Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2022

SUPPORTING INFORMATION

Visible-Light-Mediated Synthesis of a-Alkoxy/Hydroxy Diarylacetaldehydes from Terminal Alkynes

Jaswant Kumar,^{a,b} Ajaz Ahmed,^{a,b} Sourav Kumar,^{a,b} Shabnam Raheem,^c Masood Ahmad Rizvi*,^c and Bhahwal Ali Shah^{*,a,b}

^a Academy of Scientific and Industrial Research (AcSIR), Ghaziabad-201002, India

^b Natural Product & Medicinal Chemistry, CSIR-Indian Institute of Integrative Medicine, Jammu-180001.

^c Department of Chemistry, University of Kashmir, Srinagar, 190006.

Table of contents

1. General Information	S 1
2. General Synthetic Procedures	
Method A: Synthesis of α -methoxy diaryl/alkyl methanols	S2
Method B: Substrate scope for α -Hydroxy diaryl/alkyl methanols	S2
3. Quenching Experiments and Stern-Volmer Plots	S2-S4
4. Characterization data (3-47)	S5-S19
5. NMR spectra	S20-S81

1. General Information

All reactions were carried out in oven-dried glassware. The solvents used were purified by distillation. The reactions were irradiated using a regular blue light-emitting diode (LED) strip purchased from market (Manufacturer: GM Modular, Model: Zodion 5050SMD; 60 LEDs per meter, 14 Lumens per LED, 12V strip Light at 460 nm). Irradiation occurred along the sides at a uniform distance of 5 cm. ¹H and ¹³C NMR spectra were recorded on FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent (CDCl₃, 7.26 ppm). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. Coupling constants (J) are quoted in Hz. Mass spectra were obtained using Q-TOF-LC/MS spectrometer using electron spray ionization.

Abbreviations: TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl, TLC = thin layer chromatography, DIPEA = N,N-diisopropylethylamine, EA = ethyl acetate, MeOH = methanol.

2. General Synthetic Procedures:

2.1. Method A: Synthesis of α-methoxy diaryl acetaldehydes

To the oven dried 15 mL glass vial was added phenylacetylene (100 mg, 0.98 mmol), benzoquinone (106 mg, 0.98 mmol), copper cyanide (21.9 mg, 25 mol%) followed by addition of MeOH as a solvent. The reaction mixture was then irradiated under an air atmosphere under blue light sourced from blue LED strips for 8 h. After the completion of reaction, as monitored by TLC, the reaction mixture was dried by rotavapor and the residue left is subjected to extraction with ethyl acetate and water. The aqueous layers were then again extracted with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using (hexane/EA = 95:5) as solvent system to obtain pure product **3** as yellow oil (218 mg, 90% yield).

2.2. Method B: Synthesis of α-hydroxy diaryl acetaldehydes

To the oven dried 15 mL glass vial was added phenylacetylene (100 mg, 0.98 mmol), benzoquinone (106 mg, 0.98 mmol), copper cyanide (89.5 mg) followed by addition of trifluoroacetic acid (111 mg, 0.98 mmol) and MeCN/H₂O (1:1) as a solvent. The reaction mixture was then irradiated under an air atmosphere under blue light sourced from blue LED strips for 8 h. After the completion of reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were then washed with sodium bicarbonate (NaHCO₃) and again extracted with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using (hexane/EA = 90:10) as solvent system to obtain pure product **39** as yellow oil (194 mg, 85% yield).

3. Luminescence Quenching Experiments and Stern-Volmer Plots

3.1. Absorption Studies:

Identification of the possible BQ+PA photo-adduct as the visible light absorbing system in the reaction mixture was obtained from the time dependent absorption changes monitored for a mixture of fixed concentrations of benzoquinone {BQ= 2.5×10^{-4} M} and {phenylacetylene (PA) 5×10^{-5} M}. The prepared binary mixture was irradiated for 70 minutes under blue LED (15W). The absorbance was recorded after every 10 minutes over the wavelength range of 300-800 nm. The irradiation time dependent hyperchromic effect at the λ max of 470 nm was corroborated to the excimer formation as blue light responsive absorbing system of the reaction mixture.

3.2. Stoichiometric analysis of the BQ: PA photo-adduct:

The stoichiometry of the proposed complex between BQ and PA was obtained from Job's continuous variation method using absorbance studies. The absorption spectra of equimolar

concentrations $(5x10^{-5} \text{ M})$ of BQ and PA were recorded at $\lambda \max 470 \text{ nm}$ in quartz cuvette over Shimadzu (UV-1800) spectrophotometer. From the observed jobs plot the absorbance was seen to be maximum at1:1 molar ratio of BQ and PA in methanol solvent, predicting the 1:1 stoichiometry of their adduct formed in solution.

The relative propensity of copper (I) salts towards nucleophilic step of the proposed reaction path was also attempted using the absorption studies. Upon incremental addition of copper (I) salts {CuCN, CuCl} on BQ: PA adduct under blue LED irradiation the changes in the absorption pattern predicted the influence of copper salt Lewis acidity on the reaction propensity, which was explored through binding constant calculations of CuCl and CuCN adducts with the proposed molecule in the reaction mechanism. These binding constant (K) were determined using the relevant Benesi–Hildebrand equation:

$$1/(A - A_0) = 1/(A_{max} - A) + 1/K (A_{max} - A)[M]$$

In this equation, A_0 and A are the absorbance of BQ: PA adduct before and after the increasing concentrations of copper salts respectively. A_{max} is the absorbance obtained at saturated concentration and [M] is the added copper salt concentration. The observed binding constants K_{CuCN} and K_{CuCl} were obtained from the ratio of the intercept to the slope in the plot of $1/(A-A_0)$ versus 1/[M].

3.3. Fluorescence Studies:

Fluorescence studies were carried out using Shimadzu (RF-5301PC) spectroflourometer Fluorescence quenching of BQ after addition of PA was observed for 70 minutes in methanol around 20°C temperature and blue LED irradiation. The hypochromism in fluorescence intensity of BQ was seen at the wavelength of λ 516 nm corresponding to its emission maximum. To support absorption studies suggesting the role of Lewis acidity of copper(I) cyanide on the reaction propensity, the fluorescence measurements were also carried out. The effect of CuCN addition on the fluorescence profile of equimolar concentrations of BQ:PA adduct at the wavelength of 516 nm indicated a dose dependent hyperchromic effect with a slight blue shift. The changes in the fluorescence intensity of BQ:PA adduct upon incremental addition of CuCN were analyzed using Stern Volmer analysis method Fig S1 with the calculated stern volmer constant of 6 x 10⁴. From the emission studies the corresponding binding constant of 4 x 10⁵ for CuCN binding with the proposed molecule in the reaction mechanism was calculated which is in conformity with the absorption studies.

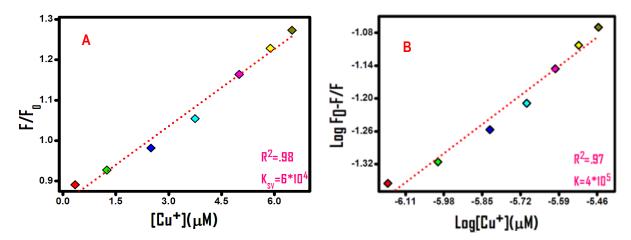
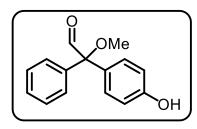


Figure S1: Stern-Volmer analysis of CuCN binding.

4. Characterization Data (3-47):

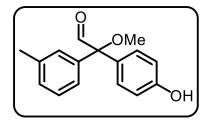
2-(4-hydroxyphenyl)-2-methoxy-2-phenylacetaldehyde (3).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (106 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 95:5) as yellow oil (218 mg, 90%). ¹H NMR (400 MHz, CDCl₃): δ - 9.65 (s, 1H), 7.32 - 7.23 (m, 5H), 7.17 - 7.13 (m, 2H), 6.78 - 6.73 (m, 2H), 3.09 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100

MHz): δ - 198.0, 156.0, 137.0, 130.5, 128.8, 128.6, 128.5, 115.5, 89.2, 52.9. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₁₅H₁₄NaO₃, 265.0835; found: 265.0848.

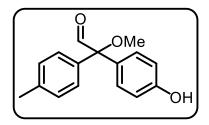
2-(4-hydroxyphenyl)-2-methoxy-2-(m-tolyl)acetaldehyde (4).



The title compound was prepared according to the method A by taking 3-methylphenylacetylene (100 mg, 0.86 mmol), 1,4benzoquinone (108 mg, 0.86 mmol), CuCN (19.2 mg, 0.22 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane:EA= 95:5) as yellow oil (212 mg, 83%). ¹H NMR (400 MHz, CDCl₃): δ - 9.64 (d, *J* = 6.1 Hz, 1H), 7.20 – 7.11 (m, 4H), 7.10 – 7.05 (m, 2H), 6.78 – 6.73 (m, 2H), 5.67 (d, *J*

= 38.1 Hz, 1H), 3.08 (d, J = 6.2 Hz, 3H), 2.25 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 198.0, 156.0, 138.4, 136.8, 130.5, 129.3, 129.3, 128.7, 128.4, 125.9, 115.5, 89.2, 52.9, 21.5. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₁₆H₁₆NaO₃, 279.0992; found: 279.1003.

2-(4-hydroxyphenyl)-2-methoxy-2-(p-tolyl)acetaldehyde (5).

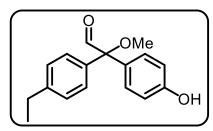


The title compound was prepared according to the method A by taking 4-methylphenylacetylene (100 mg, 0.86 mmol), 1,4benzoquinone (108 mg, 0.86 mmol), CuCN (19.2 mg, 0.22 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (228 mg, 89%). ¹H NMR (400 MHz, CDCl₃): δ - 9.63 (s, 1H), 7.19 – 7.09 (m, 6H), 6.78 – 6.72 (m, 2H), 5.73 (s, 1H), 3.08 (d, *J* = 4.2 Hz, 3H), 2.27

(s, 3H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): δ - 197.9, 156.1, 138.5, 133.7, 130.5, 129.3, 128.8, 128.6, 115.5, 89.2, 52.8, 21.1. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₁₆H₁₆NaO₃, 279.0992; found: 279.1000.

2-(4-ethylphenyl)-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (6).

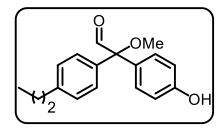
The title compound was prepared according to the method A by taking 4-ethylphenylacetylene (100 mg, 0.77 mmol), 1,4-benzoquinone (83.2 mg, 0.77 mmol), CuCN (17.2 mg, 0.19 mmol),



methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (221 mg, 82%). ¹H NMR (400 MHz, CDCl₃): δ - 9.63 (s, 1H), 7.22 - 7.11 (m, 6H), 6.78 - 6.73 (m, 2H), 5.82 (s, 1H), 3.08 (s, 3H), 2.57 (q, J= 7.6 Hz, 2H), 1.15 (t, J= 7.6 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 197.9, 156.1, 144.7, 133.7, 130.5, 128.9, 128.5, 128.1, 115.6, 89.3, 52.8, 28.5, 15.4. HRMS (ESI) (m/z):

 $[M+Na]^+$ calculated for $C_{17}H_{18}NaO_3$, 293.1148; found: 293.1161.

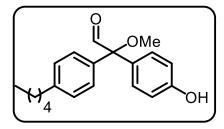
2-(4-hydroxyphenyl)-2-methoxy-2-(4-propylphenyl)acetaldehyde (7).



The title compound was prepared according to the method A by taking 4-propylphenylacetylene (100 mg, 0.69 mmol), 1,4benzoquinone (74.6 mg, 0.69 mmol), CuCN (15.4 mg, 0.17 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 93:7) as yellow oil (222 mg, 78%). ¹H NMR (400 MHz, CDCl₃): δ - ¹H NMR (400 MHz, CDCl₃) δ 9.75 (s, 1H), 7.32 – 7.21 (m, 6H), 6.89 – 6.85 (m, 2H),

5.55 (s, 1H), 3.20 (s, 3H), 2.64 – 2.59 (m, 2H), 1.72 – 1.62 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 197.9, 156.1, 143.3, 133.8, 130.5, 128.8, 128.7, 128.5, 115.6, 89.3, 52.8, 37.7, 24.4, 13.9. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₁₈H₂₀NaO₃, 307.1305; found: 307.1318.

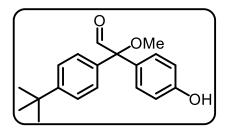
2-(4-hydroxyphenyl)-2-methoxy-2-(4-pentylphenyl)acetaldehyde (8).



The title compound was prepared according to the method A by taking 4-pentylphenylacetylene (100 mg, 0.58 mmol), 1,4-benzoquinone (62.7 mg, 0.58 mmol), CuCN (12.9 mg, 0.14 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 93:7) as yellow oil (265 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ - 9.62 (s, 1H), 7.19 – 7.14 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.76 – 6.71 (m, 2H), 4.97 (s,

1H), 3.08 (s, 3H), 2.55 – 2.45 (m, 2H), 1.51 (s, 2H), 1.22 (dt, J = 8.9, 4.3 Hz, 4H), 0.79 (t, J = 7.0 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 197.8, 155.9, 143.5, 133.9, 130.5, 128.9, 128.7, 128.6, 115.5, 89.2, 52.9, 35.6, 31.6, 31.0, 22.5, 14.1. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₂₀H₂₄NaO₃, 335.1618; found: 335.1630.

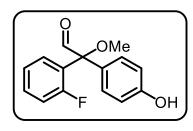
2-(4-(*tert*-butyl)phenyl)-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (9).



The title compound was prepared according to the method A by taking 4-*tert*-butylphenylacetylene (100 mg, 0.63 mmol), 1,4-benzoquinone (68 mg, 0.63 mmol), CuCN (14 mg, 0.16 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 93:7) as yellow oil (274 mg, 92%). ¹H NMR (400 MHz, CDCl₃): δ - 9.63 (d, *J* = 6.5 Hz, 1H), 7.32 - 7.27 (m, 2H), 7.21 - 7.15 (m, 4H), 6.78 - 6.71 (m, 2H),

5.14 (s, 1H), 3.08 (s, 3H), 1.22 (s, 9H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): δ - 197.8, 155.9, 151.5, 133.5, 130.6, 128.6, 128.5, 125.5, 115.5, 89.2, 52.9, 34.6, 31.3. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₁₉H₂₂NaO₃, 321.1461; found: 321.1473.

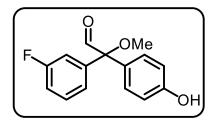
2-(2-fluorophenyl)-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (10).



The title compound was prepared according to the method A by taking 2-fluorophenylacetylene (100 mg, 0.83 mmol), 1,4benzoquinone (89.7 mg, 0.83 mmol), CuCN (18.6 mg, 0.20 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane:EA = 94:6) as yellow oil (135 mg, 52%). ¹H NMR (400 MHz, CDCl₃): δ - 9.77 (d, J = 5.8 Hz, 1H), 7.39 (tdd, J = 6.8, 4.3, 2.3 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.25 (d, J = 2.9 Hz, 1H), 7.22 –

7.17 (m, 1H), 7.14 – 7.08 (m, 1H), 6.87 – 6.83 (m, 2H), 3.23 (s, 3H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): $\delta - {}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃) $\delta - 195.6$, 155.9, 131.2 (d, J = 3.9 Hz), 131.0 (d, J = 8.6 Hz), 129.6, 127.7, 124.5 (d, J = 3.1 Hz), 116.3, 116.1, 115.6, 87.2 (d, J = 3.1 Hz), 52.9. ${}^{19}F$ NMR (377 MHz, CDCl₃): $\delta - 108.4$. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₁₅H₁₃FNaO₃, 283.0741; found: 283.0752.

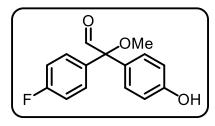
2-(3-fluorophenyl)-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (11).



