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Supporting Information

Electronic Effects of the Substituents on the Catalytic Conversion of Thiolates to Alcohols by Carboxylate Bridged Nonheme Binuclear Fe(II) and Co(II) Complexes

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EXPERIMENTAL PROCEDURES.

Construction of Calibration Curves. The calibration curves for alcohols for points 7.5 mM to 37.5 mM have previously been reported by us.[1] The present calibration curves for alcohols have been drawn with these data points along with the additional data points as mentioned below for each alcohol:

i. Benzyl alcohol: The data points, 45 mM, 52.5 mM and 60 mM, have been included in the calibration curve in the present work.
ii. 1-Hexanol: The data points, 45 mM and 60 mM, have been included in the calibration curve in the present work.
iii. 1-Decanol: The data points, 45 mM and 60 mM, have been included in the calibration curve in the present work.
iv. 1-Dodecanol: The data points, 45 mM and 60 mM, have been included in the calibration curve in the present work.
v. *tert*-Butanol: The data points, 45 mM and 60 mM, have been included in the calibration curve in the present work.

The calibration curve used here for the phenols and benzoic acid has previously been reported by us.[1]

General Procedure for Optimization Reactions.

General procedure for the optimization of the amount of aliphatic thiolates for [Co_2(PhBIMP)(μ-O_2C-C_6H_3-2,6-$(OMe)_2$)(DMF)]$(BF_4)_2$ (2d$(BF_4)_2$). To a mixture of **2d**$(BF_4)_2$ (0.015 mmol, 25.4 mg) and H_2O (300, 600, 750, 900, 1050 and 1200 equiv) in 0.5 mL of DMF was added a solution of $NaSCH_2Ph$ in varying equivalents (10, 20, 25, 30, 35, and 40 equiv.) respectively in 0.5 ml DMF in separate sets and the mixtures were stirred for 60 h resulting in the formation of a pale pink colored solution along with a deep pink solid in each case. The resulting solution was filtered. The filtrate was diluted with Et_2O and kept overnight at −35 °C. The solution was then decanted off, diluted to 10 mL with Et_2O in a volumetric flask, and GC experiment was performed using the solution. The deep pink solid obtained was found to be insoluble in CH_2Cl_2, pentane, hexane, MeCN, MeOH, EtOH, THF, Toluene, $CHCl_3$ and DMSO. The yields of $PhCH_2OH$ obtained were 8.85 equiv

(10 equiv $NaSCH_2Ph$); 18.61 equiv (20 equiv $NaSCH_2Ph$); 23.4 equiv (25 equiv $NaSCH_2Ph$); 26.81 equiv (30 equiv $NaSCH_2Ph$); 30.87 equiv (35 equiv $NaSCH_2Ph$); 29.74 equiv (40 equiv $NaSCH_2Ph$).

Same conditions were used for the catalysis using $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}F_2)(MeCN)](BF_4)_2$, (**2e**$(BF_4)_2$).

General procedure for the optimization of the amount of aromatic thiolates for $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)(DMF)](BF_4)_2$ (2d$(BF_4)_2$). To a mixture of **2d**$(BF_4)_2$ (0.0150 mmol, 25.4 mg) and H_2O (300, 450, 600 and 750 equiv) in 0.5 mL of DMF was added a solution of NaSPh in varying equivalents (10, 15, 20 and 25 equiv) respectively in 0.5 ml DMF in separate sets and the mixtures were stirred for 168 h resulting in the formation of a pale pink (for 10 and 15 equiv NaSPh)/green (for 20 and 25 equiv NaSPh) solution. The resulting solution was filtered. The filtrate was diluted with Et_2O and kept overnight at -35 ˚C. The solution was then decanted off, diluted to 10 mL with Et_2O in a volumetric flask, and GC experiment was performed using the solution. The yields of PhOH obtained were 6.76 equiv (10 equiv NaSPh); 8.96 equiv (15 equiv NaSPh); 13.86 equiv (20 equiv NaSPh); and 12.59 equiv (25 equiv NaSPh).

Same optimized conditions were used for the catalysis using $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}F_2)(MeCN)](BF_4)_2$, (**2e**$(BF_4)_2$).

General procedure for the optimization of the amount of aliphatic thiolates for $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)(DMF)](BF_4)_2$ (2f$(BF_4)_2$). To a mixture of **2f**$(BF_4)_2$ (0.0150 mmol, 25.9 mg) and H_2O (300, 600, 900, 1050, 1200 and 1350 equiv) in 0.5 mL of DMF was added a solution of $NaSCH_2Ph$ in varying equivalents (10, 20, 30, 35, 40 and 45 equiv) respectively in 0.5 ml DMF in separate sets and the mixtures were stirred for 60 h resulting in the formation of a pale pink colored solution along with a deep pink solid in each case. The resulting solution was filtered. The filtrate was diluted with Et_2O and kept overnight at −35 ˚C. The solution was then decanted off, diluted to 10 mL with Et_2O in a volumetric flask, and GC experiment was performed using the solution. The deep pink solid obtained was found to be insoluble in CH_2Cl_2, Pentane, Hexane, CH_3CN, MeOH, EtOH, THF, Toluene, $CHCl_3$ and DMSO. The yields of $PhCH_2OH$ obtained were 9.35 equiv (10 equiv $NaSCH_2Ph$); 18.77 equiv (20 equiv $NaSCH_2Ph$); 27.46 equiv (30 equiv

$NaSCH_2Ph$); 31.93 equiv (35 equiv $NaSCH_2Ph$); 37.54 equiv (40 equiv $NaSCH_2Ph$); 36.72 equiv (45 equiv $NaSCH_2Ph$).

General procedure for the optimization of the amount of aromatic thiolates for $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)(DMF)](BF_4)_2$ ($2f(BF_4)_2$). To a mixture of **2f**$(BF_4)_2$ (0.0150 mmol, 25.9 mg) and H_2O (300, 450, 600, 750 and 900 equiv) in 0.5 mL of DMF was added a solution of NaSPh in varying equivalents (10, 15, 20, 25 and 30 equiv) respectively in 0.5 ml DMF in separate sets and the mixtures were stirred for 168 h resulting in the formation of a pale pink (for 10 and 15 equiv NaSPh)/green (for 20, 25 and 30 equiv NaSPh) solution. The resulting solution was filtered. The filtrate was diluted with Et_2O and kept overnight at −35 °C. The solution was then decanted off, diluted to 10 mL with Et_2O in a volumetric flask, and GC experiment was performed using the solution. The yields of PhOH obtained were 7.35 equiv (10 equiv NaSPh); 9.38 equiv (15 equiv NaSPh); 14.62 equiv (20 equiv NaSPh); 18.17 equiv (25 equiv NaSPh); 16.48 equiv (25 equiv NaSPh).

General procedure for confirming the generation of hydrosulfide.

Generation of hydrosulfide during the catalytic hydrolysis of $NaSCH_2Ph$ using $2d(BF_4)_2$ as the catalyst. To a mixture of **2d**$(BF_4)_2$ (0.0150 mmol, 25.4 mg) and H_2O (15.75 mmol, 283.5 μL) in 0.5 mL of DMF was added a solution of $NaSCH_2Ph$ (0.525 mmol, 76.7 mg) in 0.5 ml DMF and the mixture was allowed to stir for 60 h. The reaction mixture was then filtered and a methanolic solution of $Cu(OAc)_2{\cdot}2H_2O$ (0.525 mmol, 114.3 mg) was added into the reaction mixture and further allowed to stir for 12 h which resulted into the precipitation of characteristic brown-black solid of CuS. The solid was allowed to settle down, and filtered. The brown-black solid was then washed several times with DMF followed by Et_2O and dried in vacuum to afford CuS (42.6 mg, 84.8%, 29.7 equivs.).

Generation of hydrosulfide during the catalytic hydrolysis of $NaSCH_2Ph$ using $4b(BF_4)_2$ as the catalyst. A procedure like that described for **2d**$(BF_4)_2$ but using **4b**$(BF_4)_2$ (0.0150 mmol, 25.3 mg), $NaSCH_2Ph$ (0.525 mmol, 76.7 mg) and H_2O (15.75 mmol, 283.5 μL), was followed. Yield of CuS = 30.4 mg (60.6%, 21.2 equiv).

Generation of hydrosulfide during the catalytic hydrolysis of NaSPh using 2d$(BF_4)_2$ as the catalyst. To a mixture of **2d**$(BF_4)_2$ (0.0150 mmol, 25.4 mg) and H_2O (9 mmol, 162 μL) in 0.5 mL of DMF was added a solution of NaSPh (0.300 mmol, 39.6 mg) in 0.5 ml DMF and the mixture was stirred for 168 h. The reaction mixture was then filtered and a methanolic solution of $Cu(OAc)_2 \cdot 2H_2O$ (0.300 mmol, 65.3 mg) was added into the reaction mixture and further allowed to stir for 12 h which resulted into the precipitation of characteristic brown-black solid of CuS. The solid was allowed to settle down, and filtered. The brown-black solid was then washed several times with DMF followed by Et_2O and dried in vacuum to afford CuS (18.6 mg, 64.9%, 13 equivs.).

Generation of hydrosulfide during the catalytic hydrolysis of NaSPh using 4b$(BF_4)_2$ as the catalyst. A procedure like that described for **2d**$(BF_4)_2$ but using **4b**$(BF_4)_2$ (0.0150 mmol, 25.3 mg), NaSPh (0.300 mmol, 39.6 mg) and H_2O (9 mmol, 162 μL), was followed. Yield of CuS = 10.75 mg (37.5%, 7.5 equiv).

Table S1. X-ray crystallographic data for compounds **2d**$(BF_4)_2$, **2e**$(BF_4)_2$, **2f**$(BF_4)_2$ and **4c**$(BF_4)_2$.[a]

compounds	**2d**$(BF_4)_2$·DMF	**2e**$(BF_4)_2$·2MeCN	**2f**$(BF_4)_2$·Et_2O	**4c**$(BF_4)_2$·MeCN
CCDC number	2455092	2455376	2464999	2457654
temp (K)	150(2)	130(2)	140(2)	140(2)
formula	$C_{92}H_{92}B_2Co_2F_8N_{12}O_7$	$C_{90}H_{81}B_2Co_2F_{10}N_{13}O_3$	$C_{94}H_{97}B_2Co_2F_8N_{11}O_8$	$C_{88}H_{78}B_2F_{10}Fe_2N_{12}O_3$
formula weight	1769.25	1722.15	1800.30	1674.94
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	14.1055(5)	13.9956(7)	14.0777(7)	14.2379(6)
b, Å	19.2368(6)	15.4261(6)	19.3657(11)	15.3665(6)
c, Å	19.9639(6)	21.4618(7)	20.0923(9)	21.6986(9)
α, deg	84.734(3)	90.995(3)	85.067(2)	92.180(2)
β, deg	71.040(3)	105.600(4)	71.752(2)	106.103(2)
γ, deg	76.279(3)	91.867(4)	77.266(2)	91.798(2)
V, $Å^3$	4976.4(3)	4458.8(3)	5073.4(5)	4553.5(3)
Z	2	2	2	2
ρ_{calcd}, gm/cm^3	1.181	1.283	1.178	1.222
μ, mm^{-1}	0.403	0.448	0.397	0.391
θ range, deg	1.699-25.680	1.969-25.682	2.109-25.694	1.952-25.690
completeness to θ, %	98.6	98.7	99.7	99.7
reflections collected	47916	41765	151022	125731
independent reflections	18637	16710	19240	17264
R(int)	0.0567	0.0895	0.0682	0.0805
Restraints [b]	42	77	96	82
parameters	1102	1064	1088	1038
Max., min. transmission	1.00000, 0.58218	1.00000, 0.89967	0.7453, 0.6768	0.7395, 0.6902
R1[c](wR2)[d] [I>2sigma(I)]	0.0678 (0.1823)	0.0718 (0.1982)	0.0762 (0.2032)	0.0627 (0.1624)
R1[c](wR2)[c]	0.0828 (0.1956)	0.0902 (0.2187)	0.0835 (0.2083)	0.0793 (0.1700)
GOF(F2)[e]	1.027	1.041	1.078	1.035
max, min peaks, e.$Å^{-3}$ [f]	1.020, -0.891	0.812, -0.962	1.155, -1.019	0.687, -0.920

[a]Mo Kα radiation (λ = 0.71073 Å). [b]**2d**$(BF_4)_2$·DMF, disordered BF_4^- anion; **2e**$(BF_4)_2$·2MeCN, disordered BF_4^- anion and ligand; **2f**$(BF_4)_2$·Et_2O, disordered BF_4^- anion and ligand; **4c**$(BF_4)_2$·MeCN, disordered BF_4^- anion and ligand. [c]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [d]$wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [e]$GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of data and p is the number of refined parameters. [f]electron density near: **2d**$(BF_4)_2$·DMF, disordered BF_4^- anion; **2e**$(BF_4)_2$·2MeCN, disordered BF_4^- anion; **2f**$(BF_4)_2$·Et_2O, disordered BF_4^- anion; **4c**$(BF_4)_2$·MeCN, disordered BF_4^- anion.

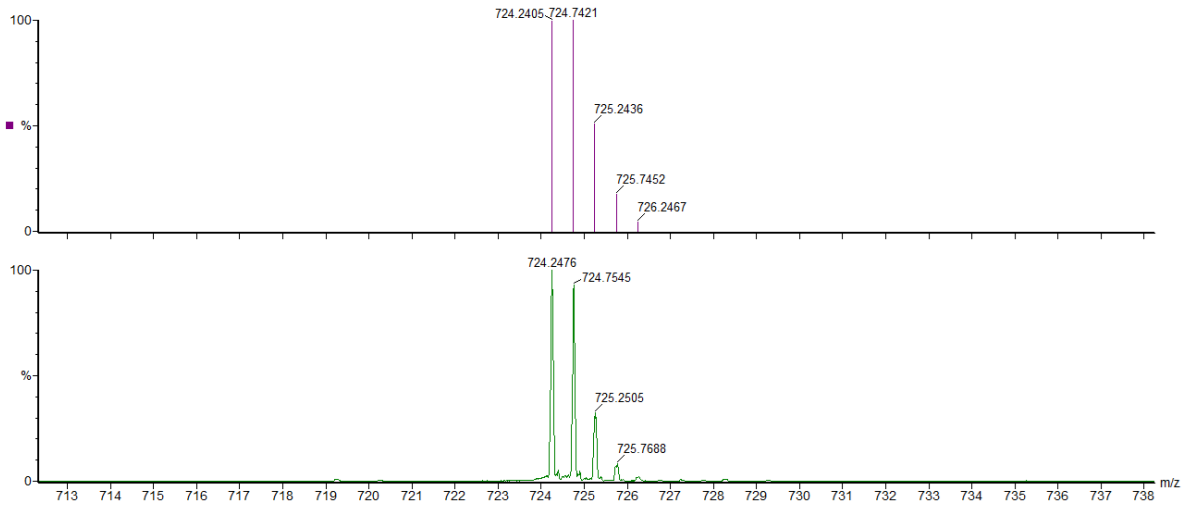


Figure S1. Mass spectrum (in MeCN) for $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)(DMF)](BF_4)_2$ (**2d**$(BF_4)_2$) shows the presence of $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{2+}$ at m/z = 724.2405 (simulated, purple line); 724.2476 (obtained, green line).

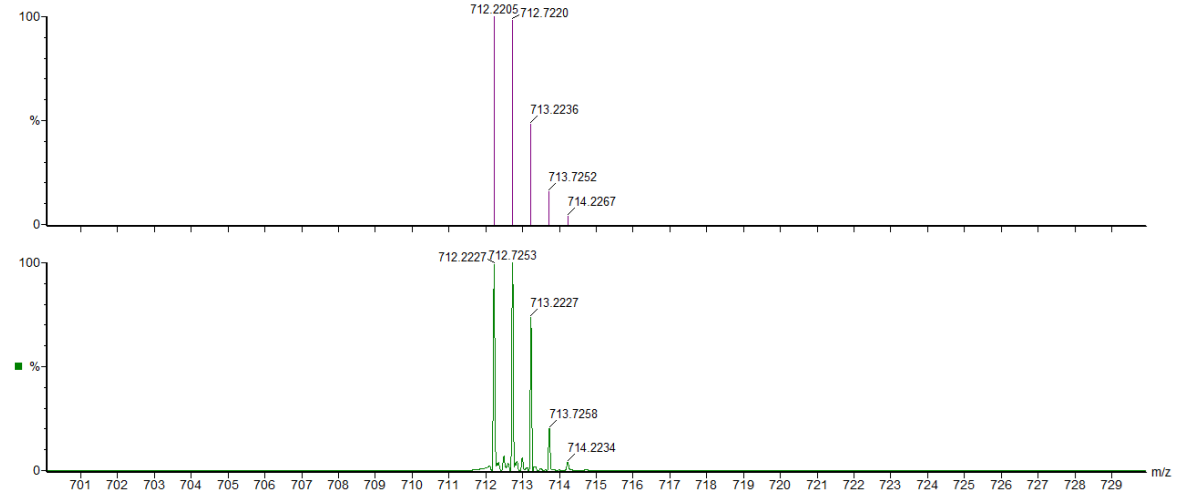


Figure S2. Mass spectrum (in MeCN) for $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}F_2)(MeCN)](BF_4)_2$, (**2e**$(BF_4)_2$) shows the presence of $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}F_2)]^{2+}$ at m/z = 712.2205 (simulated, purple line); 712.2227 (obtained, green line).

Table S2. Optimization of the ratio of **2d**$(BF_4)_2$: aliphatic thiolates. Conditions: thiolate:H_2O = 1:30, reaction time = 60 h, substrate used = $NaSCH_2Ph$, solvent = DMF, temperature = 25 °C.

$NaSCH_2Ph$ Used		Ratio of **2d**$(BF_4)_2$: $NaSCH_2Ph$	GC Yield (%) of $PhCH_2OH$	GC Yield (equiv) of $PhCH_2OH$	Yield (%) of Recovered Catalyst (**2d**)
Equiv	Amount mmol (mg)				
10	0.15 (21.9)	1:10	88.53	8.85	N/A
20	0.3 (43.8)	1:20	93	18.61	N/A
25	0.375 (54.8)	1:25	93.6	23.4	N/A
30	0.45 (65.7)	1:30	89.38	26.81	N/A
35	**0.525 (76.65)**	**1:35**	**88.21**	**30.87**	**N/A**
40	0.6 (87.6)	1:40	74.35	29.74	N/A

Amount of catalyst (**2d**$(BF_4)_2$) = 0.015 mmol (25.4 mg).

Table S3. Optimization of the ratio of **2d**$(BF_4)_2$: aromatic thiolates. Conditions: thiolate:H_2O = 1:30, reaction time = 168 h, substrate used = NaSPh, solvent = DMF, temperature = 25 °C.

NaSPh Used		Ratio of **2d**$(BF_4)_2$: NaSPh	GC Yield (%) of PhOH	GC Yield (equiv) of PhOH	Yield (%) of Recovered Catalyst (**2d**)
Equiv	Amount mmol (mg)				
10	0.15 (19.8)	1:5	67.6	6.76	N/A
15	0.225 (29.7)	1:15	59.73	8.96	N/A
20	**0.3 (39.6)**	**1:20**	**69.3**	**13.86**	**N/A**
25	0.375 (49.5)	1:25	50.37	12.59	N/A

Amount of catalyst (**2d**$(BF_4)_2$) = 0.015 mmol (25.4 mg).

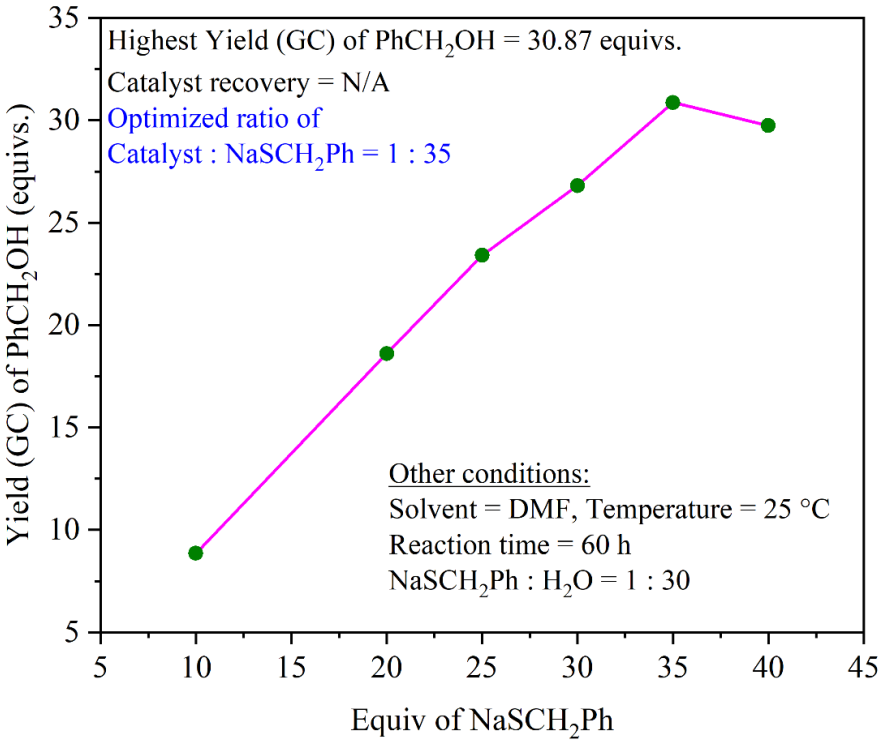


Figure S3. Optimization of the catalyst:thiolate ratio for aliphatic thiolates using **2d**$(BF_4)_2$.

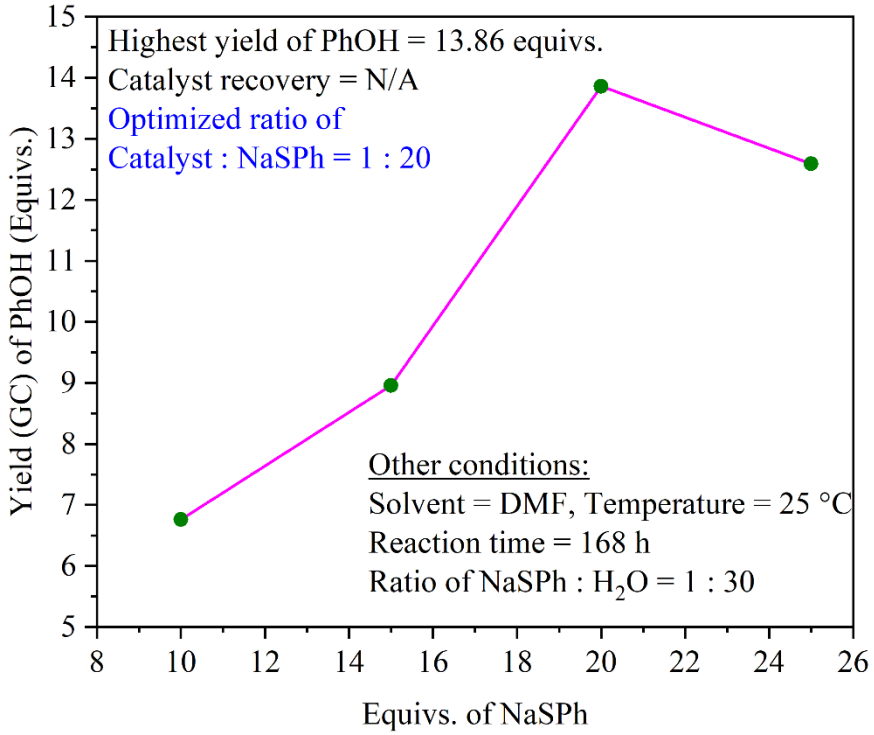


Figure S4. Optimization of the catalyst:thiolate ratio for aromatic thiolates using **2d**$(BF_4)_2$.

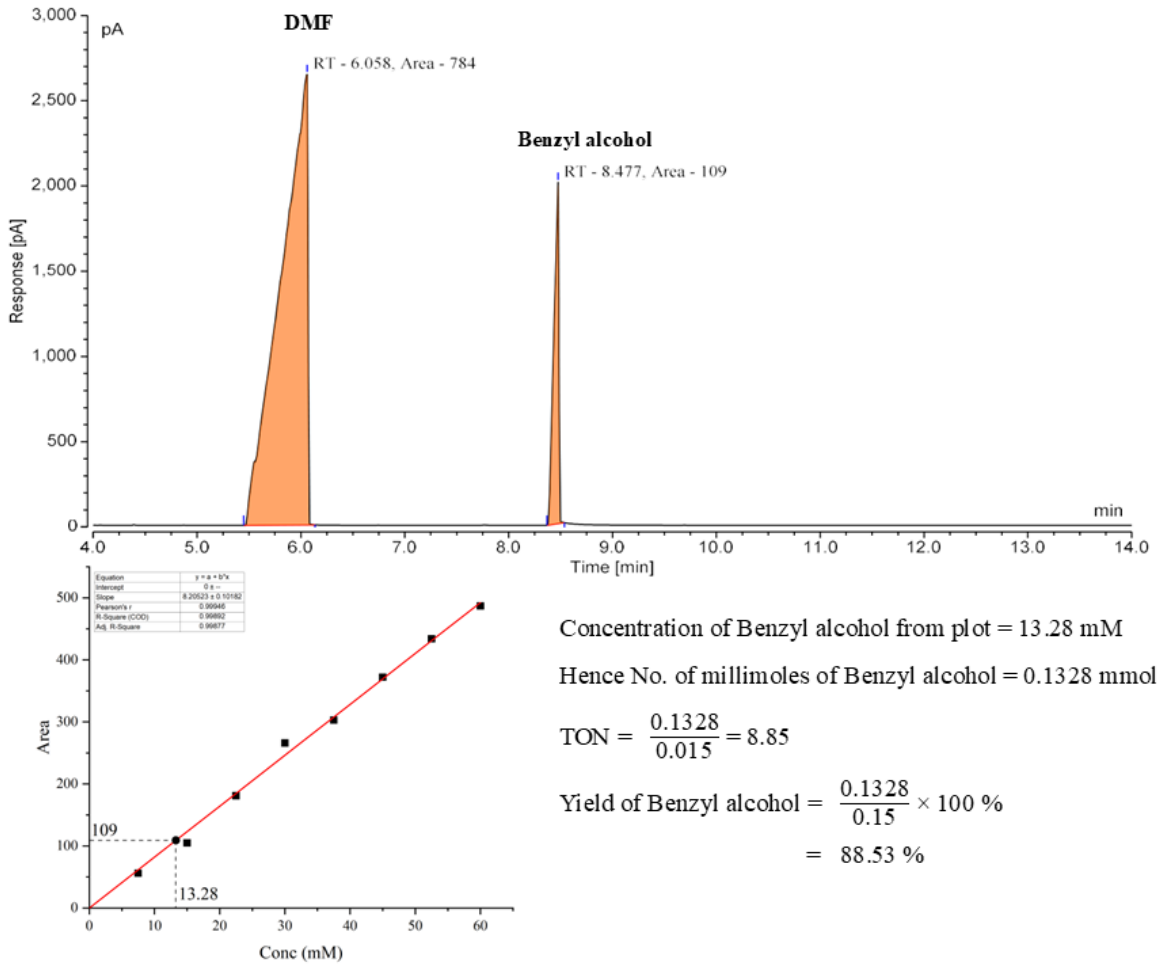


Figure S5. Calculation of yield for $PhCH_2OH$ obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:10, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 88.53 %**. The adjusted R^2 value for the calibration plot is 0.99877.

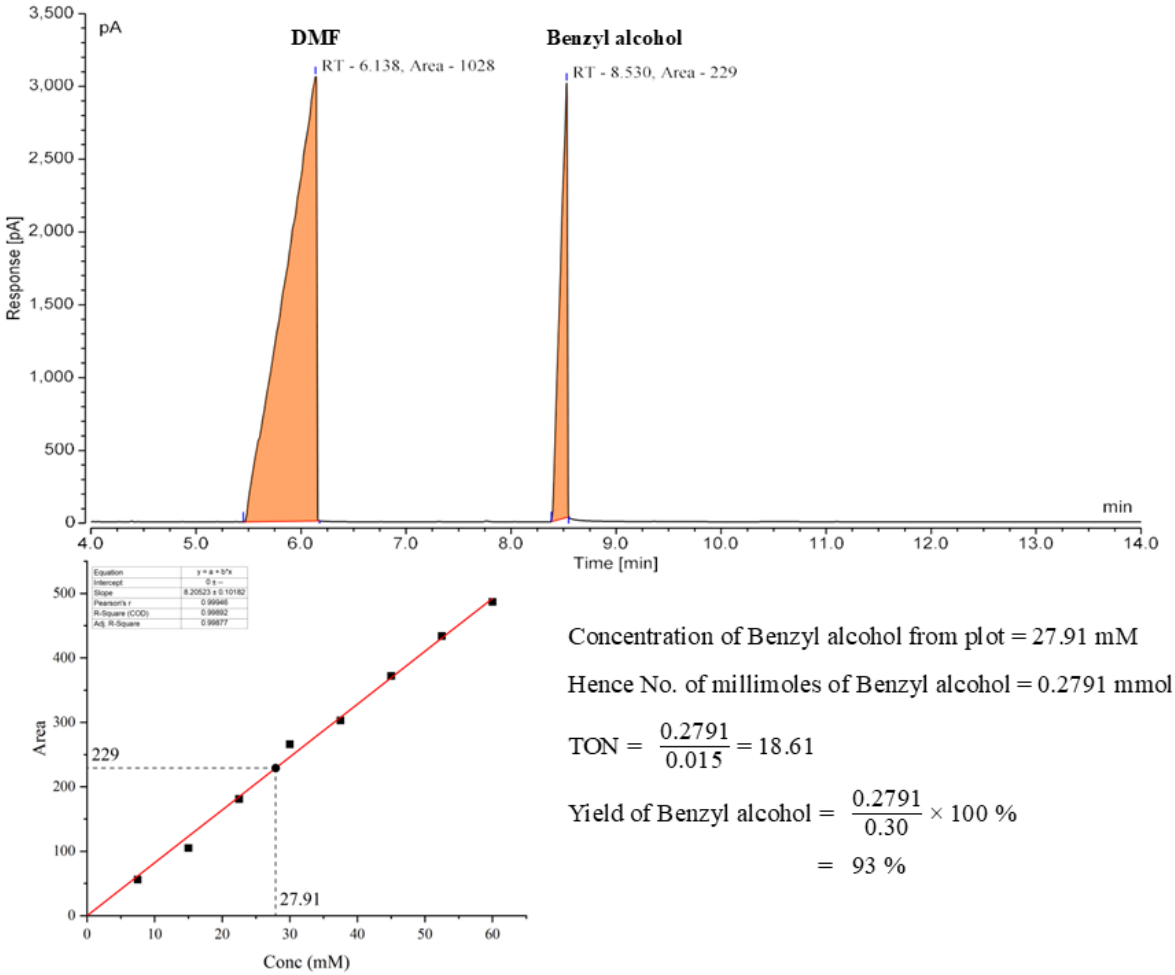
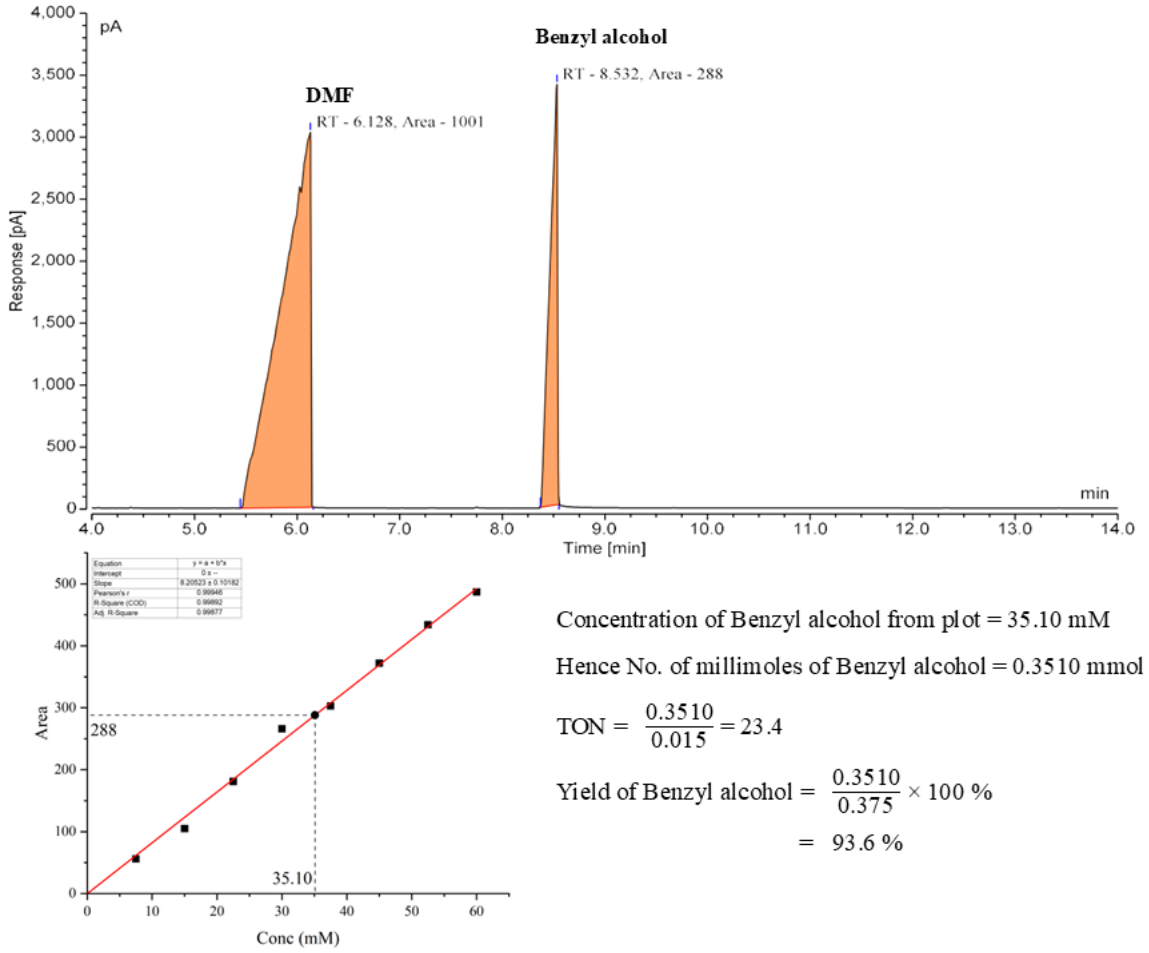


Figure S6. Calculation of yield for $PhCH_2OH$ obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 93 %**. The adjusted R^2 value for the calibration plot is 0.99877.



Concentration of Benzyl alcohol from plot = 35.10 mM

Hence No. of millimoles of Benzyl alcohol = 0.3510 mmol

$$\text{TON} = \frac{0.3510}{0.015} = 23.4$$

$$\text{Yield of Benzyl alcohol} = \frac{0.3510}{0.375} \times 100\ \% = 93.6\ \%$$

Figure S7. Calculation of yield for $PhCH_2OH$ obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 93.6 %**. The adjusted R^2 value for the calibration plot is 0.99877.

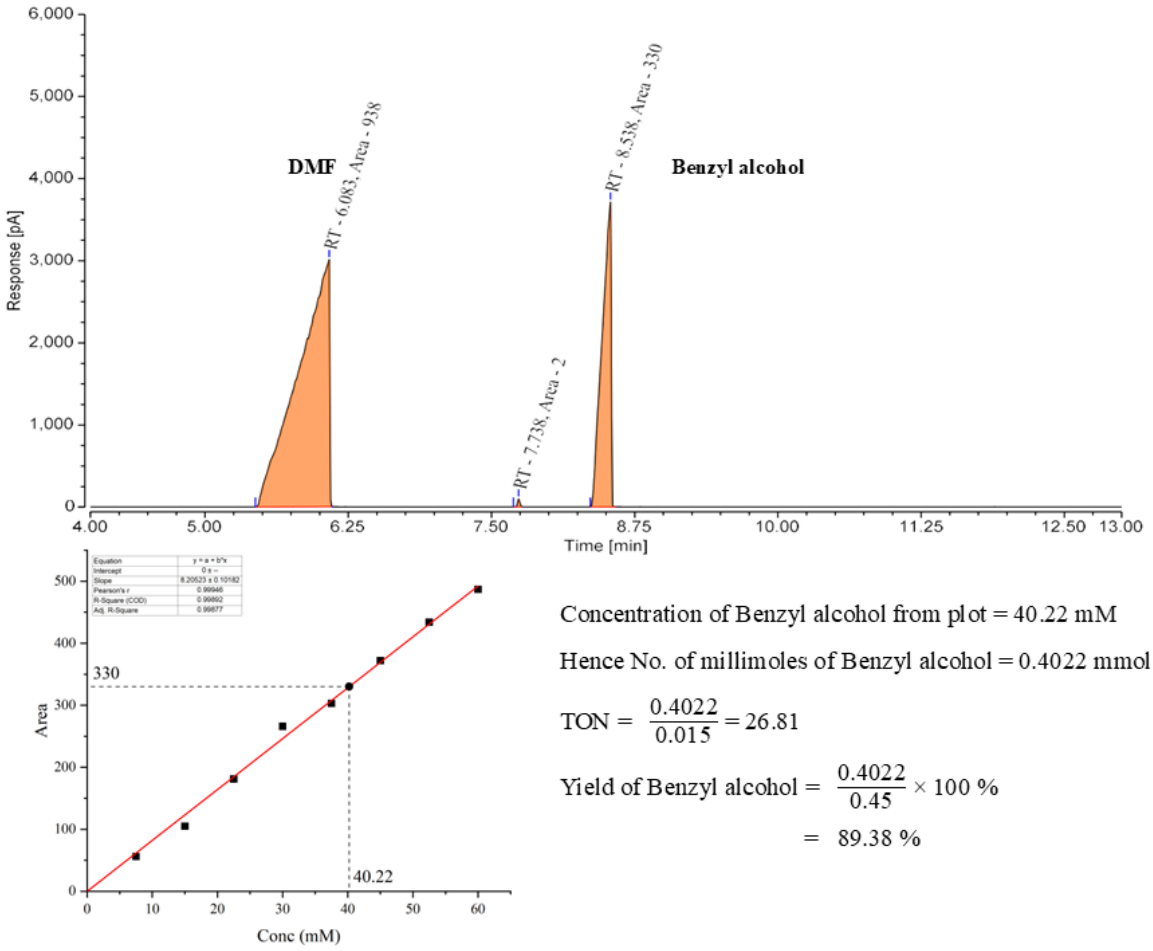
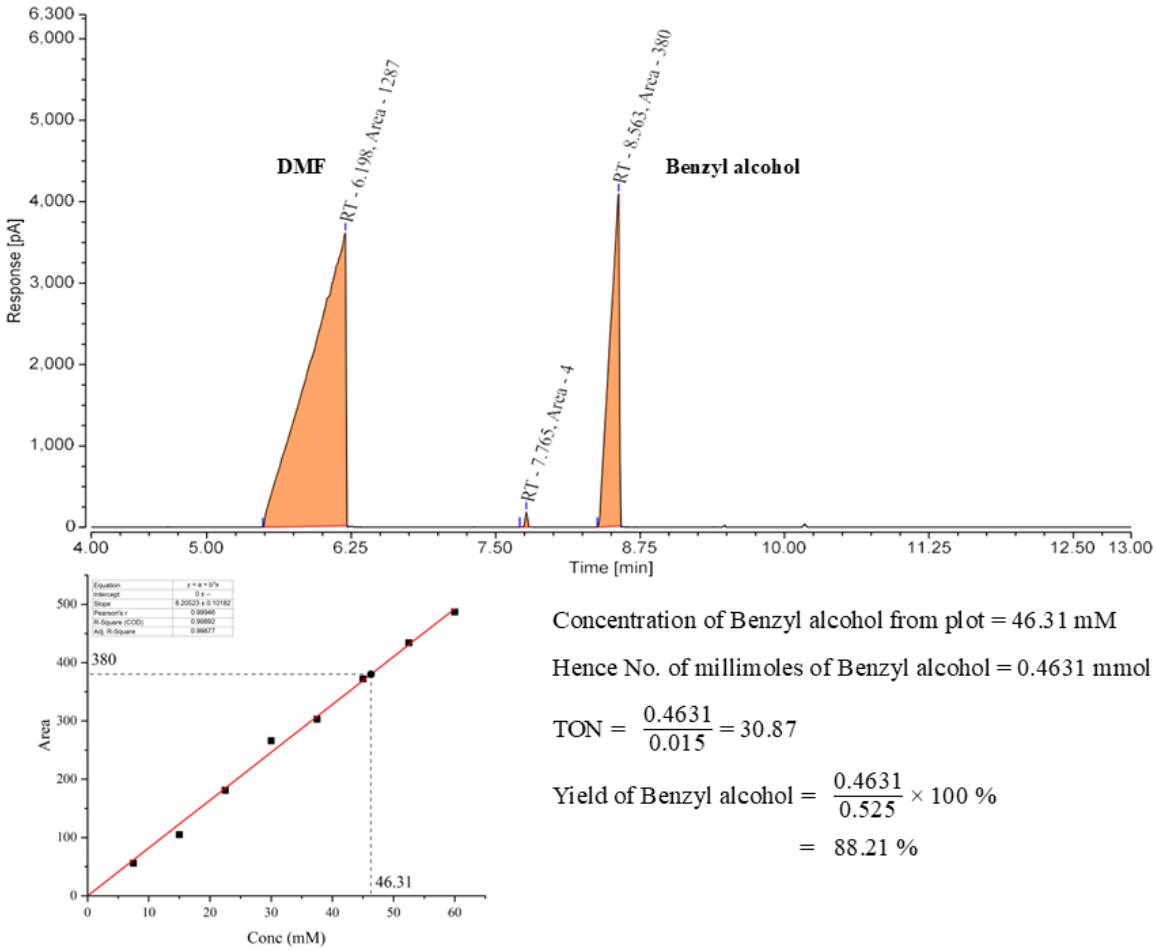


Figure S8. Calculation of yield for $PhCH_2OH$ obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:30, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 89.38 %**. The adjusted R^2 value for the calibration plot is 0.99877.



Concentration of Benzyl alcohol from plot = 46.31 mM

Hence No. of millimoles of Benzyl alcohol = 0.4631 mmol

$$\text{TON} = \frac{0.4631}{0.015} = 30.87$$

$$\text{Yield of Benzyl alcohol} = \frac{0.4631}{0.525} \times 100\ \% = 88.21\ \%$$

Figure S9. Calculation of yield for $PhCH_2OH$ obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 88.21 %**. The adjusted R^2 value for the calibration plot is 0.99877.

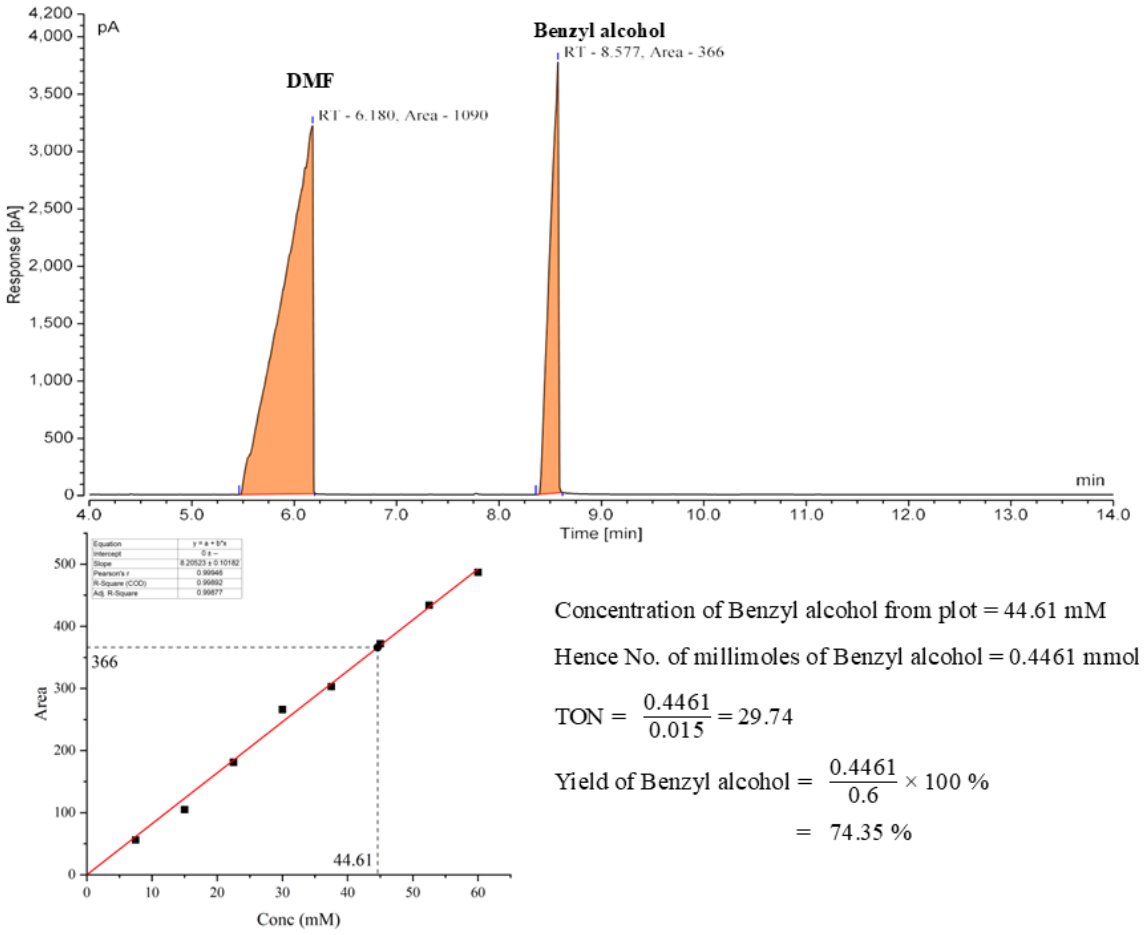


Figure S10. Calculation of yield for $PhCH_2OH$ obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 74.35 %**. The adjusted R^2 value for the calibration plot is 0.99877.

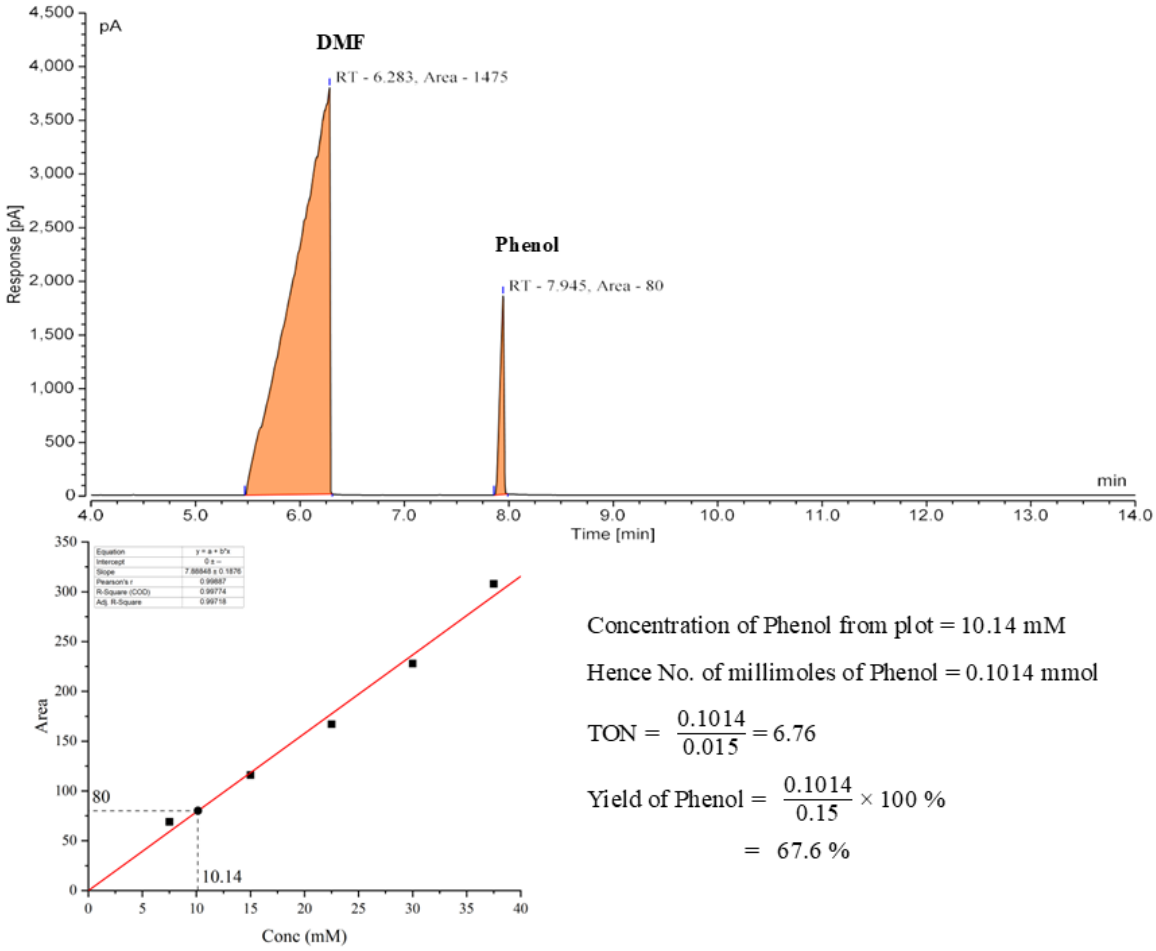


Figure S11. Calculation of yield for PhOH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:10, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 67.6 %**. The adjusted R^2 value for the calibration plot is 0.99718.

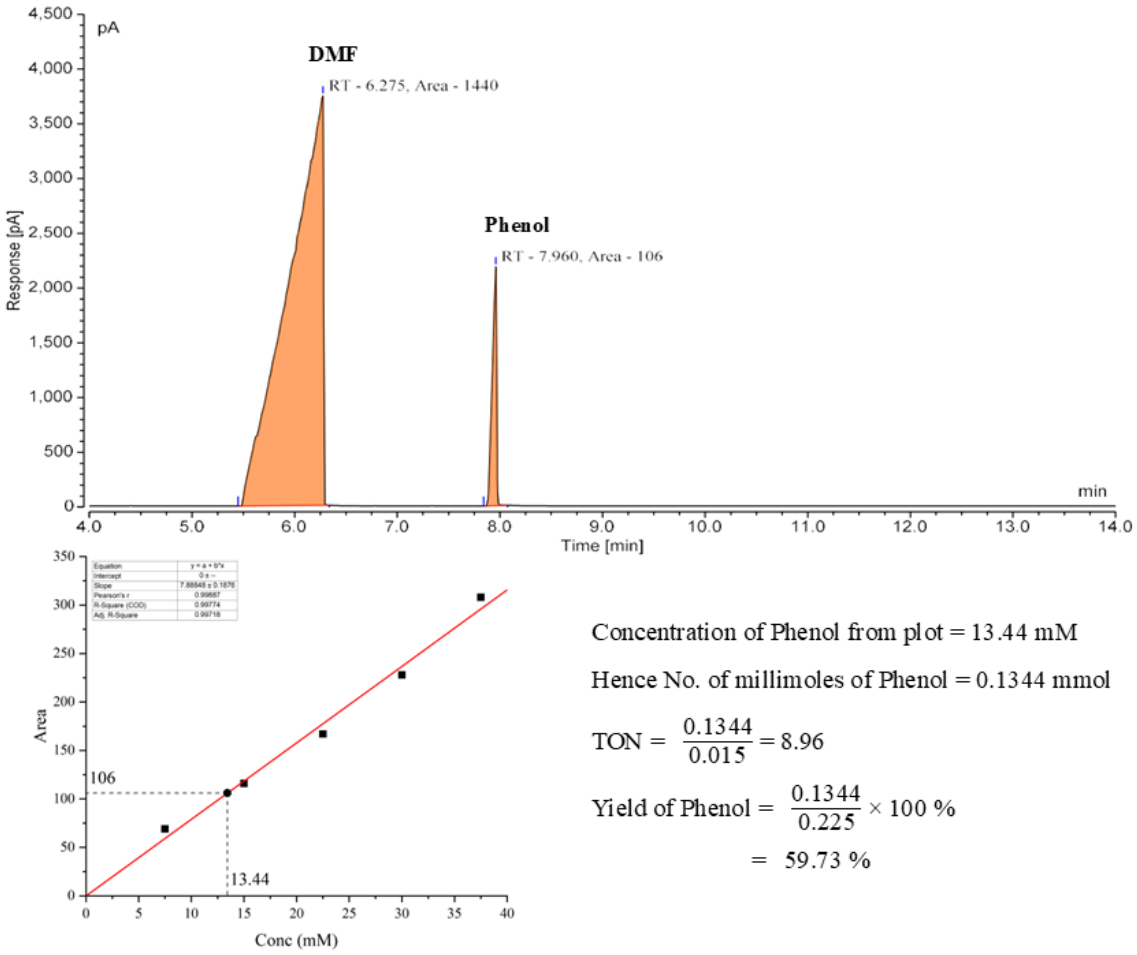


Figure S12. Calculation of yield for PhOH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:15, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 59.73 %**. The adjusted R^2 value for the calibration plot is 0.99718.

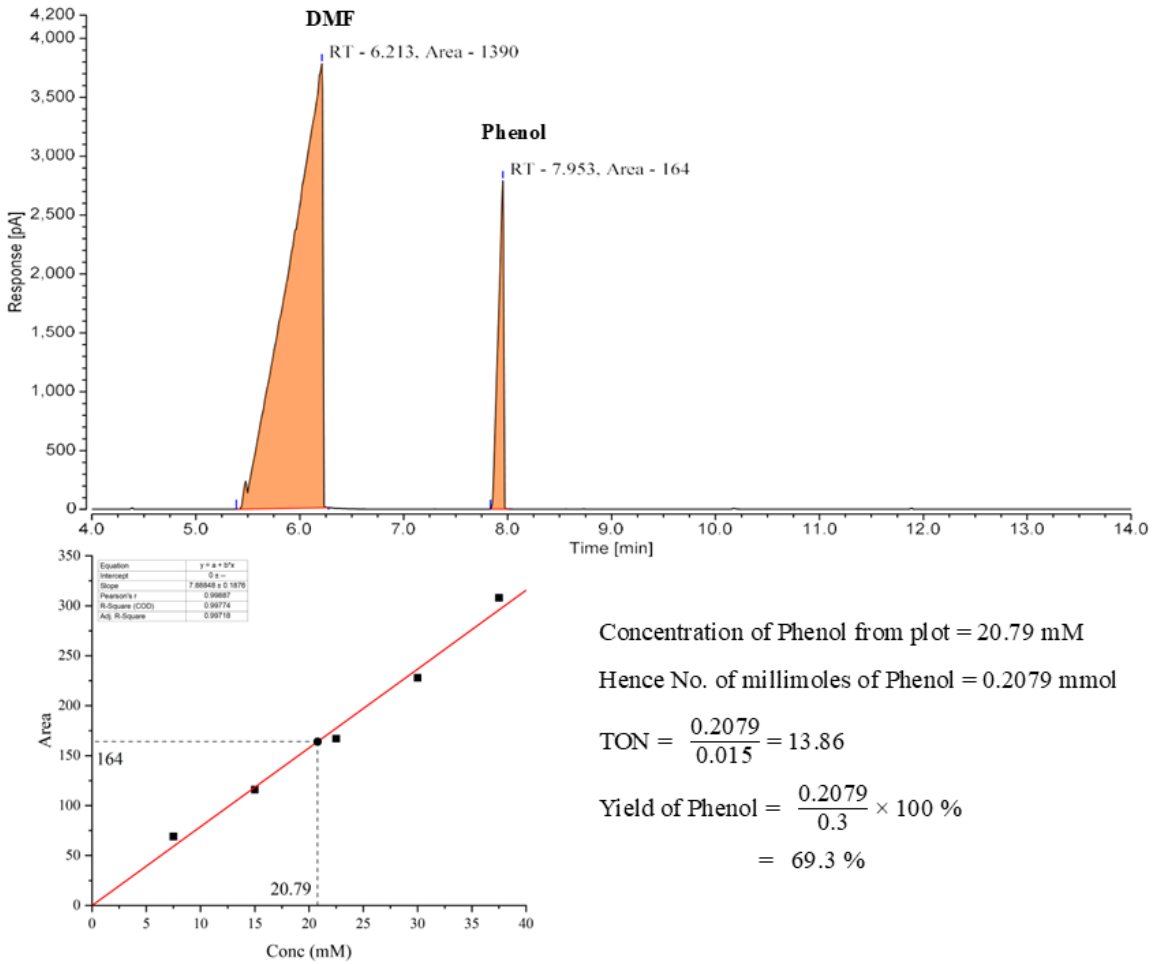


Figure S13. Calculation of yield for PhOH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 69.3 %**. The adjusted R^2 value for the calibration plot is 0.99718.

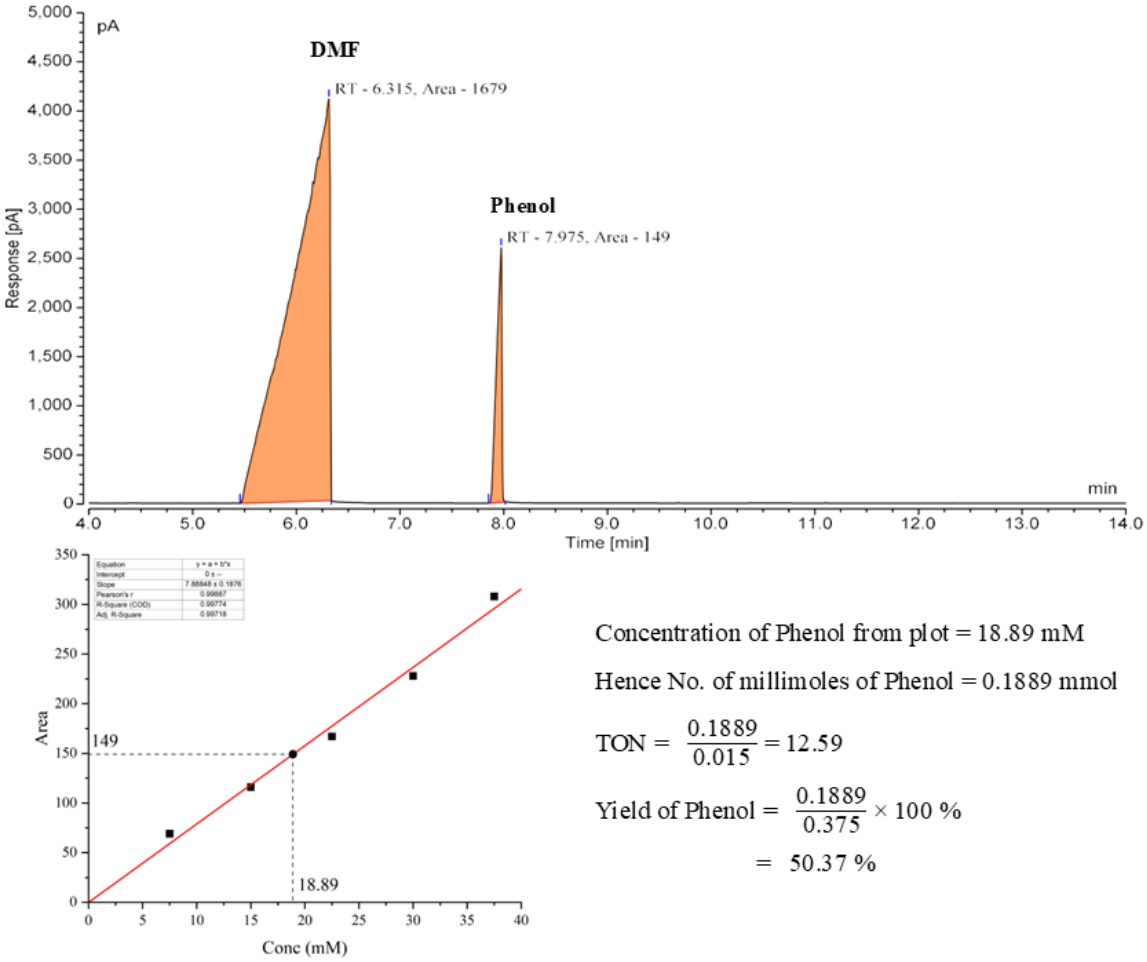


Figure S14. Calculation of yield for PhOH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 50.37 %**. The adjusted R^2 value for the calibration plot is 0.99718.

