Synthesis of Enantiopure 1,2,3-Triazolylidene-Type Mesoionic Carbenes (MICs) Conjugate Acids Featuring a Rigid Bicyclic Scaffold

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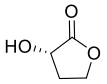
Supporting Information

General

Unless stated otherwise, all chemicals and reagents were purchased from commercial suppliers and used without further purification. All air- and moisture-sensitive manipulations were performed under Argon atmosphere using standard glovebox or Schlenk techniques. Solvents for air- and moisture-sensitive manipulations were purified, dried and degassed according to standard methods prior to use. For thin-layer chromatography (TLC), silica gel plates SiliaPlate TLC were used, and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid (AMC) or $KMnO_4$ followed by heating. Column chromatography was performed using silica gel SiliCycle-SiliaFlash P60 (particle size: 40-63 μm, pore diameter: 60 Å). ^{1}H, ^{13}C NMR, and ^{19}F spectra were recorded with Jeol ECA 500 at ambient temperature unless otherwise noted. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Jeol ECA 500. ^{1}H and ^{13}C NMR chemical shifts are given in δ relative to tetramethylsilane (TMS), 19F chemical shifts are given in δ relative to trichlorofluoromethane ($CFCl_3$) as external standard. ^{1}H chemical shifts are referenced to the residual protio-solvent (^{1}H) resonance of $CDCl_3$ (δ: 7.26), CD_3CN (δ: 1.94), CD_3OD (δ: 3.31), THF-d_8 (δ: 3.58 and 1.72). ^{13}C chemical shifts are referenced to the solvent (^{13}C) resonance of $CDCl_3$ (δ: 77.16), CD_3CN (δ: 118.26 and 1.32), CD_3OD (δ: 49.00), THF-d_8 (δ: 67.21 and 25.31). Chiral HPLC was carried out using a LC20AD Shimadzu liquid chromatograph with SPD-M20A diode array detector with columns Daicel Daicel Chiralpak® IB, and Daicel Chiralpak® IH. Samples for measurement of chiral HPLC were prepared by dissolving the corresponding sample in *i*-PrOH. Optical rotations were measured on Jasco P-1010 polarimeter. Specific optical rotations are given in concentrations *c* [g/100 ml]. High-resolution mass spectra were recorded with a LCQ Fleet spectrometer. Samples for measurement of HRMS were prepared in methanol. The x-ray measurements were carried on a Bruker APEX-II CCD diffractometer by micro-focus rotating anode MoKα (λ= 0.71073 Å) for **MIC-H$^+$f**. The structure was solved by direct methods (XT)[1] and refined by full matrix least squares based on F^2 (SHELXL2019).[2]

Experimental part

(*S*)-3-Hydroxydihydrofuran-2(3*H*)-one (3)



The title compound was prepared according to slightly modified previously reported procedures.[3]

$TsOH \cdot H_2O$ (709 mg, 3.7 mmol, 0.01 equiv.) was added in one portion to a stirred solution of L-malic acid (50.0 g, 373.0 mmol, 1.0 equiv.) in 2,2-dimethoxypropane (200 ml) at room temperature. At this temperature, the reaction mixture was stirred overnight. After the full disappearance of starting acid (according to ^{1}H NMR of crude mixture), a solution of $NaHCO_3$ (315 mg, 3.7 mmol, 0.01 equiv.) in water (200 ml) was added. The resulting mixture was extracted with DCM (5 × 100ml). The organic fractions were gathered, washed with brine (1 × 50 ml) and dried over anhydrous $MgSO_4$. After filtration, solvents and volatiles were removed under reduced pressure. The crude (52.3 g, 81 % yield) was checked by 1H NMR to confirm suitable purity and was used in the second step without further purification.

Crude carboxylic acid (52.3 g, 300 mmol, 1.0 equiv.) was dissolved in anhydrous THF (150 ml) and cooled to 0°C (water/ice bath). $BH_3 \cdot Me_2S$ (10M solution, 42 ml, 418 mmol, 1.4 equiv.) was added dropwise to a cooled and stirred solution of acid (gas evolution). After addition, reaction mixture was stirred at 0 °C for 1 hour. Then, the mixture was slowly heated up to room temperature and stirred overnight. After the full disappearance of starting acid (according to ^{1}H NMR of crude mixture), MeOH (50 ml) was added dropwise to quench the unreacted borane (beware of H_2 evolution) and the mixture stirred until gas evolution stopped (1 hour). Solvents and volatiles were removed under reduced pressure. The crude alcohol (45.0 g, 94% yield, slightly contaminated with lactone **3**) was used in the second step without further purification.

The crude alcohol (45.0 g, 281 mmol, 1.0 equiv.) was dissolved in benzene (300 ml). $TsOH \cdot H_2O$ (540 mg, 2.8 mmol, 0.01 equiv.) was added in one portion to a stirred solution of alcohol at room temperature. The reaction mixture was stirred overnight. After the full disappearance of the starting alcohol (according to TLC of the crude mixture), the reaction mixture was concentrated. The residue was purified by column chromatography (silica gel, hex/EtOAc – 1/1-1/2) and **3** was isolated as a colorless oil (19.8 g, 52% yield over three steps).

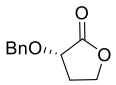
$[\alpha]_D^{22}$ = -69.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.61 – 4.37 (m, 2H), 4.30 – 4.16 (m, 1H), 3.31 (s, 1H), 2.61 (dddd, J = 14.4, 8.1, 6.0, 1.9 Hz, 1H), 2.37 – 2.18 (m, 1H) ppm.

HRMS (ESI+) m/z: calcd. for $C_4H_6O_3Na$ $[M + Na]^+$: 125.0209, found: 125.0208.

The spectral data are in agreement with those reported.[4]

(*S*)-3-(Benzyloxy)dihydrofuran-2(3*H*)-one (4a)

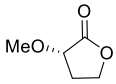


The title compound was prepared according to a slightly modified previously reported procedure.[5]

TfOH (0.3 ml, 2.9 mmol, 0.05 equiv.) was added in one portion to a stirred solution of **3** (6.0 g, 58.8 mmol, 1.0 equiv.) and benzyl 2,2,2-trichloroacetimidate (13.1 ml, 70.5 mmol, 1.2 equiv.) in anhydrous pentane/DCM (1/1, *v*/*v*, 120 ml) at 0 °C (ice/water bath). The reaction mixture was slowly heated to room temperature followed by stirring overnight. After the full disappearance of starting lactone (according to TLC), the mixture was cooled to -30 °C (freezer), the resulting solids were filtered off. The filtrate was diluted with EtOAc (200 ml) washed with a saturated solution of $NaHCO_3$ (1 × 50 ml), and brine (1 × 50 ml). The organic phase was dried over anhydrous $MgSO_4$. After filtration of drying agent, solvents and volatiles were removed under reduced pressure. The residue was purified by column chromatography (silica gel, hex/acetone – 7/1-5/1) and **4a** was isolated as a colorless oil (6.5 g, 57% yield).

$[\alpha]_D^{22}$ = -99.4 (c = 0.8, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.30 (m, 5H), 4.97 (d, J = 11.8 Hz, 1H), 4.76 (d, J = 11.8 Hz, 1H), 4.49 – 4.36 (m, 1H), 4.30 – 4.12 (m, 2H), 2.48 (dddd, J = 11.4, 7.6, 7.0, 4.4 Hz, 1H), 2.31 (dq, J = 13.1, 7.9 Hz, 1H) ppm.
HRMS (ESI+) m/z: calcd. for $C_{11}H_{12}O_3Na$ $[M + Na]^+$: 215.0679, found: 215.0679.
The spectral data are in agreement with those reported.[3]

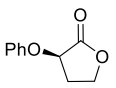
(*S*)-3-(Methyloxy)dihydrofuran-2(3*H*)-one (4b)



The title compound was prepared according to slightly a modified previously reported procedure.[6]
MeI (3.1 ml, 11.3 mmol, 5.1 equiv.) was added dropwise to a stirred suspension of **3** (1.0 g, 9.8 mmol, 1.0 equiv.), Ag_2O (2.6 g, 11.3 mmol, 1.15 equiv.) in MeCN (25 ml) loaded in round bottom flask covered by aluminum foil (light exclusion) at room temperature. The mixture was heated up to 80 °C (oil bath). At this temperature, the reaction mixture was stirred overnight. After the full disappearance of the starting lactone (according to TLC), the mixture was filtered through a short pad of Celite (washed with Et_2O). Solvents and volatiles were removed under reduced pressure and the residue was purified by column chromatography (silica gel, hex/EtOAc – 5/1-2/1) and **4b** was isolated as a colorless oil (0.8 g, 70% yield).

$[\alpha]_D^{22}$ = -80.4 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.40 (ddd, J = 9.1, 8.2, 4.2 Hz, 1H), 4.23 (ddd, J = 9.1, 8.1, 6.9 Hz, 1H), 4.02 (t, J = 7.7 Hz, 1H), 3.56 (s, 3H), 2.57 – 2.46 (m, 1H), 2.23 (dq, J = 13.1, 8.0 Hz, 1H) ppm.
HRMS (ESI+) m/z: calcd. for $C_5H_8O_3Na$ $[M + Na]^+$: 136.0366, found: 136.0366.
The spectral data are in agreement with those reported.[4]

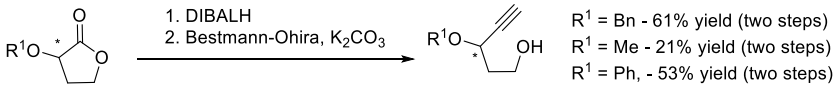
(*R*)-3-Phenoxydihydrofuran-2(3*H*)-one (4c)



DIAD (15.0 ml, 76.4 mmol, 1.2 equiv.) was added dropwise (in 5 minutes, slightly exothermic reaction) to a stirred solution of (*S*)-3-hydroxydihydrofuran-2(3*H*)-one (6.50 g, 63.7 mmol, 1.0 equiv.), phenol (7.19 g, 76.4 mmol, 1.2 equiv.) and PPh_3 (20.0 g, 76.4 mmol, 1.2 equiv.) in anhydrous THF (250 ml) at room temperature. After the full conversion of lactone (overnight, TLC monitoring), solvents and volatiles were evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, hex/EtOAc – 10/1) and **4c** was isolated as a white amorphous solid (4.89 g, 43% yield).

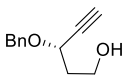
97% *ee*. The enantiomeric excess of product **4c** was determined by HPLC using a Chiralpak® IB column (*n*-heptane/*i*-PrOH – 90/10, flow rate = 1.0 mL/min, λ = 270 nm, t = 25 °C): t_R = 20.7 min, t_R = 21.8 min.
$[\alpha]_D^{22}$ = +89.3 (c = 1.5, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.24 (m, 2H), 7.08 – 6.94 (m, 3H), 4.95 (t, J = 7.9 Hz, 1H), 4.50 (ddd, J = 9.1, 8.3, 3.8 Hz, 1H), 4.33 (ddd, J = 9.0, 8.5, 6.8 Hz, 1H), 2.71 (dddd, J = 13.1, 7.7, 6.7, 3.8 Hz, 1H), 2.43 (dq, J = 13.2, 8.3 Hz, 1H) ppm.
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 173.7, 157.3, 129.7 (2C), 122.4, 115.9 (2C), 72.5, 65.4, 29.8 ppm.
HRMS (ESI+) m/z: calcd. for $C_{10}H_{11}O_3$ $[M + H]^+$: 179.0703, found: 179.0703.

General procedure 1 for alcohol synthesis (GP1)



A solution of DIBALH (1M solution in hexanes, 1.05 equiv.) was added dropwise (in 5 minutes) to a stirred solution of the lactone (1.0 equiv.) in anhydrous DCM (0.33 mol/l) at -78 °C. At this temperature, the reaction was stirred for 30 minutes (conversion was checked by TLC). After the full conversion of lactone, reaction was quenched by MeOH (1 ml per 1 mmol of lactone) at -78 °C (dry ice/acetone bath). The reaction was diluted with DCM (6 ml per 1 mmol of lactone) and aqueous saturated Rochelle´s salt solution (6 ml per 1 mmol of lactone). Heating to room temperature resulting in the formation of a heterogenous mixture. This mixture was vigorously stirred for 2 hours at room temperature. During this time, the mixture turned to a homogenous biphasic solution. The organic phase was separated, and the aqueous phase was further extracted with DCM (3 × 4 ml per 1 mmol of lactone). The organic fractions were gathered, washed with brine (1 × 4 ml per 1 mmol of lactone) and dried over anhydrous $MgSO_4$. After filtration of the drying agent, solvents were removed under reduced pressure. The crude lactol was used in the next step without further purification.
Bestmann-Ohira reagent (1.5 equiv. to lactone) was added dropwise (in 2 minutes) to a stirred suspension of lactole and K_2CO_3 (1.5 equiv. to lactone) in dry MeOH (0.33 mol/l) at 0°C (ice/water bath). The reaction was heated up to room temperature. After the full conversion of lactole (typically 1-2 hours, TLC and NMR monitoring), the reaction was quenched by water (5 ml per 1 mmol of lactone). The resulting mixture was extracted with Et_2O (3 × 5 ml per 1 mmol of lactone). The organic fractions were gathered, washed with brine (1 × 4 ml per 1 mmol of lactone) and dried over anhydrous $MgSO_4$. After filtration of the drying agent, solvents were removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes/EtOAc mixture).

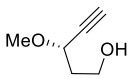
(*S*)-3-(Benzyloxy)pent-4-yn-1-ol (5a)



The title compound was synthesized according to general procedure GP1, using (*S*)-3-(benzyloxy)dihydrofuran-2(3*H*)-one (5.6 g, 29.1 mmol) as a starting material. **5a** was isolated as a colorless oil (3.40g, 61% yield over two steps).

$[\alpha]_D^{22}$ = -105.7 (*c* = 1.0, $CHCl_3$), lit.[6] $[\alpha]_D^{25}$ = -95.0 (*c* = 0.26, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 4.4 Hz, 4H), 7.31 (ddd, *J* = 8.8, 5.2, 3.7 Hz, 1H), 4.85 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.34 (td, *J* = 6.1, 2.1 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.81 – 3.74 (m, 1H), 2.54 (d, *J* = 2.1 Hz, 1H), 2.25 (br s, 1H), 2.03 (q, *J* = 6.0 Hz, 2H) ppm.
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 137.4, 128.6 (2C), 128.2 (2C), 128.1, 82.1, 74.8, 71.0, 67.4, 60.0, 38.0 ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_{12}H_{14}O_2Na$ $[M + Na]^+$: 213.0886, found: 213.0886.

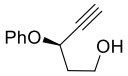
(*S*)-3-Methoxypent-4-yn-1-ol (5b)



The title compound was synthesized according to general procedure GP1, using (*S*)-3-methoxydihydrofuran-2(3*H*)-one (9.3 g, 79.4 mmol) as a starting material. **5b** was isolated as a colorless oil (1.4 g, 15% yield over two steps).

$[\alpha]_D^{22}$ = -86.1 (*c* = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.18 (td, *J* = 6.1, 2.1 Hz, 1H), 3.85 (dt, *J* = 11.3, 5.8 Hz, 1H), 3.76 (dt, *J* = 11.2, 5.4 Hz, 1H), 3.41 (s, 3H), 2.48 (d, *J* = 2.1 Hz, 1H), 2.39 (s, 1H), 1.97 (q, *J* = 5.8 Hz, 2H) ppm.
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 81.9, 74.7, 70.0, 59.9, 56.9, 37.9 ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_6H_{11}O_2$ $[M + H]^+$: 115.0754, found: 115.0755.

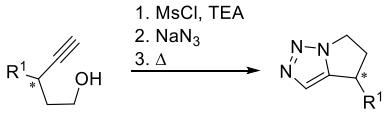
(*R*)-3-Phenoxypent-4-yn-1-ol (5c)



The title compound was synthesized according to general procedure GP1, using (*R*)-3-phenoxydihydrofuran-2(3*H*)-one (2.50 g, 14.0 mmol) as a starting material. **5c** was isolated as a colorless oil (1.3 g, 53% yield over two steps).

$[\alpha]_D^{22}$ = +138.6 (*c* = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.28 (m, 2H), 7.10 – 6.98 (m, 3H), 5.00 (ddd, *J* = 7.3, 5.5, 2.1 Hz, 1H), 3.94 (ddd, *J* = 11.8, 7.2, 4.8 Hz, 1H), 3.89 (ddd, *J* = 11.1, 6.4, 5.0 Hz, 1H), 2.53 (d, *J* = 2.0 Hz, 1H), 2.30 (br s, 1H), 2.27 – 2.13 (m, 2H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.3, 129.5 (2C), 121.8, 115.8 (2C), 81.7, 75.2, 65.5, 59.0, 38.3 ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_{11}H_{13}O_2$ $[M + H]^+$: 177.0910, found, 177.0913.

General procedure 2 for 1,2,3-triazole synthesis (GP2)

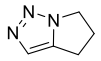


R^1 = H - 77% yield (three steps)
R^1 = OBn - 69% yield (three steps)
R^1 = OPh - 69% yield (three steps)
R^1 = OMe - 39% yield (three steps)

Caution: Azides are potentially explosive compounds. Although we have not encountered any safety problem when handling them in our experiments, proper precautions must be taken to avoid strong mechanical shock or ruction. The reactions (especially high temperature triazole synthesis) should be performed in a hood behind a blast shield.

Azides were prepared following a slightly modified literature procedure.[7]
Methanesulfonyl chloride was added dropwise to a stirred solution of alcohol (1.0 equiv.) and TEA (1.2 equiv.) in anhydrous diethyl ether (0.5 mol/l of alcohol) at 0 °C (ice/water bath). At this temperature, the reaction was stirred for 1 hour (conversion was checked by TLC). After the full conversion of alcohol, the reaction was diluted by adding water (5 ml per 1 mmol of alcohol). The organic phase was separated, the water phase was extracted by Et_2O (3 × 5 ml per 1 mmol of alcohol). The organic fractions were gathered, washed with brine (1 × 5 ml per 1 mmol of alcohol) and dried over anhydrous $MgSO_4$. After filtration, solvents and volatiles were removed under reduced pressure. The crude product was used in the next step without further purification.
Sodium azide (2.5 equiv. to mesylate) was added in one portion to a stirred solution of mesylate (1.0 equiv.) in DMF (0.5 mol/l of mesylate) at room temperature. The reaction was heated up to 70 °C (oil bath). At this temperature, the reaction was stirred for 1 hour (conversion was checked by TLC). After the full conversion of mesylate, the reaction was diluted with water (5 ml per 1 mmol of mesylate). The organic phase was separated, and the aqueous phase was further extracted with Et_2O (3 × 5 ml per 1 mmol of mesylate). The organic fractions were gathered, washed with brine (2 × 5 ml per 1 mmol of alcohol) and dried over anhydrous $MgSO_4$. After filtration of the drying agent, solvents and volatiles were removed under reduced pressure. The crude product was used in the next step without further purification.
A stirred solution of azide (1.0 equiv.) in toluene (50 mmol/l of azide) was heated up to 125 °C (oil bath). At this temperature, the reaction was stirred overnight (15 hours, the conversion was checked by TLC). After the full conversion of the azide, the reaction was cooled to room temperature and evaporated. The residue was purified by column chromatography (silica gel, hex/EtOAc or EtOAc/MeOH mixtures).

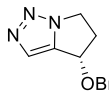
5,6-Dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazole (2)



The title compound was synthesized according to general procedure GP2, using 4-pentyn-1-ol (5.0 g, 59.4 mmol) as a starting material.
2 was isolated as a colorless oil (5.0 g, 77% yield over three steps).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (s, 1H), 4.35 – 4.25 (m, 2H), 2.97 – 2.85 (m, 2H), 2.78 (dddd, J = 13.4, 7.9, 6.7, 1.5 Hz, 2H) ppm.
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 142.0, 126.8, 46.2, 28.3, 20.6 ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_5H_8N_3$ $[M + H]^+$: 110.0713, found: 110.0713.

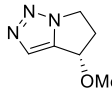
(*S*)-4-(Benzyloxy)-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazole (6a)



The title compound was synthesized according to general procedure GP2, using **5a** (2.2 g, 11.6 mmol) as a starting material.
6a was isolated as a colorless oil (1.7 g, 69% yield over three steps).

98% *ee*. The enantiomeric excess of product **6a** was determined by HPLC using a Chiralpak® IH column (*n*-heptane/*i*-PrOH – 60/40, flow rate = 1.0 mL/min, λ = 209 nm, t = 25 °C): t_R = 17.0 min, t_R = 24.5 min.
$[\alpha]_D^{22}$ = -92.3 (c = 2.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.43 – 7.28 (m, 5H), 4.98 (dd, J = 6.9, 2.4 Hz, 1H), 4.60 (d, J = 11.4 Hz, 1H), 4.57 – 4.45 (m, 2H), 4.38 – 4.30 (m, 1H), 3.06 (ddt, J = 14.2, 8.9, 7.1 Hz, 1H), 2.83 (dddd, J = 13.8, 7.8, 3.5, 2.4 Hz, 1H) ppm.
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 141.4, 137.0, 128.8 (2C), 128.3 (2C, *overlapped*), 128.2, 71.4, 70.5, 45.3, 36.9 ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_{12}H_{14}N_3O$ $[M + H]^+$: 216.1131, found: 216.1130.

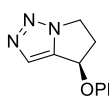
(*S*)-4-Methoxy-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazole (6b)



The title compound was synthesized according to general procedure GP2, using **5b** (1.3 g, 11.4 mmol) as a starting material.
6b was isolated as a colorless oil (620 mg, 39% yield over three steps).

$[\alpha]_D^{22}$ = -67.2 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (s, 1H), 4.74 (dt, J = 6.9, 2.4 Hz, 1H), 4.50 – 4.34 (m, 1H), 4.27 (dddd, J = 15.3, 8.3, 3.3, 1.5 Hz, 1H), 3.30 (s, 3H), 3.07 – 2.95 (m, 1H), 2.69 (dddd, J = 16.4, 8.0, 3.4, 1.6 Hz, 1H) ppm.
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 141.4, 137.0, 128.8 (2C), 128.3 (2C, *overlapped*), 128.2, 71.4, 70.5, 45.3, 36.9 ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_6H_{10}N_3O$ $[M + H]^+$: 140.0818, found: 140.0817.

(*R*)-4-Phenoxy-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazole (6c)

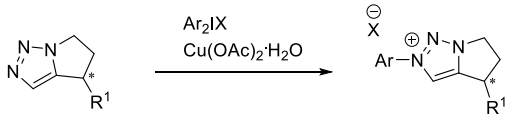


The title compound was synthesized according to general procedure GP2, using **5c** (1.3 g, 7.3 mmol) as a starting material.
6c was isolated as a white amorphous solid (1.0 g, 69% yield over three steps).

97% *ee*. The enantiomeric excess of product **6c** was determined by HPLC using a Chiralpak® IH column (*n*-heptane/*i*-PrOH – 60/40, flow rate = 1.0 mL/min, λ = 190 nm, t = 25 °C): t_R = 22.3 min, t_R = 27.7 min.
$[\alpha]_D^{22}$ = +171.5 (c = 0.9, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.41 – 7.29 (m, 2H), 7.03 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 8.1 Hz, 2H), 5.68 (dd, J = 6.9, 2.6 Hz, 1H), 4.58 (dt, J = 11.7, 7.4 Hz, 1H), 4.42 (ddd, J = 12.1, 8.8, 3.9 Hz, 1H), 3.25 (ddt, J = 13.9, 8.8, 6.9 Hz, 1H), 3.10 – 2.95 (m, 1H) ppm.
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 156.6, 140.9, 129.9 (2C), 128.9, 122.2, 115.5 (2C), 68.9, 45.2, 36.6 ppm.
HRMS (ESI+) *m/z*: calcd. for $C_{11}H_{12}N_3O$ $[M + H]^+$: 202.0975, found: 202.0973.

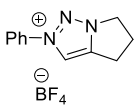
General procedure 3 for preparation of triazolium salt via arylation reaction (GP3)



R^1 = H, Ar = Ph, X = BF_4 - 98% yield
R^1 = H, Ar = Mes, X = BF_4 - 82% yield
R^1 = H, Ar = Mes, X = OTf - 68% yield
R^1 = OBn, Ar = Ph, X = BF_4 - 79% yield
R^1 = OBn, Ar = Mes, X = BF_4 - 77% yield
R^1 = OPh, Ar = Ph, X = BF_4 - 72% yield
R^1 = OPh, Ar = Mes, X = BF_4 - 86% yield
R^1 = OMe, Ar = Ph, X = BF_4 - 94% yield
R^1 = OMe, Ar = Mes, X = BF_4 - n.d.

Triazolium salts were prepared following a slightly modified literature procedure.[8]
$Cu(OAc)_2 \cdot H_2O$ (0.05 equiv.) was added in one portion to a stirred solution of triazole **6** or **2** (1.0 equiv.) and iodonium salt (1.5 equiv.) in DMF (0.25 mol/l of **6** or **2**) at room temperature. The reaction was heated up to 100 °C (oil bath). At this temperature the reaction was stirred for 4 hours (conversion was checked by TLC and ^{1}H NMR). After full conversion of triazole, solvents and volatiles were removed under reduced pressure. The residue was purified by column chromatography (silica gel, DCM/MeOH mixtures).

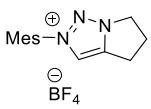
2-Phenyl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$a)



The title compound was synthesized according to general procedure GP3, using **2** (200 mg, 1.83 mmol) as a starting material.
MIC-H$^+$a was isolated as a white amorphous solid (490 mg, 98% yield).

