Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Potassium-mediated stereochemical assistance to form one indenonaphthacene isomer from Rubrene with the complementary diastereoselectivity of the acid based protocol

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SI 1 Experimental Part.

SI 1.1 General considerations.

a) Starting materials

Rubrene or 5,6,11,12-tetraphenylnaftalene (99%, CAS 517-51-1) and CF_3COOH (99%, CAS 76-01-5) were acquired from TCI America. K(0) was purchased as ingots from Aldrich (99.95%, CAS 7440-09-7). Organic solvents were purchased from Fisher Chemical. All reagents and solvents were used without any previous purification unless specified. Manipulations for the K procedure were done strictly in anhydrous conditions, inert atmosphere using vacuum line techniques and, solvents freshly distilled from metallic sodium.

b) Characterization

Solution Nuclear Magnetic Resonance Spectroscopy. ^{1}H, ^{13}C, ^{39}K, $^{1}H,^{13}C$-HMBC and 1D Selective NOESY NMR experiments were recorded on Bruker Avance III HD 400 MHz or 500 NHz spectrometers at ambient temperature. Chemical shifts are reported in ppm with respect to the TMS (Me_4Si) using a resonance of the corresponding deuterated solvent (THF-*d8*, DMF-*d7*, $CDCl_3$) for calibration. Coupling constants are given in Hz. For 1D selective NOESY, different mixing times in the range 0.5-1.5 s were tried in order to verify an NOE build-up.

Infrared Spectroscopy. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR instrument (KBr pellets).

Optical Rotations were measured in a Bellingham & Stanley ADP400+ polarimeter. Optical values are given in deg cm^2 g^{-1}.

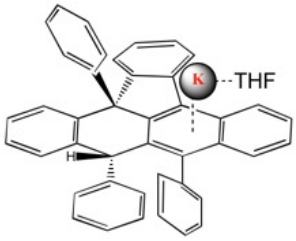
Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 aluminum plates with F-254 indicator, visualized by UV irradiation. Column chromatography was performed using Aldrich silica gel (technical grade pore size 60 A, 230-400 mesh).

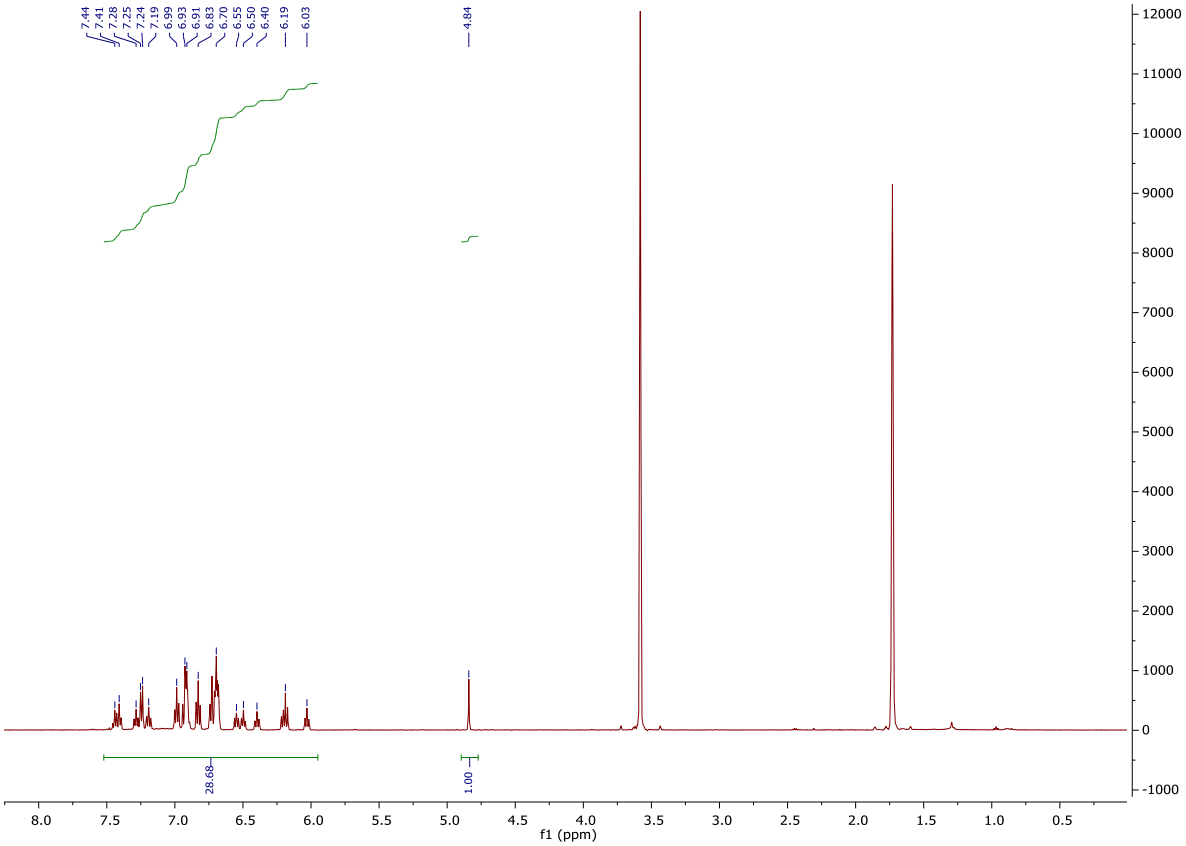
Mass Spectrometry Analysis were with a Agilent QTOF 7200 instrument with CI ionization and analysing accurate mass (High resolution mode) in a positive mode.

MM2 basic Molecular modelling computations were done using software ChemBio3D Ultra 14.0 Suite.

