STA-27, a porous Lewis acidic scandium MOF with an unexpected topology type prepared with 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine

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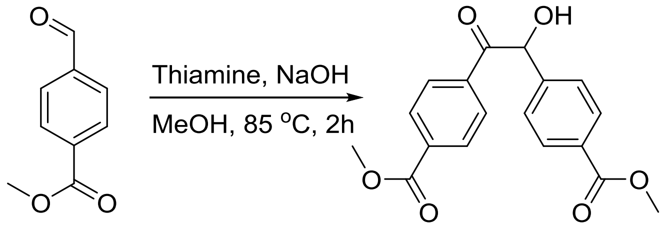
Contents

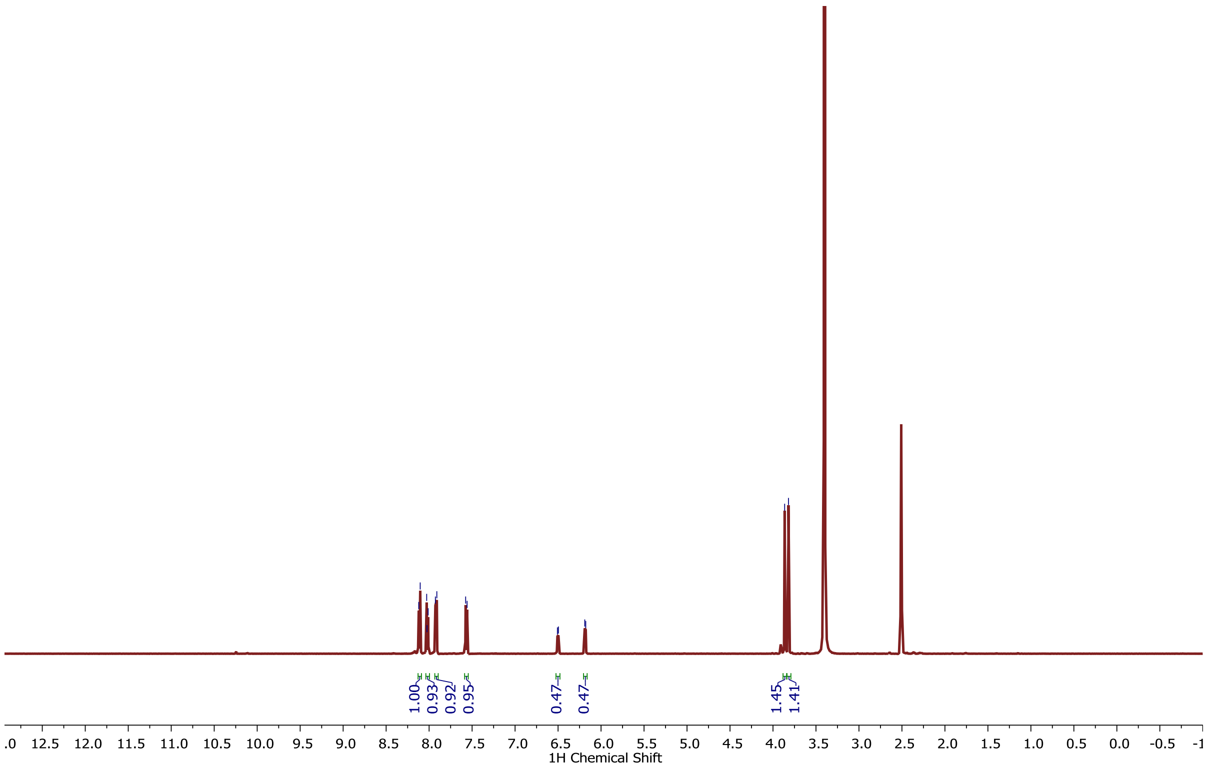
1. Synthesis of 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine (TCPP)

Synthesis of dimethyl-4,4’-(2-hydroxyacetyl)dibenzoate, 1a

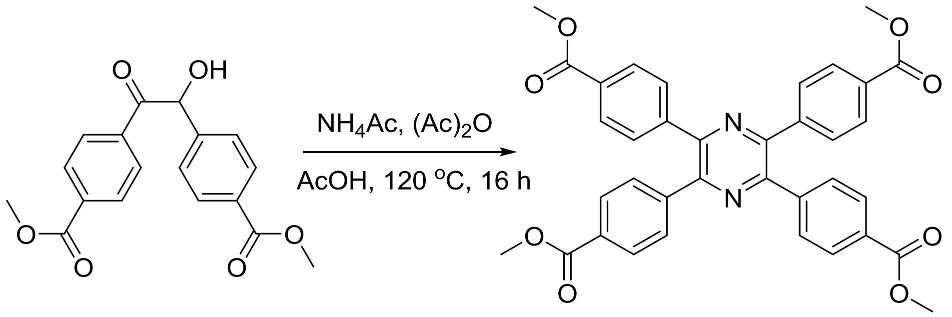


Compound 1a was synthesised by modifying the literature procedure.[S1] 3 g Thiamine hydrochloride (0.89 mmol) was dissolved in a solvent mixture of 25 mL water and methanol (1:3 ratio) and cooled using an ice-bath. To the solution kept at 0 °C, 8.3 mL of 2M NaOH solution was added dropwise for a period of 10 min (solution turns pale yellow). 24.8 g of 4-formylbenzoate (151 mmol) was added to the above solution and the mixture was heated to room temperature and kept at 60 °C for 15 min, before refluxing at 80 °C for 2 h. The resulting suspension was cooled to room temperature and the precipitated yellowish solid was washed multiple times with water, methanol and diethyl ether to obtain pale yellow solid . Yield :22. 7 g, (45%).

^{1}H NMR (400MHz, $CDCl_3$) δ(ppm): 8.11 (d, *J*=8.5Hz, 2H), 8.02 (d, *J*=8.5 Hz, 2H), 7.92(d, *J*= 8.4Hz), 7.57(d, *J*=8.3Hz, 2H), 6.50(d, *J*=6.1Hz), 6.18(d, *J*=6.1Hz), 3.86(s, 3H), 3.82(s, 3H).