^{1}H NMR (500 MHz, CD_3CN): δ 8.50 (s, 1H), 7.87 – 7.78 (m, 2H), 7.74 – 7.63 (m, 3H), 4.71 – 4.67 (m, 2H), 3.30 – 3.19 (m, 2H), 2.93 – 2.78 (m, 2H) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 149.5, 136.8, 132.8, 131.4 (2C), 124.1, 122.9 (2C), 52.0, 27.2, 23.3 ppm.
^{19}F NMR (471 MHz, CD_3CN): δ -151.8 (s, 4F) ppm.
HRMS (ESI+) *m/z*: calcd. for $C_{11}H_{12}N_3$ $[M - BF_4]^+$: 186.1026, found: 186.1024.

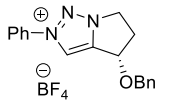
2-Mesityl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$b)



The title compound was synthesized according to general procedure GP3, using **2** (200 mg, 1.83 mmol) as a starting material.
MIC-H$^+$b was isolated as a white amorphous solid (480 mg, 82% yield).

^{1}H NMR (500 MHz, CD_3CN): δ 8.19 (s, 1H), 7.15 (s, 2H), 4.77 – 4.64 (m, 2H), 3.25 (t, J = 7.5 Hz, 2H), 2.88 (p, J = 7.6 Hz, 2H), 2.37 (s, 3H), 2.04 (s, 6H) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 149.5, 143.6, 135.8 (2C), 133.3, 130.5 (2C), 127.8, 52.2, 26.9, 23.5, 21.2, 17.2 (2C) ppm.
^{19}F NMR (471 MHz, CD_3CN): δ -152.4 (s, 4F) ppm.
HRMS (ESI+) *m/z*: calcd. for $C_{14}H_{18}N_3$ $[M - BF_4]^+$: 228.1295, found: 228.1494.

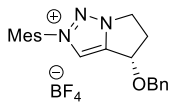
(*S*)-4-(Benzyloxy)-2-phenyl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$c)



The title compound was synthesized according to general procedure GP3, using **6a** (400 mg, 1.86 mmol) as a starting material.
MIC-H$^+$c was isolated as a yellow oil (50 mg, 69% yield).
$[\alpha]_D^{22}$ = -7.2 (*c* = 0.6, CH_3CN).

^{1}H NMR (500 MHz, CD_3OD): δ 9.06 (d, *J* = 12.0 Hz, 1H), 7.91 (ddd, *J* = 7.2, 4.9, 2.9 Hz, 2H), 7.66 (q, *J* = 4.1 Hz, 3H), 7.47 – 7.40 (m, 2H), 7.39 – 7.26 (m, 3H), 5.40 (dq, *J* = 7.0, 3.4 Hz, 1H), 4.91 (dq, *J* = 14.0, 7.3 Hz, 1H), 4.74 (qd, *J* = 10.5, 4.2 Hz, 4H), 3.29 – 3.18 (m, 1H), 2.91 – 2.76 (m, 1H) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_3OD): δ 148.0, 138.3, 137.1, 132.9, 131.4 (2C), 129.5 (2C), 129.4 (2C), 129.2, 125.5, 122.9 (2C), 73.7, 73.2, 51.0, 35.9 ppm.
^{19}F NMR (471 MHz, CD_3OD): δ -154.8 (s, 4F) ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_{18}H_{18}N_3O$ [M - BF_4]$^+$: 292.1444, found: 292.1448.

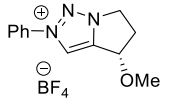
(*S*)-4-(Benzyloxy)-2-mesityl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$d)



The title compound was synthesized according to general procedure GP3, using **6a** (300 mg, 1.39 mmol) as a starting material.
MIC-H$^+$a was isolated as a white crystalline solid (450 mg, 77% yield).

$[\alpha]_D^{22}$ = -8.6 (*c* = 1.5, CH_3CN).
^{1}H NMR (500 MHz, CD_3CN): δ 8.30 (s, 1H), 7.46 – 7.31 (m, 5H), 7.17 (s, 2H), 5.41 (dd, *J* = 7.5, 3.6 Hz, 1H), 4.90 (ddd, *J* = 13.0, 8.6, 6.1 Hz, 1H), 4.79 – 4.66 (m, 3H), 3.26 (dddd, *J* = 13.8, 8.9, 7.5, 6.1 Hz, 1H), 2.86 (dddd, *J* = 13.9, 8.7, 5.2, 3.6 Hz, 1H), 2.38 (s, 3H), 2.04 (s, 6H) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 147.5, 143.7, 138.1, 135.7, 132.9, 130.5 (2C), 129.5 (2C), 129.2 (2C+1C, *overlapped*), 129.1 (2C), 129.0, 73.6, 72.9, 51.3, 35.5, 21.2, 17.2 (2C) ppm.
^{19}F NMR (471 MHz, CD_3CN): δ -152.58 (s, 4F) ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_{21}H_{24}N_3O$ [M - BF_4]$^+$: 334.1914, found: 334.1912.

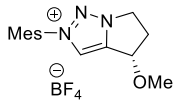
(*S*)-4-Methoxy-2-phenyl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$e)



The title compound was synthesized according to general procedure GP3, using **6b** (200 mg, 1.44 mmol) as a starting material.
MIC-H$^+$e was isolated as a white amorphous solid (410 mg, 94% yield).

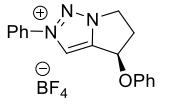
$[\alpha]_D^{22}$ = -22.6 (*c* = 0.9, MeCN).
^{1}H NMR (500 MHz, CD_3CN): δ 8.88 (s, 1H), 7.91 – 7.79 (m, 2H), 7.79 – 7.61 (m, 3H), 5.18 (dd, *J* = 7.4, 3.6 Hz, 1H), 4.83 (dt, *J* = 15.2, 7.6 Hz, 1H), 4.78 – 4.66 (m, 1H), 3.48 (s, 3H), 3.18 (ttd, *J* = 12.0, 5.6, 3.7 Hz, 1H), 2.83 – 2.72 (m, 1H) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 147.3, 136.6, 133.0, 131.4 (2C), 125.5, 122.9 (2C), 74.9, 57.8, 51.1, 35.3 ppm.
^{19}F NMR (471 MHz, CD_3CN): δ -151.79 (s, 4F) ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_{12}H_{14}N_3O$ [M - BF_4]$^+$: 216.1131, found: 216.1132.

(*S*)-2-Mesityl-4-methoxy-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate



The title compound was synthesized following to general procedure GP3, using **6b** (200 mg, 1.44 mmol) as a starting material. We obtained corresponding product in high yield, but we were not able to purify them from mesitylene-based by-product even after several column chromatography and crystallizations.

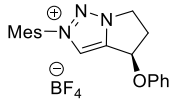
(*R*)-4-Phenoxy-2-phenyl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$f)



The title compound was synthesized according to general procedure GP3, using **6c** (300 mg, 1.49 mmol) as a starting material.
MIC-H$^+$f was isolated as a white amorphous solid (390 mg, 72% yield).

$[\alpha]_D^{22}$ = +30.4 (*c* = 1.3, MeCN).
^{1}H NMR (500 MHz, CD_3CN): δ 8.78 (s, 1H), 7.90 – 7.77 (m, 2H), 7.76 – 7.62 (m, 3H), 7.54 – 7.38 (m, 2H), 7.19 – 7.03 (m, 3H), 6.11 (dd, *J* = 7.3, 3.2 Hz, 1H), 4.96 (ddd, *J* = 13.1, 8.4, 6.5 Hz, 1H), 4.82 (ddd, *J* = 13.3, 8.9, 4.6 Hz, 1H), 3.42 (ddt, *J* = 14.0, 8.8, 6.8 Hz, 1H), 3.09 – 2.92 (m, 1H) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 157.2, 146.8, 136.5, 133.0, 131.3 (2C), 131.1 (2C), 125.9, 123.5, 123.0 (2C), 116.4 (2C), 71.6, 51.1, 35.4 ppm.
^{19}F NMR (471 MHz, CD_3CN): δ -151.75 (s, 4F) ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_{17}H_{16}N_3O$ [M - BF_4]$^+$: 278.1288, found: 278.1290.

(*R*)-2-Mesityl-4-phenoxy-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$g)



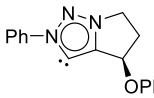
The title compound was synthesized according to general procedure GP3, using **6c** (300 mg, 1.49 mmol) as a starting material.
MIC-H$^+$g was isolated as a white amorphous solid (520 mg, 86% yield).

$[\alpha]_D^{22}$ = +54.6 (*c* = 1.3, MeCN).
^{1}H NMR (500 MHz, CD_3CN): δ 8.44 (s, 1H), 7.40 (t, *J* = 7.1 Hz, 2H), 7.17 – 7.03 (m, 5H), 6.13 (tq, *J* = 7.6, 4.1 Hz, 1H), 4.99 (ddd, *J* = 13.7, 8.6, 5.3 Hz, 1H), 4.83 (dh, *J* = 13.3, 5.2 Hz, 1H), 3.46 (tt, *J* = 12.9, 7.3 Hz, 1H), 3.03 (ddt, *J* = 13.2, 8.6, 4.0 Hz, 1H), 2.37 (s, 3H), 2.02 (s, 6H) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 157.23, 146.7, 143.7, 135.7, 132.9, 131.0 (2C), 130.5 (2C), 129.5 (2C), 123.6, 116.7 (2C), 72.1, 51.5, 35.2, 21.1, 17.2 (2C) ppm.
^{19}F NMR (471 MHz, CD_3CN): δ -151.80 (s, 4F) ppm.
HRMS (ESI+) *m*/*z*: calcd. for $C_{20}H_{22}N_3O$ [M - BF_4]$^+$: 320.1757, found: 320.1758.

Deprotonation of triazolium salt

Triazolium salt **MIC-H$^+$** (40.7 mg, 0.1 mmol, 1.0 equiv.) was dissolved in deuterated tetrahydrofuran (1.0 ml). The resulting solution was placed to a regular NMR tube without any special precautions. The NMR sample was cooled to 0 °C and KO^{t}Bu was added in one portion to the precooled solution. The NMR spectra were recorded at 0 °C.

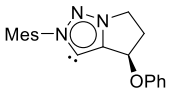
(*R*)-2-Phenyl-4-phenoxy-5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-5-ylidene (MICf)



The title compound was synthesized according to general procedure GP4, using salt **MIC-H$^+$f** (36.5 mg, 0.1 mmol) as a starting material.

^{1}H NMR (600 MHz, 0 °C, THF-d_8): δ 8.27 (d, J = 7.9 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 3H), 7.27 (t, J = 7.9 Hz, 2H), 6.92 (t, J = 7.5 Hz, 1H), 5.76 (d, J = 6.5 Hz, 1H), 4.70 (dt, J = 15.1, 8.0 Hz, 1H), 4.55 (t, J = 10.9 Hz, 1H), 3.17 (dd, J = 14.5, 7.5 Hz, 1H), 2.84 (dd, J = 14.1, 7.5 Hz, 1H) ppm.
^{13}C{^{1}H} NMR (151 MHz, 0 °C, THF-d_8): δ 195.5, 159.0, 154.0, 143.8, 130.2 (2C), 129.8 (2C), 128.8, 121.8 (2C), 119.8, 117.0 (2C), 73.0, 46.8, 32.4 ppm.

(*R*)-2-Mesityl-4-phenoxy-5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-5-ylidene (MICg)

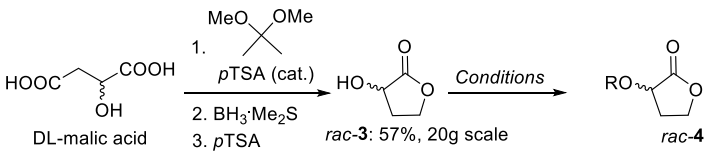


The title compound was synthesized according to general procedure GP4, using salt **MIC-H$^+$g** (40.7 mg, 0.1 mmol) as a starting material.

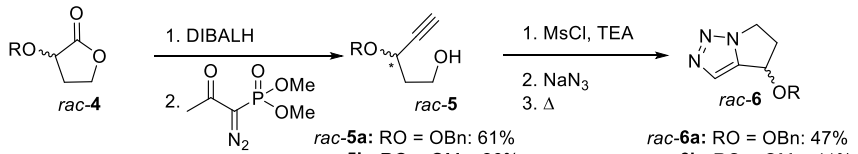
^{1}H NMR (600 MHz, 0 °C, THF-d_8): δ 7.39 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 7.7 Hz, 2H), 6.95 (s, 2H), 6.90 (t, J = 7.4 Hz, 1H), 5.75 (d, J = 6.8 Hz, 1H), 4.69 (dt, J = 14.9, 8.0 Hz, 1H), 4.53 (dt, J = 12.2, 5.9 Hz, 1H), 3.20 (dq, J = 15.5, 7.9 Hz, 1H), 2.84 (m, J = 14.3, 7.8 Hz, 1H), 2.31 (s, 3H), 1.94 (s, 6H) ppm.
^{13}C{^{1}H} NMR (151 MHz, 0 °C, THF-d_8): δ 199.7, 159.2, 153.7, 140.8, 139.0, 135.4 (2C), 130.1 (2C), 129.4 (2C, *overlapped*), 121.8, 117.3 (2C, *overlapped*), 73.5, 46.7, 33.4, 21.3, 18.01 (2C, *overlapped*) ppm.

Preparation of racemic samples

The optical purity of compounds **4c**, **6a** and **6c** was determined by chiral HPLC. The corresponding racemic samples were prepared according to previously reported procedures (see below), starting from DL-malic acid. In all cases, the spectral data were in agreement with those of enantioenriched analogs. We were not able to determine the optical purity of triazole **6b** by chiral HPLC due to lack of detection of triazole **6b** by the diode array detector used.



Conditions:
rac-**4a**: R^1 = OBn: benzyl 2,2,2-trichloroacetimidate,TfOH (cat.), 64%, *rac*-**4b:** R^1 = OMe: CH_3I, Ag_2O, 72%,
rac-**4c:** R^1 = OPh: phenol, DIAD, PPh_3, 41%



rac-**5a:** RO = OBn: 61%
rac-**5b:** RO = OMe: 26%
rac-**5c:** RO = OPh: 55%

rac-**6a:** RO = OBn: 47%
rac-**6b:** RO = OMe: 41%
rac-**6c:** RO = OPh: 67%

Control experiments

Stability of free carbene

The stability of carbene derived from salt **MIC-H$^+$g** was checked at 0 °C, and 40 °C by the following control experiments.

Triazolium salt **MIC-H$^+$g** (40.7 mg, 0.1 mmol, 1.0 equiv.) was dissolved in THF-d_8 (1.0 ml). The resulting solution was placed in a regular NMR tube without any special precautions. The NMR sample was cooled to 0 °C and KO^{t}Bu (22.4 mg, 0.2 mmol, 2.0 equiv.) was added in one portion. The NMR spectra were recorded at 0 °C at different intervals over a 48-hour period (Figure S3).

Triazolium salt **MIC-H$^+$g** (40.7 mg, 0.1 mmol, 1.0 equiv.) was dissolved in THF-d_8 (1.0 ml). The resulting solution was placed in a regular NMR tube without any special precautions. The resulting solution was placed in a regular NMR tube without any special precautions. The NMR sample was heated to 40 °C and KO^{t}Bu (22.4 mg, 0.2 mmol, 2.0 equiv.) was added in one portion. The NMR spectra were recorded at 40 °C at different intervals over a 48-hour period (Figure S4).

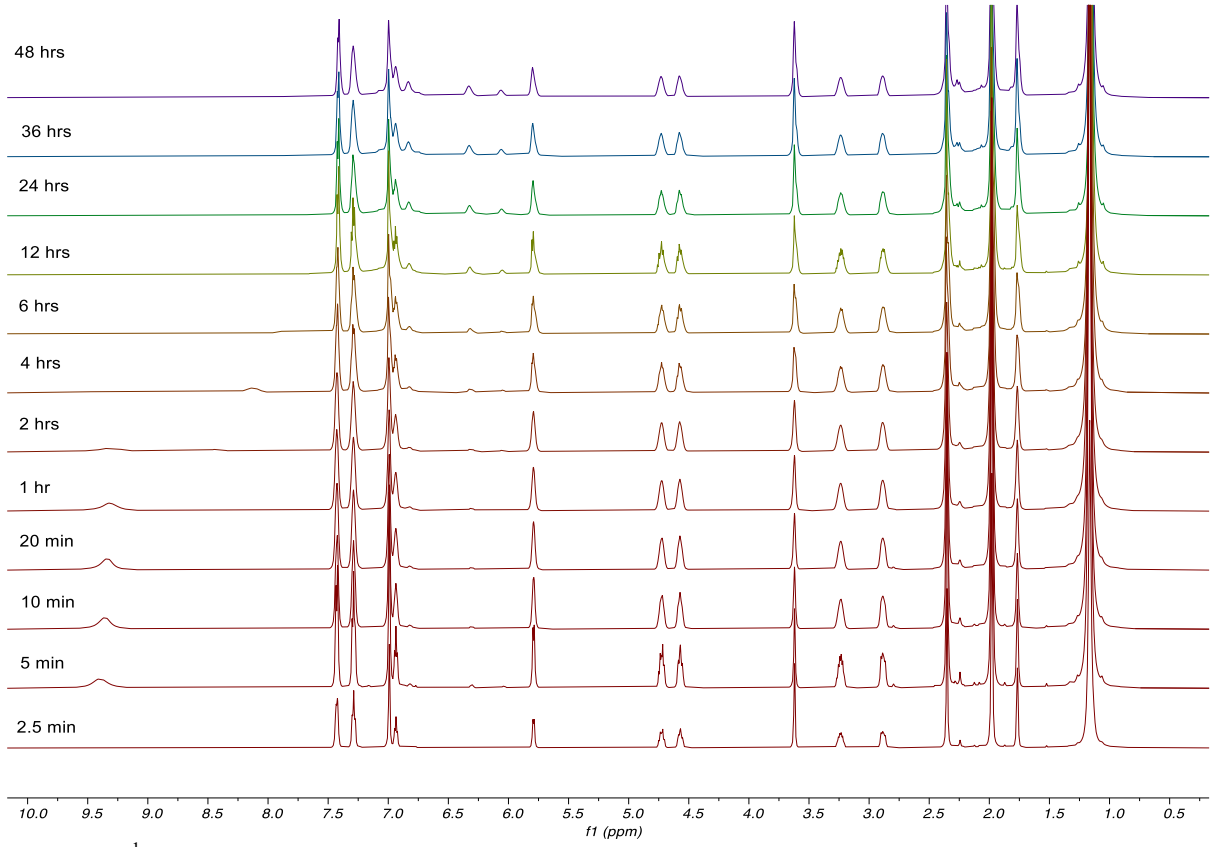


Figure S1. ^{1}H spectra at 0°C from 2.5 minutes to 48 hours.

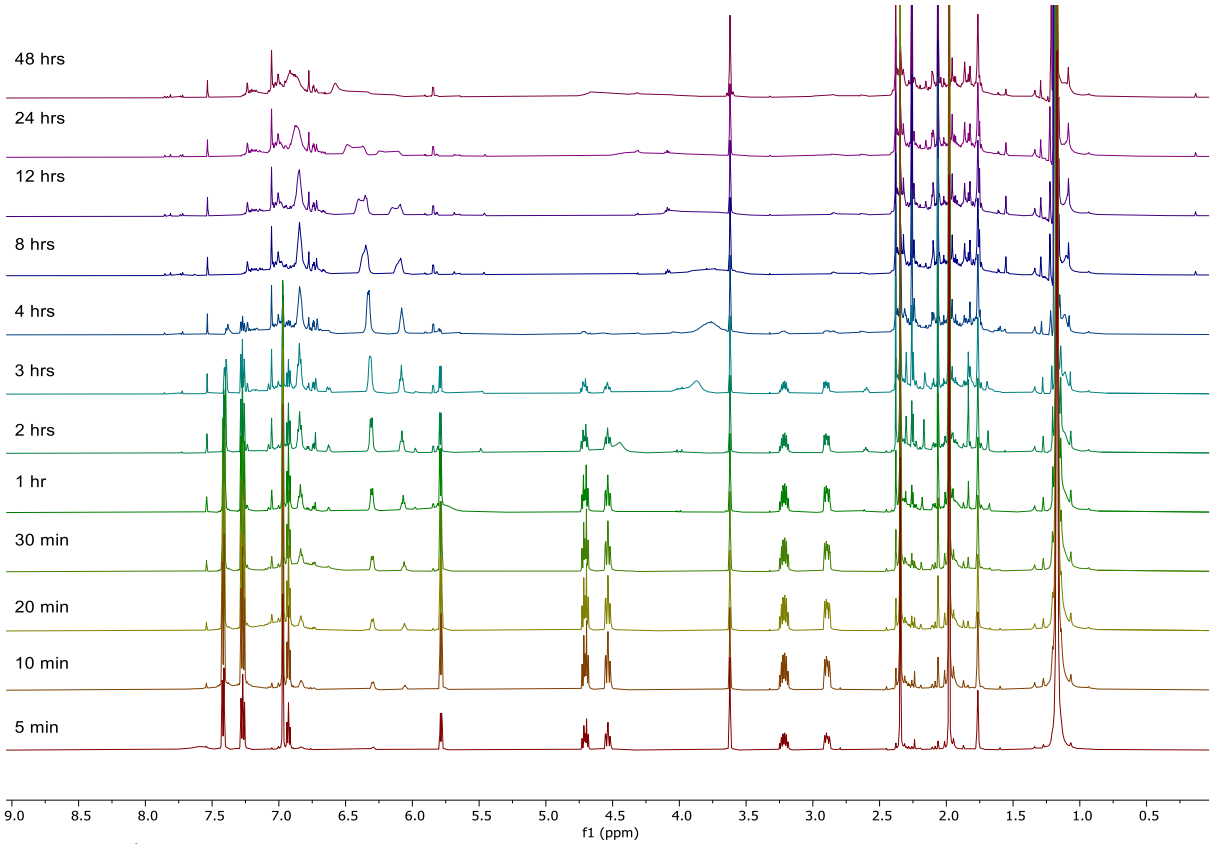


Figure S2. ^{1}H spectra at 40°C from 5 minutes to 48 hours.

Conformation stability

Triazolium salt **MIC-H$^+$f** (36.5 mg, 0.1 mmol, 1.0 equiv.) was dissolved in anhydrous THF (1.0 ml) and cooled to 0 °C (water/ice bath) under argon. KO*t*Bu (22.4 mg, 0.2 mmol, 2.0 equiv.) was added in one portion at this temperature. The resulting orange solution of free carbene was stirred at 0 °C for 15 minutes. Then, HBF_4 (48% *w*/*w*, aqueous solution, 39 µl, 0.3 mmol. 3.0 equiv.). The reaction mixture becomes colorless during the addition. The resulting heterogenous mixture was passed through a short pad of silica and directly analyzed by NMR without additional purification. Based on that, triazolium salt **MIC-H$^+$f** was identified as virtually pure (Figure S5). The checked value of optical rotation corresponds with the value for **MIC-H$^+$f** obtained in straightforward synthesis. This experiment non-directly confirmed conformational stability under deprotonation conditions.

$[\alpha]_D^{22}$ = +29.6 (*c* = 1.6, MeCN)

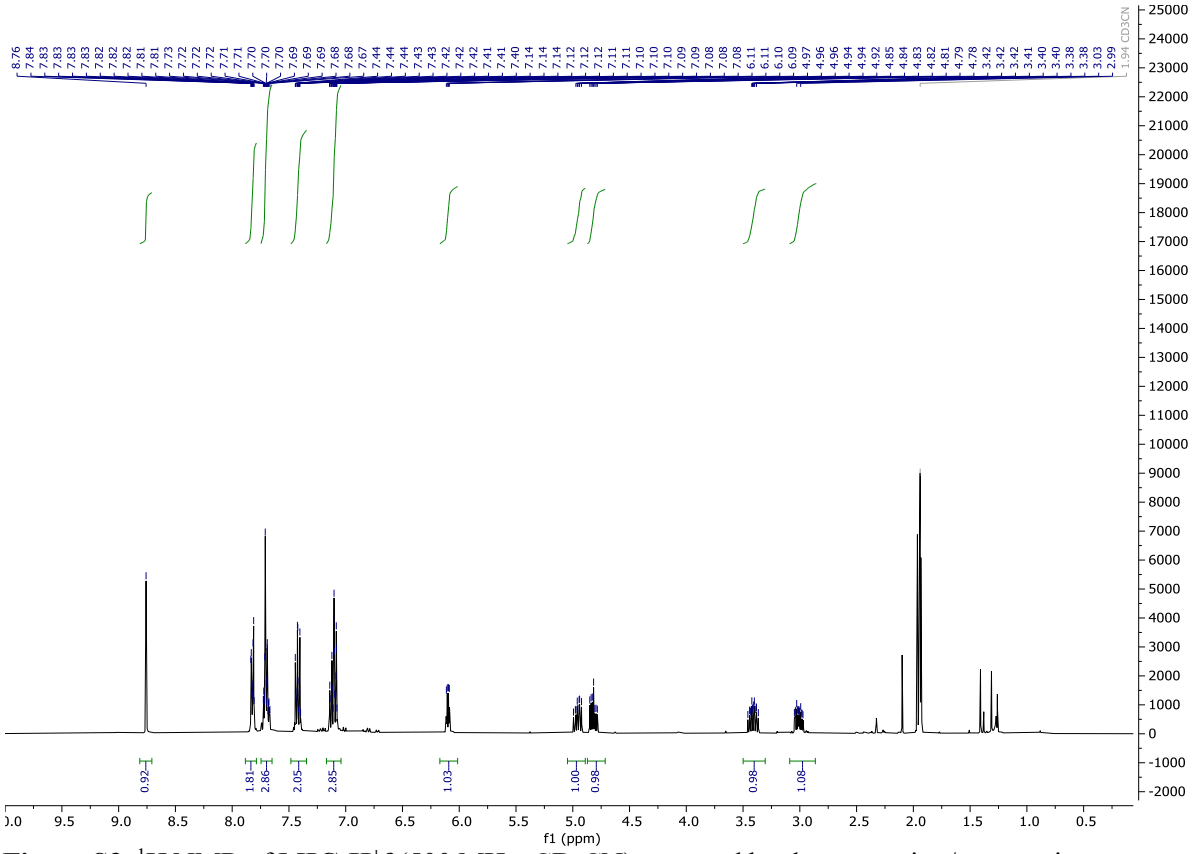


Figure S3. ^{1}H NMR of **MIC-H$^+$f** (500 MHz, CD_3CN) prepared by deprotonation/protonation sequence.

