

ELECTRONIC SUPPLEMENTARY INFORMATION

Sc₃N@I_h-C₈₀ endohedral fullerene derived donor-acceptor conjugate: Role of thiophene spacer in promoting ultrafast excited state charge separation[†]

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1. Experimental Conditions

$\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ was synthesized by an arc-discharge method with Sc_2O_3 oxide packed rods under reactive gas atmosphere using ammonia. The obtained soot was extracted with CS_2 and pyridine in a Soxhlet extractor under reflux for 6hrs. The extract was then purified by HPLC using Varian Prostar instrument in a Buckyprep column ($\phi = 10 \text{ ID} \times 250 \text{ mm}$, Cosmosil) in 3 steps using toluene as eluent at 1mL/min and monitored by a UV detector at 320nm. To separate the $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ and $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ isomers, additional HPLC steps (and recycling) were required operating a LC-9130NEXT apparatus (Japan Analytical Industry Co. Ltd.), a 5-PBB column ($\phi = 4.6 \text{ ID} \times 250 \text{ mm}$) monitored by a UV detector at 320nm and using toluene as eluent at 1mL/min flowrate. Buckminsterfullerene C_{60} (+99.95%) was purchased from BuckyUSA (Bellaire, TX). Solvents and chemicals were purchased from Aldrich Chemicals (Milwaukee, WI). Anhydrous solvents, where indicated, were dried using a Pure-Sov 400 or using standard techniques. Chromatographic purifications on silica were performed using silica gel 60 from VWR (particle size 0.040-0.063 mm). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. ^1H NMR spectra were recorded as solutions in a partial deuterated solvent on a Bruker-Topspin AV 400 instrument or in an Avance III 700. ^1H NMR chemical shifts are reported relative to residual non deuterated solvent peaks. ^{13}C NMR chemical shifts are reported relative to the deuterated solvent peak. Chemical shifts are given as δ values. FT-IR spectra were recorded in an AVATAR 370 FT-IR Thermo Nicolet spectrometer. MALDI-TOF/TOF mass spectra were recorded on a Bruker UltrafleXtreme mass spectrometer using dithranol as matrix. ESI-QTOF mass spectra were recorded on a 3200 QTRAP LC-MS/MS. The main peaks are expressed as m/z . Steady state UV/Vis spectra were recorded on a Shimadzu UV-VIS-NIR spectrophotometer UV-3600 in quartz cuvettes with a path length of 1 cm. The emission measurements were carried out on Cary Eclipse fluorescence spectrophotometer. Cyclic and Oyster-Young Square wave voltammetry (OYSWV) were performed in a $\mu\text{AUTOLAB}$ Type II

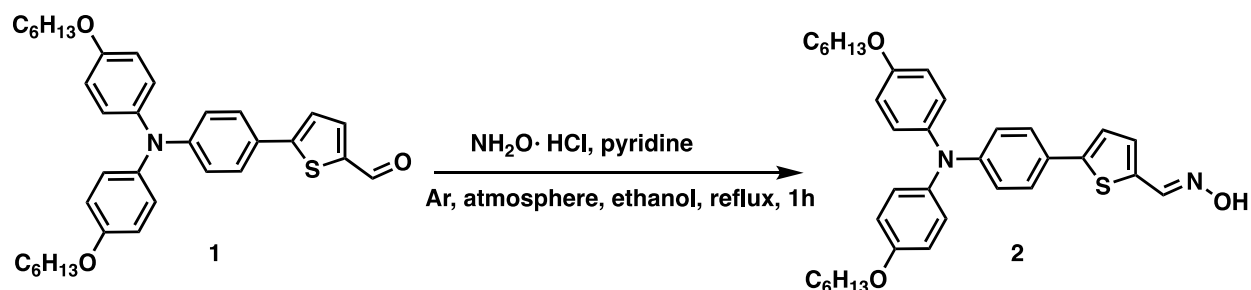
potentiostat, using 0.1M solution of Tetrabutylammonium hexafluorophosphate in 1,2-dichlorobenzene:acetonitrile 4:1 as a solvent. Solutions were deoxygenated by bubbling argon through prior to each measurement which was run under an argon atmosphere. Experiments were carried out in a one-compartment cell equipped with a glassy carbon electrode, a platinum wire counter electrode and an Ag/AgNO₃ as pseudo reference electrode. All Potentials were checked against the ferrocene/ferrocenium couple (Fc/Fc⁺) after each experiment.

Femtosecond Transient Absorption Spectrometer.

Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with 290-2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K. The estimated error in the reported rate constants is $\pm 10\%$.

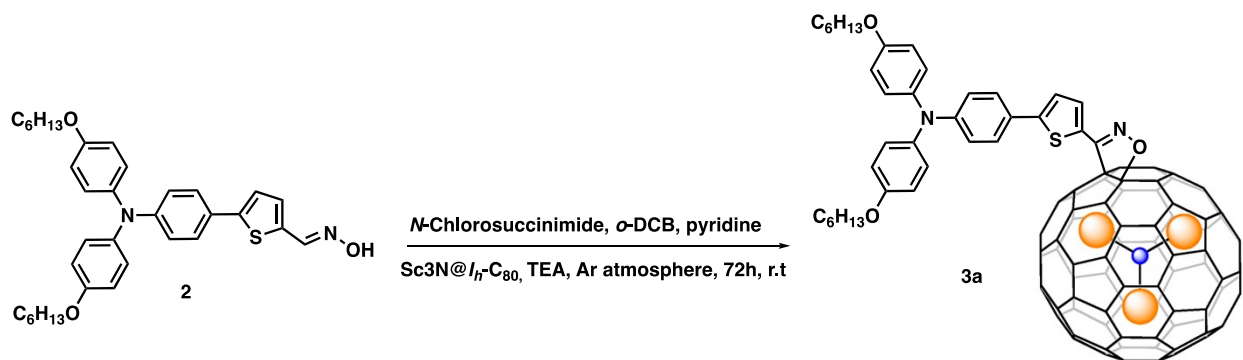
2. Synthesis

Synthesis of Compound 2.



Under argon atmosphere, a stirred solution of **1** (1.01 g, 1.83 mol) pyridine (0.43 g, 5.48 mmol) and hydroxylamine hydrochloride (0.38 g, 5.48 mmol) in ethanol (10 mL) was refluxed for 1 hour. After cooling, the solid formed was filtered and recrystallized in ethanol to obtain a mixture of Z and E isomers of **2** as a yellow solid. (0.81 g, 77%). FT-IR (neat) ν/cm^{-1} : 2929.8, 2886.5, 1603.17, 1505.0, 1441.7, 1330.9, 1232.7, 1156.8, 1023.8, 957.3, 900.3, 824.3, 795.8. $^1\text{H-NMR}$ (DMSO- D_6 , 400 MHz) δ/ppm for **2**: 11.86 (s, 1H). 7.77 (s, 1H), 7.50 (d, 2H, $^3J=8.6\text{Hz}$), 7.39 (d, 1H, $^3J=3.4\text{Hz}$), 7.31 (d, 1H, $^3J=3.4\text{Hz}$), 7.02 (d, 4H, $^3J=8.6\text{Hz}$), 6.89 (d, 4H, $^3J=8.6\text{Hz}$), 6.74 (d, 2H, $^3J=8.6\text{Hz}$), 3.92 (t, 4H, $^3J=6.3\text{Hz}$), 1.69 (m 4H), 1.39 (m, 4H), 1.29 (m, 8H), 0.87 (m, 6H). for **2'**: 11.16 (s, 1H). 8.26 (s, 1H), 7.46 (d, 2H, $^3J=8.6\text{Hz}$), 7.27 (d, 1H, $^3J=3.4\text{Hz}$), 7.25 (d, 1H, $^3J=3.4\text{Hz}$), 7.07 (d, 4H, $^3J=8.6\text{Hz}$), 6.89 (d, 4H, $^3J=8.6\text{Hz}$), 6.74 (d, 2H, $^3J=8.6\text{Hz}$), 3.92 (t, 4H, $^3J=6.3\text{Hz}$), 1.69 (m 4H), 1.39 (m, 4H), 1.29 (m, 8H), 0.87 (m, 6H). $^{13}\text{C-NMR}$ (DMSO- D_6 , 100 MHz) δ/ppm : 155.9, 148.9, 148.8, 148.3, 144.8, 143.9, 140.5, 139.9, 134.7, 132.8, 131.1, 129.3, 127.5, 126.9, 125.4, 125.2, 122.5, 121.6, 119.4, 115.9, 68.1, 31.5, 29.2, 25.7, 22.6, 14.4. MS (ESI-QTOF) m/z : Calculated for $\text{C}_{35}\text{H}_{42}\text{N}_2\text{O}_3\text{S}$: 570.3; found: 570.4 (M^+). UV-Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 390 (4.60).

