Supplementary Information

Site-selective aromatic C–H λ^3-iodanation with cyclic iodine(III) electrophile in solution and solid phases

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Contents

1. Materials and Methods

General. All reactions dealing with air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere or in an argon-filled glove box. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed as described by Still et al., using 40–63 μm silica gel (Si 60, Merck). ^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-300 (300 MHz) or Bruker AV-400/BBFO-400 (400 MHz) NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and $CDCl_3$ (77.0 ppm) or DMSO (39.0 ppm), respectively. High-resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points were determined using a capillary melting point apparatus. The mechanochemical reactions were placed onto Retsch Mixer Mill MM400 machine and subjected to 30 Hz milling.

Materials. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, or other commercial suppliers and were used as received. Toluene, THF, and Et_2O were distilled over Na/benzophenone, and stored under N_2. MeCN and CH_2Cl_2 were distilled over CaH_2, and stored under N_2. 3,3-Bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl trifluoromethanesulfonate (benziodoxole triflate, BXT; **1**) was synthesized according to the literature procedure.[1] Mostly arenes were commercially available compounds. **2aa** was synthesized according to the literature procedure, and the spectral data showed good agreement with the literature data.[2]

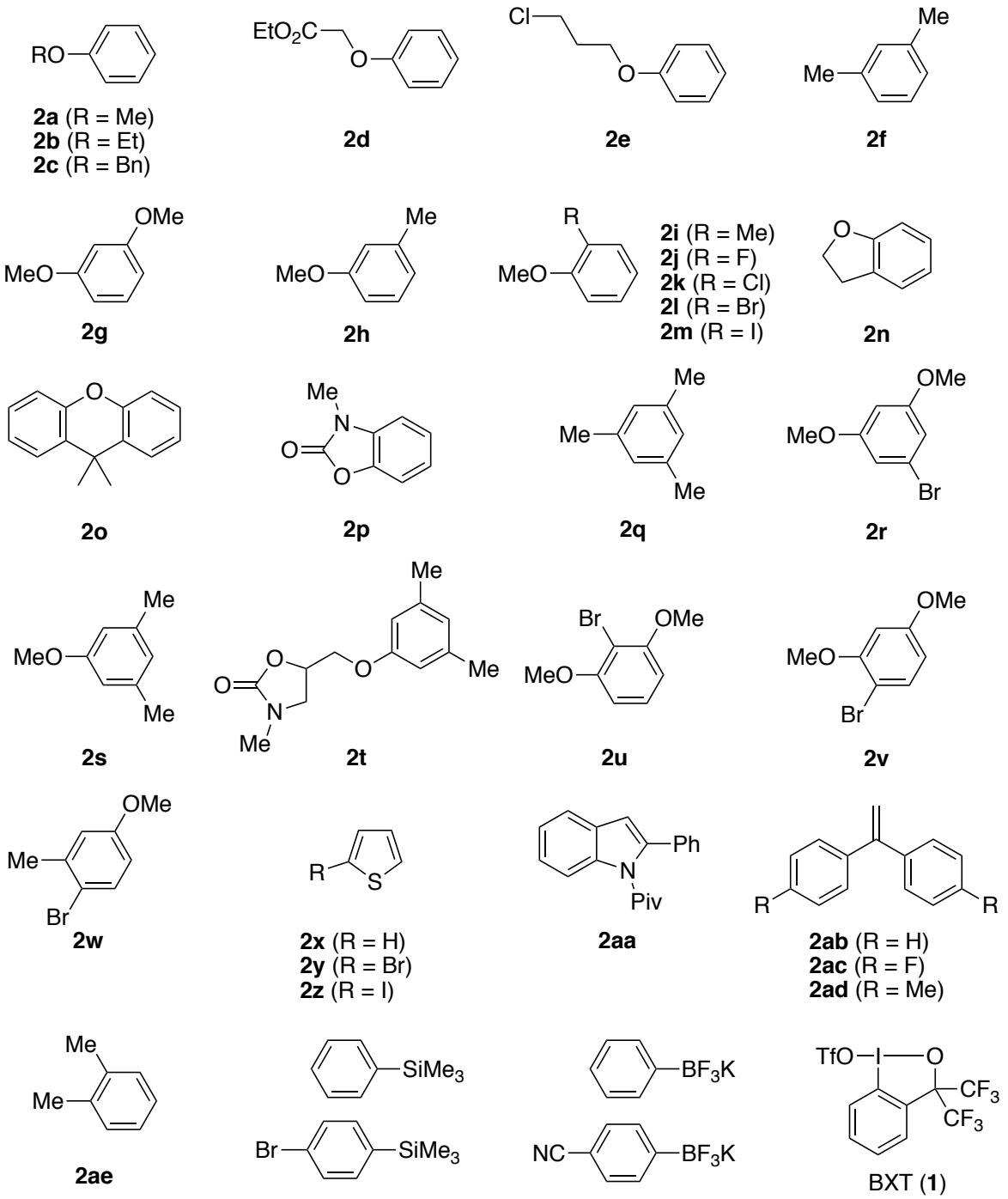
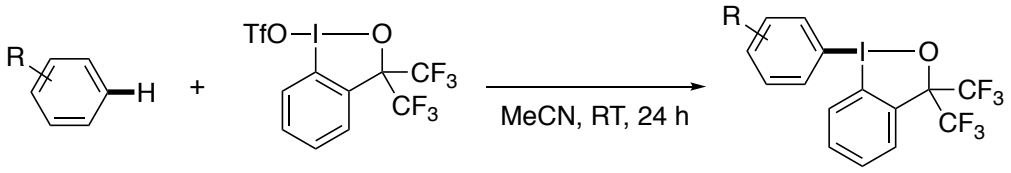


Figure S1. Starting materials used in this study.

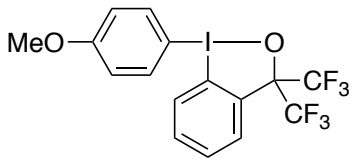
2. Aromatic C–H λ³-Iodanation with Benziodoxole Triflate



2a–2ad BXT (**1**) **3a–3ad**

General Procedure: In an argon-filled glove box, a 4 mL vial equipped with a magnetic stir bar was charged sequentially with aromatic compound **2** (0.30 mmol) and MeCN (0.5 mL), followed by the addition of BXT (**1**, 103.6 mg, 0.20 mmol). The vial was closed and taken out of the glove box. The mixture was stirred at room temperature for 24 h. Saturated aq. Na_2CO_3 (4 mL) was added, and then the mixture was extracted with EtOAc (5 mL x 3). The combined organic layer was washed with H_2O (5 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

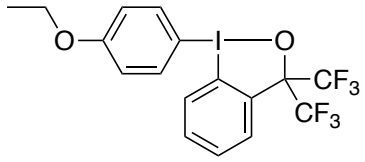
Note: While all the λ³-iodanation products reported below were synthesized according to the above procedure using a glove box, the reaction proved not to require particular care to exclude air and moisture. Thus, the model reaction was performed by charging a vial with **2a**, MeCN, and **1** in an open air, closing the vial, and stirring the mixture at room temperature for 24 h to afford the desired product **3a** in 95% yield as determined by ^{19}F NMR using 1,4-bis(trifluoromethyl)benzene as an internal standard.



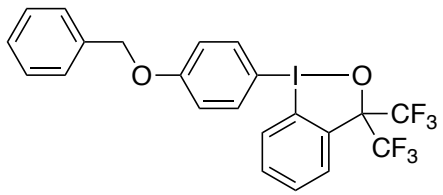
1-(4-Methoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ³-benzo[*d*][1,2]iodaoxole (3a): Prepared according to the general procedure; White solid (87.6 mg, 92% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 199-201 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (app. d, J = 7.6 Hz, 1H), 7.78 (d, J = 8.6 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.39-7.31 (m, 1H), 7.00 (d, J = 8.7 Hz, 2H), 6.82 (dd, J = 8.3, 0.8 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 138.7, 131.9, 131.0, 130.2 (two signals overlapped), 127.3, 124.1 (q, J_{C-F} = 290.1 Hz), 117.0, 111.8, 108.1, 81.9-80.8 (m), 55.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{16}H_{12}O_2F_6I$ $[M + H]^+$ 476.9786, found 476.9788.

Procedure for 3 mmol-scale reaction: A 25 mL Schlenk tube equipped with a magnetic stir

bar was charged sequentially with anisole **2a** (0.49 g, 4.5 mmol) and MeCN (7.5 mL), followed by the addition of BXT (1.55 g, 3.0 mmol). The mixture was stirred at room temperature for 24 h. Saturated aq. Na_2CO_3 (30 mL) was added, and then the mixture was extracted with EtOAc (20 mL x 3). The combined organic layer was washed with H_2O (30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: hexane (100 mL) → hexane/EtOAc = 5/1 (approx. 120 mL) → hexane/EtOAc = 2/1 (approx. 300 mL)) to afford the desired product **3a** (1.23 g, 86% yield).

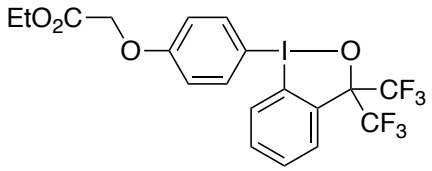


1-(4-Ethoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3b): Prepared according to the general procedure; White solid (83.3 mg, 85% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (app. d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.7 Hz, 2H), 7.54 (t, J = 7.1 Hz, 1H), 7.39-7.31 (m, 1H), 6.99 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 7.8 Hz, 1H), 4.13 (q, J = 7.0 Hz, 2H), 1.48 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 138.6, 131.9, 131.0, 130.1 (two signals overlapped), 127.3, 124.1 (q, $J_{C\text{-}F}$ = 290.3 Hz), 117.4, 111.8, 107.7, 81.9-80.7 (m), 63.9, 14.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.3; HRMS (ESI) Calcd for $C_{17}H_{14}O_2F_6I$ $[M + H]^+$ 490.9943, found 490.9949.

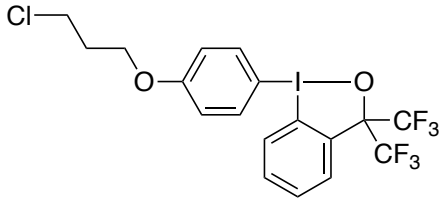


1-(4-(Benzyloxy)phenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3c): Prepared according to the general procedure; Brown solid (100.5 mg, 91% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (app. d, J = 7.6 Hz, 1H), 7.76 (d, J = 8.7 Hz, 2H), 7.59-7.50 (m, 1H), 7.49-7.39 (m, 4H), 7.39-7.30 (m, 2H), 7.07 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 7.6 Hz, 1H), 5.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 138.7, 135.8, 131.9, 131.0, 130.2 (two signals overlapped), 128.8, 128.4, 127.5, 127.4, 124.1 (q, $J_{C\text{-}F}$ = 290.4 Hz), 117.8, 111.8, 108.5, 81.9-80.7 (m), 70.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{22}H_{16}O_2F_6I$ $[M + H]^+$ 553.0099, found

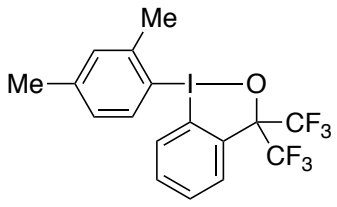
553.0106.



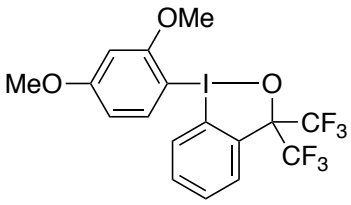
Ethyl 2-(4-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)phenoxy)acetate (3d): Prepared according to the general procedure with a modified temperature (60 °C); White solid (80.0 mg, 73% yield); R_f 0.3 (hexane/EtOAc = 1/1); m.p. 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (app. d, J = 7.7 Hz, 1H), 7.79 (d, J = 8.7 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.41-7.32 (m, 1H), 7.01 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.3 Hz, 1H), 4.73 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 160.6, 138.7, 132.0, 130.9, 130.2 (two signals overlapped), 127.4, 124.1 (q, $J_{C\text{-}F}$ = 290.2 Hz), 117.5, 111.6, 109.5, 81.8-80.7 (m), 65.1, 61.7, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1; HRMS (ESI) Calcd for $C_{19}H_{16}O_4F_6I$ $[M + H]^+$ 548.9998, found 548.9996.



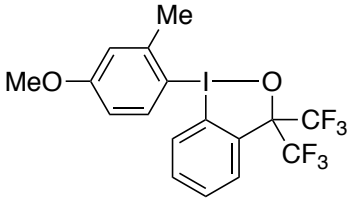
1-(4-(3-Chloropropoxy)phenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3e): Prepared according to the general procedure; White solid (80.8 mg, 75% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 149-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (app. d, J = 7.7 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H), 7.58-7.50 (m, 1H), 7.41-7.32 (m, 1H), 7.01 (d, J = 8.8 Hz, 2H), 6.83 (dd, J = 8.3, 0.9 Hz, 1H), 4.22 (t, J = 5.8 Hz, 2H), 3.79 (t, J = 6.2 Hz, 2H), 2.37-2.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 138.7, 131.9, 130.9, 130.2 (two signals overlapped), 127.3, 124.1 (q, $J_{C\text{-}F}$ = 290.0 Hz), 117.4, 111.8, 108.4, 81.9-80.7 (m), 64.5, 41.2, 31.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.9; HRMS (ESI) Calcd for $C_{18}H_{15}O_2F_6ClI$ $[M + H]^+$ 538.9709, found 538.9710.



1-(2,4-Dimethylphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3f): Prepared according to the general procedure with a modified temperature (60 °C); White solid (58.8 mg, 62% yield, regioisomer ratio = 21:1 as determined by ^{1}H NMR); R_f 0.4 (hexane/EtOAc = 3/1); m.p. 204-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (app. d, J = 6.8 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.60-7.51 (m, 1H), 7.39-7.31 (m, 1H), 7.29 (s, 1H), 7.07 (d, J = 7.7 Hz, 1H), 6.77 (dd, J = 8.3, 0.8 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.7, 138.3, 132.0, 131.7, 131.4, 130.4, 130.3, 129.5, 126.8, 124.2 (q, $J_{C\text{-}F}$ = 290.2 Hz), 118.1, 110.9, 81.9-80.8 (m), 24.3, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{17}H_{14}OF_6I$ $[M + H]^+$ 474.9994, found 474.9994.

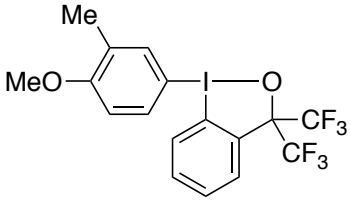


1-(2,4-Dimethoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3g): Prepared according to the general procedure; White solid (87.1 mg, 86% yield); R_f 0.4 (hexane/EtOAc = 1/1); m.p. 217-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (app. d, J = 7.0 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.57-7.48 (m, 1H), 7.39-7.30 (m, 1H), 6.83 (dd, J = 8.3, 0.8 Hz, 1H), 6.64-6.49 (m, 2H), 3.91 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 161.3, 139.5, 131.7, 131.4, 130.0, 129.9, 127.0, 124.2 (q, $J_{C\text{-}F}$ = 290.0 Hz), 111.6, 107.6, 99.2, 98.8, 82.1-80.9 (m), 56.2, 55.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{17}H_{14}O_3F_6I$ $[M + H]^+$ 506.9892, found 506.9888.

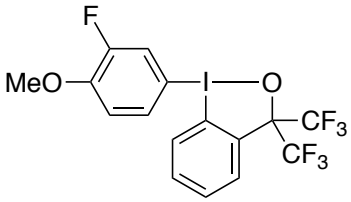


1-(4-Methoxy-2-methylphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3h): Prepared according to the general procedure; White solid (79.4 mg, 81% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 193-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (app. d, J = 6.8 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.59-7.51 (m, 1H), 7.40-7.32 (m, 1H), 6.99 (d, J = 2.7 Hz, 1H), 6.84-6.73 (m, 2H), 3.89 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 144.9, 140.0, 132.0, 131.4, 130.4, 130.2, 126.6, 124.1 (q, $J_{C\text{-}F}$ = 290.7 Hz),

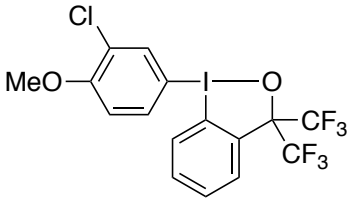
116.8, 114.1, 111.2, 111.1, 81.8-80.7 (m), 55.4, 24.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.9; HRMS (ESI) Calcd for $C_{17}H_{14}O_2F_6I$ $[M + H]^+$ 490.9943, found 490.9953.



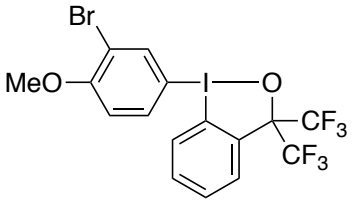
1-(4-Methoxy-3-methylphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3i): Prepared according to the general procedure; Brown solid (84.3 mg, 86% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 197-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (app. d, J = 7.4 Hz, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.60 (s, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 3.93 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 138.7, 136.4, 131.9, 131.0, 130.6, 130.1 (two signals overlapped), 127.4, 124.1 (q, $J_{C\text{-}F}$ = 290.4 Hz), 112.3, 111.8, 107.4, 81.9-81.0 (m), 55.5, 16.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.3; HRMS (ESI) Calcd for $C_{17}H_{14}O_2F_6I$ $[M + H]^+$ 490.9943, found 490.9947.



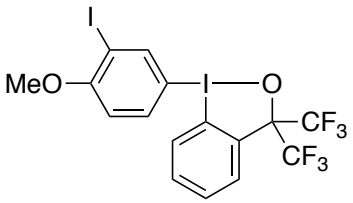
1-(3-Fluoro-4-methoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3j): Prepared according to the general procedure with a modified temperature (80 °C); White solid (75.1 mg, 76% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (app. d, J = 7.3 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.60-7.50 (m, 2H), 7.45-7.34 (m, 1H), 7.09 (t, J = 8.2 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0 (d, $^1J_{C\text{-}F}$ = 254.4 Hz), 151.1 (d, $^2J_{C\text{-}F}$ = 10.2 Hz), 133.8 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 132.1, 130.9, 130.33, 130.27, 127.3, 124.1 (d, $^2J_{C\text{-}F}$ = 18.4 Hz), 124.0 (q, $J_{C\text{-}F}$ = 289.9 Hz), 115.6, 111.6, 108.0, 81.9-81.1 (m), 56.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0, -129.9; HRMS (ESI) Calcd for $C_{16}H_{11}O_2F_7I$ $[M + H]^+$ 494.9692, found 494.9695.



1-(3-Chloro-4-methoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3k): Prepared according to the general procedure with a modified temperature (60 °C); White solid (71.5 mg, 70% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 248-250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.82 (m, 2H), 7.74 (dd, J = 8.4, 1.9 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.44-7.35 (m, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 138.0, 136.8, 132.1, 130.9, 130.4 (two signals overlapped), 127.4, 125.4, 124.0 (q, $J_{C\text{-}F}$ = 289.5 Hz), 114.3, 111.7, 108.9, 81.6-81.0 (m), 56.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{16}H_{11}O_2F_6ClI$ $[M + H]^+$ 510.9396, found 510.9400.

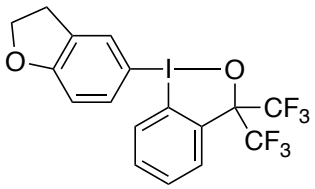


1-(3-Bromo-4-methoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3l): Prepared according to the general procedure with a modified temperature (80 °C); White solid (75.5 mg, 68% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 271-273 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 1.9 Hz, 1H), 7.87 (app. d, J = 6.6 Hz, 1H), 7.77 (dd, J = 8.4, 1.9 Hz, 1H), 7.61-7.53 (m, 1H), 7.44-7.35 (m, 1H), 7.00 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 141.0, 137.5, 132.1, 130.9, 130.4 (two signals overlapped), 127.4, 124.0 (q, $J_{C\text{-}F}$ = 288.7 Hz), 114.5, 114.1, 111.7, 109.5, 81.6-81.0 (m), 56.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1; HRMS (ESI) Calcd for $C_{16}H_{11}O_2F_6BrI$ $[M + H]^+$ 554.8891, found 554.8889.

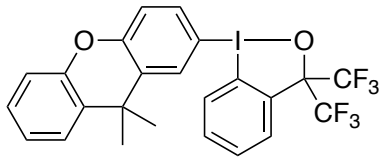


1-(3-Iodo-4-methoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]

iodaoxole (3m): Prepared according to the general procedure with a modified temperature (60 °C); Brown solid (78.3 mg, 65% yield); R_f 0.4 (hexane/EtOAc = 2/1); m.p. 259-261 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.38 (d, J = 1.9 Hz, 1H), 7.99 (dd, J = 8.4, 1.9 Hz, 1H), 7.71 (app. d, J = 7.6 Hz, 1H), 7.66-7.58 (m, 1H), 7.56-7.46 (m, 1H), 7.14 (d, J = 8.5 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 159.5, 145.7, 138.2, 131.8, 130.8, 129.6, 128.7, 128.0, 123.7 (q, $J_{C\text{-}F}$ = 291.5 Hz), 113.3, 112.0, 110.5, 88.2, 81.4-80.6 (m), 56.2; ^{19}F NMR (282 MHz, DMSO) δ -75.4; HRMS (ESI) Calcd for $C_{16}H_{11}O_2F_6I_2$ $[M + H]^+$ 602.8753, found 602.8750.

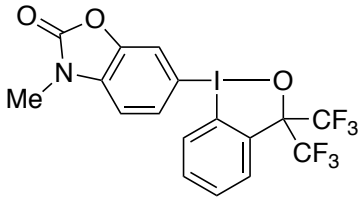


1-(2,3-Dihydrobenzofuran-5-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3n): Prepared according to the general procedure; Brown solid (72.2 mg, 74% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (app. d, J = 7.6 Hz, 1H), 7.71 (s, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.55 (t, J = 7.1 Hz, 1H), 7.42-7.33 (m, 1H), 6.89 (d, J = 8.2 Hz, 2H), 4.71 (t, J = 8.8 Hz, 2H), 3.31 (t, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 138.1, 133.9, 132.0, 131.4, 131.0, 130.2 (two signals overlapped), 127.6, 124.0 (q, $J_{C\text{-}F}$ = 289.6 Hz), 112.6, 111.7, 106.5, 81.5-80.4 (m), 72.1, 29.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{17}H_{12}O_2F_6I$ $[M + H]^+$ 488.9786, found 488.9789.



1-(9,9-Dimethyl-9*H*-xanthen-2-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3o): Prepared according to the general procedure; Brown solid (89.1 mg, 77% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 206-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.81 (m, 2H), 7.69 (dd, J = 8.3, 1.9 Hz, 1H), 7.60-7.51 (m, 1H), 7.44 (dd, J = 7.8, 1.5 Hz, 1H), 7.40-7.32 (m, 1H), 7.31-7.22 (m, 1H), 7.20-7.07 (m, 3H), 6.83 (dd, J = 8.3, 0.7 Hz, 1H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 149.6, 136.2, 135.4, 134.0, 132.0, 131.0, 130.32, 130.25, 129.2, 127.9, 127.3, 126.0, 124.12, 124.1 (q, $J_{C\text{-}F}$ = 290.2 Hz), 119.6, 116.5,

111.8, 111.2, 81.9-80.8 (m), 34.3, 32.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{24}H_{18}O_2F_6I$ $[M + H]^+$ 579.0256, found 579.0255.



6-(3,3-Bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3p): Prepared according to the general procedure; White solid (78.6 mg, 76% yield); R_f 0.3 (hexane/EtOAc = 1/2); m.p. 271-273 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.08 (d, J = 1.3 Hz, 1H), 7.86 (dd, J = 8.0, 1.3 Hz, 1H), 7.69 (app. d, J = 7.6 Hz, 1H), 7.63-7.55 (m, 1H), 7.45-7.34 (m, 2H), 6.75 (dd, J = 8.3, 0.8 Hz, 1H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 153.1, 142.3, 134.1, 132.7, 131.8, 130.8, 129.7, 128.7, 128.2, 123.8 (q, $J_{C\text{-}F}$ = 291.2 Hz), 117.0, 112.1, 110.9, 110.3, 81.8-80.7, 27.8; ^{19}F NMR (282 MHz, DMSO) δ -76.7; HRMS (ESI) Calcd for $C_{17}H_{11}NO_3F_6I$ $[M + H]^+$ 517.9688, found 517.9687. Recrystallization from CH_2Cl_2/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the T-shaped λ^3-iodane geometry and the site-selectivity of **3p** (Figure S2).[3]

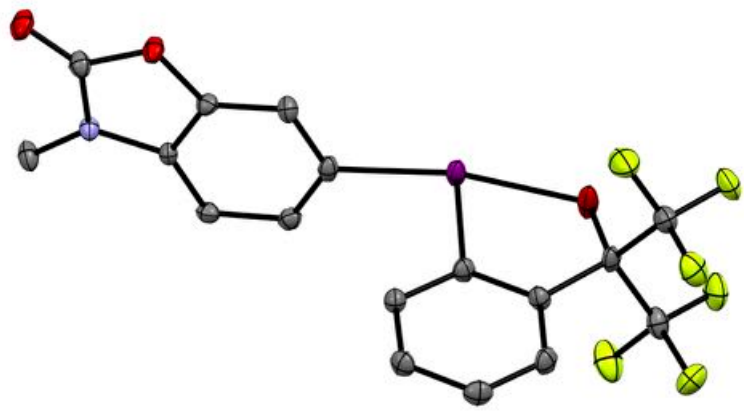
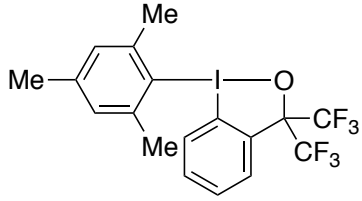
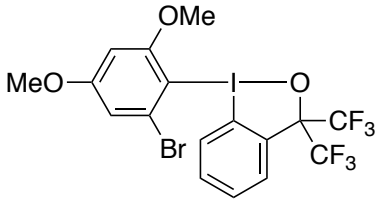


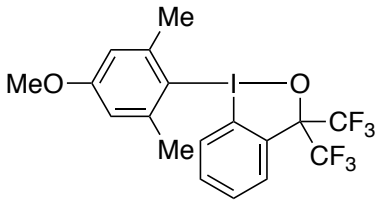
Figure S2. ORTEP drawing of **3p** (thermal ellipsoids set at 50% probability).



1-Mesityl-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3q): Prepared according to the general procedure; White solid (81.0 mg, 83% yield); R_f 0.3 (hexane/EtOAc = 3/1); m.p. 197-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (app. d, J = 7.3 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.39-7.29 (m, 1H), 7.09 (s, 2H), 6.76 (d, J = 8.1 Hz, 1H), 2.48 (s, 6H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.9, 132.2, 131.8, 130.4, 130.3, 129.2, 125.9, 124.2 (q, $J_{C\text{-}F}$ = 290.3 Hz), 121.3, 110.3, 81.5-80.7 (m), 25.8, 21.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.9; HRMS (ESI) Calcd for $C_{18}H_{16}OF_6I$ $[M + H]^+$ 489.0150, found 489.0151.

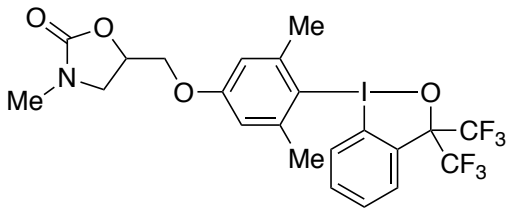


1-(2-Bromo-4,6-dimethoxyphenyl)-3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxole (3r): Prepared according to the general procedure; White solid (98.3 mg, 84% yield); R_f 0.3 (hexane/EtOAc = 1/1); m.p. 185-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (app. d, J = 7.3 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 6.94 (s, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.48 (s, 1H), 3.90 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.6, 132.2, 132.0, 131.4, 130.1 (two signals overlapped), 126.5, 124.0 (q, $J_{C\text{-}F}$ = 288.8 Hz), 111.8, 110.3, 106.4, 97.5, 81.7-80.9 (m), 56.6, 55.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.8, -76.1 (The ^{19}F NMR showed two signals, presumably due to slow rotation of the aryl-I bond); HRMS (ESI) Calcd for $C_{17}H_{13}O_3F_6BrI$ $[M + H]^+$ 584.8997, found 584.8986.

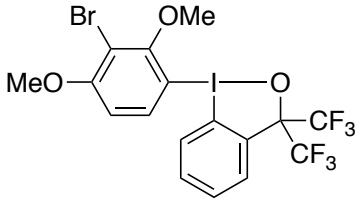


1-(4-Methoxy-2,6-dimethylphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3s): Prepared according to the general procedure; White solid (88.7 mg, 88% yield, regioisomer ratio = 15:1 as determined by ^{1}H NMR); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 205-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (app. d, J = 7.6 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.39-7.29 (m, 1H), 6.84-6.72 (m, 3H), 3.87 (s, 3H), 2.50 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 145.6, 132.1, 132.0, 130.4, 130.2, 125.8, 124.2 (q, $J_{C\text{-}F}$ = 290.4 Hz), 114.9, 114.0, 110.9, 81.9-80.8 (m), 55.3, 26.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.9; HRMS (ESI)

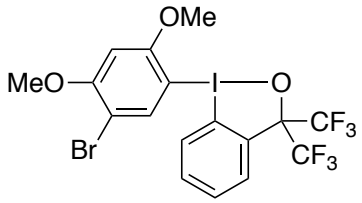
Calcd for $C_{18}H_{16}O_2F_6I$ $[M + H]^+$ 505.0099, found 505.0093.



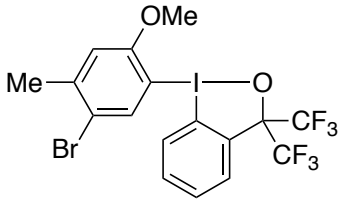
5-((4-(3,3-Bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3,5-dimethylphenoxy)methyl)-3-methyloxazolidin-2-one (3t): Prepared according to the general procedure; White solid (92.9 mg, 77% yield); R_f 0.3 (hexane/EtOAc = 1/2); m.p. 234-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (app. d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.43-7.32 (m, 1H), 6.82 (s, 2H), 6.74 (d, J = 8.3 Hz, 1H), 4.94-4.81 (m, 1H), 4.29-4.16 (m, 2H), 3.77 (t, J = 8.9 Hz, 1H), 3.58 (dd, J = 8.8, 6.1 Hz, 1H), 2.95 (s, 3H), 2.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 157.5, 145.7, 132.2, 131.8, 130.4, 130.3, 125.7, 124.2 (q, $J_{C\text{-}F}$ = 290.4 Hz), 116.2, 114.5, 114.4, 110.6, 81.9-80.8 (m), 70.4, 68.2, 48.5, 30.9, 26.03, 26.01; ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.9; HRMS (ESI) Calcd for $C_{22}H_{21}NO_4F_6I$ $[M + H]^+$ 604.0420, found 604.0415.



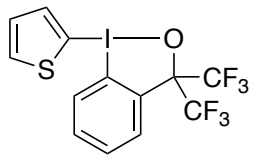
1-(3-Bromo-2,4-dimethoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3u): Prepared according to the general procedure; White solid (106.5 mg, 91% yield); R_f 0.3 (hexane/EtOAc = 1/1); m.p. 201-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (app. d, J = 7.6 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.60-7.52 (m, 1H), 7.44-7.35 (m, 1H), 6.81 (d, J = 8.6 Hz, 2H), 4.01 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 159.7, 137.3, 132.1, 131.1, 130.3, 130.1, 127.2, 124.0 (q, $J_{C\text{-}F}$ = 289.8 Hz), 111.8, 110.0, 107.3, 106.5, 81.8-80.7 (m), 62.1, 56.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.1; HRMS (ESI) Calcd for $C_{17}H_{13}O_3F_6BrI$ $[M + H]^+$ 584.8997, found 584.9000.



1-(5-Bromo-2,4-dimethoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3v): Prepared according to the general procedure; Yellow solid (74.9 mg, 64% yield); R_f 0.3 (hexane/EtOAc = 1/1); m.p. 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.84 (app. d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H), 6.60 (s, 1H), 4.02 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 160.5, 141.2, 131.9, 131.2, 130.2 (two signals overlapped), 126.9, 124.1 (q, $J_{C\text{-}F}$ = 290.2 Hz), 111.3, 104.2, 99.8, 95.8, 81.7-80.8 (m), 56.6, 56.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{17}H_{13}O_3F_6BrI$ $[M + H]^+$ 584.8997, found 584.8997.

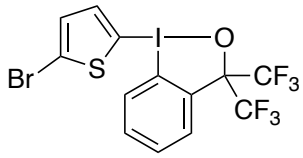


1-(5-Bromo-2-methoxy-4-methylphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3w): Prepared according to the general procedure; White solid (85.4 mg, 75% yield, regioisomer ratio = 10:1 as determined by ^{1}H NMR); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.84 (app. d, J = 7.2 Hz, 1H), 7.59-7.53 (m, 1H), 7.41-7.33 (m, 1H), 6.96 (s, 1H), 6.82 (d, J = 8.3 Hz, 1H), 3.81 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 144.6, 140.7, 132.0, 131.2, 130.2 (two signals overlapped), 127.2, 124.1 (q, $J_{C\text{-}F}$ = 289.9 Hz), 117.2, 113.4, 111.0, 107.5, 81.9-80.8 (m), 56.5, 23.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{17}H_{13}O_2F_6BrI$ $[M + H]^+$ 568.9048, found 568.9041.

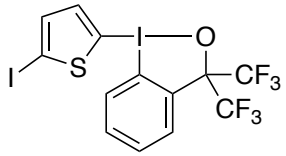


1-(Thiophen-2-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3x): Prepared according to the general procedure; White solid (66.9 mg, 74% yield); R_f 0.3 (hexane/EtOAc = 5/1); m.p. 217-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.81 (m, 1H),

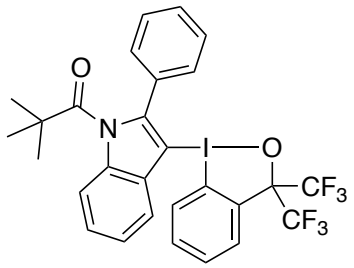
7.70 (dd, J = 5.1, 0.9 Hz, 1H), 7.62 (dd, J = 3.5, 0.9 Hz, 1H), 7.61-7.53 (m, 1H), 7.46-7.38 (m, 1H), 7.20 (dd, J = 5.1, 3.6 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 135.9, 132.3, 130.9, 130.5, 130.1, 129.8, 127.0, 123.9 (q, $J_{C\text{-}F}$ = 289.8 Hz), 113.3, 109.0, 82.2-81.0 (m); ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.1; HRMS (ESI) Calcd for $C_{13}H_8OF_6SI$ $[M + H]^+$ 452.9245, found 452.9237.



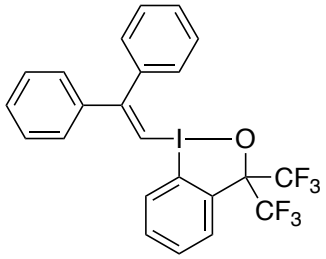
1-(5-Bromothiophen-2-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3y): Prepared according to the general procedure; White solid (87.1 mg, 82% yield); R_f 0.3 (hexane/EtOAc = 5/1); m.p. 198-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (app. d, J = 7.6 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.40 (d, J = 3.7 Hz, 1H), 7.15 (d, J = 3.7 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 132.6, 132.5, 131.0, 130.6, 130.2, 127.0, 123.8 (q, $J_{C\text{-}F}$ = 289.5 Hz), 122.1, 113.3, 110.8, 82.3-81.1 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{13}H_7OF_6SBrI$ $[M + H]^+$ 530.8350, found 530.8353.



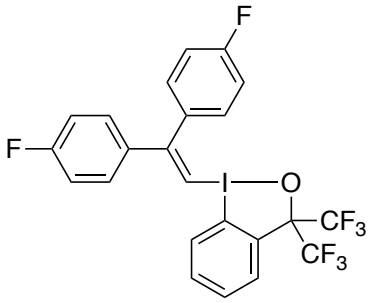
1-(5-Iodothiophen-2-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3z): Prepared according to the general procedure; White solid (102.9 mg, 89% yield); R_f 0.3 (hexane/EtOAc = 5/1); m.p. 180-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (app. d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 3.6 Hz, 1H), 7.29 (d, J = 3.6 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 139.6, 132.5, 131.0, 130.6, 130.2, 127.0, 123.8 (q, $J_{C\text{-}F}$ = 289.4 Hz), 114.9, 113.5, 84.0, 82.3-81.1 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{13}H_7OF_6SI_2$ $[M + H]^+$ 578.8211, found 578.8213.



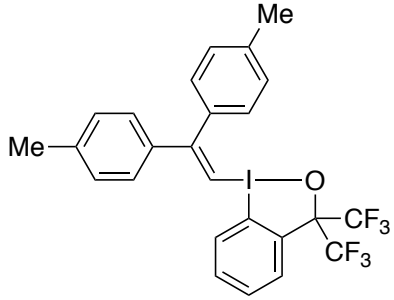
1-(3-(3,3-Bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-2-phenyl-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (3aa): Prepared according to the general procedure; Red solid (90.4 mg, 70% yield); R_f 0.3 (hexane/EtOAc = 1/2); m.p. 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (app. d, J = 7.7 Hz, 1H), 7.58-7.52 (m, 2H), 7.48-7.35 (m, 7H), 7.35-7.28 (m, 2H), 7.04 (dd, J = 8.3, 0.8 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 144.4, 136.6, 132.1, 131.6, 130.5, 130.3 (two signals overlapped), 130.0, 129.9, 129.3, 126.6, 125.4, 124.1 (q, $J_{C\text{-}F}$ = 288.2 Hz), 123.4, 120.7, 112.2, 111.8, 90.7, 82.0-81.2 (m), 44.8, 27.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.4 (q, J = 8.5 Hz), -77.1 (q, J = 8.7 Hz) (The ^{19}F NMR showed two signals, presumably due to slow rotation of the indolyl-I bond); HRMS (ESI) Calcd for $C_{28}H_{23}NO_2F_6I$ $[M + H]^+$ 646.0678, found 646.0671.



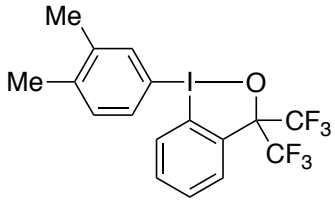
1-(2,2-Diphenylvinyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3ab): Prepared according to the general procedure with a modified MeCN volume (1.0 mL); White solid (99.8 mg, 91% yield); R_f 0.3 (hexane/EtOAc = 3/1); m.p. 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (app. d, J = 6.7 Hz, 1H), 7.75-7.68 (m, 1H), 7.64-7.56 (m, 2H), 7.47-7.28 (m, 8H), 7.22 (s, 1H), 7.17-7.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 139.5, 139.3, 132.1, 131.4, 130.4 (two signals overlapped), 129.9, 129.5, 128.9, 128.8, 128.7, 128.2, 127.2, 124.0 (q, $J_{C\text{-}F}$ = 290.3 Hz), 111.9, 106.0, 81.8-80.7 (m); ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.1; HRMS (ESI) Calcd for $C_{23}H_{16}OF_6I$ $[M + H]^+$ 549.0150, found 549.0154.



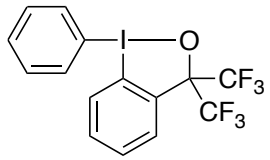
1-(2,2-Bis(4-fluorophenyl)vinyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (3ac): Prepared according to the general procedure with a modified MeCN volume (1.0 mL); White solid (94.6 mg, 81% yield); R_f 0.3 (hexane/EtOAc = 3/1); m.p. 163-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (app. d, J = 6.7 Hz, 1H), 7.72-7.57 (m, 3H), 7.37-7.29 (m, 2H), 7.18 (s, 1H), 7.16-7.00 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (d, $^1J_{C\text{-}F}$ = 250.2 Hz), 163.2 (d, $^1J_{C\text{-}F}$ = 249.1 Hz), 158.3, 135.6 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 135.1 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 132.2, 131.3, 130.8 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 130.5 (two signals overlapped), 130.1 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 127.0, 124.0 (q, $J_{C\text{-}F}$ = 290.2 Hz), 116.1 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 115.9 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 111.9, 106.2, 81.8-80.6 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1, -110.2, -110.6; HRMS (ESI) Calcd for $C_{23}H_{14}OF_8I$ $[M + H]^+$ 584.9962, found 584.9960.



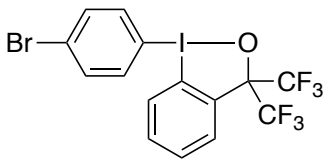
1-(2,2-Di-*p*-tolylvinyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3ad): The general procedure was modified by the change of the stoichiometry (0.2 mmol of **2ad** and 0.3 mmol of **1**), the addition of Na_2CO_3 (0.4 mmol), and the use of chlorobenzene (1.0 mL) as the solvent; Yellow solid (81.8 mg, 71% yield); R_f 0.3 (hexane/EtOAc = 3/1); m.p. 161-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (app. d, J = 6.6 Hz, 1H), 7.75-7.68 (m, 1H), 7.64-7.54 (m, 2H), 7.28-7.22 (m, 2H), 7.19 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 7.12 (s, 1H), 7.01 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 140.2, 139.6, 136.9, 136.5, 131.9, 131.6, 130.4, 130.3, 129.5, 129.4, 128.8, 128.2, 127.1, 124.1 (q, $J_{C\text{-}F}$ = 290.2 Hz), 112.1, 104.4, 82.0-80.8 (m), 21.24, 21.22; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{25}H_{20}OF_6I$ $[M + H]^+$ 577.0463, found 577.0468.



1-(3,4-Dimethylphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3ae): Prepared by modifying the general procedure with the addition of $Sc(OTf)_3$ (19.7 mg, 0.04 mmol) and the use of CH_2Cl_2 (0.5 mL) as the solvent at 60 °C; Light brown solid (52.2 mg, 55% yield); R_f 0.3 (hexane/EtOAc = 3/1); m.p. 215-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (app. d, J = 7.7 Hz, 1H), 7.64 (s, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.57-7.50 (m, 1H), 7.38-7.31 (m, 1H), 7.26 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 140.3, 137.6, 134.4, 132.3, 131.9, 131.0, 130.2, 130.1, 127.6, 124.1 (q, $J_{C\text{-}F}$ = 290.8 Hz), 115.1, 111.5, 81.9-80.7 (m), 20.0, 19.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1; HRMS (ESI) Calcd for $C_{17}H_{14}OF_6I$ $[M + H]^+$ 474.9994, found 474.9995.

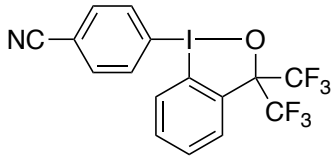


1-Phenyl-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3af): Prepared according to the general procedure using $PhSiMe_3$ or $PhBF_3K$; White solid (80.3 mg, 90% yield for $PhSiMe_3$; 83.9 mg, 94% yield for $PhBF_3K$); R_f 0.4 (hexane/EtOAc = 3/1); m.p. 237-239 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.81 (m, 3H), 7.70 (t, J = 7.5 Hz, 1H), 7.59-7.47 (m, 3H), 7.39-7.30 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.0, 131.8, 131.1, 130.8, 130.2 (two signals overlapped), 127.6, 124.1 (q, $J_{C\text{-}F}$ = 290.3 Hz), 118.7, 111.2, 81.8-80.7 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{15}H_{10}OF_6I$ $[M + H]^+$ 446.9681, found 446.9681.



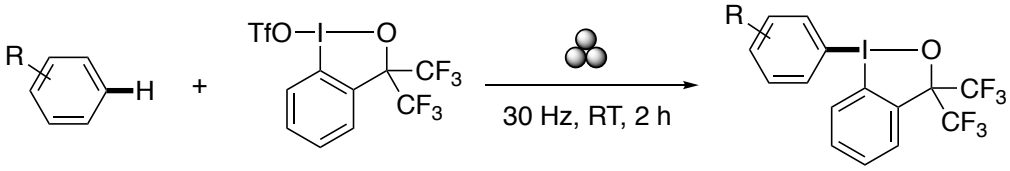
1-(4-Bromophenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole

(3ag): Prepared according to the general procedure using (4-bromophenyl)-trimethylsilane; White solid (80.9 mg, 77% yield); R_f 0.3 (hexane/EtOAc = 3/1); m.p. 228-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (app. d, J = 7.0 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.43-7.34 (m, 1H), 6.79 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 134.4, 132.2, 130.8, 130.5, 130.4, 127.5, 127.0, 124.0 (q, $J_{C\text{-}F}$ = 289.7 Hz), 117.4, 111.2, 81.8-80.6 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{15}H_9OF_6BrI$ $[M + H]^+$ 524.8786, found 524.8788.



4-(3,3-Bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)benzonitrile (3ah): Prepared according to the general procedure using potassium (4-cyanophenyl)trifluoroborate; White solid (79.5 mg, 84% yield); R_f 0.3 (hexane/EtOAc = 2/1); m.p. 270-272 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.24 (d, J = 7.7 Hz, 2H), 7.95 (d, J = 7.7 Hz, 2H), 7.71 (app. d, J = 6.8 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 137.3, 133.6, 132.2, 130.7, 129.8, 128.9, 128.5, 125.6, 123.7 (q, $J_{C\text{-}F}$ = 291.1 Hz), 117.7, 113.3, 111.8, 81.8,-80.7 (m); ^{19}F NMR (376 MHz,DMSO) δ -75.0.; HRMS (ESI) Calcd for $C_{16}H_9NOF_6I$ $[M + H]^+$ 471.9633, found 471.9636.

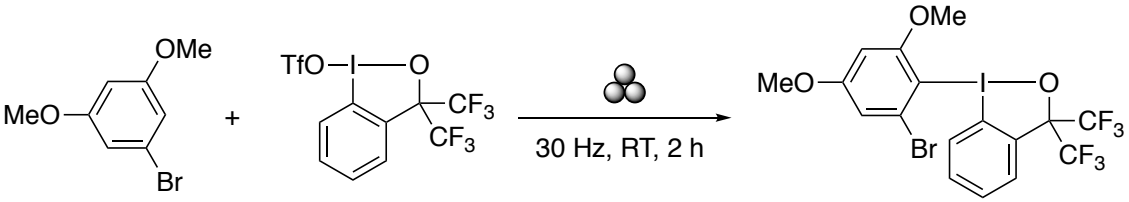
3. Mechanochemical Synthesis



2 BXT (**1**) **3**

A 15 mL stainless miller jar equipped with a 10 mm stainless steel ball was charged sequentially with aromatic compound **2** (0.30 mmol) and BXT (103.6 mg, 0.20 mmol). The jar was closed, and the mixture was subjected to 30 Hz milling for 2 h. Then the mixture was dissoved in EtOAc (15 mL), and the solution was washed with saturated aq. Na_2CO_3 (5 mL), H_2O (5 mL) and brine (5 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3**.

Gram-Scale Reaction without Chromatography Purification

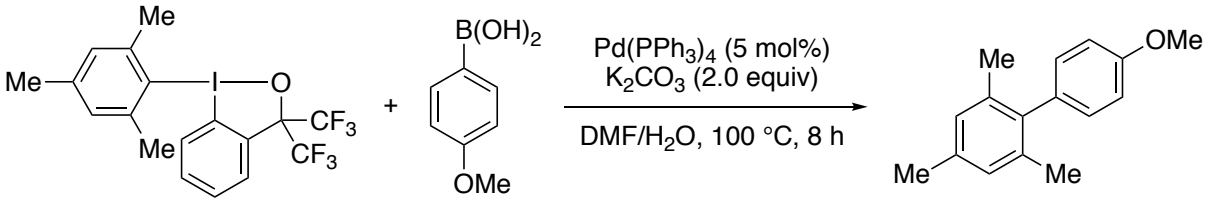


2r 0.52 g **1** 1.04 g **3r** 1.07 g

A 15 mL stainless miller jar equipped with a 10 mm stainless steel ball was charged sequentially with 1-bromo-3,5-dimethoxybenzene (**2r**, 0.52 g, 2.4 mmol) and BXT (1.04 g, 2.0 mmol). The jar was closed, and the mixture was subjected to 30 Hz milling at room temperature for 2 h. Then the crude solid mixture was collected from the miller jar using spatula and was grated. The crude product was put onto a filter funnel, and washed with saturated aq. Na_2CO_3 (10 mL) and a mixture of hexane and Et_2O (20:1, 20 mL). The residue was dried under vacuum to afford the desired product **3r** as an analytically pure light-brown solid (1.07 g, 92% yield).

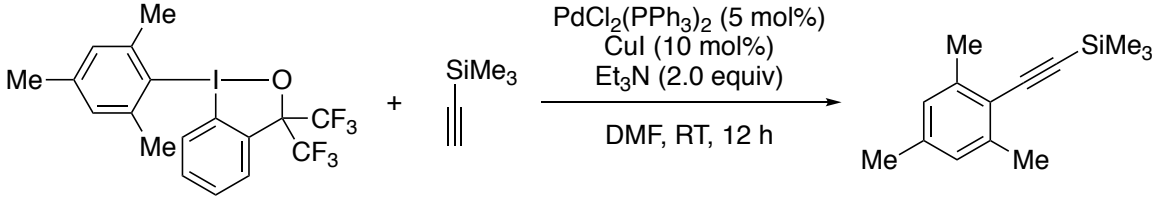
4. Product Transformations

Cross-Coupling Reactions



3q **4**, 86%

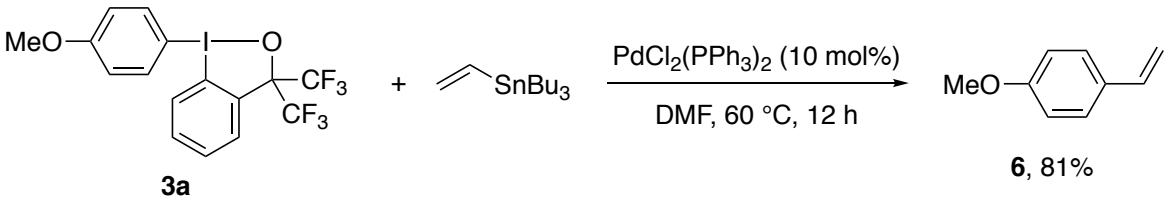
4'-Methoxy-2,4,6-trimethyl-1,1'-biphenyl (4): Under N_2 gas, a Schlenk tube equipped with a stir bar was charged with **3q** (97.6 mg, 0.20 mmol), 4-methoxyphenylboronic acid (45.6 mg, 0.30 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.010 mmol), and an aqueous solution of K_2CO_3 (1 M, 0.40 mL, 0.40 mmol), followed by the addition of DMF (2 mL). The resulting mixture was stirred at 100 °C for 8 h. The mixture was cooled to room temperature, diluted with Et_2O (10 mL), and washed with H_2O (5 mL) and brine (5 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane/Et_2O = 50/1) to afford the title compound as a white solid (38.9 mg, 86% yield); m.p. 73-75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-7.00 (m, 2H), 6.98-6.88 (m, 4H), 3.84 (s, 3H), 2.32 (s, 3H), 2.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 138.7, 136.4 (two signals overlapped), 133.3, 130.3, 128.0, 113.7, 55.2, 21.0, 20.8; HRMS (ESI) Calcd for $C_{16}H_{19}O$ $[M + H]^+$ 227.1436, found 227.1442.



3q **5**, 87%

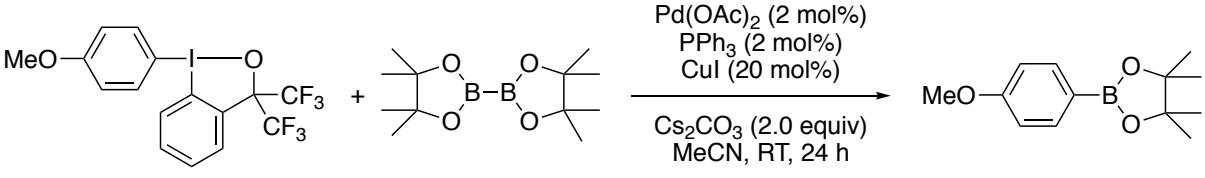
(Mesitylethynyl)trimethylsilane (5): Under N_2 gas, a Schlenk tube equipped with a stir bar was charged with **3q** (97.6 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.010 mmol), CuI (3.8 mg, 0.020 mmol), and DMF (2 mL). To the solution was added trimethylsilylacetylene (29.5 mg, 0.30 mmol) and Et_3N (40.5 mg, 0.40 mmol), and the resulting mixture was stirred at room temperature for 12 h. The mixture was diluted with Et_2O (10 mL) and washed with H_2O (5 mL) and brine (5 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel

(eluent: hexane) to afford the title compound as a light yellow oil (37.7 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 2.41 (s, 6H), 2.28 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 137.8, 127.5, 120.0, 103.0, 101.8, 21.3, 20.9, 0.2; HRMS (ESI) Calcd for $C_{14}H_{21}Si$ $[M + H]^+$ 217.1413, found 217.1420.



3a

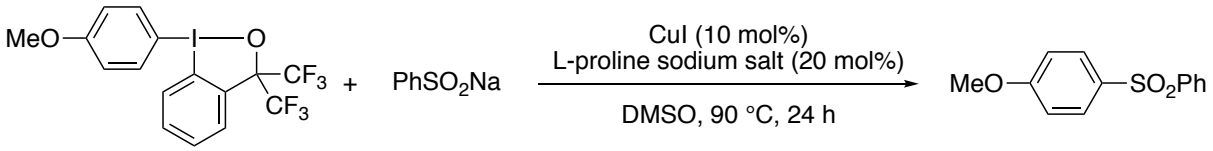
4-Vinylanisole (6): Under N_2 gas, a Schlenk tube equipped with a stir bar was charged with **3a** (95.3 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (14.0 mg, 0.020 mmol), and DMF (1 mL). To the solution was added tributyl(vinyl)tin (126.8 mg, 0.40 mmol), and the resulting mixture was stirred at 60 °C for 12 h. The mixture was cooled to room temperature, diluted with Et_2O (10 mL), and washed with H_2O (5 mL) and brine (5 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane) to afford the title compound as a colorless oil (21.8 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.66 (dd, J = 17.6, 10.9 Hz, 1H), 5.60 (d, J = 17.6 Hz, 1H), 5.12 (d, J = 10.9 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 136.2, 130.4, 127.4, 113.9, 111.5, 55.2; HRMS (ESI) Calcd for $C_9H_{11}O$ $[M + H]^+$ 135.0810, found 135.0815.



3a

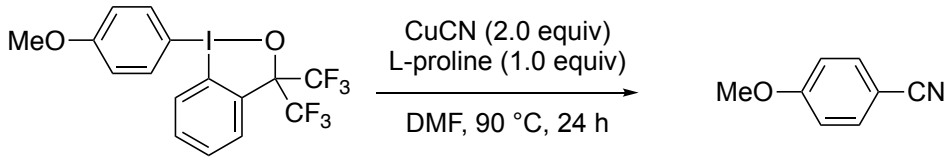
2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7): A Schlenk tube equipped with a stir bar was charged with **3a** (95.3 mg, 0.20 mmol), bis(pinacolato)diboron (101.6 mg, 0.40 mmol), $Pd(OAc)_2$ (1.0 mg, 4.0 μmol), PPh_3 (1.1 mg, 4.0 μmol), CuI (7.6 mg, 0.040 mmol), Cs_2CO_3 (130.3 mg, 0.40 mmol), and MeCN (2 mL). The resulting mixture was stirred at room temperature for 24 h. The mixture was diluted with CH_2Cl_2 (10 mL) and washed with H_2O (5 mL) and brine (5 mL). The organic layer was dried over $MgSO_4$ and

concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to afford the title compound as a colorless oil (37.6 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 136.5, 113.3, 83.5, 55.1, 24.8; HRMS (ESI) Calcd for $C_{13}H_{20}BO_3$ $[M + H]^+$ 235.1506, found 235.1507.



3a **8**, 71%

1-Methoxy-4-(phenylsulfonyl)benzene (8): Under N_2 gas, a Schlenk tube equipped with a stir bar was charged with **3a** (95.3 mg, 0.20 mmol), sodium benzenesulfonate (49.3 mg, 0.30 mmol), CuI (3.8 mg, 0.020 mmol), L-proline sodium salt (5.5 mg, 0.040 mmol), and DMSO (1 mL). The resulting mixture was stirred at 90 °C for 24 h. The mixture was cooled to room temperature. H_2O (5 mL) was added, and the mixture was extracted with EtOAc (5 mL x 3). The combined organic layer was washed with H_2O (5 mL) and brine (5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) to afford the title compound as a brown solid (35.4 mg, 71% yield); m.p. 55-57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.55-7.44 (m, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 142.3, 133.1, 132.8, 129.8, 129.2, 127.3, 114.5, 55.6; HRMS (ESI) Calcd for $C_{13}H_{13}O_3S$ $[M + H]^+$ 249.0585, found 249.0593.

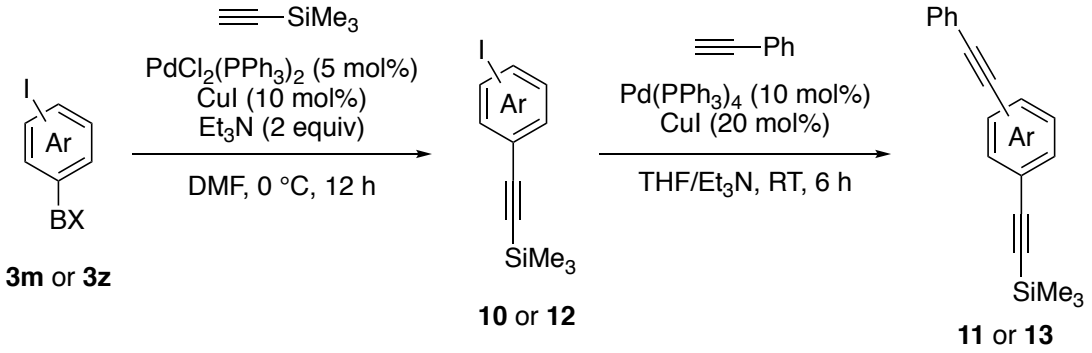


3a **9**, 86%

4-Methoxybenzonitrile (9): Under N_2 gas, a Schlenk tube equipped with a stir bar was charged with CuCN (35.8 mg, 0.40 mmol), L-proline (23.0 mg, 0.20 mmol), and DMF (1 mL). After 10 min, **3a** (95.3 mg, 0.20 mmol) was added, and the resulting mixture was stirred at 90 °C for 24 h. The mixture was cooled to room temperature and diluted with EtOAc (15 mL).

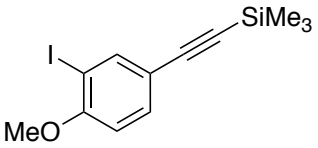
The mixture was washed with saturated aq. NH_4Cl (5 mL), H_2O (5 mL) and brine (5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to afford the title compound as a light brown solid (22.8 mg, 86% yield); m.p. 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 134.0, 119.1, 114.8, 104.0, 55.5; HRMS (ESI) Calcd for C_8H_8NO $[M + H]^+$ 134.0606, found 134.0607.

Chemoselective Sequential Sonogashira Coupling

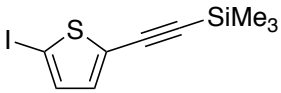


3m or **3z** **10** or **12** **11** or **13**

First step: Under N_2 gas, a Schlenk tube equipped with a stir bar was charged with **3m** or **3z** (0.22 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.010 mmol), CuI (3.8 mg, 0.020 mmol), and DMF (2 mL). To the solution was added trimethylsilylacetylene (19.6 mg, 0.20 mmol) and Et_3N (40.5 mg, 0.40 mmol) at 0 °C, and the resulting mixture was stirred at 0 °C for 12 h. The mixture was diluted with Et_2O (10 mL) and washed with H_2O (5 mL) and brine (5 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane) to afford the desired product **10** or **12**.

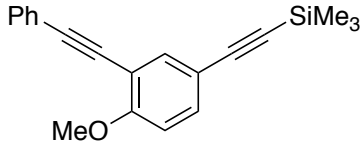


((3-Iodo-4-methoxyphenyl)ethynyl)trimethylsilane (10): Colorless oil (43.0 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 2.0 Hz, 1H), 7.41 (dd, J = 8.5, 2.0 Hz, 1H), 6.72 (d, J = 8.5 Hz, 1H), 3.88 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 142.8, 133.3, 117.3, 110.2, 103.3, 93.8, 85.2, 56.4, -0.1; HRMS (ESI) Calcd for $C_{12}H_{16}OSiI$ $[M + H]^+$ 331.0015, found 331.0010.

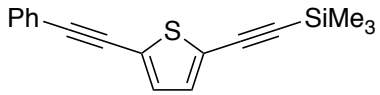


((5-Iodothiophen-2-yl)ethynyl)trimethylsilane (12): Light yellow oil (37.4 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 3.8 Hz, 1H), 6.87 (d, J = 3.8 Hz, 1H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 133.8, 129.5, 100.9, 96.1, 74.7, -0.2; HRMS (ESI) Calcd for $C_9H_{12}SiSI$ $[M + H]^+$ 306.9474, found 306.9468.

Second step: Under N_2 gas, a Schlenk tube equipped with a stir bar was charged with **10** or **12** (0.10 mmol), Pd $(PPh_3)_4$ (11.6 mg, 0.010 mmol), CuI (3.8 mg, 0.020 mmol), THF (1 mL), and Et_3N (0.5 mL). To the solution was added phenylacetylene (20.4 mg, 0.20 mmol), and the resulting mixture was stirred at room temperature for 6 h. The mixture was diluted with Et_2O (10 mL) and washed with H_2O (5 mL) and brine (5 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane) to afford the desired product **11** or **13**.

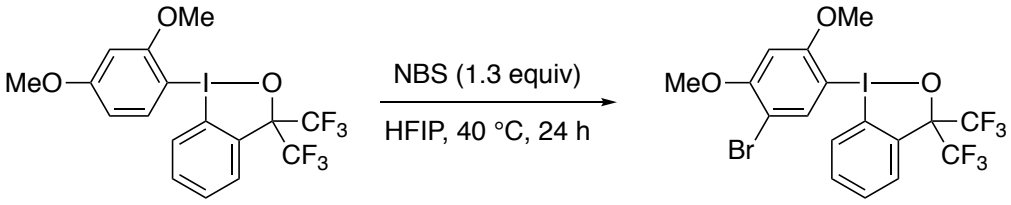


((4-Methoxy-3-(phenylethynyl)phenyl)ethynyl)trimethylsilane (11): White solid (26.2 mg, 86% yield); m.p. 52-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 2.1 Hz, 1H), 7.58-7.49 (m, 2H), 7.40 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.35-7.31 (m, 3H), 6.82 (d, *J* = 8.6 Hz, 1H), 3.91 (s, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 137.2, 133.4, 131.7, 128.3 (two signals overlapped), 123.3, 115.4, 112.8, 110.6, 104.2, 93.8, 93.1, 84.7, 56.0, 0.0; HRMS (ESI) Calcd for $C_{20}H_{21}OSi$ $[M + H]^+$ 305.1362, found 305.1364.



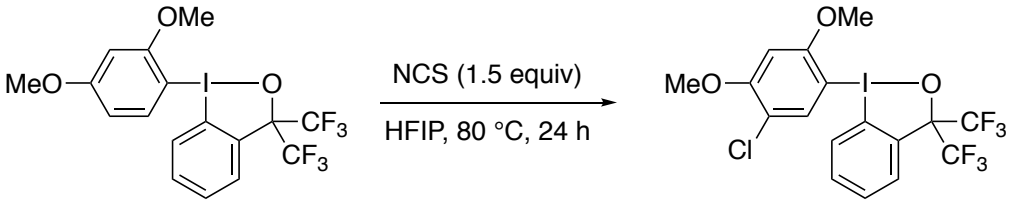
Trimethyl((5-(phenylethynyl)thiophen-2-yl)ethynyl)silane (13): White solid (23.6 mg, 84% yield); m.p. 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.48 (m, 2H), 7.37-7.31 (m, 3H), 7.10 (d, *J* = 3.8 Hz, 1H), 7.09 (d, *J* = 3.8 Hz, 1H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 131.54, 131.49, 128.7, 128.4, 124.7, 124.5, 122.6, 100.1, 96.9, 93.8, 82.2, -0.2; HRMS (ESI) Calcd for $C_{17}H_{16}KSiS$ $[M + K]^+$ 319.0379, found 319.0374.

Halogenation of Aryl-BX Product



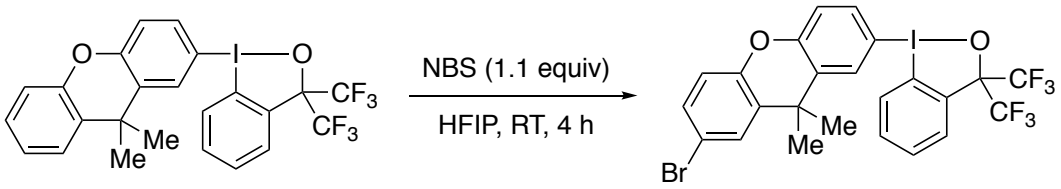
3g **3v,** 86%

1-(5-Bromo-2,4-dimethoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (3v): A Schlenk tube equipped with a stir bar was charged with **3g** (101.2 mg, 0.20 mmol) and hexafluoroisopropanol (0.8 mL), followed by the addition of N-bromosuccinimide (46.3 mg, 0.26 mmol) under air. The resulting mixture was stirred at 40 °C for 24 h. The mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc = 1/1) to afford the title compound the title compound as a yellow solid (95.8 mg, 82% yield), with NMR spectra identical to that described above.



3g **14,** 88%

1-(5-Chloro-2,4-dimethoxyphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2] iodaoxole (14): A Schlenk tube equipped with a stir bar was charged with **3g** (101.2 mg, 0.20 mmol) and hexafluoroisopropanol (0.8 mL), followed by the addition of N-chlorosuccinimide (40.1 mg, 0.30 mmol) under air. The resulting mixture was stirred at 80 °C for 24 h. The mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc = 1/1) to afford the title compound as a white solid (95.4 mg, 88% yield); m.p. 231-233 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (app. d, J = 7.2 Hz, 1H), 7.77 (s, 1H), 7.60-7.51 (m, 1H), 7.41-7.32 (m, 1H), 6.82 (dd, J = 8.3, 0.7 Hz, 1H), 6.63 (s, 1H), 4.03 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 159.6, 138.4, 131.9, 131.3, 130.2 (two signals overlapped), 126.9, 124.1 (q, $J_{C\text{-}F}$ = 290.5 Hz), 116.3, 111.4, 99.3, 96.0, 81.8-81.2 (m), 56.6, 56.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{17}H_{13}ClF_6IO_3$ $[M + H]^+$ 540.9502, found 540.9505.



3o **15**, 93%

1-(7-Bromo-9,9-dimethyl-9*H*-xanthen-2-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (15): A Schlenk tube equipped with a stir bar was charged with **3o** (115.7 mg, 0.20 mmol) and hexafluoroisopropanol (0.8 mL), followed by the addition of N-bromosuccinimide (39.2 mg, 0.22 mmol) under air. The resulting reaction mixture was stirred at room temperature for 4 h. The mixture was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc = 3/1) to afford the title compound as a white solid (121.9 mg, 93% yield); m.p. 260-262 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 7.71 (dd, J = 8.3, 1.7 Hz, 1H), 7.61-7.50 (m, 2H), 7.42-7.32 (m, 2H), 7.16 (d, J = 8.3 Hz, 1H), 7.01 (d, J = 8.7 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 148.7, 136.3, 135.3, 133.2, 132.0, 131.4, 131.0, 130.9, 130.3 (two signals overlapped), 129.0, 127.2, 124.1 (q, $J_{C\text{-}F}$ = 289.8 Hz), 119.6, 118.4, 116.4, 111.9, 111.7, 81.6-80.8 (m), 34.5, 32.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0; HRMS (ESI) Calcd for $C_{24}H_{17}BrF_6IO_2$ $[M + H]^+$ 656.9361, found 656.9358.

5. DFT Calculation

All the calculations were carried out using Gaussian 09 packages.[4] Geometry optimizations were performed using the B3LYP functional[5] with a combined basis set BSI (i.e., SDD[6] for iodine and 6-31G(d) for the other atoms). Harmonic frequency calculations were performed using the same method as optimization to confirm each stationary point to be either a local minimum (zero imaginary frequency) or a transition state (one imaginary frequency). Intrinsic reaction coordinate (IRC)[7] analysis was used to ensure that each transition state connects the right reactant and product. M06 functional[8] with the BSII basis set (i.e., SDD for iodine and 6-311++G(2df,2p) for the other atoms) was used to calculate the single-point energies of all the optimized geometries. All the optimizations, frequency calculations and single-point energy calculations were simulated in acetonitrile by using SMD[9] solvation model. The energies reported in this work were calculated by adding the Gibbs free energy corrections (obtained from frequency calculations) to the single-point energies, corresponding to the reference state of 1 mol/L, 298.15 K. The 3D structures were drawn using the CYLview program.[10]

Reaction pathway for *para* C–H λ^3-iodanation of anisole

The experimentally observed, *para* C–H λ^3-iodanation of anisole (**2a**) with BXT (**1**) was explored (Figure S4). Isomerization of **1** through **TS1** brings the triflate ligand to the *trans* position of the aryl ligand, with endergonicity of 8.5 kcal mol^{-1}. This allows **2a** to bind to the *cis* position of the aryl ligand, forming the pre-C–H cleavage complex **CP1**. The C–H cleavage occurs through a six-centered TS (**TS2*p***) with an overall activation energy of 19.3 kcal mol^{-1}, where C–I bond formation and C–H deprotonation occur concertedly to afford the aryl–BX product **3a** and TfOH. The slightly higher free energy of [**3a** + TfOH] (2.1 kcal mol^{-1}) than that of [**1** + **2a**] may reflect computational artifact, which does not take intermolecular hydrogen bonding between TfOH molecules into account. Binding of **2a** to the *trans* position of the aryl ligand of **1** is also feasible, and the resulting complex **CP1'** is more stable than **CP1**. However, C–H λ^3-iodanation from **CP1'** requires extremely high activation energy (**TS2*p*'**, 37.3 kcal mol^{-1}) and leads to much less stable product **3a'**, and hence is not realistically feasible.

