Electronic Supplementary Information

Effect of Noncovalent Interactions in Ion Pairs on Hypervalent Iodines: Inversion of Regioselectivity in Sulfonyloxylactonization

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Contents

General

NMR spectra were recorded on JEOL JNM-400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometer. Chemical shifts were reported in ppm on the δ scale relative to tetramethylsilane (δ = 0 for ^{1}H NMR) and residual $CHCl_3$ (δ = 77.16 for ^{13}C NMR) as an internal reference. New compounds were characterized by ^{1}H, ^{13}C, ^{13}C off-resonance techniques, COSY, HMQC, and HMBC. Infrared (IR) spectra were recorded on a JASCO FT/IR-6200 Fourier transform infrared spectrophotometer or METTLER TOLEDO ReactIR15. Column chromatography was performed with silica gel. Purification by recycle HPLC was performed on SHIMADZU recycle HPLC system (SPD-20A, RID-10A, DGU-20A, LC-6AD, and FCV-20H2) and Japan Analytical Industry Co. (NEXT recycling preparative HPLC). Reactions were carried out in dry solvents under nitrogen atmosphere, unless otherwise stated. Reagents were purchased from Aldrich or Tokyo Chemical Industry Co., Ltd. (TCI), Wako Pure Chemical Industries, Ltd., and used after purification by distillation or used without purification for solid substrates. X-ray diffraction analysis was carried out by Rigaku XtaLAB Synergy with Hypix-6000HE.

Materials

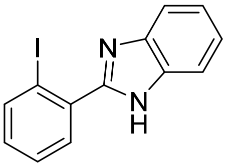
Dehydrated solvents were purchased from Wako Pure Chemical Industries and used as obtained. All sulfonic acids, *p*-TsOH•H_2O **5a**, $PhSO_3H$ **5b**, 4-ethylbenzenesulfonic acid **5c**, *m*-xylenesulfonic acid **5d**, *p*-chlorobenzenesulfonic acid **5e**, 2-naphthalenesulfonic acid (hydrate) **5f**, methanesulfonic acid **5g**, ethanesulfonic acid **5h** were purchased and used as obtained. $PhI(OAc)_2$, PhI(OH)OTs, 1-butyl-3-methylimidazolium tetrafluoroborate, and pyrone **10** was purchased and used as obtained.

The preparation and characterization of new compounds were described below. Carboxylic acids **2d** (S. Ram, S. Shankar, K. Ajay, A. S. Chauhan, P. Das, *Chem. Commun.* **2020**, *56*, 10674.), **2e** (T. Ishida, M. Iwasaki, Y. Kazao, Y. Nishihara, *Org. Lett.* **2020**, *22*, 7343.), and **2i** (P. Dydio, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2013**, *52*, 3878.) were reported compounds.

Syntheses of Hypervalent Iodines $ArI(OAc)_2$

ArI(OAc)₂ 1a

(S1) 2-(2-iodophenyl)-1*H*-benzo[*d*]imidazole



This manipulation was carried out according to the reported method (I. H. Lee, E. H. Jeoung, M. M. Kreevoy, *J. Am. Chem. Soc.* **1997**, *119*, 2722). To the round-bottom flask was added polyphosphoric acid (81.6 g), 2-iodobenzoic acid (25.1 g, 101 mmol) and *o*-phenylenediamine (11.0 g, 102 mmol). The mixture was allowed to warm to 175-180 °C and stirred for 4 h. After cooling to room temperature, the reaction mixture was neutralized by 1 M NaOH aq to pH about 7. Then the solid was collected with Büchner funnel and washed with water. The collected solid was dried with an oven to give the titled product as a light brown solid (31.3 g, 97%). The spectral data was agreement with the reported data (Y. A. Vlasenko, P. S. Postnikov, M. E. Trusova, A. Shafir, V. V. Zhdankin, A. Yoshimura, M. S.

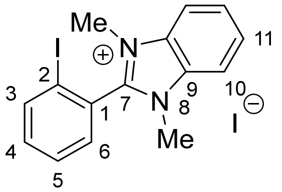
Yusubov, *J. Org. Chem.* **2018**, *83*, 12056.).

^{1}H NMR (DMSO-d_6): 12.75 (br s, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.63-7.62 (m, 3H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.29-7.23 (m, 3H)

^{13}C NMR (100 MHz, DMSO-d_6): 152.5, 139.7, 139.6, 136.54, 131.40, 131.36, 131.29, 131.24, 131.16, 128.17, 128.12, 122.1, 97.4

HRMS (EI, 70 eV) Calculated ($C_{13}H_9N_2I$) 319.9811, Found: 319.9808

(S2) 2-(2-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide



This manipulation was carried out according to the reported method (I. H. Lee, E. H. Jeoung, M. M. Kreevoy, *J. Am. Chem. Soc.* **1997**, *119*, 2722). To the microwave vial (20 mL volume) with a stirrer bar was added 2-(2-iodophenyl)-1*H*-benzo[*d*]imidazole (2.56 g, 8.23 mmol) and methanol (8 mL). Iodomethane (2 mL) and NaOH powder (0.342 g, 8.55 mmol) were added to the reaction mixture, and then the vial was capped. The mixture was heated at 110 °C for 2 h by microwave irradiation. The precipitated solid was washed with ethanol to give a light brown color solid. The product was used at the next step without further purification (3.15 g, 83%).

mp: This compound was not melted and not decomposed at 300 °C.

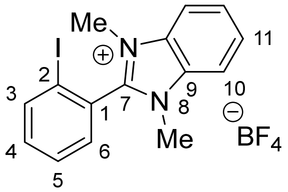
IR: (KBr) 3025, 1485, 760 cm^{-1}

^{1}H NMR (400 MHz, DMSO-d_6): 8.25 (d, *J* = 7.7 Hz, 1H, 3-H), 8.23-8.18 (m, 2H, 10-H), 7.89 (dd, *J* = 7.7, 1.4 Hz, 1H, 6-H), 7.85-7.80 (m, 3H, 5-H and 11-H), 7.61 (td, *J* = 7.7, 1.4 Hz, 1H, 4-H), 3.83 (s, 6H, CH_3 x 2)

^{13}C NMR (100 MHz, DMSO-d_6): 150.8 (s, C-7), 139.4 (d, C-3), 134.8 (d, C-4), 132.4 (d, C-6), 131.4 (s, C-9), 129.3 (d, C-5), 127.3 (d, C-11), 126.8 (s, C-2), 113.8 (d, C-10), 99.1 (s, C-1), 32.6 (q, CH_3 x 2)

Analysis: $C_{15}H_{14}I_2N_2$ (476.10) Calcd: C, 37.84; H, 2.96; N, 5.88, Found: C, 37.58; H, 2.86; N, 5.81

(S3) 2-(2-iodophenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium tetrafluoroborate



This manipulation was carried out according to the reported method (W. Qian, E. Jin, W. Bao, Y. Zhang, *Angew. Chem. Int. Ed.* **2005**, *44*, 952-955.). To the solution of 2-(2-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (2.02 g, 4.23 mmol) in chloroform (45 mL) was added silver tetrafluoroborate (0.945 g, 4.85 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was filtrated off and the obtained solid was extracted with hot chloroform. The obtained chloroform solution was evaporated to give a pale red solid. The product was used at the next step without further purification (1.88 g, 99%).

mp: 221-226 °C (decomposed)

IR: (KBr) 3357, 3080, 1525, 1139 cm^{-1}

^{1}H NMR (400 MHz, CD_3CN): 8.22 (d, *J* = 7.9 Hz, 1H, 3-H), 7.98-7.94 (m, 2H, 10-H), 7.83-7.77 (m, 3H, 5-H and 11-H), 7.65 (dd, *J* = 7.9, 1.9 Hz, 1H, 6-H), 7.59 (td, *J* = 7.9, 1.9 Hz, 1H, 4-H), 3.81 (s, 6H, CH_3 x 2)

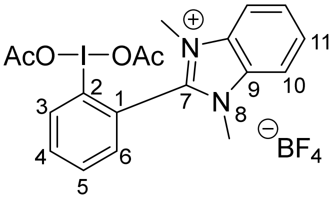
^{13}C NMR (100 MHz, CD_3CN): 151.9 (s, C-7), 141.0 (d, C-3), 135.8 (d, C-4), 133.2 (d, C-6), 132.6 (s, C-2), 130.5 (d, C-5), 128.5 (d, C-11), 127.8 (s, C-9), 114.4 (d, C-10), 98.0 (s, C-1), 33.5 (q, CH_3 x 2)

^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O): -151.8

HRMS: (EI, 70 eV) Calculated ($C_{15}H_{14}N_2I$): 349.2002 ($[M - BF_4]^+$), Found: 349.0197

Analysis: $C_{15}H_{14}BF_4IN_2$, Calcd: C, 41.32; H, 3.24; N, 6.43, Found: C, 40.99; H, 3.30; N, 6.32

(1a) 2-(2-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate



This manipulation was carried out according to the reported method (M. Uyanik, T. Yasui, K. Ishihara, *Angew. Chem. Int. Ed.* **2013**, *52*, 9215.). To the flame-dried flask was added 2-(2-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate (1.32 g, 3.2 mmol) and 9% peracetic acid (12 mL). The reaction mixture was stirred at 45 ºC for 12 h. After cooling to room temperature, the solvent was evaporated. Then, the precipitated solid was washed with acetic acid over 3 times. The solid was washed with diethyl ether (anhydrous) to remove acetic acid. The volatiles were evaporated to give the product as a white solid (1.17 g, 70%). The structure was determined by X-ray crystallography.

mp: 207-209 °C (decomposed)

IR: (KBr) 1645, 1369, 1278, 1064 cm^{-1}

^{1}H NMR (400 MHz, CD_3CN): 8.67 (d, *J* = 8.0 Hz, 1H, 3-H), 8.09 (t, *J* = 8.0 Hz, 1H, 5-H), 8.01 (t, *J* = 8.0 Hz, 1H, 4-H), 7.99-7.92 (3H, m, 6-H and 10-H), 7.86-7.78 (2H, m, 11-H), 3.88 (6H, s, Me x 2), 1.88 (6H, s, OAc x 2)

^{13}C NMR (100 MHz, CD_3CN): 177.8 (s, *C*OCH$_3$ x 2), 149.4 (s, C-7), 139.5 (d, C-3), 136.9 (d, C-4), 134.8 (d), 134.2 (d), 133.0 (s, C-9), 128.8 (d, C-11), 125.9 (s, C-2), 123.7 (s, C-1), 114.7 (d, C-10), 34.2 (q, Me x 2), 20.3 (q, OAc x 2)

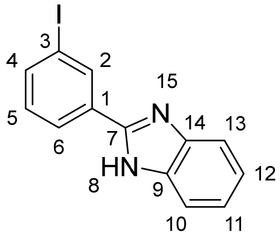
^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O): -151.8

HRMS: (ESI) Calculated ($C_{19}H_{20}N_2O_4I$) 467.04623 ($[M - BF_4]^+$), Found: 467.04656

X-ray crystallographic data have been deposited at the Cambridge Crystallographic Centre: CCDC 2044394.

ArI(OAc)₂ 1b

(S4) 2-(3-iodophenyl)-1*H*-benzo[*d*]imidazole



This manipulation was carried out according to the reported method (I. H. Lee, E. H. Jeoung, M. M. Kreevoy, *J. Am. Chem. Soc.* **1997**, *119*, 2722). To a round-bottom flask was added 3-iodobenzoic acid (1 mmol, 0.25 g), *o*-phenylenediamine (1 mmol, 0.11 g) and polyphosphoric acid (3.7 g). The mixture was stirred for 1.5 h at 175-180 ºC. The reaction mixture was allowed to room temperature and neutralized by 6% NaOH aqueous solution. After neutralizing viscous mixture, the precipitated solid was washed with water and dried to give the soil color product (0.298 g, 93%).

mp: 262-264 °C

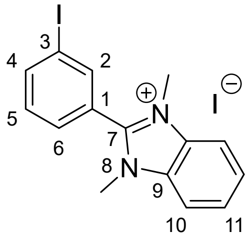
IR: (KBr) 2913, 1439, 744 cm^{-1}

^{1}H NMR (400 MHz, DMSO-*d*$_6$): 13.04 (br s, 1H, 8-H), 8.55 (s, 1H, 2-H), 8.19 (d, *J* = 7.9 Hz, 1H, 6-H), 7.85 (d, *J* = 7.9 Hz, 1H, 4-H), 7.67 (d, *J* = 7.7 Hz, 1H, 10-H or 13-H), 7.54 (d, *J* = 7.2 Hz, 1H, 10-H or 13-H), 7.36 (t, *J* = 7.9 Hz, 1H, 5-H), 7.28-7.16 (m, 2H, 11-H and 12-H)

^{13}C NMR (100 MHz, DMSO-*d*$_6$): 149.6 (s, C-7), 143.7 (s, C-9 or C-14), 138.3 (d, C-4), 135.0 (s, C-9 or C-14), 134.6 (d, C-2), 132.2 (s, C-1), 131.2 (d, C-5), 125.7 (d, C-6), 122.9 (d, C-11 or C-12), 122.0 (d, C-11 or C-12), 119.1 (d, C-10 or C-13), 111.6 (d, C-10 or C-13), 95.4 (s, C-3)

HRMS: (EI, 70 eV) Calculated ($C_{13}H_9N_2I$) 319.9811, Found: 319.9806

(S5) 2-(3-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide



This manipulation was carried out according to the reported method (I. H. Lee, E. H. Jeoung, M. M. Kreevoy, *J. Am. Chem. Soc.* **1997**, *119*, 2722). To the microwave vial (5 mL volume) with a stirrer bar was added 2-(3-iodophenyl)-1*H*-benzo[*d*]imidazole (0.300 g, 0.937 mmol) and methanol (1 mL). Iodomethane (0.45 mL) and NaOH powder (0.060 g, 1.5 mmol) were added to the reaction mixture, and then the vial was capped. The mixture was heated at 110 °C for 2 h by microwave irradiation. The precipitated solid was washed with ethanol to give a light brown color solid. The product was used at the next step without further purification (0.345 g, 77%).

mp: 298-299 °C

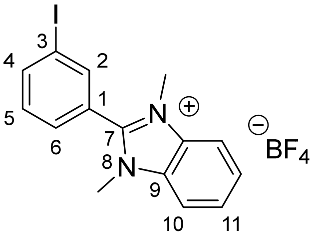
IR: (KBr) 1519, 1483, 1455 cm^{-1}

^{1}H NMR (400MHz, DMSO-d_6): 8.31 (s, 1H, 2-H), 8.21 (d, *J* = 8.0 Hz, 1H, 4-H), 8.14 (dd, *J* = 5.9, 3.0 Hz, 2H, 10-H), 7.94 (d, *J* = 8.0 Hz, 1H, 6-H), 7.77 (dd, *J* = 5.9, 3.0 Hz, 2H, 11-H), 7.58 (t, *J* = 8.0 Hz, 1H, 5-H), 3.89 (s, 6H, CH_3 x 2)

^{13}C NMR (100 MHz, DMSO-d_6): 148.7 (s, C-7), 141.5 (d, C-4), 138.5 (d, C-2), 131.6 (s, C-9), 131.2 (d, C-5), 130.1 (d, C-6), 126.7 (d, C-11), 123.0 (s, C-3), 113.4 (d, C-10), 95.8 (s, C-1), 32.8 (q, CH_3 x 2)

HRMS: (EI, 70 eV) Calculated ($C_{15}H_{14}N_2I$) 349.0202 ([M - I]$^+$), Found: 349.0199

(S6) 2-(3-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate



This manipulation was carried out according to the reported method (W. Qian, E. Jin, W. Bao, Y. Zhang, *Angew. Chem. Int. Ed.* **2005**, *44*, 952-955.). To the solution of 2-(3-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (0.959 g, 2.01 mmol) in $CHCl_3$ (20 mL) was added silver tetrafluoroborate (0.440 g, 2.26 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was filtrated off and the obtained solid was extracted with hot chloroform. The obtained chloroform solution was evaporated to give a white solid The product was used at the next step without further purification (0.665 g, 76%).

mp: 230-234 °C

IR: (KBr) 1520, 1486, 1057 cm^{-1}

^{1}H NMR (400 MHz, CD_3OD): 8.25-8.23 (m, 2H, 2-H and 6-H), 8.04-7.98 (m, 2H, 10-H), 7.84 (dt, *J* = 8.1, 1.3 Hz, 1H, 4-H), 7.81-7.76 (m, 2H, 11-H), 7.57 (t, *J* = 8.1 Hz, 1H, 5-H), 3.96 (s, 6H, CH_3 x 2)

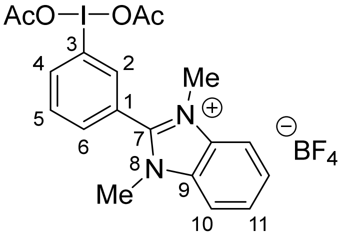
^{13}C NMR (100 MHz, CD_3OD): 150.3 (s, C-7), 143.6 (d), 140.0 (d), 133.5 (s, C-9), 132.5 (d, C-5), 131.0 (d, C-4), 128.4 (d, C-11), 124.3 (s, C-1), 114.2 (d, C-10), 95.7 (s, C-3), 33.3 (q, CH_3 x 2)

^{19}F NMR (377 MHz, CD_3OD, external standard: TFA in D_2O): -154.9

HRMS: (EI, 70 eV) Calculated ($C_{15}H_{14}N_2I$): 349.2002 ([M - BF_4]$^+$), Found: 349.0196

Analysis: $C_{15}H_{14}BF_4IN_2$, Calcd: C, 41.32; H, 3.24; N, 6.43, Found: C, 41.21; H, 3.21; N, 6.41

(1b) 2-(3-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium tetrafluoroborate



This manipulation was carried out according to the reported method (M. Uyanik, T. Yasui, K. Ishihara, *Angew. Chem. Int. Ed.* **2013**, *52*, 9215.). To the flame-dried flask was added 2-(3-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate (0.418 g, 0.959 mmol) and 9% peracetic acid (4 mL). The reaction mixture was stirred at 45 ºC for 12 h. After cooling to room temperature, the solvent was evaporated. Then, the precipitated solid was washed with acetic acid over 3 times. The solid was washed with diethyl ether (anhydrous) to remove acetic acid. The remained ether was evaporated to give the product as a white solid (0.355 g, 67%).

mp: 221-224 °C

IR: (KBr) 1643, 1274, 1056 cm^{-1}

^{1}H NMR (400 MHz, CD_3CN): 8.56-8.53 (m, 1H, 4-H), 8.49 (t, J = 1.7 Hz, 1H, 2-H), 8.00 (dt, J = 7.9, 1.7 Hz, 1H, 6-H), 7.96-7.92 (m, 3H, 5-H and 10-H), 7.78 (dd, J = 6.3, 3.4 Hz, 2H, 11-H), 3.90 (s, 6H, 8-Me x 2), 1.98 (s, 6H, $COCH_3$ x 2)

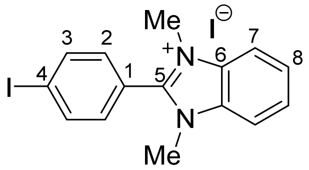
^{13}C NMR (100 MHz, CD_3CN): 177.6 (s, $\mathit{C}OCH_3$ x 2), 149.3 (s, C-7), 140.0 (d, C-4), 137.8 (d, C-2), 135.0 (d, C-6), 133.1 (d, C-5), 133.1 (s, C-9), 128.4 (d, C-11), 124.1 (s, C-1), 122.0 (s, C-3), 114.2 (d, C-10), 33.9 (q, 8-Me x 2), 20.4 (q, $CO\mathit{C}H_3$ x 2)

^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O): -151.3

HRMS: (ESI) Calculated ($C_{19}H_{20}N_2O_4I$) 467.0462 ($[M - BF_4]^+$), Found: 467.0448

ArI(OAc)₂ 1c

(S7) 2-(4-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide



This manipulation was carried out according to the reported method (I. H. Lee, E. H. Jeoung, M. M. Kreevoy, *J. Am. Chem. Soc.* **1997**, *119*, 2722). To the vial (5 mL volume) with a stirrer bar was added 2-(4-iodophenyl)-1*H*-benzo[*d*]imidazole (0.785 g, 2.45 mmol) and methanol (3 mL). Iodomethane (0.6 mL) and NaOH powder (0.130 g, 3.25 mmol) were added to the reaction mixture, and then the vial was capped. The mixture was heated at 110 °C for 8 h by microwave irradiation. The precipitated solid was washed with ethanol to give a light brown color solid. The product was used at the next step without further purification (0.833 g, 71%).

Caution: Dimethyl ether (b.p. -24 °C) is generated during the reaction. Be careful to the pressure in a vial.

mp: This compound does not melt and not decompose at 300 °C.

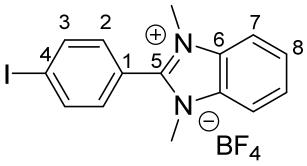
IR: (KBr) 1593, 1463, 766 cm^{-1}

^{1}H NMR (400 MHz, DMSO-d_6): 8.18 (d, J = 8.2 Hz, 2H, 3-H), 8.13 (dd, J = 6.3, 3.4 Hz, 2H, 7-H), 7.77 (dd, J = 6.3, 3.4 Hz, 2H, 8-H), 7.68 (d, J = 8.2 Hz, 2H, 2-H), 3.89 (s, 6H, CH_3 x 2)

^{13}C NMR (100 MHz, DMSO-d_6): 149.7 (s, C-5), 138.3 (d, C-3), 132.4 (d, C-2), 131.7 (s, C-6), 126.7 (d, C-8), 120.4 (s, C-1), 113.4 (d, C-7), 101.7 (s, C-4), 32.8 (q, CH_3 x 2)

HRMS: (FAB) Calculated ($C_{15}H_{14}N_2I$): 349.2002 ($[M - I]^+$), Found: 349.0198

(S8) 2-(4-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate



This manipulation was carried out according to the reported method (W. Qian, E. Jin, W. Bao, Y. Zhang, *Angew. Chem. Int. Ed.* **2005**, *44*, 952-955.). To the solution of 2-(4-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (1.42 g, 2.98 mmol) in CH_3CN (30 mL) was added silver tetrafluoroborate (0.641 g, 3.29 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was filtrated off, and additionally the obtained solid was extracted with CH_3CN. The combined CH_3CN solution was evaporated to give a grey solid. The obtained product was used at the next step without further purification (1.11 g, 85%).

mp: This compound does not melt and not decompose at 300 °C.

IR: (KBr) 1486, 1070, 764 cm^{-1}

^{1}H NMR (400 MHz, DMSO-*d*$_6$): 8.19 (d, *J* = 8.5 Hz, 2H, 3-H), 8.13 (dd, *J* = 6.0, 3.1 Hz, 2H, 7-H), 7.77 (dd, *J* = 6.0, 3.1 Hz, 2H, 8-H), 7.68 (d, *J* = 8.5 Hz, 2H, 2-H), 3.89 (s, 6H, Me x 2)

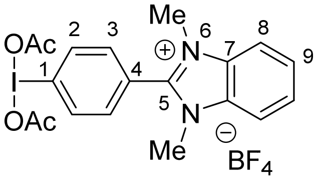
^{13}C NMR (100 Hz, DMSO-*d*$_6$): 149.7 (s, C-5), 138.4 (d, C-3), 132.4 (d, C-2), 131.8 (s, C-6), 126.7 (d, C-8), 120.4 (s, C-1), 113.4 (d, C-7), 101.6 (s, C-4), 32.7 (q, Me)

^{19}F NMR (377 MHz, DMSO-*d*$_6$, external standard: TFA in D_2O): -148.4

HRMS: (EI, 70 eV) Calculated ($C_{15}H_{14}N_2I$): 349.2002 ($[M - BF_4]^+$), Found: 349.0206

Analysis: $C_{15}H_{14}BF_4IN_2$, Calcd: C, 41.32; H, 3.24; N, 6.43, Found: C, 41.24; H, 3.14; N, 6.44

(1c) 2-(4-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium tetrafluoroborate



This manipulation was carried out according to the reported method (M. Uyanik, T. Yasui, K. Ishihara, *Angew. Chem. Int. Ed.* **2013**, *52*, 9215.). To the flame-dried flask was added 2-(4-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate (0.172 g, 0.393 mmol) and 9% peracetic acid (1.5 mL). The reaction mixture was stirred at 45 ºC for 12 h. After cooling to room temperature, the solvent was evaporated. Then, the precipitated solid was washed with acetic acid over 3 times. The solid was washed with diethyl ether (anhydrous) to remove acetic acid. The remained ether was evaporated to give the product as a white solid (0.100 g, 46%).

mp: 289-293 °C

IR: (KBr) 1644, 1276, 1062 cm^{-1}

^{1}H NMR (400 MHz, CD_3CN): 8.51 (d, *J* = 8.6 Hz, 2H, 2-H), 7.93 (dd, *J* = 6.3, 3.1 Hz, 2H, 8-H), 7.89 (d, *J* = 8.6 Hz, 2H, 3-H), 7.78 (dd, *J* = 6.3, 3.1 Hz, 2H, 9-H), 3.89 (s, 6H, 6-Me x 2), 1.99 (s, 6H, $COCH_3$ x 2)

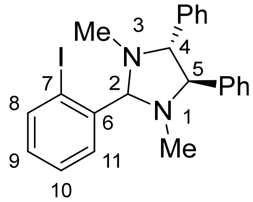
^{13}C NMR (100 MHz, CD_3CN): 177.7 (s, *C*OCH$_3$ x 2), 149.7 (s, C-5), 137.1 (d, C-2), 133.9 (d, C-3), 133.1 (s, C-7), 128.4 (d, C-9), 126.1 (s, C-4), 125.1 (s, C-1), 114.2 (d, C-8), 33.9 (q, 6-Me x 2), 20.5 (q, CO*C*H$_3$ x 2)

^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O): -151.8

HRMS: (ESI) Calculated ($C_{19}H_{20}N_2O_4I$): 467.0462 ($[M - BF_4]^+$), Found: 467.0464

ArI(OAc)₂ 1d ((R,R)-1d)

(S9) (*4R,5R*)-2-(2-iodophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine



This manipulation was carried out according to the reported method (V. Jurčík, R. Wilhelm, *Tetrahedron: Asymmetry* **2006**, *17*, 801.). The mixture of 2-iodobenzaldehyde (1.06 g, 4.57 mmol) and (*1R*,*2R*)-N,N-dimethyl-1,2-diphenylethanediamine (1.10 g, 4.57 mmol) was grinded with spatula for 10 min. The mixture exothermically became solid. The reaction mixture was purified by flash column chromatography (hexane/EtOAc) to give a white solid containing 2-iodobenzaldehyde (1.12 g). This mixture was used next reaction without further purification. The further purification was carried out for the characterization.

mp: 148-149 °C

IR: (KBr) 2790, 1602, 1008, 748, 700 cm^{-1}

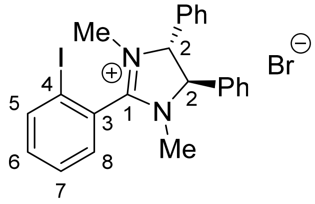
^{1}H NMR (400 MHz, $CDCl_3$): 7.92 (dd, 1H, J = 7.8 Hz, 11-H), 7.88 (dd, 1H, J = 7.8 Hz, 8-H), 7.47 (t, 1H, J = 7.8 Hz, 10-H), 7.29-7.19 (m, 10H, Ph x 2), 7.06 (td, 1H, J = 7.8 Hz, 9-H), 5.13 (s, 1H, 2-H), 3.87 (d, 1H, J = 8.7 Hz), 3.61 (d, 1H, J = 8.7 Hz), 2.16 (s, 3H, NMe), 1.91 (s, 3H, NMe)

^{13}C NMR (100 MHz, $CDCl_3$): 141.5 (s, C-6), 140.1 (s), 139.6 (d, C-8), 139.4 (s), 131.1 (d, C-9), 130.1 (d, C-11), 128.4 (d), 128.3 (d), 128.2 (d), 128.1 (d), 127.7 (d), 127.5 (d), 102.2 (s, C-7), 90.8 (d, C-2), 77.9 (d), 77.3 (d), 37.6 (q, NMe), 36.3 (q, NMe)

$[\alpha]_D^{20}$ = +84.9 (c = 0.62, $CHCl_3$)

HRMS: (CI, 70 eV) Calculated ($C_{23}H_{24}N_2I$) : 455.0984 ([M + H]), Found: 455.0989

(S10) (4*R*,5*R*)-2-(2-iodophenyl)-1,3-dimethyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium bromide



This manipulation was carried out according to the reported method (V. Jurčík, R. Wilhelm, *Tetrahedron: Asymmetry* **2006**, *17*, 801.). To the solution of (*4R*,*5R*)-2-(2-iodophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine (3.56 g, 7.84 mmol) in DME (23 mL) was added N-bromoacetamide (1.09 g, 7.90 mmol). The reaction mixture was stirred at room temperature overnight. After diethyl ether was added to the reaction mixture, a white solid was precipitated. The supernatant solution was removed and the precipitated solid was washed with diethyl ether. The solid was dried under reduced pressure to give a product as a white solid (4.14 g, 99%).

mp: 145-150 °C (sublimation)

IR: (KBr) 3404, 1602, 760, 703 cm^{-1}

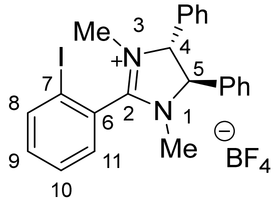
^{1}H NMR (400 MHz, $CDCl_3$): 8.81 (dd, *J* = 7.7, 1.4 Hz, 1H, 8-H), 8.03 (d, *J* = 8.2 Hz, 1H, 5-H), 7.87 (d, *J* = 6.8 Hz, 2H), 7.76 (t, *J* = 7.7 Hz, 1H, 7-H), 7.51-7.40 (m, 9H), 5.92 (d, *J* = 13.3 Hz, 1H, 2-H), 5.04 (d, *J* = 13.3 Hz, 1H, 2-H), 2.99 (s, 3H, NMe), 2.78 (s, 3H, NMe)

^{13}C NMR (100 MHz, $CDCl_3$): 167.0 (s, C-1), 139.4 (d, C-5), 134.3 (s, C-3), 134.2 (d, C-6), 133.0 (d, C-8), 132.5 (s), 130.4 (d), 130.3 (d), 130.1 (d), 129.8 (d), 129.7 (d), 128.6 (d), 128.3 (s), 93.9 (s, C-4), 76.6 (d, C-2), 74.7 (d, C-2), 33.8 (q, Me), 32.8 (q, Me)

$[\alpha]_D^{20}$ = +93.7 (c = 0.54, $CHCl_3$)

HRMS: (FAB+, 70 eV) Calculated ($C_{23}H_{22}N_2I$) 453.0828 ($[M - Br]^+$), Found: 453.0834

(S11) (*4R*,*5R*)-2-(2-iodophenyl)-1,3-dimethyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium



This manipulation was carried out according to the reported method (W. Qian, E. Jin, W. Bao, Y. Zhang, *Angew. Chem. Int. Ed.* **2005**, *44*, 952-955.). To the solution of (*4R*,*5R*)-2-(2-iodophenyl)-1,3-dimethyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium bromide (0.853 g, 1.60 mmol) in chloroform (16 mL) was added silver tetrafluoroborate (0.411 g, 2.11 mmol). The mixture was stirred at room temperature overnight. The resulting residue was filtrated off and the solution was evaporated. After the evaporation, the crude product was purified by silica gel chromatography (MeOH) to give a white solid (0.617 g, 72%).

mp: 169-172 °C

IR (KBr): 1607, 1059 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (dd, *J* = 7.6, 1.4 Hz, 1H, 11-H), 8.05 (d, *J* = 7.2 Hz, 1H, 8-H), 7.74 (t, *J* = 7.6 Hz, 1H, 10-H), 7.60 (d, *J* = 7.7 Hz, 2H, Ph-*o*), 7.52-7.40 (m, 9H, 9-H, Ph-*m* and *p*), 5.56 (d, *J* = 12.8 Hz, 1H), 5.02 (d, *J* = 12.8 Hz, 1H), 2.85 (s, 3H, NMe), 2.76 (s, 3H, NMe)

^{13}C NMR (100 MHz, $CDCl_3$): 166.9 (s, C-2), 139.6 (d, C-8), 134.32 (d), 134.28 (s, Ph-*i*), 132.7 (s, Ph-*i*), 131.6 (d, C-11), 130.5 (d), 130.4 (d), 130.2 (d), 129.9 (d), 129.8 (d), 128.9 (d), 128.5 (d), 128.3 (s, C-6), 93.4 (s, C-7), 76.2 (d), 74.5 (d), 33.0 (q, NMe), 32.7 (q, NMe)

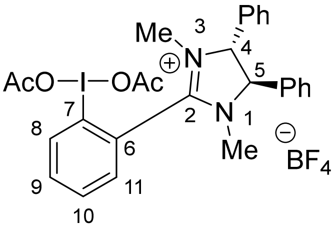
^{19}F NMR (377 MHz, $CDCl_3$, external standard: TFA in D_2O): -152.0

$[\alpha]_D^{20}$ = +91.1 (c = 2.35, $CHCl_3$)

HRMS: (FAB+, 70 eV) Calculated ($C_{23}H_{22}N_2I$): 453.0828 ($[M-BF_4]^+$), Found: 453.0823

Analysis: $C_{23}H_{22}BF_4IN_2$, Calcd: C, 51.14; H, 4.11; N, 5.19, Found: C, 51.02; H, 4.06; N, 5.15

((*R*,*R*)-1d) (*4R*,*5R*)-2-(2-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate



This manipulation was carried out according to the reported method (M. Uyanik, T. Yasui, K. Ishihara, *Angew. Chem. Int. Ed.* **2013**, *52*, 9215.). To the flame-dried flask was added (*4R*,*5R*)-2-(2-iodophenyl)-1,3-dimethyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (0.541 g, 1.00 mmol) and 9% peracetic acid (5 mL). The reaction mixture was stirred at 45 ºC for 12 h under N_2. After cooling to room temperature, the solvent was evaporated. Then, the precipitated solid was washed with diethyl ether (anhydrous) under N_2. The solid was further washed with anhydrous diethyl ether in a glove box. Remained ether was evaporated to give the product as a white solid (0.585 g). The hypervalent iodine included a small amount of starting material.

mp: 101-103 °C

IR: (KBr) 3425, 1602, 1056 cm^{-1}

$[\alpha]_D^{20}$ = +79.2 (c = 0.68, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): 8.57 (d, *J* = 7.7 Hz, 1H, 11-H), 8.48 (d, *J* = 7.7 Hz, 1H, 8-H), 8.07 (t, *J* = 7.7 Hz, 1H, 10-H), 7.84 (t, *J* = 7.7 Hz, 1H, 9-H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.53-7.41 (m, 6H), 7.32 (t, *J* = 3.4 Hz, 2H), 5.58 (d, *J* = 12.8 Hz, 1H), 5.05 (d, *J* = 12.8 Hz, 1H), 2.91 (s, 3H, NMe), 2.77 (s, 3H, NMe), 1.93 (broadening singlet, 6H, OAc x 2)

^{13}C NMR (100 MHz, $CDCl_3$): 177.1 (s, *C*OCH$_3$), 165.1 (s, C-2), 138.3 (d, C-8), 135.3 (d, C-9), 134.6 (d, C-10), 133.9 (s), 132.8 (d, C-11), 132.1 (s), 130.7 (d), 130.5 (d), 130.10 (d), 130.07 (d), 129.1 (d), 128.3 (d), 126.3 (s, C-7), 120.3 (s, C-6), 76.1 (d), 75.0 (d), 34.1 (q, NMe), 33.3 (q, NMe), 20.3 (q, CO*C*H$_3$)

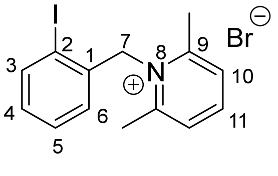
^{19}F NMR (377 MHz, $CDCl_3$, external standard: TFA in D_2O): -151.6

HRMS: (ESI+) Calculated ($C_{27}H_{28}IN_2O_4$) 571.1088 ([M - BF_4])

Found: 571.1059

ArI(OAc)$_2$ 1e

(S12) 1-(2-iodobenzyl)-2,6-dimethylpyridin-1-ium bromide



This manipulation was carried out according to the reported method (W. Qian, E. Jin, W. Bao, Y. Zhang, *Angew. Chem. Int. Ed.* **2005**, *44*, 952.). To the solution of 1-(bromomethyl)-2-iodobenzene (1.19 g, 4.01 mmol) in CH_3CN (2 mL) was added 2,6-lutidine (0.504 g, 4.70 mmol). The reaction mixture was stirred at reflux temperature for 28 h.

After cooling to room temperature, to the reaction mixture was added ether and the precipitated solid was washed with ether to give the product as a pale red solid (0.714 g, 44%).

mp: The product was sublimated during 260-274 °C.

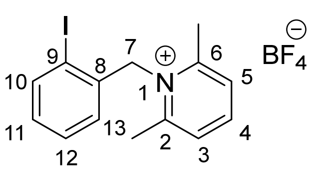
IR: (KBr) 2978, 1619, 1489, 753 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 8.51 (t, *J* = 7.7 Hz, 1H, 11-H), 8.10 (d, *J* = 7.7 Hz, 2H, 10-H), 8.00 (d, *J* = 7.7 Hz, 1H, 3-H), 7.30 (t, *J* = 7.7 Hz, 1H, 5-H), 7.11 (t, *J* = 7.7 Hz, 1H, 4-H), 6.11 (d, *J* = 7.7 Hz, 1H, 6-H), 5.82 (s, 2H, 7-H_2), 2.89 (s, 6H, 9-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 156.5 (s, C-9), 146.1 (d, C-11), 140.9 (d, C-3), 133.4 (s, C-2), 130.7 (d, C-4), 129.5 (d, C-5), 129.1 (d, C-10), 124.5 (d, C-6), 97.2 (s, C-1), 62.5 (t, C-7), 22.3 (q, 9-Me)

HRMS: (EI, 70 eV) Calculated ($C_{14}H_{14}IN$): 323.0171 ([M - H - Br]$^+$), Found: 323.0167

(S13) 1-(2-iodobenzyl)-2,6-dimethylpyridin-1-ium tetrafluoroborate



This manipulation was carried out according to the reported method (W. Qian, E. Jin, W. Bao, Y. Zhang, *Angew. Chem. Int. Ed.* **2005**, *44*, 952-955.). To a solution of 1-(2-iodobenzyl)-2,6-dimethylpyridin-1-ium bromide (1.50 mmol, 0.606 g) in chloroform (15 mL) was added silver tetrafluoroborate (1.6 mmol, 0.311 g). The mixture was stirred at room temperature for 12 h. After the reaction, black precipitates were filtered off and the solvent was evaporated to give the product as white solid (0.577 g, 94%).

mp: 188-190 °C

IR: (KBr) 1621, 1494, 1083 cm^{-1}

^{1}H NMR: (400 MHz, $CDCl_3$) 8.34 (t, 1H, 4-H), 7.99 (d, 1H, 10-H), 7.85 (d, 2H, 3-H and 5-H), 7.31 (t, 1H, 12-H), 7.10 (t, 1H, 11-H), 6.08 (d, 1H, 13-H), 5.68 (s, 2H, 7-H_2), 2.74 (s, 6H, 2-Me and 6-Me)

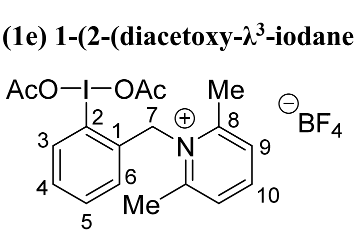
^{13}C NMR: (100 MHz, $CDCl_3$) 156.4 (s, C-2 and C-6), 145.9 (d, C-4), 140.8 (d, C-10), 133.5 (s, C-8), 130.7 (d, C-11), 129.7 (d, C-12), 128.6 (d, C-3), 124.4 (d, C-13), 97.0 (s, C-9), 61.7 (t, C-7), 21.5 (q, 2-Me and 6-Me)

^{19}F NMR (377 MHz, $CDCl_3$, external standard: TFA in D_2O): -153.7

HRMS: (FAB+) Calculated ($C_{14}H_{15}NI$): 324.0249 ([M – BF_4]), Found: 324.0248

Analysis: $C_{14}H_{15}BF_4IN$ (410.99) Calcd: C, 40.91; H, 3.68; N, 3.41, Found: C, 40.63; H, 3.62; N, 3.44

(1e) 1-(2-(diacetoxy-λ^3-iodaneyl)benzyl)-2,6-dimethylpyridin-1-ium tetrafluoroborate



This manipulation was carried out according to the reported method (M. Uyanik, T. Yasui, K. Ishihara, *Angew. Chem. Int. Ed.* **2013**, *52*, 9215.). To the flame-dried flask was added 1-(2-iodobenzyl)-2,6-dimethylpyridin-1-ium tetrafluoroborate (0.290 g, 0.704 mmol) and 9% peracetic acid (3 mL). The reaction mixture was stirred at room temperature overnight. After the reaction, the solvent was evaporated. Then, the precipitated solid was washed with acetic acid briefly. The solid was washed with diethyl ether (anhydrous) to remove acetic acid. Remained ether was evaporated to give the product as a white solid (0.322 g, 87%). The structure was determined by X-ray crystallography.

mp: 121-124 ºC

IR (KBr): 3421, 1565, 1084 cm^{-1}

^{1}H NMR (400 MHz, CD_3CN): 8.41 (m, 2H, 3-H and 10-H), 7.90 (d, *J* = 7.7 Hz, 2H, 9-H), 7.61-7.53 (m, 2H, 4-H and 5-H), 6.46 (d, *J* = 7.2 Hz, 1H, 6-H), 6.13 (s, 2H, 7-H), 2.70 (s, 6H, 8-Me x 2), 1.96 (s, 6H, OAc x 2)

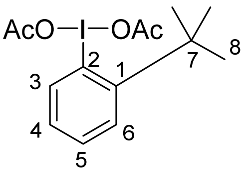
^{13}C NMR (100 MHz, CD_3CN): 177.3 (s, *C*OCH$_3$), 158.0 (s, C-8), 147.1 (d), 139.2 (d), 134.7 (d), 133.7 (s, C-2), 132.4 (d), 129.7 (d, C-9), 126.2 (d, C-6), 124.0 (s, C-1), 59.6 (t, C-7), 21.7 (q, 8-Me), 20.3 (q, CO*C*H$_3$)

^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O): -151.8

HRMS: (ESI) Calculated ($C_{18}H_{21}NO_4I$): 442.05098 ([M - BF$_4$]$^+$), Found: 442.04964

X-ray crystallographic data was deposited at the Cambridge Crystallographic Centre: CCDC 2044652

(1f) (2-(*tert*-butyl)phenyl)-λ^3-iodanediyl diacetate



To the flame-dried flask was added 1-(*tert*-butyl)-2-iodobenzene (0.212 g, 0.815 mmol) and 9% peracetic acid (3.5 mL). The reaction mixture was stirred at room temperature over 12 h. The solvent was evaporated and the sluggish liquid was washed with hexane briefly to give the product as a white solid (0.188 g, 61%).

mp: 91-95 °C

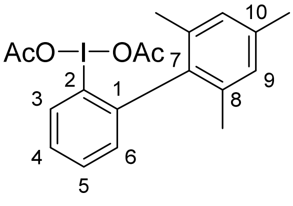
IR: (KBr) 1650, 1366, 1287, 1262 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 8.44 (d, *J* = 7.7 Hz, 1H, 3-H), 7.74 (d, *J* = 7.7 Hz, 1H, 6-H), 7.59 (t, *J* = 7.7 Hz, 1H, 5-H), 7.26 (t, *J* = 7.7 Hz, 1H, 4-H), 1.98 (s, 6H, COCH$_3$ x 2), 1.54 (s, 9H, C(CH$_3$)$_3$)

^{13}C NMR (100 MHz, $CDCl_3$): 176.6 (s, *C*OCH$_3$), 150.2 (s, C-1), 142.9 (d, C-3), 132.6 (d, C-5), 129.2 (d, C-4), 128.8 (d, C-6), 122.5 (s, C-2), 38.0 (s, *C*(CH$_3$)$_3$), 31.6 (q, C(*C*H$_3$)$_3$), 20.6 (q, CO*C*H$_3$)

HRMS: (ESI) Calculated ($C_{14}H_{19}O_4NaI$) 401.0220 ([M + Na]$^+$), Found: 401.0224

(1g) (2',4',6'-trimethyl-[1,1'-biphenyl]-2-yl)-λ^3-iodanediyl diacetate



To 2'-iodo-2,4,6-trimethyl-1,1'-biphenyl (0.346 g, 1.07 g) was added 9% peracetic acid (4 mL) and stirred at room temperature overnight. AcOH was evaporated under vacuum condition, then the resulting solid was washed with ether and dried to give a white solid (0.285 g, 60%).

mp: 154-156 °C

IR: (KBr) 1644, 1269, 668 cm^{-1}

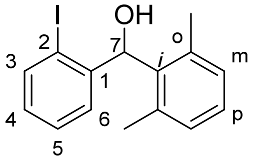
^{1}H NMR (400 MHz, $CDCl_3$): 8.39 (dd, *J* = 8.5, 1.2 Hz, 1H, 3-H), 7.70 (td, *J* = 7.5, 1.2 Hz, 1H, 5-H), 7.47-7.42 (m, 2H, 4-H and 6-H), 6.92 (s, 2H, 9-H), 2.34 (s, 3H, 10-Me), 2.01 (s, 6H, 8-Me x 2), 1.92 (s, 6H, $COCH_3$ x 2)

^{13}C NMR (100 MHz, $CDCl_3$): 176.4 (s, *C*OCH_3), 145.2 (s, C-2), 138.6 (s, C-10), 138.2 (d, C-3), 138.0 (s, C-7), 136.5 (s, C-8), 132.9 (d, C-5), 131.2 (d, C-4 or C-6), 129.6 (d, C-4 or C-6), 128.4 (d, C-9), 127.0 (s, C-1), 21.3 (q, 8-Me), 20.6 (q), 20.4 (q)

HRMS: (ESI) Calculated ($C_{19}H_{21}O_4INa$) 463.0377 ($[M + Na]^+$), Found: 463.0394

ArI(OAc)$_2$ 1h

(S14) (2,6-dimethylphenyl)(2-iodophenyl)methanol



Magnesium turnings (6.7 mmol, 0.18 g) was placed into a three-necked flask equipped with a dropping funnel. The flask was flame-dried under reduced pressure and filled with N_2. THF (8 mL) was added to the flask and the solution of 2-bromo-*m*-xylene (6.7 mmol, 1.28 g) in THF (3.6 mL) was added dropwise over 20 min. Additional THF was added to the flask and the reaction mixture was stirred for 1 h at room temperature. Then, the flask was cooled to 0 °C and 2-iodobenzaldehyde (6.7 mmol, 1.28 g) in THF (2.4 mL) was added dropwise over 16 min. The reaction mixture was allowed to room temperature and stirred for 2.5 h. Then, the reaction was quenched by saturated aqueous Na_2CO_3 and the aqueous layer was extracted with diethyl ether. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 90:10, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (1.42 g, 84%).

mp: 92-93 °C

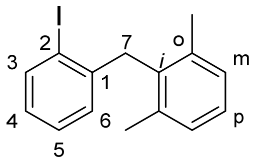
IR: (KBr) 3308 (OH) cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 7.88 (d, *J* = 7.7 Hz, 1H, 6-H), 7.30-7.21 (m, 2H, 3-H and 4-H), 7.14 (t, *J* = 7.7 Hz, 1H, *p*), 7.04 (d, *J* = 7.7 Hz, 2H, *m*), 6.97 (td, *J* = 7.7, 2.4 Hz, 1H, 5-H), 6.20 (d, *J* = 4.7 Hz, 1H, 7-H), 2.49 (d, *J* = 4.7 Hz, 1H, OH), 2.28 (s, 6H, CH_3 x 2)

^{13}C NMR (100 MHz, $CDCl_3$): 144.0 (s, C-1), 140.2 (d, C-6), 137.4 (s, *o*), 137.0 (s, *i*), 129.6 (d, *m*), 129.5 (d), 129.2 (d), 128.3 (d), 127.9 (d), 99.3 (s, C-2), 76.5 (d, C-7), 21.7 (q, CH_3 x 2)

HRMS: (EI, 70 eV) Calculated ($C_{15}H_{15}OI$) 338.0168, Found 338.0162

(S15) 2-(2-iodobenzyl)-1,3-dimethylbenzene



This manipulation was carried out according to the reported method (M. Yasuda, Y. Onishi, M. Ueba, T. Miyai, A. Baba, *J. Org. Chem.* **2001**, *66*, 7741.). To a solution of (2,6-dimethylphenyl)(2-iodophenyl)methanol (1.0 mmol, 0.337 g) in dichloromethane (1 mL) was added indium trichloride (0.16 mmol, 0.0371 g) and chlorodiphenylsilane (2 mmol, 0.41 mL). The mixture was stirred at room temperature for 2 h. Then, the reaction mixture was diluted by diethyl ether and water. The mixture was extracted with diethyl ether. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The crude product was purified by silica gel column chromatography (only hexane, column length 10 cm, diameter 26 mm silica gel) to give the titled product as a white solid (0.265 g, 83%).

mp: 60-65 °C

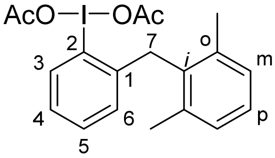
IR: (KBr) 2946, 1467, 1011, 775 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) 7.88 (dd, *J* = 7.7, 1.0 Hz, 1H, 6-H), 7.15-7.07 (m, 4H, 4-H, *m* and *p*), 6.88 (t, 1H, *J* = 7.7 Hz, 5-H), 6.50 (d, 1H, *J* = 7.7 Hz, 3-H), 3.97 (s, 2H, 7-H_2), 2.17 (s, 6H, CH_3 x 2)

^{13}C NMR (100 MHz, $CDCl_3$) 142.0 (s, C-1), 139.3 (d, C-6), 137.5 (s), 136.6 (s), 128.5 (d, *p*), 128.3 (d, *m*), 127.9 (d), 127.8, (d), 126.8 (d), 102.0 (s, C-2), 41.5 (t, C-7), 20.2 (q, CH_3 x 2)

HRMS: (FAB) Calculated ($C_{15}H_{15}I$) 322.0219, Found: 322.0128

(1h) (2-(2,6-dimethylbenzyl)phenyl)-λ^3-iodanediyl diacetate



To the flame-dried flask was added 2-(2-iodobenzyl)-1,3-dimethylbenzene (0.974 g, 3.02 mmol) and 9% peracetic acid (10 mL). The reaction mixture was stirred at room temperature over 12 h. The solvent was evaporated and the precipitated solid was washed with hexane. The remained hexane was evaporated to give the product as a white solid (1.21 g, 91%).

mp: 126-129 °C

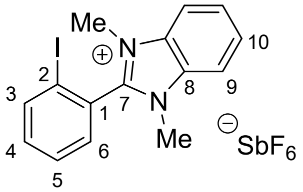
IR: (KBr) 1654 (C=O), 1278, 666 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (d, *J* = 7.6 Hz, 1H, 3-H), 7.40 (t, *J* = 7.6 Hz, 1H, 5-H), 7.27 (t, *J* = 7.6 Hz, 1H, 4-H), 7.17 (t, *J* = 7.2 Hz, 1H, *p*), 7.11 (d, *J* = 7.2 Hz, 2H, *m*), 6.76 (d, *J* = 7.6 Hz, 1H, 6-H), 4.37 (s, 2H, C-7), 2.21 (s, 6H, *o*-Me x 2), 2.02 (s, 6H, $COCH_3$ x 2)

^{13}C NMR (100 MHz, $CDCl_3$): 176.5 (s, *C*OCH$_3$), 141.3 (s, C-2), 137.6 (s, C-1), 137.5 (d, C-3), 134.8 (s, C-*o*), 132.9 (d, C-5), 128.9 (d), 128.52 (d), 128.48 (d), 127.8 (s, C-*i*), 127.2 (d), 38.3 (t, C-7), 20.4 (q, CO*C*H$_3$), 20.1 (q, *o*-Me)

HRMS: (ESI) Calculated ($C_{19}H_{21}IO_4Na$): 463.03767 ([M + Na]$^+$) Found: 463.03639

(S16) 2-(2-iodophenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium hexafluoroantimonate



To the solution of 2-(2-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (0.946 g, 1.99 mmol) in chloroform (20 mL) was added silver hexafluoroantimonate (0.815 g, 2.37 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was filtrated off and the obtained solid was extracted with hot chloroform. The obtained chloroform solution was evaporated to give a pale yellow solid. The product was used at the next step without further purification (1.12 g, 96%).

mp: 175-182 °C

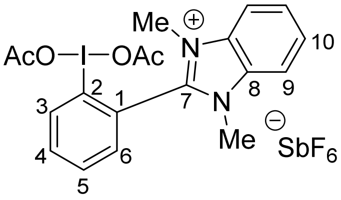
IR: (KBr) 1524, 1487, 1452, 756 cm^{-1}

^{1}H NMR (400 MHz, CD_3CN): 8.22 (d, *J* = 8.2 Hz, 1H, 3-H), 7.96 (dd, *J* = 6.3, 3.4 Hz, 2H, 9-H), 7.83-7.77 (m, 3H, 5-H and 10-H), 7.66 (dd, *J* = 8.2, 1.4 Hz, 1H, 6-H), 7.59 (td, *J* = 8.2, 1.4 Hz, 1H, 4-H), 3.81 (s, 6H, Me x 2)

^{13}C NMR (100 MHz, CD_3CN): 152.0 (s, C-7), 141.1 (d, C-3), 135.8 (d, C-4), 133.2 (d, C-6), 132.7 (s, C-8), 130.6 (d, C-5), 128.6 (d, C-10), 127.8 (s, C-1), 114.5 (d, C-9), 98.0 (s, C-2), 33.6 (q, Me)

HRMS: (FAB, 70 eV) Calculated ($C_{15}H_{14}N_2I$): 349.2002 ($[M - SbF_6]^+$), Found: 349.0198

(1k) 2-(2-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium hexafluoroantimonate



This manipulation was carried out according to the reported method (M. Uyanik, T. Yasui, K. Ishihara, *Angew. Chem. Int. Ed.* **2013**, *52*, 9215.). To the flame-dried flask was added 2-(2-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium hexafluoroantimonate (0.879 g, 1.50 mmol) and 9% peracetic acid (7 mL). The reaction mixture was stirred at 45 ºC over 12 h. After cooling to room temperature, the solvent was evaporated. Then, the precipitated solid was washed with acetic acid over 3 times. The solid was washed with diethyl ether (anhydrous) to remove acetic acid. Remained ether was evaporated to give the product as a white solid (0.661 g, 63%).

mp: 117-132 °C (decomposed)

IR: (KBr) 1646 (C=O), 1274, 658 cm^{-1}

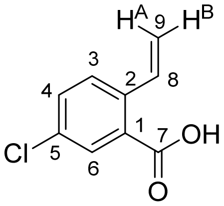
^{1}H NMR (400 MHz, CD_3CN): 8.66 (d, *J* = 7.7, 1.3 Hz, 1H, 3-H), 8.08 (td, *J* = 7.7, 1.3 Hz, 1H, 5-H), 8.01 (td, *J* = 7.7, 1.8 Hz, 1H, 4-H), 7.97-7.93 (m, 3H, 6-H and 9-H), 7.83-7.79 (m, 2H, 10-H), 3.87 (s, 6H, NMe x 2), 1.89 (s, 6H, OAc x 2)

^{13}C NMR (100 MHz, CD_3CN): 177.8 (s, *C*OCH$_3$), 149.4 (s, C-7), 139.5 (d, C-3), 136.9 (d, C-4), 134.8 (d, C-5), 134.2 (d, C-6), 133.0 (s, C-8), 128.8 (d, C-10), 125.9 (s, C-2), 123.7 (s, C-1), 114.7 (d, C-9), 34.2 (q, NMe), 20.3 (q, CO*C*H$_3$)

HRMS: (ESI) Calculated ($C_{19}H_{20}N_2O_4I$): 467.0462 ($[M - BF_4]^+$), Found: 467.0476

Syntheses of 2-Vinylbenzoic Acids 2

(2a) 5-chrolo-2-vinylbenzoic acid



To a solution of methyl 5-chrolo-2-vinylbenzoate (0.195 g, 0.99 mmol) in a THF/MeOH/H_2O (4:1:1) mixture (6 mL) was added LiOH (0.0806 g, 3.37 mmol). The reaction mixture was stirred at 70 °C overnight. After cooled to room temperature, the mixture was diluted by water. Then, THF and MeOH were removed under a reduced pressure. The aqueous layer was washed by CH_2Cl_2 and acidified by 1 M HCl aq, and then, the target benzoic acid was precipitated. The resulting solid was extracted by CH_2Cl_2. The CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated to give a white solid (0.158 g, 88%). This is known compound and spectroscopic data were identical with those from the reported literature.[1]

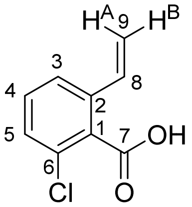
^{1}H NMR (400 MHz, $CDCl_3$): 11.85 (br s, 1H, COOH), 8.03 (d, J = 2.2 Hz, 1H, 6-H), 7.58-7.47 (m, 3H), 5.67 (d, J = 17.4 Hz, 1H, 9-H^A), 5.42 (d, J = 11.1 Hz, 1H, 9-H^B)

^{13}C NMR (100 MHz, $CDCl_3$): 172.0, 139.2, 135.0, 133.5, 133.4, 131.3, 129.1, 128.3, 117.7

HRMS: (EI, 70 eV)

Calculated ($C_9H_7ClO_2$): 182.0135; Found: 182.0131

(2b) 6-chloro-2-vinylbenzoic acid



To a solution of methyl 6-chloro-2-vinylbenzoate (0.278 g, 1.41 mmol) in a THF/MeOH/H_2O (4:1:1) mixture (6.4 mL) was added LiOH (0.0962 g, 4.02 mmol). The reaction mixture was stirred at 70 °C overnight. After cooled to room temperature, the mixture was diluted by water. Then, THF and MeOH were removed under a reduced pressure. The aqueous layer was washed by CH_2Cl_2 and acidified by 1 M HCl aq, and then, the target benzoic acid was precipitated. The resulting solid was extracted by CH_2Cl_2. The CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated to give a white solid (0.124 g, 48%).

mp: 99-101 °C

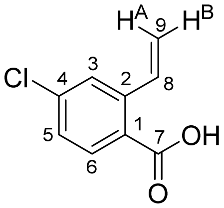
IR: (KBr) 3018 (O-H), 1705 (C=O), 1282 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 11.72 (br s, 1H, COOH), 7.54-7.50 (m, 1H, 4-H), 7.39-7.34 (m, 2H, 3-H and 5-H), 6.88 (dd, J = 17.3, 11.0 Hz, 1H, 8-H), 5.82 (d, J = 17.3 Hz, 1H, 9-H^A), 5.47 (d, J = 11.0 Hz, 1H, 9-H^B)

^{13}C NMR (100 MHz, $CDCl_3$): 172.9 (s, C-7), 137.2 (s, C-2), 132.8 (d, C-8), 131.3 (s), 131.03 (s), 130.96 (d), 128.8 (d), 124.0 (d, C-4), 118.9 (t, C-9)

HRMS: (EI, 70 eV) Calculated ($C_9H_7ClO_2$) 182.0135, Found: 182.0134

(2c) 4-chloro-2-vinylbenzoic acid



A sealable reactor vessel was charged with methyl 4-chloro-2-vinylbenzoate (0.551 g, 2.80 mmol), lithium hydroxide (0.186 g, 7.78 mmol), a THF/methanol/water (4:1:1) mixture (10 ml), sealed and stirred at 70 °C overnight. The reaction mixture was diluted with water, followed by evaporation of THF and methanol under reduced pressure. Then, the water phase residue was washed with DCM, acidified with 1M HCl to pH = 3, and extracted with DCM. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum, yielding 0.451 g (89%) of the titled product. This procedure was referred to the reported literature.[2]

mp: 152-153 °C

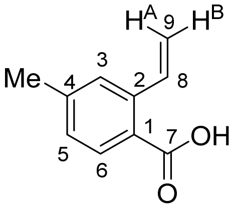
IR: (KBr) 2817 (OH), 1685 (C=O) cm^{-1}

^1H NMR (400 MHz, $CDCl_3$): 8.00 (d, J = 8.4 Hz, 1H, 6-H), 7.58-7.51 (m, 2H, 3-H and 8-H), 7.34 (dd, J = 8.4, 2.2 Hz, 1H, 5-H), 5.69 (d, J = 17.4 Hz, 1H, 9-H^A), 5.44 (d, J = 10.6 Hz, 1H, 9-H^B)

^{13}C NMR (100 MHz, $CDCl_3$): 172.0 (s, C-7), 142.6 (s, C-2), 139.7 (s, C-4), 135.1 (d, C-8), 133.0 (d, C-6), 127.85 (d), 127.80 (d), 125.4 (s, C-1), 118.2 (t, C-9)

HRMS: (EI, 70 eV) Calculated ($C_9H_7ClO_2$): 182.0135; Found: 182.0132

(2f) 4-methyl-2-vinylbenzoic acid

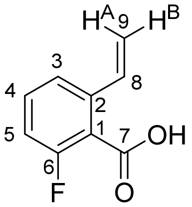


To a solution of methyl 5-chrolo-2-vinylbenzoate (0.124 g, 0.70 mmol) in a THF/MeOH/H_2O (4:1:1) mixture (4 mL) was added LiOH (0.0539 g, 2.25 mmol). The reaction mixture was stirred at 70 °C overnight. After cooled to room temperature, the mixture was diluted by water. Then, THF and MeOH were removed under a reduced pressure. The aqueous layer was washed by CH_2Cl_2 and acidified by 1 M HCl aq, and then, the target benzoic acid was precipitated. The resulting solid was extracted by CH_2Cl_2. The CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated to give a white solid (0.103 g, 90%). This is known compound and spectroscopic data were identical with those from literature.[2]

^1H NMR (400 MHz, $CDCl_3$): 12.46 (br s, 1H, COOH), 7.97 (d, J = 8.3 Hz, 1H), 7.60 (dd, J = 17.4, 10.9 Hz, 1H, 8-H), 7.41 (s, 1H, 3-H), 7.18 (d, J = 8.3 Hz, 1H), 5.66 (d, J = 17.4 Hz, 1H, 9-H^A), 5.37 (d, J = 10.9 Hz, 1H, 9-H^B), 2.43 (s, 3H, Me)

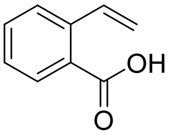
^{13}C NMR (100 MHz, $CDCl_3$): 173.1, 144.0, 140.9, 136.5, 131.7, 128.5, 128.5, 124.4, 116.6, 21.8
HRMS: (EI, 70 eV) Calculated ($C_{10}H_{10}O_2$) 162.0681, Found: 162.0677

(2g) 6-fluoro-2-vinylbenzoic acid



To a solution of methyl 6-fluoro-2-vinylbenzoate (0.402 g, 2.04 mmol) in a THF/MeOH/H_2O (4:1:1) mixture (4 mL) was added LiOH (0.132 g, 5.52 mmol). The reaction mixture was stirred at 70 °C overnight. After cooled to room temperature, the mixture was diluted by water. Then, THF and MeOH were removed under a reduced pressure. The aqueous layer was washed by CH_2Cl_2 and acidified by 1 M HCl aq, and then, the target benzoic acid was precipitated. The resulting solid was extracted by CH_2Cl_2. The CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated to give a white solid (0.337 g, 99%).
mp: 126-127 °C
IR: (KBr) 2998 (OH), 1707 (C=O) cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): 7.47-7.39 (m, 2H, 3-H and 4-H), 7.11-7.02 (m, 2H, 8-H and 5-H), 5.78 (d, J = 17.4 Hz, 1H, 9-H^A), 5.44 (d, J = 10.6 Hz, 1H, 9-H^B)
^{13}C NMR (100 MHz, $CDCl_3$): 170.5 (s, C-7), 160.6 (s, d, $^1J_{CF}$ = 253 Hz, C-6), 139.5 (s, C-2), 133.5 (d, d, $^4J_{CF}$ = 2.5 Hz, C-8), 132.5 (d, d, $^3J_{CF}$ = 9.0 Hz, C-4), 122.0 (d, d, $^4J_{CF}$ = 3.3 Hz, C-3), 118.9 (s, $^2J_{CF}$ = 14.7 Hz, C-1), 118.6 (t, C-9), 115.3 (d, d, $^2J_{CF}$ = 22.1 Hz, C-5)
^{19}F NMR (377 MHz, $CDCl_3$, external standard:TFA in D_2O): -115.36
HRMS: (EI, 70 eV) Calculated ($C_9H_7FO_2$) 166.0430, Found: 166.0428

(2h) 2-vinylbenzoic acid



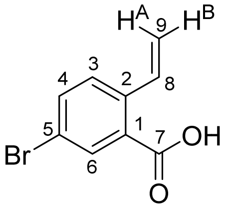
To a dried 100 mL three necked round bottom flask equipped with a reflux condenser and a dropping funnel was added magnesium metal turnings (0.378 g, 16 mmol). THF (30 mL) was added to the flask. The solution of 2-bromostyrene (2.76 g, 15 mmol) in THF was added dropwise by dropping funnel into the flask at room temperature. After exothermic reaction, the mixture was stirred at 70 °C for 2 h. Then, the mixture was allowed to room temperature and poured onto dry ice in a beaker. The mixture was washed with ether, and then, water was added poured into the beaker. The water phase was acidified to pH ~ 1 with 1 N HCl aq and extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure to yield 2-vinylbenzoic acid (1.54 g, 69%). The spectral data accorded with reference data.[3]

^{1}H NMR (400 MHz, $CDCl_3$): 11.93 (br s, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.63-7.54 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 5.68 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.40 (dd, *J* = 11.0, 1.3 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): 173.3, 140.8, 136.2, 133.3, 131.5, 127.8, 127.7, 127.2, 117.0

HRMS: (EI, 70 eV) Calculated ($C_9H_8O_2$): 148.0524, Found: 148.0522

(2j) 5-bromo-2-vinylbenzoic acid



A sealable reactor vessel was charged with methyl 5-bromo-2-vinylbenzoate (0.125 g, 0.518 mmol), lithium hydroxide (0.0435 g, 1.82 mmol), a THF/methanol/water (4:1:1) mixture (3 ml), sealed and stirred at 70 °C overnight. The reaction mixture was diluted with water, followed by evaporation of THF and methanol under reduced pressure. Then, the water phase residue was washed with DCM, acidified with 1M HCl to pH = 3, and extracted with DCM. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum, yielding 0.105 g (89%) of the titled product. This procedure was referred by the reported literature.[2]

mp: 134-135 °C

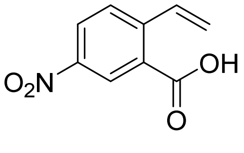
IR: (KBr) 2995 (OH), 1698 (C=O) cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 8.18 (d, *J* = 1.9 Hz, 1H, 6-H), 7.66 (dd, *J* = 8.7, 1.9 Hz, 1H, 4-H), 7.54-7.47 (m, 2H, 3-H and 8-H), 5.68 (d, *J* = 17.4 Hz, 1H, 9-H^A), 5.42 (d, *J* = 11.1 Hz, 1H, 9-H^B)

^{13}C NMR (100 MHz, $CDCl_3$): 171.9 (s, C-7), 139.7 (s, C-2), 136.3 (d, C-4), 135.1 (d, C-8), 134.2 (d, C-6), 129.3 (d, C-3), 128.7 (s, C-1), 121.4 (s, C-5), 117.8 (t, C-9)

HRMS: (EI, 70 eV) Calculated ($C_9H_7BrO_2$): 225.9629, Found: 225.9630

(2k) 5-nitro-2-vinylbenzoic acid



A sealable reactor vessel was charged with methyl 5-nitro-2-vinylbenzoate (0.603 g, 2.9 mmol), lithium hydroxide (0.817 g, 34 mmol), a THF/methanol/water (4:1:1) mixture (10 ml), sealed and stirred at rt overnight. The reaction mixture was diluted with water, followed by evaporation of THF and methanol under reduced pressure. Then, the water phase residue was washed with DCM, acidified with 1M HCl to pH = 3, and extracted with DCM. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum, yielding 0.519 g (92%) of the titled product. This procedure was referred to the following literature and the NMR data were agreement with the reported data.[2]

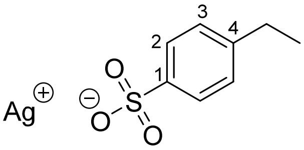
^{1}H NMR (400 MHz, $CDCl_3$): 8.92 (d, *J* = 2.4 Hz, 1H), 8.39 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.64 (dd, *J* = 17.3, 11.4 Hz, 1H), 5.86 (d, *J* = 17.3 Hz, 1H), 5.63 (d, *J* = 11.4 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): 170.9, 146.9, 146.7, 134.4, 129.0, 127.9, 127.7, 126.9, 121.2

HRMS: (EI, 70 eV) Calculated ($C_9H_7NO_4$): 193.0375, Found: 193.0371

Syntheses of ethylbenzenesulfonate salts 12 and 13

silver 4-ethylbenzenesulfonate



To a solution of 4-ethylbenzenesulfonic acid (2.08 g, 11.2 mmol) in deionized H_2O (16 mL) was added $AgNO_3$ (1.96 g, 11.5 mmol). The mixture was stirred over night at room temperature. H_2O in the reaction mixture was evaporated and the precipitated solid was washed with small amount of deionized water. Then the solid was dried with dried N_2 flow to give a white solid (1.25 g, 37%). This procedure was referred by the following report.[4]

mp: This compound was decomposed and did not melt during 200-297 °C

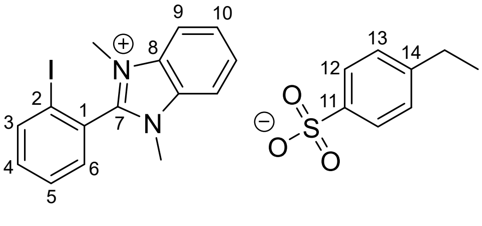
IR: (KBr) 2894, 1406, 1189, 1038, 1011 cm^{-1}

^1H NMR (400 MHz, D_2O): 7.75 (d, J = 7.5 Hz, 2H, 2-H), 7.42 (d, J = 7.5 Hz, 2H, 3-H), 2.72 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.23 (t, J = 7.6 Hz, 3H, CH_2CH_3)

^{13}C NMR (100 MHz, D_2O): 165.9 (s, C-1), 156.8 (s, C-4), 145.4 (d, C-3), 142.6 (d, C-2), 45.3 (t, CH_2CH_3), 31.9 (q, CH_2CH_3)

Analysis: $C_8H_9AgO_3S\bullet 1/3H_2O$ (299.09) Calcd: C, 32.13; H, 3.26, Found: C, 32.21; H, 3.24

(12) 2-(2-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium 4-ethylbenzenesulfonate



To a solution of 2-(2-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (0.0949 g, 0.199 mmol) in $CHCl_3$ (2 mL) was added silver 4-ethylbenzenesulfonate (0.0695 g, 0.0237 mmol) under N_2 atmosphere. The mixture was stirred over night at room temperature. The reaction mixture was filtrated off to remove AgI and the $CHCl_3$ solution was evaporated under reduced pressure. The product was washed with dried THF to give a white solid (0.0579 g, 54%).

mp: 163-165 ºC

IR: (KBr) 3518, 1219, 1194, 1035, 1012, 676 cm^{-1}

^1H NMR (400 MHz, CD_2Cl_2): 8.10 (m, 2H, 3-H and 6-H), 7.80 (dd, J = 6.3, 3.2 Hz, 2H, 9-H), 7.72 (t, J = 7.7 Hz, 1H), 7.67 (dd, J = 6.3, 3.2 Hz, 2H, 10-H), 7.49 (td, J = 7.7, 1.2 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H, 12-H), 7.01 (d, J = 8.2 Hz, 2H, 13-H), 3.81 (s, 6H, Me x 2), 2.59 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.18 (t, J = 7.6 Hz, 3H, CH_2CH_3)

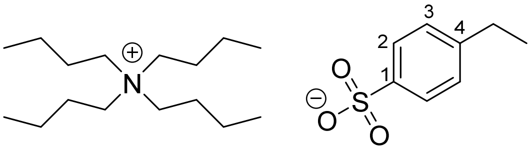
^{13}C NMR (100 MHz, CD_2Cl_2): 151.3 (s, C-7), 145.3 (s), 140.1 (d), 135.0 (d), 134.0 (d), 132.1 (s, C-8), 130.2 (d), 127.7 (d), 127.5 (d), 127.4 (s, C-1), 126.0 (d, C-12), 113.6 (d, C-9), 97.2 (s, C-2), 33.2 (q, NMe x 2), 29.0 (t, $\mathit{C}H_2CH_3$), 15.8 (q, $CH_2\mathit{C}H_3$)

^{1}H NMR (400 MHz, CD_3CN): 8.20 (d, $J = 7.7$ Hz, 1H, 3-H), 7.97-7.95 (m, 2H, 9-H), 7.78-7.73 (m, 4H, 5-H, 6-H and 10-H), 7.59-7.53 (m, 3H, 4-H and 12-H), 7.13 (d, $J = 7.7$ Hz, 2H, 13-H), 3.80 (s, 6H, NMe x 2), 2.62 (q, $J = 7.6$ Hz, 2H, $C\mathit{H_2}CH_3$), 1.19 (t, $J = 7.6$ Hz, 3H, $CH_2C\mathit{H_3}$)

^{13}C NMR (100 MHz, CD_3CN): 151.9 (s, C-7), 147.1 (s), 145.7 (s), 140.9 (d, C-3), 135.7 (d), 133.4 (d), 132.6 (s, C-8), 130.4 (d), 128.4 (d), 128.0 (d), 127.8 (s, C-1), 126.7 (d, C-12), 114.4 (d, C-9), 98.1 (s, C-2), 33.5 (q, NMe x 2), 29.1 (t, $\mathit{C}H_2CH_3$), 16.0 (q, $CH_2\mathit{C}H_3$)

Analysis: $C_{23}H_{23}IN_2O_3S$ (534.41) Calcd: C, 51.69; H, 4.34; N, 5.24, Found: C, 51.36; H, 4.44; N, 5.24

(13) tetrabutylammonium 4-ethylbenzenesulfonate



To a solution of Bu_4NBr (0.0676 g, 0.210 mmol) in $CHCl_3$ (2 mL) was added silver 4-ethylbenzenesulfonate (0.0702 g, 0.240 mmol) under N_2 atmosphere. The mixture was stirred over night at room temperature. The reaction mixture was filtrated off to remove AgI and the $CHCl_3$ solution was evaporated under reduced pressure to give a white solid (0.0859 g, 96%).

mp: 85-88 ºC

IR: (KBr) 2963, 2873, 1638, 1487, 1461, 1190 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 7.80 (d, $J = 8.2$ Hz, 2H, 2-H), 7.13 (d, $J = 8.2$ Hz, 2H, 3-H), 3.24-3.20 (m, 8H, $C\mathit{H_2}CH_2CH_2CH_3$ x 4), 2.62 (q, $J = 7.6$ Hz, 2H, 4-$C\mathit{H_2}CH_3$), 1.61-1.53 (m, 8H, $CH_2C\mathit{H_2}CH_2CH_3$ x 4), 1.42-1.32 (m, 8H, $CH_2CH_2C\mathit{H_2}CH_3$ x 4), 1.19 (t, $J = 7.6$ Hz, 3H, 4-$CH_2C\mathit{H_3}$), 0.95 (t, $J = 7.5$ Hz, 12H, $CH_2CH_2CH_2C\mathit{H_3}$ x 4)

^{13}C NMR (100 MHz, $CDCl_3$): 145.1 (s), 144.8 (s), 127.3 (d, C-3), 126.3 (d, C-2), 58.7 (t, $\mathit{C}H_2CH_2CH_2CH_3$), 28.8 (t, 4-$\mathit{C}H_2CH_3$), 24.0 (t, $CH_2\mathit{C}H_2CH_2CH_3$), 19.7 (t, $CH_2CH_2\mathit{C}H_2CH_3$), 15.7 (q, 4-$CH_2\mathit{C}H_3$), 13.7 (q, $CH_2CH_2CH_2\mathit{C}H_3$)

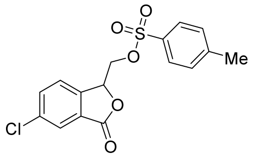
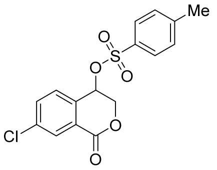
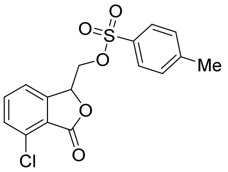
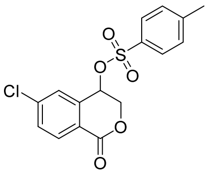
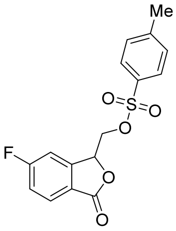
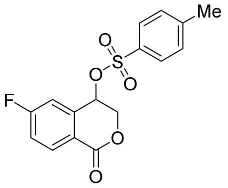
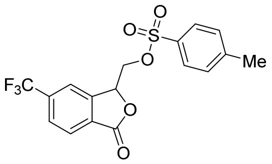
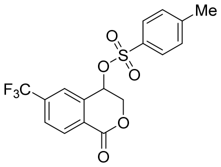
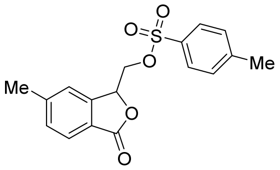
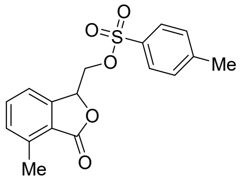
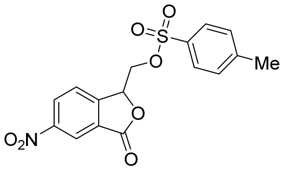
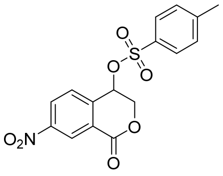
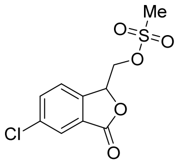
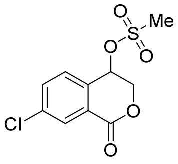
Analysis: $C_{24}H_{45}NO_3S$ (427.69) Calcd: C, 67.40; H, 10.61; N, 3.28, Found: C, 67.17; H, 10.71; N, 3.33

Products

The preparation and characterization of new compounds were described below. Products **4ha** and **3ha** were reported compounds (The spectral data was agreement with the reference[5]). Compounds **3ia** and **3ab** could not be isolated because they were decomposed by a silica gel column chromatography.

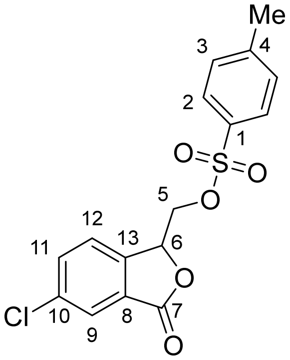
List of X-ray crystal structures

The structures of following products were determined by X-ray diffraction analysis.

4a (from 2a and 5a)  CCDC 2044374	**3a (from 2a and 5a)**  CCDC 2044375	**4ba (from 2b and 5a)**  CCDC 2044376
3ca (from 2c and 5a)  CCDC 2044377	**4da (from 2d and 5a)**  CCDC 2044378	**3da (from 2d and 5a)**  CCDC 2044379
4ea (from 2e and 5a)  CCDC 2044380	**4ea (from 2e and 5a)**  CCDC 2049845	**4fa (from 2f and 5a)**  CCDC 2044382
4ia (from 2i and 5a)  CCDC 2044390	**4ka (from 2k and 5a)**  CCDC 2044391	**3ka (from 2k and 5a)**  CCDC 2044392
4ag (from 2a and 5g)  CCDC 2049846	**3ag (from 2a and 5g)**  CCDC 2049847	

4a (from 2a and 5a)

(5-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.103 g, 0.87 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0290 g, 0.152 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0287 g, 0.157 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water phase was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4a** and **3a**; 64%, ratio **4a**/**3a** = 91:9). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0207 g, 37%).

The structure was determined by X-ray crystallography (Deposition number: CCDC 2044374)

Rf (hexane/ethyl acetate = 50:50): 0.61

mp: 146-152 °C

IR: (KBr) 1755 cm^{-1} (C=O)

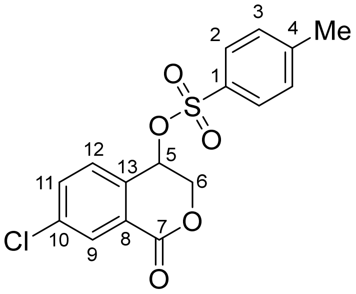
^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (d, J = 1.7 Hz, 1H, 9-H), 7.71 (d, J = 8.2 Hz, 2H, 2-H), 7.64 (dd, J = 8.2, 1.7 Hz, 1H, 11-H), 7.45 (d, J = 8.2 Hz, 1H, 12-H), 7.35 (d, J = 8.2 Hz, 2H, 3-H), 5.60 (t, J = 4.7 Hz, 1H, 6-H), 4.41-4.33 (m, 2H, 5-H_2), 2.46 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 168.0 (s, C-7), 145.7 (s, C-1), 143.4 (s, C-13), 136.7 (s, C-10), 134.8 (d, C-11), 132.2 (s, C-4), 130.2 (d, C-3), 128.2 (s, C-8), 128.0 (d, C-2), 126.1 (d, C-9), 123.9 (d, C-12), 77.4 (d, C-6), 68.4 (t, C-5), 21.8 (q, 4-Me)

HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}ClO_5S$) 352.0172, Found: 352.0174

3a (from 2a and 5a)

7-chloro-1-oxoisochroman-4-yl 4-methylbenzenesulfonate



To a solution of PhI(OH)(OTs) (0.177 g, 0.300 mmol) in CH_2Cl_2 (5 mL) was added 5-chloro-2-vinylbenzoic acid (0.0554 g, 0.450 mmol). The reaction mixture was stirred for 3 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4a** and **3a**; 69%, ratio **4a**/**3a** = 4:96). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0332 g, 31%).

The structure was determined by X-ray crystallography (Deposition number: CCDC 2044375).

Rf (hexane/ethyl acetate = 50:50): 0.78

mp: 107-109 °CIR: (KBr) 1718 (C=O) cm^{-1}

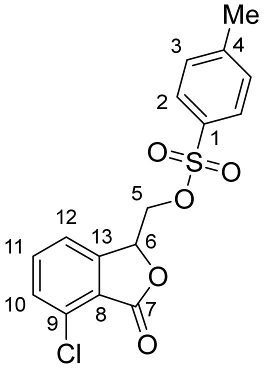
^{1}H NMR (400 MHz, $CDCl_3$): 8.08 (d, *J* = 2.4 Hz, 1H, 9-H), 7.76 (d, *J* = 8.2 Hz, 2H, 2-H), 7.57 (dd, *J* = 8.2, 2.4 Hz, 1H, 11-H), 7.36 (d, *J* = 8.2 Hz, 2H, 3-H), 7.28 (d, *J* = 8.2 Hz, 1H, 12-H), 5.66 (t, *J* = 2.7 Hz, 1H, 5-H), 4.69 (dd, *J* = 12.7, 2.7 Hz, 1H, 6-H), 4.55 (dd, *J* = 12.7, 2.7 Hz, 1H, 6-H), 2.47 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 161.9 (s, C-7), 145.8 (s, C-1), 137.5 (s, C-10), 134.6 (d, C-11), 133.4 (s, C-4), 132.4 (s, C-13), 130.5 (d), 130.2 (d, C-3), 129.7 (d), 127.9 (d, C-2), 126.5 (s, C-8), 70.8 (d, C-5), 69.6 (t, C-6), 21.8 (q, 4-Me)

HRMS: (FAB, 70 eV) Calculated ($C_{16}H_{14}ClO_5S$) 353.0250 ([M + H]$^+$), Found: 353.0248

4ba (from 2b and 5a)

(4-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.103 g, 0.185 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0295 g, 0.155 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The aforementioned procedure was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 6-chloro-2-vinylbenzoic acid (0.0277 g, 0.152 mmol) and the reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ba** and **3ba**; 51%, ratio **4ba**/**3ba** = 88:12). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0221 g, 0.0626 mmol, 41%).

The structure was determined by X-ray crystallography (Deposition number: CCDC 2044376)

Rf (hexane/ethyl acetate = 50:50): 0.55

mp: 128-130 °C

IR: (KBr) 1768 (C=O) cm^{-1}

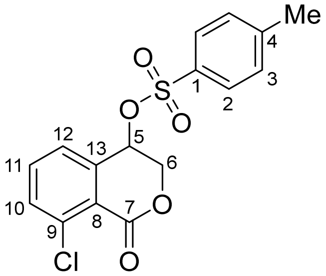
^{1}H NMR (400 MHz, $CDCl_3$): 7.73 (d, *J* = 8.4 Hz, 2H, 2-H), 7.62 (t, *J* = 7.7 Hz, 1H, 11-H), 7.53 (d, *J* = 7.7 Hz, 1H, 12-H), 7.42 (d, *J* = 7.5 Hz, 1H, 10-H), 7.36 (d, *J* = 8.4 Hz, 2H, 3-H), 5.55 (t, *J* = 4.8 Hz, 1H, 6-H), 4.36 (d, *J* = 4.8 Hz, 2H, 5-H_2), 2.46 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 166.2 (s, C-7), 147.4 (s, C-13), 145.6 (s, C-1), 135.3 (d, C-11), 133.8 (s, C-9), 132.0 (s, C-4), 131.5 (d, C-12), 130.1 (d, C-3), 127.9 (d, C-2), 122.9 (s, C-8), 120.9 (d, C-10), 76.0 (d, C-6), 68.3 (t, C-5), 21.7 (q, 4-Me)

HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}ClO_5S$) 352.0172, Found: 352.0166

3ba (from 2b and 5a)

8-chloro-1-oxoisochroman-4-yl 4-methylbenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0572 g, 0.177 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH· H_2O (0.0282 g, 0.148 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation were repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 6-chloro-2-vinylbenzoic acid (0.0273 g, 0.150 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a yellow solid (0.0280 g, 53%).

Rf (hexane/ethyl acetate = 50:50): 0.63

mp: 154-156 °C

IR (KBr): 1750 (C=O) cm^{-1}

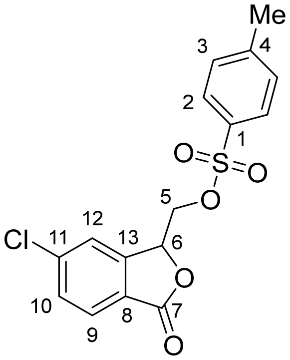
^{1}H NMR (400 MHz, $CDCl_3$): 7.76 (d, J = 8.4 Hz, 2H, 2-H), 7.59 (dd, J = 7.8, 1.0 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H, 11-H), 7.34 (d, J = 8.4 Hz, 2H, 3-H), 7.29 (d, J = 7.8 Hz, 1H), 5.66 (t, J = 2.9 Hz, 1H, 5-H), 4.60 (dd, J = 12.6, 2.9 Hz, 1H, 6-H), 4.48 (dd, J = 12.6, 2.9 Hz, 1H, 6-H), 2.46 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 159.4 (s, C-7), 145.8 (s, C-1), 137.3 (s), 137.0 (s), 134.3 (d), 134.2 (d), 133.4 (s), 130.2 (d, C-3), 127.9 (d, C-2), 126.7 (d), 122.6 (s, C-13), 71.8 (d, C-5), 68.7 (t, C-6), 21.9 (q, 4-Me)

HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}ClO_5S$): 352.0172, Found: 352.0168

4ca (from 2c and 5a)

(6-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.104 g, 0.188 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0283 g, 0.157 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, CH_2Cl_2 (0.3 mL) and 4-chrolo-2-vinylbenzoic acid (0.0279 g, 0.153 mmol) were added to the flask and stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted by CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ca** and **3ca**; 73%, ratio **4a**/**3a** = >99:<1). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0306 g, 0.0867 mmol, 60%).

Rf (hexane/ethyl acetate = 50:50): 0.72

mp: 170-173 °C

IR: (KBr) 1765 (C=O) cm^{-1}

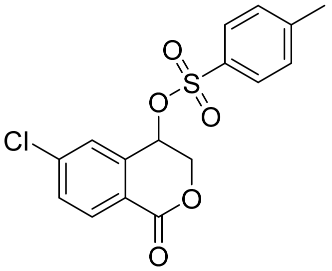
^{1}H NMR (400 MHz, $CDCl_3$): 7.83 (d, *J* = 7.5 Hz, 1H, 9-H), 7.73 (d, *J* = 8.7 Hz, 2H, 2-H), 7.55 (d, *J* = 7.5 Hz, 1H, 10-H), 7.43 (s, 1H, 12-H), 7.36 (d, *J* = 8.2 Hz, 2H, 3-H), 5.57 (t, *J* = 4.8 Hz, 1H, 6-H), 4.36 (d, *J* = 4.8 Hz, 2H, 5-H_2), 2.47 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 168.3 (s, C-7), 146.9 (s, C-13), 145.7 (s, C-1), 141.4 (s, C-8), 132.0 (s, C-4), 131.0 (d, C-10), 130.2 (d, C-3), 128.1 (d, C-2), 127.3 (d, C-9), 124.9 (s, C-11), 123.0 (d, C-12), 76.8 (d, C-6), 68.3 (t, C-5), 21.9 (q, 4-Me)

HRMS: (EI, 70 mV) Calculated ($C_{16}H_{13}ClO_5S$) 352.0172, Found: 352.0178

3ca (from 2c and 5a)

6-chloro-1-oxoisochroman-4-yl 4-methylbenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0576 g, 0.179 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0300 g, 0.158 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The aforementioned procedure was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 4-chloro-2-vinylbenzoic acid (0.0267 g, 0.147 mmol) and stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ca** and **3ca**; 74%, ratio **4ca**/**3ca** = 37:63). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) and recycle HPLC (hexane/ethyl acetate = 50:50) to give the titled compound as a white solid (0.0031 g, 0.0093 mmol, 6%). The structure was determined by X-ray crystallography (Deposition number: CCDC 2044377)

Rf (hexane/ethyl acetate = 50:50): 0.67

mp: 149-150 °C

IR: (KBr) 1724 (C=O) cm^{-1}

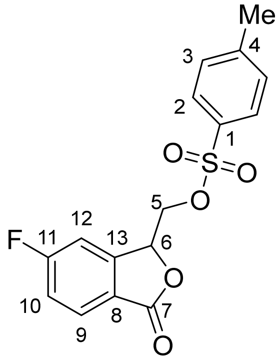
^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.51 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 1.9 Hz, 1H), 5.60 (t, *J* = 2.9 Hz, 1H), 4.68 (dd, *J* = 12.6, 3.4 Hz, 1H), 4.55 (dd, *J* = 13.0, 2.9 Hz, 1H), 2.47 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 162.2 (s), 145.9 (s), 140.9 (s), 135.6 (s), 133.2 (s), 132.3 (d), 131.4 (d), 130.3 (d), 128.03 (d), 127.98 (d), 123.3 (s), 70.9 (d), 69.5 (t), 21.8 (q)

HRMS: (ESI) Calculated ($C_{16}H_{13}O_5NaSCl$):375.0064 ([M + Na]$^+$), Found: 375.0058

4da (from 2d and 5a)

(6-fluoro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.0994 g, 0.179 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0293 g, 0.154 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The aforementioned procedure was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 4-fluoro-2-vinylbenzoic acid (0.0266 g, 0.160 mmol) and the reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4da** and **3da**; 67%, ratio **4da**/**3da** = 90:10). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0312 g, 0.0928 mmol, 58%). The structure was determined by X-ray crystallography (Deposition number: CCDC 2044378)

Rf (hexane/ethyl acetate = 50:50): 0.64

mp: 179-181 °C

IR: (KBr) 1763 (C=O) cm^{-1}

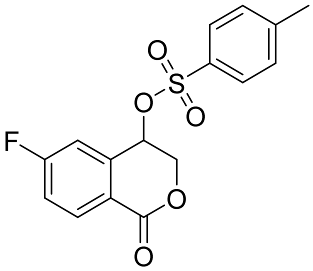
^{1}H NMR (400 MHz, $CDCl_3$): 7.90 (d, J = 8.6 Hz, d, $^4J_{HF}$ = 4.8 Hz, 1H, 9-H), 7.73 (d, J = 8.2 Hz, 2H, 2-H), 7.36 (d, J = 8.2 Hz, 2H, 3-H), 7.27 (dd, J = 8.6, 2.2 Hz, d, $^3J_{HF}$ = 8.6 Hz, 1H, 10-H), 7.13 (d, J = 2.2 Hz, d, $^3J_{HF}$ = 7.7 Hz, 1H, 12-H), 5.57 (t, J = 4.8 Hz, 1H, 6-H), 4.40-4.32 (m, 2H, 5-H_2) 2.47 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 168.0 (s, C-7), 166.8 (s, d, $^1J_{CF}$ = 284 Hz, C-11), 148.0 (s, d, $^3J_{CF}$ = 11 Hz, C-13), 145.8 (s, C-1), 132.0 (s, C-4), 130.2 (d, C-3), 128.6 (d, d, $^3J_{CF}$ = 11 Hz, C-9), 128.1 (d, C-2), 122.4 (s, d, $^4J_{CF}$ = 2 Hz, C-8), 118.5 (d, d, $^2J_{CF}$ = 25 Hz, C-10), 110.1 (d, d, $^2J_{CF}$ = 25 Hz, C-12), 76.7 (d, d, $^4J_{CF}$ = 3 Hz, C-6), 68.3 (t, C-5), 21.9 (q, 4-Me)

^{19}F NMR (377 MHz, $CDCl_3$, external standard:TFA in D_2O): -101.37

HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}FO_5S$) 336.0468, Found: 336.0466

3da (from 2d and 5a)



To a solution of PhI(OAc)$_2$ (0.0568 g, 0.176 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added *p*-TsOH•H$_2$O (0.0295 g, 0.155 mmol) under N$_2$ atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH$_2$Cl$_2$ and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N$_2$. The evaporation and N$_2$-filling manipulation was repeated twice. After evaporation, to the mixture was added CH$_2$Cl$_2$ (0.3 mL) and 4-fluoro-2-vinylbenzoic acid (0.0259 g, 0.156 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CH$_2$Cl$_2$. The collected organic layer was dried over MgSO$_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4da** and **3da**; 47%, ratio **4da**/**3da** = 53:47). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0059 g, 0.0175 mmol, 11%). The structure was determined by X-ray crystallography (CCDC 2044379).

Rf (hexane/ethyl acetate = 50:50): 0.67

mp: 143-145 °C

IR: (KBr) 1714 (C=O) cm^{-1}

^{1}H NMR (400 MHz, CDCl$_3$): 8.15 (d, J = 8.7, d, J_{HF} = 5.8 Hz, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.23 (dd, J = 8.7, 2.4 Hz, d, J_{HF} = 8.5 Hz, 1H), 6.96 (d, J = 2.4 Hz, d, J_{HF} = 8.2 Hz, 1H), 5.63 (t, J = 3.4 Hz, 1H), 4.65 (dd, J = 12.8, 3.4 Hz, 1H), 4.56 (dd, J = 12.8, 3.4 Hz, 1H), 2.48 (s, 3H)

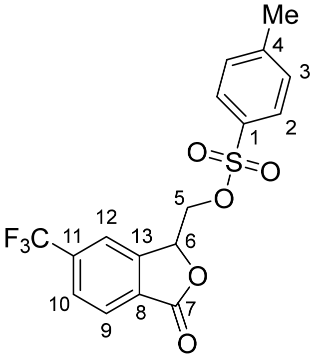
^{13}C NMR (100 MHz, CDCl$_3$): 167.2 (s), 163.4 (s, d, $^1J_{CF}$ = 245.0 Hz), 146.0 (s), 137.2 (s, d, $^3J_{CF}$ = 9.0 Hz), 134.0 (d, d, $^3J_{CF}$ = 9.0 Hz), 133.2 (s), 130.3 (d), 128.0 (d), 121.2 (s, d, $^4J_{CF}$ = 3.3 Hz), 118.6 (d, d, $^2J_{CF}$ = 21.3 Hz), 115.0 (d, d, $^2J_{CF}$ = 22.9 Hz), 70.9 (d), 69.4 (t), 21.9 (q)

^{19}F NMR (377 MHz, CDCl$_3$, external standard: TFA in D$_2$O): -101.0

HRMS: (EI, 70 eV) Calculated (C$_{16}$H$_{13}$FO$_5$S):336.0468, Found: 336.0469

4ea (from 2e and 5a)

(3-oxo-6-(trifluoromethyl)-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.100 g, 0.181 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0288 g, 0.151 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 4-(trifluoromethyl)-2-vinylbenzoic acid (0.0334 g, 0.155 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ea** and **3ea**; 58%, ratio **4ea**/**3ea** = >99:<1). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0134 g, 22%). The structure was determined by X-ray crystallography (CCDC 2044380).

