.6
55.5
48.1
44.3
36.4
35.6
31.7
31.2
22.7
22.3
14.2
7.5
0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

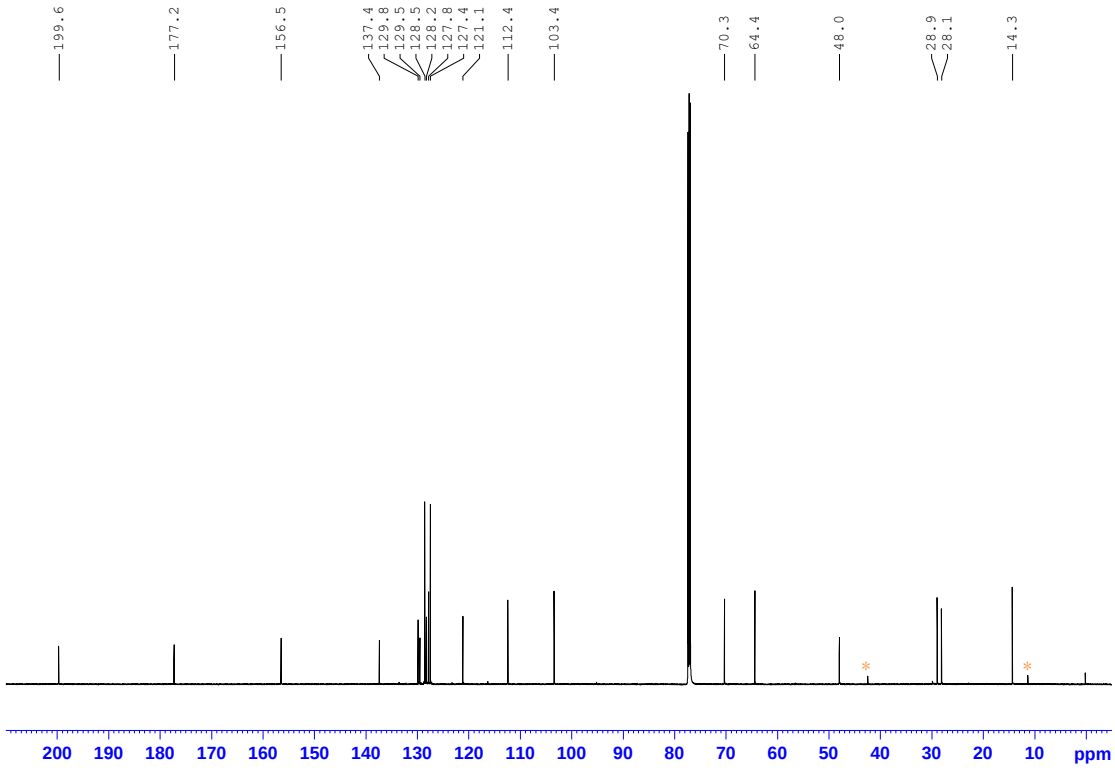

7.43 7.42 7.41 7.40 7.39 7.35 7.34 7.33 7.26 7.25 7.24 7.23 7.07 7.07 7.06 7.06 6.99 6.98 6.93 6.92 6.91 5.60 5.12 4.23 4.22 3.98 3.97 3.96 3.95 3.95 3.94 3.93 3.90 3.89 3.89 3.88 3.88 3.87 3.86 3.85 2.30 2.28 2.28 2.27 2.26 2.25 2.25 2.24 2.17 2.16 2.16 2.15 2.14 1.27 1.26 1.25
O
OEt
BnO
2av
600 MHz
3.93 0.95 1.20 1.00 1.00 1.01 1.03 2.03 0.99 1.05 1.06 3.06 1.09 3.31
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

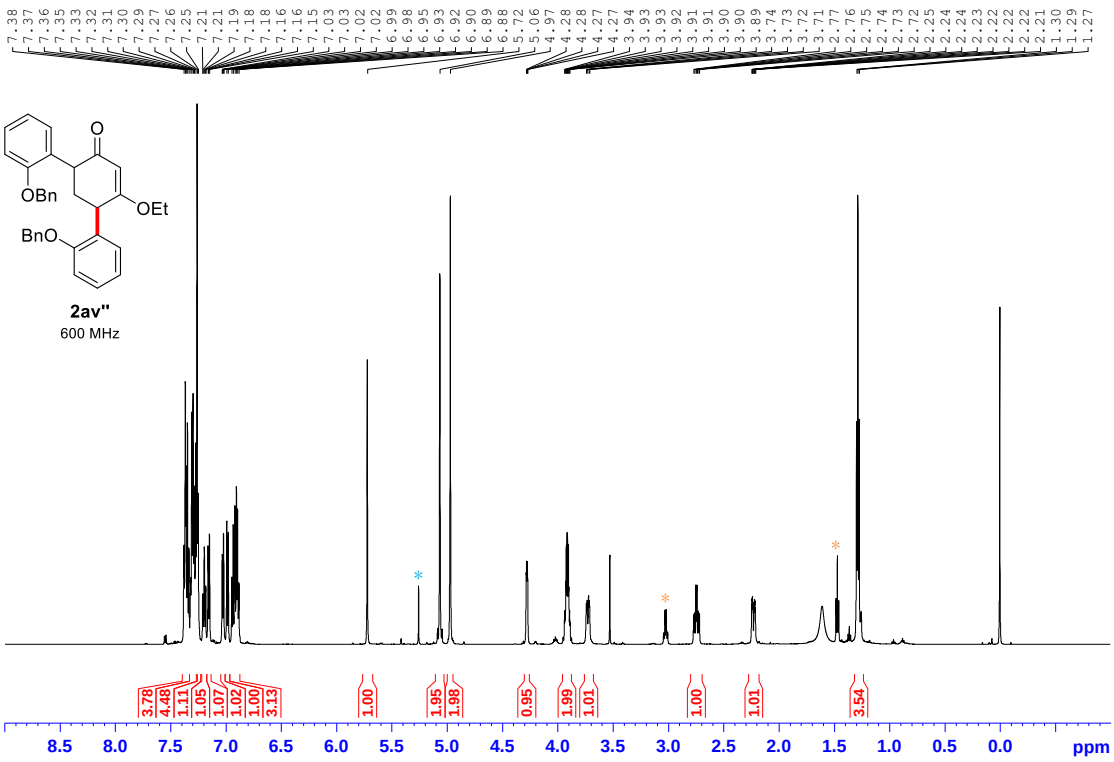
* $NHEt_2$


200.5 178.2 156.3 137.1 128.7 128.3 128.1 128.0 127.9 127.2 120.7 112.0 104.9 70.0 64.5 39.2 33.8 27.8 14.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


OBn
OEt
O
2av'
600 MHz
3.88
1.03
1.02
0.98
2.03
1.00
2.04
2.02
0.98
1.02
2.10
1.00
3.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

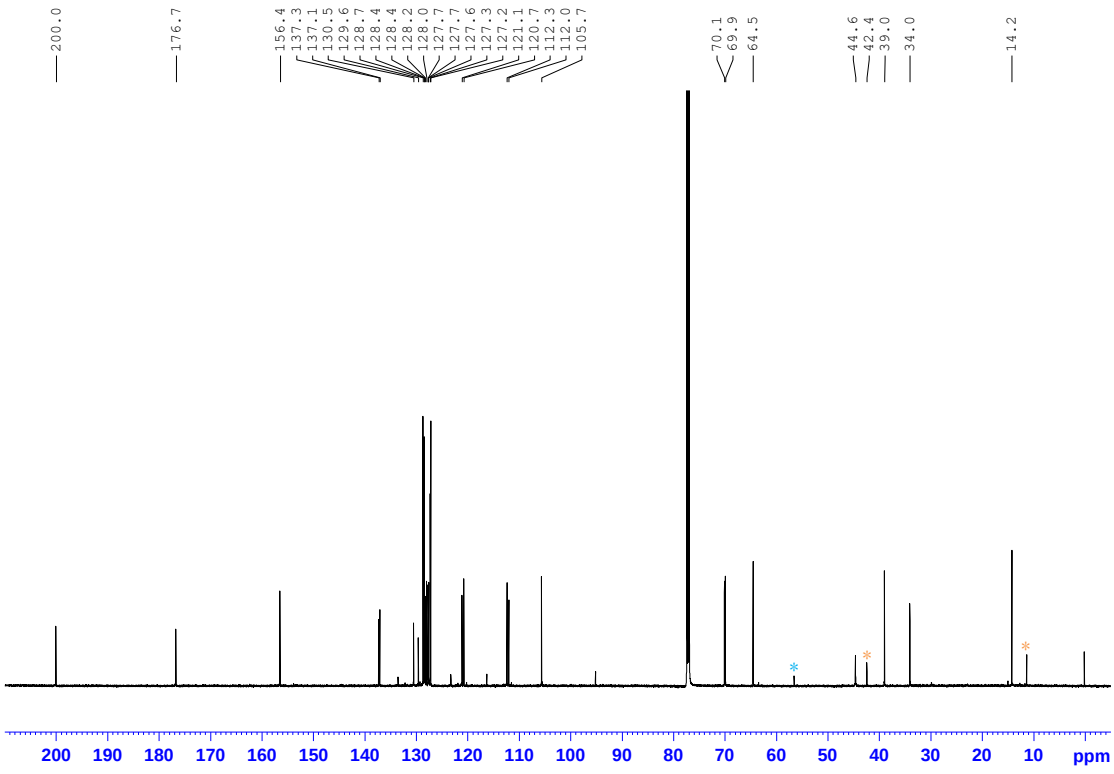
* $NHEt_2$

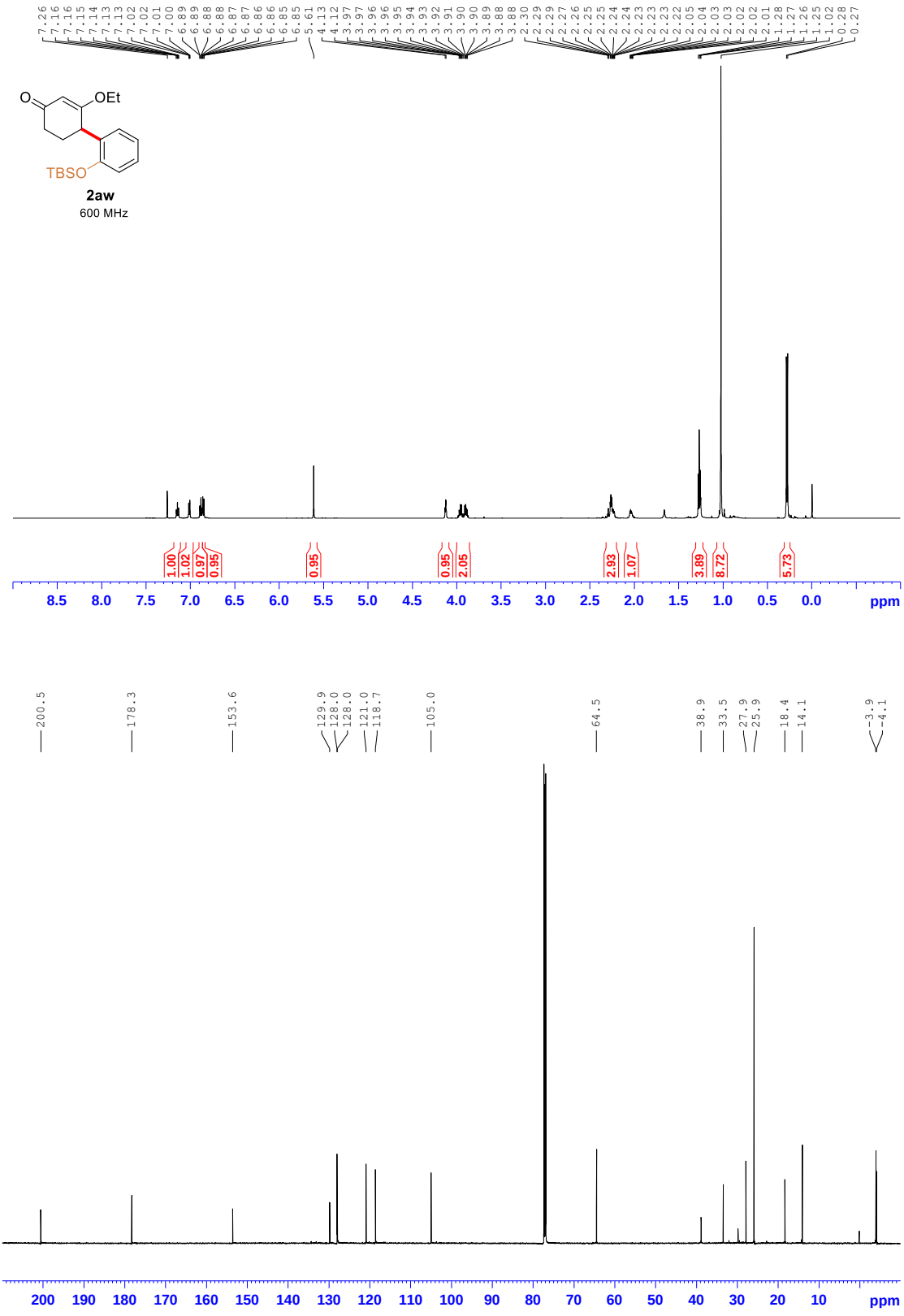

199.6
177.2
156.5
137.4
129.8
129.5
128.5
128.2
127.8
127.4
121.1
112.4
103.4
70.3
64.4
48.0
28.9
28.1
14.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.38 7.37 7.36 7.35 7.33 7.32 7.31 7.30 7.29 7.27 7.26 7.25 7.21 7.21 7.19 7.18 7.18 7.16 7.16 7.15 7.03 7.03 7.02 7.02 6.99 6.98 6.95 6.93 6.92 6.90 6.89 6.88 5.72 5.06 4.97 4.28 4.28 4.27 4.27 3.94 3.93 3.93 3.92 3.91 3.91 3.90 3.90 3.89 3.74 3.73 3.72 3.71 2.77 2.76 2.75 2.74 2.73 2.72 2.25 2.24 2.24 2.23 2.22 2.22 2.22 2.21 1.30 1.29 1.27
O
OBn
OEt
BnO
2av"
600 MHz
3.78 4.48 1.11 1.05 1.07 1.02 1.00 3.13 1.00 1.95 1.98 0.95 1.99 1.01 1.00 1.01 3.54
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