The title compound was prepared according to the method A by taking 3-fluorophenylacetylene (100 mg, 0.83 mmol), 1,4benzoquinone (89.7 mg, 0.83 mmol), CuCN (18.6 mg, 0.20 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (182 mg, 70%). ¹H NMR (400 MHz, CDCl₃): δ - 9.66 (s, 1H), 7.32 – 7.25 (m, 1H), 7.18 – 7.09 (m, 4H), 6.98 (tdd, *J* = 8.4, 2.2, 1.4 Hz, 1H),

6.82 – 6.76 (m, 2H), 5.48 (s, 1H), 3.14 (s, 3H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ - 197.8, 164.1, 161.6, 156.1, 139.9 (d, J = 9.6 Hz), 130.4, 130.1 (d, J = 8.1 Hz), 128.5 (d, J = 6.9 Hz), 124.3 (d, J = 2.9 Hz), 115.7 (d, J = 19.3 Hz), 115.5 (d, J = 22.0 Hz), 88.5, 53.1. ¹⁹F NMR (377 MHz, CDCl₃): δ -111.9. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₅H₁₂FO₃, 259.0765; found: 259.0768.

2-(4-fluorophenyl)-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (12).

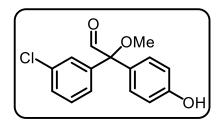


The title compound was prepared according to the method A by taking 4-fluorophenylacetylene (100 mg, 0.83 mmol), 1,4benzoquinone (89.7 mg, 0.83 mmol), CuCN (18.6 mg, 0.20 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (179 mg, 69%). ¹H NMR (400 MHz, CDCl₃): δ - ¹H NMR (400 MHz, CDCl₃) δ 9.65 (s, 1H), 7.36 – 7.29 (m, 2H), 7.16 (d, *J* = 8.4 Hz,

2H), 7.04 - 6.97 (m, 2H), 6.82 - 6.75 (m, 2H), 3.11 (s, 3H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): δ - 198.0, 162.7 (d, J = 248.2 Hz), 156.0 (d, J = 2.8 Hz), 132.9 (d, J = 3.2 Hz), 130.6 (d, J = 8.3 Hz),

130.4, 128.7 (d, J = 4.9 Hz), 115.6 (d, J = 5.7 Hz), 115.4, 88.6, 53.0. ¹⁹F NMR (377 MHz, CDCl₃): δ -113.2. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₅H₁₂FO₃, 259.0765; found: 259.0773.

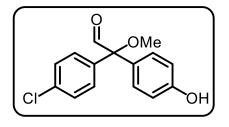
2-(3-chlorophenyl)-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (13).



The title compound was prepared according to the method A by taking 3-chlorophenylacetylene (100 mg, 0.73 mmol), 1,4benzoquinone (78.9 mg, 0.73 mmol), CuCN (16.3 mg, 0.18 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (204 mg, 74%). ¹H NMR (400 MHz, CDCl₃): δ - 9.73 (s, 1H), 7.46 (dd, *J* = 2.6, 1.4 Hz, 1H), 7.34 - 7.32 (m, 1H), 7.32 - 7.27 (m, 2H),

7.24 – 7.19 (m, 2H), 6.88 – 6.83 (m, 2H), 3.20 (s, 3H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): δ - 197.8, 156.1, 139.4, 134.6, 130.4, 129.8, 128.7, 128.6, 128.4, 126.8, 115.7, 88.5, 53.1. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₅H₁₂ClO₃, 275.0469; found: 275.0476.

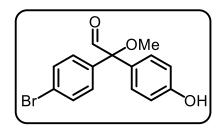
2-(4-chlorophenyl)-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (14).



The title compound was prepared according to the method A by taking 4-chlorophenylacetylene (100 mg, 0.73 mmol), 1,4benzoquinone (78.9 mg, 0.73 mmol), CuCN (16.3 mg, 0.18 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (209 mg, 76%). ¹H NMR (400 MHz, CDCl₃): δ - 9.71 (s, 1H), 7.36 (s, 4H), 7.25 - 7.13 (m, 2H), 6.90 - 6.77 (m, 2H), 3.19 (s, 3H).

¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 198.0, 156.2, 135.7, 134.6, 130.4, 130.1, 128.8, 128.4, 115.6, 88.6, 53.0. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₅H₁₂ClO₃, 275.0469; found: 275.0466.

2-(4-bromophenyl)-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (15).

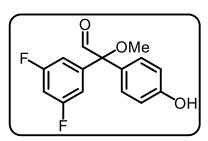


The title compound was prepared according to the method A by taking 4-bromophenylacetylene (100 mg, 0.55 mmol), 1,4-benzoquinone (59.4 mg, 0.55 mmol), CuCN (12.5 mg, 0.14 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane:EA= 93:7) as yellow oil (272 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 9.71 (s, 1H), 7.54 – 7.49 (m, 2H), 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 2H), 6.88 – 6.82

(m, 2H), 3.19 (s, 3H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): δ - 197.9, 156.1, 136.3, 131.7, 130.4, 128.5, 122.8, 115.6, 88.6, 53.0. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₅H₁₂BrO₃, 318.9964; found: 318.9965.

2-(3,5-difluorophenyl)-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (16).

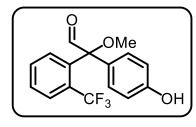
The title compound was prepared according to the method A by taking 3,5difluorophenylacetylene (100 mg, 0.72 mmol), 1,4-benzoquinone (77.8 mg, 0.72 mmol), CuCN



(16 mg, 0.18 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (189 mg, 68%). ¹H NMR (400 MHz, CDCl₃): δ - 9.71 (s, 1H), 7.24 – 7.20 (m, 2H), 7.04 – 6.98 (m, 2H), 6.88 – 6.84 (m, 2H), 6.78 (ddd, J = 8.7, 5.5, 2.4 Hz, 1H), 5.27 (s, 1H), 3.22 (s, 3H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ - 197.6, 156.1, 130.2, 128.4, 115.7, 111.6 (d, J = 7.6 Hz), 111.4, 103.9 (t, J = 25.1 Hz), 87.9 (d, J = 2.1 Hz), 53.3. ¹⁹F NMR (377 MHz, CDCl₃): δ -108.5, -108.6. HRMS (ESI)

(m/z): [M-H]⁻ calculated for C₁₅H₁₁F₂O₃, 277.0671; found: 277.0676.

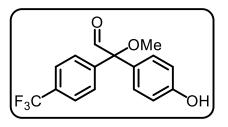
2-(4-hydroxyphenyl)-2-methoxy-2-(2-(trifluoromethyl)phenyl)acetaldehyde (17).



The title compound was prepared according to the method A by taking 2-trifluorophenylacetylene (100 mg, 0.58 mmol), 1,4benzoquinone (62.7 mg, 0.58 mmol), CuCN (13 mg, 0.14 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (161 mg, 52%). ¹H NMR (400 MHz, CDCl₃): δ - 9.78 (q, J = 1.6 Hz, 1H), 7.82 - 7.78 (m, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.53 (dt, J = 9.3, 6.5 Hz, 2H), 7.24 - 7.21

(m, 2H), 6.86 - 6.82 (m, 2H), 3.26 (s, 3H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): δ - 194.6, 154.4, 135.6, 130.1, 130.1, 128.7, 127.6, 127.3 (dd, J = 6.3, 3.8 Hz), 127.2, 114.1, 86.9, 51.7. ${}^{19}F$ NMR (377 MHz, CDCl₃) δ -56.2. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₆H₁₂F₃O₃, 309.0733; found: 309.0735.

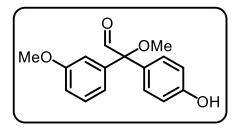
2-(4-hydroxyphenyl)-2-methoxy-2-(4-(trifluoromethyl)phenyl)acetaldehyde (18).



The title compound was prepared according to the method A by taking 4-trifluorophenylacetylene (100 mg, 0.58 mmol), 1,4-benzoquinone (62.7 mg, 0.58 mmol), CuCN (13 mg, 0.14 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (192 mg, 62%). ¹H NMR (400 MHz, CDCl₃): δ - 9.76 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.7 Hz,

2H), 6.86 (d, J = 8.7 Hz, 2H), 3.22 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 198.0, 156.1, 130.4, 129.8 (d, J = 3.8 Hz), 129.5 (d, J = 2.9 Hz), 128.9, 128.7, 125.4 (dd, J = 9.7, 6.2 Hz), 115.7, 88.5, 53.2. ¹⁹F NMR (377 MHz, CDCl₃): δ -62.7. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₆H₁₂F₃O₃, 309.0733; found: 309.0747.

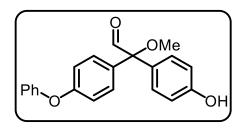
2-(4-hydroxyphenyl)-2-methoxy-2-(3-methoxyphenyl)acetaldehyde (19).



The title compound was prepared according to the method A by taking 3-methoxyphenylacetylene (100 mg, 0.75 mmol), 1,4-benzoquinone (81 mg, 0.75 mmol), CuCN (16.8 mg, 0.18 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 90:10) as yellow oil (204 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ - 9.74 (s, 1H), 7.33 – 7.27 (m, 1H), 7.26 – 7.24 (m, 2H), 7.00 – 6.95 (m, 2H), 6.89

(ddd, J = 8.2, 2.5, 0.9 Hz, 1H), 6.86 - 6.82 (m, 2H), 3.79 (s, 3H), 3.20 (s, 3H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): $\delta - 197.7, 159.7, 155.8, 138.7, 130.5, 129.5, 129.0, 121.1, 115.5, 114.2, 114.0, 89.0, 55.3, 53.0. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₆H₁₅O₄, 271.0965; found: 271.0955.$

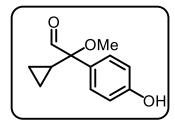
2-(4-hydroxyphenyl)-2-methoxy-2-(4-phenoxyphenyl)acetaldehyde (20).



The title compound was prepared according to the method A by taking 4-phenoxyphenylacetylene (100 mg, 0.51 mmol), 1,4-benzoquinone (55 mg, 0.51 mmol), CuCN (11.4 mg, 0.12 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 92:8) as yellow oil (261 mg, 78%). ¹H NMR (400 MHz, CDCl₃): δ - 9.62 (s, 1H), 7.25 (tt, J = 7.7, 2.4 Hz, 4H), 7.17 - 7.14 (m, 2H), 7.05 - 7.01 (m,

1H), 6.95 - 6.87 (m, 4H), 6.77 - 6.73 (m, 2H), 5.23 (d, J = 30.6 Hz, 1H), 3.09 (s, 3H). ${}^{13}C{}^{1}H$ } NMR (CDCl₃, 100 MHz): δ - 197.9, 157.7, 156.4, 156.0, 131.2, 130.5, 130.4, 129.9, 128.6, 123.9, 119.5, 118.3, 115.6, 88.9, 52.9. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₂₁H₁₈NaO₄, 357.1097; found: 357.1110.

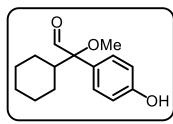
2-cyclopropyl-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (21).



The title compound was prepared according to the method A by taking cyclopropylacetylene (100 mg, 1.51 mmol), 1,4-benzoquinone (163.2 mg, 1.51 mmol), CuCN (33.7 mg, 0.37 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 95:5) as colourless oil (119 mg, 58%). ¹H NMR (400 MHz, CDCl₃): δ - 9.57 (s, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.09 – 6.00 (m, 1H), 5.03 (s, 1H), 3.29 (s, 3H), 2.19 (d, *J* = 3.4 Hz, 1H), 1.61 –

1.58 (m, 4H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 198.7, 155.4, 133.8, 130.5, 129.3, 115.4, 89.6, 52.7, 25.6, 24.5, 22.5. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₂H₁₃O₃, 205.0859; found: 205.0852.

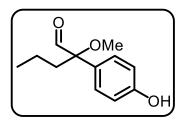
2-cyclohexyl-2-(4-hydroxyphenyl)-2-methoxyacetaldehyde (22).



The title compound was prepared according to the method A by taking ethynylcyclohexane (100 mg, 0.92 mmol), 1,4-benzoquinone (100 mg, 0.92 mmol), CuCN (20.6 mg, 0.23 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as colourless oil (210 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ - 9.56 (s, 1H), 7.35 – 7.33 (m, 2H), 6.88 – 6.86 (m, 2H), 6.06 (s,

1H), 3.30 (s, 3H), 2.03 (s, 1H), 1.34 (tt, J = 8.4, 5.5 Hz, 2H), 0.72 – 0.56 (m, 6H), 0.48 (dtd, J = 8.9, 5.3, 3.6 Hz, 2H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 200.4, 155.9, 129.2, 127.8, 115.4, 84.9, 52.3, 14.4, 1.8, 0.9. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₅H₁₉O₃, 247.1329; found: 247.1320.

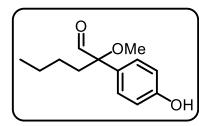
2-(4-hydroxyphenyl)-2-methoxypentanal (23).



The title compound was prepared according to the method A by taking 1-pentyne (100 mg, 1.47 mmol), 1,4-benzoquinone (158.9 mg, 1.47 mmol), CuCN (32.9 mg, 0.36 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 96:4) as colourless oil (94 mg, 45%). ¹H NMR (400 MHz, CDCl₃): δ - 9.44 (s, 1H), 7.26 (d, *J* = 2.4 Hz, 2H), 6.87 - 6.83 (m, 2H), 3.25 (s, 3H), 2.17

(ddd, J = 14.6, 10.7, 5.9 Hz, 1H), 1.99 (ddd, J = 14.6, 11.0, 5.6 Hz, 1H), 1.25 – 1.24 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ - 200.6, 155.6, 128.5, 115.7, 86.4, 51.2, 32.6, 29.7, 16.0, 14.4. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₂H₁₅O₃, 207.1016; found: 207.1009.

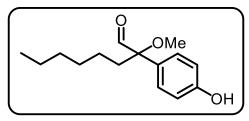
2-(4-hydroxyphenyl)-2-methoxyhexanal (24).



The title compound was prepared according to the method A by taking 1-hexyne (100 mg, 1.21 mmol), 1,4-benzoquinone (130.8 mg, 1.21 mmol), CuCN (26.8 mg, 0.30 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 96:4) as colourless oil (140 mg, 63%). ¹H NMR (400 MHz, CDCl₃): δ - 9.45 (s, 1H), 7.29 – 7.26 (m, 2H), 6.87 – 6.82 (m, 2H),

5.02 (s, 1H), 3.25 (s, 3H), 2.18 (ddd, J = 14.5, 10.0, 6.4 Hz, 1H), 2.00 (ddd, J = 14.5, 10.4, 6.2 Hz, 1H), 1.38 – 1.30 (m, 2H), 1.22 – 1.15 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 200.7, 155.6, 128.6, 128.5, 115.6, 86.3, 51.2, 30.1, 24.7, 23.0, 14.0. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₃H₁₇O₃, 221.1172; found: 221.1168.

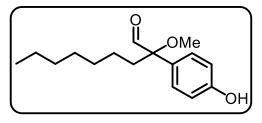
2-(4-hydroxyphenyl)-2-methoxyoctanal (25).



The title compound was prepared according to the method A by taking 1-octyne (100 mg, 0.90 mmol), 1,4benzoquinone (97.3 mg, 0.90 mmol), CuCN (19.7 mg, 0.22 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 96:4) as colourless oil (175 mg, 70%). ¹H NMR (400 MHz, CDCl₃): δ - 9.44

(s, 1H), 7.27 (d, J = 3.7 Hz, 1H), 6.84 (t, J = 5.8 Hz, 2H), 6.79 (dd, J = 5.3, 1.9 Hz, 1H), 3.24 (s, 3H), 2.18 (ddd, J = 14.5, 10.6, 5.6 Hz, 1H), 2.00 (ddd, J = 14.4, 11.0, 5.3 Hz, 1H), 1.32 – 1.21 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 200.7, 155.7, 128.5, 115.7, 114.8, 86.4, 51.2, 31.6, 30.3, 29.6, 22.6, 22.5, 14.0. HRMS (ESI) (m/z): [M+H]⁺ calculated for C₁₅H₂₂NaO₃, 273.1461; found: 273.1470.

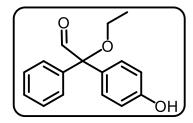
2-(4-hydroxyphenyl)-2-methoxynonanal (26).