Rf (hexane/ethyl acetate = 50:50): 0.77

mp: 143-144 °C

IR: (KBr) 1775 (C=O) cm^{-1}

^{1}H NMR (600 MHz, $CDCl_3$): 8.03 (d, *J* = 8.1 Hz, 1H, 9-H), 7.85 (d, *J* = 8.1 Hz, 1H, 10-H), 7.73 (s, 1H, 12-H), 7.72 (d, *J* = 8.4 Hz, 2H, 2-H), 7.35 (d, *J* = 8.4 Hz, 2H, 3-H), 5.67 (t, *J* = 4.8 Hz, 1H, 6-H), 4.43 (dd, *J* = 11.2, 4.8 Hz, 1H, 5-H), 4.40 (dd, *J* = 11.2, 4.8 Hz, 1H, 5-H), 2.46 (s, 3H, 4-Me)

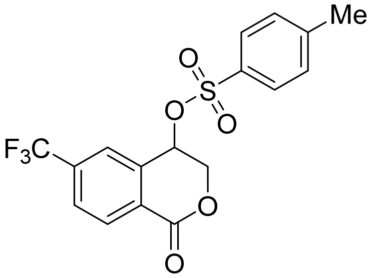
^{13}C NMR (150 MHz, $CDCl_3$): 167.7 (C, C-7), 145.7 (C), 145.6 (C), 136.3 (C, q, $^2J_{CF}$ = 32.9 Hz, C-11), 131.9 (C, C-4), 130.1 (CH, C-3), 129.5 (C, C-8), 127.9 (CH, C-2), 127.5 (CH, q, $^3J_{CF}$ = 3.3 Hz, C-10), 126.9 (CH, C-9), 123.1 (C, q, $^1J_{CF}$ = 273 Hz, CF_3), 119.9 (CH, q, $^3J_{CF}$ = 3.9 Hz, C-12), 77.3 (CH, C-6), 67.9 (CH_2, C-5), 21.7 (CH_3, 4-Me)

^{19}F NMR (372 MHz, $CDCl_3$, external standard:TFA in D_2O): -62.84

HRMS: (EI, 70 eV) Calculated ($C_{17}H_{13}F_3O_5S$) 386.0436, Found: 386.0433

3ea (from 2e and 5a)

1-oxo-6-(trifluoromethyl)isochroman-4-yl 4-methylbenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0587 g, 0.182 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added *p*-TsOH•H$_2$O (0.0297 g, 0.156 mmol) under N$_2$ atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH$_2$Cl$_2$ and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N$_2$. The evaporation and N$_2$-filling manipulation was repeated twice. After evaporation, to the mixture was added CH$_2$Cl$_2$ (0.3 mL) and 4-(trifluoromethyl)-2-vinylbenzoic acid (0.0332 g, 0.154 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH$_2$Cl$_2$. The collected organic layer was dried over MgSO$_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0151 g, 25%). The structure was determined by X-ray crystallography (CCDC 2049845).

Rf (hexane/ethyl acetate = 50:50): 0.73

mp: 160-161 °C

IR: (KBr) 1716 (C=O) cm^{-1}

^{1}H NMR (400 MHz, CDCl$_3$): 8.24 (d, J = 8.2 Hz, 1H), 7.79-7.76 (m, 3H), 7.36 (d, J = 8.2 Hz, 2H), 7.29 (s, 1H), 5.67 (t, J = 2.8 Hz, 1H), 4.77 (dd, J = 12.8, 2.8 Hz, 1H), 4.61 (dd, J = 12.8, 2.8 Hz, 1H), 2.46 (s, 3H)

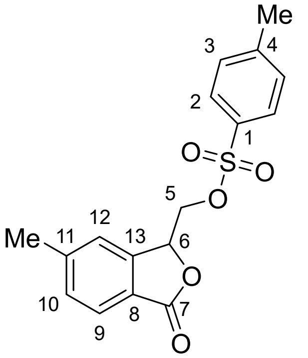
^{13}C NMR (100 MHz, CDCl$_3$): 161.7 (s), 146.1 (s), 135.8 (s, q, $^2J_{CF}$ = 33.3 Hz), 134.9 (s), 133.3 (s), 131.6 (d), 130.3 (d), 128.04 (s), 128.00 (d), 127.8 (d, q, ^3J = 3.8 Hz), 125.1 (d, q, $^3J_{CF}$ = 3.8 Hz), 122.9 (s, q, $^1J_{CF}$ = 273 Hz), 70.8 (d), 69.7 (t), 21.8 (q)

^{19}F NMR (372 MHz, CDCl$_3$, external standard:TFA in D$_2$O): -63.52

HRMS: (EI, 70 eV) Calculated (C$_{17}$H$_{13}$F$_3$O$_5$S) 386.0436, Found: 386.0436

4fa (from 2f and 5a)

(6-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.0996 g, 0.180 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0301 g, 0.158 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 4-methyl-2-vinylbenzoic acid (0.0248 g, 0.153 mmol) and stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the solvent was evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4fa** and **3fa**; 58%, ratio **4fa**/**3fa** = 83:17). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0190 g, 0.0523 mmol, 37%). The structure was determined by X-ray crystallography (CCDC 2044382).

Rf (hexane/ethyl acetate = 50:50): 0.59

mp: 159-160 °C

IR: (KBr) 1757 cm^{-1} (C=O)

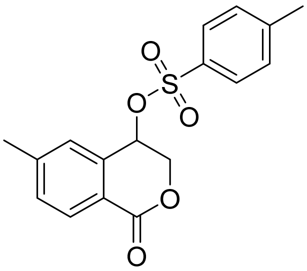
^{1}H NMR (400 MHz, $CDCl_3$): 7.78-7.74 (m, 3H, 2-H and 9-H), 7.38-7.34 (m, 3H, 3-H and 10-H), 7.27 (s, 1H, 12-H), 5.55 (t, J = 4.8 Hz, 1H, 6-H), 4.38 (dd, J = 10.9, 4.8 Hz, 1H, 5-H), 4.29 (dd, J = 10.9, 4.8 Hz, 1H, 5-H), 2.49 (s, 3H, CH_3, 11-Me), 2.46 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 169.5 (s, C-7), 146.0 (s), 145.8 (s), 145.5 (s), 132.3 (s, C-4), 131.4 (d, C-10), 130.2 (d, C-3), 128.1 (d, C-2), 126.0 (d, C-9), 123.8 (s, C-11), 122.9 (d, C-12), 77.3 (d, C-6), 69.1 (t, C-5), 22.2 (q, Me), 21.8 (q, Me)

HRMS: (EI, 70 eV) Calculated ($C_{17}H_{16}O_5S$) 332.0718, Found: 332.0717

3fa (from 2f and 5a)

6-methyl-1-oxoisochroman-4-yl 4-methylbenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0592 g, 0.184 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added *p*-TsOH•H$_2$O (0.0300 g, 0.152 mmol) under N$_2$ atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH$_2$Cl$_2$ and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N$_2$. The evaporation and N$_2$-filling manipulation were repeated twice. After evaporation, to the mixture was added CH$_2$Cl$_2$ (0.3 mL) and 4-methyl-2-vinylbenzoic acid (0.0237 g, 0.146 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH$_2$Cl$_2$. The collected organic layer was dried over MgSO$_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4fa** and **3fa**; 58%, ratio **4fa**/**3fa** = 29:71). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) and recycle HPLC (hexane/ethyl acetate) to give the titled compound as a white solid (0.0037 g, 0.0111 mmol, 8%).

Rf (hexane/ethyl acetate = 50:50): 0.67

mp: 86-89 °C

IR (KBr): 1714 (C=O) cm^{-1}

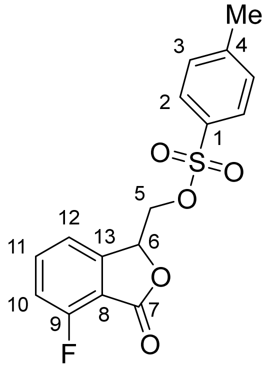
^{1}H NMR (400 MHz, CDCl$_3$): 8.00 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.35 (m, 3H), 7.03 (s, 1H), 5.62 (t, *J* = 2.5 Hz, 1H), 4.65 (dd, *J* = 12.9, 2.5 Hz, 1H), 4.52 (dd, *J* = 12.9, 2.5 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H)

^{13}C NMR (100 MHz, CDCl$_3$): 163.2 (C), 145.7 (C), 145.6 (C), 133.9 (C), 133.7 (C), 131.9 (CH), 130.8 (CH), 130.1 (CH), 128.6 (CH), 128.0 (CH), 122.3 (C), 72.0 (CH), 69.5 (CH$_2$), 21.91 (CH$_3$), 21.85 (CH$_3$)

HRMS: (EI, 70 eV) Calculated (C$_{17}$H$_{16}$O$_5$S): 332.0718, Found: 332.0713

4ga (from 2g and 5a)

(4-fluoro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.0997 g, 0.180 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0292 g, 0.154 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 6-fluoro-2-vinylbenzoic acid (0.0255 g, 0.154 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ga** and **3ga**; 80%, ratio **4ga**/**3ga** = 90:10). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) and recycle HPLC (hexane/ethyl acetate) to give the titled compound as a white solid (0.0072 g, 14%).

Rf (hexane/ethyl acetate = 50:50): 0.44

mp: 145-147 °C

IR: (KBr) 1762 (C=O) cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 7.79-7.67 (m, 3H, 2-H and 11-H), 7.36 (d, J = 8.2 Hz, 2H, 3-H), 7.31 (d, J = 8.1 Hz, 1H, 12-H), 7.22 (d, J = 8.1 Hz, d, $^3J_{HF}$ = 8.1 Hz, 1H, 10-H), 5.60 (t, J = 4.7 Hz, 1H, 6-H), 4.37 (d, J = 4.7 Hz, 2H, 5-H), 2.46 (s, 3H, 4-Me)

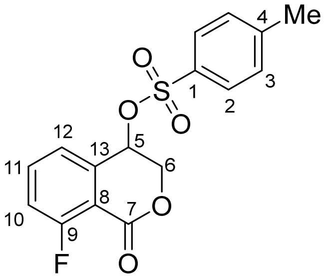
^{13}C NMR (100 MHz, $CDCl_3$): 165.5 (s, C-7), 159.8 (s, d, $^1J_{CF}$ = 265.4 Hz, C-9), 147.7 (s, C-13), 145.7 (s, C-1), 137.2 (d, d, $^3J_{CF}$ = 6.6 Hz, C-11), 132.0 (s, C-4), 130.2 (d, C-3), 128.1 (d, C-2), 118.6 (d, d, $^4J_{CF}$ = 4.1 Hz, C-12), 117.3 (d, d, $^2J_{CF}$ = 18.8 Hz, C-10), 114.2 (s, d, $^2J_{CF}$ = 14.7 Hz, C-8), 77.2 (d, C-6), 68.4 (t, C-5), 21.9 (q, 4-Me)

^{19}F NMR (377 MHz, $CDCl_3$, external standard: TFA in D_2O): -115.6

HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}FO_5S$) 336.0468, Found: 336.0463

3ga (from 2g and 5a)

8-fluoro-1-oxoisochroman-4-yl 4-methylbenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0580 g, 0.180 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added *p*-TsOH•H$_2$O (0.0268 g, 0.141 mmol) under N$_2$ atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH$_2$Cl$_2$ and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N$_2$. The evaporation and N$_2$-filling manipulation were repeated twice. After evaporation, to the mixture was added CH$_2$Cl$_2$ (0.3 mL) and 6-fluoro-2-vinylbenzoic acid (0.0248 g, 0.149 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CH$_2$Cl$_2$. The collected organic layer was dried over MgSO$_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ga** and **3ga**; 83%, ratio **4ga**/**3ga** = 42:58). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) and recycle HPLC (hexane/ethyl acetate) to give the titled compound as a white solid (0.0071 g, 0.0211 mmol, 14%).

Rf (hexane/ethyl acetate = 50:50): 0.44

mp: 129-132 ºC

IR: (KBr) 1728 cm^{-1} (C=O)

^{1}H NMR (400 MHz, CDCl$_3$): 7.78 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.9 Hz, d, $^4J_{HF}$ = 4.8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.9 Hz, d, $^3J_{HF}$ = 9.4 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 5.68 (s, 1H), 4.63 (dd, J = 12.8, 2.9 Hz, 1H), 4.51 (dd, J = 12.8, 2.9 Hz, 1H), 2.46 (s, 3H)

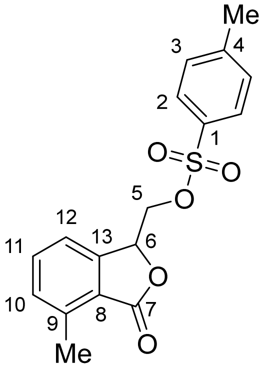
^{13}C NMR (100 MHz, CDCl$_3$): 162.8 (s, d, $^1J_{CF}$ = 267.1 Hz), 158.6 (s, d, $^3J_{CF}$ = 4.9 Hz), 145.8 (s), 136.5 (s), 136.1 (d, d, $^3J_{CF}$ = 9.8 Hz), 133.3 (s), 130.2 (d), 127.9 (d), 123.9 (d, d, $^4J_{CF}$ = 4.1 Hz), 119.6 (d, d, $^2J_{CF}$ = 21.3 Hz), 113.4 (s), 71.2 (d), 69.2 (t), 21.9 (q)

^{19}F NMR (377 MHz, CDCl$_3$, external standard: TFA in D$_2$O): -106.6

HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}FO_5S$) 336.0468, Found: 336.0469

4ia (from 2i and 5a)

(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.0993 g, 0.179 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0277 g, 0.146 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The aforementioned procedure was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 6-methyl-2-vinylbenzoic acid (0.0241 g, 0.149 mmol) and the reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ia** and **3ia**; 55%, ratio **4ia**/**3ia** = 93:7). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0248 g, 0.0746 mmol, 50%). The structure was determined by X-ray crystallography (CCDC 2044390).

Rf (hexane/ethyl acetate = 50:50): 0.66

mp: 98-99 °C

IR: (KBr) 1750 (C=O) cm^{-1}

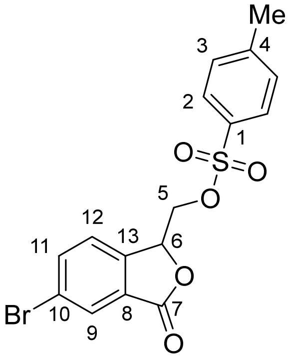
^{1}H NMR (400 MHz, $CDCl_3$): 7.74 (d, *J* = 8.7 Hz, 2H, 2-H), 7.54 (t, *J* = 7.5 Hz, 1H, 11-H), 7.38-7.21 (m, 4H, 3-H, 10-H and 12-H), 5.53 (t, *J* = 4.8 Hz, 1H, 6-H), 4.38 (dd, *J* = 11.0, 4.8 Hz, 1H, 5-H), 4.28 (dd, *J* = 11.0, 4.8 Hz, 1H, 5-H), 2.66 (s, 3H, 9-Me), 2.46 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 169.6 (s, C-7), 145.6 (s), 145.5 (s), 140.4 (s, C-9), 134.2 (d, C-11), 132.4 (s, C-1), 131.9 (d), 130.2 (d, C-3), 128.1 (d, C-2), 123.8 (s, C-8), 119.8 (d), 76.7 (d, C-6), 69.2 (t, C-5), 21.8 (q, 9-Me), 17.5 (q, 4-Me)

HRMS: (EI, 70 eV) Calculated ($C_{17}H_{16}O_5S$) 332.0718; Found: 332.0716

4ja (from 2j and 5a)

(5-bromo-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.100 g, 0.181 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0295 g, 0.155 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-bromo-2-vinylbenzoic acid (0.0361 g, 0.159 mmol) and stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ja** and **3ja**; 62%, ratio **4ja**/**3ja** = >99:<1). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0296 g, 0.0745 mmol, 47%).

Rf (hexane/ethyl acetate = 50:50): 0.65

mp: 146-148 °C

IR: (KBr) 1755 cm^{-1} (C=O)

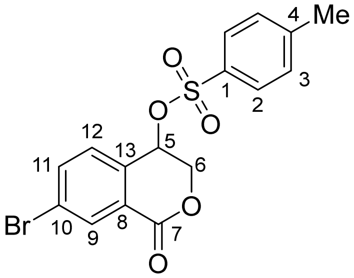
^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (s, 1H, 9-H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H, 2-H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H, 3-H), 5.57 (t, *J* = 4.8 Hz, 1H, 6-H), 4.40-4.32 (m, 2H, 5-H_2), 2.47 (s, 3H, 4-Me)

^{13}C NMR: (100 MHz, $CDCl_3$): 167.8 (s, C-7), 145.7 (s, C-1), 143.9 (s, C-13), 137.6 (d), 132.1 (s, C-4), 130.2 (d, C-3), 129.2 (d, C-9), 128.4 (s, C-8), 128.1 (d, C-2), 124.4 (s, C-10), 124.2 (d), 77.4 (d, C-6), 68.3 (d, C-5), 21.9 (d, 4-Me)

HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}BrO_5S$) 395.9667, Found: 395.9670

3ja (from 2j and 5a)

7-bromo-1-oxoisochroman-4-yl 4-methylbenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0579 g, 0.180 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added *p*-TsOH•H$_2$O (0.0300 g, 0.158 mmol) under N$_2$ atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH$_2$Cl$_2$ and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N$_2$. The evaporation and N$_2$-filling manipulation was repeated twice. After evaporation, to the mixture was added CH$_2$Cl$_2$ (0.3 mL) and 5-bromo-2-vinylbenzoic acid (0.0348 g, 0.153 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH$_2$Cl$_2$. The collected organic layer was dried over MgSO$_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ja** and **3ja**; 62%, ratio **4ja**/**3ja** = 6:94). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0221 g, 36%).

Rf (hexane/ethyl acetate = 50:50): 0.48

mp: 102-103 °C

IR: (KBr) 1718 cm^{-1} (C=O)

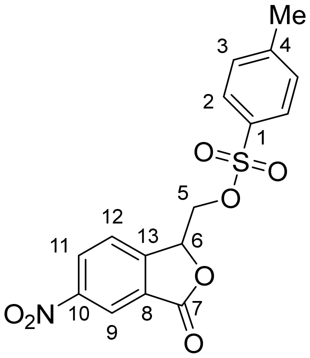
^{1}H NMR (400 MHz, CDCl$_3$): 8.25 (d, *J* = 2.1 Hz, 1H, 9-H), 7.77 (d, *J* = 8.2 Hz, 2H, 2-H), 7.73 (dd, *J* = 8.1, 2.1 Hz, 1H, 11-H), 7.36 (d, *J* = 8.2 Hz, 2H, 3-H), 7.21 (d, *J* = 8.1 Hz, 1H, 12-H), 5.64 (t, *J* = 2.9 Hz, 1H, 5-H), 4.69 (dd, *J* = 13.0, 2.9 Hz, 1H, 6-H), 4.55 (dd, *J* = 13.0, 2.9 Hz, 1H, 6-H), 2.47 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, CDCl$_3$): 161.7 (s, C-7), 145.8 (s, C-1), 137.5 (d, C-11), 133.6 (d, C-9), 133.3 (s), 132.9 (s), 130.2 (d, C-3), 129.8 (d, C-12), 127.9 (d, C-2), 126.6 (s), 125.4 (s), 70.8 (d, C-5), 69.6 (t, C-6), 21.9 (q, 4-Me)

HRMS: (EI, 70 eV) Calculated (C$_{16}$H$_{13}$BrO$_5$S) 395.9667, Found: 395.9660

4ka (from 2k and 5a)

(5-nitro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-methylbenzenesulfonate



To a solution of **1a** (0.0997 g, 0.180 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0316 g, 0.166 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-nitro-2-vinylbenzoic acid (0.0302 g, 0.156 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water phase was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^1H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ka** and **3ka**; 59%, ratio **4ka**/**3ka** = >99:<1). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel)) to give the titled compound as a white solid (0.0303 g, 53%). The structure was determined by X-ray crystallography (CCDC 2044391).

Rf (hexane/ethyl acetate = 50:50): 0.40

mp: 152-155 °C

IR: (KBr) 1769 cm^{-1} (C=O)

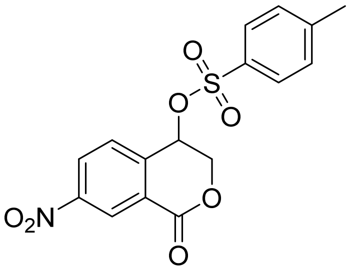
^1H NMR (400 MHz, $CDCl_3$): 8.73 (d, *J* = 2.1 Hz, 1H, 9-H), 8.57 (dd, *J* = 8.5, 2.1 Hz, 1H, 11-H), 7.76-7.69 (m, 3H, 2-H and 12-H), 7.36 (d, *J* = 8.2 Hz, 2H, 3-H), 5.73 (t, *J* = 4.5 Hz, 1H, 6-H), 4.52 (dd, *J* = 11.1, 4.5 Hz, 1H, 5-H), 4.39 (dd, *J* = 11.1, 4.5 Hz, 1H, 5-H), 2.47 (s, 3H, 4-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 166.9 (s, C-7), 150.6 (s, C-10), 149.7 (s, C-8), 146.0 (s, C-1), 131.9 (s, C-4), 130.3 (d, C-3), 129.4 (d, C-11), 128.3 (s, C-13), 128.1 (d, C-2), 124.2 (d, C-12), 121.7 (d, C-9), 77.4 (d, C-6), 67.7 (t, C-5), 21.9 (q, C-4-Me)

HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}NO_7S$) 363.0413, Found: 363.0419

3ka (from 2k and 5a)

7-nitro-1-oxoisochroman-4-yl 4-methylbenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0583 g, 0.181 mmol) in CH_2Cl_2 (0.3 mL) was added *p*-TsOH•H_2O (0.0307 g, 0.161 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-nitro-2-vinylbenzoic acid (0.0299 g, 0.155 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ka** and **3ka**; 46%, ratio **4ka**/**3ka** = 54:46). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 90:10 to 50:50, column length 10 cm, diameter 26 mm silica gel) and recycle HPLC (hexane/ethyl acetate) to give the titled compound as a white solid (0.0069 g, 0.0190 mmol, 12%). The structure was determined by X-ray crystallography (CCDC 2044392).

Rf (hexane/ethyl acetate = 50:50): 0.50

mp: 161-165 °C

IR: (KBr) 1742 (C=O) cm^{-1}

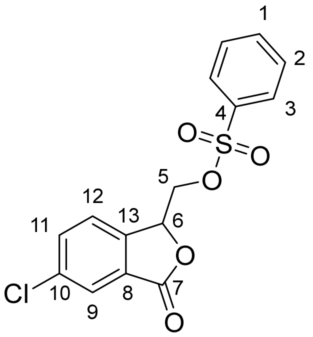
^{1}H NMR (400 MHz, $CDCl_3$): 8.95 (d, *J* = 2.2 Hz, 1H), 8.46 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 5.78 (t, *J* = 3.3 Hz, 1H), 4.69 (dd, *J* = 12.8, 3.9 Hz, 1H), 4.60 (dd, *J* = 12.8, 2.9 Hz, 1H), 2.48 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 161.0 (s), 149.4 (s), 146.3 (s), 140.2 (s), 132.8 (s), 130.4 (d), 129.6 (d), 128.7 (d), 128.0 (d), 126.5 (s), 125.9 (d), 69.8 (d), 69.2 (t), 21.9 (q)

HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}NO_7S$): 363.0413, Found: 363.0407

4ab (from 2a and 5b)

(5-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl benzenesulfonate



To a solution of **1a** (0.102 g, 0.183 mmol) in CH_2Cl_2 (0.3 mL) was added $PhSO_3H$ (0.0247 g, 0.156 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0282 g, 0.154 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ab** and **3ab**; 80%, ratio **4ab**/**3ab** = 80:20). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 90:10 to 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a viscous colorless liquid (0.0171 g, 33%).

Rf (hexane/ethyl acetate = 50:50): 0.55

IR: (neat) 1773 cm^{-1} (C=O)

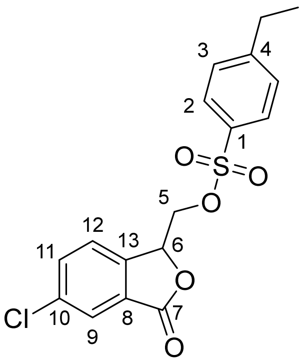
^{1}H NMR (400 MHz, $CDCl_3$): 7.85-7.83 (m, 3H, 3-H and 9-H), 7.69 (t, J = 7.7 Hz, 1H, 1-H), 7.65 (dd, J = 8.0, 1.9 Hz, 1H, 11-H), 7.57 (t, J = 7.7 Hz, 2H, 2-H), 7.45 (d, J = 8.0 Hz, 1H, 12-H), 5.61 (t, J = 4.6 Hz, 1H, 6-H), 4.40 (d, J = 4.6 Hz, 2H, 5-H_2)

^{13}C NMR (100 MHz, $CDCl_3$): 167.9 (s, C-7), 143.3 (s, C-13), 136.7 (s, C-10), 135.2 (s, C-4), 134.9 (d), 134.5 (d), 129.6 (d, C-2), 128.2 (s, C-8), 128.0 (d), 126.2 (d), 123.9 (d, C-12), 77.3 (d, C-6), 68.5 (t, C-5)

HRMS: (ESI) Calculated ($C_{15}H_{11}O_5NaSCl$):360.99079 ($[M + Na]^+$), Found: 360.99042

4ac (from 2a and 5c)

(5-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-ethylbenzenesulfonate



To a solution of **1a** (0.102 g, 0.185 mmol) in CH_2Cl_2 (0.3 mL) was added 4-ethylbenzenesulfonic acid (0.0290 g) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The aforementioned procedure was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0283 g, 0.155 mmol) and the reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ac** and **3ac**; 63%, ratio **4ac**/**3ac** = 86:14). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) and recycle HPLC to give the titled compound as a white solid (0.0217 g, 38%).

Rf (hexane/ethyl acetate = 50:50): 0.66

mp: 115-116 °C

IR: (KBr) 1754 (C=O) cm^{-1}

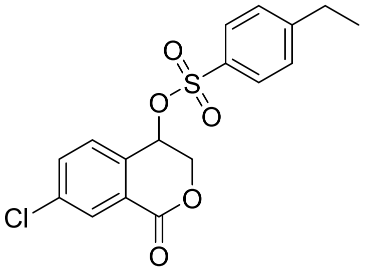
^{1}H NMR (400 MHz, $CDCl_3$): 7.85 (d, J = 1.9 Hz, 1H, 9-H), 7.74 (d, J = 8.5 Hz, 2H, 2-H), 7.65 (dd, J = 8.2, 1.9 Hz, 1H, 11-H), 7.46 (d, J = 8.2 Hz, 1H, 12-H), 7.37 (d, J = 8.5 Hz, 2H, 3-H), 5.60 (t, J = 4.8 Hz, 1H, 6-H), 4.41-4.33 (m, 2H, 5-H_2), 2.75 (q, J = 7.7 Hz, 2H, CH_2CH_3), 1.28 (t, J = 7.7 Hz, 3H, CH_2CH_3)

^{13}C NMR (100 MHz, $CDCl_3$): 168.0 (s, C-7), 151.8 (s, C-1), 143.5 (s, C-13), 136.7 (s, C-10), 134.8 (d, C-11), 132.4 (s, C-4), 129.1 (d, C-3), 128.21 (s, C-8), 128.16 (d, C-2), 126.1 (d, C-9), 124.0 (d, C-12), 77.3 (d, C-6), 68.4 (t, C-5), 29.1 (t, CH_2CH_3), 15.1 (q, CH_2CH_3)

HRMS: (EI, 70 eV) Calculated ($C_{17}H_{15}ClO_5S$) 366.0329, Found: 366.0324

3ac (from 2a and 5c)

7-chloro-1-oxoisochroman-4-yl 4-ethylbenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0562 g, 0.174 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added 4-ethylbenzenesulfonic acid (0.0256 g) under N$_2$ atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH$_2$Cl$_2$ and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N$_2$. The evaporation and N$_2$-filling manipulation were repeated twice. After evaporation, to the mixture was added CH$_2$Cl$_2$ (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0291 g, 0.159 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CHCl$_3$. The collected organic layer was dried over MgSO$_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ac** and **3ac**; 62%, ratio **4ac**/**3ac** = 29:71). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0187 g, 32%).

Rf (hexane/ethyl acetate = 50:50): 0.71

mp: 110-112 °C

IR: (KBr) 1715 (C=O) cm^{-1}

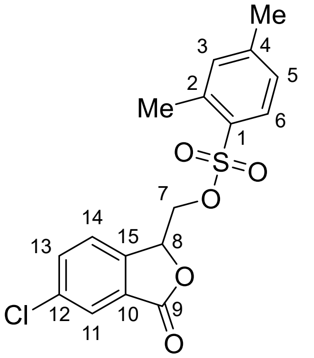
^{1}H NMR (400 MHz, CDCl$_3$): 8.09 (d, *J* = 2.1 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.56 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 1H), 5.66 (s, 1H), 4.70 (dd, *J* = 12.8, 2.7 Hz, 1H), 4.55 (dd, *J* = 12.8, 2.7 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H)

^{13}C NMR (100 MHz, CDCl$_3$): 161.9 (s), 151.9 (s), 137.5 (s), 134.5 (d), 133.5 (s), 132.4 (s), 130.6 (d), 129.8 (d), 129.1 (d), 128.0 (d), 126.5 (s), 70.8 (d), 69.7 (t), 29.1 (t), 15.3 (q)

HRMS: (FAB+, 70 eV) Calculated ($C_{17}H_{15}ClO_5SNa$): 389.0226 ([M + Na]$^+$), Found: 389.0233

4ad (from 2a and 5d)

(5-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 2,4-dimethylbenzenesulfonate



To a solution of **1a** (0.100 g, 0.181 mmol) in CH_2Cl_2 (0.3 mL) was added 2,4-$Me_2C_6H_3SO_3H$•nH_2O (0.0347 g) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0283 g, 0.155 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ad** and **3ad**; 79%, ratio **4ad**/**3ad** = 87:13). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0300 g, 53%).

Rf (hexane/ethyl acetate = 50:50): 0.67

mp: 124-126 °C

IR: (KBr) 1767 (C=O) cm^{-1}

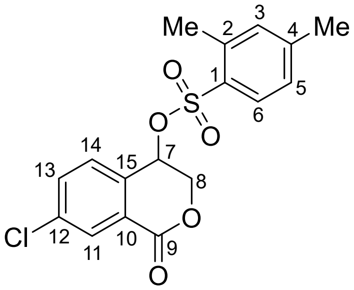
^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (d, J = 1.8 Hz, 1H, 11-H), 7.79 (d, J = 8.2 Hz, 1H, 6-H), 7.63 (dd, J = 8.2, 1.8 Hz, 1H, 13-H), 7.42 (d, J = 8.2 Hz, 1H, 14-H), 7.14-7.12 (m, 2H, 3-H and 5-H), 5.61 (t, J = 4.4 Hz, 1H, 8-H), 4.39 (dd, J = 11.2, 4.4 Hz, 1H, 7-H), 4.31 (dd, J = 11.2, 4.4 Hz, 1H, 7-H), 2.45 (s, 3H, 4-Me), 2.40 (s, 3H, 2-Me)

^{13}C NMR (100 MHz, $CDCl_3$): 167.9 (s, C-9), 145.5 (s, C-1), 143.3 (s, C-15), 138.6 (s, C-4), 136.7 (s, C-12), 134.8 (d, C-13), 133.7 (d, C-3), 130.5 (s, C-2), 130.2 (d, C-6), 128.3 (s, C-10), 126.9 (d, C-5), 126.0 (d, C-11), 123.8 (d, C-14), 77.5 (d, C-8), 68.2 (t, C-7), 21.6 (q, 2-Me), 20.1 (q, 4-Me)

HRMS: (EI, 70 eV) Calculated ($C_{17}H_{15}ClO_5S$) 366.0329, Found: 366.0325

3ad (from 2a and 5d)

7-chloro-1-oxoisochroman-4-yl 2,4-dimethylbenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0597 g, 0.185 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added 2,4-dimethylbenzenesulfonic acid hydrate (0.0362 g) under N$_2$ atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH$_2$Cl$_2$ and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N$_2$. The evaporation and N$_2$-filling manipulation was repeated twice. After evaporation, to the mixture was added CH$_2$Cl$_2$ (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0282 g, 0.154 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH$_2$Cl$_2$. The collected organic layer was dried over MgSO$_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ad** and **3ad**; 91%, ratio **4ad**/**3ad** = 11:89). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a yellow oil (0.0223 g, 39%).

Rf (hexane/ethyl acetate = 50:50): 0.71

IR: (neat) 1725 (C=O) cm^{-1}

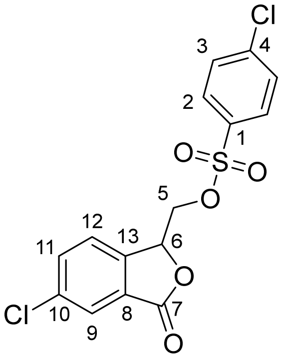
^{1}H NMR (400 MHz, CDCl$_3$): 8.08 (d, J = 2.3 Hz, 1H, 11-H), 7.84 (d, J = 8.7 Hz, 1H, 6-H), 7.54 (dd, J = 8.1, 2.3 Hz, 1H, 13-H), 7.22 (d, J = 8.1 Hz, 1H, 14-H), 7.15-7.14 (m, 2H, 3-H and 5-H), 5.61 (t, J = 2.4 Hz, 1H, 7-H), 4.70 (dd, J = 13.0, 2.4 Hz, 1H, 8-H), 4.53 (dd, J = 13.0, 2.4 Hz, 1H, 8-H), 2.48 (s, 3H, 4-Me), 2.40 (s, 3H, 2-Me)

^{13}C NMR (100 MHz, CDCl$_3$): 161.9 (s, C-9), 145.6 (s, C-1), 138.5 (s, C-4), 137.5 (s, C-10), 134.5 (d, C-13), 133.7 (d), 132.1 (s), 132.0 (s), 130.5 (d, C-11), 129.9 (d, C-6), 129.9 (d, C-14), 127.0 (d), 126.6 (s, C-2), 70.8 (d, C-7), 69.7 (t, C-8), 21.6 (q, 2-Me), 20.1 (q, 4-Me)

HRMS: (EI, 70 eV) Calculated ($C_{17}H_{15}ClO_5S$) 366.0329, Found: 366.0323

4ae (from 2a and 5e)

(5-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl 4-chlorobenzenesulfonate



To a solution of **1a** (0.100 g, 0.181 mmol) in CH_2Cl_2 (0.3 mL) was added 4-chlorobenzenesulfonic acid (0.0321 g) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0282 g, 0.154 mmol) and the reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ae** and **3ae**; 59%, ratio **4ae**/**3ae** = 32:68). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) and recycle HPLC (hexane/ethyl acetate = 50:50) to give the titled compound as a white solid (0.0213 g, 37%).

Rf (hexane/ethyl acetate = 50:50): 0.64

mp: 147-148 °C

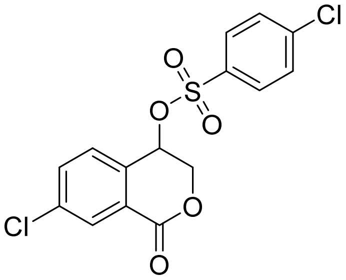
IR: (KBr) 1762 (C=O) cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (d, *J* = 1.7 Hz, 1H, 9-H), 7.77 (d, *J* = 8.7 Hz, 2H, 2-H), 7.67 (dd, *J* = 8.2, 1.7 Hz, 1H, 11-H), 7.54 (d, *J* = 8.7 Hz, 2H, 3-H), 7.45 (d, *J* = 8.2 Hz, 1H, 12-H), 5.61 (dd, *J* = 4.8, 4.3 Hz, 1H, 6-H), 4.44 (dd, *J* = 11.1, 4.3 Hz, 1H, 5-H), 4.40 (dd, *J* = 11.1, 4.8 Hz, 1H, 5-H)

^{13}C NMR (100 MHz, $CDCl_3$): 167.8 (s, C-7), 143.1 (s, C-13), 141.3 (s, C-1), 136.9 (s, C-10), 134.9 (d, C-11), 133.7 (s, C-4), 130.0 (d, C-3), 129.4 (d, C-2), 128.3 (s, C-8), 126.2 (d, C-9), 123.8 (d, C-12), 77.3 (d, C-6), 68.7 (t, C-5)

HRMS: (CI, 70 eV) Calculated ($C_{15}H_{11}Cl_2O_5S$) 372.9704 ([M + H]$^+$), Found: 372.9708

3ae (from 2a and 5e) 7-chloro-1-oxoisochroman-4-yl 4-chlorobenzenesulfonate



To a solution of PhI(OAc)$_2$ (0.0564 g, 0.175 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added 4-chlorobenzenesulfonic acid (0.0305 g) under N$_2$ atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH$_2$Cl$_2$ and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N$_2$. The evaporation and N$_2$-filling manipulation were repeated twice. After evaporation, to the mixture was added CH$_2$Cl$_2$ (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0730 g, 0.400 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CHCl$_3$. The collected organic layer was dried over MgSO$_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ae** and **3ae**; 32%, ratio **4ae**/**3ae** = 19:81). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0137 g, 23%).

Rf (hexane/ethyl acetate = 50:50): 0.78

mp: 80-82 °C

IR: (KBr) 1719 (C=O) cm^{-1}

^{1}H NMR (400 MHz, CDCl$_3$): 8.10 (s, 1H), 7.81 (d, J = 8.7 Hz, 2H), 7.60 (dd, J = 8.2, 2.2 Hz, 1H), 7.54 (d, J = 8.7 Hz, 2H), 7.34 (d, J = 8.2 Hz, 1H), 5.72 (t, J = 2.4 Hz, 1H), 4.74 (dd, J = 13.0, 2.4 Hz, 1H), 4.59 (dd, J = 13.0, 2.4 Hz, 1H)

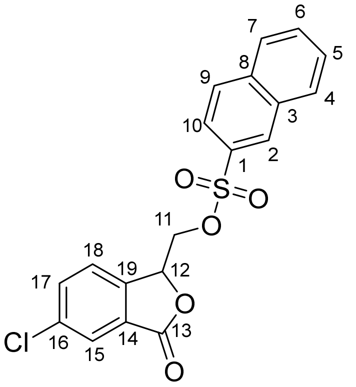
^{13}C NMR (100 MHz, CDCl$_3$): 161.7 (s), 141.3 (s), 137.8 (s), 134.8 (s), 134.7 (d), 131.9 (s), 130.7 (d), 130.0 (d), 129.8 (d), 129.3 (d), 126.6 (s), 71.3 (d), 69.7 (t)

HRMS: (FAB+, 70 eV)

Calculated ($C_{15}H_{10}Cl_2O_5SNa$): 394.9524 ([M + Na]$^+$), Found: 394.9524.

4af (from 2a and 5f)

(5-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl naphthalene-2-sulfonate



To a solution of **1a** (0.101 g, 0.182 mmol) in CH_2Cl_2 (0.3 mL) was added 2-naphtylSO$_3$H•nH$_2$O (0.0362 g) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0281 g, 0.154 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4af** and **3af**; 60%, ratio **4af**/**3af** = 85:15). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a pale yellow solid (0.0305 g, 51%).

Rf (hexane/ethyl acetate = 50:50): 0.63

mp: 111-112 °C

IR: (KBr) 1763 (C=O) cm^{-1}

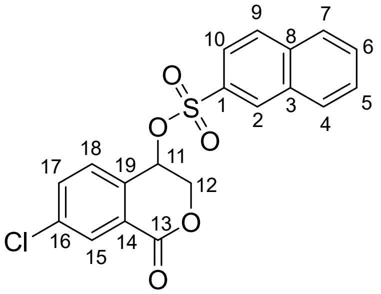
^{1}H NMR (400 MHz, $CDCl_3$): 8.42 (s, 1H, 2-H), 8.00-7.94 (m, 3H), 7.81 (d, J = 1.9 Hz, 1H, 15-H), 7.76-7.65 (m, 3H), 7.55 (dd, J = 8.2, 1.9 Hz, 1H, 10-H), 7.40 (d, J = 8.2 Hz, 1H, 9-H), 5.60 (t, J = 4.5 Hz, 1H, 12-H), 4.43 (d, J = 4.5 Hz, 2H, 11-H$_2$)

^{13}C NMR (100 MHz, $CDCl_3$): 167.9 (s, C-13), 143.3 (s, C-1), 136.7 (s), 135.6 (s), 134.8 (d, C-10), 132.0 (s), 131.9 (s), 130.1 (d), 130.0 (d), 129.9 (d), 129.5 (d), 128.2 (d), 128.2 (s), 126.1 (d, C-15), 123.8 (d, C-9), 122.3 (d), 77.3 (d, C-12), 68.6 (t, C-11)

HRMS: (EI, 70 eV) Calculated ($C_{19}H_{13}ClO_5S$) 388.0172, Found: 388.0166

3af (from 2a and 5f)

7-chloro-1-oxoisochroman-4-yl naphthalene-2-sulfonate



To a solution of PhI(OAc)$_2$ (0.0589 g, 0.183 mmol) in CH_2Cl_2 (0.3 mL) was added 2-naphtalenesulfonic acid hydrate (0.0358 g) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0280 g, 0.153 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4af** and **3af**; 67%, ratio **4af**/**3af** = 28:72). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) and recycle GPC ($CHCl_3$) to give the titled compound as a yellow sluggish liquid (0.0072 g, 12%).

Rf (hexane/ethyl acetate = 50:50): 0.70

IR: (neat) 1746 (C=O) cm^{-1}

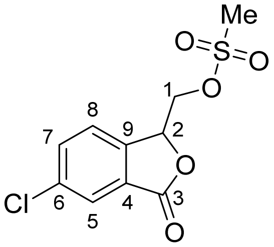
^{1}H NMR (400 MHz, $CDCl_3$): 8.47 (s, 1H, 2-H), 8.06 (d, *J* = 2.2 Hz, 1H, 15-H), 8.02-7.94 (m, 3H), 7.80 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.75-7.66 (m, 2H), 7.51 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.30-7.23 (m, 1H), 5.72 (t, *J* = 2.7 Hz, 1H, 11-H), 4.72 (dd, *J* = 12.9, 2.7 Hz, 1H, 12-H), 4.56 (dd, *J* = 12.9, 2.7 Hz, 1H, 12-H)

^{13}C NMR (100 MHz, $CDCl_3$): 161.8 (s, C-13), 137.6 (s), 135.5 (s), 134.5 (d), 133.1 (s), 132.2 (s), 131.9 (s), 130.6 (d), 130.2 (d), 130.0 (d), 129.9 (d), 129.8 (d), 129.5 (d), 128.33 (d), 128.25 (d), 126.6 (s), 122.2 (d), 71.1 (d, C-11), 69.7 (t, C-12)

HRMS: (EI, 70 eV) Calculated ($C_{19}H_{13}ClO_5S$): 388.0172, Found: 388.0169.

4ag (from 2a and 5g)

(5-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl methanesulfonate



To a solution of **1a** (0.204 g, 0.368 mmol) in CH_2Cl_2 (0.6 mL) was added CH_3SO_3H (0.0273 g, 0.284 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.6 mL) and 5-chloro-2-vinylbenzoic acid (0.0558 g, 0.306 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by and the aqueous layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ag** and **3ag**; 62%, ratio **4ag**/**3ag** = 82:18). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a yellow solid (0.0408 g, 0.147 mmol, 48%). The structure was determined by X-ray crystallography (CCDC 2049846)

Rf (hexane/ethyl acetate = 50:50): 0.37

mp: 81-83 °C

IR: (KBr) 1759 (C=O) cm^{-1}

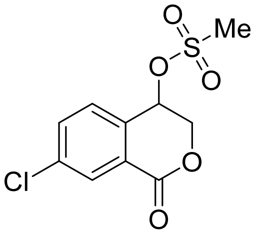
^{1}H NMR (400 MHz, $CDCl_3$): 7.91 (d, *J* = 1.7 Hz, 1H, 5-H), 7.72 (dd, *J* = 8.2, 1.7 Hz, 1H, 7-H), 7.53 (d, *J* = 8.2 Hz, 1H, 8-H), 5.71 (t, *J* = 4.3 Hz, 1H, 2-H), 4.67 (dd, *J* = 11.6, 4.3 Hz, 1H, 1-H), 4.52 (dd, *J* = 11.6, 4.3 Hz, 1H, 1-H), 3.05 (s, 3H, Me)

^{13}C NMR (100 MHz, $CDCl_3$): 168.0 (s, C-3), 143.0 (s, C-9), 136.8 (s, C-6), 135.0 (d, C-7), 128.2 (s, C-4), 126.2 (d, C-5), 123.9 (d, C-8), 77.7 (d, C-2), 68.2 (t, C-1), 38.0 (q, Me)

HRMS: (CI, 70 eV) Calculated ($C_{10}H_{10}ClO_5S$) 276.9937 ([M + H]$^+$), Found: 276.9937

3ag (from 2a and 5g)

7-chloro-1-oxoisochroman-4-yl methanesulfonate



To a solution of PhI(OAc)$_2$ (0.0566 g, 0.176 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added CH$_3$SO$_3$H (0.0197 g, 0.205 mmol) under N$_2$ atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH$_2$Cl$_2$ and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N$_2$. The evaporation and N$_2$-filling manipulation were repeated twice. After evaporation, to the mixture was added CH$_2$Cl$_2$ (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0263 g, 0.144 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the aqueous layer was extracted with CHCl$_3$. The collected organic layer was dried over MgSO$_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ag** and **3ag**; 67%, ratio **4ag**/**3ag** = 4:96). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the titled compound as a white solid (0.0235 g, 59%). The structure was determined by X-ray crystallography (CCDC 2049847).

Rf (hexane/ethyl acetate = 50:50): 0.70

mp: 79-81 °C

IR: (KBr) 1736 (C=O) cm^{-1}

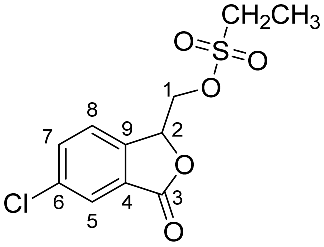
^{1}H NMR (400 MHz, CDCl$_3$): 8.17 (s, 1H), 7.69 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 5.83 (t, *J* = 2.3 Hz, 1H), 4.89 (dd, *J* = 13.2, 2.3 Hz, 1H), 4.68 (dd, *J* = 13.2, 2.3 Hz, 1H), 3.04 (s, 3H)

^{13}C NMR (100 MHz, CDCl$_3$): 161.9 (s), 137.8 (s), 134.8 (d), 132.2 (s), 130.7 (d), 130.2 (d), 126.7 (s), 70.0 (t), 69.8 (d), 39.4 (q)

HRMS: (EI, 70 eV) Calculated (C$_{10}$H$_9$ClO$_5$S) 275.9859, Found: 275.9863

4ah (from 2a and 5h)

(5-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl ethanesulfonate



To a solution of **1a** (0.0997 g, 0.180 mmol) in CH_2Cl_2 (0.3 mL) was added $EtSO_3H$ (0.0178 g, 0.162 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0278 g, 0.152 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ah** and **3ah**; 56%, ratio **4ah**/**3ah** = 89:11). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel) and recycle HPLC (hexane/ethyl acetate = 50:50) to give the titled compound as a colorless oil (0.0067 g, 15%).

Rf (hexane/ethyl acetate = 50:50): 0.43

IR: (neat) 1773 (C=O) cm^{-1}

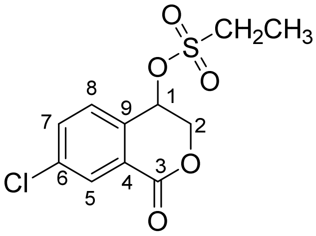
^{1}H NMR (400 MHz, $CDCl_3$): 7.92 (d, *J* = 1.9 Hz, 1H, 5-H), 7.71 (dd, *J* = 8.2, 1.9 Hz, 1H, 7-H), 7.53 (d, *J* = 8.2 Hz, 1H, 8-H), 5.70 (dd, *J* = 5.2, 4.0 Hz, 1H, 2-H), 4.64 (dd, *J* = 11.6, 4.0 Hz, 1H, 1-H), 4.50 (dd, *J* = 11.6, 5.2 Hz, 1H, 1-H), 3.15 (q, *J* = 7.4 Hz, 2H, CH_2CH_3), 1.37 (t, *J* = 7.4 Hz, 3H, CH_2CH_3)

^{13}C NMR (100 MHz, $CDCl_3$): 168.1 (s, C-3), 143.1 (s, C-9), 136.9 (s, C-6), 135.0 (d, C-7), 128.3 (s, C-4), 126.2 (d, C-5), 123.9 (d, C-8), 77.9 (d, C-2), 67.7 (t, C-1), 45.7 (t, CH_2CH_3), 8.2 (q, CH_2CH_3)

HRMS: (CI, 70 eV) Calculated ($C_{11}H_{12}ClO_5S$) 291.0094 ([M + H]$^+$), Found: 291.0090.

3ah (from 2a and 5h)

7-chloro-1-oxoisochroman-4-yl ethanesulfonate



To a solution of PhI(OAc)$_2$ (0.0579 g, 0.180 mmol) in CH_2Cl_2 (0.3 mL) was added $EtSO_3H$ (0.0159 g, 0.144 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0284 g, 0.156 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard (total yield of **4ah** and **3ah**; 58%, ratio **4ah**/**3ah** = 22:78). The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 50:50, column length 10 cm, diameter 26 mm silica gel and recycle HPLC (hexane/ethyl acetate = 50:50) to give the titled compound as a colorless liquid (0.0145 g, 0.0175 mmol, 32%).

Rf (hexane/ethyl acetate = 50:50): 0.51

IR: (neat) 1764 (C=O) cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): 8.18 (d, *J* = 2.4 Hz, 1H, 5-H), 7.68 (dd, *J* = 8.2, 2.4 Hz, 1H, 7-H), 7.58 (d, *J* = 8.2 Hz, 1H, 8-H), 5.82 (t, *J* = 2.3 Hz, 1H, 1-H), 4.88 (dd, *J* = 13.2, 2.3 Hz, 1H, 2-H), 4.67 (dd, *J* = 13.2, 2.3 Hz, 1H, 2-H), 3.14 (q, *J* = 7.5 Hz, 2H, $C\mathit{H_2}CH_3$), 1.38 (t, *J* = 7.5 Hz, 3H, $CH_2C\mathit{H_3}$)

^{13}C NMR (100 MHz, $CDCl_3$): 162.0 (s, C-3), 137.8 (s, C-4), 134.8 (d, C-7), 132.4 (s, C-6), 130.8 (d, C-5), 130.2 (d, C-8), 126.7 (s, C-9), 70.1 (t, C-2), 69.2 (d, C-1), 46.7 (t, $\mathit{C}H_2CH_3$), 8.2 (q, $CH_2\mathit{C}H_3$)

HRMS: (CI, 70 eV) Calculated ($C_{11}H_{12}ClO_5S$): 291.0094 ([M + H]$^+$), Found: 291.0098

General Procedures

Method A: Tosyloxylactonization of 2-vinyl benzoic acid 2a using PhI(OAc)$_2$ (Table 1, Entry 1)

To a solution of PhI(OAc)$_2$ (0.18 mmol) in CH_2Cl_2 (0.3 mL) was added TsOH·H_2O (*p*-toluenesulfonic acid monohydrate) (0.15 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid **2a** (0.15 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* product **4a** and 6-*endo* product **3a** were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.

Tosyloxylactonization of 2-vinyl benzoic acid 2a using PhI(OH)OTs (Table 1, Entry 2)

To a solution of PhI(OH)OTs (0.18 mmol) in CH_2Cl_2 (0.3 mL) was added 5-chloro-2-vinylbenzoic acid **2a** (0.15 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* product **4a** and 6-*endo* product **3a** were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.

Method B: Tosyloxylactonization of 2-vinyl benzoic acid 2a using ArI(OAc)$_2$ 1a and TsOH·H_2O (Table 1, Entry 3)

To a solution of **1a** (0.18 mmol) in CH_2Cl_2 (0.3 mL) was added TsOH·H_2O (*p*-toluenesulfonic acid monohydrate) (0.15 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid **2a** (0.15 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* product **4a** and 6-*endo* product **3a** were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.

Tosyloxylactonization of 2-vinyl benzoic acid 2a using ArI(OAc)$_2$ 1a and TsOH·H_2O in the presence of 1-butyl-3-methylimidazolium tetrafluoroborate (Table 1, Entry 4)

To a solution of PhI(OH)OTs (0.18 mmol) in CH_2Cl_2 (0.3 mL) was added 1-butyl-3-methylimidazolium tetrafluoroborate (0.65 mmol) and 5-chloro-2-vinylbenzoic acid **2a** (0.15 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* product **4a** and 6-*endo* product **3a** were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.

Tosyloxylactonization of 2-vinyl benzoic acid 2 using $ArI(OAc)_2$ 1a and $TsOH\cdot H_2O$ (Table 2, Scope of 2)

All experiments were carried out according to Method B.

Tosyloxylactonization of 2-vinyl benzoic acid 2 using $PhI(OAc)_2$ and $TsOH\cdot H_2O$ (Table 2, Scope of 2)

All experiments were carried out according to Method A.

Sulfonyloxylactonization of 2-vinyl benzoic acid 2a using $ArI(OAc)_2$ 1a and RSO_3H 5 (Table 3, Scope of 5)

All experiments were carried out according to Method B.

Sulfonyloxylactonization of 2-vinyl benzoic acid 2a using $PhI(OAc)_2$ and RSO_3H 5 (Table 3, Scope of 5)

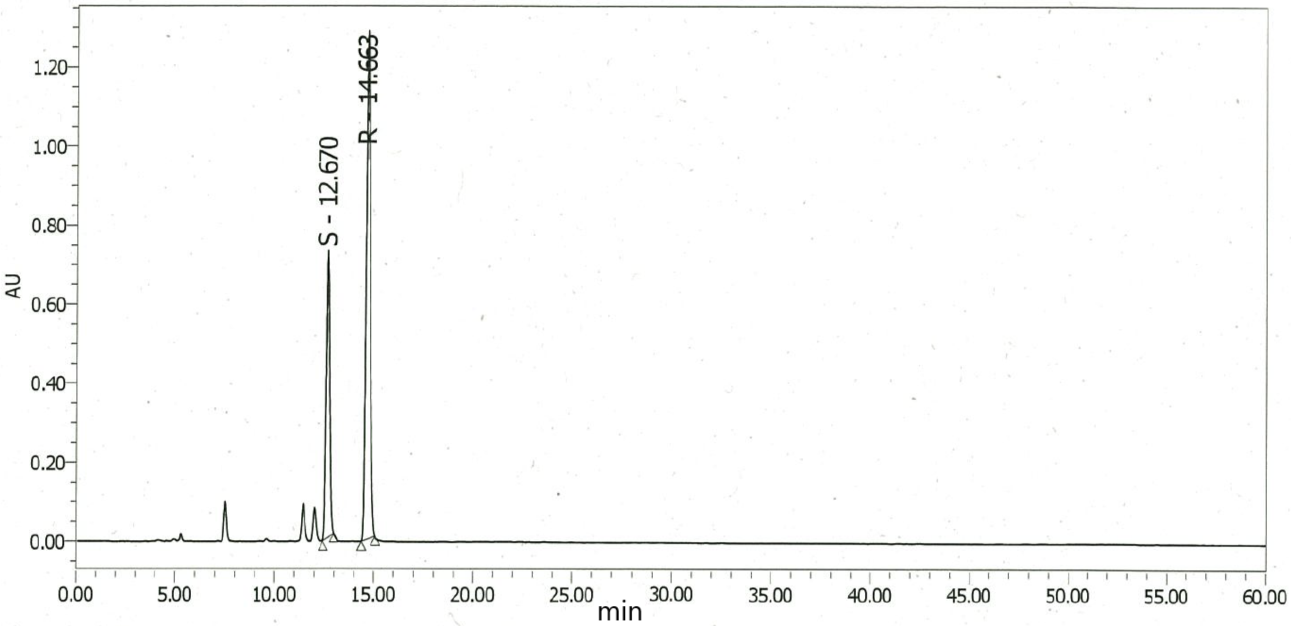
All experiments were carried out according to Method A.

Tosyloxylactonization of 2-vinyl benzoic acid 2a using $ArI(OAc)_2$ 1 and $TsOH\cdot H_2O$ (Table 4)

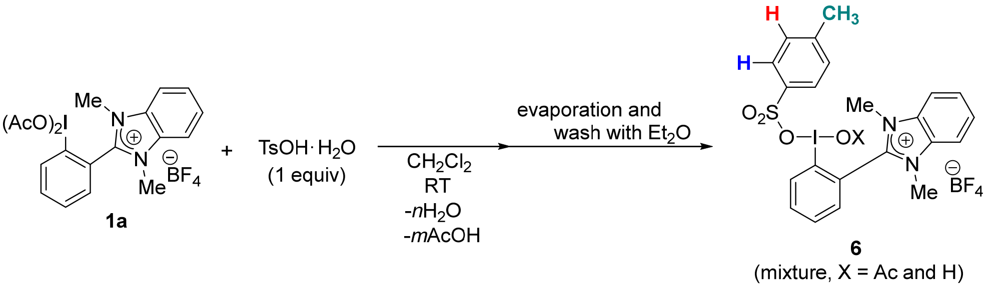
All experiments were carried out according to Method B.

Enantioselective tosyloxylactonization using optically active hypervalent iodine (***R*,*R***)-1d (Scheme 2)

The experiment was carried out according to Method B. Retention times of (*S*)-**9a** and (*R*)-**9a** were 12.7 and 14.7 min, respectively, for HLPC analyses using a chiral column Chiralpak IA (0.46 cm φ × 25 cm) (eluent: CH_2Cl_2/hexane = 40:60, the flow rate = 0.7 mL/min). The retention time was referred to reported values (M. Fujita, Y. Yoshida, K. Miyata, A. Wakisaka, T. Sugimura, *Angew. Chem. Int. Ed.* **2010**, *49*, 7068.).



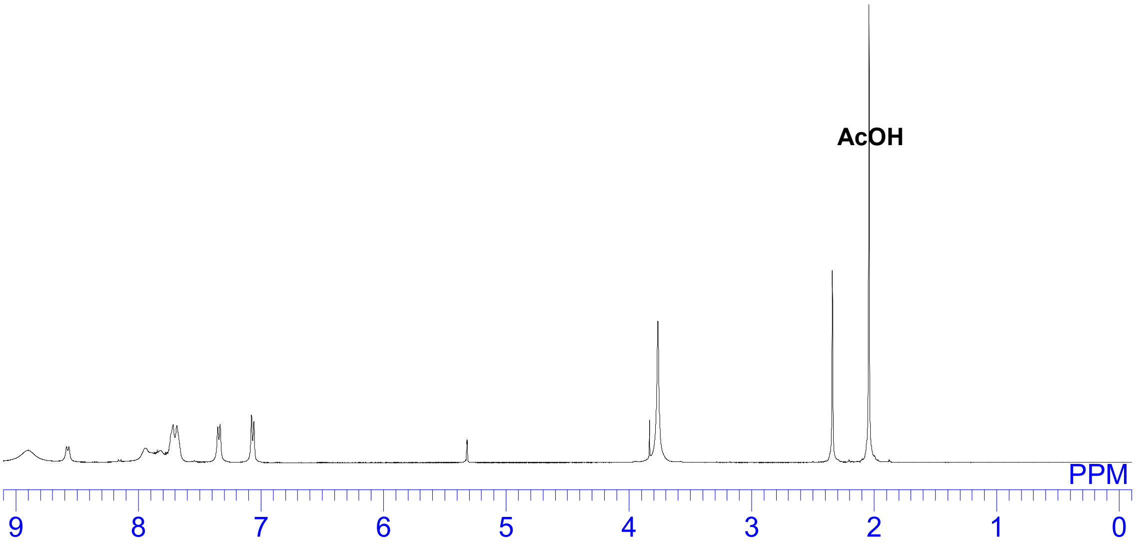
Isolation and identification of intermediate 6 (Fig. 3, A)



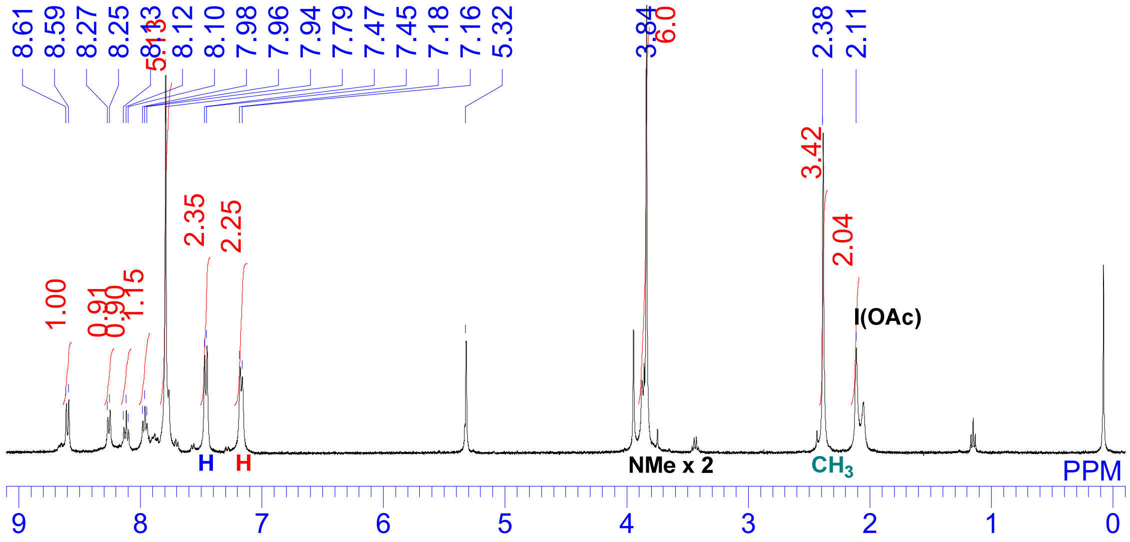
All manipulations were carried out in glove box filled with dry nitrogen gas. To the solution of **1a** (0.05 mmol) in CH_2Cl_2 (0.5 mL) was added $TsOH·H_2O$ (0.06 mmol) at room temperature, and the reaction mixture was stirred for 30 min. Then, the volatiles were evaporated in vacuo, the residue was washed with Et_2O to remove AcOH and H_2O. The volatiles were evaporated again to obtain compound **6**.

^{1}H NMR (400 MHz, CD_2Cl_2)

Before evaporation and washing with Et_2O



After evaporation and washing with Et_2O

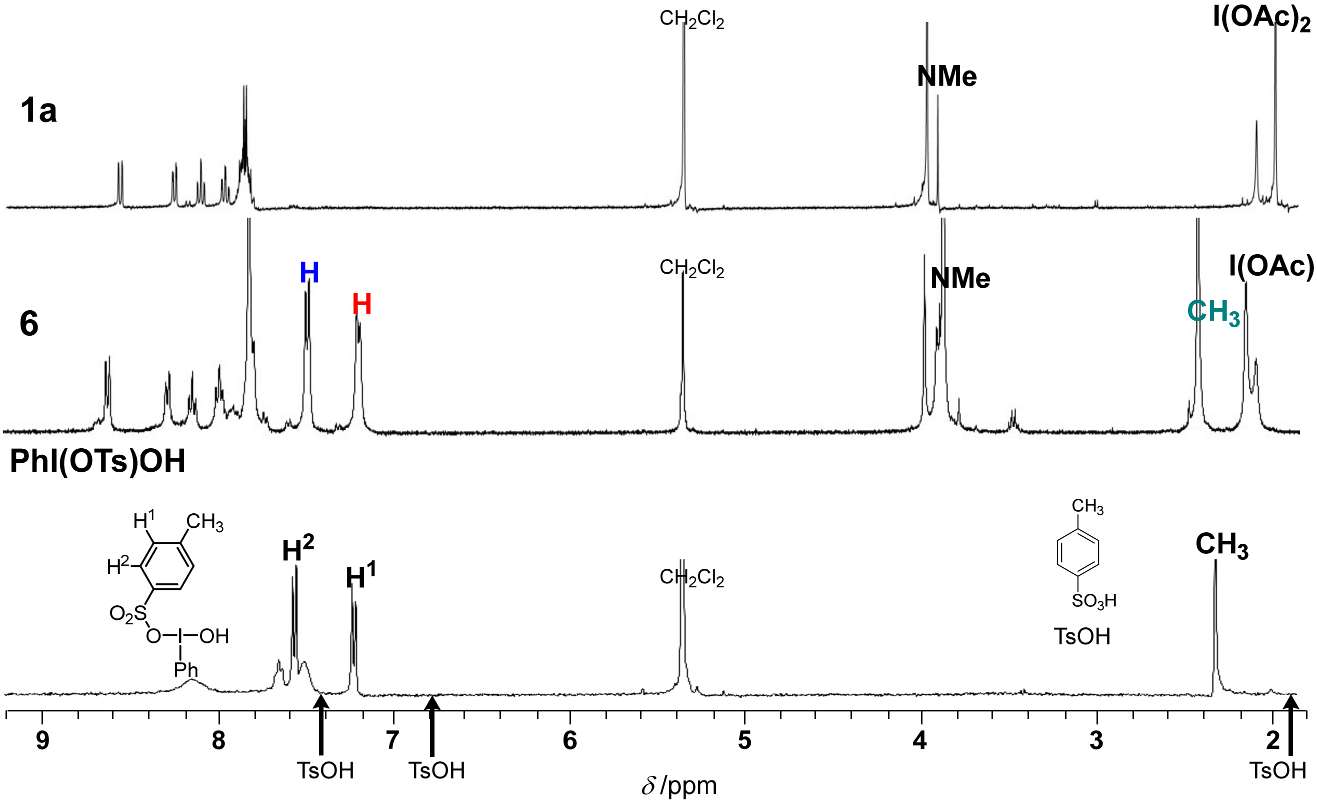


Scheme S1

Comparison among ^{1}H NMR spectra of 1a, intermediate 6, Ph(OH)OTs, and TsOH·H_2O (Fig. 3, B)

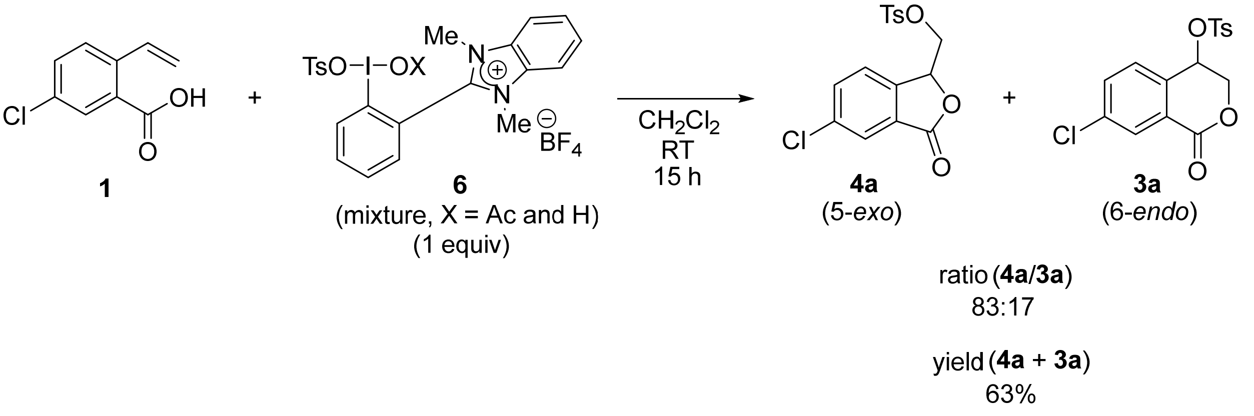
The comparison among ^{1}H NMR of spectra of **1a**, intermediate **6**, Ph(OH)OTs, and TsOH·H_2O is shown below.

^{1}H NMR (400 MHz, CD_2Cl_2)



Scheme S2

Tosyloxylation using intermediate 6 (Fig. 3, C)



Scheme S3

To the solution of compound **6** (0.1121 g, ca. 0.15 mmol), which was prepared and isolated by the procedure described above, in CH_2Cl_2 (0.5 mL) was added carboxylic acid **1** (0.0279 g, 0.168 mmol) at room temperature, and then the reaction mixture was stirred for 15 h at room temperature. The reaction was quenched with water (5 mL), and the mixture was extracted by CH_2Cl_2 (10 mL x 3). The corrected organic layers were dried over $MgSO_4$. The solvent was evaporated, and the NMR yield and the ratio in the crude product was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Observation of 4-EtPhSO$_3$ anion in the presence of pyrone (Fig. 5)

Preparation of compound 9 (Chart D, Fig. 5)

All manipulations were carried out in glove box filled with dry nitrogen gas. To the solution of **1a** (0.05 mmol) in CH_2Cl_2 (0.5 mL) was added 4-EtSO$_3$H (0.06 mmol) at room temperature, and the reaction mixture was stirred for 30 min. Then, the volatiles were evaporated in vacuo, the residue was washed with Et_2O to remove AcOH. The volatiles were evaporated again to obtain compound **9**.

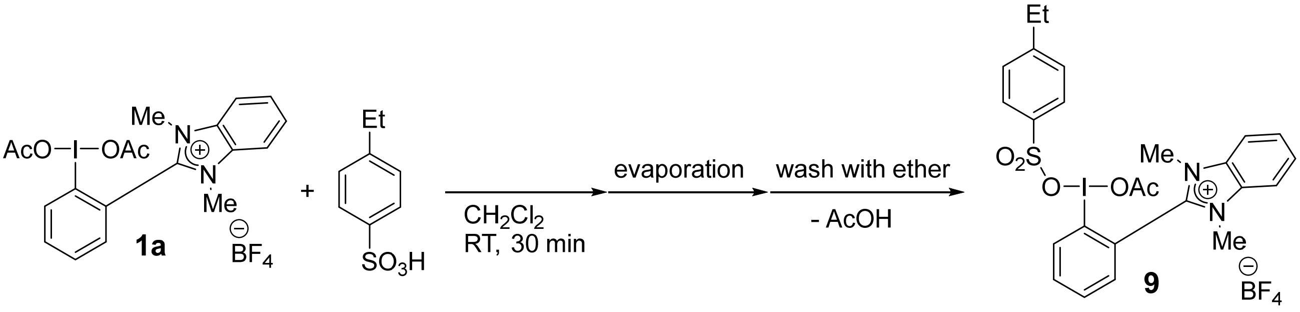
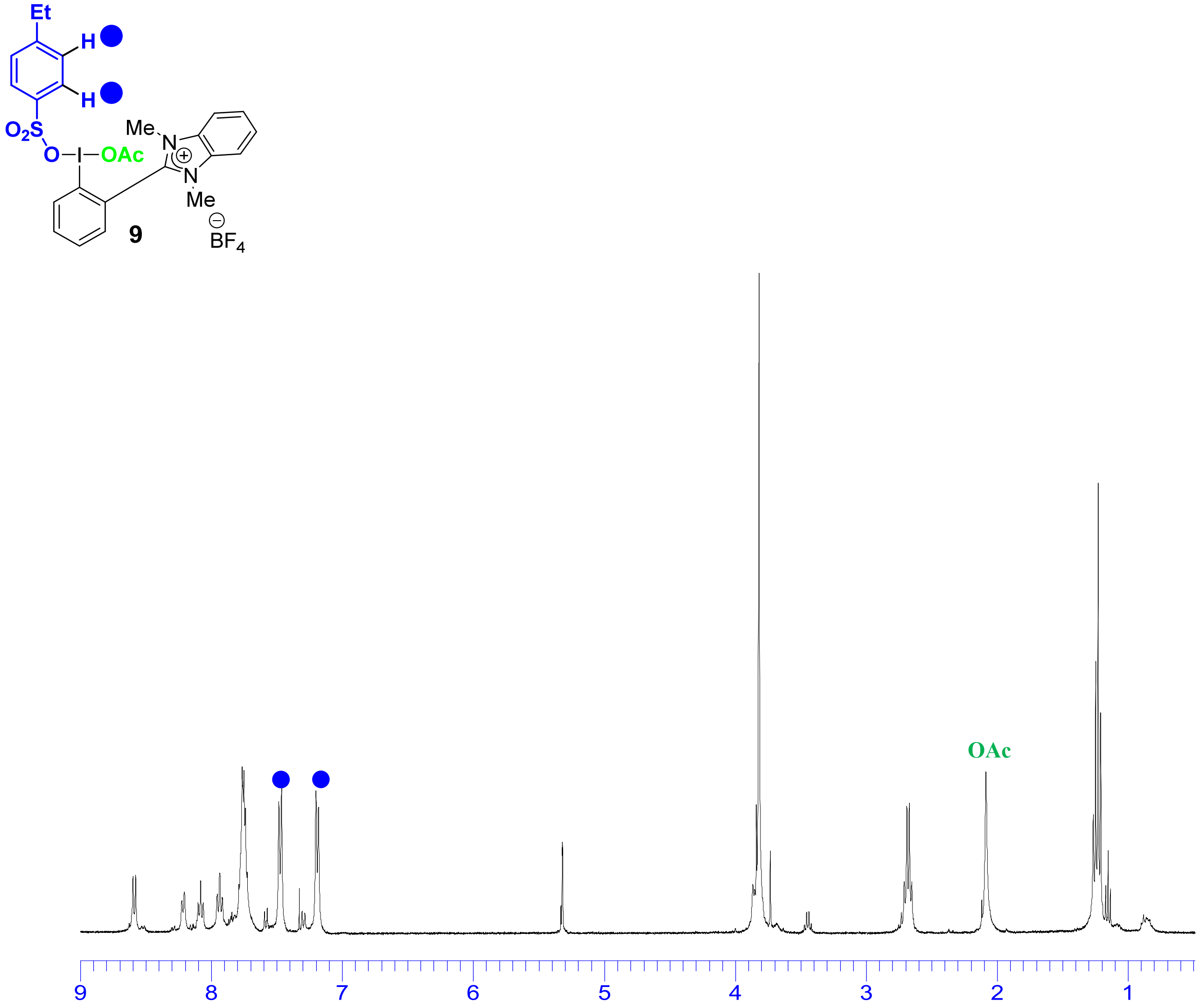


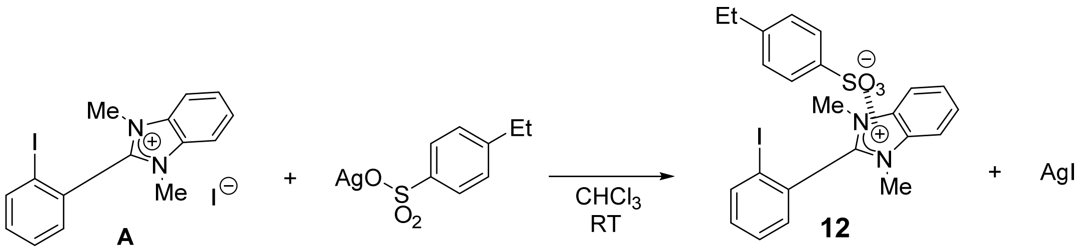
Chart D in full scale

^{1}H NMR (400 MHz, CD_2Cl_2) at 20 °C



Scheme S4

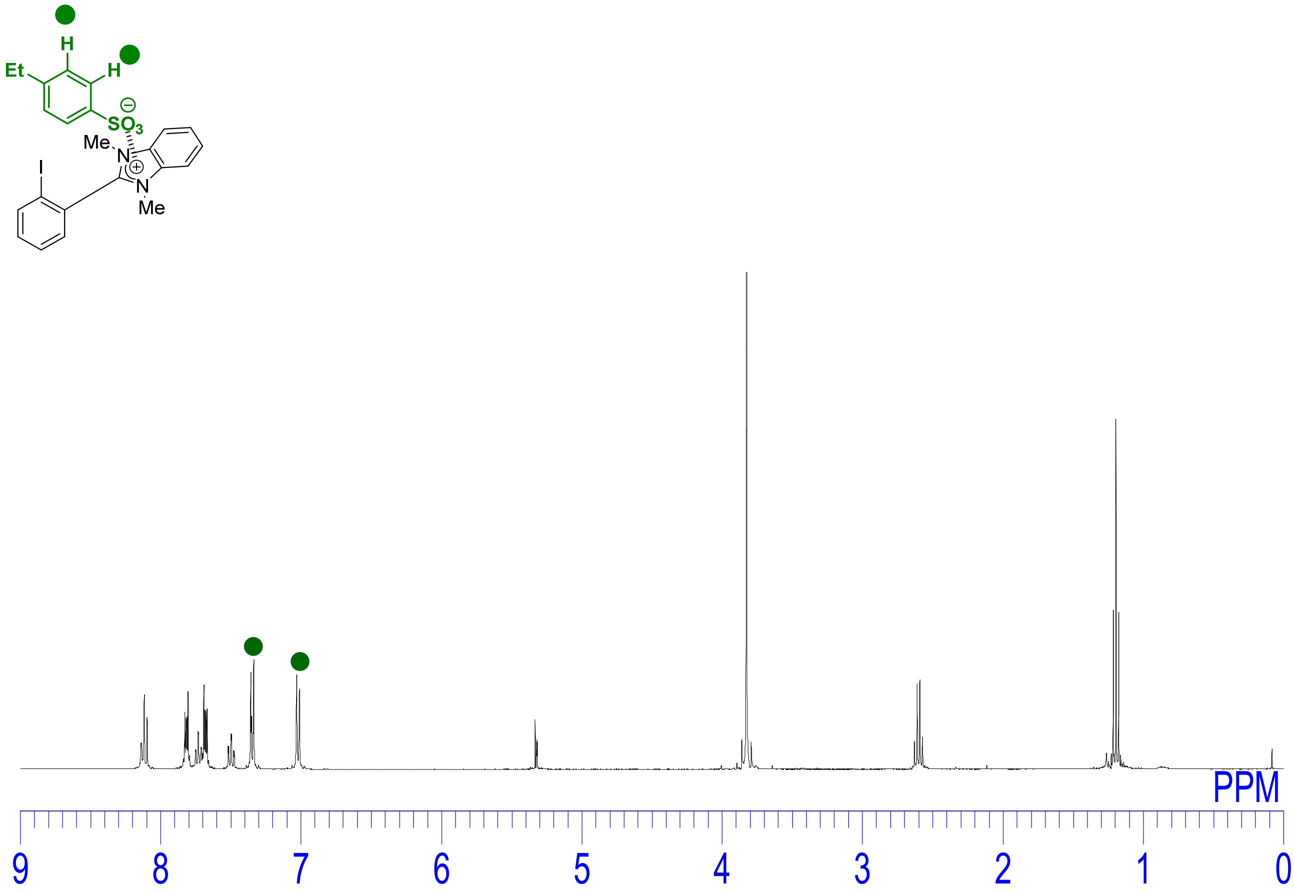
Preparation of imidazolium 4-ethylbenzene sulfonate 12 (Chart B, Fig. 5)



To the solution of imidazolium iodide **A** (0.2 mmol) in $CHCl_3$ was added silver 4-ethylbenzenesulfonate (0.22 mmol), and the reaction mixture was stirred at room temperature for overnight. Then, precipitating AgI was removed by filtration and the filtrate was concentrated to obtain compound **12**.

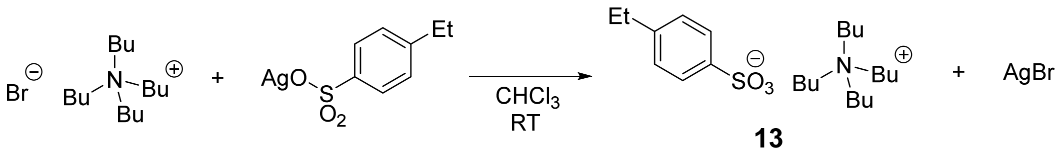
Chart B in full scale

^{1}H NMR (400 MHz, CD_2Cl_2) at 20 °C



Scheme S5

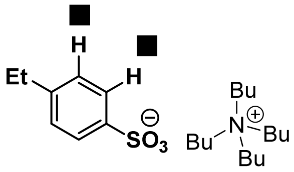
Preparation of tetrabutylammonium 4-ethylbenzene sulfonate 13 (Chart A, Fig. 5)



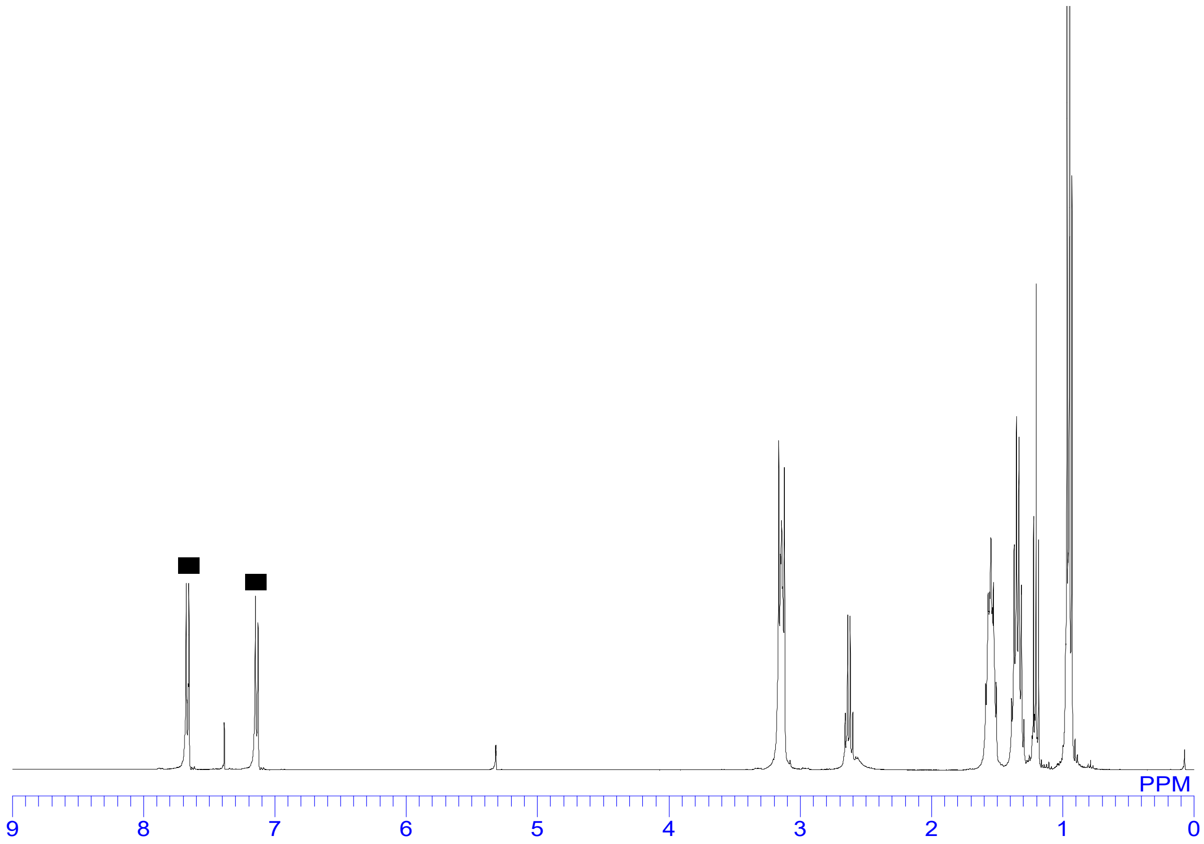
To the solution of tetrabutylammonium bromide (0.2 mmol) in CHCl$_3$ was added silver 4-ethylbenzenesulfonate (0.22 mmol), and the reaction mixture was stirred at room temperature for overnight. Then, precipitating AgI was removed by filtration and the filtrate was concentrated to obtain compound **13**.

Chart A in full scale

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) at 20 °C



13



Scheme S6

Reaction of **9** with γ-pyrone **10** (Chart C, Fig. 5)

To the solution of **9** (0.05 mmol) in CD_2Cl_2 (0.5 mL) was γ-pyrone **10** (0.125 mmol) at room temperature, and the reaction mixture was stirred for 30 min. The ^1H NMR spectrum is shown below at room temperature.

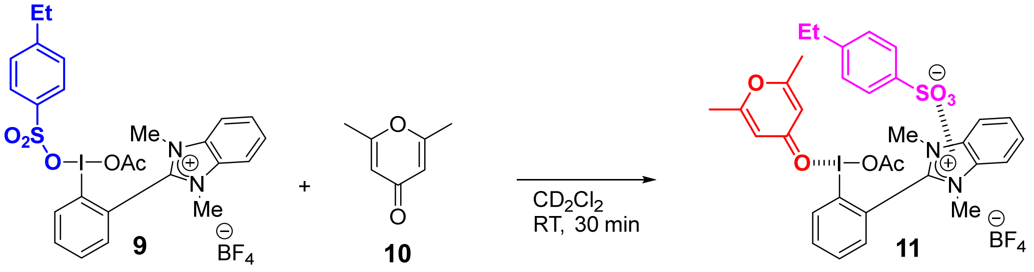
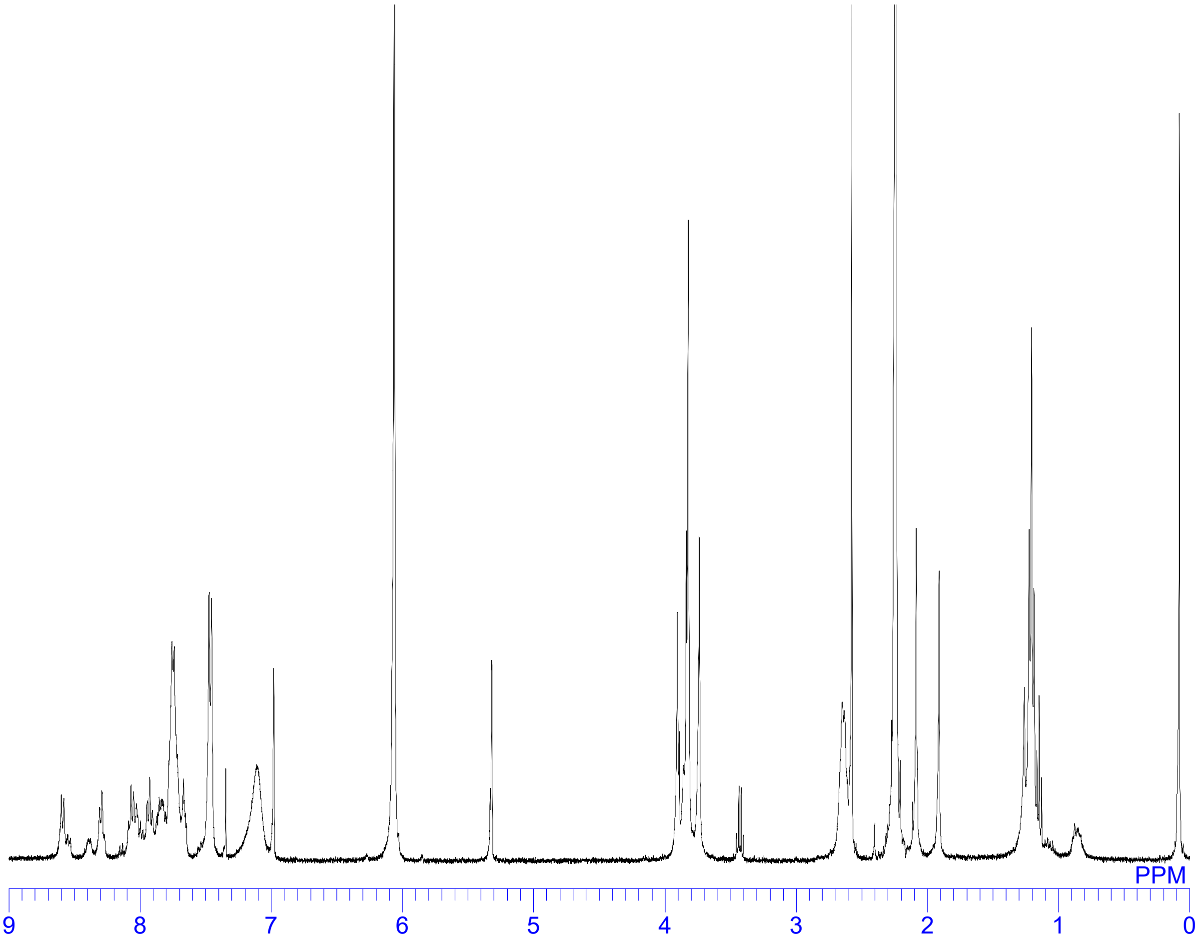


Chart C in full scale

^1H NMR (400 MHz, CD_2Cl_2) at 20 °C

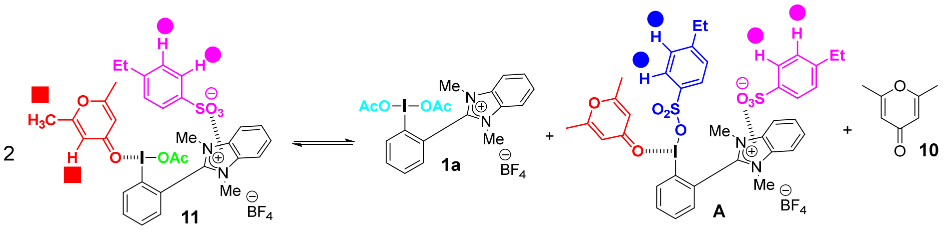


Scheme S7

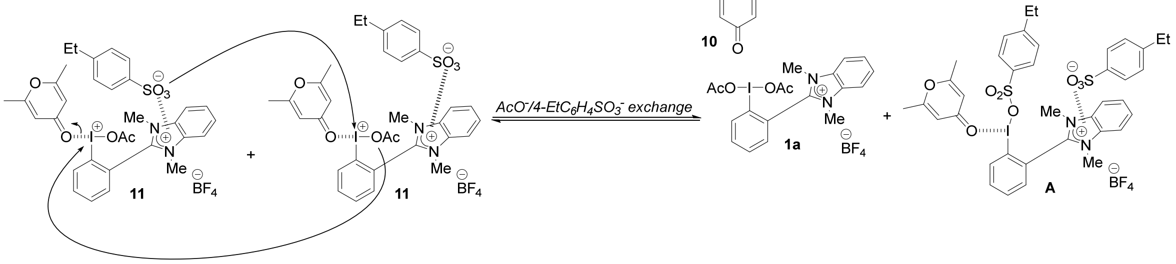
VT NMR study on reaction of 9 with γ-pyrone 10 (VT NMR of Chart C)

The broadening of aromatic proton signals of 4-$EtC_6H_4SO_3$ group in Chart C (Fig. 5) indicates fast equilibrium among a few kinds of 4-ethylbenzenesulfonate. Therefore, we carried out the VT NMR study (20, -10, -30, and -50 °C) as shown below, and then discovered that disproportionation between two molecules of **11** via AcO^-/4-$EtC_6H_4SO_3^-$ exchange occurred to give the mixture of **11**, **1a**, **A**, and **10** (Eq. 1 and Reaction Mechanism in Scheme 8). There are two types of 4-$EtC_6H_4SO_3^-$ in this equilibrium: one (colored by blue) is on the iodine atom, and another (colored by pink) is trapped by the imidazolium moiety. Focusing on aromatic proton signals in ^1H NMR spectra (7.0-7.5 ppm), the equilibrium at 20 °C is fast so the signals of 4-$EtC_6H_4SO_3$ groups of **11** and **A** coalesce. At low temperature (-10, -30, and -50 °C), the aromatic proton signals of 4-$EtC_6H_4SO_3$ group trapped by the imidazolium moiety (colored by pink) and the signals of 4-$EtC_6H_4SO_3$ group on the iodine atom (colored by blue) appear independently. Thus, it is important that the coalesce signals of 4-$EtC_6H_4SO_3$ group at 20 °C reflects the property of 4-$EtC_6H_4SO_3$ group trapped by the imidazolium moiety in **11**.

(Eq. 1)

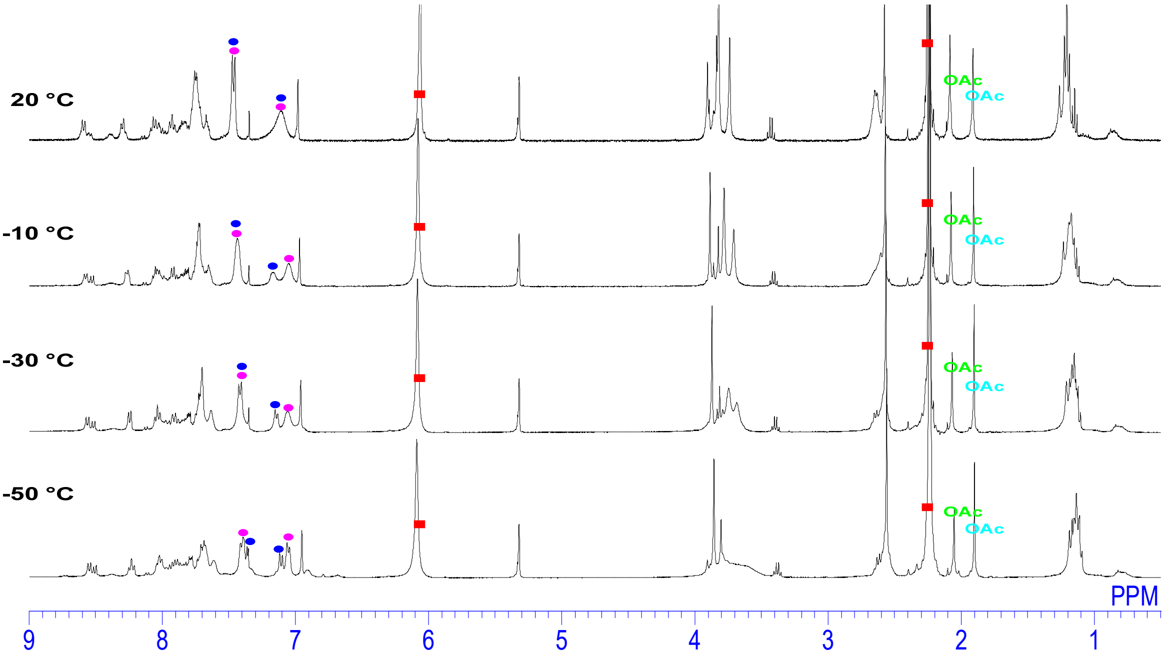


Reaction Mechanism



VT NMR spectra of Chart C on Fig. 5

^1H NMR (400 MHz, CD_2Cl_2)

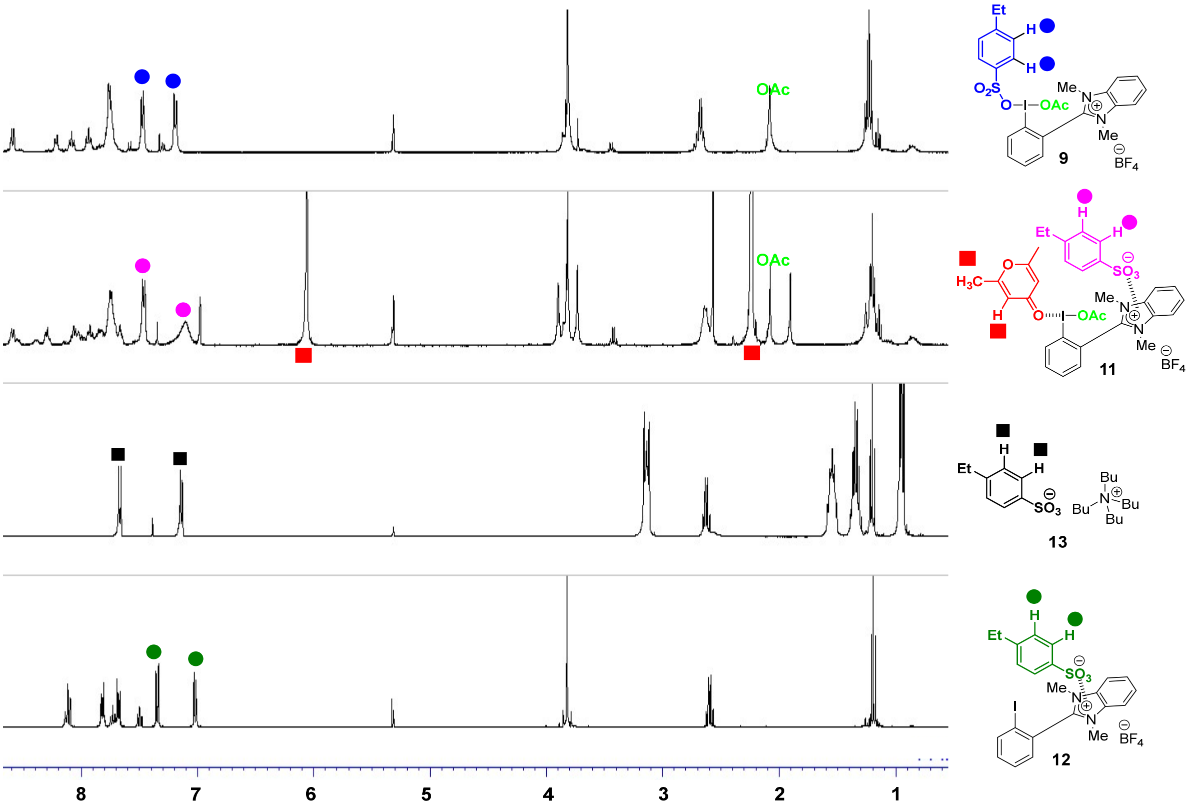


Scheme S8

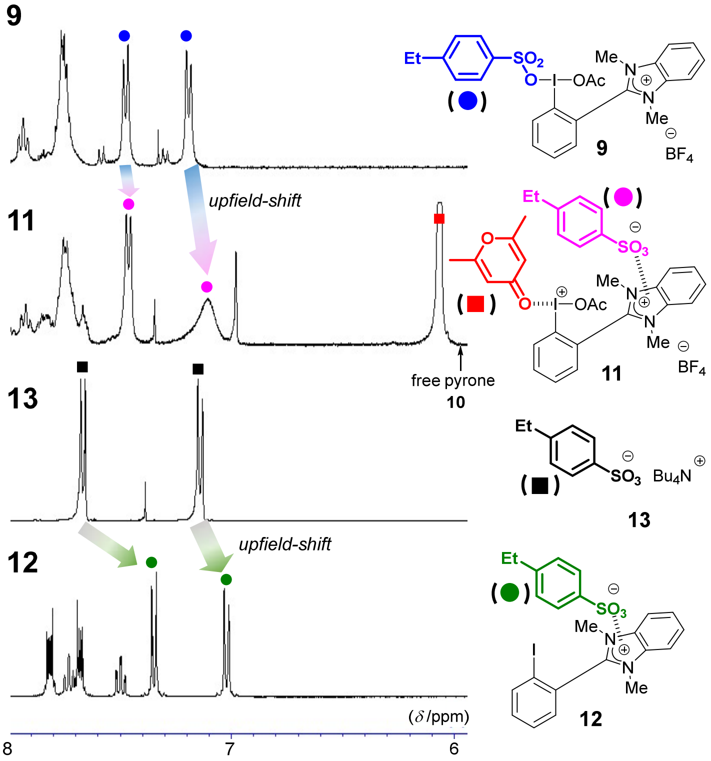
Comparison among compounds 9, 11, 12, and 13 of ^{1}H NMR (Fig. 5)

We show the comparison among ^{1}H NMR spectra (5.8-8.0 ppm) at 20 °C of compounds **9**, **11**, **12**, and **13** in Fig. 5 of the main text. ^{1}H NMR spectra at 20 °C in full scale (0.4-8.8 ppm) are shown below.

