Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Iron(III) Halide or Iodine-Promoted Synthesis of 3-Haloindene Derivatives from *o*-Alkynylarene Chalcones

Sikkandarkani Akbar and Kannupal Srinivasan*

School of Chemistry, Bharathidasan University, Tiruchirapalli 620 024, Tamil Nadu, India

srinivasank@bdu.ac.in

Contents

Experimental details and products characterization:

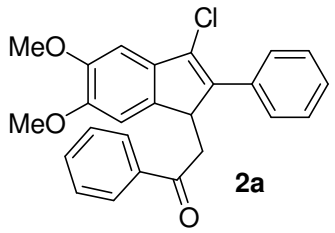
General remarks:

Melting points were determined using an apparatus by the open capillary tube method and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. HRMS (ESI) were recorded on Q-TOF mass spectrometers. Low resolution mass spectra (ESI) were recorded on LC-MS spectrometers. Elemental analyses were performed on a CHN analyzer. X-ray crystallographic data were collected on a CCD diffractometer using graphite-monochromated Mo-Ka radiation. Thin layer chromatography (TLC) was performed on pre-coated alumina sheets and detected under UV light. Silica gel (100-200 mesh) was used for column chromatography.

General procedure for the Synthesis of 3-haloindenes:

To a solution of *o*-alkynylarene chalcone **1** (0.25 mmol) in dichloroethane (3 mL) was added ferric chloride, ferric bromide or iodine (0.25 mmol) and the reaction mixture was heated under reflux. After completion of the reaction (2 h), the reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was diluted with water and extracted with dichloromethane. The combined organic layer was washed with water (when iodine was used as the reagent, it was washed with sodium thiosulphate solution first), dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product obtained was purified by column chromatography (SiO_2; EtOAc: hexane, 1:9 v/v) to afford the pure product **2**, **3** or **4**.

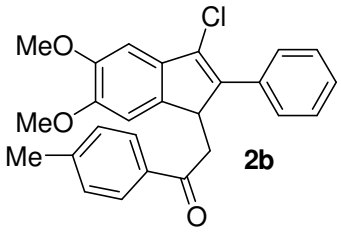
2-(3-Chloro-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-phenyl-ethanone (2a):



2a

Brown oil. Yield: 86% (87 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.46 -7.39 (m, 4H), 7.31 (t, *J* = 7.6 Hz, 1H),7.04 (s, 1H), 7.02 (s,1H), 4.77 (dd, *J* = 10.4, 2.4 Hz, 1H) 3.96 (s, 3H), 3.79 (s, 3H), 3.25 (dd, *J* = 18.0, 2.8 Hz, 1H), 2.98 (dd, *J* = 18.0, 10.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 149.1, 148.4, 140.7, 137.6, 136.9, 134.7, 133.4, 133.2, 128.7, 128.6, 128.1, 127.7, 126.6, 108.0, 102.6, 56.21, 56.17, 45.0, 41.0 ppm. MS (ESI): *m/z* = 405 $[M+H]^+$. Anal. calcd. for $C_{25}H_{21}ClO_3$: C 74.16, H 5.23; found: C 74.25, H 5.36.

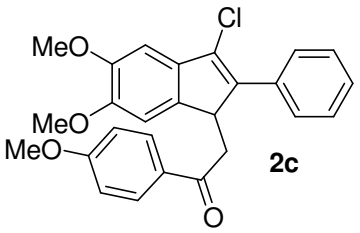
2-(3-Chloro-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-p-tolyl-ethanone (2b):



2b

Yellow oil. Yield: 78% (82 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.7 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.04 (s, 1H), 7.01 (s, 1H), 4.77 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.95 (s, 3H), 3.78, (s, 3H), 3.21 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.95 (dd, *J* = 18.4, 10.8 Hz, 1H) 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 149.1, 148.5, 144.3, 140.8, 137.7, 134.7, 134.5, 133.2, 129.3, 128.7, 128.6, 128.3, 127.64, 126.56, 108.1, 102.7, 56.23, 56.19, 45.1, 40.9, 21.6. ppm. MS (ESI): *m/z* = 441 $[M+Na]^+$. Anal. calcd. for $C_{26}H_{23}ClO_3$: C 74.55, H 5.53; found: C 74.80, H 5.63.

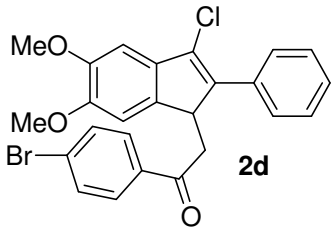
2-(3-Chloro-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-(4-methoxyphenyl)-ethanone (2c):



2c

Yellow oil. Yield: 75% (81 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.7 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 7.01 (s, 1H), 6.87 (d, *J* = 8.8Hz, 2H), 4.77 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.95 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 3.18 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.92 (dd, *J* = 17.6, 10.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 163.7, 149.1, 148.5, 140.9, 137.8, 134.7, 133.3, 130.5, 130.1, 128.63, 128.60, 127.6 126.5, 113.8, 108.1, 102.6, 56.24, 56.16, 55.5, 45.2, 40.6 ppm. MS (ESI): *m/z* = 457 $[M+Na]^+$. Anal. calcd. for $C_{26}H_{23}ClO_4$: C 71.80, H 5.33; found: C 71.66, H 5.47.

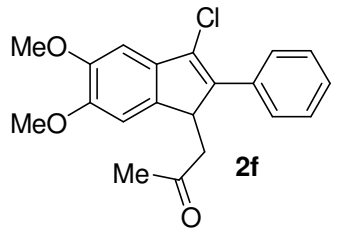
1-(4-Bromophenyl)-2-(3-chloro-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-ethanone (2d):



2d

Brown oil. Yield: 80% (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H) 7.42 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.03 (s, 1H), 6.99 (s, 1H), 4.73 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.95 (s, 3H), 3.80, (s, 3H), 3.20 (dd, *J* = 18.0, 2.0 Hz, 1H), 2.92 (dd, *J*= 17.6, 10.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ198.2, 149.3, 148.6, 140.6, 137.4, 135.6, 134.8, 133.1, 132.0, 129.6, 128.7, 128.62, 128.58, 127.7, 126.8, 108.1, 102.8, 56.3, 56.2, 45.0, 41.0 ppm. MS (ESI): *m/z* = 482 $[M]^+$. Anal. calcd. for $C_{25}H_{20}BrClO_3$: C 62.07, H 4.17; found: C 62.25, H 4.02.

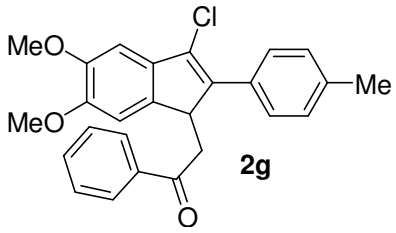
1-(3-Chloro-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-propan-2-one (2f):



2f

Yellow oil. Yield: 74% (63 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.02 (s, 2H), 4.52 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.97 (s, 3H), 3.90, (s, 3H), 2.82 (dd, *J* = 18.4, 3.2 Hz 1H), 2.37 (dd, *J* = 18.0, 10.0 Hz, 1H) 2.10 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 149.2, 148.6, 140.6, 137.4, 134.7, 133.2, 128.64, 128.57, 127.7, 126.6, 107.8, 102.7, 56.4, 56.2, 45.7, 44.7, 30.6 ppm. MS (ESI): *m/z* = 343 $[M+H]^+$. Anal. calcd. for $C_{20}H_{19}ClO_3$: C 70.07, H 5.59; found: C 70.25, H 5.41

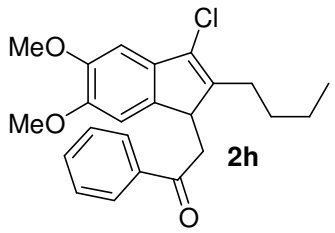
2-(3-Chloro-5,6-dimethoxy-2-p-tolyl-1*H*-inden-1-yl)-1-phenyl-ethanone (2g):



2g

Yellow oil. Yield: 72% (75 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.58-7.51 (m, 3H), 7.41 (t, *J* = 8 Hz, 2H), 7.24 (t, *J* = 2.4 Hz, 2H), 7.03 (s, 1H), 7.01 (s, 1H), 4.74 (dd, *J* = 10.8, 2.4, 1H), 3.95 (s, 3H), 3.79, (s, 3H), 3.25 (dd, *J* = 18.0, 2.8 Hz, 1H), 2.96 (dd, *J* = 17.6, 10.4 Hz, 1H), 21.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 149.1, 148.3, 140.8, 137.6, 137.5, 136.9, 134.8, 133.4, 130.3, 129.4, 128.6, 128.5, 128.1, 125.9, 108.1, 102.5, 56.22, 56.16, 44.9, 41.2, 21.3 ppm. MS (ESI): *m/z* = 441 $[M+Na]^+$. Anal. calcd. for $C_{26}H_{23}ClO_3$: C74.55, H 5.53; found: C 74.73, H 5.66.

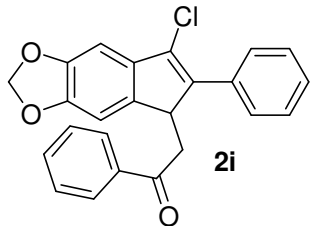
2-(2-Butyl-3-chloro-5,6-dimethoxy-1*H*-inden-1-yl)-1-phenyl-ethanone (2h):



2h

Brown oil. Yield: 68% (65 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8 Hz, 2H), 6.93 (s, 1H), 6.91 (s, 1H), 4.17 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.93 (s, 3H), 3.76, (s, 3H), 3.34 (dd, *J* = 17.2, 4.0 Hz, 1H), 3.02 (dd, *J* = 17.6, 9.2 Hz, 1H), 2.73-2.66 (m, 1H), 2.66 - 2.19 (m, 1H), 1.60- 1.42 (m, 2H) 1.41- 1.31 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0, 149.0, 147.7, 143.7, 137.3, 137.1, 134.5, 133.4, 128.8, 128.2, 126.6, 108.2, 102.3, 56.3, 56.2, 44.4, 39.9, 31.1, 26.3, 22.6, 13.8 ppm MS (ESI): *m/z* = 407 $[M+Na]^+$. Anal. calcd. for $C_{23}H_{25}ClO_3$: C 71.77, H 6.55; found: C 71.95, H 6.75.

2-(7-Chloro-6-phenyl-5*H*-indeno[5,6-d][1,3]dioxol-5-yl)-1-phenyl-ethanone (2i):

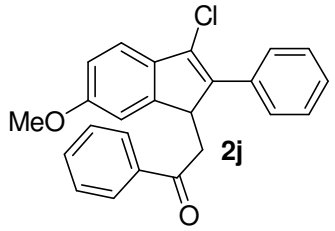


2i

Orange solid. Yield: 72% (70 mg). M.p.: 210-212 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.44 - 7.39 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 2H), 6.99 (s, 1H) 6.96 (s, 1H) 5.96 (dd, *J* = 11.6, 1.2 Hz, 1H), 4.77 (dd, *J* = 10.4, 2.4 Hz, 1H), 3.23 (dd, *J* = 18.0, 2.8 Hz, 1H), 2.97 (dd, *J* = 18.0, 10.4 Hz, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 147.5, 147.1, 141.1, 139.4, 136.7, 136.1, 133.4, 133.1, 128.7, 128.6, 128.5,

128.1, 127.7, 126.5, 105.6, 101.3, 100.5, 44.7, 41.0 ppm. MS (ESI): *m/z* = 389 $[M+H]^+$. Anal. calcd. for $C_{24}H_{19}ClO_3$: C 74.13; H 4.41; found: C 74.32, H 4.57.

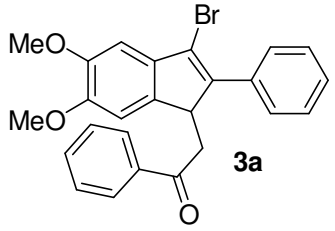
2-(3-Chloro-6-methoxy-2-phenyl-1*H*-inden-1-yl)-1-phenyl-ethanone (2j):



2j

Orange solid. Yield: 78% (73 mg). M.p.: 195-197 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 6.8 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.46 - 7.39 (m, 5H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 2 Hz, 1H)), 6.93 (dd, *J* = 8.4, 2.4Hz, 1H) 4.83 (dd, *J* = 10.4, 2.8 Hz, 1H) 3.77 (s, 3H), 3.23 (dd, *J* = 17.6, 2.8 Hz, 1H), 3.04 (dd, *J* = 18.0, 10.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 159.2, 146.8, 139.9, 136.8, 135.0, 133.3, 133.2, 128.64, 126.61, 128.60, 128.1, 127.7, 126.8, 120.1, 113.1, 110.4, 55.6, 45.0, 40.9 ppm. MS (ESI): *m/z* = 375 $[M+H]^+$. Anal. calcd. for $C_{24}H_{19}ClO_2$: C 76.90; H 5.11; found: C 76.75, H 5.20.

2-(3-Bromo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-phenyl-ethanone (3a):

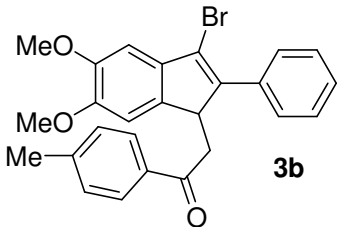


3a

Brown oil. Yield: 77% (86 mg).^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.45 - 7.39 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.03 (s, 1H), 7.01 (s, 1H), 4.74 (dd, *J* = 10.8, 2.8 Hz, 1H) 3.97 (s, 3H), 3.80 (s, 3H), 3.21 (dd, *J* = 18.0, 3.2 Hz, 1H), 2.98 (dd, *J* = 17.6, 10.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 149.19, 149.16, 148.49, 148.46, 144.5, 137.7, 136.92, 136.89, 135.9, 133.9, 133.4, 128.8, 128.7,

128.6, 128.1, 127.8, 116.6, 107.9, 104.0, 56.3, 56.2, 46.6, 40.9 ppm. MS (ESI): *m/z* = 449 $[M+H]^+$. Anal. calcd. for $C_{25}H_{21}BrO_3$: C 66.83, H 4.71; found: C 66.99, H 4.66.

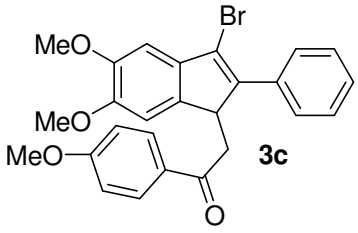
2-(3-Bromo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-p-tolyl-ethanone (3b):



3b

Brown oil. Yield: 70% (81 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.02 (s, 1H), 7.00 (s, 1H), 4.74 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.96 (s, 3H), 3.78, (s, 3H), 3.17 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.95 (dd, *J* = 17.6, 10.8 Hz, 1H) 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ .198.8, 149.1, 148.4, 144.6, 144.3, 137.7, 135.9, 134.5, 133.9, 129.3, 128.8, 128.6, 128.3, 127.8, 116.5, 107.9, 103.9, 56.24, 56.21, 46.6, 40.7, 21.6. ppm. MS (ESI): *m/z* = 485 $[M+Na]^+$. Anal. calcd. for $C_{26}H_{23}BrO_3$: C 67.39; H 5.00; found: C 67.51, H 5.15.

2-(3-Bromo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-(4-methoxy-phenyl)-ethanone (3c):

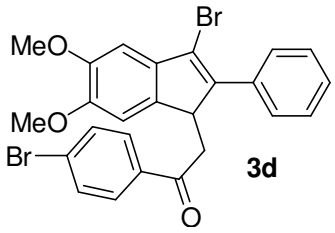


3c

Yellow oil. Yield: 73% (87 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8 Hz, 2H), 6.80 (s, 1H), 6.78 (s, 1H), 4.66 (dd, *J* = 10.4, 2.4 Hz, 1H), 3.88 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.06 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.85 (dd, *J* = 17.2, 10.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 163.7, 149.1, 148.4, 144.7, 137.8, 135.9, 134.0, 130.5, 130.0, 128.8, 128.6,

127.8, 116.4, 113.8, 108.0, 103.9, 56.3, 56.2, 55.5, 46.7, 40.4 ppm. MS (ESI): *m/z* = 501 $[M+Na]^+$. Anal. calcd. for $C_{26}H_{23}BrO_4$: C 65.14, H 4.84; found: C 65.30, H 4.76.

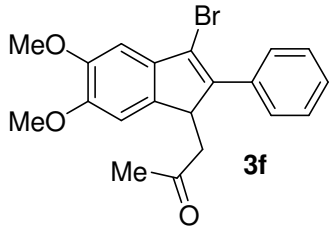
2-(3-Bromo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-(4-bromo-phenyl)-ethanone (3d):



3d

Brown oil. Yield: 80% (105 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H) 7.42 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.03 (s, 1H), 6.99 (s, 1H), 4.71 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.96 (s, 3H), 3.80, (s, 3H), 3.17 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.93 (dd, *J* = 18.0, 10.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 149.2, 148.5, 144.3, 137.4, 135.9, 135.5, 133.8, 131.9, 129.6, 128.7, 128.62, 126.60, 127.9, 116.7, 107.8, 104.0, 56.3, 56.2, 46.4, 40.8 ppm. MS (ESI): *m/z* = 527 [$[M+H]^+$. Anal. calcd. for $C_{25}H_{20}Br_2O_3$: C 56.84; H 3.82; found: C 56.75, H 3.91.

1-(3-bromo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)propan-2-one (3f):

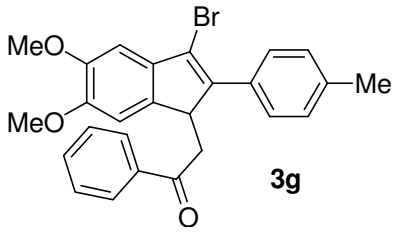


3f

Brown oil. Yield: 69% (66 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.01 (s, 2H), 4.45 (dd, *J* = 10.0, 2.8 Hz, 1H), 3.97 (s, 3H), 3.90, (s, 3H), 2.78 (dd, *J* = 18.0, 3.2 Hz, 1H), 2.38 (dd, *J*= 18.0, 10.0 Hz, 1H) 2.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 149.2, 148.5, 144.3, 137.5, 135.9, 133.9, 128.7,

128.6, 127.9, 116.5, 107.6, 104.0, 56.4, 56.2, 46.2, 45.5, 30.6 ppm. MS (ESI): *m/z* = 409 $[M+Na]^+$. Anal. calcd. for $C_{20}H_{19}BrO_3$: C 62.03; H 4.95; found: C 62.21, H 5.04.

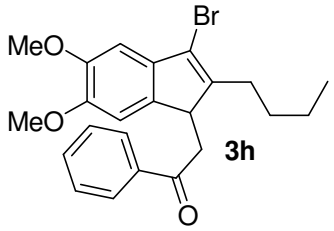
2-(3-Bromo-5,6-dimethoxy-2-p-tolyl-1*H*-inden-1-yl)-1-phenyl-ethanone (3g):



3g

Brown oil. Yield: 71% (82 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8 Hz, 2H), 7.50 (t, *J* = 6.4 Hz, 1H), 7.39 (t, *J* = 8 Hz, 2H), 7.24 (t, *J* = 8 Hz, 2H), 7.02 (s, 1H), 7.01 (s, 1H), 4.71(dd, *J* = 10.4, 2.8 Hz, 1H), 3.96 (s, 3H), 3.79, (s, 3H), 3.20 (dd, *J* = 17.6, 4.0 Hz, 1H), 2.96 (dd, *J* = 17.6, 10.4 Hz, 1H) 2.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 149.1, 148.3, 144.5, 137.8, 137.5, 136.9, 136.0, 133.3, 130.9, 129.3, 128.6, 128.1, 115.9, 107.9, 103.8, 56.22, 56.17, 46.4, 41.0, 21.3 ppm. MS (ESI): *m/z* = 485 $[M+Na]^+$. Anal. calcd.f or $C_{26}H_{23}BrO_3$: C 67.39; H 5.00; found: C 67.58, H 4.98**.**

2-(3-Bromo-2-butyl-5,6-dimethoxy-1*H*-inden-1-yl)-1-phenyl-ethanone (3h):

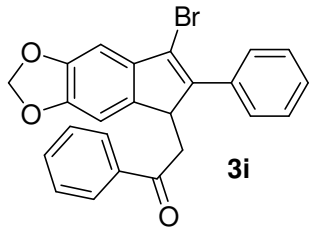


3h

Brown oil. Yield: 65% (70 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8 Hz, 2H), 6.92 (s, 1H), 6.89 (s, 1H), 4.17 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.93 (s, 3H), 3.76, (s, 3H), 3.35 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.03 (dd, *J* = 17.2, 9.2 Hz, 1H), 2.72 - 2.61 (m, 1H), 2.28 - 2.01 (m, 1H), 1.57 - 1.41 (m, 2H) 1.39 - 1.29 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0, 148.9, 147.7, 147.3, 137.4, 137.1, 135.5,

133.4, 128.8, 128.2, 116.9, 108.0, 103.4, 56.3, 56.2, 45.5, 39.9, 31.1, 27.9, 22.6, 13.9. ppm. MS (ESI): *m/z* = 451 $[M+Na]^+$. Anal. calcd. for $C_{23}H_{25}BrO_3$: C 64.34, H 5.87; found: C 64.52, H 5.68.

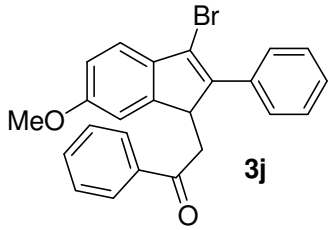
2-(7-Bromo-6-phenyl-5*H*-indeno[5,6-d][1,3]dioxol-5-yl)-1-phenyl-ethanone (3i):



3i

Orange solid. Yield: 70% (76 mg). M.p.: 199-201 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H),7.43-7.37 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.99 (s, 1H), 6.94 (s, 1H), 5.95 (dd, *J* = 11.6, 1.6 Hz, 2H), 4.73 (dd, *J* = 10.0, 2.4 Hz, 1H), 3.18 (dd, *J* = 18.0, 2.8 Hz, 1H), 2.97 (dd, *J* = 18.0, 10.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 147.5, 147.1, 144.9, 139.5, 137.3, 136.7, 133.8, 133.4, 128.7, 128.63, 128.60, 128.1, 127.9, 116.3, 105.4, 101.8, 101.3, 46.1, 40.8 ppm. MS (ESI): *m/z* = 455 $[M+Na]^+$. Anal. calcd. for $C_{24}H_{17}BrO_3$: C 66.53, H 3.95; found: C 66.65, H 4.09.

2-(3-Bromo-6-methoxy-2-phenyl-1*H*-inden-1-yl)-1-phenyl-ethanone (3j):

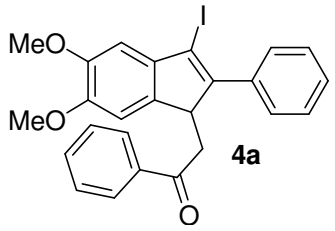


3j

Orange solid. Yield: 70% (73 mg). M.p.: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.43-7.32 (m, 5H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H)), 6.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.81 (dd, *J* = 10.4, 2.8 Hz, 1H) 3.75 (s, 3H), 3.20 (dd, *J* = 18, 3.2 Hz, 1H), 3.02 (dd, *J* = 17.6, 10.0, 1H) ppm. ^{13}C NMR (100

MHz, $CDCl_3$): δ 198.8, 159.3, 146.9, 143.7, 136.8, 136.2, 134.0, 133.4, 128.8, 128.6, 128.2, 127.9, 121.3, 116.6, 113.2, 110.2, 55.6, 46.6, 40.8 ppm. MS (ESI): *m/z* = 441 $[M+Na]^+$. Anal. calcd. for $C_{24}H_{19}BrO_2$: C 68.75, H 4.57; found: C 68.85, H 4.75.

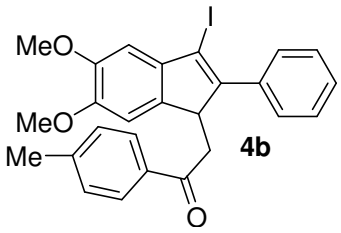
2-(3-Iodo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-phenyl-ethanone (4a):



4a

Yellow oil. Yield: 90% (112 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45-7.38 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 4.74 (dd, *J* = 10.4, 2.8 Hz, 1H) 3.98 (s, 3H), 3.80 (s, 3H), 3.17 (dd, *J* = 18.0, 3.2 Hz, 1H), 2.98 (dd, *J* = 18.0, 10.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1,151.8, 149.1, 148.4, 138.2, 137.7, 136.9, 135.5, 133.4, 128.9, 128.7, 128.5,128.1, 128.0, 107.7, 106.4, 92.8, 56.3, 56.2, 48.3, 40.8. ppm. HRMS (ESI) calcd. for $C_{25}H_{21}IO_3$: 497.0608 $[M+H]^+$; found 497.0613.

2-(3-Iodo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-p-tolyl-ethanone (4b):

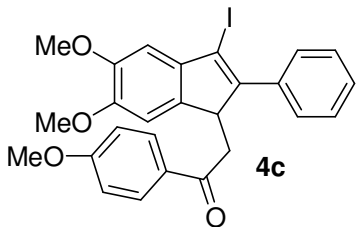


4b

Yellow oil.Yield: 83% (106 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8 Hz, 2H), 6.99 (s, 1H), 6.98 (s, 1H), 4.74 (dd, *J* = 10.4, 2.4 Hz, 1H), 3.98 (s, 3H), 3.79, (s, 3H), 3.13 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.96 (dd, *J* = 17.6, 10.4 Hz, 1H) 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ 198.6, 151.9, 149.1, 148.4, 144.2, 138.2, 137.8, 135.5, 134.5, 129.3, 128.9, 128.5, 128.3, 128.0, 107.8, 106.4, 92.7, 56.30, 56.25, 48.4, 40.6, 21.6 ppm. HRMS (ESI): Calcd. for $C_{26}H_{23}IO_3$: 511.0765 $[M+H]^+$; found 511.0770.

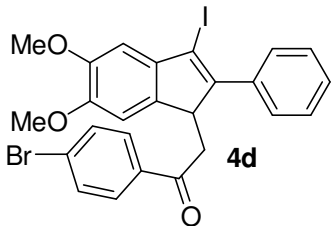
2-(3-Iodo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-1-(4-methoxy-phenyl)-ethanone (4c):



4c

Yellow oil. Yield: 85%. (112 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.98 (s, 1H), 6.97 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.73 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.97 (s, 3H), 3.82, (s, 3H) 3.78 (s, 3H), 3.09 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.92 (dd, *J* = 17.2, 10.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 163.7, 152.0, 149.1, 148.4, 138.2, 137.8, 135.5, 130.5, 130.0, 128.9, 128.5, 128.0, 113.8, 107.8, 106.3, 92.6, 56.3, 56.2, 55.5, 48.5, 40.3. ppm. HRMS (ESI): Calcd. for $C_{26}H_{23}IO_4$: 527.0714 $[M+H]^+$; found 527.0720.

1-(4-Bromophenyl)-2-(3-iodo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-ethanone (4d):

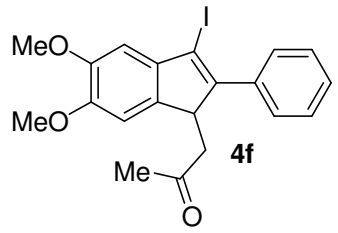


4d

Brown oil. Yield: 83% (119 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H) 7.43 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 6.97 (s, 1H), 6.96 (s, 1H), 4.70 (dd, *J* = 10.4, 3.2 Hz, 1H), 3.98 (s, 3H), 3.81, (s, 3H), 3.12 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.92 (dd, *J* = 17.6, 10.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ

198.0, 151.6, 149.2, 148.4, 138.2, 137.4, 135.6, 135.4, 131.9, 129.6, 128.9,128.62, 128.55, 128.1, 107.6, 106.4, 93.0, 56.33, 56.25, 48.2, 40.7 ppm. HRMS (ESI): Calcd. for $C_{25}H_{20}BrIO_3$: 574.9713 $[M+H]^+$; found 574.9717.

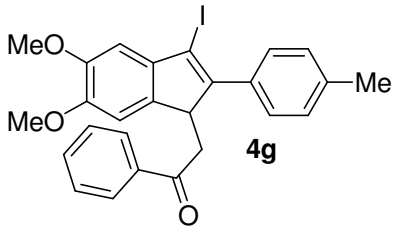
1-(3-Iodo-5,6-dimethoxy-2-phenyl-1*H*-inden-1-yl)-propan-2-one (4f):



4f

Brown oil.Yield: 74% (80 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 6.99 (s, 1H), 6.95 (s, 1H), 4.46 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.96 (s, 3H), 3.89, (s, 3H), 2.71 (dd, *J* = 18, 3.2 Hz, 1H), 2.36 (dd, *J* = 17.6, 10.0 Hz, 1H) 2.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 151.6, 149.2, 148.5, 138.2, 137.5, 135.5, 128.9, 128.5, 128.0, 107.5, 106.4, 92.7, 56.4, 56.3, 48.0, 45.4, 30.6. ppm. HRMS (ESI): Calcd. for $C_{20}H_{19}IO_3$: 457.0271 $[M+Na]^+$; found 457.0277.

2-(3-Iodo-5,6-dimethoxy-2-p-tolyl-1*H*-inden-1-yl)-1-phenyl-ethanone (4g):

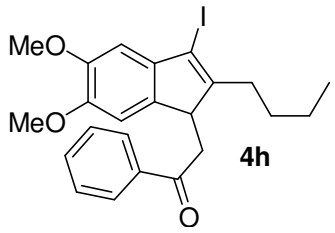


4g

Yellow oil. Yield: 78% (99 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.54-7.49 (m, 3H), 7.40 (t, *J* = 8 Hz, 2H), 7.24 (t, *J* = 5.6 Hz, 2H), 6.98 (s, 1H), 6.96 (s, 1H), 4.71 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.97 (s, 3H), 3.79, (s, 3H), 3.15 (dd, *J* = 17.6, 3.2 Hz, 1H), 2.96 (dd, *J* = 17.6, 10.4 Hz, 1H) 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 151.8, 149.1, 148.3, 138.3, 137.9, 137.6, 136.9, 133.3, 132.5, 129.2, 128.8, 128.6, 128.2, 128.1, 107.1, 106.3,

92.0, 56.3, 56.2, 48.2, 40.9, 21.3. ppm. HRMS (ESI): Calcd. for $C_{26}H_{23}IO_3$: 511.0765 $[M+H]^+$; found 511.0770.

