Supporting Information

TfOH-Catalyzed Tandem Cyclopropane Ring Enlargement/C－C Formation/Etherification of Alkynylcyclopropanes and 1,3-Diketones to Cyclobutane-fused Dihydrofurans

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Contents

1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. 1,2-Dichloroethane was distilled from CaH_2 prior to use. 1,1,2,2-tetrachloroethane was dried over anhydrous K_2CO_3 and distilled prior to use. Synthetic reagents purchased from Acros and Alfa Aesar were used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates containing a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash column chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Bruker ARX400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) and Bruker Avance 600 (^{1}H at 600 MHz, ^{13}C at 150 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on Bruker APEX IV (ESI) mass spectrometers.

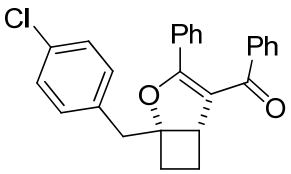
Abbreviations:
PE = petroleum ether
EA = ethyl acetate
DCE = 1,2-dichloroethane
TCE = 1,1,2,2-tetrachloroethane
m.p. = melting point

2. Experimental procedures and characterization data

The alkynylcyclopropanes[1] (**1a** to **1l**), 1,3-diketones (**4** and **5**)[2] and cycloheptane-1,3-dione[3] were prepared by following the literature procedures. Other 1,3-dicarbonyl compounds (**2**, **6**, **7**, **8**, and **9)** were commercially available. All the products were assigned to have the dihydrofuran skeleton by compared to product **3g**, which was determined by X-ray crystallographic analysis.

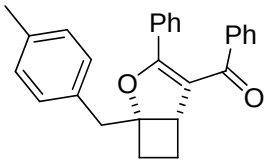
General procedure for the tandem reaction: Under argon atmosphere, TfOH (4 μL, 0.05 mmol, 10 mol %) was added to a solution of the alkynylcyclopropane derivative (0.5 mmol) and the 1,3-diketone (0.55 mmol) in 5 mL dry DCE (or TCE). The resulting mixture was heated at the indicated temperature. When TLC indicated the disappearance of the alkynylcyclopropane derivative, the reaction mixture was cooled to room temperature and purified by flash column chromatography on silica gel (eluted with PE to PE/EA = 10 : 1) to afford the corresponding product.

(1-(4-chlorobenzyl)-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-4-yl)phenylmethanone (3a):



white solid (75% yield, DCE as solvent, 80 °C, 23 h), m.p.: 102－103 °C, R_f = 0.15 (hexane/AE = 10 : 1)
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31－7.24 (m, 6H), 7.21－7.14 (m, 4H), 7.08－7.04 (m, 4H), 3.88－3.85 (m, 1H), 3.20 (d, J = 14.6 Hz, 1H), 3.12 (d, J = 14.6 Hz, 1H), 2.72－2.65 (m, 1H), 2.43－2.36 (m, 1H), 2.32－2.23 (m, 1H), 2.15－2.07 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.9, 166.0, 139.1, 134.6, 132.6, 131.3, 131.2, 130.3, 129.9, 129.0, 128.8, 128.4, 127.63, 127.60, 117.8, 90.6, 48.8, 41.6, 33.5, 24.3.
FT-IR (neat): ν 3062, 2941, 1610, 1590, 1572, 1491, 1446 cm^{-1}.
HRMS (ESI) calcd for $C_{26}H_{22}ClO_2$ [M+H$^+$]: 401.1303. Found: 401.1300.

(1-(4-methylbenzyl)-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-4-yl)phenylmethanone (3b):

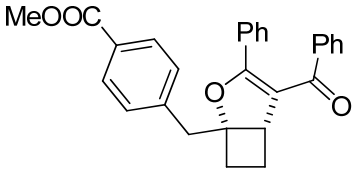


light yellow oil (40% yield, DCE as solvent, 80 °C, 7 h), R_f = 0.20 (hexane/AE = 10 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29－7.11 (m, 10H), 7.07－7.01 (m, 4H), 3.92－3.88 (m, 1H), 3.19 (d, J = 14.3 Hz, 1H), 3.12 (d, J = 14.3 Hz, 1H), 2.71－2.63 (m, 1H), 2.46－2.39 (m, 1H), 2.33 (s, 3H), 2.28－2.18 (m, 1H), 2.11－2.04 (m, 1H).

(1) S. Ye and Z.-X. Yu, *Org. Lett*., 2010, ***12***, 804.
(2) P. K. Dhondi, P. Carberry and J. D. Chisholm, *Tetrahedron Lett*., 2007, ***48***, 8743.
(3) G. S. Thompson and J. A. Hirsch, *J. Org. Chem.*, 1998, ***63***, 1098.

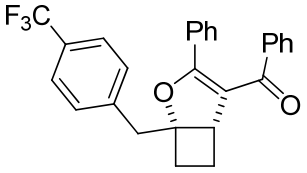
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 166.3, 139.3, 136.1, 133.0, 131.0, 130.5, 129.8, 129.7, 129.0, 128.9, 128.8, 127.5, 117.8, 91.1, 48.7, 41.8, 33.4, 24.3, 21.0.
FT-IR (neat): ν 3054, 2939, 1610, 1590, 1572, 1515, 1490 cm^{-1}.
HRMS (ESI) calcd for $C_{27}H_{24}NaO_2$ [M+Na$^+$]: 403.1669. Found: 403.1661.

methyl 4-(4-benzoyl-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-1-yl)methylbenzoate (3d):



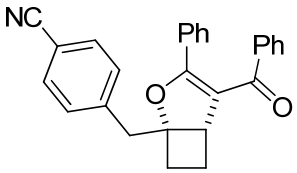
light yellow oil (76% yield, DCE as solvent, 80 ^{o}C, 20 h), R_f = 0.17 (hexane/AE = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.28－7.26 (m, 2H), 7.21－7.14 (m, 4H), 7.07－7.01 (m, 4H), 3.92－3.88 (m, 1H), 3.89 (s, 3H), 3.29 (d, J = 14.3 Hz, 1H), 3.22 (d, J = 14.3 Hz, 1H), 2.74－2.66 (m, 1H), 2.46－2.38 (m, 1H), 2.33－2.24 (m, 1H), 2.14－2.06 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.6, 166.9, 165.8, 141.5, 139.0, 131.1, 130.2, 129.9, 129.8, 129.5, 128.9, 128.62, 128.59, 127.5, 117.7, 90.3, 51.9, 48.8, 42.1, 33.6, 24.2.
FT-IR (neat): ν 2989, 2948, 1719, 1610, 1590, 1573, 1491 cm^{-1}.
HRMS (ESI) calcd for $C_{28}H_{25}O_4$ [M+H$^+$]: 425.1747. Found: 425.1741.

(3-phenyl-1-(4-trifluoromethylbenzyl)-2-oxabicyclo[3.2.0]hept-3-en-4-yl)phenylmethanone (3e):



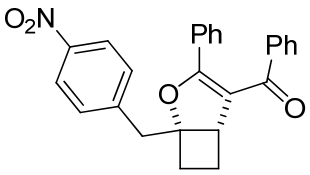
light yellow oil (70% yield, DCE as solvent, 80 ^{o}C, 23 h), R_f = 0.17 (hexane/AE = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 7.9 Hz, 2H), 7.28－7.24 (m, 2H), 7.21－7.14 (m, 4H), 7.07－7.01 (m, 4H), 3.93－3.89 (m, 1H), 3.29 (d, J = 14.3 Hz, 1H), 3.22 (d, J = 14.3 Hz, 1H), 2.75－2.67 (m, 1H), 2.46－2.38 (m, 1H), 2.36－2.27 (m, 1H), 2.16－2.08 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 165.9, 140.3, 139.0, 131.2, 130.21, 130.17, 129.9, 129.0 (q, J = 32.0 Hz), 128.9, 128.7, 127.6, 125.1 (q, J = 3.1 Hz), 124.2 (q, J = 272.3 Hz), 117.7, 90.3, 48.9, 42.0, 33.6, 24.3.
FT-IR (neat): ν 3064, 2939, 1618, 1590, 1573, 1491, 1447, 1324 cm^{-1}.
HRMS (ESI) calcd for $C_{27}H_{22}F_3O_2$ [M+H$^+$]: 435.1566. Found: 435.1559.

4-(4-benzoyl-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-1-yl)methylbenzonitrile (3f):



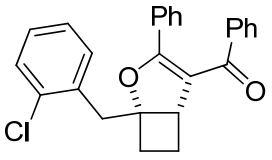
light brown oil (32% yield, TCE as solvent, 100 °C, 7 h), R_f = 0.22 (hexane/AE = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.31－7.29 (m, 2H), 7.23－7.15 (m, 4H), 7.08－7.04 (m, 4H), 3.92－3.88 (m, 1H), 3.30 (d, J = 14.3 Hz, 1H), 3.23 (d, J = 14.3 Hz, 1H), 2.76－2.68 (m, 1H), 2.45－2.28 (m, 2H), 2.15－2.08 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 165.7, 141.8, 138.9, 131.9, 131.2, 130.6, 130.0, 129.9, 128.9, 128.6, 127.6, 118.7, 117.6, 110.6, 89.9, 48.9, 42.2, 33.5, 24.1.
FT-IR (neat): ν 3058, 2941, 2228, 1608, 1590, 1573, 1491, 1446 cm^{-1}.
HRMS (ESI) calcd for $C_{27}H_{22}NO_2$ [M+H$^+$]: 392.1645. Found: 392.1641.

(1-(4-nitrobenzyl)-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-4-yl)phenylmethanone (3g):



light yellow solid (41% yield, TCE as solvent, 100 °C, 22 h), m.p. = 138－139 °C, R_f = 0.26 (hexane/AE = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.33－7.31 (m, 2H), 7.24－7.16 (m, 4H), 7.09－7.03 (m, 4H), 3.94－3.91 (m, 1H), 3.36 (d, J = 14.3 Hz, 1H), 3.30 (d, J = 14.3 Hz, 1H), 2.78－2.70 (m, 1H), 2.47－2.30 (m, 2H), 2.16－2.09 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 165.6, 146.9, 143.9, 138.9, 131.2, 130.7, 129.97, 129.94, 128.9, 128.6, 127.6, 123.3, 117.6, 89.8, 49.0, 41.8, 33.5, 24.0.
FT-IR (neat): ν 3066, 2943, 1606, 1590, 1573, 1518, 1491, 1446 cm^{-1}.
HRMS (ESI) calcd for $C_{26}H_{22}NO_4$ [M+H$^+$]: 412.1543. Found: 412.1538.

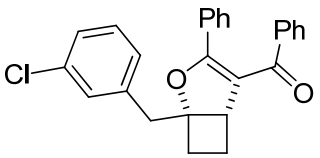
(1-(2-chlorobenzyl)-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-4-yl)phenylmethanone (3h):



light yellow oil (61% yield, TCE as solvent, 100 °C, 21 h), R_f = 0.13 (hexane/AE = 10 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43－7.39 (m, 2H), 7.33 (s, 1H), 7.31 (s, 1H), 7.24－7.14 (m, 6H), 7.07－7.03 (m, 4H), 4.00－3.97 (m, 1H), 3.45 (d, J = 14.5 Hz, 1H), 3.40 (d, J = 14.5 Hz, 1H), 2.77－2.69 (m, 1H), 2.53－2.46 (m, 1H), 2.38－2.29 (m, 1H), 2.14－2.06 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 166.0, 139.2, 134.7, 134.1, 131.6, 131.1, 130.3, 129.8, 129.5, 129.0, 128.7, 128.0, 127.55, 127.53, 126.6, 117.8, 90.8, 49.1, 38.4, 33.8, 24.4.
FT-IR (neat): ν 3058, 2939, 1610, 1590, 1572, 1491, 1475, 1446 cm^{-1}.

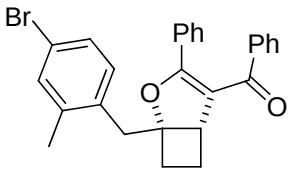
HRMS (ESI) calcd for $C_{26}H_{21}ClNaO_2$ [M+Na^+]: 423.1122. Found: 423.1120.