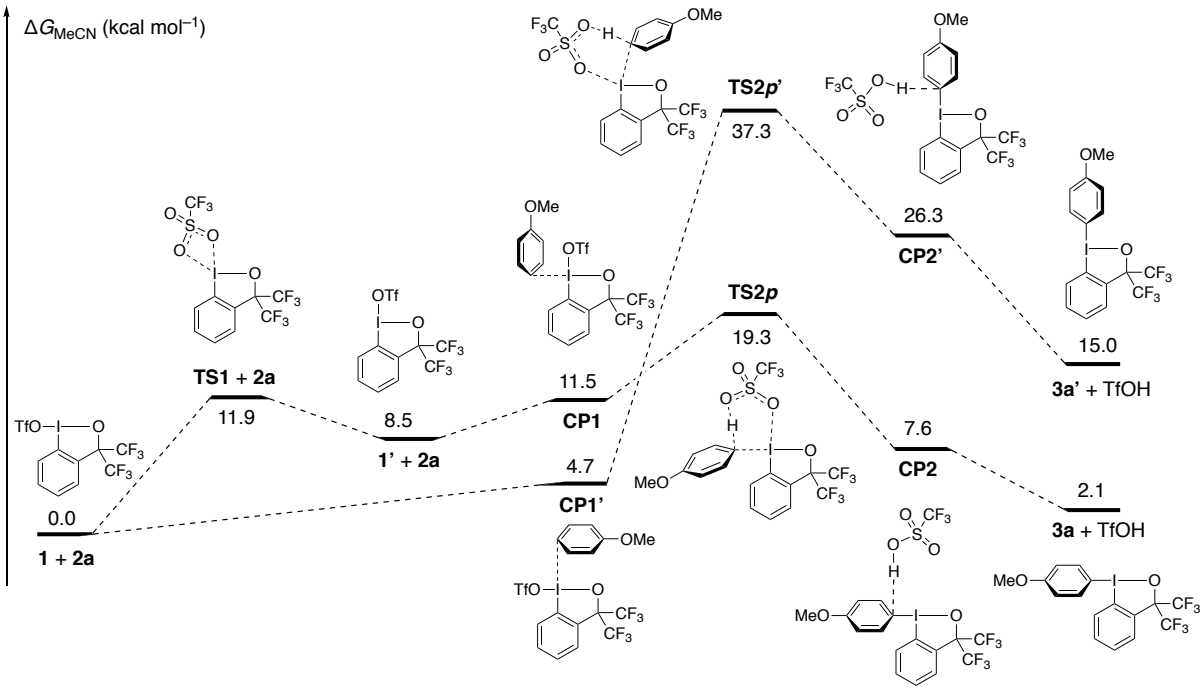
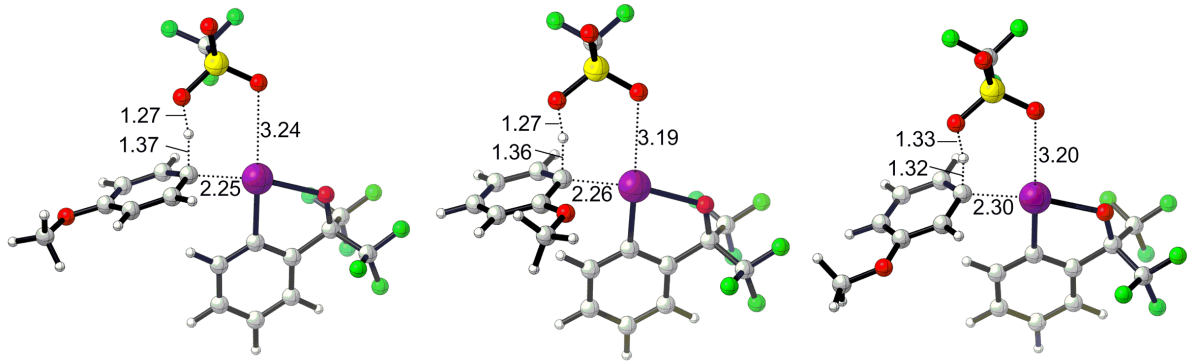


Figure S4. Energy diagram for the *para* C–H λ³-iodanation of anisole (**2a**) with BXT (**1**).

Regioselectivity of C–H λ³-iodanation

Having clarified the reaction pathway for *para* C–H λ³-iodanation and its rate-determining TS (**TS2*p***), we also located TSs for the λ³-iodanation of the *ortho*- (**TS2*o***) and *meta*- (**TS2*m***) positions (Figure S5). Consistent with the experiment, these TSs were higher in energy than **TS2*p***.



TS2*p*
(ΔG_MeCN = 19.3)

TS2*o*
(ΔG_MeCN = 20.5)

TS2*m*
(ΔG_MeCN = 27.5)

Figure S5. Structures of transition states for C–H λ³-iodanation of anisole (**2a**) with BXT (**1**). In the parentheses are shown Gibbs free energies (in MeCN, kcal mol⁻¹) in reference to that of [**1** + **2a**]. Bond distances are in Å.

Thermal correction to Gibbs Free Energies (TCG), single-point electronic energies (E) and Cartesian coordinates of reactants and transition states

BXT (1)

TCG = 0.091313 a.u.

E = -1992.319526 a.u.

I	0.337241000	-1.079619000	-0.181085000
O	-1.639701000	-1.271364000	0.471131000
C	-0.336025000	0.955651000	-0.440877000
C	-1.704425000	1.064976000	-0.223457000
C	-2.275854000	2.332013000	-0.404390000
C	-1.476953000	3.415948000	-0.769482000
C	-0.104929000	3.256643000	-0.963700000
C	0.492071000	2.001145000	-0.803283000
H	0.514327000	4.103688000	-1.242287000
H	1.554135000	1.864317000	-0.955422000
H	-3.338904000	2.474400000	-0.255791000
H	-1.935172000	4.391022000	-0.901094000
C	-2.481730000	-0.190008000	0.173886000
C	-3.284843000	0.044003000	1.486942000
C	-3.420434000	-0.635450000	-0.985045000
F	-2.460736000	0.486962000	2.450092000
F	-4.267888000	0.953285000	1.327202000
F	-3.851405000	-1.092890000	1.917998000
F	-4.105387000	-1.745213000	-0.665715000
F	-4.311512000	0.318510000	-1.316183000
F	-2.680547000	-0.909527000	-2.075461000
O	3.571574000	-1.849953000	0.641771000
S	3.726132000	-0.750879000	-0.317112000
O	2.395504000	-0.385687000	-1.016622000
O	4.819148000	-0.793419000	-1.289332000
C	4.034259000	0.765304000	0.713466000
F	5.172563000	0.613580000	1.395234000
F	4.132517000	1.846218000	-0.068489000
F	3.027359000	0.944906000	1.575984000

Anisole (2a)

TCG = 0.102002 a.u.

E = -346.6366701 a.u.

C	1.857117000	-0.998674000	0.000945000
C	2.285733000	0.335009000	0.000757000
C	1.333577000	1.354452000	-0.000221000
C	-0.035914000	1.063135000	-0.001285000
C	-0.456155000	-0.274335000	-0.001145000
C	0.499246000	-1.305096000	-0.000135000
H	-0.756326000	1.873370000	-0.002224000
H	3.346005000	0.571785000	0.001503000
H	0.154809000	-2.335386000	0.000033000
O	-1.759019000	-0.675343000	-0.002240000
H	1.649420000	2.394807000	-0.000423000
H	2.585380000	-1.805905000	0.001823000
C	-2.774853000	0.326026000	0.002240000
H	-3.724312000	-0.213423000	0.004293000
H	-2.714807000	0.955853000	0.898585000
H	-2.720526000	0.958543000	-0.892610000

TS1

TCG = 0.091659 a.u.

E = -1992.300833 a.u.

I	-0.414197000	0.662730000	-0.388620000
O	0.881984000	-0.926930000	-0.495331000
C	1.402389000	1.699643000	0.064105000
C	2.474147000	0.818678000	0.188604000
C	3.721527000	1.362932000	0.519024000
C	3.852167000	2.739976000	0.705502000
C	2.752535000	3.588692000	0.569892000
C	1.495563000	3.068270000	0.245280000
H	2.863084000	4.658694000	0.716343000
H	0.629571000	3.712000000	0.140211000

H	4.587882000	0.721846000	0.626427000
H	4.825103000	3.148506000	0.959271000
C	2.201940000	-0.663268000	-0.030988000
C	3.104471000	-1.239991000	-1.162872000
C	2.362472000	-1.465171000	1.293428000
F	2.973365000	-0.492846000	-2.269033000
F	4.401197000	-1.242323000	-0.803599000
F	2.758962000	-2.498432000	-1.467200000
F	2.089223000	-2.765704000	1.112232000
F	3.608901000	-1.366505000	1.787864000
F	1.506518000	-0.985305000	2.211585000
O	-3.163241000	1.353023000	-0.636556000
S	-3.688717000	-0.039412000	-0.772371000
O	-2.581069000	-1.038822000	-0.891109000
O	-4.806103000	-0.213624000	-1.708994000
C	-4.420623000	-0.395167000	0.896223000
F	-5.409766000	0.469023000	1.159873000
F	-4.916058000	-1.638889000	0.931845000
F	-3.486323000	-0.280341000	1.851906000

1’

TCG = 0.090119 a.u.

E = -1992.304771 a.u.

I	-0.319626000	1.139587000	-0.270298000
O	0.558378000	-0.705574000	-0.430500000
C	1.707441000	1.704083000	0.109394000
C	2.556801000	0.605374000	0.159519000
C	3.913082000	0.834448000	0.422161000
C	4.366324000	2.140494000	0.614454000
C	3.484556000	3.221510000	0.553534000
C	2.125681000	3.011377000	0.299150000
H	3.847381000	4.233872000	0.702750000
H	1.428339000	3.840562000	0.250828000
H	4.612696000	0.009224000	0.474351000

H	5.419636000	2.310496000	0.813800000
C	1.926720000	-0.766619000	-0.053474000
C	2.598915000	-1.518593000	-1.239903000
C	1.970775000	-1.606030000	1.256245000
F	2.558800000	-0.752550000	-2.340606000
F	3.885196000	-1.810145000	-0.973261000
F	1.963885000	-2.668018000	-1.509745000
F	1.360370000	-2.789797000	1.099014000
F	3.233808000	-1.838795000	1.655500000
F	1.335736000	-0.939128000	2.235441000
O	-3.476064000	1.498072000	-0.804070000
S	-3.534660000	0.021057000	-0.800131000
O	-2.157868000	-0.606145000	-0.788756000
O	-4.467424000	-0.625116000	-1.732569000
C	-4.182943000	-0.406027000	0.886519000
F	-5.409115000	0.107289000	1.052840000
F	-4.248229000	-1.733838000	1.045388000
F	-3.377514000	0.098407000	1.834064000

CP1

TCG = 0.214212 a.u.

E = -2338.955726 a.u.

C	-2.509955000	1.913710000	1.012377000
C	-2.454295000	1.491748000	-0.348497000
C	-2.301041000	2.478522000	-1.361564000
C	-2.190302000	3.820390000	-1.043662000
C	-2.249484000	4.215044000	0.313028000
C	-2.397220000	3.246535000	1.337922000
I	-0.179204000	-0.000583000	-0.486685000
O	1.554103000	-1.279823000	-0.617224000
C	1.406501000	1.389118000	-0.046222000
C	2.641870000	0.769061000	0.124484000
C	3.729747000	1.582626000	0.468323000
C	3.559734000	2.960324000	0.611318000

C	2.307846000	3.545050000	0.419558000
C	1.204720000	2.751971000	0.088717000
H	2.178403000	4.617802000	0.526894000
H	0.227276000	3.189241000	-0.059273000
H	4.709915000	1.146086000	0.616085000
H	4.414637000	3.576233000	0.872496000
H	-2.078610000	4.556906000	-1.830071000
H	-2.867473000	0.519539000	-0.619295000
H	-2.439351000	3.585787000	2.367873000
C	2.714813000	-0.749026000	-0.052073000
C	3.842033000	-1.141963000	-1.053765000
C	2.937879000	-1.439597000	1.325667000
F	3.689577000	-0.462646000	-2.203178000
F	5.074519000	-0.873828000	-0.573406000
F	3.800812000	-2.451967000	-1.341349000
F	2.989722000	-2.776404000	1.202831000
F	4.075871000	-1.037856000	1.926339000
F	1.913501000	-1.143904000	2.148929000
O	-3.792451000	-1.533057000	-1.195134000
S	-2.966335000	-2.708538000	-0.830357000
O	-1.497988000	-2.508951000	-1.018501000
O	-3.470496000	-4.018753000	-1.283130000
C	-3.134808000	-2.782907000	1.017057000
O	-2.171977000	5.482167000	0.729454000
H	-2.294844000	2.171277000	-2.403181000
H	-2.661520000	1.171683000	1.790248000
C	-2.009601000	6.538305000	-0.233904000
H	-1.958328000	7.456802000	0.351397000
H	-1.082613000	6.406937000	-0.800804000
H	-2.866065000	6.579888000	-0.914083000
F	-4.413266000	-2.984592000	1.373694000
F	-2.394563000	-3.780281000	1.527330000
F	-2.723106000	-1.630387000	1.581638000

TS2*p*

TCG = 0.209668 a.u.

E = -2338.938826 a.u.

C	-2.117721000	1.342546000	1.109956000
C	-1.736570000	0.988778000	-0.227207000
C	-2.029400000	1.922939000	-1.269624000
C	-2.786654000	3.052447000	-1.032633000
C	-3.211629000	3.334728000	0.287284000
C	-2.862905000	2.469916000	1.355938000
I	0.121551000	-0.261649000	-0.456059000
O	2.243685000	-1.209826000	-0.613680000
C	1.494305000	1.363516000	0.064477000
C	2.831753000	1.002058000	0.178287000
C	3.731501000	2.013669000	0.553050000
C	3.292947000	3.318162000	0.776609000
C	1.943531000	3.639705000	0.637481000
C	1.023785000	2.649518000	0.280013000
H	1.595101000	4.654583000	0.804830000
H	-0.023888000	2.900024000	0.175641000
H	4.783083000	1.781900000	0.665327000
H	4.010631000	4.082272000	1.059851000
H	-3.042239000	3.713591000	-1.851884000
H	-2.617463000	-0.021317000	-0.520194000
H	-3.197626000	2.721509000	2.357277000
C	3.249762000	-0.464710000	-0.089976000
C	4.425303000	-0.502905000	-1.114509000
C	3.702518000	-1.110954000	1.256359000
F	4.081262000	0.162368000	-2.236255000
F	5.578724000	0.048352000	-0.659504000
F	4.718508000	-1.767141000	-1.469672000
F	4.069776000	-2.396091000	1.087590000
F	4.740178000	-0.478303000	1.854257000
F	2.673780000	-1.099023000	2.131690000
O	-3.594644000	-0.792892000	-0.778090000

S	-3.344958000	-2.311821000	-0.826215000
O	-1.954567000	-2.634148000	-1.182344000
O	-4.432764000	-3.010805000	-1.510498000
C	-3.496137000	-2.767138000	0.968808000
O	-3.944389000	4.392157000	0.627356000
H	-1.697803000	1.706994000	-2.281414000
H	-1.862388000	0.675018000	1.927483000
C	-4.369165000	5.327763000	-0.383072000
H	-4.970265000	6.067084000	0.146391000
H	-3.505682000	5.813873000	-0.846930000
H	-4.977929000	4.826206000	-1.141117000
F	-4.717249000	-2.476299000	1.424403000
F	-3.272501000	-4.075718000	1.120907000
F	-2.590955000	-2.084960000	1.685022000

CP2

TCG = 0.211415 a.u.

E = -2338.959098 a.u.

C	-1.971742000	1.418046000	1.204860000
C	-1.416937000	1.248136000	-0.073819000
C	-1.967965000	1.919461000	-1.170117000
C	-3.080852000	2.750997000	-1.004159000
C	-3.634008000	2.921612000	0.274502000
C	-3.070725000	2.248515000	1.376373000
I	0.268143000	-0.092381000	-0.358012000
O	2.376605000	-1.190542000	-0.587308000
C	1.777368000	1.430833000	0.109480000
C	3.096203000	1.002230000	0.155621000
C	4.059541000	1.971435000	0.485910000
C	3.694537000	3.294421000	0.733391000
C	2.355900000	3.680358000	0.665539000
C	1.375416000	2.734925000	0.352369000
H	2.064759000	4.709570000	0.854451000
H	0.331750000	3.022632000	0.302039000

H	5.103761000	1.691713000	0.545378000
H	4.461522000	4.022653000	0.980284000
H	-3.498618000	3.254885000	-1.867721000
H	-3.122862000	-0.156553000	-0.812657000
H	-3.515390000	2.388136000	2.357111000
C	3.433887000	-0.489187000	-0.131765000
C	4.556752000	-0.572146000	-1.212992000
C	3.939292000	-1.141505000	1.194509000
F	4.183681000	0.103242000	-2.320683000
F	5.756083000	-0.066350000	-0.823456000
F	4.783705000	-1.847936000	-1.579218000
F	4.250164000	-2.441548000	1.017460000
F	5.032301000	-0.547754000	1.734507000
F	2.962162000	-1.087501000	2.126446000
O	-3.991231000	-0.632806000	-0.793616000
S	-3.782512000	-2.229265000	-0.818748000
O	-2.545245000	-2.577608000	-1.505384000
O	-5.063282000	-2.810309000	-1.180122000
C	-3.510643000	-2.558603000	0.998386000
O	-4.703123000	3.702304000	0.549378000
H	-1.539264000	1.799365000	-2.160751000
H	-1.548866000	0.902022000	2.061041000
C	-5.343435000	4.393302000	-0.527974000
H	-6.168270000	4.945223000	-0.074192000
H	-4.657246000	5.096901000	-1.012967000
H	-5.738737000	3.690429000	-1.270379000
F	-4.595271000	-2.213985000	1.683678000
F	-3.265299000	-3.856436000	1.156521000
F	-2.464112000	-1.847043000	1.419047000

3a

TCG = 0.187872 a.u.

E = -1376.894785 a.u.

C	-3.198152000	-0.543622000	1.304238000

C	-2.582774000	-0.576460000	0.046476000
C	-3.322051000	-0.309446000	-1.105612000
C	-4.682982000	-0.004558000	-1.014962000
C	-5.302804000	0.031061000	0.243537000
C	-4.551623000	-0.242723000	1.401330000
I	-0.504026000	-1.163863000	-0.119597000
O	1.884984000	-1.367328000	-0.264784000
C	0.276176000	0.883848000	0.029994000
C	1.655811000	1.030271000	0.036211000
C	2.145857000	2.343526000	0.152457000
C	1.278315000	3.431598000	0.243362000
C	-0.102480000	3.234819000	0.225025000
C	-0.617134000	1.939971000	0.118979000
H	-0.784579000	4.077332000	0.293383000
H	-1.687962000	1.772290000	0.107182000
H	3.214047000	2.518072000	0.169642000
H	1.686448000	4.434453000	0.328832000
H	-5.242356000	0.199289000	-1.920680000
H	-5.047698000	-0.212603000	2.366897000
C	2.570831000	-0.225681000	-0.068231000
C	3.554975000	-0.047174000	-1.267583000
C	3.383960000	-0.354491000	1.259277000
F	2.858904000	0.156920000	-2.406437000
F	4.423799000	0.989581000	-1.143303000
F	4.304499000	-1.152102000	-1.450045000
F	4.176800000	-1.444993000	1.247190000
F	4.185011000	0.704787000	1.538849000
F	2.534024000	-0.490021000	2.300813000
O	-6.612711000	0.315613000	0.446210000
H	-2.848906000	-0.334800000	-2.082716000
H	-2.628131000	-0.751532000	2.204782000
C	-7.425712000	0.635493000	-0.685397000
H	-8.420911000	0.838189000	-0.285588000
H	-7.052835000	1.526233000	-1.204823000

H	-7.480537000	-0.204568000	-1.387890000

HOTf

TCG = 0.004532 a.u.

E = -962.0572 a.u.

H	1.378286000	1.953280000	-0.075949000
O	1.264403000	1.214608000	-0.718013000
S	0.851210000	-0.142944000	0.057491000
O	1.246991000	-0.071254000	1.457257000
O	1.226703000	-1.246557000	-0.807869000
C	-1.008133000	0.009061000	-0.002671000
F	-1.416363000	-0.007684000	-1.266751000
F	-1.530801000	-1.020766000	0.657891000
F	-1.369906000	1.151237000	0.577873000

CP1'

TCG = 0.211928 a.u.

E = -2338.964328 a.u.

C	-0.549403000	3.928530000	1.066992000
C	-1.156383000	4.114710000	-0.182267000
C	-0.364440000	4.096226000	-1.331597000
C	1.018840000	3.896548000	-1.253100000
C	1.619612000	3.710400000	0.000738000
C	0.825701000	3.724831000	1.162305000
I	-0.397412000	0.272953000	0.204803000
O	1.534237000	-0.117311000	0.903009000
C	-0.070894000	-1.673746000	-0.669856000
C	1.235716000	-2.106949000	-0.473296000
C	1.588188000	-3.344366000	-1.029471000
C	0.643371000	-4.090406000	-1.734506000
C	-0.657489000	-3.615785000	-1.901756000
C	-1.034802000	-2.379365000	-1.366203000
H	-1.390716000	-4.199476000	-2.449789000
H	-2.039386000	-2.000238000	-1.496205000

H	2.594023000	-3.727430000	-0.909904000
H	0.931153000	-5.048581000	-2.155500000
H	1.610842000	3.890812000	-2.161321000
H	-2.228105000	4.276724000	-0.254054000
H	1.308422000	3.587558000	2.125852000
C	2.190162000	-1.201255000	0.304589000
C	2.840072000	-1.962677000	1.496582000
C	3.277245000	-0.620790000	-0.647179000
F	1.881997000	-2.511429000	2.261651000
F	3.661280000	-2.948976000	1.083168000
F	3.559349000	-1.133382000	2.267564000
F	4.110896000	0.207324000	0.002224000
F	4.019715000	-1.583971000	-1.224955000
F	2.679598000	0.084544000	-1.628427000
O	-3.543889000	1.166730000	1.295520000
S	-3.800910000	0.543589000	-0.007161000
O	-2.504216000	0.261980000	-0.800088000
O	-4.823896000	1.114461000	-0.884957000
C	-4.381438000	-1.180361000	0.377411000
O	2.953084000	3.520739000	0.198772000
H	-0.819833000	4.242267000	-2.307971000
H	-1.149579000	3.945789000	1.973175000
C	3.801565000	3.428917000	-0.944634000
H	4.806628000	3.250574000	-0.557394000
H	3.509986000	2.597052000	-1.594816000
H	3.798443000	4.362485000	-1.520551000
F	-5.536559000	-1.126208000	1.045138000
F	-4.563456000	-1.870596000	-0.754746000
F	-3.471797000	-1.812974000	1.128601000

TS2*p*'

TCG = 0.206453 a.u.

E = -2338.906895 a.u.

C	-1.158933000	1.549047000	1.040883000

C	-1.084072000	1.004044000	-0.278899000
C	-0.762089000	1.880414000	-1.355553000
C	-0.754108000	3.249195000	-1.176216000
C	-0.951507000	3.775408000	0.122205000
C	-1.151184000	2.910070000	1.228367000
I	-0.191066000	-1.100902000	-0.433419000
O	1.512063000	0.523812000	0.036813000
C	1.749534000	-2.160273000	-0.258383000
C	2.899791000	-1.460238000	0.008567000
C	4.100324000	-2.183809000	0.113567000
C	4.092668000	-3.569292000	-0.051754000
C	2.902294000	-4.249079000	-0.323850000
C	1.703073000	-3.538093000	-0.430216000
H	2.901021000	-5.327862000	-0.452983000
H	0.768964000	-4.053504000	-0.639434000
H	5.033885000	-1.676522000	0.323087000
H	5.025083000	-4.119945000	0.032937000
H	-0.582276000	3.904401000	-2.021551000
H	-2.415075000	0.602852000	-0.542175000
H	-1.282055000	3.348026000	2.212843000
C	2.786522000	0.084369000	0.164167000
C	3.293360000	0.496980000	1.577724000
C	3.641710000	0.767351000	-0.944164000
F	2.578525000	-0.143101000	2.524705000
F	4.599386000	0.213595000	1.796696000
F	3.141852000	1.819593000	1.783554000
F	3.534059000	2.109333000	-0.888688000
F	4.962000000	0.475595000	-0.876311000
F	3.206663000	0.378616000	-2.159898000
O	-3.622231000	0.509561000	-0.744715000
S	-4.299411000	-0.880672000	-0.725124000
O	-3.388312000	-1.952104000	-1.145566000
O	-5.639739000	-0.810741000	-1.306049000
C	-4.545006000	-1.141594000	1.098253000

O	-0.956373000	5.075566000	0.409941000
H	-0.597950000	1.470857000	-2.347877000
H	-1.312745000	0.886089000	1.886591000
C	-0.733632000	6.043491000	-0.633525000
H	-0.798444000	7.014331000	-0.142090000
H	0.259400000	5.914350000	-1.074071000
H	-1.505222000	5.966264000	-1.405590000
F	-5.367446000	-0.216937000	1.598094000
F	-5.067545000	-2.353412000	1.308134000
F	-3.364521000	-1.061892000	1.728502000

CP2'

TCG = 0.207905 a.u.

E = -2338.925845 a.u.

C	-1.171008000	1.517043000	1.349914000
C	-0.832966000	1.024675000	0.084902000
C	-1.050991000	1.770785000	-1.071461000
C	-1.673634000	3.020984000	-0.974434000
C	-2.040467000	3.520539000	0.285139000
C	-1.784133000	2.760391000	1.443186000
I	0.057690000	-0.976649000	-0.075407000
O	1.811070000	0.790362000	0.062200000
C	2.096602000	-1.919781000	-0.162379000
C	3.234799000	-1.161172000	-0.096860000
C	4.463730000	-1.844780000	-0.157701000
C	4.488351000	-3.234316000	-0.282509000
C	3.299854000	-3.966577000	-0.346866000
C	2.071129000	-3.301287000	-0.286578000
H	3.321333000	-5.048534000	-0.444232000
H	1.135649000	-3.853415000	-0.335682000
H	5.397586000	-1.298475000	-0.108939000
H	5.444702000	-3.747292000	-0.329477000
H	-1.860754000	3.585853000	-1.880080000
H	-2.964713000	0.470652000	-0.526079000

H	-2.075847000	3.161804000	2.409014000
C	3.090645000	0.391666000	0.048329000
C	3.762539000	0.823271000	1.388066000
C	3.808972000	1.074736000	-1.155779000
F	3.171110000	0.188223000	2.422127000
F	5.090003000	0.554082000	1.462643000
F	3.624057000	2.147526000	1.600817000
F	3.666255000	2.414748000	-1.111494000
F	5.141385000	0.829869000	-1.229072000
F	3.263646000	0.651935000	-2.315573000
O	-3.952952000	0.391746000	-0.525859000
S	-4.410423000	-1.118962000	-0.844130000
O	-3.363042000	-1.830130000	-1.566476000
O	-5.780830000	-1.055557000	-1.320313000
C	-4.450289000	-1.813725000	0.888057000
O	-2.645895000	4.712555000	0.490533000
H	-0.758142000	1.392648000	-2.045482000
H	-0.974300000	0.939951000	2.247391000
C	-2.959037000	5.527576000	-0.643031000
H	-3.448772000	6.416087000	-0.240850000
H	-2.052034000	5.823638000	-1.182646000
H	-3.643659000	5.010799000	-1.325372000
F	-5.383332000	-1.190627000	1.599543000
F	-4.726217000	-3.113030000	0.814007000
F	-3.256154000	-1.638273000	1.455275000

3a'

TCG = 0.186616 a.u.

E = -1376.872975 a.u.

C	-2.036419000	0.877185000	0.518583000
C	-2.183882000	-0.506265000	0.460641000
C	-3.367952000	-1.130799000	0.088697000
C	-4.471297000	-0.333144000	-0.228947000
C	-4.358480000	1.065352000	-0.178552000

C	-3.137522000	1.660560000	0.191640000
I	-0.510361000	-1.759304000	1.003036000
O	0.878450000	0.744041000	1.211688000
C	0.881296000	-1.477323000	-0.678509000
C	1.746780000	-0.394989000	-0.787934000
C	2.592555000	-0.419747000	-1.915624000
C	2.550051000	-1.448692000	-2.855470000
C	1.657541000	-2.508603000	-2.701054000
C	0.808136000	-2.525009000	-1.595015000
H	1.614266000	-3.315341000	-3.426969000
H	0.106137000	-3.339183000	-1.451985000
H	3.297637000	0.386935000	-2.065321000
H	3.220193000	-1.417188000	-3.710058000
H	-5.399880000	-0.811709000	-0.516830000
H	-3.070993000	2.744387000	0.216111000
C	1.809465000	0.776169000	0.277783000
C	3.219429000	0.686298000	0.964468000
C	1.714272000	2.144485000	-0.493786000
F	3.331561000	-0.490010000	1.623366000
F	4.293269000	0.765041000	0.132347000
F	3.378017000	1.668673000	1.877327000
F	1.634607000	3.173441000	0.374380000
F	2.748186000	2.444173000	-1.330780000
F	0.588218000	2.174627000	-1.245556000
O	-5.364467000	1.924009000	-0.471603000
H	-3.450114000	-2.211392000	0.041796000
H	-1.069922000	1.299228000	0.790262000
C	-6.625603000	1.387857000	-0.880079000
H	-7.267614000	2.251039000	-1.063951000
H	-6.529150000	0.802660000	-1.802150000
H	-7.068224000	0.765733000	-0.093324000

TS2*o*

TCG = 0.210047 a.u.

E = -2338.937206 a.u.

C	1.904500000	1.580543000	-1.668614000
C	1.652931000	1.417472000	-0.266285000
C	1.840251000	2.556707000	0.598480000
C	2.401429000	3.735351000	0.078265000
C	2.690075000	3.816033000	-1.279333000
C	2.448049000	2.746230000	-2.163893000
I	0.032018000	-0.061078000	0.285280000
O	-1.877454000	-1.299473000	0.686384000
C	-1.597272000	1.207499000	-0.445932000
C	-2.863251000	0.635999000	-0.389780000
C	-3.931630000	1.413366000	-0.867321000
C	-3.719521000	2.700347000	-1.359525000
C	-2.433556000	3.237463000	-1.391198000
C	-1.351013000	2.482484000	-0.930858000
H	-2.259695000	4.239844000	-1.770988000
H	-0.353544000	2.901214000	-0.960950000
H	-4.936936000	1.012066000	-0.851751000
H	-4.563879000	3.281178000	-1.718433000
H	2.594384000	4.586041000	0.720896000
H	2.703034000	0.625099000	0.097048000
H	2.683456000	2.844489000	-3.218488000
C	-3.028103000	-0.799061000	0.163651000
C	-4.089354000	-0.807754000	1.305993000
C	-3.486604000	-1.735762000	-0.996196000
F	-3.744239000	0.082720000	2.258604000
F	-5.344950000	-0.495082000	0.900359000
F	-4.163593000	-2.016740000	1.891418000
F	-3.624338000	-3.007685000	-0.575898000
F	-4.662340000	-1.378038000	-1.565085000
F	-2.554386000	-1.732252000	-1.972804000
O	3.804750000	0.069062000	0.412262000
S	3.787918000	-1.422015000	0.796005000
O	2.468891000	-1.851904000	1.285973000

O	4.981781000	-1.795401000	1.554301000
C	3.968413000	-2.227663000	-0.867949000
H	1.716635000	0.734359000	-2.323042000
F	5.119363000	-1.863874000	-1.439167000
F	3.949753000	-3.556569000	-0.728714000
F	2.952811000	-1.858957000	-1.661237000
H	3.113087000	4.739342000	-1.665477000
O	1.513878000	2.384827000	1.877244000
C	1.768919000	3.435981000	2.830292000
H	1.190072000	4.330171000	2.581288000
H	1.439975000	3.036219000	3.789447000
H	2.836697000	3.669375000	2.869133000

TS2*m*

TCG = 0.209025 a.u.

E = -2338.925127 a.u.

C	-2.097971000	1.333860000	1.472241000
C	-1.761267000	1.131987000	0.099837000
C	-1.938935000	2.198296000	-0.823626000
C	-2.540198000	3.394242000	-0.422671000
C	-2.913509000	3.549628000	0.926681000
C	-2.693330000	2.524895000	1.857784000
I	0.045029000	-0.237243000	-0.316860000
O	2.048610000	-1.289179000	-0.623159000
C	1.507905000	1.227577000	0.379334000
C	2.828257000	0.791719000	0.350849000
C	3.804186000	1.690990000	0.810722000
C	3.451023000	2.961265000	1.263760000
C	2.115144000	3.359459000	1.269353000
C	1.122375000	2.482094000	0.823473000
H	1.832284000	4.348050000	1.618337000
H	0.086628000	2.793824000	0.831196000
H	4.846298000	1.398056000	0.813015000
H	4.225098000	3.638277000	1.612262000

H	-2.622630000	0.215360000	-0.298296000
H	-2.993750000	2.677805000	2.890007000
C	3.150033000	-0.626862000	-0.166120000
C	4.151211000	-0.536793000	-1.357660000
C	3.765450000	-1.471130000	0.990842000
F	3.635407000	0.246883000	-2.326302000
F	5.359114000	-0.022157000	-1.024366000
F	4.378743000	-1.748300000	-1.896416000
F	4.014955000	-2.733746000	0.596949000
F	4.925695000	-0.972984000	1.478746000
F	2.892666000	-1.532873000	2.018020000
O	-3.676504000	-0.513759000	-0.662463000
S	-3.514173000	-2.025164000	-0.862812000
O	-2.136984000	-2.395800000	-1.229973000
O	-4.622371000	-2.595909000	-1.631096000
C	-3.727963000	-2.657607000	0.870207000
H	-1.942669000	0.531308000	2.185729000
F	-4.943688000	-2.353787000	1.333778000
F	-3.572675000	-3.985437000	0.890090000
F	-2.807492000	-2.103274000	1.673428000
H	-3.378956000	4.470066000	1.261206000
H	-1.656212000	2.071898000	-1.864540000
O	-2.711323000	4.329968000	-1.382889000
C	-3.290519000	5.589094000	-1.020673000
H	-3.323805000	6.171489000	-1.942614000
H	-4.307159000	5.462147000	-0.631650000
H	-2.672231000	6.110449000	-0.280783000

6. References

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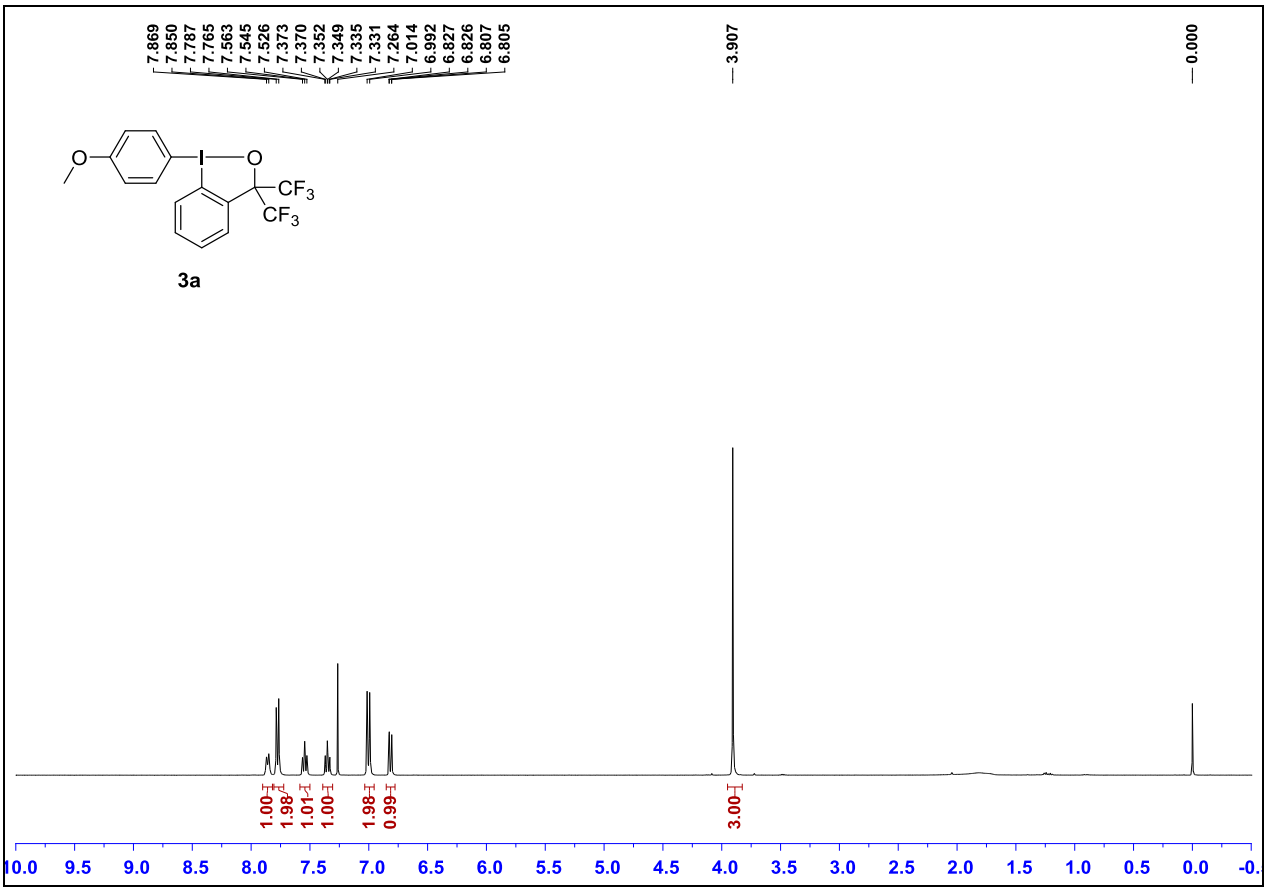
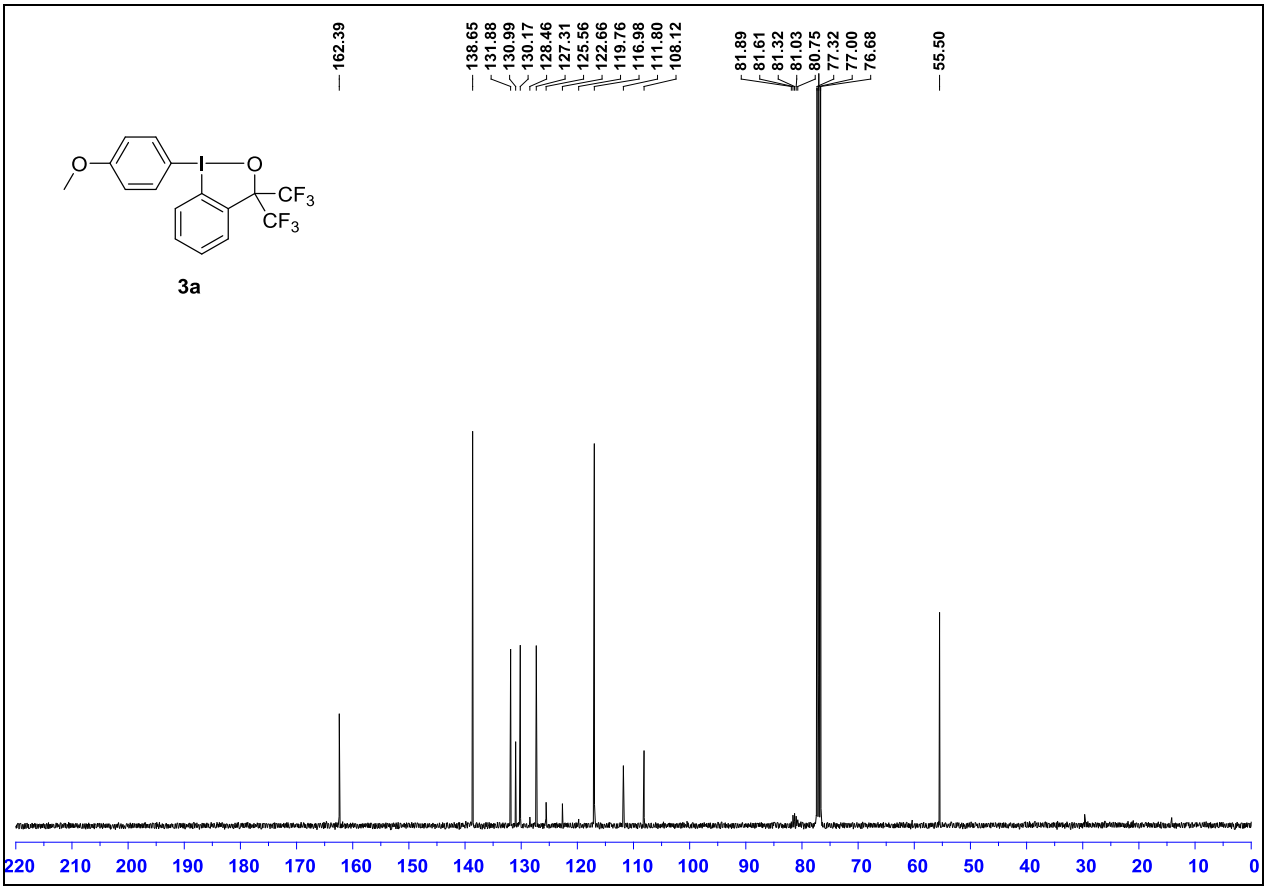
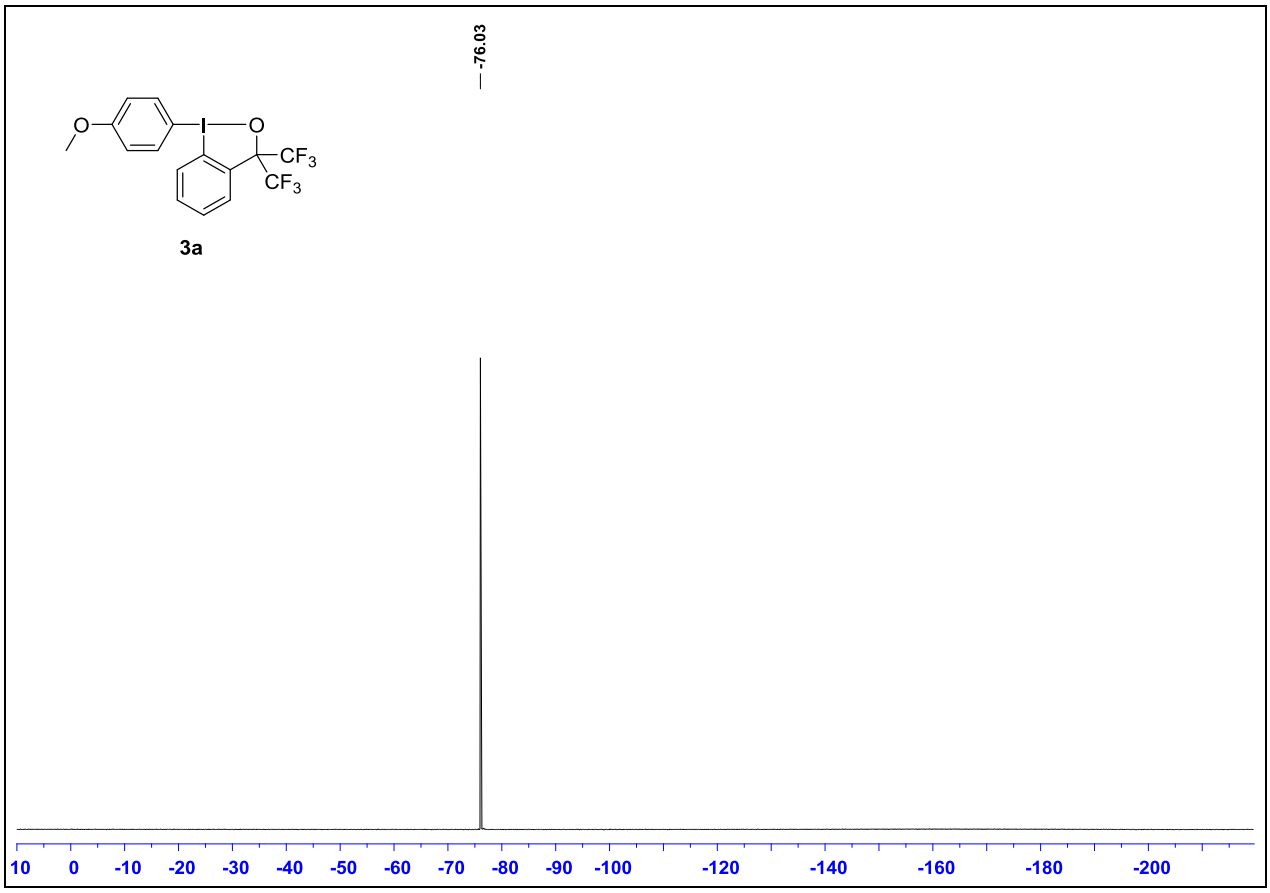
7. NMR Spectra

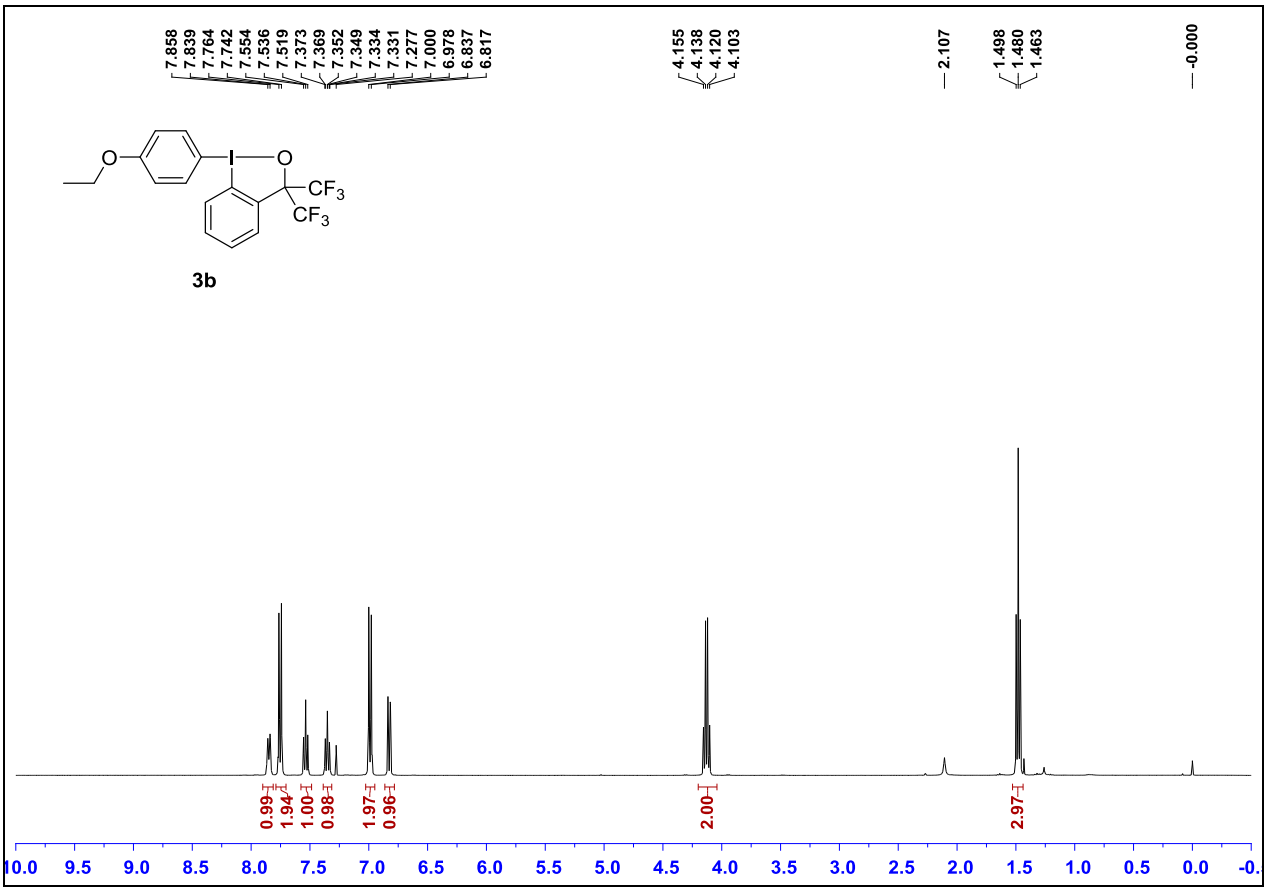
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

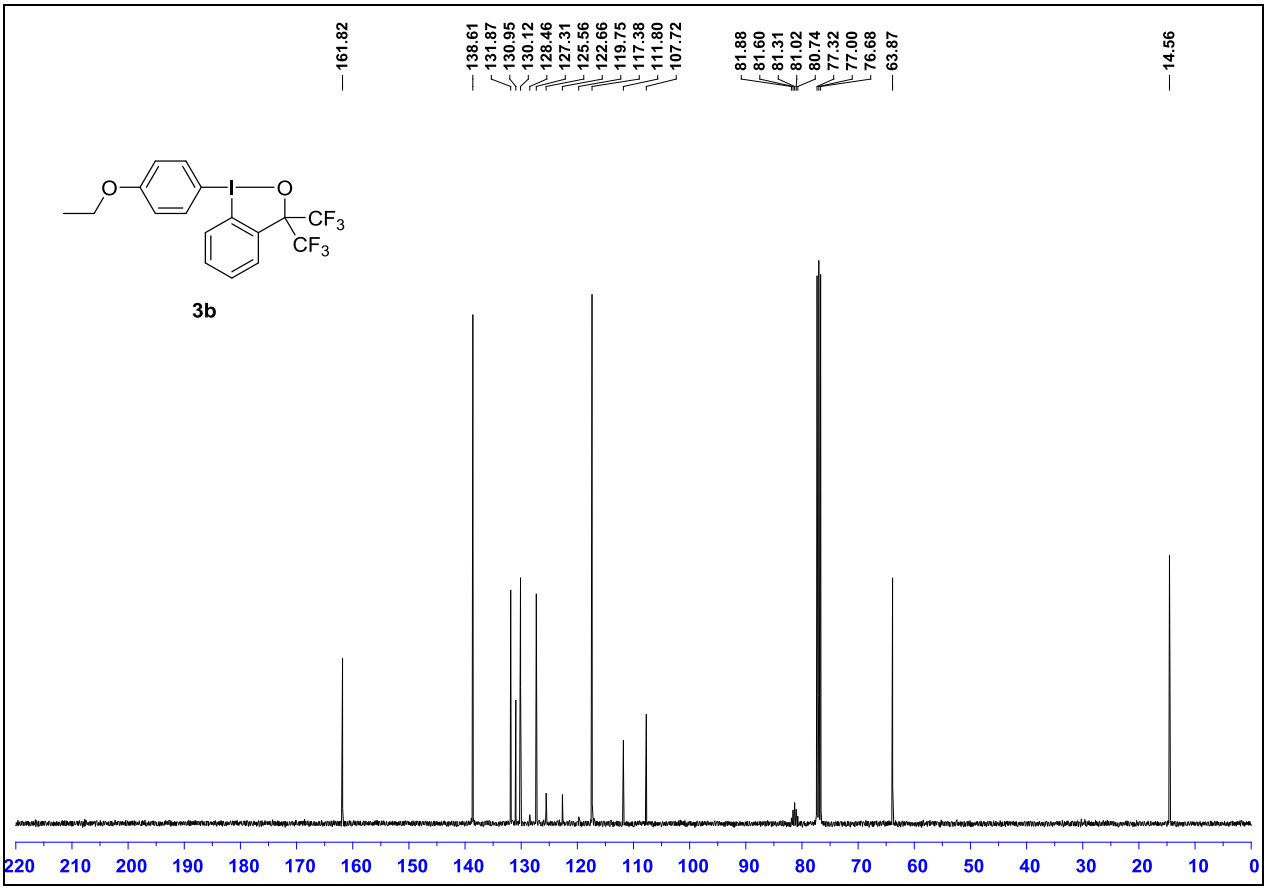


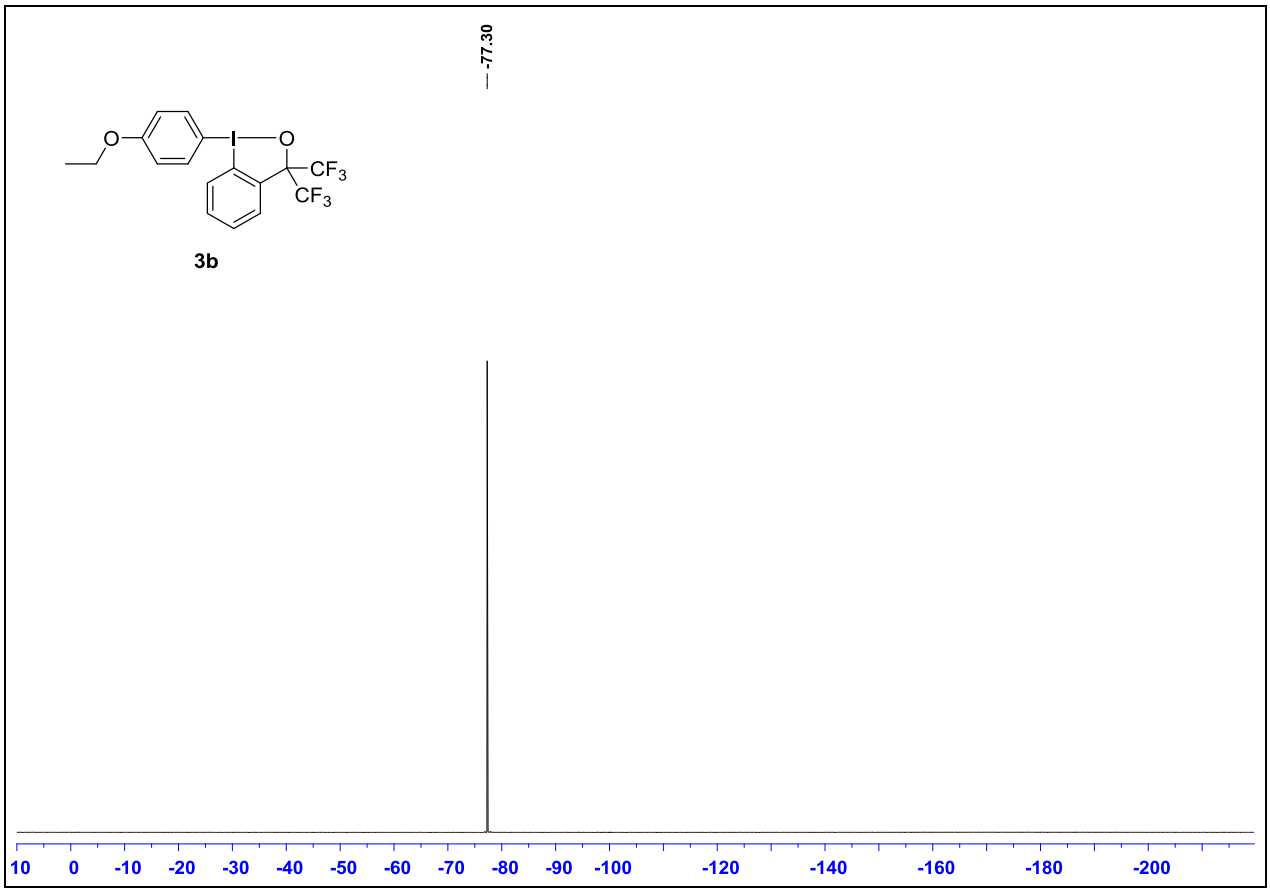



-76.03
O
I
O
CF3
CF3
3a
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

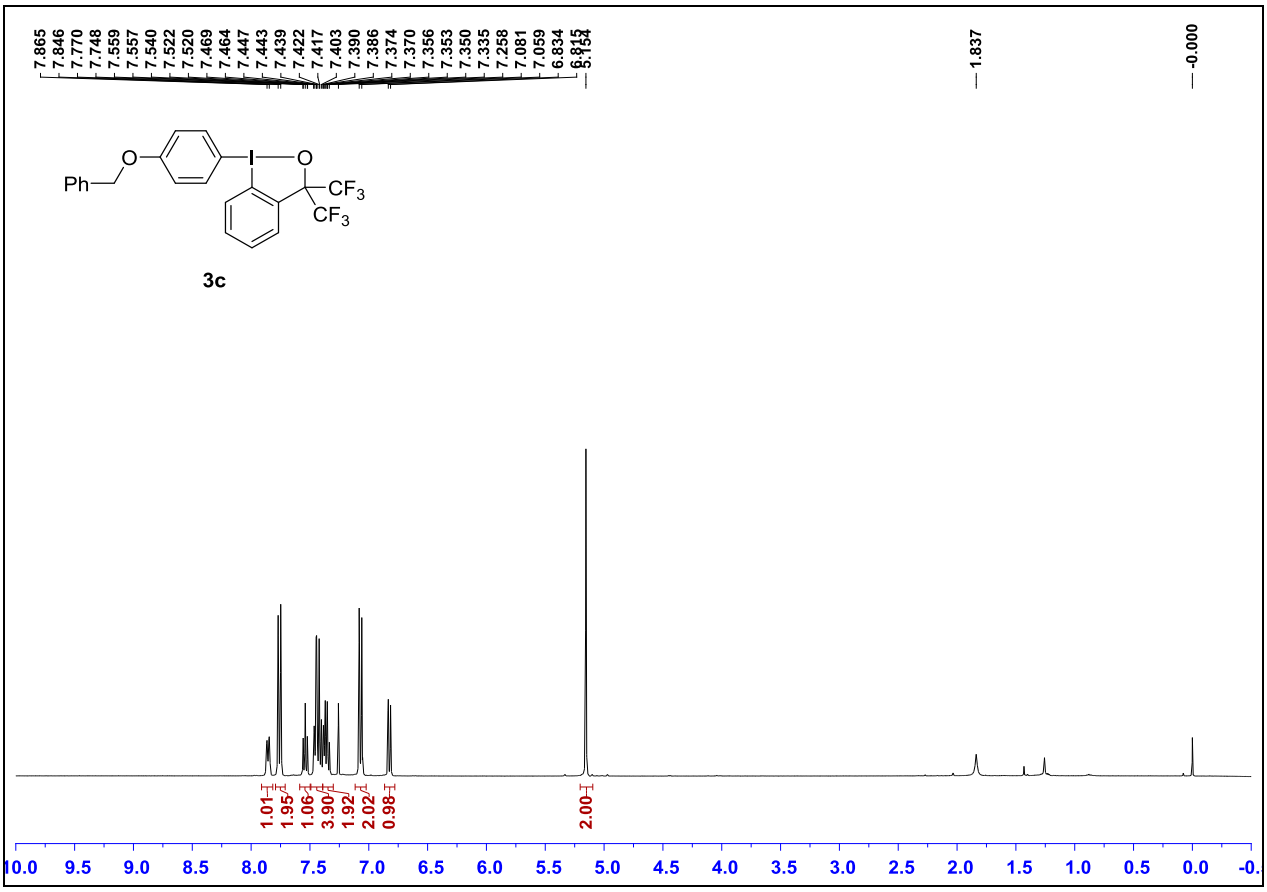
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

