Supplementary Information

Carbon–iodine atropisomerism on triazole and triazolium frameworks: A breathing axle with divergent adaptivity

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Contents

1. Materials and Methods

General. All reactions dealing with air- or moisture-sensitive compounds were performed by standard Schlenk technique in oven-dried reaction vessels under an argon atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed using 40–50 μm silica gel (silica gel 60N, Kanto Chemical). ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on JEOL JNM-ECA600 (600 MHz) or JNM-ECZL400S (400 MHz) spectrometers. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and $CHCl_3$ (77.0 ppm), respectively. $^{19}F\{^{1}H\}$ NMR spectra are referenced to an external standard (CF_3CO_2H, –76.6 ppm). $^{31}P\{^{1}H\}$ NMR spectra are referenced to external standard (PPh_3, –6.0 ppm). High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 spectrometer equipped with a double-focusing mass analyzer or a JMS-T100GC spectrometer equipped with a TOF mass analyzer. Chiral stationary phase HPLC analysis was performed on a Jasco LC-4000 Series system with Daicel Chiralpak columns (4.6 mm I.D. × 150 mm length). Optical rotations were measured on a Horiba SEPA-300 high-sensitive polarimeter.

Materials. Unless otherwise noted, commercial reagents were purchased from TCI, Kanto Chemical, Sigma-Aldrich, or other commercial suppliers and were used as received. Anhydrous THF and Et_2O were supplied from KANTO Chemical Co., Inc. as "Dehydrated solvent system" and were used as received. Anhydrous toluene was purchased from FUJIFILM Wako Pure Chemical and was used as received. 1-Cyclohexyl-4-octyl-1*H*-1,2,3-triazole (**SM-1a**)[1], (3*s*,5*s*,7*s*)-1-azidoadamantane (**SM-2**)[2], (3*r*,5*r*,7*r*)-1-ethynyladamantane (**SM-3**)[3], 1-chloro-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodoxole (chlorobenziodoxole, CBX)[4], and sodium (*R*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide ((*R*)-CPA-Na)[5] were synthesized according to the reported procedures (Figure S1).

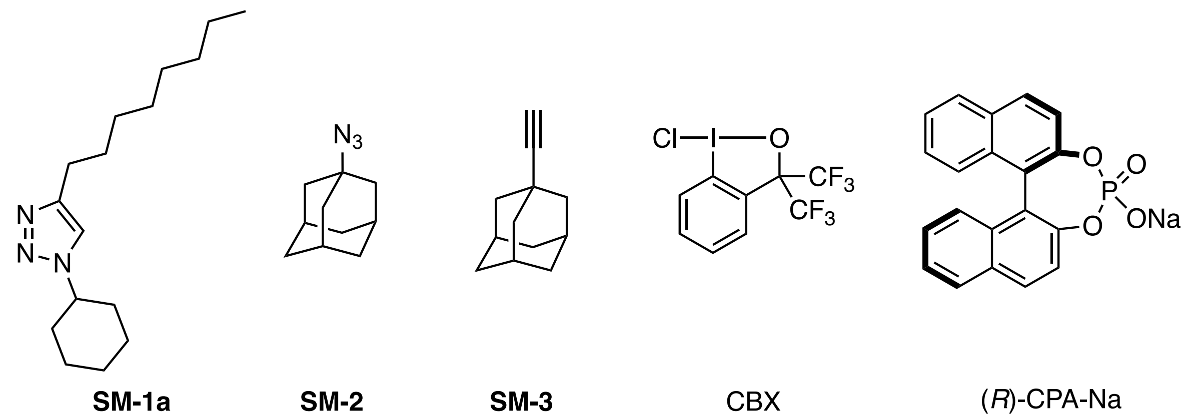
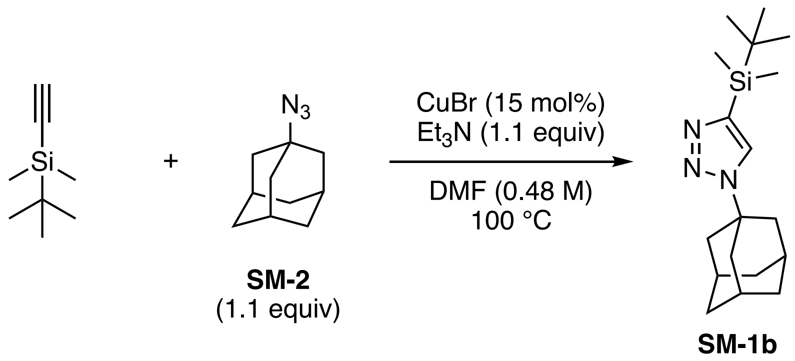


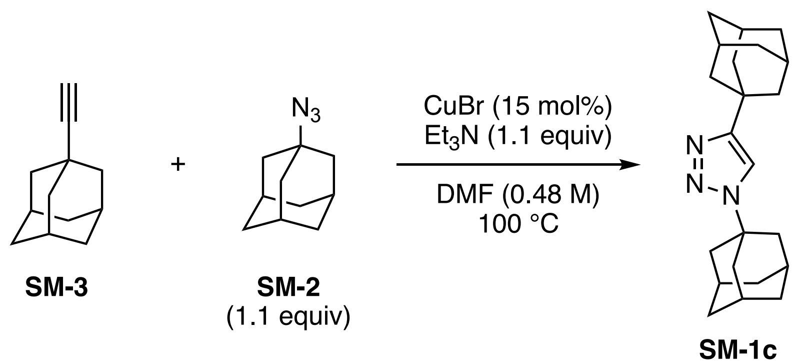
Figure S1. Known compounds synthesized according to the literature procedure.

2. Preparation of Triazole- and Triazolium-Benziodoxoles

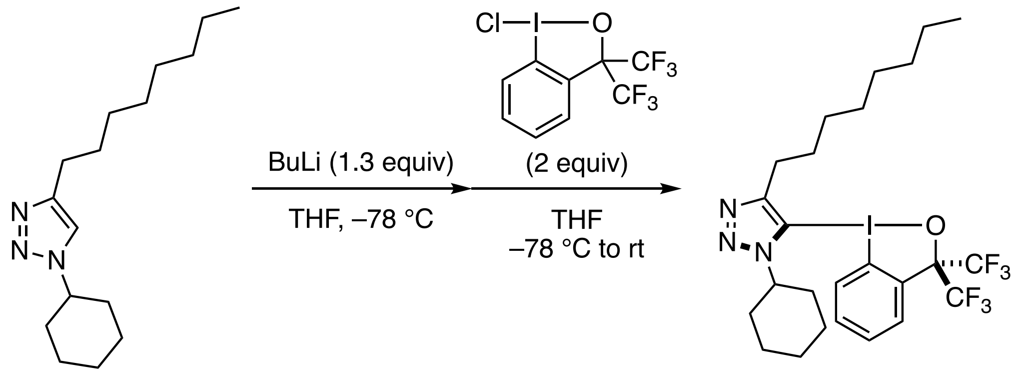


1-((3*s*,5*s*,7*s*)-Adamantan-1-yl)-4-(*tert*-butyldimethylsilyl)-1*H*-1,2,3-triazole (SM-1b): To a solution of (3*s*,5*s*,7*s*)-1-azidoadamantane **SM-2** (974.9 mg, 5.5 mmol) and CuBr (107.6 mg, 0.75 mmol) in DMF (10 mL) was added *tert*-butyl(ethynyl)dimethylsilane (0.91 mL, 5.0 mmol) and triethylamine (0.76 mL, 5.5 mmol) at room temperature. The reaction mixture was stirred at 100 °C for 2.5 h. Upon cooling to room temperature, the mixture was quenched with saturated NH_4Cl aq. and extracted with hexane/EtOAc (4:1). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the title compound **SM-1b** as a white solid (1.37 g, 86% yield).

R_f 0.43 (hexane/EtOAc = 6/1); m.p. 219–221 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 (s, 1H), 2.27–2.24 (m, 9H), 1.84–1.75 (m, 6H), 0.94 (s, 9H), 0.28 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 143.0, 125.6, 58.9, 43.1, 36.0, 29.5, 26.3, 16.5, –5.7; **HRMS** (EI) *m/z:* $[M]^+$ calcd for $C_{18}H_{31}N_3Si$ 317.2282; found 317.2280.

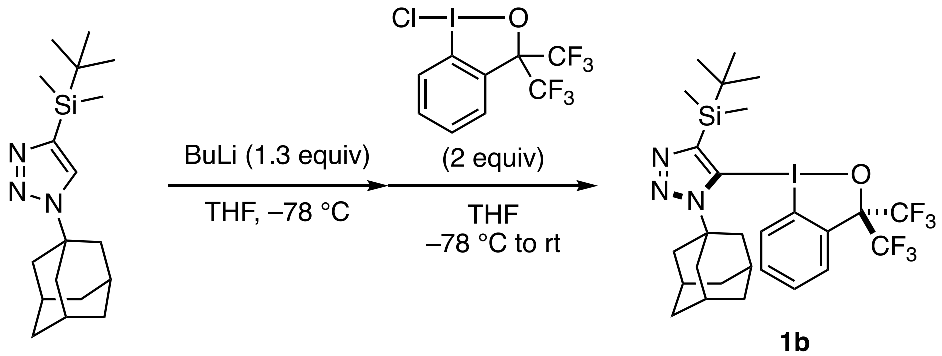


1-((1*r*,3*R*)-Adamantan-1-yl)-4-((1*s*,3*S*)-adamantan-1-yl)-1*H*-1,2,3-triazole (SM-1c): To a solution of (3*s*,5*s*,7*s*)-1-azidoadamantane **SM-2** (2.61 g, 14.7 mmol) and CuBr (286.9 mg, 2.0 mmol) in DMF (28 mL) was added (3*r*,5*r*,7*r*)-1-ethynyladamantane **SM-3** (2.15 g, 13.4 mmol) and triethylamine (2.0 mL, 14.7 mmol) at room temperature. The reaction mixture was stirred at 100 °C for 2.5 h. Upon cooling to room temperature, the mixture was quenched with saturated NH_4Cl aq. and extracted with hexane/EtOAc (4:1). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the title compound **SM-1c** as a white solid (4.05 g, 80% yield). The spectral data were consistent with those reported in the literature[6].



5-(3,3-Bis(trifluoromethyl)-1λ³-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-1-cyclohexyl-4-octyl-1*H*-1,2,3-triazole (1a): Under an argon atmosphere, a two-necked flask equipped with a magnetic stir bar was charged with **SM-1a** (26.3 mg, 0.1 mmol) and THF (1 mL). To the solution was added BuLi (1.54 M in hexane, 84.4 µL, 0.13 mmol) dropwise at –78 °C. The resulting mixture was stirred at –78 °C for 30 min, and a solution of CBX (80.9 mg, 0.2 mmol) in THF (0.2 mL) was added slowly. The resulting mixture was then warmed to room temperature and stirred for 24 h before being quenched with saturated NH_4Cl aq. After separation of the organic layer, the aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic layer extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, followed by recrystallization from hexane/CH_2Cl_2 to afford the title compound **1a** as a white solid (51.3 mg, 99% yield).

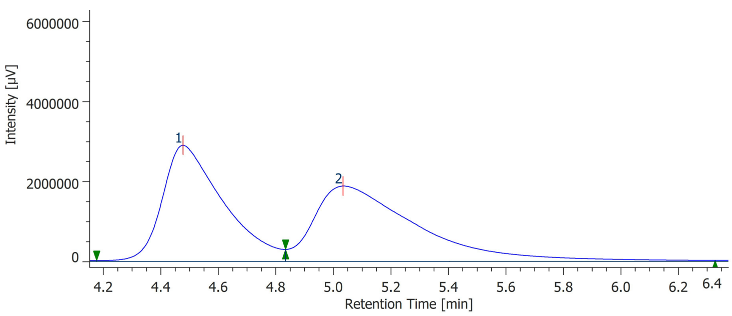
R_f 0.50 (hexane/EtOAc = 2/1); m.p. 125–127 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 1H), 7.68–7.64 (m, 1H), 7.47–7.43 (m, 1H), 6.55 (dd, J = 8.4 Hz, 0.9 Hz, 1H), 4.31–4.24 (m, 1H), 2.82–2.74 (m, 1H), 2.74–2.67 (m, 1H), 2.17–1.98 (m, 3H), 1.96–1.90 (m, 1H), 1.89–1.83 (m, 2H), 1.76–1.70 (m, 1H), 1.70–1.63 (m, 2H), 1.45–1.36 (m, 1H), 1.34–1.16 (m, 12H), 0.85 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 155.0, 132.8, 131.3, 131.1, 130.7, 126.3, 123.8 (q, $J_{C–F}$ = 290.4 Hz), 123.6 (q, $J_{C–F}$ = 290.4 Hz), 112.5, 108.2, 82.1–80.8 (m), 61.6, 33.8, 33.3, 31.7, 29.7, 29.3, 29.1, 29.0, 26.1, 25.3, 24.8, 22.6, 14.0, one aliphatic resonance not resolved due to overlap; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ –75.7 (q, $J_{F–F}$ = 8.5 Hz, 3F), –76.0 (q, $J_{F–F}$ = 8.5 Hz, 3F); **HRMS** (FAB) *m/z:* $[M+H]^+$ calcd for $C_{25}H_{33}F_6IN_3O$ 632.1567; found 632.1557.



SM-1b **1b**

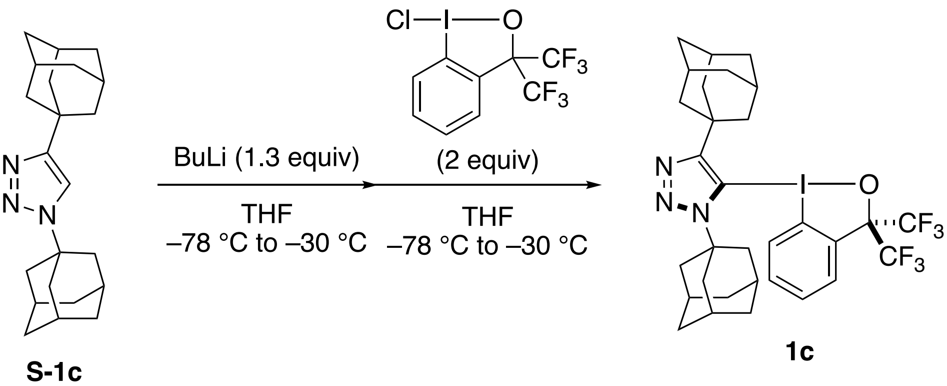
1-((1*s*,3*s*)-Adamantan-1-yl)-5-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-4-(*tert*-butyldimethylsilyl)-1*H*-1,2,3-triazole (1b): Under an argon atmosphere, a two-necked flask equipped with a magnetic stir bar was charged with **SM-1b** (1.37 g, 4.3 mmol) and THF (43 mL). To the solution was added BuLi (1.54 M in hexane, 3.6 mL, 5.6 mmol) dropwise at –78 °C. The resulting mixture was stirred at this temperature for 30 min, and a solution of CBX (3.48 g, 8.6 mmol) in THF (8.6 mL) was added slowly. The reaction mixture was warmed to room temperature and stirred for 26 h before being quenched with saturated NH_4Cl aq. After separation of the organic layer, the aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, followed by recrystallization (hexane/CH_2Cl_2) to afford the title compound **1b** as a yellow solid (871 mg, 30% yield).

R_f 0.45 (hexane/EtOAc = 4/1); m.p. 125–127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.3 Hz, 1H), 7.68–7.62 (m, 1H), 7.49–7.43 (m, 1H), 6.49 (dd, J = 8.5 Hz, 0.9 Hz, 1H), 2.47–2.40 (m, 3H), 2.39–2.32 (m, 3H), 2.25–2.18 (m, 3H), 1.79–1.67 (m, 6H), 0.95 (s, 9H), 0.31 (s, 3H), 0.20 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 155.2, 132.6, 131.2, 130.8, 130.3, 127.1, 123.7 (q, $J_{C–F}$ = 290.0 Hz), 123.4 (q, $J_{C–F}$ = 289.5 Hz), 115.2, 112.5, 82.1–80.4 (m), 64.4, 43.2, 35.5, 29.7, 26.5, 17.2, –4.7, –4.9; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ –75.8 (q, $J_{F–F}$ = 8.3 Hz, 3F), –76.6 (q, $J_{F–F}$ = 8.3 Hz, 3F); **HRMS** (FAB) *m/z:* $[M+H]^+$ calcd for $C_{27}H_{35}F_6IN_3OSi$ 686.1493; found 686.1488; HPLC analysis: Daicel Chiralpak ID column (hexane:*i*PrOH = 97/3, 1.0 mL/min, 25 °C, 230 nm).



Peak	Ret. Time (min)	Area (%)
1	4.477	47.735
2	5.033	52.265

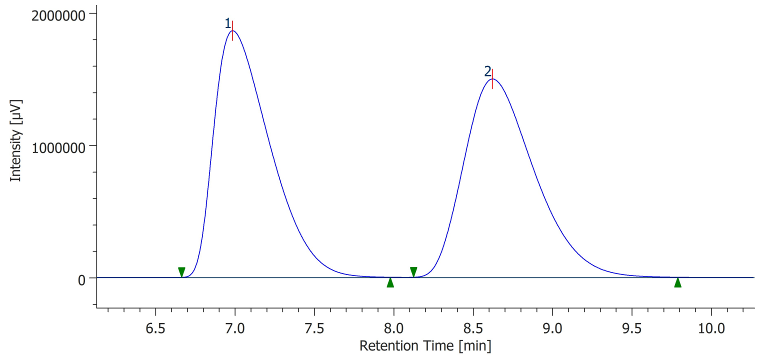
Figure S2. HPLC traces of racemic **1b**.



4-((1*R*,3*S*)-Adamantan-1-yl)-1-(adamantan-1-yl)-5-(3,3-bis(trifluoromethyl)-1λ³-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-1*H*-1,2,3-triazole (1c): Under an argon atmosphere, a two-necked flask equipped with a magnetic stir bar was charged with **SM-1c** (1.17 g, 3.1 mmol) and THF (31 mL). To the solution was added BuLi (1.54 M in hexane, 2.62 mL, 4.0 mmol) dropwise at –78 °C. The resulting mixture was warmed to –30 °C and stirred for 15 h (referred to as suspension A). In a separate two-necked flask equipped with a magnetic stirrer bar, CBX (2.51 g, 6.2 mmol) was dissolved in THF (6.2 mL) under an argon atmosphere and the mixture was cooled to –78 °C. Suspension A was added dropwise to this mixture through a cannula at –78 °C. The resulting mixture was stirred at this temperature for 1 h, warmed to –30 °C, and stirred for 22 h. The mixture was then warmed to room temperature and quenched with saturated NH_4Cl aq. After separation of the organic layer, the aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, followed by recrystallization (hexane/CH_2Cl_2) to afford the title compound **1c** as a white solid (1.18 g, 54%).

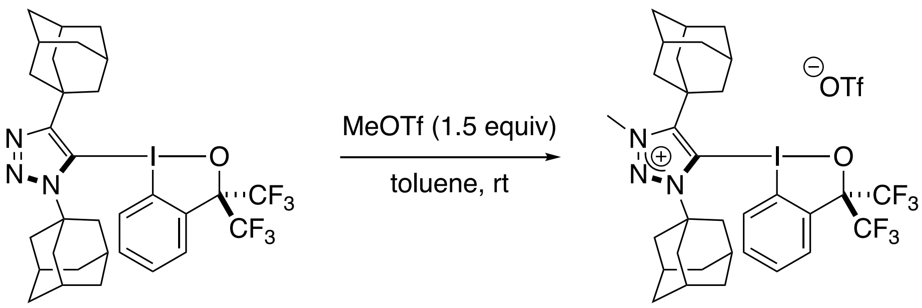
R_f 0.30 (hexane/EtOAc = 4/1); m.p. 198–200 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89–7.81 (m, 1H), 7.69–7.58 (m, 1H), 7.48 (t, J = 7.9 Hz, 1H), 6.56 (d, J = 8.4 Hz, 1H), 2.45–2.38 (m, 3H), 2.37–2.27 (m, 3H), 2.22–1.91 (m, 12H), 1.77–1.58 (m, 12H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 161.7, 132.6, 131.2, 131.1, 130.1, 127.3, 123.7 (q, $J_{C–F}$ = 289.7 Hz), 123.5 (q, $J_{C–F}$ = 291.5 Hz), 116.2, 101.5, 81.9–81.1 (m), 65.1, 43.0, 42.4, 36.3, 35.5, 35.2, 29.7, 28.4; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ –75.9 (q, $J_{F–F}$ = 8.3 Hz, 3F), –76.2 (q, $J_{F–F}$ = 8.5 Hz, 3F); **HRMS** (FAB) *m/z:* $[M+H]^+$ calcd for $C_{31}H_{35}F_6IN_3O$ 706.1724; found 706.1713; $[\alpha]_D^{25}$ +29.4 (*c* 0.22, $CHCl_3$, 99% ee), $[\alpha]_D^{25}$ –64.8 (*c* 0.18, $CHCl_3$, 99% ee); HPLC analysis: Daicel Chiralpak IH column (4.6 mm I.D. × 150 mm L; hexane:CH_2Cl_2 = 80/20, 1.0 mL/min, 25 °C, 250 nm).

Enantiomerically pure samples of **1c** were obtained on the milligram scale by repeated injections on an analytical chiral HPLC column (Daicel Chiralpak IH; the same conditions noted above). Although the separation capacity per injection is limited, the atropisomers elute with clean baseline separation, allowing straightforward collection of each enantiomer through multiple runs (typically ~1 mg per run). The combined fractions were then concentrated to give multi-milligram quantities of each atropisomer in high enantiomeric purity, which were then subjected to racemization and recognition experiments.



Peak	Ret. Time (min)	Area (%)
1	6.983	49.620
2	8.620	50.380

Figure S3. HPLC traces of racemic **1c**.

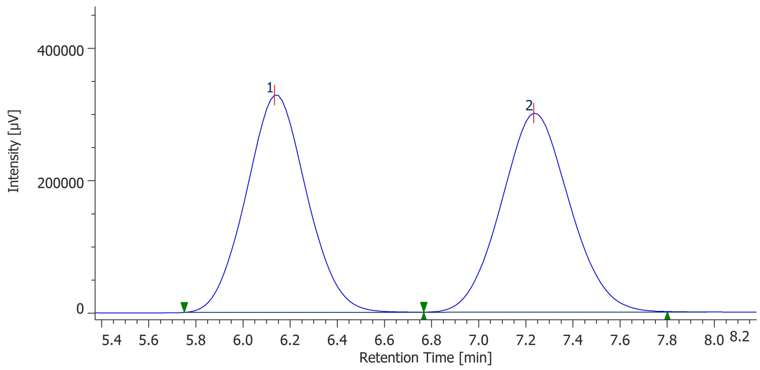


1c **2c**

1-((1*r*,3*R*)-Adamantan-1-yl)-4-((1*s*,3*S*)-adamantan-1-yl)-5-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-methyl-1*H*-1,2,3-triazol-3-ium trifluoromethanesulfonate (2c): Under an argon atmosphere, a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1c** (211.7 mg, 0.3 mmol) and toluene (2.4 mL). To the solution was added MeOTf (49.2 µL, 0.45 mmol) and the resulting mixture was stirred for 20 h. After completion of the reaction, the mixture was filtered and washed with toluene to afford the title compound **2c** as a white solid (240 mg, 92% yield).