Crystallographic data

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 2301453 and can be obtained free of charge from the Centre via its website (https://www.ccdc.cam.ac.uk/structures/).

Table S1. Summary of crystallographic data for **MIC-H$^+$f** and structure refinement parameters.

Compound	**MIC-H+f**
Formula	$C_{17}H_{16}BF_4N_3O$
M	365.14
Crystal system	Monoclinic
Space group	P 1 2_1 1
T/K	100
a/Å	7.8608(3)
b/Å	9.5883(4)
c/Å	11.0615(5)
α/°	90
β/°	96.807(2)
γ/°	90
V/Å^3	827.85(6)
Z	2
μ(Mo Kα)/mm^{-1}	0.123
Diffrns collected	17888
Independent diffrns	3356
Observed[b] diffrns	3135
R_{int}[c]/%	0.0399
No. of parameters	235
R[c] obsd diffrns/%	0.0286
R, wR[c] all data/%	0.0330, 0.0652
Δρ/e Å^{-3}	0.142, -0.171
CCDC entry	2301453

[a] The range of transmission factors. [b] Diffractions with $I > 2\sigma(I)$. [c] Definitions: $R_{int} = \Sigma\,|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, where F_o^2(mean) is the average intensity of symmetry-equivalent diffractions. $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$.

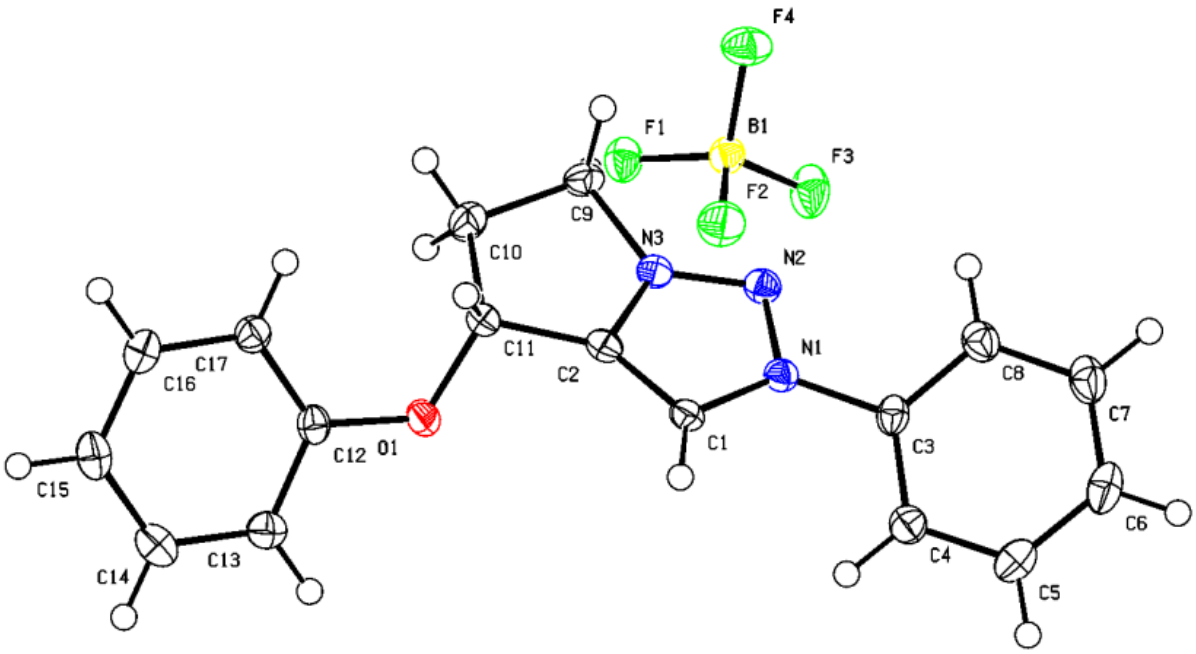


Figure S4. View on molecule of **MIC-H$^+$f** with atom numbering schema, the displacement ellipsoid is drawn on 50% probability level.

NMR spectra

(*R*)-3-Phenoxydihydrofuran-2(3H)-one (4c)

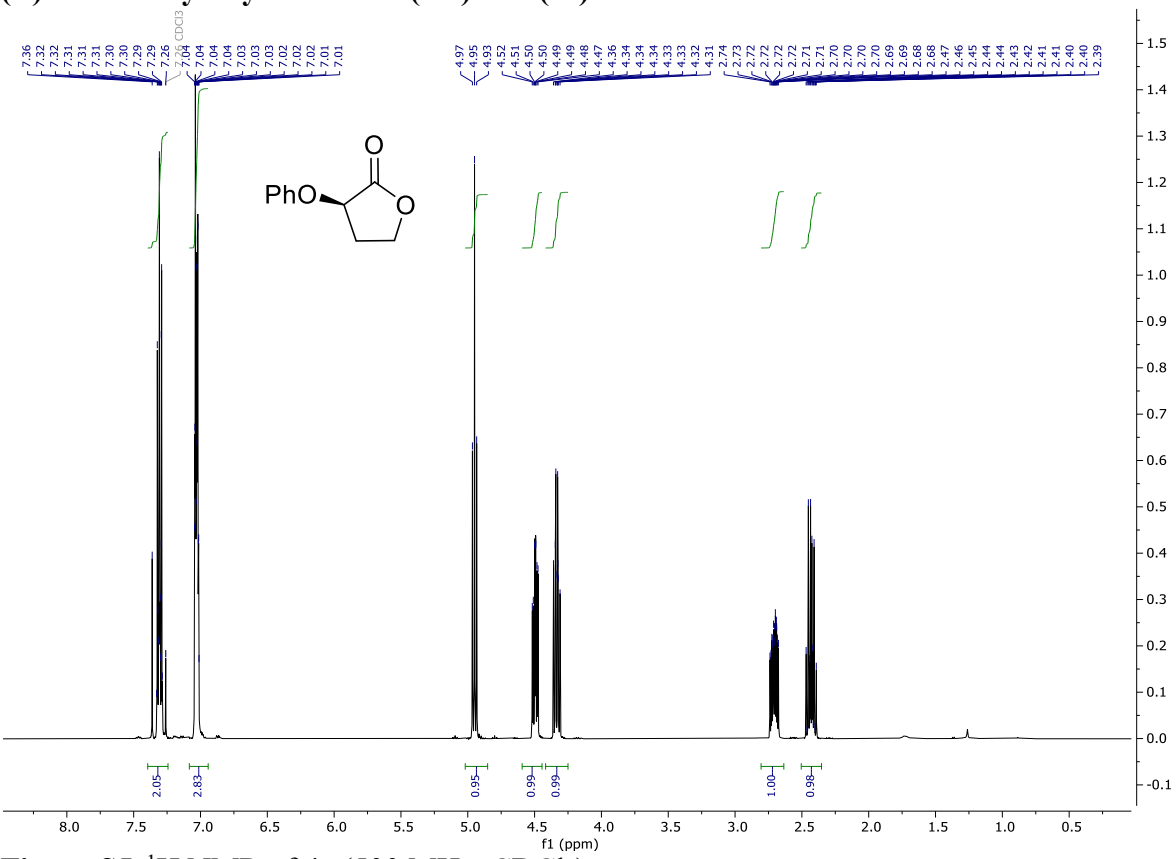


Figure S5. ^{1}H NMR of **4c** (500 MHz, $CDCl_3$)

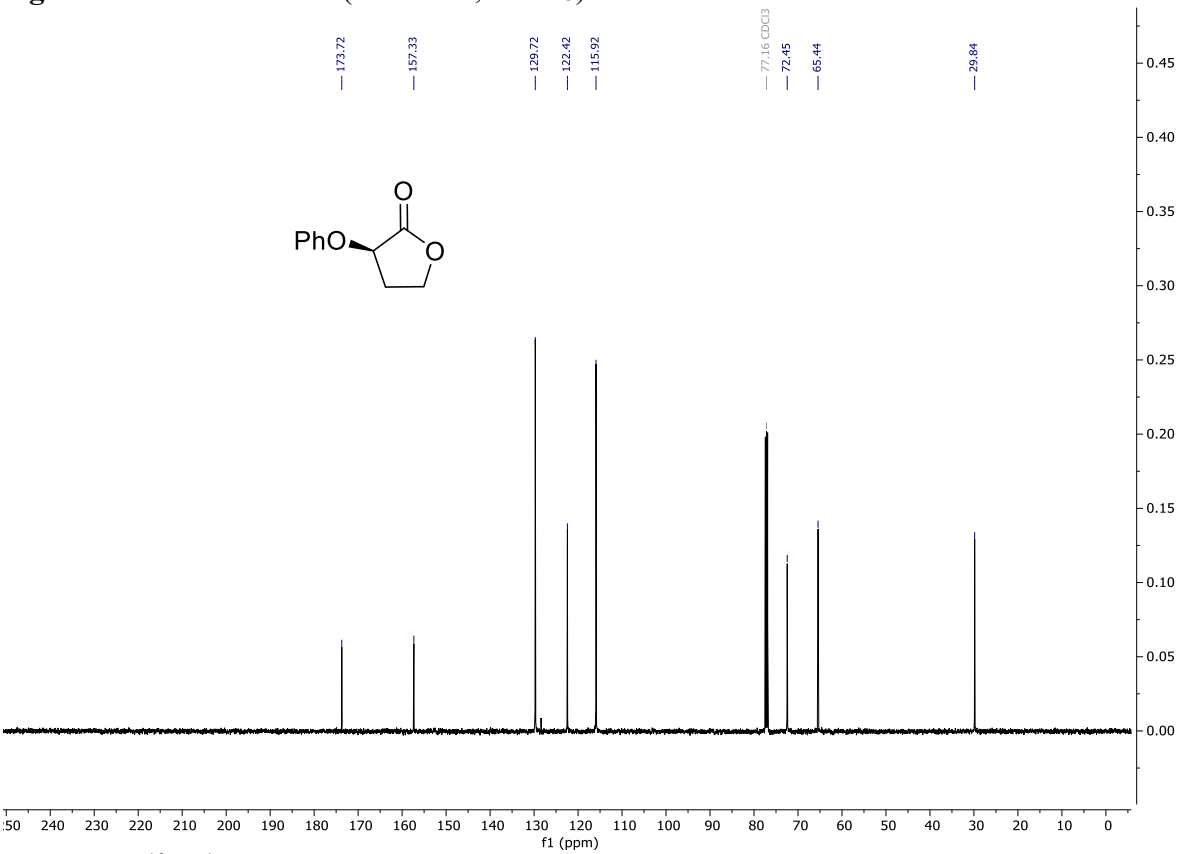


Figure S6. $^{13}C\{^{1}H\}$ NMR of **4c** (126 MHz, $CDCl_3$)

(*S*)-3-(Benzyloxy)pent-4-yn-1-ol (5a)

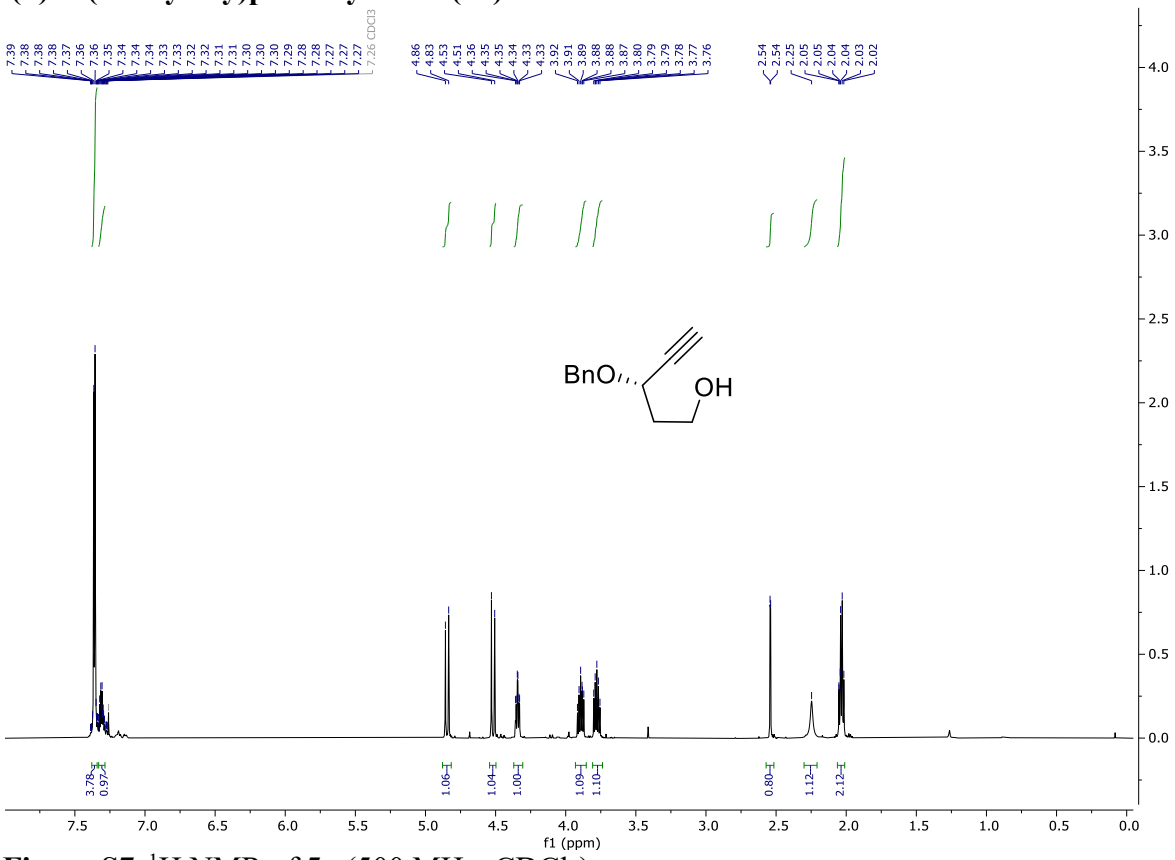


Figure S7. ^{1}H NMR of **5a** (500 MHz, $CDCl_3$)

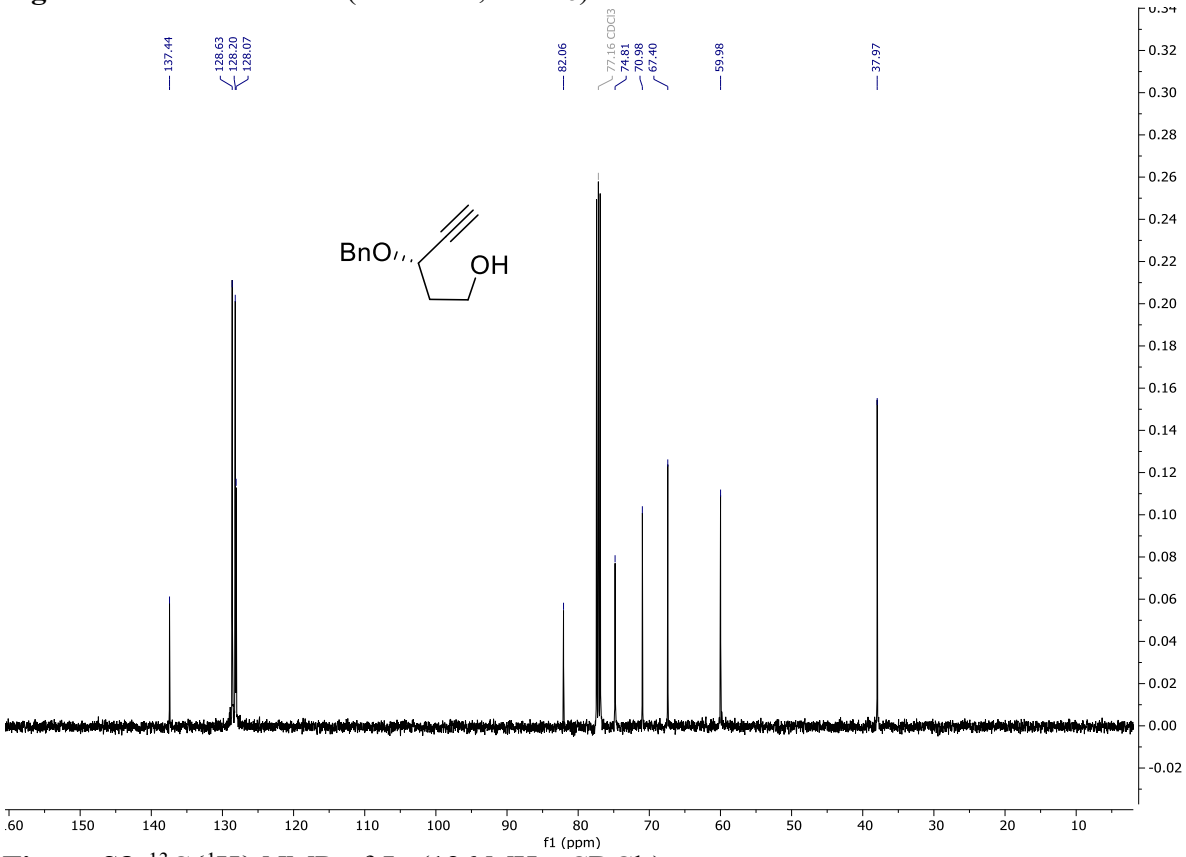


Figure S8. $^{13}C\{^{1}H\}$ NMR of **5a** (126 MHz, $CDCl_3$)

(*S*)-3-Methoxypent-4-yn-1-ol (5b)

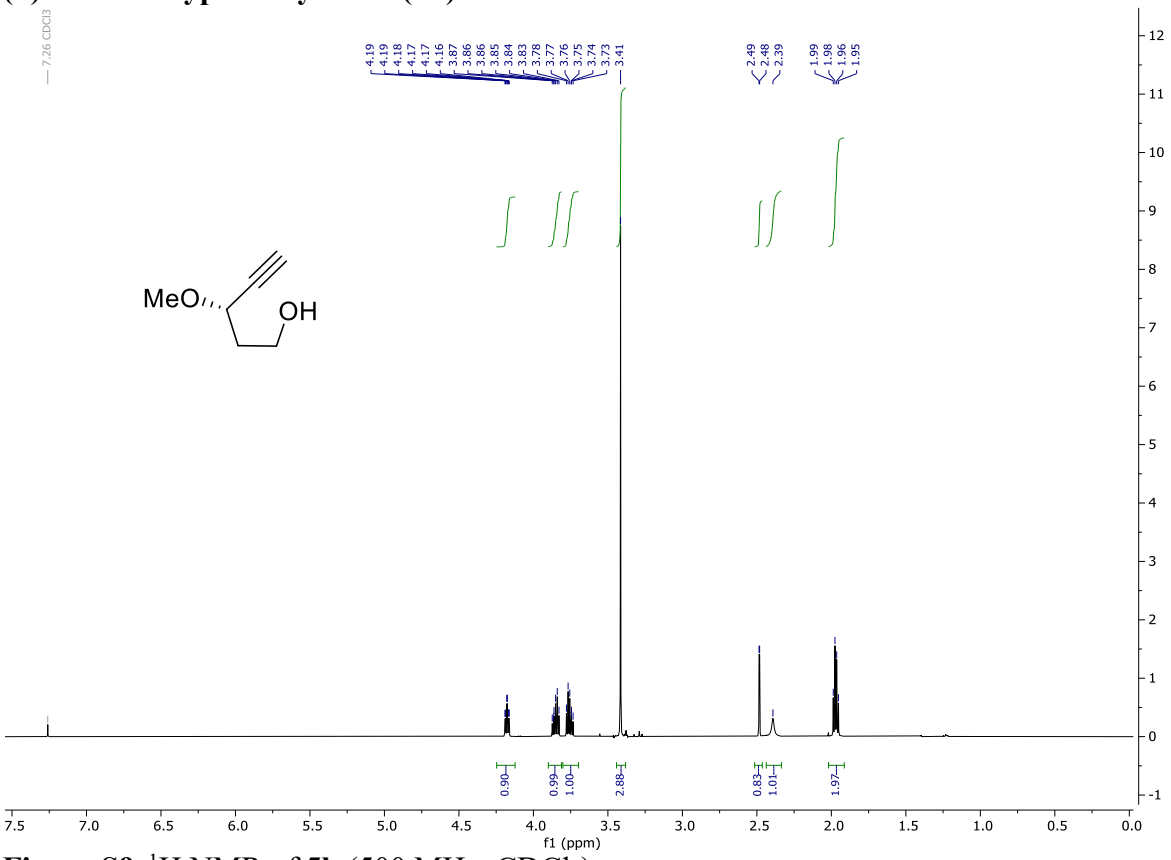


Figure S9. ^{1}H NMR of **5b** (500 MHz, $CDCl_3$)

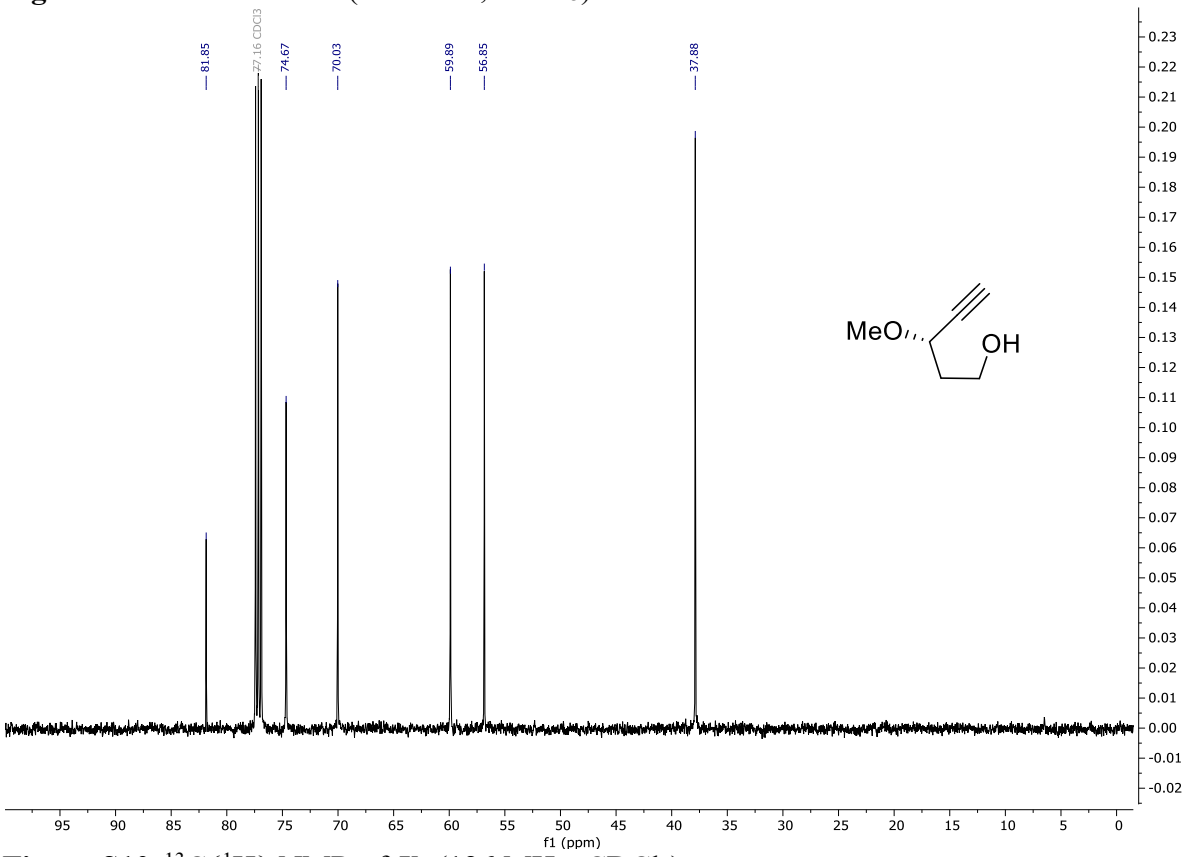


Figure S10. ^{13}C{^{1}H} NMR of **5b** (126 MHz, $CDCl_3$)

(*R*)-3-Phenoxypent-4-yn-1-ol (5c)