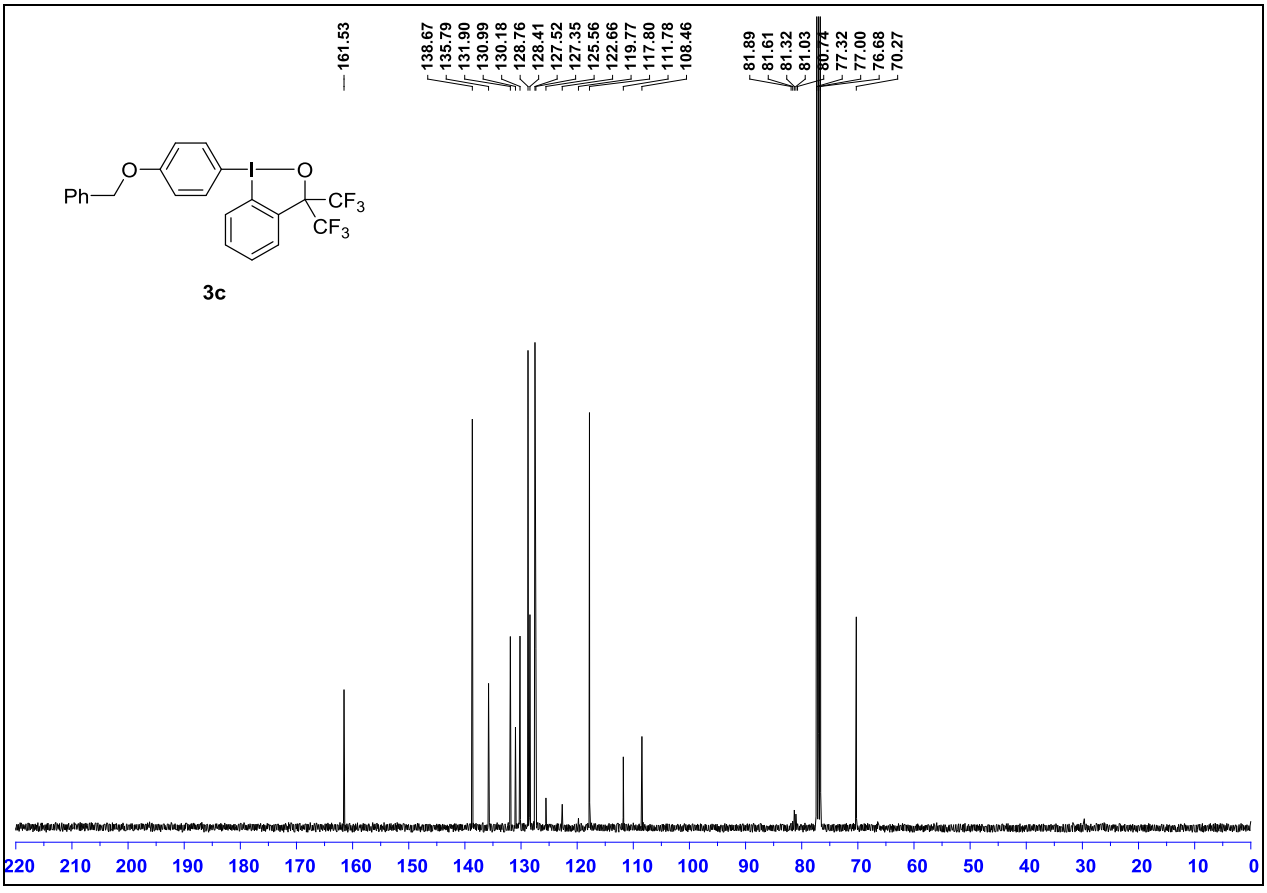


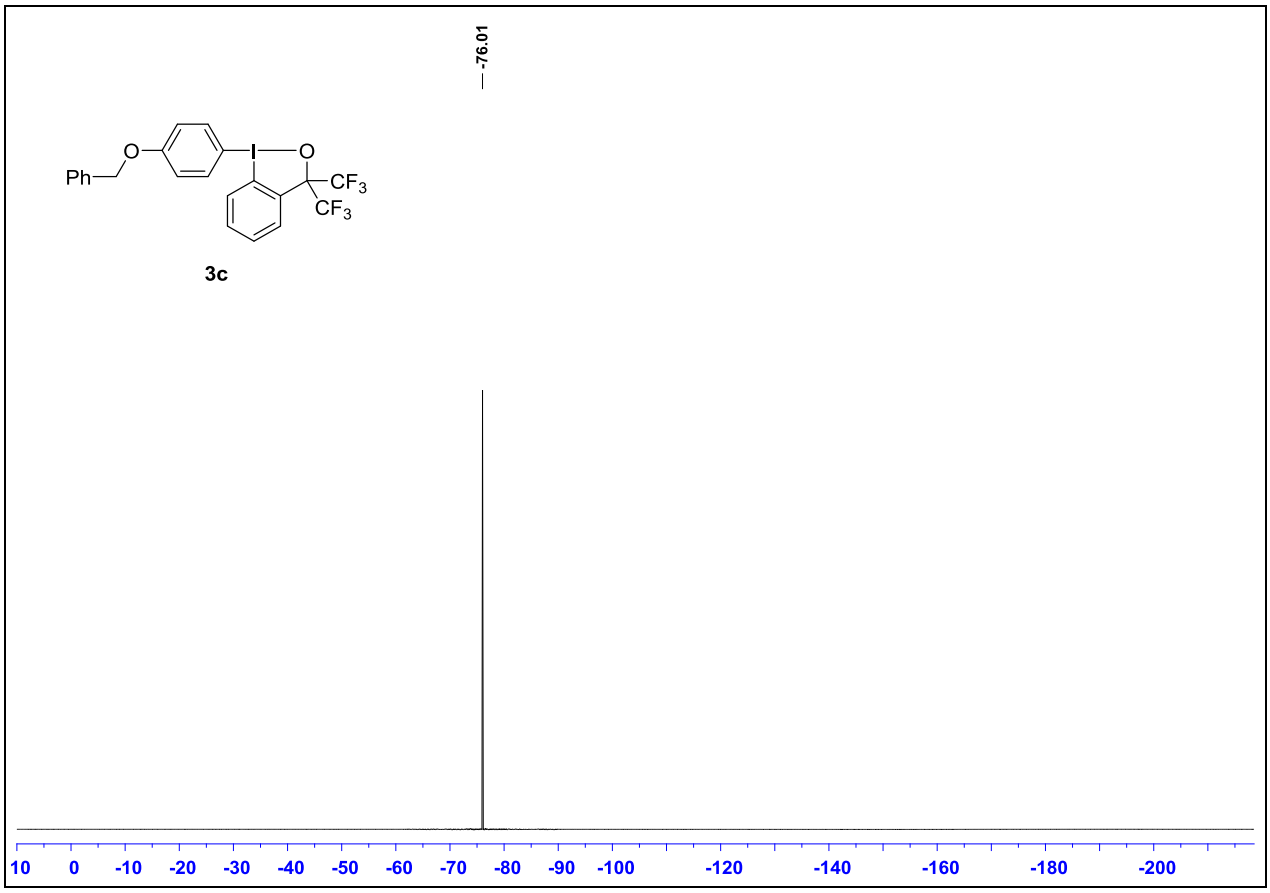



-77.30
O
I
O
CF3
CF3
3b
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

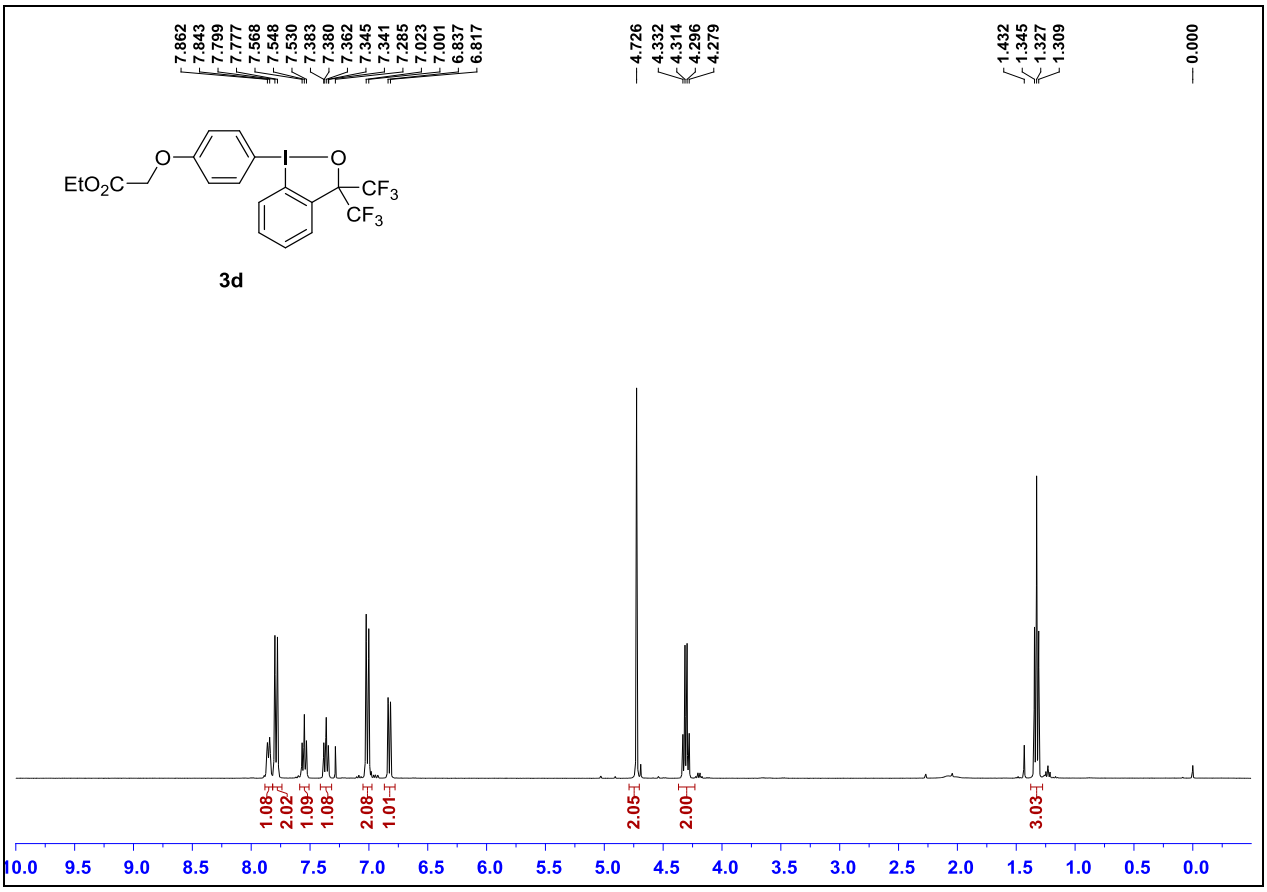


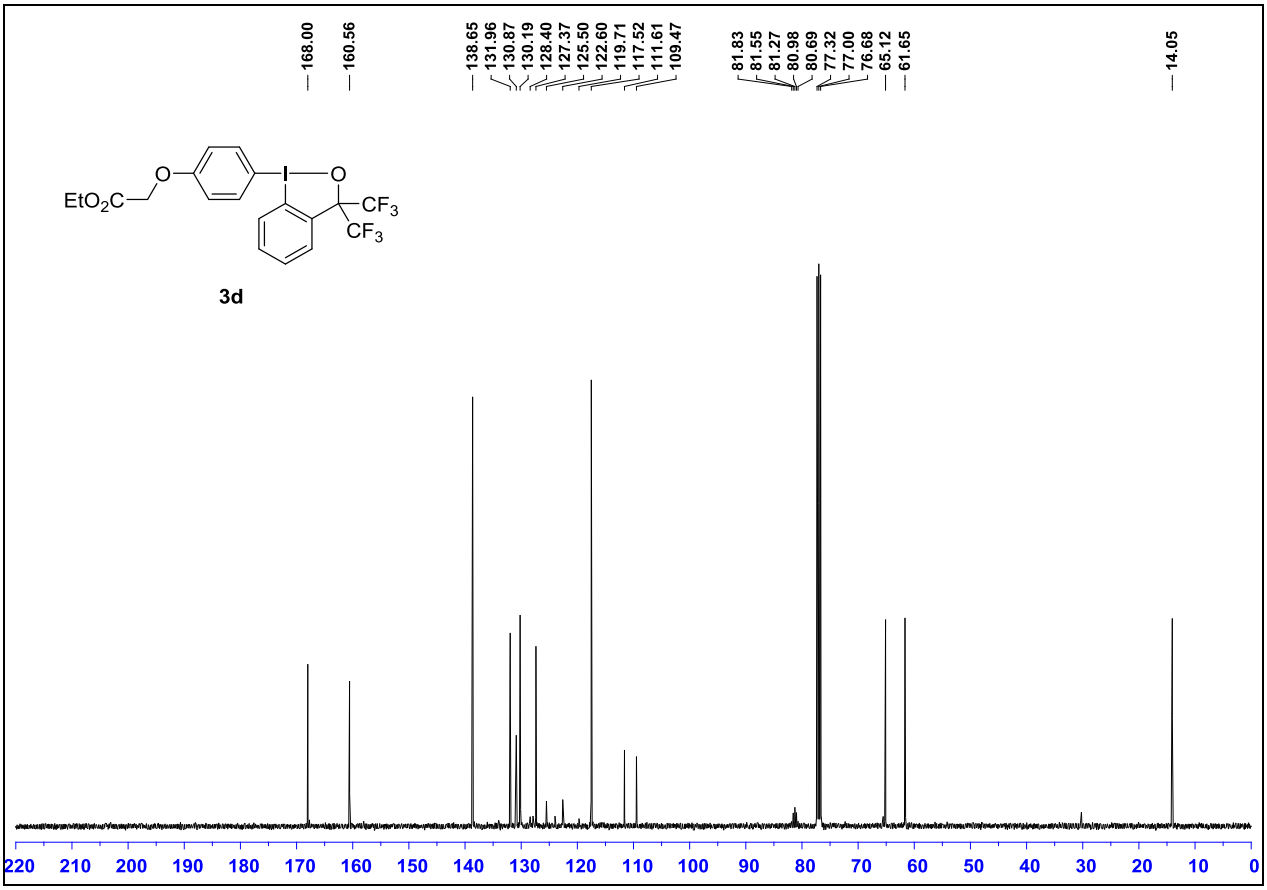


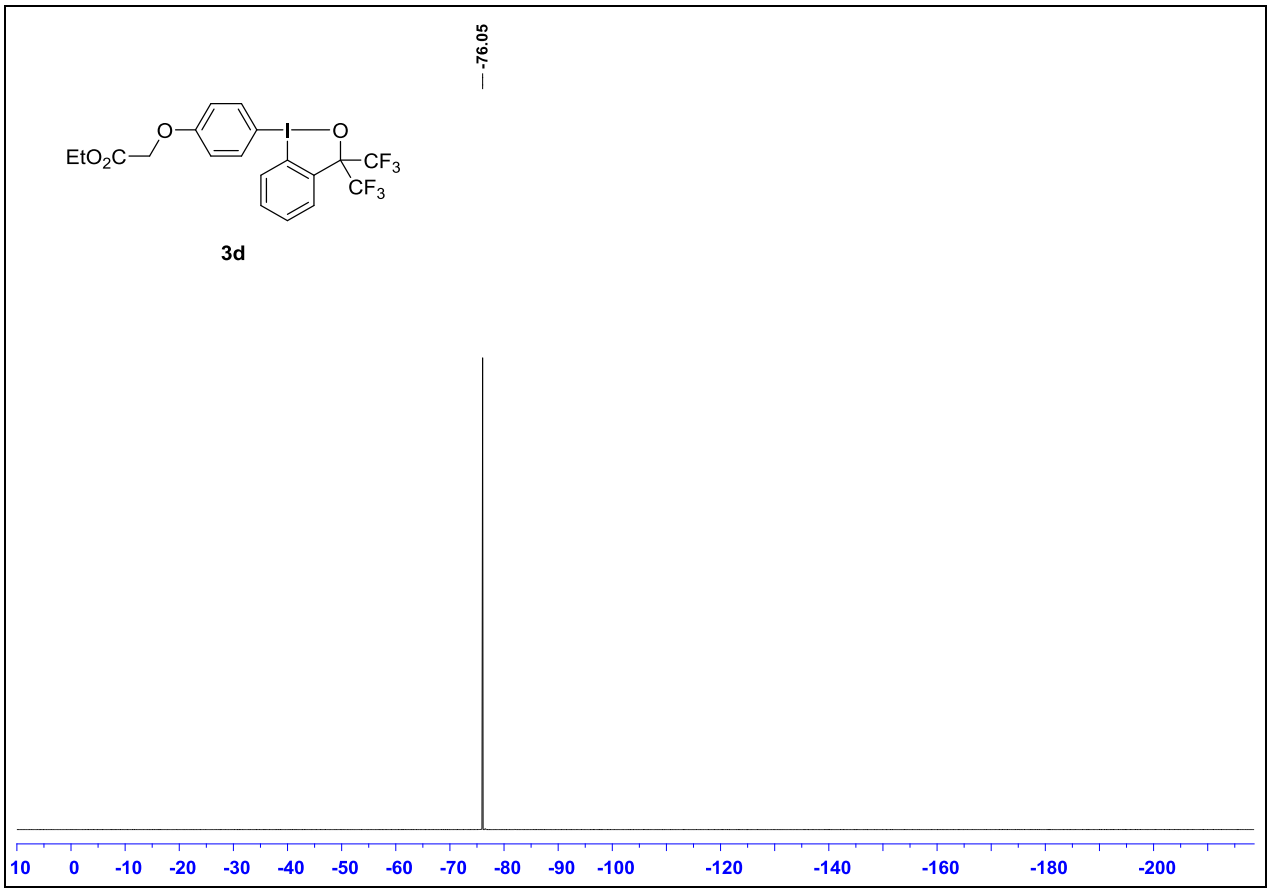

-76.01
Ph
O
I
O
CF3
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

3c

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum



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O
I
O
EtO2C
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CF3
10
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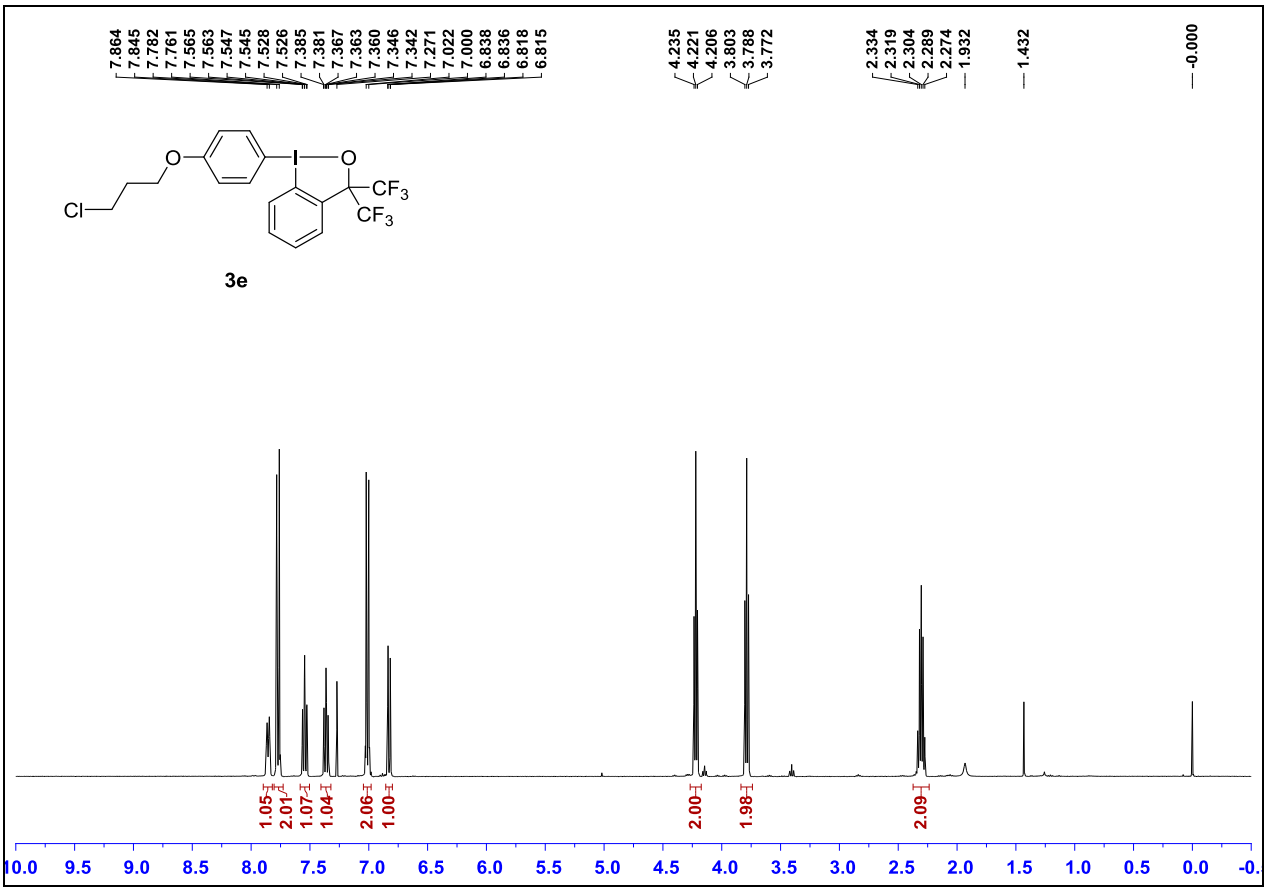
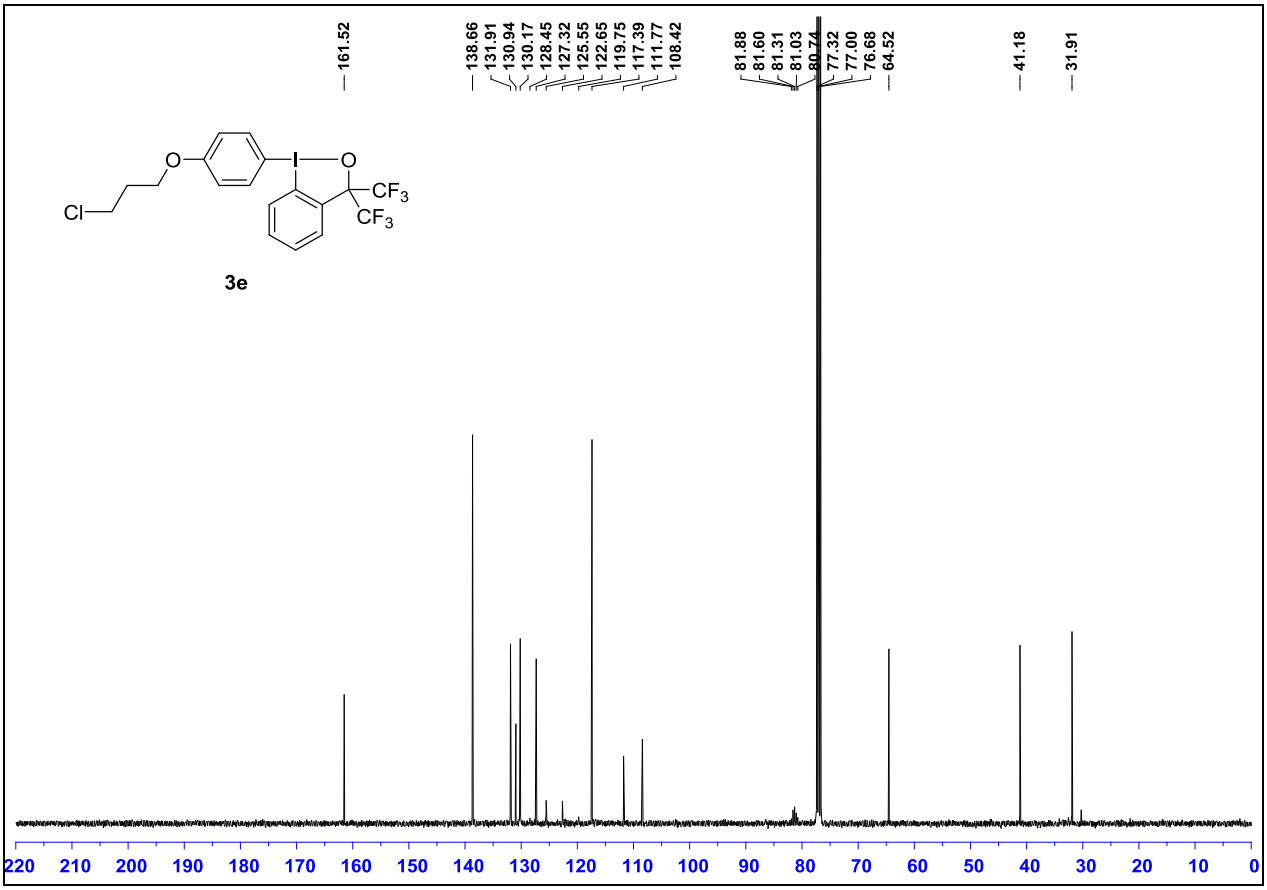
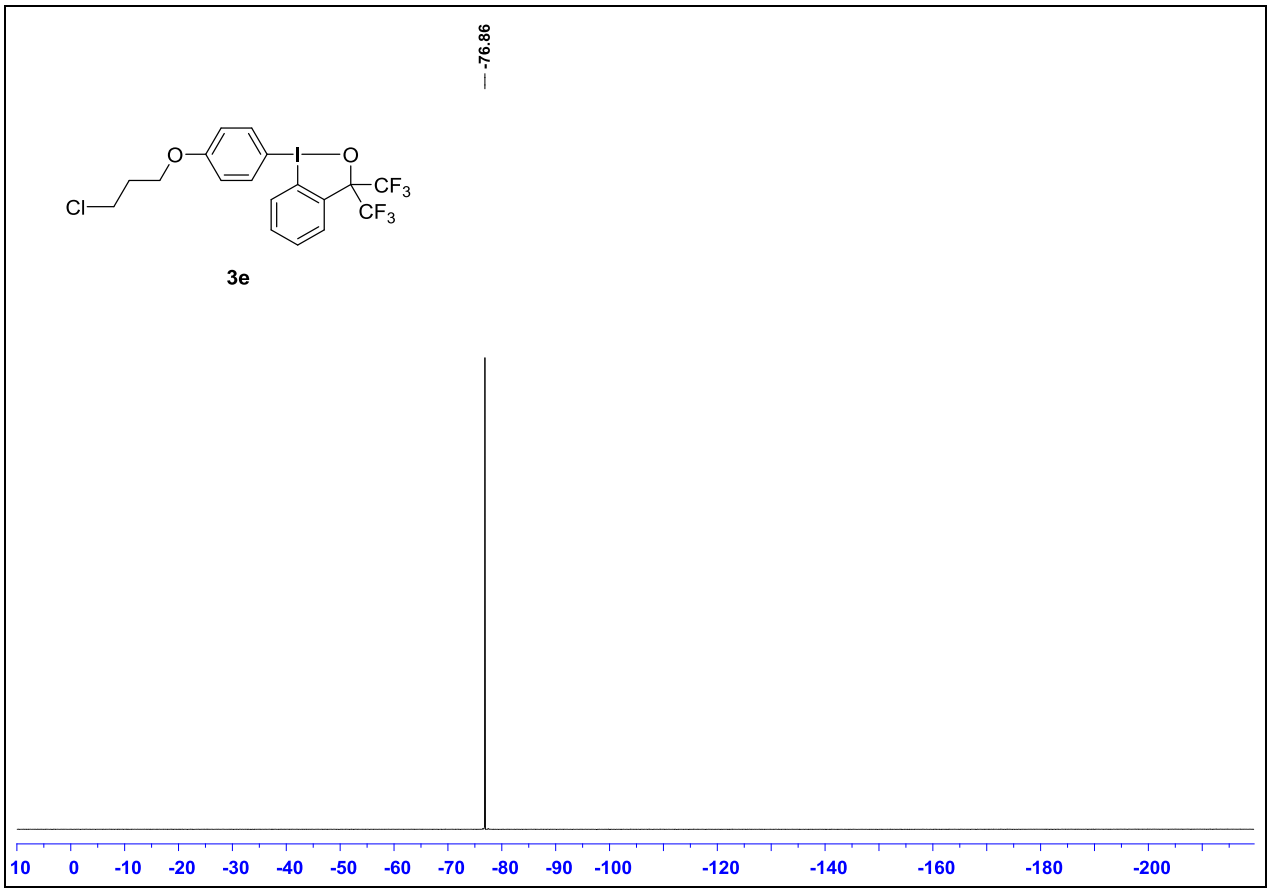
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

3d

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum



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CF3
CF3
Cl
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-20
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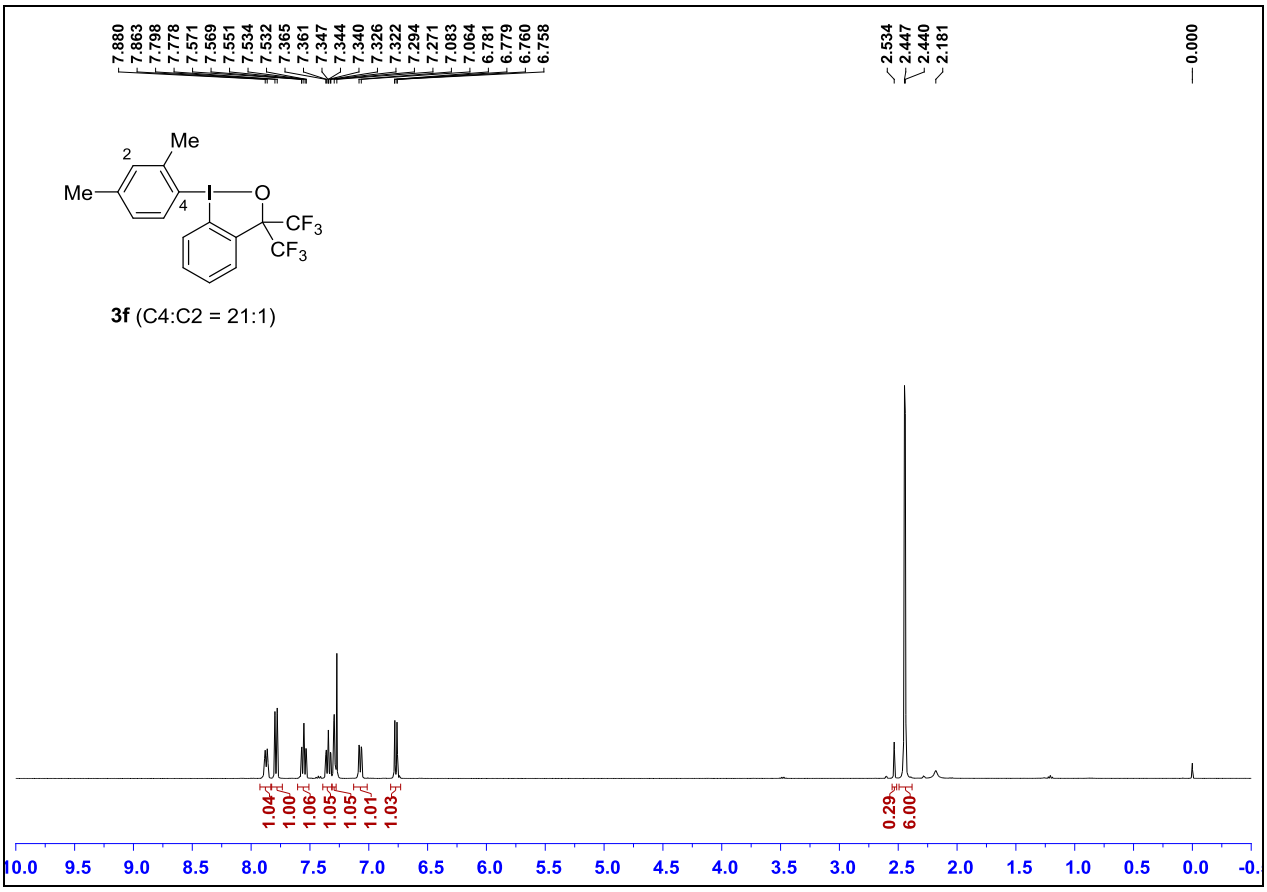
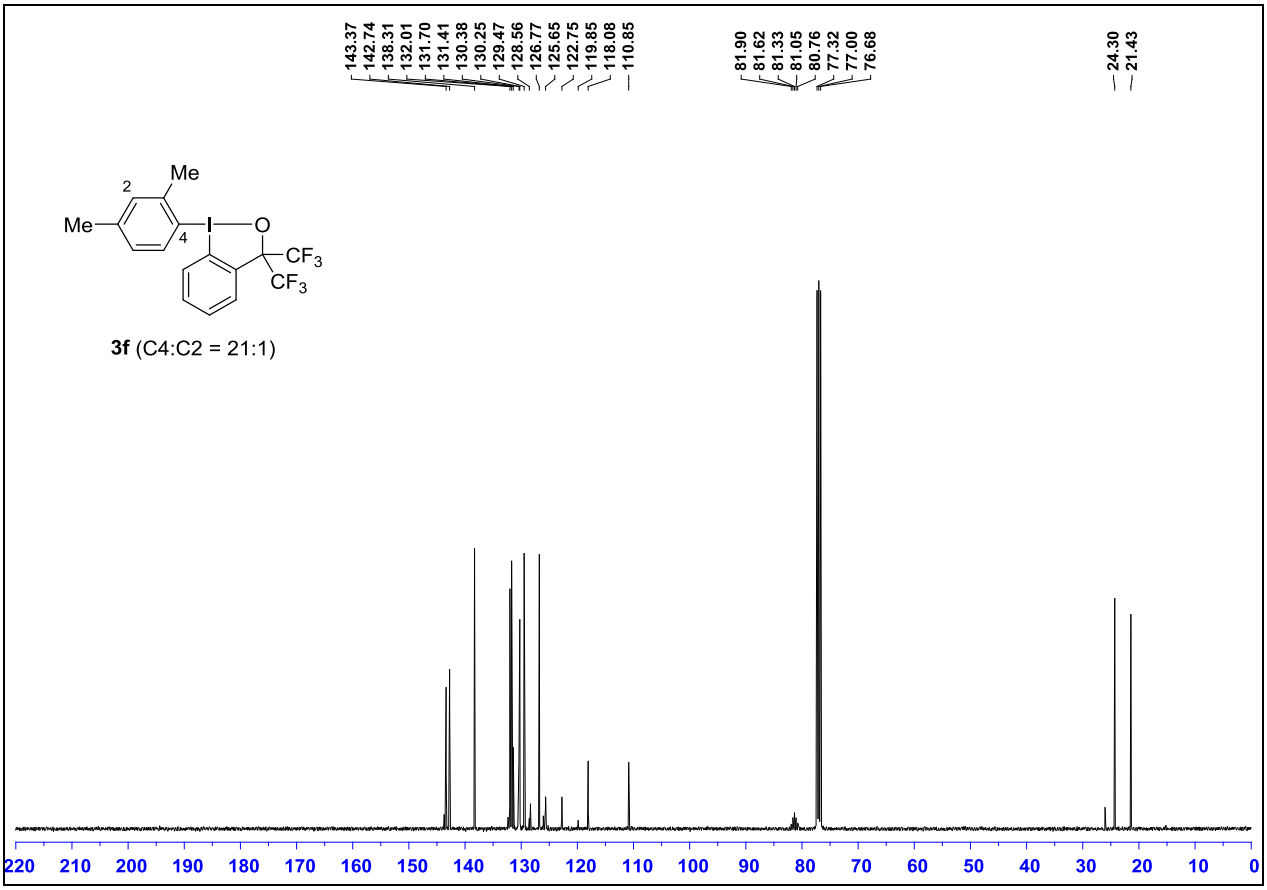
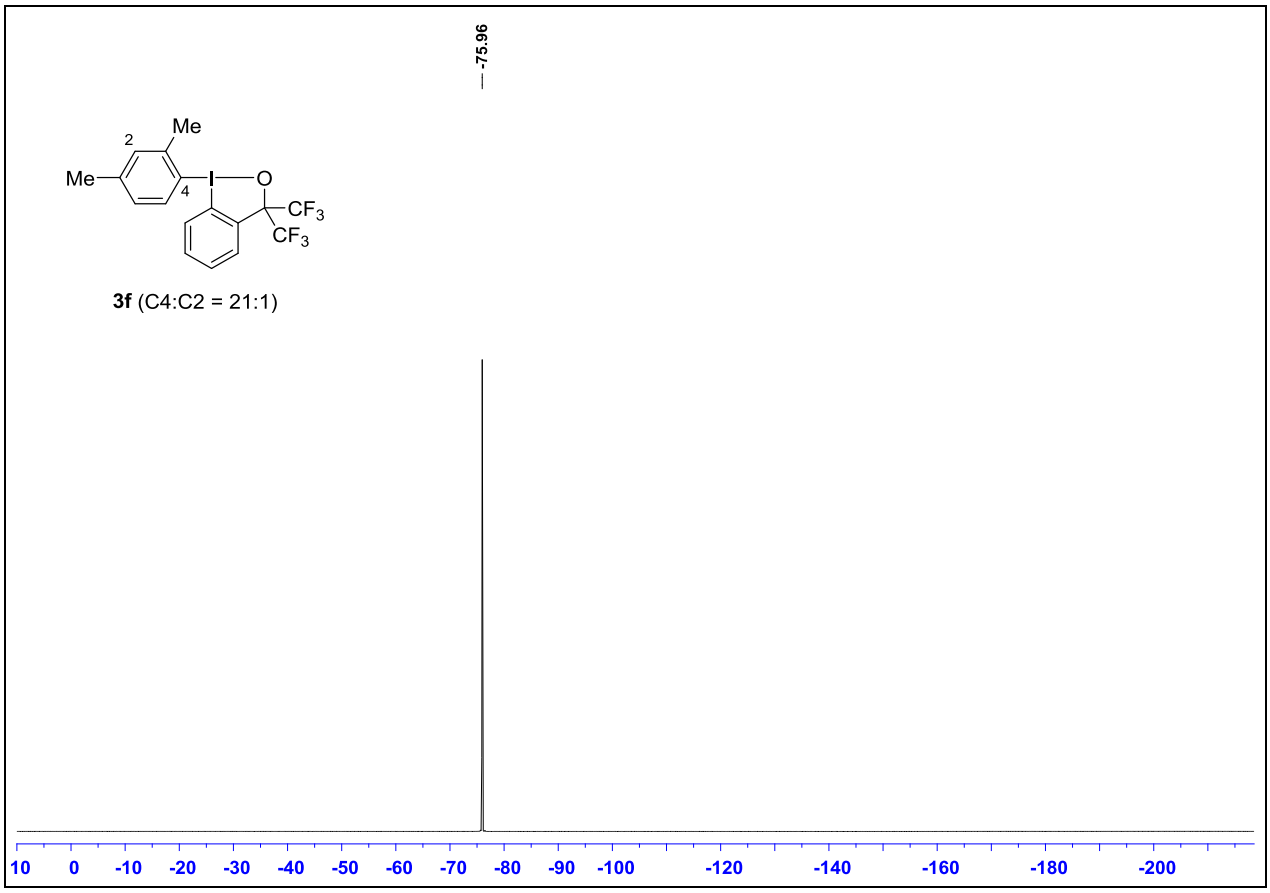
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum



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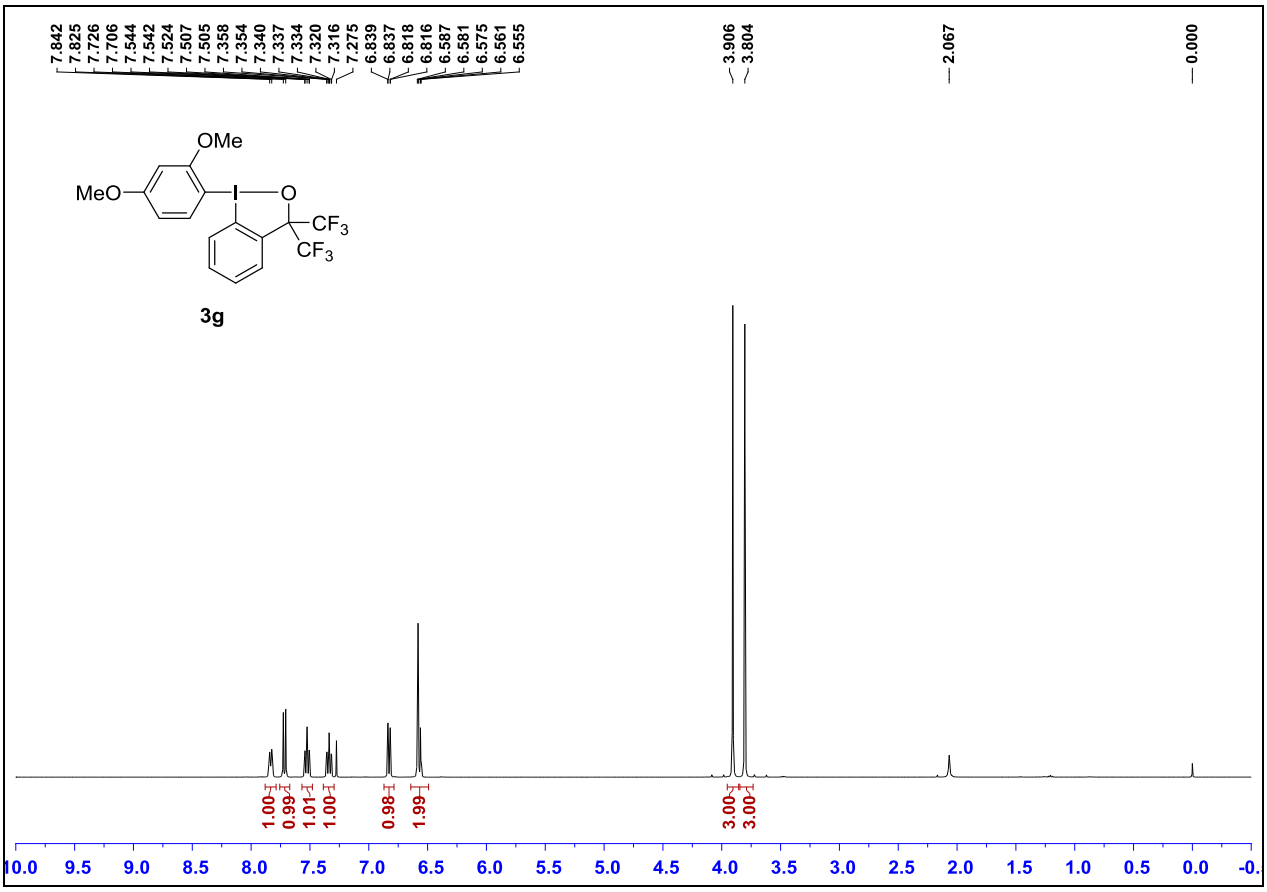
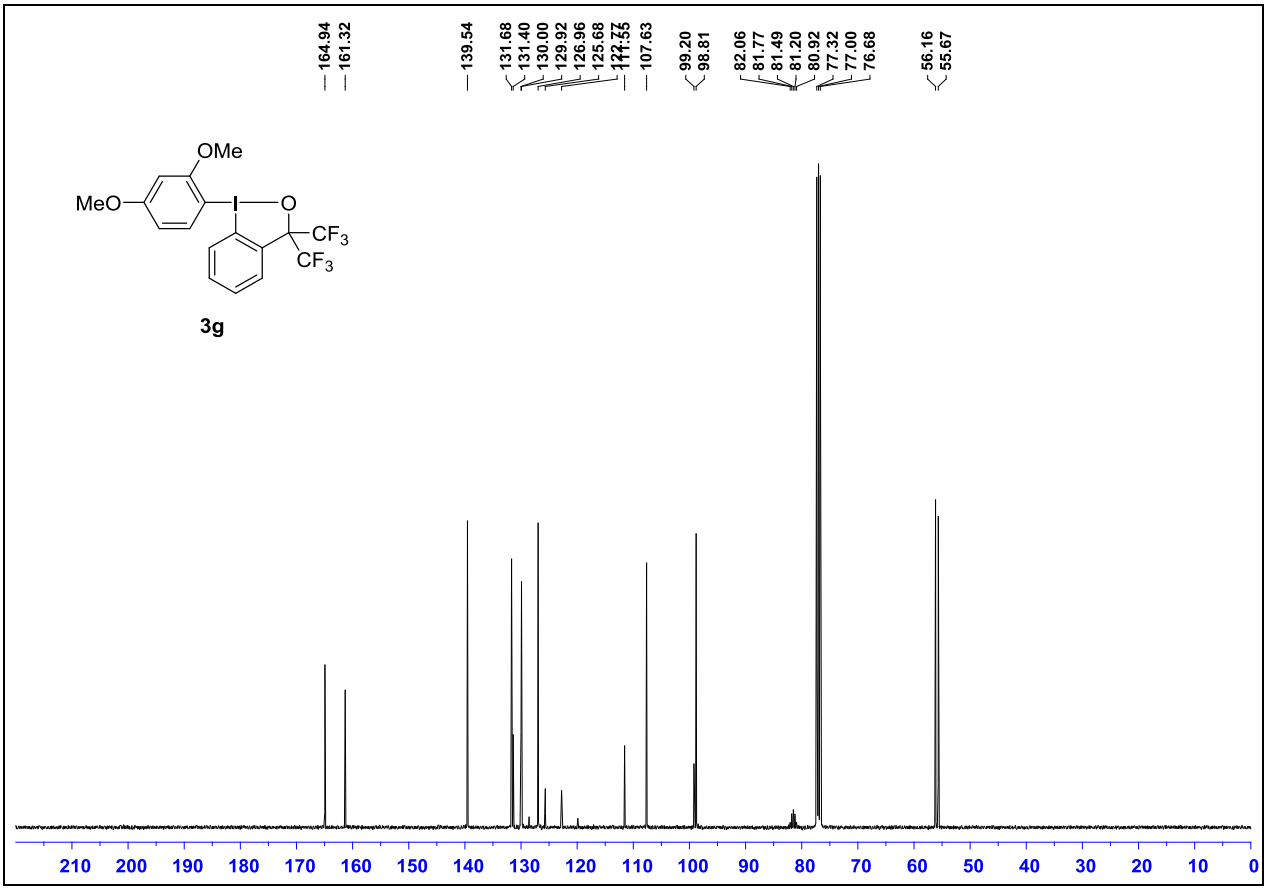
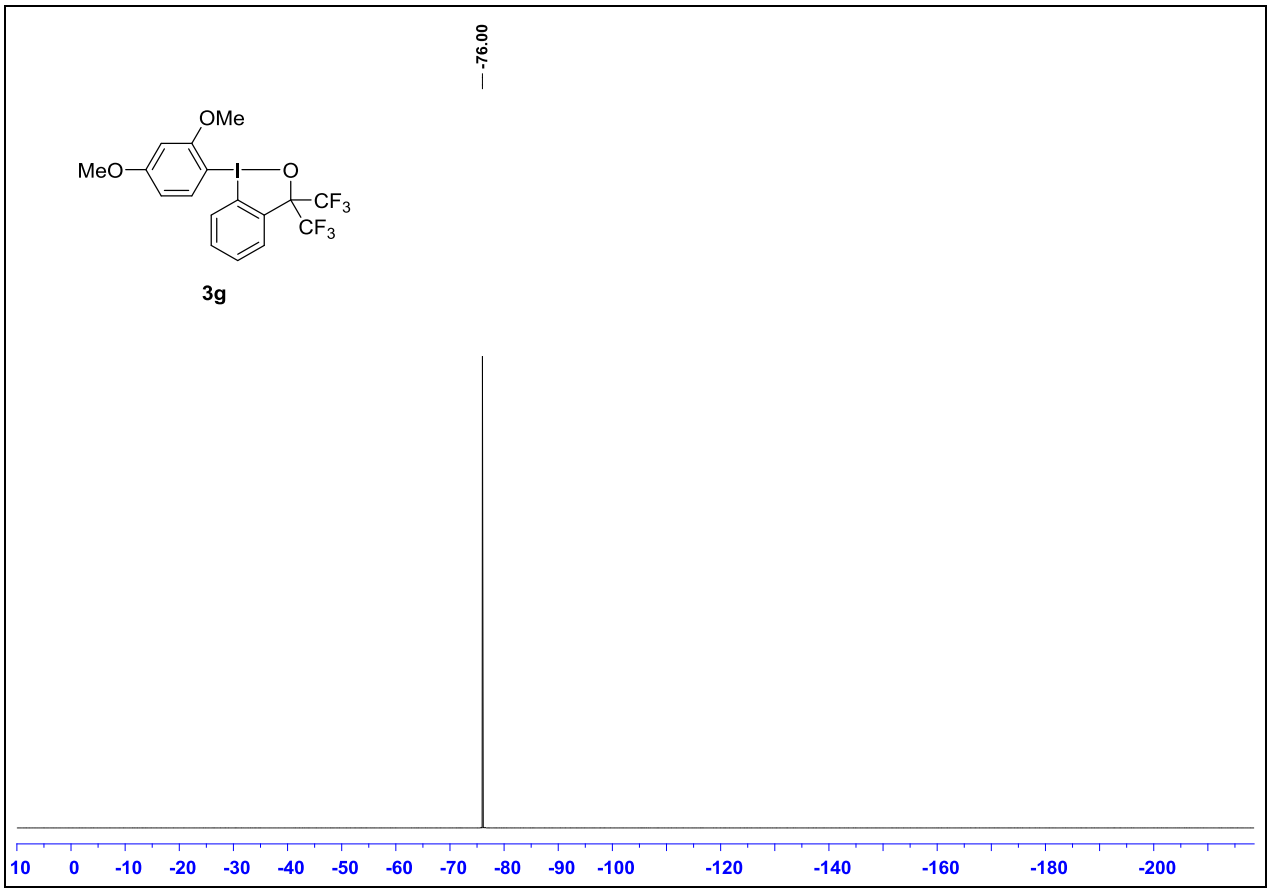
Me
2
Me
4
I
O
CF3
CF3
3f (C4:C2 = 21:1)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum



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OMe
MeO
I
O
CF3
CF3
3g
10
0
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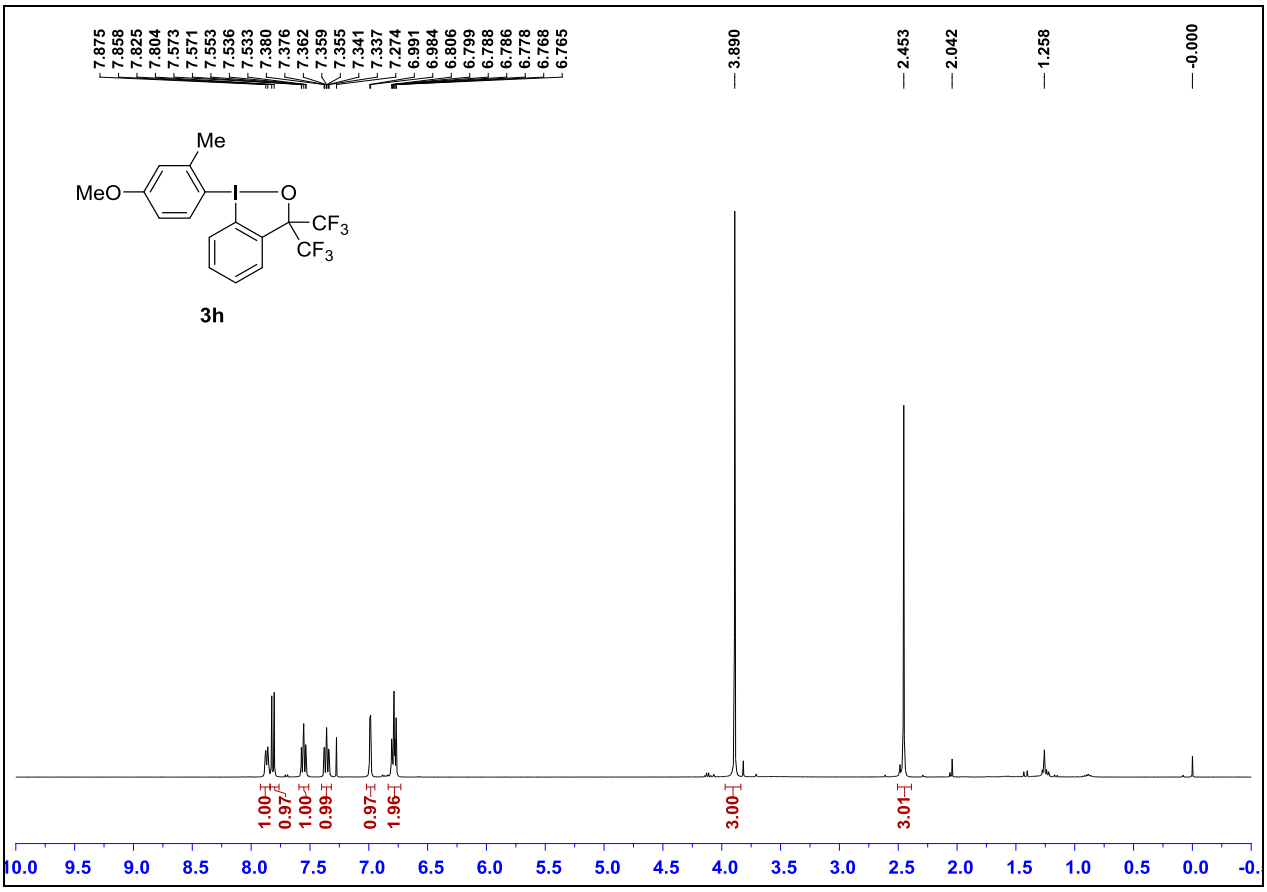
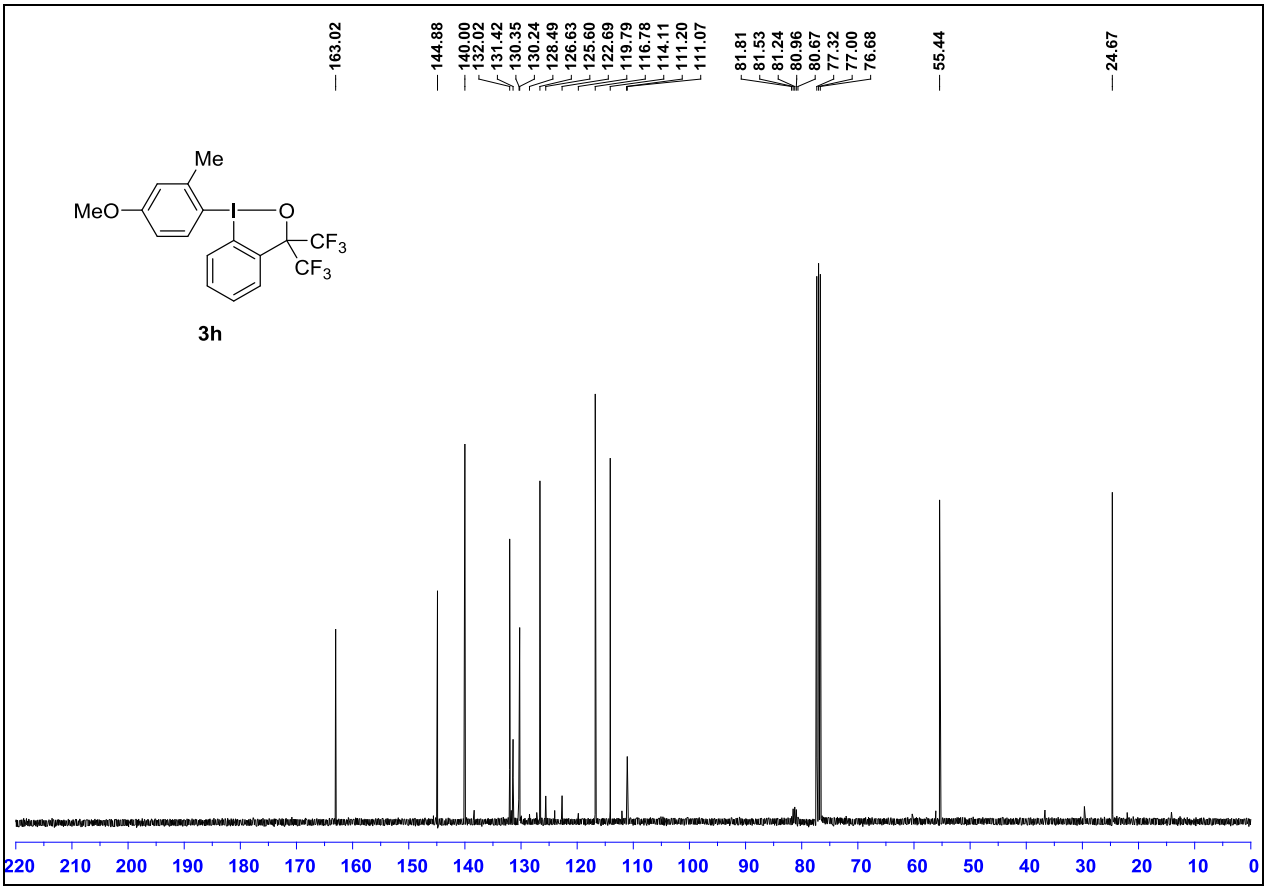
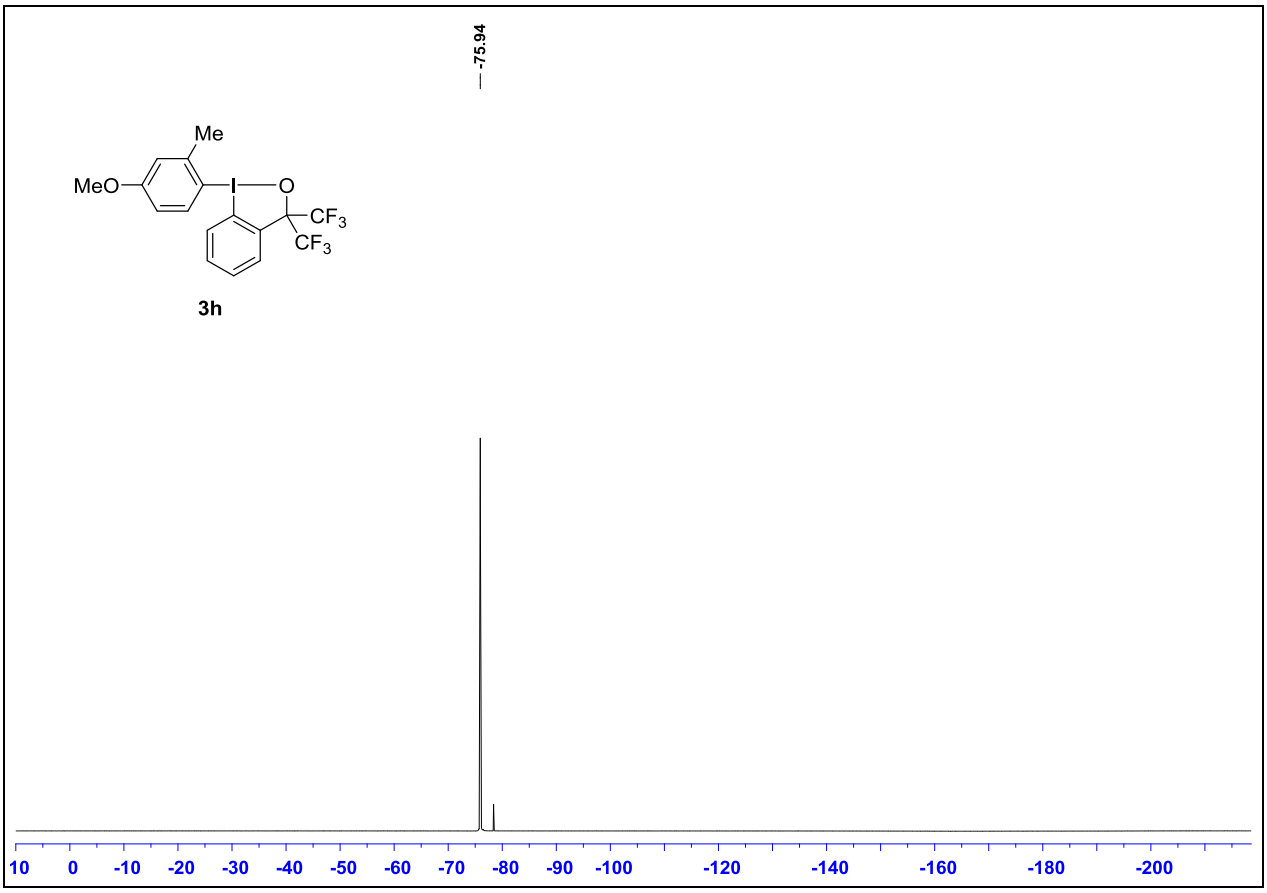
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

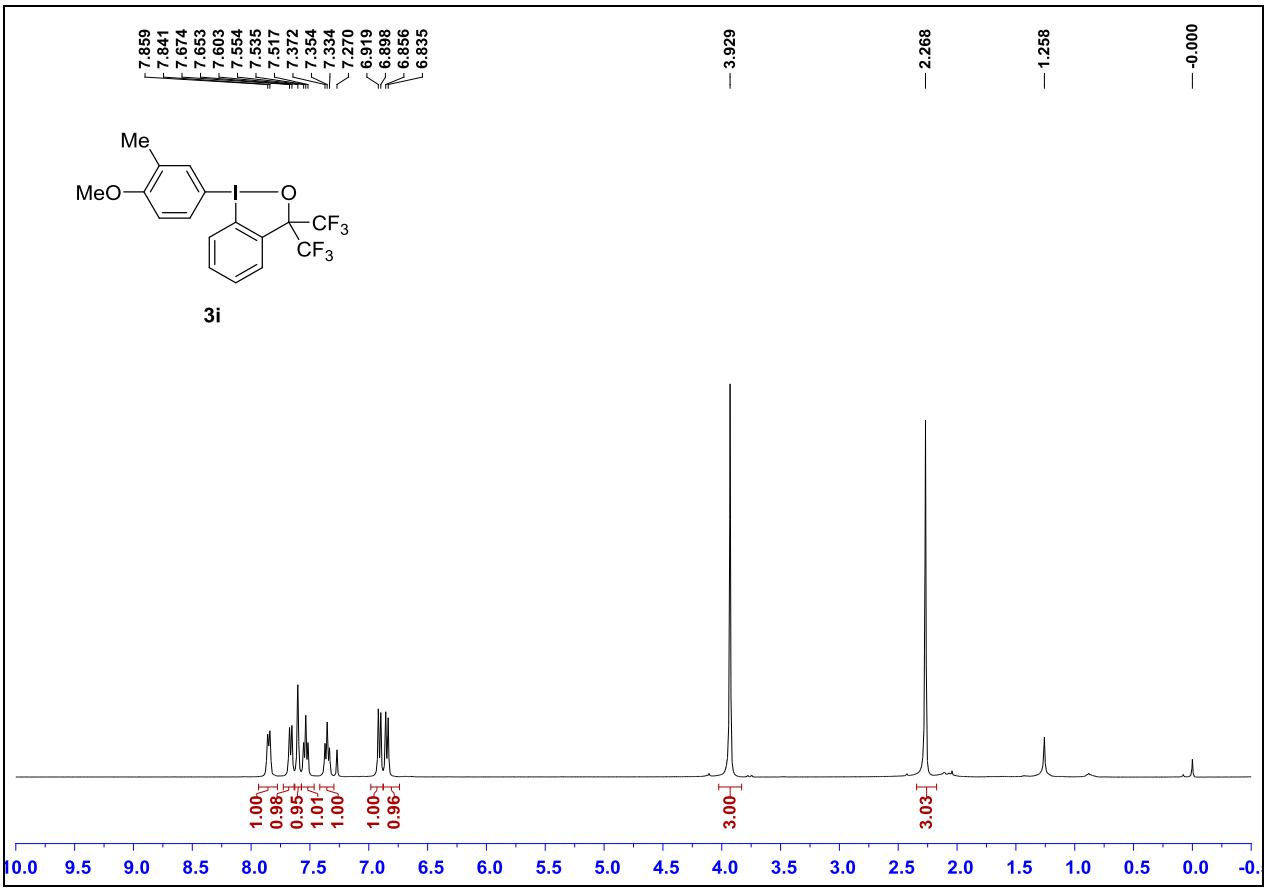
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

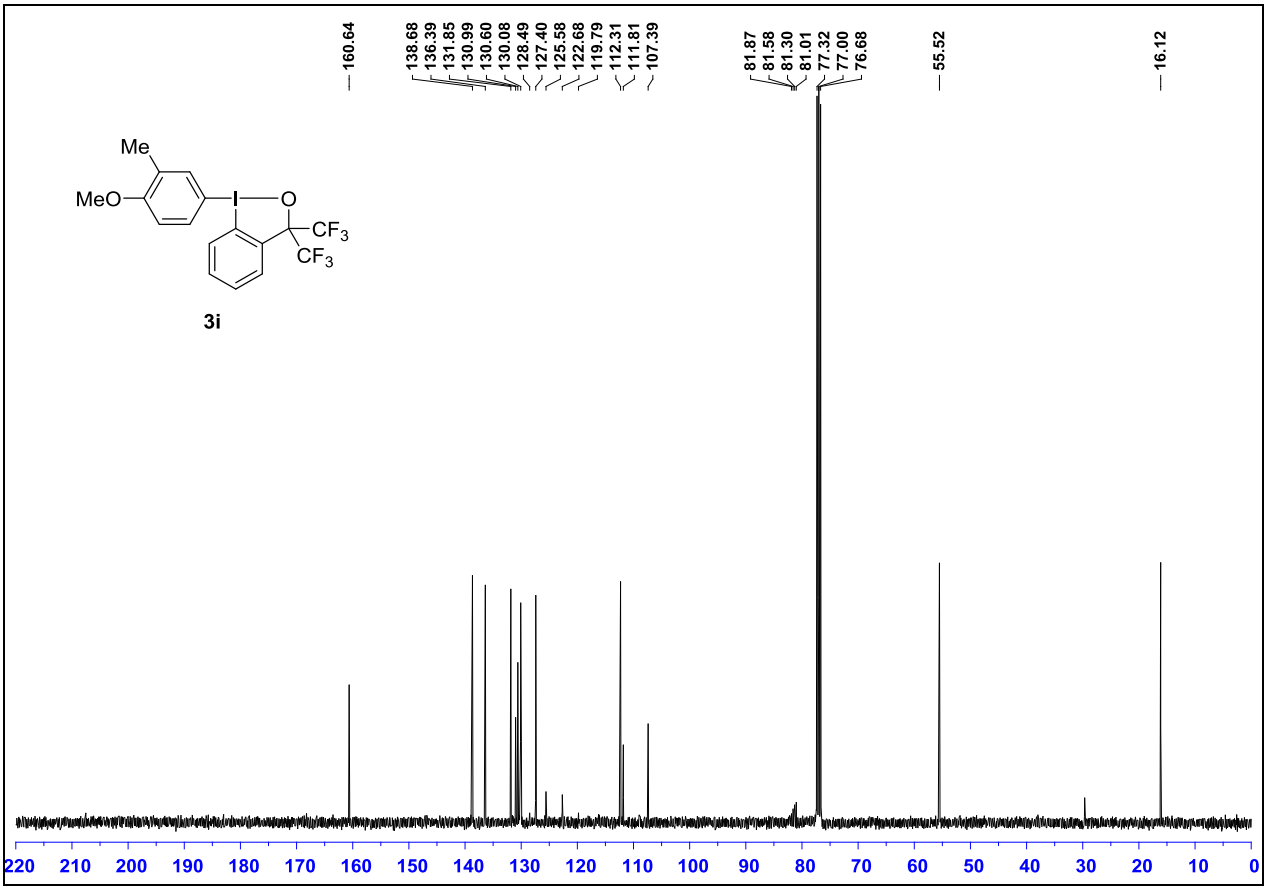


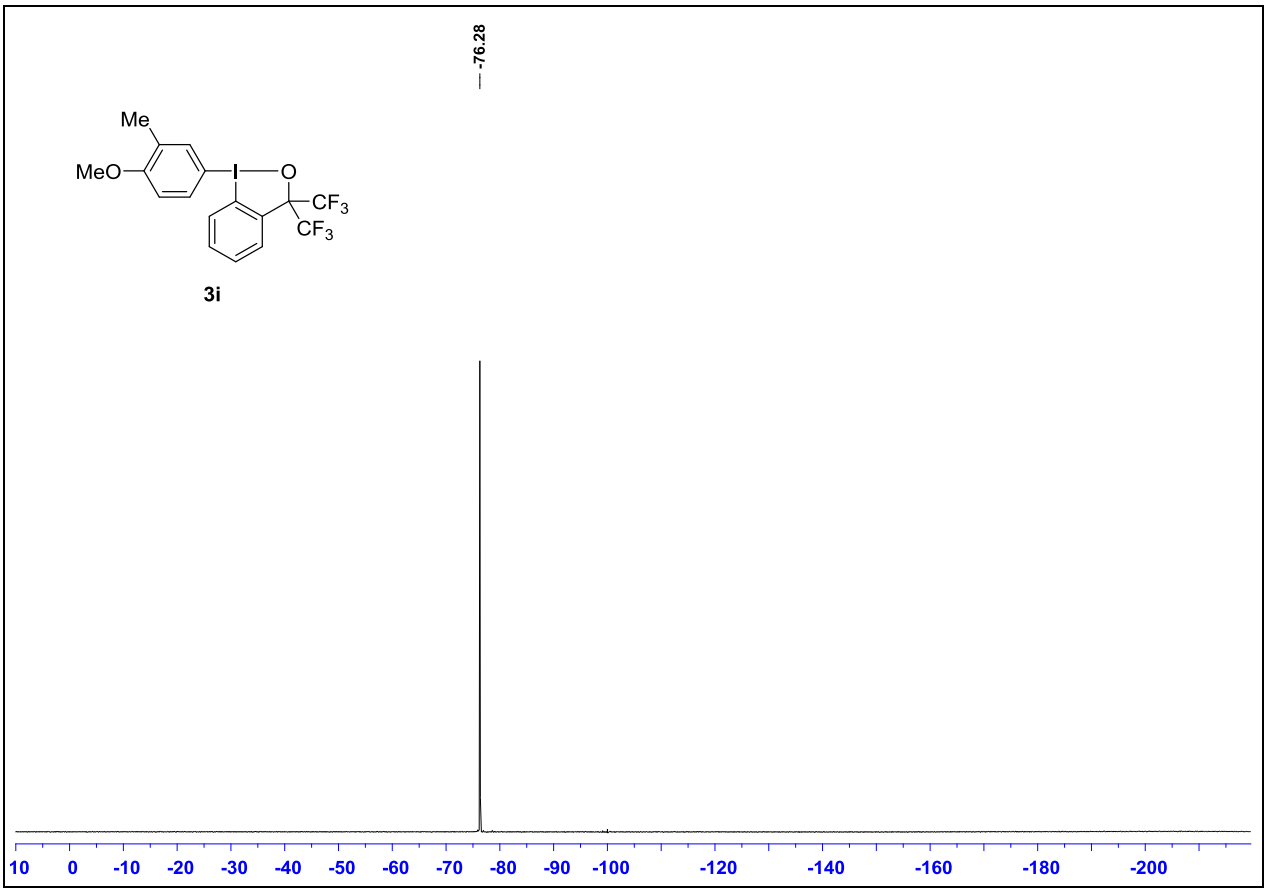



-75.94
Me
MeO
I
O
CF3
CF3
3h
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

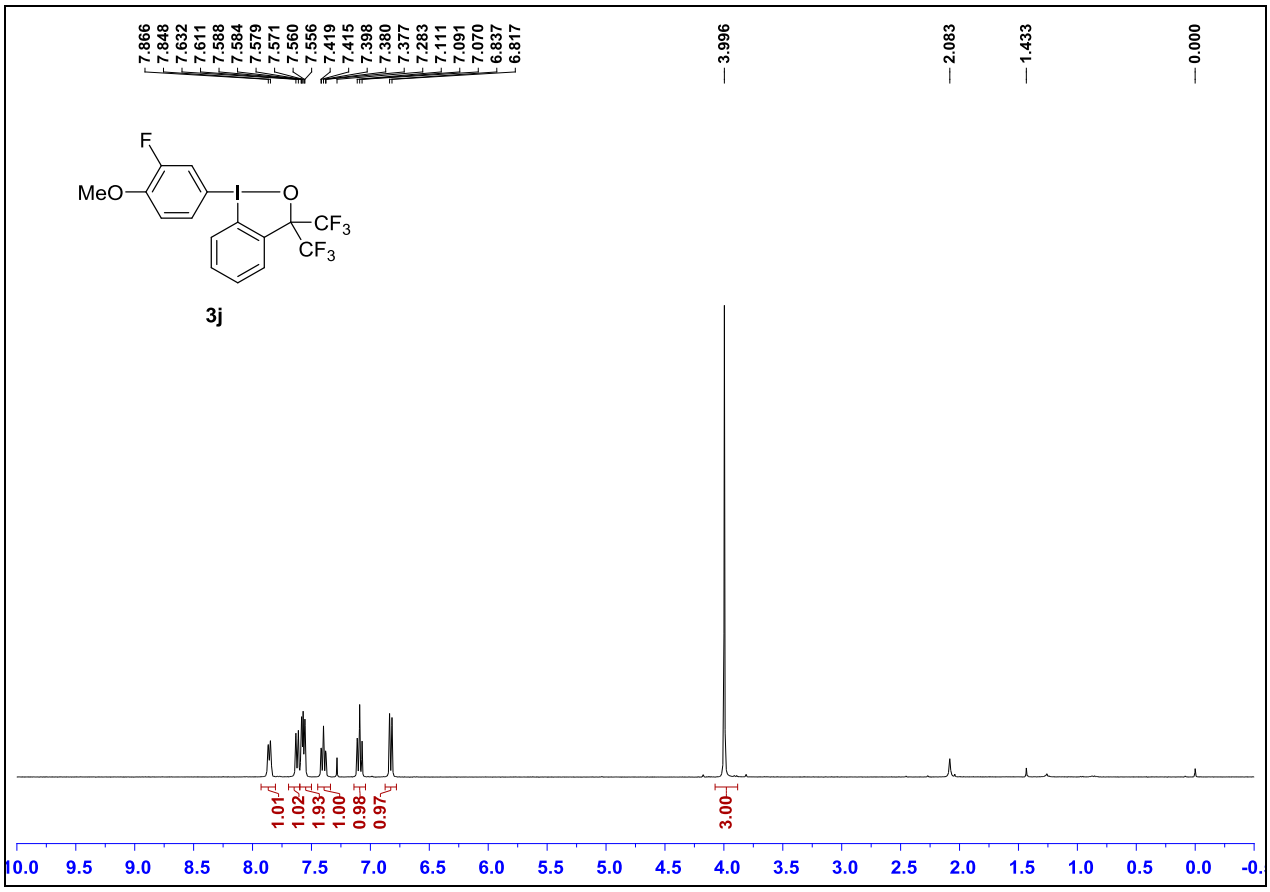
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

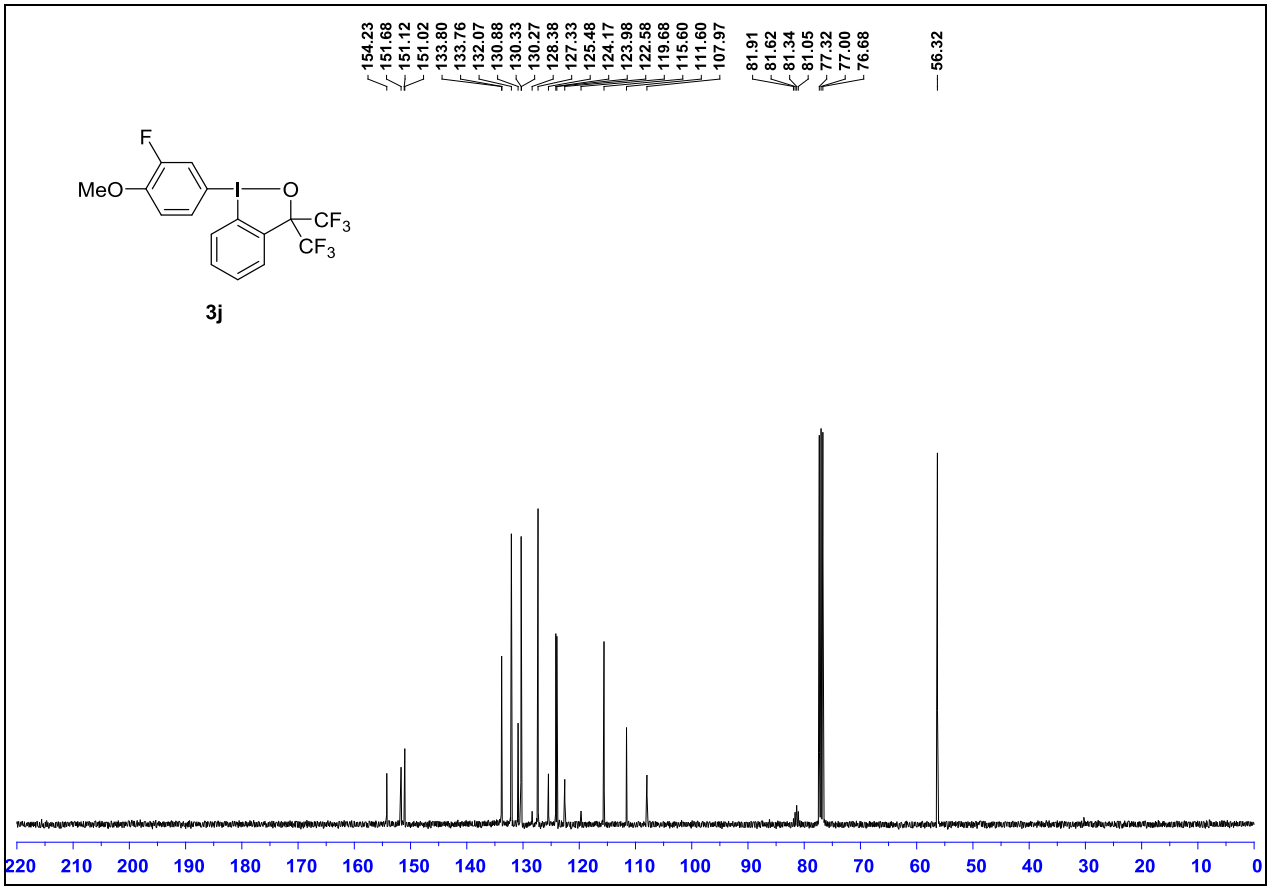


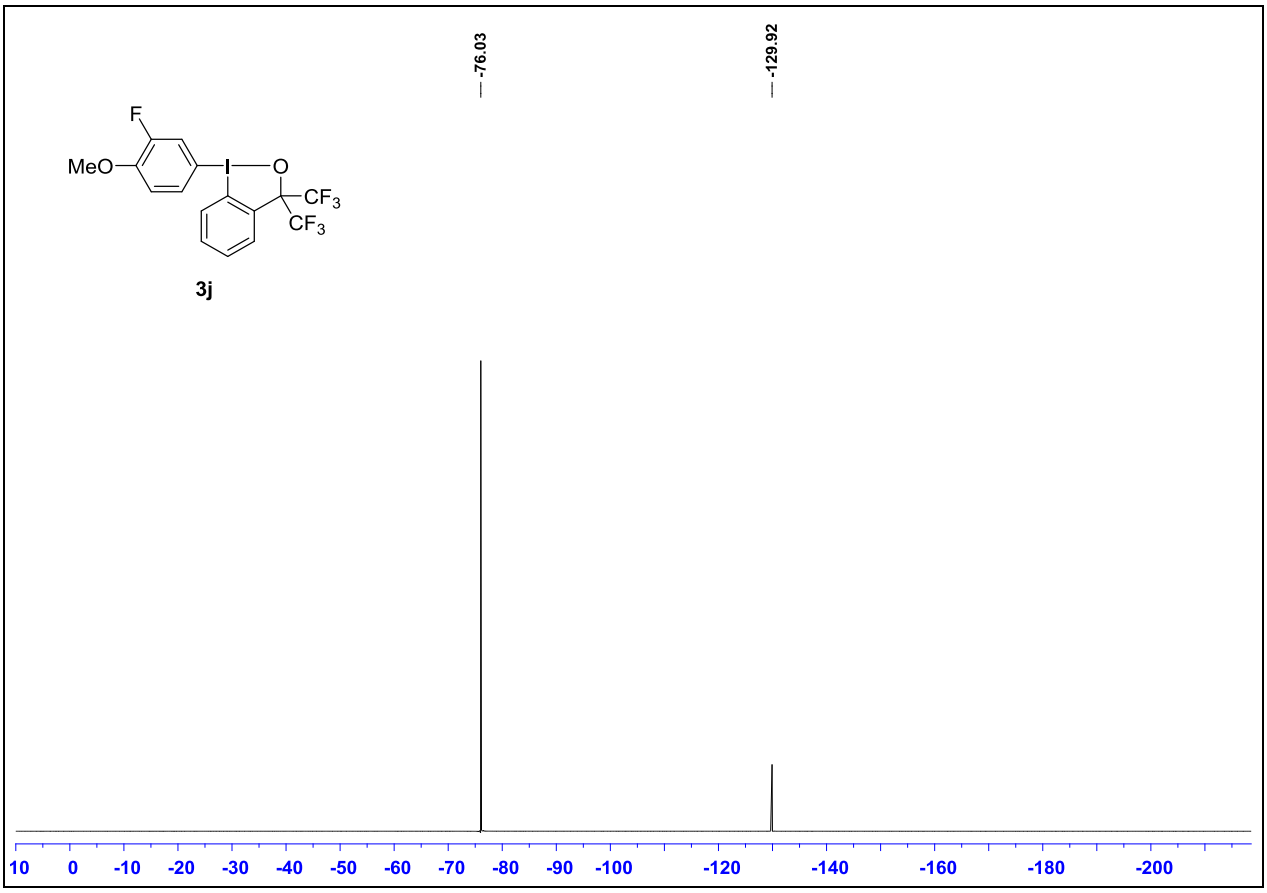



-76.28
Me
MeO
I
O
CF3
CF3
3i
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

