Supporting Information for

Quaternary ammonium salts interact with enolates and sulfonates via formation of multiple $^{+}$N-C-H hydrogen bonding interactions

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Contents

1. ^{1}H-NMR and ^{13}C-NMR spectra.

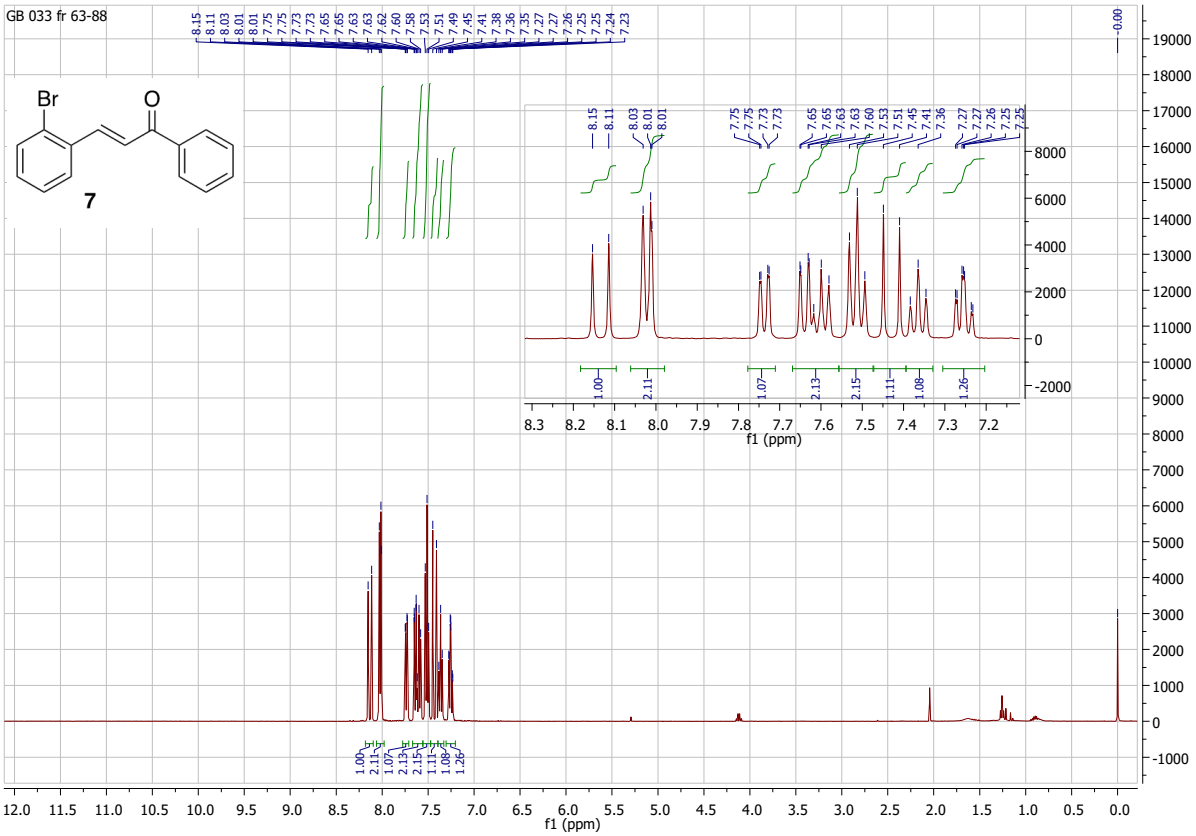


Figure S1. ^{1}H NMR spectrum for compound 7.

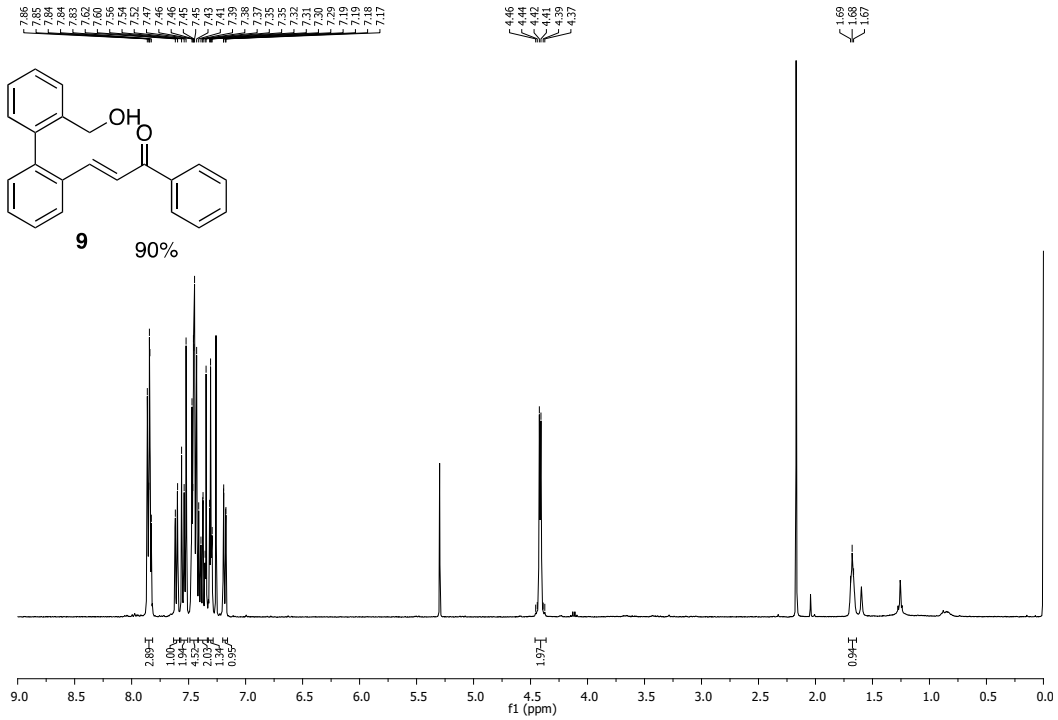


Figure S2. ^{13}C NMR spectrum for compound 9.