R_f 0.50 (CH_2Cl_2/MeOH = 19/1); m.p. 189–191 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88–7.82 (m, 2H), 7.73 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 9.0 Hz, 1H), 4.59 (s, 3H), 2.58–2.51 (m, 3H), 2.44–2.38 (m, 3H), 2.37–2.31 (m, 3H), 2.29–2.21 (m, 6H), 2.11–2.05 (m, 3H), 1.79–1.63 (m, 12H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 152.8, 134.6, 131.8, 131.0, 130.0, 129.9, 123.4 (q, $J_{C–F}$ = 288.6 Hz), 123.3 (q, $J_{C–F}$ = 290.4 Hz), 120.6 (q, $J_{C–F}$ = 320.8 Hz), 116.9, 114.3, 82.6–81.9 (m), 73.1, 43.5, 41.9, 40.1, 37.0, 35.6, 35.1, 30.0, 27.8; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ –75.9 (q, $J_{F–F}$ = 8.1 Hz, 3F), –76.2 (q, $J_{F–F}$ = 8.4 Hz, 3F), –78.0 (s, 3F); **HRMS** (FAB) *m/z:* $[M]^+$ calcd for $C_{32}H_{37}F_6IN_3O$ 720.1880; found 720.1873; $[\alpha]_D^{25}$ +60.0 (*c* 0.06, $CHCl_3$, 99% ee), $[\alpha]_D^{25}$ –86.0 (*c* 0.11, $CHCl_3$, 99% ee); HPLC analysis: Daicel Chiralpak IC column (4.6 mm I.D. × 150 mm L; hexane:250 mM NaOTf in EtOH = 80/20, 1.0 mL/min, 25 °C, 250 nm).

Enantiomerically pure samples of **2c** were obtained on the milligram scale by repeated injections on an analytical chiral HPLC column (Daicel Chiralpak IC; the same conditions noted above). Although the separation capacity per injection is limited, the atropisomers elute with clean baseline separation, allowing straightforward collection of each enantiomer through multiple runs (typically ~1 mg per run). The combined fractions were then concentrated to give multi-milligram quantities of each atropisomer in high enantiomeric purity, which were then subjected to racemization and recognition experiments.



Peak	Ret. Time (min)	Area (%)
1	6.133	49.209
2	7.233	50.791

Figure S4. HPLC traces of racemic **2c**.

3. X-ray Crystallographic Analysis

X-ray crystal structure analysis of *rac*-1c

Single crystals of **1c** suitable for X-ray crystallography were obtained by recrystallization from THF/hexane. A suitable crystal was selected and mounted on a Rigaku Saturn CCD diffractometer. The crystal was kept at 153 K during data collection. Using ShelXle[7], the structure was solved with the SHELXS[8] structure solution program and refined with the SHELXL-2019/3[8] refinement package using Least Squares minimization. The asymmetric unit consists of a weakly associated dimer composed of two molecules, together with one solvent molecule. Because the two adamantyl groups inserted into the triazole ring have similar geometries, orientational disorder of the triazole units was observed. The atom on the disordered triazole ring, which could be modeled as either carbon or nitrogen, was refined the corresponding site occupancy with EXYZ and EADP constraints. The crystal structure contains disordered CH_2Cl_2 solvent molecules located around inversion center. The DSR program[9] was used to assign solvent molecules to the disordered part with restraints. Crystallographic data of *rac*-**1c** has been deposited on Cambridge Crystallographic Data Center, with deposition no. CCDC 2505927.

Table S1. Crystal data and structure refinements for 4-((1*R*,3*S*)-adamantan-1-yl)-1-(adamantan-1-yl)-5-(3,3-bis(trifluoromethyl)-1λ[3]-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-1*H*-1,2,3-triazole (*rac*-**1c**).

CCDC number	2505927
Empirical formula	$2(C_{31}H_{34}F_6IN_3O)\cdot CH_2Cl_2$
Formula weight	1495.95
Space system	Triclinic
Space group	$P\overline{1}$
a/Å	13.07355 (16)
b/Å	16.1140 (2)
c/Å	16.95238 (19)
α/°	63.4079 (12)
β/°	75.5952 (10)
γ/°	76.6091 (11)
Volume/Å^3	3063.17 (7)
Z	2
Temperature/K	153
2θ range for data collection/°	2.1 to 36.3
ρ_{calcd} g/cm^3	1.622
μ/mm^{-1}	1.20

F 000	1508
Crystal_size/mm^3	0.18 × 0.14 × 0.09
Radiation	Mo Kα
Reflections collected	106454
Independent	28351
Index ranges	−21≦h≦21, −26≦k≦26, −28≦l≦27
Data/restraints/parameters	28351/47/813
Final R indexes R [I>2σ(I)]gt	R_1 = 0.0392, wR_2 = 0.1055
Final R indexes R [all data]	R_1 = 0.0444, wR_2 = 0.1107
Goodness-of-fit on F^2	1.034
Largest peak/deepest hole eÅ^{-3}	2.82/−2.26
Absolute structure parameter	-

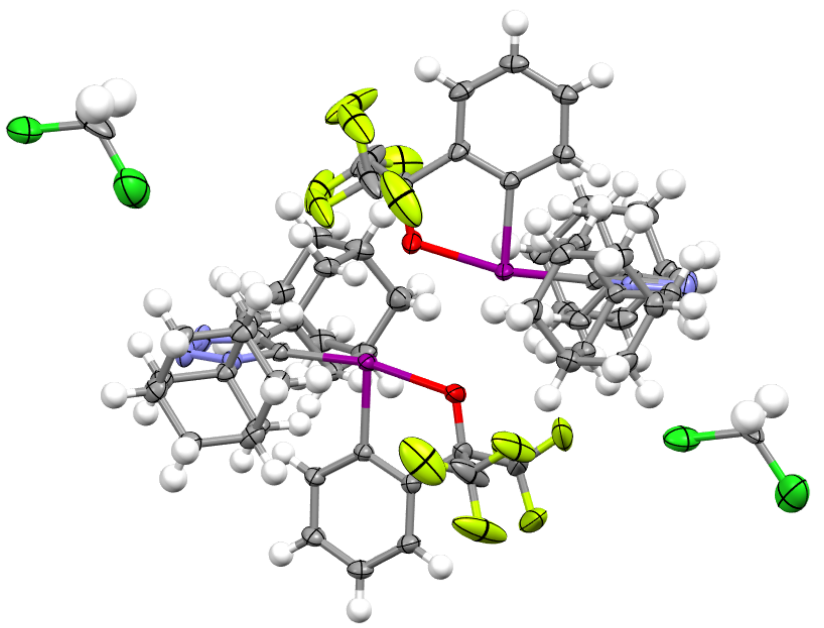


Figure S5. Thermal ellipsoid (50 % probability) plot of *rac*-**1c**, CCDC No. 2505927. Color code of atoms: hydrogen, white; carbon, gray; fluorine, yellow; iodine, purple; oxygen, red.

X-ray crystal structure analysis of *rac*-2c

Single crystals of **2c** suitable for X-ray crystallography were obtained by recrystallization from MeCN. A suitable crystal was selected and mounted on a Rigaku Saturn CCD diffractometer. The crystal was kept at 153 K during data collection. Using ShelXle, the structure was solved with the SHELXS structure solution program and refined with the SHELXL-2019/3 refinement package using Least Squares minimization. The crystal structure contains disordered trifluoromethanesulfonate molecule. The DSR program[9] was used to assign trifluoromethanesulfonate molecules to the disordered part with restraints. Although the crystal is a racemate, it adopts a polar structure, and the Flack parameter was refined as an inversion twin along the polar axis. Crystallographic data of *rac*-**2c** has been deposited on Cambridge Crystallographic Data Center, with deposition no. CCDC 2505926.

Table S2. Crystal data and structure refinements for 1-((1*r*,3*R*)-adamantan-1-yl)-4-((1*s*,3*S*)-adamantan-1-yl)-5-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-methyl-1*H*-1,2,3-triazol-3-ium trifluoromethanesulfonate (*rac*-**2c**).

CCDC number	2505926
Empirical formula	$C_{33}H_{37}F_9IN_3O_4S$
Formula weight	869.61
Space system	Orthorhombic
Space group	$Pna2_1$
a/Å	17.0458 (2)
b/Å	17.9934 (2)
c/Å	22.7406 (3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6974.81 (15)
Z	8
Temperature/K	153
2θ range for data collection/°	2.2 to 36.4
ρ_{calcd} g/cm^3	1.656
μ/mm^{-1}	1.07
F 000	3504
Crystal_size/mm^3	0.24 × 0.20 × 0.13
Radiation	Mo Kα

Reflections collected	193691,
Independent	33180
Index ranges	−28≦h≦27, −29≦k≦30, −37≦l≦37
Data/restraints/parameters	29336/541/995
Final R indexes R [I>2σ(I)]gt	R_1 = 0.0363, wR_2 = 0.0877
Final R indexes R [all data]	R_1 = 0.0428, wR_2 = 0.0914
Goodness-of-fit on F^2	1.053
Largest peak/deepest hole eÅ^{-3}	1.61/−1.19
Absolute structure parameter	0.209(10) Refined as an inversion twin

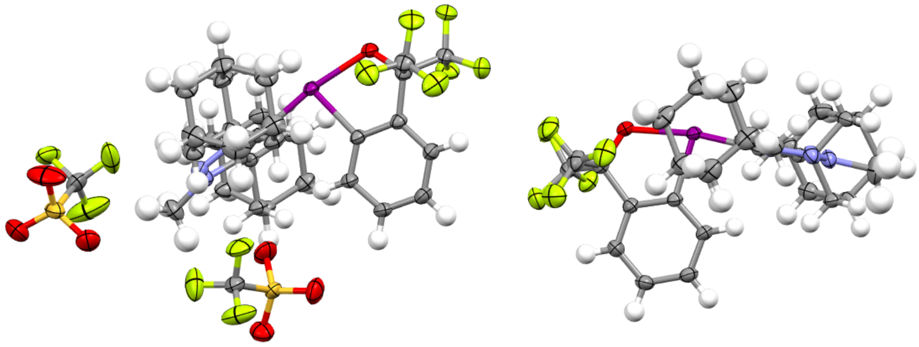


Figure S6. Thermal ellipsoid (50 % probability) plot of *rac*-**2c**, CCDC No. 2505926. Color code of atoms: hydrogen, white; carbon, gray; fluorine, yellow; iodine, purple; oxygen, red.

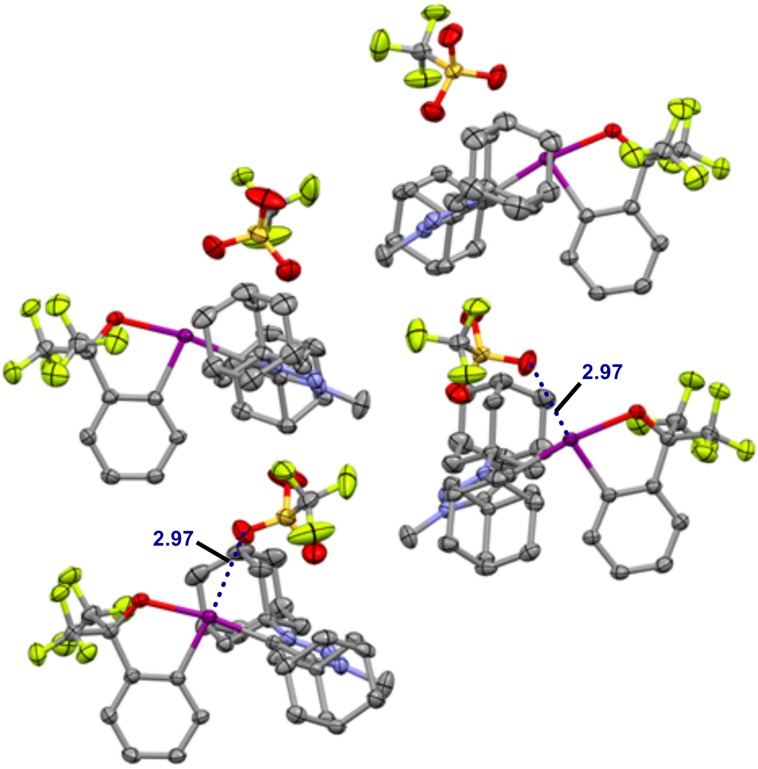


Figure S7. Packing structure of *rac*-**2c**. The triflate anion engages in a halogen-bonding interaction with the iodine center, forming a contact ion pair in which the anion occupies the σ-hole region opposite the C–I bond. The TfO⁻···I distance is 2.97 Å.

4. Variable-Temperature $^{19}F\{^1H\}$ NMR Study

The ^{19}F NMR spectra of a solution of compound **1a** in DMSO-d_6 were recorded at different temperatures until coalescence was reached to determine the rotational barriers around the C–I bond.[10] The coalescence temperature (T_c) was determined to be 115 °C (388.15 K), where the signals corresponding to the two CF_3 groups in compound **1a** merged into a single peak. From the frequency difference between the two signals of CF_3 groups when the exchange is slow ($\Delta\nu$), coupling constant (J), and T_c, the rotational barrier ($\Delta G^{\ddagger}_{rot}$), and racemization half-life ($t_{1/2}$ *rac*) at 25 °C (298.15 K) were calculated according to the following equations. The $\Delta G^{\ddagger}_{rot}$ value is reported to one decimal place. To ensure internal consistency, k_{ent} and $t_{1/2}$ *rac* at 25 °C were calculated using the rounded $\Delta G^{\ddagger}_{rot}$:

$$\Delta G^{\ddagger}_{rot} = RT_c \ln(\kappa k_B T / k_{ent} h)$$

$$t_{1/2}\, rac = \ln(2)/k_{rac}$$

Where:

$$k_{ent} \text{ at } T_c = \pi\sqrt{\frac{\Delta\nu^2 + 6J^2}{2}} = 362.4\ (s^{-1})$$

$\Delta\nu$ (frequency difference between the two signals when the exchange is slow) = 161.9 (Hz)

J (coupling constant) = 8.2 (Hz)

$k_{rac} = 2k_{ent}$

R (gas constant) = 8.31446 ($J \cdot K^{-1} \cdot mol^{-1}$)

T_c (coalescence temperature) = 388.15 (K)

T (temperature for half-life calculation) = 298.15 (K)

h (Planck's constant) = 6.626×10^{-34} ($J \cdot s$)

k_B (Boltzmann constant) = 1.381×10^{-23} ($J \cdot K^{-1}$)

κ (transmission coefficient) = 0.5

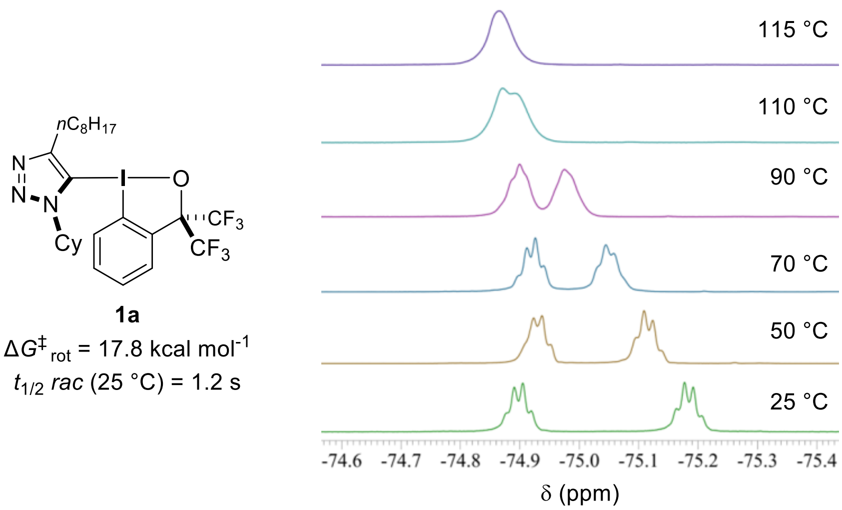


Figure S8. Variable temperature $^{19}F\{^1H\}$ NMR spectra of compound **1a** (565 MHz, DMSO-d_6).

5. Enantiomeric Excess Decay of Enantioenriched Samples

The enantiomers of compounds **1b, 1c,** and **2c** were separated using chiral HPLC. Each separated enantiomer was collected individually, and the solvent was removed under reduced pressure to obtain enantioenriched samples. The rotational barriers ($\Delta G^{\ddagger}_{\mathrm{rot}}$) of compounds **1b, 1c,** and **2c** were calculated by monitoring the decay of enantiomeric excess (ee) of the enantioenriched samples over time (t) by chiral HPLC[9]. To estimate the $\Delta G^{\ddagger}_{\mathrm{rot}}$ values, the $\ln(\mathrm{ee}_t/\mathrm{ee}_0)$ was plotted against t, and the data set was fitted linearly. The slopes of the resulting first-order kinetic line give the racemization constant ($k_{rac} = 2k_{ent}$) at the measured temperature. Using the following equations, the rotational barriers and racemization half-lives at 25 °C (298.15 K) were calculated. The $\Delta G^{\ddagger}_{\mathrm{rot}}$ values are reported to one decimal place. To ensure internal consistency, k_{ent} and $t_{1/2}\ rac$ at 25 °C were calculated using the rounded $\Delta G^{\ddagger}_{\mathrm{rot}}$:

$$\Delta G^{\ddagger}_{\mathrm{rot}} = RT\ln(\kappa k_B T/\ k_{ent} h)$$

$$\ln(\mathrm{ee}_t/\mathrm{ee}_0) = -k_{rac} t$$

$$t_{1/2}\ rac = \ln(2)/k_{rac}$$

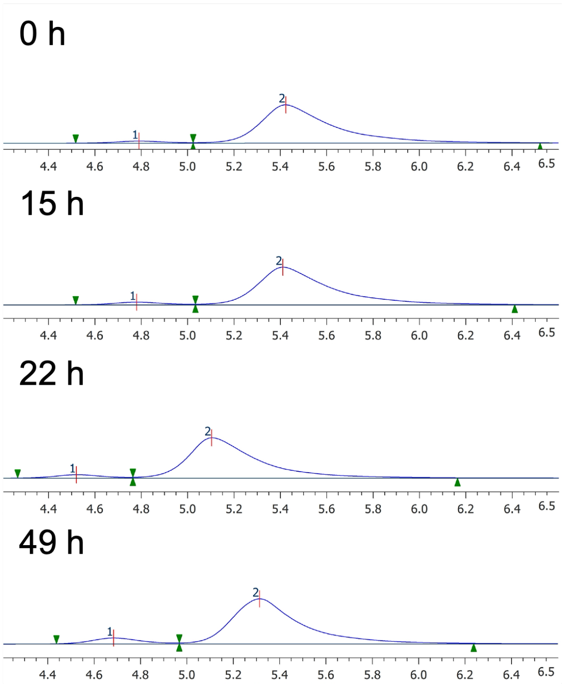
Where:

ee_t is the enantiomeric excess at time t

ee_0 is the initial enantiomeric excess

For compound **1b**:

Enantioenriched **1b** was dissolved in CH_2Cl_2 in a screw-cap vial and maintained at room temperature. The ee values were monitored at predetermined time intervals by chiral HPLC analysis, and the $\ln(ee_t/ee_0)$ values were plotted against time to determine the racemization rate constant at the measurement temperature (Figure S9). From this rate constant, the rotational barrier $\Delta G^{\ddagger}_{rot}$ and racemization half-life at 25 °C were calculated.



ee (%)	time (h)	time (s)
92.9	0	0
90.1	15	54000
88.7	22	79200
82.5	49	176400

$\Delta G^{\ddagger}_{rot}$ = 25.9 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 12.5 days

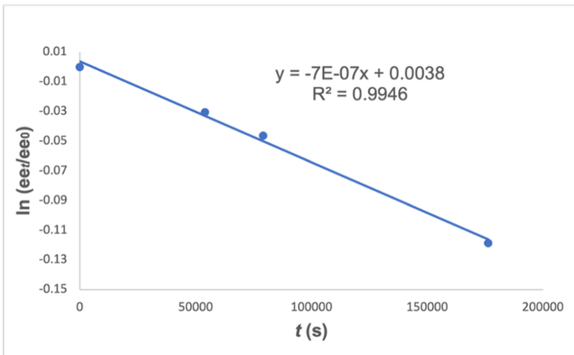
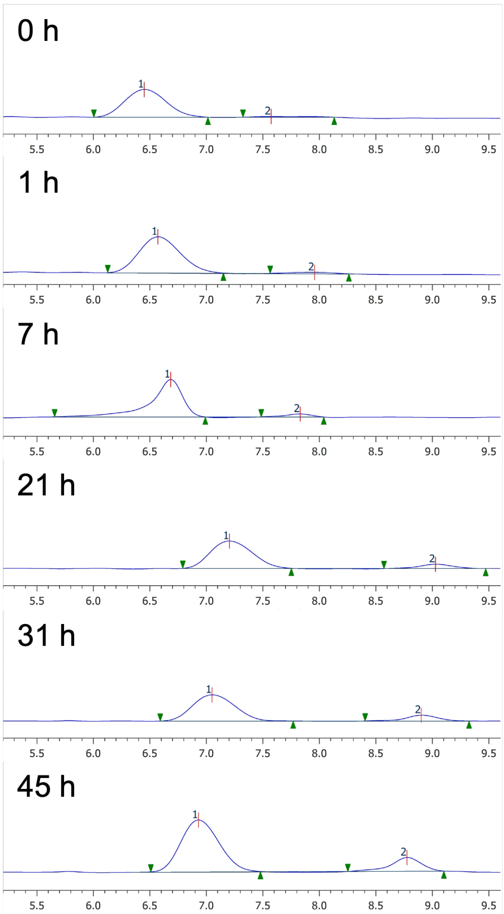


Figure S9. Enantiomeric excess (ee) decay of enantioenriched **1b** over time in CH_2Cl_2 at rt monitored by chiral HPLC (Chiralpak ID, hexane:*i*PrOH = 97/3, 1.0 mL/min, 25 °C, 220 nm) and plot of $\ln(ee_t/ee_0)$ against time.