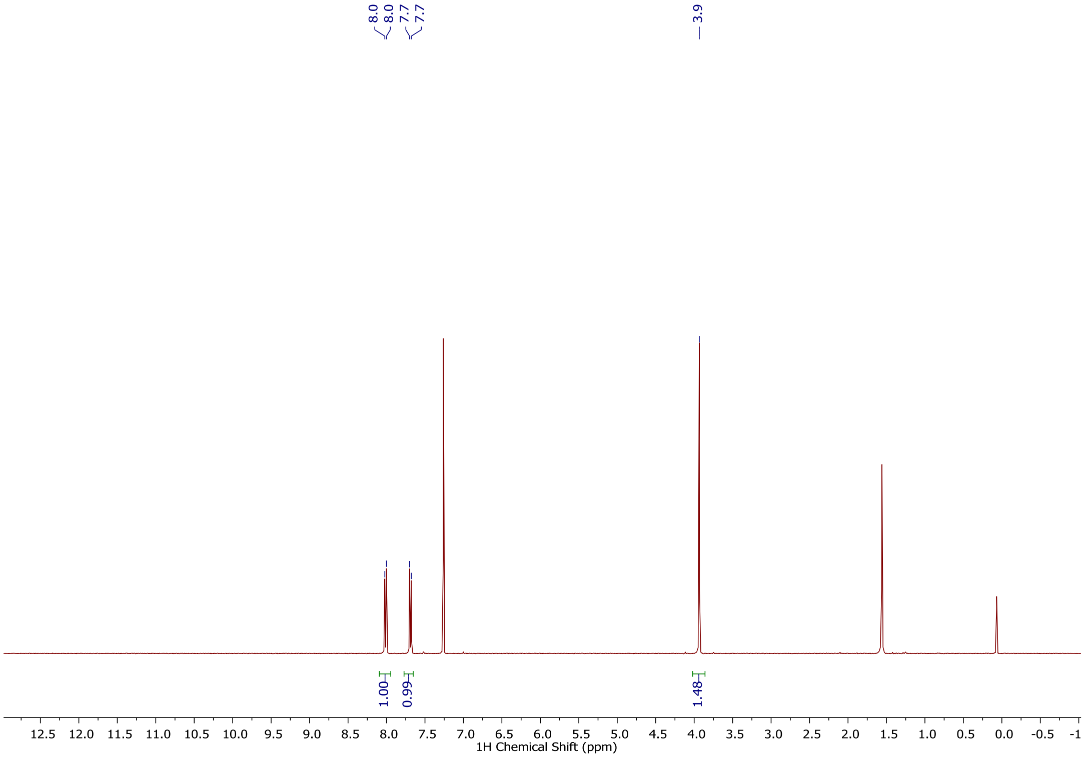


Synthesis of 2,3,5,6-tetrakis(4-methoxycarbonyl)phenyl)pyrazine, 1b

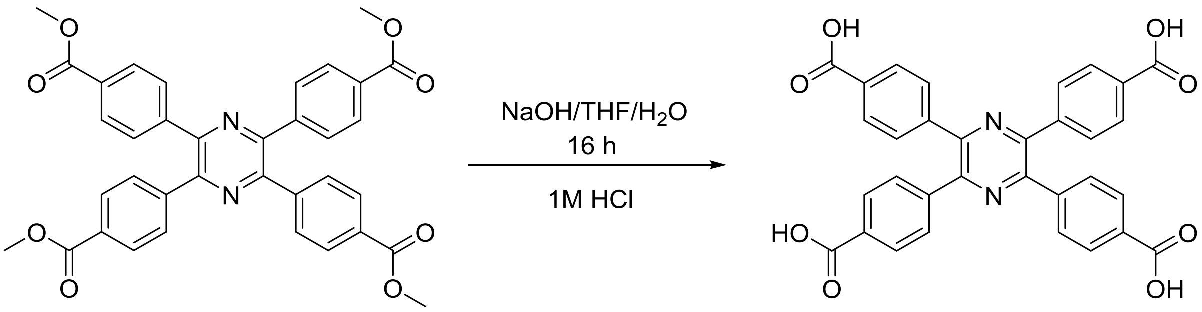


1b was synthesised by following the literature procedure.[S2] 15 g dimethyl-4,4'-(2-hydroxyacetyl)dibenzoate (45.7 mmol)(**1a**) and 10.6 g ammonium acetate (137 mmol) was dissolved in a solvent mixture of 46 mL acetic acid and 6.48 mL of acetic anhydride and stirred at 120 °C for 12 h. The precipitate obtained was washed multiple times with water and diethyl ether to isolate the product as yellow solid. Yield : 4. 73 g (17%).

^{1}H NMR (400MHz, $CDCl_3$) δ(ppm): 8.01(d, *J*=8.6Hz, 8H), 7.69(d, *J*=8.6 Hz, 8H), 3.93(s, 12H).

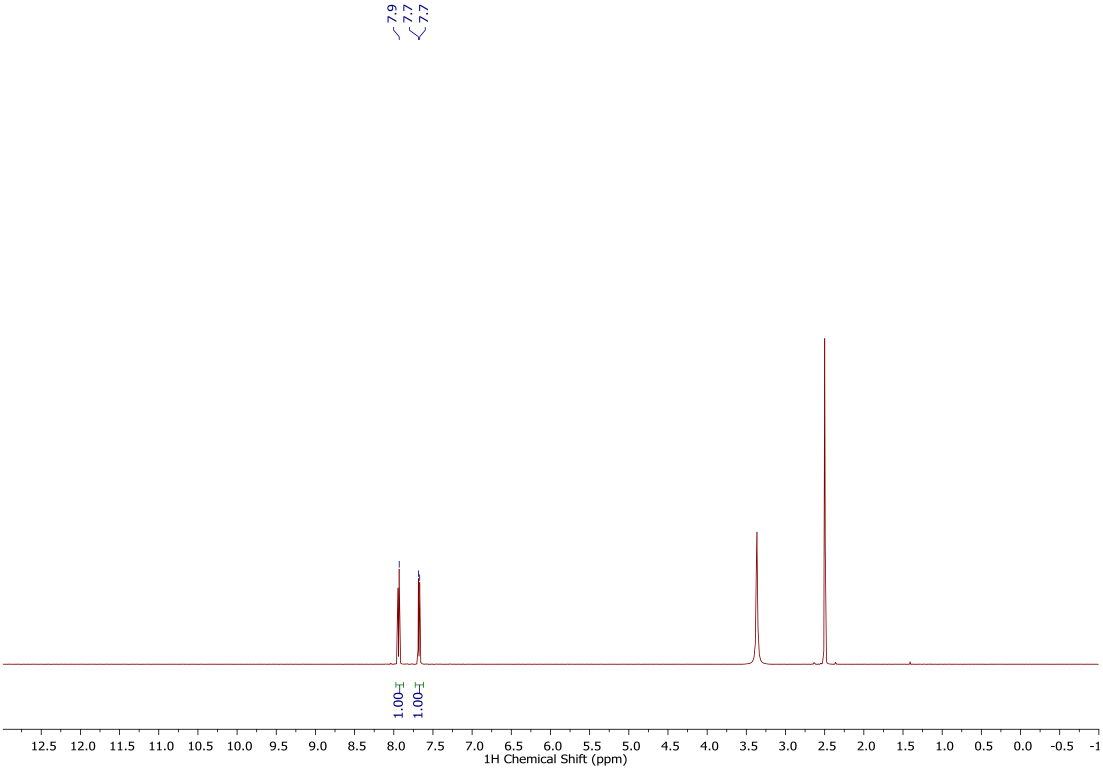


Synthesis of 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine (H_4TCPP)



The product was synthesised following the literature procedure reported.[S2] 4.73 g tetramethyl-4,4’,4’’,4’’’-(pyrazine-2,3,5,6-tetrayl)tetrabenzoate (7.67 mmol) was added to a solvent mixture of 140 mL THF and H_2O in 1:1 ratio with 3.68 g NaOH. The mixture was refluxed for 12 h at 90 °C and the solvent was reduced under vacuum. The solution was then acidified with 1M HCl to reach pH 4-5. The off-white precipitate thus obtained was washed multiple times with water and dried at 100 °C overnight. Yield : 3.82 g (89%). Data in accordance with the literature.

^{1}H NMR (400MHz, DMSO-*d*$_6$) δ(ppm): 7.93(d, *J*=8.5Hz, 8H), 7.68(d, *J*=8.5 Hz, 8H).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1H Chemical Shift (ppm)

2. Characterisation

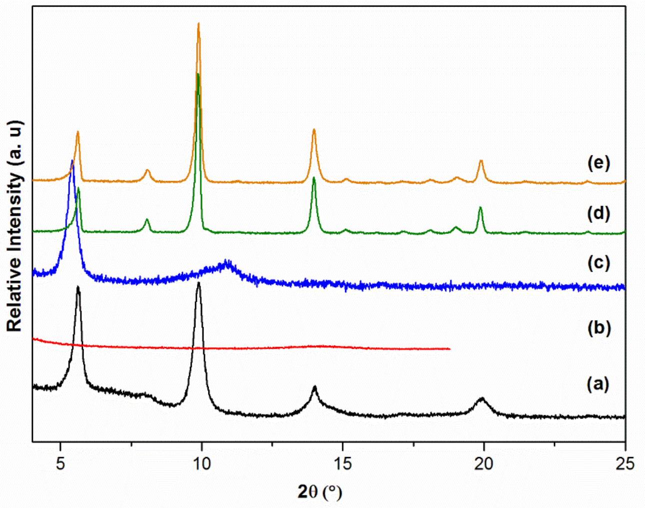


Figure S1: PXRD patterns of $Al_2(OH)_2$TCPP synthesis attempts: a) In equivolume DMF - 3.5 M aq. HNO_3 - AcCN at 150 °C for 30 h using $Al(NO_3)_3.9H_2O$ and H_4TCPP as precursors b) In DMF at 150 °C for 30 h using $Al(NO_3)_3.9H_2O$ and H_4TCPP as precursors, c) in equivolume DMF and AcCN at 150 °C for 30 h using $Al(NO_3)_3.9H_2O$ and H_4TCPP as precursors, d) In equivolume DMF and 3.5 M aq. HNO_3 at 150 °C for 30 h using $Al(NO_3)_3.9H_2O$ and H_4TCPP as precursors and e) In equivolume DMF and 3.5 M Aq. HNO_3 at 150 °C for 30 h using $AlCl_3.6H_2O$ and H_4TCPP as precursors.