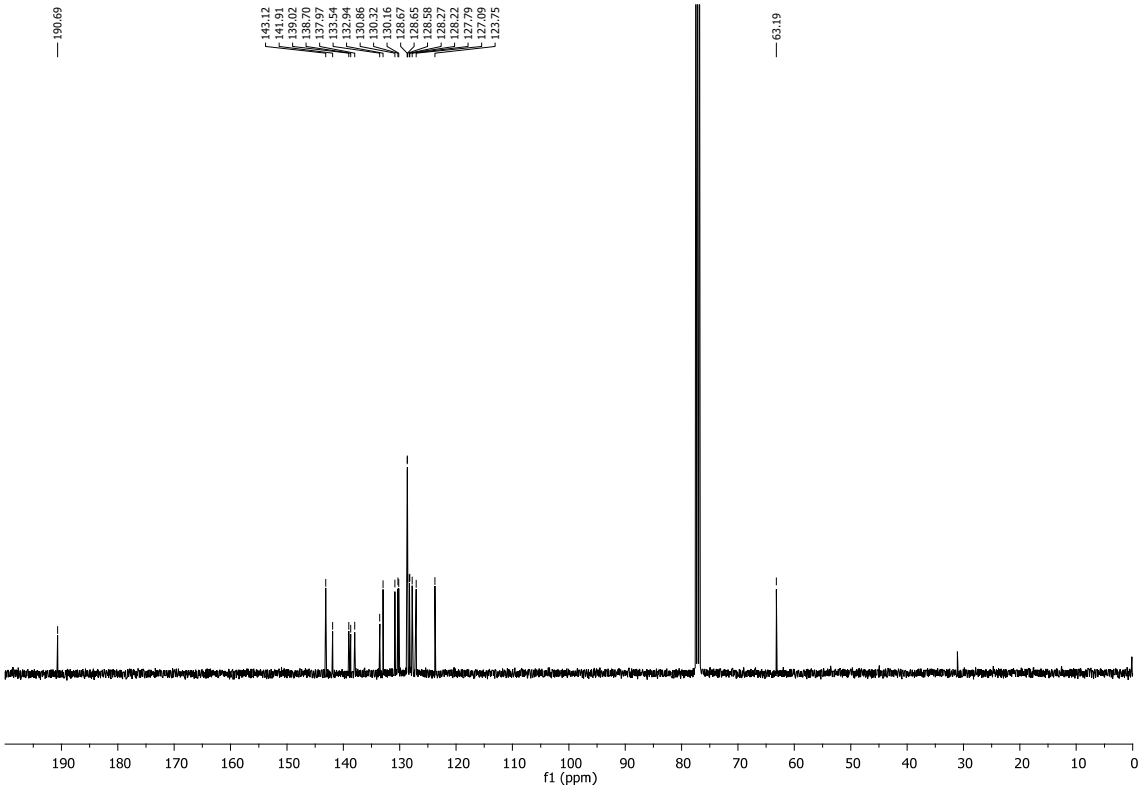


Figure S3. ^{1}C NMR spectrum for compound 9.

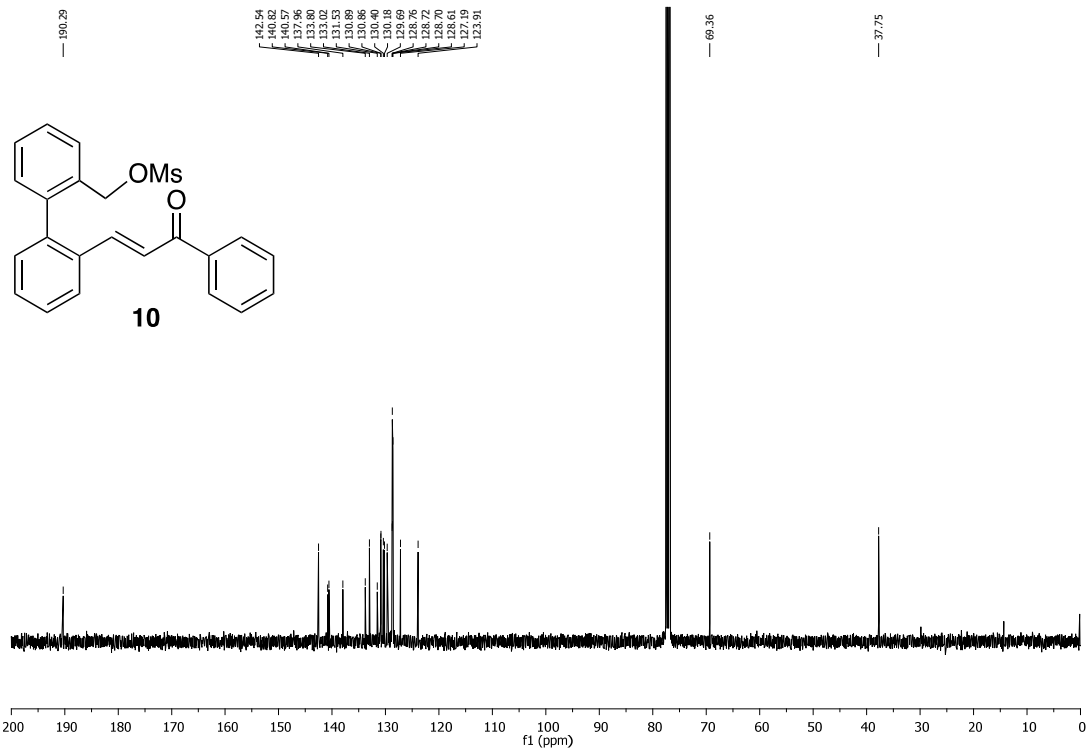


Figure S4. ^{13}C NMR spectrum for compound 10.

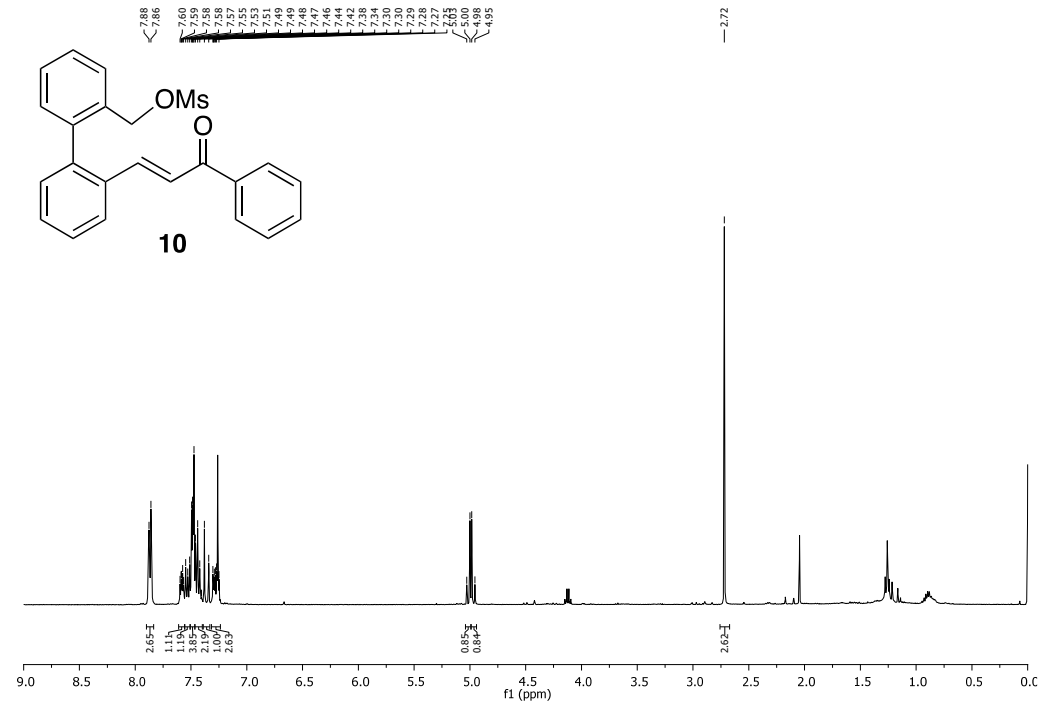


Figure S5. ^{1}H NMR spectrum for compound 10.