For compound **1c** and **2c**:

Enantioenriched **1c** (2.0 mg) and **2c** (2.0 mg) were individually dissolved in chlorobenzene (2.0 mL) and maintained at 70 °C. At predetermined time intervals, an aliquot of each solution was transferred to a screw cap vial, diluted with CH_2Cl_2, and the enantiomeric excess was determined by chiral HPLC analysis (Figures S10 for **1c** and S11 for **2c**). For each compound, the recorded time points and the corresponding ln(ee_t/ee_0) values were plotted to determine racemization rate constants at the measurement temperature. From these rate constants, the rotational barriers $\Delta G^{\ddagger}_{rot}$ and racemization half-lives at 25 °C were calculated.



ee (%)	time (h)	time (s)
93.2	0	0
91.9	1	3600
87.4	7	25200
78.3	21	75600
71.2	31	111600
65.0	45	162000

$\Delta G^{\ddagger}_{rot}$ = 29.1 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 7.6 years

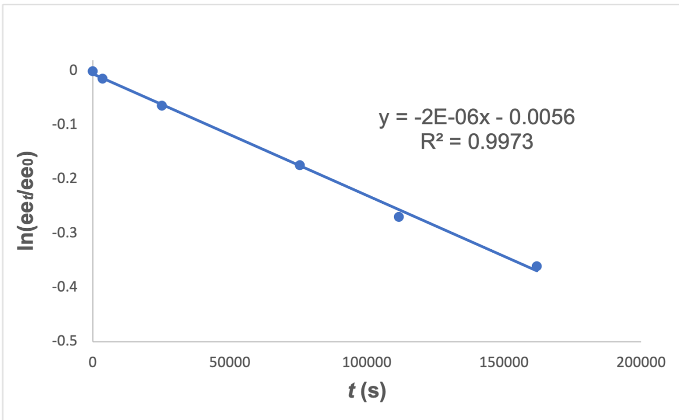
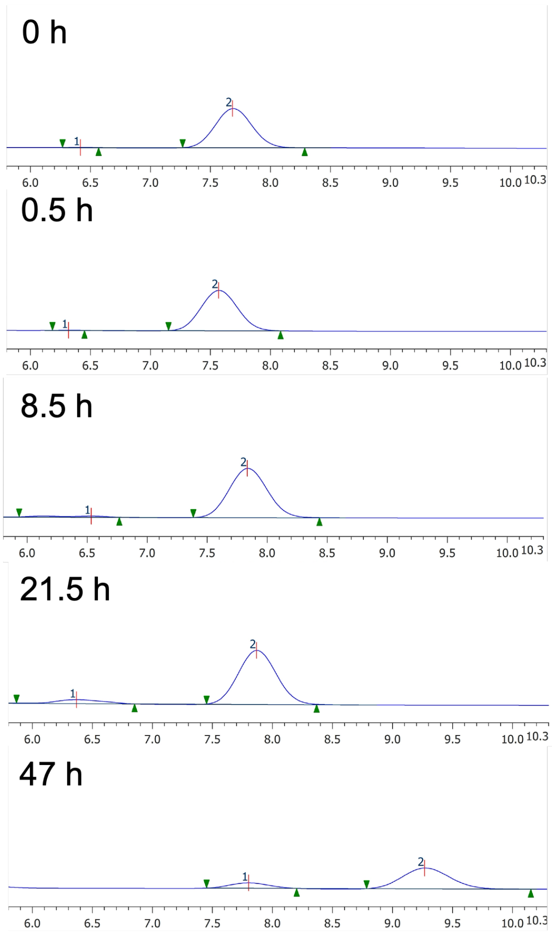


Figure S10. Enantiomeric excess (ee) decay of enantioenriched **1c** over time in chlorobenzene at 70 °C monitored by chiral HPLC (Chiralpak IH, hexane:CH_2Cl_2 = 80/20, 1.0 mL/min, 25 °C, 240 nm) and plot of ln(ee_t/ee_0) against time.



ee (%)	time (h)	time (s)
99.5	0	0
99.2	0.5	1800
93.2	8.5	30600
83.8	21.5	77400
65.2	47	169200

$\Delta G^{\ddagger}_{rot}$ = 29.0 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 6.4 years

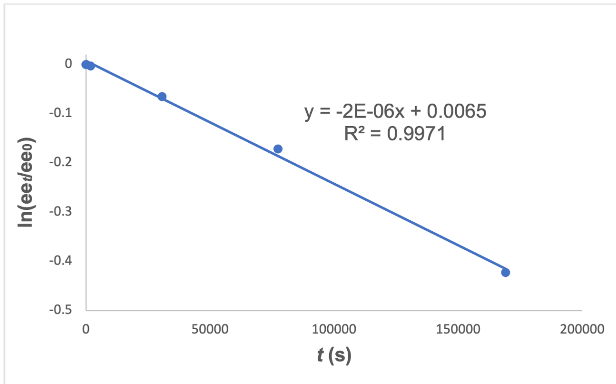


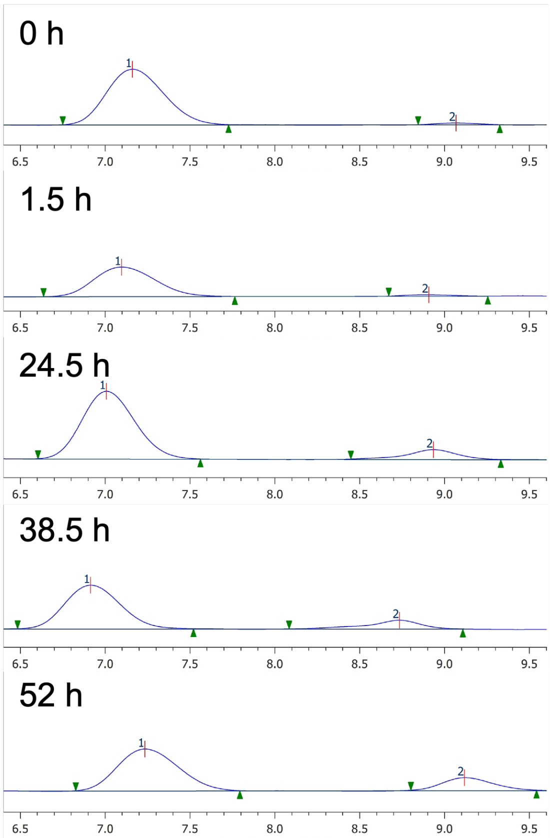
Figure S11. Enantiomeric excess (ee) decay of enantioenriched **2c** over time in chlorobenzene at 70 °C monitored by chiral HPLC (Chiralpak IC, hexane:250 mM NaOTf in EtOH = 80/20, 1.0 mL/min, 25 °C, 240 nm) and plot of ln(ee_t/ee_0) against time.

Solvent- and additive-responsive racemization kinetics of 1c

The racemization kinetics of enantiomerically enriched **1c** were studied under various solvent conditions and in the presence of different additives.

a) Solvent Effect on Racemization

Enantioenriched **1c** (2.0 mg) was dissolved separately in toluene, THF, Et_3N, AcOH (2.0 mL each) in individual vials, and the solutions were maintained at the indicated temperature. At predetermined time intervals, an aliquot of each solution was transferred to a screw cap vial, diluted with CH_2Cl_2, and the enantiomeric excess was determined by chiral HPLC analysis (Figures S12–S15). The recorded time points and the corresponding $\ln(ee_t/ee_0)$ values were plotted to determine racemization rate constants at the measurement temperature. From these rate constants, the rotational barriers $\Delta G^{\ddagger}_{rot}$ and racemization half-lives at 25 °C were calculated.



ee (%)	time (h)	time (s)
95.8	0	0
93.1	1.5	5400
75.1	24.5	88200
67.3	38.5	138600
58.8	52	187200

$\Delta G^{\ddagger}_{rot}$ = 29.0 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 6.4 years

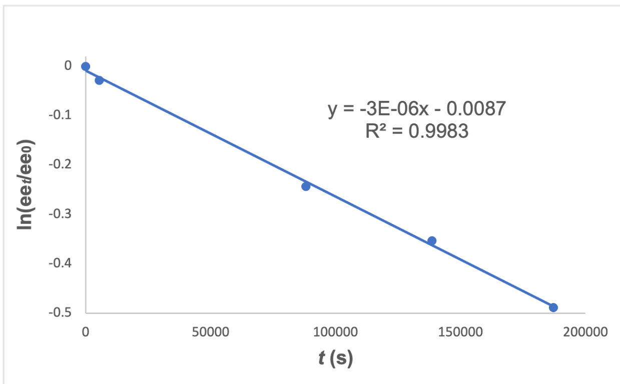
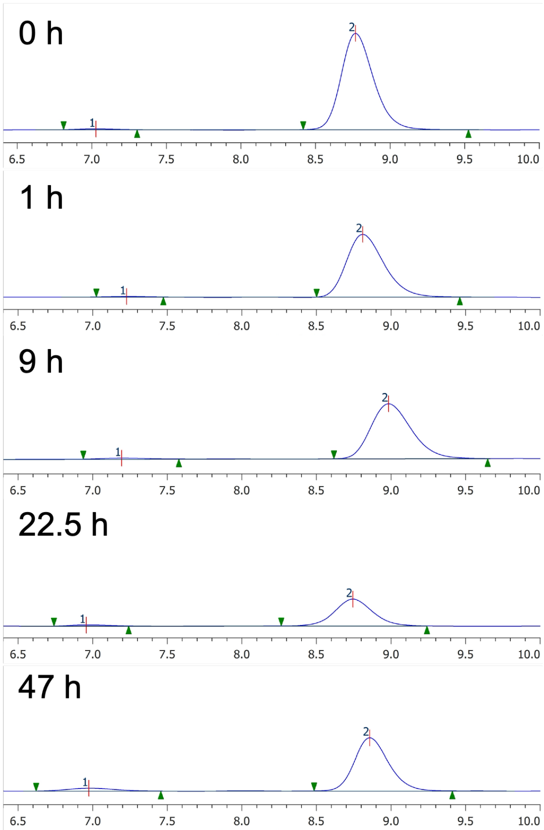


Figure S12. Enantiomeric excess (ee) decay of enantioenriched **1c** over time in toluene at 70 °C monitored by chiral HPLC (Chiralpak IH, hexane:CH_2Cl_2 = 80/20, 1.0 mL/min, 25 °C, 240 nm) and plot of $\ln(ee_t/ee_0)$ against time.



ee (%)	time (h)	time (s)
98.0	0	0
97.8	1	3600
95.2	9	32400
91.7	22.5	81000
85.5	47	169200

$\Delta G^{\ddagger}_{rot}$ = 29.3 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 10.6 years

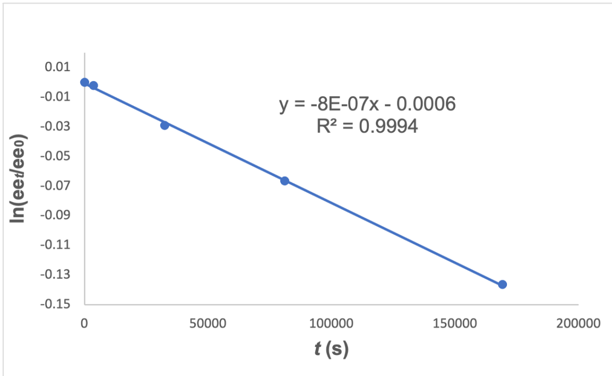
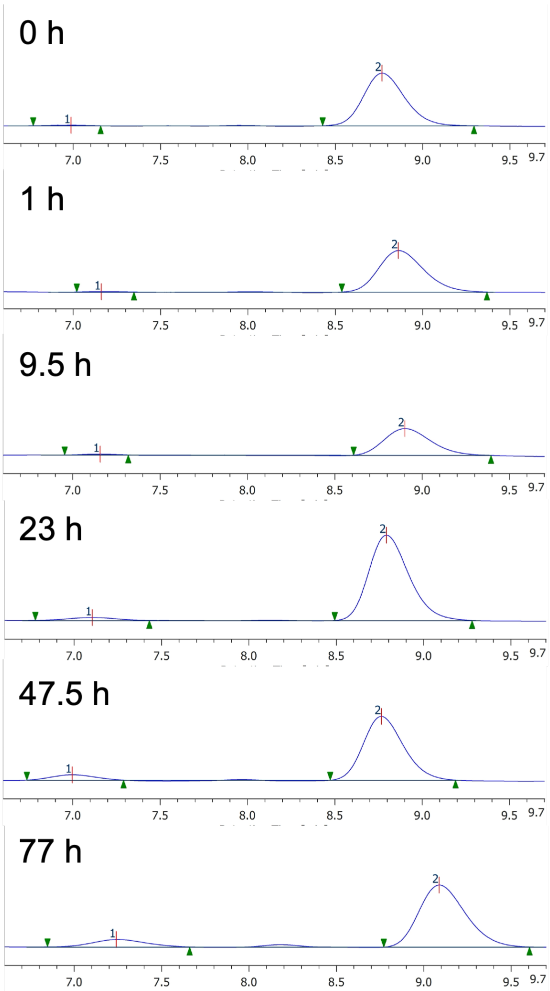


Figure S13. Enantiomeric excess (ee) decay of enantioenriched **1c** over time in THF at 65 °C monitored by chiral HPLC (Chiralpak IH, hexane:CH_2Cl_2 = 80/20, 1.0 mL/min, 25 °C, 240 nm) and plot of ln(ee$_t$/ee$_0$) against time.



ee (%)	time (h)	time (s)
98.0	0	0
97.7	1	3600
95.2	9	32400
91.7	22.5	81000
83.6	47	169200
75.8	77	277200

$\Delta G^{\ddagger}_{rot}$ = 29.2 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 9.0 years

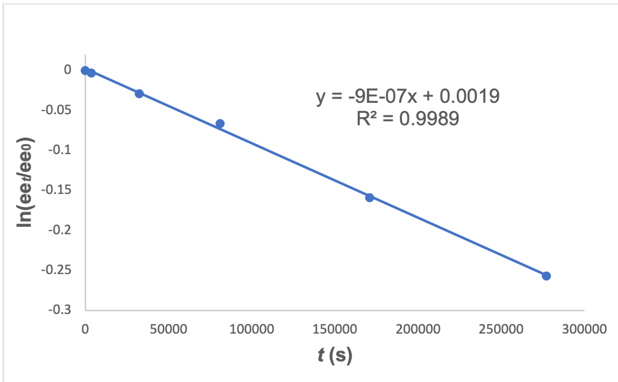
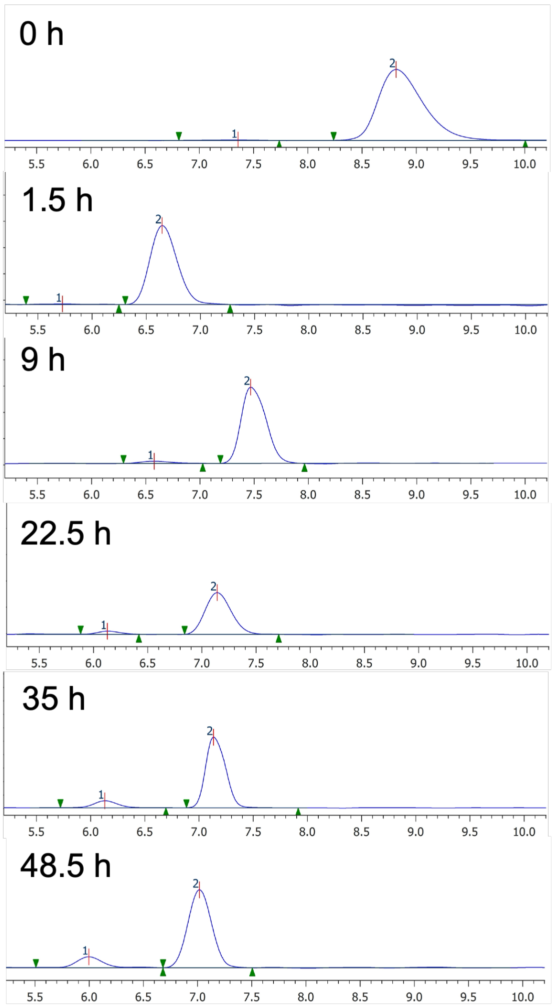


Figure S14. Enantiomeric excess (ee) decay of enantioenriched **1c** over time in Et_3N at 65 °C monitored by chiral HPLC (Chiralpak IH, hexane:CH_2Cl_2 = 80/20, 1.0 mL/min, 25 °C, 260 nm) and plot of $\ln(ee_t/ee_0)$ against time.



ee (%)	time (h)	time (s)
98.8	0	0
97.1	1.5	5400
93.3	9	32400
87.0	22.5	81000
77.7	35	126000
72.9	48.5	174600

$\Delta G^{\ddagger}_{rot}$ = 25.3 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 4.5 days

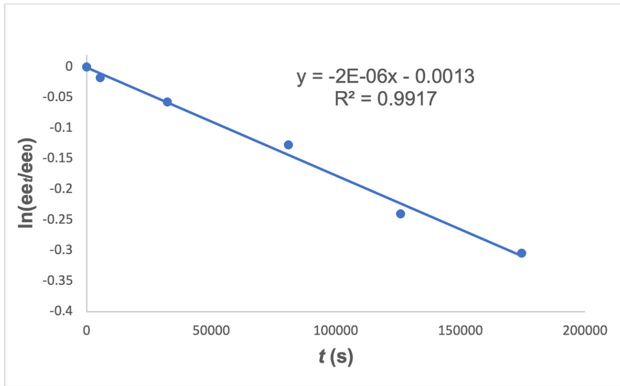
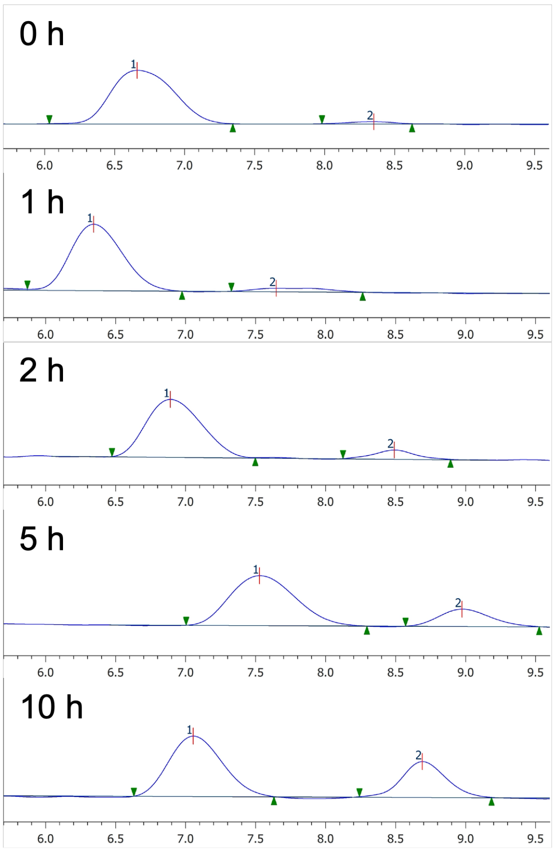


Figure S15. Enantiomeric excess (ee) decay of enantioenriched **1c** over time in AcOH at rt monitored by chiral HPLC (Chiralpak IH, hexane:CH_2Cl_2 = 80/20, 1.0 mL/min, 25 °C, 250 nm) and plot of ln(ee_t/ee_0) against time.

b) Additive Effect on Racemization

To a solution of enantioenriched **1c** (2.0 mg) in toluene (2.0 mL), TFA (1 equiv) was added, and the solution was kept at room temperature. At predetermined time intervals, an aliquot of each solution was transferred to a screw cap vial, diluted with CH_2Cl_2, and the enantiomeric excess was determined by chiral HPLC analysis (Figure S16). The time points and the corresponding ee erosions were plotted to determine racemization rate constants at the measurement temperature. From these rate constants, the rotational barriers $\Delta G^{\ddagger}_{rot}$ and racemization half-lives at 25 °C were calculated.



ee (%)	time (h)	time (s)
94.1	0	0
86.1	1	3600
78.6	2	7200
57.1	5	18000
33.8	10	36000

$\Delta G^{\ddagger}_{rot}$ = 23.6 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 6.2 h

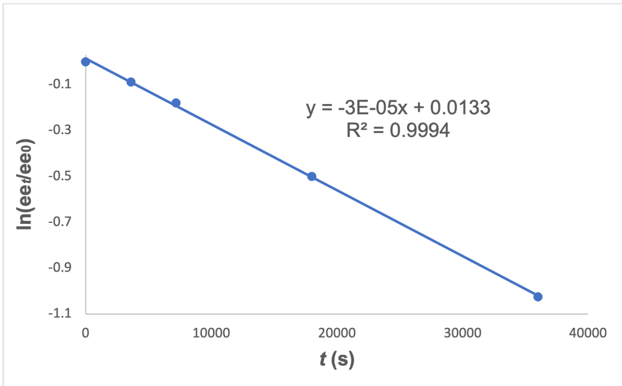


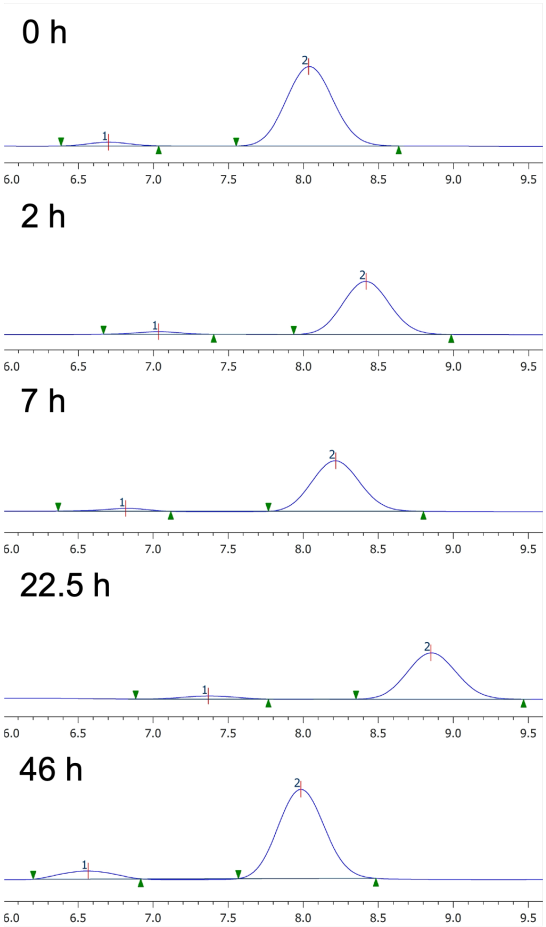
Figure S16. Enantiomeric excess (ee) decay of enantioenriched **1c** over time in toluene with TFA (1 equiv) at rt monitored by chiral HPLC (Chiralpak IH, hexane:CH_2Cl_2 = 80/20, 1.0 mL/min, 25 °C, 250 nm) and plot of ln(ee_t/ee_0) against time.