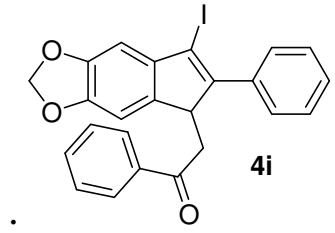
2-(2-Butyl-3-iodo-5,6-dimethoxy-1*H*-inden-1-yl)-1-phenyl-ethanone (4h):



4h

Yellow oil. Yield: 72% (86 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8 Hz, 2H), 6.90 (s, 1H), 6.82 (s, 1H), 4.22 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.94 (s, 3H), 3.76 (s, 3H), 3.35 (dd, *J* = 17.2,4.0 Hz, 1H), 3.03 (dd, *J* = 17.2, 9.2 Hz, 1H), 2.66-2.59 (m, 1H), 2.36- 2.29 (m, 2H),1.58- 1.45 (m, 2H) 1.43- 1.29 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 154.2, 148.9, 147.7, 137.7, 137.6, 137.1, 133.5, 128.8, 128.2, 107.8, 105.6, 93.5, 56.3, 56.2, 46.6, 40.0, 31.3, 31.0, 22.6, 13.9. ppm. HRMS (ESI): Calcd. for $C_{23}H_{25}IO_3$: 477.0921 $[M+H]^+$; found 477.0924.

2-(7-Iodo-6-phenyl-5*H*-indeno[5,6-d][1,3]dioxol-5-yl)-1-phenyl-ethanone (4i):

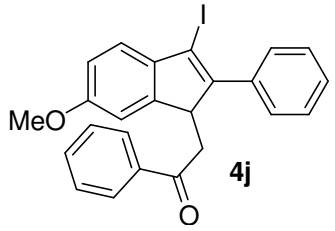


4i

Orange solid. Yield: 78% (94 mg). M.p.: 185-187 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H),7.43-7.37 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.95 (s, 1H), 6.91 (s, 1H), 5.95 (dd, *J* = 11.6, 1.6 Hz, 2H) 4.72 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.14 (dd, *J* = 18.0, 2.8 Hz, 1H), 2.97 (dd, *J* = 17.6, 10.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 152.2, 147.4, 147.0, 139.7, 139.5, 136.7, 135.4, 133.3, 128.9, 128.6, 128.5,

128.1, 128.0, 105.1, 104.2, 101.3, 92.4, 47.8, 40.7 ppm. HRMS (ESI): Calcd. for $C_{24}H_{17}IO_3$: 481.0295$[M+H]^+$; found 481.0288.

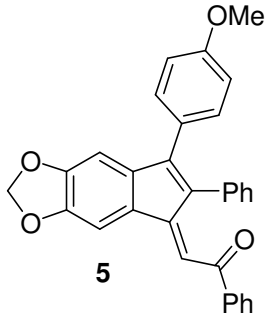
2-(3-Iodo-6-methoxy-2-phenyl-1*H*-inden-1-yl)-1-phenyl-ethanone (4j):



4j

Orange solid. Yield: 85% (99 mg). M.p.: 182-184 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 6.8 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H),7.45-7.38 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 2.4 Hz, 1H)), 6.93 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.82 (dd, *J* = 10.4, 3.2 Hz, 1H), 3.77 (s, 3H), 3.17 (dd, *J* = 17.6, 2.4 Hz, 1H), 3.03 (dd, *J* = 18.0, 10.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 159.2, 150.9, 146.9, 138.5, 136.8, 135.5, 133.3, 128.9, 128.6, 128.5, 128.1, 128.0, 123.6, 113.1, 110.0, 92.6, 55.6, 48.3, 40.6 ppm. HRMS (ESI): Calcd. for $C_{24}H_{19}IO_2$: 489.0322 $[M+Na]^+$; found 489.0328.

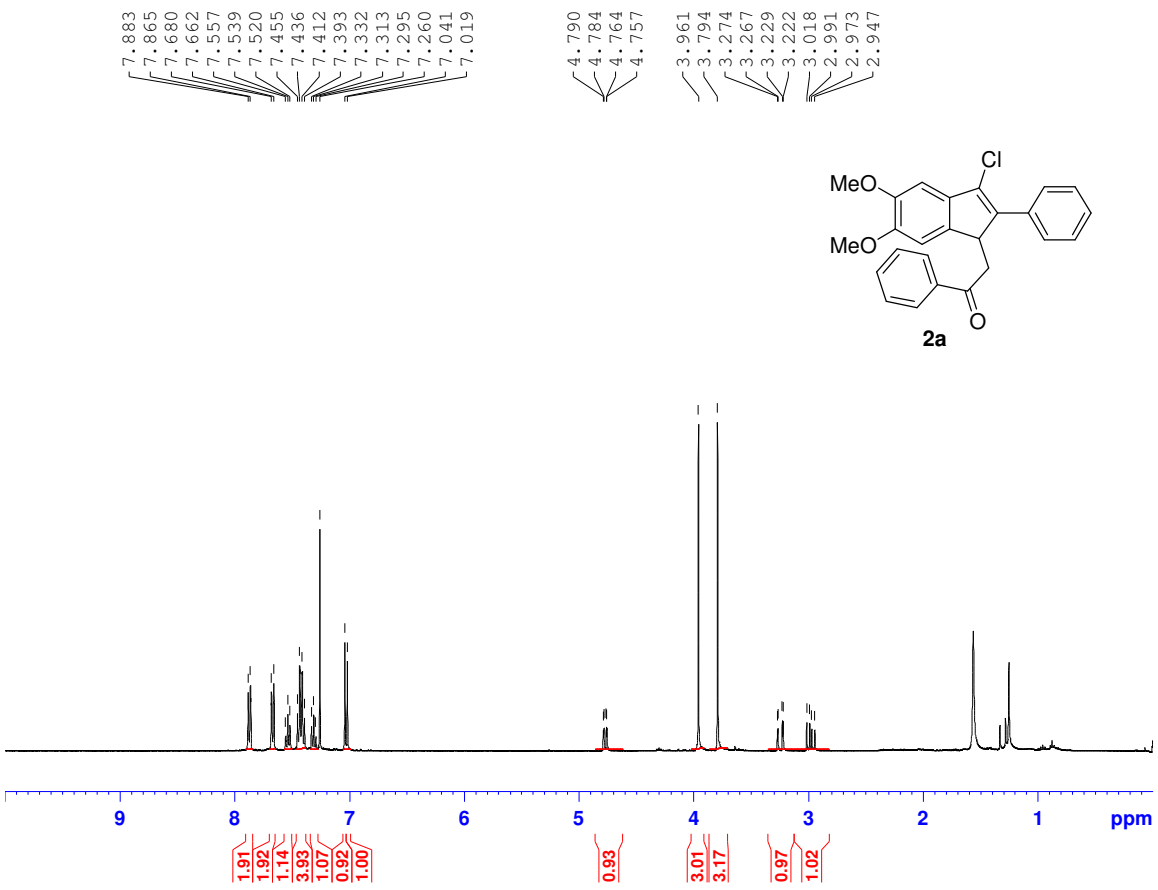
Procedure for the Synthesis of 2-[7-(4-Methoxy-phenyl)-6-phenyl-indeno[5,6-d][1,3]dioxol-5-ylidene]-1-phenyl-ethanone (5):

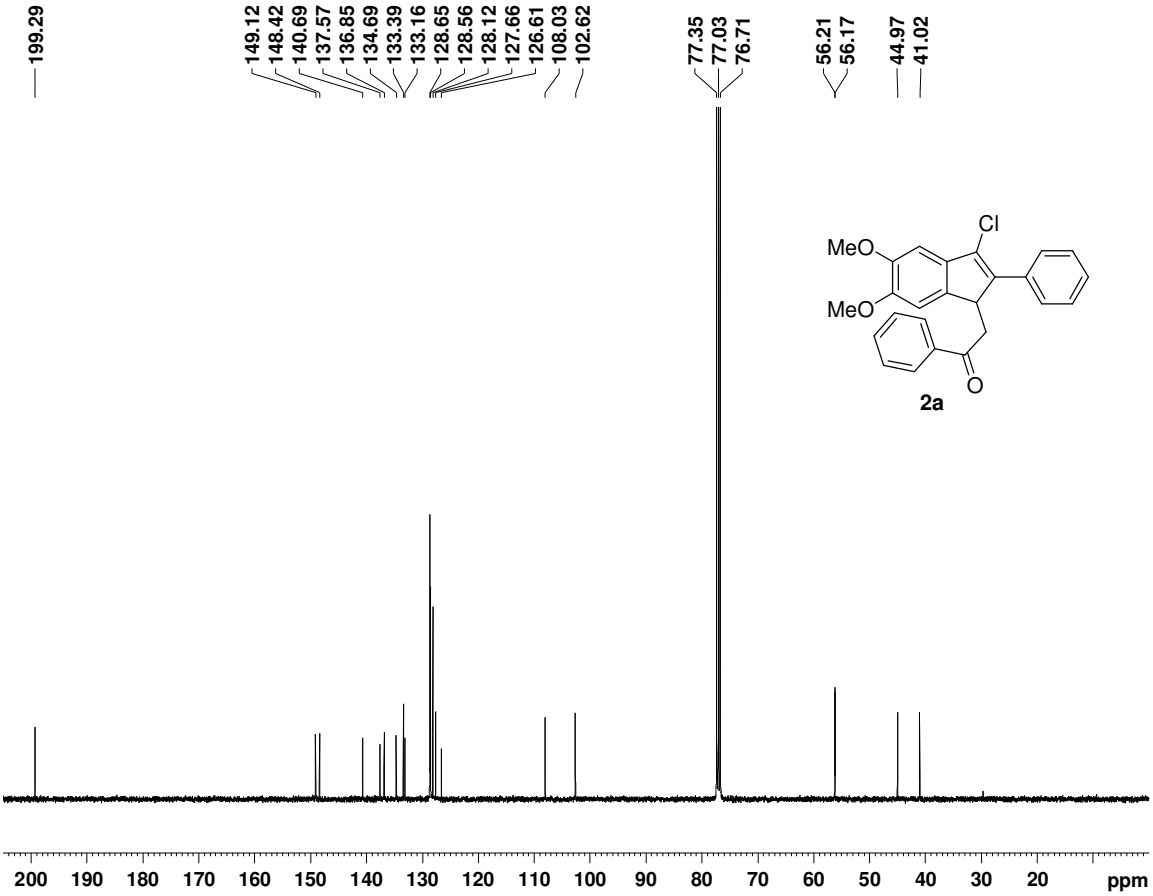


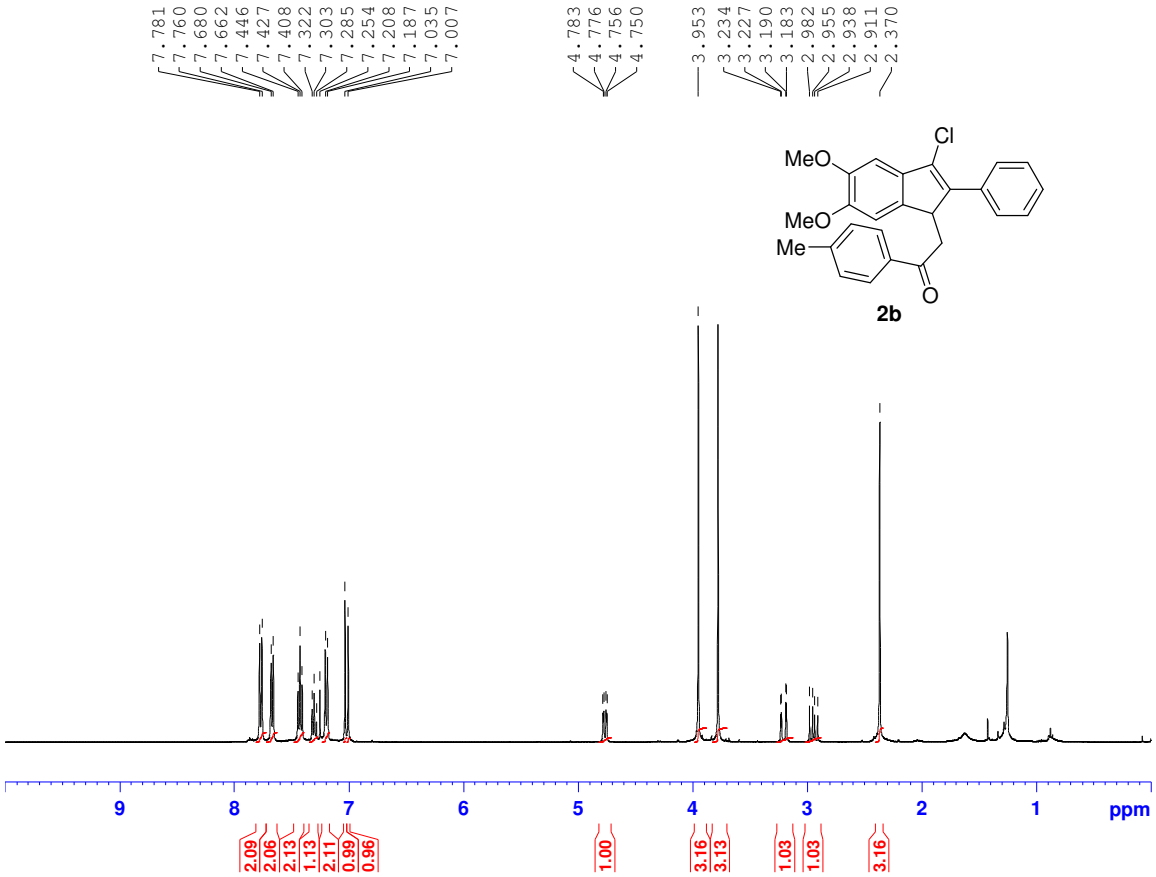
5

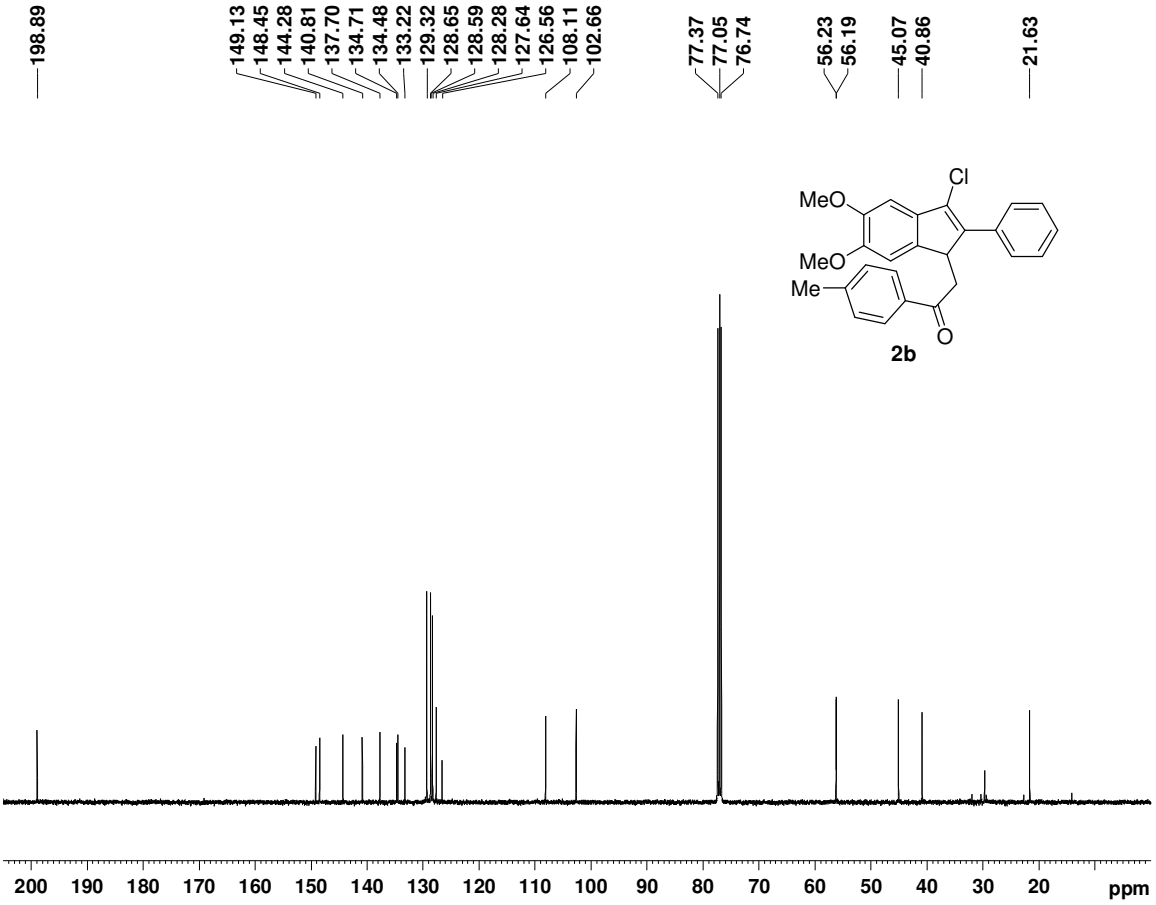
To a solution of **4i** (48 mg; 0.1 mmol) in toluene (2 mL) were added 4-methoxyphenyl boronic acid (23 mg; 0.15 mmol), K_3PO_4 (42 mg, 0.2 mmol), $Pd(OAc)_2$ (1 mg, 5 mol%) and

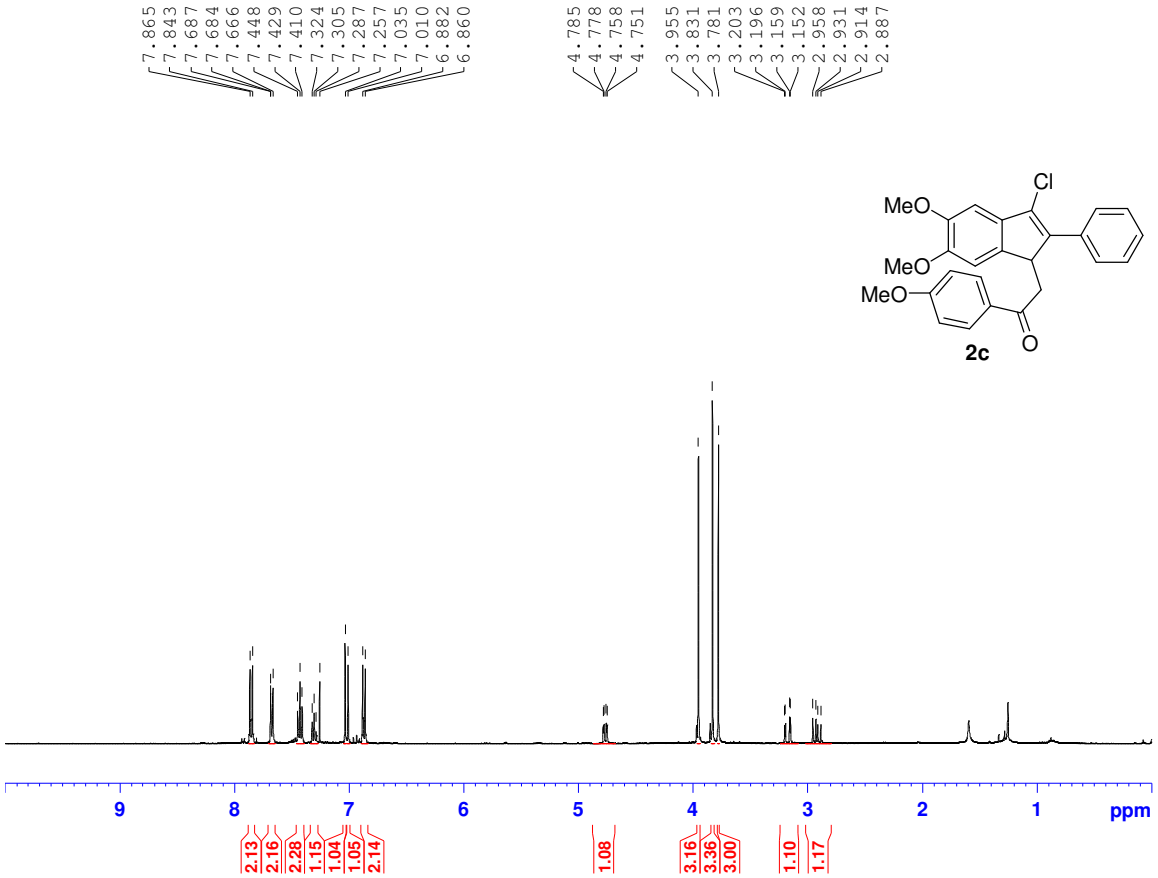
SPhos (4 mg, 10 mol%). The reaction mixture was heated to 60 °C and stirred for 4 h. The mixture was cooled to room temperature and the solvent was evaporated. The residue was diluted with water and extracted with EtOAc. The combined organic layer was washed with water, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2; EtOAc: hexane, 0.5:9.5 v/v) to afford the pure product **5**. Purple oil. Yield: 76% (35 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.6 (d, *J* = 7.6 Hz, 2H), 7.78 (s, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.35-7.17 (m, 7H), 6.96 (s, 1H), 6.84-6.81 (m, 3H), 5.96 (s, 2H), 3.80 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.1, 159.3, 149.9, 148.8, 146.6, 143.8, 140.1, 138.1, 137.5, 133.3, 131.0, 130.5, 128.8, 128.7, 128.2, 126.2, 124.9, 113.8, 107.9, 102.4, 101.4, 55.2 ppm. MS (ESI): *m/z* = 481 $[M+Na]^+$. Anal. calcd. for. $C_{31}H_{22}O_4$: C 81.21, H 4.84; found: C 81.40, H 4.98.

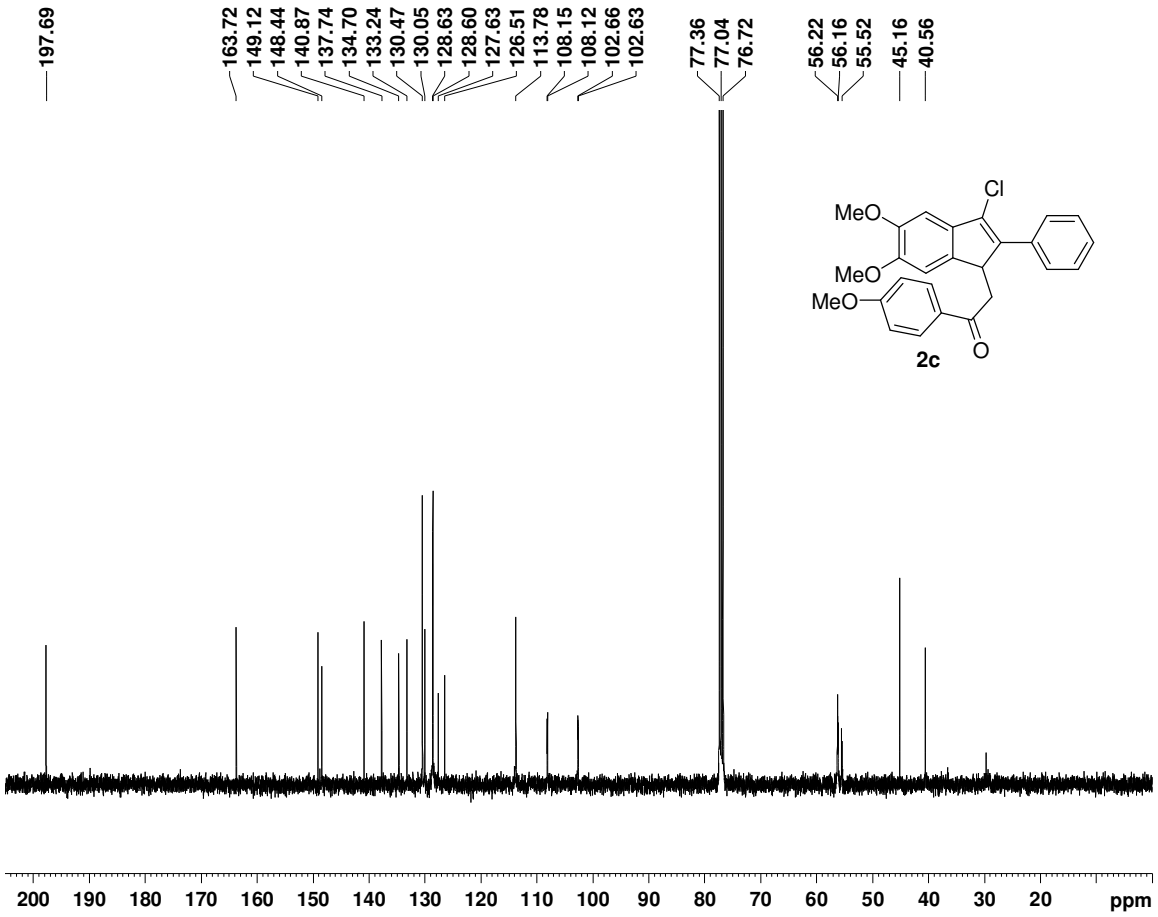

7.883
7.865
7.680
7.662
7.557
7.539
7.520
7.455
7.436
7.412
7.393
7.332
7.313
7.295
7.260
7.041
7.019
4.790
4.784
4.764
4.757
3.961
3.794
3.274
3.267
3.229
3.222
3.018
2.991
2.973
2.947
Cl
MeO
MeO
O
2a
9
8
7
6
5
4
3
2
1
ppm
1.91
1.92
1.14
3.93
1.07
0.92
1.00
0.93
3.01
3.17
0.97
1.02

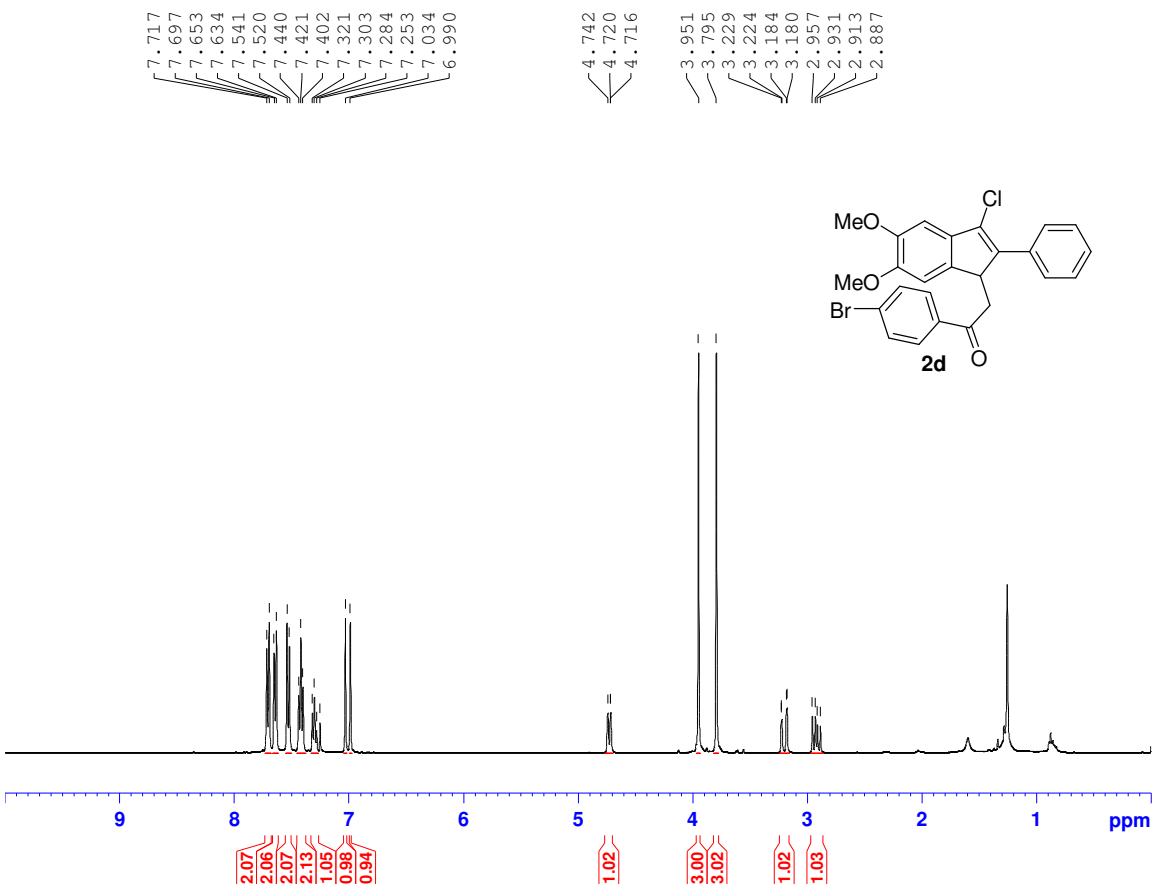

199.29
149.12
148.42
140.69
137.57
136.85
134.69
133.39
133.16
128.65
128.56
128.12
127.66
126.61
108.03
102.62
77.35
77.03
76.71
56.21
56.17
44.97
41.02
Cl
MeO
MeO
O
2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