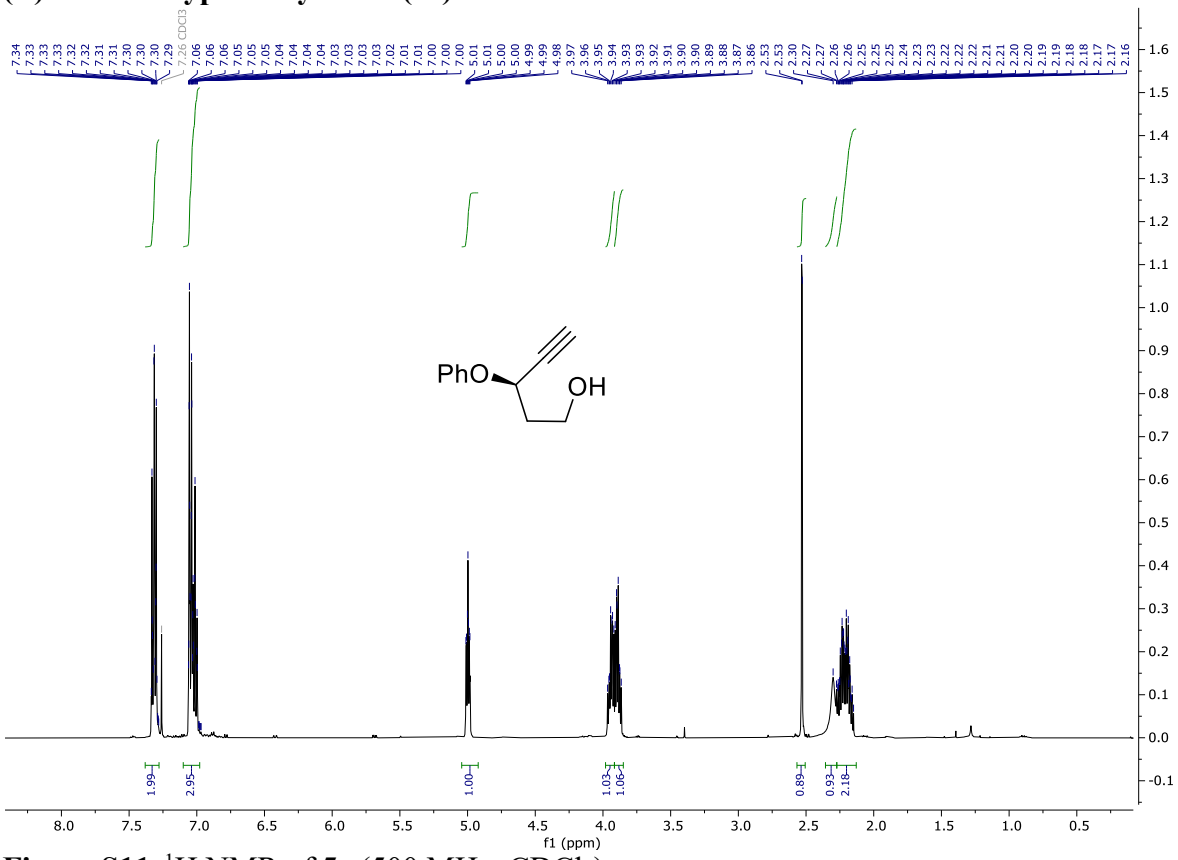


Figure S11. ^{1}H NMR of **5c** (500 MHz, $CDCl_3$)

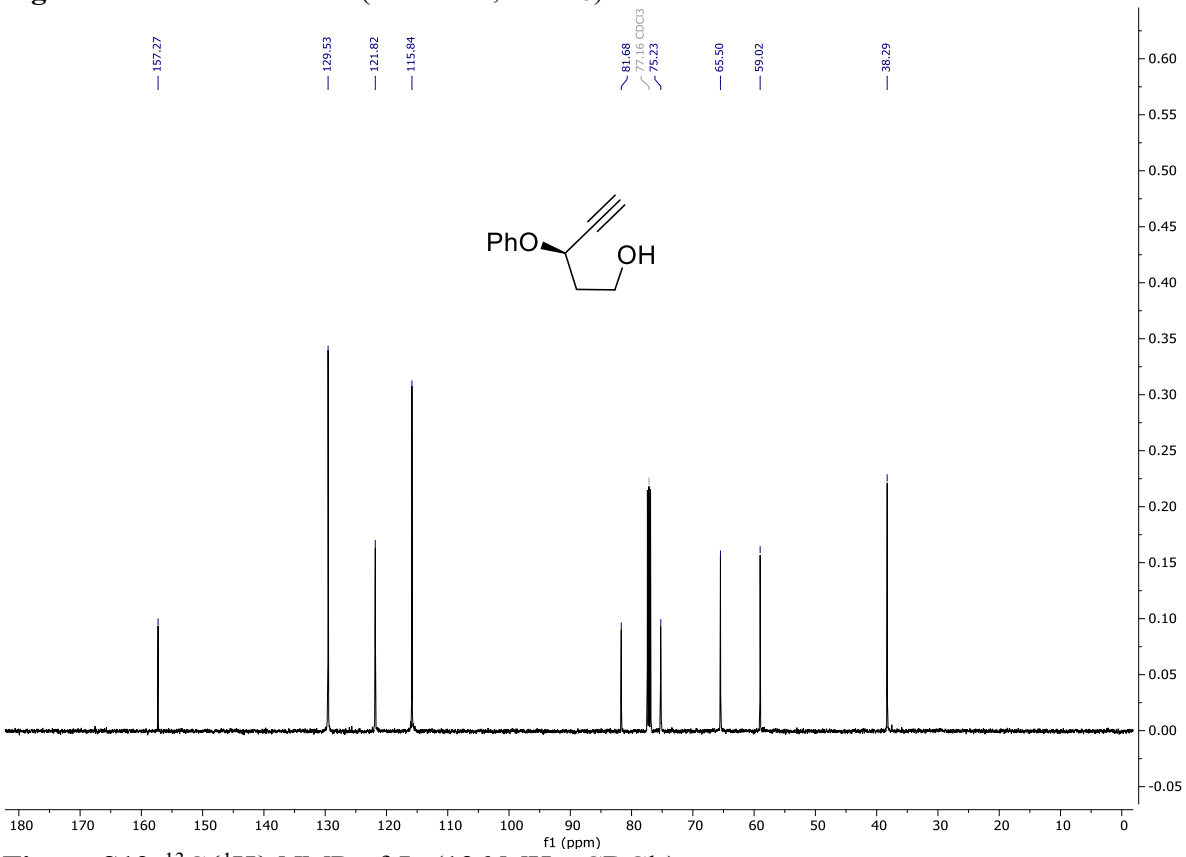


Figure S12. $^{13}C\{^{1}H\}$ NMR of **5c** (126 MHz, $CDCl_3$)

5,6-Dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazole (2)

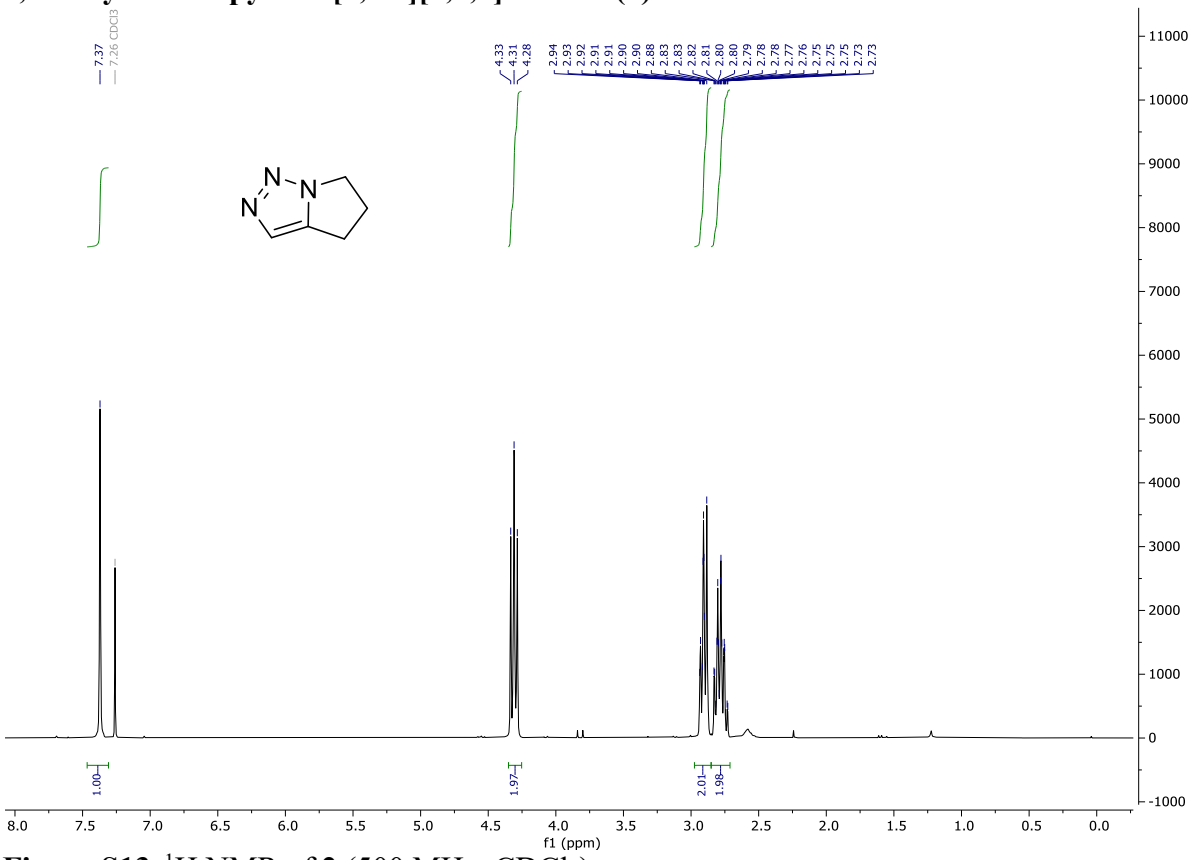


Figure S13. ^{1}H NMR of **2** (500 MHz, $CDCl_3$)

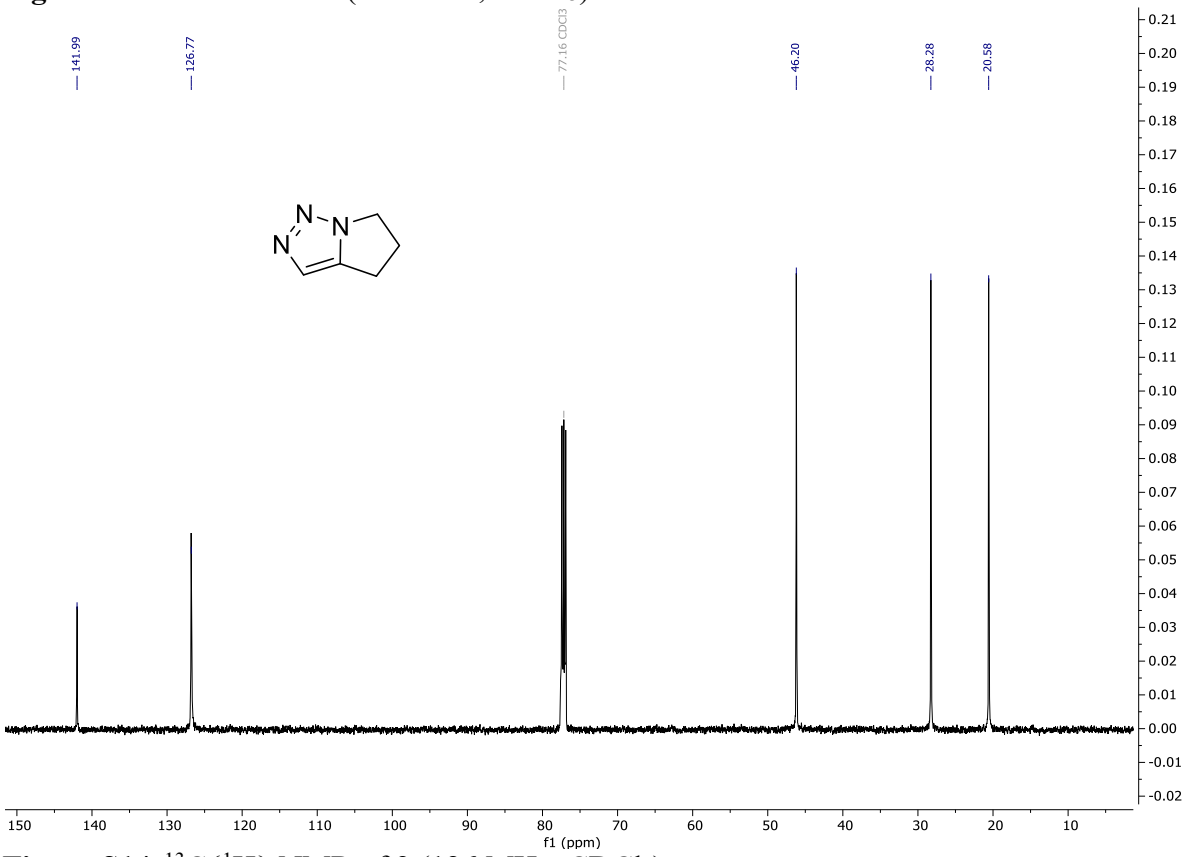


Figure S14. ^{13}C{^{1}H} NMR of **2** (126 MHz, $CDCl_3$)

(*S*)-4-(Benzyloxy)-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazole (6a)

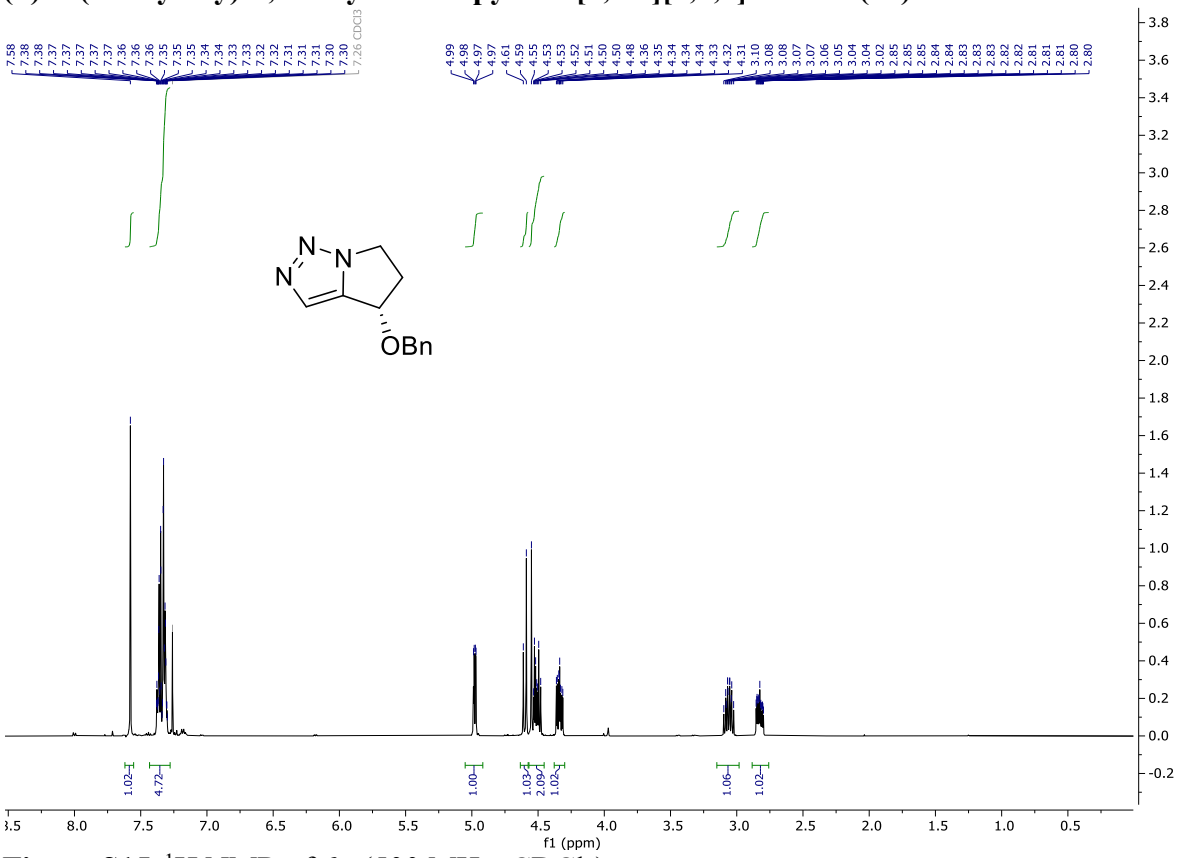


Figure S15. ^{1}H NMR of **6a** (500 MHz, $CDCl_3$)

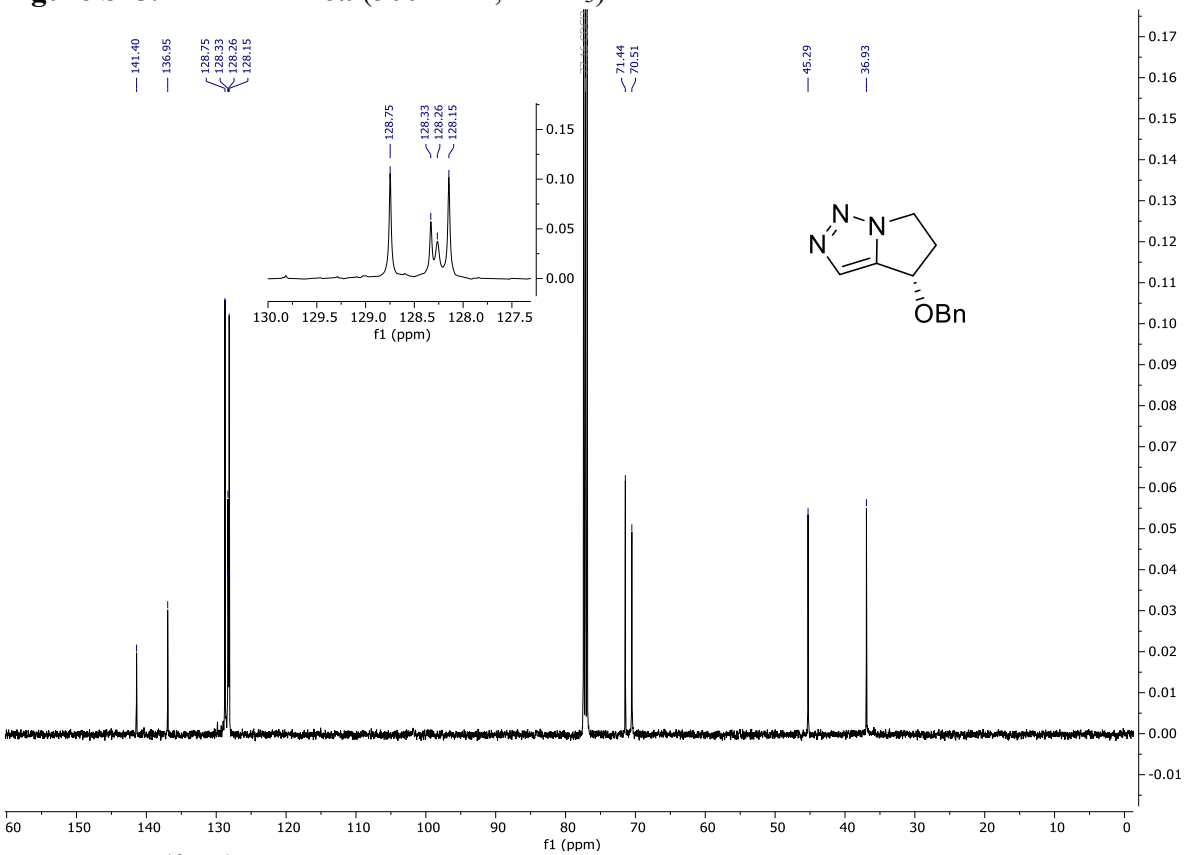


Figure S16. ^{13}C{^{1}H} NMR of **6a** (126 MHz, $CDCl_3$)

(*S*)-4-Methoxy-5,6-dihydro-4H-pyrrolo[1,2-c][1,2,3]triazole (6b)

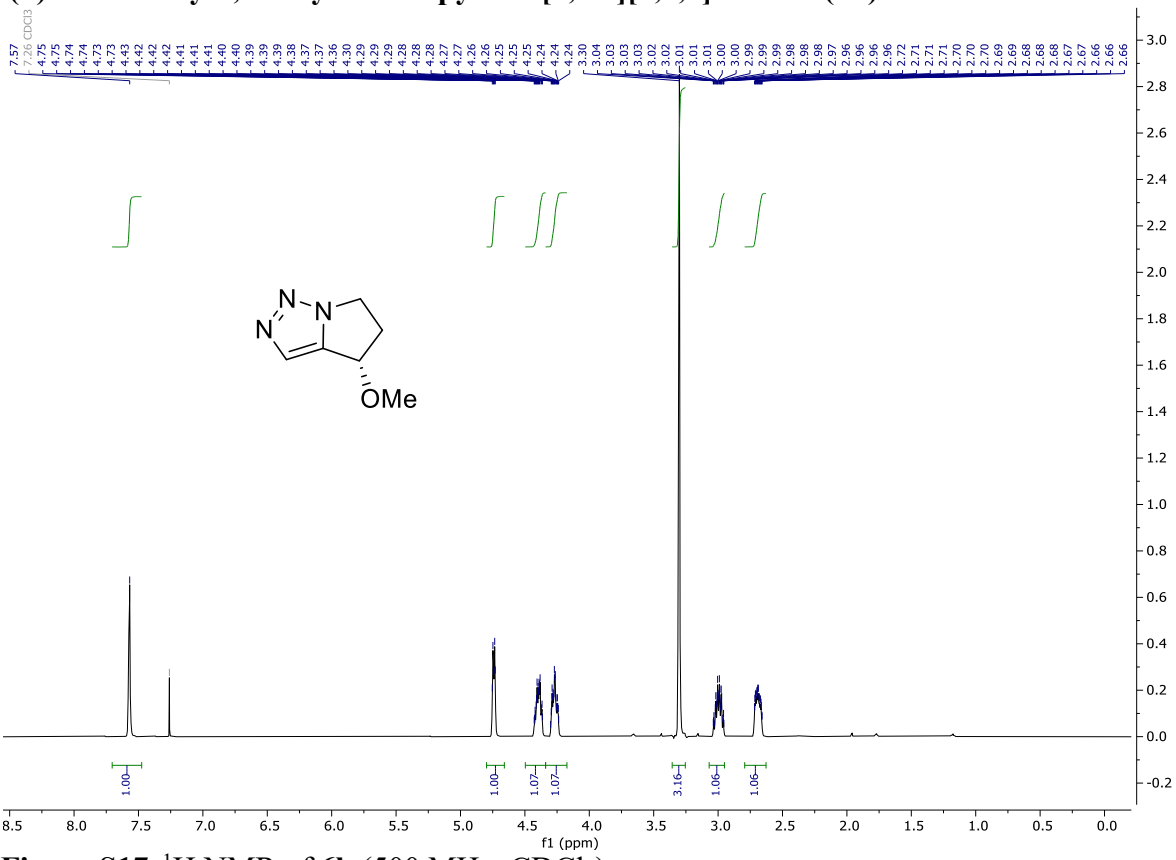


Figure S17. ^{1}H NMR of **6b** (500 MHz, $CDCl_3$)

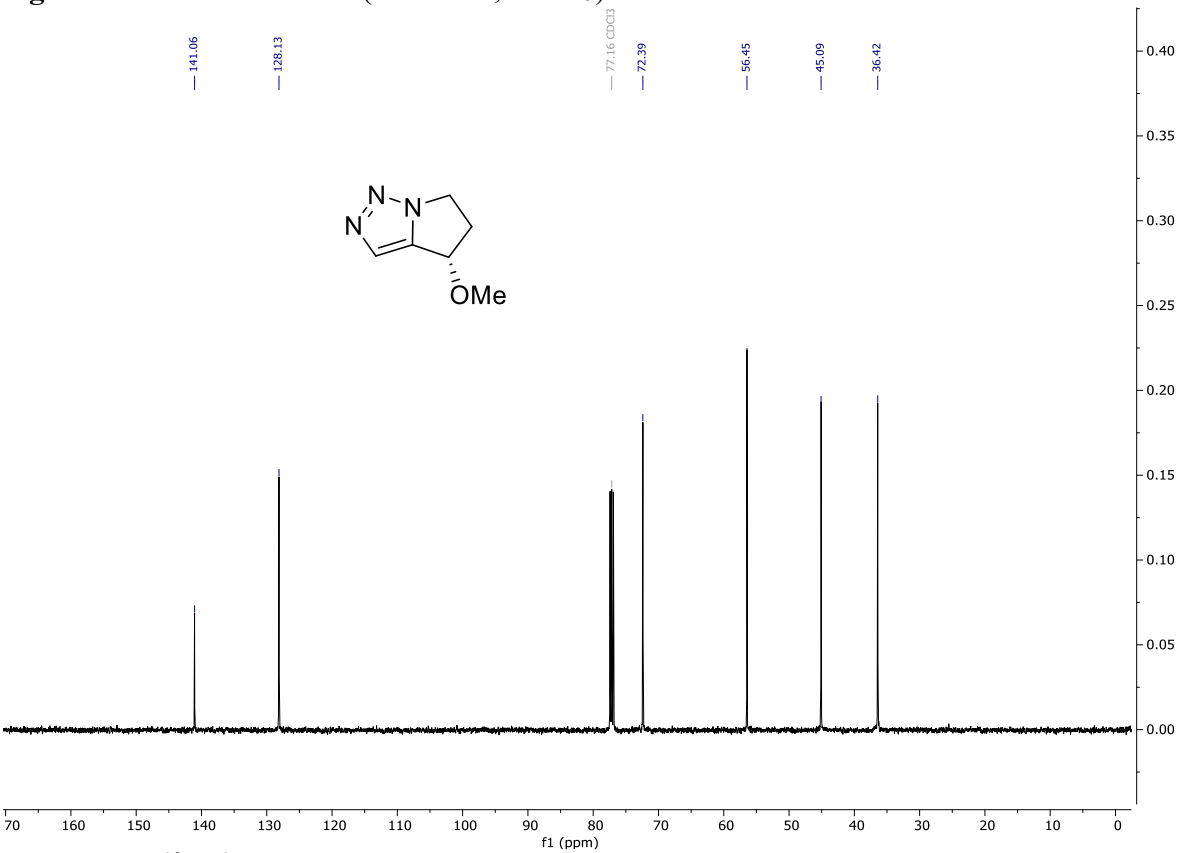


Figure S18. $^{13}C\{^{1}H\}$ NMR of **6b** (126 MHz, $CDCl_3$)

(*R*)-4-Phenoxy-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazole (6c)