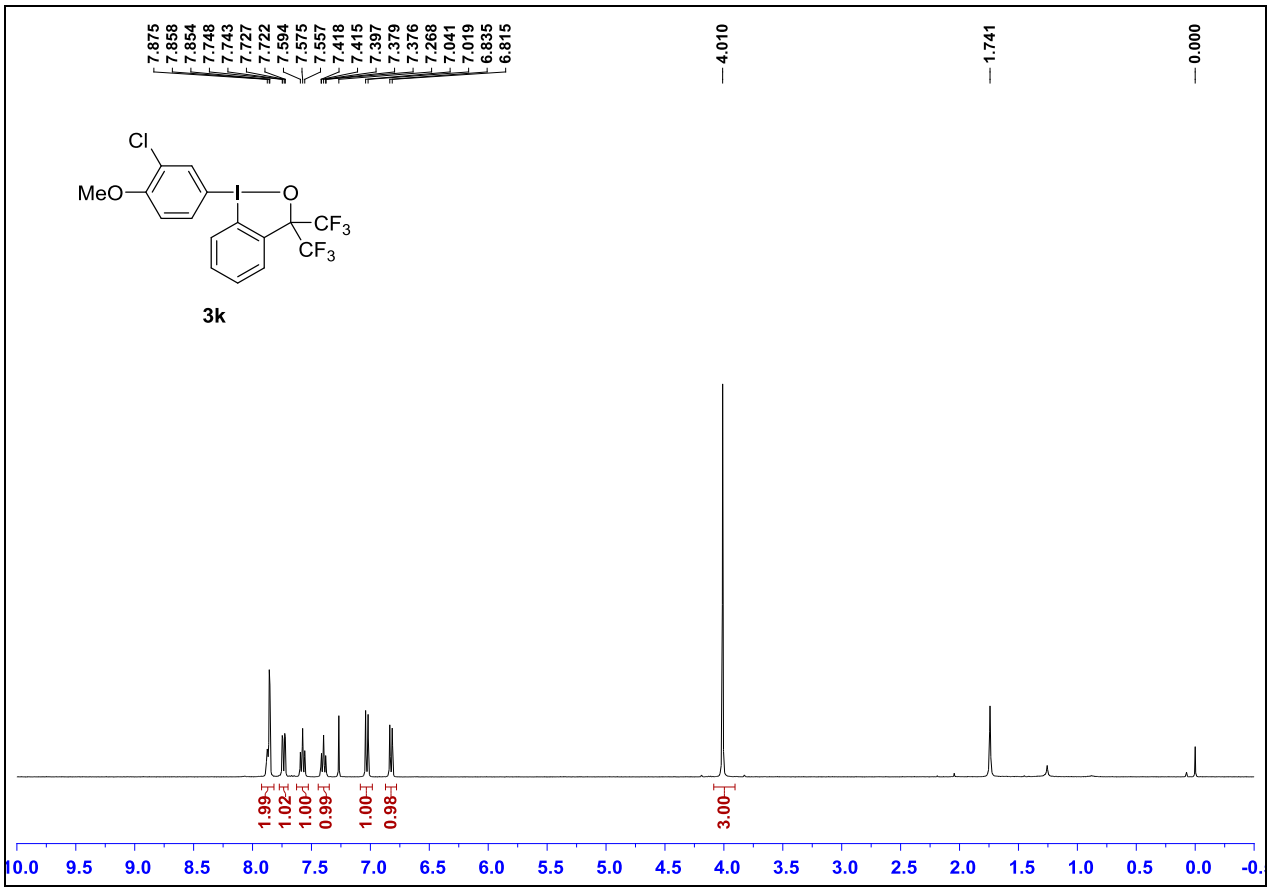
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

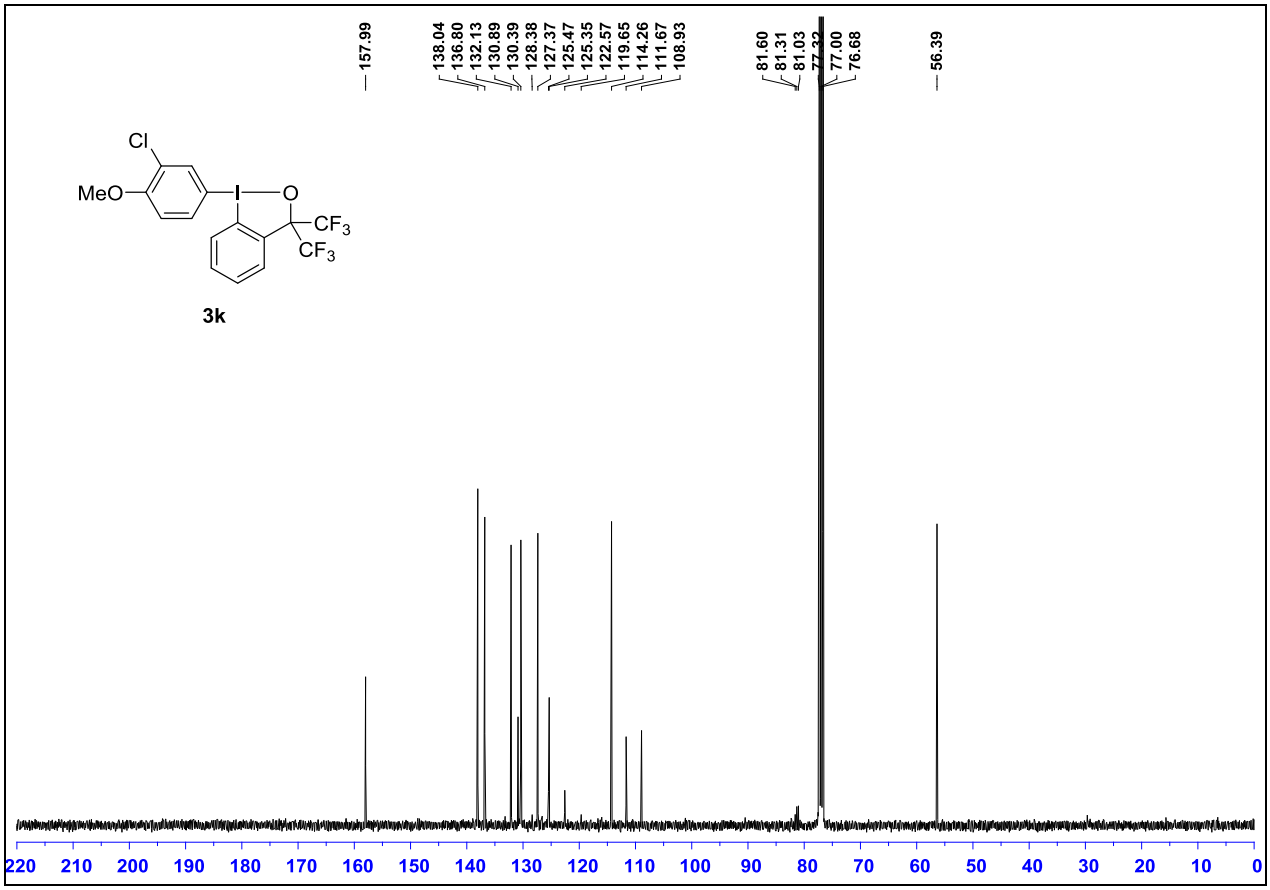


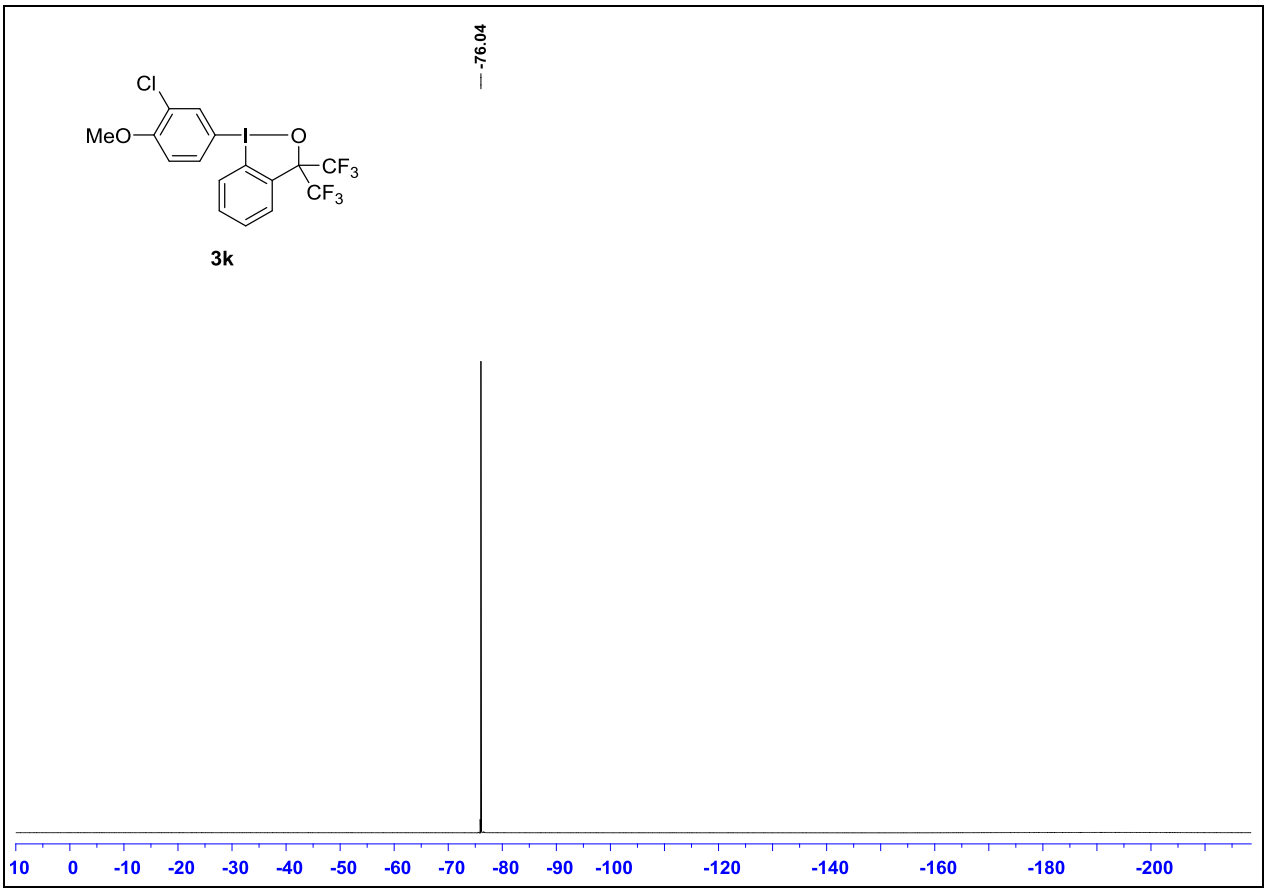



-76.03
-129.92
F
MeO
I
O
CF3
CF3
3j
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

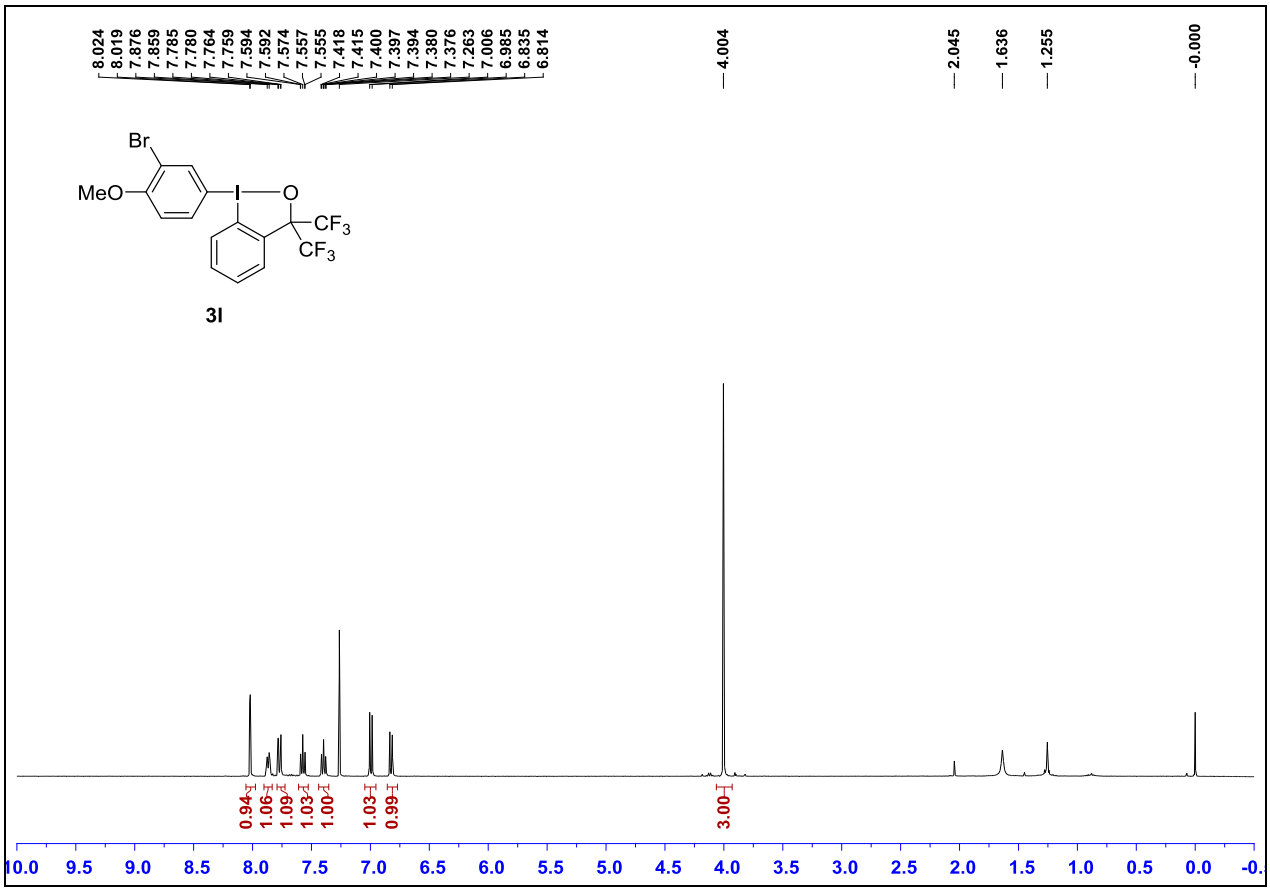
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

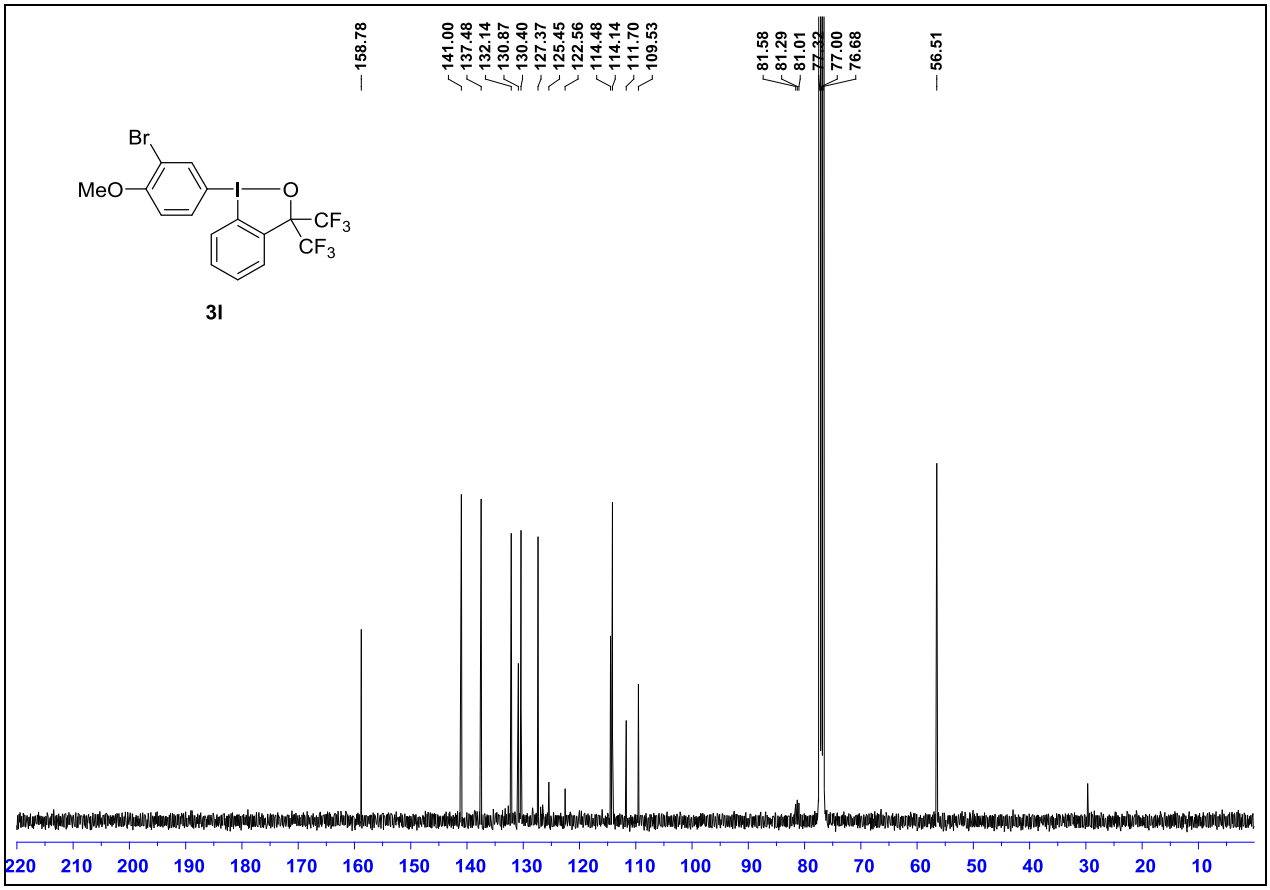


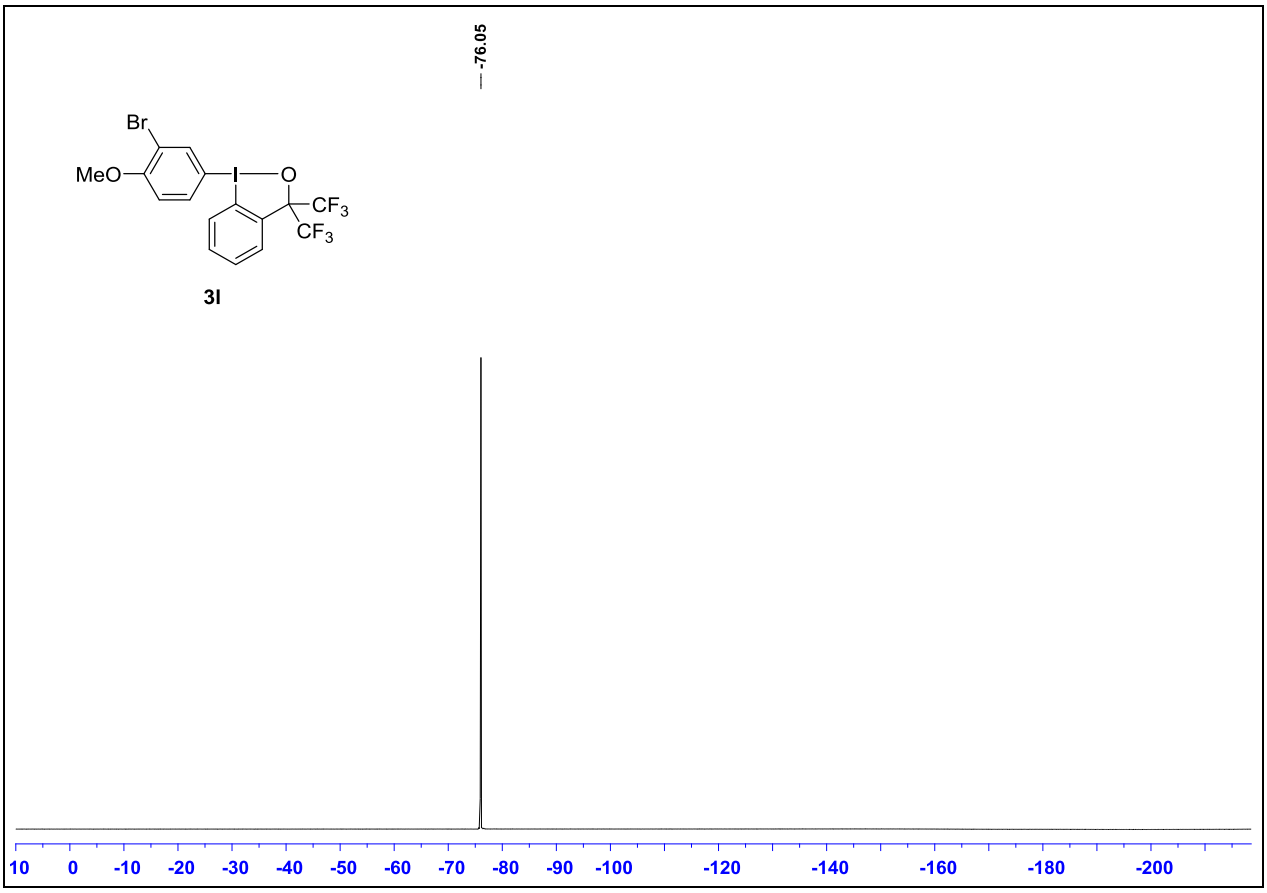



-76.04
Cl
MeO
I
O
CF3
CF3
3k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

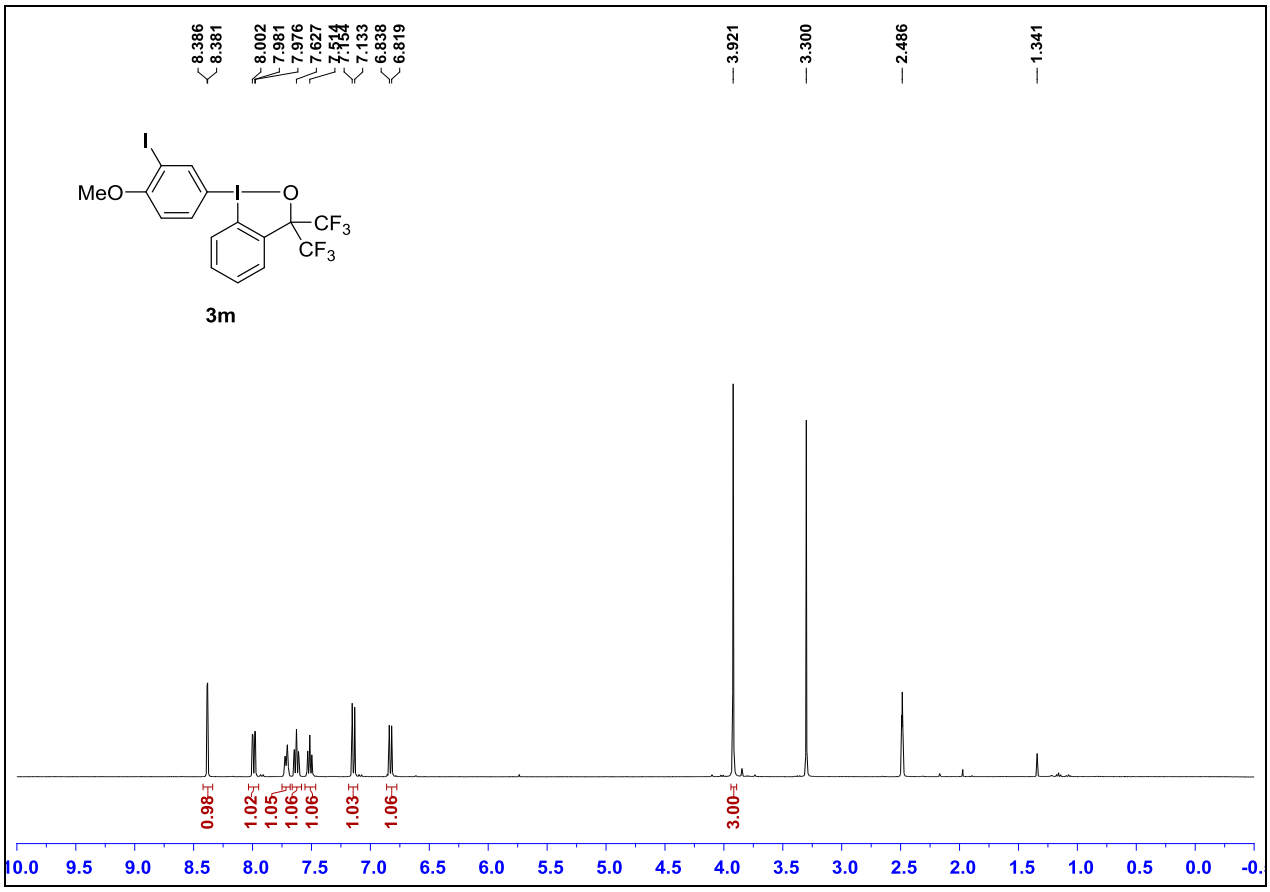
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

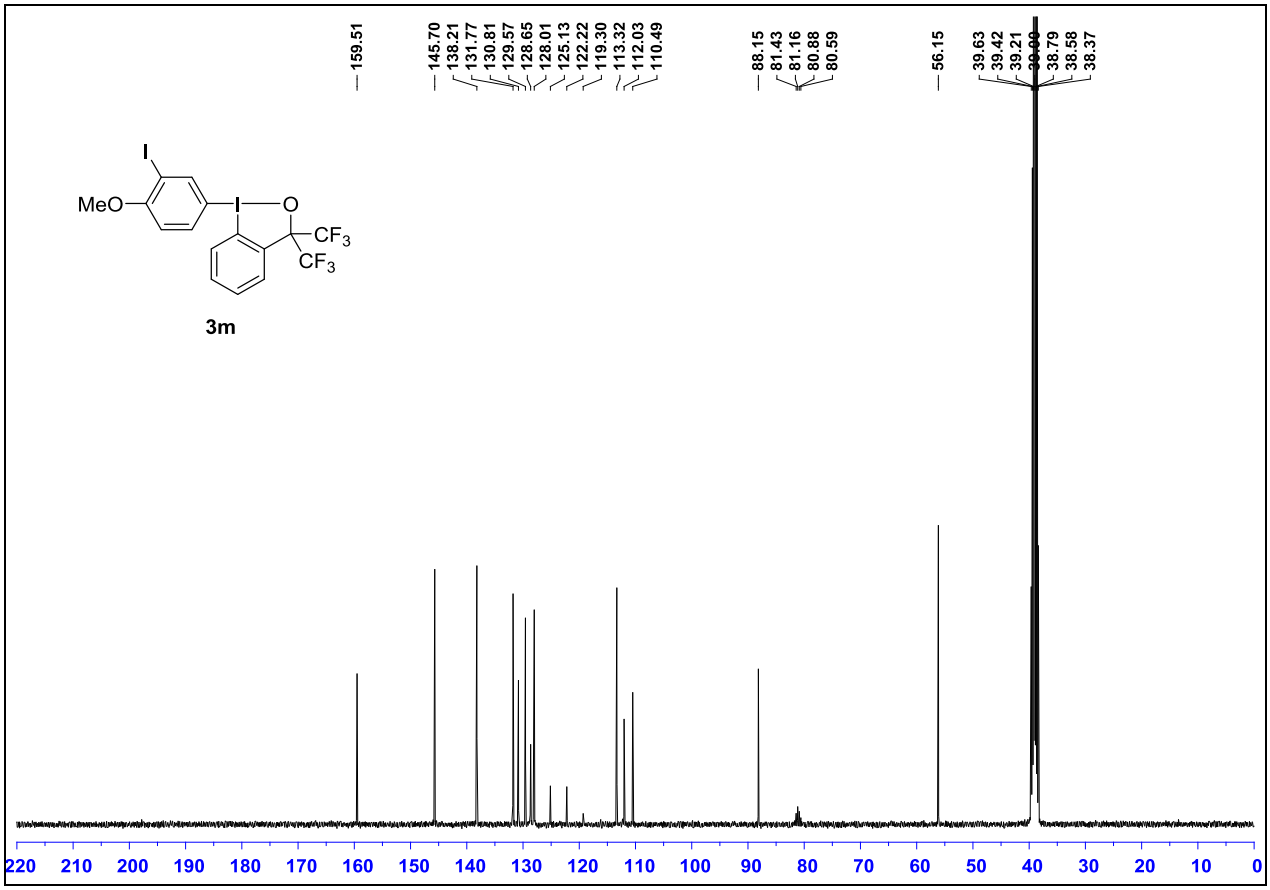


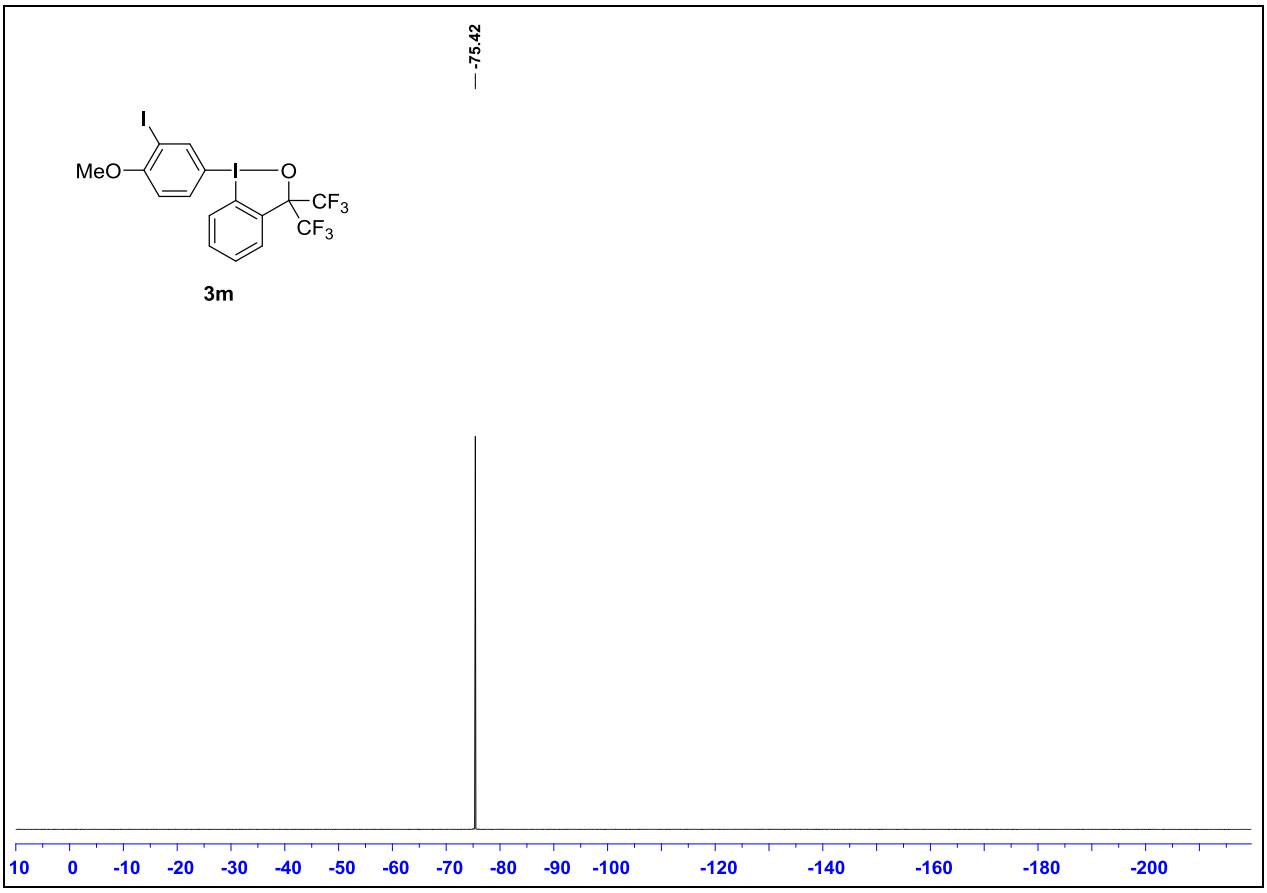



-76.05
Br
MeO
I
O
CF3
CF3
3l
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

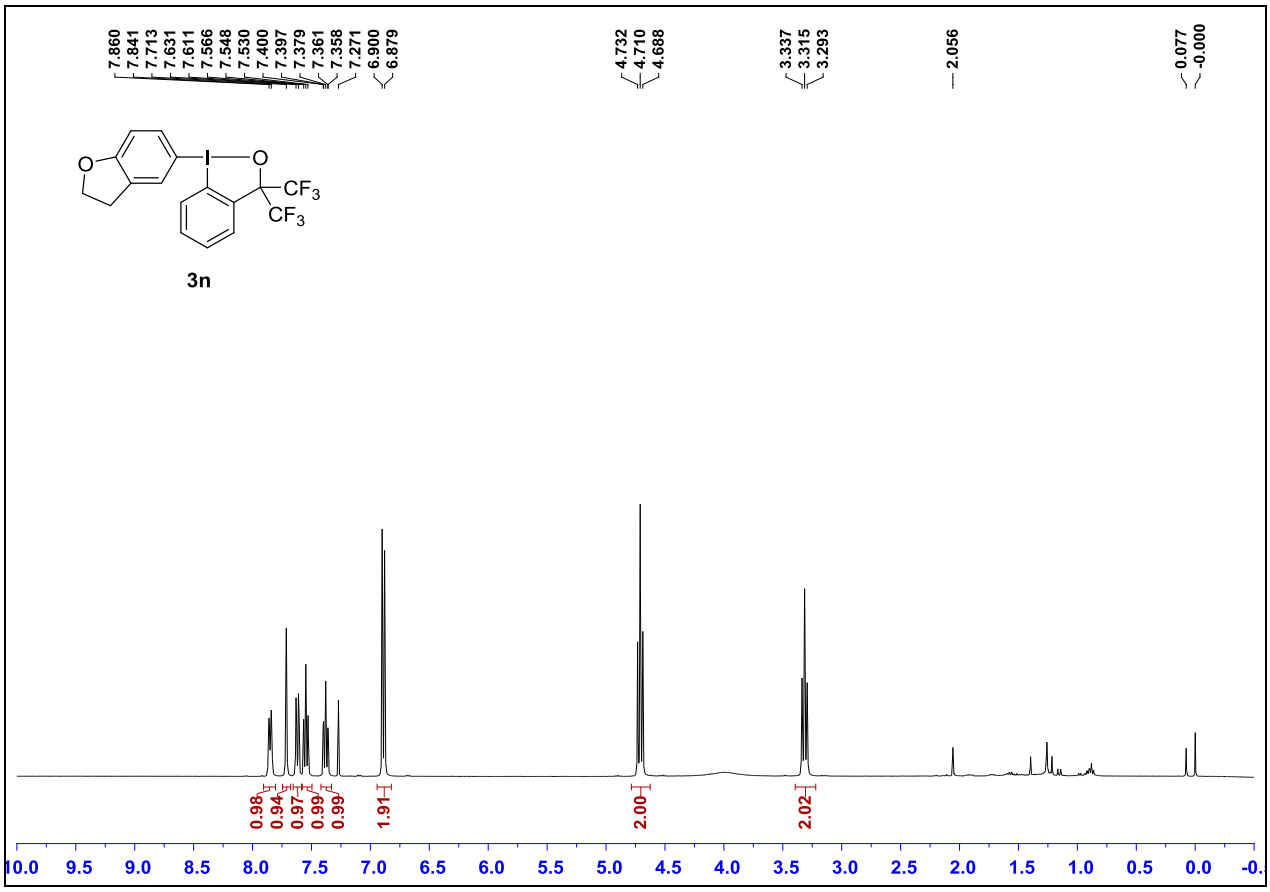
^{1}H NMR (400 MHz, DMSO), ^{13}C NMR (100 MHz, DMSO) and ^{19}F NMR (282 MHz, DMSO) spectrum

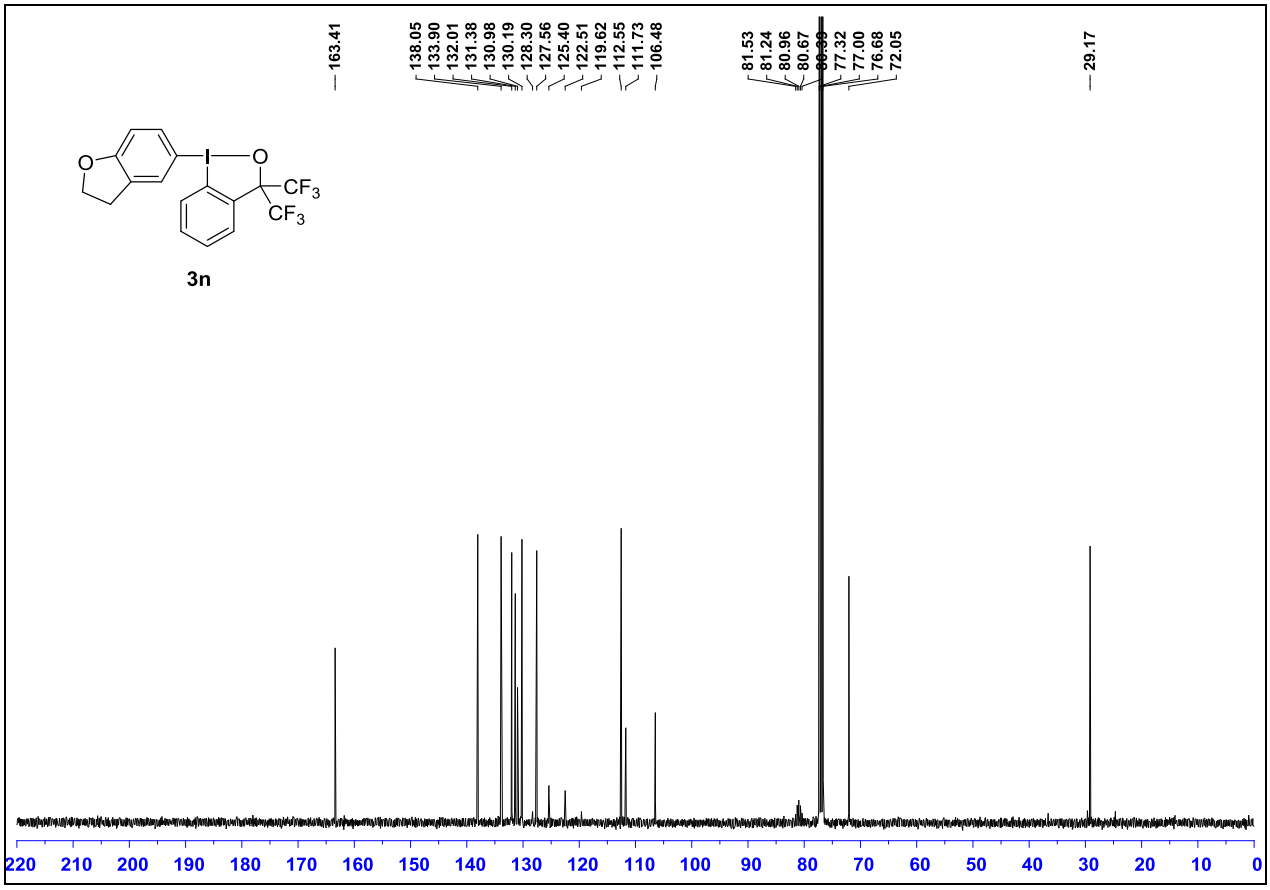


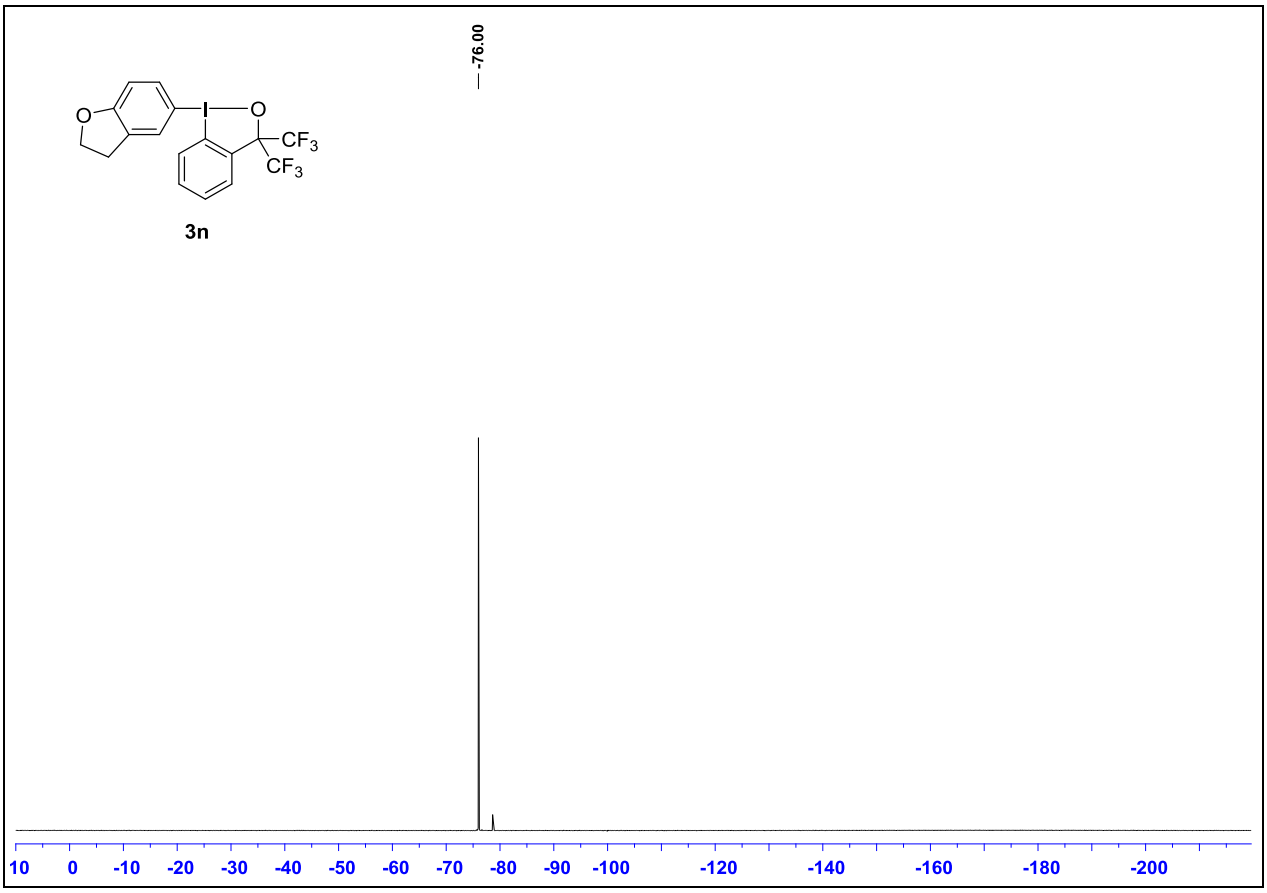



-75.42
I
MeO
I
O
CF3
CF3
3m
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

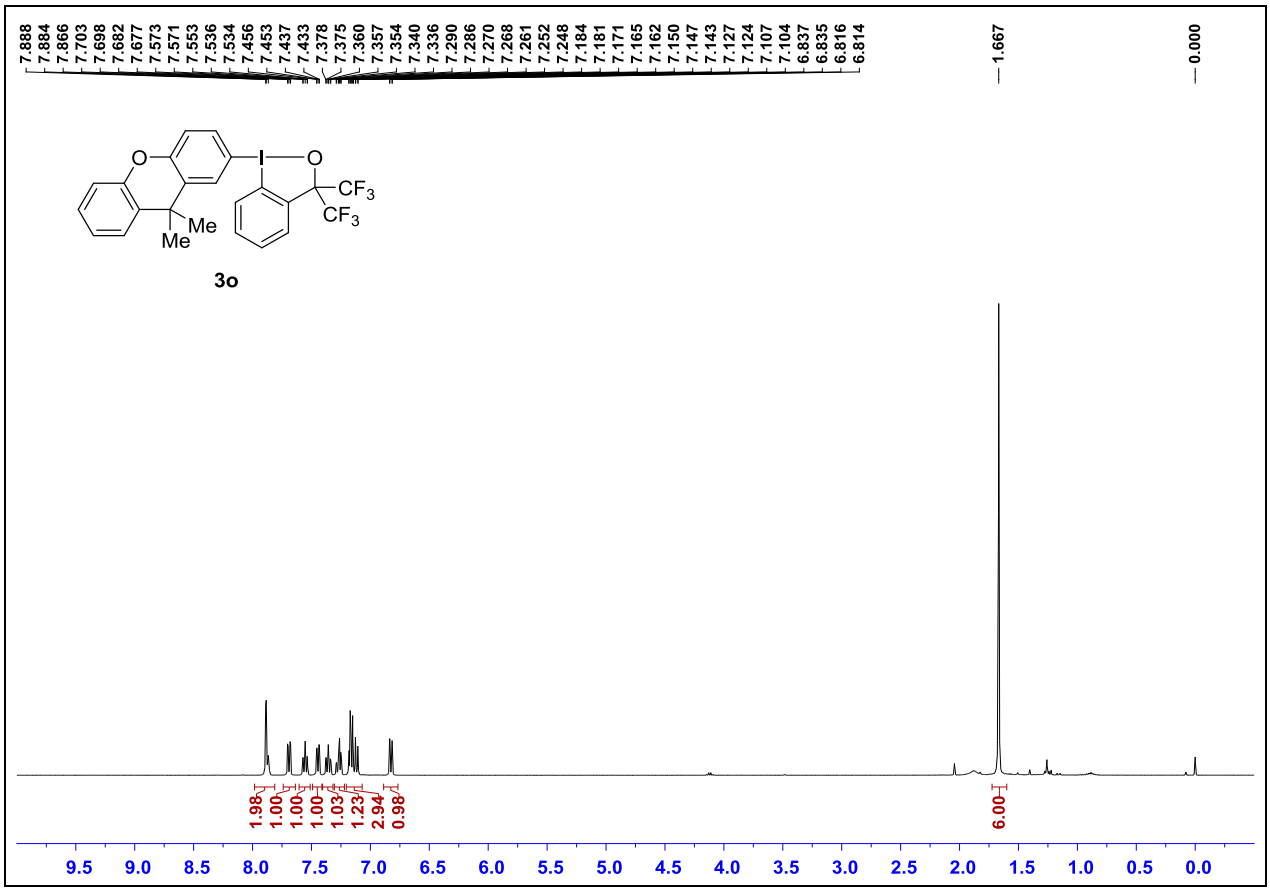
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

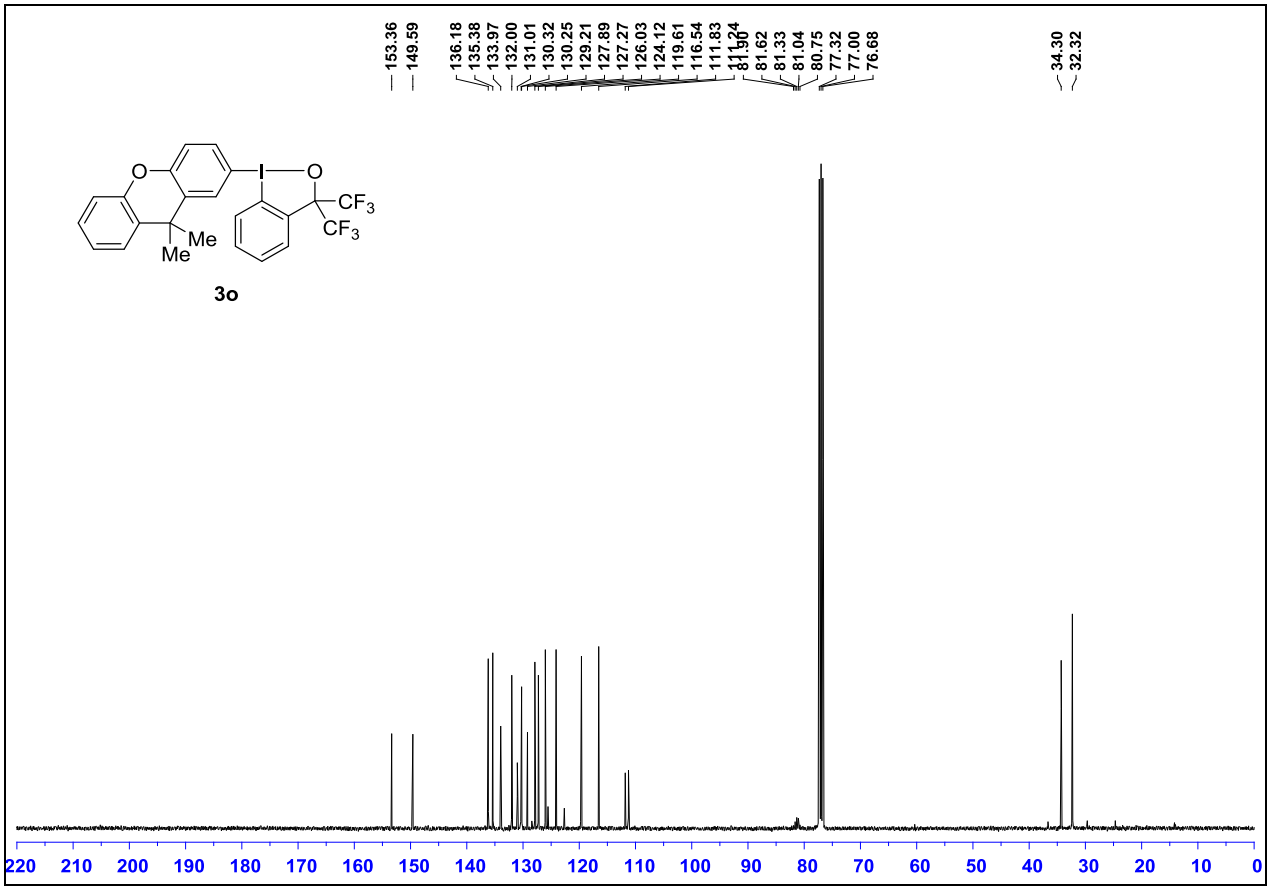


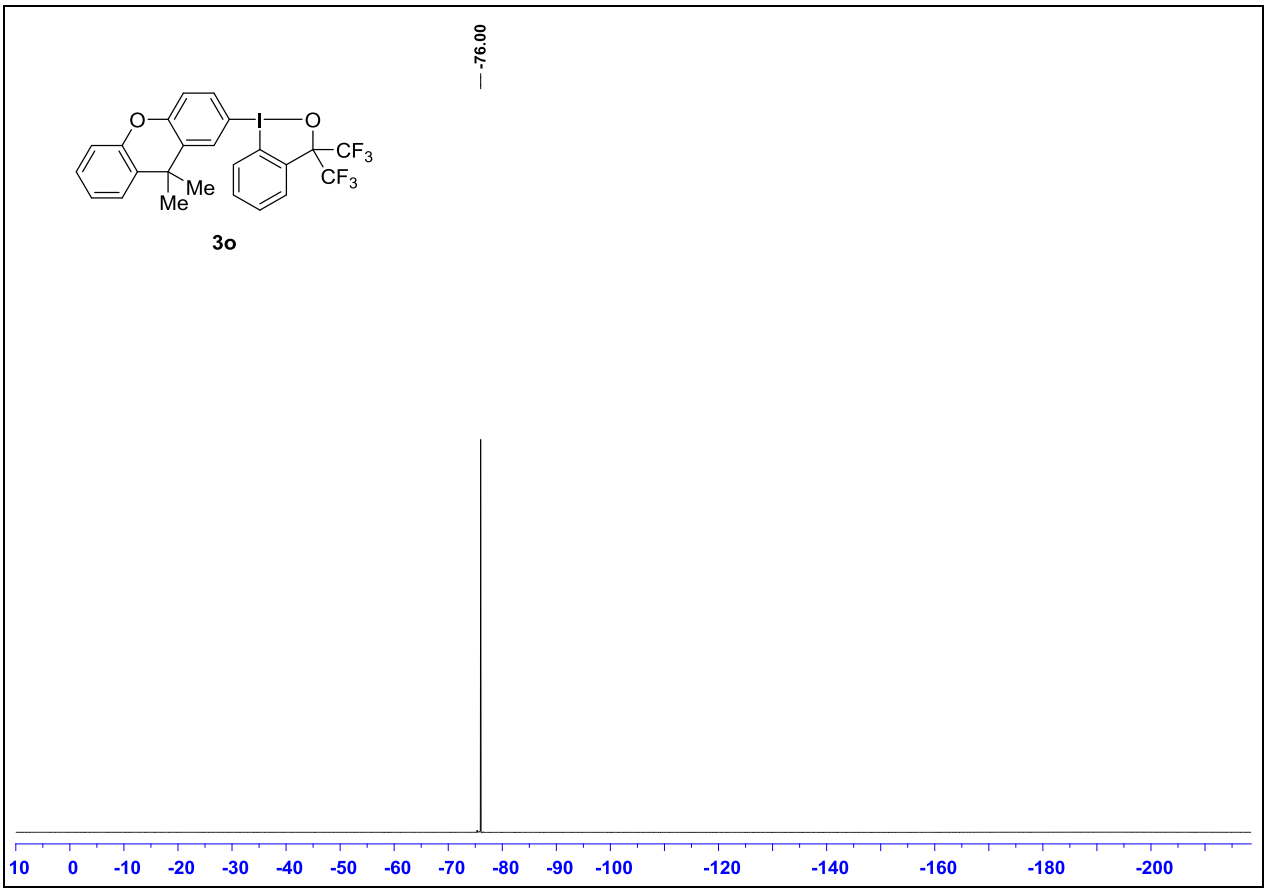



-76.00
O
I
O
CF3
CF3
3n
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

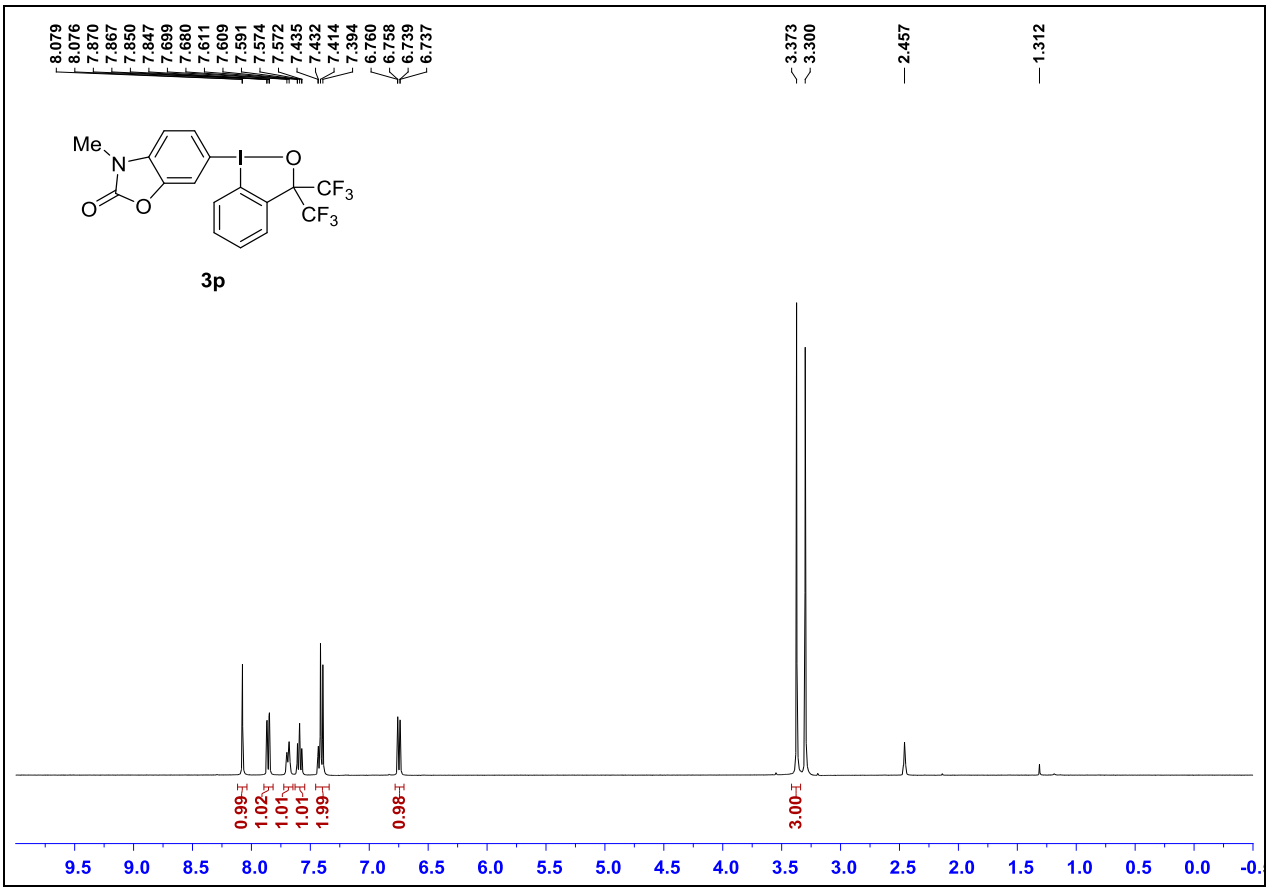
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

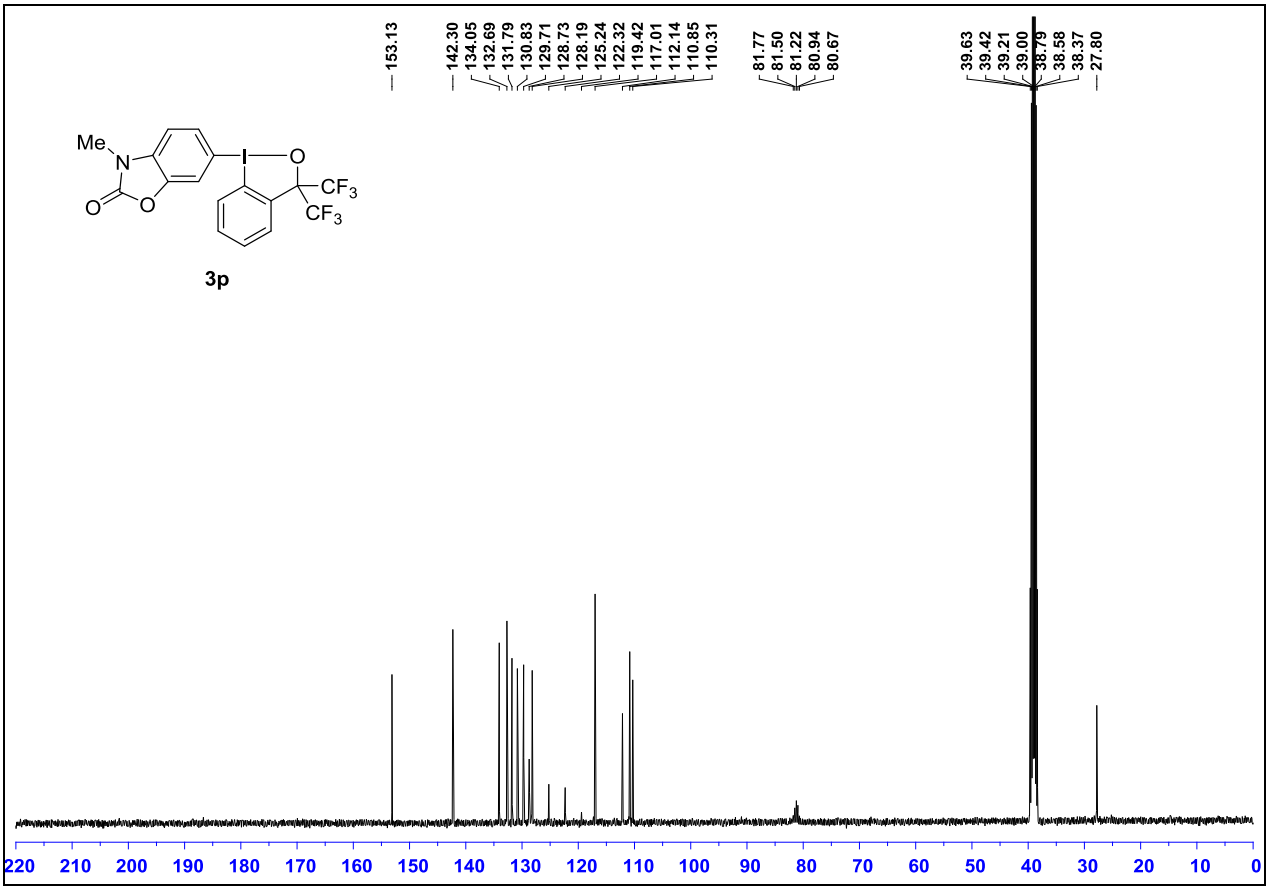


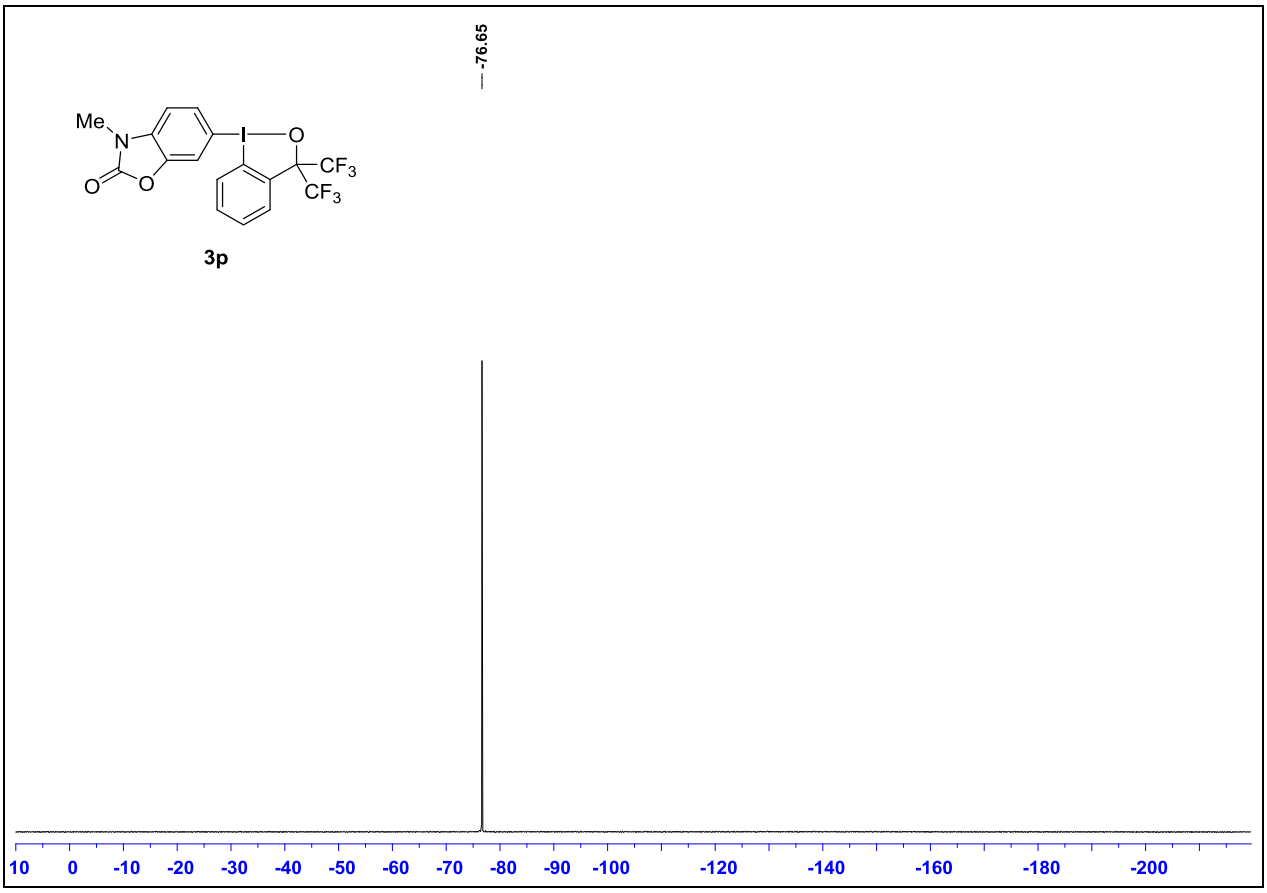



-76.00
O
I
O
CF3
CF3
Me
Me
3o
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

^{1}H NMR (400 MHz, DMSO), ^{13}C NMR (100 MHz, DMSO) and ^{19}F NMR (282 MHz, DMSO) spectrum