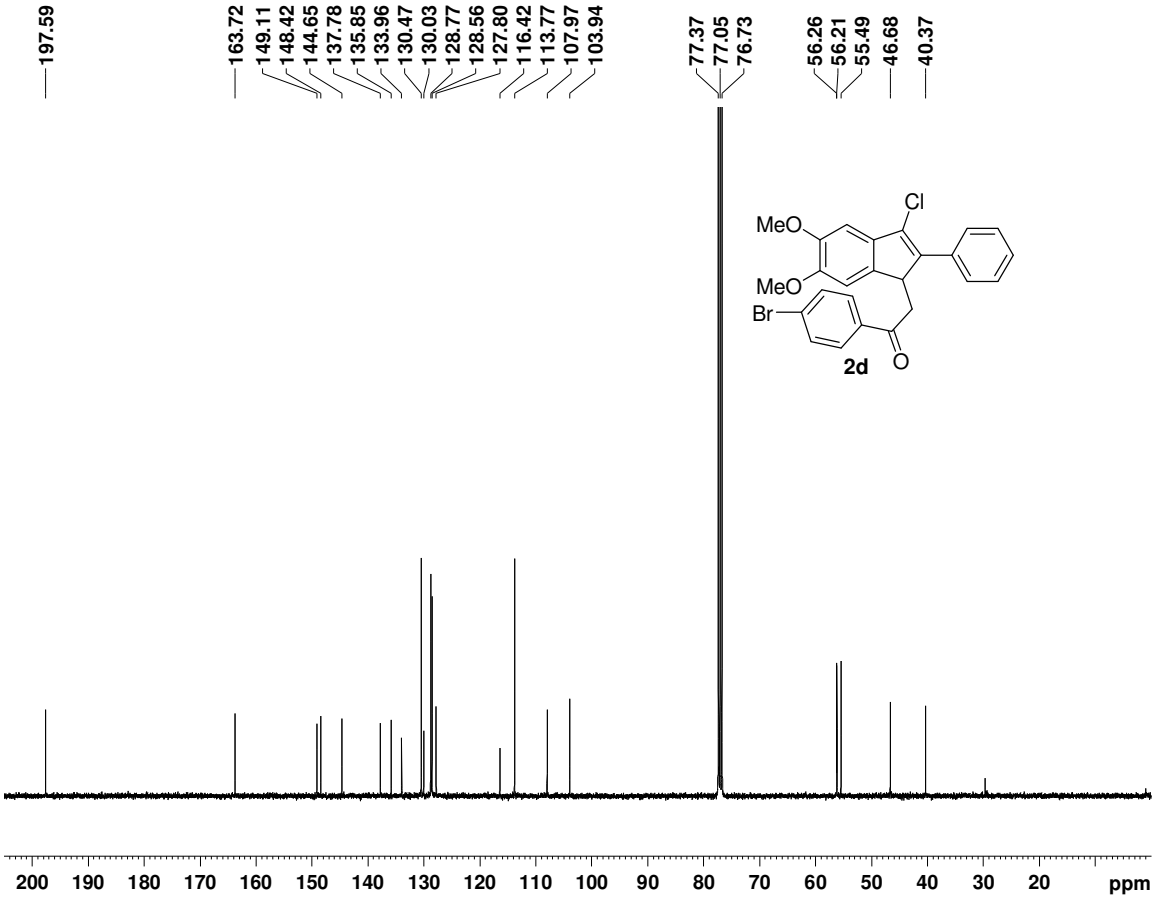

7.781
7.760
7.680
7.662
7.446
7.427
7.408
7.322
7.303
7.285
7.254
7.208
7.187
7.035
7.007
4.783
4.776
4.756
4.750
3.953
3.234
3.227
3.190
3.183
2.982
2.955
2.938
2.911
2.370
Cl
MeO
MeO
Me
O
2b
9
8
7
6
5
4
3
2
1
ppm
2.09
2.06
2.13
1.13
2.11
0.99
0.96
1.00
3.16
3.13
1.03
1.03
3.16

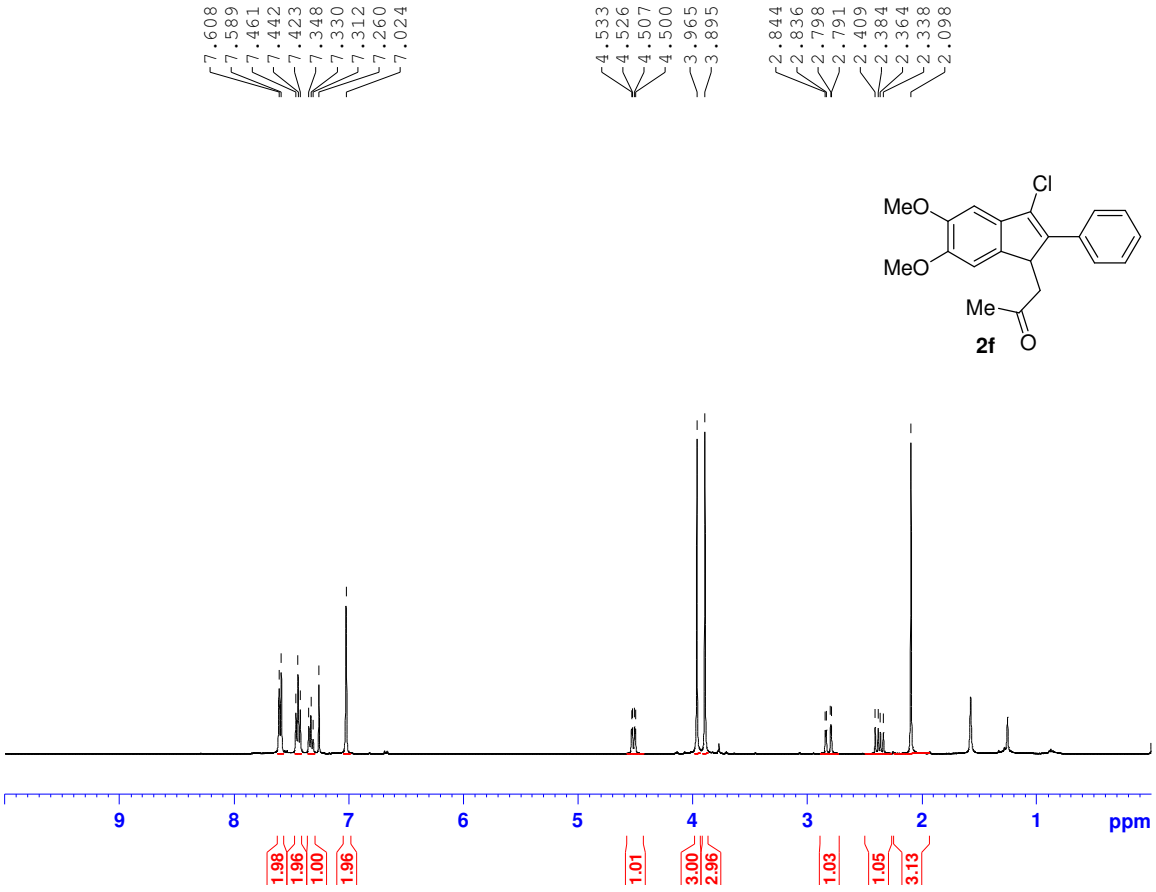

198.89
149.13
148.45
144.28
140.81
137.70
134.71
134.48
133.22
129.32
128.65
128.59
128.28
127.64
126.56
108.11
102.66
77.37
77.05
76.74
56.23
56.19
45.07
40.86
21.63
Cl
MeO
MeO
Me
O
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

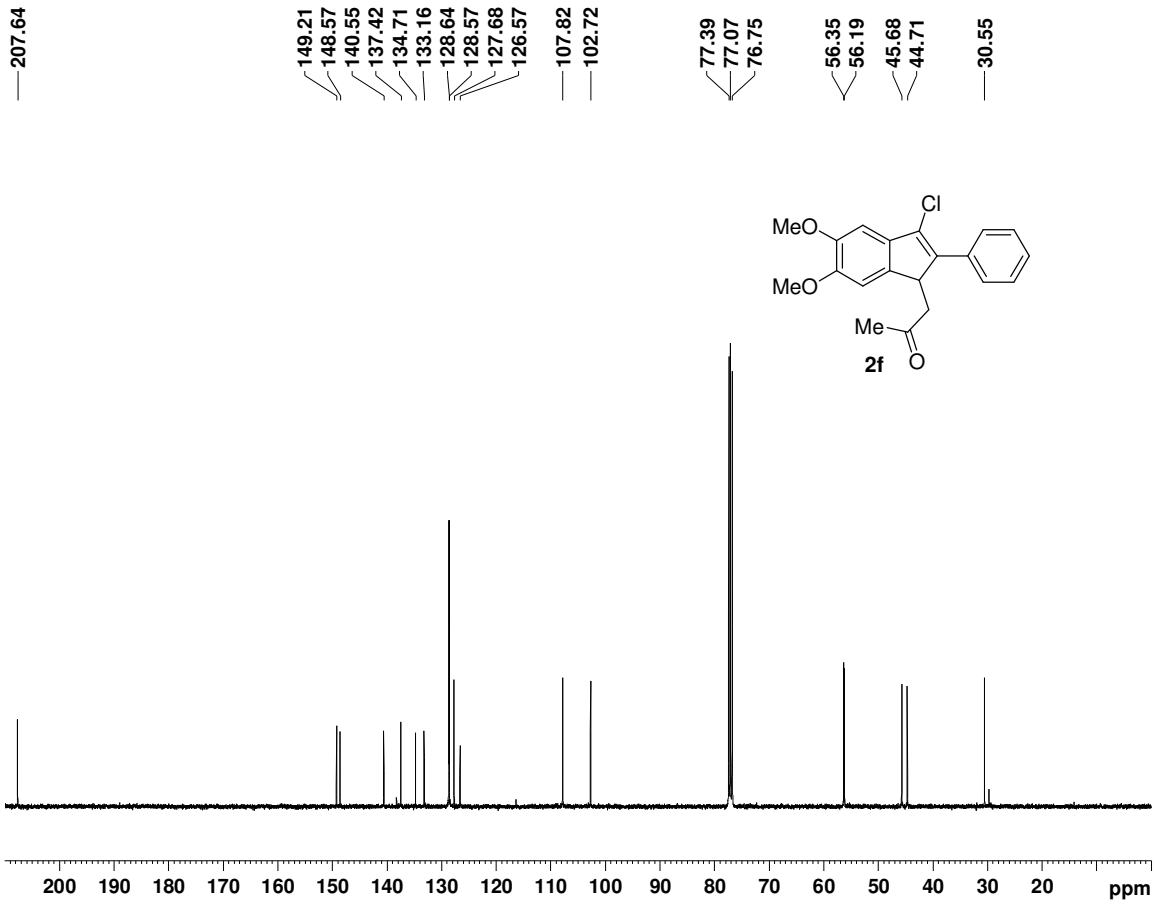

7.865
7.843
7.687
7.684
7.666
7.448
7.429
7.410
7.324
7.305
7.287
7.257
7.035
7.010
6.882
6.860
4.785
4.778
4.758
4.751
3.955
3.831
3.781
3.203
3.196
3.159
3.152
2.958
2.931
2.914
2.887
Cl
MeO
MeO
MeO
O
2c
9
8
7
6
5
4
3
2
1
ppm
2.13
2.16
2.28
1.15
1.04
1.05
2.14
1.08
3.16
3.36
3.00
1.10
1.17

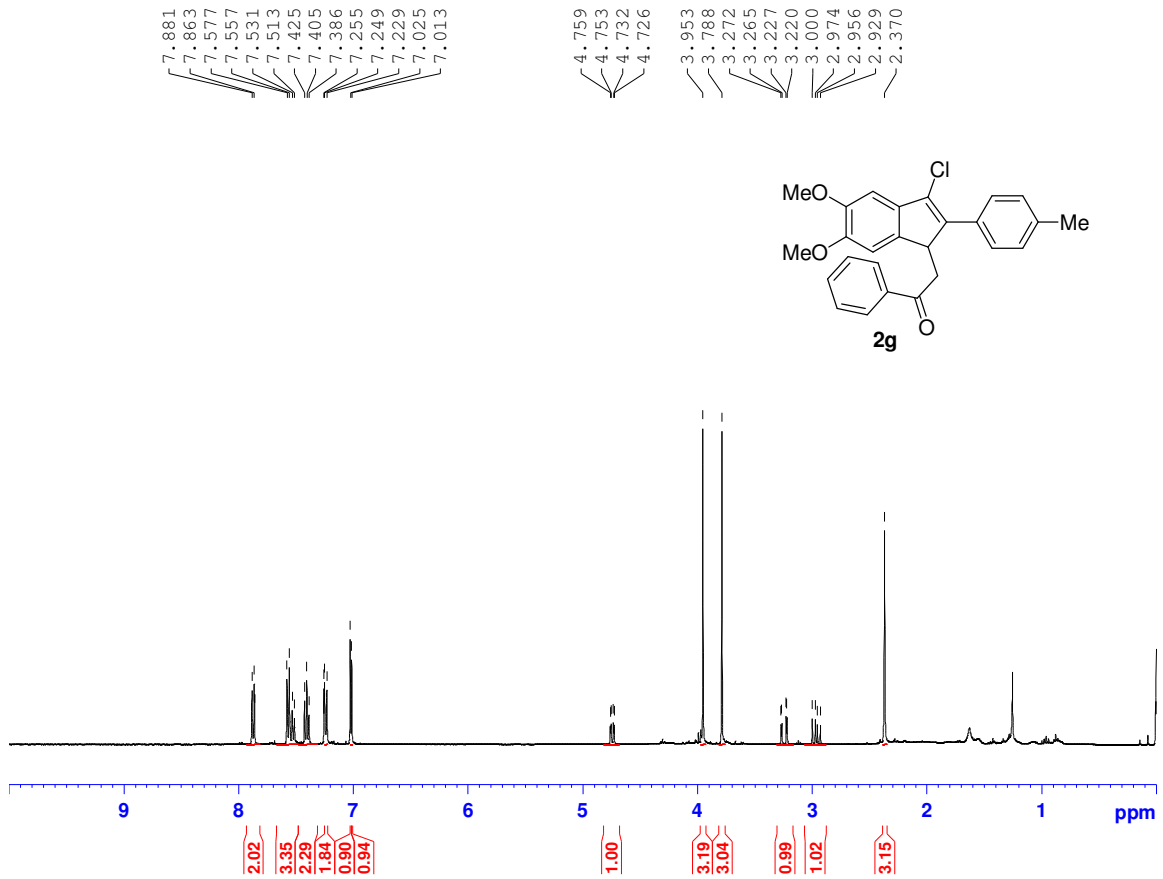

197.69
163.72
149.12
148.44
140.87
137.74
134.70
133.24
130.47
130.05
128.63
128.60
127.63
126.51
113.78
108.15
108.12
102.66
102.63
77.36
77.04
76.72
56.22
56.16
55.52
45.16
40.56
Cl
MeO
MeO
MeO
O
2c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

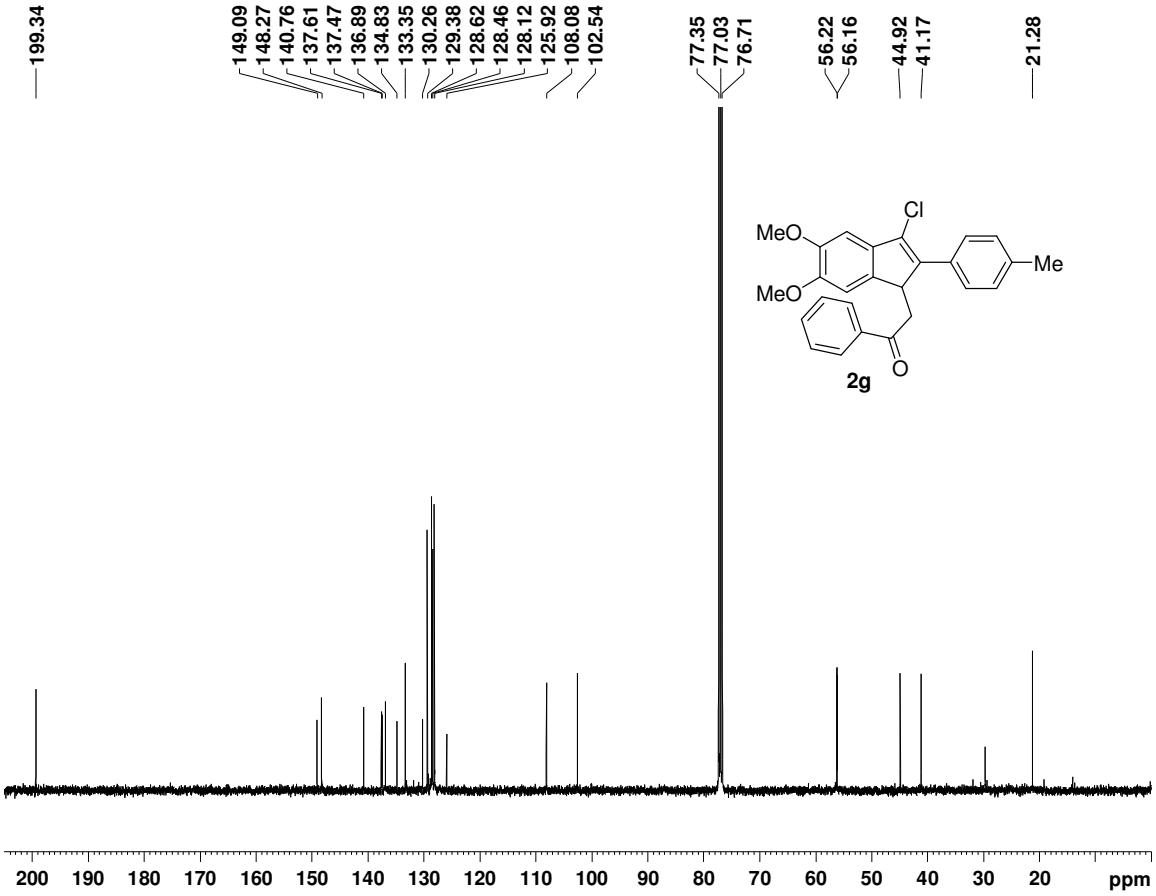

7.717
7.697
7.653
7.634
7.541
7.520
7.440
7.421
7.402
7.321
7.303
7.284
7.253
7.034
6.990
4.742
4.720
4.716
3.951
3.795
3.229
3.224
3.184
3.180
2.957
2.931
2.913
2.887
Cl
MeO
MeO
Br
O
2d
9
8
7
6
5
4
3
2
1
ppm
2.07
2.06
2.07
2.13
1.05
0.98
0.94
1.02
3.00
3.02
1.02
1.03

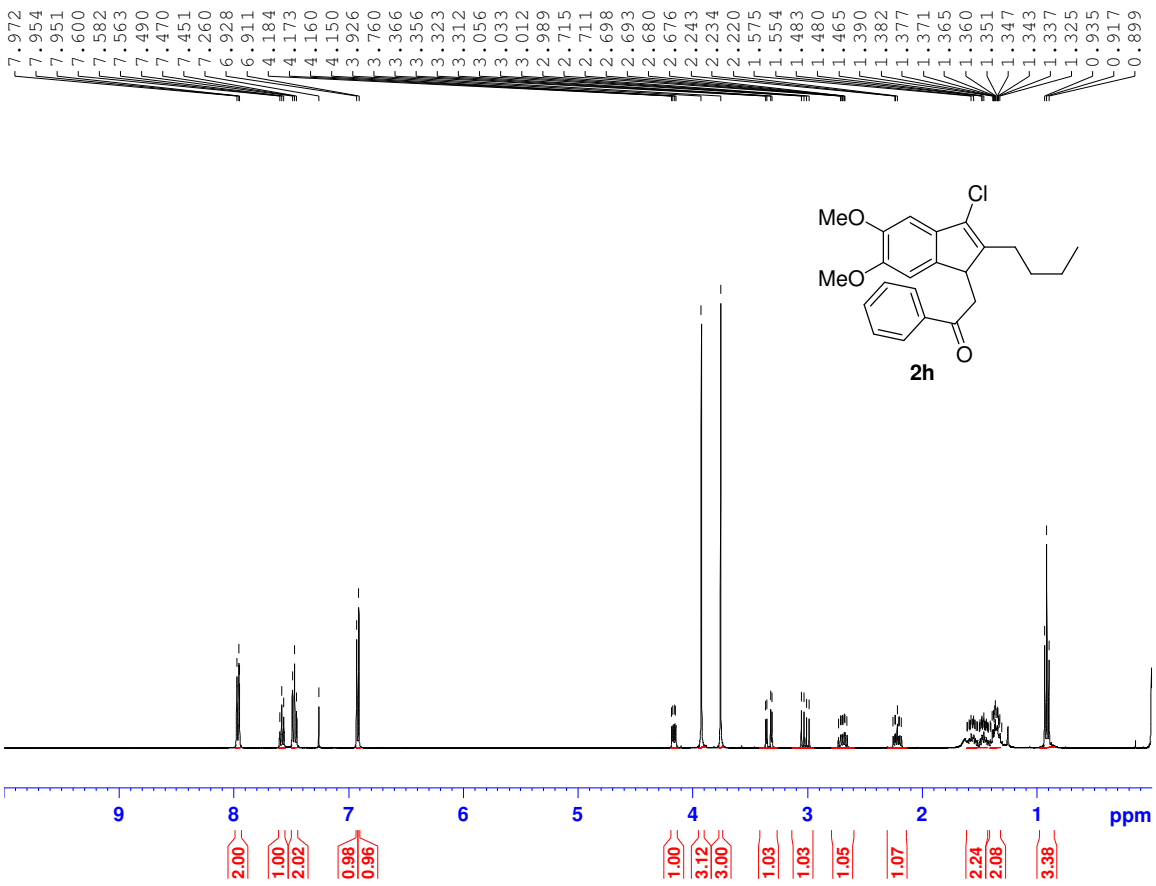

197.59
163.72
149.11
148.42
144.65
137.78
135.85
133.96
130.47
130.03
128.77
128.56
127.80
116.42
113.77
107.97
103.94
77.37
77.05
76.73
56.26
56.21
55.49
46.68
40.37
Cl
MeO
MeO
Br
O
2d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

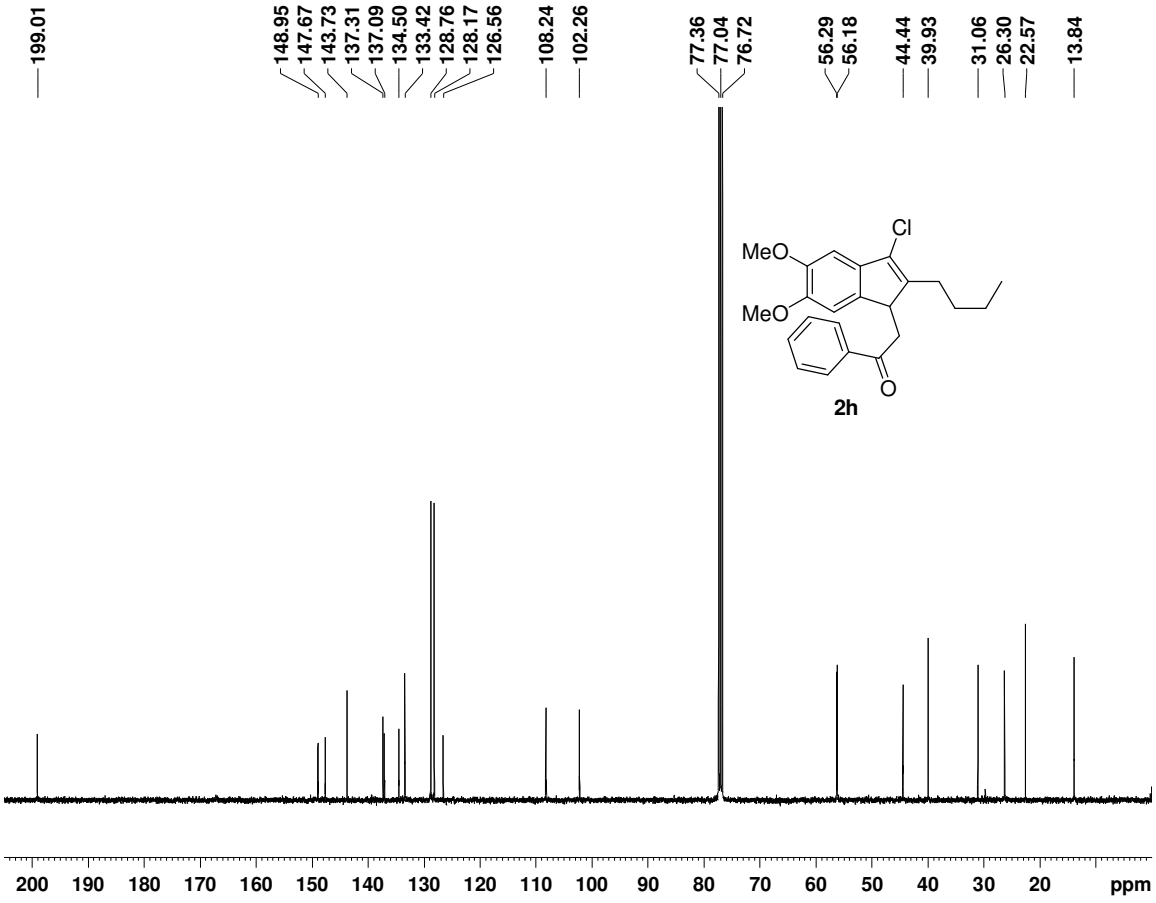

7.608
7.589
7.461
7.442
7.423
7.348
7.330
7.312
7.260
7.024
4.533
4.526
4.507
4.500
3.965
3.895
2.844
2.836
2.798
2.791
2.409
2.384
2.364
2.338
2.098
Cl
MeO
MeO
Me
O
2f
9
8
7
6
5
4
3
2
1
ppm
1.98
1.96
1.00
1.96
1.01
3.00
2.96
1.03
1.05
3.13

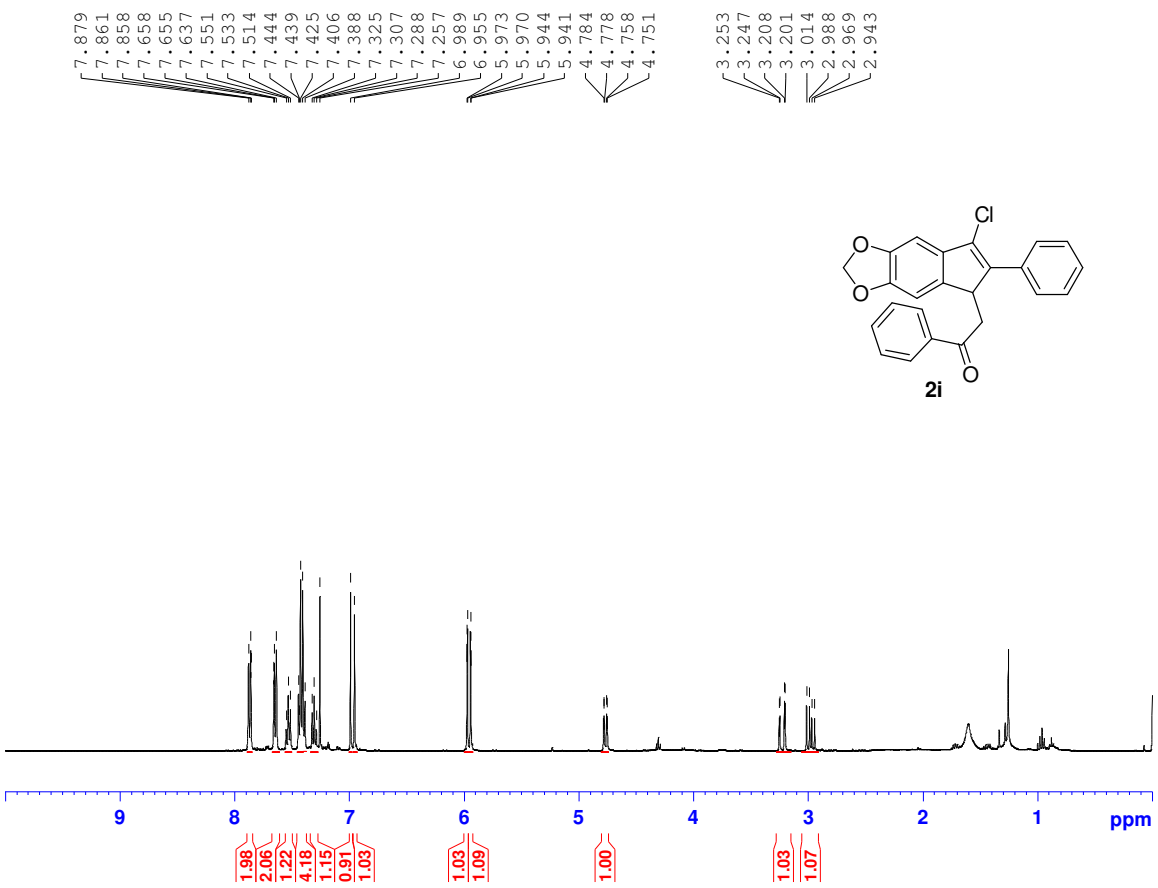

207.64
149.21
148.57
140.55
137.42
134.71
133.16
128.64
128.57
127.68
126.57
107.82
102.72
77.39
77.07
76.75
56.35
56.19
45.68
44.71
30.55
Cl
MeO
MeO
Me
O
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

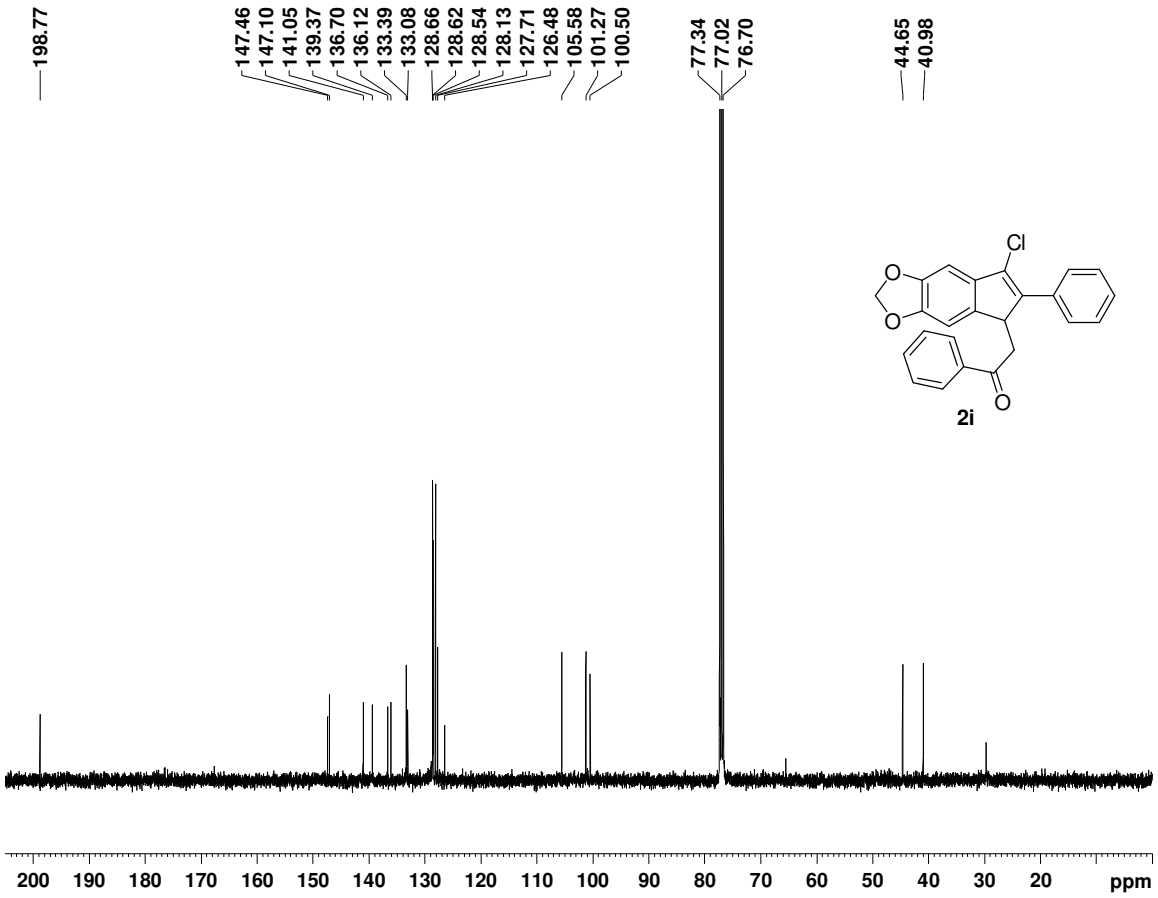

7.881
7.863
7.577
7.557
7.531
7.513
7.425
7.405
7.386
7.255
7.249
7.229
7.025
7.013
4.759
4.753
4.732
4.726
3.953
3.788
3.272
3.265
3.227
3.220
3.000
2.974
2.956
2.929
2.370
Cl
MeO
MeO
Me
O
2g
9
8
7
6
5
4
3
2
1
ppm
2.02
3.35
2.29
1.84
0.90
0.94
1.00
3.19
3.04
0.99
1.02
3.15

