Electronic Supplementary Material (ESI) for Analyst.

Selective mass spectrometric analysis of thiols using charge-tagged disulfides

Supporting Information

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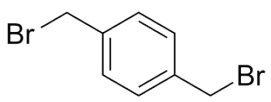
List of Compounds by Number



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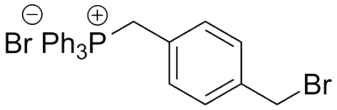

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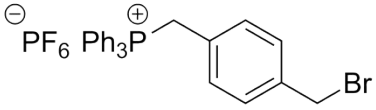

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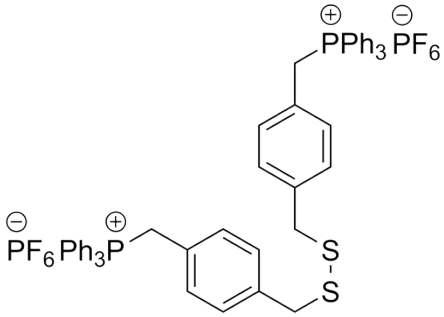

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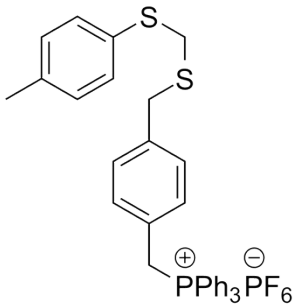


5

Figure S1. List of relevant species by number (as they appear in the main body of the manuscript)

Instrumental Parameters

Table S1: Complete list of QTOF Micro Quadrupole parameters

Ion Energy (V)	**2.0**
Collison Energy	2.0
Low mass resolution	4.1
High mass resolution	4.2
RF Lens 1	0.4
Pre/Post Filter	4.8
RF Lens 2	5.5
Aperture (V)	6.1
Set mass	0.0
Plate one	1.1
Entrance	110.0
Gas cell RF	600.0
Can	0.0
Plate two	-3.2
Pusher cycle time	Auto (47.0)
Pusher frequency	21276.60

Table S2: Complete list of QTOF Micro TOF parameters

Acceleration (V)	**200.0**
Focus (V)	0.0
Steering (V)	1.5
Tube Lens (V)	76.0
Grid 2 (V)	0.0
TOF Flight Tube (V)	5630.0
Reflectron (V)	1780.0
Pusher offset	0.0
Pusher	818.0
Puller	634.7

Table S3: Complete list of QTOF Micro TDC parameters

Inhibit Push	**13.0**
Np Multiplier	0.70
Resolution	5000.0
Lteff	1080.00
Veff	5630.00