The title compound was prepared according to the method A by taking 1-nonyne (100 mg, 0.80 mmol), 1,4benzoquinone (86.5 mg, 0.80 mmol), CuCN (17.9 mg, 0.20 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 96:4) as colourless oil (180 mg, 68%). ¹H NMR (400 MHz, CDCl₃): δ - 9.44 (s, 1H), 7.26 (dd, J = 6.5, 2.3 Hz, 2H),

6.85 (dd, J = 9.2, 2.4 Hz, 2H), 5.49 (s, 1H), 3.24 (s, 3H), 2.18 (ddd, J = 16.0, 10.7, 5.5 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.28 (dd, J = 11.1, 4.8 Hz, 10H), 0.87 (t, J = 6.9 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 200.8, 155.7, 128.5, 128.4, 115.7, 86.4, 51.2, 31.8, 30.3, 29.9, 29.2, 22.6, 22.5, 14.1. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₆H₂₃O₃, 263.1642; found: 263.1655.

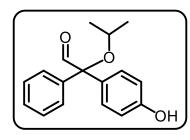
2-ethoxy-2-(4-hydroxyphenyl)-2-phenylacetaldehyde (27).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (106 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), ethanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 95:5) as yellow oil (225 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ - 9.74 (s, 1H), 7.43 - 7.33 (m, 5H), 7.24 (dt, *J* = 9.6, 2.5 Hz, 2H), 6.85 - 6.81 (m, 2H), 5.77 (s, 1H), 3.32 - 3.25 (m, 2H), 1.24 (t, *J* =

7.0 Hz, 3H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): δ - 198.6, 155.9, 137.6, 130.4, 129.4, 128.7, 128.5, 128.4, 115.5, 88.8, 60.8, 15.4. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₁₆H₁₆NaO₃, 279.0992; found: 279.0991.

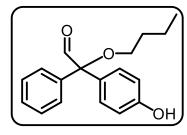
2-(4-hydroxyphenyl)-2-isopropoxy-2-phenylacetaldehyde (28).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (106 mg, 0.98 mmol), CuCN (21.4 mg, 0.24 mmol), isopropyl alcohol (3 ml) as solvent and purified by column chromatography (hexane: EA= 94:6) as yellow oil (194 mg, 72%). ¹H NMR (400 MHz, CDCl₃): δ - 9.75 (d, *J* = 5.7 Hz, 1H), 7.46 - 7.41 (m, 2H), 7.38 - 7.31 (m, 3H), 7.31 - 7.27 (m, 2H), 6.85 - 6.78 (m, 2H), 5.22 (d, *J*

= 69.2 Hz, 1H), 3.71 (dt, J = 12.2, 6.1 Hz, 1H), 1.03 (dd, J = 6.1, 2.8 Hz, 6H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 199.3, 155.6, 139.0, 131.0, 130.6, 128.9, 128.3, 128.2, 115.2, 88.6, 68.3, 23.9. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₇H₁₇O₃, 269.1172; found: 269.1166.

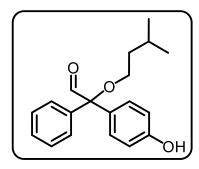
2-butoxy-2-(4-hydroxyphenyl)-2-phenylacetaldehyde (29).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (105.9 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), n-butanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 95:5) as yellow oil (170 mg, 60%). ¹H NMR (400 MHz, CDCl₃): δ - 9.75 (s, 1H), 7.45 – 7.32 (m, 5H), 7.29 – 7.27 (m, 1H), 7.26 (s, 1H), 6.85 – 6.80 (m, 2H), 5.20 (s, 1H), 3.27 – 3.20 (m, 2H),

1.63 – 1.57 (m, 2H), 1.45 – 1.38 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 198.9, 155.6, 138.1, 130.3, 130.1, 128.6, 128.4, 128.3, 115.3, 88.2, 64.9, 32.1, 19.4, 13.9. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₁₈H₂₀NaO₃, 307.1305; found: 307.1318.

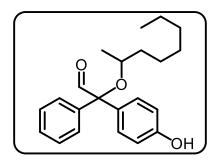
2-(4-hydroxyphenyl)-2-(isopentyloxy)-2-phenylacetaldehyde (30).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (105.9 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), iso-amyl alcohol (3 ml) as solvent and purified by column chromatography (hexane: EA= 97:3) as yellow oil (224 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ - 9.75 (s, 1H), 7.44 - 7.32 (m, 5H), 7.28 - 7.25 (m, 2H), 6.86 - 6.80 (m, 2H), 3.39 - 3.17 (m, 2H), 1.76 (td, *J* = 13.4, 6.7 Hz, 1H), 1.56 - 1.49 (m, 2H), 0.88 - 0.81 (m, 6H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 198.9, 155.7, 138.1, 130.3,

130.0, 128.6, 128.4, 128.3, 115.3, 88.3, 63.5, 38.9, 25.0, 22.6. HRMS (ESI) (m/z): $[M-H]^{-1}$ calculated for $C_{19}H_{21}O_3$, 297.1485; found: 297.1481.

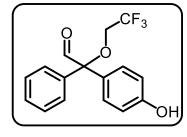
2-(4-hydroxyphenyl)-2-(octan-2-yloxy)-2-phenylacetaldehyde (31).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (105.9 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), 2-octanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 97:3) as yellow oil (129 mg, 38%). ¹H NMR (400 MHz, CDCl₃): δ - 9.72 (d, J = 0.8 Hz, 1H), 7.45 - 7.42 (m, 2H), 7.36 - 7.32 (m, 3H), 7.29 (d, J = 8.3 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 5.11 (s, 1H), 3.50 (dd, J = 12.0, 6.0 Hz, 1H), 1.49 - 1.41 (m, 2H), 1.23 - 1.13 (m, 8H), 0.96 (dd, J = 8.0, 4.3 Hz, 3H), 0.85 (d,

J = 6.6 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): $\delta - 199.8, 155.5, 130.8, 130.6, 129.1, 128.8, 128.3, 128.2, 115.2, 115.1, 71.7, 37.7, 31.8, 29.3, 25.3, 22.6, 21.3, 14.1. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₂₂H₂₇O₃, 339.1955; found: 339.1954.$

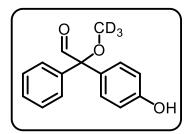
2-(4-hydroxyphenyl)-2-phenyl-2-(2,2,2-trifluoroethoxy)acetaldehyde (32).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (105.9 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), 2,2,2-trifluoroethanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 93:7) as yellow oil (269 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ - 9.83 (s, 1H), 7.43 – 7.37 (m, 5H), 7.24 – 7.18 (m, 2H), 6.90 – 6.84 (m, 2H), 3.76 – 3.67 (m, 2H).

¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 197.0, 156.6, 136.3, 130.4, 128.9, 128.6, 127.9, 125.1, 122.4, 115.9, 89.4, 62.8 (q, J = 34.9 Hz). ¹⁹F NMR (377 MHz, CDCl₃): δ -73.9. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₆H₁₂F₃O₃, 309.0733; found: 309.0740.

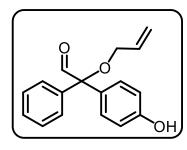
2-(4-hydroxyphenyl)-2-(methoxy-d₃)-2-phenylacetaldehyde (33).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (105.9 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), methanol-44 (3 ml) as solvent and purified by column chromatography (hexane: EA= 93:7) as yellow oil (42 mg, 90%). ¹H NMR (400 MHz, CDCl₃): δ - 9.68 (s, 1H), 7.35 - 7.31 (m, 4H), 7.31 - 7.28 (m, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.73 (s, 1H). ¹³C{¹H} NMR

 $\begin{array}{l} (CDCl_3, 100 \text{ MHz}): \delta - 198.0, 156.0, 137.2, 130.6, 129.1, 128.9, 128.7, 128.6, 115.6, 77.4. \ HRMS \\ (ESI) \ (m/z): \ [M-H]^- \ calculated \ for \ C_{15}H_{10}D_3O_3, 244.1048; \ found: 244.1061. \end{array}$

2-(allyloxy)-2-(4-hydroxyphenyl)-2-phenylacetaldehyde (34).

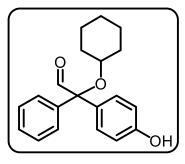


The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (105.9 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), allyl alcohol (3 ml) as solvent and purified by column chromatography (hexane: EA= 95:5) as yellow oil (198 mg, 74%). ¹H NMR (400 MHz, CDCl₃): δ - 9.78 (s, 1H), 7.43 (ddd, J = 4.6, 3.9, 2.2 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.27 (d, J = 8.7 Hz, 2H), 6.90 – 6.80 (m, 2H), 5.94 (ddt, J = 17.2, 10.5, 5.3 Hz, 1H), 5.34 (dq, J = 17.3, 1.7 Hz, 1H),

5.17 (ddd, J = 10.5, 3.1, 1.5 Hz, 1H), 3.83 – 3.77 (m, 2H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 198.3, 155.9, 137.6, 134.4, 130.4, 129.5, 128.7, 128.6, 128.5, 116.6, 115.5, 88.7, 66.3. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₇H₁₅O₃, 267.1016; found: 267.1011.

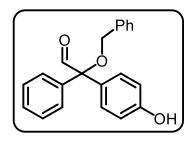
2-(cyclohexyloxy)-2-(4-hydroxyphenyl)-2-phenylacetaldehyde (35).

The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (105.9 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol),



cyclohexanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 95:5) as yellow oil (108 mg, 35%). ¹H NMR (400 MHz, CDCl₃): δ - 9.74 (s, 1H), 7.47 – 7.43 (m, 2H), 7.36 – 7.28 (m, 5H), 6.80 (d, J = 8.8 Hz, 2H), 5.07 (s, 1H), 3.42 – 3.35 (m, 1H), 1.62 (s, 4H), 1.43 – 1.36 (m, 2H), 1.29 (dd, J = 5.4, 3.0 Hz, 2H), 1.15 – 1.09 (m, 2H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 199.4, 155.5, 139.7, 139.2, 130.6, 128.8, 128.3, 128.2, 115.1, 88.4, 73.8, 33.9, 25.6, 24.3. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₂₀H₂₁O₃, 309.1485; found: 309.1501.

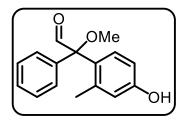
2-(benzyloxy)-2-(4-hydroxyphenyl)-2-phenylacetaldehyde (36).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (105.9 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), benzyl alcohol (3 ml) as solvent and purified by column chromatography (hexane: EA= 93:7) as yellow oil (175 mg, 55%). ¹H NMR (400 MHz, CDCl₃): δ - 9.86 (s, 1H), 7.49 – 7.47 (m, 2H), 7.41 – 7.30 (m, 10H), 6.88 – 6.82 (m, 2H), 4.34 (s, 2H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ - 198.3, 155.9, 138.2, 137.8, 132.9, 130.4, 128.7, 128.6, 128.5,

128.4, 127.6, 127.5, 115.5, 88.8, 67.2. HRMS (ESI) (m/z): $[M-H]^-$ calculated for $C_{21}H_{17}O_3$, 317.1172; found: 317.1158.

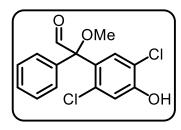
2-(4-hydroxy-2-methylphenyl)-2-methoxy-2-phenylacetaldehyde (37).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), methyl-*p*-benzoquinone (119.6 mg, 0.98 mmol), CuCN (21.9 mg, 0.24 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 92:8) as yellow oil (215 mg, 84%). ¹H NMR (400 MHz, CDCl₃): δ - 9.66 (s, 1H), 7.33 – 7.25 (m, 5H), 7.03 (d, *J* = 1.7 Hz, 1H), 6.95 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.45 (d,

J = 21.7 Hz, 1H), 3.09 (s, 3H), 2.13 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 197.9, 154.4, 136.9, 131.6, 128.8, 128.6, 128.5, 127.9, 127.8, 124.4, 115.0, 89.3, 52.9, 16.0. HRMS (ESI) (m/z): [M+Na]⁺ calculated for C₁₆H₁₆NaO₃, 279.0992; found: 279.0999.

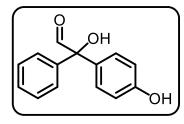
2-(2,5-dichloro-4-hydroxyphenyl)-2-methoxy-2-phenylacetaldehyde (38).



The title compound was prepared according to the method A by taking phenylacetylene (100 mg, 0.98 mmol), 2,5-dichlorobenzoquinone (172.4 mg, 0.98 mmol), CuCN (25.9 mg, 0.24 mmol), methanol (3 ml) as solvent and purified by column chromatography (hexane: EA= 92:8) as yellow oil (207 mg, 67%). ¹H NMR (400 MHz, CDCl₃): δ - 9.80 (s, 1H), 7.57 (s, 1H), 7.42 – 7.37

(m, 5H), 7.10 (s, 1H), 3.21 (s, 3H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100 MHz): δ - 195.8, 152.2, 135.3, 133.5, 131.5, 129.3, 128.7, 128.6, 128.4, 118.7, 118.6, 87.8, 52.9. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₅H₁₁Cl₂O₃, 309.0080; found: 309.1752.

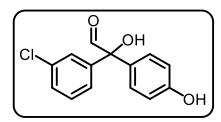
2-hydroxy-2-(4-hydroxyphenyl)-2-phenylacetaldehyde (39).



The title compound was prepared according to the method B by taking phenylacetylene (100 mg, 0.98 mmol), 1,4-benzoquinone (106 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), TFA (56 mg, 0.5 mmol) and MeCN/H₂O (1:1) as solvent and purified by column chromatography (hexane: EA= 88:12) as yellow oil (171 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ - 9.91 (s, 1H), 7.44 – 7.40 (m, 1H), 7.38 (dd, *J* = 4.2, 1.7 Hz, 3H), 7.37 – 7.33 (m, 1H), 7.21 – 7.17 (m,

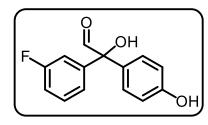
2H), 6.84 - 6.80 (m, 2H), 5.36 (s, 1H), 4.39 (s, 1H). ${}^{13}C{}^{1}H}$ NMR (CDCl₃, 100 MHz): $\delta - 198.0$, 155.9, 139.2, 131.4, 129.1, 128.8, 128.5, 127.4, 115.8, 83.2. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₄H₁₁O₃, 227.0703; found: 227.0716.

2-(3-chlorophenyl)-2-hydroxy-2-(4-hydroxyphenyl)acetaldehyde (40)



The title compound was prepared according to the method B by taking 3-chlorophenylacetylene (100 mg, 0.73 mmol), 1,4benzoquinone (78.9 mg, 0.73 mmol), CuCN (16.3 mg, 0.18 mmol), TFA (41 mg, 0.36 mmol) and MeCN/H₂O (1:1) as solvent and purified by column chromatography (hexane: EA= 90:10) as yellow oil (180 mg, 69%). ¹H NMR (400 MHz, CDCl₃): δ - 9.90 (s, 1H), 7.43 - 7.40 (m, 1H), 7.37 - 7.32 (m, 2H), 7.29 - 7.26 (m, 1H), 7.20 - 7.16 (m, 2H), 6.88 - 6.83 (m, 2H), 5.26 (d, *J* = 29.1 Hz, 1H), 4.38 (s, 1H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 197.3, 156.0, 141.2, 135.0, 131.1, 130.0, 129.0, 128.7, 127.6, 125.5, 115.9, 82.8. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₄H₁₀ClO₃, 261.0313; found: 261.0324.