(1-(3-chlorobenzyl)-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-4-yl)phenylmethanone (3i):



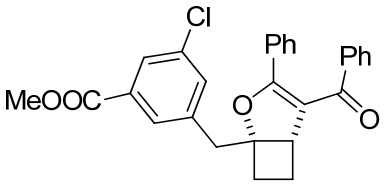
light yellow oil (78% yield, DCE as solvent, 80 °C, 21 h), R_f = 0.21 (hexane/AE = 10 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36－7.35 (m, 1H), 7.29－7.27 (m, 2H), 7.24－7.14 (m, 7H), 7.07－7.02 (m, 4H), 3.90－3.87 (m, 1H), 3.20 (d, J = 14.3 Hz, 1H), 3.13 (d, J = 14.3 Hz, 1H), 2.74－2.66 (m, 1H), 2.45－2.37 (m, 1H), 2.34－2.24 (m, 1H), 2.15－2.08 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 166.1, 139.0, 138.1, 134.0, 131.1, 130.2, 129.9, 129.8, 129.5, 128.9, 128.7, 128.0, 127.6, 126.8, 117.7, 90.4, 48.7, 41.8, 33.6, 24.3.
FT-IR (neat): ν 3058, 2943, 1609, 1590, 1572, 1490, 1446 cm^{-1}.
HRMS (ESI) calcd for $C_{26}H_{21}ClNaO_2$ [M+Na^+]: 423.1122. Found: 423.1115.

(1-(4-bromo-2-methylbenzyl)-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-4-yl)phenylmethanone (3j):



light yellow oil (63% yield, TCE as solvent, 100 °C, 19 h), R_f = 0.33 (hexane/AE = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34－7.32 (m, 3H), 7.26 (dd, J = 8.4 and 2.0 Hz, 1H), 7.22－7.13 (m, 5H), 7.08－7.02 (m, 4H), 3.92－3.88 (m, 1H), 3.21 (d, J = 14.8 Hz, 1H), 3.14 (d, J = 14.8 Hz, 1H), 2.77－2.69 (m, 1H), 2.45－2.28 (m, 2H), 2.35 (s, 3H), 2.14－2.07 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 165.9, 139.3, 139.1, 133.7, 133.0, 131.6, 131.1, 130.2, 129.8, 128.9, 128.7, 127.6, 127.5, 120.3, 117.6, 90.9, 49.2, 37.9, 33.8, 24.2, 20.1.
FT-IR (neat): ν 2941, 1610, 1590, 1572, 1490, 1446 cm^{-1}.
HRMS (ESI) calcd for $C_{27}H_{24}BrO_2$ [M+H^+]: 459.0954. Found: 459.0947.

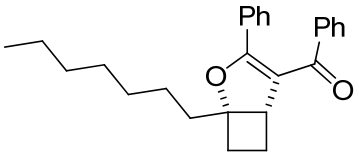
methyl 3-(4-benzoyl-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-1-yl)methyl-5-chlorobenzoate (3k):



light yellow oil (61% yield, TCE as solvent, 100 °C, 19 h), R_f = 0.22 (hexane/AE = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.933 (s, 1H), 7.927 (s, 1H), 7.54 (t, J = 1.8 Hz, 1H), 7.30－7.28 (m, 2H), 7.22－7.16 (m, 4H), 7.09－7.03 (m, 4H), 3.89 (s, 3H), 3.89－3.86 (m, 1H), 3.28 (d, J = 14.6 Hz, 1H), 3.20 (d, J = 14.6 Hz, 1H), 2.76－2.68 (m, 1H), 2.46－2.29 (m, 2H), 2.18－2.11 (m,

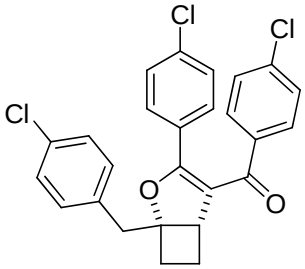
1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 165.9, 165.7, 139.0, 138.5, 134.3, 134.2, 131.7, 131.2, 130.1, 129.9, 129.2, 129.0, 128.7, 128.0, 127.6, 117.7, 90.1, 52.3, 48.7, 41.6, 33.6, 24.3.
FT-IR (neat): ν 3061, 2951, 1725, 1609, 1590, 1574, 1491, 1447, 1433 cm^{-1}.
HRMS (ESI) calcd for $C_{28}H_{23}ClNaO_4$ [M+Na^+]: 481.1177. Found: 481.1171.

(1-heptyl-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-4-yl)phenylmethanone (3l):



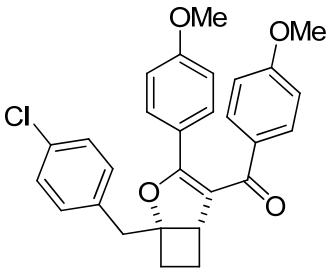
light yellow oil (19% yield, DCE as solvent, 40 °C, 22 h), R_f = 0.31 (hexane/AE = 10 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47－7.45 (m, 2H), 7.24－7.14 (m, 4H), 7.10－7.04 (m, 4H), 3.89－3.85 (m, 1H), 2.71－2.63 (m, 1H), 2.37－2.27 (m, 2H), 2.11－2.04 (m, 1H), 1.95－1.82 (m, 2H), 1.53－1.43 (m, 2H), 1.41－1.23 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 166.7, 139.6, 131.0, 130.7, 129.8, 129.1, 128.8, 127.57, 127.55, 118.0, 91.6, 48.8, 36.0, 33.6, 31.8, 29.7, 29.2, 24.2, 23.4, 22.6, 14.1.
FT-IR (neat): ν 3057, 2929, 2855, 1610, 1590, 1572, 1490, 1446 cm^{-1}.
HRMS (ESI) calcd for $C_{26}H_{30}NaO_2$ [M+Na^+]: 397.2138. Found: 397.2140.

(1-(4-chlorobenzyl)-3-(4-chlorophenyl)-2-oxabicyclo[3.2.0]hept-3-en-4-yl)(4-chlorophenyl)methanone (3m):



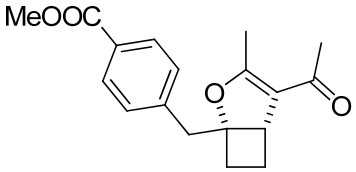
white solid (75% yield, DCE as solvent, 80 °C, 20 h), m.p. = 100－102 °C, R_f = 0.16 (hexane/AE = 10 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.9 Hz, 2H), 7.10 (d, J = 8.9 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 3.85－3.82 (m, 1H), 3.19 (d, J = 14.3 Hz, 1H), 3.11 (d, J = 14.3 Hz, 1H), 2.71－2.63 (m, 1H), 2.46－2.38 (m, 1H), 2.34－2.24 (m, 1H), 2.12－2.04 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 164.6, 137.8, 137.3, 136.3, 134.4, 132.7, 131.2, 130.2, 130.0, 128.5, 128.4, 128.13, 128.09, 117.7, 90.9, 48.8, 41.6, 33.6, 24.3.
FT-IR (neat): ν 3034, 2937, 1606, 1586, 1566, 1490, 1400 cm^{-1}.
HRMS (ESI) calcd for $C_{26}H_{20}Cl_3O_2$ [M+H^+]: 469.0523. Found: 469.0515.

(1-(4-chlorobenzyl)-3-(4-methoxyphenyl)-2-oxabicyclo[3.2.0]hept-3-en-4-yl)(4-methoxypheny l)methanone (3n):



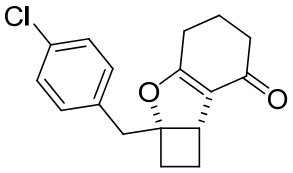
light yellow oil (72% yield, TCE as solvent, 100 °C, 21 h), R_f = 0.21 (hexane/AE = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 9.0 Hz, 2H), 7.27 (s, 4H), 7.22 (d, J = 9.0 Hz, 2H), 6.63 (d, J = 9.0 Hz, 2H), 6.61 (d, J = 9.0 Hz, 2H), 3.84—3.81 (m, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.18 (d, J = 14.1 Hz, 1H), 3.10 (d, J = 14.1 Hz, 1H), 2.70—2.62 (m, 1H), 2.41—2.34 (m, 1H), 2.28—2.19 (m, 1H), 2.10—2.03 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 192.7, 163.8, 162.2, 160.6, 134.8, 132.4, 131.7, 131.2, 131.0, 130.4, 128.3, 122.8, 115.9, 113.1, 113.0, 89.8, 55.2, 55.1, 49.3, 41.6, 33.4, 24.2.
FT-IR (neat): ν 2939, 2838, 1598, 1571, 1508, 1492, 1463, 1441, 1418 cm^{-1}.
HRMS (ESI) calcd for $C_{28}H_{26}ClO_4$ [M+H$^+$]: 461.1514. Found: 461.1508.

methyl 4-(4-acetyl-3-methyl-2-oxabicyclo[3.2.0]hept-3-en-1-yl)methylbenzoate (3o):



white solid (29% yield, TCE as solvent, 100 °C, 22 h), m.p. = 124—125 °C, R_f = 0.20 (hexane/AE = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 3.91 (s, 3H), 3.48—3.44 (m, 1H), 3.16 (d, J = 14.1 Hz, 1H), 3.10 (d, J = 14.1 Hz, 1H), 2.47—2.39 (m, 1H), 2.32—2.12 (m, 2H), 2.22 (s, 3H), 2.08 (s, 3H), 1.92—1.85 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 169.1, 166.9, 141.4, 129.8, 129.5, 128.7, 117.6, 90.2, 52.0, 46.0, 41.9, 33.2, 29.3, 23.9, 15.2.
FT-IR (neat): ν 2948, 1719, 1666, 1587, 1434 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{21}O_4$ [M+H$^+$]: 301.1434. Found: 301.1430.

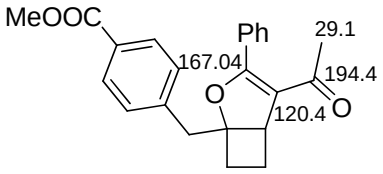
2a-(4-chlorobenzyl)-1,2,2a,5,6,7b-hexahydrobenzo[*d*]cyclobuta[*b*]furan-7(4*H*)-one (3q):



light yellow oil (45% yield, TCE as solvent, 120 °C, 22 h), R_f = 0.28 (hexane/AE = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 3.44—3.41 (m,

1H), 3.11 (d, *J* = 14.5 Hz, 1H), 3.05 (d, *J* = 14.5 Hz, 1H), 2.49－2.24 (m, 6H), 2.17－1.85 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 178.2, 134.2, 132.6, 131.0, 128.3, 118.8, 94.3, 42.3, 41.0, 36.5, 33.0, 24.1, 23.0, 21.6.
FT-IR (neat): *v* 2942, 1648, 1617, 1492, 1453, 1400 cm^{-1}.
HRMS (ESI) calcd for $C_{17}H_{18}ClO_2$ [M+H$^+$]: 289.0990. Found: 289.0987.

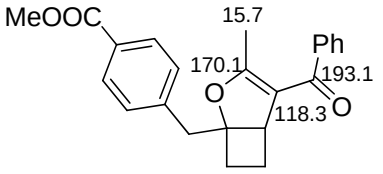
methyl 4-(4-acetyl-3-phenyl-2-oxabicyclo[3.2.0]hept-3-en-1-yl)methylbenzoate (3s):



(confirmed by HMBC)

light yellow oil (21% yield, TCE as solvent, 100 ^{o}C, 19 h), R_f = 0.20 (hexane/AE = 4 : 1).
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.49－7.41 (m, 5H), 7.36 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.72－3.69 (m, 1H), 3.24 (d, *J* = 14.3 Hz, 1H), 3.17 (d, *J* = 14.3 Hz, 1H), 2.63－2.58 (m, 1H), 2.37－2.32 (m, 1H), 2.30－2.24 (m, 1H), 2.04－1.99 (m, 1H), 1.87 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$): δ 194.4, 167.04, 166.97, 141.4, 131.1, 130.4, 129.9, 129.5, 128.9, 128.7, 128.2, 120.4, 90.2, 52.0, 47.1, 41.9, 33.4, 29.1, 24.1.
FT-IR (neat): *v* 2949, 1719, 1666, 1612, 1588, 1491, 1435 cm^{-1}.
HRMS (ESI) calcd for $C_{23}H_{23}O_4$ [M+H$^+$]: 363.1591. Found: 363.1591.

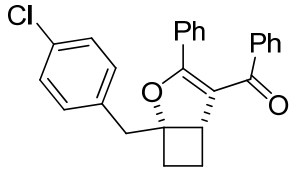
methyl 4-(4-benzoyl-3-methyl-2-oxabicyclo[3.2.0]hept-3-en-1-yl)methylbenzoate (3t):



(confirmed by HMBC)

light yellow oil (38% yield, TCE as solvent, 100 ^{o}C, 19 h), R_f = 0.30 (hexane/AE = 4 : 1).
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.45－7.43 (m, 3H), 7.38－7.35 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 3.70－3.67 (m, 1H), 3.16 (d, *J* = 14.3 Hz, 1H), 3.10 (d, *J* = 14.3 Hz, 1H), 2.51－2.46 (m, 1H), 2.34－2.29 (m, 1H), 2.23－2.17 (m, 1H), 1.98－1.93 (m, 1H), 1.85 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$): δ 193.1, 170.1, 167.0, 141.4, 141.0, 130.9, 129.8, 129.5, 128.6, 128.1, 127.5, 118.3, 90.7, 52.0, 46.7, 42.1, 33.1, 24.4, 15.7.
FT-IR (neat): *v* 2950, 1719, 1610, 1575, 1434, 1384 cm^{-1}.
HRMS (ESI) calcd for $C_{23}H_{23}O_4$ [M+H$^+$]: 363.1591. Found: 363.1589.

