SUPPORTING INFORMATION

IBX-I_2 Redox Couple for Facile Generation of IOH and I^+: Expedient Protocol for Iodohydroxylation of Olefins and Iodination of Aromatics

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EXPERIMENTAL SECTION

General Aspects. The melting points were determined with a Melting Point apparatus and are uncorrected. Column chromatography was conducted with silica-gel of 100-200 mesh particle size. NMR spectra were recorded on 400 MHz and 500 MHz spectrometers. IR spectra were recorded on a FT-IR spectrophotometer. Mass spectral analyses were carried out with Waters ESI-Q^{TOF} instrument.

General Procedure for Iodohydroxylation of Olefins. In a typical experimental procedure, 0.5-1.5 mmol of the olefin, 1.5 equiv of I_2 and 1.5 equiv of IBX in 2.0- 3.0 mL of DMSO were stirred at room temperature. The progress of the reaction was monitored by TLC analysis. After completion of the reaction as judged by TLC analysis, the reaction mixture was quenched with water (10 mL) and extracted with ethyl acetate (2 × 20 mL). The combined organic extracts were washed with 10% aq. sodium thiosulfate solution (5 mL), water (10 mL), brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by column chromatography over silica gel.

For e-rich olefins, the reagent was prepared first by stirring I_2 and IBX for 30 min in DMSO and then olefin was added to it. While the duration of reaction was typically 30 min for e-rich olefins, it varied from 1-12 h for e-deficient olefins such as α,β-unsaturated carbonyl compounds.

General Procedure for One-pot Epoxidation of Olefins. After the disappearance of the olefin in the iodohydroxylation reaction described above, 1.5 equiv of 10% aq. NaOH solution was added to the reaction mixture in the same pot at room temperature. The progress of the reaction was monitored by TLC analysis. After the iodohydrin was consumed in the reaction, the reaction mixture was quenched with water (10 mL) and extracted with ethyl acetate (2 × 20 mL). The combined organic extracts were washed with 10% aq. sodium thiosulfate solution (5 mL), water (10 mL), brine (10 mL) and dried over anhydrous

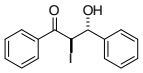
Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by column chromatography using silica gel.

General Procedure for the Iodination of Aromatics. In a typical experimental procedure, the iodinating reagent was prepared by adding 2.2 equivalents of molecular iodine to IBX in 2.0-3.0 mL of DMSO/CH_3CN-TFA (9:1) at room temperature for 30 min. Subsequently, the 1-2 mmol of the substrate was added to the above prepared reagent and stirring was continued. The progress of the reaction was monitored by TLC analysis. After completion of the reaction, the reaction mixture was quenched with 10% aq. sodium thiosulfate solution (5 mL) and extracted with ethyl acetate (2 × 10 mL). The combined organic extracts were washed with water (10 mL × 2), brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography using silica gel. It should be noted that for phenols, the aqueous reaction mixture was neutralized with NH_4Cl before extraction.

For phenol and aniline derivatives, the reagent was first made by stirring I_2 and IBX for 30 min and then the substrate was added. The same procedure as mentioned above was followed for iodination of *p*-nitrotolune except that 5 equiv of Conc. H_2SO_4 was used in place of TFA in AcOH medium.

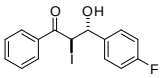
The Spectral Data of the Products

(2R*,3R*)-3-Hydroxy-2-iodo-1,3-diphenylpropan-1-one[1]



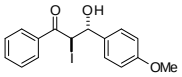
White solid; mp 120-122 °C (lit. mp 122-124 °C)[1]; IR (KBr) cm^{-1} 3481, 1660; ^1H NMR (400 MHz, $CDCl_3$): δ 5.36 (d, *J* = 8.0 Hz, 1H), 5.54 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.46-7.50 (m, 4H), 7.60 (t, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 2H).

(2R*,3R*)-3-(4-Fluorophenyl)-3-hydroxy-2-iodo-1-phenylpropan-1-one



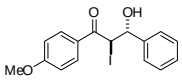
White solid; mp 57-58 °C; IR (KBr) cm^{-1} 3442, 1672; ^1H NMR (500 MHz, $CDCl_3$): δ 3.83 (br s, 1H), 5.36 (d, *J* = 8.3 Hz, 1H), 5.47 (d, *J* = 8.3 Hz, 1H), 7.07 (t, *J* = 8.6 Hz, 2H), 7.44-7.50 (m, 4H), 7.61 (t , *J* = 7.3 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.3, 75.3, 115.3 (d, *J* = 21.5 Hz), 128.7, 128.8, 129.0 (d, *J* = 8.3 Hz), 134.0, 134.1, 135.7 (d, *J* = 2.4 Hz), 162.6 (d, *J* = 245.6 Hz), 196.0; ESI-MS^+ *m/z* Calcd for $C_{15}H_{12}IFO_2$ 368.9787 [M-H], found 368.9789.

(2R*,3R*)-3-Hydroxy-2-iodo-3-(4-methoxyphenyl)-1-phenylpropan-1-one



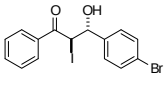
Colorless semisolid; IR (KBr) cm^{-1} 3467, 1673; ^1H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 3H), 5.33 (d, *J* = 8.1 Hz, 1 H), 5.51 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.7, 55.2, 75.5, 113.8, 128.4, 128.7, 128.8, 132.1, 133.9, 134.2, 159.6, 196.1; ESI-MS^+ *m/z* Calcd for $C_{16}H_{15}IO_3$ 404.9963 [M+Na], found 404.9965.

(2R*,3R*)-3-Hydroxy-2-iodo-1-(4-methoxyphenyl)-3-phenylpropan-1-one



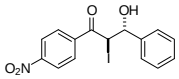
White solid; mp 122-123 °C; IR (KBr) cm^{-1} 3479, 1649; ^1H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 3H), 3.94 (d, *J* = 5.7 Hz, 1H), 5.33 (t, *J* = 6.7 Hz, 1H), 5.50 (d, *J* = 8.0Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.97 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.8, 55.6, 76.2, 114.0, 126.9, 127.2, 128.4, 131.2, 139.9, 164.2, 194.8; ESI-MS^+ *m/z* Calcd for $C_{16}H_{15}IO_3$ 383.0144 [M+H], found 383.0144.

(2R*,3R*)-3-(4-Bromophenyl)-3-hydroxy-2-iodo-1-phenylpropan-1-one



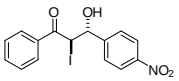
White solid; mp 92-94 °C; IR (KBr) cm^{-1} 3495, 1671; ^1H NMR (500 MHz, $CDCl_3$): δ 5.32 (d, *J* = 8.0 Hz, 1H), 5.46 (d, *J* = 8.0 Hz, 1Hz), 7.36 (d, *J* = 8.6 Hz, 2H), 7.47-7.52 (m, 4H), 7.61-7.62 (m, 1H), 7.99 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.7, 75.4, 122.5, 128.9, 129.0, 131.5, 131.7, 134.0, 134.3, 138.8, 195.9; ESI-MS^+ *m/z* Calcd for $C_{15}H_{12}BrIO_2$ 428.8987 [M-H], found 428.8987.

(2R*,3R*)-3-Hydroxy-2-iodo-1-(4-nitrophenyl)-3-phenylpropan-1-one



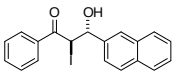
White solid; mp 116-117 °C; IR (KBr) cm^{-1} 3495, 1683; ^1H NMR (500 MHz, $CDCl_3$): δ 5.36 (d, *J* = 8.6 Hz, 1H), 5.49 (d, *J* = 8.6 Hz, 1H), 7.30-7.42 (m, 3H), 7.46 (d, *J* = 6.9 Hz, 2H), 8.13 (d, *J* = 8.6 Hz, 2H), 8.29 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.6, 75.6, 123.9, 127.2, 128.6, 128.8, 129.8, 138.9, 139.5, 150.5, 194.1; ESI-MS^+ *m/z* Calcd for $C_{15}H_{12}INO_4$ 395.9732 [M-H], found 395.9734.

(2R*,3R*)-3-Hydroxy-2-iodo-3-(4-nitrophenyl)-1-phenylpropan-1-one



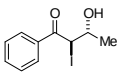
White solid; mp 109-110 °C; IR (KBr) cm^{-1} 3408, 1655; ^1H NMR (500 MHz, $CDCl_3$): δ 5.46 (s, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.61-7.64 (m, 1H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.3 Hz, 2H), 8.24 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.9, 75.1, 123.6, 128.4, 128.8, 128.9, 133.7, 134.4, 146.8, 147.9, 195.6; ESI-MS^+ *m/z* Calcd for $C_{15}H_{12}INO_4$ 395.9732 [M-H], found 395.9736.

(2R*,3S*)-3-Hydroxy-2-iodo-3-(naphthalen-2-yl)-1-phenylpropan-1-one



White solid; mp 124-125 °C; IR (KBr) cm^{-1} 3484, 1666; ^1H NMR (500 MHz, $CDCl_3$): δ 3.94 (br s, H), 5.54 (d, *J* = 8.0 Hz, 1H), 5.66 (d, *J* = 8.0 Hz, 1H), 7.46-7.53 (m, 4H), 7.58-7.61 (m, 2H), 7.84-7.89 (m, 3H), 7.94 (s, 1H), 8.02 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.9, 76.3, 124.4, 126.3, 126.9, 127.7, 128.2, 128.5, 128.80, 128.83, 133.0, 133.3, 134.1, 134.2, 137.2, 196.1; ESI-MS^+ *m/z* Calcd for $C_{19}H_{15}IO_2$ 425.0014 [M+Na], found 425.0014.

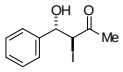
(2R*,3R*)-3-Hydroxy-2-iodo-1-phenylbutan-1-one



White solid; ^1H NMR (500 MHz, $CDCl_3$): δ 1.58 (d, *J* = 6.2 Hz, 3H), 4.43-4.48 (m, 1H), 5.22

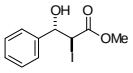
(d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 8.00 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.9, 30.1, 69.4, 128.85, 128.88, 133.9, 134.2, 195.9; ESI-MS$^+$ *m/z* Calcd for $C_{10}H_{11}IO_2$ 290.9882 [M+H], found 290.9887.

(3R*,4R*)-4-Hydroxy-3-iodo-4-phenylbutan-2-one[1]



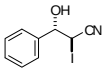
White solid; mp 63-64 °C (lit. mp 63.7-65.5 °C)[1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 3.62 (br s, 1H), 4.72 (d, J = 8.5 Hz, 1H), 5.10 (d, J = 8.5 Hz, 1H), 7.39 (m, 5H).

Methyl (2R*,3R*)-3-hydroxy-2-iodo-3-phenylpropanoate[1]



White solid; mp 59-60 °C (lit. mp 60-62 °C)[1]; IR (KBr) cm^{-1} 3423, 1709; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.43 (br s, 1H), 3.77 (s, 3H), 4.57 (d, J = 8.3 Hz, 1H), 5.08 (d, J = 8.3 Hz, 1H), 7.35-7.37 (m, 5H).

3-Hydroxy-2-iodo-3-phenylpropanenitrile[1]

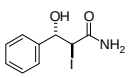


White solid; IR (KBr) cm^{-1} 3416, 2249; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.89 (br s, 1H), 4.45 (d, J = 4.5 Hz, 1H), 4.96 (d, J = 4.5 Hz, 1H), 7.40-7.47 (m, 5H).

Methyl 3-hydroxy-2-iodo-3-propanoate

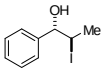
Colorless liquid; IR (KBr) cm^{-1} 3397, 1730; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.84 (br s, 1H), 3.77 (s, 3H), 3.81 (dd, J_1 = 12.0 Hz, J_2 = 4.9 Hz, 1H), 3.97 (dd, J_1 = 12.0 Hz, J_2 = 8.9 Hz, 1H), 4.44 (dd, J_1 = 8.9 Hz, J_2 = 4.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 53.1, 64.9, 171.4; ESI-MS$^+$ *m/z* Calcd for $C_4H_7IO_3$ 252.9337 [M+Na], found 252.9339.

(2R*,3R*)-3-Hydroxy-2-iodo-3-phenylpropaneamide



White solid; mp 131-132 °C; IR (KBr) cm^{-1} 3326, 3187, 1688, 1630; ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.40 (d, J = 9.5 Hz, 1H), 4.84 (dd, J_1 = 9.5 Hz, J_2 = 5.5 Hz, 1H), 5.93 (d, J = 5.5 Hz, 1H), 7.12 (s, 1H), 7.26-7.35 (m, 5H), 7.63 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.2, 74.7, 127.4, 127.7, 127.9, 142.5, 171.3; ESI-MS$^+$ *m/z* Calcd for $C_9H_{10}INO_2$ 291.9834 [M+H], found 291.9834.

(1R*,2S*)-2-Iodo-1-phenylpropan-1-ol[2]

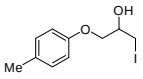


Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.74 (d, J = 7.0 Hz, 3H), 4.52 (dq, J_1 = 7.0 Hz, J_2 = 4.0 Hz, 1H), 7.30-7.39 (m, 5H).

2-Iodo-1-phenylethanol[3]

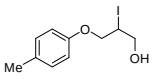
Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.25 (br s, 1H), 3.40 (dd, J_1 = 10.2 Hz, J_2 = 8.8 Hz, 1H), 3.49 (dd, J_1 = 10.2 Hz, J_2 = 3.5 Hz, 1H), 4.83 (dd, J_1 = 8.8 Hz, J_2 = 3.5 Hz, 1H), 7.31-7.37 (m, 5H).

1-Iodo-3-(*p*-tolyloxy)propan-2-ol[4]



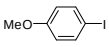
Pale yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.55 (br s, 1H), 3.38 (dd, J_1 = 10.3 Hz, J_2 = 5.5 Hz 1H), 3.46 (dd, J_1 = 10.3 Hz, J_2 = 5.1 Hz, 1H), 3.95-3.99 (m, 1H), 4.01-4.07 (m, 2H), 6.81 (d, J = 8.4 Hz , 2H), 7.08 (d, J = 8.4 Hz, 2H).

2-Iodo-3-(*p*-tolyloxy)propan-1-ol[5]



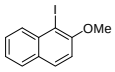
Pale yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.29 (s, 3H), 3.95 (dd, J_1 = 5.1 Hz, J_2 = 1.7 Hz, 2H), 4.26 (dd, J_1 = 10.3 Hz, J_2 = 8.3 Hz, 1H), 4.30-4.33 (m, 1H), 4.42-4.46 (m, 1H), 6.81 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H).

4-Iodoanisole[6]



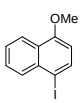
White solid; mp 50-51 °C (lit. mp 51-52 °C)[6]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 (s, 3H), 6.68 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H).

1-Iodo-2-methoxynaphthalene[7a]



White solid; mp 87-88 °C (lit. mp 87-88 °C)[7b]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.03 (s, 3H), 7.21 (d, J = 8.6 Hz, 1H), 7.37-7.40 (m, 1H), 7.53-7.56 (m, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 8.6 Hz, 1H).

2-Iodo-1-methoxynaphthalene[6]



White solid; mp 53-54 °C (lit. mp 53-55 °C)[7b]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.99 (s, 3H), 6.60

(d, J = 8.1 Hz, 1H), 7.51 (td, J_1 = 6.8 Hz, J_2 = 1.1 Hz, 1H), 7.57-7.60 (m, 1H), 7.95 (d, J = 8.6 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 8.23 (d, J = 8.6 Hz, 1H).

2,4,6-Triiodophenol[8a]

Brown solid; mp 152-153 °C (lit. mp 156-159 °C)[8a]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.76 (s, 1H), 7.93 (s, 2H).

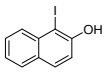
4-Iodoaniline[9a]

Brown solid; mp 61-62 °C (lit. mp 62-64 °C)[9b]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.67 (br s, 2H), 6.47 (d, J = 9.0 Hz, 2H), 7.40 (d, J = 9.0 Hz, 2H).

2,4,6-Triiodoaniline[10a]

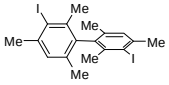
Solid; mp 177-179 °C (lit. mp 183-185 °C)[10b]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.67 (br s, 2H), 7.86 (s, 2H).

1-Iodonaphthalen-2-ol[11]



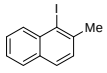
White solid; mp 93-94 °C (lit. mp 92-94 °C)[7a]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.78 (s, 1H), 7.26 (d, J = 8.9 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.74 (d, J = 8.9 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H).

3,3'-Diiodobimesityl[12]



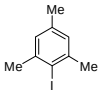
White solid; mp 154-156 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.79 (s, 6H), 2.08 (s, 6H), 2.49 (s, 6H), 7.04 (s, 2H).

1-Iodo-2-methylnaphthalene[13]



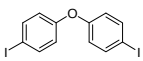
Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.7 (s, 3H), 7.37 (d, J = 8.3 Hz, 1H), 7.44-7.47 (m, 1H), 7.54-7.57 (m, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 8.23 (d, J = 8.6 Hz, 1H).

2-Iodo-1,3,5-trimethylbenzene[6]



White solid; mp 30-31 °C (lit. mp 92-94 °C)[6] ;^{1}H NMR (500 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.43 (s, 6H), 6.89 (s, 2H).

4,4'-Diiododiphenylether[14a]



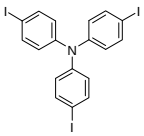
White solid; mp 135-136 °C (lit. mp 139-141 °C)[14b]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.76 (d, J = 9.0 Hz, 4H), 7.63 (d, J = 9.0 Hz, 4H).

Monoiodotoluene (inseperable mixture of *o* & *p*)[15]

(*o*-iodotoluene) ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 6.85-6.88 (m, 1H), 7.23-7.25 (m, 2H), 7.81 (d, J = 7.9 Hz, 1H).

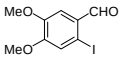
(*p*-iodotoluene) ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.29 (s, 3H), 6.93 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H).

Tris(4-iodophenyl)amine[16]



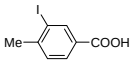
White solid; mp 151-152 °C (lit. mp 169 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (d, J = 8.6 Hz, 6H), 7.53 (d, J = 8.6 Hz, 6H).

2-Iodo-4,5-dimethoxybenzaldehyde[17a]



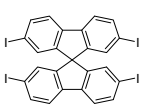
White solid; mp 137-139 °C (lit. mp 137-139 °C)[17b]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.92 (s, 3H), 3.96 (s, 3H), 7.31 (s, 1H), 7.42 (s, 1H), 9.86 (s, 1H).

3-Iodo-4-methylbenzoic acid[18]



White solid; mp 209-210 °C (lit. mp 208-209 °C)[18]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.51 (s, 3H), 7.33 (d, J = 7.9 Hz, 1H), 7.97 (dd J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 8.52 (d, J = 1.7 Hz, 1H).

2,2',7,7'-Tetraiodo-9,9'-spirobifluorene[19]



White solid; mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (d, J = 1.4 Hz, 4H), 7.56 (d, J

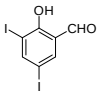
= 8.3 Hz, 4H), 7.73 (dd, J_1 = 8.3 Hz, J_2 = 1.4 Hz, 4H).

Iodobromobenzene (inseperable mixture of *ortho* and *para* isomers)[20]

(*o*-iodobromobenzene) ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (td J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1H), 7.20 (td, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 7.63 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 7.86 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H).

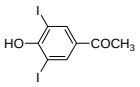
(*p*-iodobromobenzene) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H).

2-Hydroxy-3,5-diiodobenzaldehyde[21]



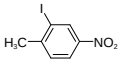
White solid; mp 106-107 °C (lit. mp 108 °C)[21]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 2.1 Hz, 1H), 8.25 (d, J = 2.1 Hz, 1H), 9.71 (s, 1H).

1-(4-Hydroxy-3,5-diiodophenyl)ethanone[22]



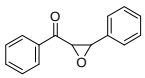
White solid; mp 158-160 °C (lit. mp 160 °C)[22]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53 (s, 3H), 6.18 (s, 1H), 8.27 (s, 2H).

2-Iodo-4-nitrotoluene[23]



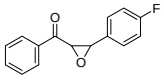
White solid; mp 52-54 °C (lit. mp 52-54°C)[24]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.53 (s, 3H), 7.38 (d, J = 8.6 Hz, 1H), 8.11 (dd, J_1 = 8.6 Hz, J_2 = 2.1 Hz, 1H), 8.65 (d, J = 2.1 Hz, 1H).

***trans*-Epoxy-1,3-diphenylpropan-1-one**[24a]



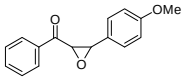
White solid; mp 87-89 °C (lit. mp 89-90 °C)[24b]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.08 (d, J = 1.7 Hz, 1H), 4.30 (d, J = 1.7 Hz, 1H), 7.36-7.42 (m, 5H), 7.48-7.51(m, 2H), 7.60-7.64 (m, 1H), 8.00-8.02 (m, 2H).

***trans*-Epoxy-3-(4-fluorophenyl)-1-phenylpropan-1-one**[24a]



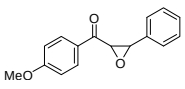
Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.07 (d, J = 1.6 Hz, 1H), 4.26 (d, J = 1.9 Hz, 1H), 7.07-7.11 (m, 2H), 7.33-7.36 (m, 2H), 7.48-7.51 (m, 2H), 7.61-7.64 (m, 1H), 7.99-8.01 (m, 2H).

***trans*-Epoxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one**[24a]



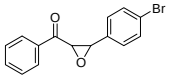
Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 3H), 4.02 (d, *J* = 1.7 Hz, 1H), 4.29 (d, *J* = 1.7 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.46-7.49 (m, 2H), 7.59-7.62 (m, 1H), 8.00 (d, *J* = 7.2 Hz, 2H).

***trans*-Epoxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one**[25]



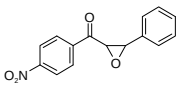
White solid; mp 77-78 °C (lit. mp 79-80 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (s, 3H), 4.07 (d, *J* = 1.9 Hz, 1H), 4.25 (d, *J* = 1.9 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 2H), 7.36-7.40 (m, 5H), 8.00 (d, *J* = 9.0 Hz, 2H).

***trans*-Epoxy-3-(4-bromophenyl)-1-phenylpropan-1-one**[24a]



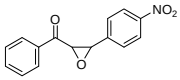
White solid; mp 88-90 °C (lit. mp 89-90 °C)[24c]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.04 (d, *J* = 1.5 Hz, 1H), 4.24 (d, *J* = 1.5 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.47-7.53 (m, 4H), 7.60-7.63 (m, 1H), 7.99 (d, *J* = 7.6 Hz, 2H).

***trans*-Epoxy-1-(4-nitrophenyl)-3-phenylpropan-1-one**[25]



White solid; mp 118-120 °C (lit. mp 142-144 °C)[24d] ;^{1}H NMR (500 MHz, $CDCl_3$): δ 4.10 (d, *J* = 1.5 Hz, 1H), 4.26 (d, *J* = 1.5 Hz, 1H), 7.35-7.37 (m, 2H), 7.41-7.43 (m, 3H), 8.19 (d, *J* = 8.8 Hz, 2H), 8.34 (d, *J* = 8.8 Hz, 2H).

***trans*-Epoxy-3-(4-nitrophenyl)-1-phenylpropan-1-one**[24]



White solid; mp 140-141 °C (lit. mp 139-141 °C)[24d]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.20 (d, *J* = 1.7 Hz, 1H), 4.28 (d, *J* = 1.7 Hz, 1H), 7.50-7.53 (m, 2H), 7.56 (d, *J* = 8.8 Hz, 2H). 7.64-7.67 (m, 1H), 8.01 (dd, J_1 = 8.6, J_2 = 1.4 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 2H).

