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COPPER MEDIATED FORMATION OF CARBON-HETEROATOM BONDS USING ORGANOBORON REAGENTS AND ULTRASOUND

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Abstract – This report summarizes research efforts focused on copper acetate mediated reactions to form new carbon-heteroatom bonds using organoboron reagents under ultrasound irradiation. The method involves the application of ultrasound irradiation to the Chan-Evans-Lam reaction to achieve *O*-arylation of phenols, *N*-arylation of anilines and indoles, and *S*-arylation of thiols. Ultrasound irradiation was found to decrease reaction times from 72 hours to 4 hours while improving the product yields an average of 20%.[1] Representative C-O, C-N, and C-S coupling reactions were successfully scaled-up from the milligram to gram levels while maintaining good product yields offering potential applications in industrial processes.

INTRODUCTION

Over the past century, there have been numerous methods developed to achieve aryl-aryl coupling reactions under a variety of conditions while employing a variety of catalysts. However, the corresponding reactions involving the *N*-arylation, *O*-arylation, and *S*-arylation have not been investigated as fully; especially reactions involving thermally sensitive compounds that are of importance to the pharmaceutical industry.[2] In 1998, the Chan-Lam reaction was developed for the C-N coupling reaction; it employs mild reaction conditions. The coupling reaction was then expanded to include the formation of C-S and C-O bonds and is now known as the Chan-Evans-Lam reaction.[3] Unlike earlier syntheses that employed expensive or toxic metal catalysts, the Chan-Evans-Lam reaction uses a copper(II) acetate salts, under anhydrous conditions, to perform coupling reactions. The relatively mild conditions have allowed its application in a variety of syntheses that could not have been accomplished using previously reported procedures.[2a,4] The primary downsides to the Chan-Evans-Lam reaction are time, typically 24-72 hours, and the requirement that anhydrous reaction conditions be employed.[1c]

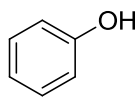
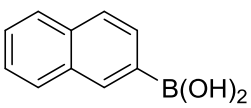
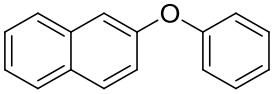
We recently reported the use of copper(II) acetate, in the presence of ultrasonic radiation, for the homocoupling of several aryltrifluoroborate compounds.[5] We then investigate the possibility of coupling various arylborates to phenols, anilines, indoles, and thiols. Herein, we report the results of our investigation which has led to successful coupling of phenols, anilines, indoles, and thiols with organoboron reagents while decreasing reaction times, increasing product yields, and eliminating the requirement the need for anhydrous reaction conditions.

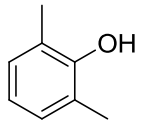
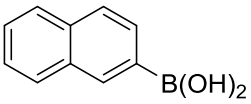
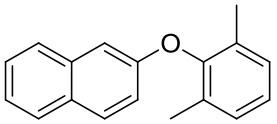
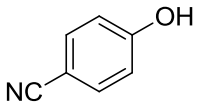
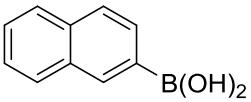
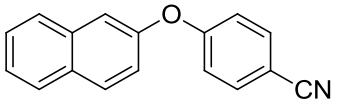
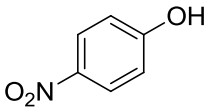
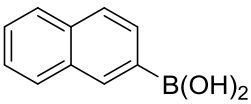
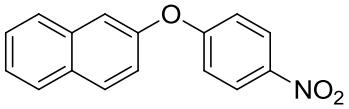
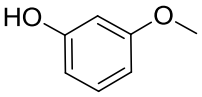
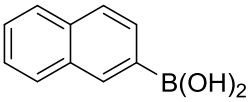
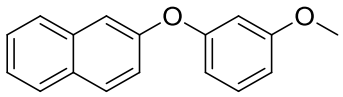
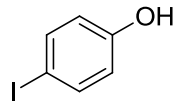
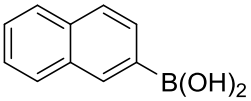
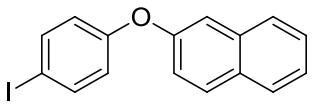
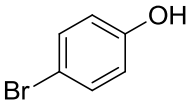
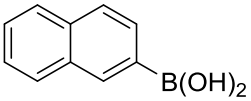
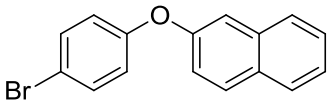
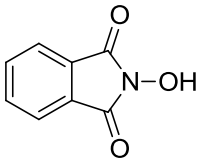
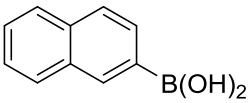
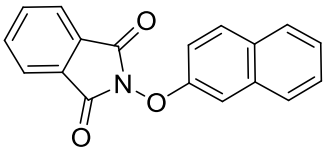
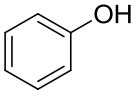
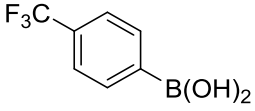
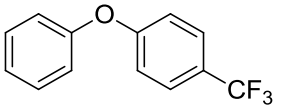
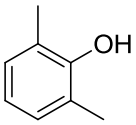
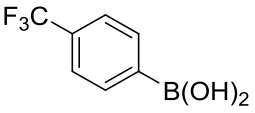
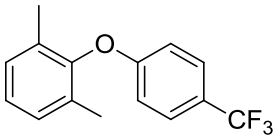
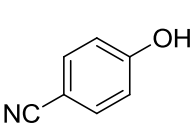
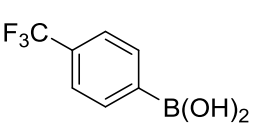
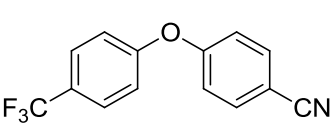
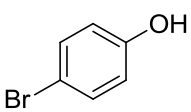
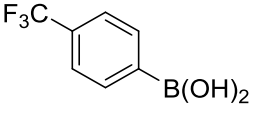
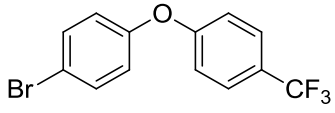
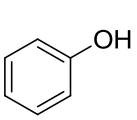
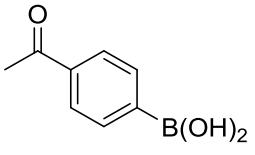
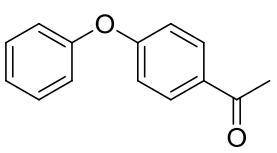
RESULTS AND DISCUSSION

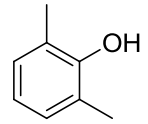
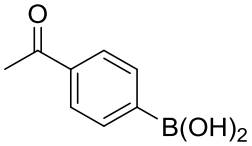
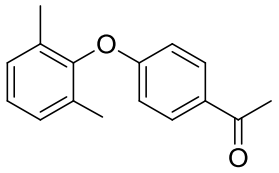
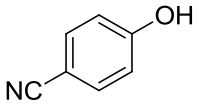
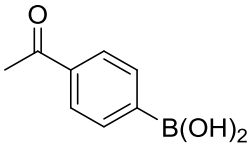
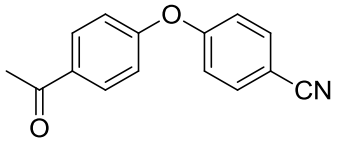
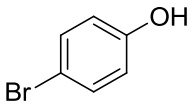
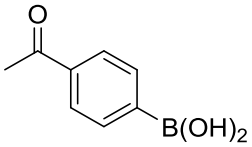
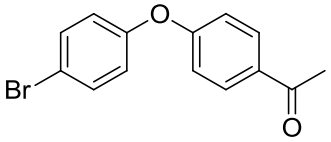
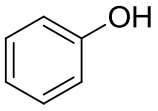
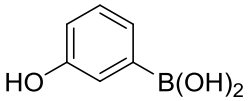
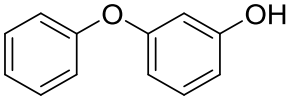
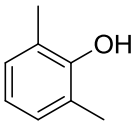
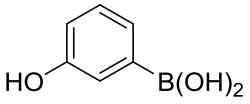
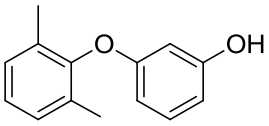
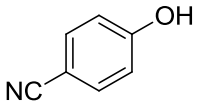
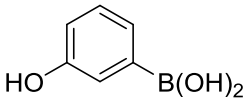
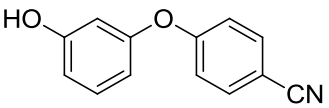
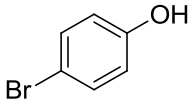
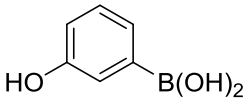
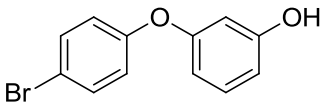
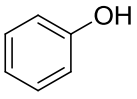
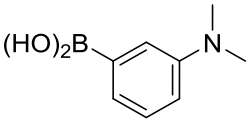
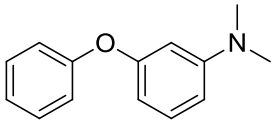
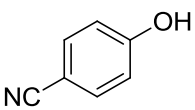
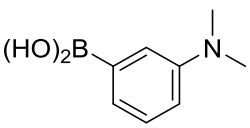
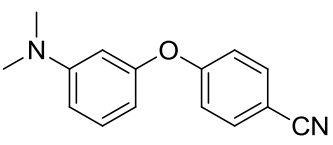
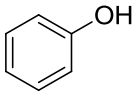
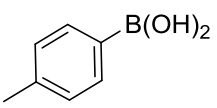
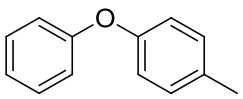
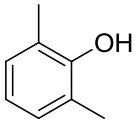
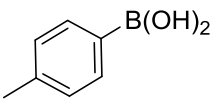
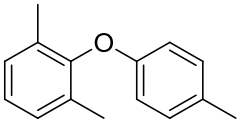
Survey experiments were conducted using naphthylboronic acid and phenol to determine the most effective reaction conditions. The first series of experiments employed one equivalent of phenol and 1.5 equivalents of naphthylboronic acid in DCM in the presence of 5.0 equivalents of triethylamine, and 4 equivalents of copper(II) acetate under ultrasound irradiation for six hours. Since the heat generated by the ultrasound is sufficiently high to evaporate DCM, the reaction vessel was placed in an ice/water bath maintained at 0-5 °C. A control experiment was carried out using identical conditions while stirring at room temperature for periods of 6 to 72 hours in the absence of ultrasound irradiation. The ultrasound experiment produced a product yield of 94%, the 6 hour control produced a yield of 23%, and the 72 hour control resulted in a yield of 72%. Subsequent experiments were conducted in which the ultrasound irradiation time was reduced to 4 hours, and the quantity of copper(II) acetate was decreased from 4 equivalents to 1 equivalent. The product yield was found to be essentially the same. It is possible that the cooling of the ice bath has a beneficial effect on the reaction: with a cooler solvent system the ultrasound probe is able to more easily shed built up internal heat, and thus improve the heat transfer from the probe to the surrounding media.[6]

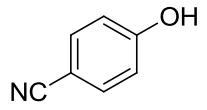
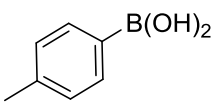
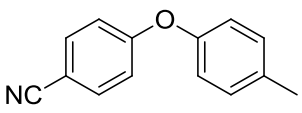
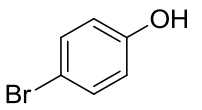
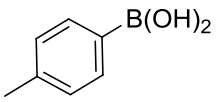
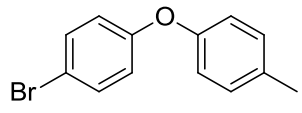
The new method was evaluated employing various arylboronic acids with a variety of substituted phenols, anilines, indoles, and thiols. Arylboronic acids and the heteroatom aryls were chosen to include electron donating groups, electron withdrawing groups, and sterically hindered groups. The results are summarized in the Tables 1 - 3.