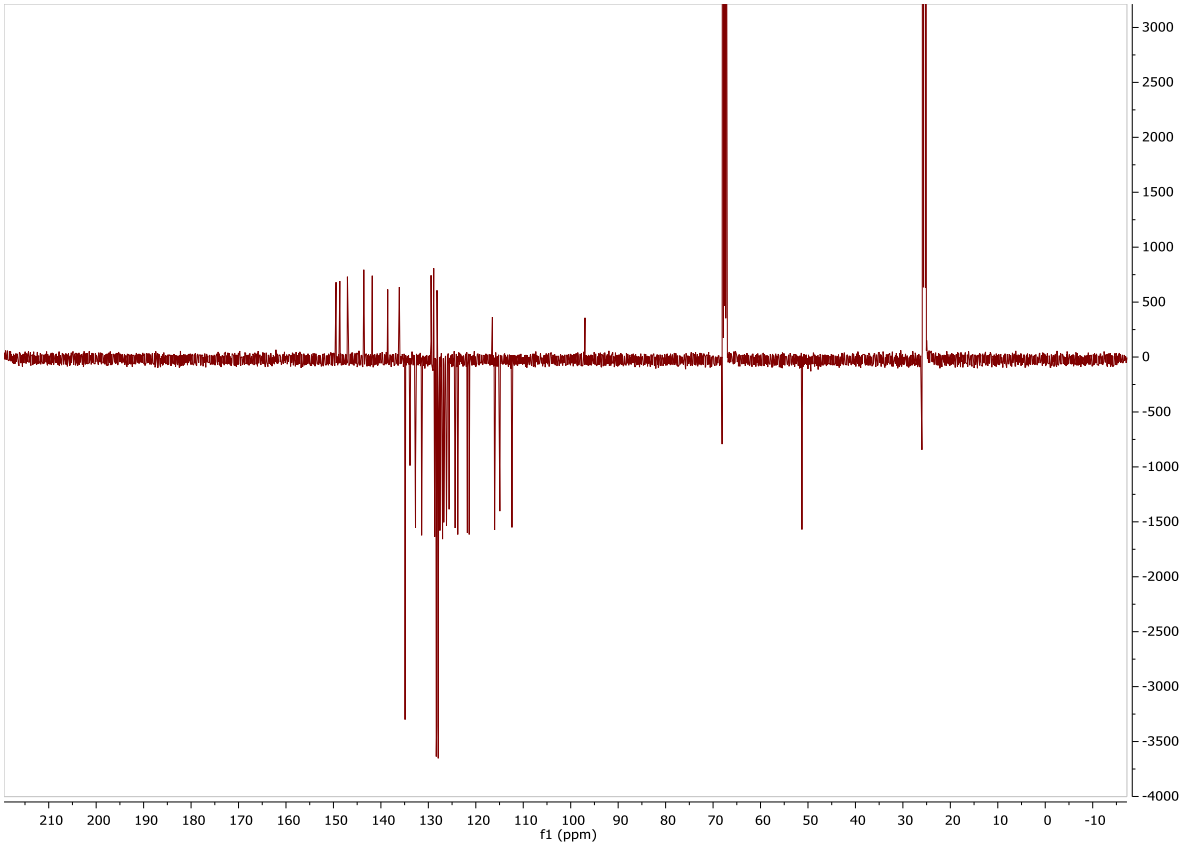
SI 2 Product's Characterization.

SI 2.1 Characterization for [K(((*S,S*)+(*R,R*))-R*)(THF)x].