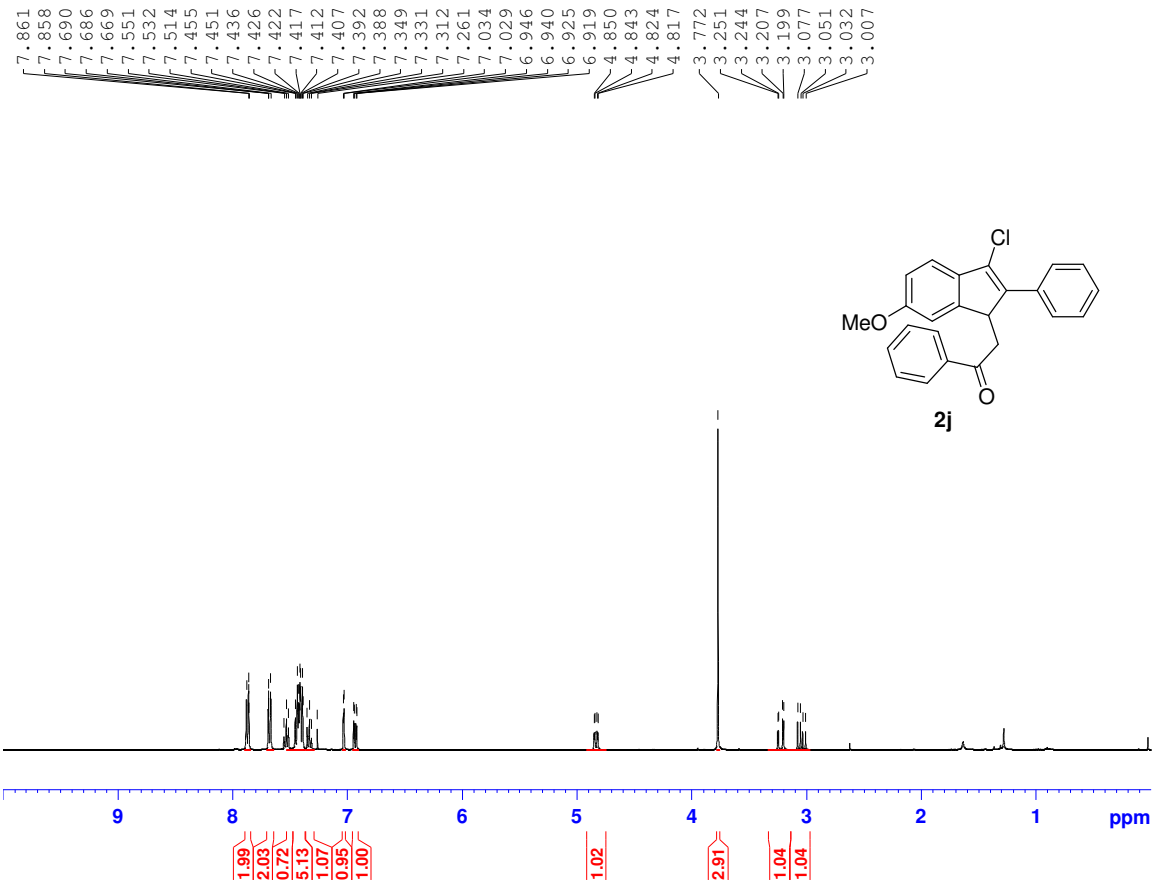

199.34
149.09
148.27
140.76
137.61
137.47
136.89
134.83
133.35
130.26
129.38
128.62
128.46
128.12
125.92
108.08
102.54
77.35
77.03
76.71
56.22
56.16
44.92
41.17
21.28
Cl
MeO
MeO
Me
O
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

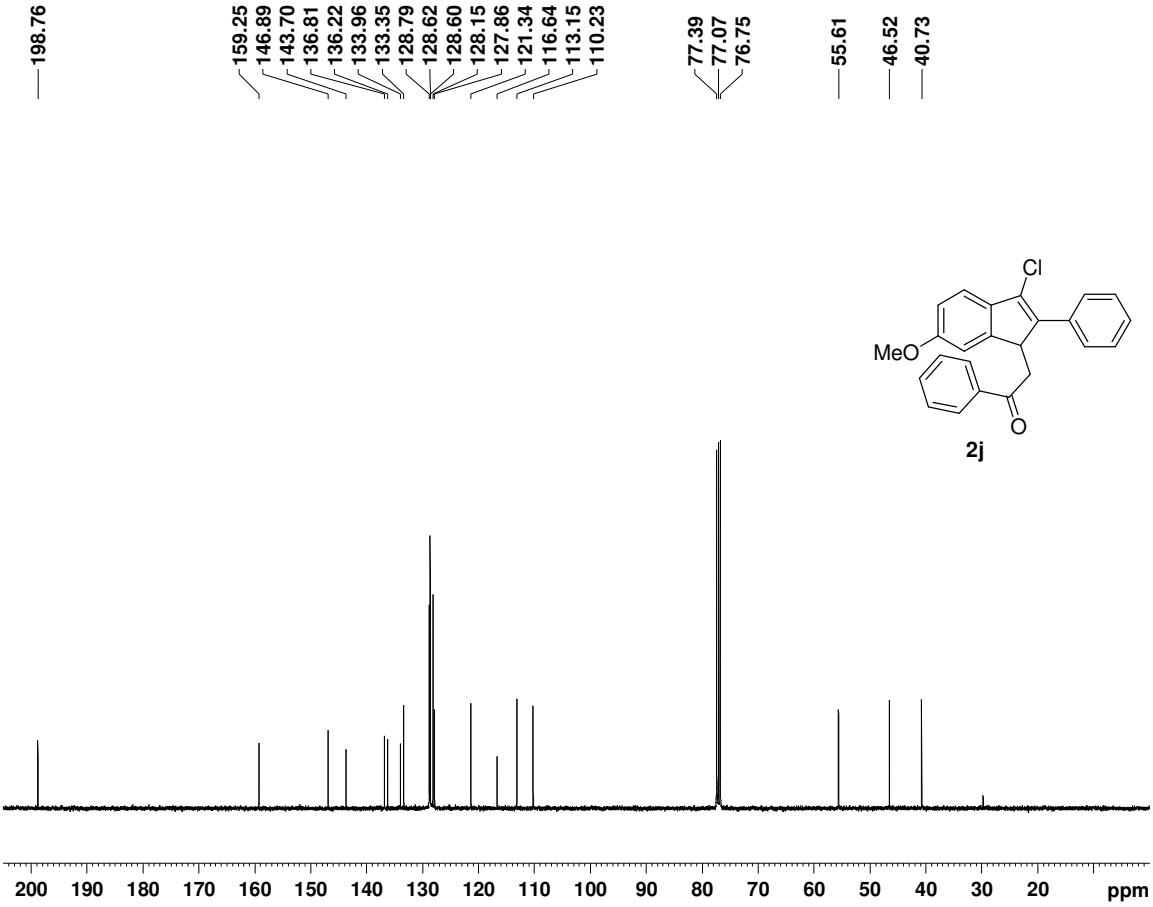

7.972
7.954
7.951
7.600
7.582
7.563
7.490
7.470
7.451
7.260
6.928
6.911
4.184
4.173
4.160
4.150
3.926
3.760
3.366
3.356
3.323
3.312
3.056
3.033
3.012
2.989
2.715
2.711
2.698
2.693
2.680
2.676
2.243
2.234
2.220
1.575
1.554
1.483
1.480
1.465
1.390
1.382
1.377
1.371
1.365
1.360
1.351
1.347
1.343
1.337
1.325
0.935
0.917
0.899
MeO
MeO
Cl
O
2h
9
8
7
6
5
4
3
2
1
ppm
2.00
1.00
2.02
0.98
0.96
1.00
3.12
3.00
1.03
1.03
1.05
1.07
2.24
2.08
3.38

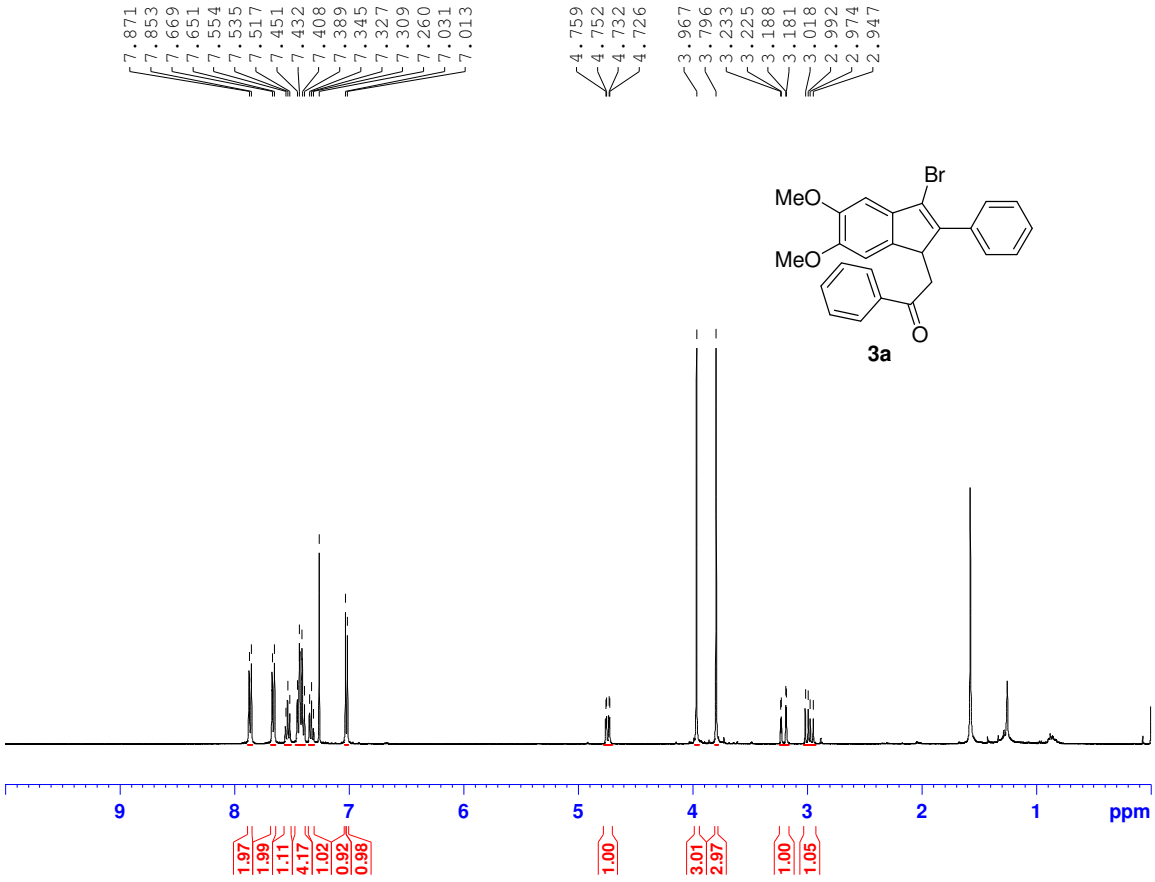

199.01
148.95
147.67
143.73
137.31
137.09
134.50
133.42
128.76
128.17
126.56
108.24
102.26
77.36
77.04
76.72
56.29
56.18
44.44
39.93
31.06
26.30
22.57
13.84
Cl
MeO
MeO
O
2h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

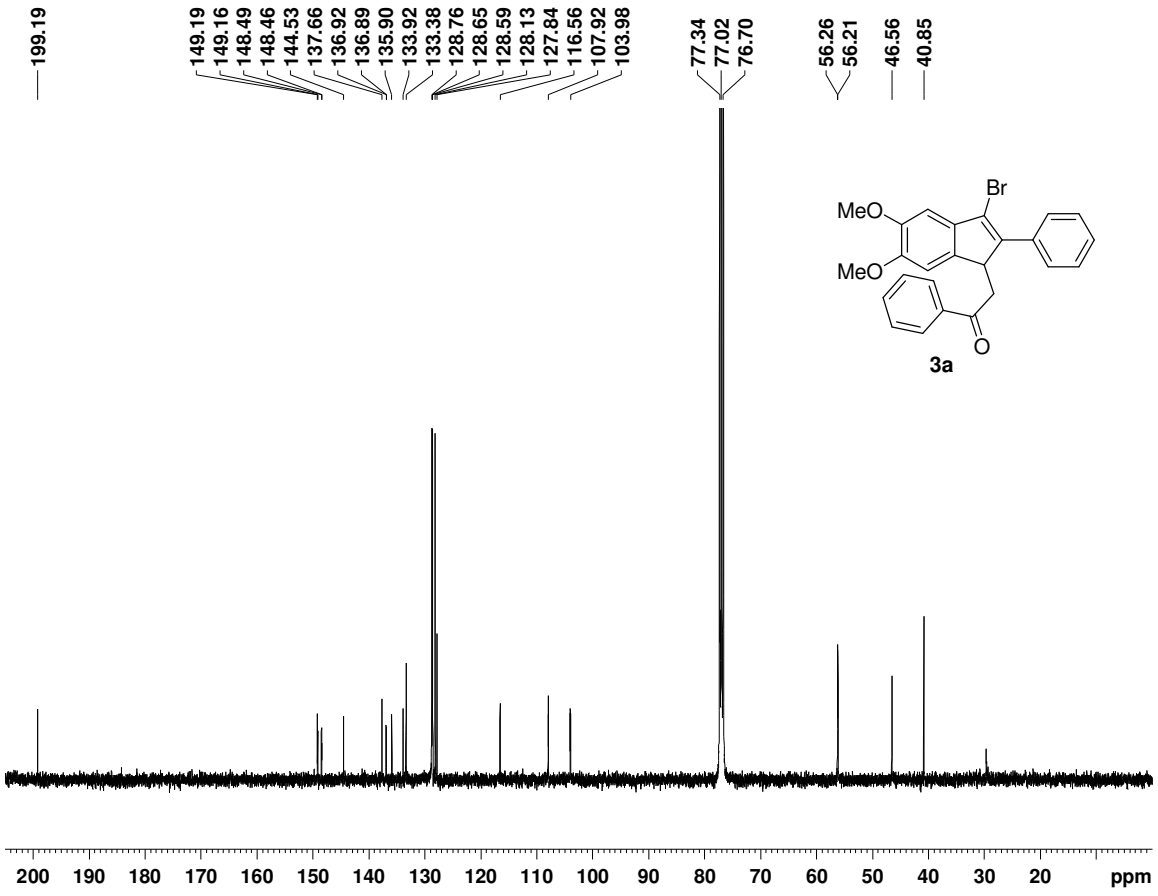

7.879
7.861
7.858
7.658
7.655
7.637
7.551
7.533
7.514
7.444
7.439
7.425
7.406
7.388
7.325
7.307
7.288
7.257
6.989
6.955
5.973
5.970
5.944
5.941
4.784
4.778
4.758
4.751
3.253
3.247
3.208
3.201
3.014
2.988
2.969
2.943
Cl
O
O
O
2i
9
8
7
6
5
4
3
2
1
ppm
1.98
2.06
1.22
4.18
1.15
0.91
1.03
1.03
1.09
1.00
1.03
1.07

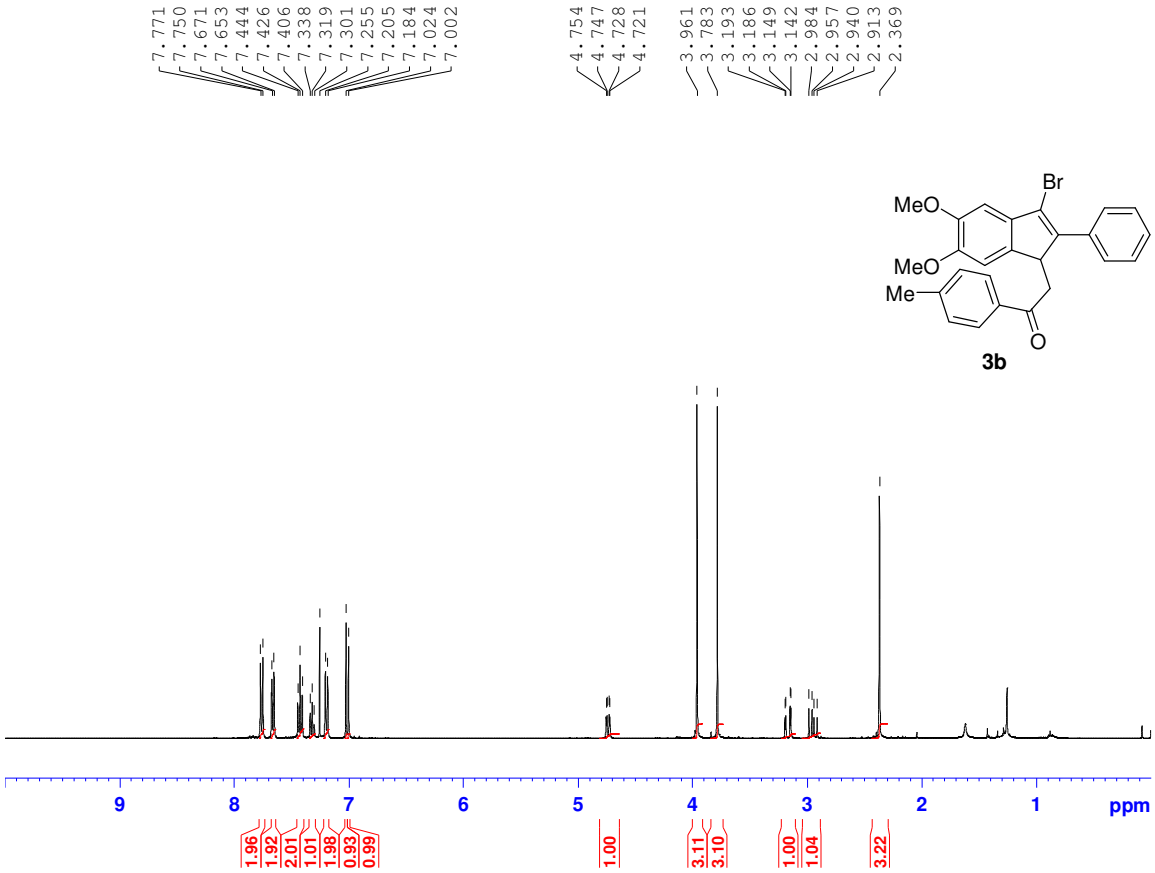

198.77
147.46
147.10
141.05
139.37
136.70
136.12
133.39
133.08
128.66
128.62
128.54
128.13
127.71
126.48
105.58
101.27
100.50
77.34
77.02
76.70
44.65
40.98
Cl
O
O
O
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

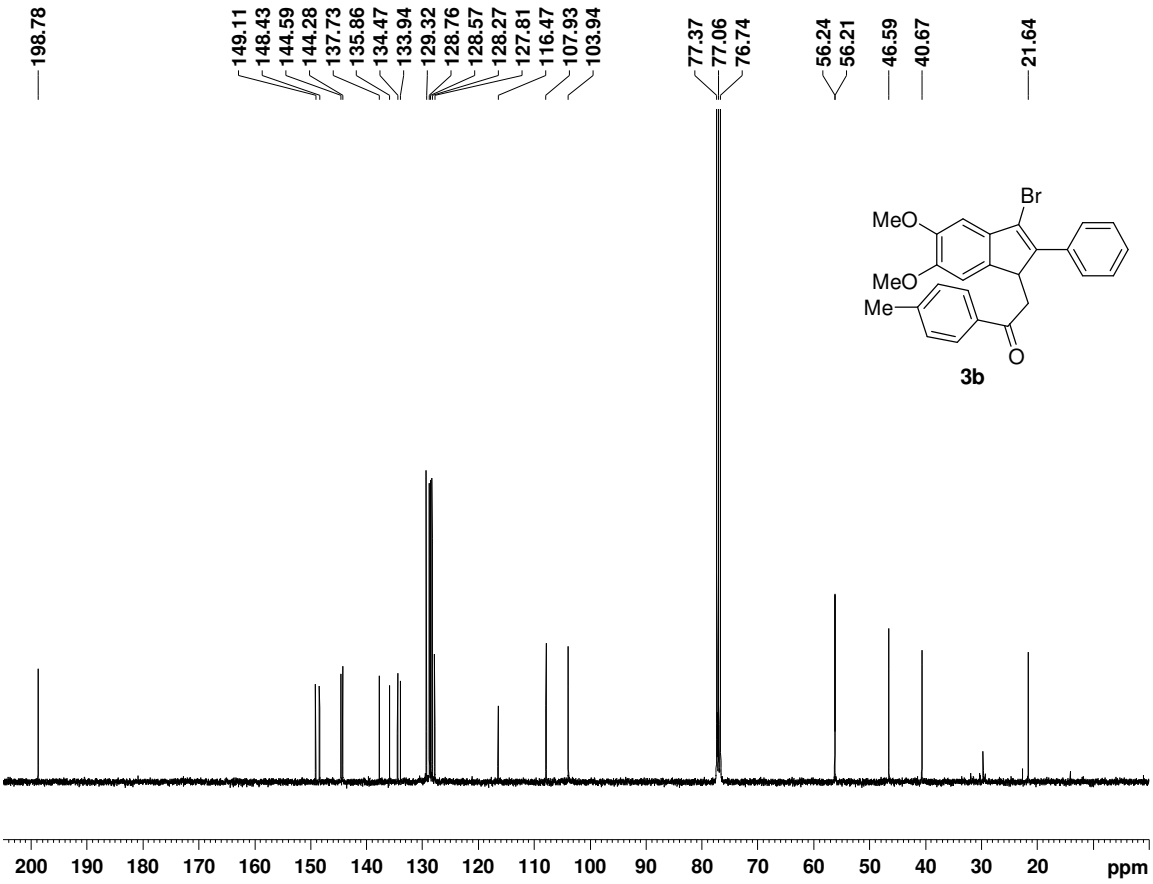

7.861
7.858
7.690
7.686
7.669
7.551
7.532
7.514
7.455
7.451
7.436
7.426
7.422
7.417
7.412
7.407
7.392
7.388
7.349
7.331
7.312
7.261
7.034
7.029
6.946
6.940
6.925
6.919
4.850
4.843
4.824
4.817
3.772
3.251
3.244
3.207
3.199
3.077
3.051
3.032
3.007
Cl
MeO
O
2j
9
8
7
6
5
4
3
2
1
ppm
1.99
2.03
0.72
5.13
1.07
0.95
1.00
1.02
2.91
1.04
1.04

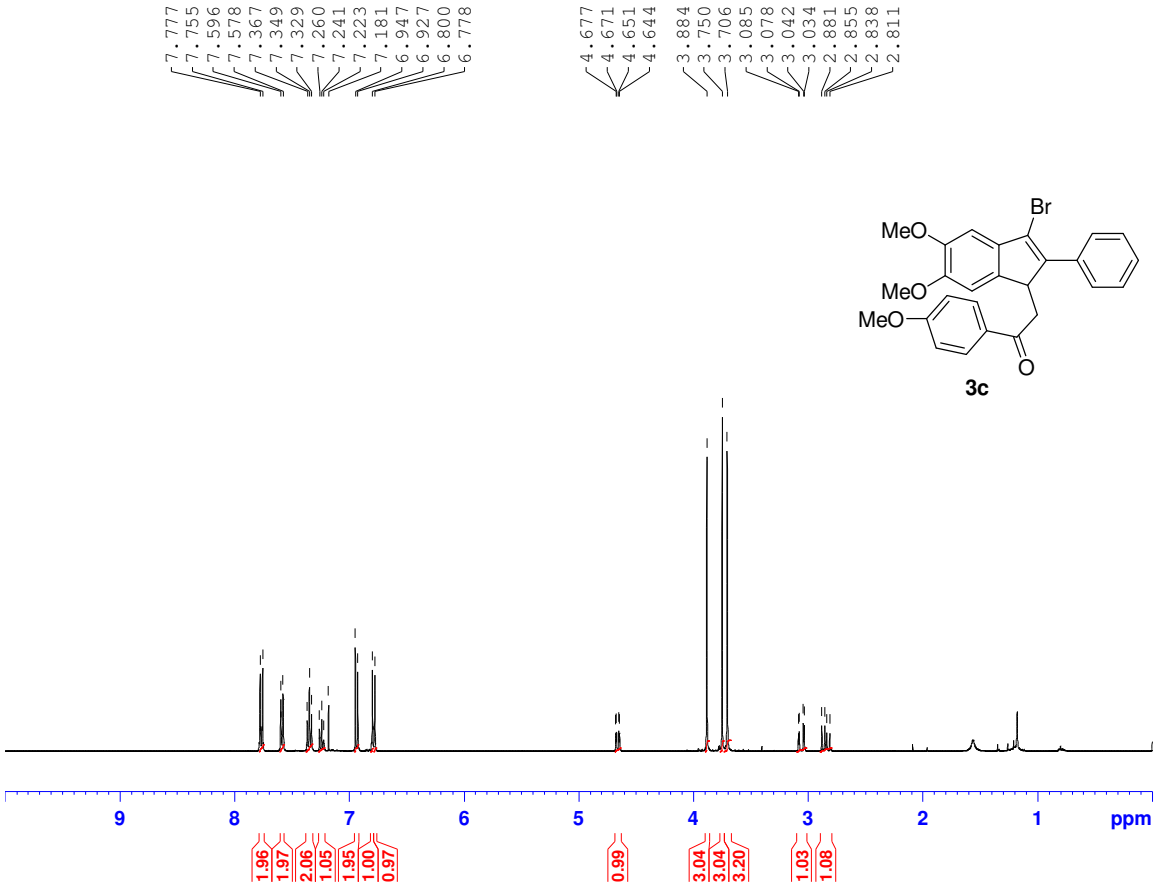

198.76
159.25
146.89
143.70
136.81
136.22
133.96
133.35
128.79
128.62
128.60
128.15
127.86
121.34
116.64
113.15
110.23
77.39
77.07
76.75
55.61
46.52
40.73
Cl
MeO
O
2j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

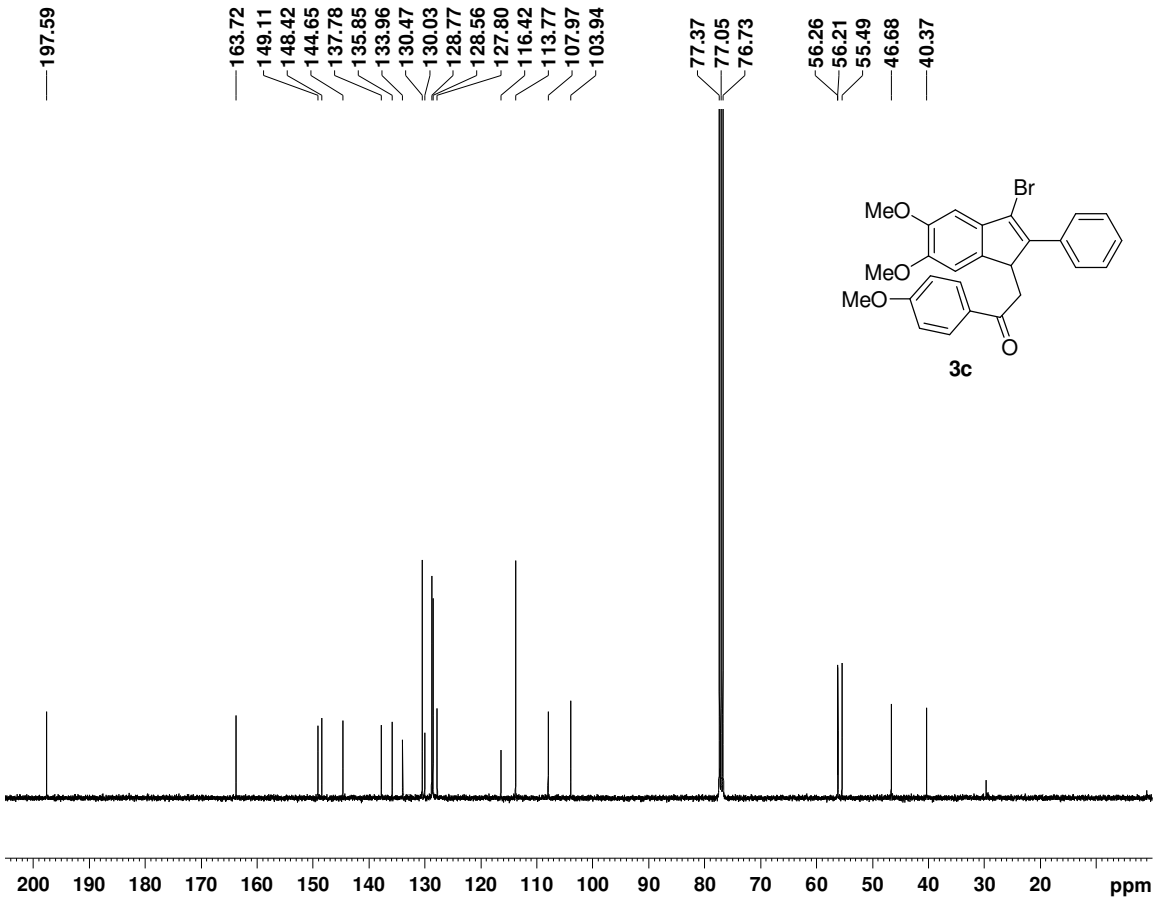

7.871
7.853
7.669
7.651
7.554
7.535
7.517
7.451
7.432
7.408
7.389
7.345
7.327
7.309
7.260
7.031
7.013
4.759
4.752
4.732
4.726
3.967
3.796
3.233
3.225
3.188
3.181
3.018
2.992
2.974
2.947
Br
MeO
MeO
O
3a
9
8
7
6
5
4
3
2
1
ppm
1.97
1.99
1.11
4.17
1.02
0.92
0.98
1.00
3.01
2.97
1.00
1.05