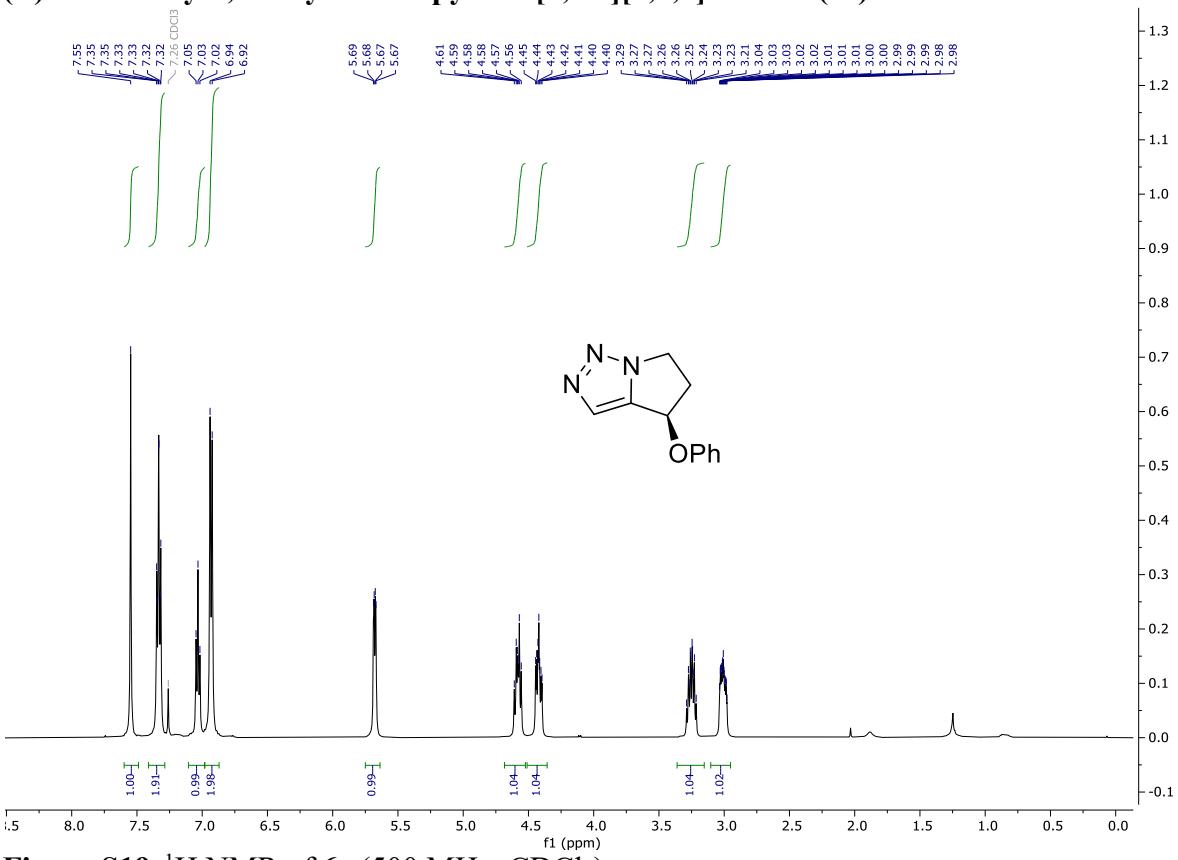


Figure S19. ^{1}H NMR of **6c** (500 MHz, $CDCl_3$)

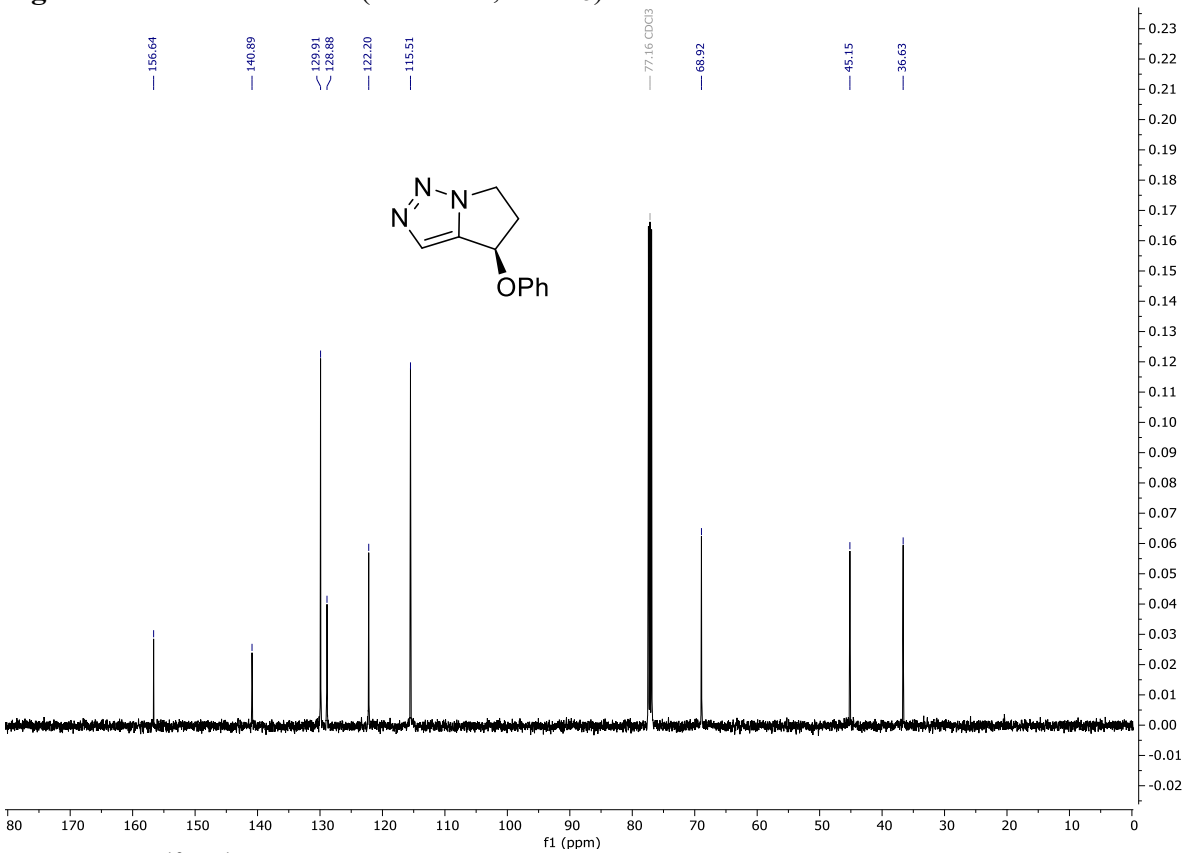


Figure S20. ^{13}C{^{1}H} NMR of **6c** (126 MHz, $CDCl_3$)

2-Phenyl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$a)

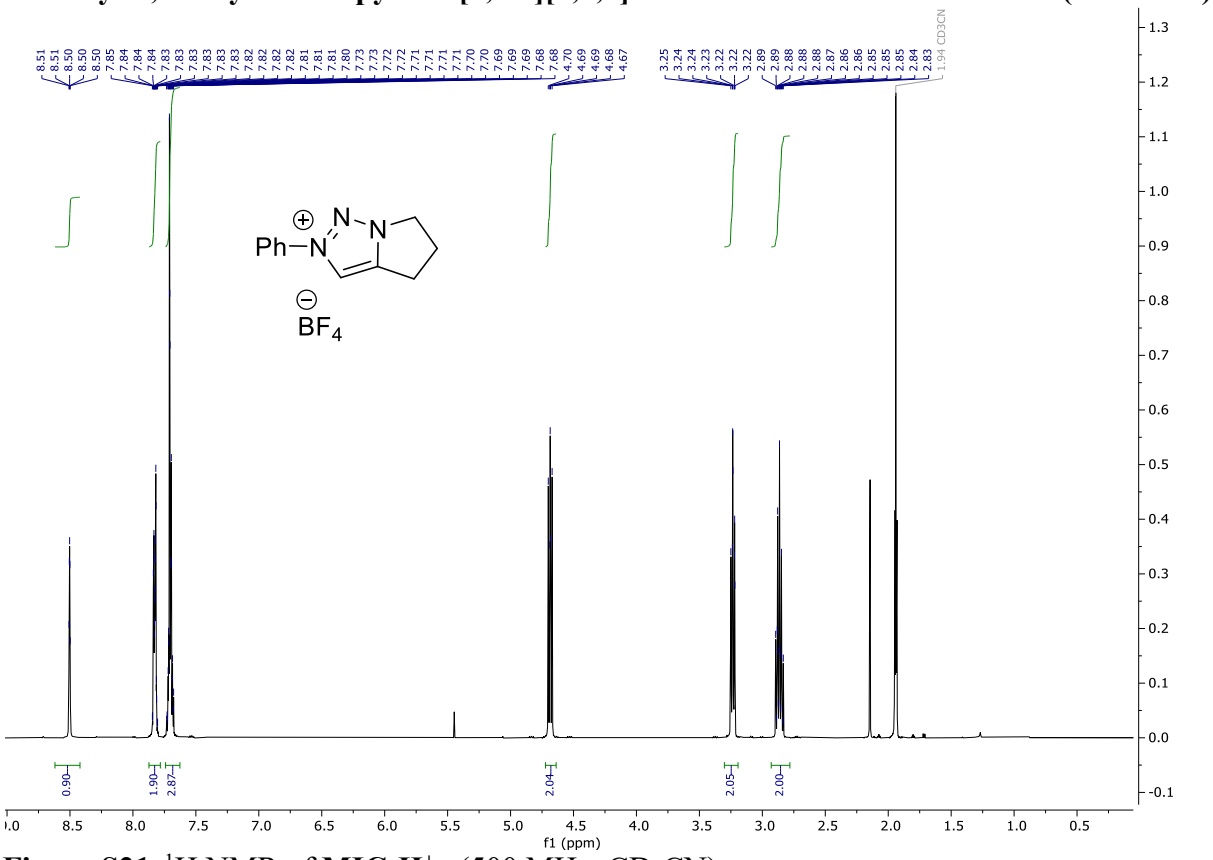


Figure S21. ^{1}H NMR of **MIC-H$^+$a** (500 MHz, CD_3CN)

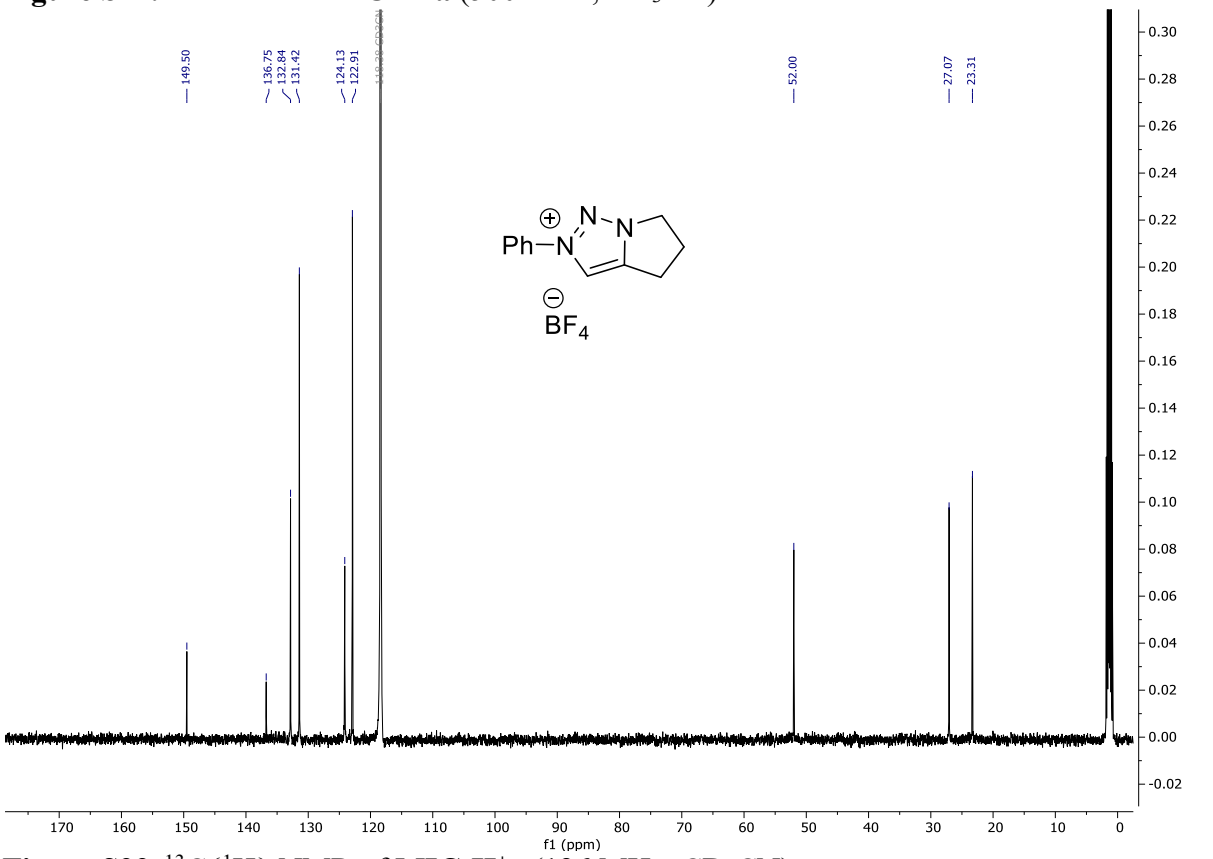


Figure S22. $^{13}C\{^1H\}$ NMR of **MIC-H$^+$a** (126 MHz, CD_3CN)

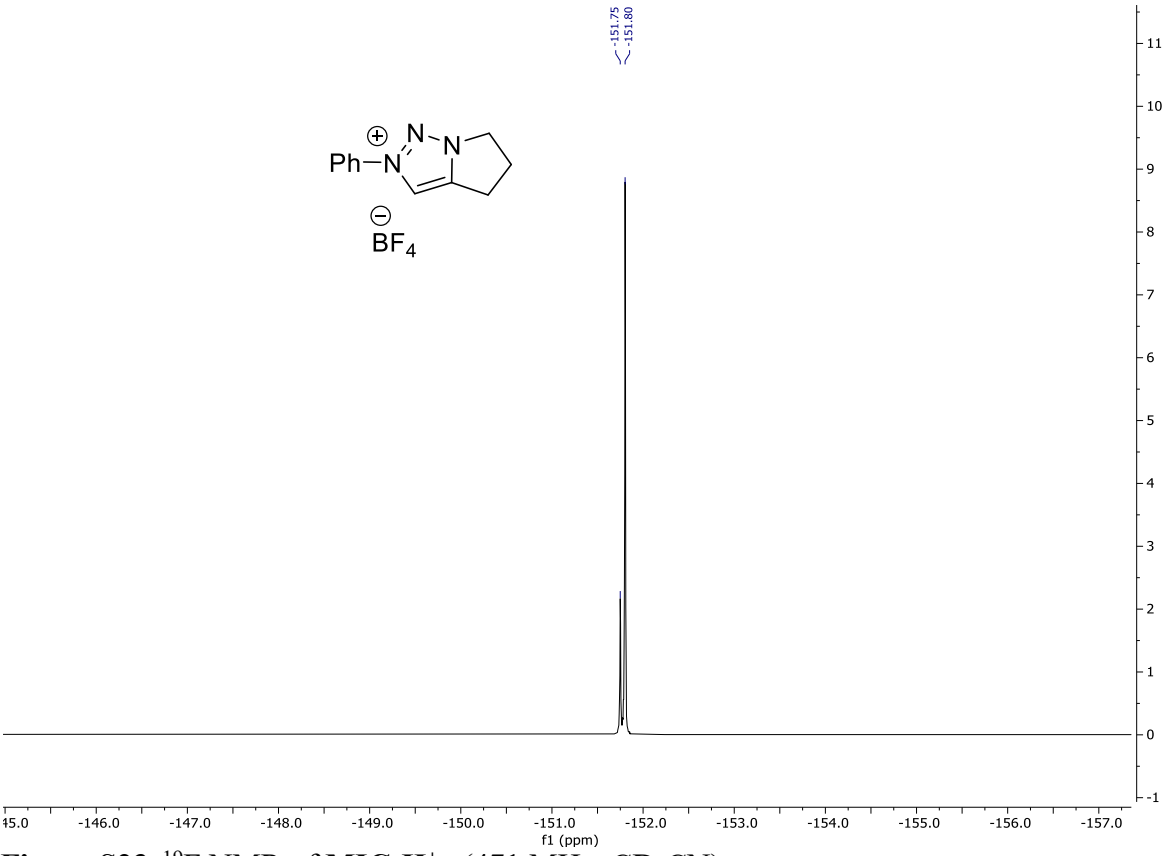


Figure S23. ^{19}F NMR of **MIC-H$^+$a** (471 MHz, CD_3CN)

2-Mesityl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$b)

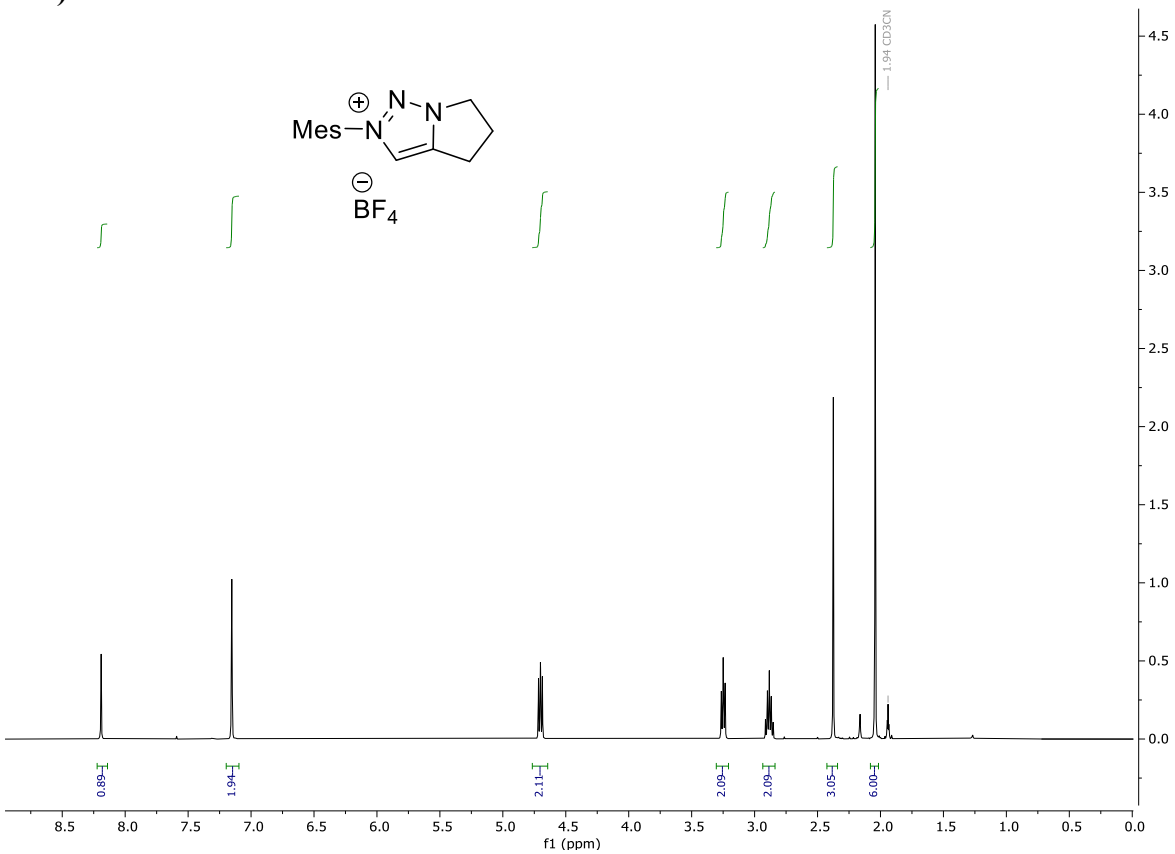


Figure S24. ^{1}H NMR of **MIC-H$^+$b** (500 MHz, CD_3CN)

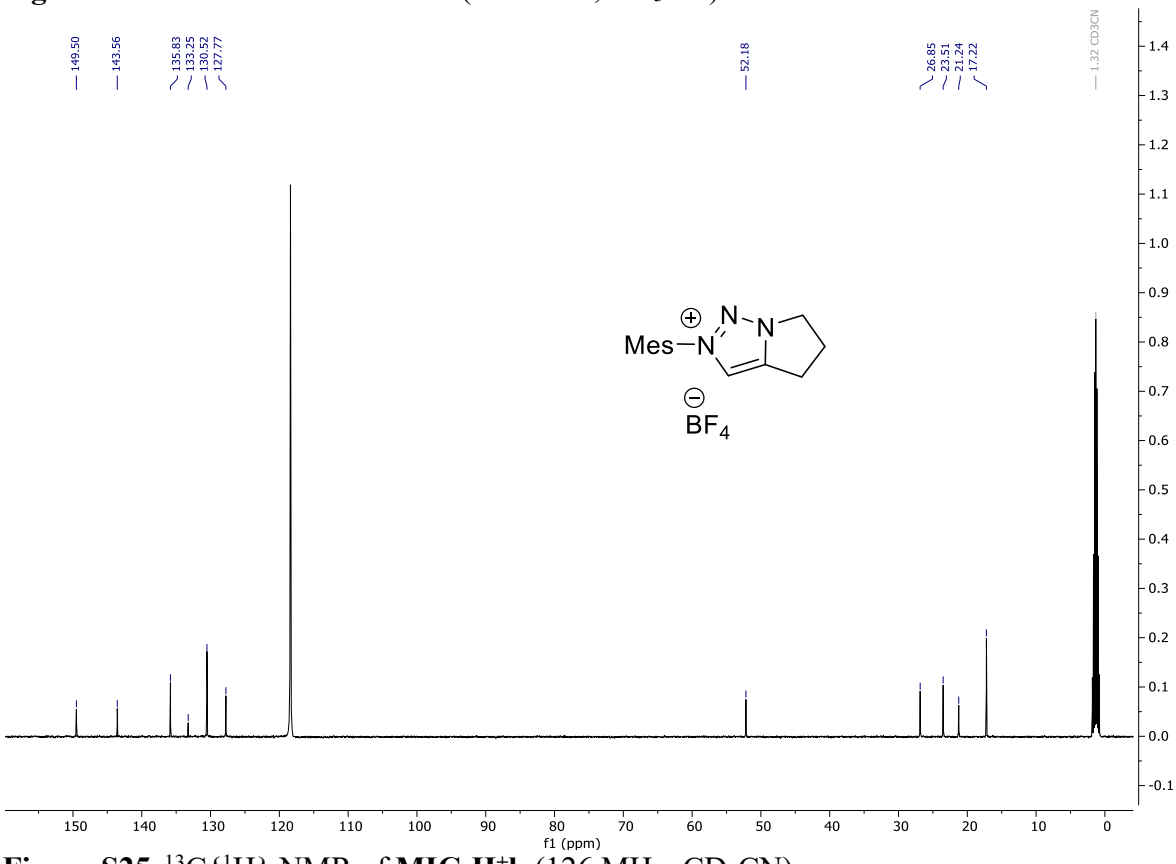


Figure S25. $^{13}C\{^1H\}$ NMR of **MIC-H$^+$b** (126 MHz, CD_3CN)

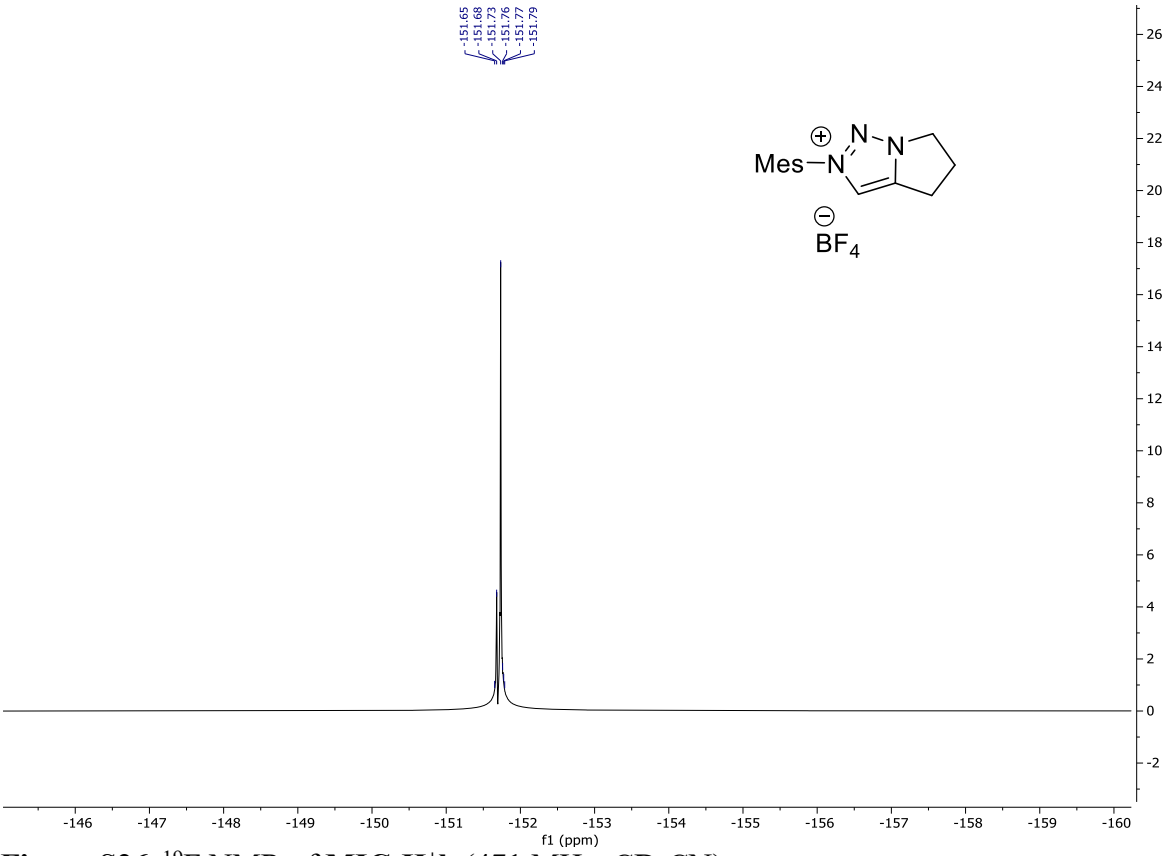


Figure S26. ^{19}F NMR of **MIC-H$^+$b** (471 MHz, CD_3CN)