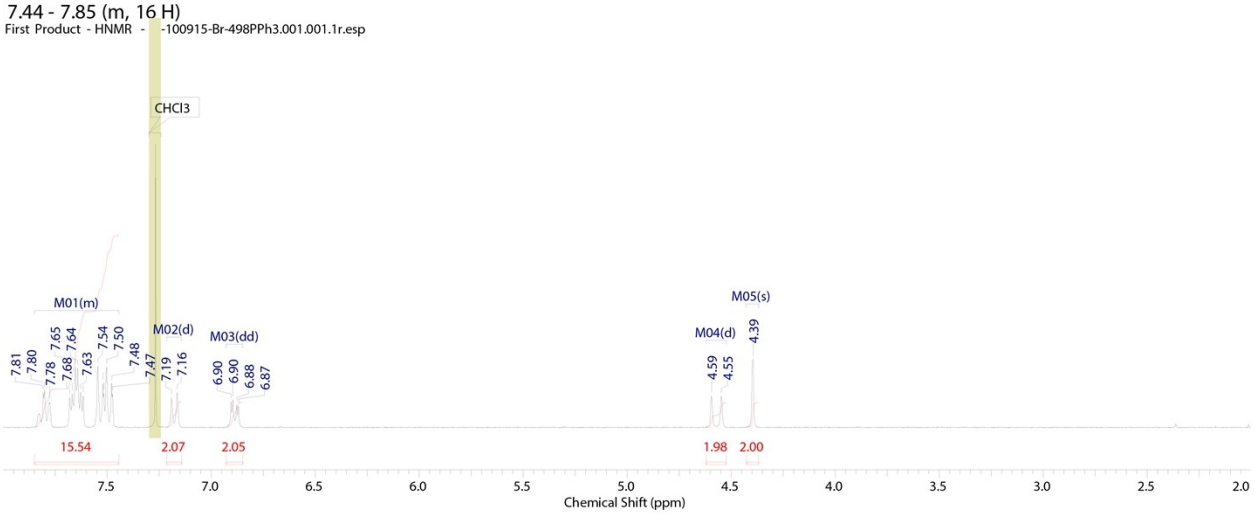
NMR Data

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	3.4166	Comment	EJ - 100915 - Pure Br-Phosphonium Salt			Date	10 Sep 2015 15:21:52
Date Stamp	10 Sep 2015 15:21:52						
Frequency (MHz)	300.27	Nucleus	1H	Number of Transients	16	Origin	spect
Original Points Count	16384	Owner	av300user	Points Count	16384	Pulse Sequence	zg30
Receiver Gain	203.00	SW(cyclical) (Hz)	4795.40	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	1800.8390	Spectrum Type	STANDARD	Sweep Width (Hz)	4795.10	Temperature (degree C)	27.000

^{1}H NMR (300 MHz, CHLOROFORM- d) δ ppm4.39 (s, 2 H) 4.57 (d, J=14.05 Hz, 2 H) 6.89 (dd, J=8.20, 2.34 Hz, 2 H) 7.18 (d, J=7.90 Hz, 2 H) 7.44 - 7.85 (m, 16 H)

First Product - HNMR - -100915-Br-498PPh3.001.001.1r.esp



No.	(ppm)	Annotation	Layer No.	Created By	Created At	Modified By	Modified At
1	[1.47 .. 1.63]	Water	1	Eric	Mon 14/09/2015 2:18:36 PM	Eric	Tue 15/09/2015 10:50:49 AM
2	[7.24 .. 7.30]	CHCl3	1	Eric	Mon 14/09/2015 2:18:48 PM	Eric	Tue 15/09/2015 10:57:27 AM

No.	Shift1 (ppm)	H's	Type	J (Hz)	Multiplet1	(ppm)
1	4.39	2	s	-	M05	[4.37 .. 4.43]
2	4.57	2	d	14.05	M04	[4.52 .. 4.62]
3	6.89	2	dd	8.20, 2.34	M03	[6.85 .. 6.93]
4	7.18	2	d	7.90	M02	[7.14 .. 7.21]
5	7.62	16	m	-	M01	[7.44 .. 7.85]

No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[4.3678 .. 4.42	2.00000000	5.78073800e+6	2.00000000
2	[4.5238 .. 4.61	1.97551250	5.70996000e+6	1.97551250
3	[6.8483 .. 6.92	2.04578424	5.91307150e+6	2.04578424
4	[7.1421 .. 7.21	2.07188320	5.98850700e+6	2.07188320
5	[7.4431 .. 7.84	15.53992558	4.49161200e+7	15.53992558

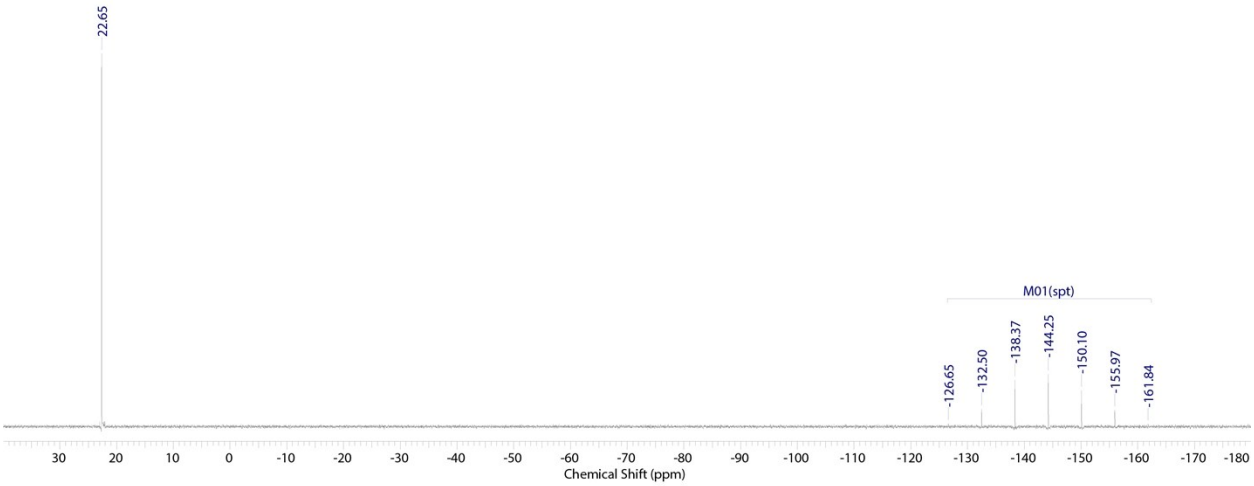
Figure S2. 300 MHz Proton NMR report of **(3)**; 4-(bromomethyl)benzyl)triphenylphosphonium hexafluorophosphate