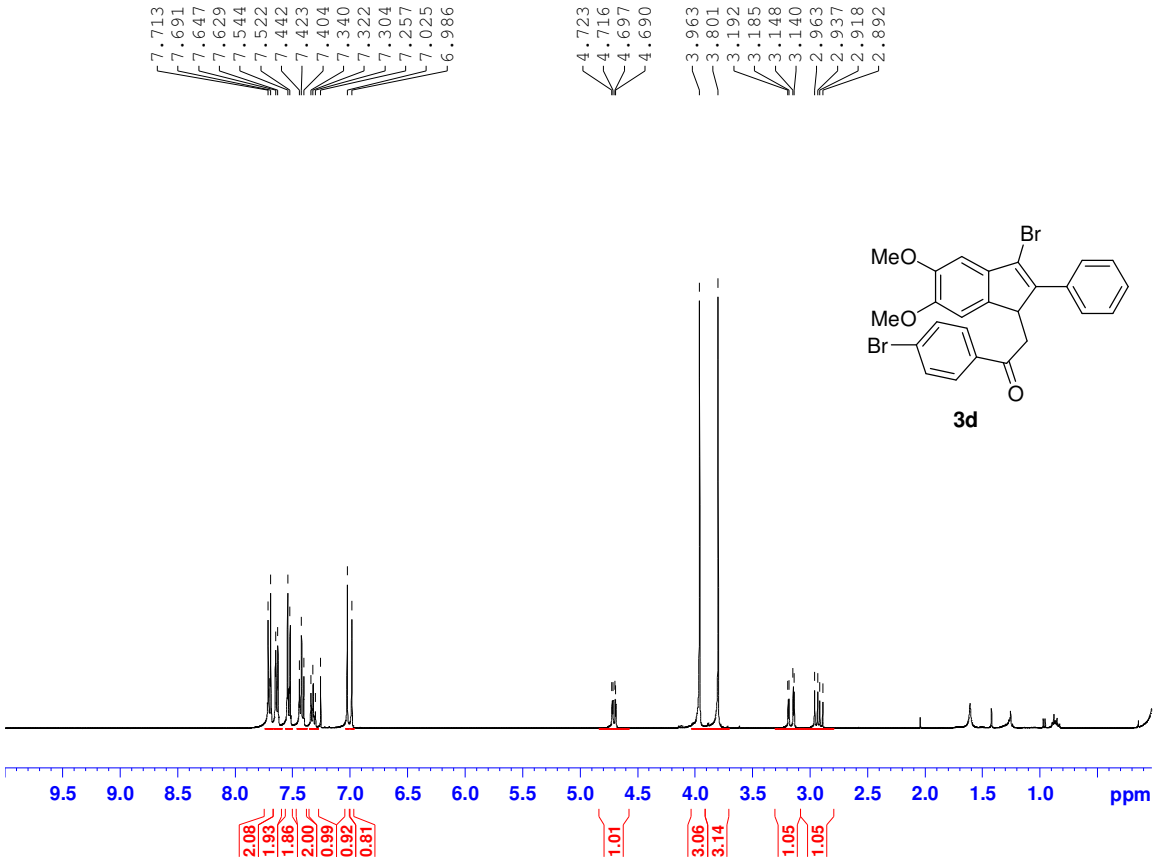

199.19
149.19
149.16
148.49
148.46
144.53
137.66
136.92
136.89
135.90
133.92
133.38
128.76
128.65
128.59
128.13
127.84
116.56
107.92
103.98
77.34
77.02
76.70
56.26
56.21
46.56
40.85
Br
MeO
MeO
O
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

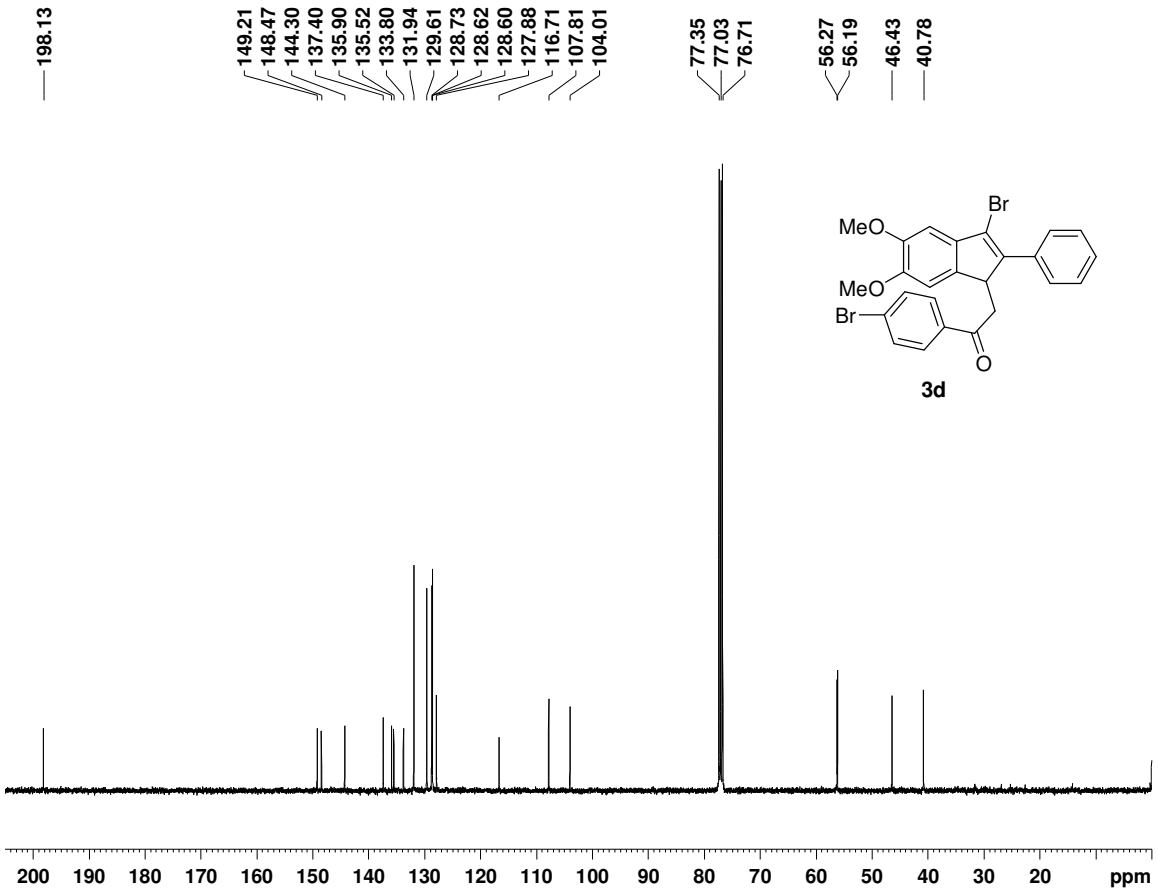

7.771
7.750
7.671
7.653
7.444
7.426
7.406
7.338
7.319
7.301
7.255
7.205
7.184
7.024
7.002
4.754
4.747
4.728
4.721
3.961
3.783
3.193
3.186
3.149
3.142
2.984
2.957
2.940
2.913
2.369
Br
MeO
MeO
Me
O
3b
9
8
7
6
5
4
3
2
1
ppm
1.96
1.92
2.01
1.01
1.98
0.93
0.99
1.00
3.11
3.10
1.00
1.04
3.22

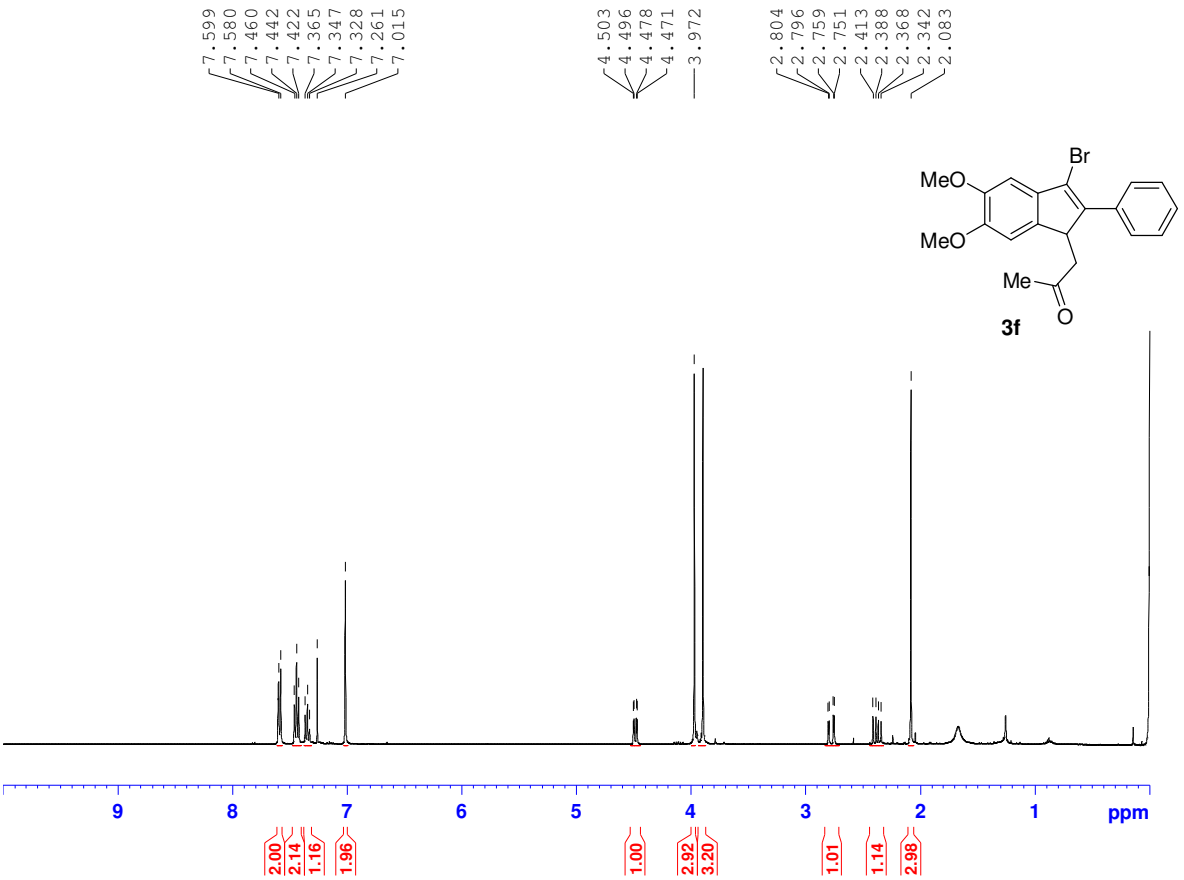

198.78
149.11
148.43
144.59
144.28
137.73
135.86
134.47
133.94
129.32
128.76
128.57
128.27
127.81
116.47
107.93
103.94
77.37
77.06
76.74
56.24
56.21
46.59
40.67
21.64
Br
MeO
MeO
Me
O
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

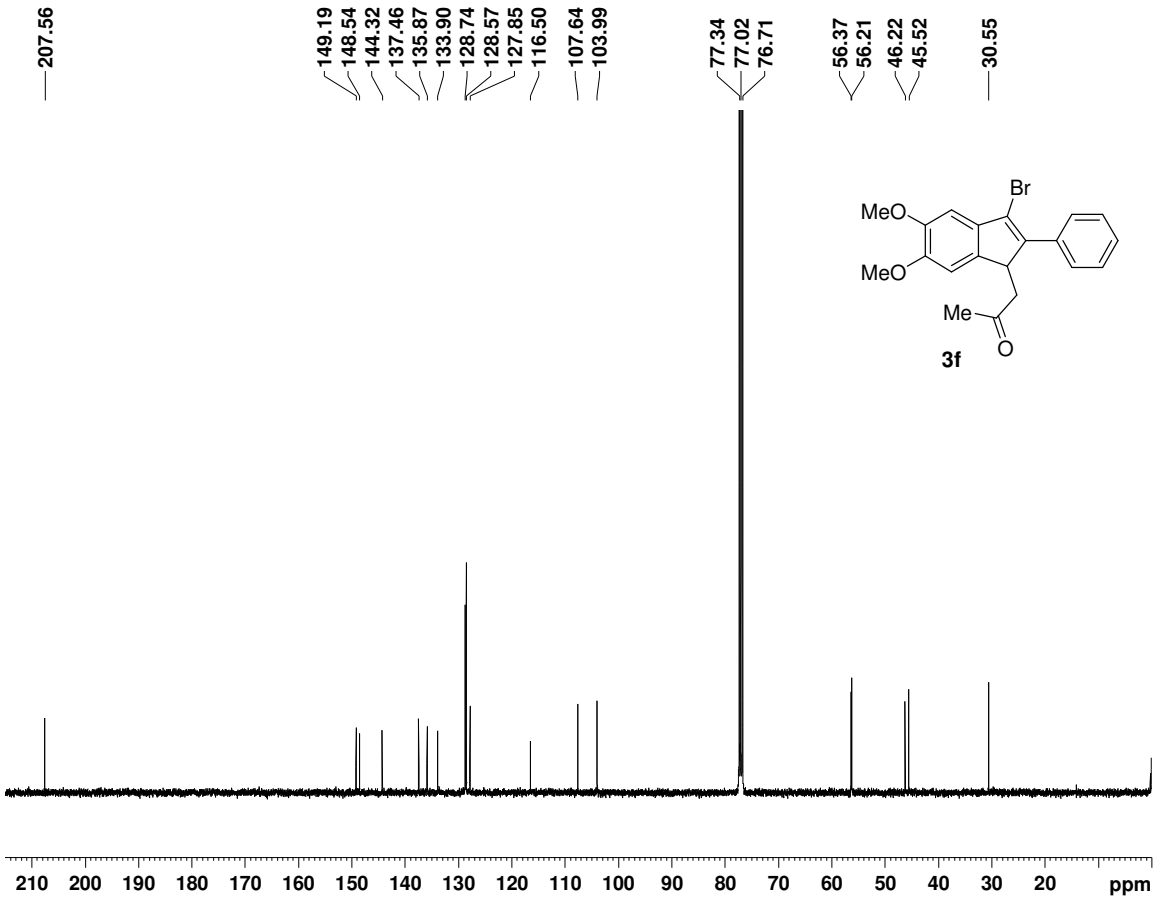

7.777
7.755
7.596
7.578
7.367
7.349
7.329
7.260
7.241
7.223
7.181
6.947
6.927
6.800
6.778
4.677
4.671
4.651
4.644
3.884
3.750
3.706
3.085
3.078
3.042
3.034
2.881
2.855
2.838
2.811
Br
MeO
MeO
MeO
O
3c
9
8
7
6
5
4
3
2
1
ppm
1.96
1.97
2.06
1.05
1.95
1.00
0.97
0.99
3.04
3.04
3.20
1.03
1.08

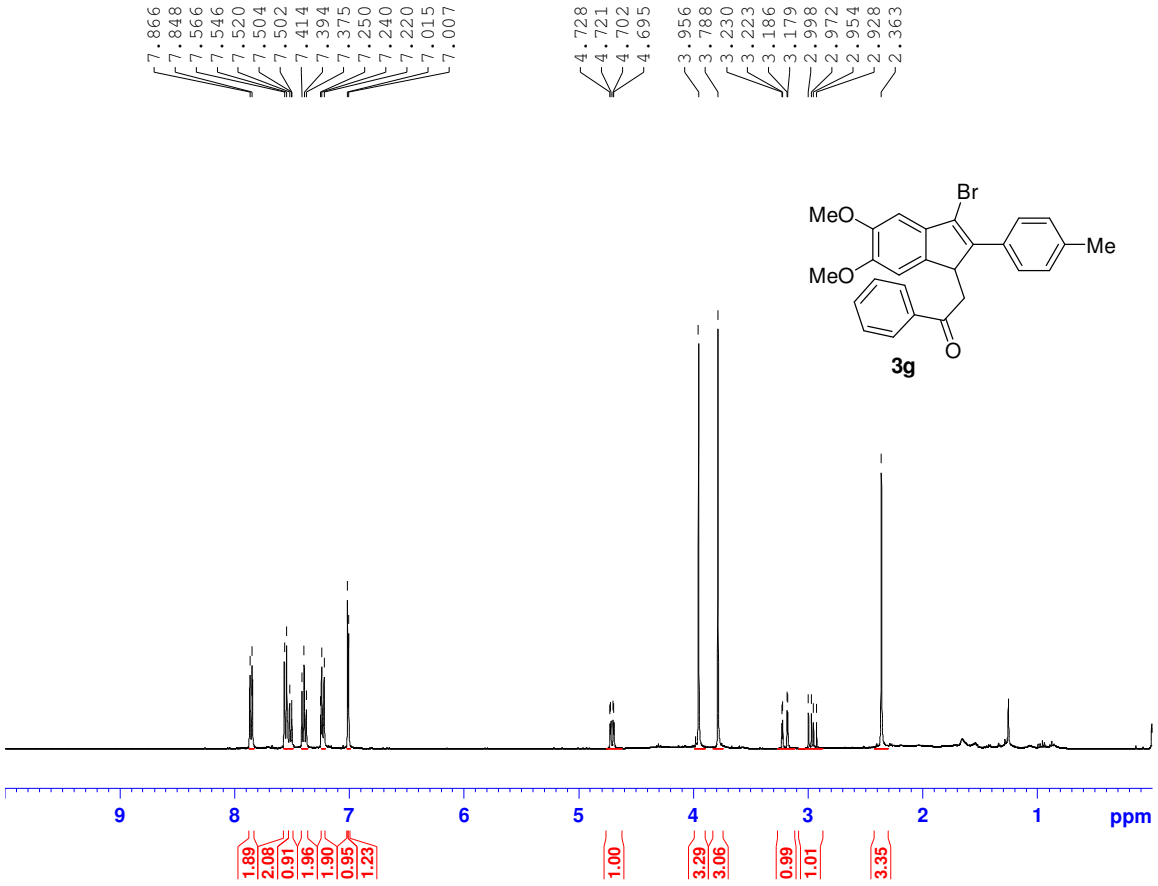

197.59
163.72
149.11
148.42
144.65
137.78
135.85
133.96
130.47
130.03
128.77
128.56
127.80
116.42
113.77
107.97
103.94
77.37
77.05
76.73
56.26
56.21
55.49
46.68
40.37
Br
MeO
MeO
MeO
O
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

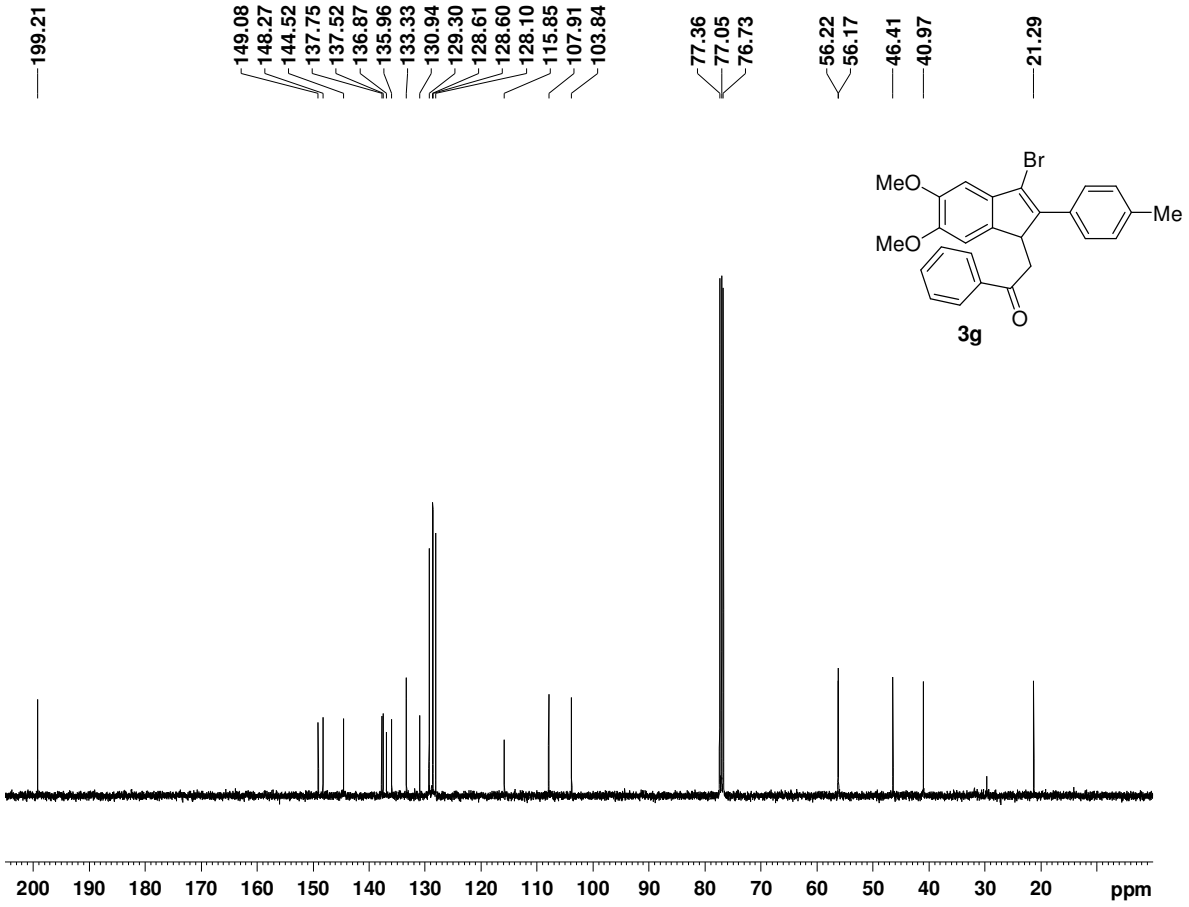

7.713
7.691
7.647
7.629
7.544
7.522
7.442
7.423
7.404
7.340
7.322
7.304
7.257
7.025
6.986
4.723
4.716
4.697
4.690
3.963
3.801
3.192
3.185
3.148
3.140
2.963
2.937
2.918
2.892
MeO
MeO
Br
Br
O
3d
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.08
1.93
1.86
2.00
0.99
0.92
0.81
1.01
3.06
3.14
1.05
1.05

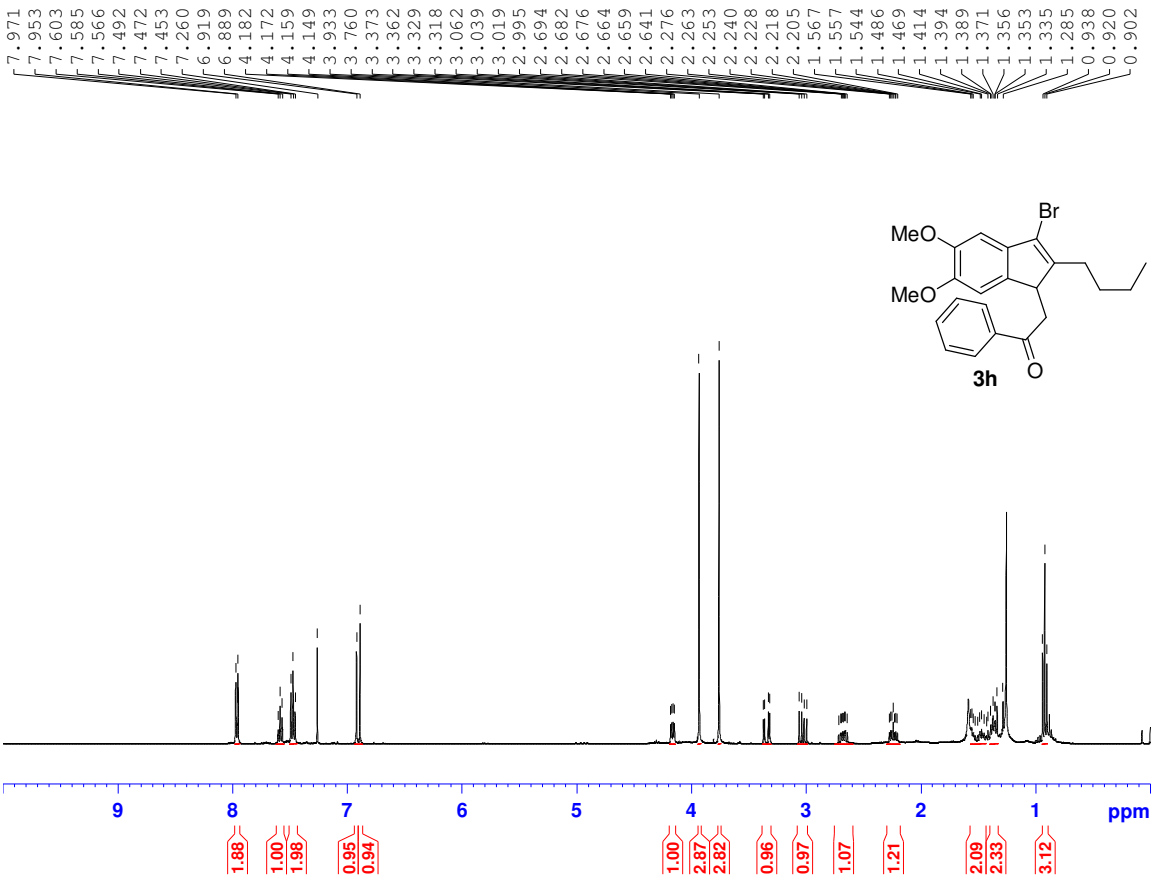

198.13
149.21
148.47
144.30
137.40
135.90
135.52
133.80
131.94
129.61
128.73
128.62
128.60
127.88
116.71
107.81
104.01
77.35
77.03
76.71
56.27
56.19
46.43
40.78
Br
MeO
MeO
Br
O
3d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

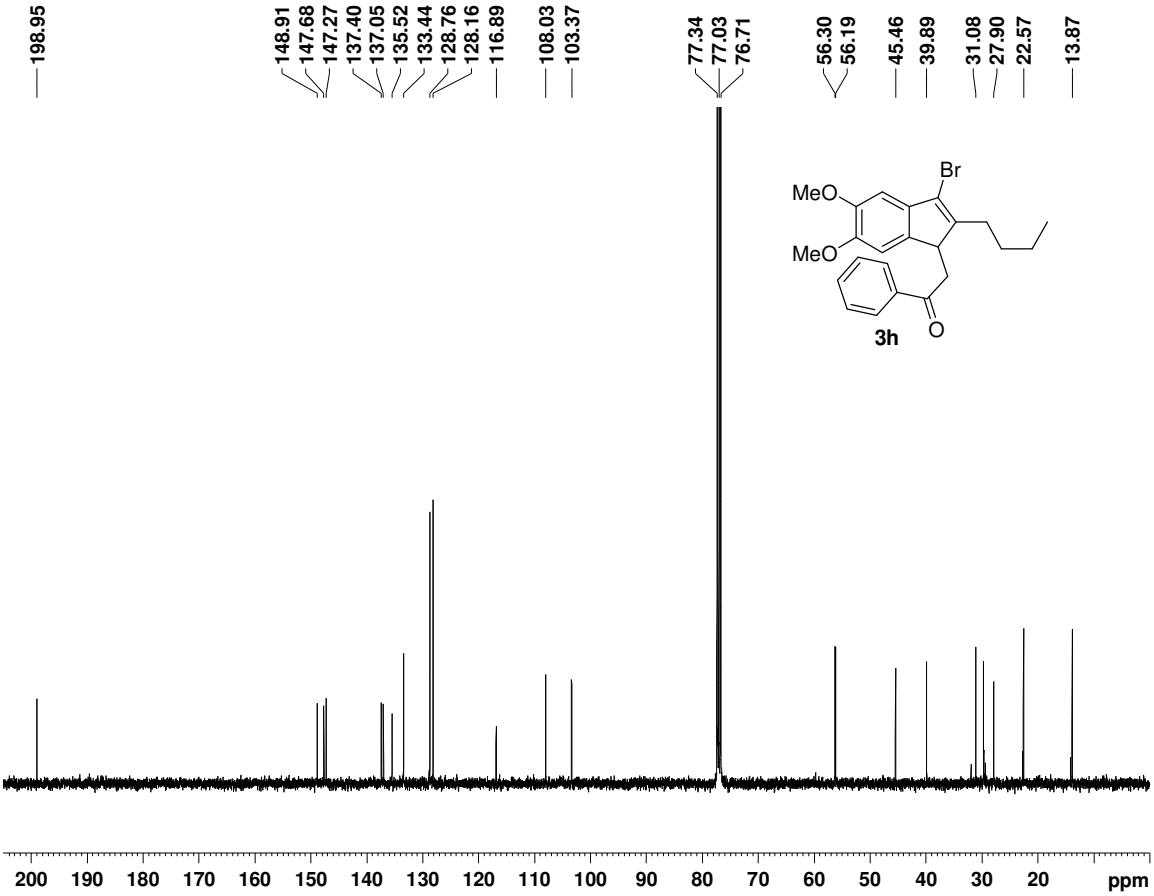

7.599
7.580
7.460
7.442
7.422
7.365
7.347
7.328
7.261
7.015
4.503
4.496
4.478
4.471
3.972
2.804
2.796
2.759
2.751
2.413
2.388
2.368
2.342
2.083
Br
MeO
MeO
Me
O
3f
9
8
7
6
5
4
3
2
1
ppm
2.00
2.14
1.16
1.96
1.00
2.92
3.20
1.01
1.14
2.98