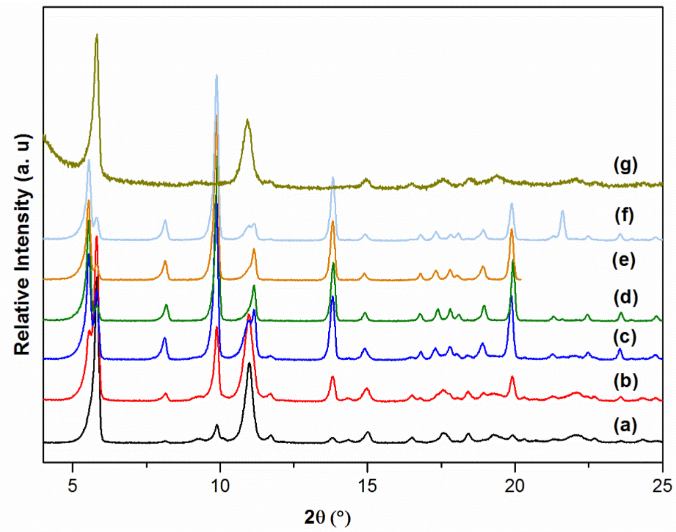


Figure S2: PXRD patterns of $Ga_2(OH)_2$TCPP synthesis attempts in equivolume DMF and 3.5 M aq. HNO_3 using $Ga(NO_3)_3.6H_2O$ and H_4TCPP as precursors: a) at 150 °C for 30 h, b) at 150 °C for 16 h, c) at 150 °C for 35 h, d) at 150 °C for 40 h, e) at 150 °C for 48 h, f) at 150 °C for 72 h and e) at 150 °C for 96 h.

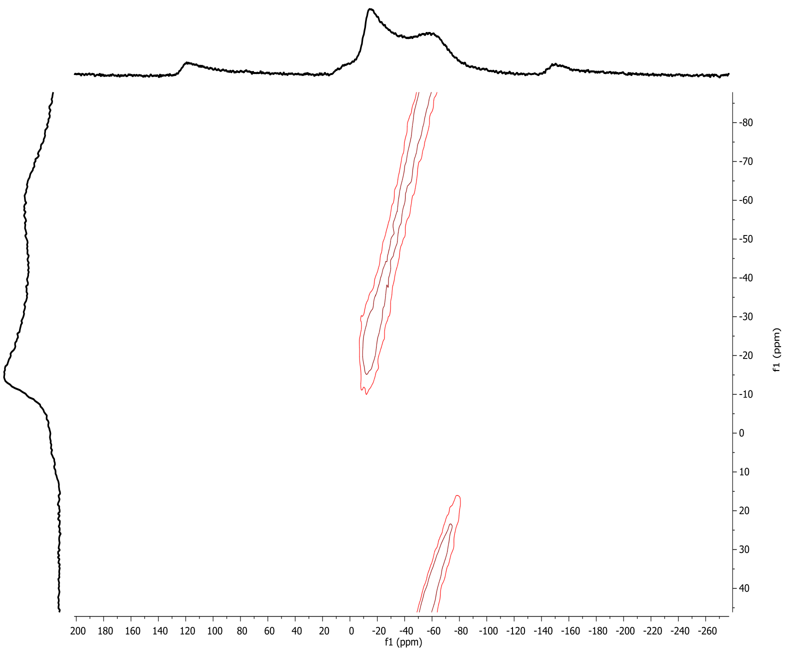


Figure S3: ^{27}Al MQ MAS NMR of $Al_2(OH)_2$TCPP.

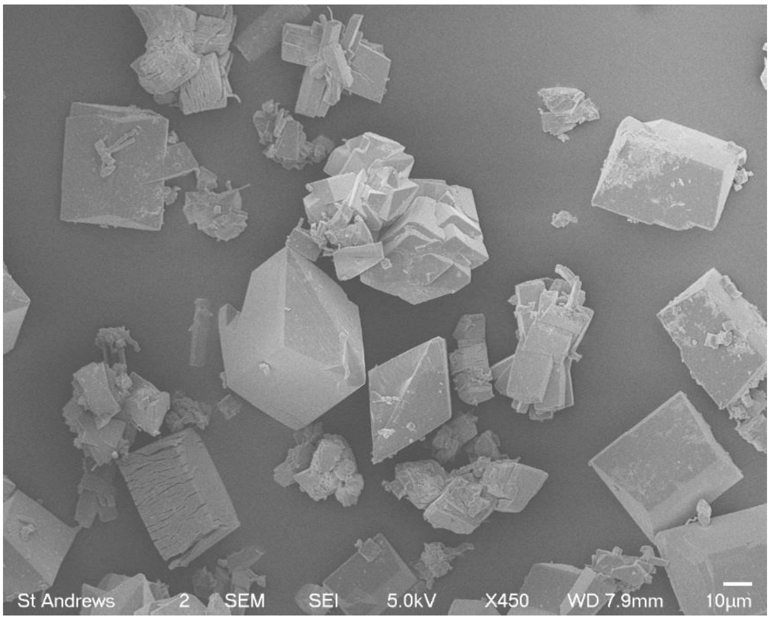


Figure S4: SEM images of $Ga_2(OH)_2$TCPP.

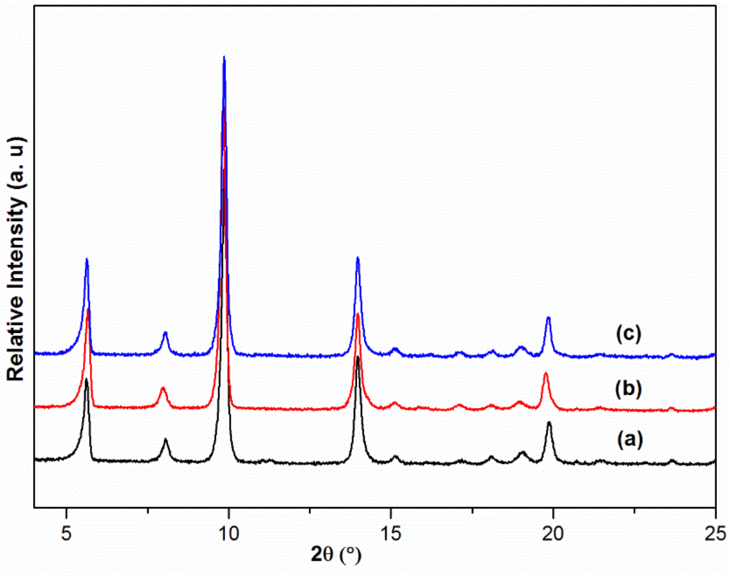
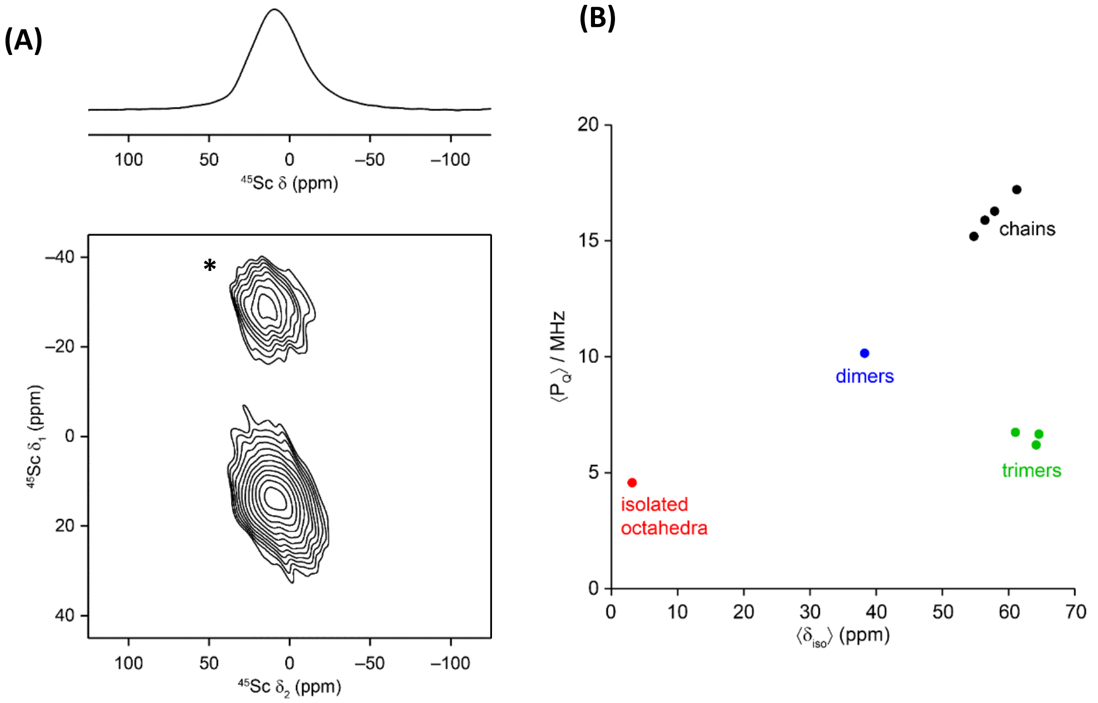