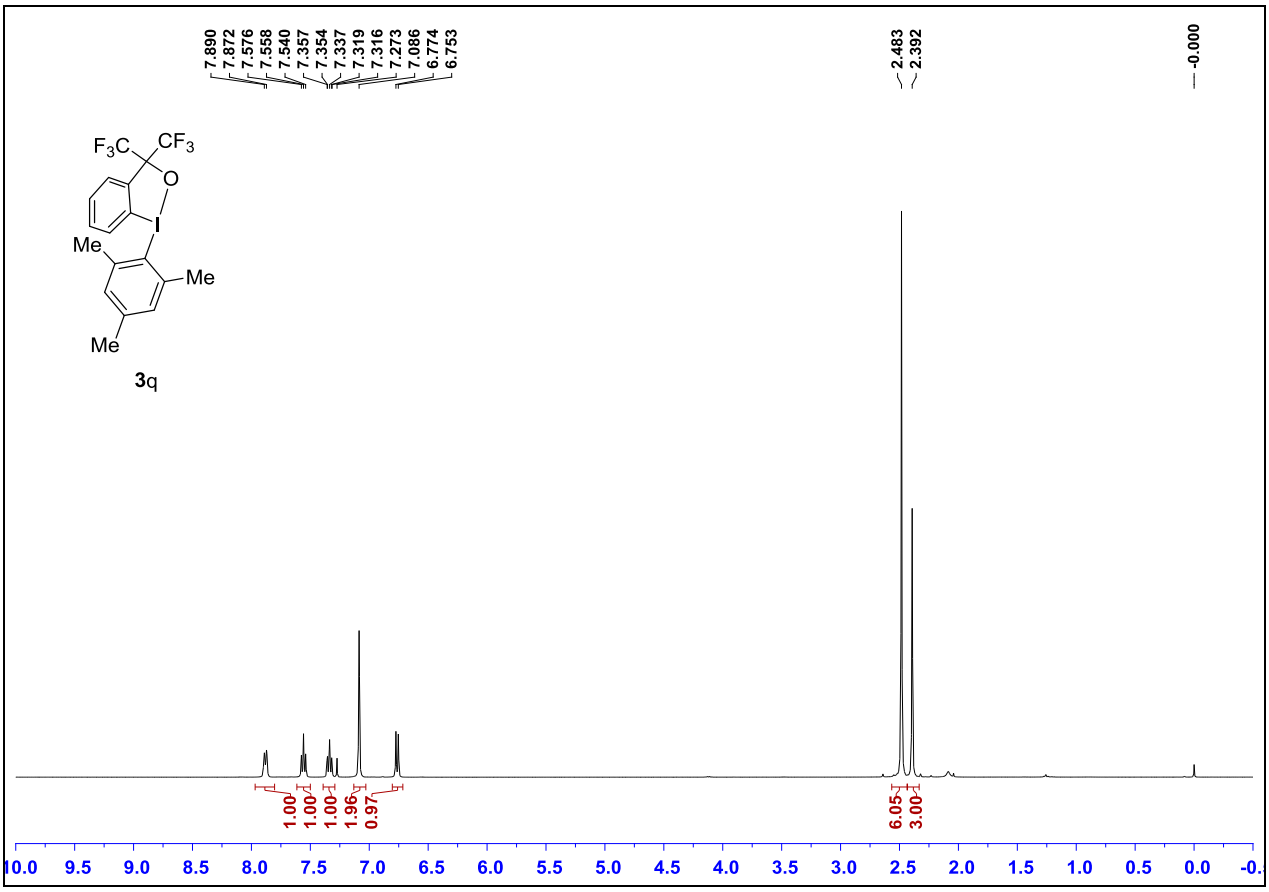


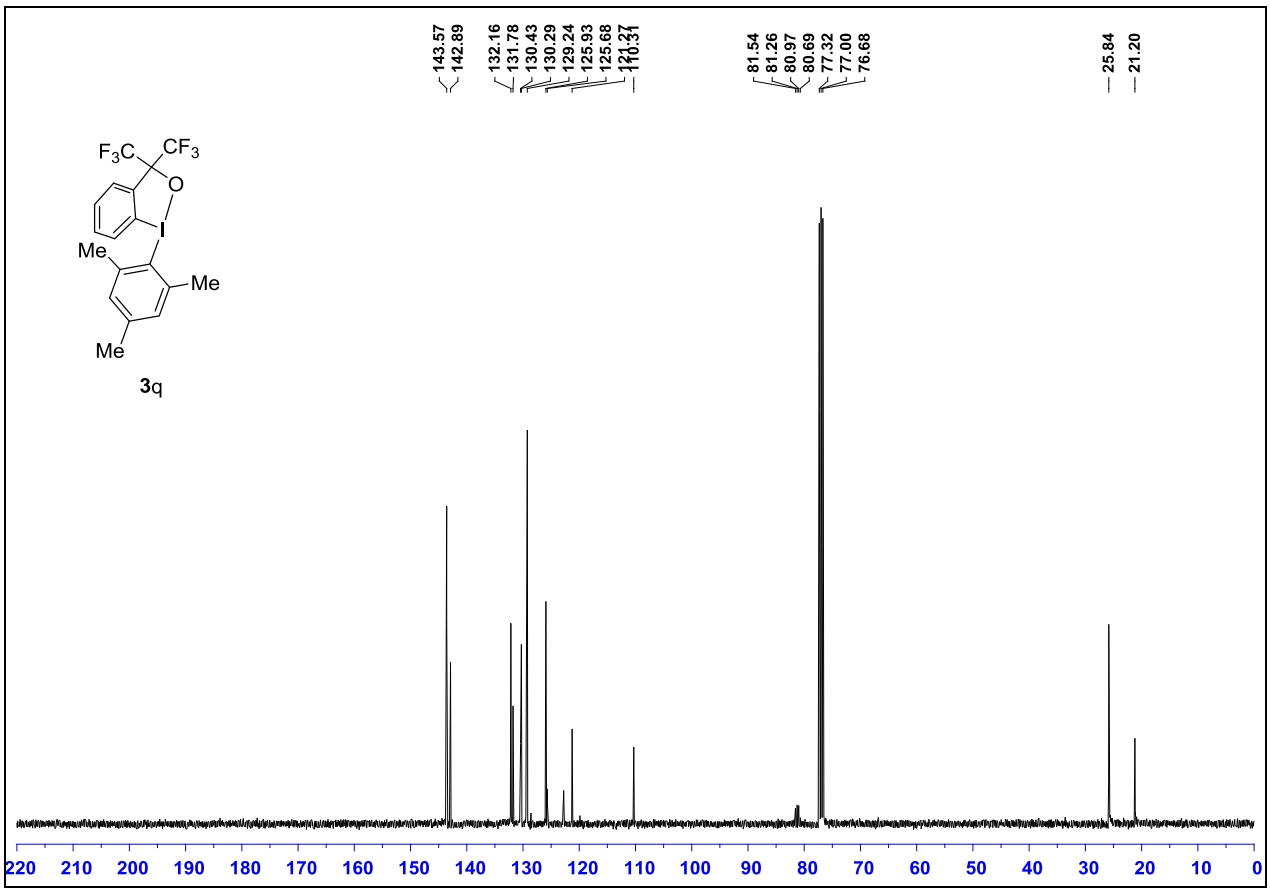


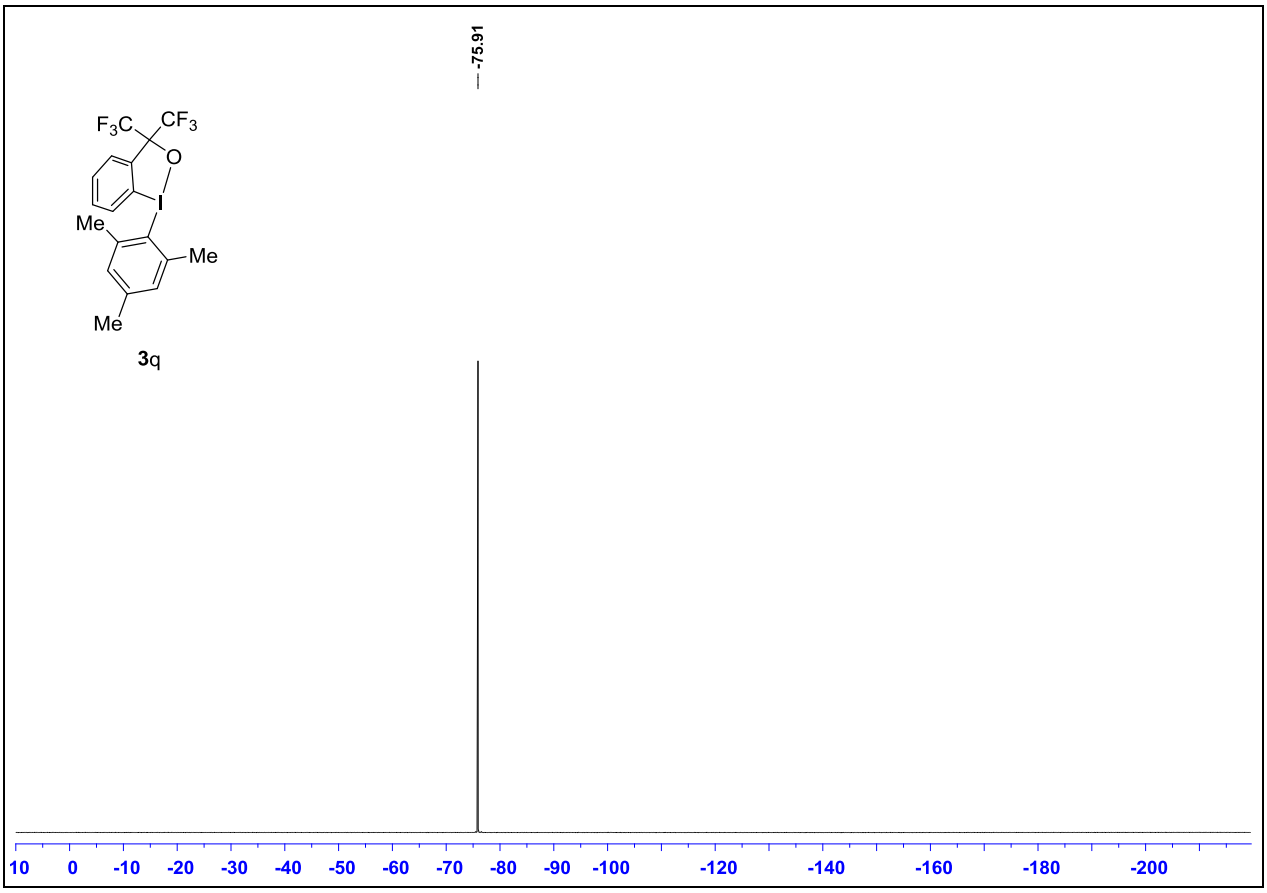

-76.65
Me
N
O
O
I
O
CF3
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

3p

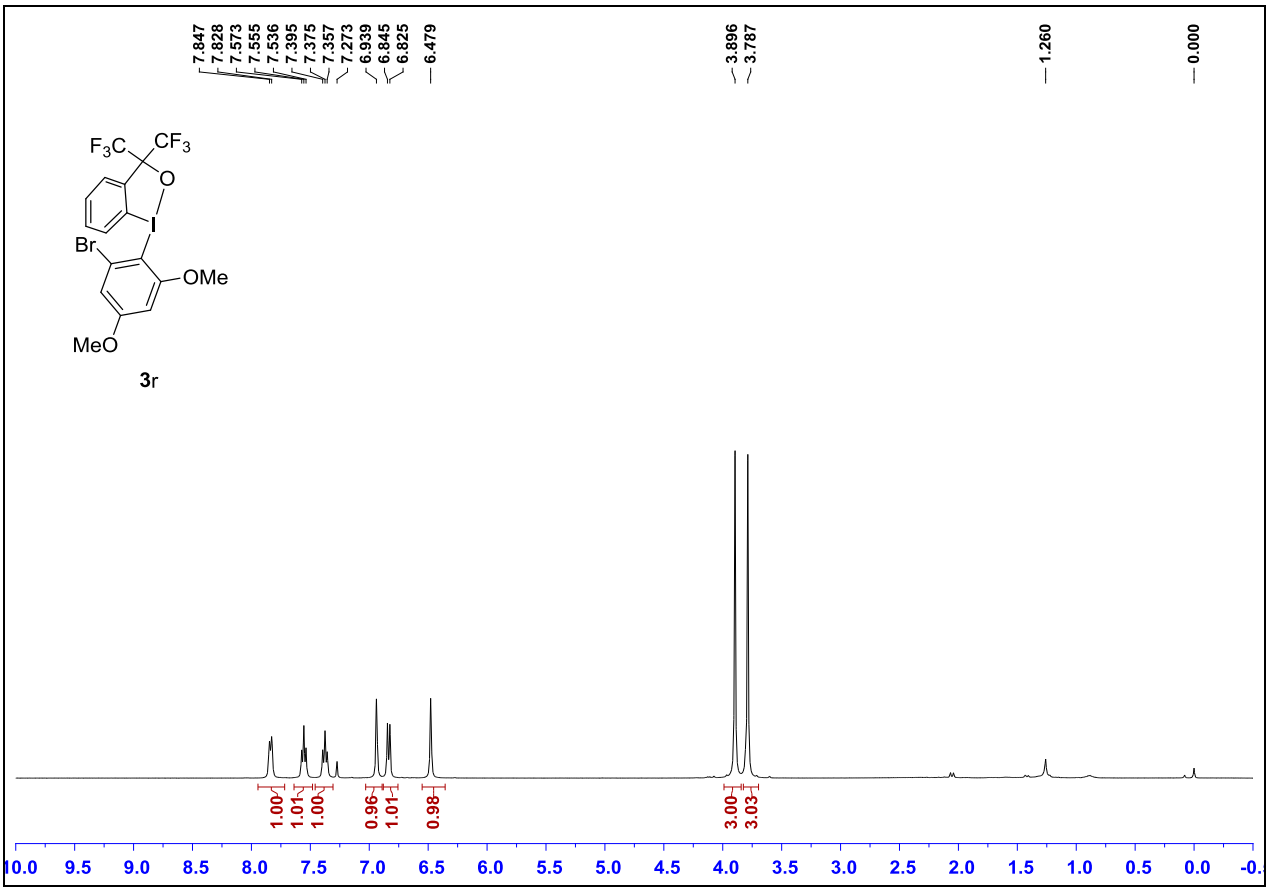
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

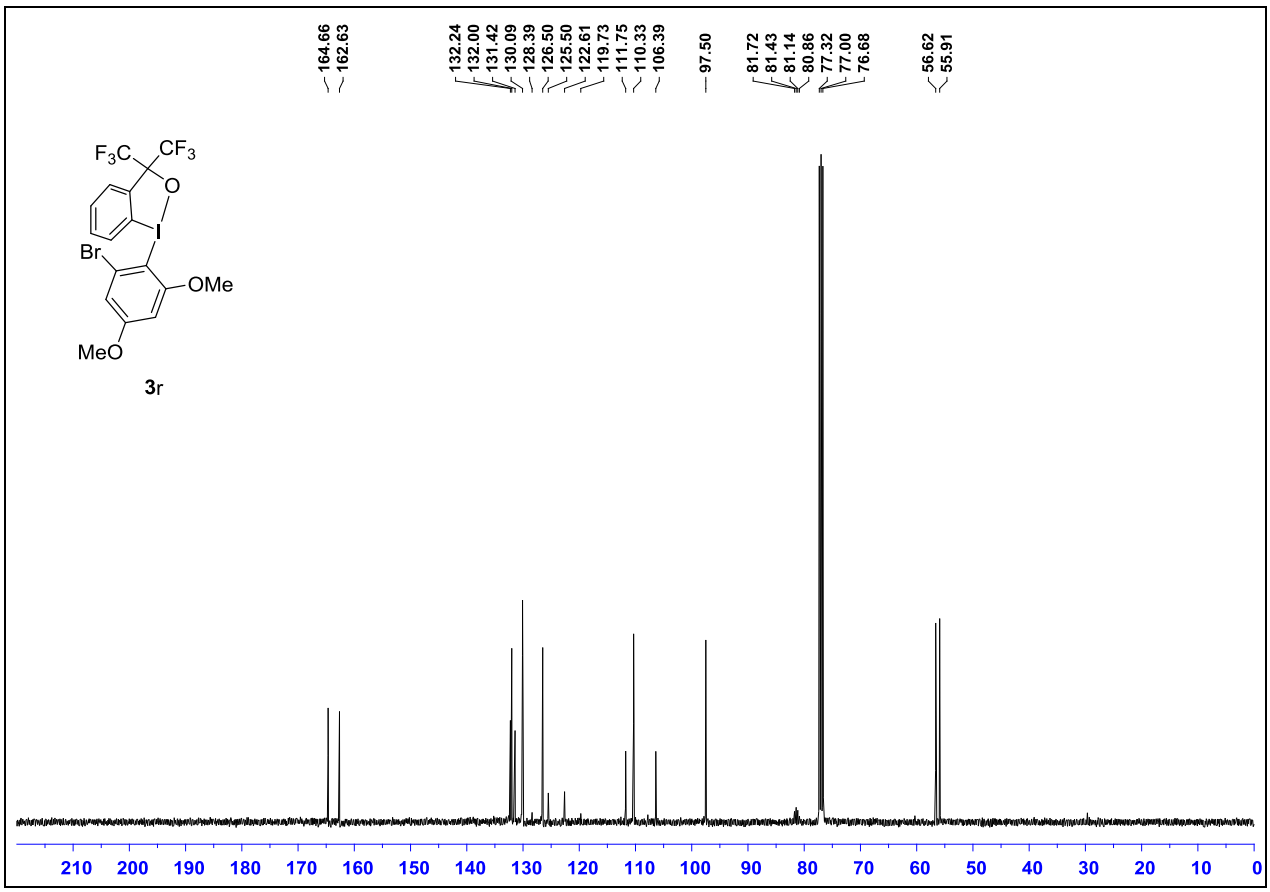


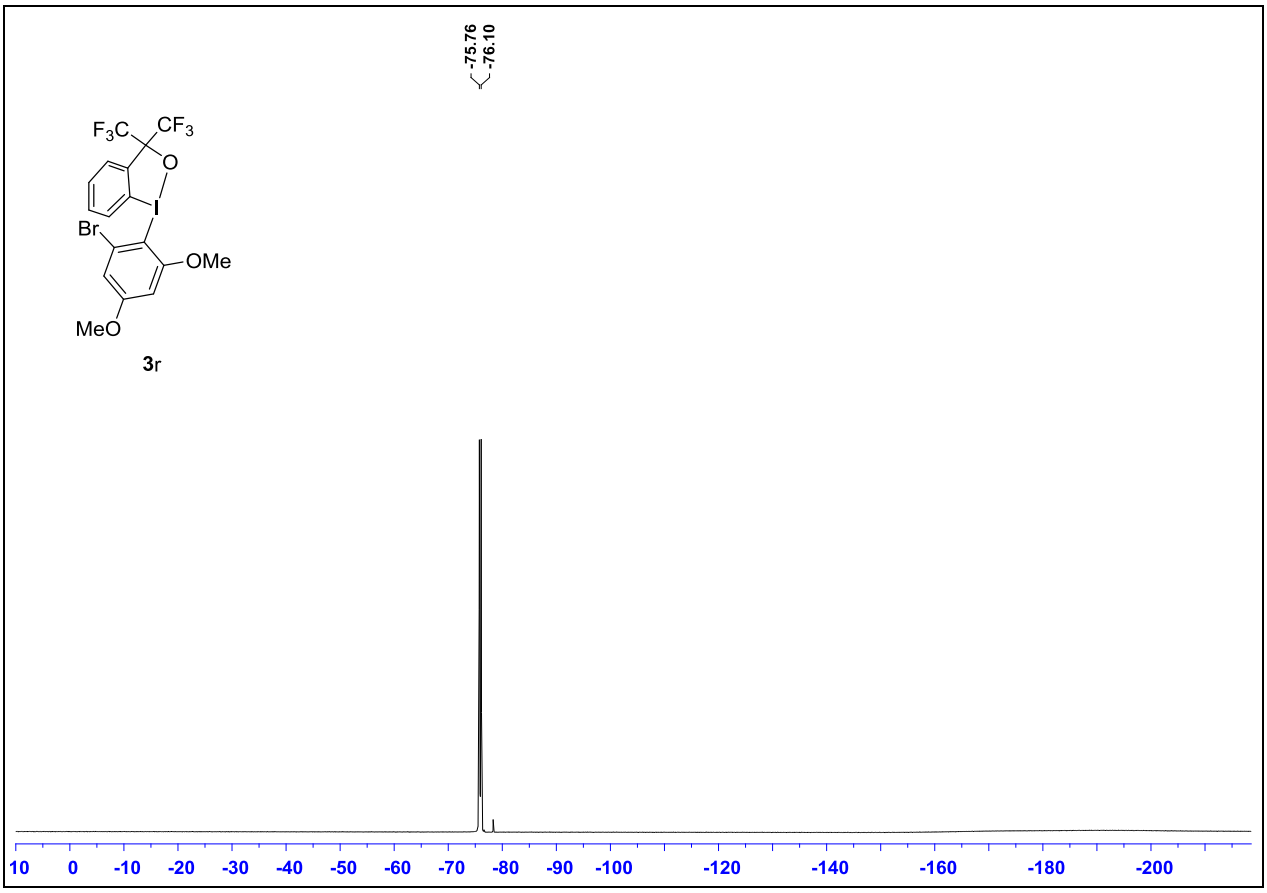



-75.91
F3C
CF3
O
I
Me
Me
Me
3q
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

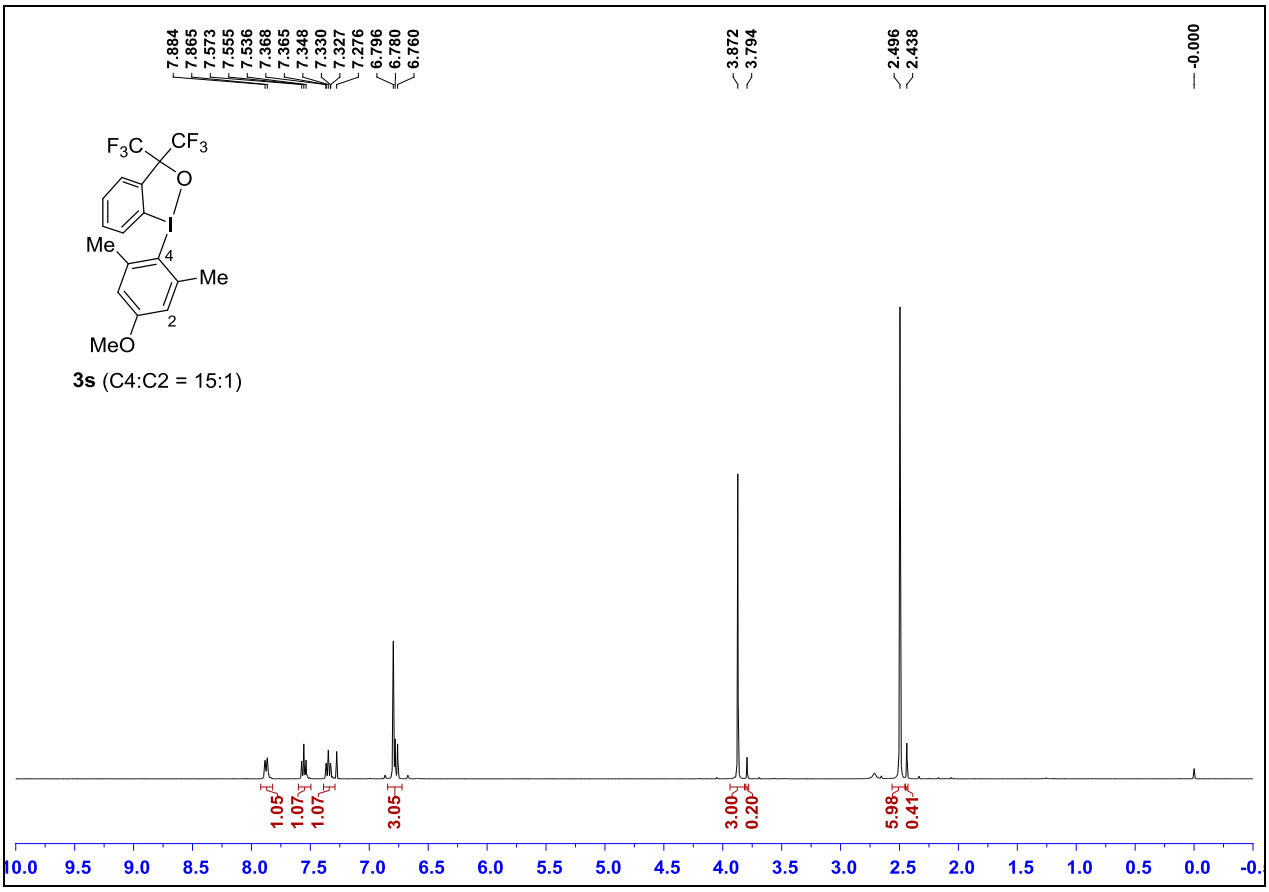
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

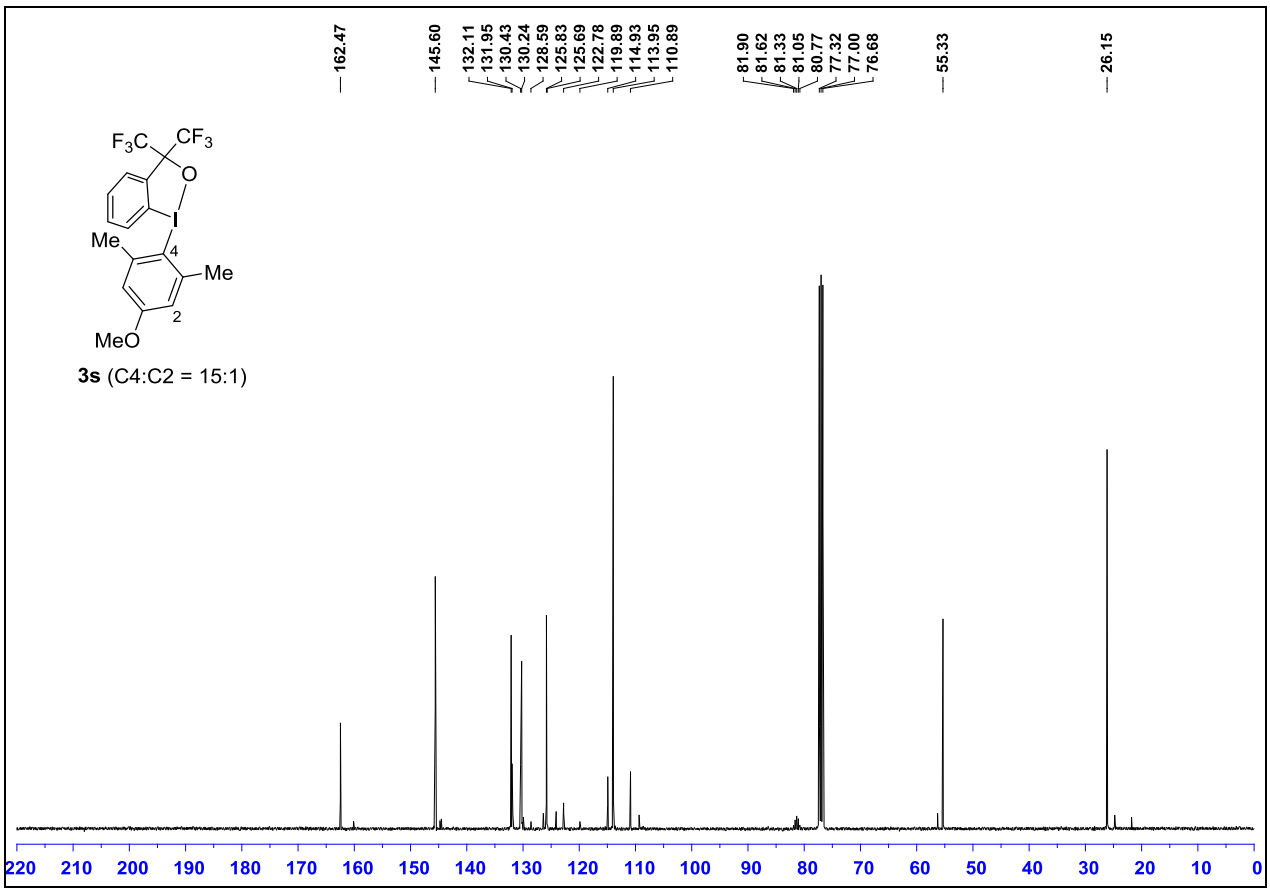


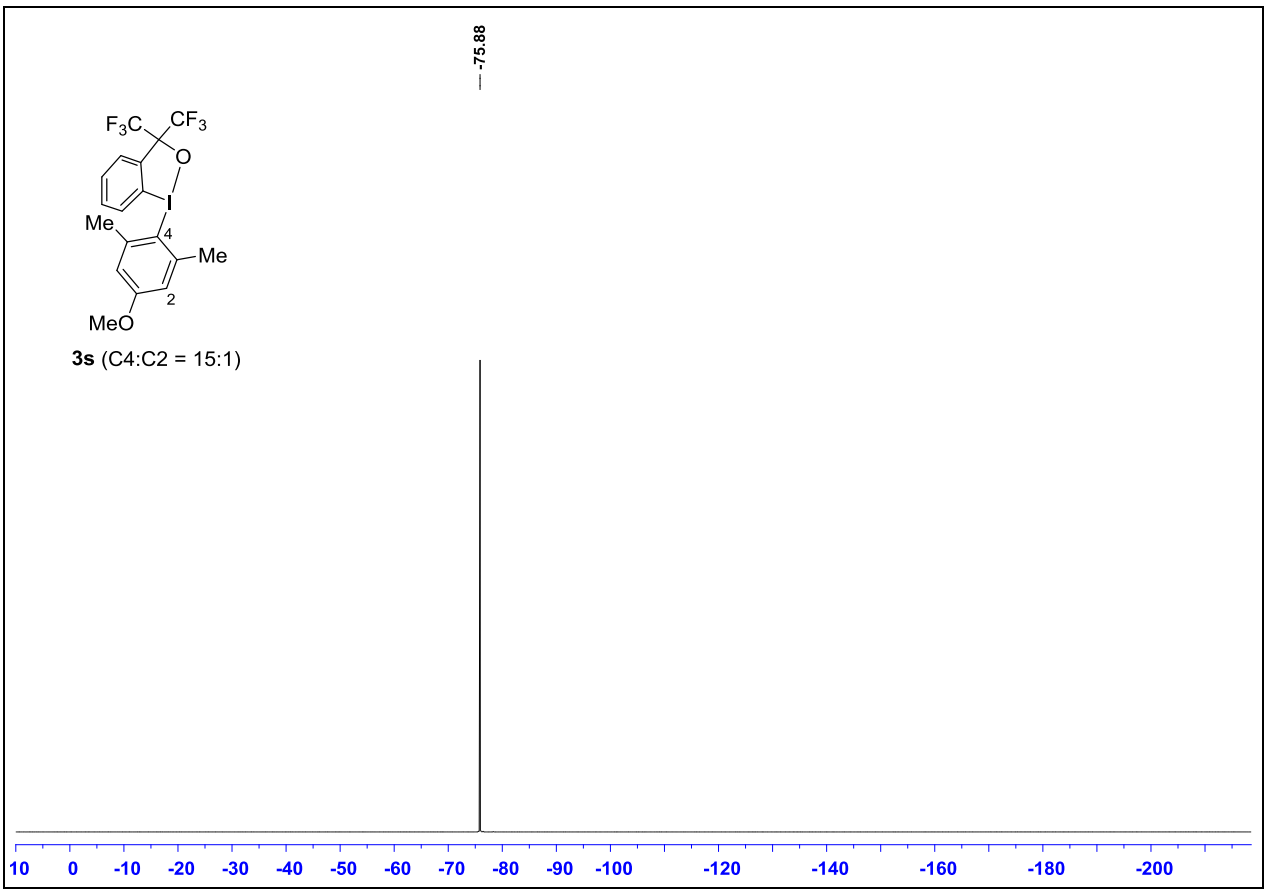



-75.76
-76.10
F3C
CF3
O
I
Br
OMe
MeO
3r
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

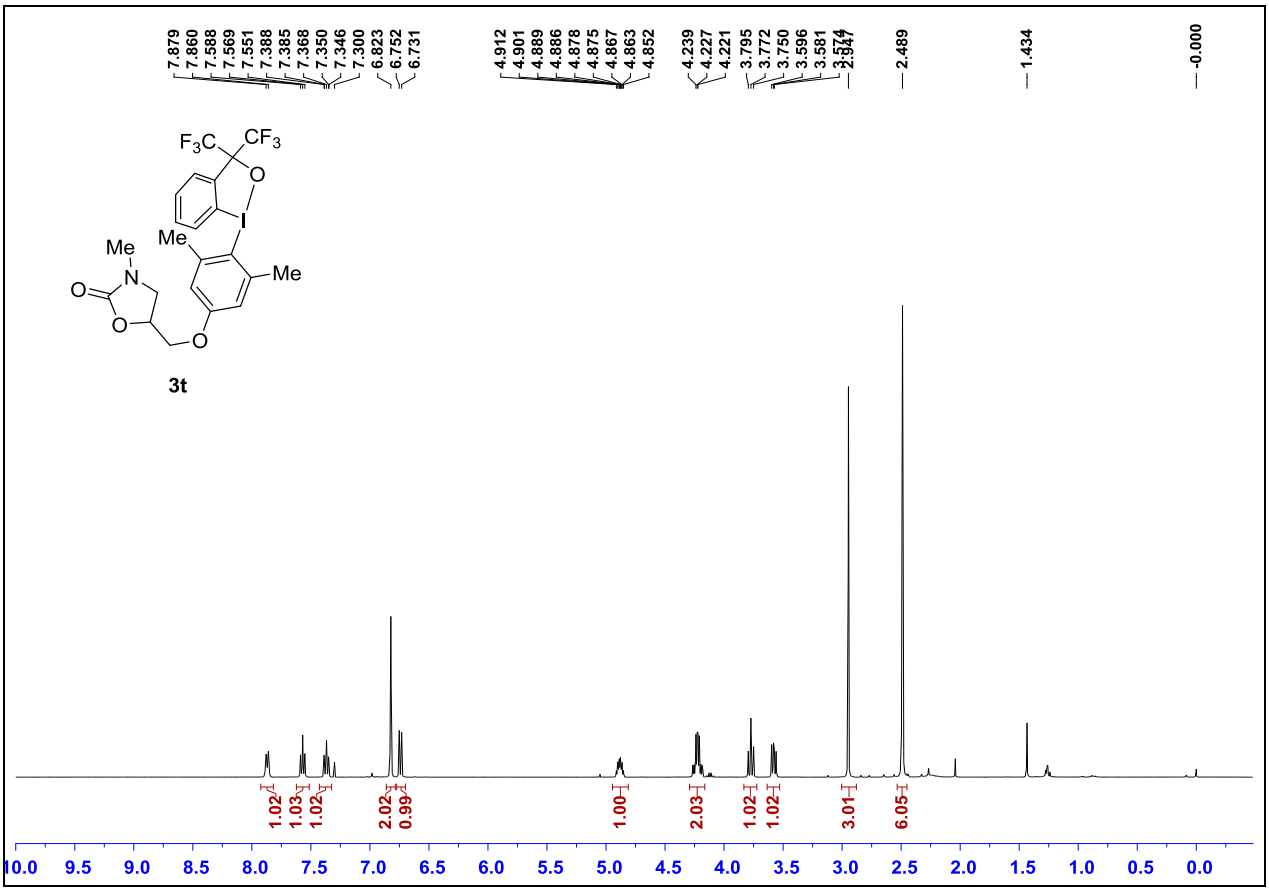


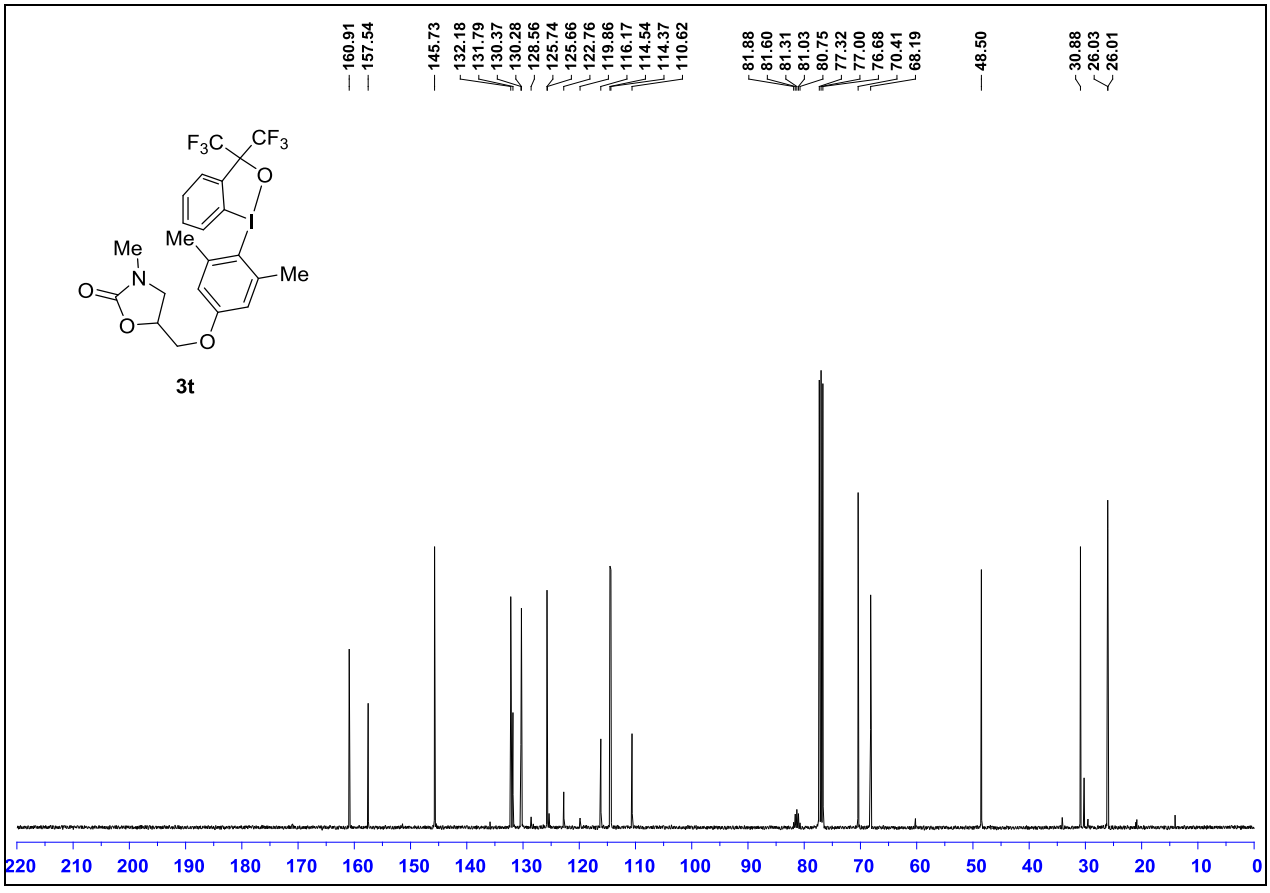


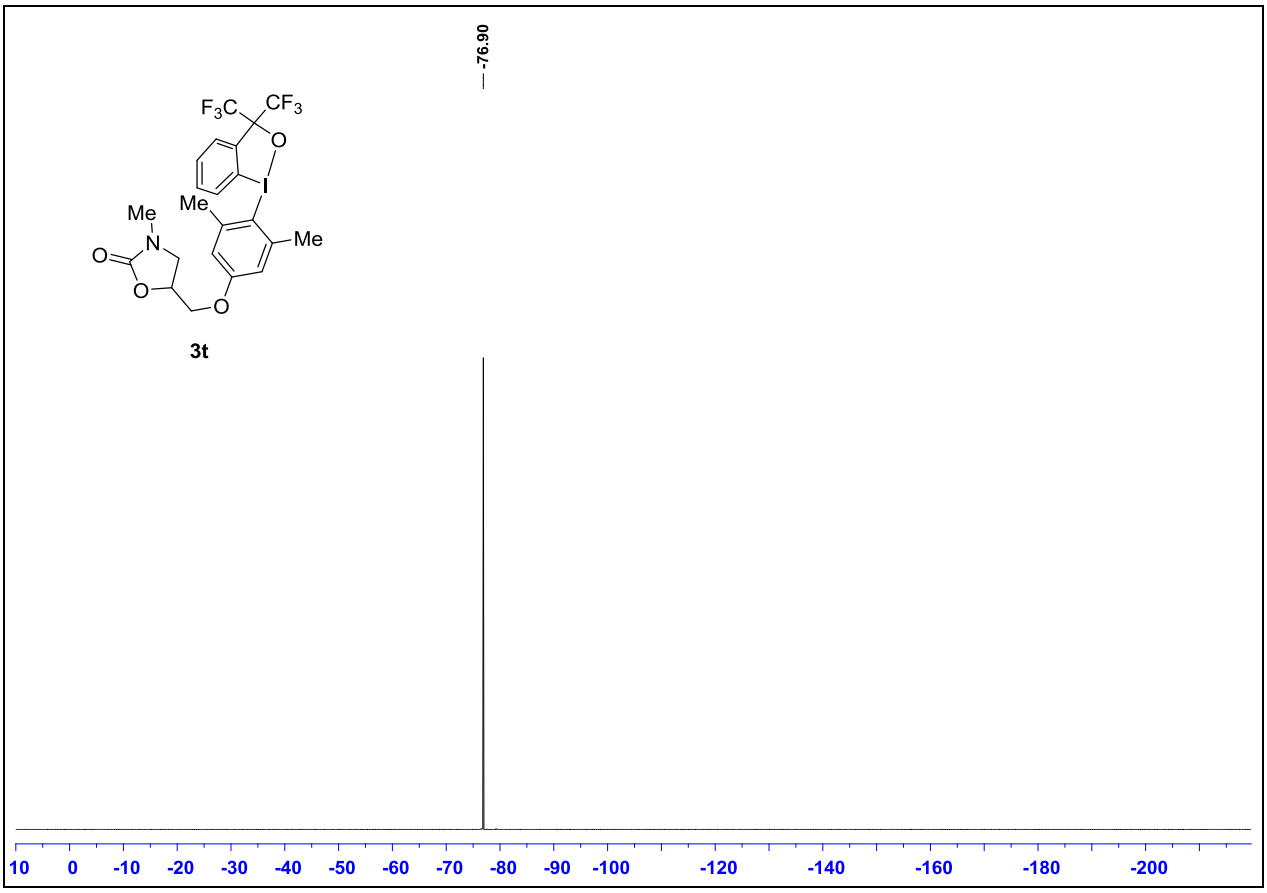

-75.88
F3C
CF3
O
I
Me
4
Me
2
MeO
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

3s (C4:C2 = 15:1)

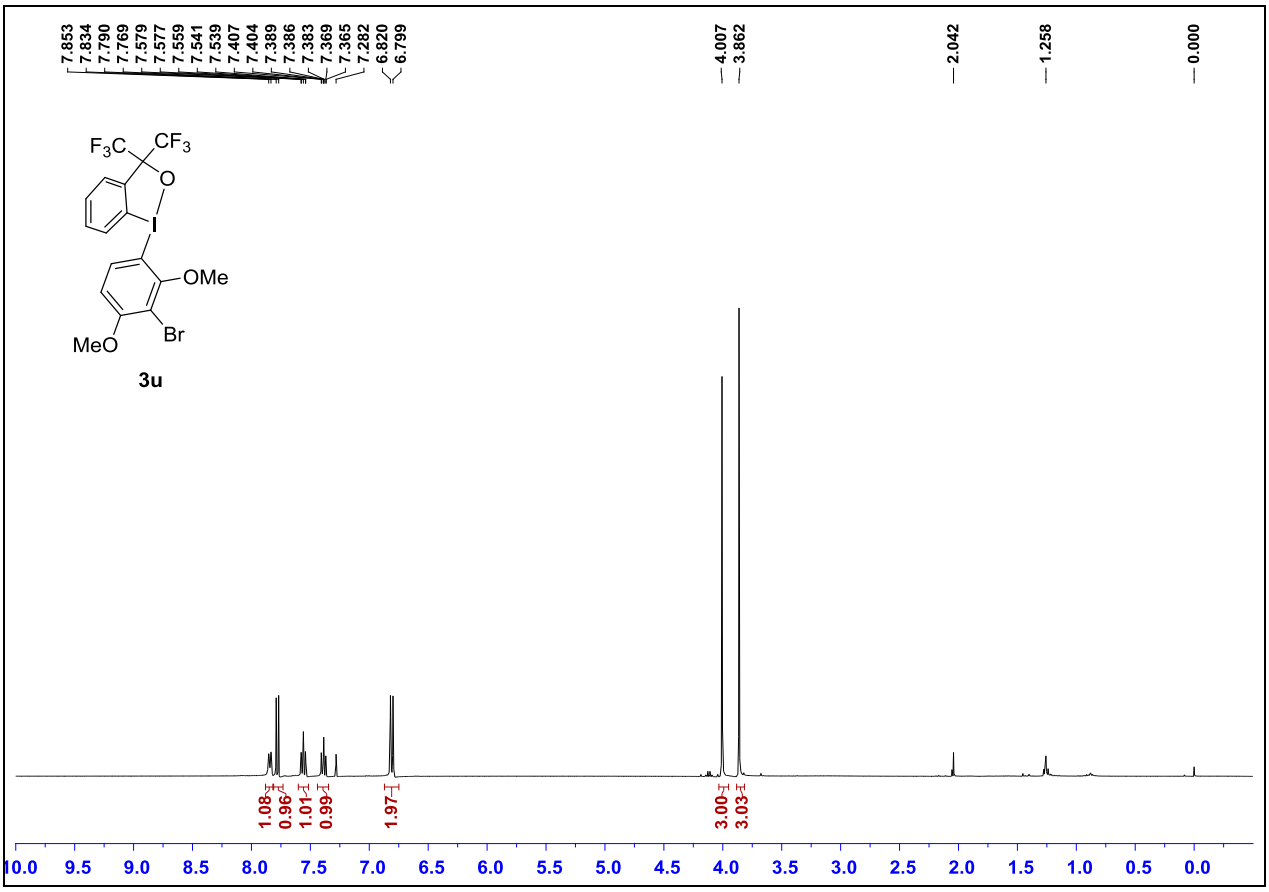
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

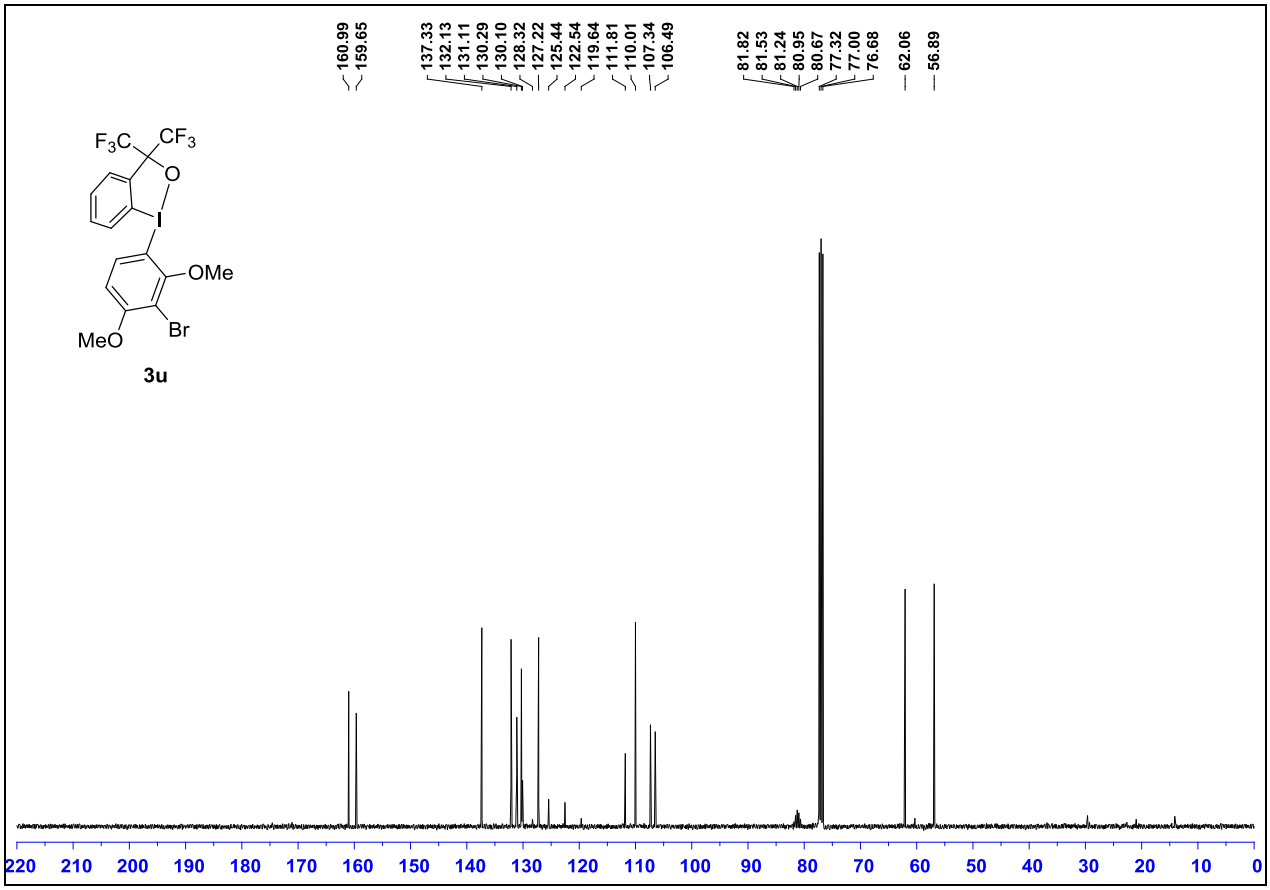


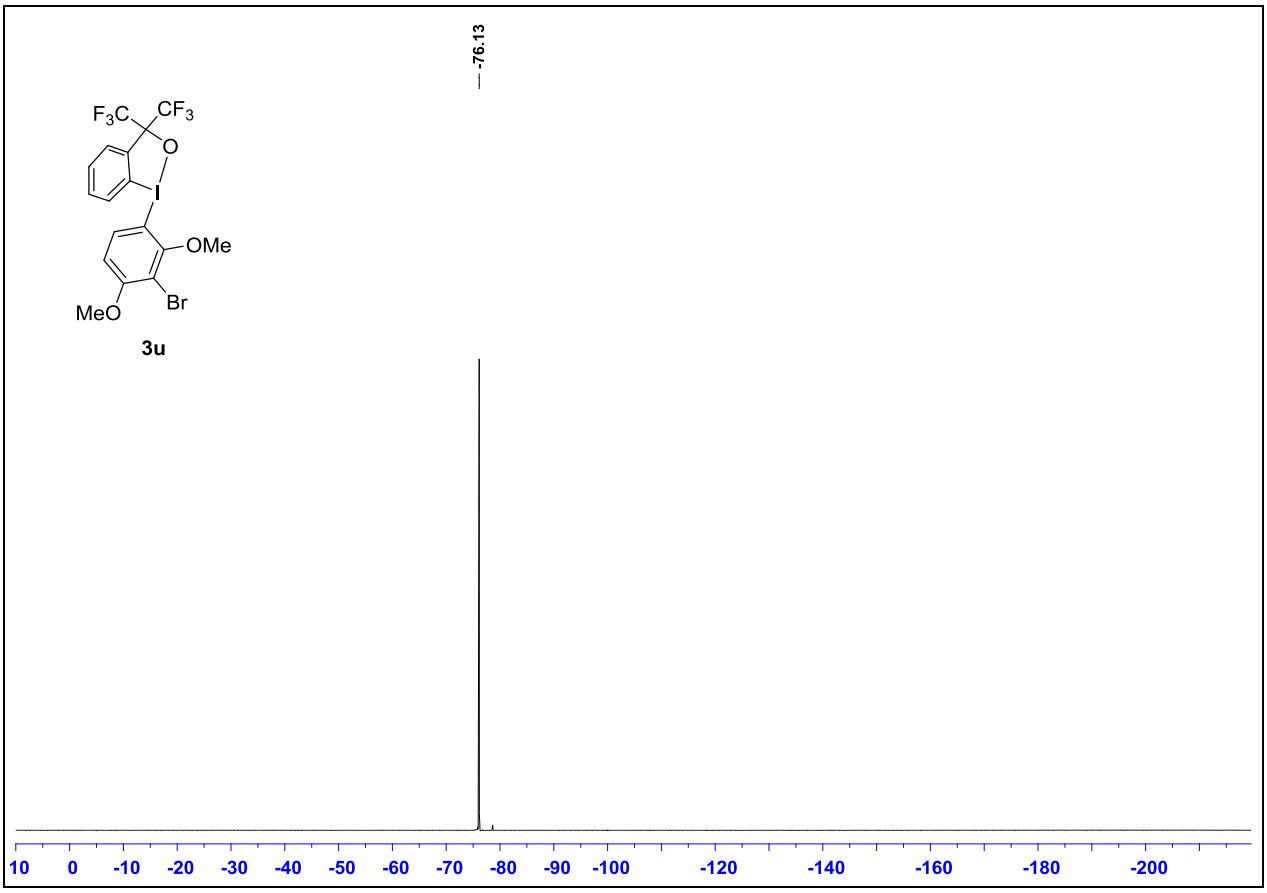



-76.90
F3C
CF3
O
I
Me
Me
Me
N
O
O
O
3t
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

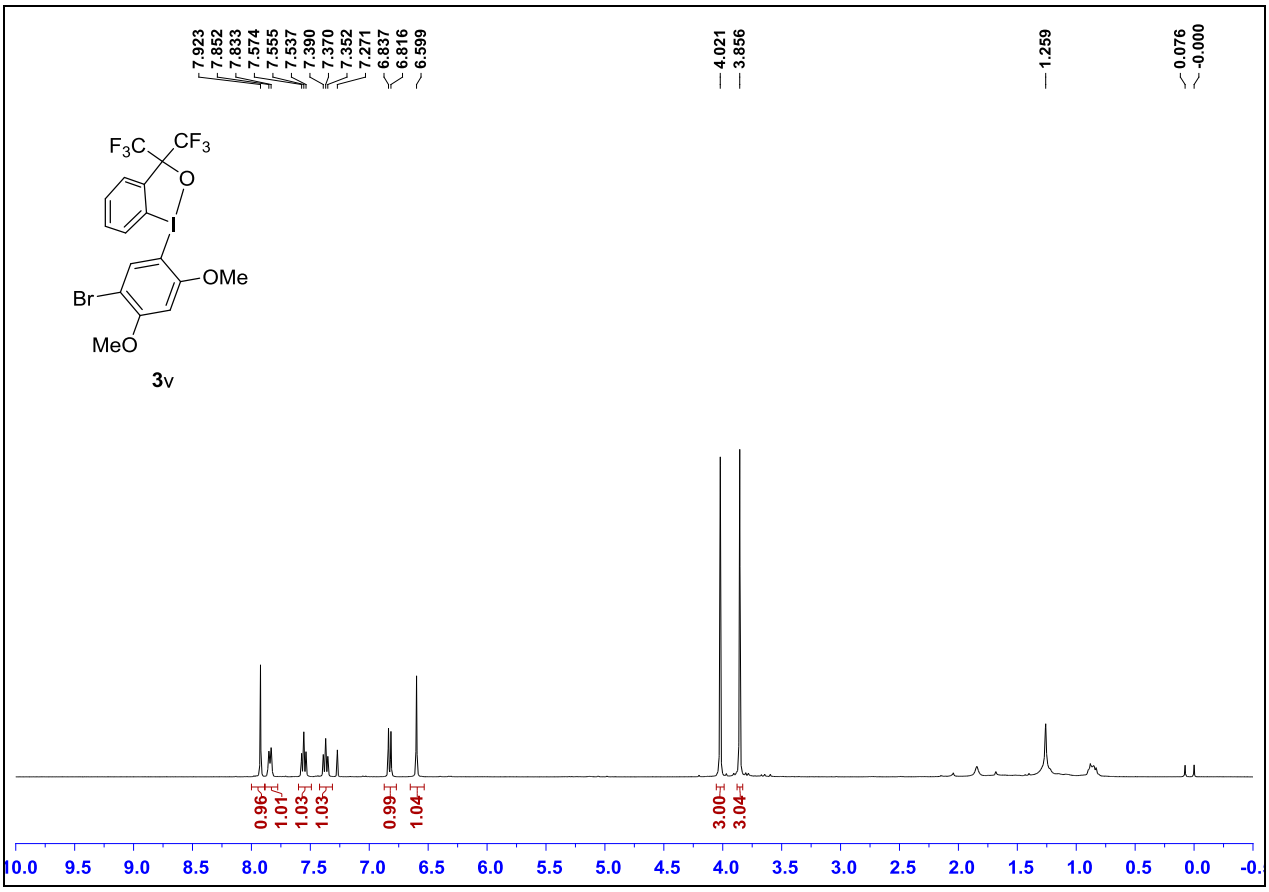
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

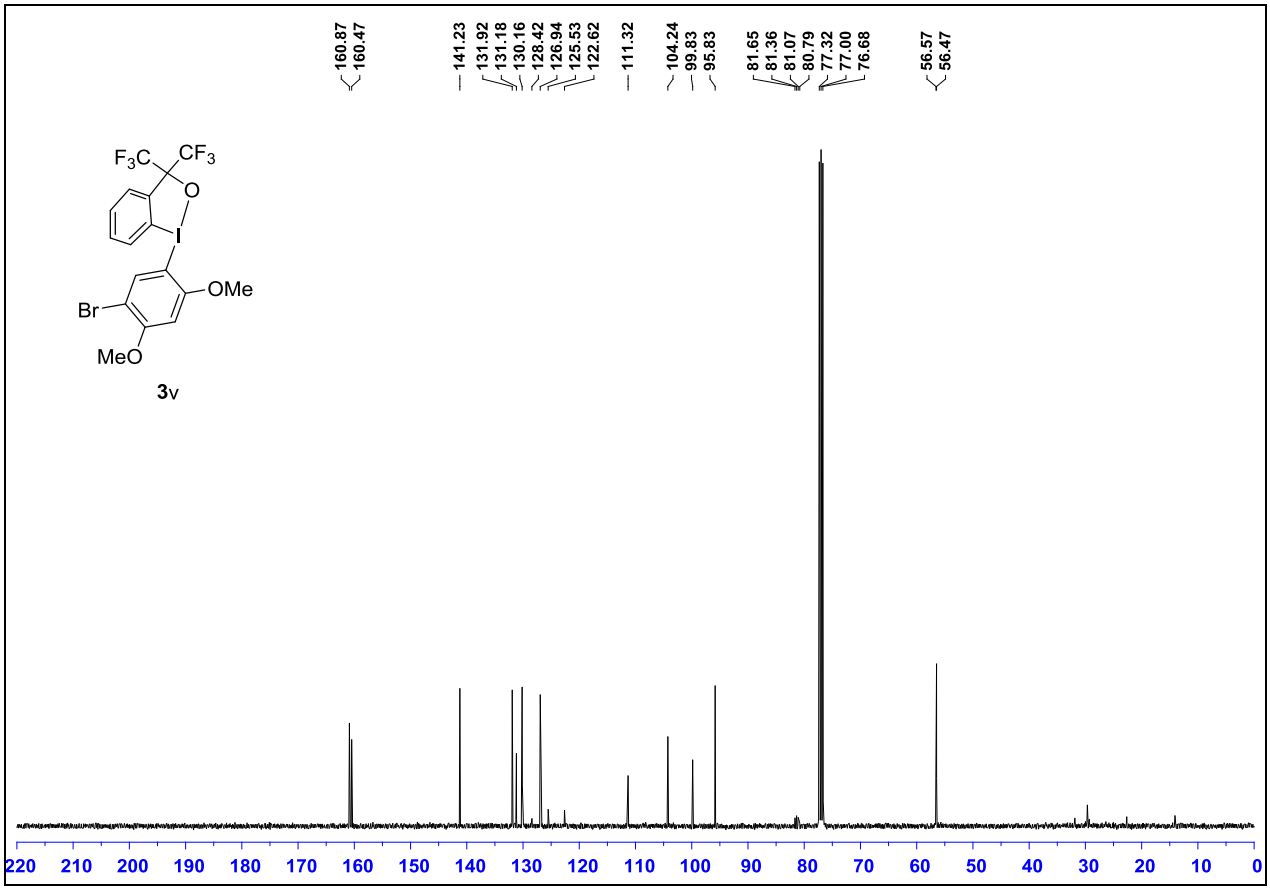


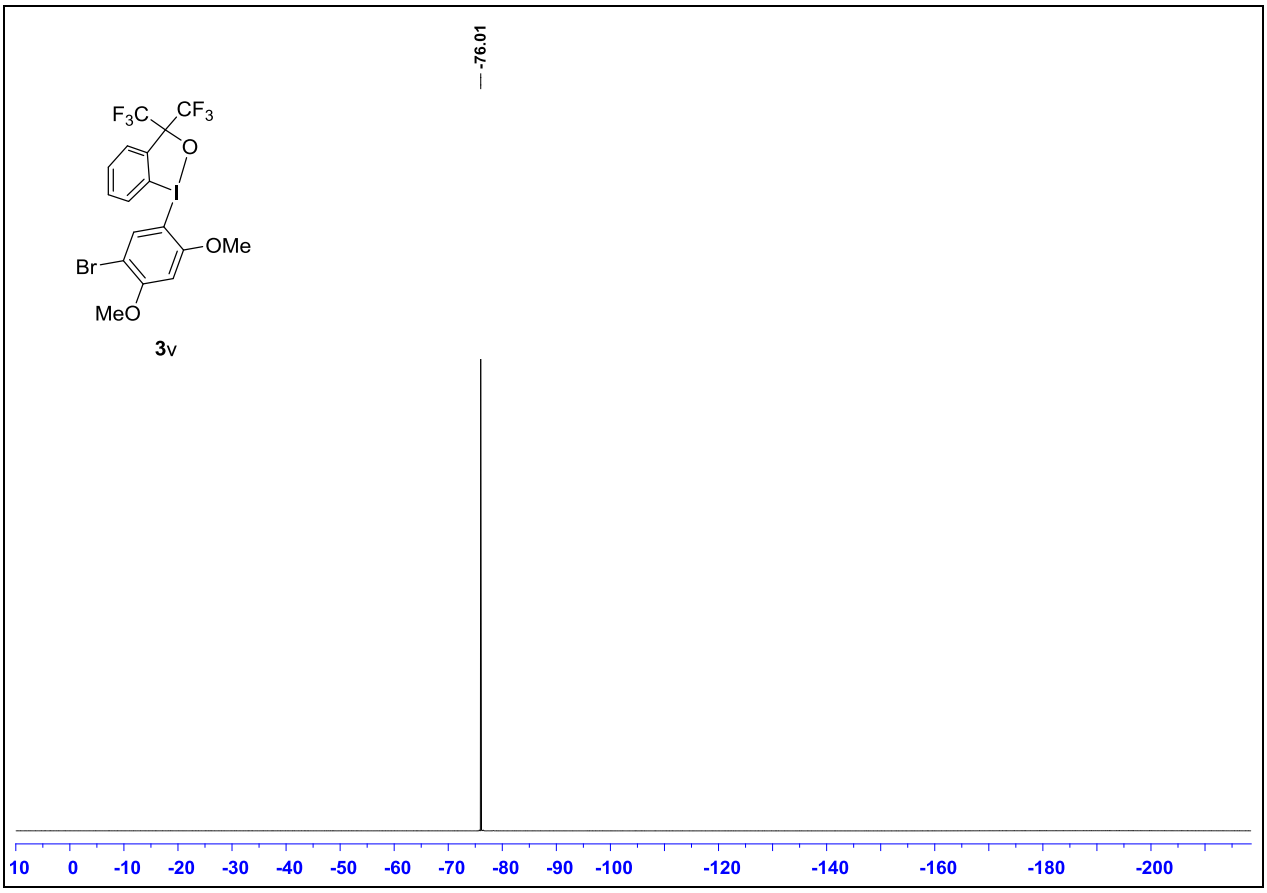



-76.13
F3C
CF3
O
I
OMe
MeO
Br
3u
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

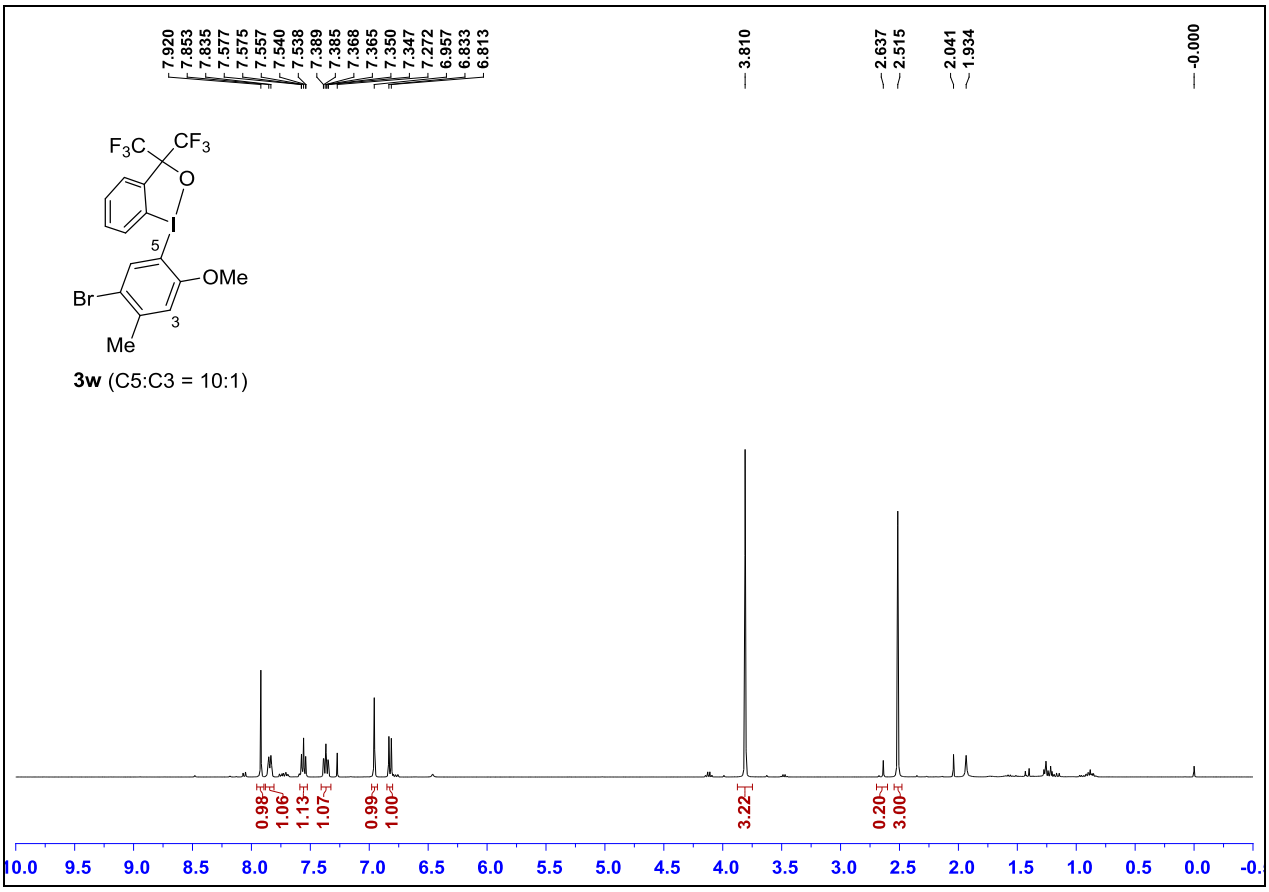
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

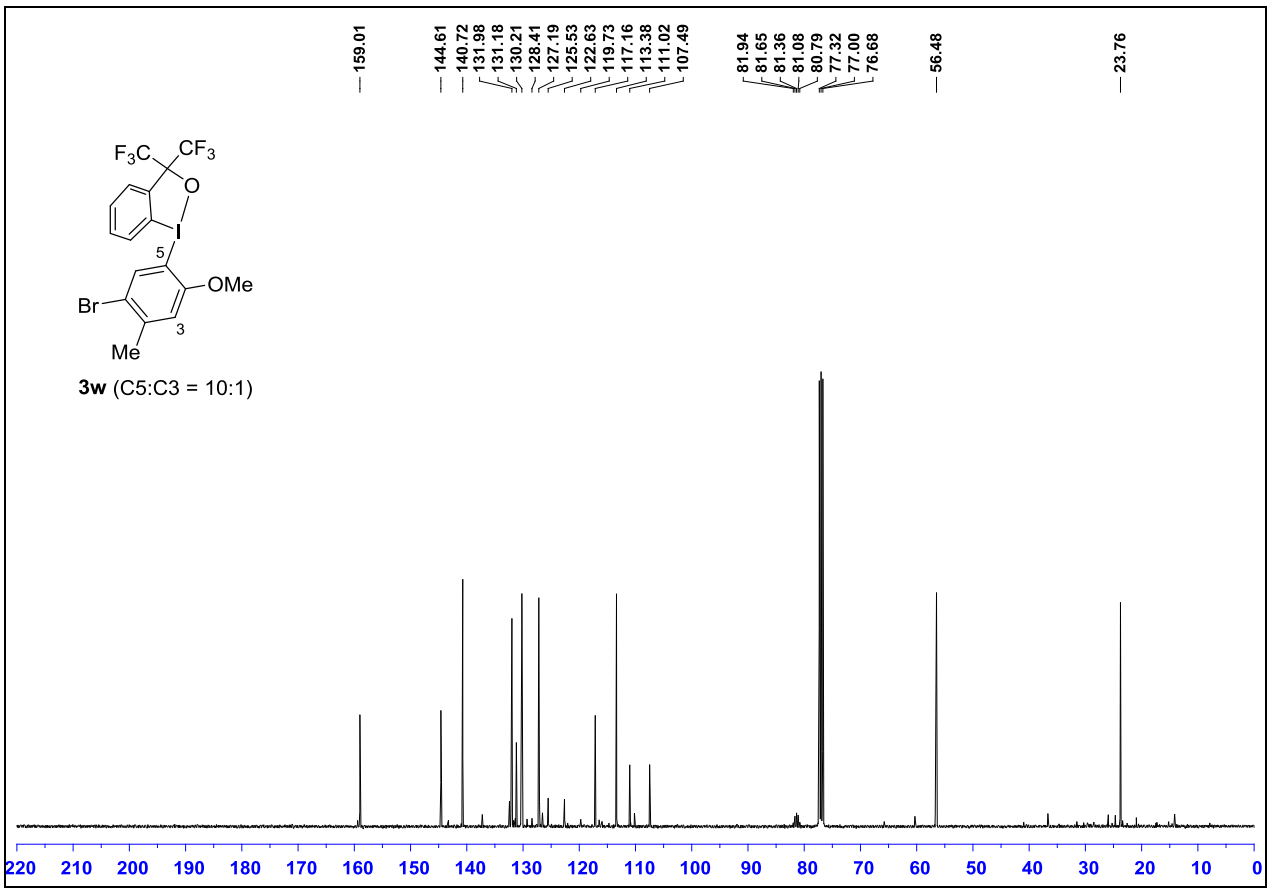


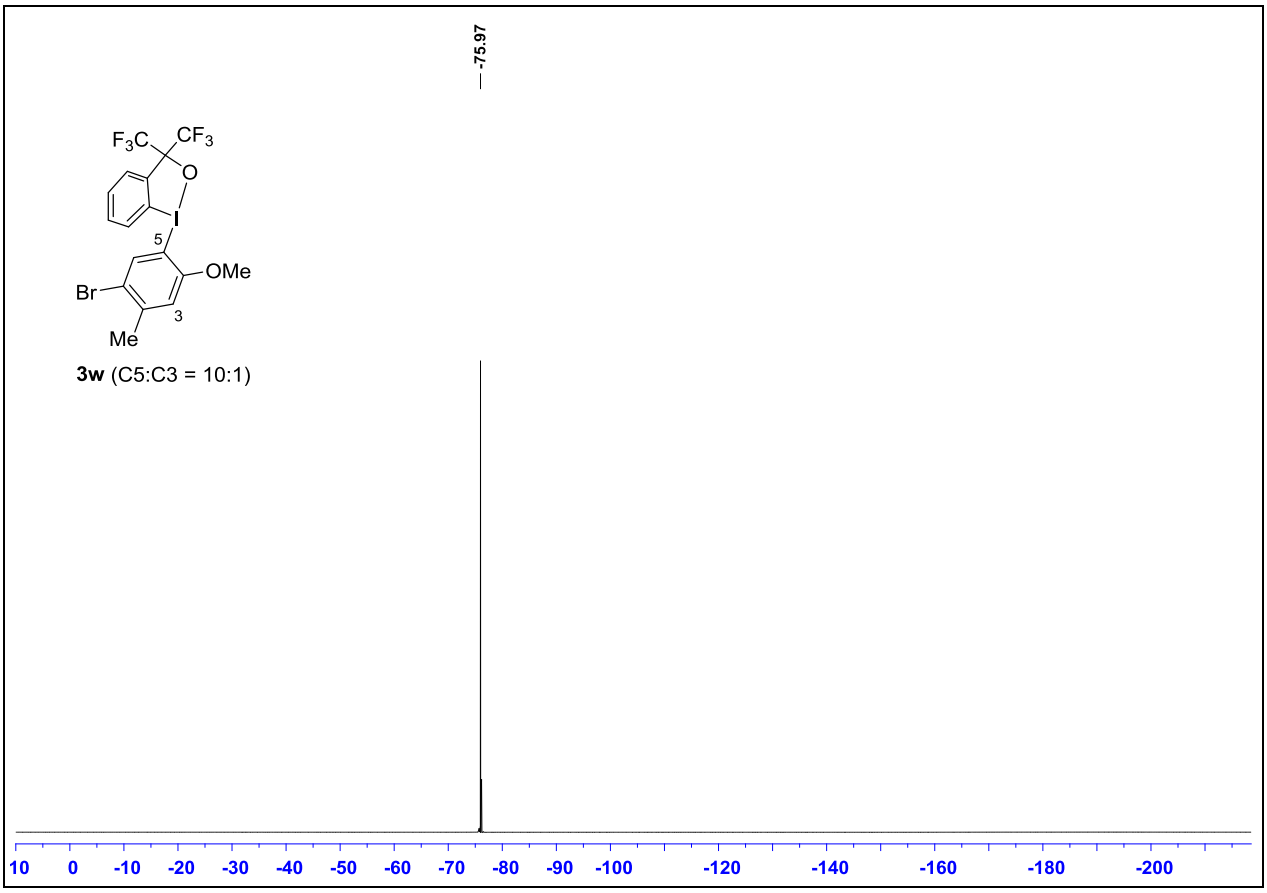



-76.01
F3C
CF3
O
I
Br
OMe
MeO
3v
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