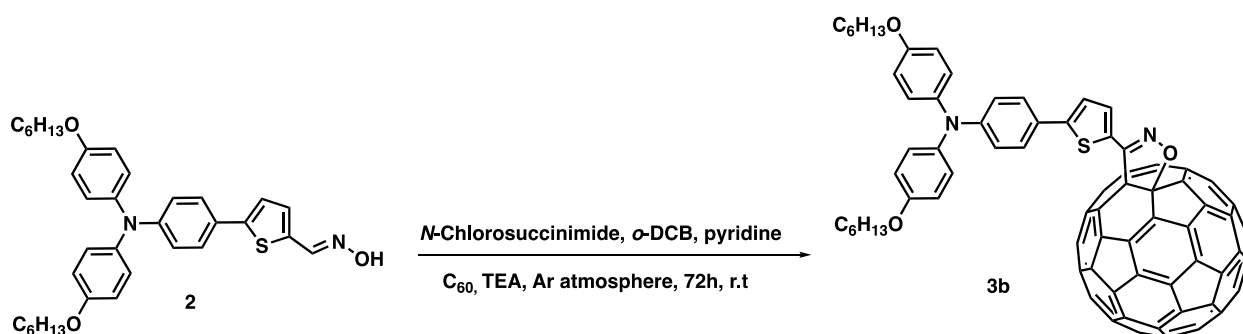
Synthesis of Compound 3a.



Under argon atmosphere, over a stirred solution of oxime **2** (0,1 g, 0.18 mmol) and *N*-Chlorosuccinimide (0,05 g, 0,36 mmol,) in 20 mL of dry 1,2-dichlorobenzene, was added pyridine (30 μl 0,36 mmol) and the reaction mixture was stirred at room temperature for 30 min. Then a degassed solution of fullerene $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ (16 mg, 0,015 mmol) in 100 mL of dry 1,2-dichlorobenzene and triethylamine (30 μl 0,22 mmol) were added. The mixture was stirred at room temperature for 72 hours, then the solvent was evaporated under reduced pressure and the crude obtained was purified by column chromatography (SiO_2) using first CS_2 as eluent to remove unreacted $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ and then a mixture of CS_2 :Toluene 1:1 to elute the final product. The same procedure was repeated two times with unreacted $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$. All the fractions containing **3a** were further purified by preparative HPLC (Buckyprep column, 20IDx250 mm, Toluene 20 mL/min) to obtain **3a** as a black powder. (6 mg, 25%) FT-IR (KBr) ν/cm^{-1} : 3442.7, 2933.0, 2853.8, 2353.6, 2337.7, 1495.5, 1444.9, 1381.5, 1248.6, 1055.4, 811.6, 589.6, 526.6, 469.7. $^1\text{H-NMR}$ (CD_2Cl_2 : CS_2 9:1, 400 MHz) δ/ppm : 7.96 (bs, 1H), 7.45 (d, 2H, $^3J=7.9\text{Hz}$), 7.24 (bs, 1H), 7.06 (d, 4H, $^3J=8.2\text{Hz}$), 6.89 (d, 2H, $^3J=7.9\text{Hz}$), 6.82 (d, 4H, $^3J=8.2\text{Hz}$), 3.93 (t, 4H, $^3J=6.4\text{Hz}$), 1.78, m (4H), 1.47 (m, 4H), 1.36 (m, 8H), 0.93 (t, 6H, $^3J=6.4\text{Hz}$). $^{13}\text{C NMR}$ (175 MHz, CDCl_3 : CS_2 1:1) δ/ppm : 157.8, 156.8, 156.6, 156.3, 155.9, 154.8, 154.6, 153.0, 152.7, 152.2, 150.8, 150.2, 149.7, 149.6, 149.1, 148.9, 148.8, 148.3, 147.9, 147.4, 147.3, 147.1, 146.4, 146.3, 146.0, 145.9, 145.3, 145.1, 144.7, 144.5, 144.4, 144.3, 143.8, 143.7, 143.2, 142.9, 142.5, 142.1, 141.9, 141.8, 141.4,

141.0, 140.9, 140.8, 140.1, 140.0, 139.9, 139.7, 139.5, 139.4, 139.3, 139.2, 139.1, 139.0, 138.9, 138.4, 138.2, 138.1, 138.0, 137.5, 137.3, 137.2, 136.6, 136.5, 135.7, 135.3, 135.2, 134.9, 134.8, 134.1, 133.7, 133.5, 132.7, 132.1, 131.9, 131.2, 130.9, 130.5, 130.4, 130.2, 129.0, 128.6, 128.4, 127.1, 127.0, 126.9, 124.7, 121.9, 121.7, 121.1, 119.9, 119.8, 118.9, 115.4, 114.6, 110.9, 110.3, 97.7, 70.3, 68.2, 31.9, 29.6, 26.1, 23.0, 14.4. MS (MALDI-TOF) m/z : Calculated for $C_{115}H_{40}N_3O_3SSc_3$:1677.15 found: 1677.28 (M)⁻. UV-Vis (CH_2Cl_2) λ_{max}/nm (log ϵ): 413 (4.74).

Synthesis of Compound 3b.



Under argon atmosphere, over a stirred solution of oxime **2** (0.23 g, 0.39 mmol) and *N*-Chlorosuccinimide (0.11 g, 0.8 mmol) in 20 mL of dry dichloromethane, was added pyridine (64 μ l 0.8 mmol) and the reaction mixture was stirred at room temperature for 30 min. Then, the solvent was evaporated and a degassed solution of fullerene C_{60} (0.57 g, 0.8 mmol) in 190 mL of dry toluene and triethylamine (228 μ l 1.59 mmol) were added. The mixture was stirred at room temperature for 1 hour, then the solvent was evaporated under reduced pressure and the crude obtained was purified by column chromatography (SiO_2) using first CS_2 as eluent to remove unreacted C_{60} and then a mixture of CS_2 :Toluene 1:1 to elute the final product. The solid obtained was washed with methanol, ethyl ether and cyclohexane to obtain **3b** as a black powder. (0.14 gr, 27%). FT-IR (KBr) ν/cm^{-1} : 2329.5, 2860.2, 2366.2, 2640.9, 1603.2, 1508.2, 1444.9, 1235.9, 8630.6, 529.61. 1H -NMR (CD_2Cl_2 , 400 MHz) δ/ppm : 8.01 (d, 2H, $^3J=3.9$ Hz), 7.47 (d, 2H, $^3J=8.8$ Hz), 7.23 (d, 2H, $^3J=3.9$ Hz), 7.06 (d, 4H, $^3J=8.9$ Hz), 6.88 (d, 2H, $^3J=8.8$ Hz), 6.83 (d, 4H,