(*S*)-4-(Benzyloxy)-2-phenyl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$c)

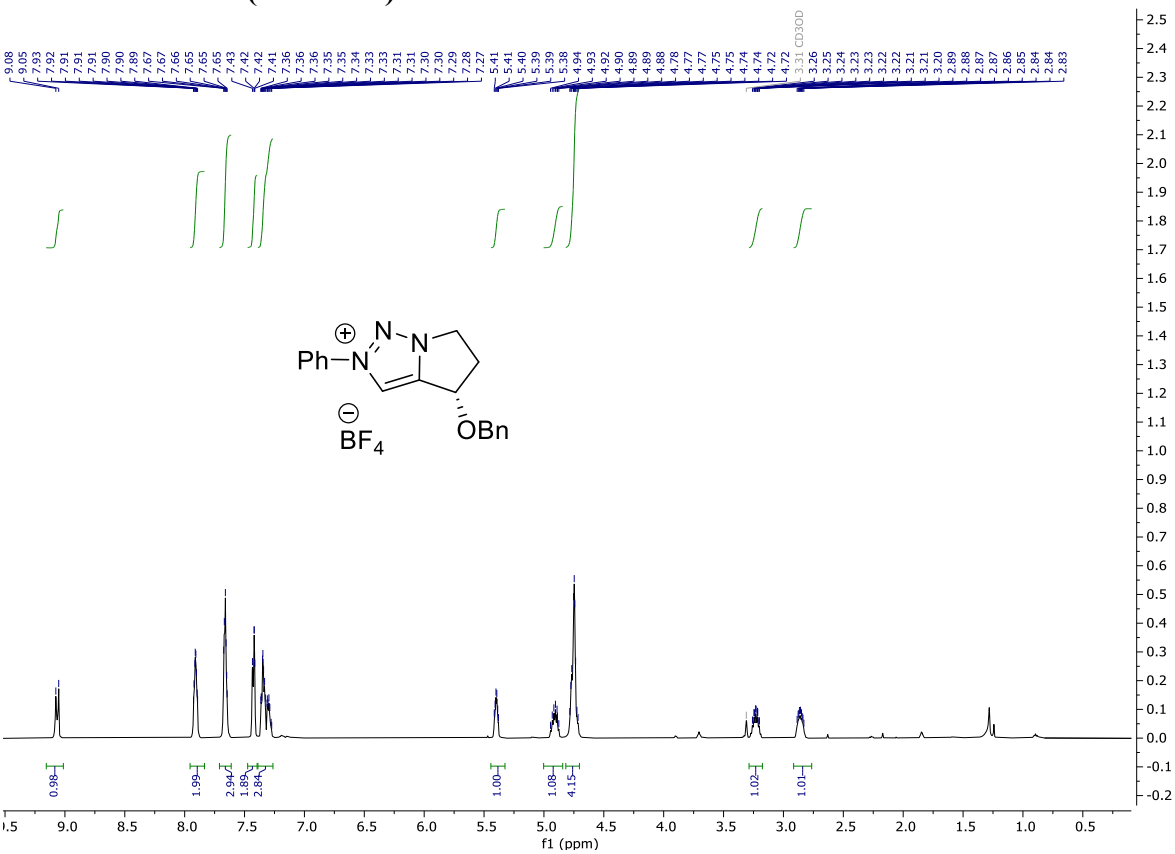


Figure S27. ^{1}H NMR of **MIC-H$^+$c** (500 MHz, CD_3OD)

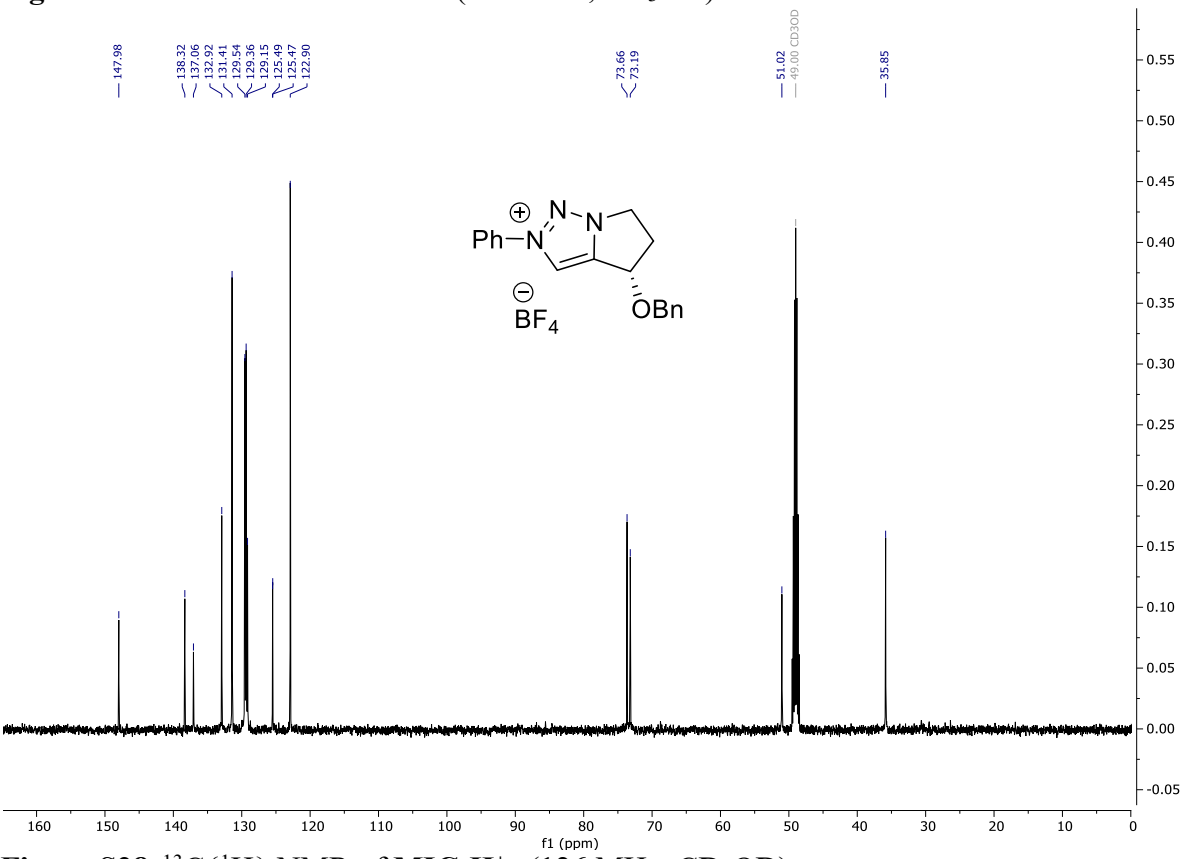


Figure S28. $^{13}C\{^1H\}$ NMR of **MIC-H$^+$c** (126 MHz, CD_3OD)

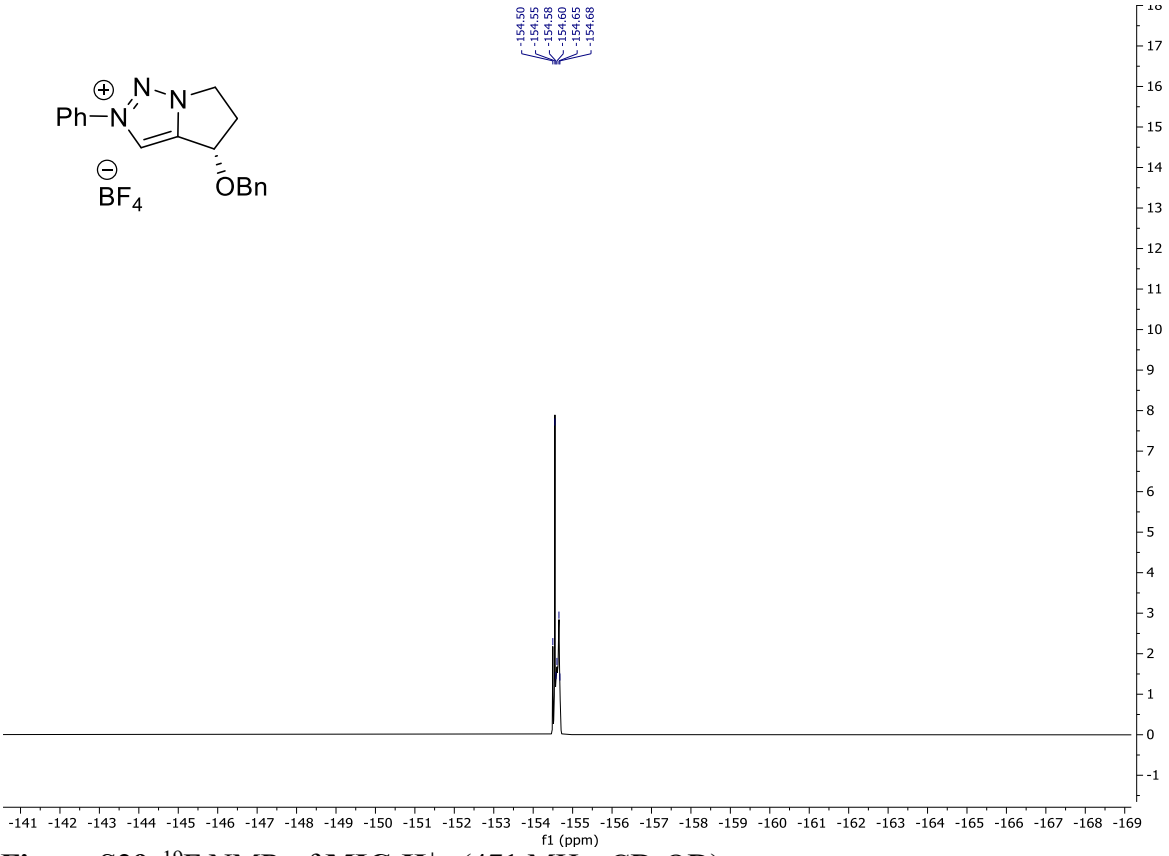


Figure S29. ^{19}F NMR of **MIC-H$^+$c** (471 MHz, CD_3OD)

(*S*)-4-(Benzyloxy)-2-mesityl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$d)

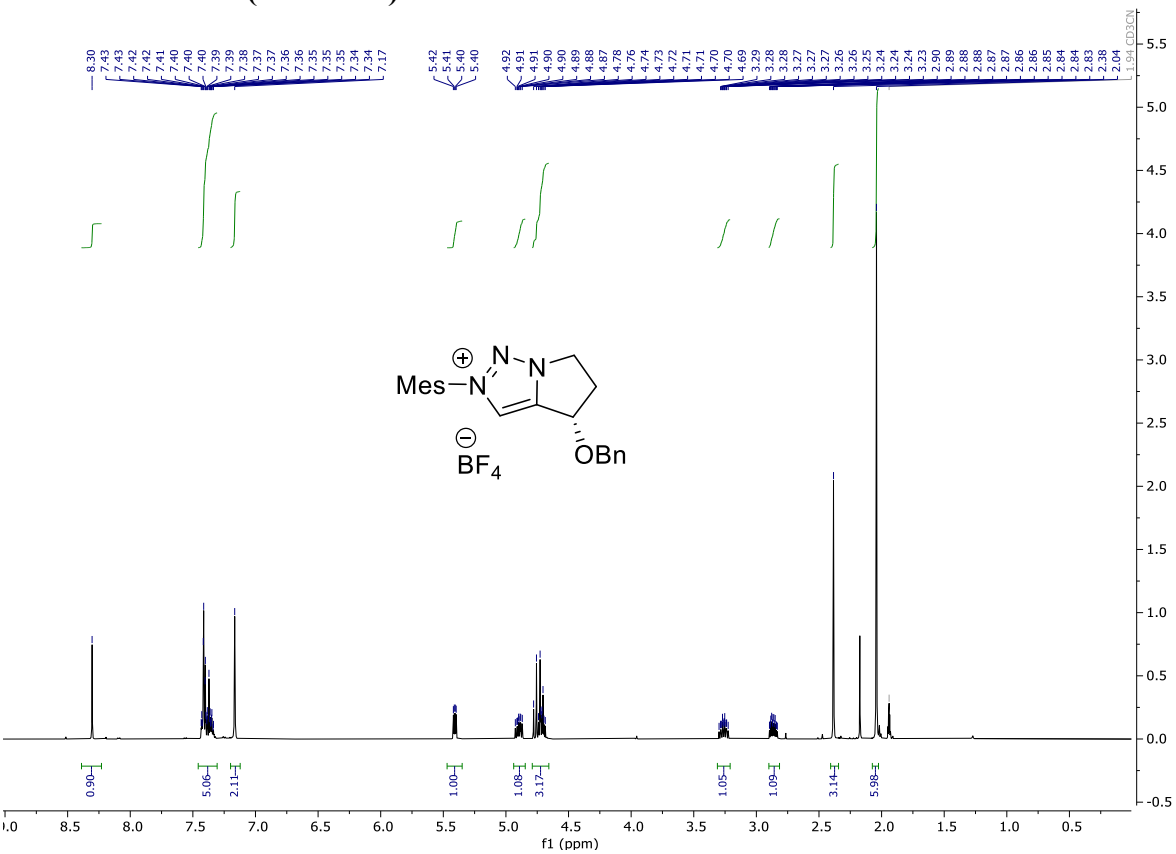


Figure S30. ^{1}H NMR of **MIC-H$^+$d** (500 MHz, CD_3CN)

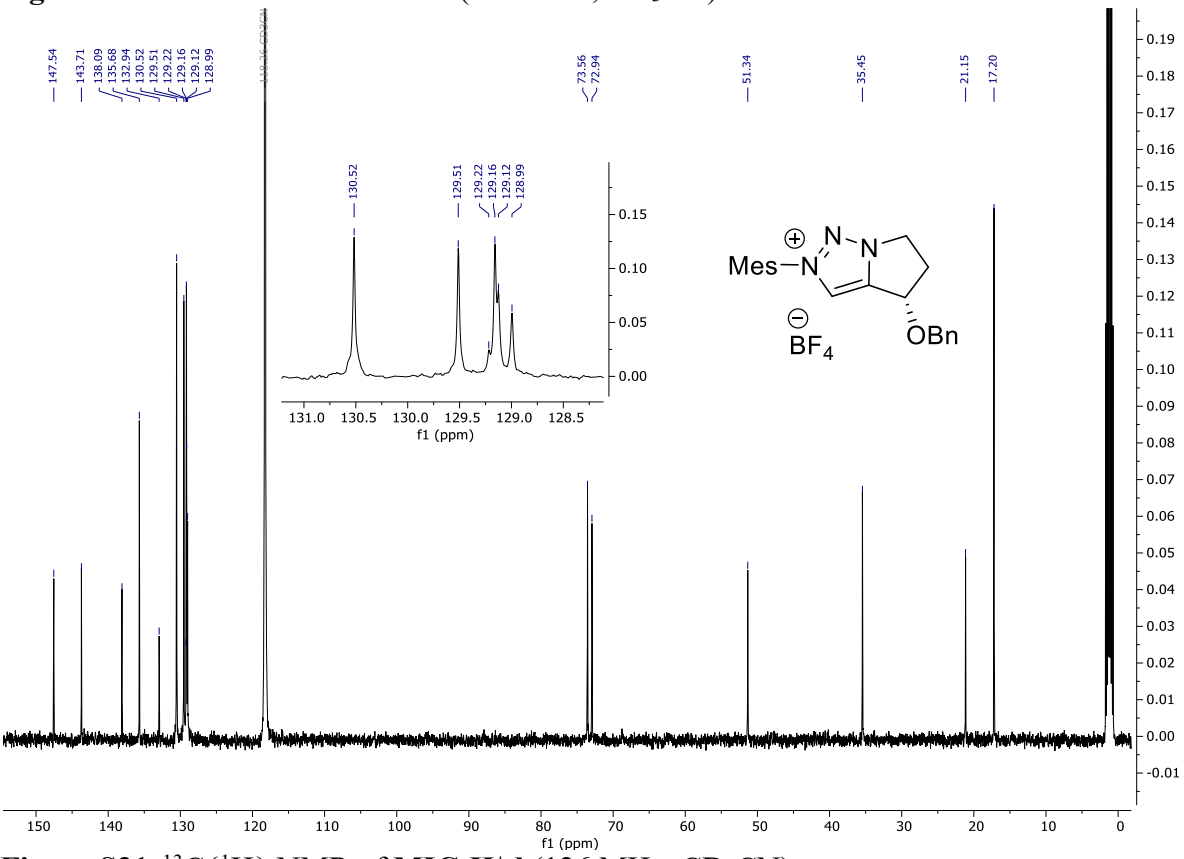


Figure S31. $^{13}C\{^1H\}$ NMR of **MIC-H$^+$d** (126 MHz, CD_3CN)

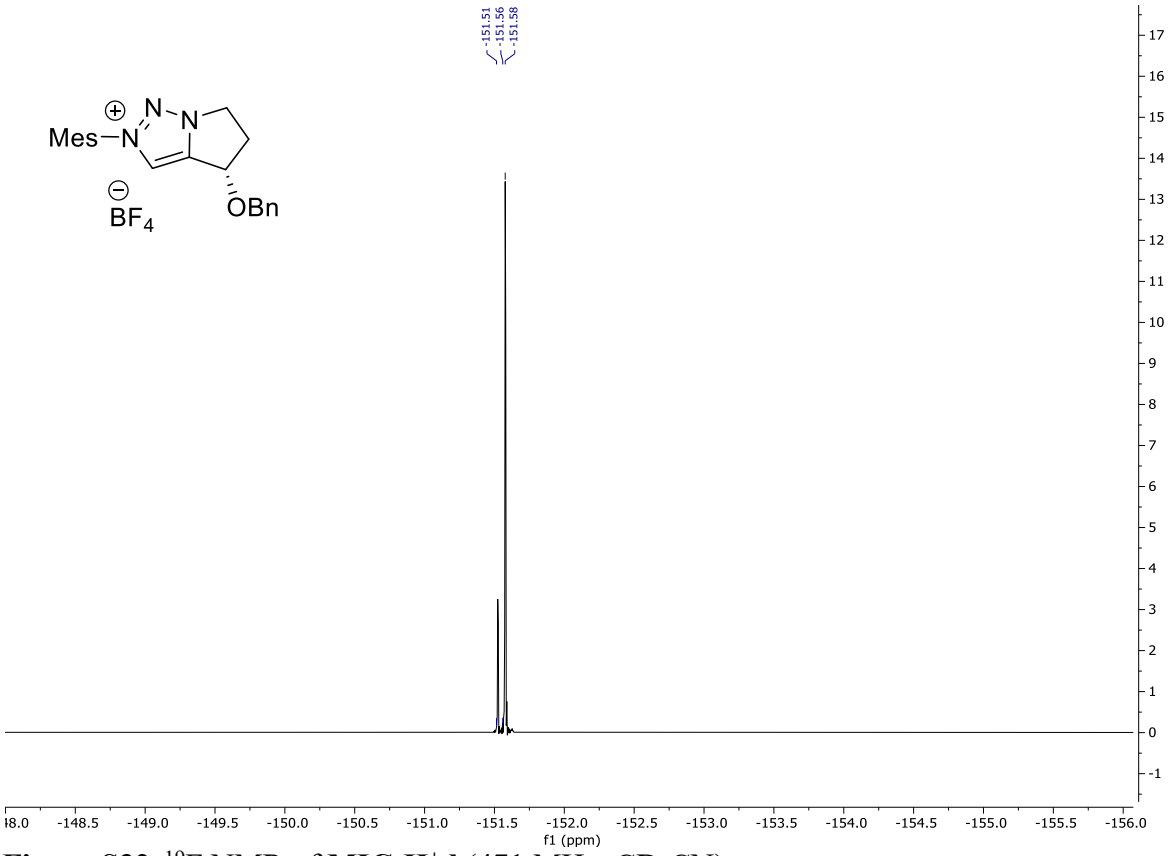


Figure S32. ^{19}F NMR of **MIC-H$^+$d** (471 MHz, CD_3CN)

(*S*)-4-Methoxy-2-phenyl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$e)

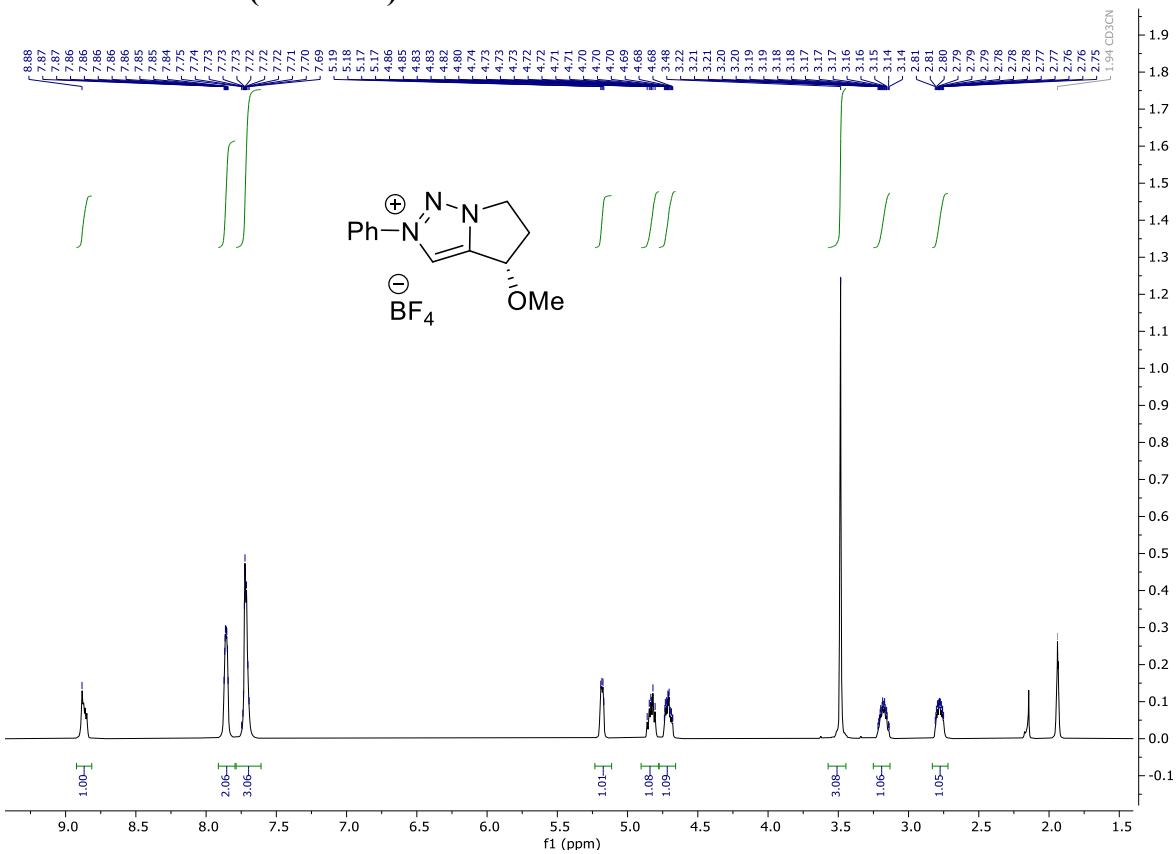


Figure S33. ^{1}H NMR of **MIC-H$^+$e** (500 MHz, CD_3CN)

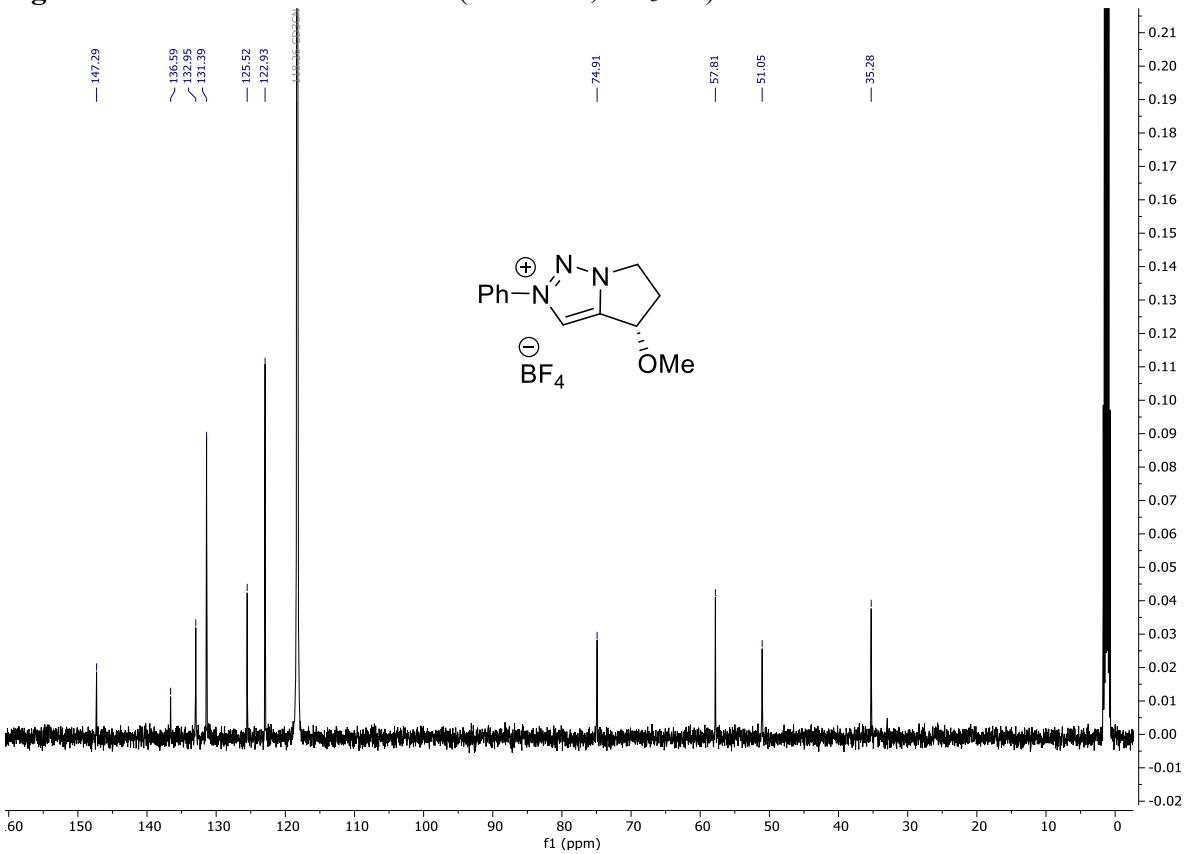


Figure S34. ^{13}C{^{1}H} NMR of **MIC-H$^+$e** (126 MHz, CD_3CN)