Solvent- and additive-responsive racemization kinetics of 2c

The racemization kinetics of enantiomerically enriched **2c** were studied under various solvent conditions and in the presence of different additives.

a) Solvent Effect on Racemization

Enantioenriched **2c** (2.0 mg) was dissolved separately in THF, AcOH (2.0 mL each) in a vial, and the solution was maintained the indicated temperature. At predetermined time intervals, an aliquot of the solution was transferred to a screw cap vial, diluted with CH_2Cl_2, and the enantiomeric excess was determined by chiral HPLC analysis (Figures S17 and S18). The recorded time points and the corresponding $\ln(ee_t/ee_0)$ values were plotted to determine racemization rate constants at the measurement temperature. From these rate constants, the rotational barriers $\Delta G^{\ddagger}_{rot}$ and racemization half-lives at 25 °C were calculated.



ee (%)	time (h)	time (s)
91.9	0	0
91.7	2	7200
90.6	7	25200
87.3	22.5	81000
81.7	46	165600

$\Delta G^{\ddagger}_{rot}$ = 28.9 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 5.4 years

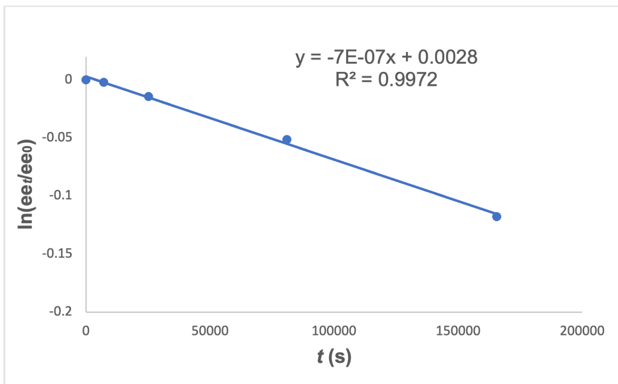
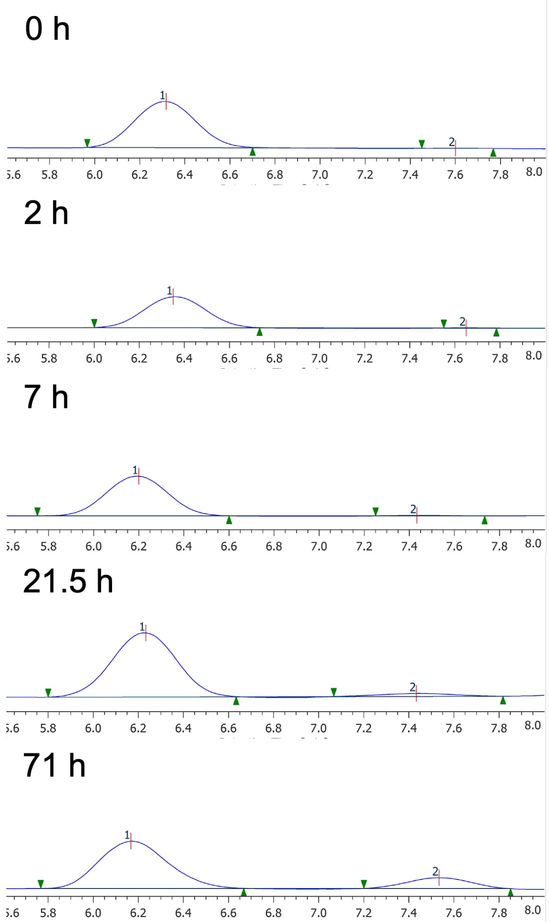


Figure S17. Enantiomeric excess (ee) decay of enantioenriched **2c** over time in THF at 60 °C monitored by chiral HPLC (Chiralpak IC, hexane:250 mM NaOTf in EtOH = 80/20, 1.0 mL/min, 25 °C, 250 nm) and plot of $\ln(ee_t/ee_0)$ against time.



ee (%)	time (h)	time (s)
99.6	0	0
99.6	2	7200
97.6	7	25200
89.8	21.5	77400
65.1	71	255600

$\Delta G^{\ddagger}_{rot}$ = 27.5 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 0.51 years

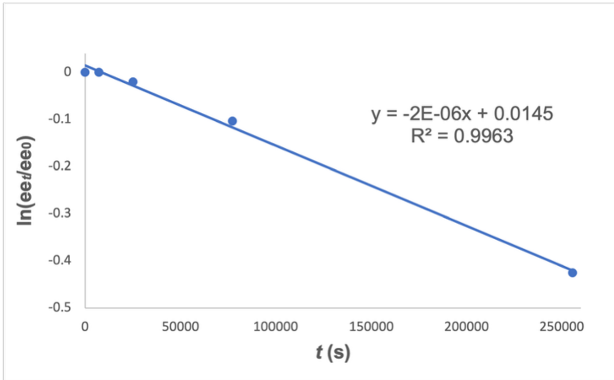
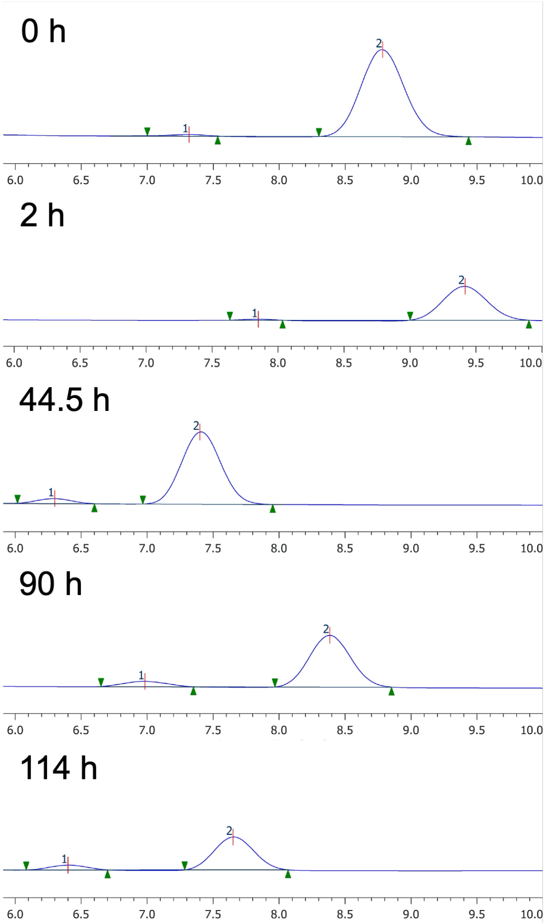


Figure S18. Enantiomeric excess (ee) decay of enantioenriched **2c** over time in AcOH at 50 °C monitored by chiral HPLC (Chiralpak IC, hexane:250 mM NaOTf in EtOH = 80/20, 1.0 mL/min, 25 °C, 240 nm) and plot of ln(ee$_t$/ee$_0$) against time.

b) Additive Effect on Racemization

To a solution of enantioenriched **2c** (2.0 mg) in chlorobenzene (2.0 mL), the additive (1 equiv each) was added in separate experiments. The solutions were maintained at 60 °C. At predetermined time intervals, an aliquot of each solution was transferred to a screw cap vial, diluted with CH_2Cl_2, and the enantiomeric excess was determined by chiral HPLC analysis (Figure S19 and S20). The time points and the corresponding ee erosions were plotted to determine racemization rate constants at the measurement temperature. From these rate constants, the rotational barriers $\Delta G^{\ddagger}_{rot}$ and racemization half-lives at 25 °C were calculated.



ee (%)	time (h)	time (s)
97.0	0	0
96.2	2	7200
88.5	44.5	160200
80.6	90	324000
75.9	114	410400

$\Delta G^{\ddagger}_{rot}$ = 29.1 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 7.6 years

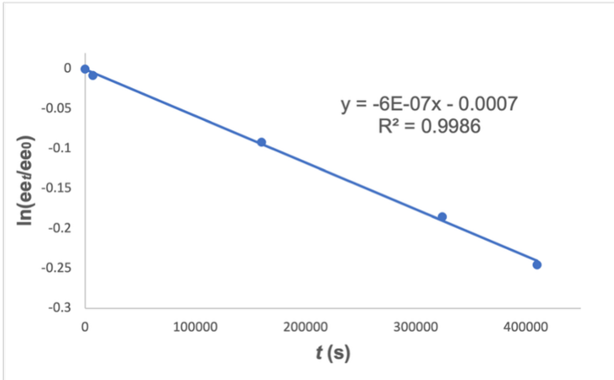
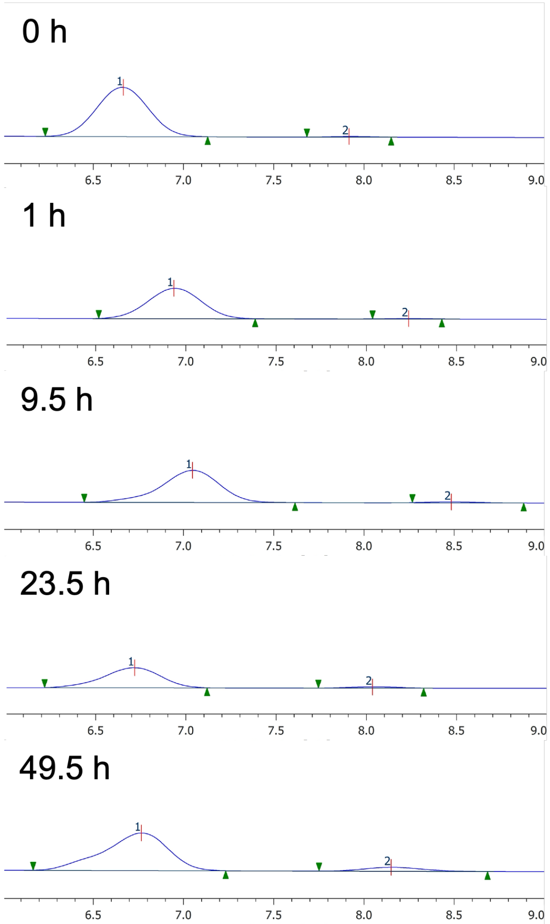


Figure S19. Enantiomeric excess (ee) decay of enantioenriched **2c** over time in toluene with pyridine (1 equiv) at 60 °C monitored by chiral HPLC (Chiralpak IC, hexane:250 mM NaOTf in EtOH = 80/20, 1.0 mL/min, 25 °C, 240 nm) and plot of ln(ee$_t$/ee$_0$) against time.



ee (%)	time (h)	time (s)
98.1	0	0
97.5	1	3600
94.8	9.5	34200
90.4	23.5	84600
82.5	49.5	178200

$\Delta G^{\ddagger}_{rot}$ = 28.7 kcal mol^{-1}

$t_{1/2}$ *rac* (25 °C) = 3.9 years

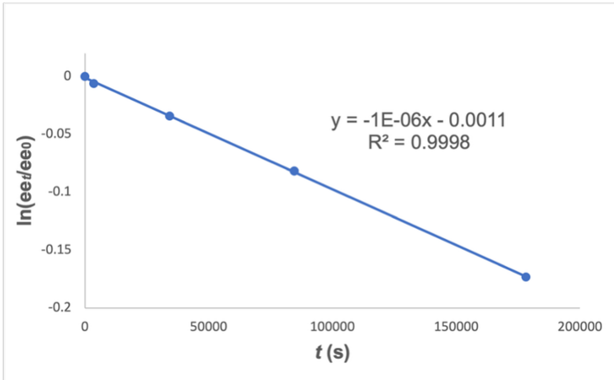


Figure S20. Enantiomeric excess (ee) decay of enantioenriched **2c** over time in toluene with TFA (1 equiv) at 60 °C monitored by chiral HPLC (Chiralpak IC, hexane:250 mM NaOTf in EtOH = 80/20, 1.0 mL/min, 25 °C, 240 nm) and plot of ln(ee$_t$/ee$_0$) against time.

6. Chiral Recognition Experiments

(a) NMR experiments with **1c** and (*R*)-BINOL

To an NMR tube, compound **1c** ((+)-**1c**, (–)-**1c**, or *rac*-**1c**; 7.1 mg, 0.01 mmol) and (*R*)-[1,1'-binaphthalene]-2,2'-diol ((*R*)-BINOL: 14.3 mg, 5.0 equiv) were dissolved in toluene-d_8 (0.5 mL). The $^{19}F\{^1H\}$ NMR spectrum of the resulting solution was then recorded.

(b) NMR experiments with **2c** and (*R*)-CPA–Na

To an NMR tube, compound **2c** ((+)-**2c**, (–)-**2c**, or *rac*-**2c**; 8.7 mg, 0.01 mmol) and sodium (*R*)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-olate 4-oxide ((*R*)-CPA–Na: 18.5 mg, 5.0 equiv) were dissolved in $CDCl_3$ (0.5 mL). The $^{19}F\{^1H\}$ NMR spectrum of the resulting solution was then recorded.

(c) Additional NMR experiments

An experiment using *rac*-**2c** (8.7 mg, 0.01 mmol) or *rac*-**3** (6.9 mg, 0.01 mmol) with (*R*)-BINOL (14.3 mg, 5.0 equiv) in $CDCl_3$ or toluene-d_8 (0.5 mL) showed the formation of diastereomeric complexes; however, peak overlap hindered effective chiral discrimination (Figure S21). In contrast, an experiment using *rac*-**1c** (7.1 mg, 0.01 mmol) and (*R*)-CPA–Na (18.5 mg, 5.0 equiv) in $CDCl_3$ (0.5 mL) caused no discernible change in the CF_3 quartet pattern, indicating the absence of measurable chiral discrimination.

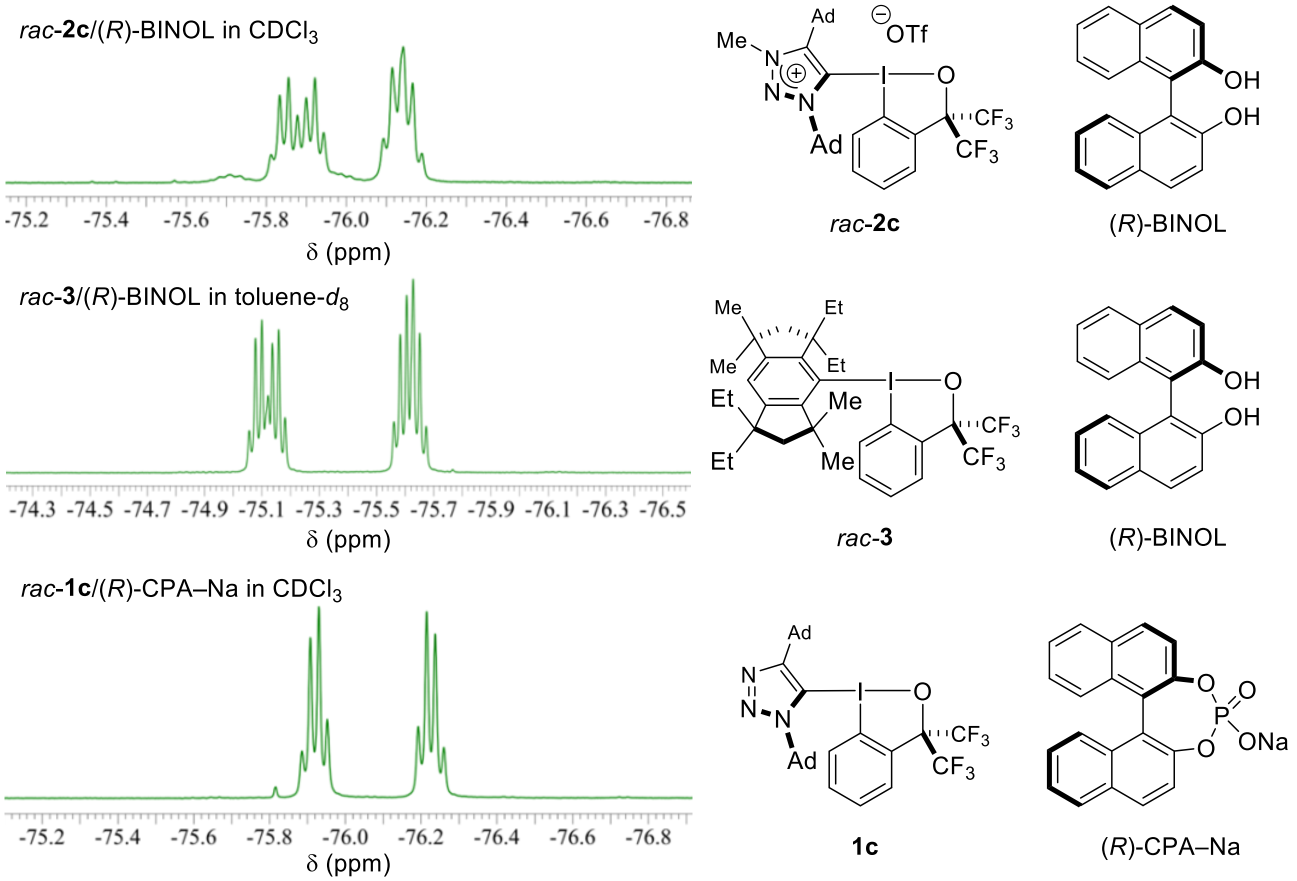


Figure S21. $^{19}F\{^1H\}$ NMR spectra of additional chiral recognition experiments.

7. Evaluation of Halogen-Bond Strength by $^{31}P\{^1H\}$ NMR Spectroscopy

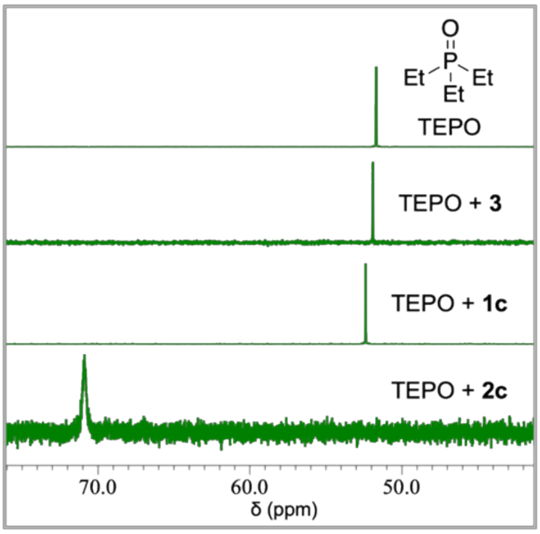
The halogen-bonding abilities of compounds **1c** and **2c** were evaluated using the $^{31}P\{^1H\}$ NMR spectroscopic method[11]. In this approach, a Lewis basic phosphine oxide interacts with a halogen bonding donor at the phosphoryl oxygen, altering the electronic environment around the phosphorus atom. This interaction results in a characteristic downfield shift of the ^{31}P NMR spectrum, and the magnitude of this shift ($\Delta\delta$) serves as a qualitative indicator of halogen-bonding strength.

Experimental procedure: To an NMR tube, triethylphosphine oxide (TEPO, 1.4 mg, 0.01 mmol) and **1c** or **2c** (0.1 mmol, 10 equiv) were dissolved in CD_2Cl_2 (0.5 mL). The ^{31}P NMR spectra (16 scans) were immediately recorded at room temperature. A reference ^{31}P NMR spectrum of TEPO alone (0.01 mmol in 0.5 mL CD_2Cl_2) was also recorded under identical conditions. For each BX compound, two independent measurements were performed, and the averaged chemical-shift change ($\Delta\delta$) was used for analysis. The $\Delta\delta$ values were calculated according to the following equation:

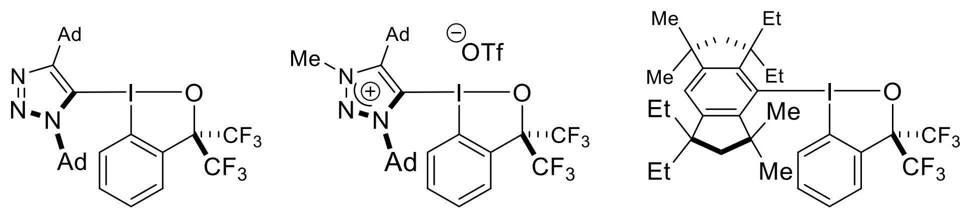
$$\Delta\delta = \delta_{obs} - \delta_0$$

where δ_0 is the ^{31}P chemical shift of free TEPO and δ_{obs} is the chemical shift observed in the presence of the BX compound.

A pronounced downfield shift was observed for **2c**, whereas **1c** and **3** induced only minimal changes in the ^{31}P chemical shift. These results indicate that **2c** behaves as a significantly stronger halogen-bond donor than the other BX derivatives examined.



compound	$\Delta\delta(^{31}P)$ (ppm) trial 1	$\Delta\delta(^{31}P)$ (ppm) trial 2	$\Delta\delta(^{31}P)$ (ppm) avg.
1c	0.70	0.50	0.60
2c	19.2	20.0	19.6
3	0.22	0.22	0.22



1c **2c** **3**

Figure S22. $^{31}P\{^1H\}$ NMR chemical shift changes ($\Delta\delta$) of triethylphosphine oxide (TEPO) in the presence of BX compounds.

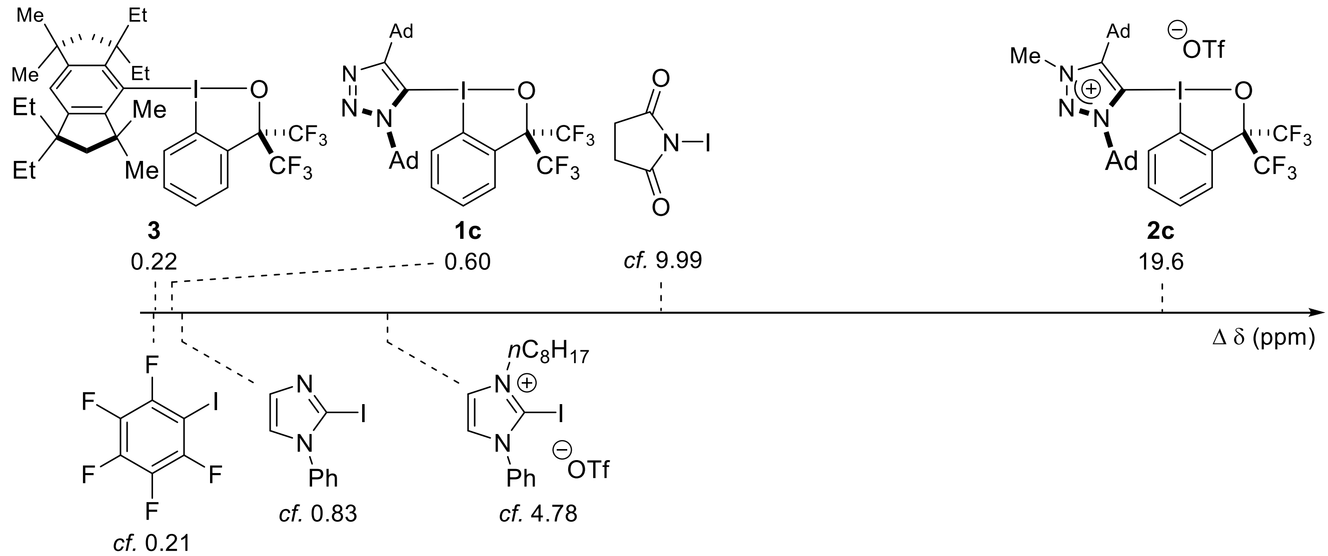


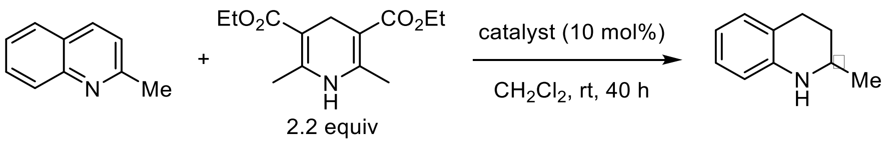
Figure S23. Comparison of $^{31}P\{^{1}H\}$ NMR chemical shift changes (Δδ) of TEPO in the presence of various halogen bonding donors.

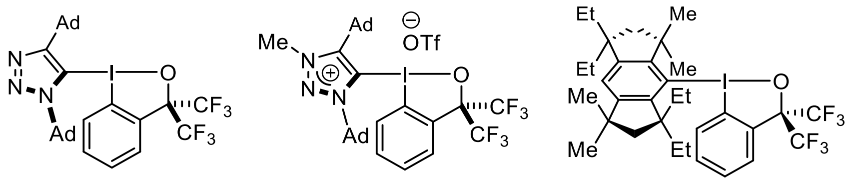
8. Attempted Application as Halogen-Bond Catalyst

Reduction of 2-methylquinoline with Hantzsch ester in the presence of chiral iodine compounds

Experimental procedure (Table S3, entry 2): Under an argon atmosphere, a 4 ml vial equipped with a magnetic stir bar was charged with 2-methylquinoline (14.3 mg, 0.10 mmol), Hantzsch ester (55.7 mg, 0.22 mmol), (+)-**2c** (8.7 mg, 0.01 mmol), and CH_2Cl_2 (1.4 mL). The mixture was stirred at room temperature for 40 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel to afford 2-methyl-1,2,3,4-tetrahydroquinoline as a white solid (11.0 mg, 75% yield).

Table S3. Reduction of 2-methylquinoline with Hantzsch ester in the presence of chiral iodine compounds.





entry	catalyst	yield (%)	%ee
1	(+)-**1c**	23	1
2	(+)-**2c**	75	2
3	(*S*)-**3**	15	0

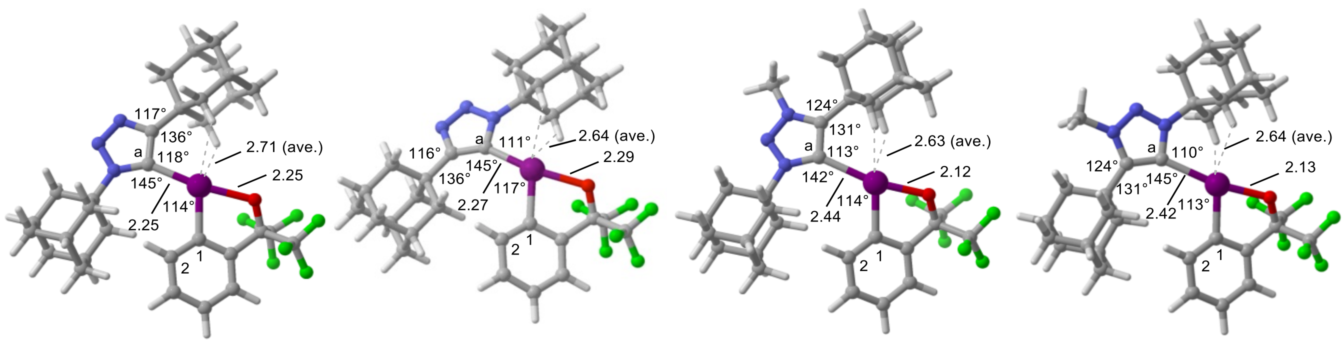
[a] Isolated yields. [b] Determined by HPLC analysis on a chiral stationary phase.