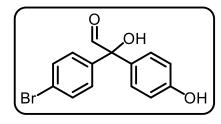
2-(3-fluorophenyl)-2-hydroxy-2-(4-hydroxyphenyl)acetaldehyde (41)



The title compound was prepared according to the method B by taking 3-fluorophenylacetylene (100 mg, 0.83 mmol), 1,4benzoquinone (89.7 mg, 0.83 mmol), CuCN (18.6 mg, 0.20 mmol), TFA (46 mg, 0.4 mmol) and MeCN/H₂O (1:1) as solvent and purified by column chromatography (hexane: EA= 90:10) as yellow oil (159 mg, 65%). ¹H NMR (400 MHz, CDCl₃): δ - 9.90 (d, J = 1.1 Hz, 1H), 7.38 (td, J = 8.1, 5.9 Hz, 1H), 7.20 – 7.13 (m,

4H), 7.06 (tdd, J = 8.3, 2.5, 1.0 Hz, 1H), 6.88 – 6.83 (m, 2H), 5.28 (d, J = 21.9 Hz, 1H), 4.38 (d, J = 1.2 Hz, 1H). $^{13}C{^{1}H}$ NMR (CDCl₃, 100 MHz): δ - 197.4, 155.6 (d, J = 85.8 Hz), 131.0, 130.3 (d, J = 8.2 Hz), 128.6 (d, J = 28.3 Hz), 127.6 (d, J = 31.8 Hz), 123.0, 116.2, 115.9, 115.7 (d, J = 9.1 Hz), 115.3 (d, J = 19.9 Hz), 114.6 (d, J = 23.1 Hz), 82.8. ^{19}F NMR (377 MHz, CDCl₃): δ - 111.3. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₄H₁₀FO₃, 245.0608; found: 245.0624.

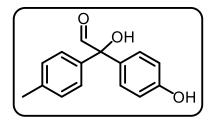
2-(4-bromophenyl)-2-hydroxy-2-(4-hydroxyphenyl)acetaldehyde (42)



The title compound was prepared according to the method B by taking 4-bromophenylacetylene (100 mg, 0.73 mmol), 1,4-benzoquinone (78.9 mg, 0.73 mmol), CuCN (16.3 mg, 0.18 mmol), TFA (41 mg, 0.36 mmol) and MeCN/H₂O (1:1) as solvent and purified by column chromatography (hexane: EA= 90:10) as yellow oil (185 mg, 60%). ¹H NMR (400 MHz, CDCl₃): δ - 9.88 (d, *J* = 1.0 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.29

-7.26 (m, 2H), 7.19 -7.14 (m, 2H), 6.86 -6.82 (m, 2H), 5.36 (s, 1H), 4.37 (d, *J* = 1.2 Hz, 1H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 197.4, 156.0, 138.2, 132.0, 131.0, 129.1, 129.0, 122.8, 115.9, 82.9. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₄H₁₀BrO₃, 304.9809; found: 304.9816.

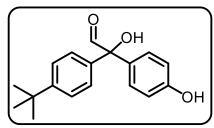
2-hydroxy-2-(4-hydroxyphenyl)-2-(p-tolyl)acetaldehyde (43)



The title compound was prepared according to the method B by taking 4-methylphenylacetylene (100 mg, 0.86 mmol), 1,4benzoquinone (108 mg, 0.86 mmol), CuCN (19.2 mg, 0.22 mmol), TFA (49 mg, 0.43 mmol) and MeCN/H₂O (1:1) as solvent and purified by column chromatography (hexane: EA= 89:11) as yellow oil (164 mg, 68%). ¹H NMR (400 MHz, CDCl₃): δ - 9.89

(s, 1H), 7.26 - 7.24 (m, 2H), 7.22 - 7.19 (m, 4H), 6.85 - 6.82 (m, 2H), 4.34 (s, 1H), 2.36 (s, 3H). $^{13}C{^{1}H}$ NMR (CDCl₃, 100 MHz): δ - 198.0, 155.9, 138.4, 136.3, 131.4, 129.5, 129.1, 127.4, 115.7, 83.1, 21.1. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₅H₁₃O₃, 241.0859; found: 241.0870.

2-(4-(tert-butyl)phenyl)-2-hydroxy-2-(4-hydroxyphenyl)acetaldehyde (44)

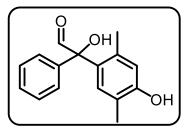


The title compound was prepared according to the method B by taking 4-*tert*-butylphenylacetylene (100 mg, 0.63 mmol), 1,4-benzoquinone (68 mg, 0.63 mmol), CuCN (14 mg, 0.16 mmol), TFA (56 mg, 0.5 mmol) and MeCN/H₂O (1:1) as solvent and purified by column chromatography (hexane: EA= 88:12) as yellow oil (213 mg, 75%). ¹H NMR (400 MHz,

CDCl₃): δ - 9.90 (s, 1H), 7.43 – 7.40 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.88 – 6.82 (m, 2H), 4.33 (s, 1H), 1.32 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 198.0, 155.8, 151.6, 136.2, 131.4, 129.1, 127.1, 125.8, 115.7, 83.0, 31.3, 29.7. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₈H₁₉O₃, 283.1329; found: 283.1335.

2-hydroxy-2-(4-hydroxy-2,5-dimethylphenyl)-2-phenylacetaldehyde (45)

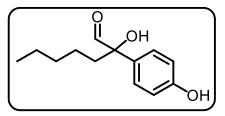
The title compound was prepared according to the method B by taking phenylacetylene (100 mg,



0.98 mmol), 2,5-dimethylbenzoquinone (133 mg, 0.98 mmol), CuCN (21.9 mg, 0.25 mmol), TFA (56 mg, 0.5 mmol) and MeCN/H₂O (1:1) as solvent and purified by column chromatography (hexane: EA= 88:12) as yellow oil (158 mg, 62%). ¹H NMR (400 MHz, CDCl₃): δ - 9.96 (d, *J* = 1.4 Hz, 1H), 7.42 - 7.36 (m, 4H), 7.33 (ddd, *J* = 8.6, 4.7, 3.7 Hz, 1H), 6.88 (s, 1H), 6.63 (s, 1H), 4.86 (s, 1H), 4.33 (d, *J* = 1.4 Hz, 1H), 2.19 (d, *J* = 7.6 Hz, 3H), 1.95 (s, 3H). ¹³C{¹H} NMR (CDCl₃,

100 MHz): δ - 197.7, 153.8, 138.3, 137.5, 132.5, 128.6, 128.0, 127.7, 120.2, 119.2, 89.5, 53.0, 20.2, 15.5. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₆H₁₅O₃, 255.1016; found: 255.1028.

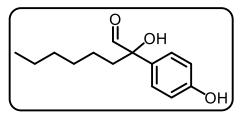
2-hydroxy-2-(4-hydroxyphenyl)heptanal (46)



The title compound was prepared according to the method B by taking 1-heptyne (100 mg, 1 mmol), 1,4-benzoquinone (108 mg, 1 mmol), CuCN (22.3 mg, 0.25 mmol), TFA (57 mg, 0.5 mmol) and MeCN/H₂O (1:1) as solvent and purified by column chromatography (hexane: EA= 92:8) as colourless oil (122 mg, 55%). ¹H NMR (400 MHz, CDCl₃): δ - 9.51 (s, 1H), 7.34 (d, *J*

= 8.8 Hz, 2H), 6.88 – 6.84 (m, 2H), 5.11 (s, 1H), 3.79 (s, 1H), 1.99 (ddd, J = 18.4, 9.6, 3.9 Hz, 2H), 1.29 (dd, J = 6.1, 2.1 Hz, 6H), 0.86 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 200.2, 155.4, 130.5, 127.4, 115.7, 81.5, 36.5, 32.0, 29.7, 22.5, 14.0. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₃H₁₇O₃, 221.1172; found: 221.1174.

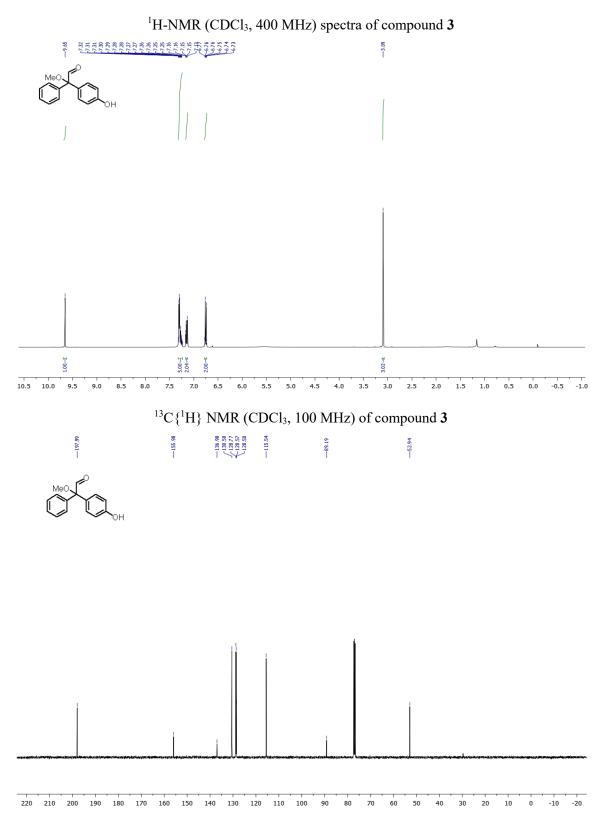
2-hydroxy-2-(4-hydroxyphenyl)octanal (47)

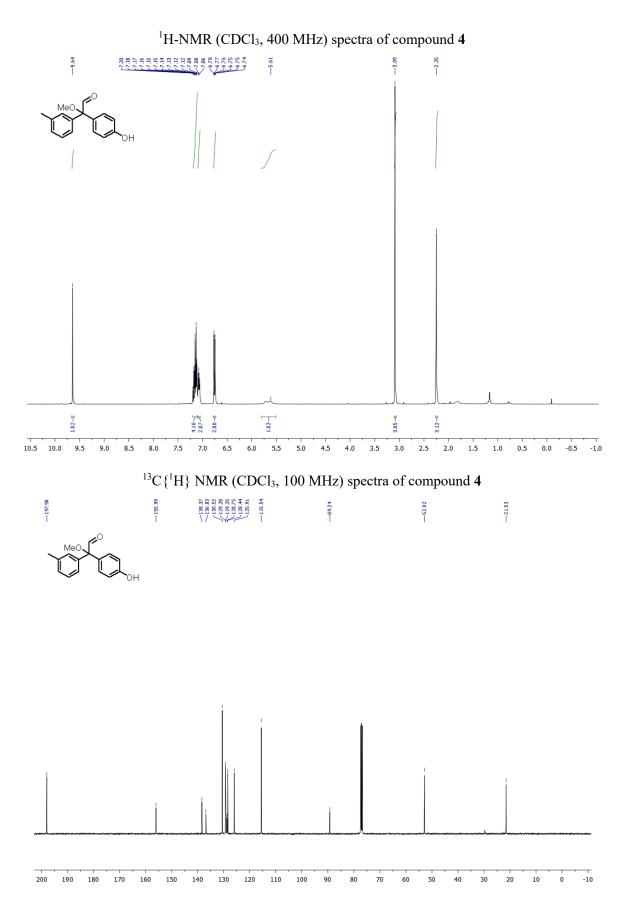


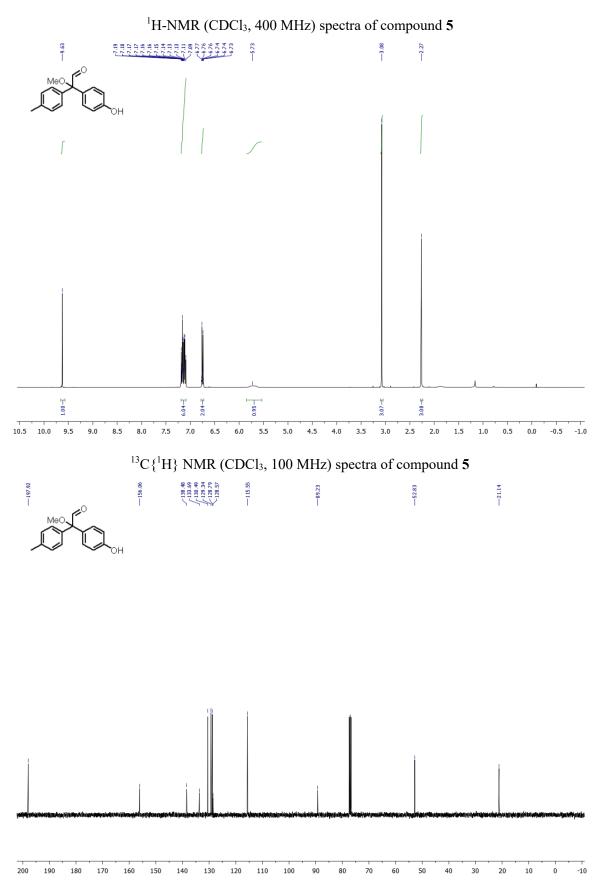
The title compound was prepared according to the method B by taking 1-octyne (100 mg, 0.89 mmol), 1,4benzoquinone (96 mg, 0.89 mmol), CuCN (20 mg, 0.22 mmol), TFA (46 mg, 0.4 mmol) and MeCN/H₂O (1:1) as solvent and purified by column chromatography (hexane: EA= 92:8) as yellow oil (146 mg, 52%). ¹H NMR (400

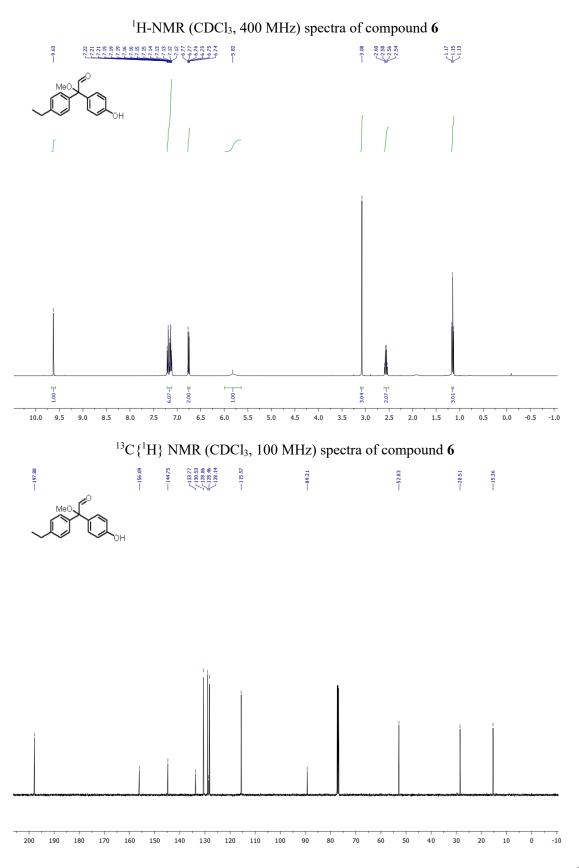
MHz, CDCl₃): δ - 9.51 (s, 1H), 7.34 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.06 (s, 1H), 3.79 (s, 1H), 2.06 - 1.93 (m, 2H), 1.31 (dd, J = 13.4, 6.0 Hz, 8H), 0.86 (t, J = 6.8 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ - 200.2, 155.4, 130.5, 127.4, 115.7, 81.5, 36.5, 31.6, 29.5, 22.6, 22.5, 14.1. HRMS (ESI) (m/z): [M-H]⁻ calculated for C₁₄H₁₉O₃, 235.1329; found: 235.1329.