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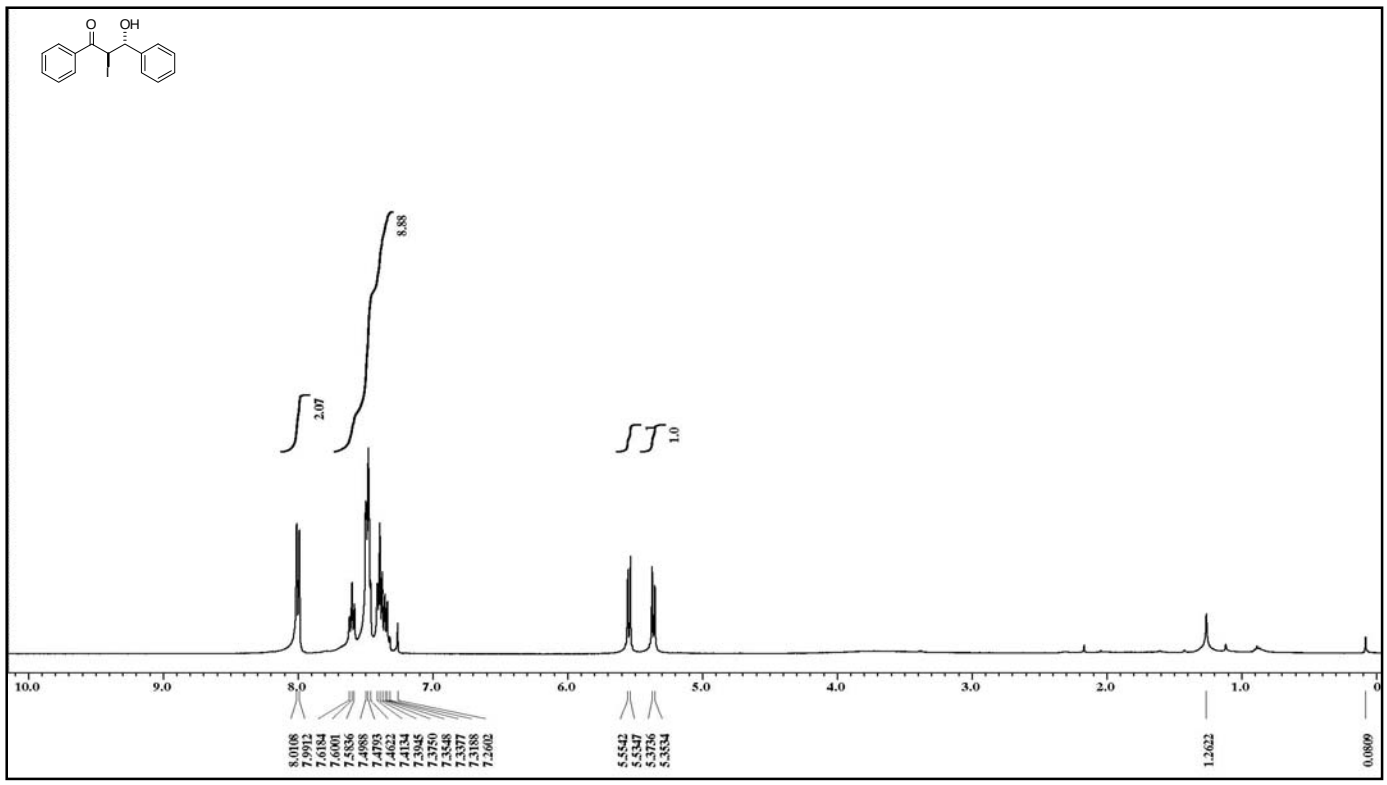
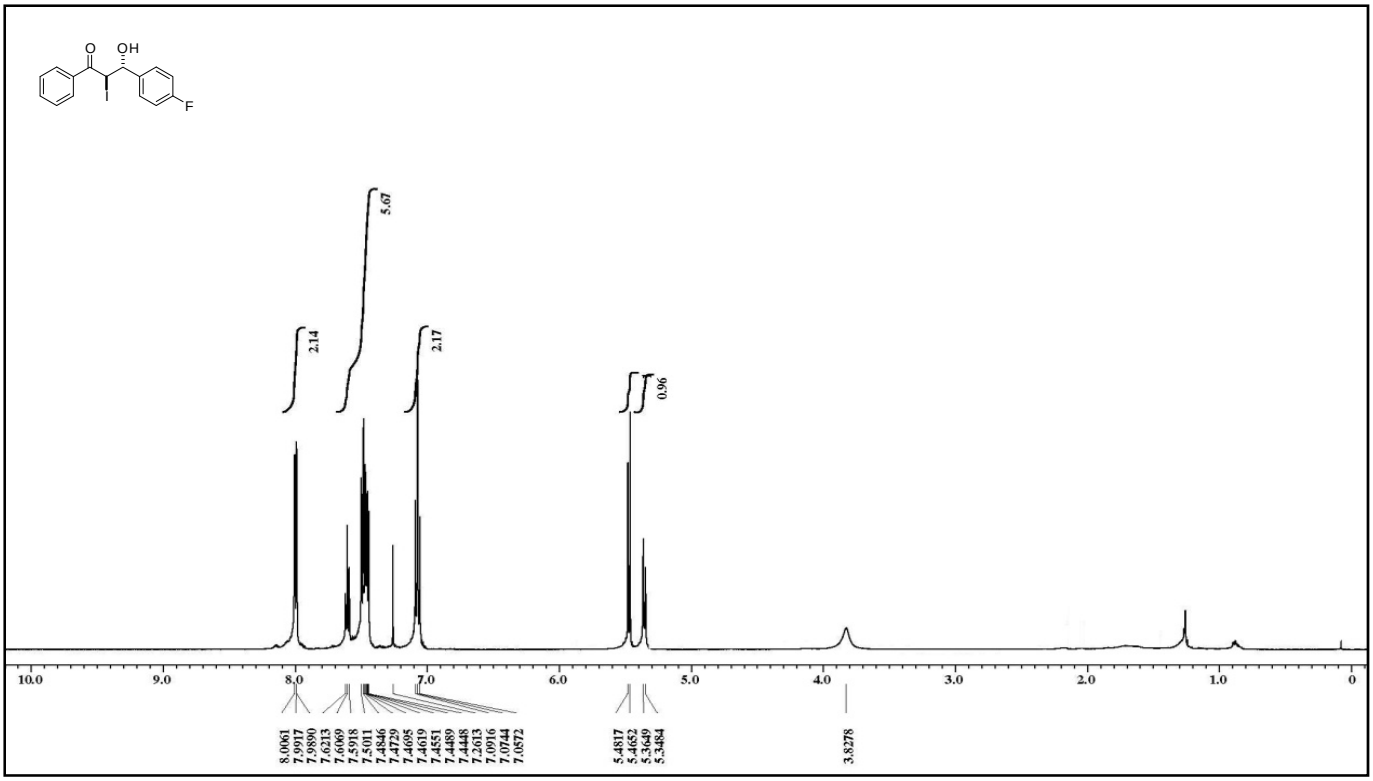


Figure S1. ^{1}H NMR spectrum of 3-hydroxy-2-iodo-1,3-diphenylpropan-1-one.



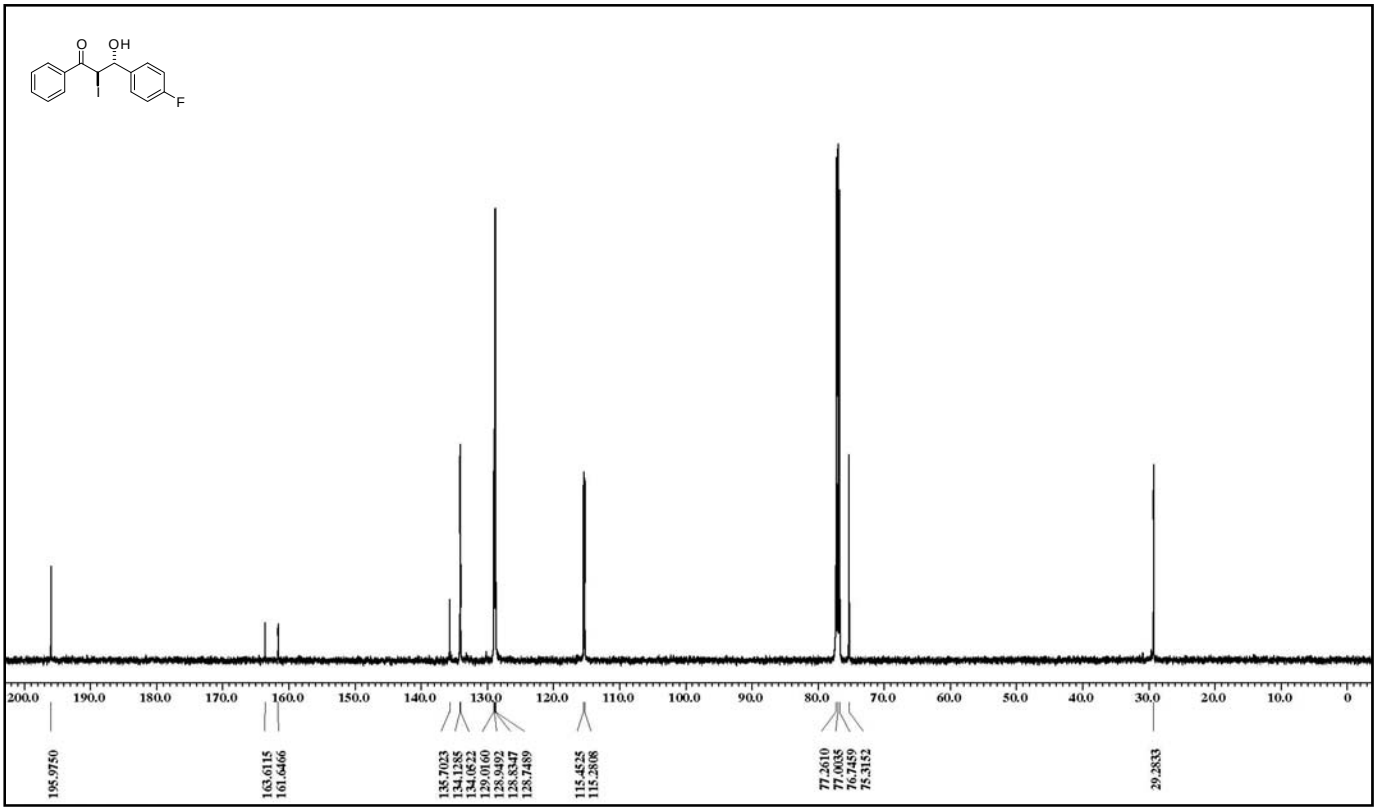
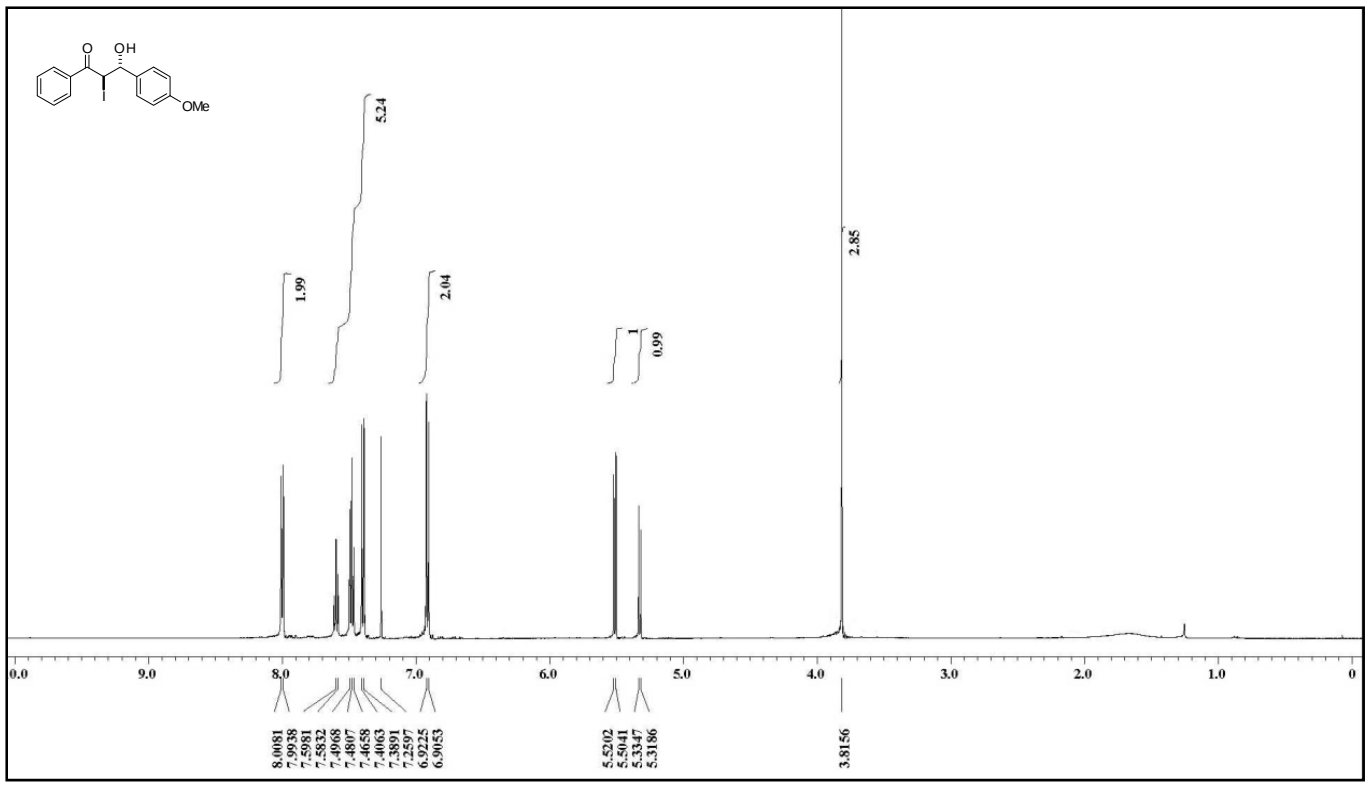


Figure S2. ^{1}H and ^{13}C NMR spectra of 3-(4-fluorophenyl)-3-hydroxy-2-iodo-1-phenylpropan-1-one.



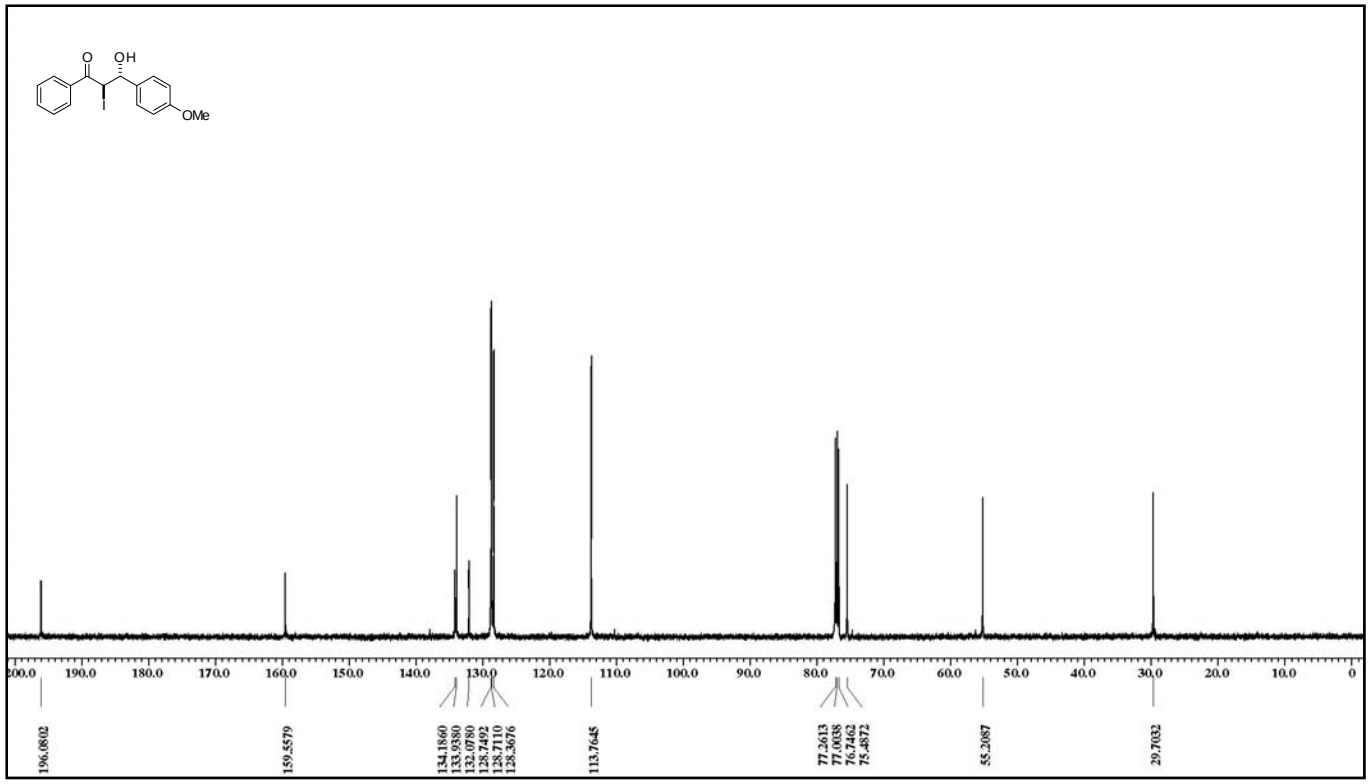


Figure S3. ^{1}H and ^{13}C NMR spectra of 3-hydroxy-2-iodo-3-(4-methoxyphenyl)-1-phenylpropan-1-one.

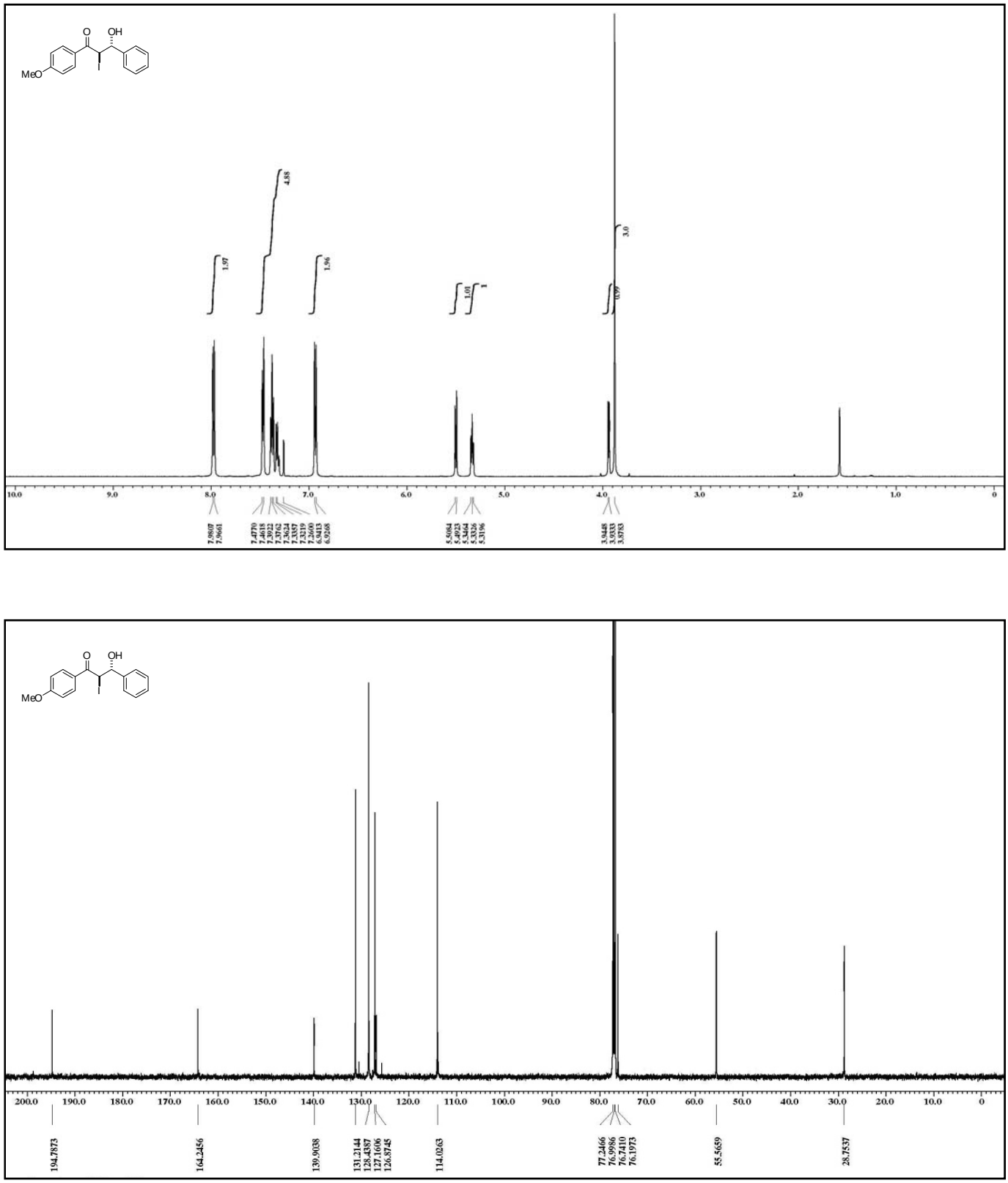
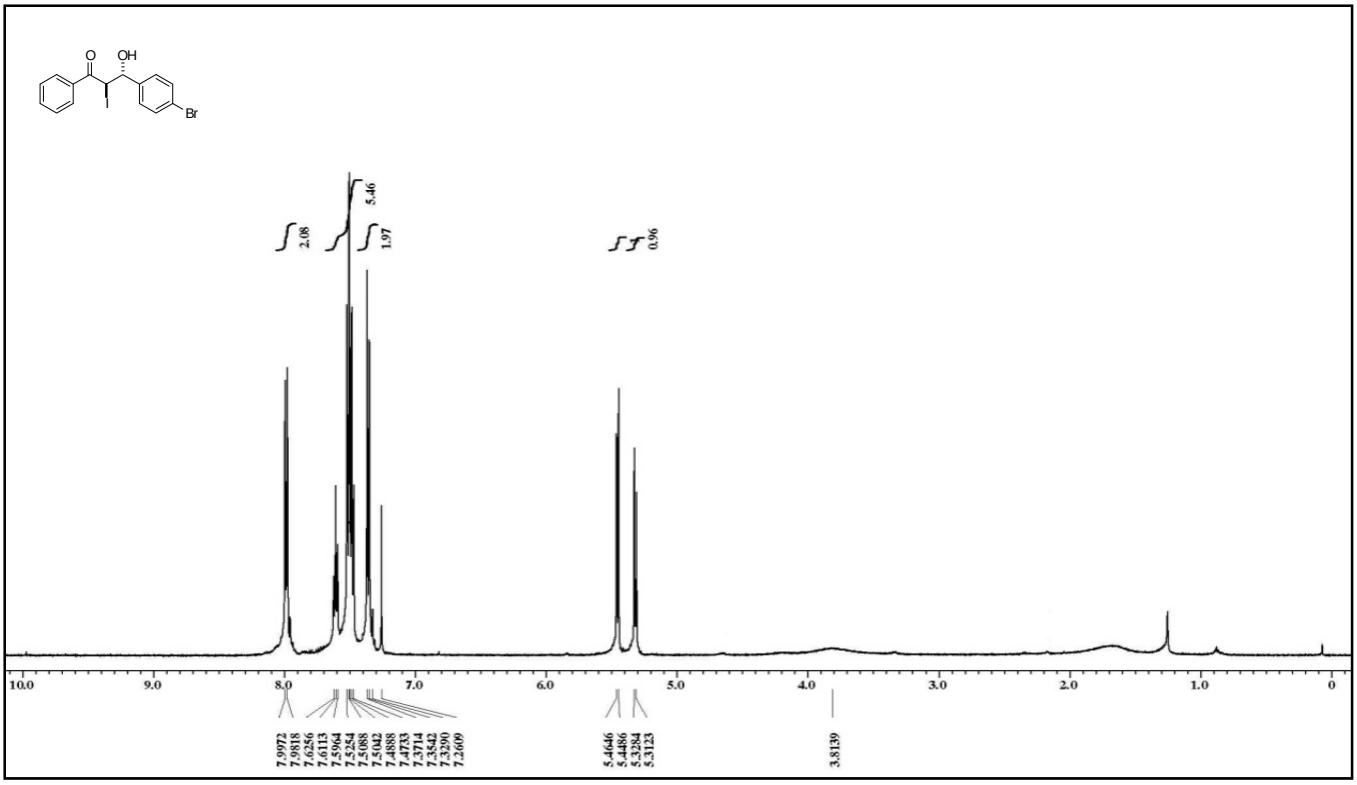


Figure S4. ^{1}H and ^{13}C NMR spectra of 3-hydroxy-2-iodo-1-(4-methoxyphenyl)-3-phenylpropan-1-one.



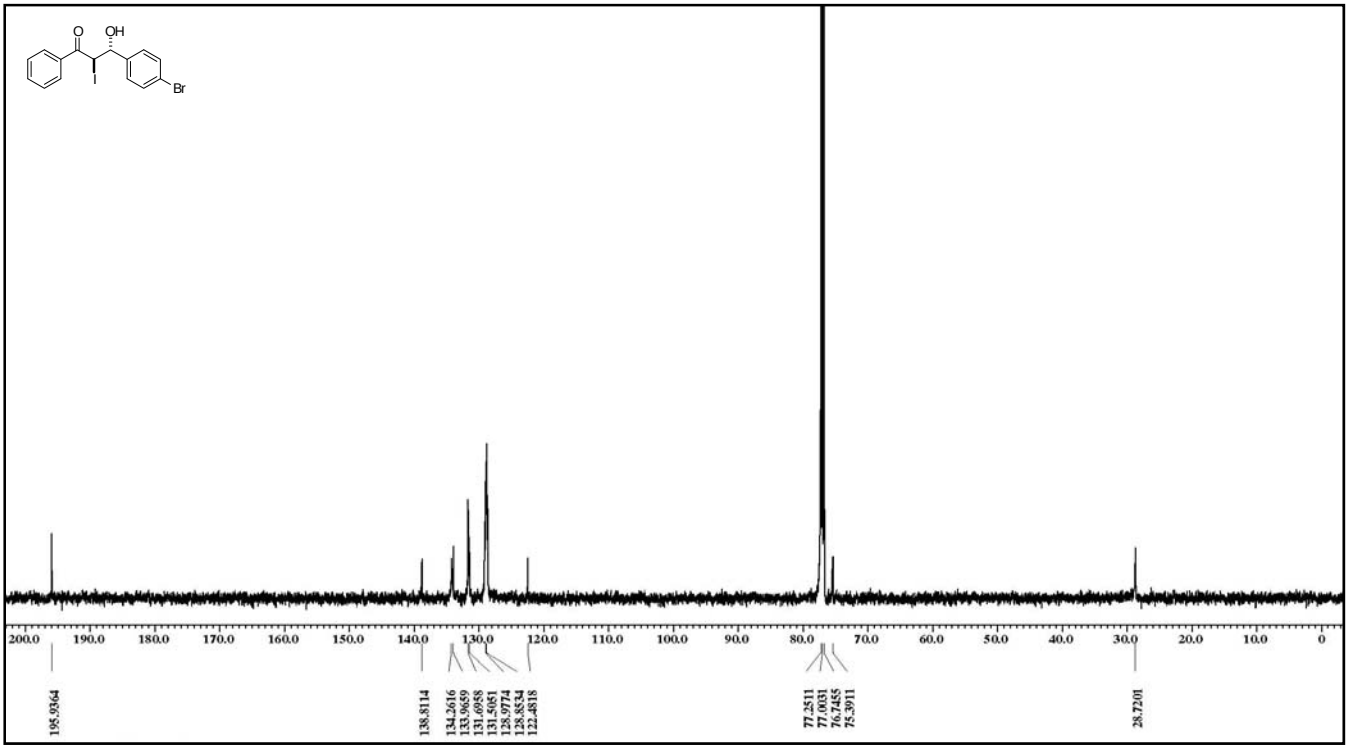


Figure S5. ^{1}H and ^{13}C NMR spectra of 3-(4-bromophenyl)-3-hydroxy-2-iodo-1-phenylpropan-1-one.

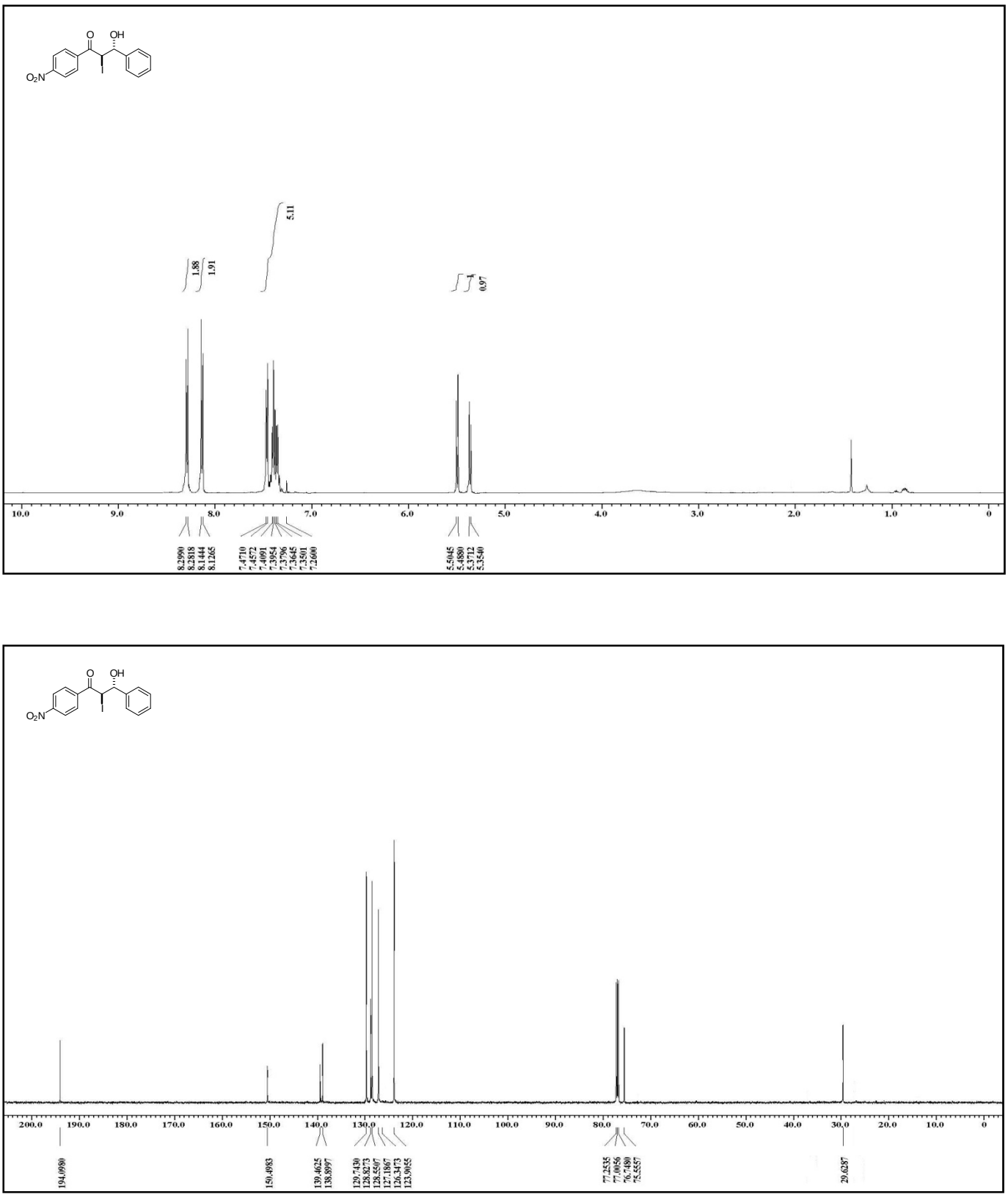


Figure S6. ^{1}H and ^{13}C NMR spectra of 3-hydroxy-2-iodo-1-(4-nitro-phenyl)-3-phenylpropan-1-one.