3. ^{1}H and ^{13}C-NMR spectra for new compounds



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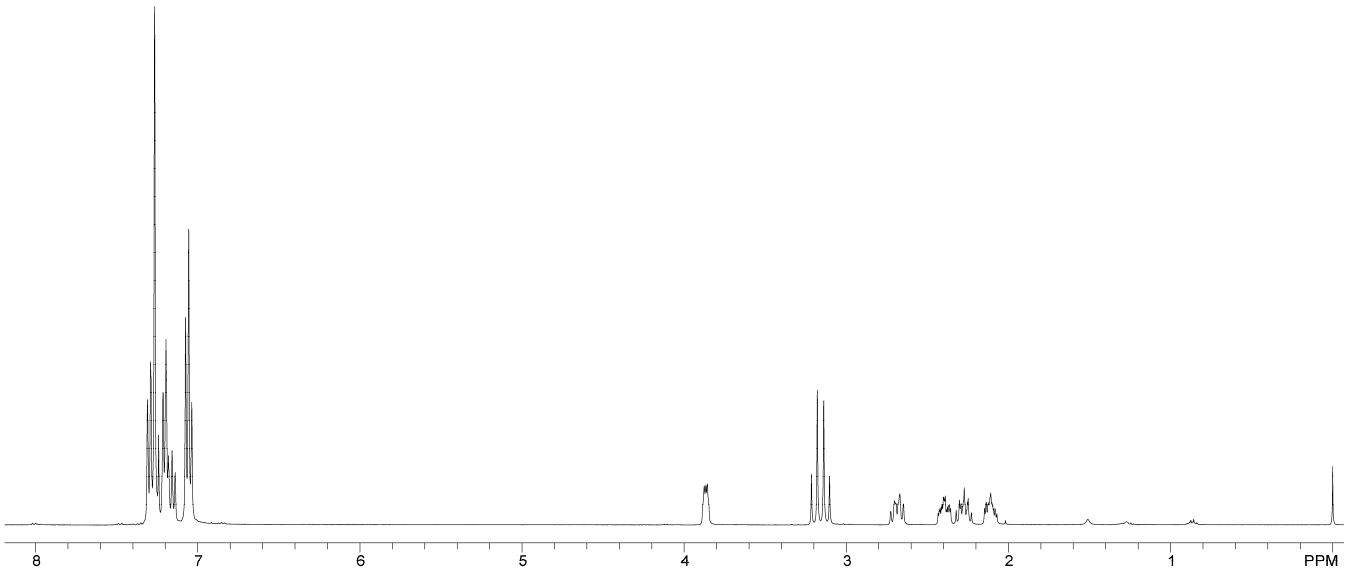
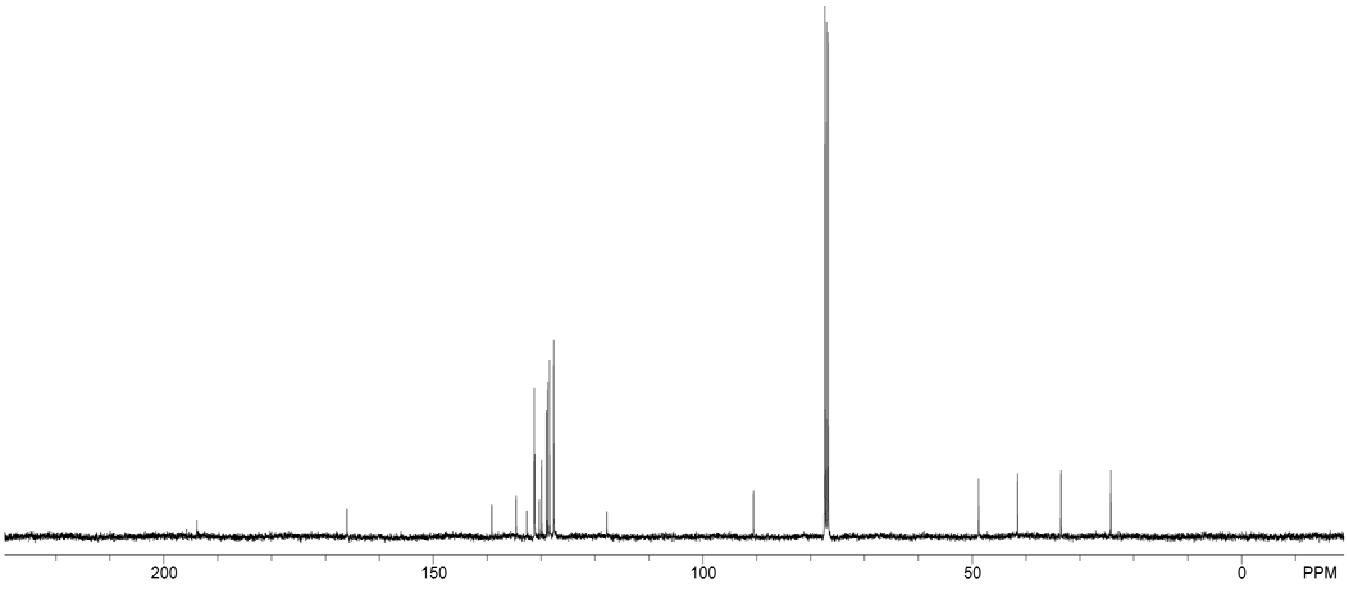
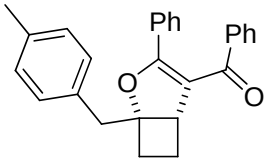
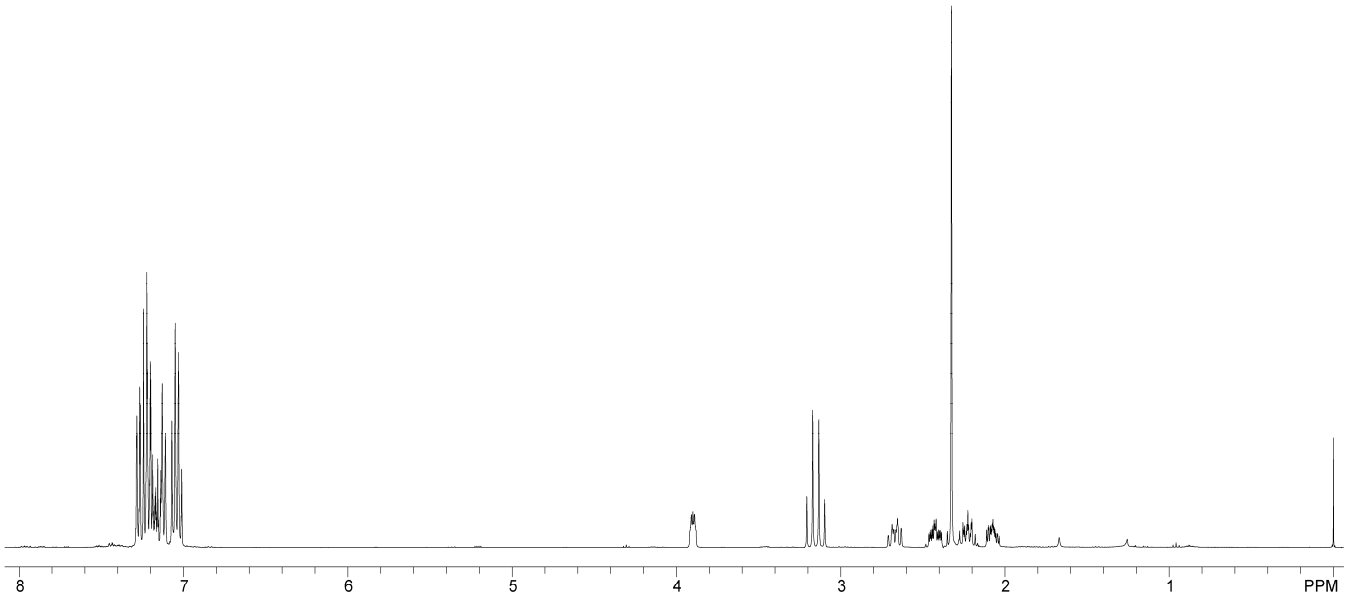
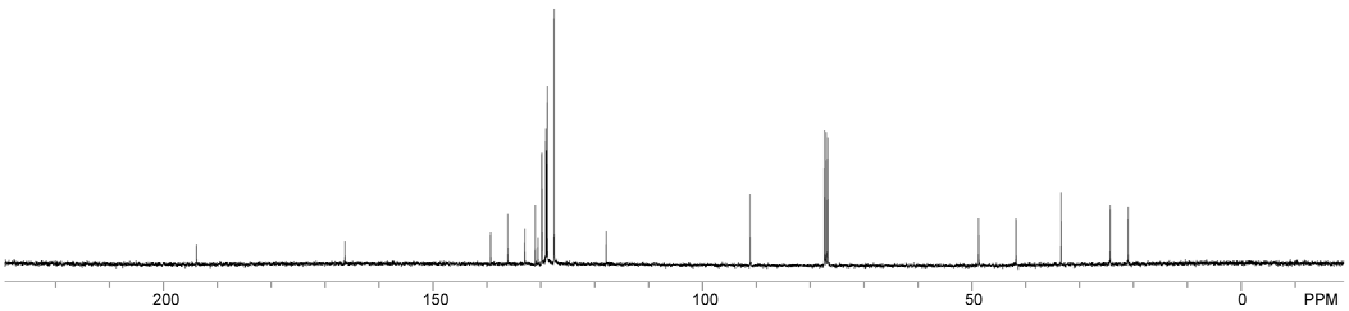