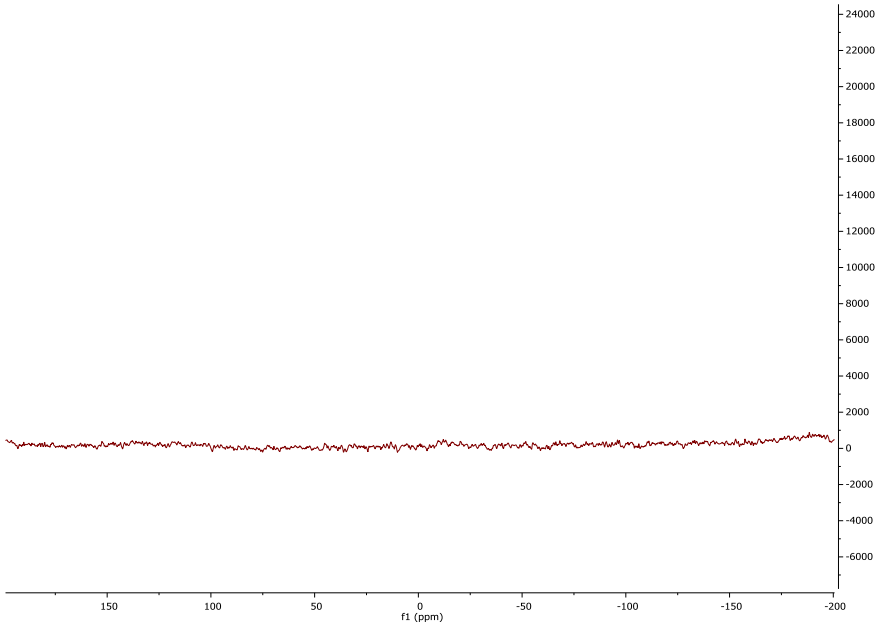




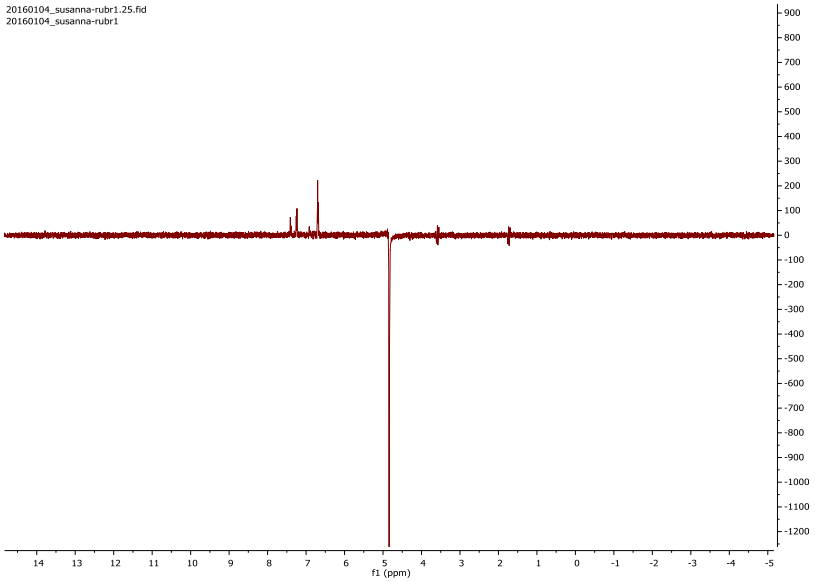
^{1}H NMR (500 MHz; THF-*d8*; Me_4Si) δH 7.44 (1H, pd, *J* = 6.0), 7.40 (1H, pt, *J* = 8.0), 7.28 (1H, t, *J* = 7.3), 7.24 (2H, d, *J* = 7.2), 7.19 (s, 1H), 7.19 (1H, *J* = 7.2), 6.98 (2H, t, *J* = 7.7 Hz), 6.91 (5H, m), 6.83 (2H, t, *J* = 7.0), 6.73 (2H, t, J = 7.0), 6.70 (3H, m), 6.54 (1H, pt, *J* = 7.5), 6.49 (1H, t, *J* = 7.2), 6.40 (1H, s, *J* = 7.5), 6.21 (2H, m), 6.07 (1H, t, *J* = 8.5), 4.84 (1H, s).



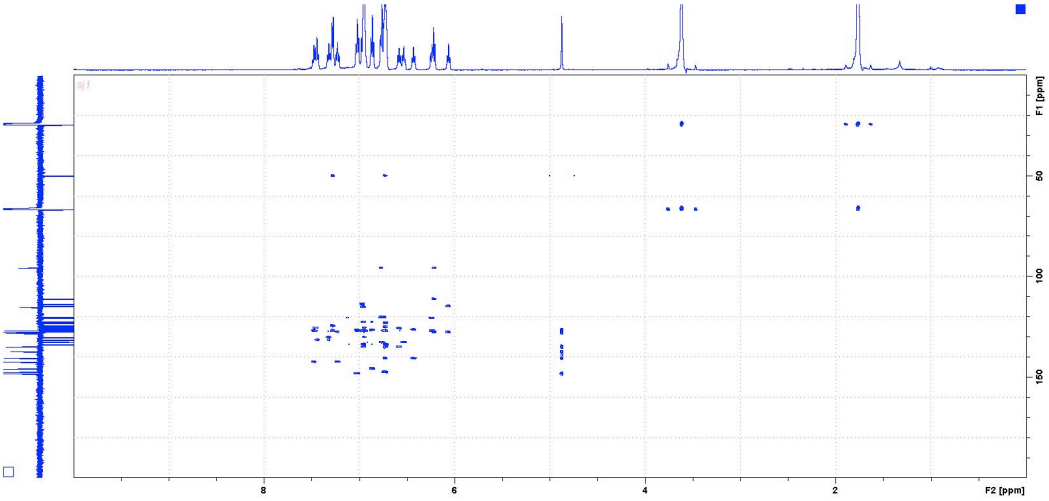
^{13}C NMR (126 MHz; THF-d8) δCq, 149.4, 148.6, 147.0, 143.6, 141.8, 138.6, 136.1, 136.1, 129.4, 128.9, 128.2, 116.50, 97.0; δCH, 134.9, 133.9, 132.7, 131.4, 128.7, 128.3, 128.2, 128.2, 127.9, 127.8, 127.6, 127.0, 126.7, 126.2, 125.6, 124.4, 123.8, 121.8, 121.4, 116.0, 114.9, 112.3, 51.3.



^{39}K NMR (26 MHz, THF-d8)

