Supporting Information St. Amant, Frazier, Newmeyer, Fruehauf and Read de Alaniz*

Direct Synthesis of Anilines and Nitrosobenzenes from Phenols

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Supporting Information – Table of Contents

Materials and Methods. Unless stated otherwise, reactions were conducted under an atmosphere of N_2 using reagent grade solvents. MeOH, EtOH, and iPrOH were stored over 3Å molecular sieves. All commercially obtained reagents were used as received. The phenols we prepared are reported in **SI-1** to **SI-15**. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with *p*-anisaldehyde or potassium permanganate. Flash column chromatography was performed using normal phase silica gel (60 Å, 0.040 – 0.063 mm, Geduran). ^{1}H NMR spectra were recorded on Varian spectrometers (400, 500, or 600 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Spectrometers (100, 125, or 150 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm). Mass spectra were obtained from the UC Santa Barbara Mass Spectrometry Facility on a (Waters Corp.) GCT Premier high resolution Time-of-flight mass spectrometer with an electron ionization (EI) source.

General Procedure **A**: Reaction with 4-substituted phenols

PIDA (0.71 g, 2.2 mmol, 1.1 equiv) was suspended in MeOH (10 mL) and cooled on an ice bath. The phenol (2.0 mmol, 1 equiv) was dissolved in MeOH (10 mL) and added dropwise over 1 min. The ice bath was removed and the reaction mixture was stirred for 30 min or until consumption of the starting material. The reagents Et_3N (2.5 mL, 18 mmol, 9 equiv), H_2O (1 mL), and ethyl glycinate hydrochloride (1.95 g, 14 mmol, 7 equiv) were added sequentially and the reaction mixture was stirred at 40 °C overnight or until consumption of the quinone. The solvent was evaporated, DCM (100 mL) was added then transferred to a separatory funnel. The organic layer was extracted with $HCl_{(aq)}$ (1 M, 6 x 10 mL). The aqueous layers were combined, neutralized with saturated $NaHCO_{3(aq)}$ (140 mL), and extracted with DCM (3 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The yield was determined through ^{1}H NMR using an internal standard.

General Procedure **B**: Reaction with 4-unsubstituted phenols

PIDA (1.35 g, 4.2 mmol, 2.1 equiv) was suspended in MeOH (10 mL) and cooled on an ice bath. The phenol (2.0 mmol, 1 equiv) was dissolved in MeOH (10 mL) and added dropwise over 1 min. The ice bath was removed and the reaction mixture was stirred for 30 min or until consumption of the starting material. The reagents Et_3N (2.5 mL, 18 mmol, 9 equiv), H_2O (1 mL), and ethyl glycinate hydrochloride (1.95 g, 14 mmol, 7 equiv) were added sequentially and the reaction mixture was stirred at 40 °C overnight or until consumption of the quinone. The solvent was evaporated, DCM (100 mL) was added then transferred to a separatory funnel. The organic layer extracted with $HCl_{(aq)}$ (1 M, 6 x 10 mL). The aqueous layers were combined, neutralized with saturated $NaHCO_{3(aq)}$ (140 mL), and extracted with DCM (3 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The yield was determined through ^{1}H NMR using an internal standard.

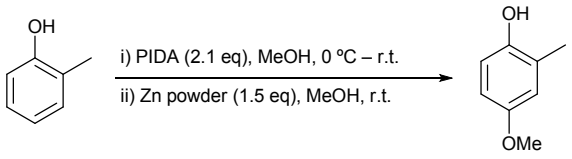
General Procedure **C**:

PIDA (81 mg, 0.25 mmol, 1 equiv) was suspended in MeOH (2.5 mL) and cooled on an ice bath. Phenol (0.25 mmol, 1 equiv) was added and the reaction mixture stirred at room temperature until consumption of the starting material (~30 min). Pyridine (40 μL, 0.50 mmol, 2 equiv) then hydroxylammonium sulfate (41 mg, 0.25 mmol, 1 equiv) were added and the reaction was stirred

until complete consumption of the quinone (overnight to 70 hr). The reaction was quenched with a saturated ammonium chloride solution and extracted with Et_2O (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 15:1 to 1:1) to yield the nitrosobenzene. Note: some of the nitrosobenzenes were found to be volatile, and care must be taken while removing solvent.

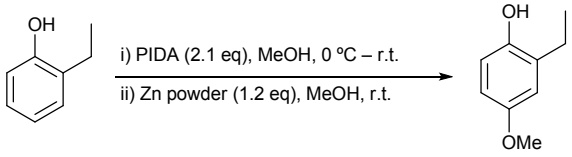
General Procedure for determining yield through ^1H NMR:
A known amount of dimethyl terephthalate (DMT) was weighed and added to the crude product. The mixture was dissolved in $CDCl_3$ and a ^1H NMR experiment was performed (relaxation delay set to 40 s). To determine the yield the integration for DMT's aromatic peak (8.09 ppm, 4H) is set to:
[4 * (mass DMT in mg) / 194.18] / (scale of reaction in mmol)

Gram-scale synthesis of **1**:
PIDA (6.76 g, 21.0 mmol, 1.05 equiv) was suspended in MeOH (90 mL) and cooled on an ice bath. 4-Methoxyphenol (2.48 g, 20.0 mmol, 1 equiv) was dissolved in MeOH (10 mL) and added dropwise over 2 min. The ice bath was removed and the reaction mixture was stirred for 30 min. The reagents Et_3N (11 mL, 80. mmol, 4 equiv), H_2O (5 mL), and ethyl glycinate hydrochloride (5.6 g, 40. mmol, 2 equiv) were added sequentially and the reaction mixture was stirred at 40 °C overnight. The solvent was evaporated until ~20 mL remained. DCM (50 mL) and H_2O (50 mL) were added and the pH was adjusted to 1-2 with $HCl_{(conc)}$ (~7 mL). The mixture was transferred to a separatory funnel and the layers separated. The aqueous layer's pH was adjusted to 7-8 with solid Na_2CO_3 then extracted with DCM (2 x 50 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 2:1 → 1:1, with 2% Et_3N) to yield **1** (1.41 g, 57%) as a flaky orange solid.



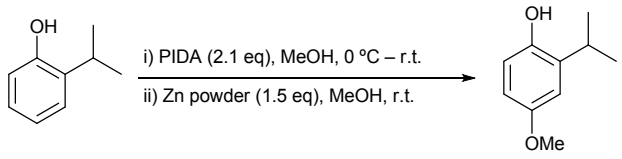
SI-1

4-Methoxy-2-methylphenol (**SI-1**): PIDA (6.8 g, 21 mmol, 2.1 eq) was added to MeOH (90 mL) and cooled on an ice bath. *o*-Cresol (1.08 g, 10.0 mmol, 1 eq) was dissolved in MeOH (10 mL) and added dropwise over 2 min with vigorous stirring. The ice bath was removed and the reaction mixture was stirred 30 min. The reaction mixture was cooled on an ice bath and zinc powder (0.98 g, 15 mmol, 1.5 eq) was added in one portion. The reaction mixture was taken off of the ice bath and stirred 1 hr. The solvent was removed, Et_2O (100 mL) was added, and the solution was transferred to a separatory funnel. The solution was washed with water (50 mL), then extracted with $NaOH_{(aq)}$ (3 M, 2 x 20 mL). The combined basic layers were acidified with $HCl_{(aq)}$ (1 M, 140 mL), then extracted with DCM (3 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 6:1 → 4:1) to yield **SI-1** (0.546 g, 40%) as white solid. Spectral data matched that of literature reported data.[1] Rf (Hexane:EtOAc, 4:1): 0.34; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 - 6.68 (m, 2 H), 6.64 (dd, *J* = 2.7, 8.6 Hz, 1 H), 4.35 (br. s., 1 H), 3.76 (s, 3 H), 2.25 (s, 3 H) ppm.



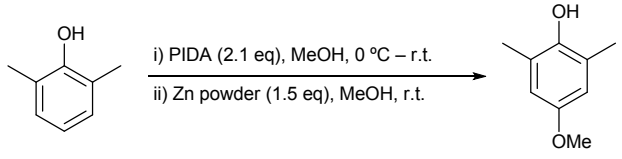
SI-2

2-Ethyl-4-methoxyphenol (**SI-2**): PIDA (2.1 g, 6.6 mmol, 1.1 eq) was added to MeOH (55 mL) and cooled on an ice bath. 2-Ethylphenol (0.72 mL, 6.0 mmol, 1 eq) was dissolved in MeOH (5 mL) and added dropwise over 5 min with vigorous stirring. The reaction mixture was taken off of the ice bath, stirred for 1 hr, a second portion of PIDA (1.9 g, 6.0 mmol, 1 eq) was added and stirring continued for 30 min. The reaction mixture was cooled on an ice bath and zinc powder (0.47 g, 7.2 mmol, 1.2 eq) was added in one portion. The reaction mixture was taken off of the ice bath and stirred 1 hr. The reaction mixture was filtered through Celite® and the solvent removed. EtOAc (50 mL) and $HCl_{(aq)}$ (1 M, 50 mL) were added, the solution was transferred to a separatory funnel and the layers separated. The aqueous layer was extracted again with EtOAc (50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 6:1) to yield **SI-2** (0.517 g, 57%). Spectral data matched that of literature reported data.[2] Rf (Hexane:EtOAc, 4:1): 0.41; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 - 6.68 (m, 2 H), 6.67 - 6.61 (m, 1 H), 4.59 (br. s, 1 H), 3.77 (s, 3 H), 2.62 (q, *J* = 7.6 Hz, 2 H), 1.25 (t, *J* = 7.5 Hz, 3 H) ppm.



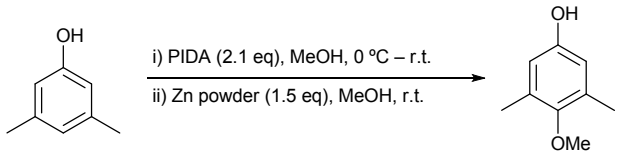
SI-3

2-Isopropyl-4-methoxyphenol (**SI-3**): PIDA (5.4 g, 17 mmol, 2.1 eq) was added to MeOH (70 mL) and cooled on an ice bath. 2-Isopropylphenol (1.1 mL, 8.0 mmol, 1 eq) was dissolved in MeOH (10 mL) and added dropwise over 2 min with vigorous stirring. The reaction mixture was taken off of the ice bath, stirred for 30 min. The reaction mixture was cooled on an ice bath and zinc powder (0.79 g, 12 mmol, 1.5 eq) was added in one portion. The reaction mixture was taken off of the ice bath and stirred 1 hr. The solvent was removed, Et_2O (50 mL) and $HCl_{(aq)}$ (1 M, 50 mL) were added, the solution was transferred to a separatory funnel, and the layers separated. The aqueous layer was extracted again with Et_2O (50 mL). The organic layers were combined and extracted with $NaOH_{(aq)}$ (1 M, 4 x 20 mL). The basic aqueous layers were combined, acidified with $HCl_{(aq)}$ (1 M, 100 mL), and extracted with DCM (2 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 6:1) to yield **SI-3** (0.50 g, 38%) as a peach oil. Spectral data matched that of literature reported data.[3] Rf (Hexane:EtOAc, 4:1): 0.42; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78 (d, *J* = 2.8 Hz, 1 H), 6.70 (d, *J* = 8.7 Hz, 1 H), 6.62 (dd, *J* = 2.8, 8.7 Hz, 1 H), 4.37 (br. s., 1 H), 3.78 (s, 3 H), 3.19 (spt, *J* = 6.9 Hz, 1 H), 1.26 (d, *J* = 6.6 Hz, 6 H) ppm.



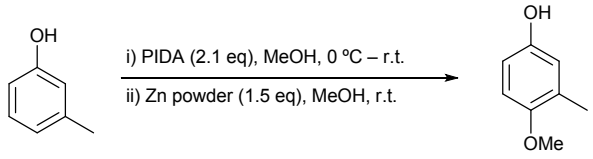
SI-4

4-Methoxy-2,6-dimethylphenol (**SI-4**): PIDA (5.4 g, 17 mmol, 2.1 eq) was added to MeOH (70 mL) and cooled on an ice bath. 2,6-Dimethylphenol (0.98 g, 8.0 mmol, 1 eq) was dissolved in MeOH (10 mL) and added dropwise over 2 min with vigorous stirring. The reaction mixture was taken off of the ice bath, stirred for 30 min. The reaction mixture was cooled on an ice bath and zinc powder (0.79 g, 12 mmol, 1.5 eq) was added in one portion. The reaction mixture was taken off of the ice bath and stirred 1 hr. The solvent was removed, Et_2O (50 mL) and $HCl_{(aq)}$ (1 M, 50 mL) were added, the solution was transferred to a separatory funnel, and the layers separated. The aqueous layer was extracted again with Et_2O (50 mL). The organic layers were combined and extracted with $NaOH_{(aq)}$ (1 M, 2 x 20 mL). The basic aqueous layers were combined, acidified with $HCl_{(aq)}$ (1 M, 50 mL), and extracted with DCM (2 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 15:1 → 9:1) to yield **SI-4** (0.40 g, 33%) as a white powder. Spectral data matched that of literature reported data.[4] Rf (Hexane:EtOAc, 9:1): 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (s, 2 H), 4.23 (br. s, 1 H), 3.75 (s, 3 H), 2.24 (s, 6 H) ppm.



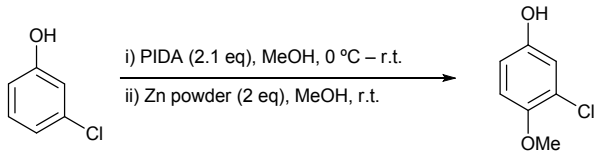
SI-5

4-Methoxy-3,5-dimethylphenol (**SI-5**): PIDA (5.4 g, 17 mmol, 2.1 eq) was added to MeOH (70 mL) and cooled on an ice bath. 3,5-Dimethylphenol (0.98 g, 8.0 mmol, 1 eq) was dissolved in MeOH (10 mL) and added dropwise over 2 min with vigorous stirring. The reaction mixture was taken off of the ice bath, stirred for 30 min. The reaction mixture was cooled on an ice bath and zinc powder (0.79 g, 12 mmol, 1.5 eq) was added in one portion. The reaction mixture was taken off of the ice bath and stirred 1 hr. The solvent was removed, Et_2O (50 mL) and water (50 mL) were added, the solution was transferred to a separatory funnel, and the layers separated. The organic layer was extracted with $NaOH_{(aq)}$ (1 M, 2 x 40 mL). The basic aqueous layers were combined, acidified with $HCl_{(aq)}$ (1 M, 100 mL), and extracted with DCM (3 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 6:1) to yield **SI-5** (0.54 g, 44%). Spectral data matched that of literature reported data.[5] Rf (Hexane:EtOAc, 4:1): 0.31; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 2 H), 4.45 (br. s., 1 H), 3.68 (s, 3 H), 2.24 (s, 6 H) ppm.



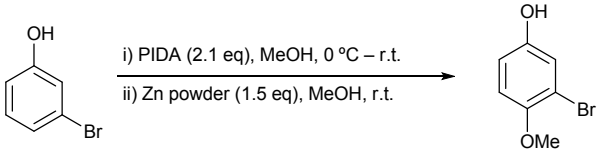
SI-6

4-methoxy-3-methylphenol (SI-6): PIDA (6.8 g, 21 mmol, 2.1 eq) was added to MeOH (100 mL) and cooled on an ice bath. *m*-Cresol (1.05 g, 10.0 mmol, 1 eq) was added dropwise over 2 min with vigorous stirring. The reaction mixture was taken off of the ice bath and stirred 30 min. The reaction mixture was cooled on an ice bath and zinc powder (0.98 g, 15 mmol, 1.5 eq) was added in one portion. The reaction mixture was taken off of the ice bath and stirred 1 hr. The solvent was removed, Et_2O (100 mL) was added, and the solution was transferred to a separatory funnel. The solution was washed with water (50 mL), then extracted with $NaOH_{(aq)}$ (3 M, 2 x 20 mL). The combined basic layers were acidified with $HCl_{(aq)}$ (1 M, 140 mL) and extracted with DCM (3 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 4:1) to yield **SI-6** (0.77 g, 56%). Spectral data matched that of literature reported data.[6] Rf (Hexane:EtOAc, 4:1): 0.26; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 - 6.59 (m, 3 H), 4.37 (br. s., 1 H), 3.79 (s, 3 H), 2.19 (s, 3 H) ppm.



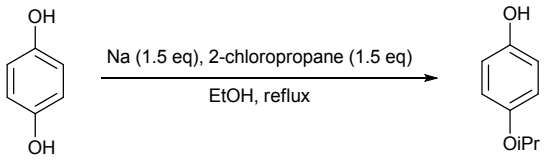
SI-7

3-Chloro-4-methoxyphenol (SI-7): PIDA (5.4 g, 17 mmol, 2.1 eq) was added to MeOH (70 mL) and cooled on an ice bath. 3-Chlorophenol (1.03 g, 8.00 mmol, 1 eq) was dissolved in MeOH (10 mL) and added dropwise over 2 min with vigorous stirring. The reaction mixture was taken off of the ice bath, stirred for 30 min. The reaction mixture was cooled on an ice bath and zinc powder (0.79 g, 12 mmol, 1.5 eq) was added in one portion. The reaction mixture was taken off of the ice bath and stirred 1 hr. Another portion of zinc powder (0.26 g, 4.0 mmol, 0.5 eq) was added and the reaction stirred for 30 min. The solvent was removed, Et_2O (50 mL) and water (50 mL) were added, the solution was transferred to a separatory funnel, and the layers separated. The organic layer was extracted again with Et_2O (50 mL). The organic layers were combined and extracted with $NaOH_{(aq)}$ (1 M, 2 x 40 mL). The basic aqueous layers were combined, acidified with $HCl_{(aq)}$ (1 M, 100 mL), and extracted with DCM (2 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 6:1 → 4:1) to yield **SI-7** (0.30 g, 24%). Spectral data matched that of literature reported data.[7] Rf (Hexane:EtOAc, 4:1): 0.24; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (d, *J* = 3.1 Hz, 1 H), 6.82 (d, *J* = 8.8 Hz, 1 H), 6.71 (dd, *J* = 3.1, 8.8 Hz, 1 H), 4.50 (br. s., 1 H), 3.85 (s, 3 H) ppm.



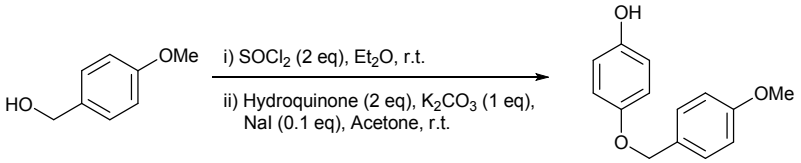
SI-8

3-Bromo-4-methoxyphenol (SI-8): PIDA (5.4 g, 17 mmol, 2.1 eq) was added to MeOH (70 mL) and cooled on an ice bath. 3-Bromophenol (1.38 g, 8.00 mmol, 1 eq) was dissolved in MeOH (10 mL) and added dropwise over 2 min with vigorous stirring. The reaction mixture was taken off of the ice bath, stirred for 30 min. The reaction mixture was cooled on an ice bath and zinc powder (0.79 g, 12 mmol, 1.5 eq) was added in one portion. The reaction mixture was taken off of the ice bath and stirred 1 hr. The solvent was removed, Et_2O (50 mL) and water (50 mL) were added, the solution was transferred to a separatory funnel, and the layers separated. The organic layer was extracted with $NaOH_{(aq)}$ (1 M, 2 x 40 mL). The basic aqueous layers were combined, acidified with $HCl_{(aq)}$ (1 M, 100 mL), and extracted with DCM (2 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 6:1 → 4:1) to yield **SI-8** (0.42 g, 26%). Spectral data matched that of literature reported data.[8] Rf (Hexane:EtOAc, 4:1): 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 2.7 Hz, 1 H), 6.83 - 6.74 (m, 2 H), 4.57 (br. s., 1 H), 3.85 (s, 3 H) ppm.



SI-9

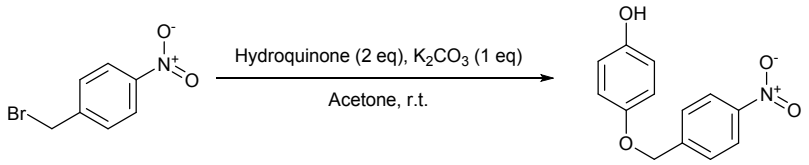
4-Isopropoxyphenol (SI-9): Sodium metal (0.69 g, 30. mmol, 1.5 eq) was added to EtOH (50 mL). The solution was stirred until complete reaction of the sodium (40 min). Hydroquinone (2.2 g, 20. mmol, 1 eq) and 2-chloropropane (2.7 mL, 30. mmol, 1.5 eq) were added and the reaction was heated to reflux overnight. The solvent was removed, DCM (100 mL) was added, and the solution was transferred to a separatory funnel. The organic layer was washed with $HCl_{(aq)}$ (0.4 M, 100 mL) then brine (2 x 50 mL). The organic layer was extracted with $NaOH_{(aq)}$ (1 M, 3 x 10 mL). The basic aqueous layers were combined, washed with DCM (30 mL), acidified with $HCl_{(aq)}$ (1 M, 40 mL), and extracted with DCM (2 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed to yield **SI-9** (0.89 g, 29%). Spectral data matched that of literature reported data.[9] Rf (Hexane:EtOAc, 2:1): 0.53; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 - 6.78 (m, 2 H), 6.78 - 6.73 (m, 2 H), 4.49 (s, 1 H), 4.41 (spt, J = 6.1 Hz, 1 H), 1.31 (d, J = 6.3 Hz, 6 H) ppm.



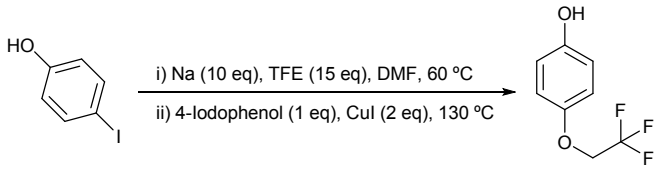
SI-10

4-(4-Methoxybenzyloxy)phenol (SI-10): To a solution of 4-methoxybenzyl alcohol (1.25 mL, 10.0 mmol, 1 eq) in Et_2O (20 mL) was added thionyl chloride (1.5 mL, 20. mmol, 2 eq) dropwise. The reaction mixture was stirred for 5 hr. Water (20 mL) was added carefully and the reaction mixture was stirred for 5 min then transferred to a separatory funnel. The layers were separated then the aqueous layer was extracted again with DCM (2 x 20 mL). The organic layers were combined, washed with water (20 mL), then brine (20 mL). The organic layers was dried over $MgSO_4$, filtered, and the solvent removed to yield 4-methoxybenzyl chloride (1.52 g, 97%) as a clear and colorless oil.

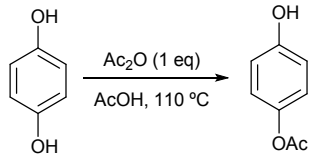
The intermediate was suspended in acetone (20 mL), then hydroquinone (2.2 g, 20. mmol, 2 eq), K_2CO_3 (1.4 g, 10 mmol, 1 eq), and NaI (0.15 g, 1.0 mmol, 0.1 eq) were added. The reaction mixture was stirred overnight, filtered through Celite® with acetone, and then the solvent was removed. EtOAc (50 mL) was added then transferred to a separatory funnel. The organic layer was washed with water and brine (3 x 50 mL). The organic layer was dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 3:1) to yield **SI-10** (0.89 g, 39% from 4-methoxybenzyl alcohol) as a crystalline peach solid. Spectral data matched that of literature reported data.[10] Rf (Hexane:EtOAc, 2:1): 0.38; ^{1}H NMR (400 MHz, DMSO) δ 8.90 (s, 1 H), 7.36 - 7.30 (m, 2 H), 6.96 - 6.89 (m, 2 H), 6.84 - 6.76 (m, 2 H), 6.72 - 6.61 (m, 2 H), 4.89 (s, 2 H), 3.75 (s, 3 H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 158.8, 151.2, 151.2, 129.4, 129.3, 115.8, 115.7, 113.7, 69.5, 55.0 ppm.



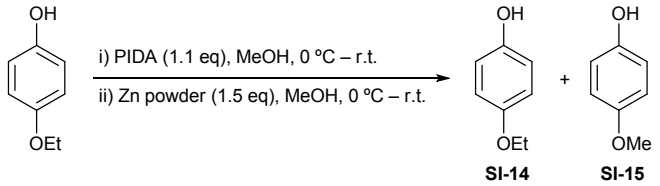
4-(4-Nitrobenzyloxy)phenol (**SI-11**): Hydroquinone (2.2 g, 20. mmol, 2 eq) and K_2CO_3 (1.4 g, 10 mmol, 1 eq) were added to acetone (20 mL). 4-Nitrobenzyl bromide (2.16 g, 10.0 mmol, 1 eq) was added in portions and the reaction mixture was stirred overnight. The reaction mixture was filtered through Celite® with acetone, and then the solvent was removed. EtOAc (50 mL) was added then transferred to a separatory funnel. The organic layer was washed with water (3 x 50 mL). The organic layer was dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 2:1 → 1:1) to yield **SI-11** (0.91 g, 37%) as a yellow powder. Rf (Hexane:EtOAc, 1:1): 0.51; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.7 Hz, 2 H), 7.60 (d, *J* = 8.7 Hz, 2 H), 6.88 - 6.84 (m, 2 H), 6.81 - 6.77 (m, 2 H), 5.13 (s, 2 H), 4.44 (s, 1 H) ppm; ^{1}H NMR (400 MHz, DMSO) δ 9.00 (br. s., 1 H), 8.23 (d, *J* = 8.6 Hz, 2 H), 7.67 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 9.0 Hz, 2 H), 6.69 (d, *J* = 9.0 Hz, 2 H), 5.15 (s, 2 H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 151.7, 150.7, 146.9, 145.6, 128.1, 128.0, 123.5, 115.8, 68.6 ppm; HRMS (EI) Exact mass cald. for $C_{13}H_{11}NO_4$ $[M]^+$: 245.0688, found: 245.0679.



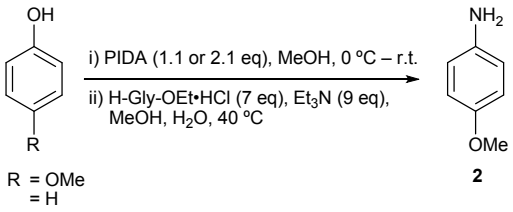
4-(2,2,2-Trifluoroethoxy)phenol (**SI-12**): Sodium metal (2.3 g, 0.10 mol, 10 eq) was added to DMF (100 mL). 2,2,2-Trifluoroethanol (7.3 mL, 0.10 mol, 10 eq) was added slowly, keeping the temperature ~20 °C with an ice bath. The solution was stirred for 1 hr, and then another portion of 2,2,2-trifluoroethanol (3.7 mL, 50. mmol, 5 eq) was added slowly. The solution was stirred at 60 °C until complete reaction of the sodium (20 min). CuI (3.8 g, 20. mmol, 2 eq), and 4-iodophenol (2.2 g, 10. mmol, 1 eq) were added and the reaction mixture was stirred at 130 °C for 6 hours. Most of the solvent was removed (< 30 mL remained) and water (100 mL) was added. The solution was filtered through Celite®, acidified (pH ~1-2) with $HCl_{(aq)}$ (1 M, ~100 mL), and extracted with DCM (3 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed. The residue was subjected to flash column chromatography (Hexane:EtOAc, 4:1 → 3:1) to yield **SI-12** (0.14 g, 7%). Spectral data matched that of literature reported data.[11] Rf (Hexane:EtOAc, 4:1): 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 - 6.83 (m, 2 H), 6.83 - 6.75 (m, 2 H), 4.58 (br. s., 1 H), 4.30 (q, *J* = 8.2 Hz, 2 H) ppm.