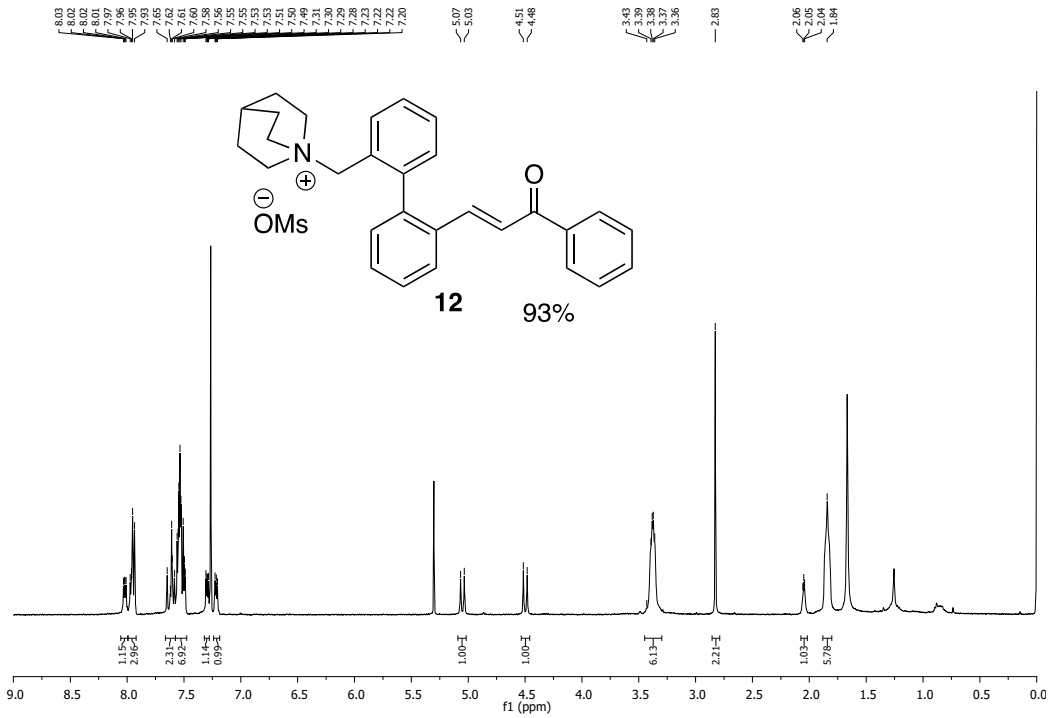


Figure S6. ^{1}H NMR spectrum for compound 12.

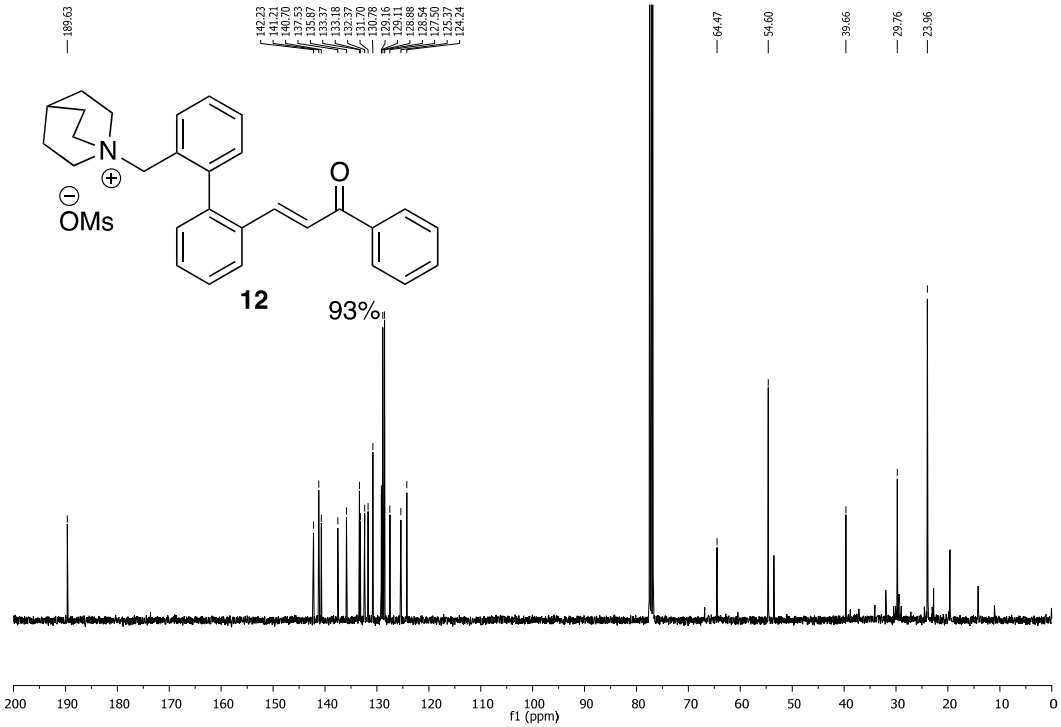


Figure S7. ^{13}C NMR spectrum for compound 12.

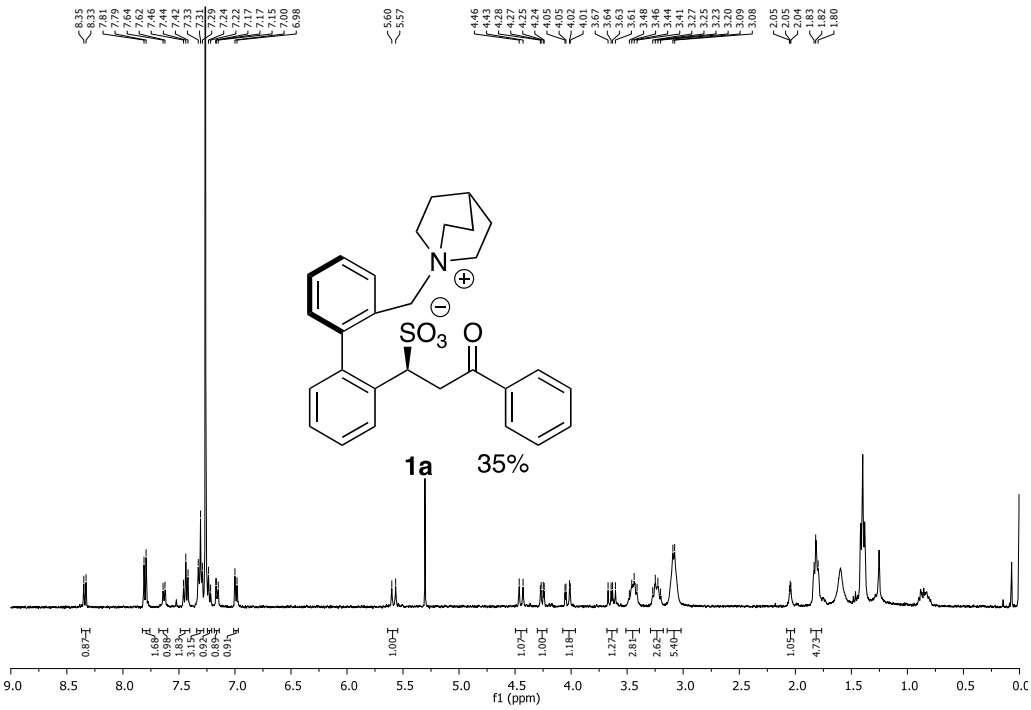


Figure S8. ^{1}H NMR spectrum for compound 1a.