$^3J=8.9\text{Hz}$), 3.92 (t, 4H, $^3J=6.7\text{Hz}$), 1.76, m (4H), 1.45 (m, 4H), 1.33 (m, 8H), 0.90 (t, 6H, $^3J=6.9\text{Hz}$).
 $^{13}\text{C-NMR}$ (CD_2Cl_2 , 100 MHz) δ/ppm : 156.1, 149.5, 148.9, 148.7, 147.8, 147.3, 146.4, 146.3, 146.2, 146.00, 145.9, 145.7, 145.3, 145.2, 145.1, 144.8, 144.7, 144.6, 144.4, 144.1, 142.9, 142.8, 142.5, 142.4, 142.3, 142.3, 142.0, 141.7, 140.3, 140.2, 139.9, 137.0, 136.9, 131.1, 128.1, 127.1, 126.8, 124.4, 122.1, 119.3, 115.3, 68.3, 31.6, 29.3, 25.7, 22.6, 13.8. MS (MALDI-TOF) m/z : Calculated for $\text{C}_{95}\text{H}_{40}\text{N}_2\text{O}_3\text{S}$:1288.27 found:1288.46 (M). UV-Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$): 254 (5.18), 317 (4.78), 407 (4.56).

3. Spectral characterization of synthesized compounds

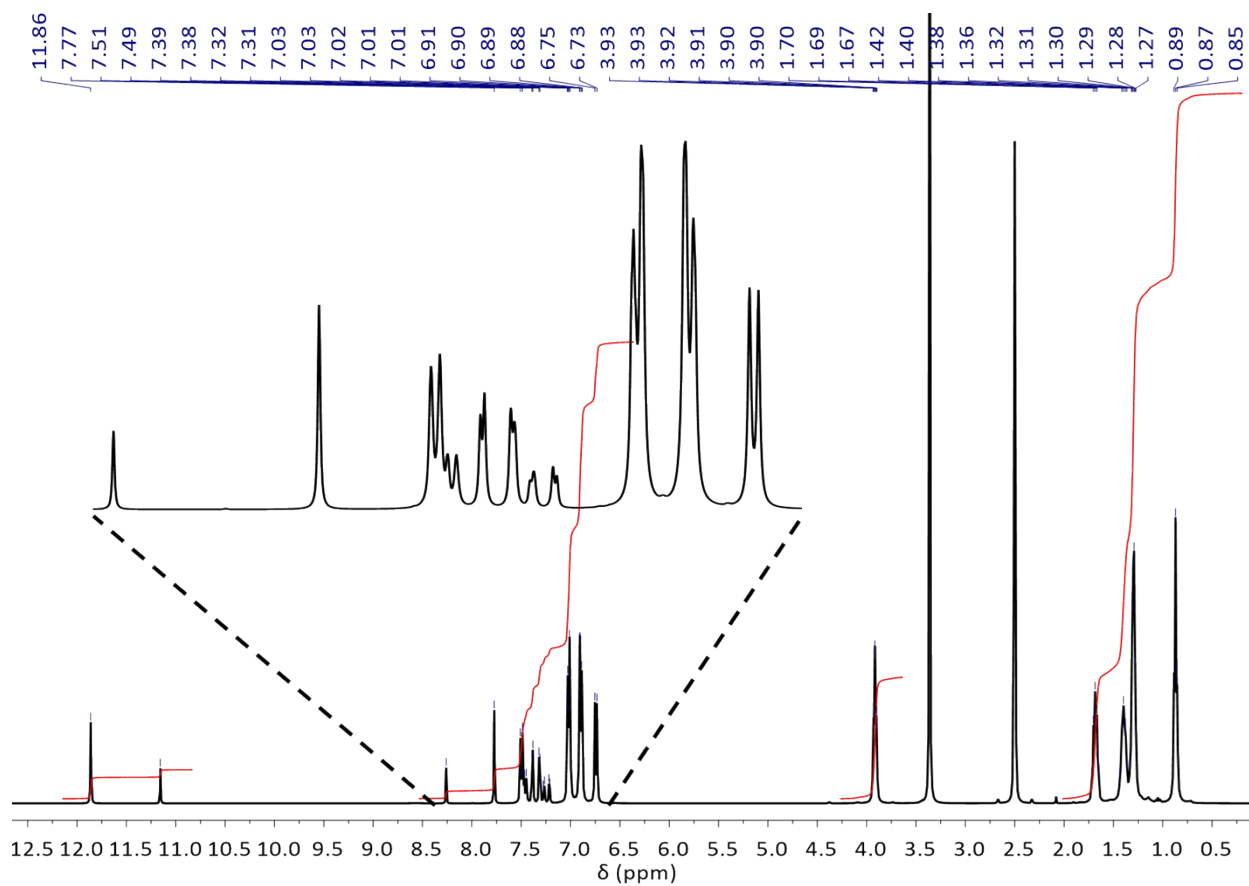


Figure S1. $^1\text{H-NMR}$ (DMSO-D_6 , 400 MHz) spectrum of compound **2**.

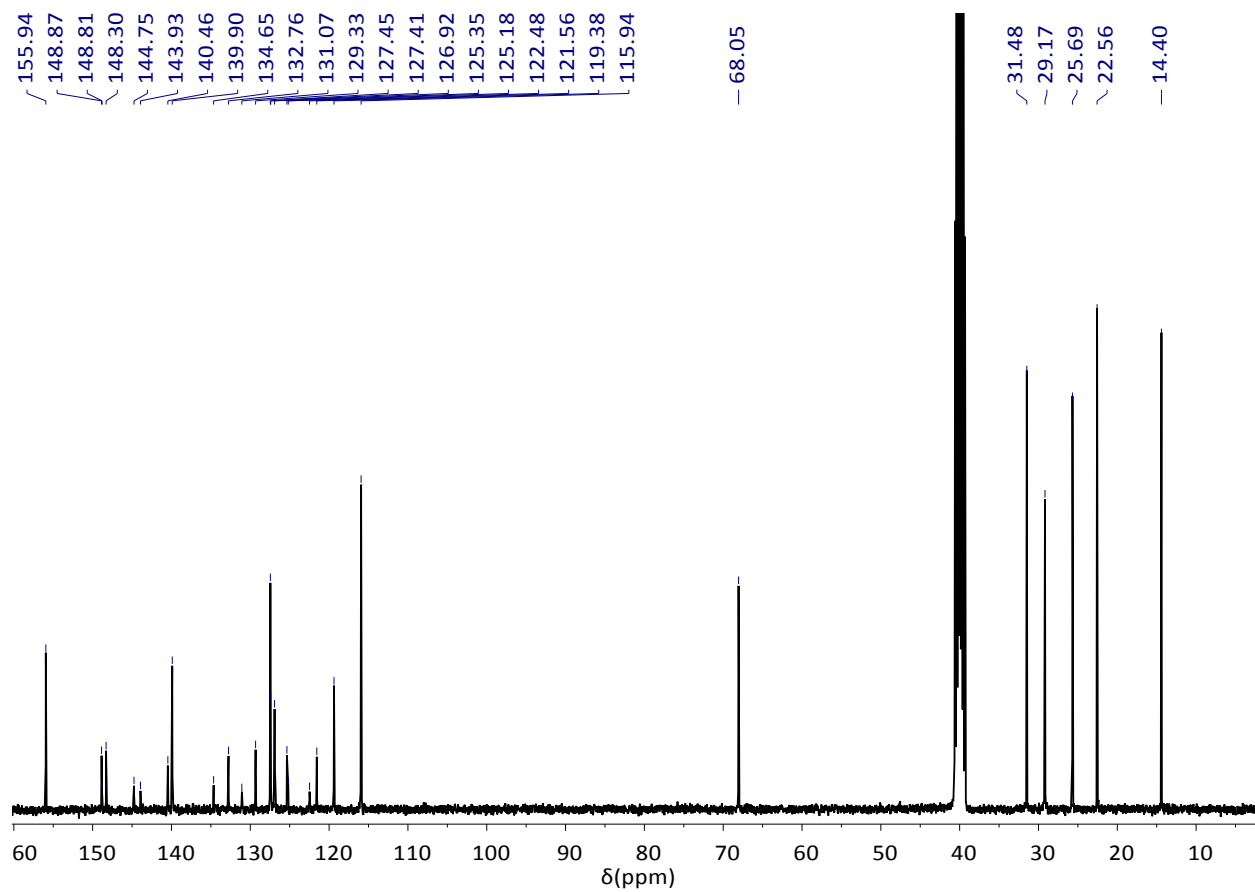


Figure S2. ^{13}C -NMR (DMSO- D_6 , 100 MHz) spectrum of compound 2.