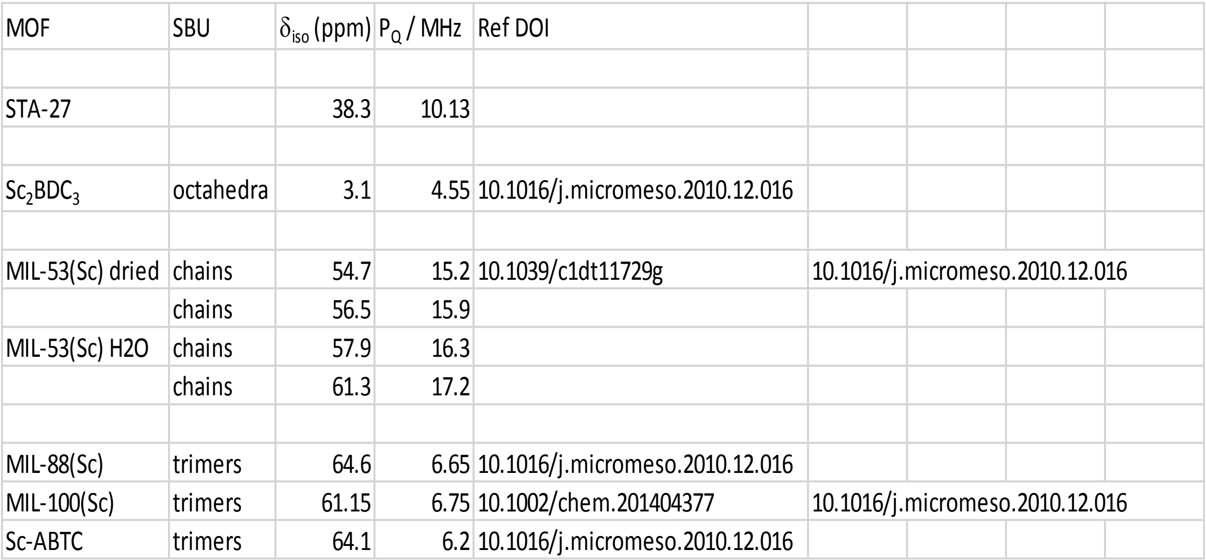
Figure S5: PXRD patterns of (a) as-synthesised $Al_2(OH)_2$TCPP compared with (b) $Al_2(OH)_2$TCPP after N_2 adsorption studies and (c) $Al_2(OH)_2$TCPP after VT-CO_2 adsorption studies.

Table ST1: Optimising synthesis conditions for STA-27, $Sc_2(O)(H_2O)_2$TCPP. In each case 0.895 mmol $ScCl_3.6H_20$ and 0.074 mml H_4TCPP are used as reagents (M:L = 12:1)

Metal Source	DMF (mL)	HNO_3 (3.5 M) (mL)	CH_3CN (mL)	Temperature (°C)	Time (h)	Phase Purity
$ScCl_3.6H_2O$	7.5	7.5	-	150	30	Unknown Impurity
$ScCl_3.6H_2O$	7.5	7.5	7.5	150	16	Microcrystalline STA-27
$ScCl_3.6H_2O$	7.5	7.5	7.5	150	30	Single crystals of STA-27



(C)



MOF	SBU	δ_{iso} (ppm)	P_Q / MHz	Ref DOI				
STA-27		38.3	10.13					
Sc_2BDC_3	octahedra	3.1	4.55	10.1016/j.micromeso.2010.12.016				
MIL-53(Sc) dried	chains	54.7	15.2	10.1039/c1dt11729g	10.1016/j.micromeso.2010.12.016			
	chains	56.5	15.9					
MIL-53(Sc) H2O	chains	57.9	16.3					
	chains	61.3	17.2					
MIL-88(Sc)	trimers	64.6	6.65	10.1016/j.micromeso.2010.12.016				
MIL-100(Sc)	trimers	61.15	6.75	10.1002/chem.201404377	10.1016/j.micromeso.2010.12.016			
Sc-ABTC	trimers	64.1	6.2	10.1016/j.micromeso.2010.12.016				

Figure S6: ^{45}Sc MAS NMR and MQ MAS NMR spectra of STA-27. (B) Plot of mean ^{47}Sc isotropic shift $<\delta_{iso}>$ and quadrupolar product $<P_Q>$ for a series of Sc-containing MOFs with different Sc coordination motifs.[S3] Red circle = isolated ScO_6 octahedra (Sc_2BDC_3 and derivatives), black circles = chains of ScO_6 octahedra (MIL-53 and derivatives) and green circles = trimers of ScO_6 octahedra (MIL-88, MIL-100 and Sc-ABTC, ABTC = 3,3´,5,5´-azobenzenetetracarboxylate). Dimer based chains of STA-27 is shown by blue circle. Reference points were obtained from multiple-quantum (MQ) MAS experiments carried out at 20.0 T, whereas spectra for STA-27 were recorded at 9.4 T as described in the experimental details. Asterisk denotes spinning side band.

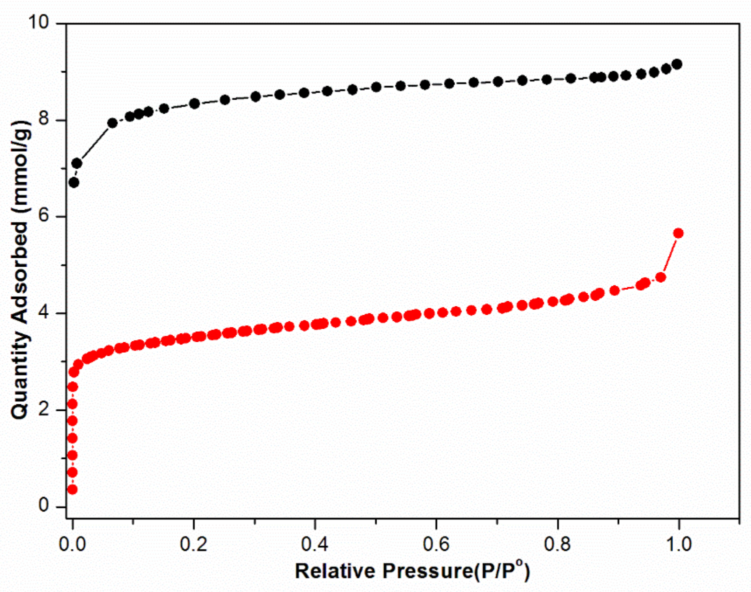


Figure S7: N_2 adsorption isotherm at -196 °C for STA-27 (black) and STA-27-*C* (red).