Table 1. Reaction of Arylboronic Acids with Phenols

Starting Material	Starting Boronic Acid	Product	Yield
			92

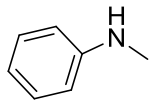
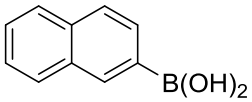
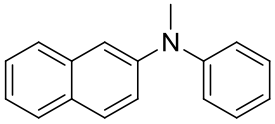
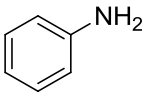
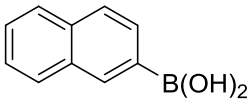
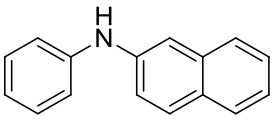
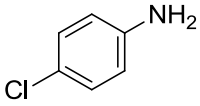
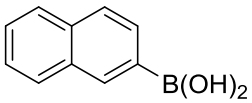
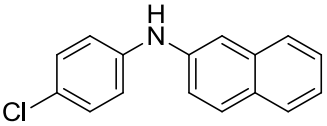
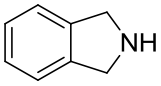
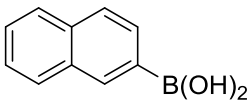
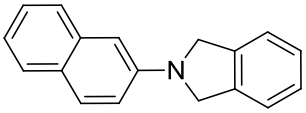
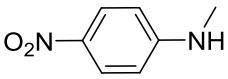
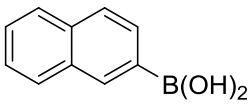
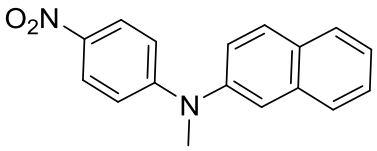
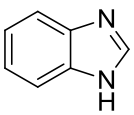
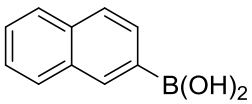
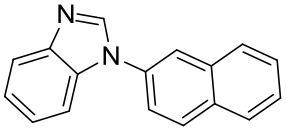
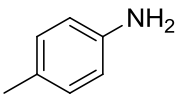
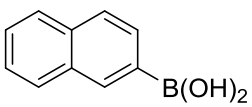
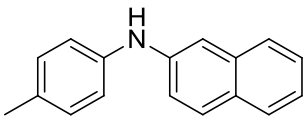
			81
			97
			91
			88
			93
			92
			53
			97
			88
			90
			97
			91

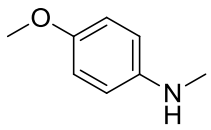
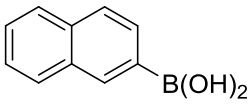
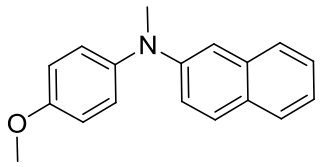
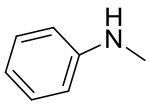
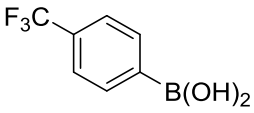
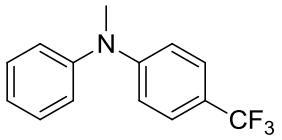
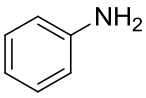
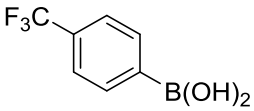
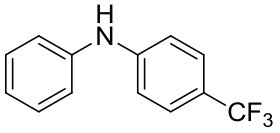
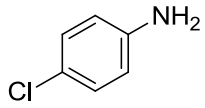
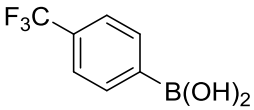
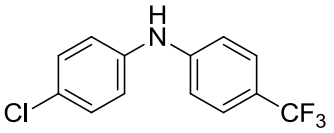
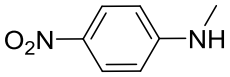
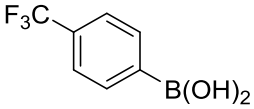
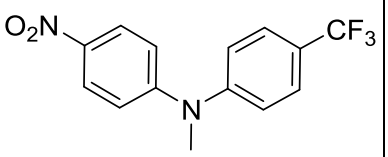
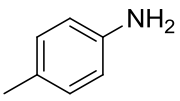
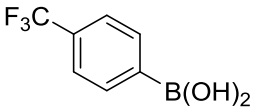
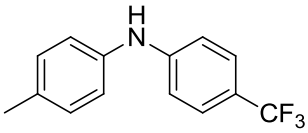
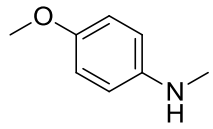
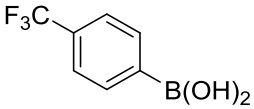
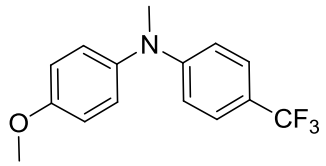
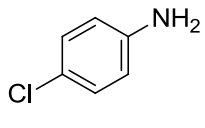
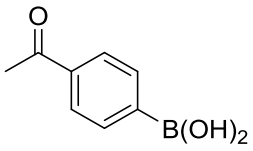
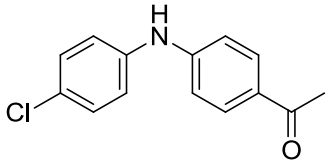
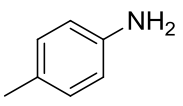
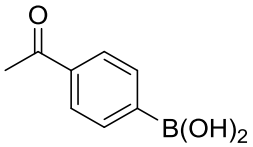
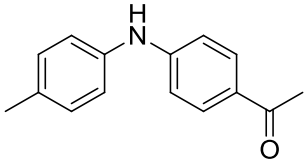
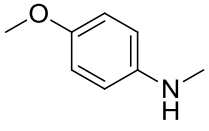
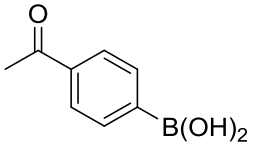
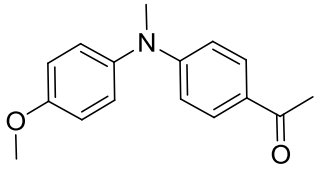
			81
			89
			88
			76
			72
			66
			76
			72
			68
			85
			88

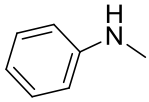
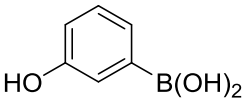
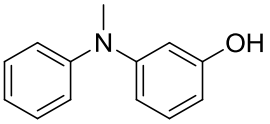
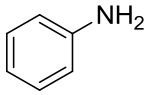
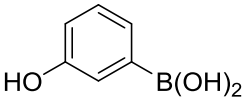
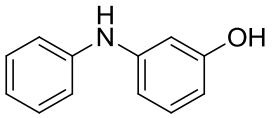
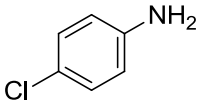
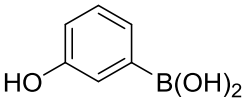
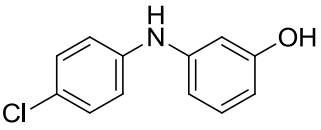
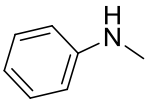
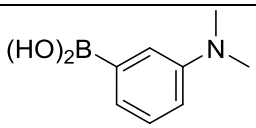
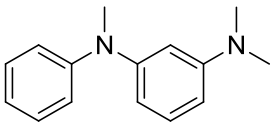
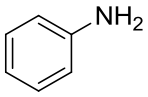
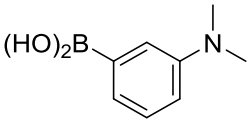
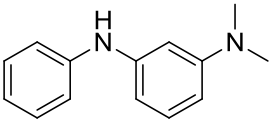
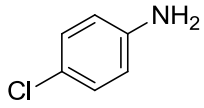
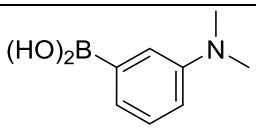
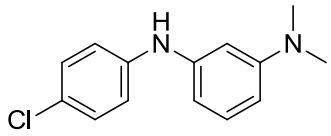
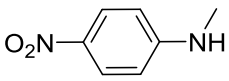
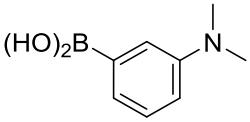
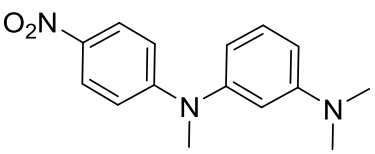
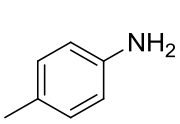
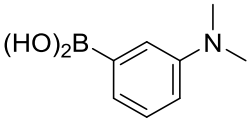
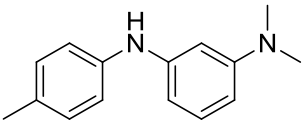
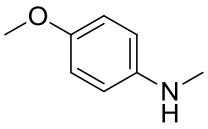
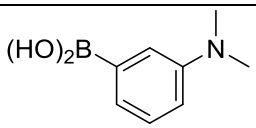
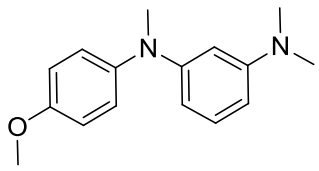
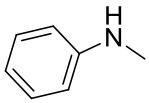
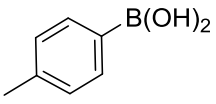
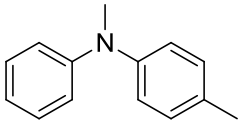
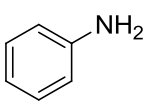
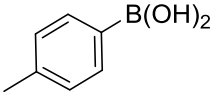
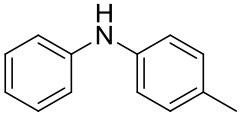
			92
			93

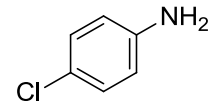
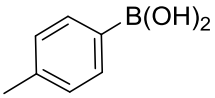
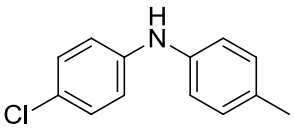
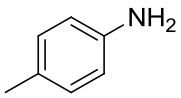
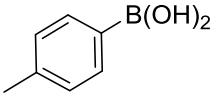
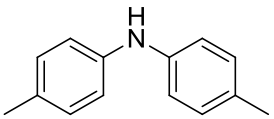
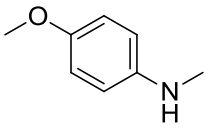
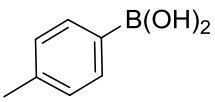
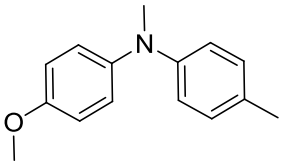
Reaction conditions: 1.5 mmol of arylboronic acid, 1.0 mmol phenol, 2.0 mmol copper(II) acetate, 5.0 mmol of triethylamine was mixed in DCM. The mixture was sonicated for 4 hours.