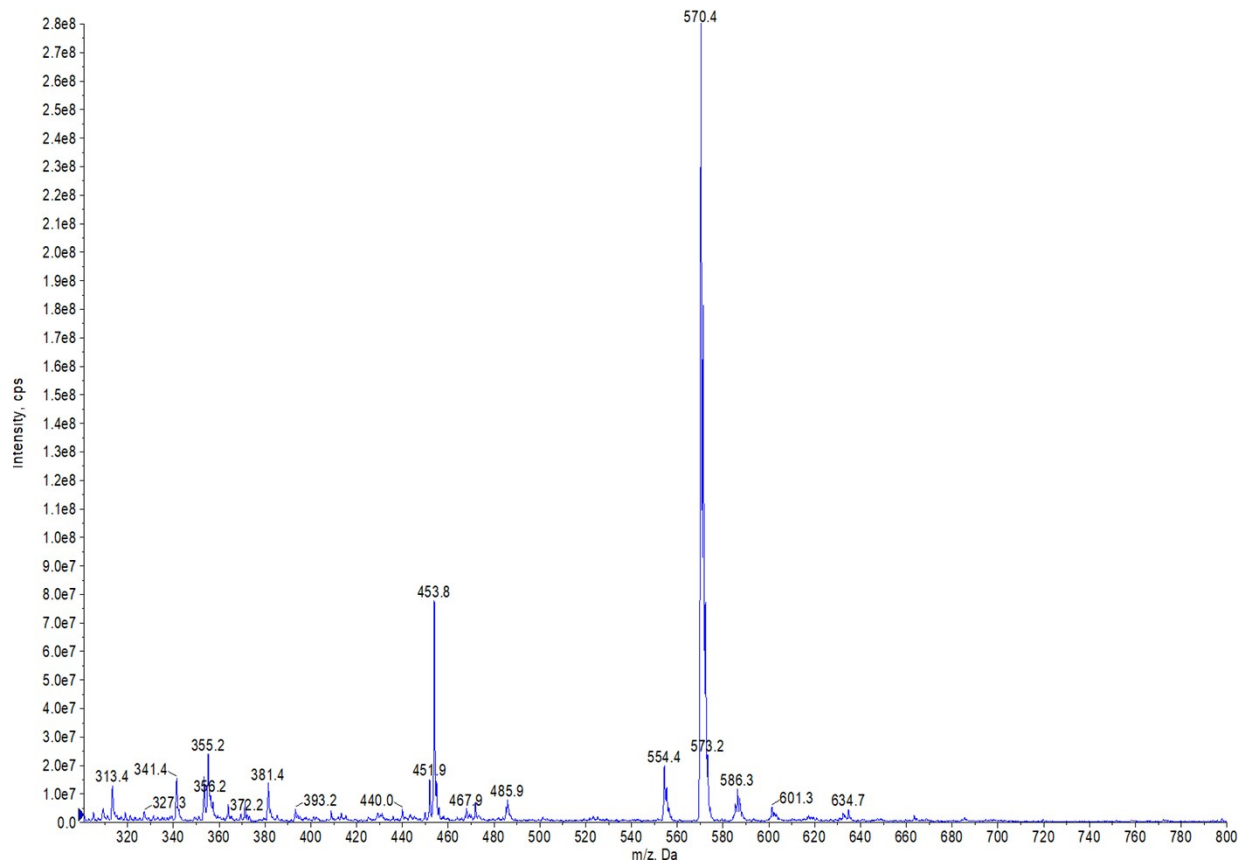


Figure S3. MS (ESI-QTOF) spectrum of compound **2**

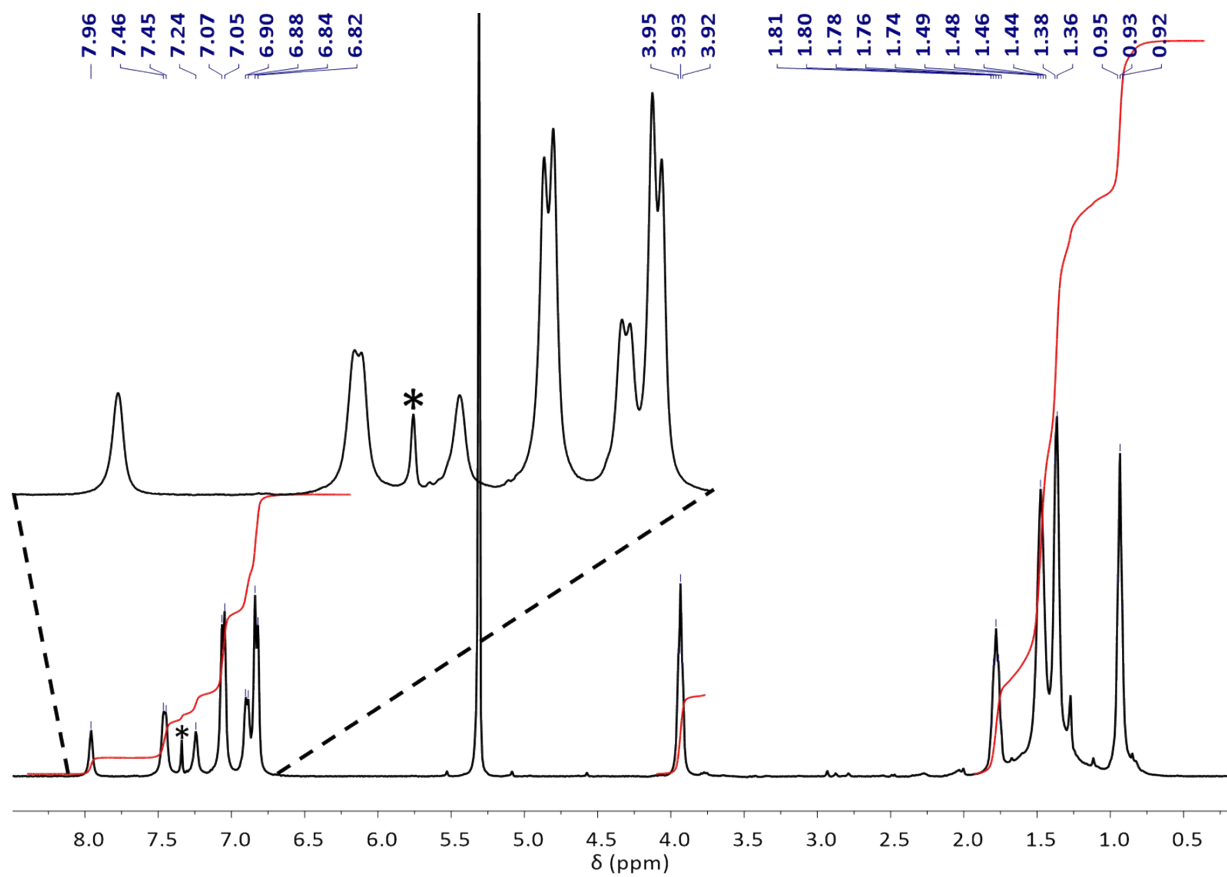


Figure S4. $^1\text{H-NMR}$ ($\text{CD}_2\text{Cl}_2:\text{CS}_2$ 9:1, 400 MHz) spectrum of compound **3a**. (* Denotes solvent impurity)