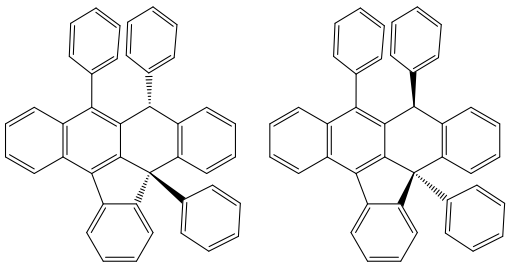


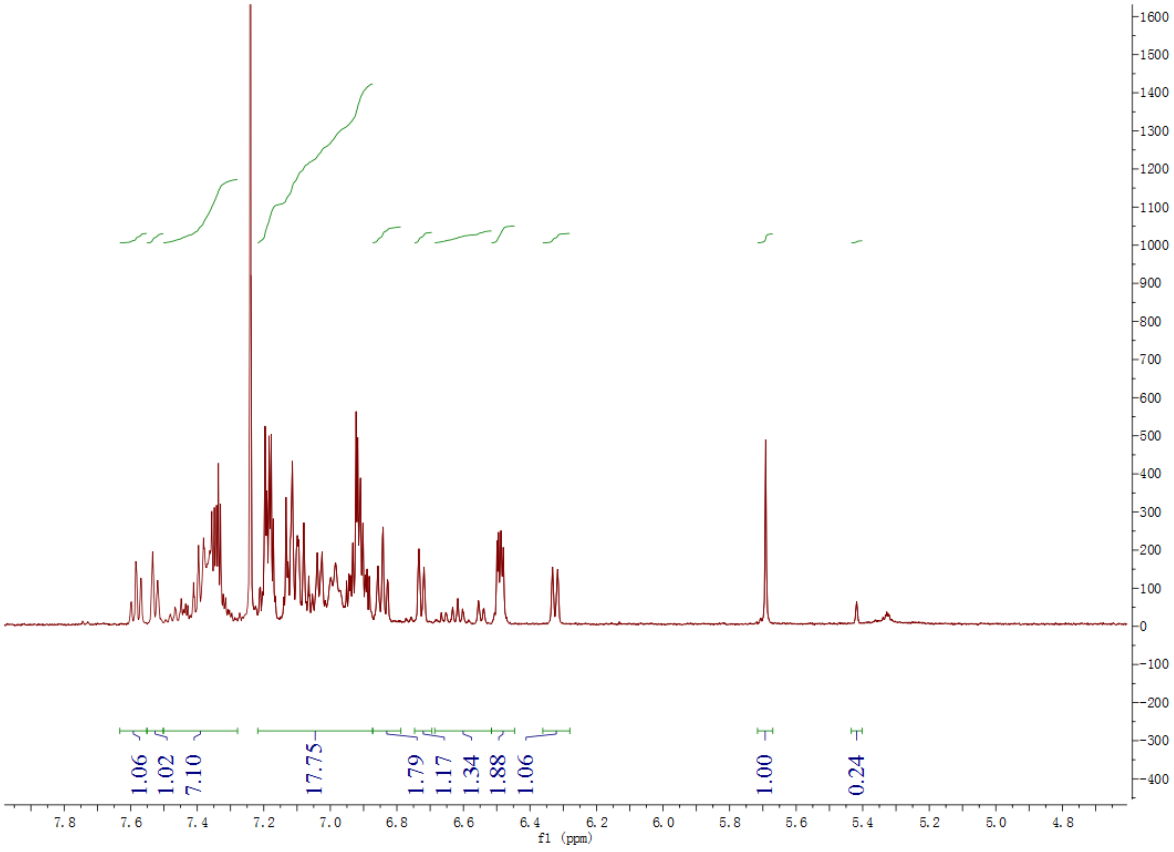
Selective 1D NOESY (500 MHz, THF-*d8*)



^{1}H,^{13}C-HMBC (500 MHz, THF-d8)

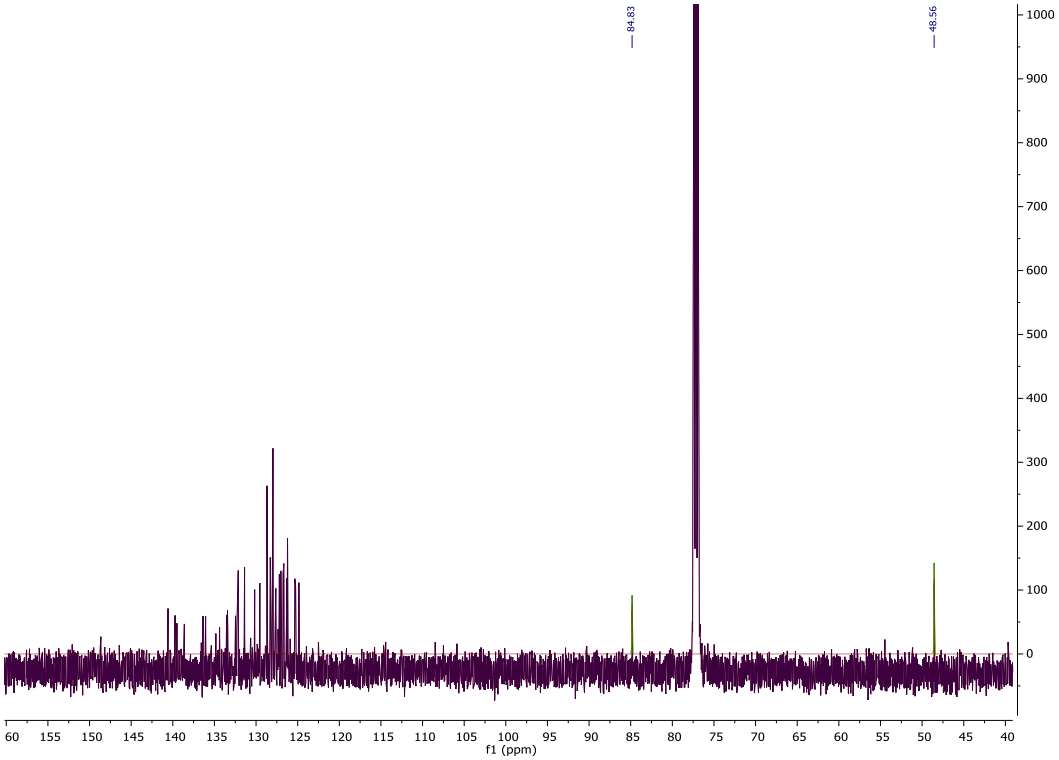
SI 2.2 Characterization for ((*S,S*)+(*R,R*))-R* where R* is (4b*R*,9*R*)-4b,9,10-triphenyl-4b,9-dihydroindeno[1,2,3-*fg*]tetracene and (4b*S*,9*R*)-4b,9,10-triphenyl-4b,9-dihydroindeno[1,2,3-*fg*]tetracene.





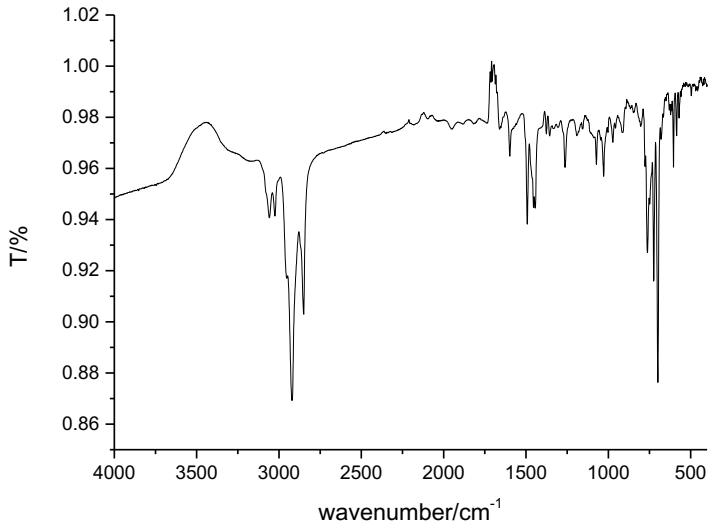
^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δH 7.58 (1H, ptd, *J*= 4), 7.52 (1H, pd, *J*= 4), 7.42-7.34 (7H, m), 7.20-6.84 (14H, m), 6.72 (1H, t, *J*= 4), 6.49 (2H, m), 6.31 (1H, d, *J*= 4), 5.76 (s, 1H); δH (*minor hydrogenated product)* 5.33 (1H, s).