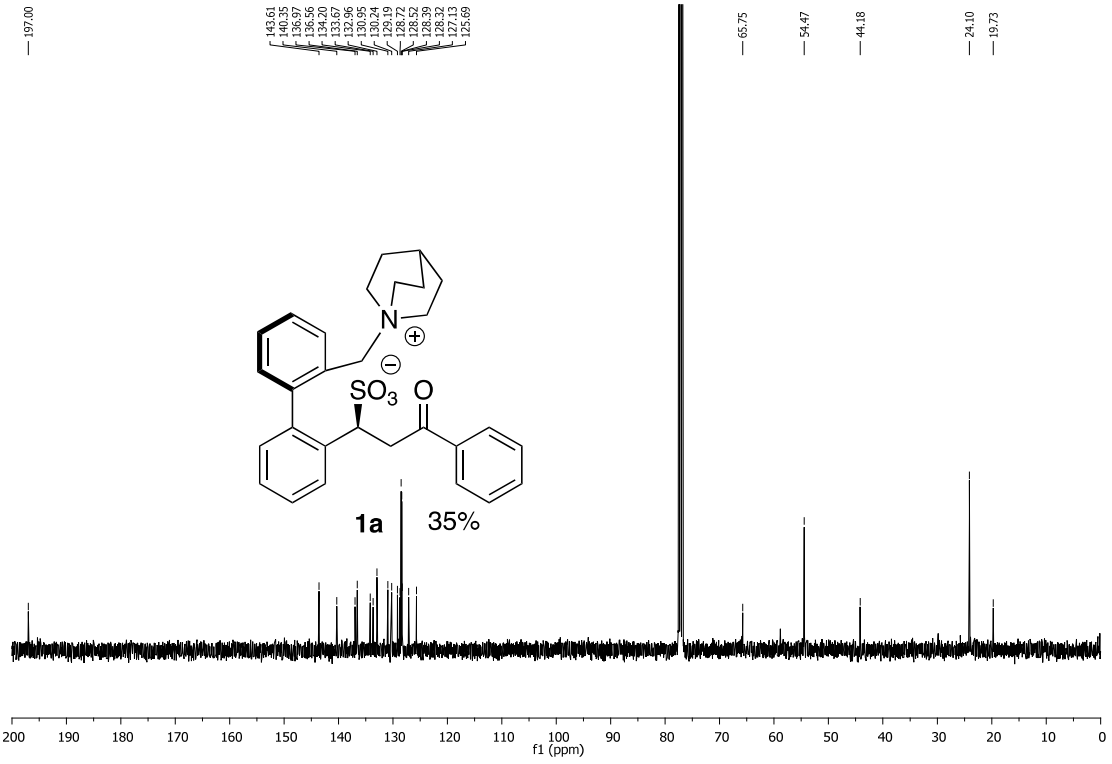


Figure S9. ^{13}C NMR spectrum for compound 1a.

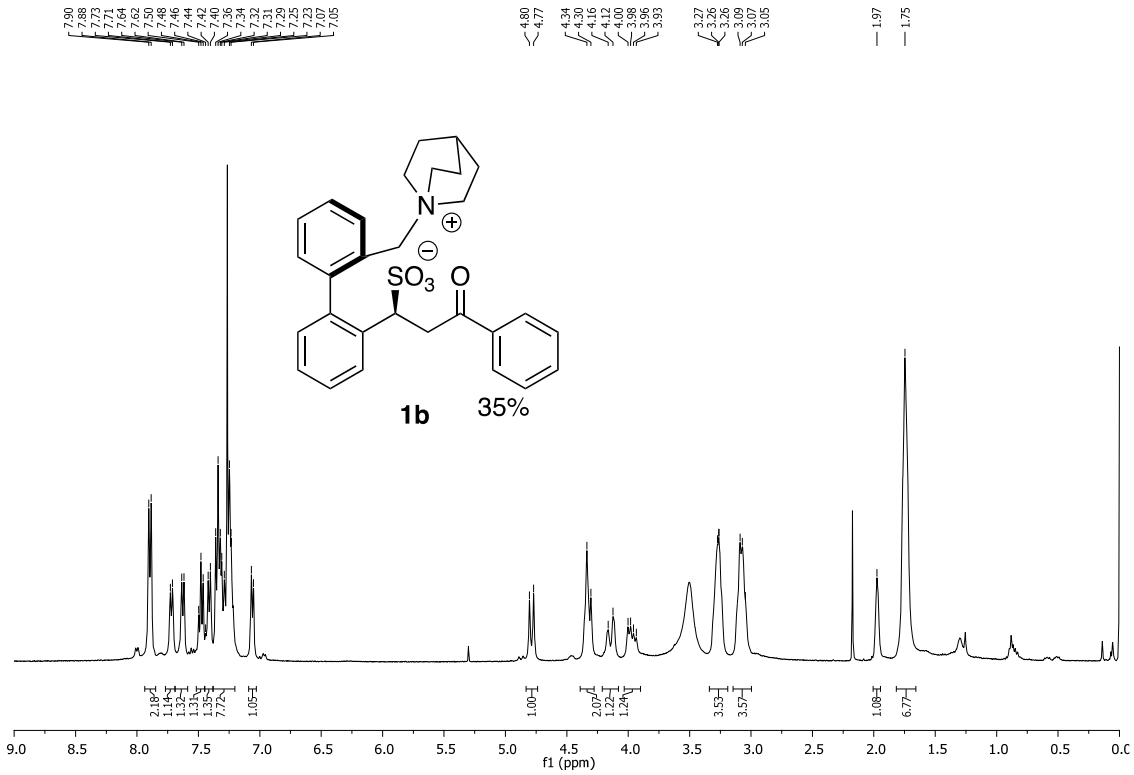


Figure S10. ^{1}H NMR spectrum for compound 1b.