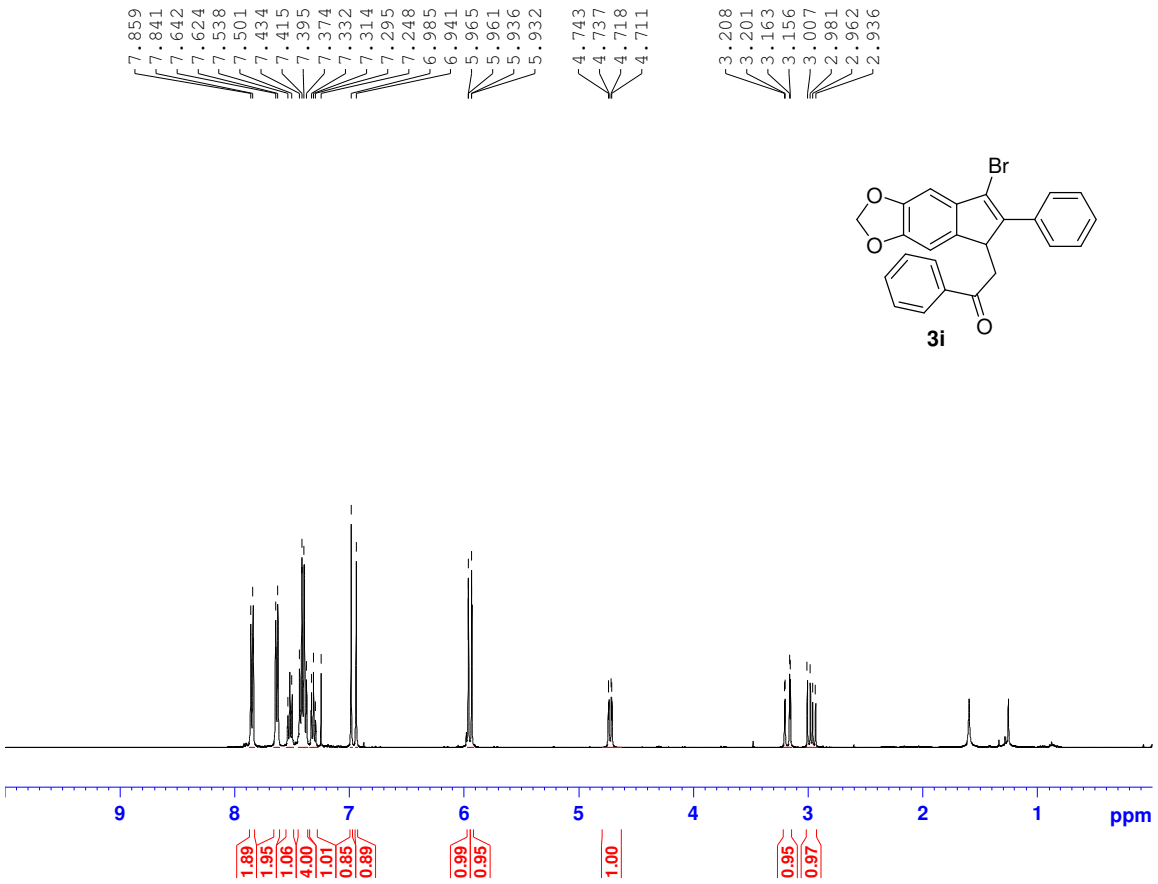

207.56
149.19
148.54
144.32
137.46
135.87
133.90
128.74
128.57
127.85
116.50
107.64
103.99
77.34
77.02
76.71
56.37
56.21
46.22
45.52
30.55
Br
MeO
MeO
Me
O
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

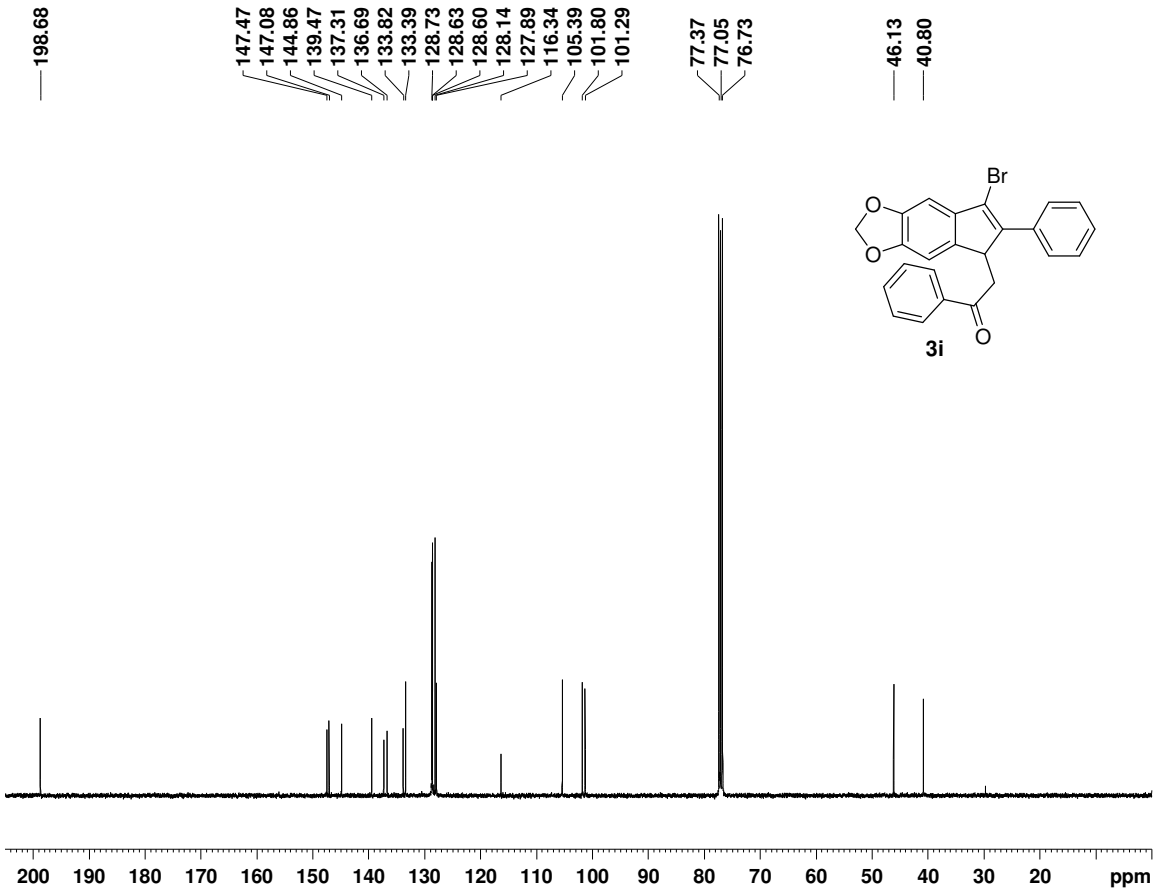

7.866
7.848
7.566
7.546
7.520
7.504
7.502
7.414
7.394
7.375
7.250
7.240
7.220
7.015
7.007
4.728
4.721
4.702
4.695
3.956
3.788
3.230
3.223
3.186
3.179
2.998
2.972
2.954
2.928
2.363
Br
MeO
MeO
Me
O
3g
9
8
7
6
5
4
3
2
1
ppm
1.89
2.08
0.91
1.96
1.90
0.95
1.23
1.00
3.29
3.06
0.99
1.01
3.35

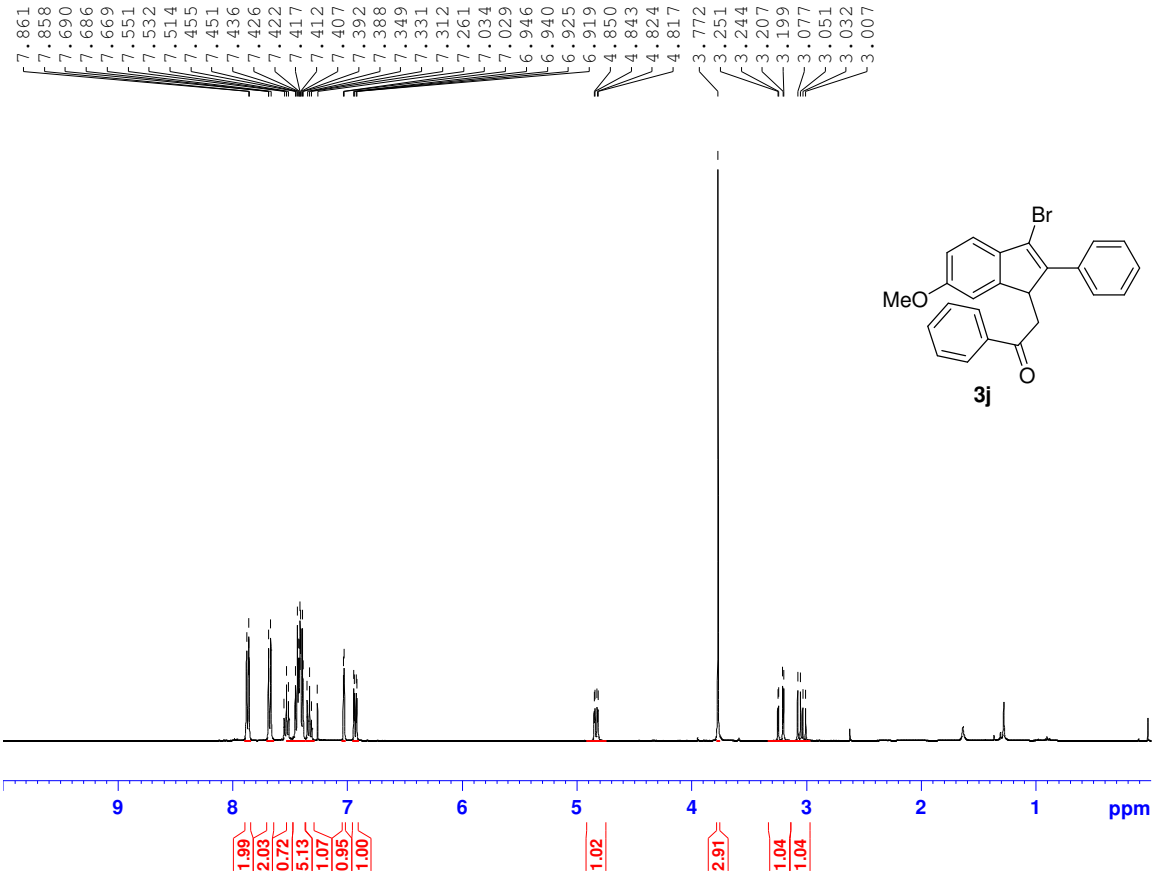

199.21
149.08
148.27
144.52
137.75
137.52
136.87
135.96
133.33
130.94
129.30
128.61
128.60
128.10
115.85
107.91
103.84
77.36
77.05
76.73
56.22
56.17
46.41
40.97
21.29
Br
MeO
MeO
Me
O
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

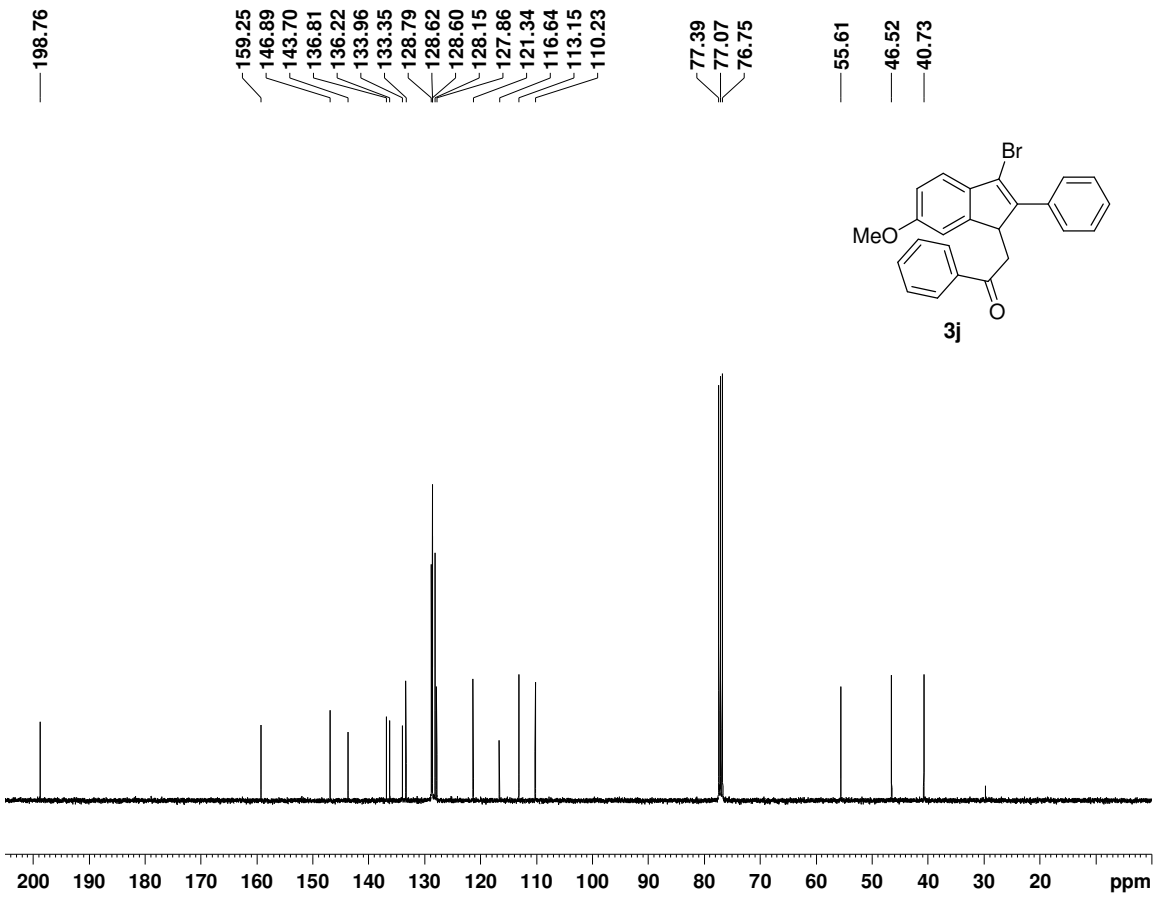

7.971
7.953
7.603
7.585
7.566
7.492
7.472
7.453
7.260
6.919
6.889
4.182
4.172
4.159
4.149
3.933
3.760
3.373
3.362
3.329
3.318
3.062
3.039
3.019
2.995
2.694
2.682
2.676
2.664
2.659
2.641
2.276
2.263
2.253
2.240
2.228
2.218
2.205
1.567
1.557
1.544
1.486
1.469
1.414
1.394
1.389
1.371
1.356
1.353
1.335
1.285
0.938
0.920
0.902
Br
MeO
MeO
O
3h
9
8
7
6
5
4
3
2
1
ppm
1.88
1.00
1.98
0.95
0.94
1.00
2.87
2.82
0.96
0.97
1.07
1.21
2.09
2.33
3.12

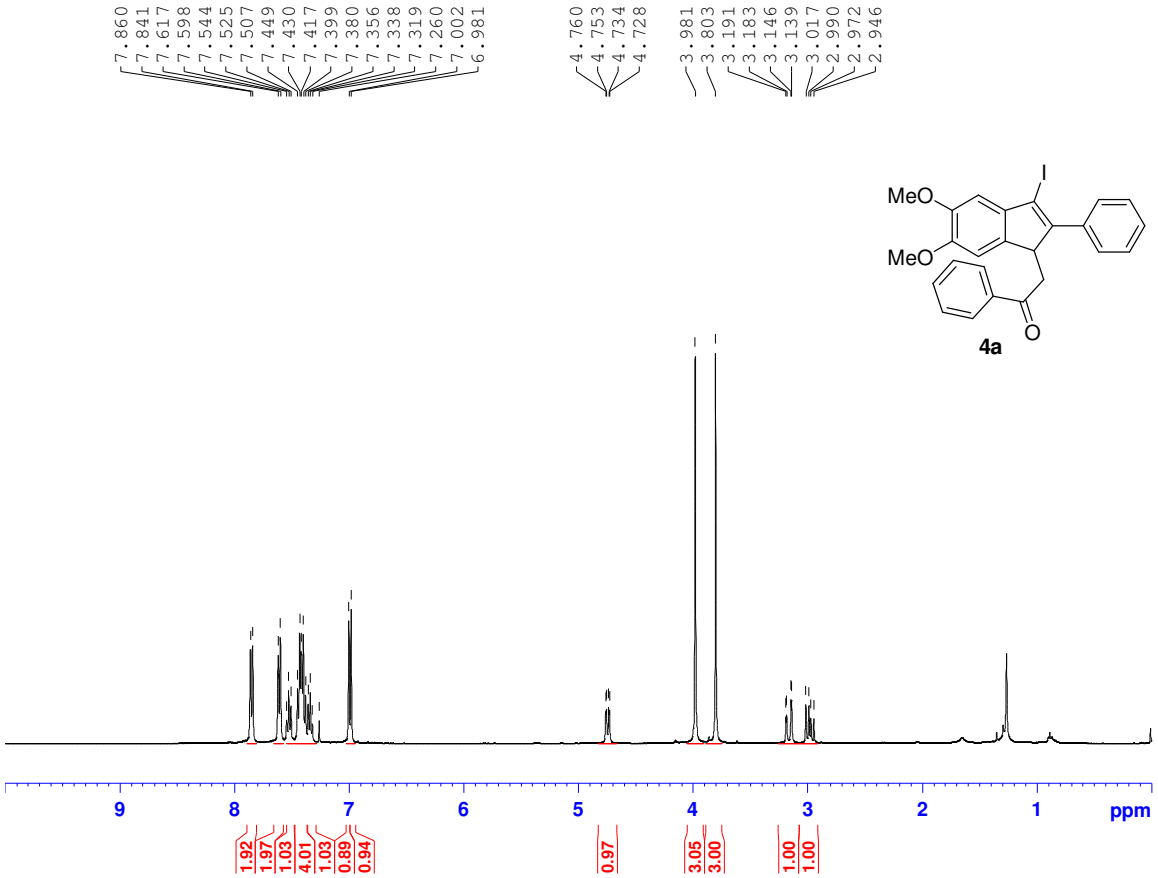

198.95
148.91
147.68
147.27
137.40
137.05
135.52
133.44
128.76
128.16
116.89
108.03
103.37
77.34
77.03
76.71
56.30
56.19
45.46
39.89
31.08
27.90
22.57
13.87
Br
MeO
MeO
O
3h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

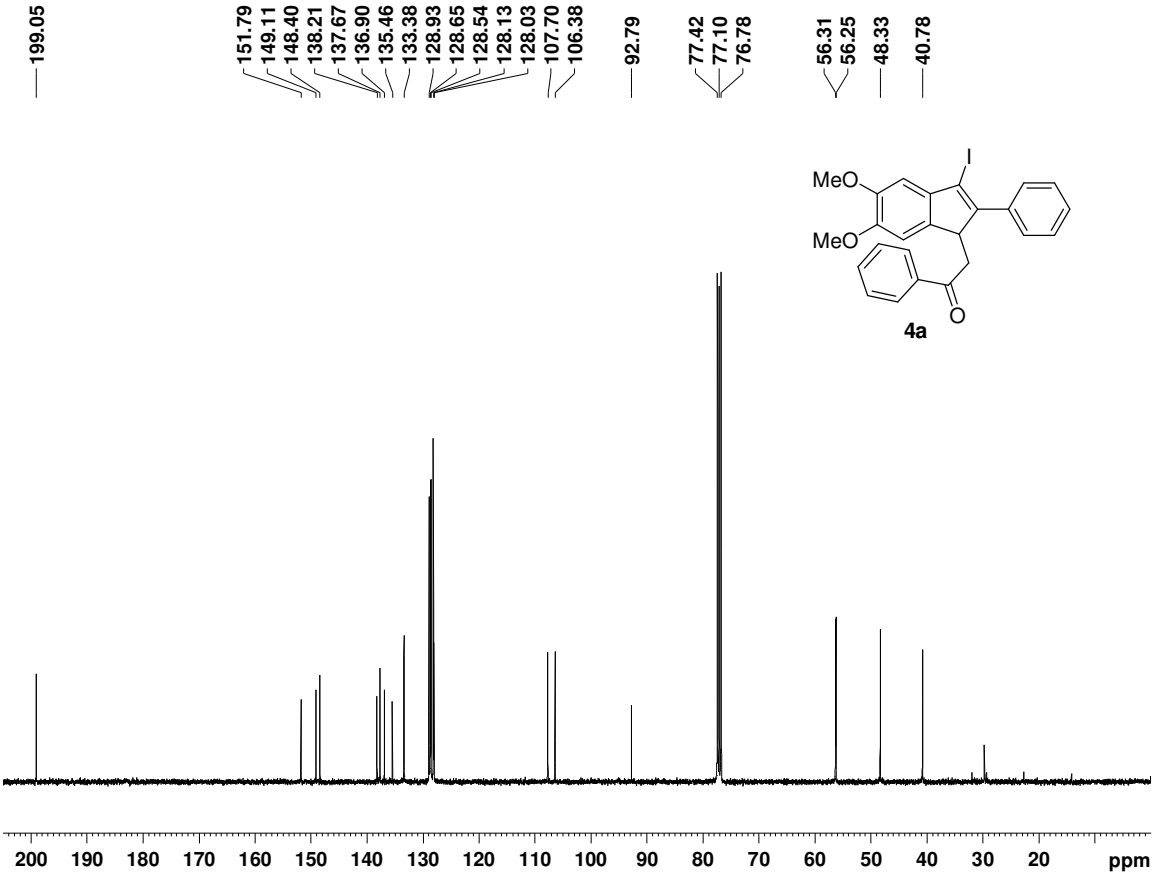

7.859
7.841
7.642
7.624
7.538
7.501
7.434
7.415
7.395
7.374
7.332
7.314
7.295
7.248
6.985
6.941
5.965
5.961
5.936
5.932
4.743
4.737
4.718
4.711
3.208
3.201
3.163
3.156
3.007
2.981
2.962
2.936
Br
O
O
O
3i
9
8
7
6
5
4
3
2
1
ppm
1.89
1.95
1.06
4.00
1.01
0.85
0.89
0.99
0.95
1.00
0.95
0.97

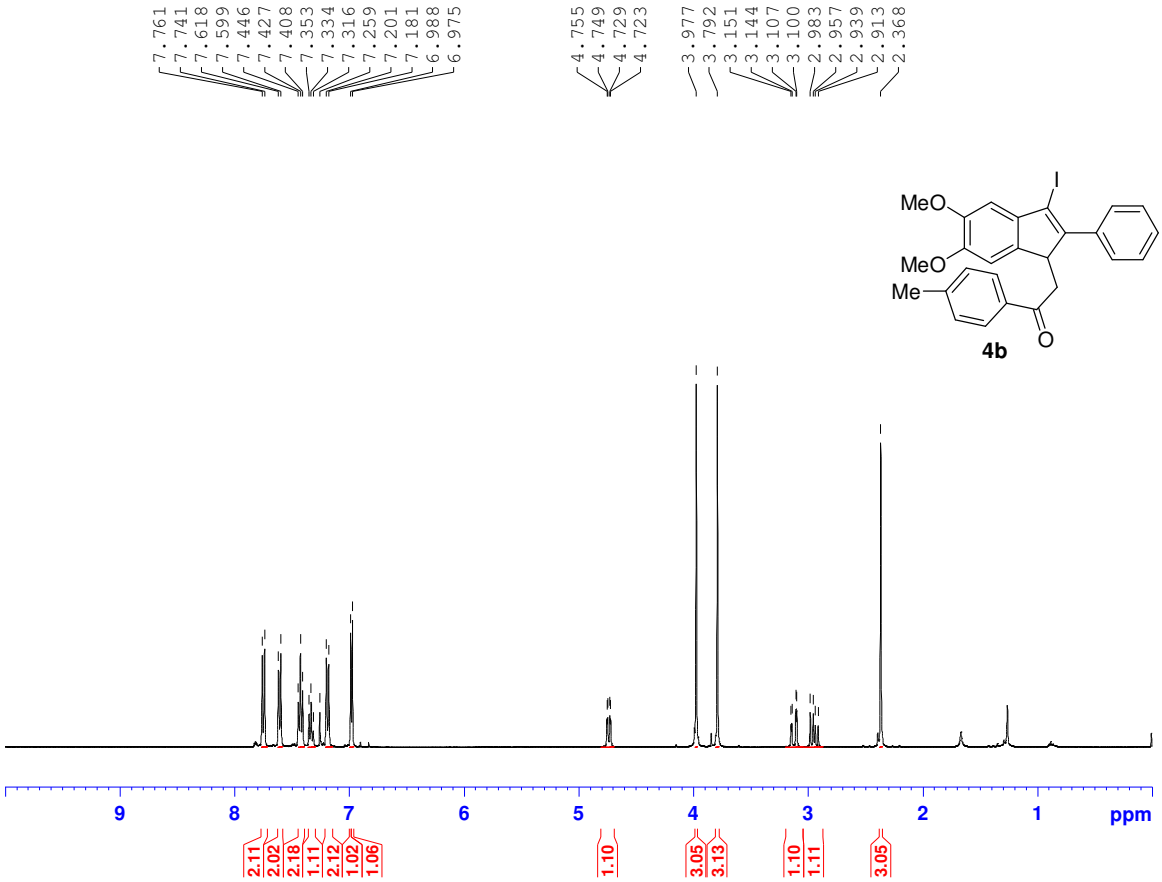

198.68
147.47
147.08
144.86
139.47
137.31
136.69
133.82
133.39
128.73
128.63
128.60
128.14
127.89
116.34
105.39
101.80
101.29
77.37
77.05
76.73
46.13
40.80
Br
O
O
O
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

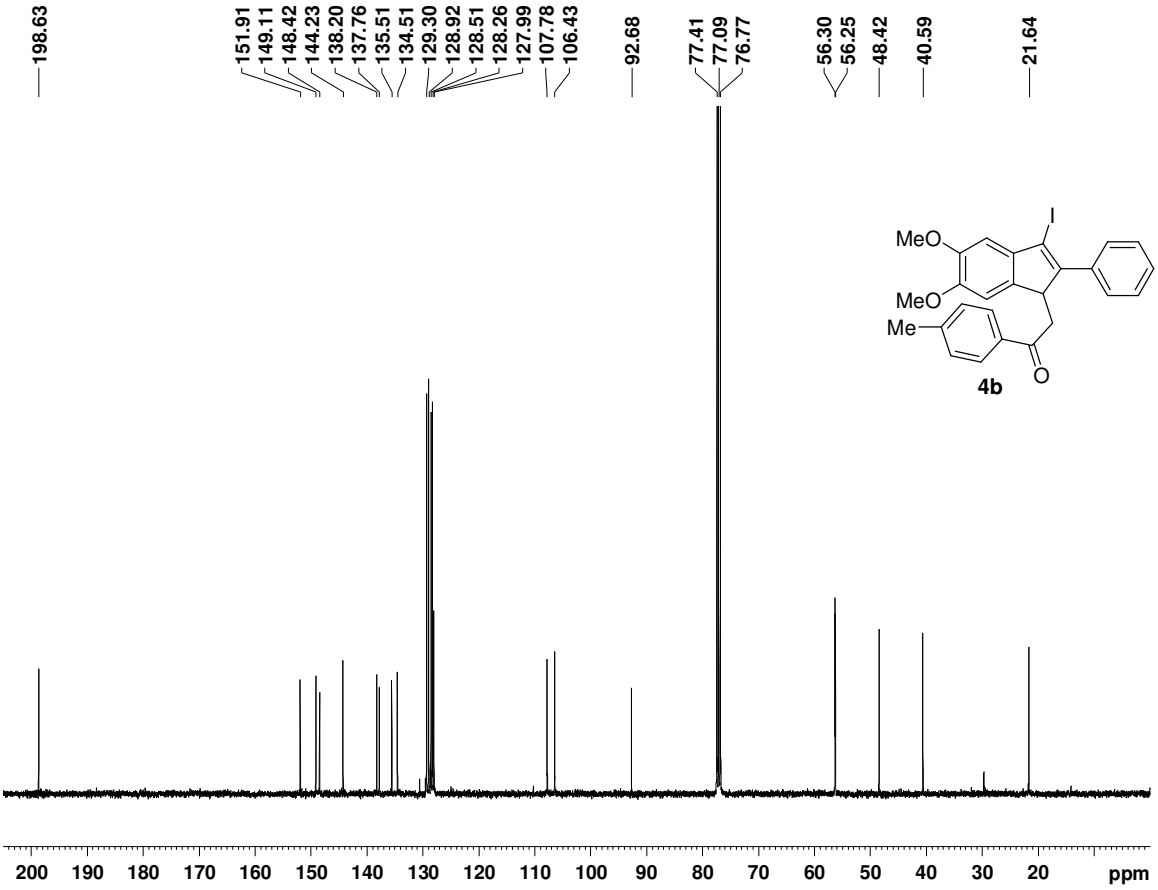

7.861
7.858
7.690
7.686
7.669
7.551
7.532
7.514
7.455
7.451
7.436
7.426
7.422
7.417
7.412
7.407
7.392
7.388
7.349
7.331
7.312
7.261
7.034
7.029
6.946
6.940
6.925
6.919
4.850
4.843
4.824
4.817
3.772
3.251
3.244
3.207
3.199
3.077
3.051
3.032
3.007
Br
MeO
O
3j
9
8
7
6
5
4
3
2
1
ppm
1.99
2.03
0.72
5.13
1.07
0.95
1.00
1.02
2.91
1.04
1.04