Table 2. Reactions of Arylboronic Acid with Anilines and Indoles

Starting Material	Starting Boronic Acid	Product	Yield
			90
			87
			94
			89
			96
			97
			95

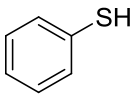
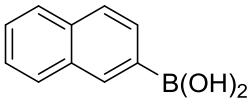
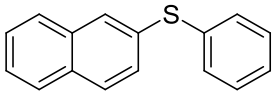
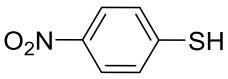
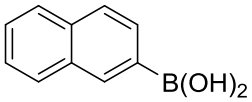
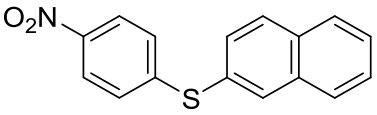
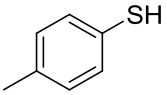
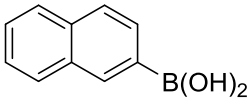
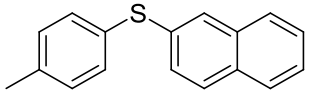
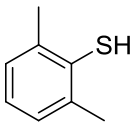
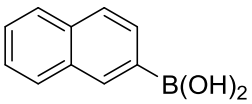
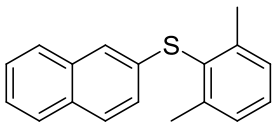
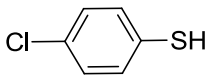
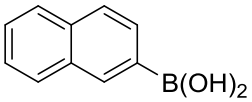
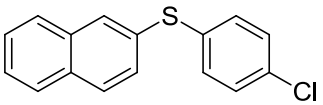
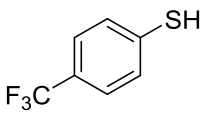
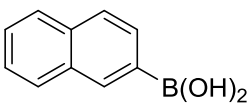
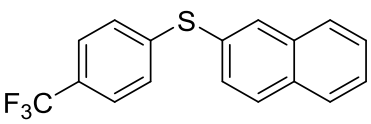
			87
			91
			86
			96
			93
			92
			97
			92
			90
			93

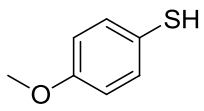
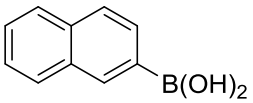
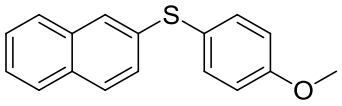
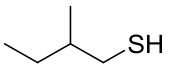
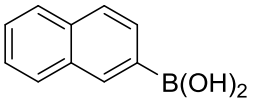
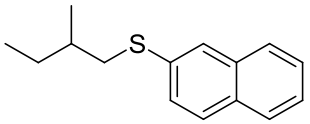
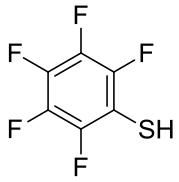
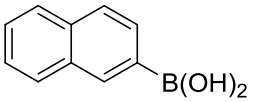
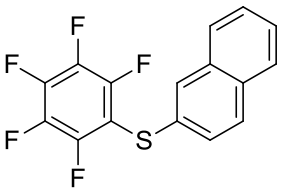
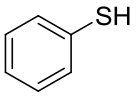
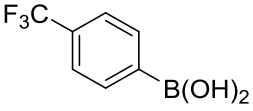
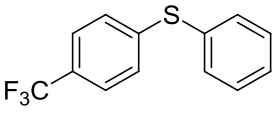
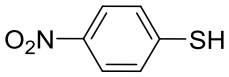
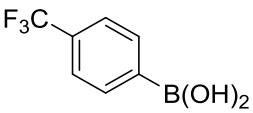
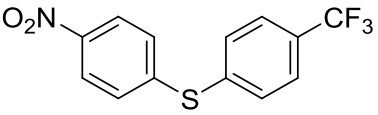
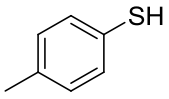
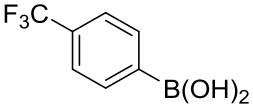
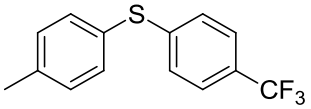
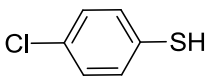
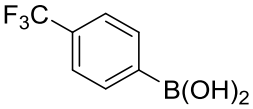
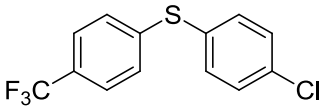
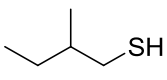
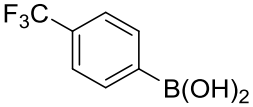
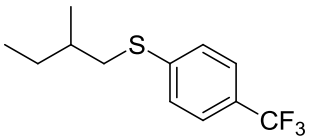
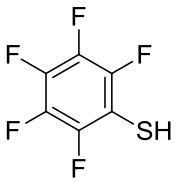
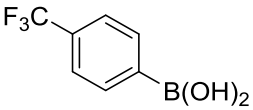
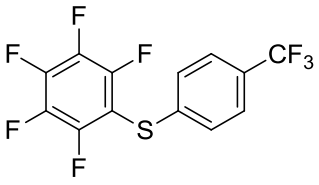
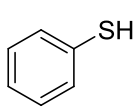
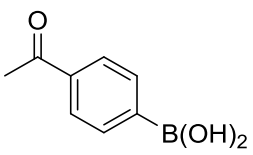
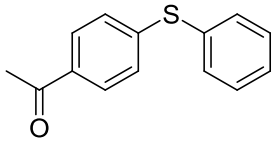
			78
			62
			66
			68
			72
			61
			66
			82
			81
			93
			67

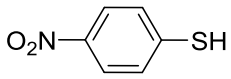
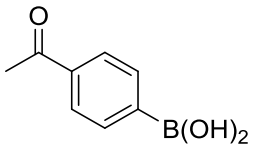
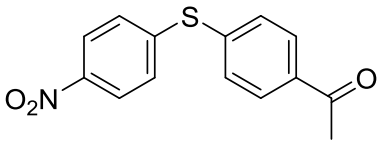
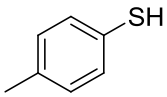
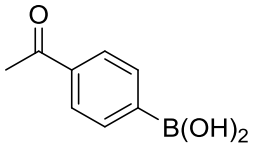
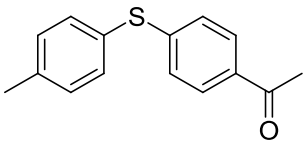
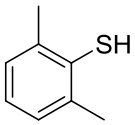
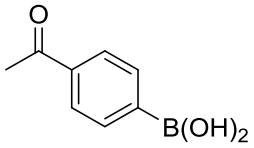
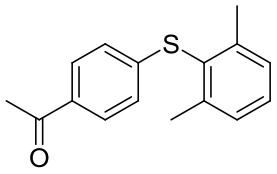
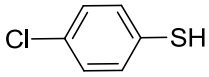
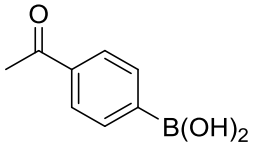
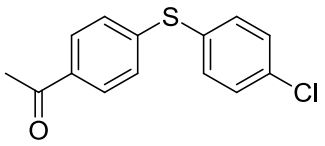
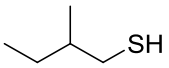
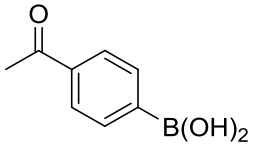
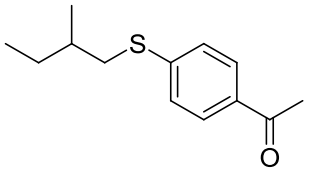
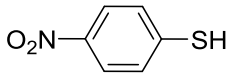
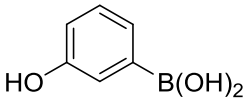
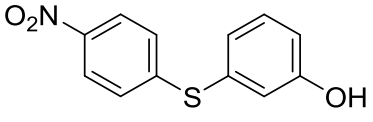
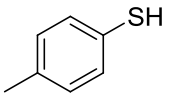
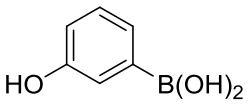
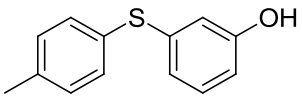
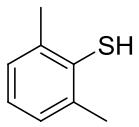
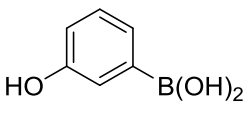
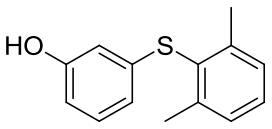
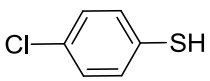
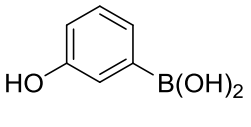
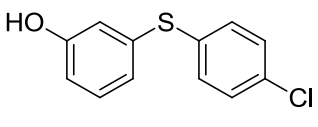
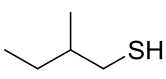
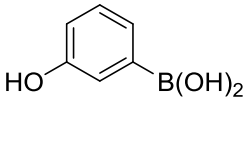
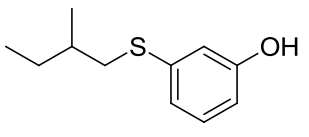
			74
			90
			96