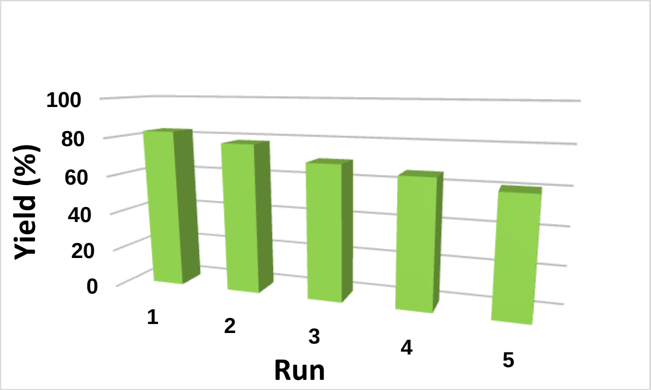


Figure S8: Plots of yields (%) of imine at different runs in the recycle experiments of STA-27 for imine condensation reaction between 4'-fluoroacetophenone and benzylamine.

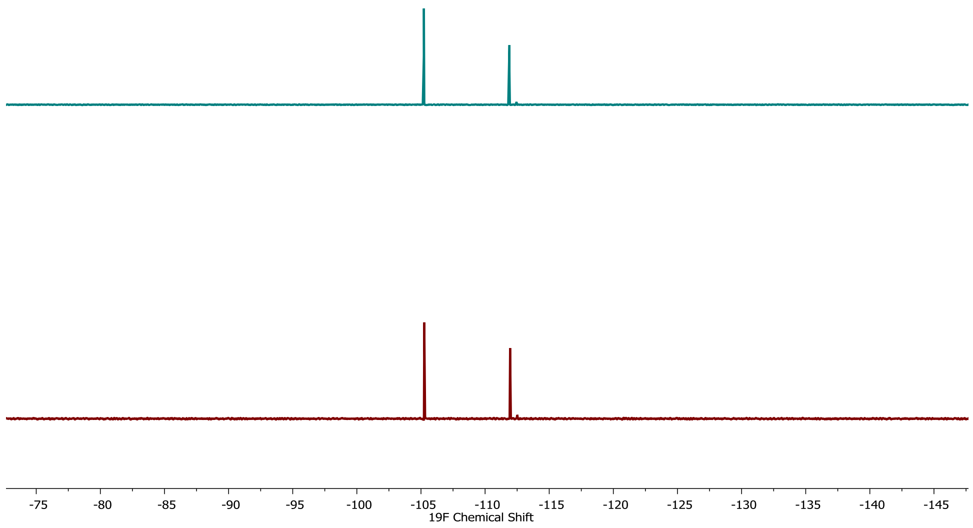


Figure S9: $^{19}F\{^{1}H\}$ NMR spectra of imine condensation between 4'-fluoroacetophenone and benzylamine catalysed by STA-27 at 90 °C in toluene under inert atmosphere stopped after 5h (below) and $^{19}F\{^{1}H\}$ NMR spectra of the filtrate after subsequent heating at 90 °C for 12 h in toluene under inert atmosphere after the removal of catalyst by hot filtration (above). No further conversion was observed once the catalyst is removed.

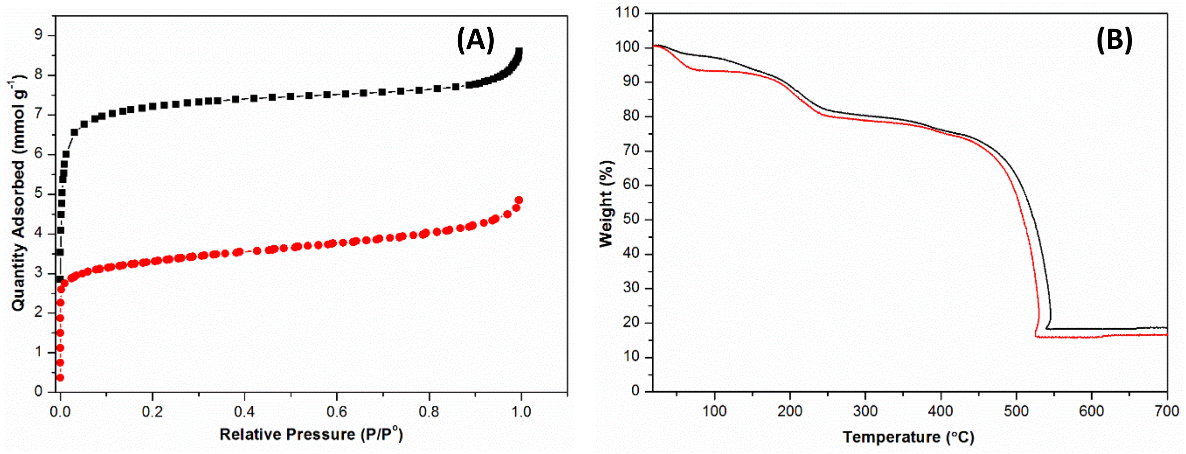


Figure S10: (A) N_2 adsorption of the STA-27 recovered after carbonyl ene reaction *via* the removal of reaction solution without acetone wash (black) and N_2 adsorption of the STA-27 recovered after catalysis after overnight soaking and multiple washes with acetone(red) and (B) TGA of STA-27 recovered after carbonyl ene reaction *via* the removal of reaction solution without acetone wash (black) and TGA of STA-27 recovered after catalysis after overnight soaking and multiple washes with acetone (red).