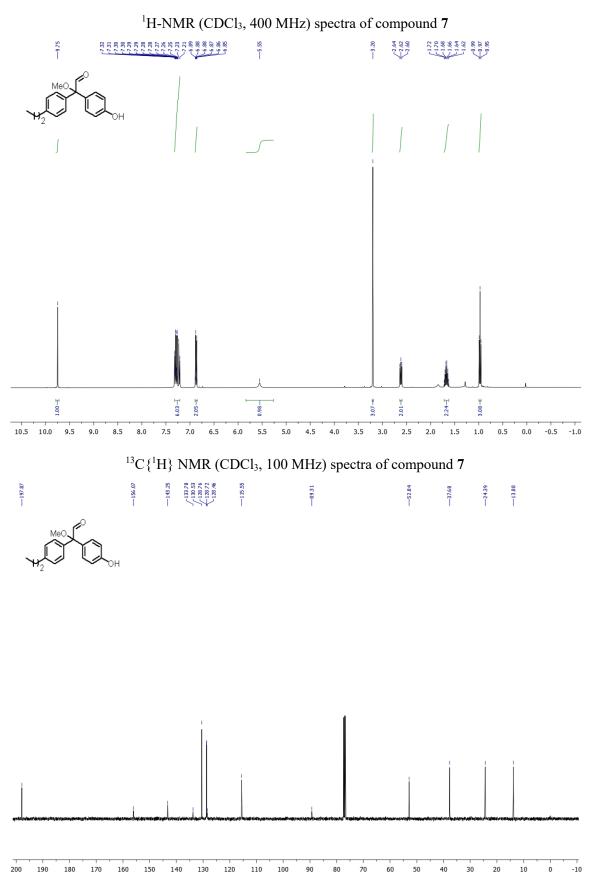
5. NMR Spectra

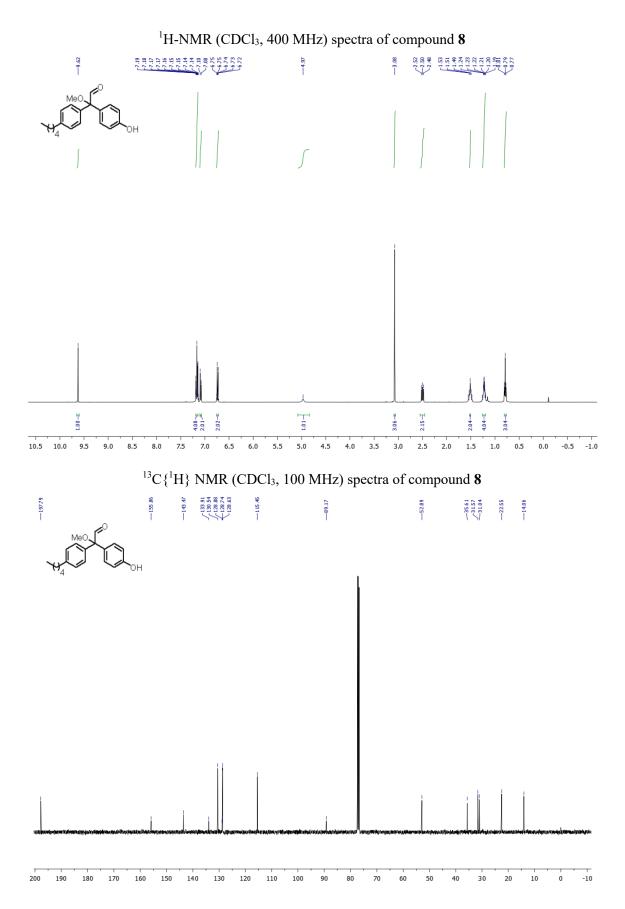


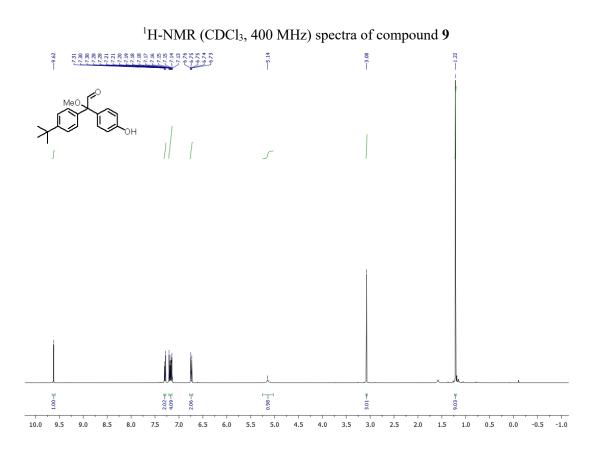


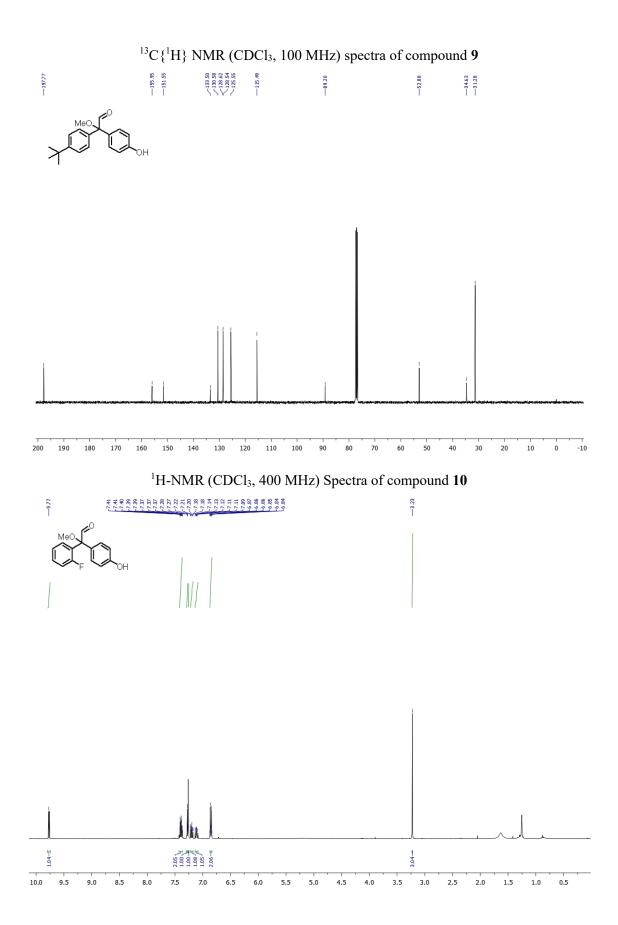


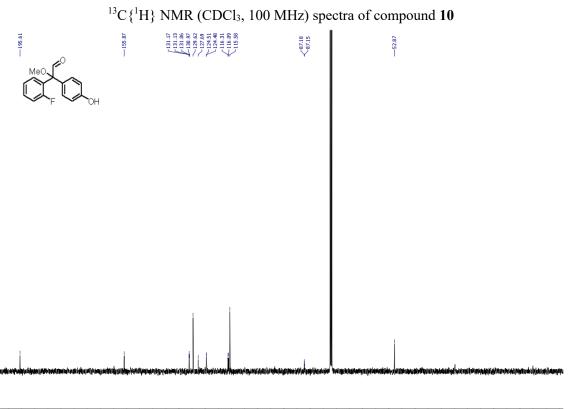










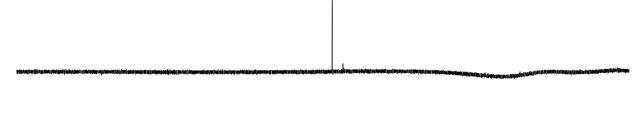


-10 ò

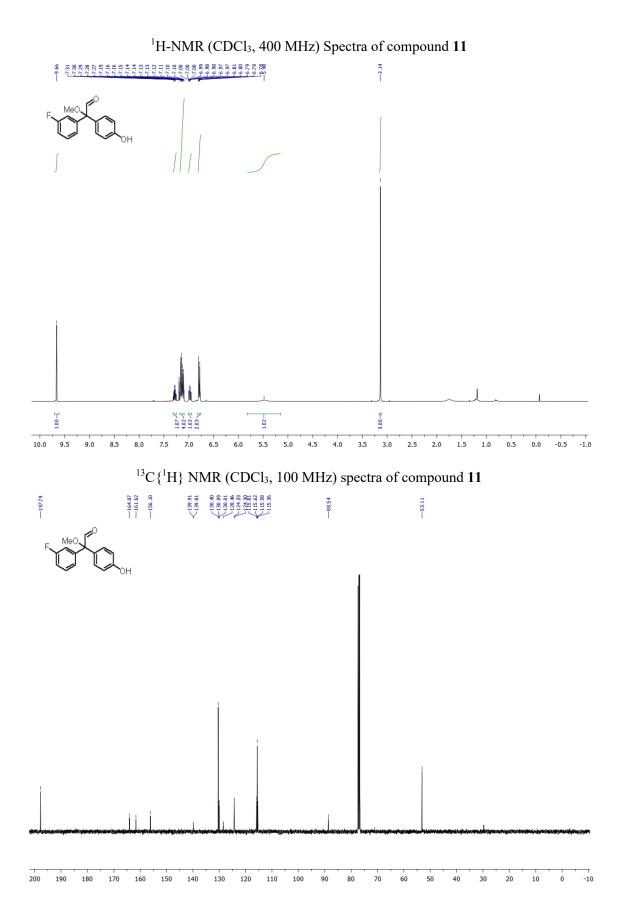
¹⁹F-NMR (CDCl₃, 377 MHz) Spectra of compound 10

----108.41





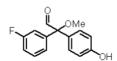
-																		· · · ·	
-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200



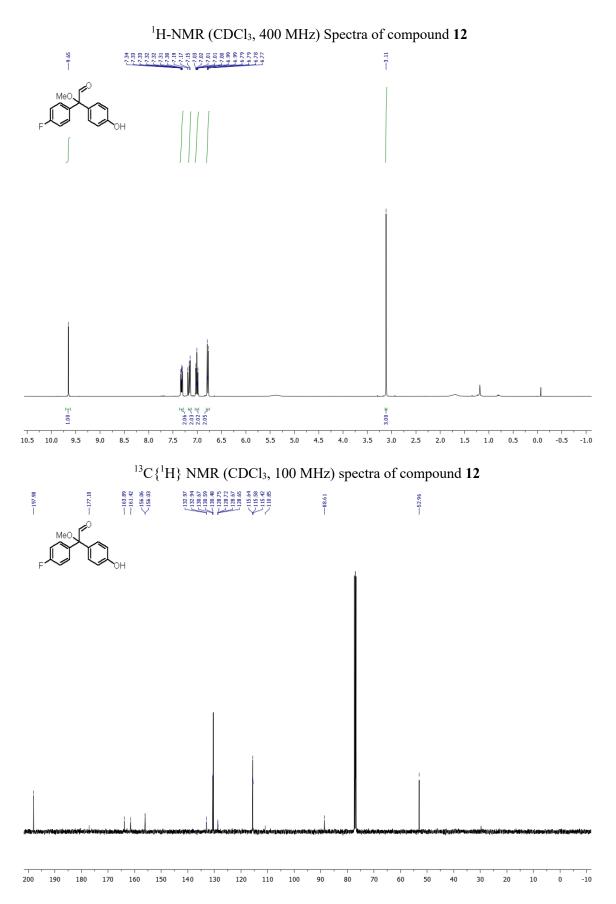
S30

¹⁹F-NMR (CDCl₃, 377 MHz) Spectra of compound 11

----111.86

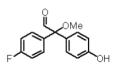


			- · ·	- I I															
-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200

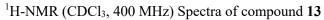


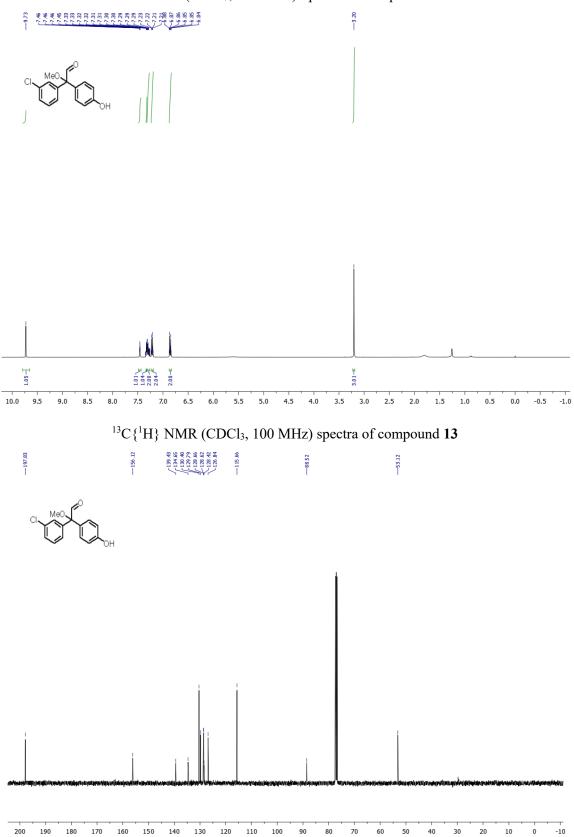
¹⁹F-NMR (CDCl₃, 377 MHz) Spectra of compound **12**

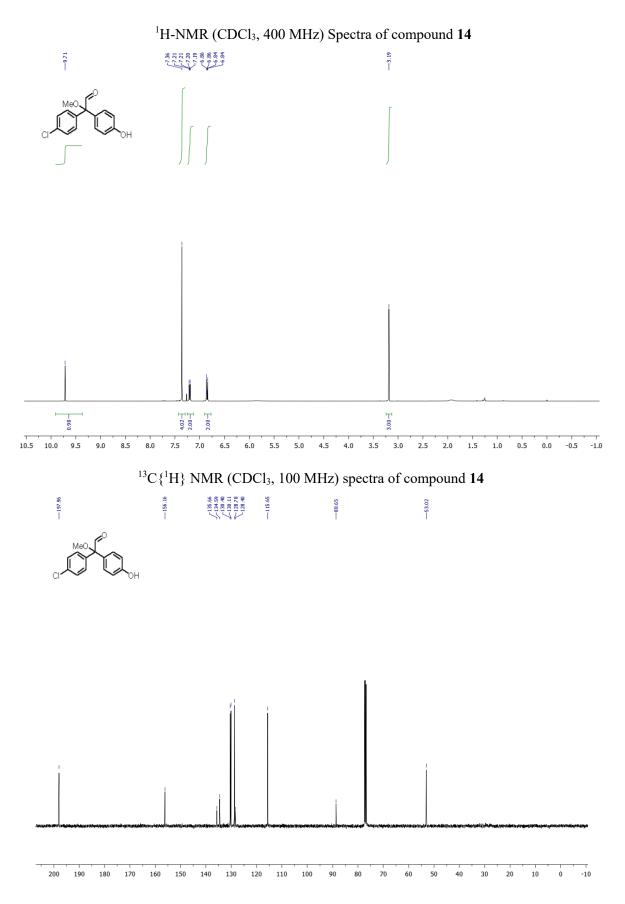
----113.21

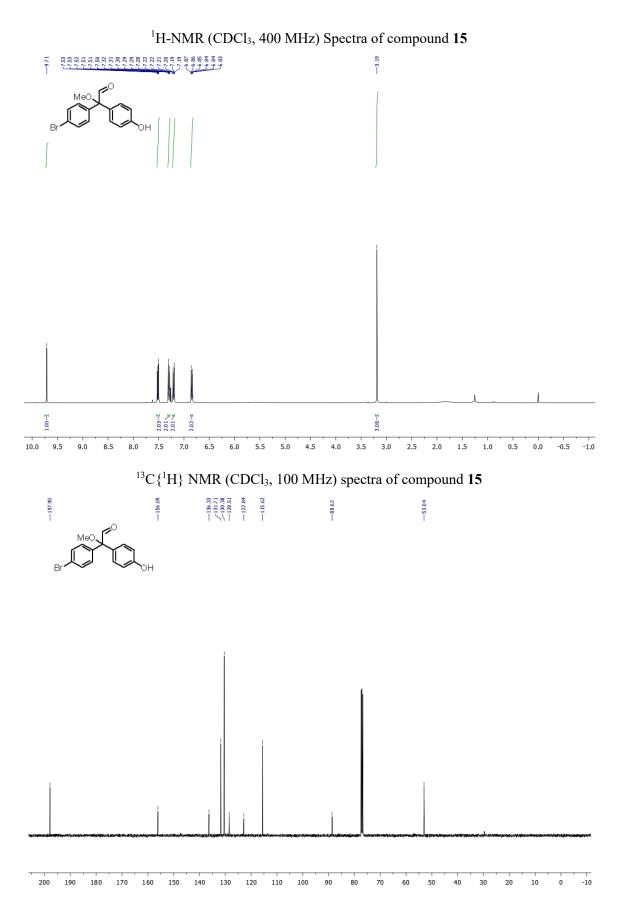


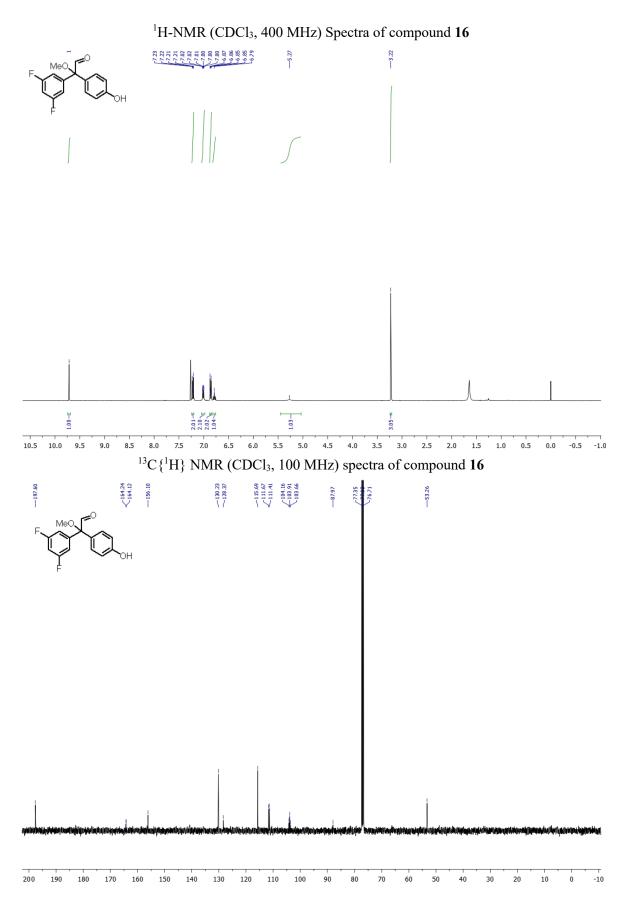
-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200