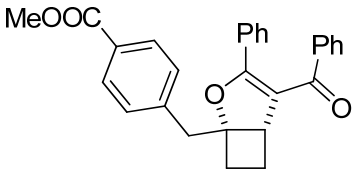




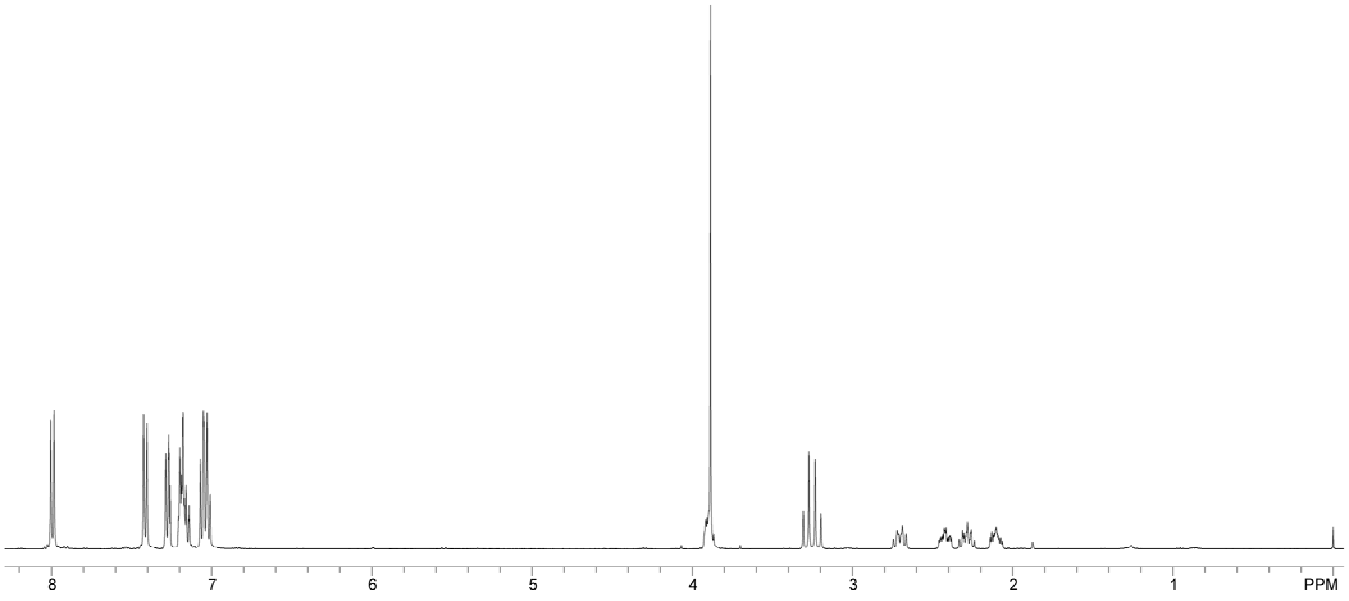
3b

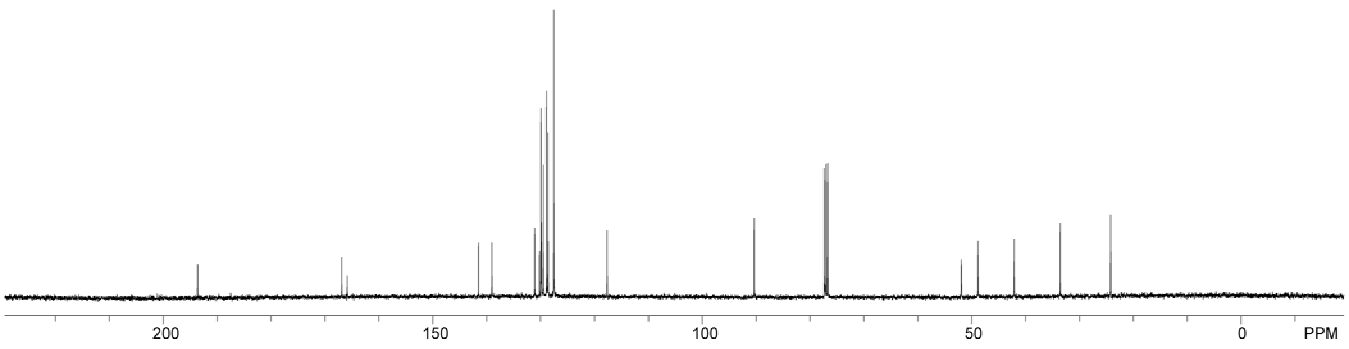


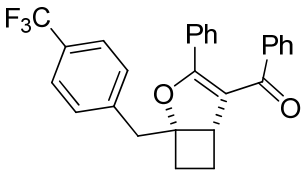




3d







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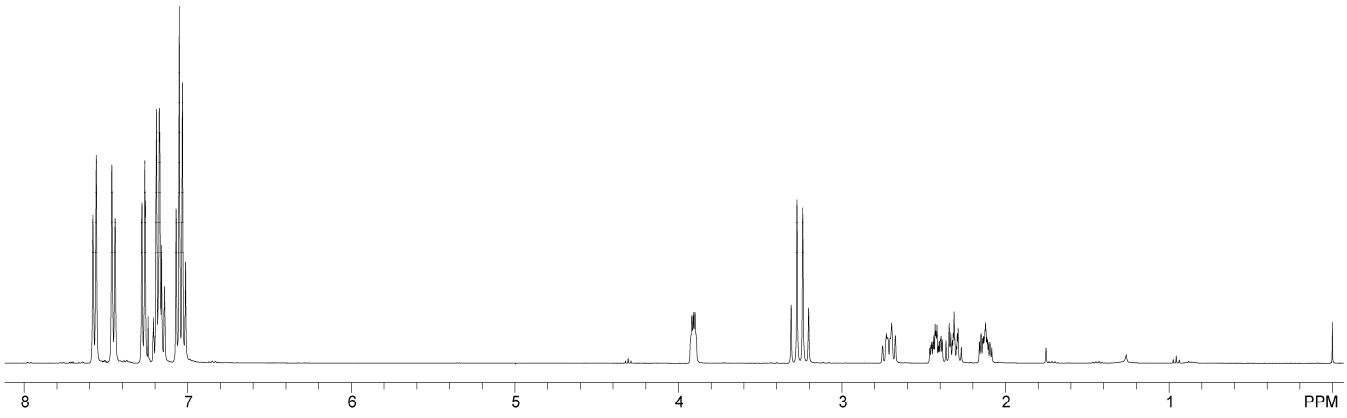

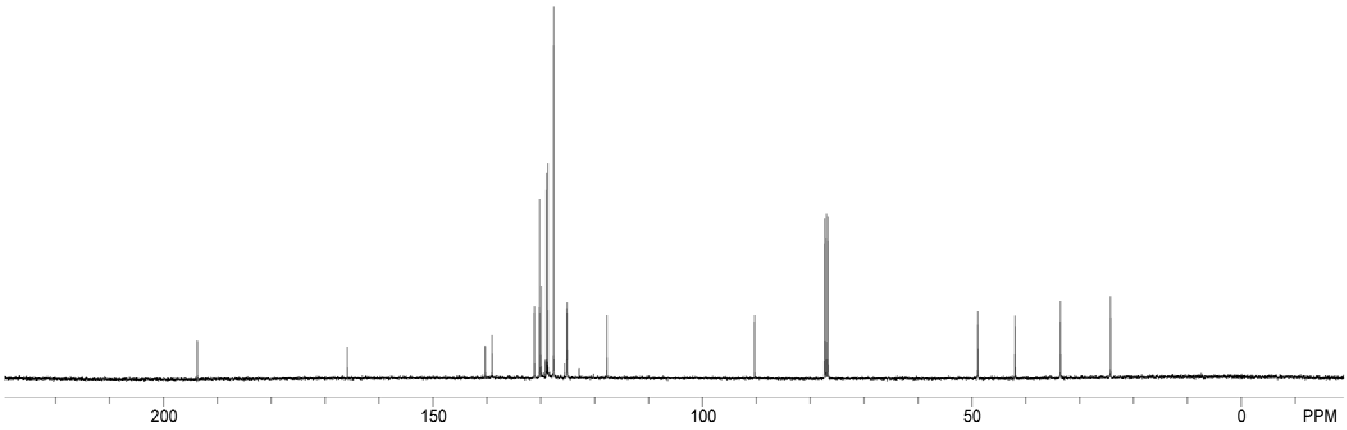

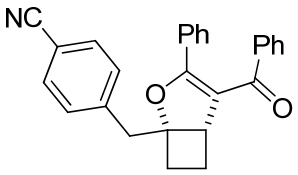

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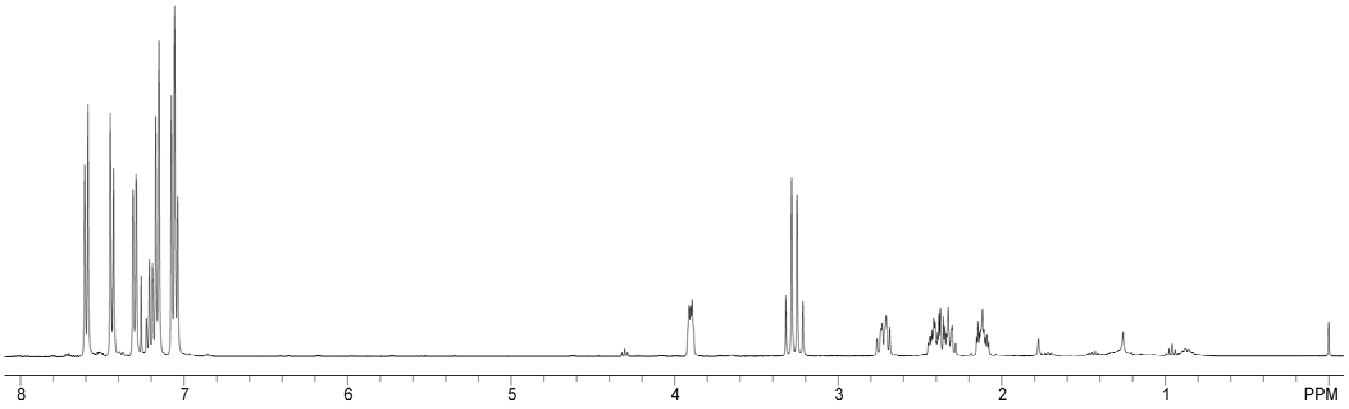

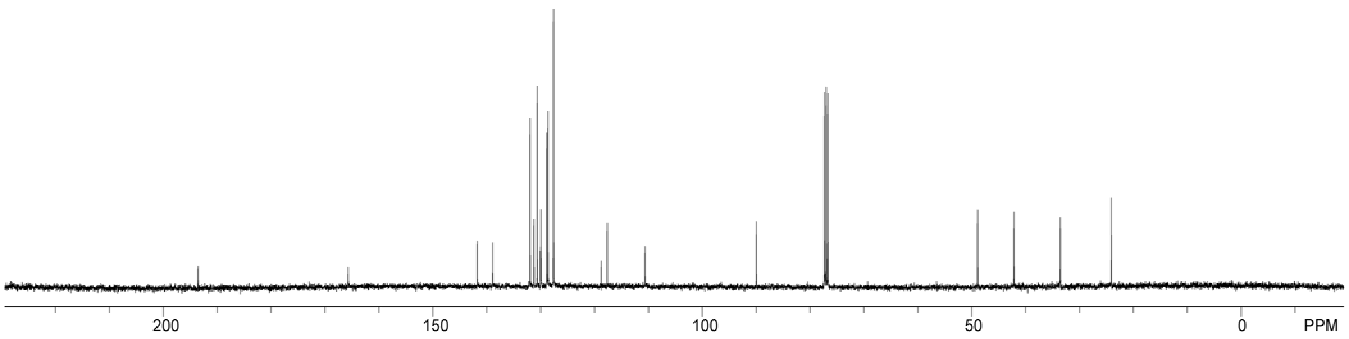

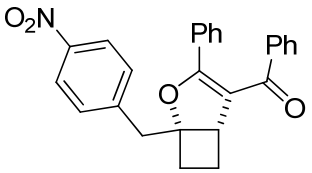

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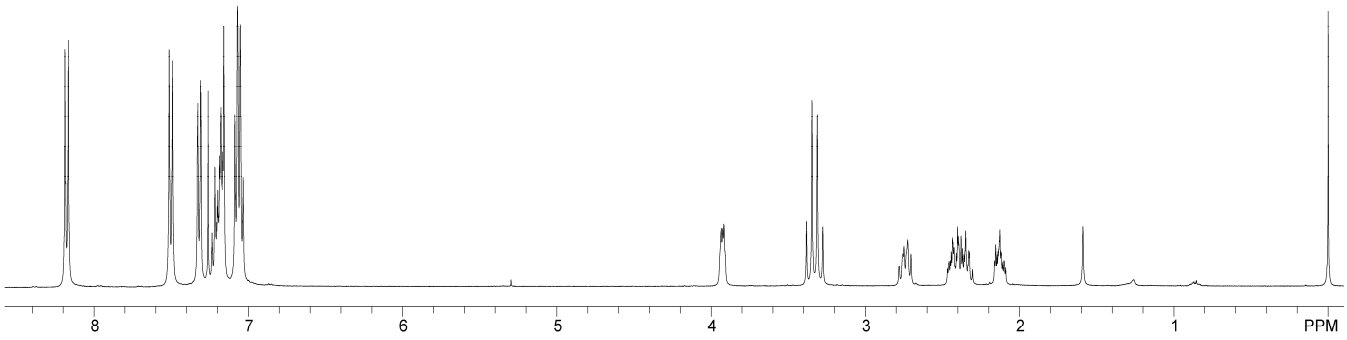