9. DFT Calculation

All the density functional theory (DFT) calculations were performed with the Gaussian 16 program[12]. Geometry optimizations were performed with the M06-2X functional[13-15] and a combined basis set B1 (i.e. the SDD effective core potential[16] for iodine, the 6-31+G(d,p) basis set for all other atoms). Harmonic frequency calculations were performed for each stationary point to ensure that it is either an energy minimum (no imaginary frequency) or a transition state (only one imaginary frequency). For each transition state, intrinsic reaction coordinate (IRC)[17] analysis was performed to ensure that it connects the correct reactant and product. The single-point energy calculations were further performed with the M06-2X functional and a combined basis set B2 (i.e., the SDD effective core potential for iodine, the 6-311+G(2df,2p) basis set for all other atoms). The SMD model[18] with toluene as the solvent was used for all the calculations. The single-point energies corrected by the thermal correction to Gibbs free energies (TCG, obtained from frequency calculations) were used as the Gibbs free energies reported in this work, corresponding to the reference state of 1 mol/L, 298.15 K. The optimized structures are visualized using CYLView 2.0[19].

Geometric Features of the C–I Rotational Transition States in 1c and 2c

For triazole–BX **1c**, the two rotational pathways show clear geometric and energetic differentiation. The clockwise pathway (**TS1cR**) features a larger dihedral distortion (∠C^a–I–C^1–C^2= –43.6° vs. –29.0° in **TS1cL**) and a more pronounced C–I–C bending (117° vs. 114° in **TS1cL**), consistent with its greater activation barrier (36.8 vs. 31.6 kcal mol^{-1}). In contrast, triazolium–BX **2c** displays no significant geometric differentiation between its two rotational pathways. Both transition states display similar dihedral twists and bond-angle changes, giving rise to nearly degenerate activation barriers.



C^a–I–C^1–C^2 = -29.0° **TS1cL** (31.6)

C^a–I–C^1–C^2 = -43.6° **TS1cR** (36.8)

C^a–I–C^1–C^2 = -29.7° **TS2cL** (31.4)

C^a–I–C^1–C^2 = -27.4° **TS2cR** (32.0)

Figure S24. Structures of the transition states of C–I bond rotation of (*S*)-**1c** and (*S*)-**2c**.

Analysis of the rotational barrier of triazole–BX (1c) under N-Protonation

The effect of N-activation of the triazole on the C–I rotational barrier of triazole–BX **1c** was examined using a bare-protonated model (Figure S25). Protonation at N(3) lowers both rotational pathways: the counterclockwise barrier decreases from 31.6 kcal mol^{-1} (**TS1cL**) to 28.6 kcal mol^{-1} (**TS1cL-H$^+$**), and the clockwise barrier from 36.8 kcal mol^{-1} (**TS1cR**) to 28.9 kcal mol^{-1} (**TS1c R-H$^+$**). Structural analysis shows that N-protonation lengthens the C–I bond but leaves the N(3)–C(4)–Ad angle essentially unchanged, indicating that no steric buttressing is introduced. This behavior is in sharp contrast to the N-methylated analogue **2c**, where the N-methyl substituent pushes the adamantyl group toward the iodine center, increasing local steric congestion and raising the rotational barrier.

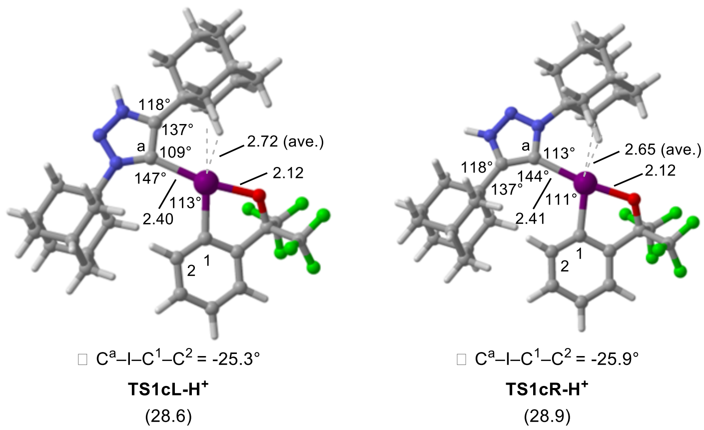


Figure S25. Transition-state structures for C–I bond rotation of N(3)-protonated triazole–BX (**TS1cL-H$^+$** and **TS1cR-H$^+$**), with key structural parameters.

Table S4. Energy data (hartrees).

Structure	E(M06-2X/B1)	TCG	E(M06-2X(SMD)/ B2)	TCG+ E(M06-2X(SMD)/ B2)	Imaginary Frequency (cm^{-1})
(*S*)-1c	-2050.918051	0.556066	-2051.558303	-2051.002237	
TS1c$_R$	-2050.860003	0.557429	-2051.501083	-2050.943654	-19.39
TS1c$_L$	-2050.868187	0.557955	-2051.509777	-2050.951822	-26.24
(*S*)-2c	-2090.583894	0.597549	-2091.272427	-2090.674878	
TS2c$_R$	-2090.536120	0.599564	-2091.223520	-2090.623956	-21.27
TS2c$_L$	-2090.536925	0.599265	-2091.224062	-2090.624797	-22.67
Tz-Ph	-1251.881779	0.539958	-1252.229118	-1251.68916	
TSTz-Ph	-1251.850308	0.545638	-1252.198079	-1251.652441	-40.56
HTz$^+$-Ph	-1252.273253	0.554676	-1252.657319	-1252.102643	
TSHTz$^+$-Ph	-1252.239316	0.560131	-1252.624966	-1252.064835	-41.22
MeTz$^+$-Ph	-1291.564099	0.581046	-1291.957531	-1291.376485	
TSMeTz$^+$-Ph	-1291.508624	0.584456	-1291.903285	-1291.318829	-91.56
1c-H$^+$	-2051.295781	0.570669	-2051.974652	-2051.403983	
TS1cL-H$^+$	-2051.253466	0.572562	-2051.930993	-2051.358431	-22.16
TS1cR-H$^+$	-2051.252429	0.572385	-2051.930293	-2051.357908	-22.01

Cartesian coordinates

(*S*)-1c

C	-0.29183700	0.93195700	3.39342300
C	-1.07757800	2.07995300	3.46839800
C	-1.53305100	2.70035800	2.30884900
C	-1.19856000	2.18450600	1.05181100
C	-0.42460700	1.04046100	1.02116200
C	0.04030400	0.39185200	2.15199800
H	0.06683000	0.44877200	4.29625000
H	-1.33962200	2.49626300	4.43523200
H	-2.15230000	3.58724400	2.37505400
H	0.64812300	-0.50423400	2.08195900
I	0.00445900	0.28357400	-0.95231800
O	-0.98786500	2.25522400	-1.34014500
C	-1.65605600	2.78836200	-0.29158700
C	-1.40095700	4.31571900	-0.30472600
C	-3.16951900	2.48868400	-0.45323800
F	-3.66806300	3.01429800	-1.57098700
F	-3.33828000	1.15219800	-0.51765300
F	-3.91739600	2.92763600	0.57369000
F	-1.62630700	4.83462900	-1.50904200
F	-2.17899600	4.98675400	0.57045400
F	-0.12673600	4.56668100	0.02281900
C	0.91666200	-1.48587000	-0.13364700
C	2.25475000	-1.70408100	0.17280600
N	0.28961300	-2.65251400	0.21330500
N	1.18093900	-3.51703100	0.69275100
N	2.35337500	-2.96205700	0.67609900
C	-1.12853800	-3.08681000	0.07478400
C	-1.52356300	-3.08819600	-1.41400000
C	-1.27102300	-4.52099700	0.61957300
C	-2.05916600	-2.16242000	0.88121000
H	-0.84608100	-3.75806000	-1.95834000
H	-1.41830600	-2.08718300	-1.84345900
C	-2.98338600	-3.54816100	-1.55886100
H	-0.96459500	-4.54623600	1.67055700
H	-0.59599100	-5.18936200	0.07646600
C	-2.72701000	-4.99063300	0.46971300
H	-1.98805000	-1.12702100	0.53769700
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C	-3.51500000	-2.63140600	0.72199700
H	-3.25595000	-3.52463900	-2.61986900
C	-3.12549100	-4.97550500	-1.01333500

C	-3.89629200	-2.59758600	-0.76717200
H	-2.80096400	-6.01097200	0.86218100
C	-3.65689600	-4.06050500	1.26155400
H	-4.16371900	-1.95017100	1.28357600
H	-2.48689200	-5.66250800	-1.58278400
H	-4.16056200	-5.32022000	-1.12837300
H	-3.80605500	-1.57489400	-1.15436000
H	-4.94341000	-2.90036300	-0.88936200
H	-4.69677400	-4.39694300	1.16697700
H	-3.40014000	-4.08847400	2.32812200
C	3.47777400	-0.82847700	0.02450000
C	3.33682500	0.47895100	0.83967100
C	4.72176200	-1.58265300	0.54455700
C	3.71882500	-0.47631500	-1.46348800
H	3.18000800	0.22796200	1.89773700
H	2.46099900	1.05153100	0.51132100
C	4.59309400	1.34904600	0.68163300
H	4.83487300	-2.52251900	-0.00778700
H	4.56785300	-1.85730600	1.59479000
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H	2.85439600	0.06024200	-1.87315000
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C	4.97417500	0.39632600	-1.61238700
H	4.46140000	2.27270400	1.25725700
C	5.81573700	0.57987100	1.20138900
C	4.79136700	1.69048900	-0.80378900
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H	5.11637100	0.64034800	-2.67180100
H	5.68837400	0.34671000	2.26642700
H	6.71668000	1.19979700	1.10850900
H	3.92506900	2.25093500	-1.17953900
H	5.67170700	2.33432700	-0.92444900
H	7.10112400	0.23706200	-1.20516800
H	6.34099200	-1.29021600	-1.66952300

TS1c$_R$

C	1.15355700	-4.24333500	-0.76480000
C	0.12876300	-4.95027700	-0.14844000
C	-1.05256600	-4.30000600	0.19609100
C	-1.21133600	-2.92917300	-0.02226100
C	-0.10315400	-2.23239200	-0.50099900
C	1.04086500	-2.86440000	-0.95087700
H	2.04663900	-4.75010000	-1.11526200
H	0.22219600	-6.01803400	0.01749900

H	-1.88391400	-4.86531400	0.60176200
H	1.82660700	-2.33127700	-1.45875000
I	-0.49544100	-0.06845000	-0.67075000
O	-2.54260200	-1.08422800	-0.70543400
C	-2.56664400	-2.20223100	0.05678900
C	-2.88407200	-1.86875800	1.53899100
C	-3.69181900	-3.11178100	-0.51378900
F	-4.81303900	-2.42030300	-0.69701900
F	-3.32199800	-3.61881100	-1.69661300
F	-3.99629300	-4.15464900	0.28930100
F	-4.09615900	-1.33217100	1.68583200
F	-2.81006100	-2.94400500	2.34211500
F	-1.98775600	-0.97585900	2.00132300
C	1.22807200	1.31574500	-0.16580700
C	2.58760300	1.39591300	0.11259200
N	0.76977200	2.60994800	0.06347800
N	1.79223800	3.38545000	0.43255400
N	2.86455900	2.67883000	0.46838300
C	-0.56772900	3.29306700	-0.00636300
C	-1.52091800	2.74728000	1.07799200
C	-0.36737700	4.80088500	0.28211000
C	-1.16834400	3.18591800	-1.42202000
H	-1.05346400	2.91003700	2.05716400
H	-1.69640800	1.67450000	0.98259300
C	-2.87414500	3.47242000	0.99084800
H	0.33331600	5.22280300	-0.44497500
H	0.08656500	4.92780200	1.26838400
C	-1.71323500	5.54184600	0.22029300
H	-1.32014700	2.15189500	-1.74058100
H	-0.46554300	3.63755400	-2.13336900
C	-2.53061000	3.89813100	-1.46715800
H	-3.54874500	3.03710400	1.73609500
C	-2.67415200	4.96683500	1.26917200
C	-3.46447400	3.27573300	-0.41546200
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C	-2.33217800	5.39019500	-1.17492900
H	-2.95925900	3.76513600	-2.46669400
H	-2.26547100	5.11054500	2.27721200
H	-3.63622200	5.49256600	1.22768300
H	-3.60484900	2.20546900	-0.61754700
H	-4.45236500	3.74862100	-0.47311700
H	-3.29414600	5.91546200	-1.22149700
H	-1.67694400	5.83851400	-1.93244900
C	3.75001400	0.44372900	0.13691700

C	3.34237900	-0.93018100	-0.36752200
C	4.89197900	0.98308200	-0.75489500
C	4.27917100	0.30264300	1.58332200
H	2.95781500	-0.81556900	-1.39217000
H	2.53478600	-1.31087300	0.27007600
C	4.52483500	-1.90706800	-0.34680500
H	5.18496200	1.97673400	-0.40012400
H	4.52309200	1.09901300	-1.78321800
C	6.08660900	0.01797800	-0.72257000
H	3.47104100	-0.06691400	2.22916800
H	4.56888800	1.29185900	1.95504800
C	5.47277000	-0.66393900	1.61548800
H	4.19771600	-2.88851400	-0.71661400
C	5.64837100	-1.36089600	-1.24123200
C	5.03249200	-2.04278800	1.09739200
H	6.88595900	0.41328000	-1.36028400
C	6.59660200	-0.11749300	0.72100000
H	5.83347200	-0.75703900	2.64653600
H	5.29850800	-1.27855100	-2.27882500
H	6.49884100	-2.05448500	-1.23818700
H	4.23874500	-2.45088700	1.73686900
H	5.87441900	-2.74581200	1.13263200
H	7.46237400	-0.79167800	0.75152700
H	6.92970300	0.85936900	1.09316900

TS1c$_L$

C	1.65795600	-3.94754300	-0.48915200
C	0.65936900	-4.82780500	-0.08924900
C	-0.63460200	-4.36293200	0.12485200
C	-0.94606500	-3.01078400	-0.03599300
C	0.09865300	-2.14522800	-0.34678300
C	1.37767200	-2.58726500	-0.62056500
H	2.65649800	-4.31149900	-0.70812700
H	0.87663800	-5.88407300	0.02637500
H	-1.42254000	-5.05636900	0.39569900
H	2.14471900	-1.90315900	-0.94632700
I	-0.52293700	-0.06776800	-0.49307800
O	-2.42864400	-1.24936900	-0.62534500
C	-2.37513200	-2.44797400	0.00394400
C	-2.81883200	-2.30733900	1.48369700
C	-3.34793800	-3.39705600	-0.74627800
F	-4.52952900	-2.81819700	-0.93602200
F	-2.84585500	-3.71632500	-1.94600700
F	-3.57226600	-4.55391400	-0.08676200
F	-4.08747200	-1.91425500	1.59302900

F	-2.68008600	-3.44886900	2.18049000
F	-2.05014300	-1.38311400	2.08865300
C	1.12474000	1.42155700	-0.11259000
C	0.60543300	2.72324200	0.00134200
N	2.47241500	1.58566500	0.05681500
N	2.75570900	2.87984400	0.24223600
N	1.66067800	3.55359800	0.20689000
C	3.62795500	0.65560800	0.08851300
C	3.38411000	-0.45669300	1.11891300
C	3.88416900	0.09110100	-1.31856800
C	4.88990700	1.43358400	0.52380200
H	2.45406400	-0.99167000	0.91152200
H	3.26460500	0.00657500	2.10615000
C	4.58559300	-1.42145600	1.13023700
H	4.08850300	0.93103100	-1.99398700
H	2.98862900	-0.40492000	-1.71053100
C	5.08907200	-0.86766300	-1.27986300
H	4.71814400	1.88476600	1.50622500
H	5.07699500	2.25489400	-0.17259100
C	6.09798200	0.48691800	0.56512400
H	4.38015900	-2.23523600	1.83500300
C	4.83757500	-2.00156500	-0.27296800
C	5.83837300	-0.64760900	1.56668800
H	5.24471100	-1.28700800	-2.28030700
C	6.33741000	-0.09010200	-0.83780400
H	6.97498100	1.06319900	0.88023400
H	3.99915700	-2.62376900	-0.59555400
H	5.71527800	-2.65924600	-0.23956300
H	5.69680400	-0.23526500	2.57332800
H	6.70223200	-1.32265200	1.60790000
H	7.20873300	-0.75664000	-0.83157000
H	6.55031700	0.72048100	-1.54562800
C	-0.78772000	3.34928700	-0.02415500
C	-1.51134300	3.14241600	-1.37819100
C	-1.67234500	2.83917900	1.14283100
C	-0.63759800	4.88230100	0.16725300
H	-1.66286600	2.08249700	-1.60927700
H	-0.88282000	3.55141100	-2.18022300
C	-2.88877200	3.82374000	-1.37058000
H	-1.15445800	3.04718800	2.08822600
H	-1.82612900	1.75646700	1.10054300
C	-3.04673200	3.52560100	1.12187700
H	-0.00173100	5.28597500	-0.62843600
H	-0.11380200	5.07898600	1.10856600

C	-2.00313900	5.58305600	0.16405500
H	-3.38428600	3.62769500	-2.32870500
C	-3.73430700	3.24554400	-0.22423300
C	-2.71137600	5.33456600	-1.17426900
H	-3.65631300	3.11817700	1.93685200
C	-2.86911700	5.03777800	1.30765700
H	-1.84265400	6.65890400	0.30273800
H	-3.86667000	2.16377300	-0.36119300
H	-4.73380200	3.69832300	-0.23417200
H	-2.11991800	5.75383000	-1.99843000
H	-3.68879000	5.83384900	-1.18537200
H	-3.84726900	5.53586600	1.31315600
H	-2.39146000	5.24383000	2.27409600

(*S*)-2c

C	0.55792300	-0.90078500	3.45409100
C	1.53316800	-1.89378000	3.52136800
C	2.07009500	-2.43934000	2.35876400
C	1.62717800	-2.00173700	1.10585000
C	0.66504600	-1.01065400	1.08407600
C	0.11285500	-0.43925800	2.21554900
H	0.13873100	-0.47974300	4.36175400
H	1.88081200	-2.24676300	4.48604800
H	2.83618000	-3.20377000	2.41902000
H	-0.64302800	0.33559000	2.15397700
I	0.12906300	-0.41076100	-0.91340000
O	1.36623300	-2.11521100	-1.28042700
C	2.15925500	-2.51609500	-0.23910900
C	2.17399100	-4.06302400	-0.26610200
C	3.57956200	-1.93534600	-0.45045600
F	4.12203200	-2.34574900	-1.58914700
F	3.47550600	-0.58756000	-0.50261300
F	4.41823300	-2.22824900	0.54961300
F	2.46236000	-4.51848500	-1.47824500
F	3.07302700	-4.57348200	0.59218900
F	0.96764200	-4.52538500	0.08311400
C	-1.11871700	1.27191900	-0.10504200
C	-2.49450900	1.31222300	0.12843700
N	-0.67289700	2.54480400	0.14198500
N	-1.64042000	3.33664000	0.49747300
C	0.70424500	3.16814000	0.00731000
C	1.09473300	3.18122400	-1.48076100
C	0.64243400	4.61761200	0.52131200
C	1.72527800	2.38454700	0.84680800
H	0.34280200	3.74706000	-2.04526900

H	1.12716000	2.16510100	-1.88512500
C	2.48491300	3.82903200	-1.62217400
H	0.32752100	4.62691400	1.57113000
H	-0.09717400	5.18740700	-0.04971200
C	2.02837700	5.26903000	0.37323100
H	1.79879200	1.34354900	0.52663000
H	1.41493700	2.39083400	1.89970100
C	3.11022200	3.03889400	0.68245700
H	2.76405000	3.81719400	-2.68062000
C	2.43275100	5.27389600	-1.10786200
C	3.50449600	3.02105000	-0.80359500
H	1.96033500	6.29690000	0.74373300
C	3.06091600	4.48395600	1.19304400
H	3.83266000	2.45644800	1.26327800
H	1.71668900	5.86143700	-1.69561900
H	3.41378100	5.74727700	-1.22623100
H	3.55434500	1.98828200	-1.16942700
H	4.50335100	3.45444200	-0.92552400
H	4.04802400	4.94965200	1.09664900
H	2.79608400	4.50257600	2.25750100
C	-3.52027900	0.19429800	-0.01446000
C	-3.08401400	-1.01979800	0.84740700
C	-4.94909800	0.57723300	0.43910400
C	-3.60046000	-0.21572900	-1.50968100
H	-3.06880900	-0.72238400	1.90503800
H	-2.07217600	-1.34238200	0.59115100
C	-4.04356200	-2.20146800	0.64089000
H	-5.32418400	1.42347800	-0.14559800
H	-4.94450700	0.86029700	1.49904700
C	-5.91856900	-0.60379100	0.24801900
H	-2.60990200	-0.48859300	-1.88624600
H	-3.94530700	0.64431800	-2.09950700
C	-4.55559300	-1.40524900	-1.68838100
H	-3.68673000	-3.04553300	1.24046400
C	-5.45310700	-1.79833200	1.08902500
C	-4.05771600	-2.59034000	-0.84589000
H	-6.91258500	-0.28187800	0.57638400
C	-5.96326300	-0.99884600	-1.23412800
H	-4.57088800	-1.68347400	-2.74742800
H	-5.45274100	-1.53808500	2.15510800
H	-6.14559700	-2.63796400	0.96144100
H	-3.05170300	-2.88941100	-1.16826000
H	-4.71307700	-3.45541000	-0.99738200
H	-6.66096300	-1.83173100	-1.37657800

H	-6.33085500	-0.16201700	-1.84146700
C	-3.95194800	3.36913700	0.83223600
H	-4.60375200	3.42635900	-0.03737200
H	-4.46497300	2.90291000	1.66826300
H	-3.61397300	4.36576600	1.10789700
N	-2.73273300	2.61367900	0.49262100

TS2c$_R$

C	0.51360100	-4.33089400	-0.03529400
C	-0.70510800	-4.88713400	0.33800000
C	-1.85461400	-4.10179300	0.37844200
C	-1.79452000	-2.73979500	0.07705700
C	-0.53949000	-2.20944600	-0.20062800
C	0.60466900	-2.96620000	-0.31525500
H	1.39888500	-4.95263600	-0.12162300
H	-0.77296900	-5.94511700	0.56540900
H	-2.81254800	-4.54888600	0.62004000
H	1.53698200	-2.52820500	-0.63313200
I	-0.66456000	-0.06872100	-0.56281000
O	-2.67525000	-0.71603200	-0.81274200
C	-3.01001200	-1.82695800	-0.07187800
C	-3.51939500	-1.39530200	1.32536600
C	-4.13735400	-2.53706600	-0.86580000
F	-5.08379600	-1.67613900	-1.21718300
F	-3.63208800	-3.08409400	-1.97475700
F	-4.71332800	-3.51579200	-0.14809500
F	-4.61968200	-0.65448000	1.24704800
F	-3.76308100	-2.43994300	2.12215100
F	-2.56533500	-0.64899500	1.92135500
C	1.41766500	1.09346900	-0.17402500
C	2.81176100	0.97763400	-0.17489600
N	1.19495700	2.46421300	-0.19645400
N	2.30456900	3.14034000	-0.27434100
C	-0.05329200	3.33295200	-0.04146300
C	-0.79507100	2.92897500	1.24647600
C	0.38307700	4.80725600	0.11853500
C	-0.93090200	3.25573900	-1.30397600
H	-0.11860700	3.07563600	2.09780900
H	-1.09200600	1.88000000	1.24935000
C	-2.05177600	3.80425500	1.39646200
H	0.94309800	5.13081400	-0.76388100
H	1.04737800	4.90436900	0.98373200
C	-0.85663400	5.70183300	0.30394200
H	-1.25854000	2.24152300	-1.54060000
H	-0.34678700	3.60843800	-2.16306400