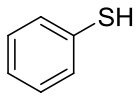
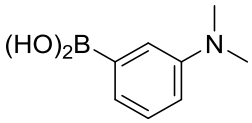
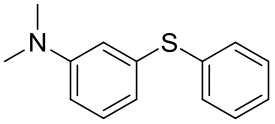
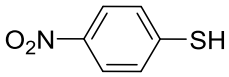
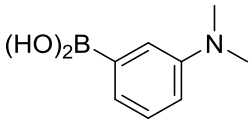
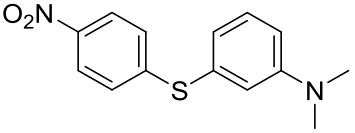
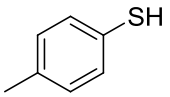
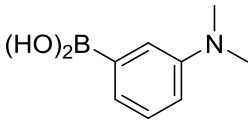
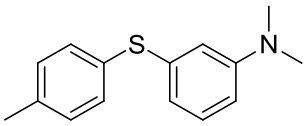
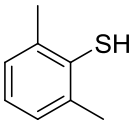
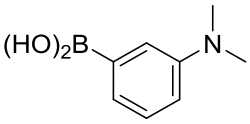
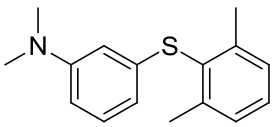
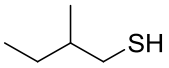
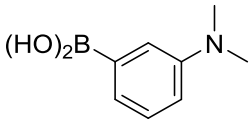
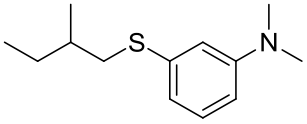
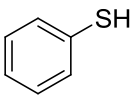
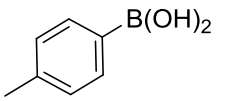
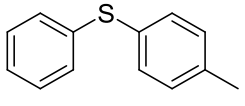
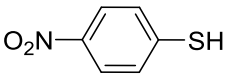
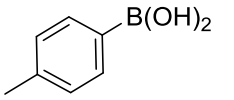
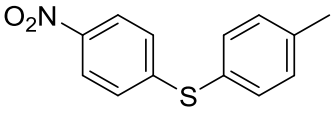
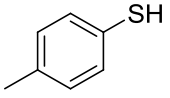
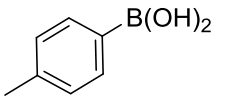
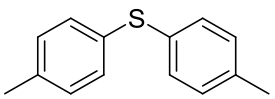
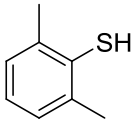
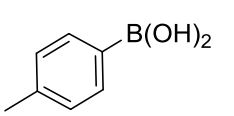
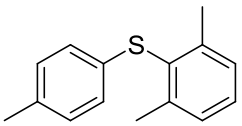
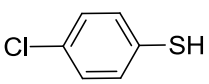
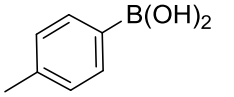
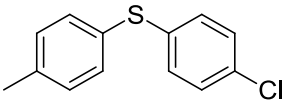
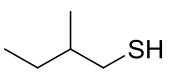
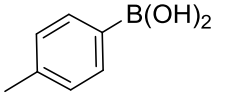
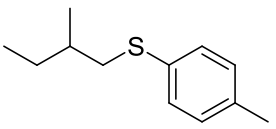
Reaction conditions: 1.5 mmol of arylboronic acid, 1.0 mmol phenol, 2.0 mmol copper(II) acetate, 5.0 mmol of triethylamine was mixed in DCM. The mixture was sonicated for 4 hours.

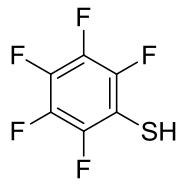
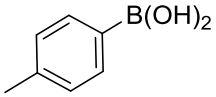
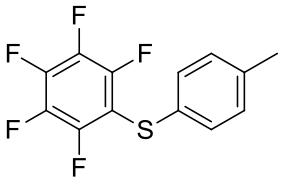
Table 3. Reactions of Naphthaboronic Acid with Thiols

Starting Material	Starting Boronic Acid	Product	Yield
			92
			88
			94
			93
			91
			92

			95
			98
			95
			95
			91
			98
			92
			94
			98
			90

			88
			89
			87
			93
			88
			73
			71
			73
			81
			96

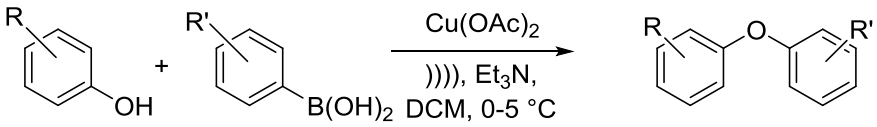
			80
			76
			82
			77
			98
			92
			88
			95
			85
			94
			98

			98

Reaction conditions: 1.5 mmol of arylboronic acid, 1.0 mmol phenol, 2.0 mmol copper(II) acetate, 5.0 mmol of triethylamine were mixed in DCM. The mixture was sonicated for 4 hours.

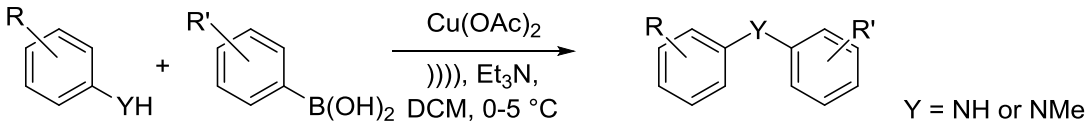
The syntheses of 2-phenoxynaphthalene, *N*-phenylnaphthalen-2-amine, and naphthalen-2-yl(phenyl)sulfane were repeated using a tenfold increase in the amount of all reagents and solvent. Sonication energy was increased to 20% amplitude (110 watts), sonication time increased to 8 hours (1 minute sonication pulse with a 3 second break), and the reaction vessel was changed to a 100 mL beaker. The external temperature was maintained at 0-5 °C. The yield was 80% using 2-phenoxynaphthalene, 78% using *N*-phenylnaphthalen-2-amine, and 87% using naphthalen-2-yl(phenyl)sulfane, indicating that the reactions are scalable to industrial standards. In an attempt to evaluate the electronic effects of the substituent groups on the reaction, the yields were plotted against the reported sigma values, Table 4 through Table 6:

Table 4. Correlation of Reactant Sigma Values with Product Yields



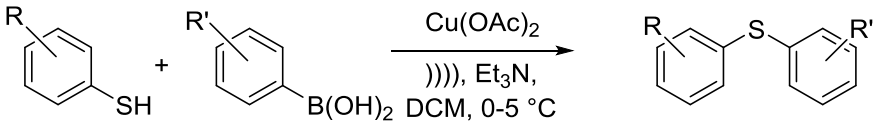
R ↓ R' →	*m* -OH	*m*-NMe_2	*p*-Me	para -C(O)Me	*p* -CF^3
p-OMe	0	0	0	0	0
H	76	72	85	91	97
p-Br	76	0	93	88	97
p-CN	66	68	92	89	90
2,6–Me	72	0	88	81	88

Table 5. Correlation of Reactant Sigma Values with Product Yields



Y	R ↓ R' →	*m* -OH	*m* -NMe_2	*p* -Me	*p* -C(O)Me	*p* -CF_3
NH	*p*-Me	0	82	90	90	92
NMe	*p*-OMe	0	81	96	93	97
NMe	H	78	68	93	0	91
NH	H	62	72	67	0	86
NH	*p*-Cl	66	61	74	92	96
NMe	*p*-NO_2	0	66	0	0	93

Table 6. Correlation of Reactant Sigma Values with Product Yields



R ↓ R' →	*m*-OH	*m*-NMe_2	*p*-Me	*p*-C(O)Me	*p*-CF_3
p-Me	71	82	95	89	98
p-OMe	0	0	0	0	0
H	0	80	92	90	95
p-Cl	81	0	94	93	92
p-NO_2	73	76	88	88	91
2,6-Me	73	77	85	87	0
2,3,4,5,6 -F		0	98		94
2-methylbutyl	96	98	98	88	98

The data indicate that the highest product yields are obtained when the boronic acid contains an electron withdrawing group, while the phenol has a sigma value close to zero.

CONCLUSION

The use of ultrasound enhances the Chan-Lam-Evans modified Ullmann reaction. The reaction times are dramatically decreased from 72 hours to 4 hours with improvement in product yields. The method was successfully scaled-up from millimole to gram scale while maintaining good product yields. The new coupling methodology can be characterized as atom efficient, scalable, environmentally friendly, inexpensive, and capable of rapidly producing high yields of products.

EXPERIMENTAL

Representative Procedure for the Synthesis of 2-phenoxynaphthalene

Naphthylboronic acid (0.25 g, 1.5 mmol) was added with 0.094 g of phenol (1.0 mmol) to 15 mL of DCM. Copper(II) acetate (0.36 g, 2.0 mmol) was then added along with triethylamine (0.5g, 5.0 mmol), and the dismembrator horn placed in the reaction vessel. The sonicator was set to 55 watts and the reaction was allowed to proceed for 4 hours (1 minute pulse with a 3 second rest). Post reaction, the product was isolated by column chromatography. Product yields were determined by weight and purity was confirmed by GC/MS and NMR.

Characterization of Compounds

^{1}H NMR and ^{13}C NMR spectra were recorded either at 250 and 63 MHz or 300 and 75 MHz respectively. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectra were referenced to TMS and the *d*-chloroform solvent shift. High quality mass spectrometry was carried out using a Qstar electron spray ionization mass spectrometer, in either positive (M+1) or negative mode (M-1), ionization energy of ±5000 e/v, injection rate of 20 μL/min.

2-Phenoxynaphthalene[7]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 - 7.80 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.44 - 7.31 (m, 6H), 7.16 - 7.01 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 154.4, 134.3, 130.6, 129.5, 127.8, 126.7, 126.4, 125.2, 123.0, 119.2, 116.9, 108.1. Anal. Calcd for $C_{16}H_{12}O$: 220.0888. Found: 221.1001 (M+1). GC RT 6.78 minutes.

2-(2,6-Dimethylphenoxy)naphthalene[8]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 3H), 7.53 – 7.49 (m, 3H), 7.23 – 7.13 (m, 2H), 7.03 (d, *J* = 7.3 Hz, 2H), 2.32 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 151.2, 133.3, 129.0, 128.5, 126.7, 126.3, 125.7, 125.1, 123.8, 123.2, 114.4, 108.0, 16.8. Anal. Calcd for $C_{18}H_{16}O$: 248.1201 Found: 249.1113 (M+1). GC RT 7.48 minutes.

4-(Naphthalen-2-yloxy)benzonitrile[9]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.83 (m, 5H), 7.66 – 7.49 (m, 3H), 7.39 (s, 1H), 7.08 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR (63 MHz, D_2O) δ 161.9, 153.9, 133.8, 132.9, 130.1, 129.2, 127.4, 125.4, 122.9, 119.5, 117.6, 116.5, 109.2, 104.6. Anal. Calcd for $C_{17}H_{11}NO$: 245.0841. Found: 244.0900 (M-1). GC RT 18.05

minutes.

2-(4-Nitrophenoxy)naphthalene[10]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 – 8.20 (m, 2H), 7.93 – 7.85 (m, 3H), 7.55 – 7.51 (m, 4H), 7.29 – 7.21 (m, 2H). ^{13}C NMR (63 MHz, D_2O) δ 162.5, 152.8, 141.9, 135.8, 130.2, 129.7, 127.8, 126.0, 125.8, 124.4, 123.7, 117.4, 116.2, 108.4. Anal. Calcd for $C_{16}H_{11}NO_3$: 265.0739. Found: 264.0811 (M-1). GC RT 20.18 minutes.

2-(3-Methoxyphenoxy)naphthalene[10]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 3H), 7.54 – 7.45 (m, 3H), 7.37 (t, *J* = 6.7 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.86 – 6.75 (m, 3H), 3.81 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 161.2, 158.6, 155.0, 134.5, 130.4, 130.2, 129.9, 127.8, 127.2, 126.6, 124.8, 120.1, 114.5, 111.3, 109.3, 105.2, 55.4. Anal. Calcd for $C_{17}H_{14}O_2$: 250.0994 Found: 249.1002 (M-1). GC RT 15.11 minutes.