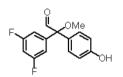




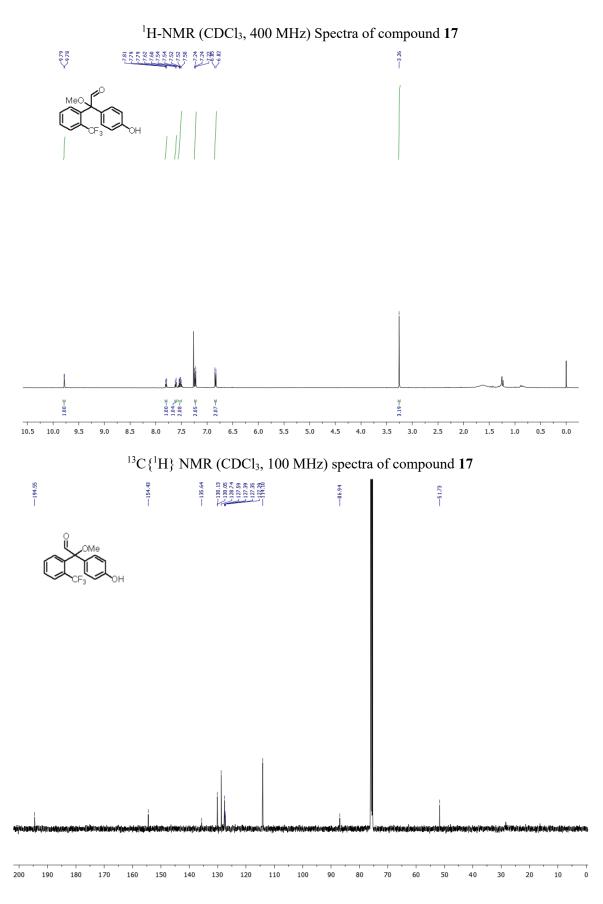


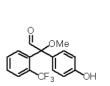






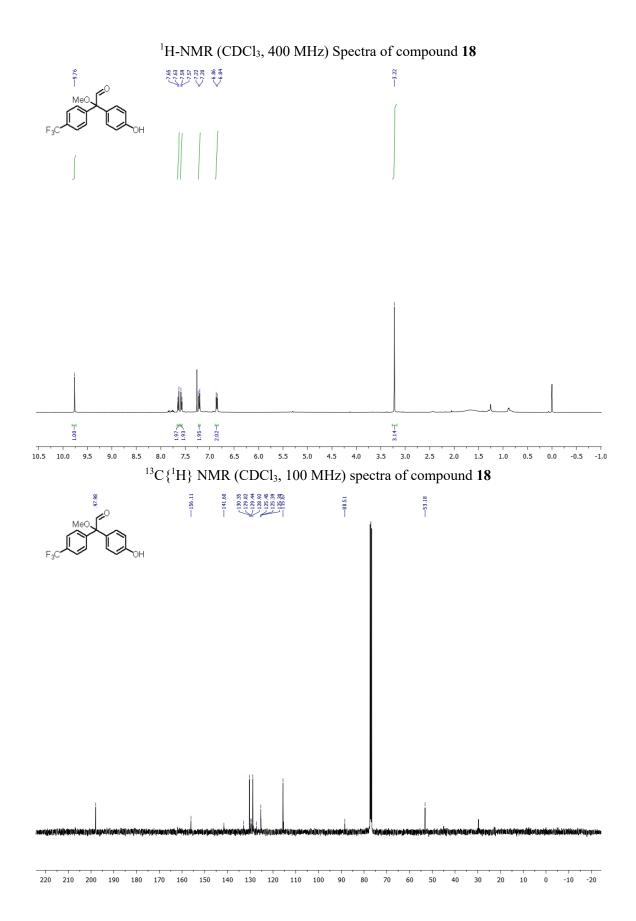
-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200

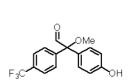




-----56.23

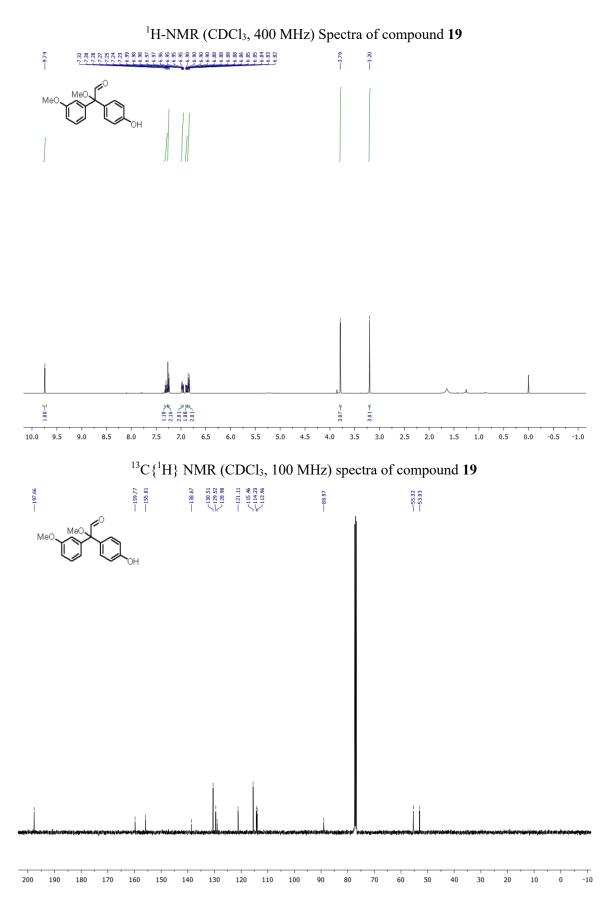
_																			· · · ·
-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200

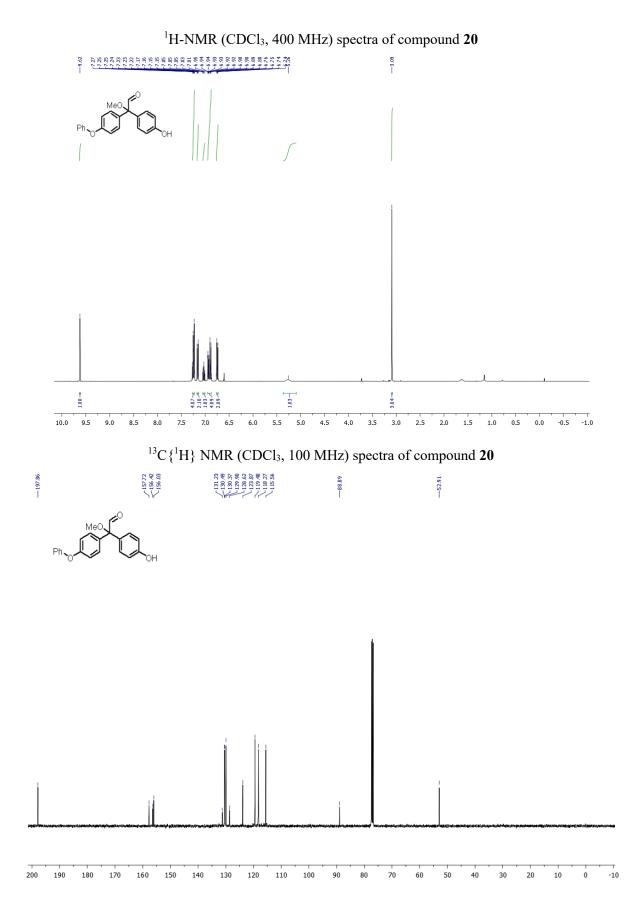


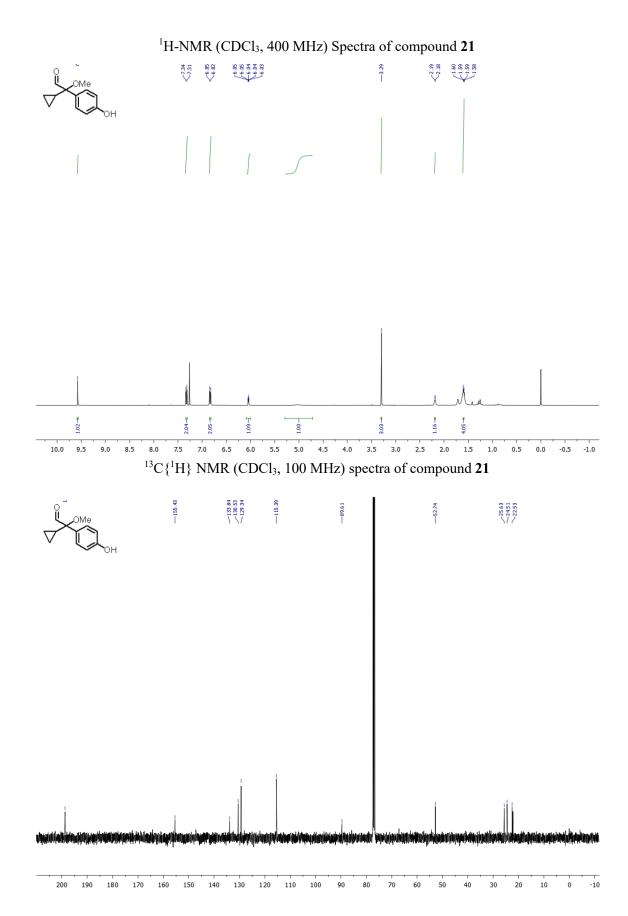


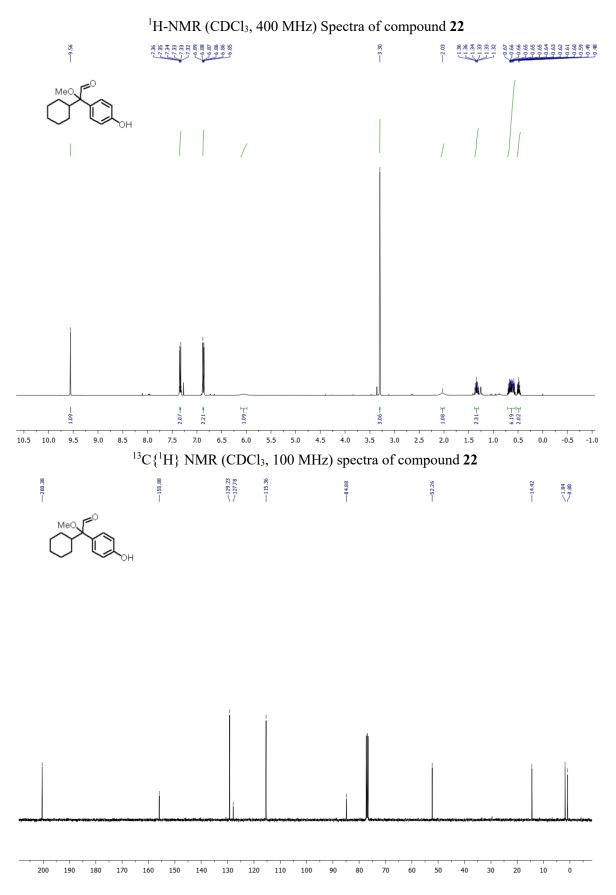
----62.69

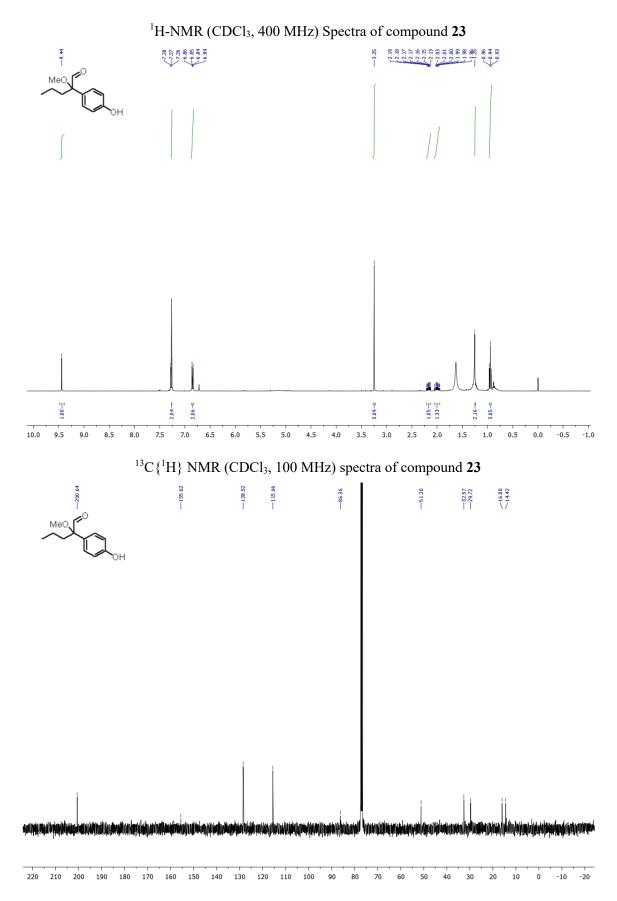
+																	· · · ·		
-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200