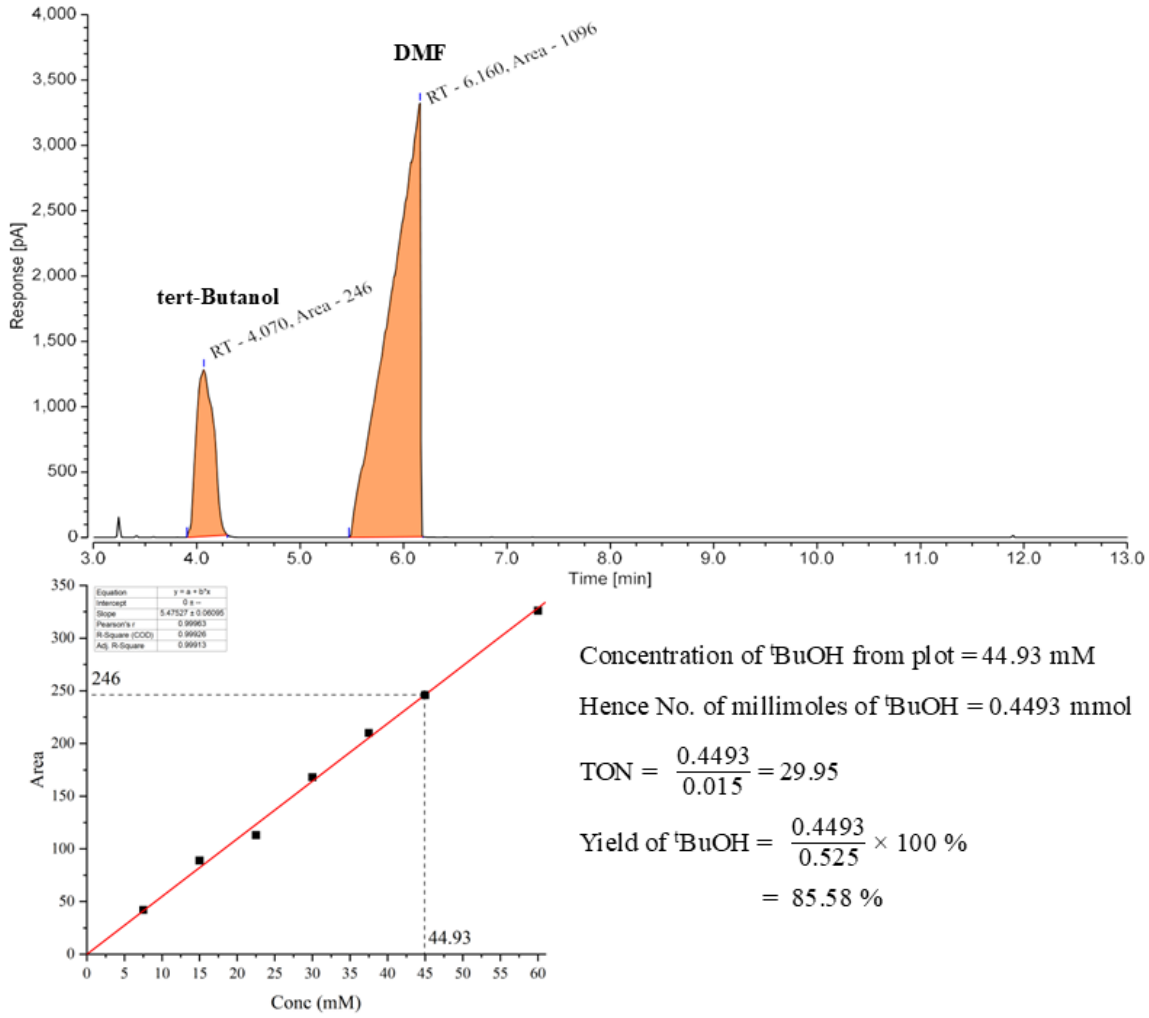


Figure S15. Calculation of yield for ^{t}BuOH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS^{t}Bu. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of ^{t}BuOH = 85.58 %**. The adjusted R^2 value for the calibration plot is 0.99913.

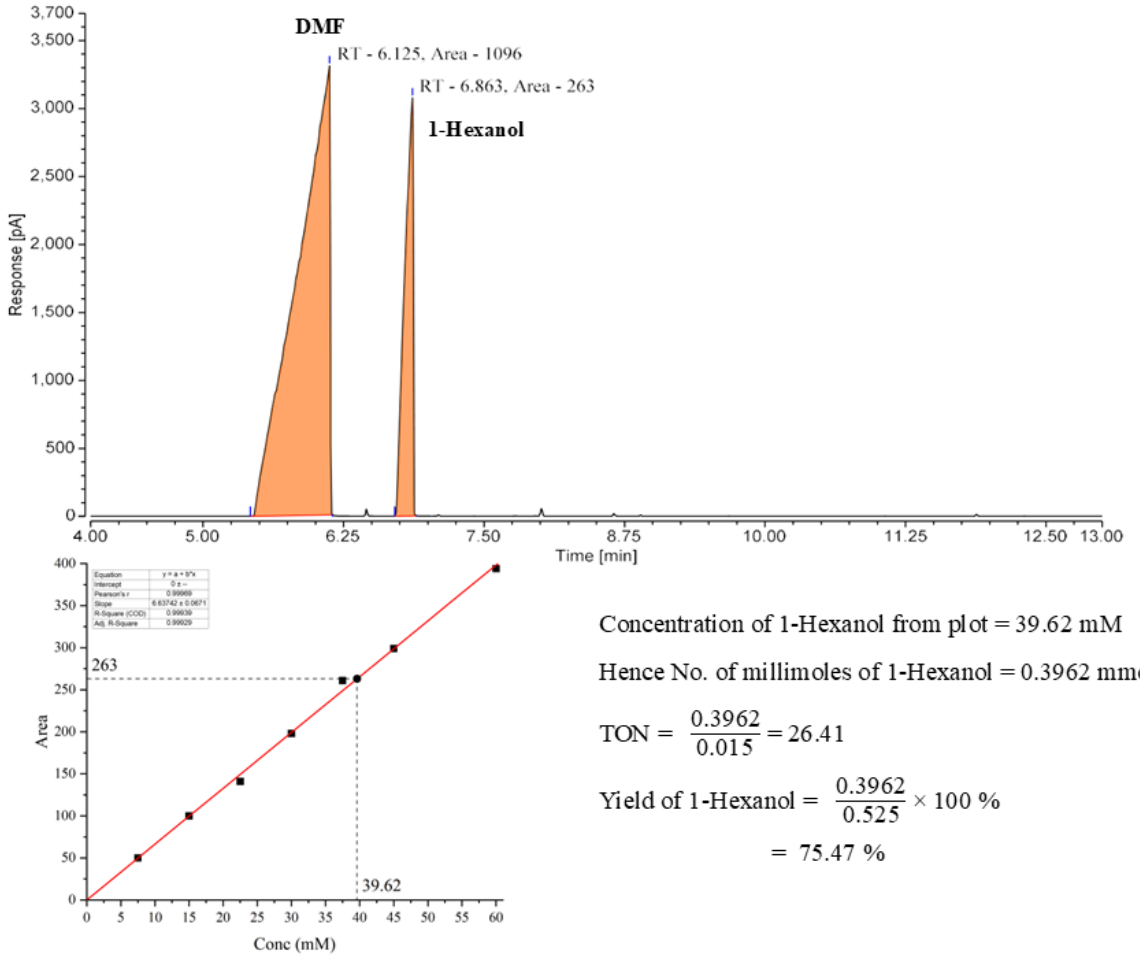


Figure S16. Calculation of yield for CH_3-$(CH_2)_4$-CH_2-OH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_4$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_4$-CH_2-OH = 75.47 %**. The adjusted R^2 value for the calibration plot is 0.99929.

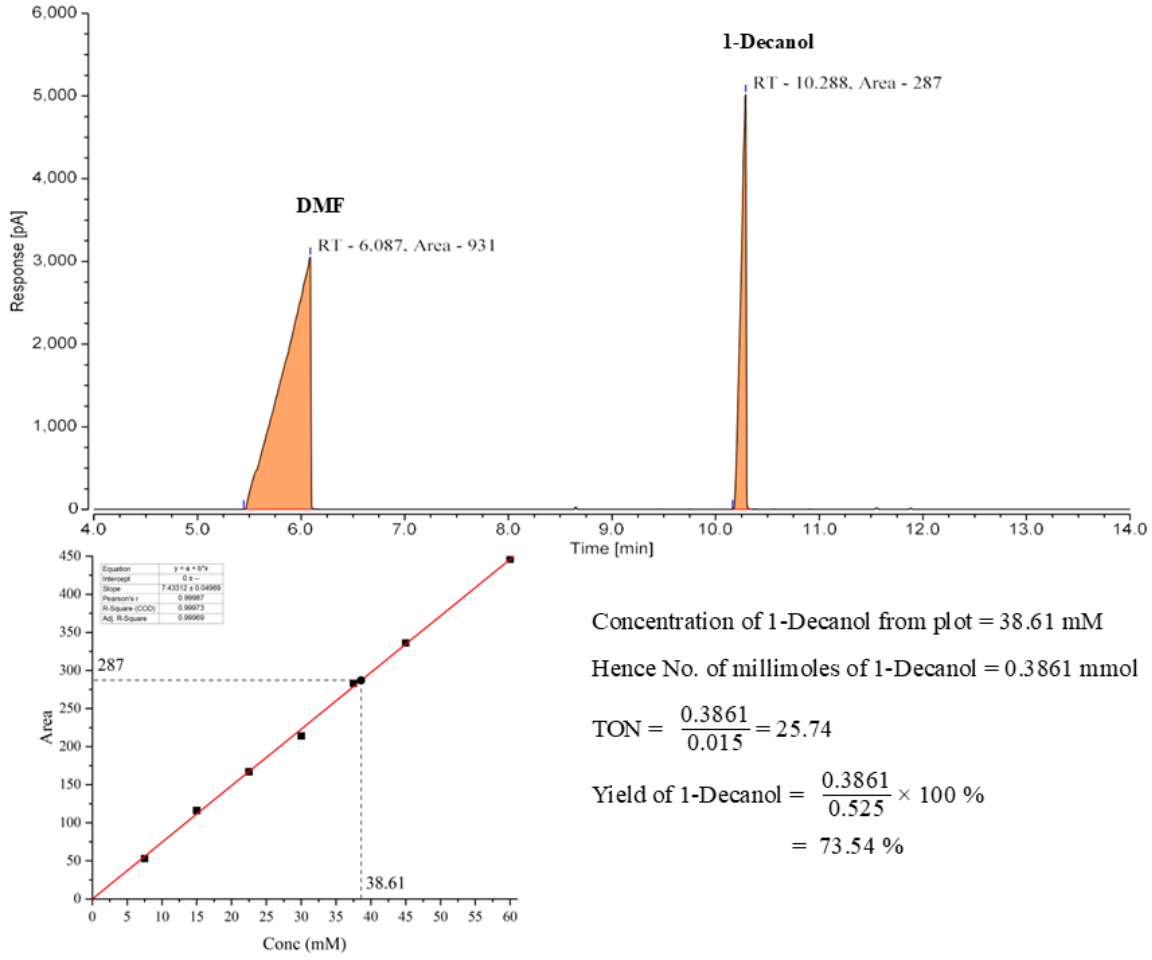


Figure S17. Calculation of yield for CH_3-$(CH_2)_8$-CH_2-OH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_8$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_8$-CH_2-OH = 73.54 %**. The adjusted R^2 value for the calibration plot is 0.99969.

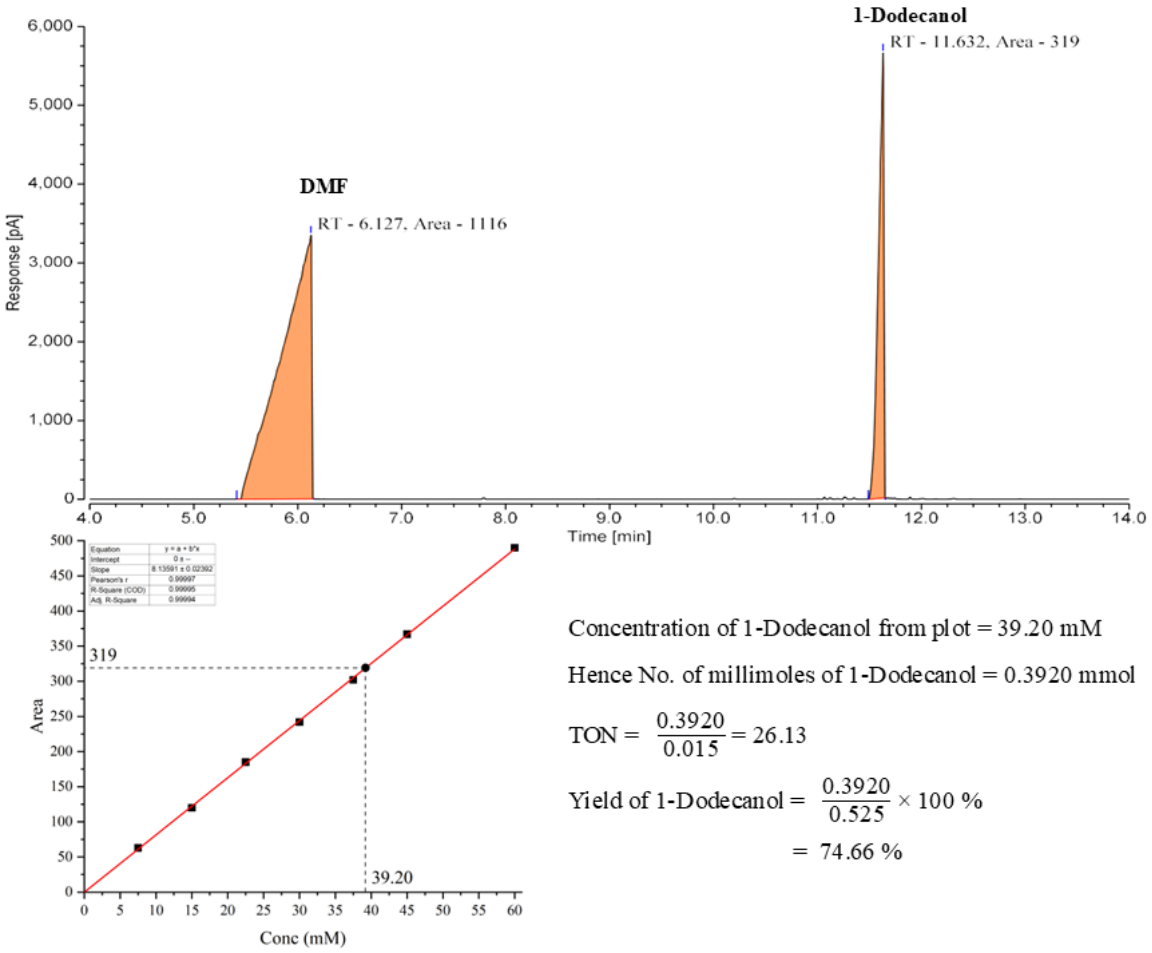


Figure S18. Calculation of yield for CH_3-$(CH_2)_{10}$-CH_2-OH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH)_{10}$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_{10}$-CH_2-OH = 74.66 %**. The adjusted R^2 value for the calibration plot is 0.99994.

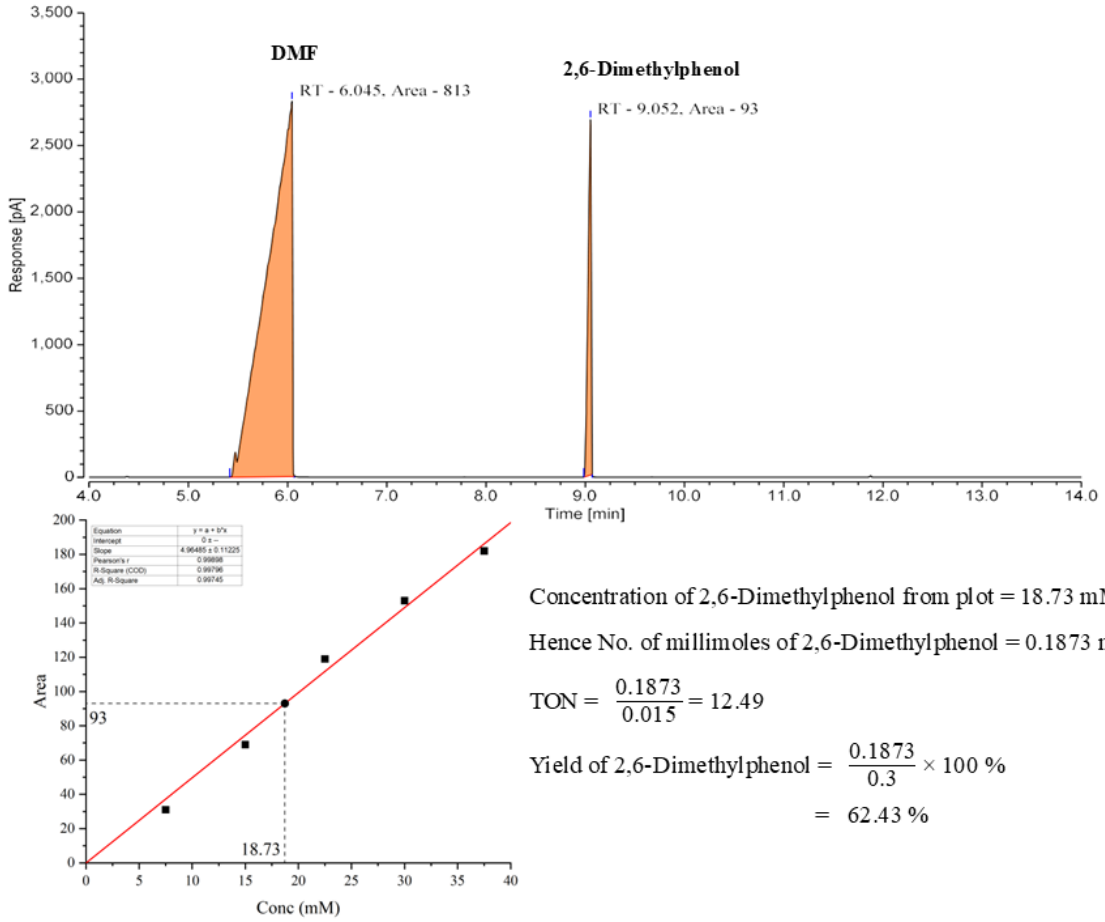


Figure S19. Calculation of yield for 2,6-Me_2-C_6H_3-OH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,6-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,6-Me_2-C_6H_3-OH = 62.43 %**. The adjusted R^2 value for the calibration plot is 0.99745.

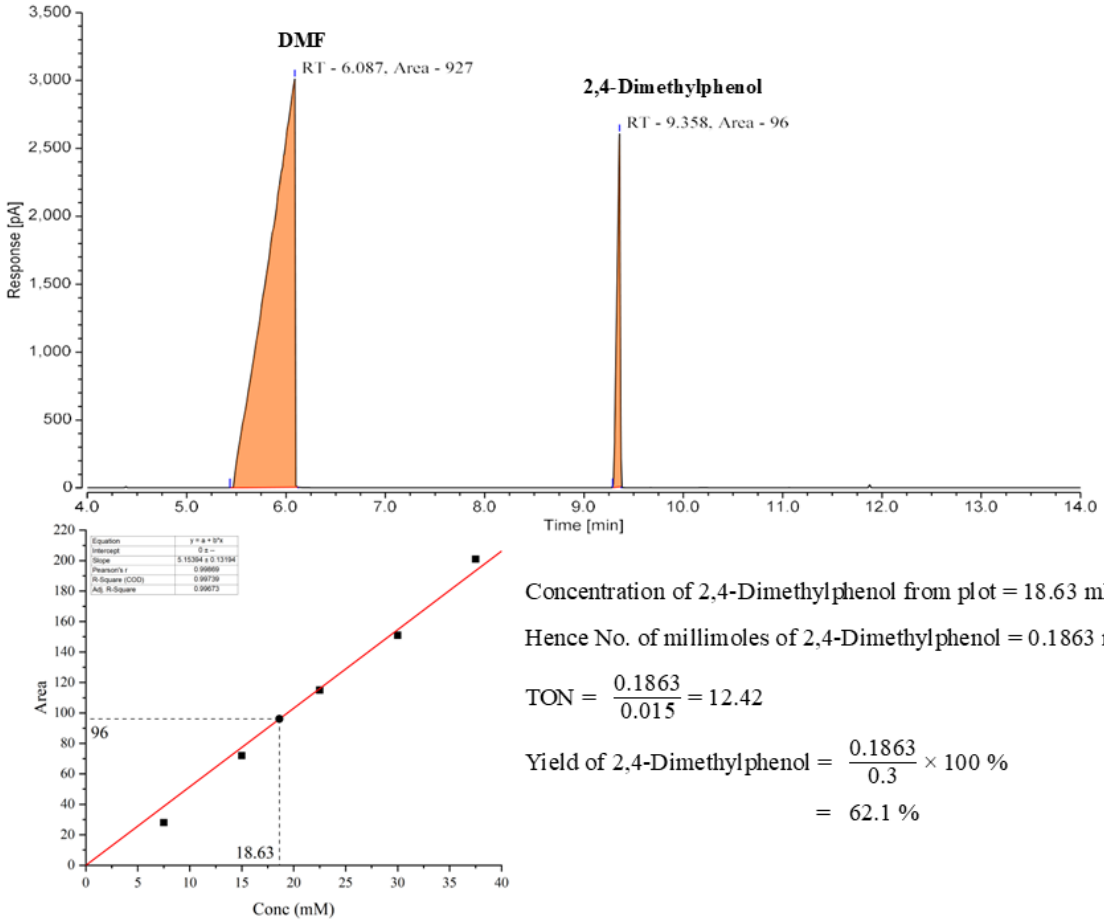


Figure S20. Calculation of yield for 2,4-Me_2-C_6H_3-OH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,4-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,4-Me_2-C_6H_3-OH = 62.1 %**. The adjusted R^2 value for the calibration plot is 0.99673.

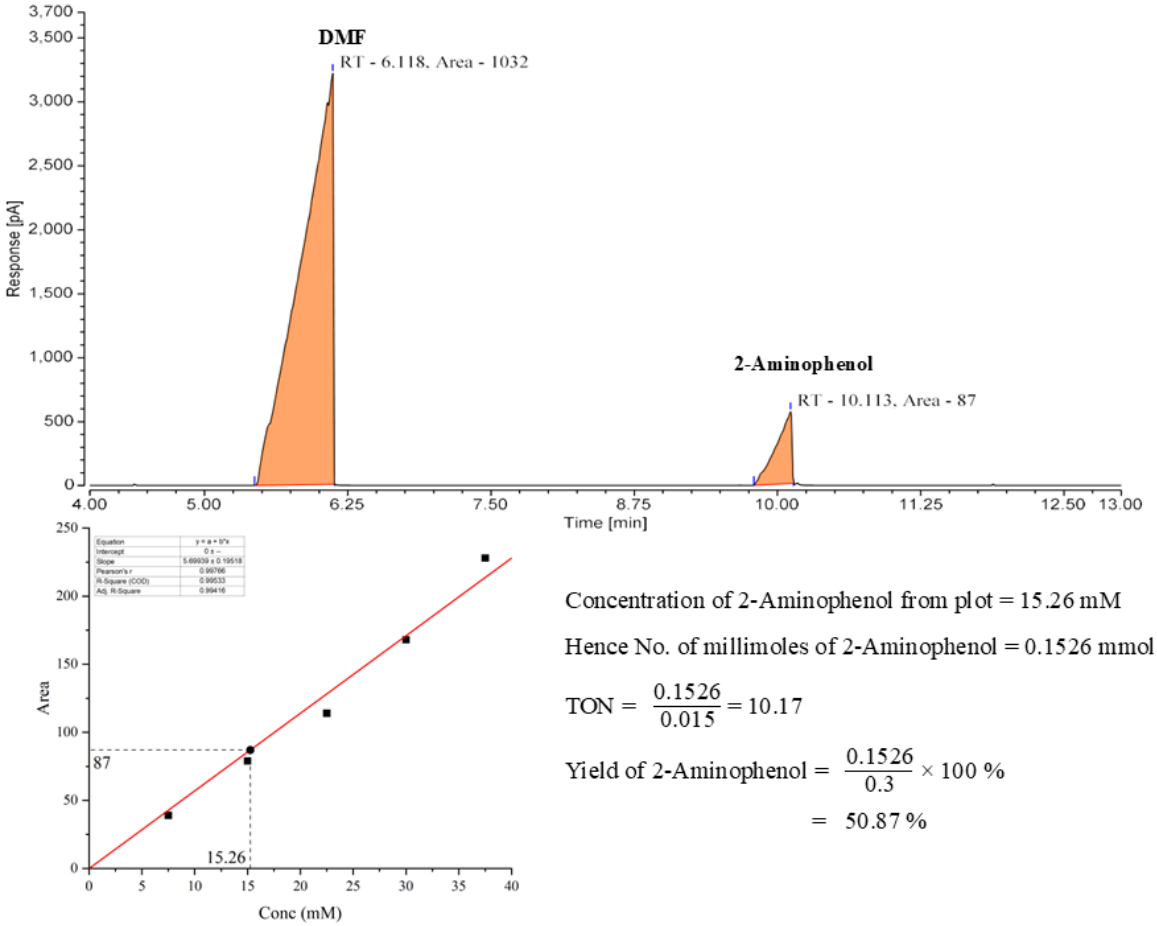


Figure S21. Calculation of yield for *o*-NH_2-C_6H_4-OH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-NH_2)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of *o*-NH_2-C_6H_4-OH = 50.87 %**. The adjusted R^2 value for the calibration plot is 0.99416.

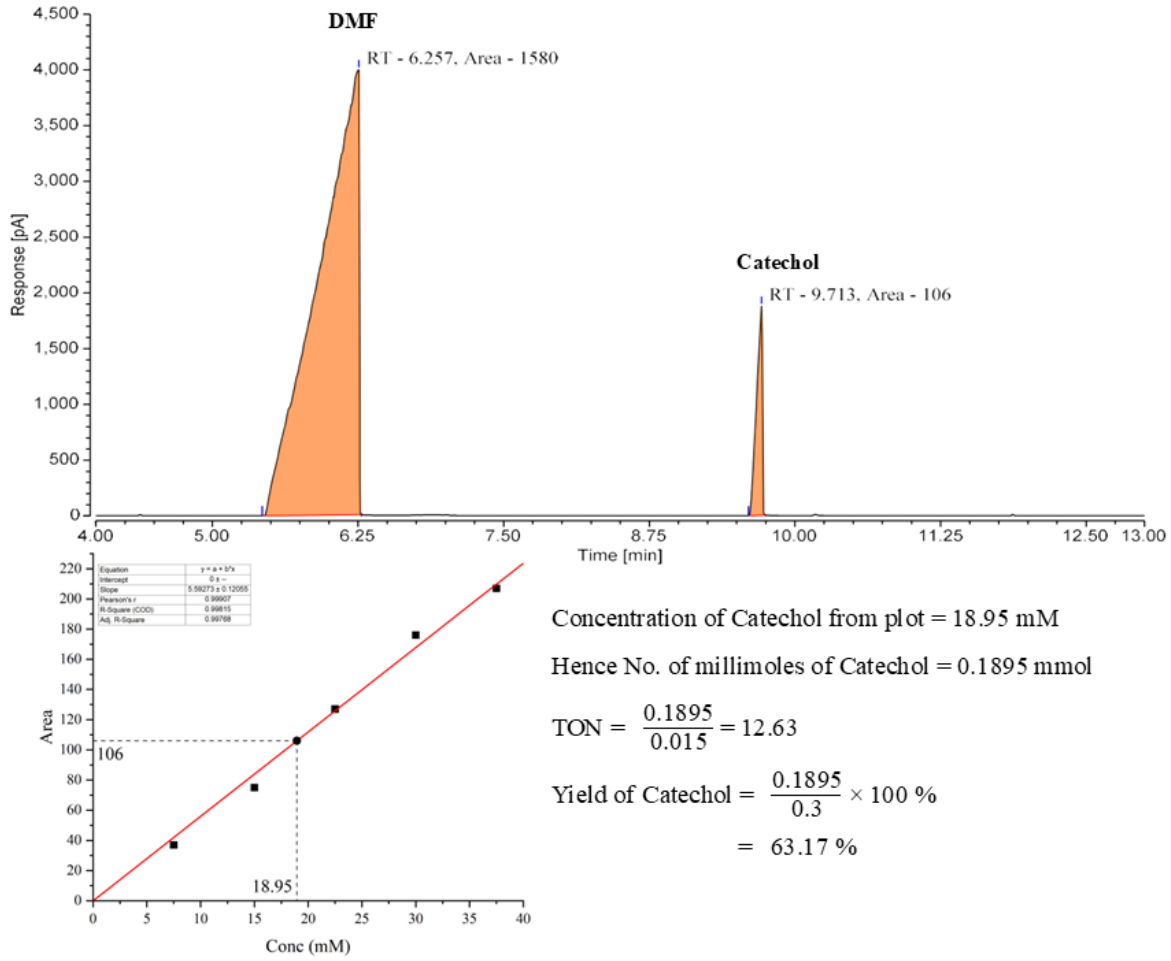


Figure S22. Calculation of yield for 1,2-$(OH)_2$-C_6H_4 obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-ONa)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 1,2-$(OH)_2$-C_6H_4 = 63.17 %**. The adjusted R^2 value for the calibration plot is 0.99768.

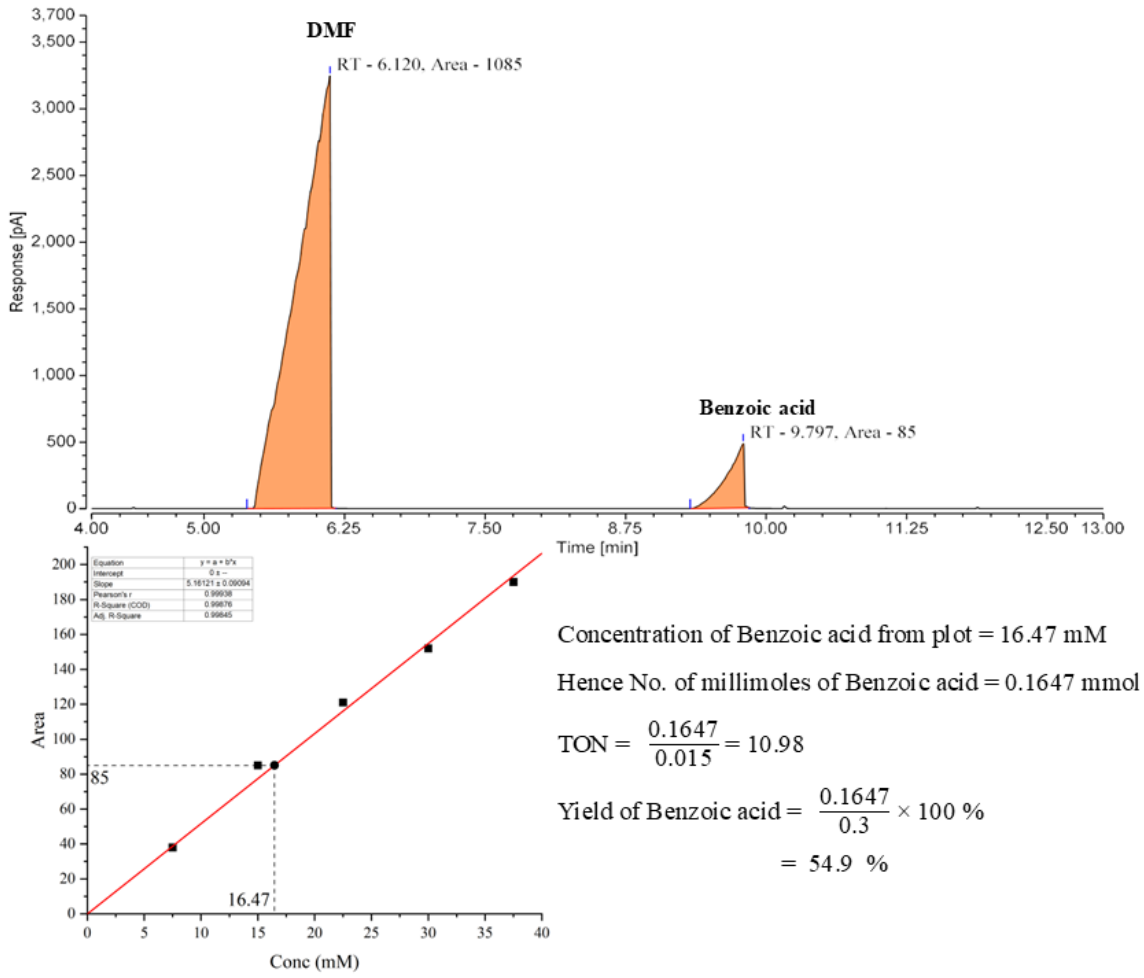


Figure S23. Calculation of yield for PhCOOH obtained from the **2d**$(BF_4)_2$ mediated catalytic hydrolysis of NaSC(O)Ph. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhCOOH = 54.9 %**. The adjusted R^2 value for the calibration plot is 0.99845.

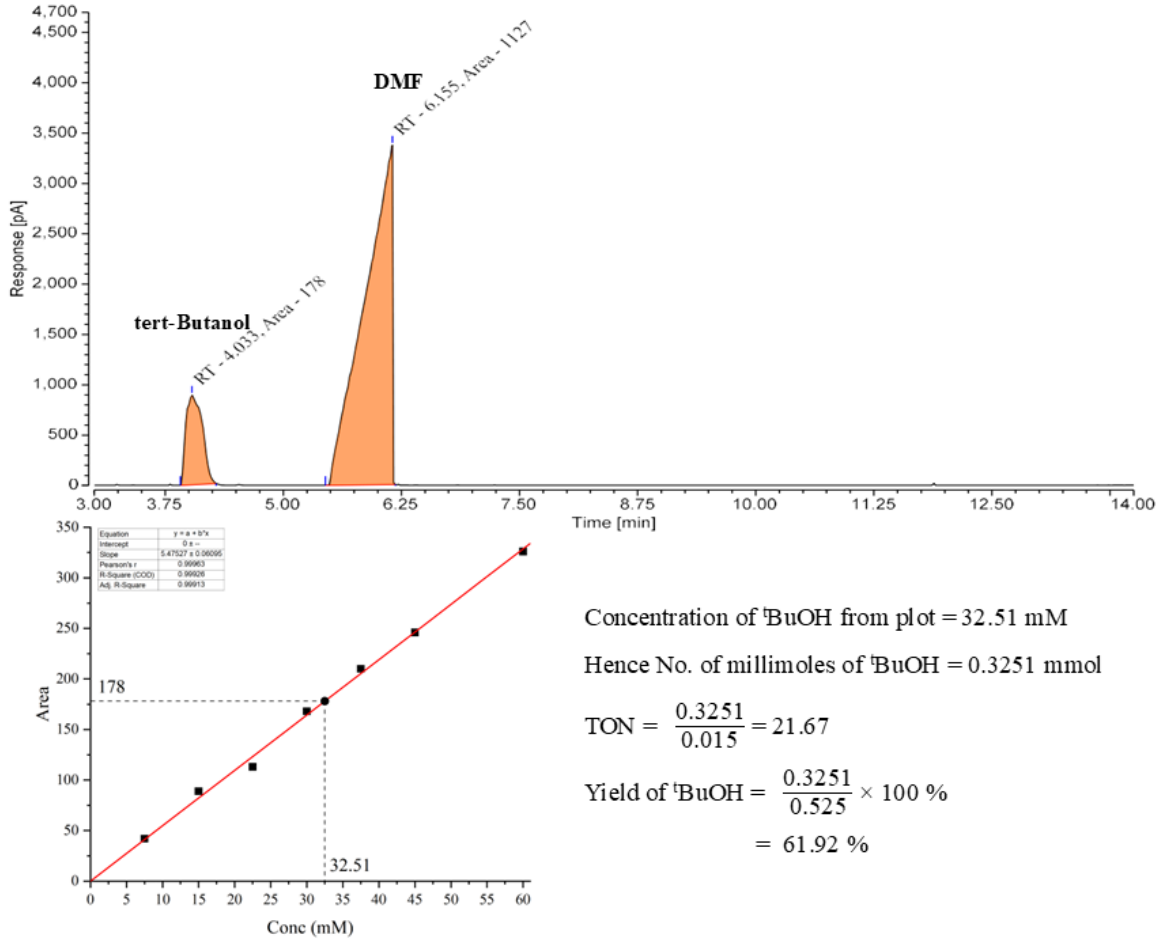


Figure S24. Calculation of yield for ^{t}BuOH obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaS^tBu. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of ^{t}BuOH = 61.92 %**. The adjusted R^2 value for the calibration plot is 0.99913.

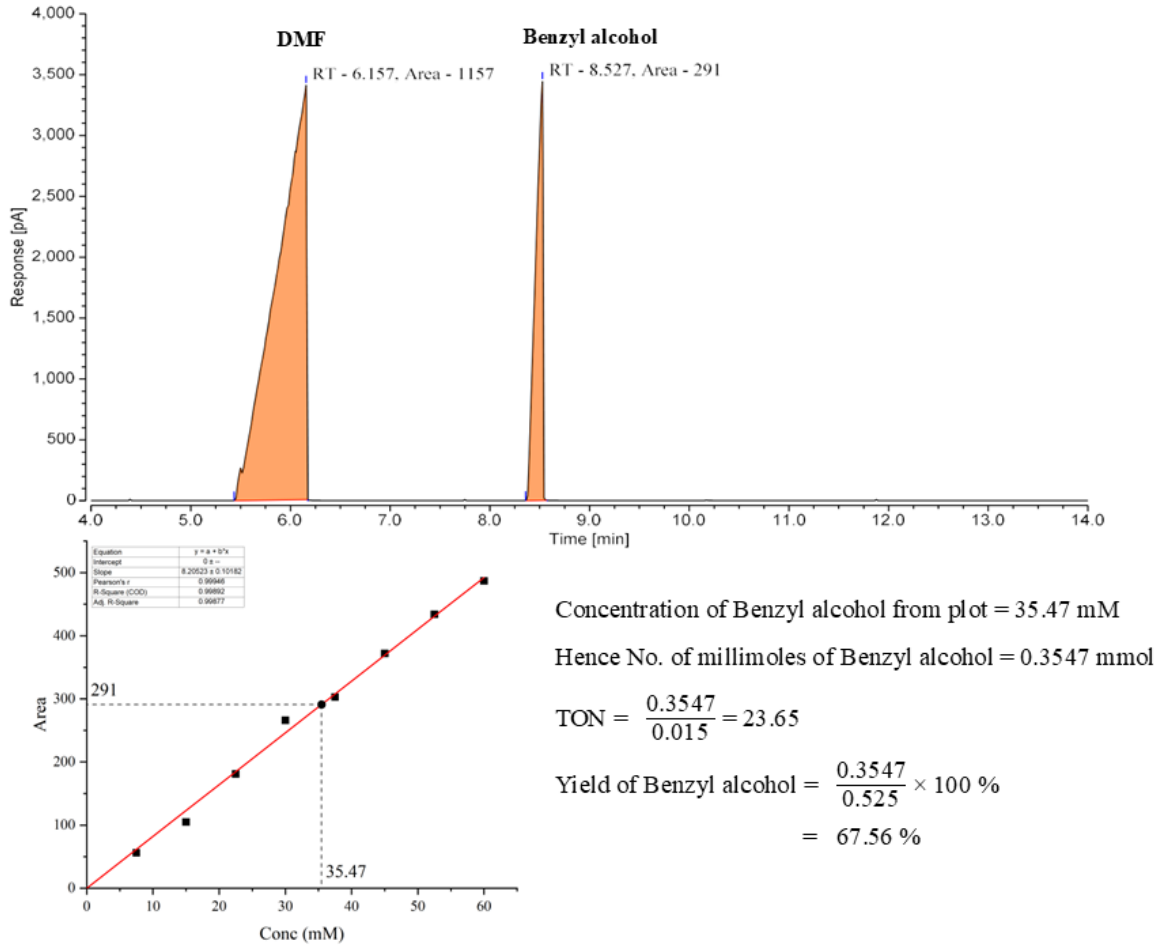


Figure S25. Calculation of yield for $PhCH_2OH$ obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 67.56 %**. The adjusted R^2 value for the calibration plot is 0.99877.

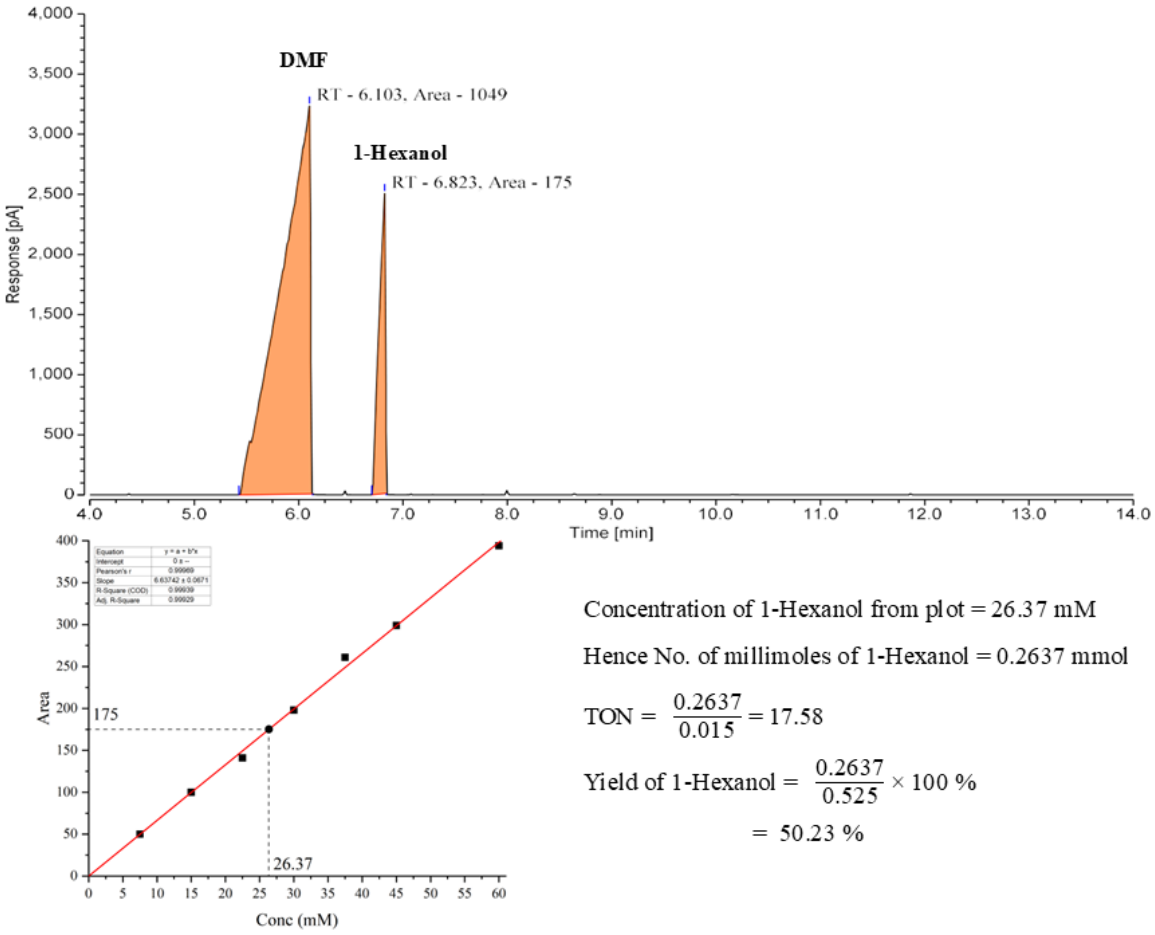


Figure S26. Calculation of yield for CH_3-$(CH_2)_4$-CH_2-OH obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_4$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_4$-CH_2-OH = 50.23 %**. The adjusted R^2 value for the calibration plot is 0.99929.

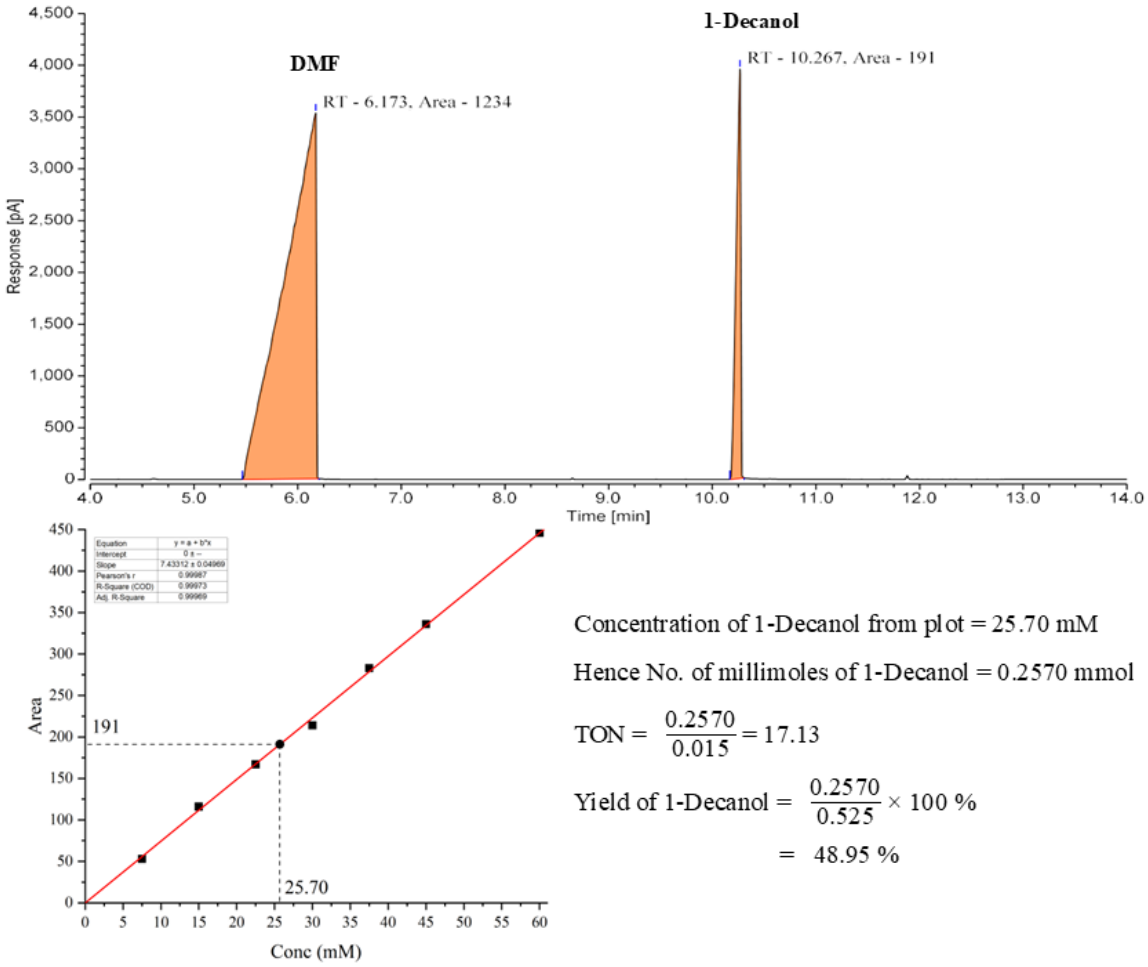


Figure S27. Calculation of yield for CH_3-$(CH_2)_8$-CH_2-OH obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_8$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_8$-CH_2-OH = 48.95 %**. The adjusted R^2 value for the calibration plot is 0.99969.

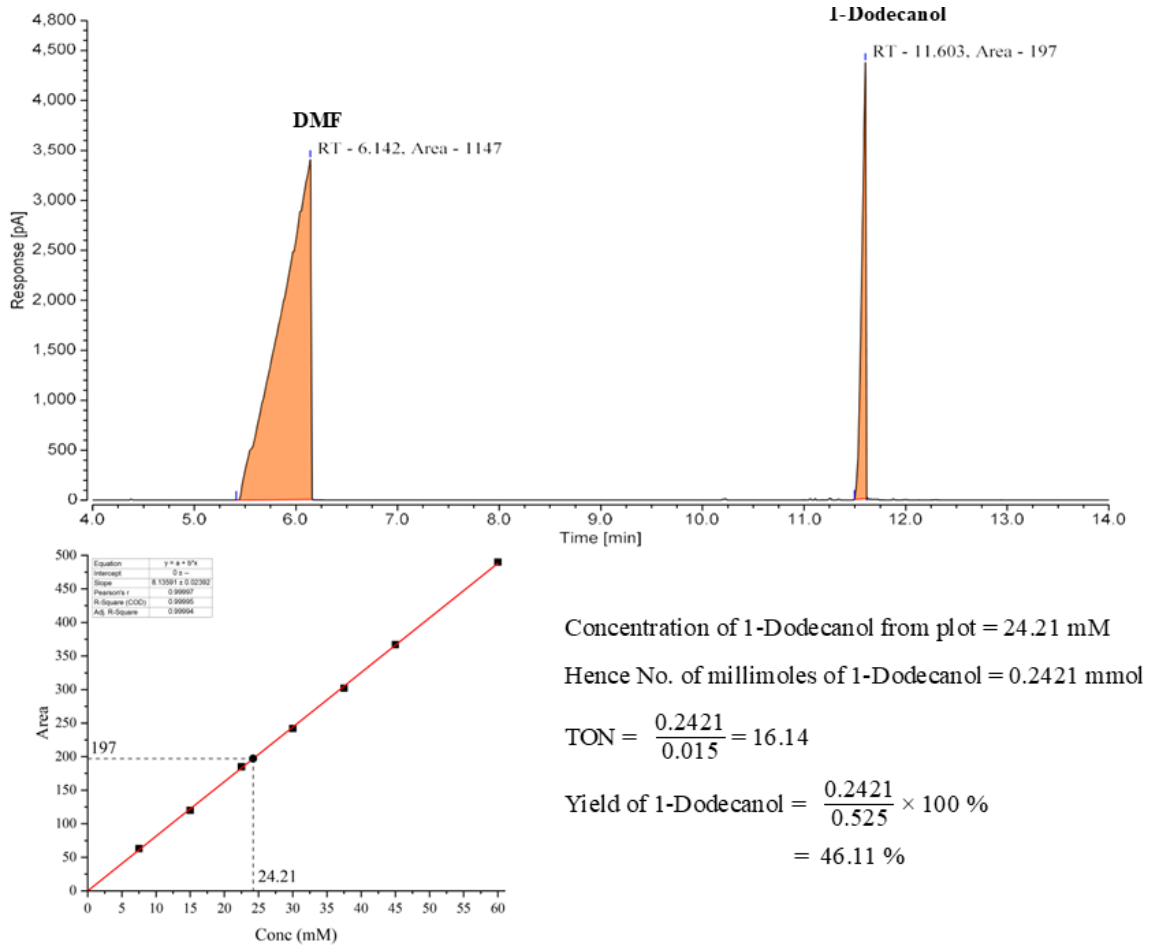


Figure S28. Calculation of yield for CH_3-$(CH_2)_{10}$-CH_2-OH obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH)_{10}$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_{10}$-CH_2-OH = 46.11 %**. The adjusted R^2 value for the calibration plot is 0.99994.

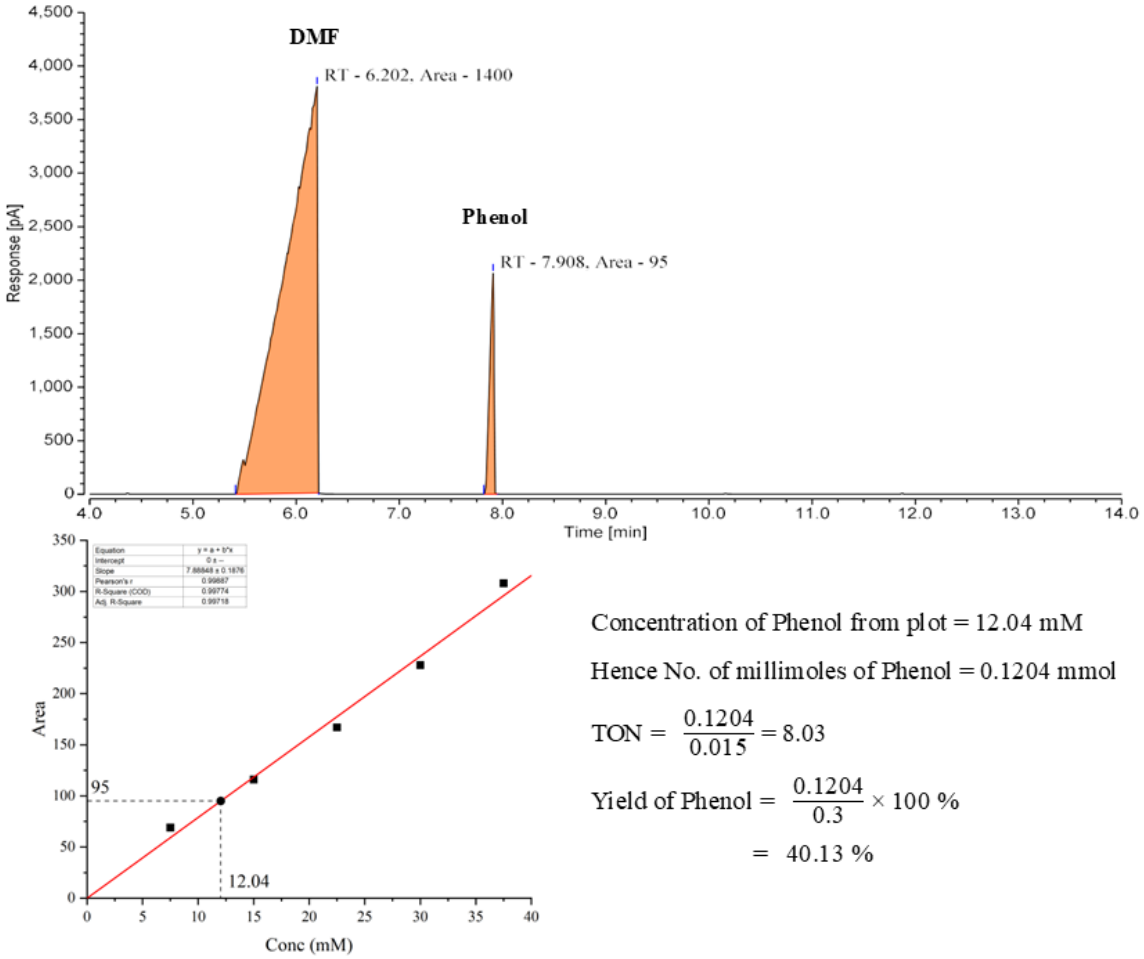
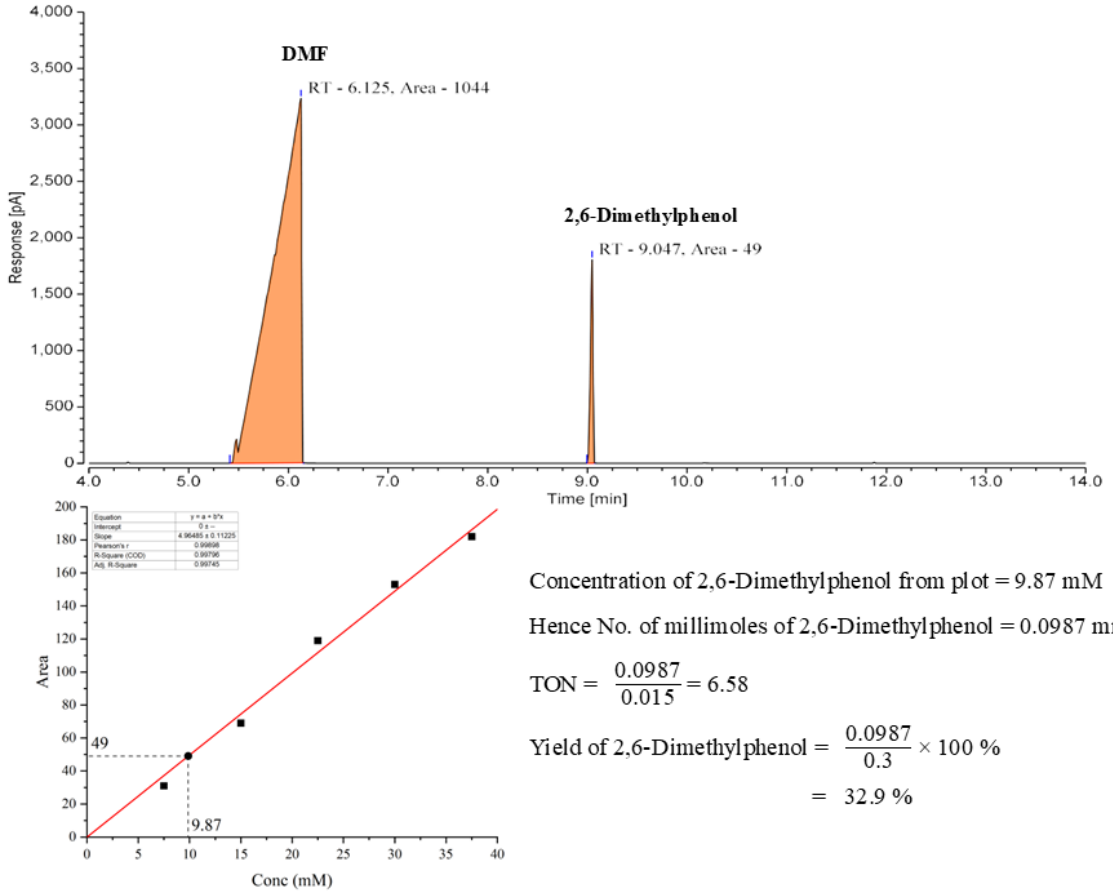


Figure S29. Calculation of yield for PhOH obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 40.13 %**. The adjusted R^2 value for the calibration plot is 0.99718.



Concentration of 2,6-Dimethylphenol from plot = 9.87 mM

Hence No. of millimoles of 2,6-Dimethylphenol = 0.0987 mmol

$$\text{TON} = \frac{0.0987}{0.015} = 6.58$$

$$\text{Yield of 2,6-Dimethylphenol} = \frac{0.0987}{0.3} \times 100\ \% = 32.9\ \%$$

Figure S30. Calculation of yield for 2,6-Me_2-C_6H_3-OH obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,6-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,6-Me_2-C_6H_3-OH = 32.9 %**. The adjusted R^2 value for the calibration plot is 0.99745.

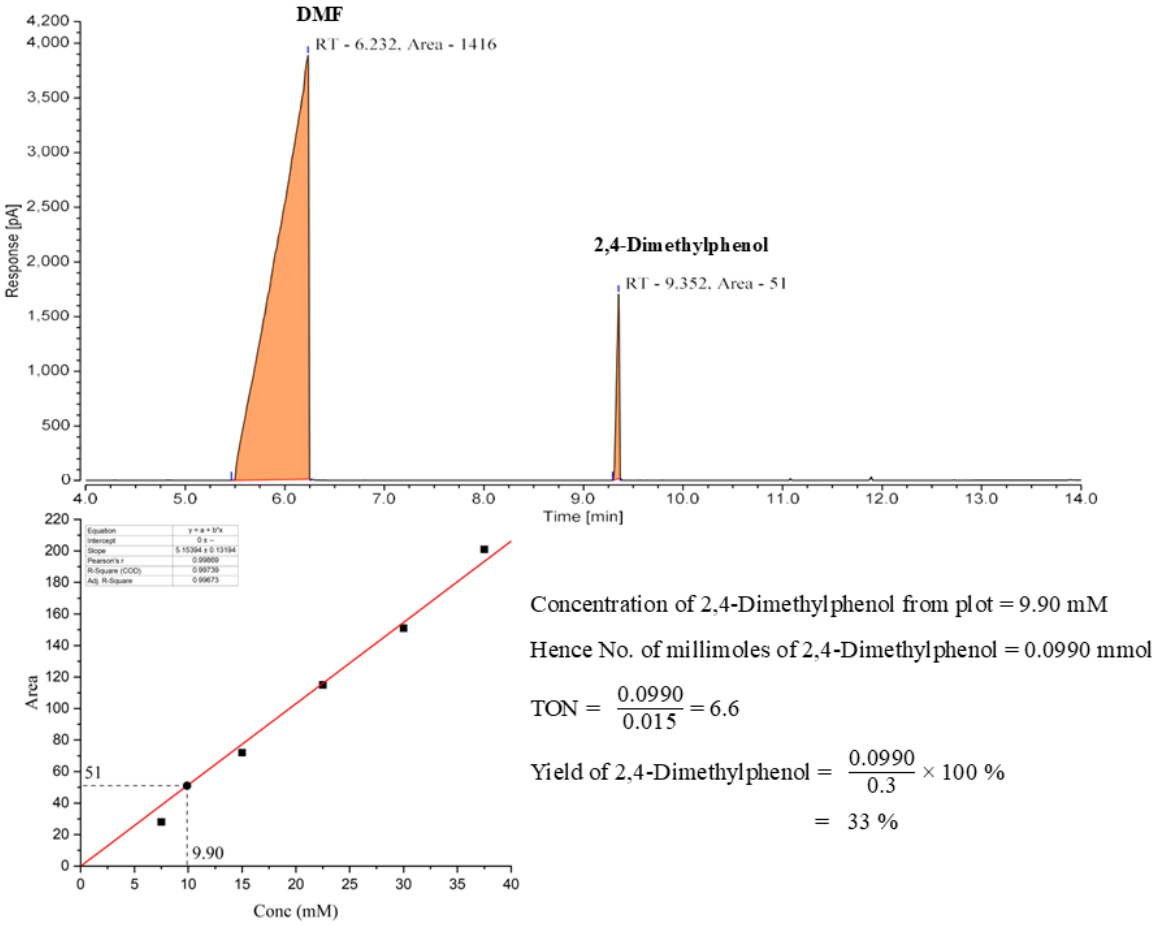


Figure S31. Calculation of yield for 2,4-Me_2-C_6H_3-OH obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,4-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,4-Me_2-C_6H_3-OH = 33 %.** The adjusted R^2 value for the calibration plot is 0.99673.

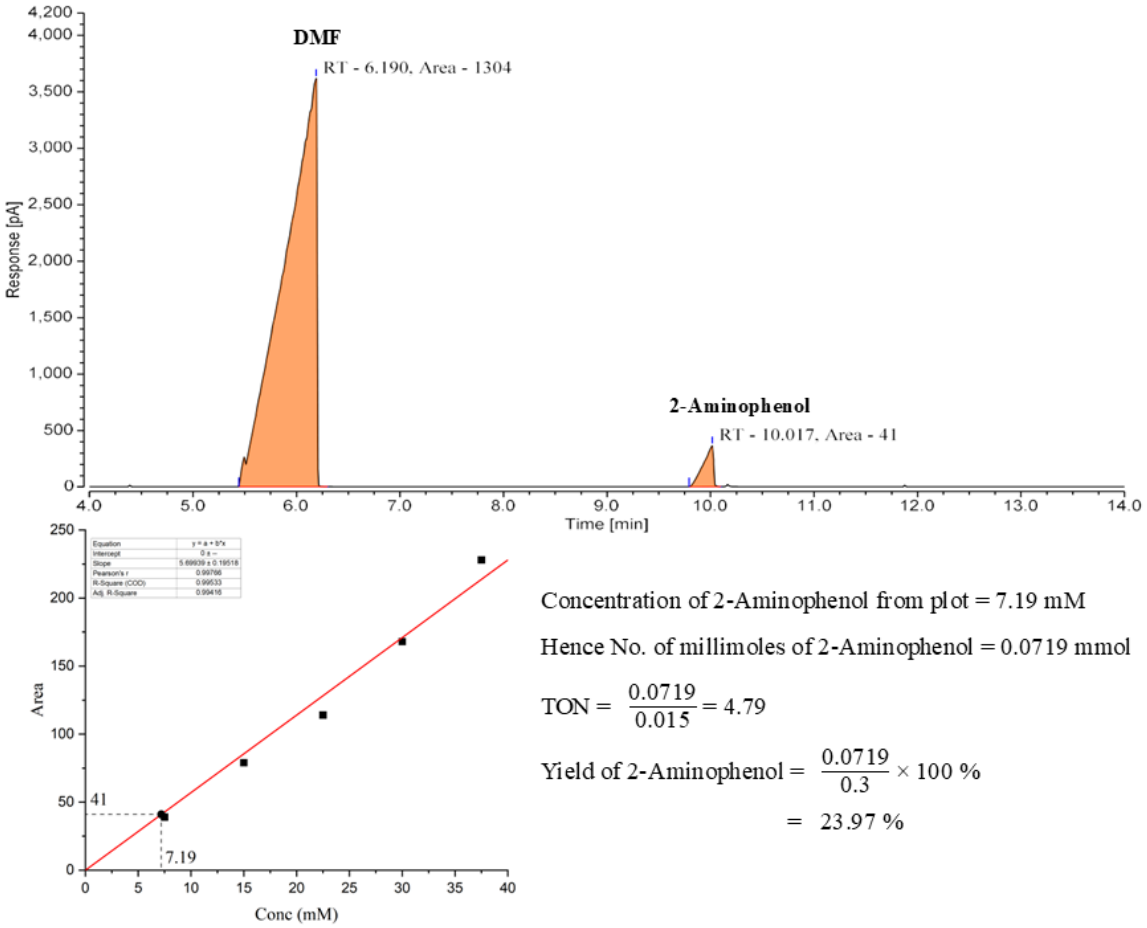


Figure S32. Calculation of yield for *o*-NH_2-C_6H_4-OH obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-NH_2)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of *o*-NH_2-C_6H_4-OH = 23.97 %.** The adjusted R^2 value for the calibration plot is 0.99416.

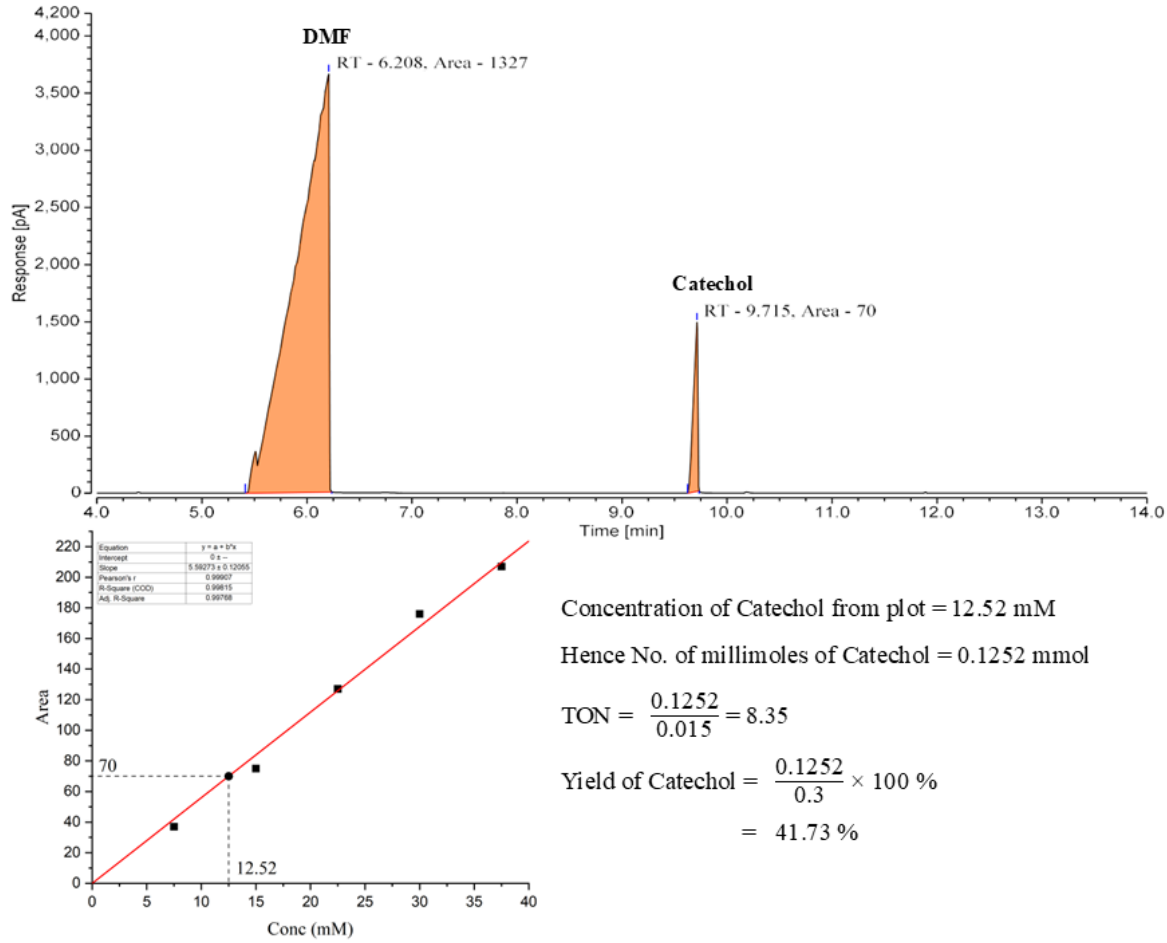


Figure S33. Calculation of yield for 1,2-$(OH)_2$-C_6H_4 obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-ONa)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 1,2-$(OH)_2$-C_6H_4 = 41.73 %**. The adjusted R^2 value for the calibration plot is 0.99768.

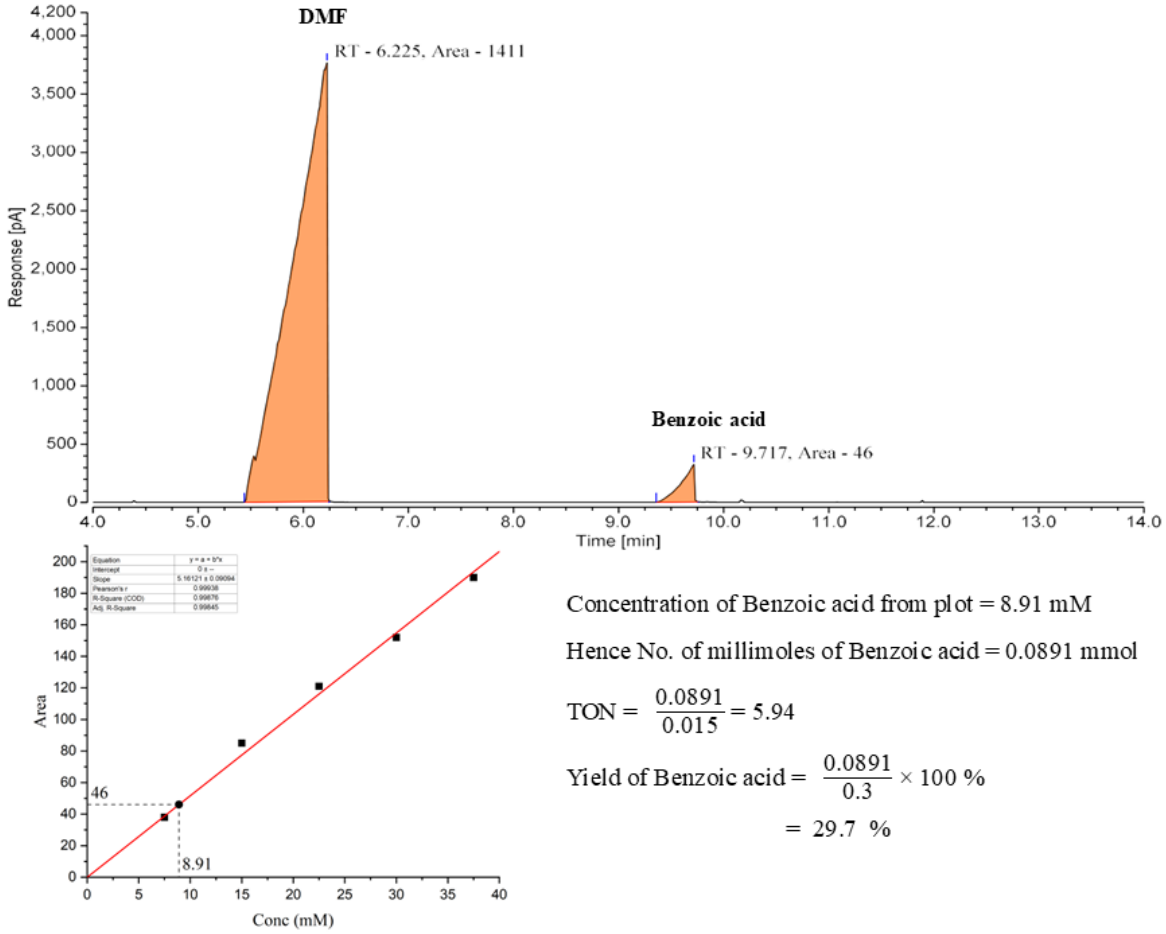


Figure S34. Calculation of yield for PhCOOH obtained from the **2e**$(BF_4)_2$ mediated catalytic hydrolysis of NaSC(O)Ph. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhCOOH = 29.7 %**. The adjusted R^2 value for the calibration plot is 0.99845.

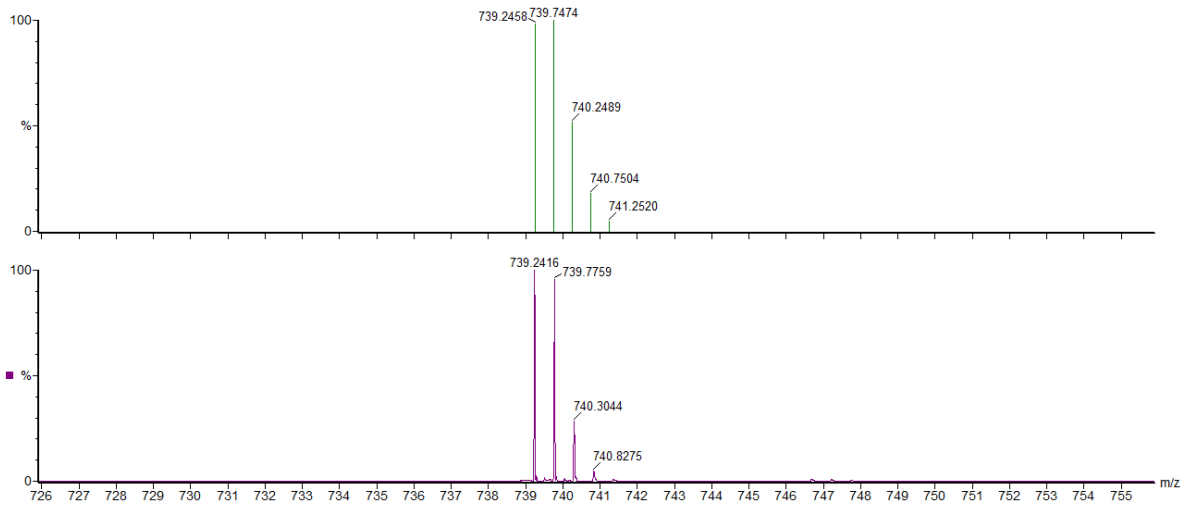


Figure S35. Mass spectrum (in MeCN) for $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)(DMF)](BF_4)_2$, **2f**$(BF_4)_2$ shows the presence of $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{2+}$ at m/z = 739.2458 (simulated, green line); 739.2416 (obtained, violet line).

Table S4. Optimization of the ratio of **2f:** aliphatic thiolates. Conditions: thiolate:H_2O = 1:30, reaction time = 60 h, substrate used = $NaSCH_2Ph$, solvent = DMF, temperature = 25 °C.

$NaSCH_2Ph$ Used		Ratio of **2f**: $NaSCH_2Ph$	GC Yield (%) of $PhCH_2OH$	GC Yield (equiv) of $PhCH_2OH$	Yield (%) of Recovered Catalyst (**2f**)
Equiv	Amount mmol (mg)				
10	0.15 (21.9)	1:10	93.46	9.35	N/A
20	0.3 (43.8)	1:20	93.83	18.77	N/A
30	0.45 (65.7)	1:30	91.53	27.46	N/A
35	0.525 (76.65)	1:35	91.24	31.93	N/A
40	**0.6 (87.6)**	**1:40**	**93.85**	**37.54**	**N/A**
45	0.675 (98.6)	1:45	81.61	36.72	N/A

Amount of catalyst (**2f**) = 0.015 mmol (25.9 mg).

Table S5. Optimization of the ratio of **2f**: aromatic thiolates. Conditions: thiolate:H_2O = 1:30, reaction time = 168 h, substrate used = NaSPh, solvent = DMF, temperature = 25 °C.

NaSPh Used		Ratio of **2f**: NaSPh	GC Yield (%) of PhOH	GC Yield (equiv) of PhOH	Yield (%) of Recovered Catalyst (**2f**)
Equiv	Amount mmol (mg)				
10	0.15 (19.8)	1:5	73.53	7.35	N/A
15	0.225 (29.7)	1:15	62.53	9.38	N/A
20	0.3 (39.6)	1:20	73.1	14.62	N/A
25	**0.375 (49.5)**	**1:25**	**72.67**	**18.17**	**N/A**
30	0.45 (59.4)	1:30	54.93	16.48	N/A

Amount of catalyst (**2f**) = 0.015 mmol (25.9 mg).

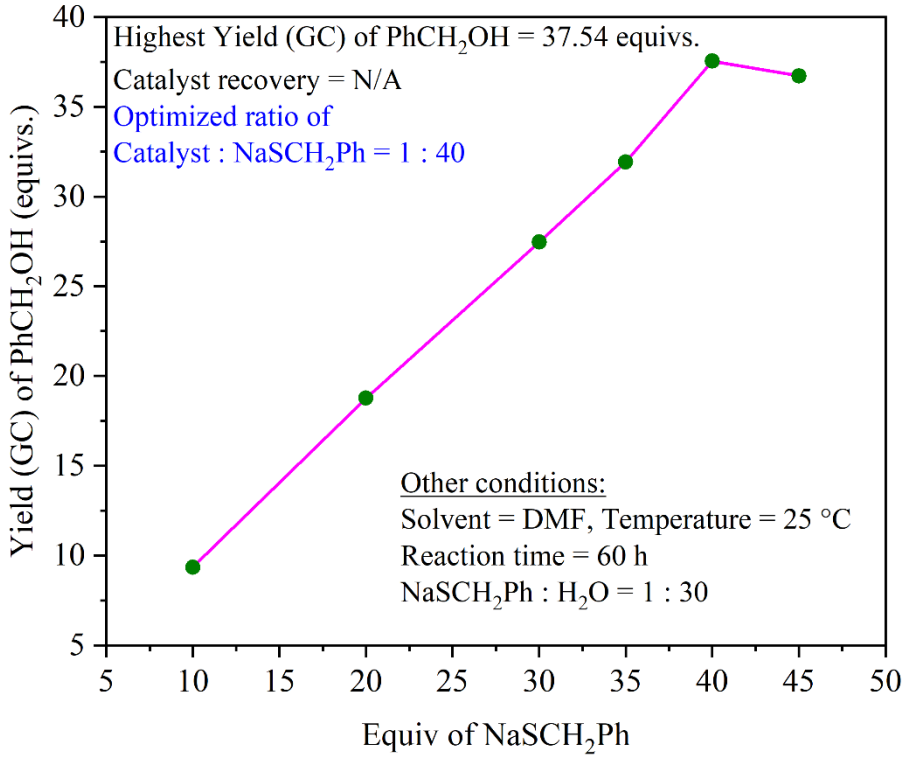


Figure S36. Optimization of the catalyst:thiolate ratio for aliphatic thiolates using **2f(BF$_4$)$_2$**.

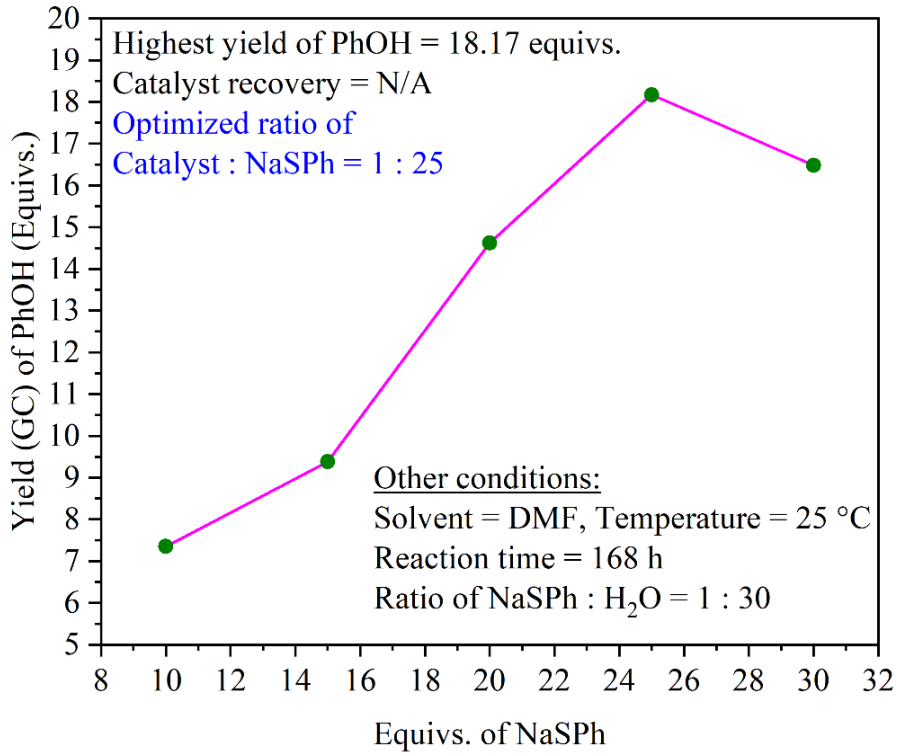


Figure S37. Optimization of the catalyst:thiolate ratio for aromatic thiolates using **2f(BF$_4$)$_2$**.

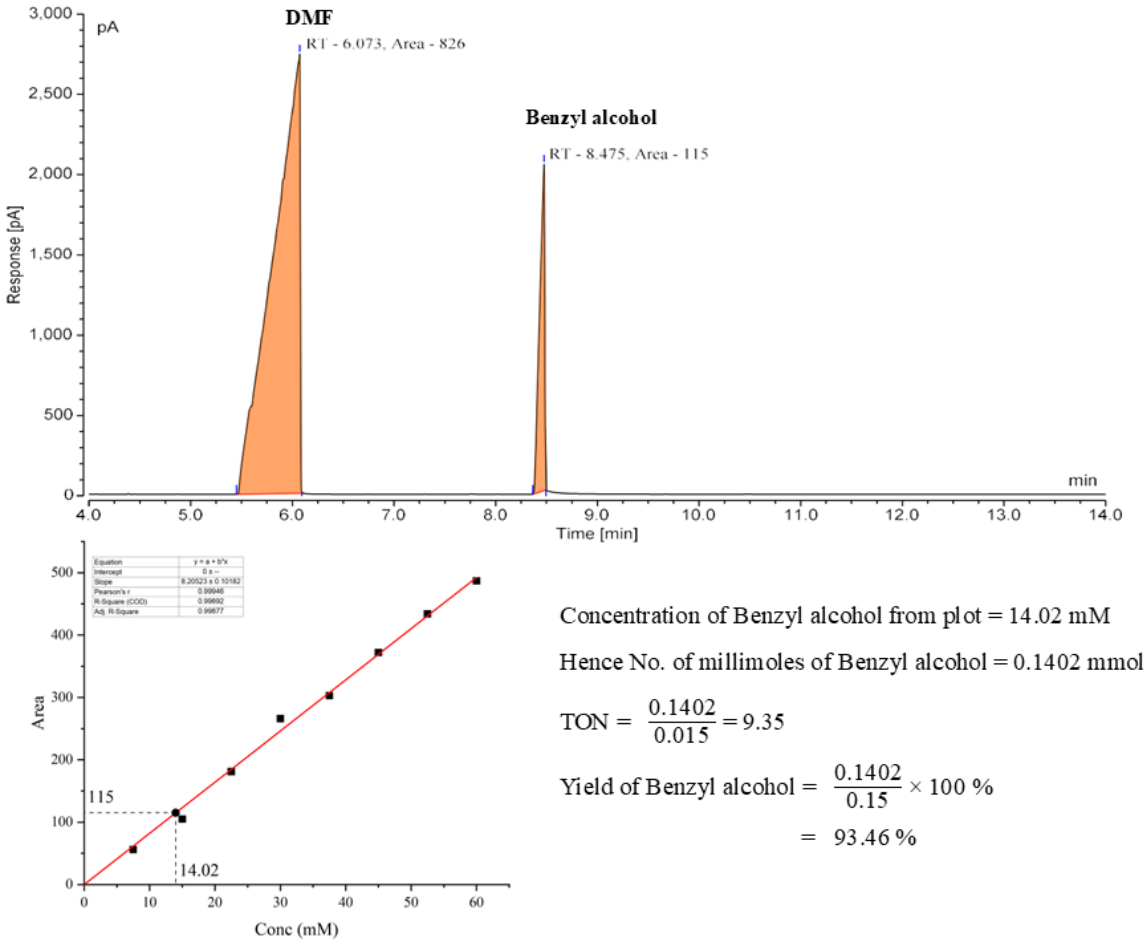


Figure S38. Calculation of yield for $PhCH_2OH$ obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:10, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 93.46 %**. The adjusted R^2 value for the calibration plot is 0.99877.

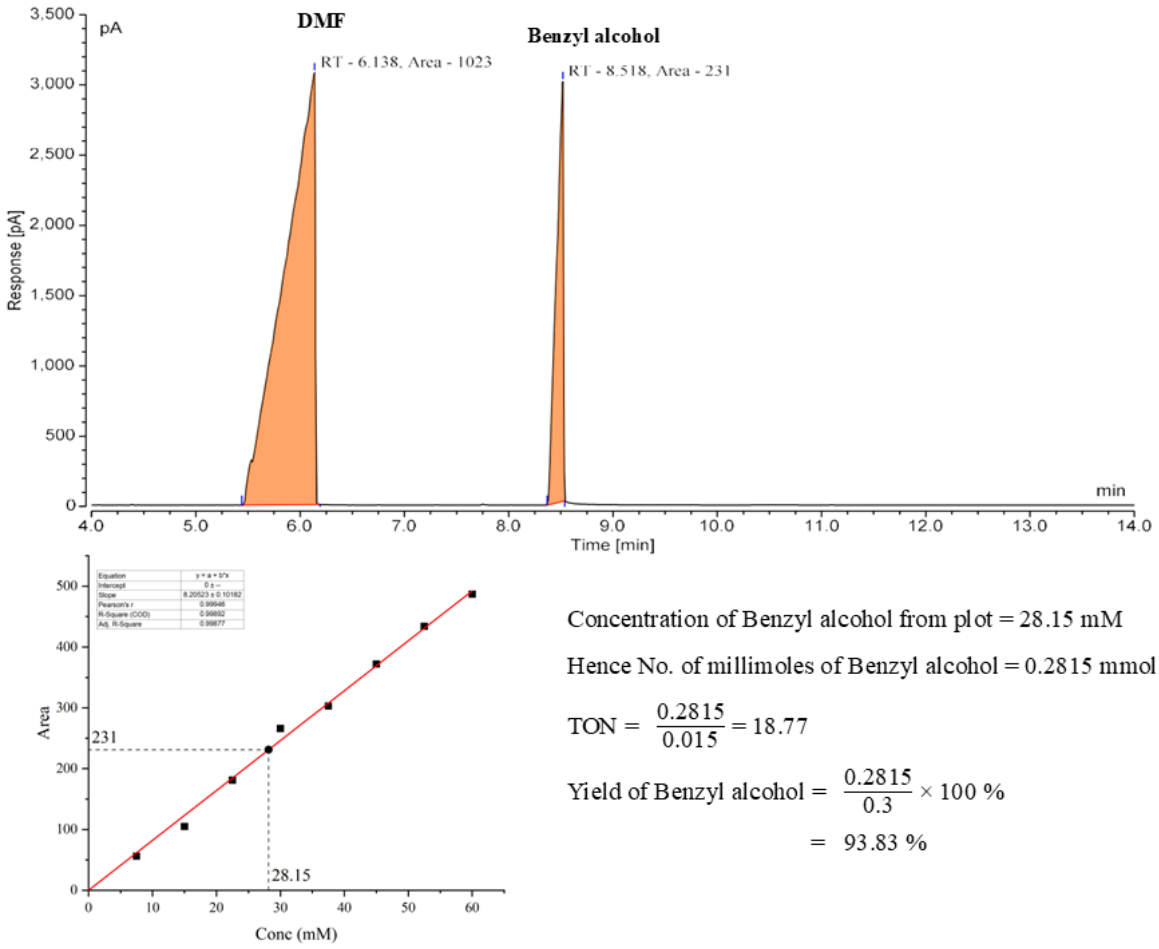


Figure S39. Calculation of yield for $PhCH_2OH$ obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 93.83 %.** The adjusted R^2 value for the calibration plot is 0.99877.

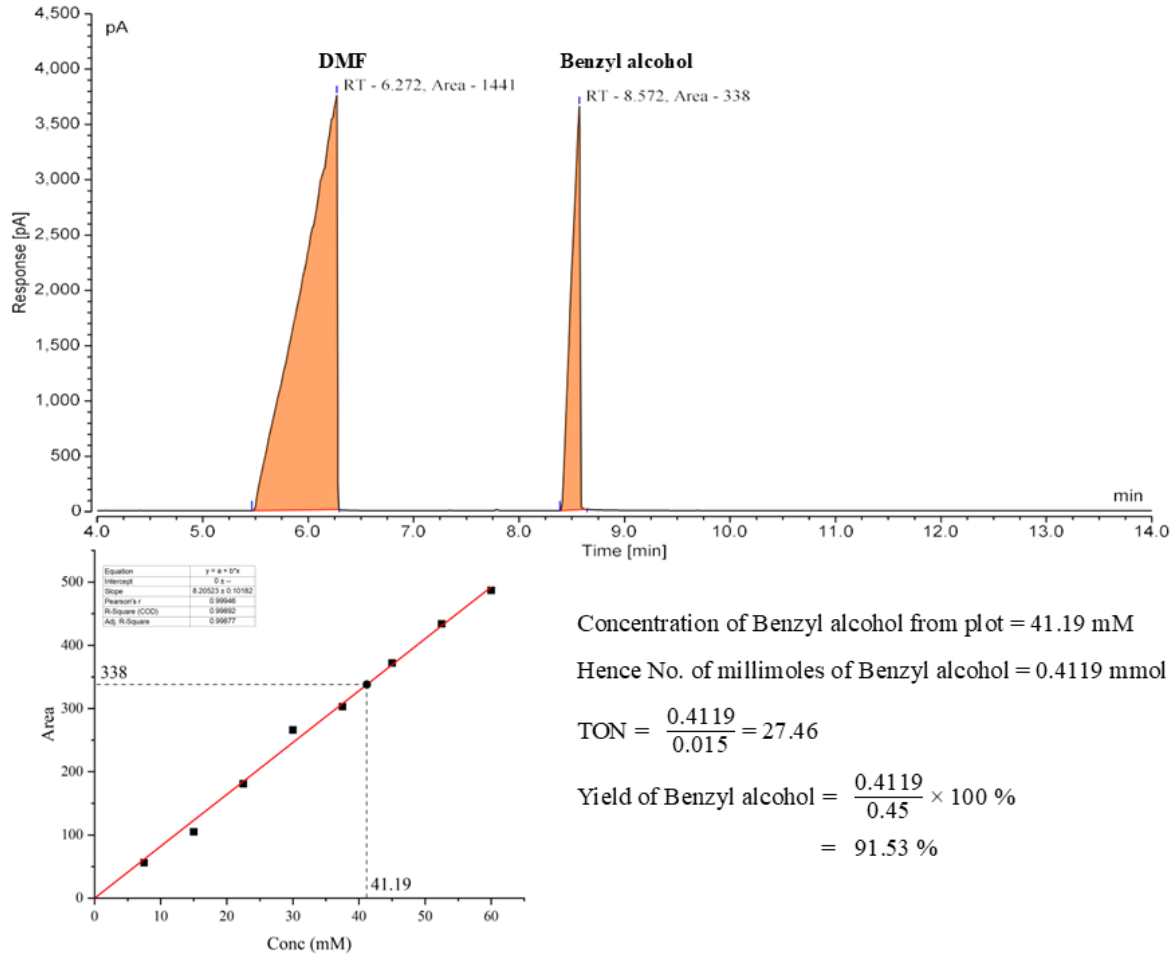


Figure S40. Calculation of yield for $PhCH_2OH$ obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:30, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 91.53 %.** The adjusted R^2 value for the calibration plot is 0.99877.

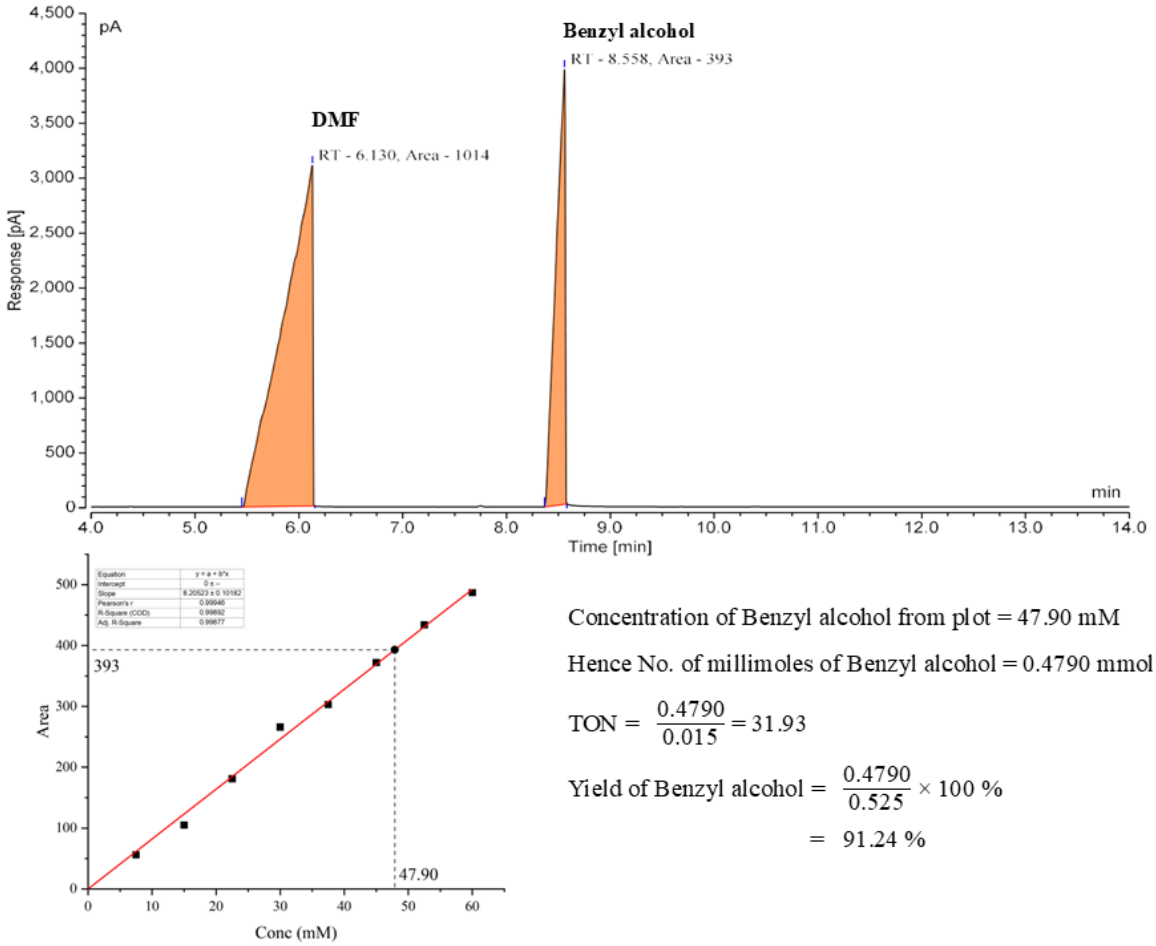


Figure S41. Calculation of yield for $PhCH_2OH$ obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 91.24 %**. The adjusted R^2 value for the calibration plot is 0.99877.

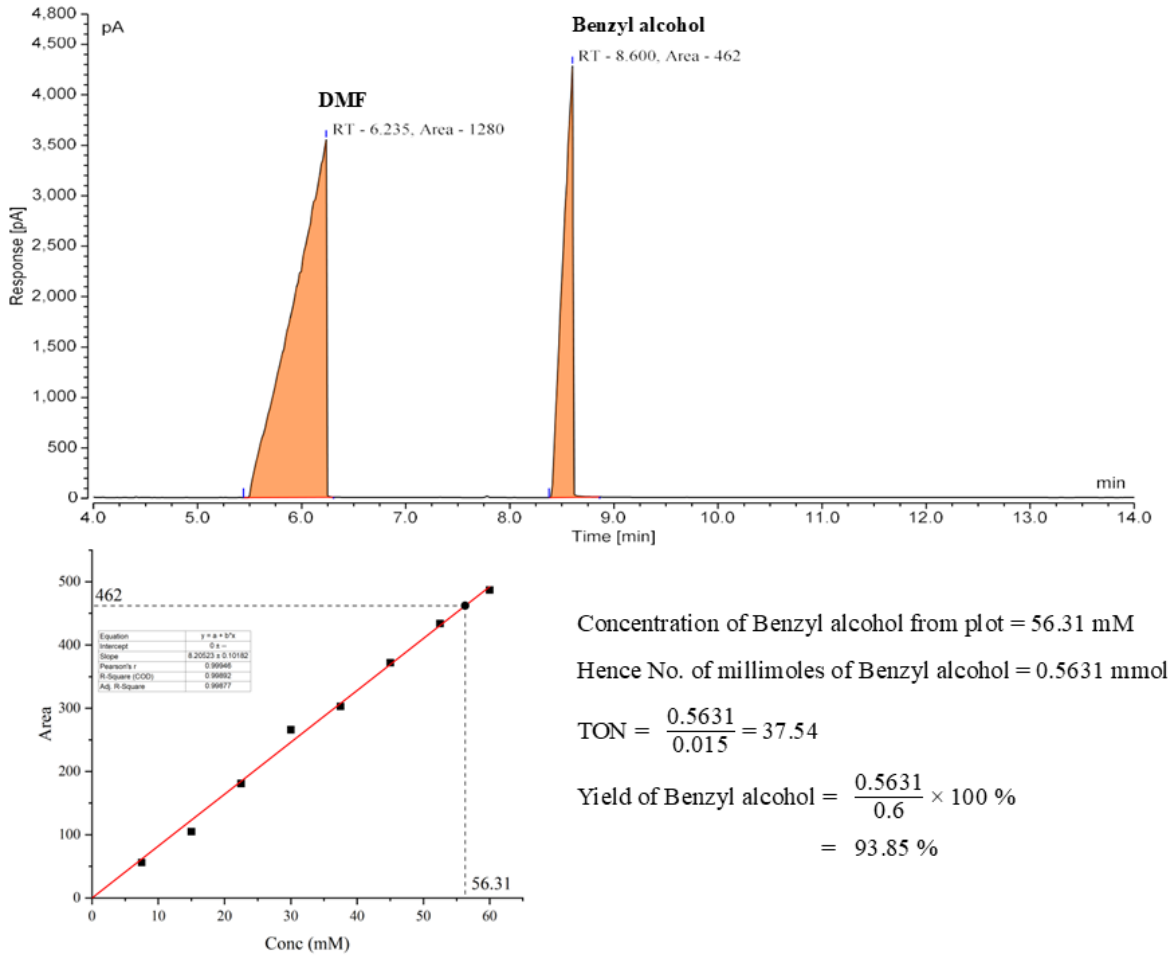


Figure S42. Calculation of yield for $PhCH_2OH$ obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 93.85 %**. The adjusted R^2 value for the calibration plot is 0.99877.

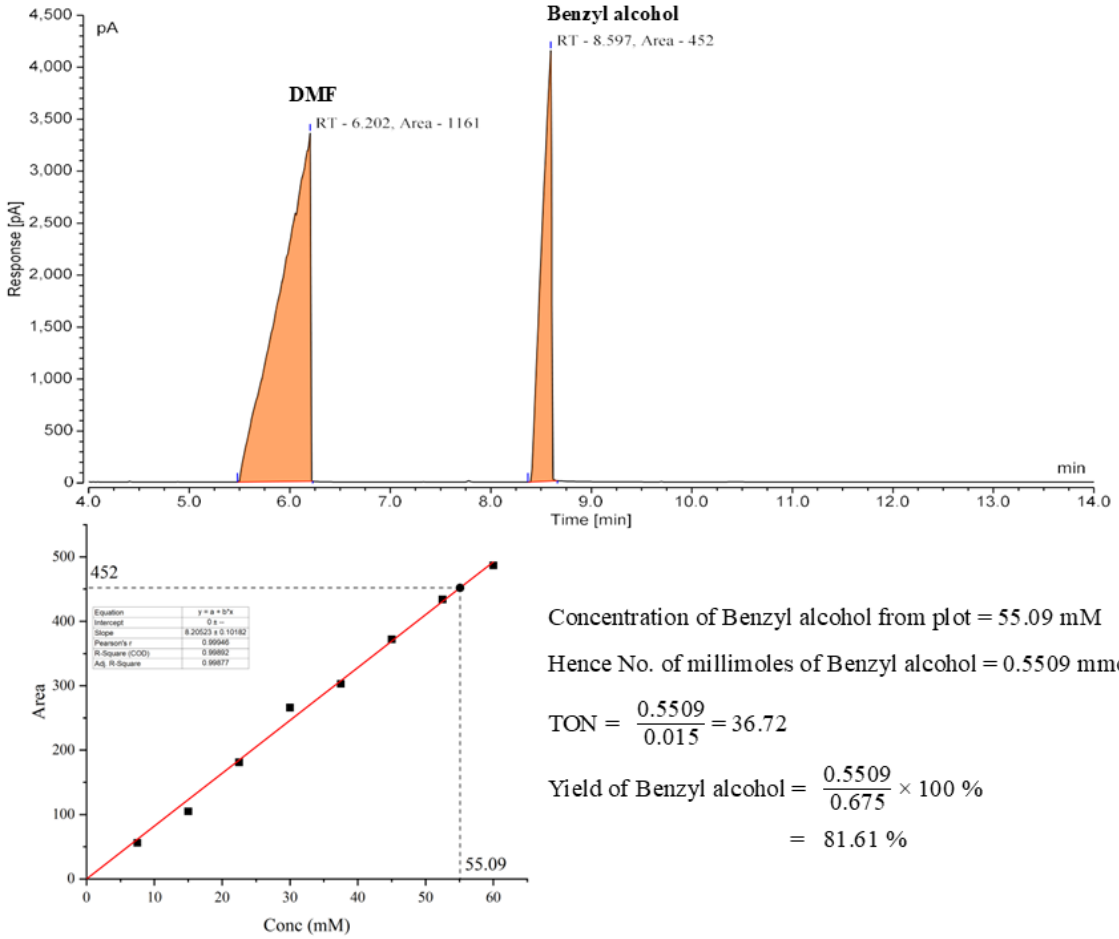


Figure S43. Calculation of yield for $PhCH_2OH$ obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:45, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 81.61 %**. The adjusted R^2 value for the calibration plot is 0.99877.

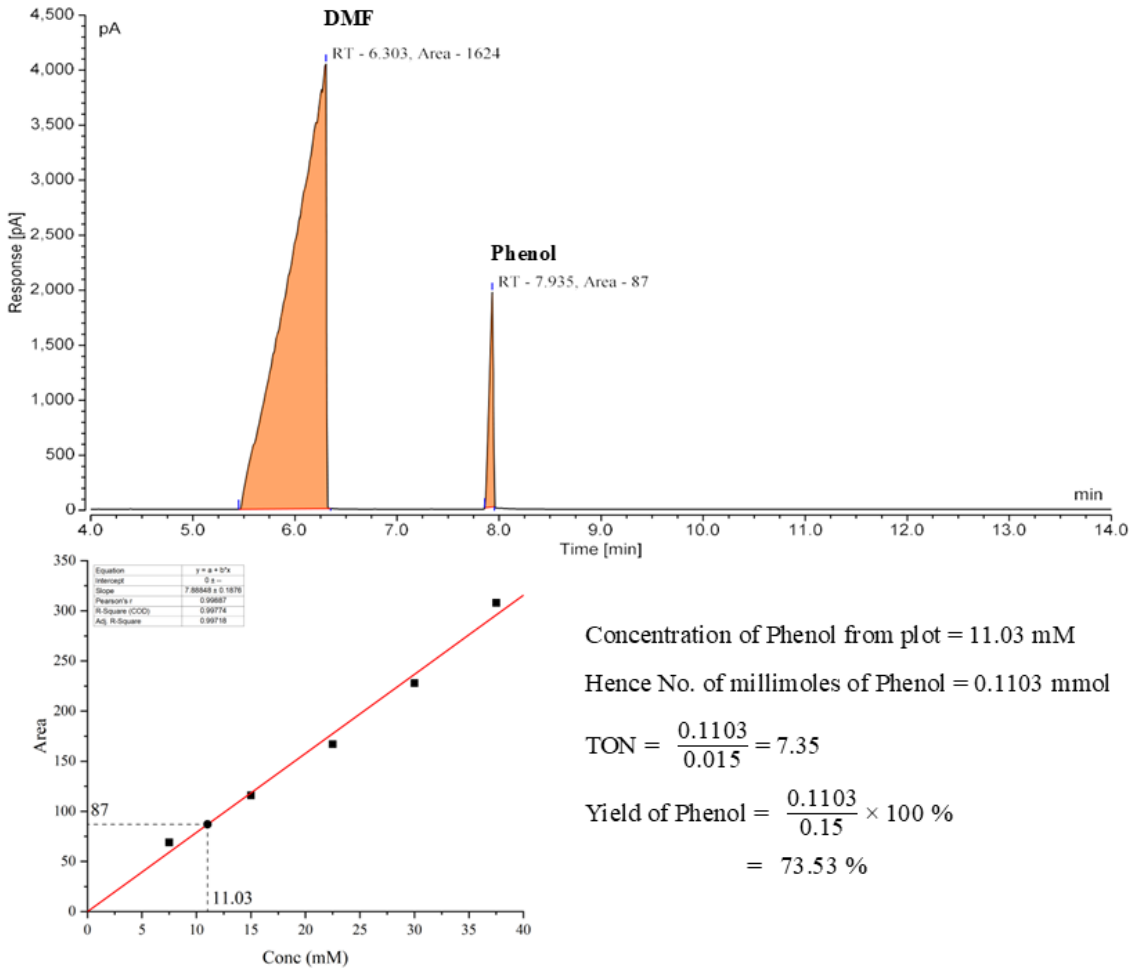


Figure S44. Calculation of yield for PhOH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:10, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 73.53 %**. The adjusted R^2 value for the calibration plot is 0.99718.

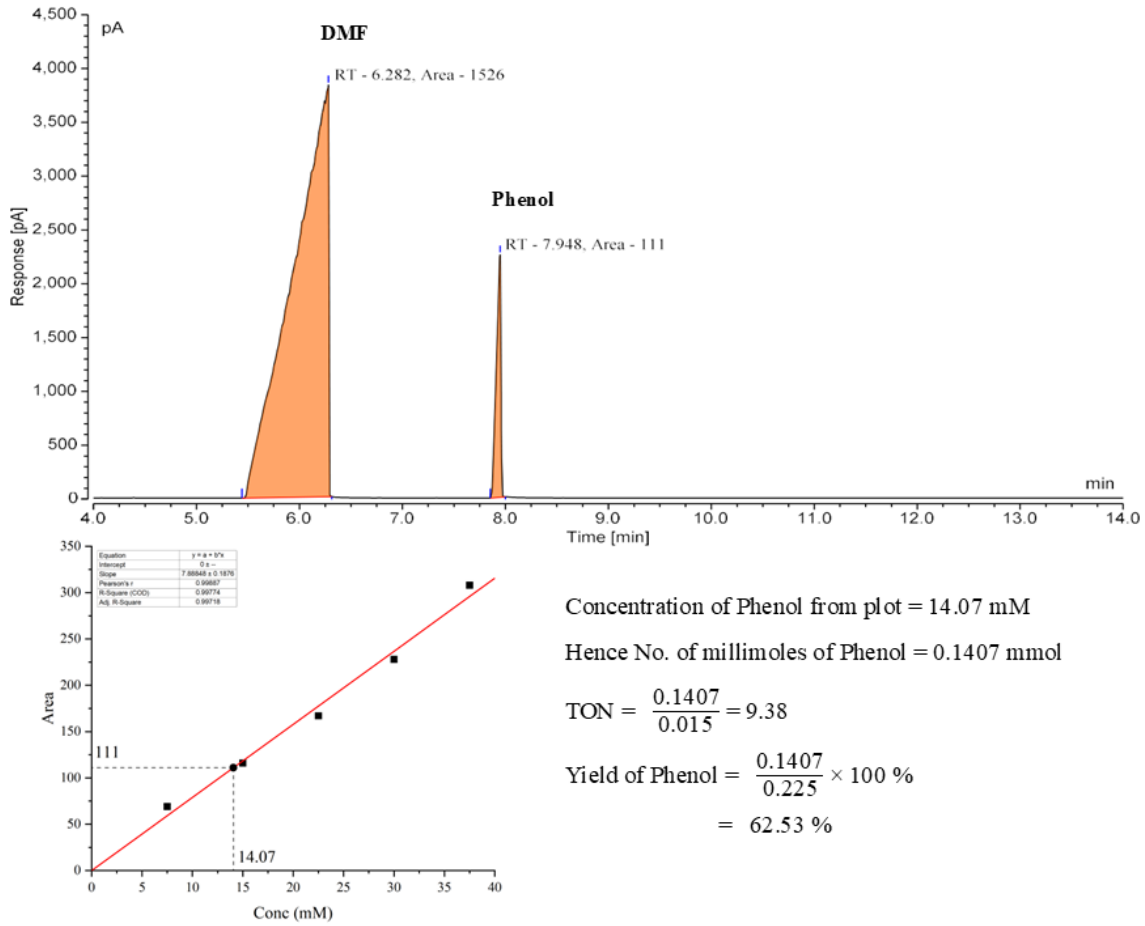


Figure S45. Calculation of yield for PhOH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:15, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 62.53 %.** The adjusted R^2 value for the calibration plot is 0.99718.

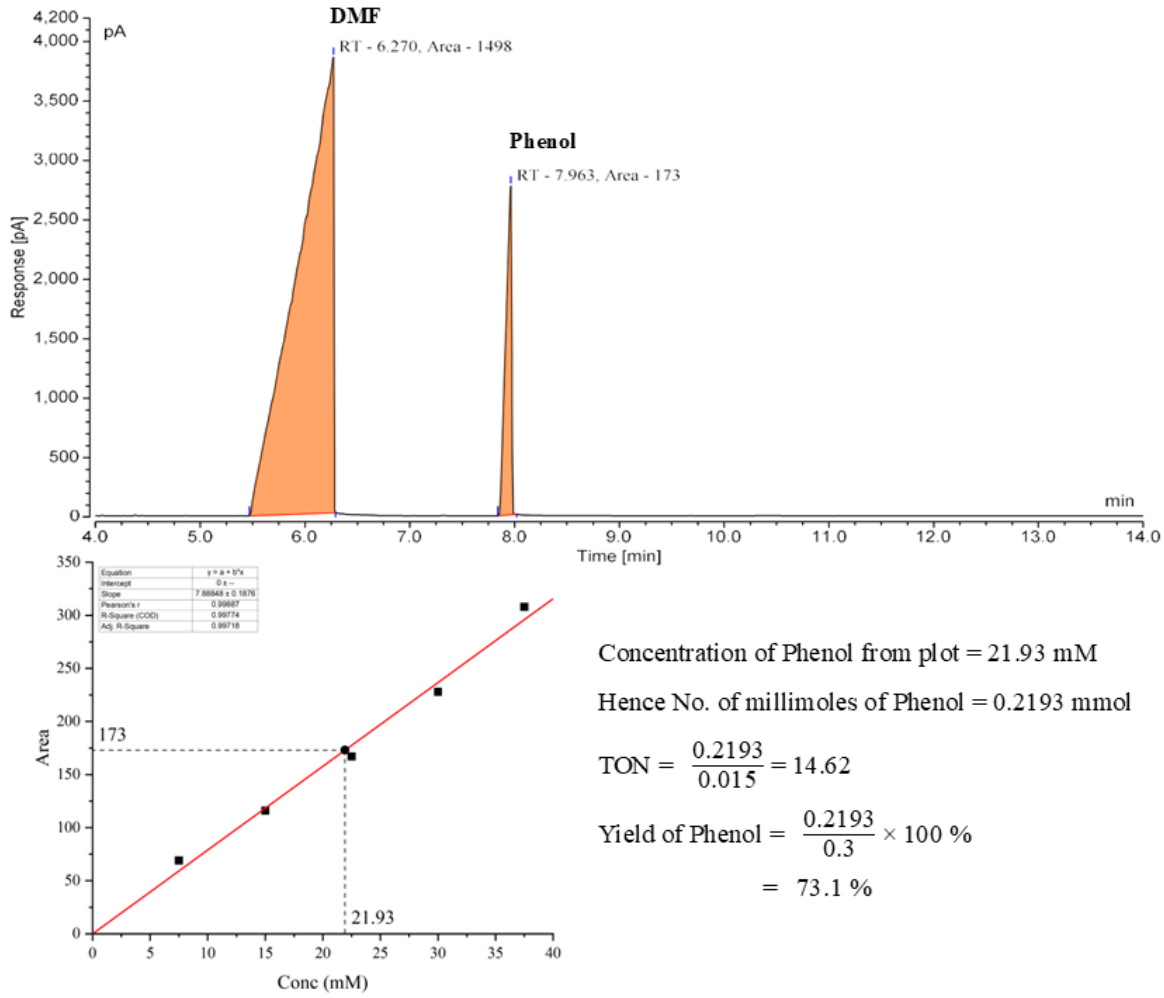


Figure S46. Calculation of yield for PhOH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 73.1 %**. The adjusted R^2 value for the calibration plot is 0.99718.

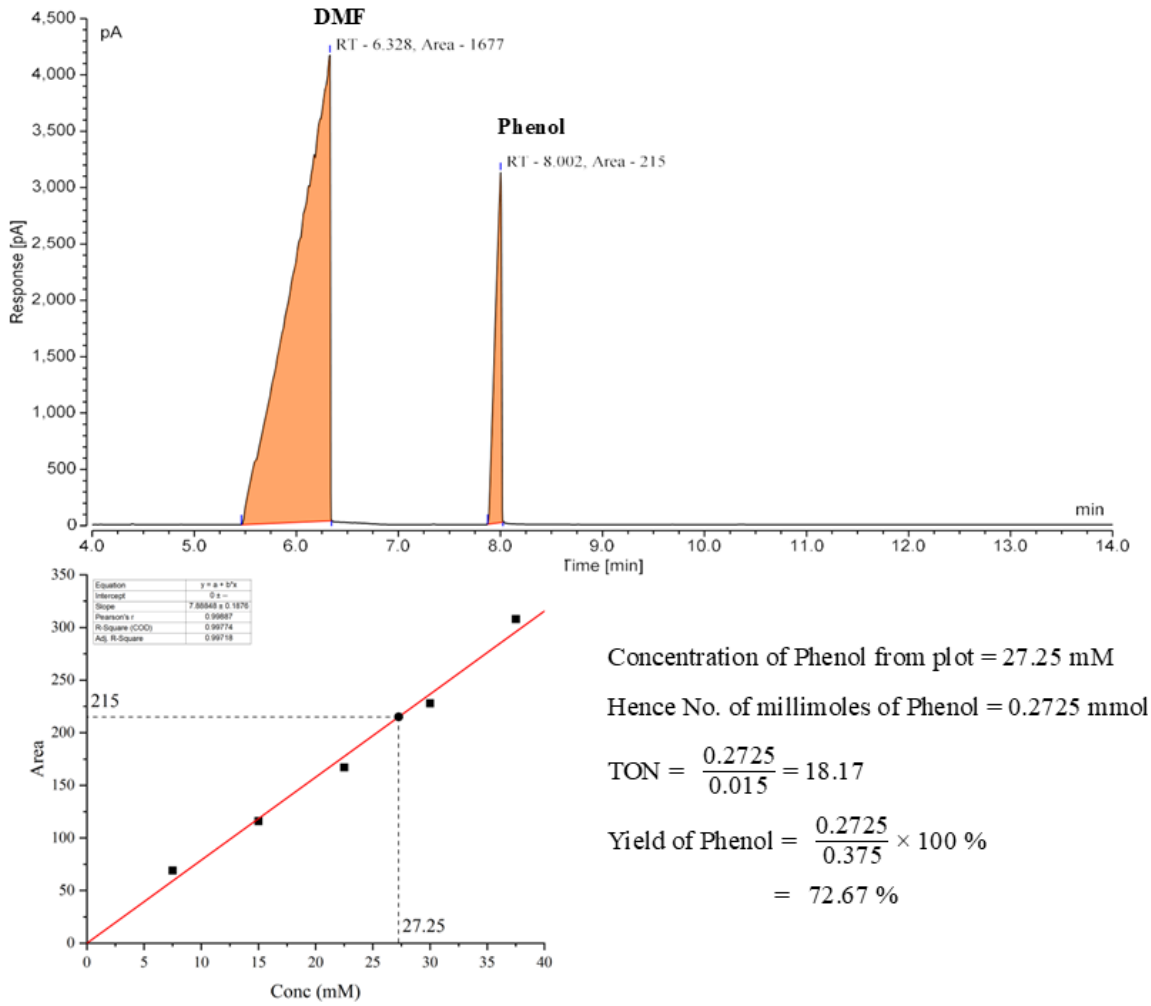


Figure S47. Calculation of yield for PhOH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 72.67 %**. The adjusted R^2 value for the calibration plot is 0.99718.

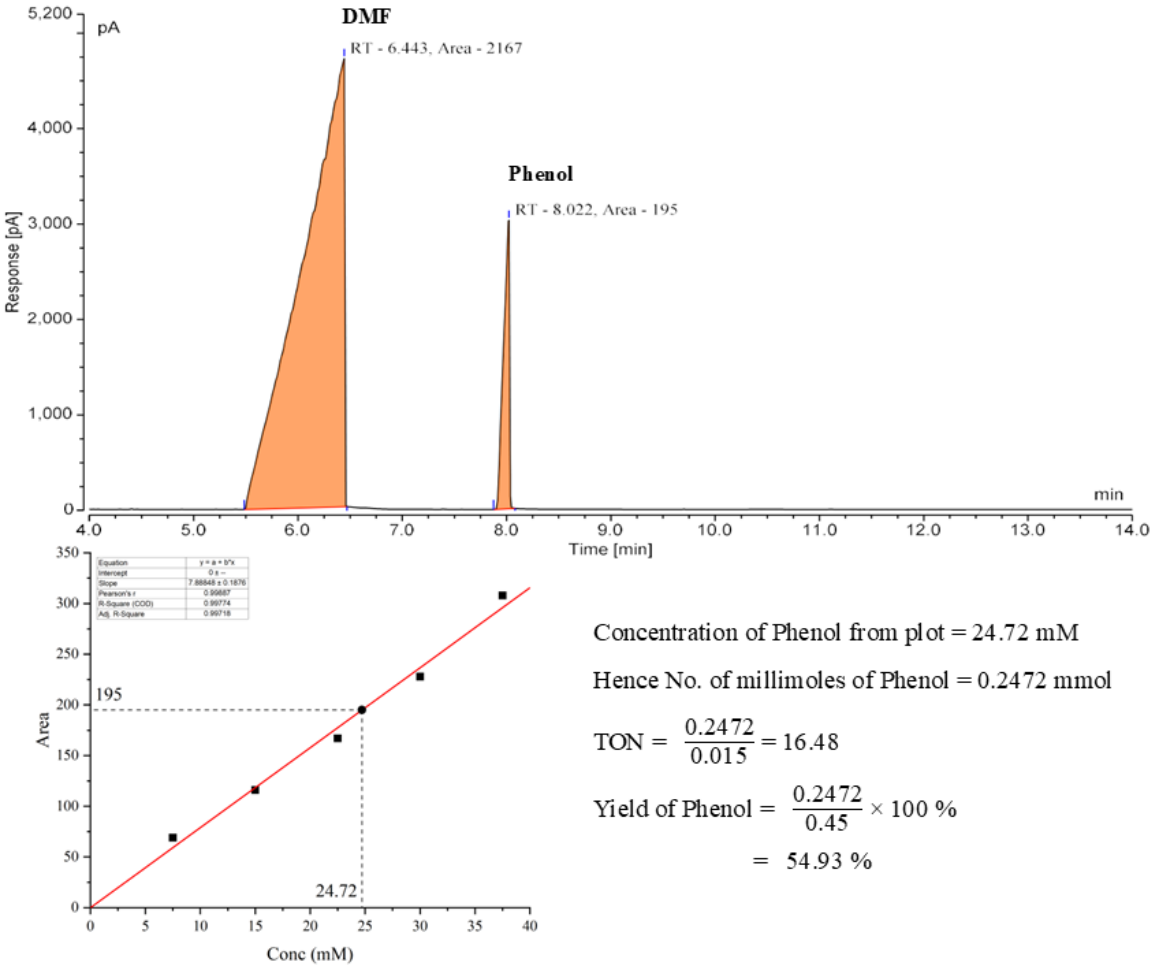


Figure S48. Calculation of yield for PhOH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:30, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 54.93 %**. The adjusted R^2 value for the calibration plot is 0.99718.

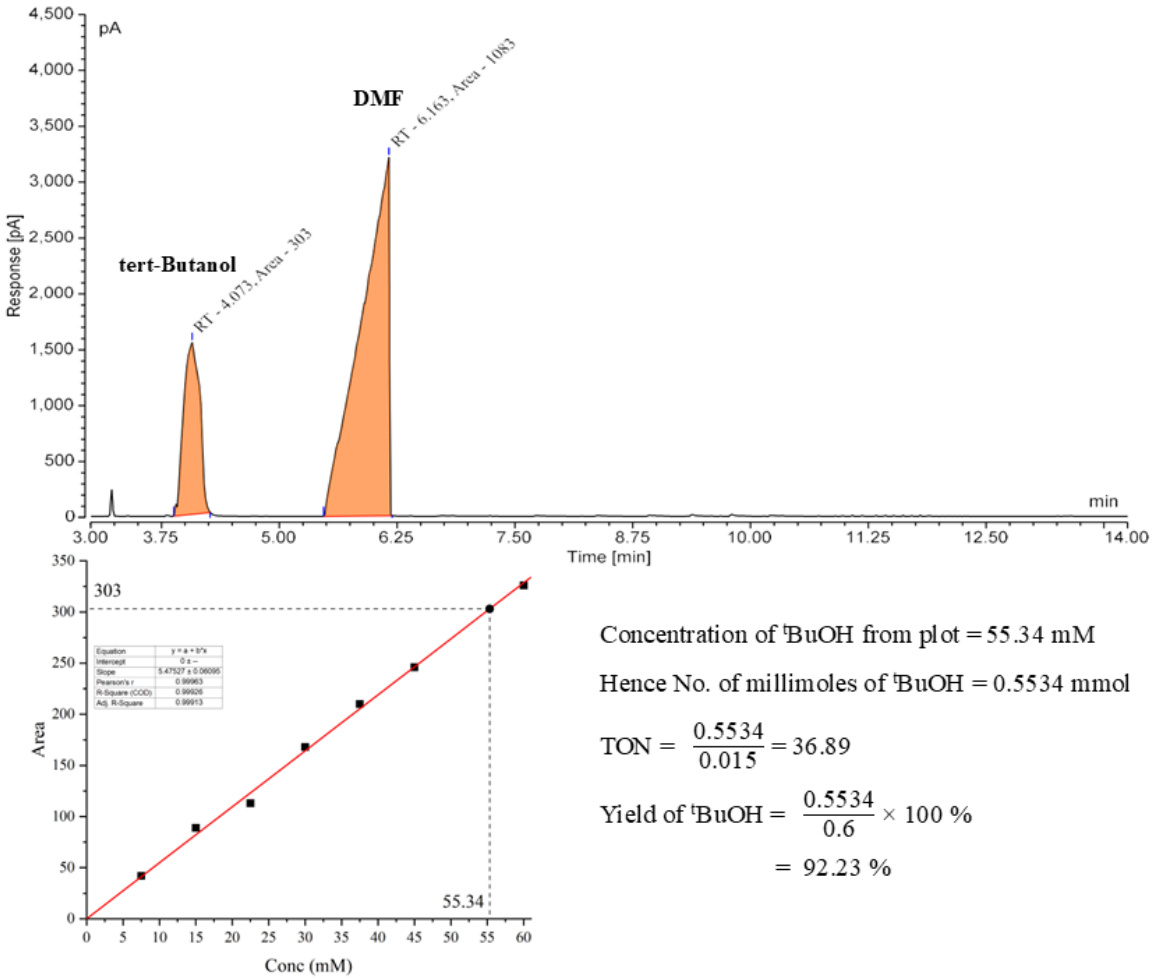


Figure S49. Calculation of yield for ᵗBuOH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaSᵗBu. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of ᵗBuOH = 92.23 %**. The adjusted R^2 value for the calibration plot is 0.99913.

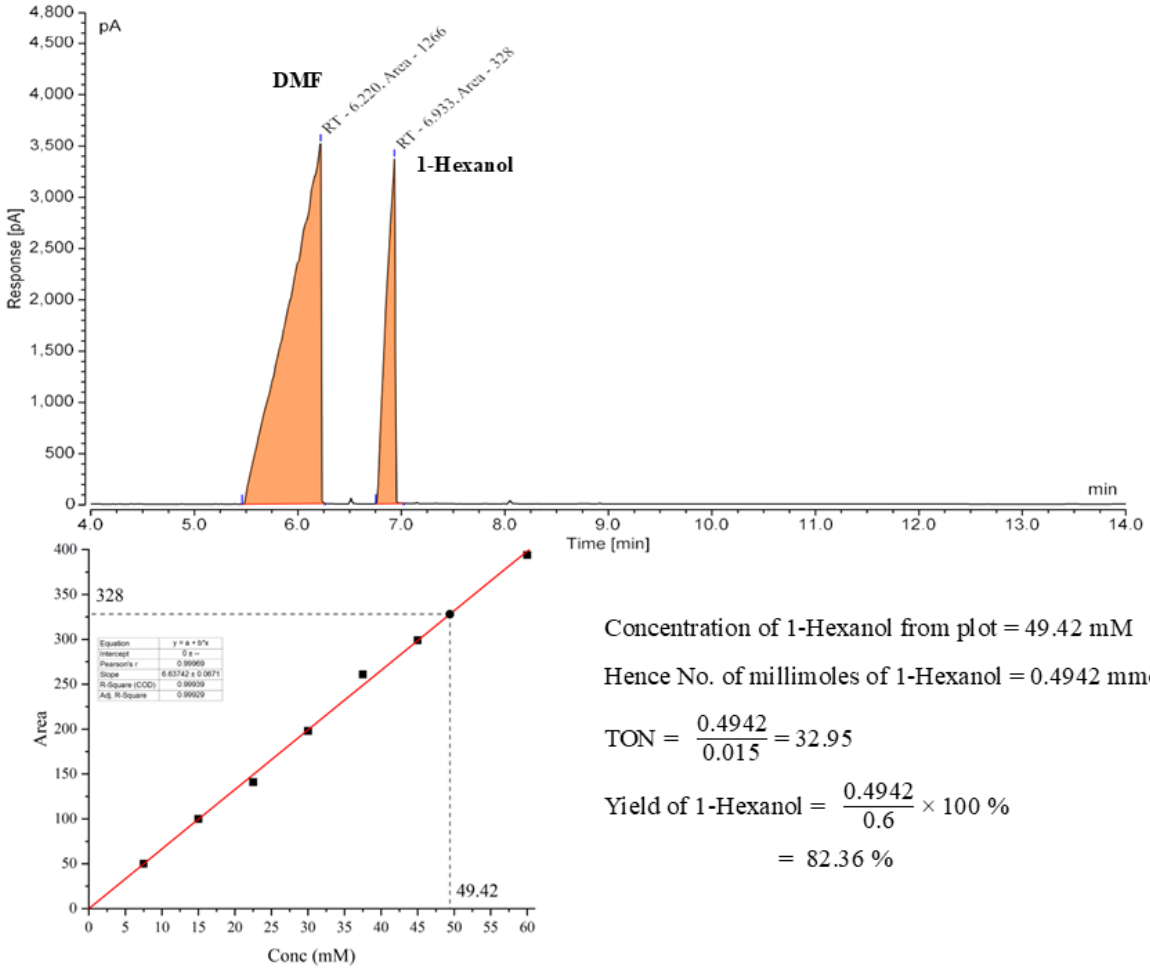


Figure S50. Calculation of yield for CH_3-$(CH_2)_4$-CH_2-OH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_4$-CH_3. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_4$-CH_2-OH = 82.36 %**. The adjusted R^2 value for the calibration plot is 0.99929.

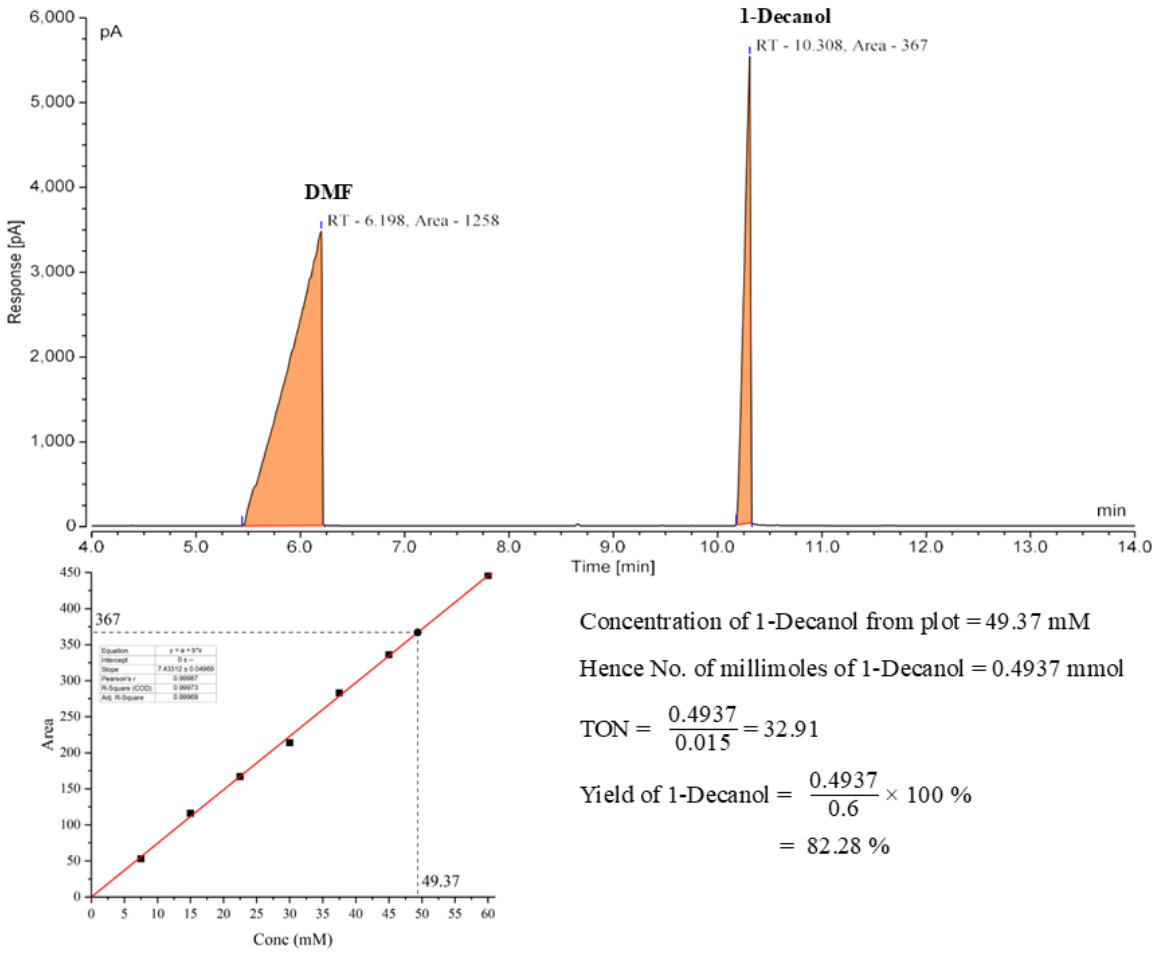


Figure S51. Calculation of yield for CH_3-$(CH_2)_8$-CH_2-OH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_8$-CH_3. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_8$-CH_2-OH = 82.28 %**. The adjusted R^2 value for the calibration plot is 0.99969.

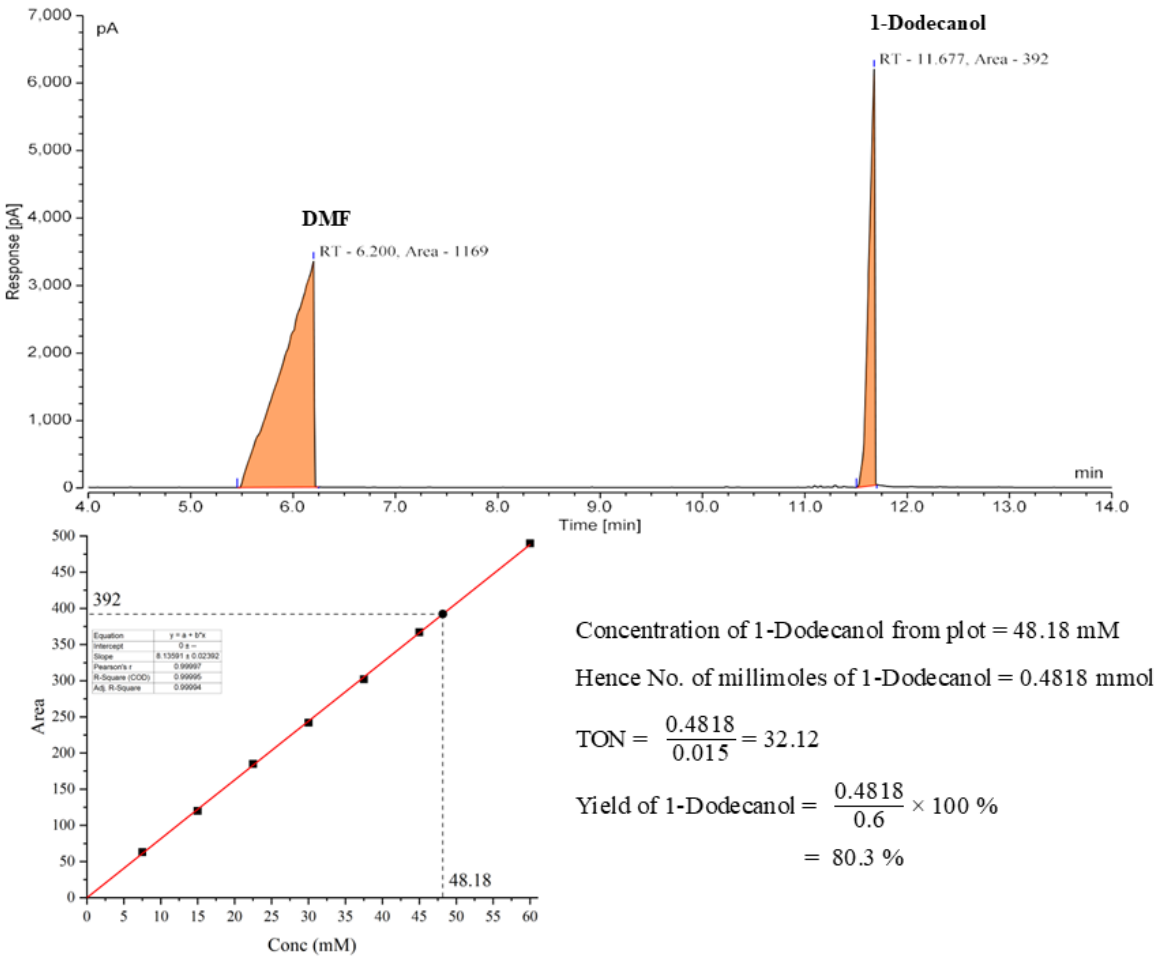


Figure S52. Calculation of yield for CH_3-$(CH_2)_{10}$-CH_2-OH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH)_{10}$-CH_3. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_{10}$-CH_2-OH = 80.30 %**. The adjusted R^2 value for the calibration plot is 0.99994.

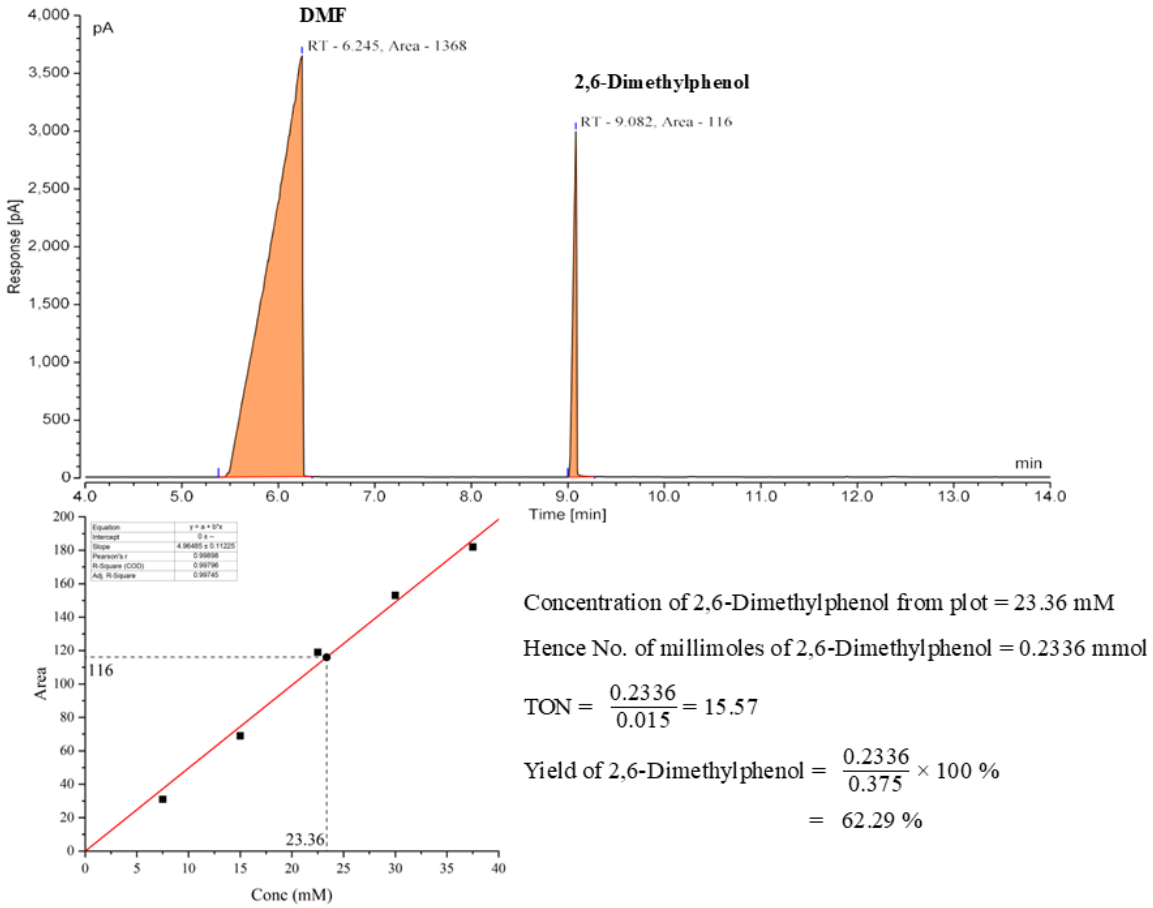


Figure S53. Calculation of yield for 2,6-Me_2-C_6H_3-OH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,6-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,6-Me_2-C_6H_3-OH = 62.29 %**. The adjusted R^2 value for the calibration plot is 0.99745.

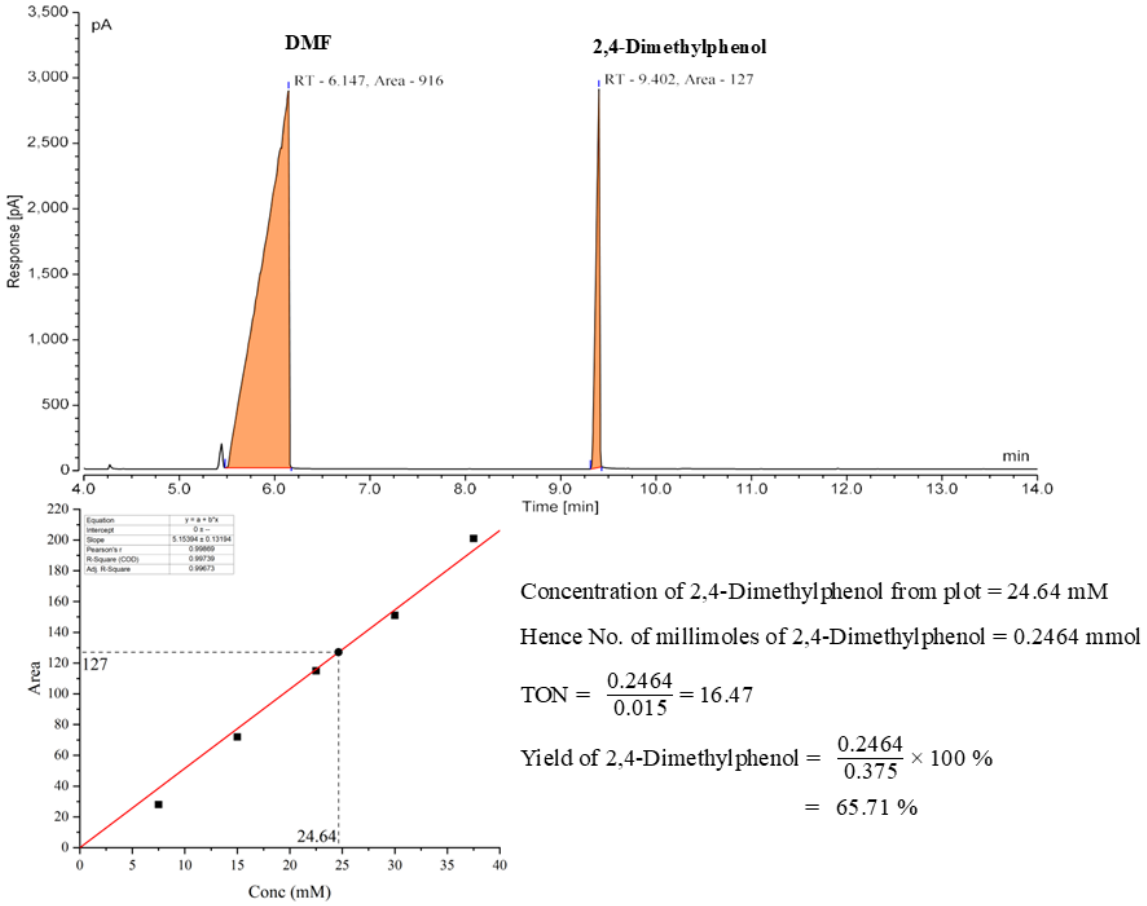


Figure S54. Calculation of yield for 2,4-Me_2-C_6H_3-OH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,4-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,4-Me_2-C_6H_3-OH = 65.71 %**. The adjusted R^2 value for the calibration plot is 0.99673.

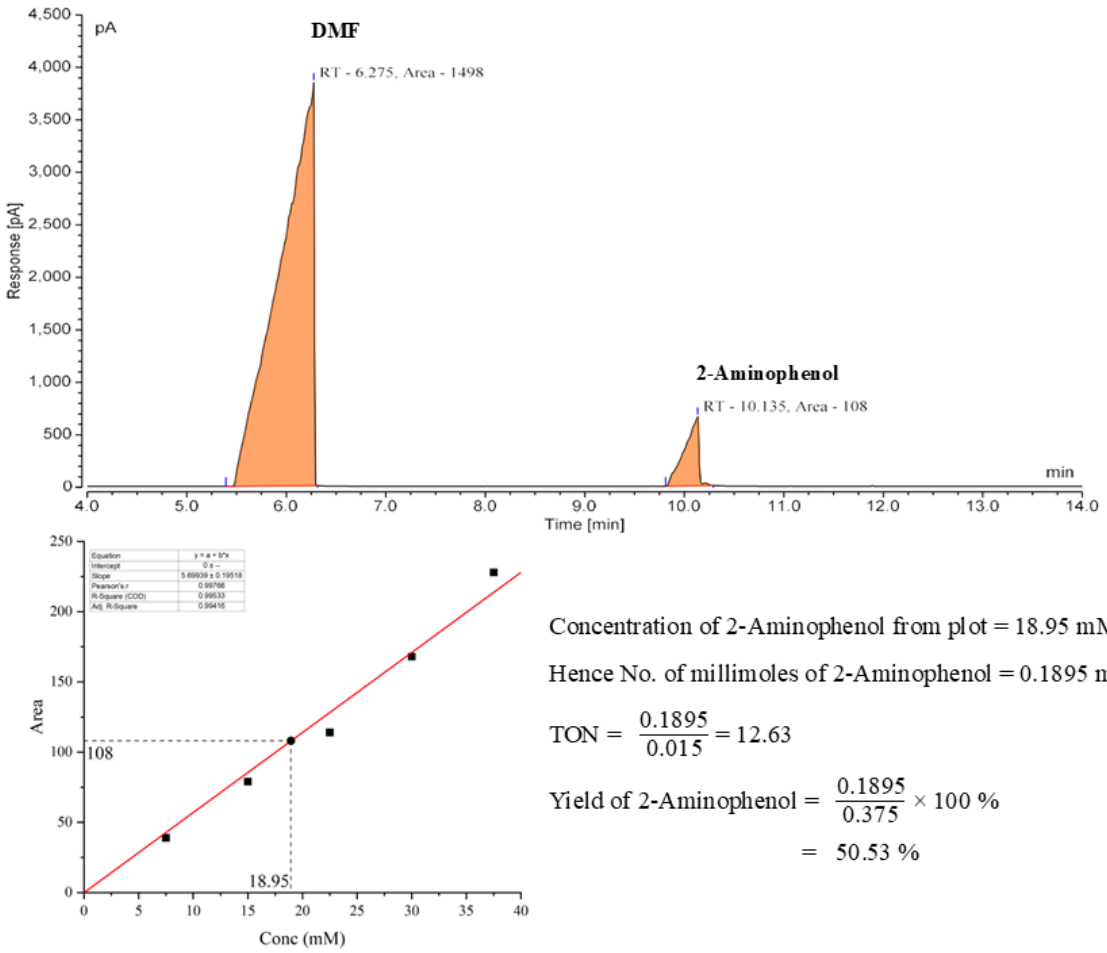


Figure S55. Calculation of yield for *o*-NH_2-C_6H_4-OH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-NH_2)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of *o*-NH_2-C_6H_4-OH = 50.53 %**. The adjusted R^2 value for the calibration plot is 0.99416.

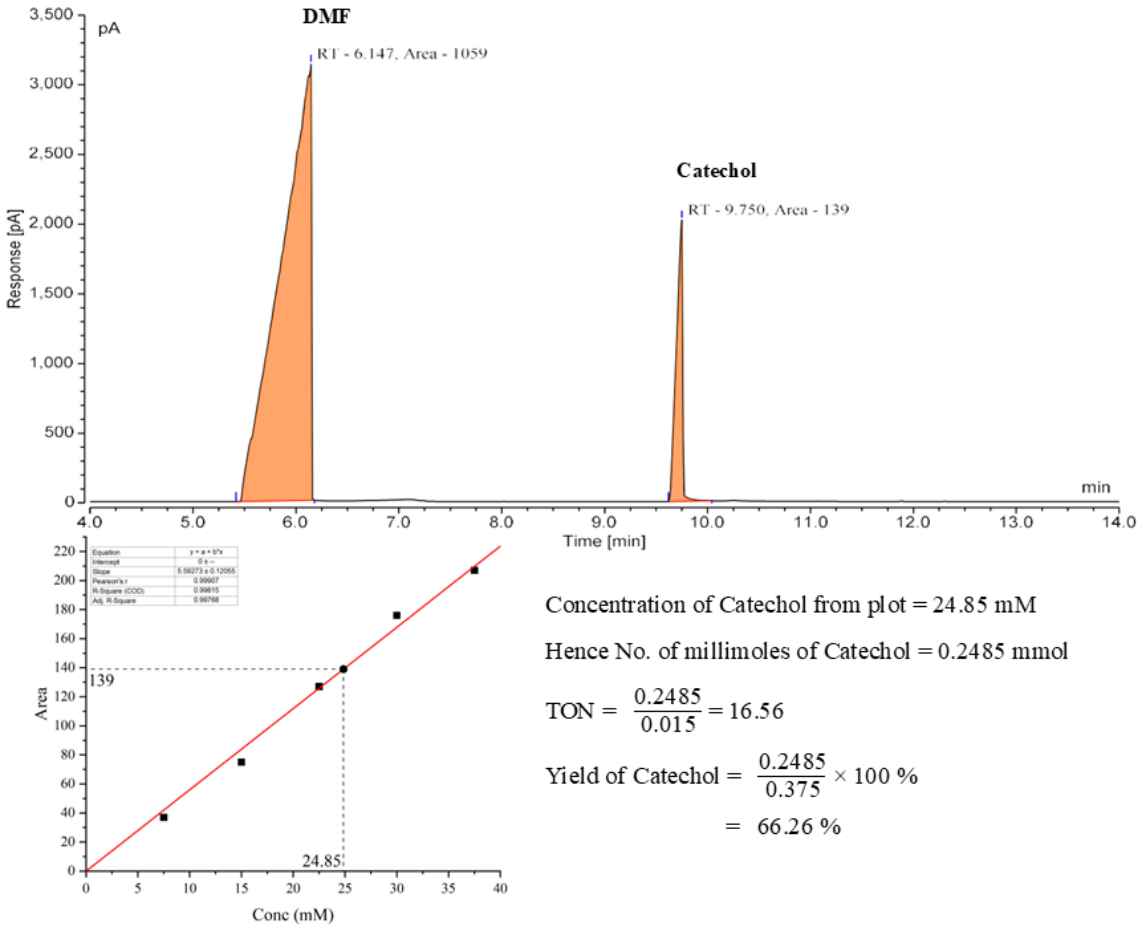


Figure S56. Calculation of yield for 1,2-$(OH)_2$-C_6H_4 obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-ONa)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 1,2-$(OH)_2$-C_6H_4 = 66.26 %**. The adjusted R^2 value for the calibration plot is 0.99768.

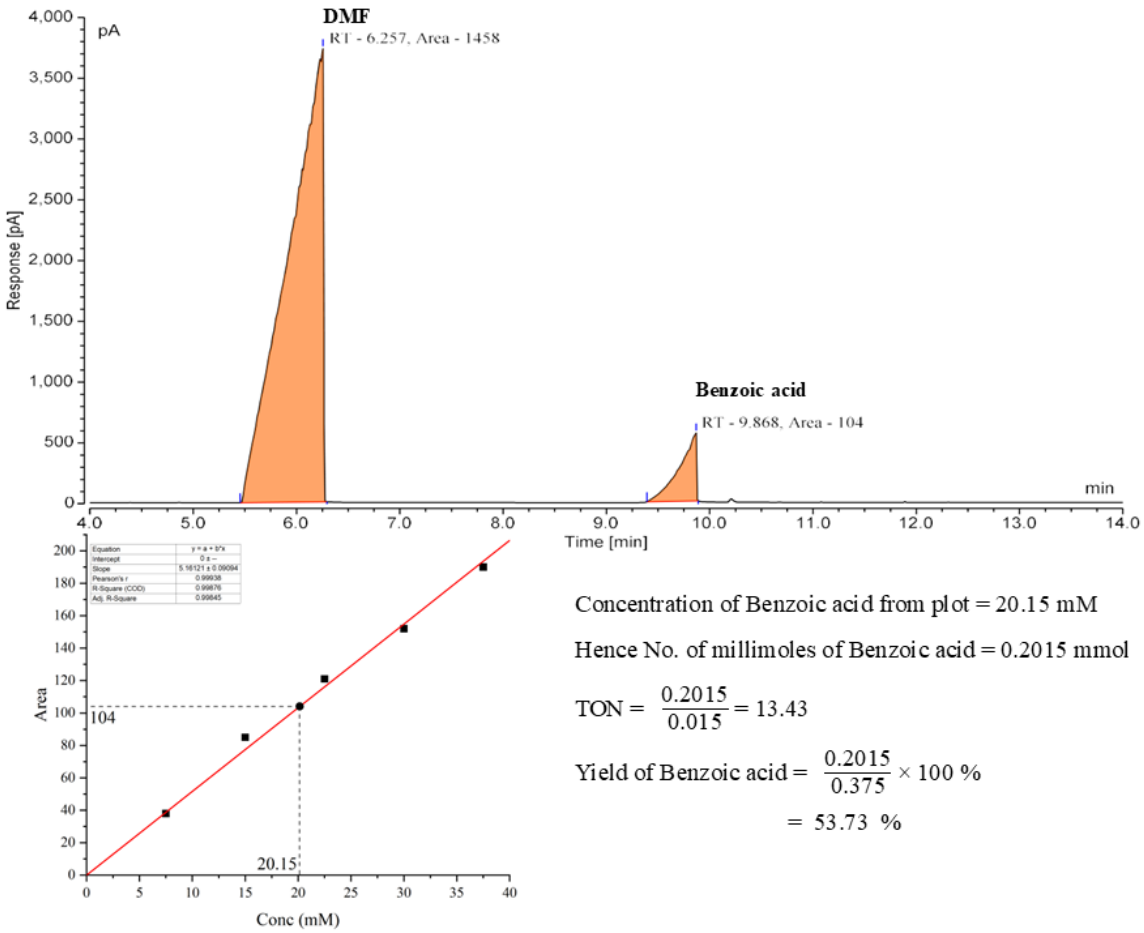


Figure S57. Calculation of yield for PhCOOH obtained from the **2f**$(BF_4)_2$ mediated catalytic hydrolysis of NaSC(O)Ph. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhCOOH = 53.73 %**. The adjusted R^2 value for the calibration plot is 0.99845.

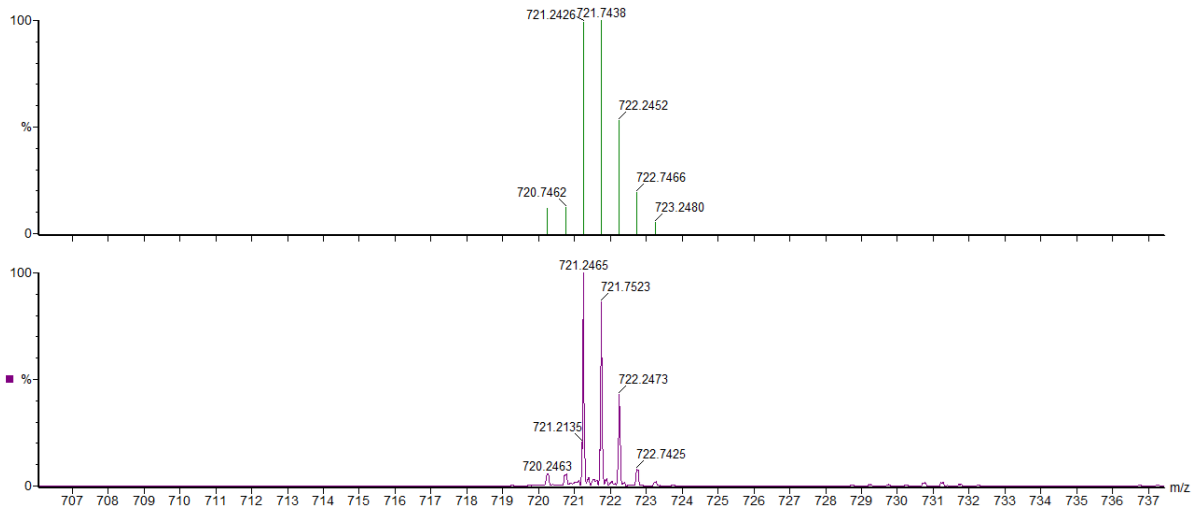


Figure S58. Mass spectrum (in MeCN) for $[Fe_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)(DMF)](BF_4)_2$ (**4b**$(BF_4)_2$) shows the presence of $[Fe_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{2+}$ at m/z = 721.2426 (simulated, green line); 721.2465 (obtained, purple line).

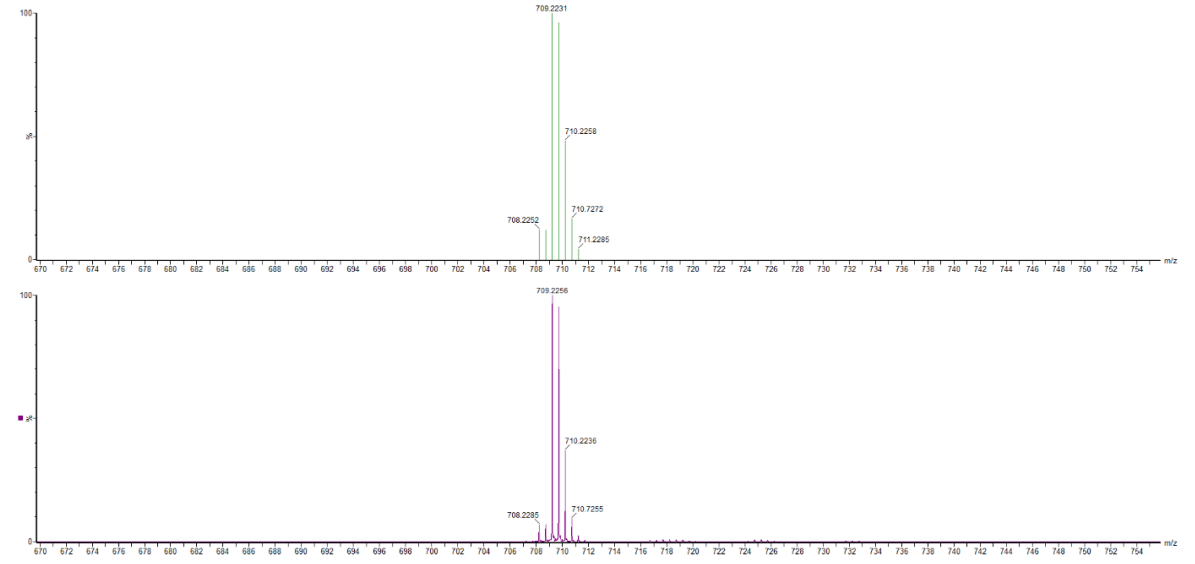


Figure S59. Mass spectrum (in MeCN) for $[Fe_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}F_2)(MeCN)](BF_4)_2$, (**4c**$(BF_4)_2$) shows the presence of $[Fe_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}F_2)]^{2+}$ at m/z = 709.2231 (simulated, green line); 709.2256 (obtained, purple line).

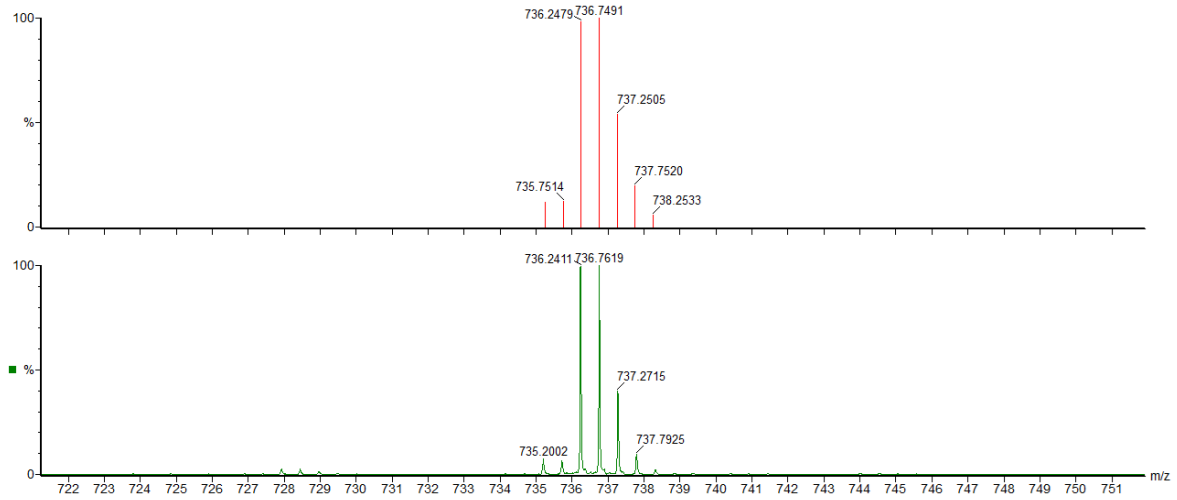


Figure S60. Mass spectrum (in MeCN) for $[Fe_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)(DMF)](BF_4)_2$, **4d**$(BF_4)_2$ shows the presence of $[Fe_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{2+}$ at m/z = 736.2479 (simulated, red line); 736.2411 (obtained, green line).

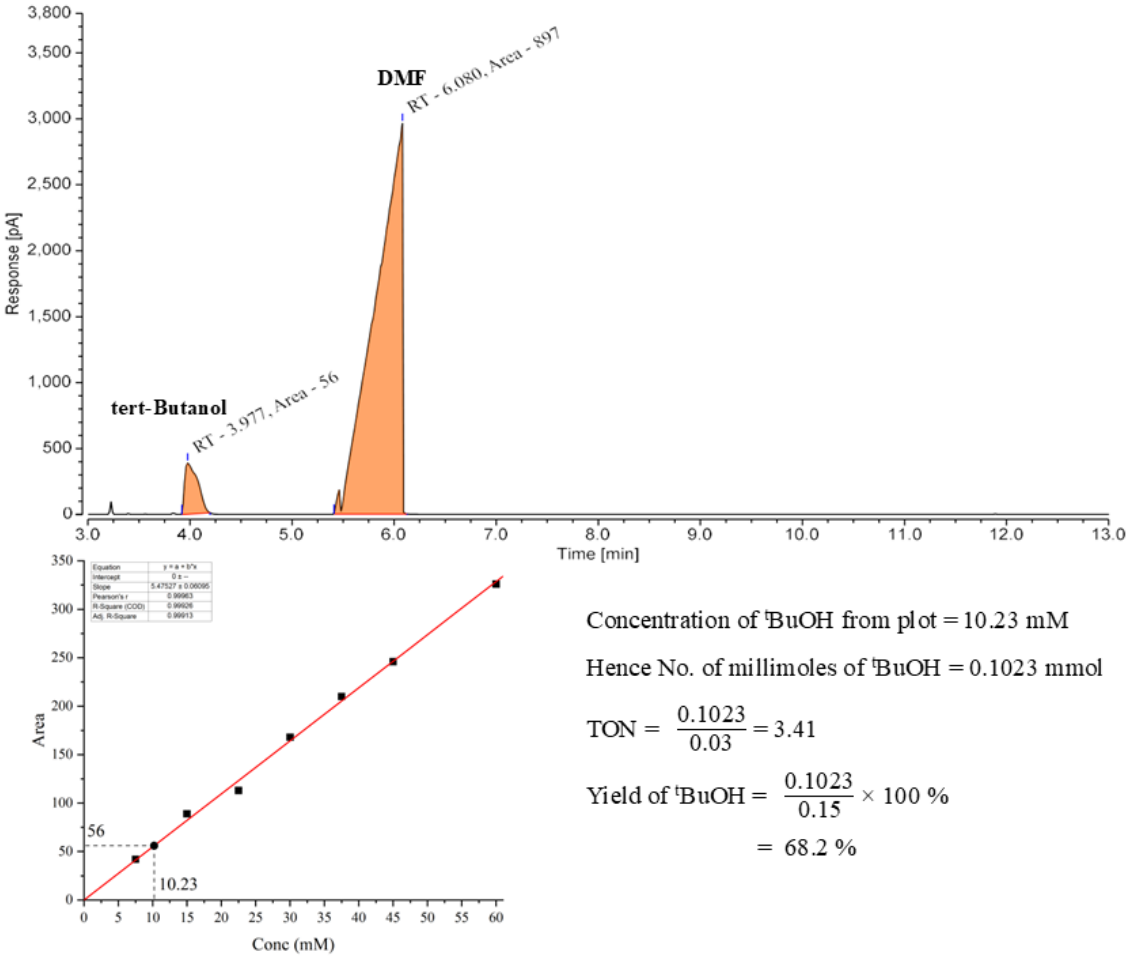


Figure S61. Calculation of yield for ^{t}BuOH obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of NaS^tBu. Reaction conditions: catalyst:thiolate = 1:5, thiolate:H_2O = 1:16, reaction time = 30h, solvent = DMF, temperature = 25°C. Note that **yield of ^{t}BuOH = 68.2 %**. The adjusted R^2 value for the calibration plot is 0.99913.

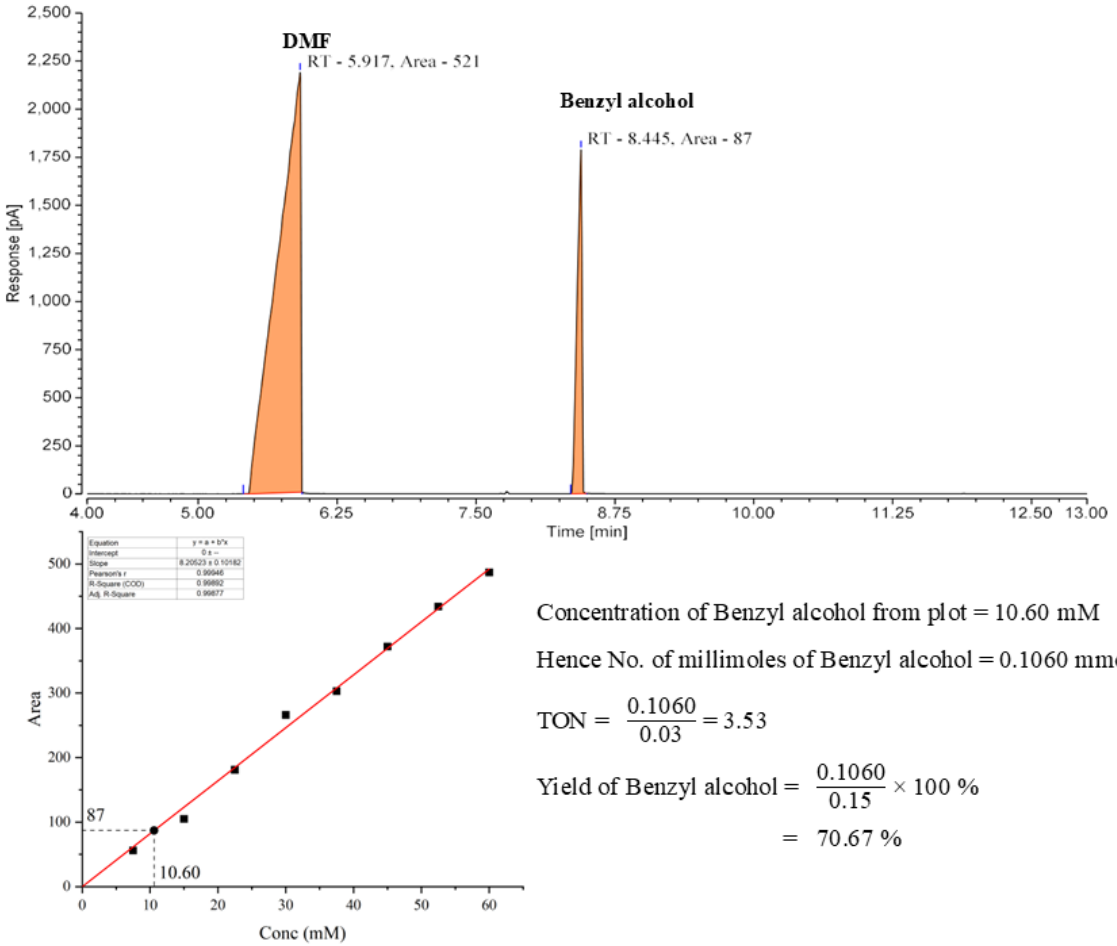


Figure S62. Calculation of yield for $PhCH_2OH$ obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:5, thiolate:H_2O = 1:16, reaction time = 30h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 70.67 %**. The adjusted R^2 value for the calibration plot is 0.99877.

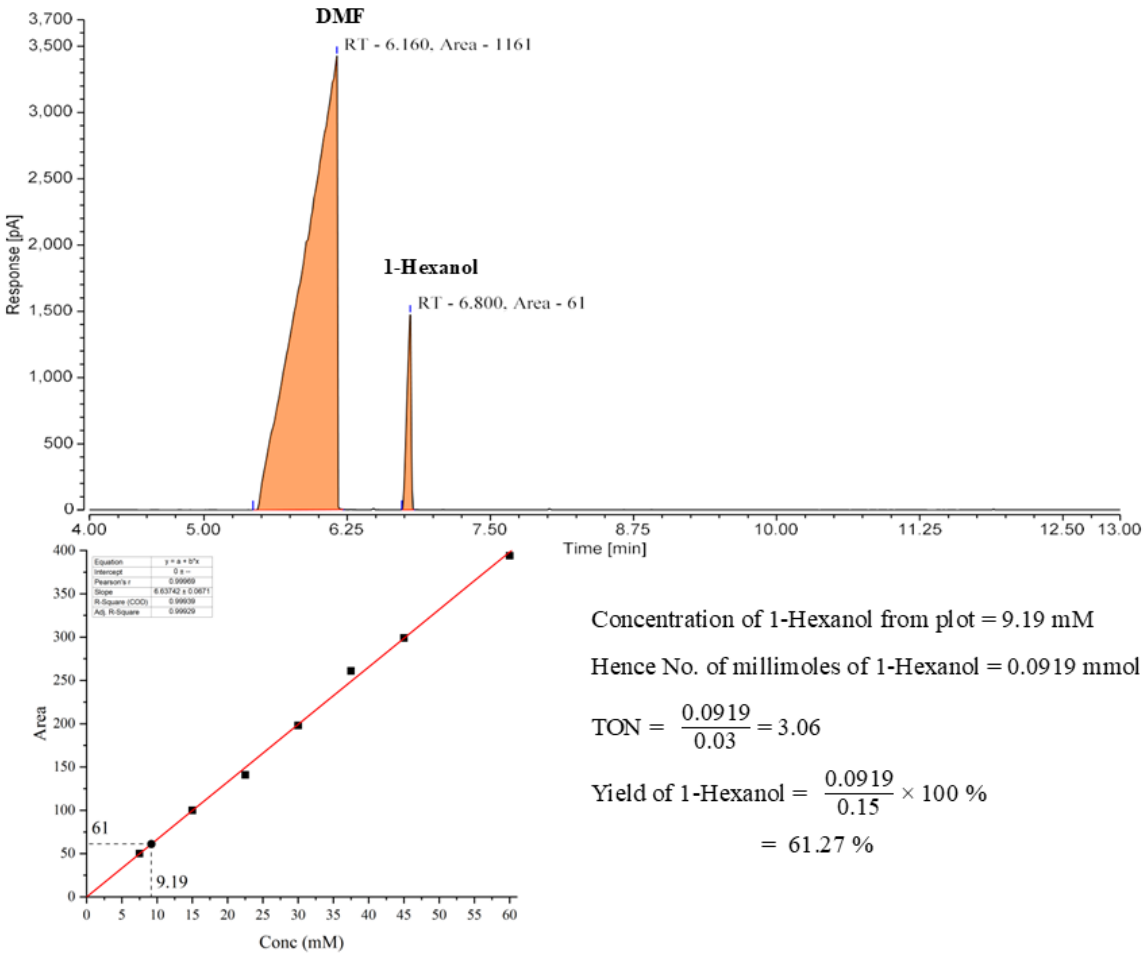


Figure S63. Calculation of yield for CH_3-$(CH_2)_4$-CH_2-OH obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_4$-CH_3. Reaction conditions: catalyst:thiolate = 1:5, thiolate:H_2O = 1:16, reaction time = 30h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_4$-CH_2-OH = 61.27 %**. The adjusted R^2 value for the calibration plot is 0.99929.

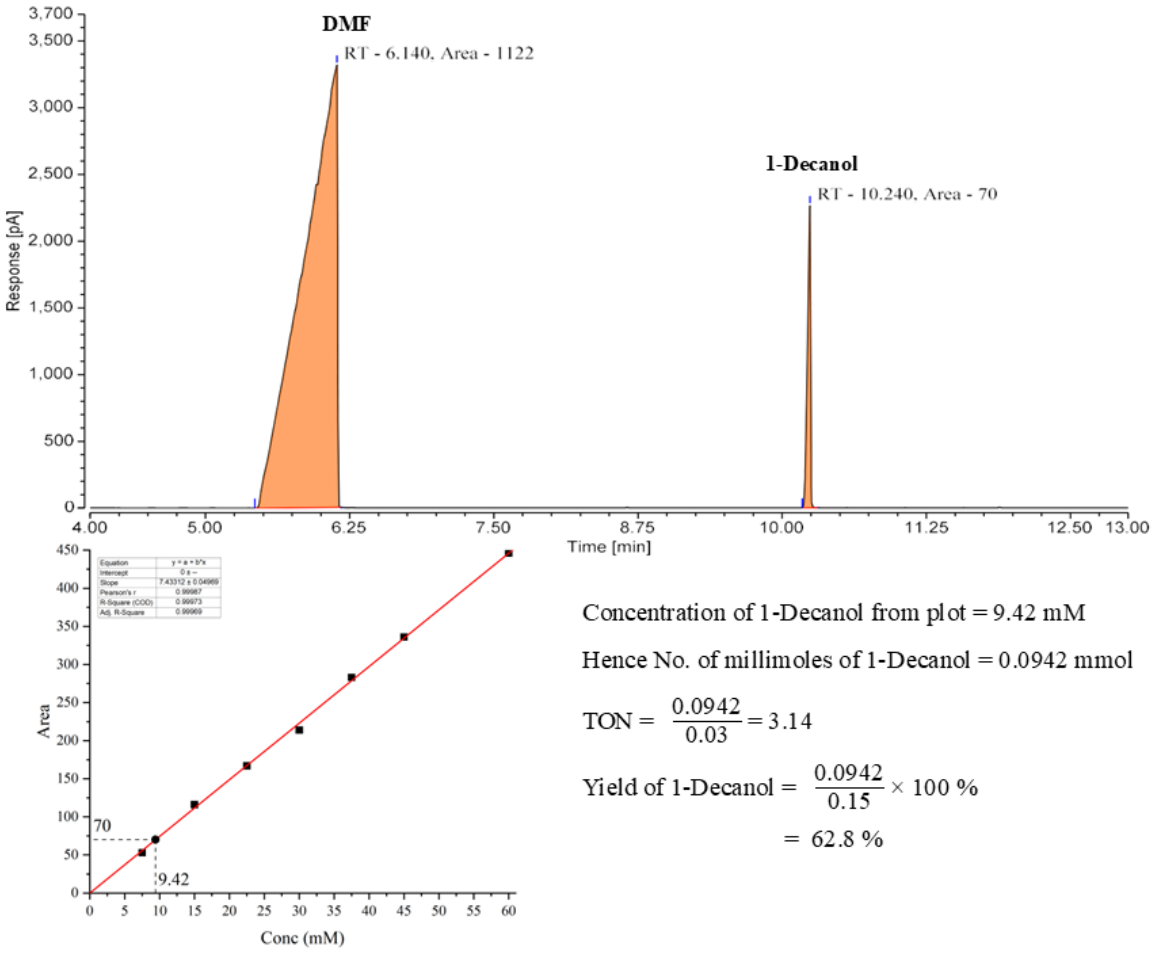


Figure S64. Calculation of yield for CH_3-$(CH_2)_8$-CH_2-OH obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_8$-CH_3. Reaction conditions: catalyst:thiolate = 1:5, thiolate:H_2O = 1:16, reaction time = 30h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_8$-CH_2-OH = 62.8 %**. The adjusted R^2 value for the calibration plot is 0.99969.

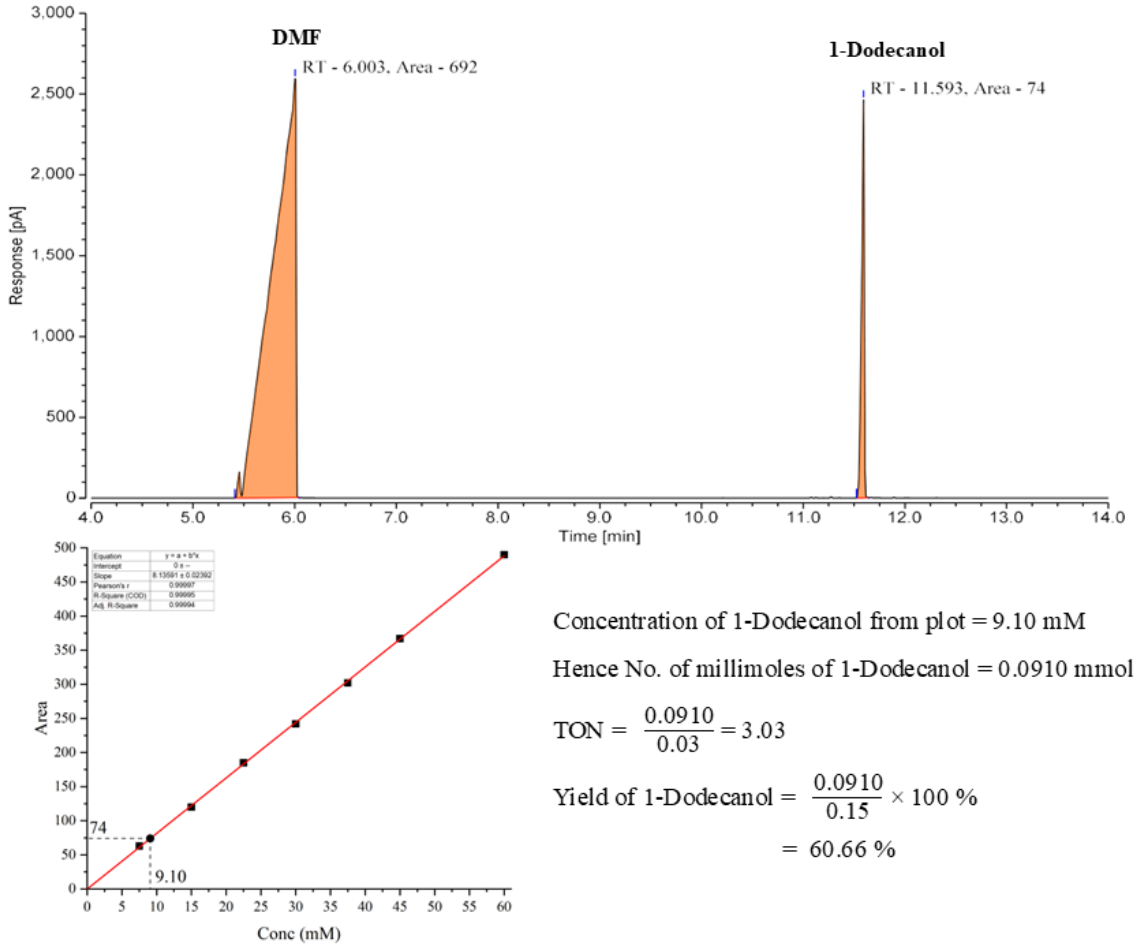


Figure S65. Calculation of yield for CH_3-$(CH_2)_{10}$-CH_2-OH obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH)_{10}$-CH_3. Reaction conditions: catalyst:thiolate = 1:5, thiolate:H_2O = 1:16, reaction time = 30h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_{10}$-CH_2-OH = 60.66 %**. The adjusted R^2 value for the calibration plot is 0.99994.

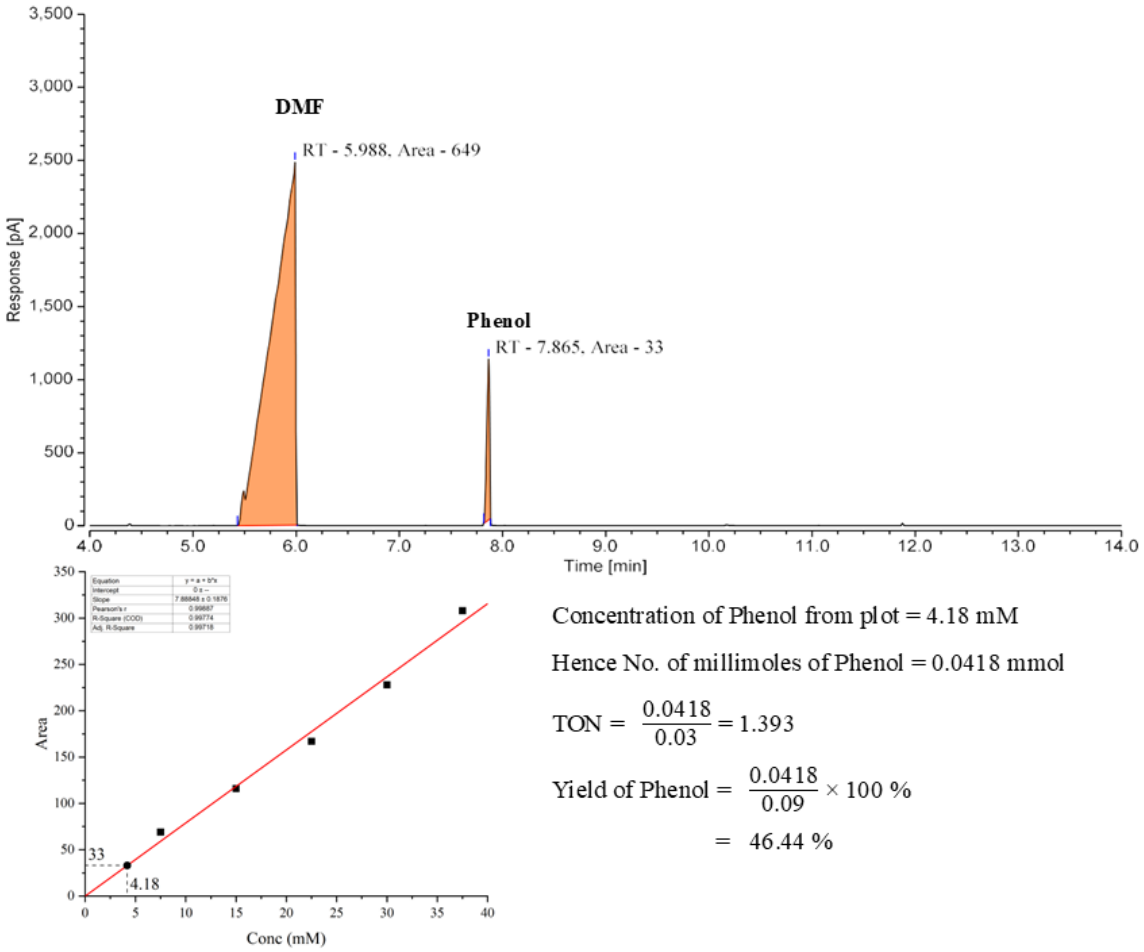


Figure S66. Calculation of yield for PhOH obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:3, thiolate:H_2O = 1:16, reaction time = 120h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 46.44 %**. The adjusted R^2 value for the calibration plot is 0.99718.

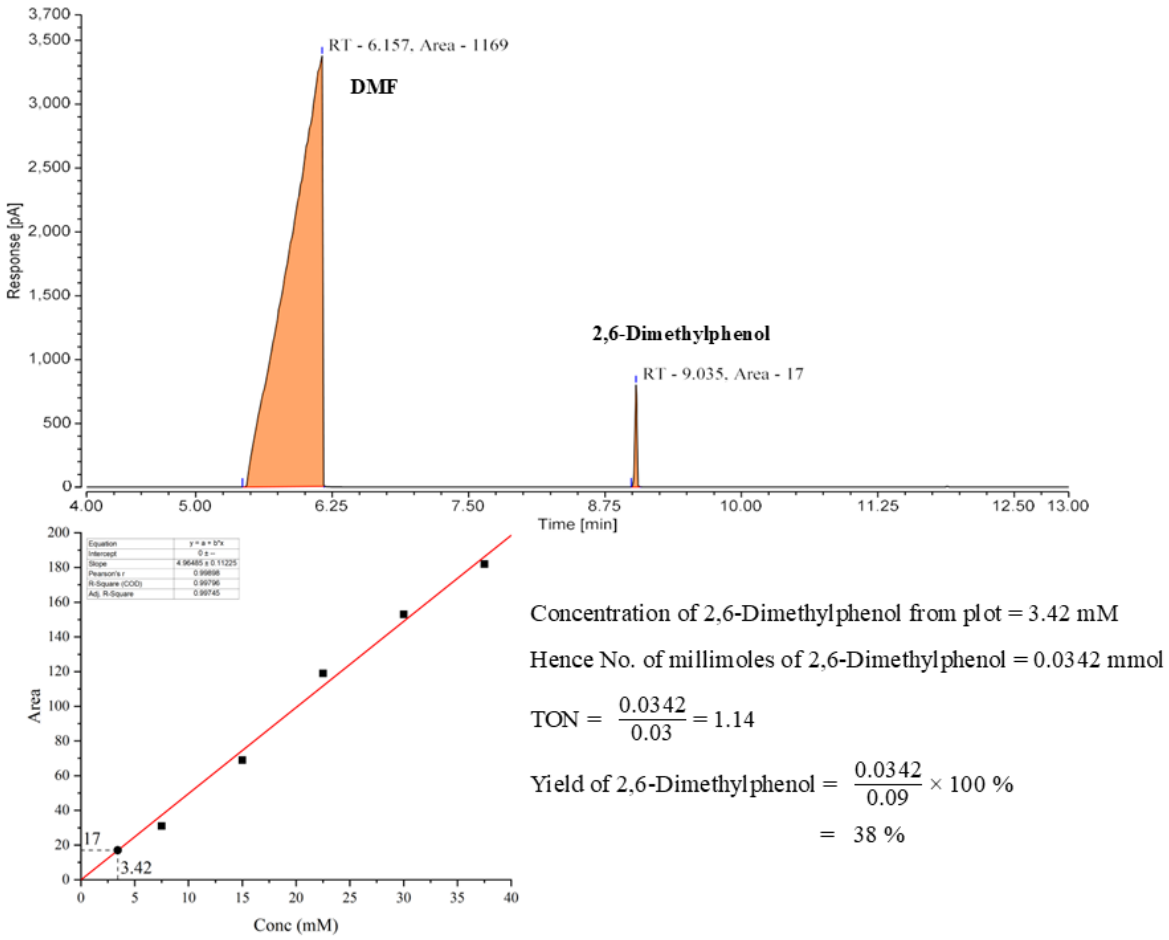
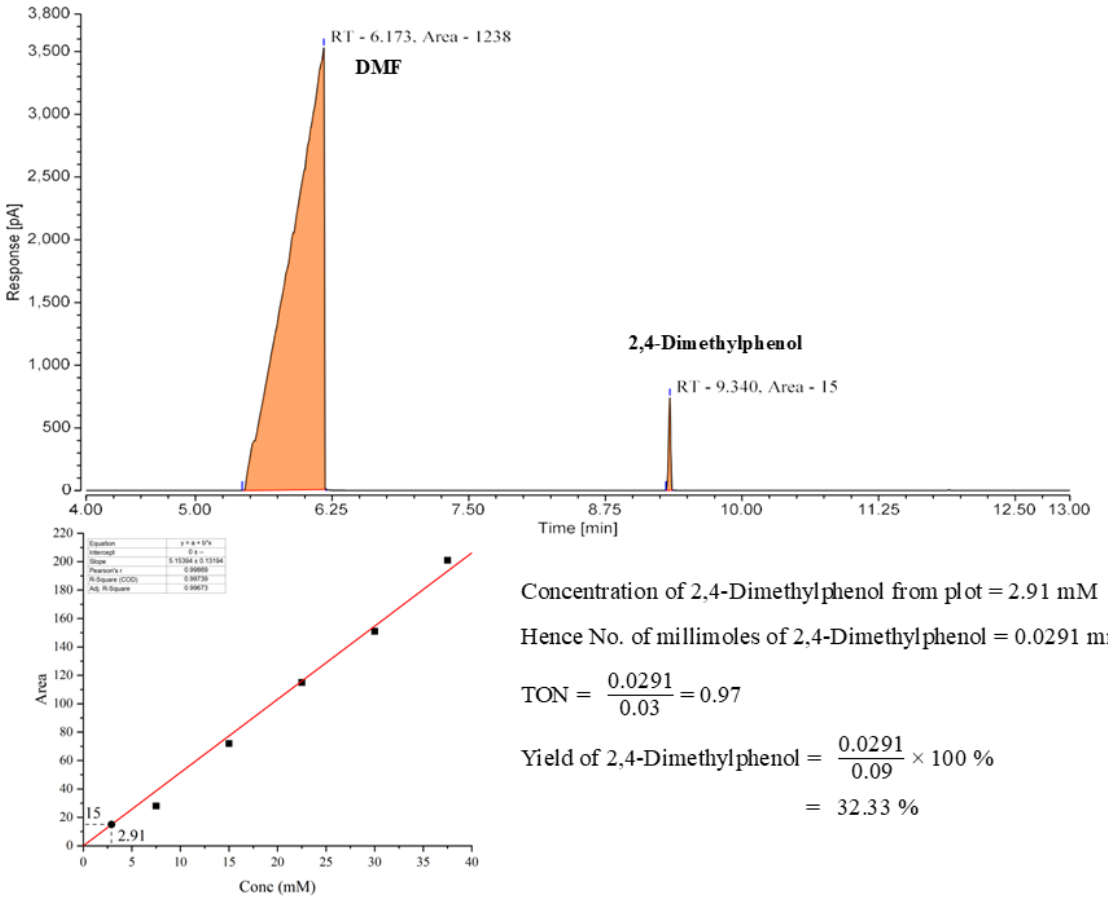


Figure S67. Calculation of yield for 2,6-Me_2-C_6H_3-OH obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,6-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:3, thiolate:H_2O = 1:16, reaction time = 120h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,6-Me_2-C_6H_3-OH = 38 %**. The adjusted R^2 value for the calibration plot is 0.99745.



Concentration of 2,4-Dimethylphenol from plot = 2.91 mM

Hence No. of millimoles of 2,4-Dimethylphenol = 0.0291 mmol

$$\text{TON} = \frac{0.0291}{0.03} = 0.97$$

$$\text{Yield of 2,4-Dimethylphenol} = \frac{0.0291}{0.09} \times 100\ \% = 32.33\ \%$$

Figure S68. Calculation of yield for 2,4-Me_2-C_6H_3-OH obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,4-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:3, thiolate:H_2O = 1:16, reaction time = 120h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,4-Me_2-C_6H_3-OH = 32.33 %**. The adjusted R^2 value for the calibration plot is 0.99673.

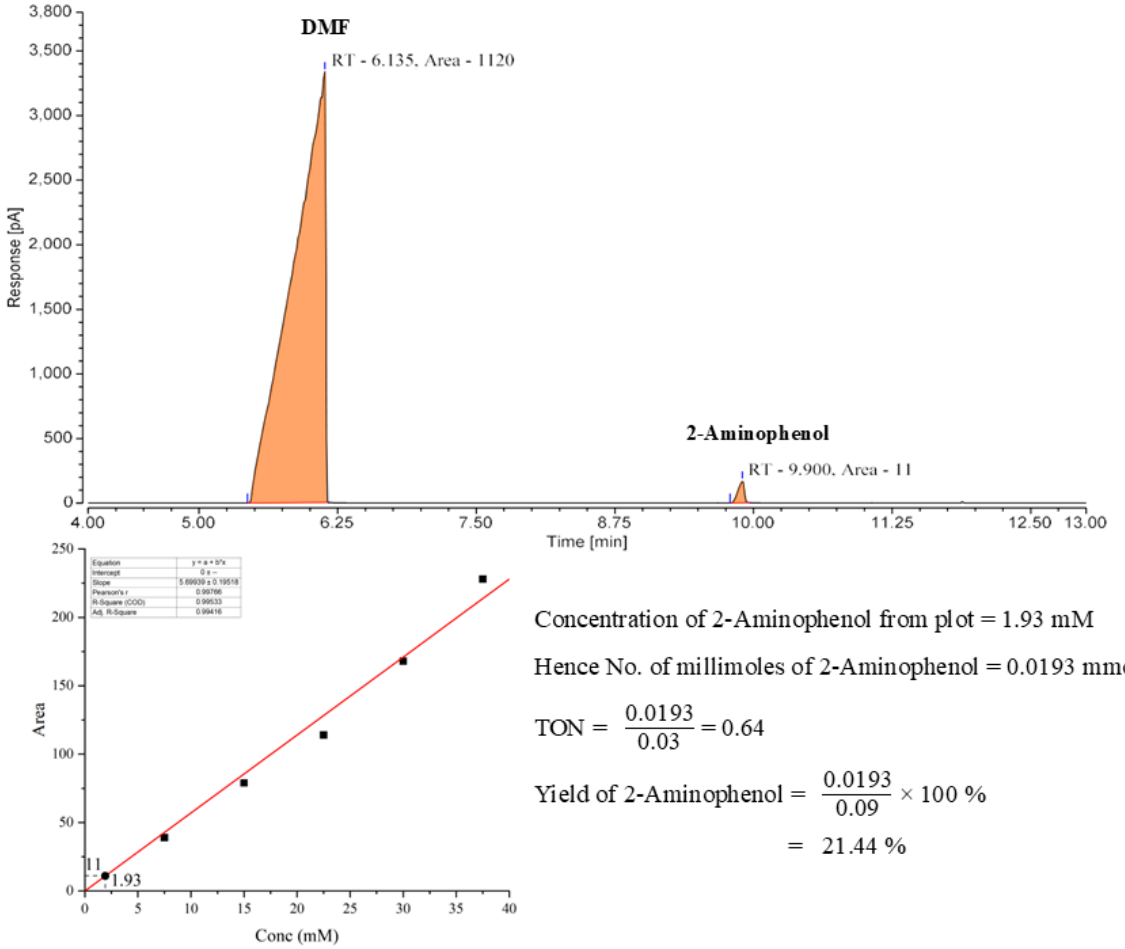


Figure S69. Calculation of yield for *o*-NH_2-C_6H_4-OH obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-NH_2)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:3, thiolate:H_2O = 1:16, reaction time = 120h, solvent = DMF, temperature = 25°C. Note that the **yield of *o*-NH_2-C_6H_4-OH = 21.44 %**. The adjusted R^2 value for the calibration plot is 0.99416.

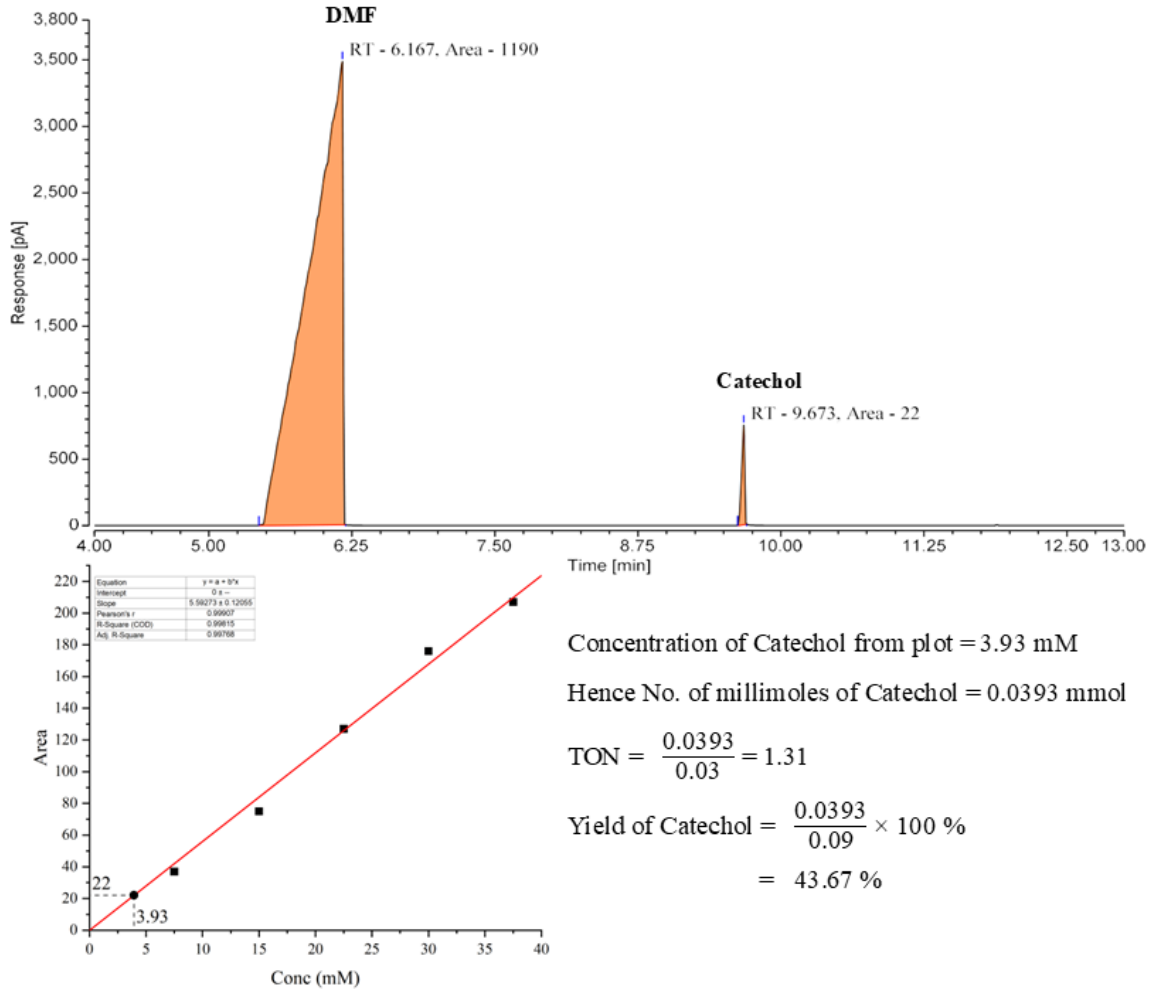


Figure S70. Calculation of yield for 1,2-$(OH)_2$-C_6H_4 obtained from the **3**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-ONa)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:3, thiolate:H_2O = 1:16, reaction time = 120h, solvent = DMF, temperature = 25°C. Note that the **yield of 1,2-$(OH)_2$-C_6H_4 = 43.67 %**. The adjusted R^2 value for the calibration plot is 0.99768.

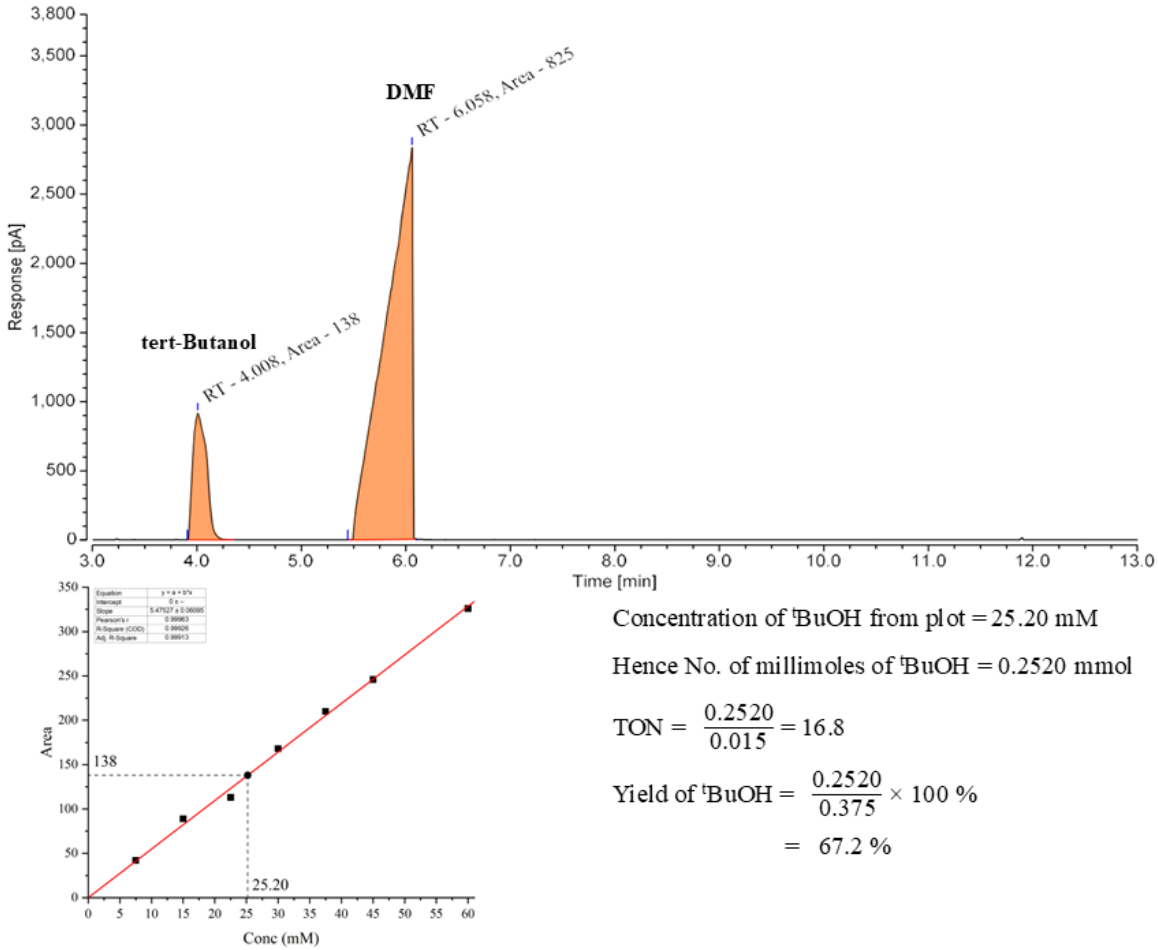


Figure S71. Calculation of yield for ᵗBuOH obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaSᵗBu. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of ᵗBuOH = 67.2 %**. The adjusted R^2 value for the calibration plot is 0.99913.

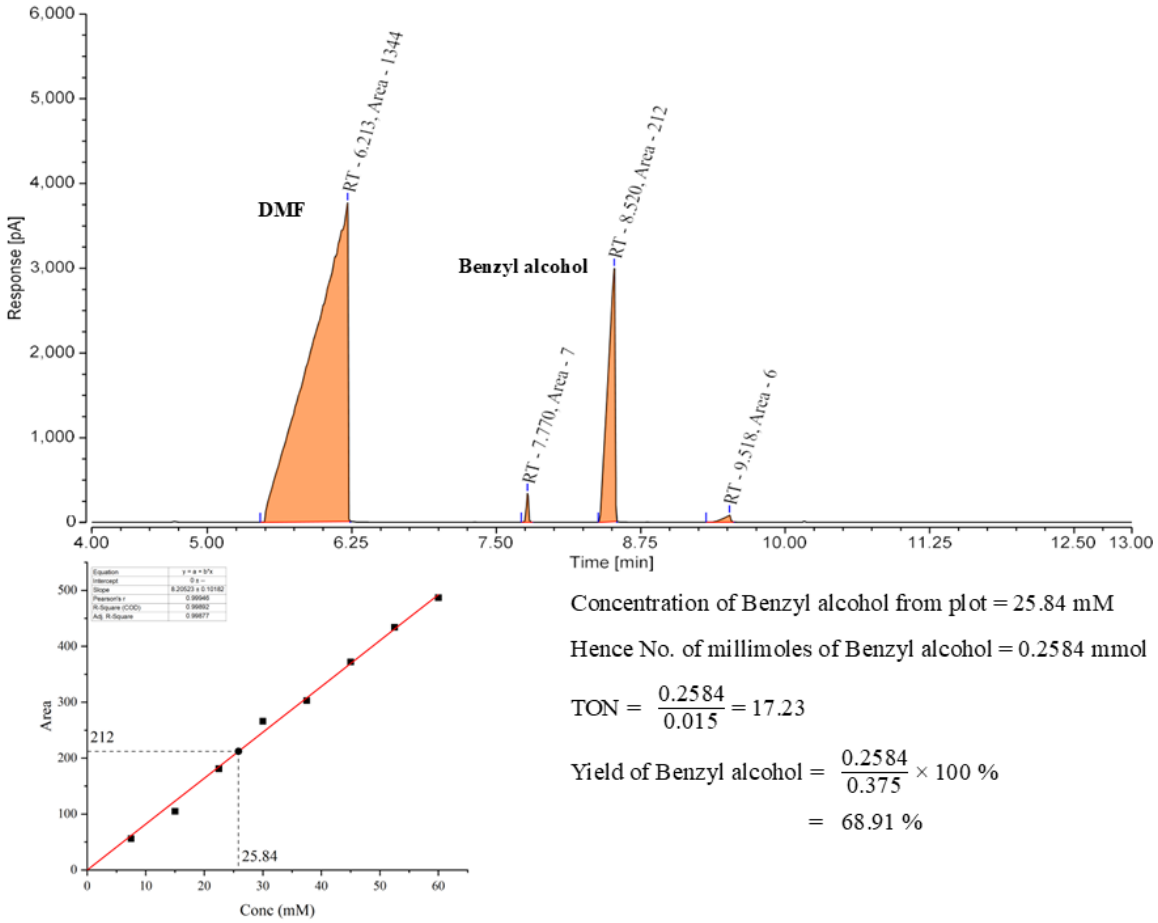


Figure S72. Calculation of yield for $PhCH_2OH$ obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 68.91 %**. The adjusted R^2 value for the calibration plot is 0.99877.

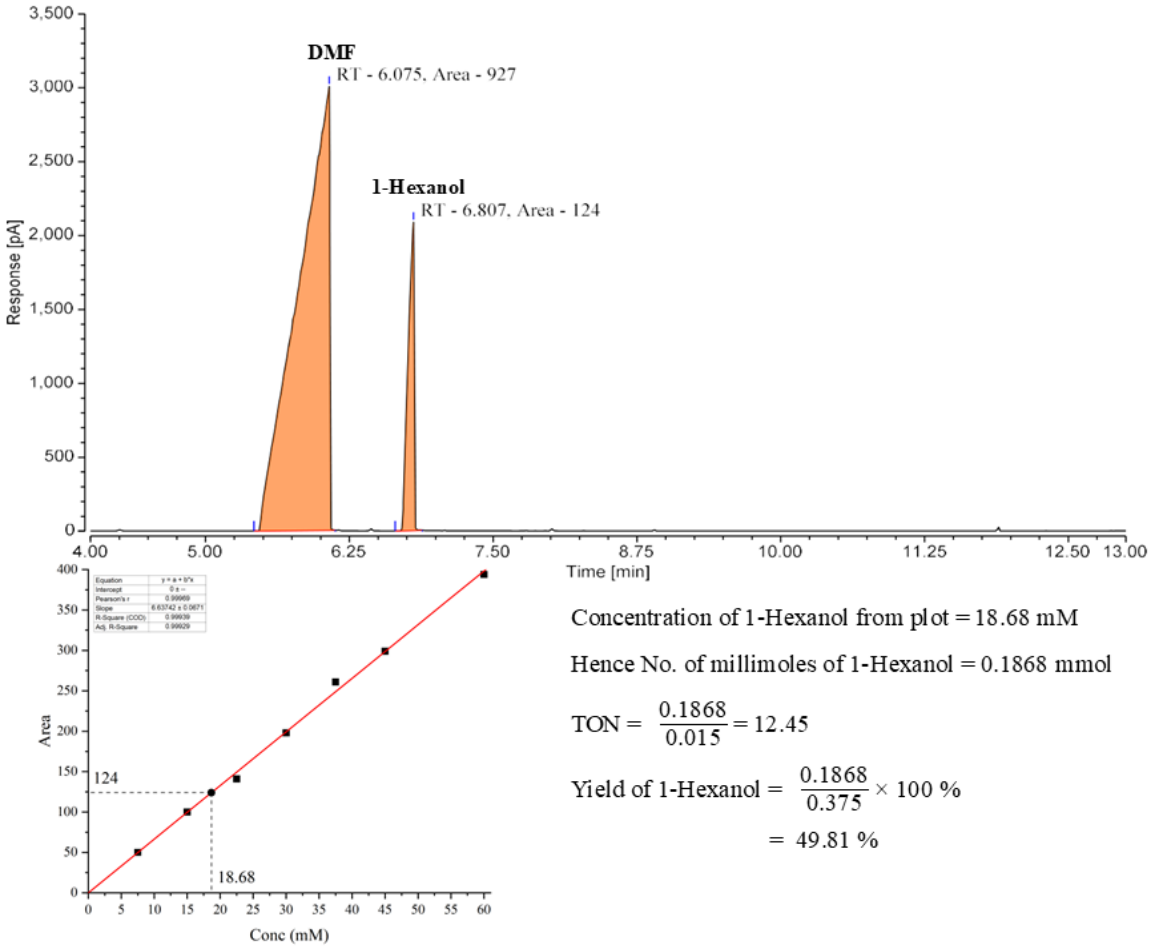


Figure S73. Calculation of yield for CH_3-$(CH_2)_4$-CH_2-OH obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_4$-CH_3. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_4$-CH_2-OH = 49.81 %**. The adjusted R^2 value for the calibration plot is 0.99929.

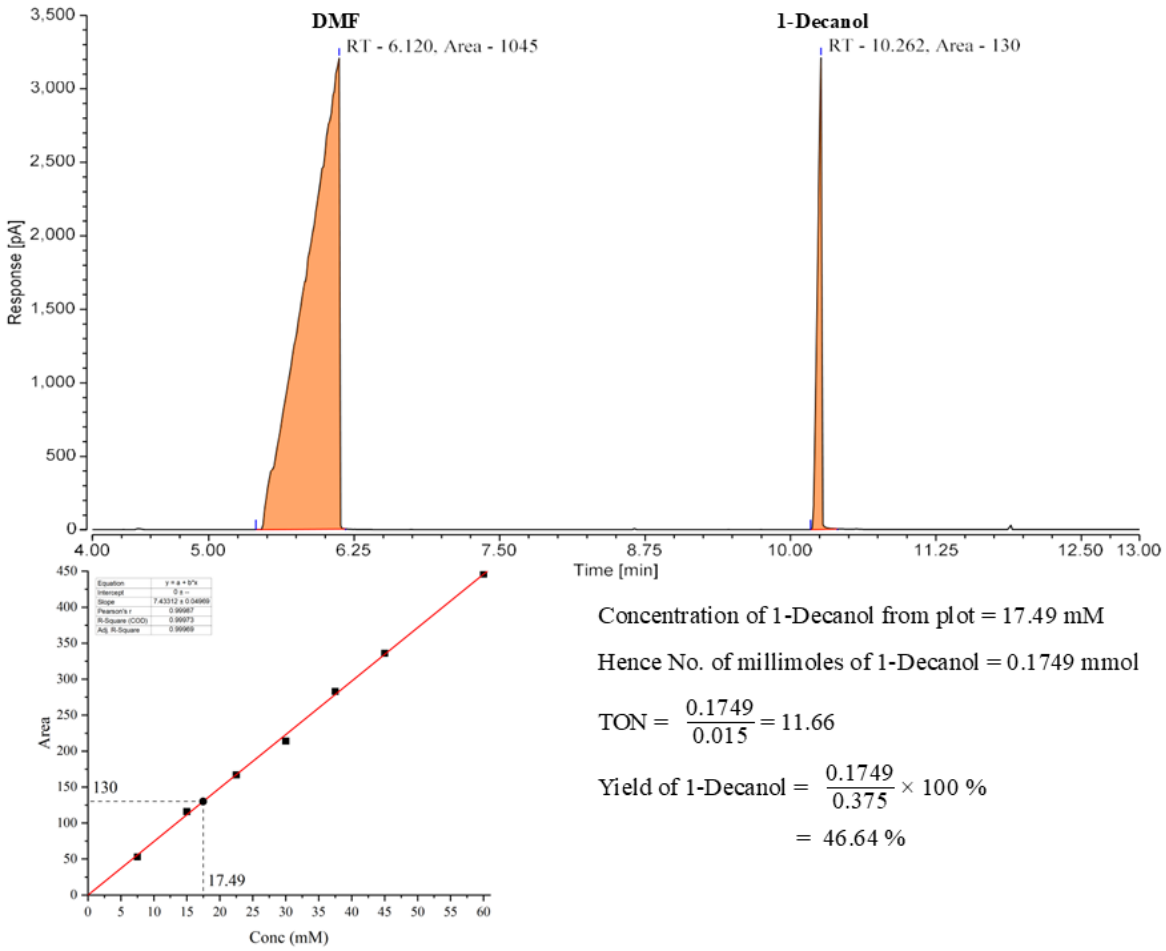


Figure S74. Calculation of yield for CH_3-$(CH_2)_8$-CH_2-OH obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_8$-CH_3. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_8$-CH_2-OH = 46.64 %**. The adjusted R^2 value for the calibration plot is 0.99969.

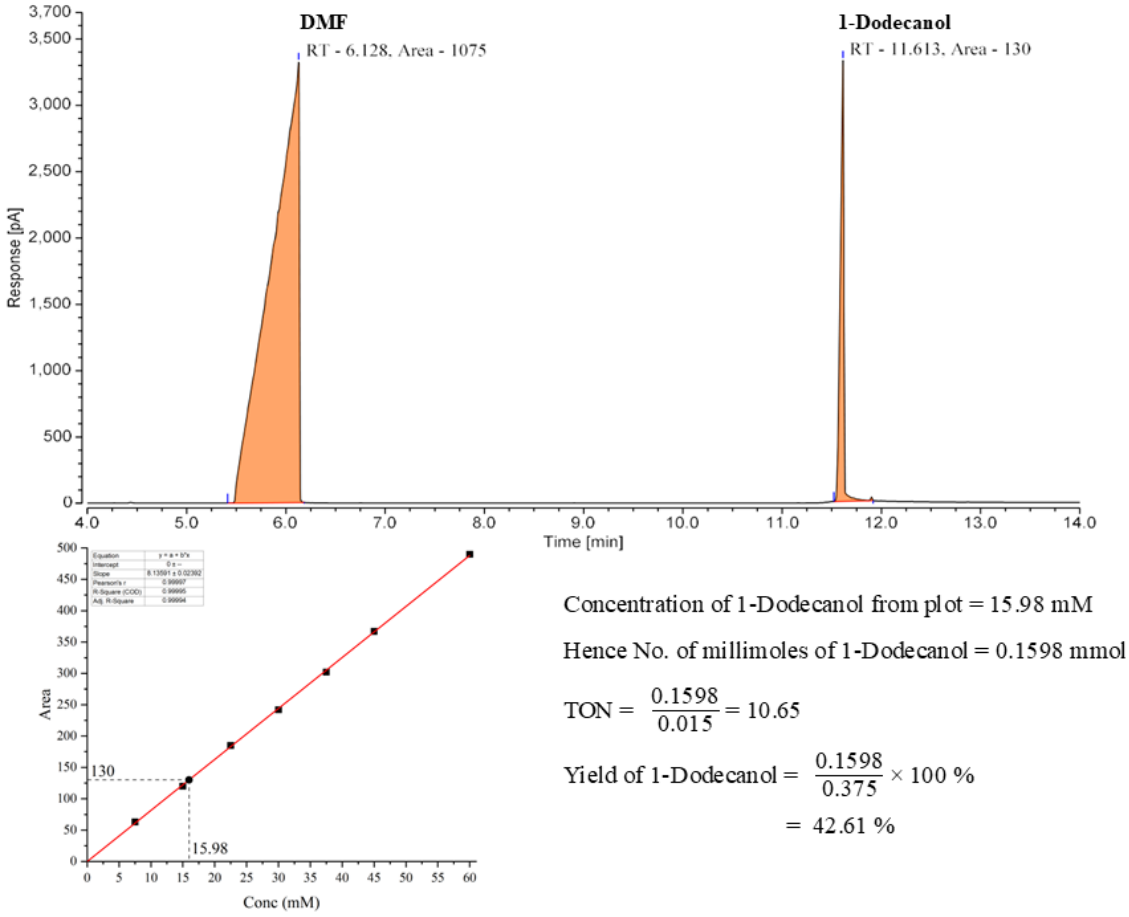


Figure S75. Calculation of yield for CH_3-$(CH_2)_{10}$-CH_2-OH obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH)_{10}$-CH_3. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_{10}$-CH_2-OH = 42.61 %**. The adjusted R^2 value for the calibration plot is 0.99994.

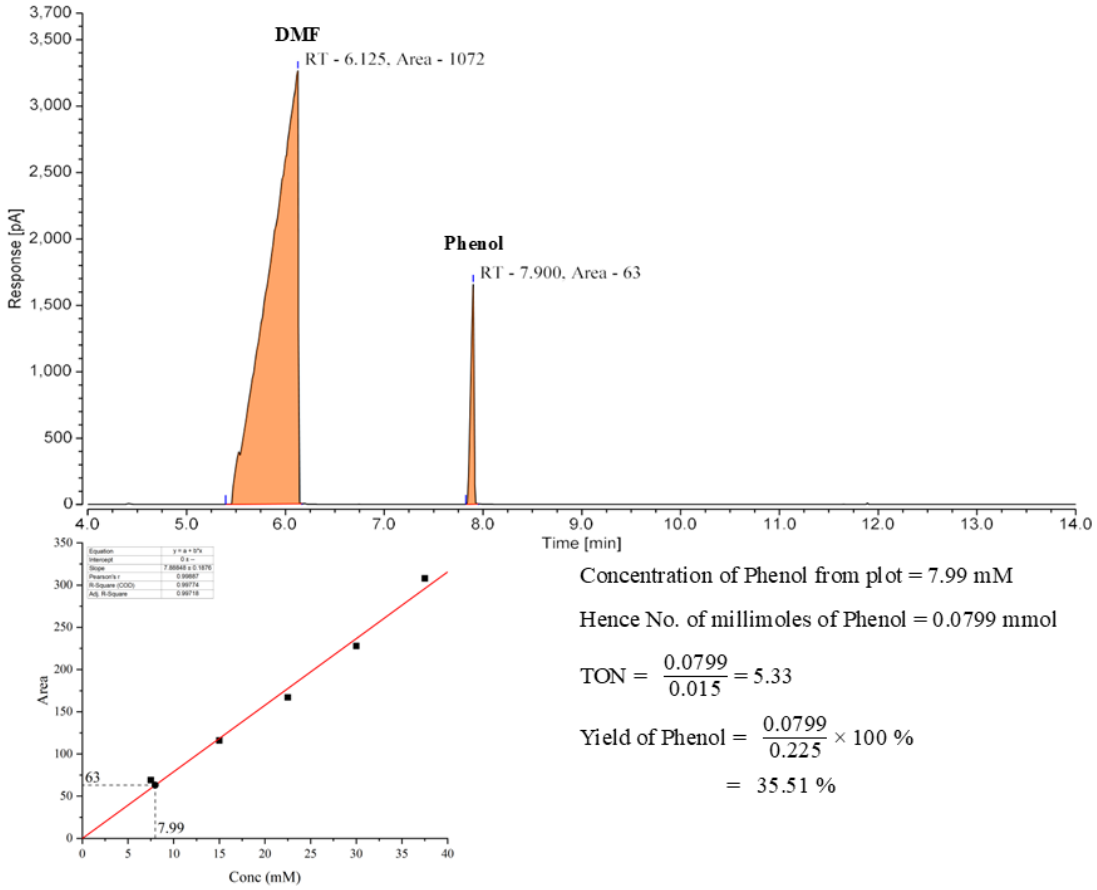


Figure S76. Calculation of yield for PhOH obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:15, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 35.51 %.** The adjusted R^2 value for the calibration plot is 0.99718.

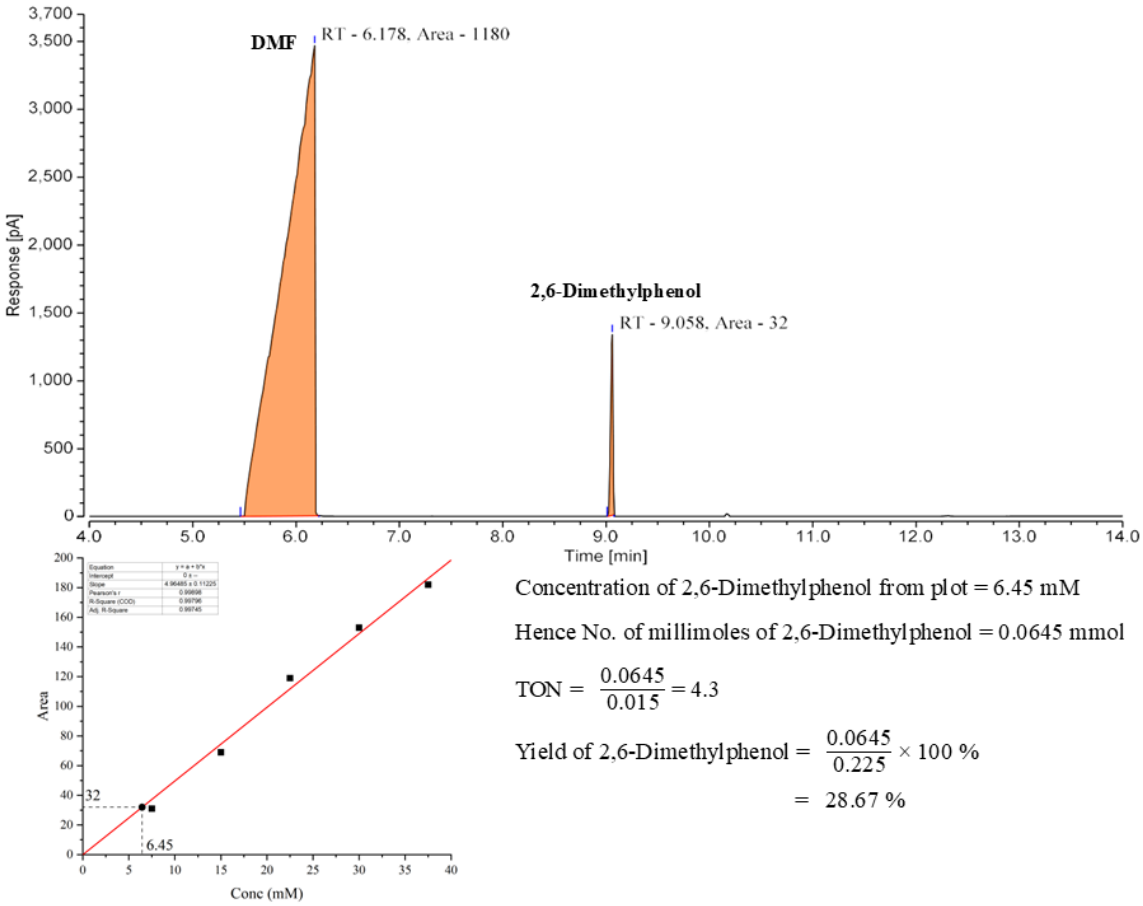


Figure S77. Calculation of yield for 2,6-Me_2-C_6H_3-OH obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,6-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:15, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,6-Me_2-C_6H_3-OH = 28.67 %**. The adjusted R^2 value for the calibration plot is 0.99745.

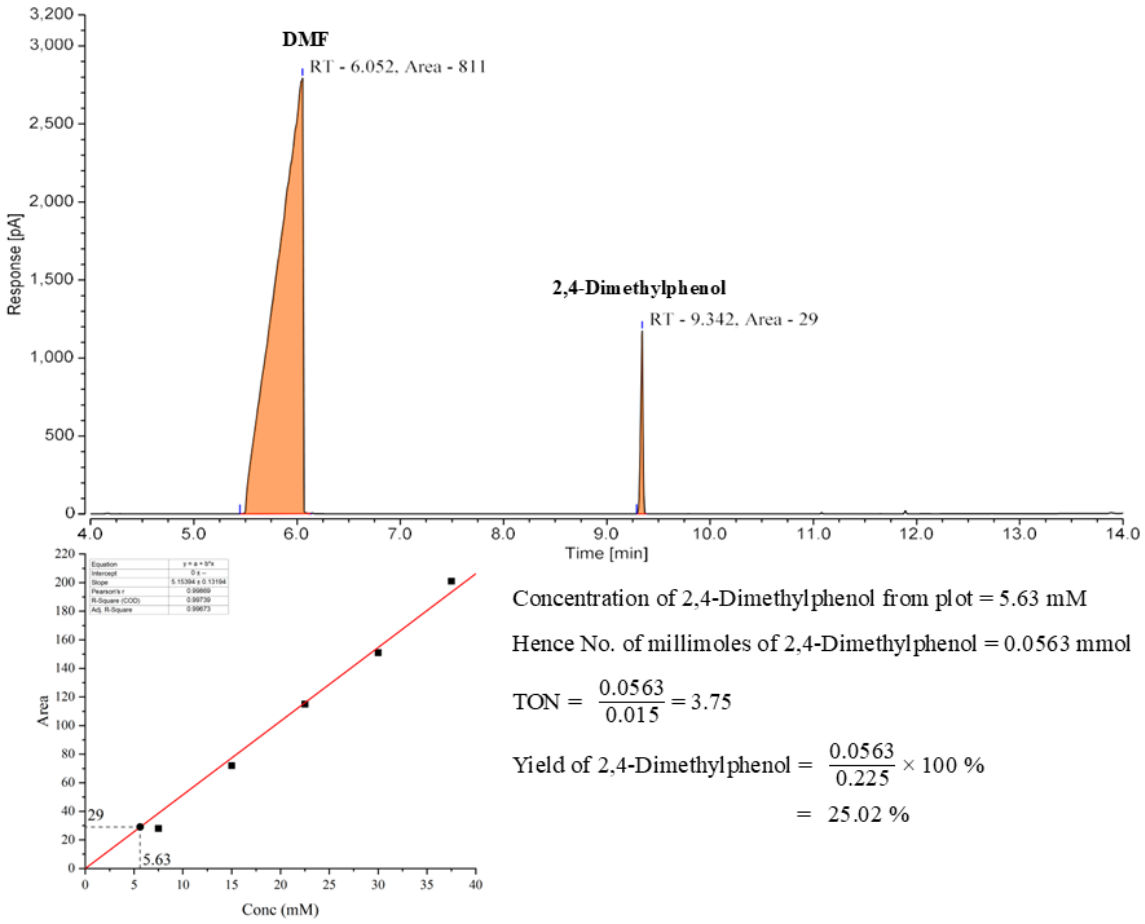


Figure S78. Calculation of yield for 2,4-Me_2-C_6H_3-OH obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,4-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:15, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,4-Me_2-C_6H_3-OH = 25.02 %**. The adjusted R^2 value for the calibration plot is 0.99673.

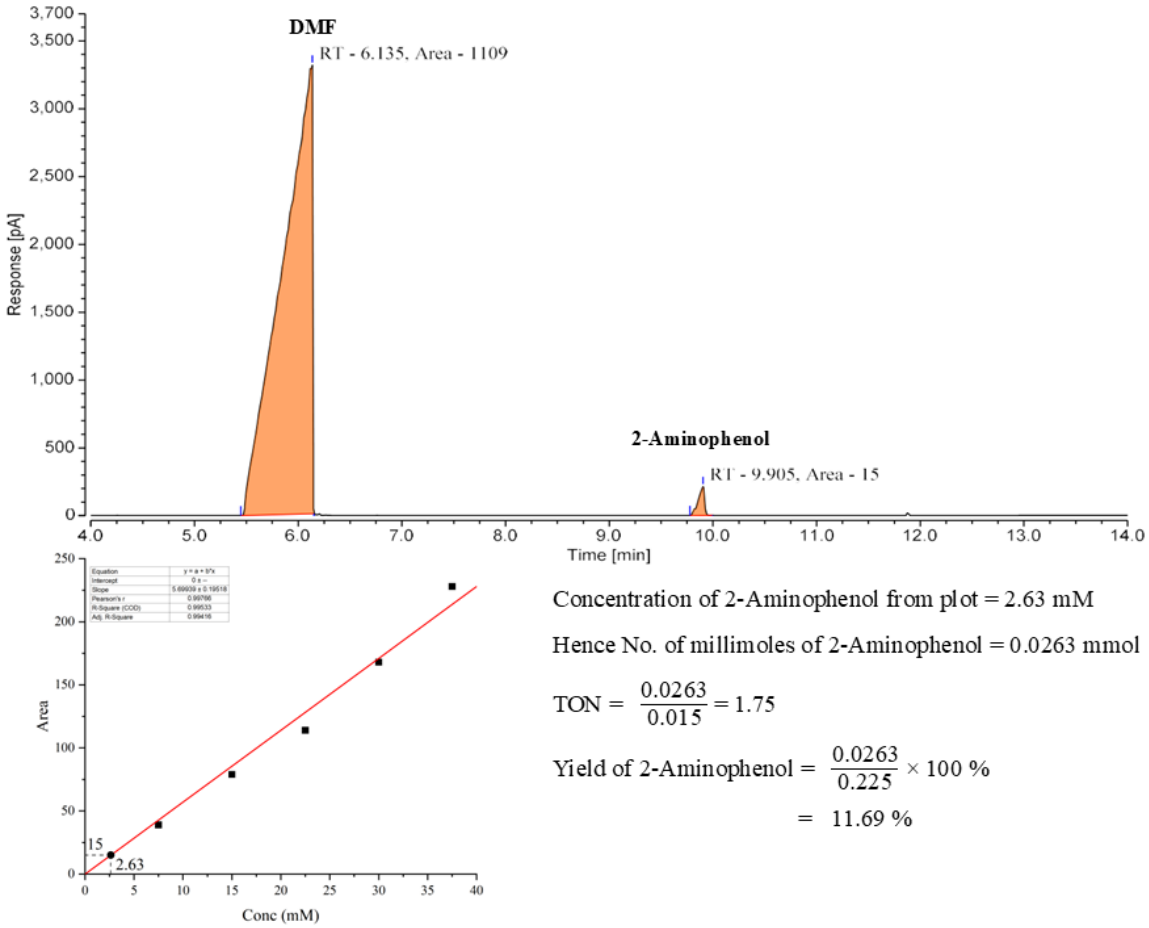


Figure S79. Calculation of yield for *o*-NH_2-C_6H_4-OH obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-NH_2)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:15, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of *o*-NH_2-C_6H_4-OH = 11.69 %**. The adjusted R^2 value for the calibration plot is 0.99416.

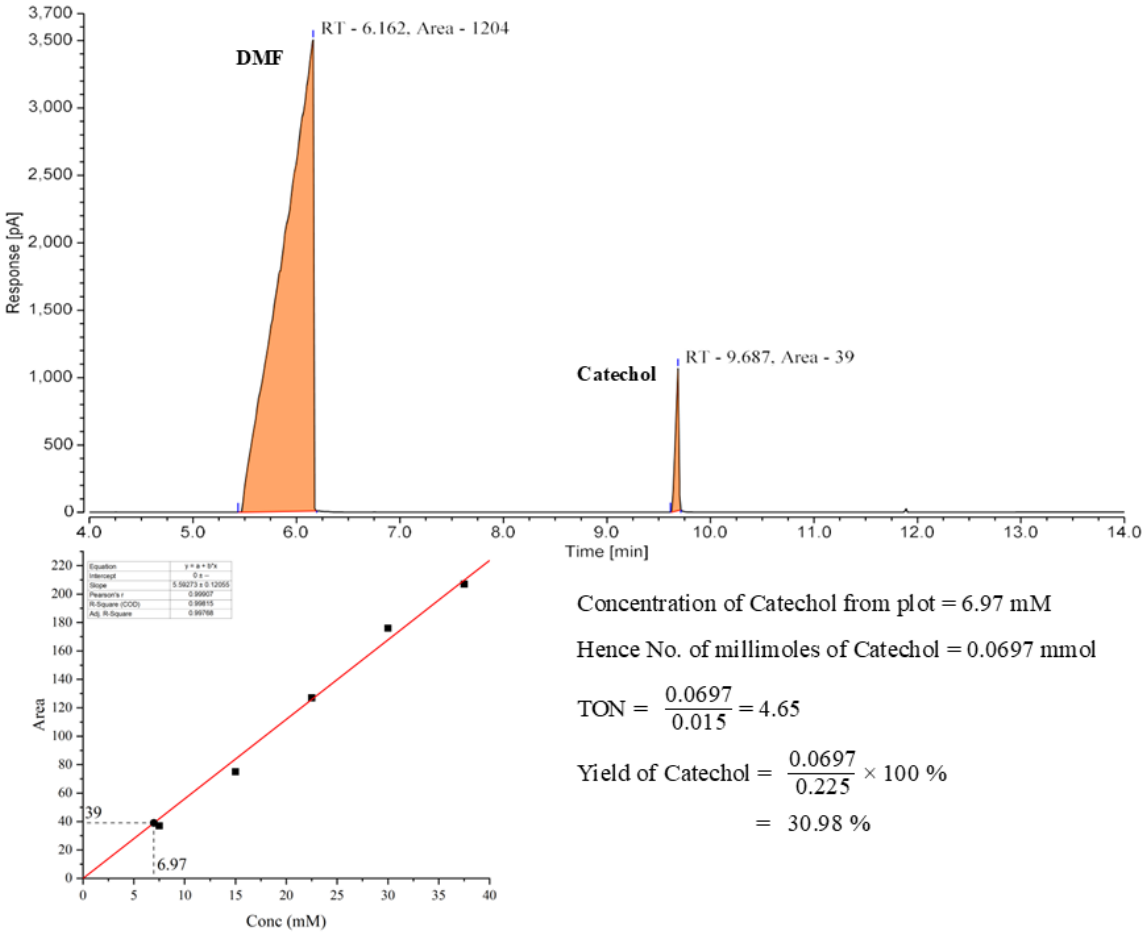


Figure S80. Calculation of yield for 1,2-$(OH)_2$-C_6H_4 obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-ONa)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:15, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 1,2-$(OH)_2$-C_6H_4 = 30.98 %**. The adjusted R^2 value for the calibration plot is 0.99768.

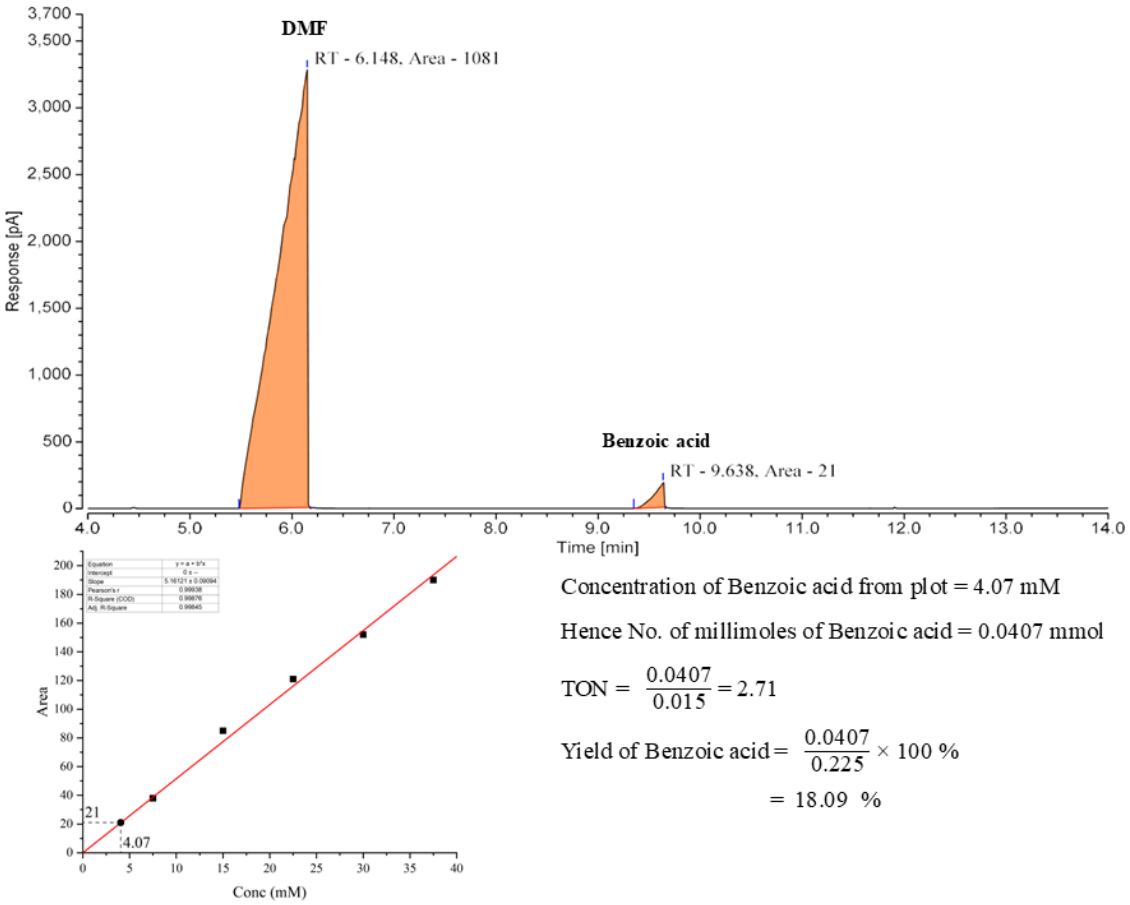


Figure S81. Calculation of yield for PhCOOH obtained from the **4a**$(BF_4)_2$ mediated catalytic hydrolysis of NaSC(O)Ph. Reaction conditions: catalyst:thiolate = 1:15, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhCOOH = 18.09 %**. The adjusted R^2 value for the calibration plot is 0.99845.

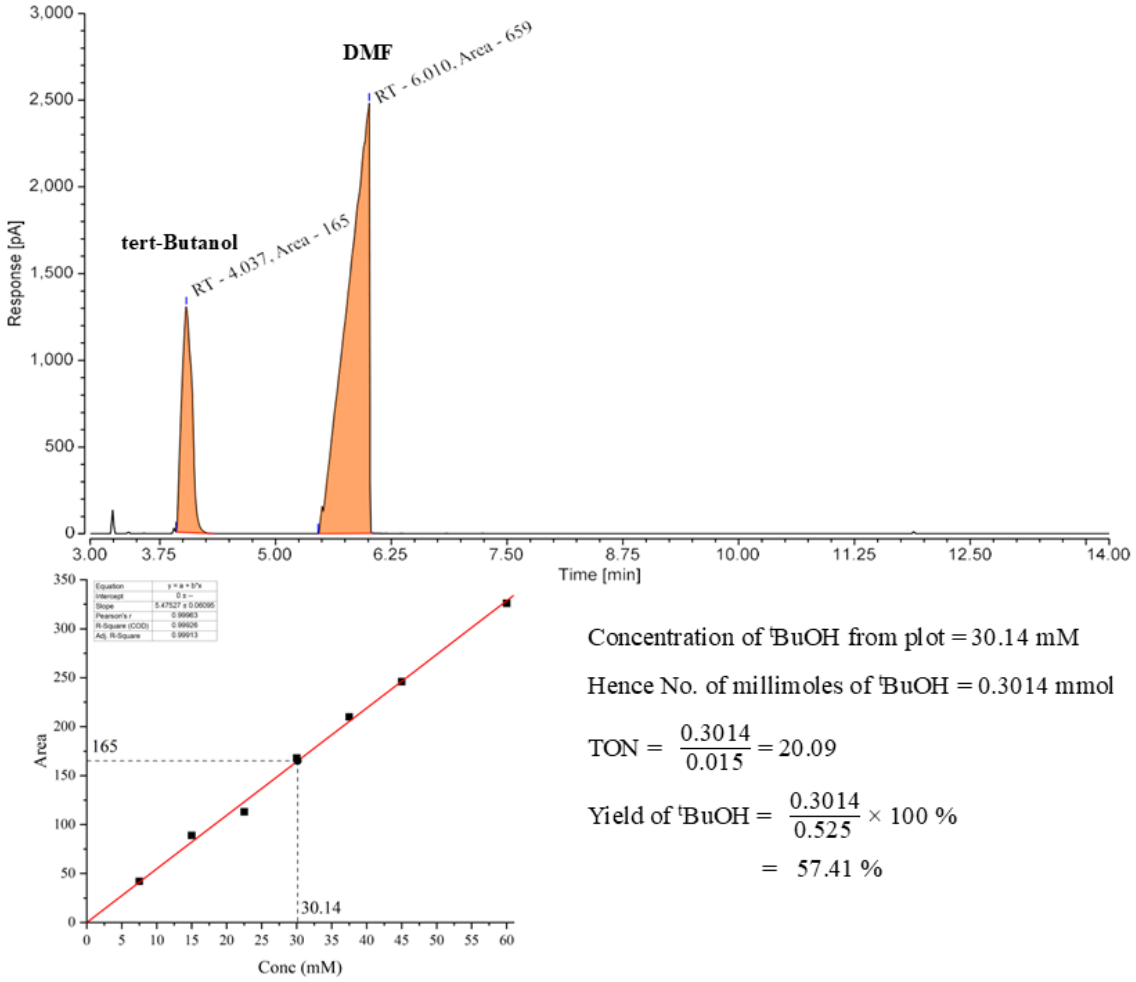


Figure S82. Calculation of yield for ᵗBuOH obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaSᵗBu. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of ᵗBuOH = 57.41 %**. The adjusted R^2 value for the calibration plot is 0.99913.

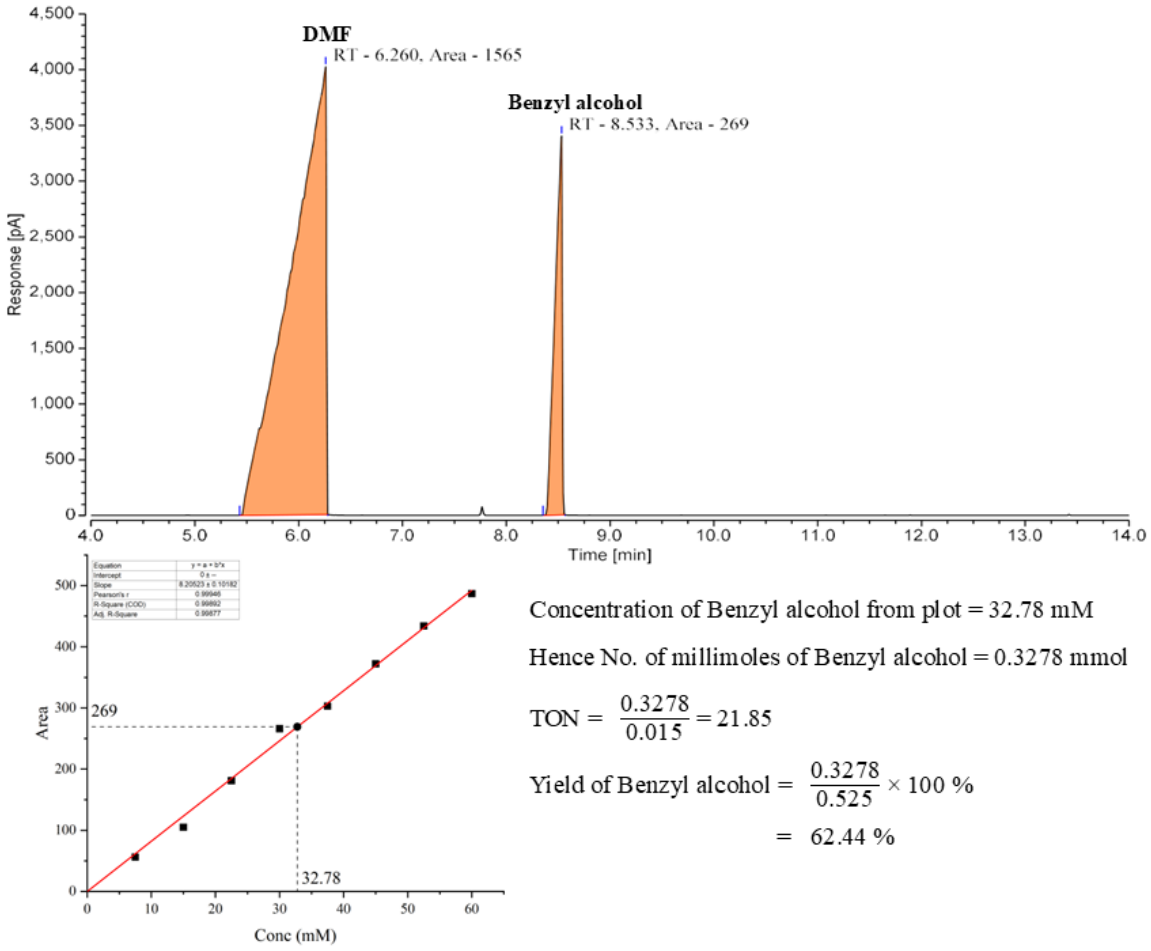


Figure S83. Calculation of yield for $PhCH_2OH$ obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 62.44 %**. The adjusted R^2 value for the calibration plot is 0.99877.

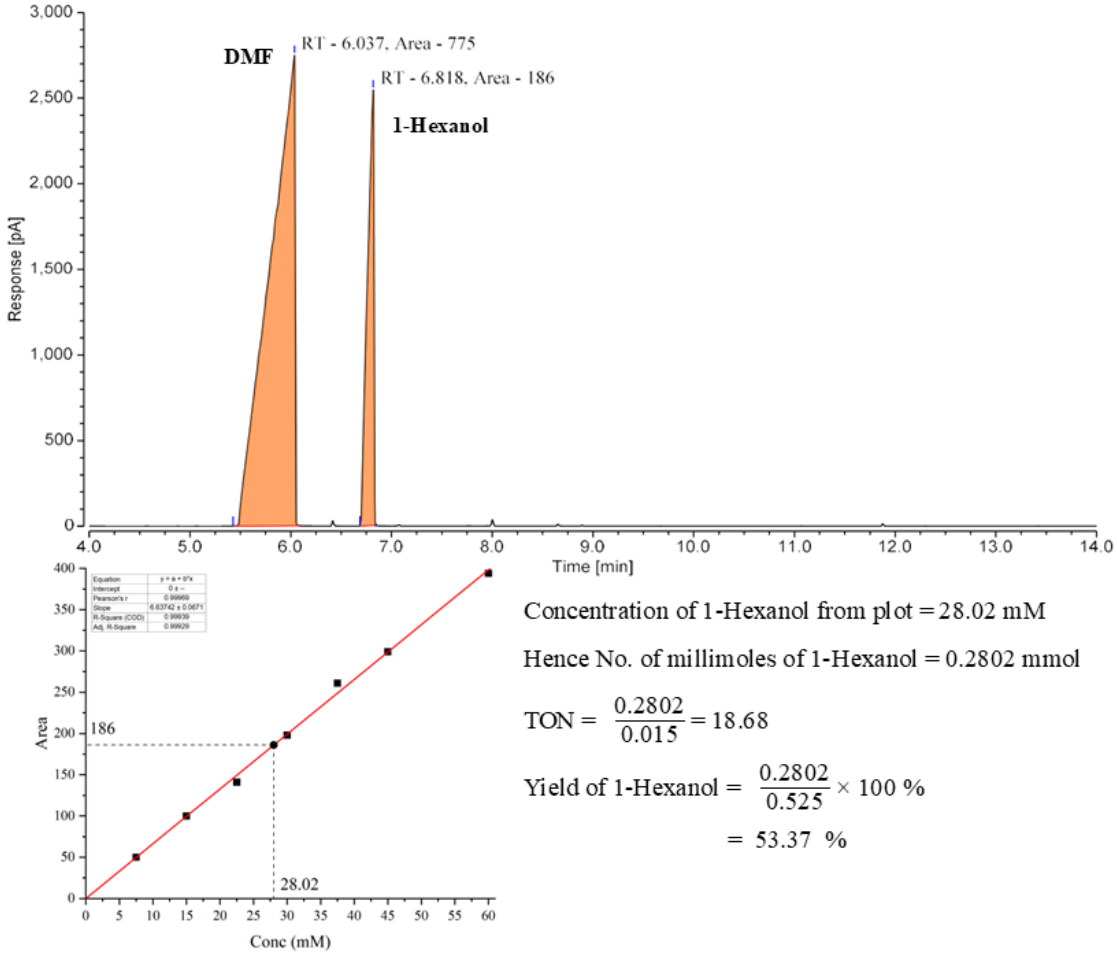


Figure S84. Calculation of yield for CH_3-$(CH_2)_4$-CH_2-OH obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_4$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_4$-CH_2-OH = 53.37 %**. The adjusted R^2 value for the calibration plot is 0.99929.

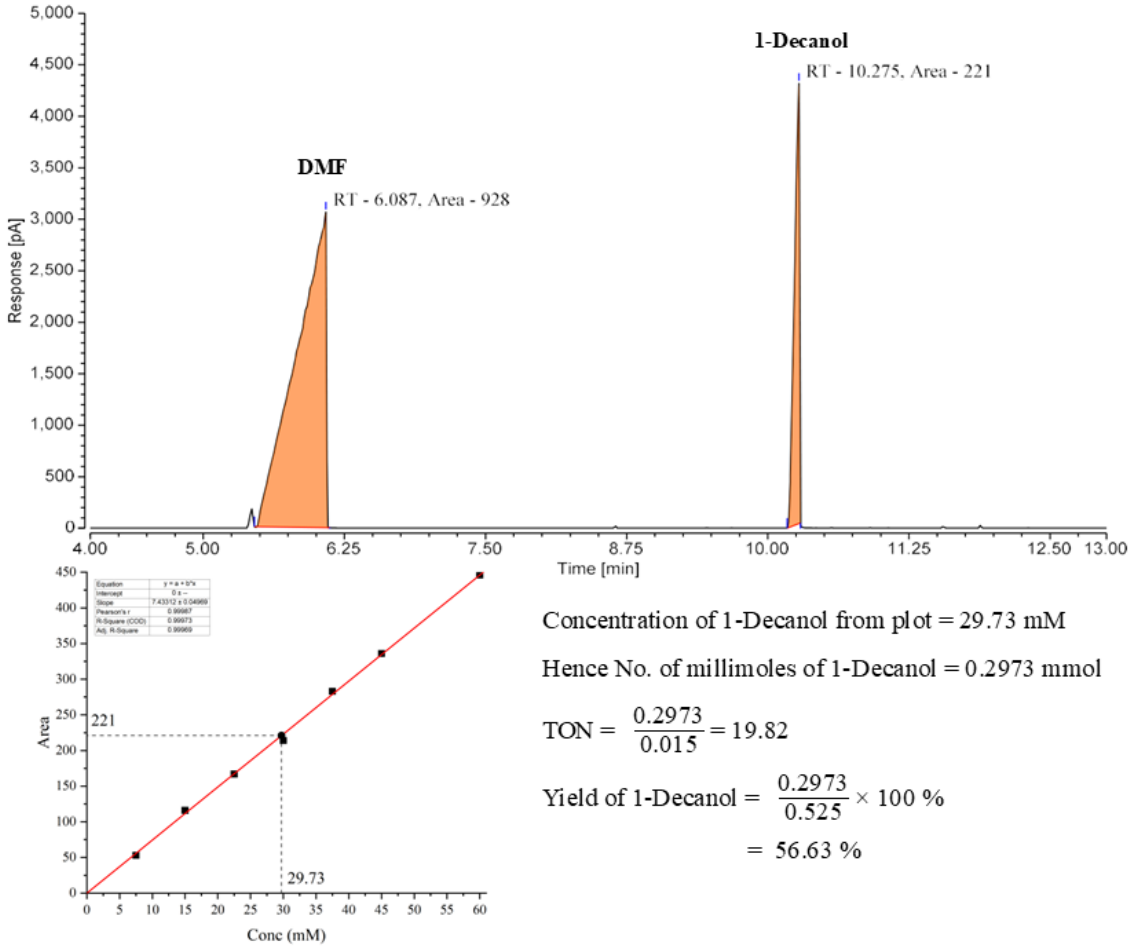


Figure S85. Calculation of yield for CH_3-$(CH_2)_8$-CH_2-OH obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_8$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_8$-CH_2-OH = 56.63 %**. The adjusted R^2 value for the calibration plot is 0.99969.

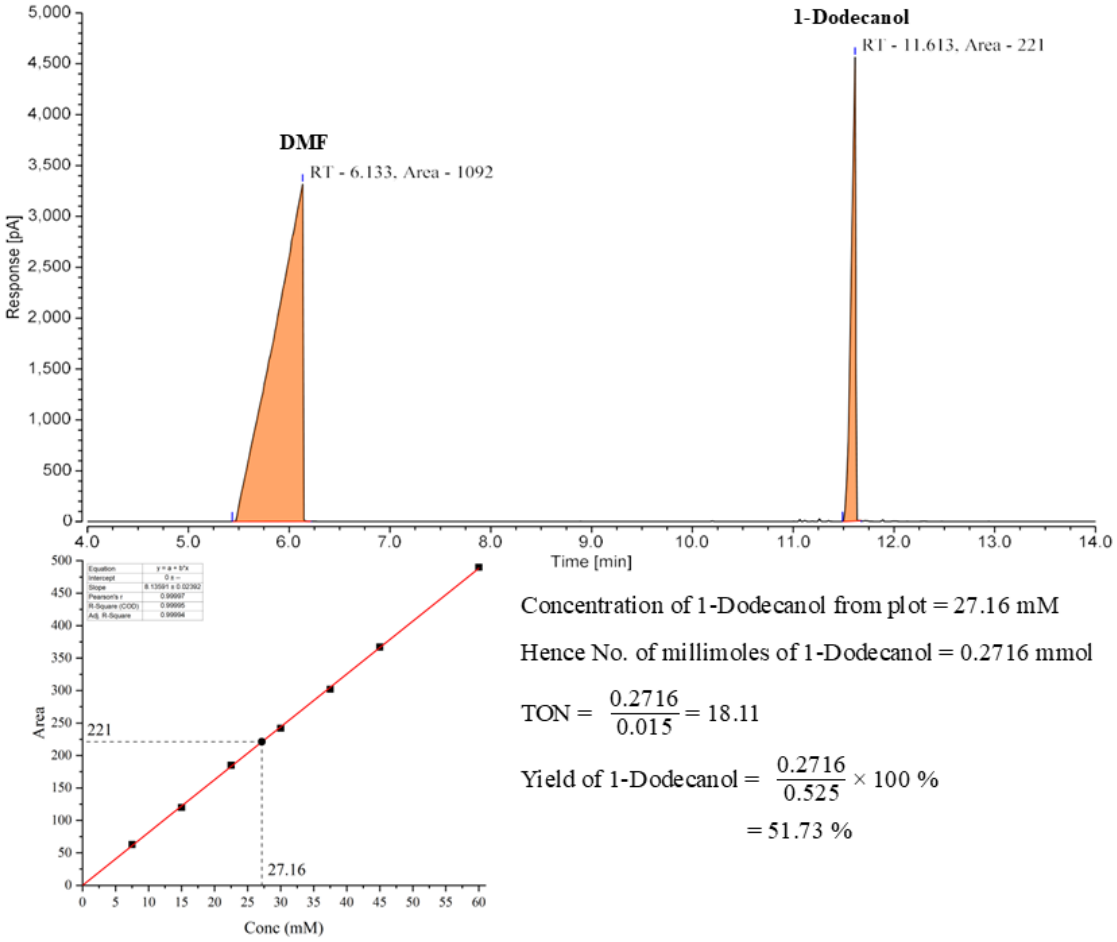


Figure S86. Calculation of yield for CH_3-$(CH_2)_{10}$-CH_2-OH obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH)_{10}$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_{10}$-CH_2-OH = 51.73 %**. The adjusted R^2 value for the calibration plot is 0.99994.

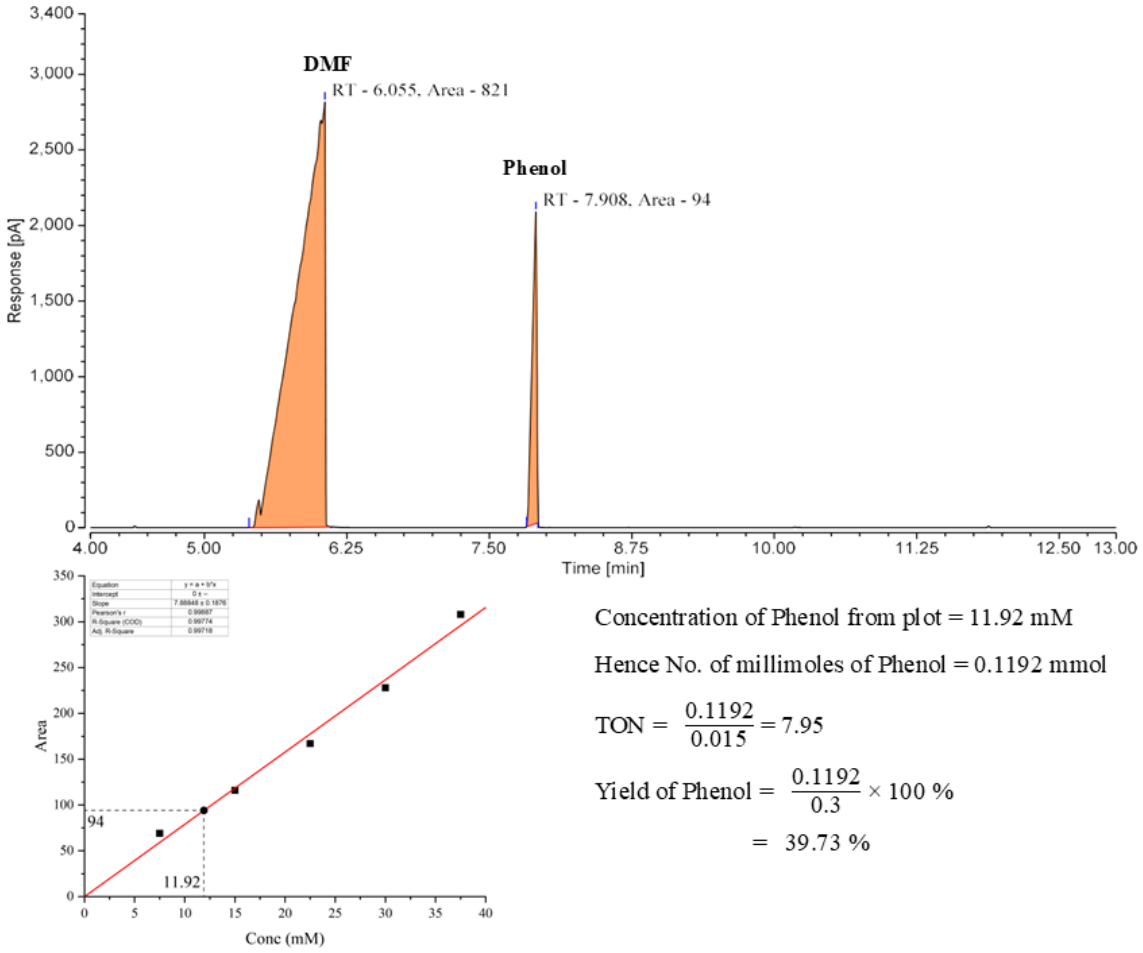


Figure S87. Calculation of yield for PhOH obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 39.73 %**. The adjusted R^2 value for the calibration plot is 0.99718.

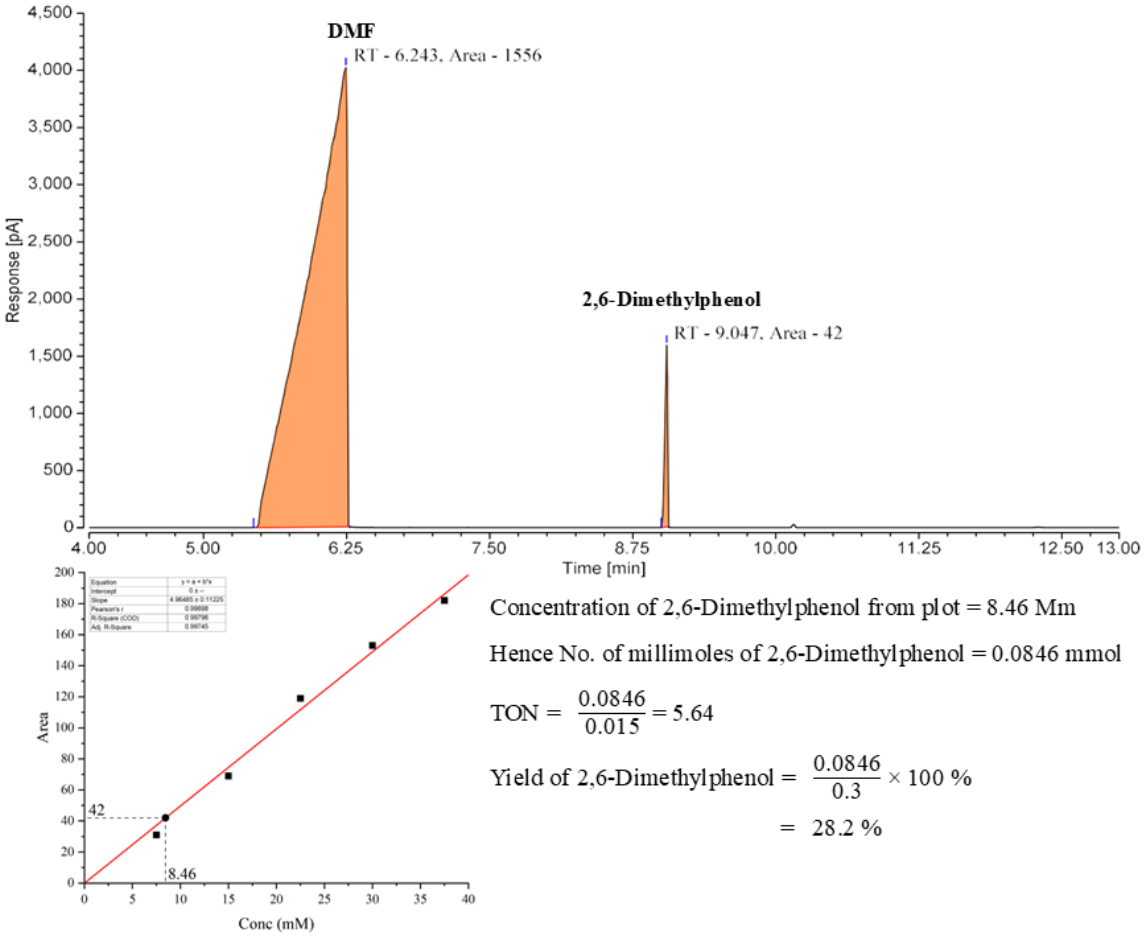


Figure S88. Calculation of yield for 2,6-Me_2-C_6H_3-OH obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,6-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,6-Me_2-C_6H_3-OH = 28.2 %**. The adjusted R^2 value for the calibration plot is 0.99745.

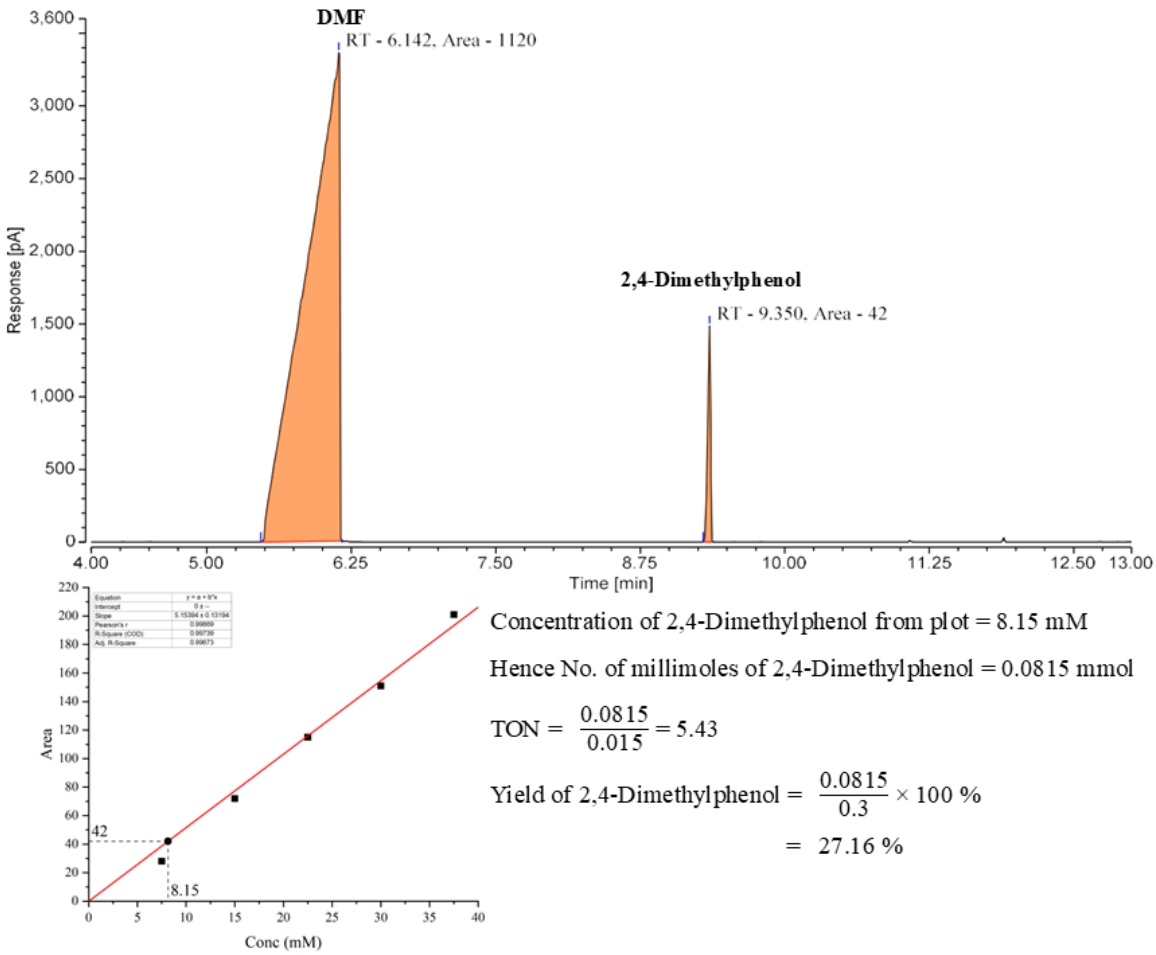


Figure S89. Calculation of yield for 2,4-Me_2-C_6H_3-OH obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,4-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,4-Me_2-C_6H_3-OH = 27.16 %**. The adjusted R^2 value for the calibration plot is 0.99673.

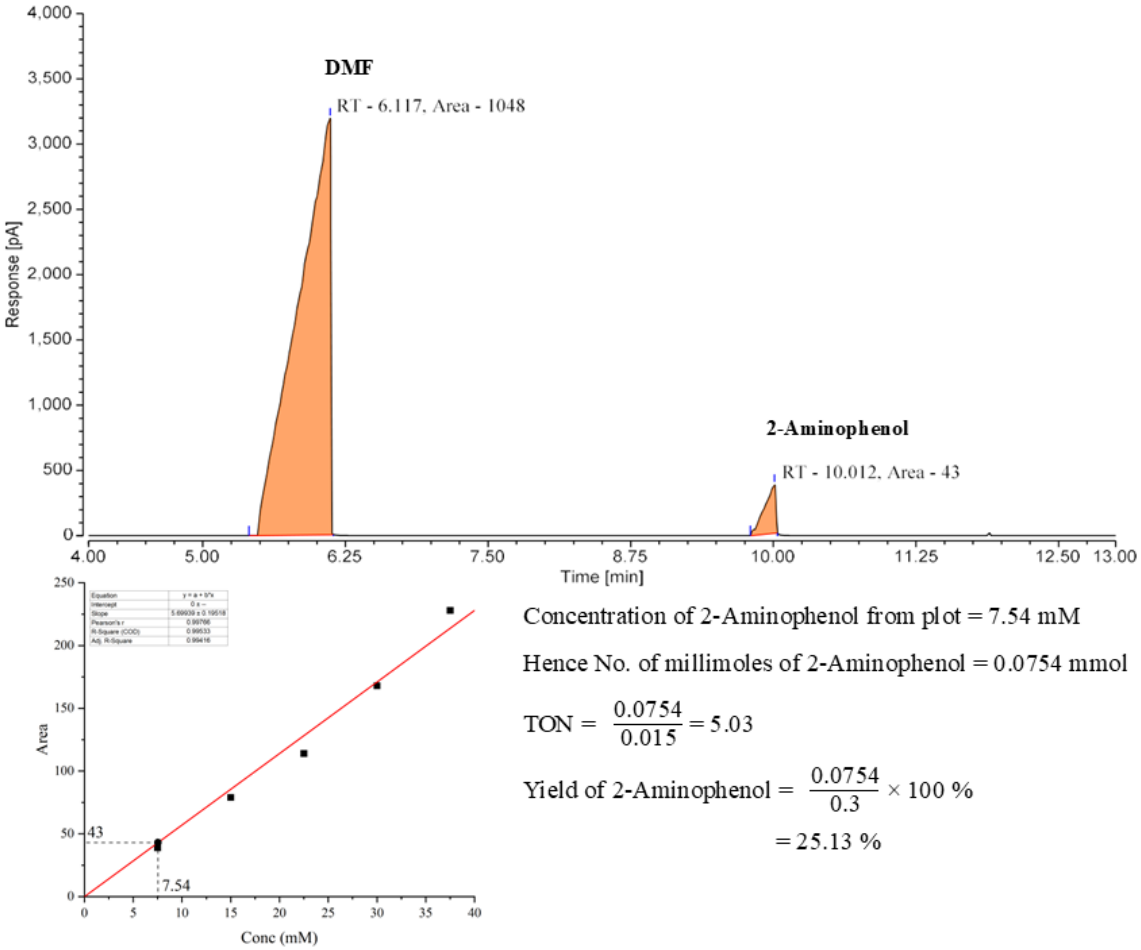


Figure S90. Calculation of yield for *o*-NH_2-C_6H_4-OH obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-NH_2)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of *o*-NH_2-C_6H_4-OH = 25.13 %**. The adjusted R^2 value for the calibration plot is 0.99416.

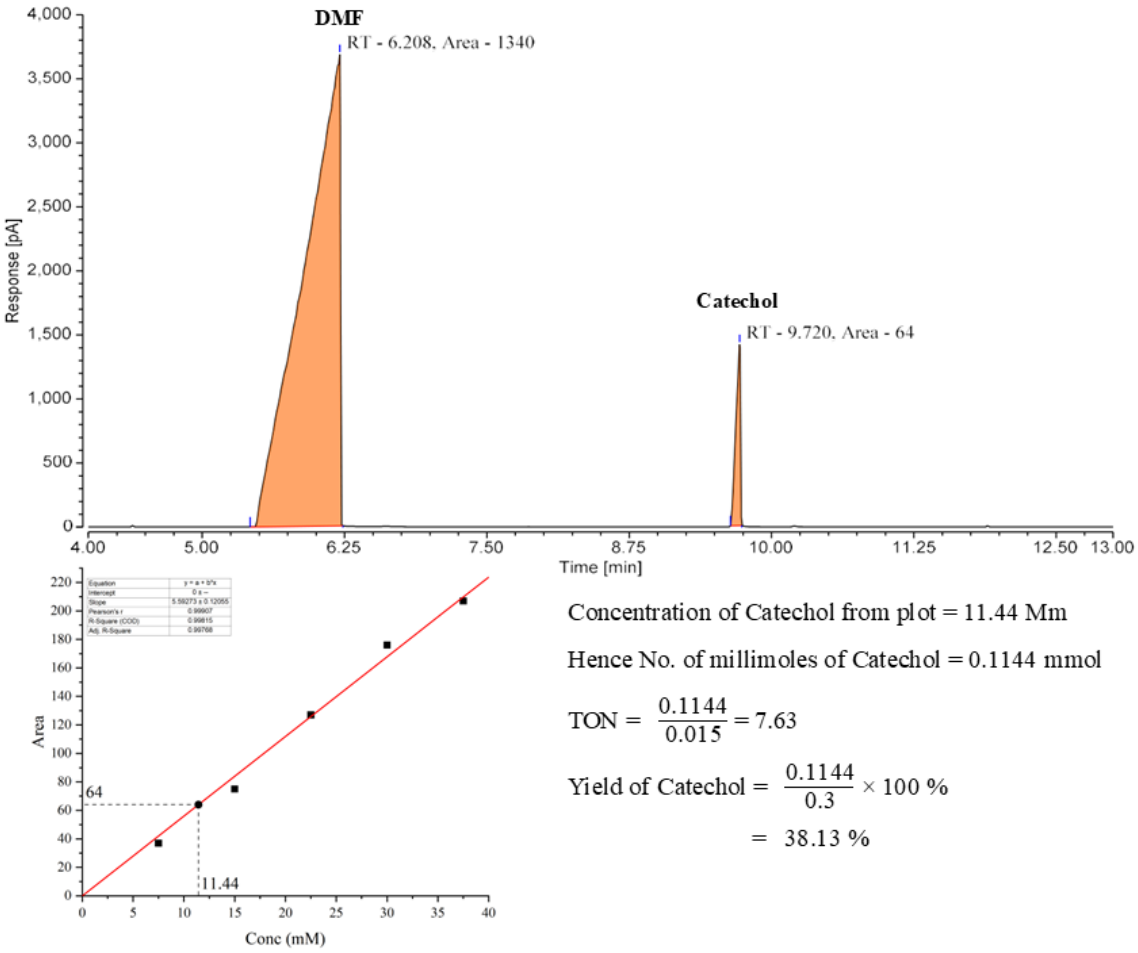


Figure S91. Calculation of yield for 1,2-$(OH)_2$-C_6H_4 obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-ONa)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 1,2-$(OH)_2$-C_6H_4 = 38.13 %**. The adjusted R^2 value for the calibration plot is 0.99768.

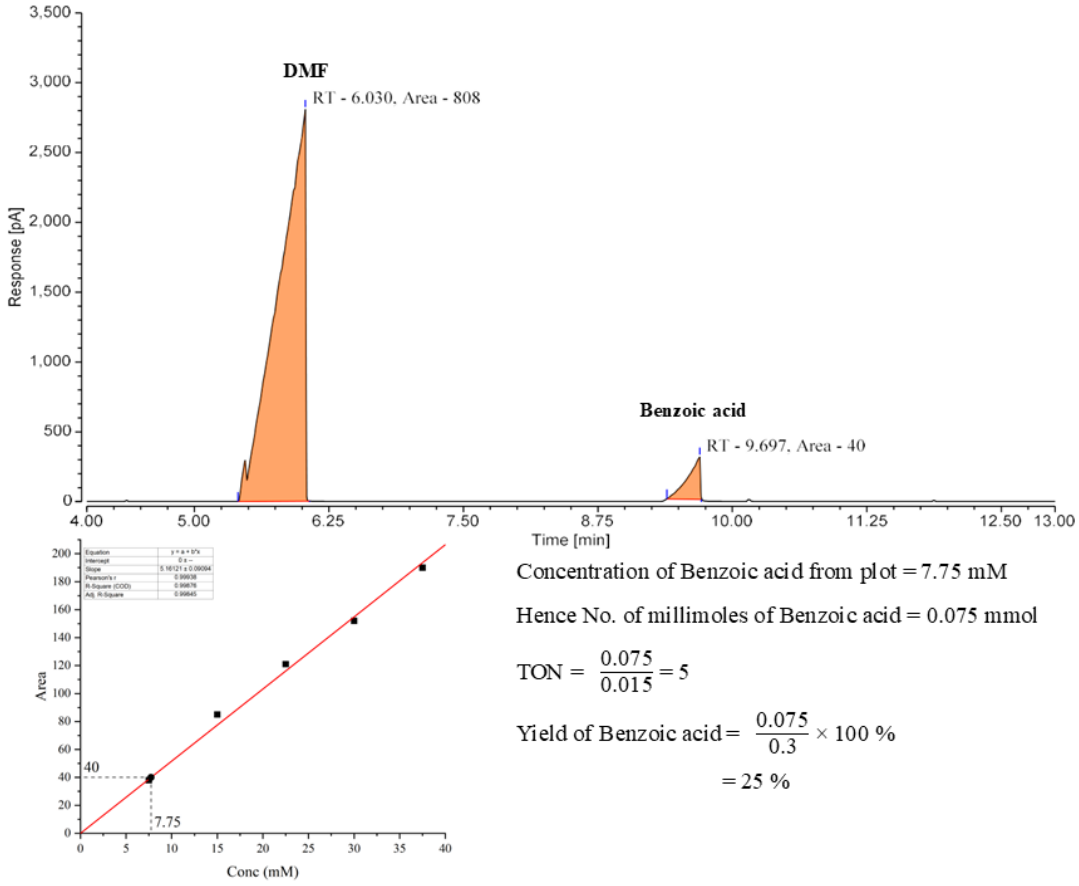
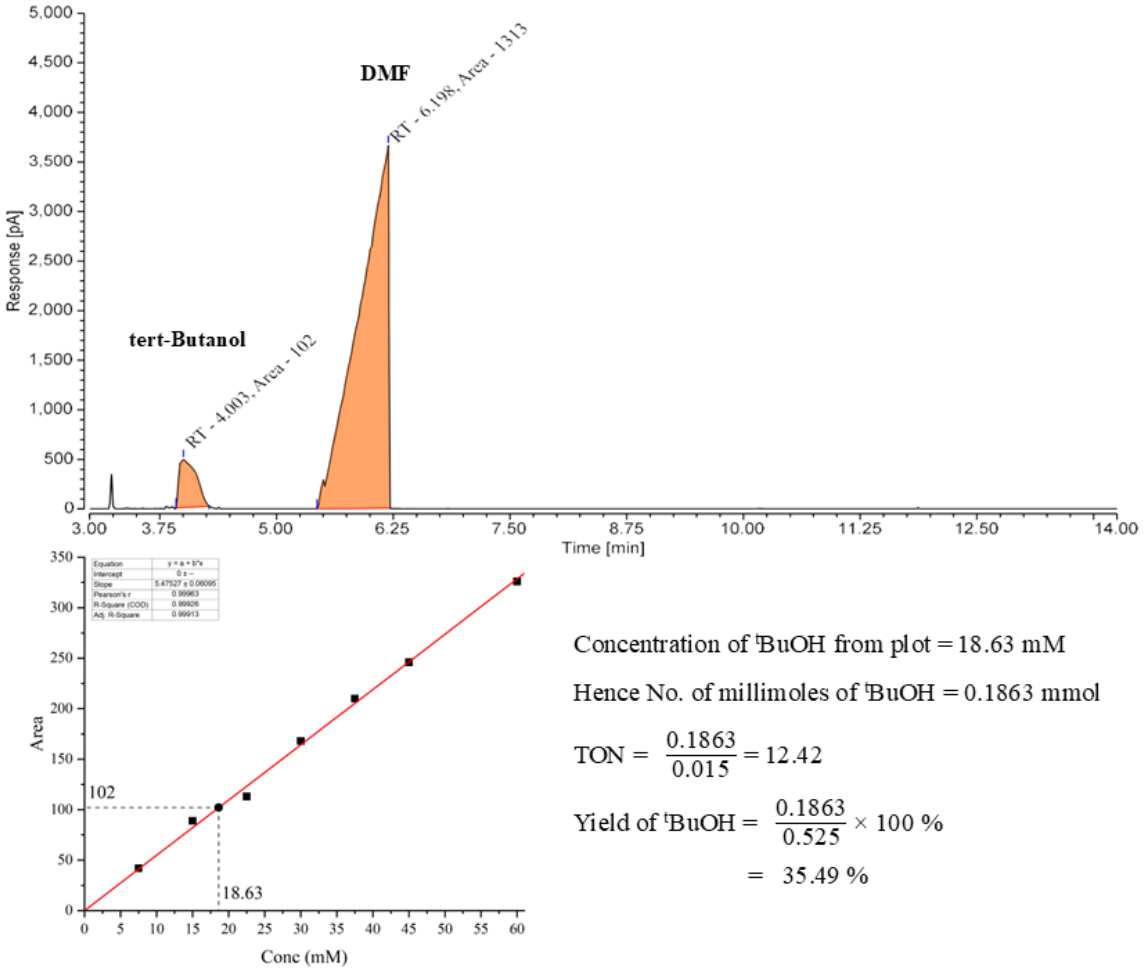


Figure S92. Calculation of yield for PhCOOH obtained from the **4b**$(BF_4)_2$ mediated catalytic hydrolysis of NaSC(O)Ph. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhCOOH = 25 %**. The adjusted R^2 value for the calibration plot is 0.99845.



Concentration of ^{t}BuOH from plot = 18.63 mM

Hence No. of millimoles of ^{t}BuOH = 0.1863 mmol

$$\text{TON} = \frac{0.1863}{0.015} = 12.42$$

$$\text{Yield of } ^{t}\text{BuOH} = \frac{0.1863}{0.525} \times 100\ \% = 35.49\ \%$$

Figure S93. Calculation of yield for ^{t}BuOH obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaS^{t}Bu. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of ^{t}BuOH = 35.49 %**. The adjusted R^2 value for the calibration plot is 0.99913.

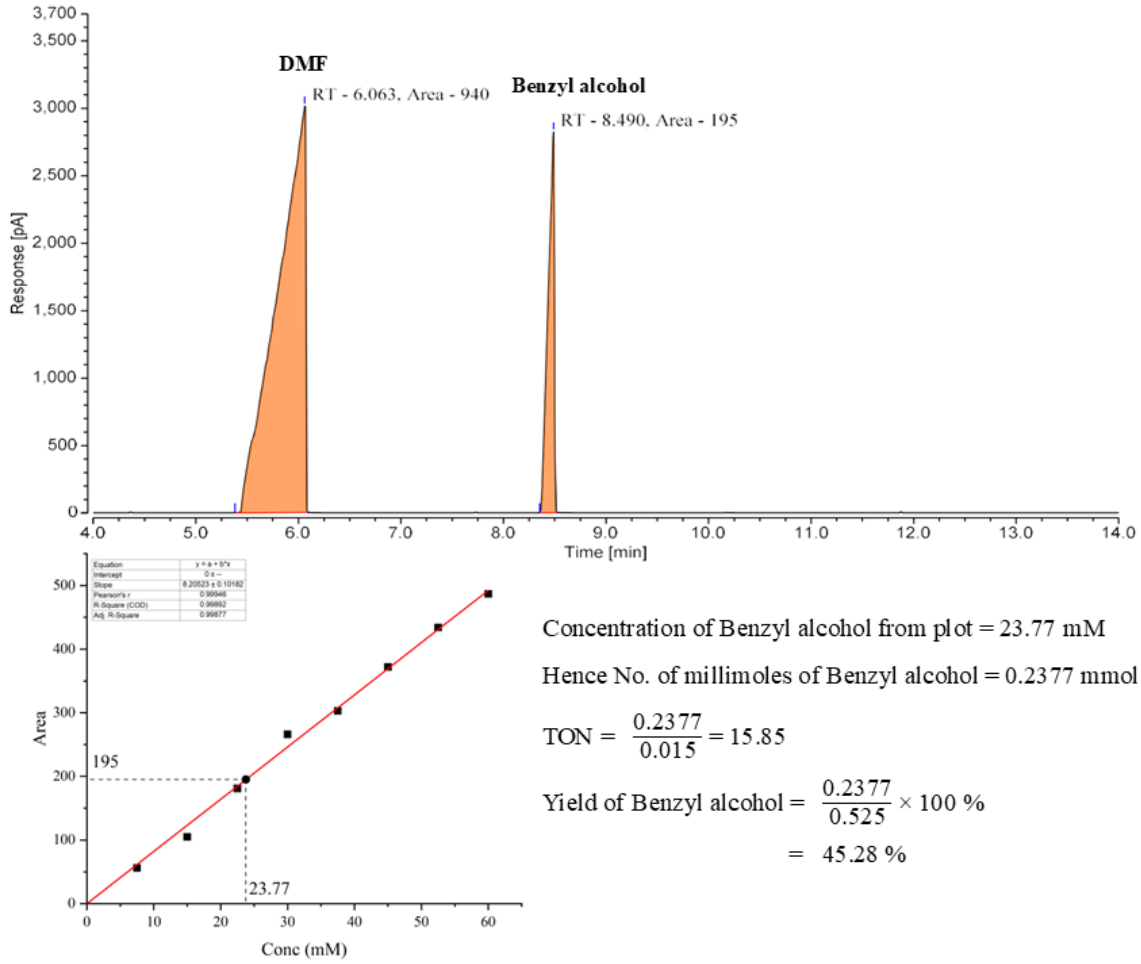


Figure S94. Calculation of yield for $PhCH_2OH$ obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 45.28 %**. The adjusted R^2 value for the calibration plot is 0.99877.

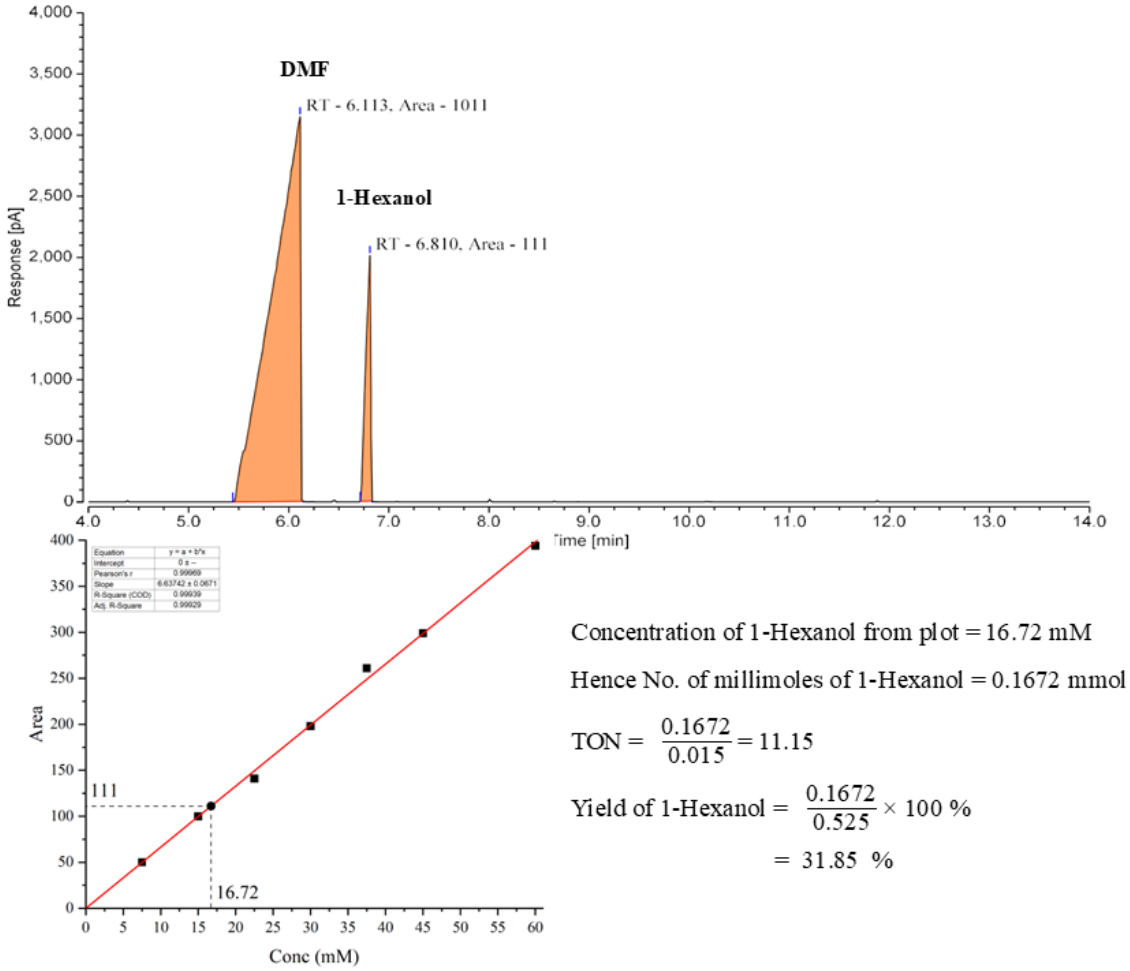


Figure S95. Calculation of yield for CH_3-$(CH_2)_4$-CH_2-OH obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_4$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_4$-CH_2-OH = 31.85 %**. The adjusted R^2 value for the calibration plot is 0.99929.

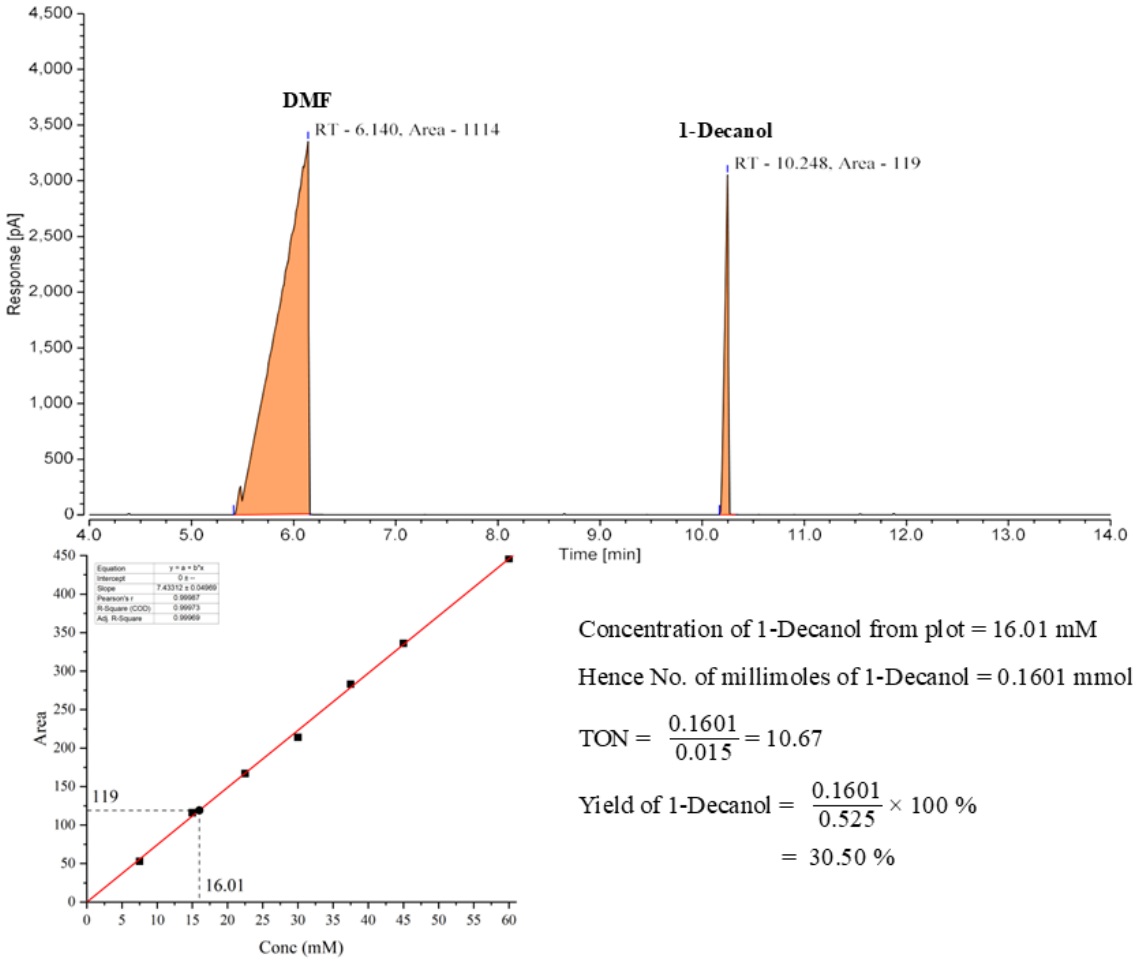


Figure S96. Calculation of yield for CH_3-$(CH_2)_8$-CH_2-OH obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_8$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_8$-CH_2-OH = 30.50 %**. The adjusted R^2 value for the calibration plot is 0.99969.

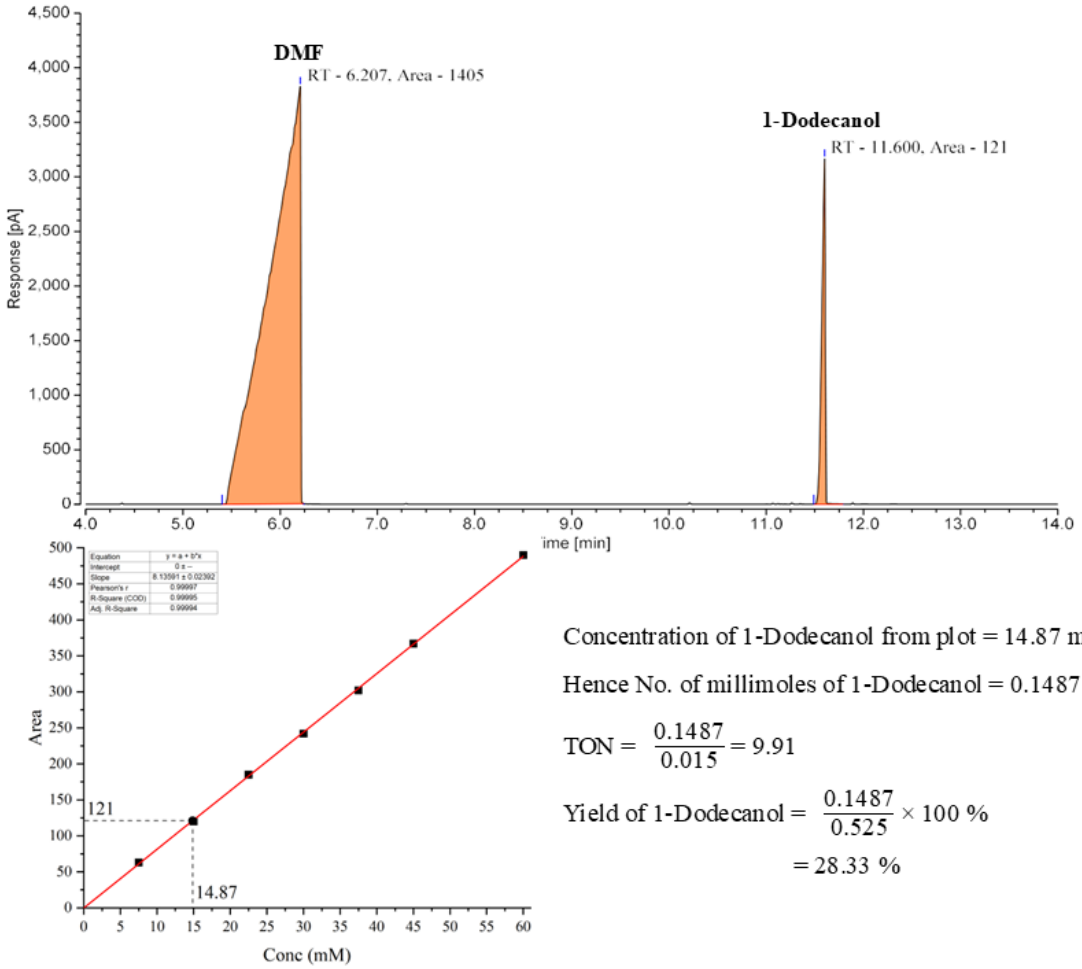


Figure S97. Calculation of yield for CH_3-$(CH_2)_{10}$-CH_2-OH obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH)_{10}$-CH_3. Reaction conditions: catalyst:thiolate = 1:35, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_{10}$-CH_2-OH = 28.33 %**. The adjusted R^2 value for the calibration plot is 0.99994.

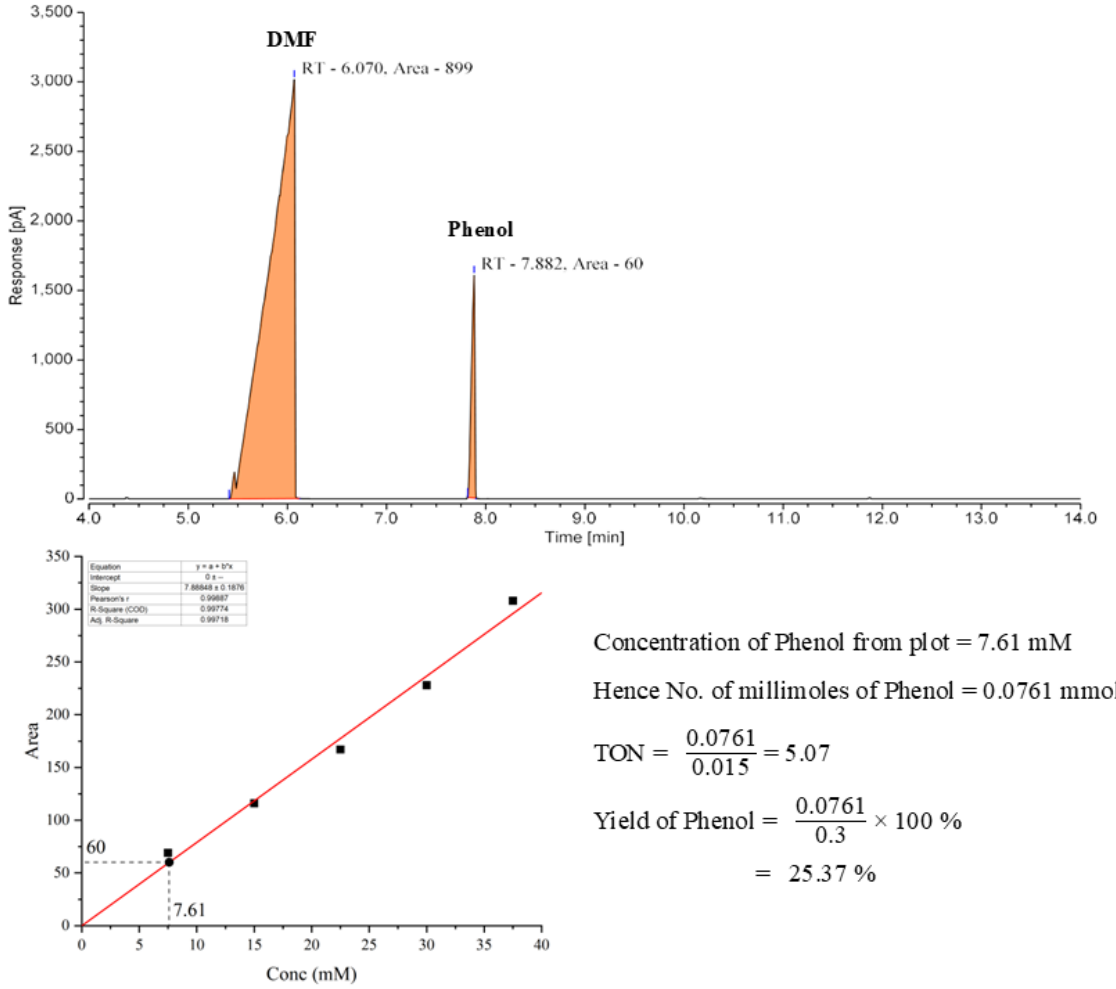
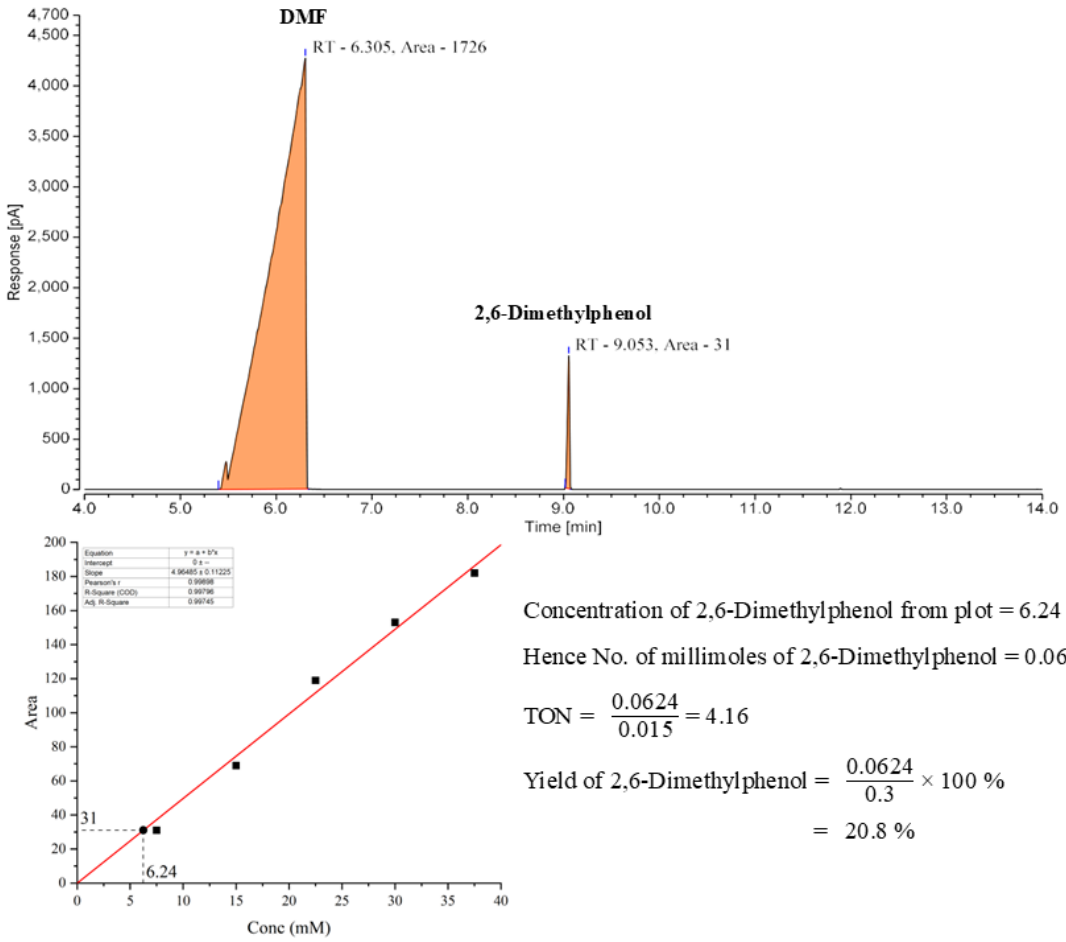


Figure S98. Calculation of yield for PhOH obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 25.37 %**. The adjusted R^2 value for the calibration plot is 0.99718.



Concentration of 2,6-Dimethylphenol from plot = 6.24 mM

Hence No. of millimoles of 2,6-Dimethylphenol = 0.0624 mmol

$$\text{TON} = \frac{0.0624}{0.015} = 4.16$$

$$\text{Yield of 2,6-Dimethylphenol} = \frac{0.0624}{0.3} \times 100\ \% = 20.8\ \%$$

Figure S99. Calculation of yield for 2,6-Me_2-C_6H_3-OH obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,6-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,6-Me_2-C_6H_3-OH = 20.8 %**. The adjusted R^2 value for the calibration plot is 0.99745.

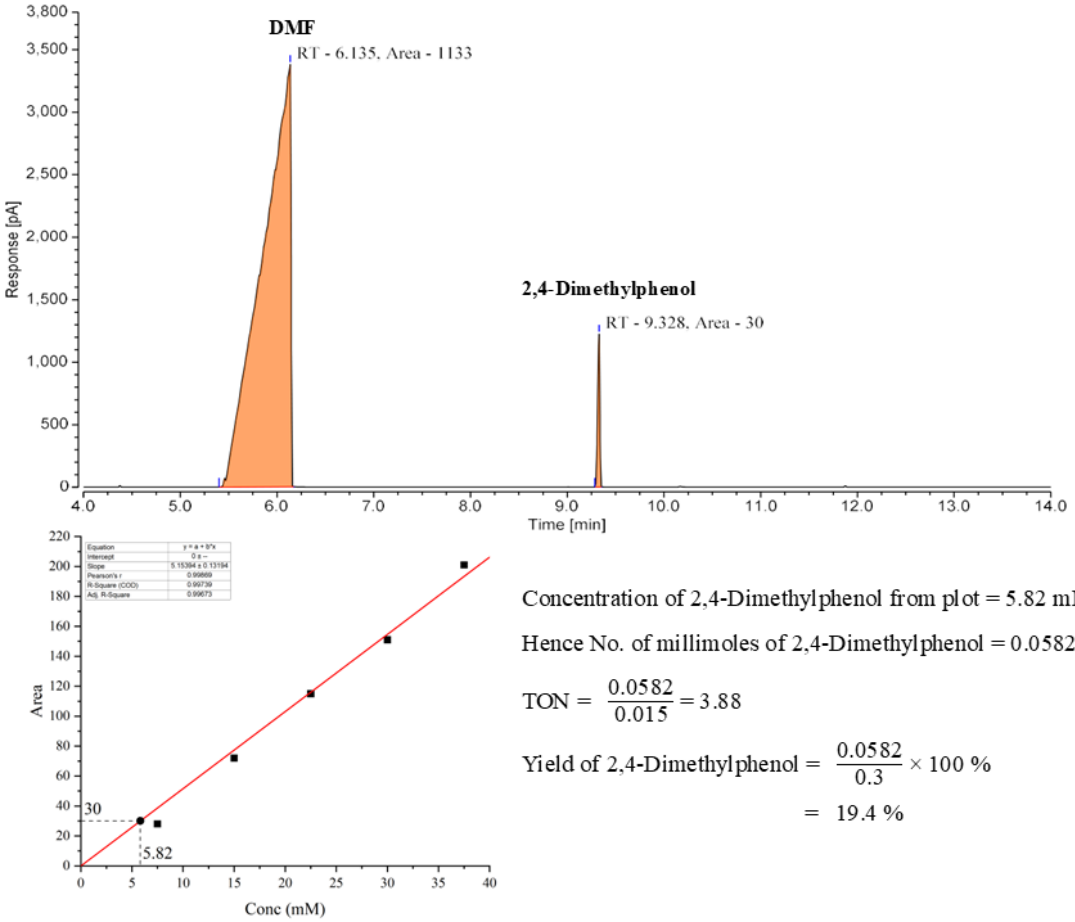


Figure S100. Calculation of yield for 2,4-Me_2-C_6H_3-OH obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,4-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,4-Me_2-C_6H_3-OH = 19.4 %**. The adjusted R^2 value for the calibration plot is 0.99673.

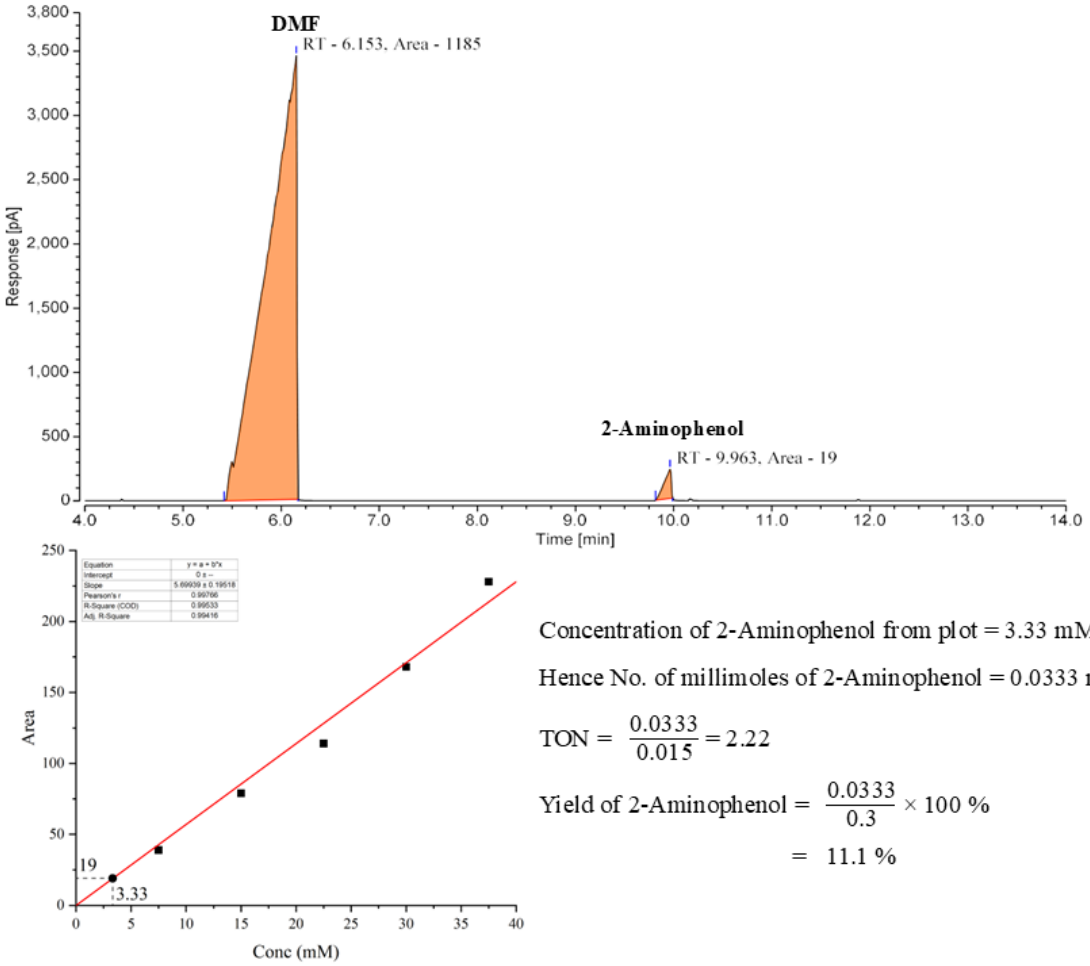


Figure S101. Calculation of yield for *o*-NH_2-C_6H_4-OH obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-NH_2)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of *o*-NH_2-C_6H_4-OH = 11.1 %**. The adjusted R^2 value for the calibration plot is 0.99416.

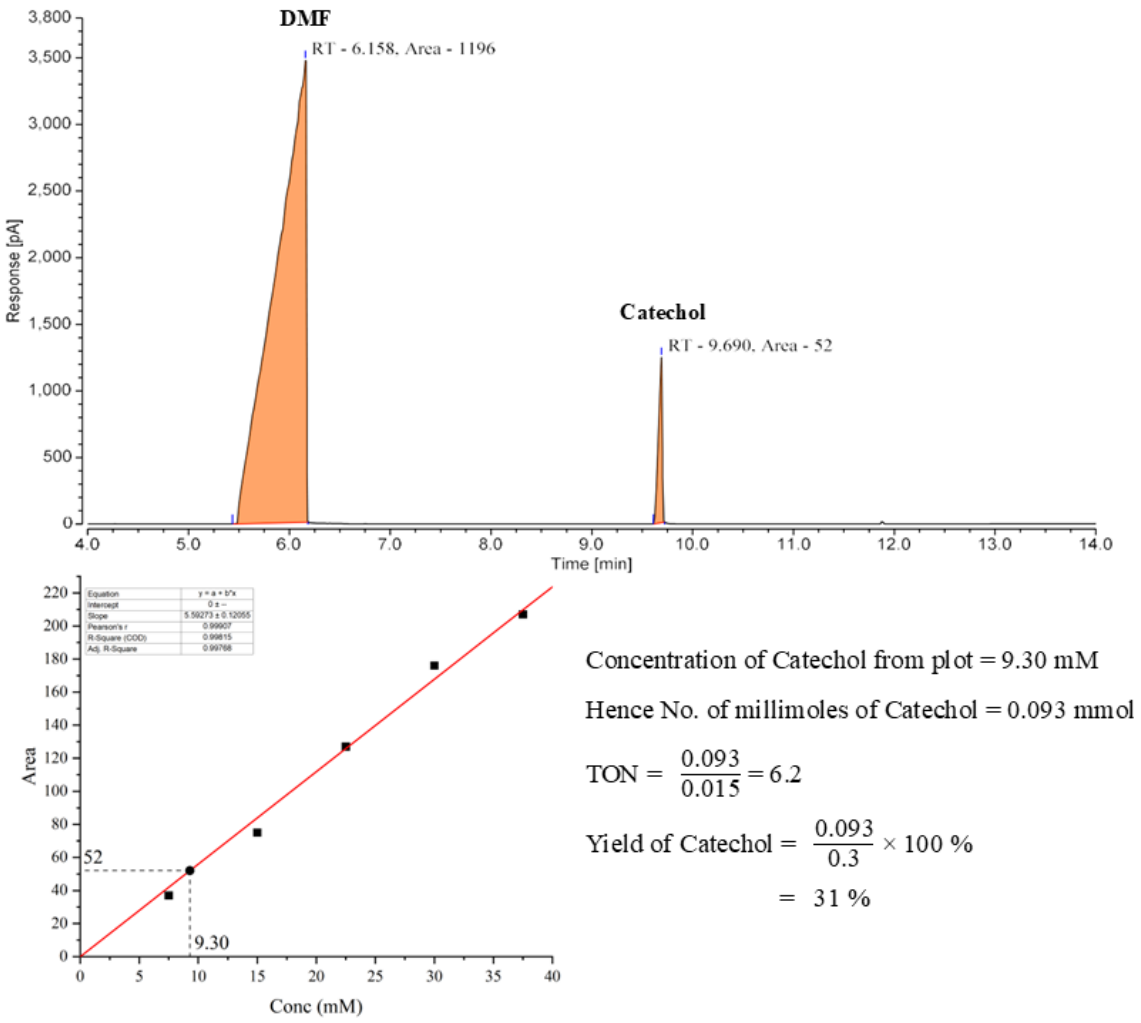


Figure S102. Calculation of yield for 1,2-$(OH)_2$-C_6H_4 obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-ONa)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 1,2-$(OH)_2$-C_6H_4 = 31 %**. The adjusted R^2 value for the calibration plot is 0.99768.

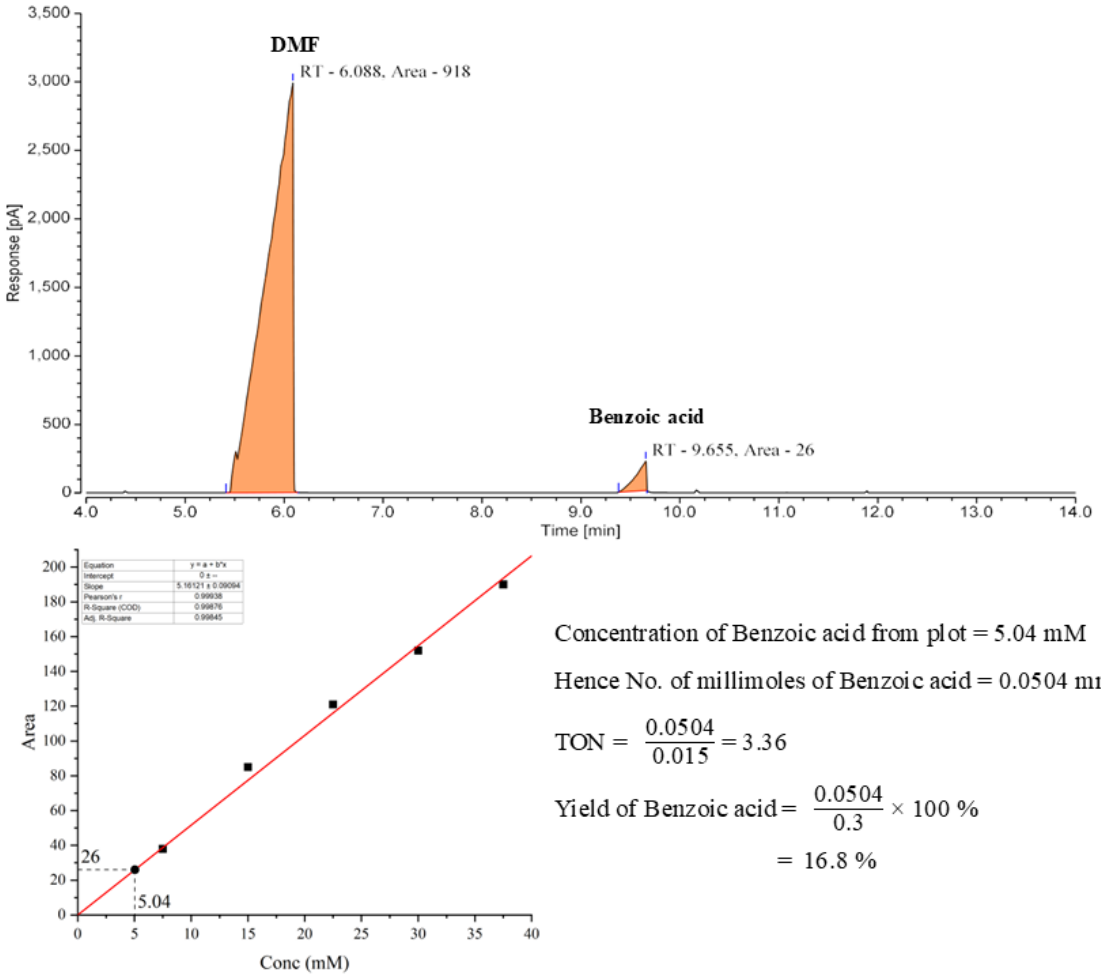
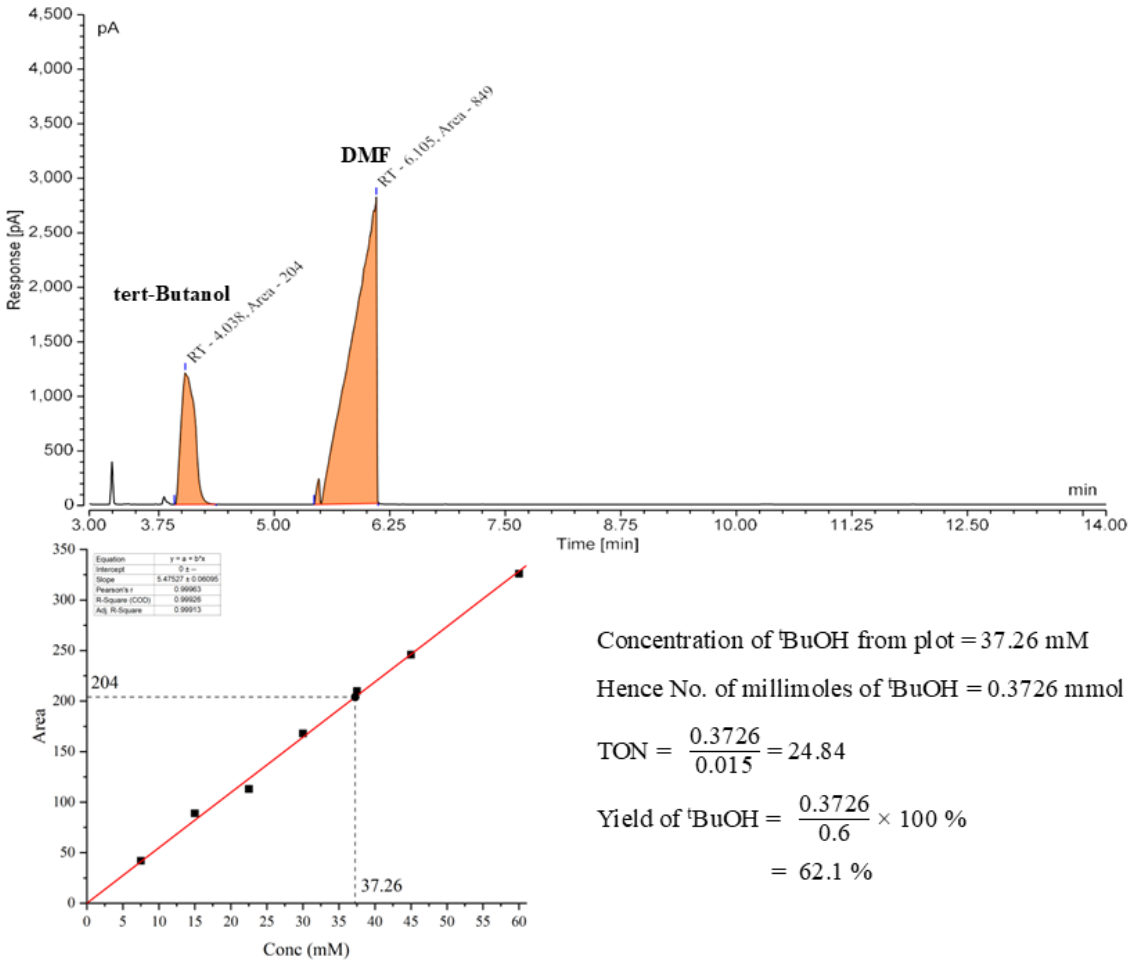


Figure S103. Calculation of yield for PhCOOH obtained from the **4c**$(BF_4)_2$ mediated catalytic hydrolysis of NaSC(O)Ph. Reaction conditions: catalyst:thiolate = 1:20, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhCOOH = 16.8 %**. The adjusted R^2 value for the calibration plot is 0.99845.



Concentration of ^{t}BuOH from plot = 37.26 mM

Hence No. of millimoles of ^{t}BuOH = 0.3726 mmol

$$\text{TON} = \frac{0.3726}{0.015} = 24.84$$

$$\text{Yield of } ^{t}\text{BuOH} = \frac{0.3726}{0.6} \times 100\ \% = 62.1\ \%$$

Figure S104. Calculation of yield for ^{t}BuOH obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS^{t}Bu. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of ^{t}BuOH = 62.1 %**. The adjusted R^2 value for the calibration plot is 0.99913.

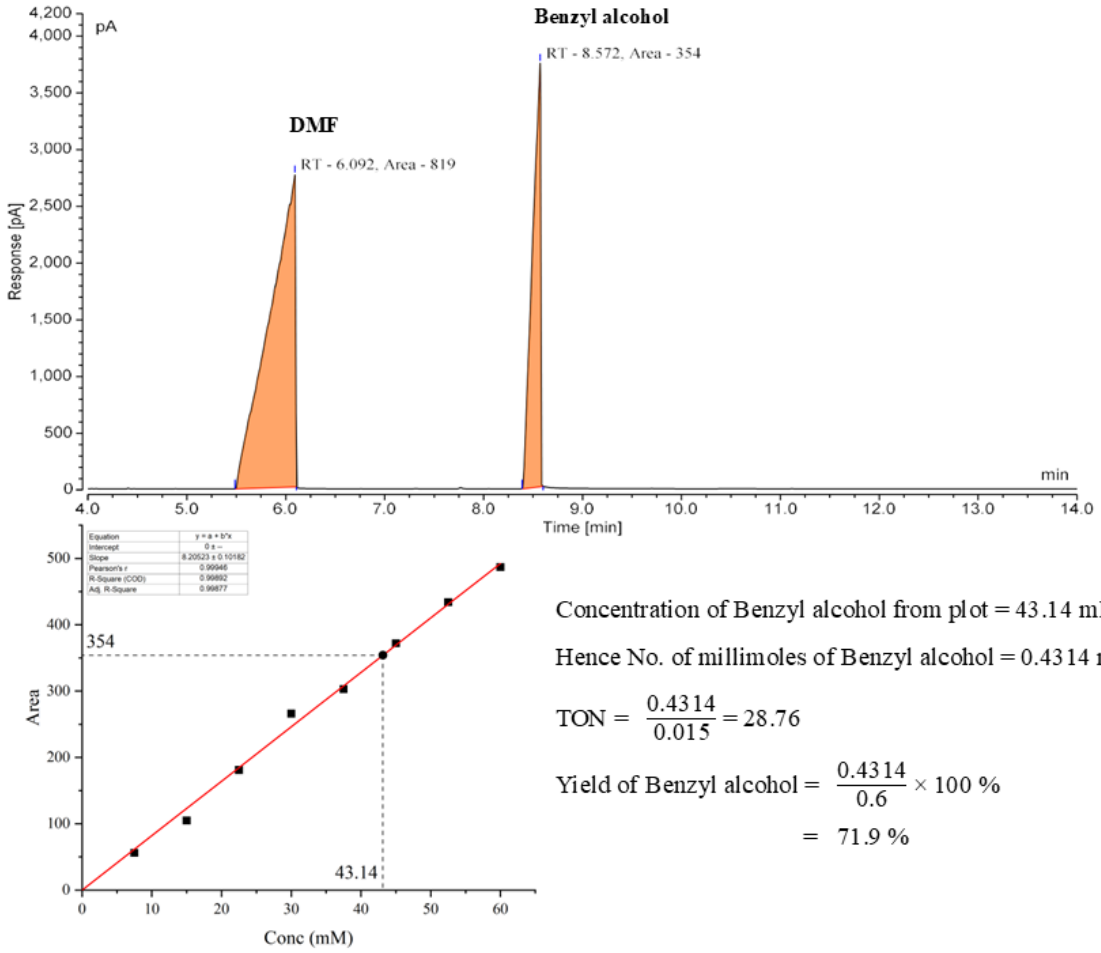


Figure S105. Calculation of yield for $PhCH_2OH$ obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of $NaSCH_2Ph$. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of $PhCH_2OH$ = 71.9 %**. The adjusted R^2 value for the calibration plot is 0.99877.

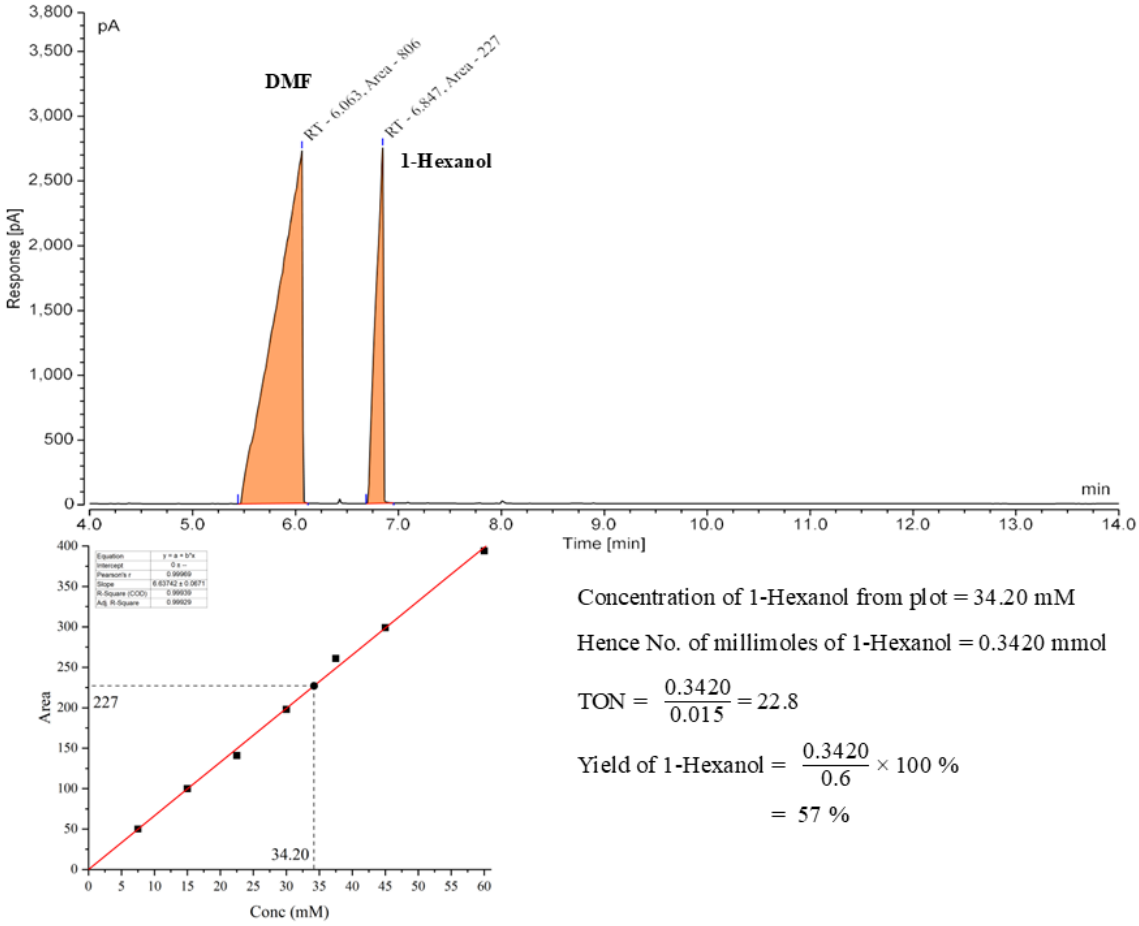


Figure S106. Calculation of yield for CH_3-$(CH_2)_4$-CH_2-OH obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_4$-CH_3. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_4$-CH_2-OH = 57 %**. The adjusted R^2 value for the calibration plot is 0.99929.

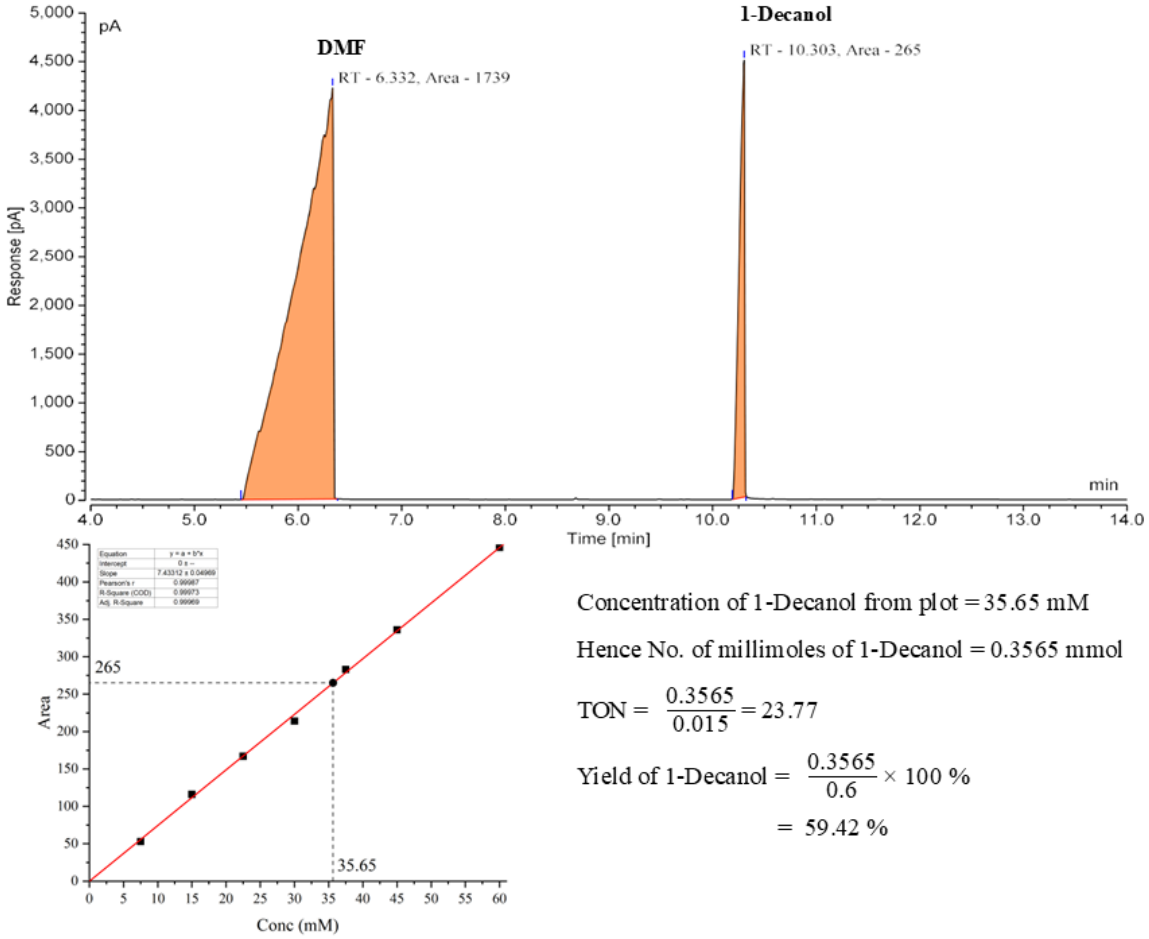


Figure S107. Calculation of yield for CH_3-$(CH_2)_8$-CH_2-OH obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH_2)_8$-CH_3. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_8$-CH_2-OH = 59.42 %**. The adjusted R^2 value for the calibration plot is 0.99969.

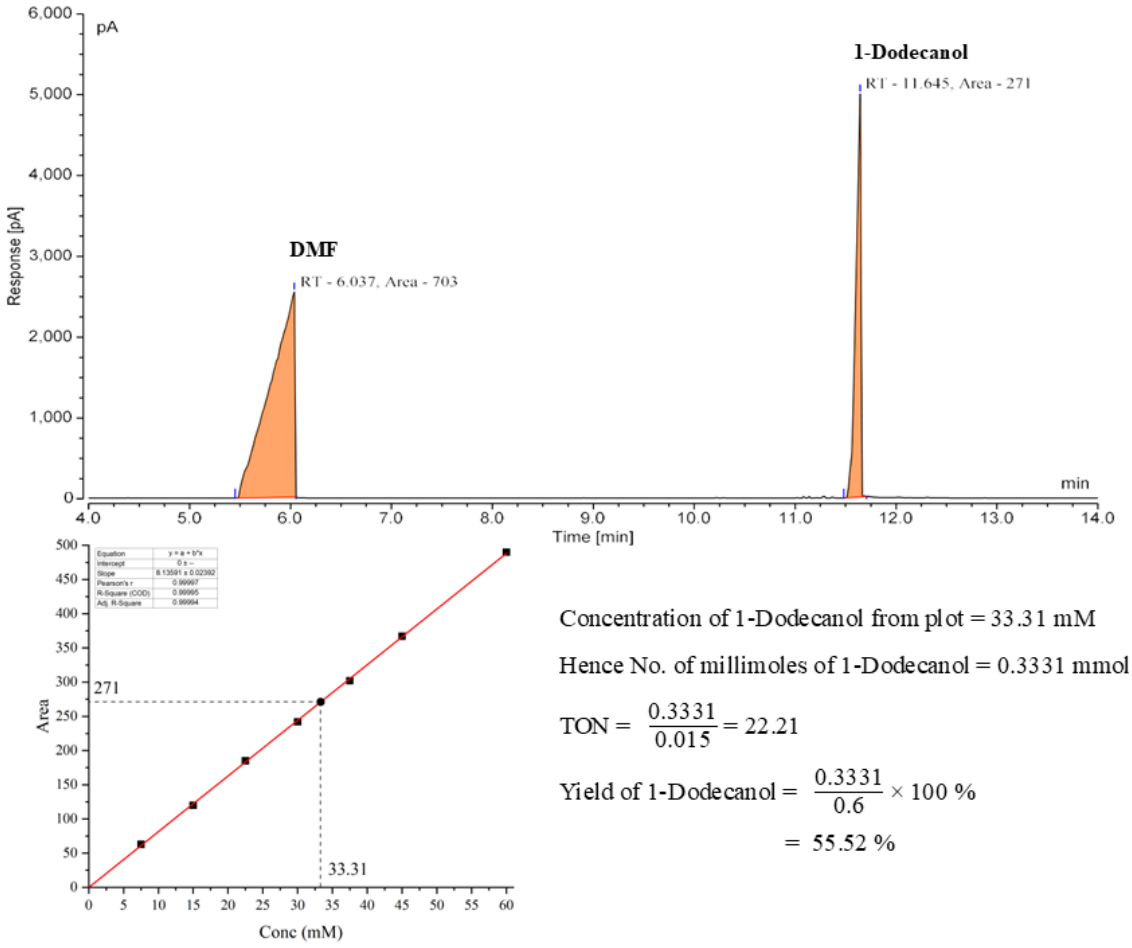


Figure S108. Calculation of yield for CH_3-$(CH_2)_{10}$-CH_2-OH obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS-$CH_2(CH)_{10}$-CH_3. Reaction conditions: catalyst:thiolate = 1:40, thiolate:H_2O = 1:30, reaction time = 60h, solvent = DMF, temperature = 25°C. Note that **yield of CH_3-$(CH_2)_{10}$-CH_2-OH = 55.52 %**. The adjusted R^2 value for the calibration plot is 0.99994.

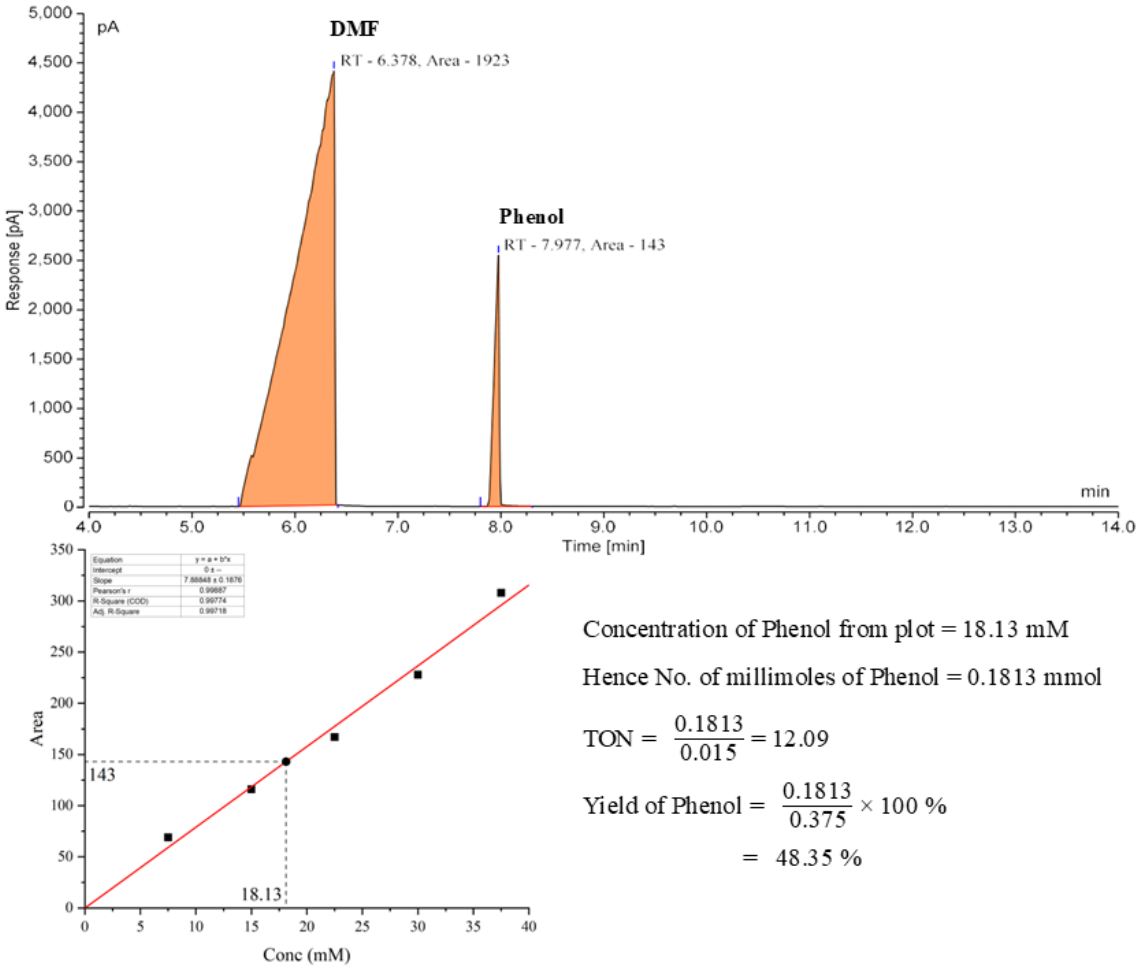


Figure S109. Calculation of yield for PhOH obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of NaSPh. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhOH = 48.35 %**. The adjusted R^2 value for the calibration plot is 0.99718.

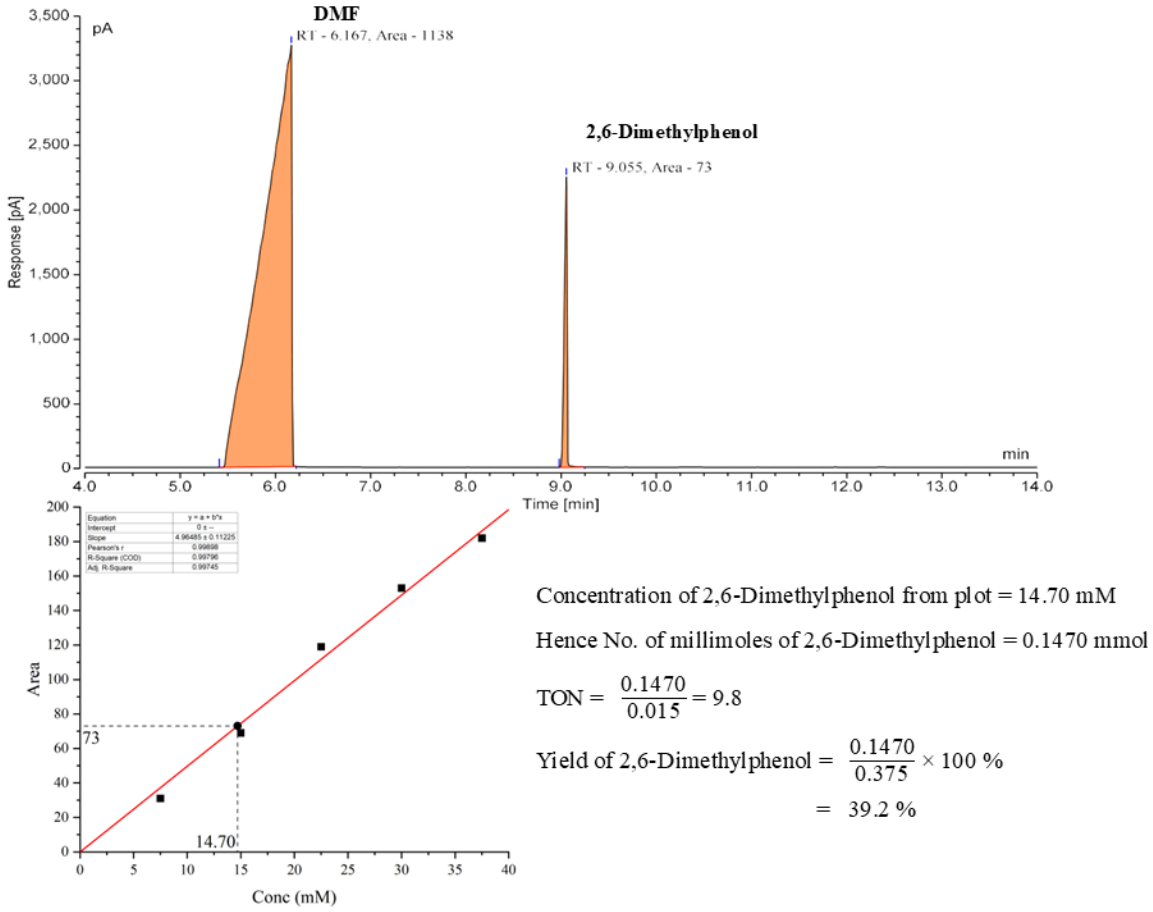


Figure S110. Calculation of yield for 2,6-Me_2-C_6H_3-OH obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,6-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,6-Me_2-C_6H_3-OH = 39.2 %**. The adjusted R^2 value for the calibration plot is 0.99745.

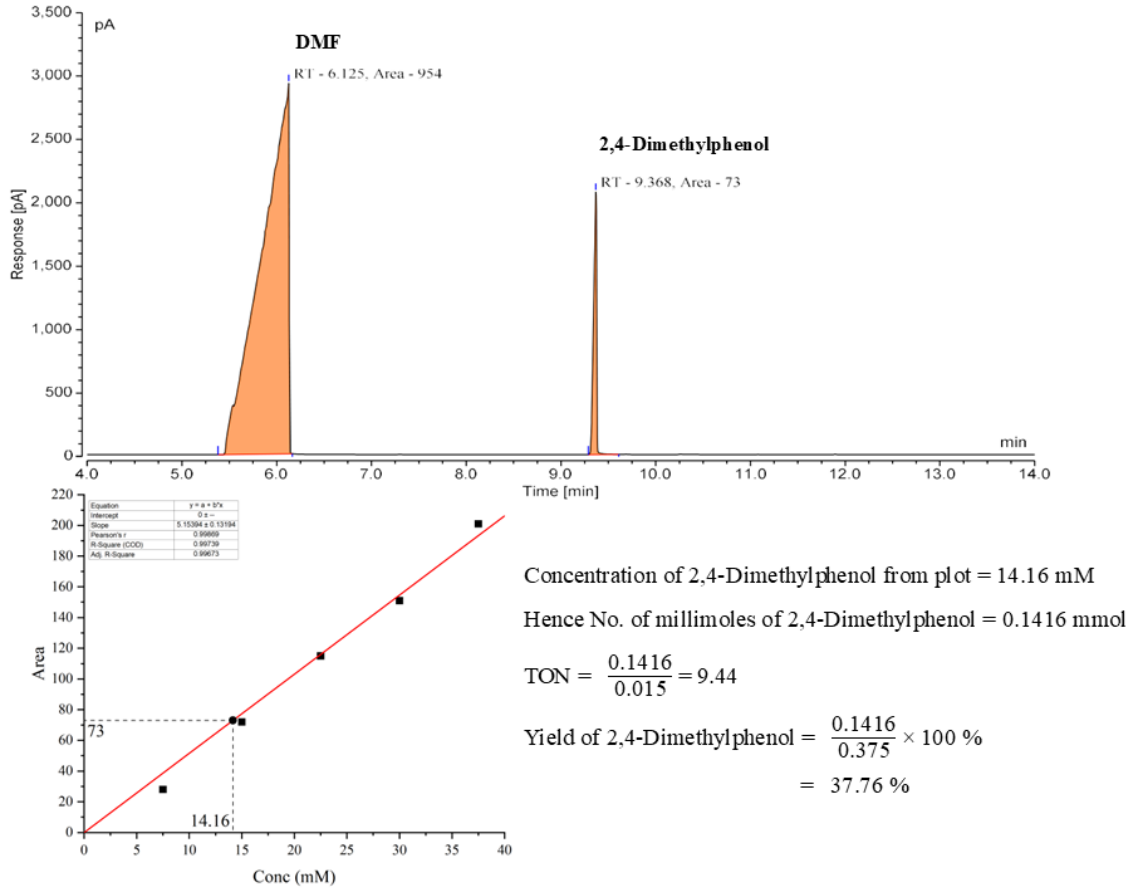


Figure S111. Calculation of yield for 2,4-Me_2-C_6H_3-OH obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(2,4-Me_2-C_6H_3). Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 2,4-Me_2-C_6H_3-OH = 37.76 %**. The adjusted R^2 value for the calibration plot is 0.99673.

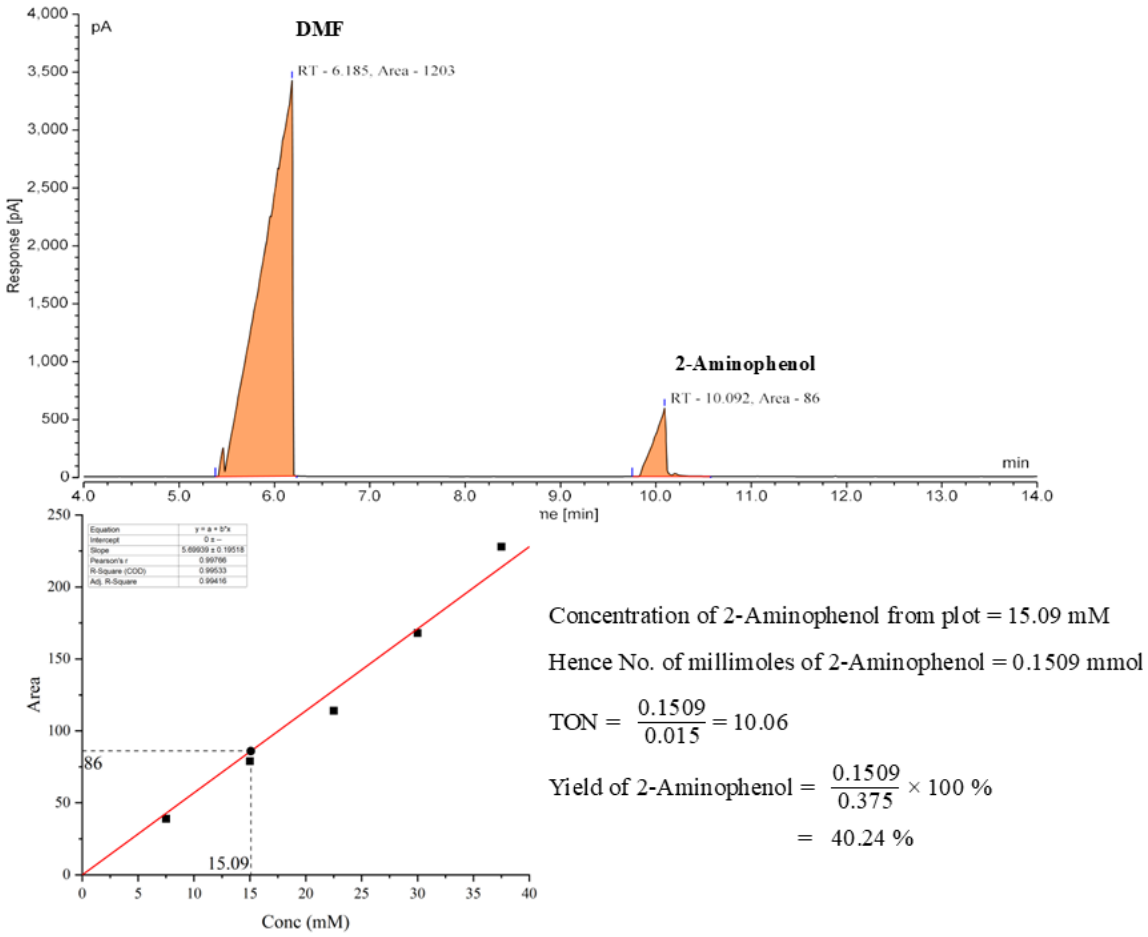


Figure S112. Calculation of yield for *o*-NH_2-C_6H_4-OH obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-NH_2)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of *o*-NH_2-C_6H_4-OH = 40.24 %**. The adjusted R^2 value for the calibration plot is 0.99416.

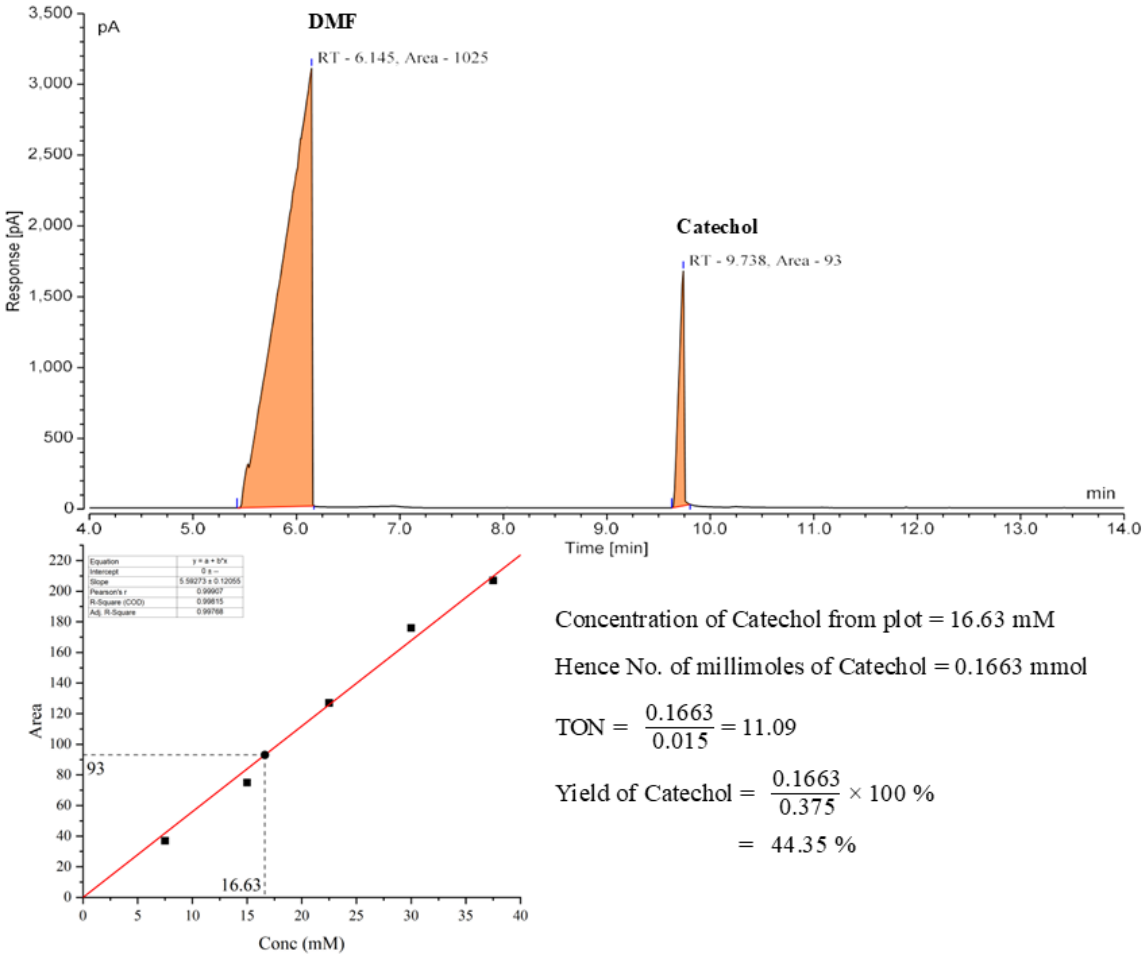


Figure S113. Calculation of yield for 1,2-$(OH)_2$-C_6H_4 obtained from the **4d**$(BF_4)_2$ mediated catalytic hydrolysis of NaS(*o*-ONa)-C_6H_4. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that the **yield of 1,2-$(OH)_2$-C_6H_4 = 44.35 %**. The adjusted R^2 value for the calibration plot is 0.99768.

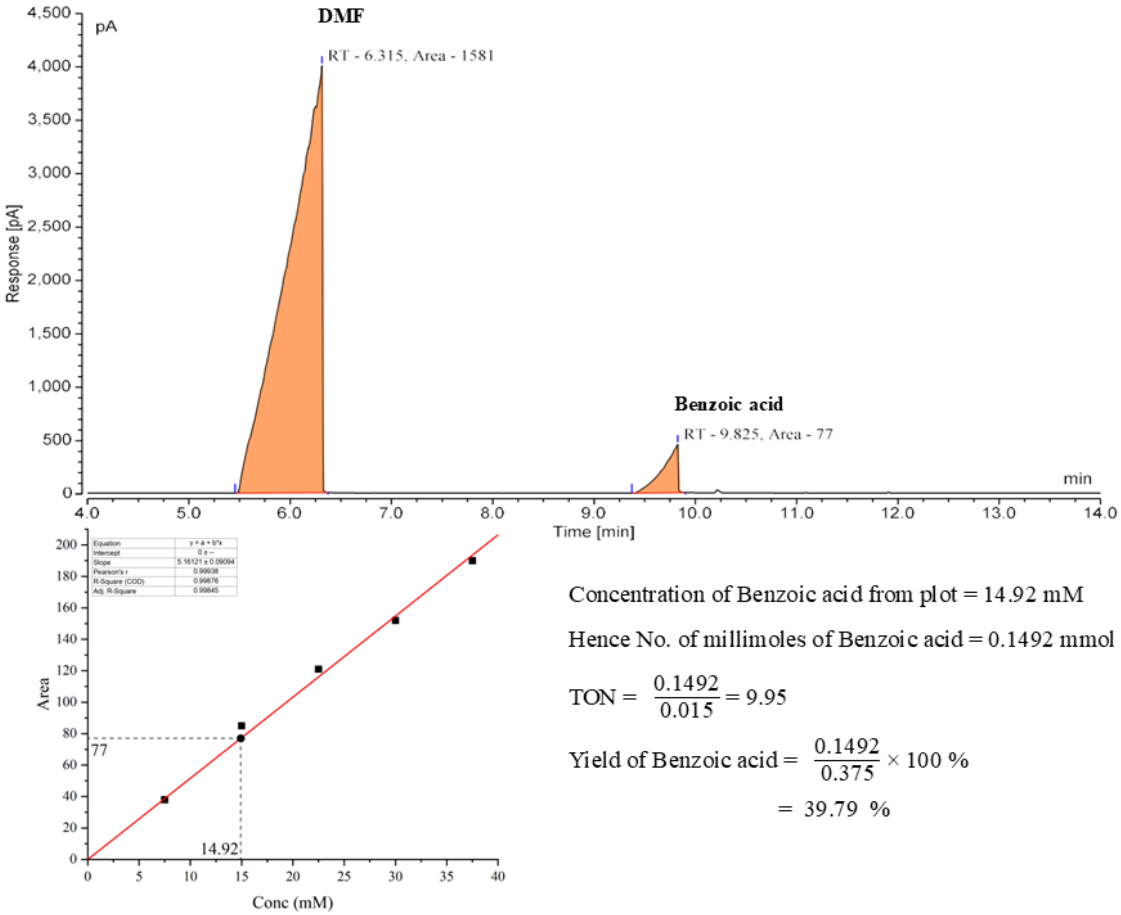


Figure S114. Calculation of yield for PhCOOH obtained from the **4d(BF$_4$)$_2$** mediated catalytic hydrolysis of NaSC(O)Ph. Reaction conditions: catalyst:thiolate = 1:25, thiolate:H_2O = 1:30, reaction time = 168h, solvent = DMF, temperature = 25°C. Note that **yield of PhCOOH = 39.79 %**. The adjusted R^2 value for the calibration plot is 0.99845.

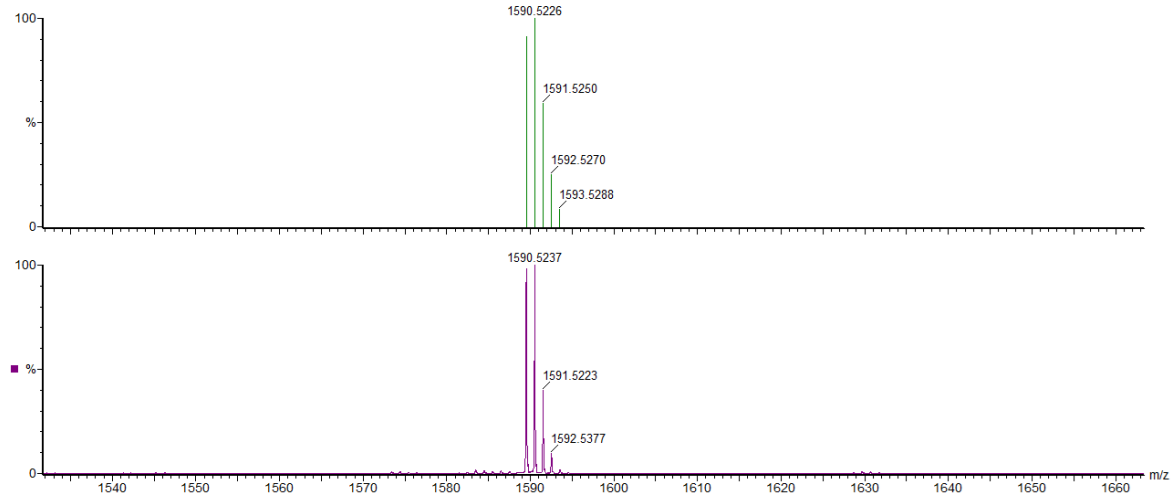


Figure S115. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2d**$(BF_4)_2$, $NaSCH_2Ph$ and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Co_2(PhBIMP)(SCH_2Ph)(H_2O)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1590.5226 (simulated, green line), 1590.5237 (obtained, purple line).

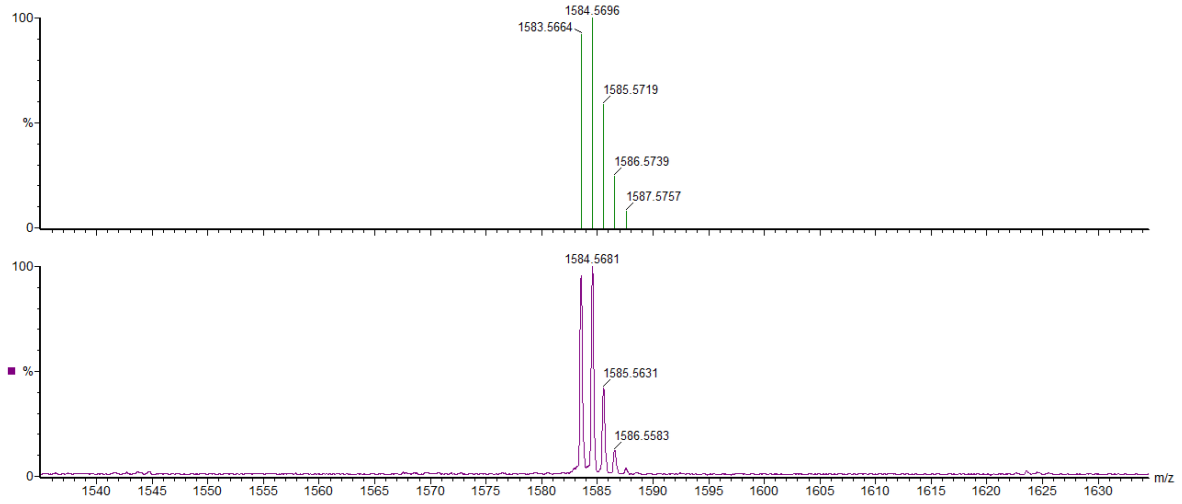


Figure S116. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2d**$(BF_4)_2$, $NaS(CH_2)_5CH_3$ and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Co_2(PhBIMP)(S(CH_2)_5CH_3)(H_2O)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1584.5696 (simulated, green line), 1584.5681 (obtained, purple line).

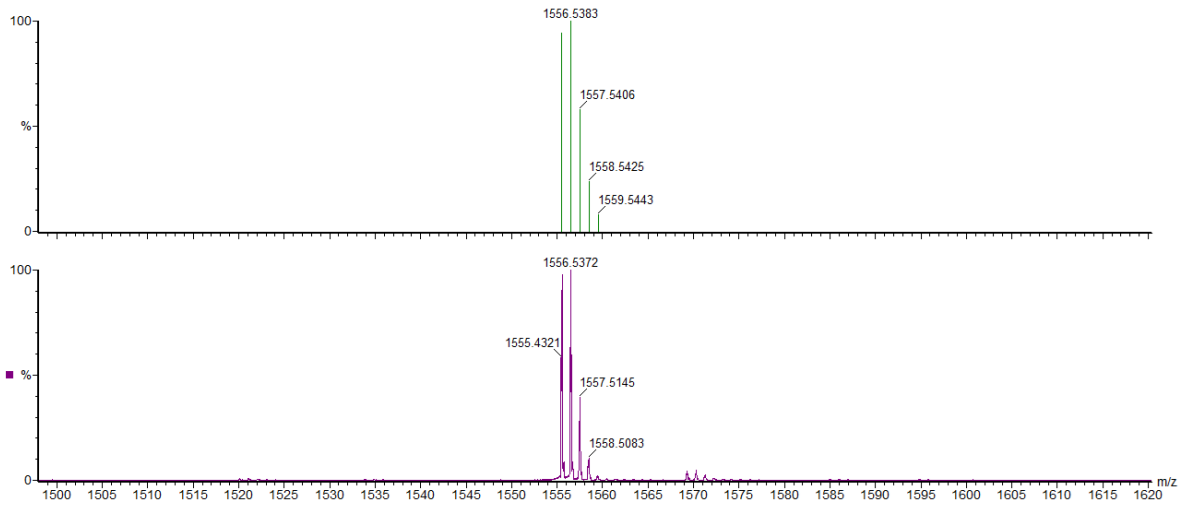


Figure S117. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2d**$(BF_4)_2$, NaS^tBu and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Co_2(PhBIMP)(S^tBu)(H_2O)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1556.5383 (simulated, green line), 1556.5372 (obtained, purple line).

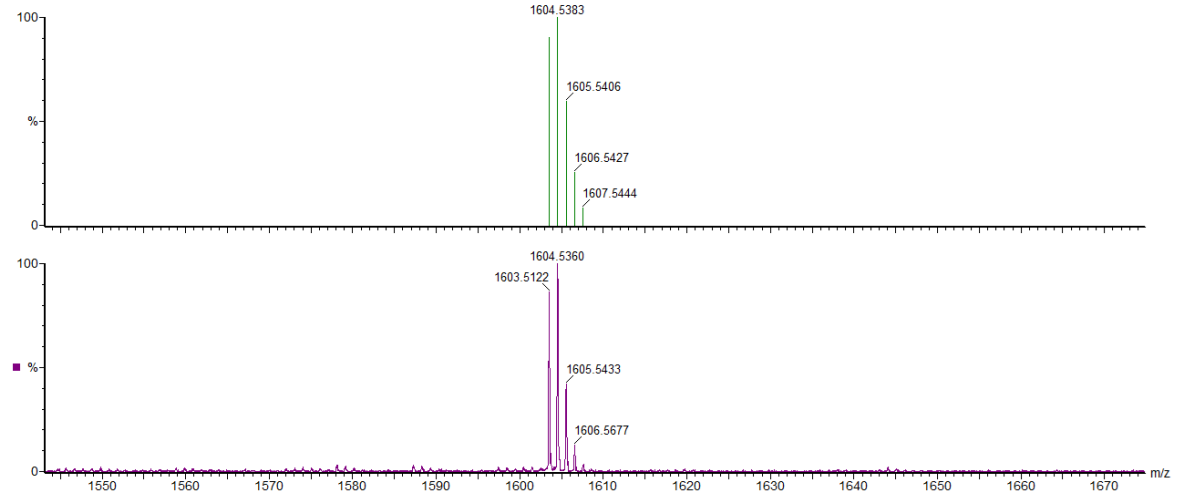


Figure S118. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2d**$(BF_4)_2$, Na$S(2,6\text{-}Me_2\text{-}C_6H_3)$ and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Co_2(PhBIMP)(S(2,6\text{-}Me_2\text{-}C_6H_3))(H_2O)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1604.5383 (simulated, green line), 1604.5360 (obtained, purple line).

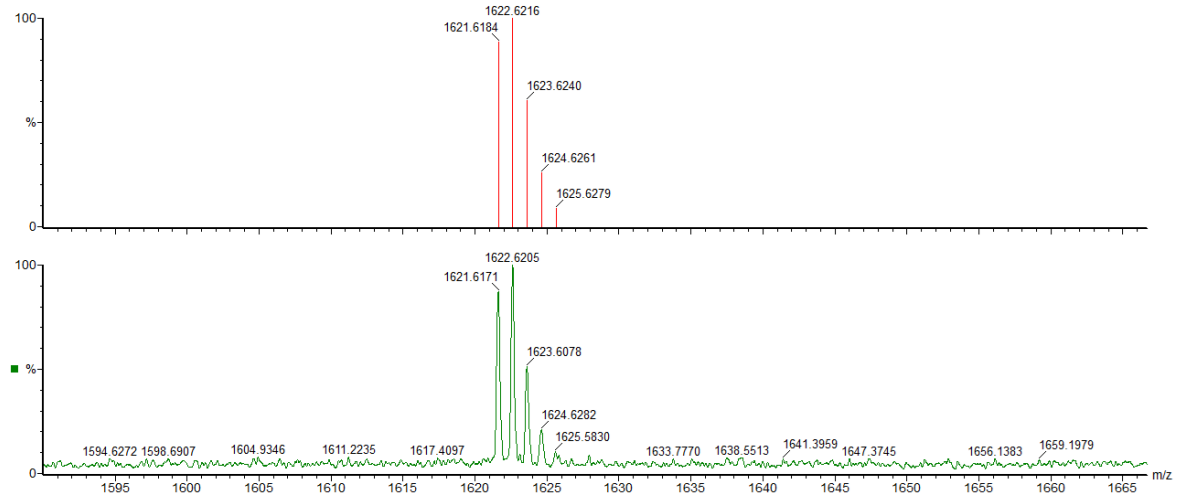


Figure S119. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2d**$(BF_4)_2$, $NaS(CH_2)_9CH_3$ and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Co_2(PhBIMP)(S(CH_2)_9CH_3)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1622.6216 (simulated, red line), 1622.6205 (obtained, green line).

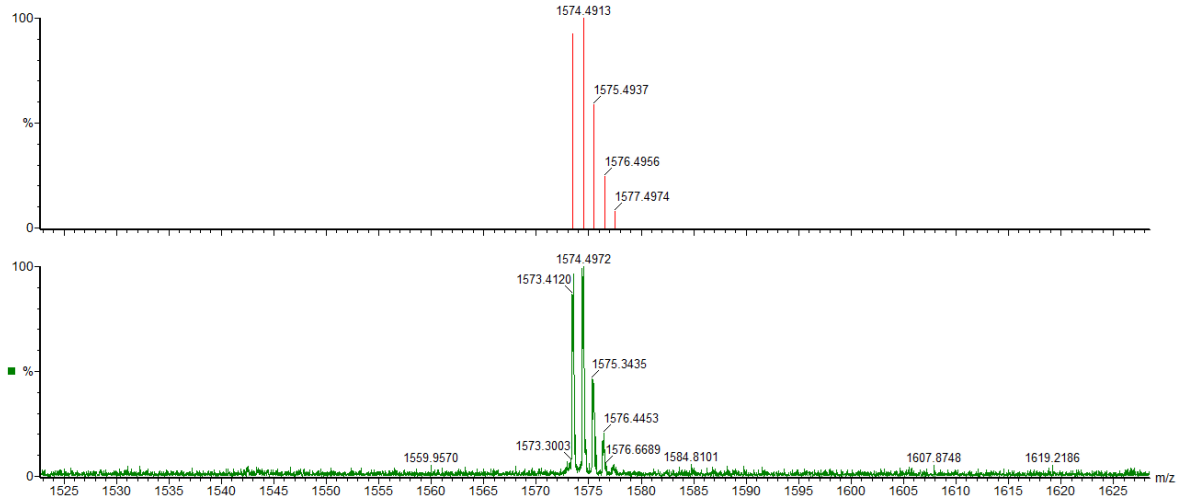


Figure S120. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2d**$(BF_4)_2$, NaS(*o*-ONa)-C_6H_4 and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Co_2(PhBIMP)(S(o\text{-}OH)\text{-}C_6H_4)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1574.4913 (simulated, red line), 1574.4972 (obtained, green line).

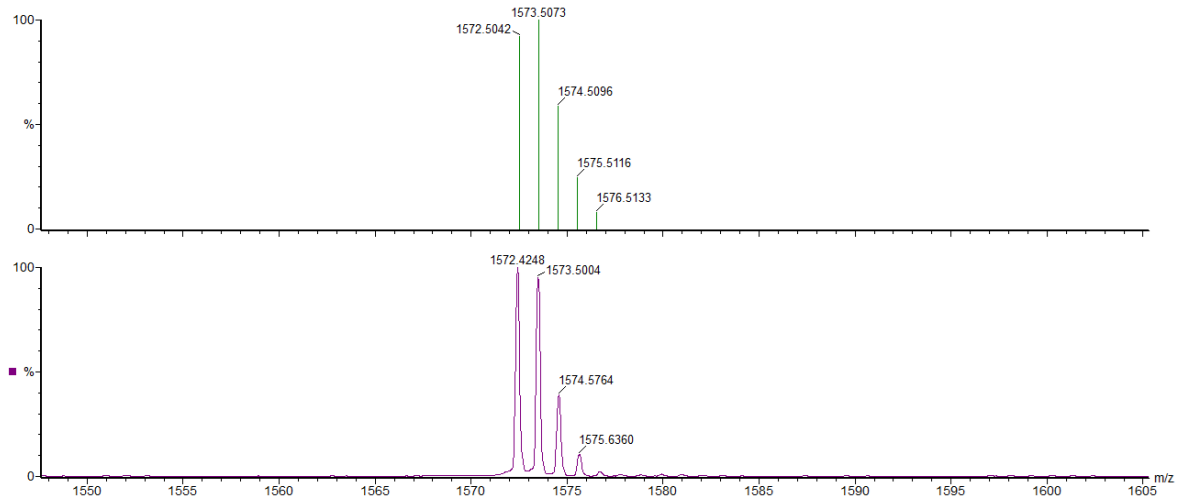


Figure S121. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2d**$(BF_4)_2$, NaS(*o*-NH_2)-C_6H_4 and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Co_2(PhBIMP)(S(o\text{-}NH_2)\text{-}C_6H_4)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1573.5073 (simulated, green line), 1573.5004 (obtained, purple line).

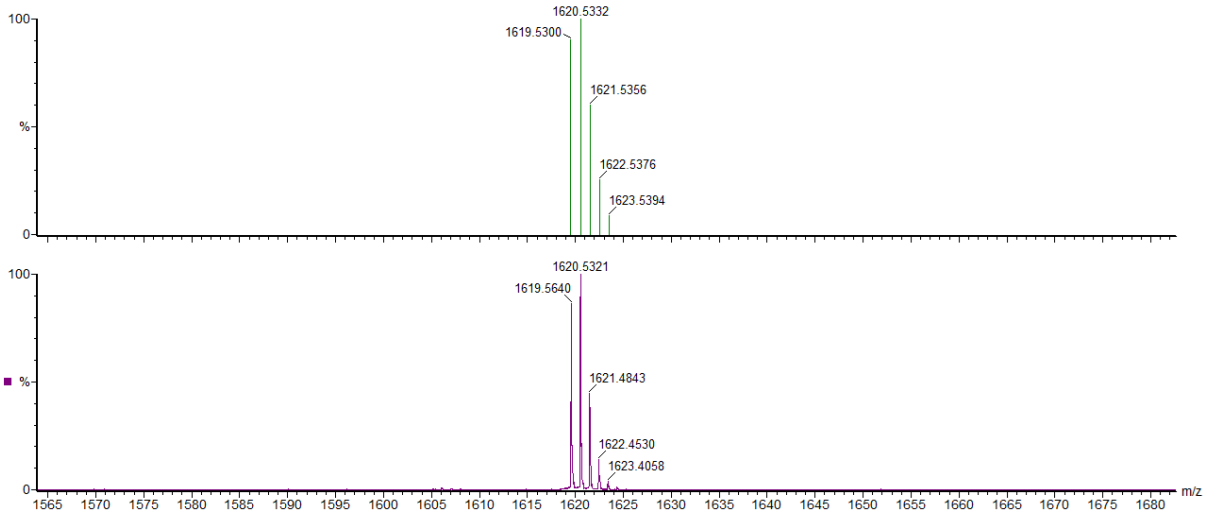


Figure S122. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2f**$(BF_4)_2$, $NaSCH_2Ph$ and H_2O in 1:40:1200 ratio indicates the formation of the proposed intermediate $[Co_2(PhBIMP)(SCH_2Ph)(H_2O)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{1+}$ at m/z = 1620.5332 (simulated, green line), 1620.5321 (obtained, purple line).

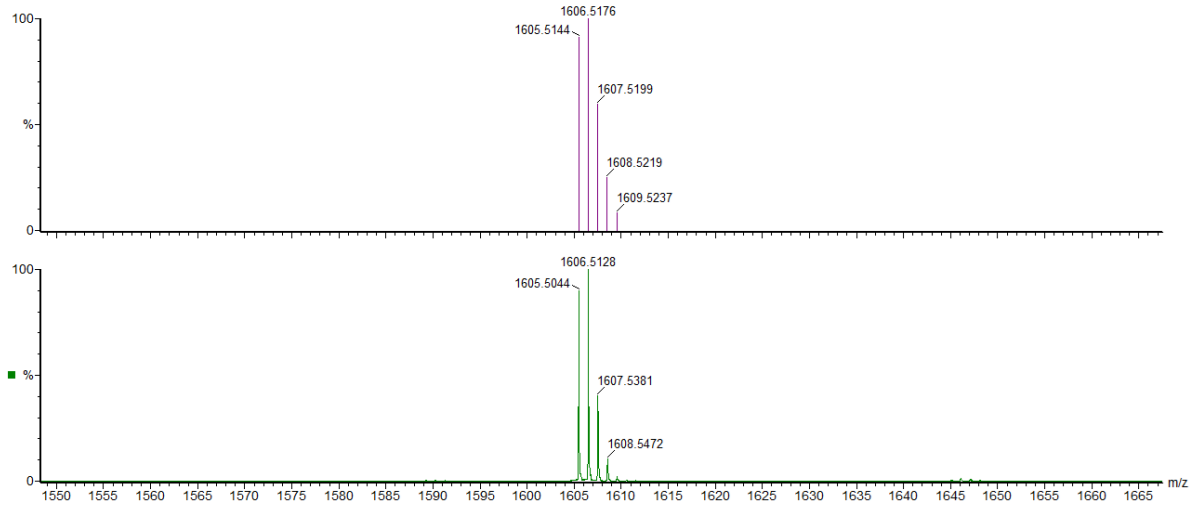


Figure S123. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2f**$(BF_4)_2$, NaSPh and H_2O in 1:25:750 ratio indicates the formation of the proposed intermediate $[Co_2(PhBIMP)(SPh)(H_2O)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{1+}$ at m/z = 1606.5176 (simulated, purple line), 1606.5128 (obtained, green line).

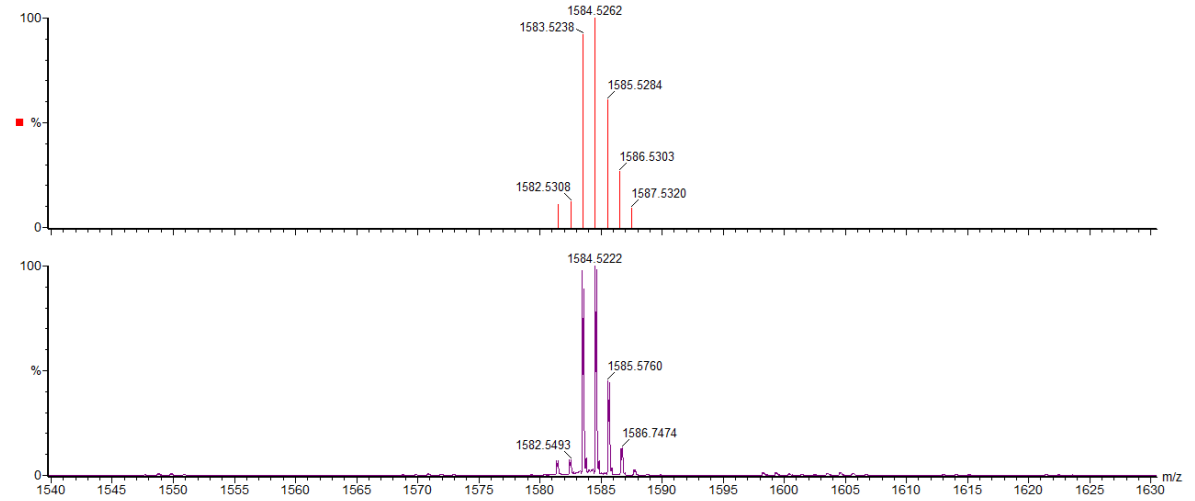


Figure S124. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4b**$(BF_4)_2$, $NaSCH_2Ph$ and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Fe_2(PhBIMP)(SCH_2Ph)(H_2O)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1584.5262 (simulated, red line), 1584.5222 (obtained, purple line).

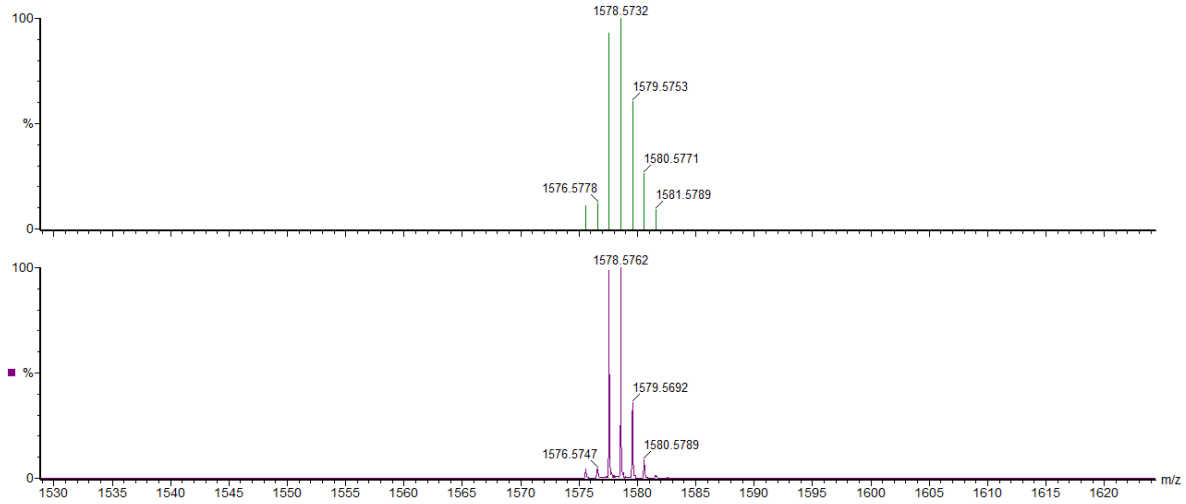


Figure S125. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4b**$(BF_4)_2$, $NaS(CH_2)_5CH_3$ and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Fe_2(PhBIMP)(S(CH_2)_5CH_3)(H_2O)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1578.5732 (simulated, green line), 1578.5762 (obtained, purple line).

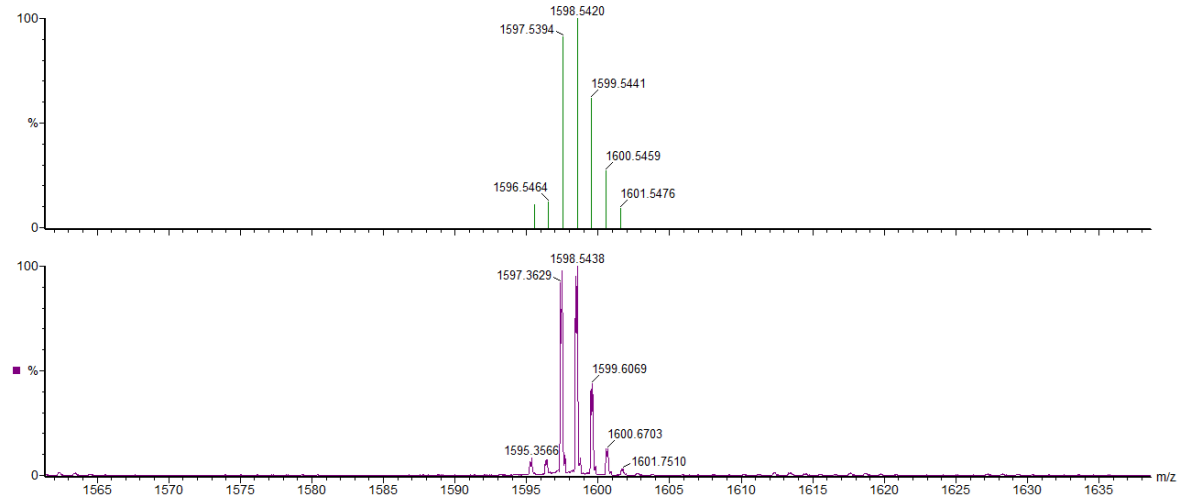


Figure S126. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4b**$(BF_4)_2$, $NaS(2,6\text{-}Me_2\text{-}C_6H_3)$ and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Fe_2(PhBIMP)(S(2,6\text{-}Me_2\text{-}C_6H_3))(H_2O)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1598.5420 (simulated, green line), 1598.5438 (obtained, purple line).

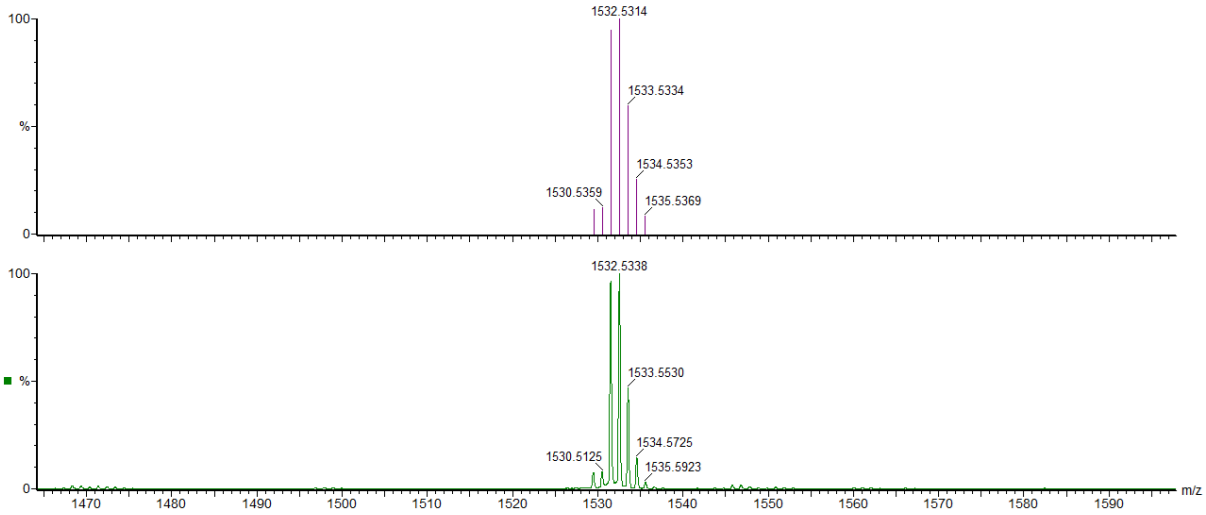


Figure S127. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4b**$(BF_4)_2$, NaS^{t}Bu and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Fe_2(PhBIMP)(S^tBu)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1532.5314 (simulated, purple line), 1532.5338 (obtained, green line).

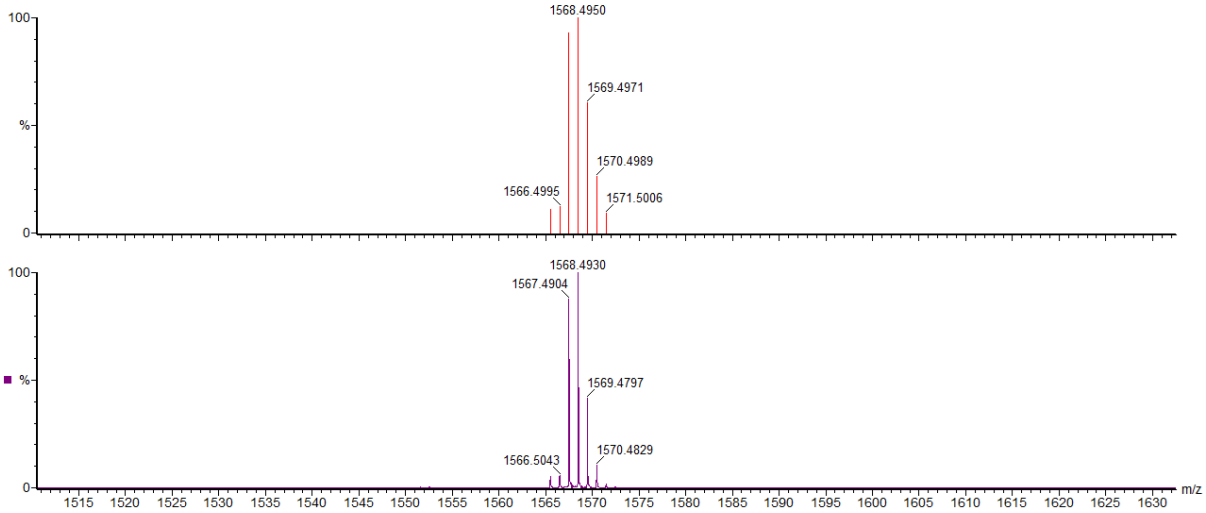


Figure S128. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4b**$(BF_4)_2$, NaS(*o*-ONa)-C_6H_4 and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Fe_2(PhBIMP)(S(o\text{-}OH)\text{-}C_6H_4)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2]^{1+}$ at m/z = 1568.4950 (simulated, red line), 1568.4930 (obtained, purple line).

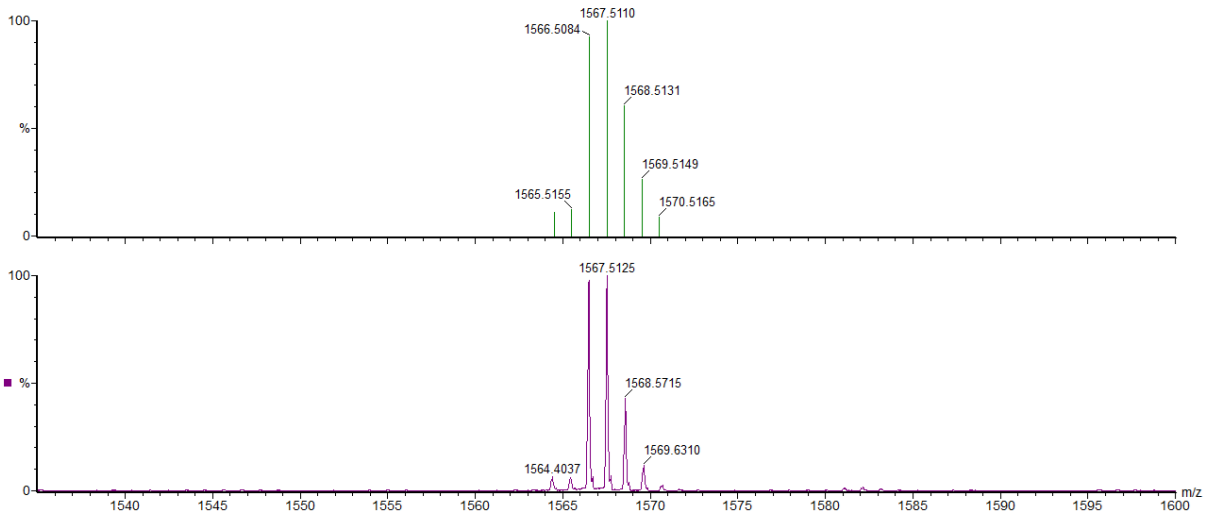


Figure S129. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4b**$(BF_4)_2$, NaS(*o*-NH_2)-C_6H_4 and H_2O in 1:10:300 ratio indicates the formation of the proposed intermediate $[Fe_2(PhBIMP)(S(o\text{-}NH_2)\text{-}C_6H_4)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1567.5110 (simulated, green line), 1567.5125 (obtained, purple line).

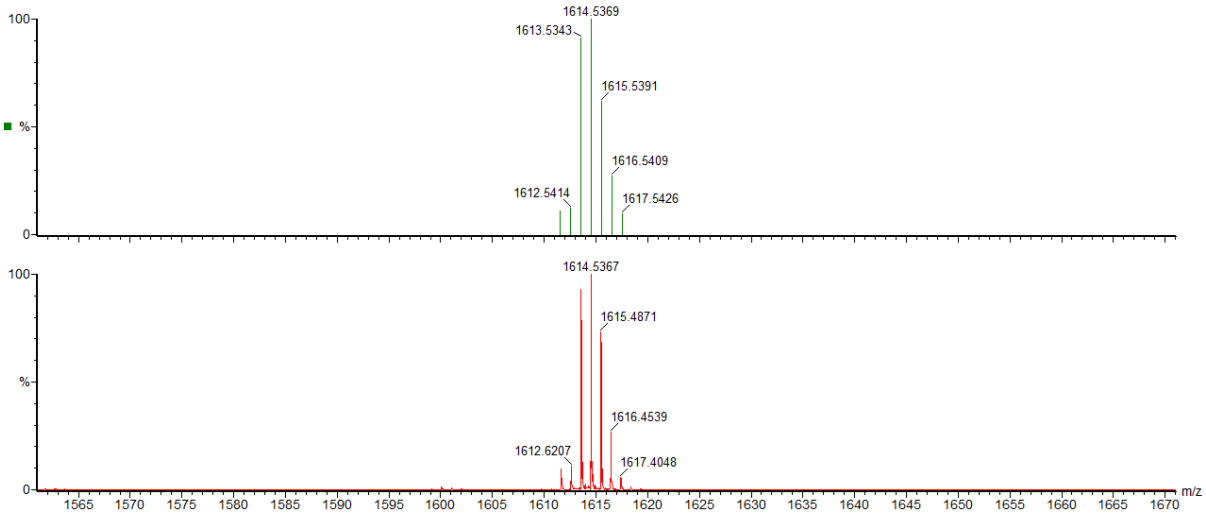


Figure S130. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4d**$(BF_4)_2$, $NaSCH_2Ph$ and H_2O in 1:40:1200 ratio indicates the formation of the proposed intermediate $[Fe_2(PhBIMP)(SCH_2Ph)(H_2O)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{1+}$ at m/z = 1614.5369 (simulated, green line), 1614.5367 (obtained, red line).

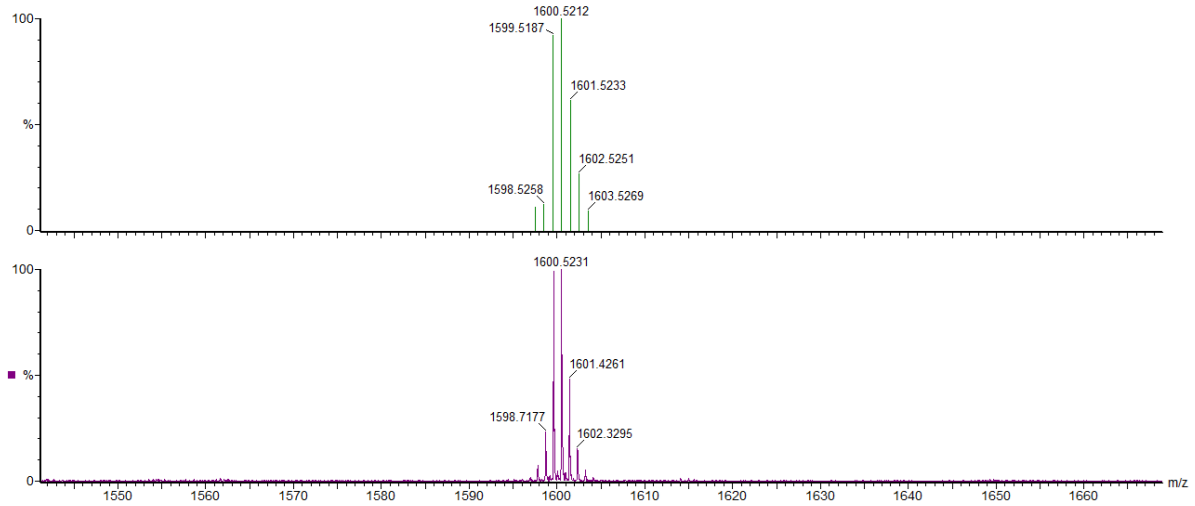


Figure S131. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2f**$(BF_4)_2$, NaSPh and H_2O in 1:25:750 ratio indicates the formation of the proposed intermediate $[Fe_2(PhBIMP)(SPh)(H_2O)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{1+}$ at m/z = 1600.5212 (simulated, green line), 1600.5231 (obtained, purple line).

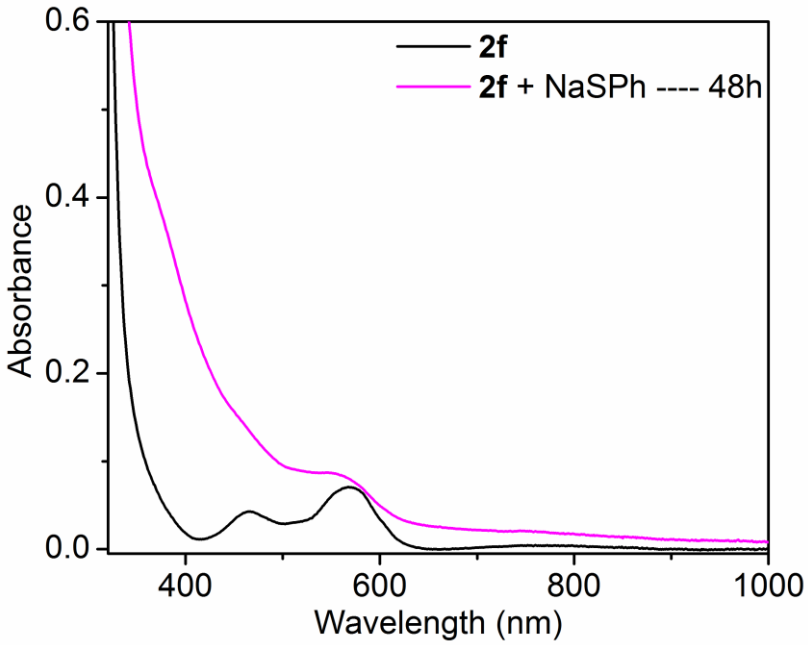


Figure S132. Electronic absorption spectra for **2f**$(BF_4)_2$ (0.5 mM) and a solution of **2f**$(BF_4)_2$ (0.5 mM) and NaSPh (12.5 mM) in DMF (after 48 h stirring).

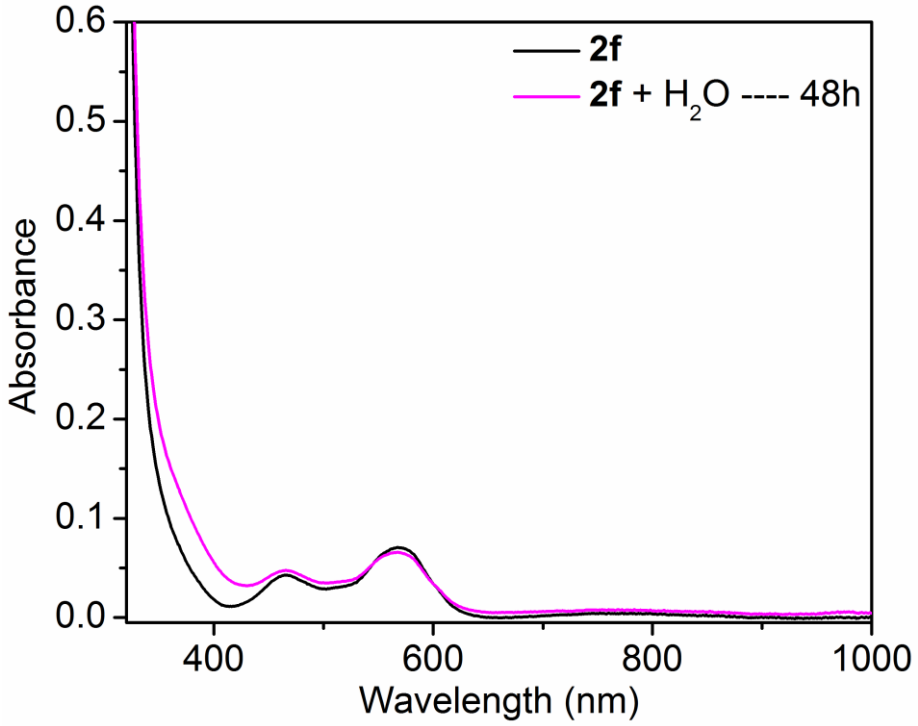


Figure S133. Electronic absorption spectra for **2f**$(BF_4)_2$ (0.5 mM) and a solution of **2f**$(BF_4)_2$ (0.5 mM) and H_2O (0.375 mM) in DMF (after 48 h stirring).

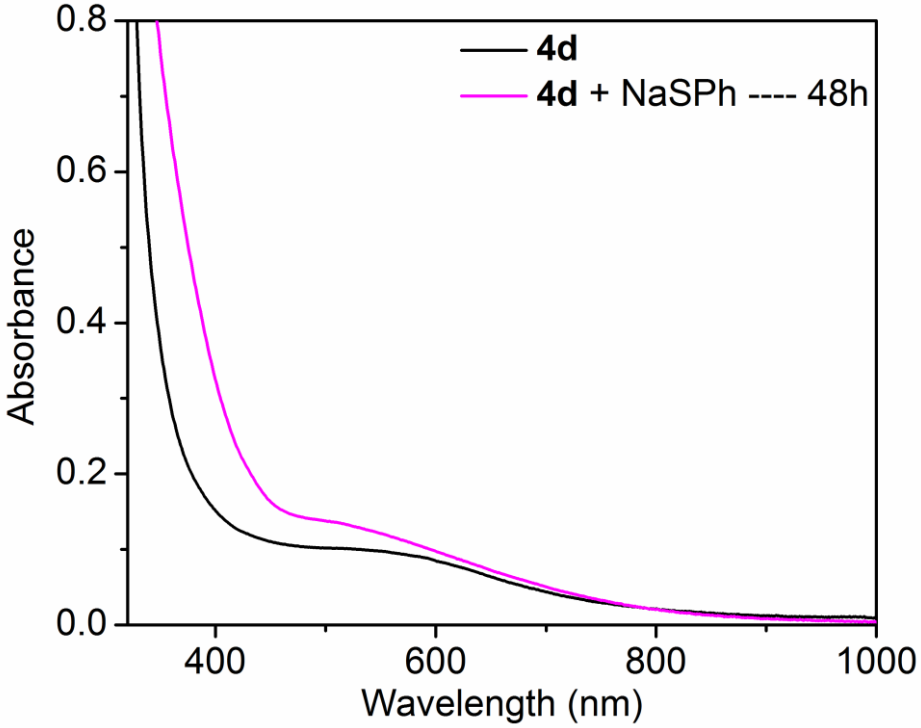


Figure S134. Electronic absorption spectra for **4d**$(BF_4)_2$ (0.5 mM) and a solution of **4d**$(BF_4)_2$ (0.5 mM) and NaSPh (12.5 mM) in DMF (after 48 h stirring).

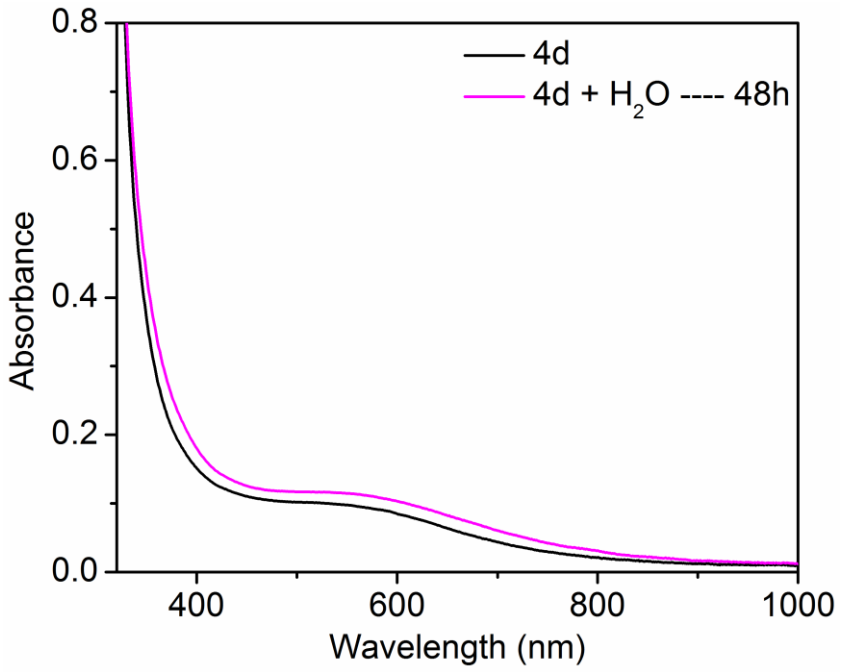


Figure S135. Electronic absorption spectra for **4d**$(BF_4)_2$ (0.5 mM) and a solution of **4d**$(BF_4)_2$ (0.5 mM) and H_2O (0.375 M) in DMF (after 48 h stirring).

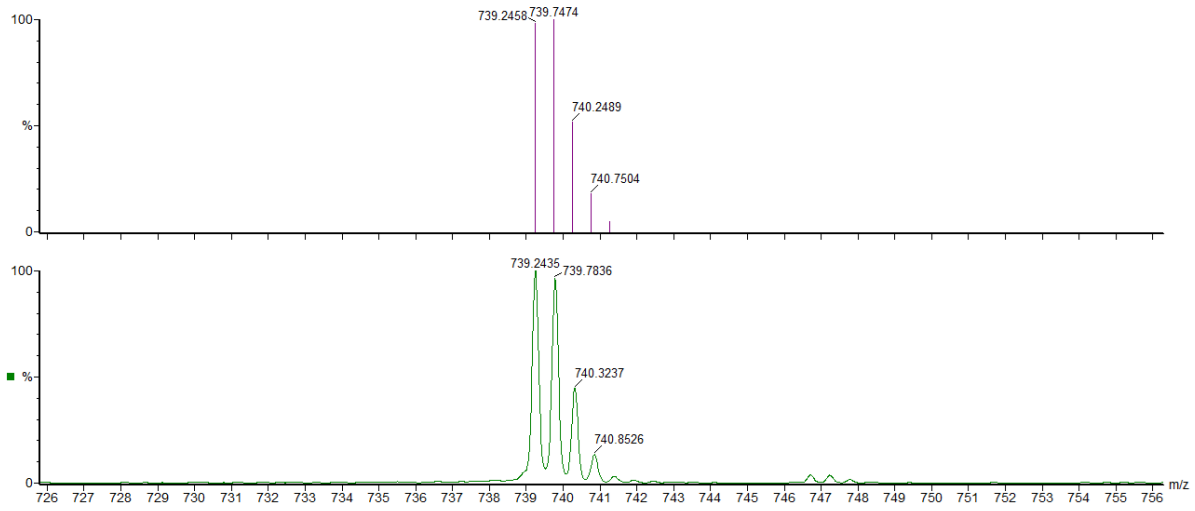


Figure S136. Mass spectrum (in DMF/MeCN) for **2f**$(BF_4)_2$ recovered from the reaction of **2f**$(BF_4)_2$ and NaSPh in 1:25 ratio in CH_2Cl_2 shows the presence of $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{2+}$ (**2f**) at m/z = 739.2458 (simulated, purple line), 739.2435 (obtained, green line).

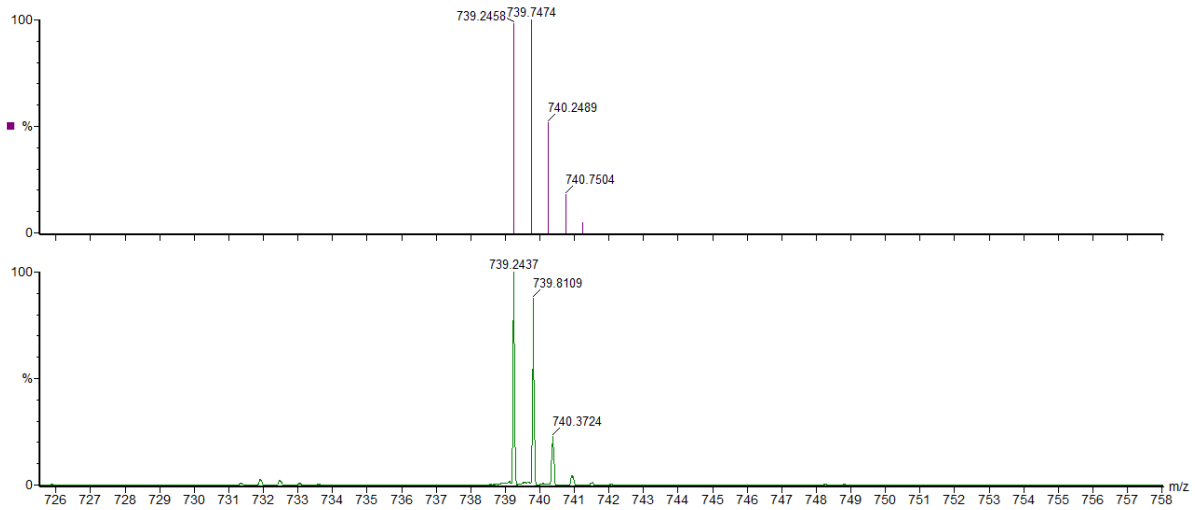


Figure S137. Mass spectrum (in DMF/MeCN) for **2f**$(BF_4)_2$ recovered from the reaction of **2f**$(BF_4)_2$ and H_2O in 1:750 ratio in DMF shows the presence of $[Co_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{2+}$ (**2f**) at m/z = 739.2458 (simulated, purple line), 739.2437 (obtained, green line).

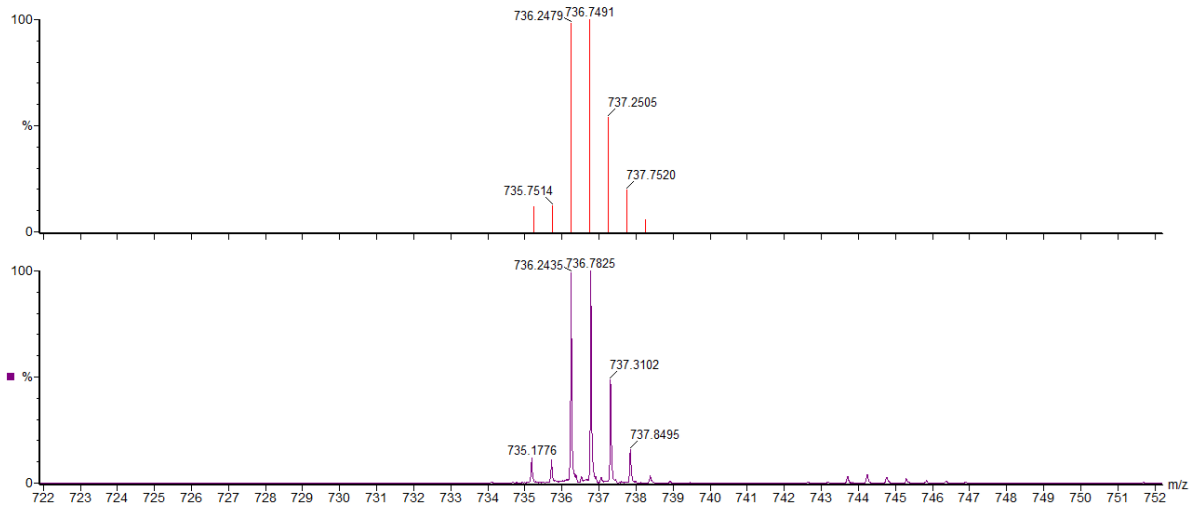


Figure S138. Mass spectrum (in DMF/MeCN) for **4d**$(BF_4)_2$ recovered from the reaction of **4d**$(BF_4)_2$ and NaSPh in 1:25 ratio in CH_2Cl_2 shows the presence of $[Fe_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{2+}$ (**4d**) at m/z = 736.2479 (simulated, red line), 736.2435 (obtained, purple line).

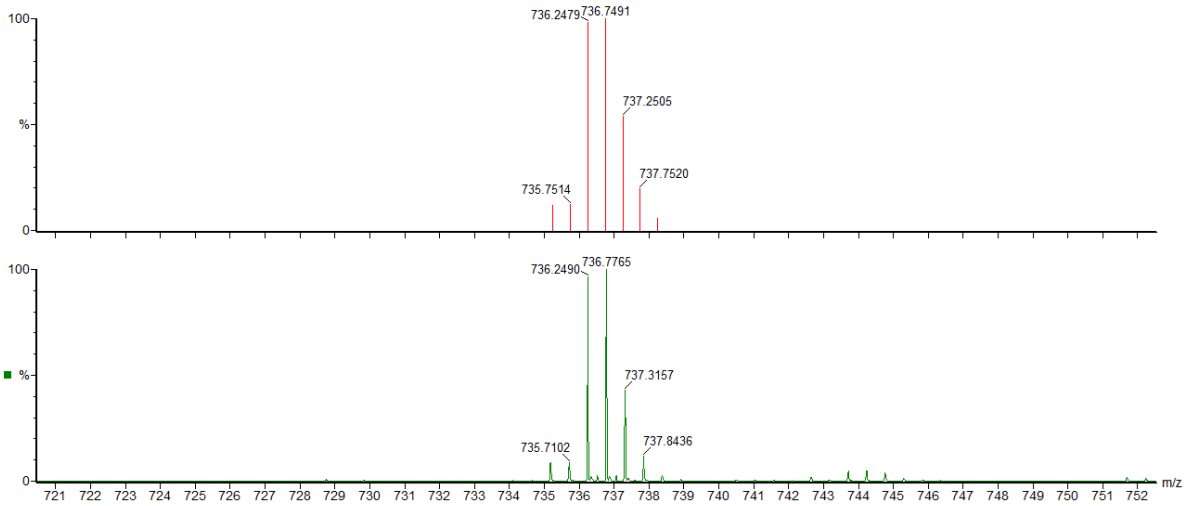


Figure S139. Mass spectrum (in DMF/MeCN) for **4d**$(BF_4)_2$ recovered from the reaction of **4d**$(BF_4)_2$ and H_2O in 1:750 ratio in DMF shows the presence of $[Fe_2(PhBIMP)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{2+}$ (**4d**) at m/z = 736.2479 (simulated, red line), 736.2490 (obtained, green line).

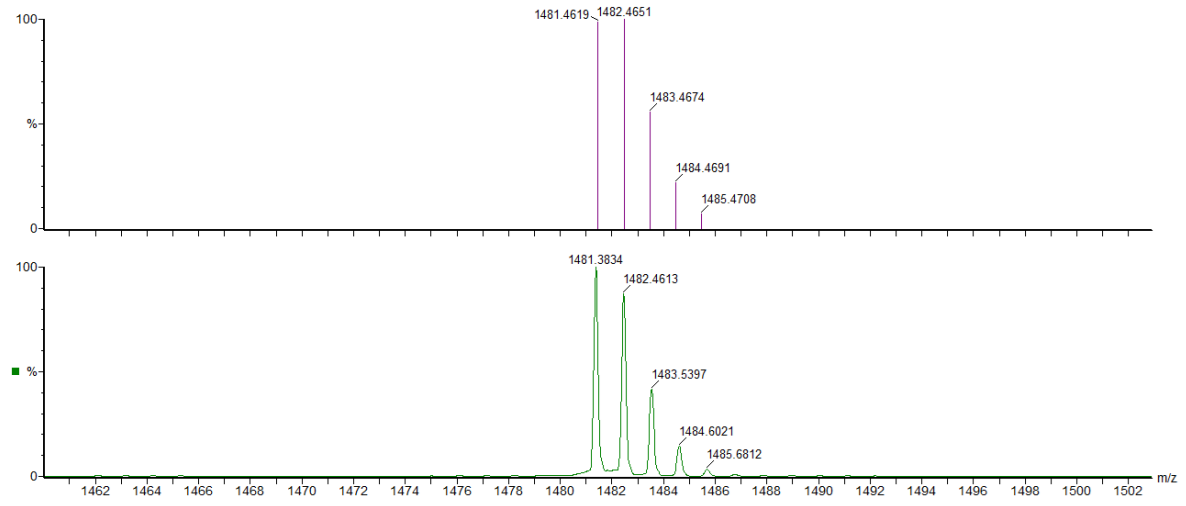


Figure S140. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2d**$(BF_4)_2$, $NaSCH_2Ph$ and H_2O in 1:30:900 (after stirring for 60 h) showed the presence of the complex, $[Co_2(PhBIMP)(SH)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1482.4651 (simulated, purple line); 1482.4613 (obtained, green line).

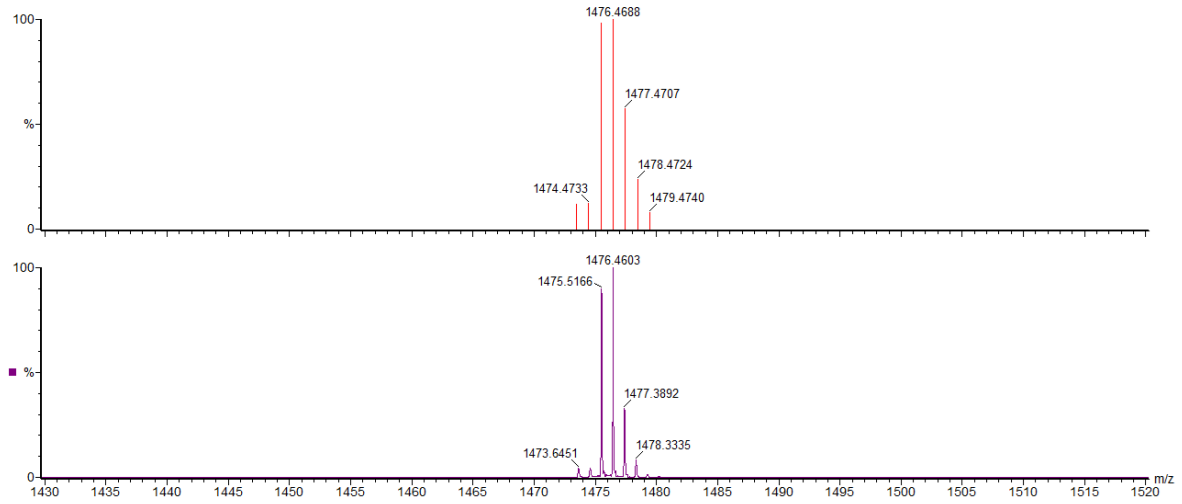


Figure S141. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4b**$(BF_4)_2$, $NaSCH_2Ph$ and H_2O in 1:30:900 (after stirring for 60 h) showed the presence of the complex, $[Fe_2(PhBIMP)(SH)(\mu\text{-}O_2C\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2)]^{1+}$ at m/z = 1476.4688 (simulated, red line); 1476.4603 (obtained, purple line).

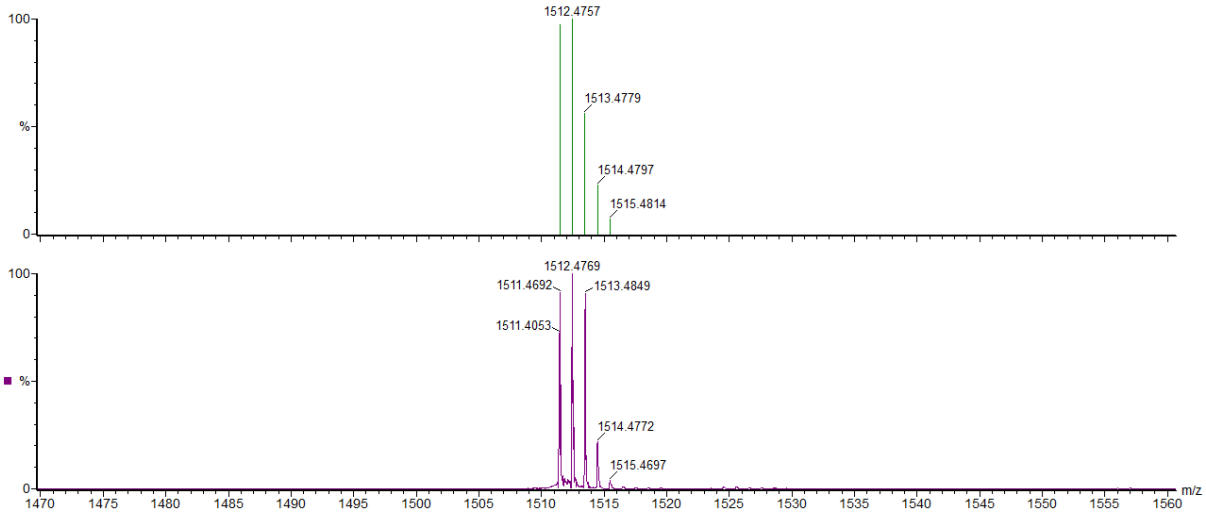


Figure S142. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2f**$(BF_4)_2$, $NaSCH_2Ph$ and H_2O in 1:40:1200 (after stirring for 60 h) showed the presence of the complex, $[Co_2(PhBIMP)(SH)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{1+}$ at m/z = 1512.4757 (simulated, green line); 1512.4769 (obtained, purple line).

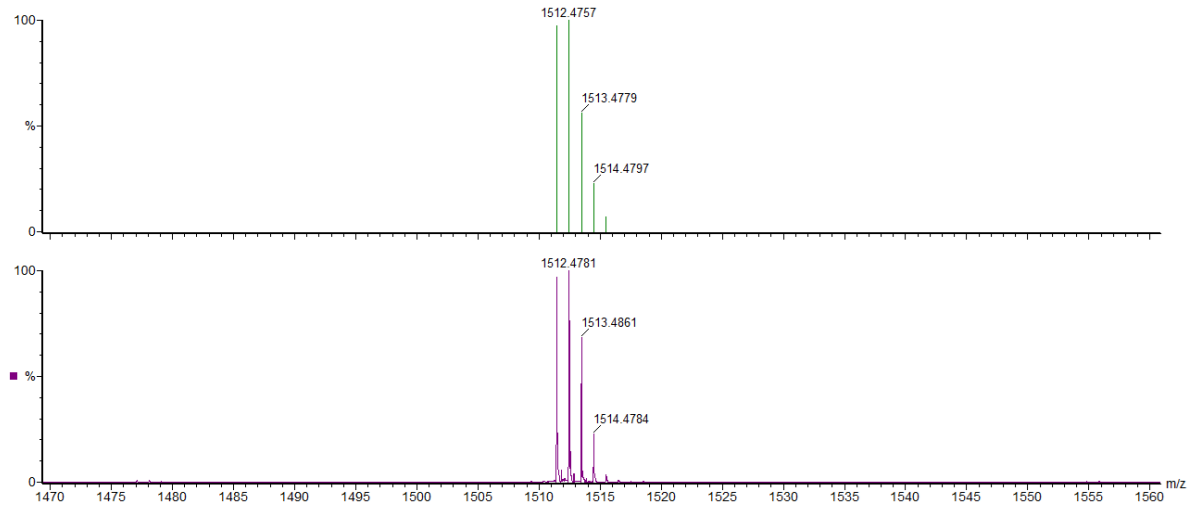


Figure S143. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **2f**$(BF_4)_2$, NaSPh and H_2O in 1:25:750 (after stirring for 168 h) showed the presence of the complex, $[Co_2(PhBIMP)(SH)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{1+}$ at m/z = 1512.4757 (simulated, green line); 1512.4781 (obtained, purple line).

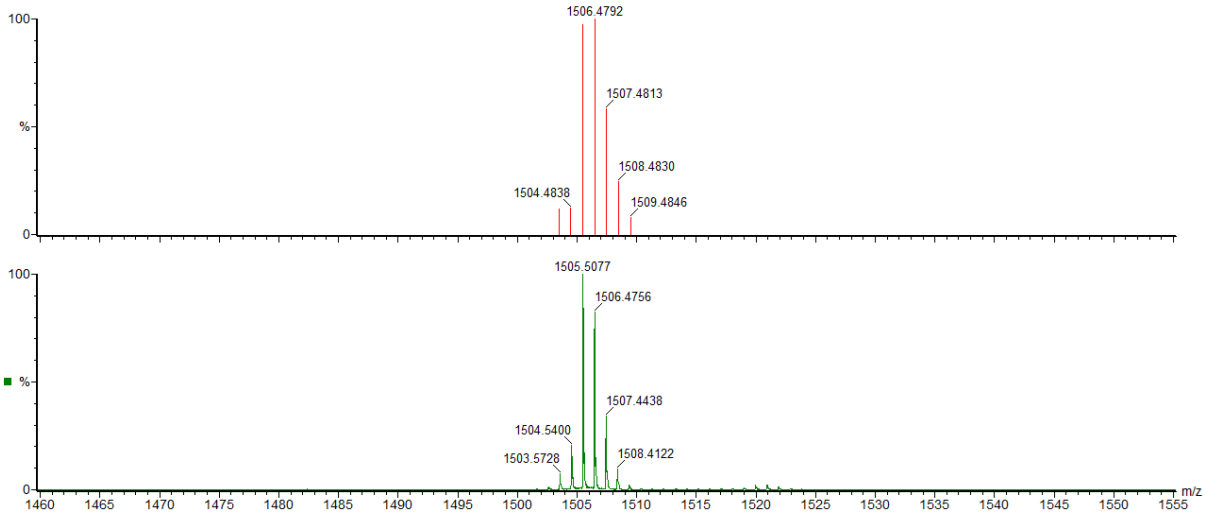


Figure S144. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4d**$(BF_4)_2$, $NaSCH_2Ph$ and H_2O in 1:40:1200 (after stirring for 60 h) showed the presence of the complex, $[Fe_2(PhBIMP)(SH)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{1+}$ at m/z = 1506.4792 (simulated, red line); 1506.4756 (obtained, green line).

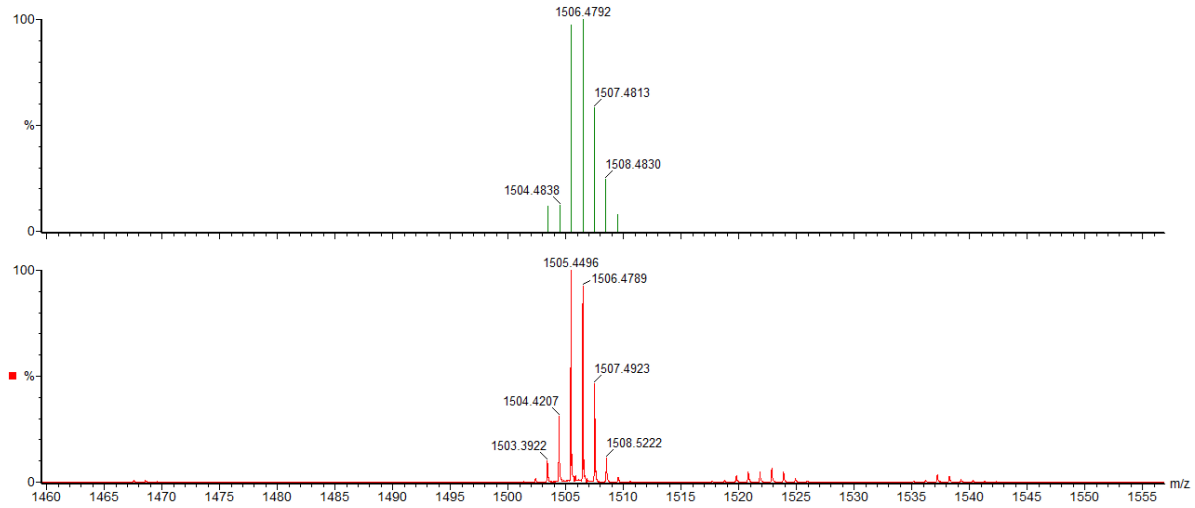


Figure S145. Mass spectrometric analysis (in DMF/MeCN) of a mixture of **4d**$(BF_4)_2$, NaSPh and H_2O in 1:25:750 (after stirring for 168 h) showed the presence of the complex, $[Fe_2(PhBIMP)(SH)(\mu\text{-}O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}(OMe)_3)]^{1+}$ at m/z = 1506.4792 (simulated, green line); 1506.4789 (obtained, red line).

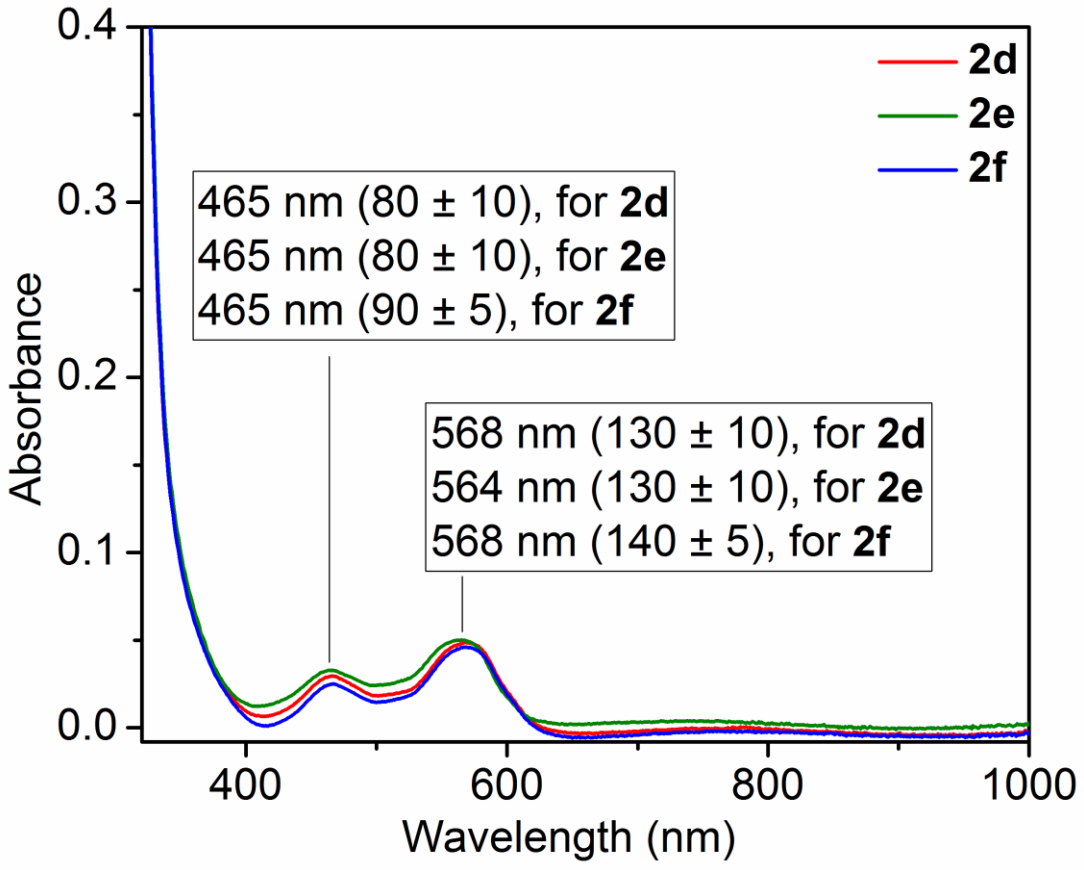


Figure S146. Electronic absorption spectra of **2d**$(BF_4)_2$, **2e**$(BF_4)_2$ and **2f**$(BF_4)_2$ (0.4 mM in DMF).

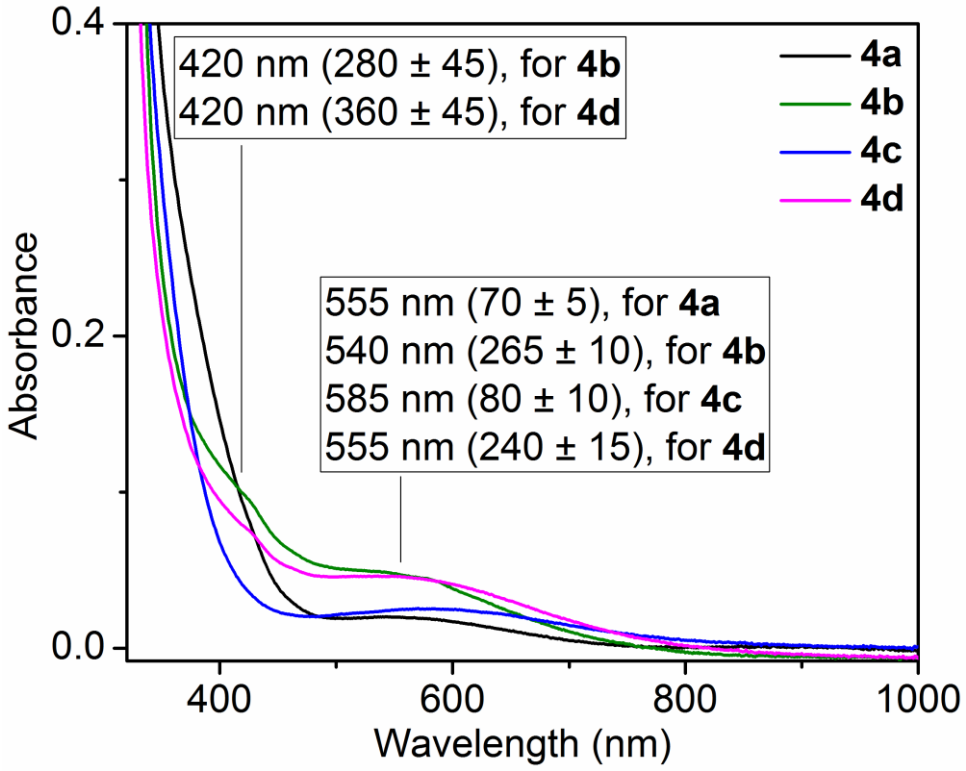


Figure S147. Electronic absorption spectra of **4a**$(BF_4)_2$, **4b**$(BF_4)_2$, **4c**$(BF_4)_2$ and **4d**$(BF_4)_2$ (0.4 mM in DMF).

References.

1. A. B. Chakraborty, T. Ganguly, A. Bera and A. Majumdar, *Eur. J. Inorg. Chem.*, 2024, **27**, e202400105.
2. T. Ganguly, A. Bera, A. B. Chakraborty and A. Majumdar, *Inorg. Chem.*, 2022, **61**, 7377-7386.