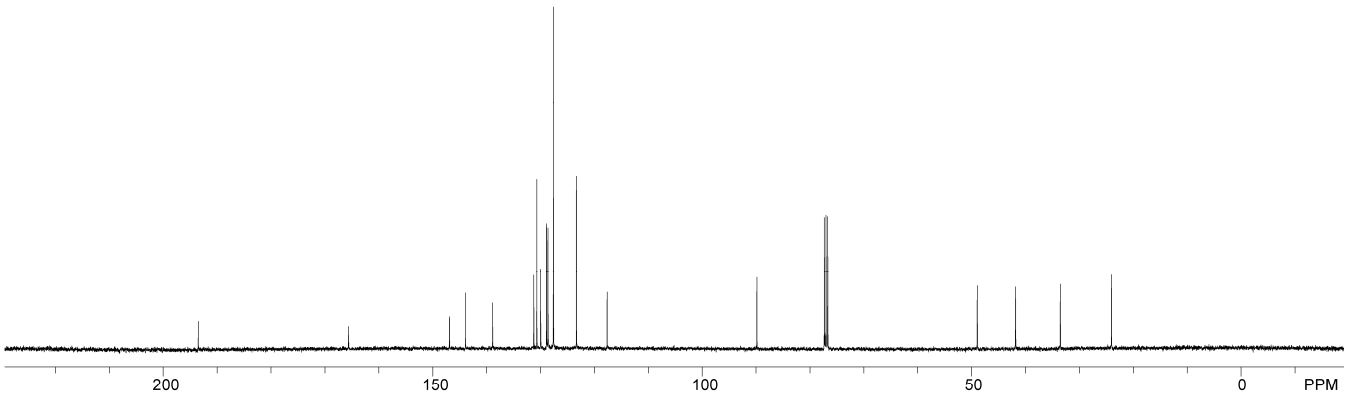

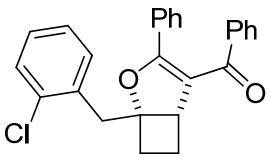

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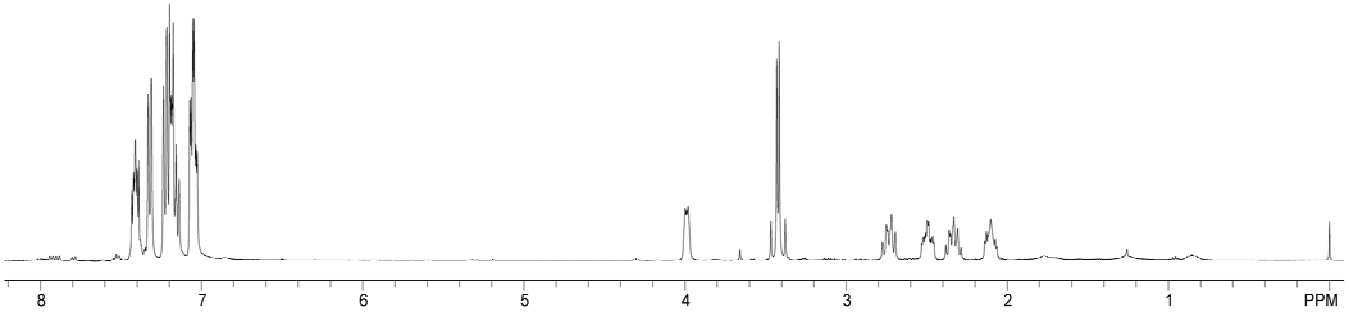
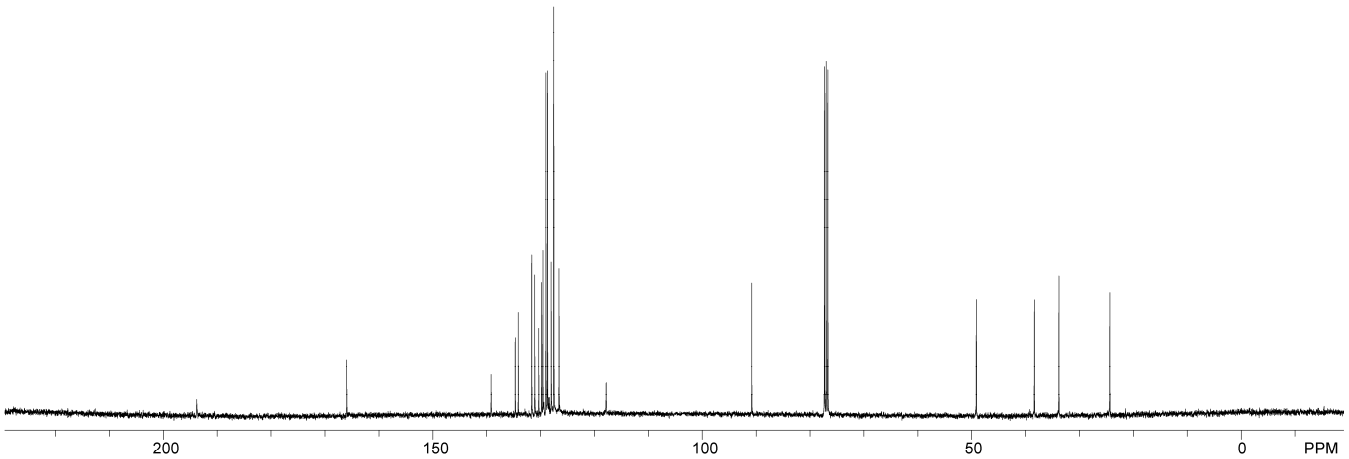
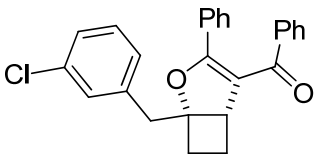
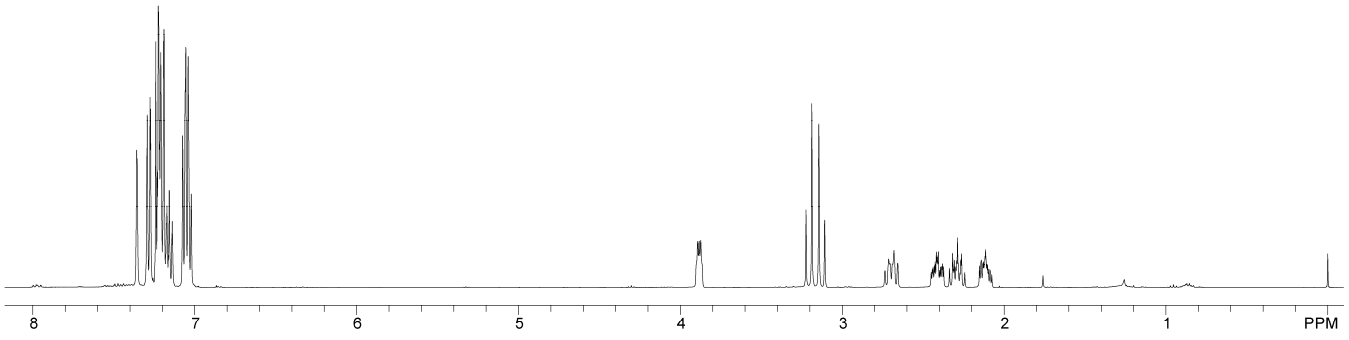
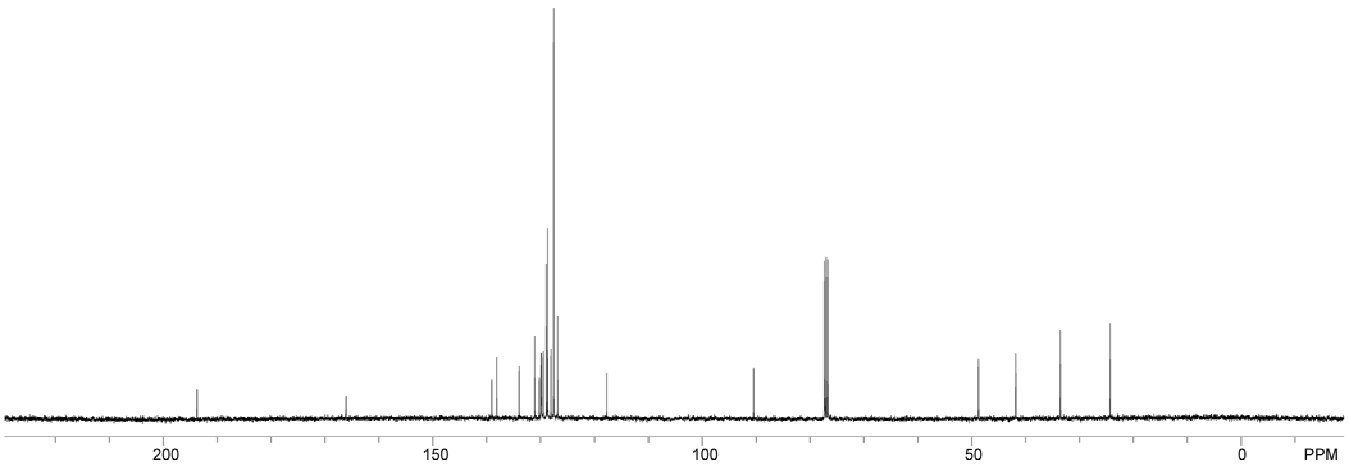


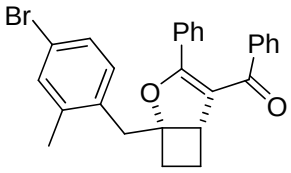




3i







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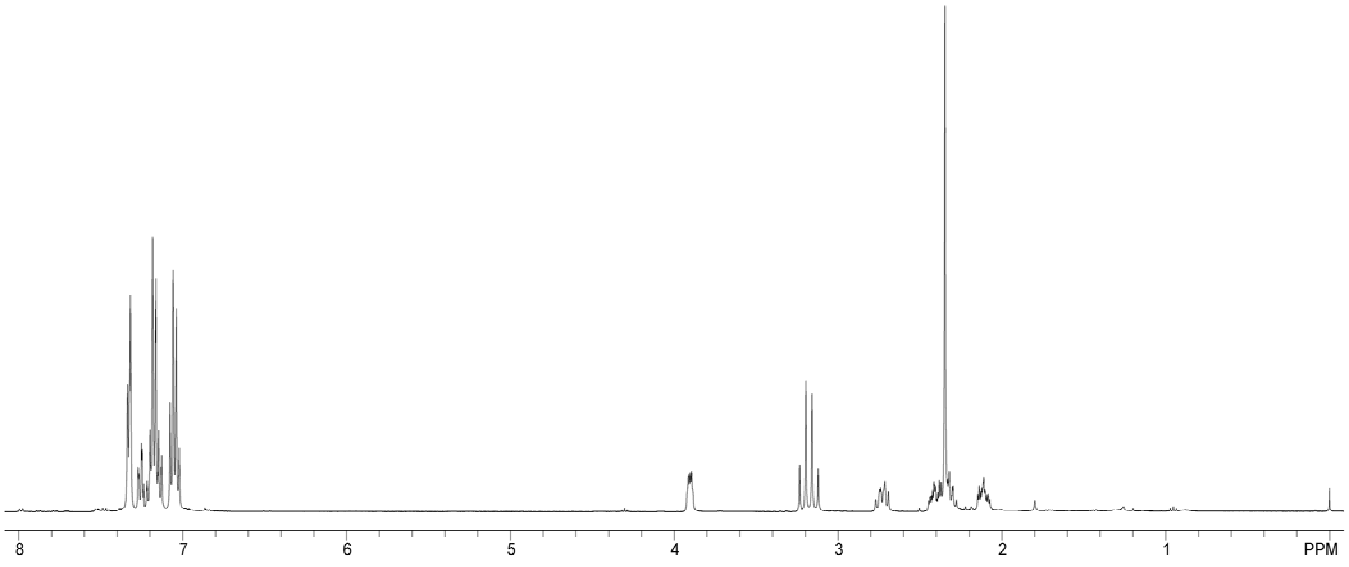
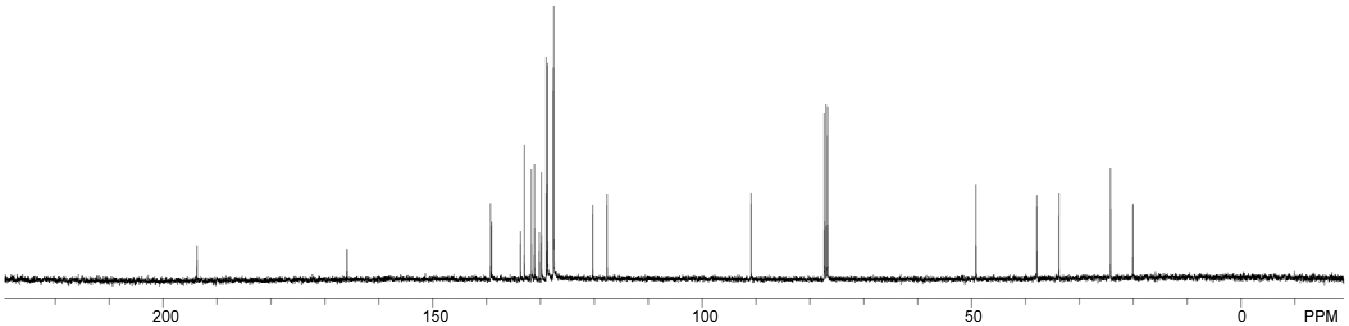
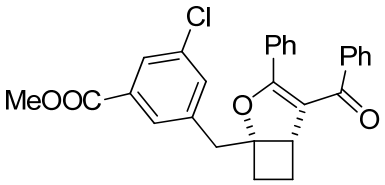
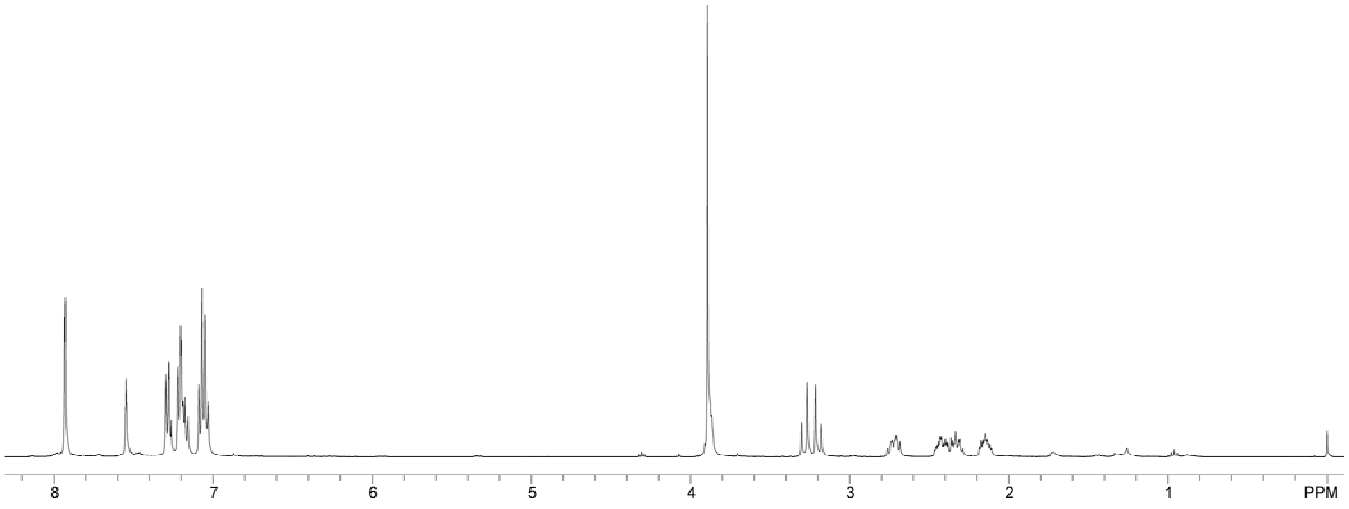
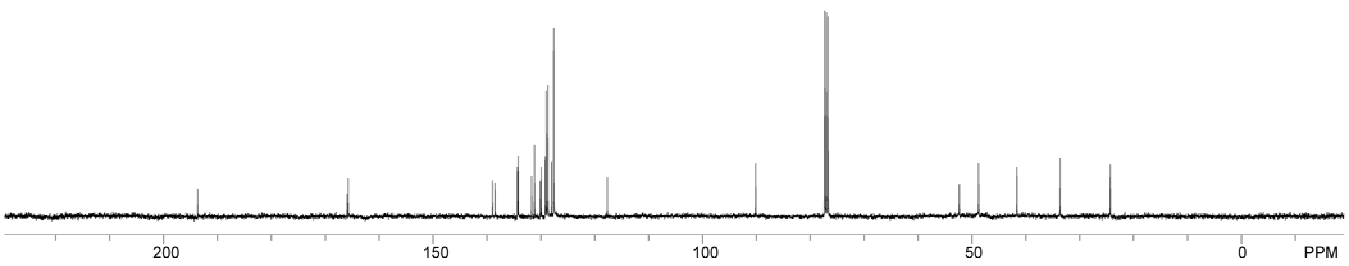