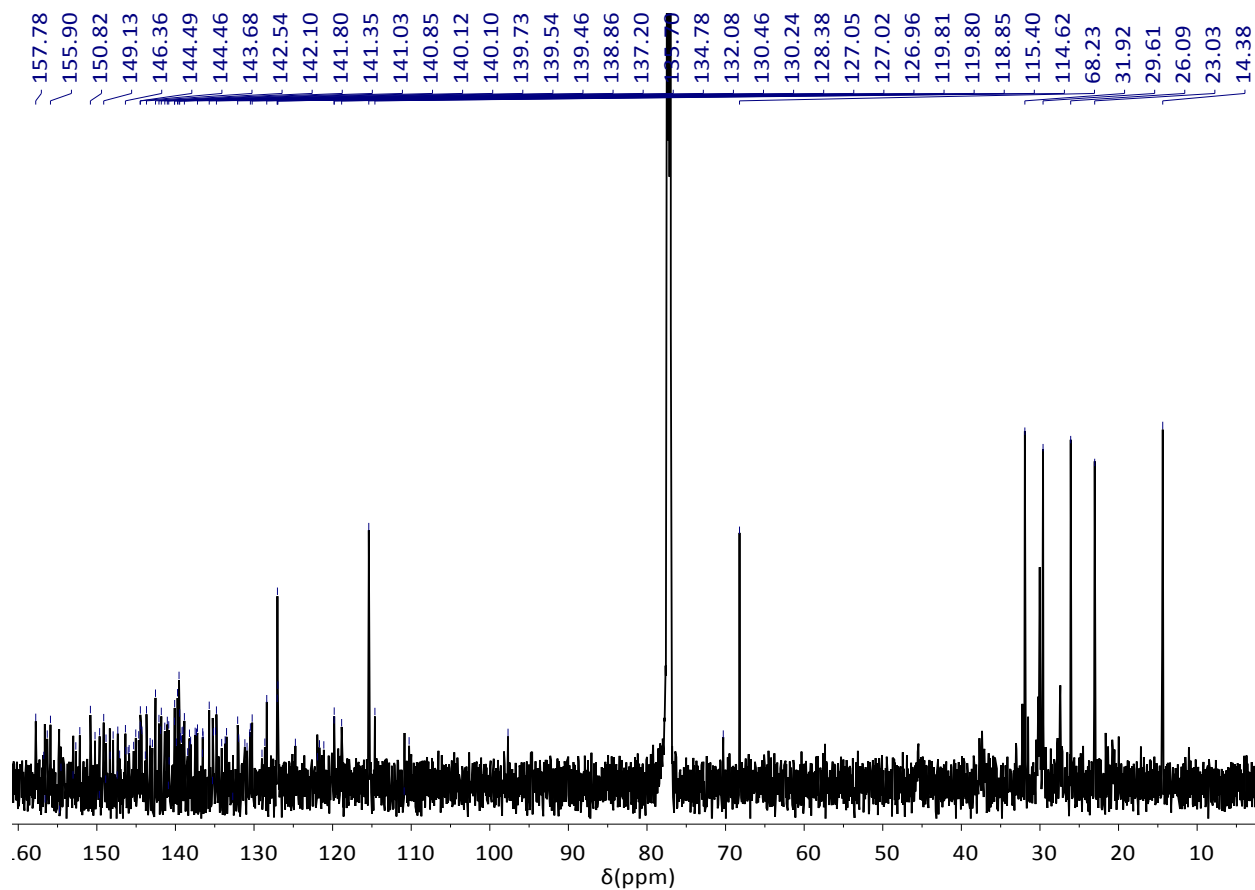


Figure S5. ^{13}C -NMR (CDCl_3 : CS_2 9:1, 175 MHz) spectrum of compound 3a.

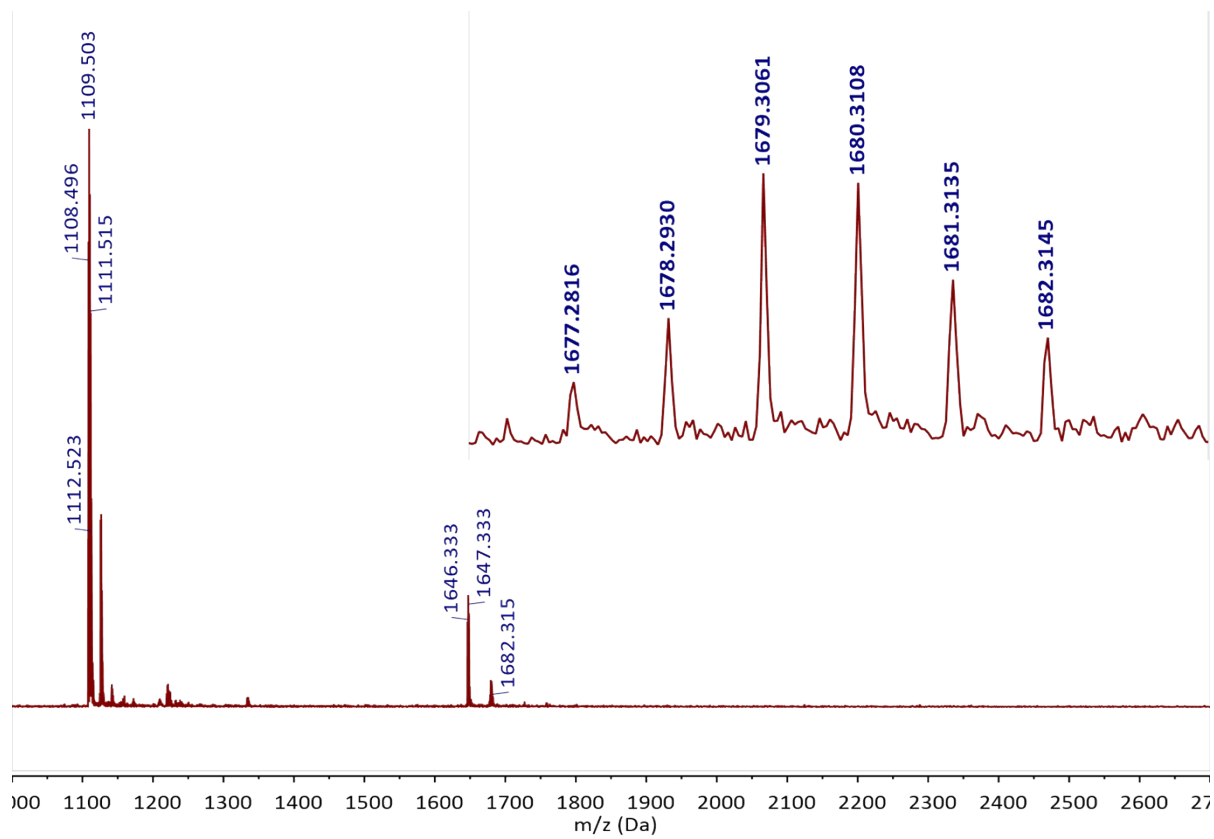


Figure S6. MS (MALDI-TOF) spectrum of compound **3a**.