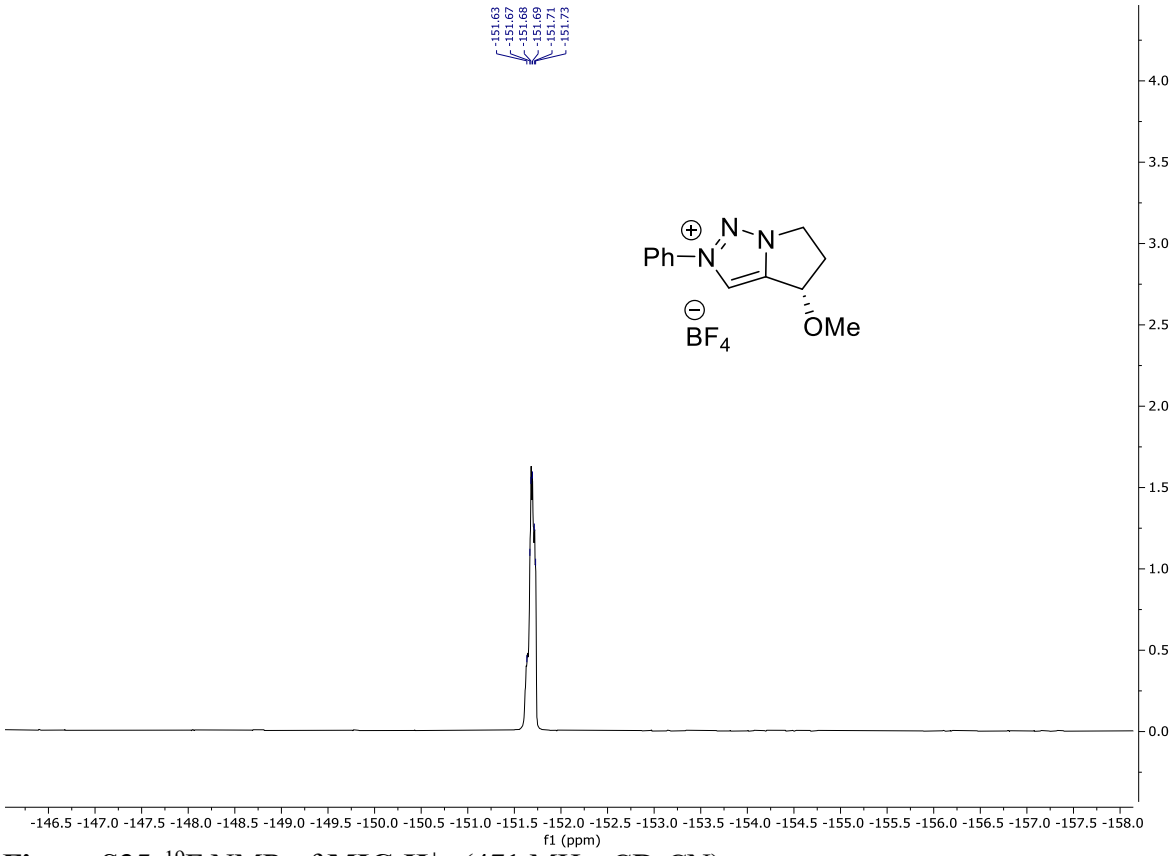


Figure S35. ^{19}F NMR of **MIC-H$^+$e** (471 MHz, CD_3CN)

(*R*)-4-Phenoxy-2-phenyl-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$f)

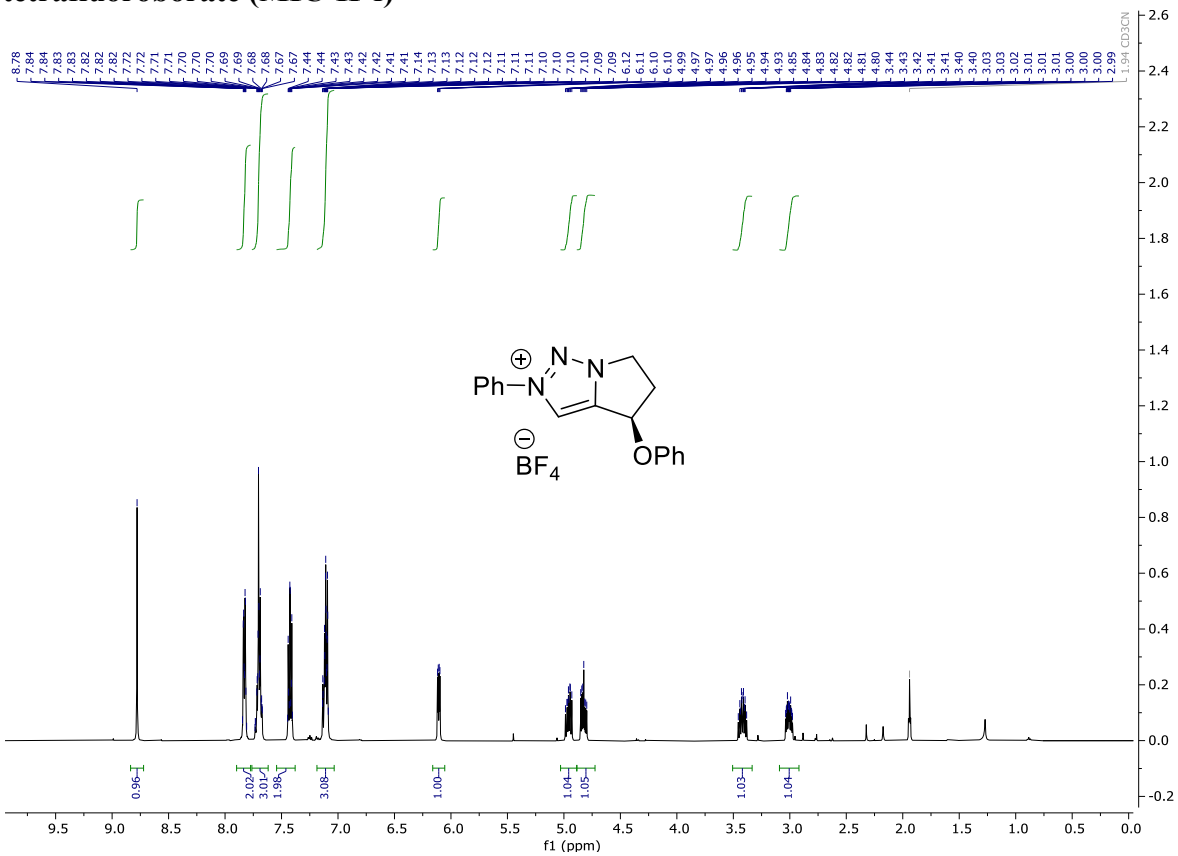


Figure S36. ^{1}H NMR of **MIC-H$^+$f** (500 MHz, CD_3CN)

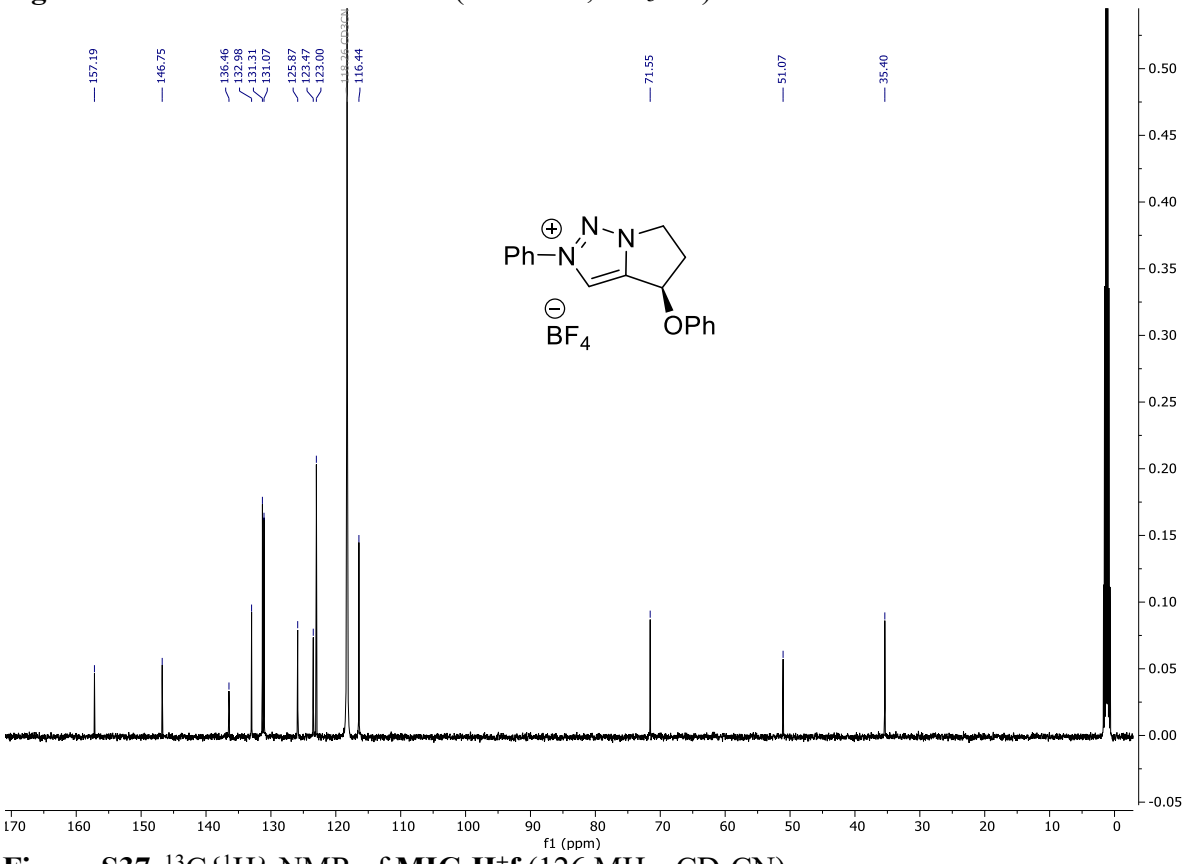


Figure S37. $^{13}C\{^1H\}$ NMR of **MIC-H$^+$f** (126 MHz, CD_3CN)

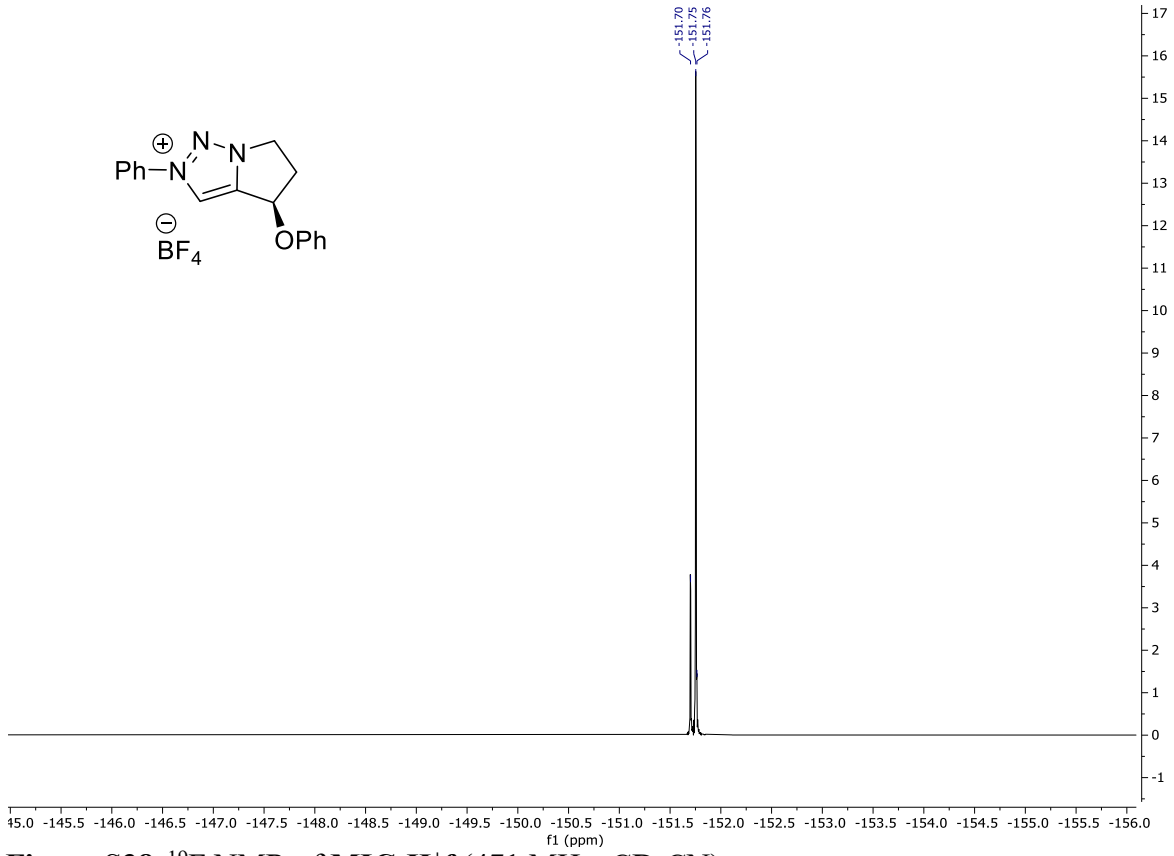


Figure S38. ^{19}F NMR of **MIC-H$^+$f** (471 MHz, CD_3CN)

(*R*)-2-Mesityl-4-phenoxy-5,6-dihydro-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-2-ium tetrafluoroborate (MIC-H$^+$g)

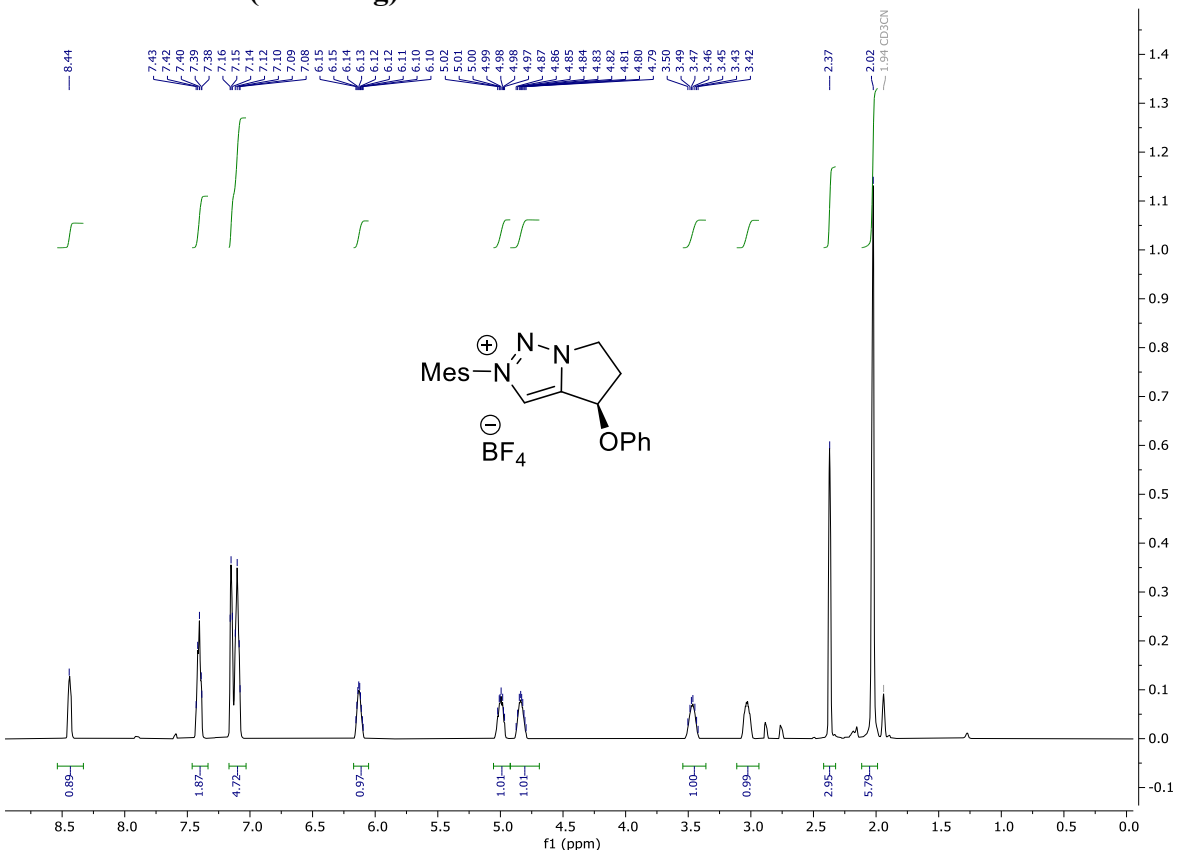


Figure S39. ^{1}H NMR of **MIC-H$^+$g** (500 MHz, CD_3CN)

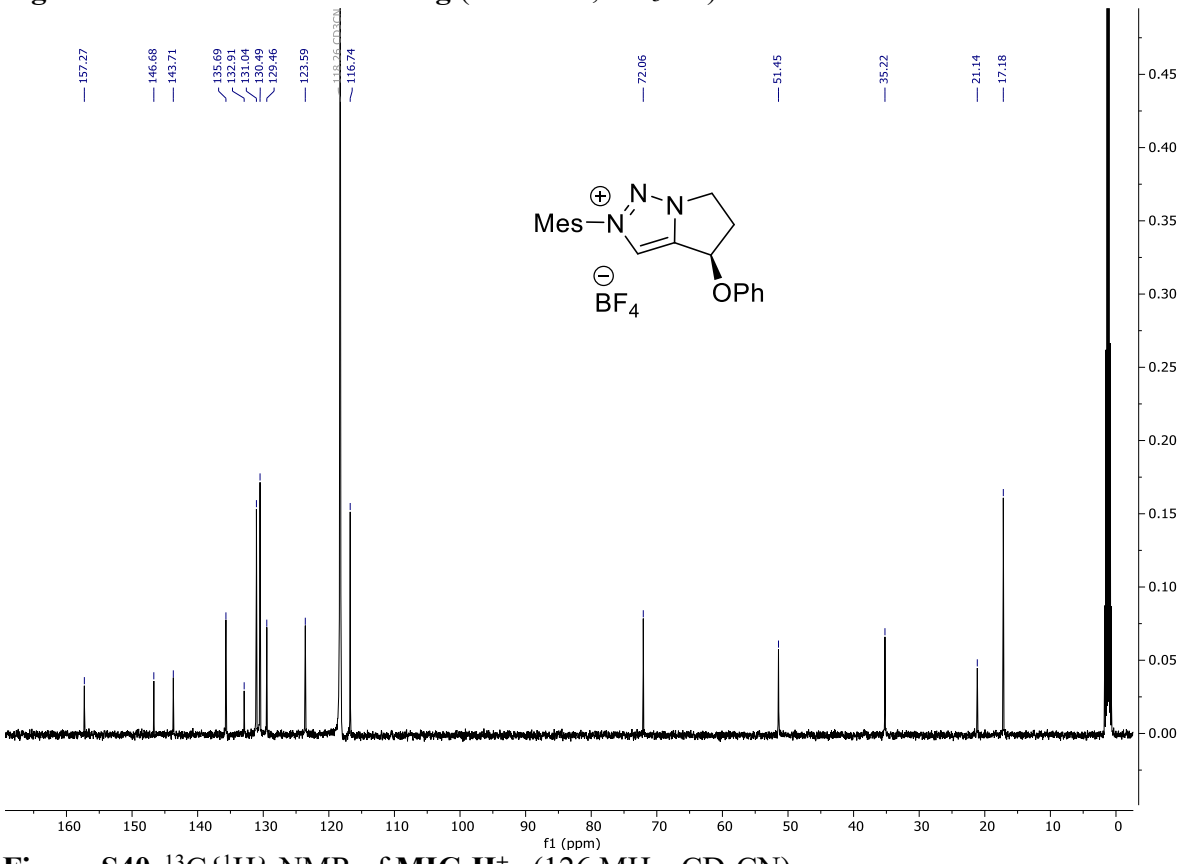


Figure S40. $^{13}C\{^1H\}$ NMR of **MIC-H$^+$g** (126 MHz, CD_3CN)

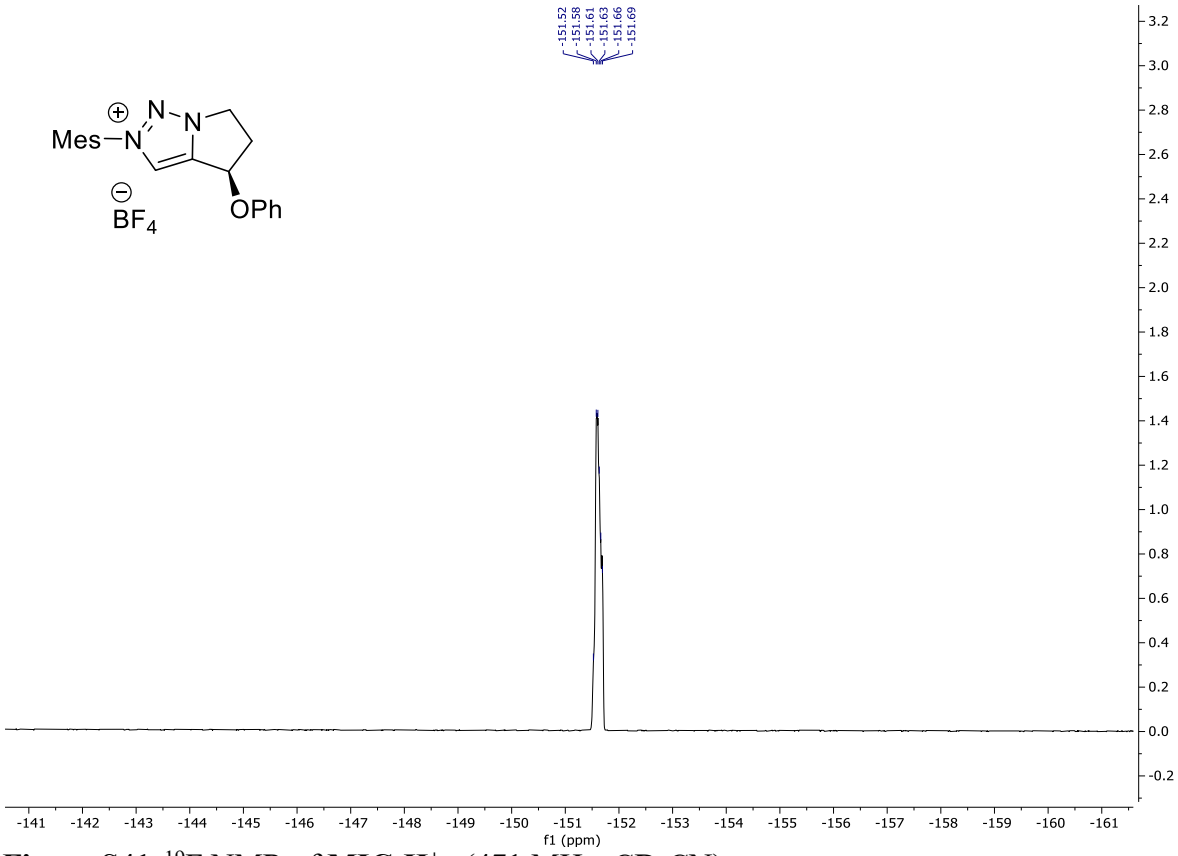


Figure S41. ^{19}F NMR of **MIC-H$^+$g** (471 MHz, CD_3CN)

(*R*)-2-Phenyl-4-phenoxy-5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-5-ylidene (MICf)