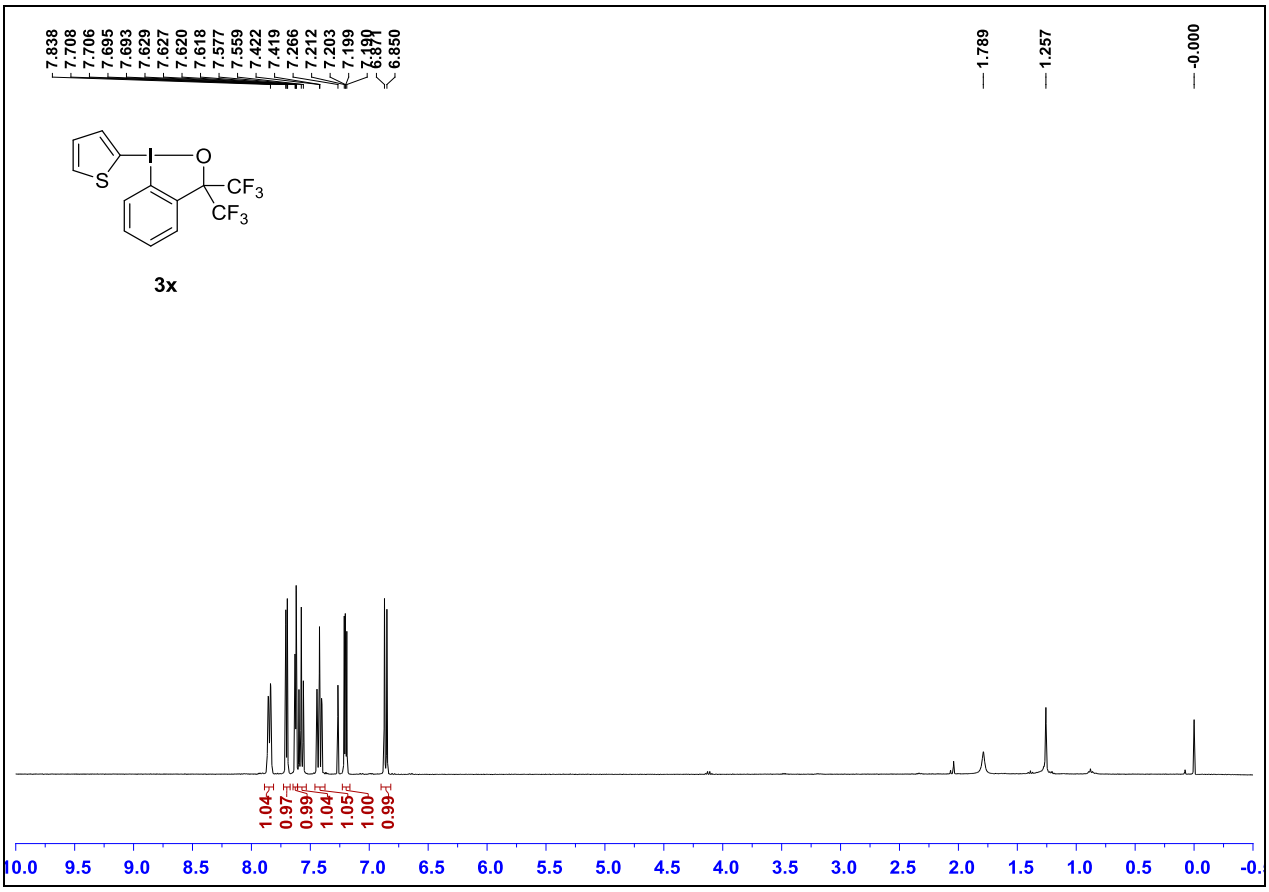
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

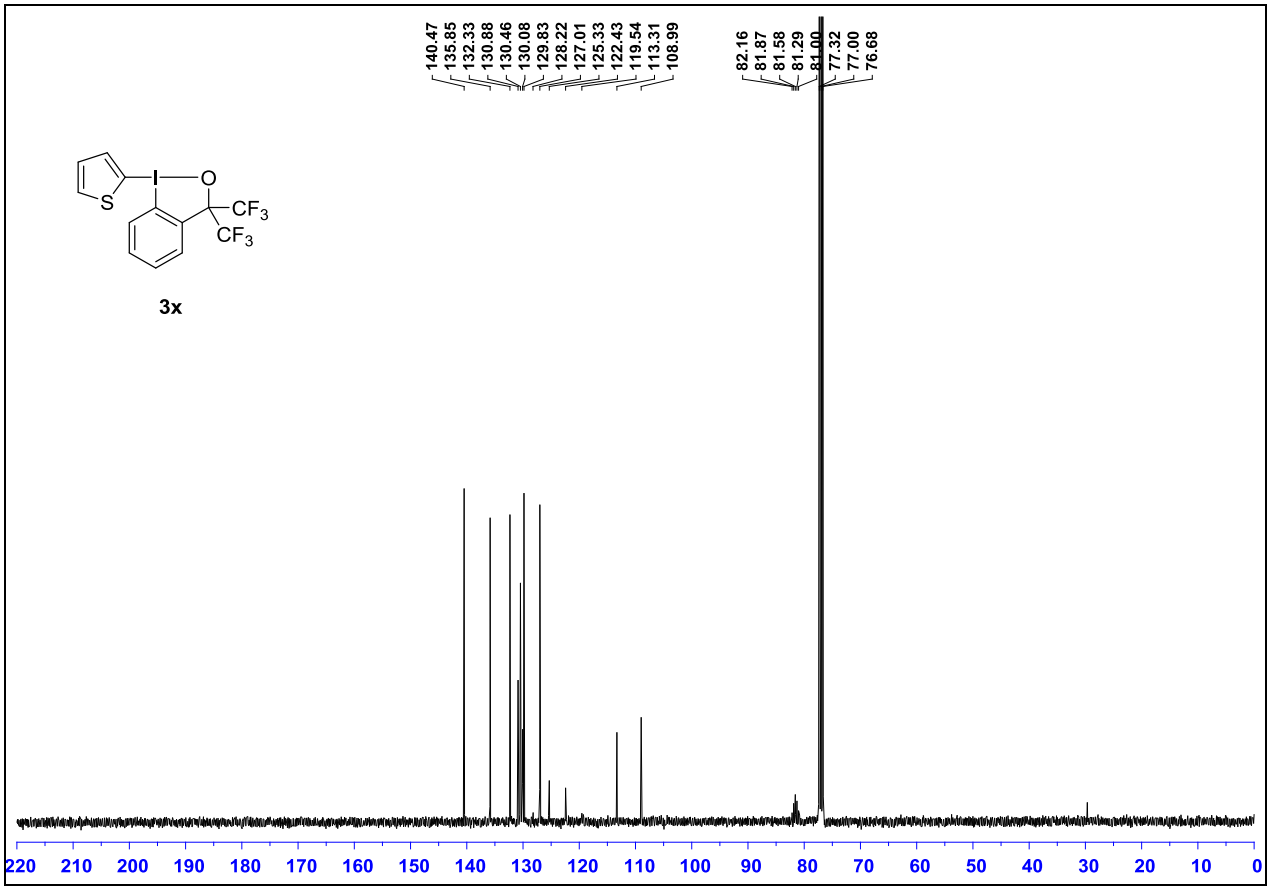


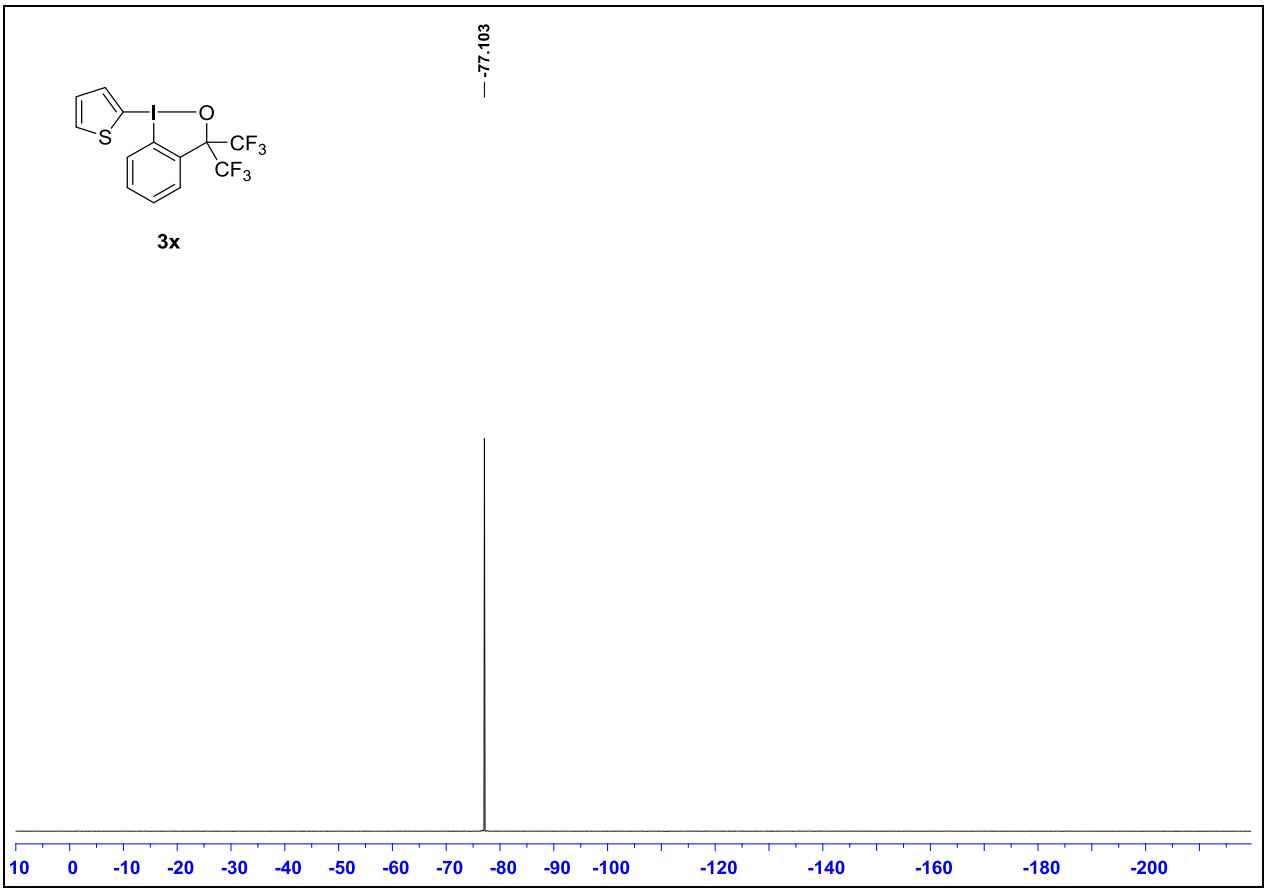



-75.97
F3C
CF3
O
I
5
OMe
Br
3
Me
3w (C5:C3 = 10:1)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

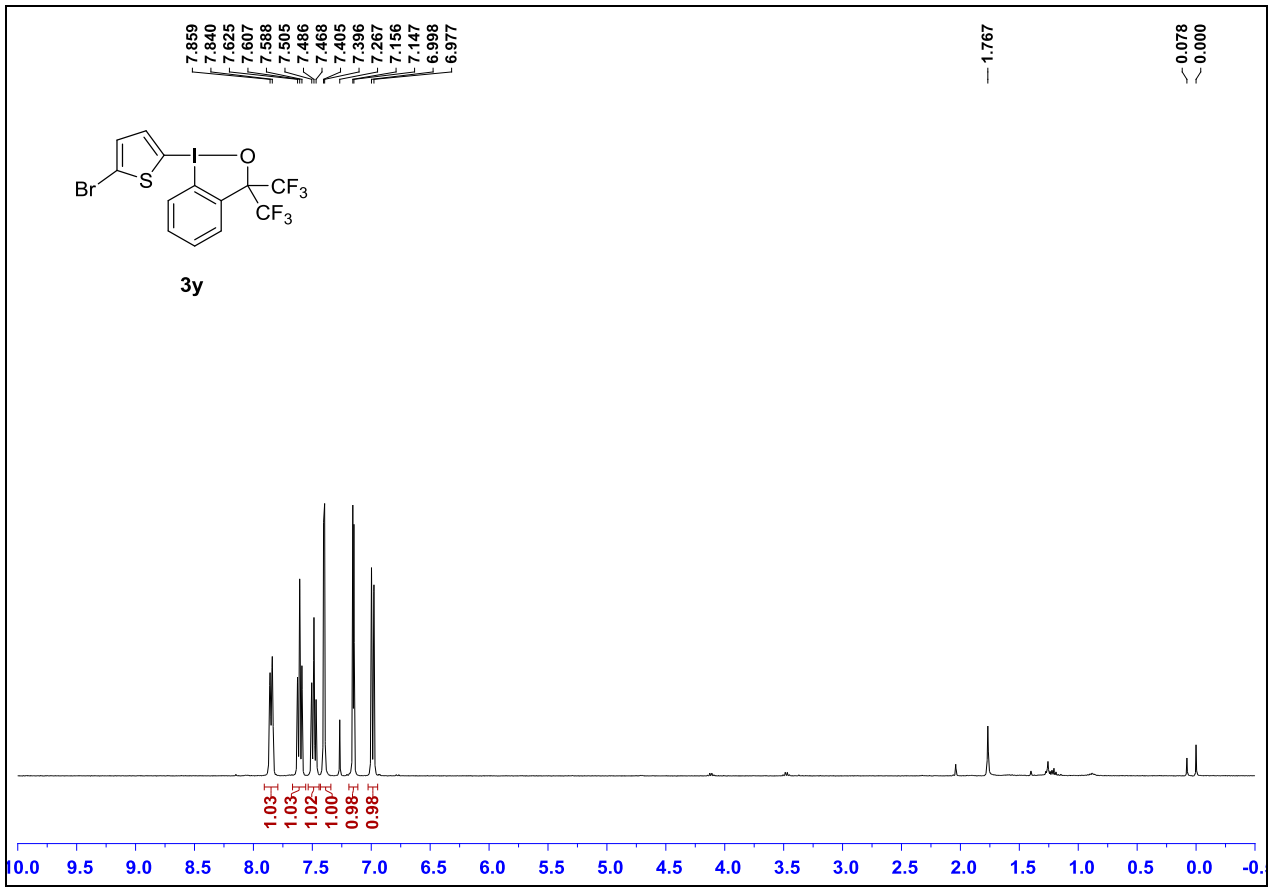
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

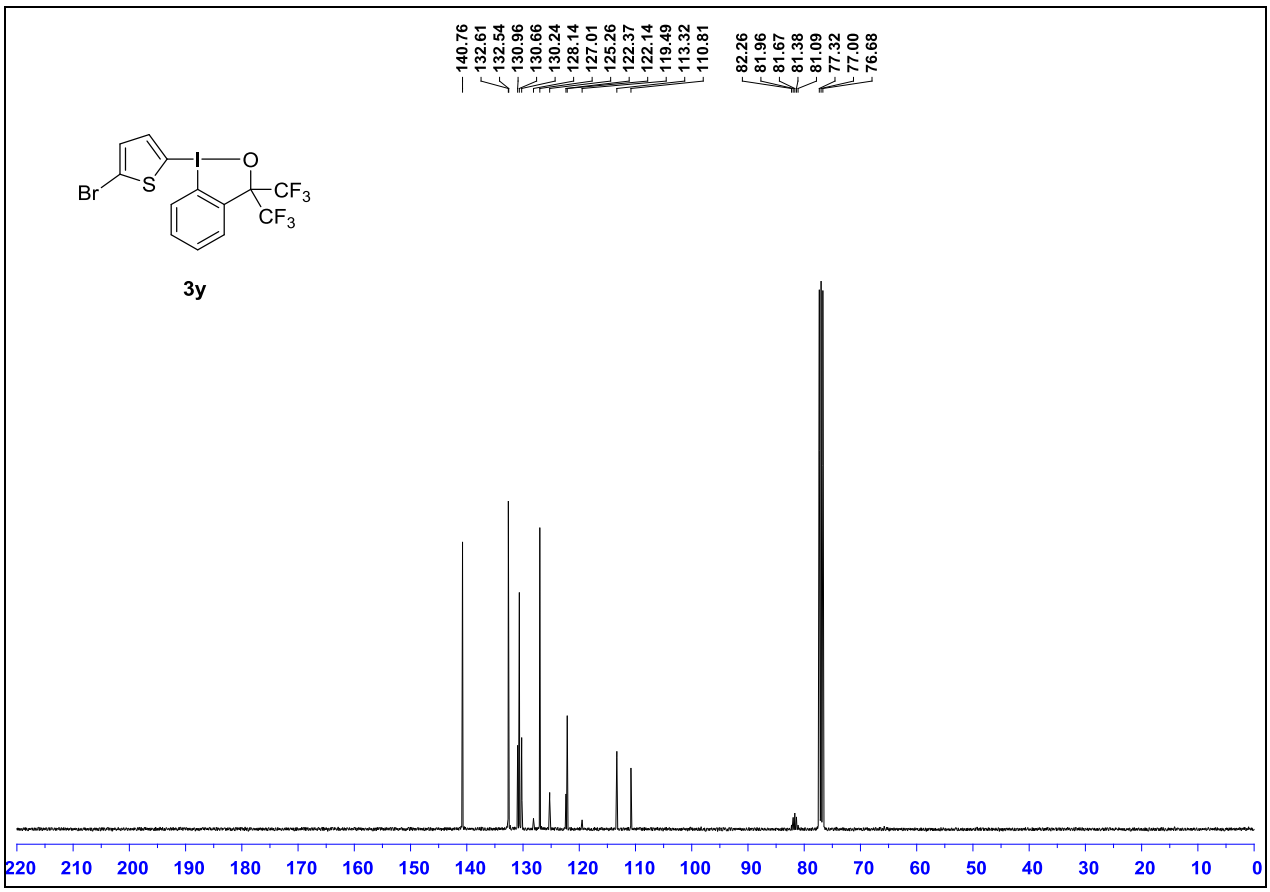


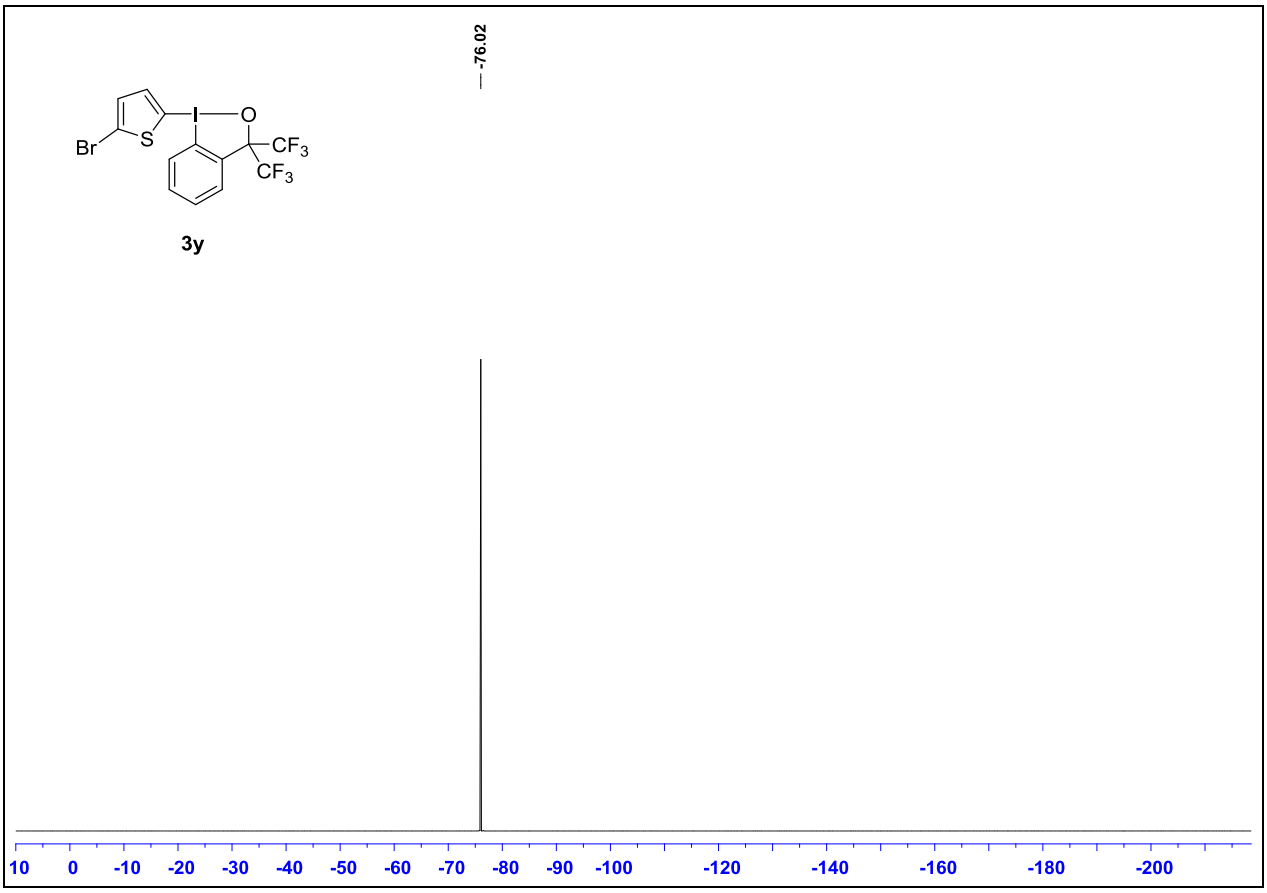



-77.103
S
I
O
CF3
CF3
3x
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

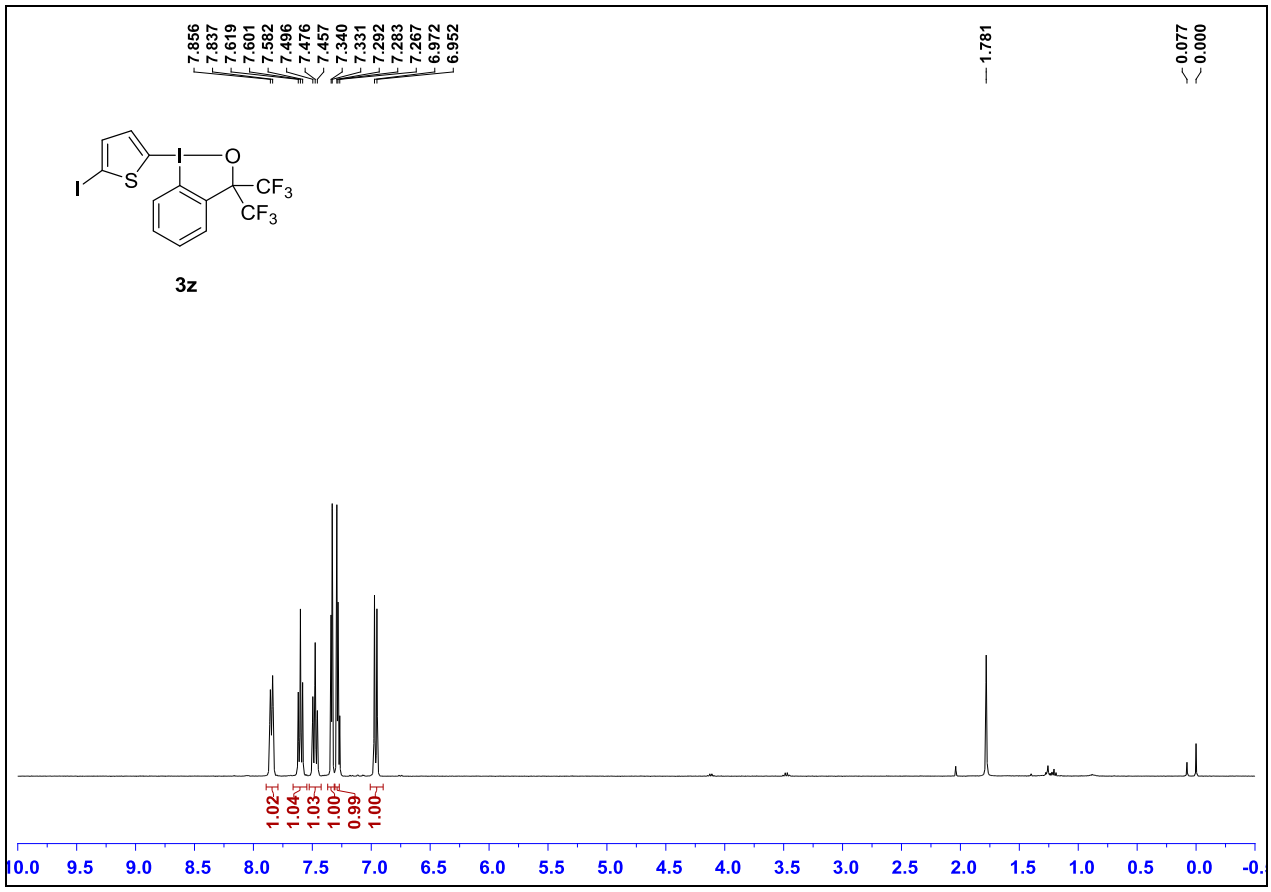
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

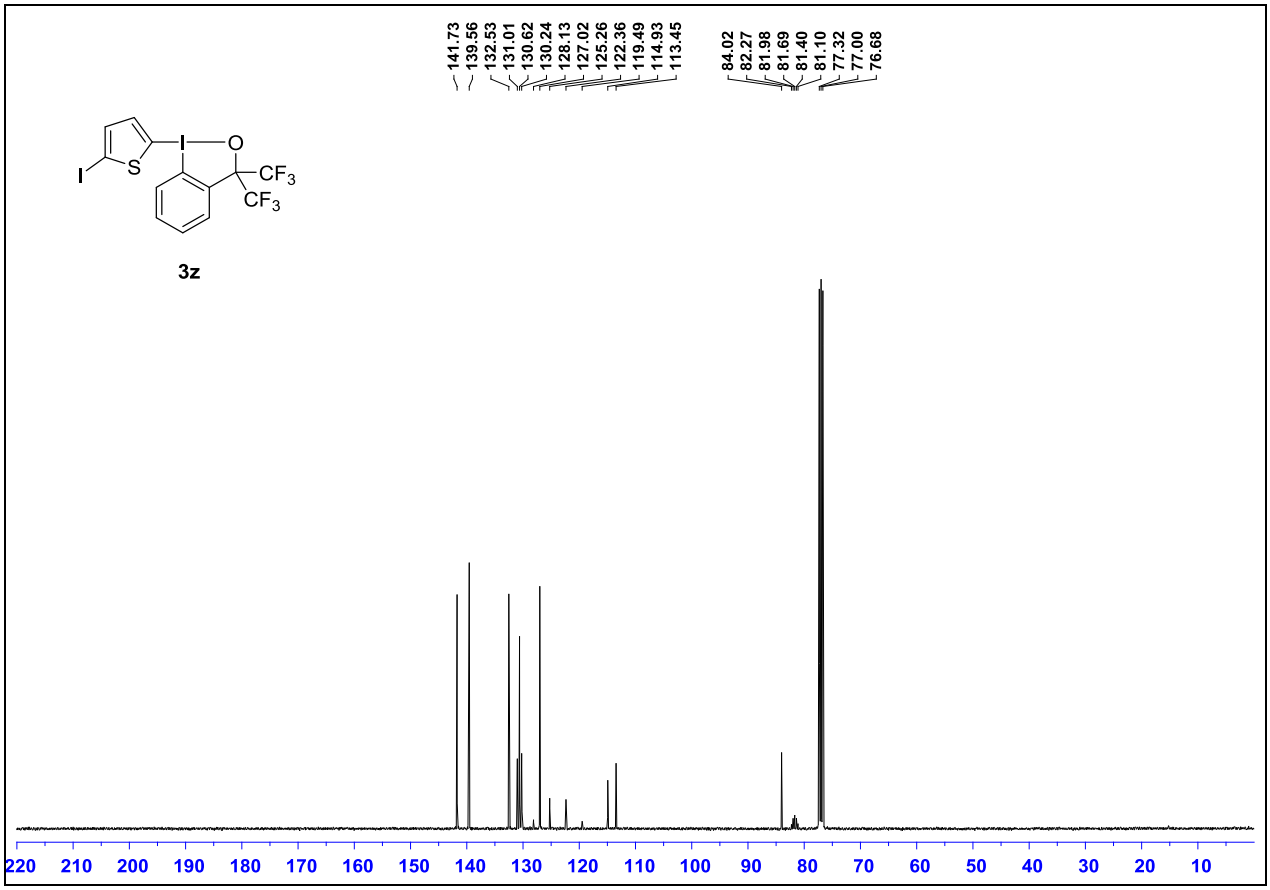


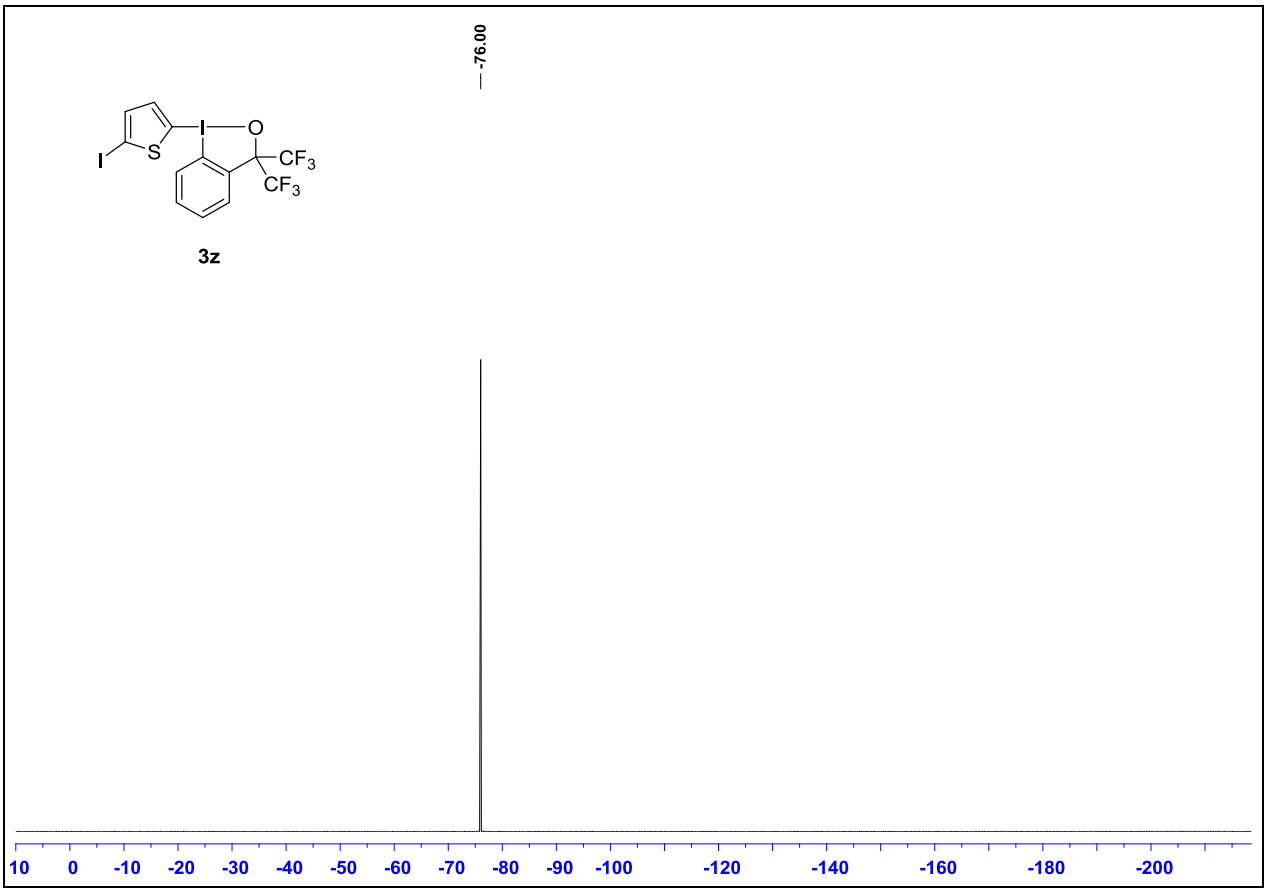



-76.02
Br
S
I
O
CF3
CF3
3y
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

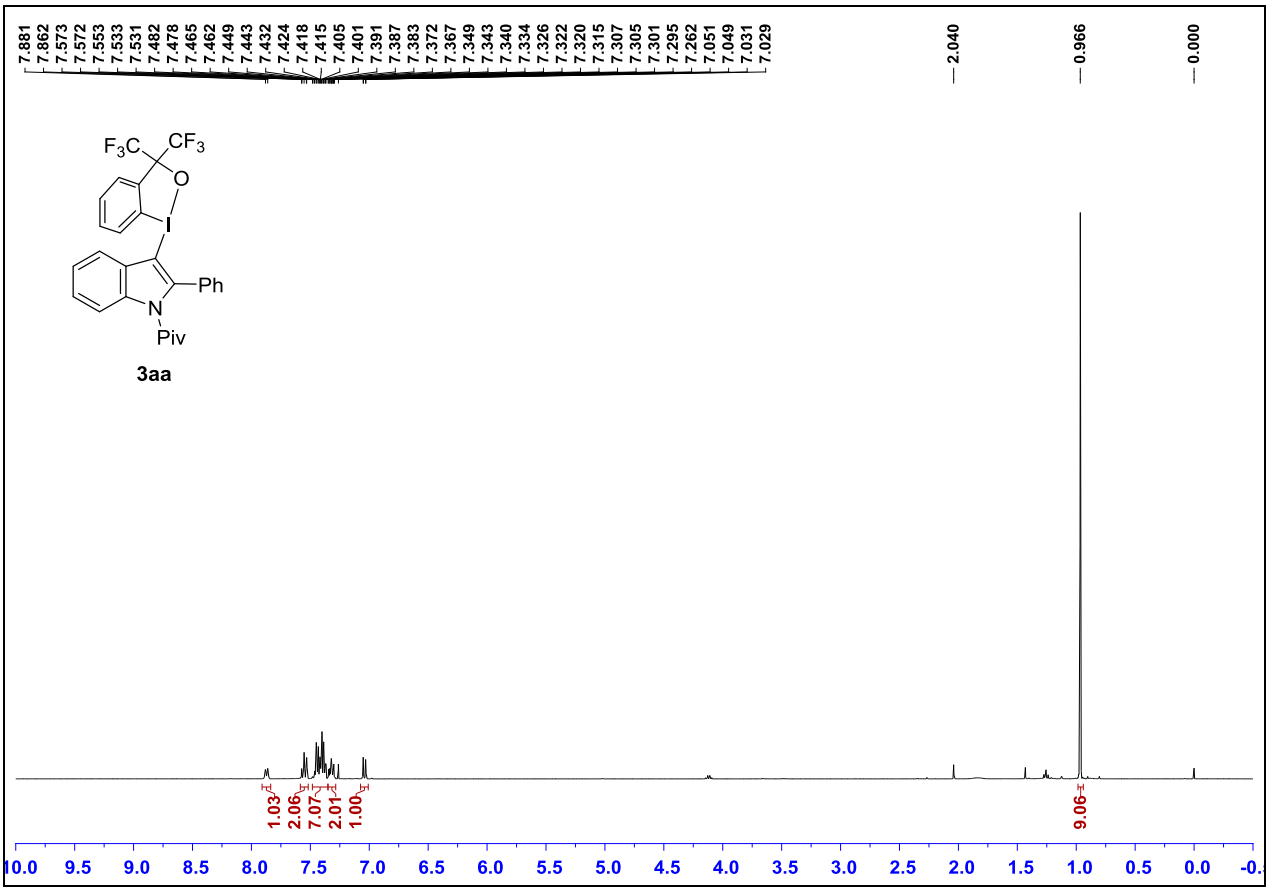
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

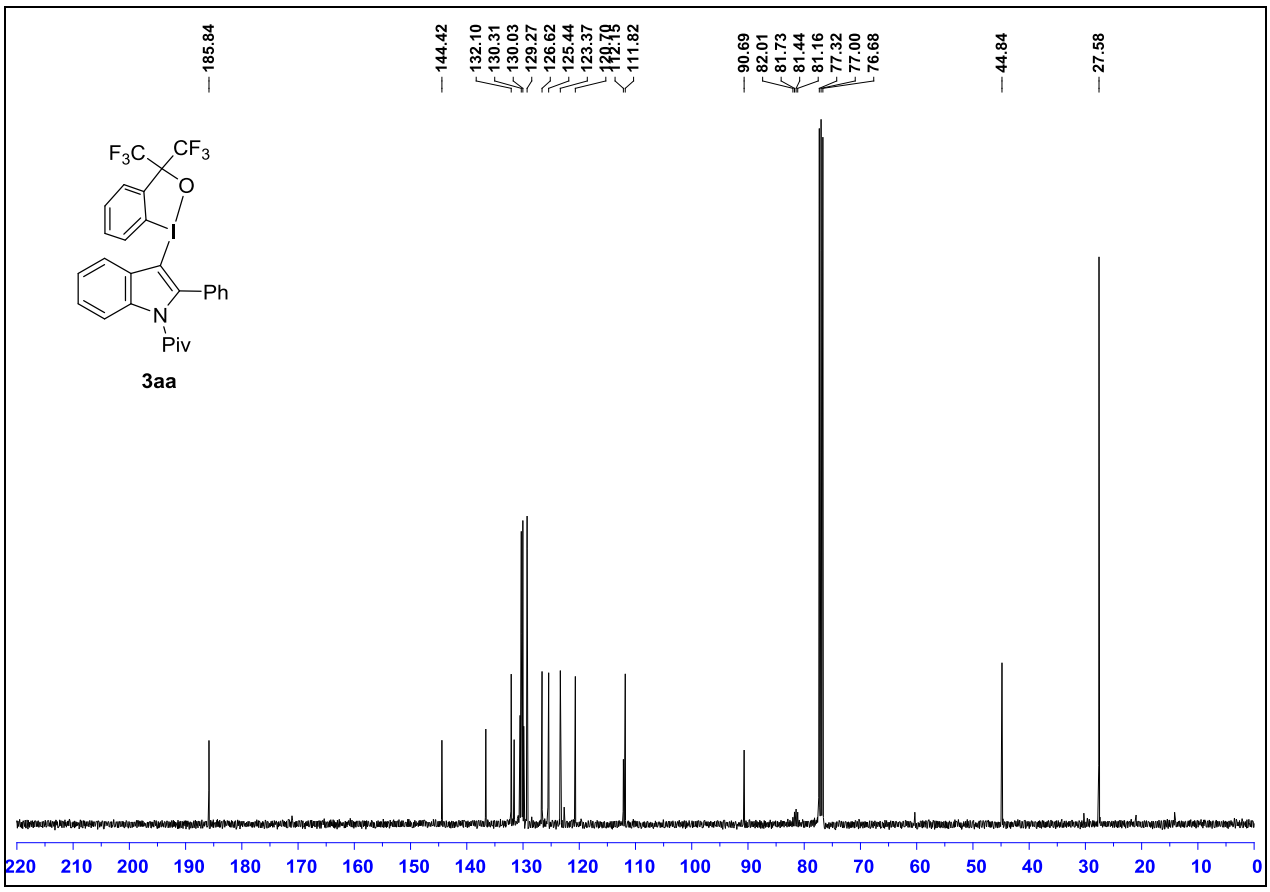


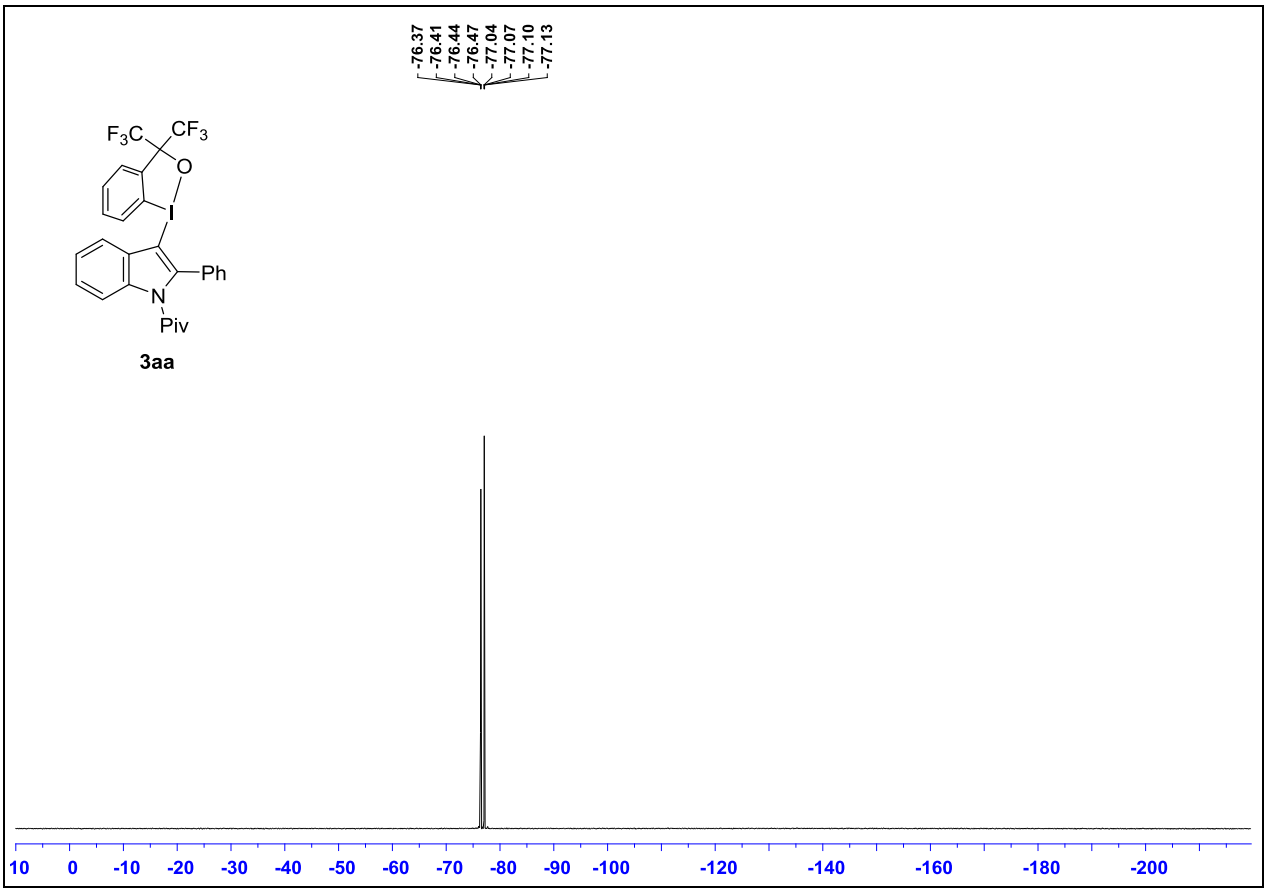



-76.00
I
S
I
O
CF3
CF3
3z
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

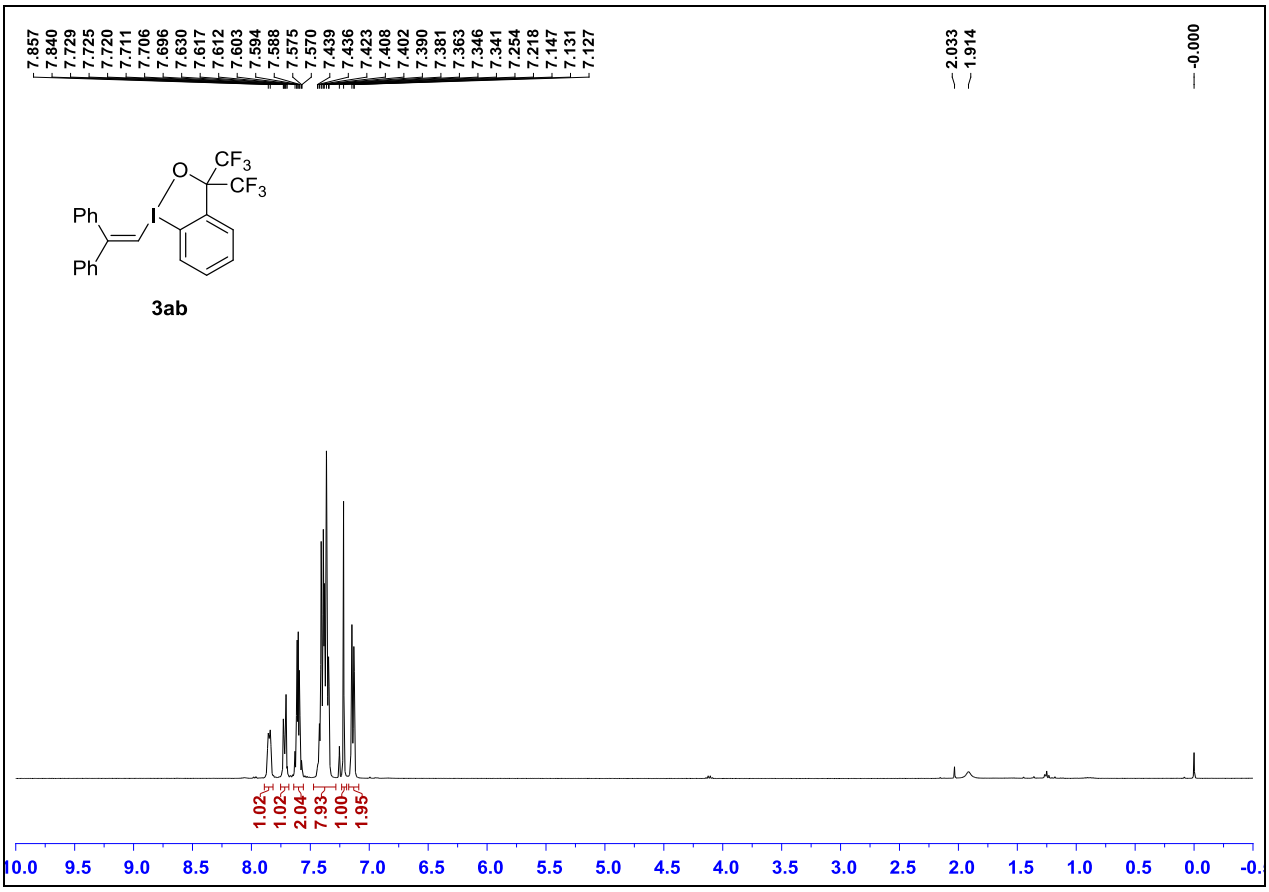
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

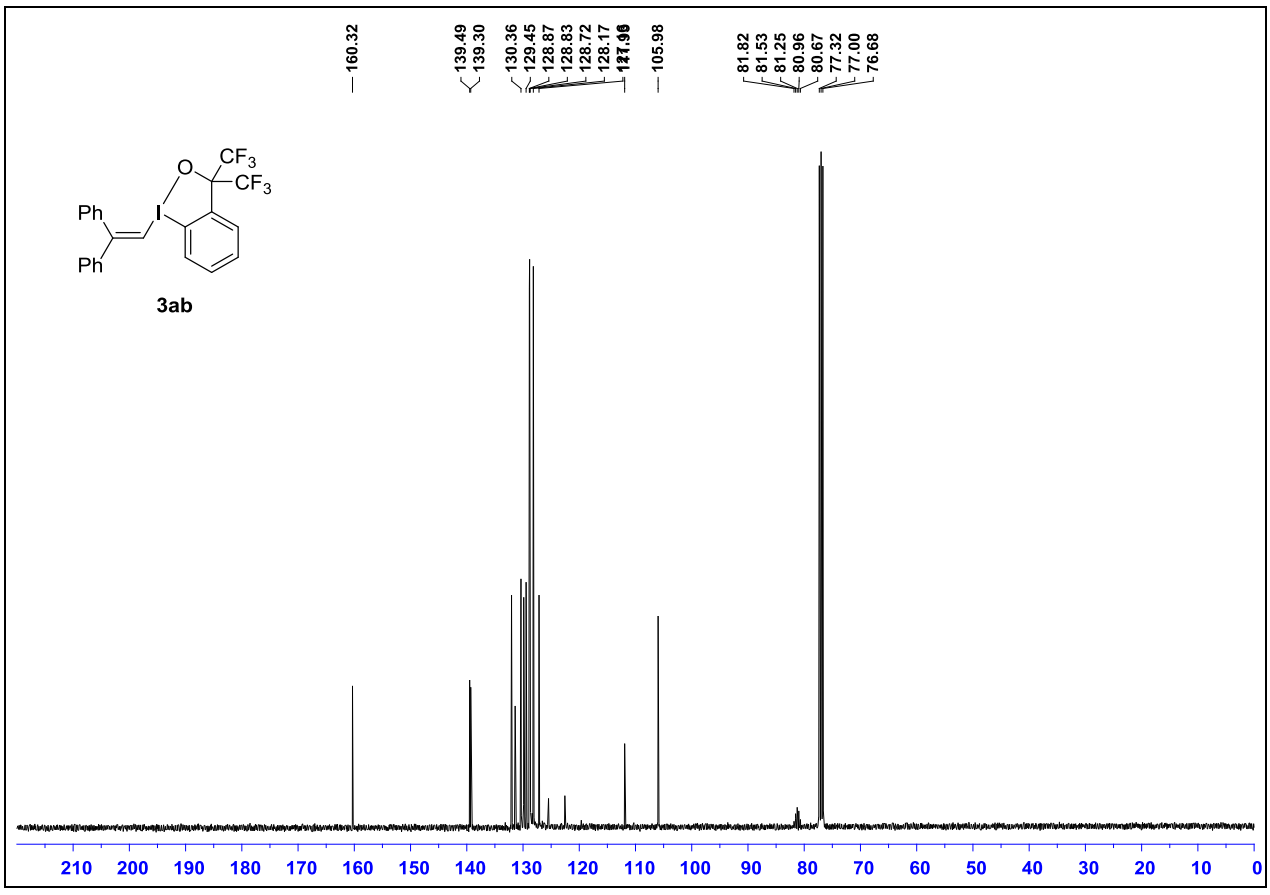


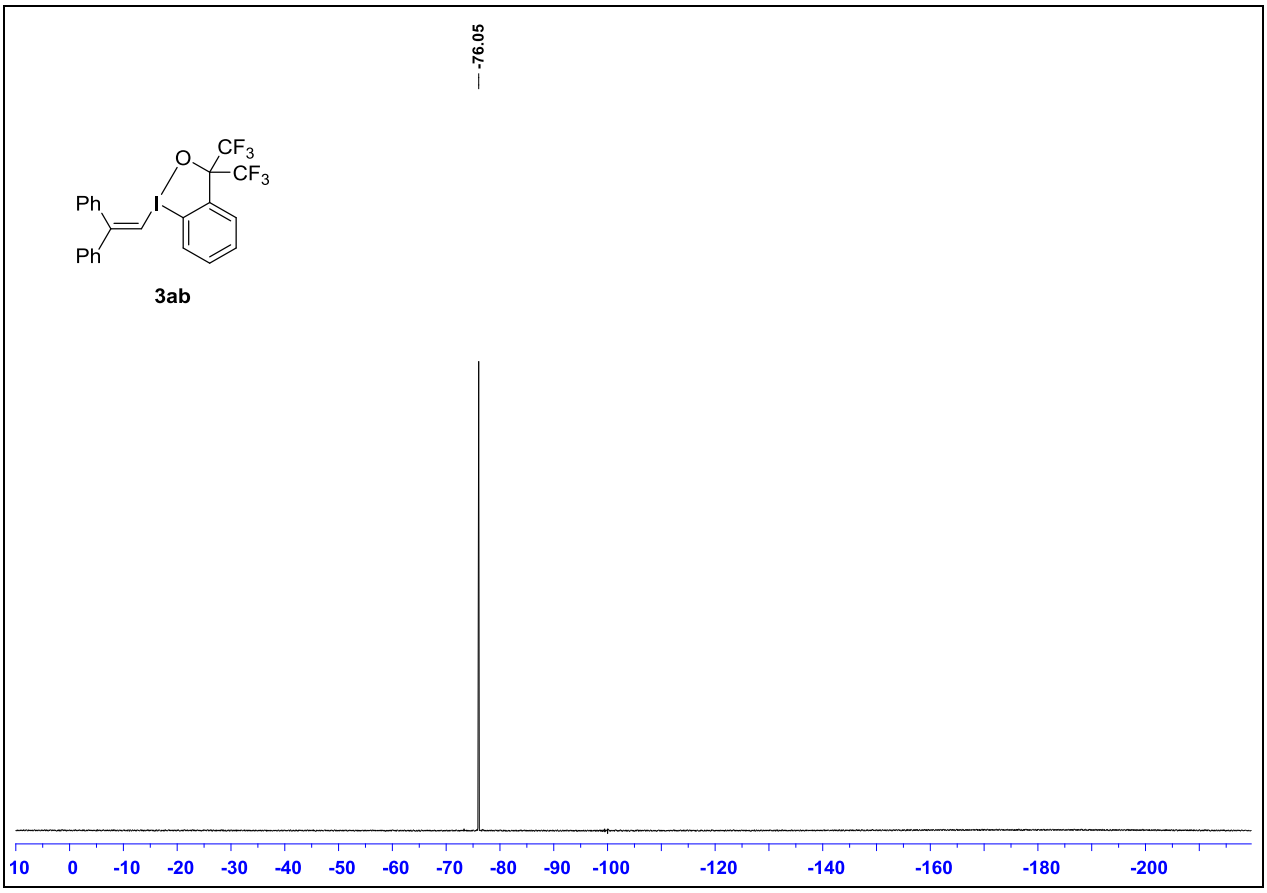



-76.37
-76.41
-76.44
-76.47
-77.04
-77.07
-77.10
-77.13
F3C
CF3
O
I
Ph
N
Piv
3aa
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

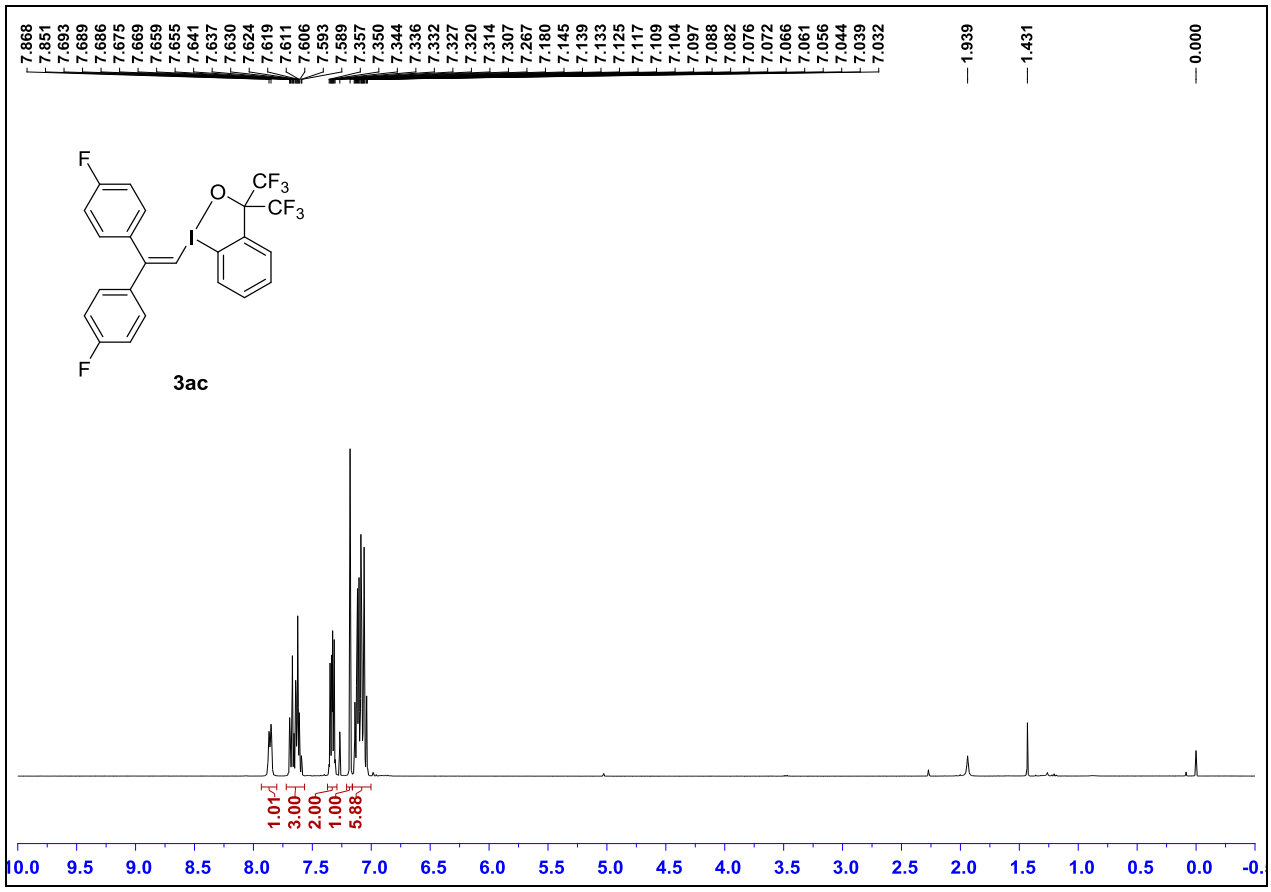
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) spectrum

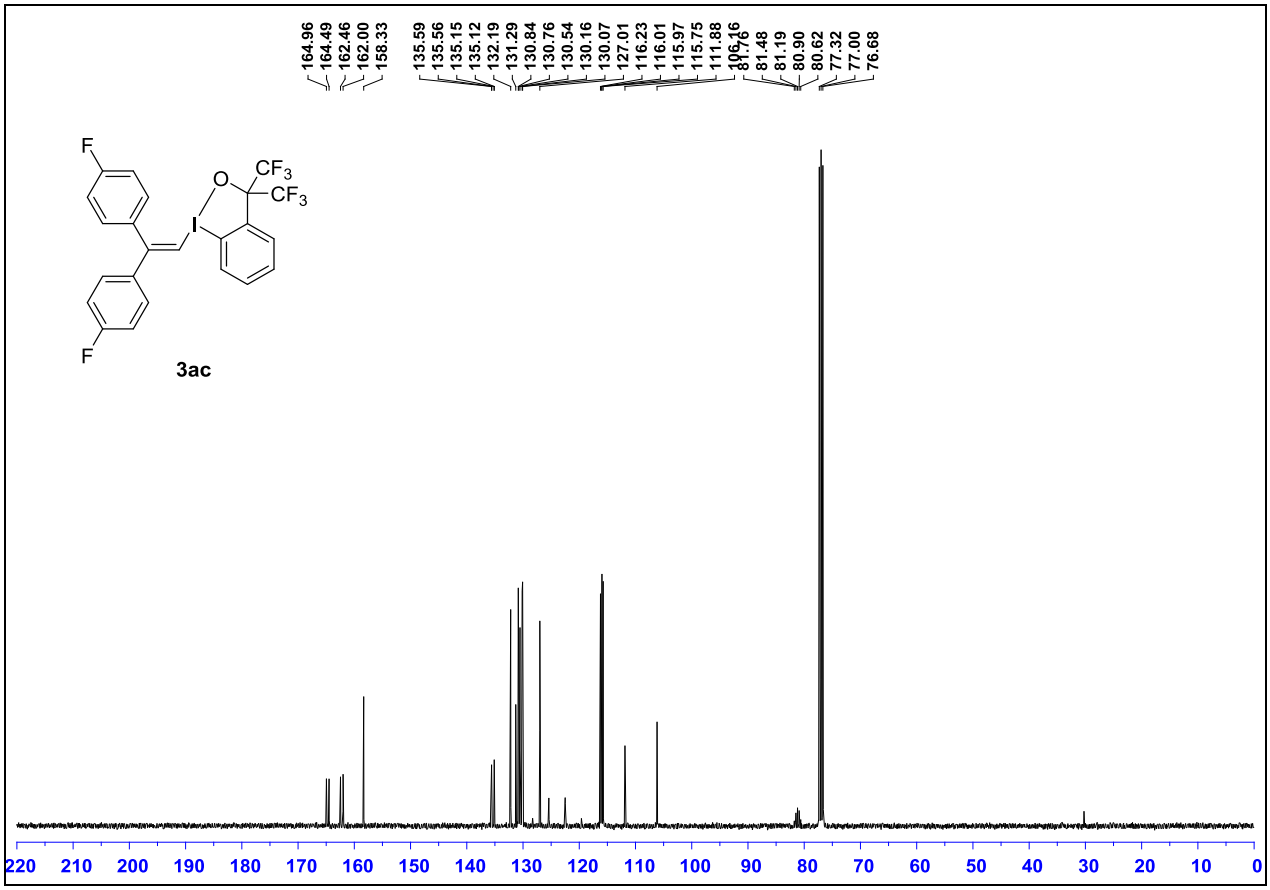


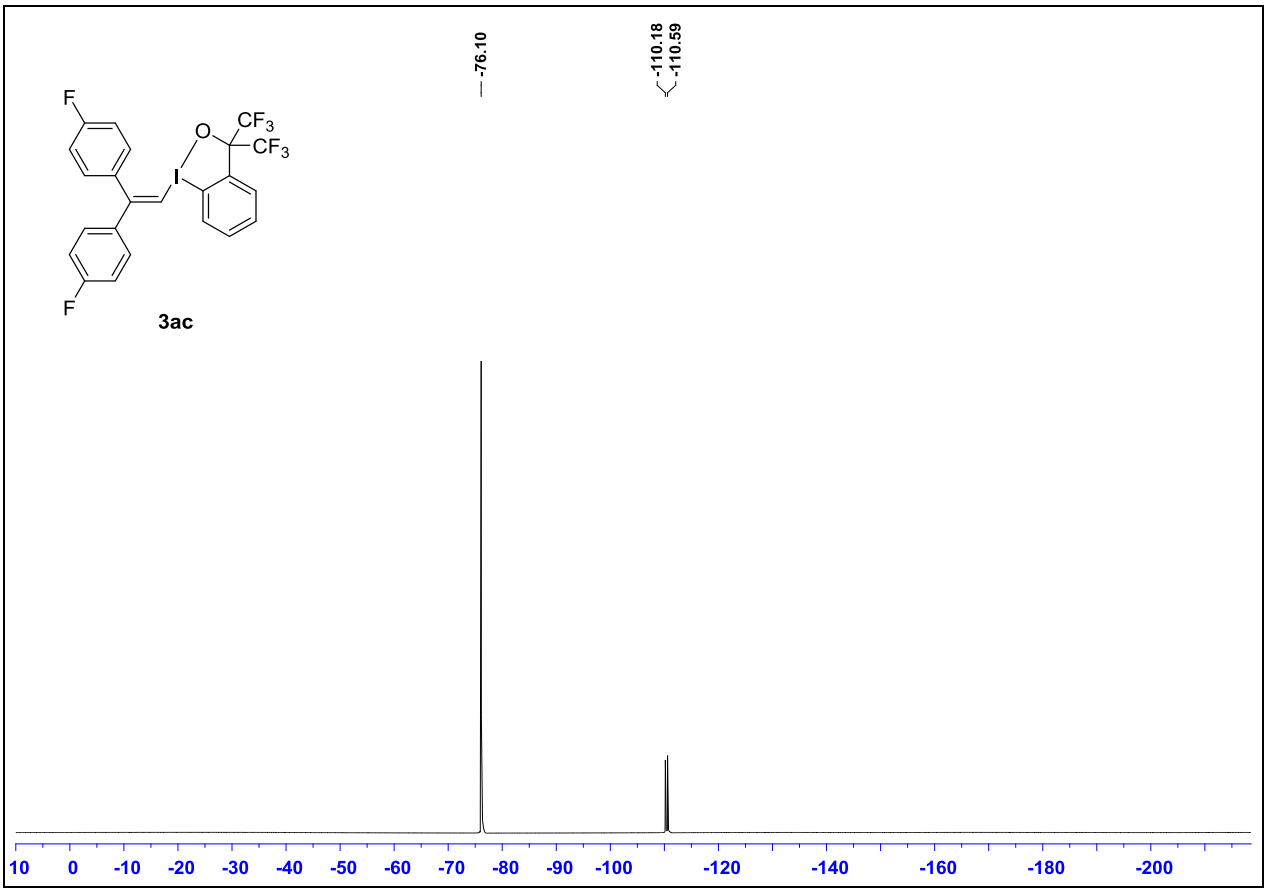



-76.05
O
CF3
CF3
I
Ph
Ph
3ab
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

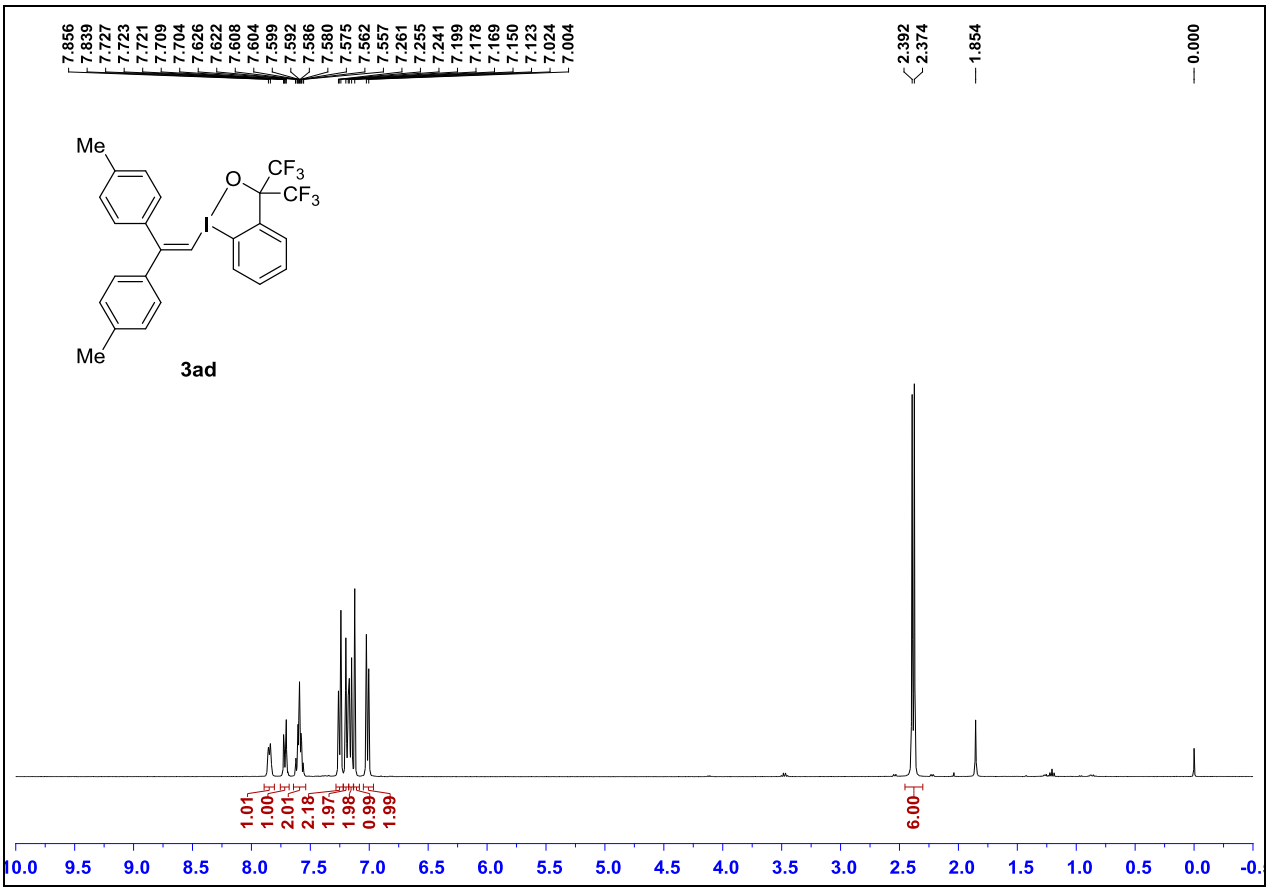
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