C	-2.18569200	4.12429800	-1.09926000
H	-2.59685500	3.46999600	2.28499200
C	-1.63267100	5.27048500	1.55470100
C	-2.93854100	3.63879100	0.15089600
H	-0.50892700	6.73386900	0.41702700
C	-1.76474100	5.58848100	-0.92715500
H	-2.82366800	4.01711200	-1.98221100
H	-1.01252400	5.39146600	2.45130900
H	-2.51668500	5.90496900	1.68373500
H	-3.23483700	2.58729600	0.03262600
H	-3.86047300	4.21772600	0.27354600
H	-2.64989300	6.22162300	-0.79984800
H	-1.24043400	5.93940800	-1.82441500
C	3.71142200	-0.23882100	-0.00567700
C	3.11447200	-1.14123700	1.10167000
C	3.82412200	-1.02603100	-1.33260500
C	5.14614900	0.12442800	0.45545300
H	2.06710800	-1.36715600	0.89202600
H	3.11778900	-0.58491300	2.04815600
C	3.94408700	-2.42886200	1.26266900
H	4.26699100	-0.37944600	-2.10228700
H	2.82424500	-1.29727000	-1.69826500
C	4.69534600	-2.28196200	-1.13837000
H	5.10110400	0.71005800	1.38353800
H	5.65922000	0.71691800	-0.30396200
C	5.99383100	-1.13934000	0.66949100
H	3.45995300	-3.06644500	2.01094000
C	4.07798300	-3.19292600	-0.06737300
C	5.35257400	-2.03955600	1.73254500
H	4.75821000	-2.81777500	-2.09145400
C	6.10107500	-1.87698200	-0.67316100
H	6.99070200	-0.82857600	1.00016300
H	3.11877900	-3.58843100	-0.40900800
H	4.72559000	-4.06443500	0.08574400
H	5.30229500	-1.51381800	2.69395900
H	5.96388800	-2.93630300	1.88472900
H	6.72734400	-2.76980400	-0.56609600
H	6.58255200	-1.23290400	-1.41989700
C	4.60322300	2.87491500	-0.46613200
H	5.08320300	2.43284800	-1.33732800
H	4.41983900	3.93252400	-0.64324400
H	5.21542500	2.74596700	0.42237400
N	3.27235600	2.27056000	-0.27452200

TS2c$_L$

C	0.57592500	-4.36044400	-0.40839900
C	-0.60910100	-4.95999100	0.00432500
C	-1.75290900	-4.19188700	0.20833200
C	-1.71906600	-2.80759900	0.02931700
C	-0.49280800	-2.24144200	-0.30167700
C	0.64060100	-2.97523900	-0.56928900
H	1.45369300	-4.96330100	-0.61825000
H	-0.65693200	-6.03494900	0.13785800
H	-2.68699900	-4.66760100	0.48594500
H	1.54543700	-2.50185200	-0.91377800
I	-0.64877200	-0.08002900	-0.46497900
O	-2.66960500	-0.71203400	-0.57811500
C	-2.93979100	-1.89316200	0.07855400
C	-3.31808800	-1.60155700	1.55155400
C	-4.13649700	-2.52595900	-0.67751800
F	-5.10961300	-1.64072400	-0.84996600
F	-3.73569500	-2.95237200	-1.87820800
F	-4.64477100	-3.57754500	-0.01425900
F	-4.41464800	-0.85783700	1.64624400
F	-3.49801700	-2.72094500	2.25910700
F	-2.30739800	-0.91889100	2.12824100
C	1.43443700	1.11283000	-0.05049100
C	1.23953800	2.48507100	0.22004900
N	2.75324600	0.89996000	0.25836700
N	3.34507000	1.97060500	0.71065900
C	3.65252000	-0.30164800	0.10971600
C	3.21443900	-1.40742500	1.07771600
C	3.61052300	-0.77469300	-1.35042700
C	5.09729800	0.11096200	0.45730700
H	2.16560100	-1.67430400	0.91895600
H	3.29577300	-1.03351700	2.10582500
C	4.14147400	-2.62895800	0.89069700
H	3.93854100	0.04524200	-2.00138800
H	2.58441900	-1.01913700	-1.65023400
C	4.54788500	-1.98881900	-1.51484600
H	5.14184200	0.47984500	1.48643600
H	5.42005500	0.92688600	-0.19796300
C	6.02877500	-1.09830300	0.29162600
H	3.80357100	-3.42787300	1.55930700
C	4.13016700	-3.12451800	-0.56668900
C	5.58017300	-2.21938300	1.24126100
H	4.49713600	-2.33142500	-2.55348200
C	5.98415200	-1.57215600	-1.16773900
H	7.04512400	-0.78211400	0.54763000

H	3.15603700	-3.53046800	-0.84756700
H	4.84034700	-3.95366300	-0.66580200
H	5.63765400	-1.87711300	2.28160400
H	6.24718700	-3.08357900	1.14694400
H	6.66146900	-2.42118500	-1.31234800
H	6.32241800	-0.77007400	-1.83497200
C	0.01806300	3.38585500	0.00984900
C	-0.49678700	3.20358900	-1.44448100
C	-1.07624300	3.06984000	1.06537700
C	0.31267000	4.90547800	0.14052800
H	-0.67701200	2.15849100	-1.69943000
H	0.28789400	3.54410700	-2.13296700
C	-1.79095800	3.99458800	-1.67522800
H	-0.68115800	3.32041300	2.05938700
H	-1.32693700	2.00733100	1.09982600
C	-2.34906700	3.88012300	0.77894900
H	1.09012300	5.19947700	-0.57614900
H	0.65809200	5.14598100	1.14900500
C	-0.95430800	5.74533900	-0.11931800
H	-2.15438600	3.78055100	-2.68591300
C	-2.84600200	3.56691100	-0.64188800
C	-1.48586000	5.48940300	-1.53309200
H	-3.11420700	3.59483100	1.50845600
C	-2.03430900	5.37567000	0.90591100
H	-0.68300000	6.80086200	-0.00863200
H	-3.06310500	2.49360500	-0.73878900
H	-3.78598400	4.09717500	-0.83159400
H	-0.74754400	5.79697400	-2.28411500
H	-2.39076300	6.08301900	-1.70538600
H	-2.93685000	5.97098400	0.72705400
H	-1.69245700	5.60413600	1.92328500
C	2.93881700	4.18677200	1.26945800
H	2.89302200	4.98222600	0.53171300
H	2.35385300	4.44090700	2.15127900
H	3.97194500	3.99926700	1.55368600
N	2.45099700	2.91757600	0.69901500

Tz-Ph

C	-0.00481700	-0.09485100	-0.03573800
C	1.11661600	-0.90896800	-0.03492300
N	-1.05876700	-0.97373700	-0.06518400
N	-0.60423000	-2.23029400	-0.07456700
N	0.68647600	-2.20122300	-0.05895600
C	-0.11833600	1.38445200	-0.02166500
C	-0.07594000	2.10512700	-1.22025200

C	-0.20109900	2.08281900	1.18638100
C	-0.13238500	3.49609600	-1.21261300
C	-0.25950900	3.47543600	1.19677600
H	-0.20407700	1.52672900	2.12015600
C	-0.22792200	4.18429200	-0.00284300
H	-0.09712800	4.04299200	-2.14955600
H	-0.32101200	4.00565500	2.14193700
H	-0.26967300	5.26888900	0.00450000
C	2.60127400	-0.63922200	-0.00941700
C	2.95630800	0.85912700	0.00948400
C	3.20824200	-1.30386400	1.24975000
C	3.24933900	-1.28150300	-1.25932100
H	2.50750800	1.34255700	0.88696200
H	2.54121100	1.35568300	-0.87668800
C	4.48207300	1.04727200	0.03750400
H	2.94849300	-2.36864300	1.24950500
H	2.75372600	-0.85677600	2.14491000
C	4.73212400	-1.11719100	1.27737400
H	2.82445200	-0.81855800	-2.16098500
H	2.99022500	-2.34602700	-1.28679400
C	4.77319300	-1.09457700	-1.23313400
H	4.70682400	2.12066000	0.05085500
C	5.06219500	0.38272000	1.29518400
C	5.10362100	0.40527900	-1.21225000
H	5.13801500	-1.59638700	2.17657000
C	5.34820500	-1.76249200	0.02594800
H	5.20884600	-1.55728100	-2.12703300
H	4.64045400	0.84951500	2.19515200
H	6.14959800	0.53042700	1.33012300
H	4.71217200	0.88895200	-2.11698800
H	6.19161000	0.55279900	-1.20835600
H	6.44031300	-1.65056100	0.04475100
H	5.12928400	-2.83781300	0.01271100
C	-2.52570300	-0.74162700	-0.03069900
C	-2.95012500	0.22035500	-1.15546600
C	-3.24871200	-2.08778000	-0.22721100
C	-2.93122400	-0.15345100	1.33341200
H	-2.64027600	-0.19884700	-2.12173800
H	-2.45398600	1.18676300	-1.03432900
C	-4.47307600	0.43015400	-1.11202400
H	-2.94197500	-2.78760200	0.55538000
H	-2.94477100	-2.52900400	-1.18274500
C	-4.76922700	-1.87311700	-0.18699700
H	-2.42257000	0.80311100	1.49029300

H	-2.61161700	-0.84170300	2.12634600
C	-4.45393100	0.06004200	1.37354000
H	-4.75482200	1.12423900	-1.91223900
C	-5.18921500	-0.91246500	-1.30807600
C	-4.85981600	1.02841500	0.25055700
H	-5.25980800	-2.84304300	-0.32724500
C	-5.16900500	-1.28396100	1.17400800
H	-4.72637400	0.48653400	2.34588100
H	-4.93031900	-1.33840600	-2.28579300
H	-6.27670500	-0.76570600	-1.29291300
H	-4.36101500	1.99647400	0.38996800
H	-5.94153200	1.20910200	0.28600300
H	-6.25618400	-1.14118800	1.21863000
H	-4.89705300	-1.97864300	1.97875900
H	0.00492200	1.56278100	-2.15875900

TSTz-Ph

C	0.02740200	0.08796500	0.00001500
C	-1.09626900	-0.77051200	0.00003900
N	1.09407700	-0.80578700	0.00021000
N	0.64643400	-2.05969900	0.00029500
N	-0.63858900	-2.04725300	0.00020900
C	0.10068200	1.58015900	0.00000500
C	-1.09234600	2.32438500	-0.00003200
C	1.27801400	2.35042300	0.00006900
C	-1.11902600	3.71426200	-0.00001200
C	1.26253700	3.74317700	0.00009000
H	2.24577300	1.88899400	0.00007700
C	0.06380400	4.44564900	0.00005100
H	-2.07992400	4.22000000	-0.00004300
H	2.20996800	4.27390400	0.00013500
H	0.05167300	5.53051600	0.00007000
C	-2.61928700	-0.62846000	-0.00001200
C	-3.13885100	0.04807300	1.29817200
C	-3.13881900	0.04805400	-1.29821900
C	-3.26361100	-2.04624900	-0.00001900
H	-2.68790900	1.02376300	1.48830000
H	-2.84061000	-0.58862500	2.14155300
C	-4.66868900	0.18165700	1.26210700
H	-2.84059000	-0.58868000	-2.14157800
H	-2.68785800	1.02372500	-1.48838900
C	-4.66865700	0.18166600	-1.26218300
H	-2.91676000	-2.60421300	0.87585500
H	-2.91670500	-2.60423300	-0.87586100
C	-4.79988500	-1.96571700	-0.00005200

H	-5.00067500	0.72736000	2.15366100
C	-5.09228900	0.95264200	-0.00004000
C	-5.29151800	-1.21989500	1.24761600
H	-5.00061500	0.72738300	-2.15373900
C	-5.29149500	-1.21988100	-1.24772100
H	-5.19900300	-2.98723200	-0.00006300
H	-4.63593600	1.95321700	-0.00002900
H	-6.18039500	1.09686000	-0.00005500
H	-5.00277200	-1.76457100	2.15554100
H	-6.38744500	-1.15236600	1.24006700
H	-6.38742200	-1.15234900	-1.24018300
H	-5.00274000	-1.76454800	-2.15564800
C	2.58430100	-0.68727300	0.00007000
C	3.06468300	-0.01987000	1.30819300
C	3.22391100	-2.10170200	0.00008700
C	3.06447800	-0.01996400	-1.30817500
H	2.78780000	-0.69018300	2.13168100
H	2.57221300	0.92911700	1.51516600
C	4.59134100	0.15484700	1.26462900
H	2.88751800	-2.66048900	-0.87752000
H	2.88758800	-2.66043600	0.87775500
C	4.76117000	-1.98783700	-0.00000100
H	2.57208600	0.92908700	-1.51504600
H	2.78736000	-0.69025000	-2.13160500
C	4.59115400	0.15467200	-1.26489300
H	4.91169900	0.70761000	2.15507000
C	5.24146000	-1.23457100	1.24785700
C	4.99704500	0.93353800	-0.00021700
H	5.17300700	-3.00356300	0.00004600
C	5.24126100	-1.23475000	-1.24803800
H	4.91138300	0.70730200	-2.15546300
H	4.96712700	-1.78496500	2.15634500
H	6.33525300	-1.14616900	1.23535800
H	4.53010700	1.92829100	-0.00025800
H	6.08241700	1.09384000	-0.00030200
H	6.33505700	-1.14635500	-1.23575000
H	4.96675800	-1.78526600	-2.15640200
H	-2.03590100	1.81578900	-0.00006500

HTz^+-Ph

C	0.01281000	-0.16251600	0.00000600
C	-1.10970000	-0.97854000	0.00003600
N	1.08940400	-1.02414600	0.00013200
N	0.71587900	-2.27130900	0.00020700
C	0.06750400	1.32024800	-0.00002400

C	0.05744200	2.02120000	1.21004900
C	0.05741300	2.02126900	-1.21002400
C	0.05849700	3.41371900	1.20857300
H	0.04777400	1.47481700	2.14966900
C	0.05848300	3.41380600	-1.20844600
C	0.06200700	4.10962600	0.00008000
H	0.05319900	3.95338300	2.14955900
H	0.05315600	3.95353000	-2.14939700
H	0.06196200	5.19460500	0.00011900
N	-0.58967200	-2.23148000	0.00012300
C	-2.59225200	-0.70705900	-0.00001100
C	-2.98309300	0.10231300	-1.26132900
C	-3.37863100	-2.03706200	0.00001300
C	-2.98311300	0.10236600	1.26126800
H	-2.69765800	-0.45956500	-2.16097600
H	-2.43577000	1.05138700	-1.27289400
C	-4.49552700	0.37505700	-1.25589900
H	-3.12269000	-2.62780400	0.89259100
H	-3.12267100	-2.62785800	-0.89252200
C	-4.89072100	-1.75887300	0.00001200
H	-2.43576700	1.05142700	1.27281700
H	-2.69771500	-0.45948000	2.16094800
C	-4.49553700	0.37517700	1.25578300
H	-4.75013800	0.94944900	-2.15289900
C	-5.25943300	-0.95683300	-1.25696700
C	-4.86157800	1.18168900	-0.00009300
H	-5.42194900	-2.71635700	0.00008100
C	-5.25943100	-0.95671900	1.25694000
H	-4.75014100	0.94961400	2.15275300
H	-5.01813300	-1.53250500	-2.15955100
H	-6.33911200	-0.76970100	-1.27303800
H	-4.33069600	2.14218800	-0.00016000
H	-5.93466400	1.40481800	-0.00011800
H	-6.33911100	-0.76960600	1.27298300
H	-5.01811800	-1.53232200	2.15956500
C	2.57628700	-0.73290300	0.00007600
C	2.93351000	0.06670400	1.26367100
C	3.34068900	-2.06645900	0.00014400
C	2.93334700	0.06649800	-1.26369800
H	2.64963700	-0.51011800	2.15339900
H	2.39010000	1.01508100	1.27974200
C	4.44758300	0.34882600	1.25670700
H	3.06899000	-2.65457300	-0.88320700
H	3.06906800	-2.65443900	0.88361300

C	4.85169800	-1.77718200	0.00003300
H	2.38988500	1.01486000	-1.27985600
H	2.64939100	-0.51048500	-2.15329100
C	4.44742200	0.34863200	-1.25696200
H	4.69355800	0.92671400	2.15346800
C	5.22131200	-0.97631600	1.25675200
C	4.80322100	1.15938900	-0.00021500
H	5.38065900	-2.73554500	0.00007700
C	5.22114600	-0.97652300	-1.25687100
H	4.69329200	0.92637200	-2.15384700
H	4.98512100	-1.55416500	2.15882100
H	6.29925700	-0.77988500	1.27127700
H	4.26237200	2.11444700	-0.00025200
H	5.87371500	1.39325800	-0.00031000
H	6.29908900	-0.78009600	-1.27156300
H	4.98484700	-1.55452800	-2.15881200
H	0.04765000	1.47496800	-2.14969100
H	-1.09580200	-3.11053600	0.00004400

TSHTz^{+}-Ph

C	-0.03366300	0.10299600	-0.00001200
C	1.11724800	-0.71898300	-0.00001200
N	-1.09694700	-0.80797900	-0.00001400
N	-0.68422400	-2.04313900	-0.00001900
C	-0.11664100	1.59509000	-0.00001100
C	1.07848300	2.33272000	0.00000200
C	-1.30162500	2.35072200	-0.00002100
C	1.09978400	3.72214700	0.00001000
C	-1.28758400	3.74203500	-0.00001300
H	-2.26760400	1.88620300	-0.00003500
C	-0.08814900	4.44438000	0.00000400
H	2.05635600	4.23431400	0.00002200
H	-2.23398700	4.27281600	-0.00002100
H	-0.07990000	5.52888000	0.00001200
C	2.64369700	-0.60551500	-0.00000400
C	3.15508600	0.06908600	-1.30414500
C	3.15507400	0.06908500	1.30414200
C	3.28225900	-2.02802200	-0.00000200
H	2.70409000	1.04515700	-1.48500900
H	2.85717800	-0.56335300	-2.15101500
C	4.68553000	0.19806600	-1.26199000
H	2.85716100	-0.56335800	2.15100700
H	2.70407300	1.04515300	1.48500800
C	4.68551700	0.19807000	1.26200000
H	2.96888200	-2.58623600	-0.89469000

H	2.96886800	-2.58623800	0.89468100
C	4.82143800	-1.94933900	0.00000900
H	5.01255900	0.74220800	-2.15416300
C	5.10703500	0.96976500	0.00000600
C	5.30469600	-1.20465300	-1.25080500
H	5.01253700	0.74221400	2.15417500
C	5.30468300	-1.20464900	1.25082500
H	5.21111100	-2.97285000	0.00001200
H	4.65433200	1.97107200	0.00000200
H	6.19344800	1.11312300	0.00001200
H	5.01922300	-1.74977300	-2.15906300
H	6.39859900	-1.14018600	-1.24237300
H	6.39858700	-1.14018400	1.24240400
H	5.01920100	-1.74976700	2.15908200
C	-2.61917300	-0.68852900	-0.00000500
C	-3.07453800	-0.02081100	-1.31375200
C	-3.24712900	-2.10453900	0.00001100
C	-3.07452000	-0.02078900	1.31373700
H	-2.80605900	-0.69499700	-2.13675500
H	-2.57836000	0.92584300	-1.52035500
C	-4.60273400	0.16042600	-1.26512700
H	-2.92077400	-2.66296700	0.88273000
H	-2.92079100	-2.66298000	-0.88270600
C	-4.78577500	-1.98142900	0.00002400
H	-2.57833500	0.92586600	1.52032100
H	-2.80603300	-0.69496500	2.13674600
C	-4.60271500	0.16045100	1.26513000
H	-4.91514600	0.71418900	-2.15617000
C	-5.25737600	-1.22666000	-1.24987100
C	-5.00119600	0.94217200	-0.00000400
H	-5.19698300	-2.99612800	0.00003700
C	-5.25735800	-1.22663500	1.24991100
H	-4.91511400	0.71423200	2.15616700
H	-4.98873500	-1.77849000	-2.15869600
H	-6.34908500	-1.13276400	-1.23762900
H	-4.53335800	1.93623200	-0.00001700
H	-6.08429500	1.10776900	0.00000300
H	-6.34906700	-1.13274000	1.23768300
H	-4.98870300	-1.77844600	2.15874200
H	2.02524600	1.82968900	0.00000500
H	1.13009000	-2.84032200	-0.00002000
N	0.60669600	-1.97290600	-0.00001800

MeTz$^+$-Ph

C	0.04289200	-0.04969900	-0.04297400

C	-1.09040800	-0.85775700	-0.04356100
N	1.11462800	-0.91162200	-0.01047300
N	0.72744400	-2.15167200	0.01746500
C	0.15611400	1.43009100	-0.02481400
C	0.14879700	2.10649400	1.19883300
C	0.19661800	2.15295900	-1.21923600
C	0.19655500	3.49774300	1.22639300
H	0.09857700	1.54165500	2.12632500
C	0.24386900	3.54441000	-1.18975000
C	0.24524400	4.21665900	0.03211300
H	0.19008200	4.01904400	2.17772300
H	0.27418000	4.10257100	-2.11947600
H	0.27894700	5.30090600	0.05359700
N	-0.57934800	-2.13084200	0.00287200
C	-1.22125800	-3.45296200	0.01618500
H	-2.10192200	-3.42978000	0.65212000
H	-1.49017100	-3.73955600	-1.00018800
H	-0.48582900	-4.14726400	0.41773400
C	-2.57546900	-0.53539800	-0.03406100
C	-2.83053200	0.96250400	-0.33324600
C	-3.33225300	-1.35368500	-1.11338400
C	-3.15867000	-0.84040000	1.37105500
H	-2.41745400	1.21873400	-1.31680300
H	-2.32519900	1.58954100	0.40683800
C	-4.33496500	1.27627800	-0.29937100
H	-3.20775800	-2.42832800	-0.96324500
H	-2.92297800	-1.11049400	-2.10298400
C	-4.83731000	-1.04291900	-1.06368300
H	-2.63509500	-0.22557100	2.11512200
H	-2.99365300	-1.88834800	1.64933000
C	-4.66587200	-0.53708900	1.39384700
H	-4.46475400	2.34331500	-0.50953300
C	-5.06786200	0.44357100	-1.35739900
C	-4.89166900	0.95126800	1.09398800
H	-5.34176600	-1.65591300	-1.81831400
C	-5.37787400	-1.39062600	0.33257500
H	-5.05561500	-0.78051800	2.38808900
H	-4.69997100	0.69272300	-2.36062900
H	-6.14023000	0.66974100	-1.33985000
H	-4.39776700	1.56955100	1.85414600
H	-5.96223100	1.18292700	1.13404300
H	-6.45738000	-1.20556200	0.37038700
H	-5.22868900	-2.45853200	0.54170800
C	2.60778000	-0.64431600	-0.00347500

C	2.97986000	0.15585700	1.25556500
C	3.34622900	-1.99349100	0.01044900
C	2.99101800	0.13529000	-1.27187000
H	2.67887100	-0.40763800	2.14831200
H	2.45992600	1.11684700	1.26349400
C	4.50012300	0.40335200	1.25343300
H	3.06506000	-2.58308600	-0.86899700
H	3.05955400	-2.56848700	0.89755200
C	4.86322400	-1.73904000	0.01412000
H	2.47023900	1.09535100	-1.29989800
H	2.69886800	-0.44283300	-2.15814600
C	4.51089700	0.38438100	-1.26006100
H	4.75501400	0.98259300	2.14688700
C	5.24542300	-0.93763200	1.26646500
C	4.87867000	1.19674200	-0.00777300
H	5.37009100	-2.70934500	0.02362000
C	5.25619000	-0.95656500	-1.24682000
H	4.77327900	0.95021300	-2.15993300
H	4.99293800	-1.50378800	2.17160000
H	6.32735700	-0.76448000	1.28419700
H	4.35799100	2.16290500	-0.01729900
H	5.95393600	1.40788300	-0.00488200
H	6.33826400	-0.78373200	-1.25784000
H	5.01138200	-1.53616600	-2.14552300
H	0.18268700	1.62574700	-2.16957300