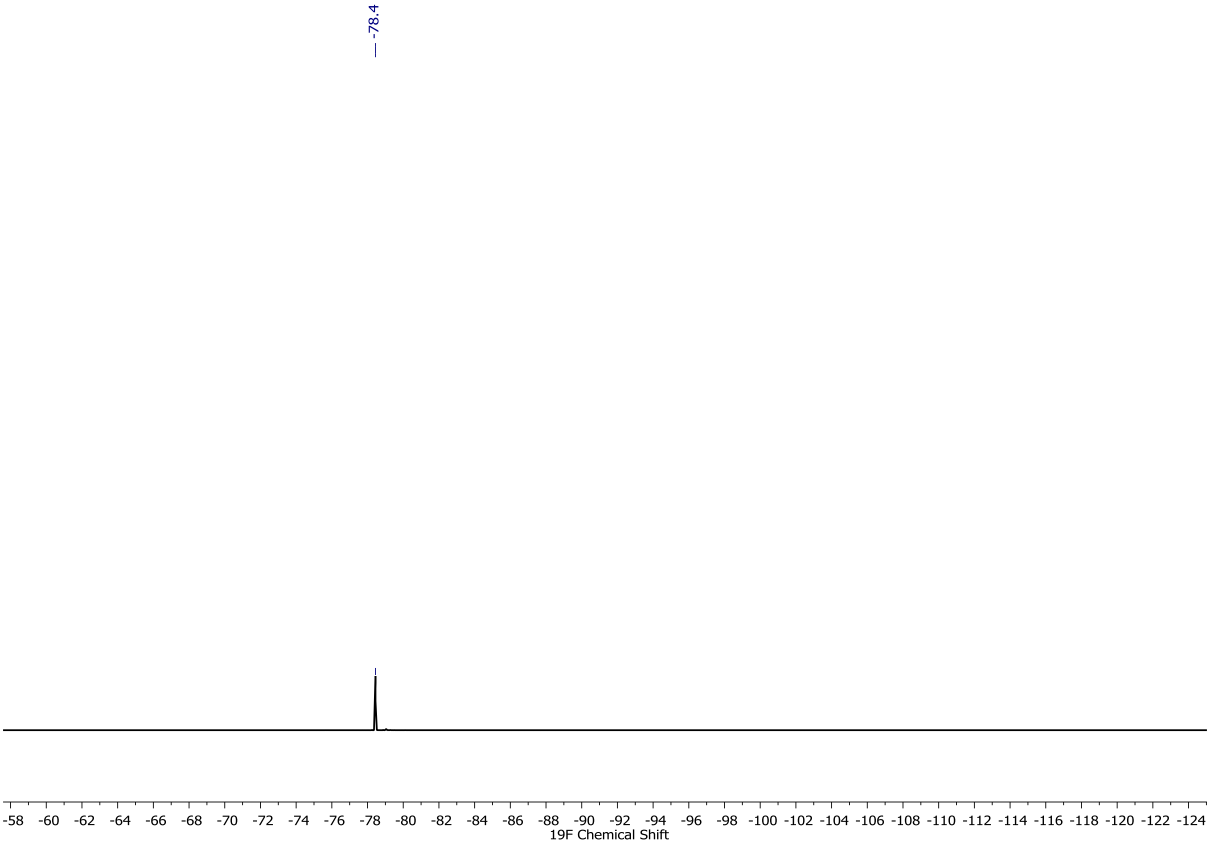
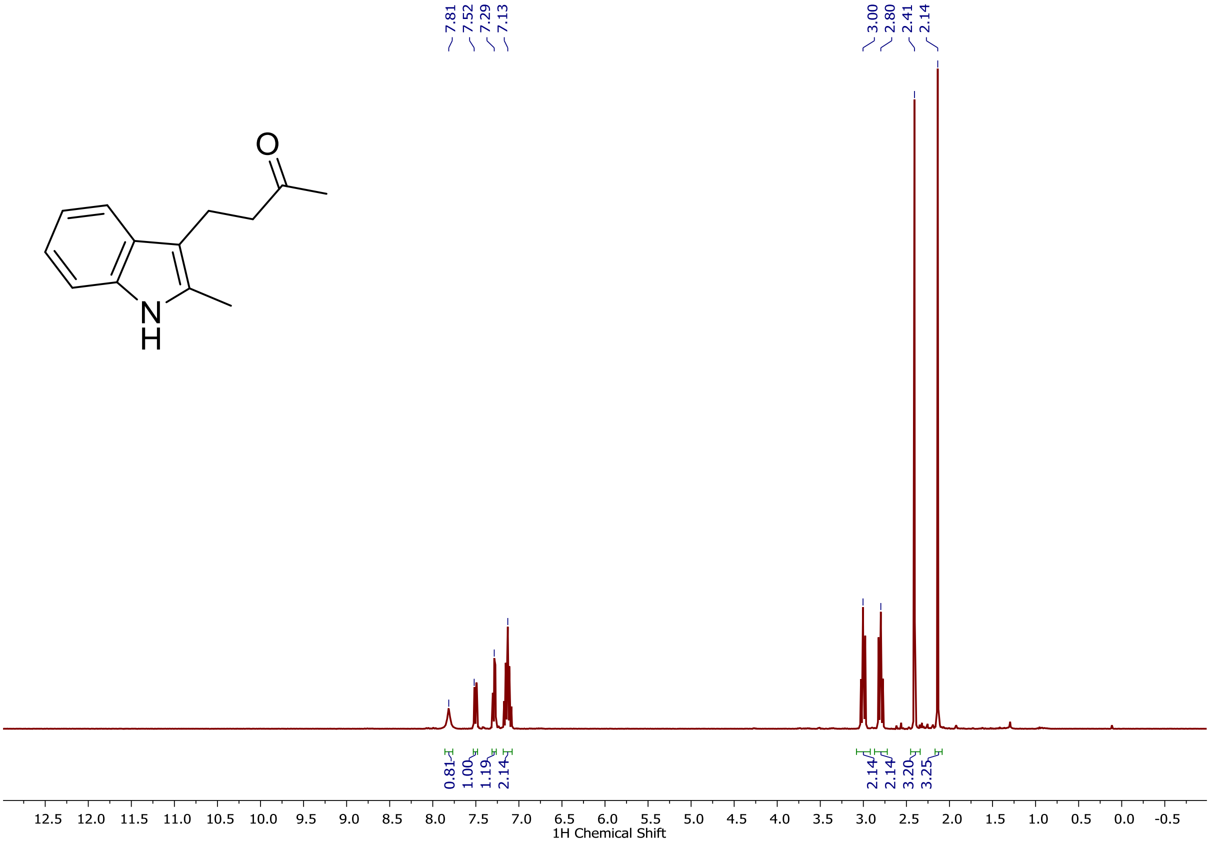
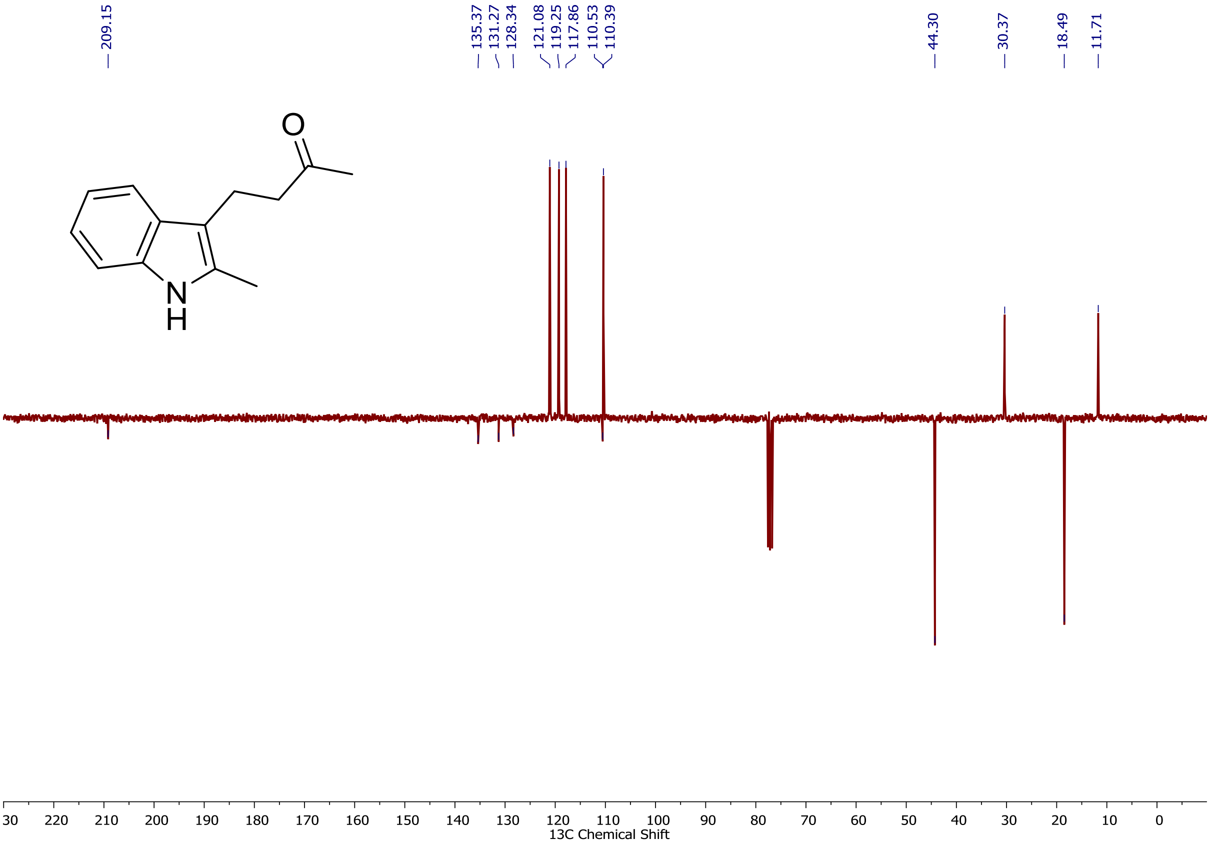
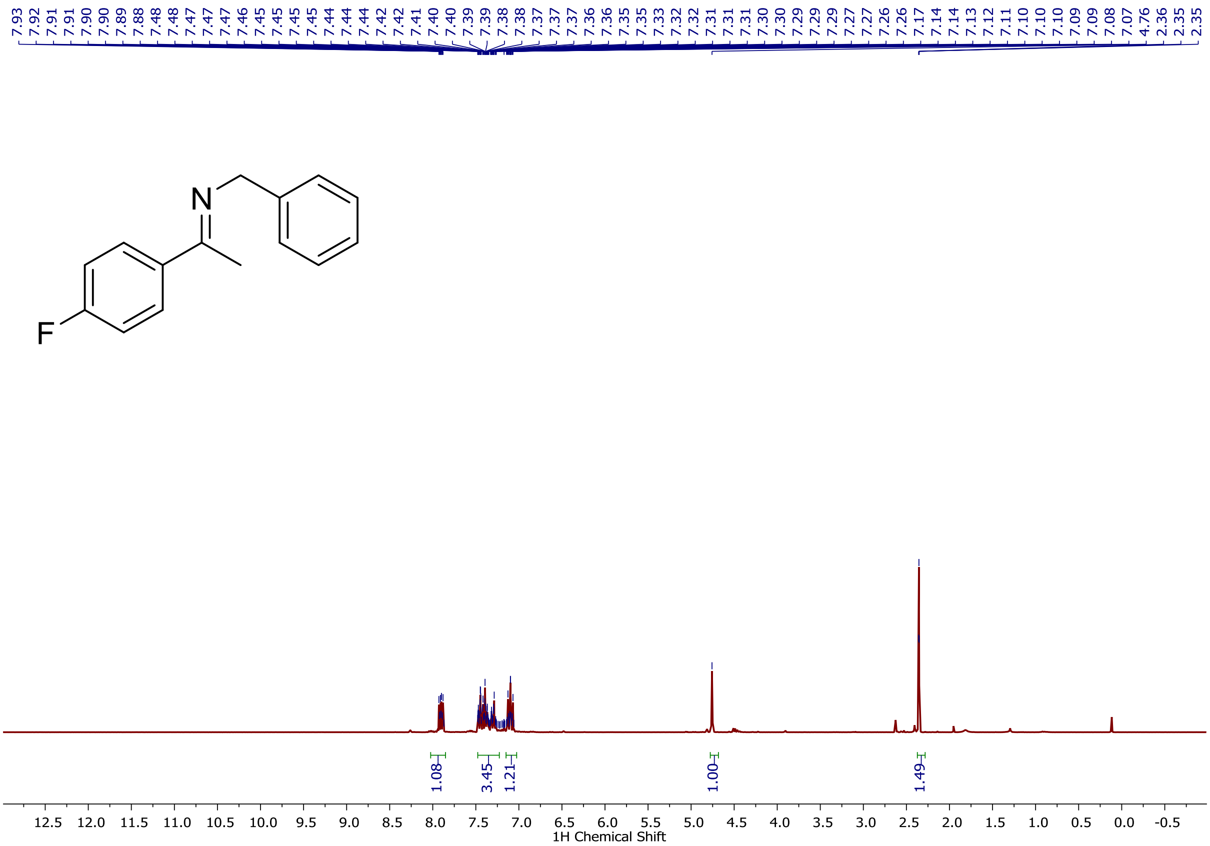


Figure S11: $^{19}F\{^1H\}$ NMR spectra of dissolved STA-27 recovered from carbonyl ene reaction after N_2 adsorption studies.

3. NMR Spectra of the products



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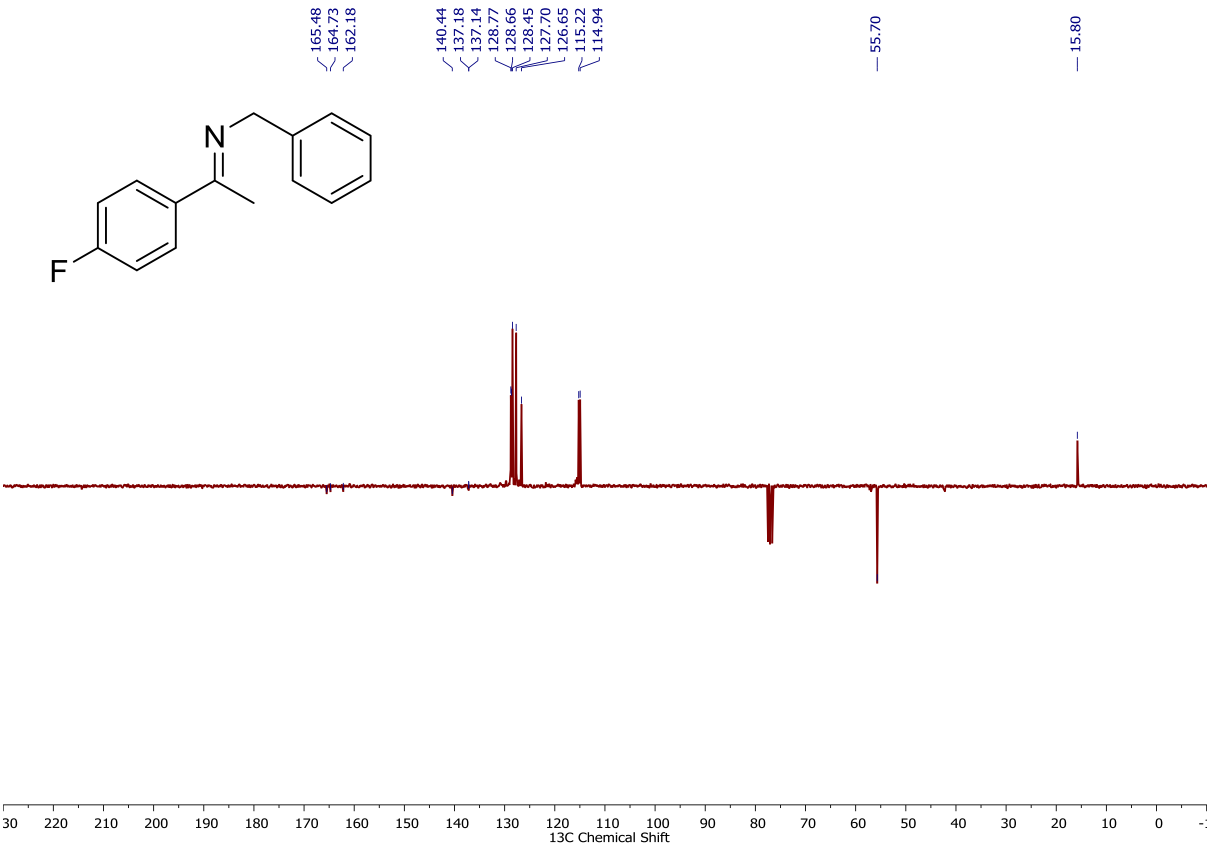
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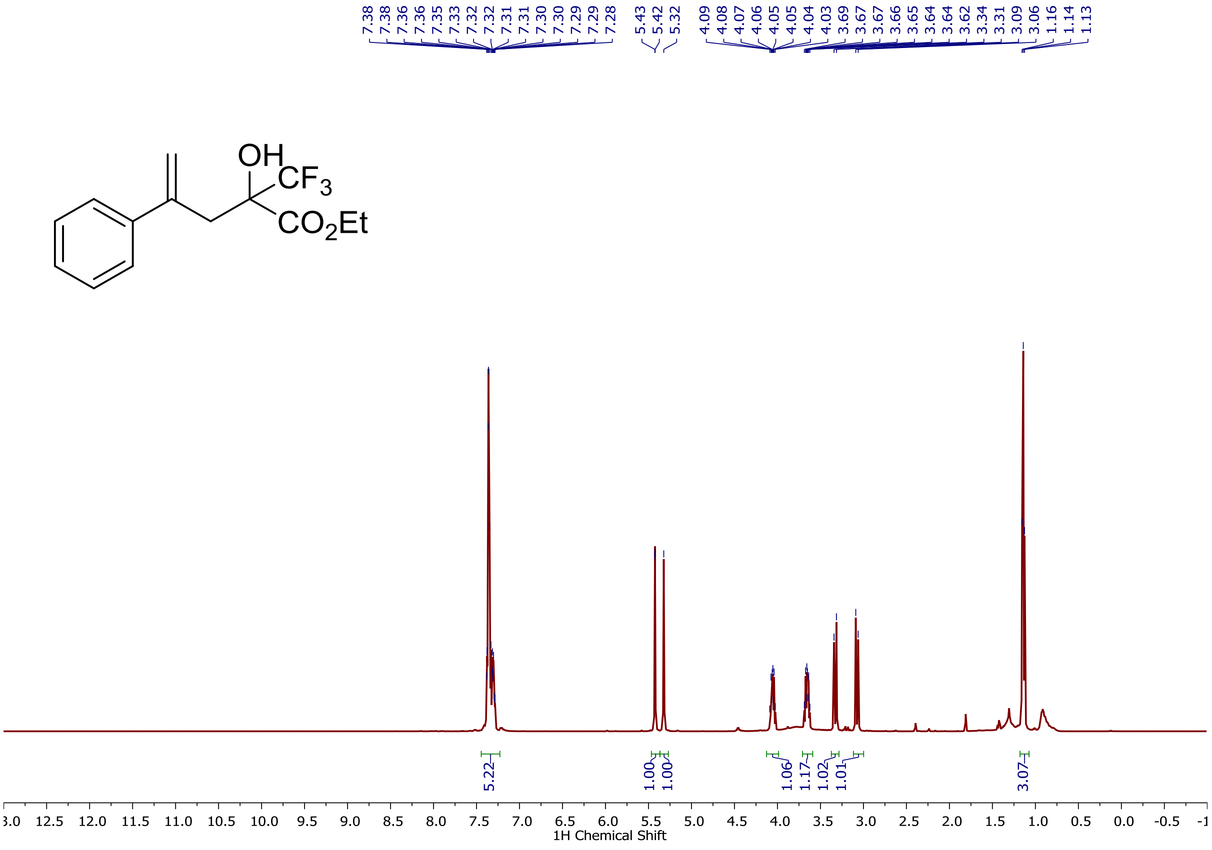