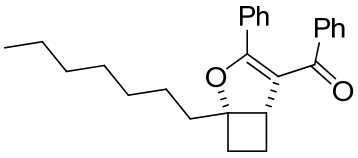




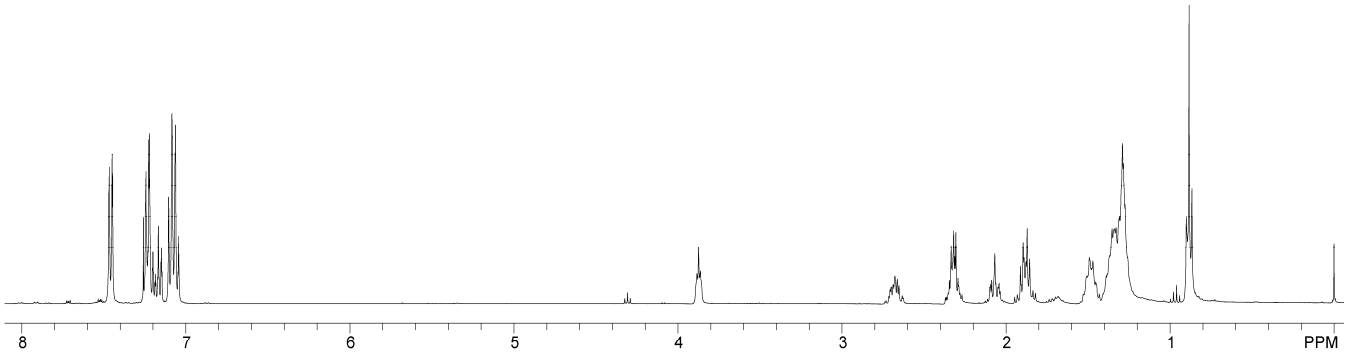
3k

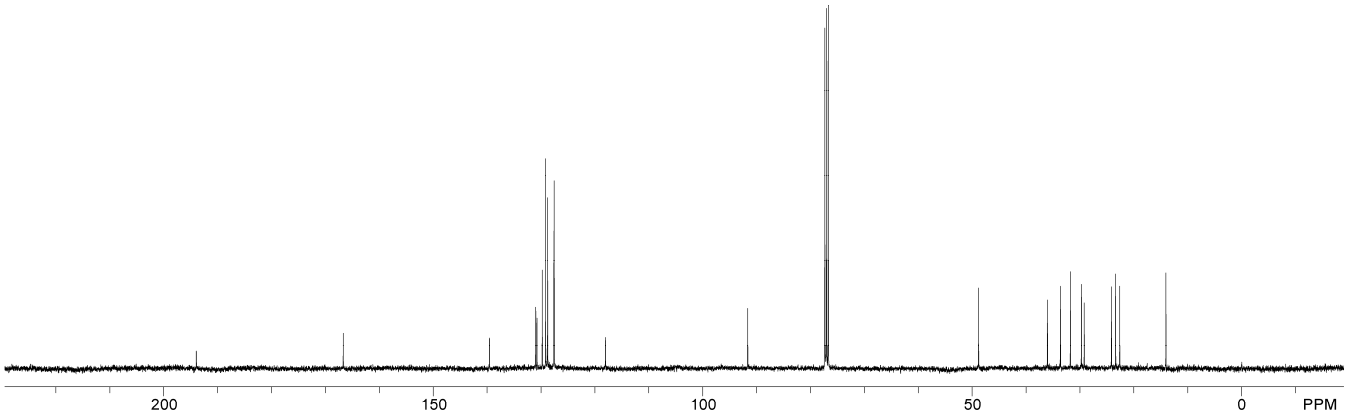


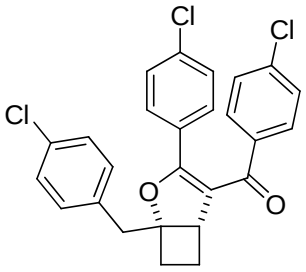




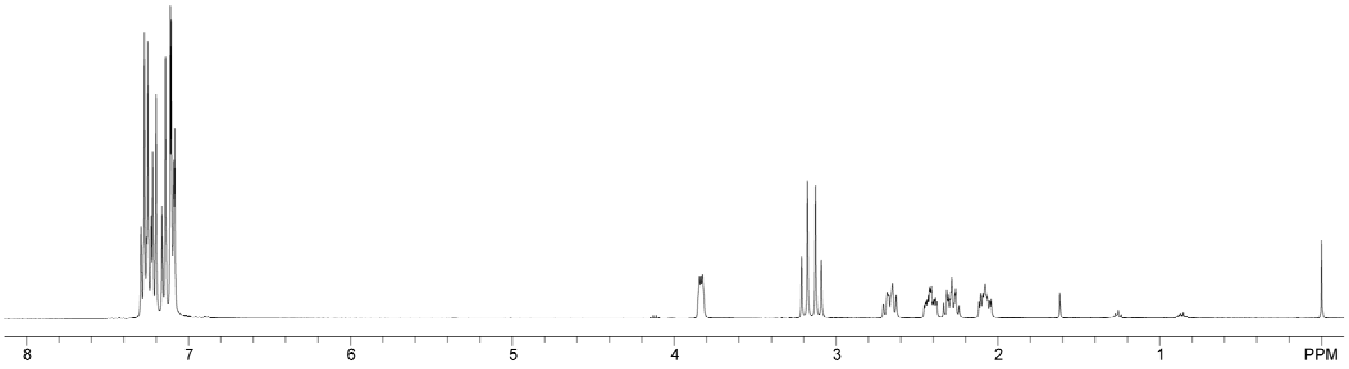
3l

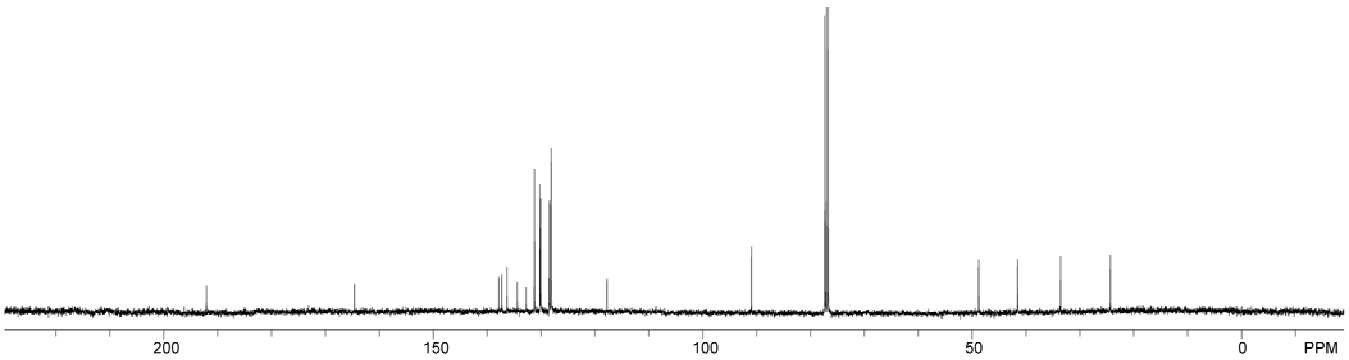


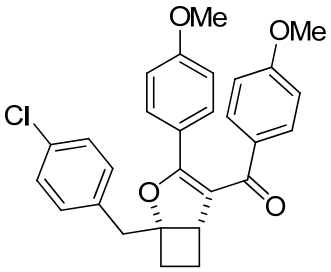




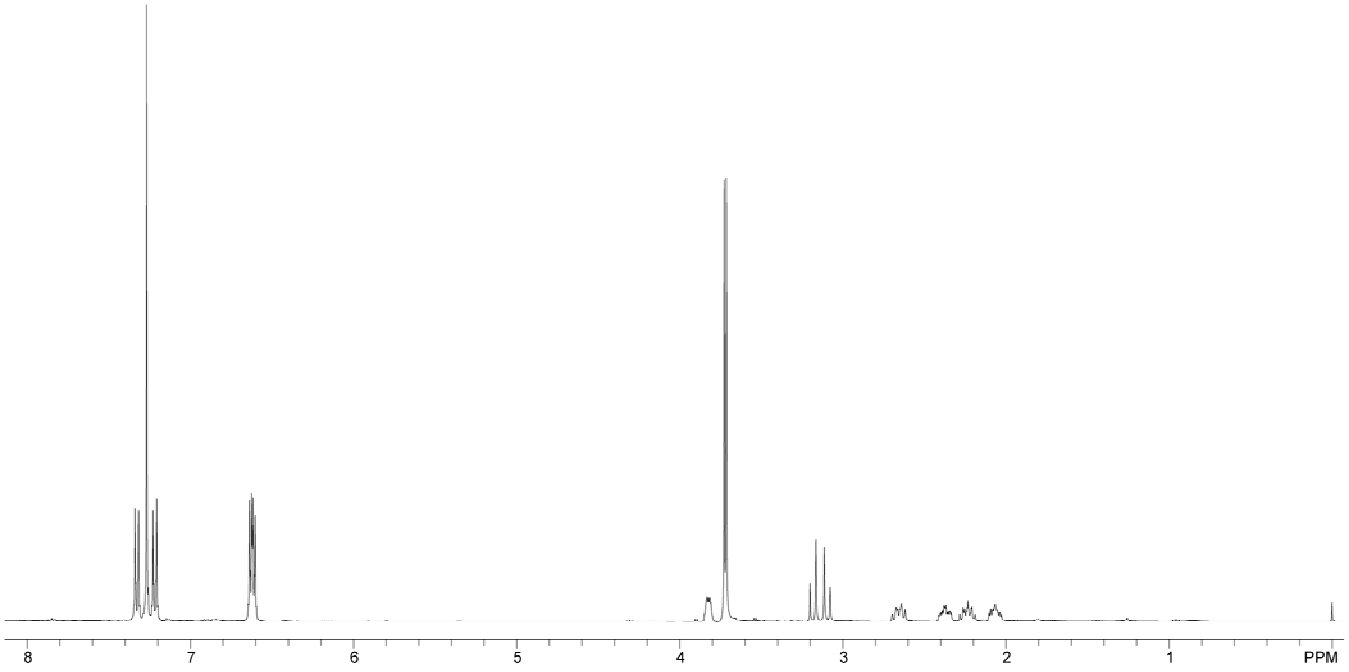
3m

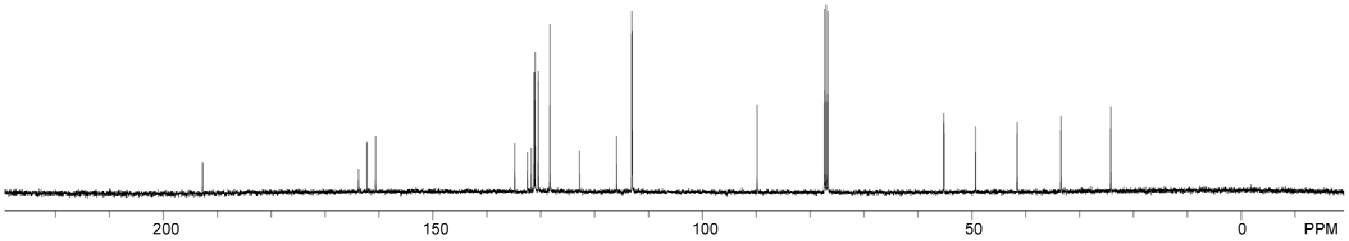


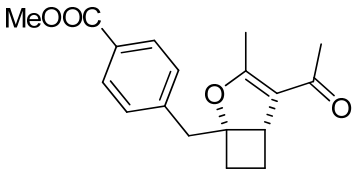




3n