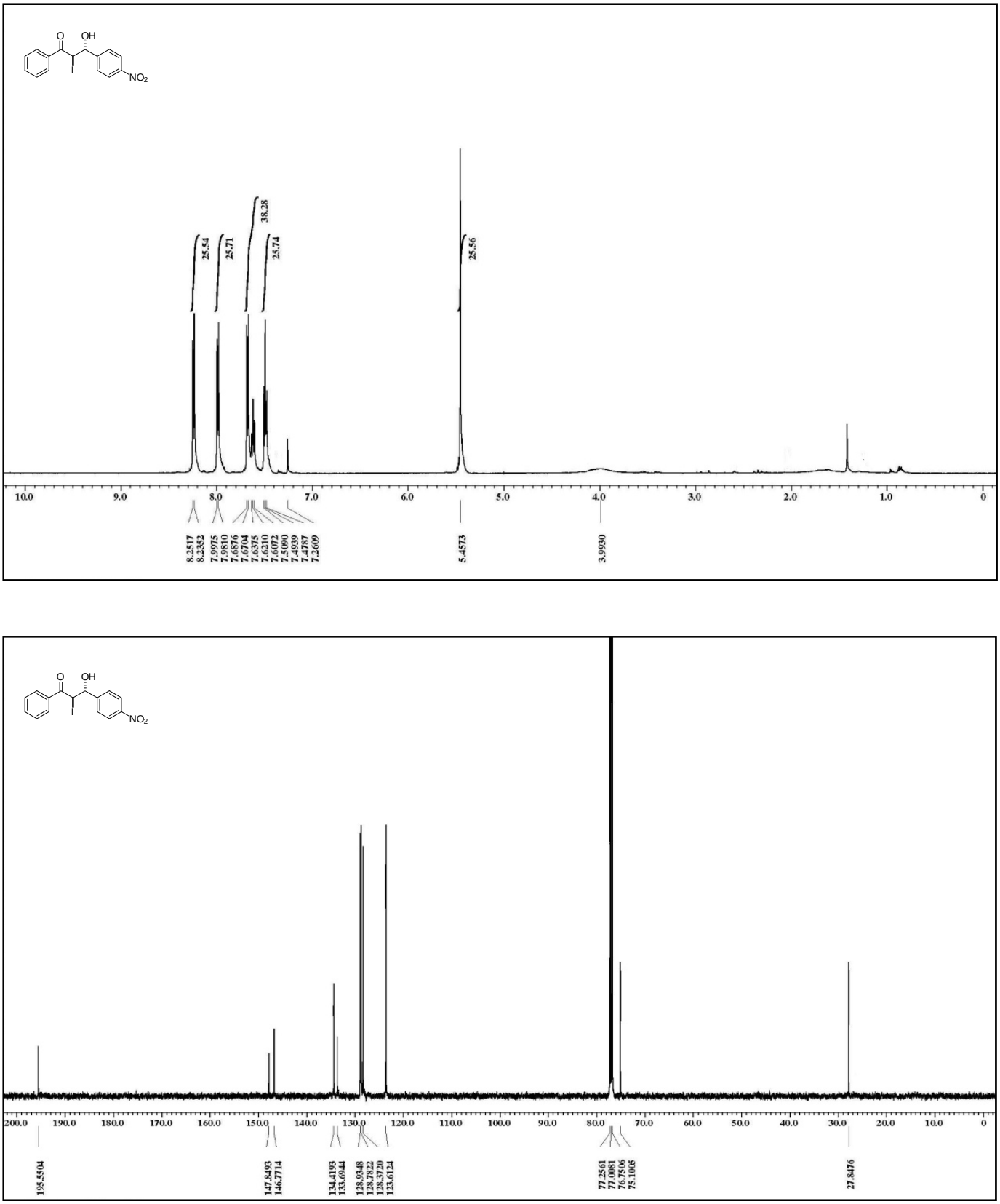


Figure S7. ^{1}H and ^{13}C NMR spectra of 3-hydroxy-2-iodo-3-(4-nitrophenyl)-1-phenylpropan-1-one.

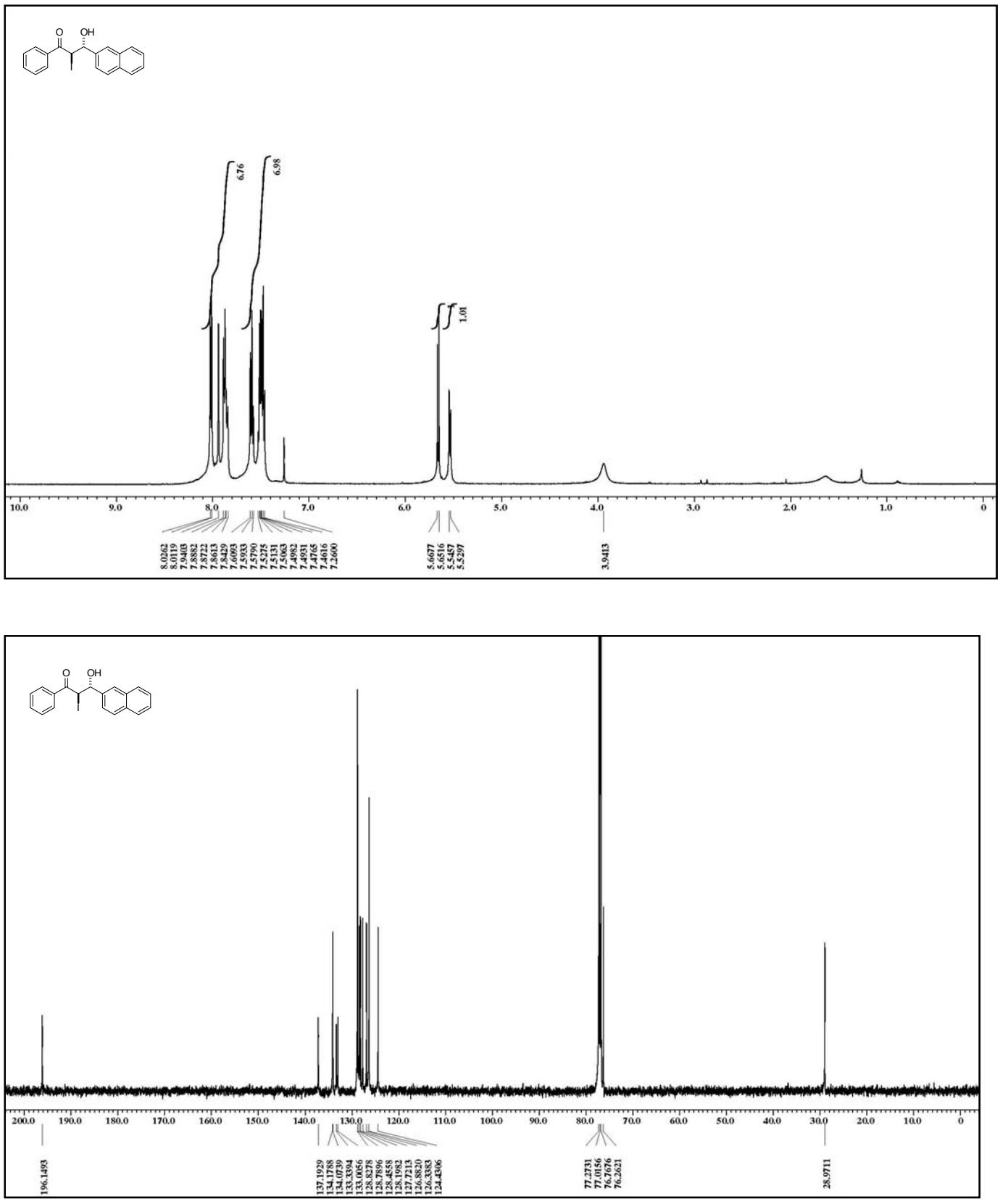
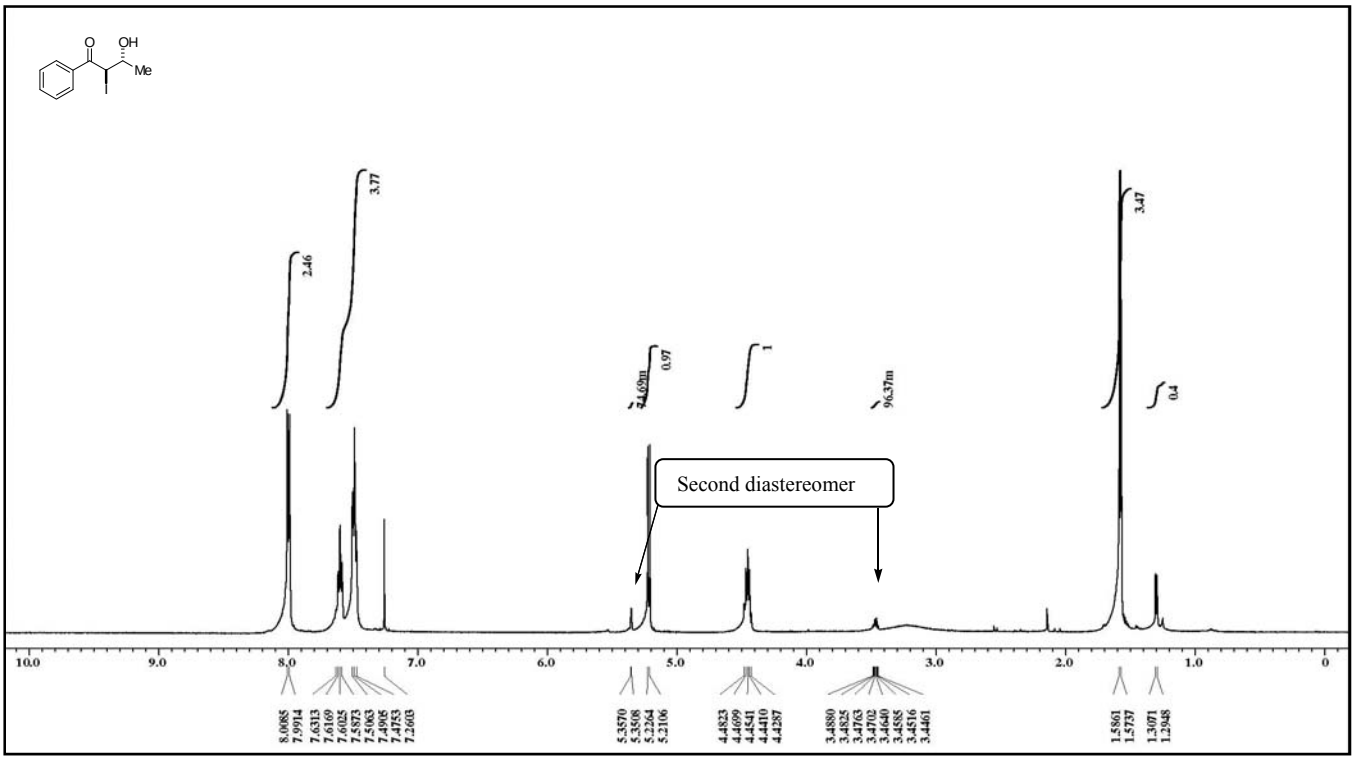


Figure S8. ^{1}H and ^{13}C NMR spectra of 3-hydroxy-2-iodo-3-(naphthalen-2-yl)-1-phenylpropan-1-one.



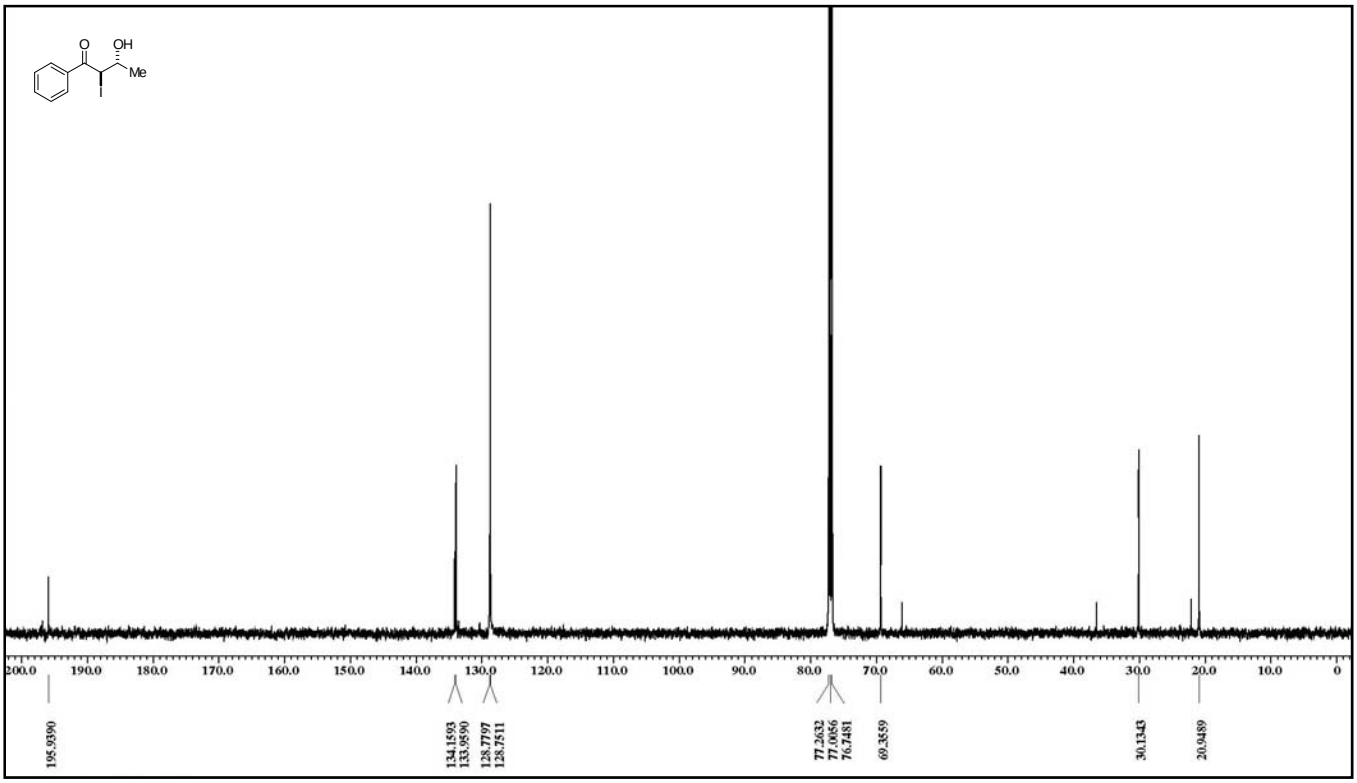


Figure S9. ^{1}H and ^{13}C NMR spectra of 3-hydroxy-2-iodo-1-phenylbutan-1-one.

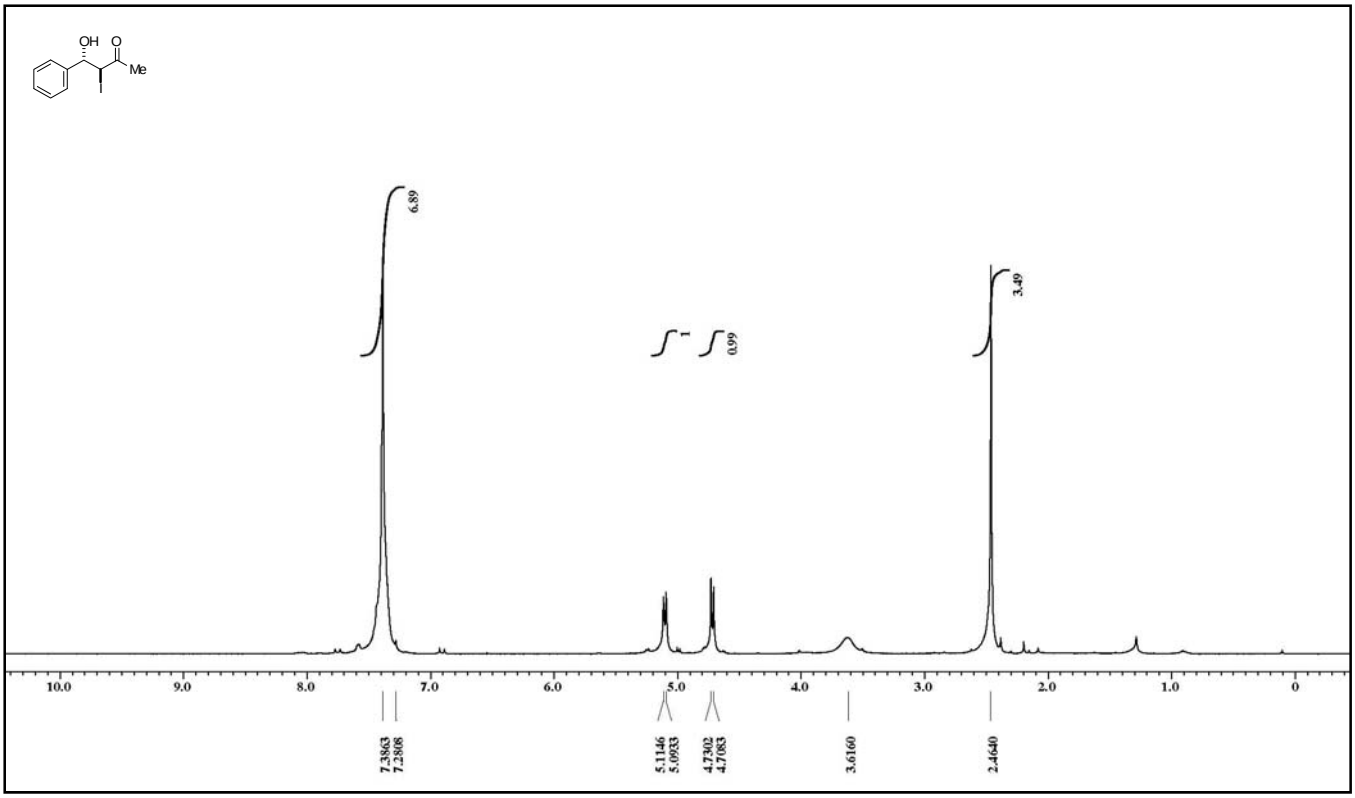


Figure S10. ^{1}H NMR spectrum of 4-hydroxy-3-iodo-4-phenylbutan-2-one.

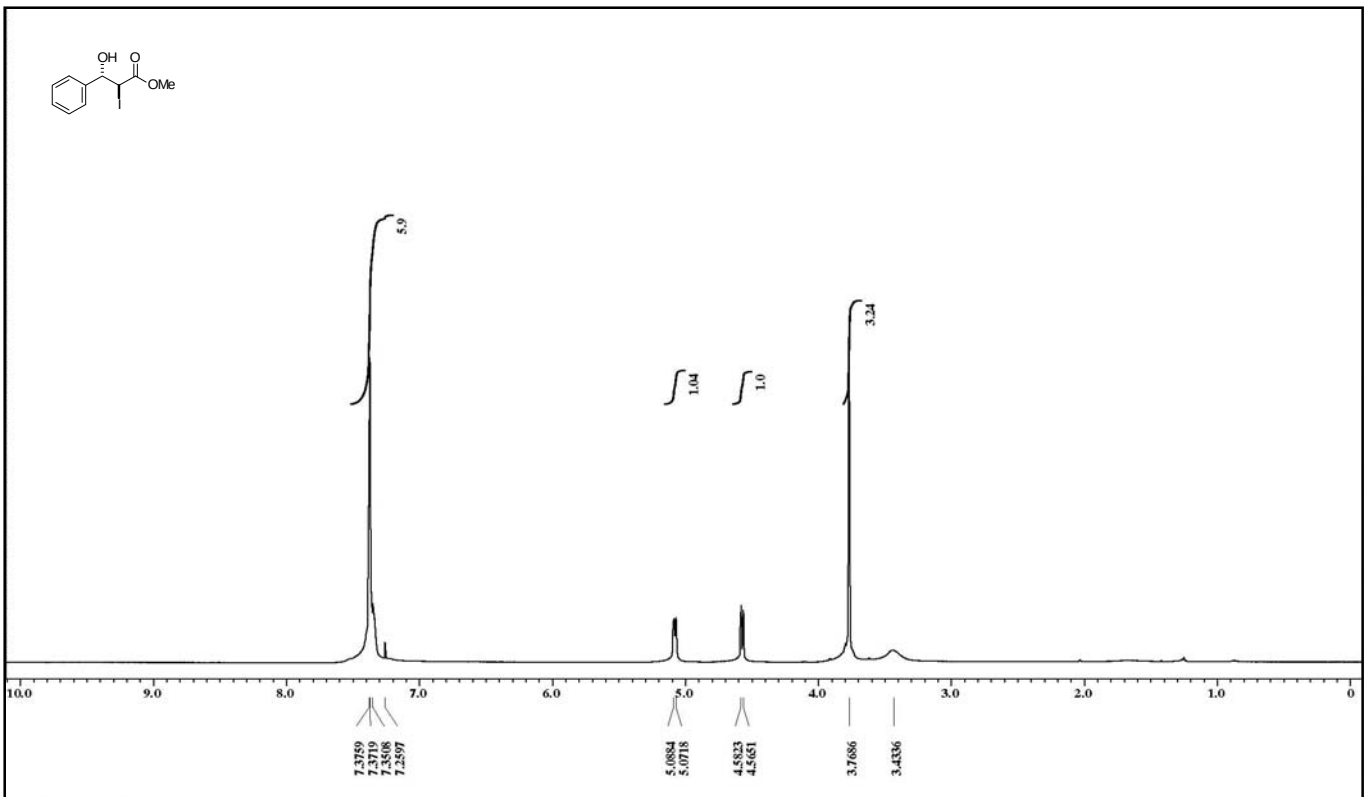


Figure S11. ^{1}H NMR spectrum of methyl 3-hydroxy-2-iodo-3-phenylpropanoate.