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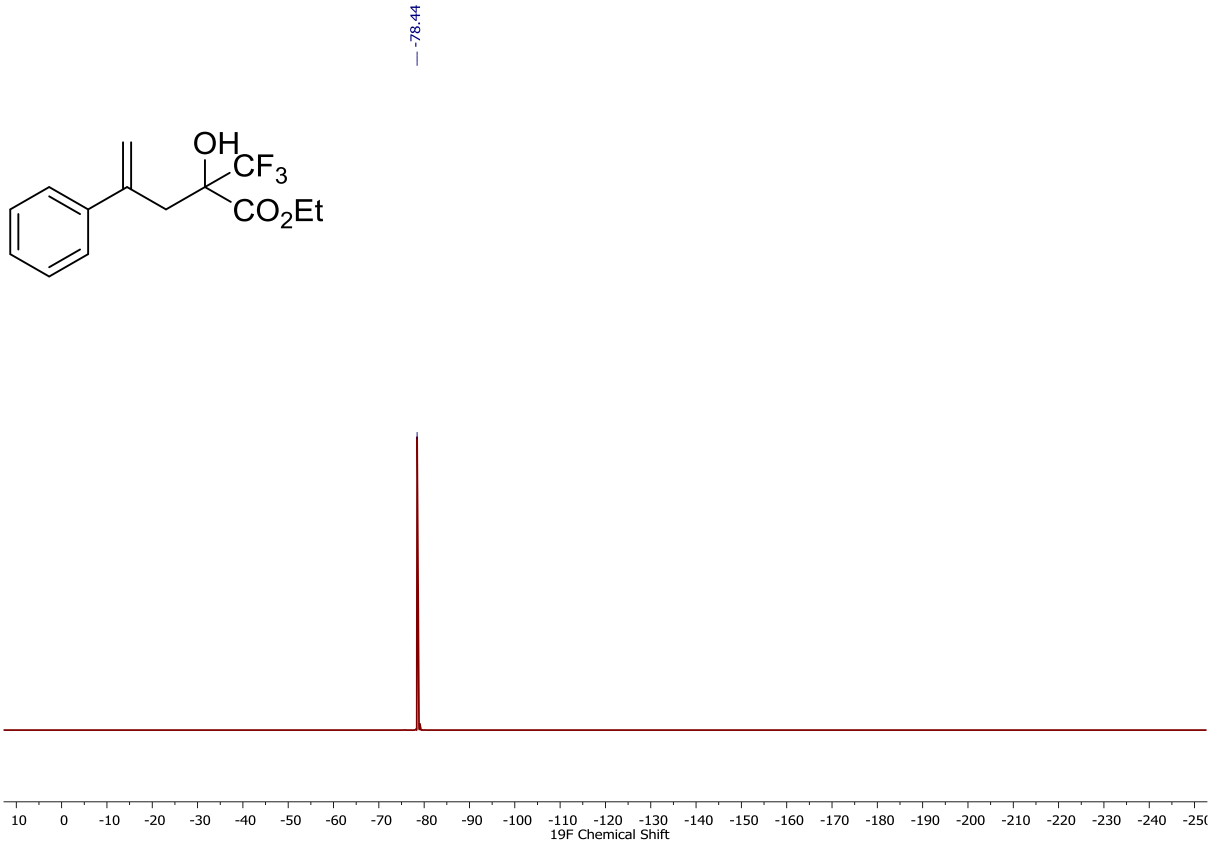
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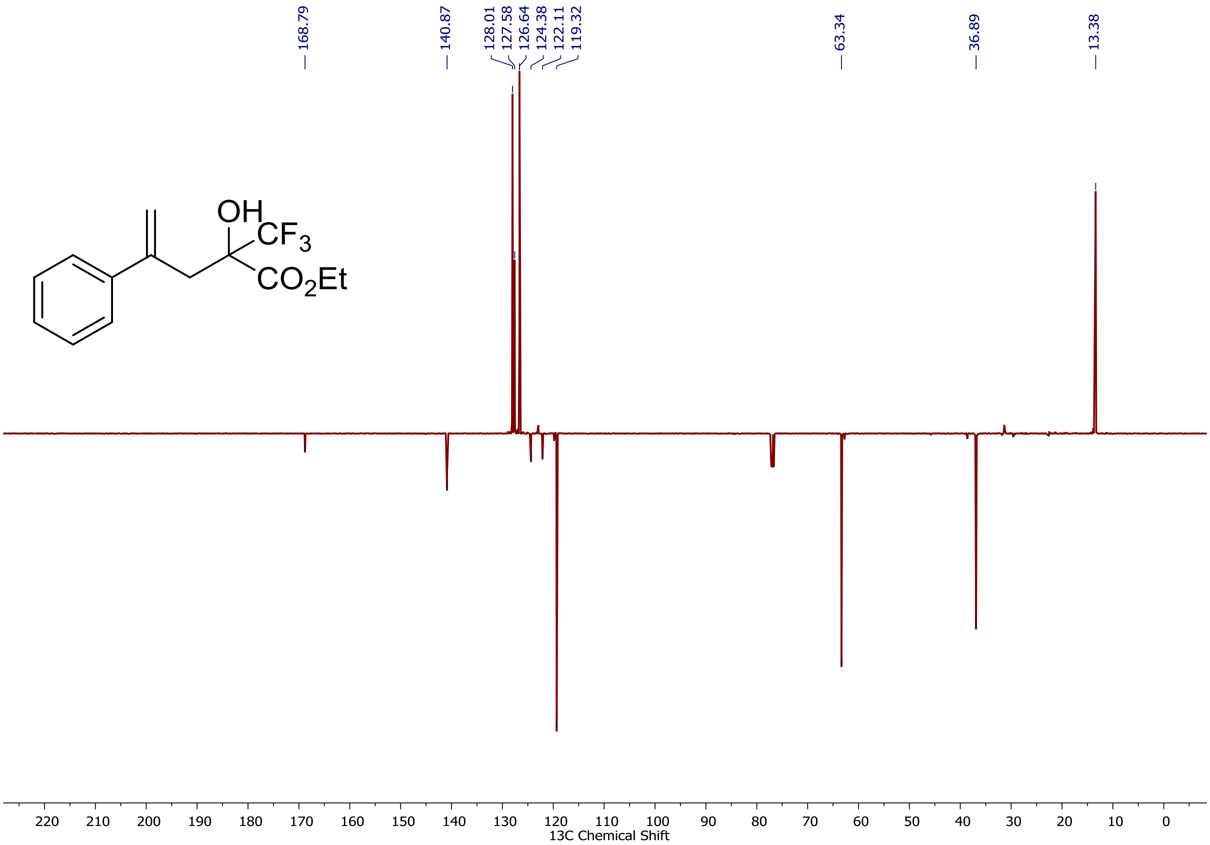
19F Chemical Shift



5. References

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