TSMeTz$^+$-Ph

C	0.04013500	0.54228500	-0.44693200
C	-1.14414800	-0.17903900	-0.73036900
N	1.07576800	-0.36119000	-0.71375700
N	0.62140100	-1.42813600	-1.30215500
C	0.27835000	2.00528800	-0.27875700
C	-0.78779800	2.90838900	-0.19116600
C	1.55775400	2.56924600	-0.40548800
C	-0.58830900	4.28246100	-0.11852400
H	-1.79638500	2.55111000	-0.21842900
C	1.76744900	3.94185000	-0.34021200
C	0.69606900	4.81304800	-0.17138600
H	-1.45011300	4.93696400	-0.04245600
H	2.77753200	4.32567100	-0.43856200
H	0.85640800	5.88439200	-0.11812800
N	-0.67031300	-1.32426700	-1.34291400
C	-1.32989700	-2.37674300	-2.13452100
H	-2.17076300	-2.80600400	-1.59888800
H	-1.66094600	-1.95167500	-3.08207200

H	-0.56951800	-3.13498000	-2.31101400
C	-2.60446300	-0.23286800	-0.20880700
C	-3.09204000	0.95296100	0.66054500
C	-3.65820800	-0.38547600	-1.33641400
C	-2.60299500	-1.47095900	0.75208500
H	-3.24769600	1.83129100	0.03242300
H	-2.35765000	1.19652500	1.43806100
C	-4.47478600	0.67072100	1.28469300
H	-3.41406600	-1.18184800	-2.03943700
H	-3.68689400	0.54659500	-1.91526800
C	-5.04435400	-0.68100300	-0.73272200
H	-1.91922100	-1.25109600	1.58314200
H	-2.21523900	-2.36848900	0.26560900
C	-4.00810600	-1.76457500	1.29074600
H	-4.74495700	1.54287700	1.88966900
C	-5.49227800	0.48992100	0.14995200
C	-4.45411100	-0.58494800	2.15826300
H	-5.75398000	-0.81968800	-1.55527600
C	-4.97688900	-1.96226500	0.11404500
H	-3.96291800	-2.67927900	1.89197500
H	-5.56703400	1.40747300	-0.44688200
H	-6.48750200	0.29152900	0.56381500
H	-3.76608500	-0.45732400	3.00305100
H	-5.45107200	-0.76717000	2.57534500
H	-5.97517900	-2.20947700	0.49234200
H	-4.65314400	-2.81099300	-0.50453400
C	2.52022900	-0.55069600	-0.18525500
C	2.65558700	0.10493600	1.20228500
C	2.73759000	-2.07252200	0.02849900
C	3.56074100	-0.09886600	-1.22616600
H	1.93362100	-0.37021100	1.87902700
H	2.43984500	1.17056400	1.20393500
C	4.09012200	-0.11514000	1.71814800
H	2.62976000	-2.60592300	-0.91804700
H	1.97588300	-2.45540200	0.71918000
C	4.14898700	-2.33095500	0.59020400
H	3.45010500	0.94144500	-1.53403100
H	3.42608400	-0.70740100	-2.12887000
C	4.96839700	-0.31765800	-0.63853400
H	4.19512900	0.42173400	2.66642800
C	4.32868800	-1.61340400	1.93188800
C	5.09347300	0.44153700	0.69349200
H	4.26019800	-3.41219600	0.72356900
C	5.19541400	-1.81702900	-0.40785100

H	5.70260000	0.06592600	-1.35423600
H	3.62402700	-2.00484100	2.67581100
H	5.33923000	-1.78789700	2.31820600
H	4.91697100	1.51440700	0.53691600
H	6.11289600	0.33951400	1.08187900
H	6.20323300	-1.99035800	-0.01407800
H	5.11961800	-2.36035400	-1.35756100
H	2.41560600	1.94876300	-0.58128000

1c-H$^+$

C	-0.33714000	0.97282500	3.43001000
C	-1.14347800	2.10741600	3.49052000
C	-1.60426700	2.71183500	2.32436400
C	-1.25209900	2.19093100	1.07490500
C	-0.45766600	1.06033500	1.05977000
C	0.01298800	0.42709300	2.19497000
H	0.02331000	0.50559200	4.34026900
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H	-2.24048000	3.58766400	2.37894900
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C	-1.71358100	2.76226400	-0.27273200
C	-1.49951400	4.29385100	-0.32259900
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F	-3.69190500	2.87649900	-1.60571200
F	-3.30321700	1.04793400	-0.51268500
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F	-1.72293100	4.76919900	-1.54061600
F	-2.30981800	4.94266800	0.53035900
F	-0.23671400	4.57769800	0.01713600
C	0.93576900	-1.47818400	-0.11528500
C	2.29247300	-1.65401100	0.12500200
N	0.36503900	-2.69566500	0.18081000
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C	-1.07471200	-3.14633100	0.06378700
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H	-0.82010100	-3.75300200	-1.99749400
H	-1.38287000	-2.08138000	-1.81613900
C	-2.94723500	-3.55005800	-1.54423000
H	-0.87093000	-4.65013800	1.61665000
H	-0.53901400	-5.25002800	-0.01195200
C	-2.65593100	-5.05330600	0.43636900

H	-1.90120100	-1.19253400	0.59746100
H	-1.64801700	-2.28558400	1.96662700
C	-3.43066300	-2.69940600	0.77263600
H	-3.23624700	-3.49398000	-2.59855400
C	-3.07925100	-4.99289300	-1.03855200
C	-3.83967000	-2.61951800	-0.70723500
H	-2.72140200	-6.08343200	0.80064200
C	-3.56296200	-4.14266300	1.27552700
H	-4.06223400	-2.03230200	1.36801900
H	-2.45634900	-5.66536500	-1.64107700
H	-4.11594000	-5.33159200	-1.14331300
H	-3.75723300	-1.58642300	-1.06699200
H	-4.88858700	-2.91620200	-0.81709600
H	-4.60421800	-4.47347500	1.19302500
H	-3.28698900	-4.20278900	2.33561400
C	3.50555300	-0.76524200	0.00300100
C	3.33940600	0.49604700	0.88530100
C	4.77253500	-1.51996600	0.46799800
C	3.70703500	-0.34524600	-1.47508400
H	3.20494000	0.19469500	1.93321000
H	2.44400700	1.05511400	0.59002300
C	4.57537800	1.39854900	0.74540100
H	4.92525300	-2.41830300	-0.14893000
H	4.66220200	-1.83302300	1.51713200
C	6.00984800	-0.61569500	0.33979600
H	2.82257200	0.18889400	-1.83923600
H	3.82832600	-1.24308000	-2.09537600
C	4.94051200	0.56317400	-1.59616500
H	4.42937300	2.28784200	1.36727200
C	5.82146400	0.63336900	1.21269500
C	4.73918500	1.81317100	-0.72528200
H	6.88733800	-1.17717600	0.67675500
C	6.18665200	-0.20154600	-1.12834200
H	5.05598600	0.85607800	-2.64488000
H	5.71958400	0.34903700	2.26771000
H	6.70604200	1.27542100	1.13602800
H	3.85623900	2.37172200	-1.06154300
H	5.60115300	2.48170100	-0.82910000
H	7.07498400	0.43180400	-1.22996200
H	6.34779500	-1.08635000	-1.75697600
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TS1cL-H$^+$

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C	-1.19528000	-2.98996500	-0.02228100
C	-0.07421300	-2.21838700	-0.30437300
C	1.17981000	-2.74138300	-0.52923400
H	2.32060200	-4.56127900	-0.56774400
H	0.39753600	-5.99111200	0.08497100
H	-1.84647400	-4.99523100	0.37802000
H	2.00583500	-2.11576500	-0.82690600
I	-0.59696400	-0.11520100	-0.45134800
O	-2.47911900	-1.06945800	-0.60274400
C	-2.55630200	-2.29958900	0.01226900
C	-3.01359300	-2.12039800	1.48087600
C	-3.60646500	-3.10611400	-0.79425400
F	-4.70961000	-2.39357300	-0.98133400
F	-3.10516700	-3.42963200	-1.98950300
F	-3.94790200	-4.24390000	-0.16763000
F	-4.22551200	-1.58294900	1.56195000
F	-3.01070000	-3.27275200	2.15737600
F	-2.15112800	-1.28753400	2.09911200
C	1.26767700	1.34966300	-0.09729400
C	0.80797400	2.67367100	0.02138900
N	2.62911500	1.46086500	0.08149200
N	3.02474300	2.69071600	0.28099200
C	3.72556500	0.42793200	0.08669500
C	3.41118000	-0.64064200	1.14152700
C	3.85156900	-0.17586800	-1.31928400
C	5.05707200	1.11103700	0.45499400
H	2.43514400	-1.09921500	0.95667600
H	3.35879400	-0.16399800	2.12820800
C	4.53401500	-1.69920700	1.12700900
H	4.08991700	0.62429500	-2.03093200
H	2.89804200	-0.60953600	-1.64333800
C	4.97744800	-1.23045000	-1.31094800
H	4.97227100	1.58370600	1.43934700
H	5.28806800	1.89903900	-0.26823700
C	6.18012400	0.06293300	0.46197100
H	4.28823100	-2.47644400	1.85816100
C	4.68135400	-2.32353500	-0.27154900
C	5.86215200	-1.02373300	1.49930100
H	5.04920100	-1.67327800	-2.30964200
C	6.30370100	-0.55074600	-0.94027300
H	7.11402800	0.56784400	0.72867800
H	3.78992800	-2.89242500	-0.54673600

H	5.50879700	-3.04227400	-0.25872200
H	5.79827000	-0.58250100	2.50128400
H	6.66561900	-1.76831800	1.52374300
H	7.11535300	-1.28647200	-0.96070300
H	6.55274200	0.22697800	-1.67233500
C	-0.52884900	3.40720600	-0.01439800
C	-1.23984400	3.22453900	-1.37904900
C	-1.44452800	2.95762800	1.15468500
C	-0.29062500	4.93173200	0.16526100
H	-1.43585500	2.17027300	-1.59633000
H	-0.58363200	3.59188600	-2.17889700
C	-2.57836100	3.97915600	-1.38846300
H	-0.92838600	3.14837600	2.10477300
H	-1.64842900	1.88404600	1.11985800
C	-2.77879800	3.71820200	1.10570700
H	0.35523200	5.30991000	-0.64109500
H	0.20168300	5.12415900	1.13010600
C	-1.61783400	5.70825800	0.13809100
H	-3.07014300	3.79963700	-2.35012700
C	-3.46428900	3.45850500	-0.24532300
C	-2.31756200	5.47982100	-1.20797800
H	-3.41437600	3.35283700	1.91896900
C	-2.51926800	5.21978400	1.27964100
H	-1.39464200	6.77258400	0.26718400
H	-3.65605200	2.38453600	-0.37252100
H	-4.43712700	3.96208000	-0.27132300
H	-1.69832400	5.85896600	-2.03063700
H	-3.26317300	6.03278300	-1.23383000
H	-3.46619300	5.77103500	1.26657200
H	-2.04584500	5.41296900	2.25044800
N	1.93681100	3.39506100	0.23960200
H	2.01338300	4.39675400	0.37549200

TS1cR-H$^+$

C	1.25330100	-4.07350400	-0.43013200
C	0.17544300	-4.87214100	-0.06513200
C	-1.08345500	-4.30922400	0.12400600
C	-1.27696600	-2.93471700	-0.02894000
C	-0.15595300	-2.16488300	-0.31891400
C	1.09344000	-2.69241700	-0.56163800
H	2.22345400	-4.51824600	-0.62537600
H	0.30462600	-5.94305000	0.04484600
H	-1.93158300	-4.93849200	0.36998200
H	1.92220100	-2.07199600	-0.86327300
I	-0.68578100	-0.05397900	-0.45454900

O	-2.56764100	-1.01927300	-0.60107600
C	-2.63863800	-2.24629400	0.01765000
C	-3.08223300	-2.06639900	1.49054700
C	-3.69645300	-3.05669500	-0.77561600
F	-4.79990200	-2.34336800	-0.95774100
F	-3.20579800	-3.38814800	-1.97320000
F	-4.03554900	-4.19061000	-0.14019700
F	-4.29548800	-1.53379300	1.58291700
F	-3.06777800	-3.21726800	2.16961500
F	-2.21722800	-1.22877000	2.09948600
C	1.24283700	1.34393900	-0.08938900
C	2.62380300	1.32145700	0.10996800
N	0.91325700	2.69002400	0.07764100
N	1.94924300	3.43545400	0.34703700
C	-0.40496300	3.45193600	0.01034600
C	-1.32465400	3.00124600	1.16003900
C	-0.12462700	4.95877500	0.20053200
C	-1.03734100	3.27090800	-1.37994300
H	-0.82319600	3.21251000	2.11268600
H	-1.53120800	1.92989700	1.13968500
C	-2.65580600	3.76839500	1.06438800
H	0.56169800	5.31148900	-0.57647000
H	0.35815900	5.12992900	1.16741900
C	-1.44742200	5.74397600	0.13218400
H	-1.22337500	2.22373900	-1.62729300
H	-0.34433700	3.65739000	-2.13753900
C	-2.37566900	4.02972800	-1.42603400
H	-3.31808800	3.40471000	1.85632700
C	-2.39131600	5.26810900	1.24428600
C	-3.29516100	3.50724100	-0.30960100
H	-1.21350000	6.80456900	0.26972900
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H	-2.83790800	3.85139900	-2.40212200
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H	-3.33385800	5.82501700	1.19883200
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C	3.45029900	-0.81526900	1.14015200
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H	3.41053200	-0.35845100	2.13767000
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H	3.87189500	2.99240600	0.56307300