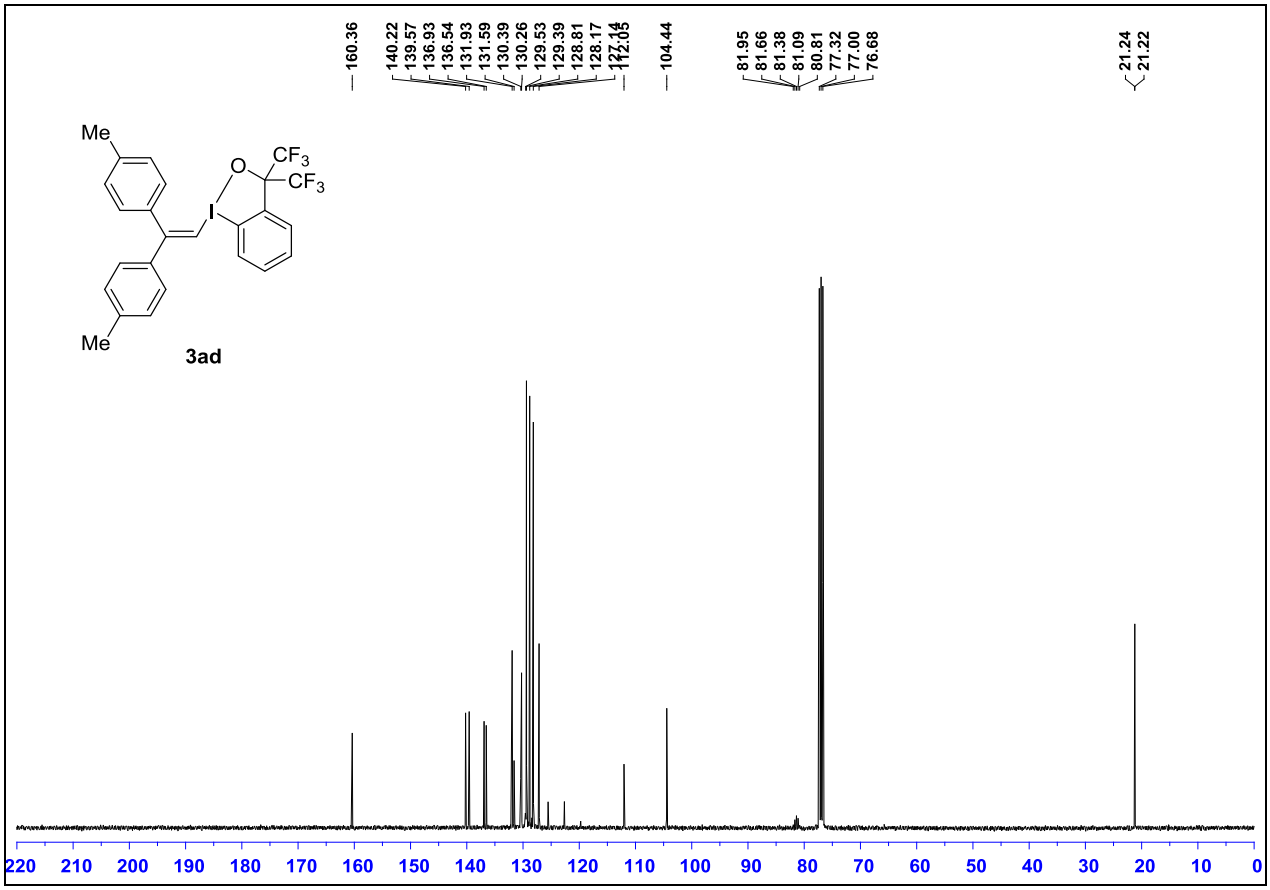


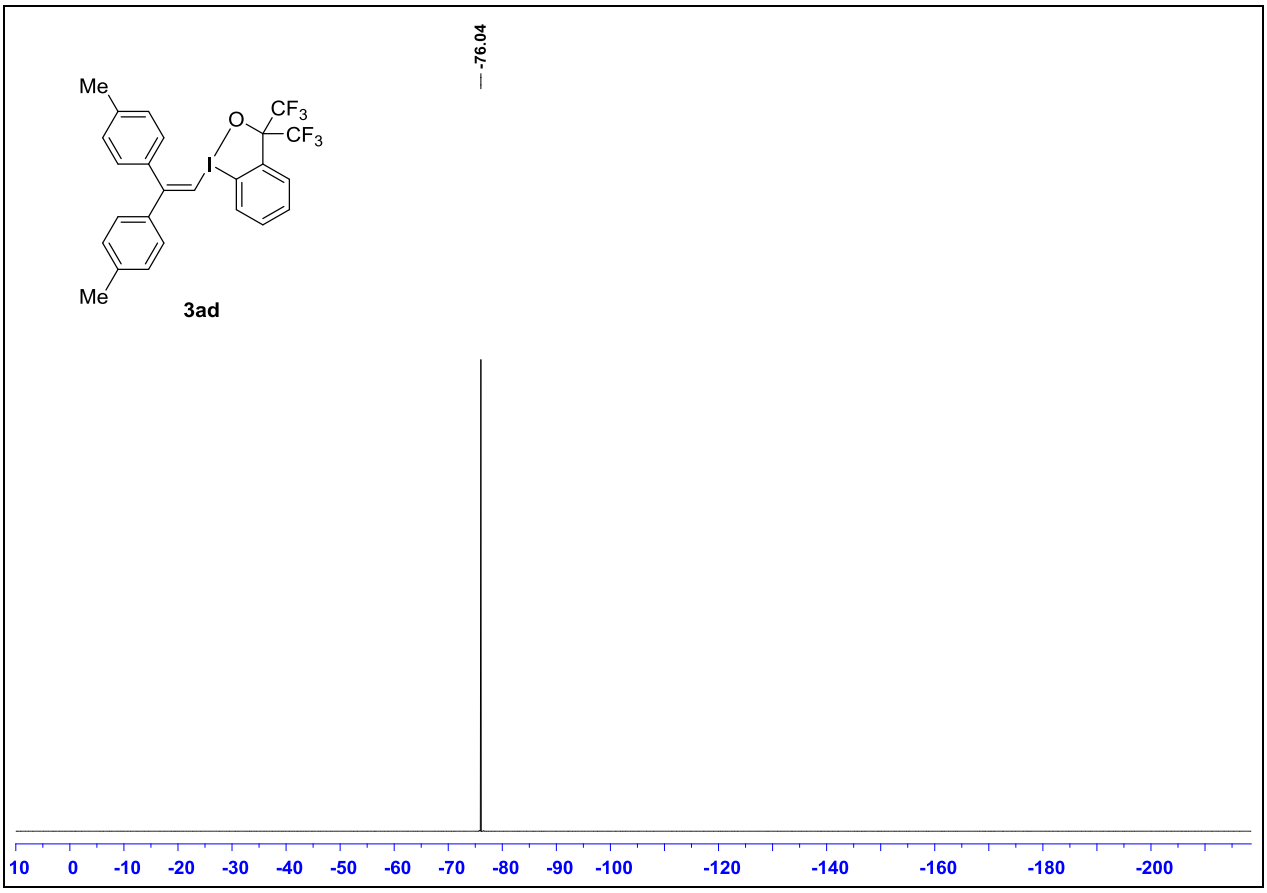



-76.10
-110.18
-110.59
F
O
CF3
CF3
I
F
3ac
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

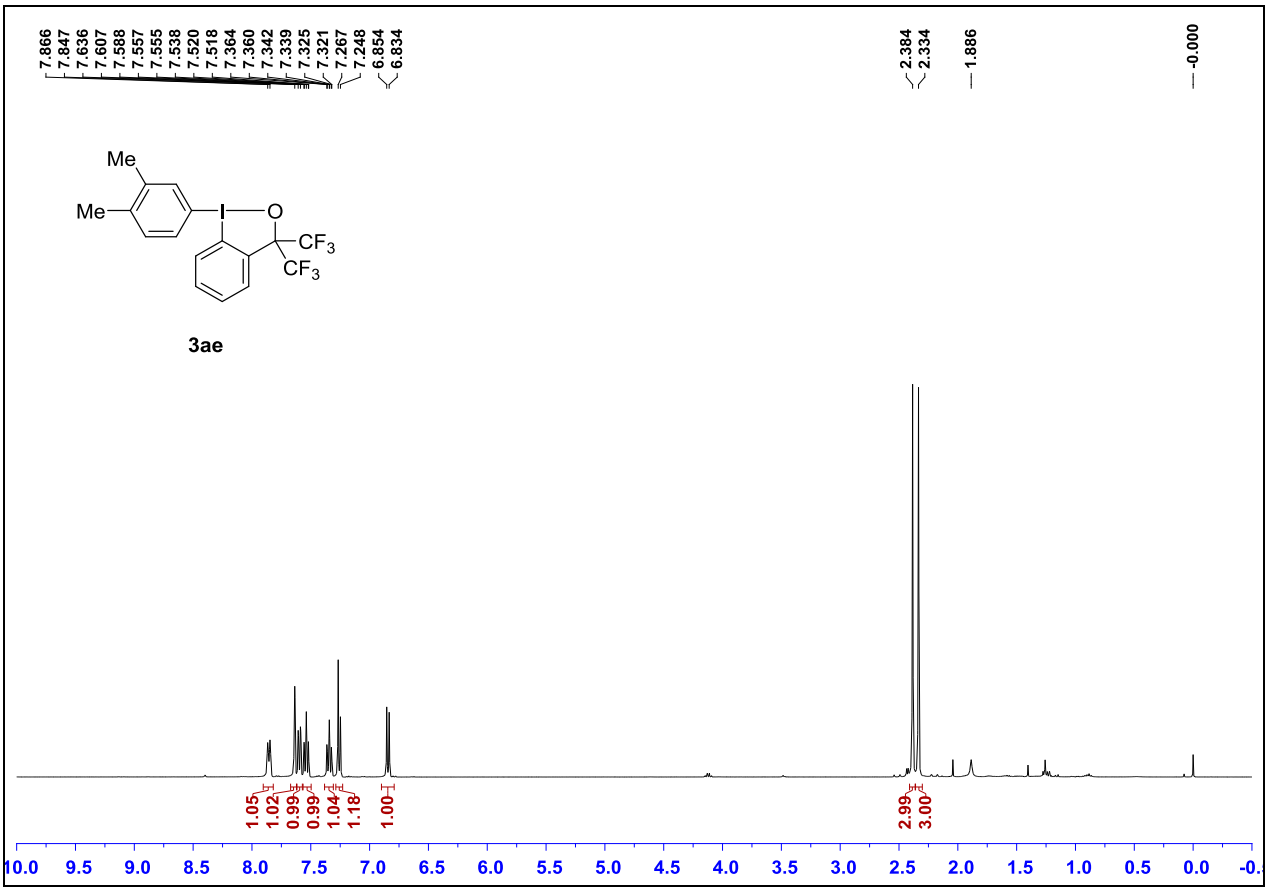
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

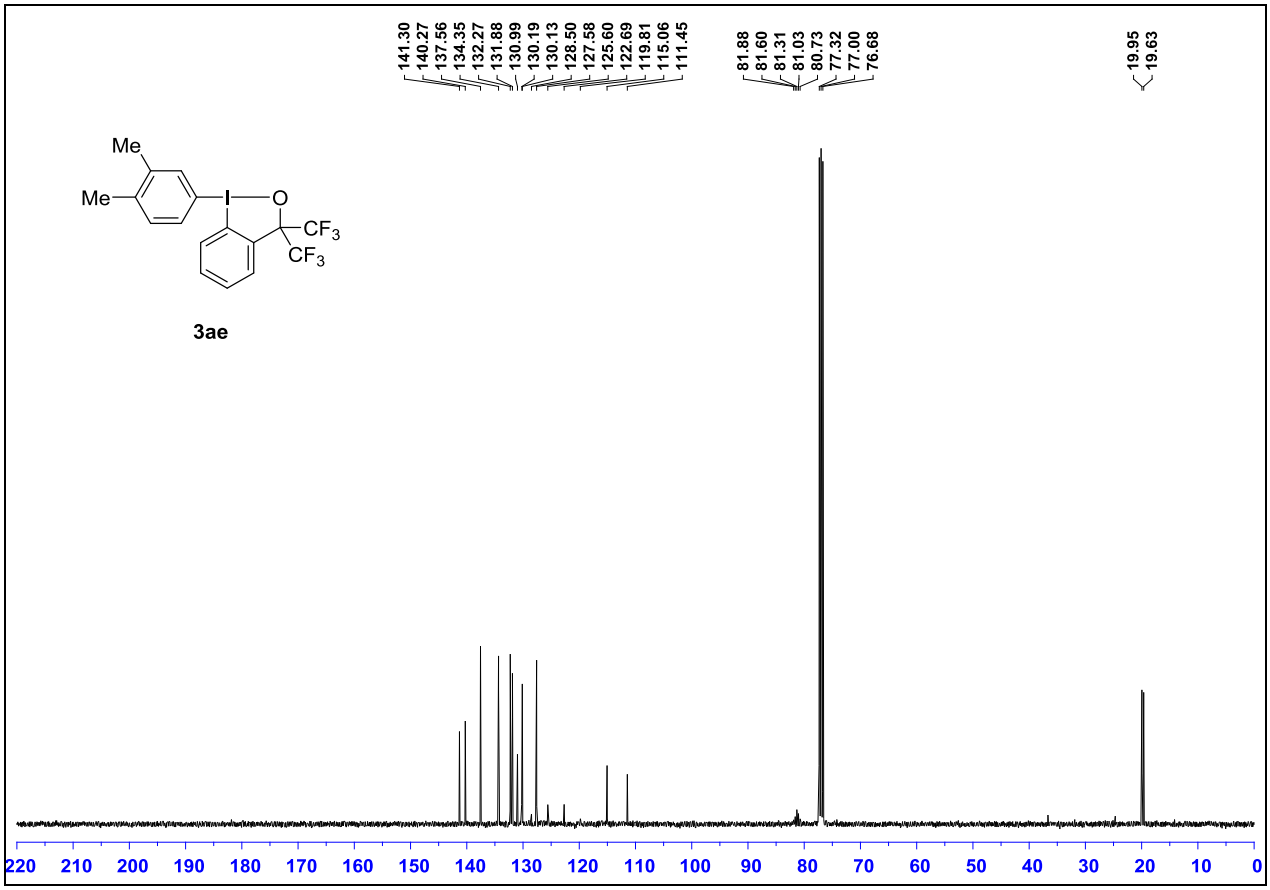


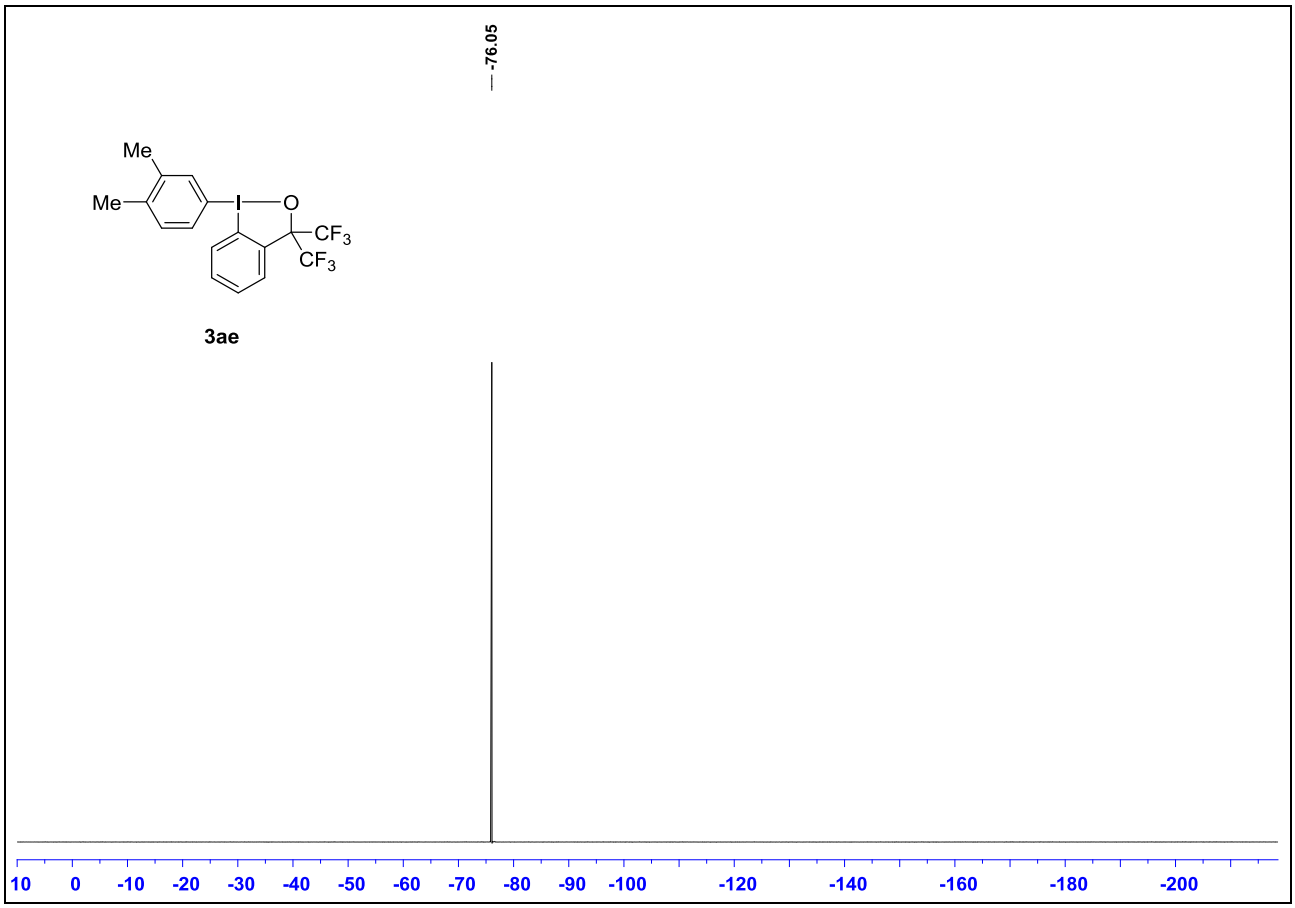



-76.04
Me
O
CF3
CF3
I
Me
3ad
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

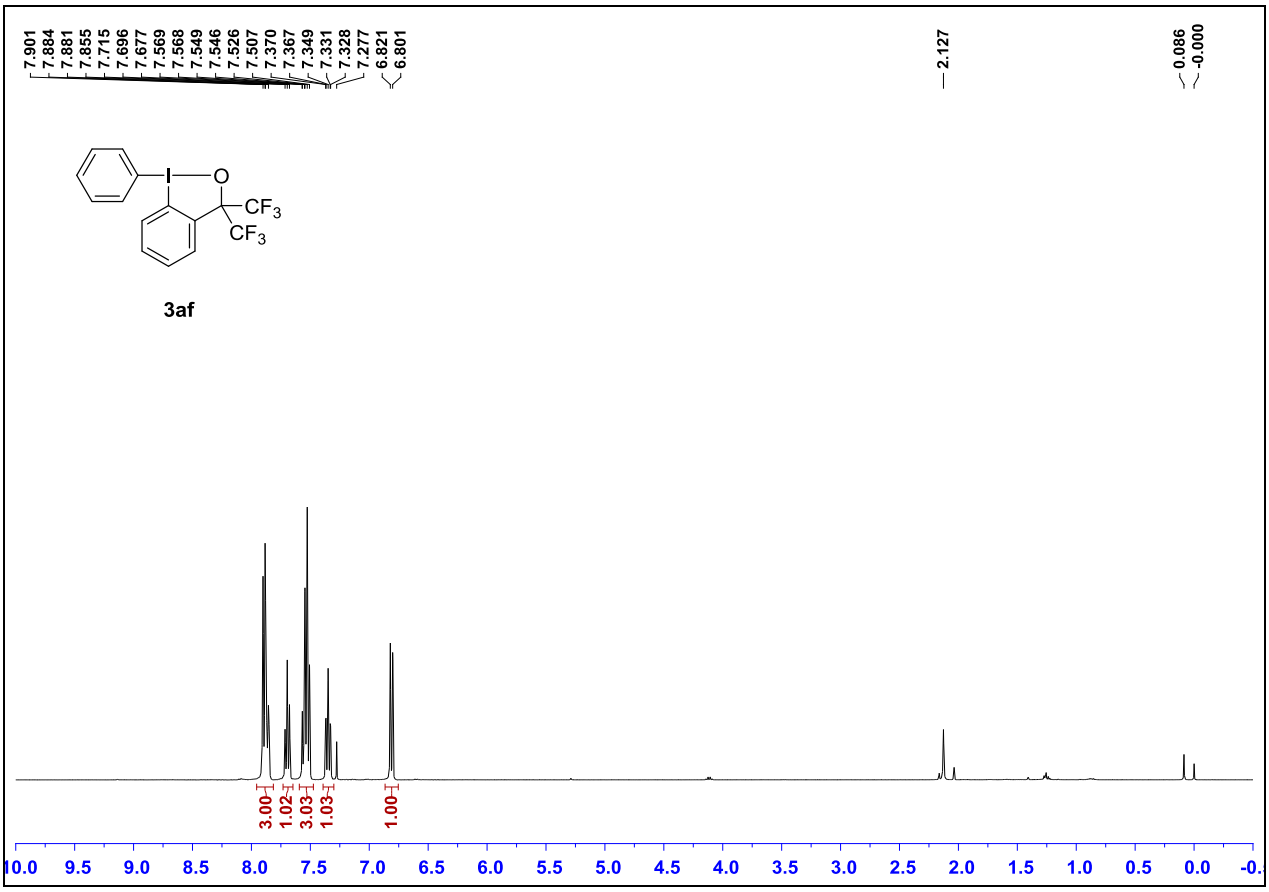
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

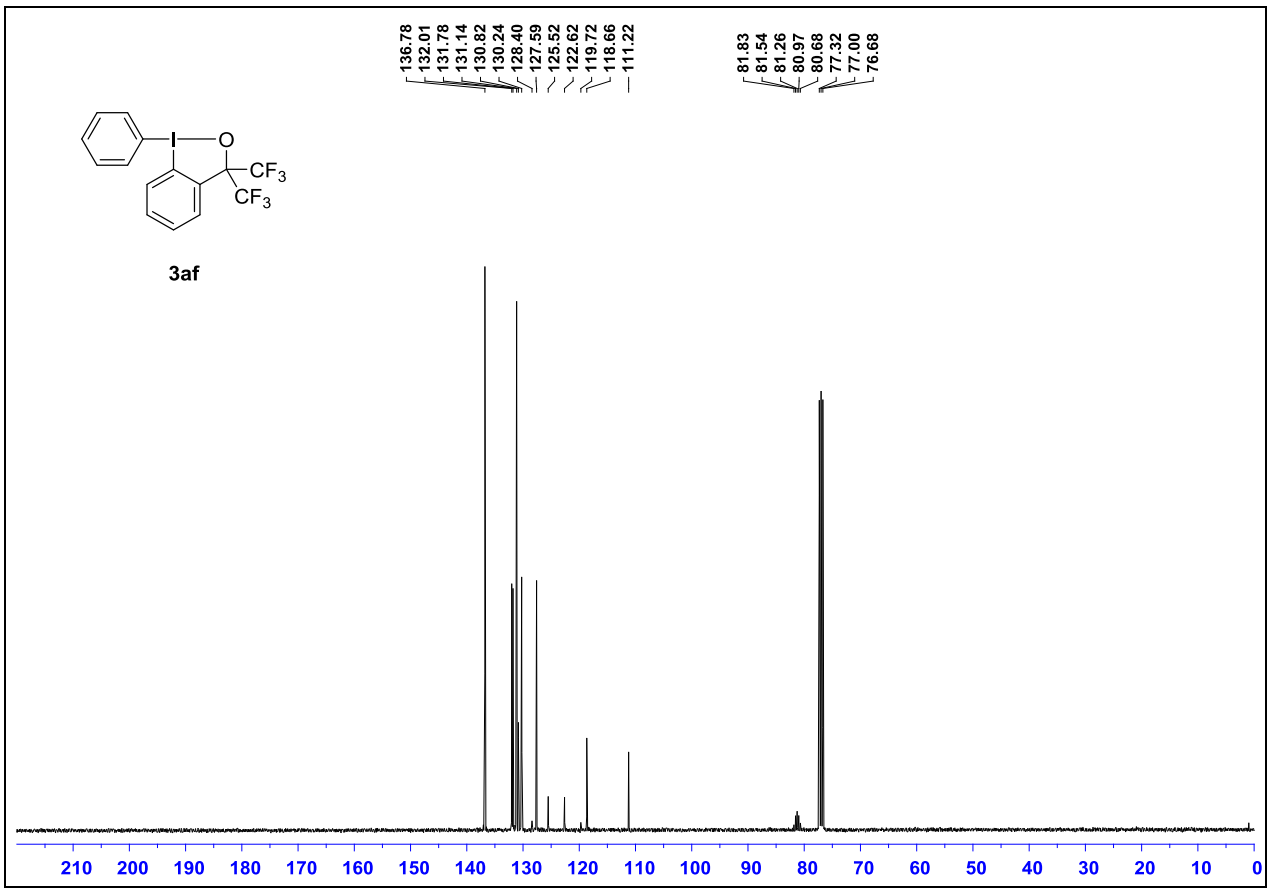


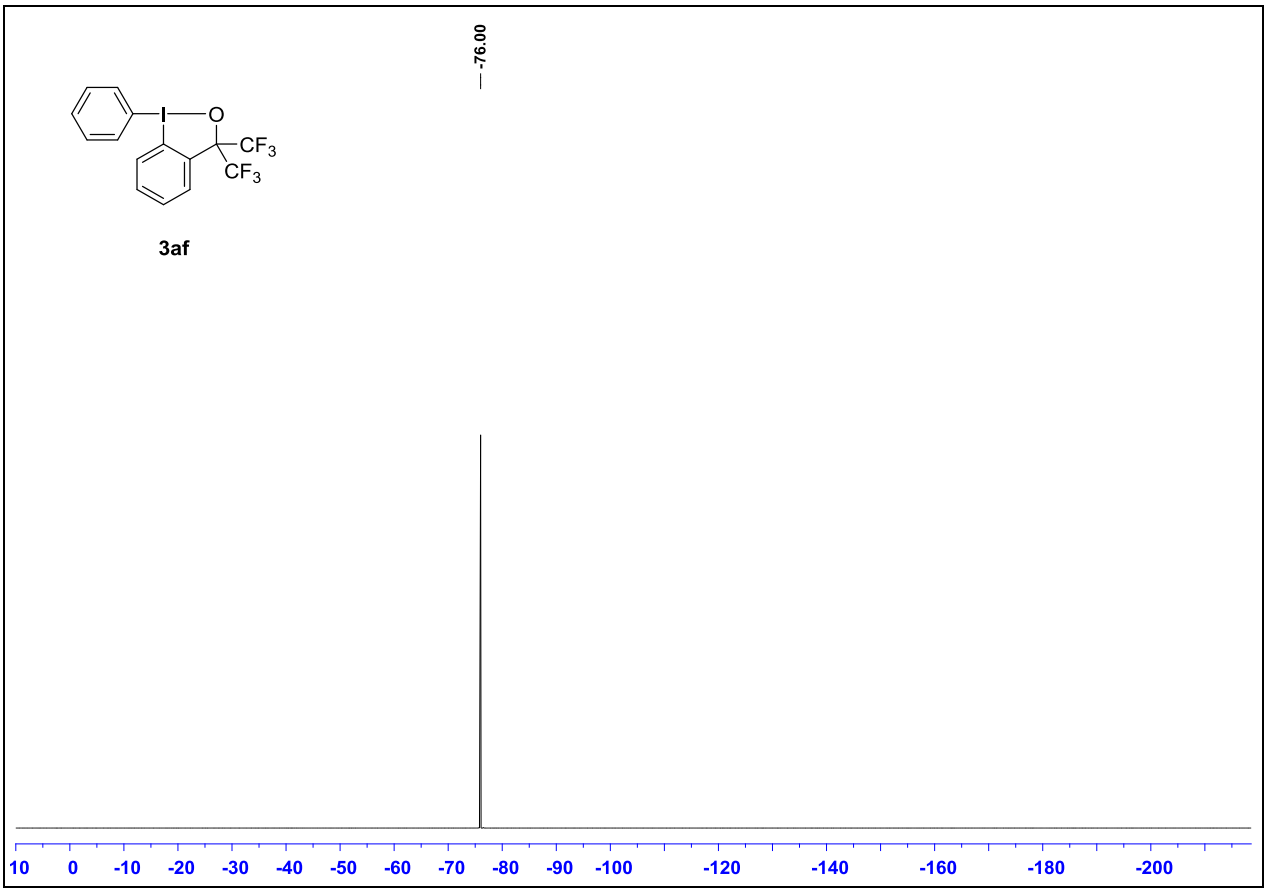



-76.05
Me
Me
I
O
CF3
CF3
3ae
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

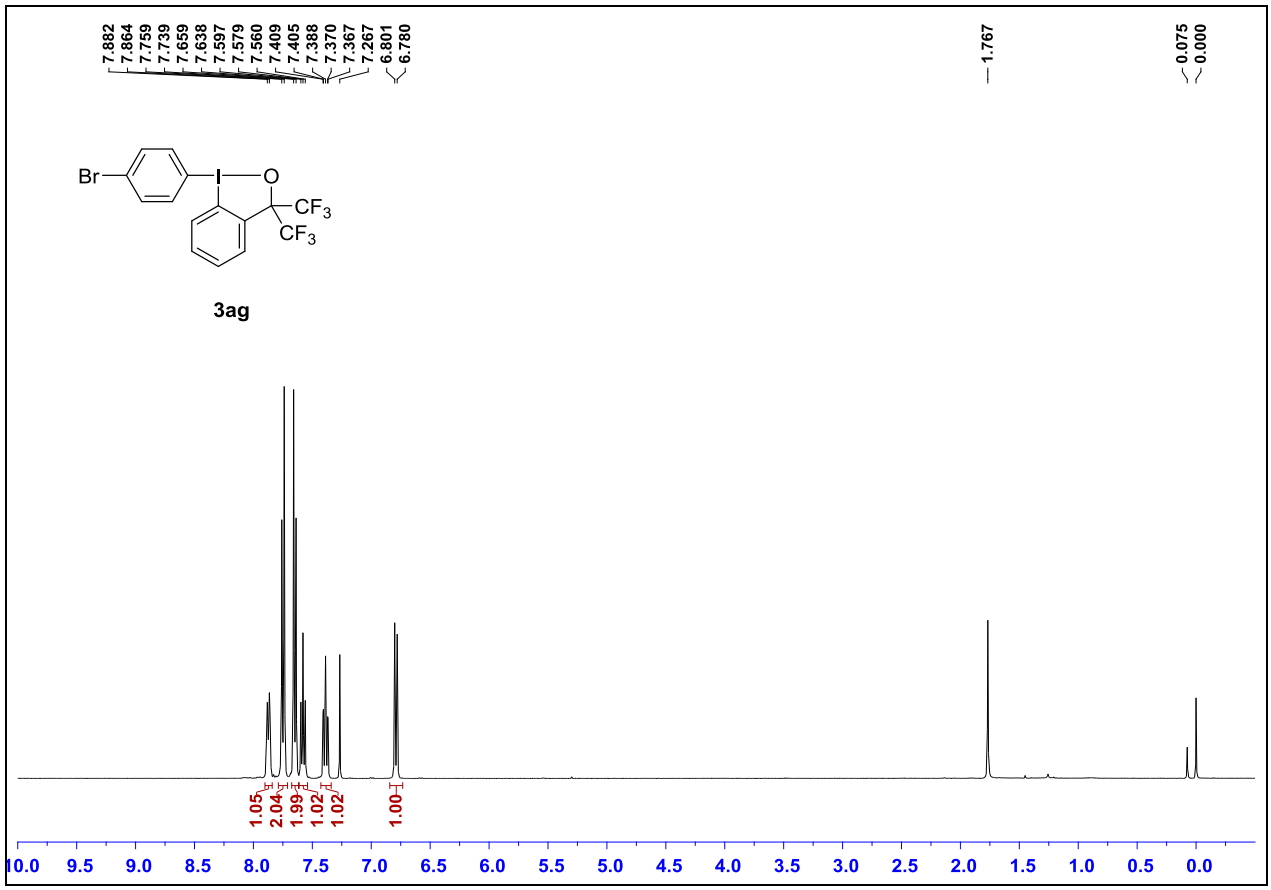
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

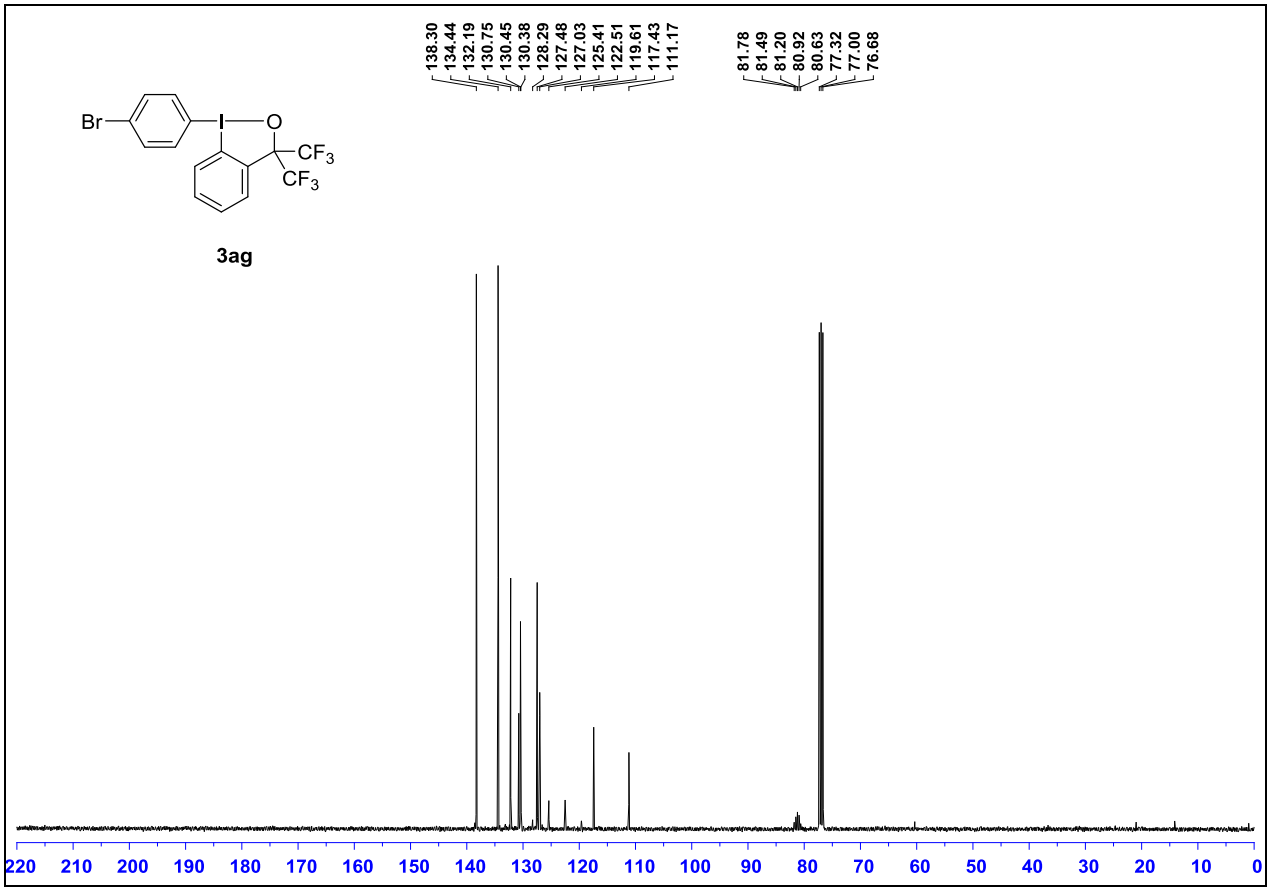


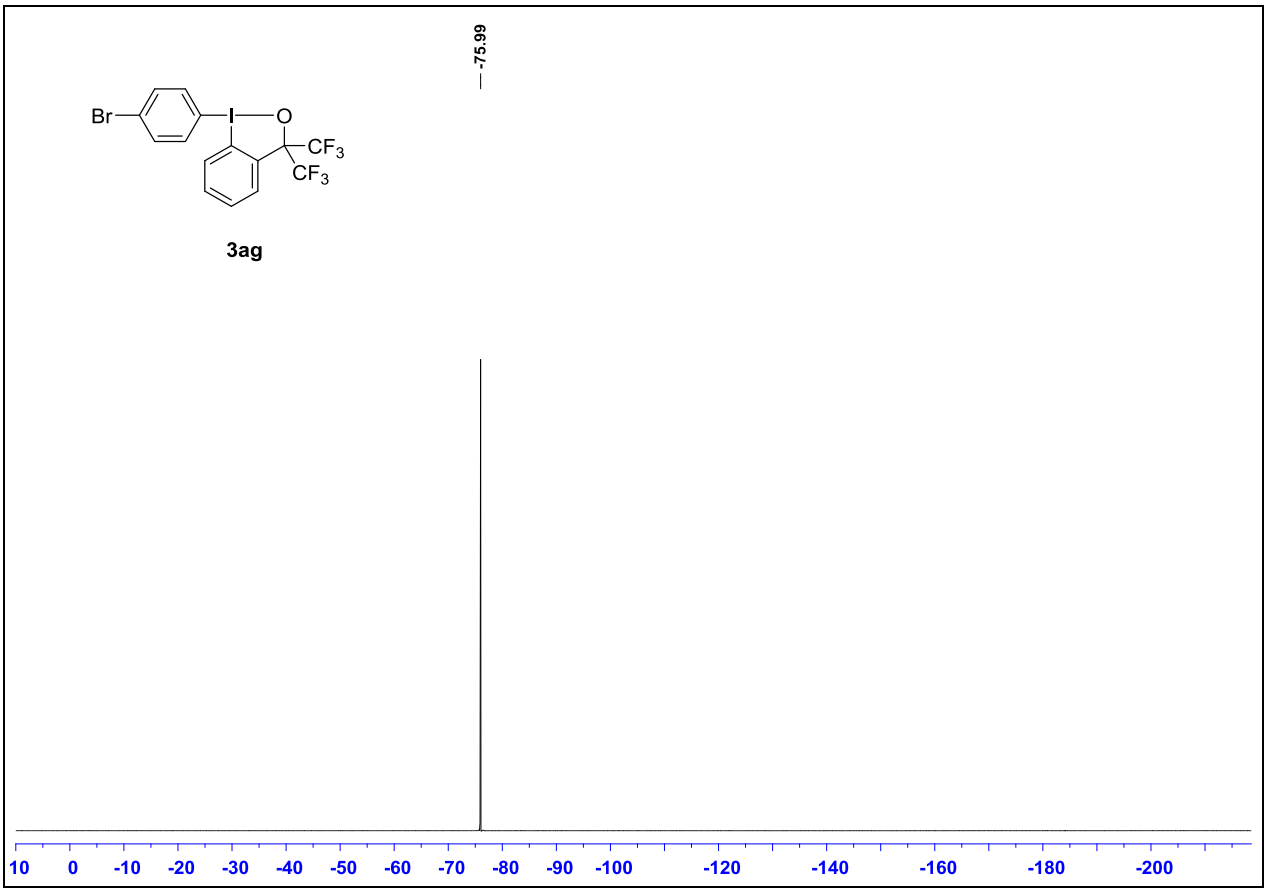



-76.00
I
O
CF3
CF3
3af
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

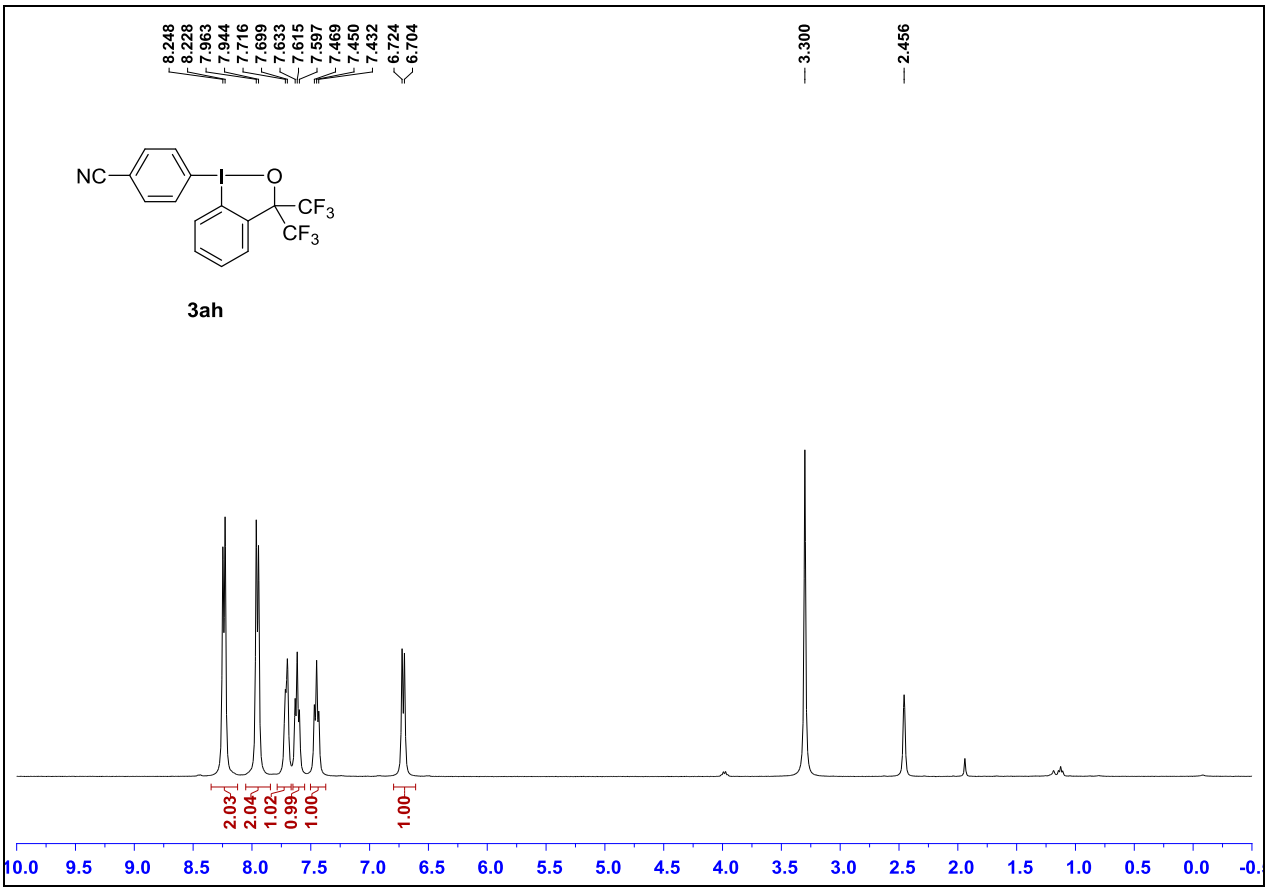
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum

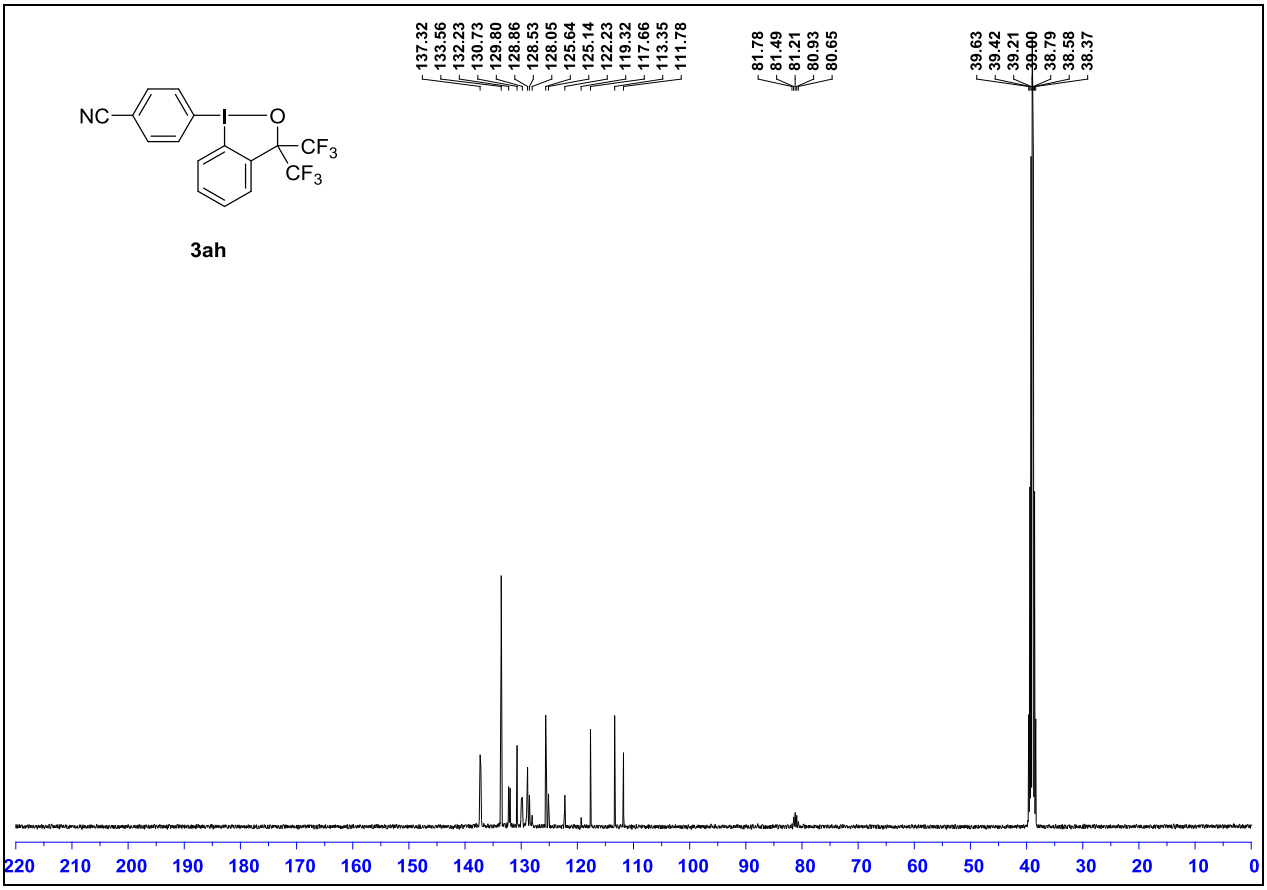


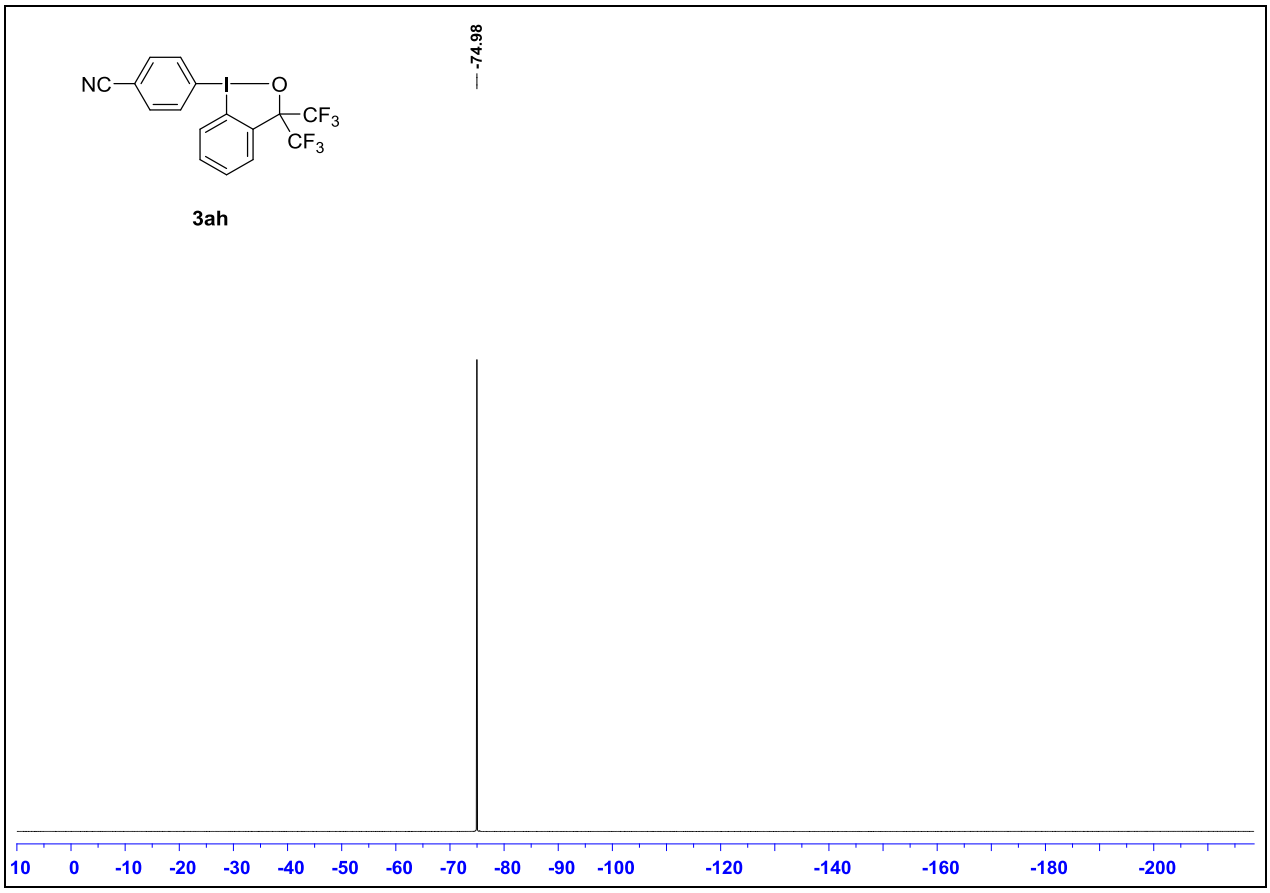



-75.99
Br
I
O
CF3
CF3
3ag
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

^{1}H NMR (400 MHz, DMSO), ^{13}C NMR (100 MHz, DMSO) and ^{19}F NMR (376 MHz, DMSO) spectrum

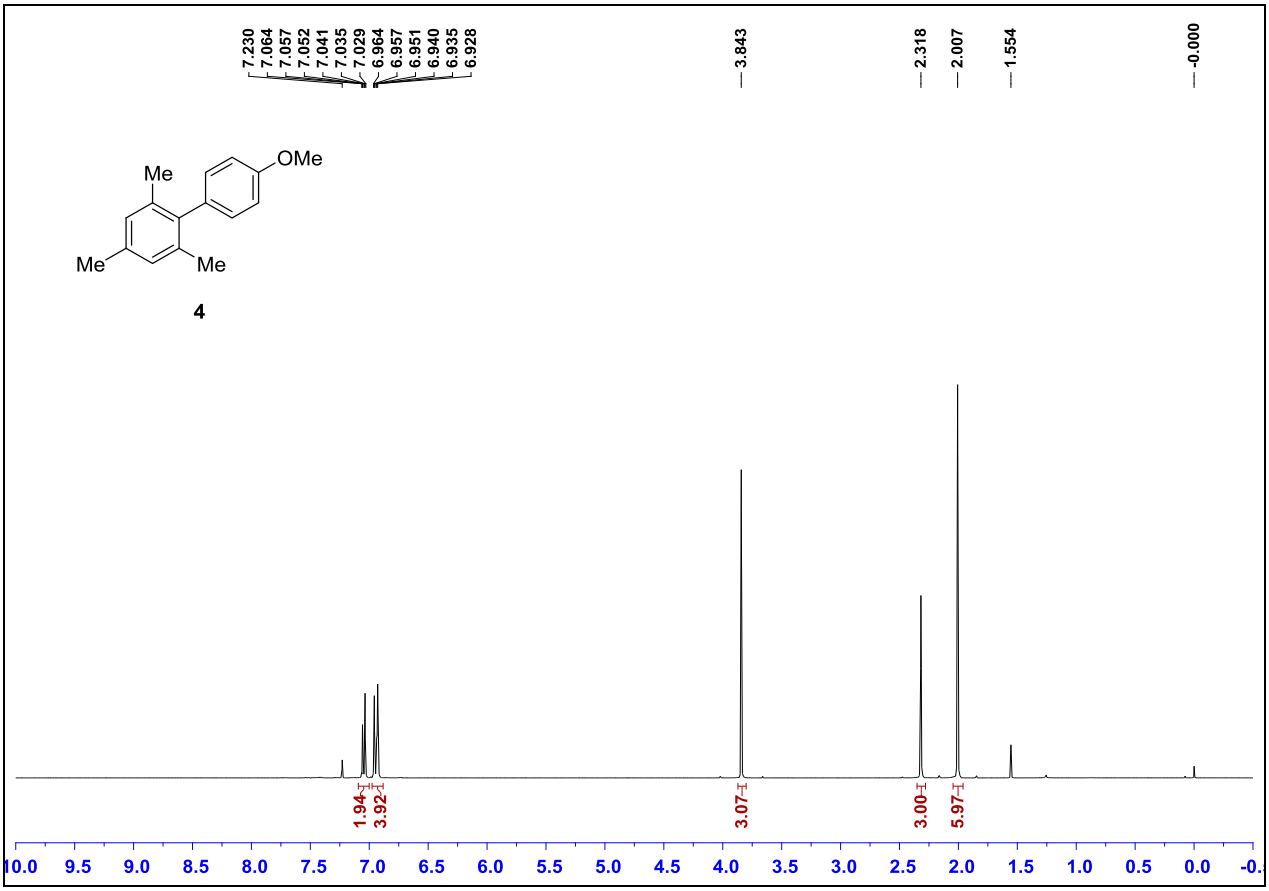


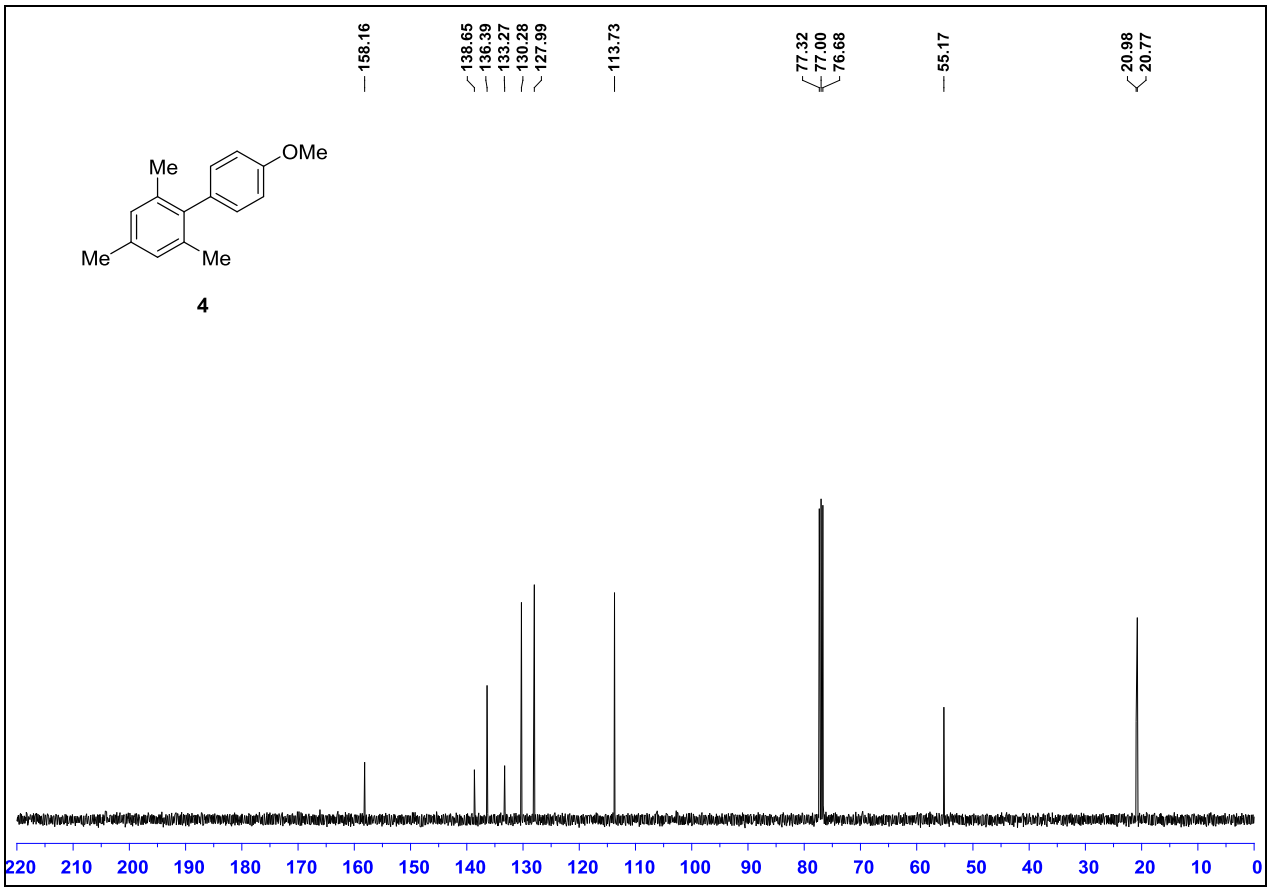



NC
I
O
CF3
CF3
-74.98
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

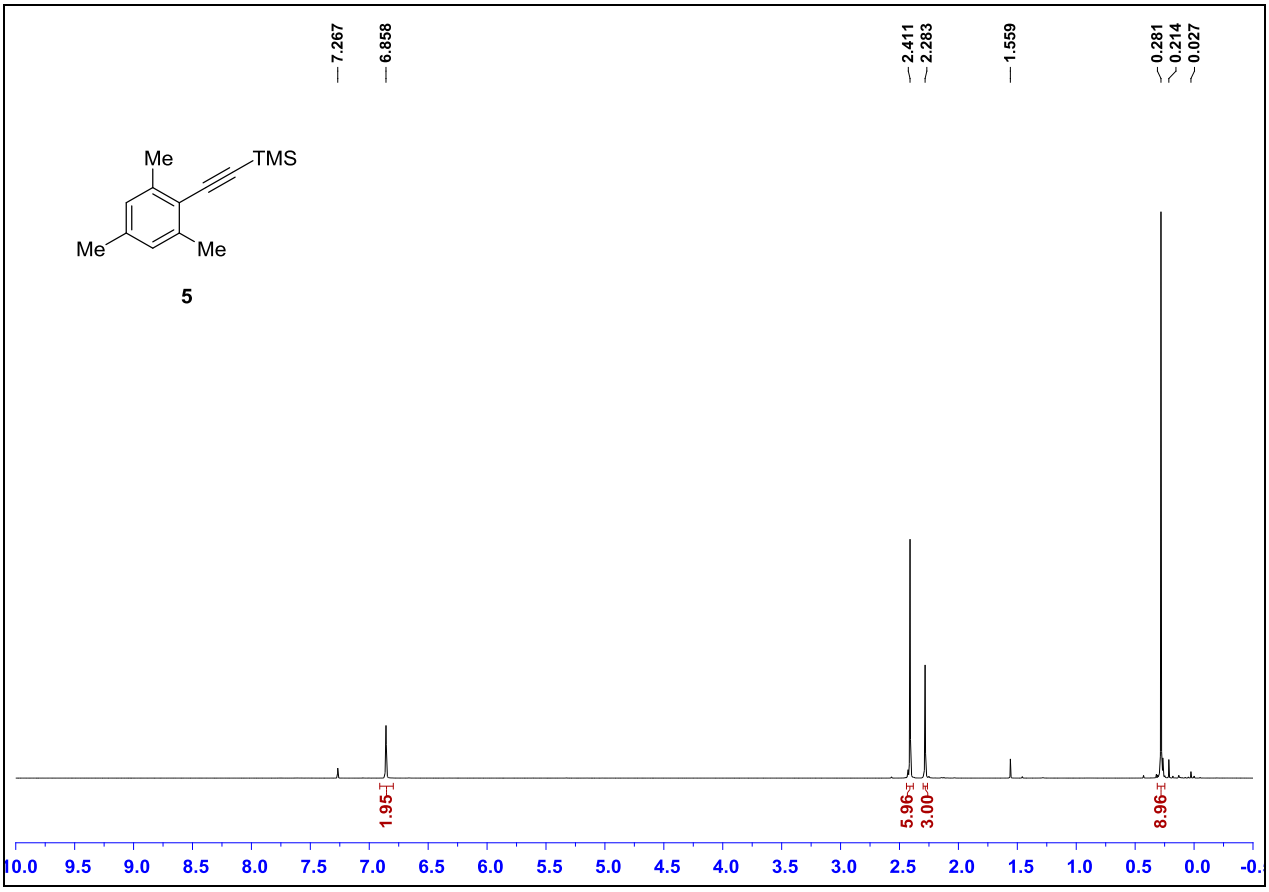
3ah

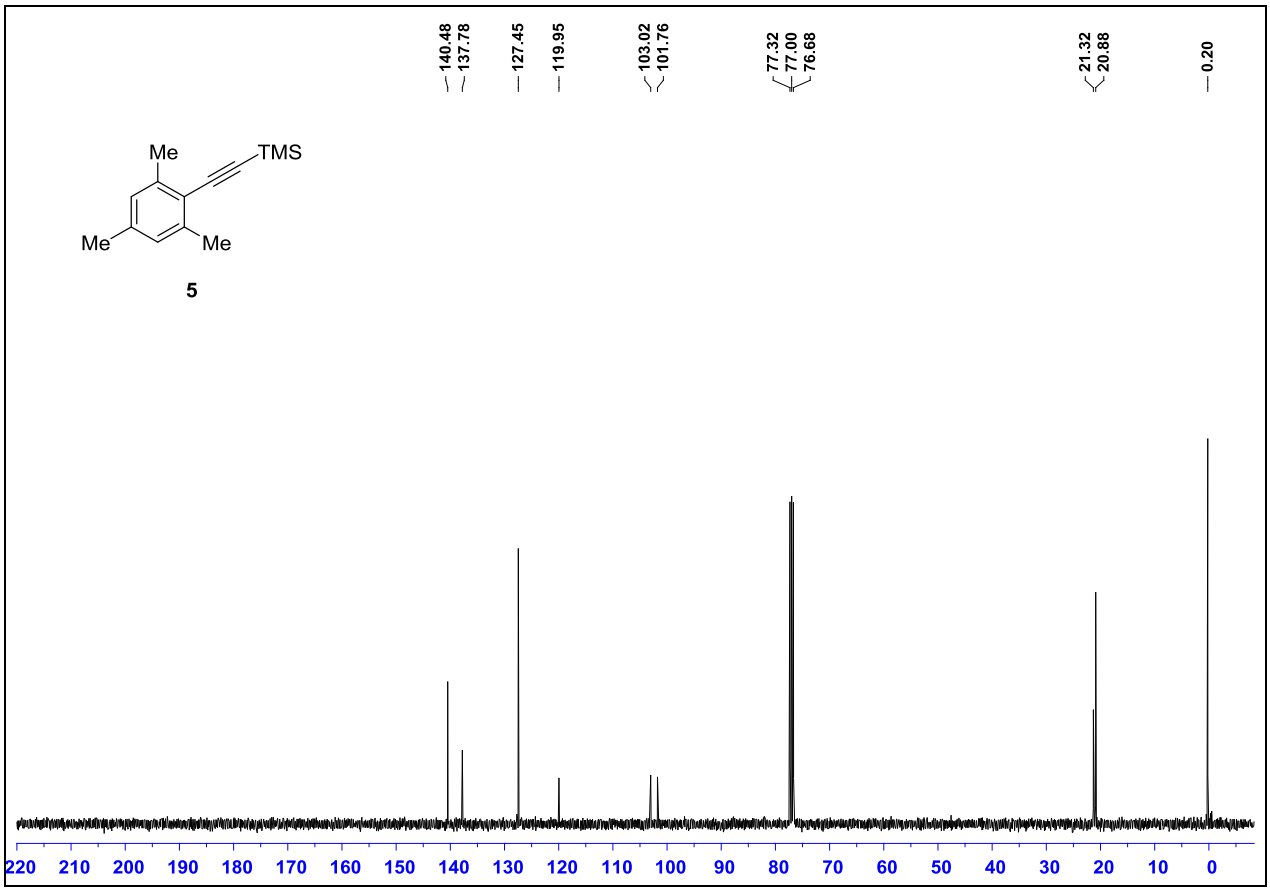
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum



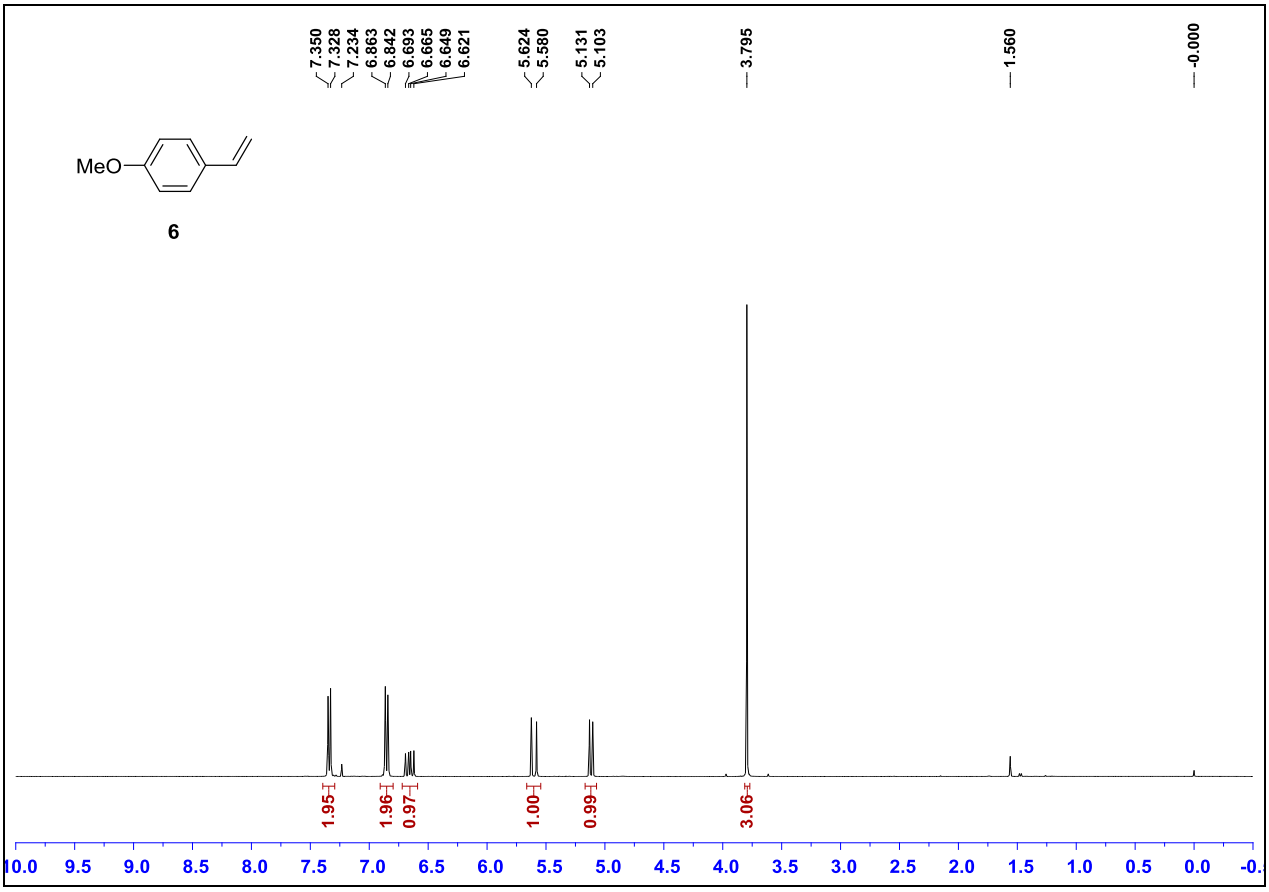


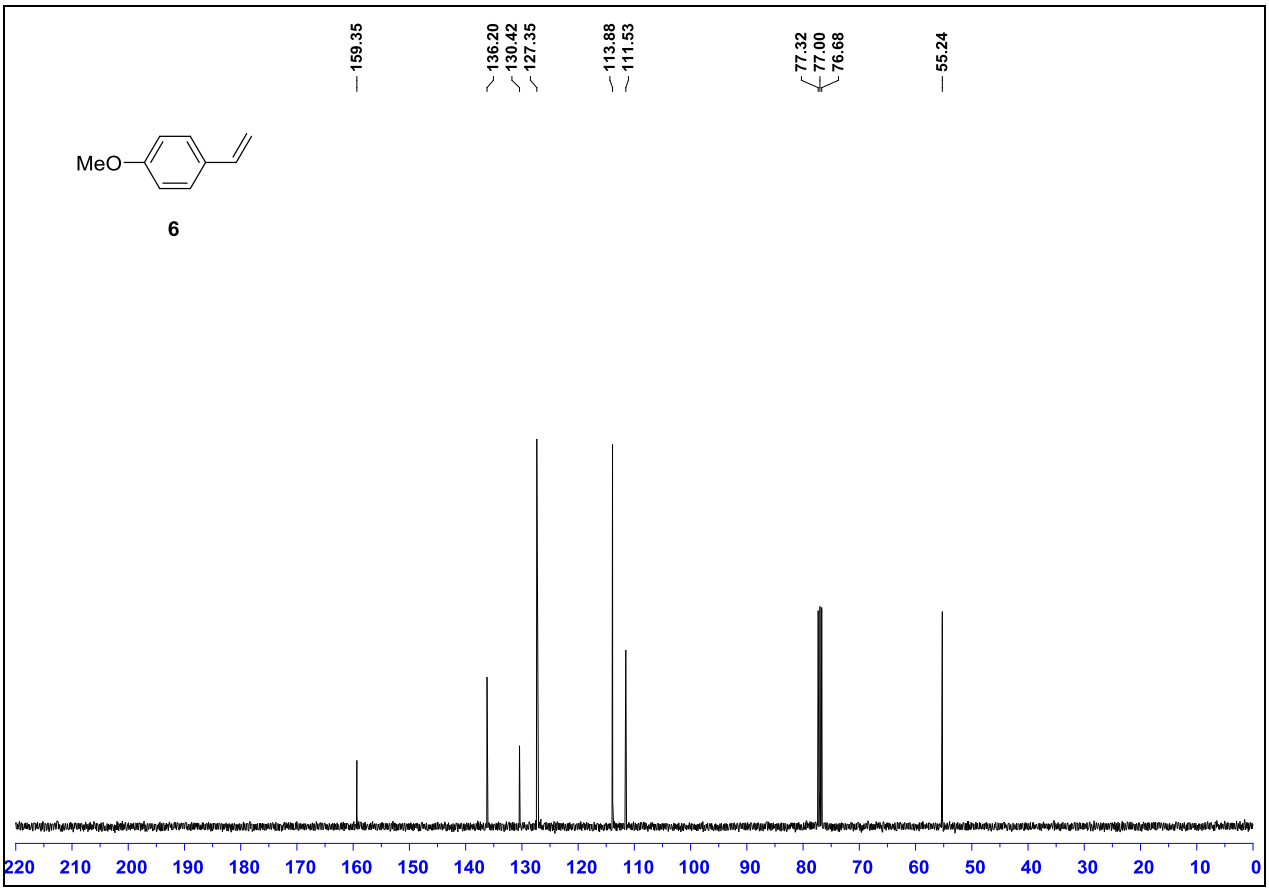
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum



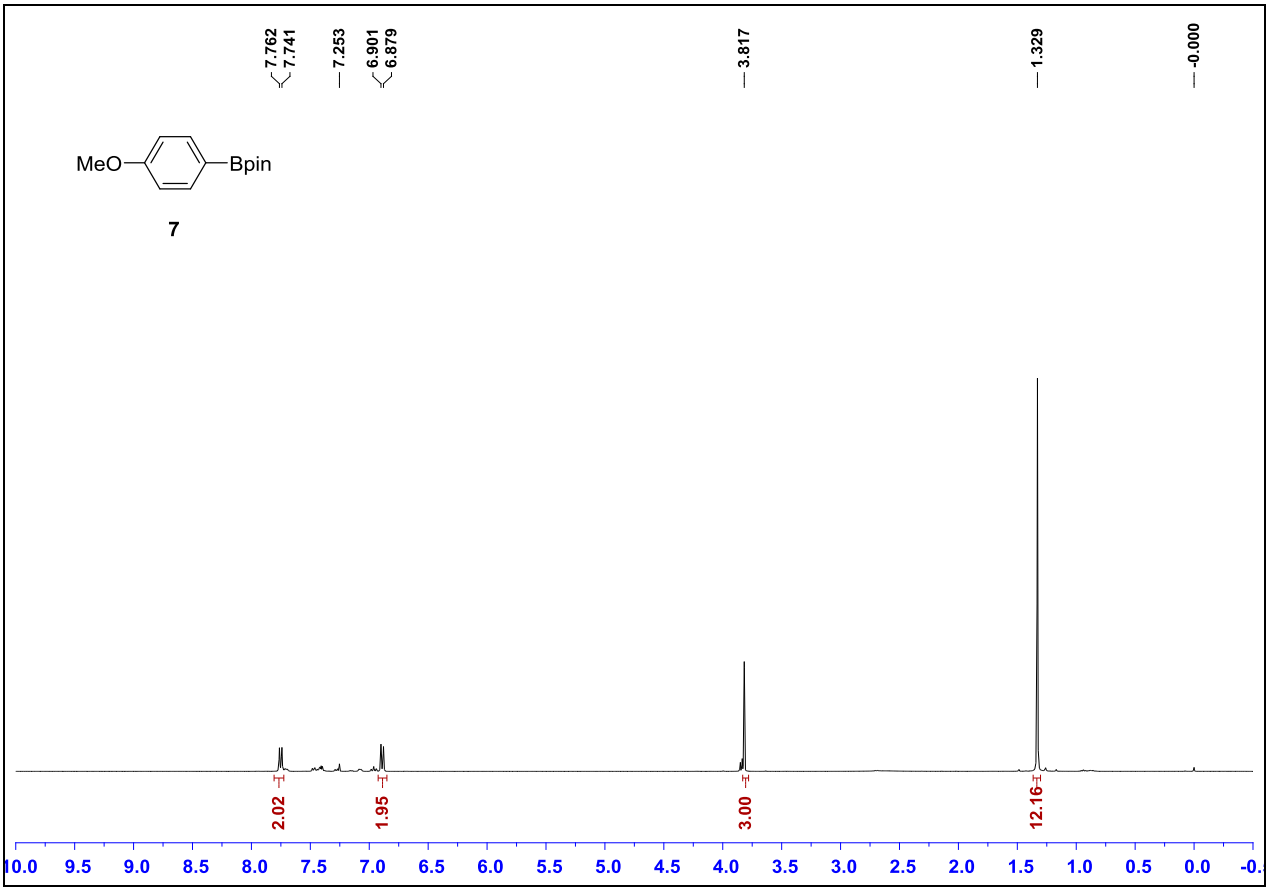


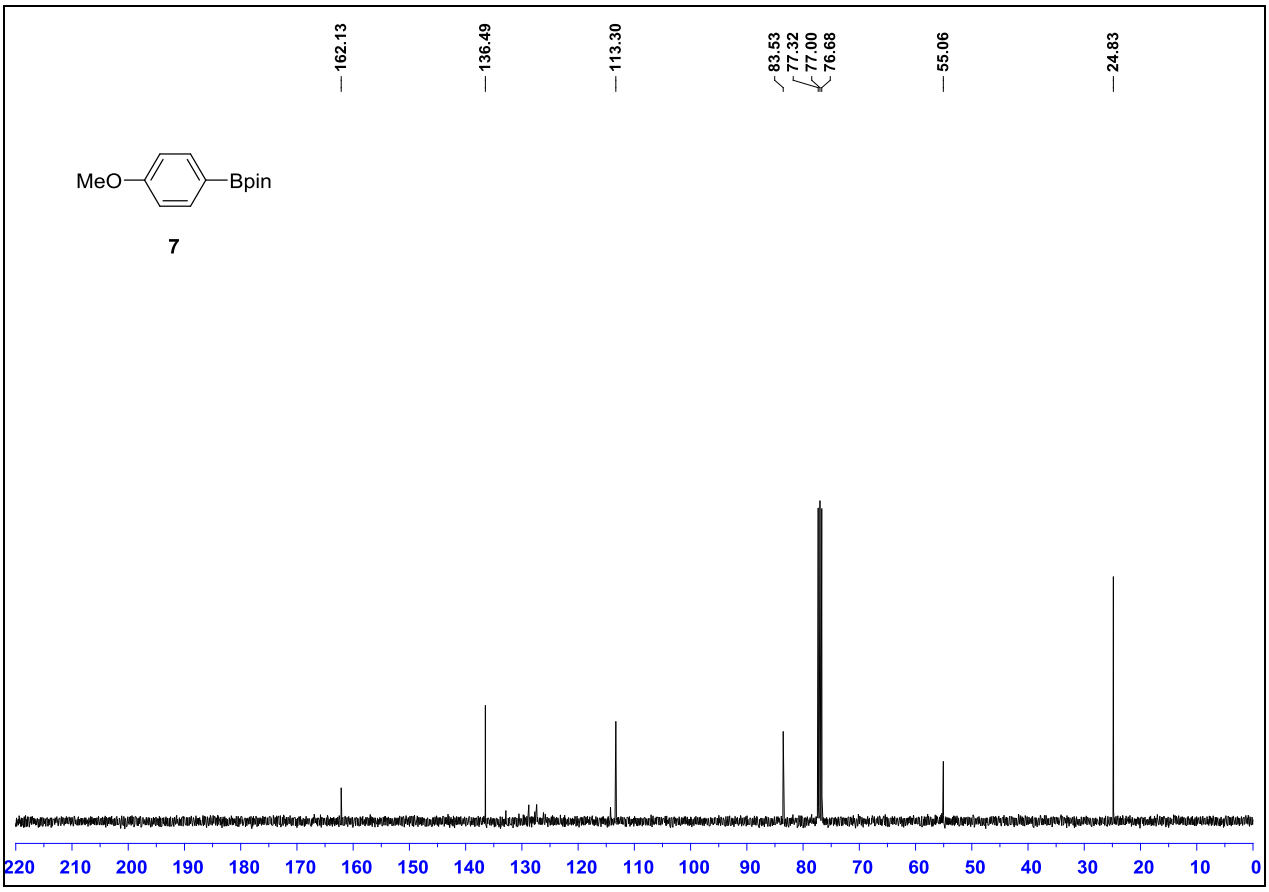
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum



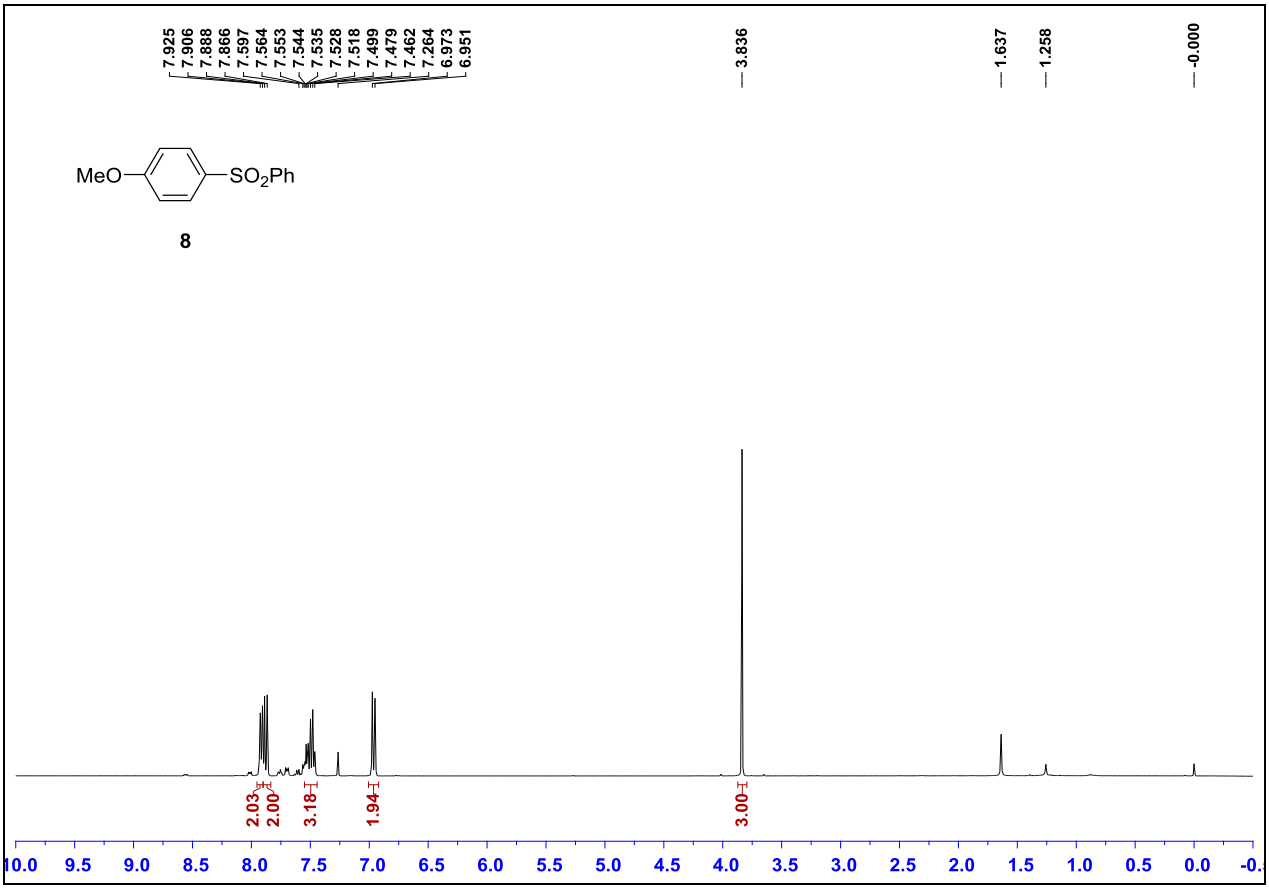


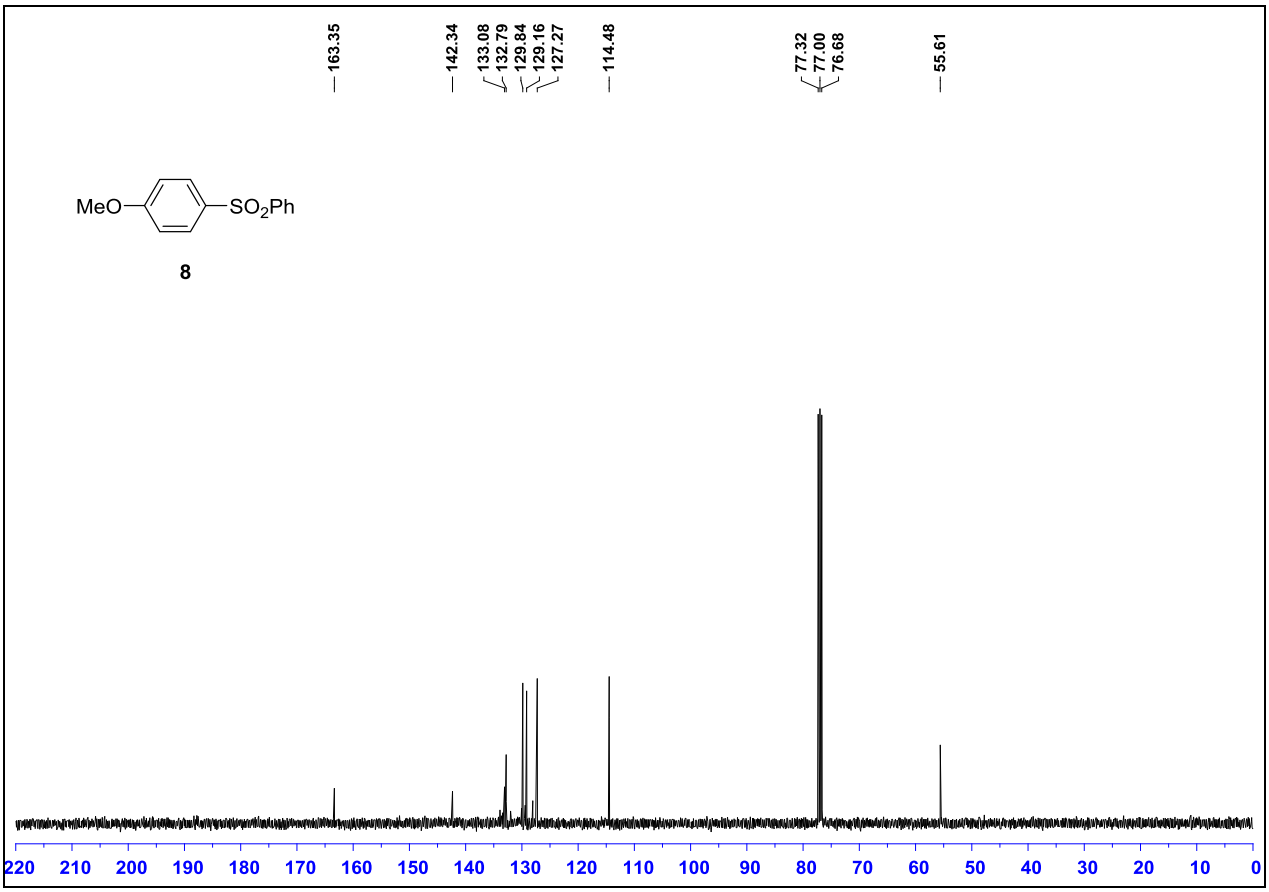
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum



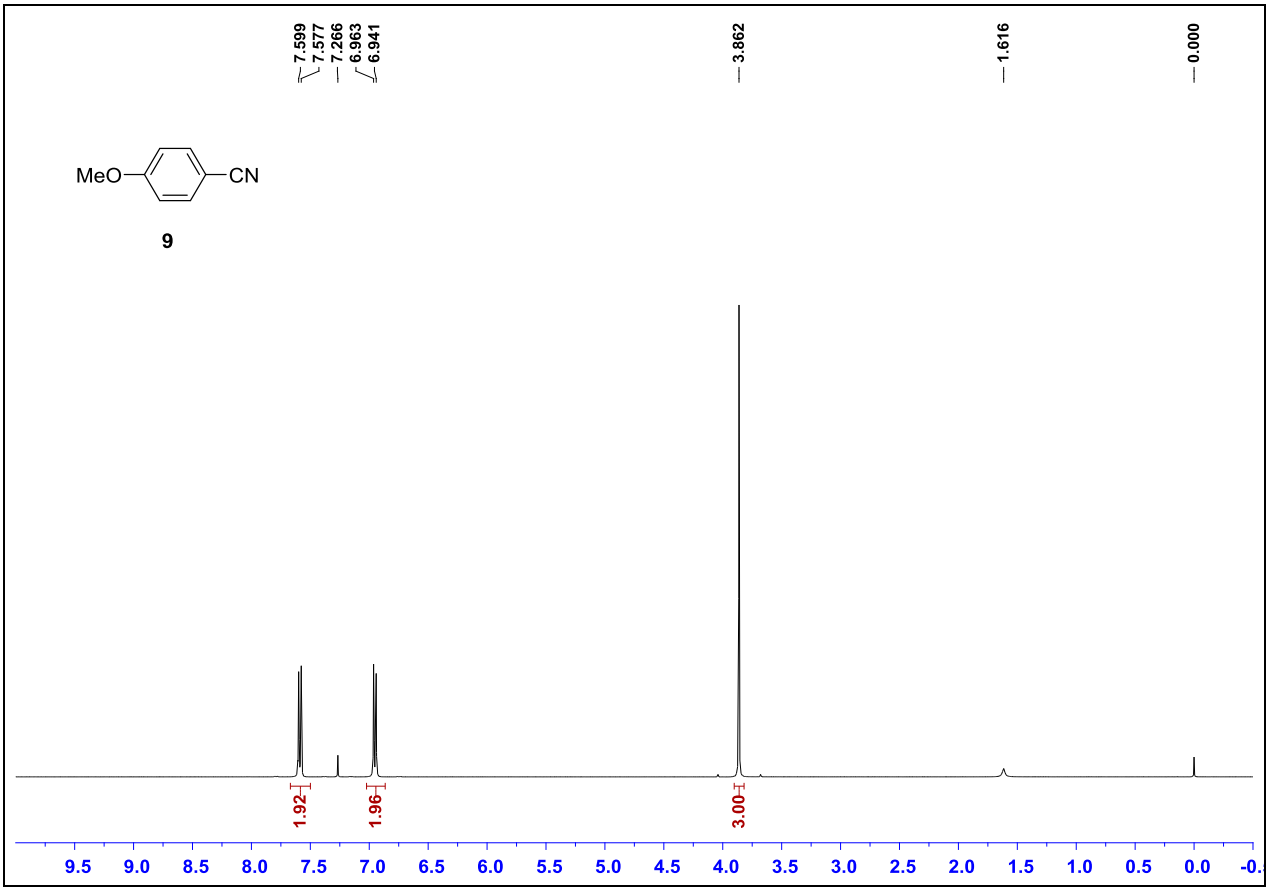


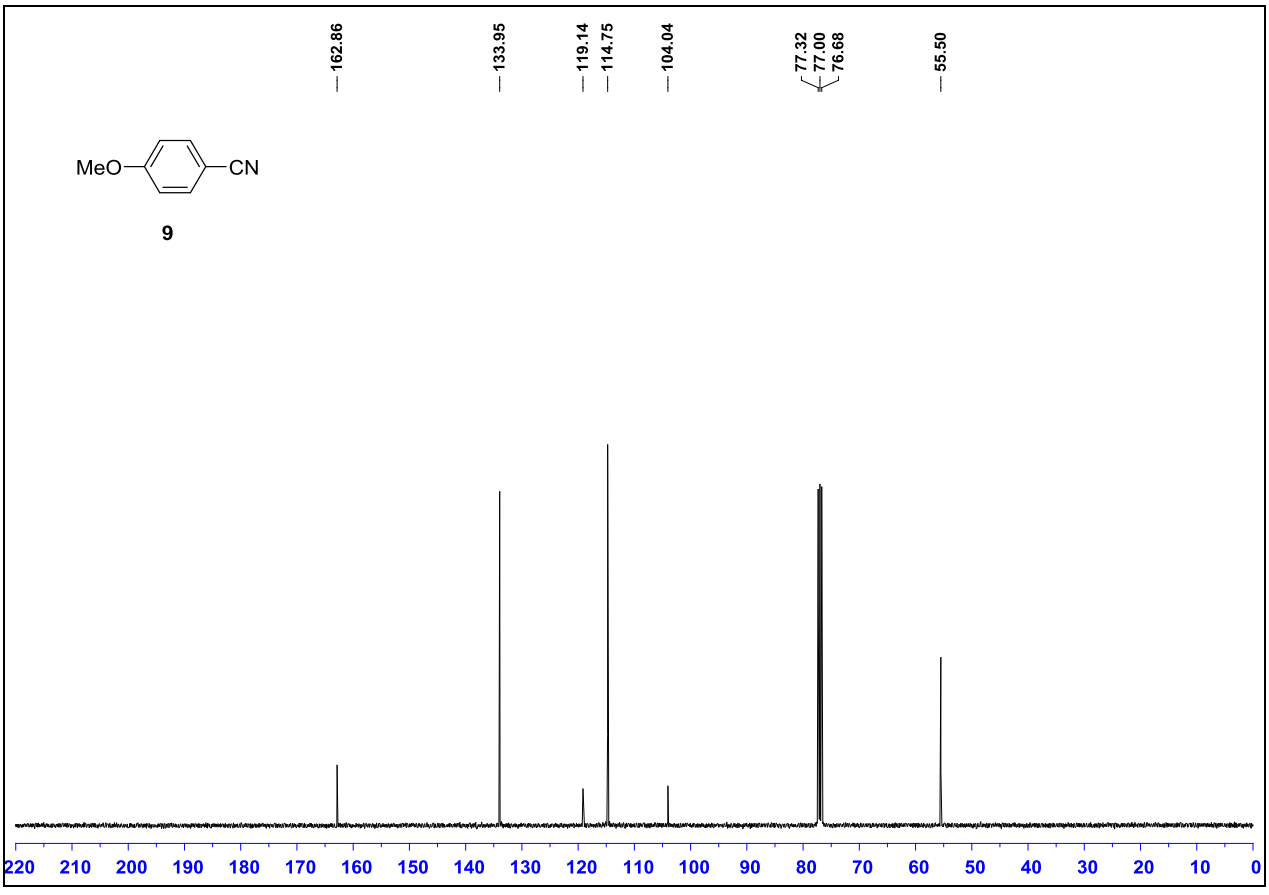
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum



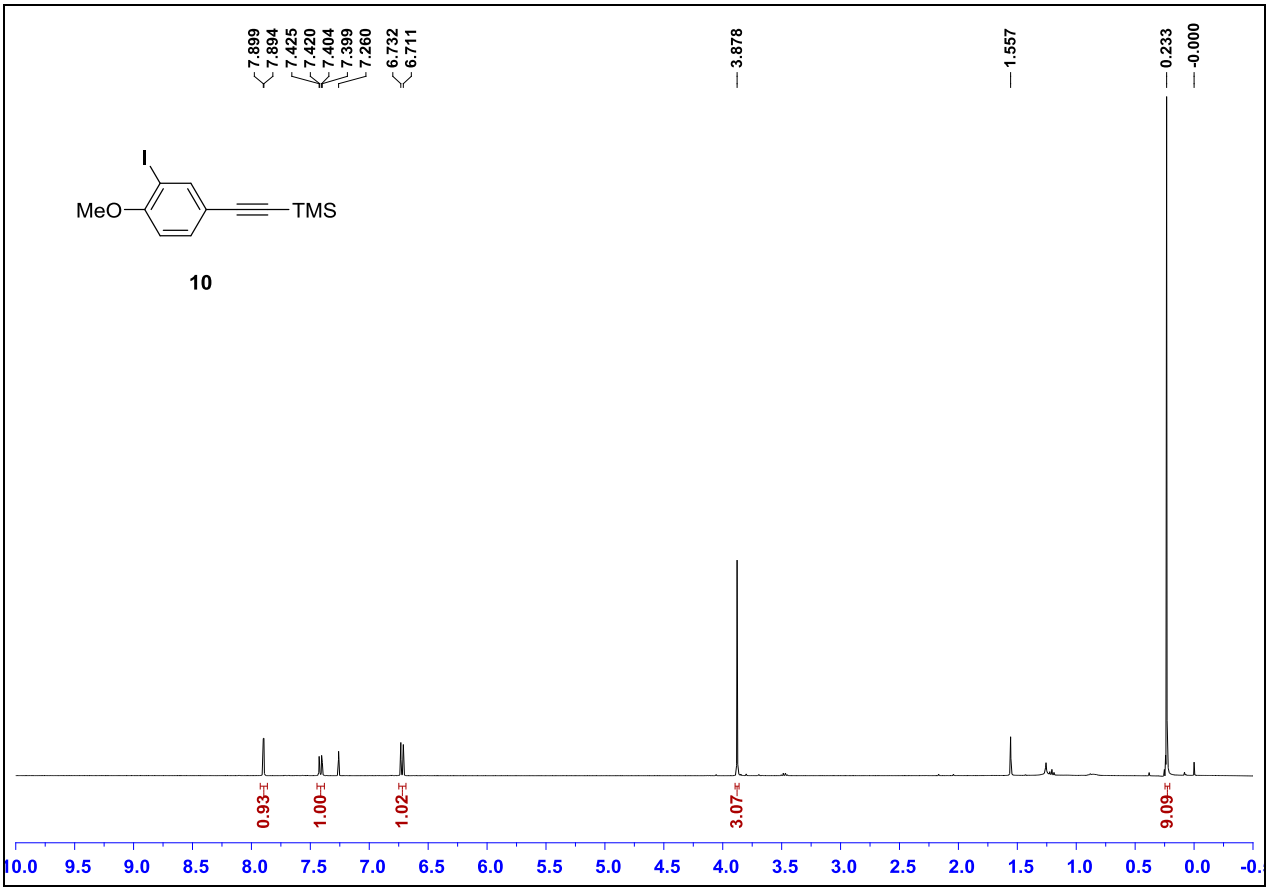


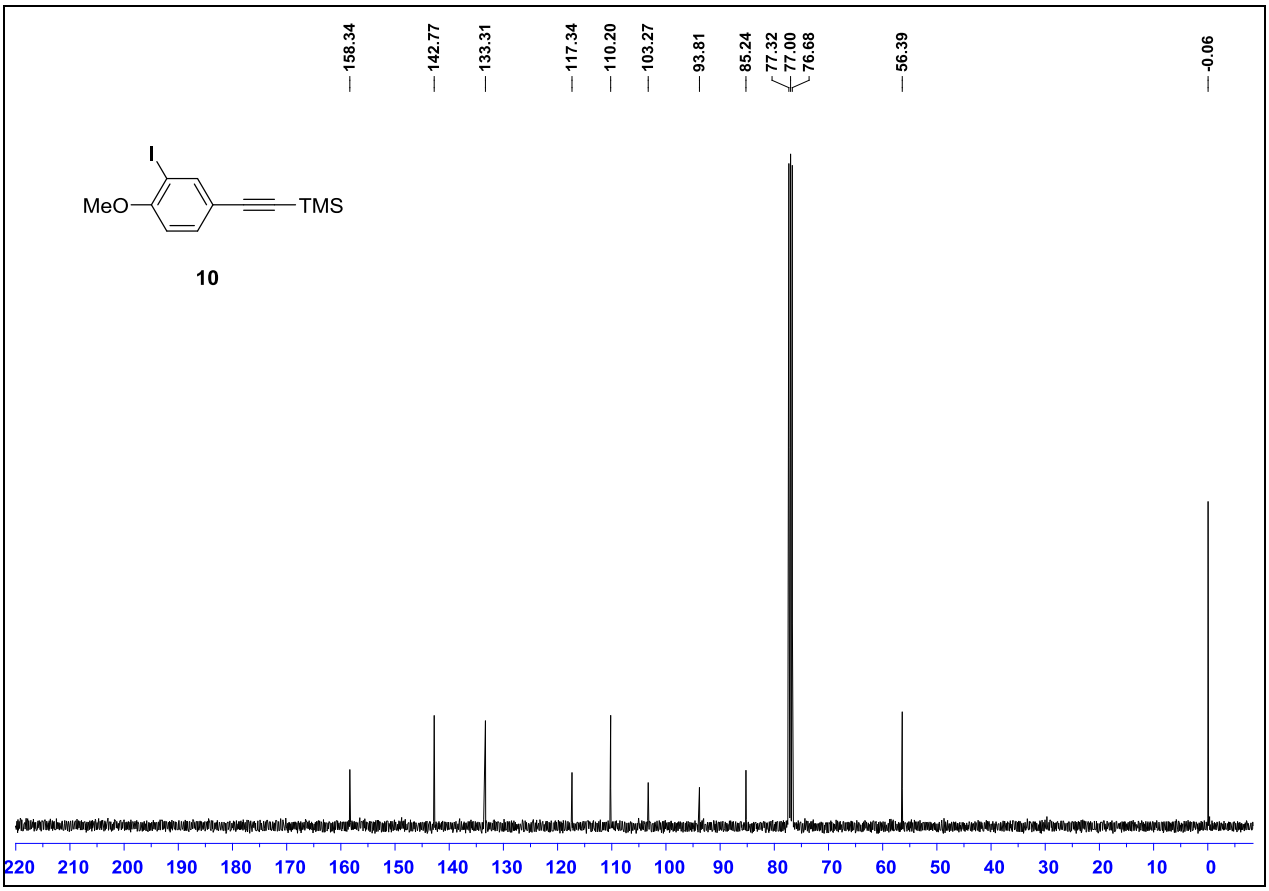
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum



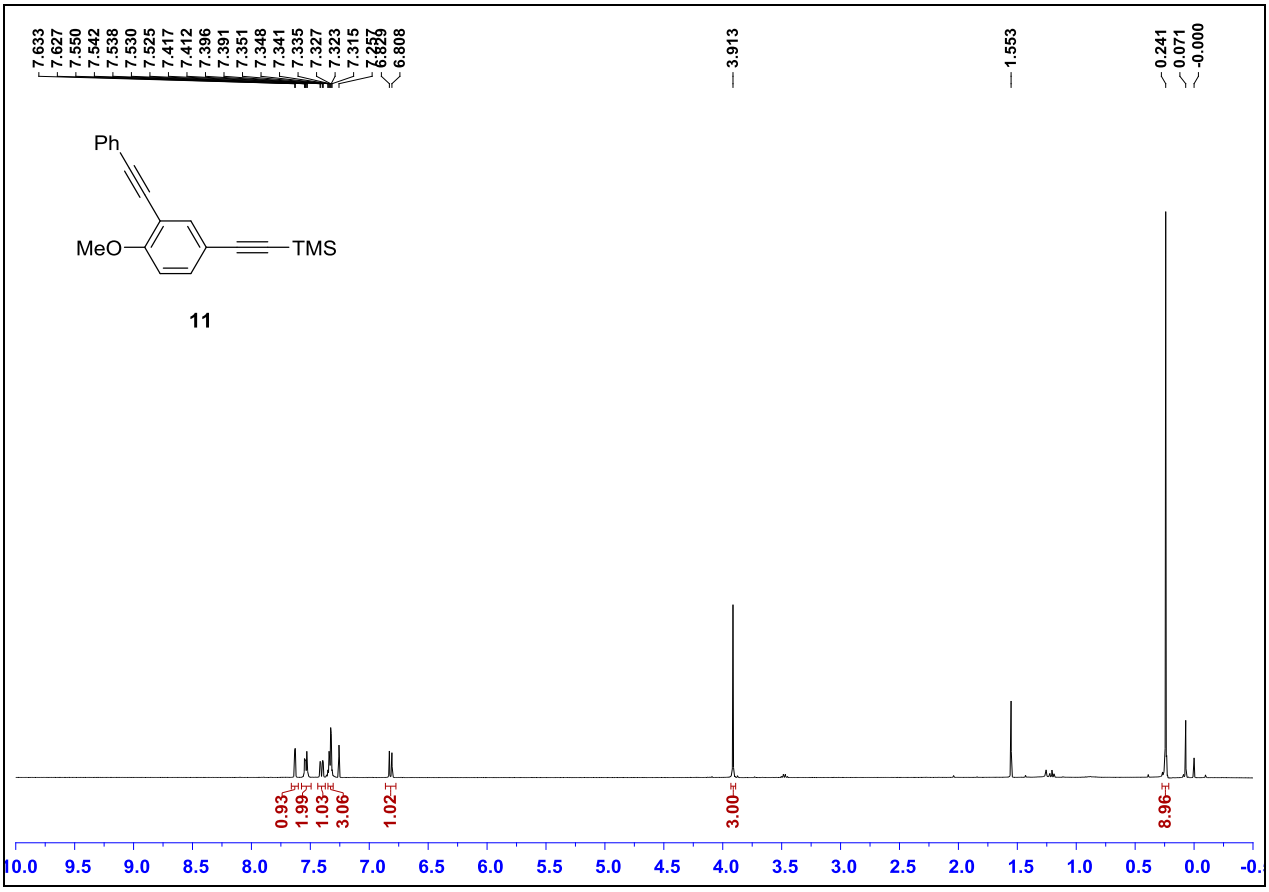


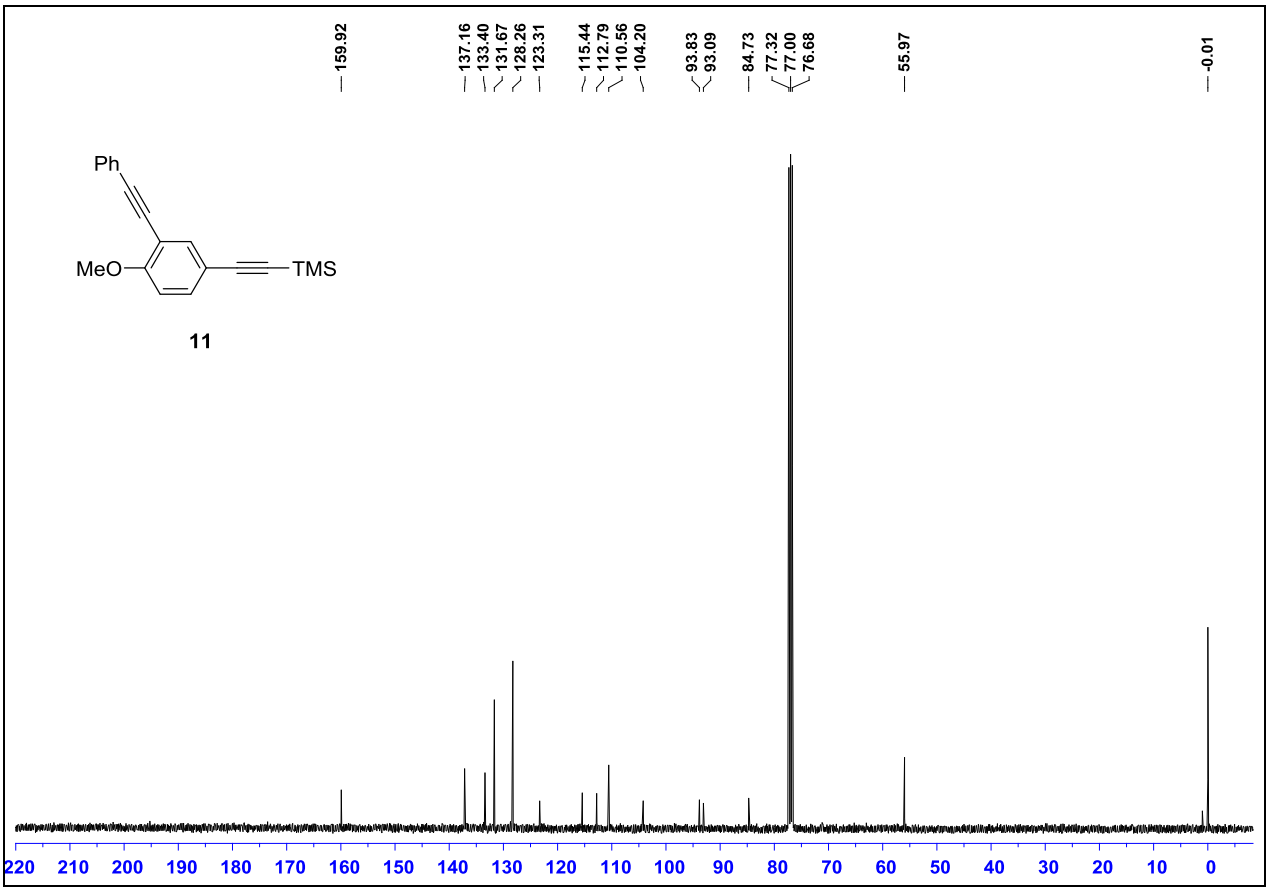
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum



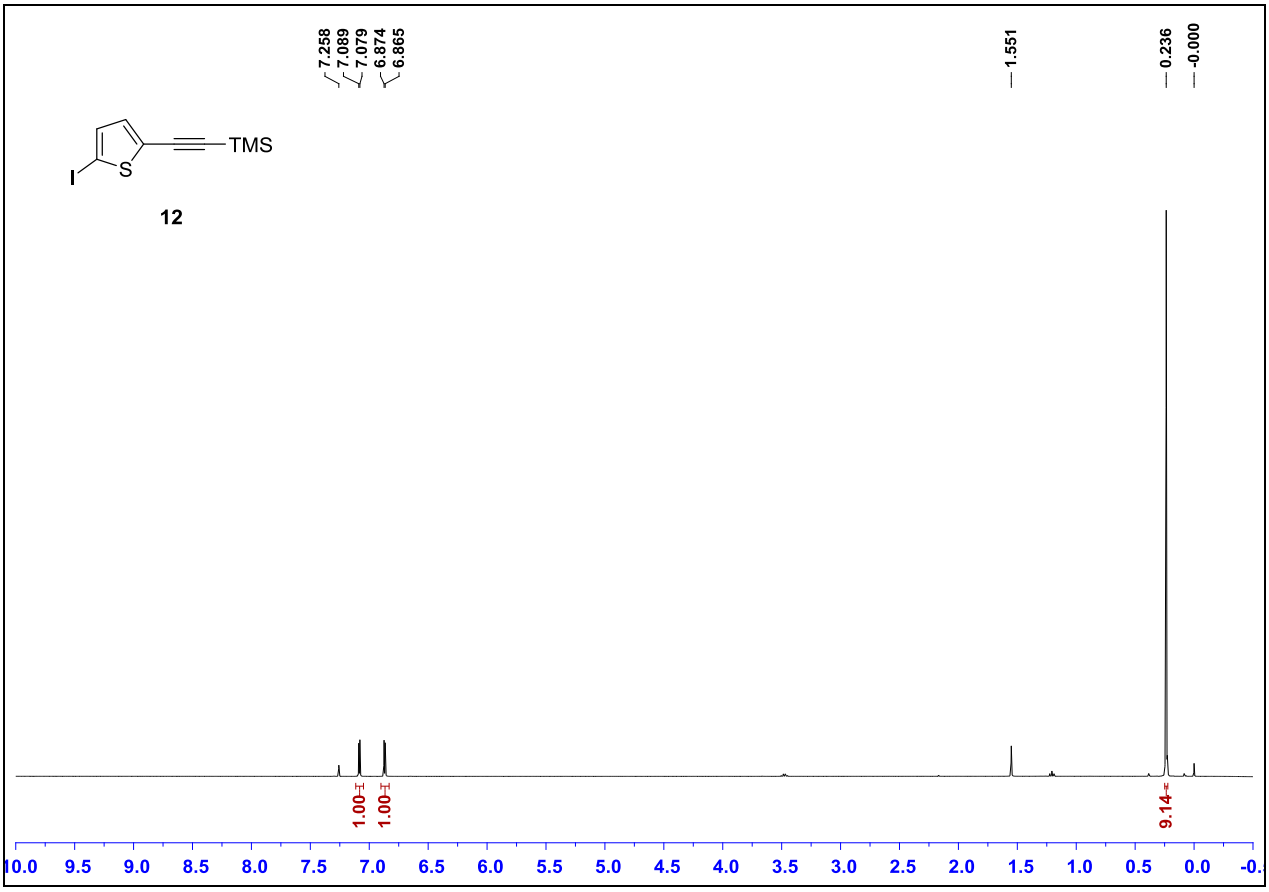


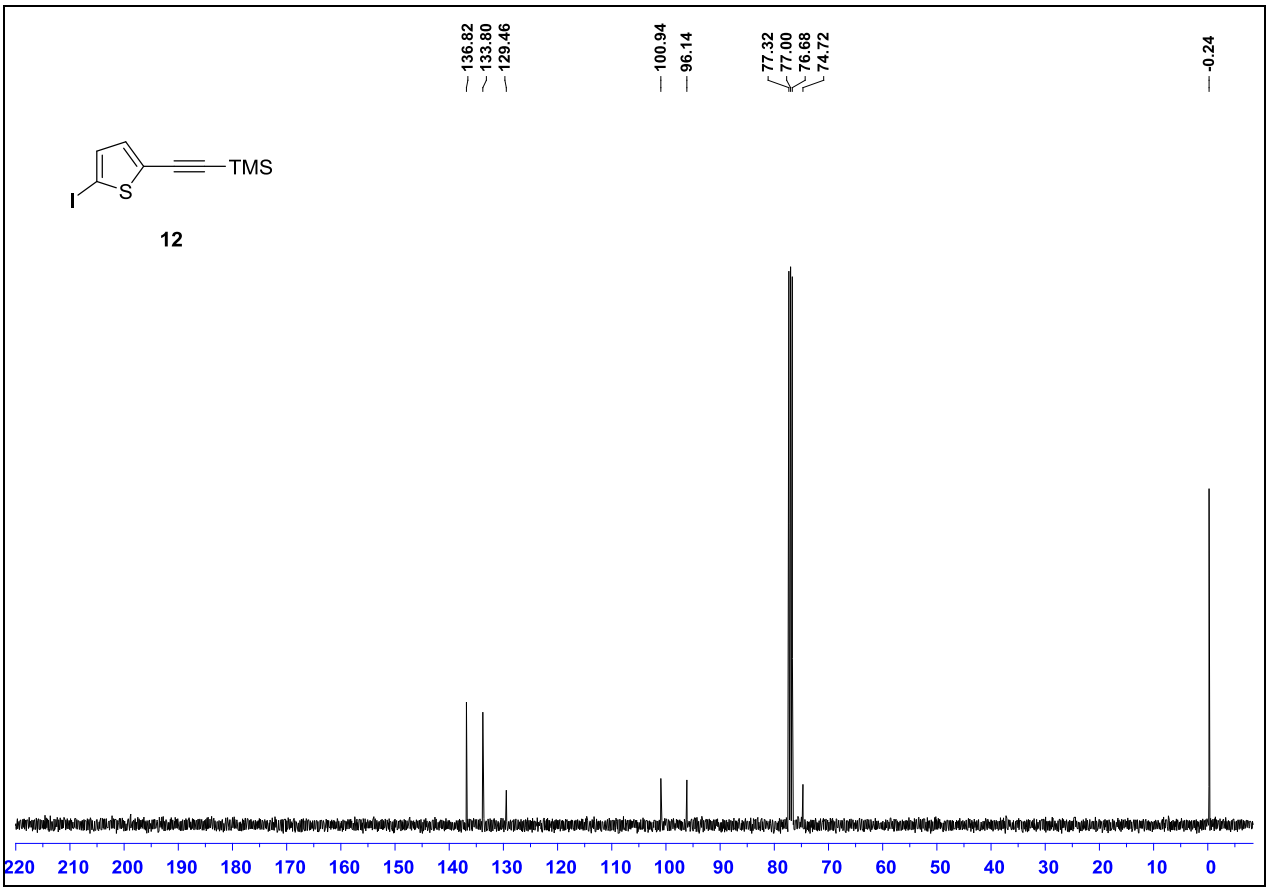
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum



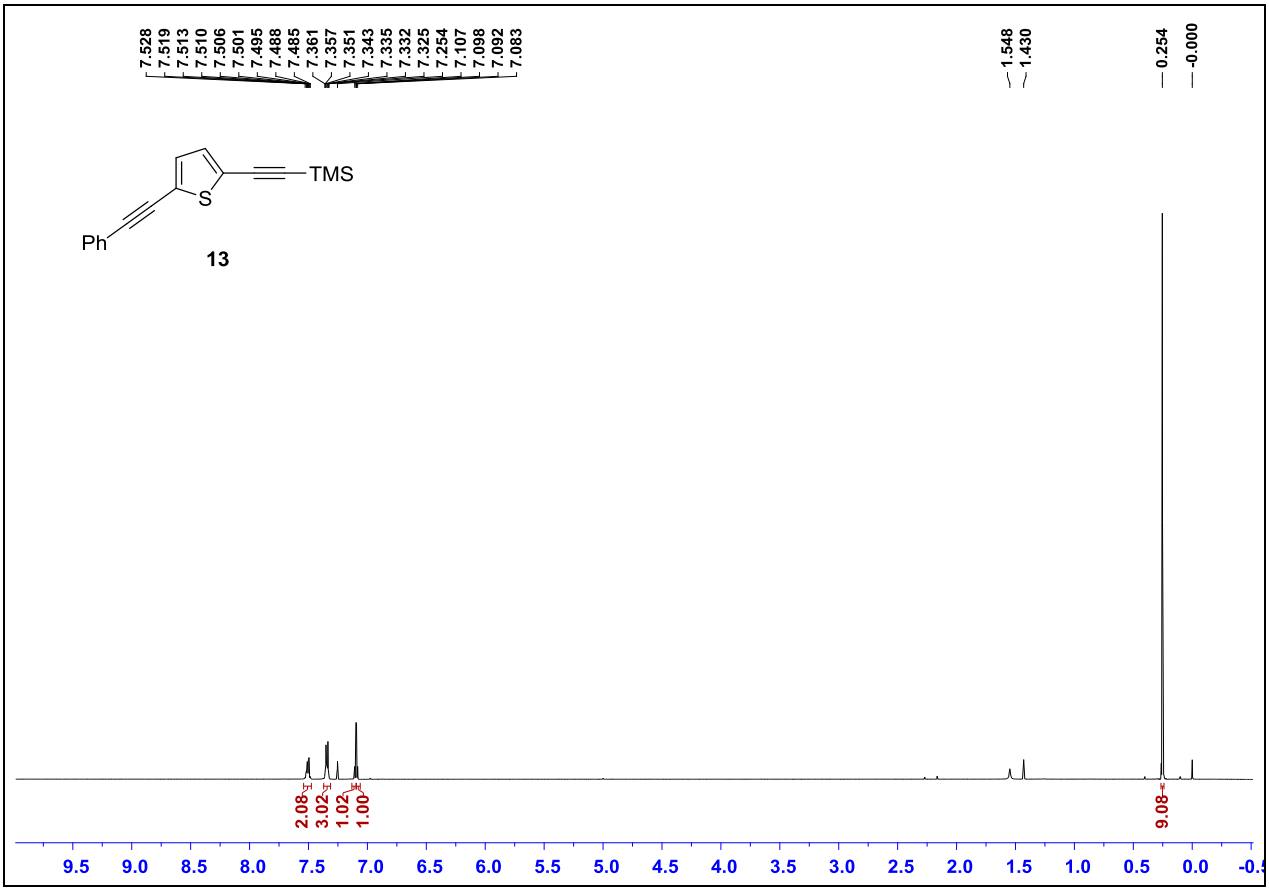


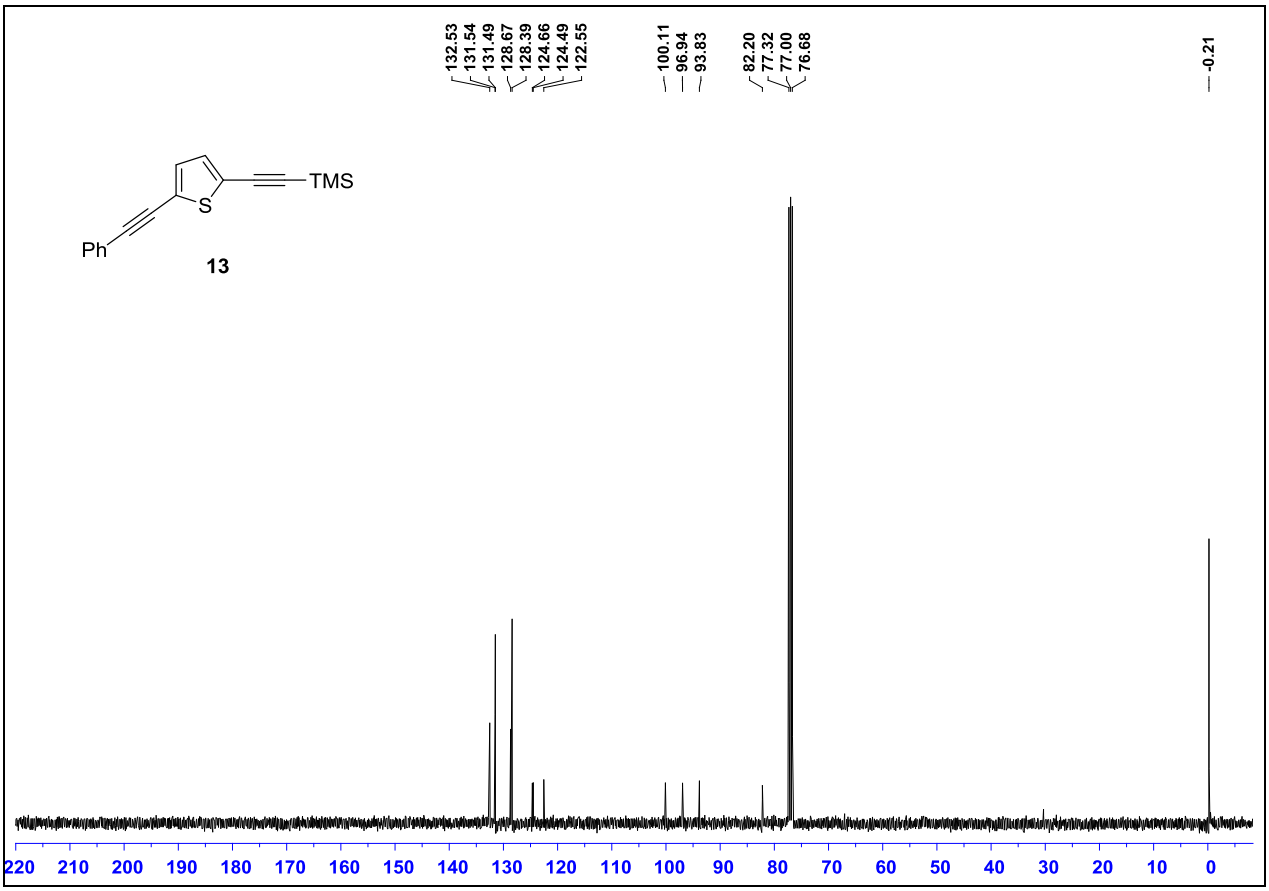
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum



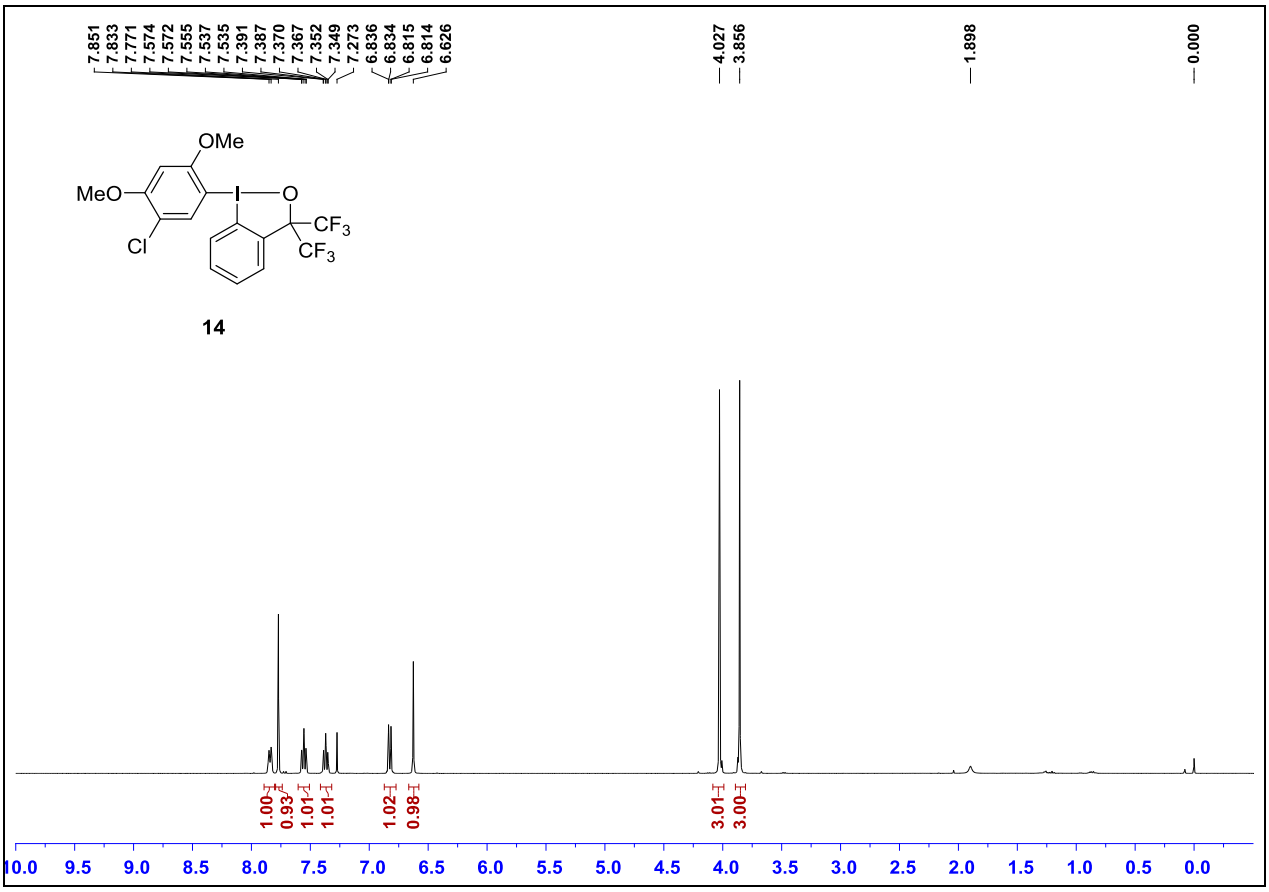


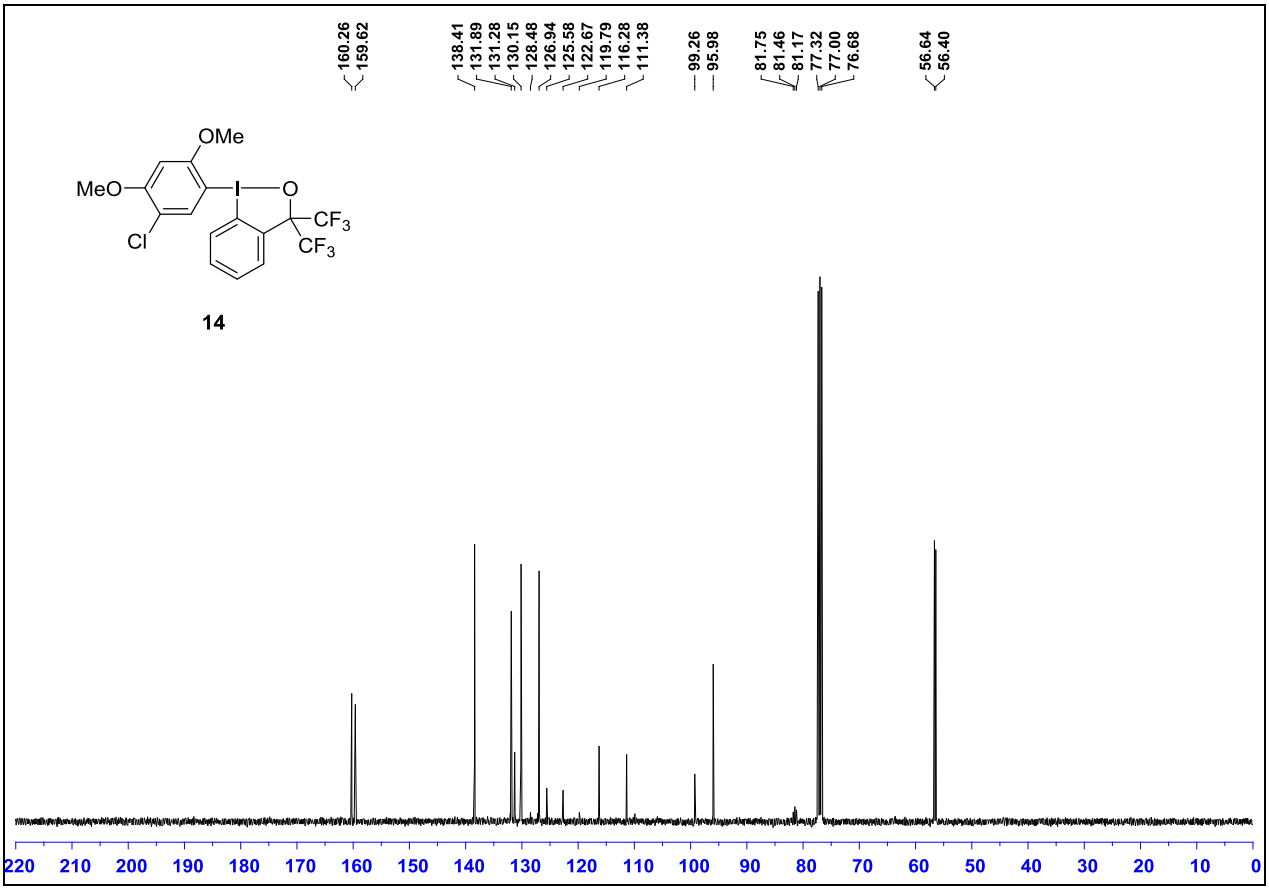
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum

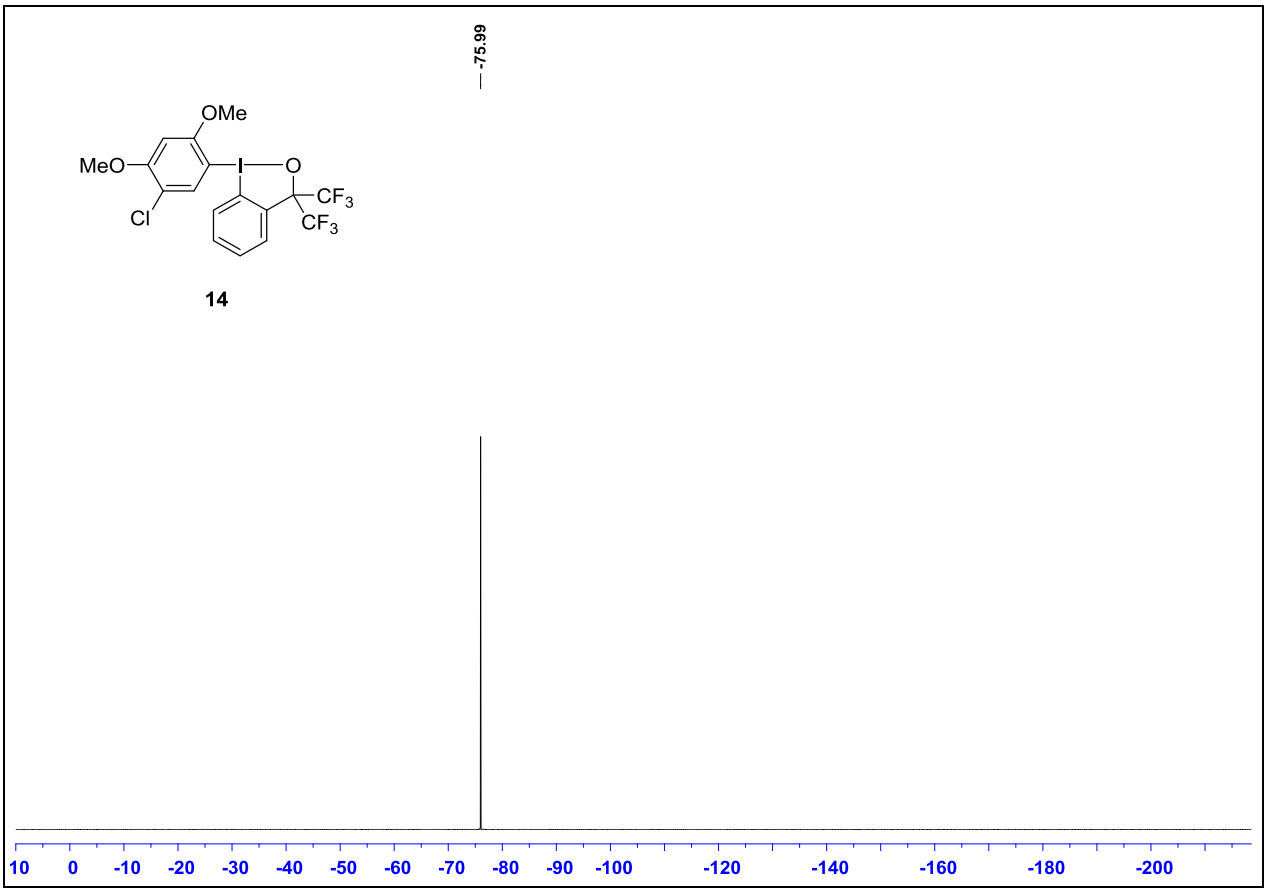




^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum



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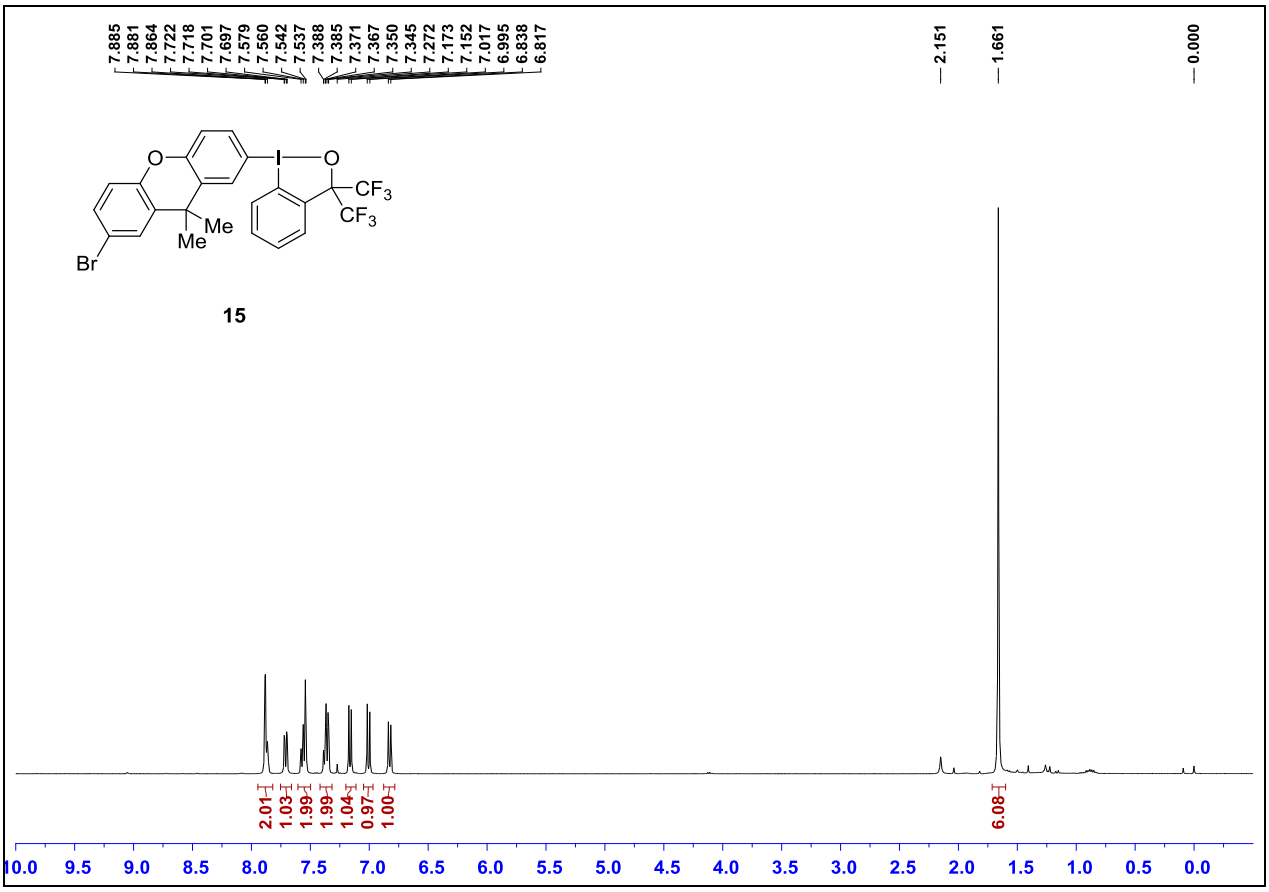
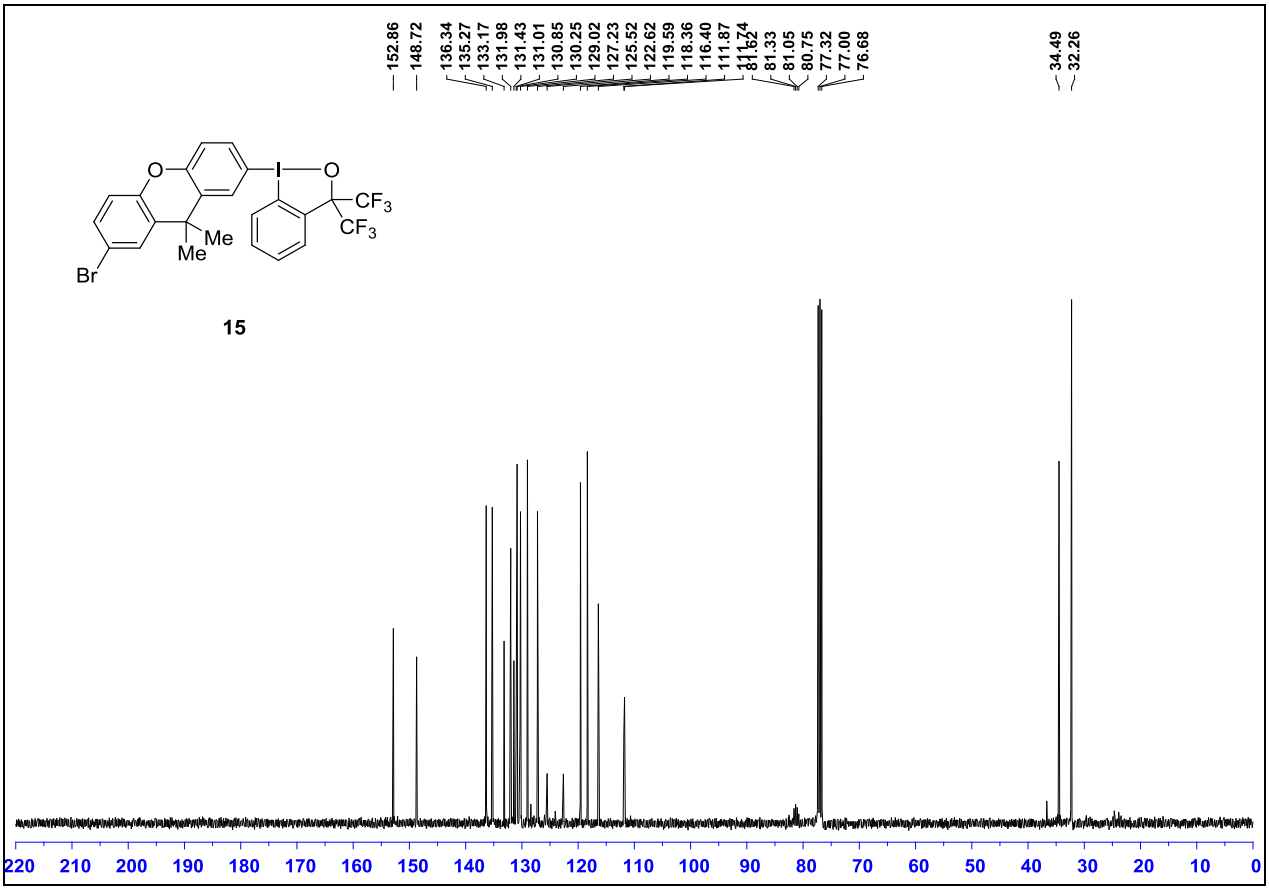
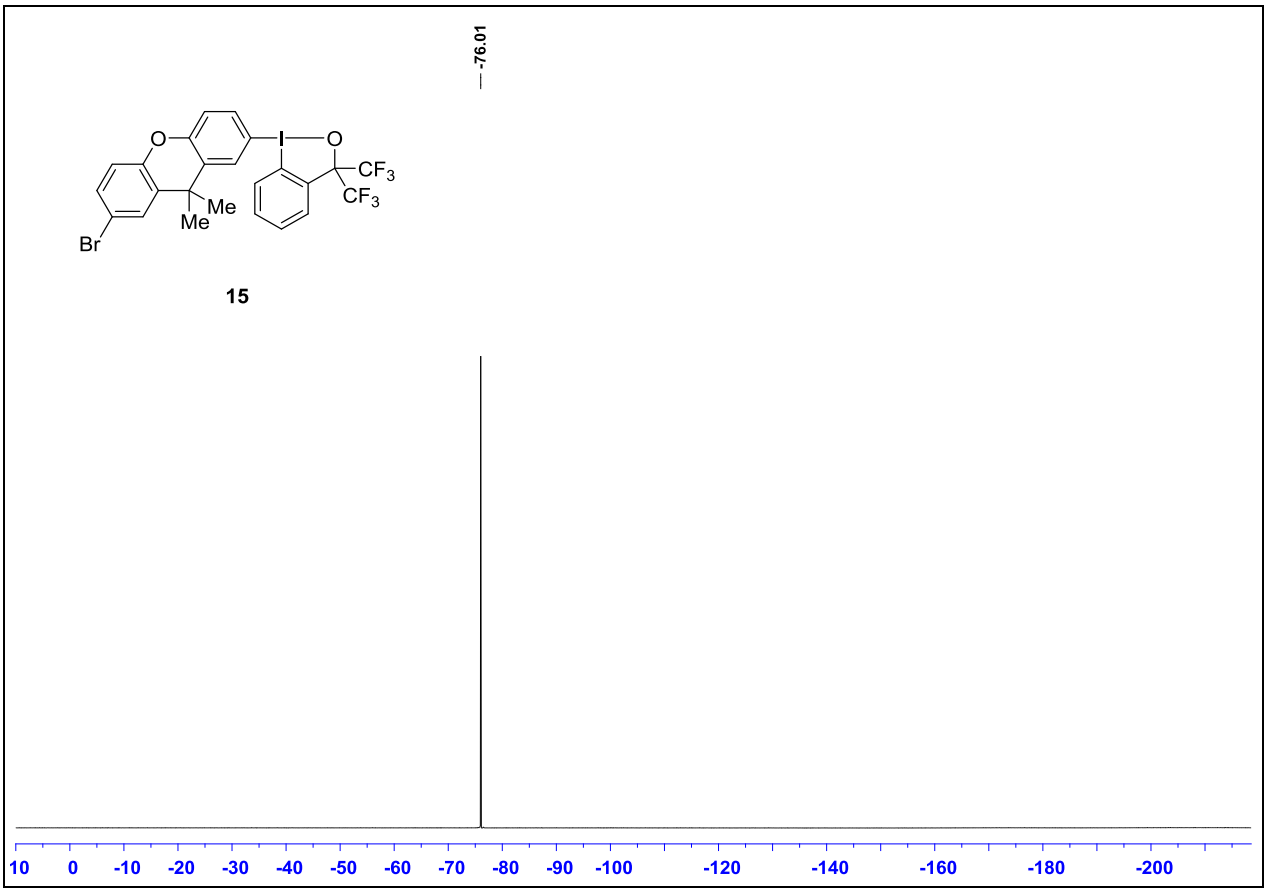
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum



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