Para-Directed Amination of Electron-Rich Arenes with Bis(2,2,2-trichloroethyl) Azodicarboxylate†

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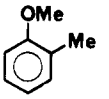
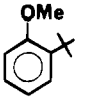
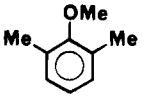
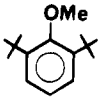
We have already depicted that electron-deficient azo molecules add to electron-rich arenes with a high degree of selectivity. In all cases the hydrazide moiety is incorporated para to the electron-donating substituent.[1,2] This paper contains results on the amination of C_2-alkyl substituted anisole with bis(2,2,2-trichloroethyl) azodicarboxylate (BTCEAD). In addition, new experimental conditions which allow rapid amination of aromatic compounds including 1,4-disubstituted substrates are described. These conditions were also applied to the bisamination of arenes. Furthermore, frontier molecular orbital calculations are presented in order to rationalize the observed selectivity.

Results and Discussion

Amination of Ortho Substituted Anisole. Comparable reactivity was observed with anisole and C_2-alkyl substituted anisole (Table 1) with $ZnCl_2$ as catalyst. For example with 2-methylanisole (**1**) and 2-*tert*-butylanisole (**2**) as substrates, the para-aminated products (**5, 6**) were isolated in 99 and 82% yields, respectively. In the case of C_2,C_6-dialkyl compounds little or no reaction was observed under the same experimental conditions. 2,6-Dimethylanisole (**3**) was converted to the hydrazide **7** in only 30% yield after 3 days whereas no aminated product was detected with 2,6-di-*tert*-butylanisole (**4**) as a substrate. These experimental results suggest that the amination reaction takes place via the formation of the Wheland intermediate as is proposed for electrophilic aromatic substitution reactions such as nitration.[3,4] The lower reactivity of C_2,C_6-dialkylanisole could be explained by unfavorable steric interactions in the σ-complex.

Amination and Bisamination with Trifluoromethanesulfonic Acid. The use of other activators was envisaged both to make possible the amination of 1,4-disubstituted arenes and to prepare bisaminated products. It has been found that CF_3SO_3H and CF_3CO_2H are powerful catalysts for this reaction; they dramatically accelerate the rate of the amination. For example, with anisole (**8**) as a substrate, the reaction was performed with 0.1 equiv of CF_3SO_3H in CH_2Cl_2 at −78 °C to give exclusively the para isomer **15**, in 99% yield within 2 h (Table 2). With TFA as a solvent the reaction took place at 0 °C to provide the hydrazide **15** in 94% yield, after 3 h. In this case 1% of both the ortho isomer **16** and the bisaminated **17** product were isolated.[5] Phenol (**9**) showed similar reactivity to anisole but lower selectivity was observed (9:1 with CF_3SO_3H and 1:1 with TFA). The lower selectivity observed for phenol compared with our previous $LiClO_4$–ether conditions is probably a direct consequence of these more drastic experimental conditions combined with a less sterically demanding ortho σ-complex as compared to anisole.

Table 1

SUBSTRATE	HYDRAZIDE[2]
 1	**5** 99% (17 hr)
 2	**6** 82% (20 hr)
 3	**7** 30% (3 days)
 4	No Reaction

These new amination conditions were applied to the 1,4-disubstituted cases. 1,4-Dimethoxybenzene (**10**) was aminated with 1.2 equiv of BTCEAD and 0.1 equiv of CF_3SO_3H as catalyst to give the hydrazide **20** in 85% yield. Similar reactivity was observed with 4-bromoanisole (**11**), the aminated product **21** being isolated in 76% yield.[10]

In addition, bisaminated compounds can be prepared in good yields with these new conditions (Scheme 1). Anisole was treated with 3 equiv of BTCEAD in CH_2Cl_2 in the presence of CF_3SO_3H to afford the bishydrazide **17** in 85% yield. 1,2- and 1,3-dimethoxybenzene were bisaminated in 85% (**32**) and 74% (**30**) yields, respectively. The hydrazides were then converted to their corresponding amines using our standard protocol.[1,2]

Frontier-MO Calculations. Molecular orbital treatment has been utilized with a certain degree of success to explain the regioselectivity of nitration reaction[6] and other reactions involving aromatic molecules.[7]

The formation of a π-complex (Figure 1) prior to the formation of σ-complex could be envisaged for the addition of azo molecules on arenes. Three center π-complexes have been proposed as intermediates in electrophilic aromatic substitution reactions.[3] For the present case the π-complex would involve the HOMO of the arene molecules with the LUMO of the azo reagent. In Figure 2 are shown the frontier orbital coefficients of given

† Dedicated to Professor S. Hanessian for his 60th birthday.