Full scale at 20 °C (^{1}H NMR in CD_2Cl_2)



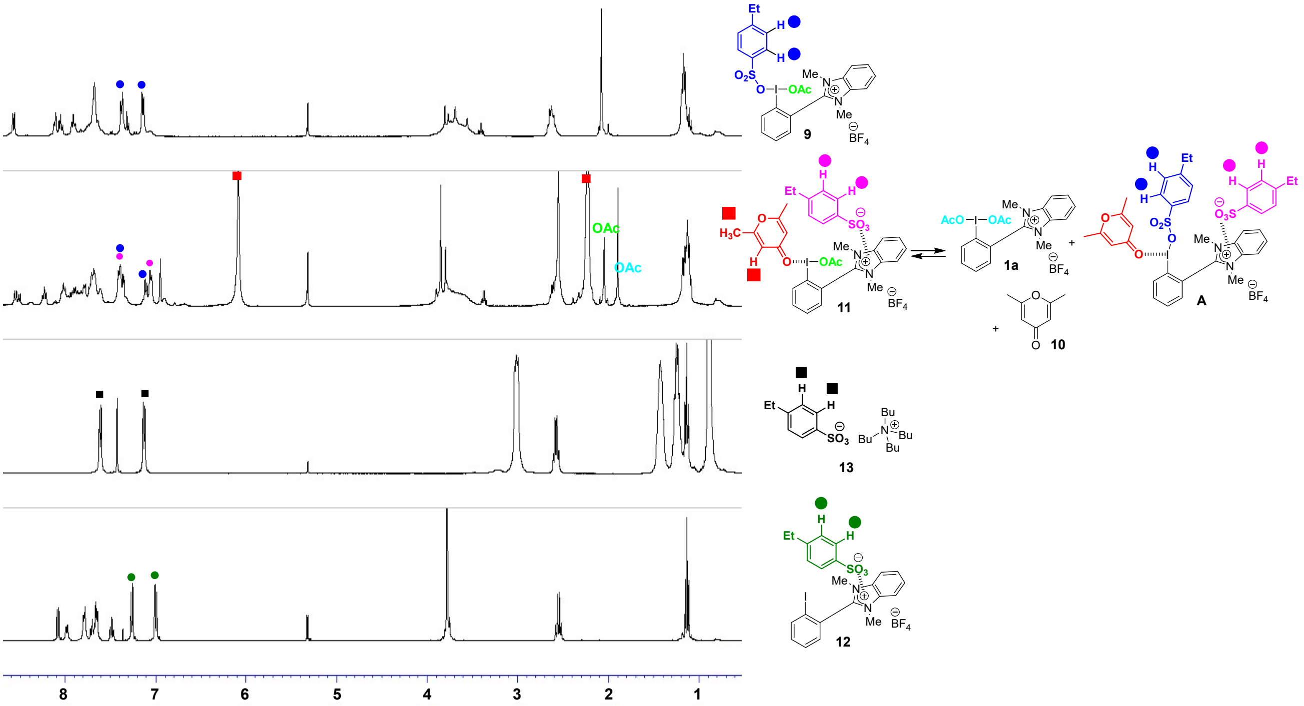
Enlarged view at 20 °C (^{1}H NMR in CD_2Cl_2)



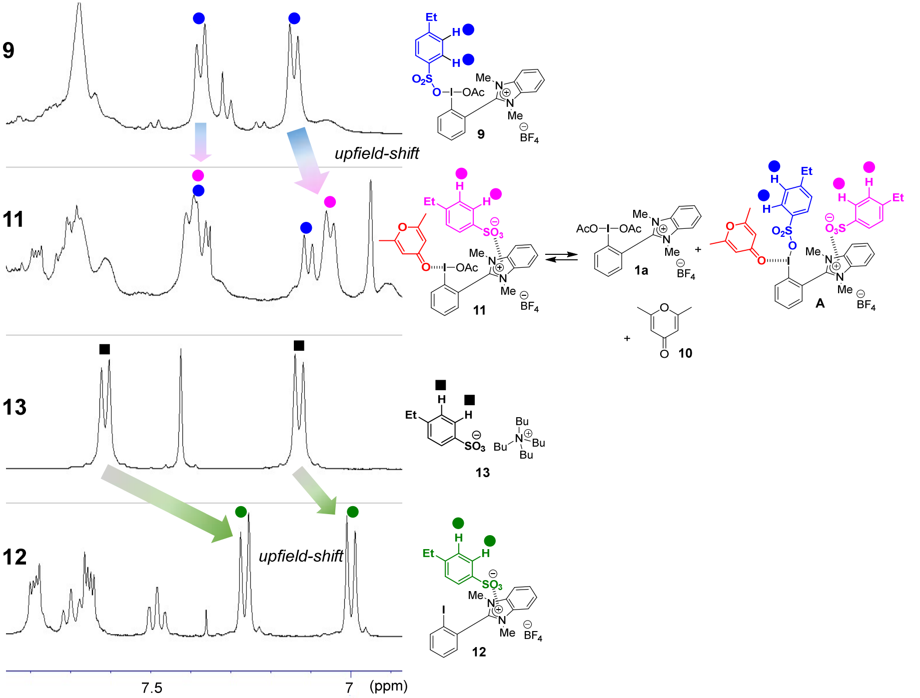
Scheme S9

Considering the result of the VT NMR study on compound **11** described above, we investigated the comparison among ^{1}H NMR spectra at -50 °C, too. In Scheme S10, the ^{1}H NMR spectra at -50 °C are shown. In the chart of 11, signals of two types of 4-$EtC_6H_4SO_3$ groups appeared (pointed by blue or pink circles). The signals (pointed by blue circles) correspond to 4-$EtC_6H_4SO_3^-$ on the iodide atom in species **A** because their chemical shift values are similar to that of **9**. Another signals (pointed by pink circles), which appear at more upfield than that of **A**, correspond to 4-$EtC_6H_4SO_3^-$ trapped by the imidazolium moiety in **11** and **A**, which are overlapped due to the same environment in the interaction with the imidazolium moiety. In fact, the chemical shift values of these signals (pointed by pink circles) are close to those of imidazolium sulfonate **12** (pointed by green circles) as a reference compound rather than Bu_4N salt **13** (pointed by black squares) Therefore, the ^{1}H NMR spectra at -50 °C supports that 4-$EtC_6H_4SO_3$ anion is kicked out and trapped by the imidazolium moiety and complex **11** is generated.

Full scale at -50 °C (^{1}H NMR in CD_2Cl_2)



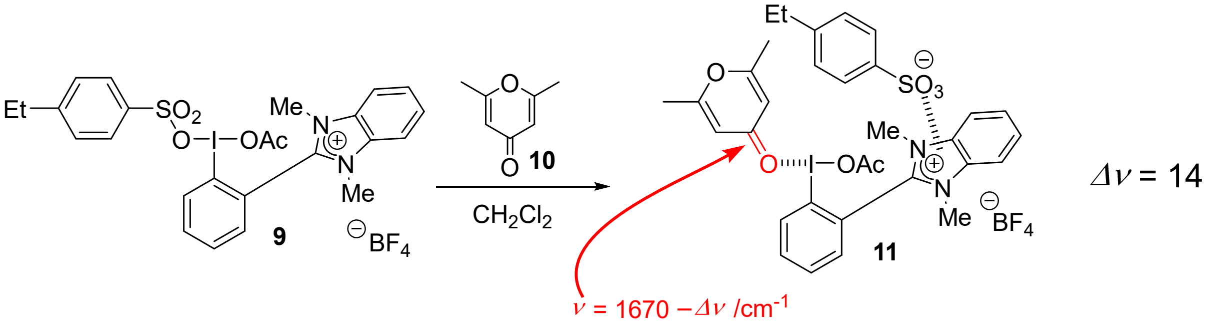
Enlarged view at -50 °C (^{1}H NMR in CD_2Cl_2)

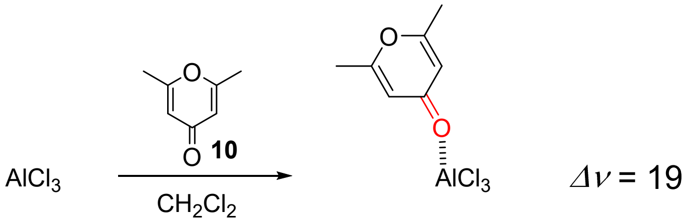


Scheme S10

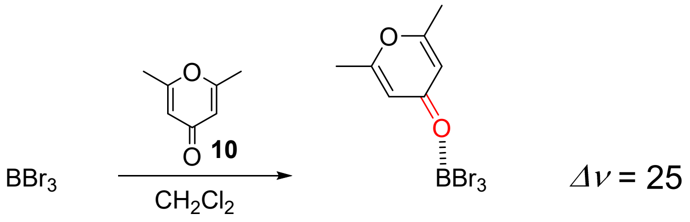
Confirmation of coordination of γ-pyrone 10 to the iodine canter by IR stretching frequency of the C=O bond

We established the evaluation of the Lewis acidity by IR stretching frequency of the C=O bond of γ-pyrone **10** in the complexation between a Lewis acid and **10**. Therefore, the coordination of the carbonyl oxygen atom of **10** to the iodine center in **9** was observed by this method. In the solution of **9** and **10** in CH_2Cl_2, $\Delta\nu$ is 14 cm^{-1}. Considering the values of $\Delta\nu$ exhibited by $AlCl_3$ and BBr_3, this value clearly suggests the the coordination of the carbonyl oxygen atom of **10** to the iodine center in **9**.





Y. Nishimoto, S. Nakao, S. Machinaka, F. Hidaka, M. Yasuda, *Chem. Eur. J.* **2019**, *25*, 10792



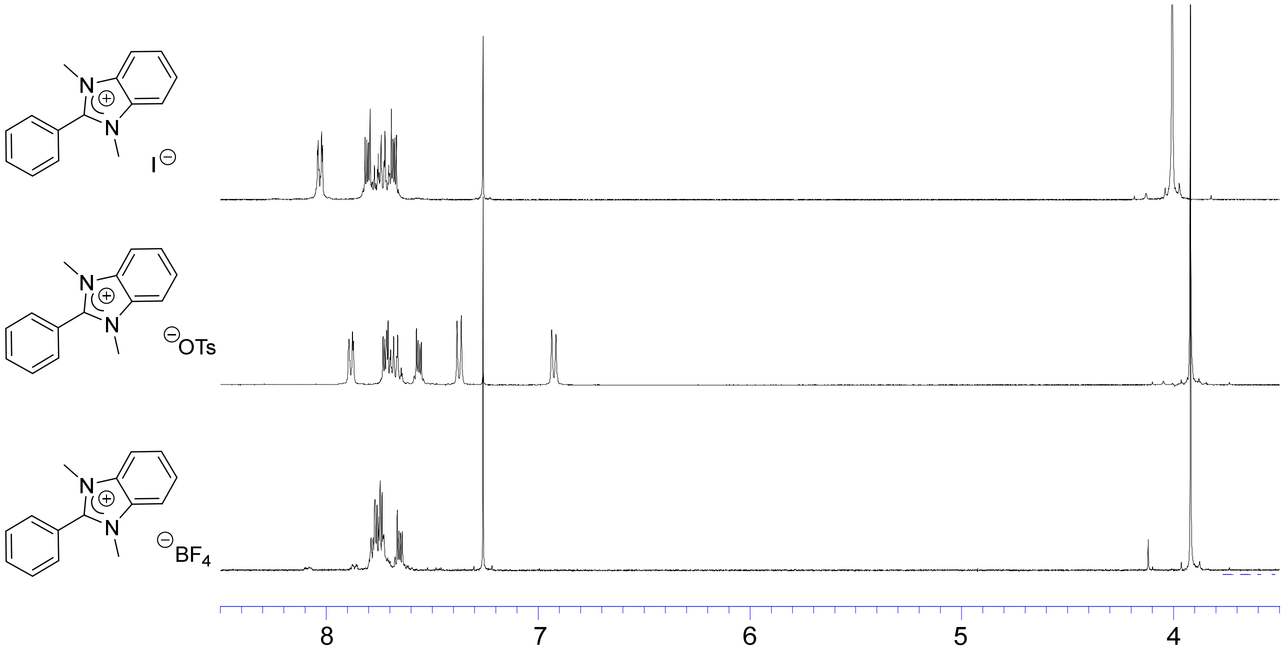
A. Konishi, R. Yasunaga, K. Chiba, M. Yasuda, *Chem. Commun.* **2016**, *52*, 3348.

Scheme S11

Effects of counter anions on ^{1}H NMR spectra of imidazolium salts

Effects of counter anions on imidazolium salts were investigated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of imidazolium iodide, tosylate, and tetrafluoroborate in $CDCl_3$ are shown below. Chemical shifts of each imidazolium salts are considerably different, which suggests that imidazolium cation interacts with each anion to form contact ion pairs.

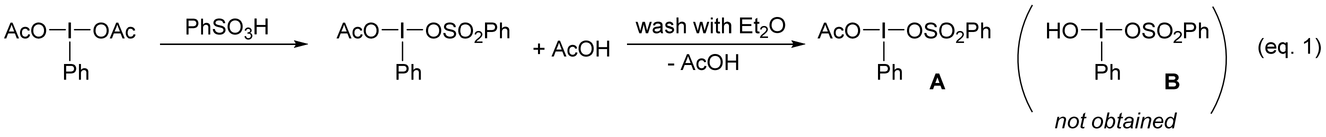
^{1}H NMR (400 MHz, $CDCl_3$)



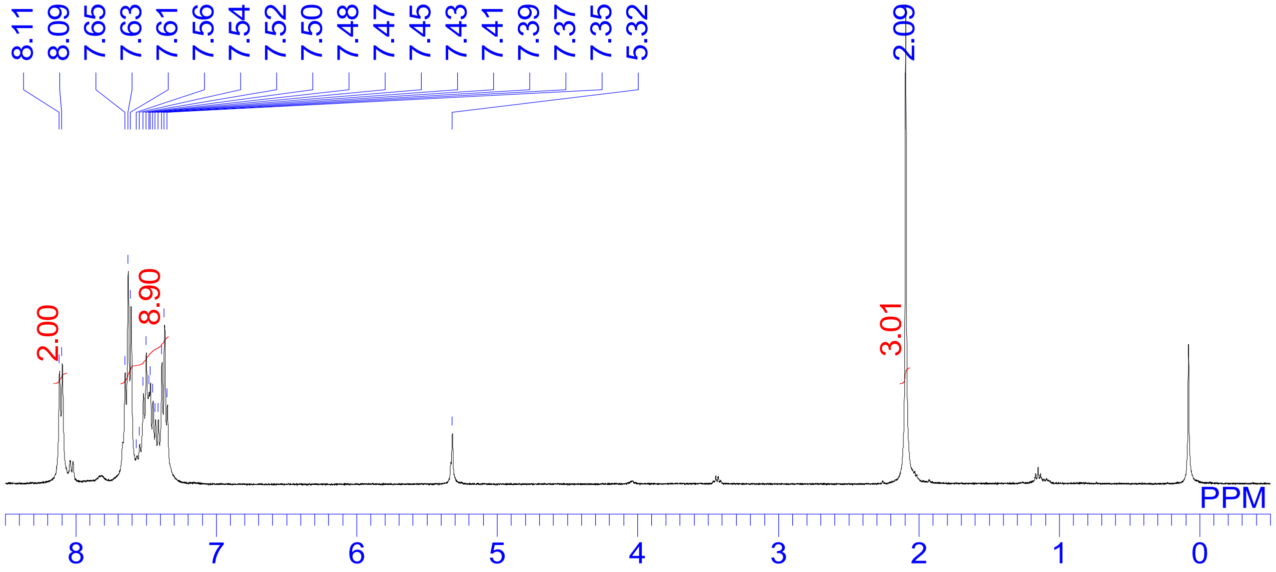
Scheme S12

Effect of OH and OAc groups on I atom of hypervalent iodines on the regioselectivity

To the solution of $PhI(OAc)_2$ in CH_2Cl_2 was added $PhSO_3H$, and the reaction mixture was stirred at room temperature for 30 min. Then, the volatiles were evaporated in vacuo and the residual oil was lightly washed Et_2O to give $PhI(OAc)OSO_2Ph$ **A** as a colorless oil (eq. 1). ^1H NMR spectra of $PhI(OAc)OSO_2Ph$ **A** is shown below. This result is contrast to the reaction of $PhI(OAc)_2$ with $TsOH{\cdot}H_2O$ giving PhI(OH)OTs. This experiment suggests that not $PhI(OH)OSO_2Ph$ **B** but $PhI(OAc)OSO_2Ph$ **A** is generated without H_2O.



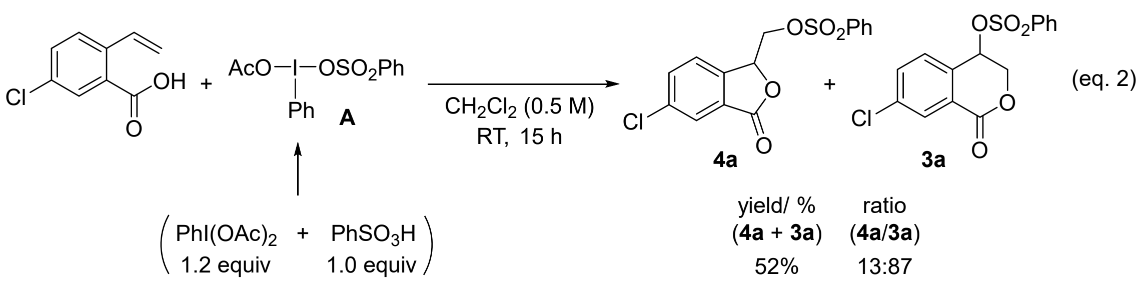
^1H NMR of $PhI(OAc)OSO_2Ph$ (400 MHz, CD_2Cl_2)



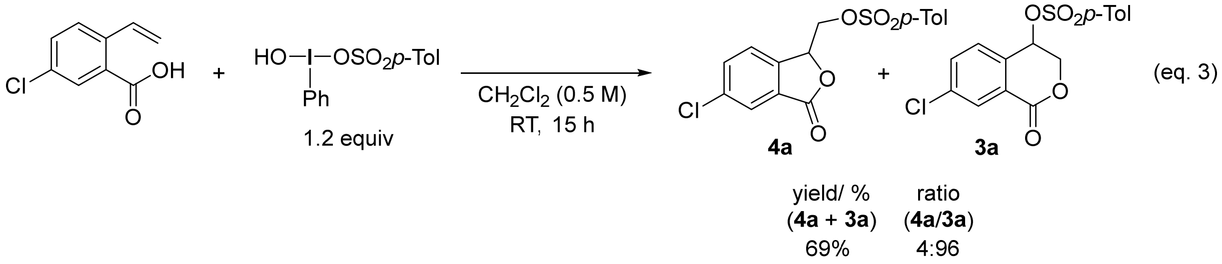
Scheme S13

Therefore, we used $PhI(OAc)OSO_2Ph$ **A** to investigate the effect of OH and OAc groups on I atom of hypervalent iodines on the regioselectivity, as shown below.

(eq. 2) To a solution of $PhI(OAc)_2$ (0.0577 g, 0.179 mmol) in CH_2Cl_2 (0.3 mL) was added $PhSO_3H$ (0.0241 g, 0.152 mmol) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature. Then, CH_2Cl_2 and AcOH were evaporated under reduced pressure (1.0 Torr) for 5 min at 30 °C and filled with N_2. The evaporation and N_2-filling manipulation was repeated twice. After evaporation, to the mixture was added CH_2Cl_2 (0.3 mL) and 5-chloro-2-vinylbenzoic acid (0.0289 g, 0.158 mmol). The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by water and the water layer was extracted with CH_2Cl_2. The collected organic layer was dried over $MgSO_4$ and the volatiles were evaporated. The yields of 5-*exo* and 6-*endo* product were determined by ^1H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.



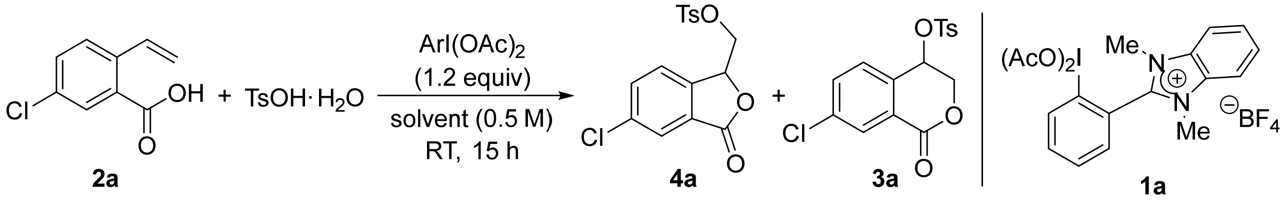
Scheme S14The result of eq. 2 revealed that PhI(OAc)OSO$_2$Ph **A** exhibited the 6-*endo* selectivity, and the level of selectivity is almost same as that exhibited by PhI(OH)OSO$_2$*p*-Tol (Koser's reagent) (eq. 3). Therefore, OH and OAc groups on I atom of hypervalent iodines do not influence on the regioselectivity of the present tosyloxylactonization.



Scheme S15

Effect of solvents on the regioselectivity of 1a and PhI(OAc)$_2$

Solvent effects on the regioselectivity in the tosyloxylactonization of **2a** with TsOH·H$_2$O using **1a** or PhI(OAc)$_2$ as shown below. In the use of CHCl$_3$, PhCl, CH$_2$Cl$_2$, ClCH$_2$CH$_2$Cl, and CH$_3$CN as solvents, **1a** and PhI(OAc)$_2$ exhibited the high level of 5-*exo* selectivity and 6-endo selectivity, respectively, regardless of the permittivity. Theexaminations in hexane, toluene, Et$_2$O, and THF resulted in no reaction because **1a** and PhI(OAc)$_2$ are insoluble in these solvents.



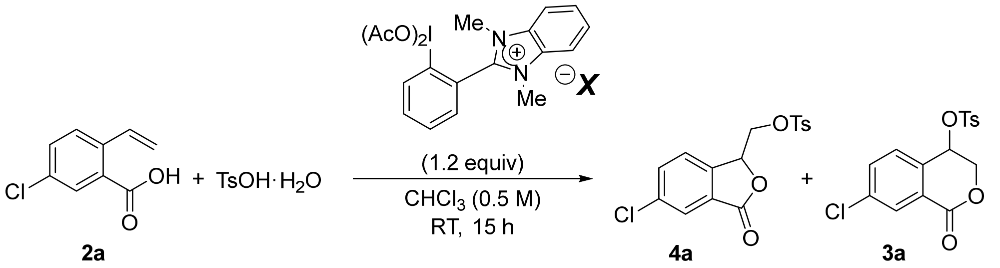
Solvent	Permittivity		regioselectivity (%) **4a** 5-*exo*	regioselectivity (%) **3a** 6-*endo*	yield (**4a**+**3a**)	
CHCl$_3$	4.8	**1a**	87	13	63%	
		PhI(OAc)$_2$	11	89	57%	
PhCl	5.7	**1a**	>99		29%	recovery of **2a** 45%
		PhI(OAc)$_2$	27	73	15%	recovery of **2a** 56%
CH$_2$Cl$_2$	9.1	**1a**	91	9	64%	
		PhI(OAc)$_2$	17	83	60%	
ClCH$_2$CH$_2$Cl	10.6	**1a**	87	13	68%	
		PhI(OAc)$_2$	21	79	71%	
CH$_3$CN	37.5	**1a**	80	20	56%	
		PhI(OAc)$_2$	17	83	42%	

The use of other solvents such as hexane, toluene, Et$_2$O, and THF resulted in no reaction because **1a** and PhI(OAc)$_2$ are insoluble in these solvents.

Scheme S16

Effect of couteranions of imidazolium moiety on the regioselectivity

The use of SbF_6^- instead of BF_4^- in $ArI(OAc)_2$ **1a** also gave 5-*exo* product **4a**. The selectiveity of the SbF_6 salt was the same level as that of the BF_4 salt. The low yield was due to the low solubility of the SbF6 salt. Other hypervalent iodines (***X*** = Br, I, OTs, PF6) could not been synthesized.



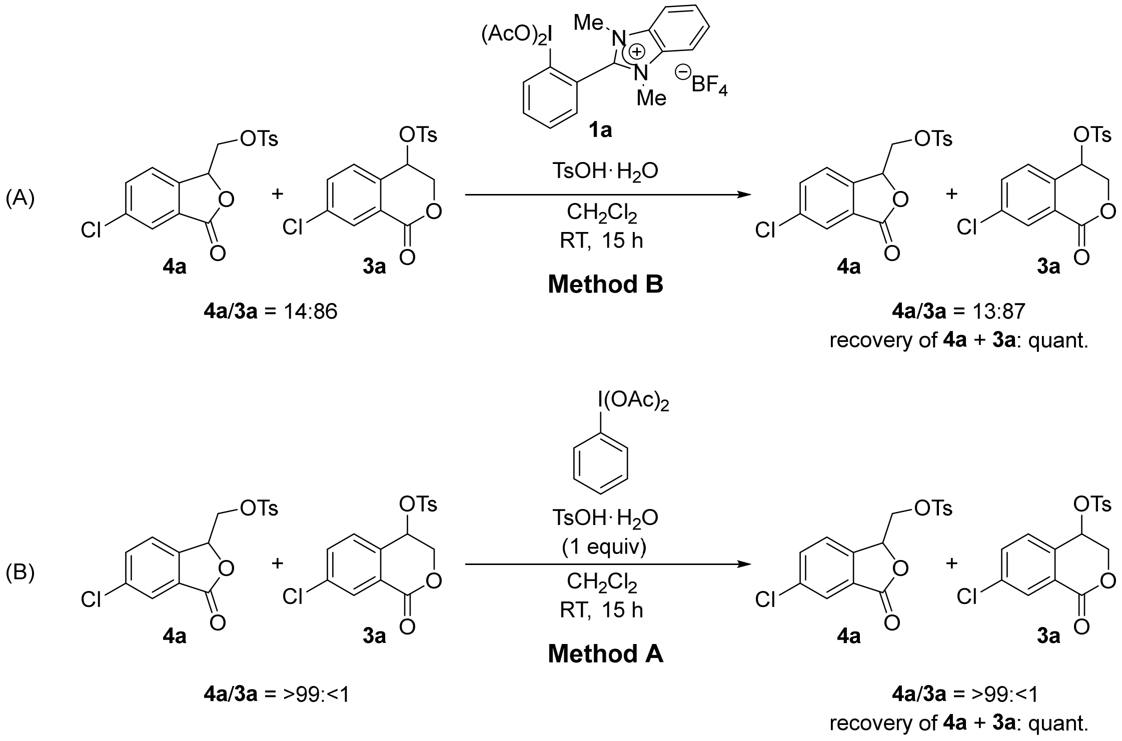
X	regioselectivity (%) **4a** 5-*exo*	 **3a** 6-*endo*	yield (**4a**+**3a**)
BF_4	87	13	63%
SbF_6	95	5	15% recovery of **2a**: 46%

Other hypervalent iodines (***X*** = Br, I, OTs, PF_6) could not been synthesized.

Scheme S17

Investigation of Isomerization between 5-*Exo* and 6-*Endo* Products

The results shown in Scheme S18 suggested the isomerization between 5-*exo* and 6-*endo* products did not occur. Method A and Method B are the reaction conditions giving preferentially 5-*exo* **4a** and 6-*endo* **3a**, respectively (See General Procedures at p. 38 in SI). After the mixture of 5-*exo* **4a** and 6-*endo* **3a** (**4a**/**3a** = 14:86) was underwent the reaction conditions using **1a** (Method B), the ratio of **4a** to **3a** was not changed, and **4a** and **3a** was recovered quantitatively. When the 5-*exo* **4a** was treated with the reaction conditions using $PhI(OAc)_2$ (Method A), 6-*endo* **3a** was not obtained and **4a** was recovered quantitatively.



Scheme S18

Computational Studies

Calculation Method Details

All geometry optimizations and thermal energy correction calculations (frequency analyses) using density functional theory (DFT) were performed with the Gaussian 16 (revision C.01). Quantum chemical calculations were performed under vacuum at 298 K and 1 bar. The geometry optimizations were carried out at ωB97X-D level of theory in gas phase with a mixed basis set; 6-311+G(d,p) for C, H, O, N, S, B, F and Lanl2DZ for I.

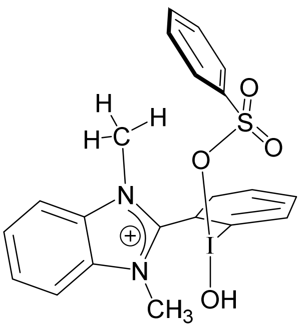
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, S112 J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT, 2016.

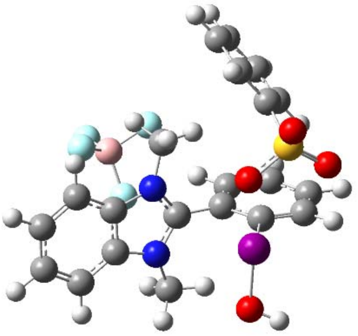
Summary of calculated energies and thermochemical parameters of the optimized structures

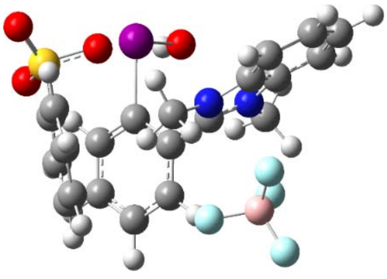
	electronic and zero-point Energies [hartree]	electronic and thermal Energies [hartree]	electronic and thermal Enthalpies [hartree]	electronic and thermal Free Energies [hartree]	imaginary frequency
***o*-7-A**	-2056.124012	-2056.090567	-2056.089623	-2056.191884	0
***o*-7-B**	-2056.120972	-2056.087956	-2056.087012	-2056.186394	0
8-B	-1522.773154	-1522.746052	-1522.745108	-1522.831828	0
PhI(OH)OSO2Ph	-1173.957596	-1173.940561	-1173.939617	-1174.004019	0
ArI(OH)OSO2Ph bearing an imidazolidinium moiety					
conformer A	-1903.730259	-1903.699333	-1903.698388	-1903.793765	0
conformer B	-1903.729659	-1903.698608	-1903.697664	-1903.793549	0
***m*-7**	-2056.129737	-2056.096809	-2056.095865	-2056.196892	0
***p*-7**	-2056.120003	-2056.087134	-2056.08619	-2056.186741	0
ArI(OH)OMs bearing an imidazolium moiety	-1864.465139	-1864.434952	-1864.434007	-1864.528787	0

Optimized Structures

***o*-7-A**

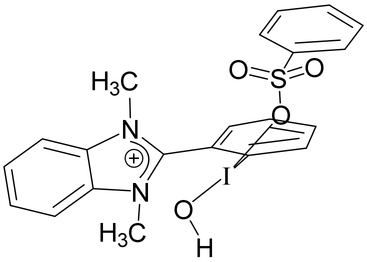


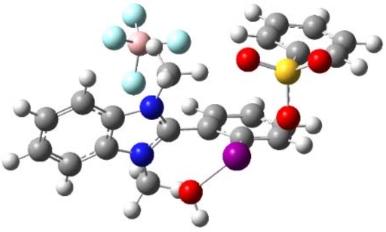


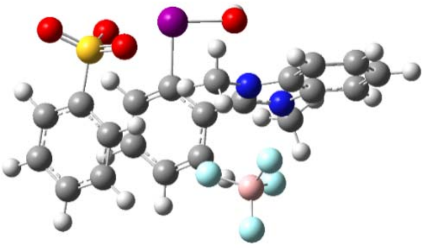


Another view

***o*-7-B**

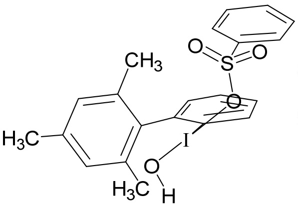


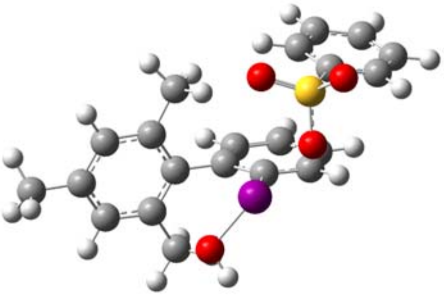


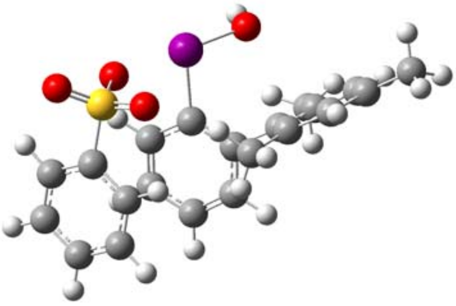


Another view

8-B

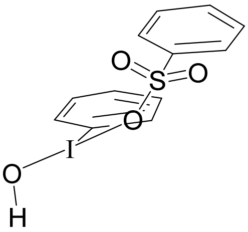


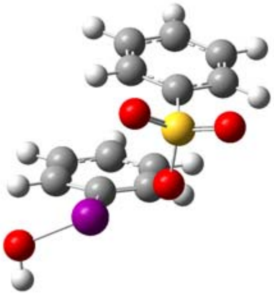


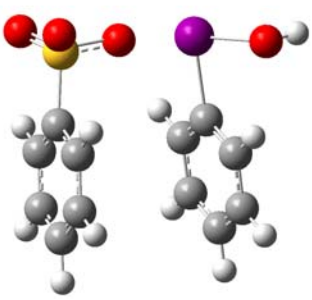


Another view

PhI(OH)OSO$_2$Ph



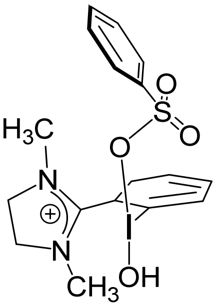


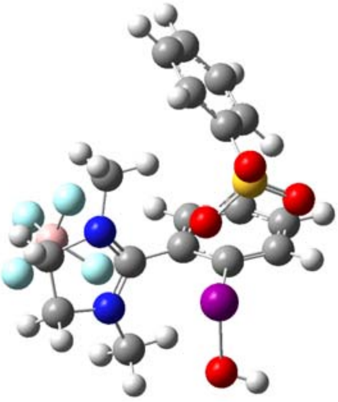


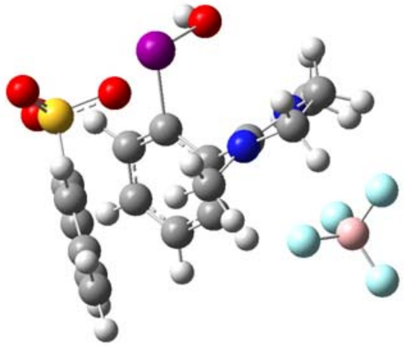
Another view

ArI(OH)OSO$_2$Ph bearing an imidazolidinium moiety

Conformer A



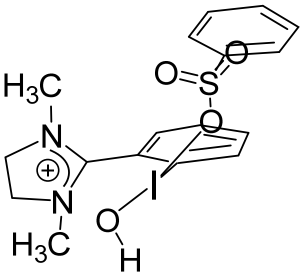


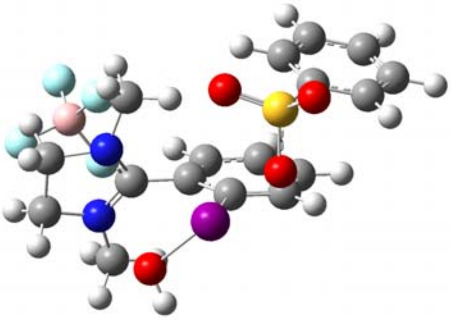


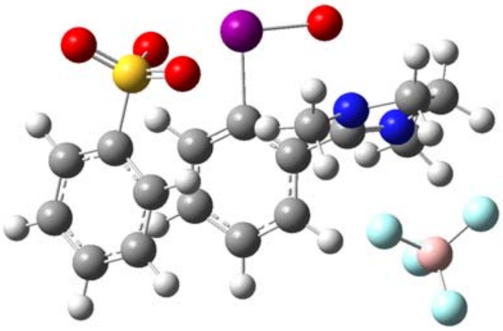
Another view

ArI(OH)OSO$_2$Ph bearing an imidazolidinium moiety

Conformer B

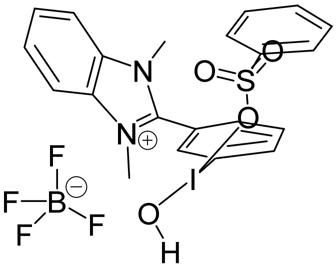


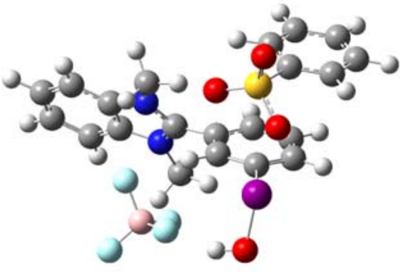


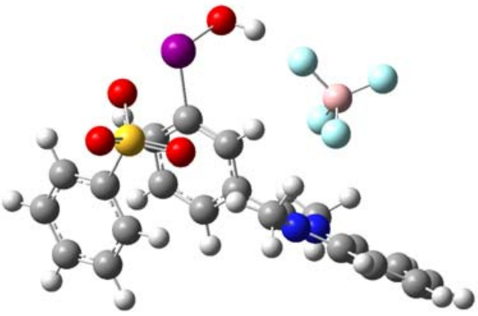


Another view

***m*-7**

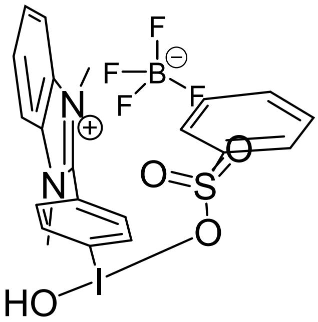


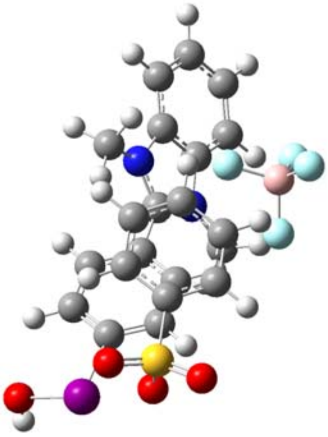


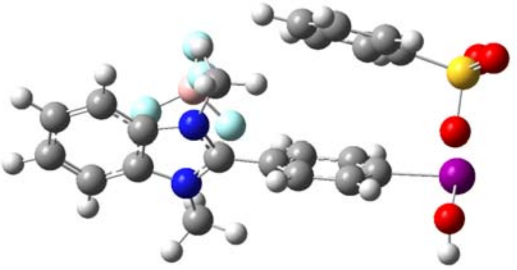


Another view

***p*-7**

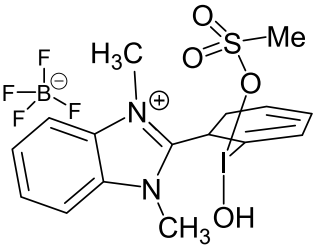


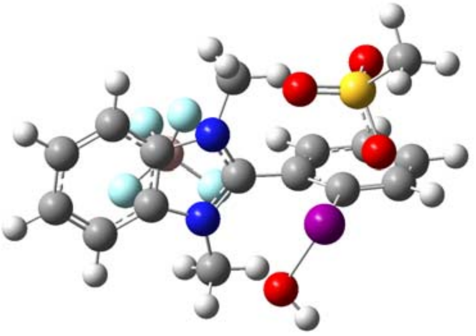


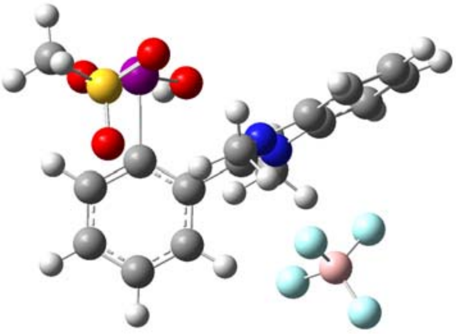


Another view

ArI(OH)OMs bearing an imidazolium moiety







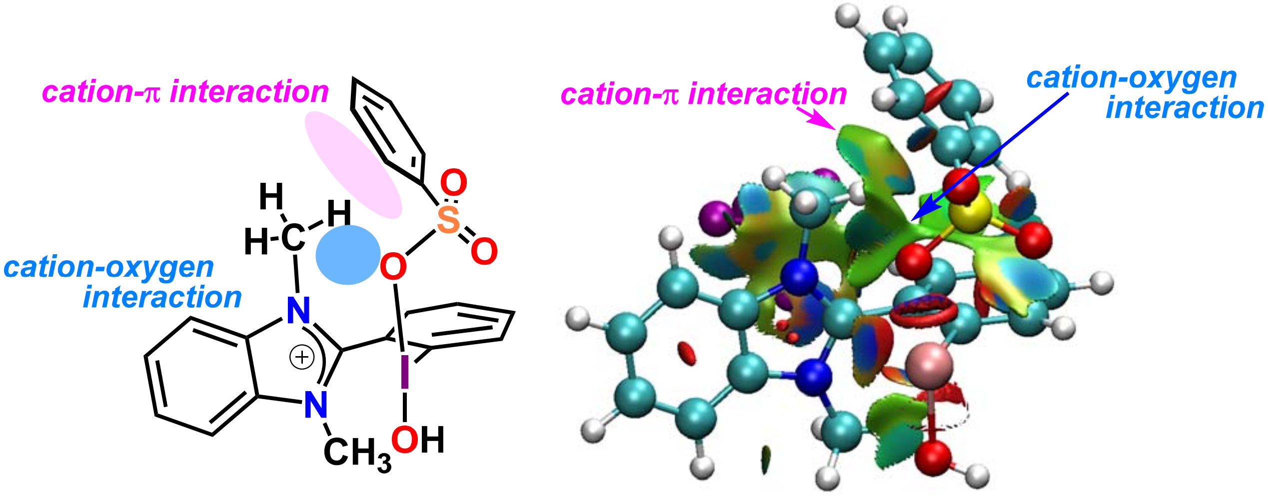
Another view

Non-Covalent Interaction (NCI)-Plot

Non-covalent interactions (NCI) were computed using the non-covalent interaction index from the optimized electron density at ωB97X-D level of theory in gas phase with a mixed basis set; cc-pVTZ for C, H, O, N, S, B, F and cc-pVTZ-DK3 for I. The wave function files (.wfn) were obtained from single point energy calculation using the optimized structures as above at ωB97X-D level of theory in gas phase with a mixed basis set; cc-pVTZ for C, H, O, N, S, B, F and cc-pVTZ-DK3 for I.

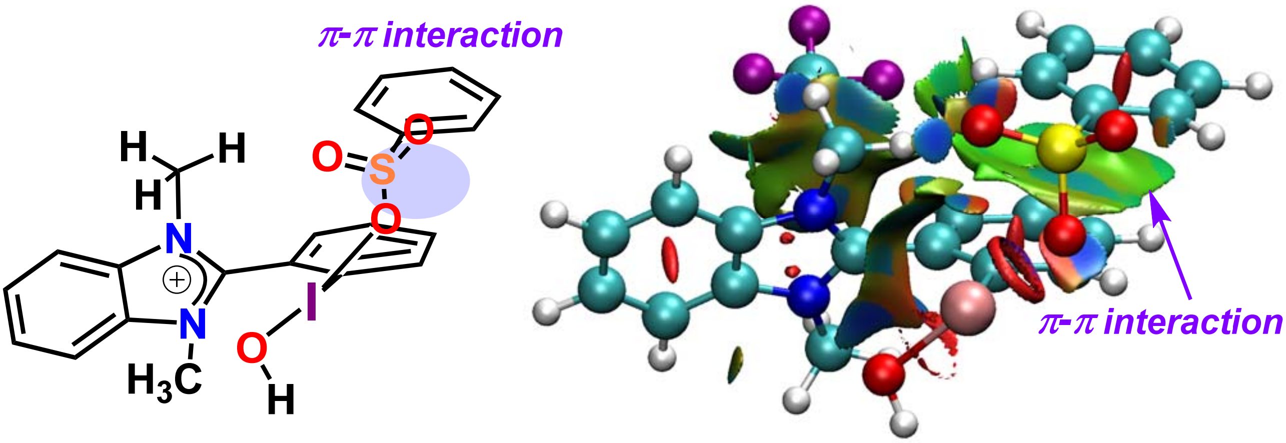
The generation of the NCI plot surfaces were obtained by NCIPLOT program.[6,7] The surfaces were colored on a blue-green-red (BGR) scale using VMD program[8] with a reduced density gradient (RDG) surfaces = 0.65 a.u. and the color range blue(attractive)-green-red(repulsive) for $-0.015 < \rho < +0.015$ a.u.. The blue region indicates strong attractive interactions and the red region indicates strong repulsive interactions.

o-7-A



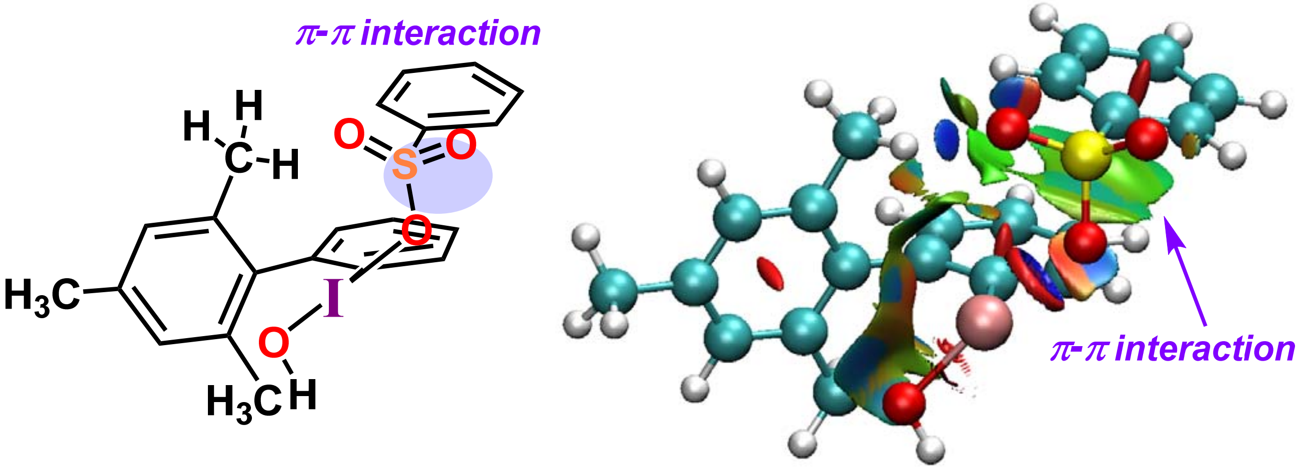
Scheme S19

o-7-B



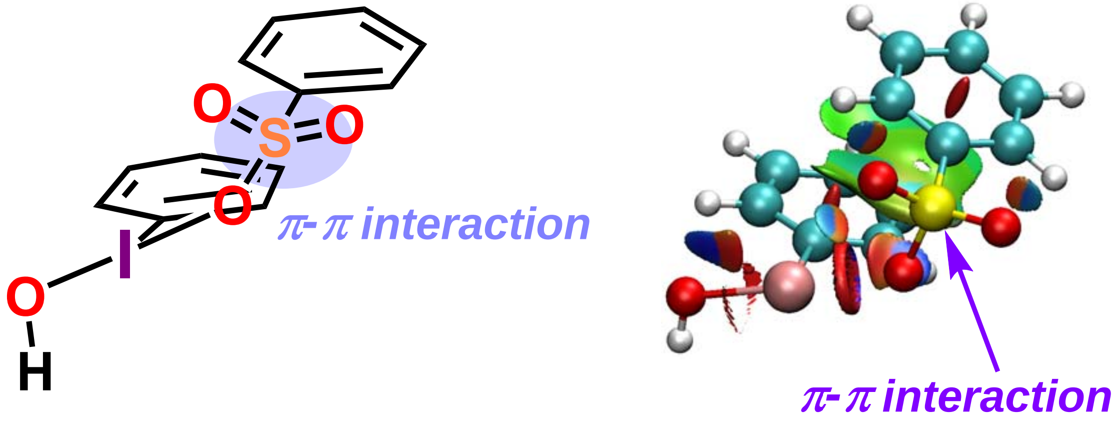
Scheme S20

8-B



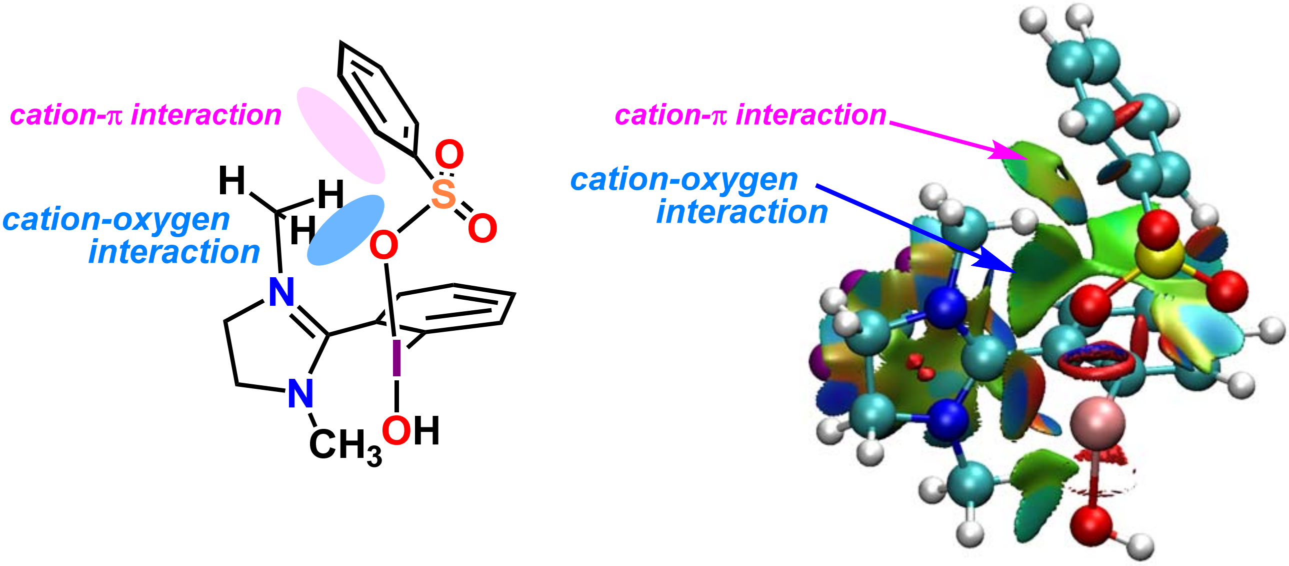
Scheme S21

PhI(OH)OSO$_2$Ph



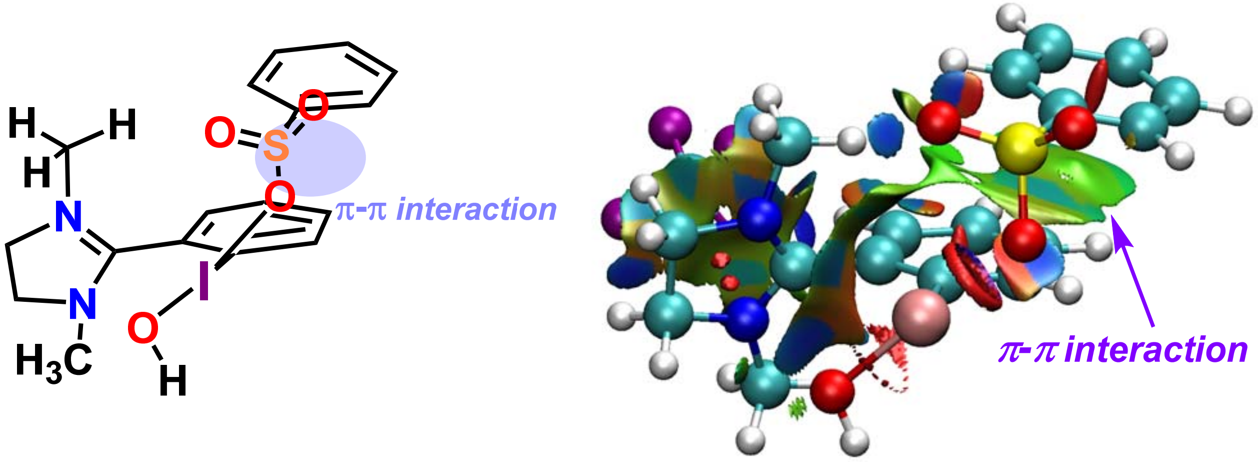
Scheme S22

ArI(OH)OSO$_2$Ph bearing an imidazolidinium moiety
Conformer A



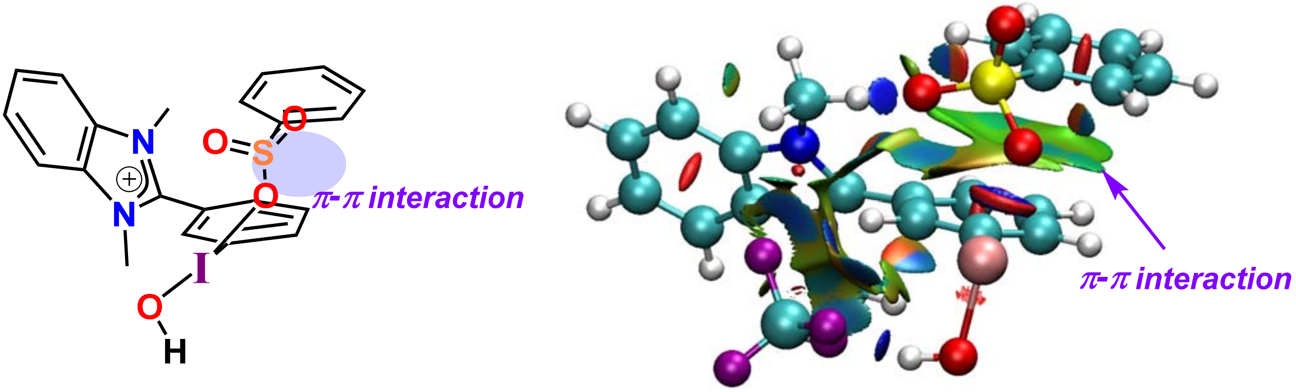
Scheme S23

ArI(OH)OSO$_2$Ph bearing an imidazolidinium moiety
Conformer B



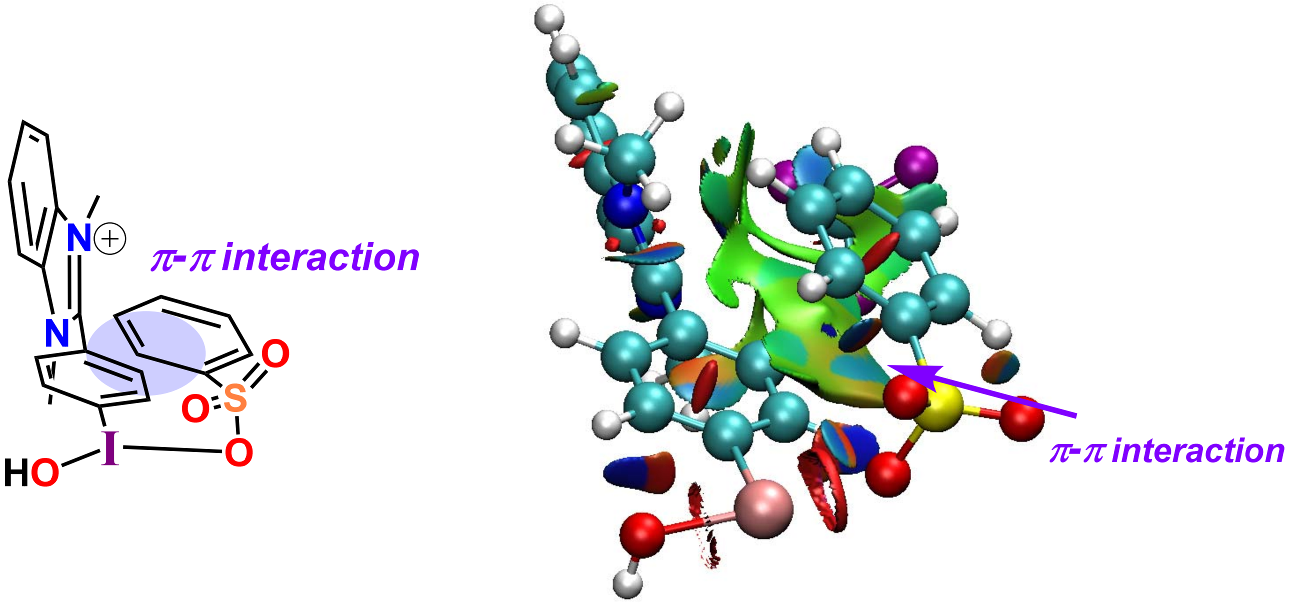
Scheme S24

***m*-7**



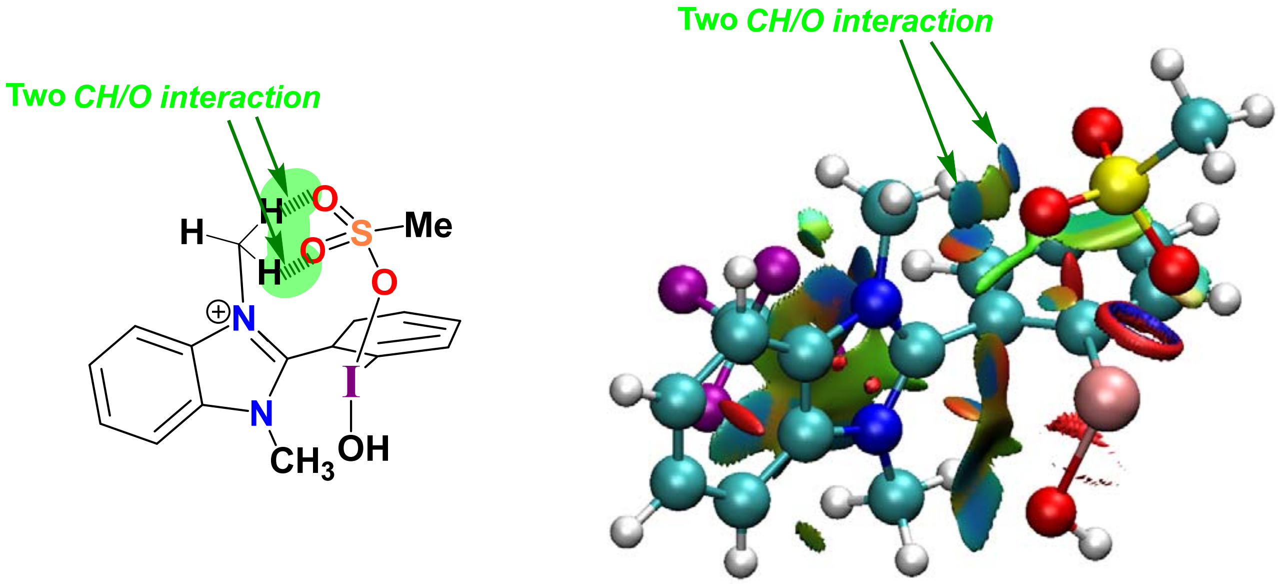
Scheme S25

***p*-7**



Scheme S26

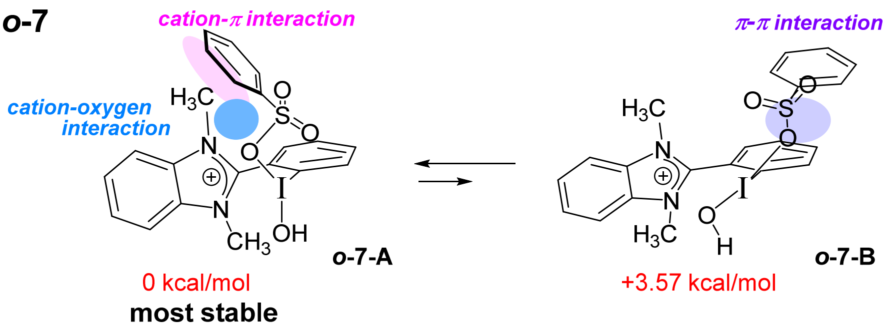
ArI(OH)OMs bearing an imidazolium moiety



Scheme S27

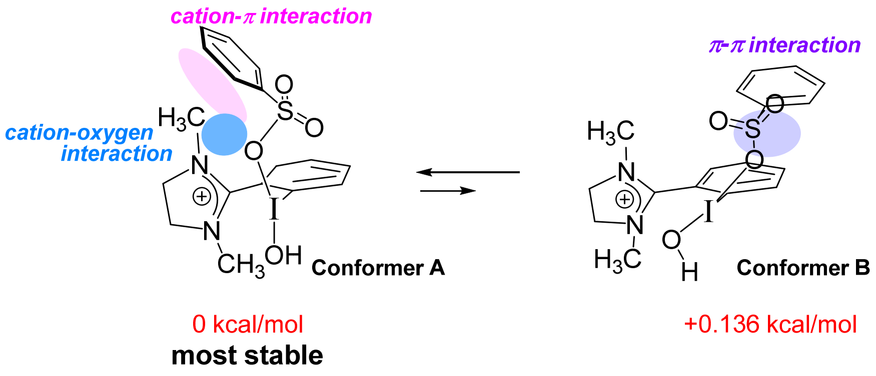
Summary of NCI analysis and thermochemical parameters

ArI(OH)OSO_2Ph ***o*-7** has two enegetic local minimums, and major conformer ***o*-7-A** is more stable than minor one ***o*-7-B** by 3.57 kcal/mol. Noncovalent interaction analysis shows that in ***o*-7-A** the Me group of the imidazolium moiety and the phenyl ring of the $PhSO_3$ group generates a cation−π interaction surface. In addition, the same Me group forms an effective cation-oxygen interaction with the oxygen atom of the $PhSO_3$ group, as evident from the large isosurface. In the minor conformer ***o*-7-B**, a π−π interaction of the $PhSO_3$ group with the iodobenzene framework contributes to the stabilization of the conformation. Therefore, the noncovalent interactions between the anionic $PhSO_3$ group and the imidazolium moiety is stronger than the π−π interaction of the $PhSO_3$ group with the iodobenzene framework. In ArI(OH)OSO_2Ph bearing an imidazolidinium moiety like **1d**, most stable **conformer A** (0.136 kcal/mol) has cation−π and cation-oxygen interactions between the imidazolidinium moiety and the $PhSO_3$ group like ***o*-7-A**. Minor **conformer B** has a π−π interaction of the $PhSO_3$ group with the iodobenzene framework. Thus, imidazolium and imidazolidinium moieties attracts the $PhSO_3$ group via the noncovalent forces in Koser-type intermediates.



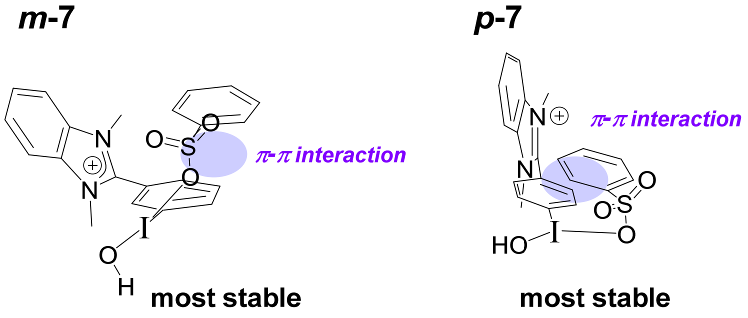
Scheme S28

ArI(OH)OSO_2Ph bearing an imidazolidinium moiety



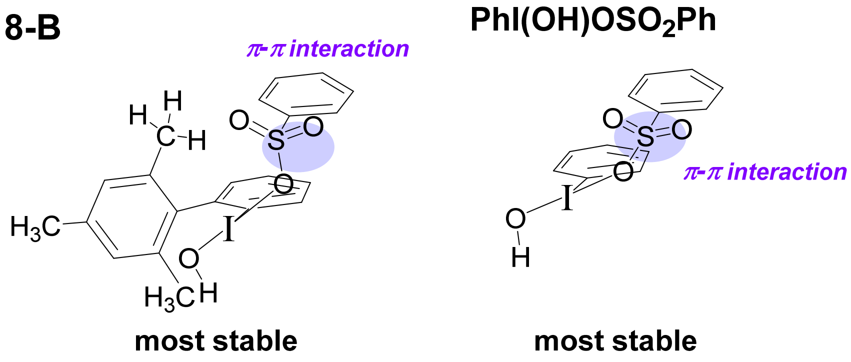
Scheme S29

In contrast to **o-7**, the most stable conformers of *meta*-substituted **m-7** and *para*-substituted **p-7**, are the structures involving a π–π interaction like **o-7-B**. Therefore, effective noncovalent interactions work only between the anionic $PhSO_3$ group and the imidazolium moiety at the *ortho* position of the iodine atom.



Scheme S30

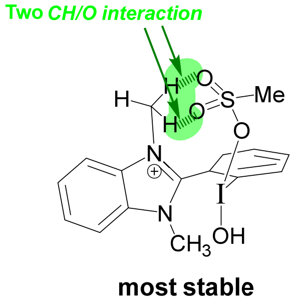
The most stable conformers of **8** and $PhI(OH)OSO_2Ph$ include the π–π interaction of the $PhSO_3$ group with the iodobenzene framework. So, this type of π–π interaction is a main factor to stabilize the conformation of Koser-type reagents.



Scheme S31

The combination of $ArI(OAc)_2$ **1a** with MsOH also exhibits the 5-*exo* selectivity. In this case, ArI(OX)OMs (X = H or OAc) would be an intermediate. The NCI analysis shows two CH/O interaction between the Me group of the imidazolium moiety and the MsO group. Thus, the imidazolium moiety effectively attracts the MsO group via the noncovalent forces.

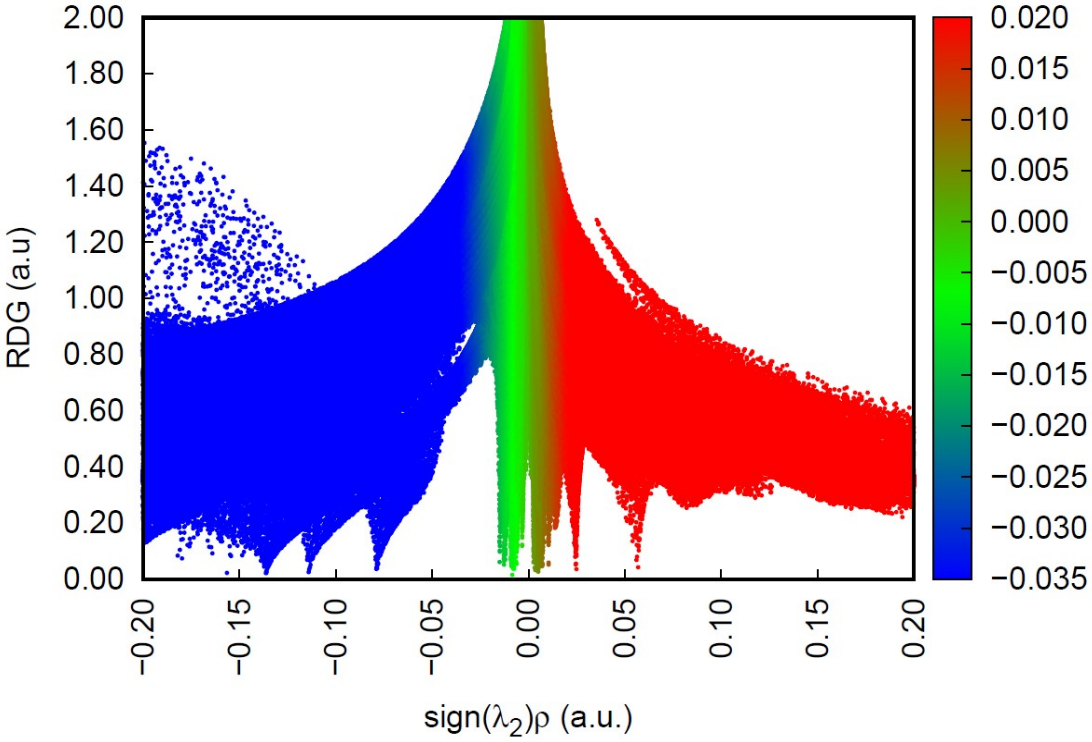
ArI(OH)OMs bearing an imidazolium moiety



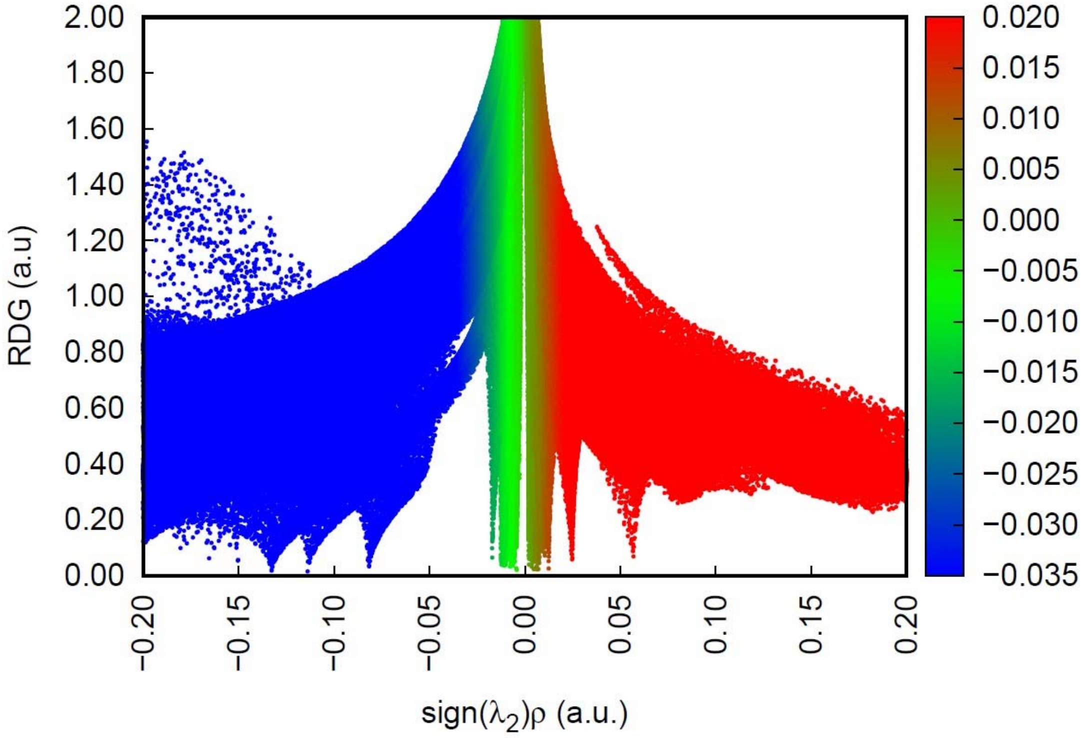
Scheme S32

Scatter plots of the non-covalent interaction index

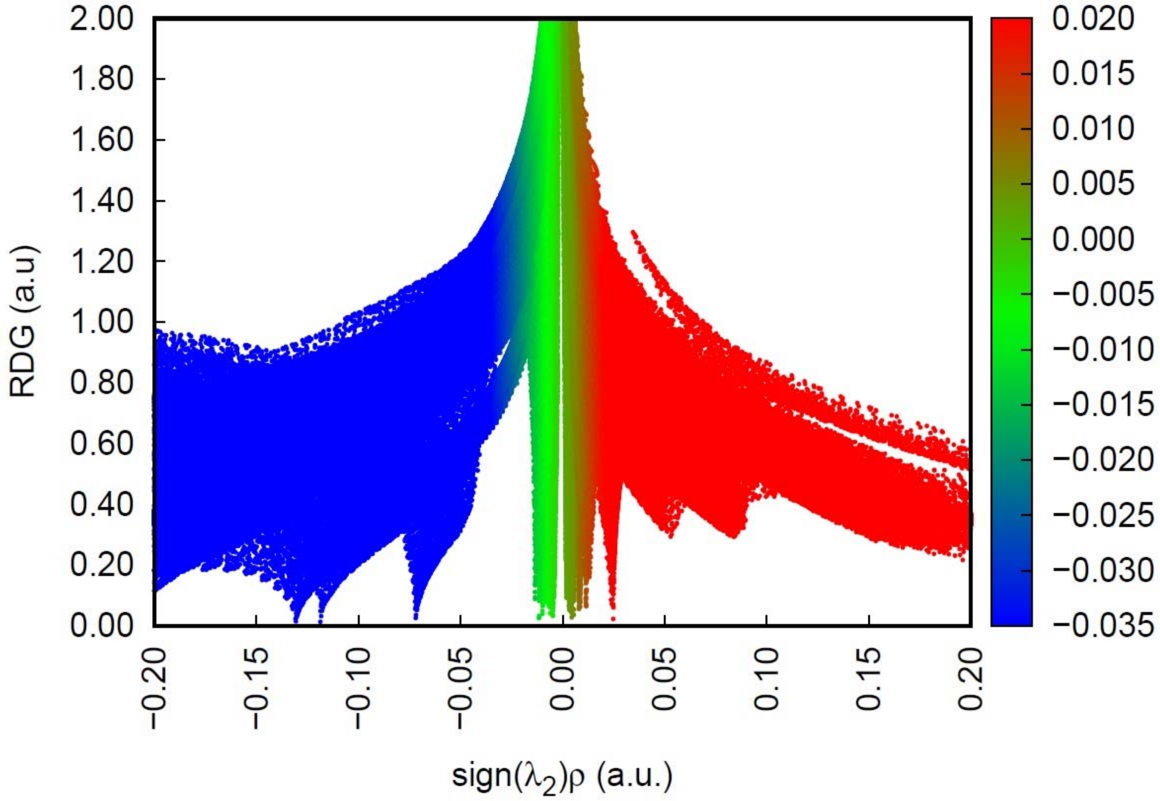
o-**7**-**A**



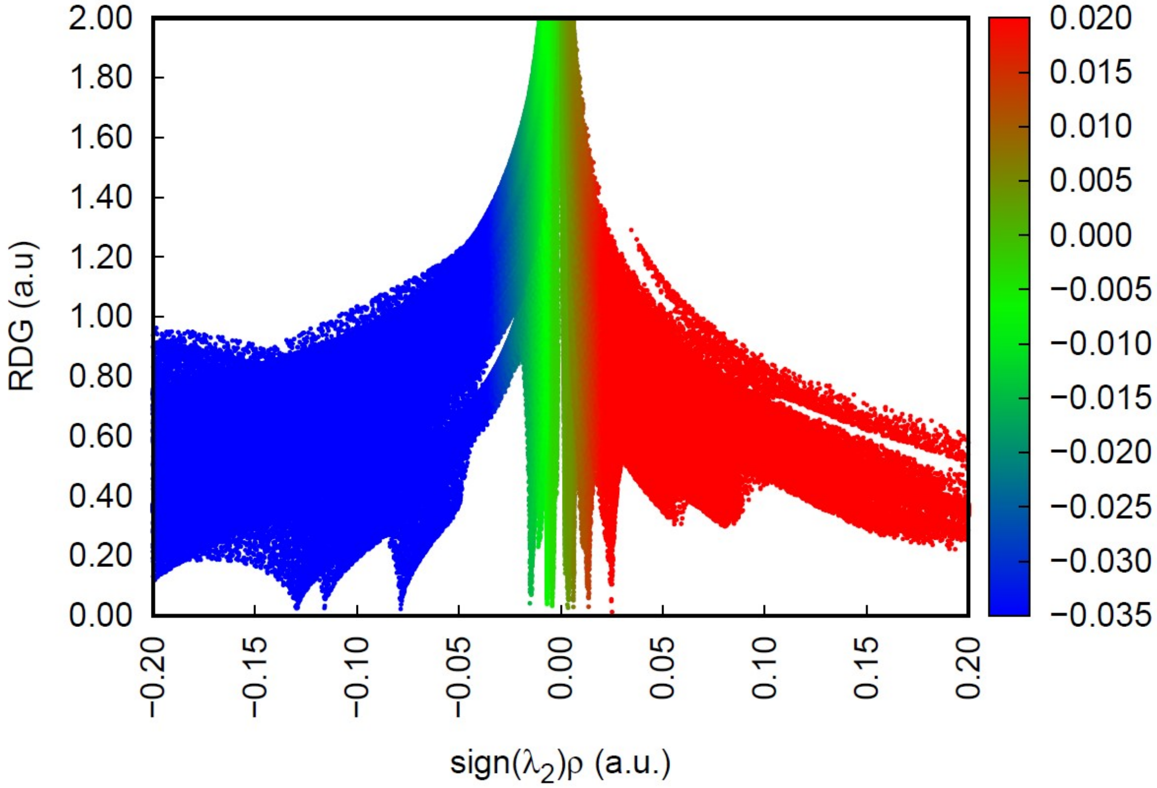
o-**7**-**B**



8-B

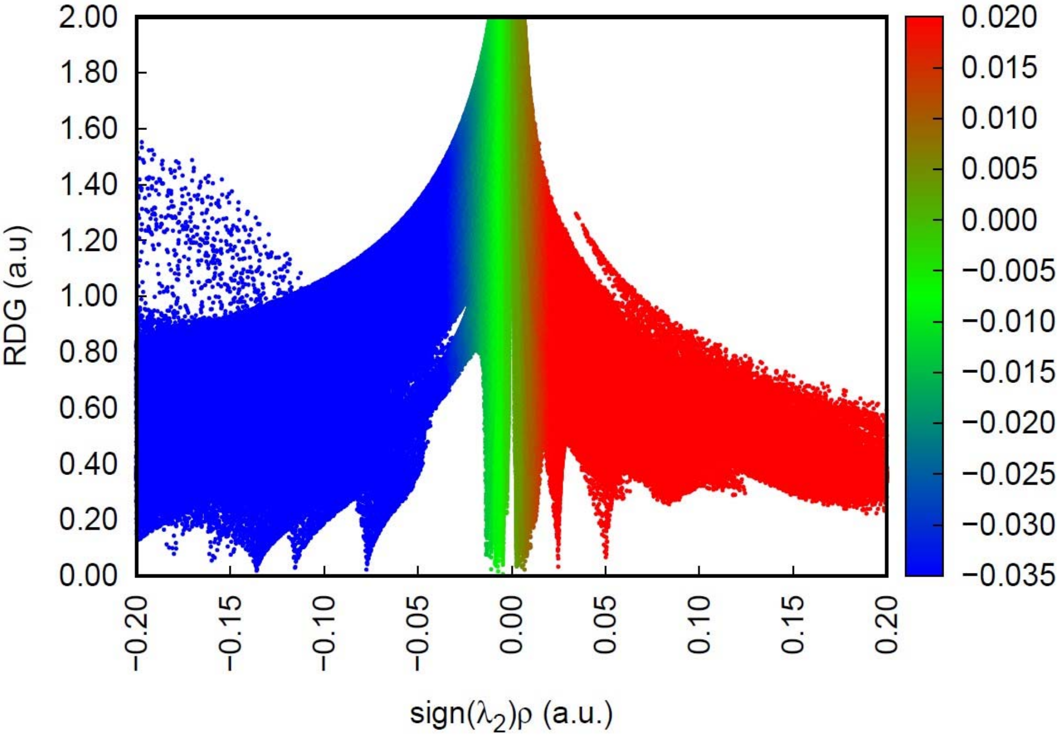


PhI(OH)OSO$_2$Ph



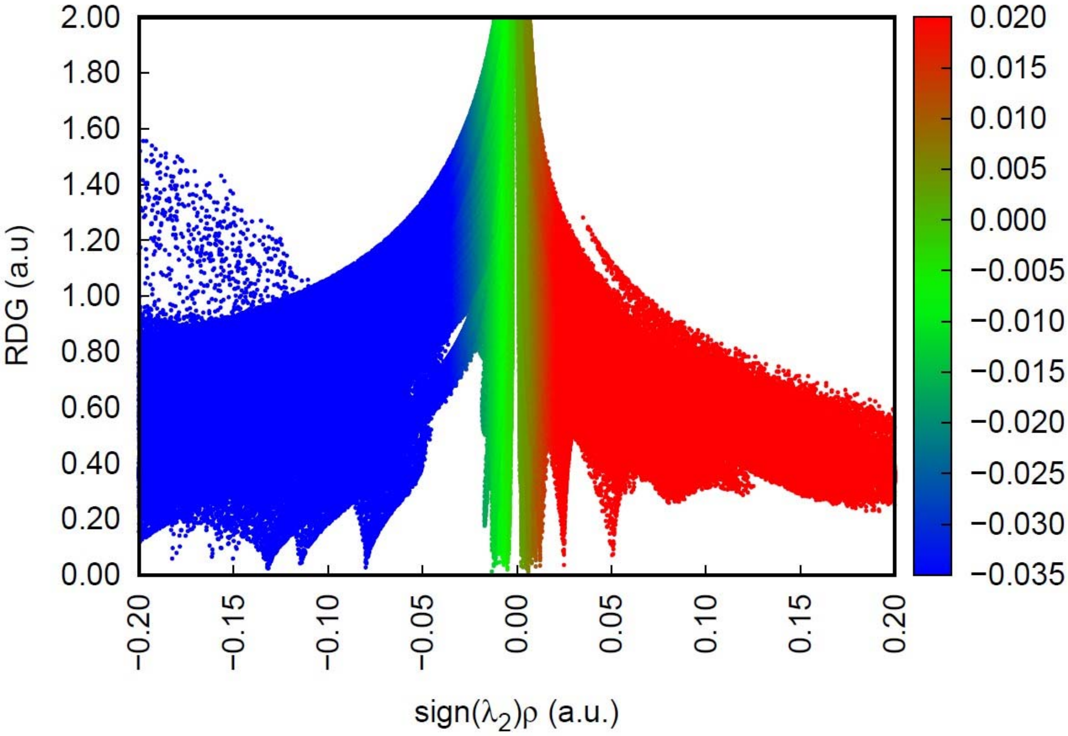
ArI(OH)OSO$_2$Ph bearing an imidazolidinium moiety

Conformer A

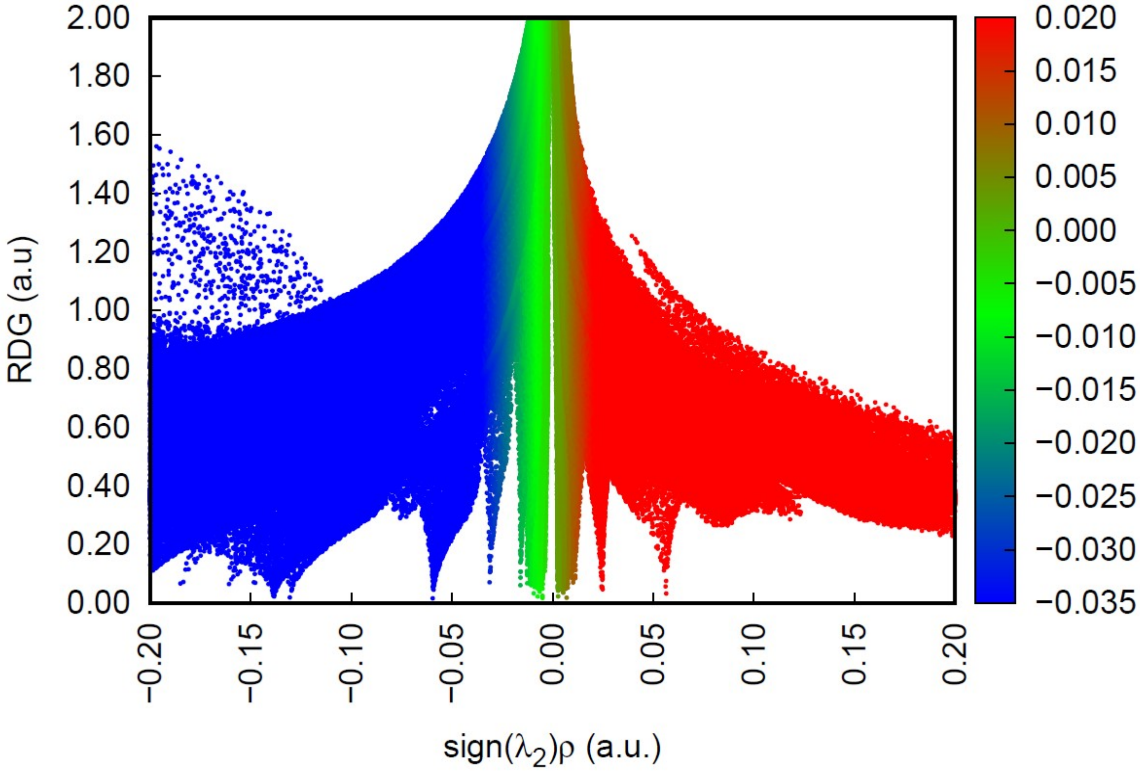


ArI(OH)OSO$_2$Ph bearing an imidazolidinium moiety

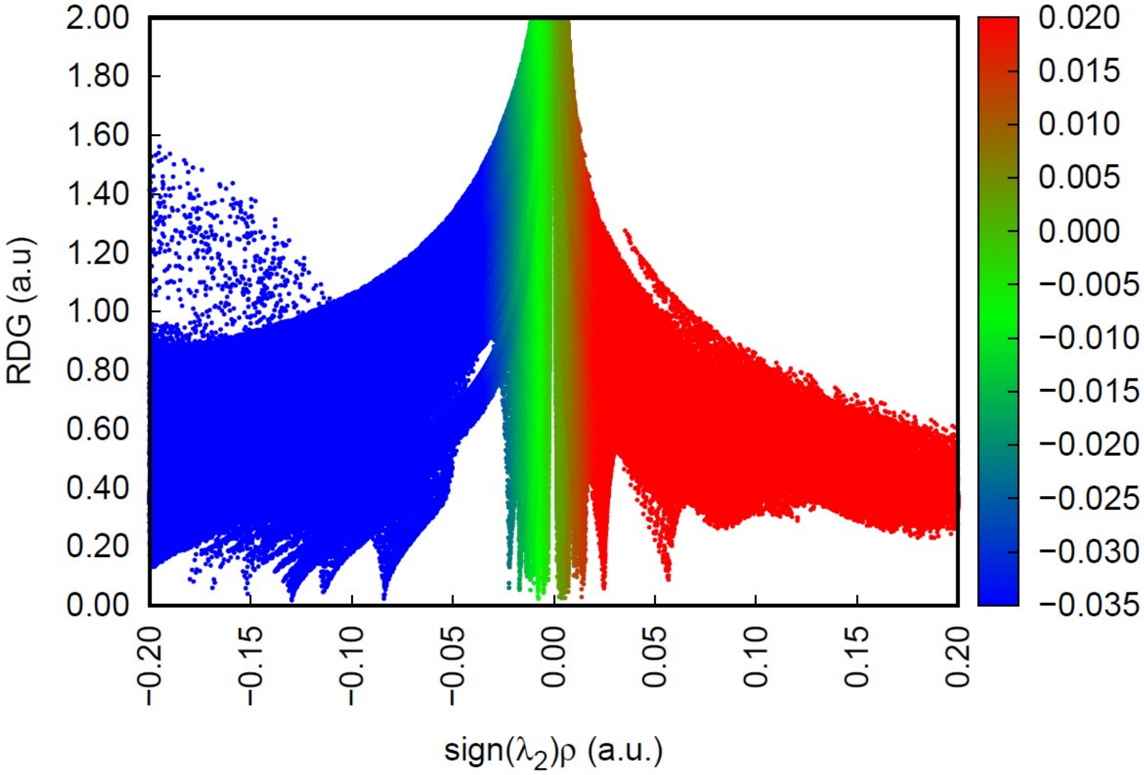
Conformer B



***m*-7**


2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
RDG (a.u)
−0.20
−0.15
−0.10
−0.05
0.00
0.05
0.10
0.15
0.20
sign(λ_2)ρ (a.u.)
0.020
0.015
0.010
0.005
0.000
−0.005
−0.010
−0.015
−0.020
−0.025
−0.030
−0.035

***p*-7**


2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
RDG (a.u)
−0.20
−0.15
−0.10
−0.05
0.00
0.05
0.10
0.15
0.20
sign(λ_2)ρ (a.u.)
0.020
0.015
0.010
0.005
0.000
−0.005
−0.010
−0.015
−0.020
−0.025
−0.030
−0.035

List of optimized structures

***o*-7-A**

1	I	0	-1.368	-2.318	-0.083	I
2	S	0	-3.386	0.185	-1.115	S
3	O	0	-0.425	-3.693	1.132	O
4	O	0	-2.041	-0.586	-1.301	O
5	O	0	-4.019	-0.275	0.117	O
6	O	0	-4.141	0.159	-2.347	O
7	C	0	-1.038	-0.870	1.426	C
8	C	0	-2.015	-0.701	2.388	C
9	C	0	-1.785	0.228	3.399	C
10	C	0	-0.612	0.968	3.418	C
11	C	0	0.360	0.786	2.440	C
12	C	0	0.156	-0.150	1.431	C
13	C	0	-2.779	1.842	-0.858	C
14	C	0	-2.504	2.277	0.431	C
15	C	0	-1.886	3.508	0.612	C
16	C	0	-1.561	4.292	-0.490	C
17	C	0	-1.874	3.858	-1.774	C
18	C	0	-2.487	2.627	-1.966	C
19	H	0	-1.047	-4.082	1.754	H
20	H	0	-2.952	-1.238	2.333	H
21	H	0	-2.542	0.378	4.160	H
22	H	0	-0.442	1.699	4.199	H
23	H	0	1.276	1.362	2.434	H
24	H	0	-2.765	1.655	1.276	H
25	H	0	-1.646	3.850	1.611	H
26	H	0	-1.632	4.478	-2.630	H
27	H	0	-2.734	2.269	-2.959	H
28	C	0	1.204	-0.423	0.429	C
29	N	0	2.108	-1.401	0.559	N
30	C	0	2.390	-2.154	1.770	C
31	H	0	2.591	-3.190	1.502	H
32	H	0	1.517	-2.132	2.417	H
33	H	0	3.247	-1.701	2.271	H
34	C	0	0.606	1.332	-1.245	C
35	H	0	-0.063	1.684	-0.466	H
36	H	0	0.030	1.038	-2.121	H

37	H	0	1.329	2.116	-1.465	H
38	N	0	1.345	0.179	-0.748	N
39	H	0	-1.059	5.242	-0.346	H
40	C	0	2.405	-0.414	-1.413	C
41	C	0	2.975	-0.144	-2.651	C
42	C	0	2.896	-1.413	-0.580	C
43	C	0	4.057	-0.923	-3.014	C
44	H	0	2.608	0.654	-3.281	H
45	C	0	3.990	-2.193	-0.938	C
46	C	0	4.557	-1.930	-2.171	C
47	H	0	4.544	-0.743	-3.965	H
48	H	0	4.387	-2.957	-0.281	H
49	H	0	5.416	-2.507	-2.492	H
50	F	0	3.576	2.133	-0.525	F
51	F	0	4.263	3.113	1.452	F
52	F	0	3.317	1.006	1.474	F
53	F	0	2.012	2.835	1.005	F
54	B	0	3.325	2.301	0.851	B

***o*-7-B**

1	I	0	0.948	-2.402	-0.355	I
2	S	0	3.252	-0.792	1.516	S
3	O	0	-0.908	-2.835	-1.153	O
4	O	0	2.944	-1.698	0.275	O
5	O	0	2.082	-0.780	2.385	O
6	O	0	4.539	-1.175	2.045	O
7	C	0	0.844	-0.497	-1.310	C
8	C	0	-0.314	0.273	-1.249	C
9	C	0	-0.295	1.514	-1.890	C
10	C	0	0.834	1.944	-2.568	C
11	C	0	1.969	1.147	-2.618	C
12	C	0	1.982	-0.085	-1.980	C
13	C	0	3.405	0.835	0.792	C
14	C	0	2.374	1.755	0.923	C
15	C	0	2.484	2.995	0.306	C
16	C	0	3.626	3.307	-0.421	C
17	C	0	4.663	2.383	-0.533	C
18	C	0	4.557	1.139	0.074	C