* DCM

* $NHEt_2$


200.0 176.7 156.4 137.3 137.1 130.5 129.6 128.7 128.4 128.4 128.2 128.0 127.7 127.7 127.6 127.3 127.2 121.1 120.7 112.3 112.0 105.7 70.1 69.9 64.5 44.6 42.4 39.0 34.0 14.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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OEt
TBSO
2aw
600 MHz
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1.02
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0.95
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0.95
2.05
2.93
1.07
3.89
8.72
5.73
ppm
200.5
178.3
153.6
129.9
128.0
128.0
121.0
118.7
105.0
64.5
38.9
33.5
27.9
25.9
18.4
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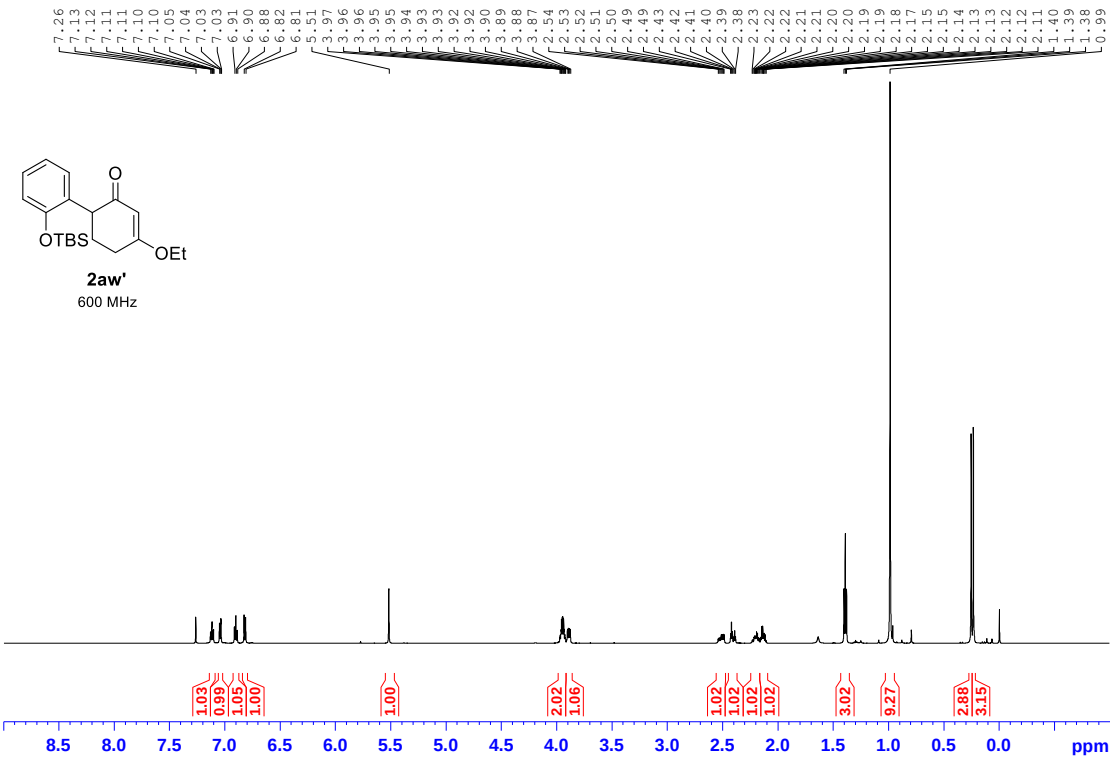
-3.9
-4.1
ppm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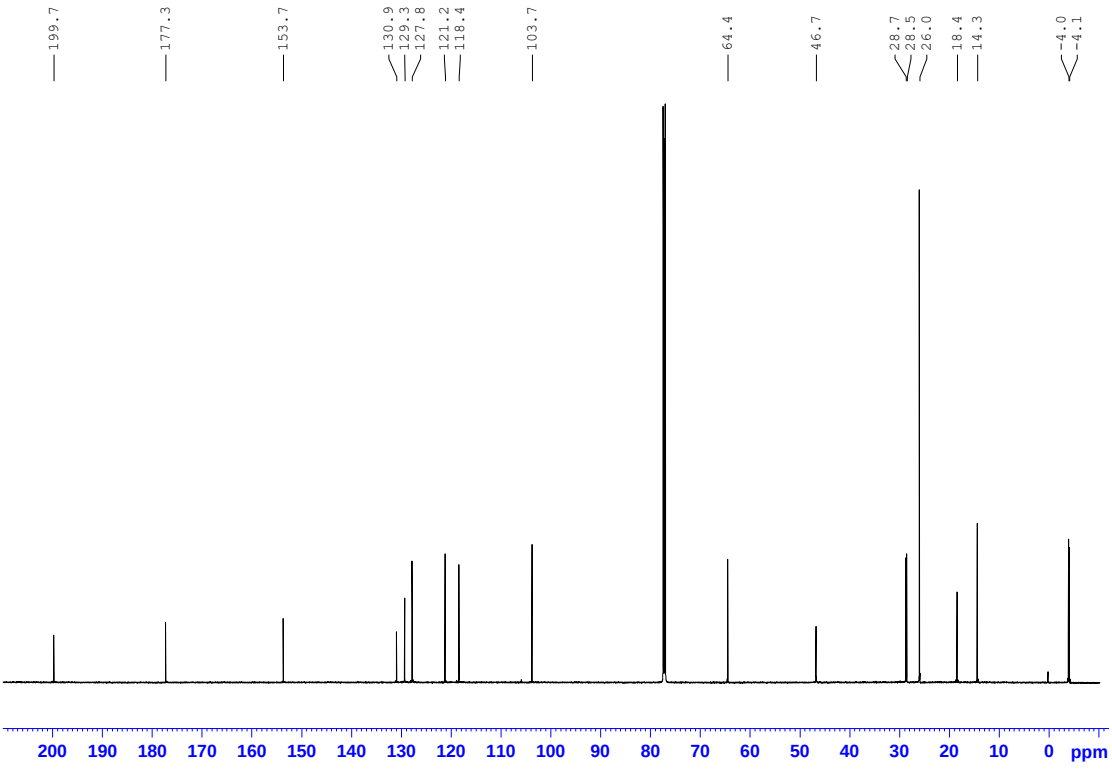
O
OTBS
OEt
2aw'
600 MHz
1.03 0.99 1.05 1.00 1.00 2.02 1.06 1.02 1.02 1.02 1.02 3.02 9.27 2.88 3.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm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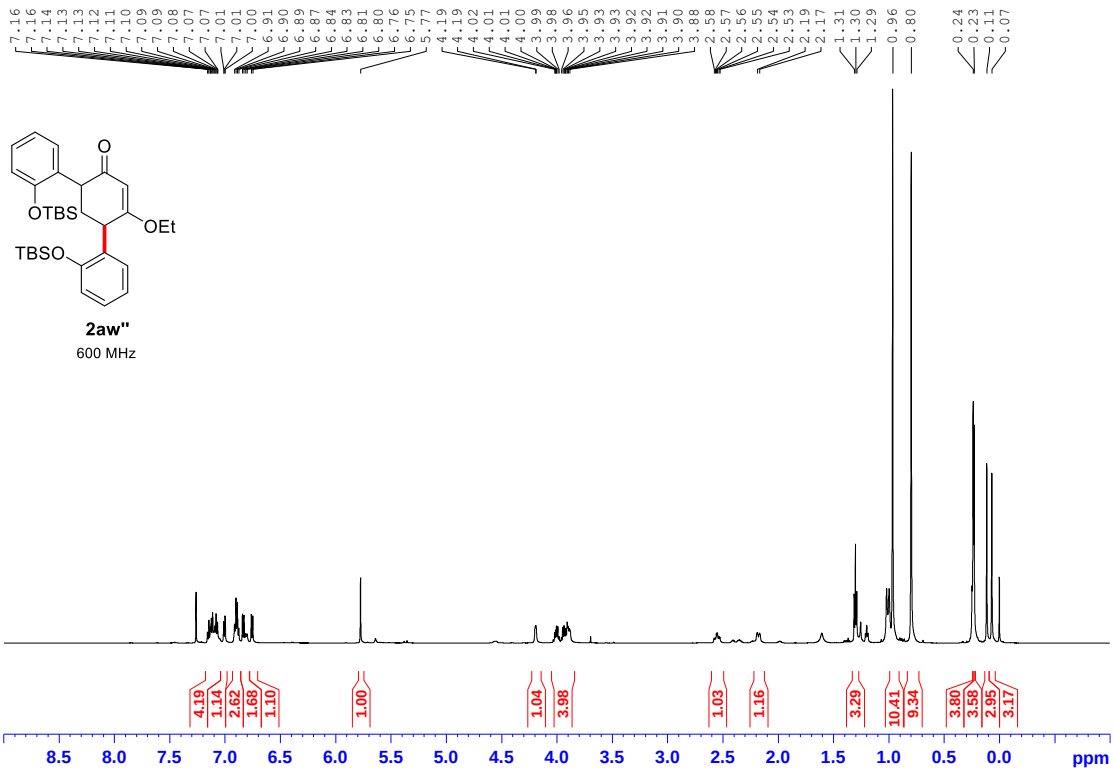
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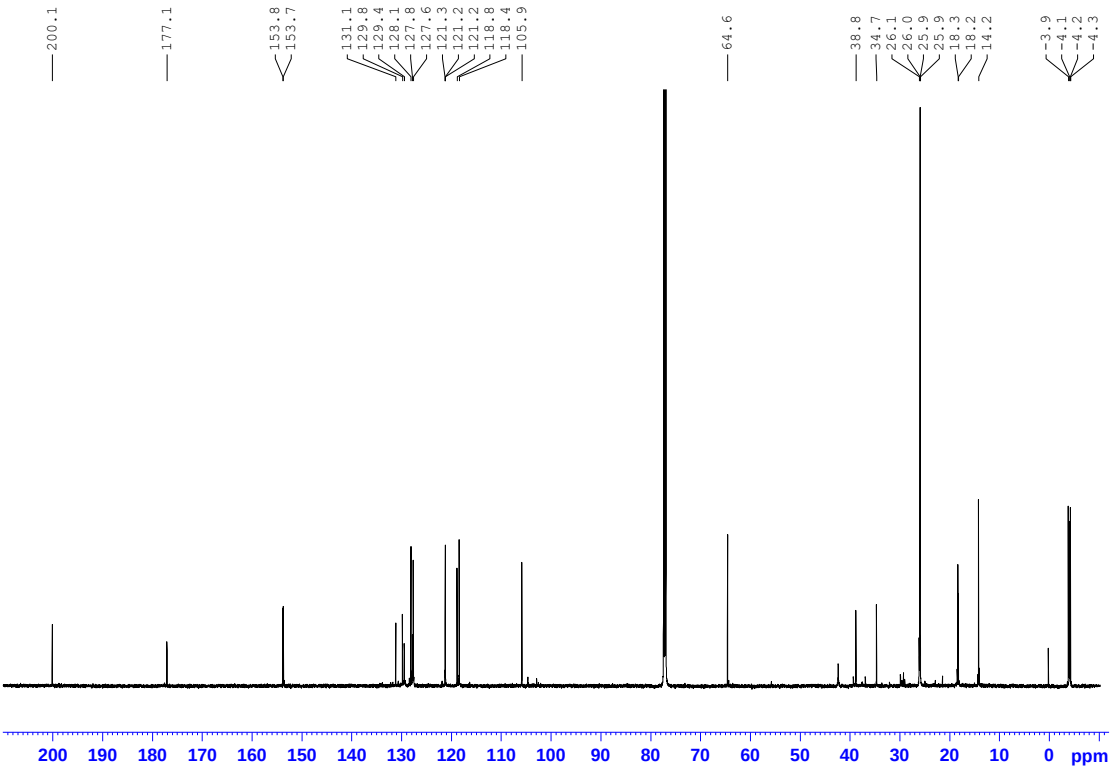
O
OTBS
OEt
TBSO
2aw''
600 MHz
4.19 1.14 2.62 1.68 1.10 1.00 1.04 3.98 1.03 1.16 3.29 10.41 9.34 3.80 3.58 2.95 3.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm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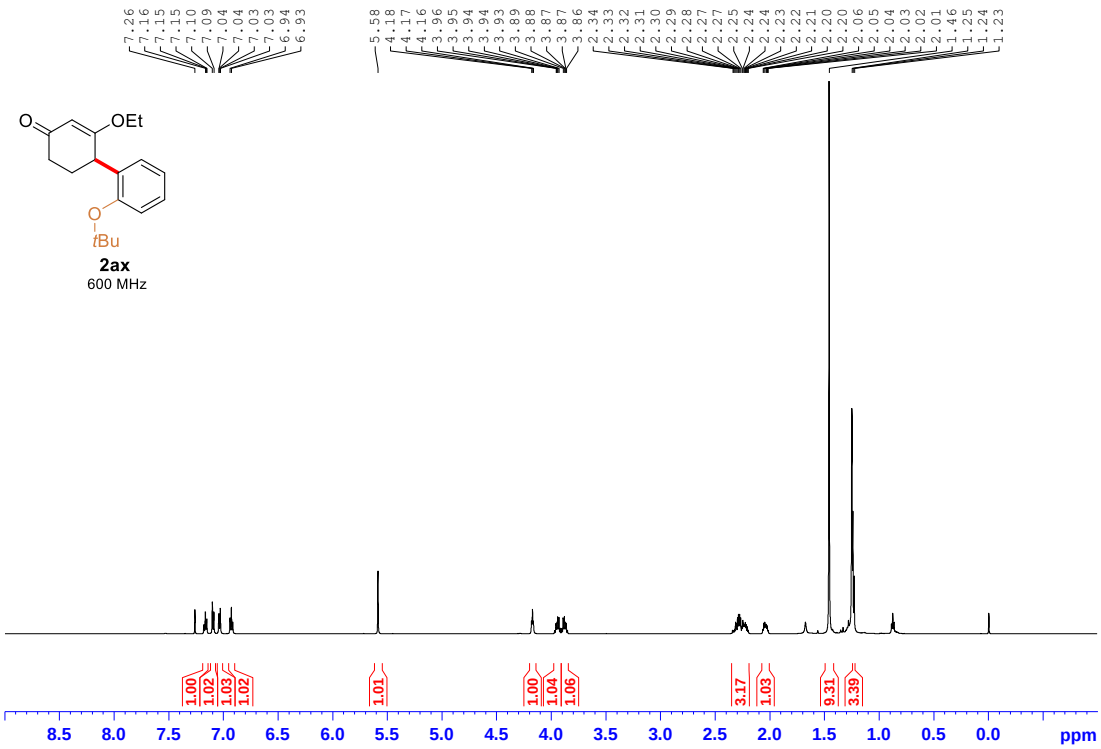
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.16
7.15
7.15
7.10
7.09
7.04
7.04
7.03
7.03
6.94
6.93
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4.18
4.17
4.16
3.96
3.95
3.94
3.94
3.93
3.89
3.88
3.87
3.87
3.86
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2.32
2.31
2.30
2.29
2.28
2.27
2.27
2.25
2.24
2.24
2.23
2.22
2.21
2.20
2.20
2.06
2.05
2.04
2.03
2.02
2.01
1.46
1.25
1.24
1.23
O
OEt
O
tBu
2ax
600 MHz
1.00
1.02
1.03
1.02
1.01
1.00
1.04
1.06
3.17
1.03
9.31
3.39
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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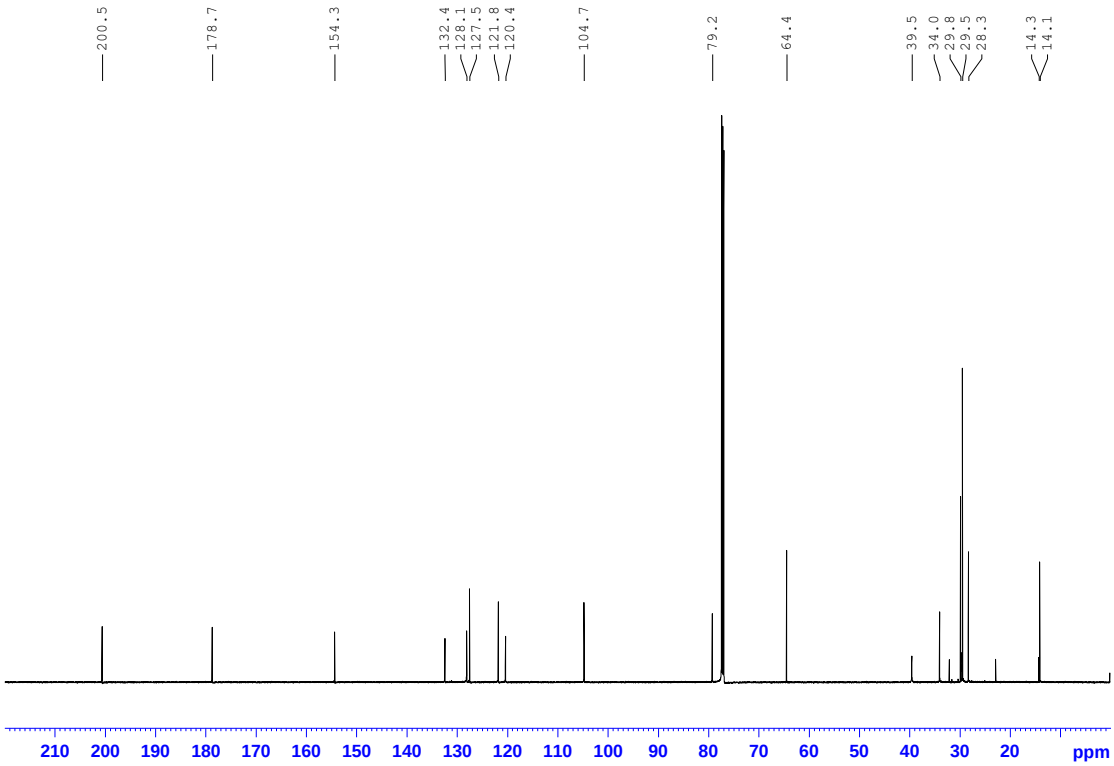
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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178.7
154.3
132.4
128.1
127.5
121.8
120.4
104.7
79.2
64.4
39.5
34.0
29.8
29.5
28.3
14.3
14.1
210
200
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160
150
140
130
120
110
100
90
80
70
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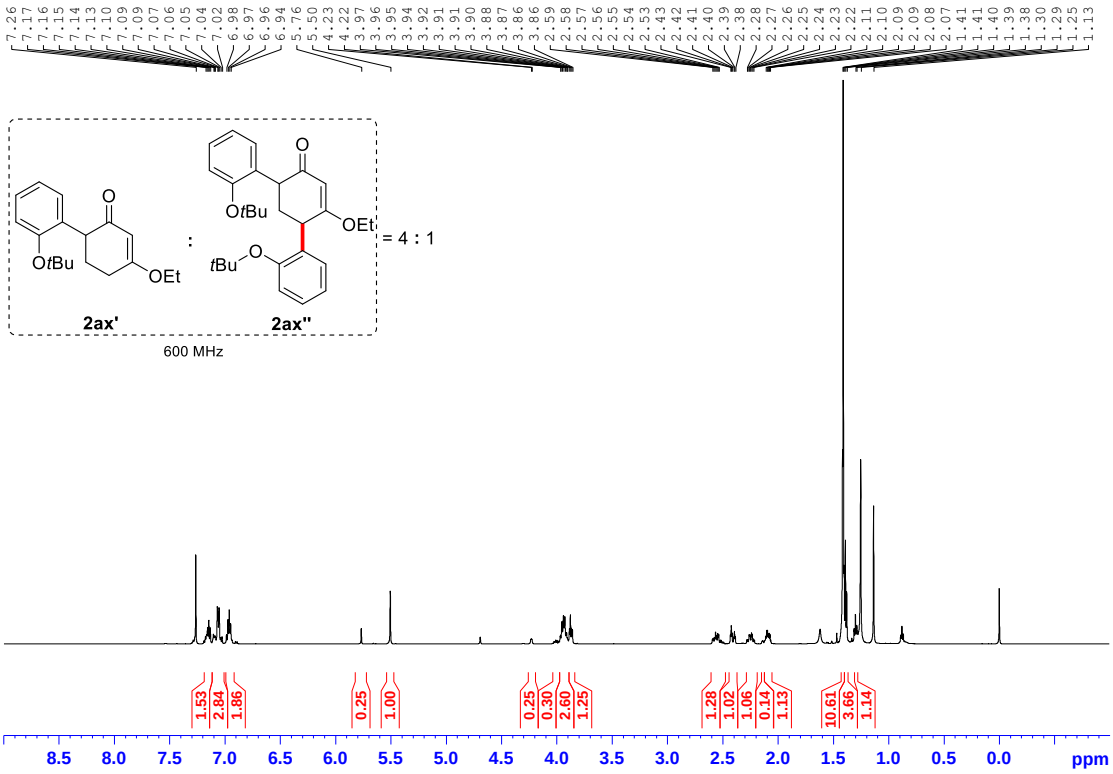
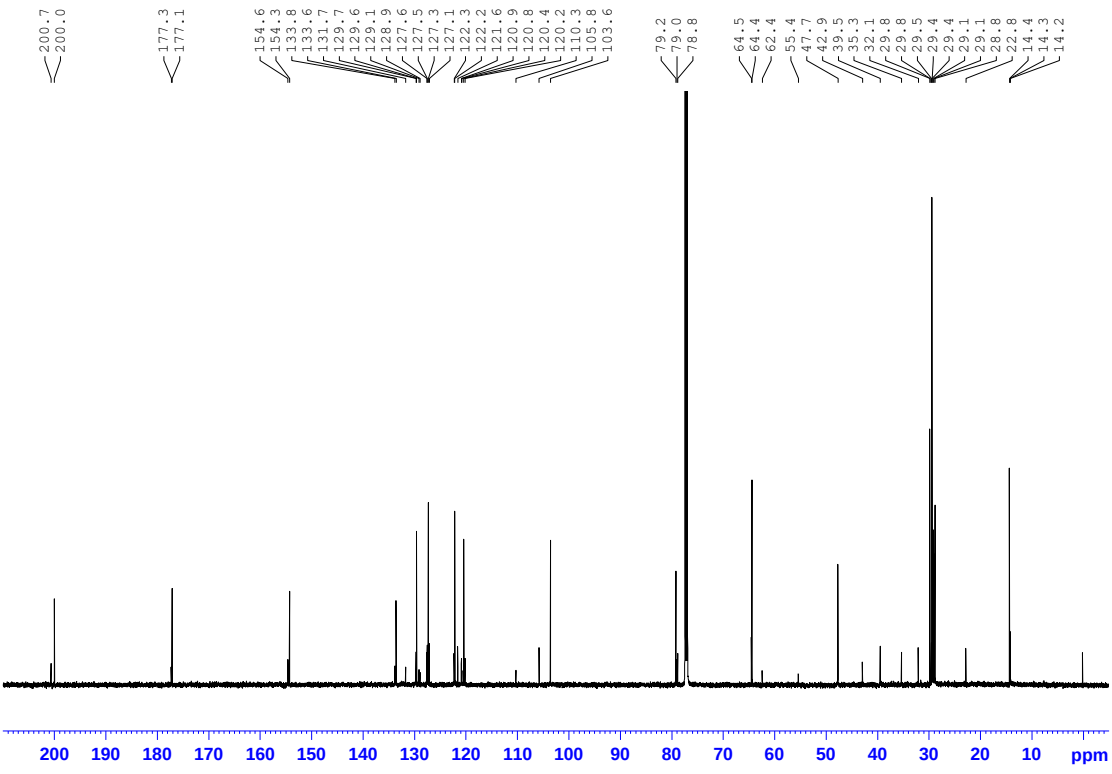
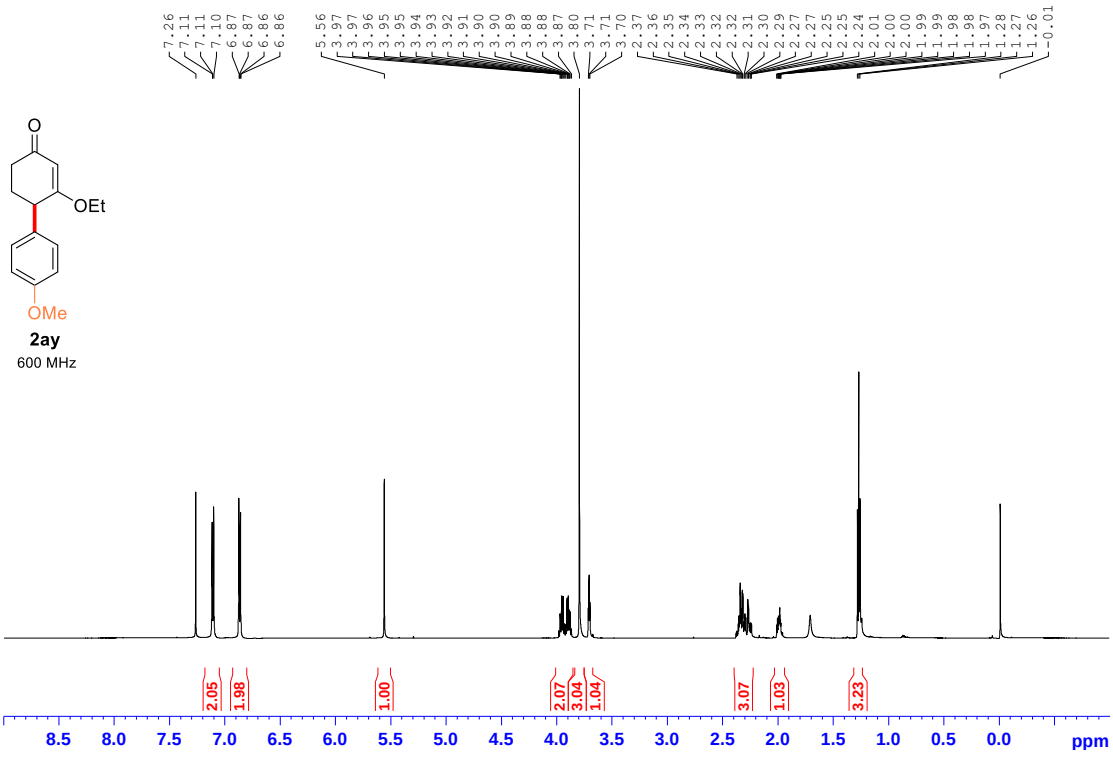
50
40
30
20
ppm