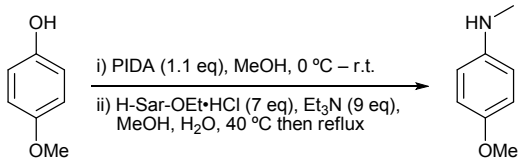
4-Hydroxyphenyl acetate (SI-13): Hydroquinone (2.2 g, 20. mmol, 2 eq) was added to AcOH (5 mL). Ac_2O (0.47 g, 5.0 mmol, 0.5 eq) was added dropwise, the reaction mixture stirred for 30 min at 110 °C, Ac_2O (0.47 g, 5.0 mmol, 0.5 eq) was added dropwise and the reaction mixture was stirred a further 1.5 hr at 110 °C. The solvent was removed and toluene (10 mL) was added. The solution was sonicated for 2 min, stirred for 5 min, filtered, and the solvent removed to yield **SI-13** (1.3 g, 85%). Spectral data matched that of literature reported data.[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 - 6.90 (m, 2 H), 6.80 - 6.75 (m, 2 H), 5.04 (br. s., 1 H), 2.29 (s, 3 H) ppm.



4-Ethoxyphenol (**SI-14**) & 4-Methoxyphenol (**SI-15**): PIDA (0.71 g, 2.2 mmol, 1.1 eq) was added to MeOH (10 mL) and cooled on an ice bath. 4-Ethoxyphenol (0.28 g, 2.0 mmol, 1 eq) dissolved in MeOH (10 mL) was added dropwise over 2 min with vigorous stirring. The reaction mixture was taken off of the ice bath and stirred 30 min. The reaction mixture was cooled on an ice bath and zinc powder (0.20 g, 3.0 mmol, 1.5 eq) was added in one portion. The reaction mixture was taken off of the ice bath and stirred 1 hr. The solvent was removed, Et_2O (100 mL) was added, and the solution was transferred to a separatory funnel. The solution was washed with water (50 mL), then extracted with $NaOH_{(aq)}$ (3 M, 40 mL). The basic layer was acidified with $HCl_{(aq)}$ (1 M, 140 mL) and extracted with DCM (3 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed yielding **SI-14** (53%) and **SI-15** (28%) (determined through ^{1}H NMR using an internal standard). Spectral data matched that of authentic samples.

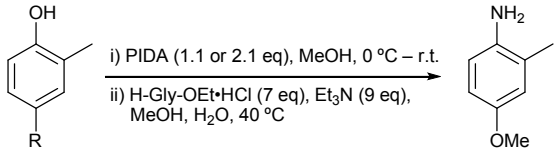


4-Methoxyaniline (2): Obtained using General Procedure **A** from 4-methoxyphenol (85%) or General Procedure **B** from phenol (44%). Spectral data matched that of literature reported data.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68 (td, J = 3.4, 8.8 Hz, 2 H), 6.56 (td, J = 3.4, 8.8 Hz, 2 H), 3.66 (s, 3 H), 3.34 (br. s., 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 139.9, 115.9, 114.3, 55.1 ppm.



7

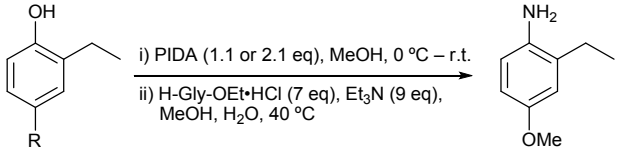
4-Methoxy-N-methylaniline (7): Obtained using General Procedure **A** from 4-methoxyphenol using sarcosine ethyl ester hydrochloride (44%). The second step was stirred at 40 °C overnight, then at reflux for 5 hr. Spectral data matched that of literature reported data.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, J = 9.0 Hz, 2 H), 6.50 (d, J = 9.0 Hz, 2 H), 3.66 (s, 3 H) 3.16 (br. s., 1 H), 2.71 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 143.4, 114.5, 113.2, 55.4, 31.2 ppm.



R = OMe (**SI-1**)
= H

8

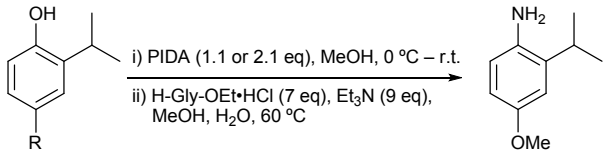
4-Methoxy-2-methylaniline (**8**): Obtained using General Procedure **A** from **SI-1** (93%) or General Procedure **B** from 2-methylphenol (56%). Spectral data matched that of literature reported data.[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 - 6.53 (m, 3 H), 3.69 (s, 3 H), 3.35 (br. s., 2 H), 2.11 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 138.0, 123.4, 115.8, 115.5, 111.6, 55.1, 17.1 ppm.



R = OMe (**SI-2**)
= H

9

2-Ethyl-4-methoxyaniline (**9**): Obtained using General Procedure **A** from **SI-2** (73%) or General Procedure **B** from 2-ethylphenol (55%). Spectral data matched that of literature reported data .[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 1 H), 6.62 - 6.56 (m, 2 H), 3.72 (s, 3 H), 3.40 (br. s., 2 H), 2.47 (q, J = 7.4 Hz, 2 H), 1.22 (t, J = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 137.4, 129.4, 116.0, 114.1, 111.3, 55.2, 23.9, 12.7 ppm.

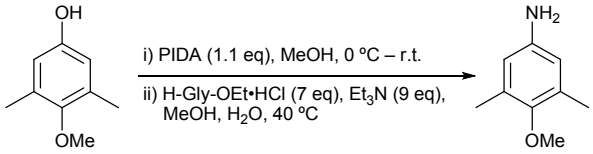


R = OMe (**SI-3**)
= H

10

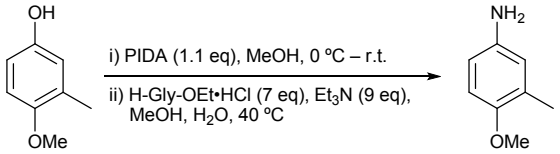
2-Isopropyl-4-methoxyaniline (10): Obtained using General Procedure **A** from **SI-3** (65%) or General Procedure **B** from 2-isopropylphenol (65%). The second step was performed at 60 °C. Spectral data matched that of literature reported data .[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 (d, J = 2.3 Hz, 1 H), 6.60 - 6.51 (m, 2 H), 3.68 (s, 3 H), 3.52 (br. s., 2 H), 2.86 (spt, J = 6.8 Hz, 1 H),

1.19 (d, J = 7.0 Hz, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 136.8, 133.6, 116.5, 111.7, 110.9, 55.3, 27.6, 22.0 ppm.



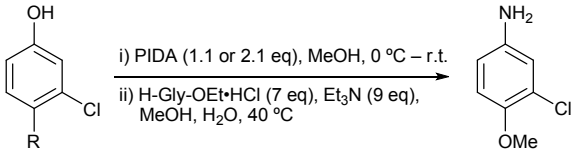
SI-5 **12**

4-Methoxy-3,5-dimethylaniline (12): Obtained using General Procedure **A** from **SI-5** (66%). The second step required 2 days to react to completion. Spectral data matched that of literature reported data.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (s, 2 H), 3.65 (s, 3 H), 3.46 (br. s., 2 H), 2.20 (s, 6 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 142.0, 131.0, 115.0, 59.6, 15.8 ppm.



SI-6 **13**

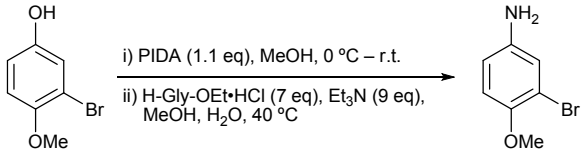
4-Methoxy-3-methylaniline (13): Obtained using General Procedure **A** from **SI-6** (78%). Spectral data matched that of literature reported data.[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (d, J = 8.6 Hz, 1 H), 6.51 - 6.43 (m, 2 H), 3.72 (s, 3 H), 3.32 (br. s., 2 H), 2.15 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 139.5, 126.9, 118.0, 112.6, 111.1, 55.4, 15.8 ppm.



R = OMe (**SI-7**)
= H

14

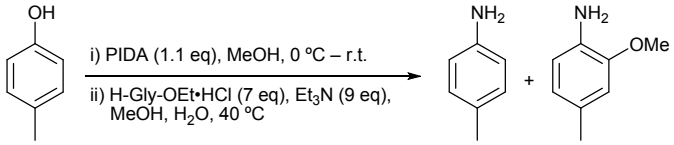
3-Chloro-4-methoxyaniline (14): Obtained using General Procedure **A** at 1 mmol scale from **SI-7** (57%) or General Procedure B from 3-chlorophenol (20%). Spectral data matched that of an authentic sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 - 6.63 (m, 2 H), 6.48 (dd, J = 2.5, 8.8 Hz, 1 H), 3.73 (s, 3 H), 3.38 (br. s., 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 140.8, 122.6, 116.9, 114.0, 113.7, 56.6 ppm.



SI-8 **15**

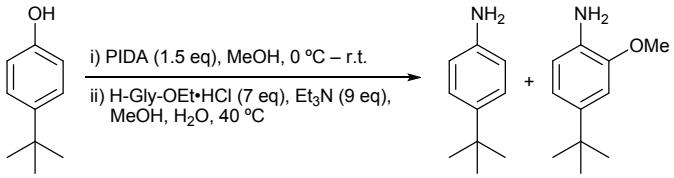
3-Bromo-4-methoxyaniline (15): Obtained using General Procedure **A** from **SI-8** (64%). Spectral data matched that of literature reported data.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, J

= 2.3 Hz, 1 H), 6.60 (d, *J* = 8.6 Hz, 1 H), 6.46 (dd, *J* = 2.3, 8.6 Hz, 1 H), 3.65 (s, 3 H), 3.33 (br. s., 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 141.1, 119.5, 114.5, 113.2, 111.6, 56.4 ppm.



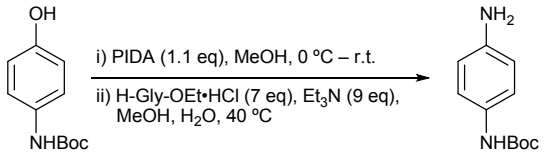
17a **17b**

***p*-Toluidine (17a) and 2-methoxy-4-methylaniline (17b):** Obtained using General Procedure **A** from *p*-cresol giving **17a** (59%) and **17b** (11%). The second step required 2 days to react to completion. Spectral data matched that of literature reported data.[21, 22] **17a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.8 Hz, 2 H), 6.59 (d, *J* = 8.2 Hz, 2 H), 3.69 (br. s., 2 H), 2.26 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 129.3, 126.9, 114.8, 20.0 ppm. **17b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 - 6.61 (m, 3 H, overlaps with **17a**), 3.81 (s, 3 H), 3.69 (br. s., 2 H, overlaps with **17a**), 2.30 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 133.2, 127.4, 120.8, 114.6, 111.1, 54.9, 20.5 ppm.



18a **18b**

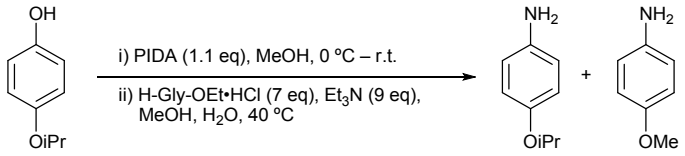
4-*tert*-Butylaniline (18a) and 4-*tert*-butyl-2-methoxyaniline (18b): Obtained using General Procedure **A** with 1.5 equivalents of PIDA from 4-*tert*-butylphenol. The residue was subjected to flash column chromatography (Hexane:EtOAc, 4:1, with 1% Et_3N) yielding **18a** (20%) as a clear and colorless oil and **18b** (19%) as a white solid. Spectral data matched that of literature reported data.[23, 24] **18a**: Rf (Hexane:EtOAc, 4:1): 0.30; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 - 7.21 (m, 2 H), 6.70 - 6.66 (m, 2 H), 3.60 (s., 2 H), 1.33 (br. s., 9 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7, 141.3, 126.0, 114.9, 33.8, 31.5 ppm. **18b**: Rf (Hexane:EtOAc, 4:1): 0.36; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (d, *J* = 2.1 Hz, 1 H), 6.85 (dd, *J* = 2.1, 8.2 Hz, 1 H), 6.69 (d, *J* = 8.2 Hz, 1 H), 3.89 (s, 3 H), 3.72 (br. s., 2 H), 1.33 (s, 9 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.0, 141.8, 133.6, 117.6, 114.7, 108.2, 55.5, 34.2, 31.6 ppm.



19

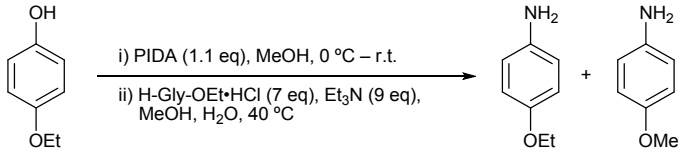
***tert*-Butyl 4-aminophenylcarbamate (19):** Obtained using General Procedure **A** from *tert*-butyl 4-hydroxyphenylcarbamate. The residue was subjected to flash column chromatography (Hexane:EtOAc, 2:1, with 1% Et_3N) to yield **19** (34%) as a flaky white solid. Spectral data matched that of literature reported data.[25] Rf (Hexane:EtOAc, 2:1): 0.16; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (br. d, *J* = 7.8 Hz, 2 H), 6.67 - 6.61 (m, 2 H), 6.26 (br. s., 1 H), 3.57 (br. s., 2 H),

1.51 (s, 9 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 142.3, 129.6, 120.9, 115.5, 79.9, 28.3 ppm.



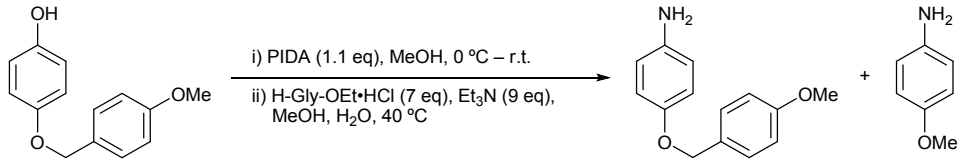
SI-9 **24** **2**

Entry 1: 4-Isopropoxyaniline (24) and 4-methoxyaniline (2): Obtained using General Procedure **A** from **SI-9** giving a mixture of **24** (75%)[26] and **2** (10%). Spectral data matched that of literature reported data. **24**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 - 6.63 (m, 2 H, overlaps with **2**), 6.59 - 6.48 (m, 2 H, overlaps with **2**), 4.29 (spt, *J* = 6.1 Hz, 1 H), 3.39 (br. s., 2 H, overlaps with **2**), 1.22 (d, *J* = 6.3 Hz, 6 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 140.1, 117.3, 115.8, 70.5, 21.7 ppm.



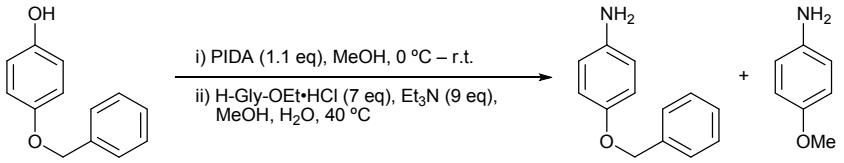
25 **2**

Entry 2: 4-Ethoxyaniline (25) and 4-methoxyaniline (2): Obtained using General Procedure **A** from 4-ethoxyphenol giving a mixture of **25** (72%)[27] and **2** (21%). Spectral data matched that of literature reported data. **25**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 (d, *J* = 8.6 Hz, 2 H, overlaps with **2**), 6.57 (d, *J* = 8.6 Hz, 2 H, overlaps with **2**), 3.90 (q, *J* = 7.0 Hz, 2 H), 3.43 (br. s., 2 H, overlaps with **2**), 1.33 (t, *J* = 7.0 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 139.8, 115.9, 115.2, 63.6, 14.6 ppm.

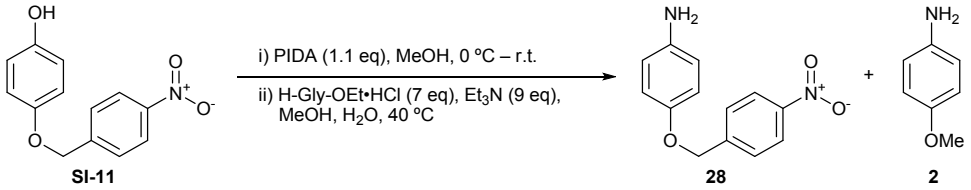


SI-10 **26** **2**

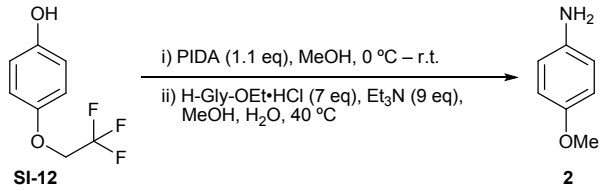
Entry 3: 4-(4-Methoxybenzyloxy)aniline (26) and 4-methoxyaniline (2): Obtained using General Procedure **A** from **SI-10** giving a mixture of **26** (37%)[28] and **2** (45%). Spectral data matched that of literature reported data. **26**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2 H), 6.91 (d, *J* = 8.6 Hz, 2 H), 6.75 (d, *J* = 8.6 Hz, 2 H), 6.67 - 6.60 (m, 2 H, overlaps with **2**), 4.90 (s, 2 H), 3.80 (s, 3 H), 3.32 (br. s., 2 H, overlaps with **2**) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 151.7, 139.8, 129.3, 129.1, 116.2, 115.8, 113.7, 70.3, 55.1 ppm.



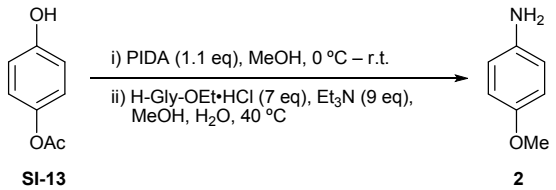
Entry 4: 4-(Benzyloxy)aniline (27) and 4-methoxyaniline (2): Obtained using General Procedure **A** from 4-benzyloxyphenol giving a mixture of **27** (33%)[29] and **2** (52%). Spectral data matched that of literature reported data. **27**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.23 (m, 5 H), 6.78 (d, *J* = 9.0 Hz, 2 H), 6.56 (d, *J* = 9.0 Hz, 2 H, overlaps with **2**), 4.92 (s, 2 H), 3.33 (br. s., 2 H, overlaps with **2**) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 140.1, 137.1, 128.0, 127.3, 127.0, 115.8, 115.5, 70.1 ppm.



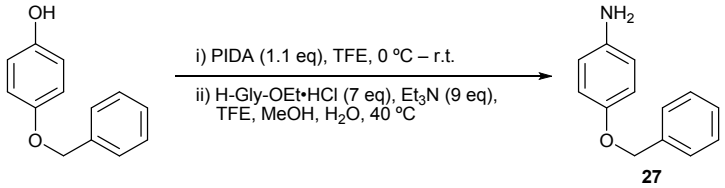
Entry 5: 4-(4-Nitrobenzyloxy)aniline (28) and 4-methoxyaniline (2): Obtained using General Procedure **A** from **SI-11** giving a mixture of **28** (5%)[30] and **2** (57%). Spectral data matched that of literature reported data. **19**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 2 H), 7.59 (d, *J* = 8.2 Hz, 2 H), 6.79 (d, *J* = 8.6 Hz, 2 H), 6.65 (d, *J* = 8.6 Hz, 2 H), 5.09 (s, 2 H), 3.18 (br. s., 2 H, overlaps with **2**) ppm; ^{1}H NMR (400 MHz, DMSO) δ 8.23 (d, *J* = 8.6 Hz, 2 H), 7.67 (d, *J* = 8.6 Hz, 2 H), 6.74 (d, *J* = 8.6 Hz, 2 H), 6.54 - 6.49 (m, 2 H, overlaps with **1**), 5.11 (s, 2 H), 4.64 (s, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 148.4, 145.0, 140.6, 127.5, 123.7, 116.4, 115.9, 69.3 ppm.



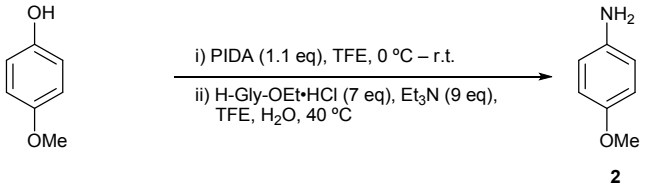
Entry 6: 4-Methoxyaniline (1): Obtained using General Procedure **A** from **SI-12** at 0.5 mmol scale giving **2** (76%) as the sole product. Spectral data matched that of literature reported data.



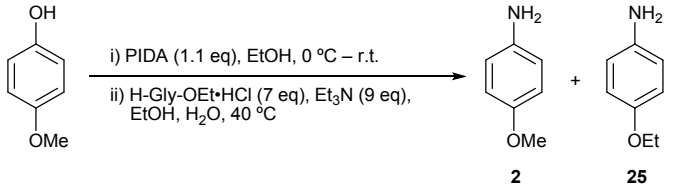
Entry 7: 4-Methoxyaniline (1): Obtained using General Procedure **A** from **SI-13** giving **2** (21%) as the sole product. Spectral data matched that of literature reported data.



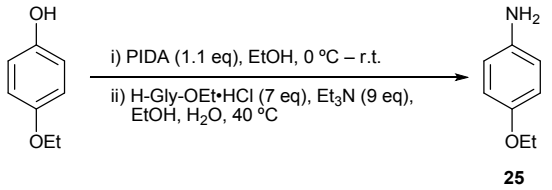
Entry 8: 4-(Benzyloxy)aniline (27): Obtained using General Procedure **A** from 4-benzyloxyphenol at 0.5 mmol scale. The first step was performed in 2,2,2-trifluoroethanol (TFE), the second step was performed in TFE:methanol (1:1) at room temperature, giving **27** (44%) as the sole product. Spectral data matched that of literature reported data.



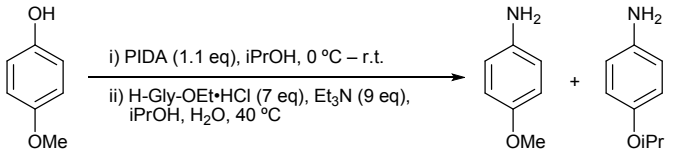
Entry 9: 4-Methoxyaniline (2): Obtained using General Procedure **A** from 4-methoxyphenol at 0.5 mmol scale. Both steps of the reaction were performed in TFE, giving **2** (43%) as the sole product. Spectral data matched that of literature reported data.



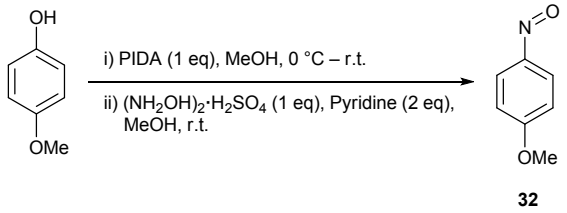
Entry 10: 4-Methoxyaniline (**2**) & 4-Ethoxyaniline (**25**)**:** Obtained using General Procedure **A** from 4-methoxyphenol with the reaction performed in ethanol giving a mixture of **2** (16%) and **25** (67%). Spectral data matched that of literature reported data.



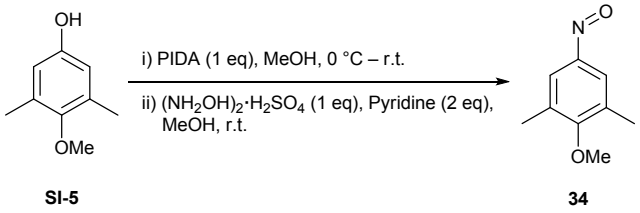
Entry 11: 4-Ethoxyaniline (25): Obtained using General Procedure **A** from 4-ethoxyphenol with the reaction performed in ethanol giving **25** (82%). Spectral data matched that of literature reported data.



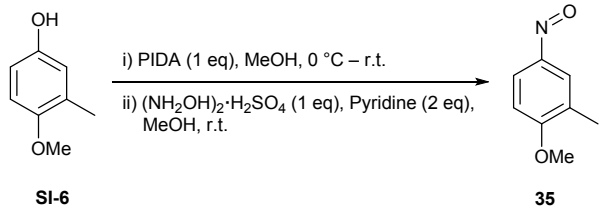
Entry 12: 4-Methoxyaniline (2) and 4-isopropoxyaniline (24): Obtained using General Procedure **A** from 4-methoxyphenol with the reaction performed in isopropanol giving a mixture of **24** (11%) and **2** (5%). There were significant solubility issues in both steps of the reaction. Spectral data matched that of literature reported data.



1-Methoxy-4-nitrosobenzene (32): Obtained using General Procedure **C** from 4-methoxyphenol giving **32** (79%). Spectral data matched that of literature reported data.[31] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 5.7 Hz, 2 H), 7.03 (d, J = 9.1 Hz, 2 H), 3.95 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 164.0, 124.4, 113.9, 56.0 ppm.

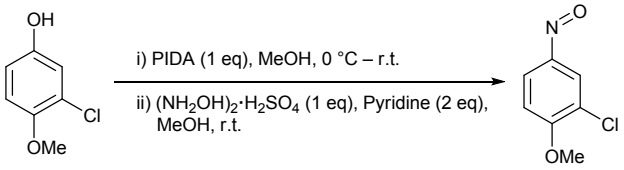


2-Methoxy-1,3-dimethyl-5-nitrosobenzene (34): Obtained using General Procedure **C** from **SI-5** giving **34** (35%). The second step required 48 hr to react to completion. Spectral data matched that of literature reported data.[32] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2 H), 3.80 (s, 3 H), 2.39 (s, 6 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 163.6, 132.0, 122.5, 59.7, 16.3 ppm; HRMS (EI) Exact mass cald. for $C_9H_{11}NO_2$ $[M]^+$: 165.0790, found: 165.0788.



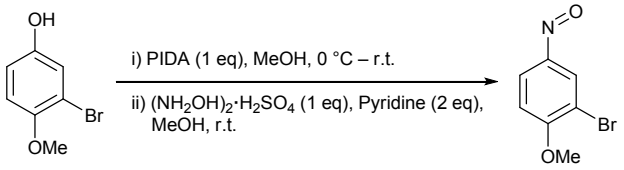
1-Methoxy-2-methyl-4-nitrosobenzene (35): Obtained using General Procedure **C** from **SI-6** giving **35** (77%). The second step required 70 hr to react to completion. Spectral data matched that of literature reported data.[32] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (br. d, J = 6.0 Hz, 1 H), 7.39 (br. s., 1 H), 7.01 (d, J = 8.6 Hz, 1 H), 4.00 - 3.96 (m, 3 H), 2.28 (s, 3 H) ppm; ^{13}C NMR (125

MHz, $CDCl_3$) δ 164.1, 163.8, 127.5, 127.0, 120.1, 109.1, 56.1, 16.2 ppm; HRMS (EI) Exact mass cald. for $C_8H_9NO_2$ $[M]^+$: 151.0633, found: 151.0632.



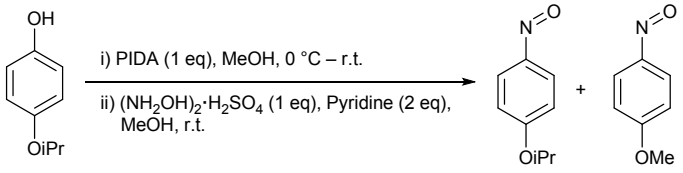
SI-7 **36**

2-Chloro-1-methoxy-4-nitrosobenzene (36): Obtained using General Procedure **C** from **SI-7** giving **36** (48%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (br. d, J = 8.0 Hz, 1 H), 7.59 (br. s., 1 H), 7.18 (d, J = 8.8 Hz, 1 H), 4.07 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 160.7, 127.1, 124.3, 119.5, 111.0, 56.9 ppm; HRMS (EI) Exact mass cald. for $C_7H_6ClNO_2$ $[M]^+$: 171.0087, found: 171.0091.