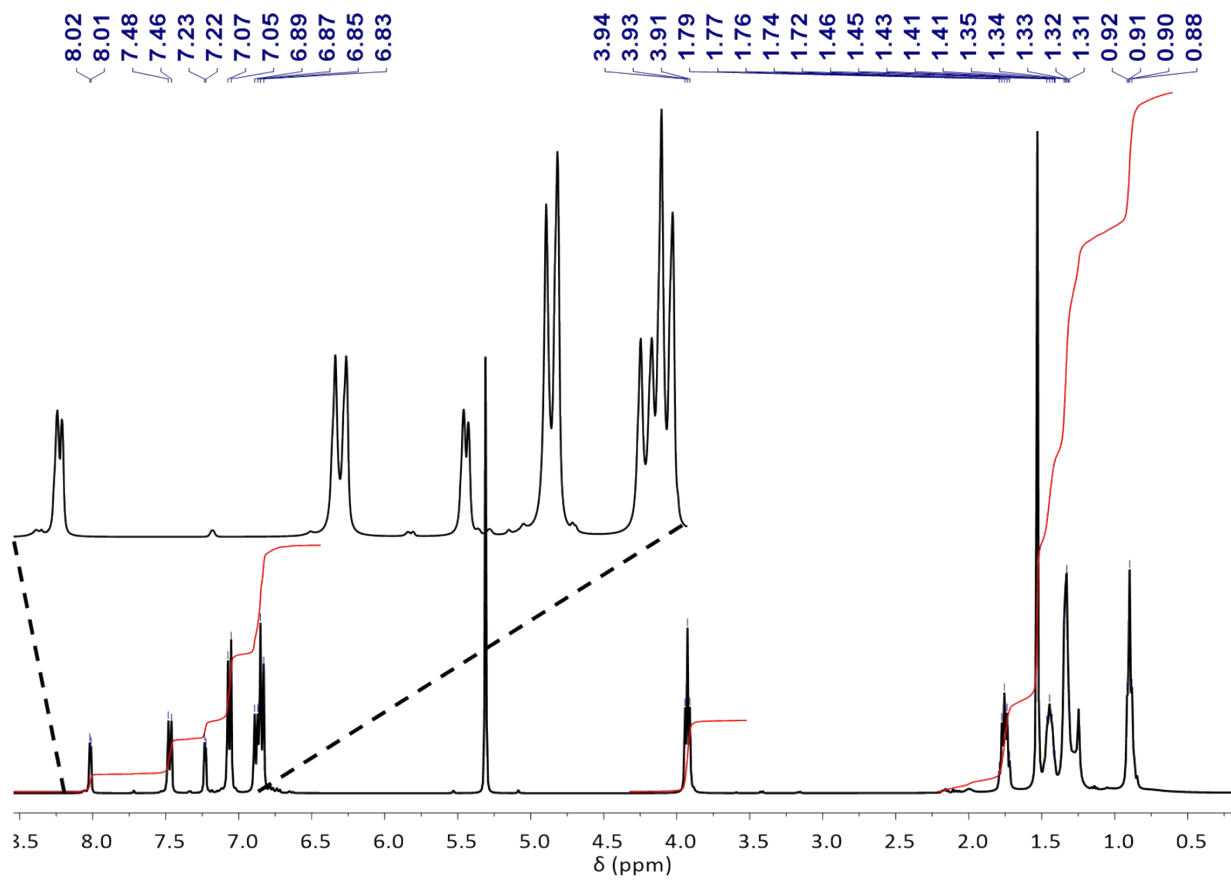


Figure S7. $^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz) spectrum of compound **3b**.

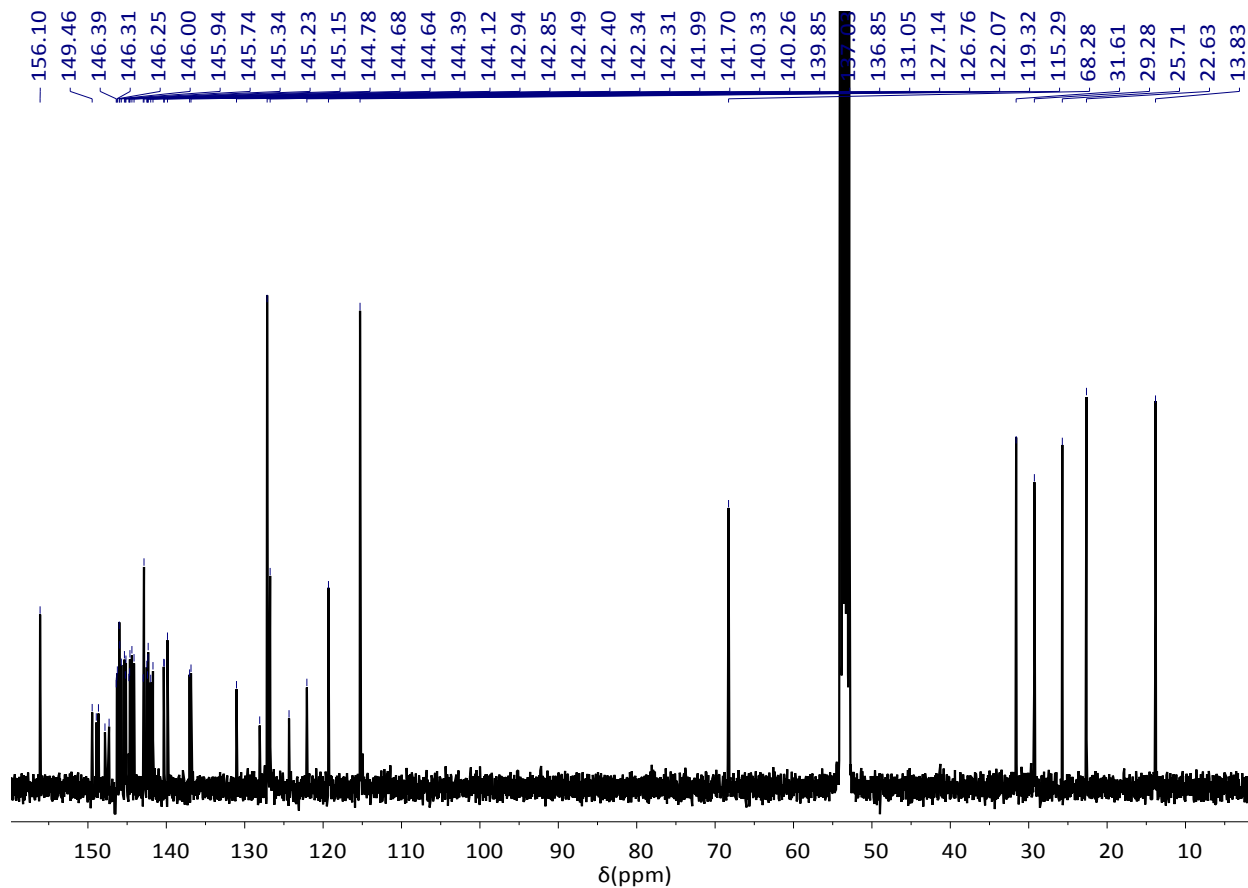


Figure S8. ^{13}C -NMR (CD_2Cl_2 , 100 MHz) spectrum of compound **3b**.