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.3369	Comment	EJ - 100915 - Pure Br-Phosphonium Salt			Date	10 Sep 2015 15:30:24
Date Stamp	10 Sep 2015 15:30:24						
Frequency (MHz)	121.55	Nucleus	31P	Number of Transients	128	Origin	spect
Original Points Count	65536	Owner	av300user	Points Count	32768	Pulse Sequence	zgpg30
Receiver Gain	203.00	SW(cyclical) (Hz)	49019.61	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	1950.9169	Spectrum Type	STANDARD	Sweep Width (Hz)	49018.11	Temperature (degree C)	27.000

^{31}P NMR (122 MHz, CHLOROFORM- d) δ ppm-144.24 (spt, J=712.10 Hz, 1 P) 22.65 (s, 119 P)

First Product 31P NMR - EJ-100915-Br-498PPh3.002.001.1r.esp



No.	Shift1 (ppm)	P's	Type	J (Hz)	Multiplet1	(ppm)
1	-144.24	1	spt	712.10	M01	[-162.38 .. -126.47]
2	22.65	119	s	-	M02	[22.39 .. 22.83]

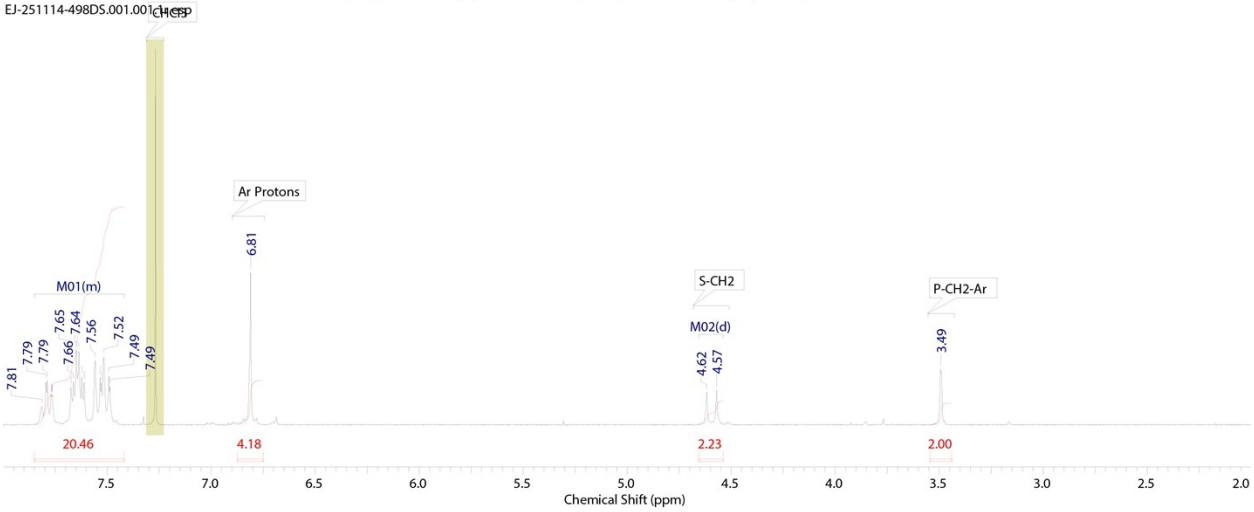
No.	(ppm)	(Hz)	Height
1	-161.84	-19672.4	0.0071
2	-155.97	-18958.9	0.0445
3	-150.10	-18245.3	0.0971
4	-144.25	-17533.2	0.1406
5	-138.37	-16819.6	0.1244
6	-132.50	-16106.1	0.0464
7	-126.65	-15394.0	0.0083
8	22.65	2753.5	1.0000

Figure S3. 300 MHz ^{31}P NMR of **(3)** (4-(bromomethyl)benzyl)triphenylphosphonium hexafluorophosphate

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	3.4166	Comment	EJ - 251114 - 498DS (Large Batch)			Date	25 Nov 2014 17:36:00
Date Stamp	25 Nov 2014 17:36:00						
Frequency (MHz)	300.27	Nucleus	1H	Number of Transients	16	Origin	spect
Original Points Count	16384	Owner	av300user	Points Count	16384	Pulse Sequence	zg30
Receiver Gain	203.00	SW(cyclical) (Hz)	4795.40	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	1800.8390	Spectrum Type	STANDARD	Sweep Width (Hz)	4795.10	Temperature (degree C)	27.000