(1) Zaltsgendler, I.; Leblanc, Y.; Bernstein, M. A. *Tetrahedron Lett.* **1993**, *34*, 2441.

(2) Mitchell, H.; Leblanc, Y. *J. Org. Chem.* **1994**, *59*, 682.

(3) Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240.

(4) Keumi, T.; Hamanaka, K.; Hasegawa, H.; Minamide, H.; Inoue, Y.; Kitajima, H. *Chem. Lett.* **1988**, 1285.

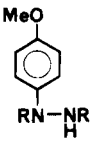
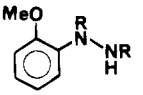
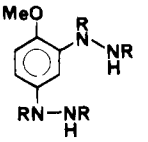
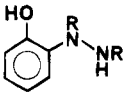
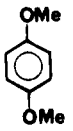
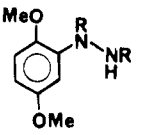
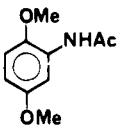
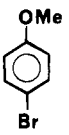
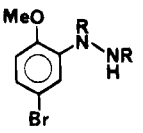
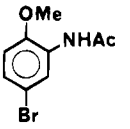
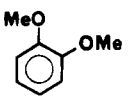
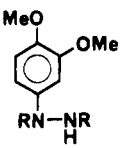
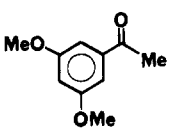
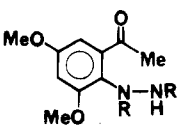
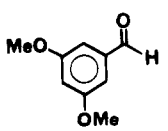
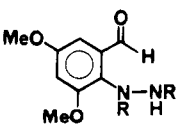
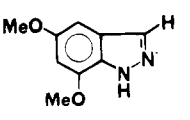
(5) These new experimental conditions have some advantages over the $ZnCl_2$ conditions. In the case of anisole, with 1 equiv of $ZnCl_2$ the reaction took 19 h. See ref 2.

(6) (a) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley-Interscience: New York, 1976. (b) Elliott, R. J.; Sackwild, V.; Richards, W. G. *J. Mol. Struct.* **1982**, *86*, 301.

(7) Sakamoto, M.; Takahashi, M.; Kimura, M.; Fujihira, M.; Fujita, T.; Iida, I.; Nishio, T.; Watanabe, S. *J. Org. Chem.* **1994**, *59*, 5117.

0022-3263/95/1960-4268$09.00/0

Table 2

SUBSTRATE		HYDRAZIDE			ANILINE
 **8**	**2** 1.2 equiv., CF_3SO_3H 0.1 equiv., CH_2Cl_2, -78°C, 2 hr	 **15** 99%	 **16** 0%	 **17** 0%	Ref 2
	2 1.2 equiv., TFA, 0°C, 3 hr	94%	1%	1%	
 **9**	**2** 1.1 equiv., CF_3SO_3H 0.1 equiv., CH_2Cl_2, -78°C to -30°C, 2 hr	 **18** 76%	 **19** 7%		Ref 2
	2 1.1 equiv., TFA, 0°C, 30 min	52%	48%		
 **10**	**2** 1.2 equiv., CF_3SO_3H 0.1 equiv, CH_2Cl_2, -78°C to 25°C, 25 min	 **20** 85%			 **25** 70%
 **11**	**2** 1.2 equiv., CH_2Cl_2, CF_3SO_3H 0.5 equiv., 25°C, 3 hr	 **21** 76%			 **26** 64%
 **12**	**2** 1.1 equiv., CH_2Cl_2, CF_3SO_3H, 0.1 equiv.	 **22**[2] 80%			Ref 1
 **13**	**2** 1.2 equiv., CH_2Cl_2, CF_3SO_3H 0.1 equiv., 0°C to 25°C, 5.5 hr	 **23**[2,9] 88%			Ref 2
 **14**	**2** 1.2 equiv., CH_2Cl_2, CF_3SO_3H 0.1 equiv., 0°C to 25°C	 **24** 74%			 **27** 68%

R = $-CO_2CH_2CCl_3$

molecules calculated by the MOPAC program.[8] From this it is clear that in all cases, except for compound **37**, a better overlap is obtained when the π-complex is formed across the carbon bearing the oxygen substituent. From the calculations, carbon 4 and 6 in compound **37** should have similar reactivity. In this case the addition to carbon 4 would give rise to the formation of an ortho σ-complex and also to a sterically unfavorable π-complex

Scheme 1

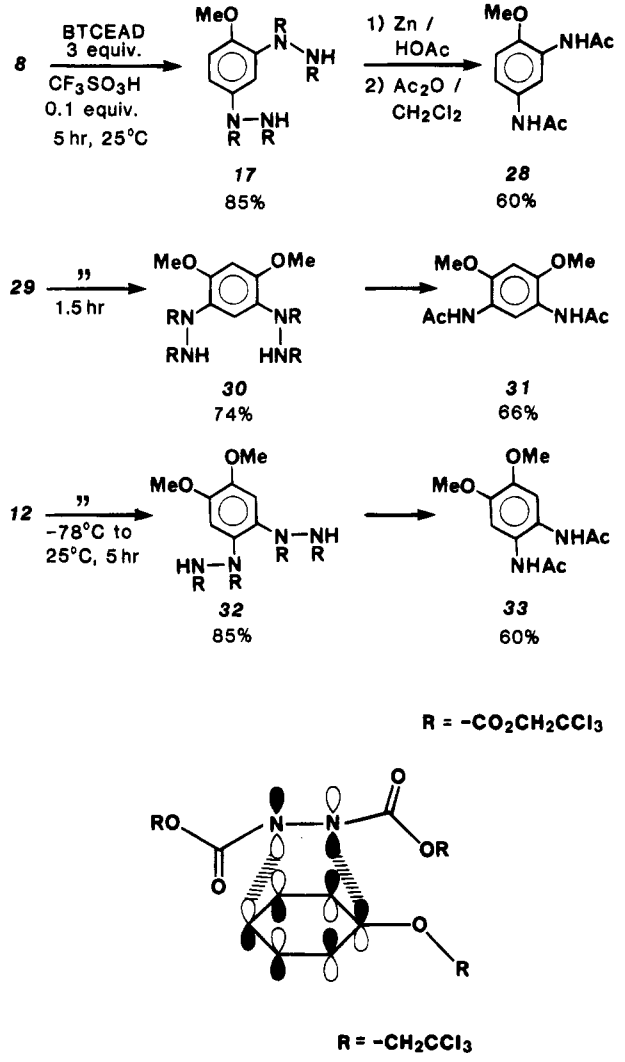


Figure 1.

due to the phenyl substituent at C_1. The previous results show that the regioselectivity for the amination reaction can be easily rationalized based on the frontier MO-calculations. The MO treatment, however, cannot be used to explain the poor reactivity of 1,4-disubstituted arenes[2] toward the $ZnCl_2$ conditions. For example, with 1,4-dimethoxybenzene (**10**) there is a good overlap across carbons 2 and 5. In this specific case it appears that the formation of an ortho σ-complex might be unfavorable, and this effect can be overcome by protonation of the azo molecule using strong acidic conditions in order to lower its LUMO and therefore make it more reactive. From our observations, the sense of the amination reaction seems to be governed firstly by the frontier MO-orbitals[11] and secondly by the nature of the σ-complex.

In conclusion, the amination of electron-rich arenes with BTCEAD is an alternative approach to the nitration

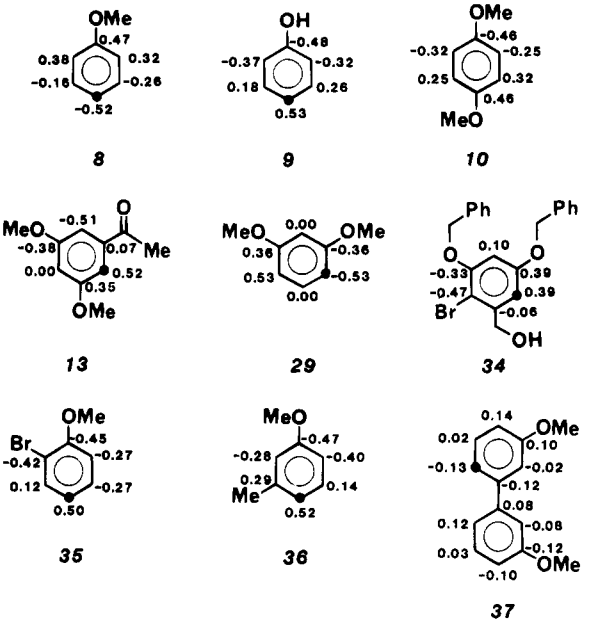


Figure 2. Characters represent the frontier orbital coefficients. The reactive site is marked by a dark dot.

reaction, and the frontier MO calculations can be used to rationalize the regioselectivity of the reaction. Finally, the degree of reactivity of the azo molecules can be modified by varying the nature of the catalyst.

Experimental Section

1-(3-Methyl-4-methoxyphenyl)-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester (5): ^1H NMR (200 MHz, acetone-d_6) δ 2.17 (s, 3H), 3.85 (s, 3H), 4.90 (s, 2H), 6.93 (d, 1H), 7.30 (s, 1H), 7.35 (d, 1H); ^{13}C NMR (100 MHz, acetone-d_6, 325 K) δ 16.06, 55.95, 75.57, 76.25, 76.94, 96.19, 110.91, 124.95, 127.35, 128.57, 134.92, 154.09, 155.21, 157.76. Anal. Calcd for $C_{14}H_{14}N_2O_5Cl_6$: C, 33.43; H, 2.81; N, 5.57. Found: C, 33.16; H, 2.96; N, 5.33.

1-(3-*tert*-Butyl-4-methoxyphenyl)-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester (6): ^1H NMR (200 MHz, acetone-d_6) δ 1.35 (s, 9H), 3.88 (s, 3H), 4.91 (s, 2H), 6.99 (d, 1H), 7.35 (dd, 1H), 7.45 (d, 1H); ^{13}C NMR (75 MHz, acetone-d_6, 325 K) δ 30.01, 36.05, 56.00, 76.05, 78.05, 96.00, 112.50, 134.60, 139.01, 153.50, 155.00, 159.00, high-resolution mass spectrum, *m/z* calcd for $C_{17}H_{21}Cl_6N_2O_5(M + H)^+$ 542.9581, found 542.9583.

1-(3,5-Dimethyl-4-methoxyphenyl)-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester (7): ^1H NMR (200 MHz, acetone-d_6) δ 2.25 (d, 6H), 3.71 (s, 3H), 4.92 (m, 2H), 7.20 (s, 1H), 7.25 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6, 325 K) δ 20.32, 64.18, 79.92, 80.63, 100.42, 129.94, 136.09, 141.57, 157.69, 159.60, 161.13, high-resolution mass spectrum, *m/z* calcd for $C_{15}H_{17}Cl_6N_2O_5$ $(M + H)^+$ 514.9268, found 514.9267.

Typical Procedure for the Amination with Trifluoromethanesulfonic Acid. 1-(2,5-Dimethoxyphenyl)-1,2-hydrazinedicarboxylic Acid Bis(2,2,2-trichloroethyl) Ester (20). To a solution of 1,4-dimethoxybenzene (180 mg, 1.30 mmol) in CH_2Cl_2 (6.5 mL) were added at −78 °C CF_3SO_3H (12 mL, 0.13 mmol) and BTCEAD (592 mg, 1.55 mmol). After a period of 5 min at −78 °C, the reaction mixture was warmed to room temperature for 25 min and quenched by the addition of 25% aqueous solution of NH_4OAc. The title compound was then extracted with ethyl acetate, dried over Na_2SO_4, filtered, evaporated, and purified by flash-chromatography (20% ethyl acetate in hexane) to afford 575 mg (85%) of a light yellow foam. ^1H NMR (400 MHz, acetone-d_6, 325 K) δ 3.76 (s, 3H), 3.84 (s, 3H), 4.88 (s, 4H), 6.94 (dd, 1H), 7.04 (d, 1H), 7.17 (s, 1H); ^{13}C NMR (100 MHz, acetone-d_6, 325 K) δ 56.19, 56.59, 75.57, 76.26, 96.16, 96.30, 113.66, 115.77, 116.01, 131.08, 150.17, 154.30, 153.63, 155.22. Anal. Calcd for $C_{14}H_{14}Cl_6N_2O_6$: C, 32.40; H, 2.72; N, 5.40. Found: C, 32.04; H, 2.75; N, 5.35.

(8) MOPAC Version 6.0: QCPE 455/SGRW, Quantum Chemistry Program Exchange, Creative Arts Building 181, Indiana University, Bloomington, IN 47405.

(9) A report describing preparation on a 10 g scale has been submitted to *Organic Synthesis*.

(10) These new experimental conditions were used for the amination of 2,6-dimethyl- and 2,6-di-*tert*-butylanisole (Table 1). The aminated products were isolated in 62 and 52% yields, respectively.

(11) The scaled electrostatic potential changes were found inconclusive to predict the selectivity.

1-(5-Bromo-2-methoxyphenyl)-1,2-hydrazinedicarboxylic acid bis(2,2,1-trichloroethyl) ester (21): ^{1}H NMR (400 MHz, acetone-d_6, 325 K) δ 3.90 (s, 3H), 4.88 (s, 4H), 7.10 (d, 1H), 7.50 (dd, 1H), 7.75 (bs, 1H), 9.60 and 9.80 (2bs, 1H); ^{13}C NMR (100 MHz, acetone-d_6, 325 K) δ 56.54, 75.66, 76.33, 96.04, 96.21, 111.80, 114.78, 151.76, 132.82, 133.35, 154.05, 155.43, 201.58, 205.87. Anal. Calcd for $C_{13}H_{11}BrCl_6N_2O_5$: C, 27.50; H, 1.95; N, 4.93. Found: C, 27.18; H, 1.96; N, 5.07.

1-(2-Formyl-4,6-dimethoxyphenyl)-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester (24): ^{1}H NMR (400 MHz, acetone-d_6, 325 K) δ 3.91 (s, 3H), 3.96 (s, 3H), 4.83 to 4.90 (m, 4H), 6.96 (d, 1H), 6.98 (d, 1H), 9.54 (bs, 1H), 10.70 (bs, 1H); ^{13}C NMR (100 MHz acetone-d_6, 325 K) δ 56.24, 56.76, 75.59, 76.46, 95.93, 96.17, 102.18, 105.54, 126.02, 135.44, 155.21, 157.75, 162.13, 191.06. Anal. Calcd for $C_{15}H_{14}Cl_6N_2O_7$: C, 32.94; H, 2.58; N, 5.12. Found: C, 32.85; H, 2.61; N, 5.04.

Typical Procedure for the Amination with Trifluoroacetic Acid. 1-(4-Hydroxyphenyl)-1,2-hydrazinedicarboxylic Acid Bis(2,2,2-trichloroethyl) Ester (18) and 1-(2-Hydroxyphenyl)-1,2-hydrazinedicarboxylic Acid Bis(2,2,2-trichloroethyl) Ester (19). To a solution of the phenol (95.0 g, 1.01 mmol) in TFA (5.0 mL) was added at 0 °C BTCEAD (456 bmg, 1.2 mmol). After a period of 30 min at 25 °C, the TFA was removed under reduced pressure and the crude mixture purified by flash chromatography (20% ethyl acetate in hexane) to afford 262 mg (48%) of the ortho isomer **19** and 280 mg (52%) of the para isomer **18**.[1] For isomer **19**: ^{1}H NMR (200 MHz, acetone-d_6) δ 4.80 to 5.00 (m, 4H), 6.90 (t, 1H), 6.95 (dd, 1H), 7.29 (t, 1H), 7.40 (dd, 1H), 8.70 (bs, 1H), 10.00 (bs, 1H); ^{13}C NMR (100 MHz, acetone-d_6, 325 K) δ 75.85, 76.93, 95.95, 101.34, 109.22, 111.08, 124.16, 125.24, 131.62, 141.94, 152.94, 154.31, high-resolution mass spectrum, *m/z* calcd for $C_{12}H_{11}Cl_6N_2O_5$ (M + H)$^+$ 472.8799, found 472.8799.

1-(2-Methoxyphenyl)-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester (17): ^{1}H NMR (300 MHz, acetone-d_6, 325 K) δ 3.79 (s, 3H), 4.85 (s, 4H), 6.97 (t, 1H), 7.10 (d, 1H), 7.35 (t, 1H), 7.55 (d, 1H), 9.45 (bs, 1H); ^{13}C NMR (75 MHz, acetone-d_6, 325 K) δ 56.30, 75.75, 113.01, 121.22, 130.28, 130.84, 142.60, 155.30, 156.20, high-resolution mass spectrum, *m/z* calcd for $C_{13}H_{13}Cl_6N_2O_5$ (M + H)$^+$ 486.8956, found 486.8957.

Typical Procedure for the Bisamination. 1-[2-Methoxy-5-[1,2-bis[(2,2,2-trichloroethyloxy)carbonyl]hydrazino]-phenyl]-1,2-hydrazinedicarboxylic Acid Bis(2,2,2-trichloroethyl) Ester (17). To a solution of anisole (99 mg, 0.93 mmol) in CH_2Cl_2 (4.6 mL) were added CF_3SO_3H (8 μL, 0.093 mmol) and BTCEAD (1.06 g, 2.79 mmol). After a period of 5 h at 25 °C and standard workup procedure with NH_4OAc, the title compound was purified by flash chromatography (20% ethyl acetate in hexane) to afford 691 mg (85%) of a yellow foam: ^{1}H NMR (400 MHz, acetone-d_6, 325 K) δ 3.91 (3H, S). 4.86 to 4.90 (m, 8H), 7.13 (d, 1H), 7.57 (bd, 1H), 7.77 (bs, 1H), 9.53 (bs, 1H), 9.71 (bs, 1H); ^{13}C NMR (100 MHz, acetone-d_6, 325 K) δ 56.54, 75.66, 76.34, 76.38, 96.04, 96.21, 112.58, 127.16, 130.56, 134.92, 153.87, 154.26, 155.23. Anal. Calcd for $C_{19}H_{16}N_4O_9Cl_6$: C, 26.24; H, 1.85; N, 6.44. Found: C, 26.23; H, 1.82; N, 6.20.

1-[2,4-Dimethoxy-5-[1,2-bis[(2,2,2-trichloroethyloxy)carbonyl]hydrazino]phenyl]-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester (30): ^{1}H NMR (400 MHz, acetone-d_6, 325 K) δ 3.94 (s, 3H), 4.86 (8H, s), 6.81 (s, 1H), 7.81 (s, 1H), 9.45 (bs, 1H); ^{13}C NMR (100 MHz, acetone-d_6, 325 K) δ 56.61, 75.56, 76.31, 96.15, 97.27, 122.84, 130.48, 154.61, 156.13, 157.42. Anal. Calcd for $C_{20}H_{18}Cl_{12}N_4O_{10}$: C, 26.70; H, 2.02; N, 6.23. Found: C, 26.72; H, 2.07; N, 6.13.