Minor isomer is present in a 10% (calculated by ^{1}H NMR integration) as the hydrogenated isomer of ((*R,R*)+(*S,S*))-R* in agreement with MS-TOF analysis.



^{13}C NMR (126 MHz; $CDCl_3$) δC 149.0, 140.4, 139.6, 139.3, 138.5, 136.2, 133.4, 133.3, 132.3, 132.0, 133.0, 131.2, 130.0, 129.4, 128.5, 128.5, 128.1, 127.8, 127.5, 127.2, 127.0, 126.9, 126.6, 126.5, 126.1, 126.1, 125.2, 125.1, 124.7, 84.7, 48.4.

In THF signal for quaternary carbon is hidden by the signal at 67 ppm from the deuterated solvent.



v_{max}/cm^{-1} (IR): 3056, 2926, 2850, 1595, 1456, 1446, 1261, 1026, 766, 724, 697.

$[\alpha]_D$ 0 (1 in $CHCl_3$)

MS (main product, TOF, +) m/z 533.2285 (MH^+, 100%), 455.1808 (MH^+-Ph, 44.45%).

MS (minor product, TOF, +) m/z 535.2443 (MH^+, 48.4%), 457.1982 (MH^+-Ph, 100%).

SI 2.3 Characterization for *rac*-R' where chirality has been assigned as (4*R,8S,12R,16S*) and, R' is (4b*S*,8b*R*,12b*S*,16b*R*)-4b,12b-diphenyl-4b,8b,12b,16b-tetrahydrodiindeno[1,2,3-*fg*:1',2',3'-op]tetracene.