OtBu
OEt
tBu
= 4 : 1
2ax'
2ax"
600 MHz
ppm


ppm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7.11
7.10
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6.87
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6.86
5.56
3.97
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3.96
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2.24
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2.00
2.00
1.99
1.99
1.98
1.98
1.97
1.28
1.27
1.26
0.01
O
OEt
OMe
2ay
600 MHz
2.05
1.98
1.00
2.07
3.04
1.04
3.07
1.03
3.23
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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3.0
2.5
2.0
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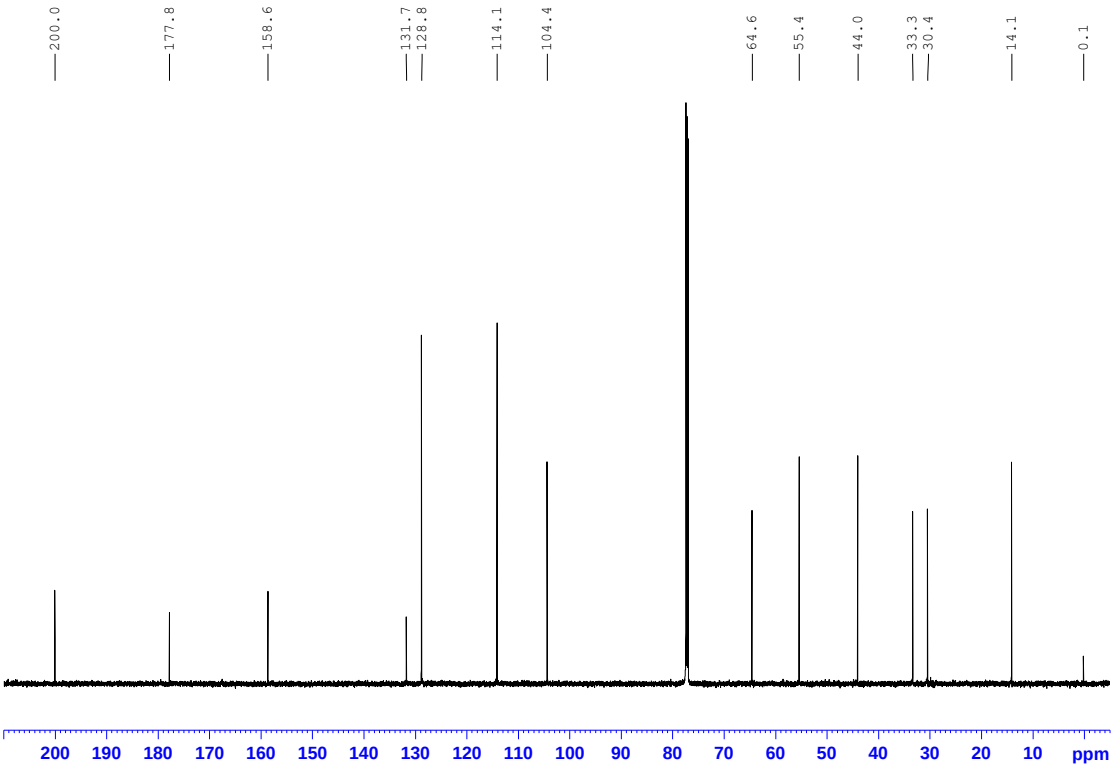
0.5
0.0
ppm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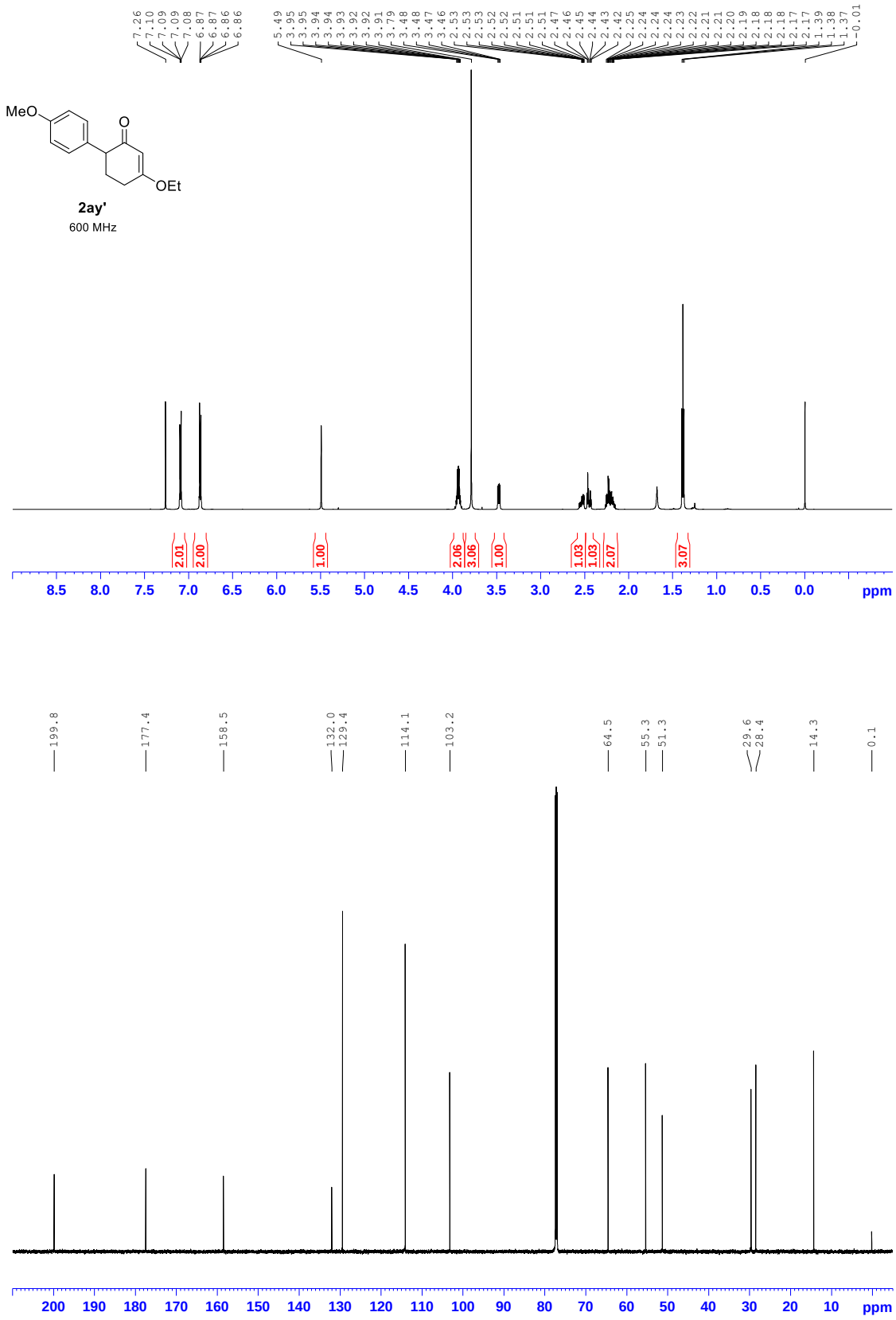
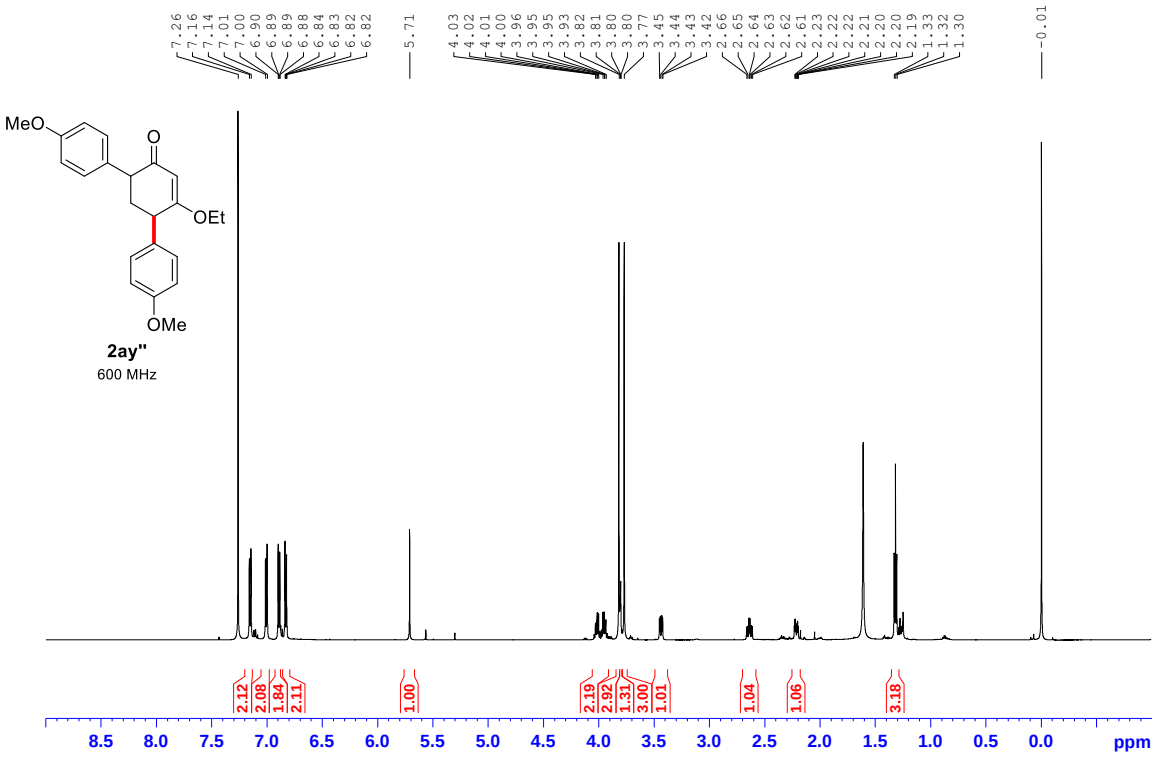
177.8
158.6
131.7
128.8
114.1
104.4
64.6
55.4
44.0
33.3
30.4
14.1
0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


MeO
O
OEt
2ay'
600 MHz
7.26 7.10 7.09 7.09 7.08 6.87 6.87 6.86 6.86
5.49 3.95 3.95 3.94 3.94 3.93 3.92 3.92 3.91 3.79 3.48 3.48 3.47 3.46 2.53 2.53 2.53 2.52 2.52 2.51 2.51 2.51 2.47 2.46 2.45 2.44 2.43 2.42 2.25 2.24 2.24 2.24 2.23 2.22 2.21 2.21 2.20 2.19 2.18 2.18 2.17 2.17 1.39 1.38 1.37 0.01
2.01 2.00 1.00 2.06 3.06 1.00 1.03 1.03 2.07 3.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
199.8 177.4 158.5 132.0 129.4 114.1 103.2 64.5 55.3 51.3 29.6 28.4 14.3 0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