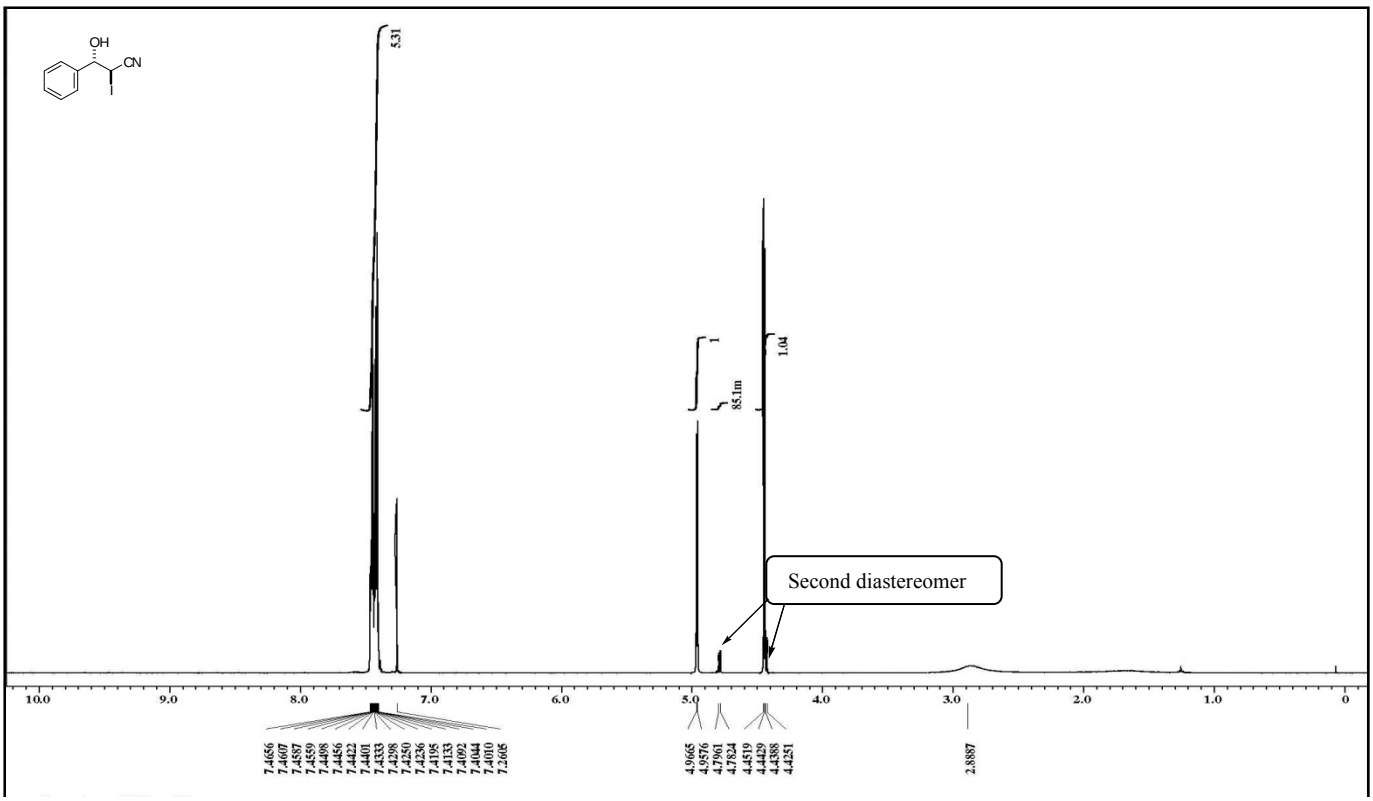
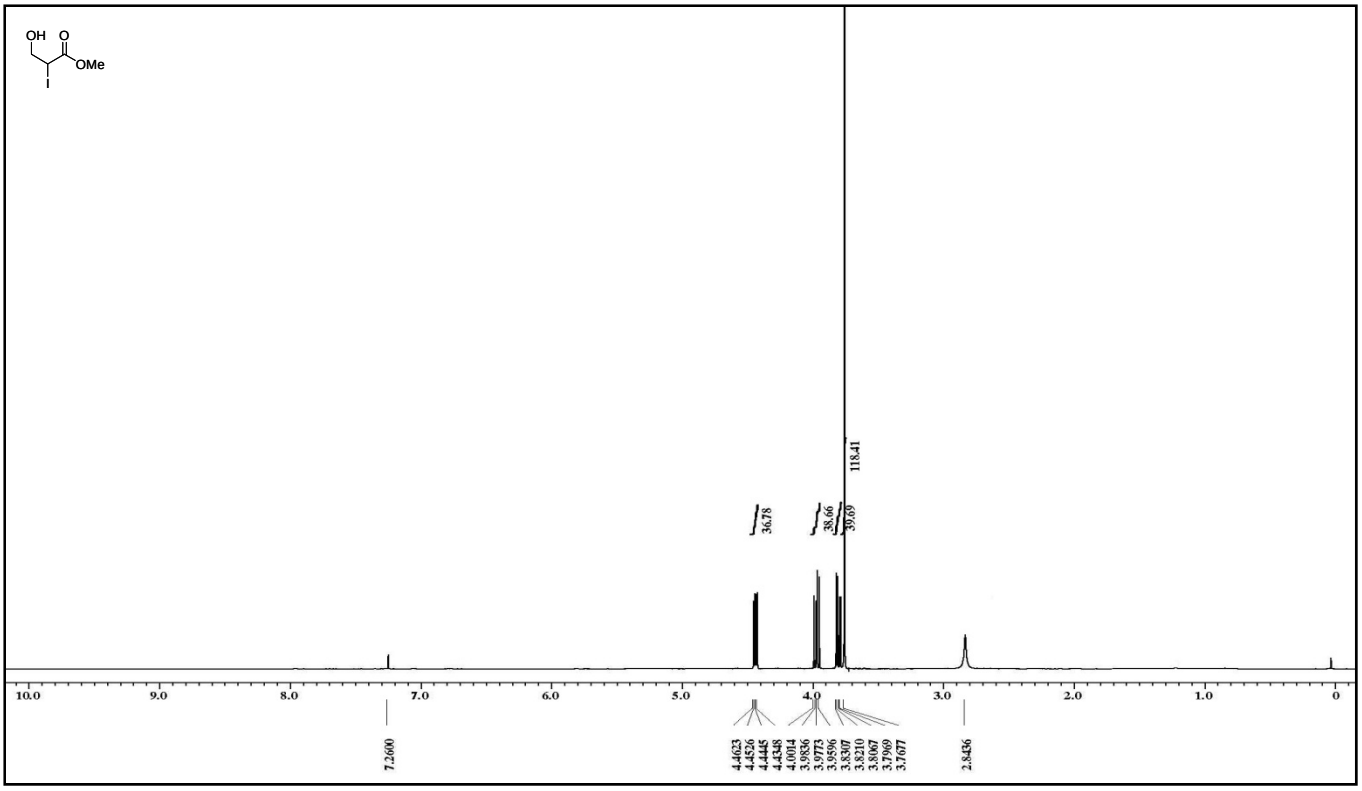


Figure S12. ^{1}H NMR spectrum of 3-hydroxy-2-iodo-3-phenylpropanenitrile.



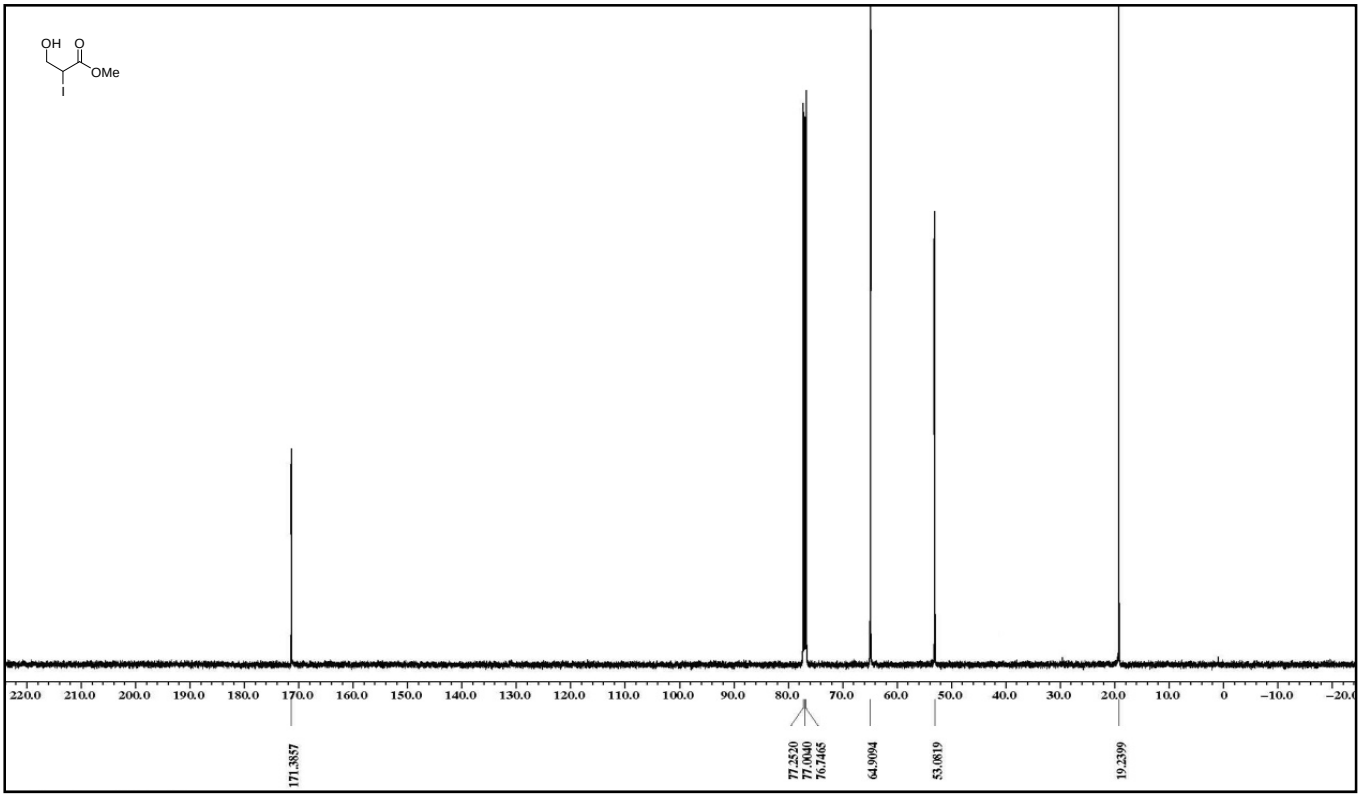
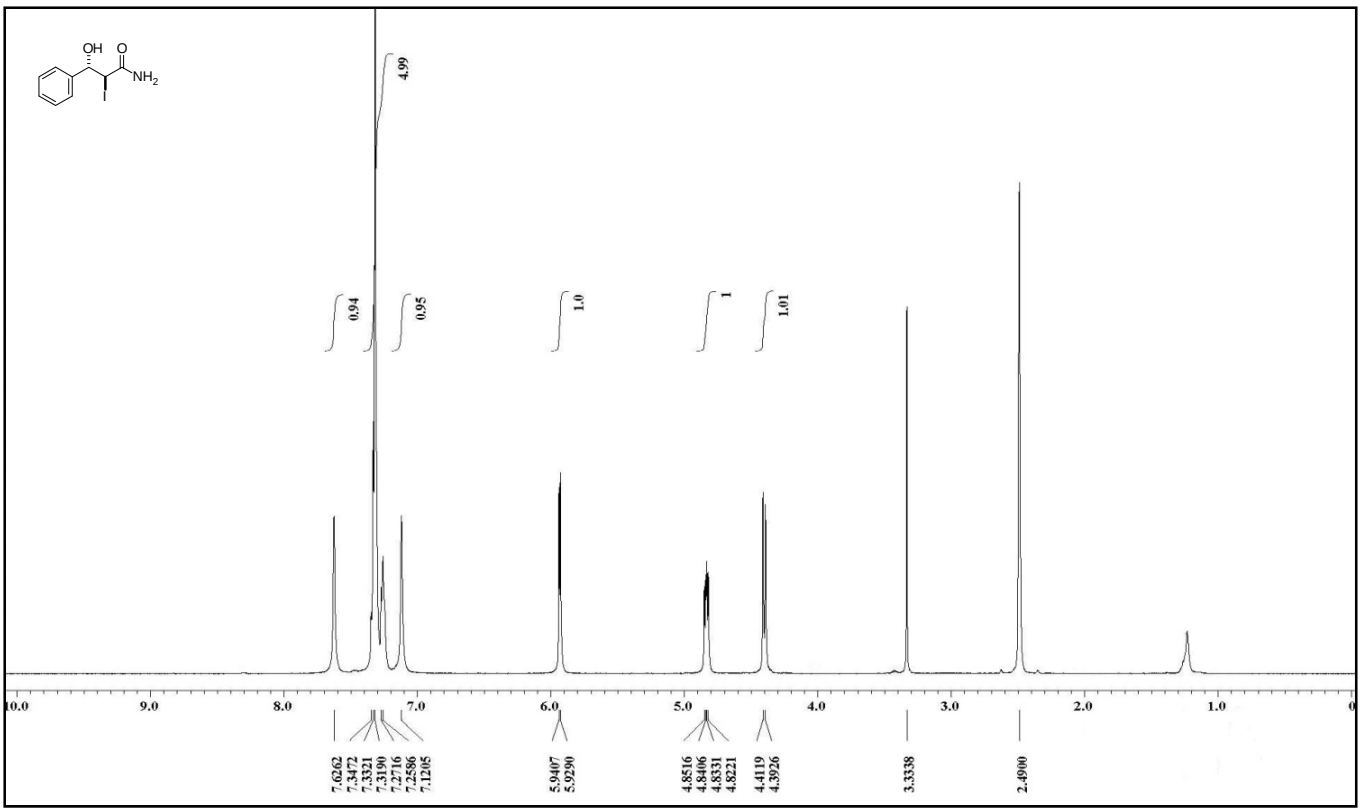


Figure S13. ^{1}H and ^{13}C NMR spectra of methyl 3-hydroxy-2-iodopropanoate.



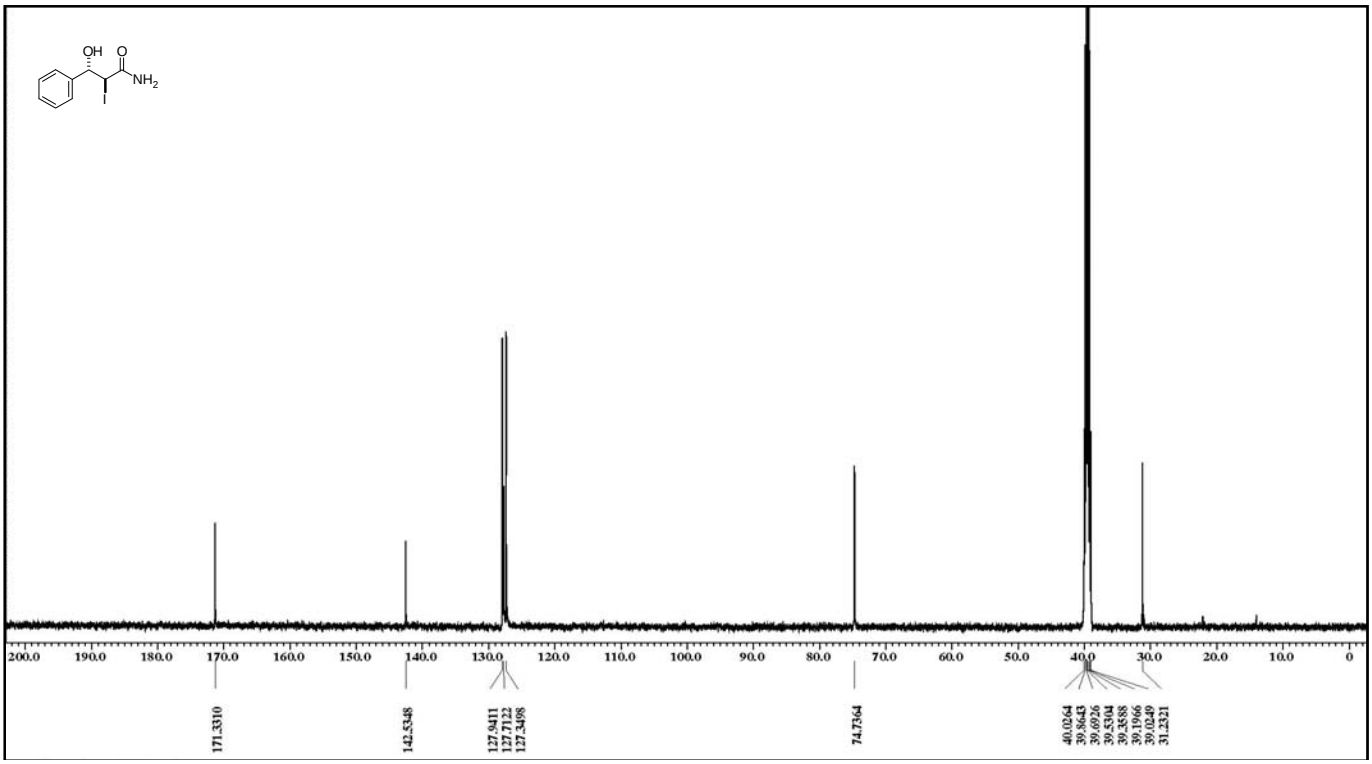


Figure S14. ^{1}H and ^{13}C NMR spectra of 3-hydroxy-2-iodo-3-phenylpropanamide.

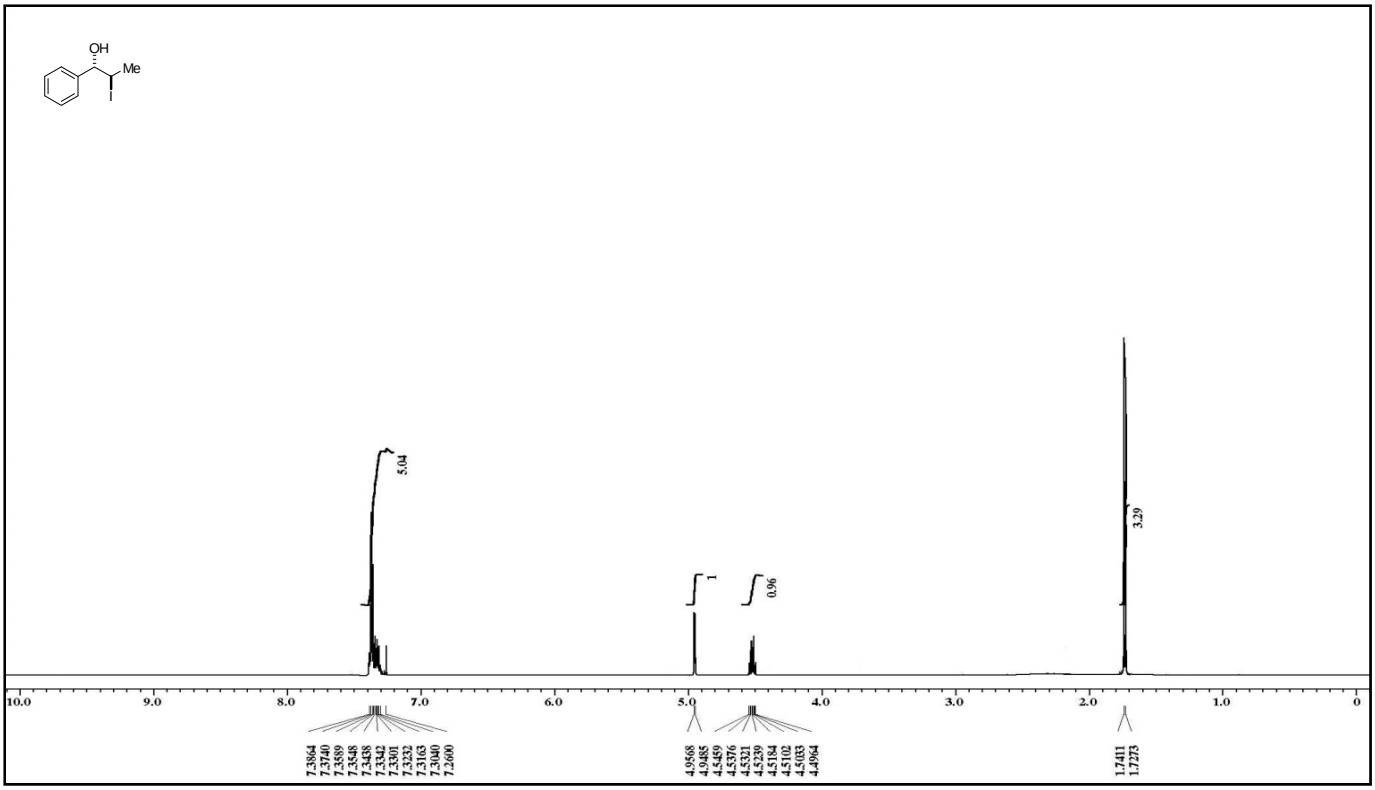


Figure S15. ^{1}H NMR spectrum of 2-iodo-1-phenylpropan-1-ol.

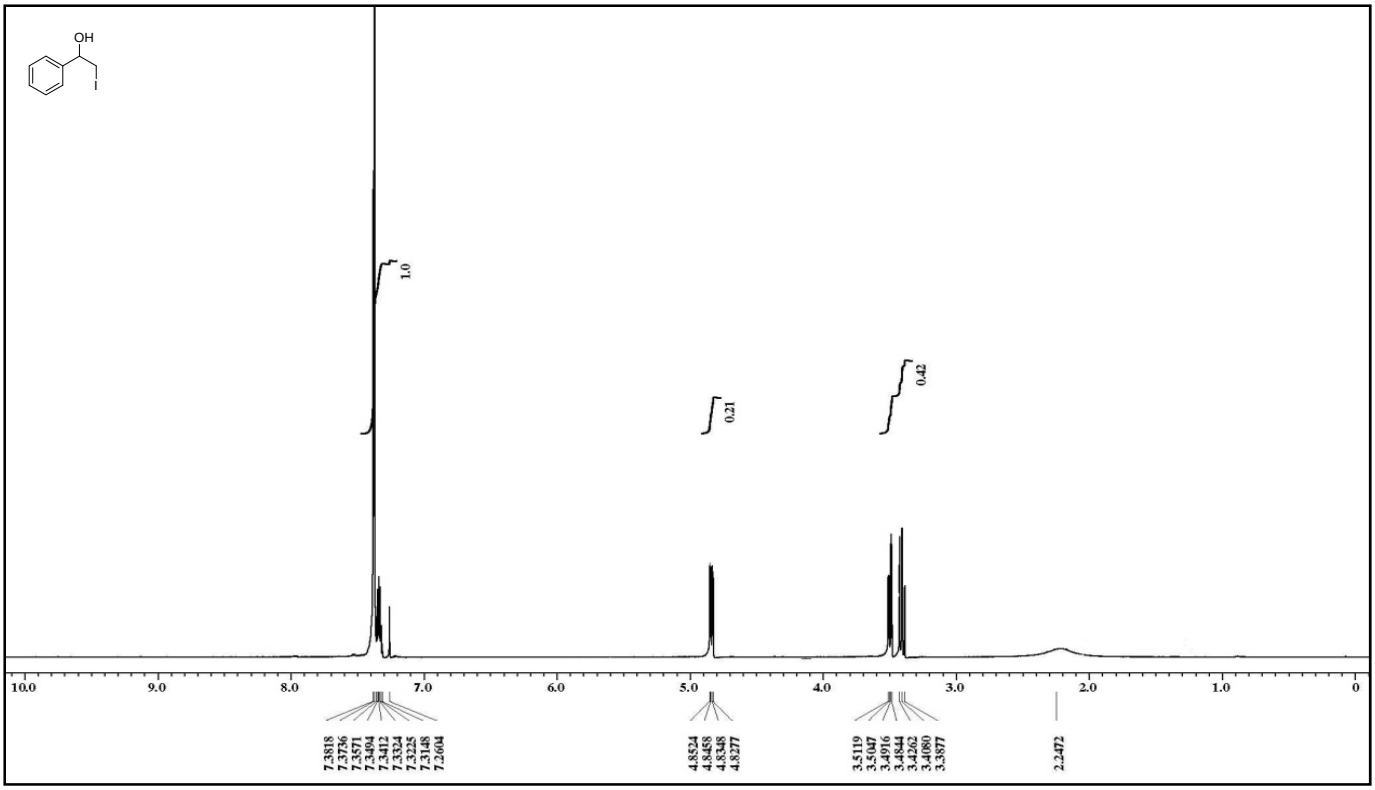


Figure S16. ^{1}H NMR spectrum of 2-iodo-1-phenylethanol.

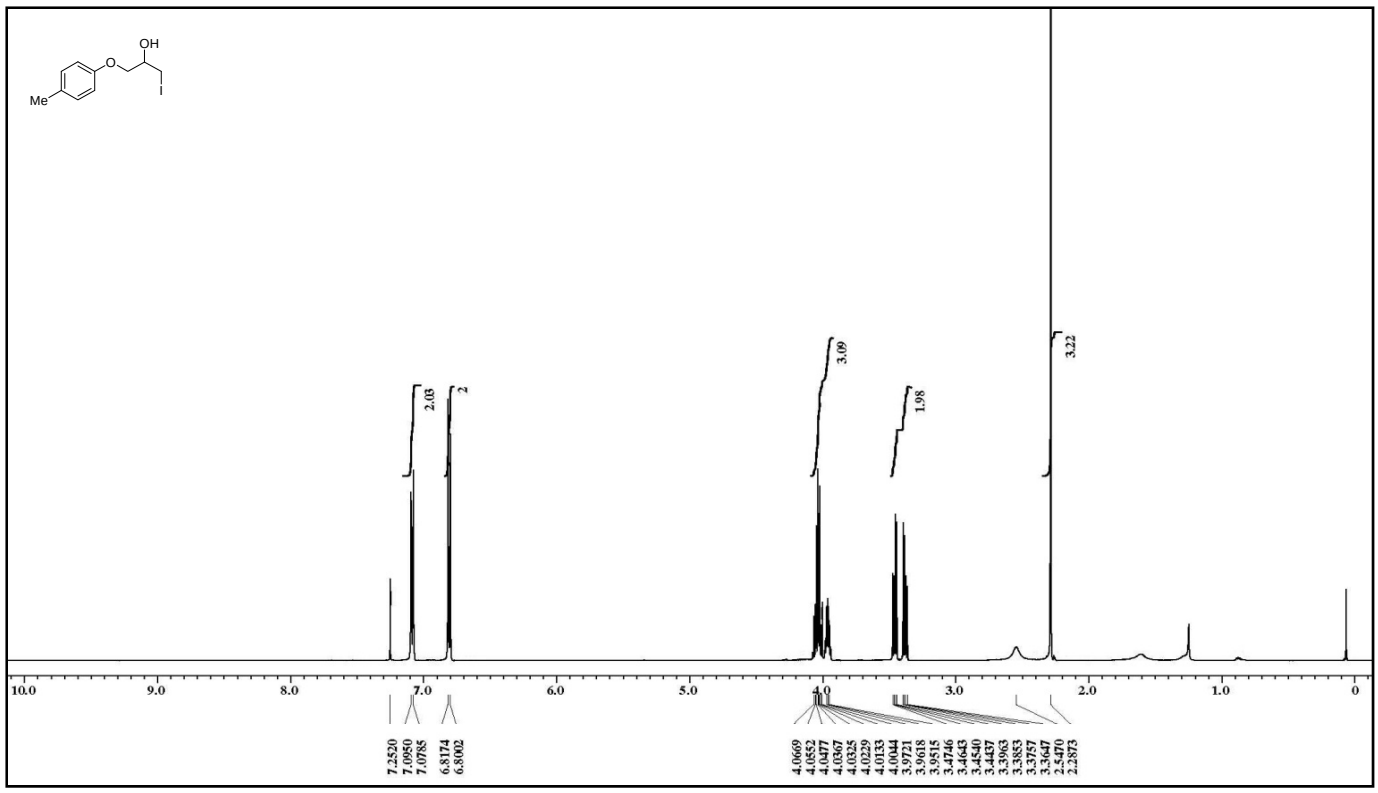


Figure S17. ^{1}H NMR spectrum of 1-iodo-3-(*p*-tolyloxy)propan-2-ol.

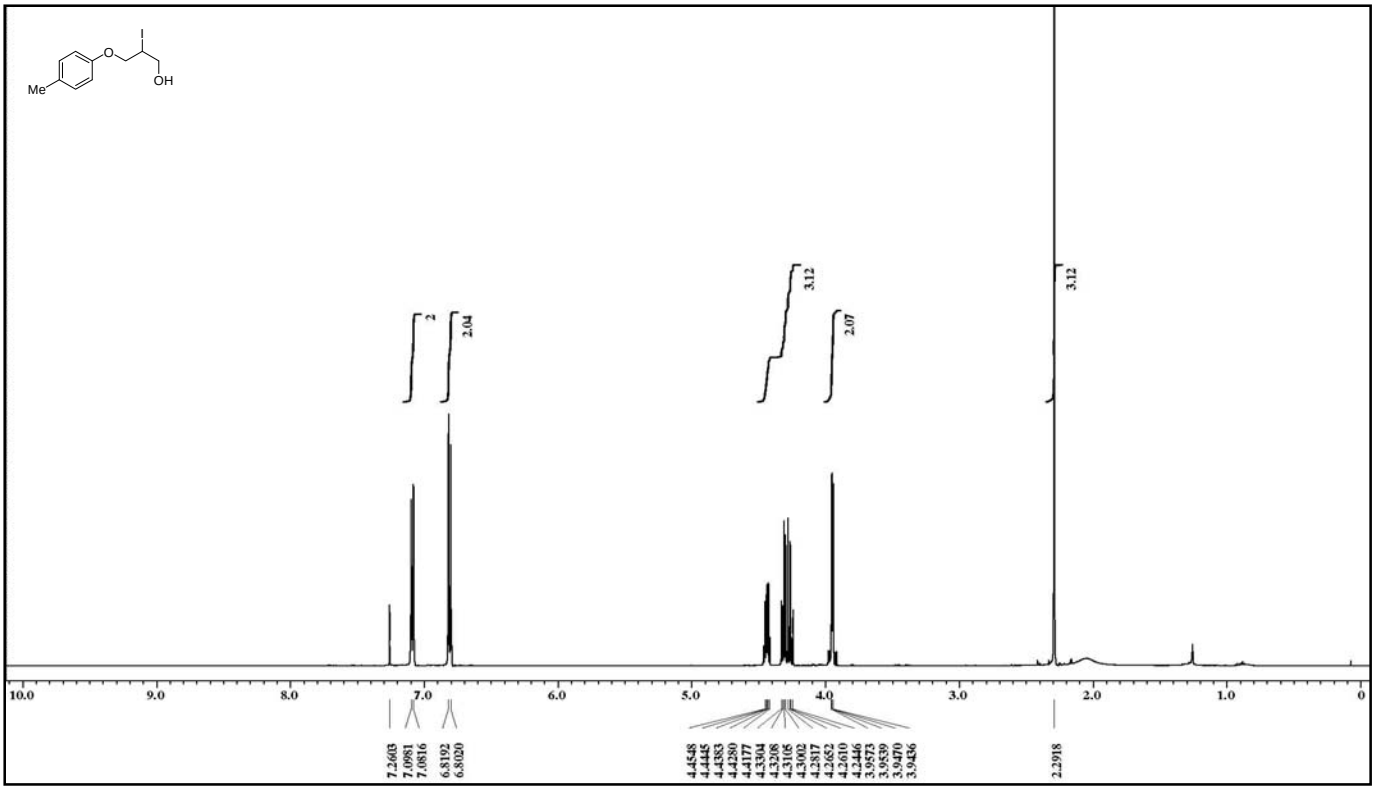


Figure S18. ^{1}H NMR spectrum of 2-iodo-3-(*p*-tolyloxy)propan-1-ol.