19	H	0	-1.173	2.143	-1.806	H
20	H	0	0.829	2.918	-3.041	H
21	H	0	2.859	1.485	-3.132	H
22	H	0	2.875	-0.694	-1.974	H
23	H	0	1.496	1.528	1.511	H
24	H	0	1.667	3.701	0.400	H
25	H	0	5.560	2.635	-1.086	H
26	H	0	5.360	0.414	0.009	H
27	C	0	-1.578	-0.137	-0.607	C
28	N	0	-1.811	-0.317	0.694	N
29	H	0	-0.805	-3.264	-2.006	H
30	C	0	-0.903	-0.095	1.810	C
31	H	0	0.088	0.125	1.436	H
32	H	0	-1.271	0.755	2.382	H
33	H	0	-0.853	-0.999	2.417	H
34	C	0	-2.885	-0.207	-2.729	C
35	H	0	-3.538	-1.009	-3.074	H
36	H	0	-3.328	0.764	-2.956	H
37	H	0	-1.921	-0.297	-3.226	H
38	N	0	-2.706	-0.337	-1.297	N
39	H	0	3.716	4.278	-0.896	H
40	C	0	-3.721	-0.636	-0.408	C
41	C	0	-5.074	-0.895	-0.598	C
42	C	0	-3.150	-0.627	0.858	C
43	C	0	-5.820	-1.145	0.539	C
44	H	0	-5.527	-0.885	-1.581	H
45	C	0	-3.898	-0.865	2.004	C
46	C	0	-5.242	-1.128	1.819	C
47	H	0	-6.881	-1.344	0.442	H
48	H	0	-3.455	-0.819	2.990	H
49	H	0	-5.870	-1.310	2.683	H
50	B	0	-2.278	2.970	0.690	B
51	F	0	-2.822	2.449	-0.532	F
52	F	0	-0.882	2.660	0.692	F
53	F	0	-2.881	2.295	1.766	F
54	F	0	-2.470	4.334	0.754	F

8-B

1	I	0	-0.383	-1.650	-0.972	I
2	S	0	2.525	-1.592	0.913	S
3	O	0	-2.283	-1.467	-1.710	O
4	O	0	1.818	-1.772	-0.449	O
5	O	0	1.537	-1.561	1.984	O
6	O	0	3.634	-2.518	1.005	O
7	C	0	-0.011	0.460	-1.061	C
8	C	0	-0.902	1.349	-0.467	C
9	C	0	-0.546	2.701	-0.542	C
10	C	0	0.615	3.119	-1.173	C
11	C	0	1.467	2.192	-1.760	C
12	C	0	1.156	0.843	-1.705	C
13	C	0	3.209	0.057	0.771	C
14	C	0	2.652	1.099	1.497	C
15	C	0	3.165	2.382	1.344	C
16	C	0	4.224	2.611	0.475	C
17	C	0	4.782	1.554	-0.240	C
18	C	0	4.278	0.270	-0.092	C
19	H	0	-1.212	3.424	-0.085	H
20	H	0	0.859	4.175	-1.202	H
21	H	0	2.383	2.508	-2.242	H
22	H	0	1.829	0.103	-2.117	H
23	H	0	1.835	0.896	2.177	H
24	H	0	2.737	3.202	1.910	H
25	H	0	5.619	1.731	-0.907	H
26	H	0	4.711	-0.566	-0.629	H
27	H	0	-2.248	-1.533	-2.668	H
28	C	0	-2.185	0.970	0.193	C
29	C	0	-3.374	1.044	-0.546	C
30	C	0	-2.207	0.603	1.545	C
31	C	0	-4.570	0.706	0.074	C
32	C	0	-3.428	0.268	2.125	C
33	C	0	-4.616	0.300	1.404	C
34	H	0	-5.491	0.752	-0.501	H
35	H	0	-3.447	-0.020	3.172	H
36	C	0	-3.373	1.511	-1.977	C
37	H	0	-4.316	1.262	-2.466	H
38	H	0	-3.238	2.596	-2.037	H

39	H	0	-2.561	1.052	-2.546	H
40	C	0	-0.952	0.595	2.375	C
41	H	0	-1.189	0.456	3.431	H
42	H	0	-0.267	-0.208	2.088	H
43	H	0	-0.413	1.542	2.271	H
44	H	0	4.625	3.612	0.361	H
45	C	0	-5.918	-0.110	2.040	C
46	H	0	-5.901	0.050	3.120	H
47	H	0	-6.758	0.450	1.623	H
48	H	0	-6.110	-1.173	1.865	H

PhI(OH)OSO$_2$Ph

1	I	0	-2.028	-0.432	-0.063	I
2	S	0	0.800	-2.234	-0.010	S
3	O	0	-3.532	0.773	0.652	O
4	O	0	-0.269	-1.525	-0.897	O
5	O	0	0.202	-2.599	1.264	O
6	O	0	1.470	-3.237	-0.808	O
7	C	0	-0.819	1.326	-0.329	C
8	C	0	-1.078	2.394	0.509	C
9	C	0	-0.274	3.522	0.380	C
10	C	0	0.743	3.556	-0.565	C
11	C	0	0.964	2.464	-1.395	C
12	C	0	0.178	1.324	-1.285	C
13	C	0	1.961	-0.909	0.299	C
14	C	0	1.760	-0.072	1.389	C
15	C	0	2.603	1.017	1.571	C
16	C	0	3.640	1.251	0.674	C
17	C	0	3.843	0.394	-0.402	C
18	C	0	3.001	-0.694	-0.596	C
19	H	0	-0.449	4.372	1.030	H
20	H	0	1.369	4.437	-0.654	H
21	H	0	1.760	2.485	-2.130	H
22	H	0	0.360	0.453	-1.899	H
23	H	0	0.959	-0.282	2.088	H
24	H	0	2.453	1.679	2.416	H
25	H	0	4.662	0.569	-1.090	H
26	H	0	3.144	-1.379	-1.423	H

27	H	0	-4.064	1.115	-0.072	H
28	H	0	4.298	2.101	0.820	H
29	H	0	-1.884	2.354	1.230	H

ArI(OH)OSO$_2$Ph bearing an imidazolidinium moiety

Conformer A

1	I	0	-1.174	-2.279	-0.250	I
2	S	0	-3.411	0.234	-0.419	S
3	O	0	0.049	-3.765	0.477	O
4	O	0	-2.155	-0.440	-1.048	O
5	O	0	-3.657	-0.364	0.890	O
6	O	0	-4.486	0.280	-1.384	O
7	C	0	-0.379	-0.950	1.193	C
8	C	0	-1.014	-0.874	2.419	C
9	C	0	-0.490	-0.012	3.377	C
10	C	0	0.625	0.762	3.089	C
11	C	0	1.247	0.679	1.848	C
12	C	0	0.752	-0.197	0.888	C
13	C	0	-2.807	1.895	-0.173	C
14	C	0	-2.223	2.238	1.039	C
15	C	0	-1.649	3.495	1.180	C
16	C	0	-1.671	4.394	0.119	C
17	C	0	-2.283	4.045	-1.081	C
18	C	0	-2.859	2.791	-1.233	C
19	H	0	-0.337	-4.179	1.253	H
20	H	0	-1.919	-1.433	2.613	H
21	H	0	-0.974	0.060	4.344	H
22	H	0	1.026	1.437	3.835	H
23	H	0	2.129	1.261	1.613	H
24	H	0	-2.222	1.527	1.855	H
25	H	0	-1.184	3.771	2.119	H
26	H	0	-2.313	4.753	-1.901	H
27	H	0	-3.343	2.502	-2.158	H
28	C	0	1.441	-0.347	-0.413	C
29	N	0	2.322	-1.294	-0.647	N
30	C	0	2.142	0.071	-2.536	C
31	C	0	2.745	-1.253	-2.050	C

32	H	0	2.896	0.861	-2.572	H
33	H	0	3.831	-1.252	-2.104	H
34	C	0	2.907	-2.224	0.299	C
35	H	0	2.474	-2.065	1.283	H
36	H	0	3.978	-2.027	0.353	H
37	H	0	2.700	-3.247	-0.020	H
38	C	0	0.471	1.656	-1.484	C
39	H	0	-0.154	1.734	-0.597	H
40	H	0	-0.171	1.696	-2.363	H
41	H	0	1.196	2.473	-1.492	H
42	N	0	1.183	0.395	-1.473	N
43	H	0	-1.215	5.371	0.230	H
44	H	0	1.628	-0.014	-3.494	H
45	H	0	2.335	-2.126	-2.569	H
46	B	0	4.479	1.223	0.110	B
47	F	0	3.250	1.900	-0.198	F
48	F	0	5.456	2.132	0.445	F
49	F	0	4.843	0.457	-1.024	F
50	F	0	4.203	0.336	1.183	F

ArI(OH)OSO$_2$Ph bearing an imidazolidinium moiety

Conformer B

1	I	0	1.087	-2.206	-0.465	I
2	S	0	3.349	-0.331	1.212	S
3	O	0	-0.738	-2.982	-1.029	O
4	O	0	3.004	-1.169	-0.058	O
5	O	0	2.288	-0.505	2.197	O
6	O	0	4.720	-0.590	1.583	O
7	C	0	0.438	-0.274	-1.113	C
8	C	0	-0.827	0.205	-0.782	C
9	C	0	-1.180	1.479	-1.228	C
10	C	0	-0.286	2.229	-1.980	C
11	C	0	0.962	1.721	-2.304	C
12	C	0	1.336	0.456	-1.870	C
13	C	0	3.240	1.346	0.604	C
14	C	0	2.207	2.168	1.031	C
15	C	0	2.109	3.456	0.516	C

16	C	0	3.040	3.907	-0.410	C
17	C	0	4.080	3.077	-0.821	C
18	C	0	4.188	1.791	-0.310	C
19	H	0	-2.165	1.858	-0.979	H
20	H	0	-0.577	3.218	-2.312	H
21	H	0	1.664	2.306	-2.886	H
22	H	0	2.320	0.065	-2.088	H
23	H	0	1.498	1.807	1.765	H
24	H	0	1.304	4.104	0.844	H
25	H	0	4.816	3.437	-1.531	H
26	H	0	5.000	1.138	-0.608	H
27	C	0	-1.829	-0.570	-0.018	C
28	N	0	-1.714	-0.869	1.269	N
29	C	0	-3.659	-1.852	0.417	C
30	C	0	-2.974	-1.468	1.729	C
31	H	0	-3.515	-2.907	0.158	H
32	H	0	-2.775	-2.320	2.379	H
33	H	0	-0.703	-3.241	-1.954	H
34	C	0	-0.887	-0.148	2.223	C
35	H	0	0.062	0.127	1.770	H
36	H	0	-1.423	0.740	2.566	H
37	H	0	-0.665	-0.810	3.060	H
38	C	0	-3.315	-1.025	-1.947	C
39	H	0	-3.431	-2.054	-2.298	H
40	H	0	-4.253	-0.478	-2.041	H
41	H	0	-2.554	-0.523	-2.540	H
42	N	0	-2.926	-1.043	-0.556	N
43	H	0	2.963	4.913	-0.807	H
44	H	0	-3.545	-0.703	2.261	H
45	H	0	-4.713	-1.583	0.407	H
46	B	0	-4.470	1.718	0.524	B
47	F	0	-3.183	1.605	1.150	F
48	F	0	-4.248	1.702	-0.883	F
49	F	0	-5.091	2.884	0.914	F
50	F	0	-5.225	0.578	0.875	F

ArI(OH)OMs bearing an imidazolium moiety

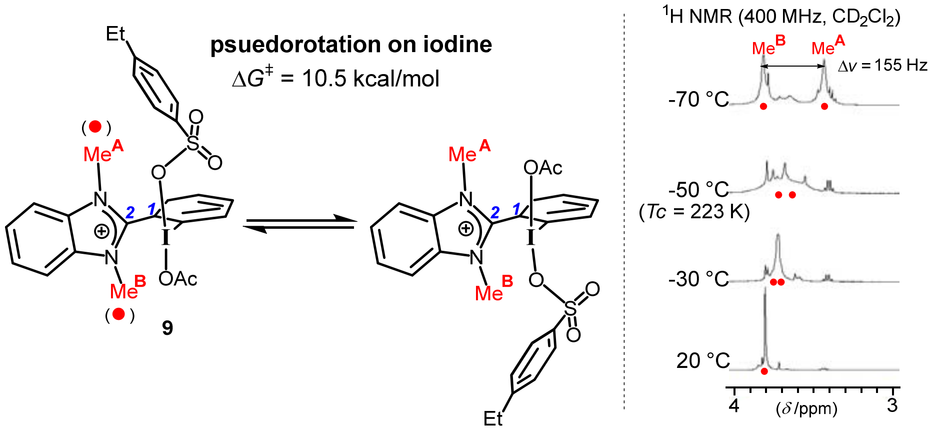
1	I	0	-2.024	-0.461	1.510	I

2	S	0	-3.476	-0.506	-1.508	S
3	O	0	-0.511	-0.476	2.892	O
4	O	0	-3.672	-0.186	-0.003	O
5	O	0	-2.768	-1.774	-1.651	O
6	O	0	-2.915	0.644	-2.201	O
7	C	0	-1.245	1.331	0.657	C
8	C	0	-2.075	2.434	0.653	C
9	C	0	-1.587	3.621	0.117	C
10	C	0	-0.298	3.680	-0.392	C
11	C	0	0.517	2.555	-0.389	C
12	C	0	0.049	1.354	0.138	C
13	H	0	-0.740	0.096	3.631	H
14	H	0	-3.088	2.370	1.026	H
15	H	0	-2.226	4.495	0.099	H
16	H	0	0.082	4.605	-0.806	H
17	H	0	1.525	2.586	-0.784	H
18	C	0	0.895	0.148	0.064	C
19	N	0	1.798	-0.234	0.966	N
20	C	0	2.240	0.507	2.136	C
21	H	0	2.078	-0.106	3.022	H
22	H	0	1.664	1.426	2.209	H
23	H	0	3.291	0.757	1.992	H
24	C	0	0.163	-0.561	-2.214	C
25	H	0	-0.536	0.270	-2.154	H
26	H	0	-0.404	-1.459	-2.455	H
27	H	0	0.928	-0.350	-2.963	H
28	N	0	0.830	-0.743	-0.931	N
29	C	0	1.743	-1.748	-0.666	C
30	C	0	2.093	-2.884	-1.388	C
31	C	0	2.356	-1.427	0.540	C
32	C	0	3.075	-3.685	-0.837	C
33	H	0	1.625	-3.123	-2.334	H
34	C	0	3.349	-2.226	1.093	C
35	C	0	3.694	-3.360	0.384	C
36	H	0	3.387	-4.579	-1.363	H
37	H	0	3.850	-1.953	2.012	H
38	H	0	4.472	-4.008	0.768	H
39	C	0	-5.158	-0.725	-2.044	C

40	H	0	-5.698	0.204	-1.866	H
41	H	0	-5.124	-0.951	-3.109	H
42	H	0	-5.593	-1.551	-1.486	H
43	B	0	4.061	1.492	-0.769	B
44	F	0	2.993	0.989	-1.584	F
45	F	0	4.571	0.433	0.010	F
46	F	0	5.035	2.067	-1.556	F
47	F	0	3.482	2.451	0.115	F

VT NMR Study on ArI(OAc)(p-EtC$_6$H$_4$SO$_3$) 9

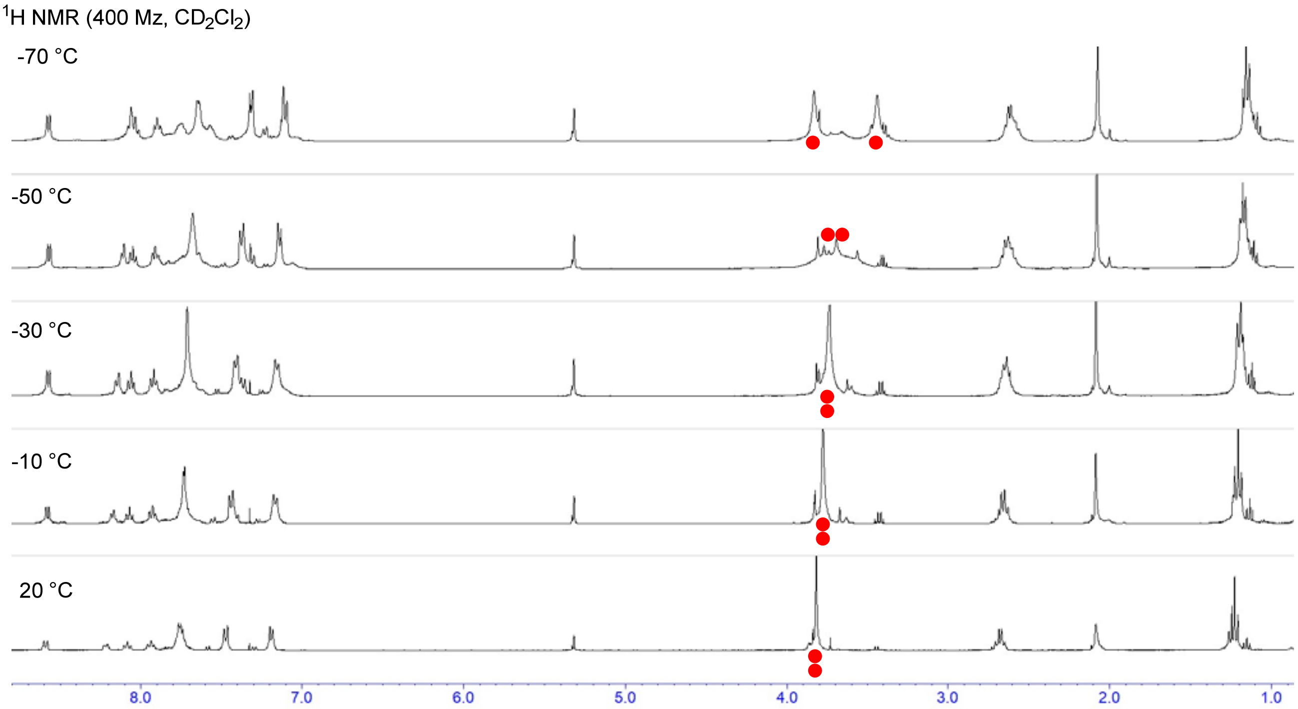
When ArI(OAc)(p-EtC$_6$H$_4$SO$_3$) **9**, which was generated from the reaction of **1a** with 4-EtC$_6$H$_4$SO$_3$H, was observed by ^{1}H NMR spectroscopy, at 20 °C and -30 °C the two Me groups on nitrogen atoms are isochronous, but at -70 °C they are anisochronous and each of singlet signals appear at 3.44 and 3.83 ppm (Schemes S33 and S34). A coalescence point is -50 °C. The signal of Me^A group interacting with p-EtC$_6$H$_4$SO$_3$ group would shift upfield compared with that of Me^B group due to cation-π interactions. A value of activation energy is estimated at 10.5 kcal/mol by equation (a). This activation energy would be small for C^1-C^2 bond rotation considering an activation energy of C-C bond rotation in 2,2'-disubstituted biphenyl skeleton (ref. G. Bott, L. D. Field, S. Sternhell, *J. Am. Chem. Soc.*, 1980, **102**, 5618.). Actually, activation energies of C^1-C^2 bond rotation in compound (*R*,*R*)-**1d** and its precursors **S10** and **S11** are much more larger than that in **9** because the two Me groups on nitrogen atoms in (*R*,*R*)-**1d**, its precursors **S10**, or **S11** are anisochronous even at 20 °C (Scheme S35), despite the fact that steric hindrance around the corresponding C^1-C^2 bond is almost same among **9**, (*R*,*R*)-**1d**, **S10**, and **S11**. Therefore, the coalescence of two Me groups in **9** would be due to psuedorotation on an iodine atom. The value of activation energy of psuedorotation on an iodine atom in λ^3-iodanes was reported to be about 15 kcal/mol by Ochiai (M. Ochiai, Y. Takaoka, Y. Masaki, *J. Am. Chem. Soc.*, 1990, **112**, 5677.) and Reich (F. J. Reich, C. S. Cooperman, *J. Am. Chem. Soc.*, 1973, **95**, 5077.).



(a) $\Delta G^{\ddagger} = 19.1 \times 10^{-3} \times Tc \times (9.97 + \log Tc - \log \Delta v) = 44.0 \text{ kJ/mol} = 10.5 \text{ kcal/mol}$

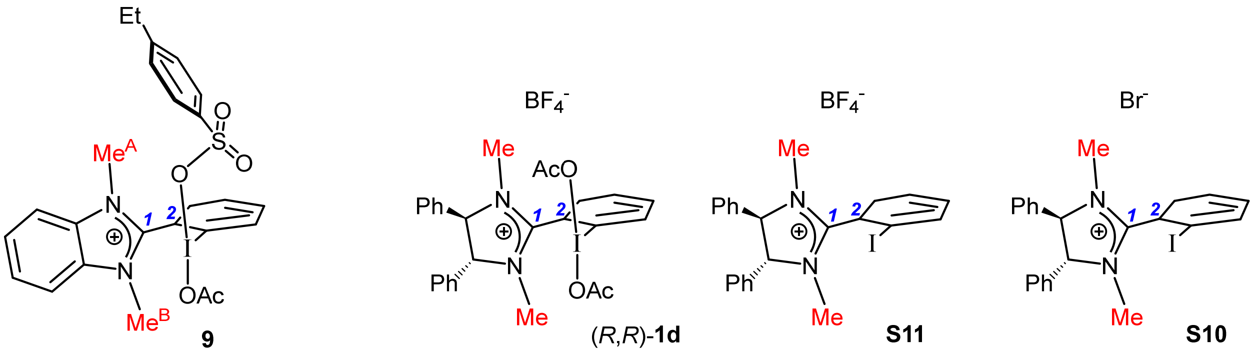
$$\begin{cases} Tc = 223 \text{ K } (-50\ ^\circ\text{C}) \\ \Delta v = 155 \text{ Hz} \end{cases}$$

Scheme S33



Scheme S34. VT ^{1}H NMR spectra of ArI(OAc)(p-$EtC_6H_4SO_3$) 9

^{1}H NMR ***at 20 °C***



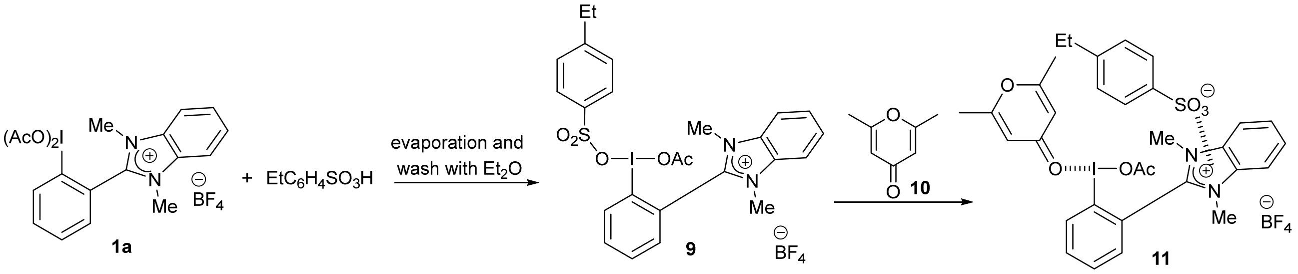
Me^A: 3.81 ppm Me^B: 3.81 ppm	Me: 2.91 ppm Me: 2.77 ppm	Me: 2.85 ppm Me: 2.76 ppm	Me: 2.99 ppm Me: 2.78 ppm
isochronous	*anisochronous*	*anisochronous*	*anisochronous*

Scheme S35.

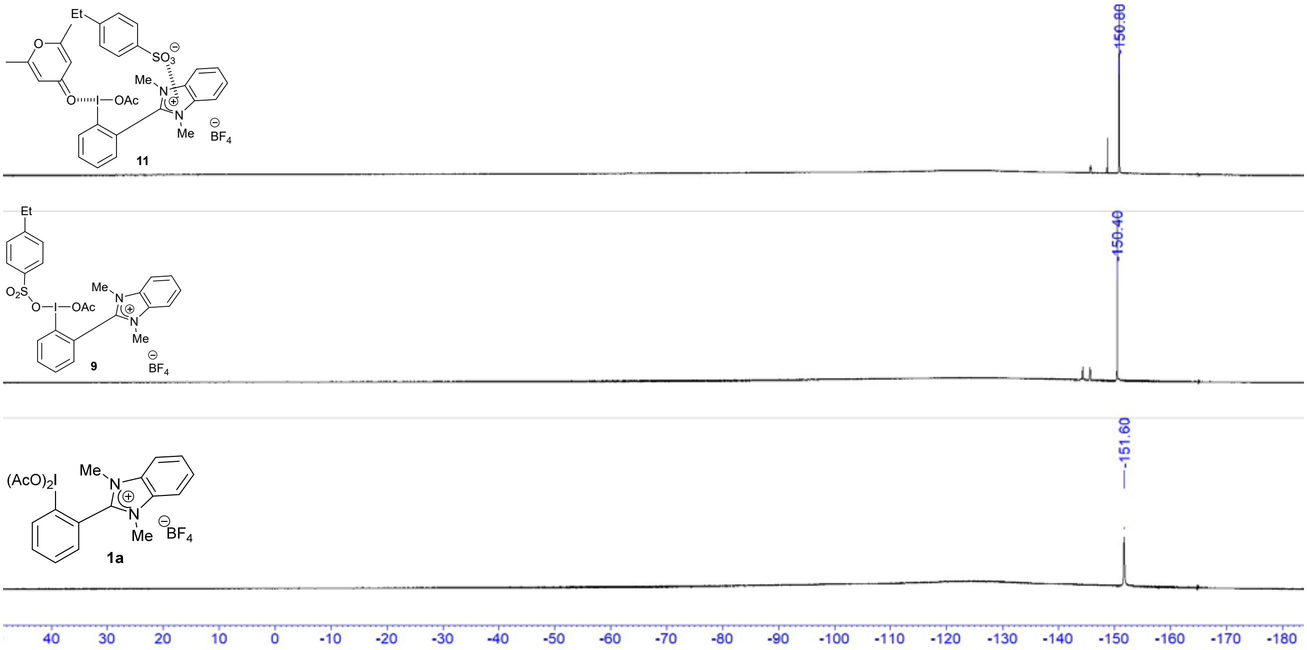
^{1}H NMR signals of two Me groups on nitrogen atoms in (*R*,*R*)-**1d**, **S10**, or **S11** are anisochronous even at 20 °C, which suggests that C^{1}-C^{2} bond rotation in (*R*,*R*)-**1d**, **S11**, **S10** are slow at 20 °C. Therefore, C^{1}-C^{2} bond rotation in **9** should be slow at 20 °C because steric hindrance around C^{1}-C^{2} bonds is almost same amoung **9**, (*R*,*R*)-**1d**, **S10**, and **S11**. But actually signals of two Me groups on nitrogen atoms in **9** are isochronous. Therefore, not C^{1}-C^{2} bond rotation but rapid psuedorotation on an iodine atom makes signals of two Me groups on nitrogen atoms in **9** isochronous at 20 °C.

Comparison of 1a with 9 and 11 in ^{19}F NMR to Investigate Effect of BF_4^- on Regioselectiviety

^{19}F NMR spectra of hypervalent iodine species **1a**, **9**, and **11** are shown in Scheme S36. The chemical shift of BF_4^- in ^{19}F NMR hardly changed among **1a**, **9**, and **11**. Therefore, noncoordinating BF_4^- is a spectator and does not affect the regioselectivity in the present sulfonyloxylactonization. In fact, we carried out calculations without BF_4^-, and the results led to the same conclusion as the results derived by calculation with BF_4^-.



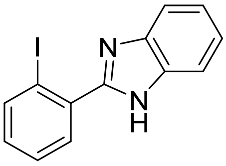
^{19}F NMR (377 MHz, $CDCl_3$, external standard: TFA in D_2O)



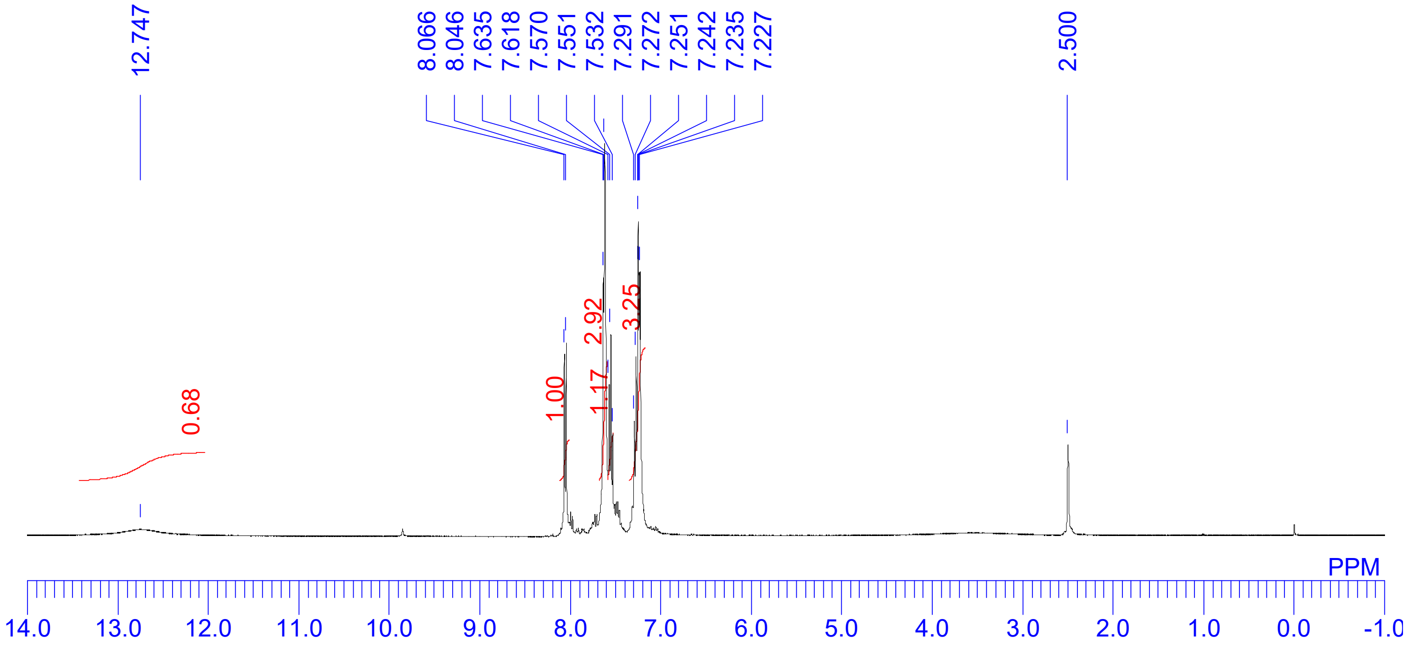
Scheme S36.

Copies of NMR Spectrum

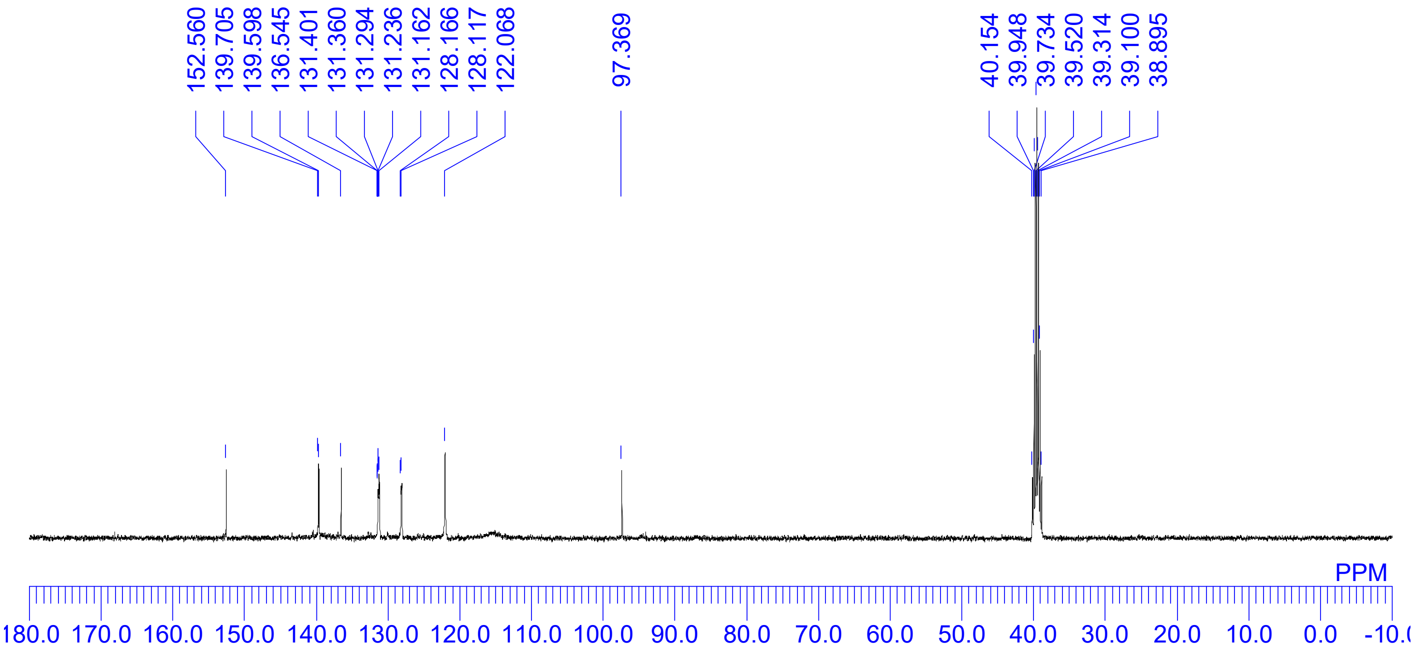
(S1) 2-(2-iodophenyl)-1*H*-benzo[*d*]imidazole



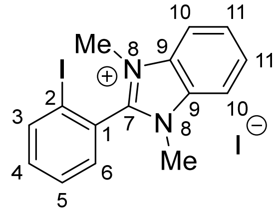
^{1}H NMR (DMSO-d_6)



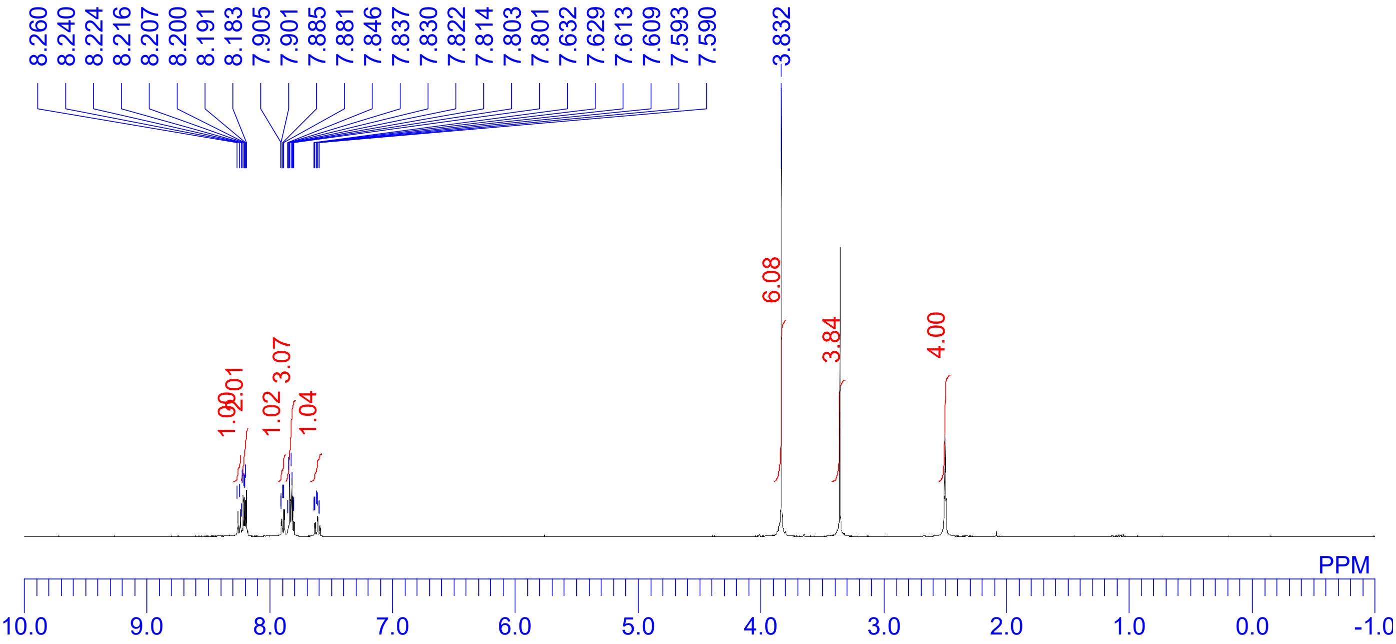
^{13}C NMR (100 MHz, DMSO-d_6)



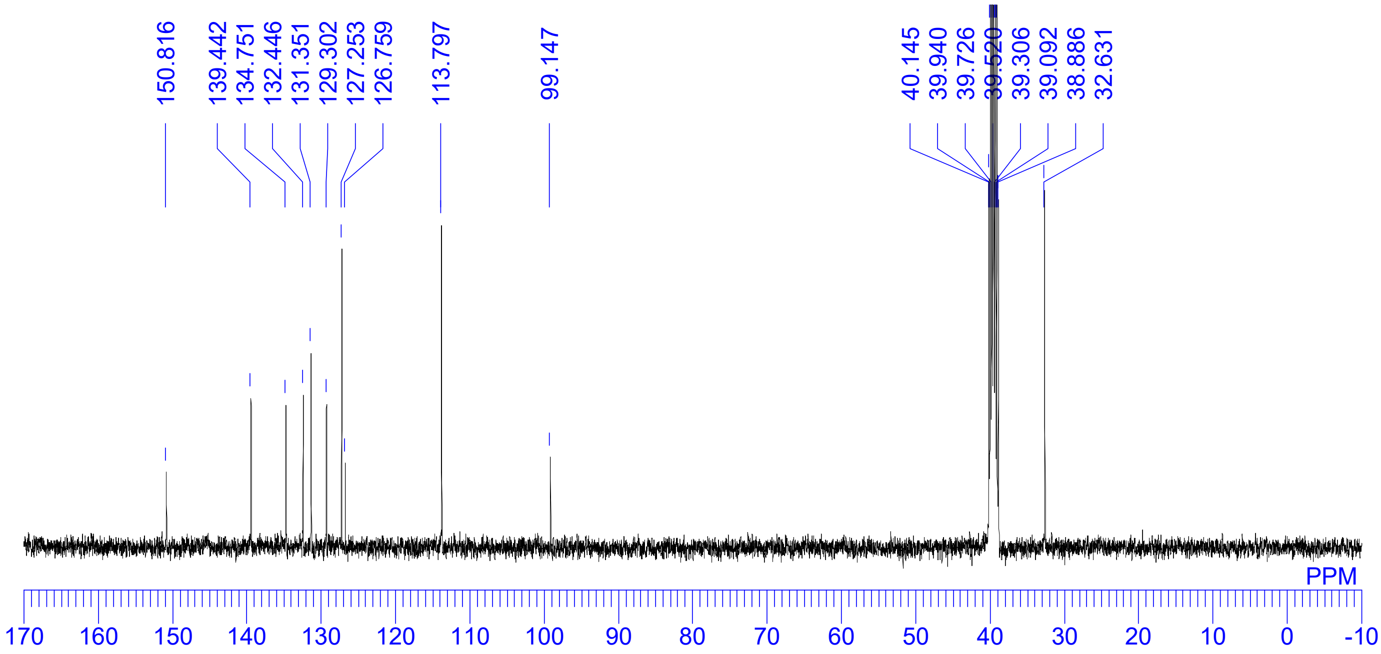
(S2) 2-(2-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide



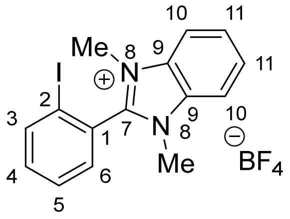
^{1}H NMR (400 MHz, DMSO-d_6)



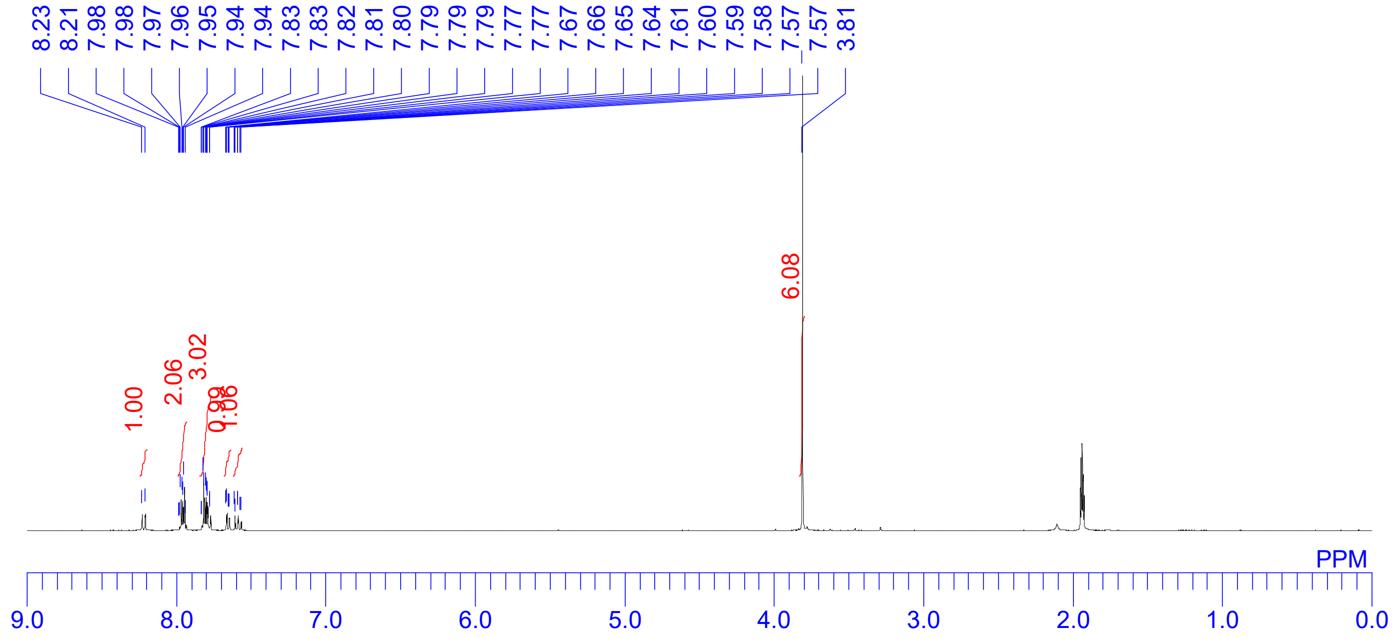
^{13}C NMR (100 MHz, DMSO-d_6)



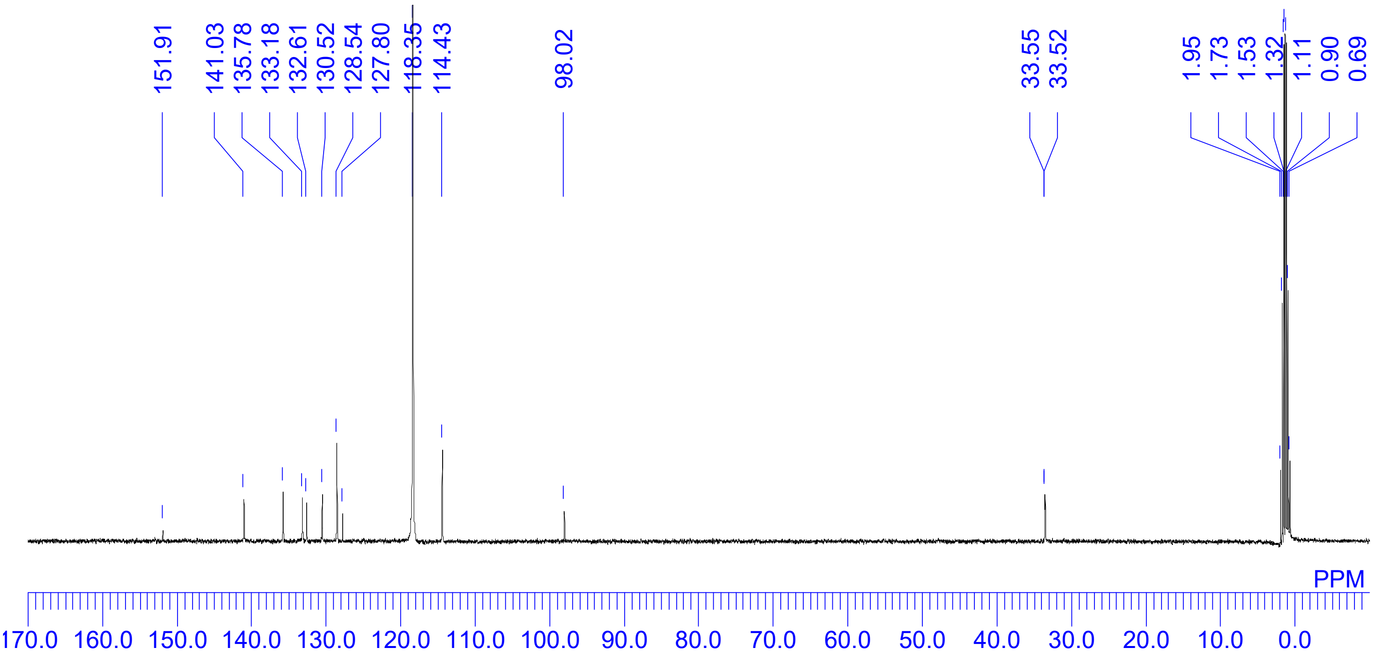
(S3) 2-(2-iodophenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium tetrafluoroborate



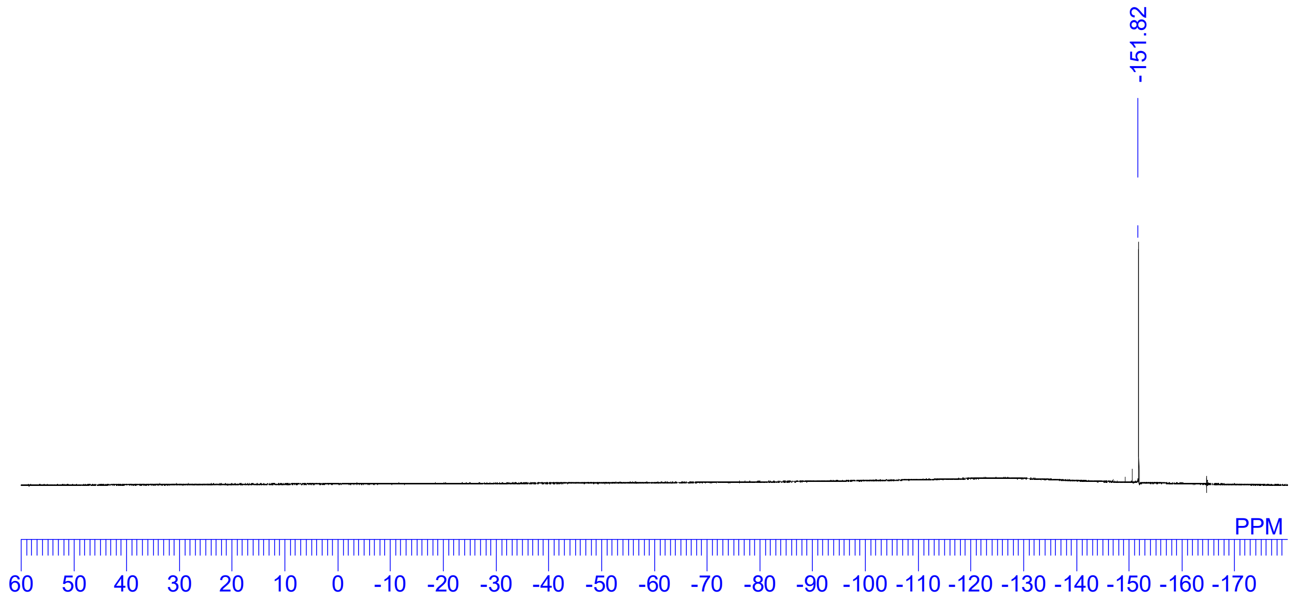
^{1}H NMR (400 MHz, CD_3CN)



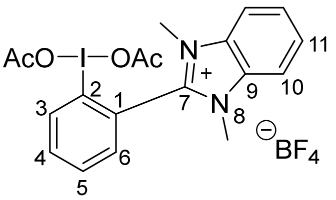
^{13}C NMR (100 MHz, CD_3CN)



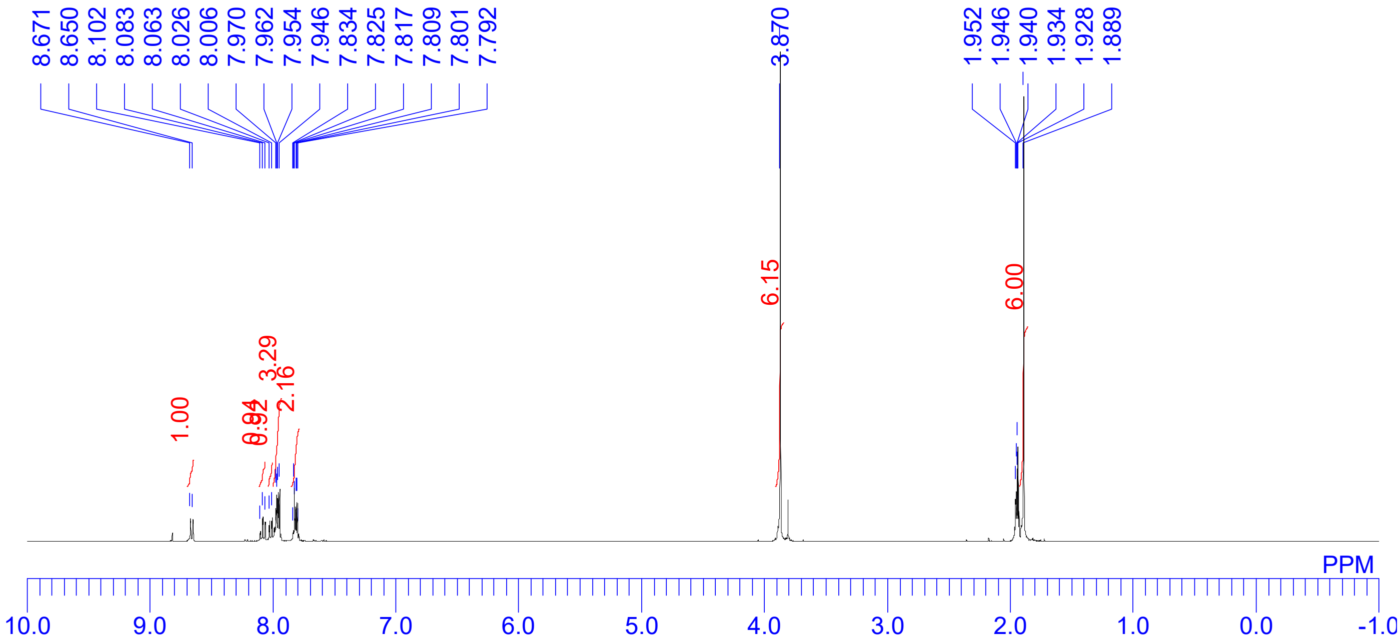
^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O)



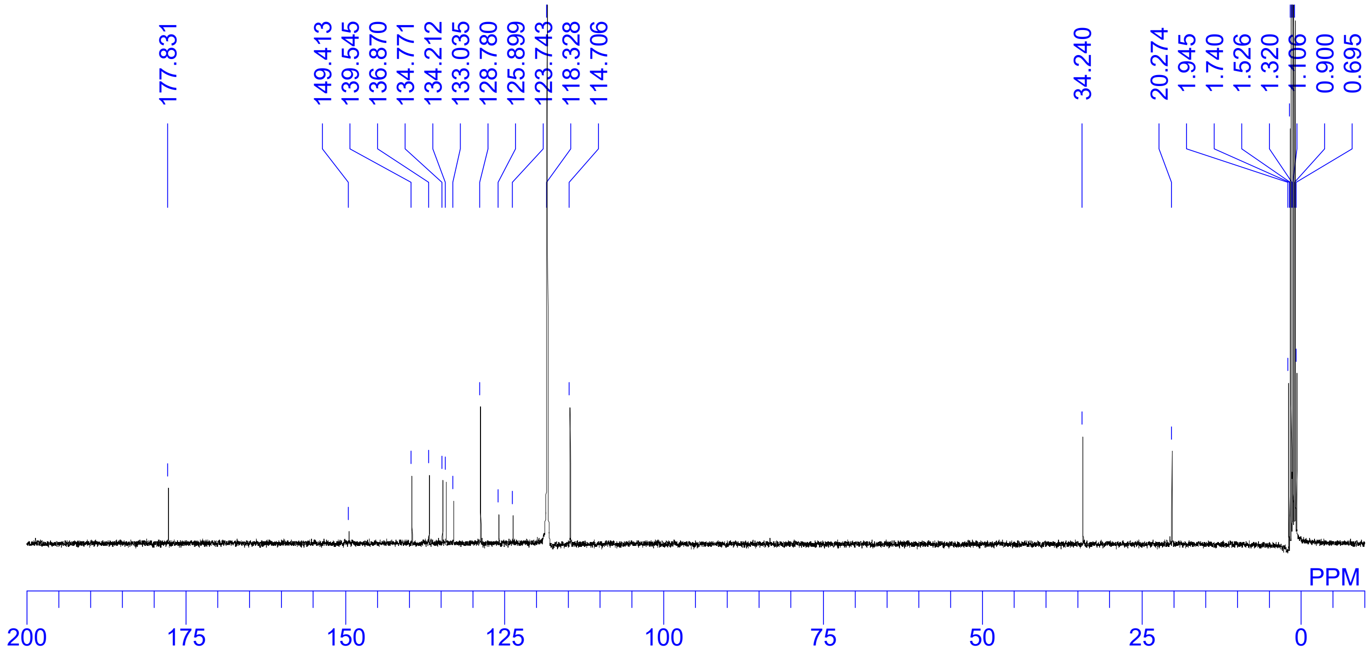
(1a) 2-(2-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate



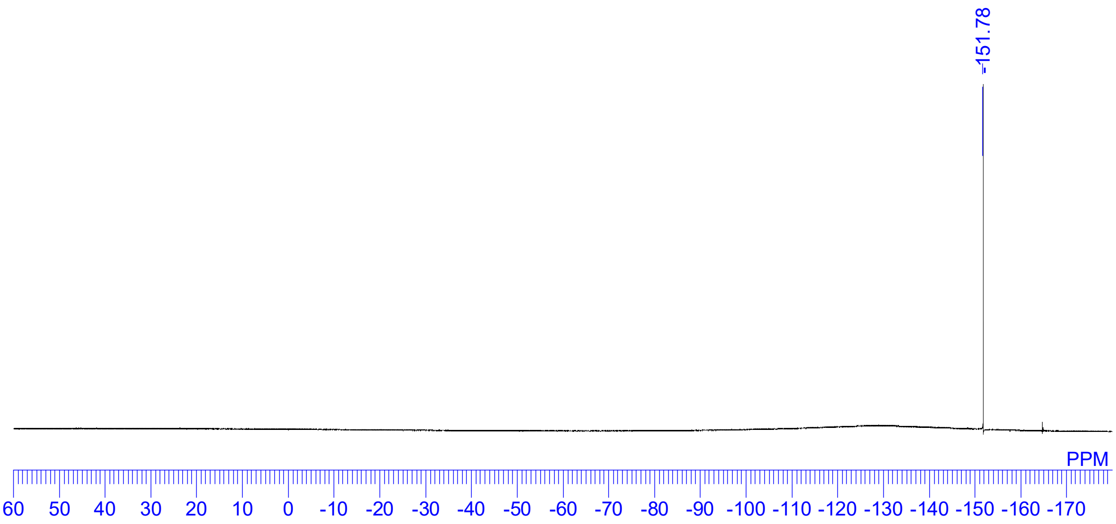
^{1}H NMR (400 MHz, CD$_3$CN)



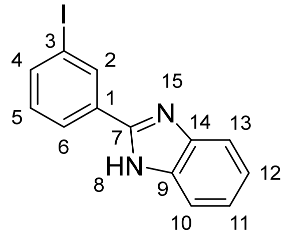
^{13}C NMR (100 MHz, CD$_3$CN)



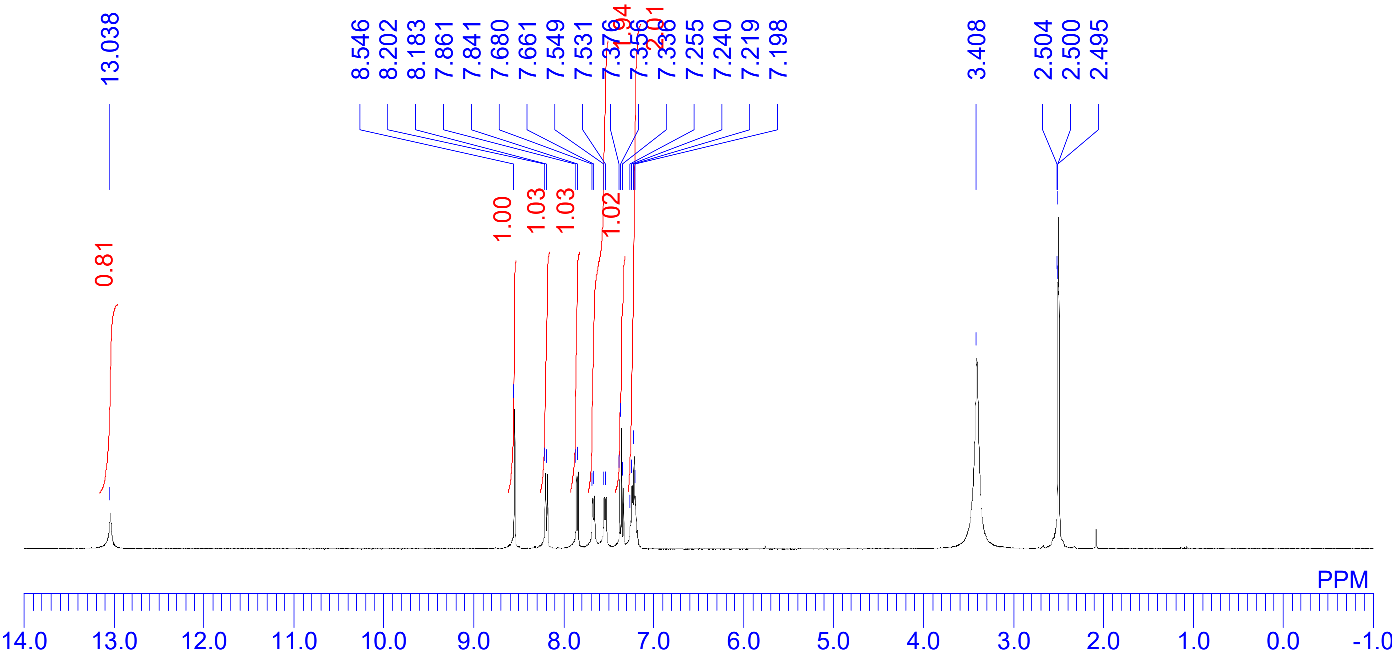
^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O)



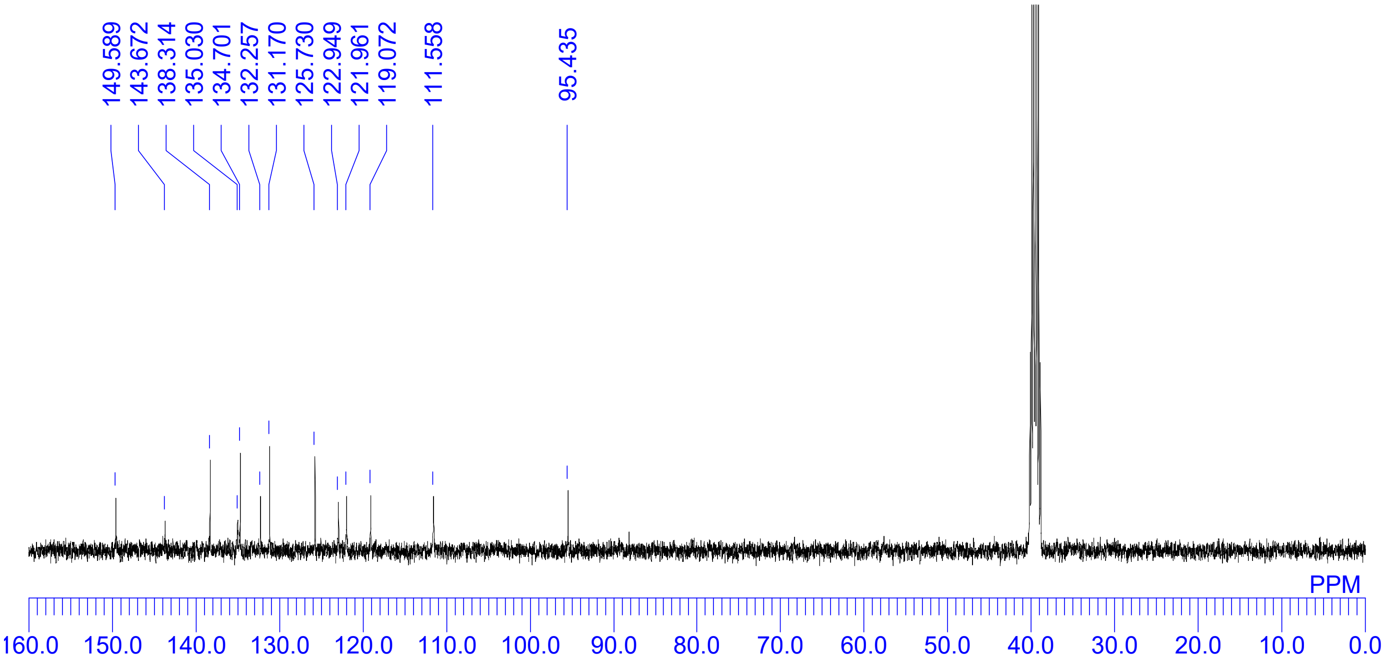
(S4) 2-(3-iodophenyl)-1H-benzo[d]imidazole



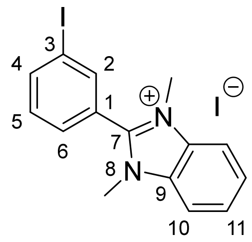
^{1}H NMR (400 MHz, DMSO-d_6)



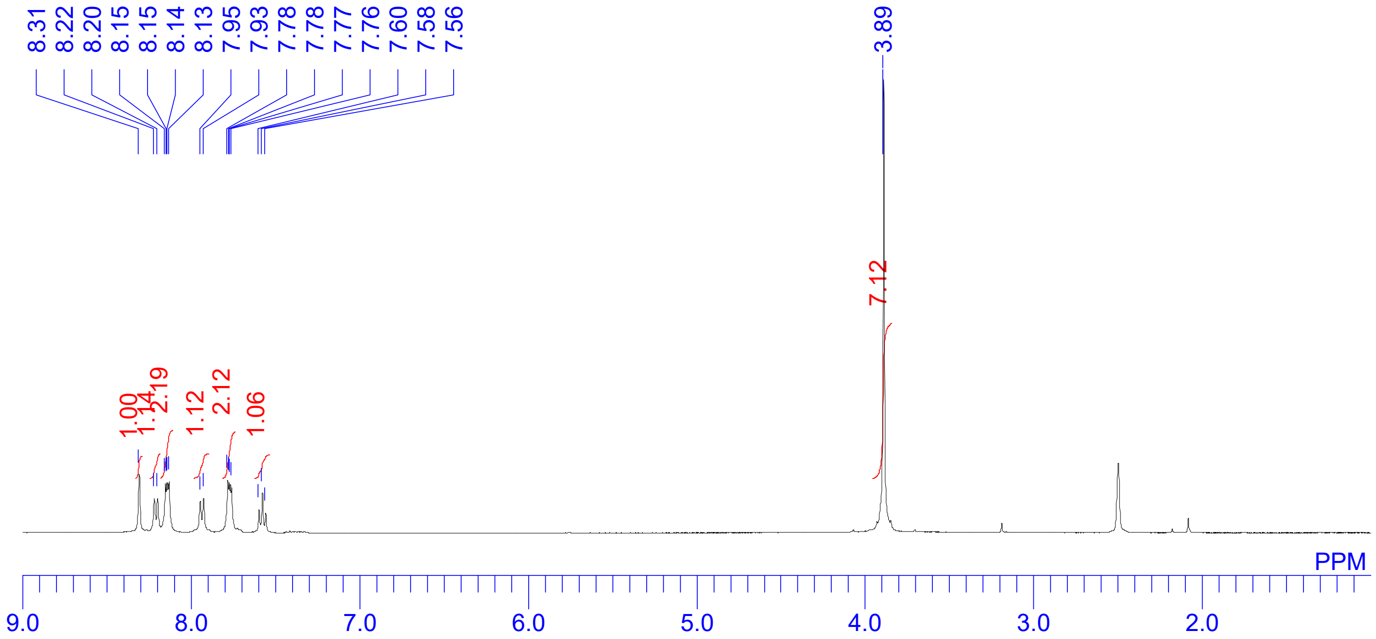
^{13}C NMR (100 MHz, DMSO-d_6)



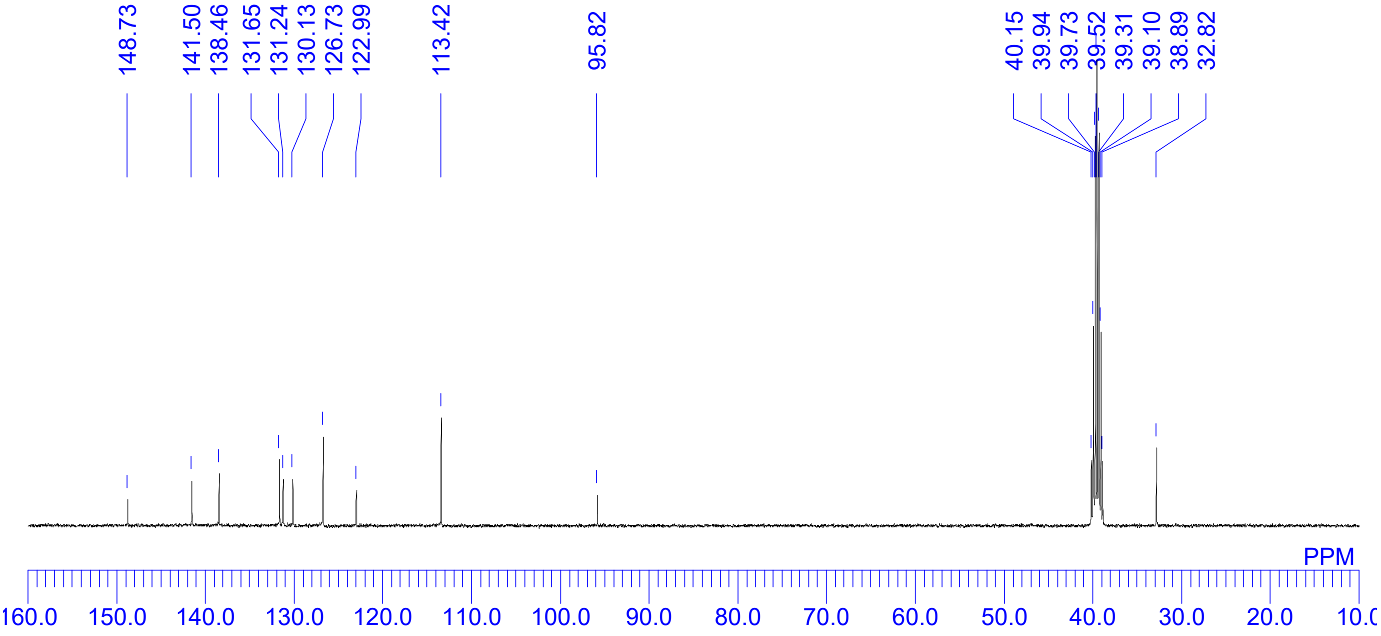
(S5) 2-(3-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazole



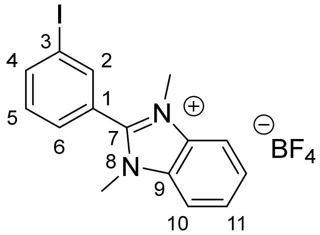
^{1}H-NMR (400MHz, DMSO-d_6)



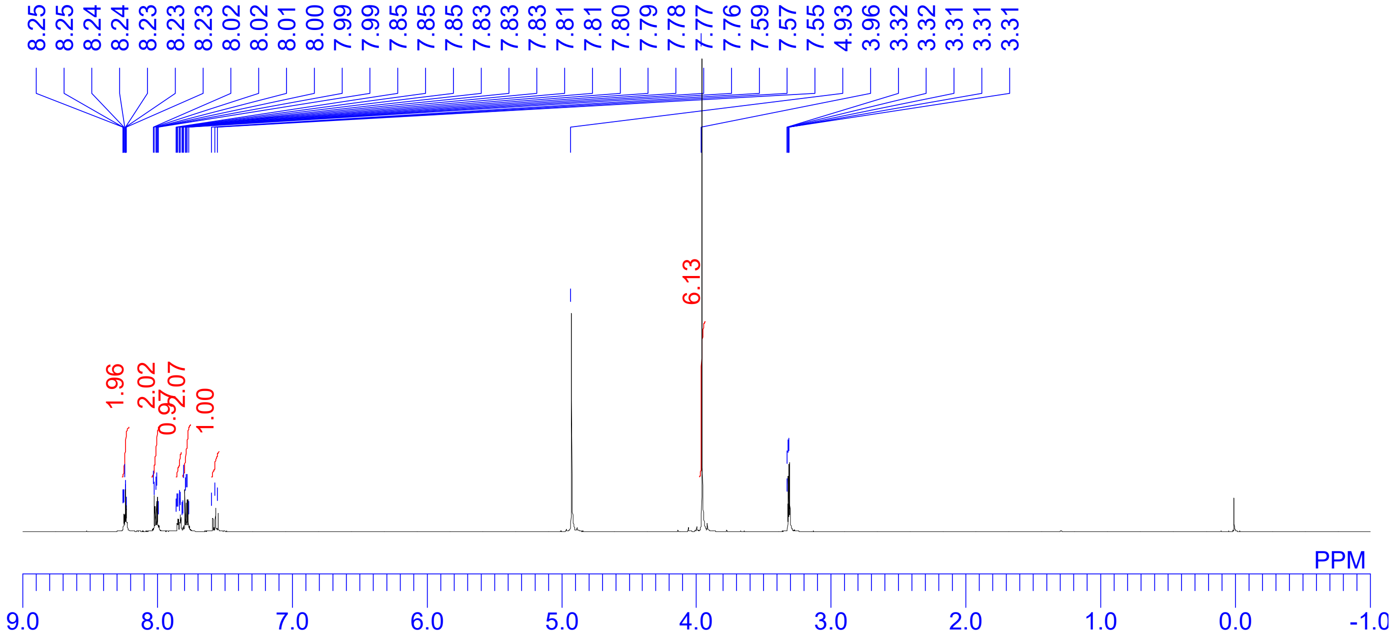
^{13}C-NMR (100 MHz, DMSO-d_6)



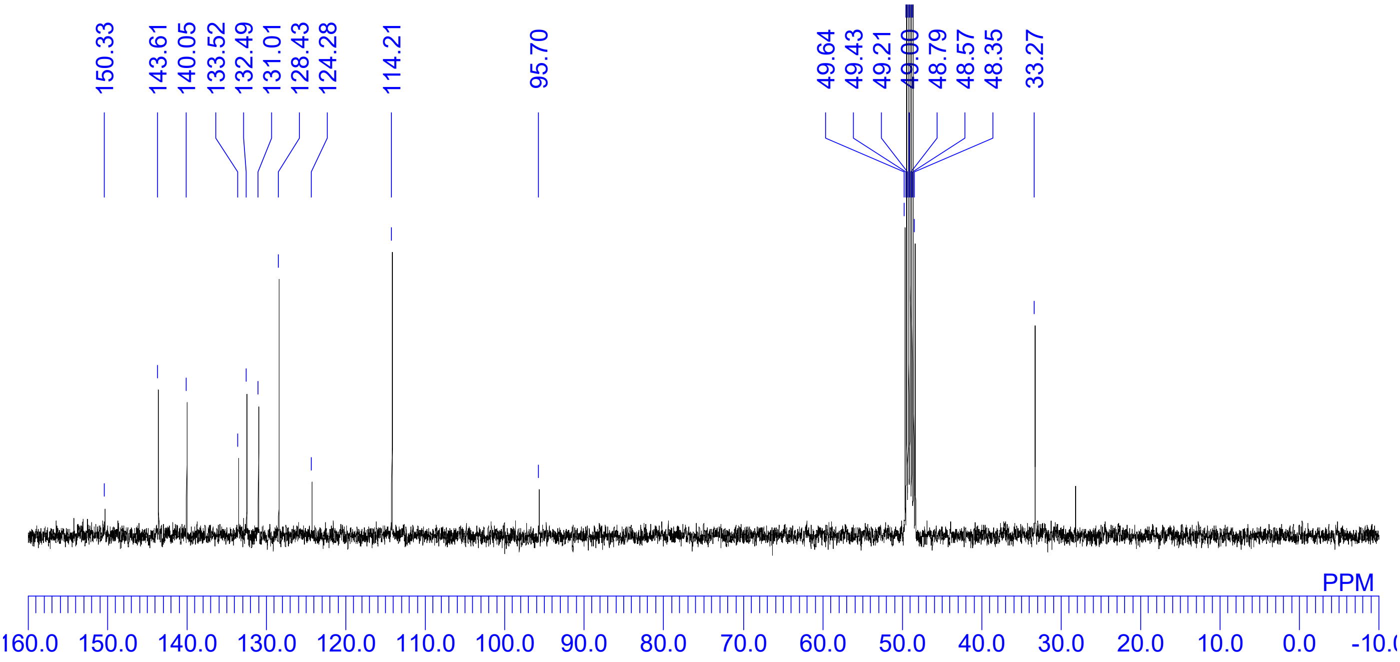
(S6) 2-(3-iodophenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium tetrafluoroborate



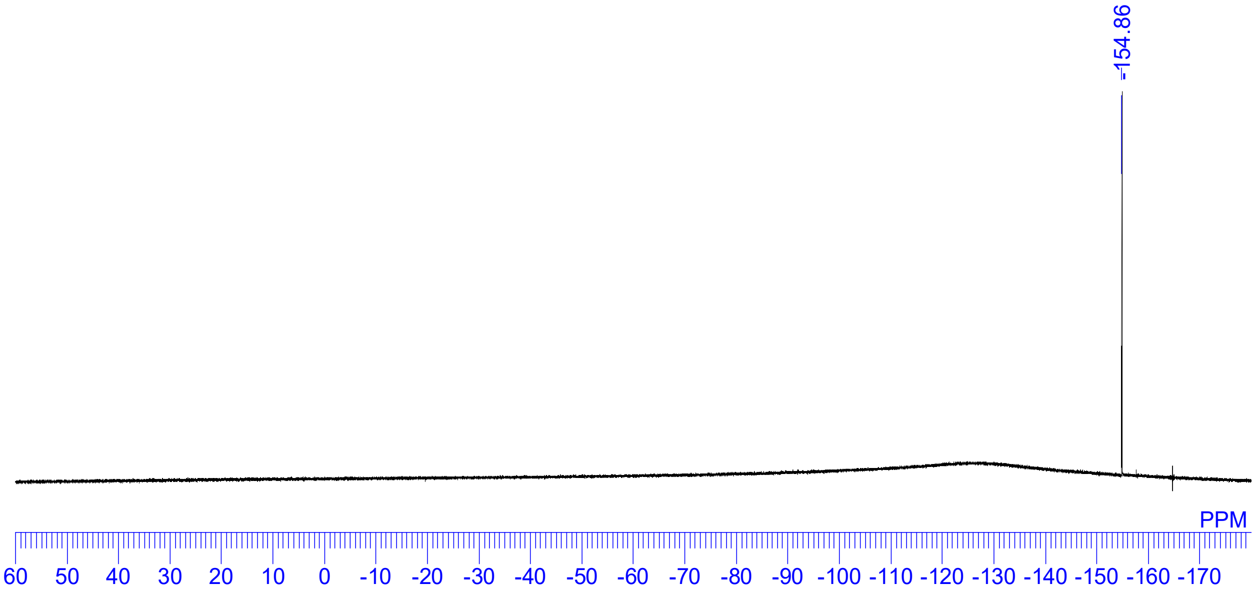
^{1}H NMR (400 MHz, CD_3OD)



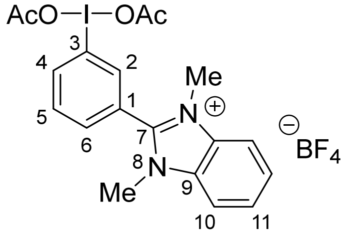
^{13}C NMR (100 MHz, CD_3OD)



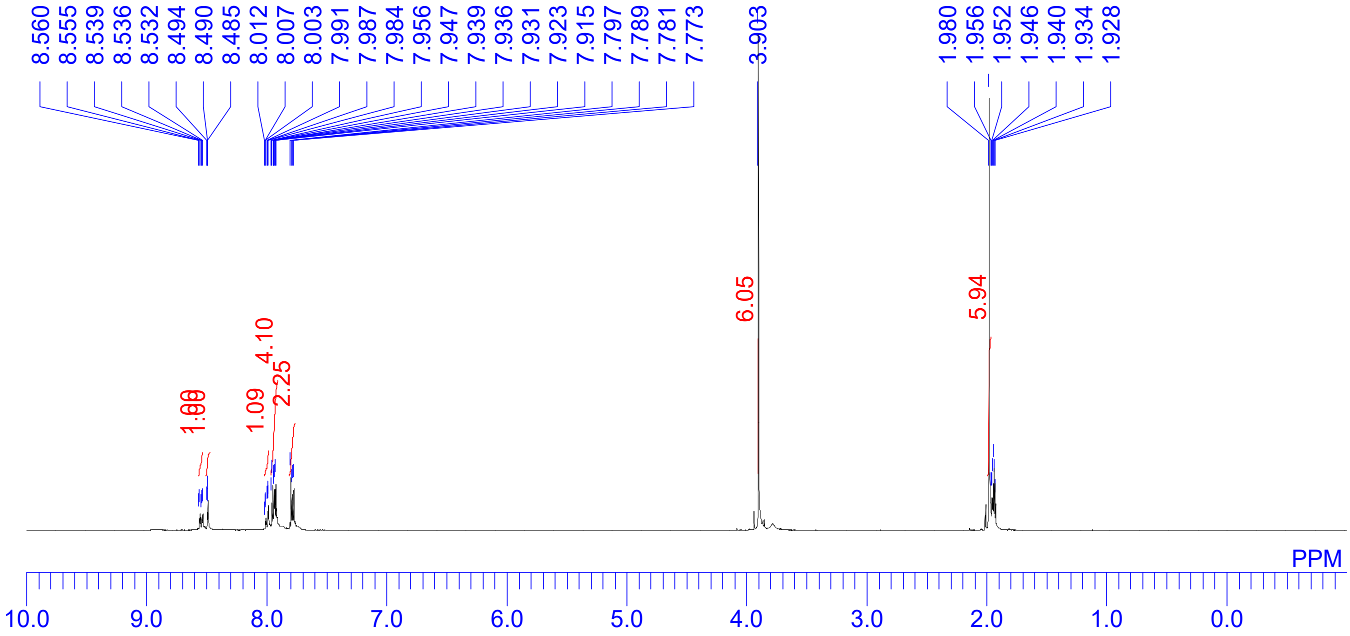
^{19}F NMR (377 MHz, CD_3OD, external standard: TFA in D_2O)



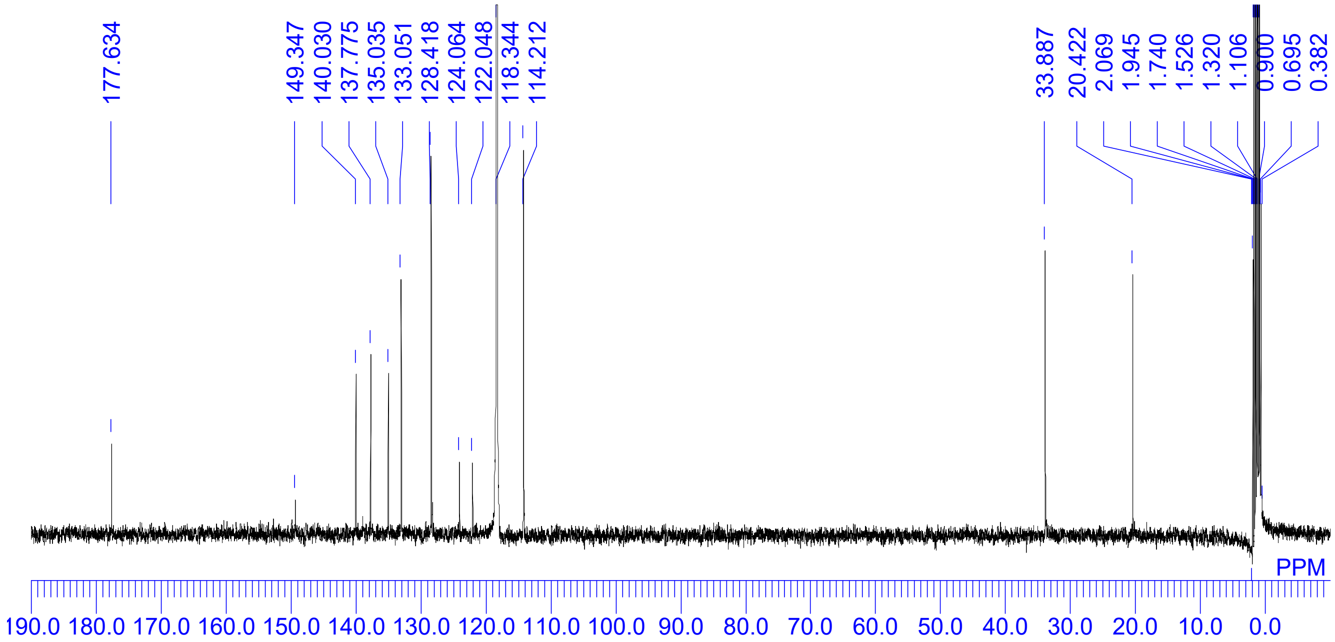
(1b) 2-(3-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium tetrafluoroborate



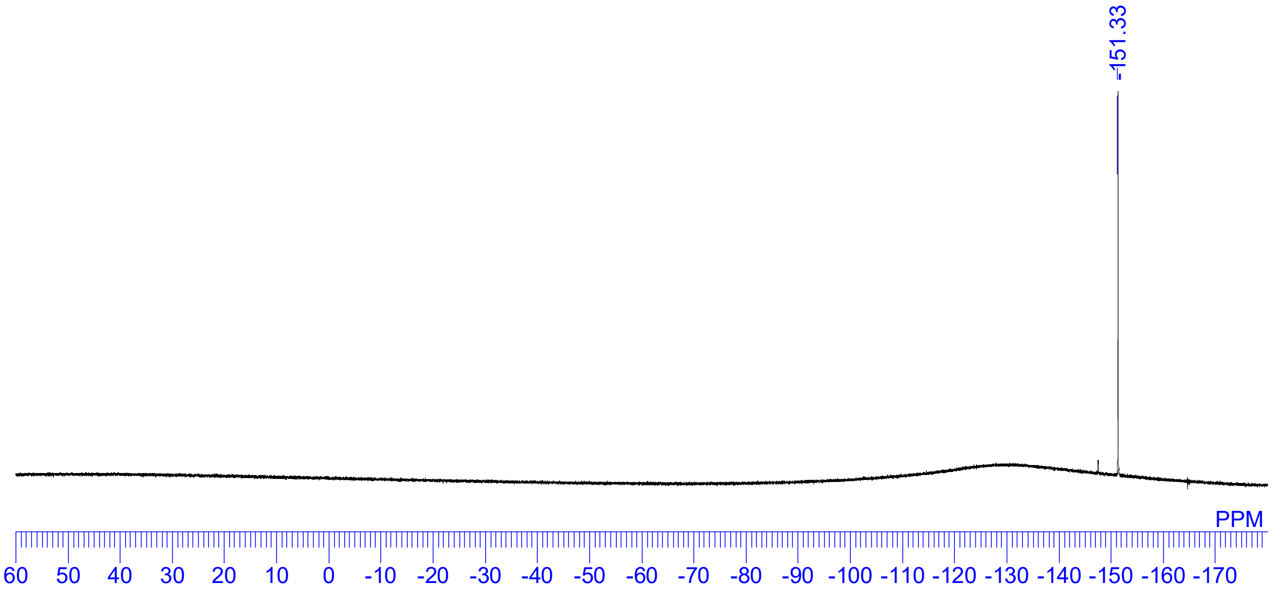
^{1}H NMR (400 MHz, CD_3CN)



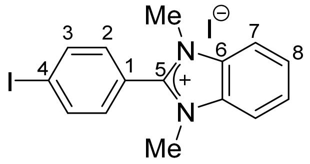
^{13}C NMR (100 MHz, CD_3CN)



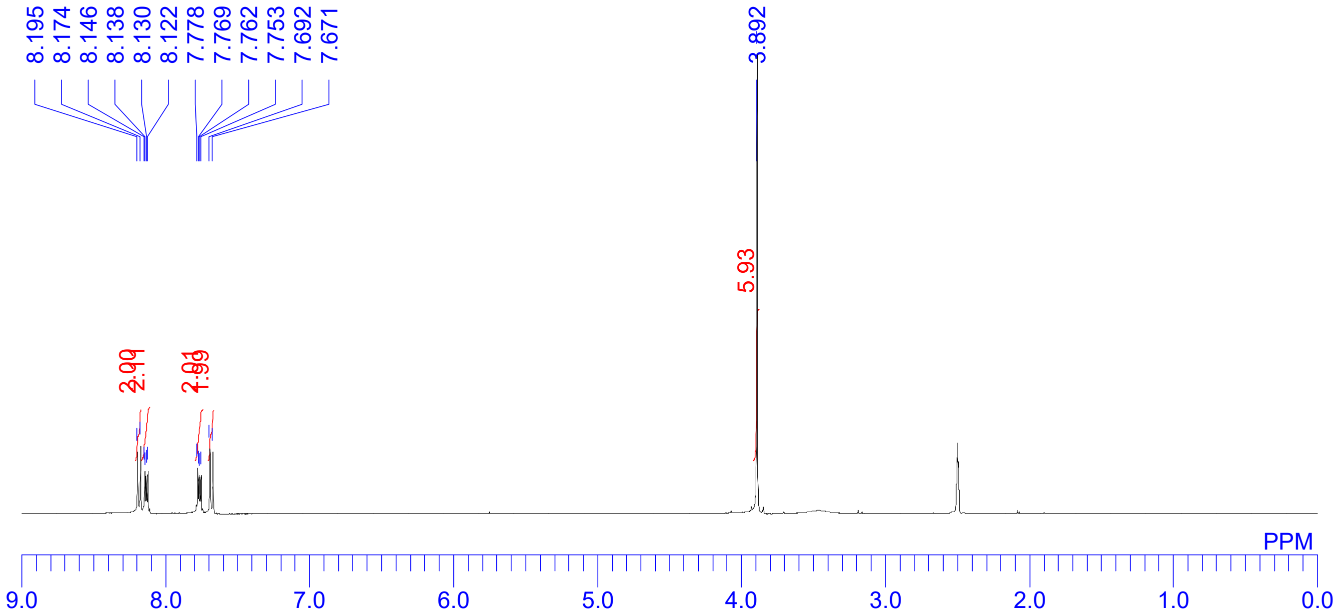
^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O)



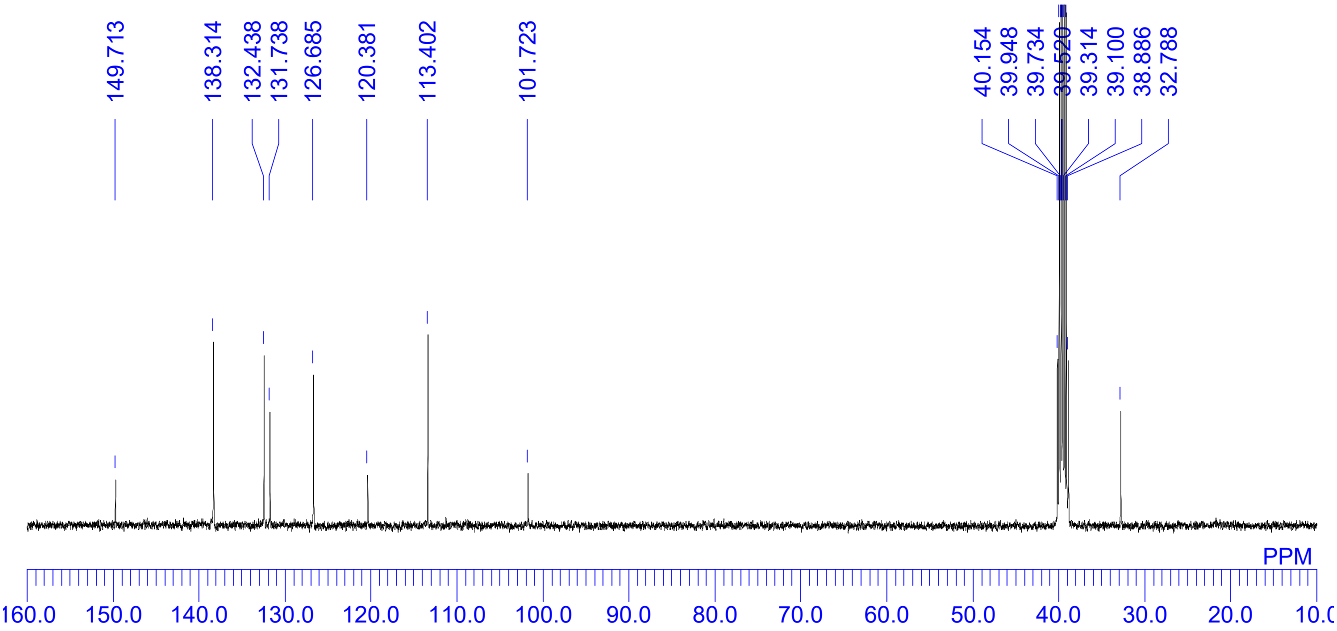
(S7) 2-(4-iodophenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium iodide



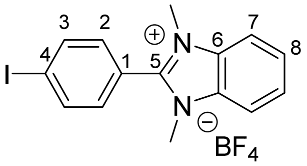
^{1}H NMR (400 MHz, DMSO-d$_6$)



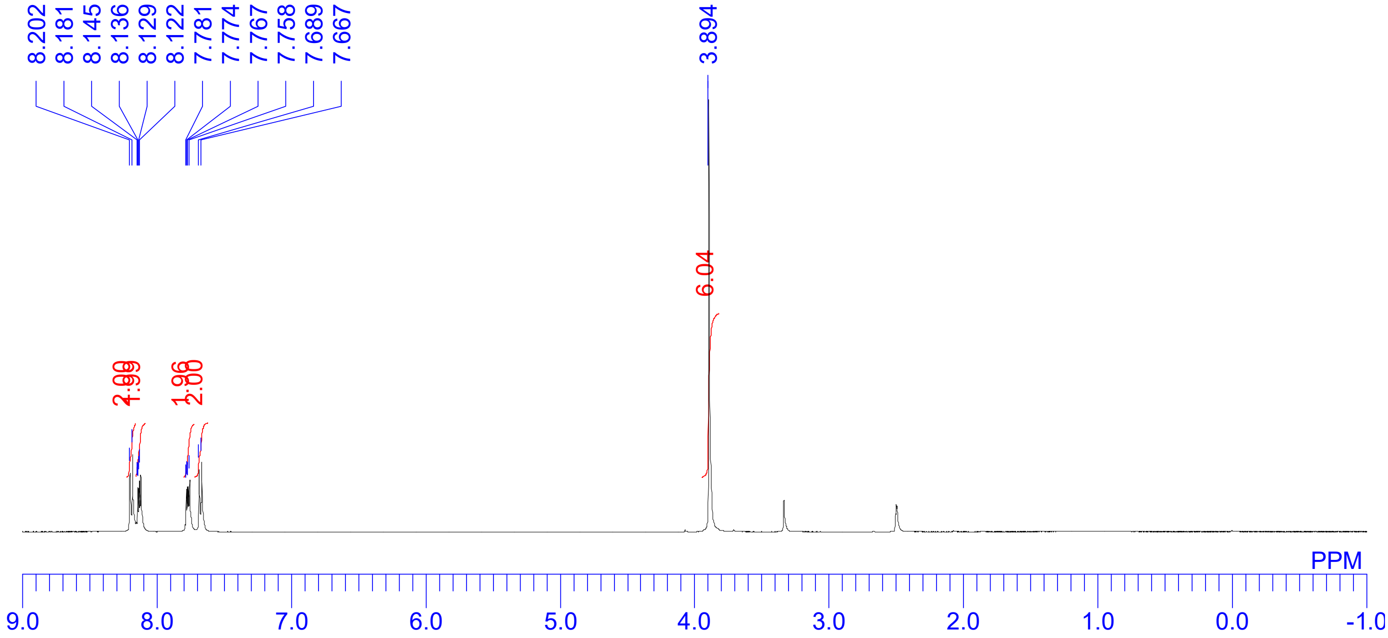
^{13}C NMR (100 MHz, DMSO-d_6)



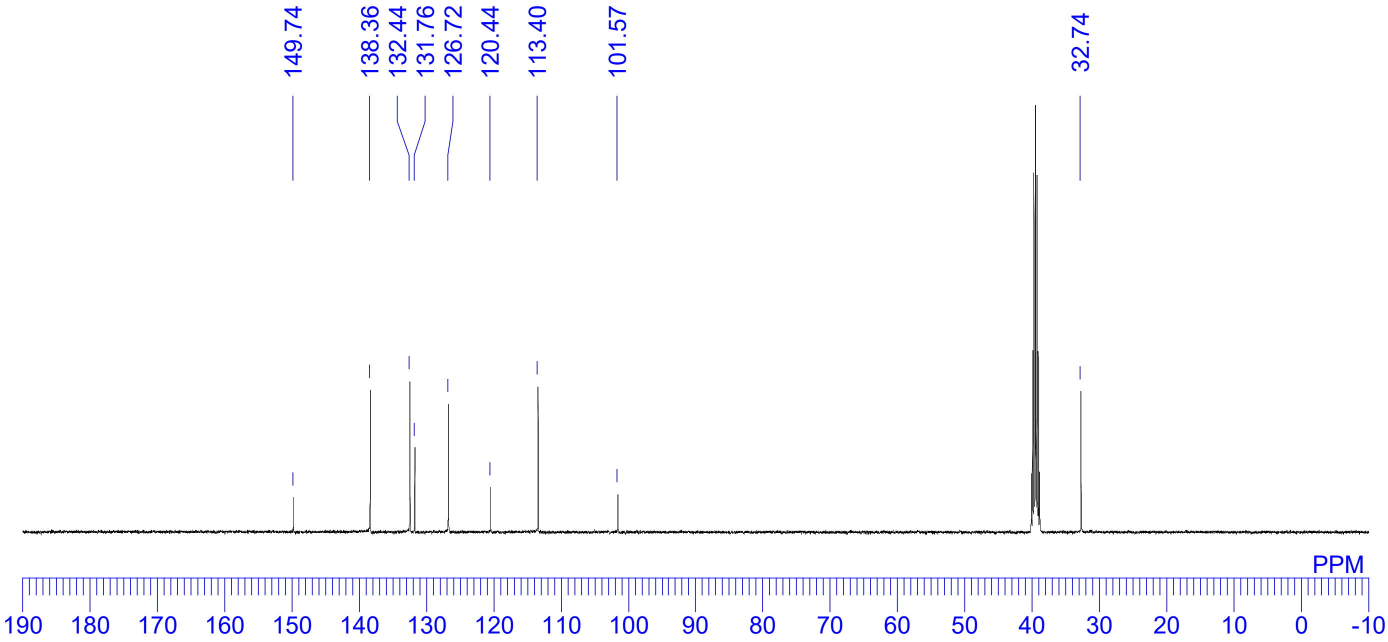
(S8) 2-(4-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate



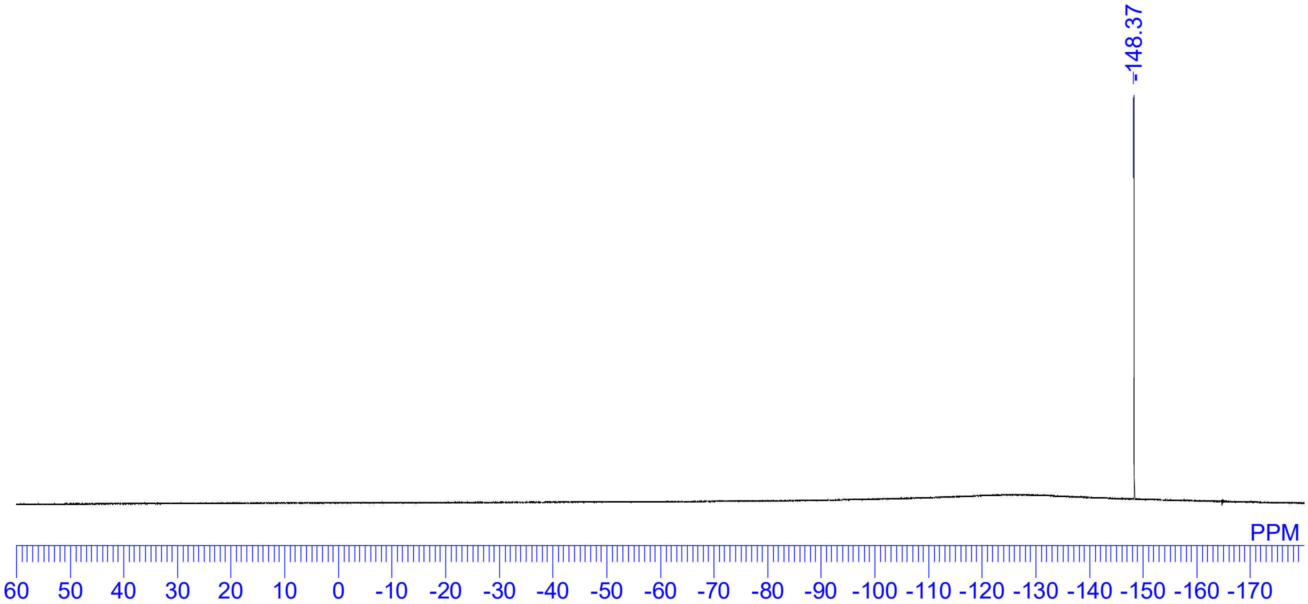
^{1}H NMR (400 MHz, DMSO-d_6)



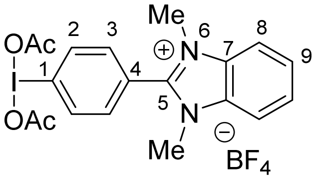
^{13}C NMR (100 Hz, DMSO-d_6)



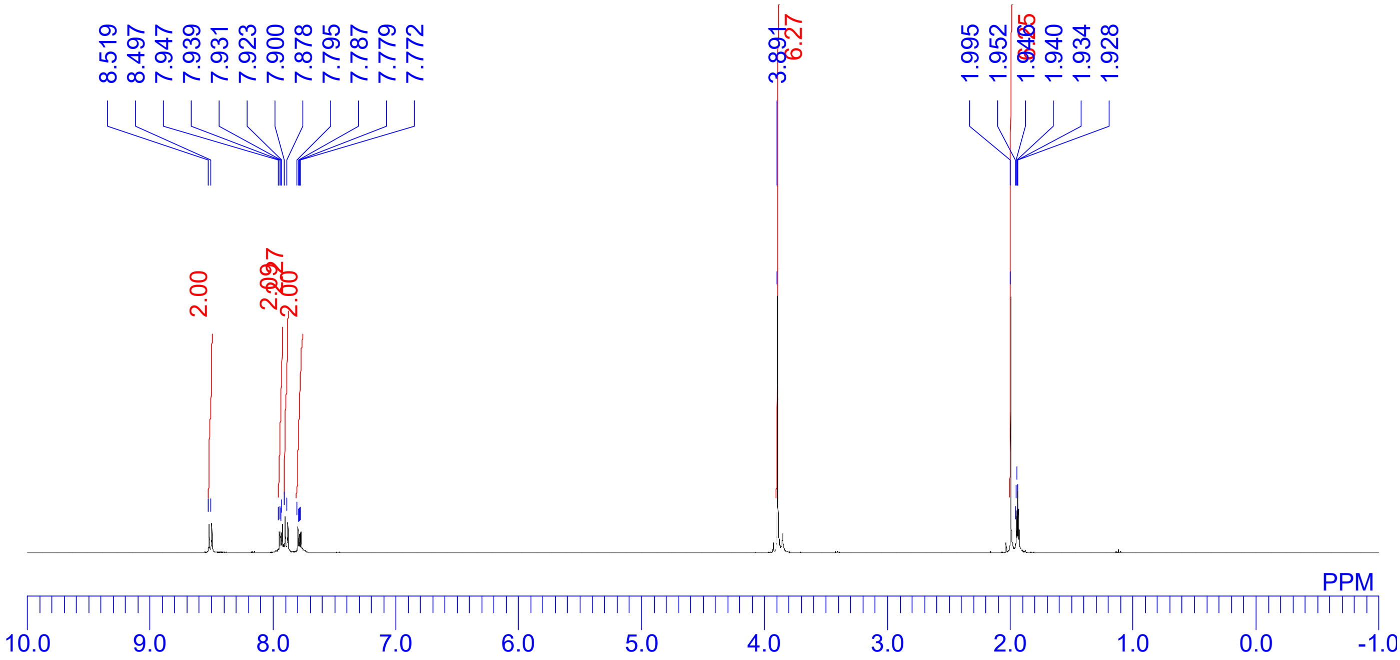
^{19}F NMR (377 MHz, DMSO-d_6, external standard: TFA in D_2O)



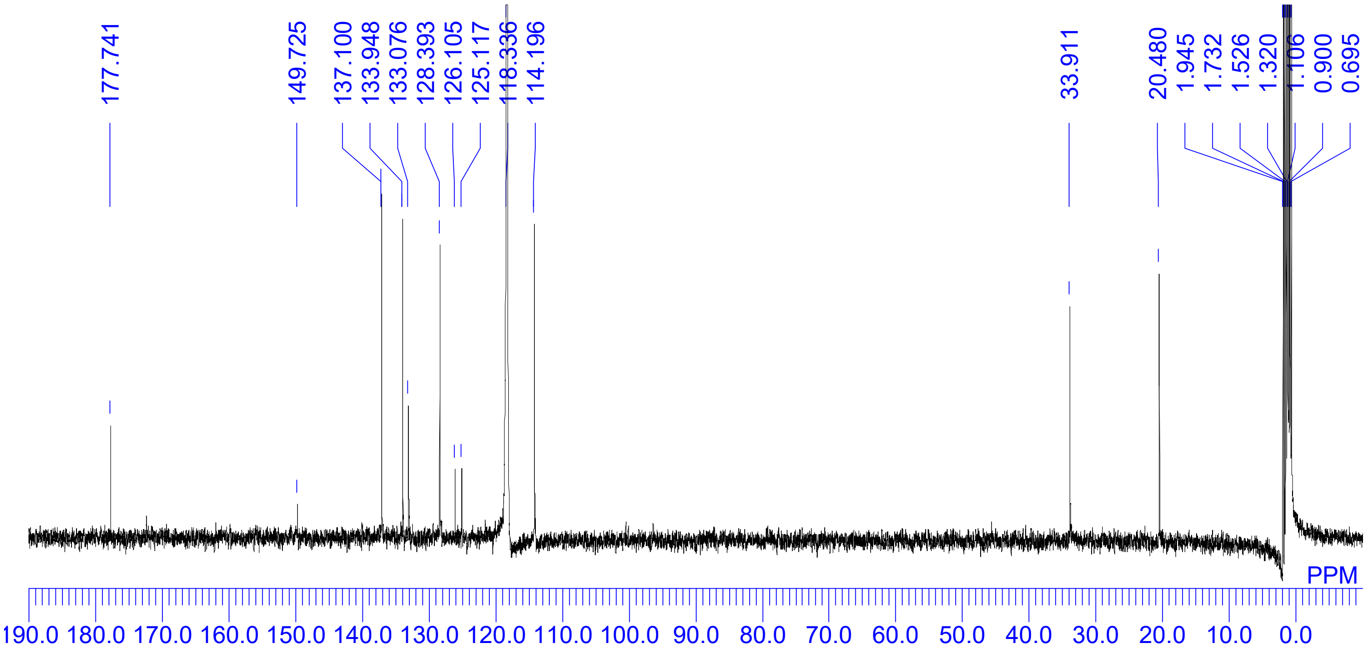
(1c) 2-(4-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium tetrafluoroborate



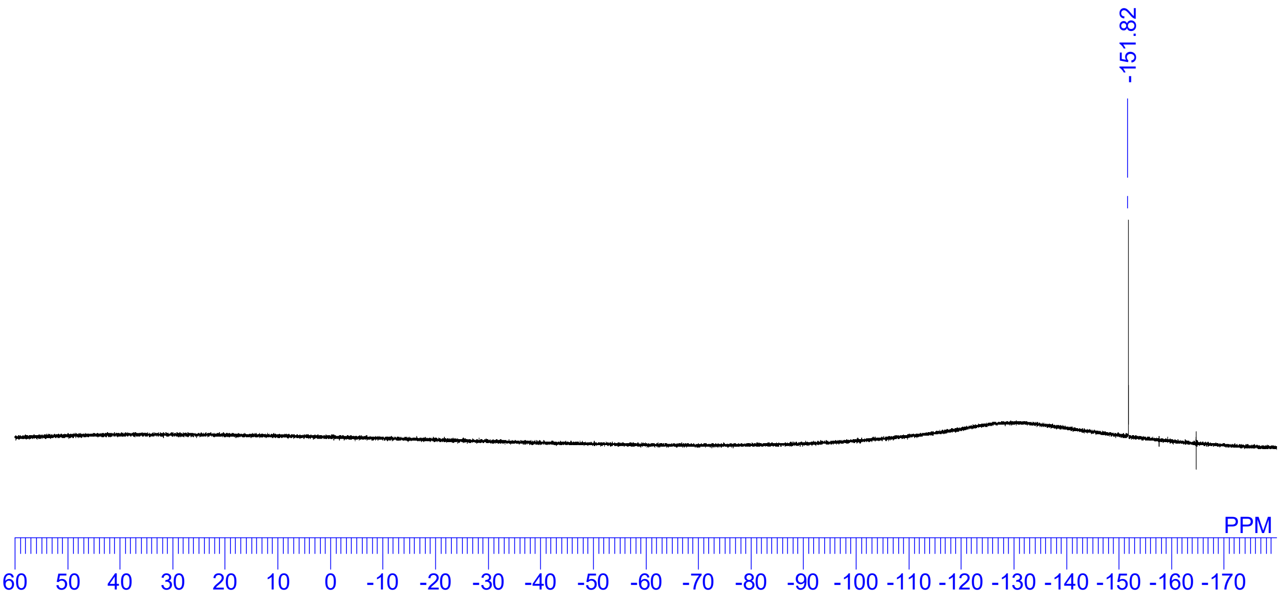
^{1}H NMR (400 MHz, CD_3CN)



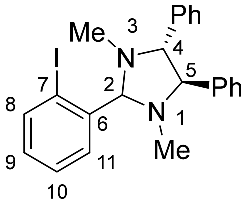
^{13}C NMR (100 MHz, CD_3CN)



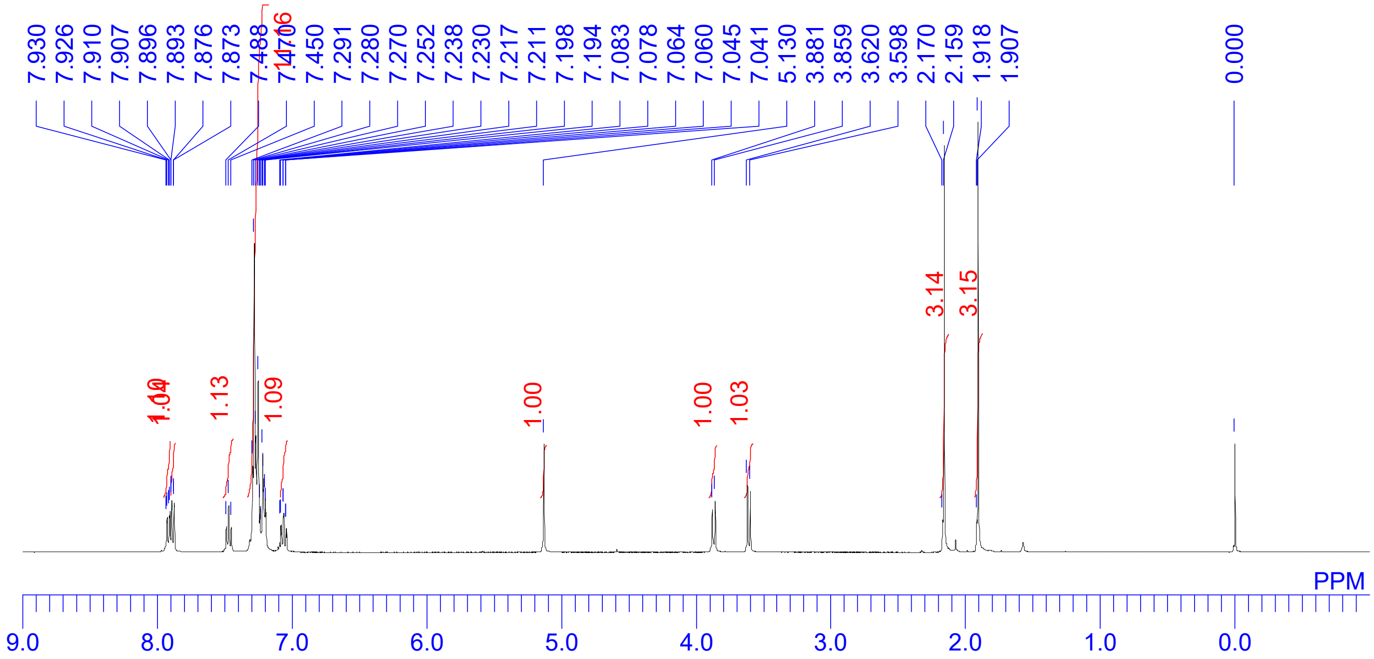
^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O)



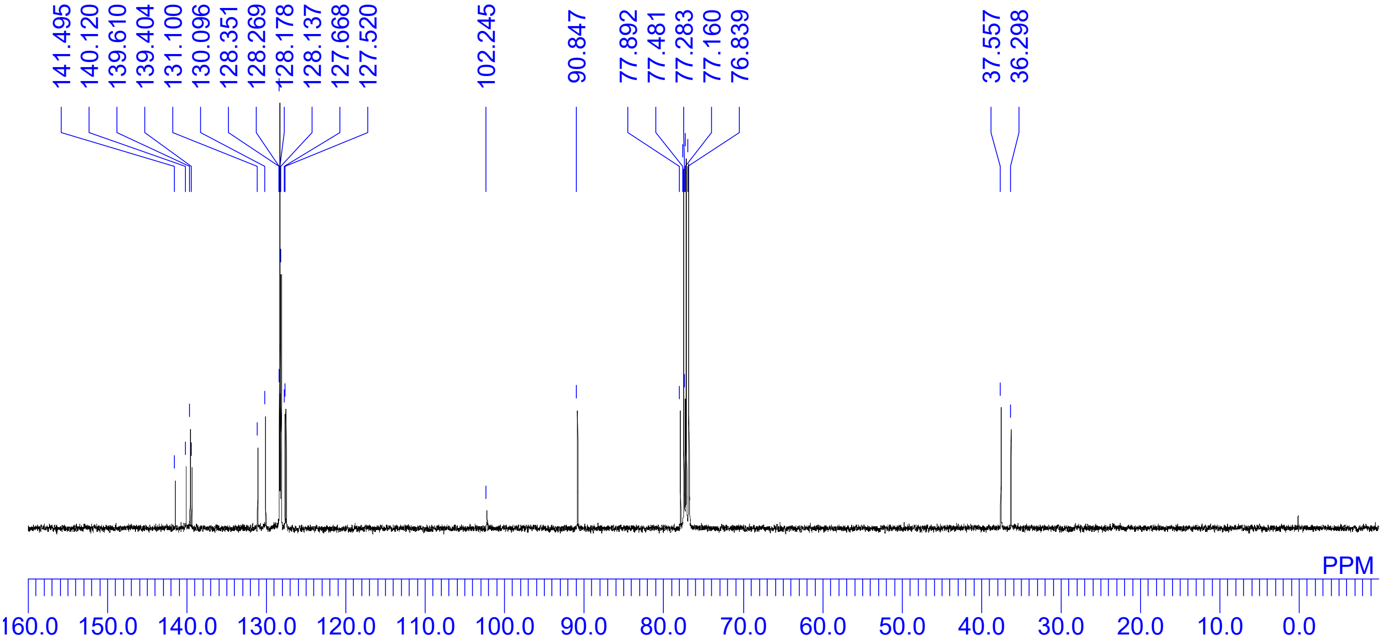
(S9) (*4R,5R*)-2-(2-iodophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine



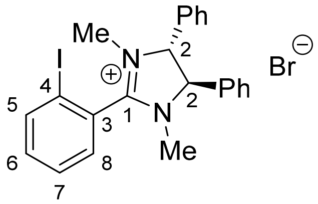
^{1}H NMR (400 MHz, CDCl$_3$)



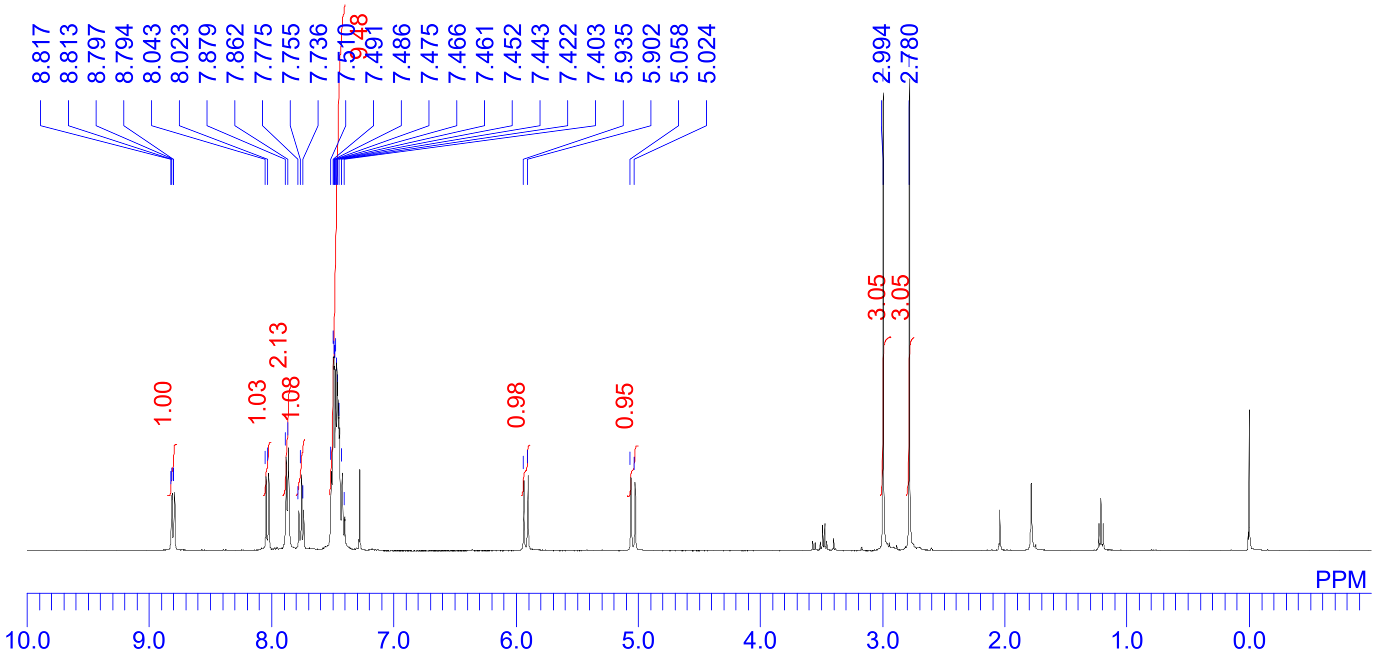
^{13}C NMR (100 MHz, CDCl$_3$)



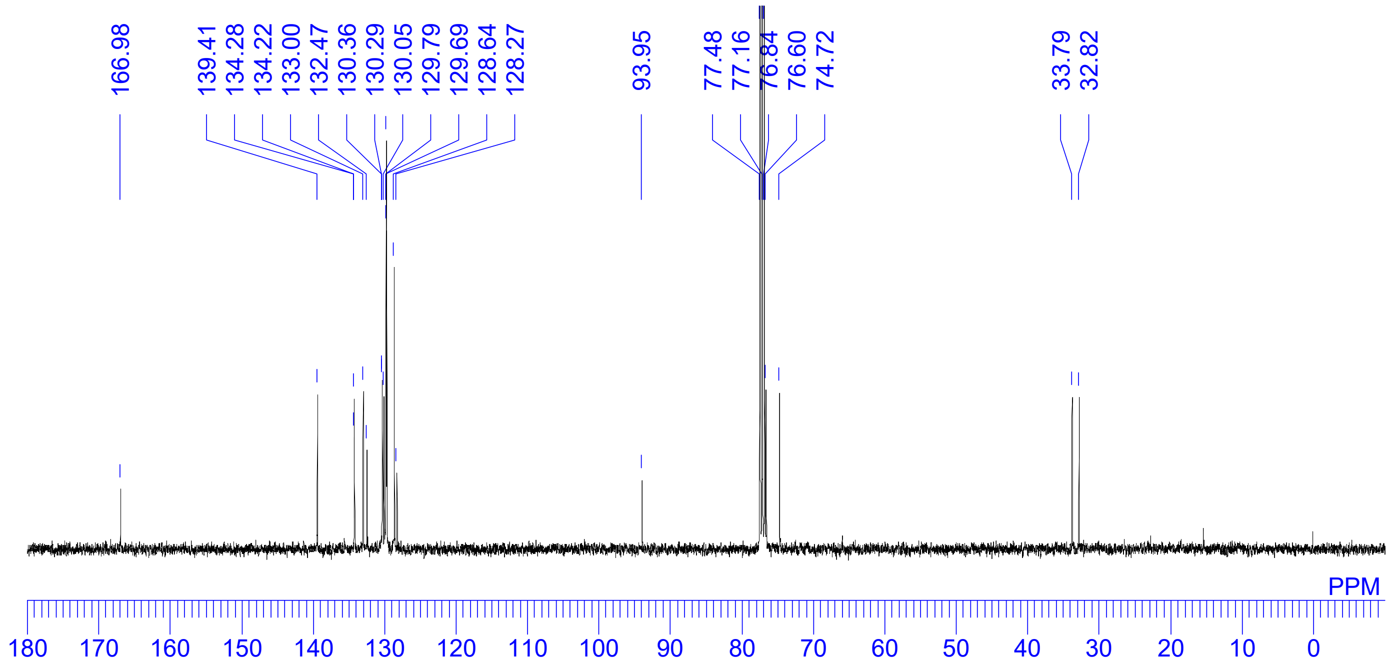
(S10) (4*R*,5*R*)-2-(2-iodophenyl)-1,3-dimethyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium bromide



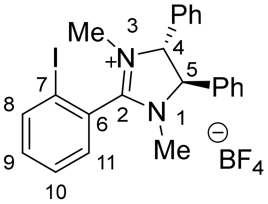
^{1}H NMR (400 MHz, CDCl$_3$)



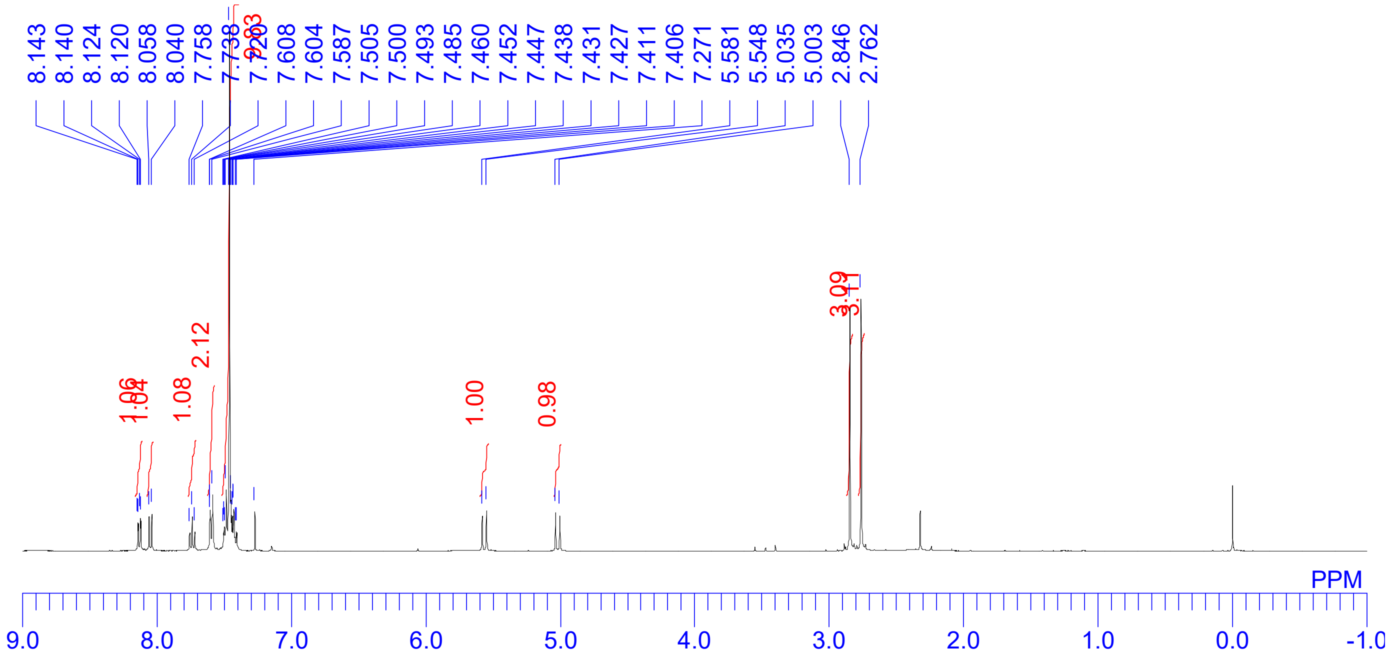
^{13}C NMR (100 MHz, CDCl$_3$)



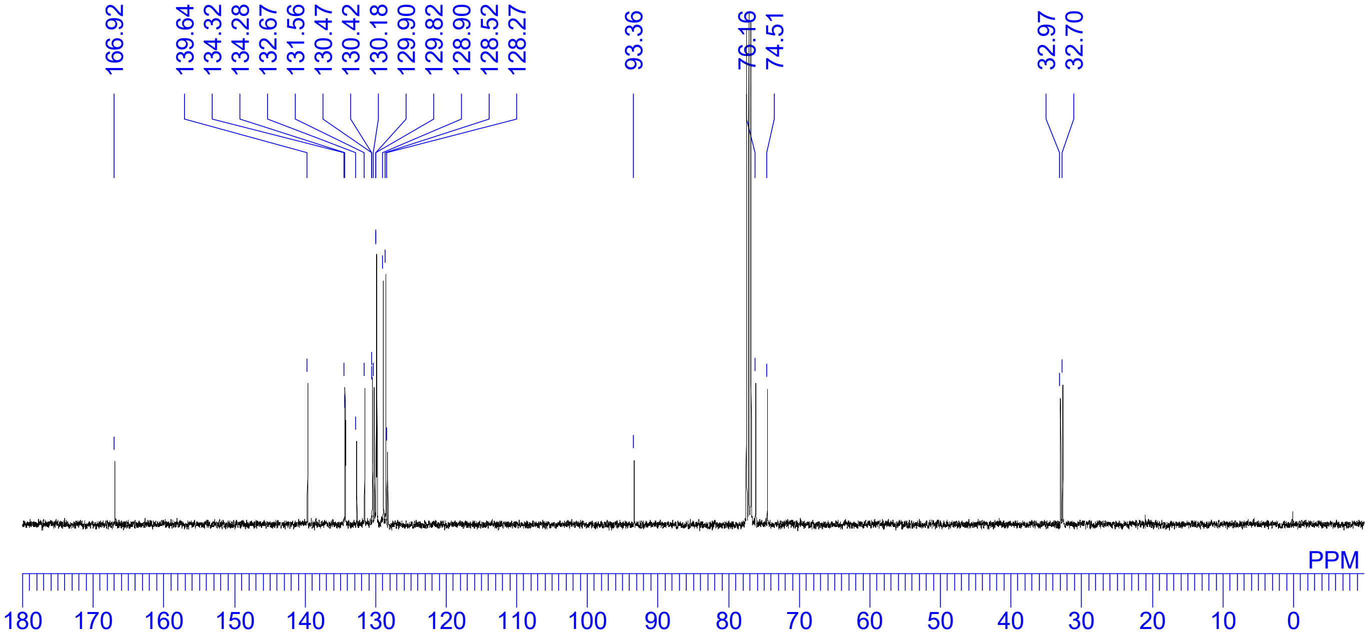
(S11) (*4R*,*5R*)-2-(2-iodophenyl)-1,3-dimethyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium



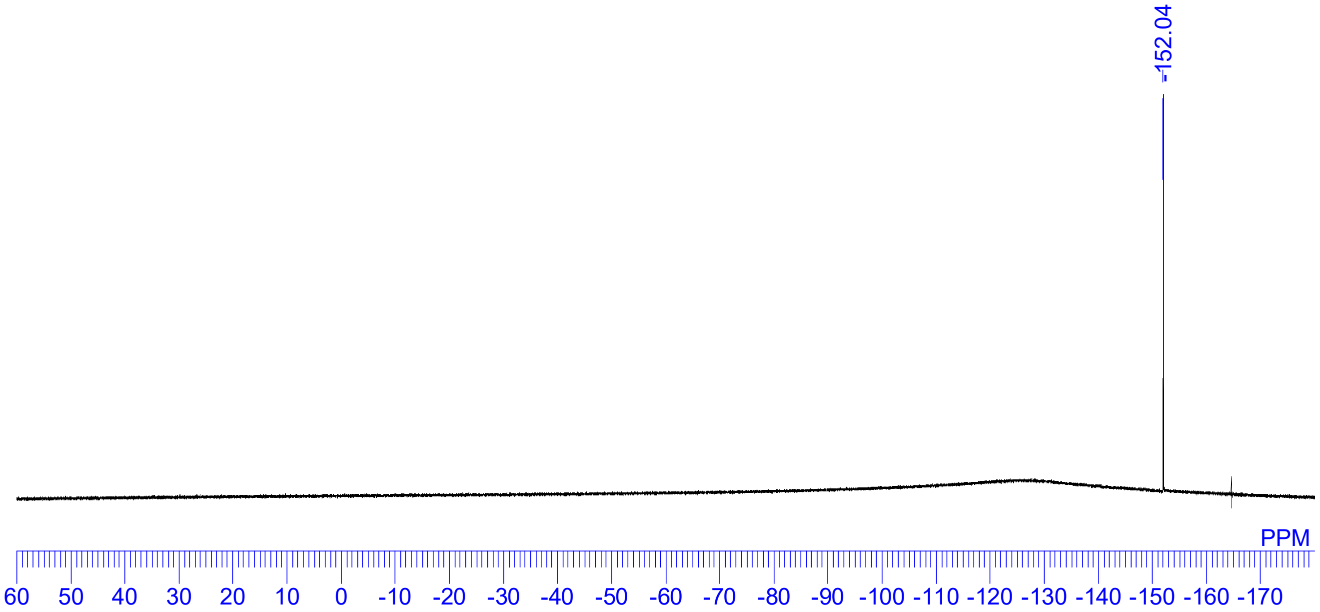
^{1}H NMR (400 MHz, CDCl$_3$):



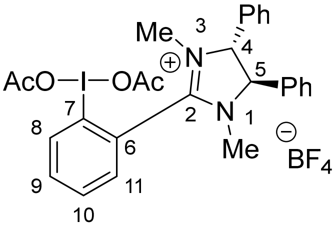
^{13}C NMR (100 MHz, CDCl$_3$):



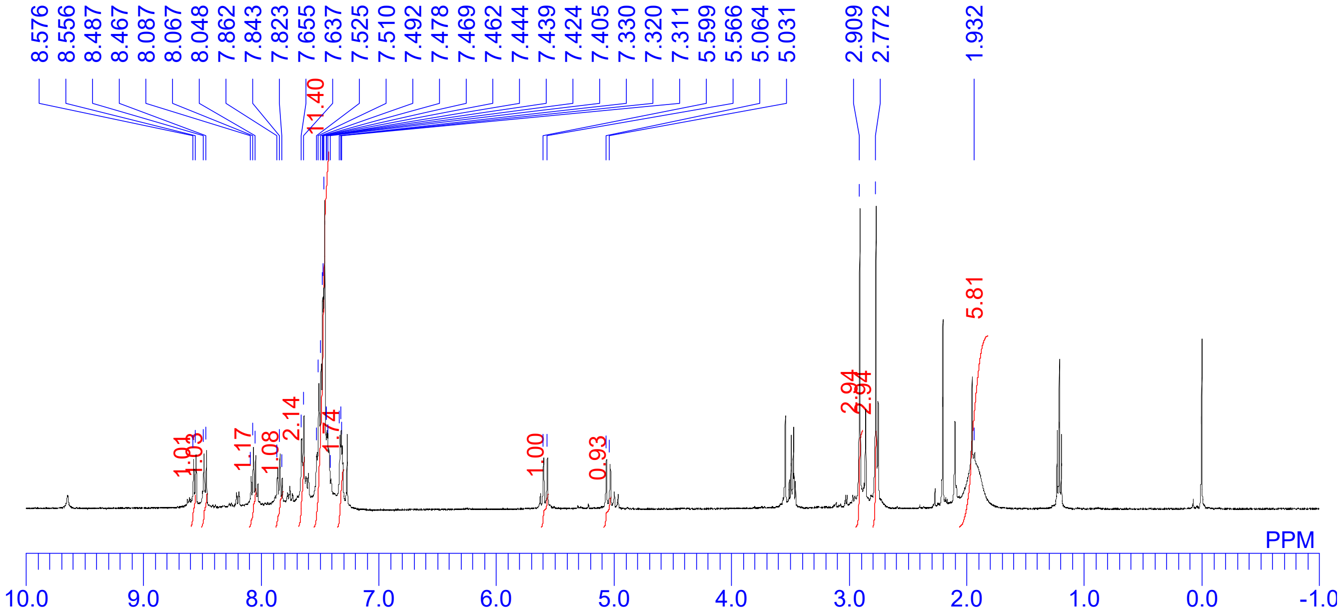
^{19}F NMR (377 MHz, $CDCl_3$, external standard: TFA in D_2O)



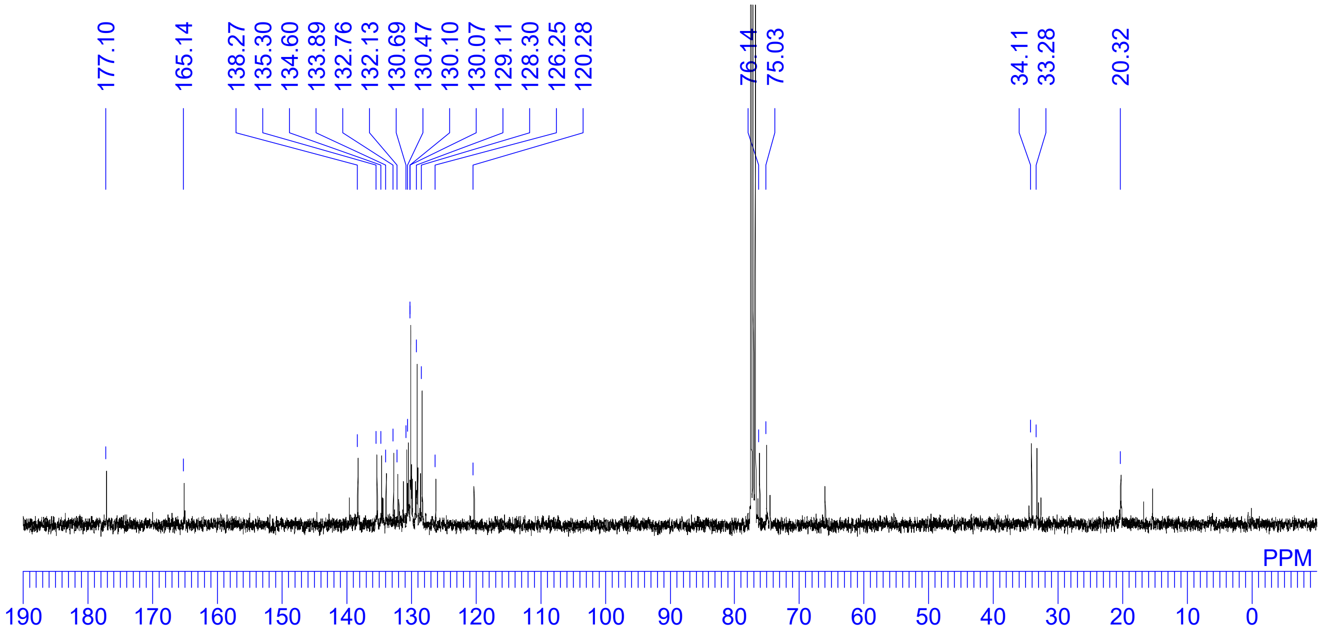
((*R*,*R*)-1d) (*4R*,*5R*)-2-(2-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate



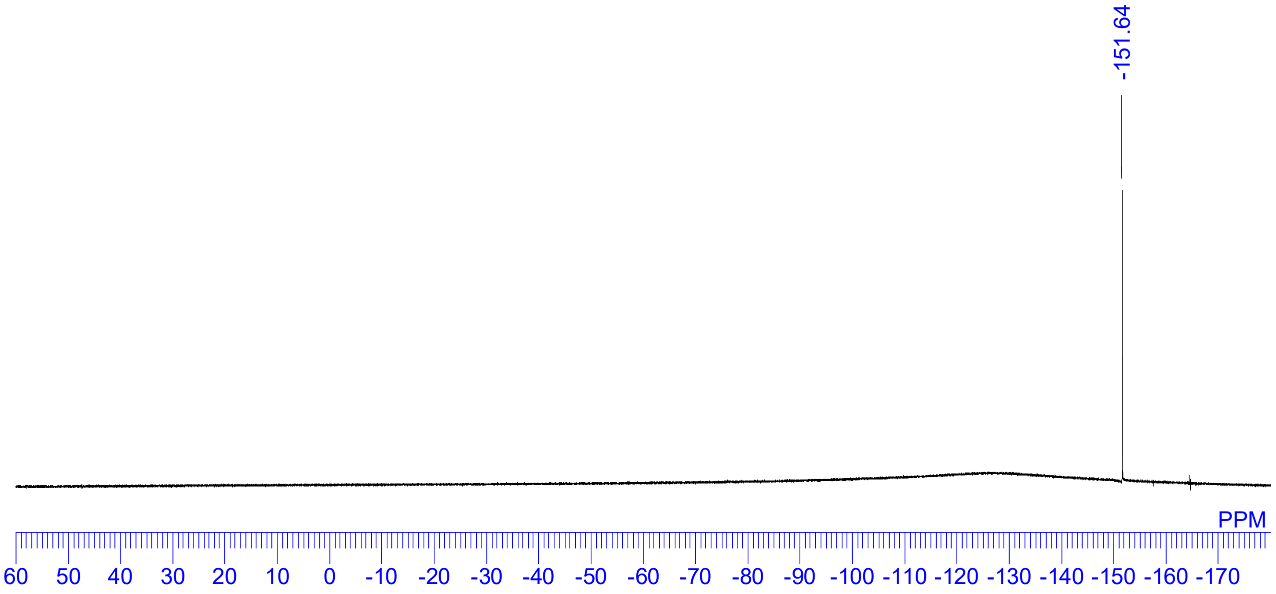
^{1}H NMR (400 MHz, CDCl$_3$)



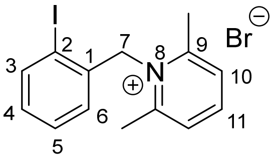
^{13}C NMR (100 MHz, CDCl$_3$)



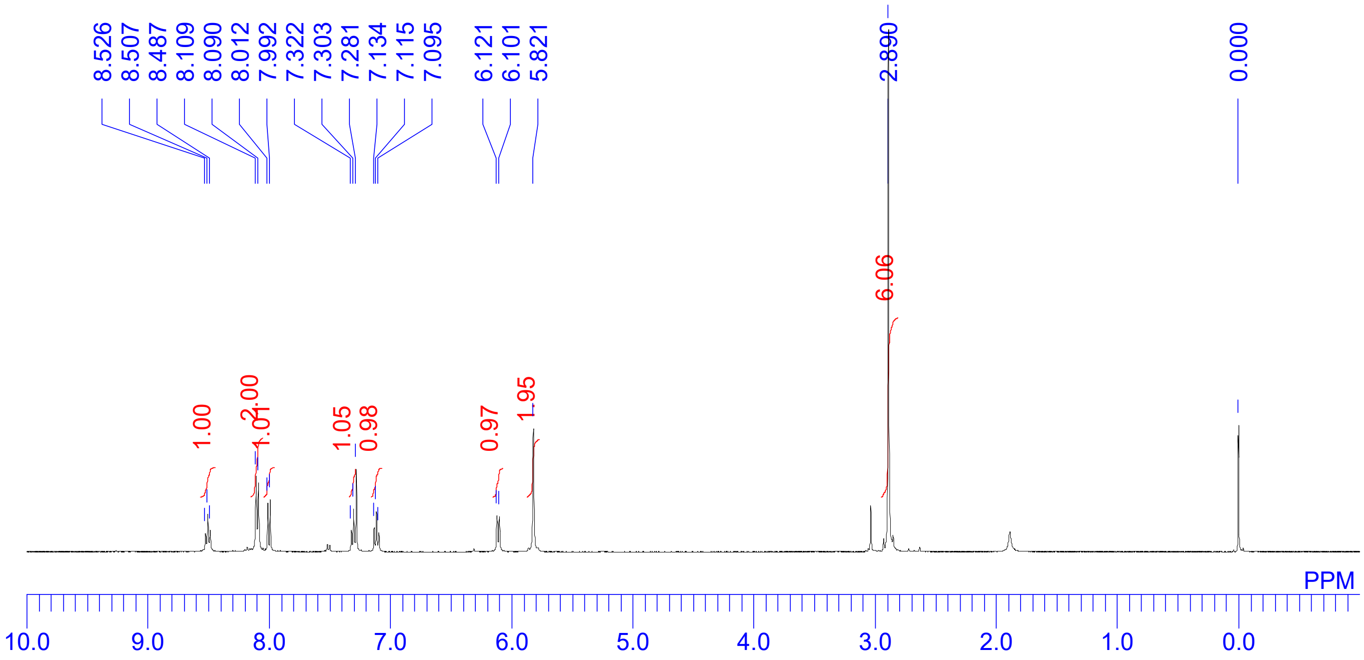
^{19}F NMR (377 MHz, $CDCl_3$, external standard: TFA in D_2O)



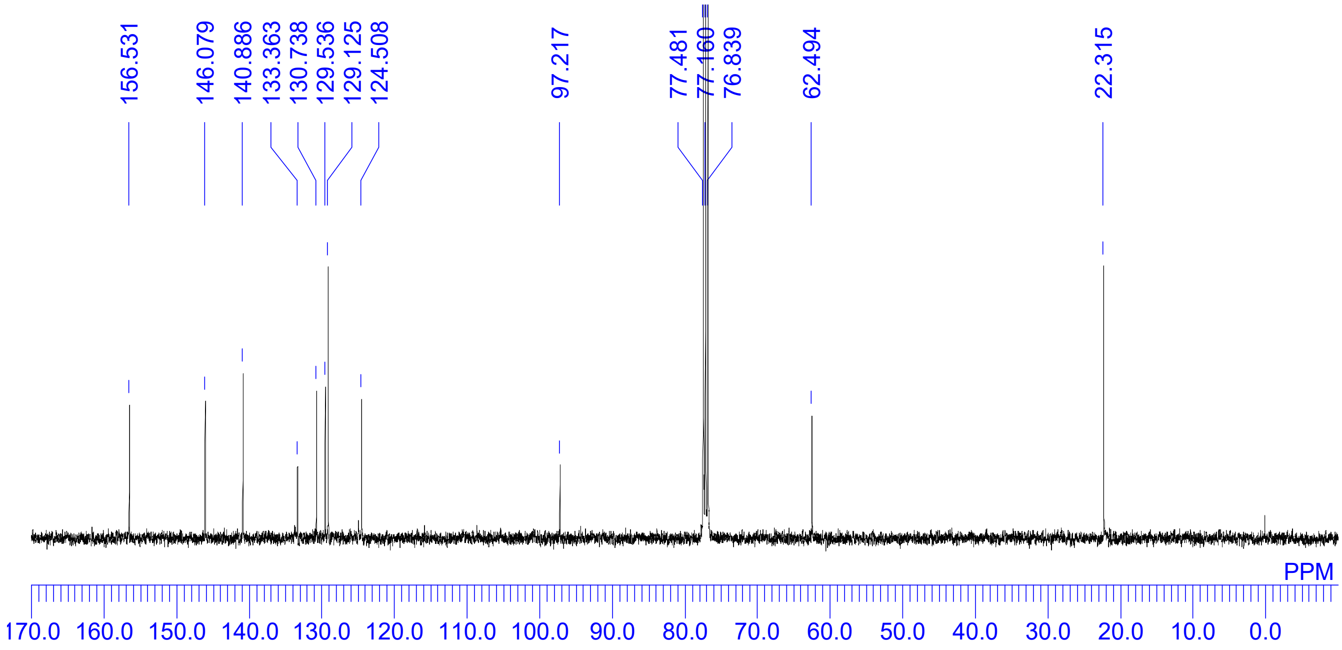
(S12) 1-(2-iodobenzyl)-2,6-dimethylpyridin-1-ium bromide



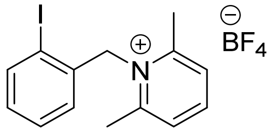
^{1}H NMR (400 MHz, CDCl$_3$)



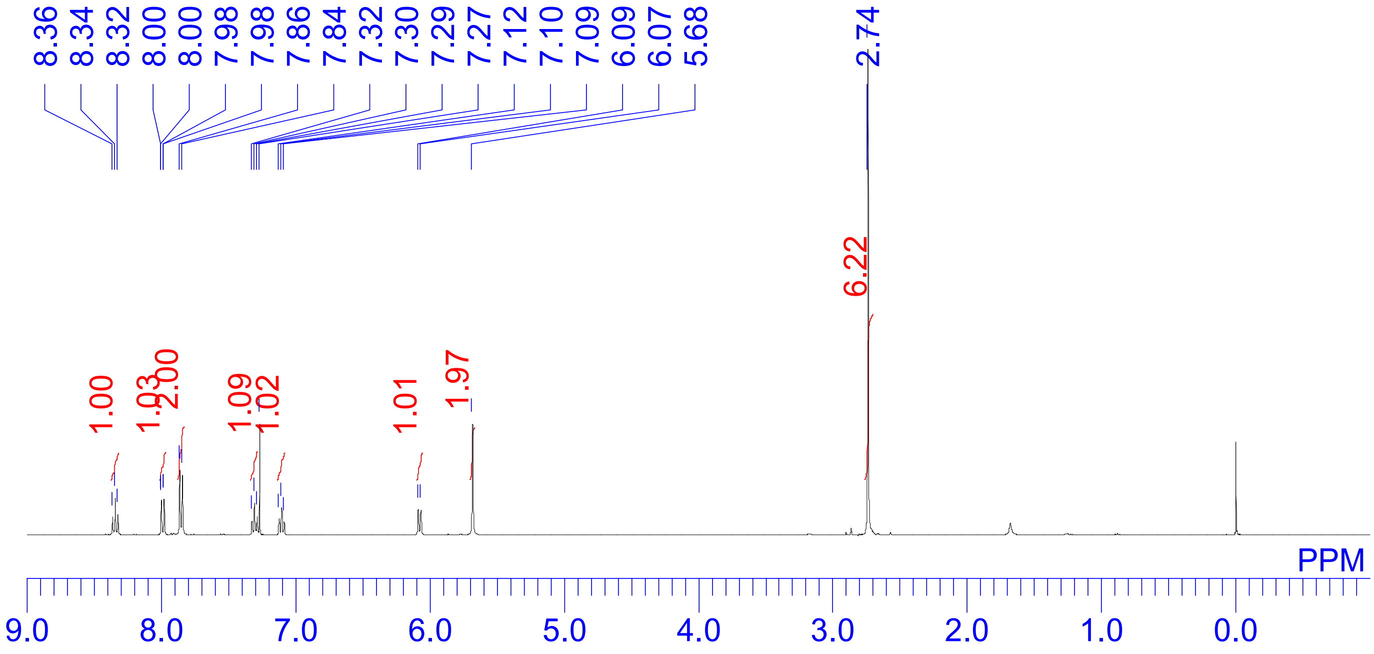
^{13}C NMR (100 MHz, CDCl$_3$)



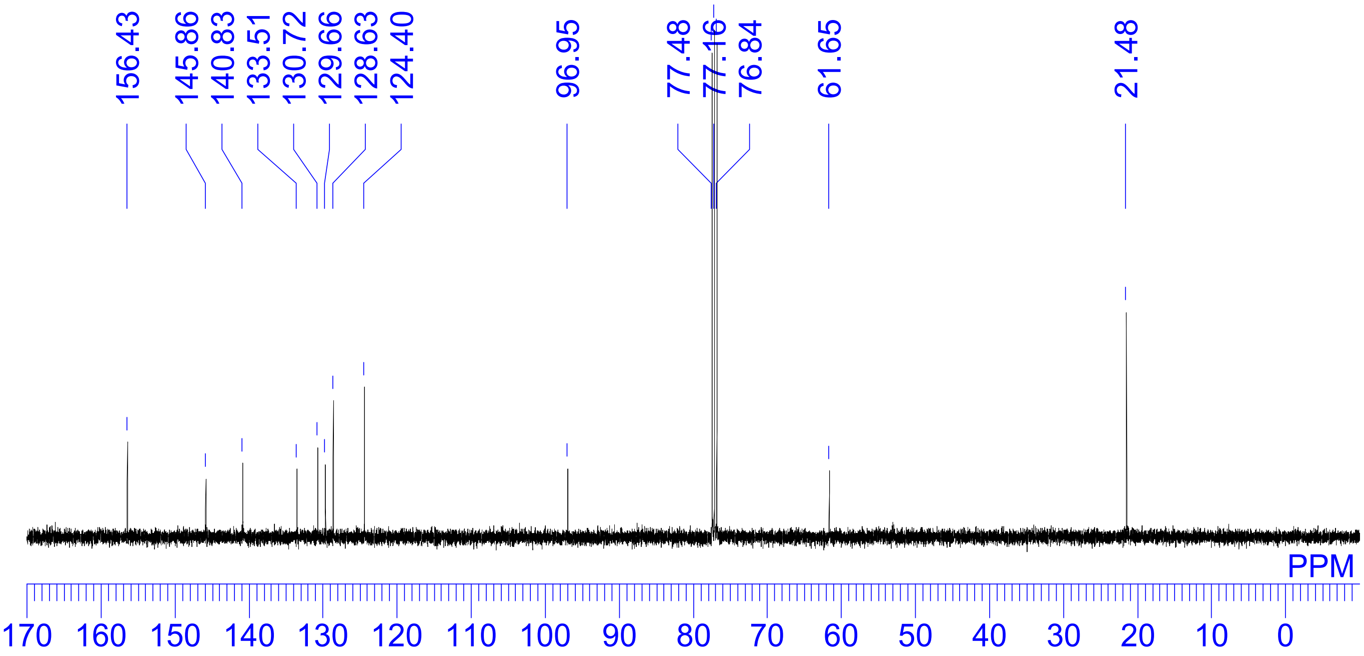
(S13) 1-(2-iodobenzyl)-2,6-dimethylpyridin-1-ium tetrafluoroborate



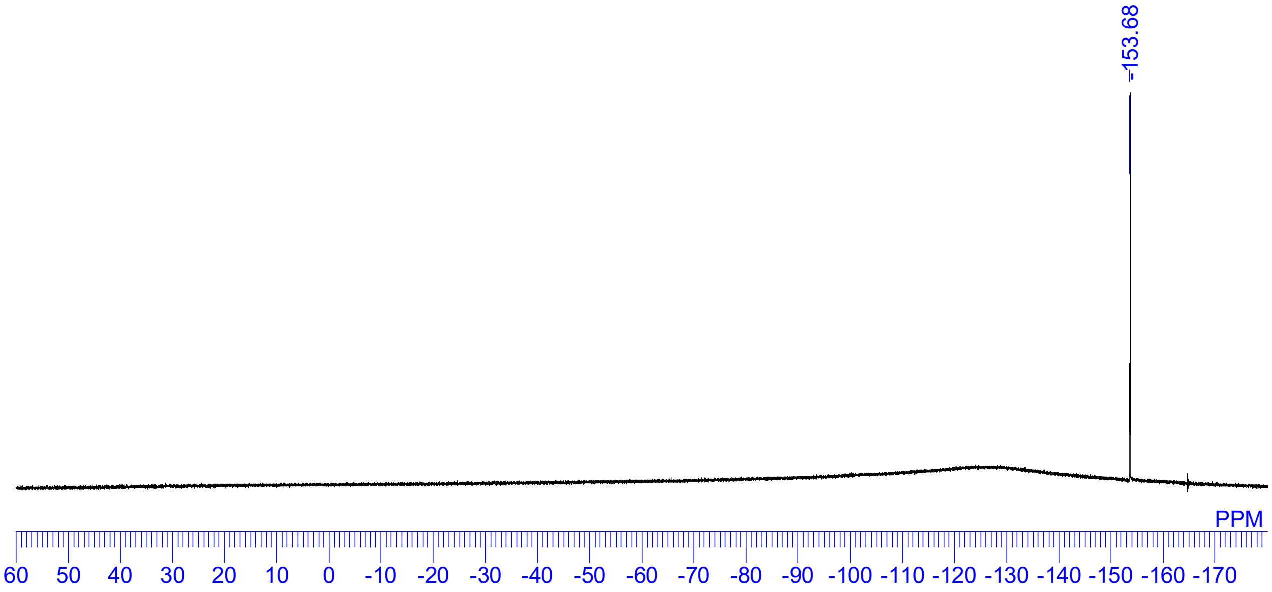
^1H NMR (400 MHz, $CDCl_3$)



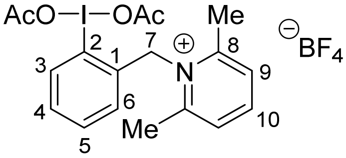
^{13}C NMR (100 MHz, $CDCl_3$)



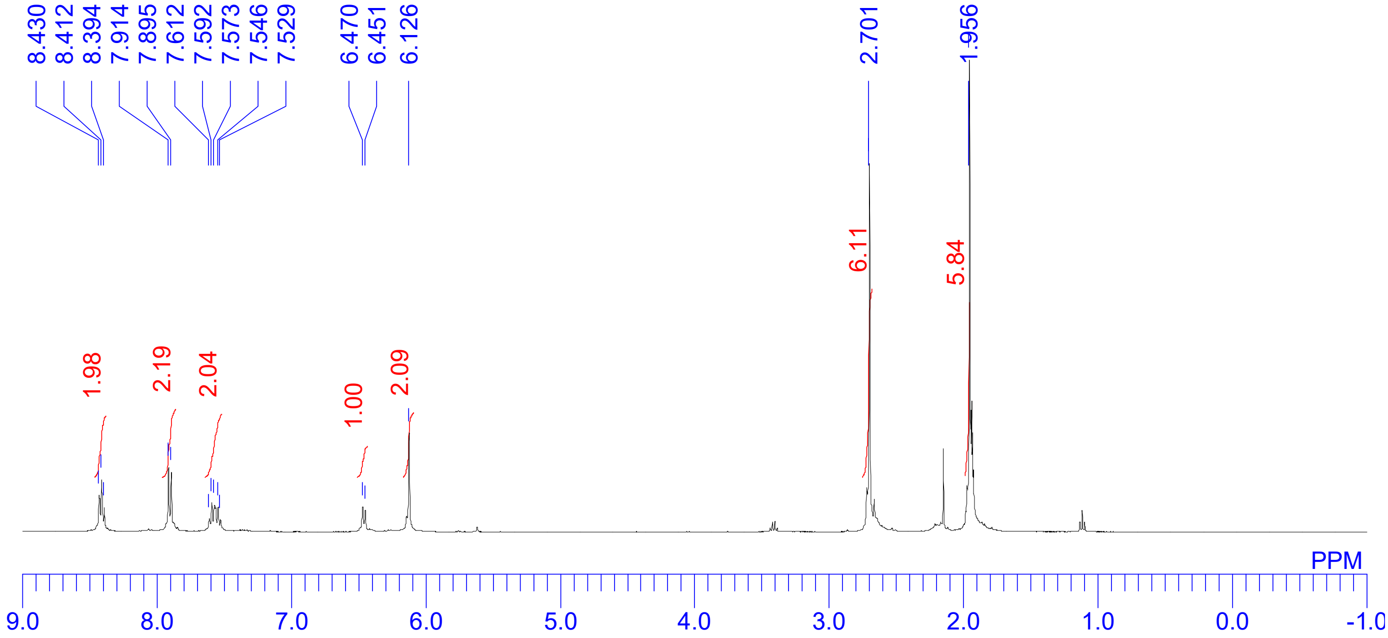
^{19}F NMR (377 MHz, $CDCl_3$, external standard: TFA in D_2O)



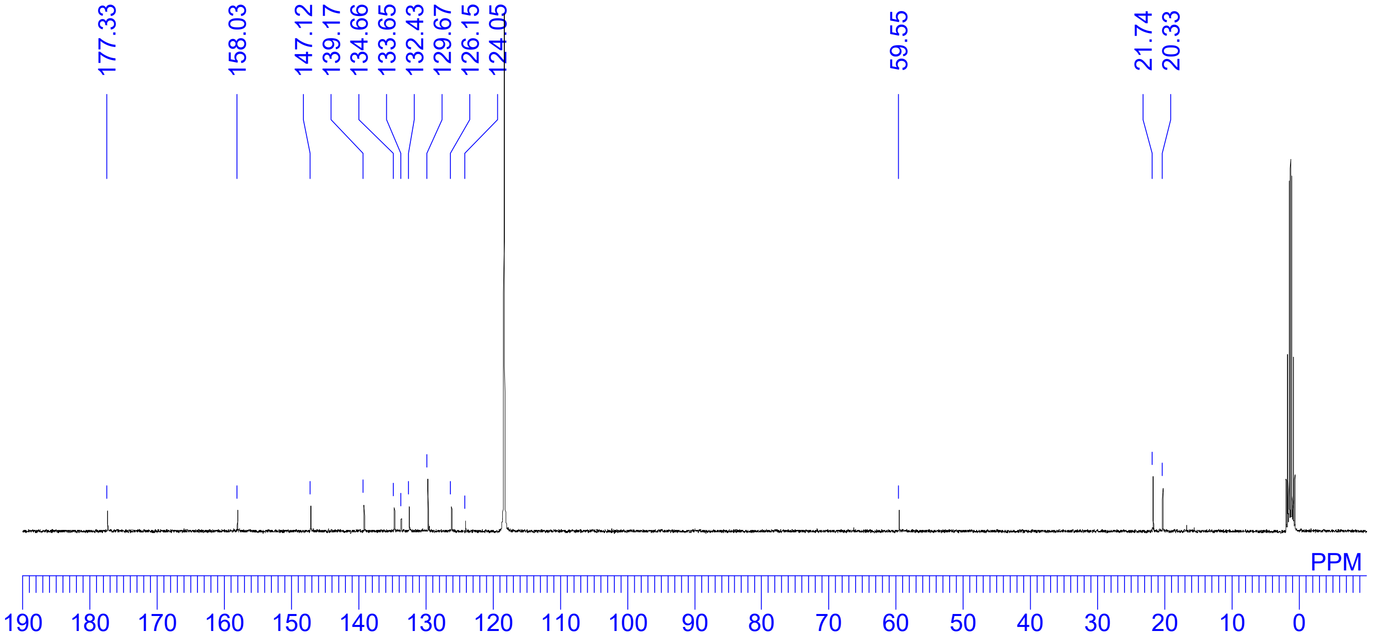
(1e) 1-(2-(diacetoxy-λ^3-iodaneyl)benzyl)-2,6-dimethylpyridin-1-ium tetrafluoroborate



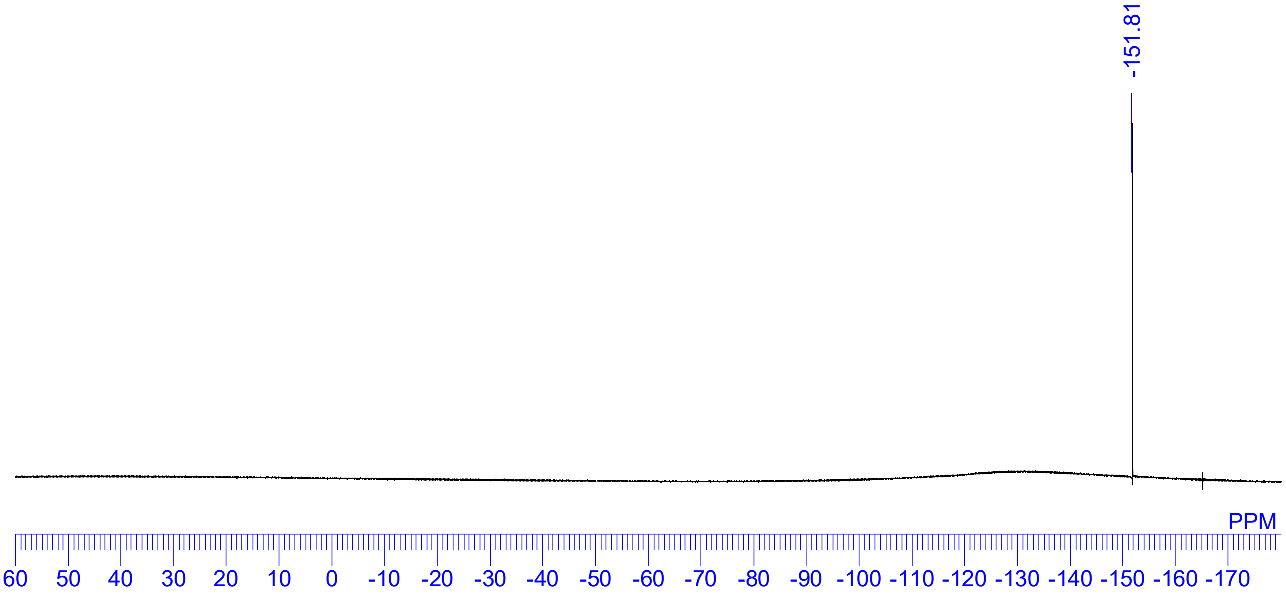
^{1}H NMR (400 MHz, CD_3CN)



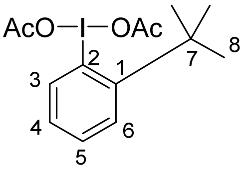
^{13}C NMR (100 MHz, CD_3CN)



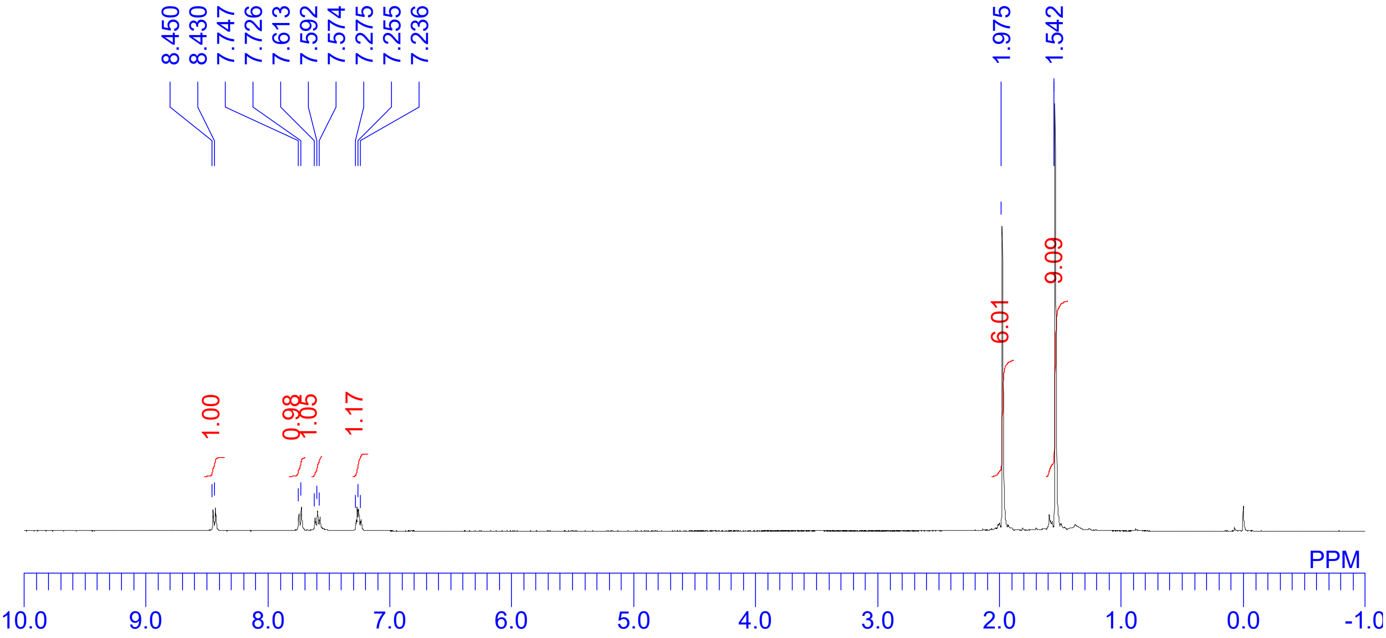
^{19}F NMR (377 MHz, CD_3CN, external standard: TFA in D_2O)



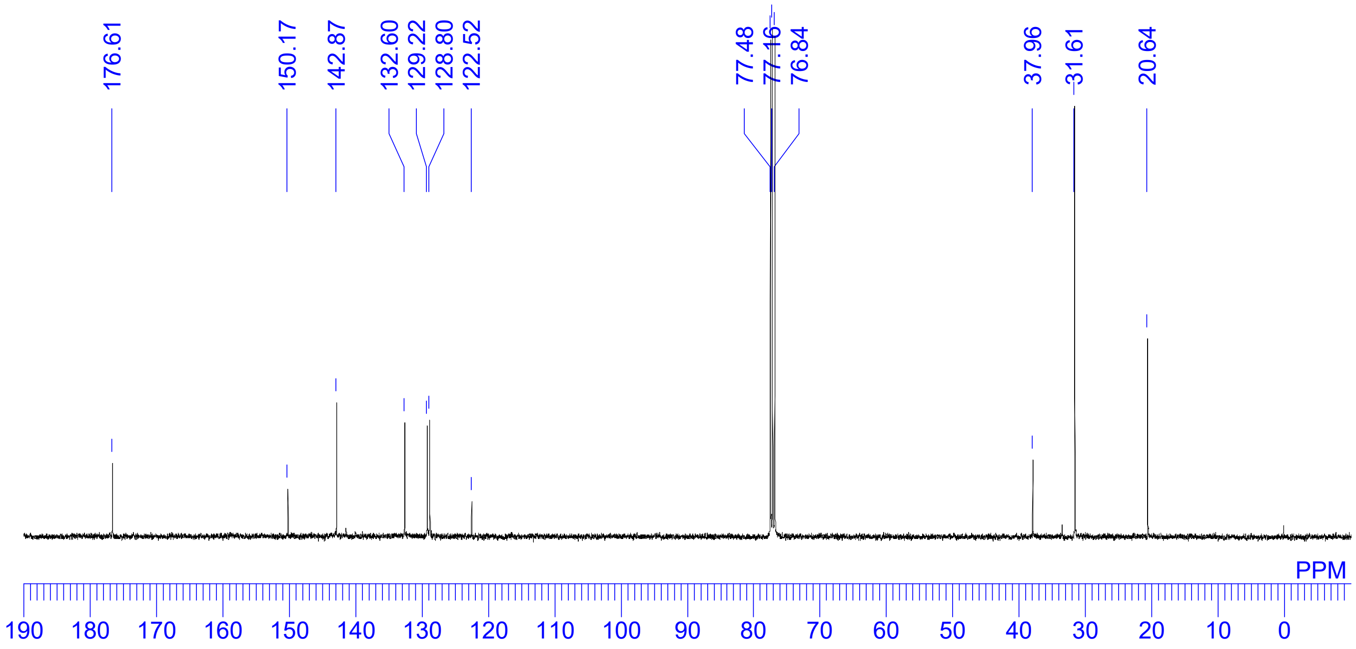
(1f) (2-(*tert*-butyl)phenyl)-λ^3-iodanediyl diacetate



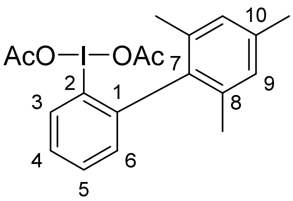
^{1}H NMR (400 MHz, CDCl$_3$)



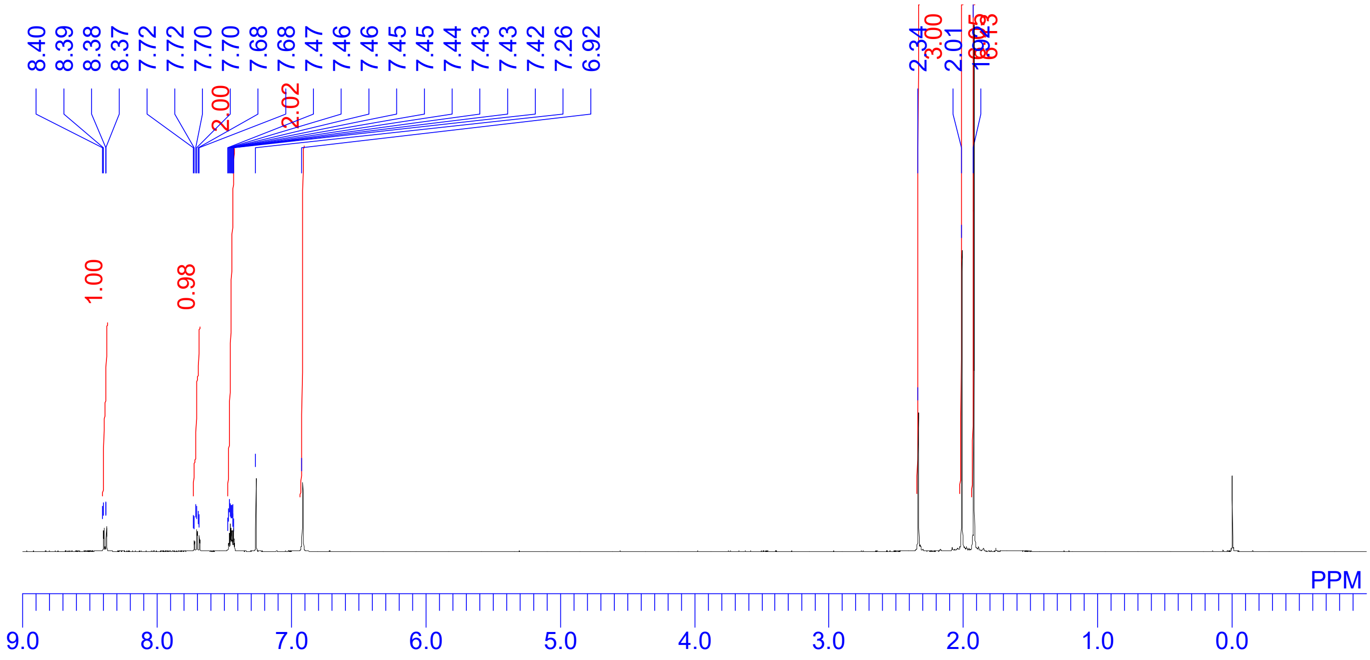
^{13}C NMR (100 MHz, CDCl$_3$)



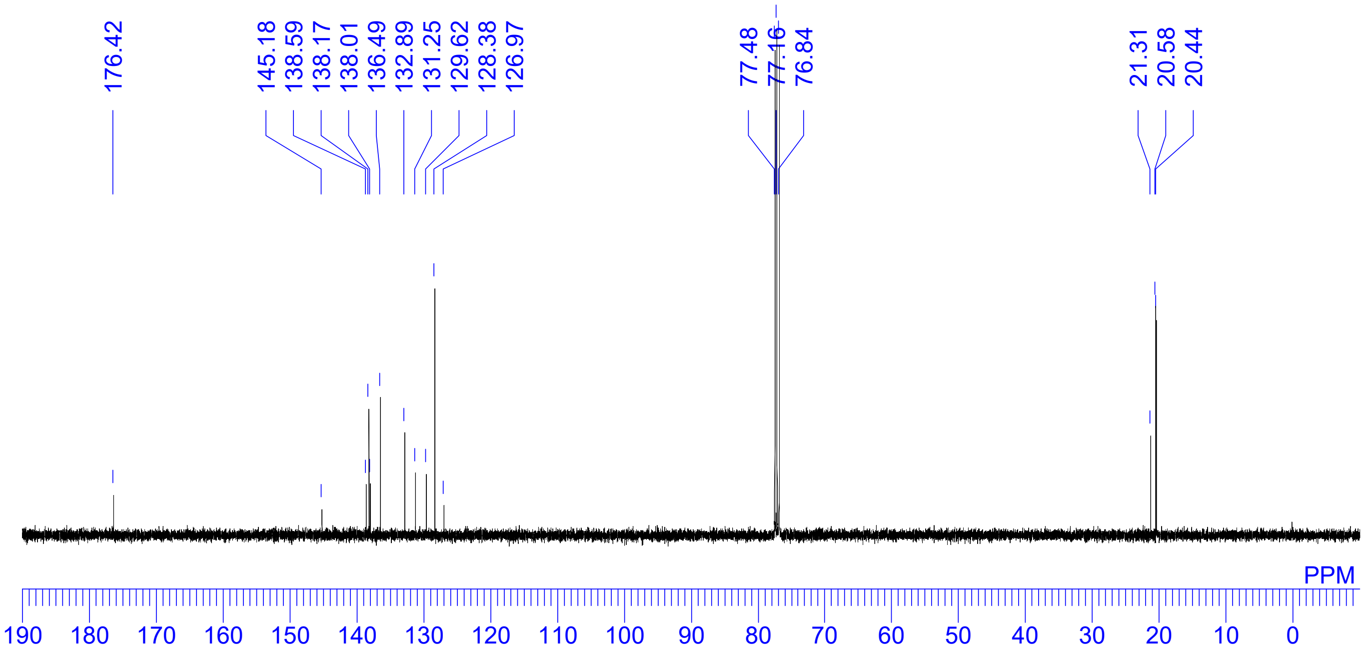
(1g) (2',4',6'-trimethyl-[1,1'-biphenyl]-2-yl)-l3-iodanediyl diacetate



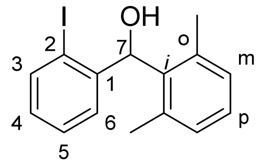
^{1}H NMR (400 MHz, CDCl$_3$)



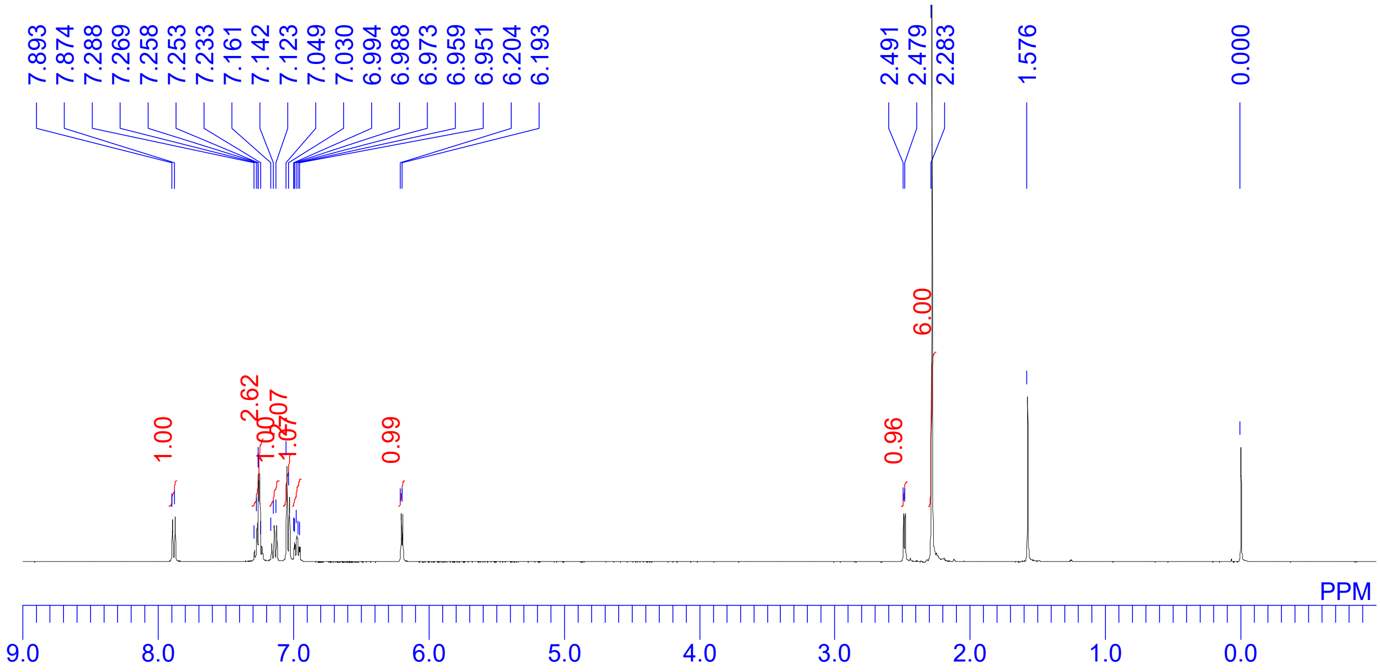
^{13}C NMR (100 MHz, CDCl$_3$)



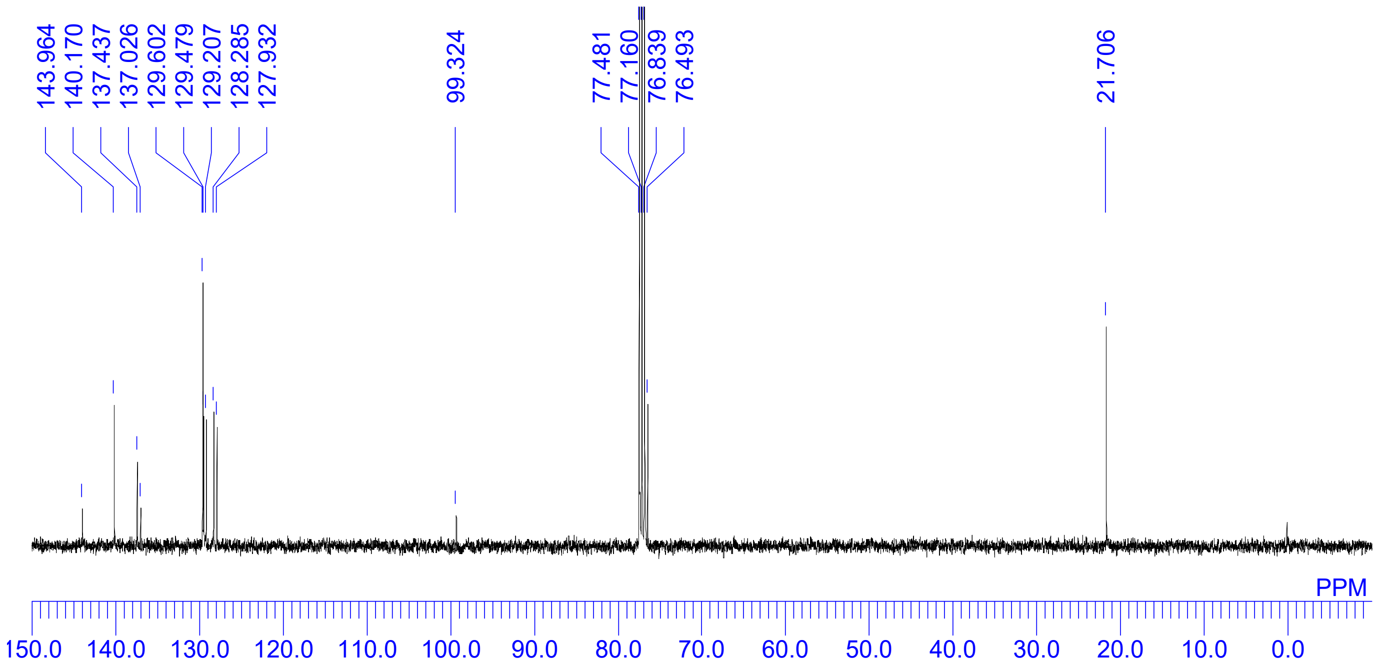
(S14) (2,6-dimethylphenyl)(2-iodophenyl)methanol



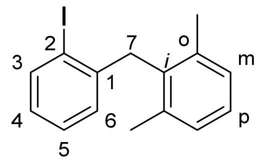
^{1}H NMR (400 MHz, CDCl$_3$)



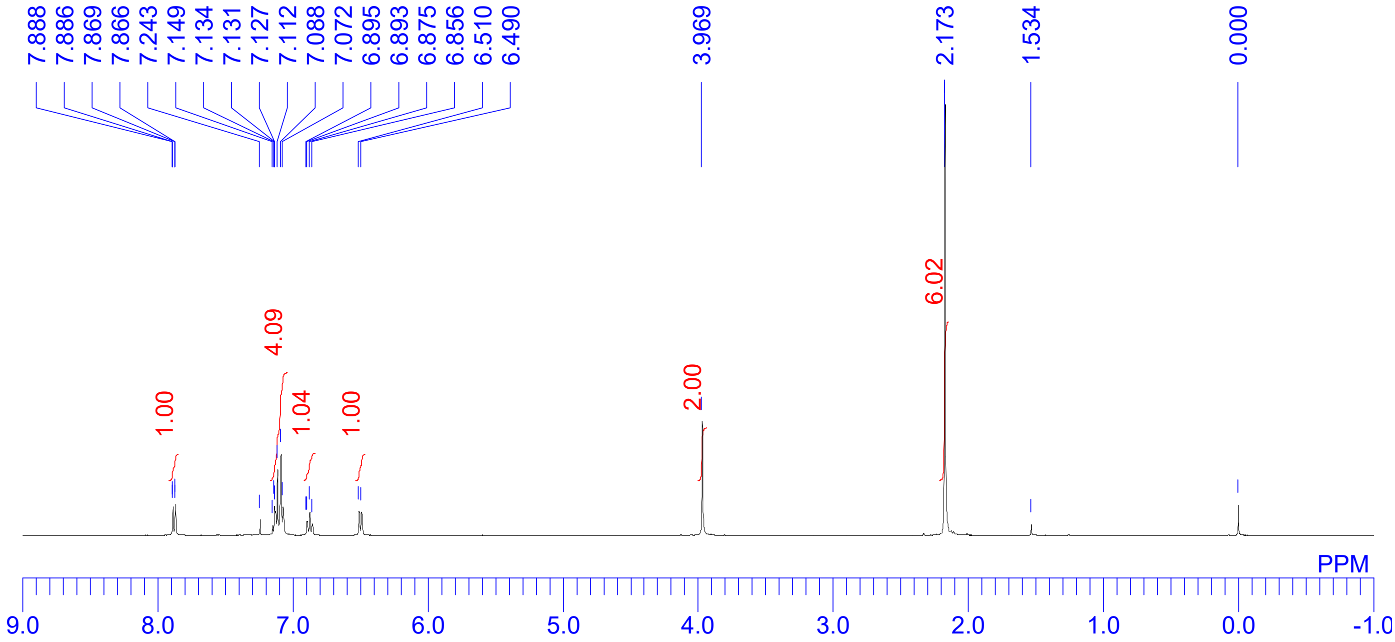
^{13}C NMR (100 MHz, CDCl$_3$)



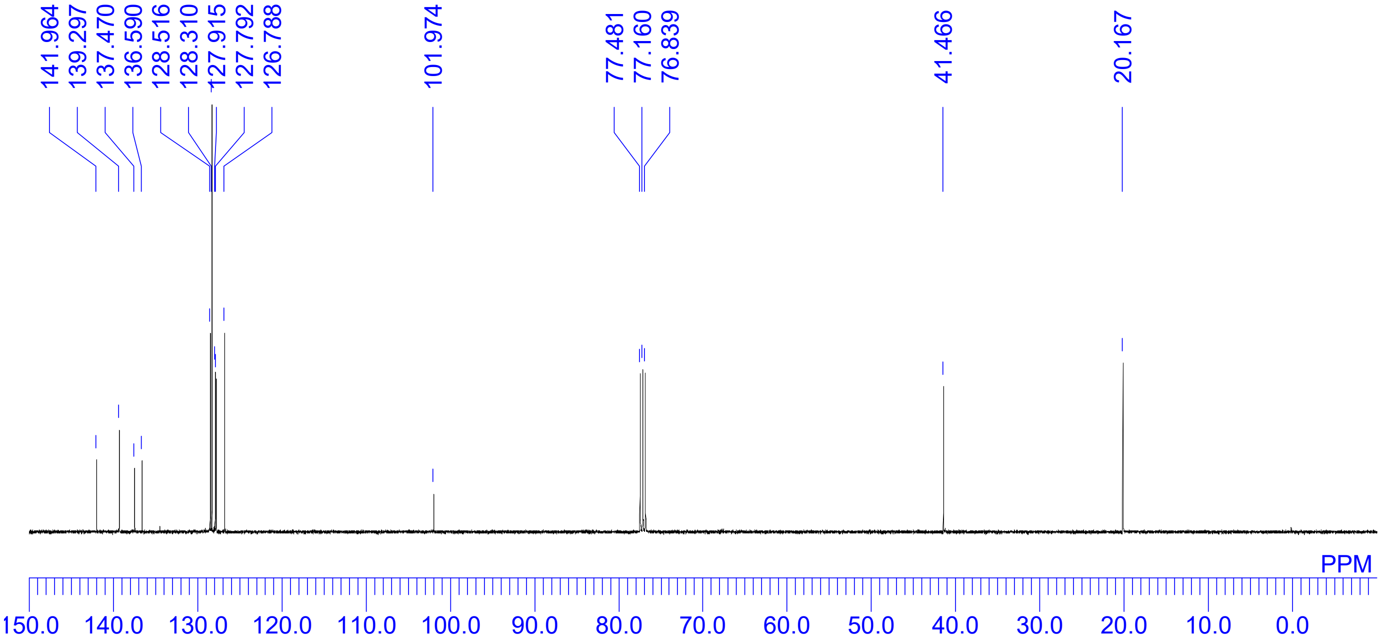
(S15) 2-(2-iodobenzyl)-1,3-dimethylbenzene



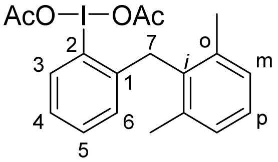
^{1}H NMR (400 MHz, CDCl$_3$)



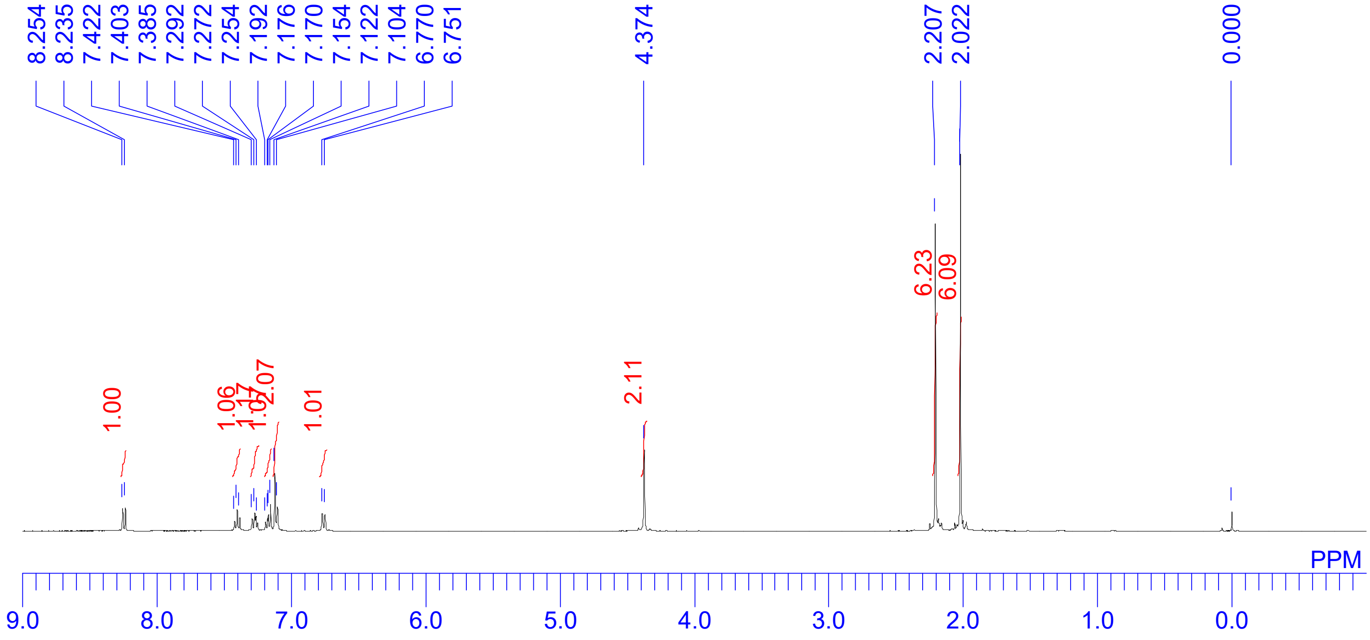
^{13}C NMR (100 MHz, CDCl$_3$)



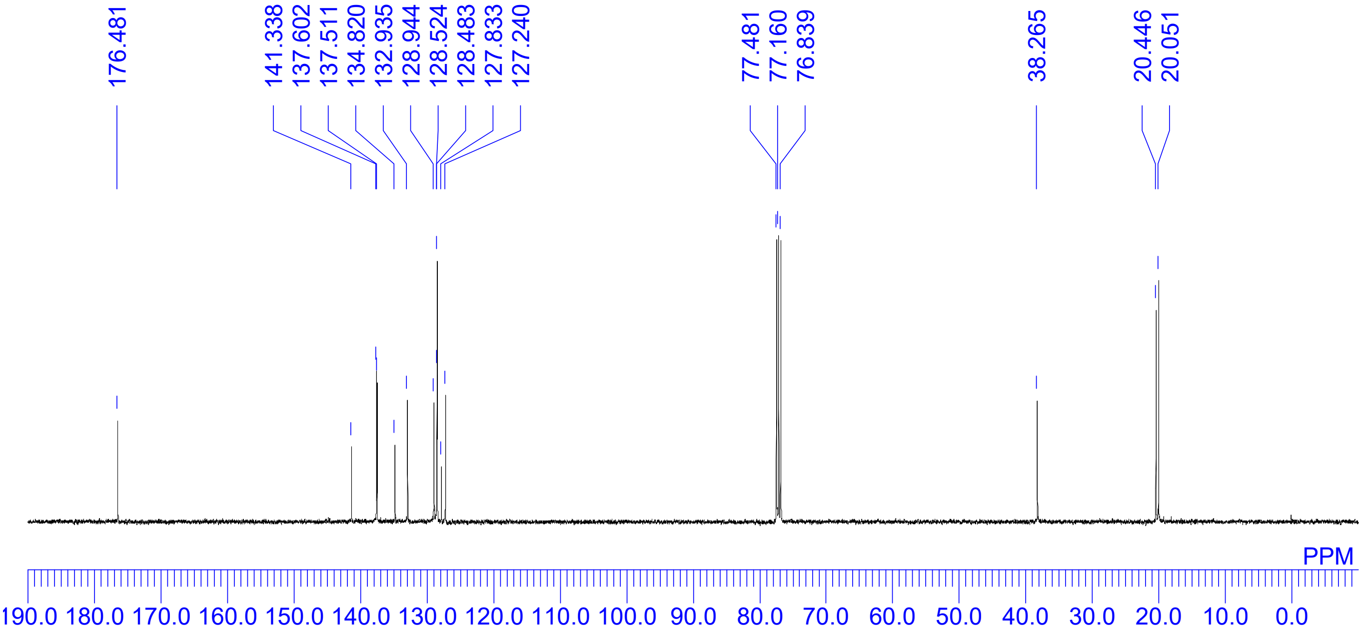
(1h) (2-(2,6-dimethylbenzyl)phenyl)-λ^3-iodanediyl diacetate



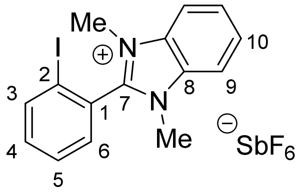
^{1}H NMR (400 MHz, CDCl$_3$)



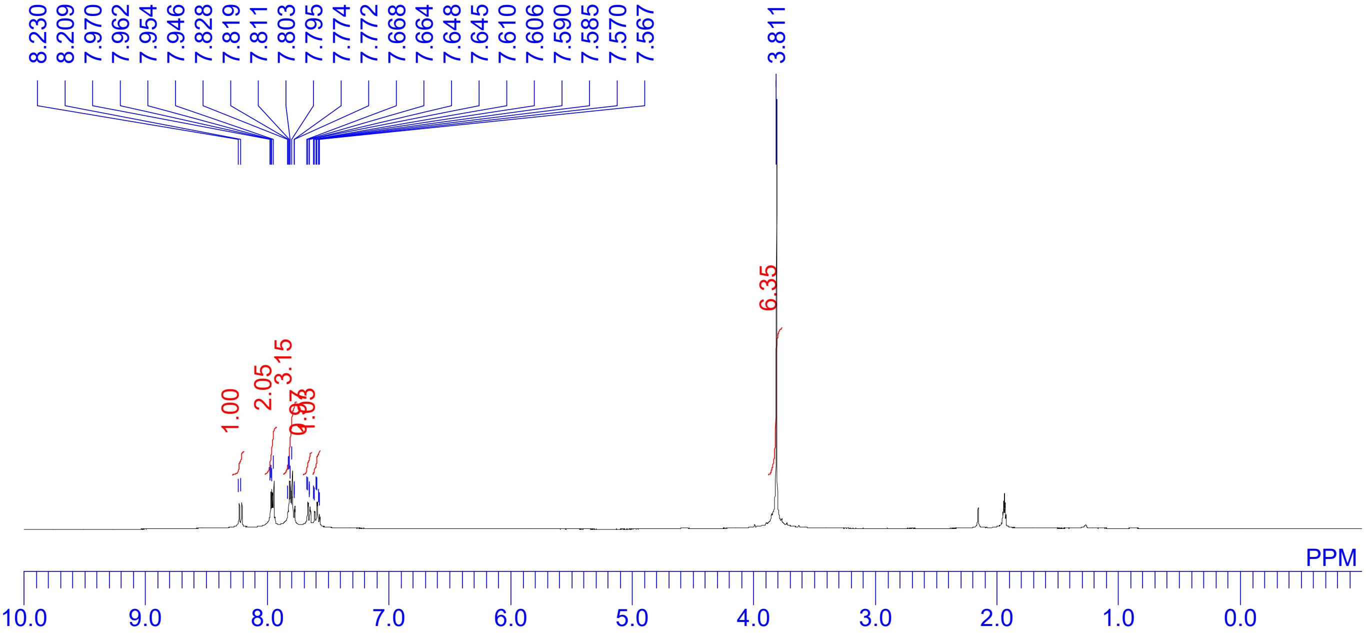
^{13}C NMR (100 MHz, CDCl$_3$)