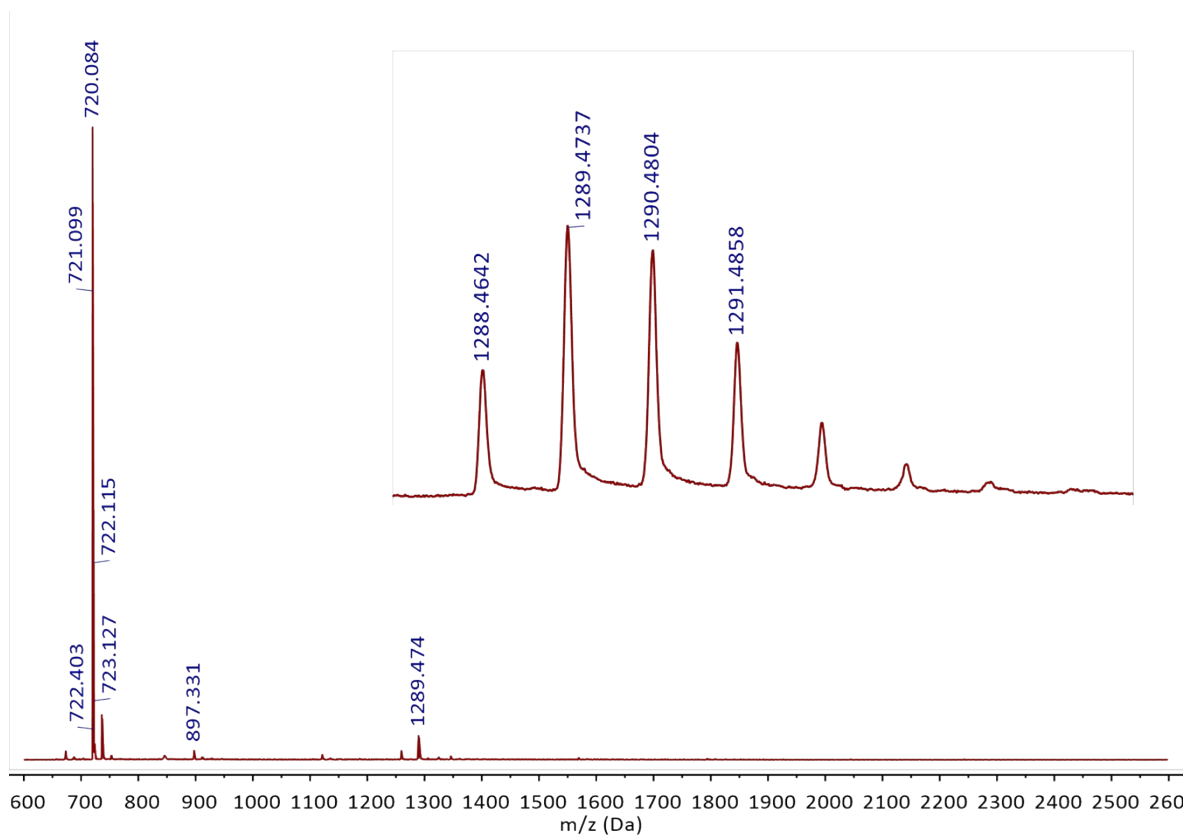


Figure S9. MS (MALDI-TOF) spectrum of compound **3b**

4. HPLC profiles of retrocycloaddition reaction of 3a and 3b.

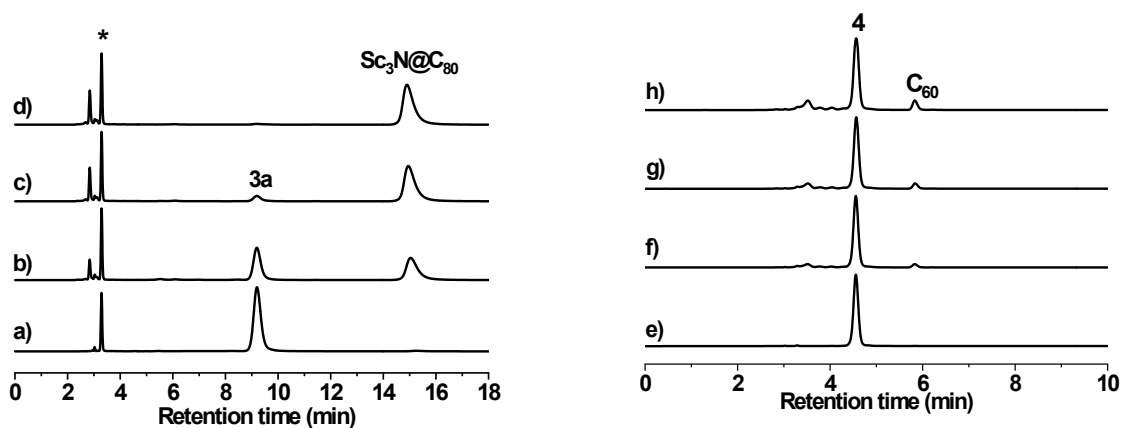


Figure S10. HPLC chromatogram of a solution of **3a** (left panel) and **3b** (right panel) in 1,2-dichlorobenzene upon heating at 170°C at different times a) 0 min, b) 0.5h, c) 1.5h, d) 2.5h, e) 0h, f) 24h, g) 48h, h) 72h. Conditions: Eluent: Toluene 2 mL/min. Column: 2 x Buckyprep 4.6ID x 250 mm. Wavelength of observation 320 nm. * denotes *o*-dichlorobenzene signal.

5. Spectrochemical oxidation of 2

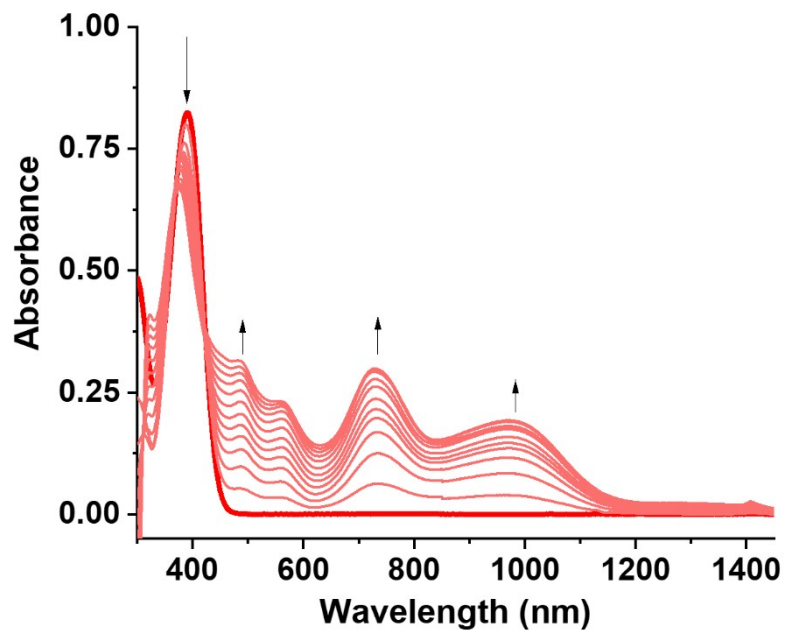


Figure S11. Spectral changes observed during chemical oxidation of **2** (NOBF_4 was used as oxidizing agent) in benzonitrile.