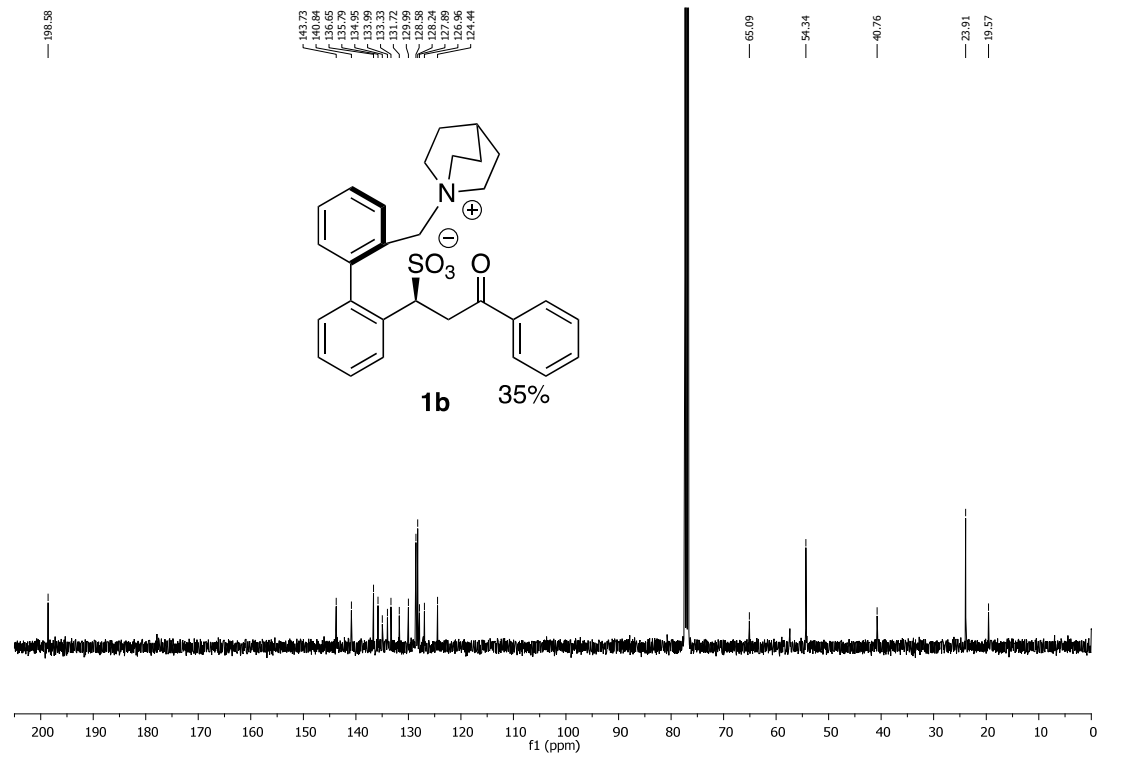


Figure S11. ^{13}C NMR spectrum for compound 1b.

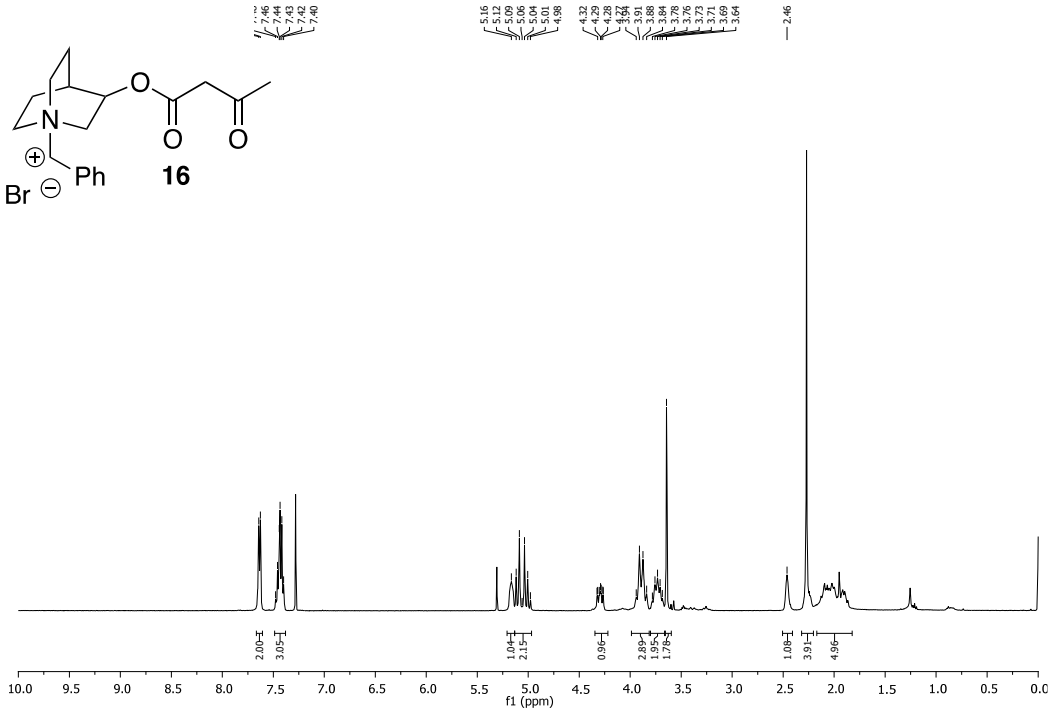


Figure S12. ^{1}H NMR spectrum for compound 16.