^{1}H NMR (300 MHz, CHLOROFORM- d) δ ppm4.59 (d, J=14.34 Hz, 2 H) 7.42 - 7.85 (m, 20 H)



No.	(ppm)	Annotation	Layer No.	Created By	Created At	Modified By	Modified At
1	[3.43 .. 3.55]	P-CH2-Ar	1	Eric	Thu 27/11/2014 11:59:21 AM		
2	[4.51 .. 4.68]	S-CH2	1	Eric	Thu 27/11/2014 12:00:18 PM		
3	[6.74 .. 6.90]	Ar Protons	1	Eric	Thu 27/11/2014 12:08:03 PM		
4	[7.23 .. 7.31]	CHCl3	1	Eric	Thu 27/11/2014 9:49:50 AM		

No.	Shift1 (ppm)	H's	Type	J (Hz)	Multiplet1	(ppm)
1	4.59	2	d	14.34	M02	[4.54 .. 4.66]
2	7.65	20	m	-	M01	[7.42 .. 7.85]

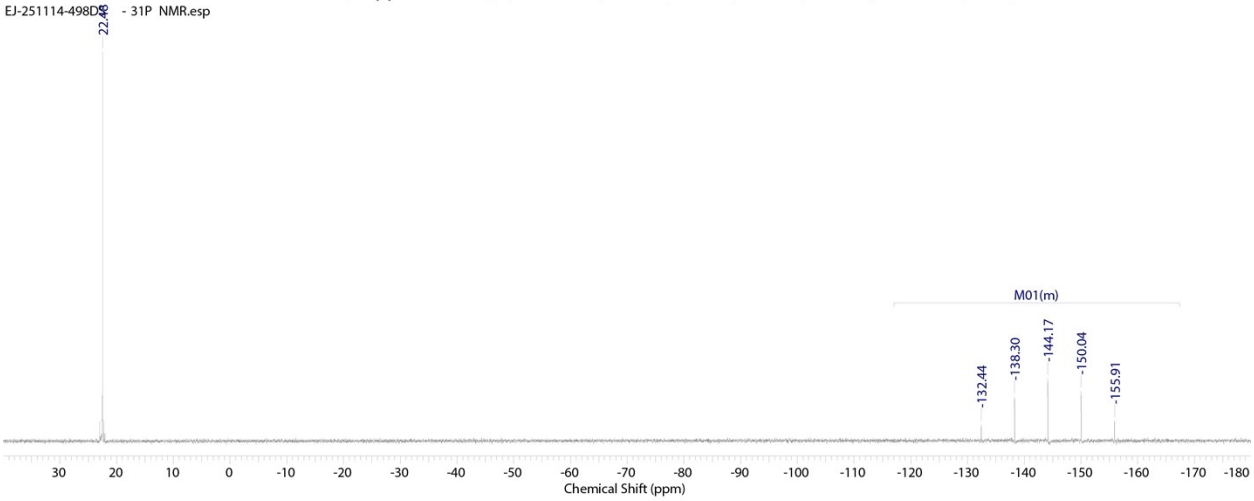
No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[3.4397 .. 3.54	2.00000000	5.22331350e+6	2.00000000
2	[4.5381 .. 4.65	2.22606540	5.81371900e+6	2.22606540
3	[6.7497 .. 6.87	4.18111277	1.09196310e+7	4.18111277
4	[7.4182 .. 7.84	20.45514679	5.34218200e+7	20.45514679

Figure S4. 300 MHz Proton NMR of compound **(4)**

Acquisition Time (sec)	1.3369	Comment	EJ - 251114 - 498DS (Large Batch)	Date	25 Nov 2014 17:42:24
Date Stamp	25 Nov 2014 17:42:24				
				Frequency (MHz)	121.55
Nucleus	31P	Number of Transients	128	Origin	spect
Owner	av300user	Points Count	32768	Pulse Sequence	zgpg30
SW(cyclical) (Hz)	49019.61	Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	1950.9169
Sweep Width (Hz)	49018.11	Temperature (degree C)	27.000	Spectrum Type	STANDARD

^{31}P NMR (122 MHz, CHLOROFORM- d) δ ppm-145.64 (m, J=713.60, 713.60, 713.60, 713.60, 713.60, 713.60 Hz, 15 P)

EJ-251114-498DS - 31P NMR.esp



No.	Shift1 (ppm)	P's	Type	J (Hz)	Multiplet1	(ppm)
1	-145.64	15	m	713.60	M01	[-167.35 .. -117.02]