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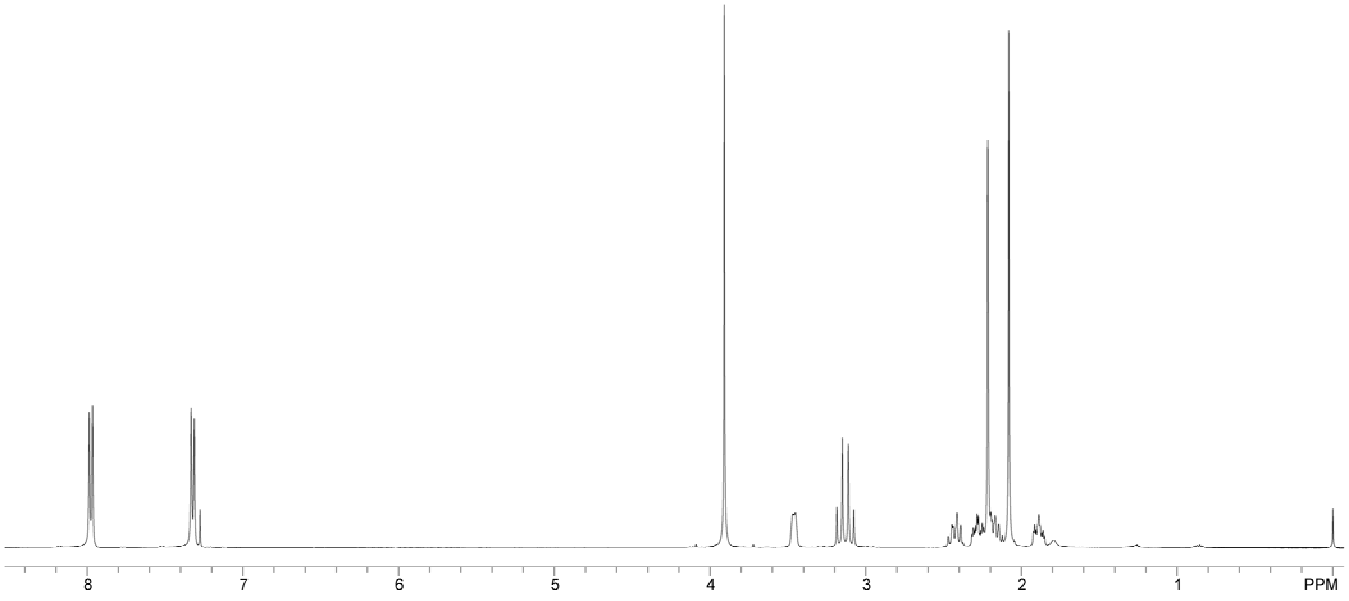

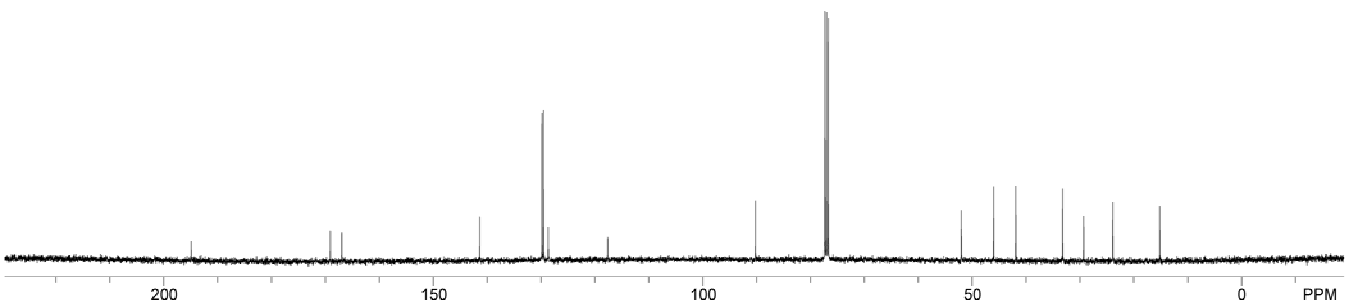

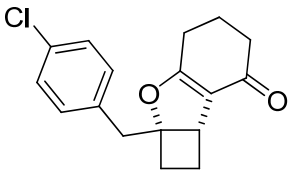

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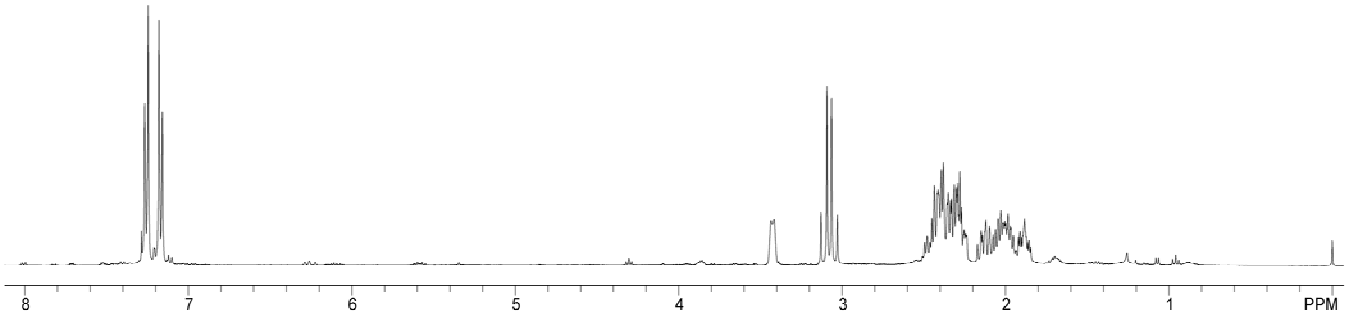

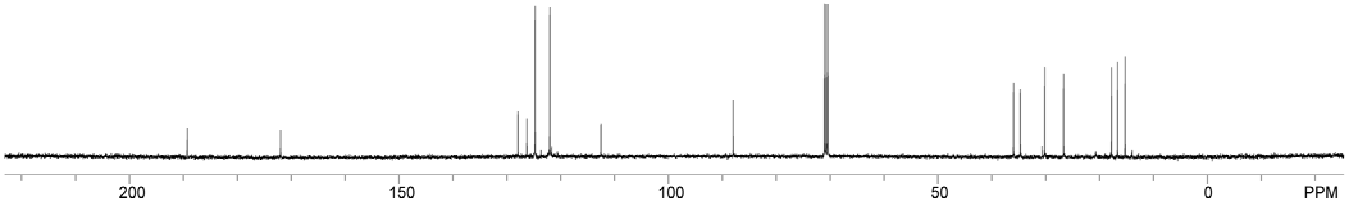

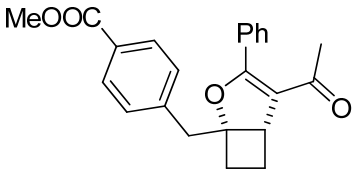

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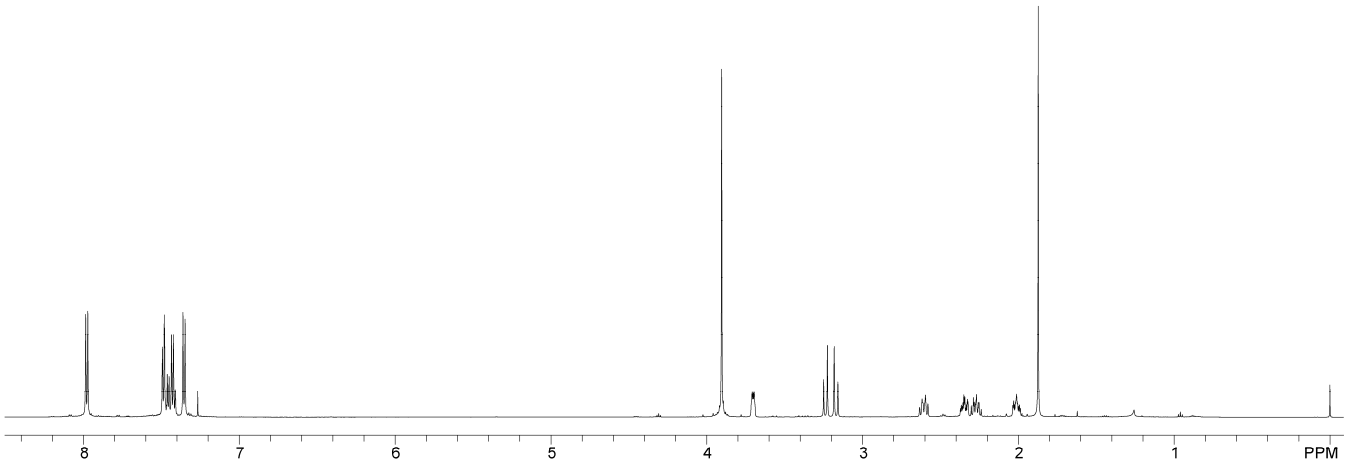