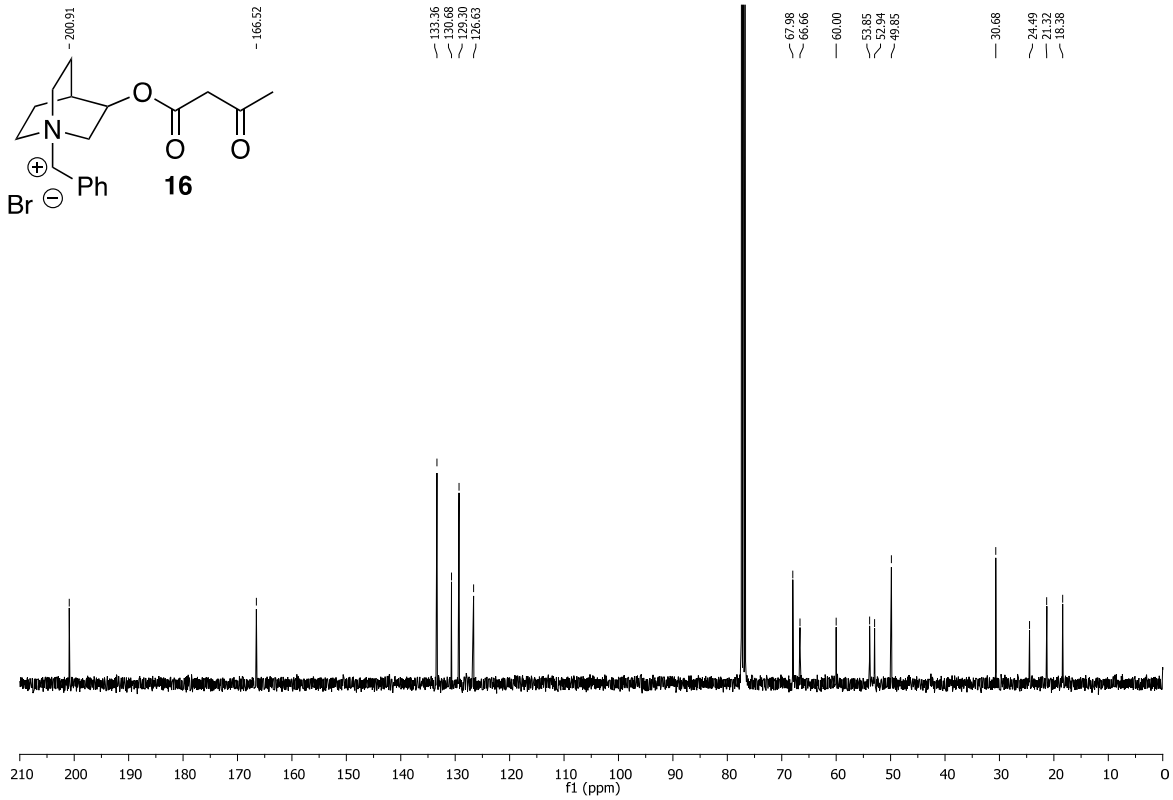


Figure S13. ^{13}C NMR spectrum for compound 16.

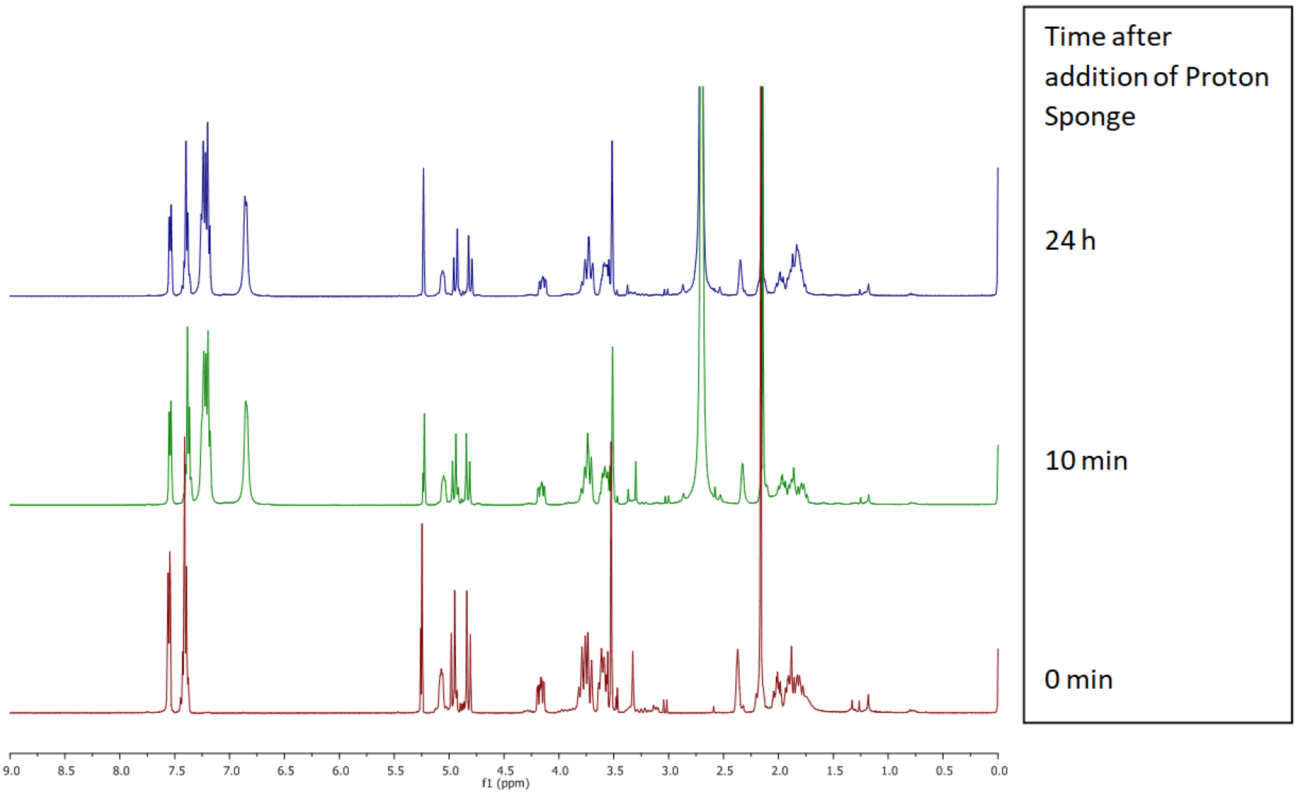
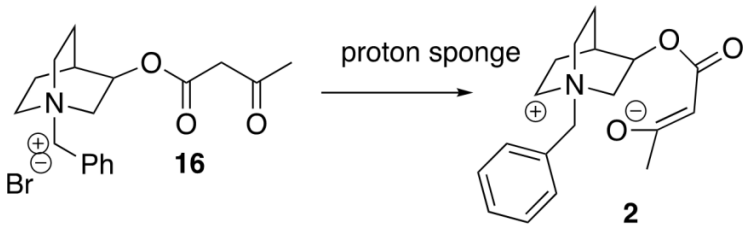


Figure S14. ^{1}H NMR spectra of compound 16 with addition of proton sponge over time revealing formation of 2.