MeO
O
OEt
OMe
2ay"
600 MHz
7.26
7.16
7.14
7.01
7.00
6.90
6.89
6.89
6.88
6.84
6.83
6.82
6.82
5.71
4.03
4.02
4.01
4.00
3.96
3.95
3.95
3.93
3.82
3.81
3.80
3.80
3.77
3.45
3.44
3.43
3.42
2.66
2.65
2.64
2.63
2.62
2.61
2.23
2.22
2.22
2.21
2.20
2.20
2.19
1.33
1.32
1.30
0.01
2.12
2.08
1.84
2.11
1.00
2.19
2.92
1.31
3.00
1.01
1.04
1.06
3.18
8.5
8.0
7.5
7.0
6.5
6.0
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3.5
3.0
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1.5
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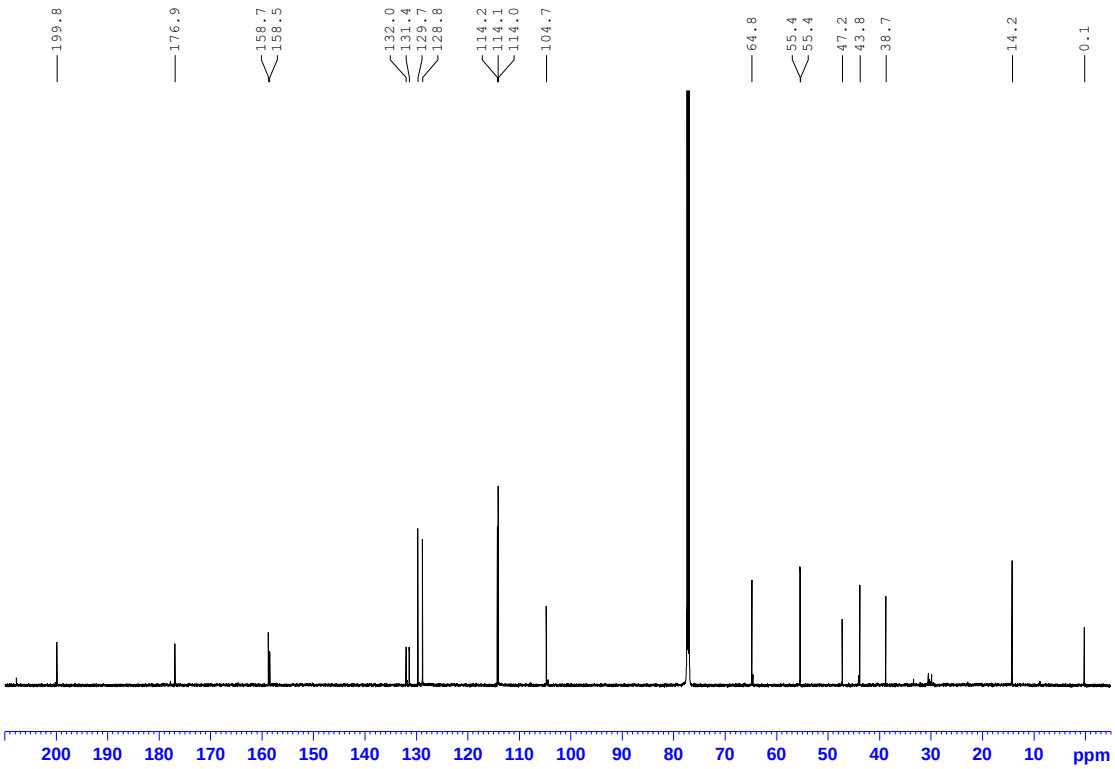
0.0
ppm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158.5
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131.4
129.7
128.8
114.2
114.1
114.0
104.7
64.8
55.4
55.4
47.2
43.8
38.7
14.2
0.1
200
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180
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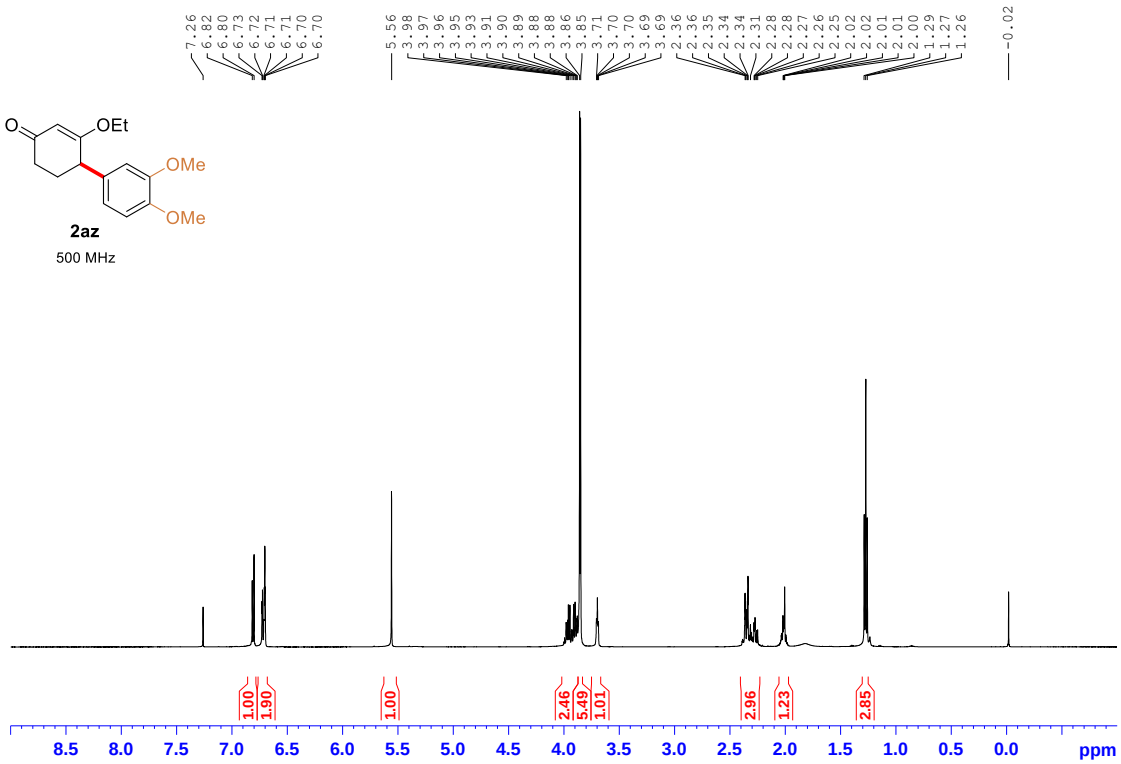
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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2.28
2.27
2.26
2.25
2.02
2.02
2.01
2.01
2.00
1.29
1.27
1.26
-0.02
O
OEt
OMe
OMe
2az
500 MHz
1.00
1.90
1.00
2.46
5.49
1.01
2.96
1.23
2.85
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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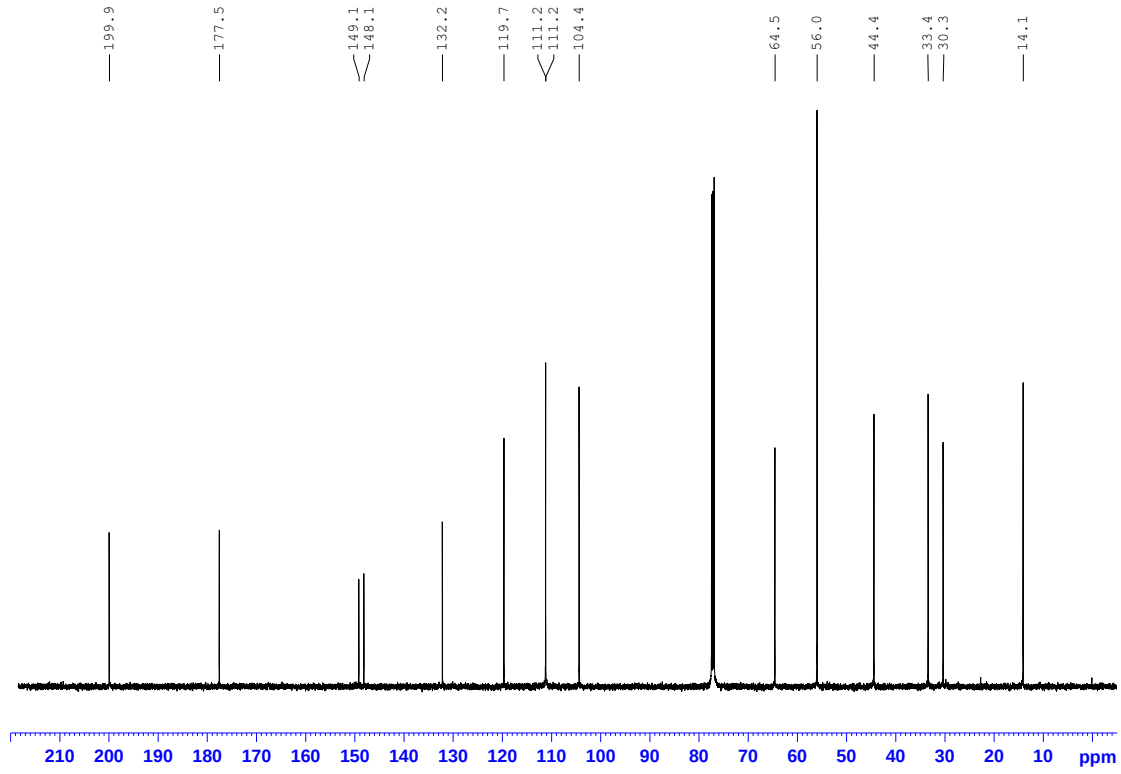
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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149.1
148.1
132.2
119.7
111.2
111.2
104.4
64.5
56.0
44.4
33.4
30.3
14.1
210
200
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180
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150
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130
120
110
100
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70
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50
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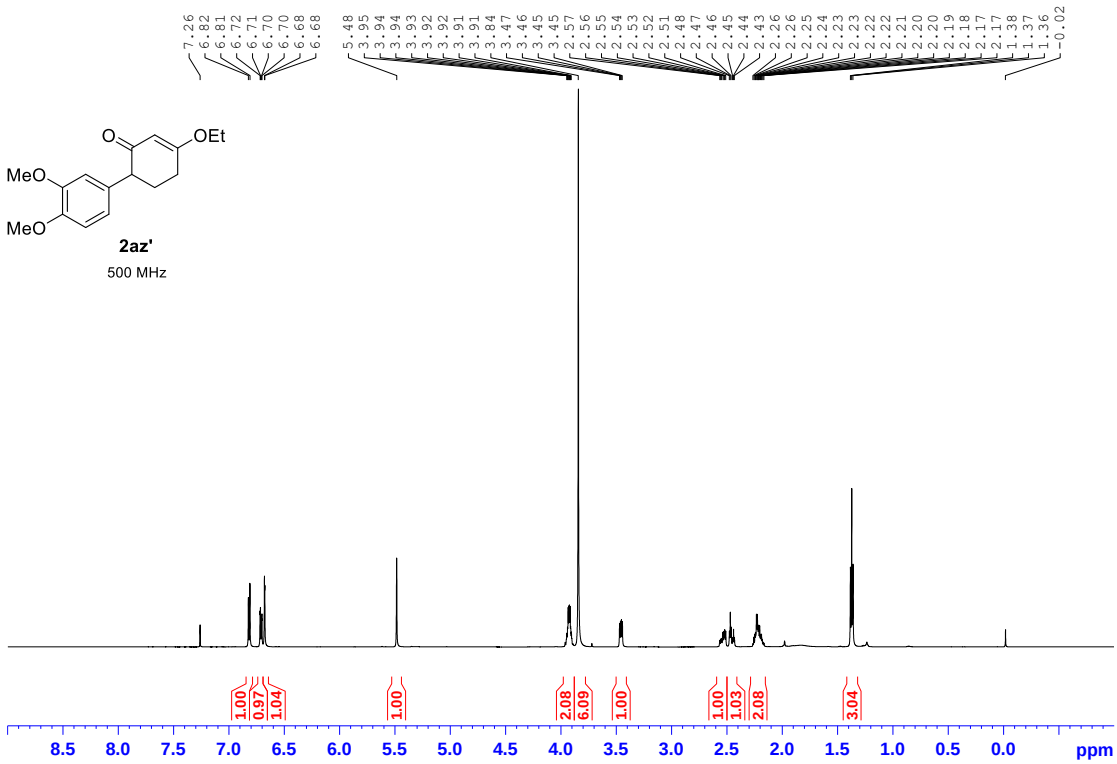
30
20
10
ppm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2.25
2.24
2.23
2.23
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2.22
2.21
2.20
2.20
2.19
2.18
2.17
2.17
1.38
1.37
1.36
-0.02
O
OEt
MeO
MeO
2az'
500 MHz
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0.97
1.04
1.00
2.08
6.09
1.00
1.00
1.03
2.08
3.04
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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1.5
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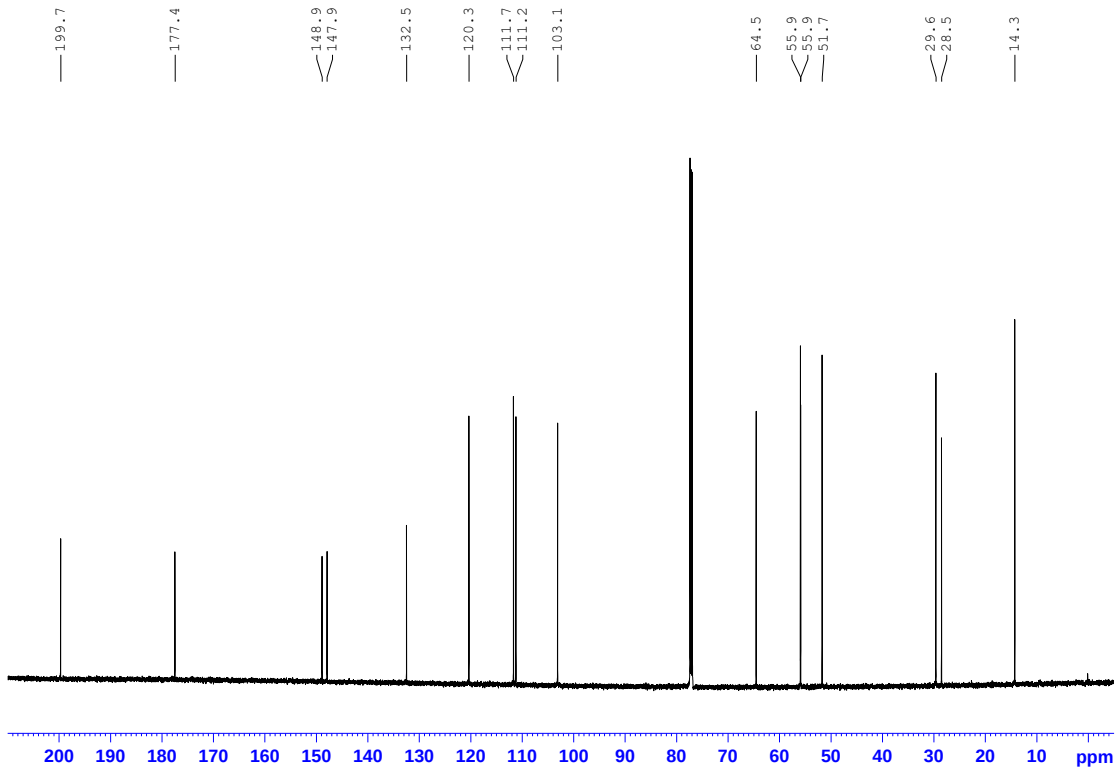
ppm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147.9
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120.3
111.7
111.2
103.1
64.5
55.9
55.9
51.7
29.6
28.5
14.3
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30
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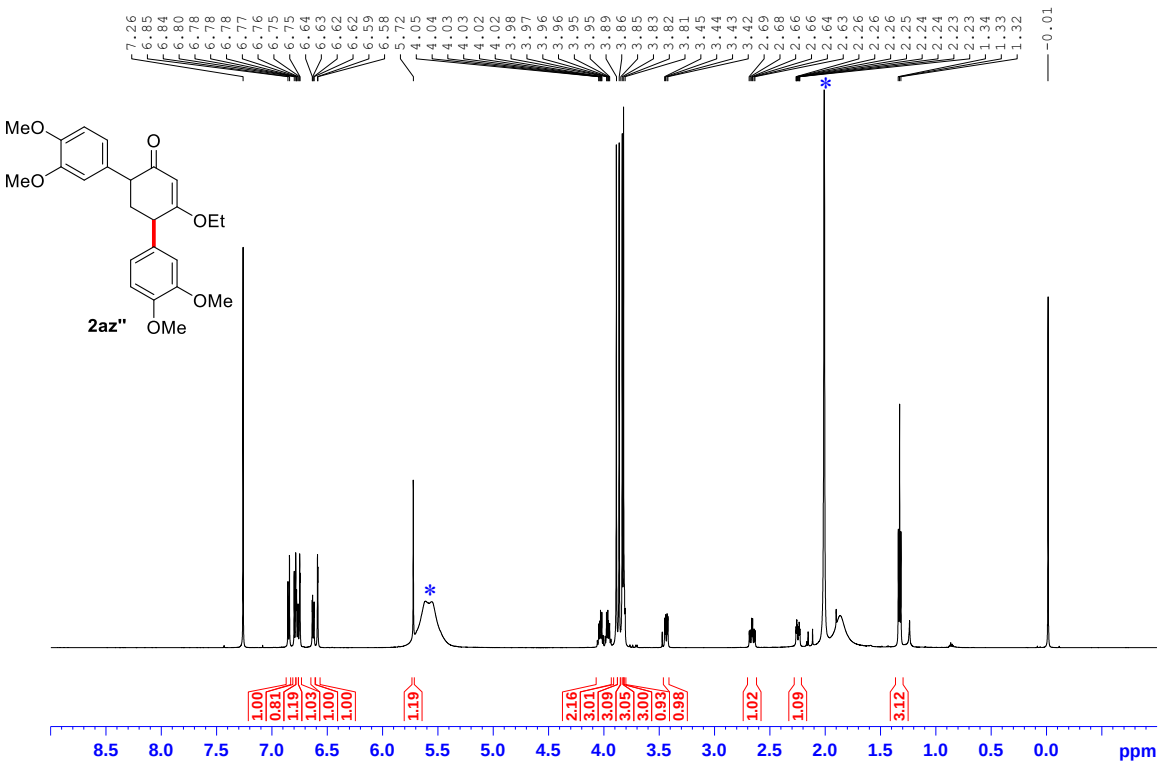
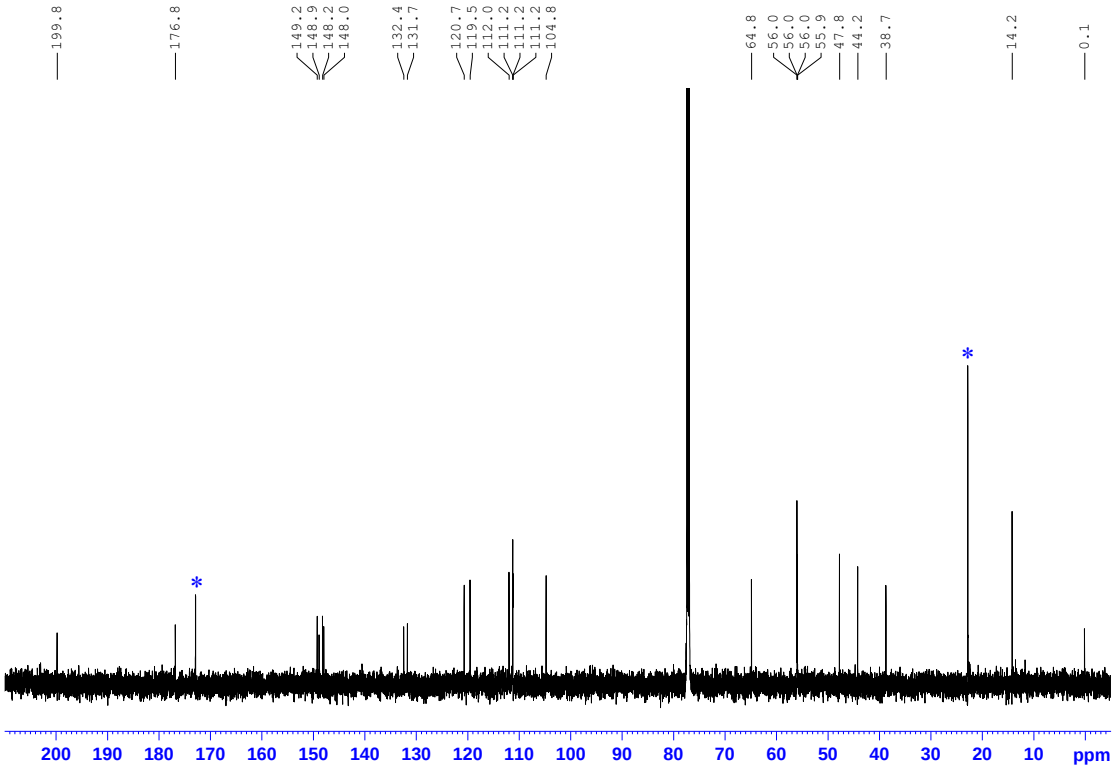
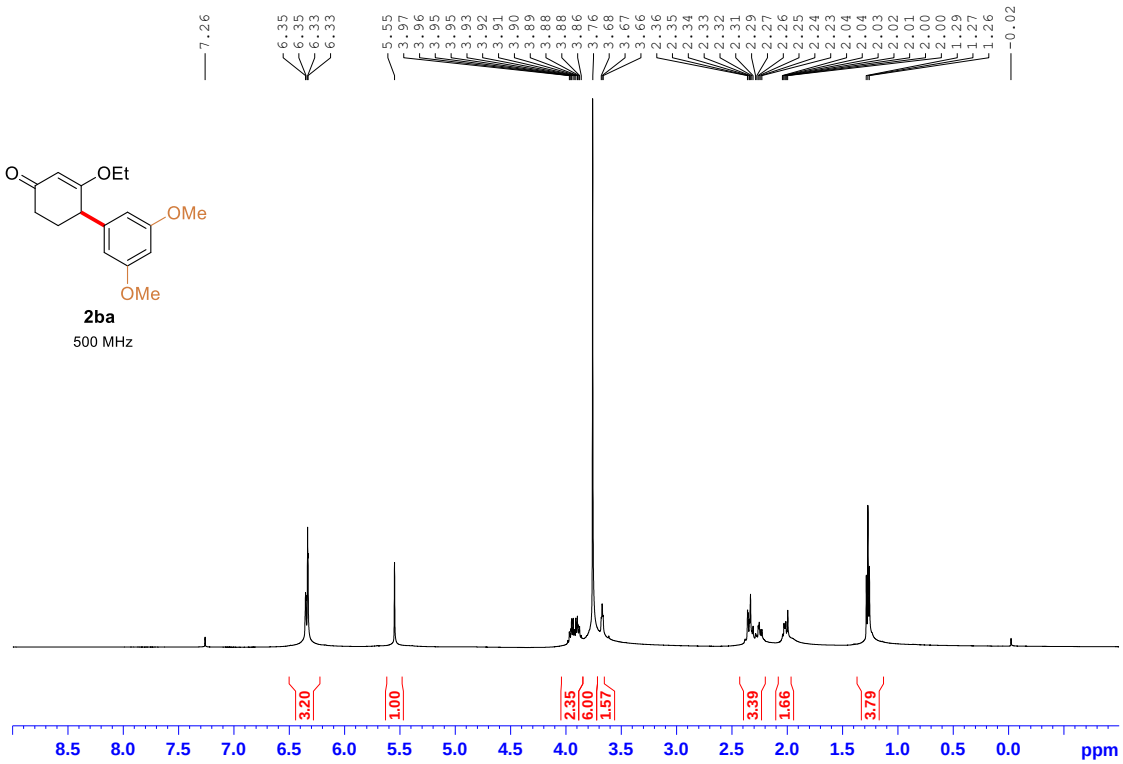
10
ppm