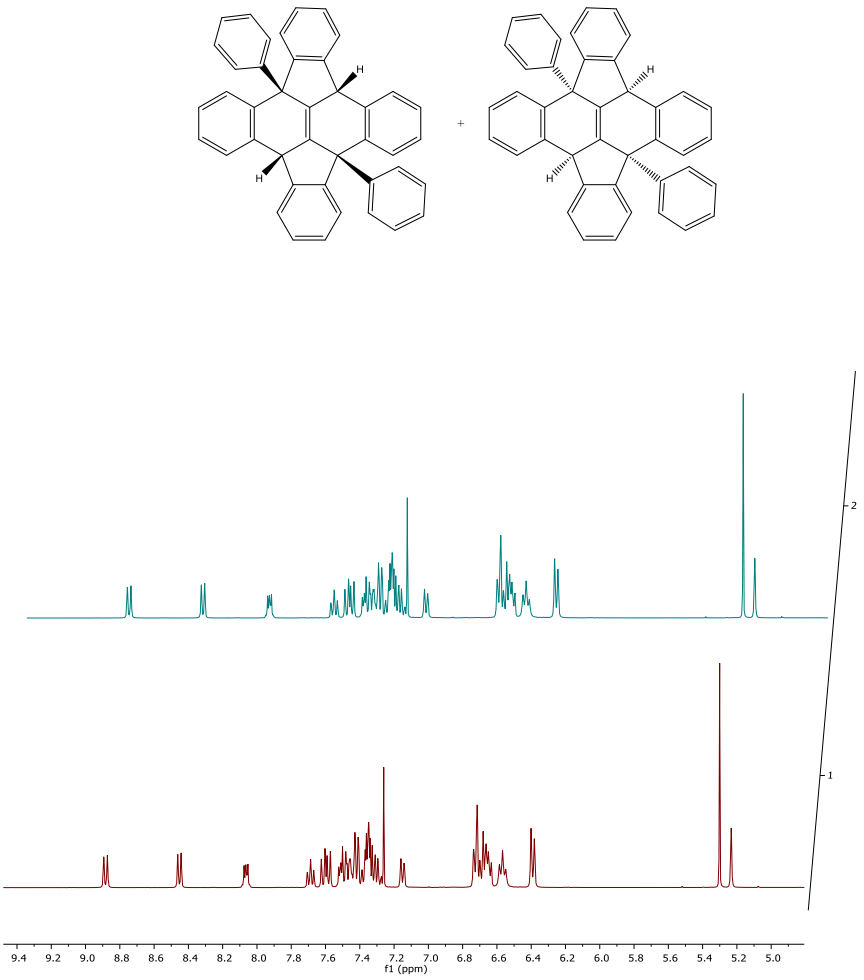
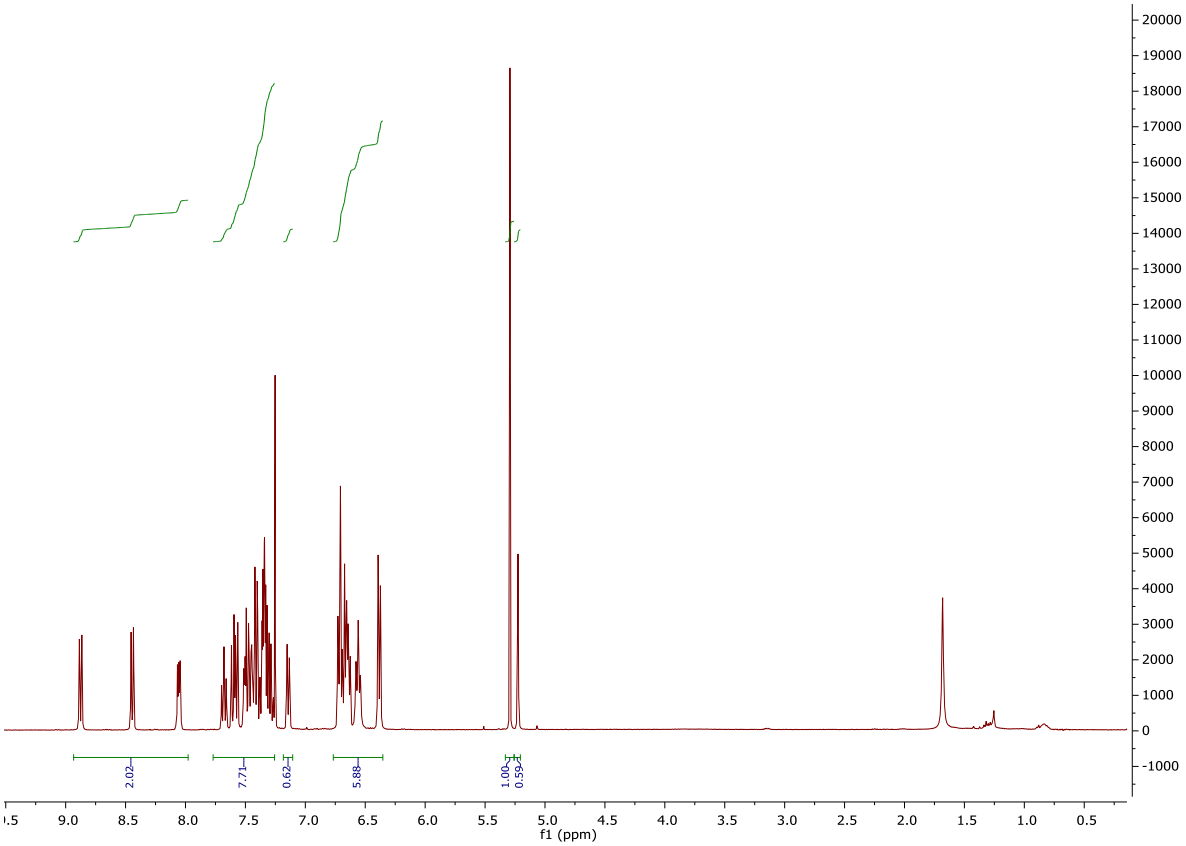
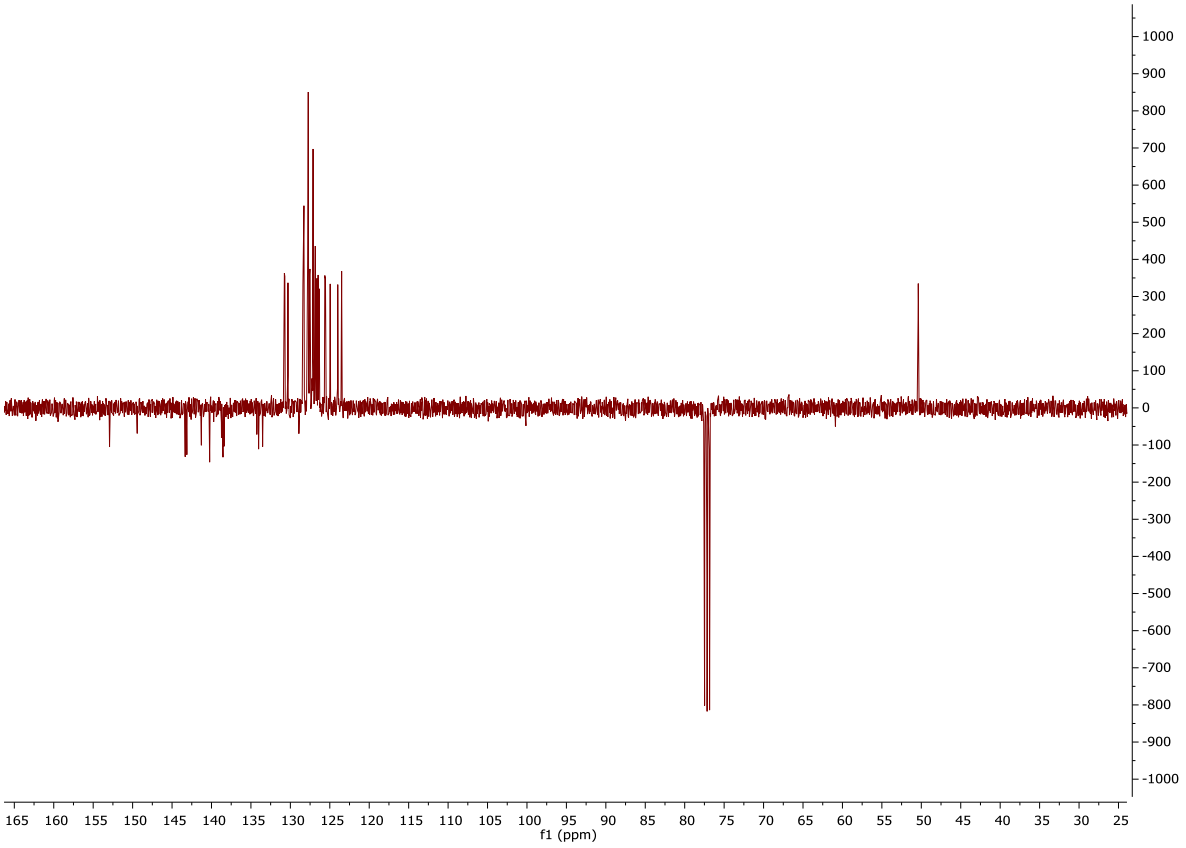