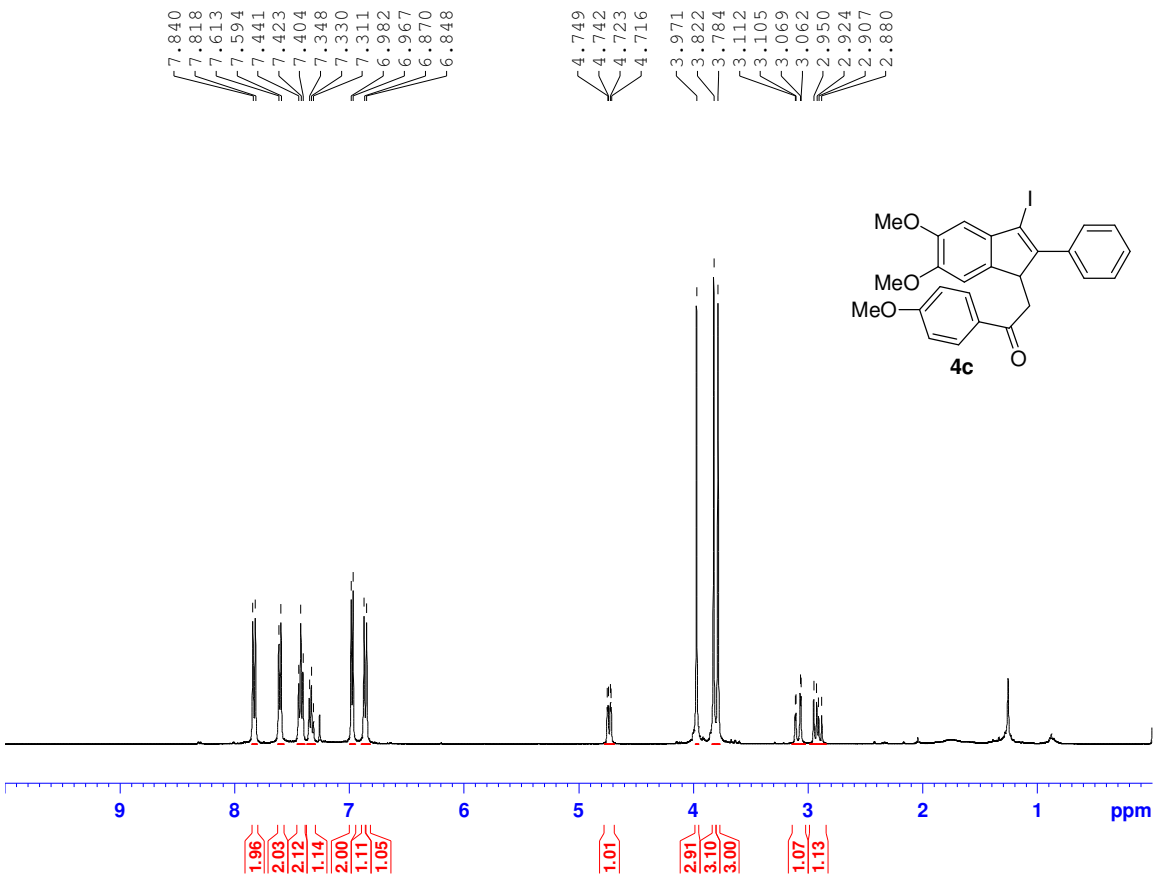

198.76
159.25
146.89
143.70
136.81
136.22
133.96
133.35
128.79
128.62
128.60
128.15
127.86
121.34
116.64
113.15
110.23
77.39
77.07
76.75
55.61
46.52
40.73
Br
MeO
O
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

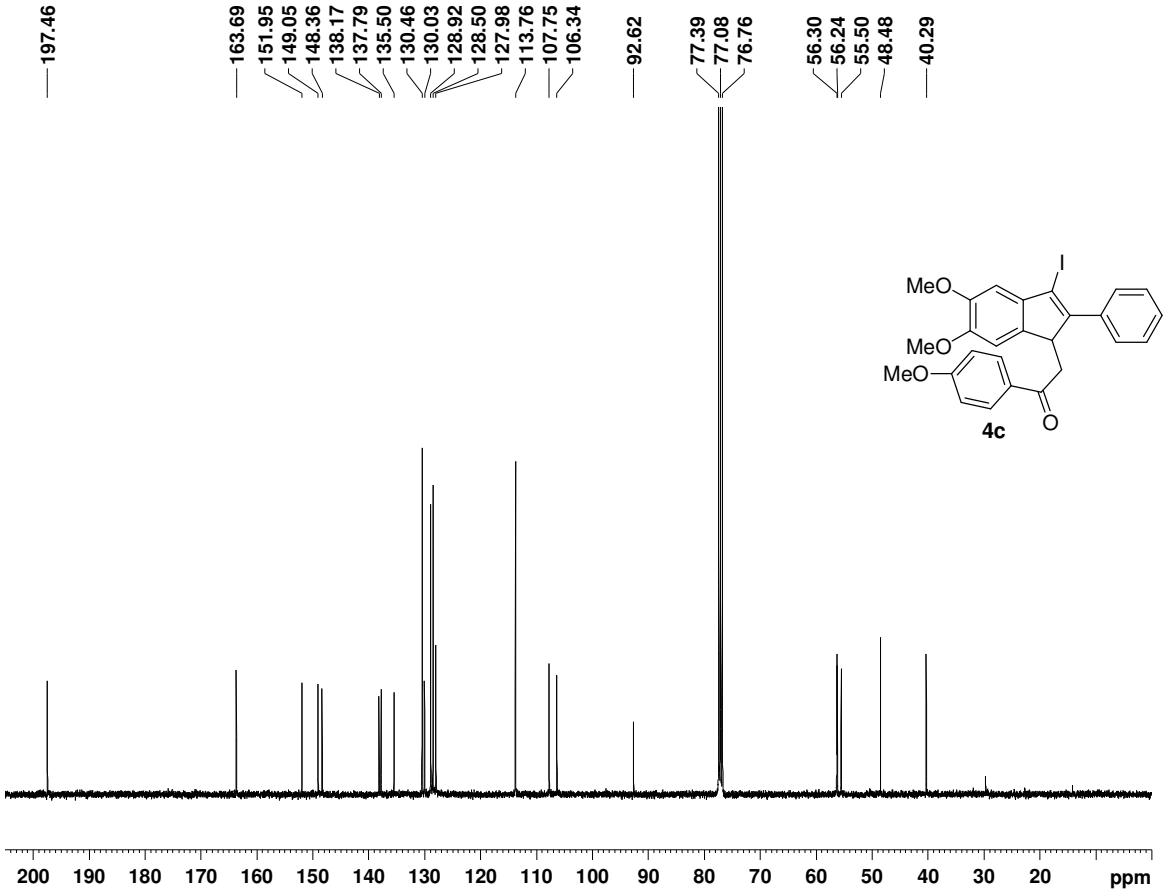

7.860
7.841
7.617
7.598
7.544
7.525
7.507
7.449
7.430
7.417
7.399
7.380
7.356
7.338
7.319
7.260
7.002
6.981
4.760
4.753
4.734
4.728
3.981
3.803
3.191
3.183
3.146
3.139
3.017
2.990
2.972
2.946
MeO
MeO
I
O
4a
9
8
7
6
5
4
3
2
1
ppm
1.92
1.97
1.03
4.01
1.03
0.89
0.94
0.97
3.05
3.00
1.00
1.00

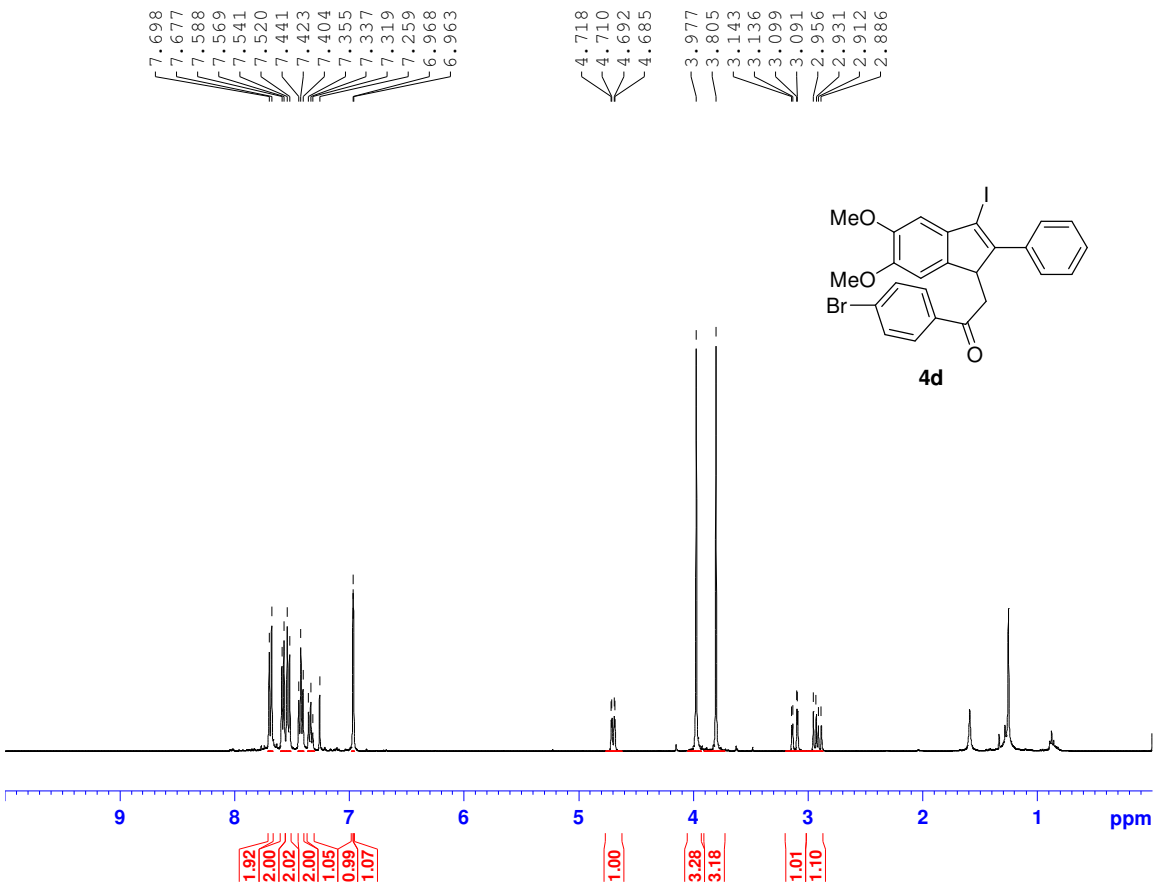

199.05
151.79
149.11
148.40
138.21
137.67
136.90
135.46
133.38
128.93
128.65
128.54
128.13
128.03
107.70
106.38
92.79
77.42
77.10
76.78
56.31
56.25
48.33
40.78
MeO
MeO
I
O
4a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

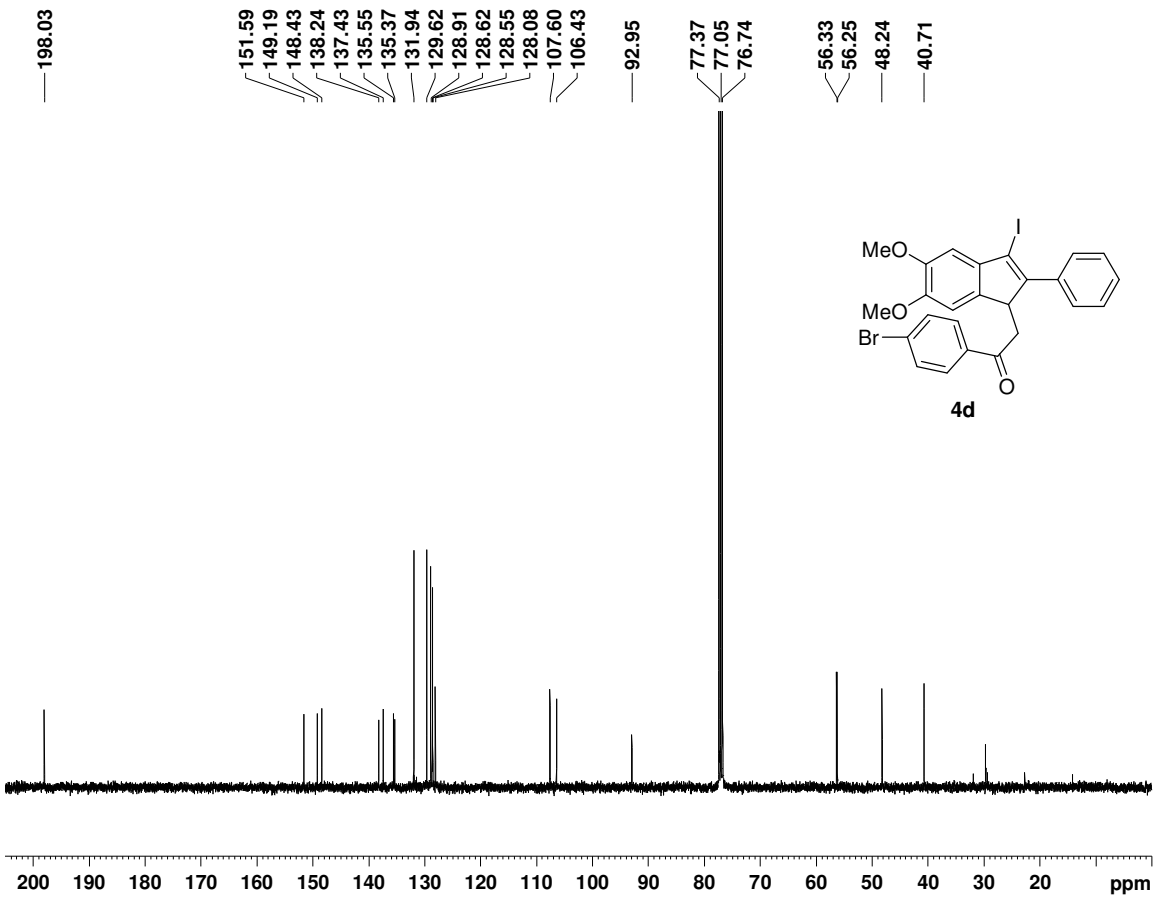

7.761
7.741
7.618
7.599
7.446
7.427
7.408
7.353
7.334
7.316
7.259
7.201
7.181
6.988
6.975
4.755
4.749
4.729
4.723
3.977
3.792
3.151
3.144
3.107
3.100
2.983
2.957
2.939
2.913
2.368
MeO
MeO
Me
I
O
4b
9
8
7
6
5
4
3
2
1
ppm
2.11
2.02
2.18
1.11
2.12
1.02
1.06
1.10
3.05
3.13
1.10
1.11
3.05

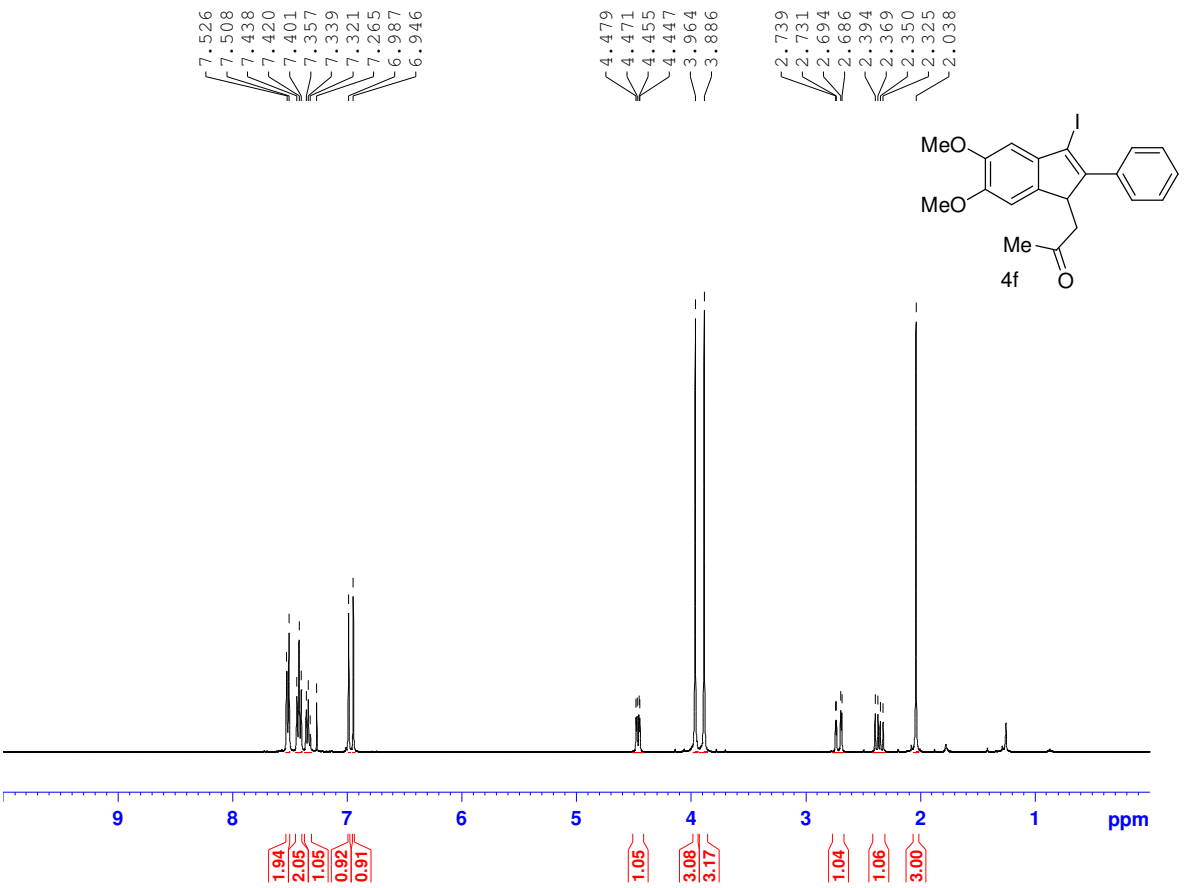

198.63
151.91
149.11
148.42
144.23
138.20
137.76
135.51
134.51
129.30
128.92
128.51
128.26
127.99
107.78
106.43
92.68
77.41
77.09
76.77
56.30
56.25
48.42
40.59
21.64
MeO
MeO
Me
I
O
4b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

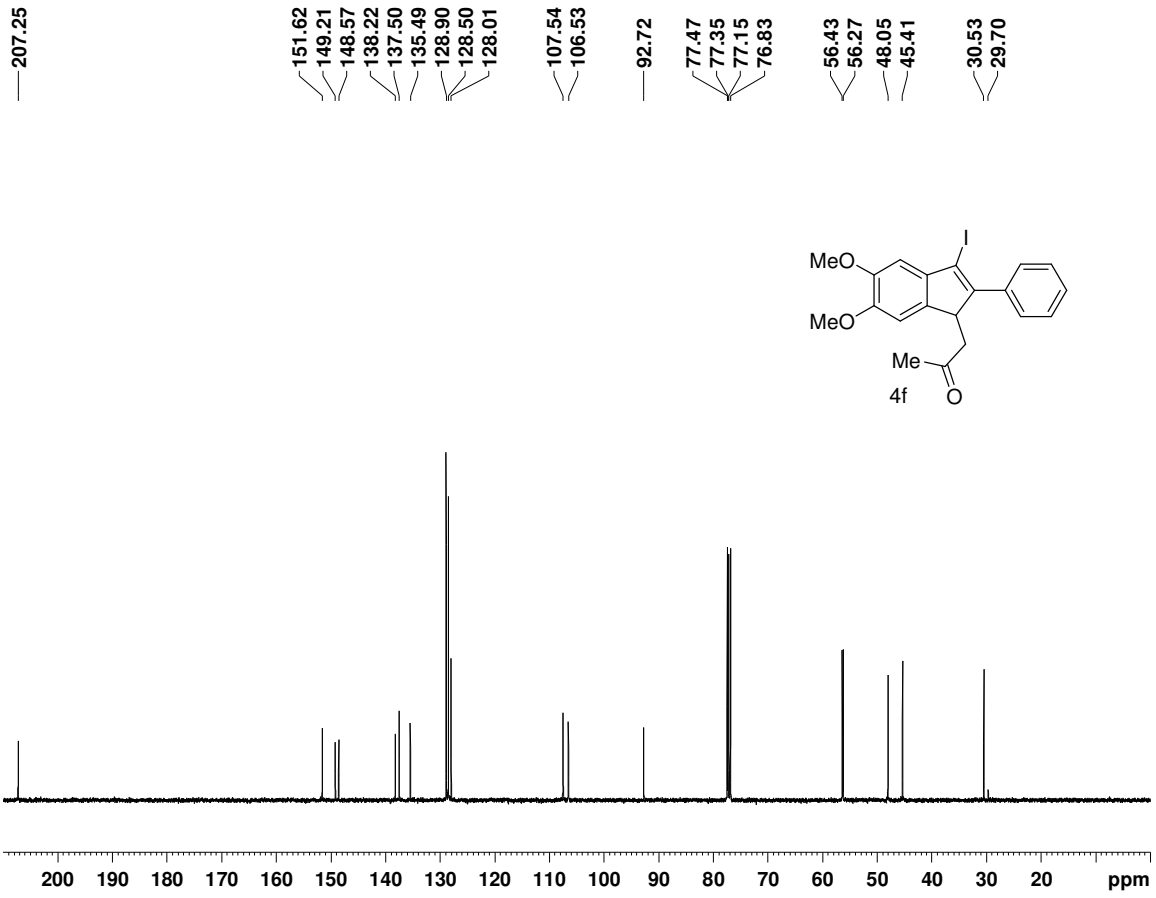

7.840
7.818
7.613
7.594
7.441
7.423
7.404
7.348
7.330
7.311
6.982
6.967
6.870
6.848
4.749
4.742
4.723
4.716
3.971
3.822
3.784
3.112
3.105
3.069
3.062
2.950
2.924
2.907
2.880
MeO
MeO
MeO
I
O
4c
9
8
7
6
5
4
3
2
1
ppm
1.96
2.03
2.12
1.14
2.00
1.11
1.05
1.01
2.91
3.10
3.00
1.07
1.13

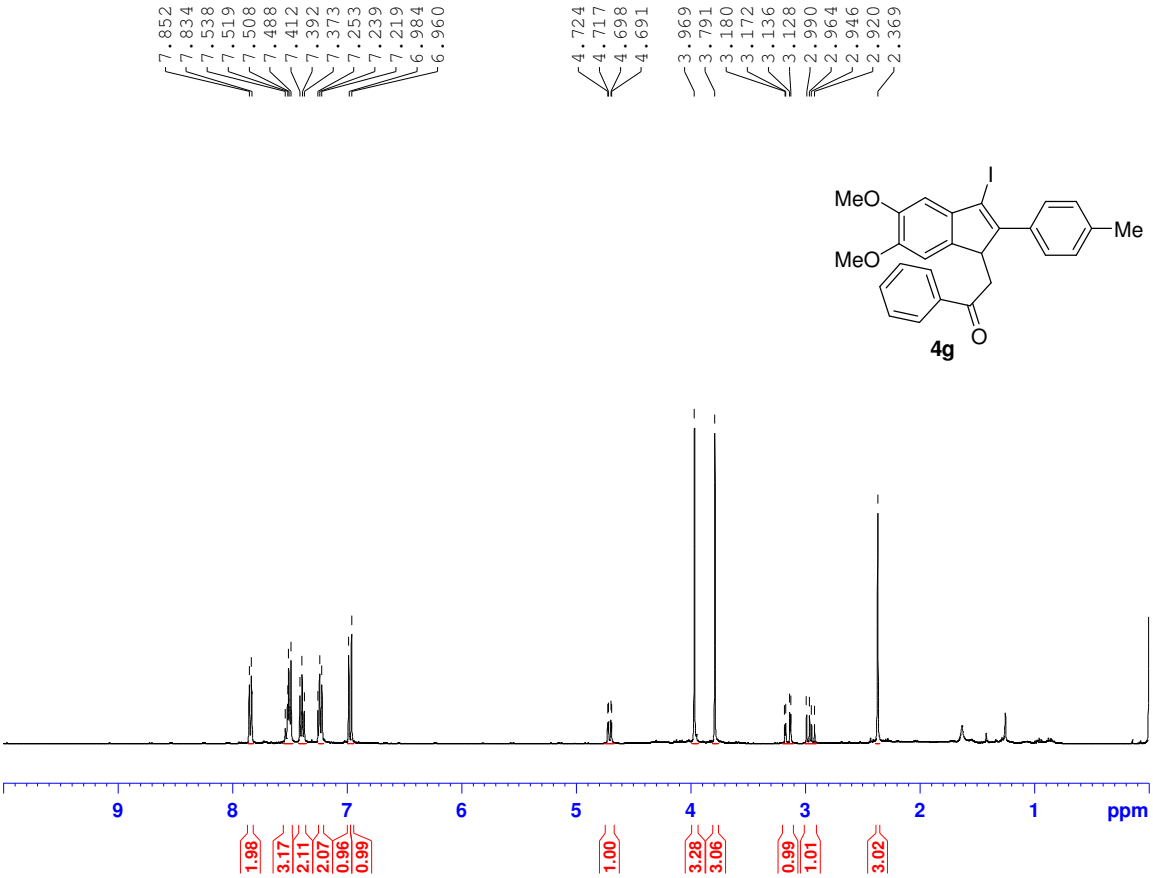

197.46
163.69
151.95
149.05
148.36
138.17
137.79
135.50
130.46
130.03
128.92
128.50
127.98
113.76
107.75
106.34
92.62
77.39
77.08
76.76
56.30
56.24
55.50
48.48
40.29
I
MeO
MeO
MeO
O
4c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

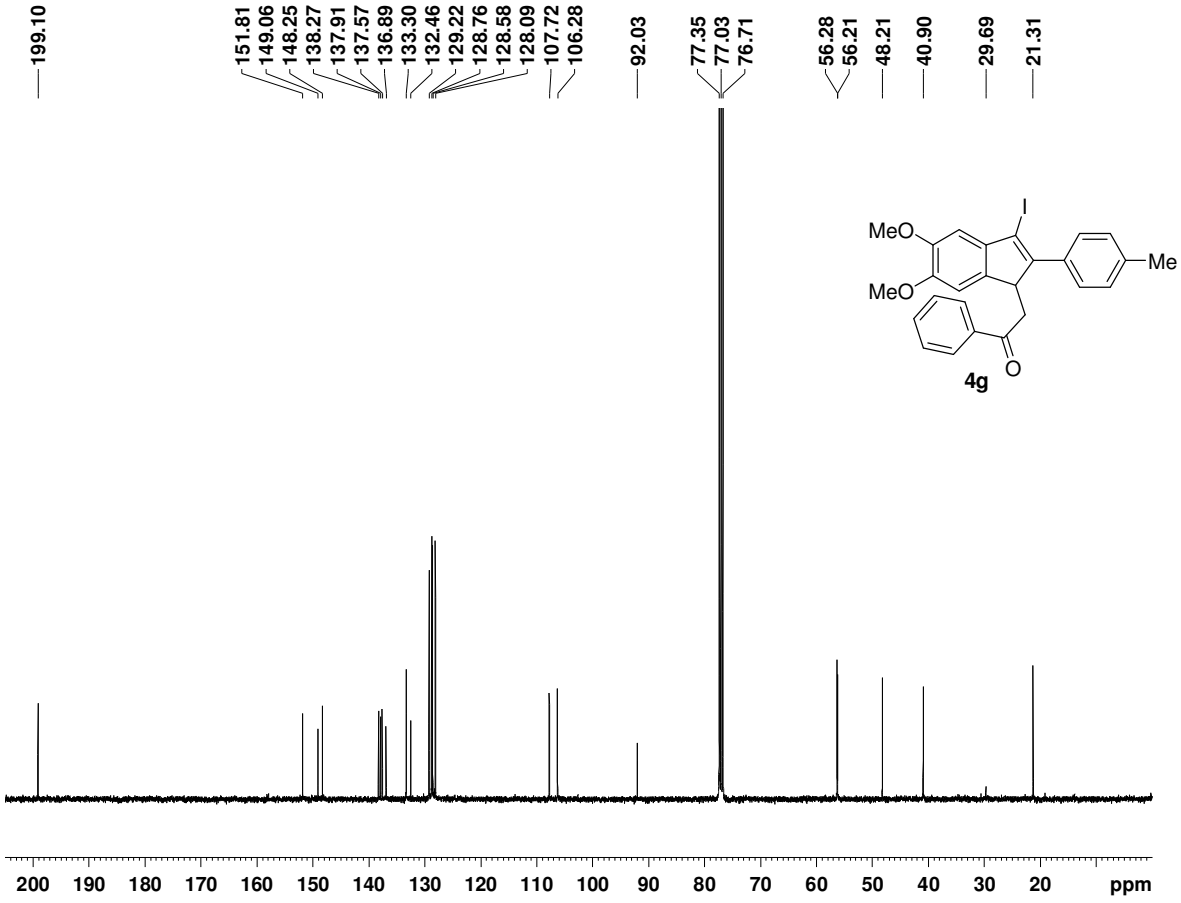

7.698
7.677
7.588
7.569
7.541
7.520
7.441
7.423
7.404
7.355
7.337
7.319
7.259
6.968
6.963
4.718
4.710
4.692
4.685
3.977
3.805
3.143
3.136
3.099
3.091
2.956
2.931
2.912
2.886
MeO
MeO
Br
I
O
4d
9
8
7
6
5
4
3
2
1
ppm
1.92
2.00
2.02
2.00
1.05
0.99
1.07
1.00
3.28
3.18
1.01
1.10