2-(4-Iodophenoxy)naphthalene[11]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 3H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.55 – 7.44 (m, 3H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (63 MHz, D_2O) δ 156.7, 154.5, 138.1, 133.2, 129.9, 127.7, 127.0, 126.5, 125.7, 118.2, 114.4, 108.8, 81.2. Anal. Calcd for $C_{16}H_{11}IO$: 345.9855. Found: 345.0005 (M-1). GC RT 19.38 minutes.

2-(4-Bromophenoxy)naphthalene[11]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 3H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.9 Hz, 1H), 7.47 – 7.35 (m, 4H), 7.05 (d *J* = 7.8 Hz, 1H). ^{13}CNMR (63 MHz, D_2O): δ 156.4, 154.5, 133.4, 132.7, 130.3, 130.1, 128.0, 127.1, 126.6, 124.9, 119.8, 117.5, 144.4, 109.5. Anal. Calcd for $C_{16}H_{11}BrO$: 297.9993. Found: 297.0011 (M-1). GC RT 17.36 minutes.

2-(Naphthalen-2-yloxy)isoindoline-1,3-dione[12]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 6H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (63 MHz, D_2O) δ 161.3, 150.7, 137.7, 133.4, 129.1, 128.5, 127.8, 127.1, 126.3, 125.6, 122.5, 121.6, 110.6, 104.9. Anal. Calcd for $C_{18}H_{11}NO_3$: 289.0739. Found: 288.0814 (M-1). GC RT 18.73 minutes.

1-Phenoxy-4-(trifluoromethyl)benzene[13]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* =7.5 Hz, 1H), 7.10 – 7.05 (m, 4H). ^{13}C NMR (63 MHz, D_2O) δ 161.2, 158.8, 128.6, 126.8, 124.1, 119.7, 118.8, 116.5. Anal. Calcd for $C_{13}H_9F_3O$: 238.0605 Found: 237.0717 (M-1). GC RT 7.48 minutes.

1,3-Dimethyl-2-(4-(trifluoromethyl)phenoxy)benzene[4]: ^{1}H NMR (250 MHz, D_2O oxide) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 6.4 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 2H), 2.32 (s, 6H). ^{13}C NMR (63 MHz, D_2O) δ 165.0, 152.0, 128.5, 127.1, 126.1, 125.5, 123.0, 120.1, 15.6. Anal. Calcd for $C_{15}H_{13}F_3O$: 266.0918. Found: 265.1101 (M-1). GC RT 7.88 minutes.

4-(4-(Trifluoromethyl)phenoxy)benzonitrile[13]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.19 (m, 4H).^{13}C NMR (63 MHz, D_2O) δ 161.2, 158.8, 128.6, 126.8, 124.1, 119.7, 118.8, 116.5. Anal. Calcd for $C_{14}H_8F_3NO$: 263.0558. Found: 262.0722 (M-1). GC RT 12.87 minutes.

1-Bromo-4-(4-(trifluoromethyl)phenoxy)benzene[14]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.41 (m, 4H), 6.99 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 157.6, 132.3, 127.1, 125.8, 123.4, 119.9, 117.8. Anal. Calcd for $C_{13}H_8BrF_3O$: 315.9711. Found: 315.0002 (M-1). GC RT 10.00 minutes.

1-(4-Phenoxyphenyl)ethanone[13]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.41 (m, 2H), 7.18 – 7.21 (m, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 198.2, 160.7, 159.1, 128.3, 128.0, 122.7, 119.0, 116.1, 26.3. Anal. Calcd for $C_{14}H_{12}O_2$: 212.0837. Found: 211.0901 (M-1). GC RT 9.90 minutes.

1-(4-(2,6-Dimethylphenoxy)phenyl)ethanone[15]: ^{1}H NMR (250 MHz, D_2O) δ 8.10 (d, *J* = 7.0 Hz, 2H), 7.26 – 7.21 (m, 3H), 7.06 (d, *J* = 7.8 Hz, 2H), 2.26 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (63 MHz, D_2O) δ 192.5, 164.0, 152.2, 133.0, 130.7, 128.3, 126.8, 125.8, 123.2, 119.8, 26.3, 15.8. Anal. Calcd for $C_{16}H_{16}O_2$: 240.1150. Found: 239.1200 (M-1). GC RT 8.91 minutes.

4-(4-Acetylphenoxy)benzonitrile[16]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.23 (m, 4H), 2.54 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 198.6, 160.7, 133.8, 130.6, 128.0, 119.0, 116.4, 102.1, 26.3. Anal. Calcd for $C_{15}H_{11}NO_2$: 237.0790. Found: 236.0881 (M-1). GC RT 9.12 minutes.

1-(4-(4-Bromophenoxy)phenyl)ethanone[15]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 6.96 – 6.90 (m, 4H), 2.63 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 198.5, 161.7, 155.1, 132.2, 130.8, 128.4, 117.2, 116.5, 115.2, 26.5. Anal. Calcd for $C_{14}H_{11}BrO_2$: 289.9942. Found: 289.0007 (M-1). GC RT 13.61 minutes.

3-Phenoxyphenol[16]: ^{1}HNMR (300 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.40 – 7.31 (m, 2H), 7.25 – 7.14 (m, 4H), 6.94 (d, *J* = 7.4, 1H), 6.50 – 6.46 (m, 2H). ^{13}CNMR (63 MHz, D_2O) δ 158.6, 155.4, 130.4, 129.6, 123.5, 120.7, 110.8, 107.4, 106.0. Anal. Calcd for $C_{12}H_{10}O_2$: 186.0681. Found: 187.0555 (M+1). GC RT 7.75 minutes.

3-(2,6-Dimethylphenoxy)phenol[17]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.29 – 7.11 (m, 2H), 7.06 (d, *J* = 5.5 Hz, 2H), 6.93 (d, *J* = 7.4 Hz, 1H), 6.82 – 6.74 (m, 2H), 2.14 (s, 6H). ^{13}C NMR (63 MHz, D_2O) δ 156.1, 154.5, 151.1, 132.3, 131.2, 129.3, 128.3, 115.1, 114.2, 108.8, 16.5. Anal. Calcd for $C_{14}H_{14}O_2$: 214.0994. Found: 215.0887 (M+1). GC RT 6.97 minutes.

4-(3-Hydroxyphenoxy)benzonitrile[18]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.17 (m, 3H), 7.04 – 6.92 (m, 3H). ^{13}C NMR (63 MHz, D_2O) δ 164.4, 159.7, 155.5, 134.0, 129.3, 119.4, 117.5, 110.5, 108.8, 104.0, 103.3. Anal. Calcd for $C_{13}H_9NO_2$: 211.0633. Found: 212.0506 (M+1). GC RT 7.77 minutes.

3-(4-Bromophenoxy)phenol[19]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.05 – 6.98 (m, 1H), 6.49 (m, 208H). ^{13}C NMR (63 MHz,

D_2O) δ 156.3, 155.6, 155.1, 132.3, 129.6, 120.5, 117.2, 115.3, 112.3, 104.9. Anal. Calcd for $C_{12}H_9BrO_2$: 263.9786. Found: 262.9523 (M-1). GC RT 8.59 minutes.

***N,N*-Dimethyl-3-phenoxyaniline[20]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.16 – 7.12 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 3H), 6.78 – 6.74 (m, 2H), 6.74 (d, *J* = 7.4 Hz, 1H), 2.90 (s, 6H). ^{13}C NMR (63 MHz, D_2O) δ 157.9, 156.6, 148.6, 129.9, 129.6, 122.8, 119.7, 107.9, 107.1, 103.7, 40.8. Anal. Calcd for $C_{14}H_{15}NO$: 213.1154. Found: 214.1010 (M+1). GC RT 8.41 minutes.

4-(3-(Dimethylamino)phenoxy)benzonitrile[18]: ^{1}H NMR (250 MHz, D_2O) δ 7.83 – 7.80 (m, 2H), 7.32 – 7.21 (m, 2H), 6.81 – 6.75 (m, 1H), 6.74 – 6.71 (m, 2H), 6.40 (d, *J* = 7.1 Hz, 1H), 3.11 (s, 6H). ^{13}C NMR (63 MHz, D_2O) δ 160.5, 158.2, 151.7, 133.7, 128.6, 117.2, 116.0, 108.8, 107.4, 106.3, 102.1, 40.4. Anal. Calcd for $C_{15}H_{14}N_2O$: 238.1106. Found: 237.1212 (M-1). GC RT 7.01 minutes.

1-Methyl-4-phenoxybenzene[7]: ^{1}H NMR (250 MHz, D_2O) δ 7.35 - 7.30 (m, 2H), 7.15 – 7.11 (m, 2H), 7.08 – 7.04 (m, 1H), 6.97 – 6.92 (m, 2H), 6.90 – 6.88 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 158.5, 155.7, 133.3, 129.6, 120.5, 118.2, 115.3, 21.2. Anal. Calcd for $C_{13}H_{12}O$: 184.0888. Found: 185.0759 (M+1). GC RT 8.41 minutes.

1,3-Dimethyl-2-(*p*-tolyloxy)benzene[21]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.00 (m, 3H), 6.81 (d, *J* = 7.2 Hz, 2H), 6.55 (d, *J* = 7.9 Hz, 2H), 2.32 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (63 MHz, D_2O) δ 154.5, 151.6, 132.5, 129.9, 128.8, 128.1, 124.8, 114.2, 22.9, 16.7. Anal. Calcd for $C_{15}H_{16}O$: 212.1201. Found: 213.1108 (M+1). GC RT 9.42 minutes.

4-(*p*-Tolyloxy)benzonitrile[13]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.11 (m, 2H), 6.81 (d, *J* = 6.4 Hz, 4H), 2.33 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 166.9, 155.4, 133.9, 133.9, 130.5, 120.2, 118.8, 117.4, 104.8, 21.4. Anal. Calcd for $C_{14}H_{11}NO$: 209.0841. Found: 208.0735 (M-1). GC RT 14.67 minutes.

1-Bromo-4-(*p*-tolyloxy)benzene[22]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 157.0, 154.4, 133.5, 132.5, 130.4,119.8, 119.2, 117.2, 115.1, 20.7. Anal. Calcd for $C_{13}H_{11}BrO$: 261.9993. Found: 261.0056 (M-1). GC RT 16.36 minutes.

***N*-Methyl-*N*-phenylnaphthalen-2-amine[23]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.66 – 7.50 (m, 4H), 7.45 (t, *J* = 6.3 Hz, 2H), 7.29 – 7.21 (m, 2H), 6.96 (d, *J* = 7.7 Hz, 2H), 3.38 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 149.9, 143.6, 136.8, 129.0, 128.3, 127.4, 127.3, 127.0, 125.7, 118.2, 116.0, 106.0, 45.2. Anal. Calcd for $C_{17}H_{15}N$: 233.1204. Found: 234.0997 (M+1). GC RT 15.76 minutes.

***N*-Phenylnaphthalen-2-amine[23]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.55 (m, 5H), 7.44 – 7.35 (m, 4H), 4.41 (s, 1H). ^{13}C NMR (63 MHz, D_2O) δ 142.7, 133.1, 129.1, 128.8, 127.6, 126.2, 125.6, 123.1, 120.9, 111.0. Anal. Calcd for $C_{16}H_{13}N$: 219.1048. Found: 220.0879 (M+1). GC RT 16.50 minutes.