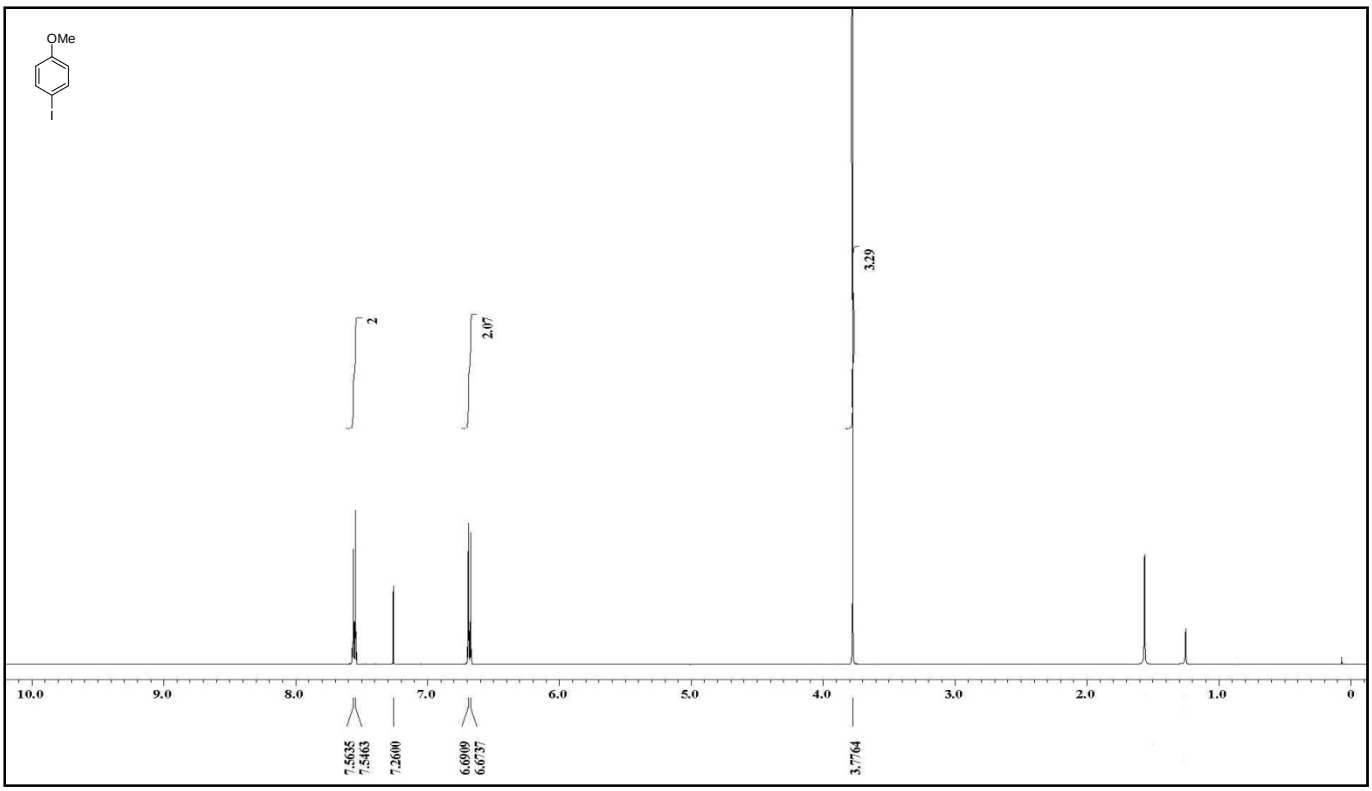


Figure S19. ^{1}H NMR spectrum of 4-iodoanisole.

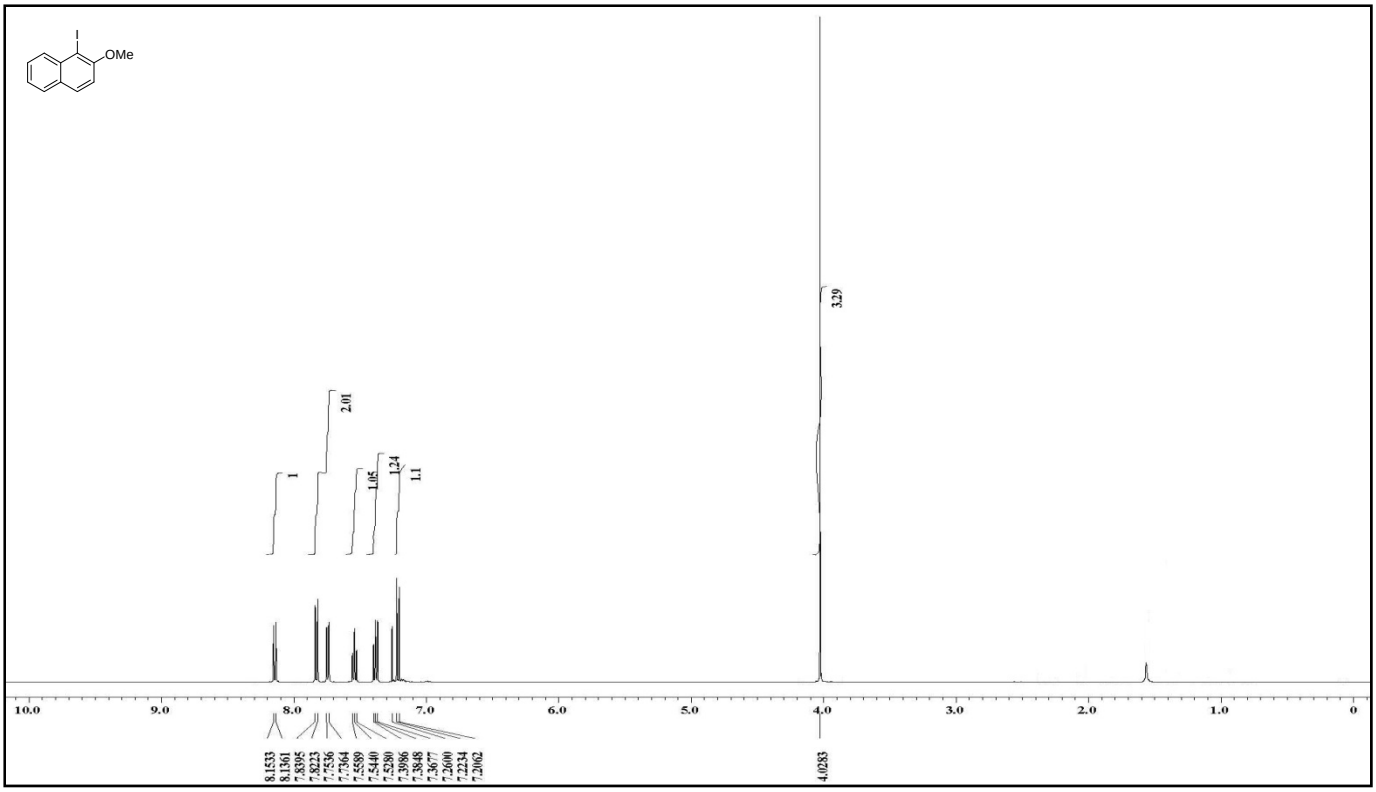


Figure S20. ^{1}H NMR spectrum of 1-iodo-2-methoxynaphthalene.

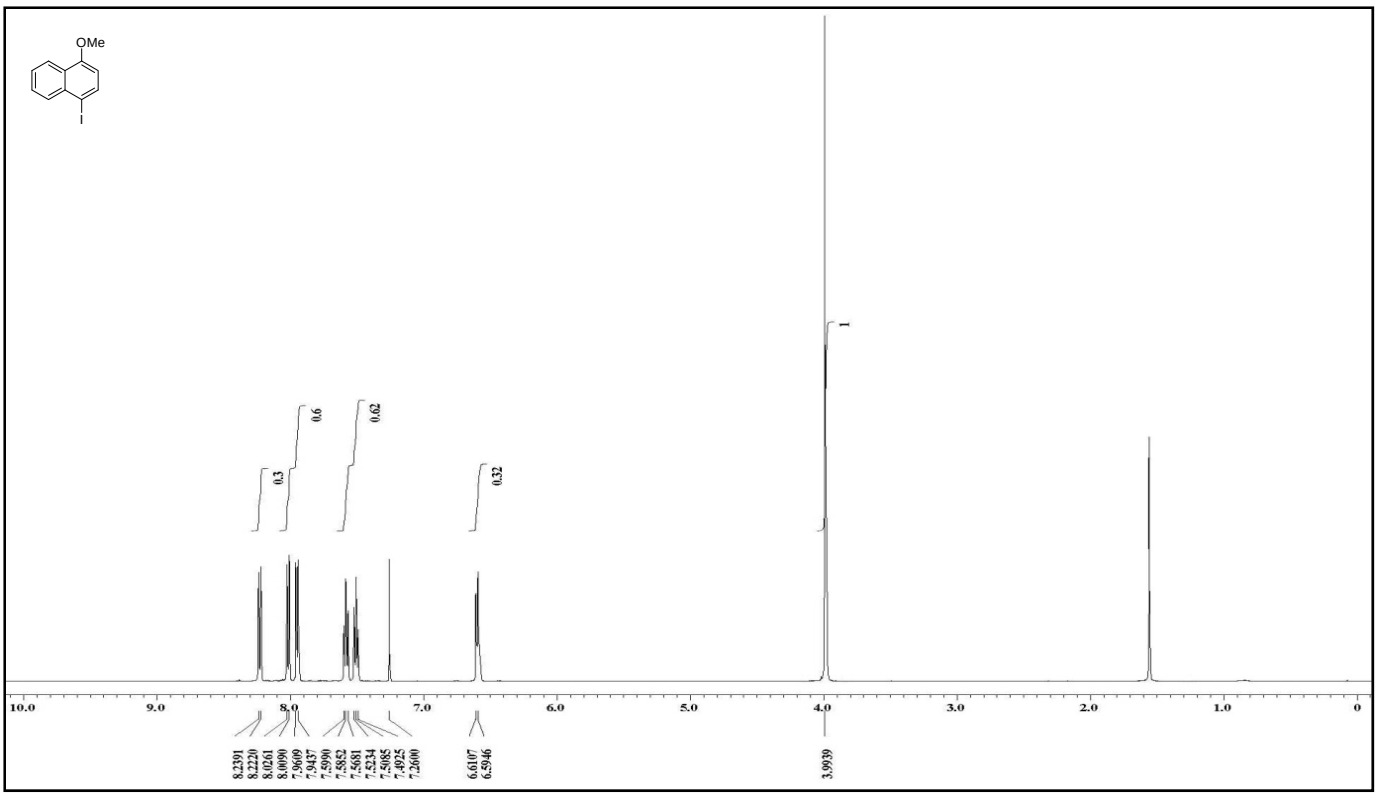


Figure S21. ^{1}H NMR spectrum of 2-iodo-1-methoxynaphthalene.

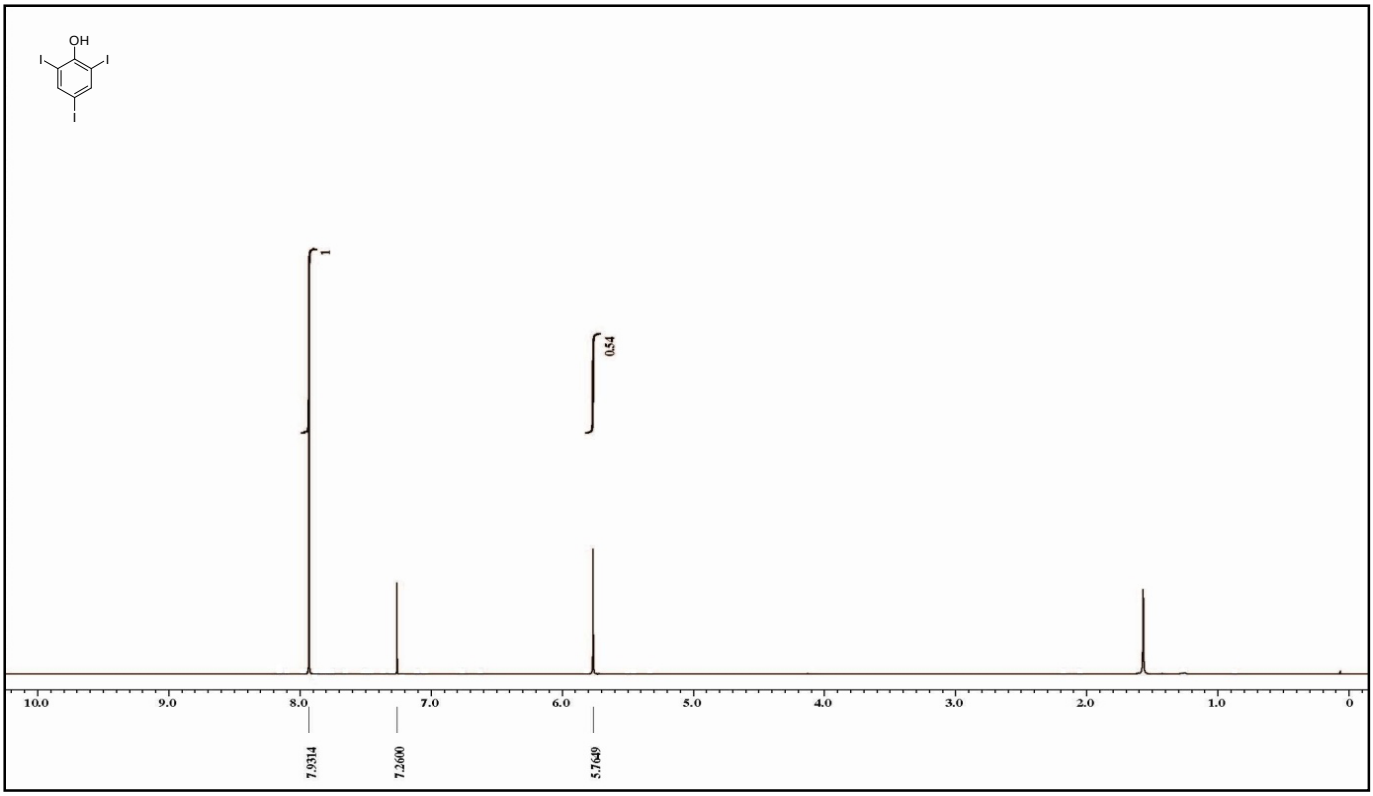


Figure S22. ^{1}H NMR spectrum of 2,4,6-triiodophenol.

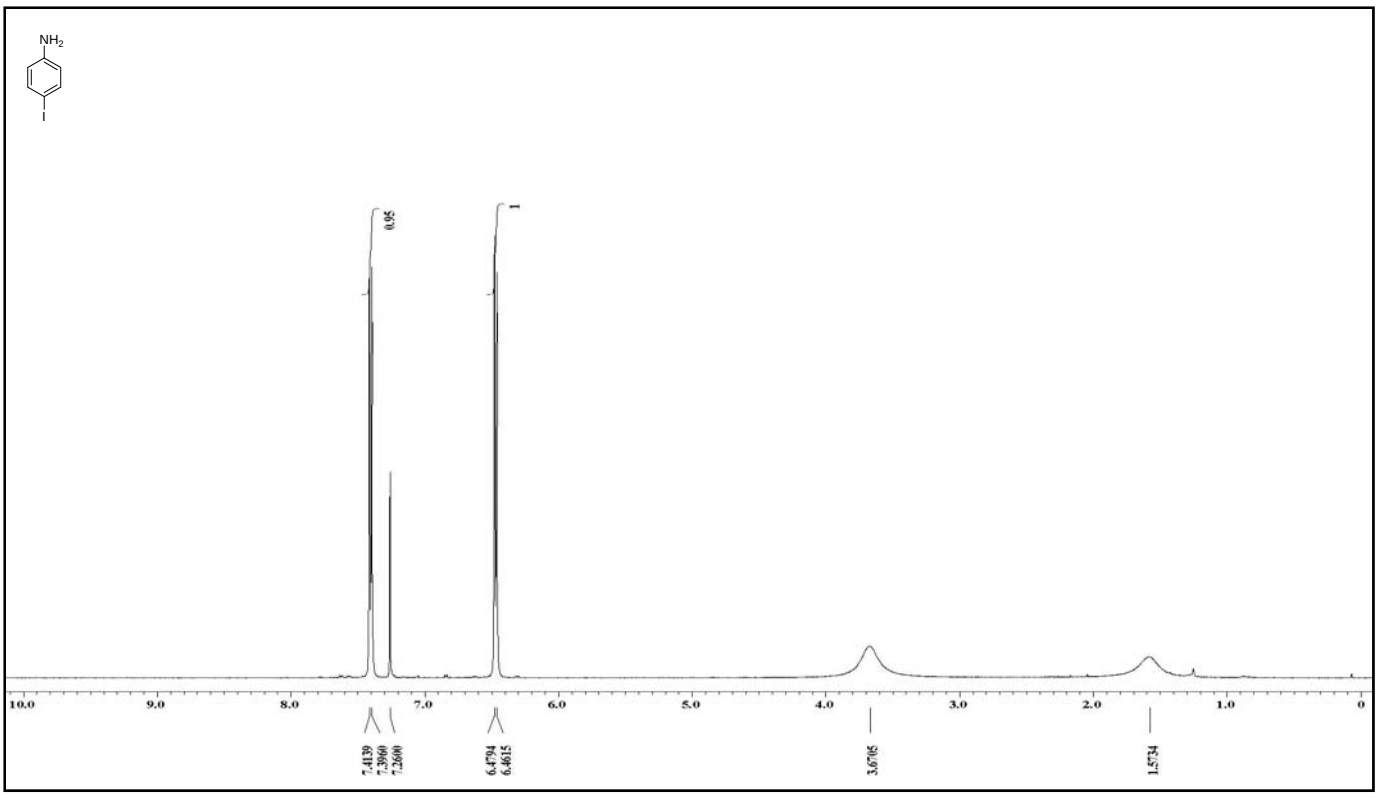


Figure S23. ^{1}H NMR spectrum of *p*-iodoaniline.

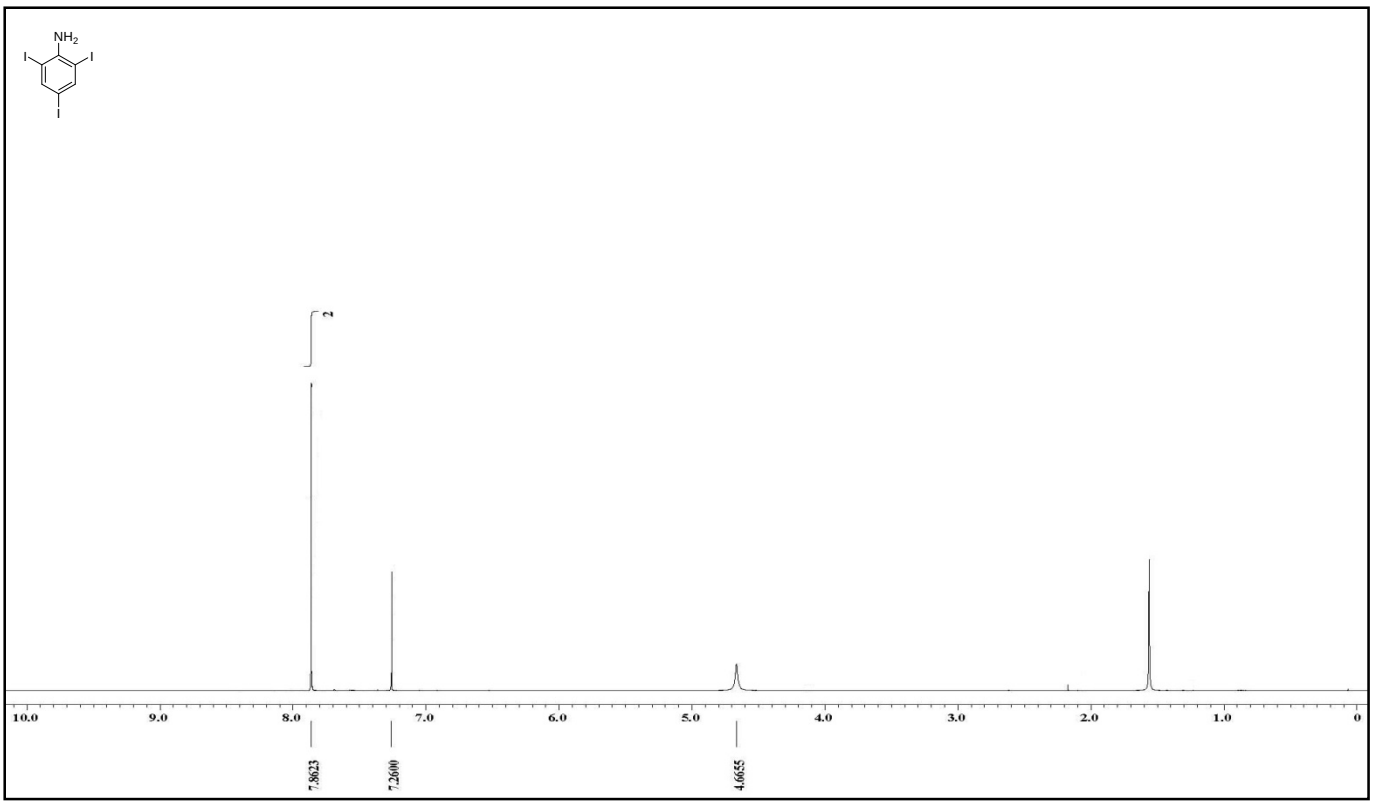


Figure S24. ^{1}H NMR spectrum of 2,4,6-triiodoaniline.

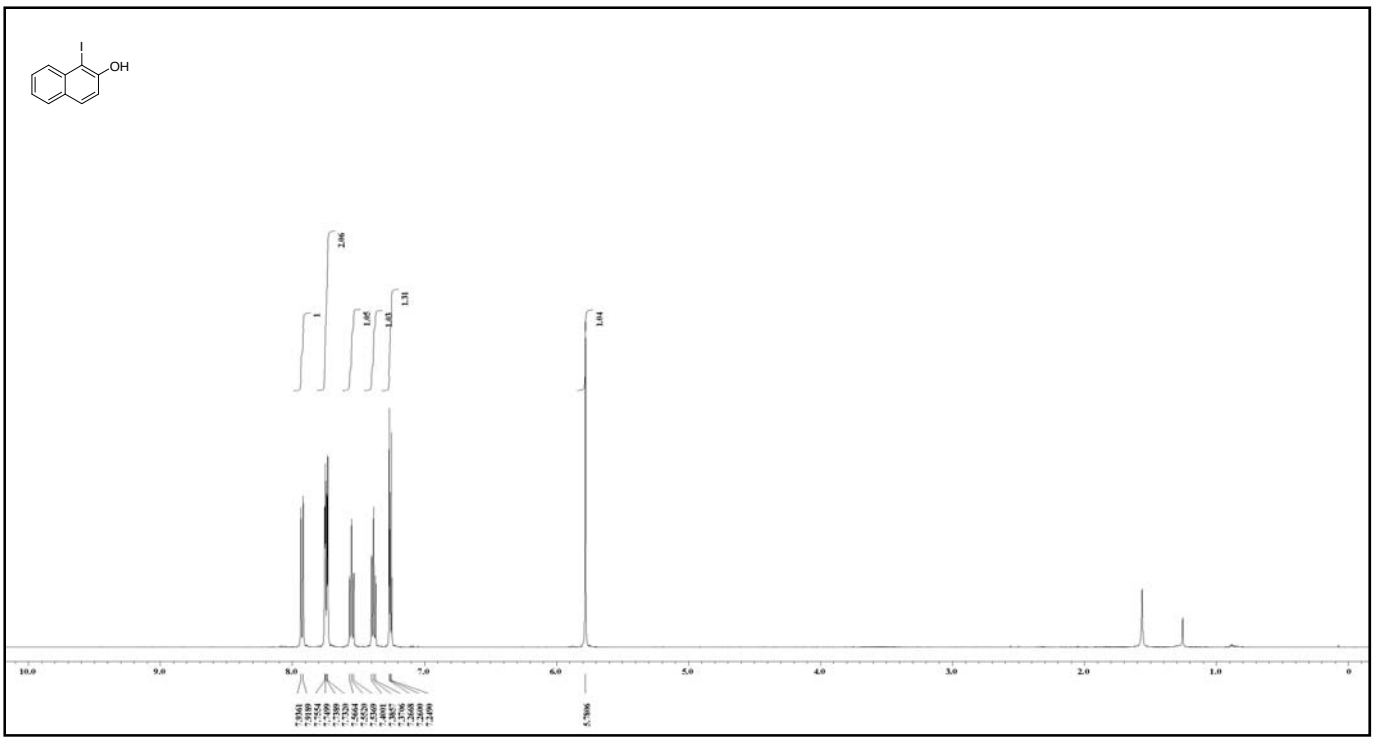


Figure S25. ^{1}H NMR spectrum of 1-iodonaphthalen-2-ol.