SI-8 **37**

2-Bromo-1-methoxy-4-nitrosobenzene (37): Obtained using General Procedure **C** from **SI-8** giving **37** (59%). The second step required 29 hr to react to completion. Spectral data matched that of literature reported data.[32] ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (br. d, J = 8.2 Hz, 1 H), 7.73 (s, 1 H), 7.11 (d, J = 9.0 Hz, 1 H), 4.03 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 161.4, 127.5, 122.9, 113.3, 110.9, 57.0 ppm; HRMS (EI) Exact mass cald. for $C_7H_6BrNO_2$ $[M]^+$: 214.9582, found: 214.9584.



SI-9 **38** **32**

1-Isopropoxy-4-nitrosobenzene (38) and 1-methoxy-4-nitrosobenzene (32): Obtained using General Procedure **C** from **SI-9** giving a mixture of **38** (47%)[31] and **32** (9%). Spectral data matched that of literature reported data for **38**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (br. s., 2 H, overlaps with **20**), 6.98 (d, J = 9.3 Hz, 2 H), 4.74 (spt, J = 6.1 Hz, 1 H), 1.41 (d, J = 6.2 Hz, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 163.9, 124.4, 115.0, 71.0, 21.9 ppm.

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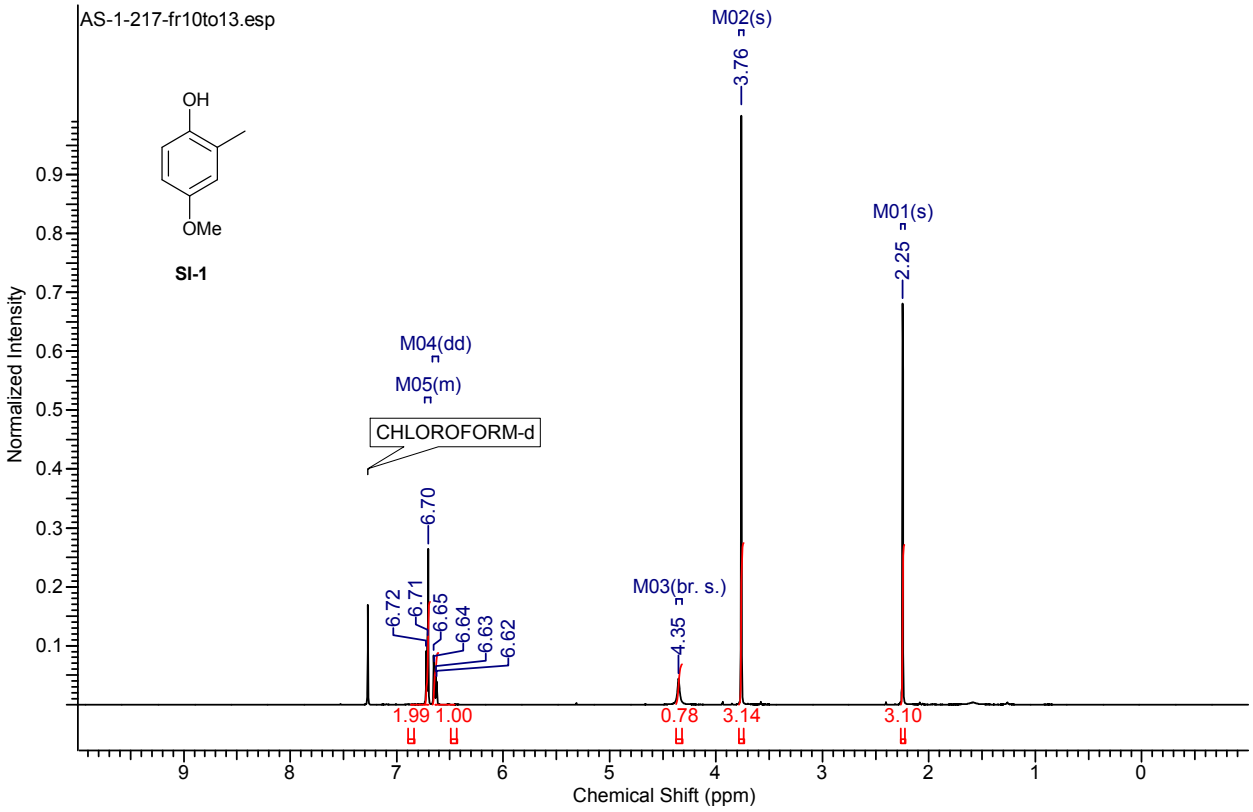
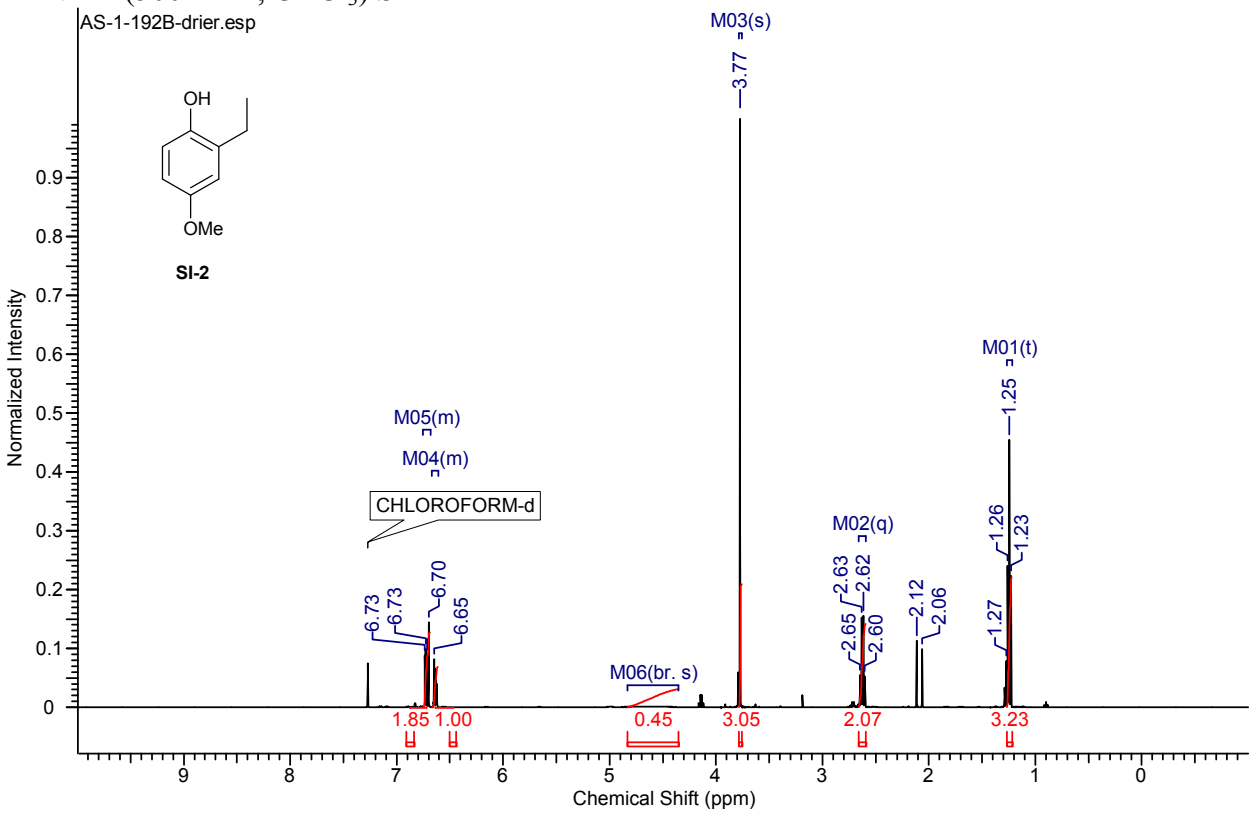
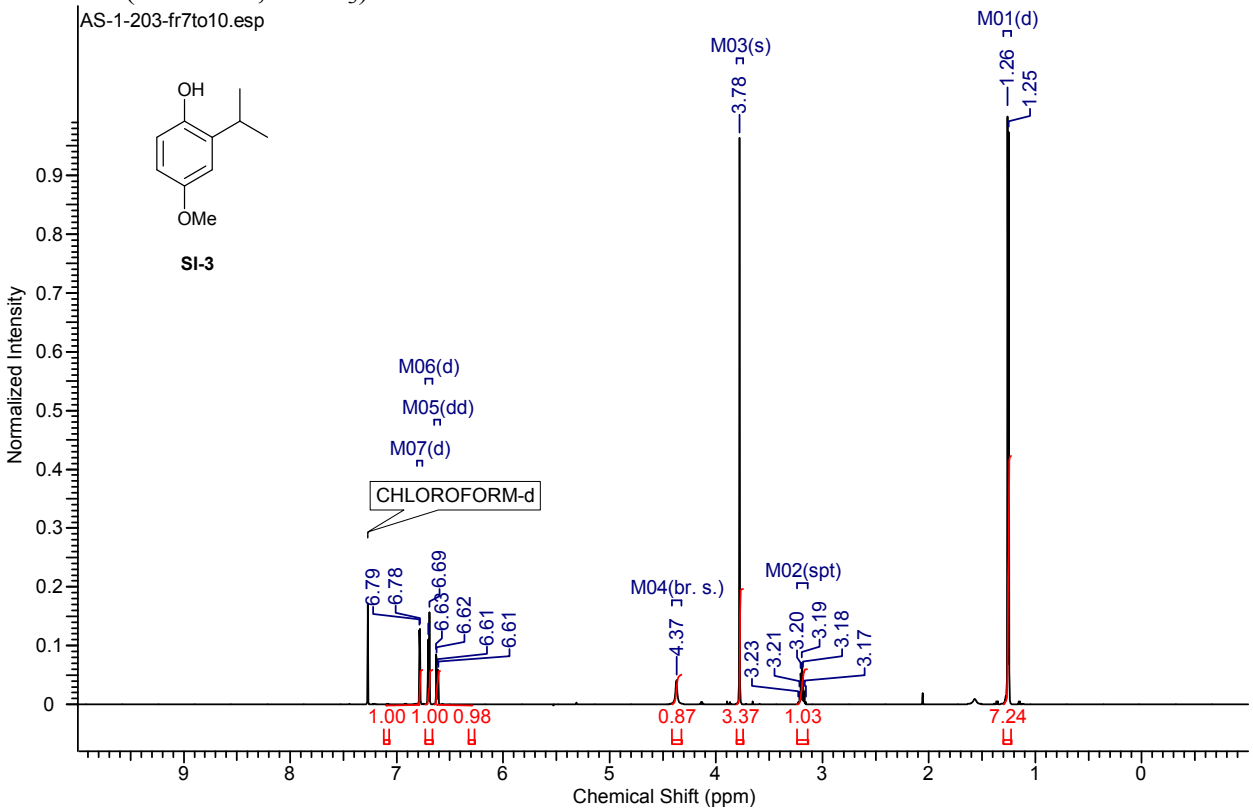
^{1}H NMR (400 MHz, $CDCl_3$) **SI-1**



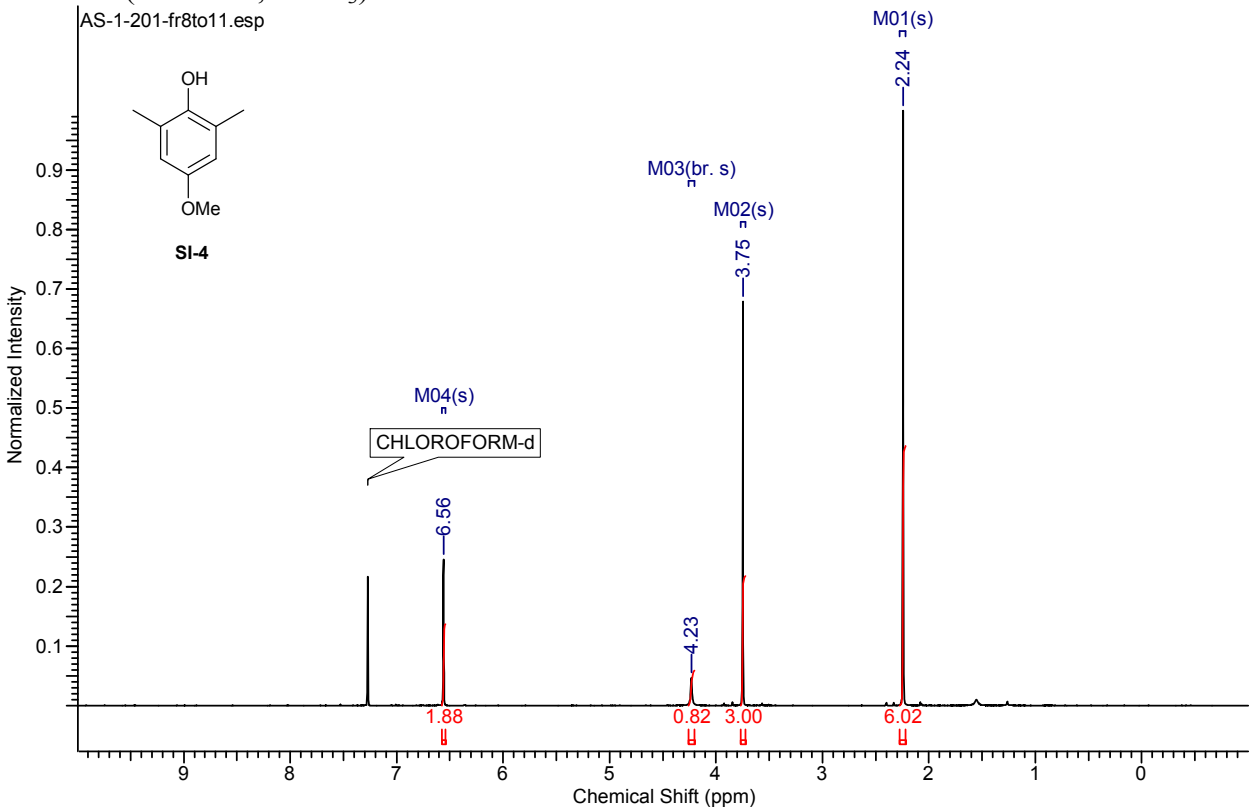
^{1}H NMR (500 MHz, $CDCl_3$) **SI-2**



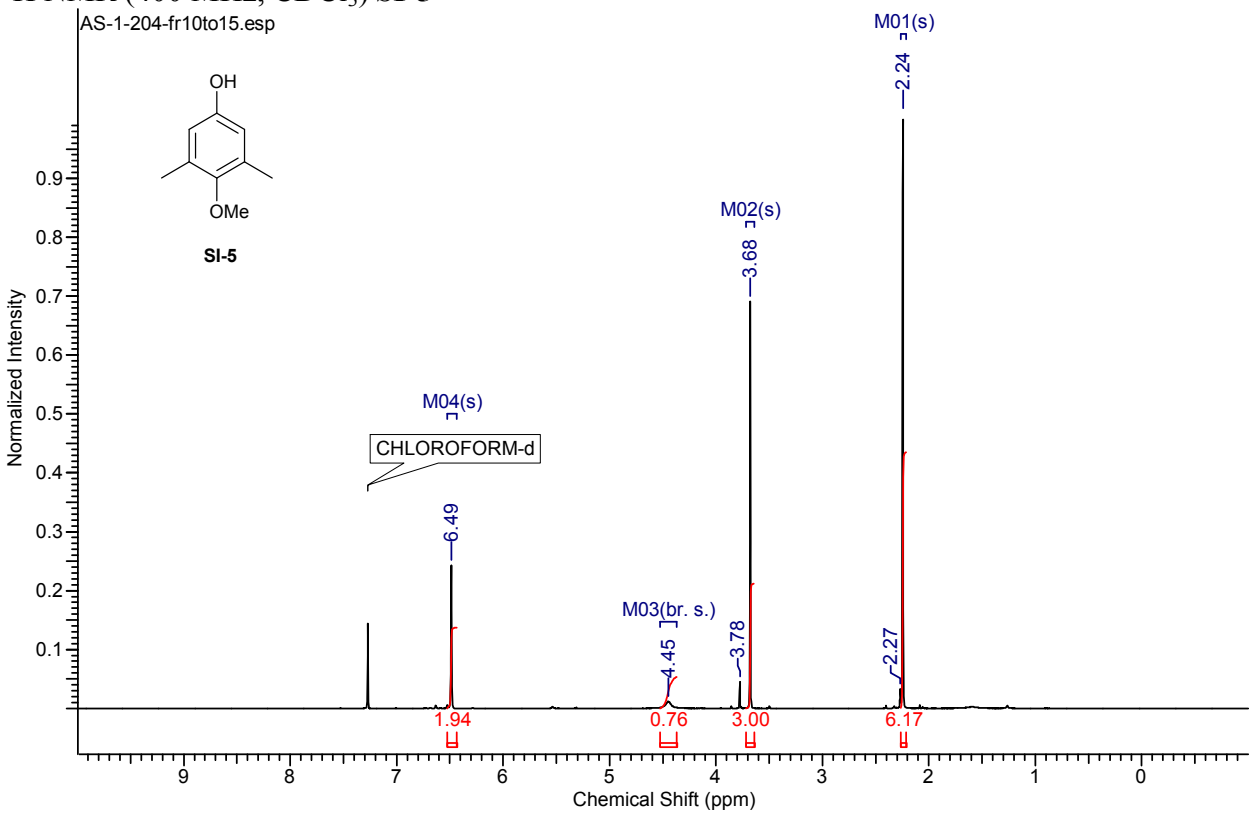
^{1}H NMR (600 MHz, $CDCl_3$) **SI-3**



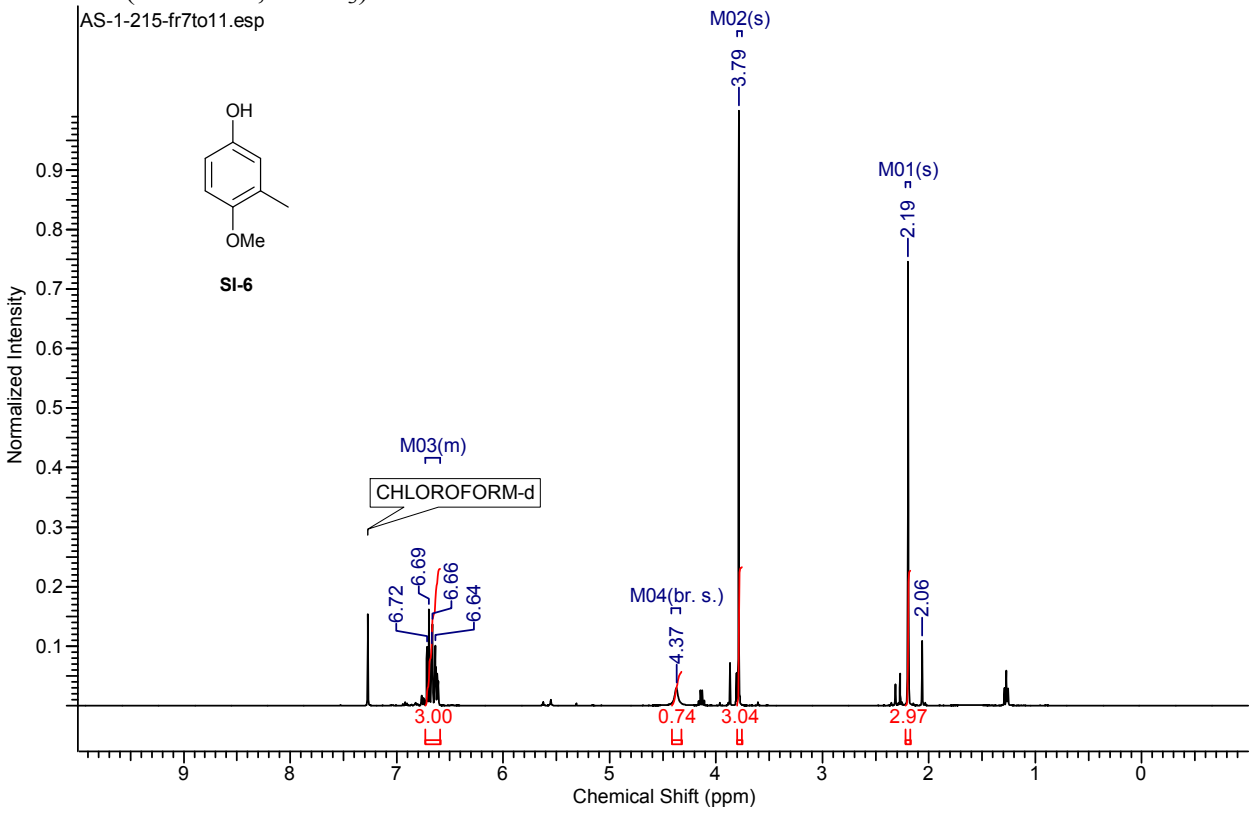
^{1}H NMR (400 MHz, $CDCl_3$) **SI-4**



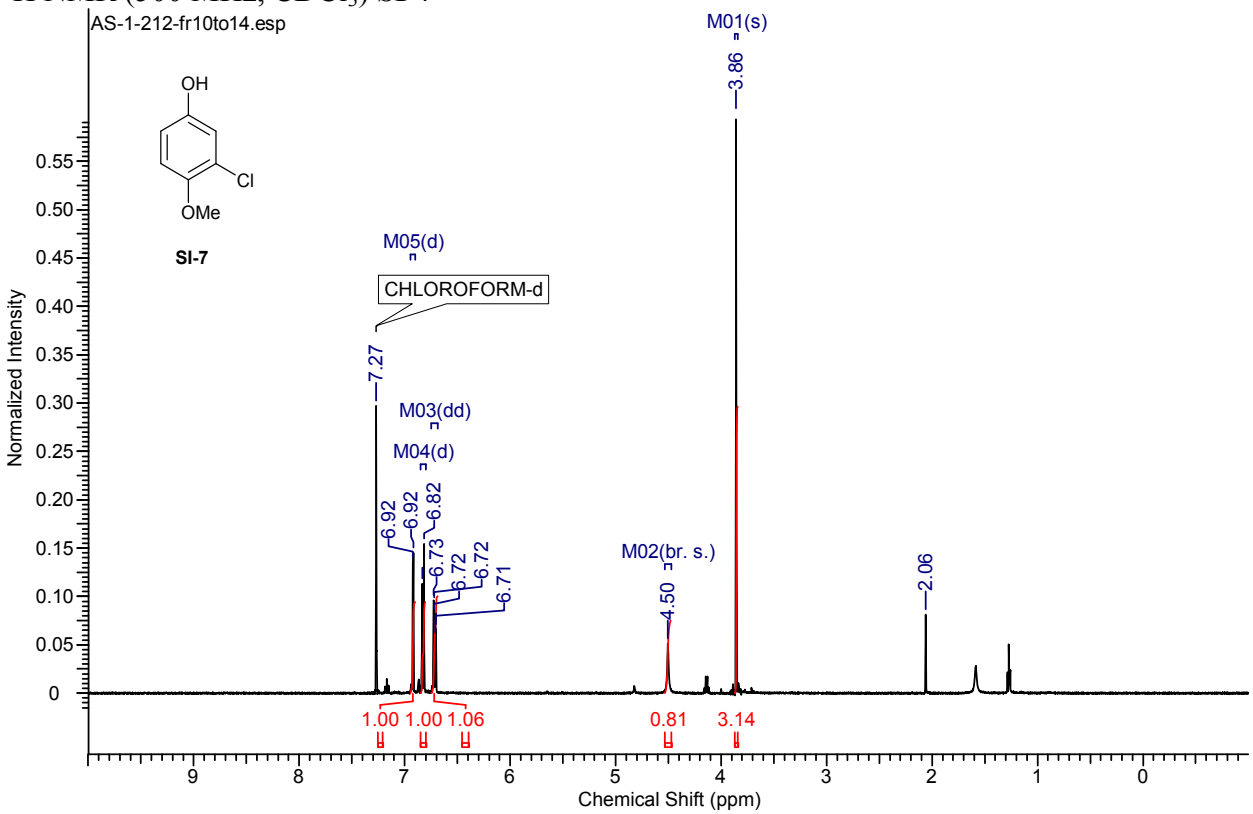
^{1}H NMR (400 MHz, $CDCl_3$) **SI-5**



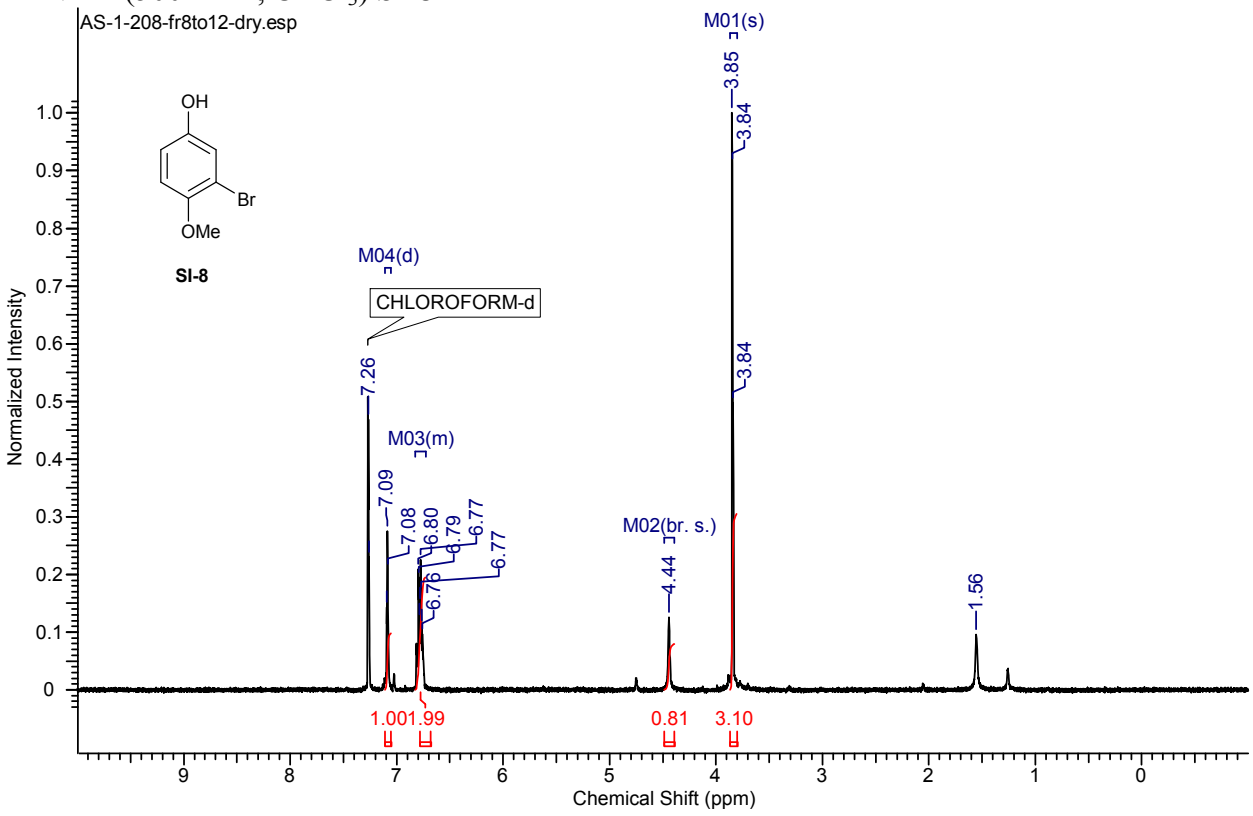
^{1}H NMR (400 MHz, $CDCl_3$) **SI-6**



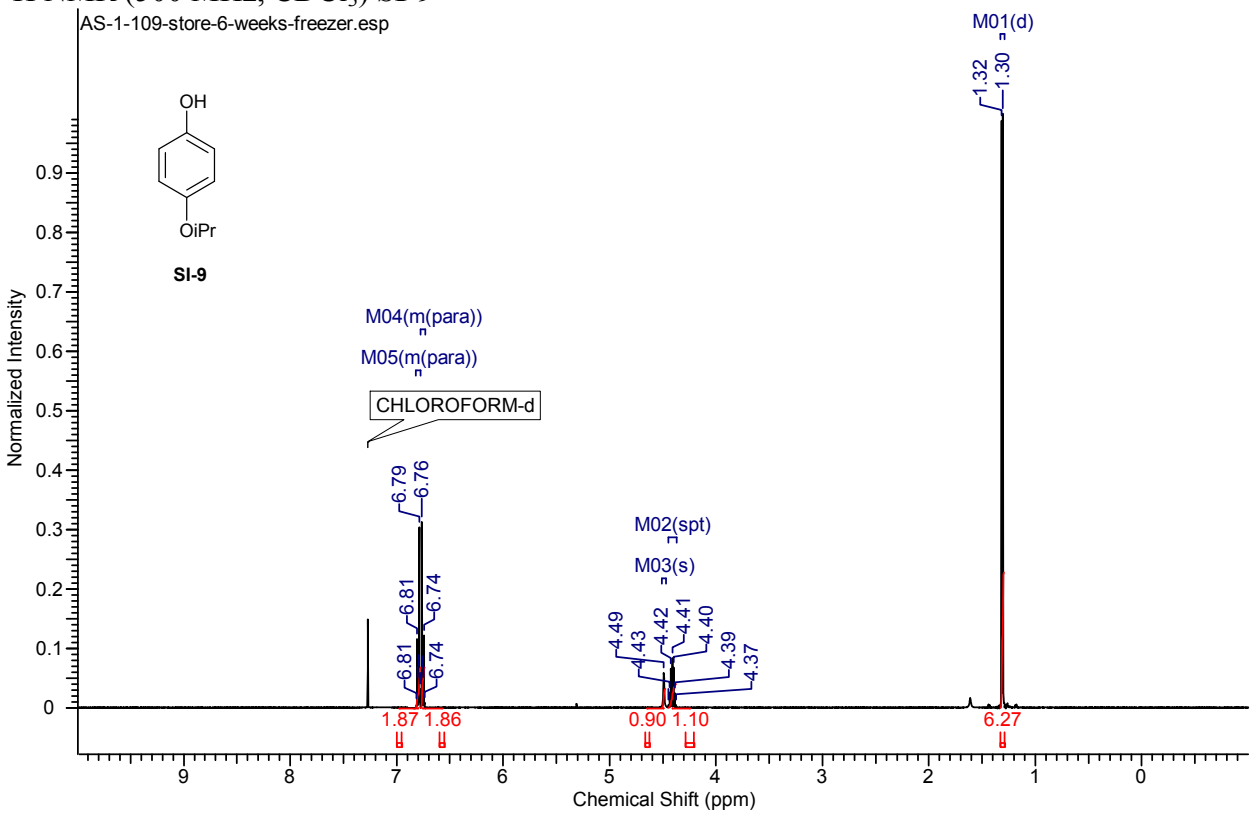
^{1}H NMR (500 MHz, $CDCl_3$) **SI-7**



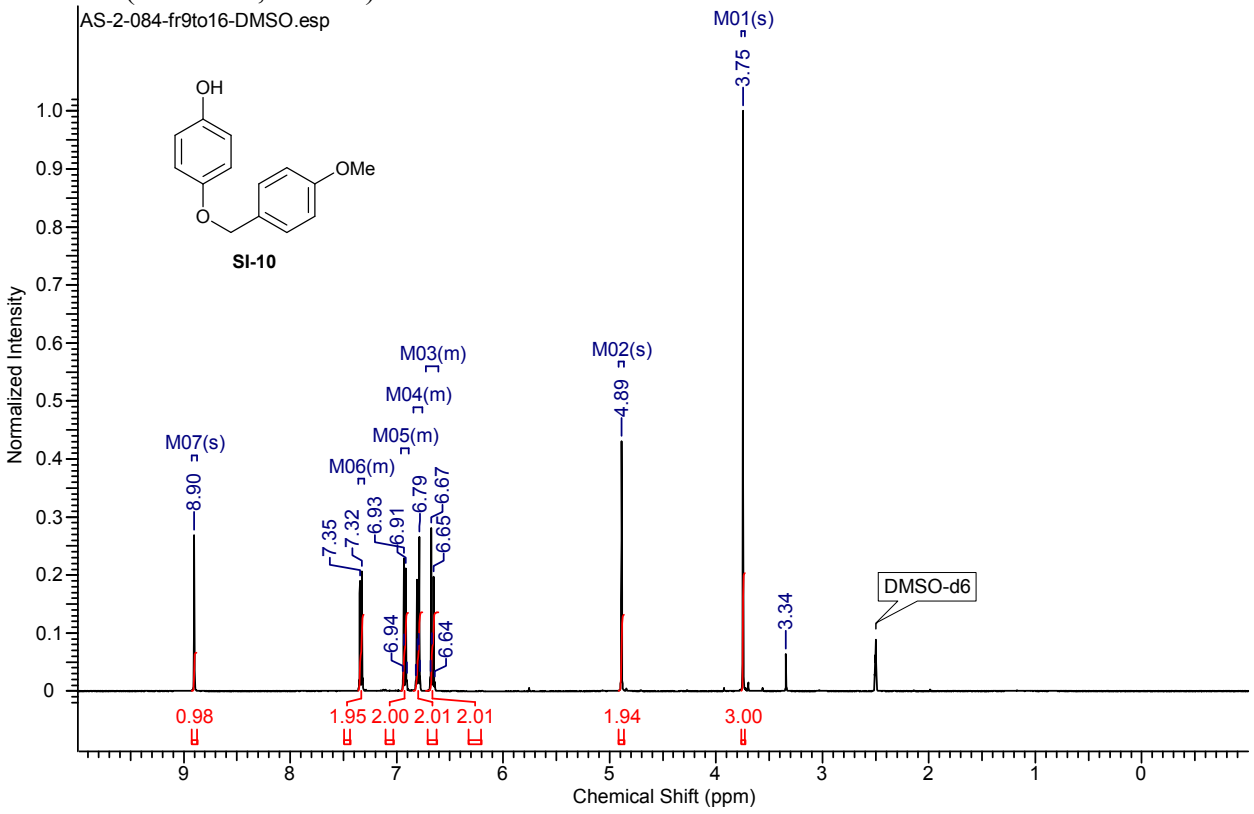
^{1}H NMR (500 MHz, $CDCl_3$) **SI-8**



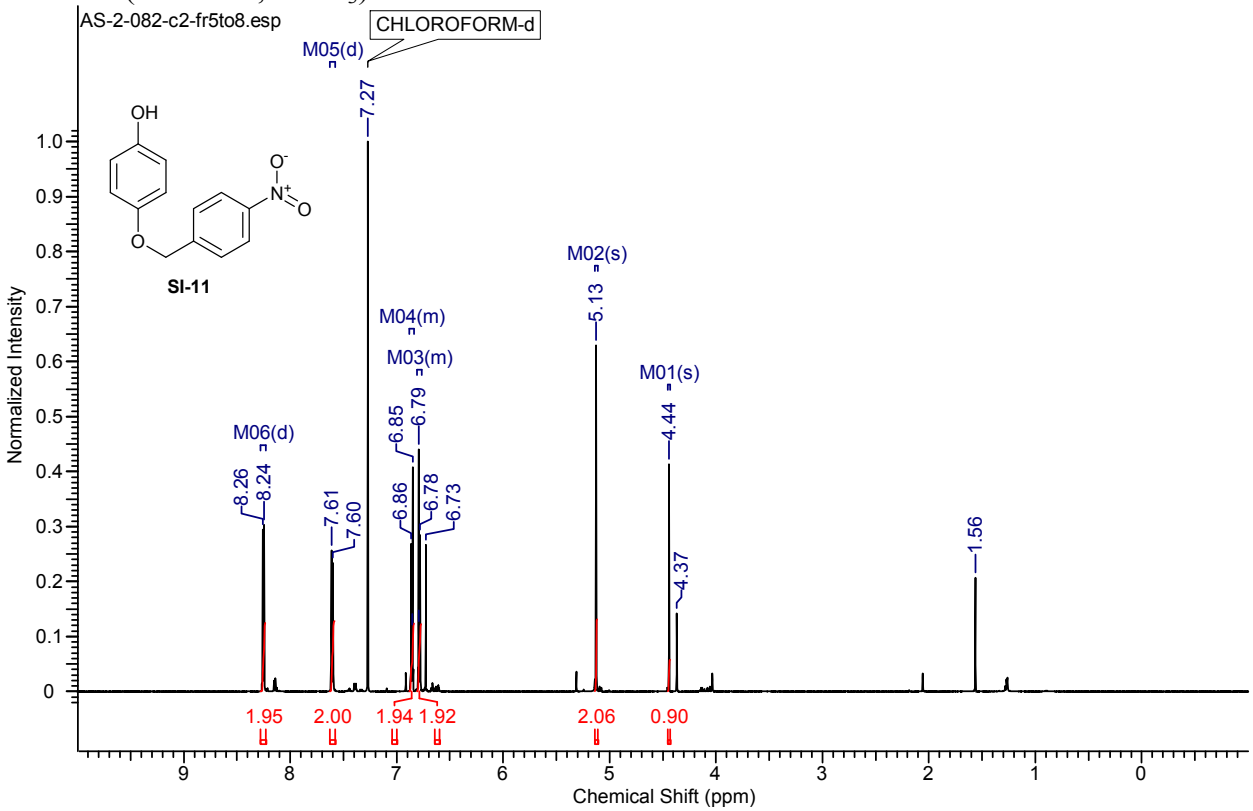
^{1}H NMR (500 MHz, $CDCl_3$) **SI-9**



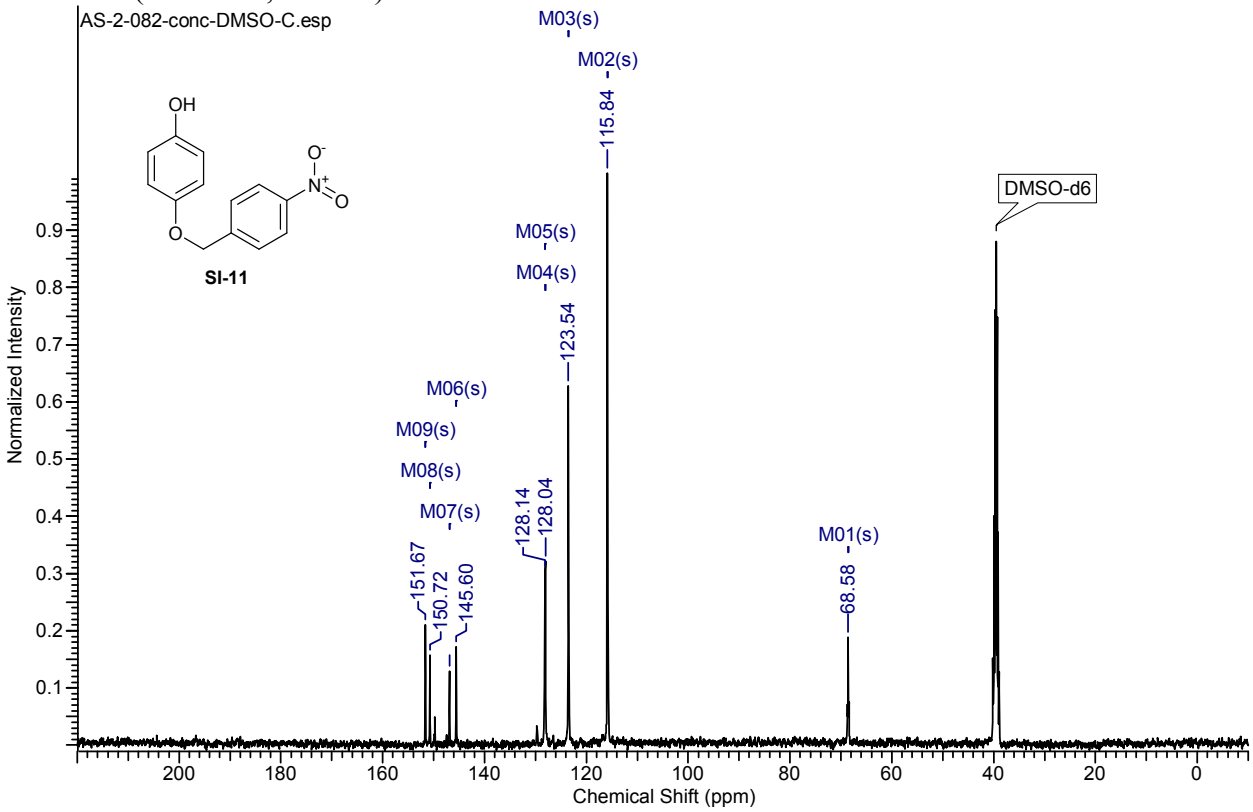
^{1}H NMR (400 MHz, DMSO) **SI-10**



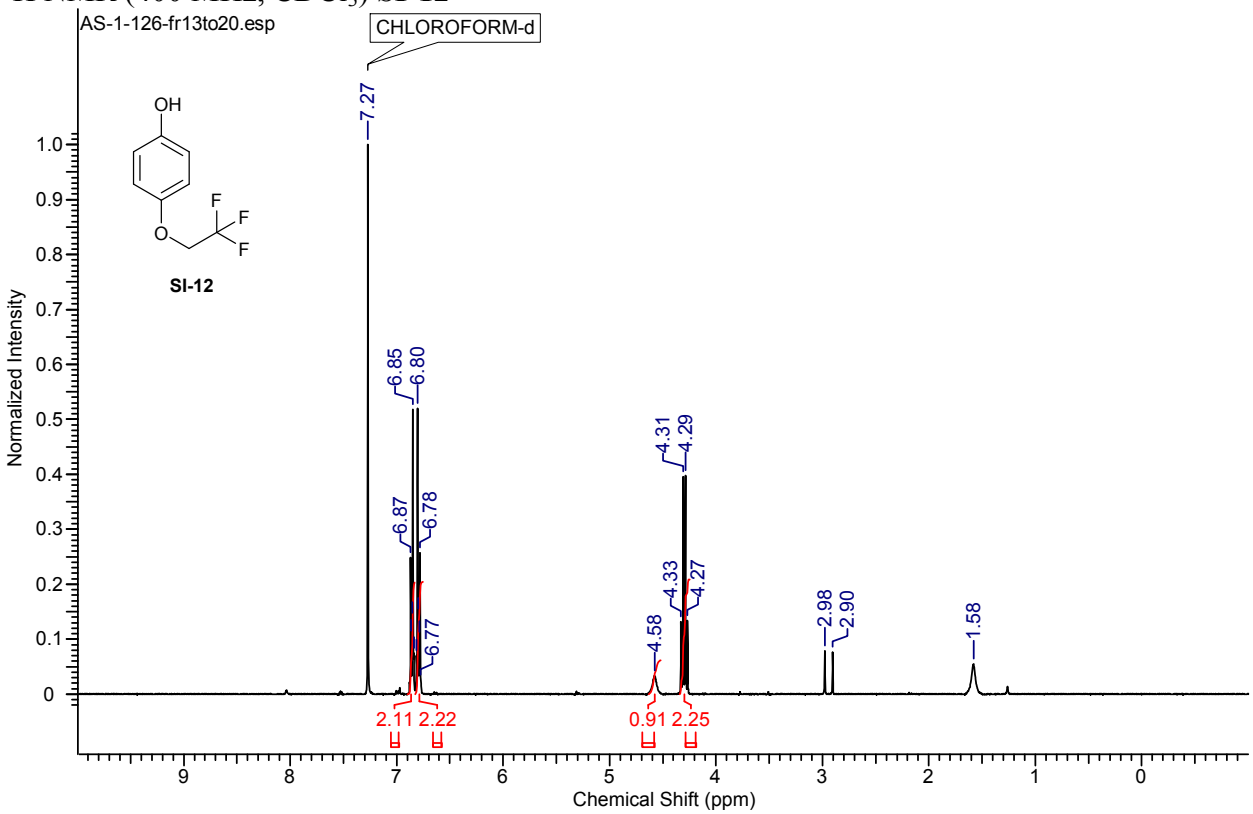
^{1}H NMR (600 MHz, $CDCl_3$) **SI-11**



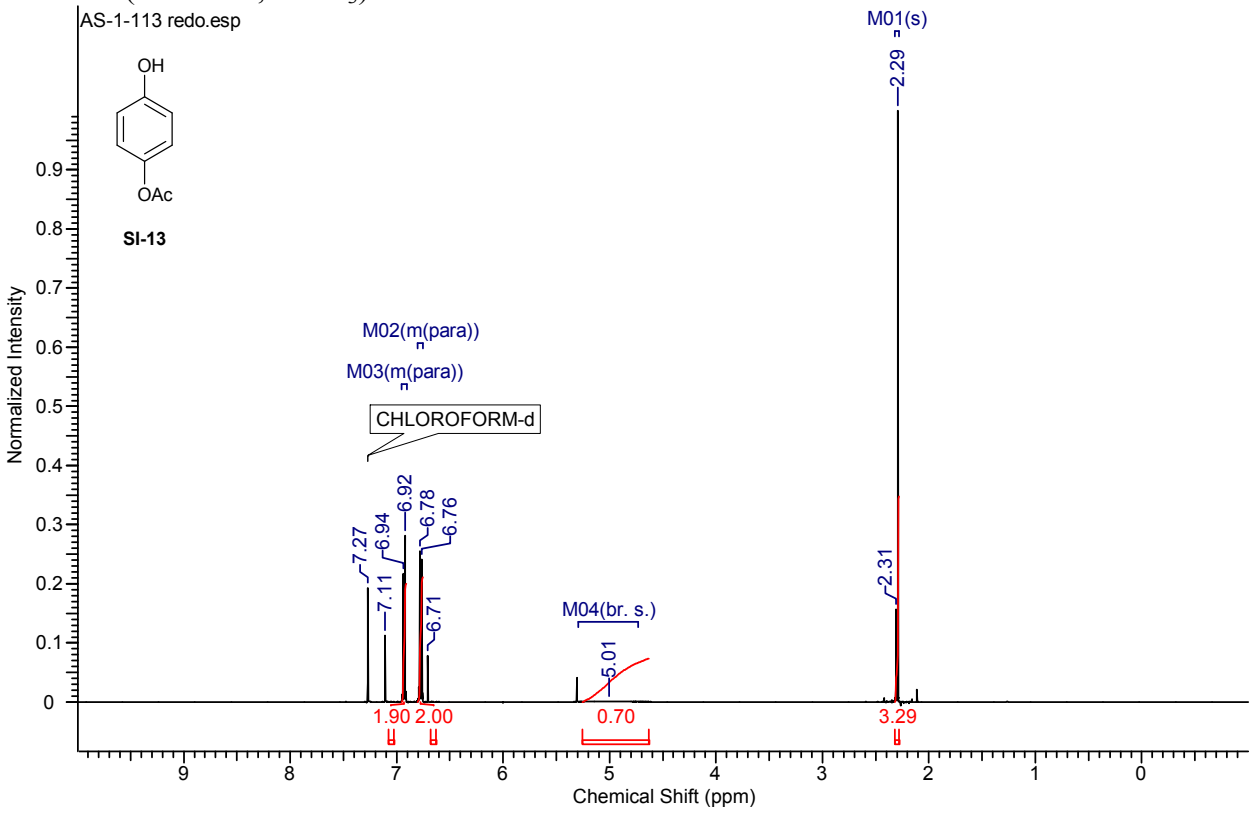
^{13}C NMR (100 MHz, DMSO) **SI-11**



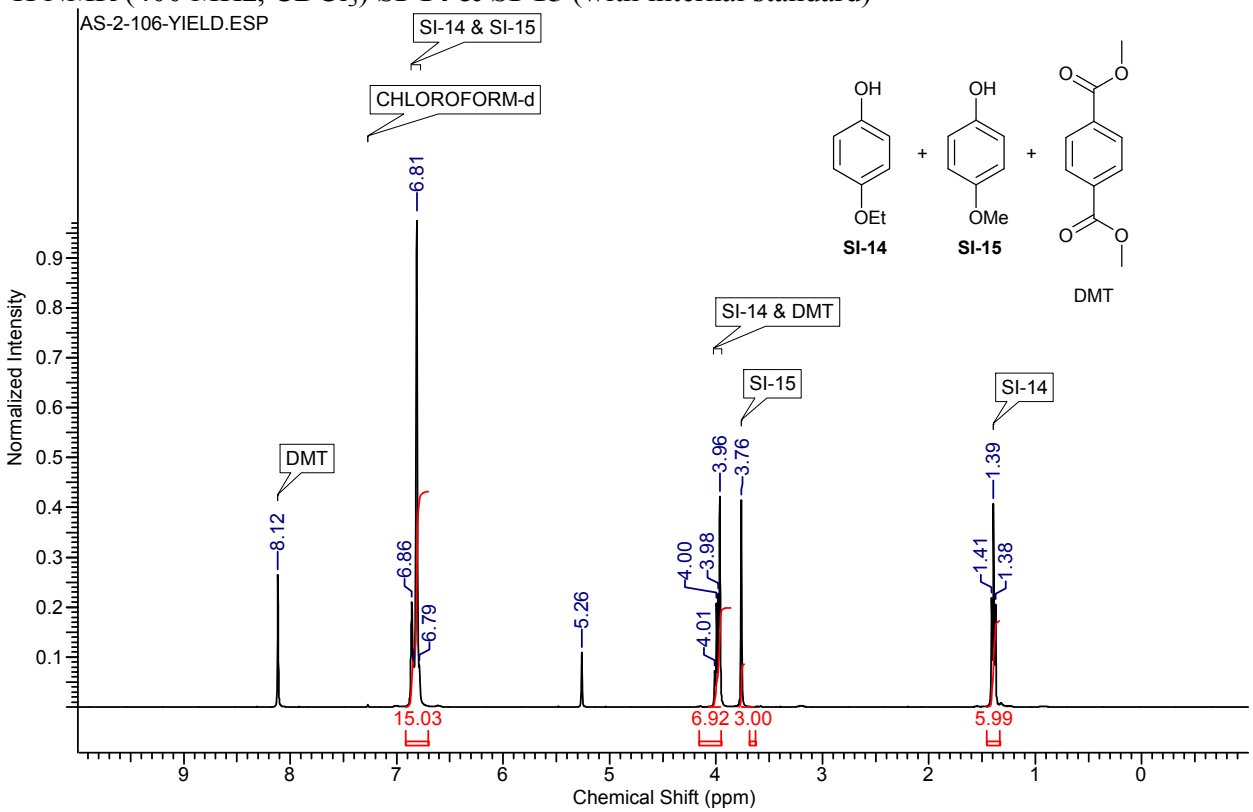
^{1}H NMR (400 MHz, $CDCl_3$) **SI-12**



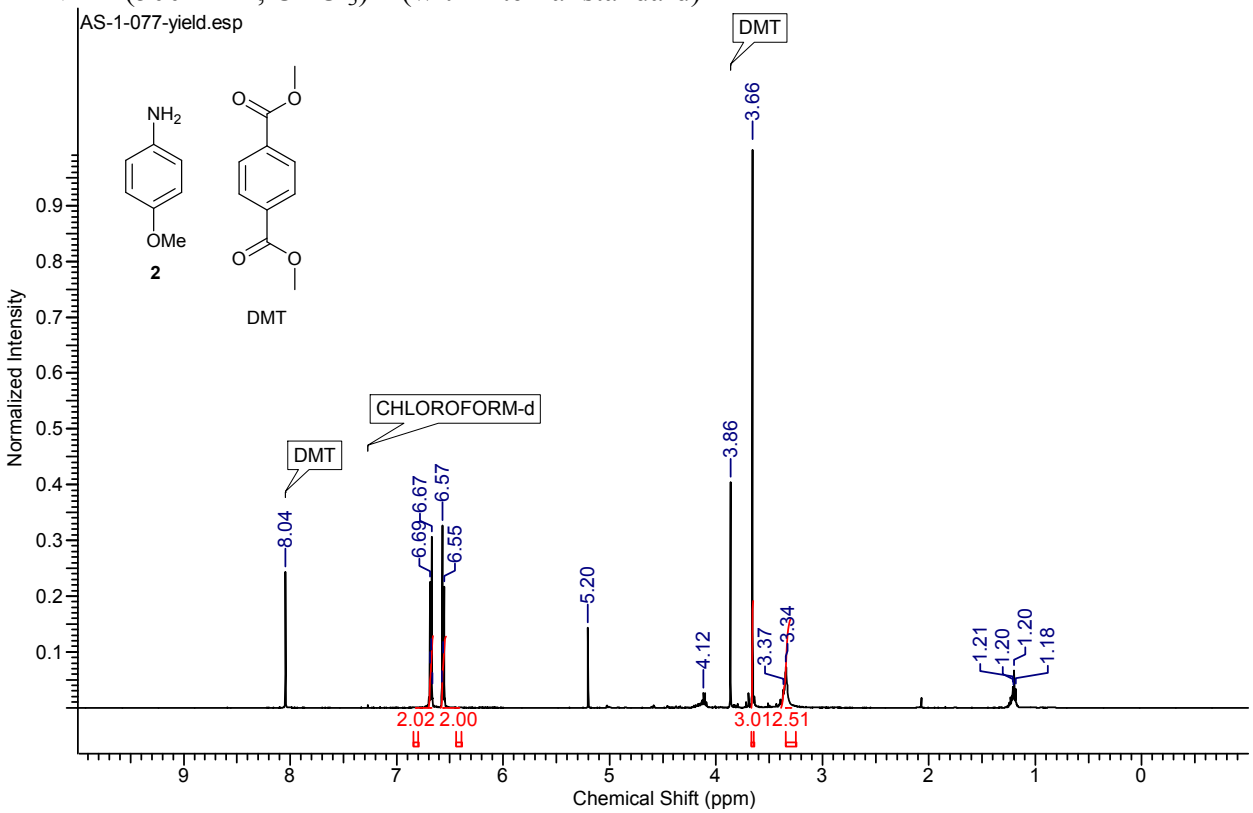
^{1}H NMR (500 MHz, $CDCl_3$) **SI-13**



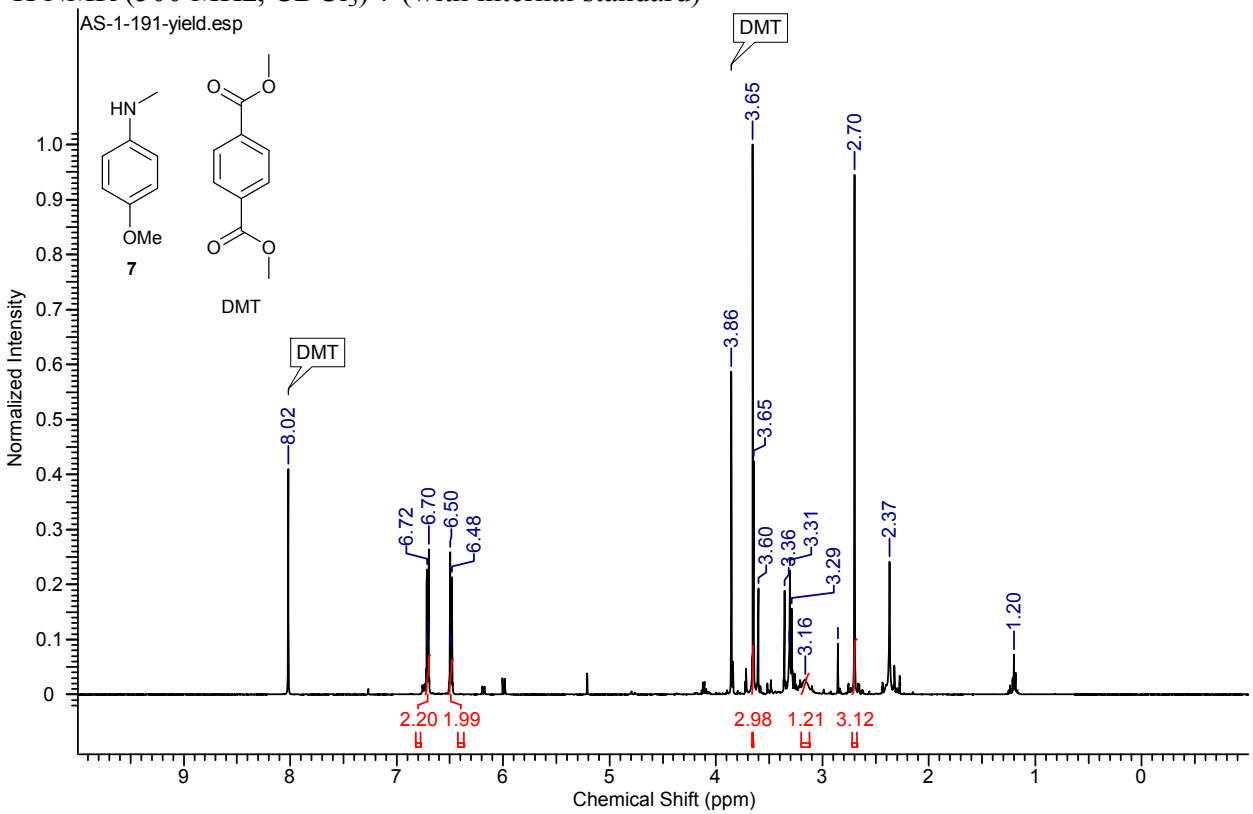
^{1}H NMR (400 MHz, $CDCl_3$) **SI-14** & **SI-15** (with internal standard)



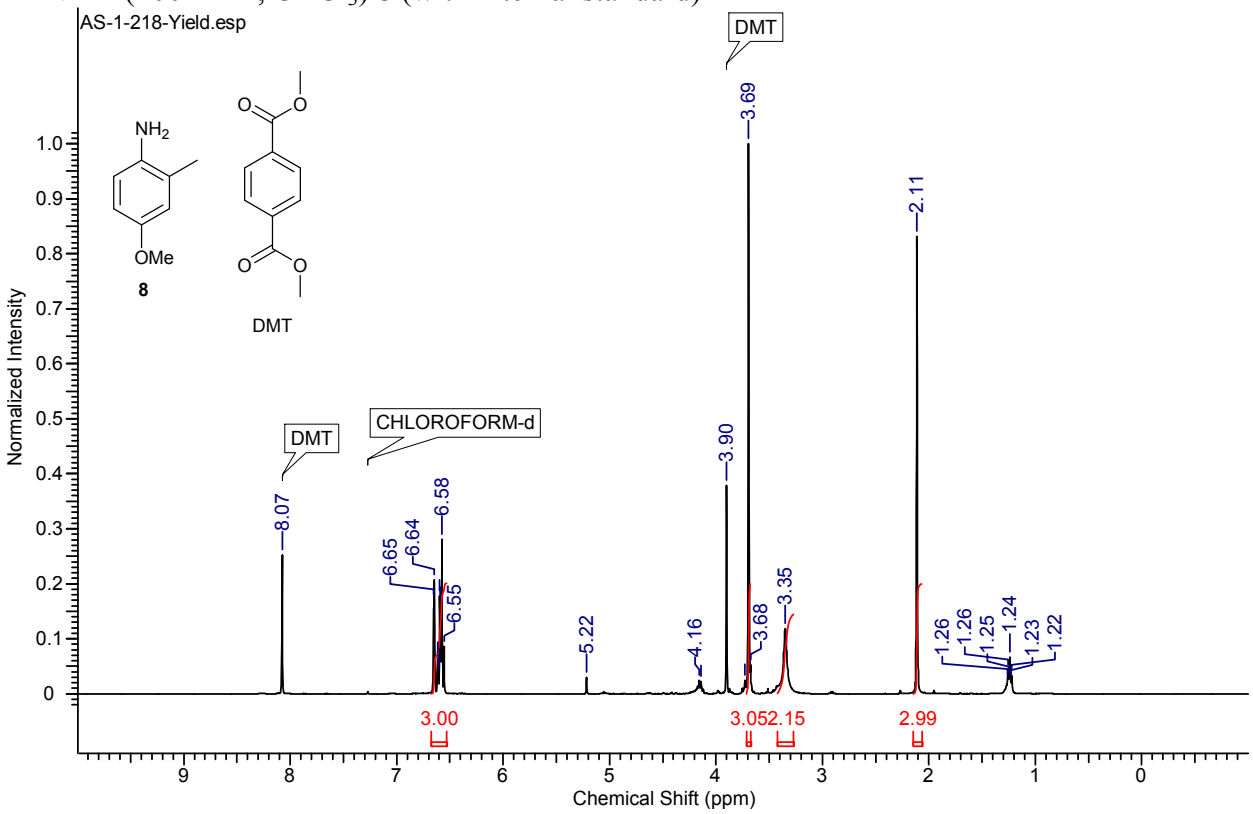
^{1}H NMR (500 MHz, $CDCl_3$) **2** (with internal standard)



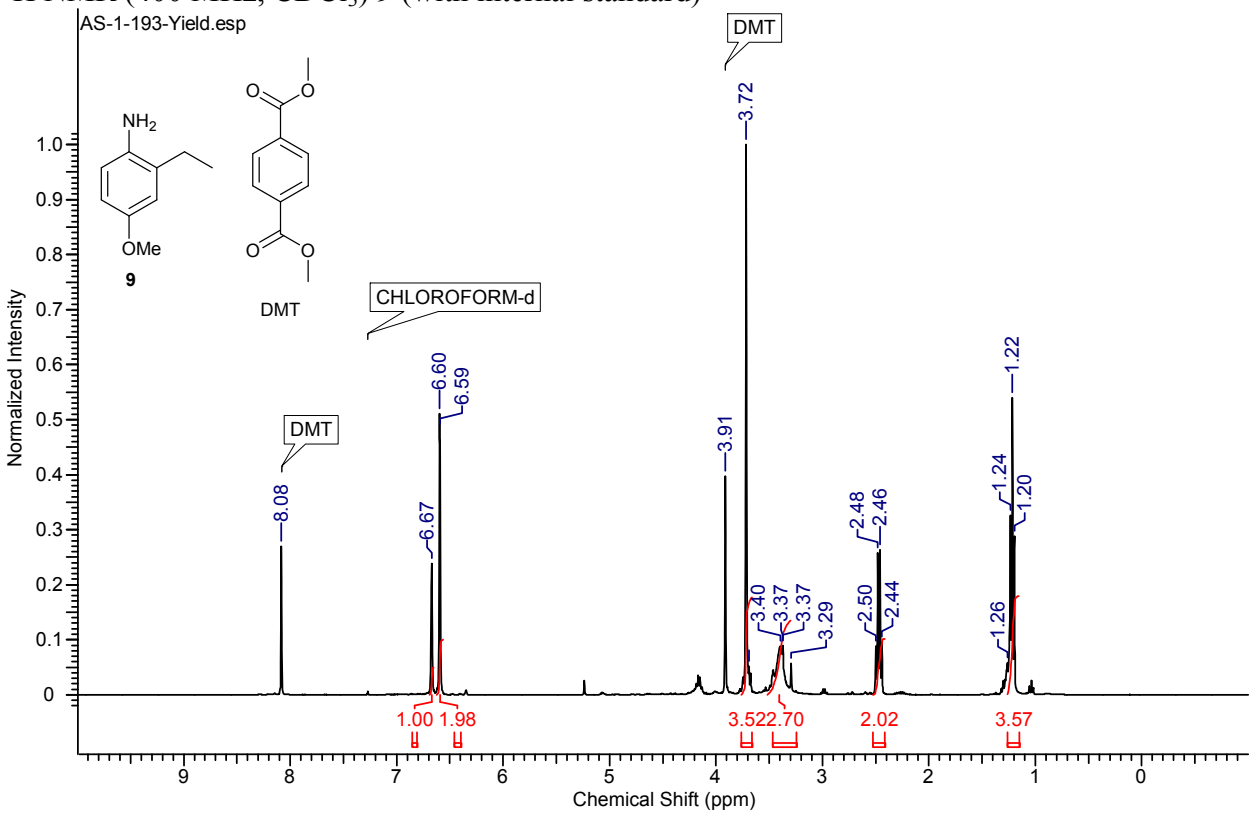
^{1}H NMR (500 MHz, $CDCl_3$) **7** (with internal standard)



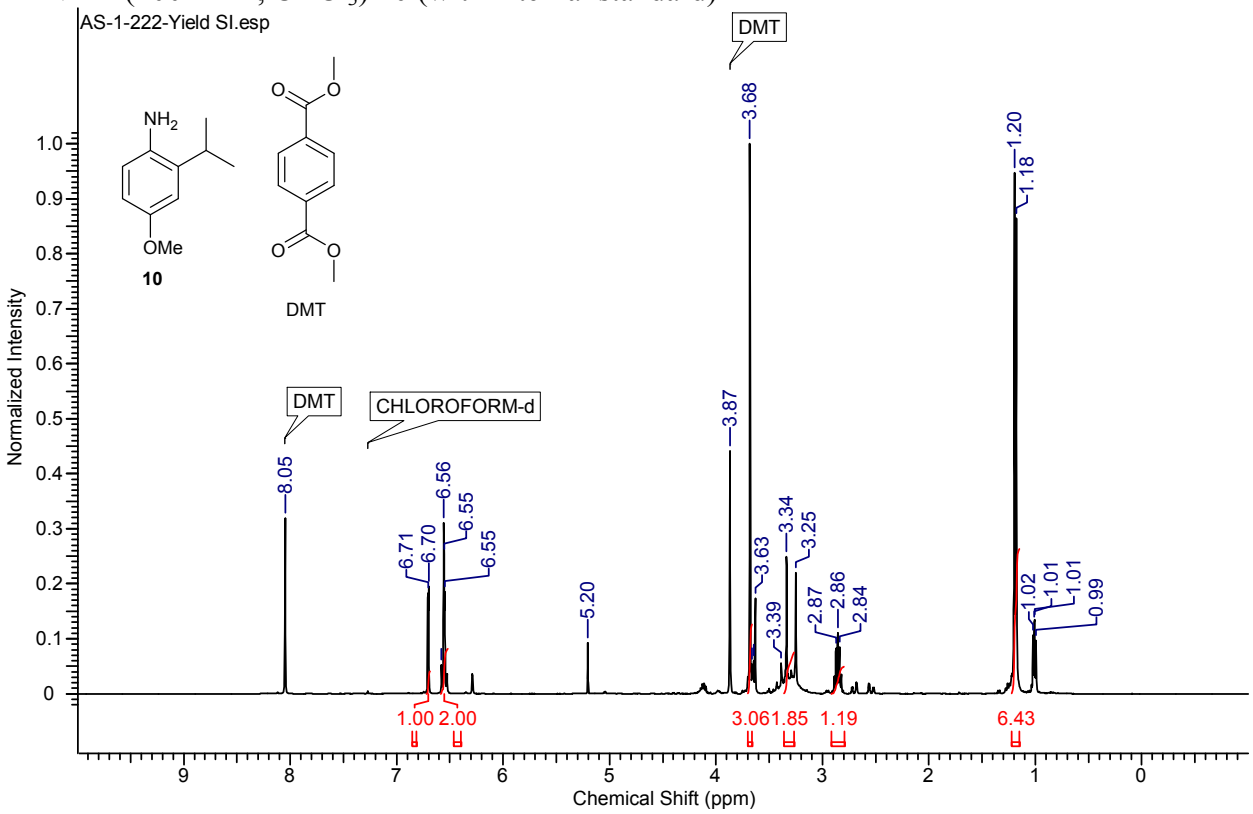
^{1}H NMR (400 MHz, $CDCl_3$) **8** (with internal standard)



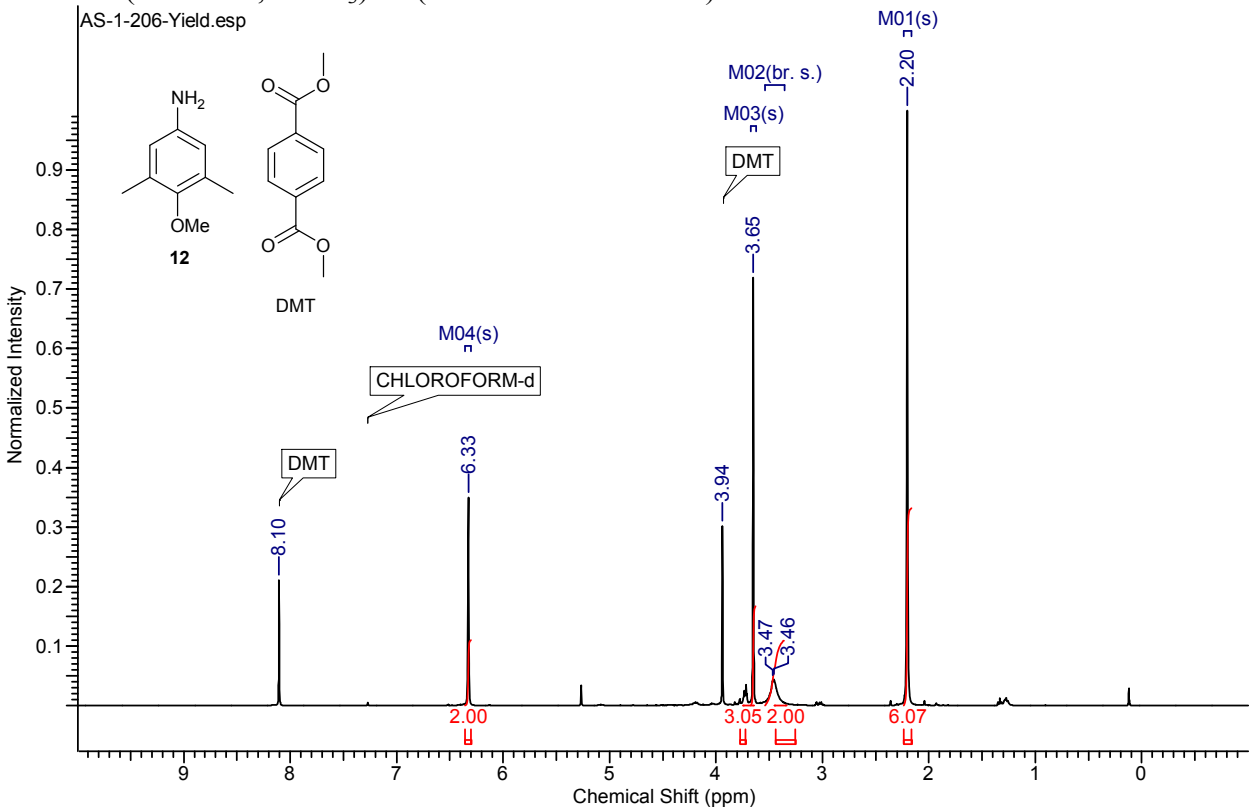
^{1}H NMR (400 MHz, $CDCl_3$) **9** (with internal standard)



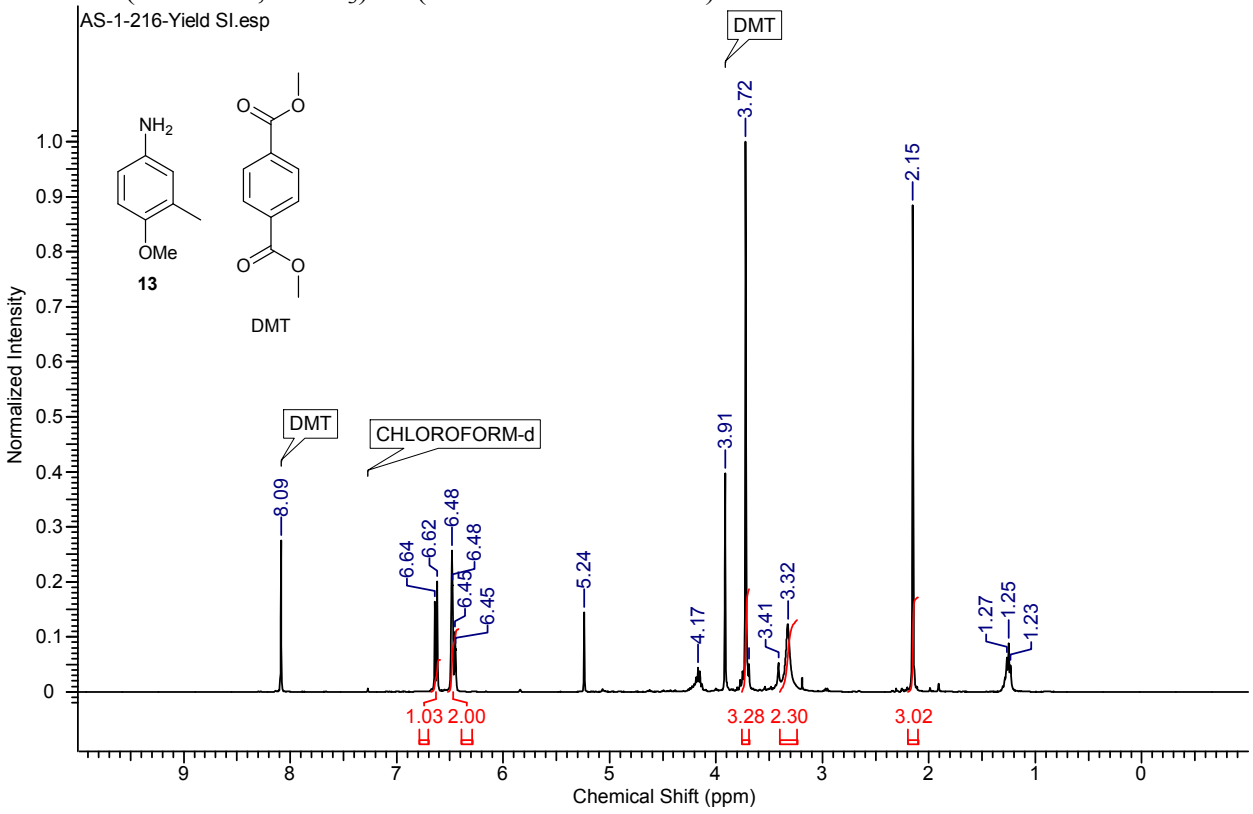
^{1}H NMR (400 MHz, $CDCl_3$) **10** (with internal standard)



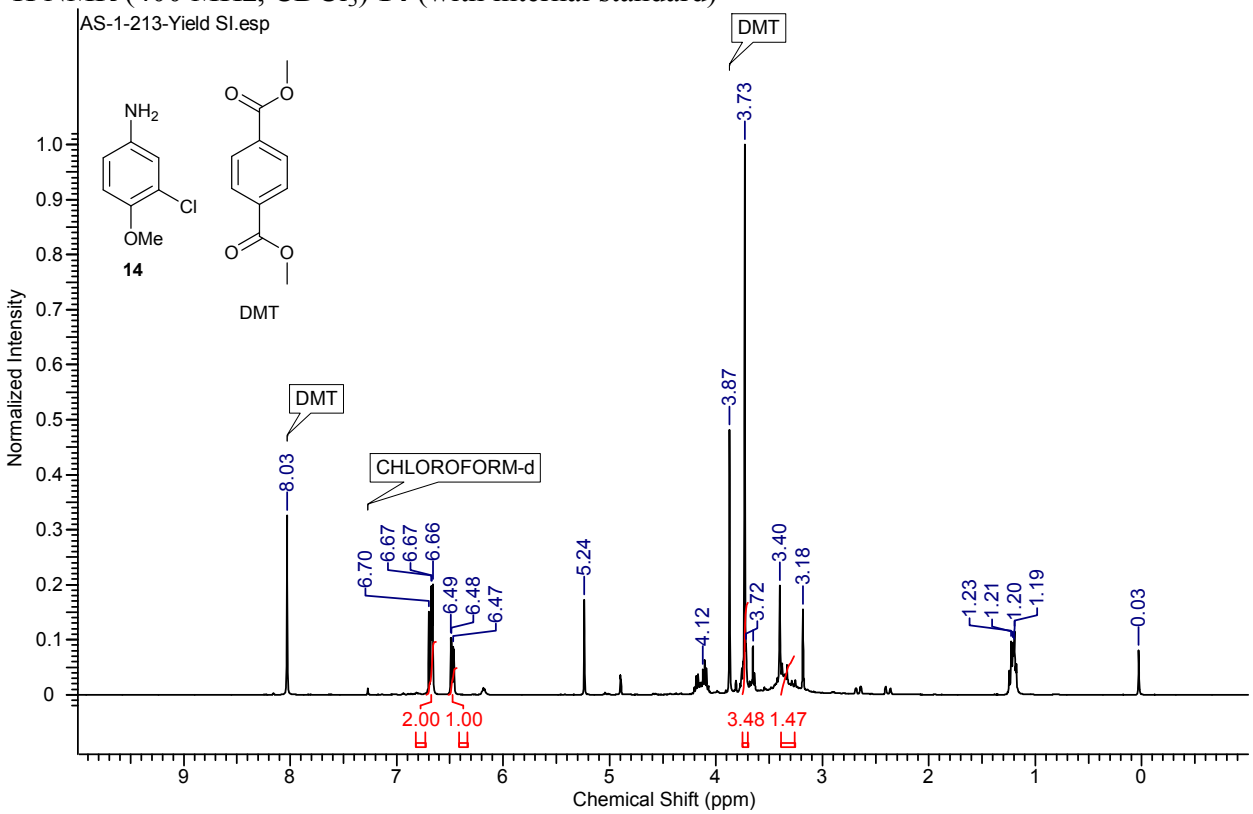
^{1}H NMR (400 MHz, $CDCl_3$) **12** (with internal standard)



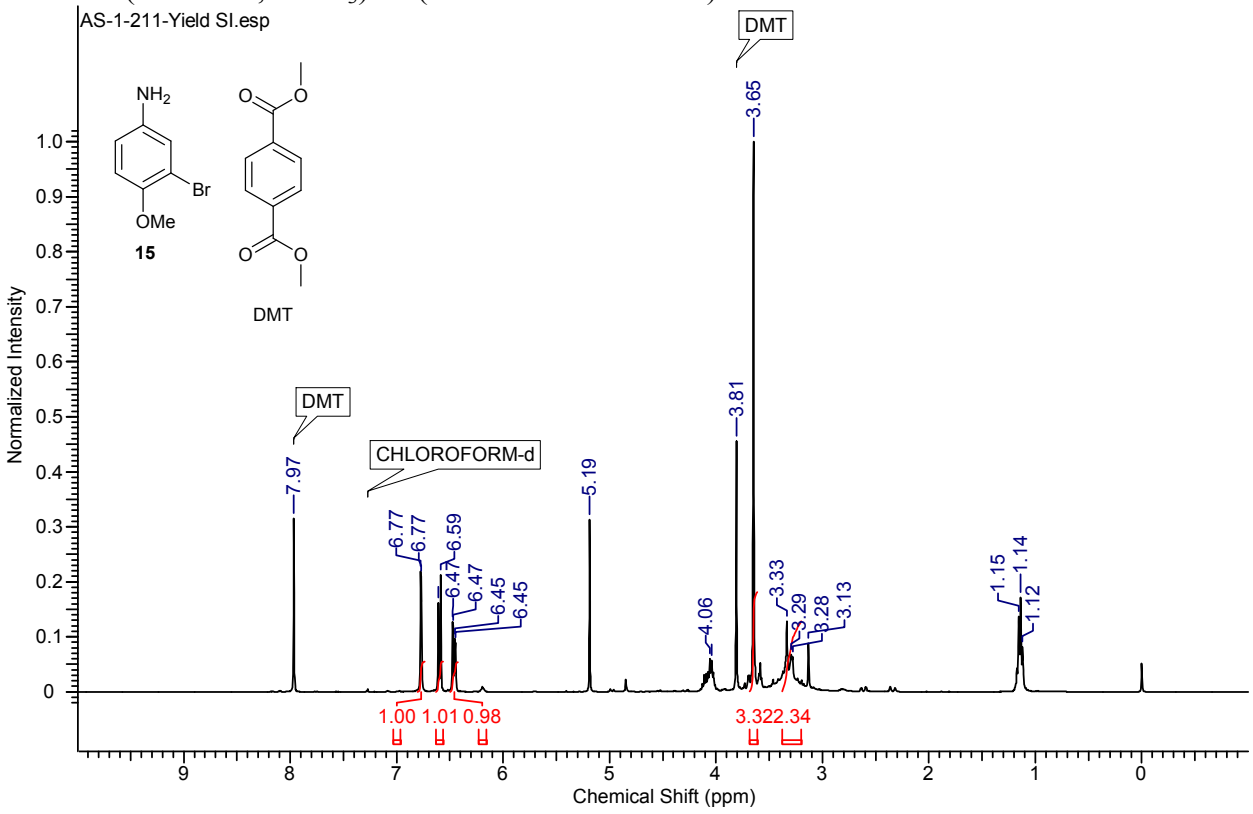
^{1}H NMR (400 MHz, $CDCl_3$) **13** (with internal standard)



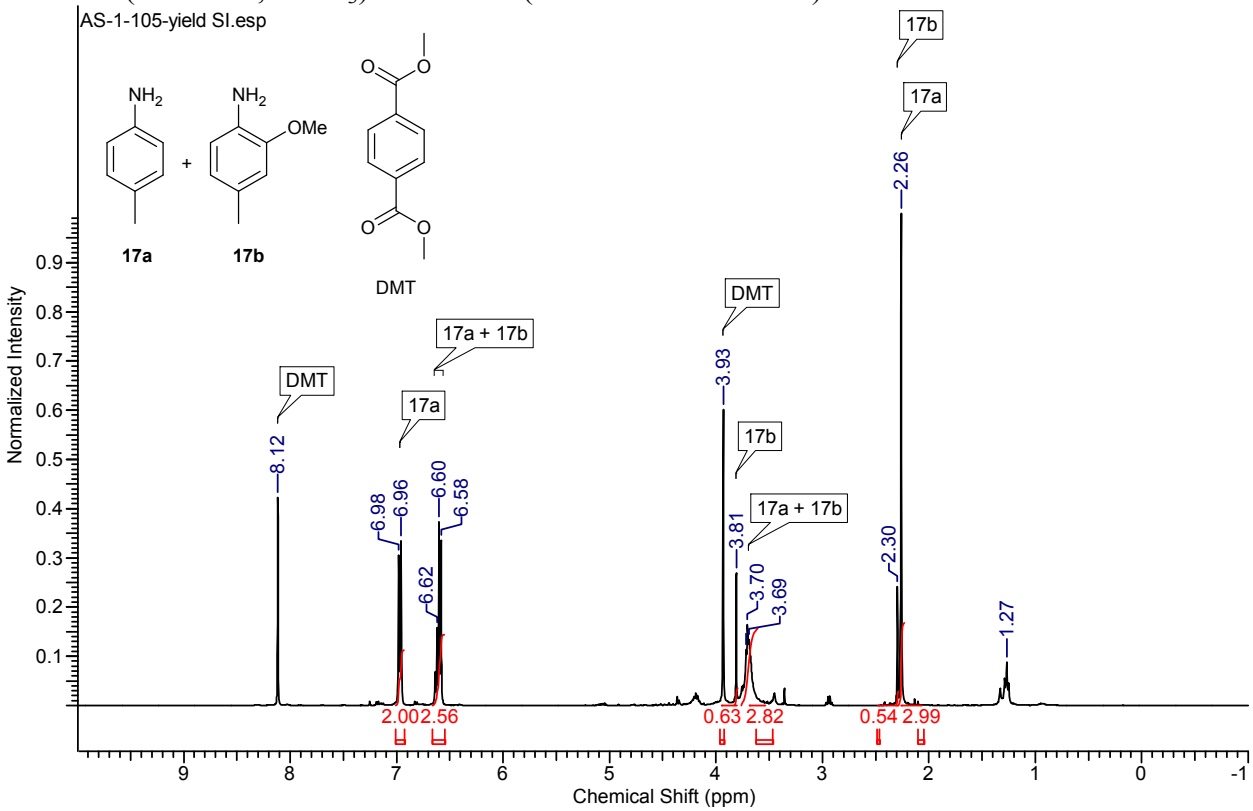
^{1}H NMR (400 MHz, $CDCl_3$) **14** (with internal standard)



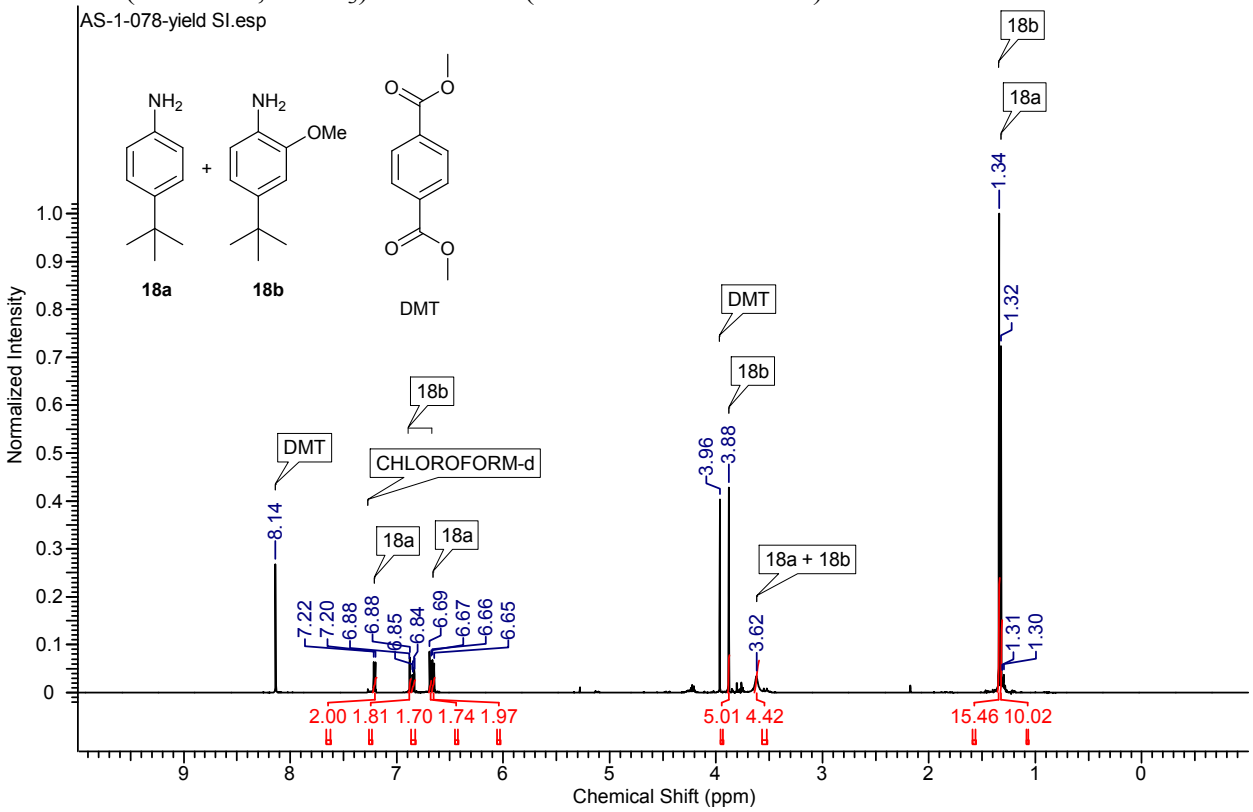
^{1}H NMR (400 MHz, $CDCl_3$) **15** (with internal standard)



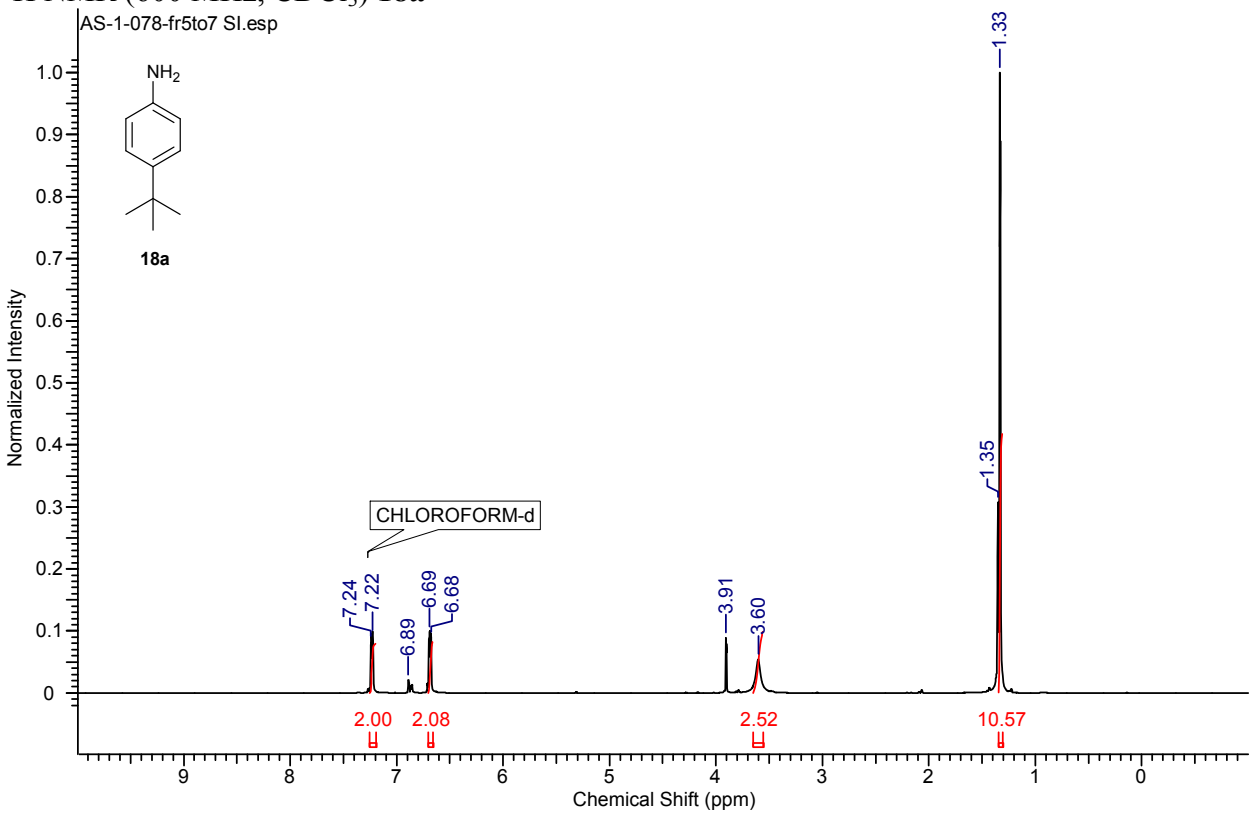
^{1}H NMR (400 MHz, $CDCl_3$) **17a** & **17b** (with internal standard)



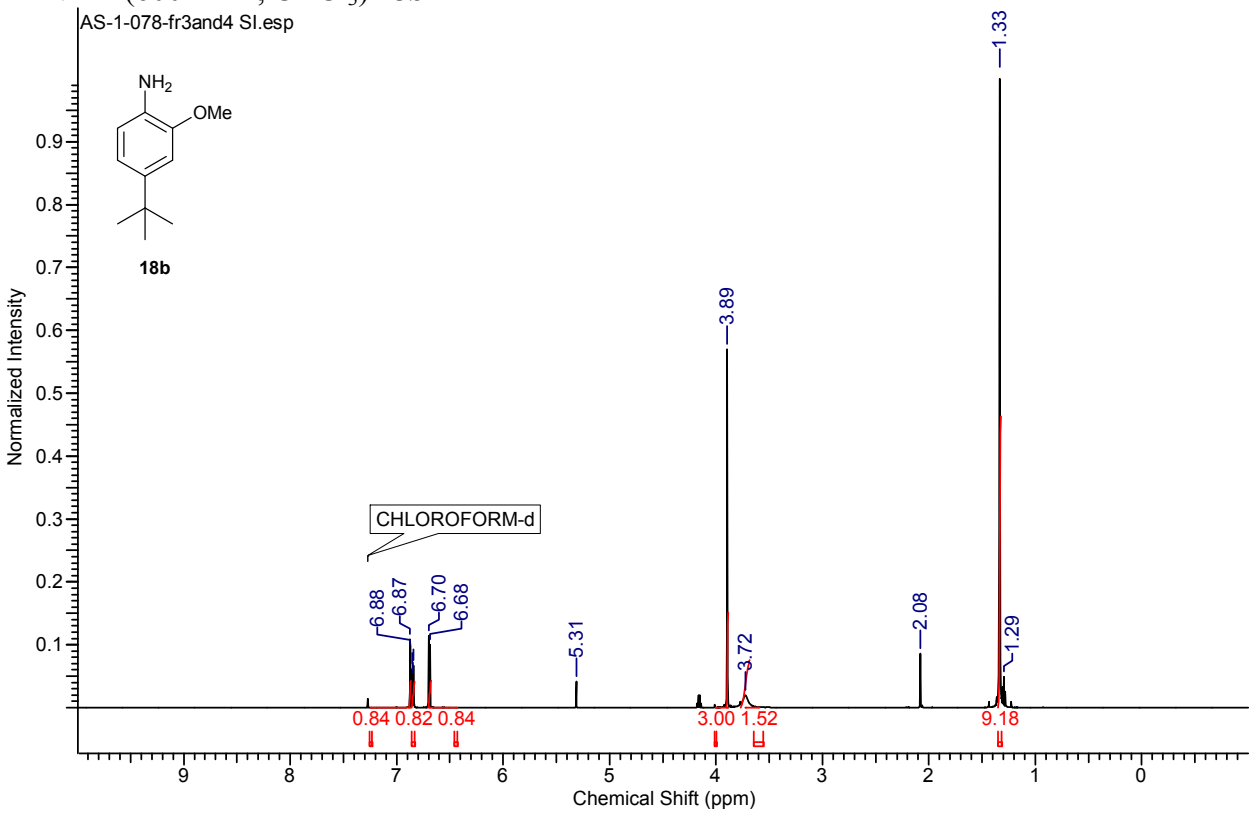
^{1}H NMR (500 MHz, $CDCl_3$) **18a** & **18b** (with internal standard)



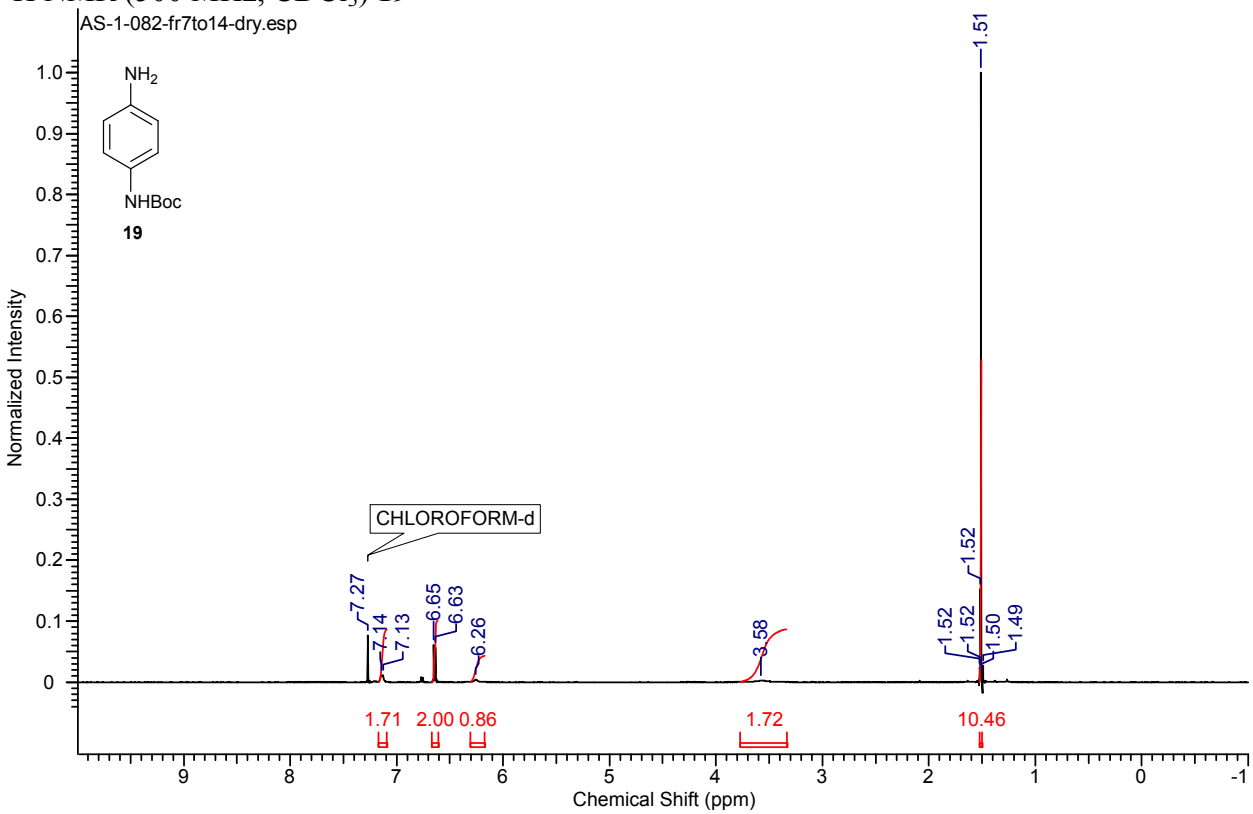
^{1}H NMR (600 MHz, $CDCl_3$) **18a**



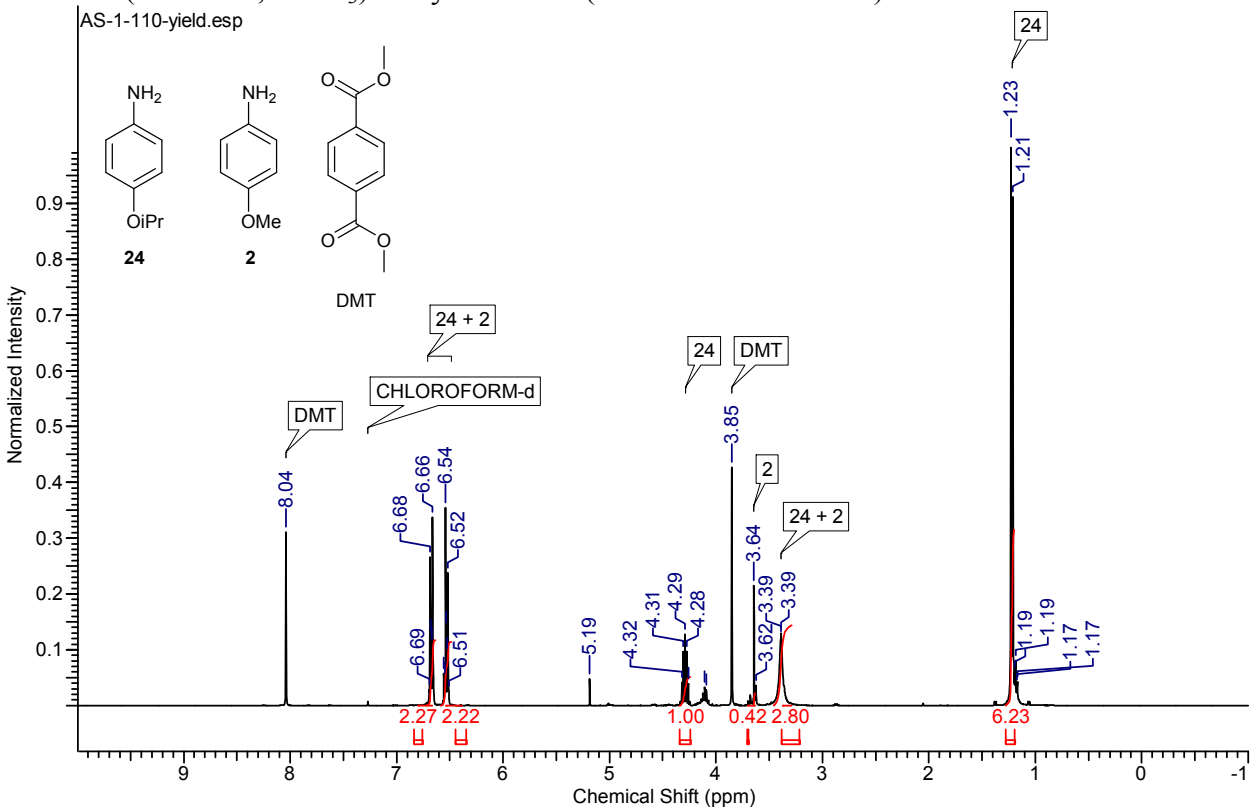
^{1}H NMR (600 MHz, $CDCl_3$) **18b**



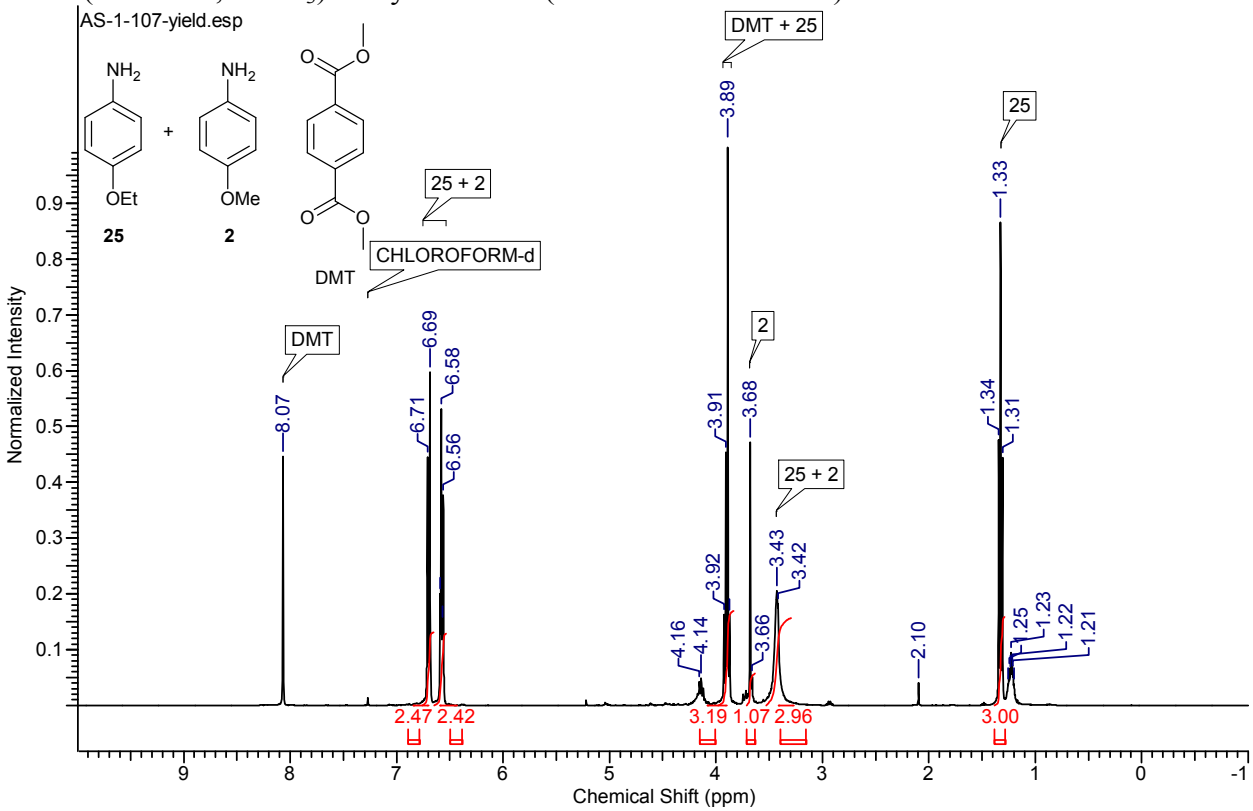
^{1}H NMR (500 MHz, $CDCl_3$) **19**



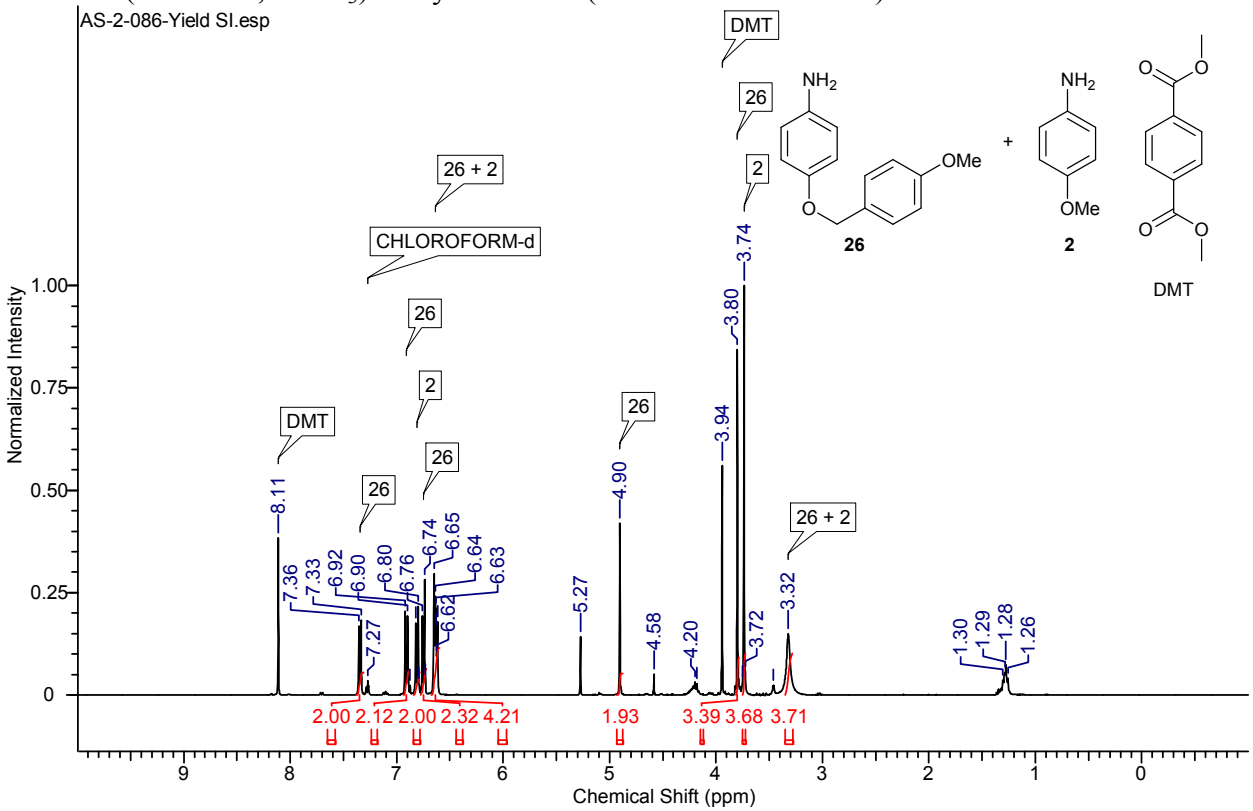
^{1}H NMR (400 MHz, $CDCl_3$) Entry **1**: **15** & **1** (with internal standard)



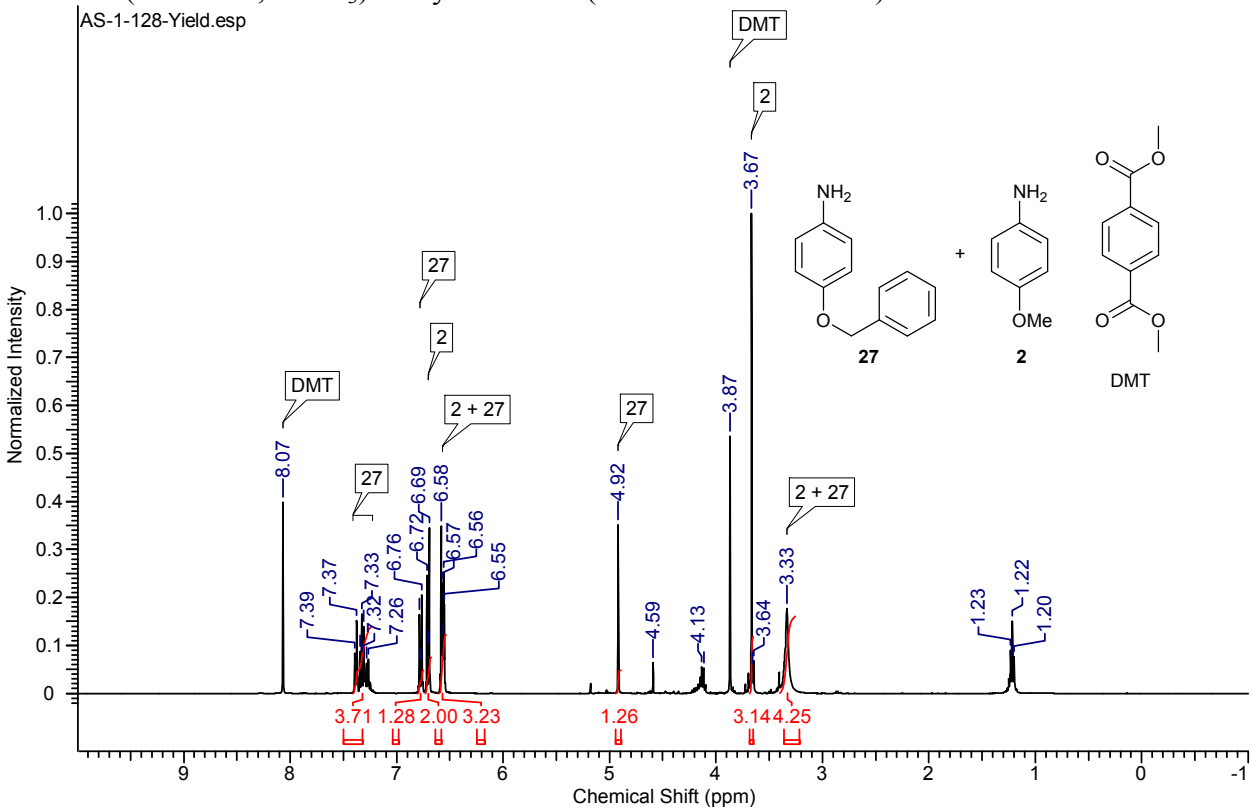
NMR (400 MHz, $CDCl_3$) Entry **2**: **25** & **2** (with internal standard) ^1H



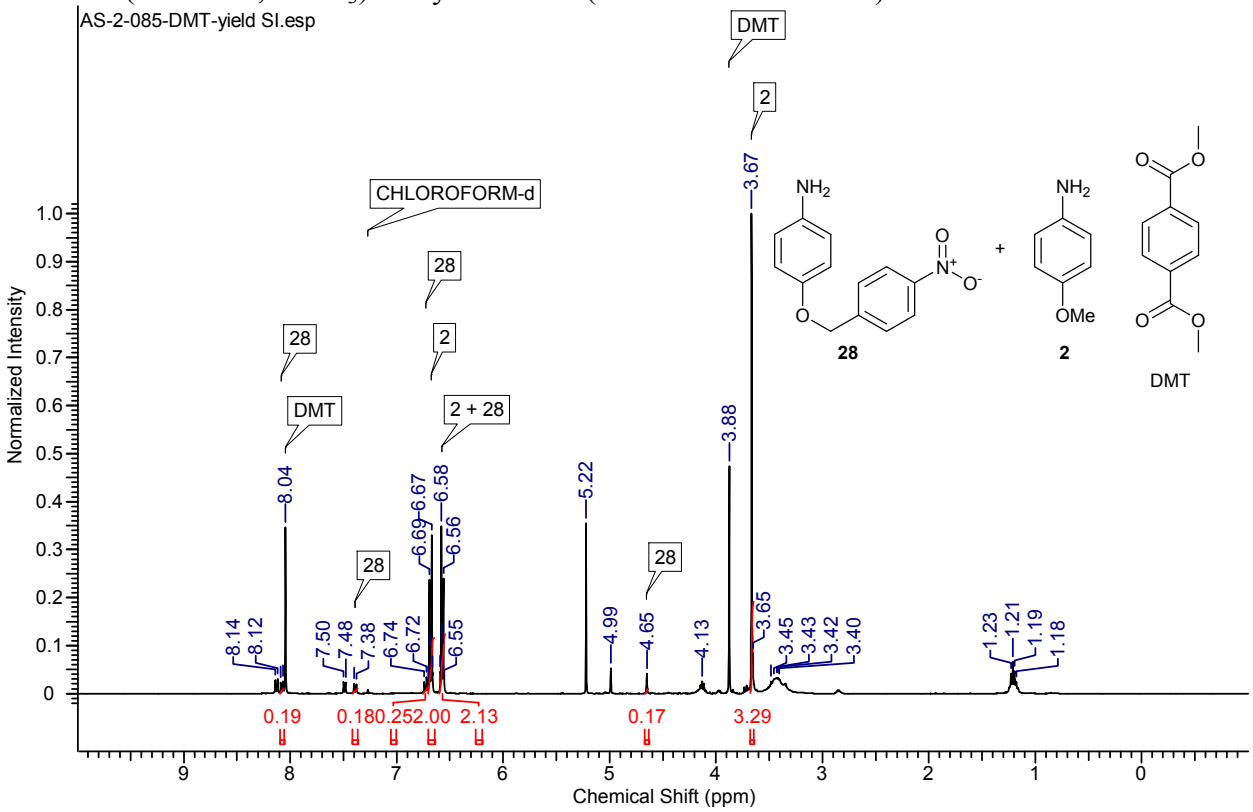
^1H NMR (400 MHz, $CDCl_3$) Entry **3**: **26** & **2** (with internal standard)



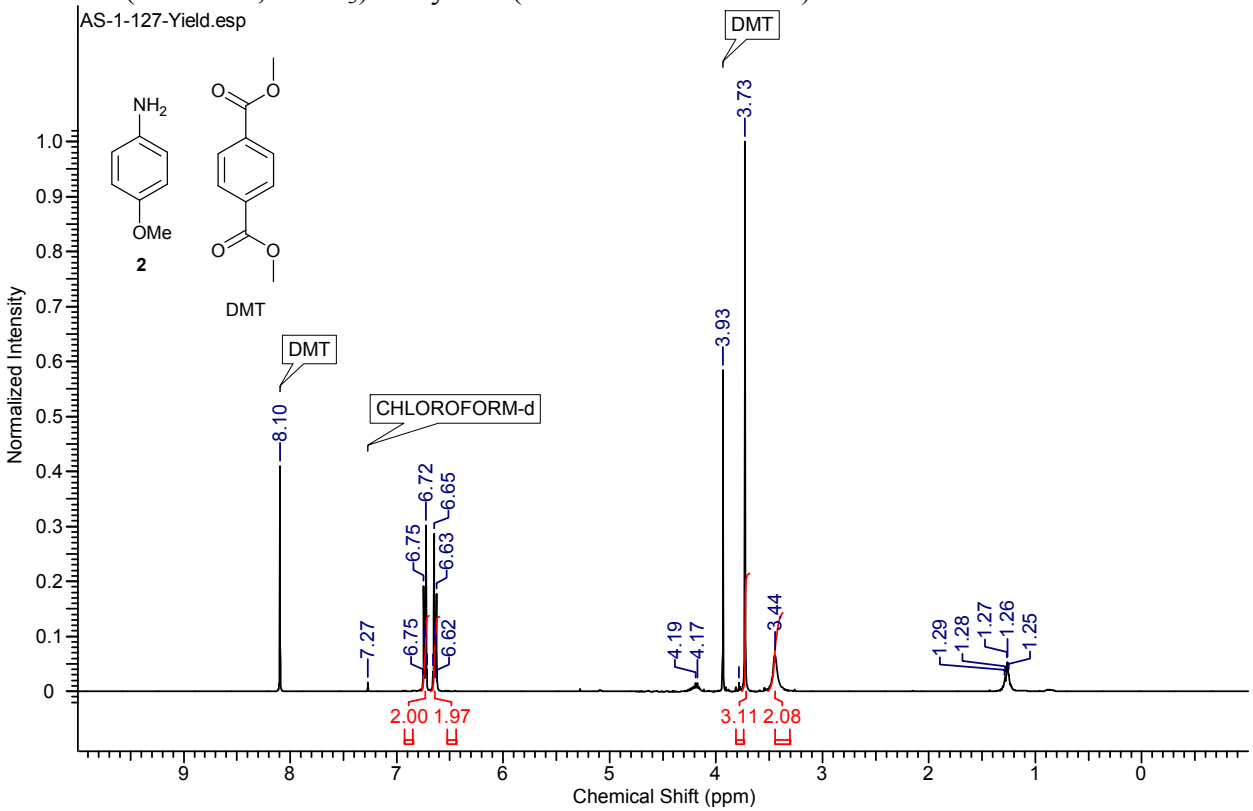
^{1}H NMR (400 MHz, $CDCl_3$) Entry **4**: **27** & **2** (with internal standard)



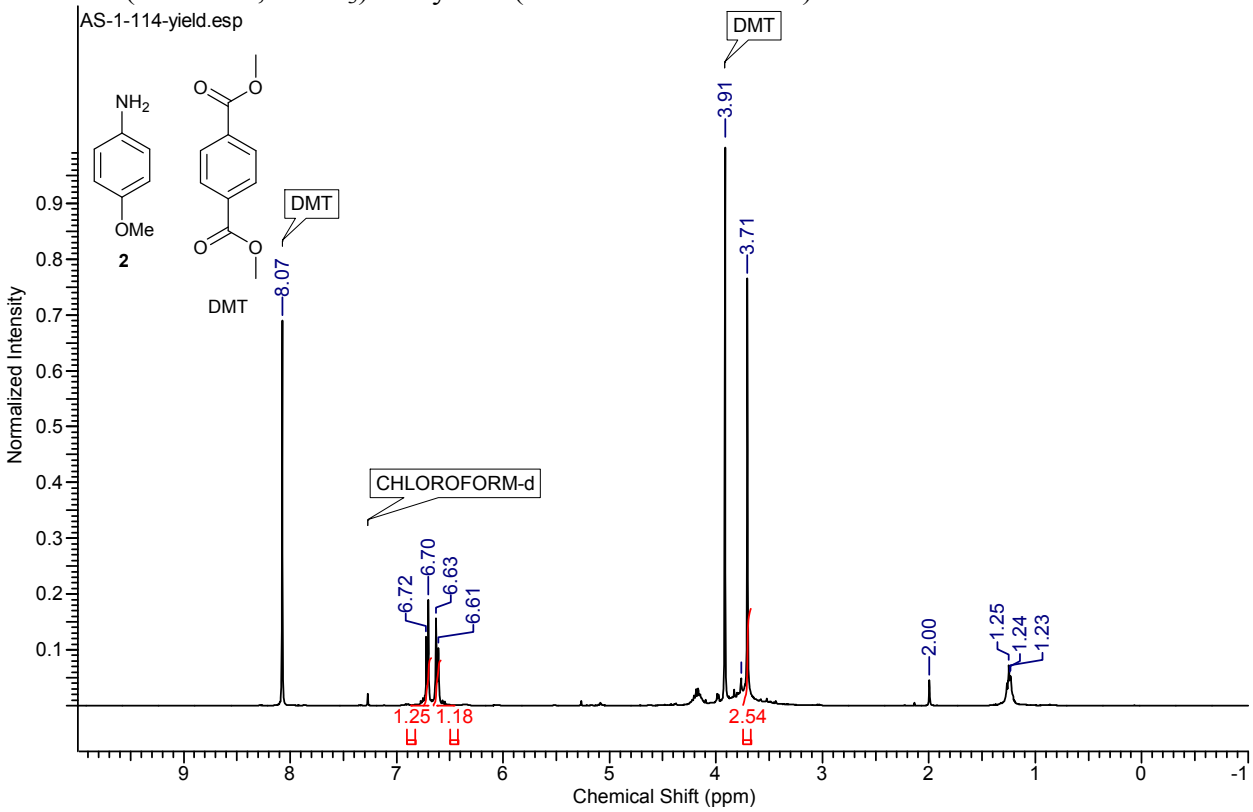
^{1}H NMR (400 MHz, $CDCl_3$) Entry **5**: **28** & **2** (with internal standard)



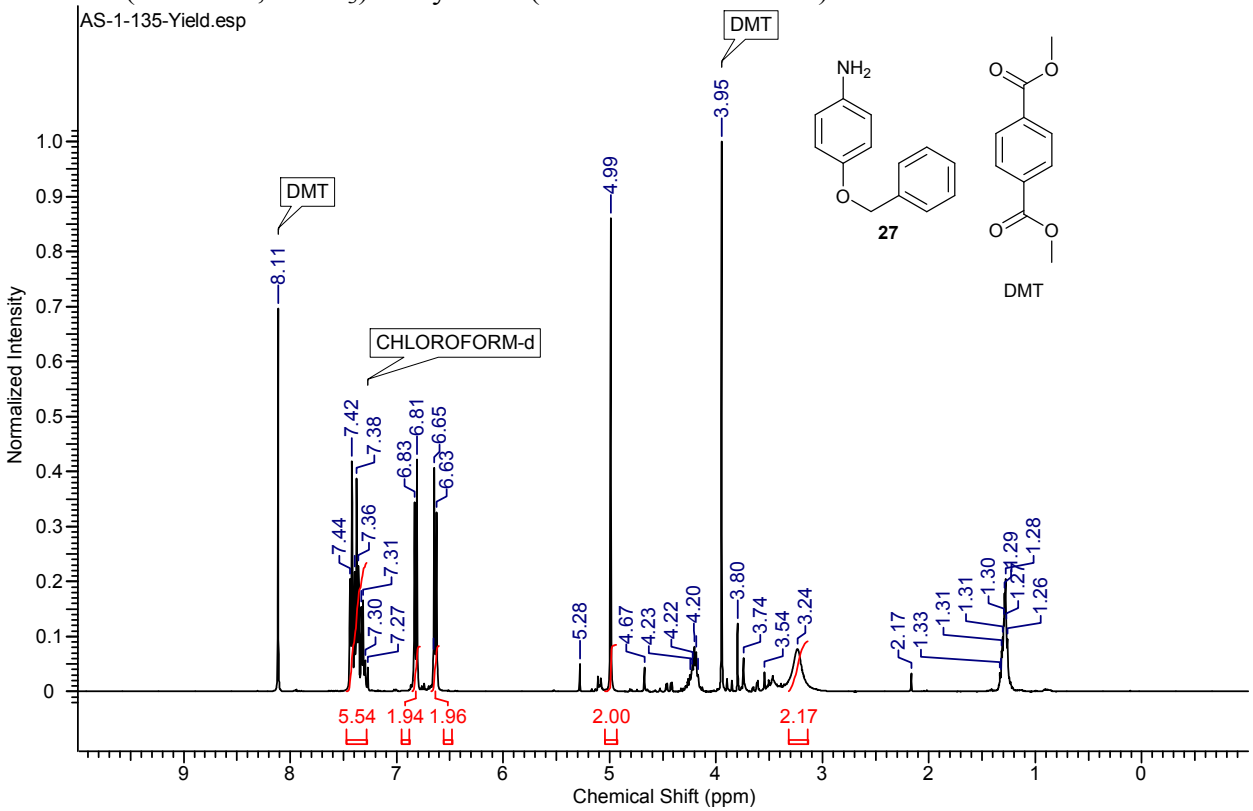
^{1}H NMR (400 MHz, $CDCl_3$) Entry **6**: **2** (with internal standard)



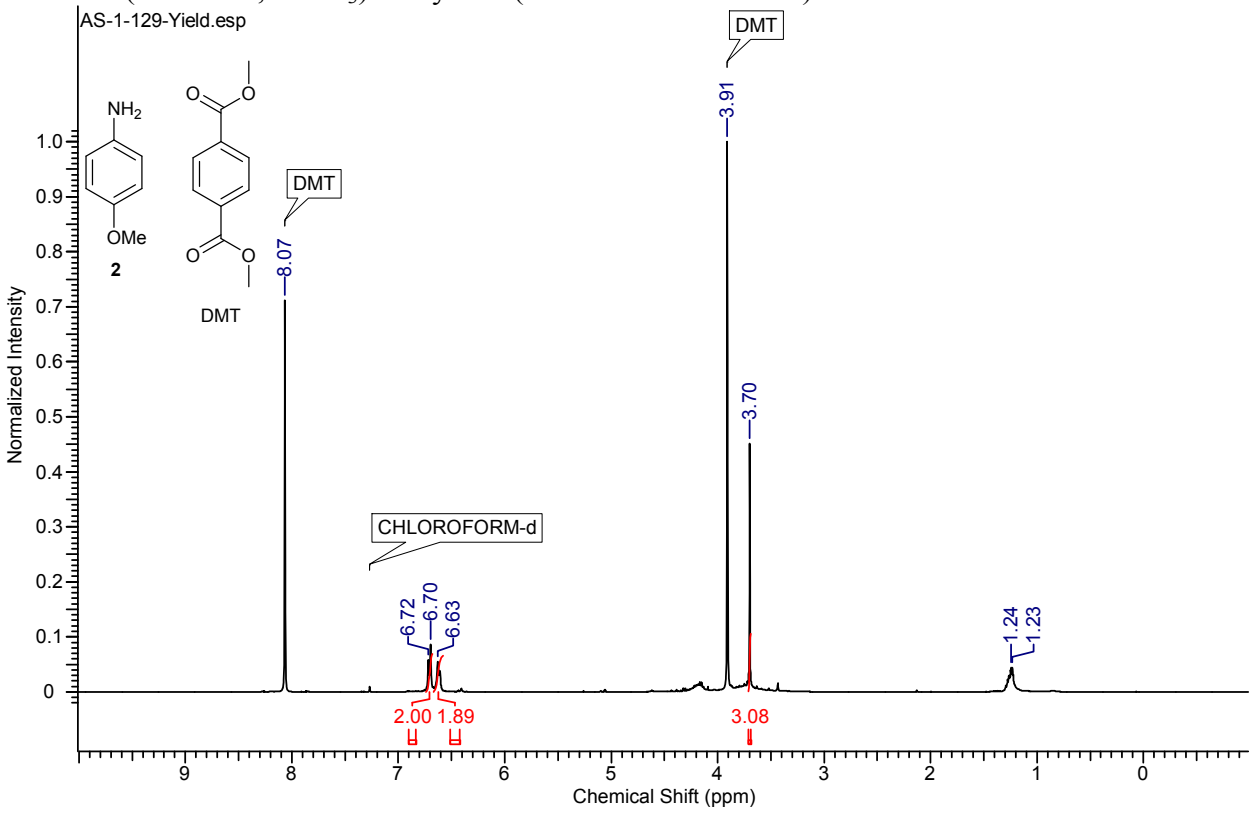
^{1}H NMR (400 MHz, $CDCl_3$) Entry **7**: **2** (with internal standard)



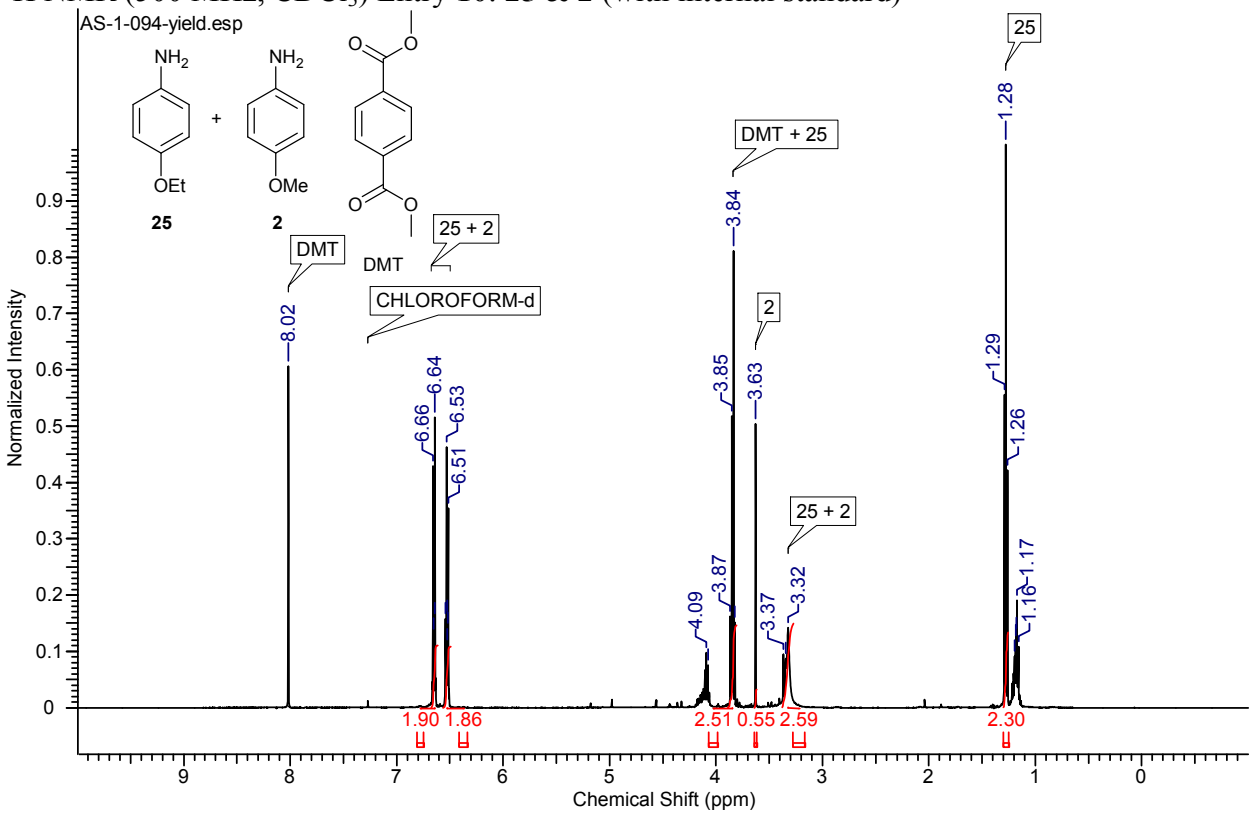
^{1}H NMR (400 MHz, $CDCl_3$) Entry **8**: **27** (with internal standard)



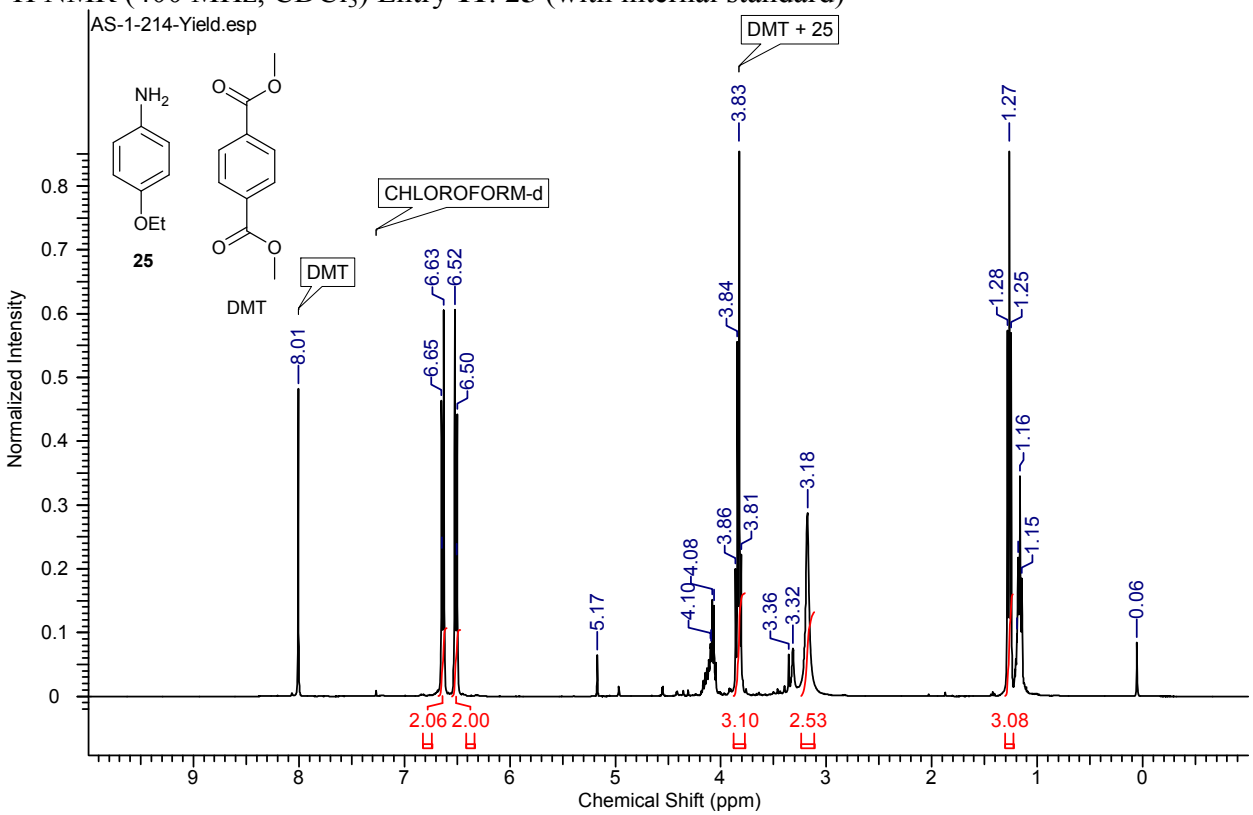
^{1}H NMR (400 MHz, $CDCl_3$) Entry **9**: **2** (with internal standard)



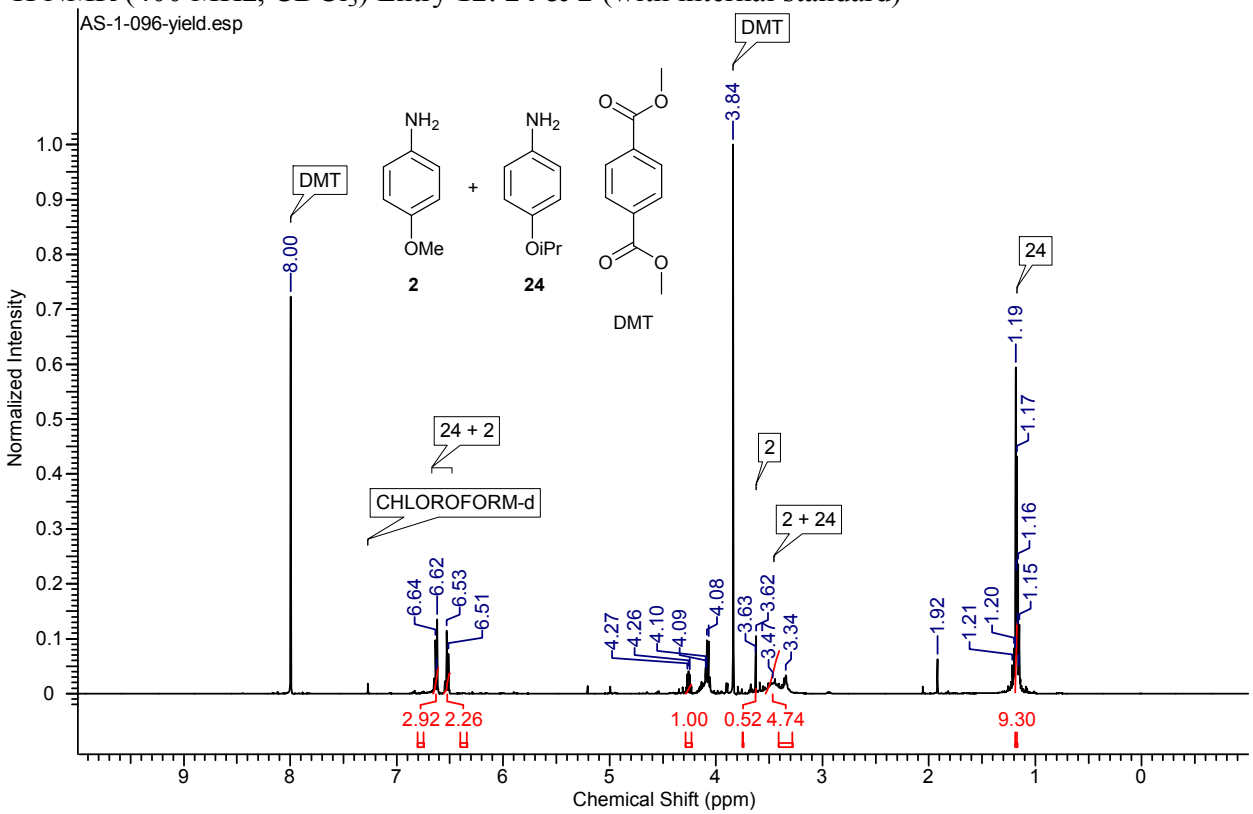
^{1}H NMR (500 MHz, $CDCl_3$) Entry **10**: **25** & **2** (with internal standard)



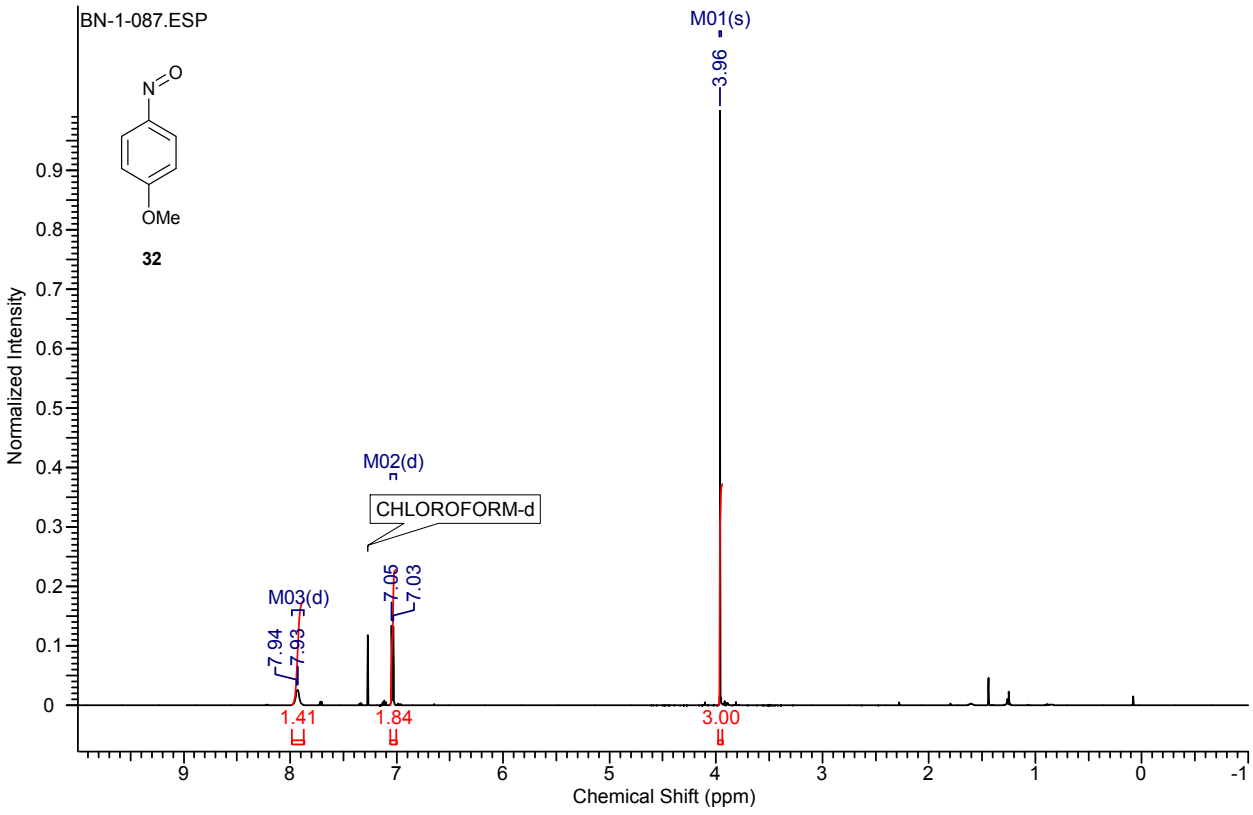
^{1}H NMR (400 MHz, $CDCl_3$) Entry **11**: **25** (with internal standard)



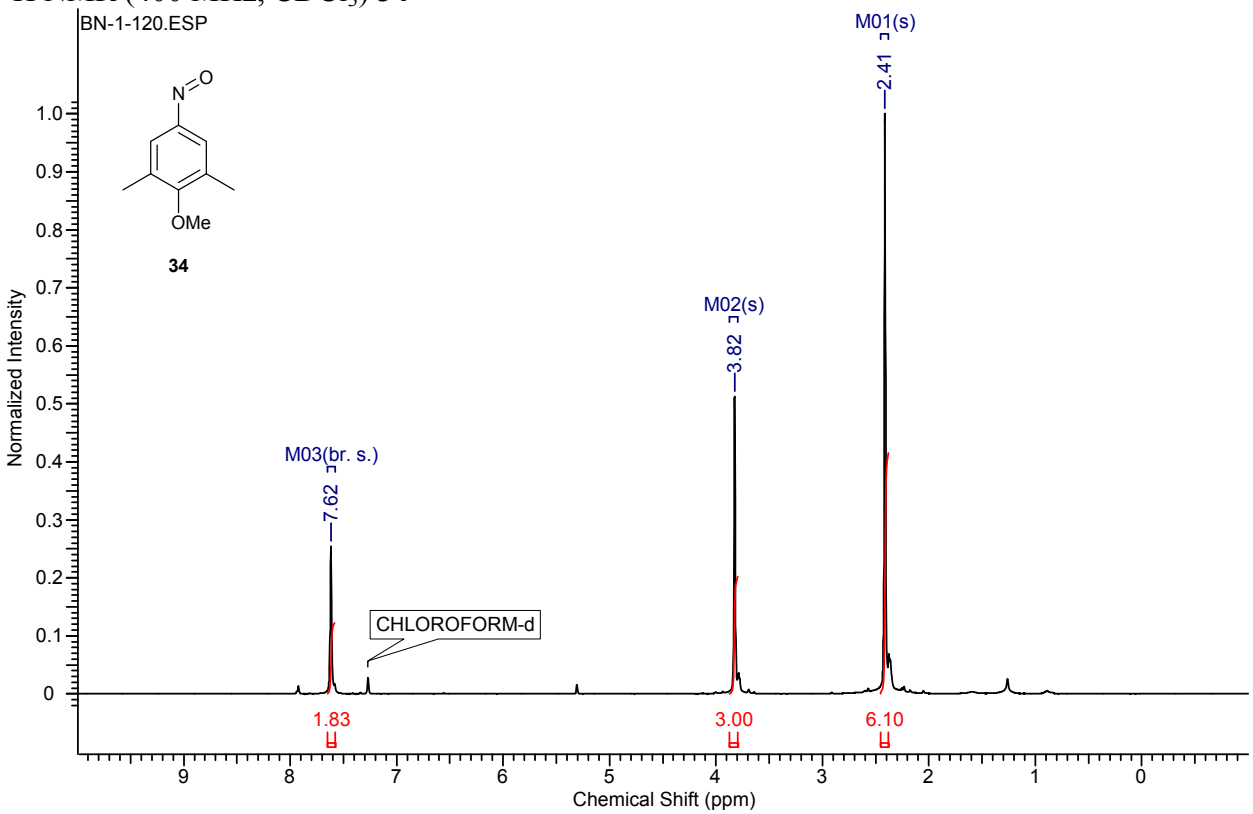
^{1}H NMR (400 MHz, $CDCl_3$) Entry **12**: **24** & **2** (with internal standard)



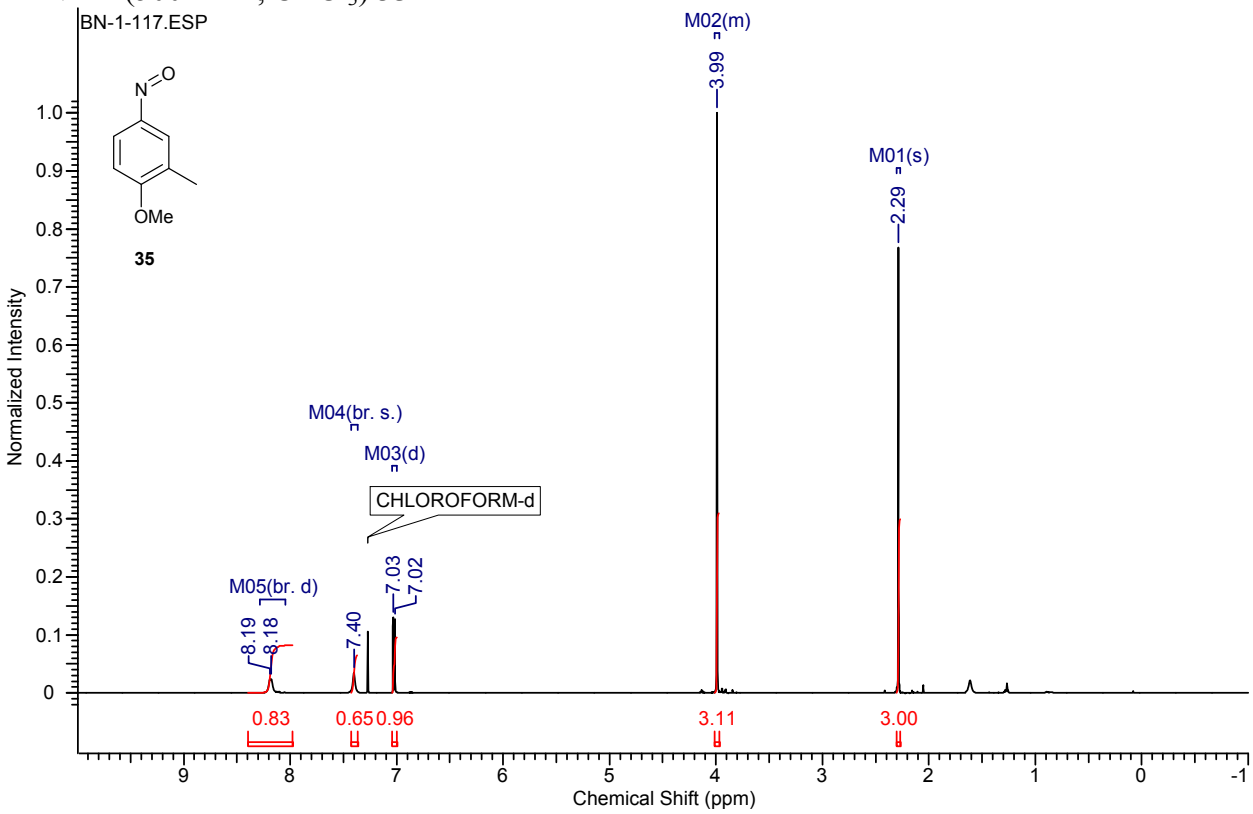
^{1}H NMR (500 MHz, $CDCl_3$) **32**



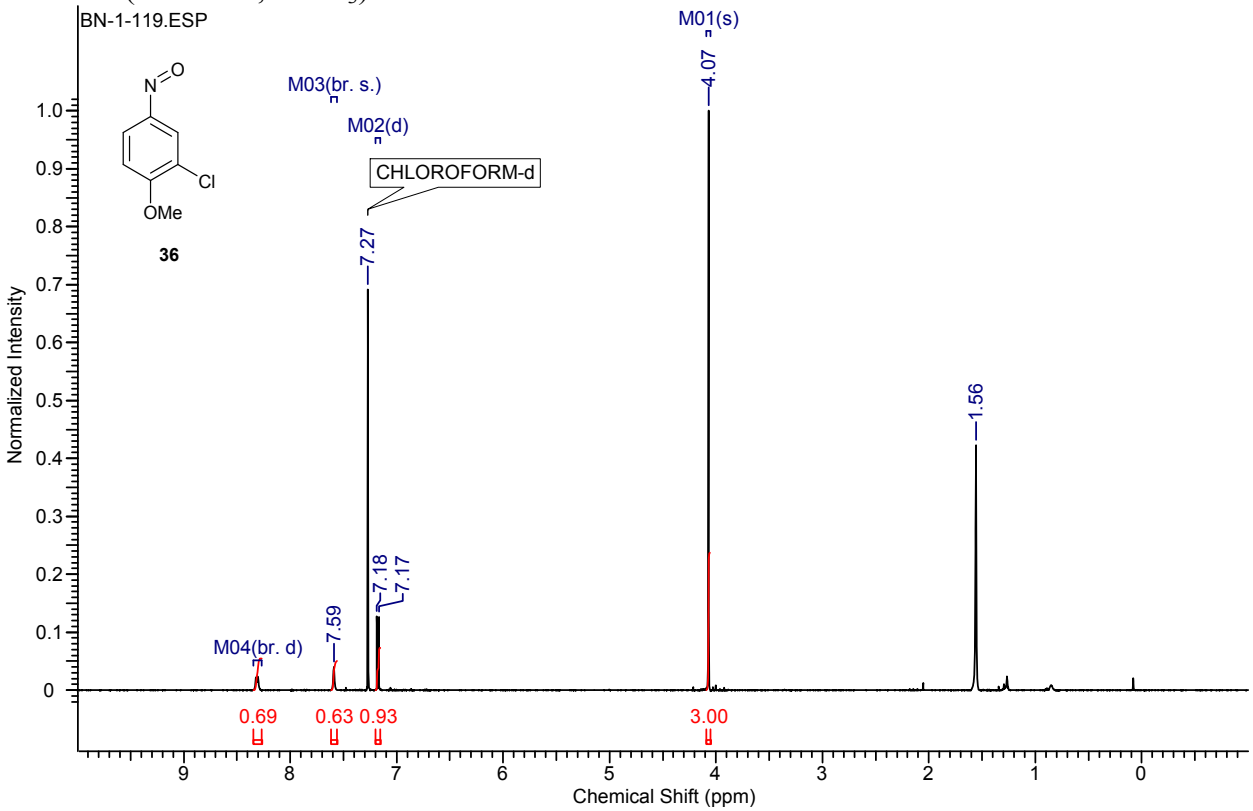
^{1}H NMR (400 MHz, $CDCl_3$) **34**



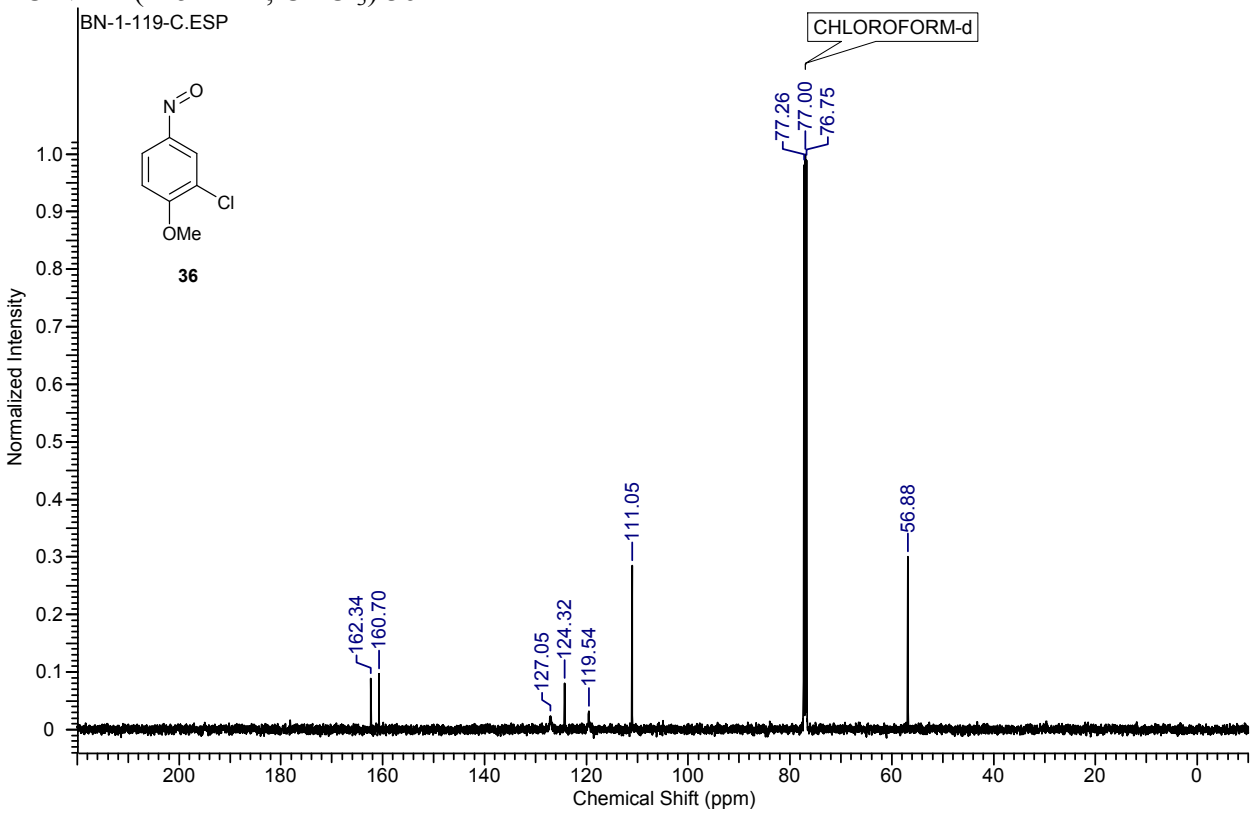
^{1}H NMR (500 MHz, $CDCl_3$) **35**



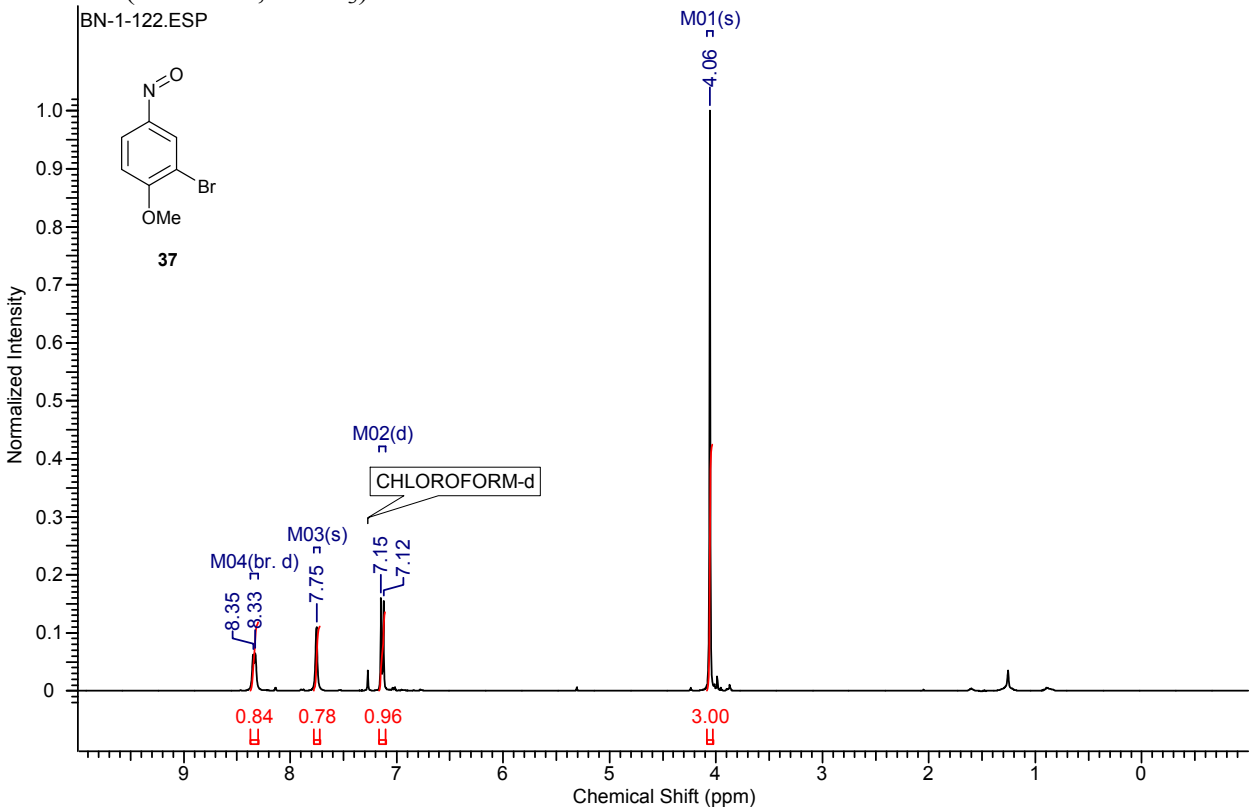
^{1}H NMR (500 MHz, $CDCl_3$) **36**



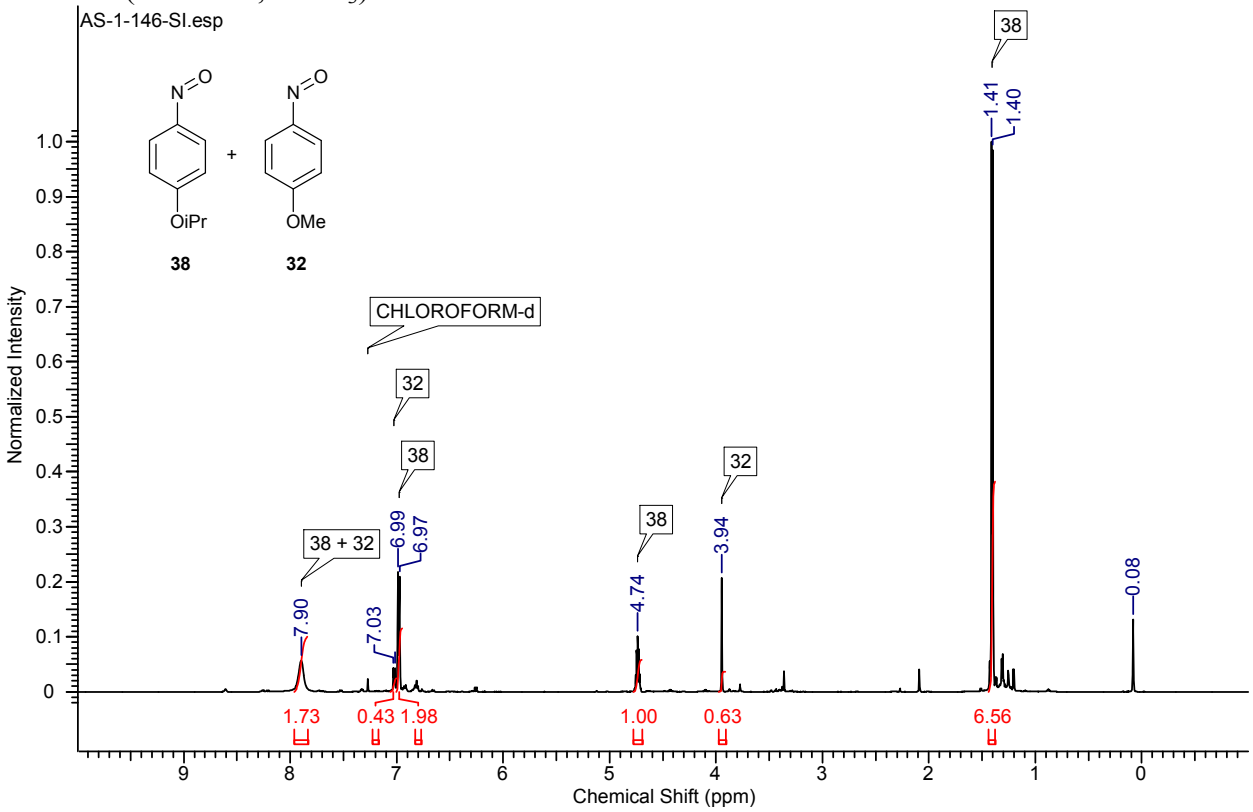
^{13}C NMR (125 MHz, $CDCl_3$) **36**



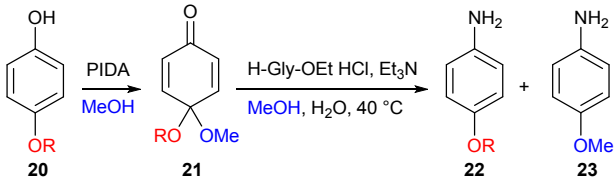
^{1}H NMR (400 MHz, $CDCl_3$) **37**



^{1}H NMR (600 MHz, $CDCl_3$) **38** & **32**



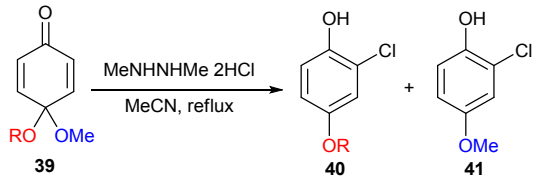
Scheme **1**:



Mixed quinone monoketals in the synthesis of anilines:

Phenol Derivative **20** (R)	pKa ROH in MeCN at 298K[33]	σ_{ROH} (pKa MeOH - pKa ROH)	**22** (R) (%)	**23** (Me) (%)	Alkoxide Retention **22** / (**22** + **23**)
iPr	16.6	-1.50	75	10	0.88
Et	15.9	-0.80	72	21	0.77
4-OMe-Bn	15.6	-0.50	37	45	0.45
Bn	15.4	-0.30	33	52	0.39
4-NO_2-Bn	14.9	0.20	5	57	0.08

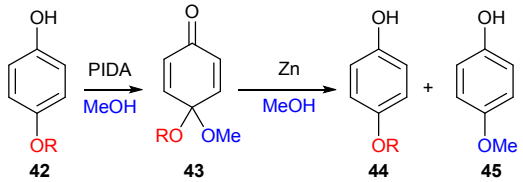
Scheme **2**:



Mixed quinone monoketals in the synthesis of *ortho*-chlorophenols (Zheng et. al.)[34]

Quinone Derivative **39** (R)	pKa ROH in MeCN at 298K[33]	σ_{ROH} (pKa MeOH - pKa ROH)	**40** (R) (%)	**41** (Me) (%)	Alkoxide Retention **40** / (**40** + **41**)
iPr	16.6	-1.50	75	10	0.88
Et	15.9	-0.80	66	19	0.78

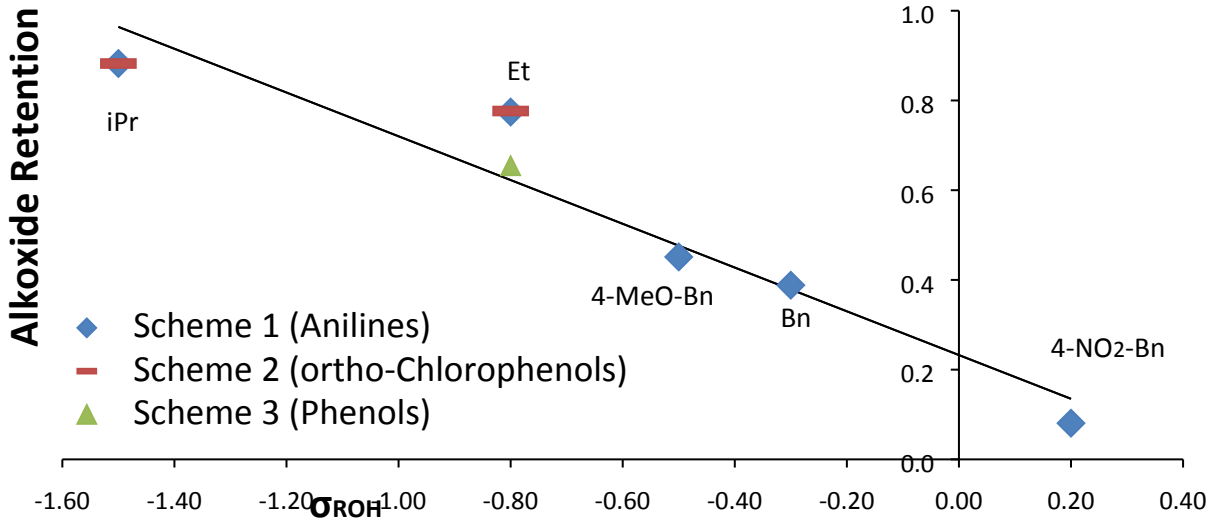
Scheme **3**:



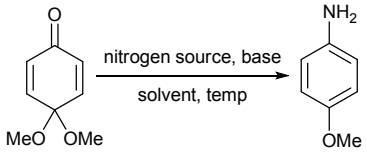
Mixed quinone monoketals in the synthesis 4-alkoxyphenols:

Phenol Derivative **42** (R)	pKa ROH in MeCN at 298K[33]	σ_{ROH} (pKa MeOH - pKa ROH)	**44** (R) (%)	**45** (Me) (%)	Alkoxide Retention **44** / (**44** + **45**)
Et	15.9	-0.80	53	28	0.65

Modified Hammett Plot:

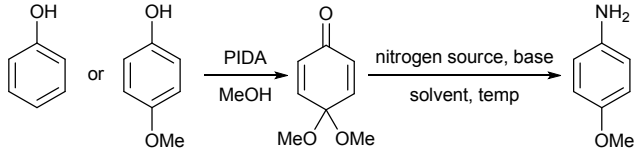


Optimization Table **S1**: Initial amine scope.



Entry	Solvent	Water	Nitrogen Source	Base	Temp	Yield (%)
1	neat	N/A	$BnNH_2$	N/A	100 °C	Decomp
2	$CHCl_3$	N/A	$BnNH_2$ (1.2 eq)	Et_xN (2.4 eq)	Reflux	No Reaction
3	$CHCl_3$	N/A	Diethyl Aminomalonate HCl (2 eq)	Et_xN (2.4 eq)	50 °C	No Reaction
4	MeOH	5%	H-Gly-OEt·HCl (7 eq)	Et_3N (6 eq)	Reflux	76%

Optimization Table **S2**: One-pot scope.



Entry	Starting Material	Solvent	PIDA	Water	Nitrogen Source	Base	Temp	Yield (%)
1	Phenol	MeOH then MeOH:EtOH (1:1)	2.1 eq	5%	H-Gly-OEt·HCl (3 eq)	$NaHCO_3$ (2.6 eq)	Reflux	35%
2	Phenol	MeOH	2.1 eq	5%	H-Gly-OEt·HCl (7 eq)	$NaHCO_3$ (6 eq)	Reflux	43%
3	Phenol	MeOH	2.1 eq	5%	H-Gly-OEt·HCl (7 eq)	Et_3N (9 eq)	Reflux	42%
4*	**Phenol**	**MeOH**	**2.1 eq**	**5%**	**H-Gly-OEt·HCl (7 eq)**	**Et_3N (9 eq)**	**40 °C**	**44%**
5	4-Methoxyphenol	MeOH	1.05 eq	5%	H-Gly-OEt·HCl (2 eq)	Et_3N (4 eq)	40 °C	57%
6*	**4-Methoxyphenol**	**MeOH**	**1.1 eq**	**5%**	**H-Gly-OEt·HCl (7 eq)**	**Et_3N (9 eq)**	**40 °C**	**85%**

*Entries 4 and 6 were used for General Procedures **B** and **A** respectively