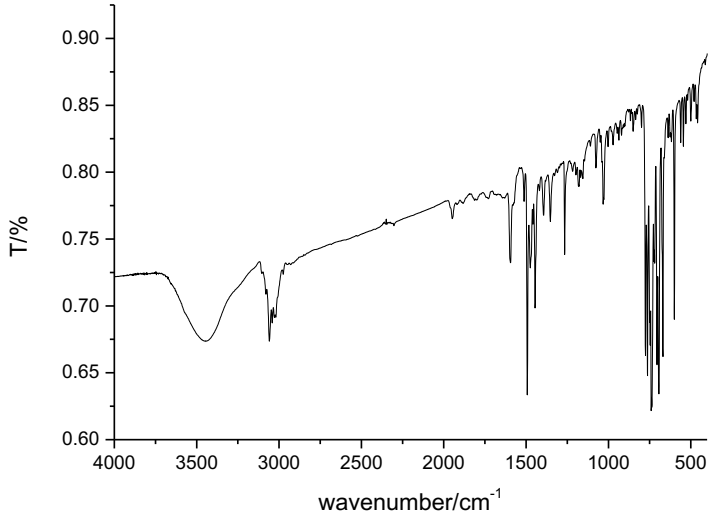
Figure SI 1: ^{1}H NMR for crude acid catalysis products at different reaction times



^{1}H NMR (mixture *rac*-R'+ ((*S*,*R*)-(*R*,*S*))-R*; 400 MHz; $CDCl_3$) δH 8.88 (1H, d, *J* = 8.3, R*), 8.44 (1H, d, *J* = 7.8, R*), 8.09 – 8.02 (m, 1H, R*), 7.64 – 7.28 (m, 9H), 6.75 – 6.60 (m, 5H), 6.56 (2H, t, *J* = 7.4, R'), 6.42 – 6.35 (2H, m, R'), 5.29 (1H, s, R'), 5.23 (1H, s, R*).



^{13}C NMR (mixture R'+ *rac*-(*R,S*)-R*; 101 MHz; $CDCl_3$) δCq 152.9, 149.4, 143.3, 143.1, 141.3, 140.2, 138.7, 138.5, 138.4, 134.2, 134.0, 133.5, 128.9, 60.9 (R'), 60.8 (R*) δCH 130.8, 130.7, 130.3, 128.4, 128.3, 127.8, 127.7, 127.7, 127.5, 127.5, 127.2, 127.1, 126.9, 126.8, 126.6, 126.5, 126.4, 125.6, 125.5, 124.9, 124.0, 123.5, 50.4 (R'), 50.2 (R*).

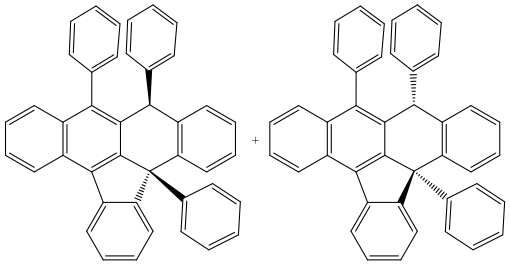


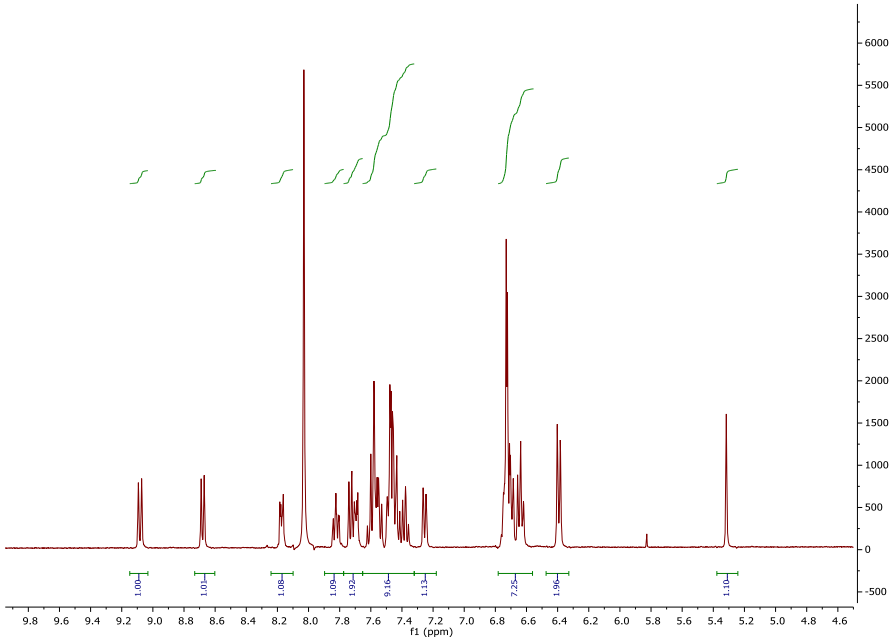
v_{max}/cm^{-1} (IR): 1599, 1491, 1446, 1267, 735, 690.

IR demined by an important intensity in bending mode in agreement with the proposed structure.

MS (main assigned product *rac*-R', TOF, +) m/z 531.2104 [MH^+-2H, 100%), 453.1654 (M –Ph, 48.79%).

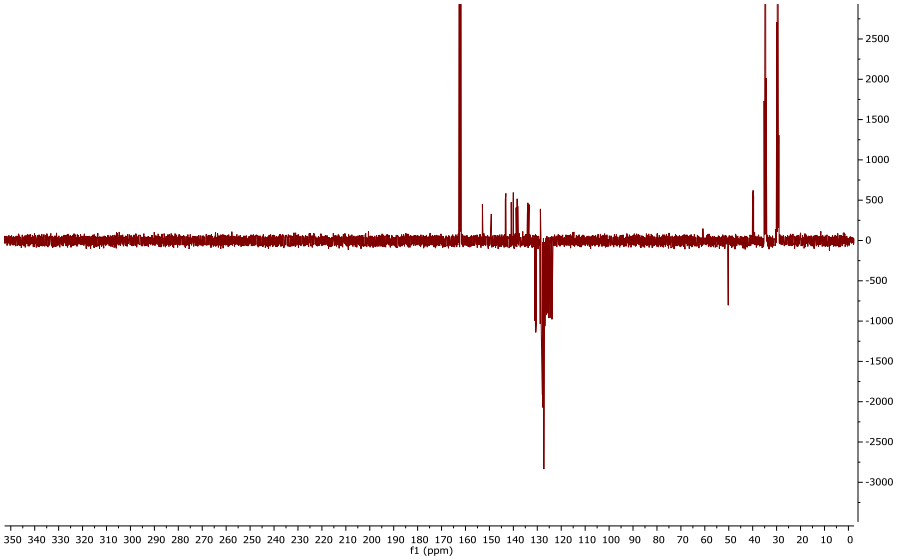
SI 2.4 Characterization for ((*S*,*R*)+(*R*,*S*))-R* where R* is (4b*R*,9*S*)-4b,9,10-triphenyl-4b,9-dihydroindeno[1,2,3-*fg*]tetracene and (4b*S*,9*R*)-4b,9,10-triphenyl-4b,9-dihydroindeno[1,2,3-*fg*]tetracene.