***N*-(4-Chlorophenyl)naphthalen-2-amine[24]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.63 (m, 4H), 7.50 – 7.41 (m, 4H), 7.34 – 7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 3.69 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 141.4, 133.2, 128.8, 127.6, 126.3, 125.6, 123.4, 122.5, 118.9, 115.9, 111.6. Anal. Calcd for $C_{16}H_{12}ClN$: 253.0658. Found: 252.0944 (M-1). GC RT 20.17 minutes.

2-(Naphthalen-2-yl)isoindoline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.63 (m, 4H), 7.41 – 7.34 (m, 6H), 7.02 (s, 1H), 4.57 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 137.7, 135.2, 129.1, 127.8, 125.5, 121.6, 115.1, 105.0, 53.8. Anal. Calcd for $C_{18}H_{15}N$: 245.1204. Found: 256.1310 (M+1). GC RT 22.56 minutes.

***N*-Methyl-*N*-(4-nitrophenyl)naphthalen-2-amine:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 9.2 Hz, 2H), 7.84 – 7.77 (m, 2H), 7.47 – 7.35 (m, 6H), 6.49 – 6.47 (m, 1H), 2.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 143.5, 137.9, 133.5, 129.0, 127.9, 126.4, 125.9, 122.8, 120.3, 118.1, 110.7, 42.3. Anal. Calcd for $C_{17}H_{14}N_2O_2$: 278.1055. Found: 277.1112 (M-1). GC RT 11.60 minutes.

1-(Naphthalen-2-yl)-1*H*-benzo[*d*]imidazole[25]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 – 8.54 (m, 1H), 8.00 – 7.89 (m, 3H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.54 – 7.46 (m, 3H), 7.25 – 7.18 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 142.8, 134.2, 134.0, 133.8, 133.0, 132.8, 130.0, 129.1, 127.3, 122.9, 122.5, 121.7, 119.4, 110.7. Anal. Calcd for $C_{17}H_{12}N_2$: 244.1000. Found: 245.1152 (M+1). GC RT 21.19 minutes.

***N*-(*p*-Tolyl)naphthalen-2-amine[23]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.49 – 7.42 (m, 4H), 7.28 – 7.24 (m, 4H), 7.11 (s, 1H), 4.21 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3, 140.1, 130.5, 129.6, 128.0, 125.1, 119.9, 118.6, 118.1, 116.6, 107.0, 20.4. Anal. Calcd for $C_{17}H_{15}N$: 233.1204. Found: 234.1178 (M+1). GC RT 14.96 minutes.

***N*-(4-Methoxyphenyl)-*N*-methylnaphthalen-2-amine[23]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 - 7.70 (m, 2H), 7.51 - 7.27 (m, 4H), 7.18 – 7.10 (m, 3H), 6.88 (d, *J* = 7.7 Hz, 2H), 4.26 (s, 1H), 3.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 144.7, 142.6, 133.5, 129.6, 127.9, 126.4, 125.9, 122.6, 120.1, 116.2, 114.6, 108.4, 55.9, 43.5. Anal. Calcd for $C_{18}H_{17}NO$: 263.1310. Found: 264.1078 (M+1). GC RT 19.83 minutes.

***N*-Methyl-*N*-phenyl-4-(trifluoromethyl)aniline[26]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 1.1 Hz, 2H), 7.30 – 7.29 (m, 2H), 6.84 (t, *J* = 1.1 Hz, 1H), 6.72 – 6.70 (m, 4H), 3.15 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 149.2, 129.1, 125.5, 123.7, 121.6, 117.2, 112.4, 44.8. Anal. Calcd for $C_{14}H_{12}F_3N$: 251.0922. Found: 250.1075 (M-1). GC RT 9.58 minutes.

***N*-Phenyl-4-(trifluoromethyl)aniline[27]:** ^{1}H NMR (250 MHz, D_2O) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 - 7.10 (m, 3H), 7.05 – 7.00 (m, 2H), 4.53 (s, 1H). ^{13}C NMR (63 MHz, D_2O) δ 147.6, 146.2, 128.9, 126.4, 122.5, 119.7, 118.2. Anal. Calcd for $C_{13}H_{10}F_3N$: 237.0765. Found: 236.0908 (M-1). GC RT 12.69 minutes.

4-Chloro-*N*-(4-(trifluoromethyl)phenyl)aniline[28]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.34 – 7.29 (m, 4H), 4.04 (s, 1H). ^{13}C NMR (63 MHz, D_2O) δ 144.5, 139.8, 129.5, 129.1, 128.6, 126.4, 122.7, 120.7. Anal. Calcd for $C_{13}H_9ClF_3N$: 271.0376. Found: 270.0500 (M-1). GC RT 16.11 minutes.

***N*-Methyl-4-nitro-*N*-(4-(trifluoromethyl)phenyl)aniline:** ^{1}H NMR (250 MHz, D_2O) δ 8.05 (d, *J* = 8.9 Hz, 2H), 7.75 – 7.61 (m, 4H), 7.30 – 7.09 (m, 2H), 3.62 (s, 1H). ^{13}C NMR (63 MHz, D_2O) δ 156.7, 147.2, 137.9, 133.5, 131.2, 125.9, 125.4, 119.4, 113.9, 43.4. Anal. Calcd for $C_{14}H_{11}F_3N_2O_2$: 296.0773. Found: 295.0972 (M-1). GC RT 7.04 minutes.

4-Methyl-*N*-(4-(trifluoromethyl)phenyl)aniline[26]: ^{1}H NMR (250 MHz, D_2O) δ 7.46 – 7.21 (m, 8H), 4.12 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 147.9, 138.8, 132.7, 129.9, 126.4, 123.3, 120.9, 20.9. Anal. Calcd for $C_{14}H_{12}F_3N$: 251.0922. Found: 250.1122 (M-1). GC RT 13.53 minutes.

4-Methoxy-*N*-methyl-*N*-(4-(trifluoromethyl)phenyl)aniline[29]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.9 Hz, 2H), 6.98 – 6.91 (m, 4H), 6.72 – 6.68 (m, 2H), 3.79 (s, 3H), 3.25 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 152.0, 143.6, 126.2, 125.3, 120.2, 116.2, 55.9, 42.0. Anal. Calcd for $C_{15}H_{14}F_3NO$: 281.1027. Found: 280.1257 (M-1). GC RT 6.67 minutes.

1-(4-((4-Chlorophenyl)amino)phenyl)ethanone[30]: ^{1}H NMR (250 MHz, D_2O) δ 7.93 (d, *J* = 7.1 Hz, 2H), 7.54 – 7.40 (m, 4H), 7.25 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 198.2, 145.0, 141.0, 128.7, 128.3, 128.0, 122.3, 121.2, 115.9, 26.3. Anal. Calcd for $C_{14}H_{12}ClNO$: 245.0607. Found: 244.0779 (M-1). GC RT 7.79 minutes.

1-(4-(*p*-Tolylamino)phenyl)ethanone[31]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.34 – 7.30 (m, 4H), 3.36 (s, 1H), 2.63 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 149.2, 137.9, 130.6, 129.7, 121.5, 113.8, 26.6, 20.3. Anal. Calcd for $C_{15}H_{15}NO$: 225.1154. Found: 226.0997 (M+1). GC RT 8.91 minutes.

1-(4-((4-Methoxyphenyl)(methyl)amino)phenyl)ethanone[30]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.40 (m, 4H), 6.55 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 3H), 3.29 (s, 1H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8, 153.0, 151.8, 140.8, 128.3, 128.0, 120.1, 120.0, 114.5, 55.4, 40.0, 26.2. Anal. Calcd for $C_{16}H_{17}NO_2$: 255.1259. Found: 256.1119 (M+1). GC RT 6.57 minutes.

3-(Methyl(phenyl)amino)phenol[32]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.19 – 7.12 (m, 2H), 6.82 – 6.79 (m, 3H), 6.73 – 6.65 (m, 4H), 4.15 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 149.1, 129.3, 129.0, 119.8, 117.1, 115.2, 112.3, 102.7, 46.2. Anal. Calcd for $C_{13}H_{13}NO$: 199.0997. Found: 198.1009 (M-1). GC RT 7.17 minutes.

3-(Phenylamino)phenol[33]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.35 – 7.32 (m, 2H), 7.10 – 7.04 (m, 5H), 6.54 – 6.49 (m, 2H), 4.21 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 146.3, 143.8, 128.1, 127.8, 123.2, 122.0, 110.2, 109.1, 105.3. Anal. Calcd for $C_{12}H_{11}NO$: 185.0841. Found:

184.0994 (M-1). GC RT 6.62 minutes.

3-((4-Chlorophenyl)amino)phenol[33]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.61 – 7.58 (m, 2H), 7.14 – 7.07 (m, 3H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.62 – 6.58 (m, 2H), 4.78 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 148.8, 144.1, 129.3, 128.9, 124.8, 122.7, 109.4, 108.1, 104.4. Anal. Calcd for $C_{12}H_{10}ClNO$: 219.0451. Found: 218.0661 (M-1). GC RT 5.19 minutes.

***N*^{1},*N*^{1},*N*^{3}-Trimethyl-*N*^{3}-phenylbenzene-1,3-diamine[34]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 4H), 6.72 – 6.66 (m, 4H), 6.46 (s, 1H), 3.32 (s, 3H), 2.95 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 150.2, 149.1, 129.6, 129.0, 120.0, 118.8, 107.0, 104.9, 41.3, 40.5. Anal. Calcd for $C_{15}H_{18}N2$: 226.1470. Found: 225.1001 (M-1). GC RT 7.92 minutes.

***N*^{1},*N*^{1}-Dimethyl-*N*^{3}-phenylbenzene-1,3-diamine[34]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.09 – 7.00 (m, 5H), 6.88 – 6.84 (m, 1H), 6.48 (s, 1H), 4.10 (s, 1H), 2.93 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 143.8, 138.1, 129.7, 129.2, 120.4, 117.6, 112.6, 106.7, 106.0, 40.5. Anal. Calcd for $C_{14}H_{16}N_2$: 212.1313. Found: 211.1219 (M-1). GC RT 9.51 minutes.

***N*^{1}-(4-Chlorophenyl)-*N*^{3},*N*^{3}-dimethylbenzene-1,3-diamine[34]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.1 Hz, 2H), 7.45 (d, *J* = 6.6 Hz, 2H), 7.27 – 7.03 (m, 2H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.43 (s, 1H), 4.11 (s, 1H), 2.89 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 141.3, 139.6, 128.6, 128.3, 127.7, 123.3, 111.9, 104.3, 39.8. Anal. Calcd for $C_{14}H_{15}ClN_2$: 246.0924. Found: 245.1008 (M-1). GC RT 5.20 minutes.

***N*^{1},*N*^{1},*N*^{3}-Trimethyl-*N*^{3}-(4-nitrophenyl)benzene-1,3-diamine[34]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 2H), 7.49 – 7.40 (m, 2H), 7.14 (t, *J* = 8.8 Hz, 1H), 6.70 – 6.65 (m, 2H), 6.53 – 6.51 (m, 1H), 4.13 (s, 1H), 2.94 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 156.4, 147.6, 133.3, 129.0, 126.4, 120.1, 112.6, 105.0, 43.0, 40.6. Anal. Calcd for $C_{15}H_{17}N_3O_2$: 271.1321. Found: 270.1259 (M-1). GC RT 11.87 minutes.