Proton sponge = 1,8-bis(dimethylamino)naphthalene



Compound 16 ^{1}H-^{1}H COSY

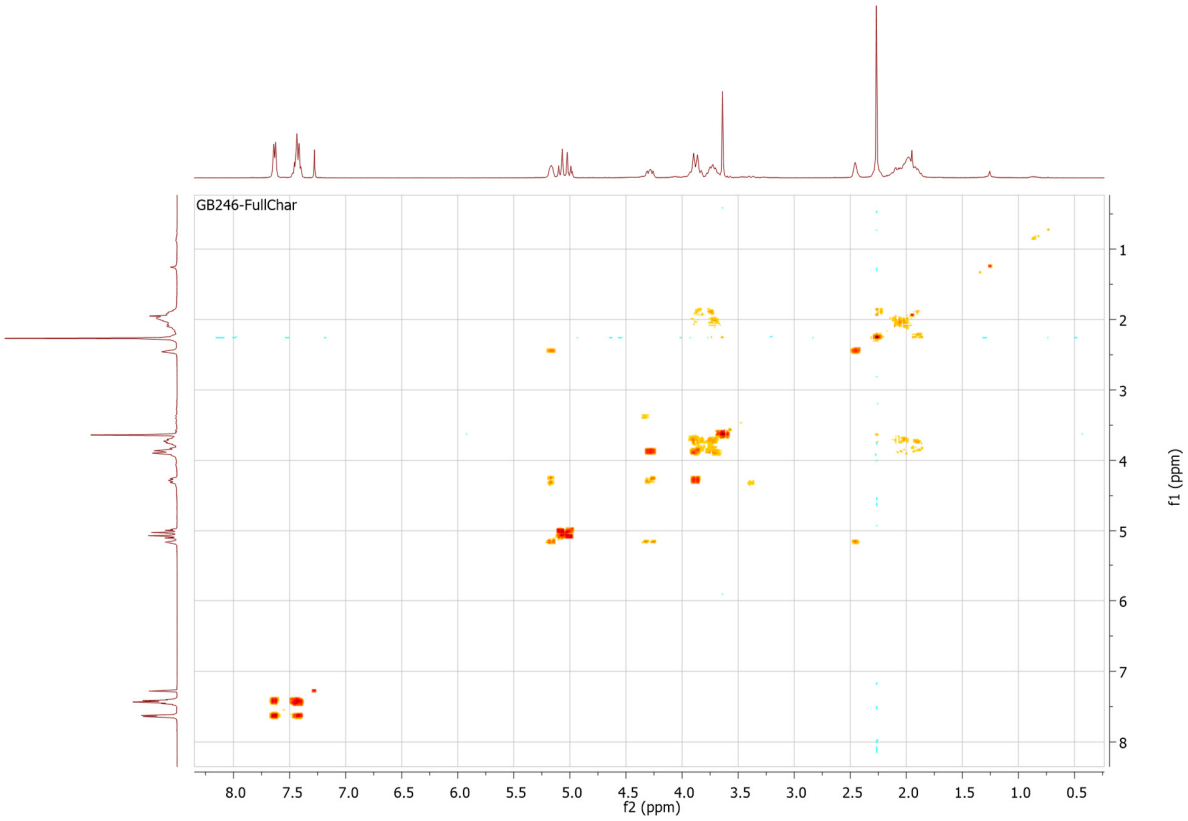


Figure S15. ^{1}H-^{1}H COSY spectrum of compound 16.

Compound 16 ^{1}H-^{13}C HSQC and enlargement

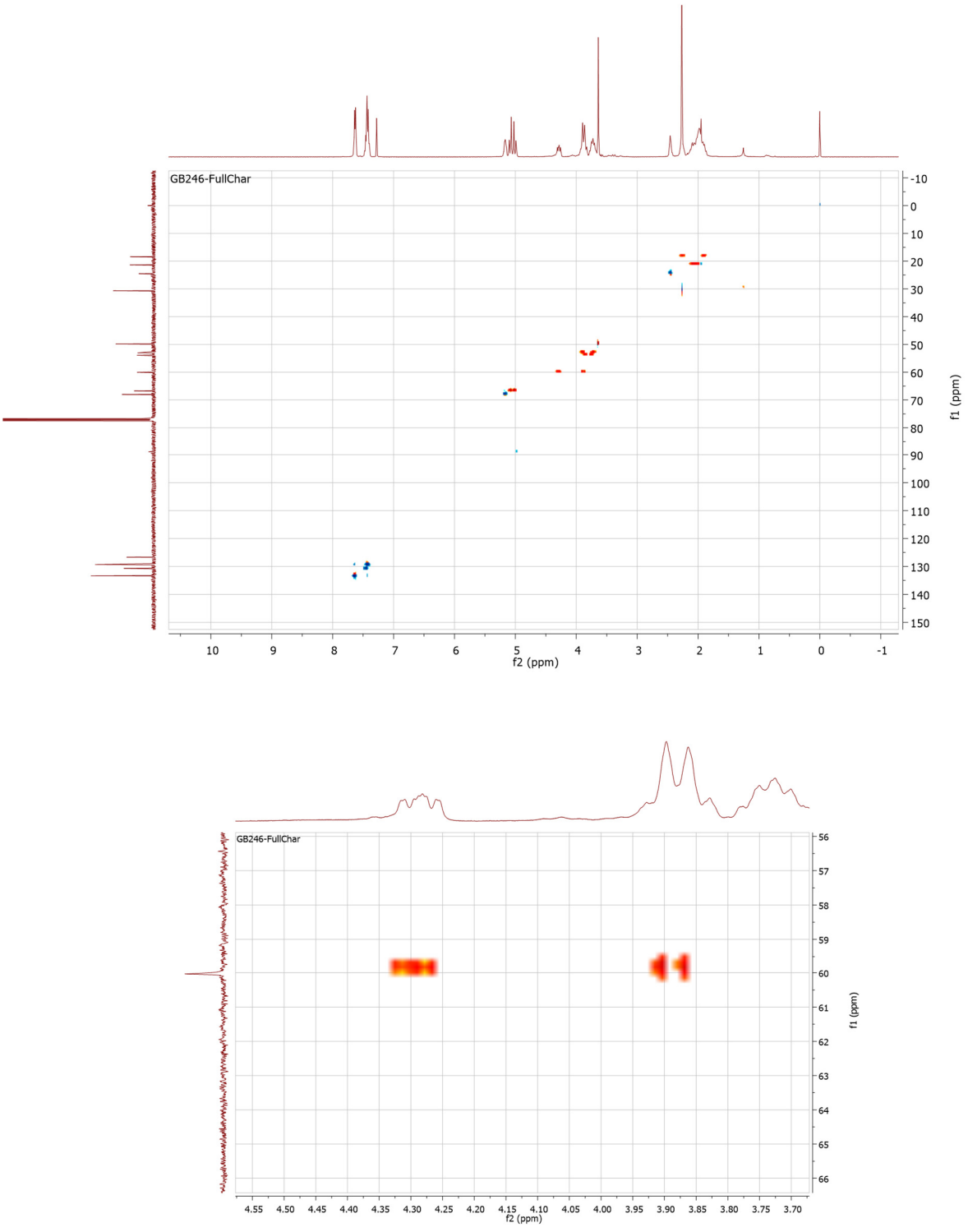


Figure S16. ^{1}H-^{13}C HSQC and enlargement for compound 16.