1-[4,5-Dimethoxy-2-[1,2-bis[(2,2,2-trichloroethyloxy)carbonyl]hydrazino]phenyl]-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester (32): ^{1}H NMR (400 MHz, acetone-d_6, 325 K) δ 3.85 (s, 6H), 4.85 to 4.90 (m, 8H), 7.18 (s, 2H), 8.81 (bs, 1H), 9.50 (bs, 1H); ^{13}C NMR (100 MHz, acetone-d_6, 325 K) δ 56.55, 56.81, 57.03, 75.74, 76.42, 76.67, 76.94, 95.41, 96.03, 100.30, 113.56, 131.44, 147.27, 150.52, 150.95, 154.26, 155.67. Anal. Calcd for $C_{20}H_{18}Cl_{12}N_4O_{10}$: C, 26.70; H, 1.79; N, 6.23. Found: C, 26.67; H, 1.98; N, 6.18.

2,5-Dimethoxyacetanilide (25): mp 92 °C (ethyl acetate/hexane); ^{1}H NMR (200 MHz, acetone-d_6) δ 2.15 (s, 3H), 3.72 (s, 3H), 3.80 (s, 3H), 6.55 (dd, 1H), 6.90 (d, 1H), 8.09 (d, 1H), 8.50 (bs, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 24.45, 55.72, 56.55, 107.64, 107.76, 111.86, 130.05, 143.44, 154.58, 168.89. Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.66; N, 7.18. Found: C, 61.47; H, 6.62; N, 6.97.

2-Acetamido-4,5-dimethoxyacetanilide (33): mp 201–202 °C (ethyl acetate–hexane); ^{1}H NMR (200 MHz, acetone-d_6) δ 2.06 (s, 6H), 3.75 (s, 6H), 7.15 (s, 2H), 8.84 (bs, 2H); ^{13}C NMR (100 MHz, acetone-d_6 + DMSO-d_6) δ 24.14, 56.49, 109.83, 124.86, 147.03, 169.34, high-resolution mass spectrum, *m/z* calcd for $C_{12}H_{17}N_2O_4$, (M + H)$^+$ 253.1188, found 253.1188.

5-Acetamido-2-methoxyacetanilide (28): ^{1}H NMR (200 MHz, acetone-d_6) δ 2.06 (s, 3H), 2.13 (s, 3H), 3.82 (s, 3H), 6.89 (d, 1H), 7.64 (dd, 1H), 8.25 (d, 1H), 8.48 (bs, 1H), 9.02 (bs, 1H). ^{13}C NMR (75 MHz, acetone-d_6 + DMSO-d_6) δ 24.00, 24.33, 56.20, 111.07, 112.96, 115.114, 128.67, 133.58, 145.35, 168.40, 168.80, high resolution mass spectrum, *m/z* calcd for $C_{11}H_{15}N_2O_3$ (M + H)$^+$ 223.1082, found 223.1082.

5-Acetamido-2,4-dimethoxyacetanilide (31): ^{1}H NMR (200 MHz, acetone-d_6) δ 2.08 (s, 6H), 3.83 (s, 6H), 6.73 (s, 1H), 8.28 (bs, 2H), 8.84 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 23.66, 56.27, 97.00, 119.15, 120.26, 148.03, 168.26, high-resolution mass spectrum, *m/z*, calcd for $C_{12}H_{17}N_2O_4$ (M + H)$^+$ 253.1188, found 253.1188.

5-Bromo-2-methoxyacetanilide (26): ^{1}H NMR (200 MHz, acetone-d_6) δ 2.15 (s, 3H), 3.86 (s, 3H), 6.95 (d, 1H), 7.16 (dd, 1H), 8.57 (d, 1H), 8.63 (bs, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 24.41, 56.40, 112.03, 113.04, 123.01, 126.40, 130.72, 148.44, 169.25. Anal. Calcd for $C_9H_{10}BrNO_2$: C, 44.29; H, 4.13; N, 5.74. Found: C, 44.10; H, 4.06; N, 5.64.

5,7-Dimethoxyindazole (27): mp 167–169 °C (ethyl acetate); ^{1}H NMR (200 MHz, acetone-d_6) δ 3.81 (s, 3H), 3.95 (s, 3H), 6.47 (d, 1H), 6.72 (d, 1H), 7.87 (s, 1H), 12.26 (bs, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 55.75, 55.82, 91.75, 98.68, 125.23, 129.37, 134.08, 146.68, 156.47. Anal. Calcd for $C_9H_{10}N_2O_2$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.40; H, 5.62; N, 15.62.

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