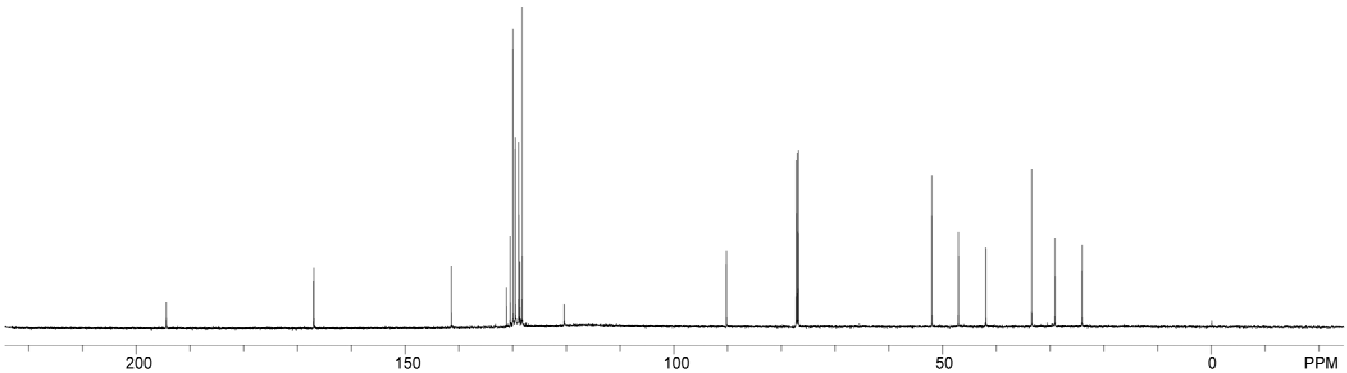

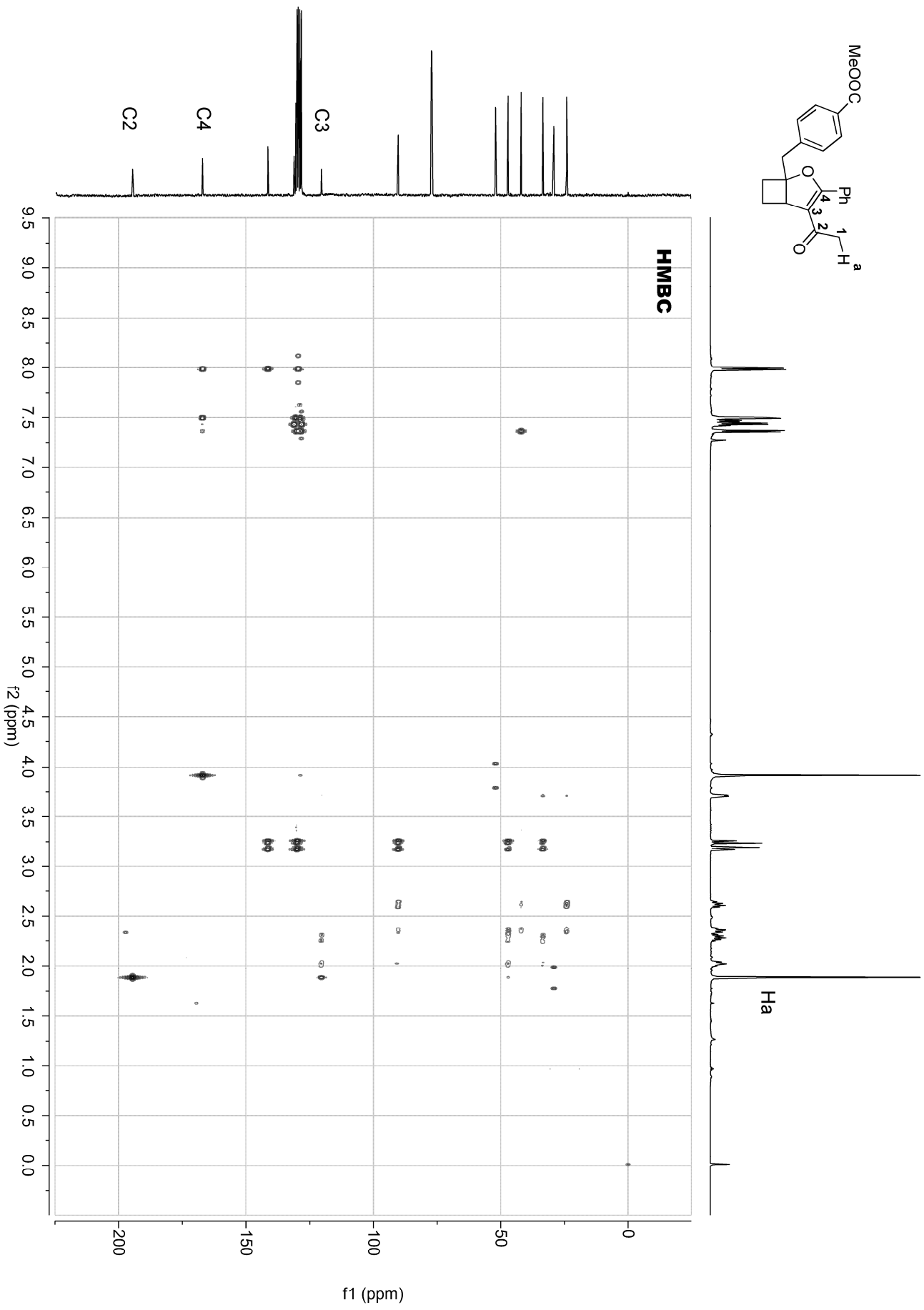
C2
C4
C3
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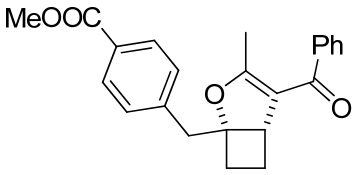
Ph
O
O
H
a
HMBC
Ha
f2 (ppm)
f1 (ppm)



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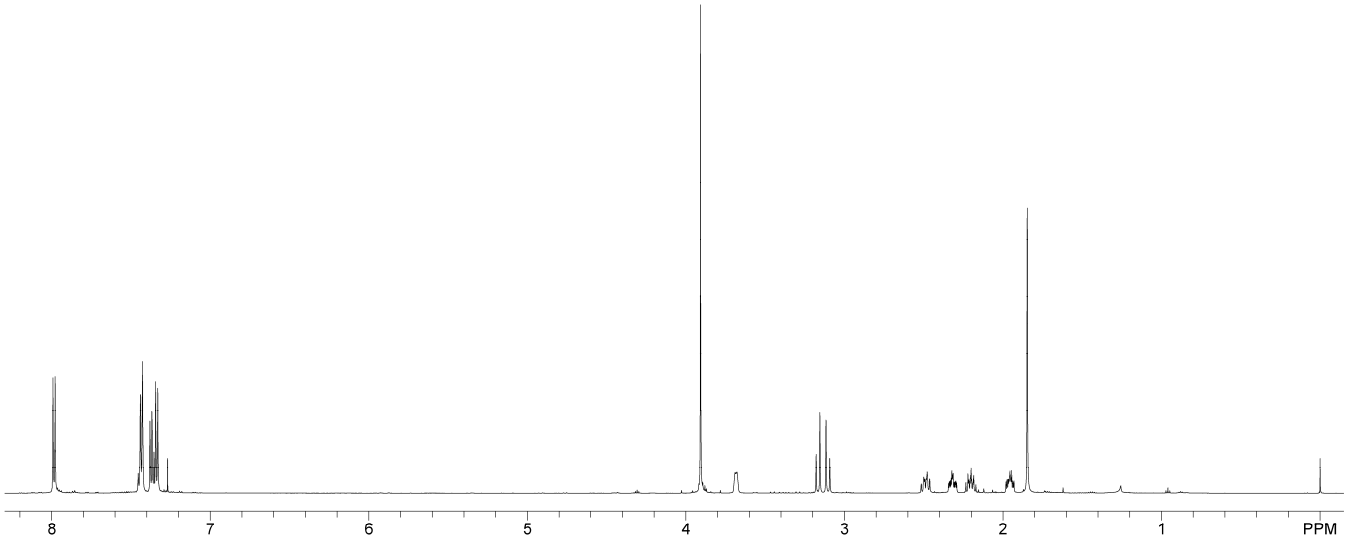

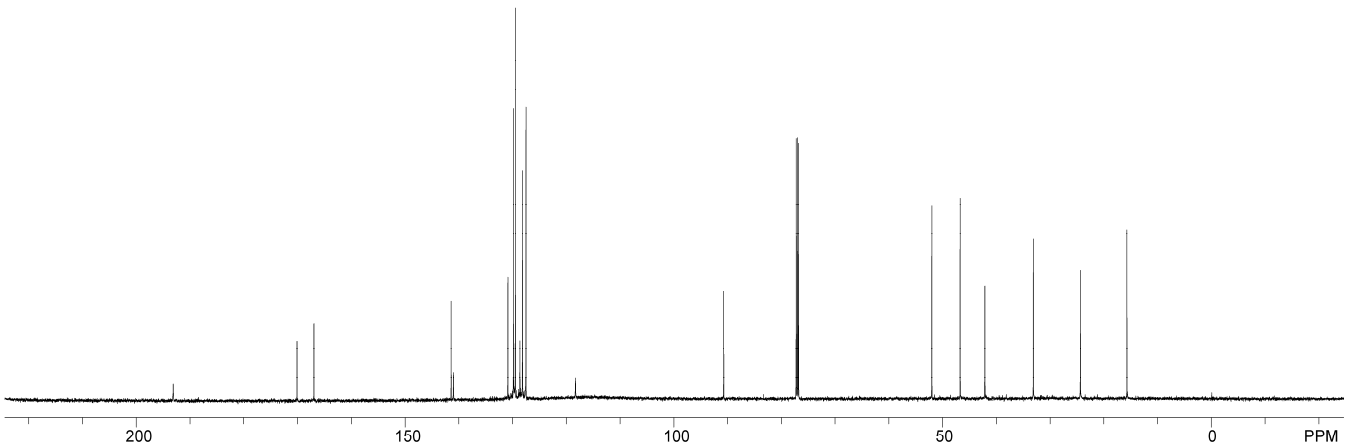

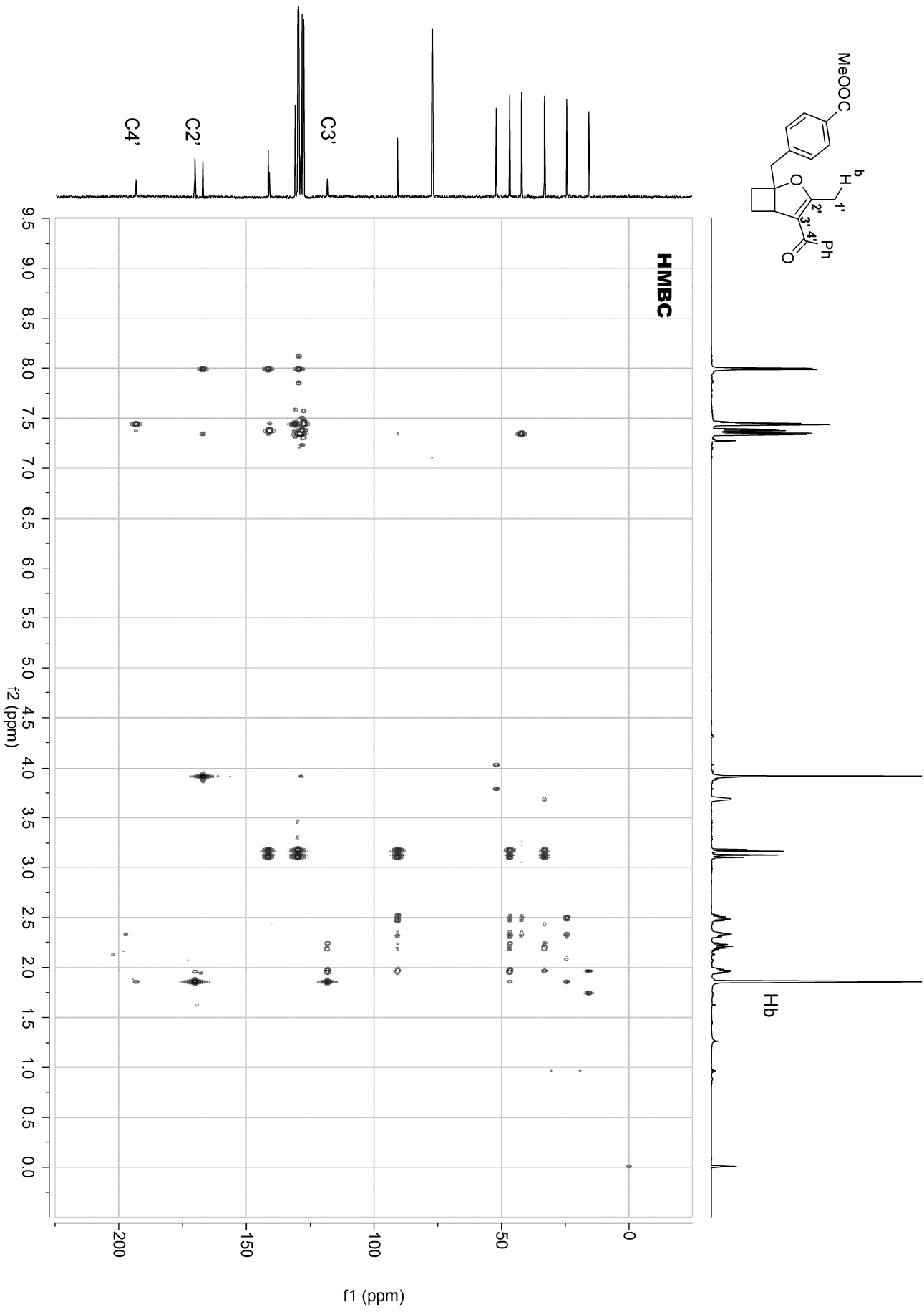
C4'
C2'
C3'
MeOOC
Ph
HMBC
Hb
f2 (ppm)
f1 (ppm)