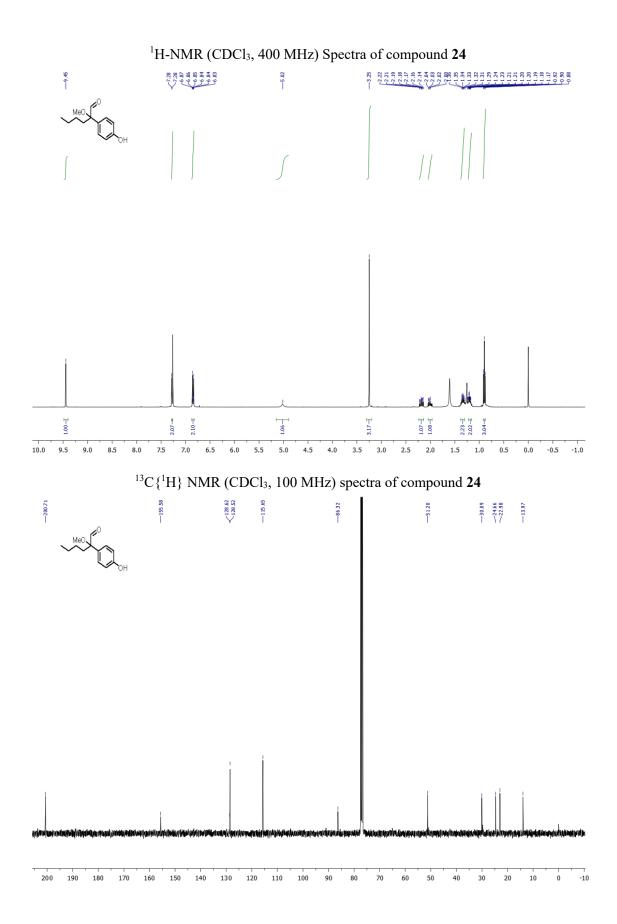


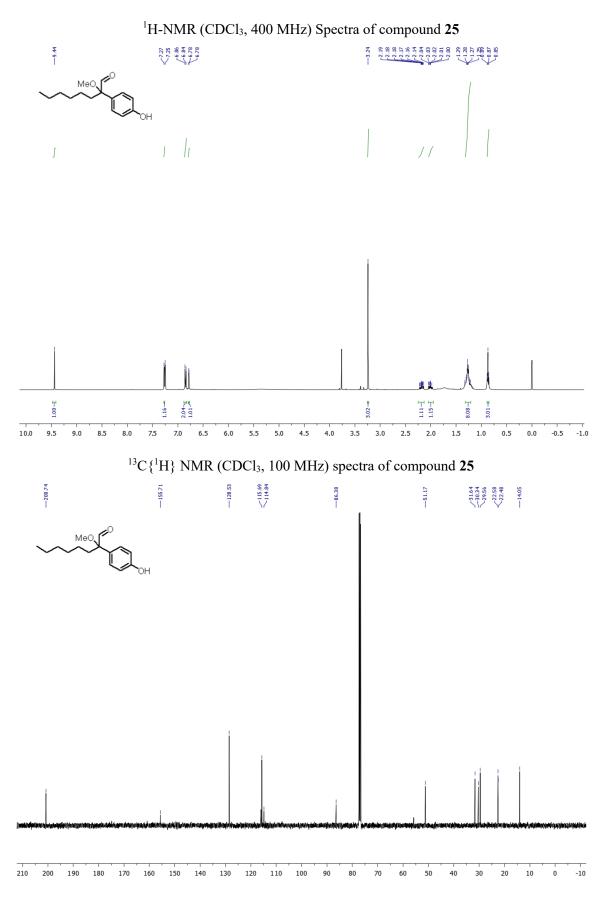


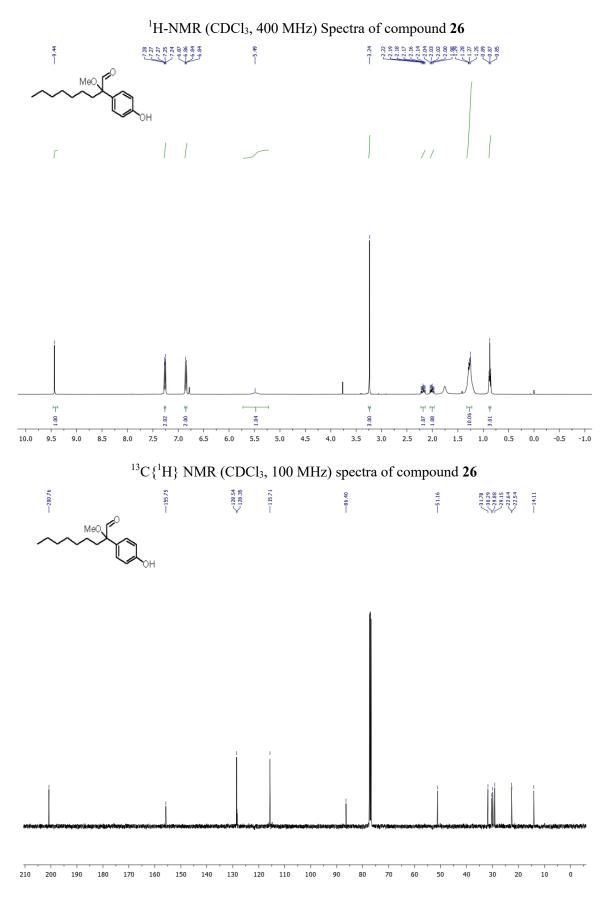


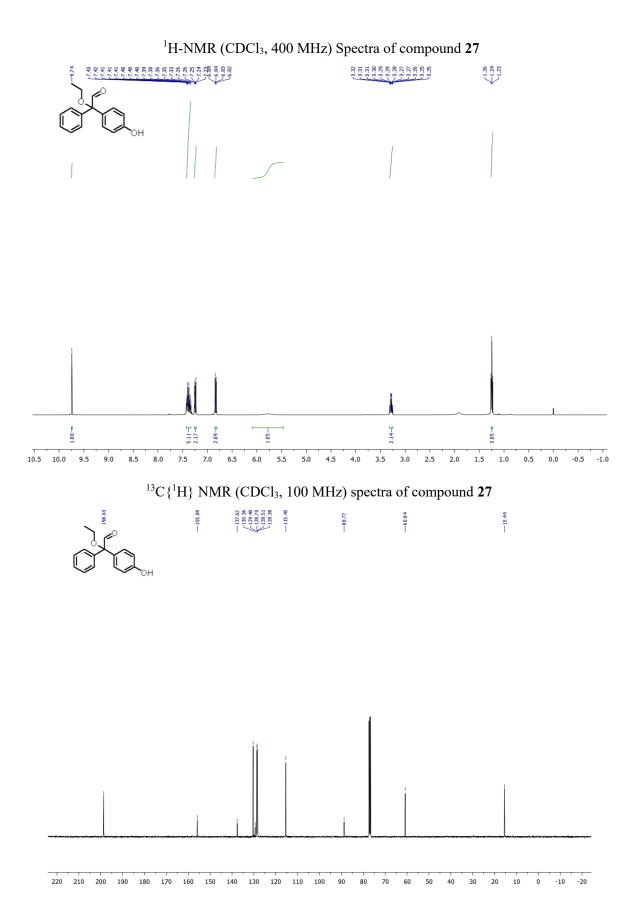


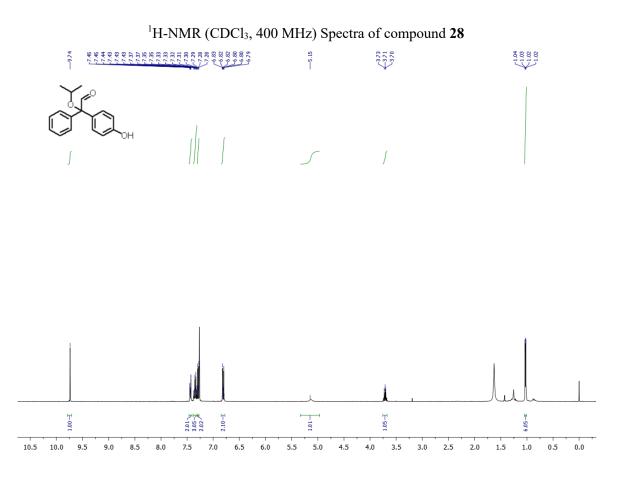


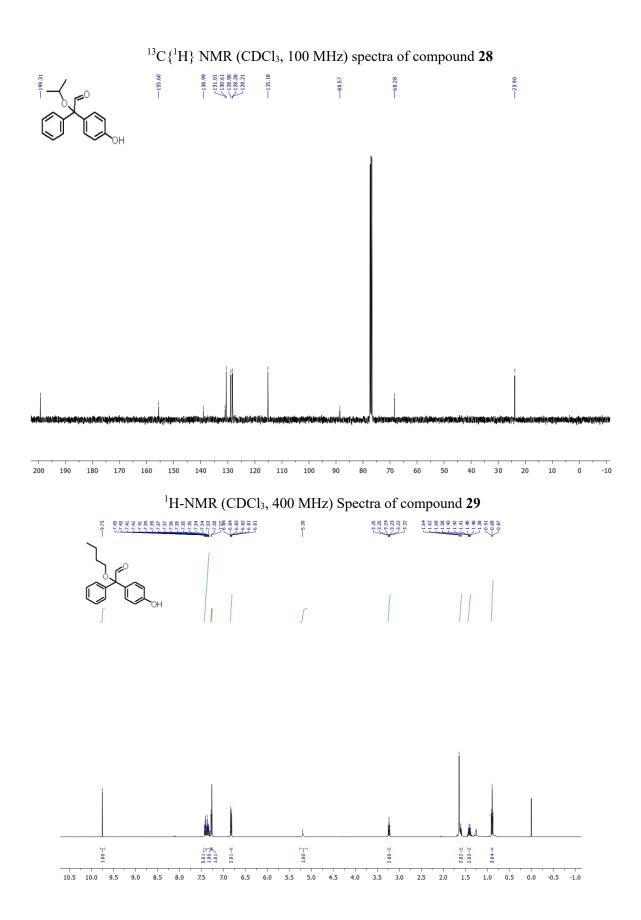


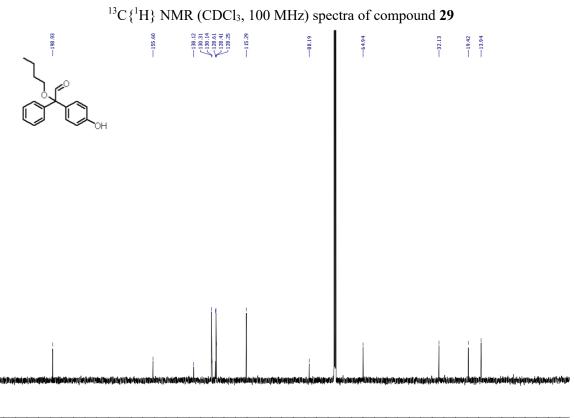


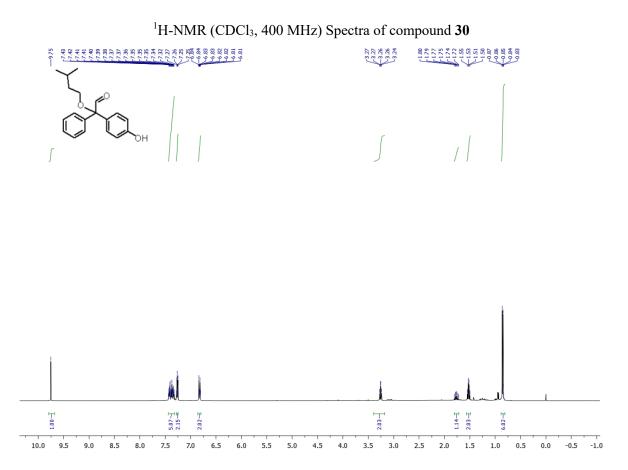


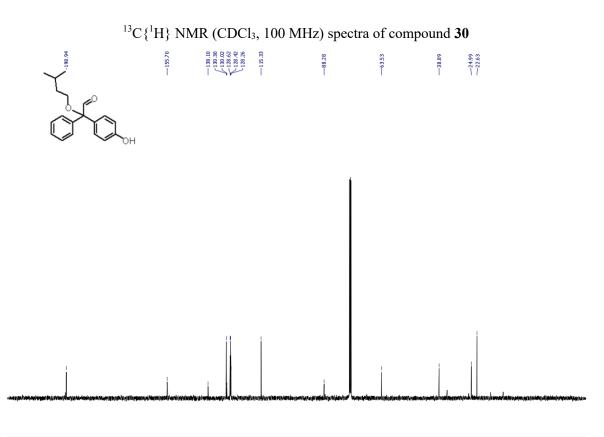


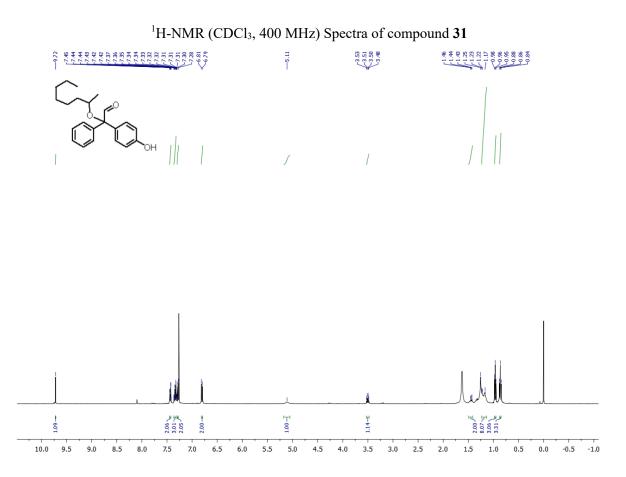


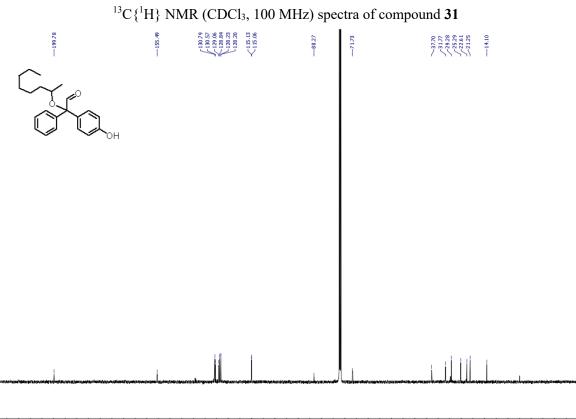


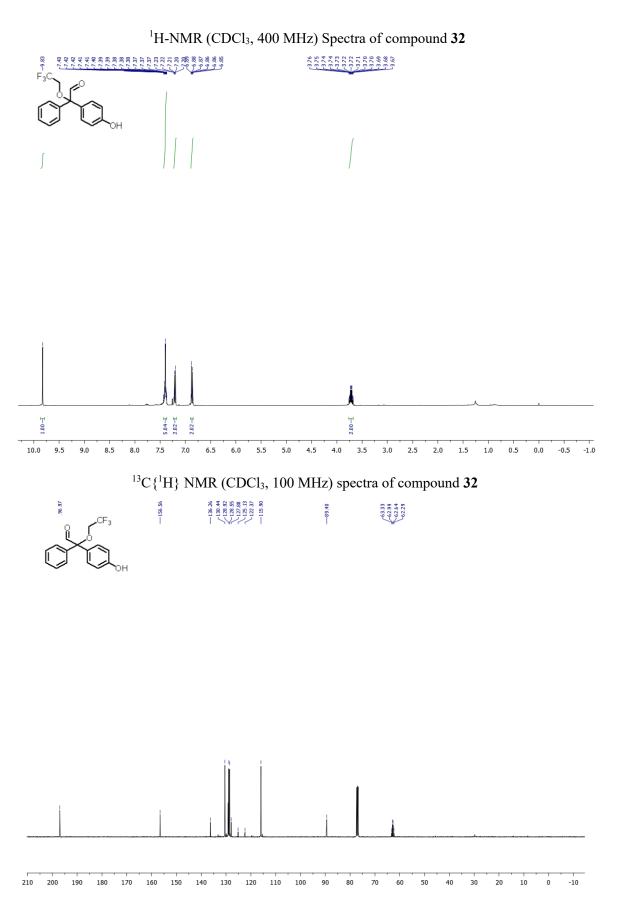






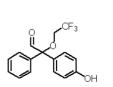




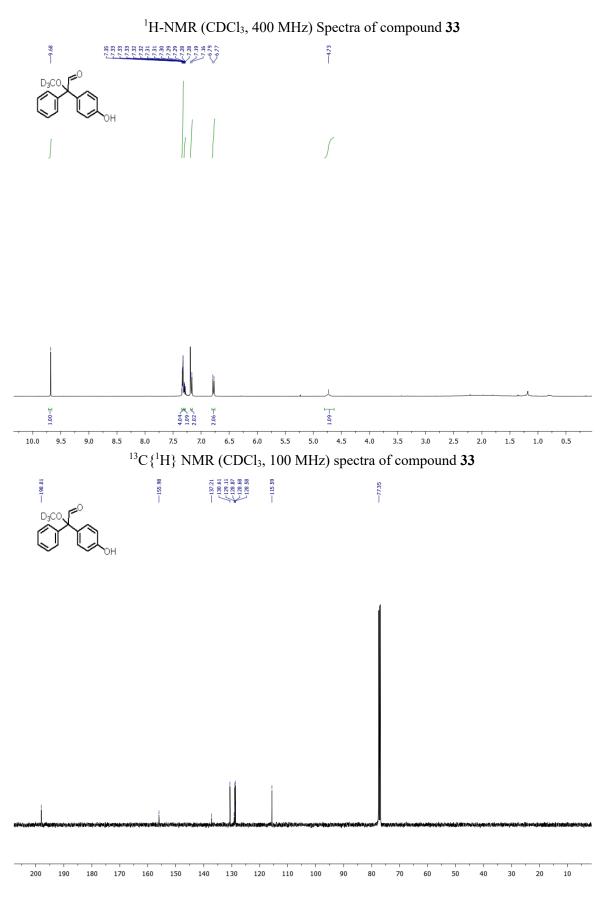


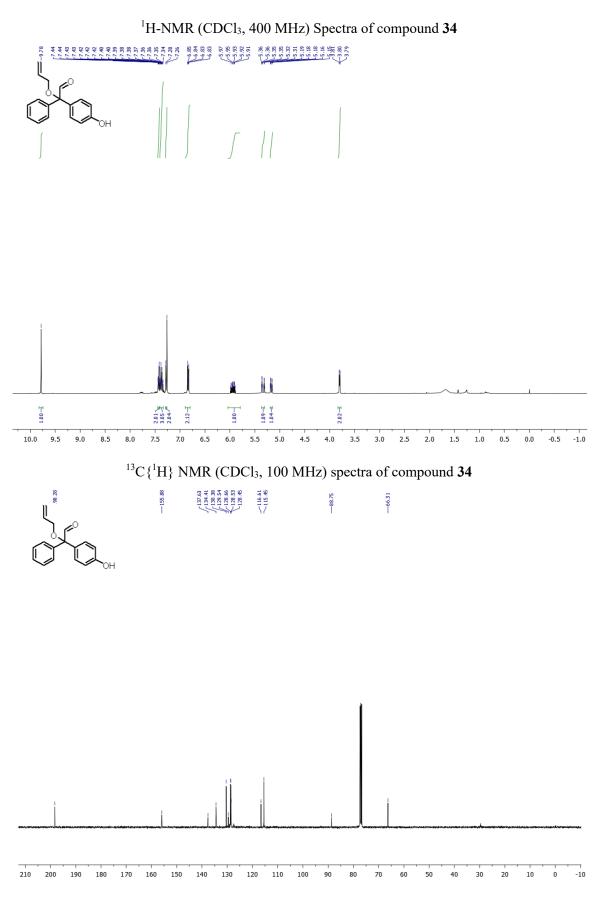
-----73.93

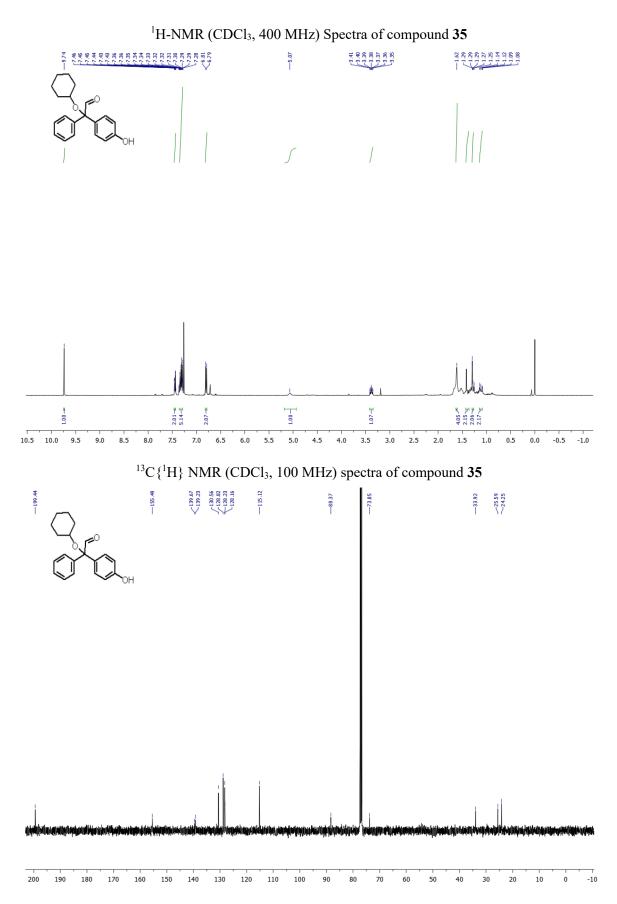
I

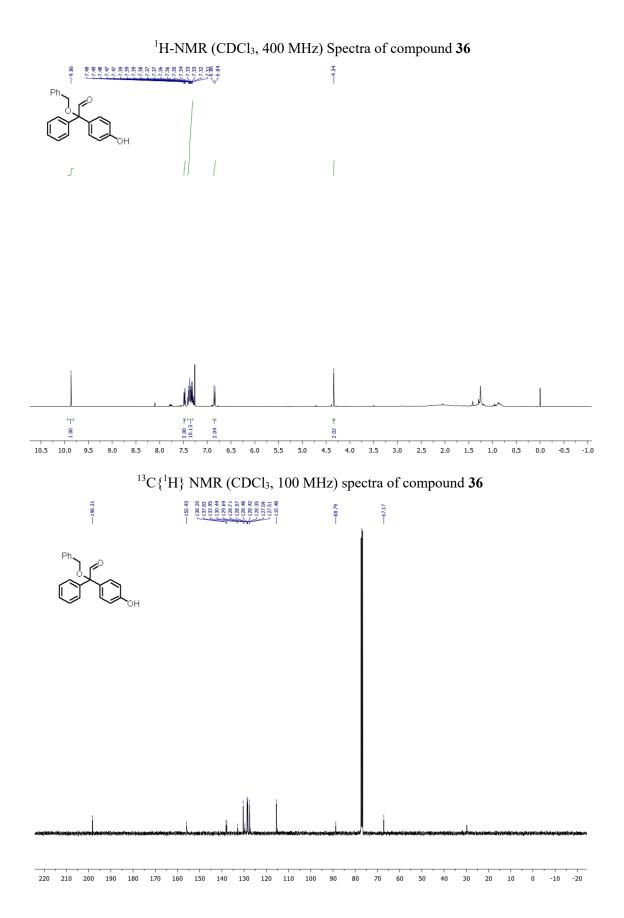


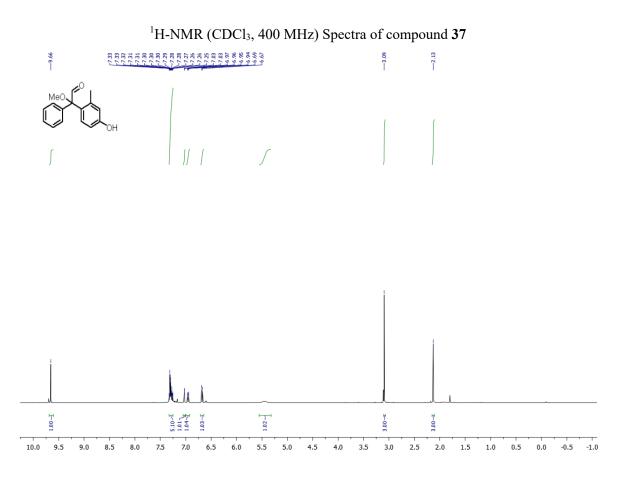
-10 -20 -200 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190