No.	(ppm)	(Hz)	Height
1	-155.91	-18951.4	0.0521
2	-150.04	-18237.8	0.1279
3	-144.17	-17524.2	0.1612
4	-138.30	-16810.7	0.1135
5	-132.44	-16098.6	0.0430
6	22.48	2732.6	1.0000

Figure S5. 300 MHz ^{31}P NMR of compound **(4)**

ESI-QTOF MS Data

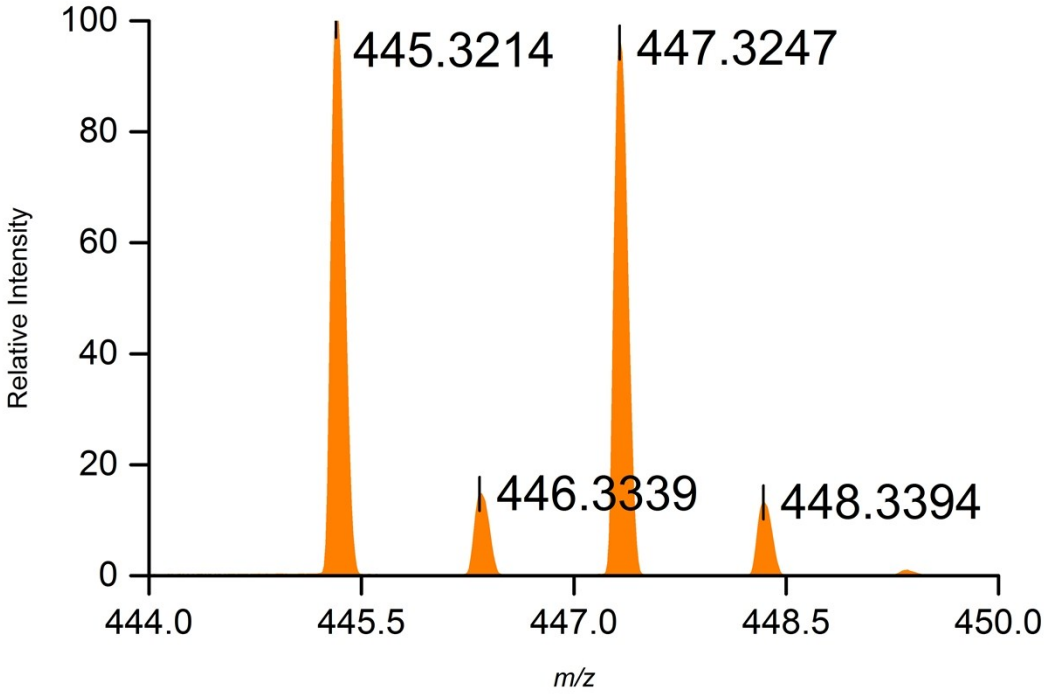


Figure S6. Positive-ion ESI-MS of (4-(bromomethyl)benzyl)triphenylphosphonium hexafluorophosphate