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11. NMR Spectra

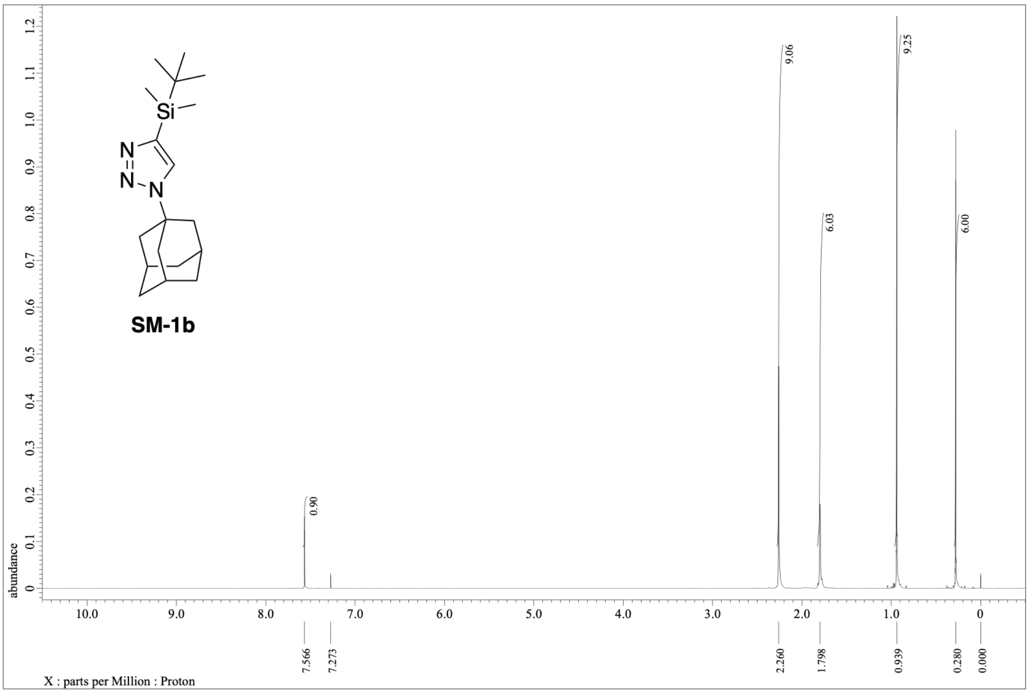

Figure S26. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **SM-1b**

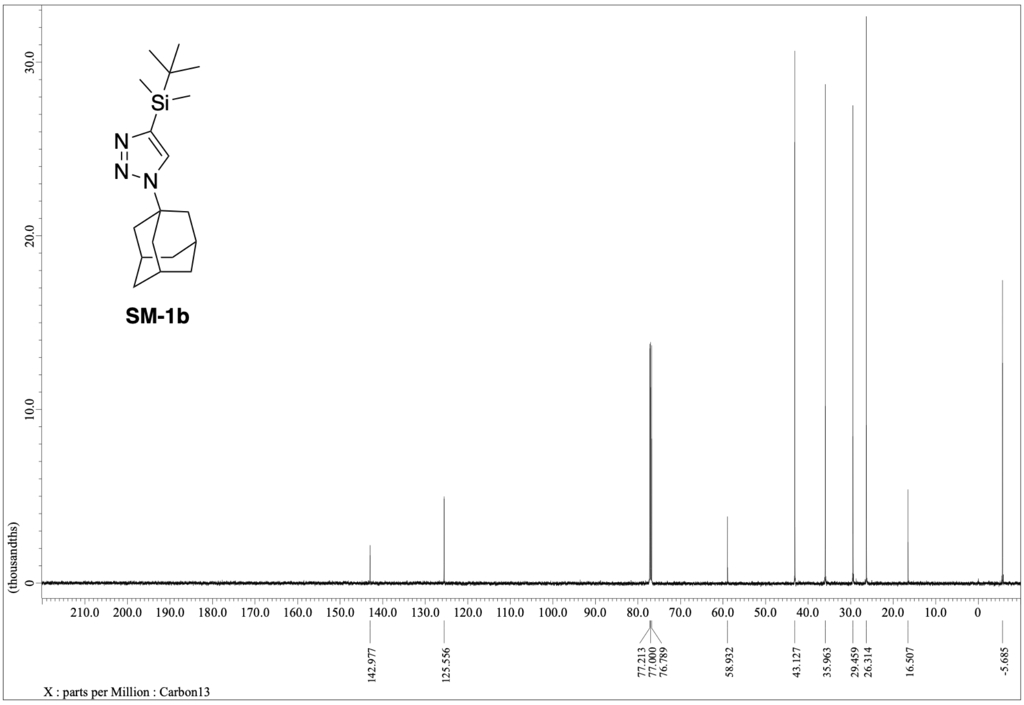

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **SM-1b**

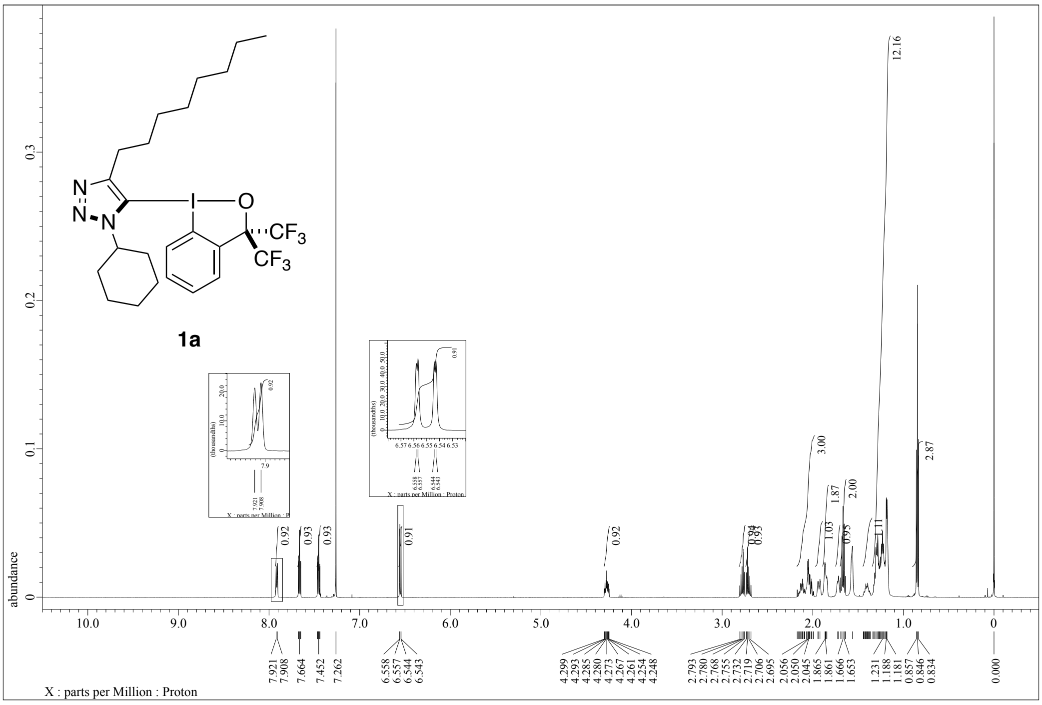

Figure S28. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1a**

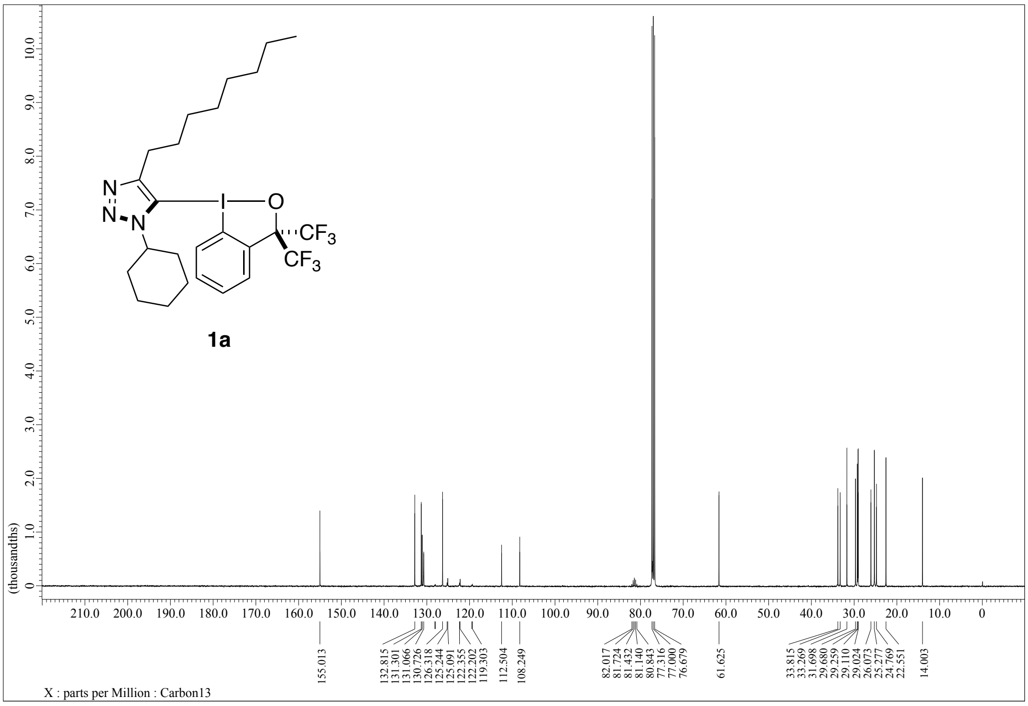

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **1a**

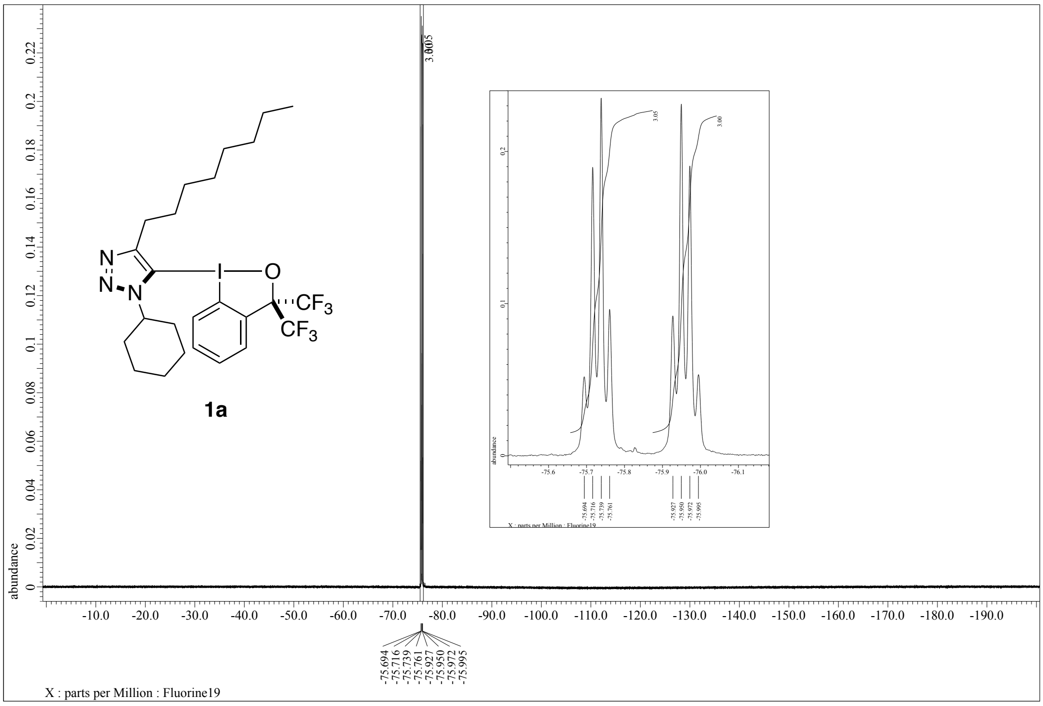

Figure S30. $^{19}F\{^{1}H\}$ NMR spectrum (565 MHz, $CDCl_3$) of **1a**

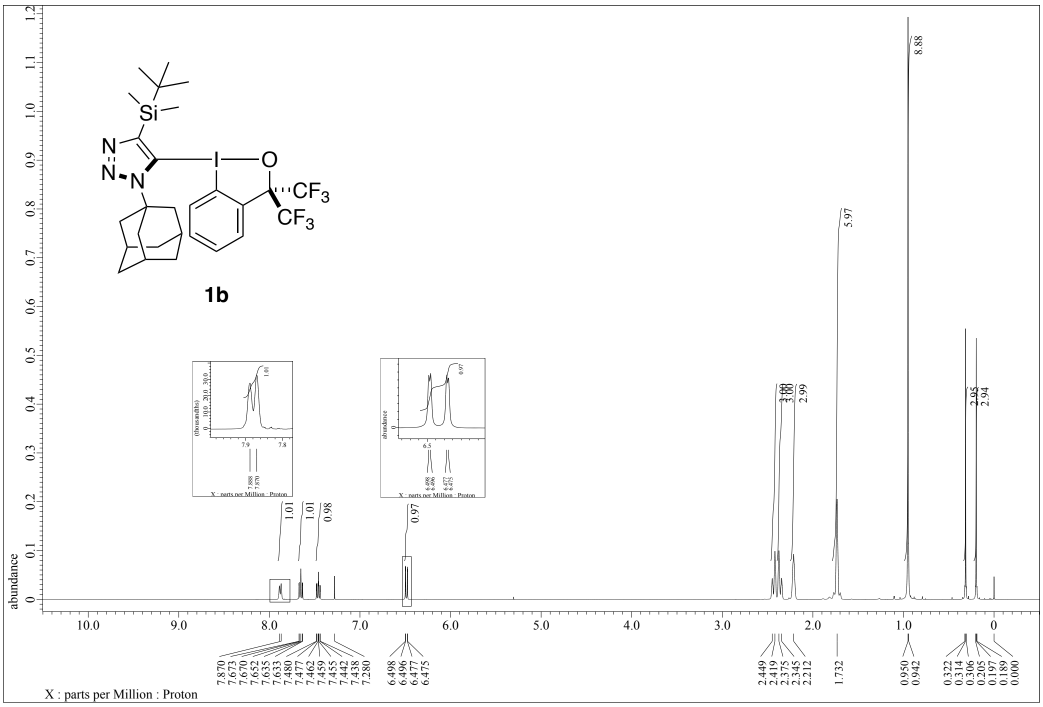

Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1b**

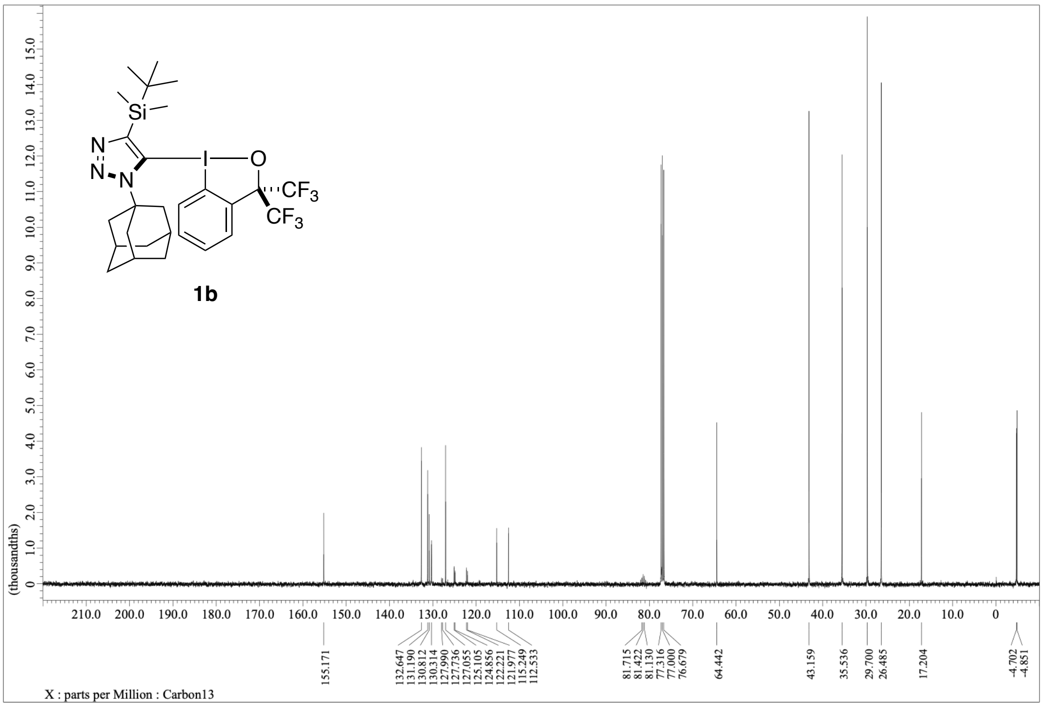

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **1b**

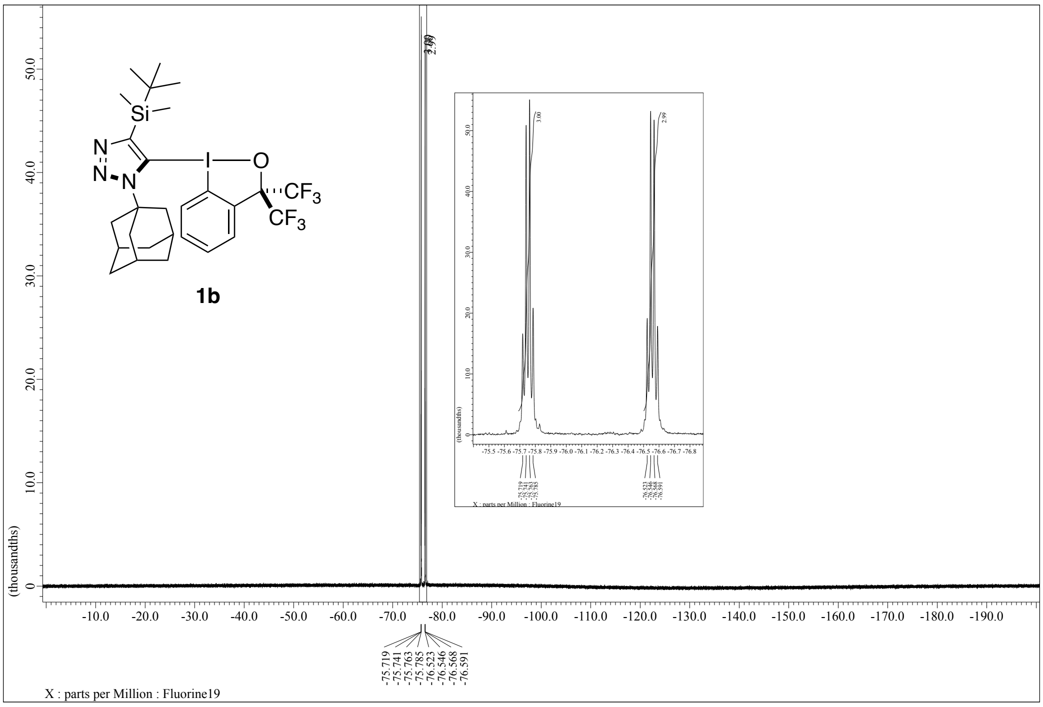

Figure S33. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, $CDCl_3$) of **1b**

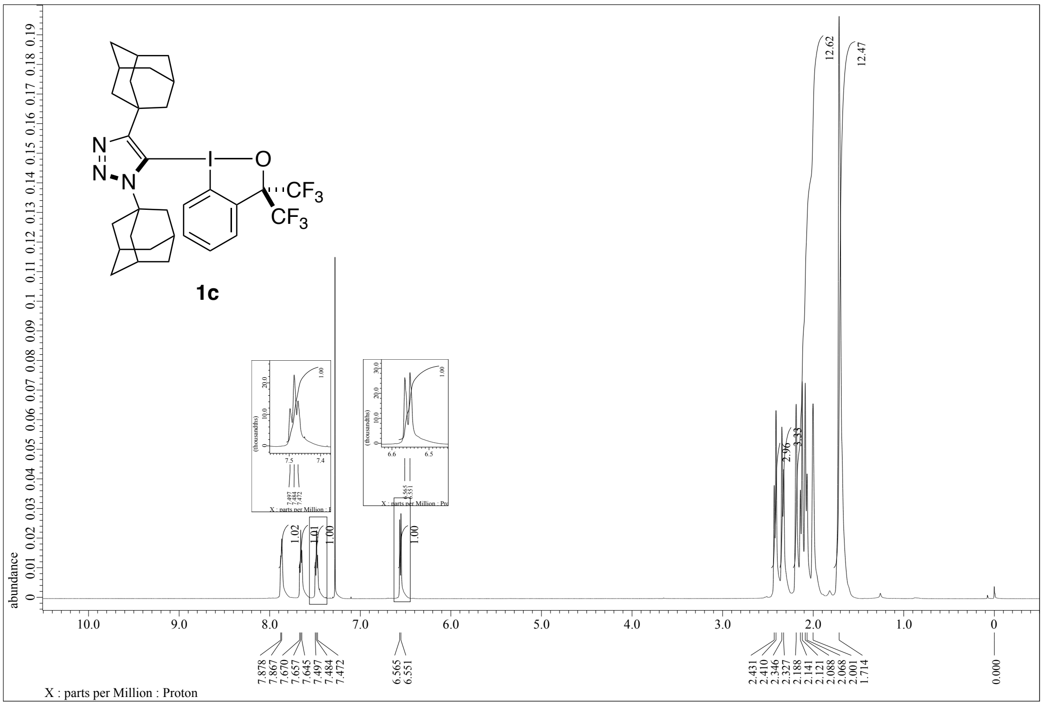

Figure S34. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1c**

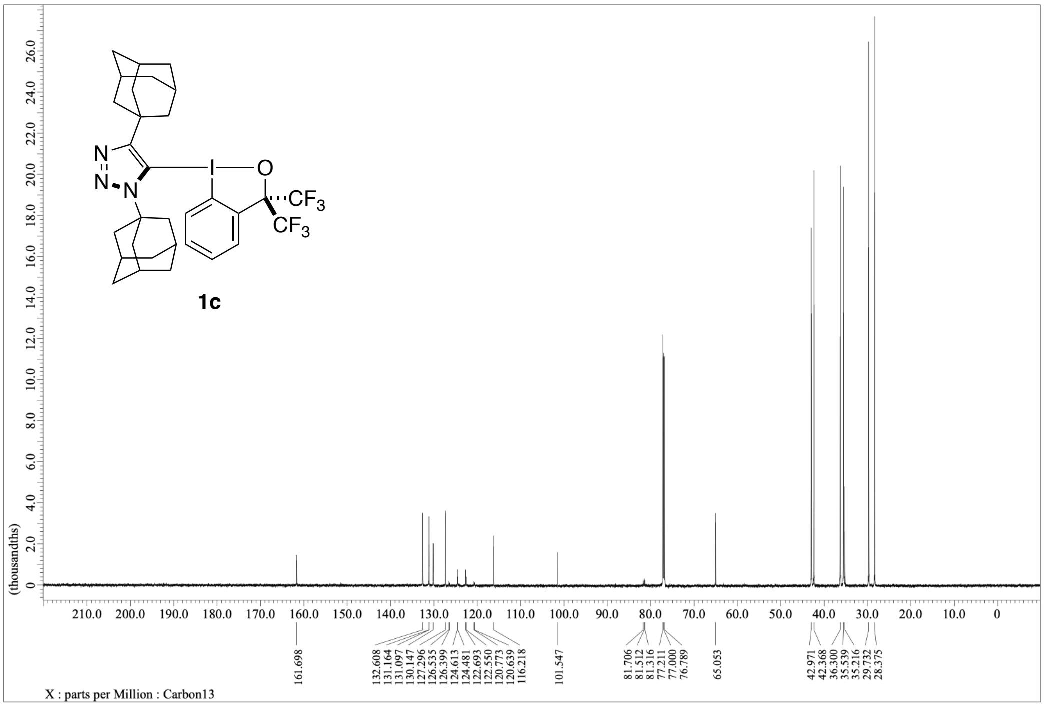

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **1c**

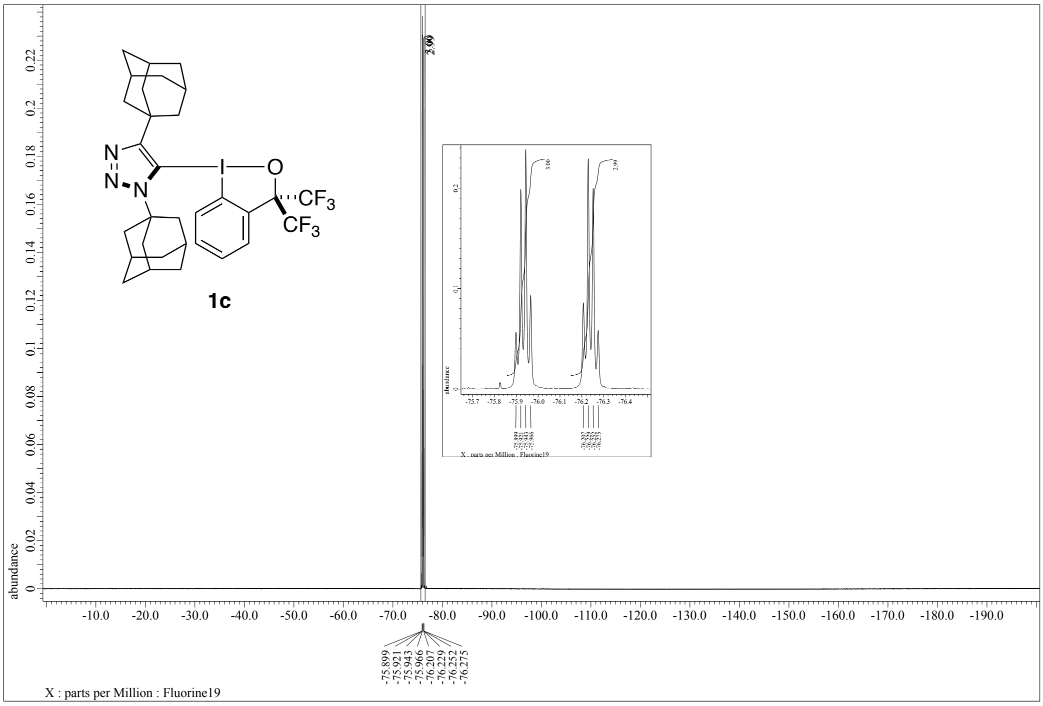

Figure S36. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, $CDCl_3$) of **1c**

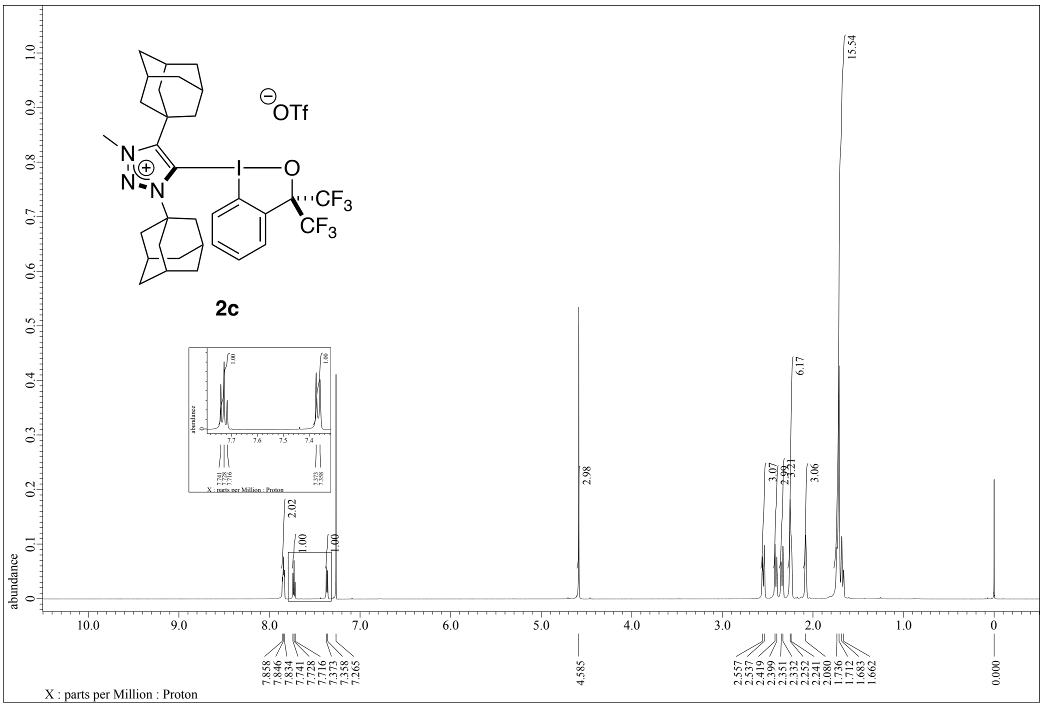

Figure S37. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2c**

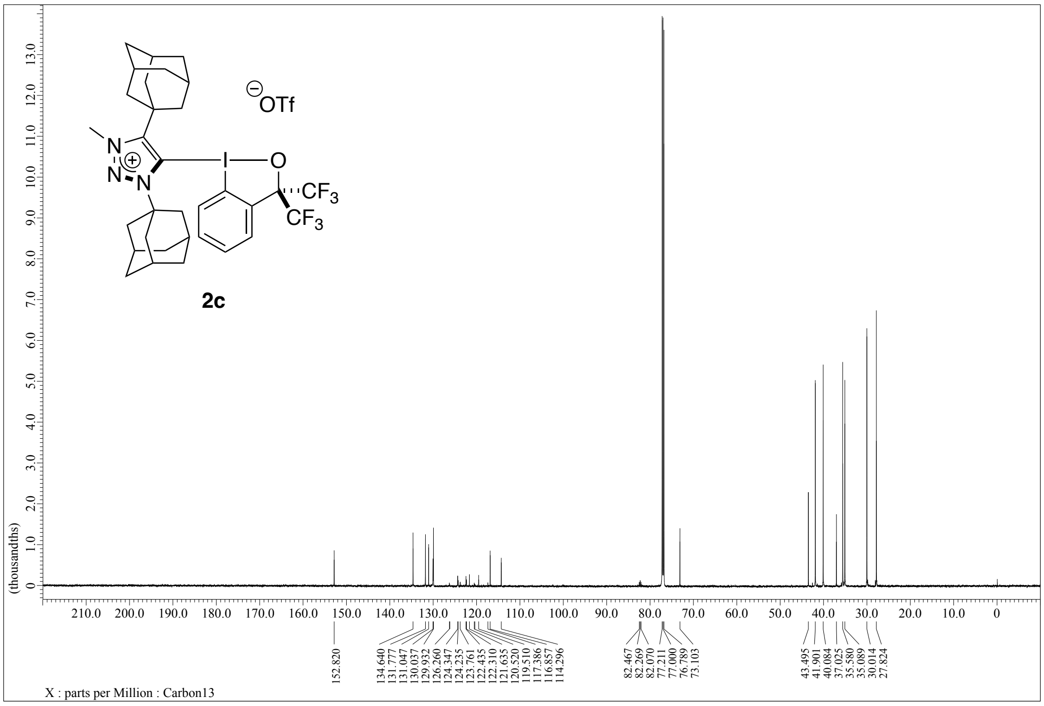

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **2c**

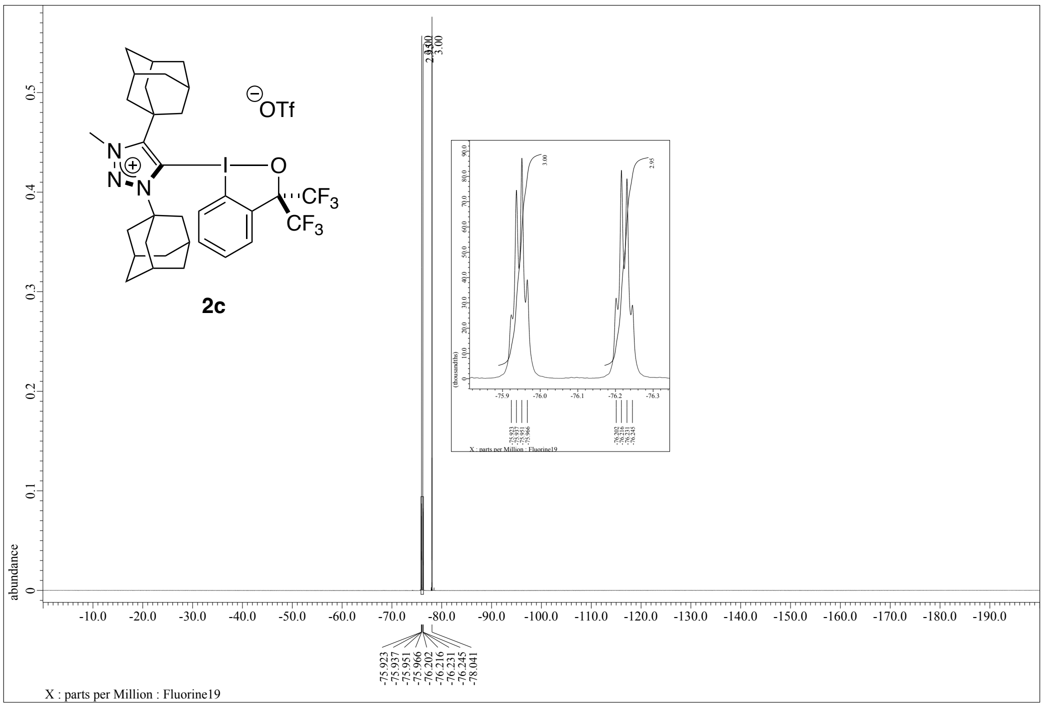

Figure S39. $^{19}F\{^{1}H\}$ NMR spectrum (565 MHz, $CDCl_3$) of **2c**