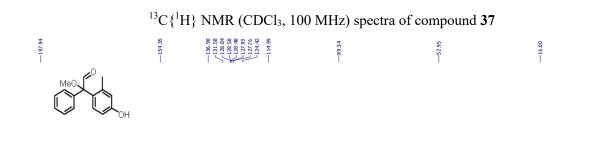


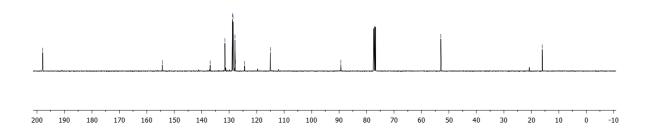


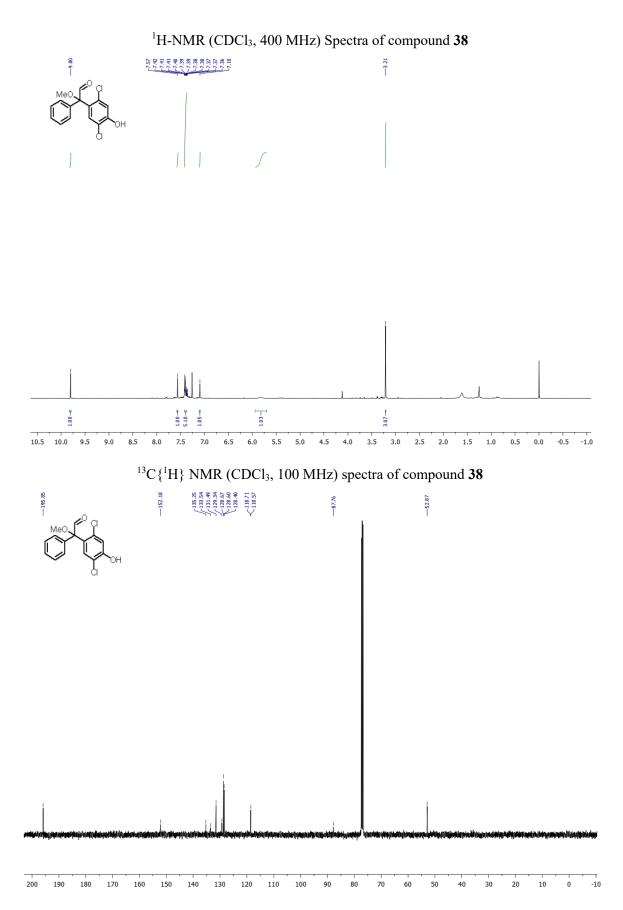


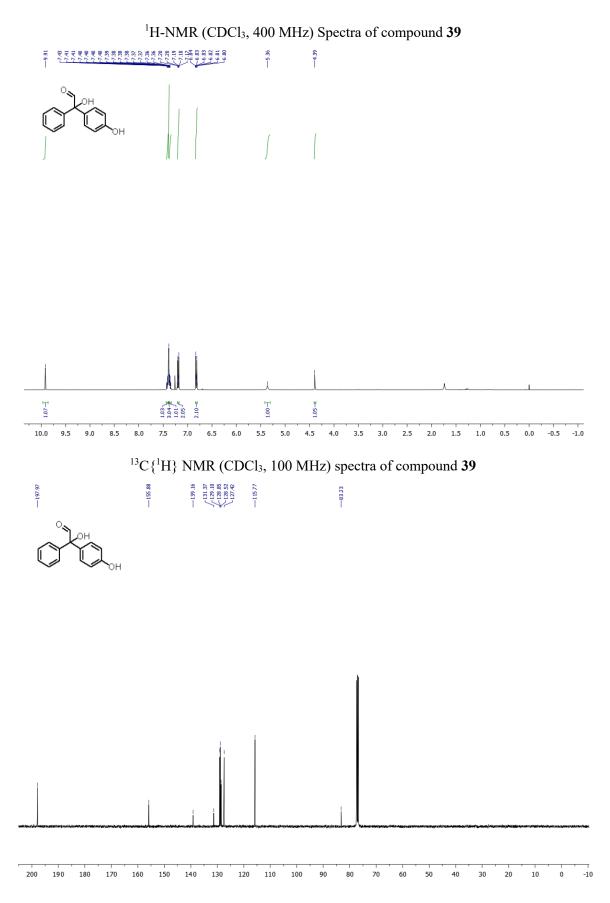


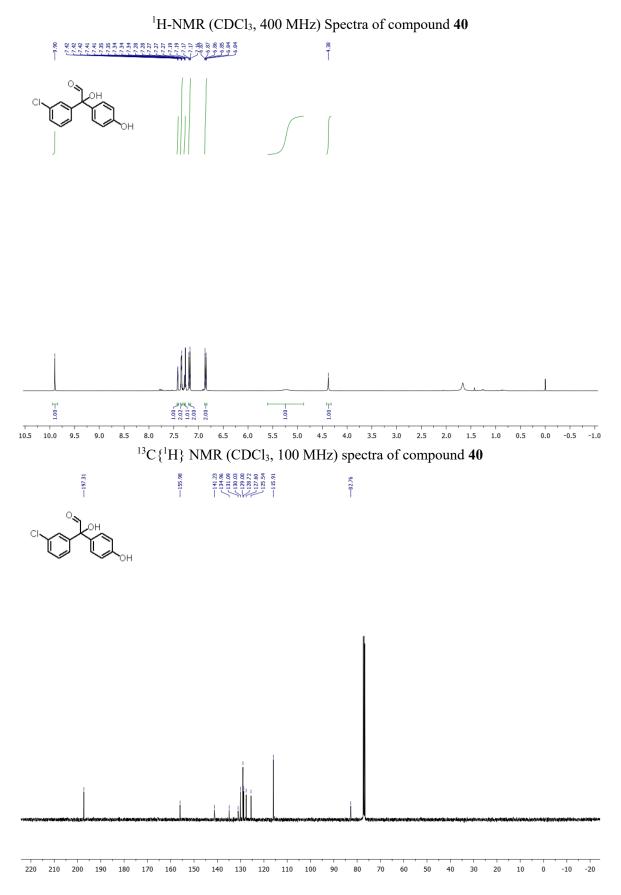




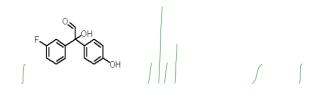


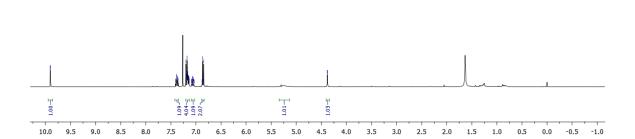


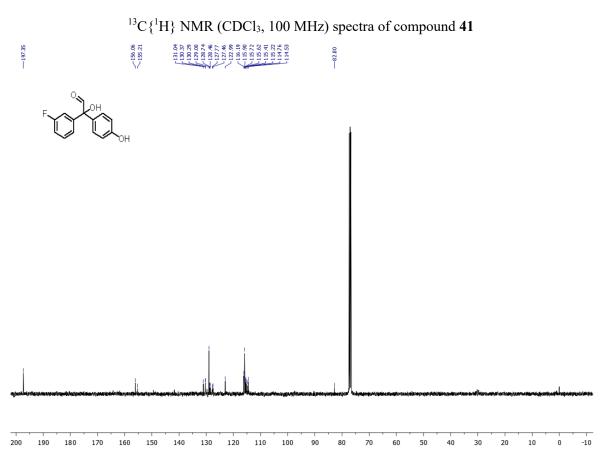




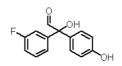








	- , ,				_	. , ,								· .		, ,				· .	· · ·
200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10

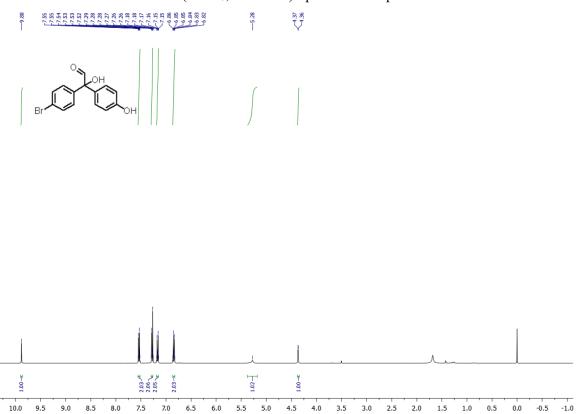


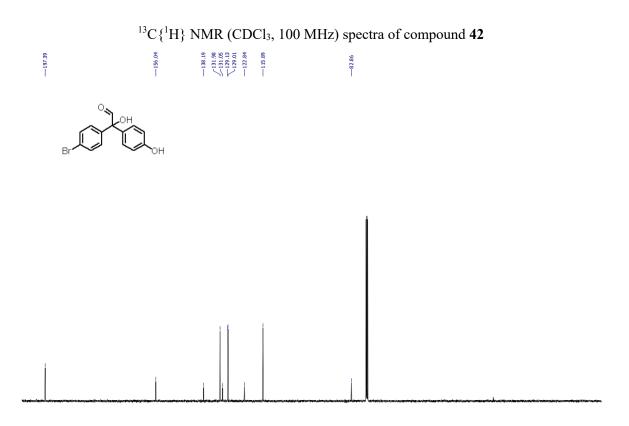
-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200

hinni

er (han ha dig i bearing in the second ship was a second state of the second s

(ninin)





					· · · ·	· · ·															F
200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10