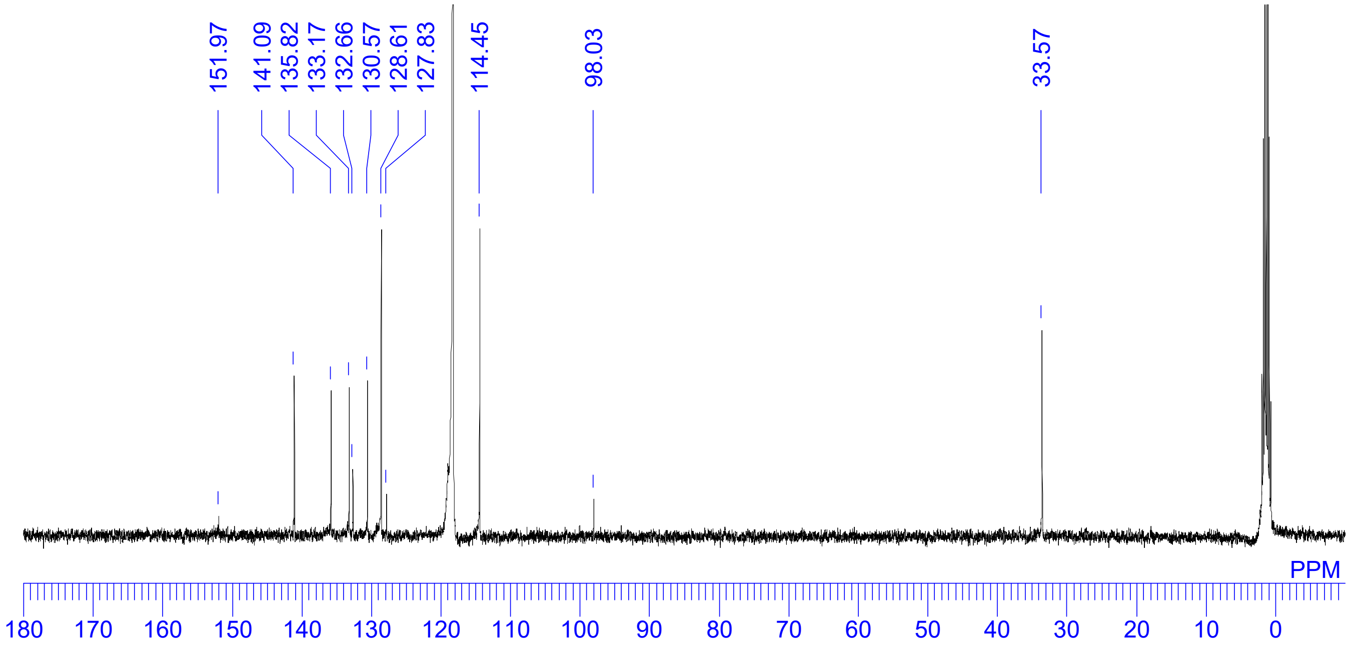
(S16) 2-(2-iodophenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium hexafluoroantimonate



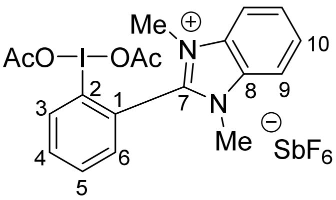
^{1}H NMR (400 MHz, CD$_3$CN)



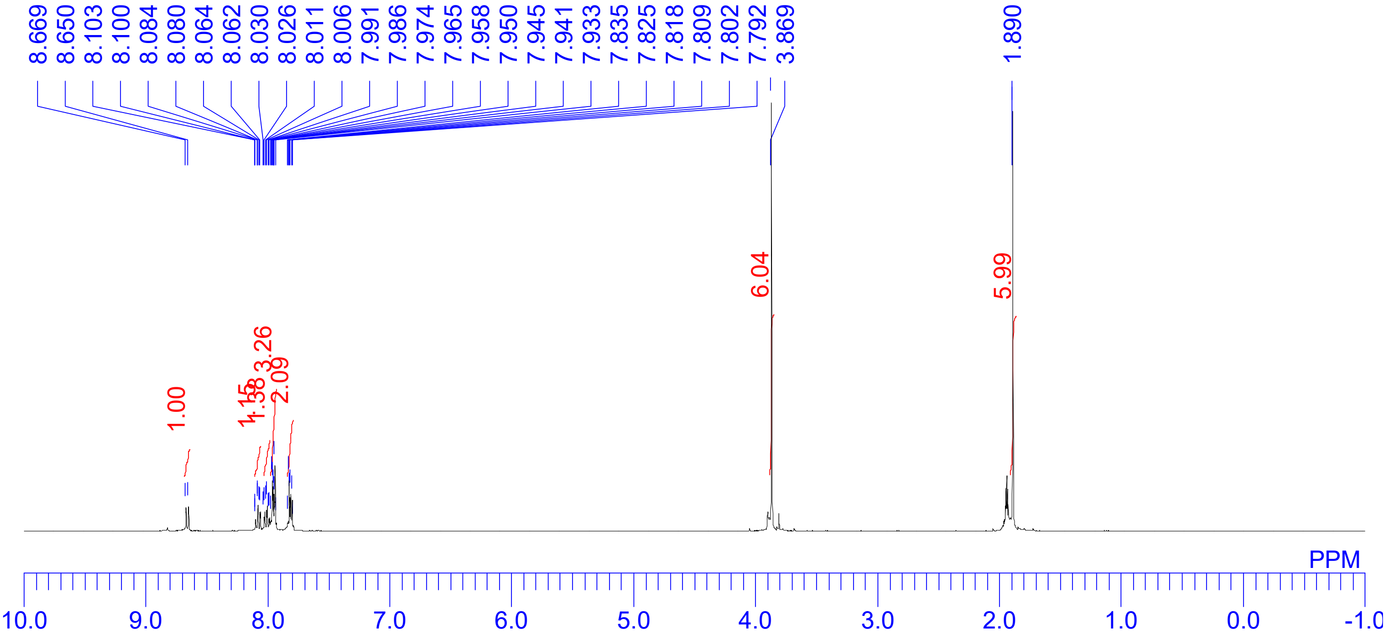
^{13}C NMR (100 MHz, CD$_3$CN)



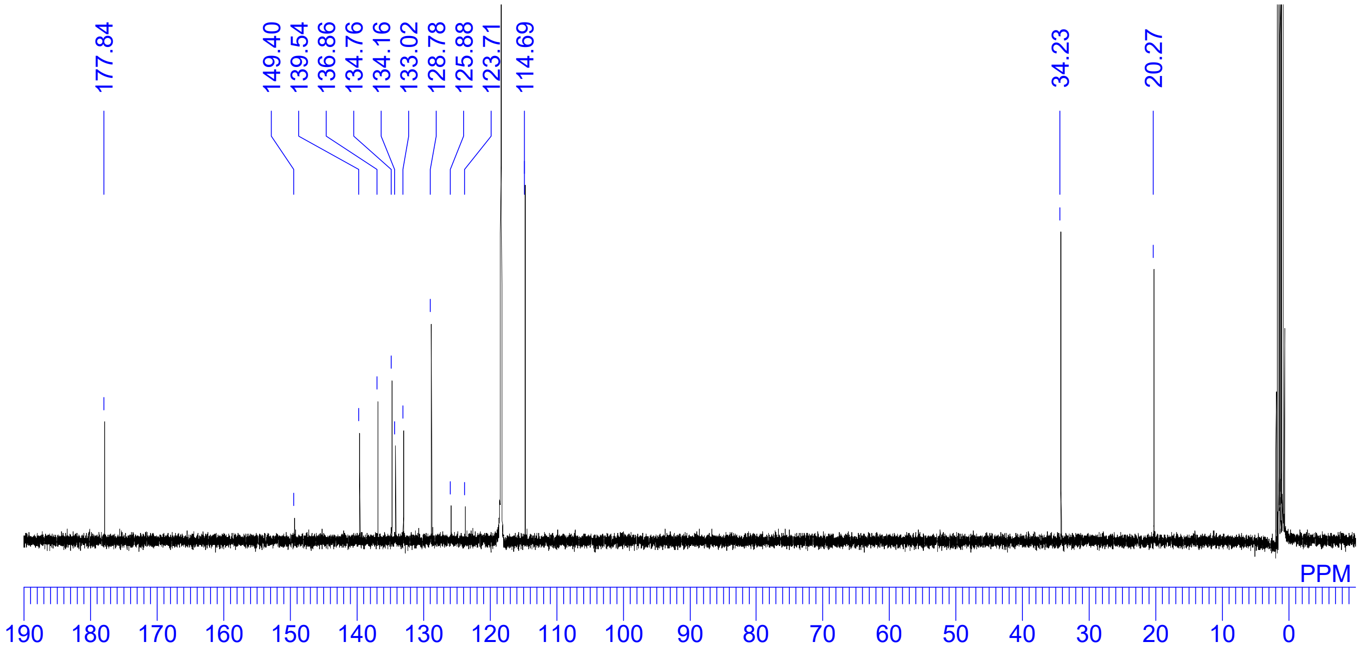
(1k) 2-(2-(diacetoxy-λ^3-iodaneyl)phenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium hexafluoroantimonate



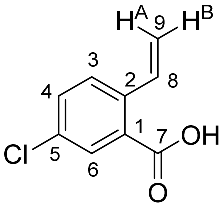
^{1}H NMR (400 MHz, CD$_3$CN)



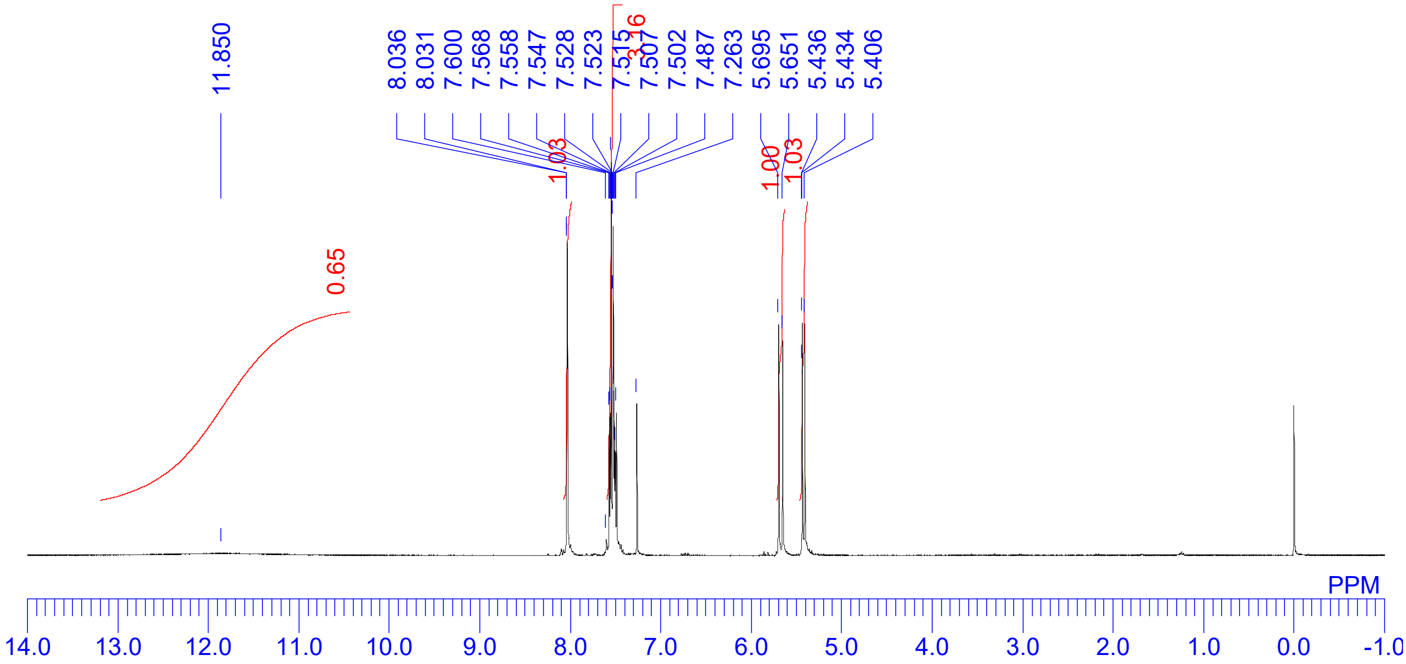
^{13}C NMR (100 MHz, CD$_3$CN)



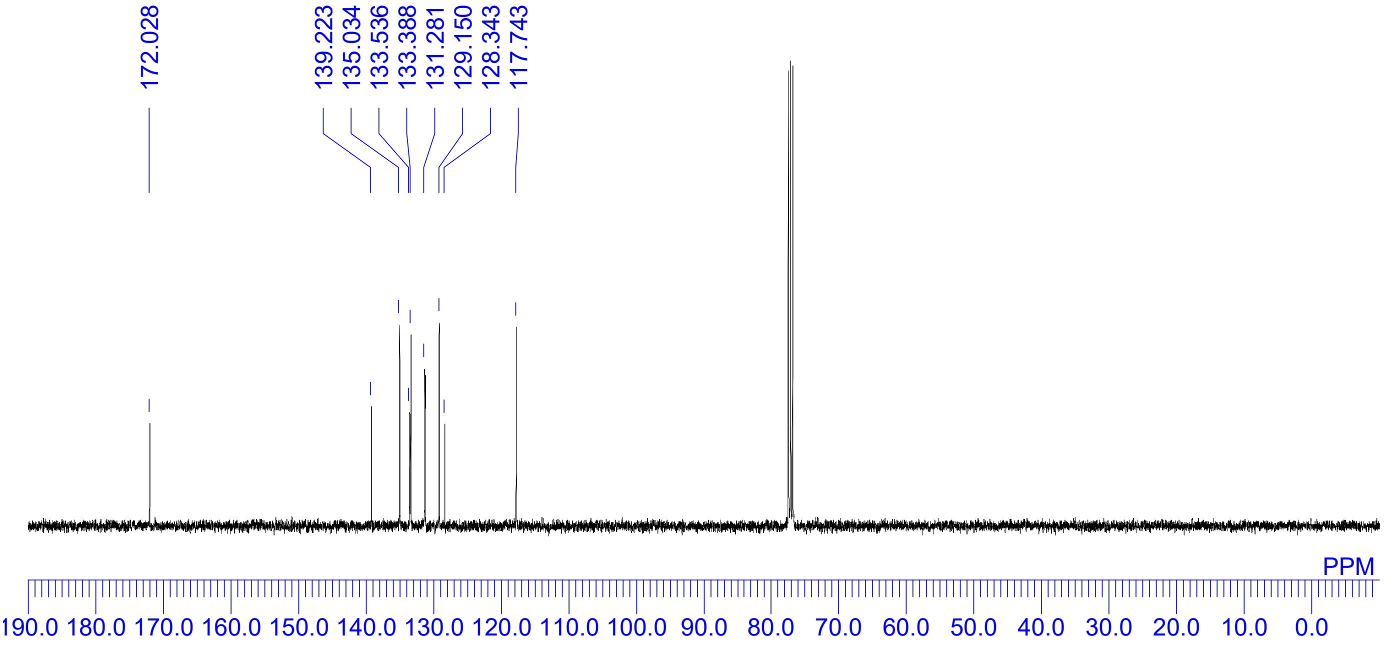
(2a) 5-chrolo-2-vinylbenzoic acid



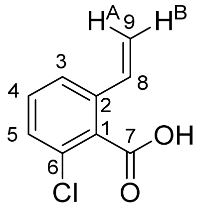
^{1}H NMR (400 MHz, CDCl$_3$)



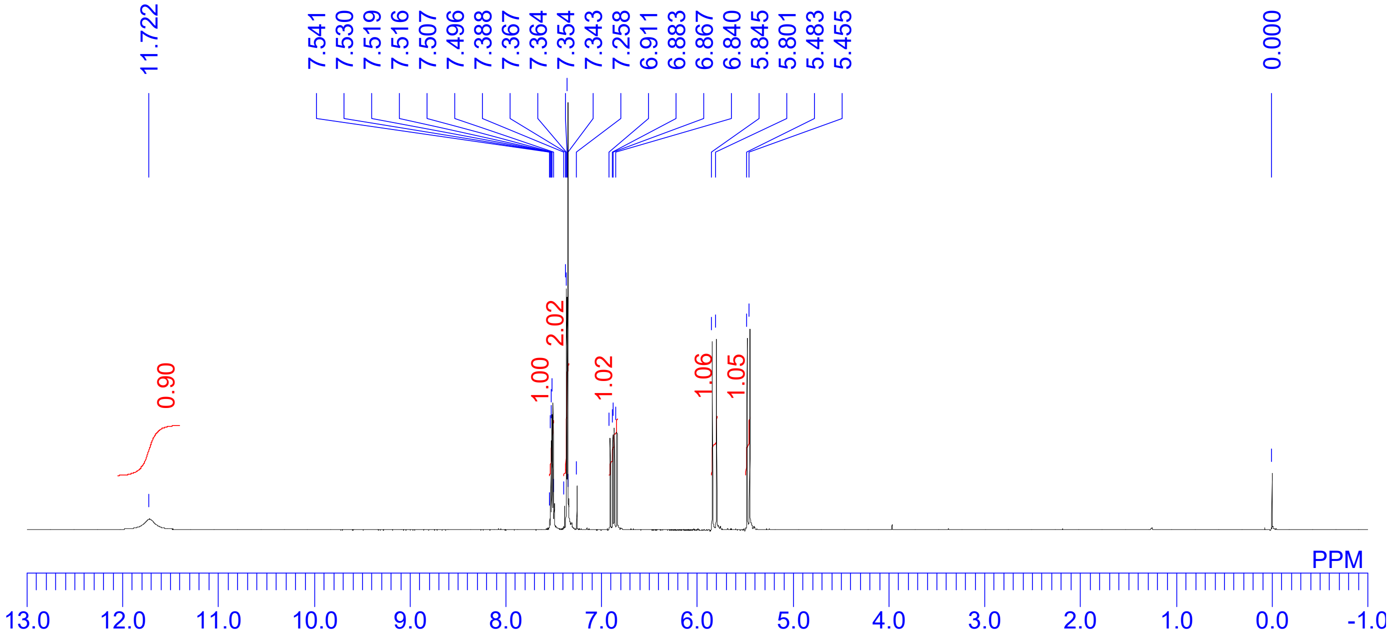
^{13}C NMR (100 MHz, CDCl$_3$)



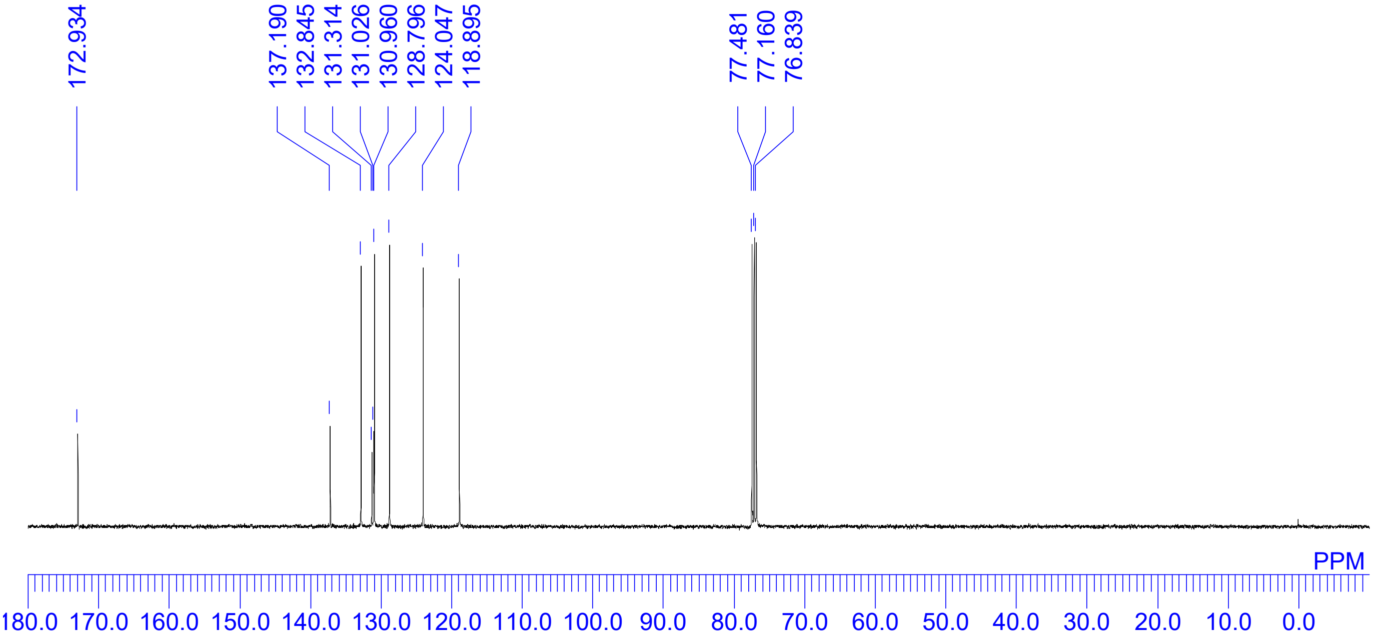
(2b) 6-chloro-2-vinylbenzoic acid



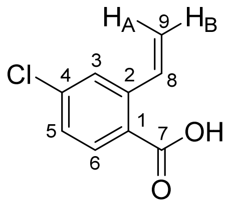
^{1}H NMR (400 MHz, $CDCl_3$)



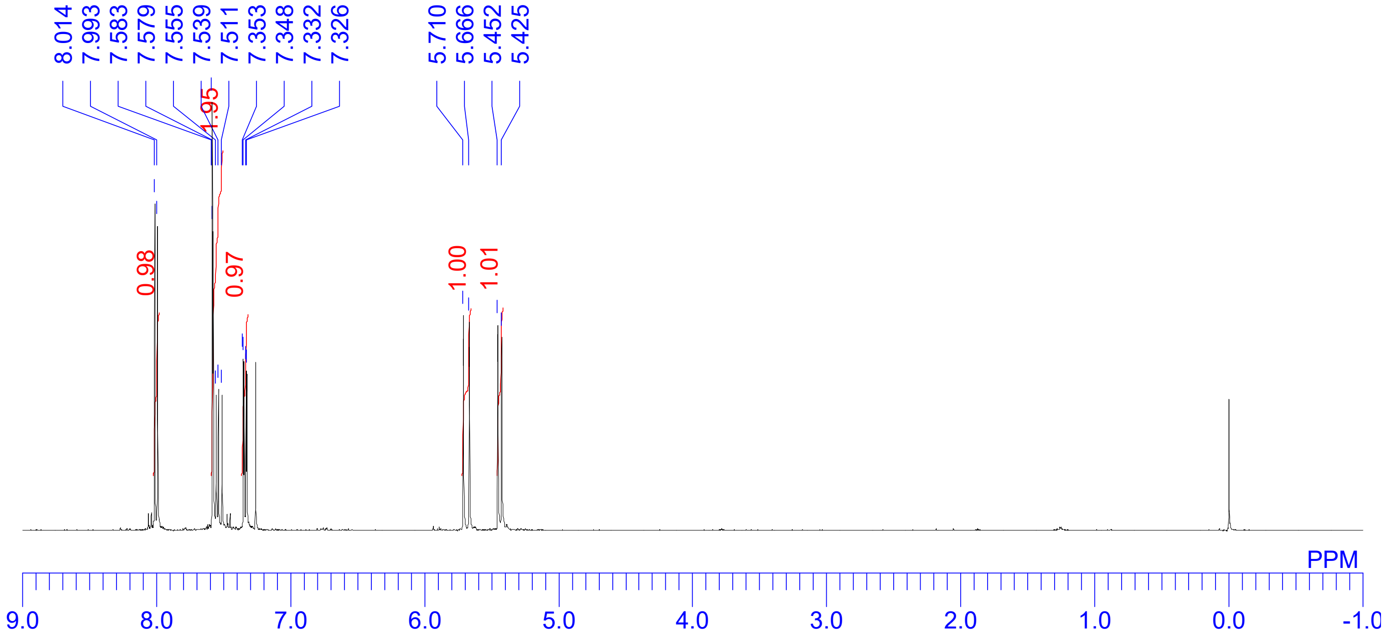
^{13}C NMR (100 MHz, $CDCl_3$)



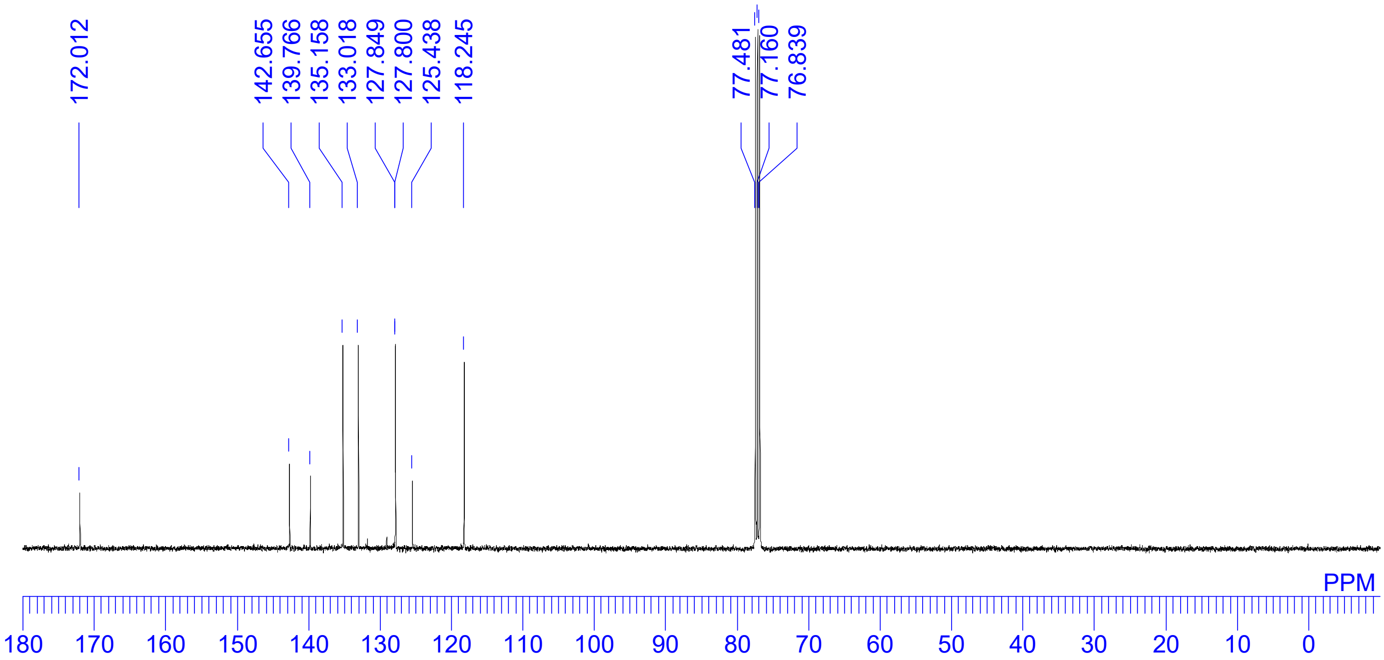
(2c) 4-chloro-2-vinylbenzoic acid



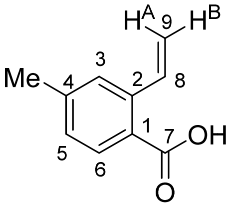
^{1}H NMR (400 MHz, CDCl$_3$)



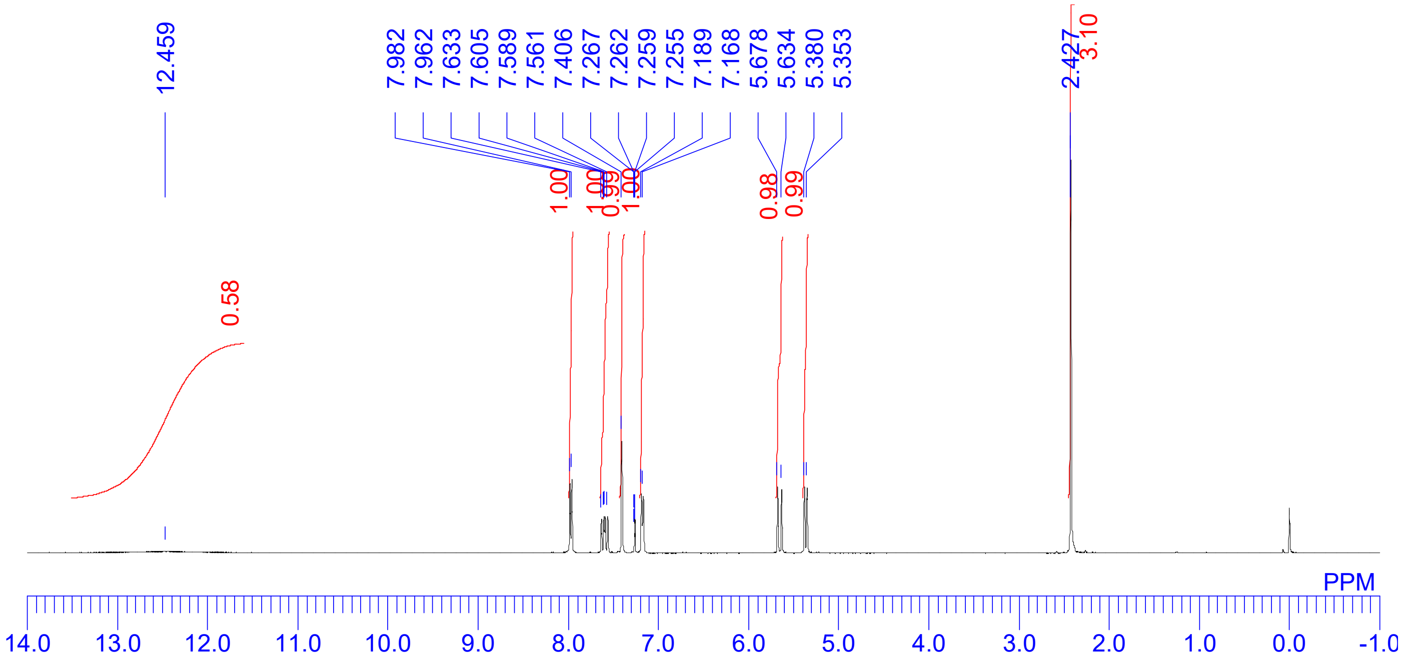
^{13}C NMR (100 MHz, CDCl$_3$)



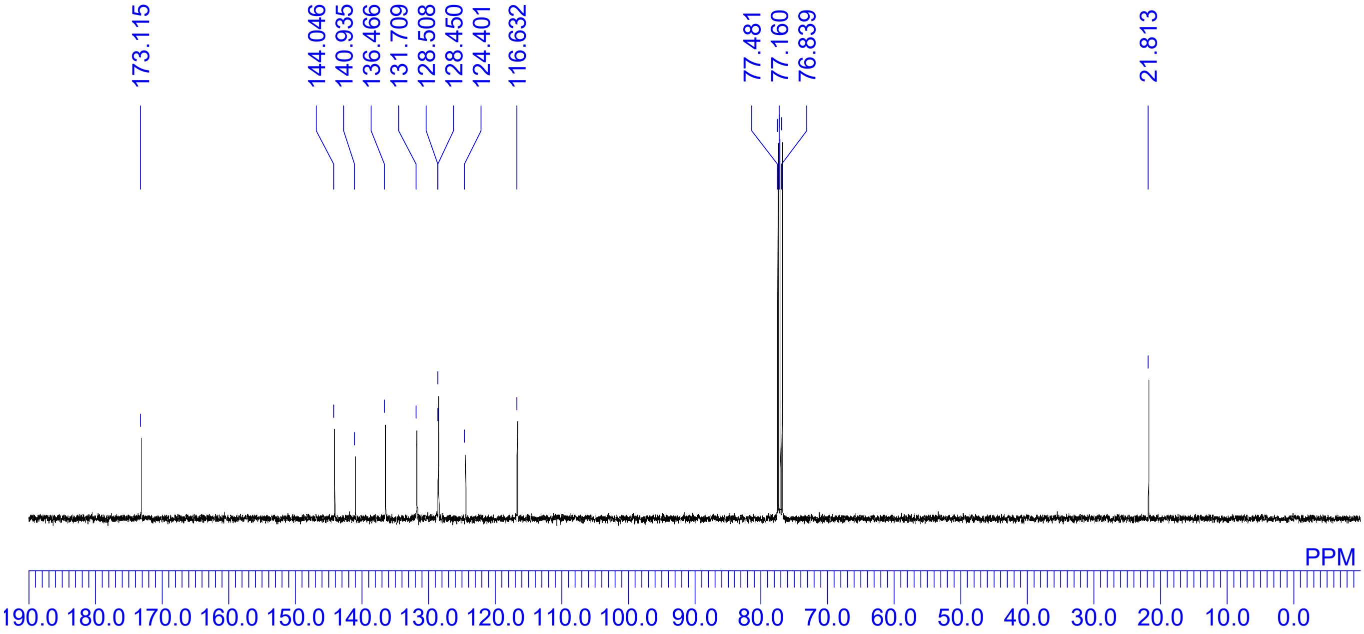
(2f) 4-methyl-2-vinylbenzoic acid



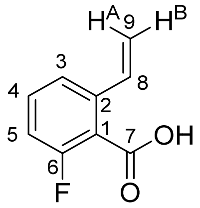
^{1}H NMR (400 MHz, CDCl$_3$)



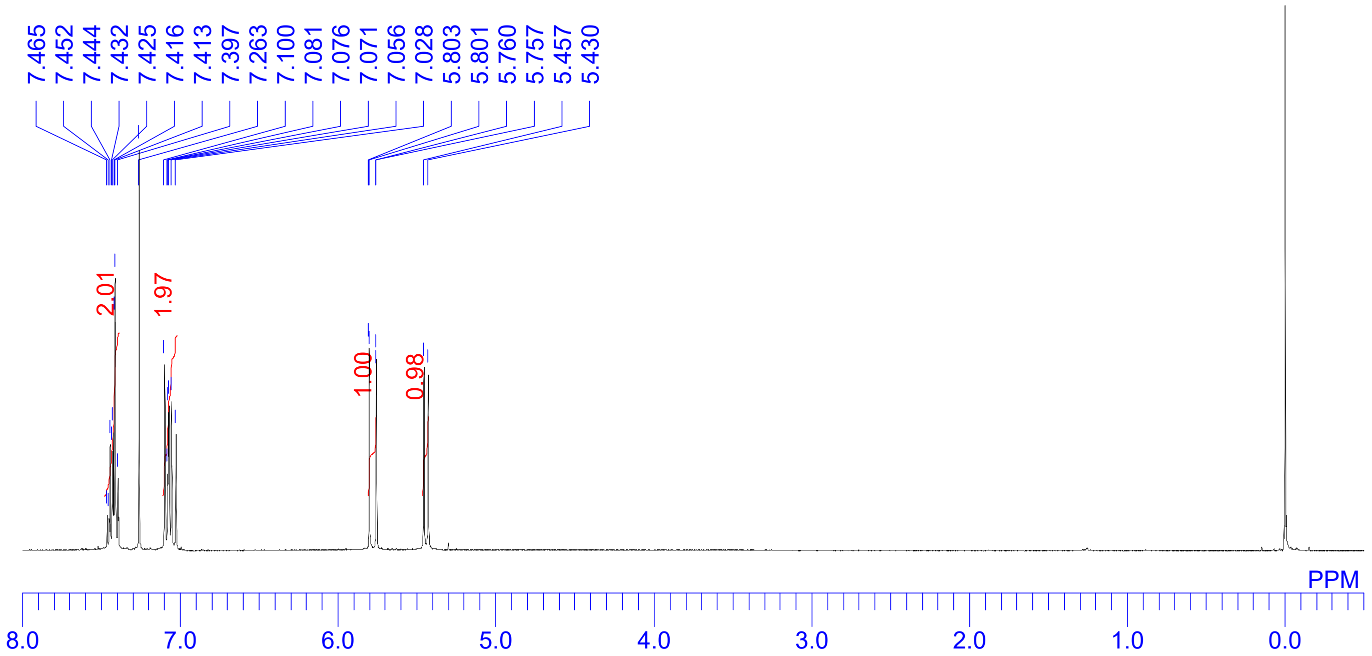
^{13}C NMR (100 MHz, CDCl$_3$)



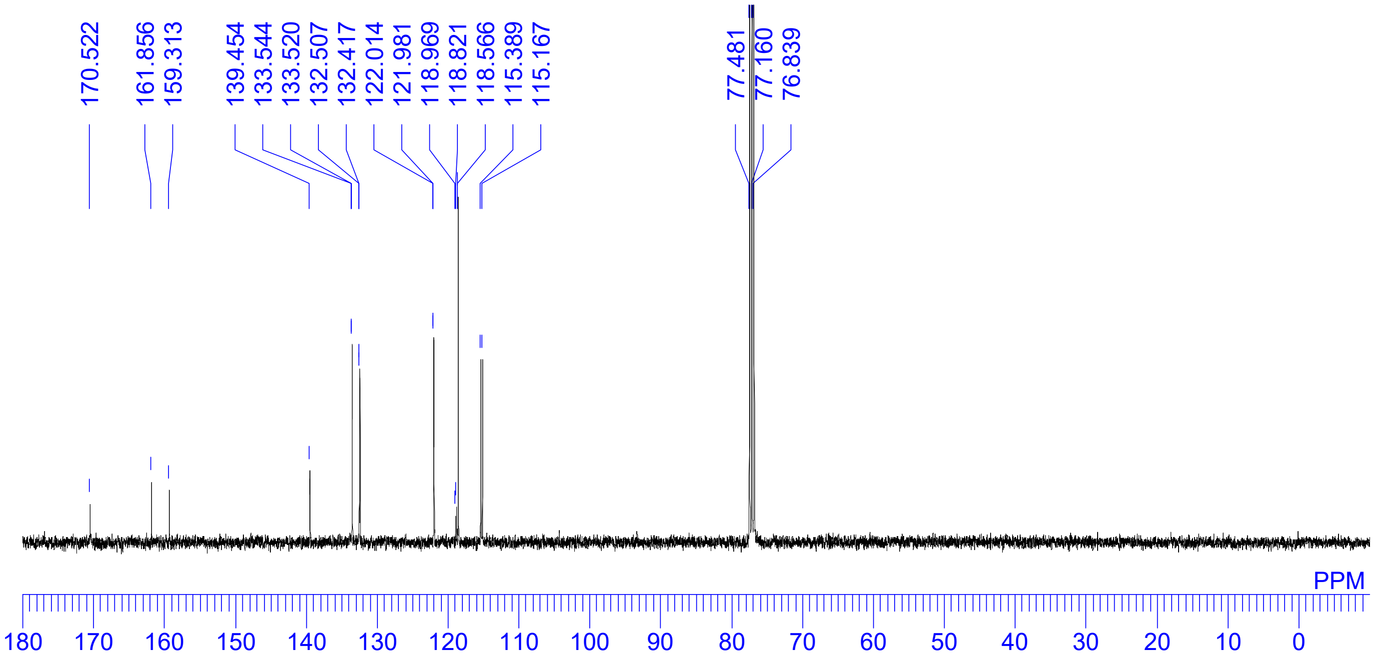
(2g) 6-fluoro-2-vinylbenzoic acid



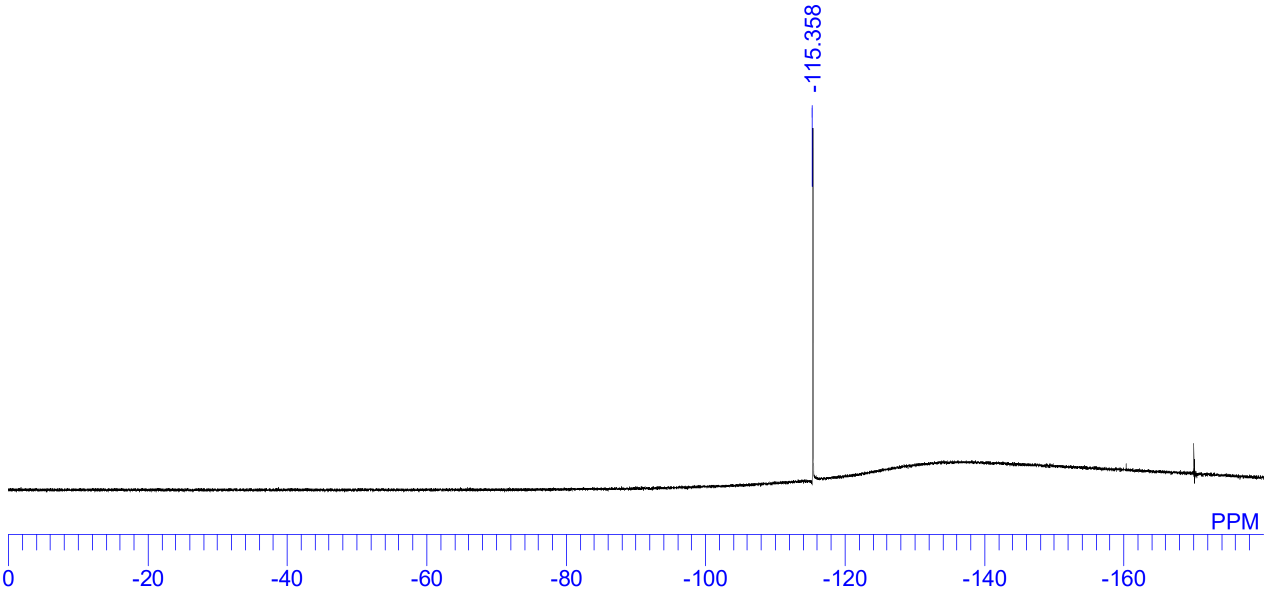
^{1}H NMR (400 MHz, $CDCl_3$)



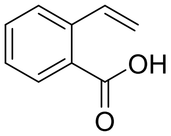
^{13}C NMR (100 MHz, $CDCl_3$)



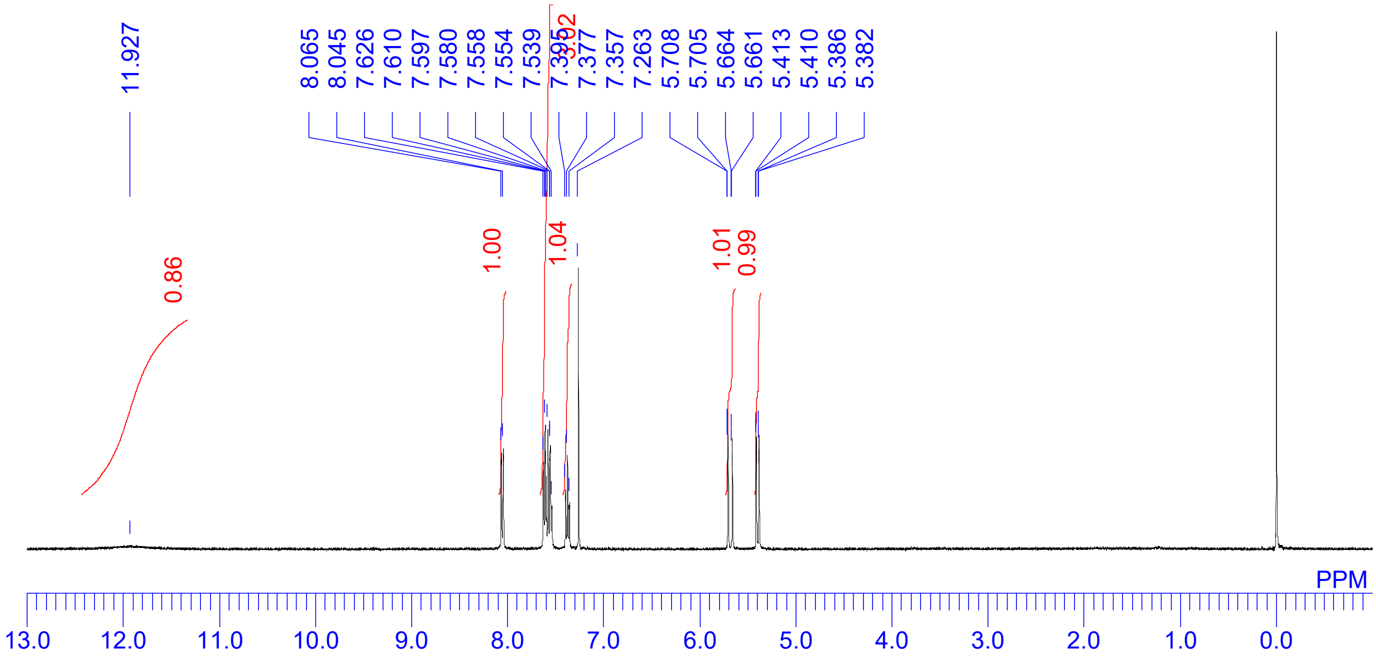
^{19}F NMR (377 MHz, $CDCl_3$, external standard:TFA in D_2O)



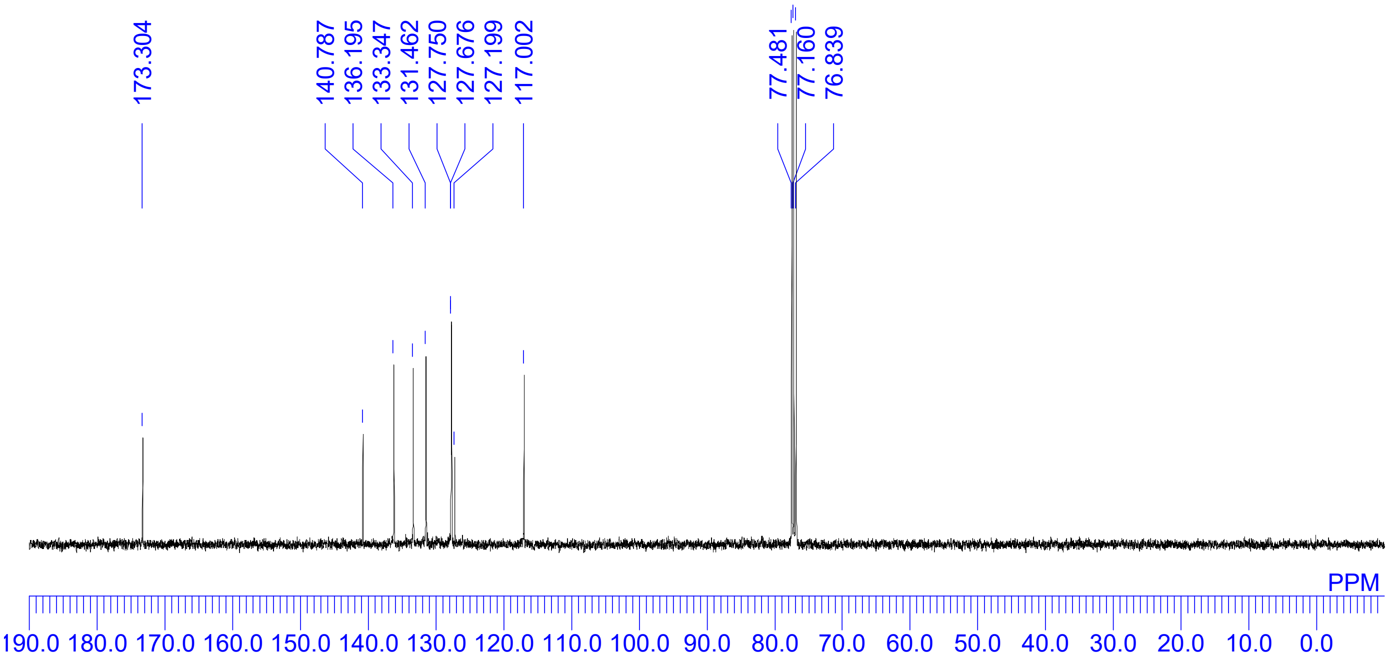
(2h) 2-vinylbenzoic acid



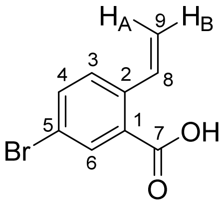
^{1}H NMR (400 MHz, CDCl$_3$)



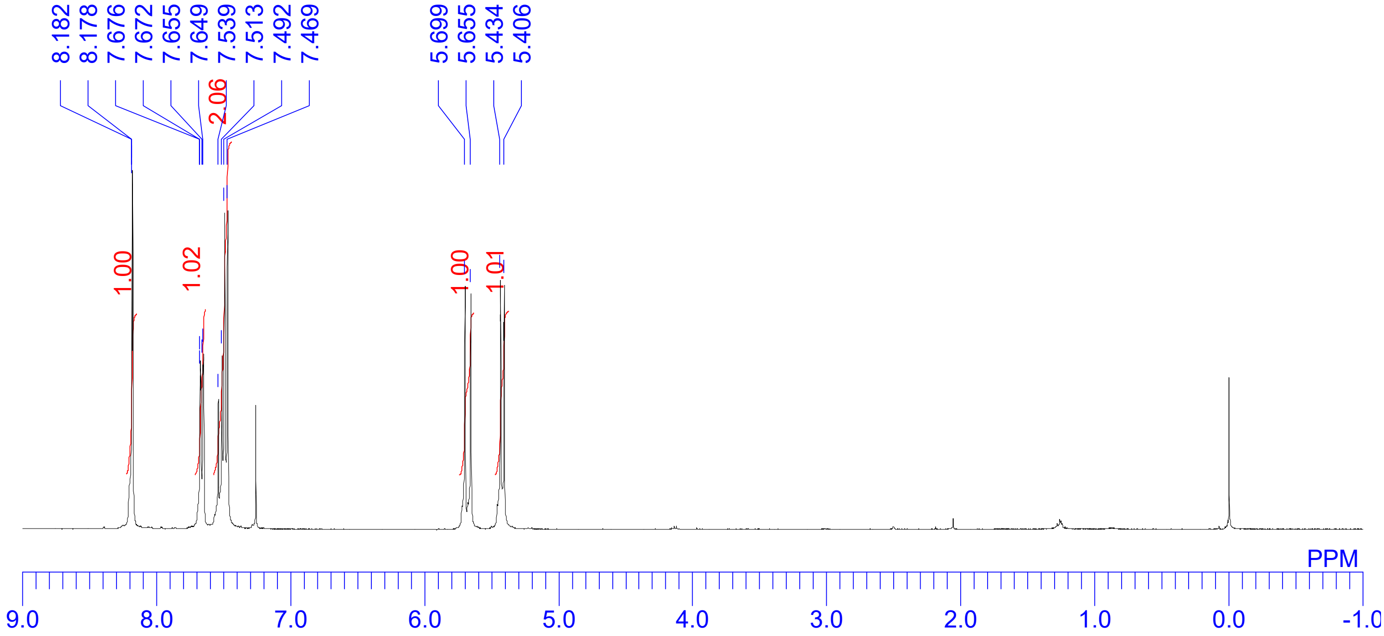
^{13}C NMR (100 MHz, CDCl$_3$)



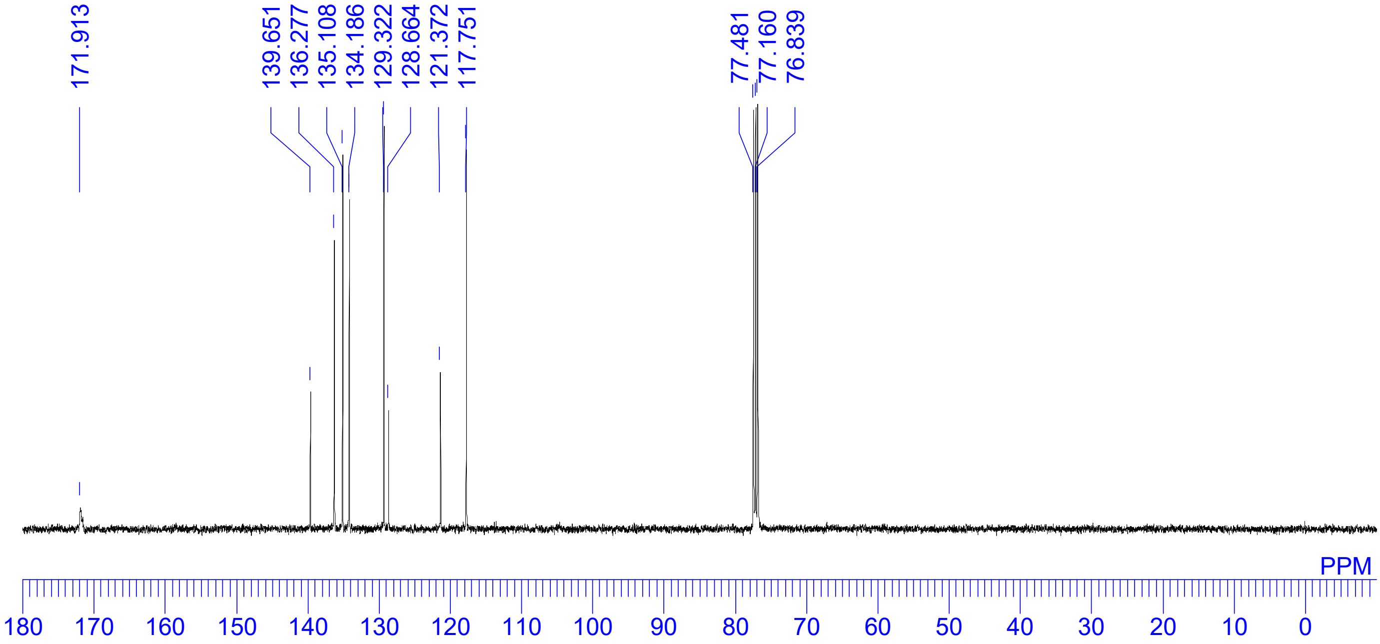
(2j) 5-bromo-2-vinylbenzoic acid



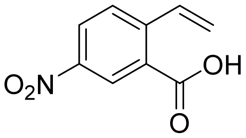
^{1}H NMR (400 MHz, CDCl$_3$)



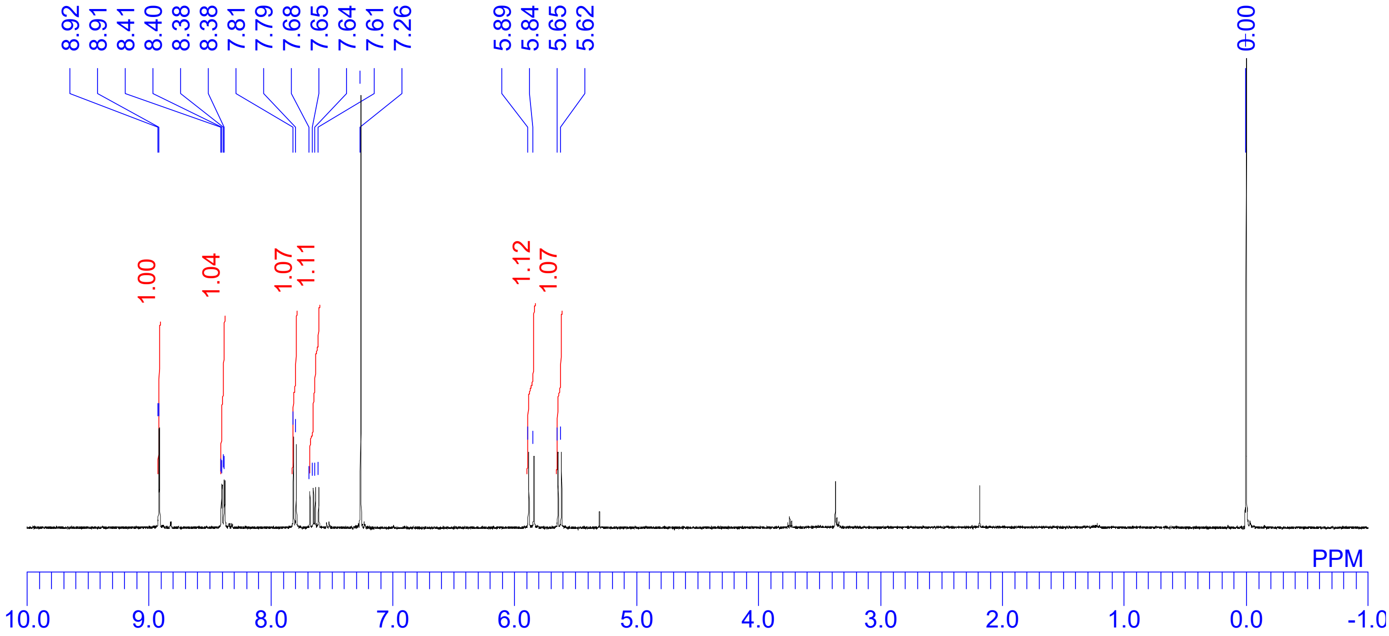
^{13}C NMR (100 MHz, CDCl$_3$)



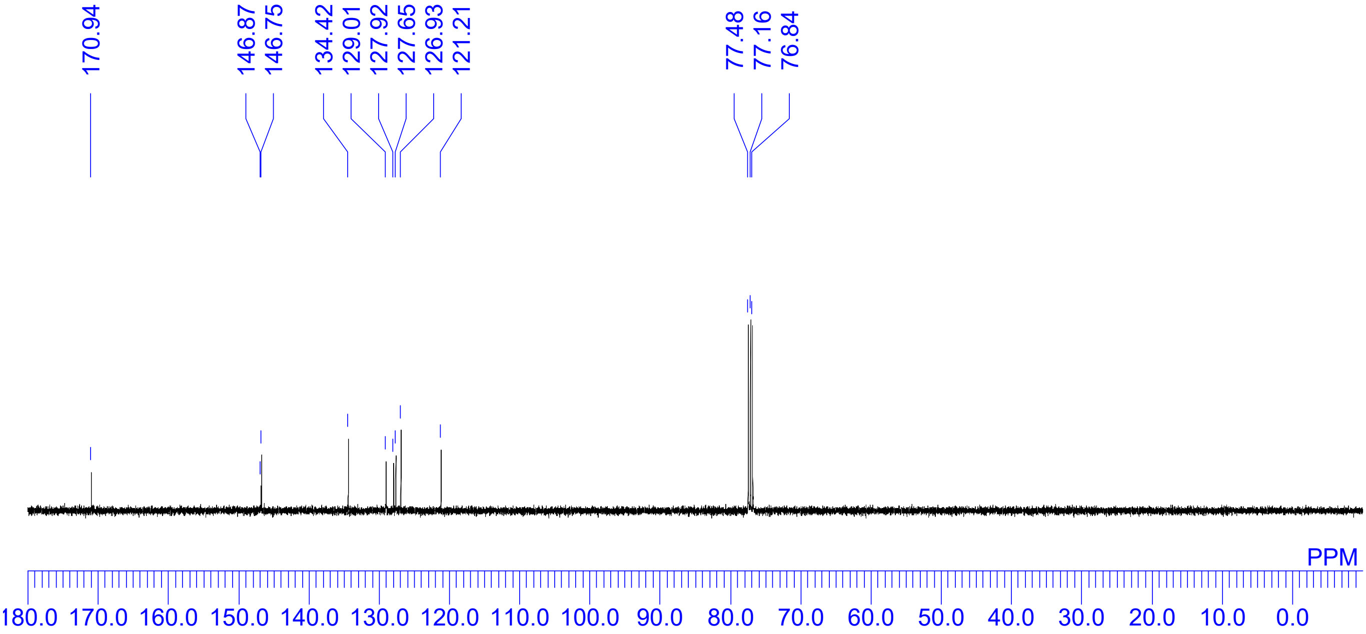
(2k) 5-nitro-2-vinylbenzoic acid



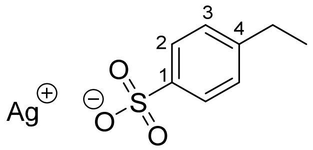
^{1}H NMR (400 MHz, $CDCl_3$)



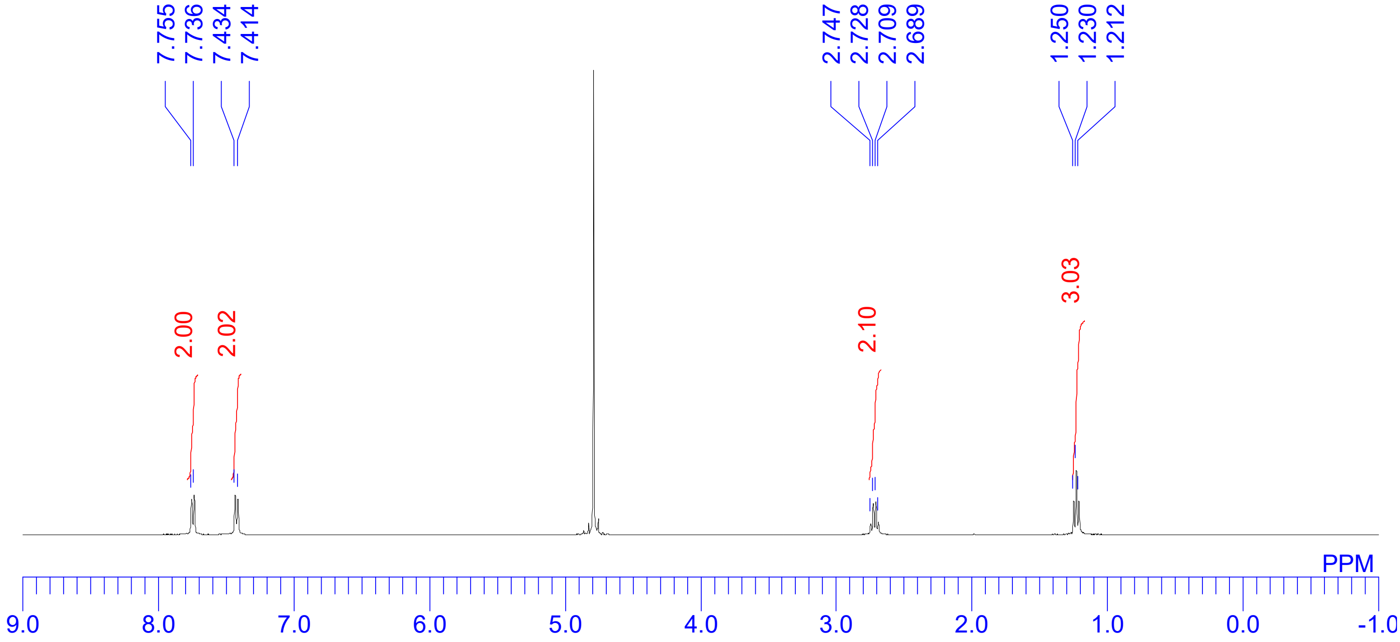
^{13}C NMR (100 MHz, $CDCl_3$)



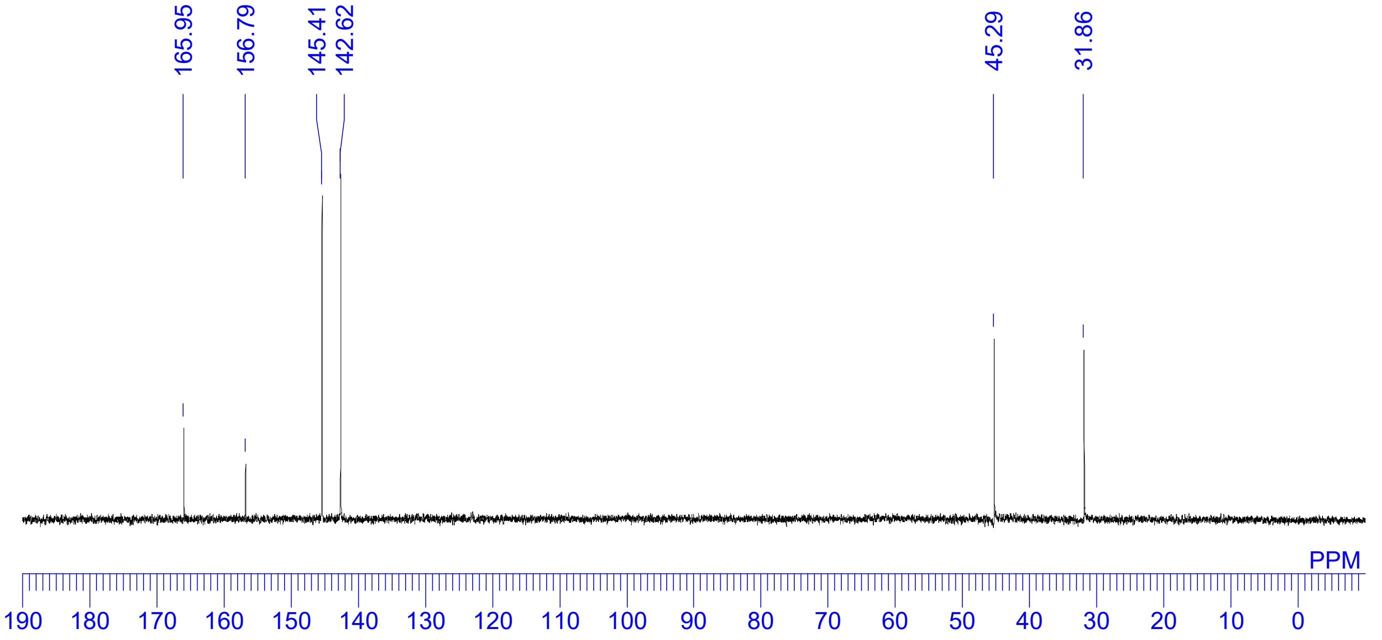
silver 4-ethylbenzenesulfonate



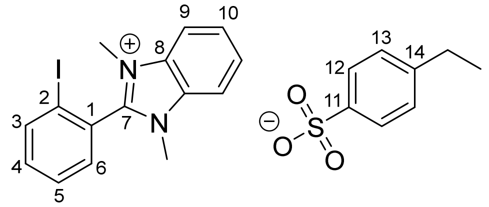
^{1}H NMR (400 MHz, D_2O)



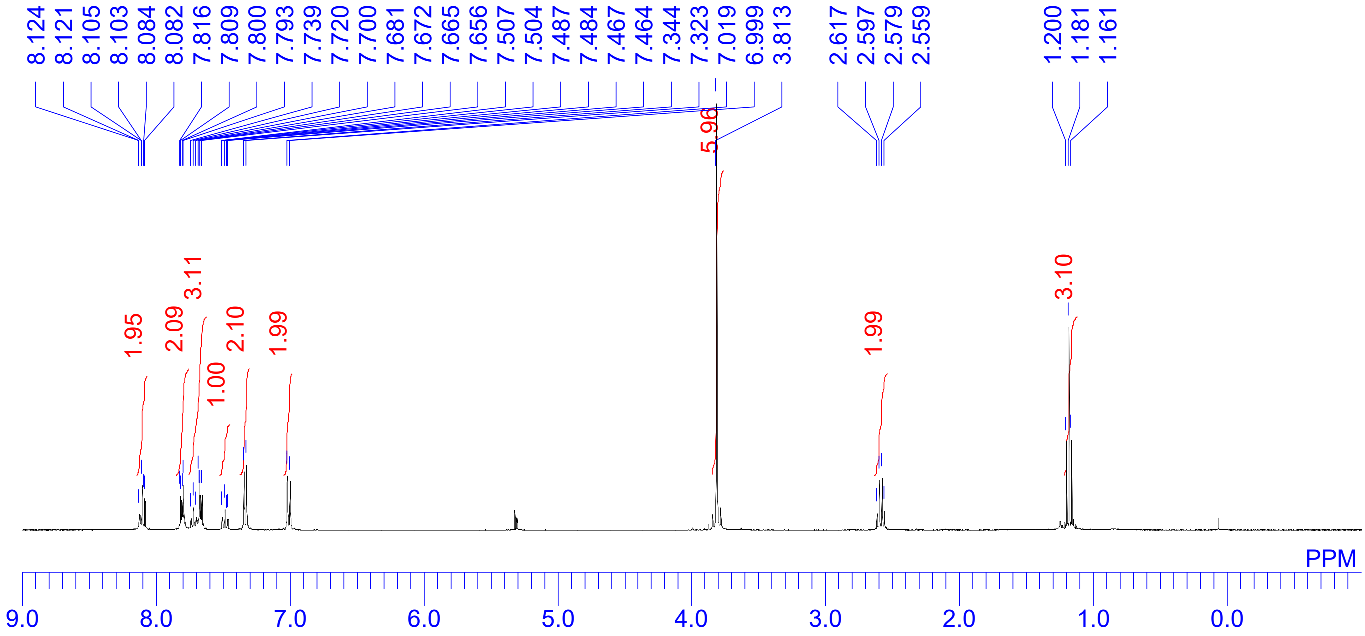
^{13}C NMR (400 MHz, D_2O)



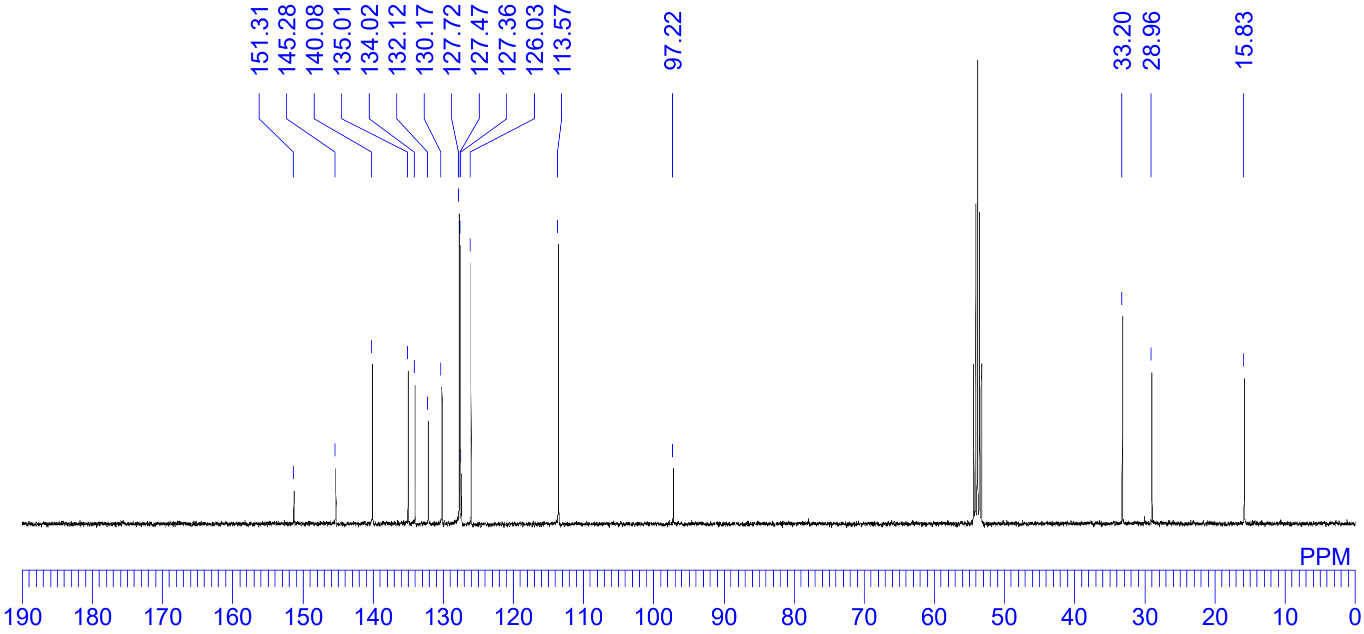
2-(2-iodophenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium 4-ethylbenzenesulfonate



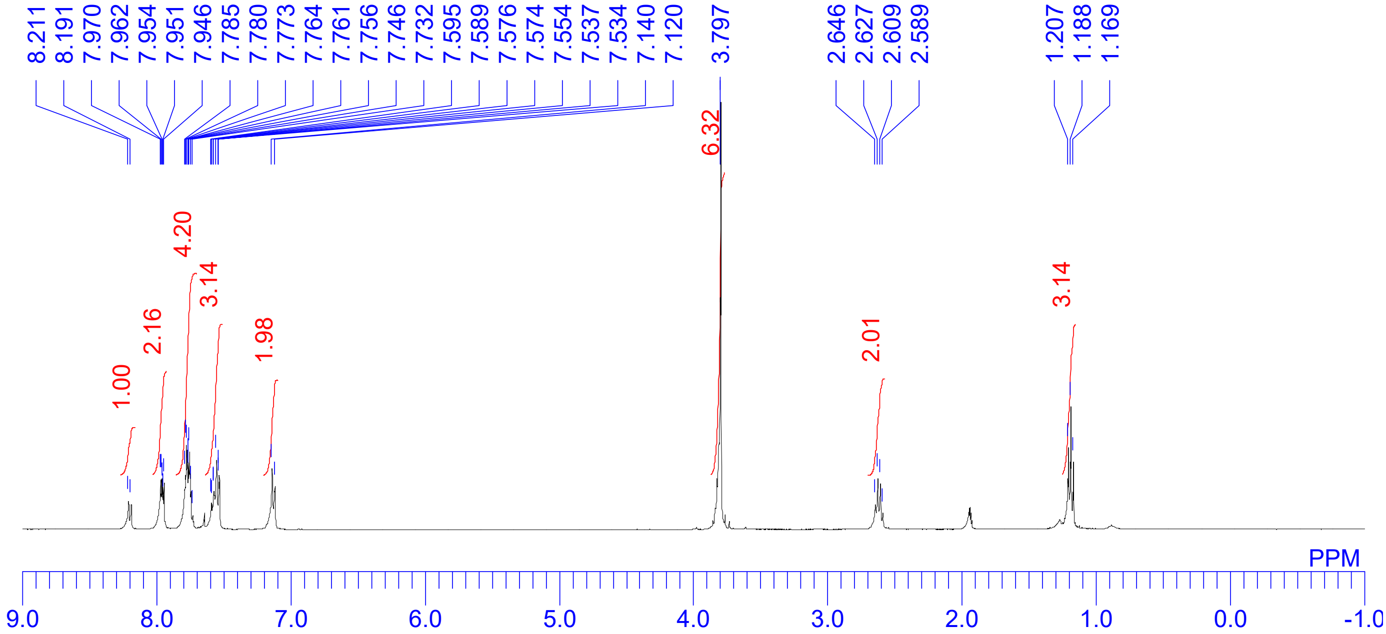
^{1}H NMR (400 MHz, CD$_2$Cl$_2$)



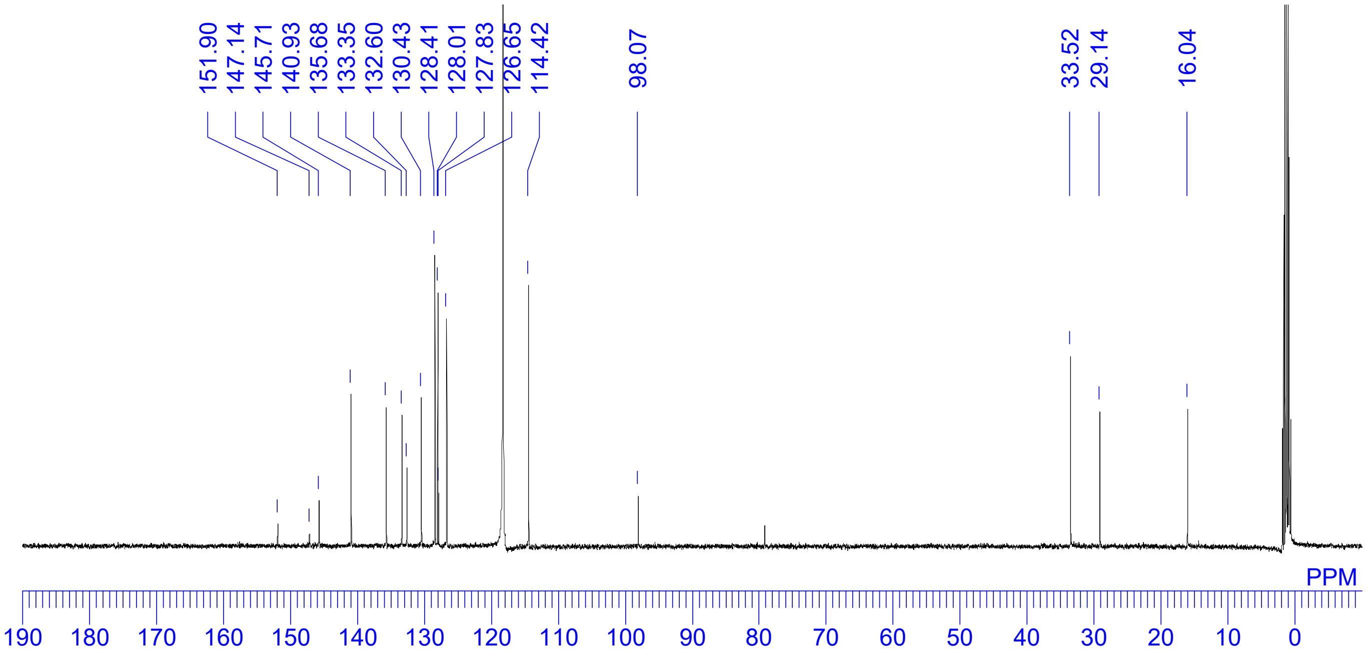
^{13}C NMR (100 MHz, CD$_2$Cl$_2$)



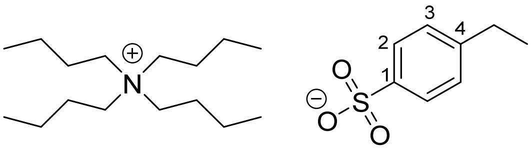
^{1}H NMR (400 MHz, CD$_3$CN)



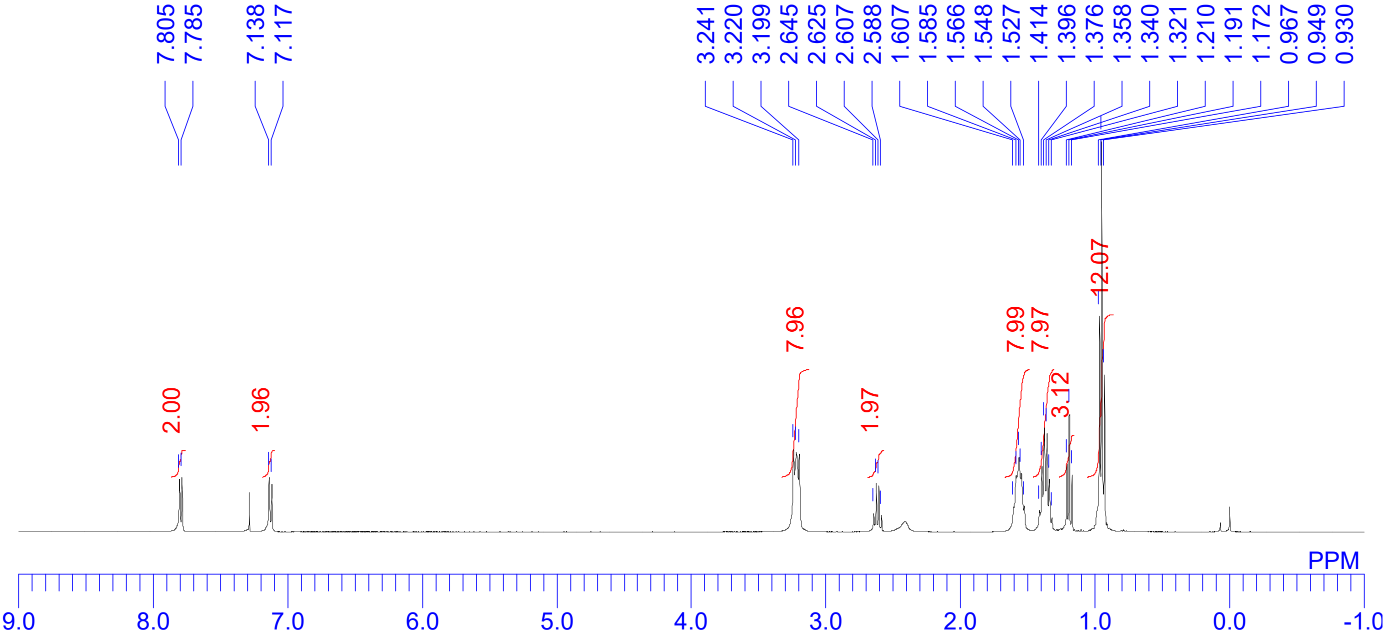
^{13}C NMR (100 MHz, CD$_3$CN)



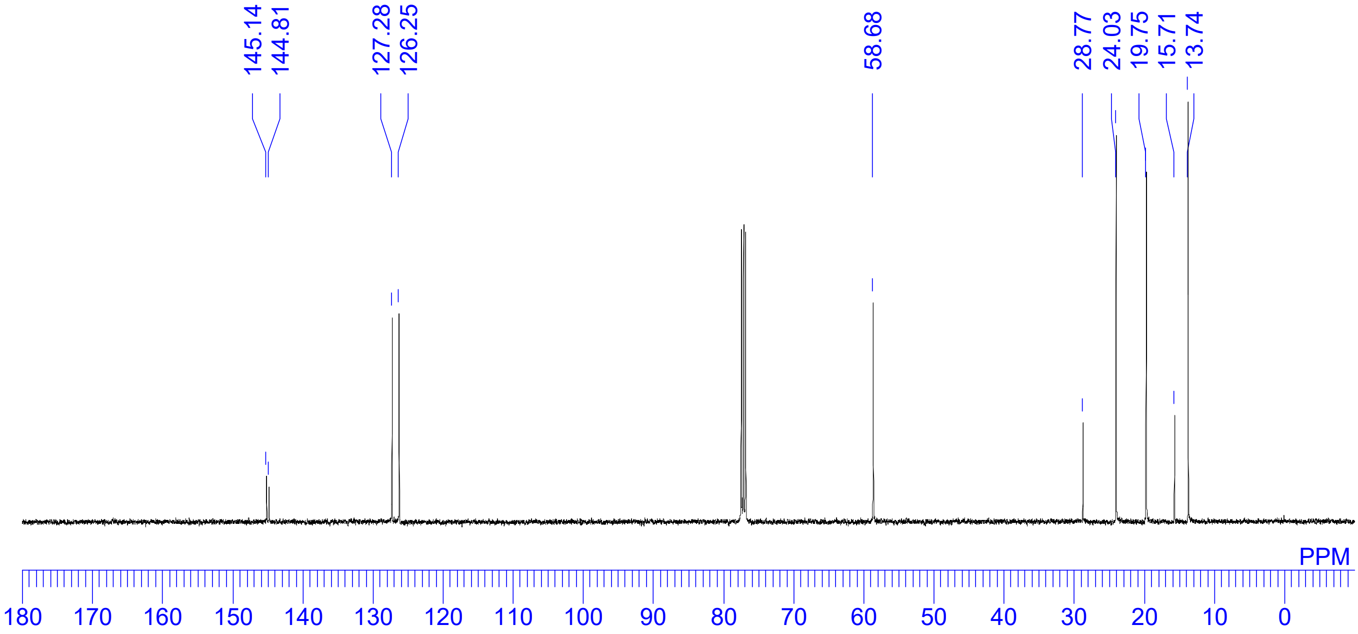
tetrabutylammonium 4-ethylbenzenesulfonate



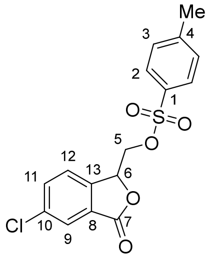
^{1}H NMR (400 MHz, CDCl$_3$)



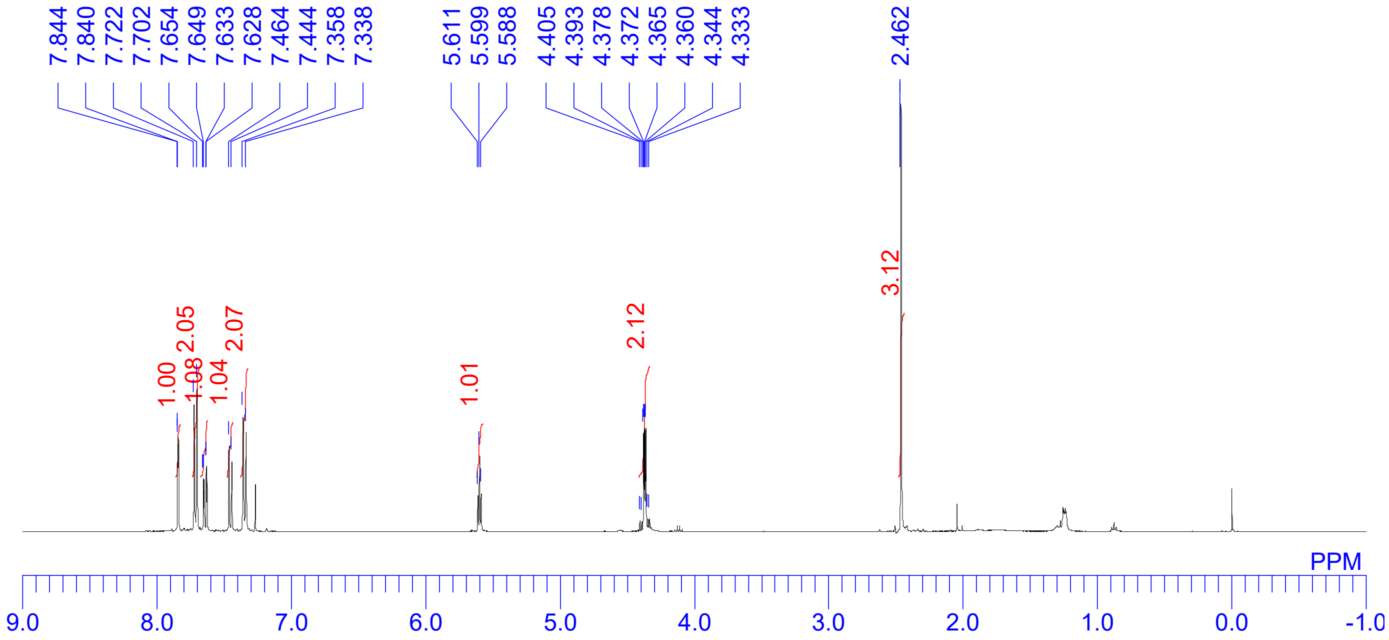
^{13}C NMR (100 MHz, CDCl$_3$)



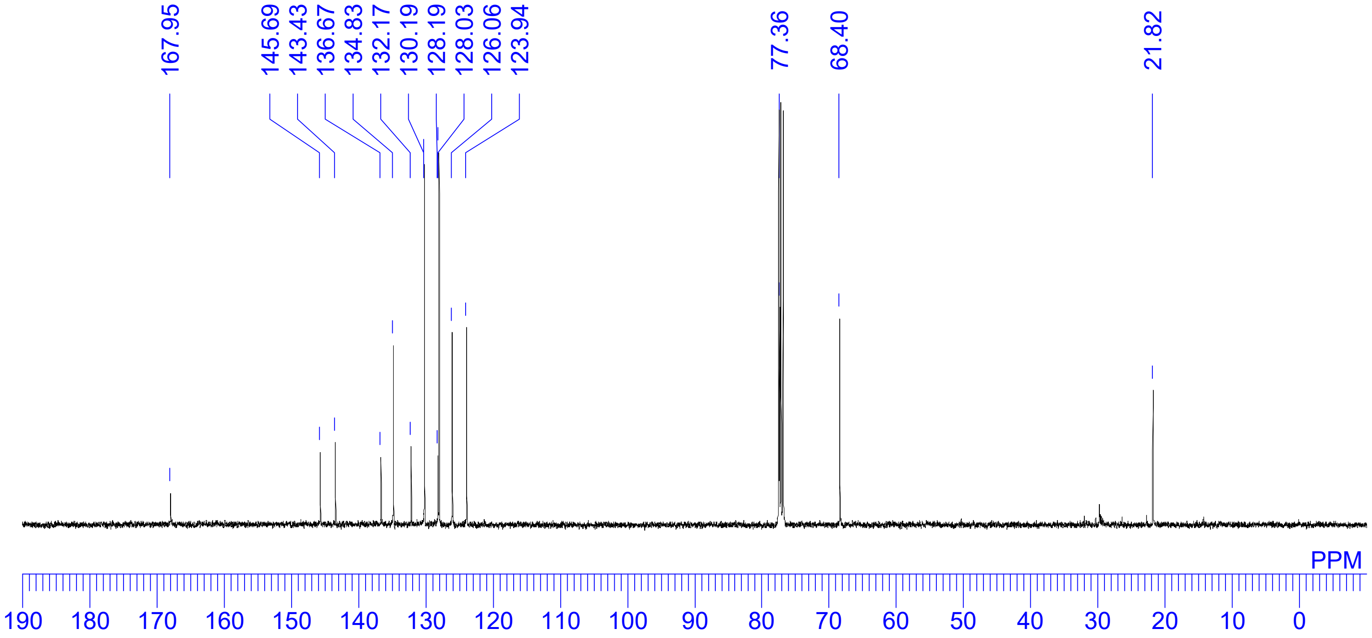
4a (from 2a and 5a)



^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (100 MHz, CDCl$_3$)



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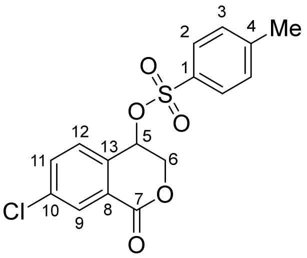
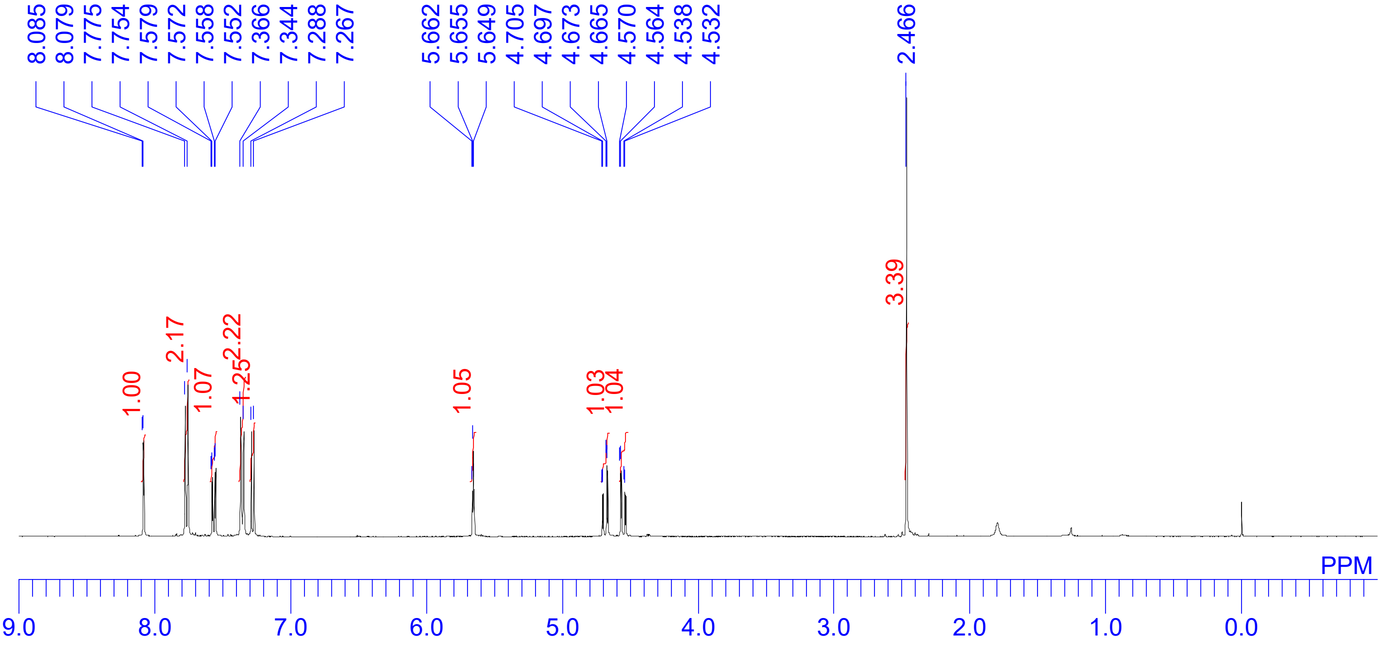
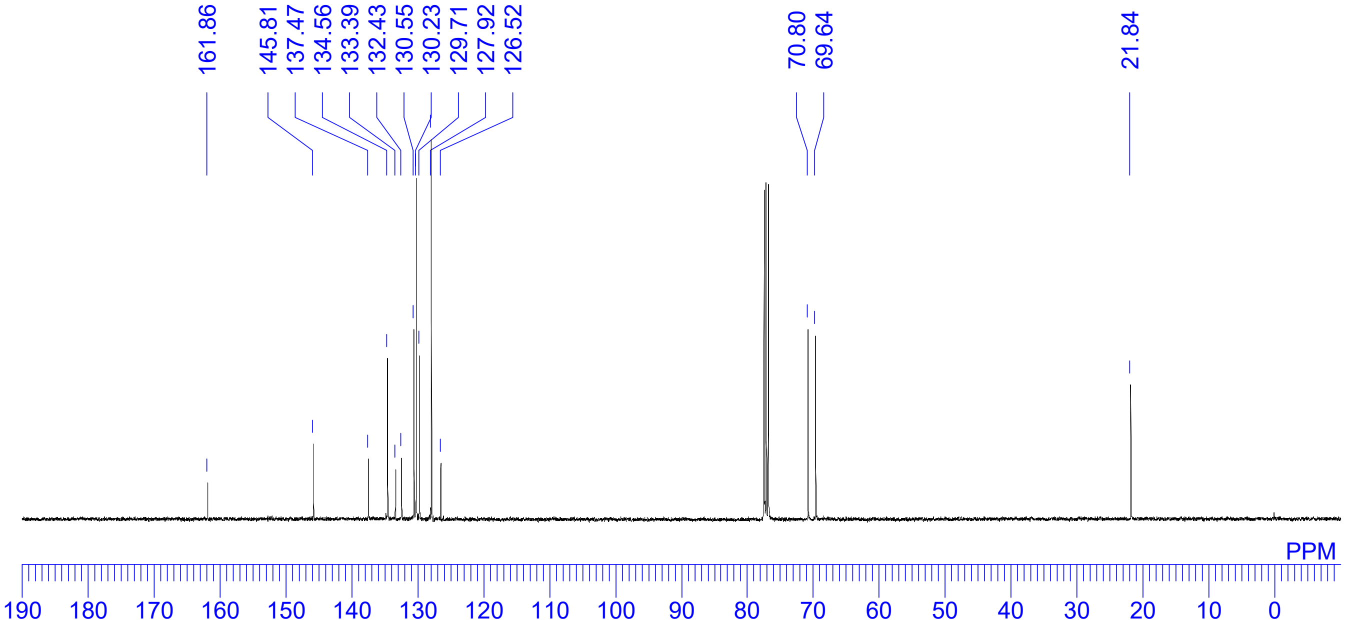


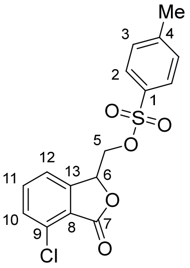
^{1}H NMR (400 MHz, CDCl$_3$)



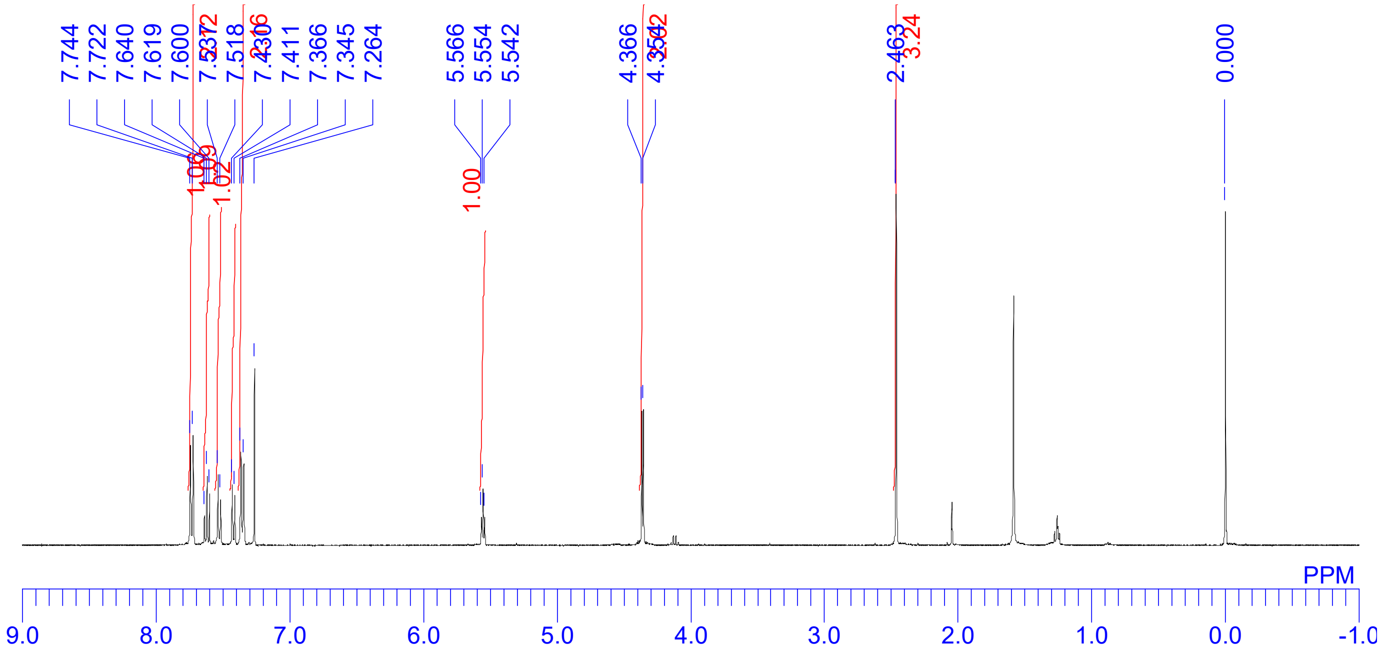
^{13}C NMR (100 MHz, CDCl$_3$)