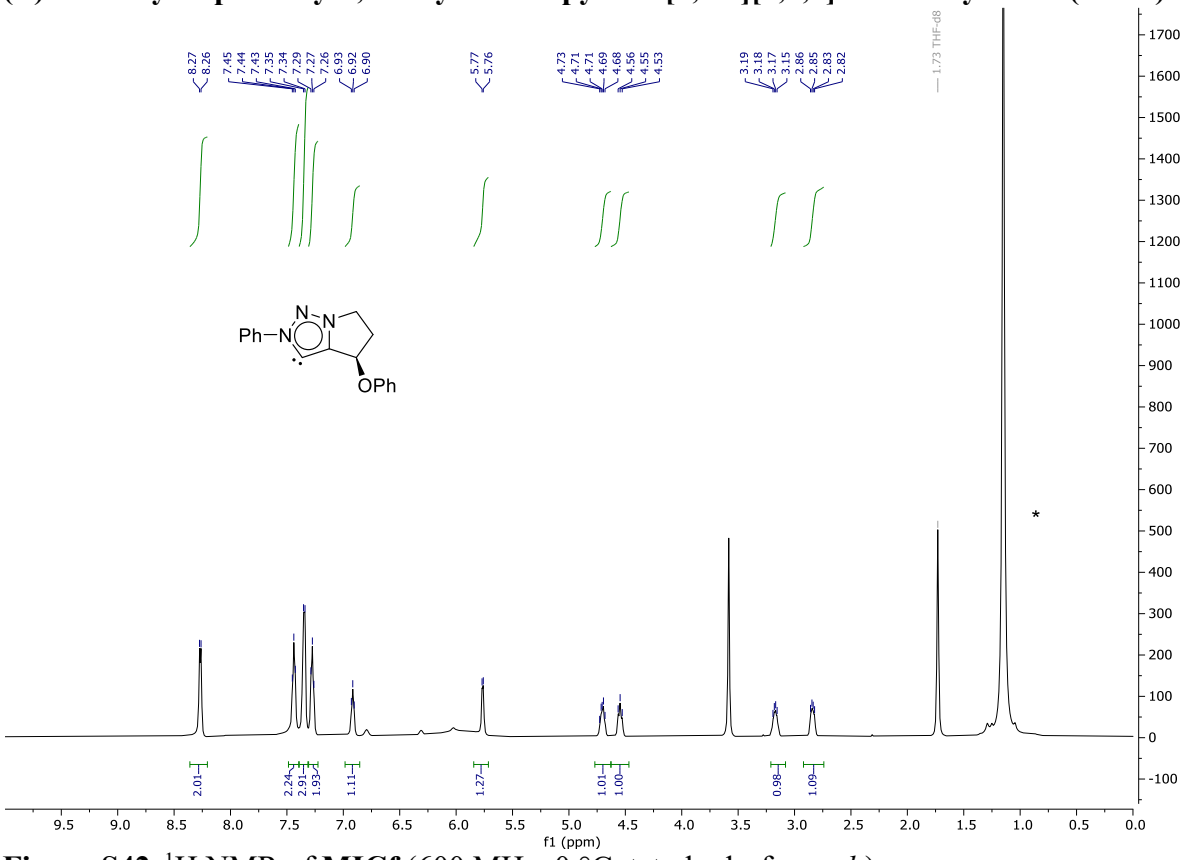


Figure S42. ^{1}H NMR of **MICf** (600 MHz, 0 °C, tetrahydrofuran-d_8)

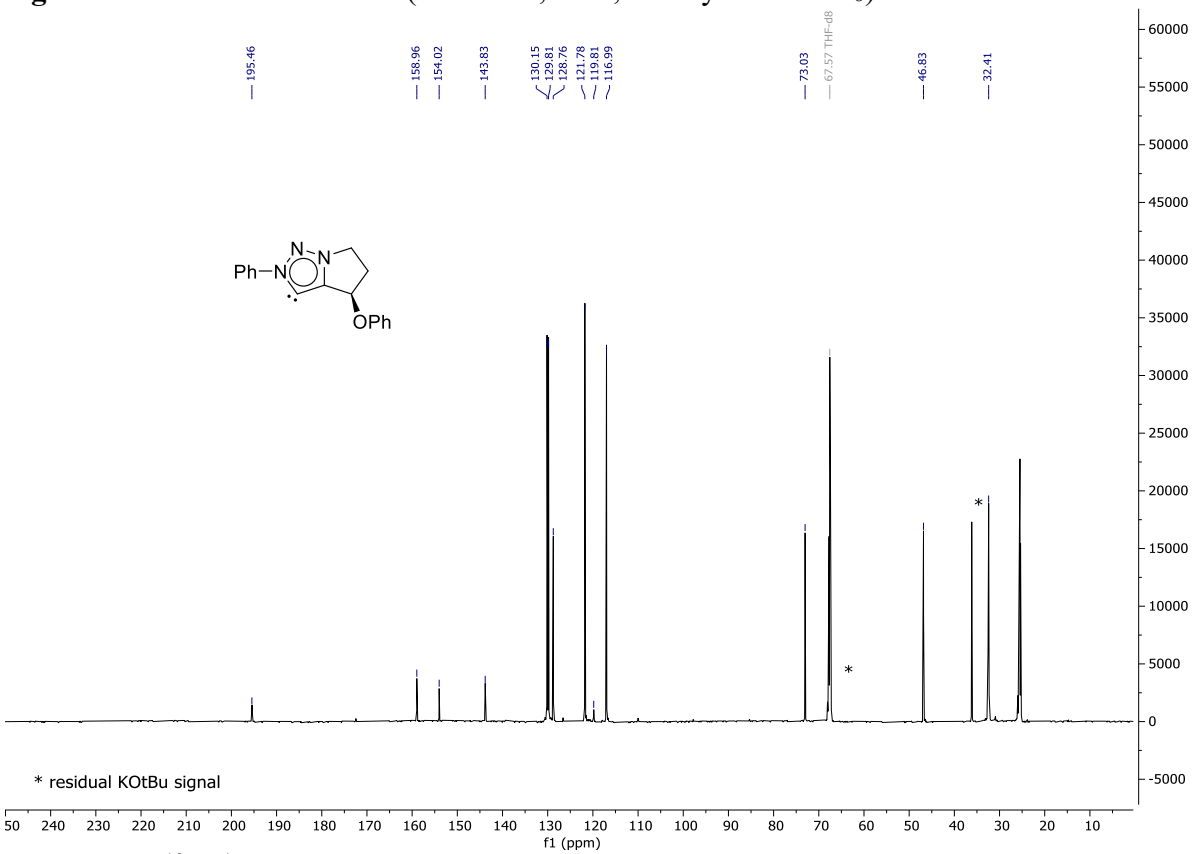


Figure S43. ^{13}C{^{1}H} NMR of **MICf** (151 MHz, 0 °C**,** tetrahydrofuran-d_8)

(*R*)-2-Mesityl-4-phenoxy-5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-5-ylidene (MICg)

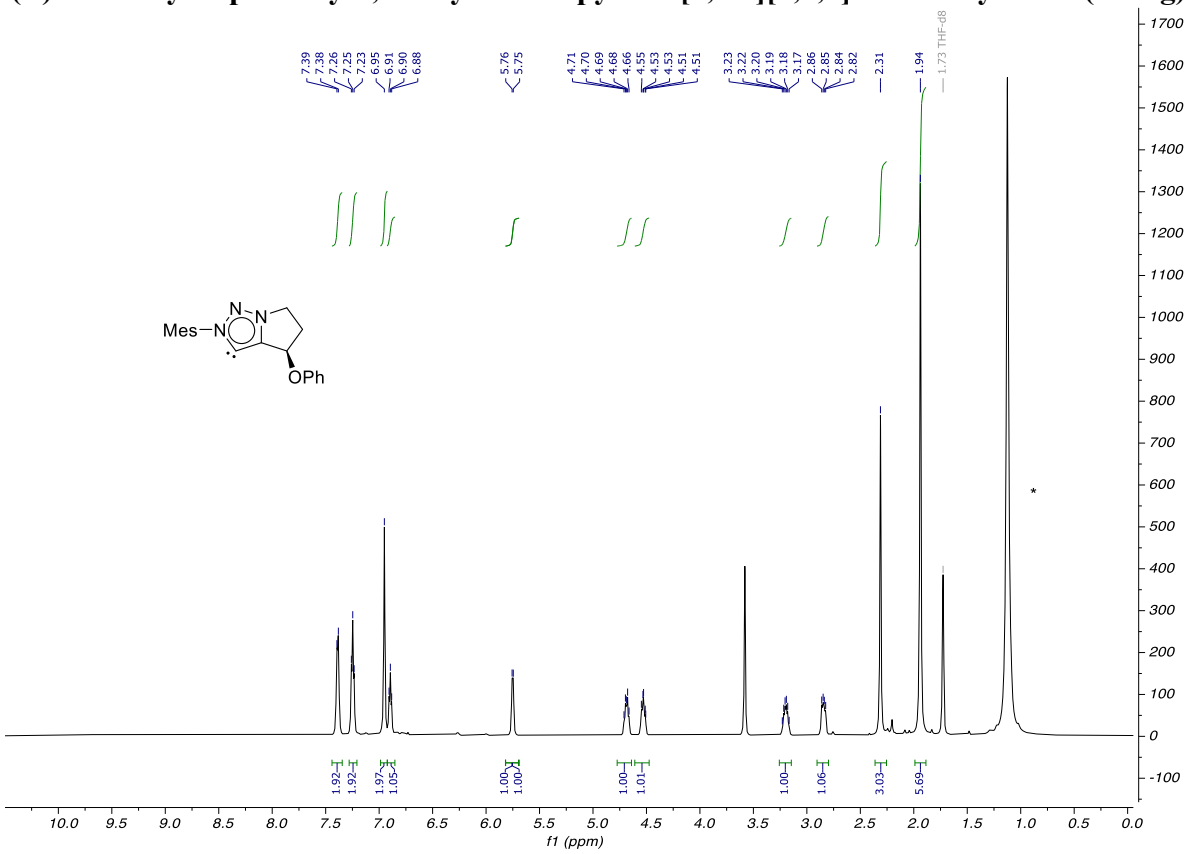


Figure S44. ^{1}H NMR of **MICg** (600 MHz, 0 °C, tetrahydrofuran-d_8)

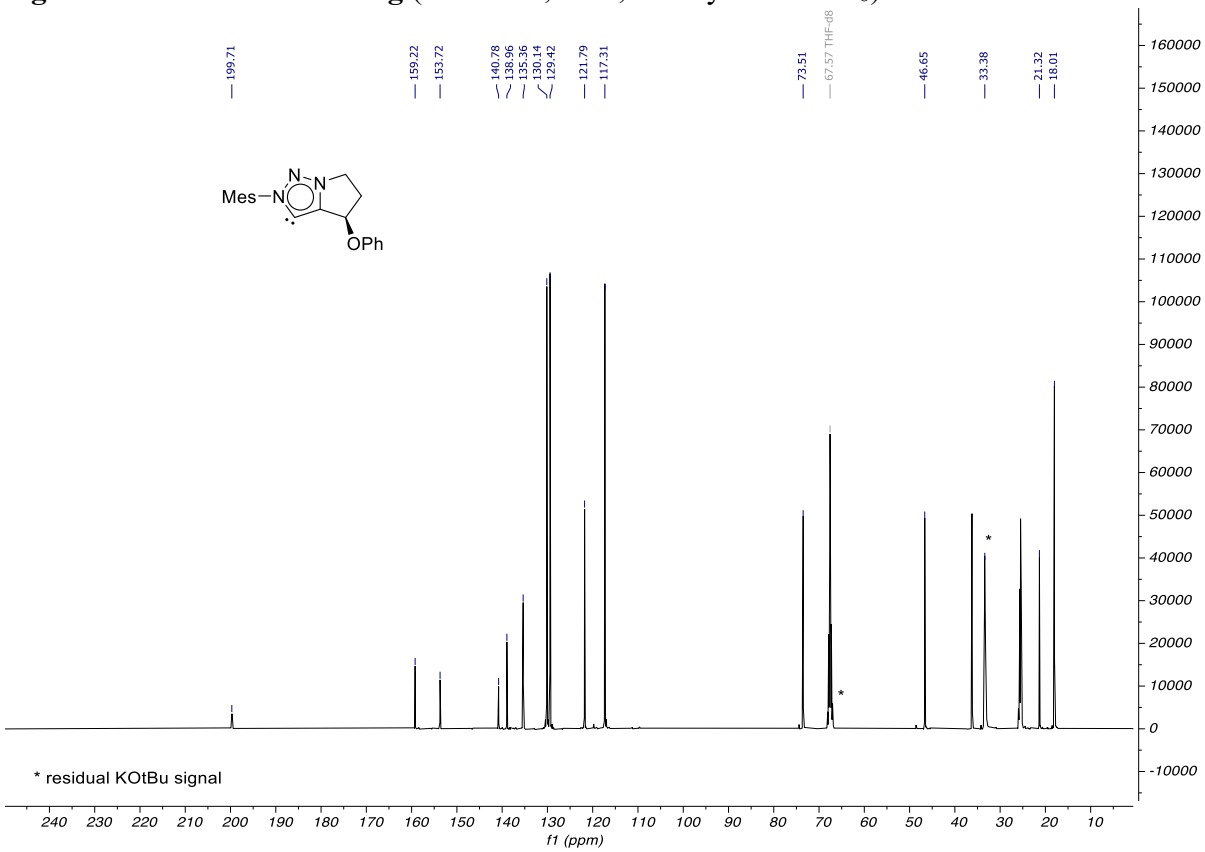
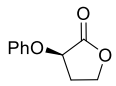


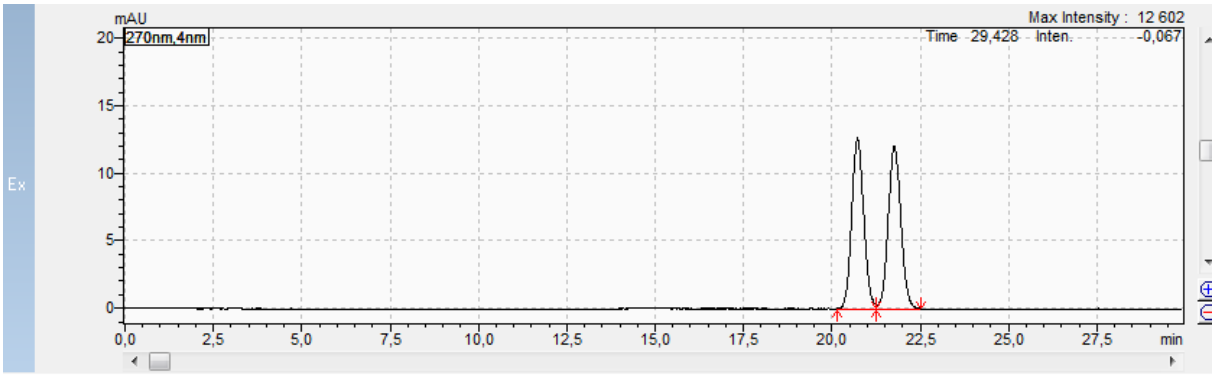
Figure S45. ^{13}C{^{1}H} NMR of **MICg** (151 MHz, 0 °C**,** tetrahydrofuran-d_8)

Chiral HPLC



Conditions: IB column
mobile phase: *n*-heptane/*i*-PrOH – 90:10
λ = 270 nm, V = 1.0 ml/min, t = 25 °C

for **4c**: t_R = 20.7 min (major), t_R = 21.8 min (minor), ***ee* = 97%**

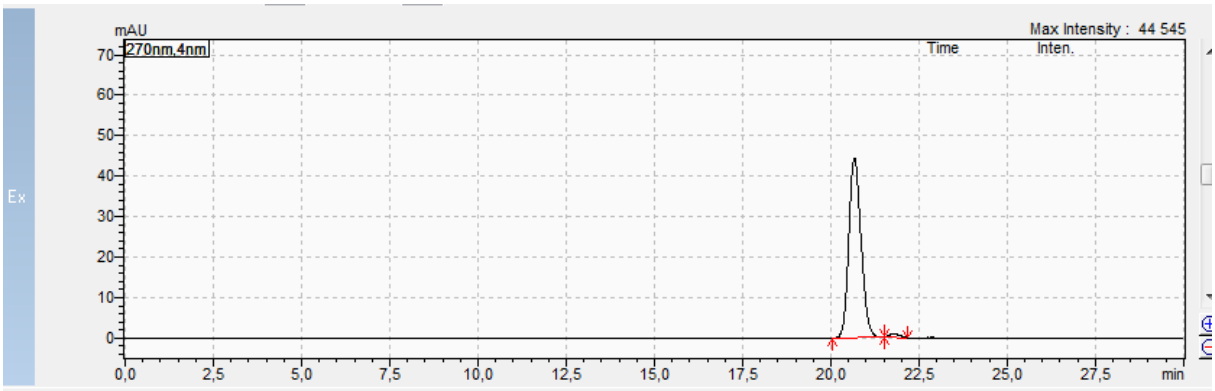


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	20,725	49,876	300728	12648	0,000000		20,149	21,259	49,876
2	21,769	50,124	302225	12062	0,000000	V	21,259	22,539	50,124
Total		100,000	602954	24710					100,000

Figure S46. Chiral HPLC trace of *rac*-**4c**

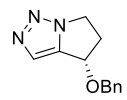


Results View - Peak Table

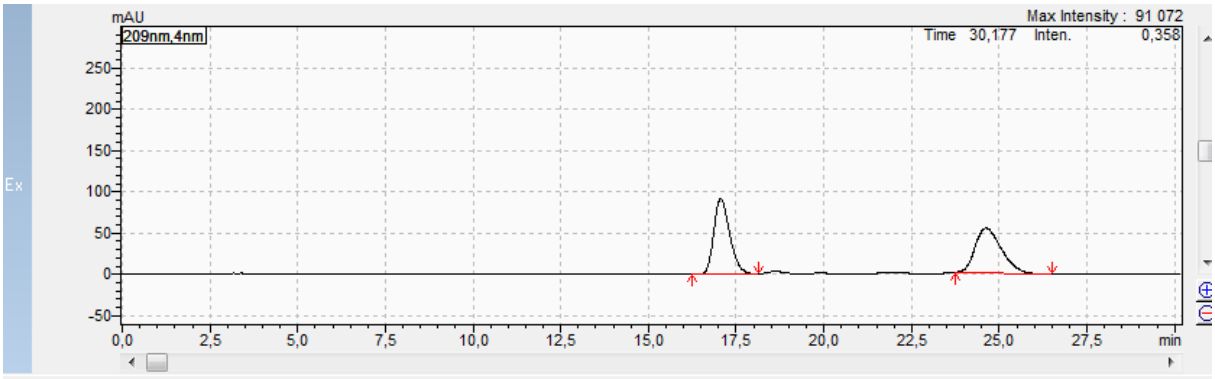
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	20,670	98,438	1071399	44430	0,000000	M	20,053	21,525	98,438
2	21,802	1,562	17006	842	0,000000	M	21,525	22,176	1,562
Total		100,000	1088406	45272					100,000

Figure S47. Chiral HPLC trace of **4c**



Conditions: IH column
mobile phase: *n*-heptane/*i*-PrOH – 60:40
λ = 209 nm, V = 1.0 ml/min, t = 25 °C
for **6a**: t_R = 17.0 min (major), t_R = 24.5 min (minor), ***ee* = 98%**

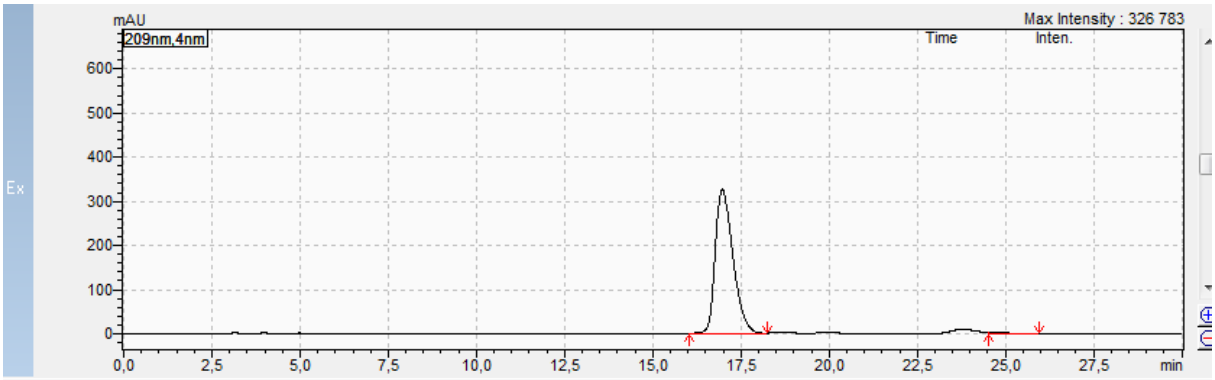


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	17,062	50,438	2858143	90466	0,000000	M	16,224	18,155	50,438
2	24,625	49,562	2808463	53878	0,000000	M	23,765	26,507	49,562
Total		100,000	5666606	144344					100,000

Figure S48. Chiral HPLC trace of *rac*-**6a**

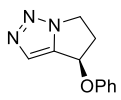


Results View - Peak Table

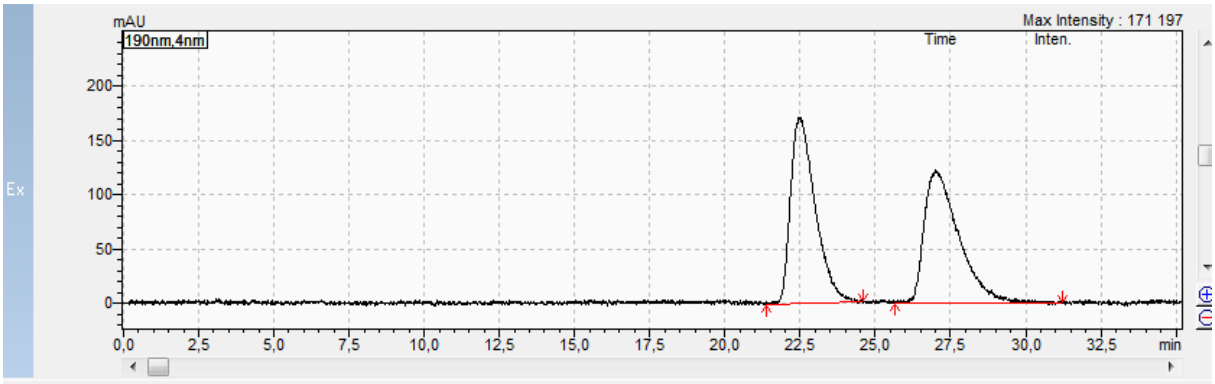
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	16,973	99,116	11420577	325996	0,000000	M	16,032	18,251	99,116
2	24,528	0,884	101884	2759	0,000000	M	24,523	25,952	0,884
Total		100,000	11522461	328756					100,000

Figure S49. Chiral HPLC trace of **6a**



Conditions: IH column
mobile phase: *n*-heptane/*i*-PrOH – 60:40
λ = 190 nm, V = 1.0 ml/min, t = 25 °C
for **6c**: t_R = 22.3 min (major), t_R = 27.7 min (minor), ***ee* = 97%**

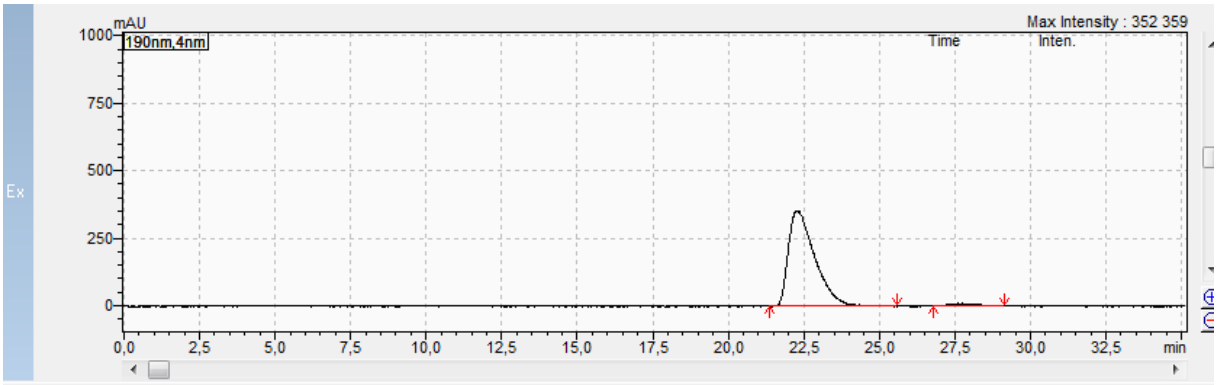


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	22,507	50,114	9779725	171063	0,000000	M	21,397	24,587	50,114
2	26,994	49,886	9735164	122012	0,000000	M	25,653	31,232	49,886
Total		100,000	19514889	293076					100,000

Figure S50. Chiral HPLC trace of *rac*-**6c**



Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	22,336	98,573	21454370	353949	0,000000	M	21,365	25,579	98,573
2	27,724	1,427	310651	8955	0,000000	M	26,773	29,131	1,427
Total		100,000	21765021	362904					100,000

Figure S51. Chiral HPLC trace of **6c**

References

1 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* 2015, **71**, 3–8.

2 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* 2015, **71**, 3–8.

3 a) S. E. Denmark and S.-M. Yang, *J. Am. Chem. Soc.*, 2004, **126**, 12432–12440. b) I. Paterson, E. A. Anderson, S. M. Dalby, J. H. Lim, P. Maltas, O. Loiseleur, J. Genovino and C. Moessnera, *Org. Biomol. Chem.*, 2012, **10**, 5861–5872.

4 H. Fan, Z. Tong, Z. Ren, K. Mishra, S. Morita, E. Edouarzin, L. Gorla, B. Averkiev, V. W. Day and D. H. Hua, *J. Org. Chem.*, 2022, **87**, 6742–6759.

5 N. G. Bandur, D. Brückner, R. W. Hoffmann and U. Koert, *Org. Lett.*, 2006, **8**, 3829–3831.

6 Q. Chen, D. Schweitzer, J. Kane, V. J. Davisson and P. Helquist, *J. Org. Chem.*, 2011, **76**, 5157–5169.

7 Y. Saito, K. Matsumoto, S. S. Bag, S. Ogasawara, K. Fujimoto, K. Hanawa and I. Saito, *Tetrahedron*, 2008, **64**, 3578–3588.

8 T. Lv, Z. Wang, J. You, J. Lan and G. Gao, *J. Org. Chem.*, 2013, **78**, 5723−5730.