***N*^{1},*N*^{1}-Dimethyl-*N*^{3}-(*p*-tolyl)benzene-1,3-diamine[35]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.27 (t, *J* = 6.4 Hz, 1H), 7.18 – 7.06 (m, 1H), 7.06 – 6.97 (m, 1H), 6.78 – 6.76 (m, 1H), 4.14 (s, 1H), 2.97 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 137.4, 129.8, 128.5, 120.6, 110.2, 105.0, 41.7, 21.1. Anal. Calcd for $C_{15}H_{18}N_2$: 226.1470. Found: 225.1301 (M-1). GC RT 10.20 minutes.

***N*^{1}-(4-Methoxyphenyl)-*N*^{1},*N*^{3},*N*^{3}-trimethylbenzene-1,3-diamine:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 – 7.02 (m, 3H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.73 – 6.68 (m, 2H), 6.26 – 6.23 (m, 1H), 4.05 (s, 1H), 3.75 (s, 3H), 2.90 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 151.9, 150.5, 142.5, 128.8, 121.1, 116.4, 105.9, 104.1, 55.6, 42.8, 40.3. Anal. Calcd for $C_{16}H_{20}N_2O$: 256.1576. Found: 255.1431 (M-1). GC RT 12.42 minutes.

Methyl-phenyl-*p*-tolylamine[23]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 7H), 6.88 – 6.81 (m, 2H), 4.88 (s, 1H), 2.68 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 148.2, 129.9, 129.2, 122.5, 117.2,

112.4, 45.3, 21.6. Anal. Calcd for $C_{14}H_{15}N$: 197.1204. Found: 196.1087 (M-1). GC RT 11.57 minutes.

4-Methyl-*N*-phenylaniline[27]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 7.09 – 7.00 (m, 4H), 6.95 - 6.90 (m, 3H), 5.60 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 138.6, 130.6, 129.2, 128.4, 122.6, 121.3, 118.9, 23.4. Anal. Calcd for $C_{12}H_{10}ClNO$: 219.0451. Found: 218.0661 (M-1). GC RT 5.19 minutes.

4-Chloro-*N*-(*p*-tolyl)aniline[28]: ^{1}H NMR (250 MHz, D_2O) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.10 – 7.00 (m, 4H), 4.04 (s, 1H), 2.80 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 144.1, 142.4, 129.9, 129.0, 126.6, 125.1, 119.9, 22.1. Anal. Calcd for $C_{13}H_{12}ClN$: 217.0658. Found: 216.0771 (M-1). GC RT 5.19 minutes.

di-*p*-Tolylamine[28]: ^{1}H NMR (250 MHz, D_2O) δ 7.29 (d, *J* = 7.9 Hz, 4H), 7.05 (d, *J* = 7.4 Hz, 4H), 5.52 (s, 1H), 2.52 (s, 6H). ^{13}C NMR (63 MHz, D_2O) δ 141.07, 130.04, 129.98, 129.40, 117.80, 20.51. Anal. Calcd for $C_{14}H_{15}N$: 197.1204. Found: 196.1107 (M-1). GC RT 14.46 minutes.

4-Methoxy-*N*-methyl-*N*-(*p*-tolyl)aniline[31]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 – 7.04 (m, 6H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.21 (s, 1H), 3.77 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 155.25, 147.33, 142.59, 129.59, 129.24, 121.22, 120.49, 114.49, 55.42, 40.31, 20.63. Anal. Calcd for $C_{15}H_{17}NO$: 227.1310. Found: 226.1214 (M-1). GC RT 8.60 minutes.

Naphthalen-2-yl(phenyl)sulfane[11]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 4H), 7.50 - 7.36 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.9, 131.4, 127.2, 126.9, 125.8, 125.8, 125.4, 125.2, 125.1, 125.0, 123.8, 123.6. Anal. Calcd for $C_{16}H_{12}S$: 236.0660. Found: 235.0772 (M-1). GC RT 15.85 minutes.

Naphthalen-2-yl(4-nitrophenyl)sulfane[36]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.65 (m, 5H), 7.52 – 7.44 (m, 3H), 7.38 – 7.25 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 141.9, 135.8, 135.0, 133.7, 130.2, 127.8, 126.3, 125.8, 125.6, 124.4. Anal. Calcd for $C_{16}H_{11}NO_2S$: 281.0510. Found: 280.0447 (M-1). GC RT 9.05 minutes.

Naphthalen-2-yl(p-tolyl)sulfane[37]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.69 (m, 3H), 7.62 (s, 1H), 7.55 – 7.37 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 135.7, 132.1, 131.7, 128.1, 126.8, 126.1, 124.1, 19.3. Anal. Calcd for $C_{17}H_{14}S$: 250.0816. Found: 249.0955 (M-1). GC RT 8.99 minutes.

(2,6-Dimethylphenyl)(naphthalen-2-yl)sulfane[38]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.55 (m, 3H), 7.69 (s, 1H), 7.46 – 7.39 (m, 3H), 6.94 – 6.89 (m, 3H), 2.23 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 134.7, 133.4, 131.3, 130.8, 129.2, 128.0, 127.8, 127.2, 125.8, 21.4. Anal. Calcd for $C_{18}H_{16}S$: 264.0973. Found: 263.1107 (M-1). GC RT 8.78 minutes.

(4-Chlorophenyl)(naphthalen-2-yl)sulfane[39]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.3 Hz, 1H),

7.83 – 7.74 (m, 5H), 7.38 – 7.31 (m, 3H), 7.26 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 135.0, 133.6, 133.1, 131.7, 131.1, 129.3, 128.2, 127.8, 127.0, 126.5, 125.8. Anal. Calcd for $C_{16}H_{11}ClS$: 270.0270. Found: 269.0644 (M-1). GC RT 9.94 minutes.

Naphthalen-2-yl(4-(trifluoromethyl)phenyl)sulfane[40]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.87 (m, 3H), 7.82 – 7.68 (m, 5H), 7.32 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, $cdcl_3$) δ 140.8, 134.7, 133.4, 129.7, 127.8, 126.5, 125.8, 125.6, 123.3. Anal. Calcd for $C_{17}H_{11}F_3S$: 304.0534. Found: 303.0728 (M-1). GC RT 11.26 minutes.

(4-Methoxyphenyl)(naphthalen-2-yl)sulfane[37]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.70 (m, 3H), 7.65 (s, 1H), 7.55 – 7.52 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 133.1, 132.2, 129.0, 128.0, 127.4, 125.4, 114.2, 54.8. Anal. Calcd for $C_{17}H_{14}OS$: 266.0765. Found: 265.1008 (M-1). GC RT 16.14 minutes.

(2-Methylbutyl)(naphthalen-2-yl)sulfane[40]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.57 (m, 3H), 7.47 (s, 1H), 7.28 – 7.13 (m, 3H), 2.73 (dd, *J* = 12.7, 5.8 Hz, 2H), 2.04 – 1.89 (m, 1H), 1.79 – 1.66 (m, 2H), 1.56 – 1.42 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 130.5, 129.7, 129.2, 128.3, 127.5, 126.0, 125.9, 44.8, 34.4, 28.4, 23.3, 11.2. Anal. Calcd for $C_{15}H_{18}S$: 230.1129. Found: 229.0918 (M-1). GC RT 12.99 minutes.

Naphthalen-2-yl(perfluorophenyl)sulfane[40]: ^{1}H NMR (250 MHz, D_2O) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.72 - 7.60 (m, 3H), 7.50 - 7.36 (m, 3H). ^{13}C NMR (63 MHz, D_2O) δ 150.0, 141.9, 138.4, 133.5, 129.7, 129.1, 128.6, 126.9, 126.7, 125.7, 100.3. Anal. Calcd for $C_{16}H_7F_5S$: 326.0189. Found: 325.0344 (M-1). GC RT 15.64 minutes.

Phenyl(4-(trifluoromethyl)phenyl)sulfane[41]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 7H), 7.22 – 7.18 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 137.0, 129.0, 127.5, 127.1, 126.7, 126.7, 124.6, 122.8. Anal. Calcd for $C_{13}H_9F_3S$: 254.0377. Found: 253.0475 (M-1). GC RT 13.75 minutes.

(4-Nitrophenyl)(4-(trifluoromethyl)phenyl)sulfane[41]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.63, 141.64, 139.66, 132.68, 129.21, 126.08, 124.53, 123.95. Anal. Calcd for $C_{13}H_8F_3NO_2S$: 299.0228. Found: 298.0500 (M-1). GC RT 12.37 minutes.

***p*-Tolyl(4-(trifluoromethyl)phenyl)sulfane[41]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 4H), 7.18 – 7.09 (m, 4H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 137.4, 130.2, 129.7, 128.6, 123.3, 119.8, 20.9. Anal. Calcd for $C_{14}H_{11}F_3S$: 268.0534. Found: 127.0784 (M-1). GC RT 12.11 minutes.

(4-Chlorophenyl)(4-(trifluoromethyl)phenyl)sulfane[41]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 135.1, 133.6, 131.7, 131.1, 129.3, 127.8, 125.8. Anal. Calcd for $C_{13}H_8ClF_3S$:

287.9987. Found: 287.0002 (M-1). GC RT 9.42 minutes.

(2-Methylbutyl)(4-(trifluoromethyl)phenyl)sulfane: ^{1}H NMR (250 MHz, D_2O) δ 7.35-7.29 (m, 4H), 2.75 (dd, *J* = 12.7, 5.8 Hz, 2H), 2.08 – 1.92 (m, 1H), 1.84 – 1.75 (m, 2H), 1.58 – 1.45 (m, 6H). ^{13}C NMR (63 MHz, D_2O) δ 142.5, 131.6, 128.5, 127.8, 125.8, 46.7, 34.5, 28.5, 18.6, 11.2. Anal. Calcd for $C_{12}H_{15}F_3S$: 248.0847. Found: 247.0747 (M-1). GC RT 6.96 minutes.

(Perfluorophenyl)(4-(trifluoromethyl)phenyl)sulfane: ^{1}H NMR (250 MHz, D_2O) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (63 MHz, D_2O) δ 149.0, 141.0, 138.2, 135.9, 133.3, 132.4, 129.0, 126.3, 100.6. Anal. Calcd for $C_{13}H_4F_8S$: 343.9906. Found: 343.0001 (M-1). GC RT 7.34 minutes.

1-(4-(Phenylthio)phenyl)ethanone[37]: ^{1}H NMR (250 MHz, D_2O) δ 7.91 (d, *J* = 5.8 Hz, 2H), 7.60 - 7.45 (m, 7H), 2.55 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 197.5, 143.0, 134.6, 133.1, 128.8, 128.0, 127.8, 126.7, 26.1. Anal. Calcd for $C_{14}H_{12}OS$: 228.0609. Found: 227.0889 (M-1). GC RT 17.60 minutes.

1-(4-((4-Nitrophenyl)thio)phenyl)ethanone[42]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 2H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 146.9, 144.0, 141.9, 133.1, 129.5, 128.3, 124.4, 26.6. Anal. Calcd for $C_{14}H_{11}NO_3S$: 273.0460. Found: 272.0551 (M-1). GC RT 12.50 minutes.

1-(4-(*p*-Tolylthio)phenyl)ethanone[43]: ^{1}H NMR (250 MHz, D_2O) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.20 (m, 4H), 6.78 (d, *J* = 8.4 Hz, 2H), 2.60 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 193.0, 137.6, 134.1, 129.7, 129.7, 128.4, 128.4, 30.6, 20.9. Anal. Calcd for $C_{15}H_{14}OS$: 242.0765. Found: 241.0510 (M-1). GC RT 13.63 minutes.

1-(4-((2,6-Dimethylphenyl)thio)phenyl)ethanone[44]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.52 – 7.42 (m, 4H), 7.10 – 7.04 (m, 1H), 2.60 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 143.3, 137.1, 134.7, 129.2, 128.5, 128.0, 127.6, 126.9, 77.4, 77.0, 76.6, 26.6, 21.4. Anal. Calcd for $C_{16}H_{16}OS$: 256.0922. Found: 255.1002 (M-1). GC RT 12.27 minutes.

1-(4-((4-Chlorophenyl)thio)phenyl)ethanone[45]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.43 – 7.38 (m, 4H), 6.82 (d, *J* = 8.4 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 144.0, 133.1, 132.6, 131.4, 129.9, 128.5, 128.3, 26.6. Anal. Calcd for $C_{14}H_{11}ClOS$: 262.0219. Found: 261.0442 (M-1). GC RT 9.46 minutes.

1-(4-((2-Methylbutyl)thio)phenyl)ethan-1-one: ^{1}H NMR (250 MHz, D_2O) δ 7.30-7.22 (m, 4H), 2.75 (dd, *J* = 12.5, 5.5 Hz, 2H), 2.45 (s, 3H), 2.06 – 1.92 (m, 1H), 1.79 – 1.66 (m, 2H), 1.55 – 1.40 (m, 6H). ^{13}C NMR (63 MHz, D_2O) δ 193.5, 137.1, 133.4, 130.4, 123.5, 46.7, 34.5, 28.5, 18.6, 11.2. Anal. Calcd for $C_{13}H_{18}OS$: 222.1078. Found: 221.0887 (M-1). GC RT 6.96 minutes.

3-((4-Nitrophenyl)thio)phenol[46]: ^{1}H NMR (250 MHz, D_2O) δ 8.90 (s, 1H), 8.15 (d, *J* = 8.6 Hz, 2H),

7.58 (d, *J* = 8.7 Hz, 2H), 6.85 – 6.79 (m, 3H), 6.72 (s, 1H). ^{13}C NMR (63 MHz, D_2O) δ 158.4, 144.0, 140.4, 137.0, 129.6, 124.4, 118.7, 115.2. Anal. Calcd for $C_{12}H_9NO_3S$: 247.0303. Found: 246.0541 (M-1). GC RT 6.15 minutes.

3-(*p*-Tolylthio)phenol[46]: ^{1}H NMR (250 MHz, D_2O) δ 8.88 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.13 – 7.07 (m, 4H), 6.93 – 6.65 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 158.9, 140.4, 137.3, 133.8, 130.0, 129.7, 129.7, 128.4, 120.1, 115.24, 113.0, 20.9. Anal. Calcd for $C_{13}H_{12}OS$: 216.0609. Found: 215.0887 (M-1). GC RT 11.62 minutes.

3-((2,6-Dimethylphenyl)thio)phenol[46]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.18 – 6.97 (m, 1H), 6.94 – 6.89 (m, 2H), 6.85 (d, *J* = 7.7 Hz, 1H), 2.25 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 143.4, 134.7, 129.6, 129.3, 128.0, 123.1, 120.7, 115.2, 21.4. Anal. Calcd for $C_{14}H_{14}OS$: 230.0765. Found: 229.0455 (M-1). GC RT 12.45 minutes.

3-((4-Chlorophenyl)thio)phenol[46]: ^{1}H NMR (250 MHz, D_2O) δ 8.78 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.91 – 6.79 (m, 2H), 6.62 – 6.42 (m, 1H), 6.25 (s, 1H). ^{13}C NMR (63 MHz, D_2O) δ 158.7, 135.1, 133.6, 129.5, 129.3, 126.3, 119.9, 115.3. Anal. Calcd for $C_{12}H_9ClOS$: 236.0063. Found: 235.0150 (M-1). GC RT 9.48 minutes.

3-((2-Methylbutyl)thio)phenol[47]: ^{1}H NMR (250 MHz, D_2O) δ 8.89 (s, 1H), 7.28-6.83 (m, 4H), 2.70 (dd, *J* = 12.8, 6.0 Hz, 2H), 2.02 – 1.89 (m, 1H), 1.80 – 1.65 (m, 2H), 1.58 – 1.43 (m, 6H). ^{13}C NMR (63 MHz, D_2O) δ 158.1, 138.3, 129.5, 120.3, 116.3, 115.3, 46.6, 34.4, 28.4, 18.5, 11.2. Anal. Calcd for $C_{11}H_{16}OS$: 196.0922. Found: 195.0504 (M-1). GC RT 6.98 minutes.

***N*,*N*-Dimethyl-3-(phenylthio)aniline[37]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 5H), 7.24 – 7.22 (m, 1H), 7.00 – 6.98 (m, 1H), 6.68 – 6.65 (m, 2H), 2.91 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 137.7, 137.0, 129.0, 127.5, 127.1, 121.2, 116.9, 112.6, 42.5. Anal. Calcd for $C_{14}H_{15}NS$: 229.0925. Found: 228.0645 (M-1). GC RT 14.67 minutes.

***N*,*N*-Dimethyl-3-((4-nitrophenyl)thio)aniline[46]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.26 (s, 1H), 7.13 – 7.11 (m, 1H), 6.75 – 6.64 (m, 2H), 6.58 (d, *J* = 9.5 Hz, 2H), 2.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 144.1, 141.3, 138.3, 131.4, 129.1, 124.5, 122.6, 118.0, 112.7, 40.6. Anal. Calcd for $C_{14}H_{14}N_2O_2S$: 274.0776. Found: 273.1141 (M-1). GC RT 6.02 minutes.

***N*,*N*-Dimethyl-3-(*p*-tolylthio)aniline:** ^{1}H NMR (250 MHz, D_2O) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.30 (s, 1H), 7.21 – 7.18 (m, 2H), 7.08 – 7.06 (m, 1H), 6.95 – 6.67 (m, 2H), 3.08 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 150.5, 141.7, 137.3, 133.8, 129.7, 129.0, 128.4, 122.7, 116.5, 112.6, 40.5, 21.0. Anal. Calcd for $C_{15}H_{17}NS$: 243.1082. Found: 242.0778 (M-1). GC RT 21.96 minutes.

3-((2,6-Dimethylphenyl)thio)-*N*,*N*-dimethylaniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.25 (m, 3H), 7.10-7.01 (m, 2H), 6.75-6.55 (m, 2H), 2.94 (s, 6H), 2.23 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6,

143.4, 138.6, 130.8, 129.2, 128.0, 127.0, 121.3, 116.6, 112.6, 40.6, 21.4. Anal. Calcd for $C_{16}H_{19}NS$: 257.1238. Found: 256.0998 (M-1). GC RT 9.78 minutes.

***N,N*-Dimethyl-3-((2-methylbutyl)thio)aniline:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.27 (m, 2H), 7.06 – 6.81 (m, 2H), 2.99 (s, 6H), 2.83 (dd, *J* = 13.4, 6.8 Hz, 2H), 2.14 – 2.00 (m, 1H), 1.84 – 1.77 (m, 2H), 1.64 – 1.57 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 138.4, 128.4, 116.2, 111.2, 109.8, 46.6, 40.9, 34.4, 28.4, 18.5, 11.1. Anal. Calcd for $C_{13}H_{21}NS$: 223.1395. Found: 222.1012 (M-1). GC RT 9.79 minutes.

Phenyl(*p*-tolyl)sulfane[11]: ^{1}H NMR (250 MHz, D_2O) δ 7.51 – 7.44 (m, 7H), 7.30 – 7.16 (m, 2H), 2.23 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 140.4, 137.0, 129.0, 128.1, 127.5, 127.1, 23.3. Anal. Calcd for $C_{13}H_{12}S$: 200.0660. Found: 199.0881 (M-1). GC RT 13.49 minutes.

(4-Nitrophenyl)(*p*-tolyl)sulfane[36]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 140.2, 137.4, 132.3, 129.6, 127.9, 124.4, 21.5. Anal. Calcd for $C_{13}H_{11}NO_2S$: 245.0510. Found: 244.0781 (M-1). GC RT 9.21 minutes.

di-*p*-Tolylsulfane[48]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 4H), 7.11 (d, *J* = 7.9 Hz, 4H), 2.33 (s, 6H). ^{13}C NMR (63 MHz, D_2O) δ 137.4, 130.5, 129.8, 128.5, 21.0. Anal. Calcd for $C_{14}H_{14}S$: 214.0816. Found: 213.0664 (M-1). GC RT 14.06 minutes.

(2,6-Dimethylphenyl)(p-tolyl)sulfane[48]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.6 Hz, 2H), 7.18 – 6.97 (m, 5H), 2.25 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 139.0, 134.2, 129.5, 128.8, 128.3, 127.6, 127.3, 21.4, 21.0. Anal. Calcd for $C_{15}H_{16}S$: 228.0973. Found: 227.1221 (M-1). GC RT 5.26 minutes.

(4-Chlorophenyl)(*p*-tolyl)sulfane[48]: ^{1}H NMR (250 MHz, D_2O) δ 7.27 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.18 – 7.13 (m, 4H), 2.35 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 140.6, 135.0, 133.5, 129.8, 129.2, 129.1, 20.4. Anal. Calcd for $C_{13}H_{11}ClS$: 234.0270. Found: 233.0478 (M-1). GC RT 5.26 minutes.

(2-Methylbutyl)(*p*-tolyl)sulfane[48]: ^{1}H NMR (250 MHz, D_2O) δ 7.22 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.3 Hz, 2H), 2.77 (dd, *J* = 12.9, 6.1 Hz, 2H), 2.44 (s, 3H), 2.07 – 1.92 (m, 1H), 1.88 – 1.75 (m, 2H), 1.62 – 1.57 (m, 6H). ^{13}C NMR (63 MHz, D_2O) δ 136.5, 132.6, 129.8, 128.9, 46.6, 34.4, 28.5, 20.4, 18.5, 11.2. Anal. Calcd for $C_{12}H_{18}S$: 194.1129. Found: 193.0889 (M-1). GC RT 6.95 minutes.

(Perfluorophenyl)(*p*-tolyl)sulfane[49]: ^{1}H NMR (250 MHz, D_2O) δ 7.27 (d, *J* = 7.3 Hz, 2H), 7.08 (d, *J* = 7.0 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (63 MHz, D_2O) δ 150.6, 141.7, 140.0, 136.0, 133.7, 131.5, 130.2, 102.2, 24.8. Anal. Calcd for $C_{13}H_7F_5S$: 290.0189. Found: 289.0471 (M-1). GC RT 8.60 minutes.

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