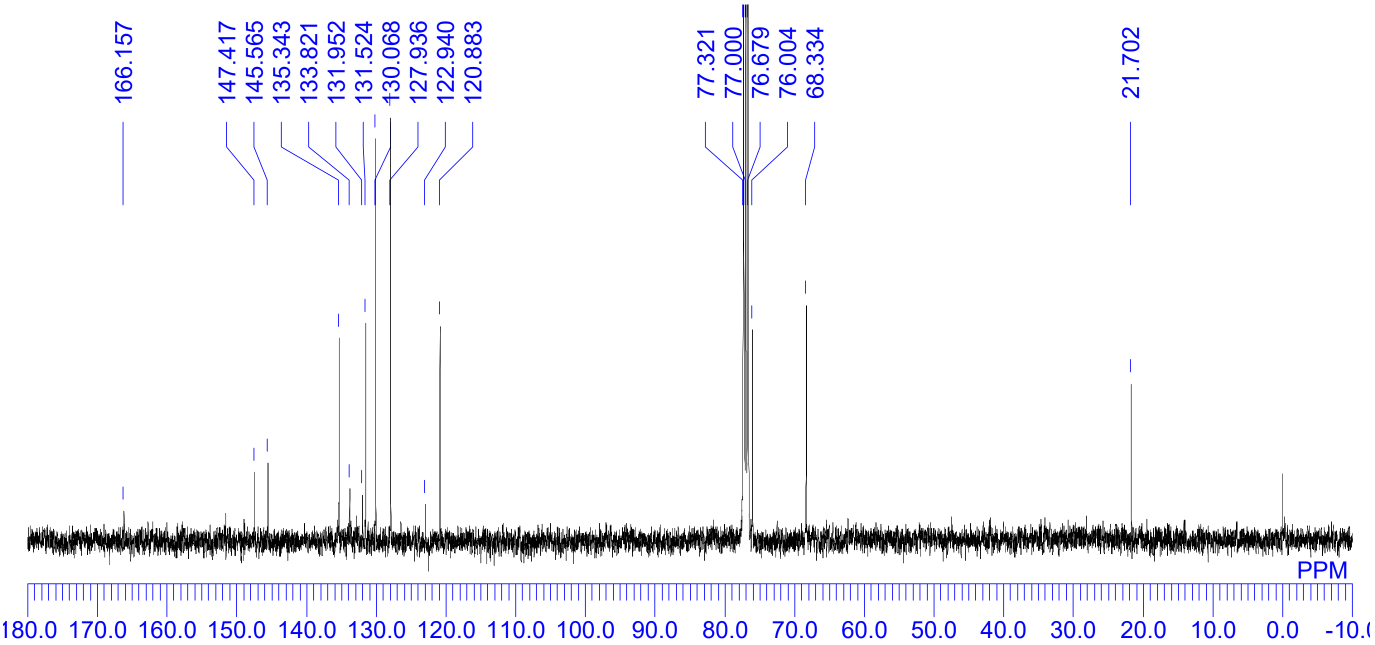
4ba (from 2b and 5a)



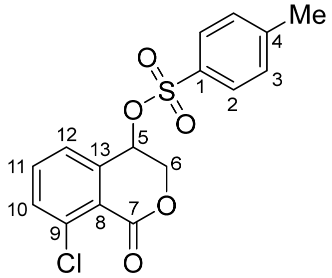
^{1}H NMR (400 MHz, CDCl$_3$)



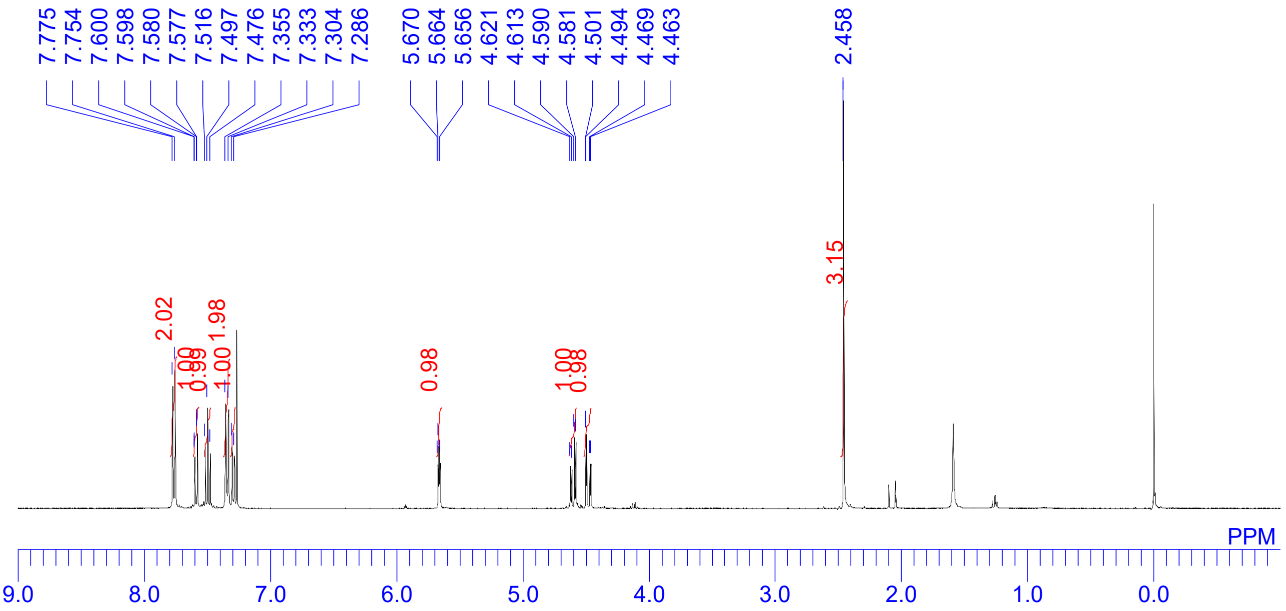
^{13}C NMR (100 MHz, CDCl$_3$)



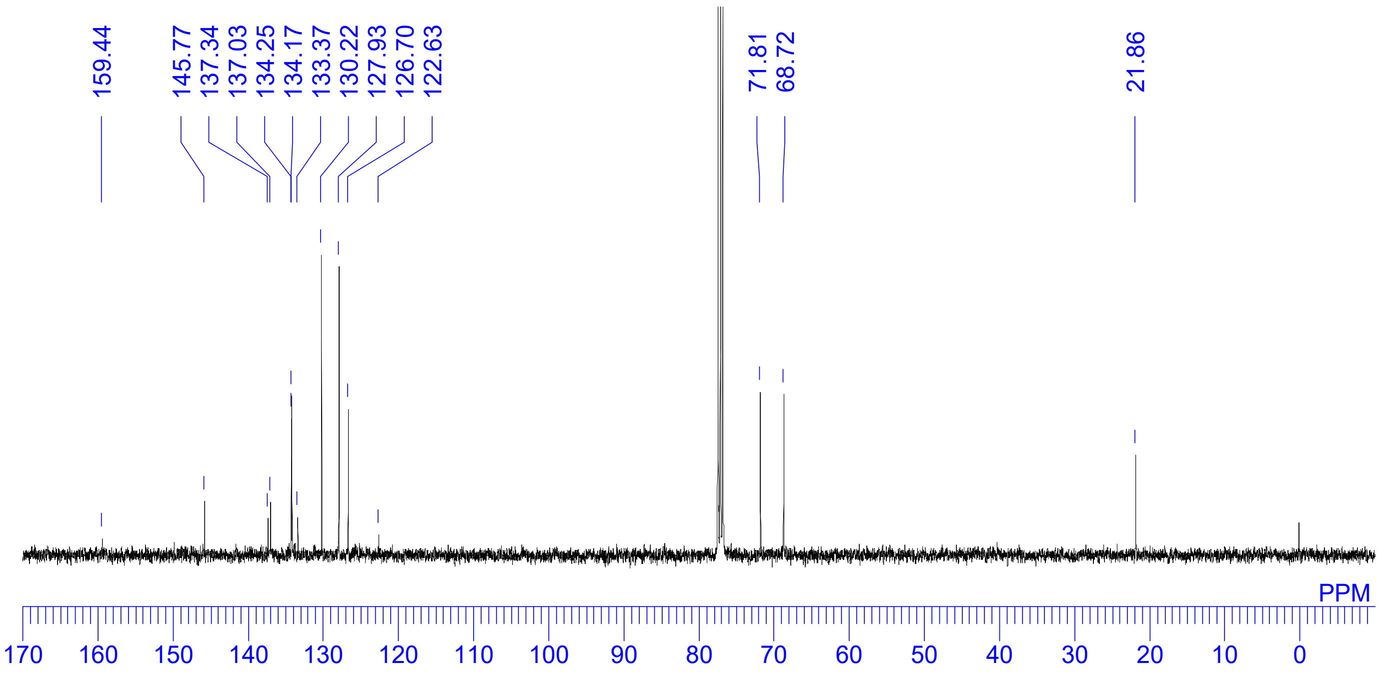
3ba (from 2b and 5a)



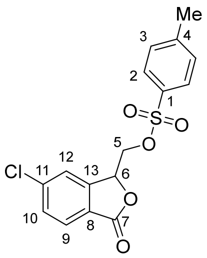
^{1}H NMR (400 MHz, CDCl$_3$)



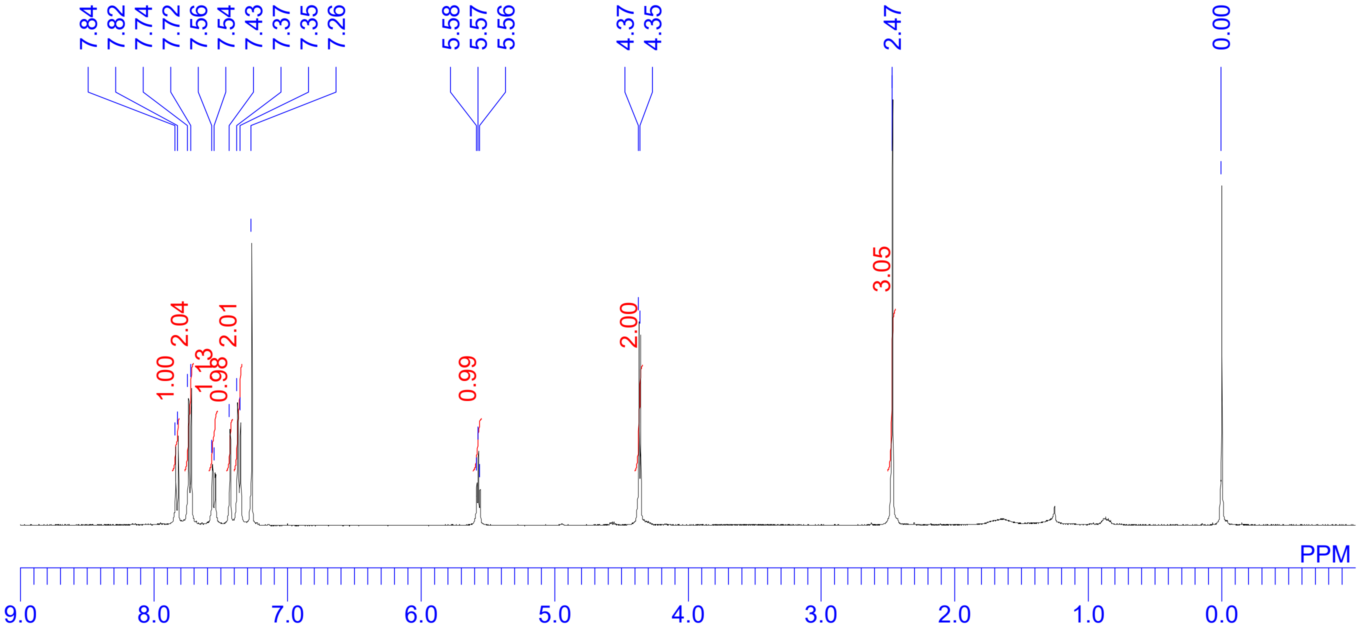
^{13}C NMR (100 MHz, CDCl$_3$)



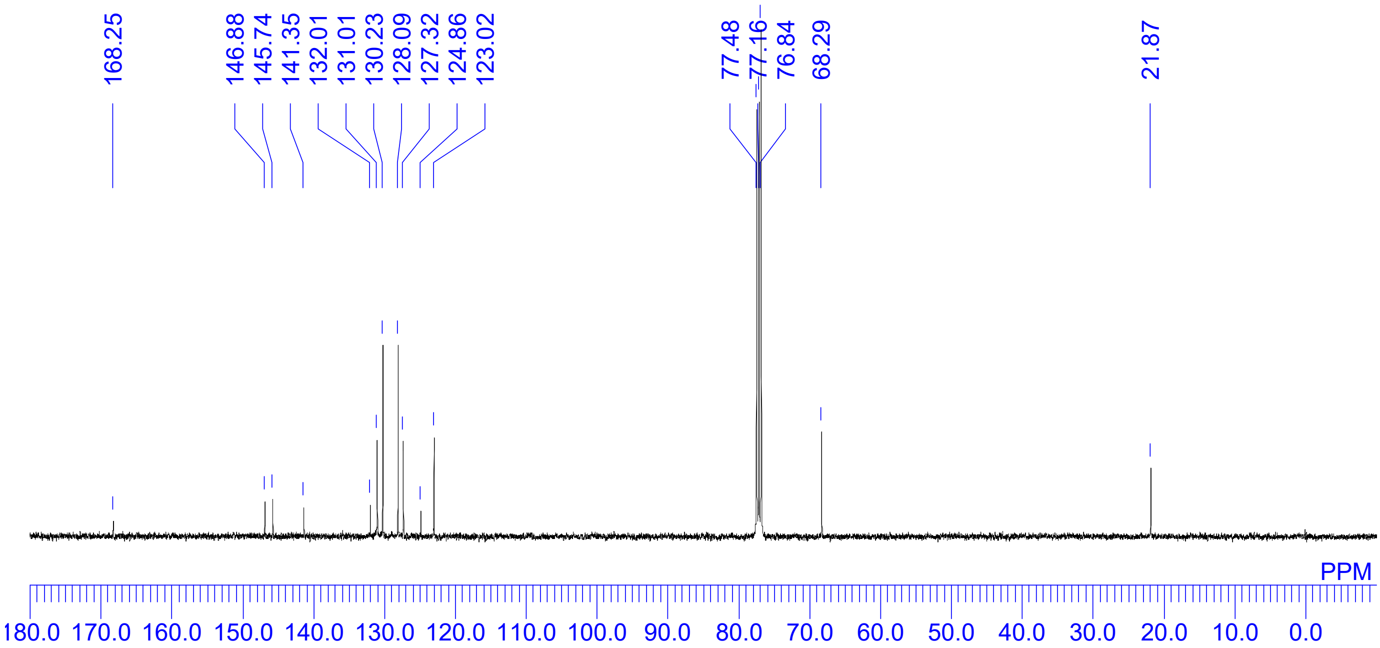
4ca (from 2c and 5a)



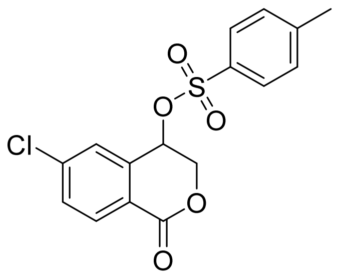
^{1}H NMR (400 MHz, CDCl$_3$)



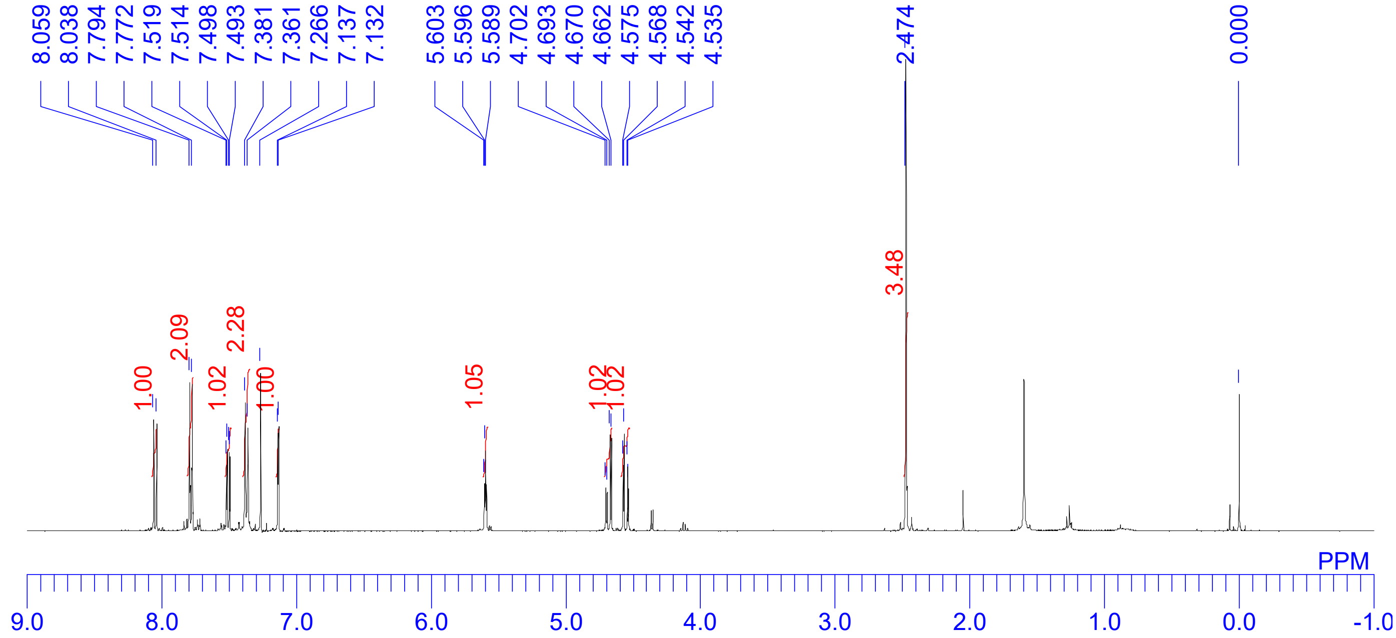
^{13}C NMR (100 MHz, CDCl$_3$)



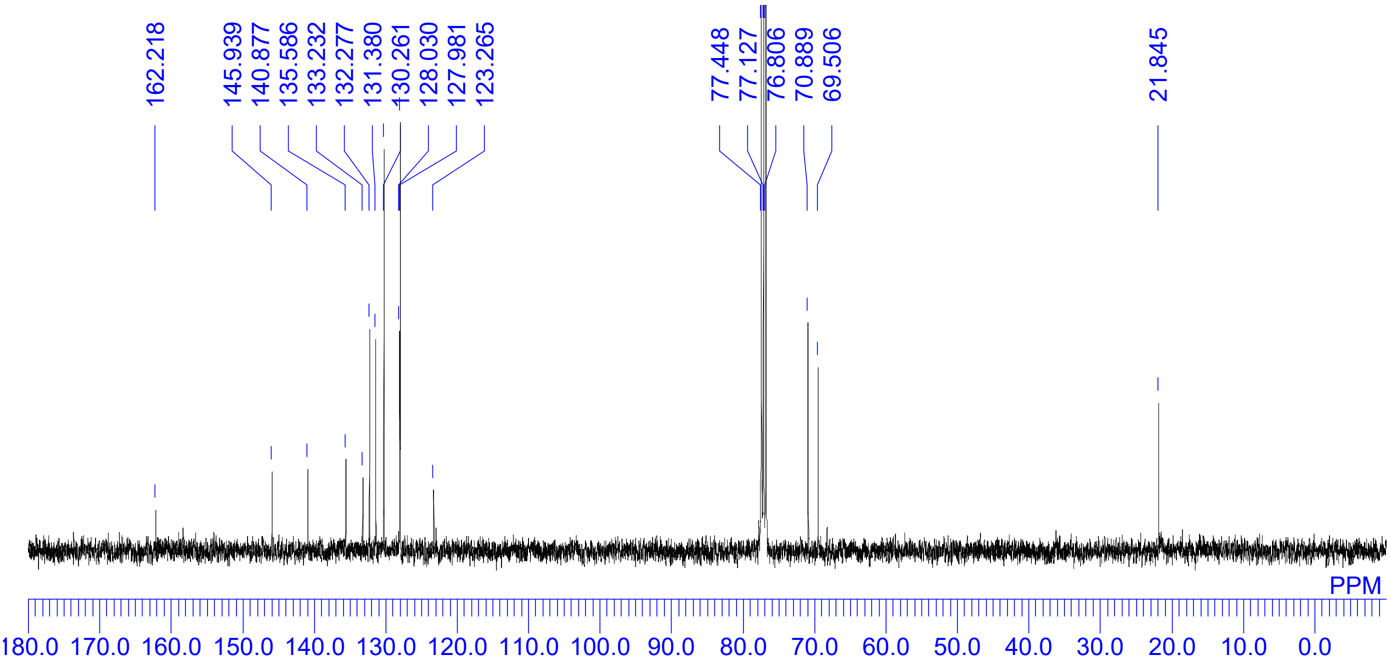
3ca (from 2c and 5a)



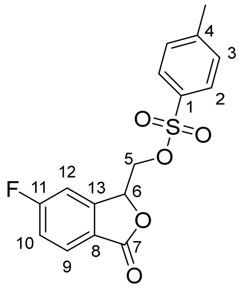
^{1}H NMR (400 MHz, CDCl$_3$)



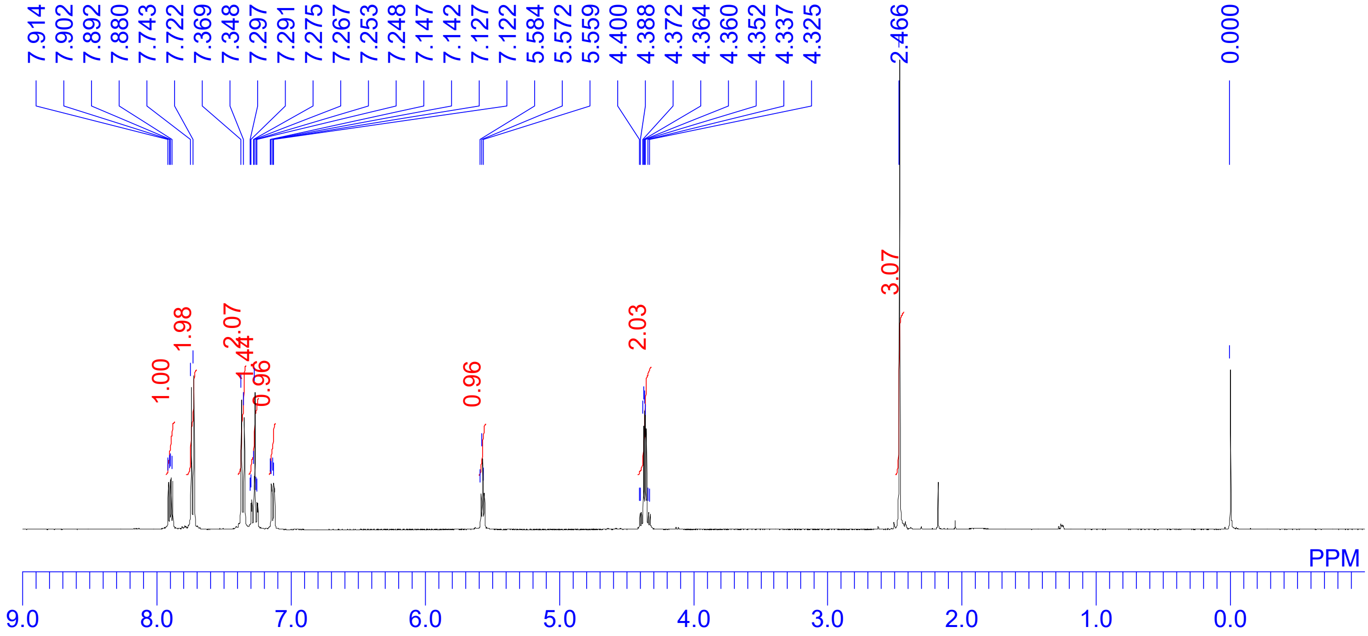
^{13}C NMR (100 MHz, CDCl$_3$)



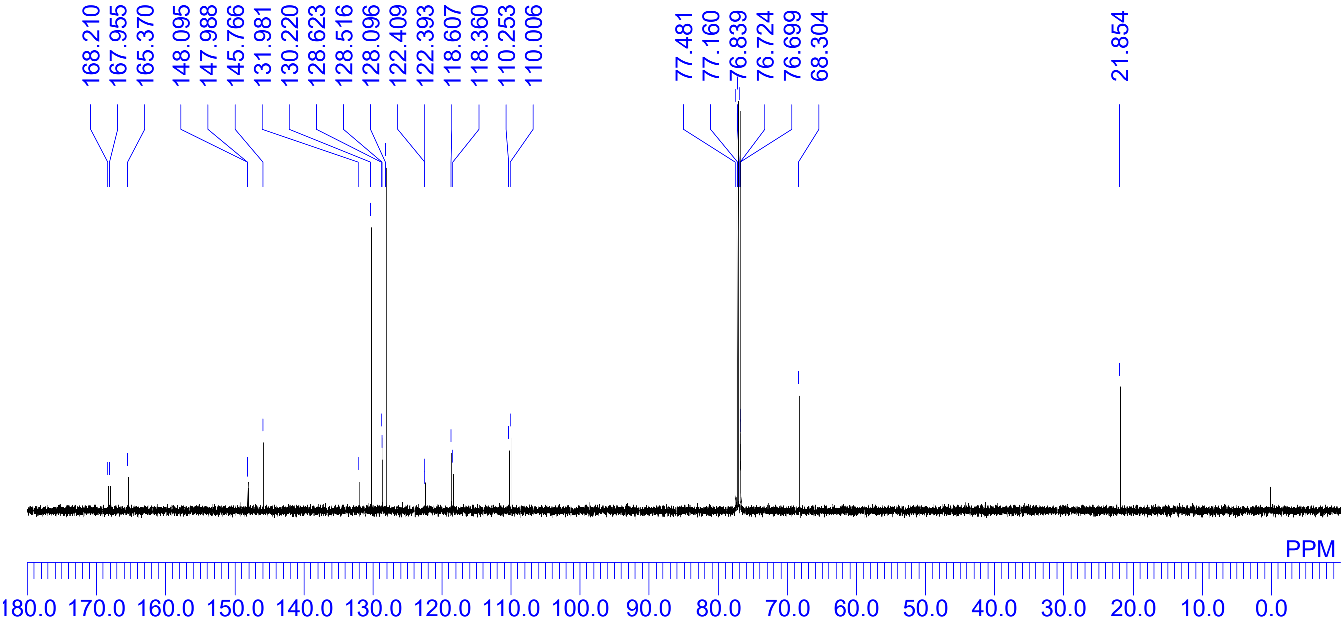
4da (from 2d and 5a)



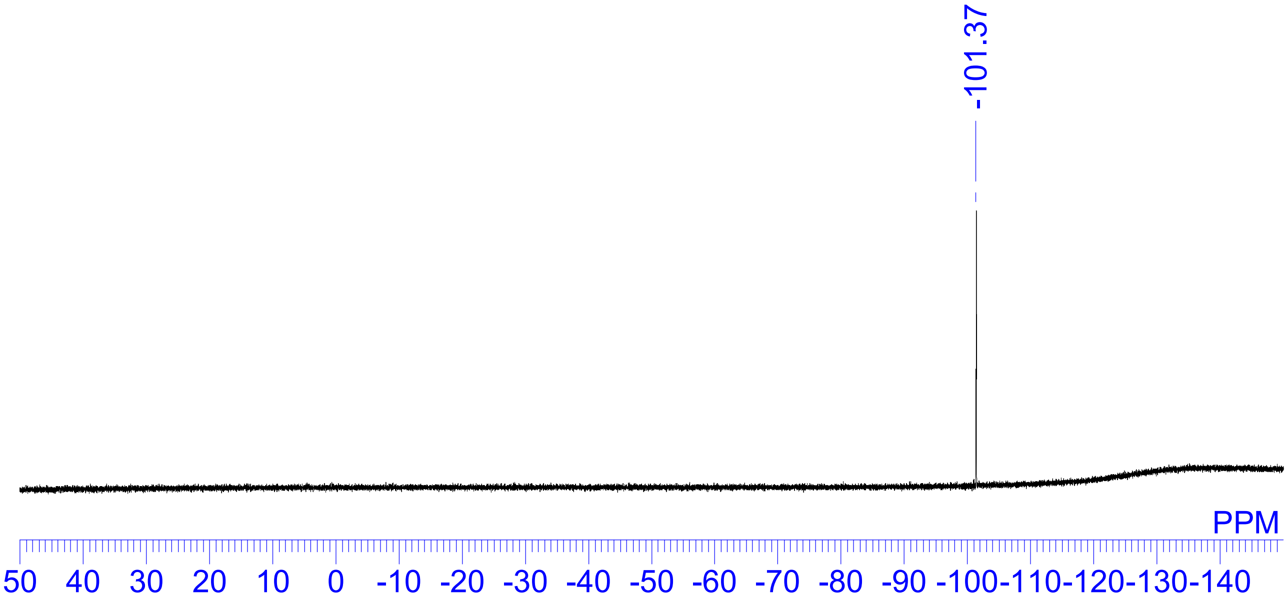
^{1}H NMR (400 MHz, CDCl$_3$)



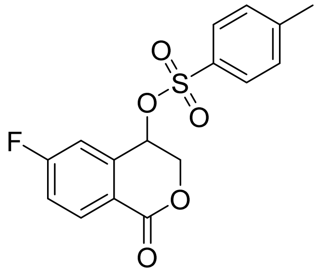
^{13}C NMR (100 MHz, CDCl$_3$)



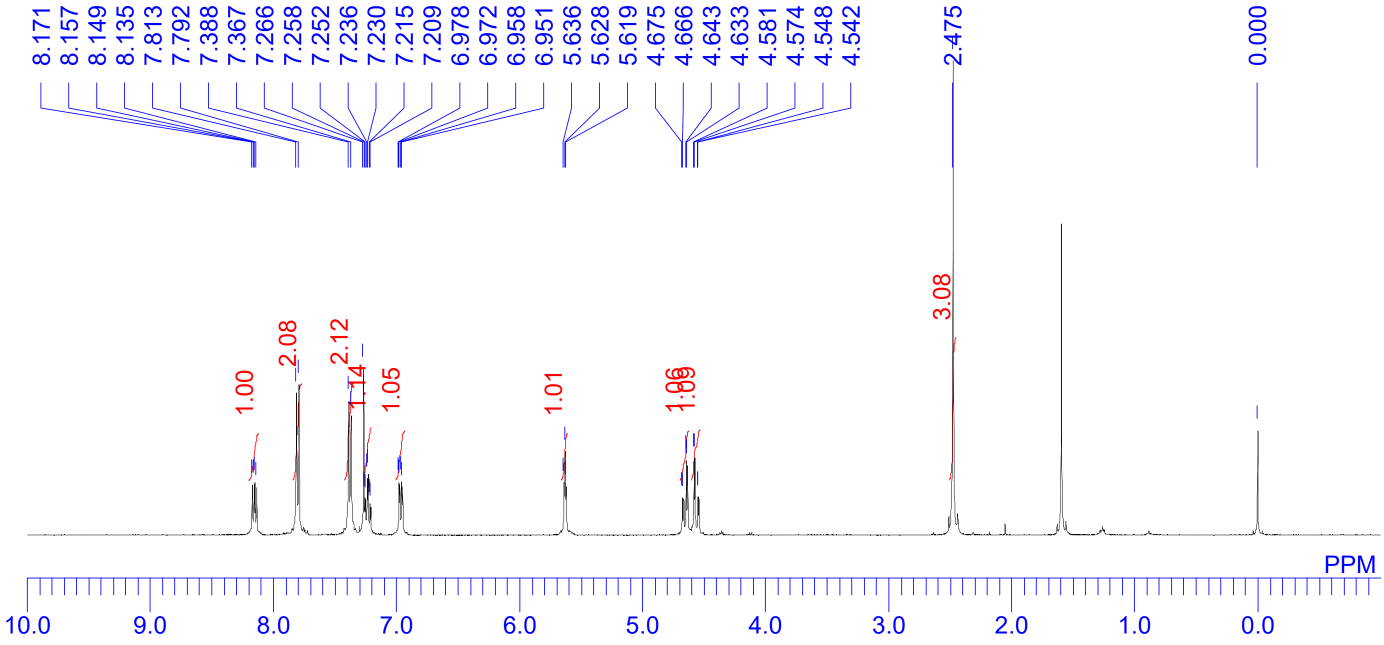
^{19}F NMR (377 MHz, $CDCl_3$, external standard:TFA in D_2O)



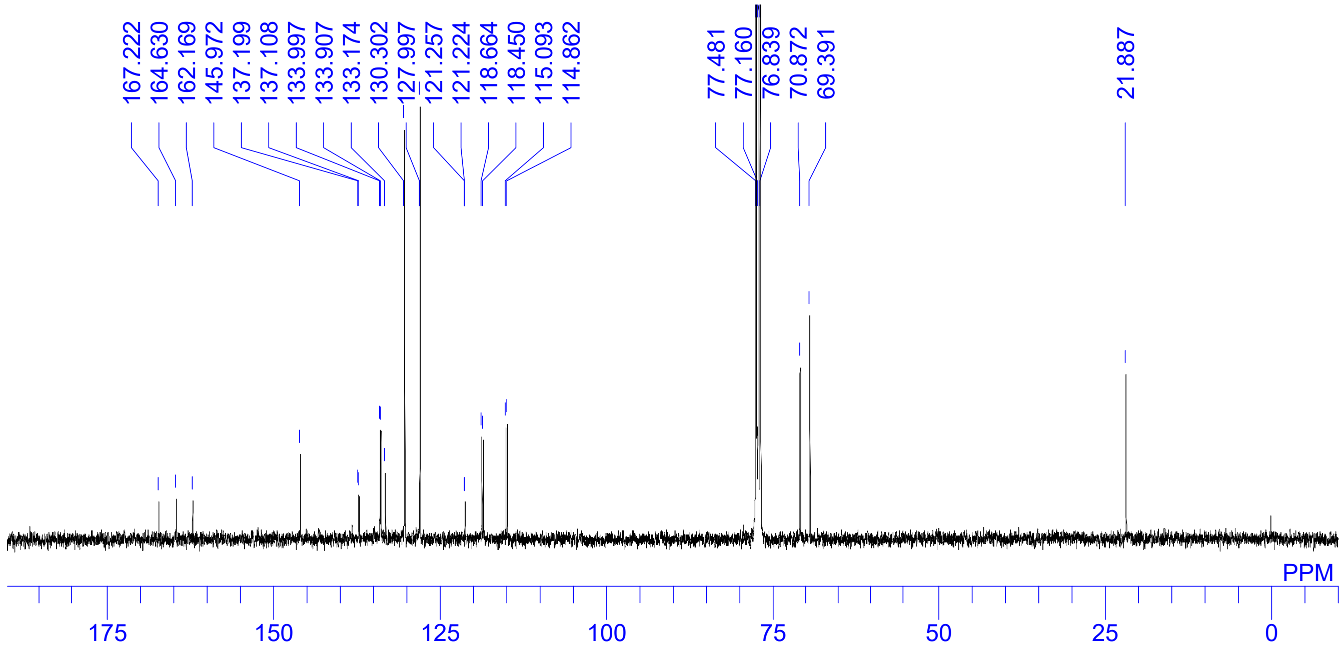
3da (from 2d and 5a)



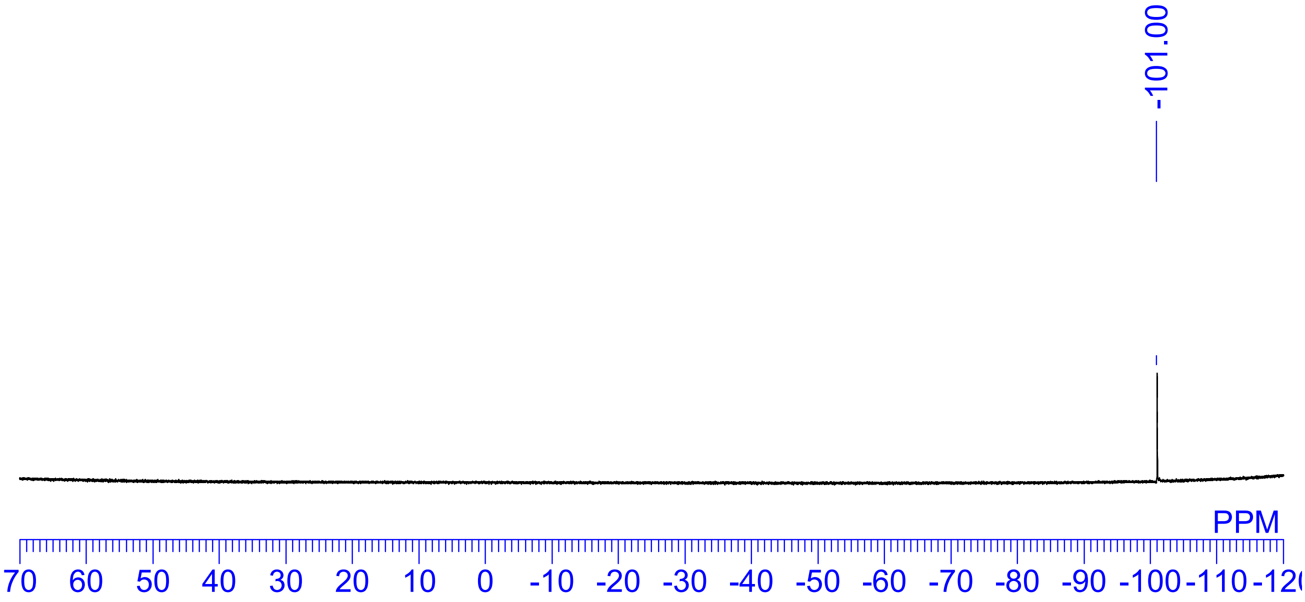
^{1}H NMR (400 MHz, CDCl$_3$)



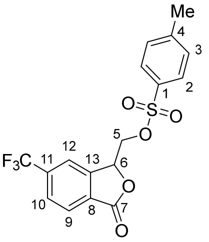
^{13}C NMR (100 MHz, CDCl$_3$)



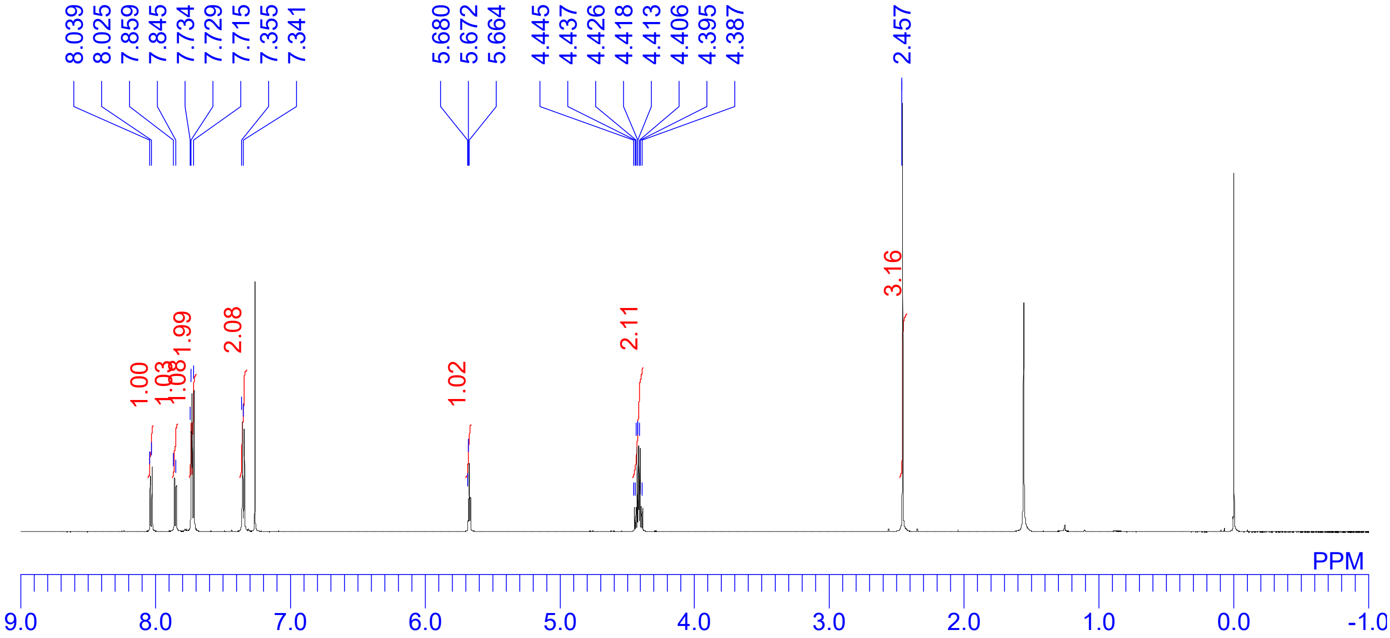
^{19}F NMR (377 MHz, $CDCl_3$, external standard:TFA in D_2O)



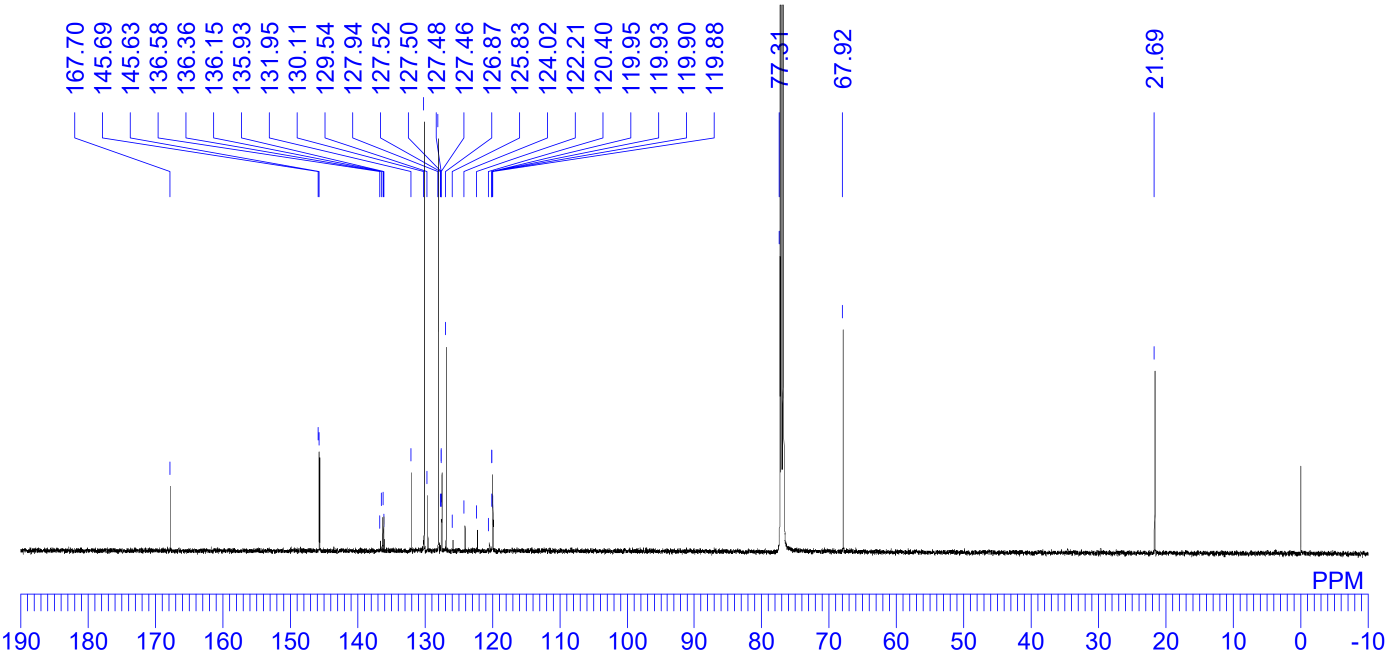
4ea (from 2e and 5a)



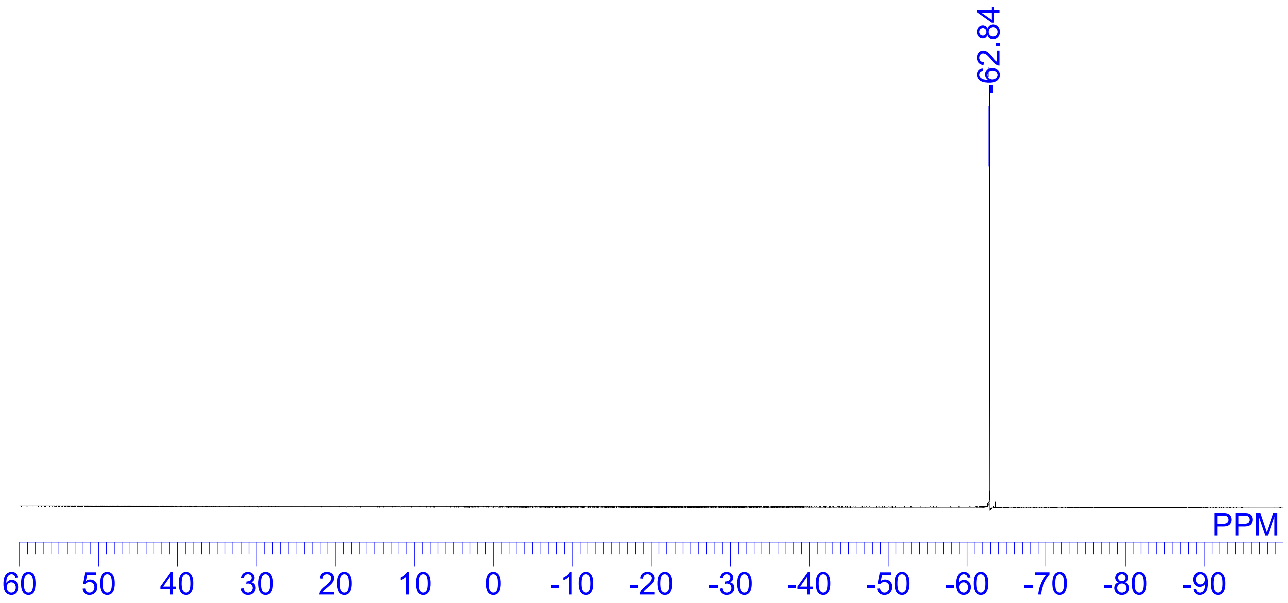
^{1}H NMR (600 MHz, CDCl$_3$)



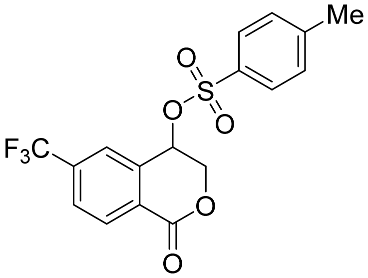
^{13}C NMR (150 MHz, CDCl$_3$)



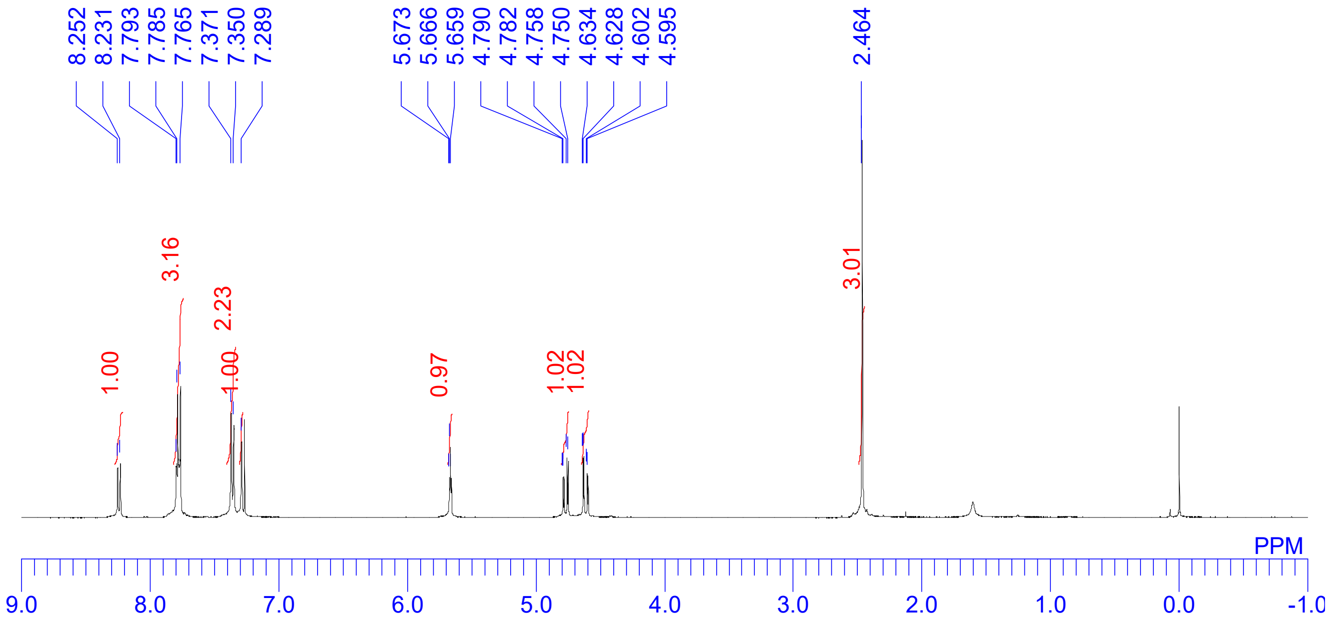
^{19}F NMR (377 MHz, $CDCl_3$, external standard:TFA in D_2O)



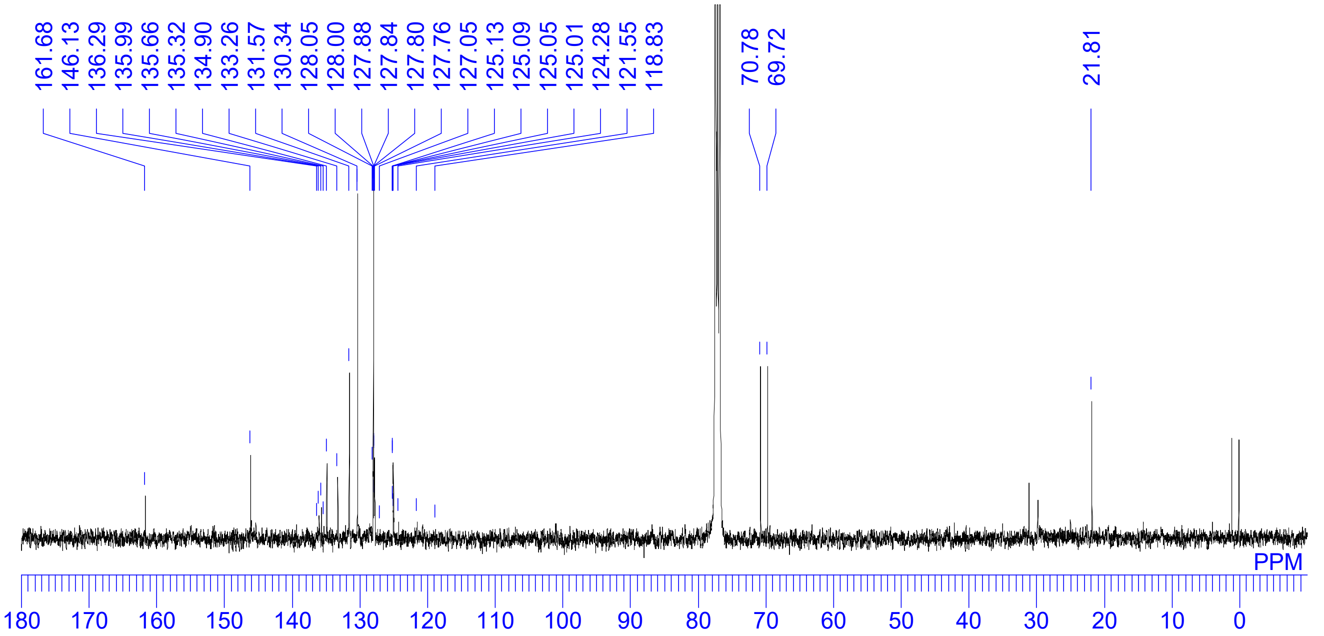
3ea (from 2e and 5a)



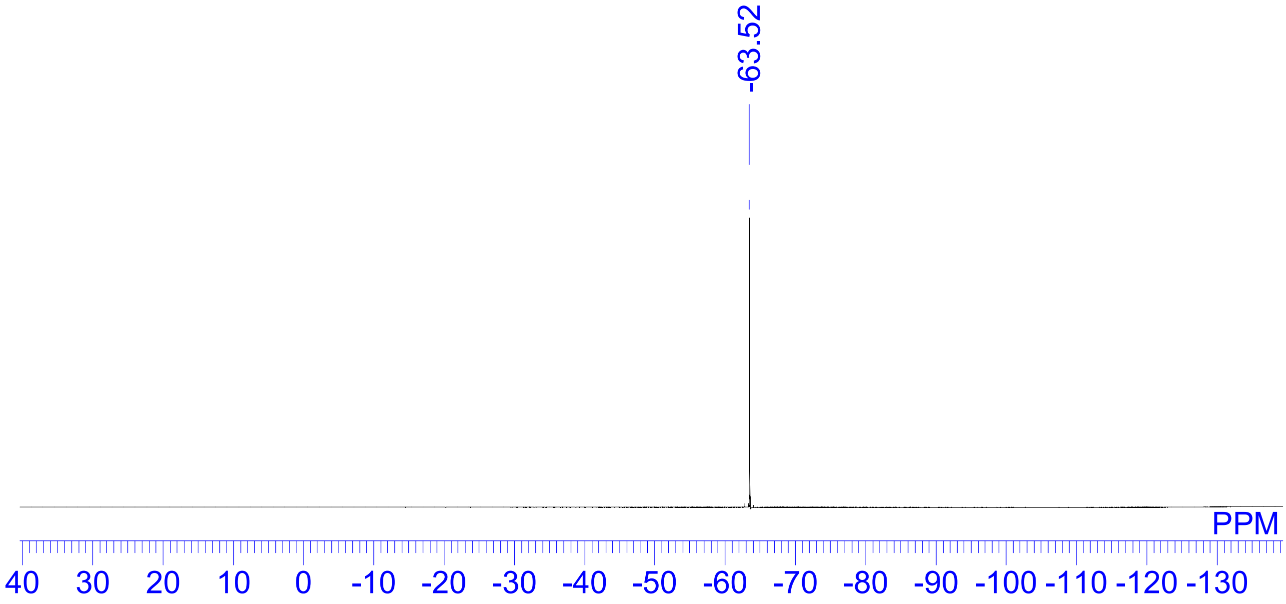
^{1}H NMR (400 MHz, CDCl$_3$)



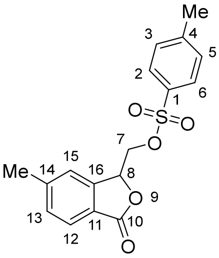
^{13}C NMR (100 MHz, CDCl$_3$)



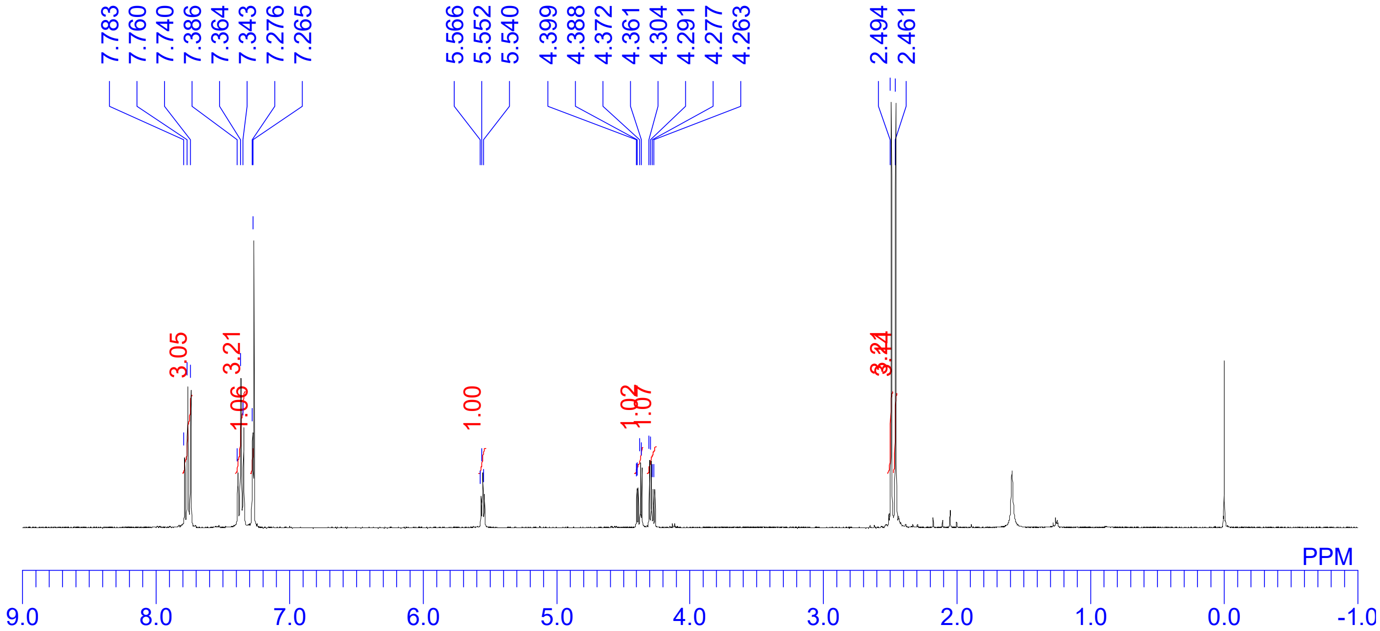
^{19}F NMR (377 MHz, $CDCl_3$, external standard:TFA in D_2O)



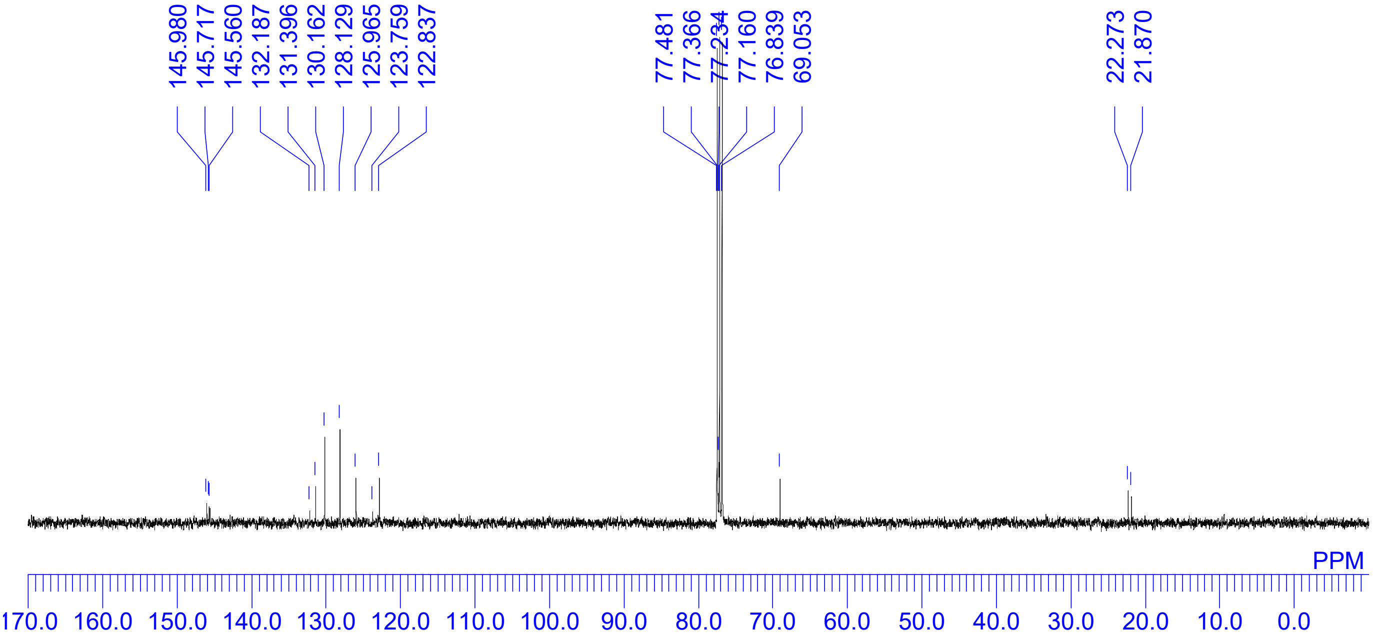
4fa (from 2f and 5a)



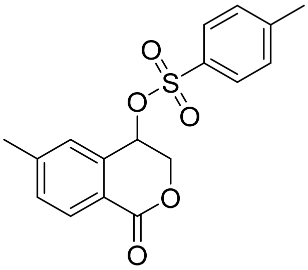
^{1}H NMR (400 MHz, CDCl$_3$)



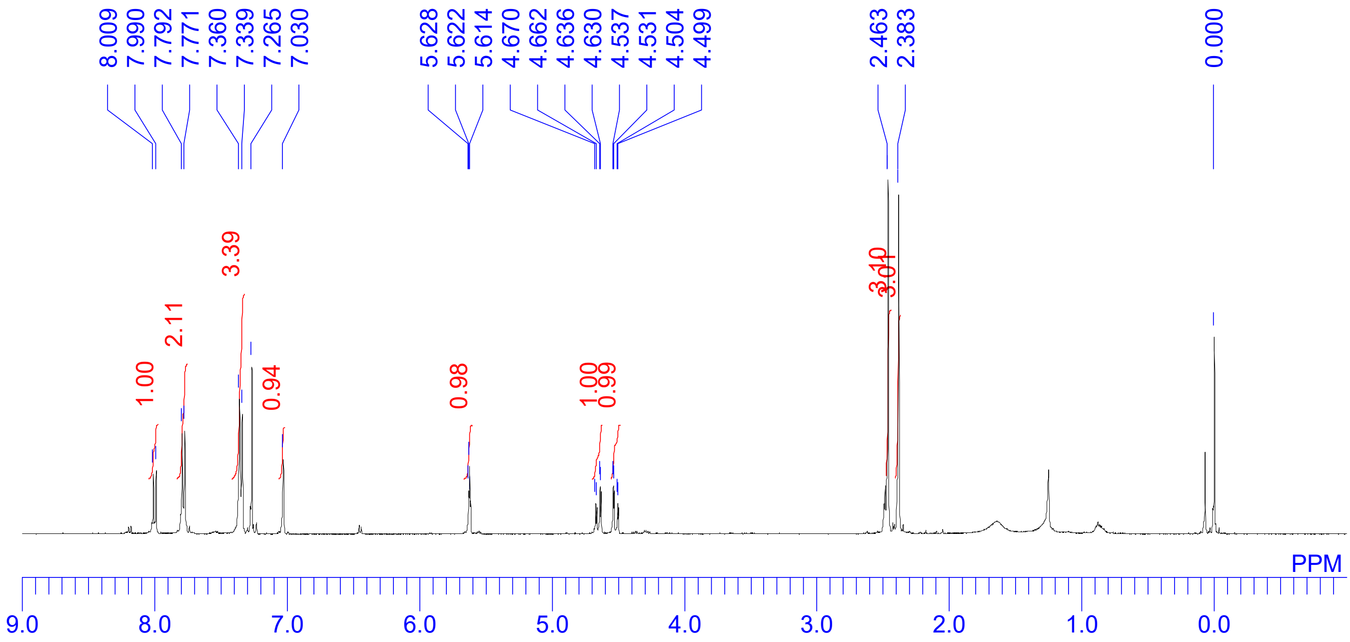
^{13}C NMR (100 MHz, CDCl$_3$)



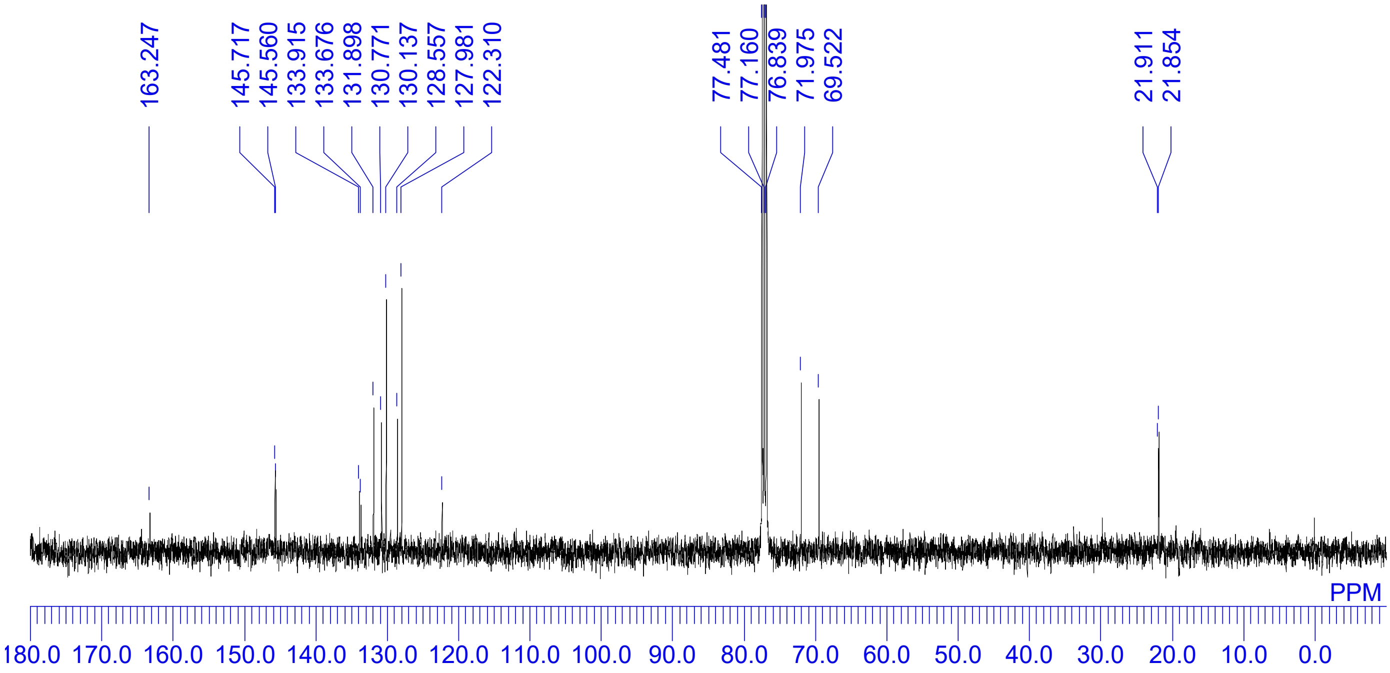
3fa (from 2f and 5a)



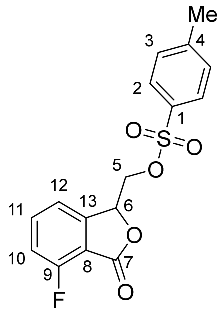
^{1}H NMR (400 MHz, CDCl$_3$)



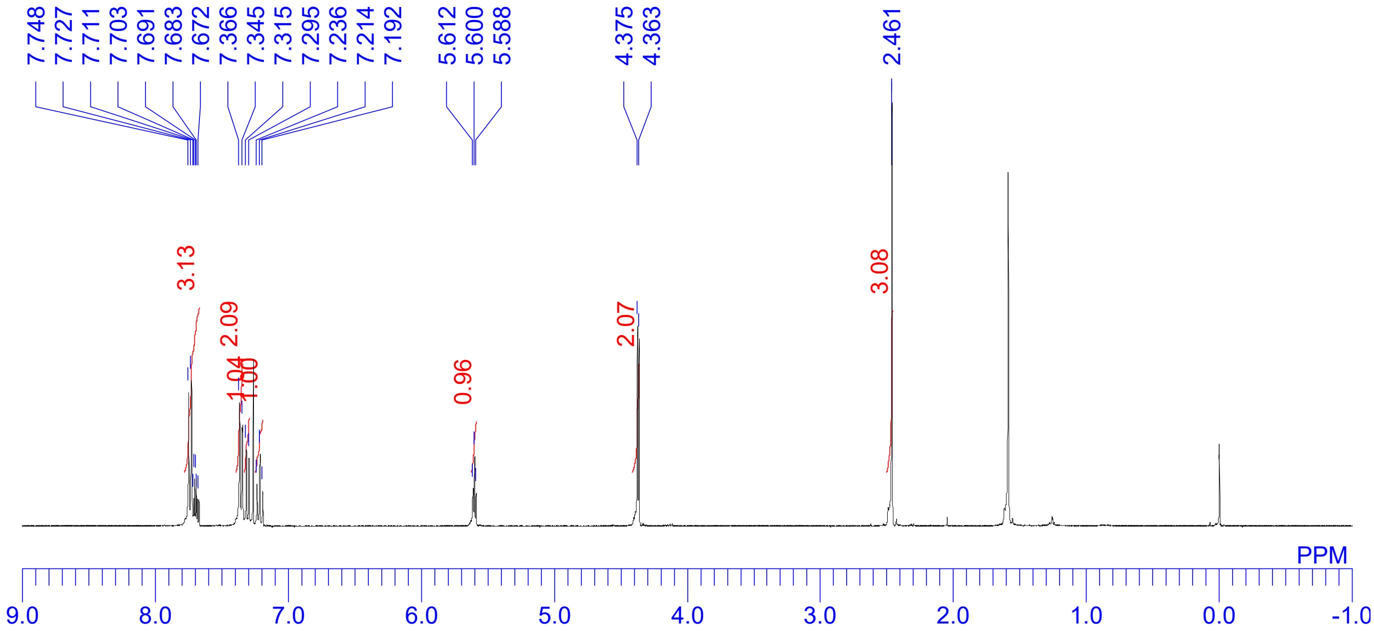
^{13}C NMR (100 MHz, CDCl$_3$)



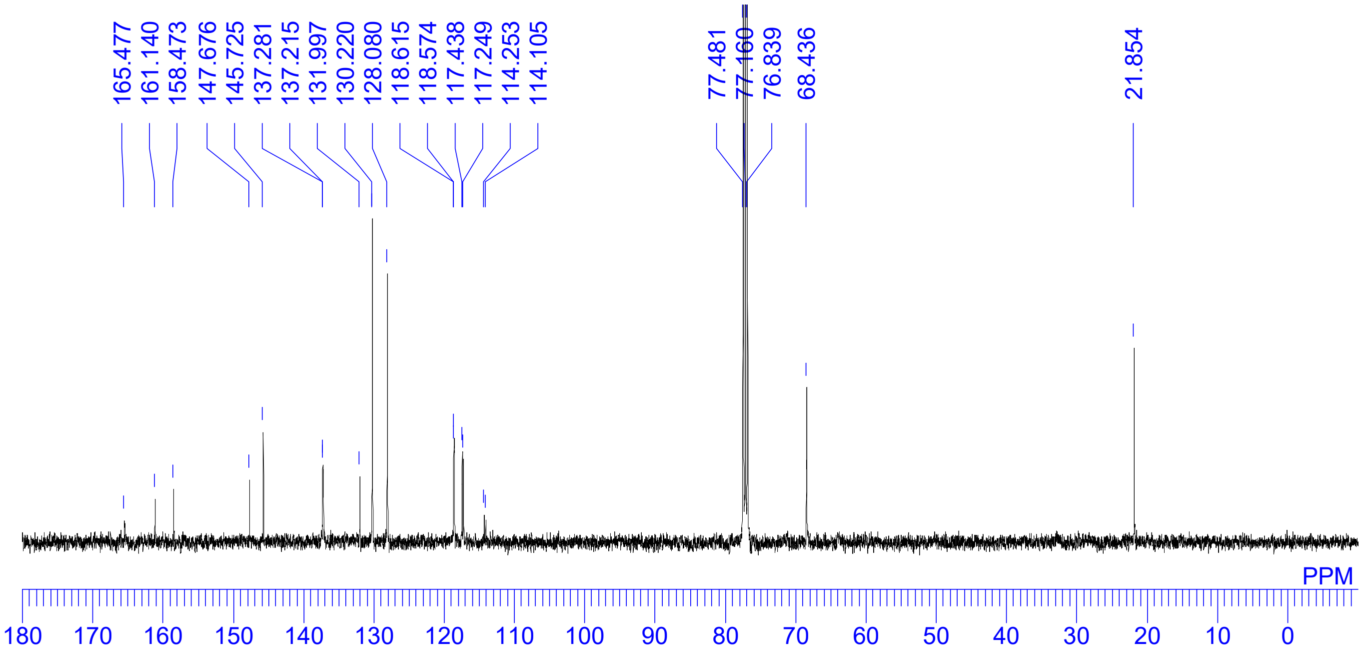
4ga (from 2g and 5a)



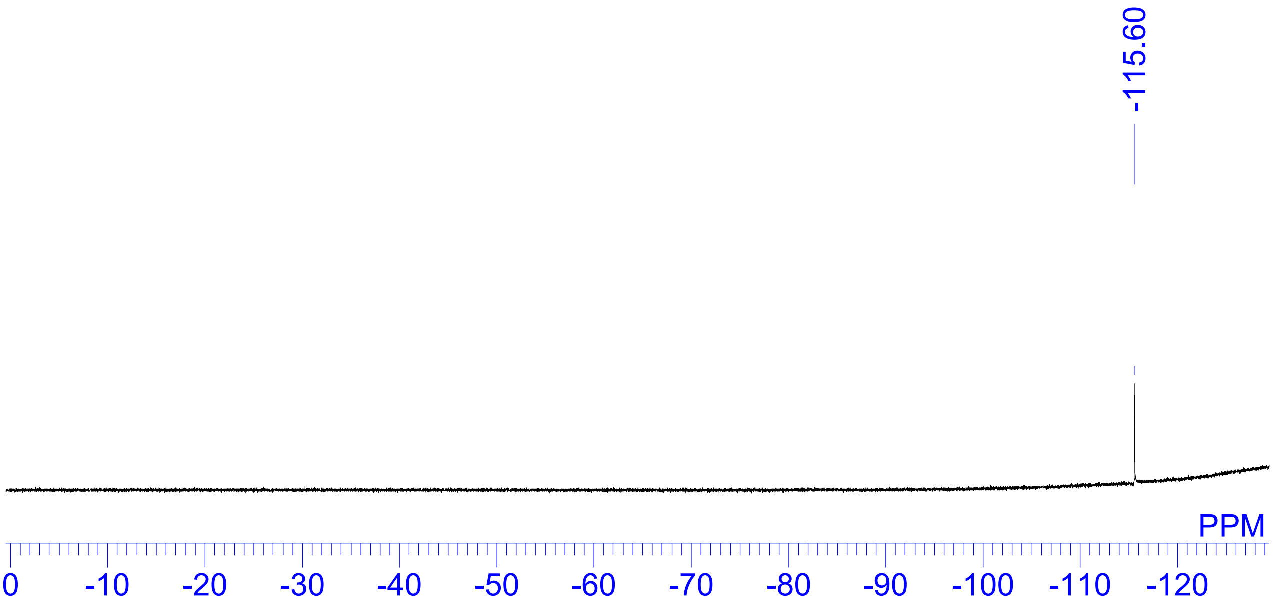
^{1}H NMR (400 MHz, CDCl$_3$)



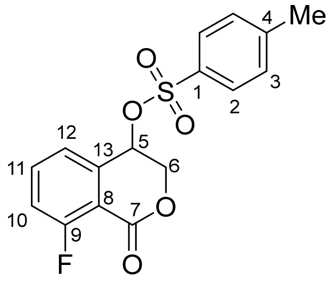
^{13}C NMR (100 MHz, CDCl$_3$)



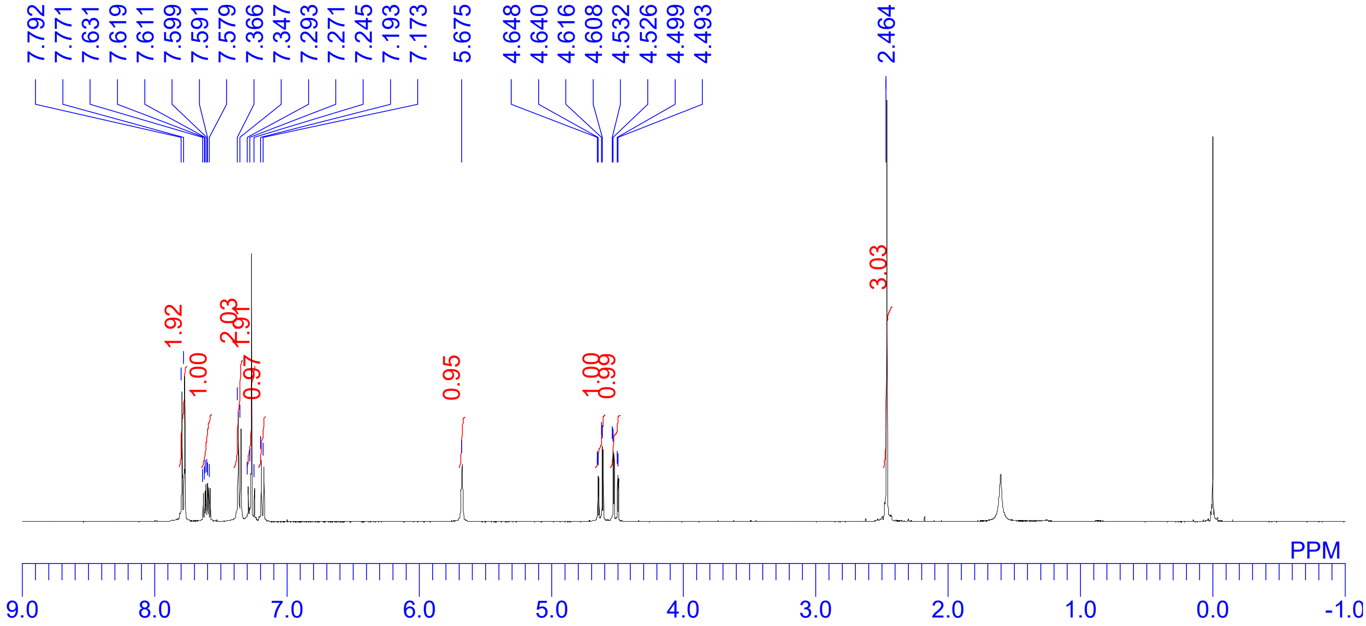
^{19}F NMR (377 MHz, CDCl$_3$, external standard:TFA in D$_2$O)



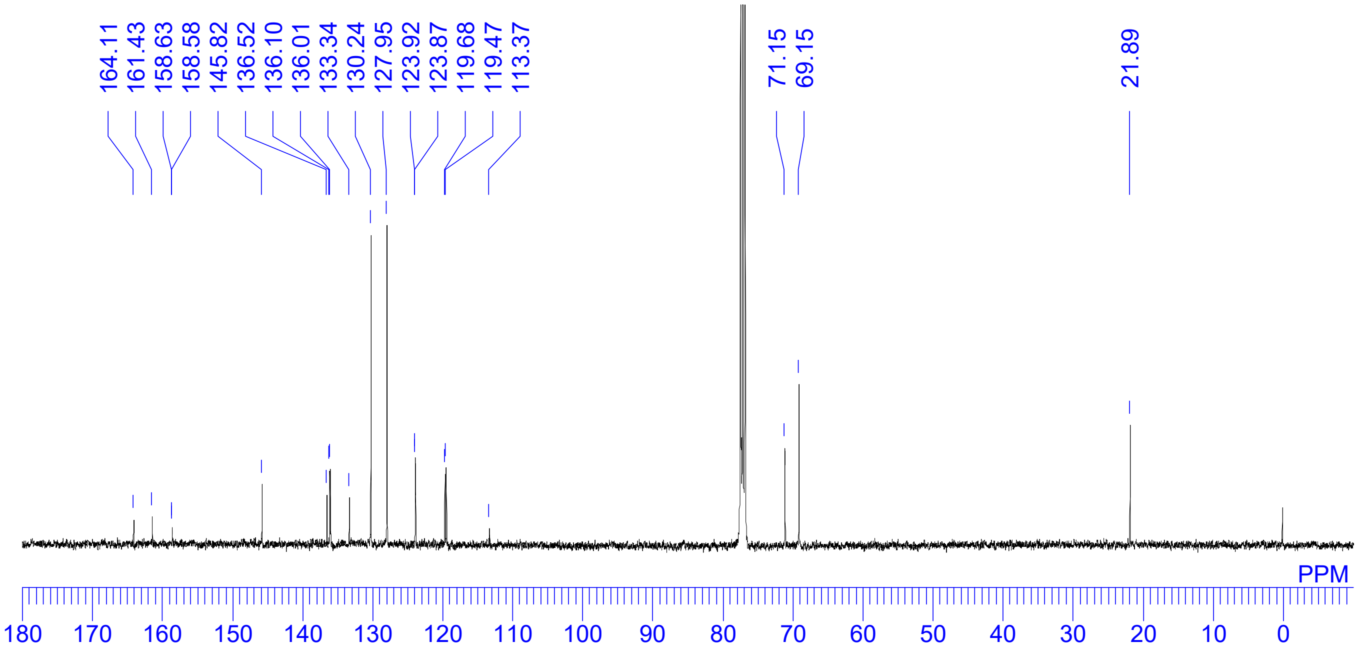
3ga (from 2g and 5a)



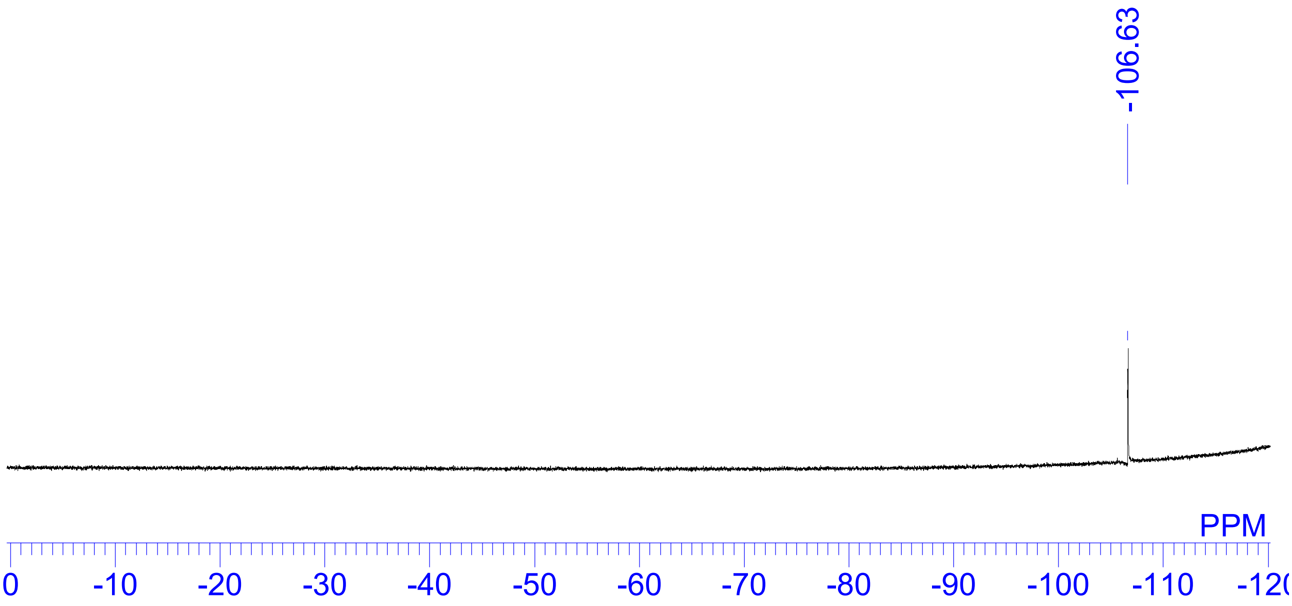
^{1}H NMR (400 MHz, CDCl$_3$)



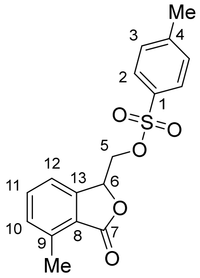
^{13}C NMR (100 MHz, CDCl$_3$)



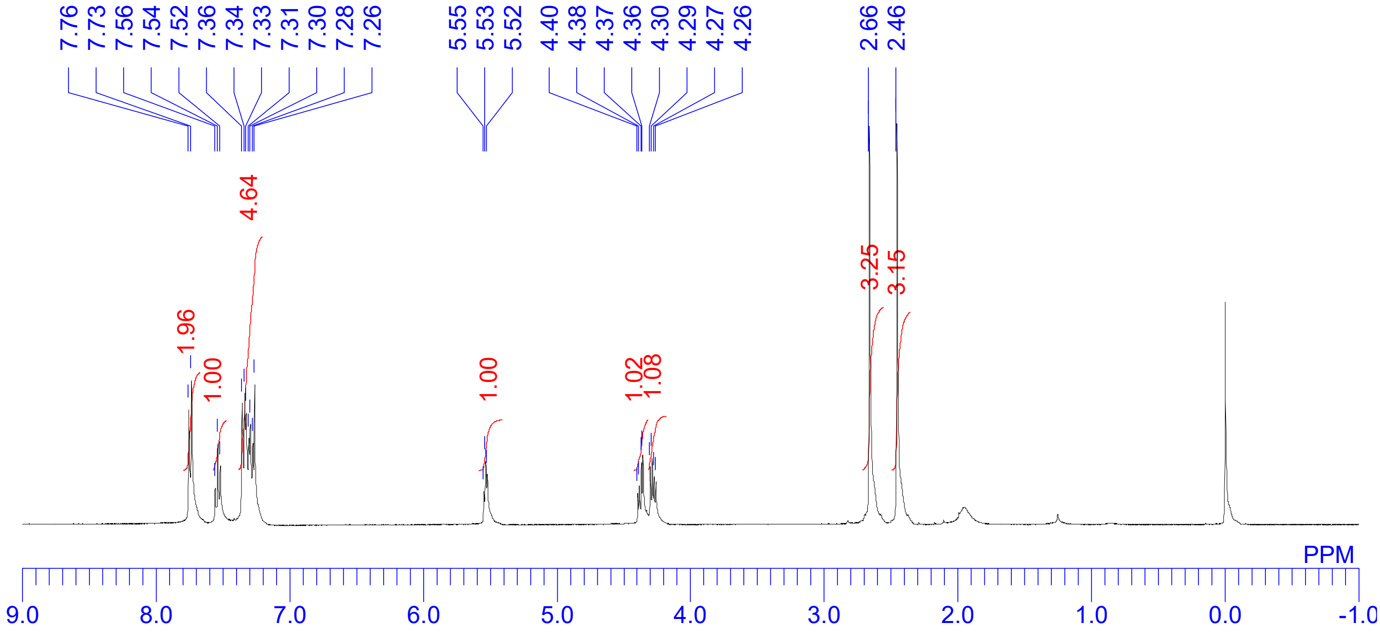
^{19}F NMR (377 MHz, $CDCl_3$, external standard:TFA in D_2O)



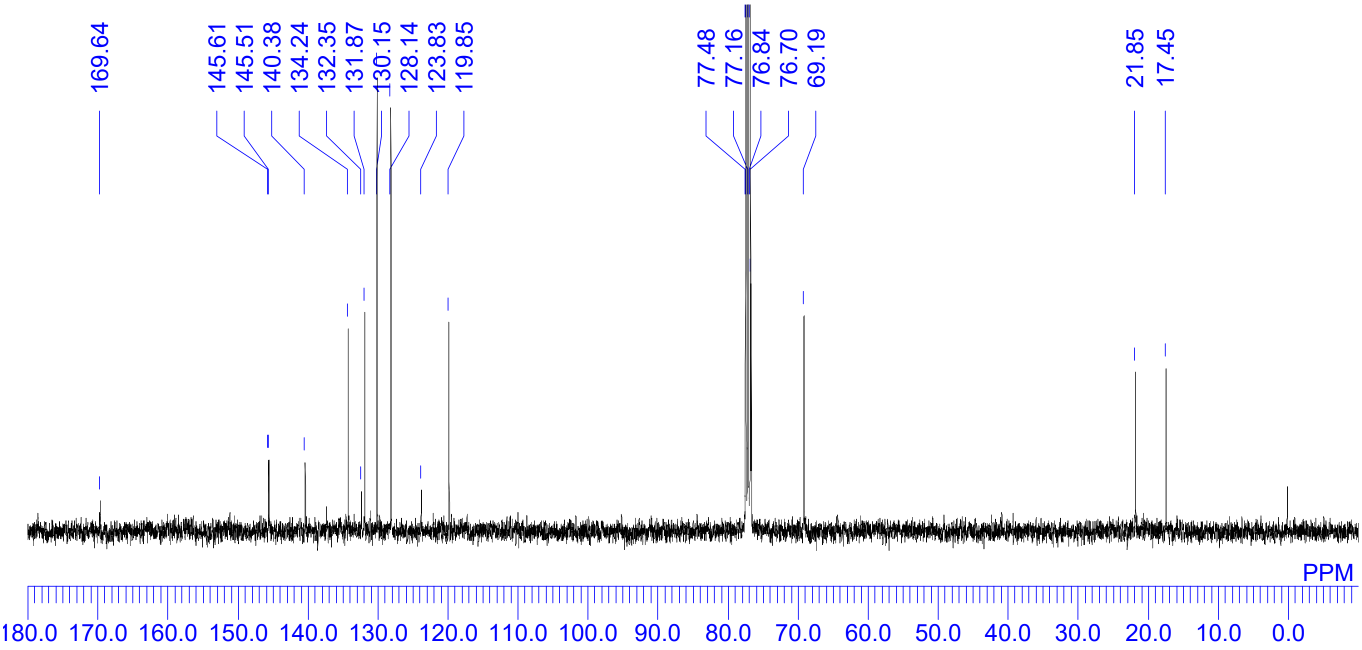
4ia (from 2i and 5a)



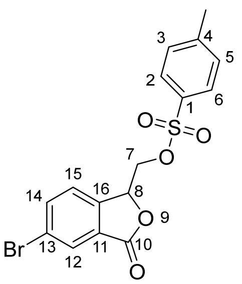
^{1}H NMR (400 MHz, $CDCl_3$)



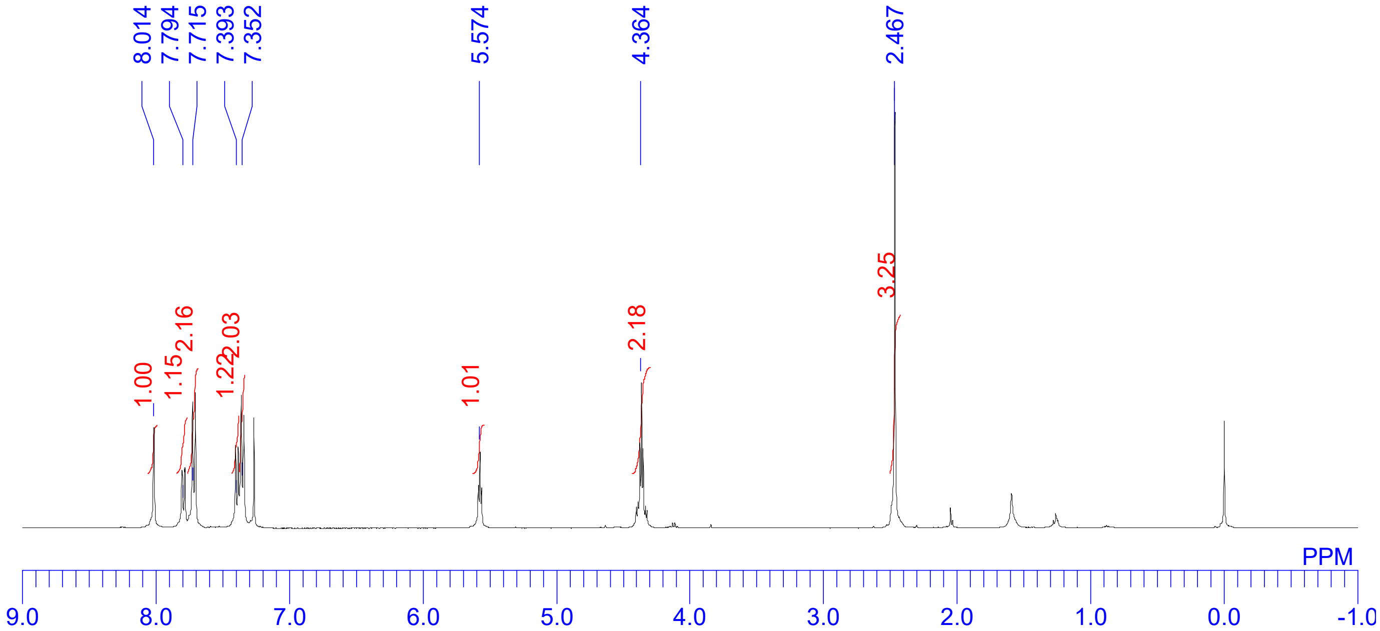
^{13}C NMR (100 MHz, $CDCl_3$)



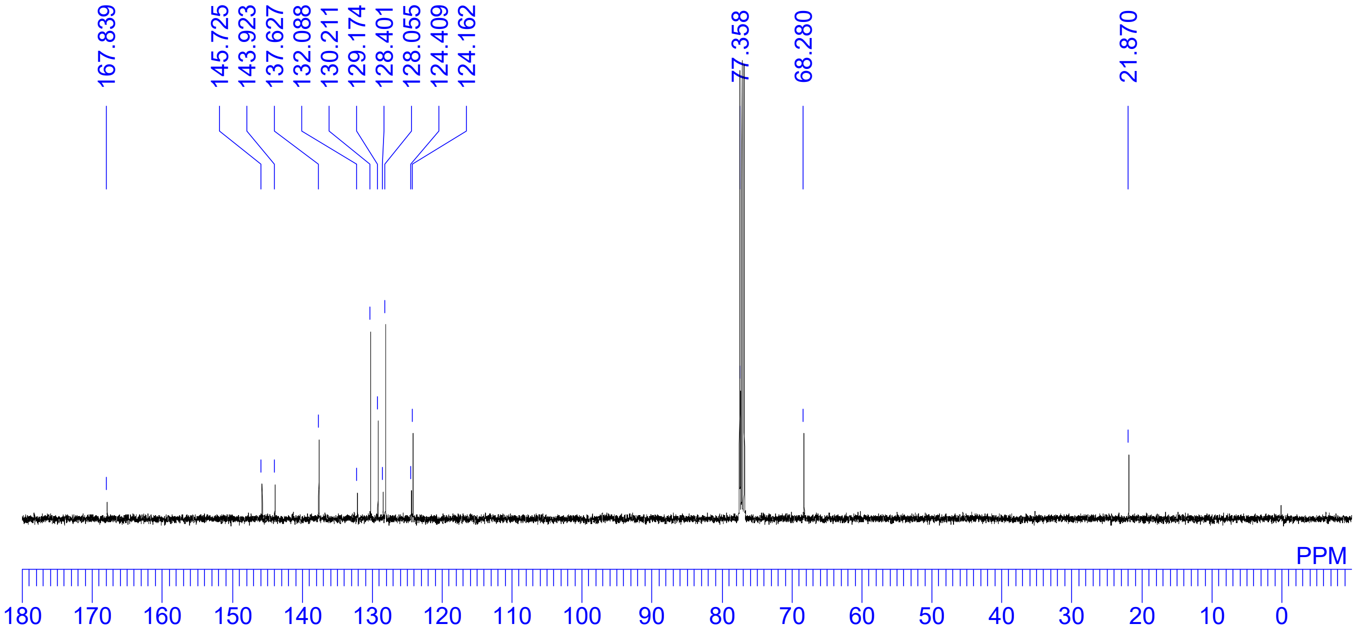
4ja (from 2j and 5a)