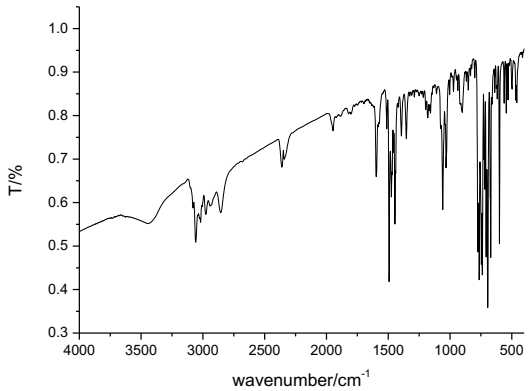


^{1}H NMR (400 MHz; DMF-*d7*; Me_4Si) δH 9.08 (1H, d, *J* = 8.0), 8.68 (1H, d, *J* = 8.0), 8.18 (1H, m), 7.84 (1H, t, *J* = 8.3), 7.87 -7.38 (19H, m), 7.25 (1H, d, *J* = 4), 6.75-6.62 (7H, m), 6.39 (2H, d, *J* = 8), 5.32 (1H, s).

Chemical shift for the aliphatic proton depends strongly on the solvent used. In DMF—*d* signal appears at 5.31 ppm, and at 5.23 and 5.22 in THF and $CDCl_3$, respectively due to the different solvation. The same is applicable to some carbon signals in less extend.



^{13}C NMR (101 MHz; DMF-*d7*) δCq 152.9, 149.2, 143.1, 141.0, 140.0, 138.8, 138.4, 138.2, 134.1, 134.0, 128.7, 60.8; δCH 131.0, 130.6, 130.4, 128.8, 128.4, 128.0, 128.0, 127.9, 127.9, 127.7, 127.3, 127.2, 127.1, 127.0, 126.8, 126.6, 126.1, 125.8, 125.1, 124.4, 123.9, 50.2.

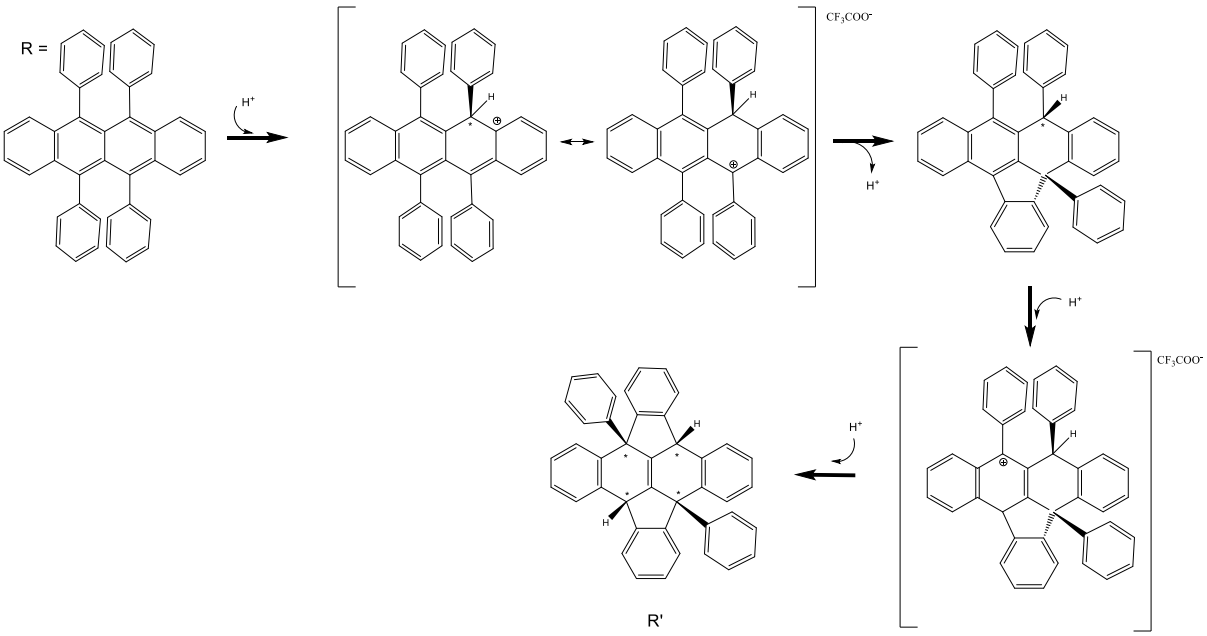


v_{max}/cm^{-1} (IR): 3060, 3008, 2972, 2849, 1598, 1492, 1449, 1058, 775, 764, 738, 694, 669, 599.

$[\alpha]_D$ 0 (1 in $CHCl_3$)

MS (((*S,R*)+(*R,S*))-R*, TOF, +) m/z 533.2266 (MH^+, 100%), 455.1813 (MH^+-Ph, 86.56%).

SI 3 Plausible mechanism of *rac*-R' formation in acidic media.



SI 4 MM2 modelling for (*R,R*)-*R and (*R,S*)-*R** showing in red distortion profile for molecule core.**