* AcOH

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2.23
2.04
2.04
2.03
2.02
2.01
2.00
2.00
1.29
1.27
1.26
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O
OEt
OMe
OMe
2ba
500 MHz
3.20
1.00
2.35
6.00
1.57
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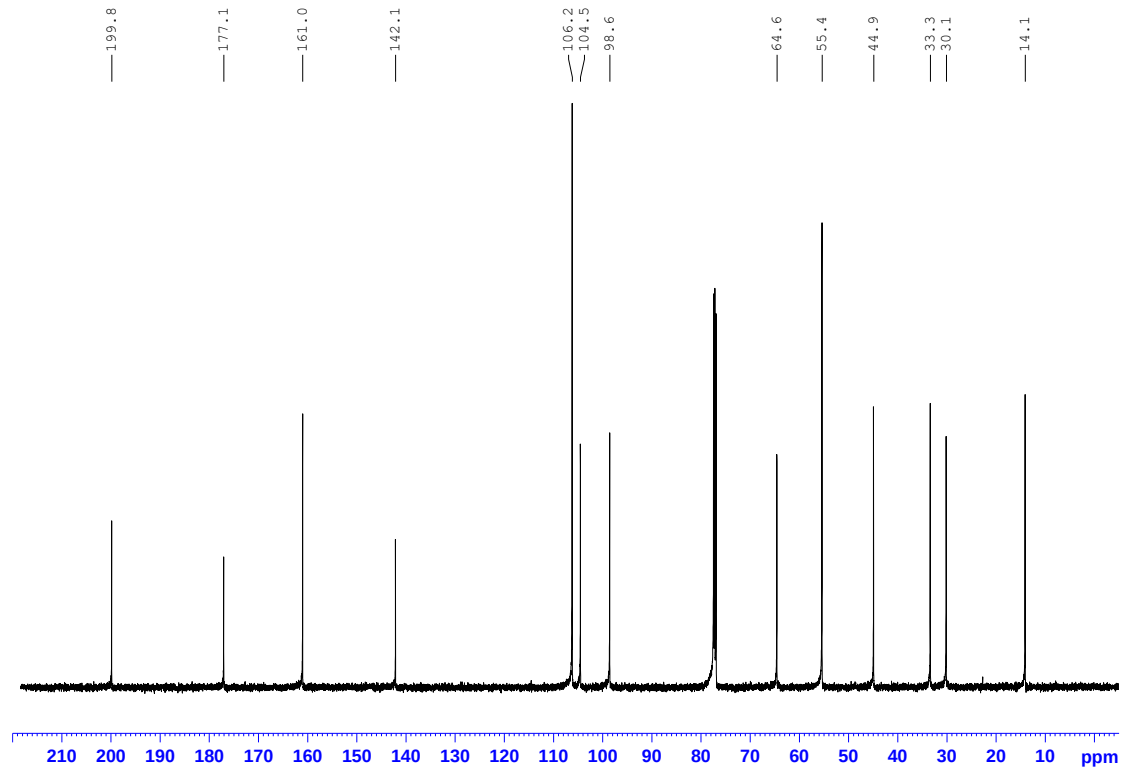
ppm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142.1
106.2
104.5
98.6
64.6
55.4
44.9
33.3
30.1
14.1
210
200
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60
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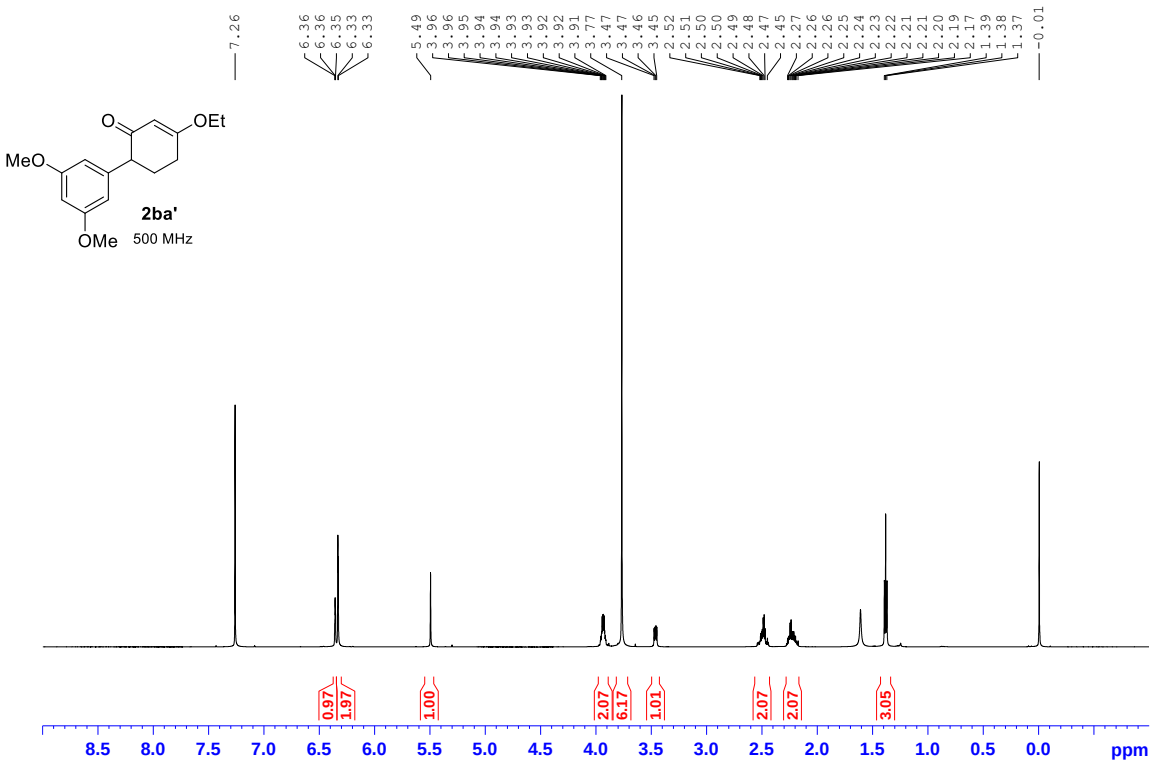
20
10
ppm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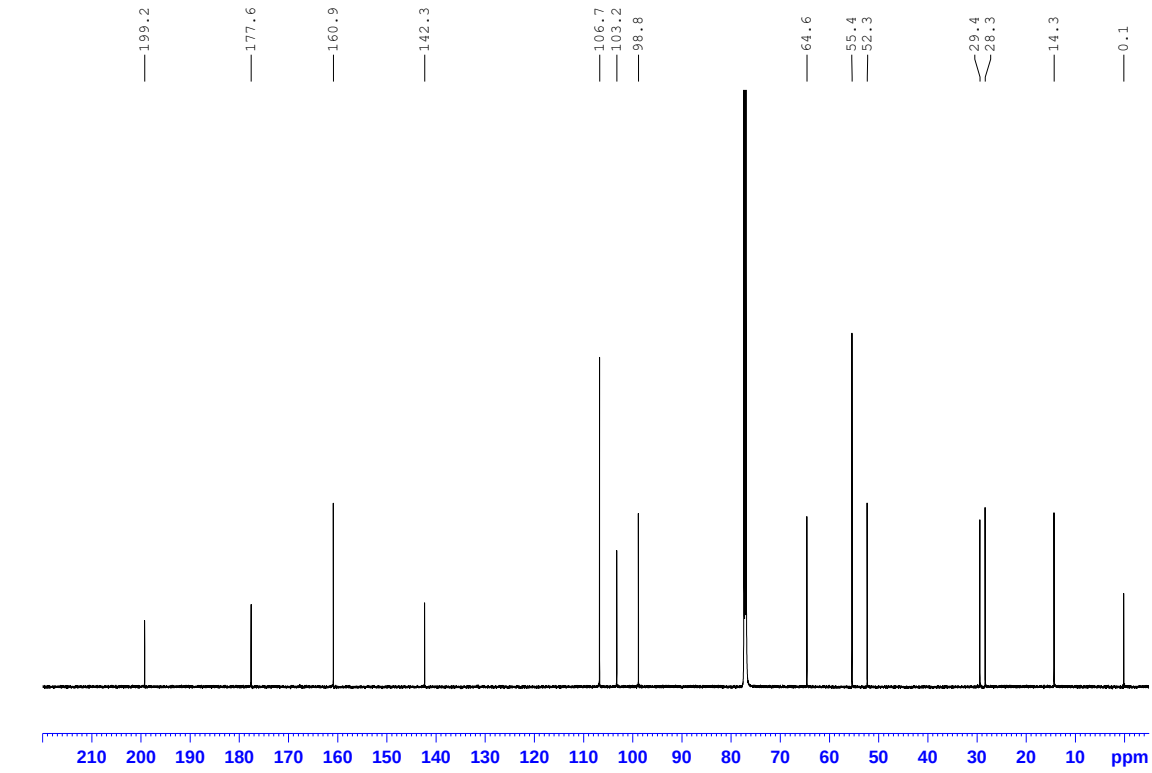
3.47
3.46
3.45
2.52
2.51
2.50
2.50
2.49
2.48
2.47
2.45
2.27
2.26
2.26
2.25
2.24
2.23
2.22
2.21
2.21
2.20
2.19
2.17
1.39
1.38
1.37
-0.01
O
OEt
MeO
OMe
2ba'
500 MHz
0.97
1.97
1.00
2.07
6.17
1.01
2.07
2.07
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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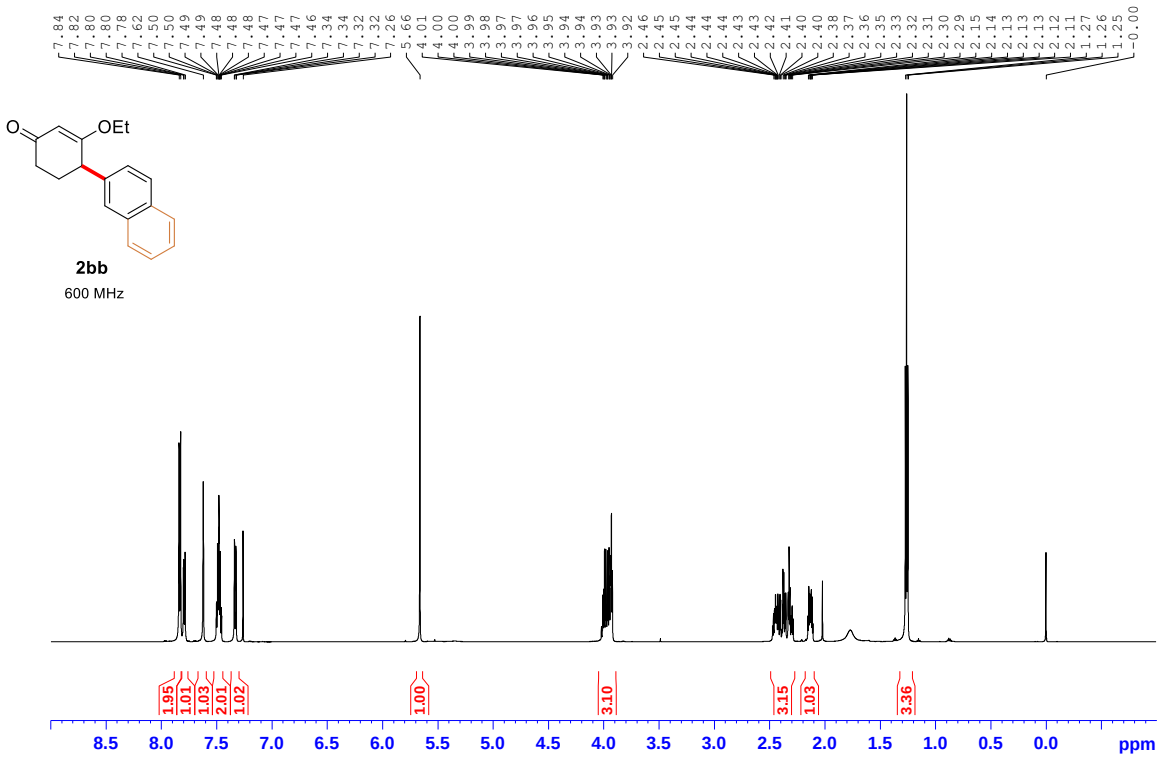
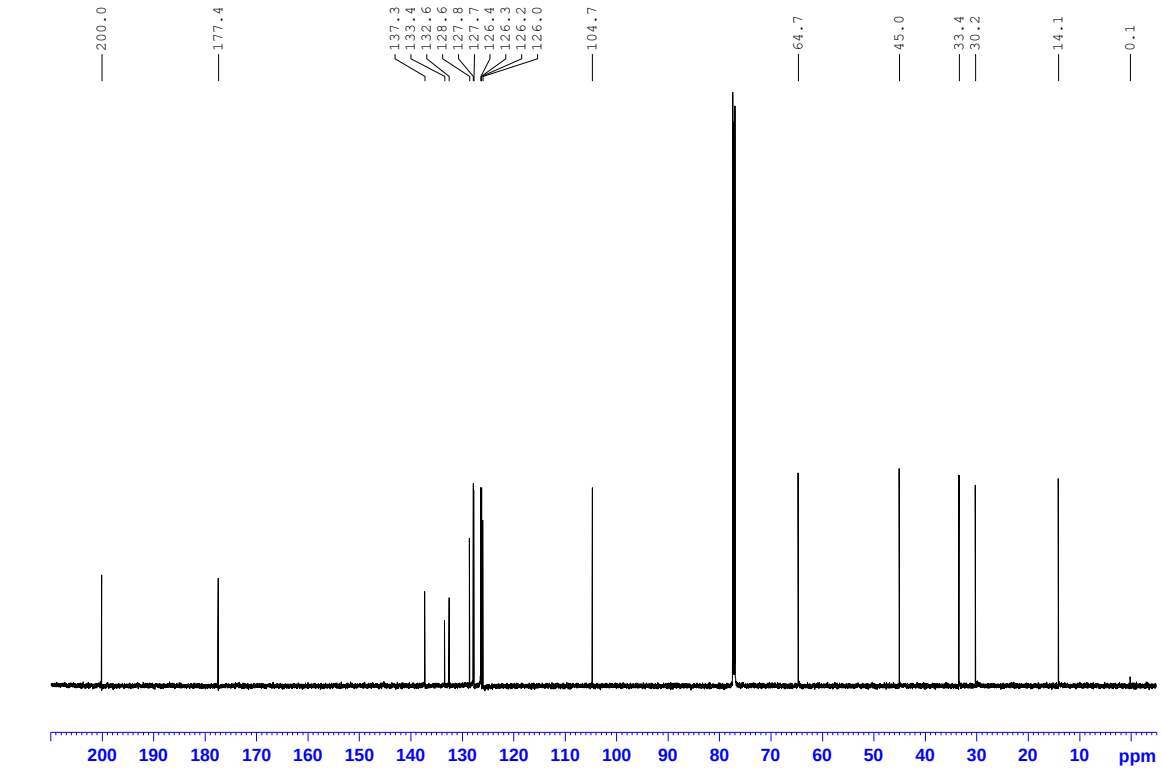
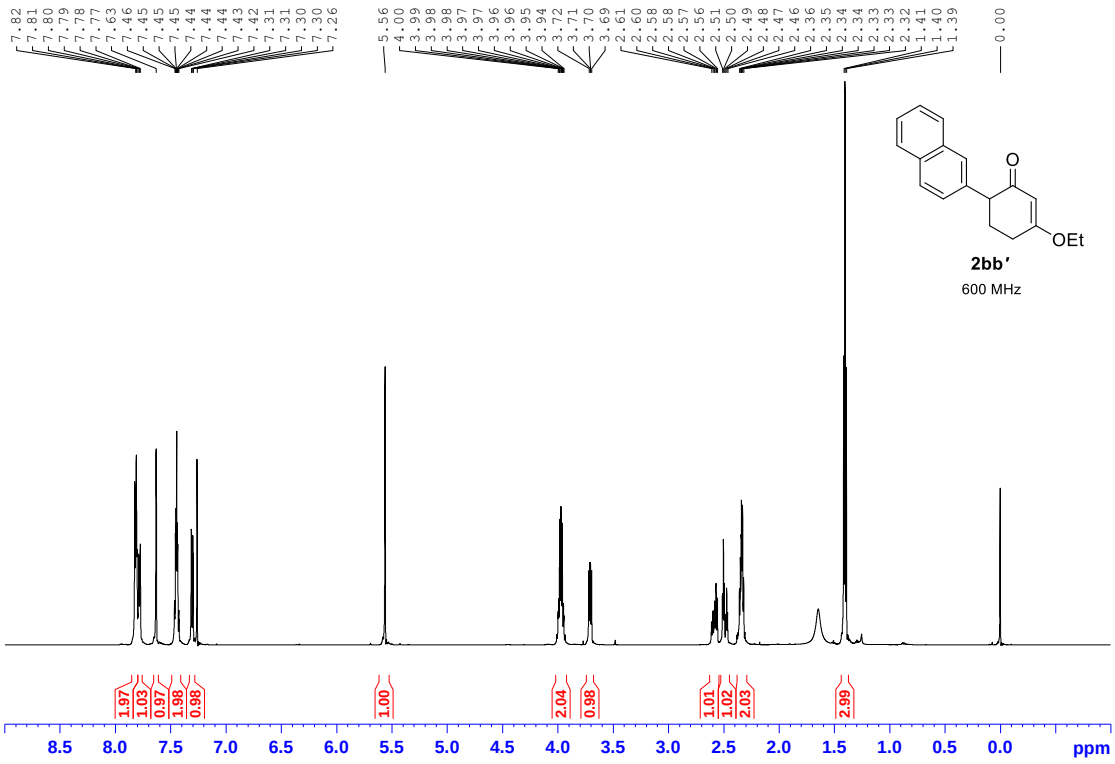
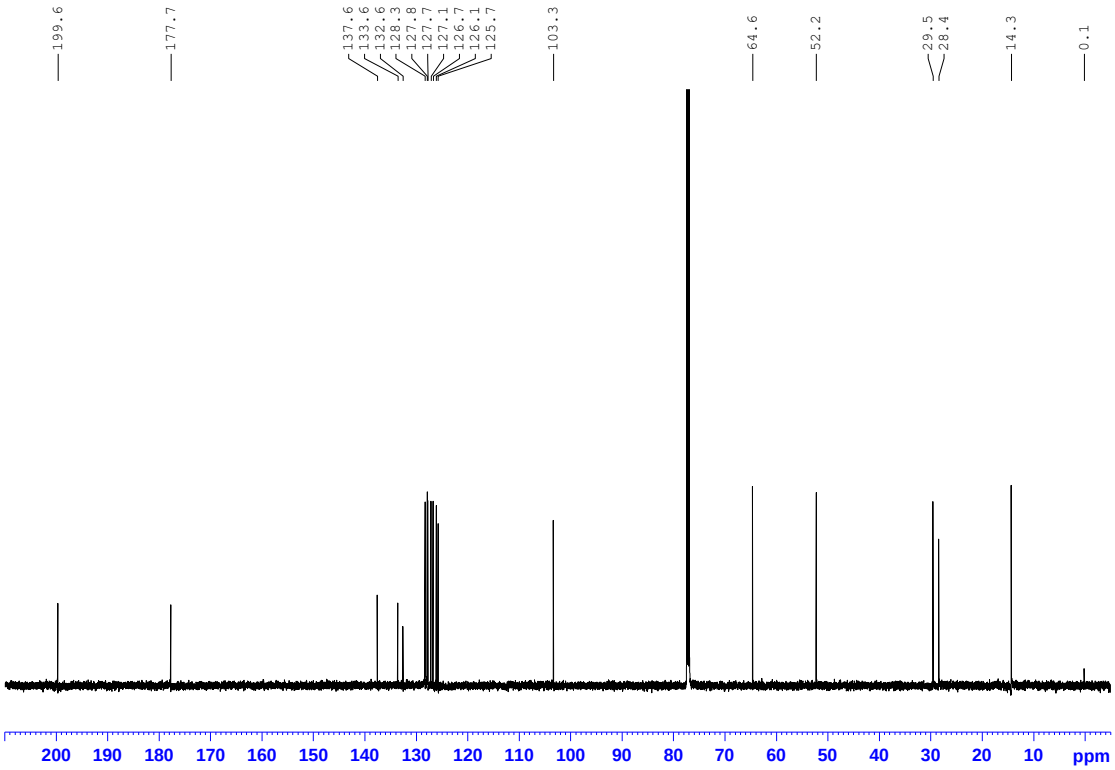
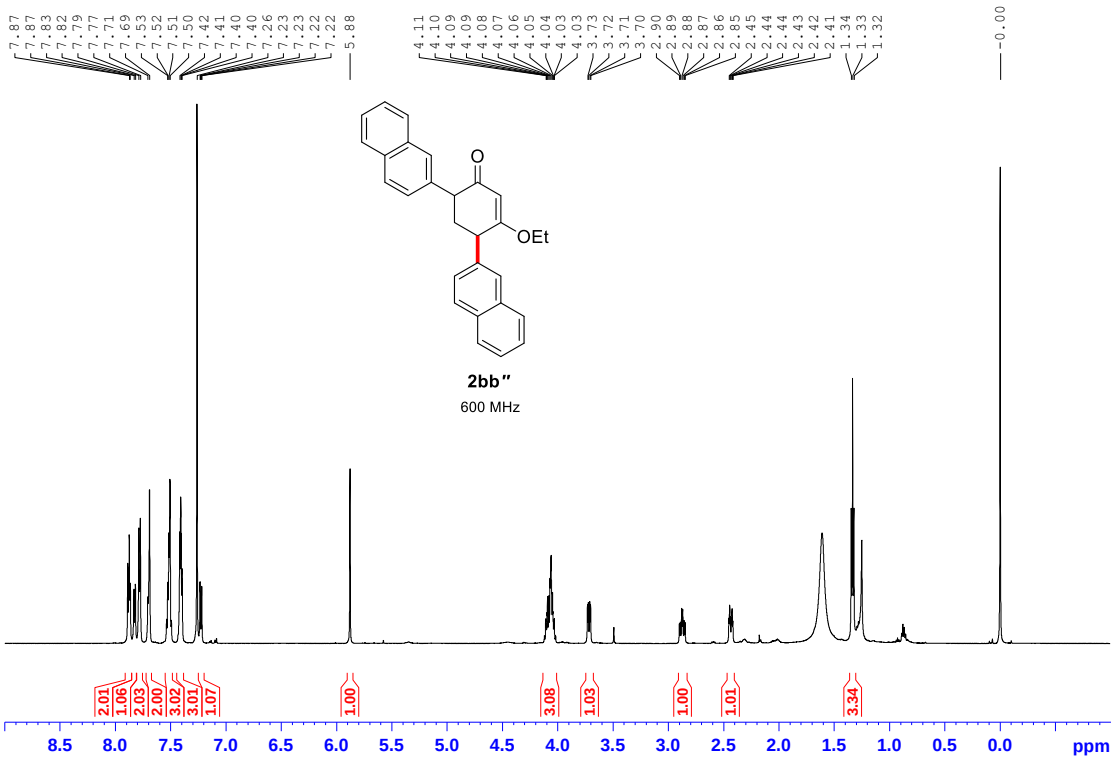
177.6
160.9
142.3
106.7
103.2
98.8
64.6
55.4
52.3
29.4
28.3
14.3
0.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.84 7.82 7.80 7.80 7.78 7.62 7.50 7.50 7.49 7.49 7.48 7.48 7.48 7.47 7.47 7.47 7.46 7.34 7.34 7.32 7.32 7.26 5.66 4.01 4.00 4.00 3.99 3.98 3.97 3.97 3.96 3.95 3.94 3.94 3.93 3.93 3.92 2.46 2.45 2.45 2.44 2.44 2.44 2.43 2.43 2.42 2.41 2.40 2.40 2.38 2.37 2.36 2.35 2.33 2.32 2.31 2.30 2.29 2.15 2.14 2.13 2.13 2.13 2.12 2.11 1.27 1.26 1.25 -0.00
O
OEt
2bb
600 MHz
1.95 1.01 1.03 2.01 1.02 1.00 3.10 3.15 1.03 3.36
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