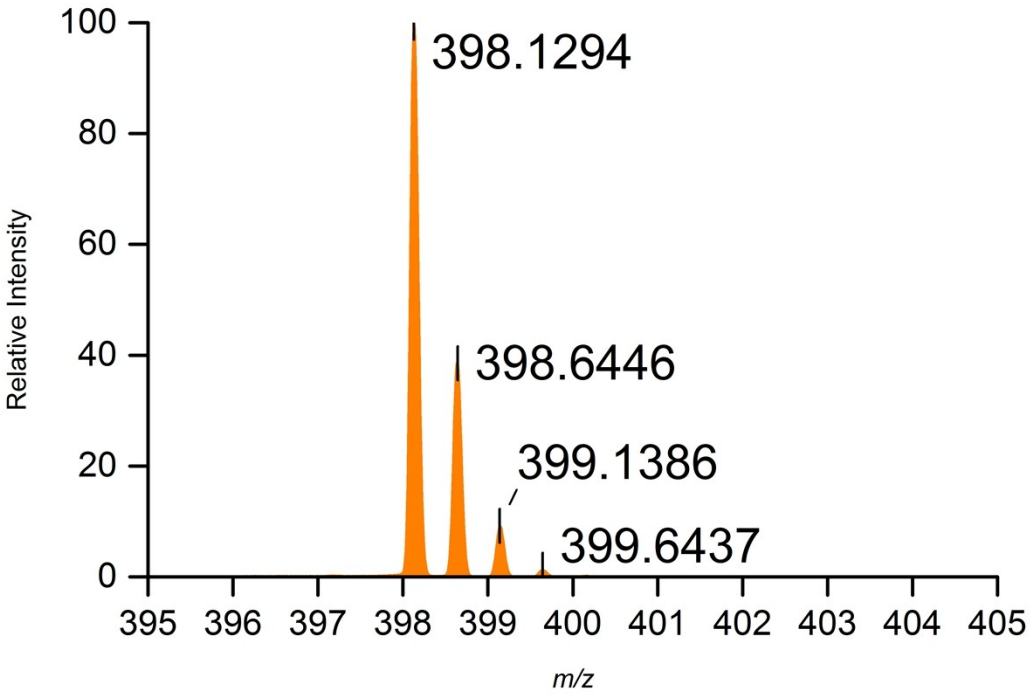


Figure S7. Positive-ion ESI-MS of the charge-tagged disulfide

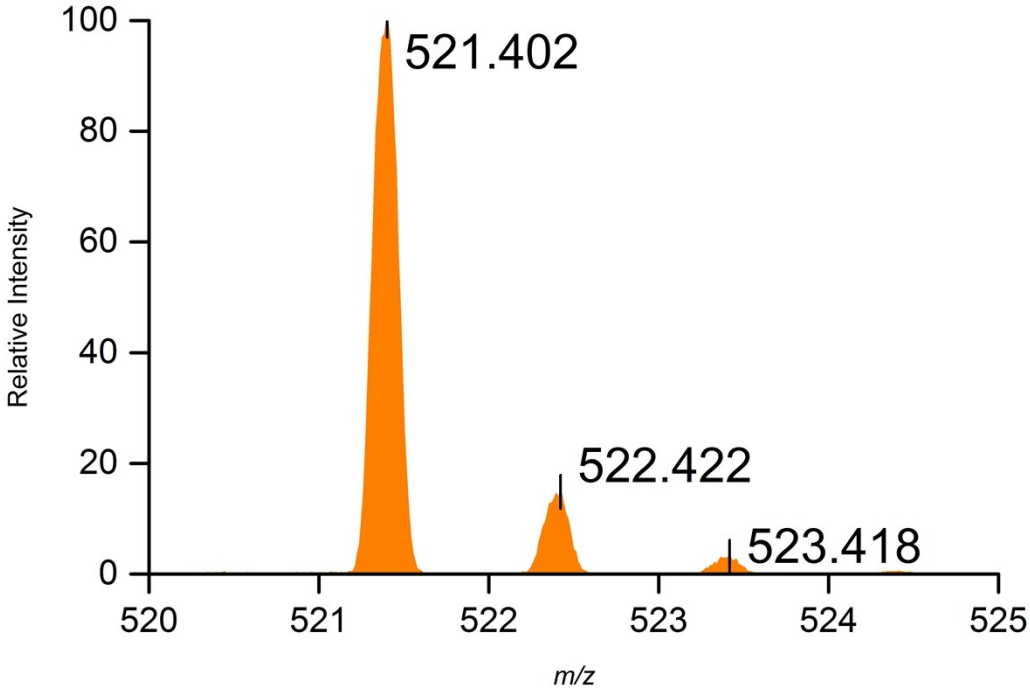


Figure S8. Positive-ion ESI-MS of the mixture of charge-tag and 4-methylbenzenethiol

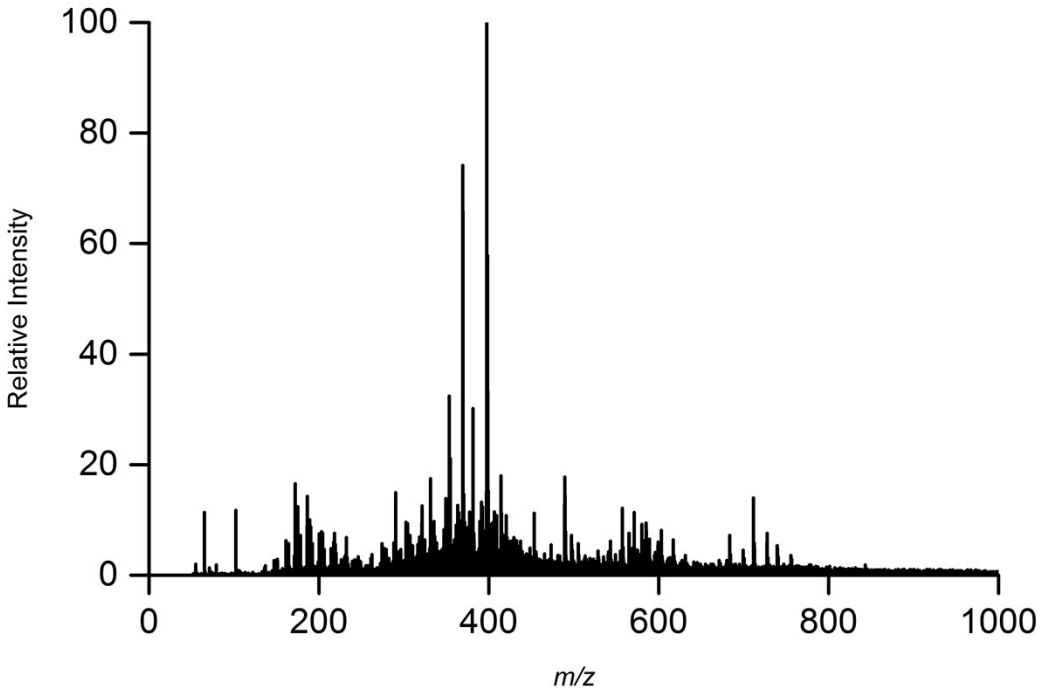


Figure S9. Positive ion ESI-MS of the mixture of charge-tagged disulfide and Basra crude petroleum

MSMS Data

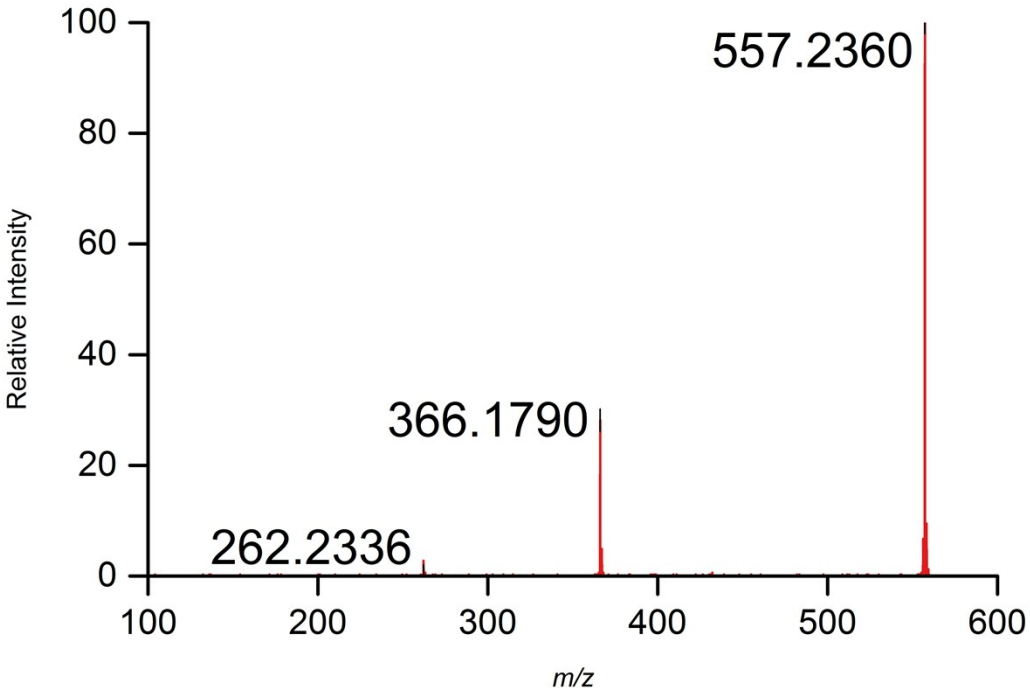


Figure S10. MSMS of nonane-1-thiol derivative with 498DS in “Sample A” (NAN-130 77229)

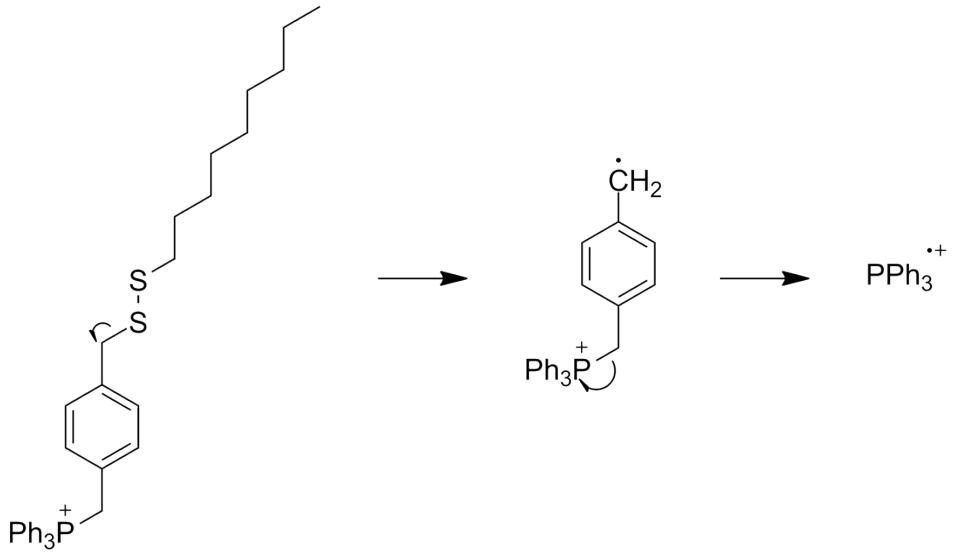


Figure S11. Fragmentation pattern using nonane-1-thiol as an example

Limit of Detection

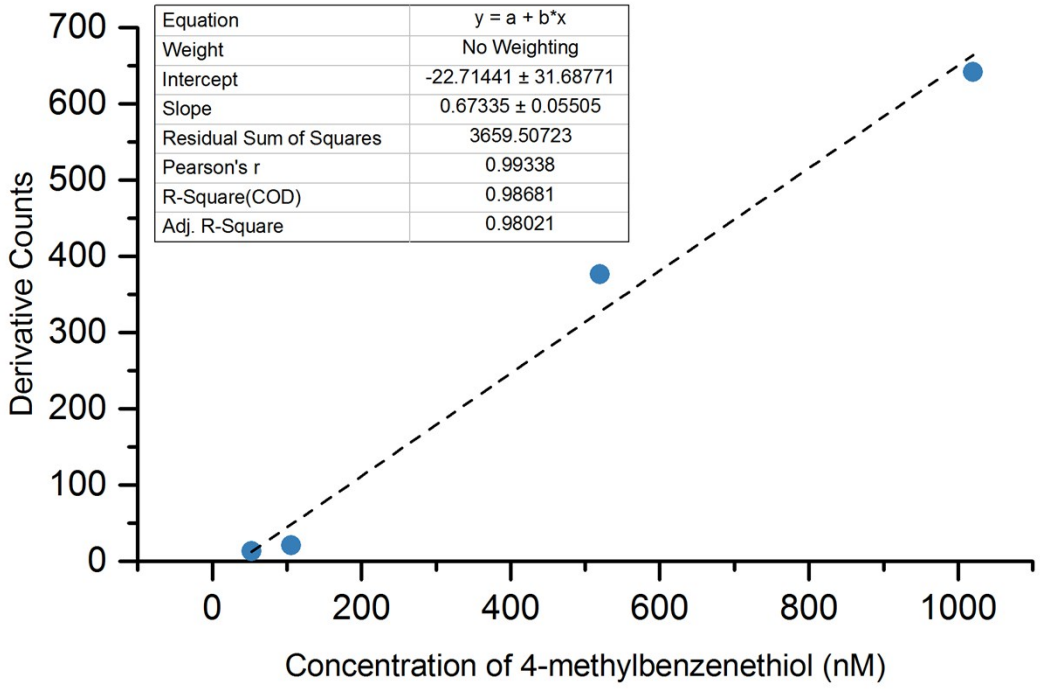


Figure S12. Response of derivative **(5)** following thiol-disulfide exchange reaction with 2.0 uM compound **(4)**

The average baseline noise was determined with a method blank sample including ethanol and 2.0 uM of compound **(4)**. The two samples analyzed in this manuscript did not exhibit significant background noise at the region of interest (that is, above *m/z* 400 and below *m/z* 2000). The response of derivative compound **(5)** was found to be linear for nano- to micromolar quantities of 4-methylbenzenethiol (Figure S10). The derivatization process is limited by the reactivity and concentration of target analytes in addition to variations in the sample matrix; therefore, the method detection limit defined here is an approximation only and will vary between samples and matrices. The general method detection limit was established based on a reaction with 2.0 uM of compound **(4)** and 4-methylbenzenethiol as an archetypal thiol (see Equation 1 in the main body of the paper). The response of the lowest identifiable derivative, **(5)**, was then used to establish the limit detection (3 times the signal-to-noise ratio) and quantitation (10 times the signal-to-noise ratio) for the jet fuel samples. The limit of detection for **(5)** was examined and found to be 39 counts (1.2 ng/L) with a limit of quantitation of 130 counts (4.0 ng/L).