6. Femtosecond Transient Absorption Spectroscopy

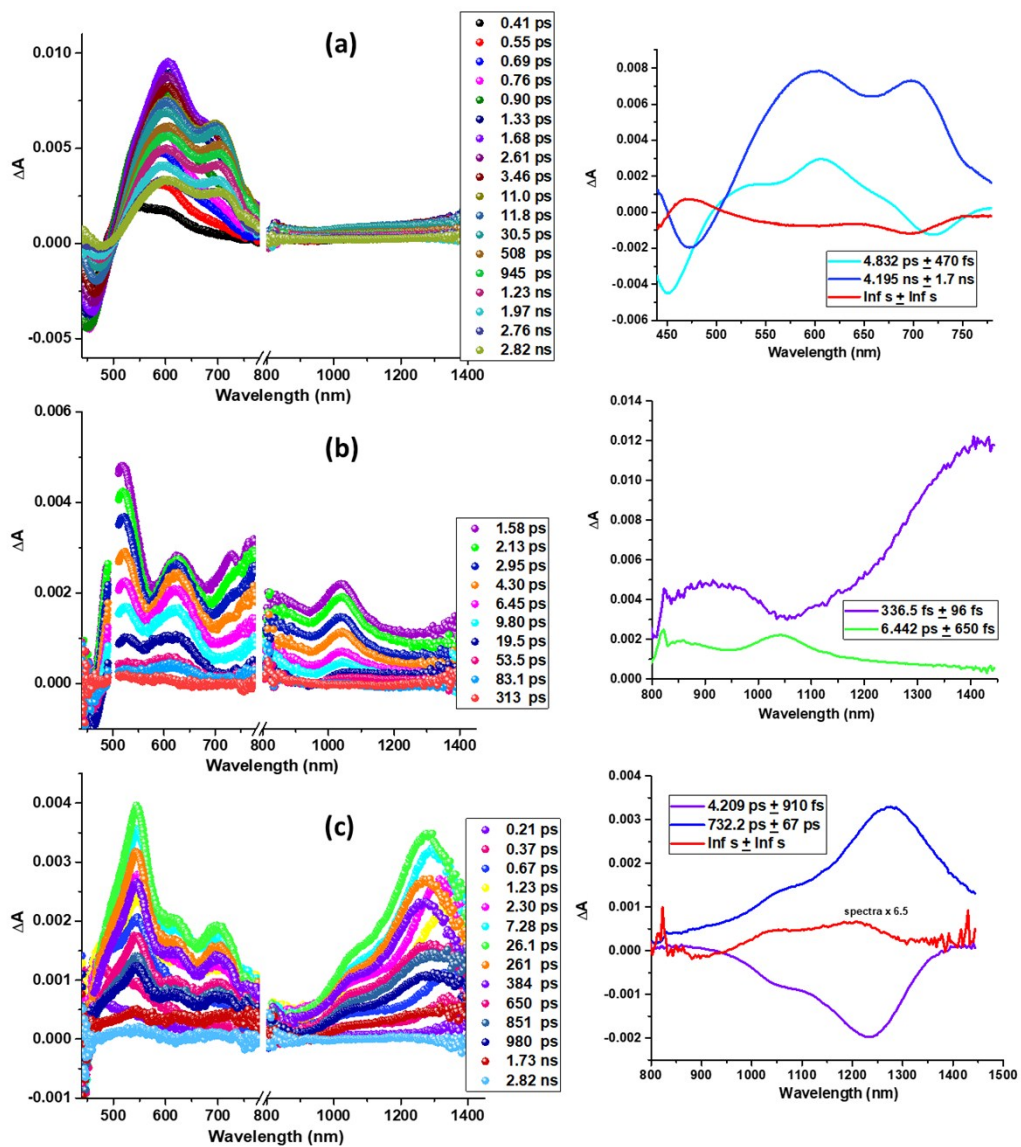


Figure S12. Fs-TA spectra at the indicated delay times of (a) **2** ($\lambda_{\text{ex}} = 390 \text{ nm}$), (b) **3a** ($\lambda_{\text{ex}} = 500 \text{ nm}$), and (c) **3b** ($\lambda_{\text{ex}} = 390 \text{ nm}$) in toluene. The DAS are shown in respective right hand panels.

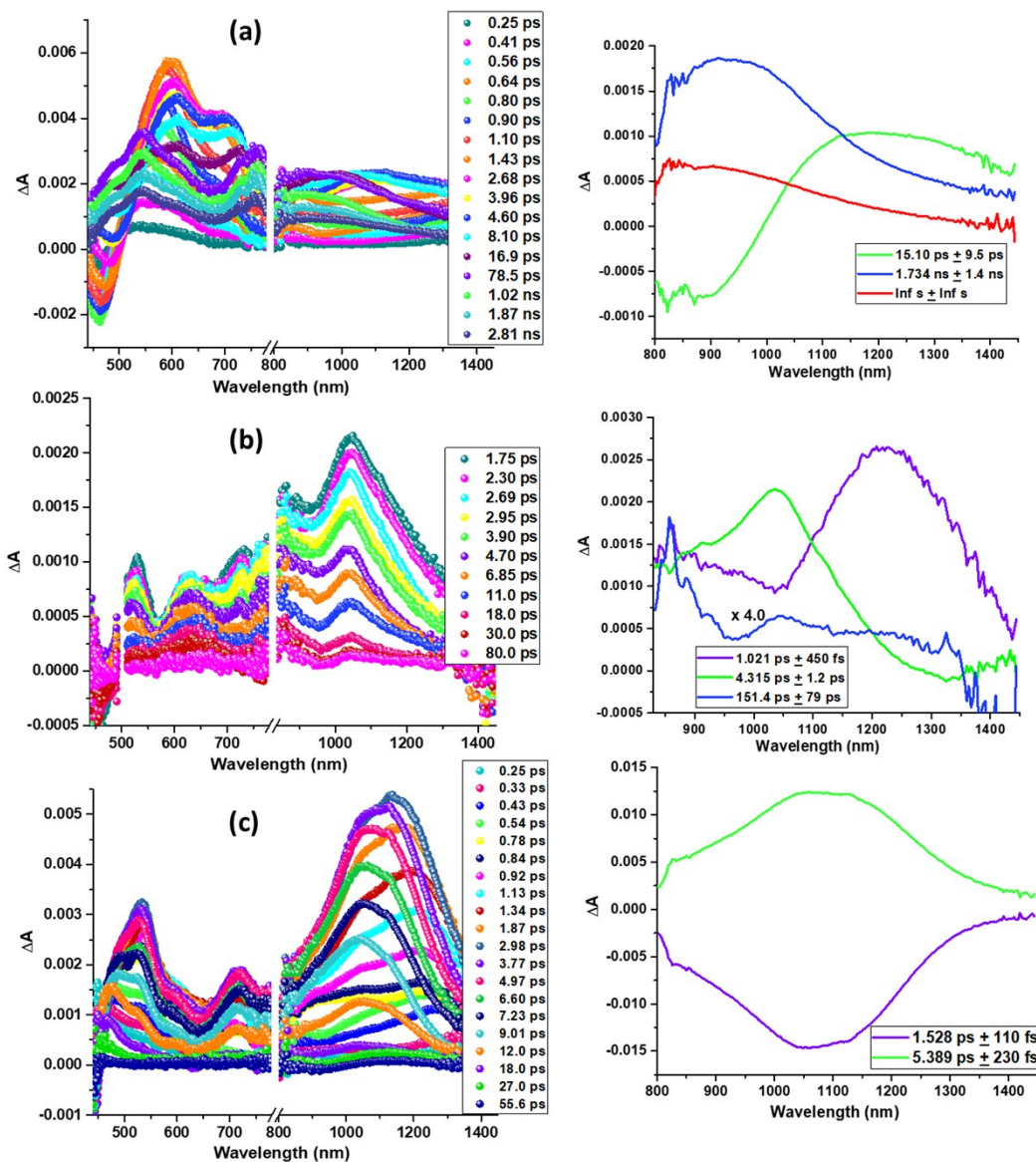


Figure S13. Fs-TA spectra at the indicated delay times of (a) **2** ($\lambda_{\text{ex}} = 390 \text{ nm}$), (b) **3a** ($\lambda_{\text{ex}} = 500 \text{ nm}$), and (c) **3b** ($\lambda_{\text{ex}} = 390 \text{ nm}$) in benzonitrile. The DAS are shown in respective right hand panels.