Compound 16 ^{1}H-^{13}C HMBC and enlargement

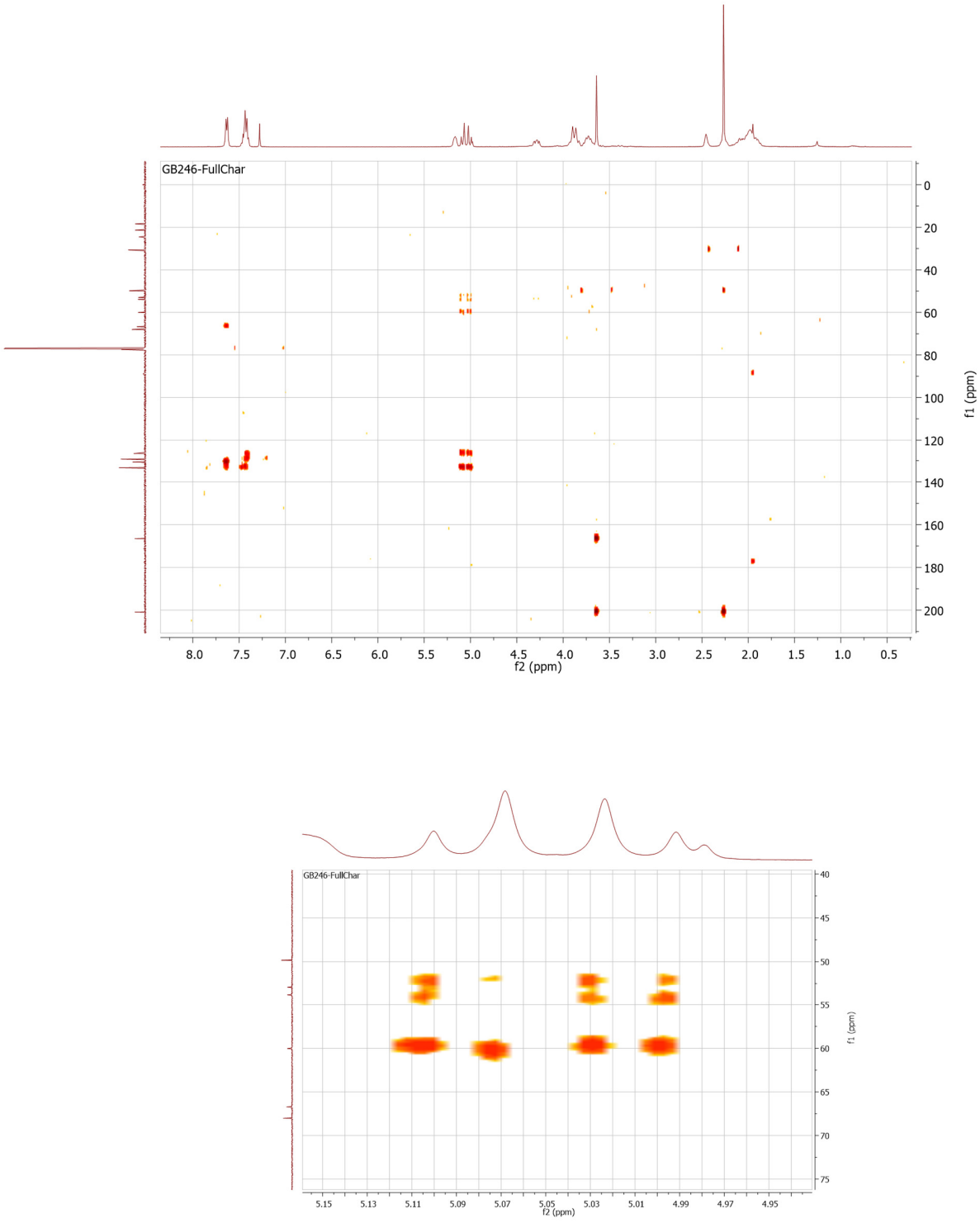


Figure S17. ^{1}H-^{13}C HMBC and enlargement for compound 16.

2. X-ray crystal structure data for compound 1a

X-ray Experimental: Data for **1a** were collected on a Bruker APEX DUO using Cu Kα radiation (λ = 1.54178 Å). The sample was mounted on a MiTeGen cryoloop and data collected at 296(2) K. Bruker APEX [S1] software was used to collect and reduce data. Absorption corrections were applied using SADABS.[S2] Structures were solved with the SHELXT structure solution program [S3] using Intrinsic Phasing. Data were refined using Least Squares method on F^2 with SHELXL.[S4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to calculated positions using a riding model with appropriately fixed isotropic thermal parameters. Molecular graphics were generated using OLEX2. [S5] Crystal data, details of data collection and refinement are given in Table S1.

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 2020518. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail:deposit@ccdc.cam.ac.uk).

X-ray Crystallography Model:

Phenyl rings on all three molecules are disordered: C1:C1a 50%; C36:C36a 64:36%; C63:C63a 49:51% and the disorder on this molecule extends to the ketone C69 and O70. Restraints used (DFIX, SADI, SIMU). Centrosymmetric space group and the model has chirality at C10 (S), C41 (S) and C72 (R). The solvent DCM molecule C2s/C3s was modelled as a rigid group in two locations with 15 % occupancy and is also disordered over an inversion centre resulting in a 0.3 occupied DCM per asymmetric unit. Restraints used (SIMU, ISOR).

Table S1. Crystal data and structure refinement for 1a.

CCDC No.	2020518
Empirical formula	$C_{88.3}H_{95.6}Cl_{2.6}N_3O_{12}S_3$
M (g/mol)	1579.22
T (K)	296(2)
Crystal System	monoclinic
SG	$P2_1/c$
a (Å)	8.7045(3)
b (Å)	32.0222(10)

c (Å)	28.3807(10)
α (°)	90
β (°)	96.283(2)
γ (°)	90
V (Å^3)	7863.2(5)
Z	4
Dcalc (g/cm^3)	1.334
μ (mm^{-1})	2.203
F(000)	3338.0
Crystal size (mm^3)	0.26 × 0.04 × 0.03
Radiation	Cu Kα (λ = 1.54178)
Reflections collected	98343
	13430
Independent reflections	R_{int} = 0.1119
	R_{sigma} = 0.0992
Data/restraints/parameters	13430/677/1132
Goodness-of-fit on F^2 (*S*)	1.031
Final R indexes [$I \geq 2\sigma(I)$]*	R_1 = 0.0634, wR_2 = 0.1775
Final R indexes [all data]	R_1 = 0.0929, R_2 = 0.2066
Largest diff. peak/hole / e Å^{-3}	0.67/-0.43

*$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, w$R_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

This data has been deposited in the Cambridge Crystallographic Data Centre (CCDC), deposition number 2020518.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) tcd1195a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: tcd1195a

Bond precision: C-C = 0.0054 A Wavelength=1.54178

Cell:	a=8.7045(3)	b=32.0222(10)	c=28.3807(10)
	alpha=90	beta=96.283(2)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	7863.2(5)	7863.2(5)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C29 H31 N O4 S, 0.433(C H2 Cl2)	1.3(C H2 Cl2), 3(C29 H31 N O4 S)

Sum formula	C29.43	H31.87	Cl0.87	N	O4	C88.30	H95.60	Cl2.60	N3	
S						O12	S3			
Mr	526.41					1579.22				
Dx,g cm-3	1.334					1.334				
Z	12					4				
Mu (mm-1)	2.203					2.203				
F000	3338.4					3338.0				
F000'	3354.97									

h,k,lmax	10,37,33	10,37,33
Nref	13462	13430
Tmin,Tmax	0.900,0.936	0.581,0.753
Tmin’	0.564	

Correction method= # Reported T Limits: Tmin=0.581 Tmax=0.753

AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 65.261

R(reflections)= 0.0634(9212) wR2(reflections)= 0.2066(13430) S = 1.031 Npar= 1132

PLATON version of 16/07/2020; check.def file version of 12/07/2020

Datablock tcd1195a - ellipsoid plot