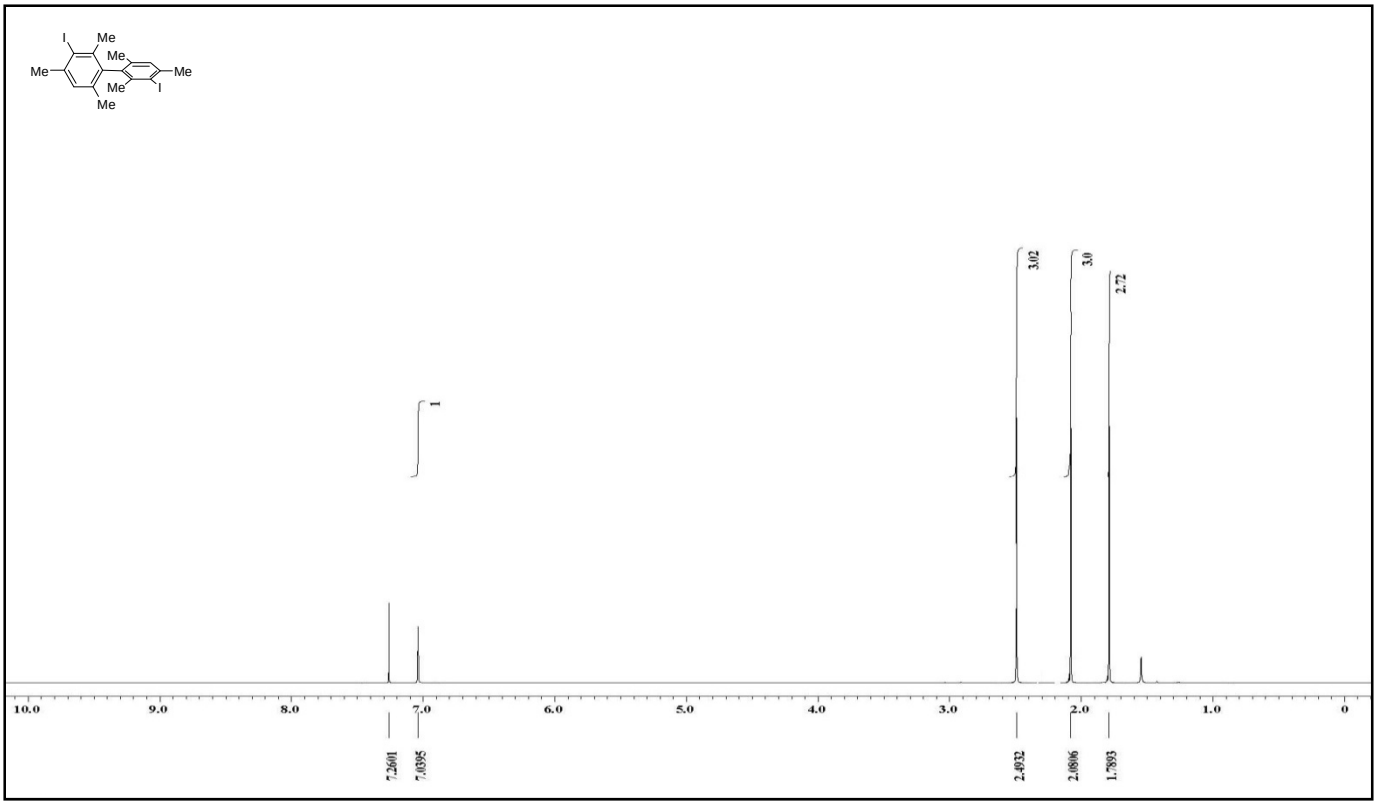


Figure S26. ^{1}H NMR spectrum of 3,3'-diiodobimesityl.

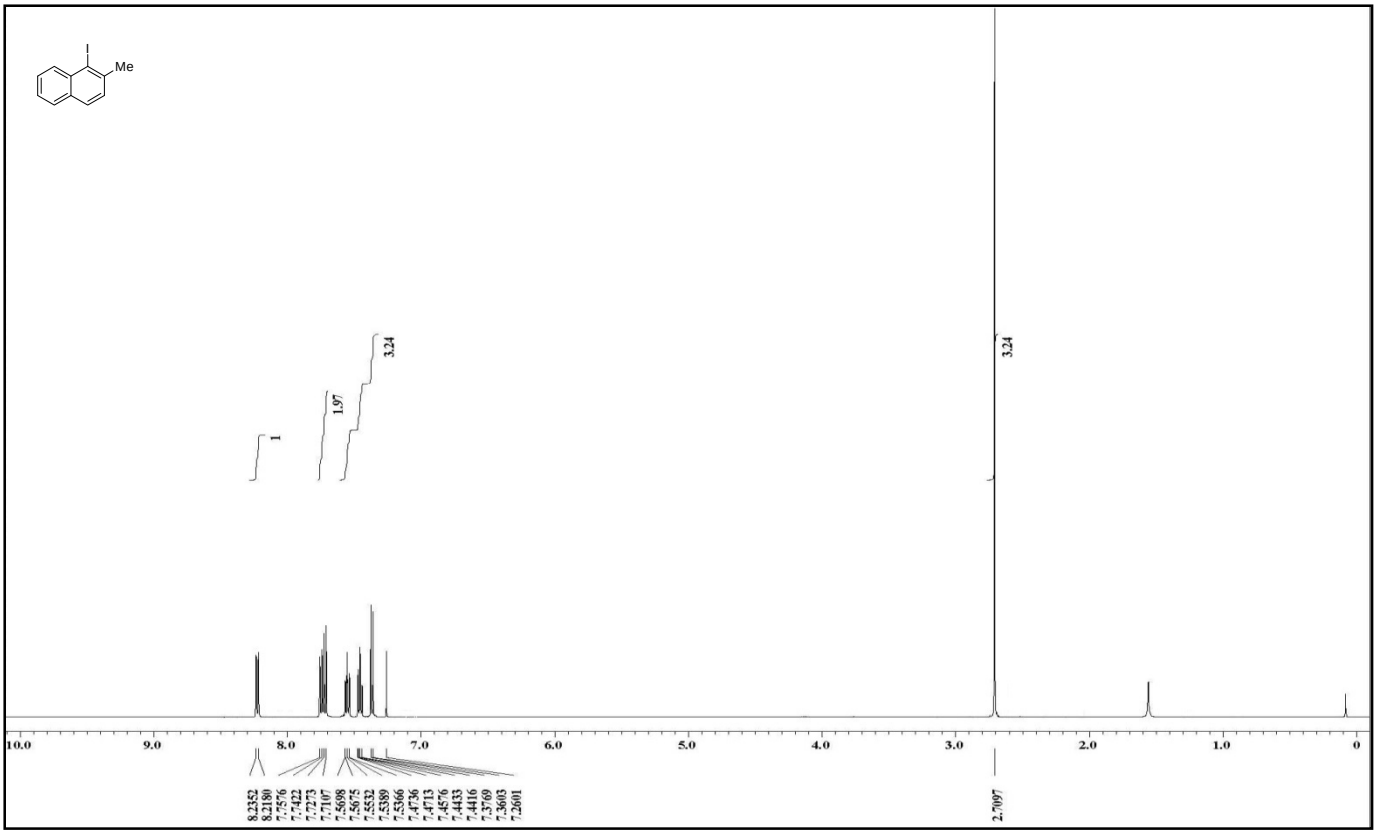


Figure S27. ^{1}H NMR spectrum of 1-iodo-2-methylnaphthalene.

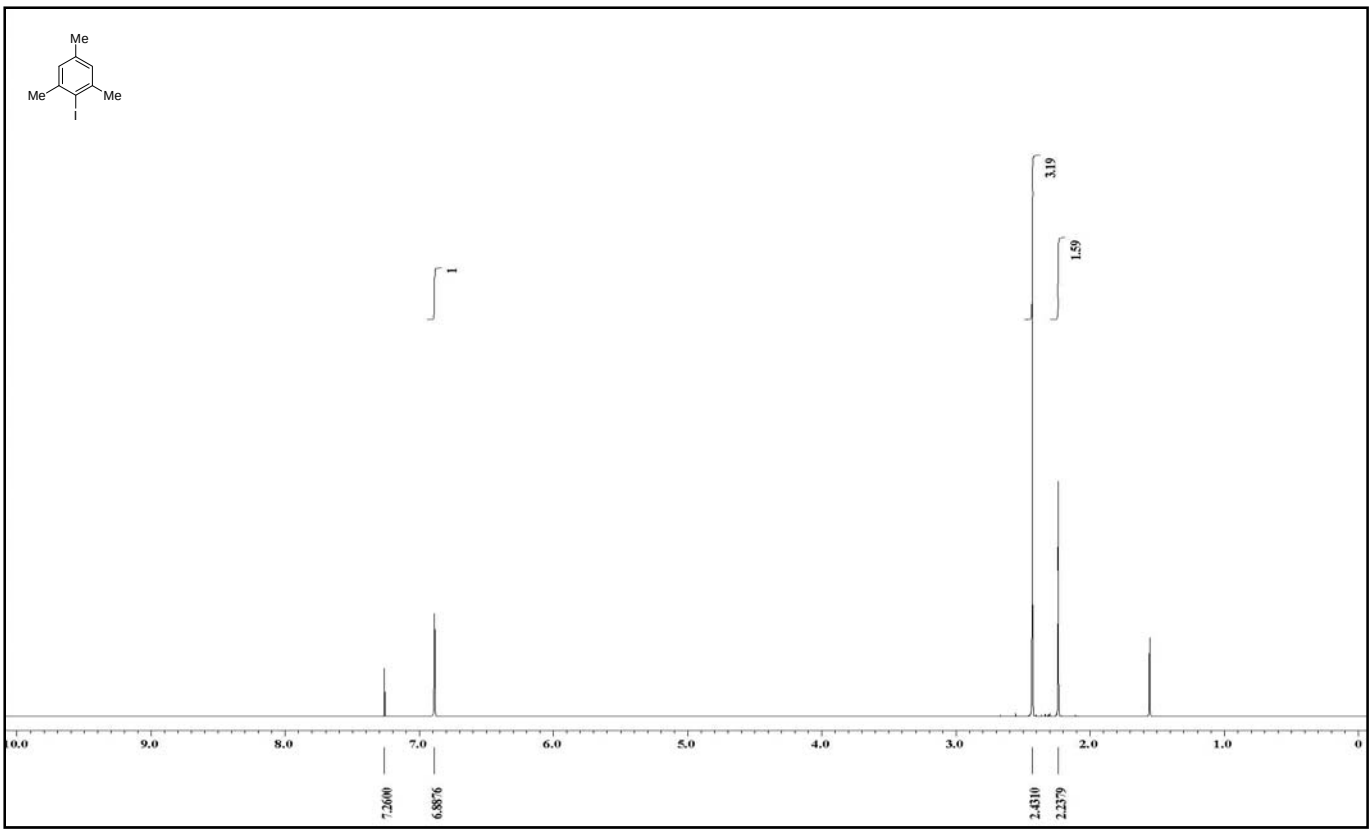


Figure S28. ^{1}H NMR spectrum of 2-iodo-1,3,5-trimethylbenzene.

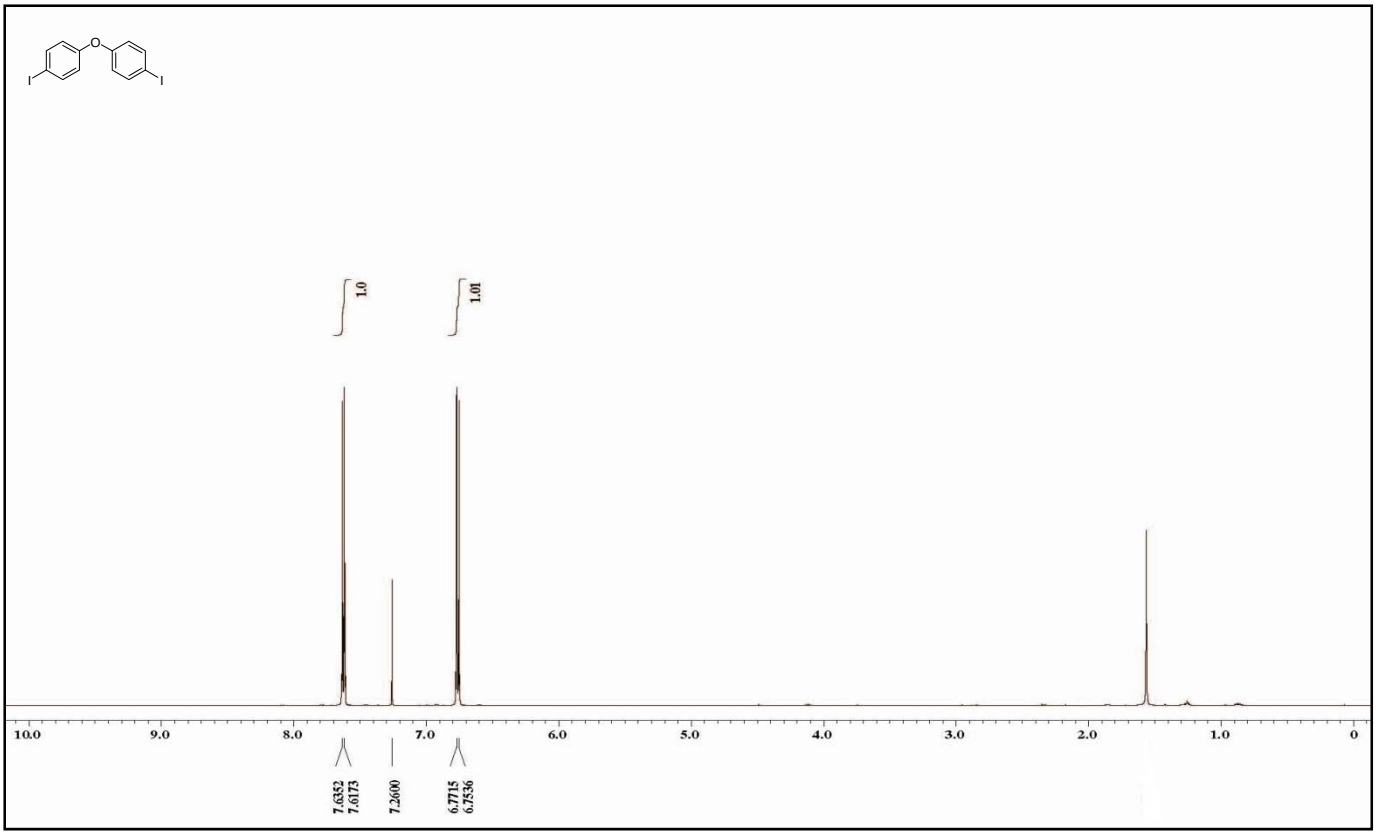


Figure S29. ^{1}H NMR spectrum of 4,4'-diiododiphenyl ether.

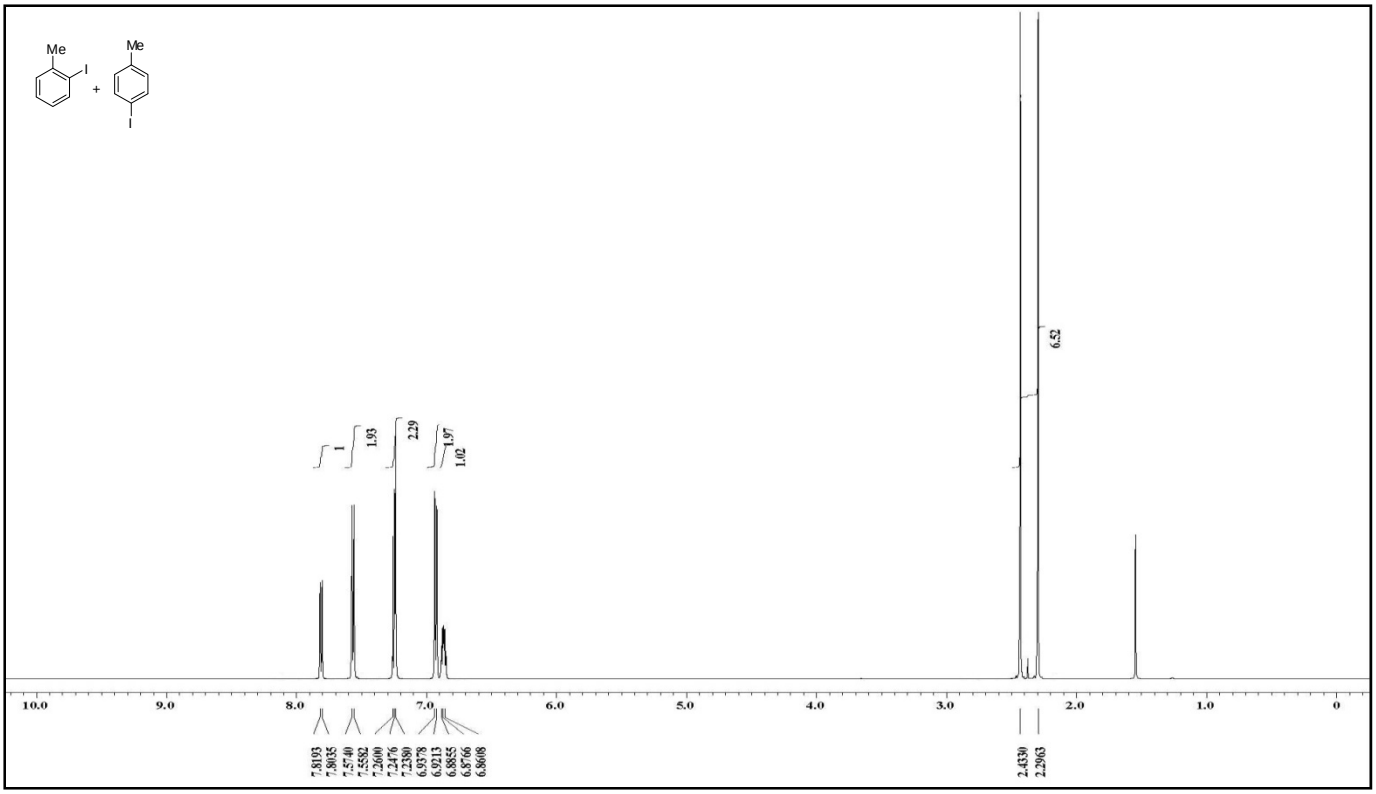


Figure S30. ^{1}H NMR spectrum of *o*- and *p*-iodotoluene (inseperable mixture).

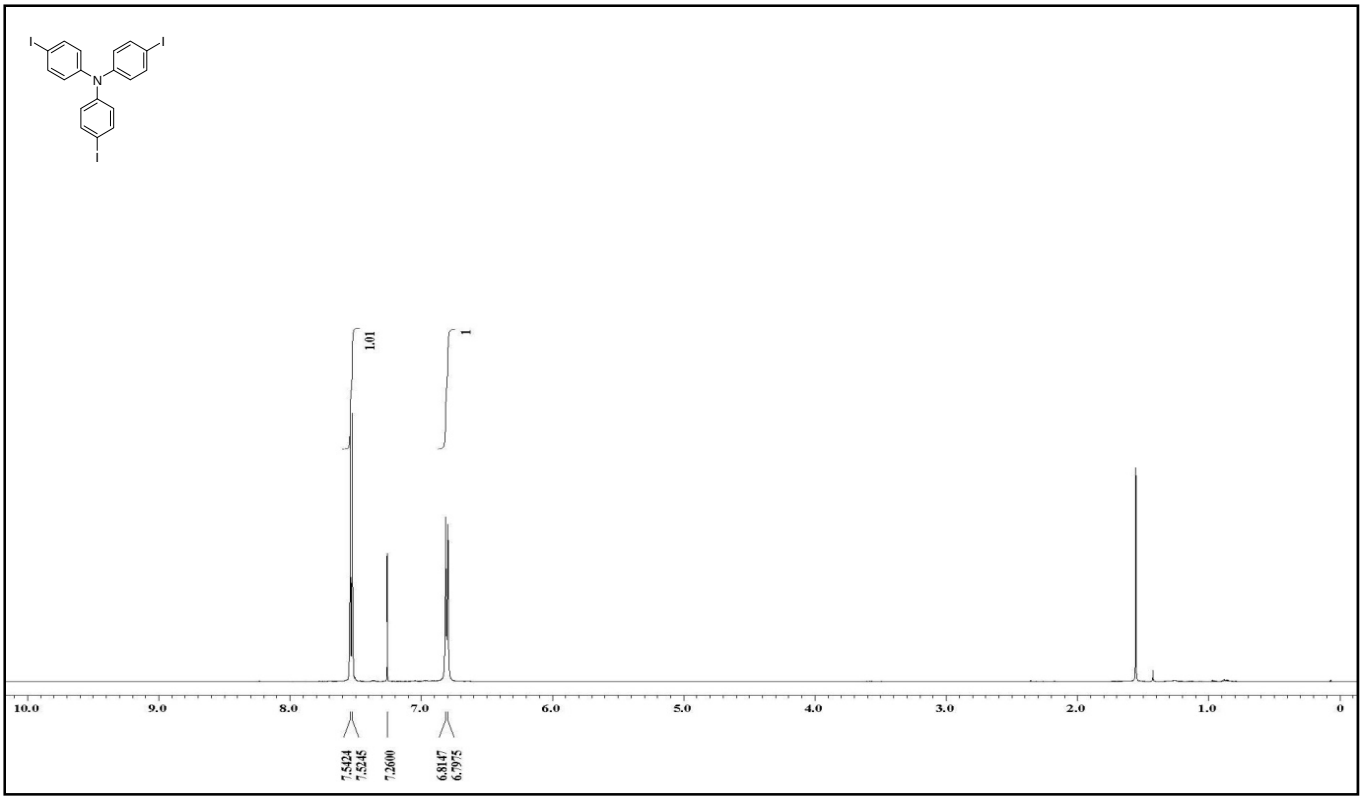


Figure S31. ^{1}H NMR spectrum of tris(4-iodophenyl)amine.

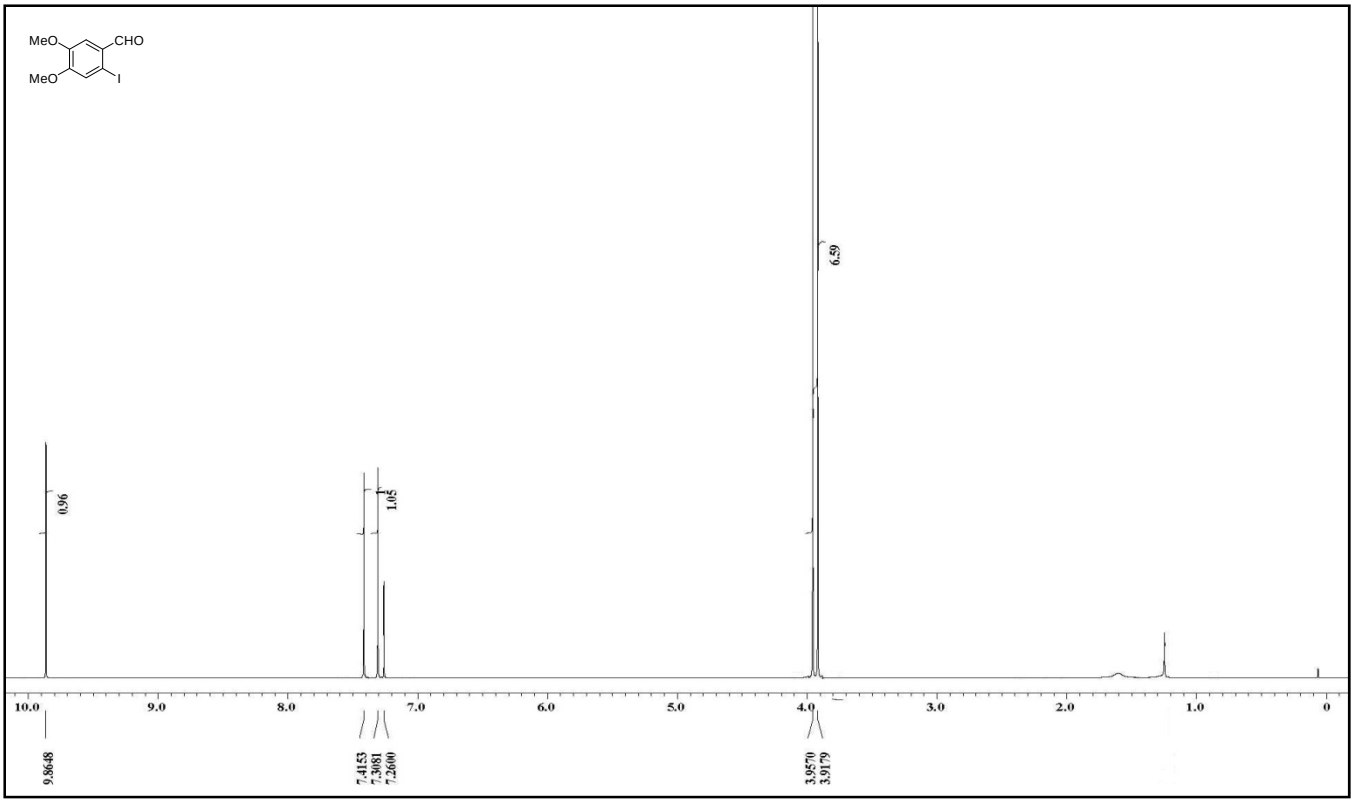


Figure S32. ^{1}H NMR spectrum of 2-iodo-4,5-dimethoxybenzaldehyde.

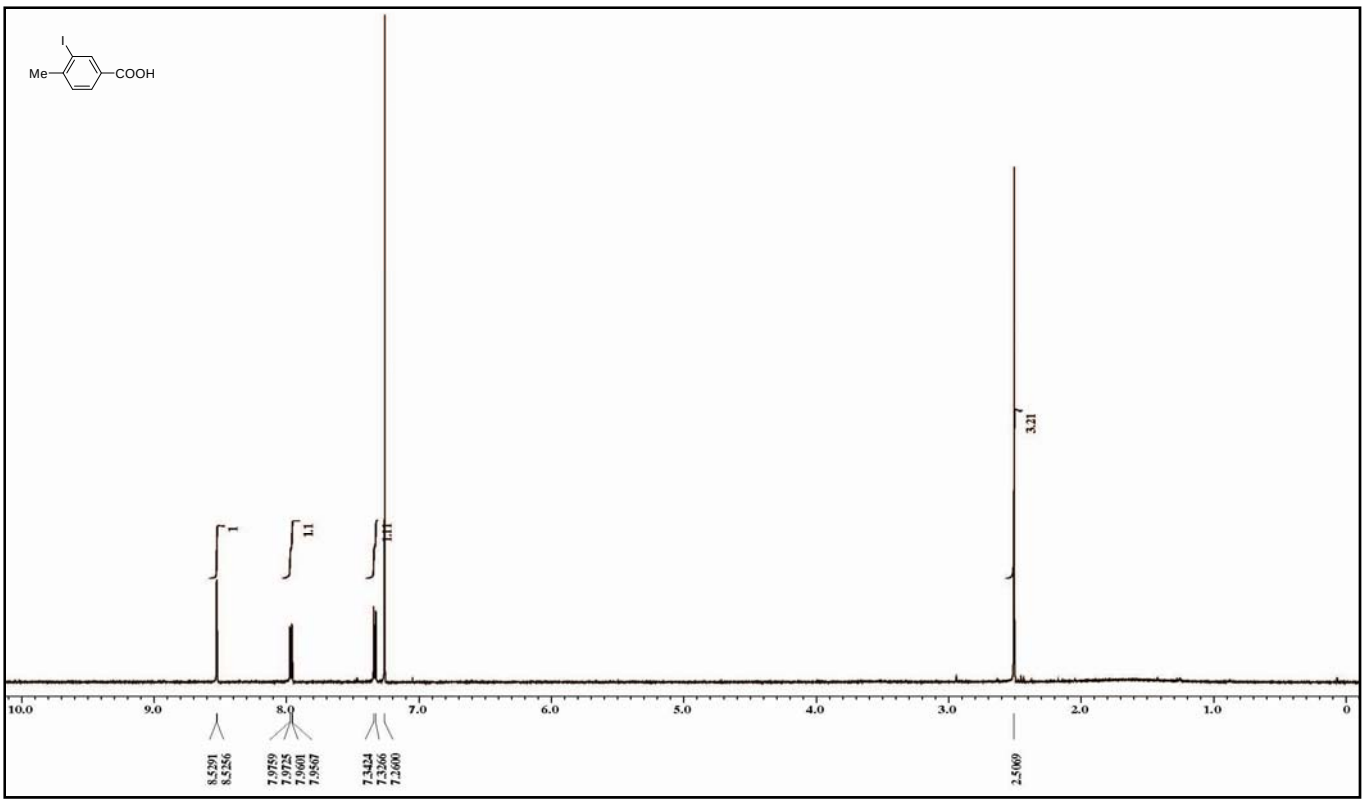


Figure S33. ^{1}H NMR spectrum of 3-iodo-4-methylbenzoic acid.