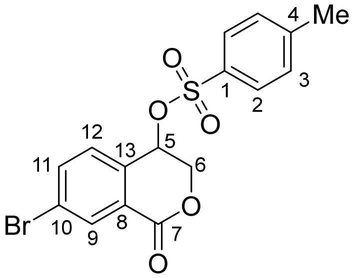
^{1}H-NMR (400 MHz, CDCl$_3$)



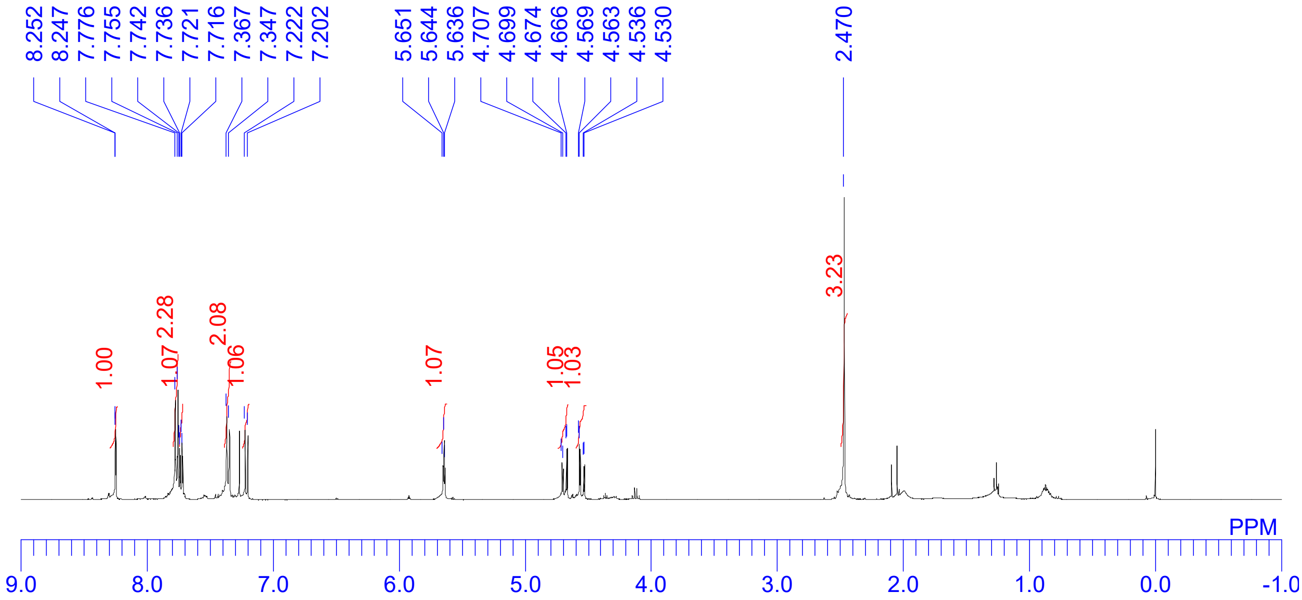
^{13}C NMR: (100 MHz, CDCl$_3$)



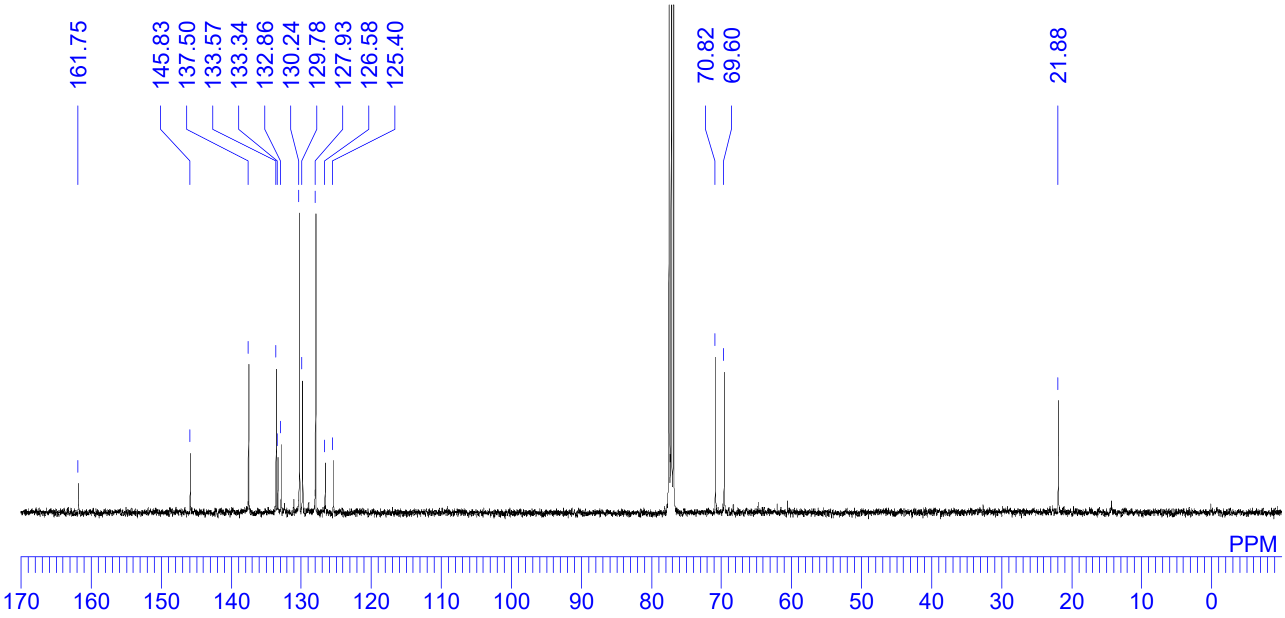
3ja (from 2j and 5a)



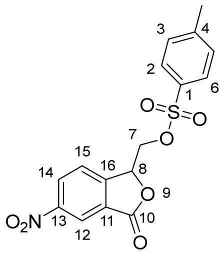
^{1}H NMR (400 MHz, CDCl$_3$)



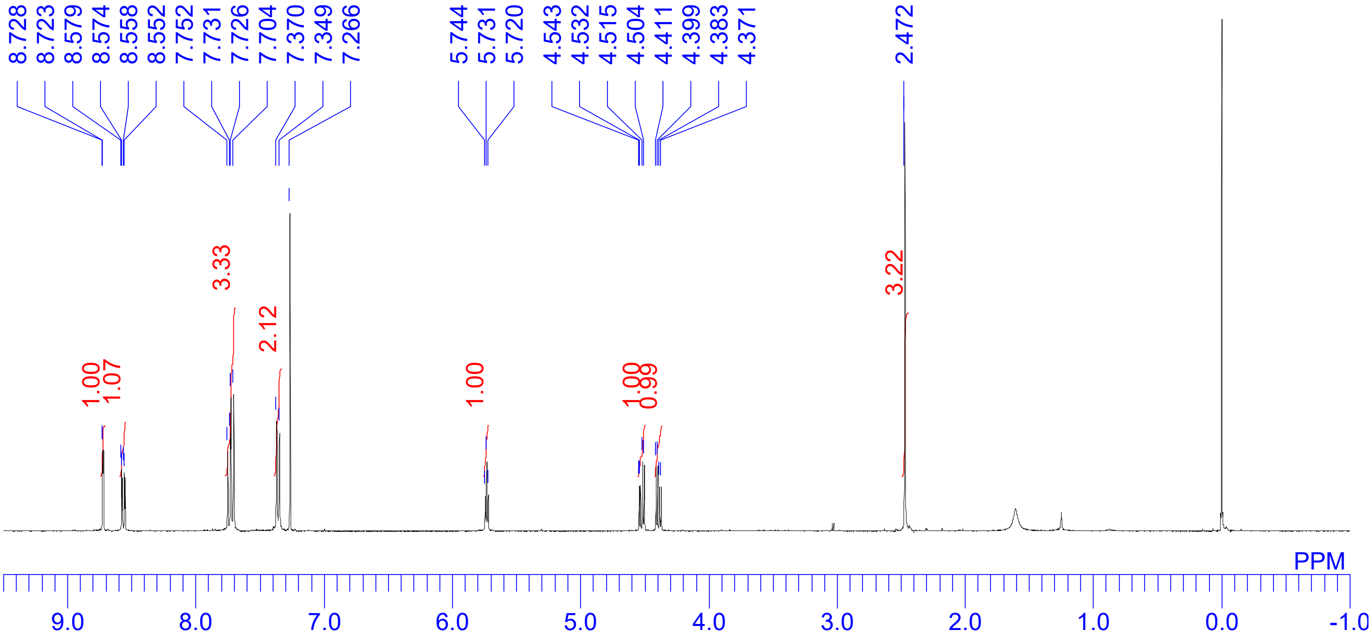
^{13}C NMR (100 MHz, CDCl$_3$)



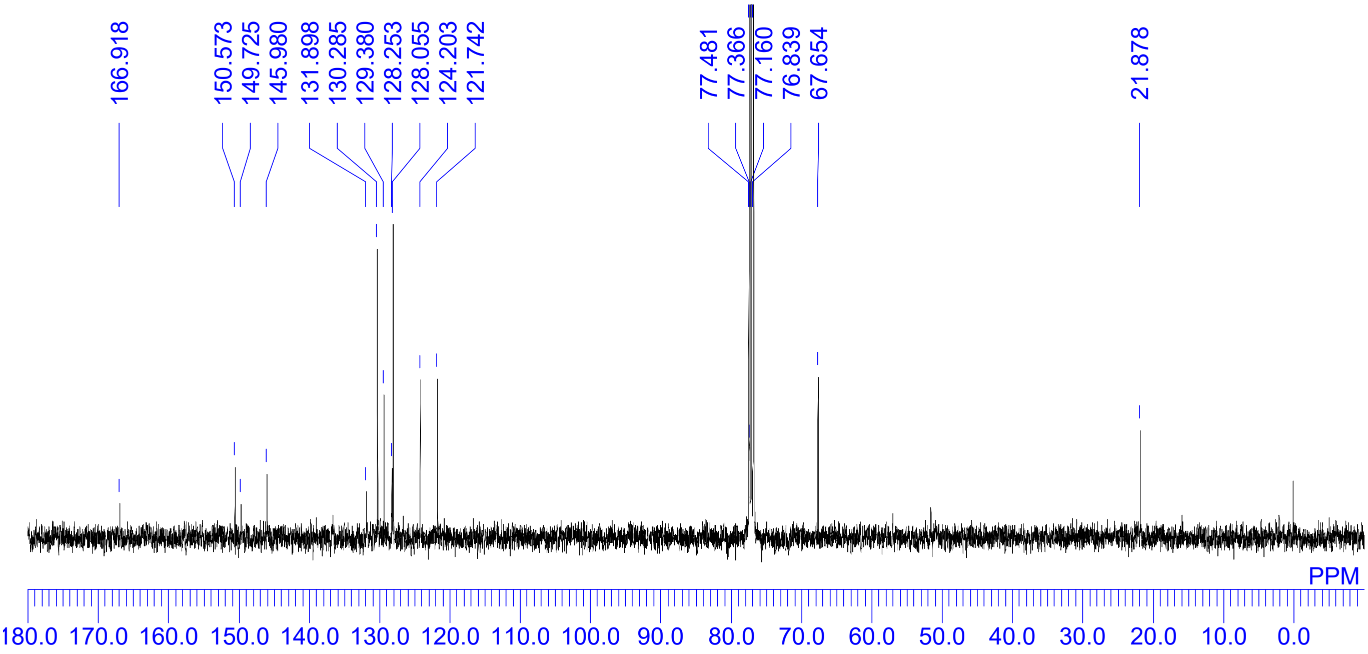
4ka (from 2k and 5a)



^{1}H NMR (400 MHz, $CDCl_3$)

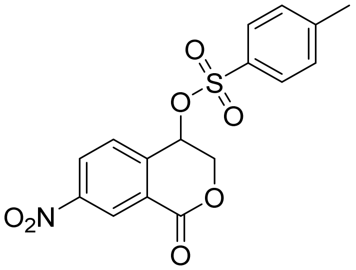


^{13}C NMR (100 MHz, $CDCl_3$)

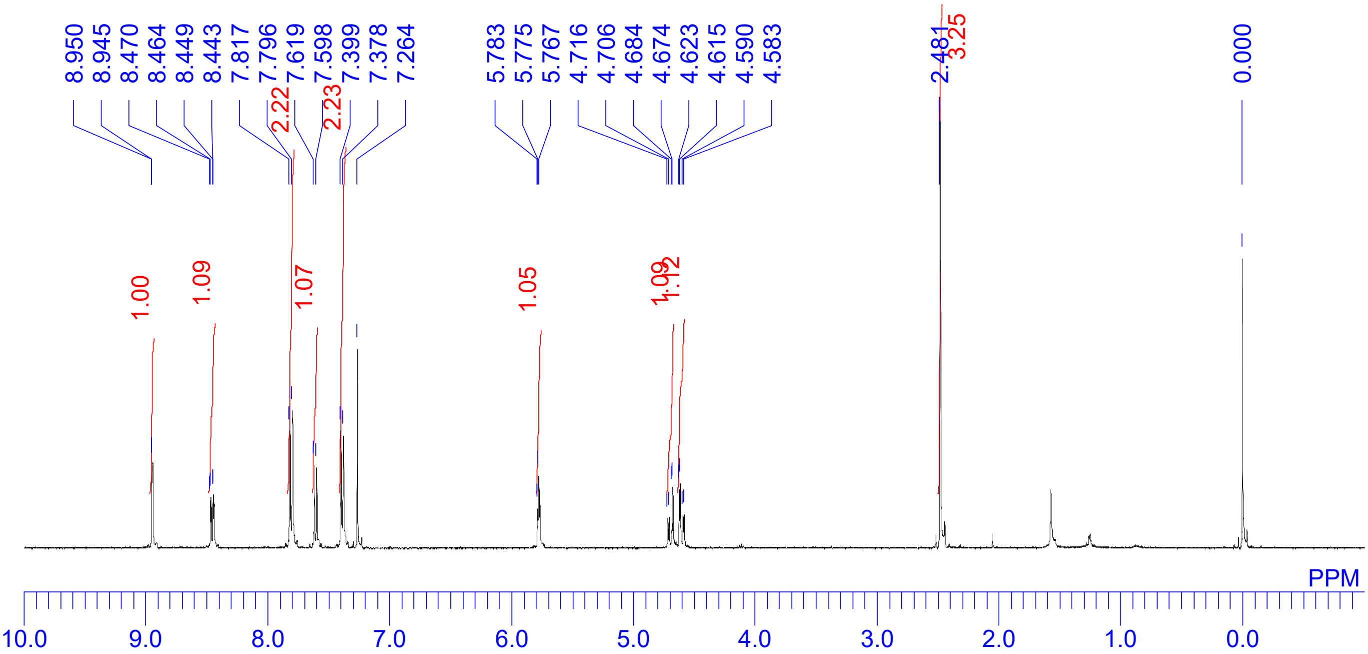


3ka (from 2k and 5a)

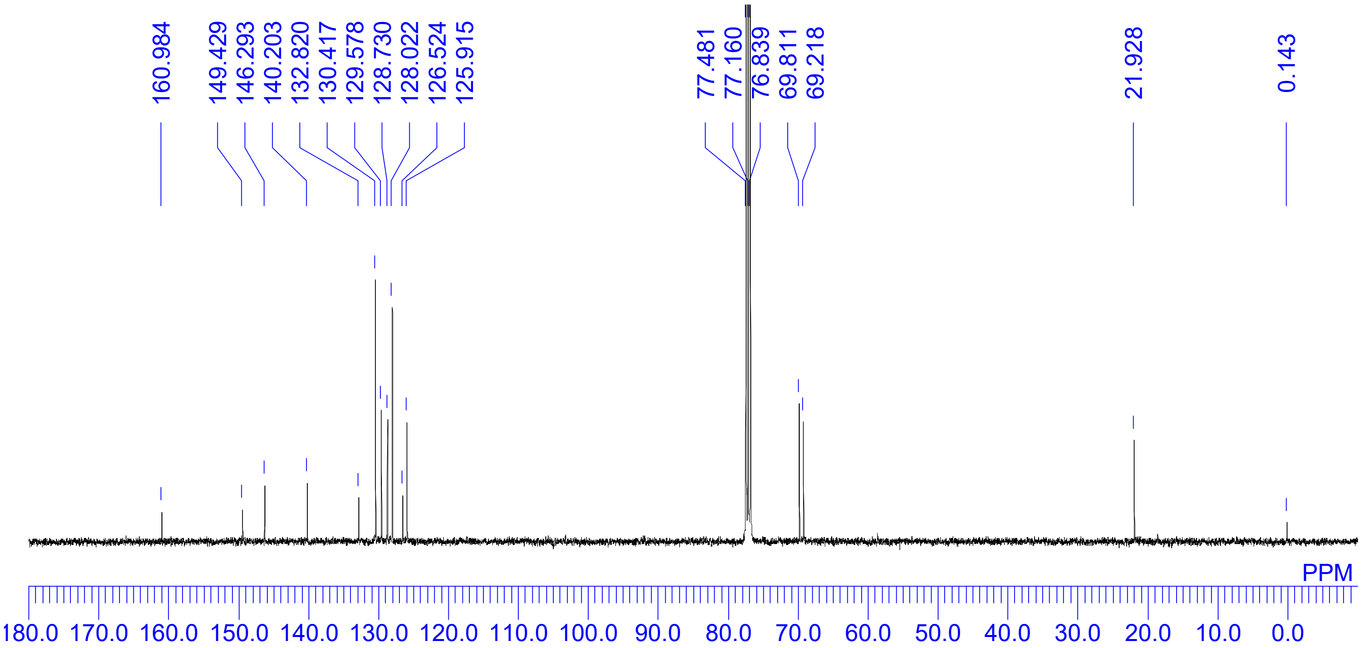
7-nitro-1-oxoisochroman-4-yl 4-methylbenzenesulfonate



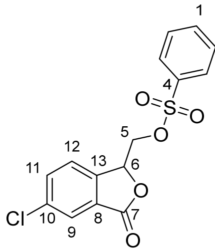
^{1}H NMR (400 MHz, $CDCl_3$)



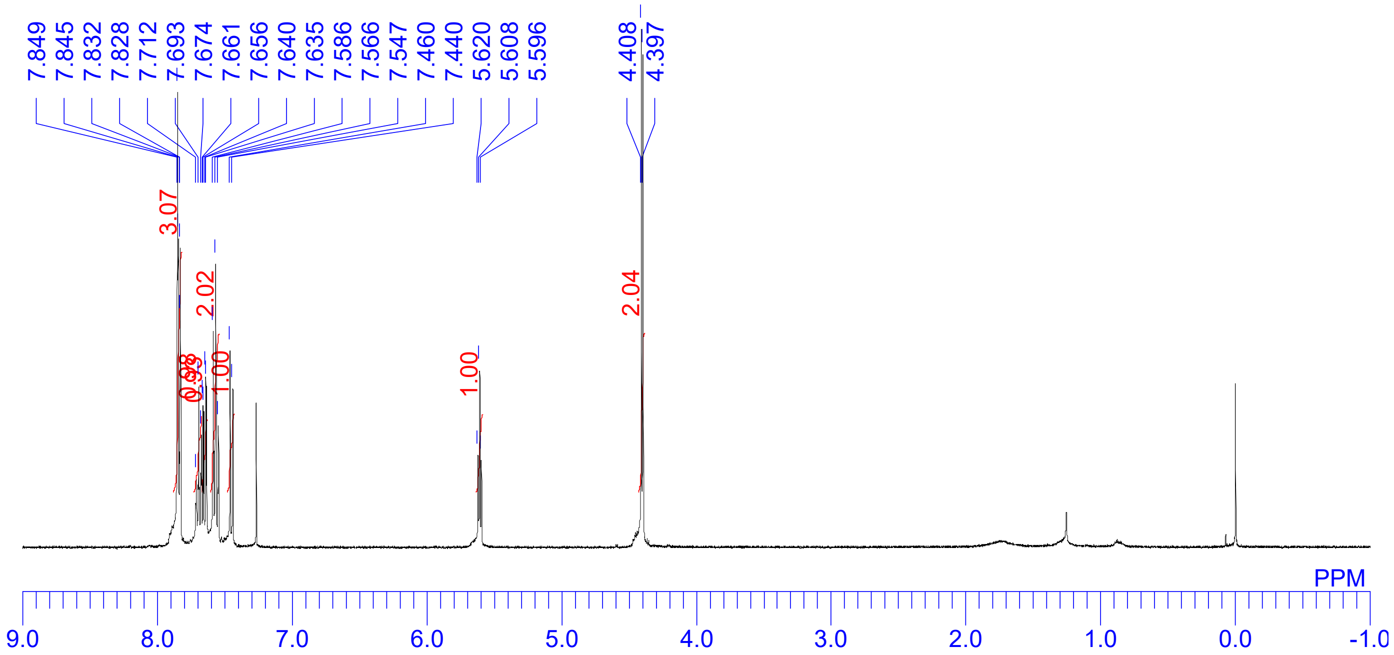
^{13}C NMR (100 MHz, $CDCl_3$)



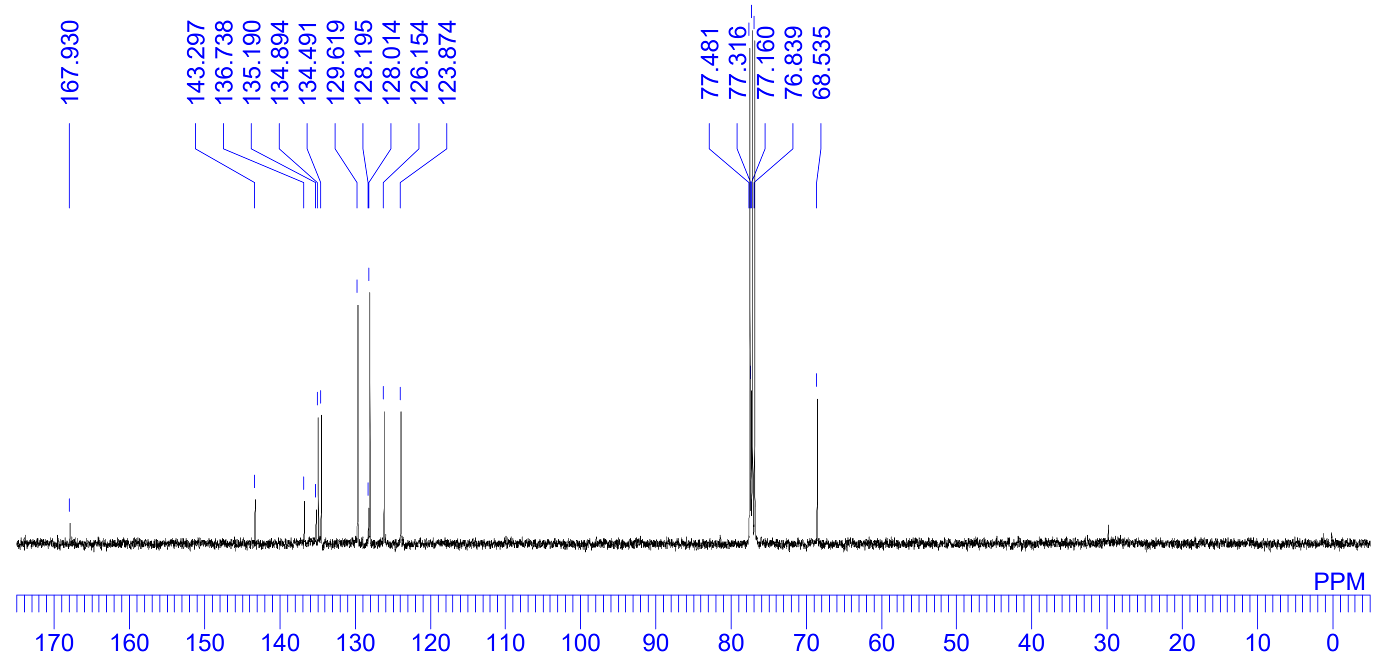
4ab (from 2a and 5b)



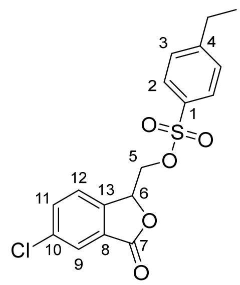
^{1}H NMR (400 MHz, CDCl$_3$)



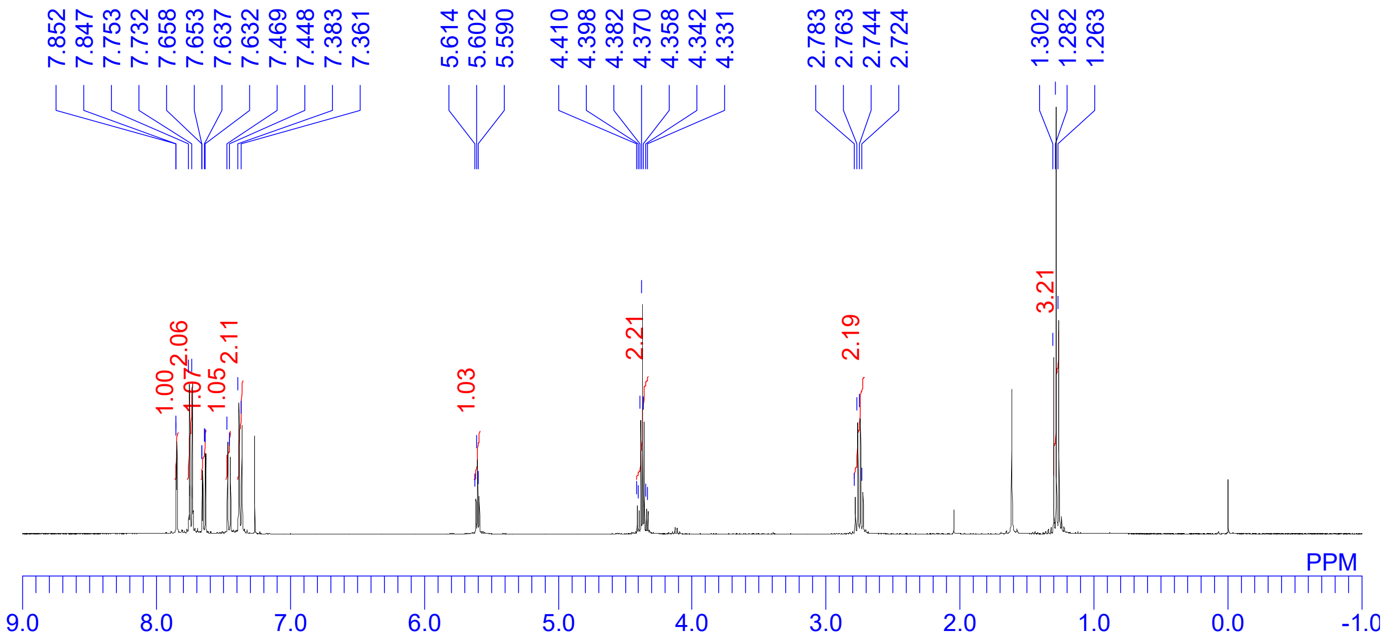
^{13}C NMR (100 MHz, CDCl$_3$)



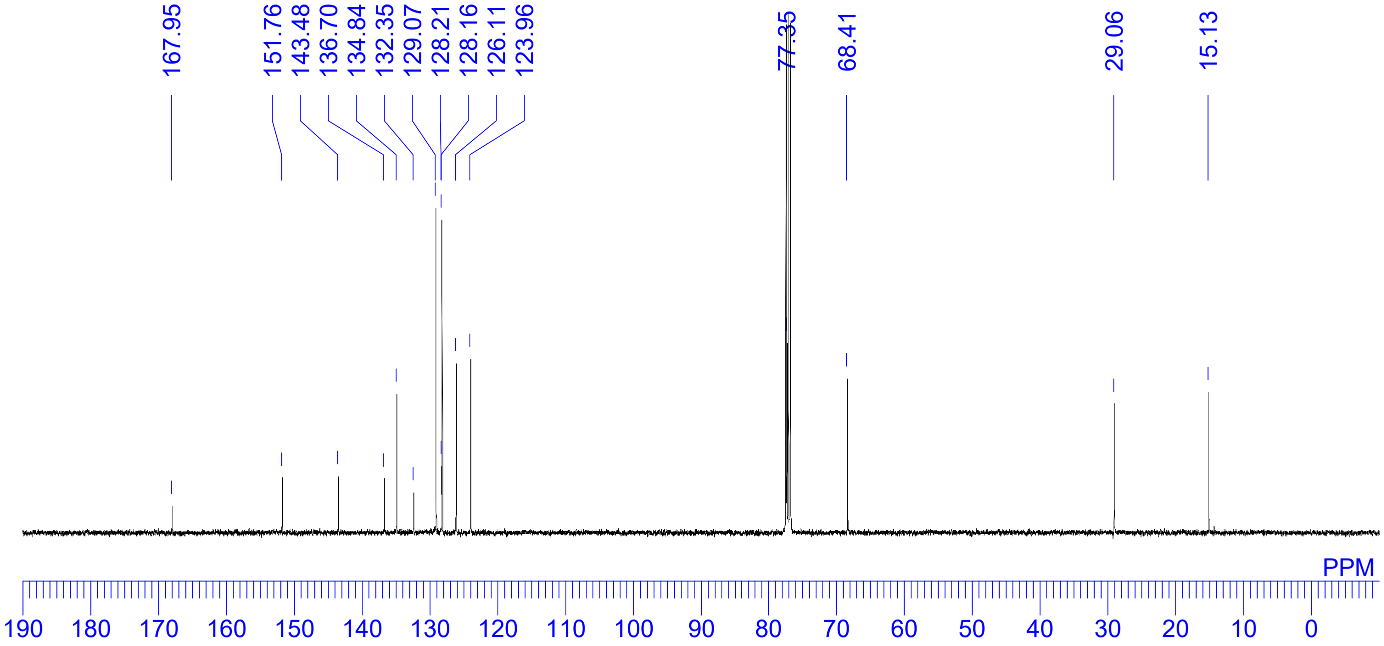
4ac (from 2a and 5c)



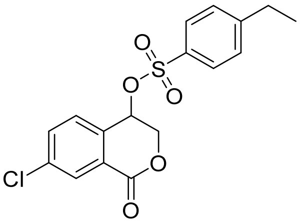
^{1}H NMR (400 MHz, CDCl$_3$)



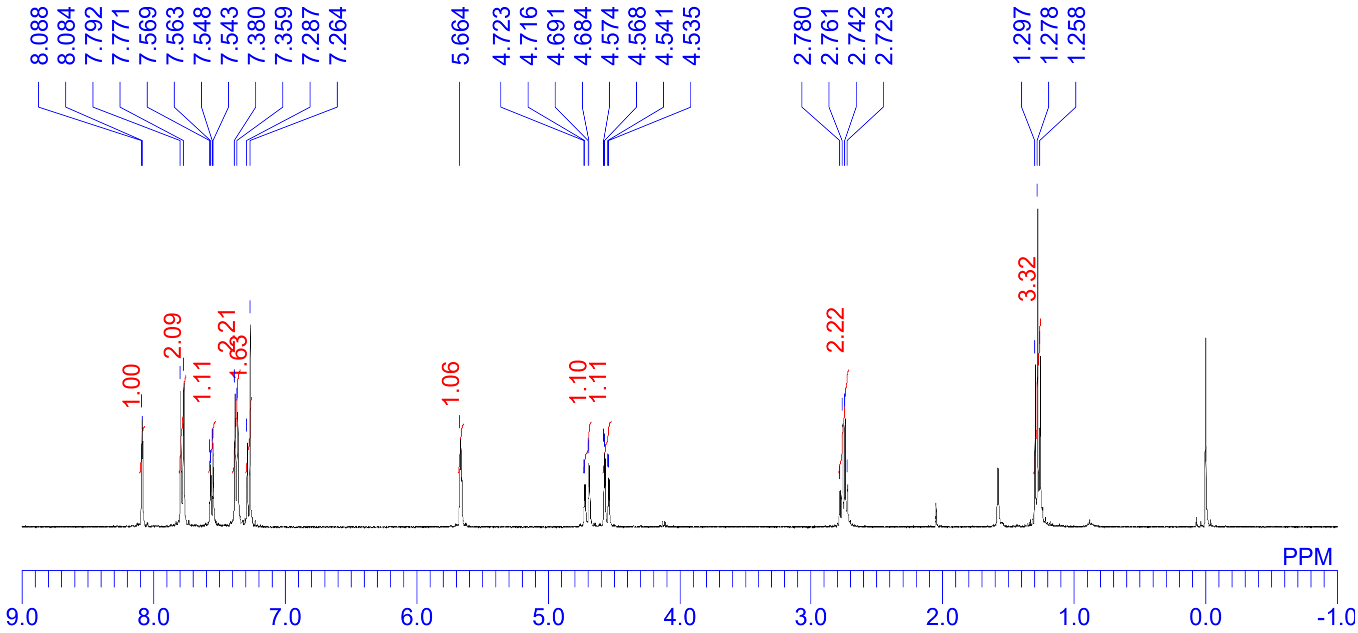
^{13}C NMR (100 MHz, CDCl$_3$)



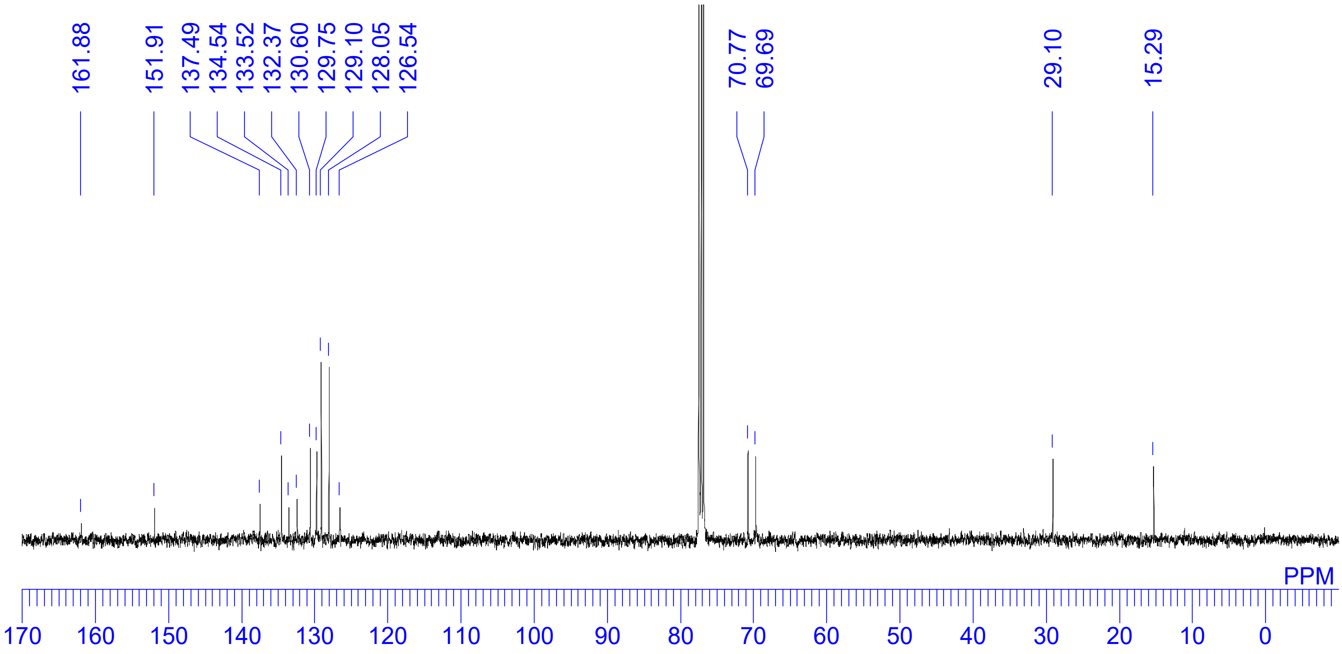
4ac (from 2a and 5c)



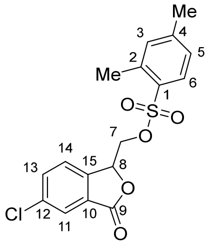
^{1}H NMR (400 MHz, CDCl$_3$)



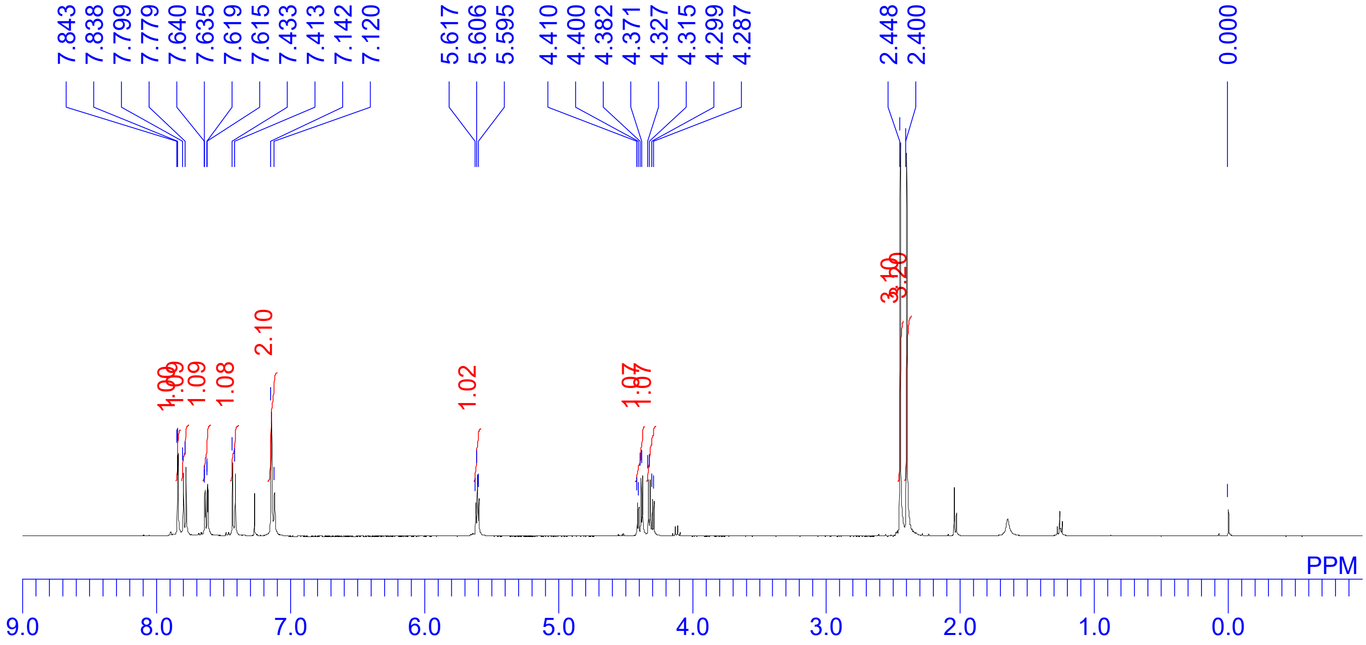
^{13}C NMR (100 MHz, CDCl$_3$)



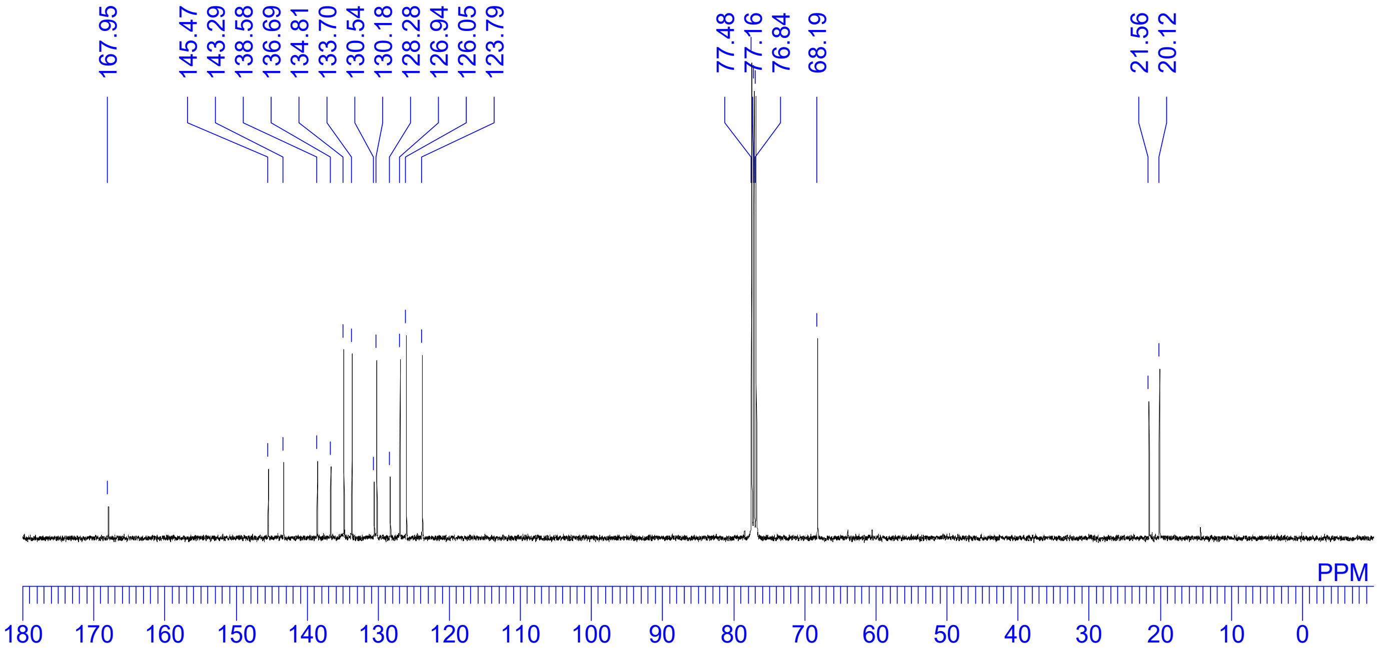
4ad (from 2a and 5d)



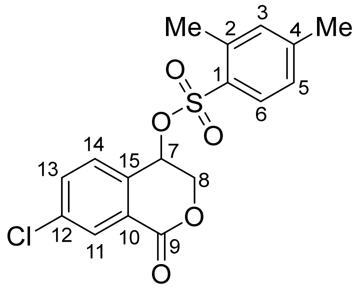
^{1}H NMR (400 MHz, CDCl$_3$)



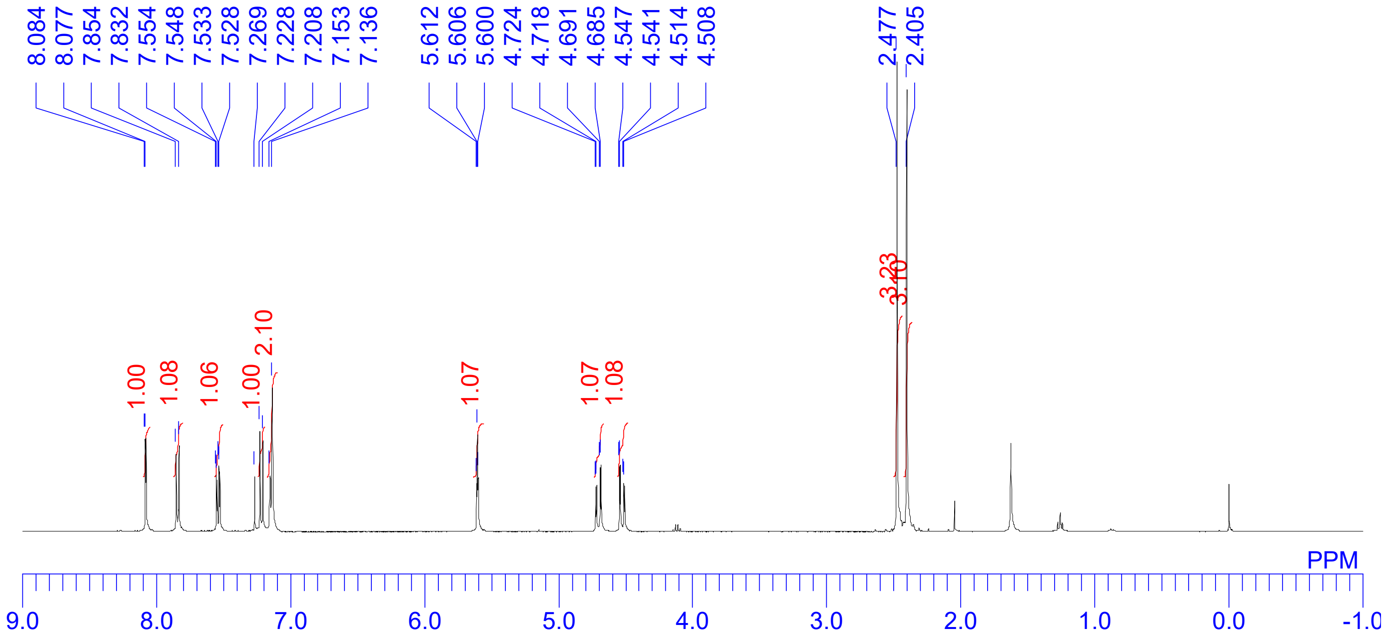
^{13}C NMR (100 MHz, CDCl$_3$)



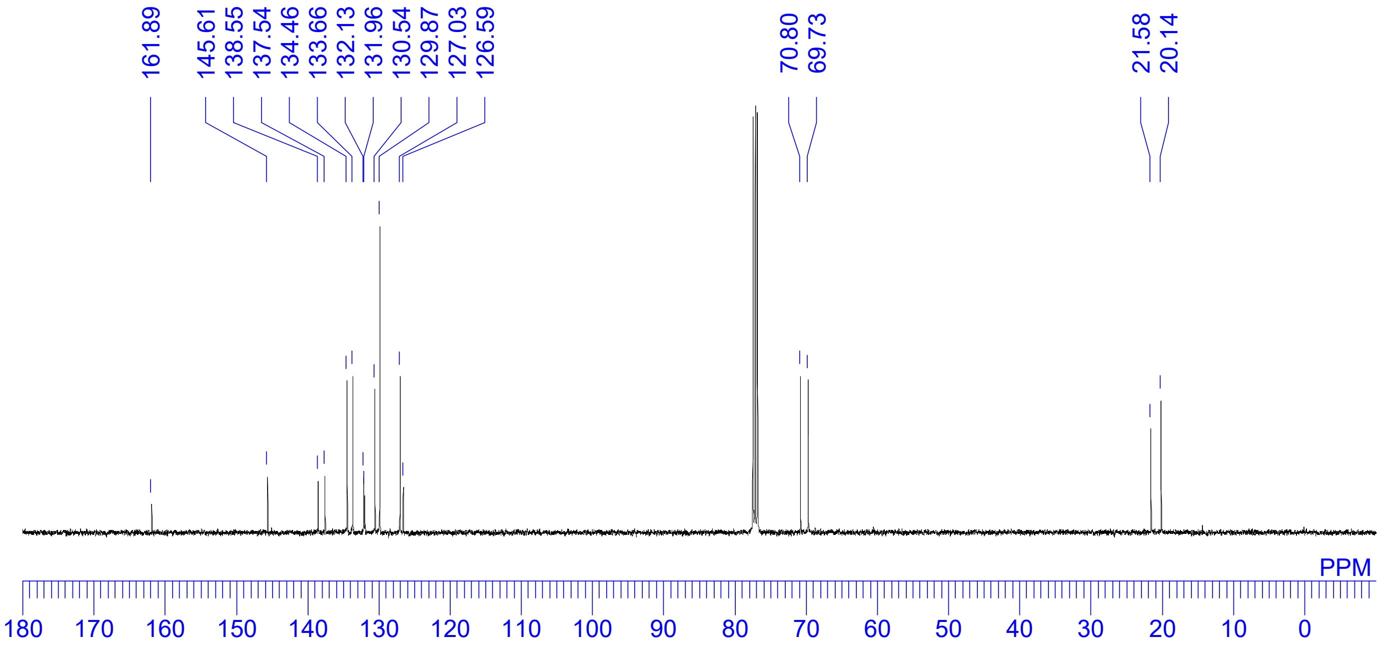
3ad (from 2a and 5d)



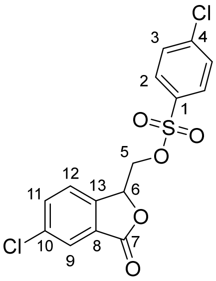
^{1}H NMR (400 MHz, CDCl$_3$)



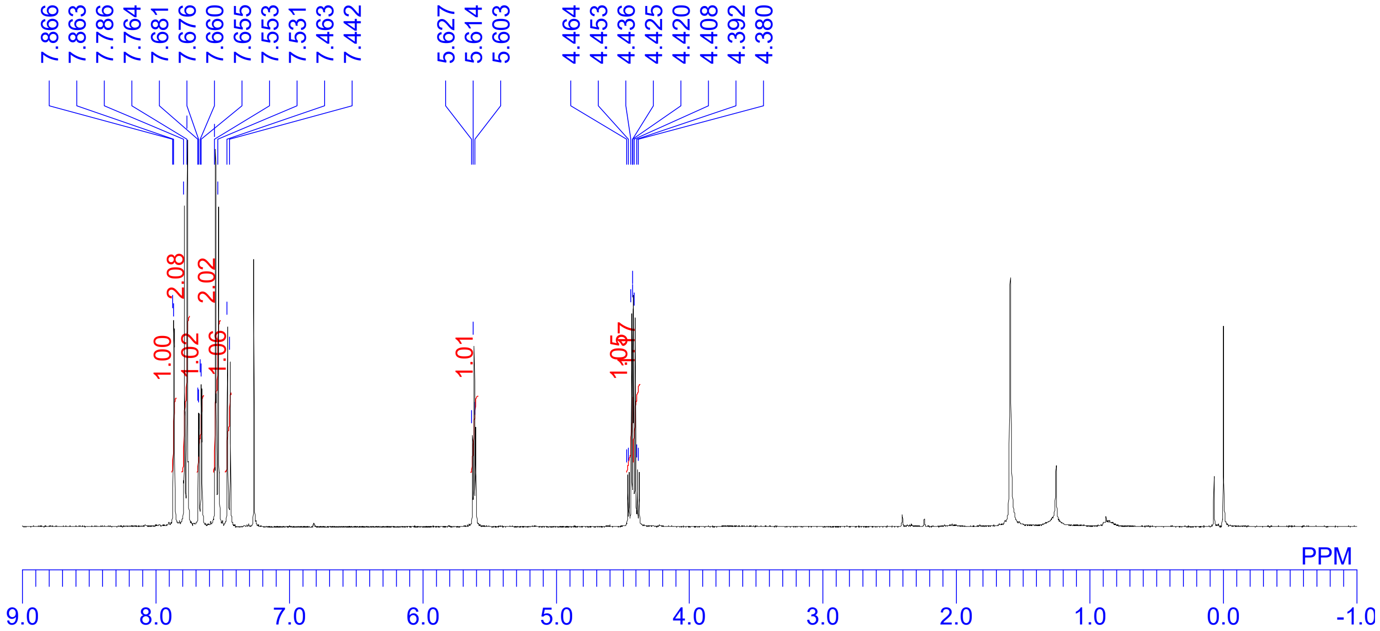
^{13}C NMR (100 MHz, CDCl$_3$)



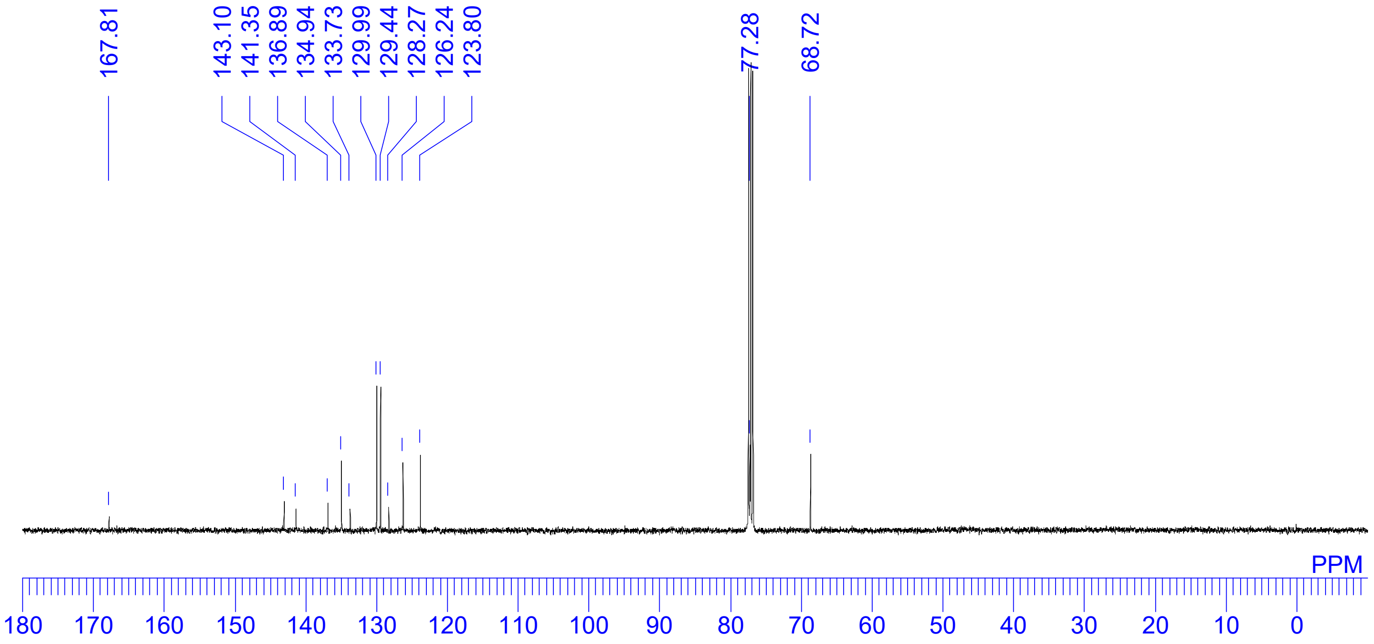
4ae (from 2a and 5e)



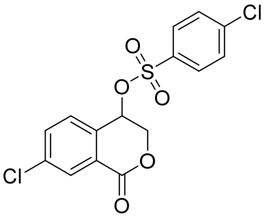
^{1}H NMR (400 MHz, CDCl$_3$)



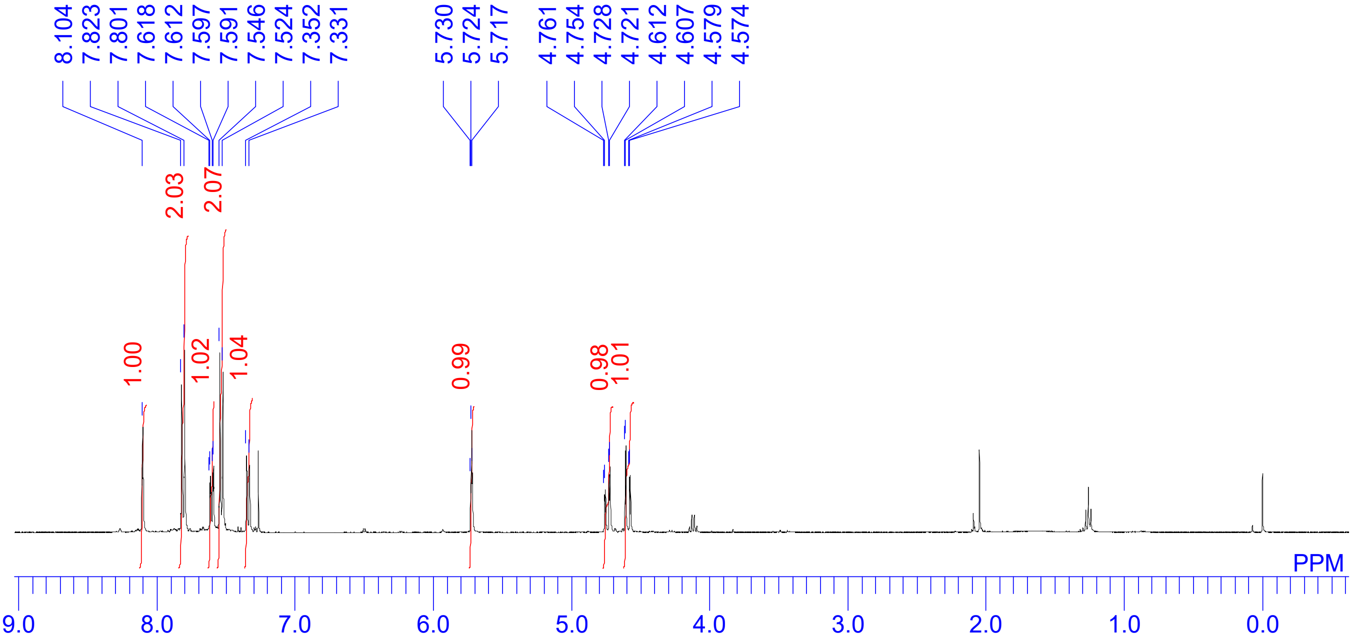
^{13}C NMR (100 MHz, CDCl$_3$)



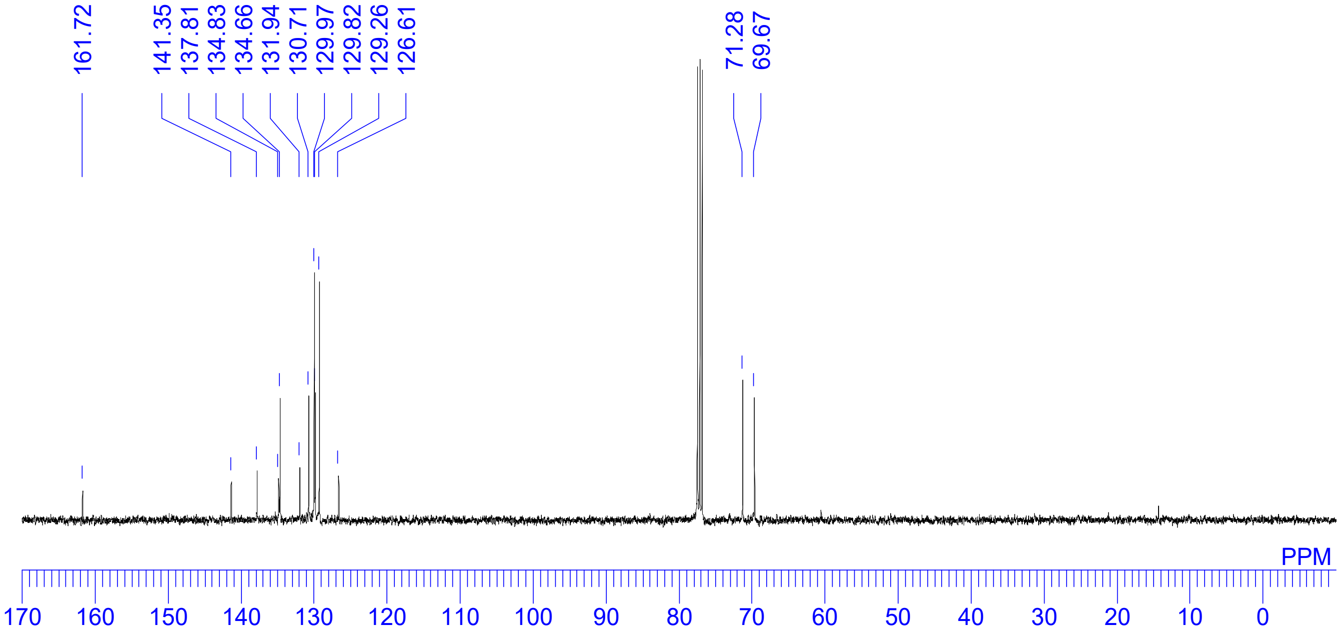
3ae (from 2a and 5e)



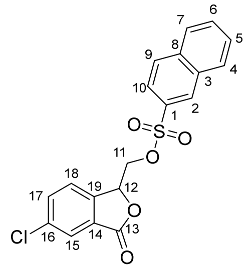
^{1}H NMR (400 MHz, CDCl$_3$)



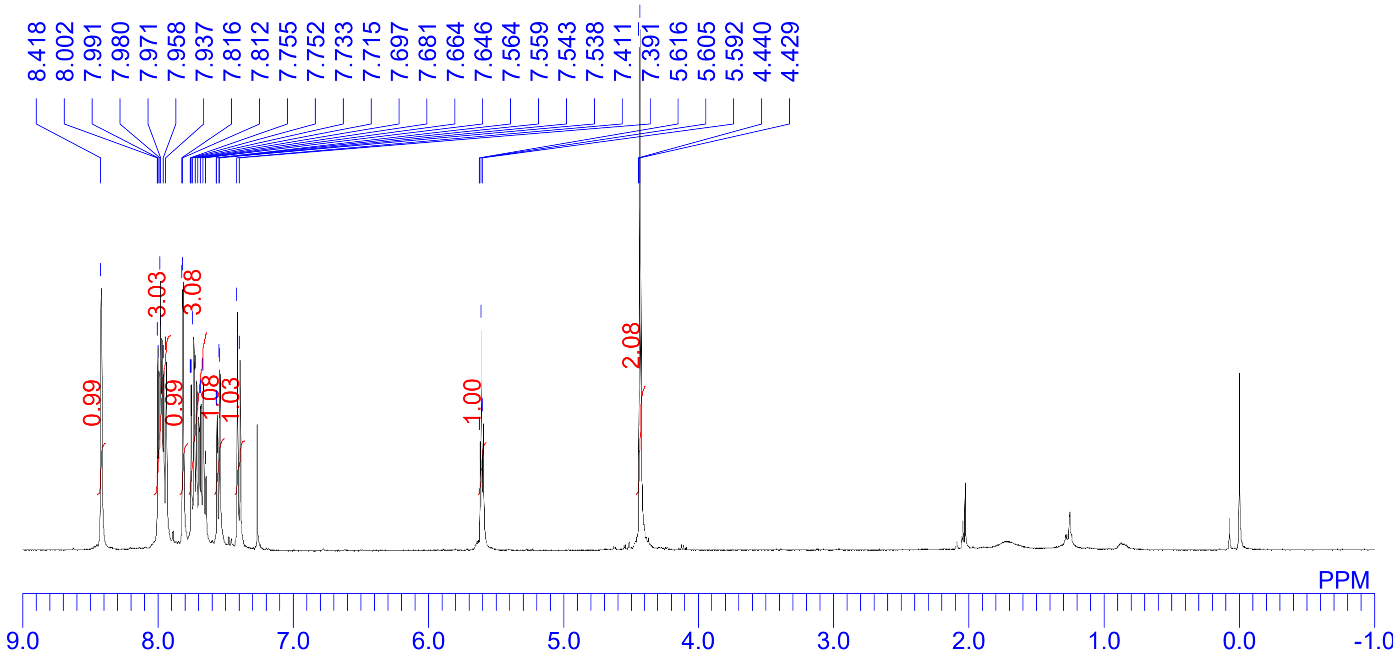
^{13}C NMR (100 MHz, CDCl$_3$)



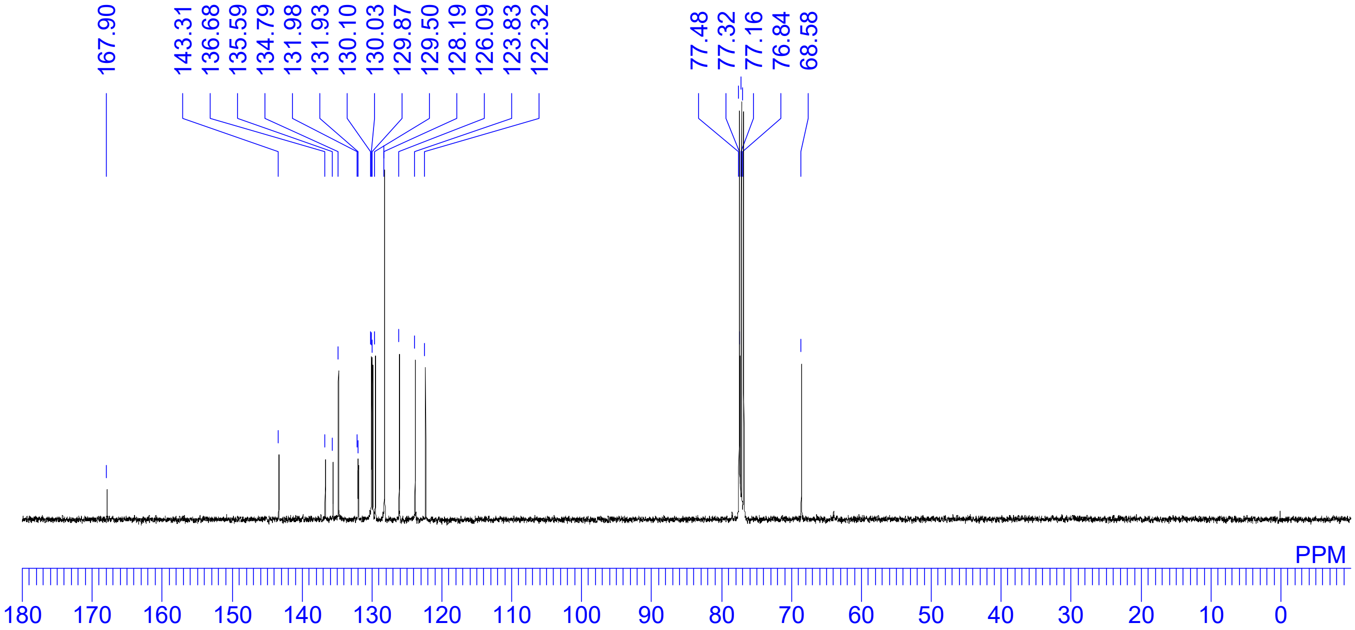
4af (from 2a and 5f)



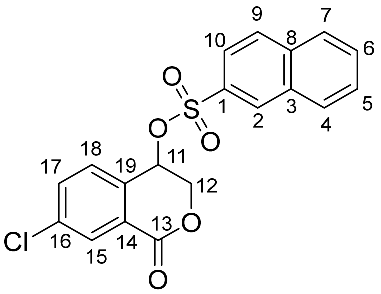
^{1}H NMR (400 MHz, CDCl$_3$)



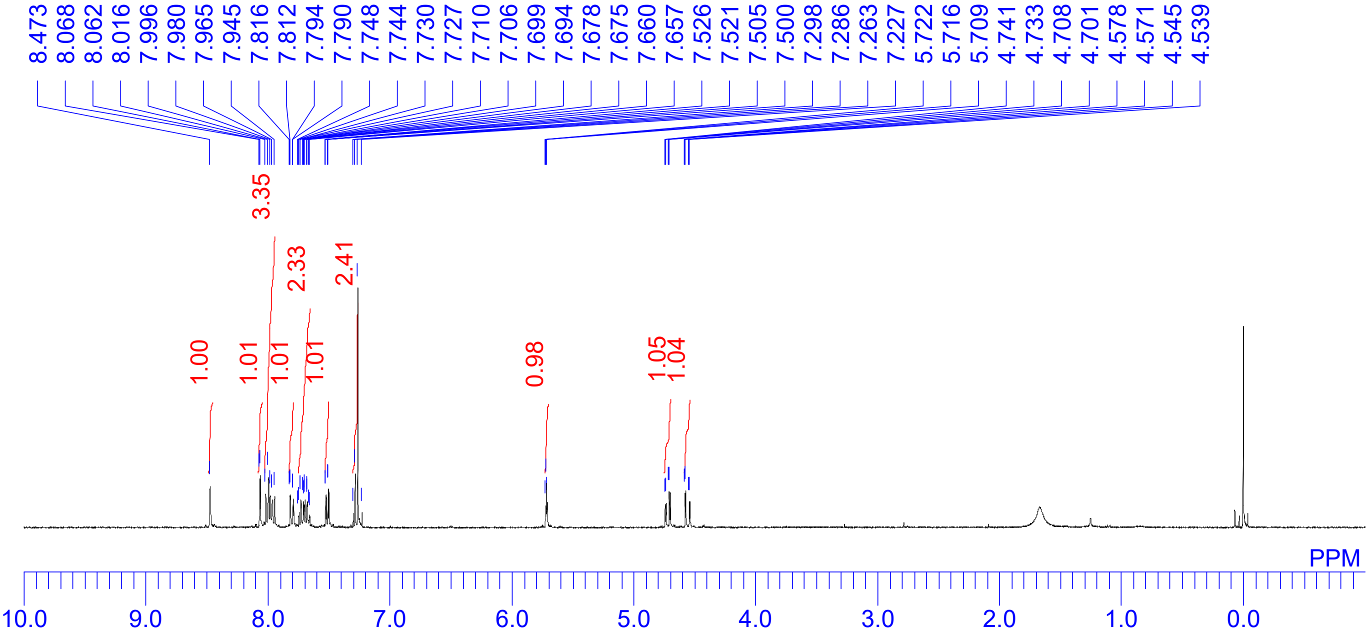
^{13}C NMR (100 MHz, CDCl$_3$)



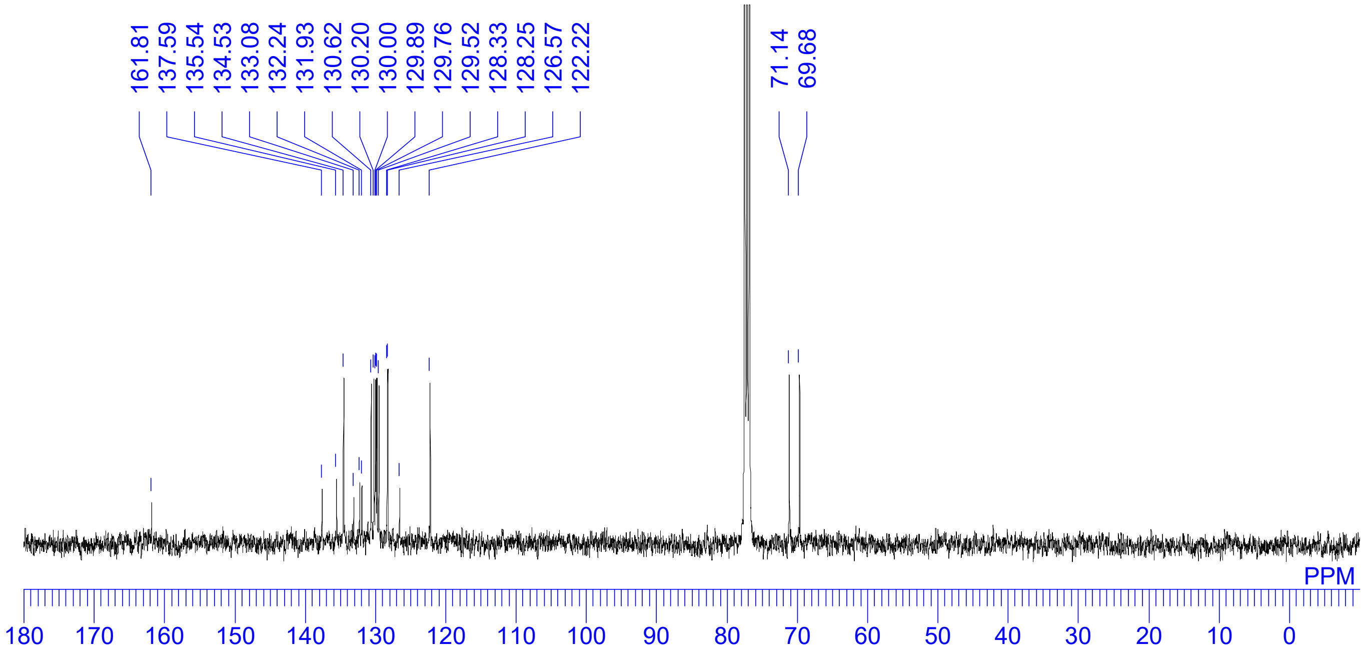
3af (from 2a and 5f)



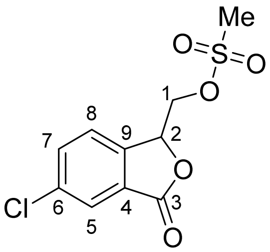
^{1}H NMR (400 MHz, CDCl$_3$)



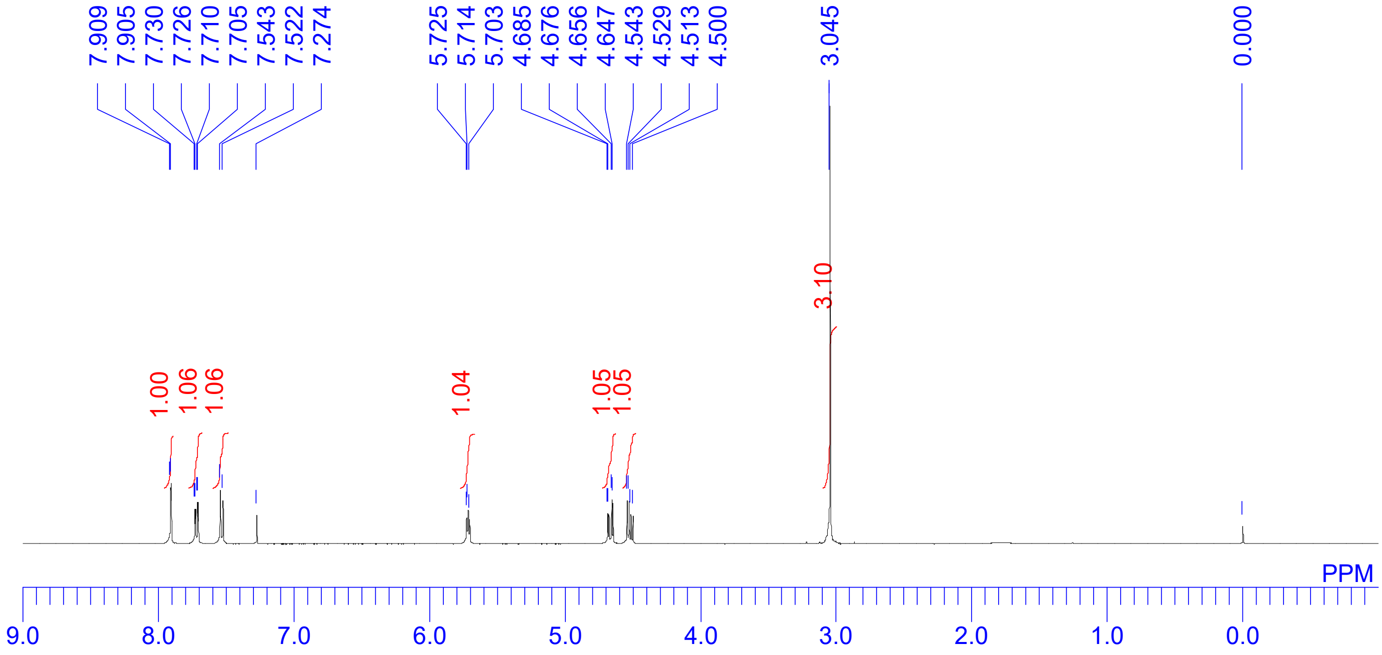
^{13}C NMR (100 MHz, CDCl$_3$)



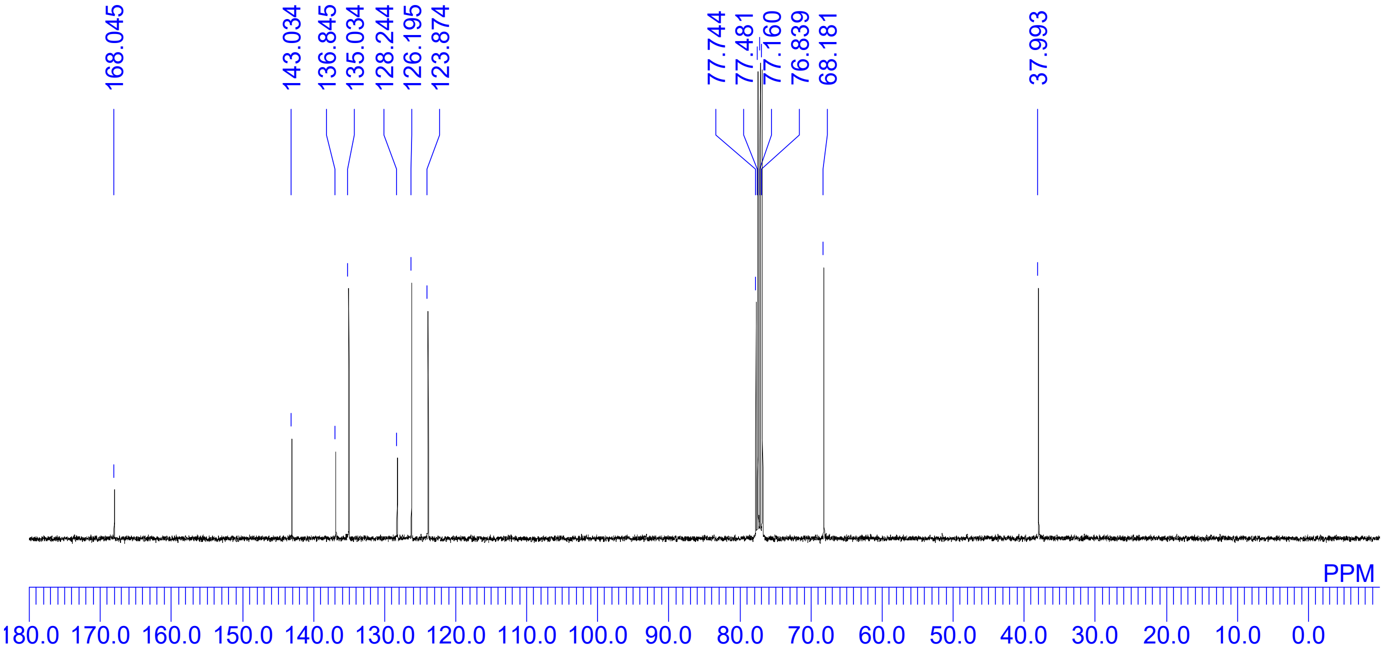
4ag (from 2a and 5g)



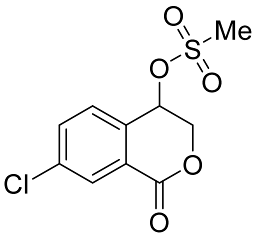
^{1}H NMR (400 MHz, CDCl$_3$)



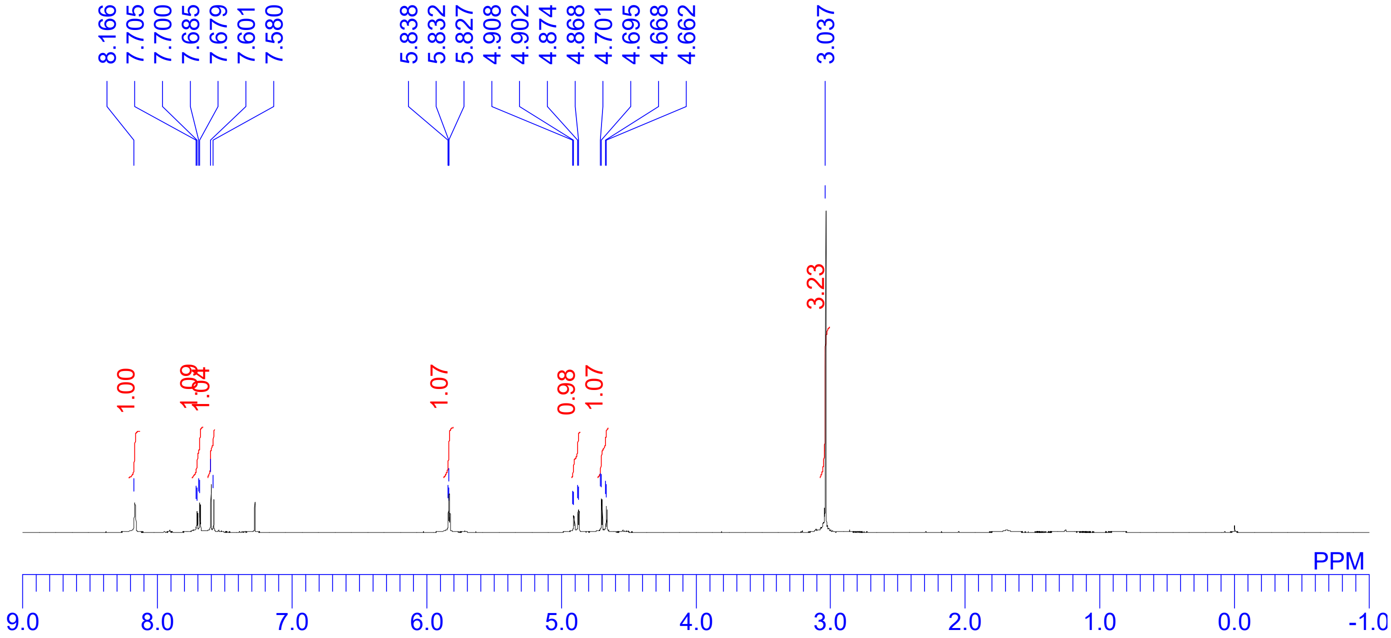
^{13}C NMR (100 MHz, CDCl$_3$)



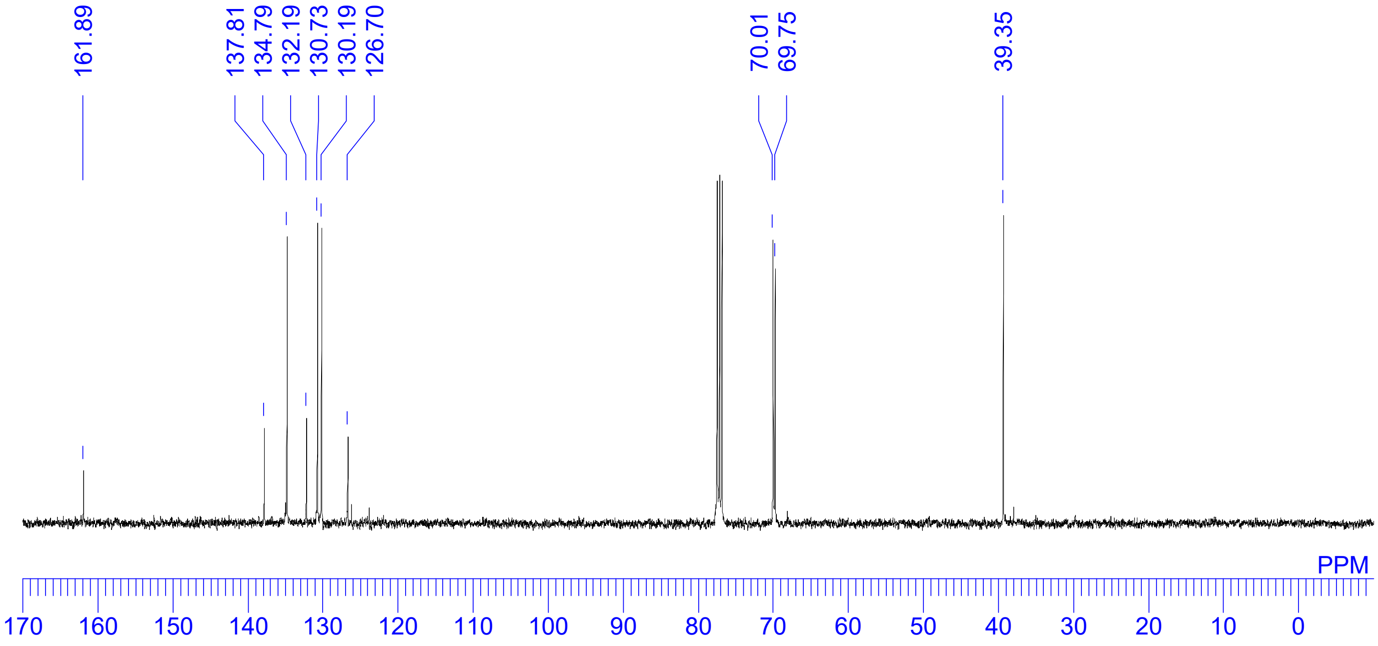
3ag (from 2a and 5g)



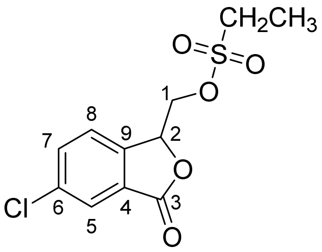
^{1}H NMR (400 MHz, $CDCl_3$)



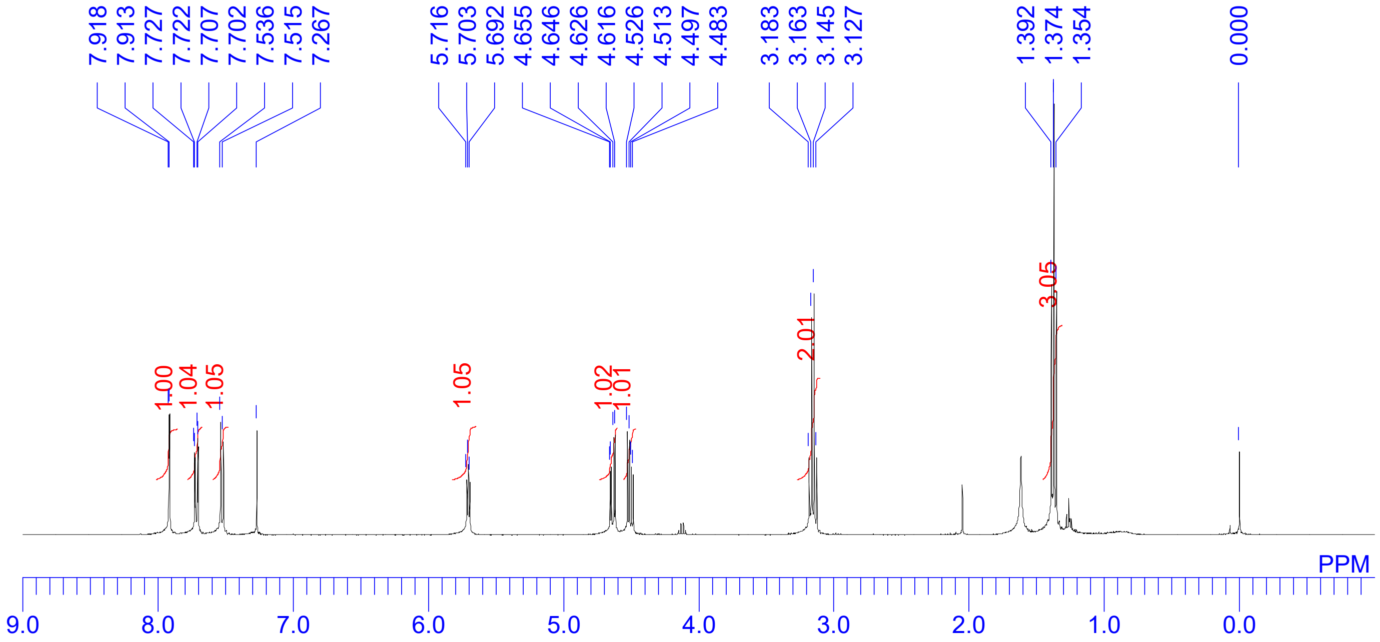
^{13}C NMR (100 MHz, $CDCl_3$)



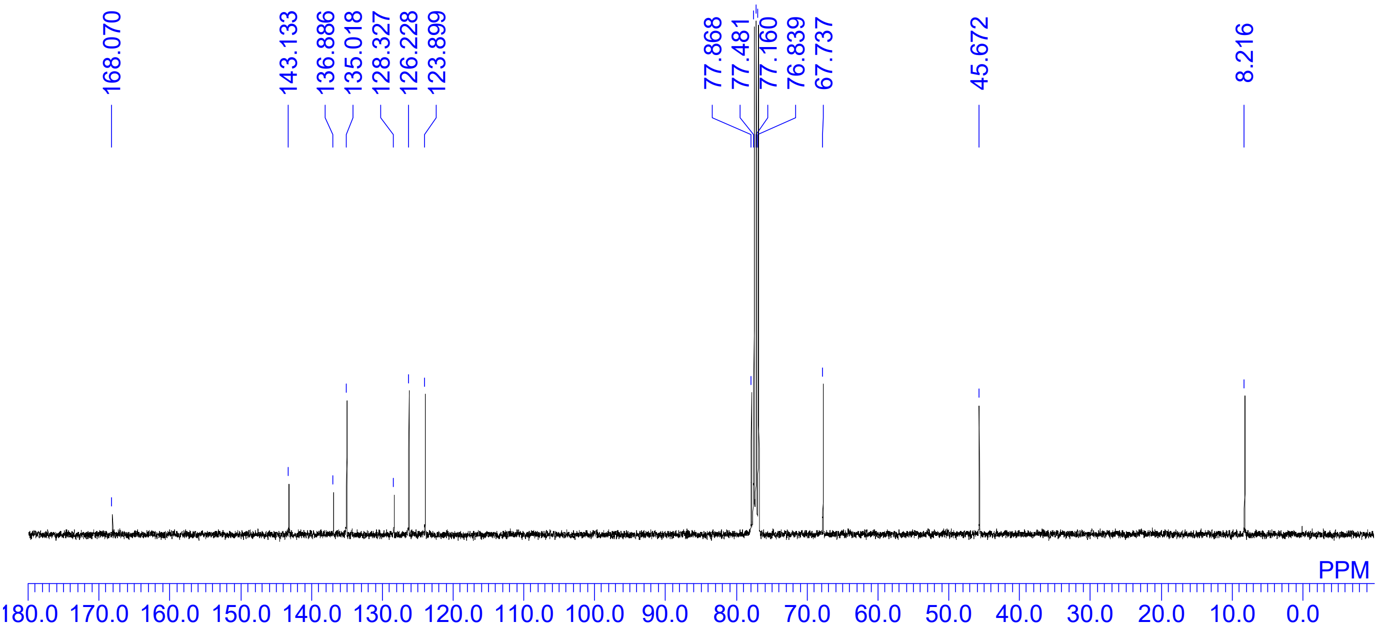
4ah (from 2a and 5h)



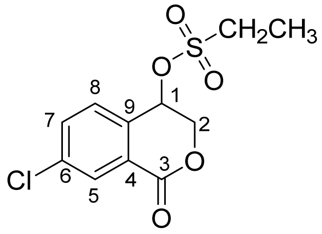
^{1}H NMR (400 MHz, CDCl$_3$)



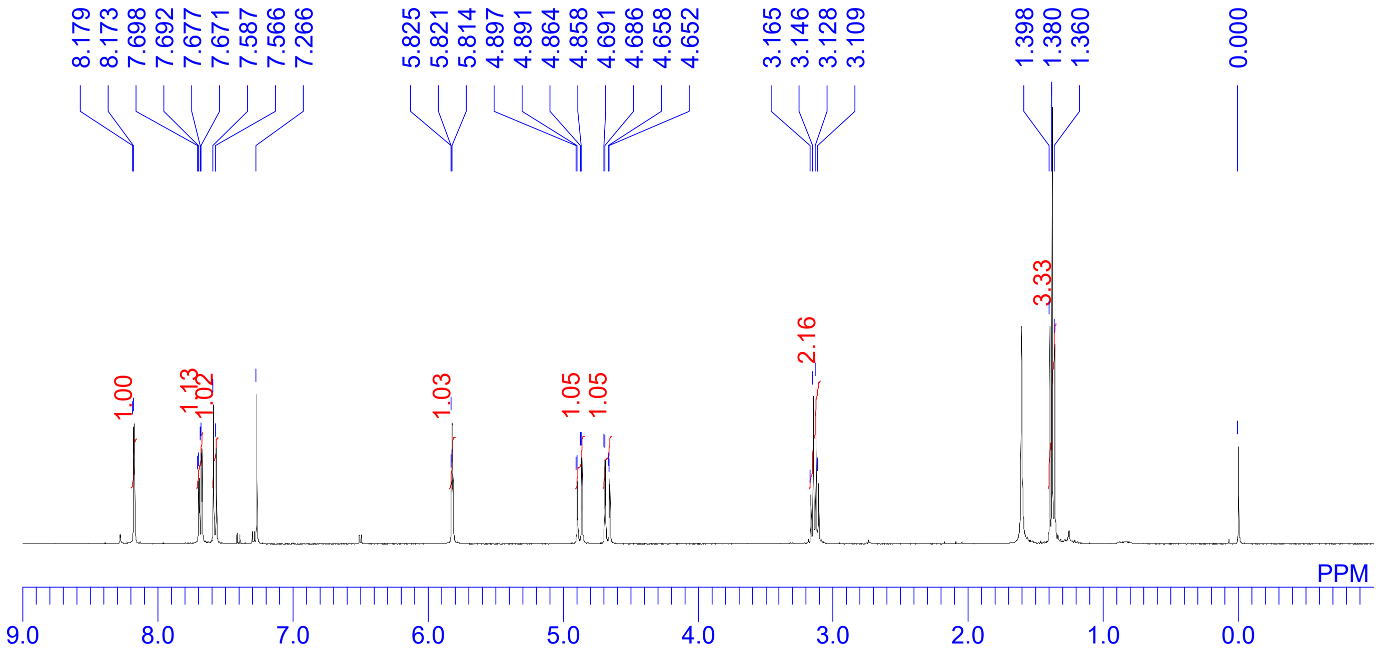
^{13}C NMR (100 MHz, CDCl$_3$)



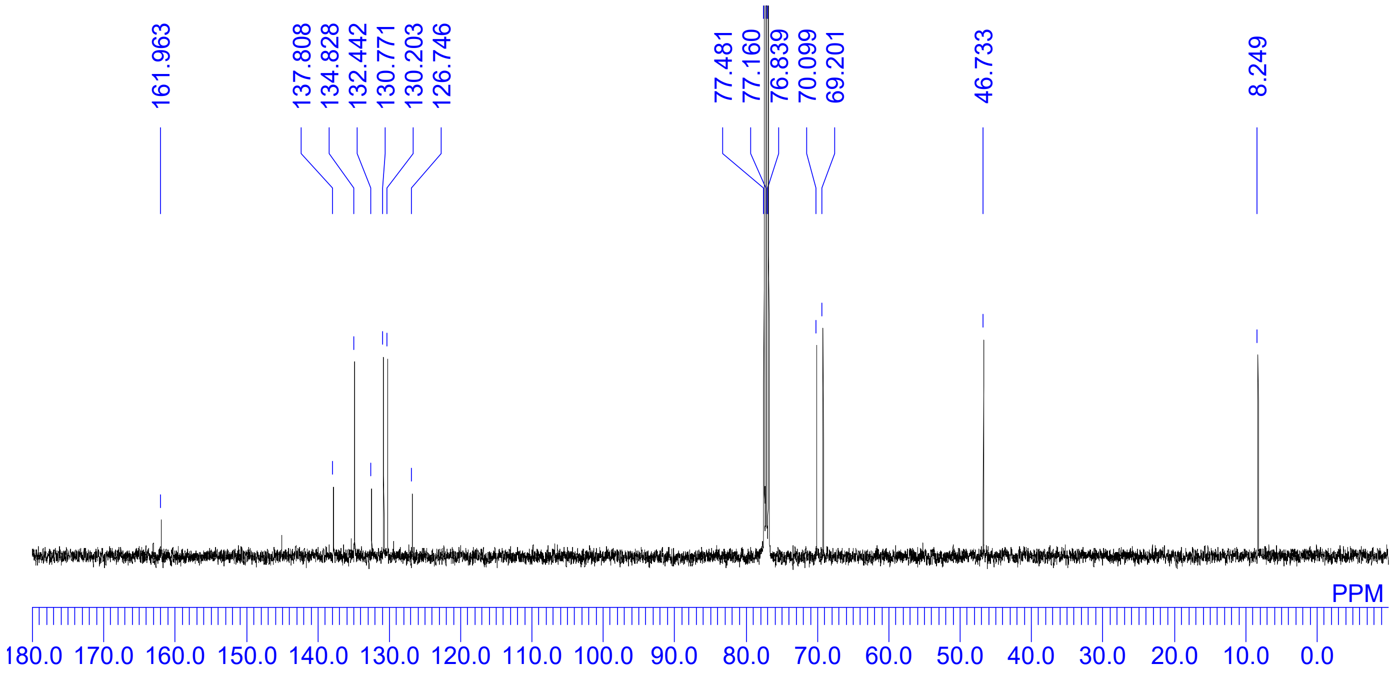
3ah (from 2a and 5h)



^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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