200.0 177.4 137.3 133.4 132.6 128.6 127.8 127.7 126.4 126.3 126.2 126.0 104.7 64.7 45.0 33.4 30.2 14.1 0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.82 7.81 7.80 7.79 7.78 7.77 7.63 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.43 7.42 7.31 7.31 7.30 7.30 7.26
5.56 4.00 3.99 3.98 3.98 3.97 3.97 3.96 3.96 3.95 3.94 3.72 3.71 3.70 3.69 2.61 2.60 2.58 2.58 2.57 2.56 2.51 2.50 2.49 2.48 2.47 2.46 2.36 2.35 2.34 2.34 2.33 2.33 2.32 1.41 1.40 1.39
0.00
O
OEt
2bb'
600 MHz
1.97 1.03 0.97 1.98 0.98
1.00
2.04 0.98
1.01 1.02 2.03
2.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


199.6
177.7
137.6 133.6 132.6 128.3 127.8 127.7 127.1 126.7 126.1 125.7
103.3
64.6
52.2
29.5 28.4
14.3
0.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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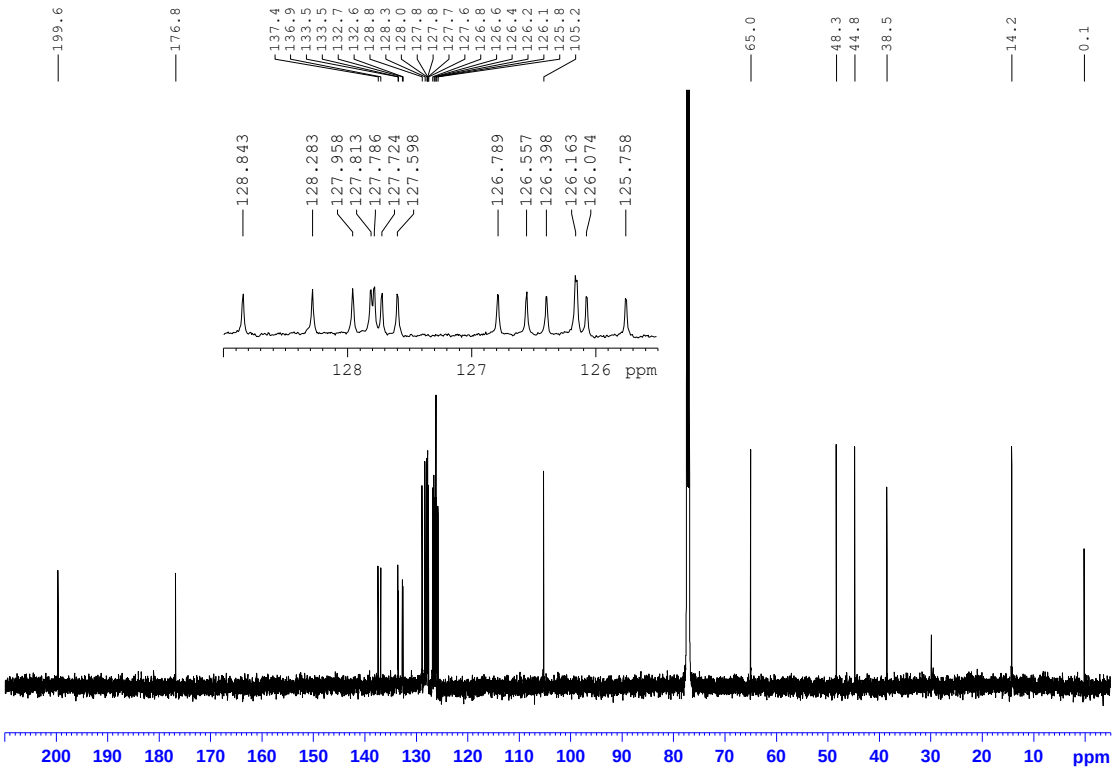
7.87
7.83
7.82
7.79
7.77
7.71
7.69
7.53
7.52
7.51
7.50
7.42
7.41
7.40
7.40
7.26
7.23
7.23
7.22
7.22
5.88
4.11
4.10
4.09
4.09
4.08
4.07
4.06
4.05
4.04
4.03
4.03
3.73
3.72
3.71
3.70
2.90
2.89
2.88
2.87
2.86
2.85
2.45
2.44
2.44
2.43
2.42
2.41
1.34
1.33
1.32
0.00
O
OEt
2bb"
600 MHz
2.01
1.06
2.03
2.00
3.02
3.01
1.07
1.00
3.08
1.03
1.00
1.01
3.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


199.6
176.8
137.4
136.9
133.5
133.5
132.7
132.6
128.8
128.3
128.0
127.8
127.8
127.7
127.6
126.8
126.6
126.4
126.2
126.1
125.8
105.2
65.0
48.3
44.8
38.5
14.2
0.1
128.843
128.283
127.958
127.813
127.786
127.724
127.598
126.789
126.557
126.398
126.163
126.074
125.758
128
127
126
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

11. Cartesian coordinates (Å) and energies of the optimized structures

ia

B3LYP SCF energy: -1749.7056644 a.u.

B3LYP enthalpy: -1748.9916544 a.u.

B3LYP free energy: -1749.1010154 a.u.

M062X SCF energy in solution: -1750.5428311 a.u.

M062X enthalpy in solution: -1749.8288211 a.u.

M062X free energy in solution: -1749.9381821 a.u.

Three lowest frequencies (cm^{-1}): 9.2904, 24.1852, 27.1396

	X	Y	Z
C	2.0053034654	-0.671061173	-1.8515781412
C	3.100710724	-1.6996815597	-1.68531123
C	4.0058729057	-1.4347718864	-0.4687185028
C	4.3562453419	0.0297917824	-0.3352995627
C	3.5183127009	0.9886087488	-0.7945428587
C	2.2694135024	0.6484125251	-1.4823676487
O	1.378607524	1.5894131186	-1.6785912139
C	-1.2514029146	2.0784565086	-0.5861594322
P	-1.5981432881	-1.1994701181	0.2605337378
C	-1.0570158953	2.9790393971	0.4822759897
C	-1.6984801939	4.2256015161	0.4891155351
C	-2.5321218746	4.5925266774	-0.5753268359
C	-2.7235149087	3.7228954972	-1.6446367104
C	-2.0771011144	2.4751518413	-1.6407472219
O	5.4623213002	0.4258837232	0.345403412
C	7.5403400947	0.2410793956	1.488259426
C	6.4439663659	-0.531969535	0.7797505414
C	-1.6259737499	-2.7131885714	-0.979316928
C	-2.6920992712	-3.7956122034	-0.7111181085
C	-0.2517204585	-3.4132757326	-0.9793923916
C	-1.8332257003	-2.149182583	-2.4048256016
C	-0.7618828975	-1.7508445677	1.9322049141
C	0.771899148	-1.7495295992	1.7399715427
C	-1.1871937927	-3.1373217988	2.4569431237
C	-1.0535780315	-0.7011037727	3.0267348305
C	-3.4584016939	-0.7253587768	0.6364594537
C	-3.5658748685	0.6534222472	1.3284247744
C	-4.1873253845	-1.7501024831	1.5342603768
C	-4.2378253074	-0.5882550192	-0.6900119983
O	-0.2293710768	2.5617951763	1.4975665538
C	0.0407839632	3.4623823645	2.563839038
H	1.2653923414	-0.8351711805	-2.6316840198

H	2.6987071078	-2.7167798925	-1.6102697396
H	3.7319789976	-1.6956784273	-2.5920468794
H	3.4968083345	-1.7442425369	0.4574533724
H	4.9037390507	-2.0536685488	-0.5485784022
H	3.7323902185	2.0387067837	-0.6177226813
H	-1.5553596811	4.9177470899	1.3122192124
H	-3.0224189891	5.562934029	-0.5569242545
H	-3.3627941608	4.0027019593	-2.4788852214
H	-2.2292071608	1.8046021214	-2.4838232973
H	8.3143429761	-0.4518576853	1.837027706
H	8.0049579904	0.9662789813	0.8115068549
H	7.1421125969	0.7795936441	2.354972106
H	5.9843024192	-1.2634212099	1.4553619621
H	6.8504534613	-1.0691735884	-0.0862744633
H	-3.7141424869	-3.4363288025	-0.8480408372
H	-2.5412527923	-4.6088499637	-1.4343677281
H	-2.6073337077	-4.2325375044	0.2873863993
H	0.5670048694	-2.705913323	-1.1197930039
H	-0.2279180112	-4.1220992301	-1.8180560199
H	-0.0702016731	-3.9875525202	-0.0678924069
H	-2.8020932269	-1.6674050076	-2.5422711807
H	-1.0568536986	-1.4222026765	-2.6654440765
H	-1.7747128666	-2.9795678616	-3.1216728243
H	1.1361928154	-0.764153728	1.4326853366
H	1.2399081016	-1.9962481072	2.7028923917
H	1.1149321659	-2.484815936	1.0122542657
H	-2.2598568005	-3.2122674423	2.6452415701
H	-0.677335315	-3.316238027	3.4138009343
H	-0.8984859276	-3.9494659313	1.7853798364
H	-0.4119856229	-0.921481969	3.8906283935
H	-0.8226919201	0.3156520433	2.6930233944
H	-2.0864919161	-0.7340356267	3.3806963109
H	-3.2738762605	1.4629720491	0.6613627113
H	-4.6202031156	0.8074826048	1.5965847029
H	-2.9842229614	0.7365610551	2.2454917035
H	-4.1337485816	-2.7747298767	1.1645703875
H	-5.2495835198	-1.4729125479	1.5735587376
H	-3.8165665937	-1.735246298	2.5625448913
H	-3.739695265	0.0847565816	-1.3940805
H	-4.4212177764	-1.5445587928	-1.1839922602
H	-5.2194665831	-0.1520267849	-0.4621621005
H	0.7427737231	2.946243092	3.2228016399
H	0.5053344077	4.389784274	2.2038473148
H	-0.8664045134	3.7098175848	3.1313175279

Pd	-0.1218930639	0.4077479945	-0.7494716298

ib

B3LYP SCF energy: -1982.1531203 a.u.
B3LYP enthalpy: -1981.3128383 a.u.
B3LYP free energy: -1981.4359063 a.u.
M062X SCF energy in solution: -1982.9668554 a.u.
M062X enthalpy in solution: -1982.1265734 a.u.
M062X free energy in solution: -1982.2496414 a.u.
Three lowest frequencies (cm^{-1}): 12.6605, 17.5572, 32.1246

	X	Y	Z
C	2.5697045911	0.4719759249	1.2581566488
C	3.8835907376	0.5421027699	2.0054893151
C	5.0694028799	0.8916472042	1.0890844556
C	5.0178573594	0.0722196186	-0.1812897647
C	3.8309166322	-0.3279997418	-0.6817184852
C	2.5434888541	0.0098619901	-0.0262477822
O	1.4884245853	-0.1918720213	-0.8066816551
C	-0.2778499932	1.9184228353	-0.5361402523
P	-3.0001395771	-0.0368982716	-0.0943891851
C	-0.1233244047	2.7906815895	0.5598568826
C	0.2023568132	4.1380179718	0.3503741565
C	0.3783958722	4.6258040419	-0.9499324036
C	0.2386510068	3.7723424751	-2.0409706586
C	-0.0790379952	2.42248074	-1.8224452403
O	6.1456186086	-0.1640140405	-0.9207678292
C	8.458683379	-0.5200207926	-1.3392076556
C	7.4391676965	-0.0603494231	-0.3123639842
C	-3.5057940284	-0.4120537681	1.7501812866
C	-4.9080637584	-1.0246184354	1.940577695
C	-3.4278500212	0.8803320162	2.5913379918
C	-2.4552662088	-1.3772567981	2.3422583832
C	-3.9993317082	1.5423146932	-0.6812584718
C	-3.4048620287	2.8449681255	-0.0965743084
C	-5.4948564332	1.5143631665	-0.2954963686
C	-3.883731867	1.6856215125	-2.214904883
C	-3.5906088882	-1.5288692859	-1.2234662963
C	-2.7957861978	-1.4517465148	-2.5496471469
C	-5.0960738605	-1.5757334563	-1.5585316723
C	-3.2374898427	-2.8793108601	-0.5607312273
O	-0.337552594	2.2622091071	1.8104772848
C	-0.0692791431	3.0800015829	2.9430155884
H	1.6458433092	0.7277704544	1.7685947423

H	3.8338048968	1.2844236359	2.8125381676
H	4.1164790835	-0.4208504776	2.5016827739
H	5.0324244861	1.958851379	0.8107304471
H	6.0088373411	0.7423476401	1.6300505319
H	3.7930934226	-0.852965767	-1.6327572702
H	0.3181117388	4.8149123226	1.1901422181
H	0.6296346409	5.6735135042	-1.0962608979
H	0.3827069754	4.1397491425	-3.0542585028
H	-0.1680279268	1.7571918199	-2.6774237267
H	9.4685703325	-0.4512694677	-0.9190556827
H	8.2752821548	-1.5596668313	-1.6319700609
H	8.4156649791	0.1054104662	-2.237721081
H	7.6396929661	0.9762037845	-0.0122546235
H	7.4874002431	-0.6912584856	0.5857305861
H	-5.007483146	-2.0098908605	1.4806089753
H	-5.0831419533	-1.1537119022	3.0176341395
H	-5.7070735873	-0.386479609	1.5580540412
H	-2.4746255447	1.4000995916	2.4599861797
H	-3.5127129394	0.6017549819	3.6507069012
H	-4.2455566407	1.5733134147	2.3784964164
H	-2.4466186233	-2.35368432	1.8571120691
H	-1.4479111366	-0.9544273146	2.279556611
H	-2.6873770359	-1.5379118284	3.4039889844
H	-2.4401912259	3.079901306	-0.5408177364
H	-4.0936052149	3.6639123801	-0.3456716235
H	-3.290292882	2.8348435286	0.9862141544
H	-6.0183921897	0.6126365379	-0.6127409534
H	-5.9867345605	2.3657198326	-0.785669148
H	-5.6428457657	1.6388383058	0.7802609102
H	-4.2842583961	2.6687782157	-2.4960545903
H	-2.8439734121	1.6491605043	-2.5532758169
H	-4.4590417325	0.9378336864	-2.7638572659
H	-1.7148412536	-1.4342480624	-2.3783428815
H	-3.0280174977	-2.3407325804	-3.1521752645
H	-3.049646069	-0.577183577	-3.1506676707
H	-5.7257187162	-1.629226525	-0.6667392291
H	-5.2829164933	-2.4887453708	-2.1407714146
H	-5.4309162019	-0.736792197	-2.1716093015
H	-2.1955047465	-2.9316662047	-0.244168148
H	-3.8783381533	-3.1042642673	0.2950884351
H	-3.4085315055	-3.6726261089	-1.3011851613
H	-0.2308475662	2.445529897	3.8173644445
H	0.9684341598	3.4367558626	2.9453181365
H	-0.7492841869	3.9405269528	2.9949649921

Pd	-0.5262163775	-0.0453116452	-0.2938825673
O	-0.1452774402	-2.4064190211	-0.0013682114
C	0.6243853583	-2.7658915659	1.1850397196
C	0.4148178413	-3.0805963285	-1.1594768153
C	1.7296522053	-3.7152503201	0.7102694551
H	1.0182844481	-1.8533573645	1.6372553772
H	-0.0640649876	-3.2525175618	1.8847008549
C	1.1509447611	-4.2885712764	-0.5918948679
H	1.0926000592	-2.386437583	-1.6651585643
H	-0.4146247456	-3.3382629813	-1.8229028966
H	1.9581027352	-4.4815461042	1.4573234918
H	2.6470537896	-3.1545175962	0.5017355893
H	1.9180945822	-4.6634662439	-1.2763544505
H	0.4468831092	-5.1023924227	-0.3796686586

Ts1a

B3LYP SCF energy: -1749.6871224 a.u.

B3LYP enthalpy: -1748.9738004 a.u.

B3LYP free energy: -1749.0815844 a.u.

M062X SCF energy in solution: -1750.5256246 a.u.

M062X enthalpy in solution: -1749.8123026 a.u.

M062X free energy in solution: -1749.9200866 a.u.

Three lowest frequencies (cm^{-1}): -73.2376, 16.3527, 21.8282

	X	Y	Z
C	0.7486079216	-1.5325817065	-1.9721900394
C	1.5686815681	-2.712829566	-1.4683411651
C	2.7285031396	-2.3111656323	-0.5409135227
C	3.4423585988	-1.0772430409	-1.0256603507
C	2.8765903171	-0.2148604295	-1.9125496314
C	1.521294448	-0.3987489183	-2.4475591179
O	1.0130337217	0.5141055733	-3.1624045751
C	0.2393005259	2.1216264855	0.112009651
P	-2.0676219042	-0.4212398419	0.2359348991
C	1.0387358035	2.3323179683	1.2590982559
C	1.4770020699	3.6159049268	1.6130873685
C	1.1221802653	4.7161158496	0.8218448676
C	0.3372933346	4.5367604785	-0.3138621741
C	-0.0981087426	3.2453134566	-0.6520237127
O	4.6608036966	-0.7542155908	-0.5425485021
C	6.5794767877	-0.8745712822	0.8648906679
C	5.3512450851	-1.6213580867	0.3809579249
C	-3.3421871159	-0.1604085972	-1.2194697955
C	-4.6750332596	-0.923518229	-1.0602037984

C	-2.6888769923	-0.5907107016	-2.5516765421
C	-3.6640492268	1.3425414443	-1.363385604
C	-2.031114555	-2.3224699631	0.7261420902
C	-1.9914097624	-3.1980538844	-0.5435594916
C	-3.2151788489	-2.82516207	1.578570847
C	-0.7200134604	-2.5796821851	1.5016342986
C	-2.7364006108	0.5488314237	1.8079415718
C	-1.9077963845	0.1266981087	3.0409099385
C	-4.2377714473	0.3116949708	2.0916079484
C	-2.546362058	2.0765670164	1.6845972313
O	1.3527720243	1.2109067777	1.9968232353
C	2.1114427643	1.3739815507	3.1879449434
H	-0.0632068842	-1.8010244041	-2.6457413797
H	0.9427307716	-3.4429219576	-0.9443346254
H	1.9990323146	-3.2514661846	-2.329985771
H	2.3588177045	-2.1098932338	0.4754577495
H	3.4318271297	-3.146312734	-0.4488891766
H	3.416133615	0.6791831359	-2.213498056
H	2.0927832783	3.7738533756	2.4925578822
H	1.4667381968	5.7080293847	1.1047356294
H	0.0608256453	5.3865682485	-0.9340586842
H	-0.7189467462	3.1234448049	-1.5374570396
H	7.1432584273	-1.5077254639	1.5590249681
H	7.2353532289	-0.61239985	0.0278048913
H	6.2977680319	0.0455835867	1.3879611159
H	4.6939035024	-1.8737916611	1.2198426809
H	5.6345063639	-2.5489922796	-0.1312323425
H	-5.2154439138	-0.6622621739	-0.1487155927
H	-5.3214265802	-0.6580748333	-1.9081628711
H	-4.5501644009	-2.0083340281	-1.0843589237
H	-2.4674870792	-1.6581594244	-2.5974852051
H	-1.7633148817	-0.040818078	-2.747123473
H	-3.3939382609	-0.369382614	-3.3645090562
H	-4.292994387	1.7210356867	-0.5547003814
H	-2.7608561853	1.957139411	-1.4267757658
H	-4.2236582461	1.4827523108	-2.297691187
H	-1.2139803742	-2.8887396583	-1.2393212788
H	-1.7774483974	-4.2308251799	-0.2379263339
H	-2.9469493088	-3.2151162261	-1.0722079709
H	-3.2516181373	-2.3769560536	2.5729831978
H	-3.0898684685	-3.907244171	1.7220743649
H	-4.1818650933	-2.674963325	1.0908242871
H	-0.6106166092	-3.6611720959	1.6596084841
H	0.1483189261	-2.2260183253	0.940358063

H	-0.7036316198	-2.1040100092	2.4835499831
H	-0.8334126703	0.2147738777	2.8506048046
H	-2.1541899986	0.806923536	3.8674380834
H	-2.1312193493	-0.8845049652	3.3859640076
H	-4.8749967985	0.8147856456	1.3594321542
H	-4.4676372914	0.7547859148	3.0702576372
H	-4.527287573	-0.7375312792	2.1373578674
H	-1.4964766649	2.3567403002	1.7275875885
H	-2.9764371817	2.5092580771	0.7826775119
H	-3.0516099517	2.5395453156	2.5433745664
H	2.2064515755	0.3757426437	3.6221555944
H	3.1140984154	1.771591331	2.9819067202
H	1.6045507031	2.0295613494	3.9083776226
Pd	0.0641515203	0.2205509674	-0.644215057

Ts2a

B3LYP SCF energy: -1749.6304046 a.u.

B3LYP enthalpy: -1748.9217546 a.u.

B3LYP free energy: -1749.0304066 a.u.

M062X SCF energy in solution: -1750.4628051 a.u.

M062X enthalpy in solution: -1749.7541551 a.u.

M062X free energy in solution: -1749.8628071 a.u.

Three lowest frequencies (cm^{-1}): -1700.4314, 14.2601, 23.3744

	X	Y	Z
C	3.0312659862	-2.2934767133	-2.0664874175
C	4.5187959526	-2.5477276833	-2.2846292568
C	4.9683136524	-2.2577540652	-0.8563057073
C	4.7470697427	-0.9034461734	-0.4585429839
C	3.6640308283	-0.2043591019	-0.9922022335
C	2.6939353569	-0.9427529038	-1.7164629899
O	1.5069819192	-0.4523822544	-2.0296557392
C	0.5821087833	1.4665335754	0.1024587021
P	-2.3263521247	-0.4079256365	0.0974574627
C	1.3953452887	1.3626260027	1.2497440038
C	1.9995631823	2.5130133215	1.7804531913
C	1.8278230828	3.7534997557	1.1574522504
C	1.0616150168	3.8555428159	0.0001921043
C	0.4482385597	2.7063030282	-0.52279113
O	5.4390774406	-0.2759987988	0.5402578267
C	7.3366478132	0.1643563	1.9148578874
C	6.6761197898	-0.8429176743	0.9914970628
C	-2.7573051868	-2.0642846186	-0.8441236694
C	-4.2576627977	-2.4070381256	-0.9170235899

C	-2.0163467932	-3.250080098	-0.1889172555
C	-2.200644561	-1.9638432982	-2.2867579055
C	-2.4541153337	-0.7057244034	2.009535031
C	-1.2225131523	-1.5079754999	2.4856576886
C	-3.7292979232	-1.4528451448	2.4519039141
C	-2.397855074	0.6525687298	2.7415499147
C	-3.5892607502	0.9731601878	-0.4309353935
C	-3.0386551751	2.3618609848	-0.0363663384
C	-4.9965374898	0.8178886117	0.1805403258
C	-3.7118280505	0.9905581099	-1.9705451778
O	1.5689737688	0.1155873329	1.7827465325
C	2.4924628855	-0.0451691243	2.8547169871
H	2.293747445	-2.8314378793	-2.6658129812
H	4.6979582643	-3.5994709359	-2.5294187265
H	4.9934500507	-1.9192316348	-3.0591790582
H	3.5823994211	-2.739033333	-0.7320205389
H	5.826637289	-2.7914552321	-0.4533398777
H	3.4488055669	0.8034016542	-0.6545369897
H	2.6196087732	2.4450605436	2.6677415002
H	2.3097692659	4.6316434309	1.5798424633
H	0.939280596	4.8109545756	-0.5035411982
H	-0.1285794666	2.7892211077	-1.4391513335
H	8.2898708892	-0.2355370168	2.2791329794
H	7.5336498546	1.1052327435	1.3893901475
H	6.7011946229	0.3779813357	2.7816269685
H	6.4858626002	-1.7845200158	1.5233667805
H	7.3184795193	-1.0650564827	0.1290860631
H	-4.8249296541	-1.684949919	-1.5090140691
H	-4.3656175427	-3.3836989785	-1.408408925
H	-4.7219513667	-2.4860256231	0.0691926379
H	-0.945525778	-3.0554372461	-0.0651885682
H	-2.1176152619	-4.1214428781	-0.8492126157
H	-2.4363691699	-3.5313887364	0.7788831494
H	-2.6316065259	-1.1530524406	-2.8733589613
H	-1.1064725851	-1.8554025545	-2.3094921146
H	-2.4220746775	-2.9046906597	-2.8084411601
H	-0.2870983046	-1.0182925938	2.2064784497
H	-1.261192956	-1.5638254592	3.5822349817
H	-1.2049976932	-2.5323753487	2.1137325821
H	-4.6501541264	-0.94053585	2.1656815572
H	-3.7220026812	-1.5237105705	3.5481528154
H	-3.7680656199	-2.4739564183	2.0648080527
H	-2.29273264	0.456467464	3.8165856819
H	-1.53804472	1.2556547662	2.4324465671

H	-3.3081825933	1.2412577393	2.6109178804
H	-2.0985178229	2.5820606457	-0.5426867231
H	-3.7705530902	3.1172246718	-0.3526478199
H	-2.883192141	2.4897099769	1.0345641211
H	-5.4521838261	-0.1529697018	-0.0255363115
H	-5.6490545345	1.585309228	-0.2576477505
H	-4.9980679735	0.9777321885	1.2618316219
H	-2.7329808912	1.0577033885	-2.4580473373
H	-4.2474144262	0.1263731504	-2.369850356
H	-4.2829814347	1.8831492337	-2.2573657282
H	2.4983459362	-1.1134770189	3.0816687588
H	3.5012740724	0.265985886	2.5602506419
H	2.1779063873	0.508558235	3.7488385408
Pd	-0.1322049989	-0.1612329163	-0.8102719156

ii'

B3LYP SCF energy: -1749.7131701 a.u.

B3LYP enthalpy: -1748.9988771 a.u.

B3LYP free energy: -1749.1094841 a.u.

M062X SCF energy in solution: -1750.5400719 a.u.

M062X enthalpy in solution: -1749.8257789 a.u.

M062X free energy in solution: -1749.936385 a.u.

Three lowest frequencies (cm^{-1}): 18.8280, 21.0196, 27.3548

	X	Y	Z
C	0.5138257021	-1.4233166624	-0.0485865435
C	1.3615875825	-1.8042535304	1.1627901147
C	2.850248406	-1.4692481738	1.0223538049
C	3.3813519117	-1.9233942461	-0.3085842764
C	2.5684784667	-2.0880507406	-1.3860843314
C	1.1386501834	-1.8000653437	-1.3626597107
O	0.4623513397	-1.8947678843	-2.400527386
C	1.6625220029	1.3223993415	-0.5444296589
P	-2.6745592648	0.3416199207	0.2881549202
C	2.3130483708	2.1461332444	0.4060174028
C	3.4032375314	2.9515137368	0.0456634018
C	3.8667502613	2.9476397935	-1.2757661034
C	3.25192818	2.1417169575	-2.2302633313
C	2.1687988202	1.3333666453	-1.8516842007
O	4.700472259	-2.1410407673	-0.4930657577
C	7.0303810143	-2.1317381884	-0.0049750287
C	5.6426144343	-1.9734487195	0.5861263746
C	-3.6805313128	-0.5546799621	-1.1136438448
C	-5.169040864	-0.8049935696	-0.8020933609

C	-2.9961808402	-1.9086128761	-1.4183714577
C	-3.5819179546	0.2628123461	-2.419978647
C	-3.1383468602	-0.44411095	2.0058394136
C	-3.0946007736	-1.9854107604	1.9105543855
C	-4.5114518759	-0.0383009901	2.5761142753
C	-2.0332099701	-0.0528472919	3.01474493
C	-3.1744480364	2.2257228748	0.3072829249
C	-2.6710387952	2.8881179877	1.6092362444
C	-4.6777435373	2.5315589479	0.1607538786
C	-2.4078458776	2.927650944	-0.8407324901
O	1.8131261713	2.1114498388	1.6894426471
C	2.4129155543	2.943582446	2.6727278719
H	-0.4655486557	-1.900124027	0.0097416242
H	0.9718464734	-1.3539953717	2.0809864482
H	1.2760358655	-2.896379044	1.2956907102
H	3.0015514787	-0.3840792685	1.1049120118
H	3.4084739736	-1.9326739382	1.8424799606
H	2.9948526038	-2.39228521	-2.3383354508
H	3.898942227	3.5811693519	0.7772583212
H	4.7116965167	3.5774094506	-1.5447624775
H	3.6088831296	2.1318268702	-3.2577554108
H	1.7120173264	0.6922140695	-2.6030893265
H	7.7813471364	-2.0244126828	0.7857391869
H	7.150057771	-3.1195623456	-0.4630164579
H	7.2191975227	-1.3684416321	-0.7672777986
H	5.5213867118	-0.9822506337	1.0368160011
H	5.4588385892	-2.7321449062	1.3565214657
H	-5.7153175266	0.1121790053	-0.5683339903
H	-5.6442638491	-1.251009348	-1.6871132325
H	-5.3108979099	-1.5078845351	0.0231772885
H	-3.0068070021	-2.6005060108	-0.57502969
H	-1.9610177866	-1.7803870324	-1.7495744754
H	-3.5468779346	-2.3929795564	-2.2371349176
H	-4.1646875899	1.1866516688	-2.3949588101
H	-2.5443966972	0.5041639737	-2.675347732
H	-3.9846274494	-0.3491075458	-3.2382134629
H	-2.1439297017	-2.3526895363	1.5104350713
H	-3.1998152482	-2.3942581725	2.9245237203
H	-3.9082744142	-2.4016319169	1.3126876245
H	-4.578568989	1.0314414988	2.788453785
H	-4.6704650031	-0.5666821413	3.5267728118
H	-5.3372427926	-0.3068765583	1.9123783608
H	-2.2138692174	-0.5842401895	3.9592469071
H	-1.0425636283	-0.341836967	2.6488207974

H	-2.0096226926	1.0132944277	3.2415875334
H	-1.6073111365	2.69720549	1.7871270262
H	-2.7955028032	3.9751893802	1.5129290854
H	-3.2341927374	2.5800606067	2.492960576
H	-5.0809429021	2.2074749036	-0.8018510911
H	-4.8250055372	3.6192562987	0.220795465
H	-5.2795191966	2.0781454886	0.9530275421
H	-1.320841289	2.7927057025	-0.7518187387
H	-2.703339622	2.5941782046	-1.8352972525
H	-2.6011200098	4.007692423	-0.7840841115
H	1.863800634	2.7591620924	3.5991727449
H	3.4708943661	2.6943673888	2.8305865364
H	2.3302004913	4.0075146276	2.4129480055
Pd	-0.1790366944	0.5585642985	-0.1277416262

iia

B3LYP SCF energy: -1749.7074669 a.u.

B3LYP enthalpy: -1748.9931149 a.u.

B3LYP free energy: -1749.1030939 a.u.

M062X SCF energy in solution: -1750.5400719 a.u.

M062X enthalpy in solution: -1749.8257199 a.u.

M062X free energy in solution: -1749.9356989 a.u.

Three lowest frequencies (cm^{-1}): 13.2108, 15.2056, 22.2799

	X	Y	Z
C	2.5007249797	-1.6656923924	0.7021290925
C	3.737030111	-2.5445653107	0.9550715581
C	5.0197369218	-1.8754003085	0.5132535869
C	4.974692988	-1.0433137	-0.5556150668
C	3.7278620617	-0.7048013193	-1.2288713588
C	2.514142014	-1.014625666	-0.6768881708
O	1.3773680808	-0.7587136988	-1.2856079808
C	0.2033390938	1.6574821229	-0.2029692157
P	-2.7176611221	-0.1957576444	0.2750972869
C	0.8331068587	2.1387558888	0.9624371896
C	1.3495268535	3.4437129402	0.985886343
C	1.2795319643	4.25363666	-0.1517559948
C	0.7025133562	3.7677146377	-1.321256373
C	0.1744448793	2.4679320206	-1.3386577024
O	6.0554186851	-0.428772897	-1.1356305609
C	8.3682493661	0.0705129261	-1.4124526008
C	7.3474905685	-0.7049716841	-0.5991824904
C	-3.0217481534	-2.1219437802	0.1583403116
C	-4.4963811362	-2.5483708885	0.0205541972

C	-2.4214876531	-2.8325049603	1.3910793974
C	-2.23259431	-2.6630651351	-1.0598871728
C	-3.1493513602	0.4074827659	2.0668550116
C	-1.9961445058	0.0166623278	3.017755316
C	-4.4711319695	-0.1592938085	2.6238674941
C	-3.2295314636	1.9493052313	2.0903457854
C	-3.8677077902	0.7037463218	-1.0096324823
C	-3.3890161353	2.1601129506	-1.197509357
C	-5.3621988924	0.7340494368	-0.6302482102
C	-3.7179743978	0.0225877225	-2.3876229817
O	0.9233877303	1.2841998255	2.030128879
C	1.6154984943	1.7216839724	3.1954661368
H	1.5842715911	-2.2579663014	0.811515304
H	3.7861968867	-2.8052664422	2.0198805125
H	3.6067104424	-3.5023287584	0.417500227
H	2.4458243552	-0.8602958192	1.4503765617
H	5.9495816344	-2.1472705583	0.9997546761
H	3.7841640266	-0.1711973013	-2.1736107032
H	1.8218835843	3.8287013624	1.883025615
H	1.6909411532	5.2590714157	-0.1148446349
H	0.6619532278	4.3798368105	-2.2185508084
H	-0.2582028343	2.0894835511	-2.2602363053
H	9.3760079491	-0.1174357025	-1.0244653151
H	8.342242849	-0.2333046398	-2.4648006926
H	8.1739247991	1.1474810785	-1.3586088926
H	7.382997644	-0.4063950236	0.4585187074
H	7.5469665387	-1.7854317255	-0.645652191
H	-4.9432767323	-2.2178675375	-0.9203094408
H	-4.5424889238	-3.6462112126	0.0295764462
H	-5.119587952	-2.1897950909	0.8437741074
H	-1.3771671535	-2.5520277524	1.5636061542
H	-2.4424441593	-3.9139600258	1.2024835478
H	-2.9888647992	-2.6572400615	2.3073342365
H	-2.5300172806	-2.228642756	-2.0134549362
H	-1.1460140534	-2.527278729	-0.9464406716
H	-2.3940717839	-3.7475747615	-1.1244342288
H	-1.0403572751	0.4252822705	2.6814741518
H	-2.2165258862	0.4360607434	4.0089349546
H	-1.8848322654	-1.0604189153	3.1438625387
H	-5.3374240123	0.0875147455	2.0059491995
H	-4.6420121637	0.2800343838	3.6160619513
H	-4.4416081761	-1.2436424317	2.7535778117
H	-3.278160428	2.2719662998	3.1386309218
H	-2.3480458035	2.4194877315	1.6432884313

H	-4.1248769253	2.3331961299	1.5959828598
H	-2.3435991817	2.2112411093	-1.5033888407
H	-3.9926090216	2.6139051272	-1.9948645113
H	-3.5127320793	2.7777825934	-0.3083509324
H	-5.7903940369	-0.2587607998	-0.4771650901
H	-5.916105929	1.2036450393	-1.454646462
H	-5.5519559908	1.3341753192	0.2633452352
H	-2.6704919052	-0.0459936941	-2.701694648
H	-4.1620317882	-0.9742618965	-2.4234274077
H	-4.2434742168	0.636462887	-3.1307601303
H	1.5949531285	0.878918379	3.8896343817
H	2.6585018134	1.9760181043	2.9702774272
H	1.1215725439	2.5837570132	3.6616407347
Pd	-0.4158607777	-0.2375839948	-0.3878876591

Ts2b

B3LYP SCF energy: -1982.0879846 a.u.

B3LYP enthalpy: -1981.2532396 a.u.

B3LYP free energy: -1981.3744376 a.u.

M062X SCF energy in solution: -1982.9024314 a.u.

M062X enthalpy in solution: -1982.0676864 a.u.

M062X free energy in solution: -1982.1888844 a.u.

Three lowest frequencies (cm^{-1}): -1697.5007, 12.9704, 18.9904

	X	Y	Z
C	-2.5017673266	-1.0450915918	1.479645443
C	-3.7701856921	-0.9655175785	2.3255962783
C	-4.6654798541	-1.8098019968	1.4252167366
C	-4.8846112968	-1.2160412407	0.142516358
C	-3.8870022367	-0.4212598147	-0.41922073
C	-2.5934180195	-0.4343641283	0.1834029403
O	-1.5734395555	-0.0008872549	-0.5191887134
C	0.5990027406	-1.7104525968	-0.3928042483
P	2.8465440941	0.67133906	0.3174787955
C	0.5559323305	-2.7072103665	0.60183026
C	0.4863639689	-4.0600548566	0.2406516503
C	0.4618154953	-4.4280566915	-1.1093696698
C	0.497327268	-3.4514051364	-2.101149902
C	0.5570656605	-2.0983183923	-1.7327003667
O	-5.9553301767	-1.4916682987	-0.6597716017
C	-8.1315874674	-2.2916522301	-1.198098624
C	-7.0667003862	-2.2139407147	-0.1188517922
C	3.2216928684	0.9650774311	2.2076213176
C	4.4766386304	1.8102634646	2.5063874073

C	3.3670862034	-0.3901363728	2.9318637959
C	1.994250718	1.6600578173	2.8367707218
C	4.1503607762	-0.623949019	-0.362078445
C	3.8143518272	-2.0676755924	0.079470868
C	5.5978939841	-0.3376481543	0.097897923
C	4.1130708318	-0.6419107445	-1.9064063732
C	3.1531426738	2.3456858249	-0.6601548247
C	2.4163868385	2.2308315912	-2.016221213
C	4.6276650517	2.7114501423	-0.9300757004
C	2.5286155662	3.5382324315	0.0976194237
O	0.6101661107	-2.2872508015	1.9087888794
C	0.4114005584	-3.2514279202	2.9362143543
H	-1.5234803763	-1.0237418561	1.9588246652
H	-3.6181955253	-1.4744148818	3.2833470992
H	-4.146562378	0.0543978497	2.5275559721
H	-3.2986838323	-2.2998176917	1.1906160545
H	-5.4680749546	-2.3918020891	1.8744486365
H	-4.0083885971	-0.0315601181	-1.4260512494
H	0.4528363134	-4.8319060054	1.0021211298
H	0.4096092075	-5.4814650827	-1.3732761558
H	0.4698199458	-3.7274390873	-3.1524906733
H	0.5646344107	-1.3401047475	-2.5115771426
H	-9.0027193948	-2.8401666456	-0.8220774413
H	-8.4577322961	-1.2904499538	-1.5008957714
H	-7.7518994976	-2.81426953	-2.0830935931
H	-6.7510772846	-3.2225800344	0.1787255643
H	-7.4469635836	-1.7011460538	0.7754656433
H	4.4002592428	2.8334103429	2.1316269762
H	4.5939394127	1.8762997534	3.5969260165
H	5.3923690393	1.3678001459	2.1102947402
H	2.5289801563	-1.060779516	2.7212842529
H	3.3764454569	-0.1979484107	4.0133714684
H	4.302653108	-0.9002439629	2.6907373788
H	1.8031024988	2.6515068499	2.4260336385
H	1.0897345319	1.0558391388	2.7156402567
H	2.176452965	1.7777079685	3.9137208405
H	2.9523148404	-2.4613169274	-0.4550324892
H	4.677040085	-2.6995342902	-0.17284699
H	3.6340818773	-2.1763396576	1.1477099103
H	5.9264679053	0.6863660261	-0.0782329148
H	6.2699708258	-0.9977335019	-0.4671231514
H	5.7431923758	-0.5692090949	1.1564657005
H	4.7038511325	-1.5015890955	-2.2497495557
H	3.0977894274	-0.7714433695	-2.2921089704

H	4.5527370538	0.2475772951	-2.3608469806
H	1.3576353998	1.9854777167	-1.8858841932
H	2.4777801919	3.1977422079	-2.534115256
H	2.8514979333	1.4797610048	-2.6773198993
H	5.2106721253	2.8168154425	-0.0113631097
H	4.6456526595	3.6863365893	-1.4366600779
H	5.138372217	2.0047623161	-1.5864634194
H	1.4896313307	3.3597990947	0.3753185563
H	3.0942948445	3.8060242298	0.99321347
H	2.556372389	4.4121288382	-0.5675312518
H	0.4135515148	-2.6938760229	3.8754601873
H	-0.5516568863	-3.7648082416	2.8249213627
H	1.2186993645	-3.9950850083	2.9613528284
Pd	0.439093983	0.2266423312	0.0457147315
O	-0.4213786968	2.4373480271	0.5105338736
C	-1.2437589828	2.56775699	1.7071806647
C	-1.0933071175	3.0783494753	-0.608786501
C	-2.5290532636	3.2750095008	1.2700751357
H	-1.4220131999	1.5720175127	2.1186035584
H	-0.676134071	3.1603767811	2.4333748209
C	-2.0774854212	4.0543449453	0.0260918293
H	-1.6024026865	2.3049810112	-1.1910754745
H	-0.3266270083	3.5590933599	-1.2217717772
H	-2.9315790441	3.9149231915	2.0611921449
H	-3.2938893661	2.5397165419	0.9981641433
H	-2.9017303393	4.3041954357	-0.6488069858
H	-1.5692889968	4.983015954	0.3124565348

iib

B3LYP SCF energy: -1982.162564 a.u.

B3LYP enthalpy: -1981.322082 a.u.

B3LYP free energy: -1981.444396 a.u.

M062X SCF energy in solution: -1982.9786672 a.u.

M062X enthalpy in solution: -1982.1381852 a.u.

M062X free energy in solution: -1982.2604992 a.u.

Three lowest frequencies (cm^{-1}): 11.0359, 17.2906, 37.0796

	X	Y	Z
C	2.8860033687	0.3522220501	1.1932840152
C	4.1054009063	-0.0235755687	2.0498883163
C	5.3925020081	0.0199927846	1.256749293
C	5.3356000886	-0.3345699127	-0.0511542463
C	4.0867405634	-0.6612318054	-0.7224798261
C	2.8701018012	-0.363526399	-0.1537793513

O	1.7399265262	-0.6171989942	-0.7614279328
C	-0.0100095941	1.5728018503	-0.5357147596
P	-2.7401898747	-0.302569279	-0.0444729515
C	0.1693276767	2.4730157615	0.5336234772
C	0.5208645995	3.8063337256	0.2794280649
C	0.6969061896	4.249245699	-1.0368070038
C	0.5328799541	3.3659322595	-2.100260281
C	0.1883484252	2.0303123774	-1.8387143288
O	6.4158216945	-0.4378503752	-0.8940249979
C	8.727450777	-0.3719936452	-1.4633240336
C	7.710061264	-0.1908076461	-0.3513524623
C	-3.2546616965	-0.5966349802	1.8124384364
C	-4.6692796277	-1.1751104524	2.0177187539
C	-3.1573510622	0.7253443273	2.6038333627
C	-2.2249155239	-1.5582730755	2.4451433077
C	-3.7064948868	1.2716887691	-0.698611504
C	-3.098429851	2.5888351279	-0.1610665688
C	-5.2038787632	1.278731405	-0.3175760025
C	-3.5835136022	1.3531753426	-2.2361934079
C	-3.350821106	-1.8280237487	-1.1185275549
C	-2.5468969614	-1.8181801206	-2.4412160974
C	-4.8551570992	-1.8566413307	-1.4615272269
C	-3.0320338196	-3.1588947018	-0.4009953609
O	-0.0321809167	1.9827260136	1.8004332263
C	0.2219409612	2.8426150506	2.9055802149
H	1.953394398	0.1526828245	1.7298618841
H	4.1607065705	0.6506282587	2.9143249872
H	3.9456468948	-1.0361191446	2.4690193846
H	2.9012814002	1.4346058178	0.9887742586
H	6.3243956359	0.2400990426	1.764532652
H	4.1389386939	-1.0812389146	-1.7233550462
H	0.6573474798	4.5064773384	1.0966231891
H	0.9679688492	5.2864989169	-1.2172924247
H	0.6767888472	3.6990232147	-3.125164579
H	0.0773760147	1.3416836357	-2.6721879166
H	9.7376667297	-0.1894215388	-1.079127159
H	8.6905864347	-1.3908979258	-1.8648908849
H	8.5388448697	0.3294928946	-2.2837992816
H	7.7559955538	0.8298553417	0.0555294289
H	7.906555011	-0.8864650576	0.4777332763
H	-4.787402679	-2.1731513194	1.5912139914
H	-4.8491144284	-1.2636395921	3.0979494778
H	-5.4538199954	-0.5341621338	1.6111135056
H	-2.1933528352	1.2207480722	2.4593864664

H	-3.2544563991	0.4886136524	3.6722058506
H	-3.9603194588	1.4248990833	2.3590579736
H	-2.23321609	-2.5525800497	1.9978764665
H	-1.2094013271	-1.1570518519	2.3715477298
H	-2.4648637045	-1.6735150865	3.5109009207
H	-2.1393034606	2.8081300009	-0.624913656
H	-3.7873501685	3.4024620411	-0.4261810001
H	-2.9700927104	2.6116173414	0.9199311487
H	-5.7375808711	0.3692179623	-0.5922107078
H	-5.683543389	2.1110668911	-0.8502359425
H	-5.3529679411	1.4571945402	0.7503412297
H	-3.96298918	2.3329371715	-2.5555652797
H	-2.5442310782	1.2828862505	-2.5699235382
H	-4.1726847294	0.5971633606	-2.7584361918
H	-1.466694188	-1.8238463241	-2.264558145
H	-2.7999593252	-2.7212295168	-3.0134047394
H	-2.7752548188	-0.9586881161	-3.0733380977
H	-5.4915562399	-1.8573887889	-0.572982401
H	-5.0573465927	-2.7904005489	-2.0041906185
H	-5.1679688758	-1.0390561315	-2.1137454423
H	-1.9933310676	-3.2233802934	-0.0769138684
H	-3.6823748071	-3.3359890246	0.4588310551
H	-3.2172898495	-3.9759330611	-1.1114716093
H	0.055209284	2.2390831515	3.8004004163
H	1.2572706588	3.2057704248	2.9060927023
H	-0.4629374699	3.7005259097	2.9189976519
Pd	-0.2823665449	-0.376638737	-0.2333198471
O	0.0655881197	-2.7416399029	0.1406310395
C	0.82238641	-3.0800426515	1.3386129182
C	0.6020623705	-3.4785139552	-0.9934453315
C	1.9472325649	-4.0143391322	0.8859112354
H	1.1868401866	-2.1574155479	1.7949037713
H	0.1349425221	-3.5740821504	2.0348069256
C	1.3591169183	-4.6517940496	-0.3811173439
H	1.263995155	-2.8106661986	-1.5518581259
H	-0.2415537507	-3.7762025932	-1.6213282571
H	2.2081767696	-4.7435692752	1.6588929898
H	2.8438407659	-3.4369823923	0.6365782625
H	2.1218241093	-5.0476170061	-1.0584707129
H	0.6681952688	-5.4636071258	-0.1228968514