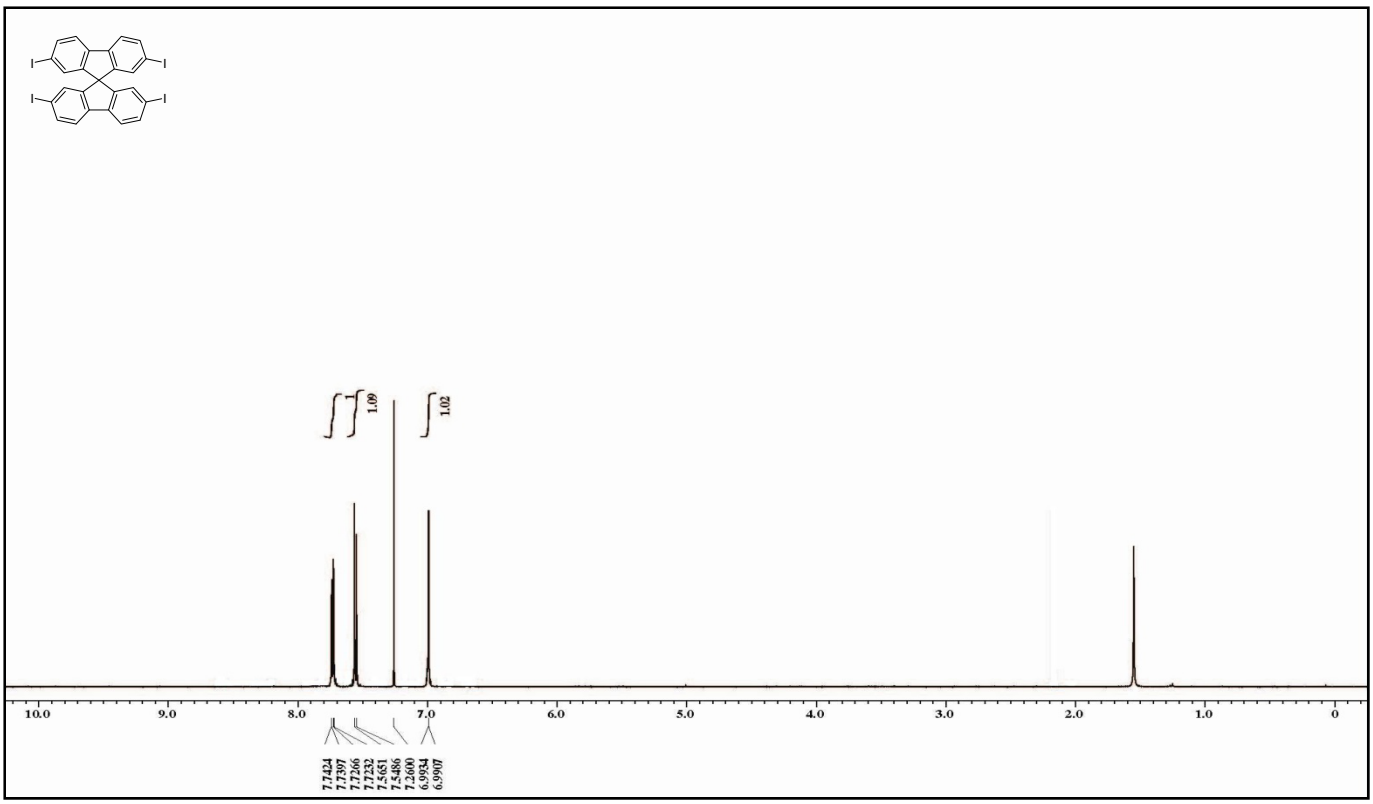


Figure S34. ^{1}H NMR spectrum of 2,2',7,7'-tetraiodo-9,9'-spirobifluorine.

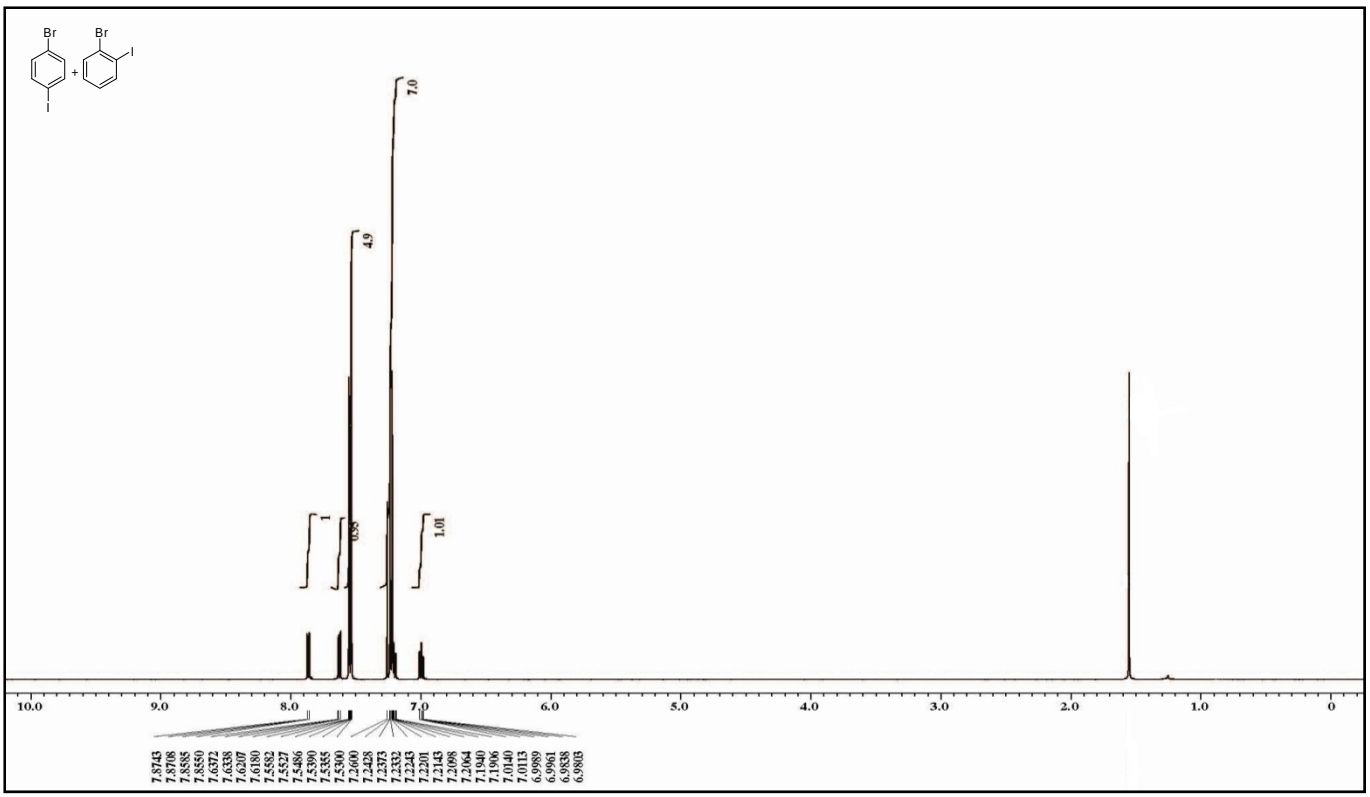


Figure S35. ^{1}H NMR spectrum of 2-iodobromobenzene and 4-iodobromobenzene (inseparable mixture).

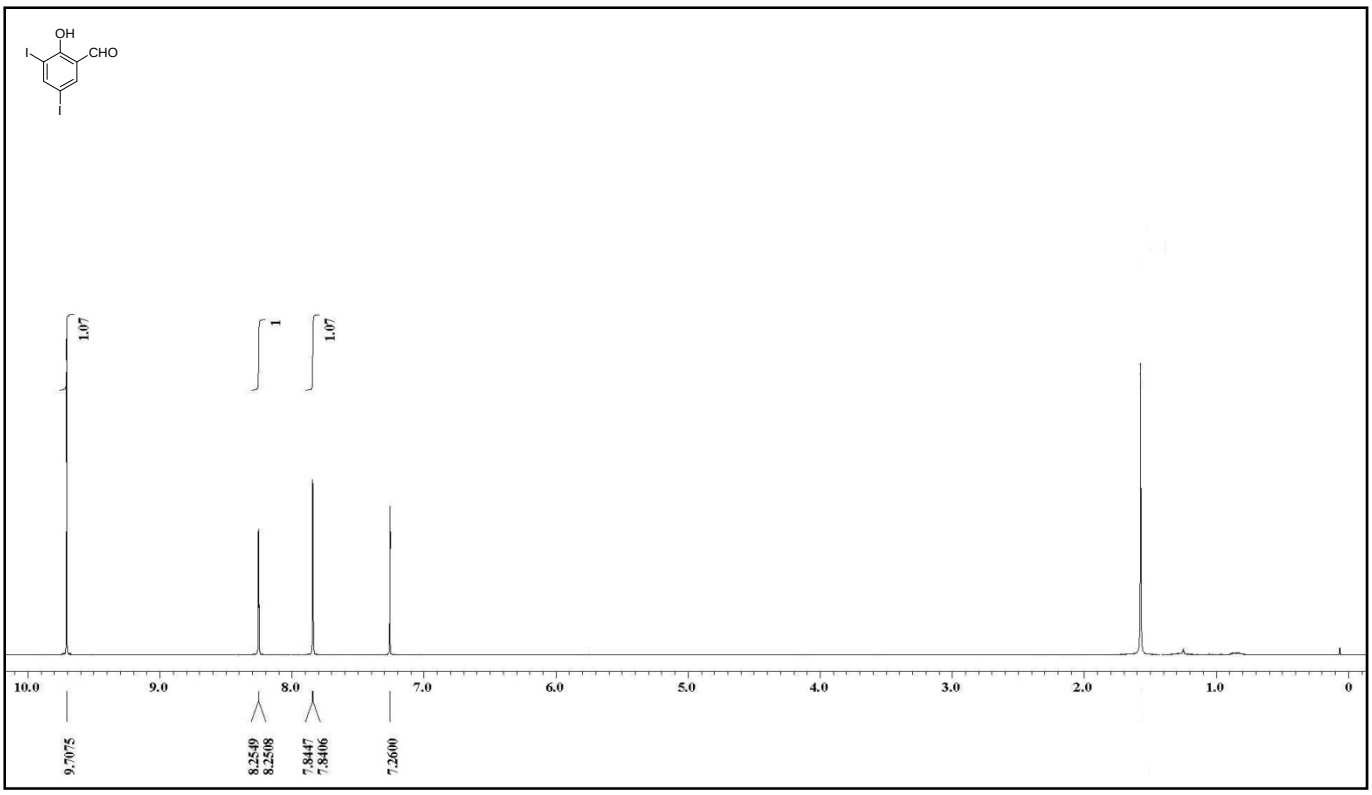


Figure S36. ^{1}H NMR spectrum of 2-hydroxy-3,5-diiodobenzaldehyde.

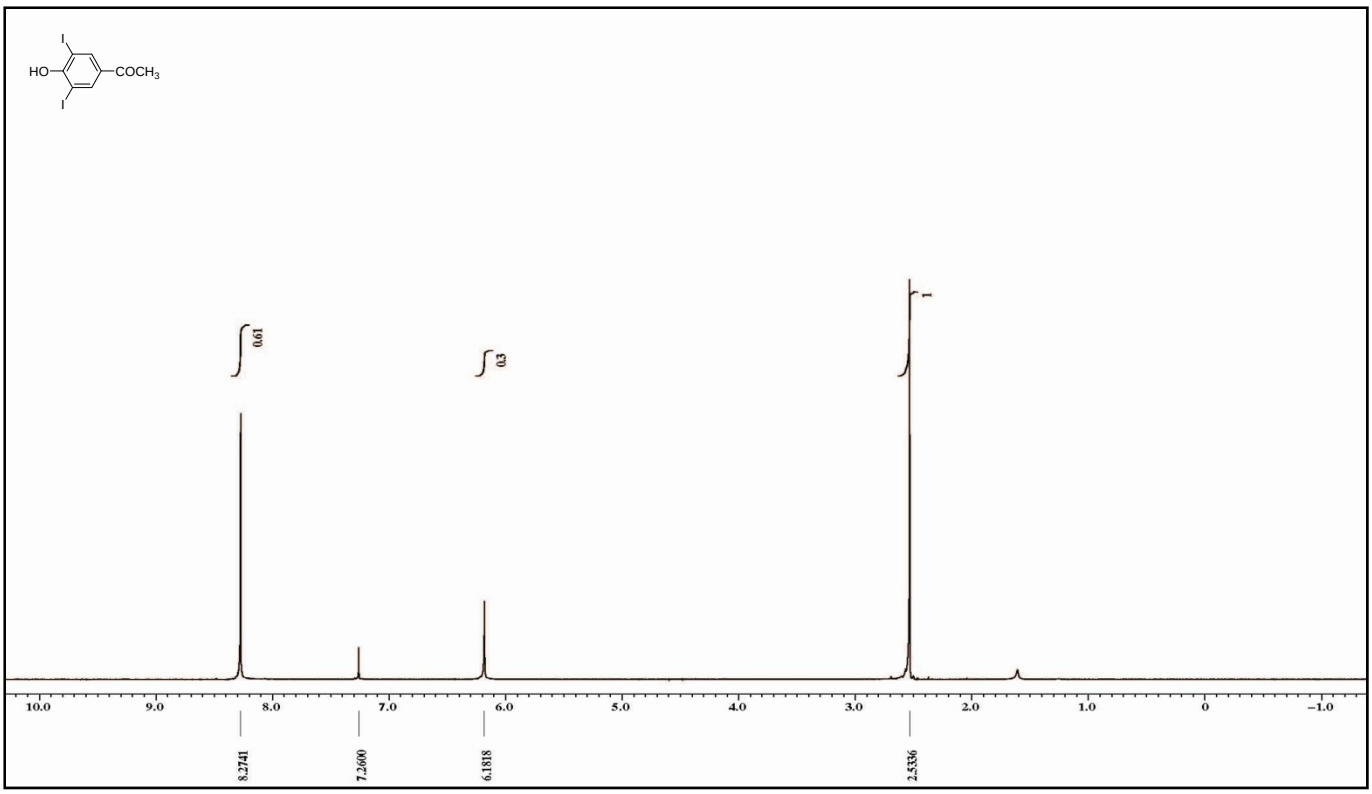


Figure S37. ^{1}H NMR spectrum of 1-(4-hydroxy-3,5-diiodophenyl)ethanone.

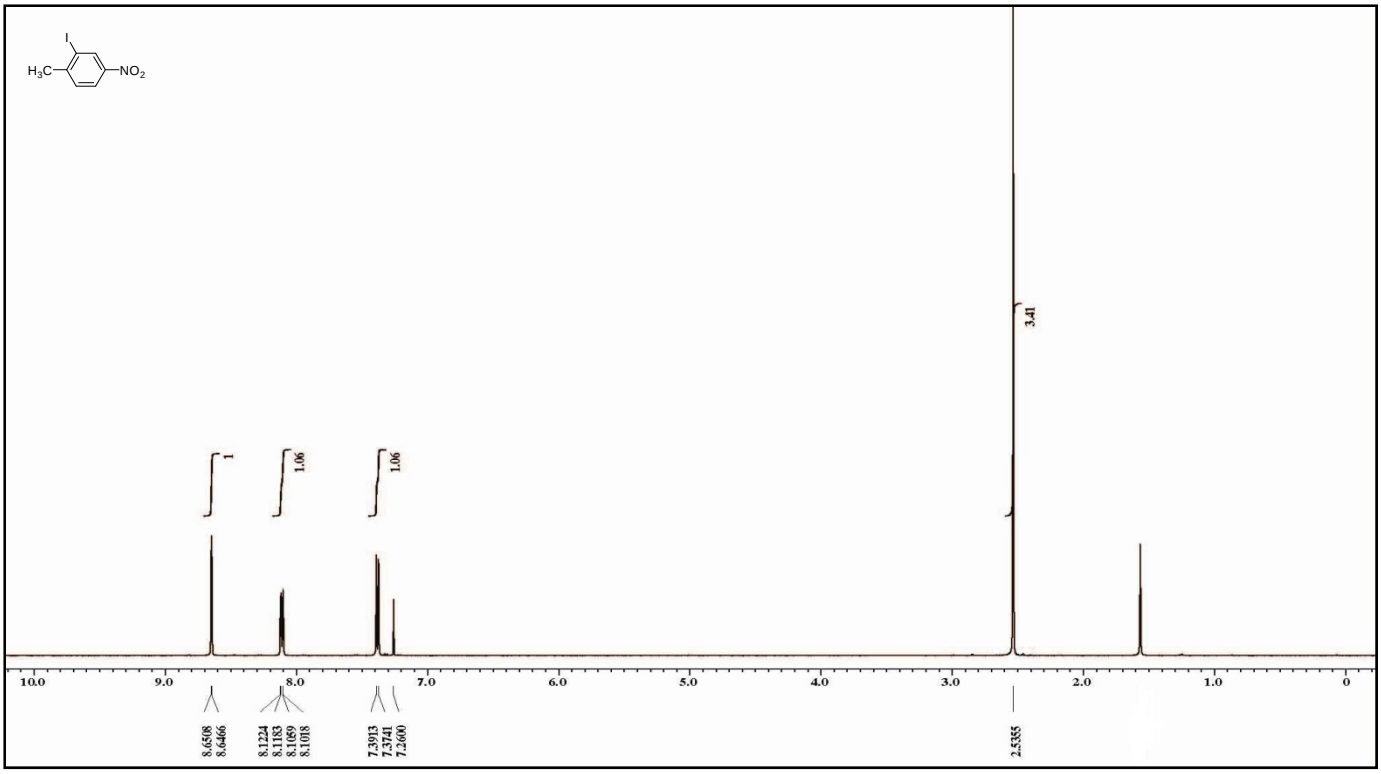


Figure S38. ^{1}H NMR spectrum of 2-iodo-4-nitrotoluene.

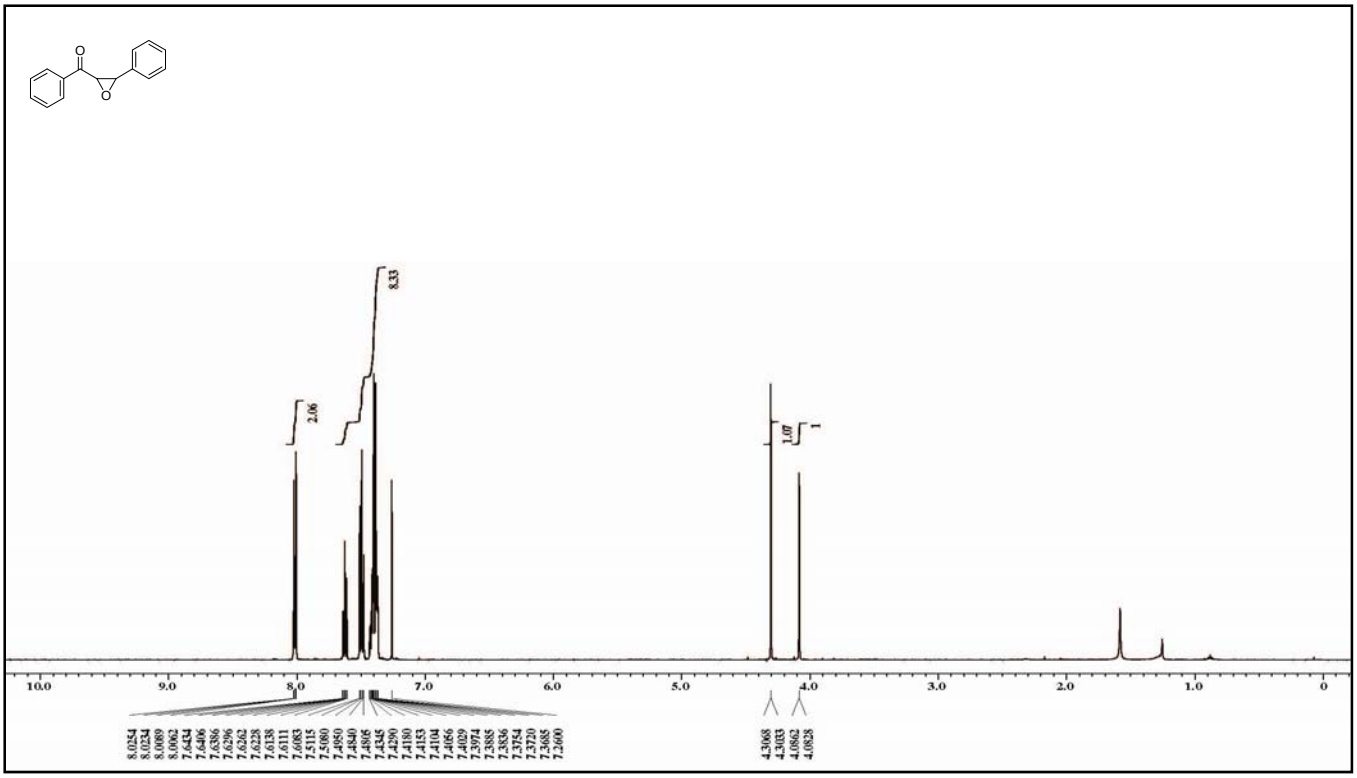


Figure S39. ^{1}H NMR spectrum of *trans*-epoxy-1,3-diphenylpropan-1-one.

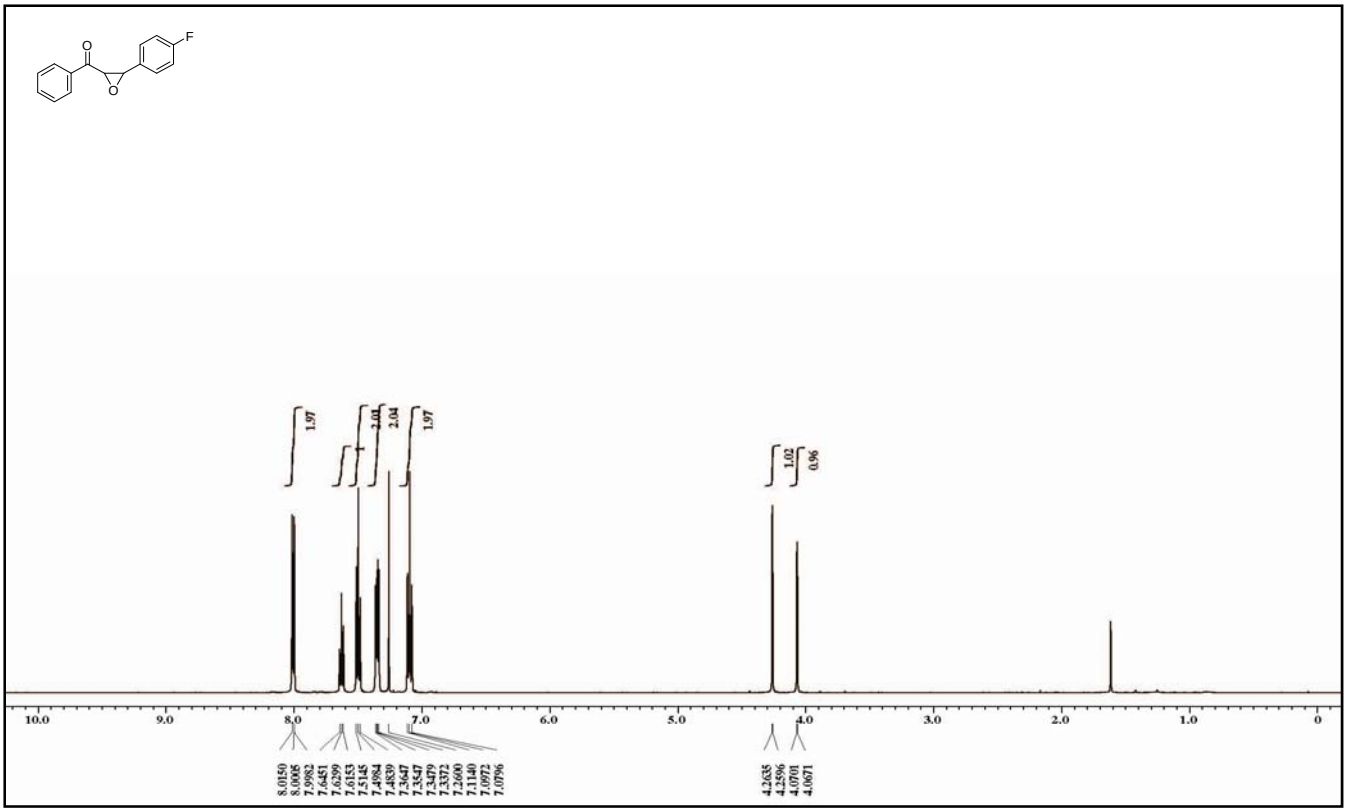


Figure S40. [1]H NMR spectrum of *trans*-epoxy-3-(4-fluorophenyl)-1-phenylpropan-1-one.

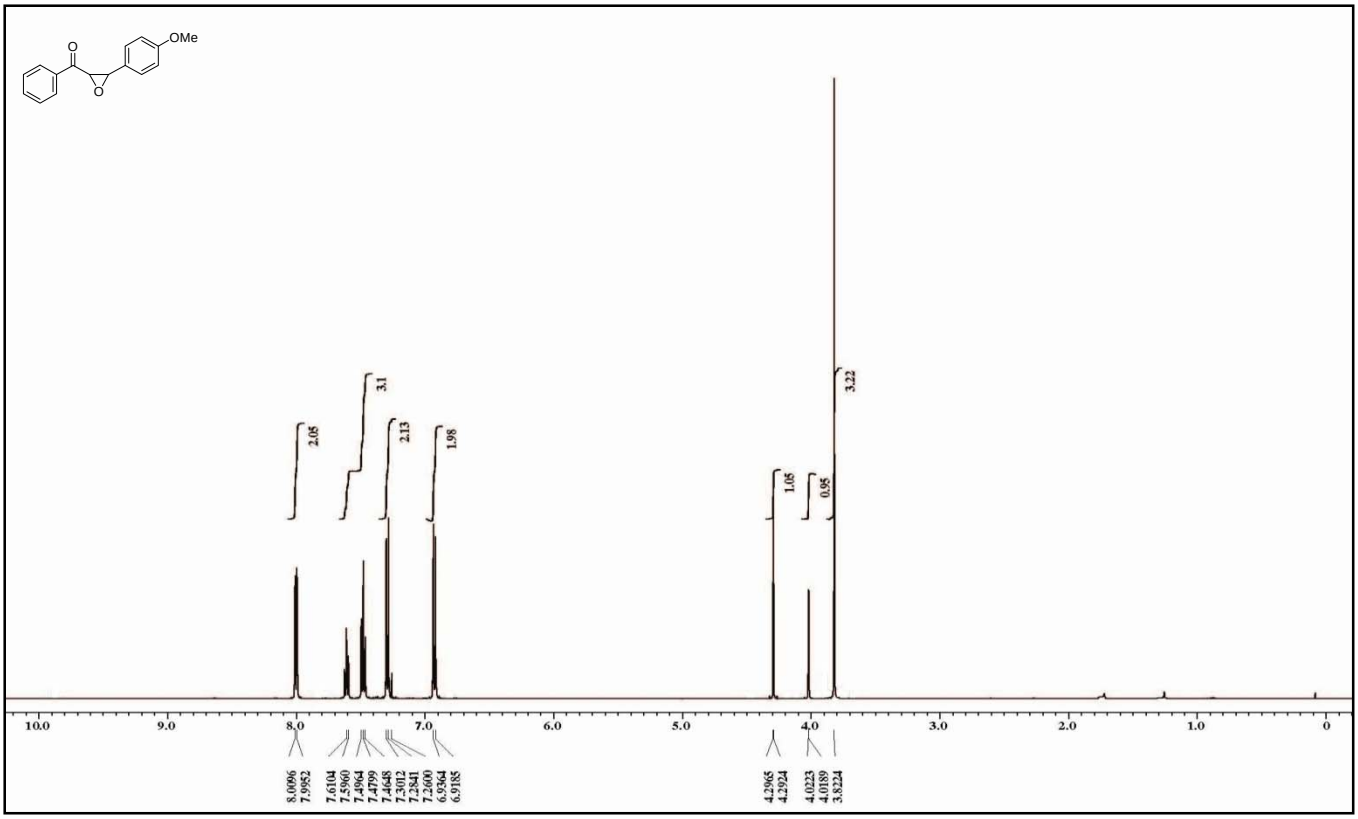


Figure S41. ^{1}H NMR spectrum of *trans*-epoxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one.

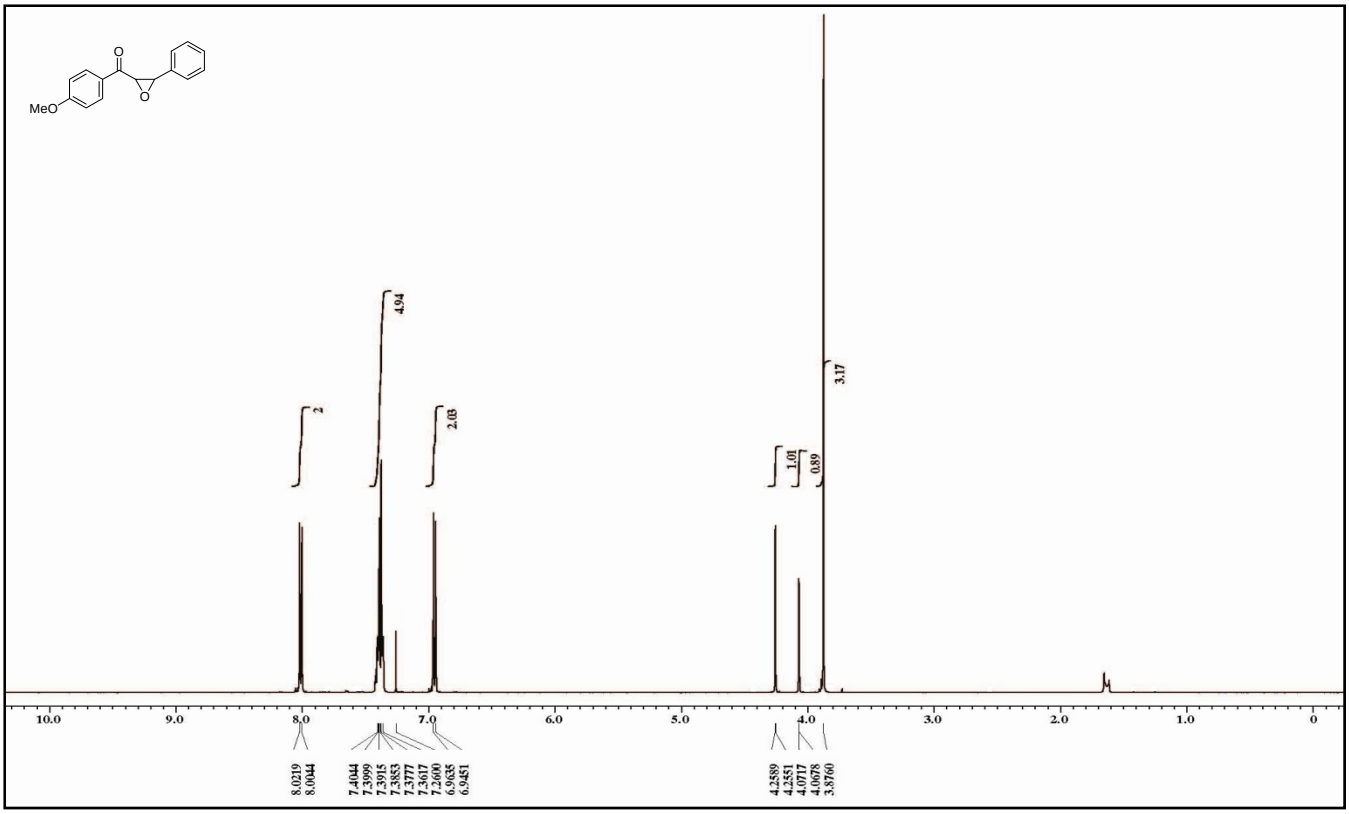


Figure S42. ^{1}H NMR spectrum of *trans*-epoxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one.

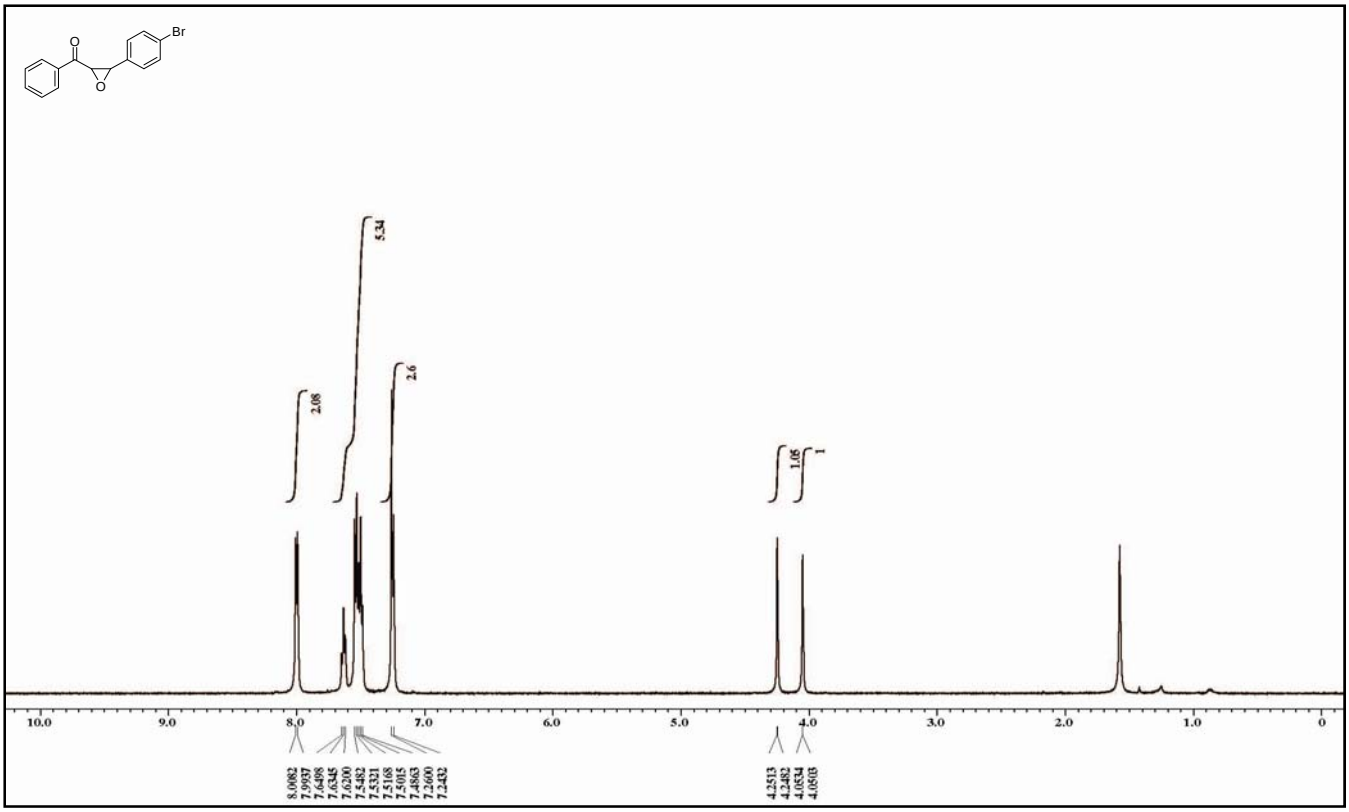


Figure S43. ^{1}H NMR spectrum of *trans*-epoxy-3-(4-bromophenyl)-1-phenylpropan-1-one.

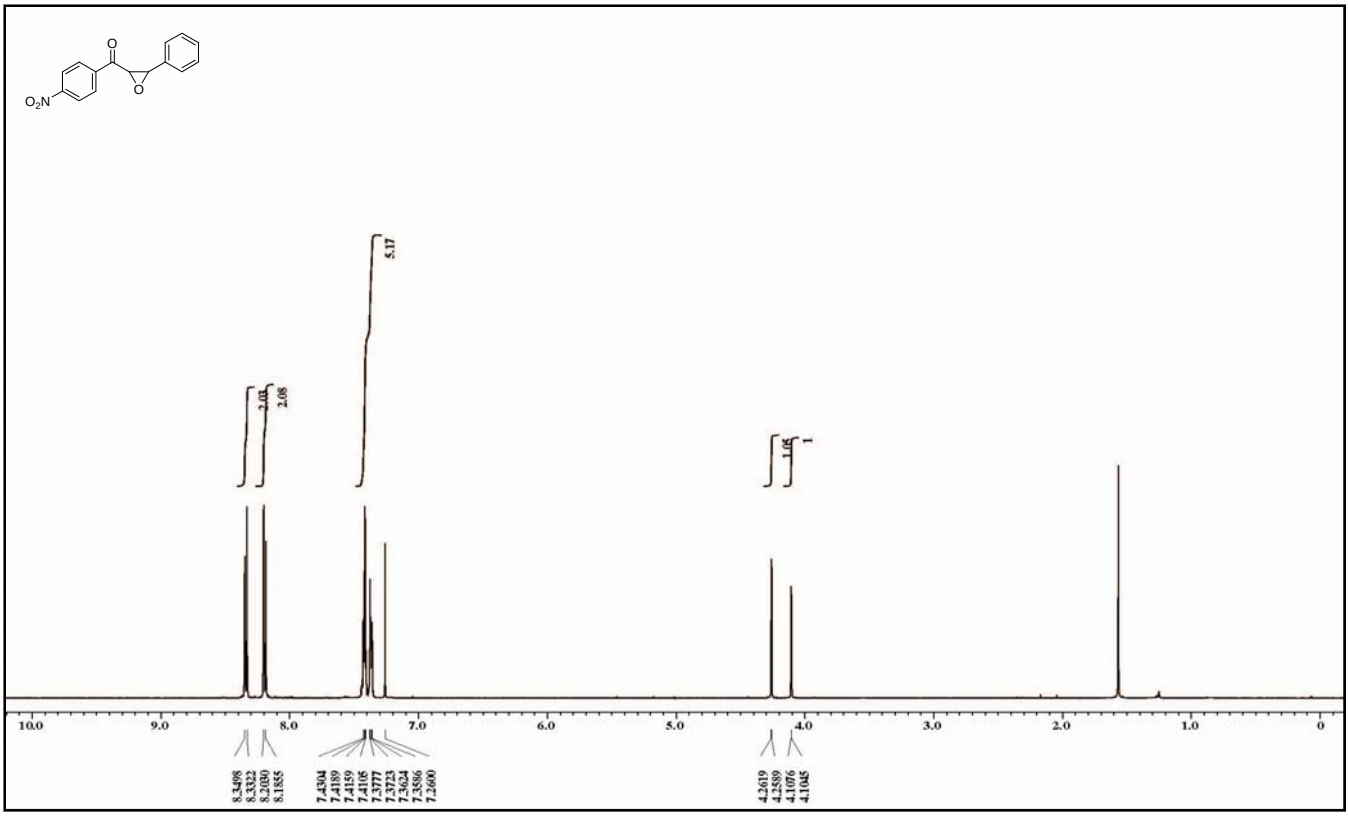


Figure S44. ^{1}H NMR spectrum of *trans*-epoxy-1-(4-nitrophenyl)-3-phenylpropan-1-one.

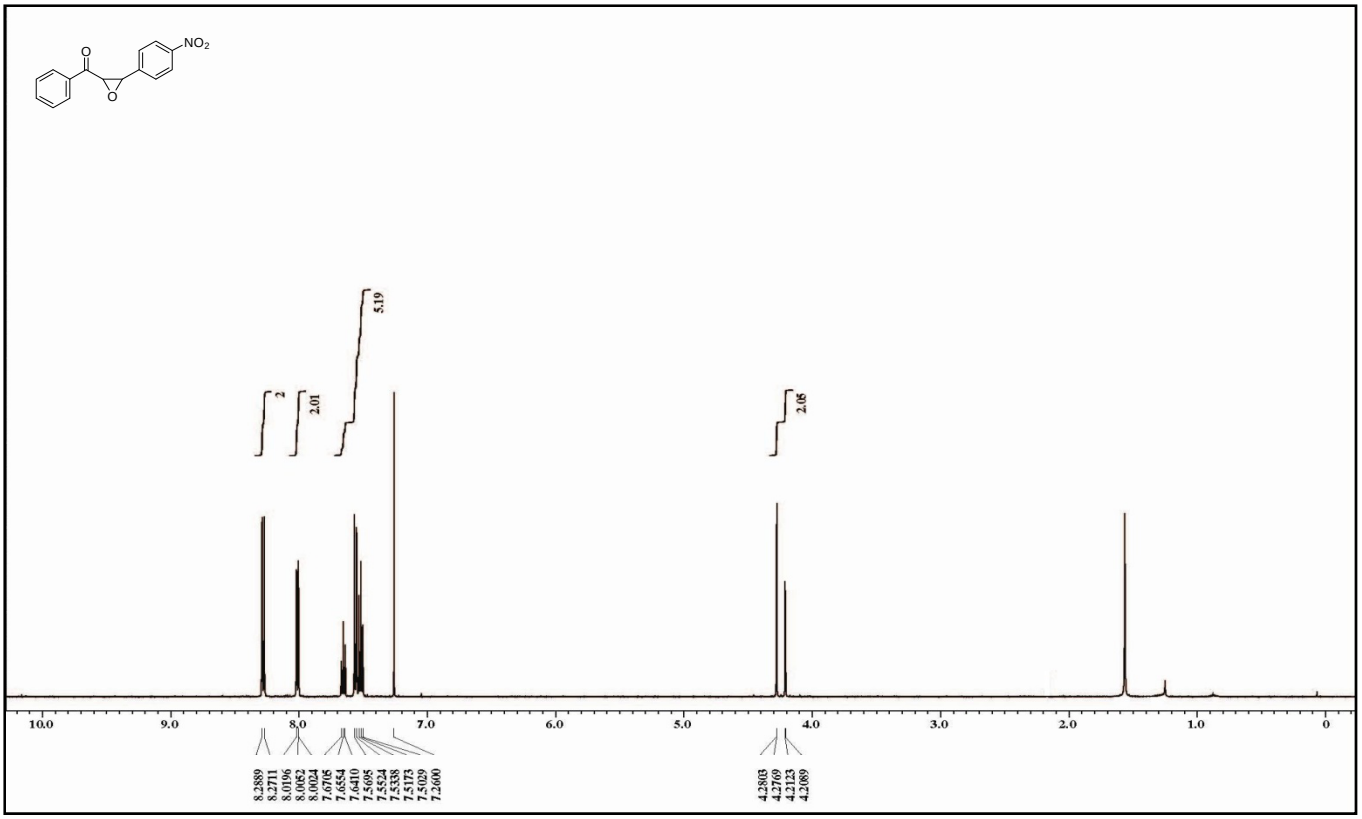


Figure S45. ^{1}H NMR spectrum of *trans*-epoxy-3-(4-nitrophenyl)-1-phenylpropan-1-one.

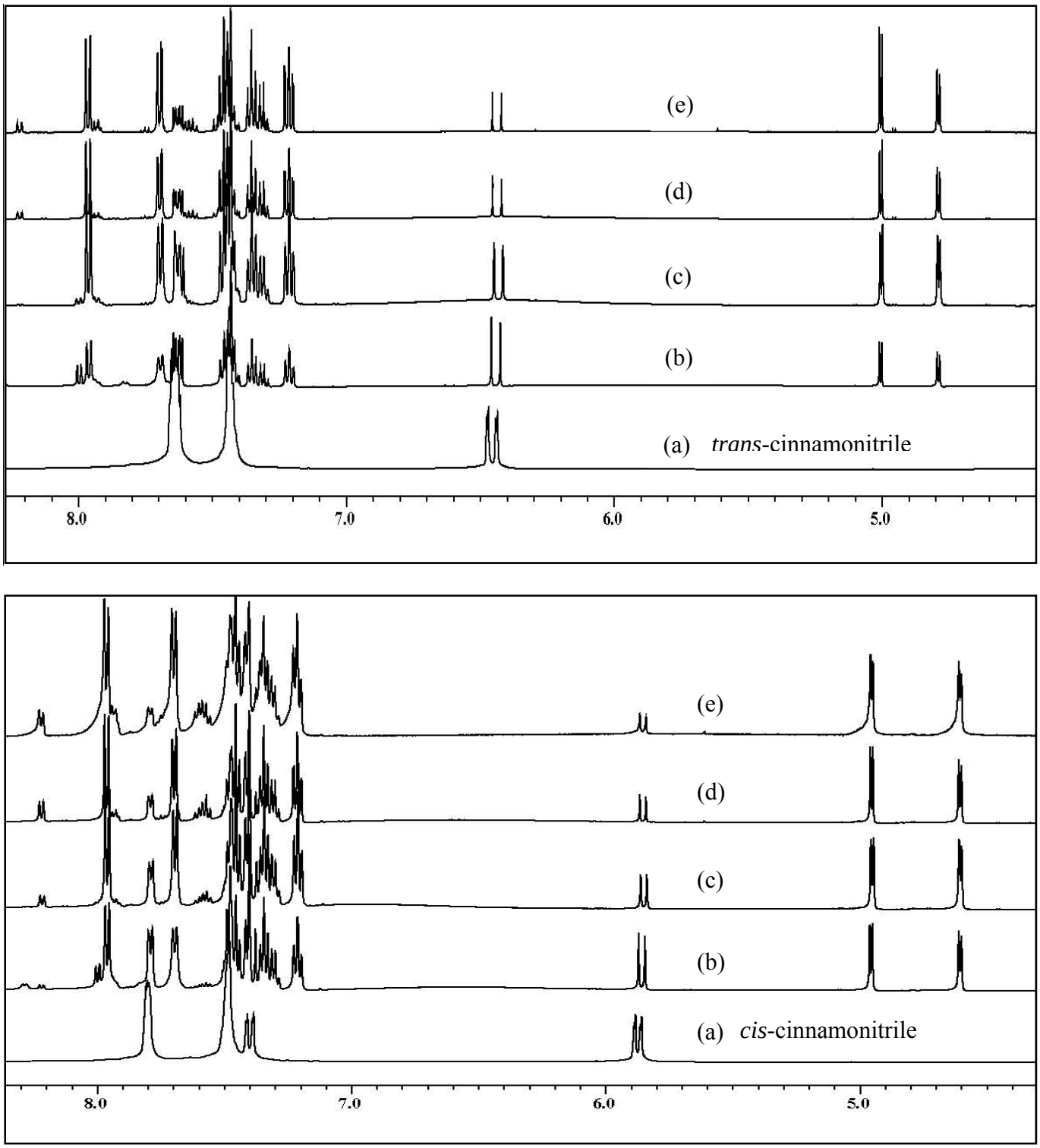


Figure S46. ^{1}H NMR monitoring of the reactions of pure trans (top) and cis (bottom) isomers of cinnamonitrile with IBX (1.0 equv) and I_2 (2.2 equiv) in DMSO-d_6 ; (a) pure isomer; (b-e) 12, 20, 36 and 60 h after the commencement of the reaction, respectively.

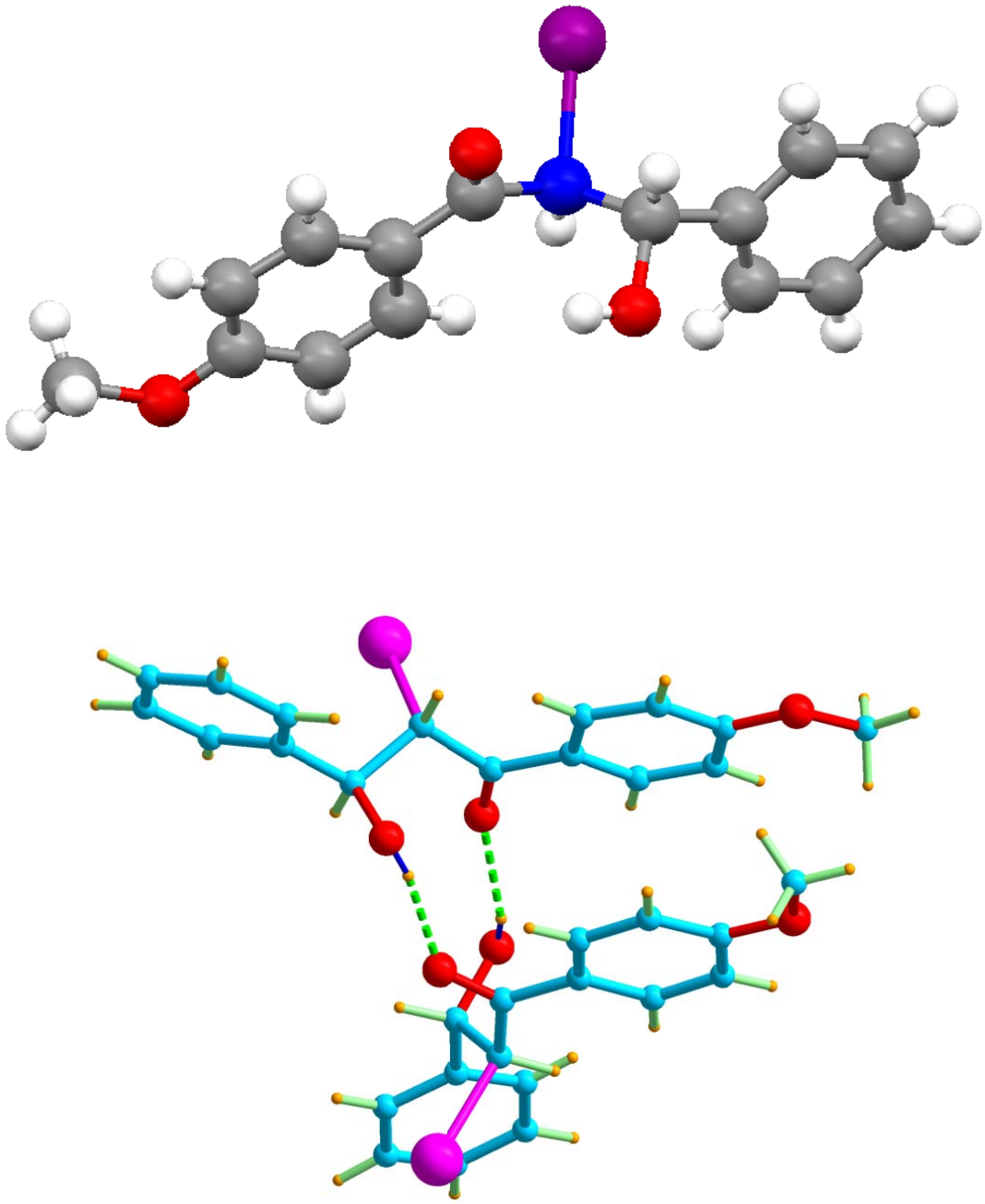


Figure S47. Molecular structure of 3-hydroxy-2-iodo-1-(4-methoxyphenyl)-3-phenylpropan-1-one (top) and its typical H-bonded association in the solid state (bottom). Note that there are two molecules in the asymmetric unit cell.

Details of X-Ray Crystal Structure Determination of 3-hydroxy-2-iodo-1-(4-methoxyphenyl)-3-phenylpropan-1-one

Empirical formula, Mw	$C_{16}H_{15}O_3I$, 382.18
Temperature	100(2) K
Radiation used, Wavelength MoKα,	0.71073 Å
Crystal system, Space group	Triclinic, P-1
Unit cell dimensions	a = 10.650(3) Å α= 68.357(5)°.
	b = 11.728(4)Å β= 89.698(5)°.
	c = 13.762(4) Å γ = 66.069(5)°.
Volume	1439.2(8) $Å^3$
Z, Calculated Density	4, 1.764 Mg/m^3
Absorption coefficient	2.229 mm^{-1}
F(000)	752
Crystal size	0.1 x 0.1 x 0.1 mm
Reflections collected	7401
Independent reflections	4057
Goodness-of-fit on F^2	1.164
Final R indices, 1196 reflections [I>2s(I)]	R1 = 0.0417, wR2 = 0.1111
R indices (all data)	R1 = 0.0533, wR2 = 0.1375