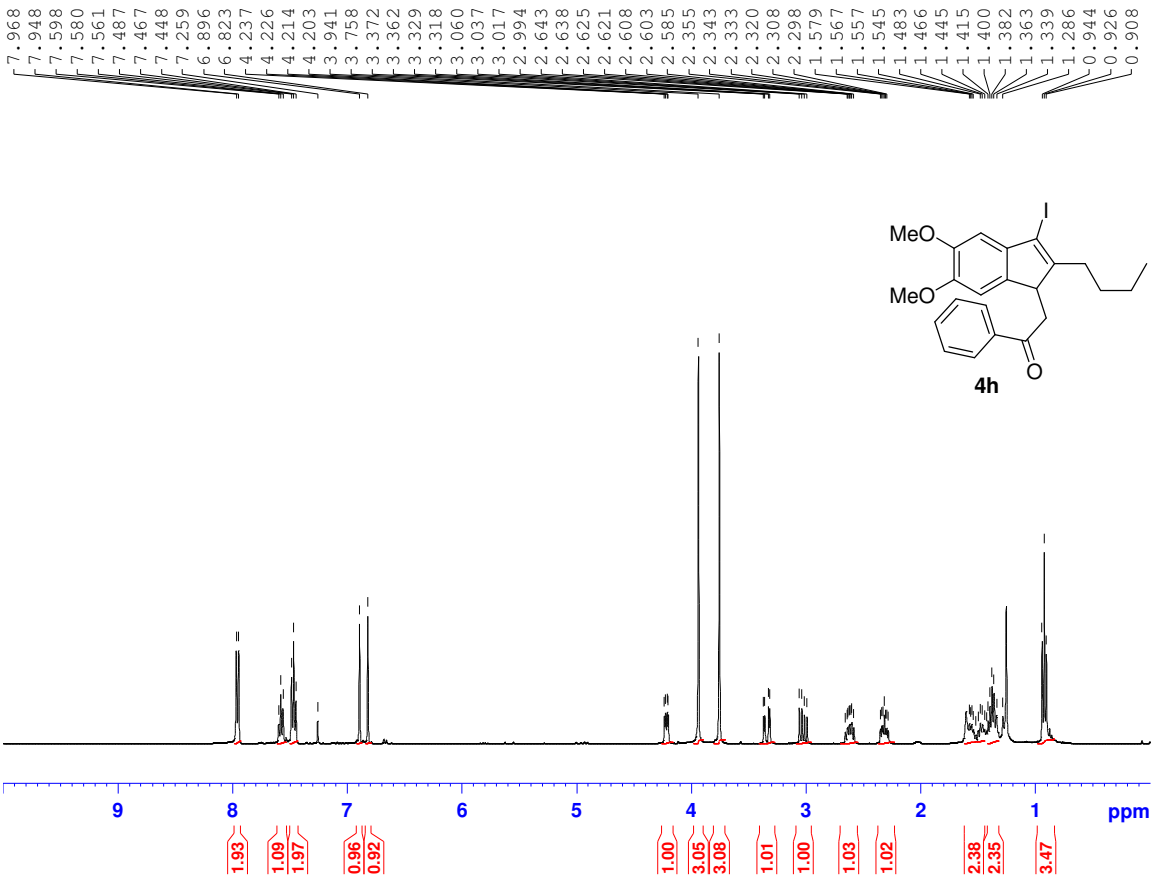

198.03
151.59
149.19
148.43
138.24
137.43
135.55
135.37
131.94
129.62
128.91
128.62
128.55
128.08
107.60
106.43
92.95
77.37
77.05
76.74
56.33
56.25
48.24
40.71
MeO
MeO
Br
I
O
4d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

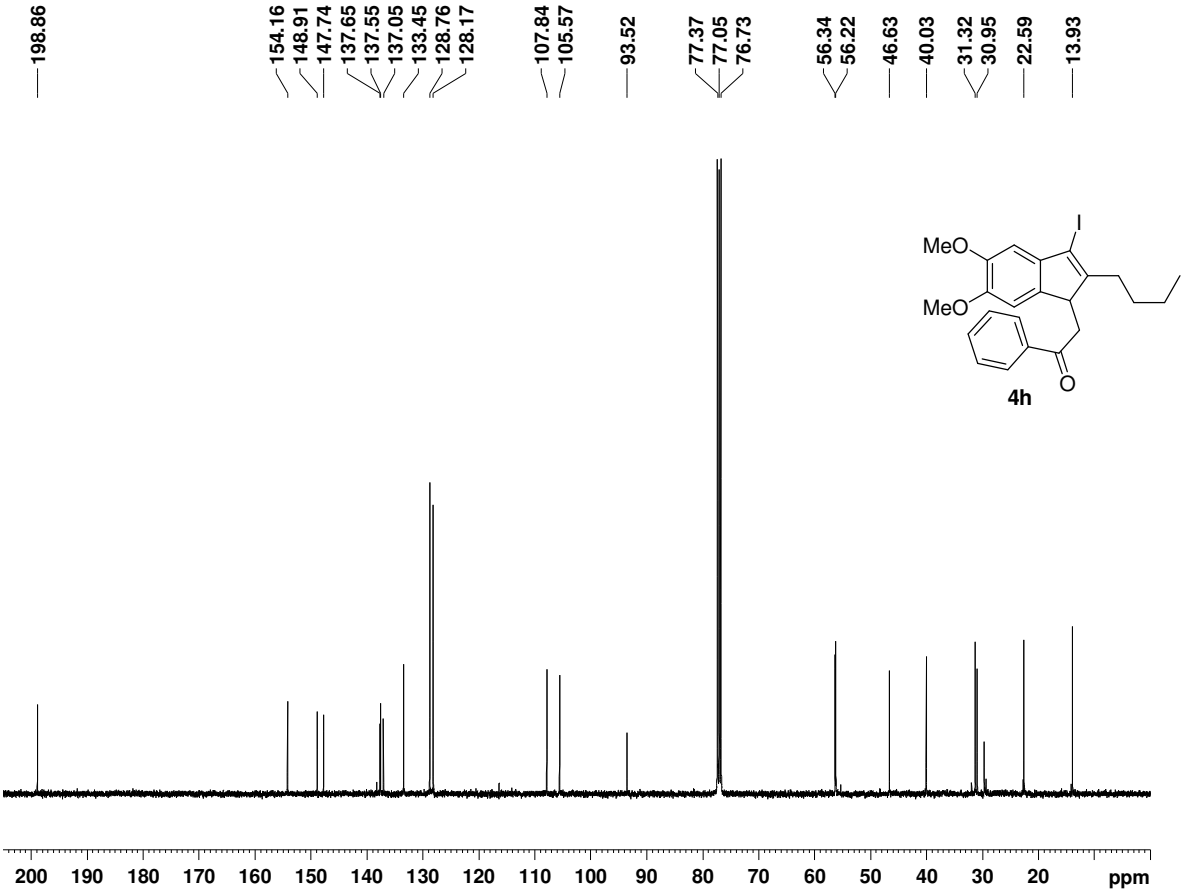

7.526
7.508
7.438
7.420
7.401
7.357
7.339
7.321
7.265
6.987
6.946
4.479
4.471
4.455
4.447
3.964
3.886
2.739
2.731
2.694
2.686
2.394
2.369
2.350
2.325
2.038
I
MeO
MeO
Me
4f
O
9
8
7
6
5
4
3
2
1
ppm
1.94
2.05
1.05
0.92
0.91
1.05
3.08
3.17
1.04
1.06
3.00

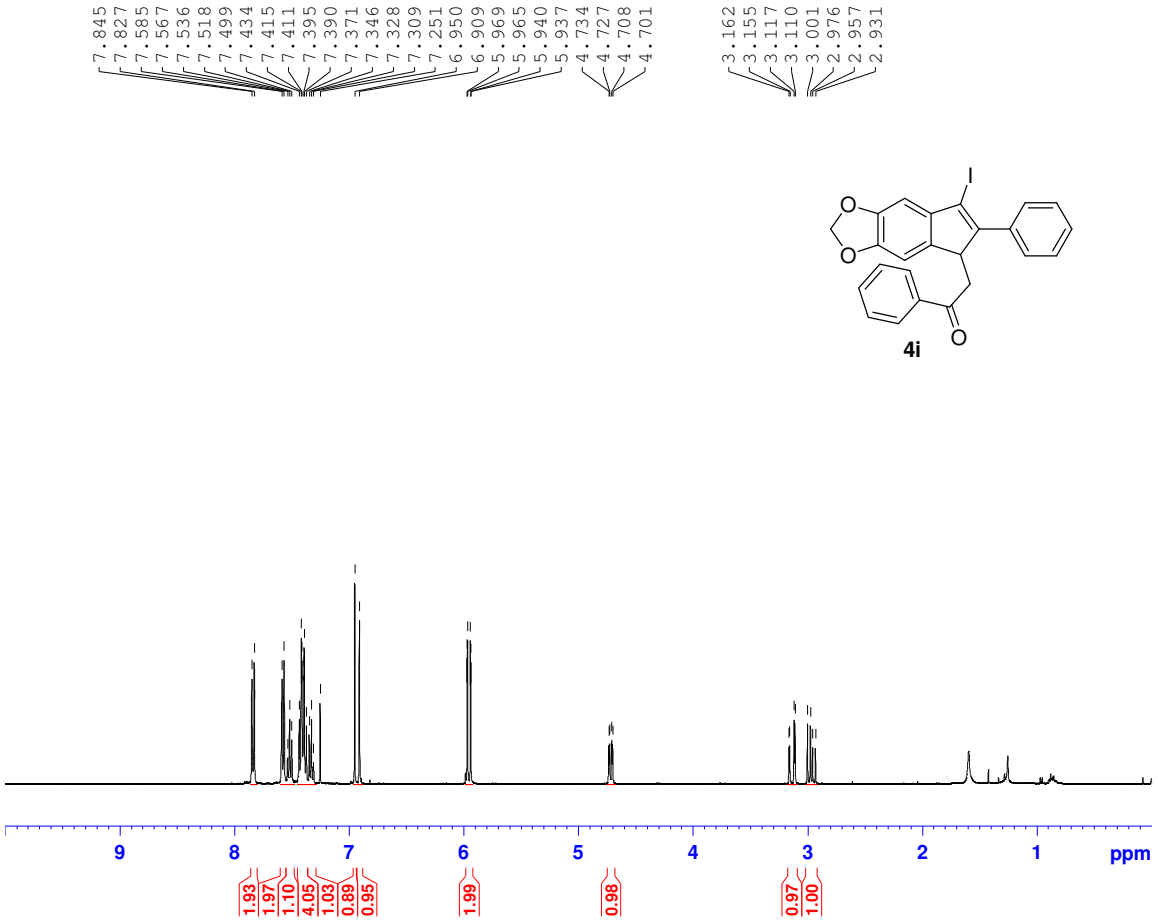

207.25
151.62
149.21
148.57
138.22
137.50
135.49
128.90
128.50
128.01
107.54
106.53
92.72
77.47
77.35
77.15
76.83
56.43
56.27
48.05
45.41
30.53
29.70
MeO
MeO
I
Me
O
4f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

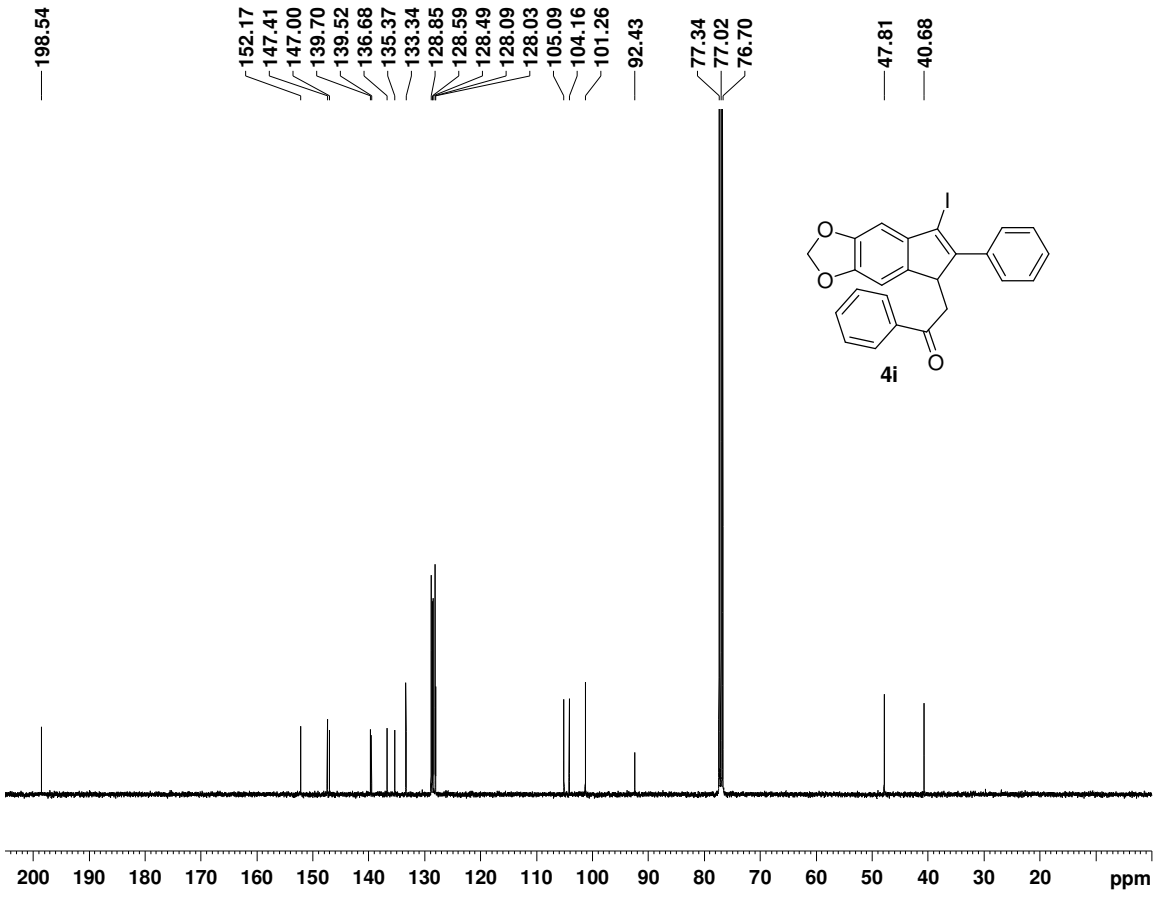

7.852
7.834
7.538
7.519
7.508
7.488
7.412
7.392
7.373
7.253
7.239
7.219
6.984
6.960
4.724
4.717
4.698
4.691
3.969
3.791
3.180
3.172
3.136
3.128
2.990
2.964
2.946
2.920
2.369
MeO
MeO
I
Me
O
4g
9
8
7
6
5
4
3
2
1
ppm
1.98
3.17
2.11
2.07
0.96
0.99
1.00
3.28
3.06
0.99
1.01
3.02

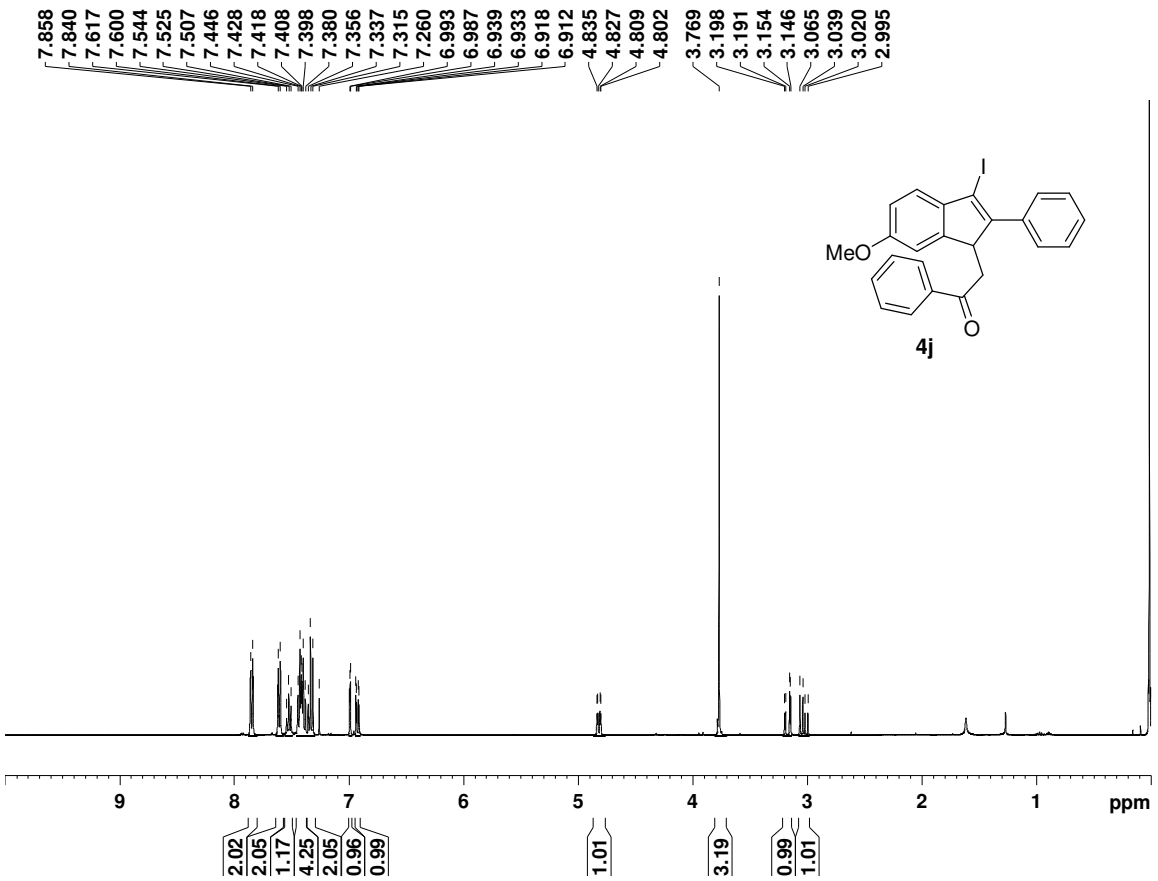

199.10
151.81
149.06
148.25
138.27
137.91
137.57
136.89
133.30
132.46
129.22
128.76
128.58
128.09
107.72
106.28
92.03
77.35
77.03
76.71
56.28
56.21
48.21
40.90
29.69
21.31
MeO
MeO
I
Me
O
4g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

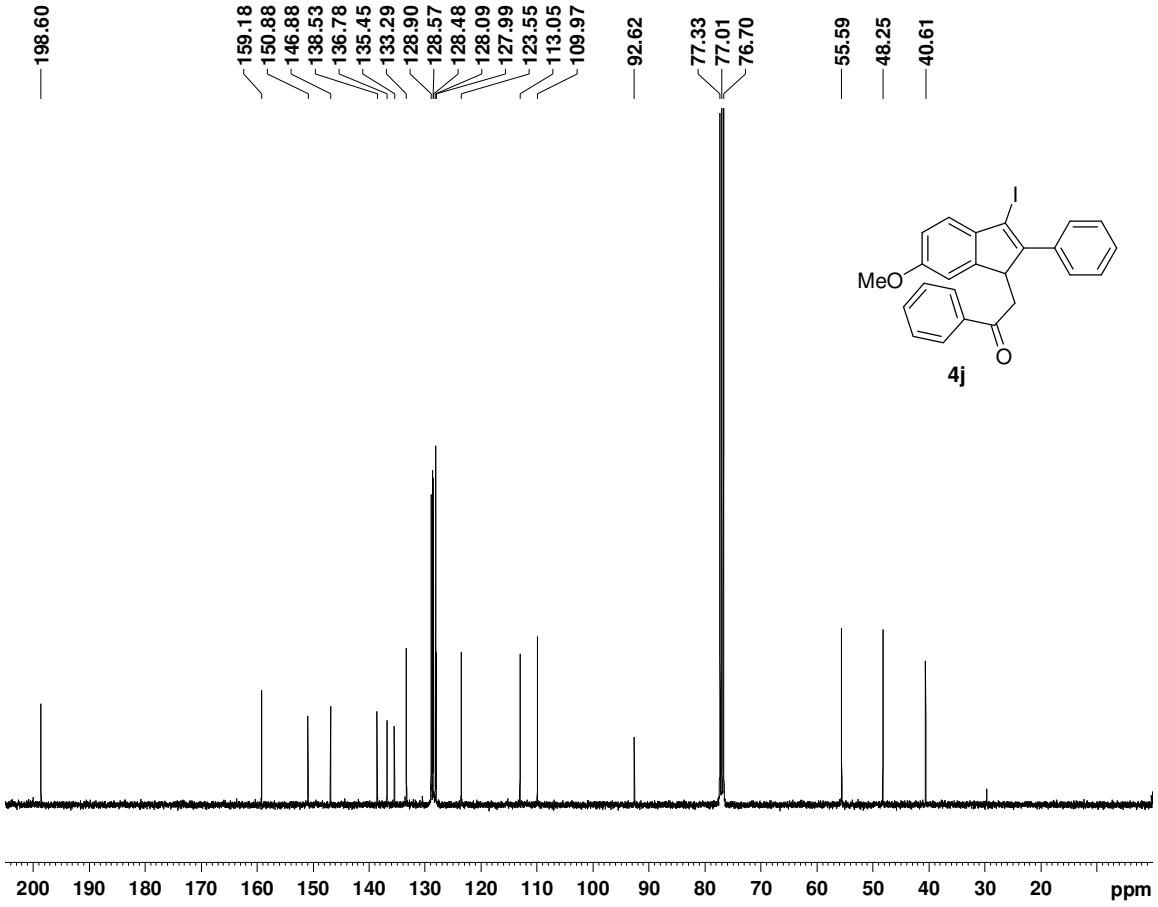

7.968
7.948
7.598
7.580
7.561
7.487
7.467
7.448
7.259
6.896
6.823
4.237
4.226
4.214
4.203
3.941
3.758
3.372
3.362
3.329
3.318
3.060
3.037
3.017
2.994
2.643
2.638
2.625
2.621
2.608
2.603
2.585
2.355
2.343
2.333
2.320
2.308
2.298
1.579
1.567
1.557
1.545
1.483
1.466
1.445
1.415
1.400
1.382
1.363
1.339
1.286
0.944
0.926
0.908
MeO
MeO
I
O
4h
9
8
7
6
5
4
3
2
1
ppm
1.93
1.09
1.97
0.96
0.92
1.00
3.05
3.08
1.01
1.00
1.03
1.02
2.38
2.35
3.47

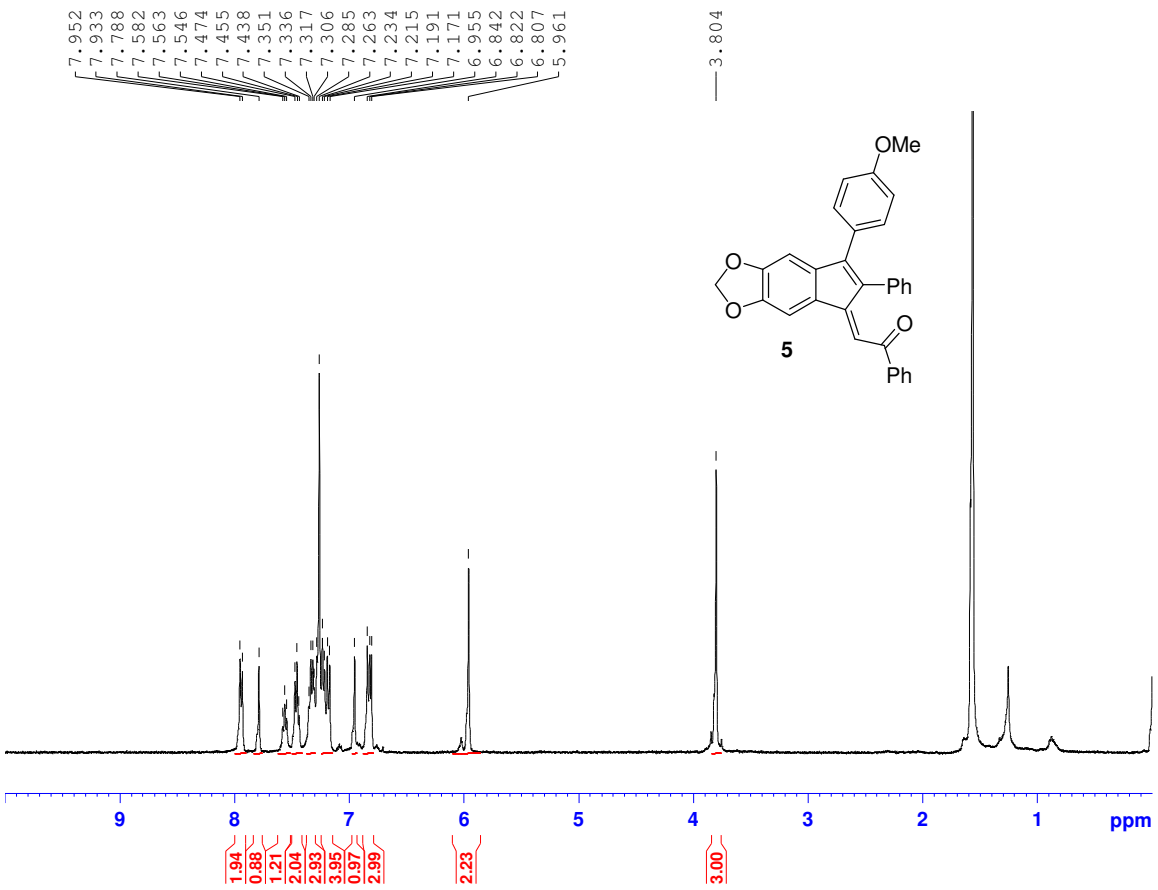

198.86
154.16
148.91
147.74
137.65
137.55
137.05
133.45
128.76
128.17
107.84
105.57
93.52
77.37
77.05
76.73
56.34
56.22
46.63
40.03
31.32
30.95
22.59
13.93
MeO
MeO
I
O
4h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

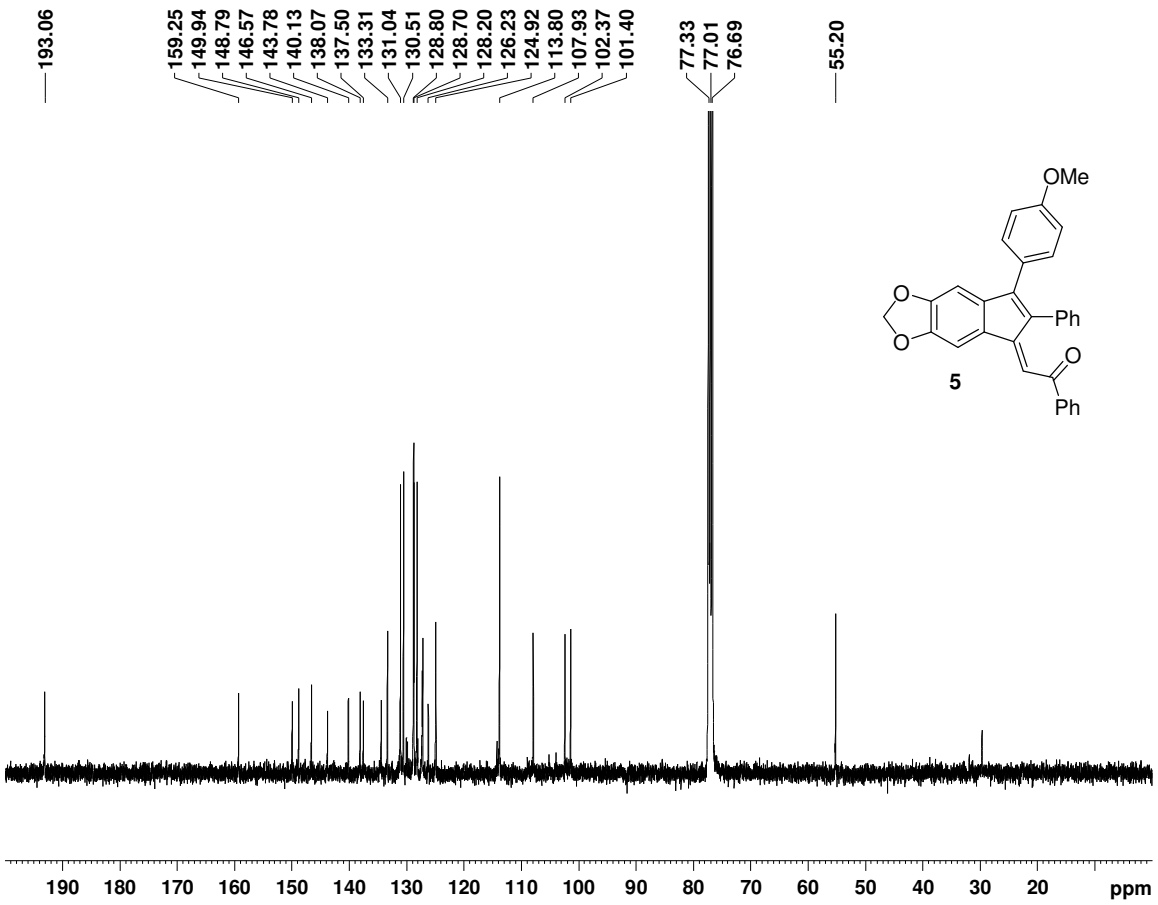

7.845
7.827
7.585
7.567
7.536
7.518
7.499
7.434
7.415
7.411
7.395
7.390
7.371
7.346
7.328
7.309
7.251
6.950
6.909
5.969
5.965
5.940
5.937
4.734
4.727
4.708
4.701
3.162
3.155
3.117
3.110
3.001
2.976
2.957
2.931
I
O
O
O
4i
9
8
7
6
5
4
3
2
1
ppm
1.93
1.97
1.10
4.05
1.03
0.89
0.95
1.99
0.98
0.97
1.00


198.54
152.17
147.41
147.00
139.70
139.52
136.68
135.37
133.34
128.85
128.59
128.49
128.09
128.03
105.09
104.16
101.26
92.43
77.34
77.02
76.70
47.81
40.68
I
O
O
O
4i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.858
7.840
7.617
7.600
7.544
7.525
7.507
7.446
7.428
7.418
7.408
7.398
7.380
7.356
7.337
7.315
7.260
6.993
6.987
6.939
6.933
6.918
6.912
4.835
4.827
4.809
4.802
3.769
3.198
3.191
3.154
3.146
3.065
3.039
3.020
2.995
I
MeO
O
4j
9
8
7
6
5
4
3
2
1
ppm
2.02
2.05
1.17
4.25
2.05
0.96
0.99
1.01
3.19
0.99
1.01


198.60
159.18
150.88
146.88
138.53
136.78
135.45
133.29
128.90
128.57
128.48
128.09
127.99
123.55
113.05
109.97
92.62
77.33
77.01
76.70
55.59
48.25
40.61
I
MeO
O
4j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.952
7.933
7.788
7.582
7.563
7.546
7.474
7.455
7.438
7.351
7.336
7.317
7.306
7.285
7.263
7.234
7.215
7.191
7.171
6.955
6.842
6.822
6.807
5.961
3.804
OMe
O
O
Ph
O
Ph
5
9
8
7
6
5
4
3
2
1
ppm
1.94
0.88
1.21
2.04
2.93
3.95
0.97
2.99
2.23
3.00


193.06
159.25
149.94
148.79
146.57
143.78
140.13
138.07
137.50
133.31
131.04
130.51
128.80
128.70
128.20
126.23
124.92
113.80
107.93
102.37
101.40
77.33
77.01
76.69
55.20
OMe
O
O
Ph
O
Ph
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm