Supporting Information

Carboxyl Radical-Assisted 1,5-Aryl Migration through Smiles Rearrangement

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Preparation of 4-Fluoro-2-phenoxybenzoic acid, 1o, Scheme 2.[1]

A mixture of 2-chloro-4-fluorobenzoic acid (873 mg, 5.0 mmol, 1.0 equiv), phenol (940 mg, 10 mmol, 2.0 equiv), K_2CO_3 (1.4 g, 10 mmol, 2.0 equiv), pyridine (0.4 mL, 5.0 mmol, 1.0 equiv), Cu powder (50 mg) and CuI (50 mg) in 5.0 mL H_2O was taken in a 50 mL round bottom flask. The reaction mixture was kept at reflux for 6 h. The mixture was then basified with Na_2CO_3 solution and extracted with Et_2O once and the aqueous phase was acidified with HCl. The resulting precipitates were extracted with dichloromethane (60 mL) and water (50 mL). The organic layer was washed with water (20 mL x 2) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (697 mg, 60%), mp 102-104 ^oC. ^1H NMR (600 MHz, DMSO-d_6): δ 7.93 (td, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.09-7.15 (m, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.0, 165 (d, *J* = 250.5 Hz), 157.5 (d, *J* = 10.5 Hz), 157.0, 134.3 (d, *J* = 10.5 Hz), 130.5, 124.0, 120.9 (d, *J* = 3.0 Hz), 118.5, 111.4 (d, *J* = 22.5 Hz), 108.2 (d, *J* = 25.5 Hz).

Preparation of 2-(*p*-Tolyloxy)-4-fluorobenzoic acid, 1p, Scheme 2.[1]

A mixture of 2-chloro-4-fluorobenzoic acid (873 mg, 5.0 mmol, 1.0 equiv), *p*-cresol (1.0 mL, 10 mmol, 2.0 equiv), K_2CO_3 (1.4 g, 10 mmol, 2.0 equiv), pyridine (0.4 mL, 5.0 mmol, 1.0 equiv), Cu powder (50 mg) and CuI (50 mg) in 5.0 mL H_2O was taken in a 50 mL round bottom flask. The reaction mixture was kept at reflux for 6 h. The mixture was then basified with Na_2CO_3 solution and extracted with Et_2O once and the aqueous phase was acidified with HCl. The resulting precipitates were extracted with dichloromethane (60 mL) and water (50 mL). The organic layer was washed with water (20 mL x 2) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (690 mg, 56%), mp 108-110 ^oC. ^1H NMR (600 MHz, DMSO-d_6): δ 12.93 (brs, 1H), 7.90 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.06 (td, *J* = 8.4 Hz, 1.8 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.71 (dd, *J* = 10.2 Hz, 1.8 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.1, 164.9 (d, *J* = 250.5 Hz), 158.2 (d, *J* = 10.5 Hz), 154.5, 134.2 (d, *J* = 10.5 Hz), 133.4, 130.9, 120.5 (d, *J* = 3.0 Hz), 118.9, 110.8 (d, *J* = 21.0 Hz), 107.3 (d, *J* = 24.0

Hz), 20.7; IR (neat): υ_{max} 1675, 1597, 1440, 1258, 851, 770 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{14}H_{11}FO_3Na$ $[M + Na]^+$: 269.0590; found: 269.0585.

Preparation of 4-Fluoro-2-(naphthalen-3-yloxy)benzoic acid, 1q, Scheme 2.[1]

A mixture of 2-chloro-4-fluorobenzoic acid (873 mg, 5.0 mmol, 1.0 equiv), naphthalen-2-ol (1.4 g, 10 mmol, 2.0 equiv), K_2CO_3 (1.4 g, 10 mmol, 2.0 equiv), pyridine (0.4 mL, 5.0 mmol, 1.0 equiv), Cu powder (50 mg) and CuI (50 mg) in 5.0 mL H_2O was taken in a 50 mL round bottom flask. The reaction mixture was kept at reflux for 6 h. The mixture was then basified with Na_2CO_3 solution and extracted with Et_2O once and the aqueous phase was acidified with HCl. The resulting precipitates were extracted with dichloromethane (60 mL) and water (50 mL). The organic layer was washed with water (20 mL x 2) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (819 mg, 58%), mp 178-180 ^oC. ^1H NMR (600 MHz, DMSO-d_6): δ 7.96-7.99 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.28-7.30 (m, 2H), 7.17 (td, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.97 (dd, *J* = 10.2 Hz, 2.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 165.9, 165.1 (d, *J* = 250.5 Hz), 157.3 (d, *J* = 10.5 Hz), 155.2, 134.4 (d, *J* = 10.5 Hz), 134.3, 130.5, 130.2, 128.1, 127.5, 127.1, 125.3, 121.1 (d, *J* = 4.5 Hz), 119.7, 113.1, 111.8 (d, *J* = 22.5 Hz), 109.4 (d, *J* = 24.0 Hz); IR (neat): υ_{max} 1681, 1603, 1429, 1293, 1232, 768, 609 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{17}H_{11}FO_3Na$ $[M + Na]^+$: 305.0590; found: 305.0591.

Preparation of 2-(Naphthalen-1-yloxy)benzoic acid, 1j, Scheme 2.[1]

A mixture of 2-ethyliodobenzoate (2.76 g, 10 mmol, 1.0 equiv), 1-naphthol (1.73 g, 12 mmol, 1.2 equiv), K_2CO_3 (1.8 g, 13 mmol, 1.3 equiv), Cu powder (0.32 g, 5.0 mmol, 0.5 equiv) and KI (830 mg, 5.0 mmol, 0.5 equiv) in 20 mL DMF was taken in a 100 mL round bottom flask. The reaction mixture was stirred at 110 °C for 24 h under nitrogen atmosphere. Then the reaction mixture was quenched through the addition of H_2O and the mixture was extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane/ ethyl acetate = 9/1) to obtain the pure desired ethyl 2-(naphthalen-1-

yloxy)benzoate in 23% (672 mg) yield as a colorless oil. Then the pure ethyl 2-(naphthalen-1-yloxy)benzoate (0.6 g, 2.05 mmol) was dissolved in a solution of 0.75 g NaOH in 10 mL H_2O and 10 mL MeOH and stirred at room temperature for 6 h. The reaction mixture was then acidified with 6N HCl. The resulting precipitates were extracted with dichloromethane (50 mL) and water (40 mL). The organic layer was washed with water (20 mL x 2) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel, hexane/ ethyl acetate = 7/3 as eluent to afford the desired white solid product 80% (435 mg) yield, mp 131-133 ^oC. ^1H NMR (600 MHz, DMSO-d_6): δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.89 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.52-7.59 (m, 3H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 167.0, 155.7, 153.4, 134.9, 134.0, 131.9, 128.2, 127.2, 126.54, 126.46, 126.0, 124.5, 124.4, 123.3, 122.0, 120.7, 112.2.

Preparation of 4-Nitro-2-phenoxybenzoic acid, 1s, Scheme 2.

To a stirred solution of 2-chloro-4-nitrobenzoic acid (1.50 g, 7.45 mmol, 1.0 equiv) and phenol (1.5 g, 16 mmol, 2.1 equiv) in MeOH (10 mL) was added a solution of NaOMe in MeOH (25 wt%, 5.0 mL, 20 mmol) under nitrogen atmosphere. After 15 minutes the solution was concentrated to dryness and the residue was taken up in dimethylacetamide (30 mL). Copper powder (50 mg) was added and the mixture was heated at 180 ^oC for 1 h under nitrogen atmosphere. The reaction mixture was cooled and acidified with 3N HCl until no more precipitate had formed. The resulting precipitates were extracted with dichloromethane (60 mL) and cold water (70 mL). The organic layer was washed with water (20 mL x 3) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 95:5 dichloromethane /methanol) afforded the desired product as a white solid, (1.35 g, 70%), mp 161-163 ^oC. ^1H NMR (600 MHz, DMSO-d_6): δ 8.01-8.05 (m, 2H), 7.62 (s, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.0, 156.2, 155.9, 150.2, 132.6, 130.8, 130.6, 124.9, 119.4, 118.5, 114.3; IR (neat): υ_{max} 1699, 1546, 1350, 1242, 800 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9NO_5Na$ $[M + Na]^+$: 282.0378; found: 282.0381.

Preparation of 2-Phenoxypyridine-3-carboxylic acid, 1w, Scheme 2.[2]

Ethyl 2-chloropyridine-3-carboxylate (1.5 g, 8.0 mmol, 1.0 equiv), phenol (1.5 g, 16 mmol, 2.0 equiv), anhydrous K_2CO_3 (3.3 g, 24 mmol, 3.0 equiv) and solvent DMF (50 mL) were taken in a single necked round bottom flask fitted with a reflux condenser and heated to 100 ^{0}C for 10 h. The formation of ethyl 2-phenoxypyridine-3-carboxylate was monitored by TLC. After the completion, the reaction mixture was cooled to room temperature. After that ice cold water was added to the reaction mixture and the product was extracted with ethyl acetate (20 x 2), the organic layer was washed with 10 % NaOH solution (10 mL), and washed with brine (10 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product ethyl 2-phenoxypyridine-3-carboxylate as a yellowish oil, (1.3 g, 65%). After that the pure ethyl 2-phenoxypyridine-3-carboxylate (730 mg, 3.0 mmol, 1.0 equiv) was taken in a 100 mL single necked round bottom flask. LiOH (400 mg, 9.0 mmol, 3.0 equiv), THF (4.0 mL) and water (1.0 mL) were added under stirring. The reaction mixture was stirred for overnight at room temperature. The reaction was monitored by TLC. After the completion of the reaction the solvent was removed under reduced pressure. The residue was cooled to 5 ^{o}C by adding ice cold water and neutralised using concentrated HCl. The solid thus obtained was filtered, washed with cold water and dried under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired 2-phenoxypyridine-3-carboxylic acid product as a white solid, (280 mg, 43%), mp 180-182 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.22-8.25 (m, 2H), 7.40 (t, *J* = 8.1 Hz, 2H), 7.17-7.23 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 165.9, 160.9, 153.9, 150.6, 141.6, 129.7, 124.6, 121.5, 119.0, 116.4; IR (neat): υ_{max} 1689, 1586, 1426, 1277, 1240, 751 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{12}H_9NO_3Na$ $[M + Na]^+$: 238.0480; found: 238.0478.

General experimental procedure for the preparation of 2-(Phenylthio)benzoic acids, Scheme 3.[3]

To a 100 mL round bottom flask equipped with magnetic stir bar, 2-iodo benzoic acid (744 mg, 3.0 mmol, 1.0 equiv) was added in 20 mL of water, followed by thiophenols (3.0 mmol, 1.0 equiv), potassium hydroxide (KOH) (841 mg, 15 mmol, 5.0 equiv) and copper(0) (19 mg, 0.3 mmol). The reaction mixture was heated to 110 ^{o}C for 12 h. Then the reaction mixture was

cooled and acidified with 3N HCl until no more precipitate was formed. The resulting precipitates were extracted with dichloromethane (60 mL) and water (50 mL). The organic layer was washed with water (10 mL x 2) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as eluent to afford the desired white solid product.

2-(Phenylthio)benzoic acid, 3a, Scheme 3.[3] The same general procedure was followed by using 2-iodo benzoic acid (744 mg, 3.0 mmol, 1.0 equiv) and benzenethiol (0.31 mL, 3.0 mmol, 1.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (636 mg, 92%), mp 166-168 ^oC. ^1H NMR (600 MHz, DMSO-d_6): δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.47-7.52 (m, 5H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 167.8, 142.1, 135.5, 132.8, 132.6, 131.3, 130.5, 129.7, 128.1, 127.3, 125.1; IR (neat): υ_{max} 1676, 1465, 1409, 1254, 744, 692 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_{10}O_2SNa$ $[M + Na]^+$: 253.0299; found: 253.0301.

2-(4-Chlorophenylthio)benzoic acid, 3c, Scheme 3. The same general procedure was followed by using 2-iodo benzoic acid (744 mg, 3.0 mmol, 1.0 equiv) and 4-chlorobenzenethiol (433 mg, 3.0 mmol, 1.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (715 mg, 90%), mp 240-242 ^oC. ^1H NMR (600 MHz, DMSO-d_6): δ 7.92 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.52-7.55 (m, 4H), 7.38 (td, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 167.8, 141.3, 137.0, 134.6, 133.0, 131.9, 131.3, 130.5, 128.4, 127.6, 125.4; IR (neat): υ_{max} 1675, 1465, 1312, 1261, 814, 741 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9ClO_2SNa$ $[M + Na]^+$: 286.9909; found: 286.9910.

2-(*p*-Tolylthio)benzoic acid, 3d, Scheme 3. The same general procedure was followed by using 2-iodo benzoic acid (744 mg, 3.0 mmol, 1.0 equiv) and 4-methylbenzenethiol (373 mg, 3.0 mmol, 1.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (667 mg, 91%), mp 206-208 ^oC. ^1H NMR (600 MHz, DMSO-d_6): δ 7.91 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.29-7.33 (m, 3H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 167.8, 142.9, 139.7, 135.8, 132.8, 131.3, 131.2, 128.8, 127.6, 126.8, 124.8, 21.2;

IR (neat): υ_{max} 1674, 1461, 1412, 1252, 806, 744 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{14}H_{12}O_2SNa$ $[M + Na]^+$: 267.0456; found: 267.0453.

Preparation of 4-Fluoro-2-(phenylthio)benzoic acid, 3b, Scheme 3.

To a 100 mL round bottom flask equipped with magnetic stir bar, 2-chloro-4-fluorobenzoic acid (524 mg, 3.0 mmol, 1.0 equiv) was added in 20 mL of dimethylformamide (DMF), followed by benzenethiol (0.31 mL, 3.0 mmol, 1.0 equiv), potassium hydroxide (KOH) (337 mg, 6.0 mmol, 2.0 equiv) and copper(0) (95 mg, 1.5 mmol, 0.5 equiv). The reaction mixture was heated to 130 ^oC for 12 h. Then the reaction mixture was cooled and acidified with 3N HCl until no more precipitate had formed. The resulting precipitates were extracted with dichloromethane (60 mL) and cold water (50 mL). The organic layer was washed with cold water (10 mL x 3) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (521 mg, 70%), mp 195-197 ^oC. ^1H NMR (600 MHz, DMSO-d_6): δ 8.02 (dd, *J* = 8.4 Hz, 6.6 Hz, 1H), 7.56-7.60 (m, 5H), 7.04 (td, *J* = 8.4 Hz, 1.8 Hz, 1H), 6.28 (dd, *J* = 10.8 Hz, 2.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.9, 164.6 (d, *J* = 250.5 Hz), 146.8 (d, *J* = 9.0 Hz), 136.1, 134.4 (d, *J* = 9.0 Hz), 131.4, 130.8, 130.5, 123.7 (d, *J* = 3.0 Hz), 113.0 (d, *J* = 25.5 Hz), 112.1 (d, *J* = 21.0 Hz); IR (neat): υ_{max} 1675, 1568, 1415, 1258, 909, 690 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9FO_2SNa$ $[M + Na]^+$: 271.0205; found: 271.0189.

Preparation of 5-Bromo-2-(phenylthio)benzoic acid, 3e, Scheme 3.

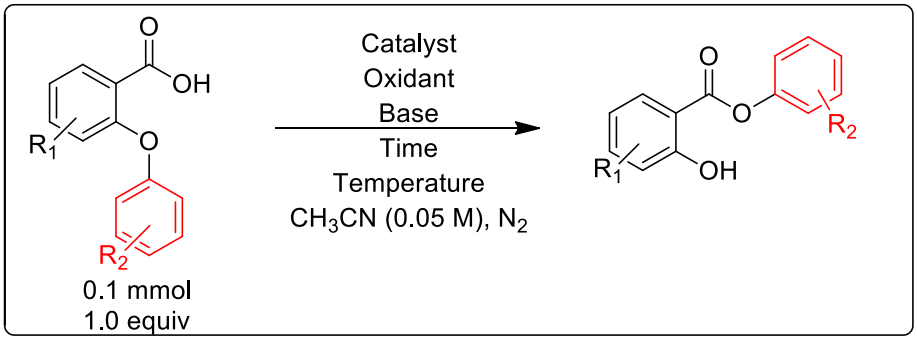
To a 100 mL round bottom flask equipped with magnetic stir bar, 2,5-dibromobenzoic acid (840 mg, 3.0 mmol, 1.0 equiv) was added in 20 mL of dimethylformamide (DMF), followed by benzenethiol (0.31 mL, 3.0 mmol, 1.0 equiv), potassium carbonate (K_2CO_3) (830 mg, 6.0 mmol, 2.0 equiv) and copper(0) (50 mg, 0.75 mmol, 0.25 equiv). The reaction mixture was heated to 150 ^oC for 12 h. Then the reaction mixture was cooled and acidified with 3N HCl until no more precipitate had formed. The resulting precipitates were extracted with dichloromethane (60 mL) and cold water (50 mL). The organic layer was washed with cold water (10 mL x 3) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 6:4 hexane/ethyl

acetate) afforded the desired product as a white solid, (556 mg, 60%), mp 168-170 ^{o}C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.00 (d, J = 2.4 Hz, 1H), 7.50-7.57 (m, 6H), 6.64 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.5, 141.9, 135.6, 135.4, 133.4, 131.9, 130.6, 130.1, 129.7, 129.2, 117.6; IR (neat): υ_{max} 1692, 1457, 1414, 1306, 1248 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9BrO_2SNa$ $[M + Na]^+$: 330.9404; found: 330.9411.

Preparation of 5-Fluoro-2-(phenylthio)benzoic acid, 3f, Scheme 3.

To a 100 mL round bottom flask equipped with magnetic stir bar, 2-bromo-5-fluorobenzoic acid (657 mg, 3.0 mmol, 1.0 equiv) was added in 20 mL of dimethylformamide (DMF), followed by benzenethiol (0.31 mL, 3.0 mmol, 1.0 equiv), potassium carbonate (K_2CO_3) (830 mg, 6.0 mmol, 2.0 equiv) and copper(0) (50 mg, 0.75 mmol, 0.25 equiv). The reaction mixture was heated to 150 ^{o}C for 12 h. Then the reaction mixture was cooled and acidified with 3N HCl until no more precipitate had formed. The resulting precipitates were extracted with dichloromethane (60 mL) and cold water (50 mL). The organic layer was washed with cold water (10 mL x 3) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (462 mg, 62%), mp 160-162 ^{o}C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.66 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 7.45-7.51 (m, 5H), 7.28 (td, *J* = 8.4 Hz, 3.0 Hz, 1H), 6.79 (dd, *J* = 9.0 Hz, 5.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.8 (d, *J* = 3.0 Hz), 159.8 (d, *J* = 243.0 Hz), 136.9 (d, *J* = 3.0 Hz), 135.0, 132.9, 130.5, 130.4 (d, *J* = 7.5 Hz), 130.1 (d, *J* = 7.5 Hz), 129.6, 120.1 (d, *J* = 22.5 Hz), 117.5 (d, *J* = 22.5 Hz); IR (neat): υ_{max} 1687, 1465, 1424, 1250, 755 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9FO_2SNa$ $[M + Na]^+$: 271.0205; found: 271.0210.

Optimization Details:



entry	catalyst	oxidant	base	time	temp.	yield
1	$AgNO_3$ 10 mol%	$K_2S_2O_8$ 3.0 equiv	-	24 h	120° C	25%
2	$AgNO_3$ 20 mol%	$K_2S_2O_8$ 3.0 equiv	-	24 h	120° C	23%
3	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 3.0 equiv	-	24 h	120° C	30%
4[a]	$Cu(OAc)_2$ 5 mol%	$[PhCO_2]_2$ 1.25 equiv	-	24 h	75° C	18%
5	$Cu(OAc)_2$ 5 mol%	aq. TBHP 3.0 equiv	-	24 h	120° C	0%
6	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 2.0 equiv	-	24 h	120° C	34%
7	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	24 h	120° C	40%
8	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.0 equiv	-	24 h	120° C	35%
9	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130° C	44%
10	$Cu(OAc)_2$ 5 mol%	TBHP in decene 3.0 equiv	-	36 h	130° C	0%
11[b]	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130° C	0%
12[c]	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130° C	0%
13[d]	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130° C	20%
14	$AgNO_3$ 5 mol%	$(NH_4)_2S_2O_8$ 1.5 equiv	-	36 h	130° C	27%
15	$AgNO_3$ 5 mol%	$PhI(OAc)_2$ 1.5 equiv	-	36 h	130° C	0%
16	$AgNO_3$ 5 mol%	$[PhCO_2]_2$ 1.5 equiv	-	36 h	130° C	trace
17	$AgNO_3$ 10 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130° C	35%
18	$AgNO_3$ 2.5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130° C	32%

19	AgOAc 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	34%
20	Ag_2O 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	33%
21	Ag_2CO_3 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	36%
22	Ag_2SO_4 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	35%
23	$Cu(OAc)_2$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	120^o C	25%
24	$Pd(TFA)_2$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	trace
25	$Fe(acac)_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	36%
26	$Fe(acac)_3$ 20 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	37%
27	$Ni(OTF)_2$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	35%
28	Fe_2O_3 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	40%
29	TBAI 5 mol%	$K_2S_2O_8$ 1.5 equiv	-	36 h	130^o C	30%
30	I_2 10 mol%	TBHP in decene 3.0 equiv	-	36 h	130^o C	0%
31	$AgNO_3$ 5 mol%	Selectflour 1.5 equiv	-	36 h	120^o C	trace
32[e]	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv.	-	36 h	130^o C	0%
33	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	$NaHCO_3$ 1.5 equiv.	36 h	130^o C	35%
34	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	K_2CO_3 2.0 equiv	36 h	130^o C	10%
35	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	Na_2CO_3 2.0 equiv	36 h	130^o C	18%
36	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	Cs_2CO_3 2 equiv	36 h	130^o C	trace
37	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	^{t}BuOK 2.0 equiv	36 h	130^o C	0%
38	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	K_2HPO_4 2.0 equiv	36 h	130^o C	34%
39	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	CF_3COONa 2.0 equiv	36 h	130^o C	50%
40	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	CH_3COONa 2.0 equiv	36 h	130^o C	30%
41	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	CF_3COONa 3.0 equiv	36 h	130^o C	48%
42	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	CF_3COOK 2.0 equiv	36 h	130^o C	64%
43	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	CF_3COOK 1.5 equiv	36 h	130^o C	57%

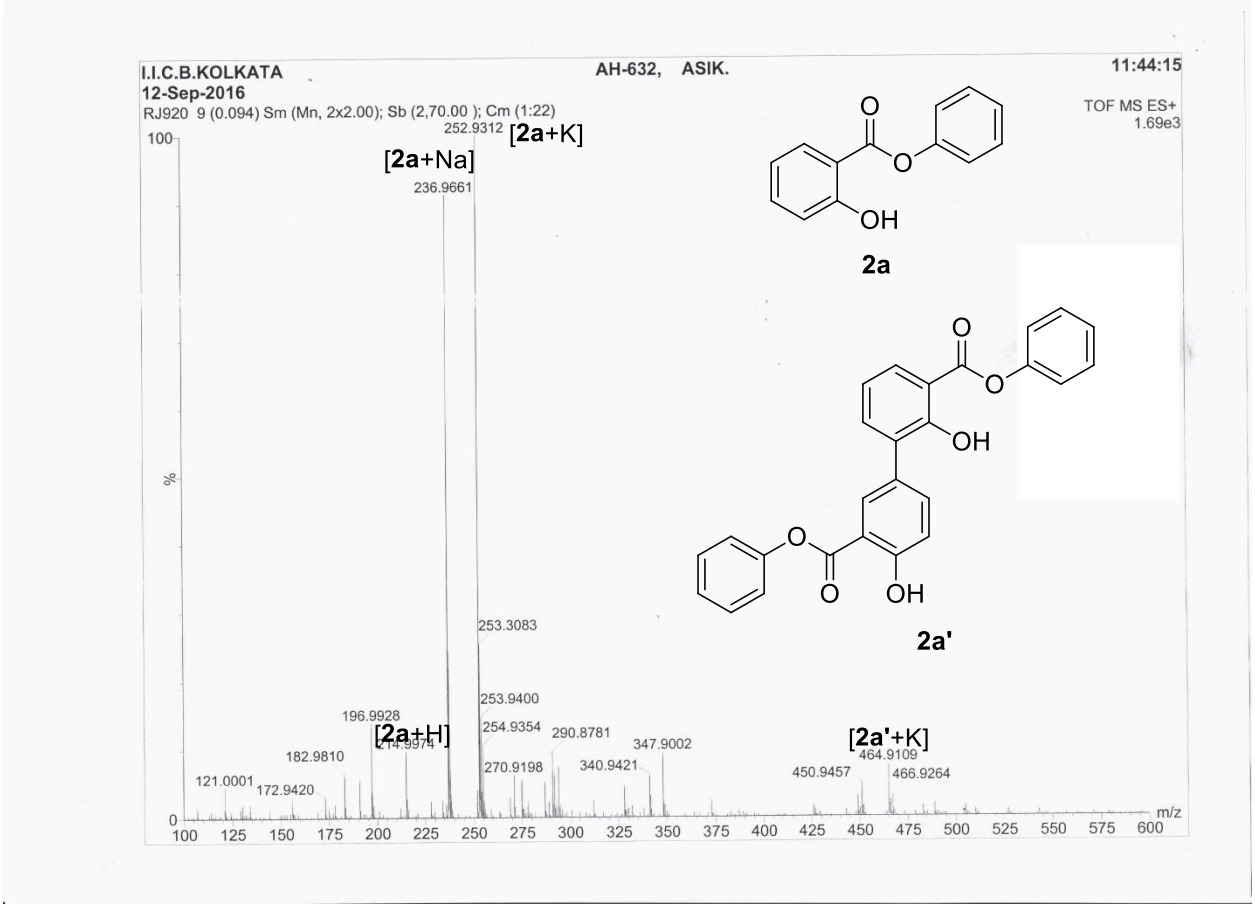
44	$AgNO_3$ 5 mol%	$Na_2S_2O_8$ 1.5 equiv	CF_3COOK 2.0 equiv	36 h	130^o C	53%
45	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv.	CH_3COOCs 2.0 equiv	36 h	130^o C	18%
46	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	DBU 2.0 equiv	36 h	130^o C	0%
47	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	$KHCO_3$ 2.0 equiv	36 h	130^o C	20%
48	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	Li_2CO_3 2.0 equiv	36 h	130^o C	32%
49	$AgNO_3$ 10 mol%	$K_2S_2O_8$ 1.5 equiv	CF_3COOK 2.0 equiv	36 h	130^o C	52%
50	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 2.0 equiv	CF_3COOK 2.0 equiv	36 h	130^o C	50%
51[f]	$AgNO_3$ 5 mol%	$K_2S_2O_8$ 1.5 equiv	CF_3COOK 2.0 equiv	36 h	130^o C	60%
52	-	$K_2S_2O_8$ 1.5 equiv	CF_3COOK 2.0 equiv	36 h	130^o C	37%
53	$AgNO_3$ 5 mol%	-	CF_3COOK 2.0 equiv	36 h	130^o C	0%
54	-	-	CF_3COOK 2.0 equiv	36 h	130^o C	0%

[a]HIFP solvent was used. [b](CH_3CN:H_2O, 1:1) solvent was used. [c]DMF, DMSO, THF, DCE, 1,4-dioxane, Ph-CF_3, Toluene and CF_3COOH solvent was used. [d]PhCN solvent was used. [e]1,10-Phenanthroline ligand was used. [f] O_2 was used.

Migratory reaction of 1a at 0.5 mmol scale, Scheme 2.

To an oven-dried 100 mL sealed tube, a mixture of 2-phenoxybenzoic acid (107 mg, 0.5 mmol, 1.0 equiv), silver nitrate (4.3 mg, 0.025 mmol), potassium persulfate (203 mg, 0.75 mmol, 1.5 equiv) and potassium trifluoroacetate (152 mg, 1.0 mmol, 2.0 equiv) was taken and dry MeCN (10 mL) was added to it. After flushing with nitrogen, the vessel was sealed with a screw cap. The reaction mixture was allowed to stir for 36 h at 130 ^{o}C. After completion (as indicated by TLC), the reaction mixture was cooled to room temperature. Then the reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (50 mL). The organic layer was washed with water (10 mL x 3) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a yellow oil, (53.5 mg, 50%).

The electrospray ionization (ESI) mass data of the crude standard reaction mixture



Control experiments, Scheme 4.

The standard reaction with radical scavenger (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO), Scheme 4a.

To an oven-dried 15 mL sealed tube, a mixture of 2-phenoxybenzoic acid (21.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv), potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) (31 mg, 0.2 mmol, 2.0 equiv) was taken and dry MeCN (2.0 mL) was added to it. After flushing with nitrogen, the vessel was sealed with a screw cap. The reaction mixture was allowed to stir for 36 h at 130 ^{o}C. The reaction mixture was cooled to room temperature. A very trace amount (>5%) product was formed as indicated by TLC.

The standard reaction with radical scavenger (Butylated hydroxytoluene (BHT), Scheme 4a.

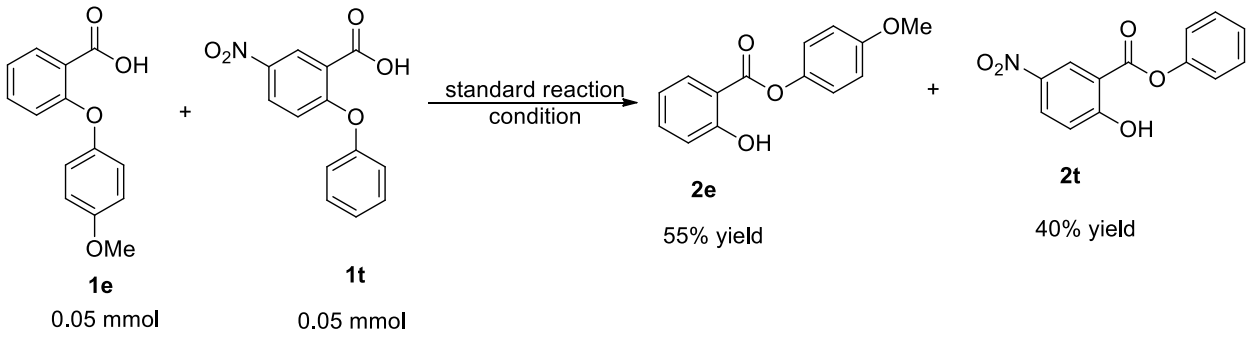
To an oven-dried 15 mL sealed tube, a mixture of 2-phenoxybenzoic acid (21.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv), potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv) and butylated hydroxytoluene (BHT) (88 mg, 0.2 mmol, 2.0 equiv) was taken and dry MeCN (2.0 mL) was added to it. After flushing with nitrogen, the vessel was sealed with a screw cap. The reaction mixture was allowed to stir for 36 h at 130 ^{o}C. The reaction mixture was cooled to room temperature. A very trace amount (>5%) product was formed as indicated by TLC.

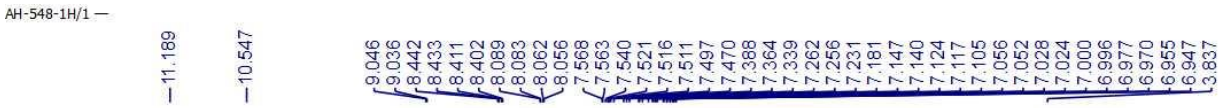
Crossover experiment, Scheme 4b.

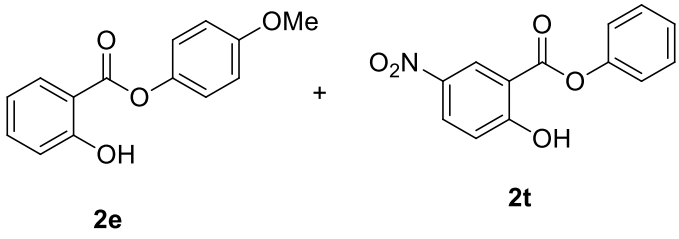
To an oven-dried 15 mL sealed tube, a mixture of 2-(4-methoxyphenoxy)benzoic acid (12.5 mg, 0.05 mmol, 1.0 equiv), 5-nitro-2-phenoxybenzoic acid (13 mg, 0.05 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv) was taken then dry MeCN (2.0 mL) was added to it. After flushing with nitrogen, the vessel was sealed with a screw cap. The reaction mixture was allowed to stir for 36 h at 130 ^{o}C. After completion (as detected by TLC), the reaction mixture was cooled to room temperature. Then the reaction mixture was poured into

water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane (9/1) as eluent to afford the desired product **2e** in 55% yield (~ 6.5 mg) and **2s** in 40% yield (5.0 mg).

Cross-over Experiments

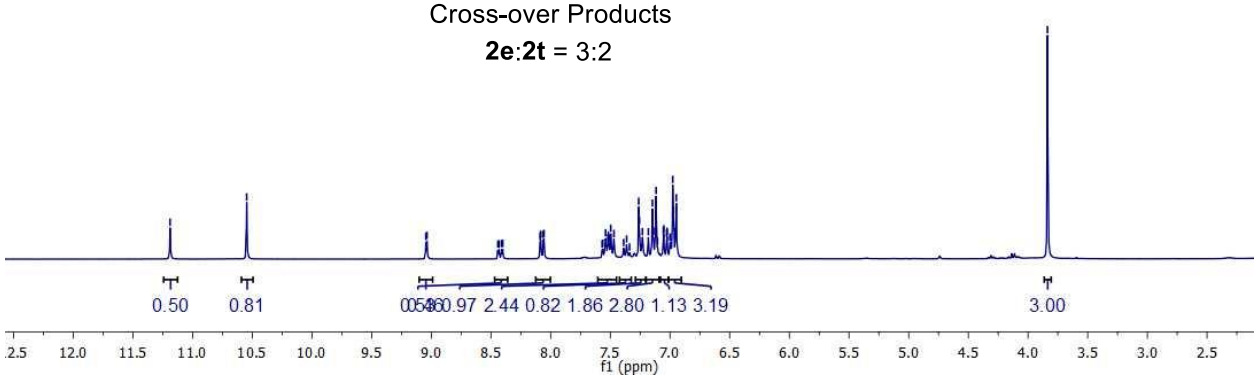


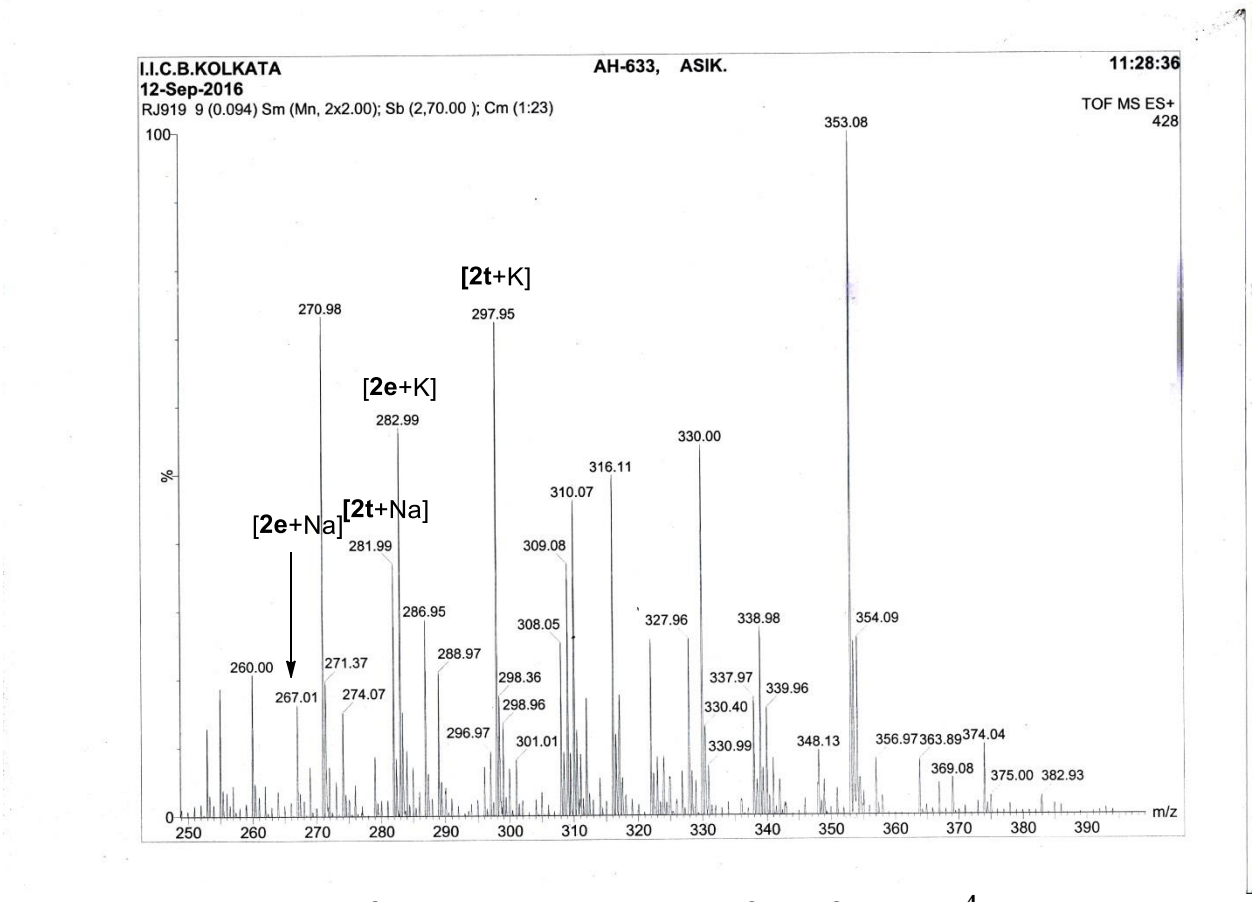




Cross-over Products

2e:**2t** = 3:2





Experimental procedure for the selective reduction of disulfide bond.[4]

To an oven-dried 10 mL round bottom flask equipped with magnetic stir bar, a mixture of diphenyl 2,2'-disulfanediyldibenzoate (**4a**) (59.5 mg, 0.13 mmol, 1.0 equiv) and triphenylphosphine (34 mg, 0.13 mmol, 1.0 equiv) was taken in a mixed solvent 1,4-dioxane (1.0 mL) and water (0.2 mL). To this reaction mixture one drop of HCl was added. The reaction mixture was stirred at 40 ^{o}C for 2.0 h under nitrogen atmosphre. After completion (as detected by TLC), the reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (30 mL). The organic layer was washed with water (10 mL x 2) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired monomer product as a white solid phenyl 2-mercaptobenzoate (**5a**)[27], (45.5 mg, 76%), mp 79-81 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.29 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 8.4 Hz, 2H), 7.39-7.43 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.24-7.28 (m, 3H), 4.78 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.3, 150.6, 139.5, 133.1, 132.2, 131.1, 129.5, 126.0, 125.0, 124.8, 121.8; IR

(neat): υ_{max} 1715, 1590, 1483, 1251, 1193, 1043, 744 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_{10}O_2SNa$ $[M + Na]^+$: 253.0299; found: 253.0284.

Experimental procedure for the hydrolysis of Phenyl 2-hydroxybenzoate ester (2a) to the corresponding Salicylic acid (6a) and Phenol.

To a 10 mL round bottom flask equipped with magnetic stir bar, the phenyl 2-hydroxybenzoate ester (**2a**) (43 mg, 0.2 mmol) was dissolved in a solution of NaOH (80 mg, 10 equiv) in 1.0 mL H_2O and 1.0 mL MeOH and stirred at room temperature for 12 h. The reaction mixture was then acidified with 6N HCl. The resulting mixture was extracted with dichloromethane (30 mL) and water (20 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel, hexane/ ethyl acetate = 7/3 as eluent to afford the desired white solid salicylic acid (**6a**) in 92% (25.5 mg) yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.4, 161.6, 136.1, 130.7, 119.6, 117.5, 113.3.

Crystal Structure:

The crystal was grown in chloroform solvent. The pure compound was dissolved in dry chloroform and slow evaporation led to the crystal **2t**. The crystal data was collected in X-ray spectroscopy (Bruker Kappa Apex-2, CCD Area Detector), and the data was analyzed using olex2 software. The structures are given below. The corresponding .cif file has been uploaded separately as supporting information.

Crystal data and structure refinement for the compound (2t) rj_ah421_0m.

Identification code	rj_ah421_0m
Empirical formula	$C_{13}H_9NO_5$
Formula weight	259.21
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.7430(9)
b/Å	16.6008(14)
c/Å	6.9203(7)

α/°	90
β/°	100.069(5)
γ/°	90
Volume/Å^3	1215.17(19)
Z	4
ρ_{calc}g/cm^3	1.417
μ/mm^{-1}	0.111
F(000)	536.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.85 to 55.052
Index ranges	-13 ≤ h ≤ 13, -21 ≤ k ≤ 16, -8 ≤ l ≤ 9
Reflections collected	11534
Independent reflections	2674 [R_{int} = 0.0374, R_{sigma} = 0.0344]
Data/restraints/parameters	2674/0/174
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0468, wR_2 = 0.1185
Final R indexes [all data]	R_1 = 0.0772, wR_2 = 0.1364
Largest diff. peak/hole / e Å^{-3}	0.18/-0.15

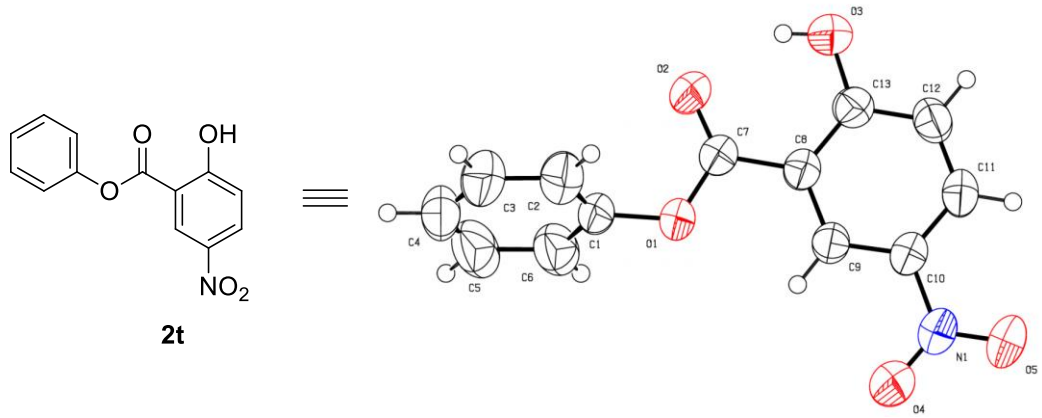
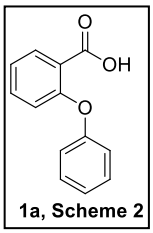


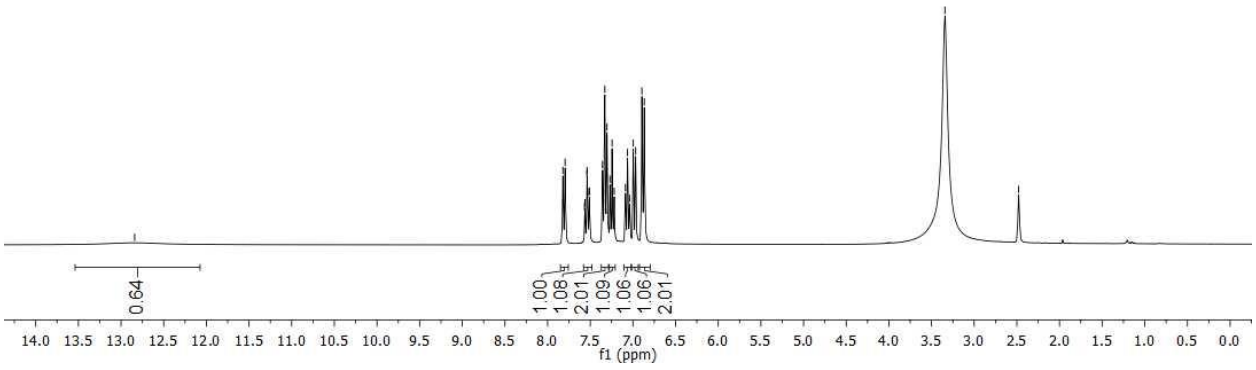
Figure 1. Crystal structure of **2t** (30% ellipsoid contour probability).

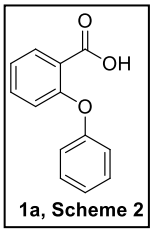
References:

1. C. Wang, I. Piel and F. Glorius, *J. Am. Chem. Soc*., 2009, **131**, 4194-4195.
2. A. Vinayak, M. Sudha, R. P. Kumar and K. Lalita. S, *Int. Res. J. Pharm*., 2013, **12**, 62-66.
3. J. D. Majmudar, H. B. Hodges-Loaiza, K. Hahne, J. L. Donelson, J. Song, L. Shrestha, M. L. Harrison, C. A. Hrycyna and R. A. Gibbs, *Bioorg. Med. Chem*., 2012, **20**, 283-295.
4. L. E. Overman, J. Smoot and J. D. Overman, *Synthesis*, 1974, 59-60.

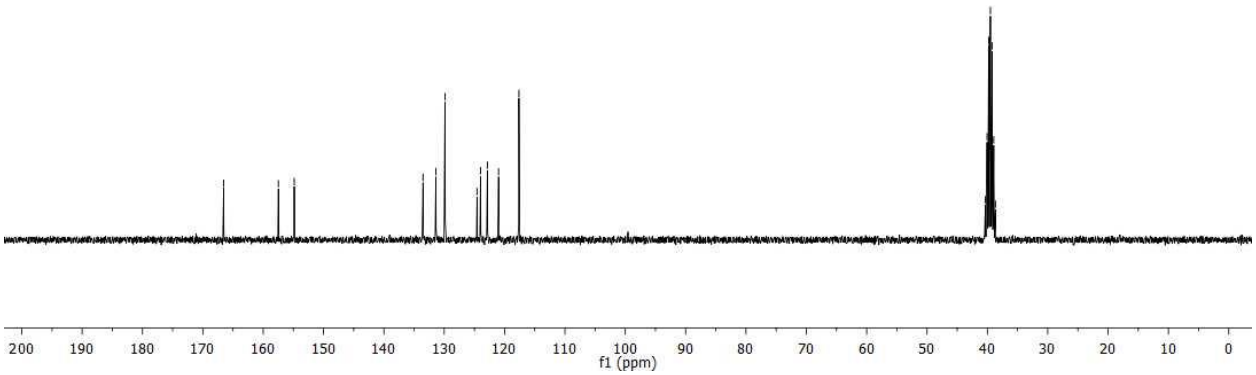


1a, Scheme 2





1a, Scheme 2

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7.815
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7.579
7.557
7.555
7.533
7.527
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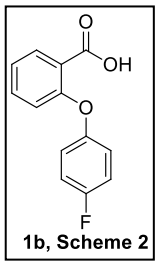
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OH
O
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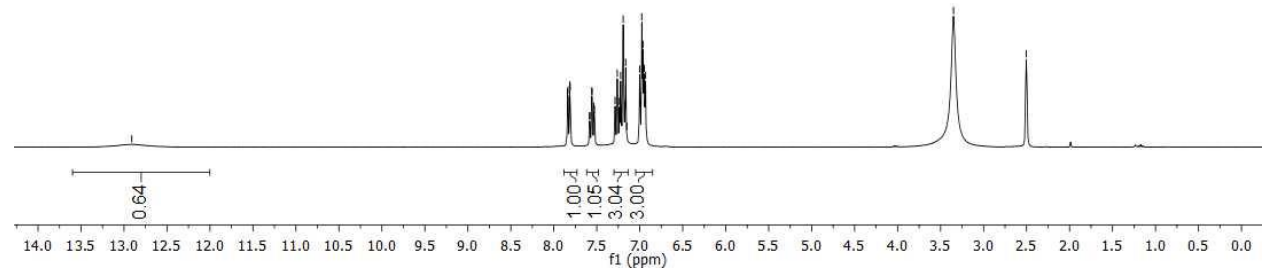
1b, Scheme 2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3.04
3.00
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f1 (ppm)


AH-368-C/1
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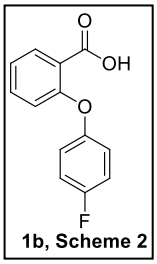
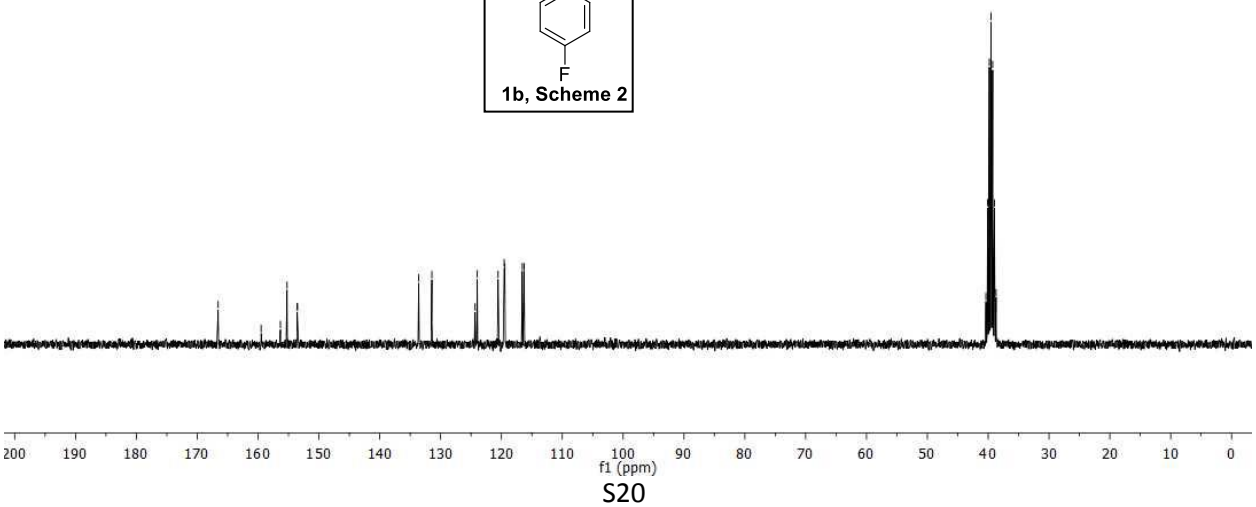

O
OH
O
F
1b, Scheme 2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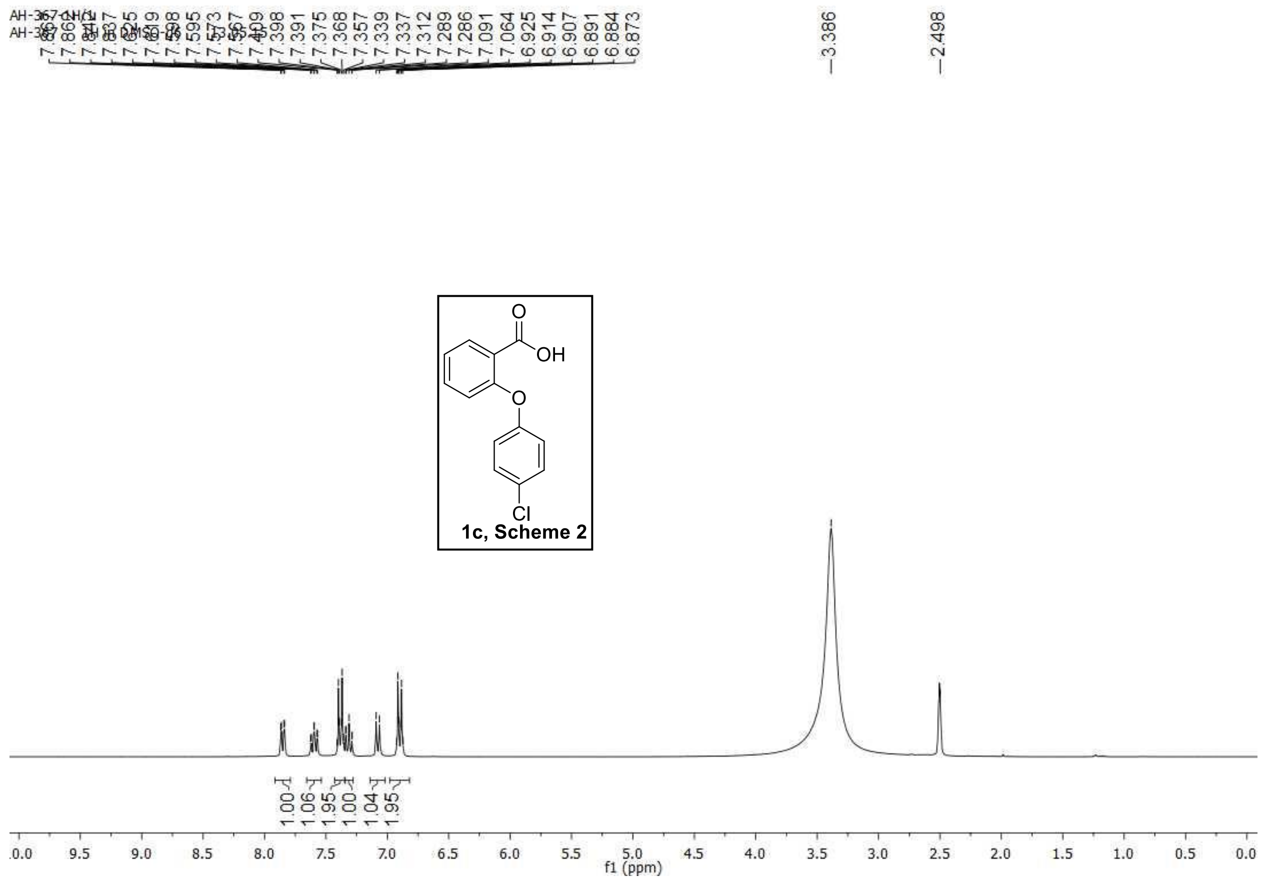
f1 (ppm)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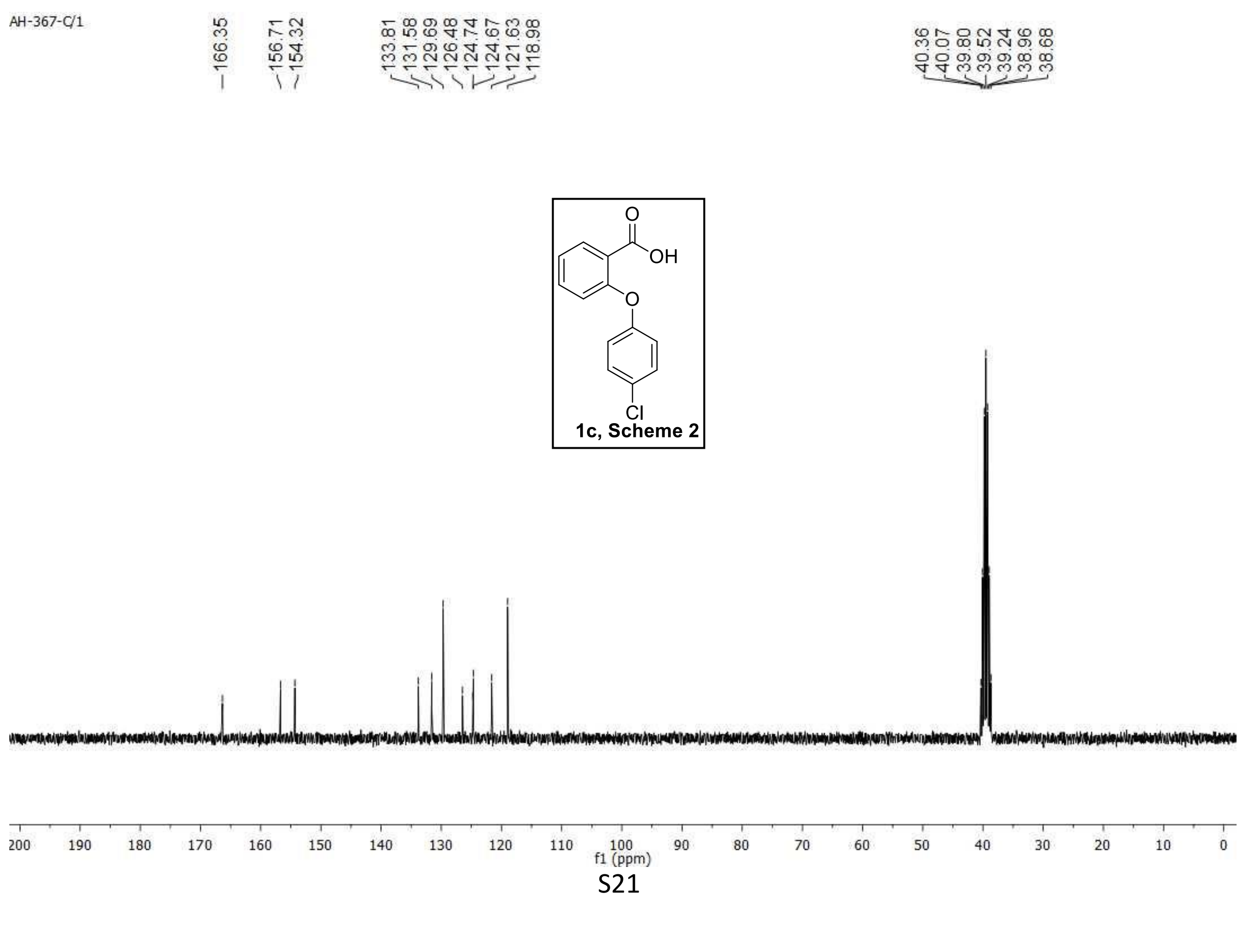
f1 (ppm)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39.80
39.52
39.24
38.96
38.68
O
OH
O
Cl
1c, Scheme 2
f1 (ppm)

AH-379-1H/1
AH-379 1H in DMSO-d6 27.5.15

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7.626
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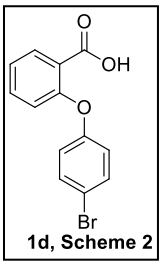
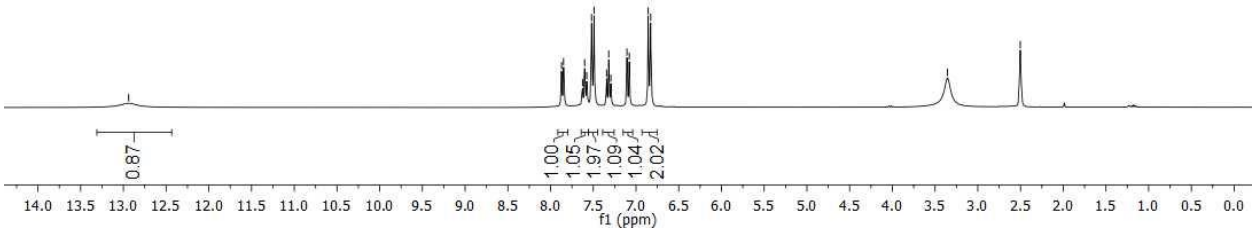


1d, Scheme 2



AH-379-C/1

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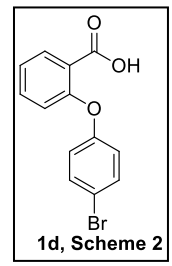

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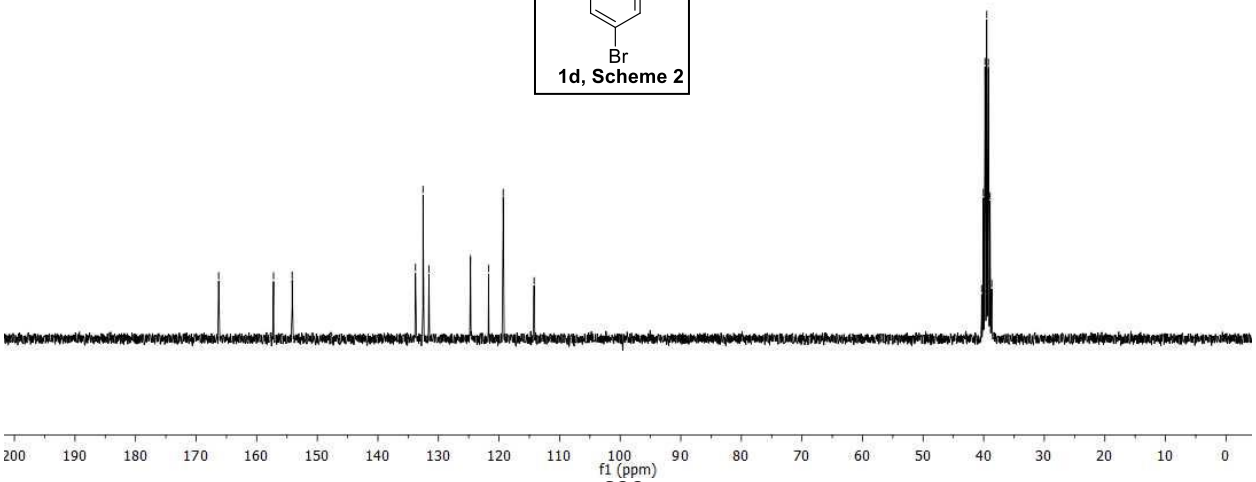

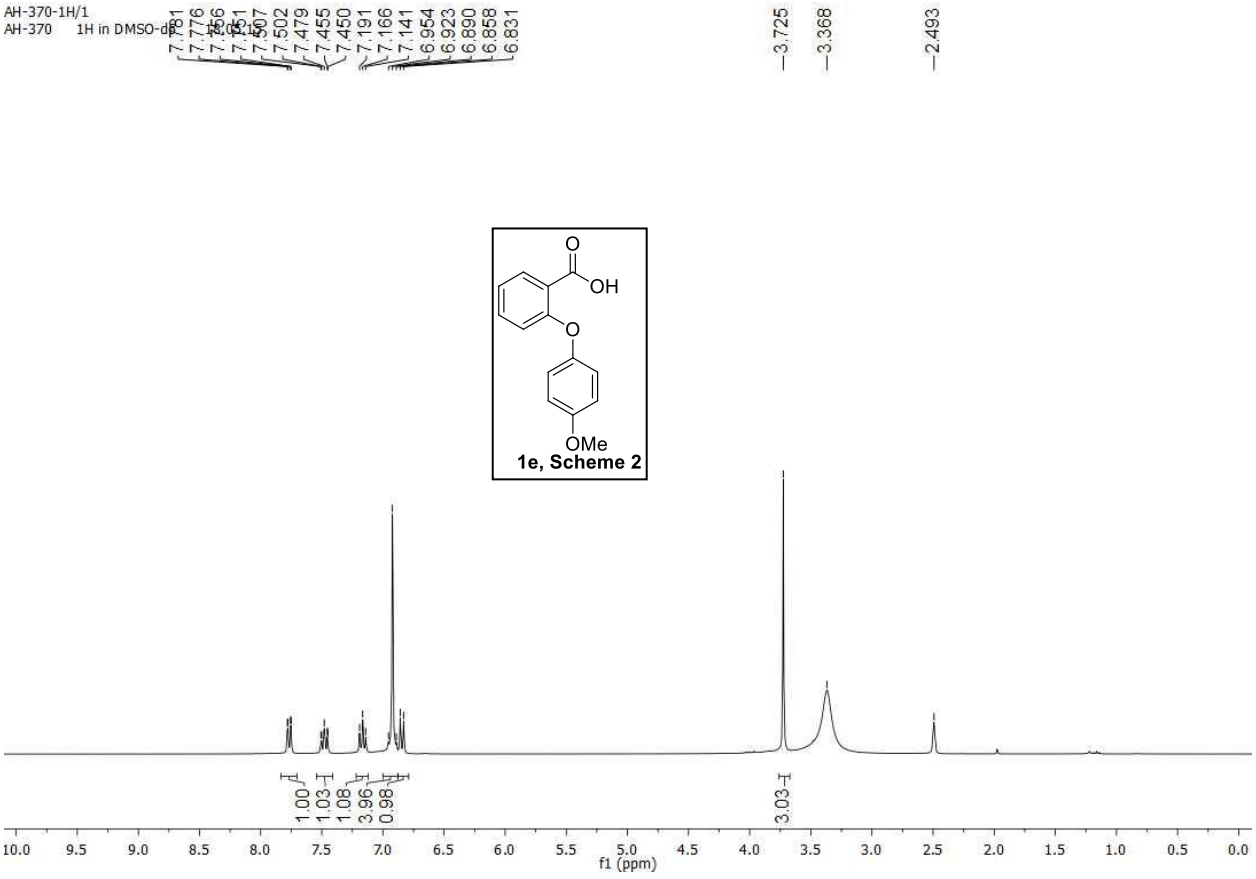
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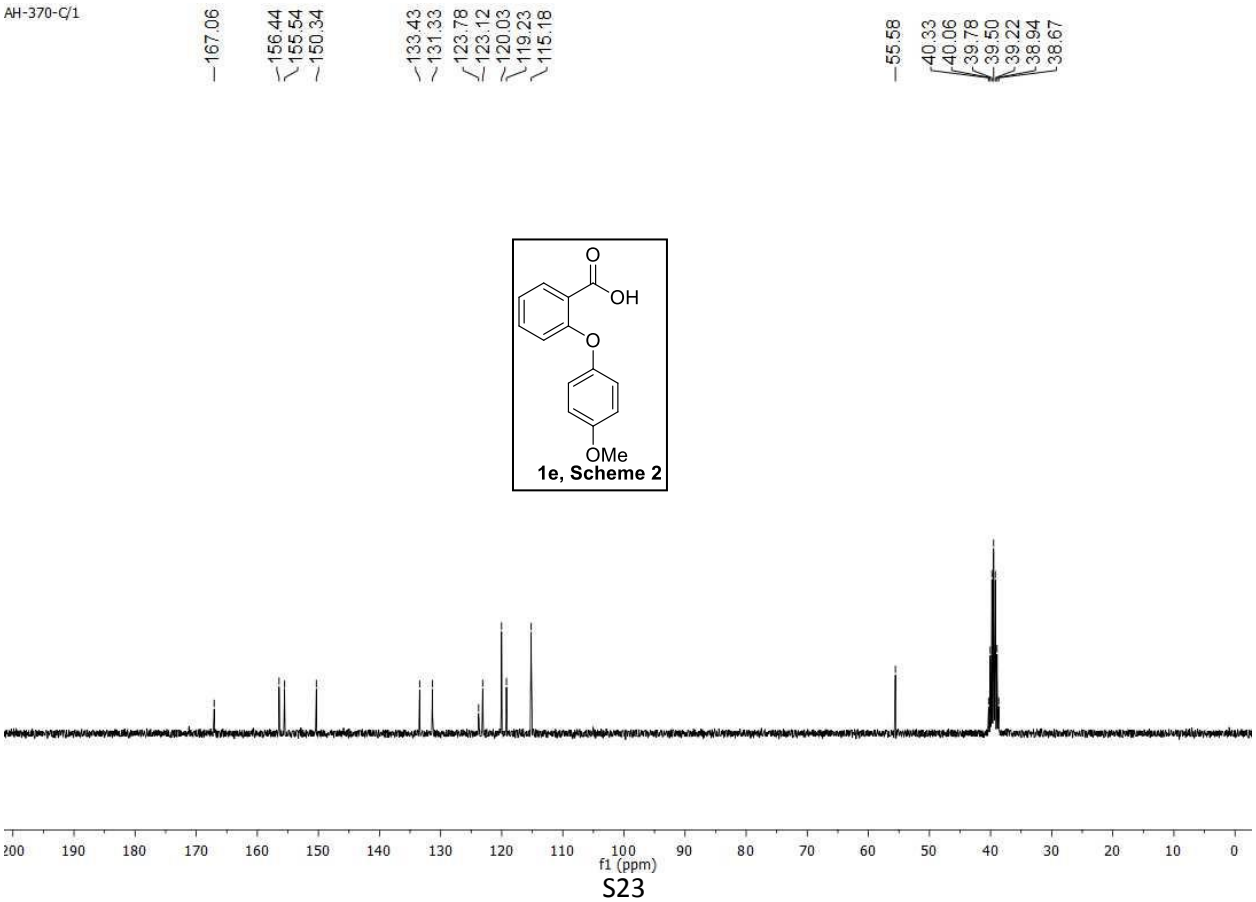
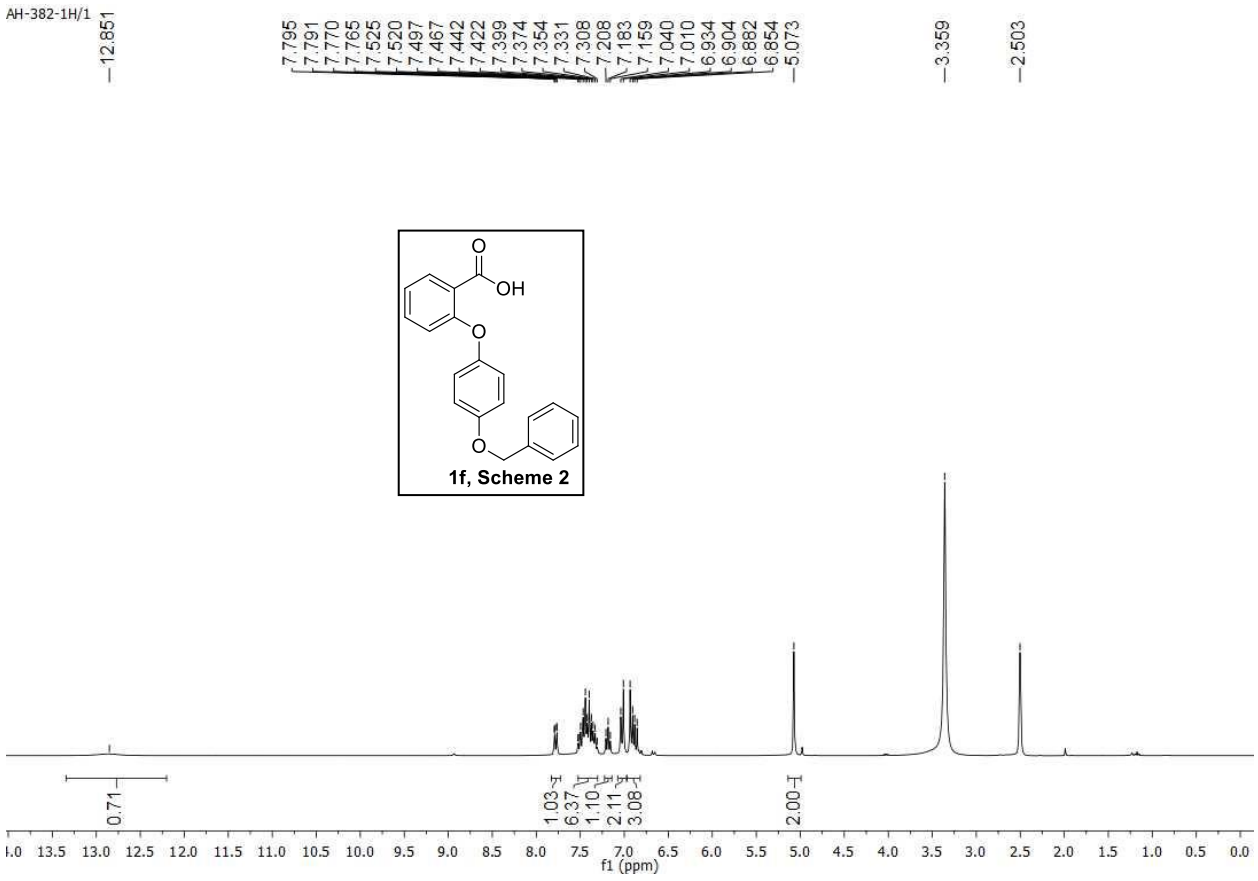
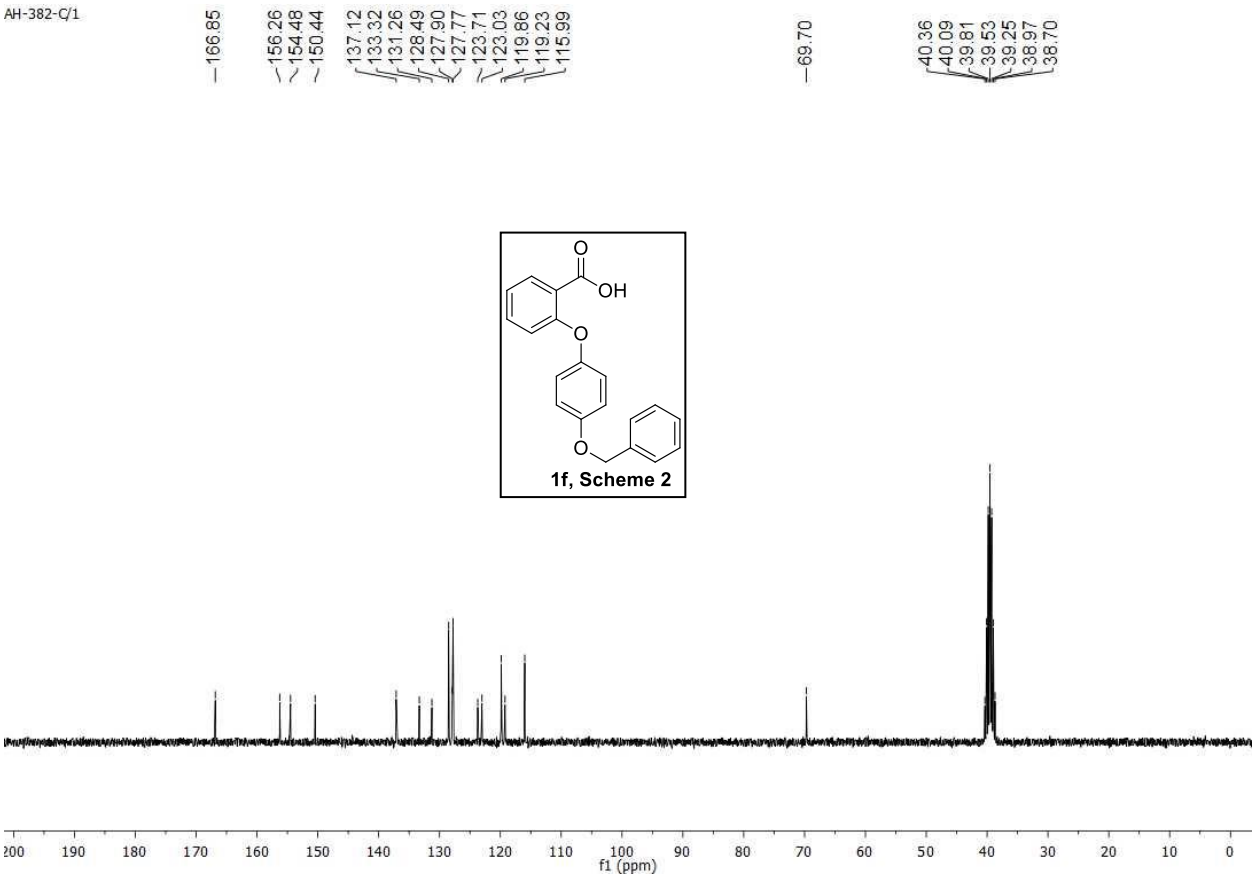
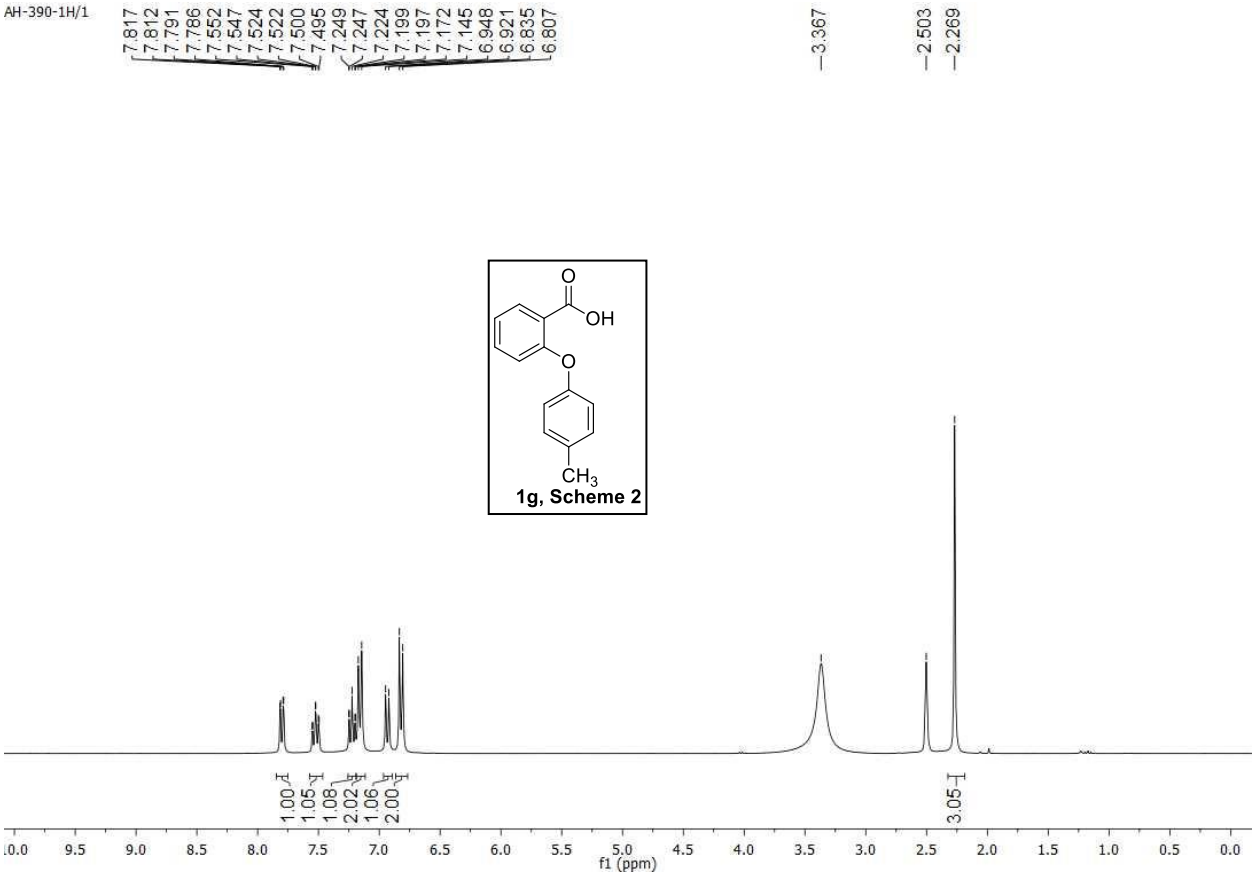
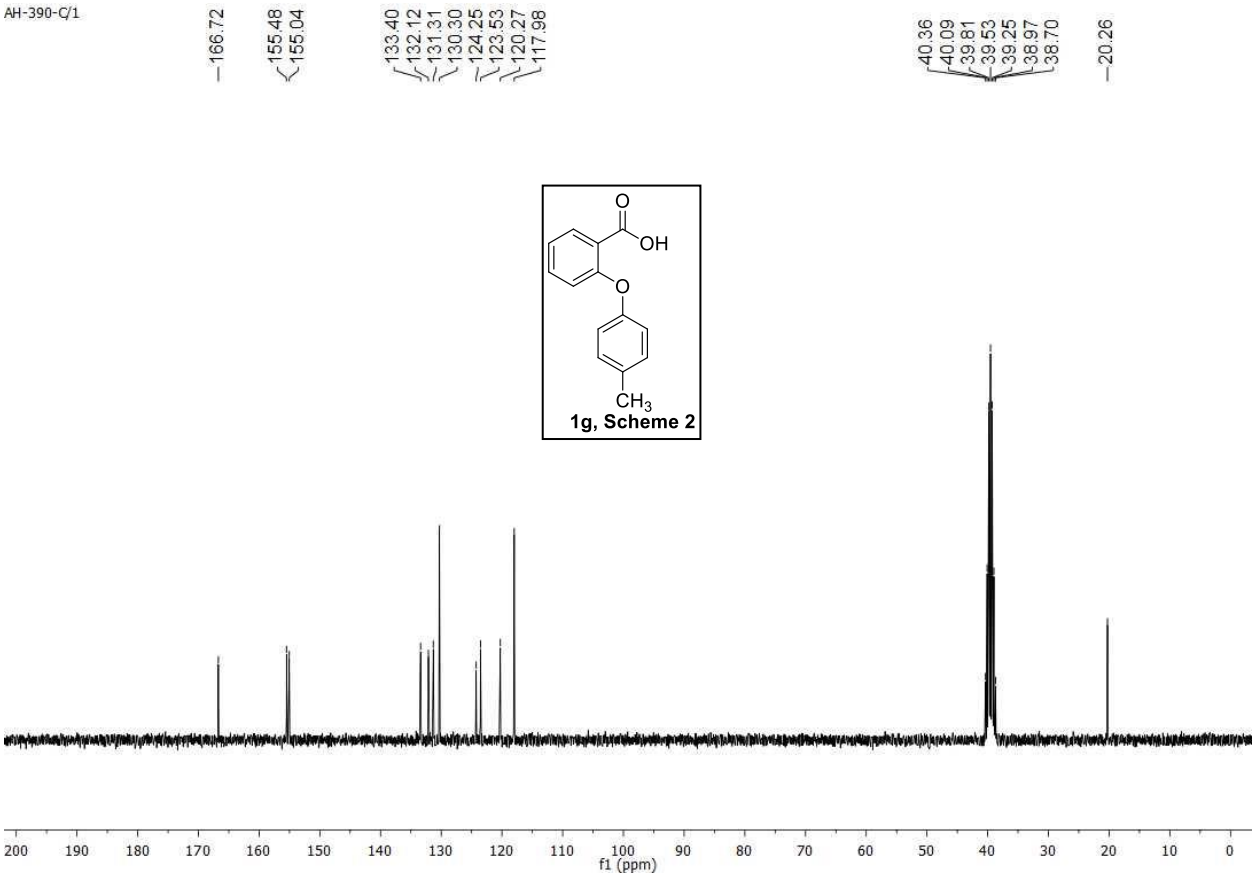
7.166
7.141
6.954
6.923
6.890
6.858
6.831
3.725
3.368
2.493
OH
OMe
1e, Scheme 2
1.00
1.03
1.08
3.96
0.98
3.03
f1 (ppm)

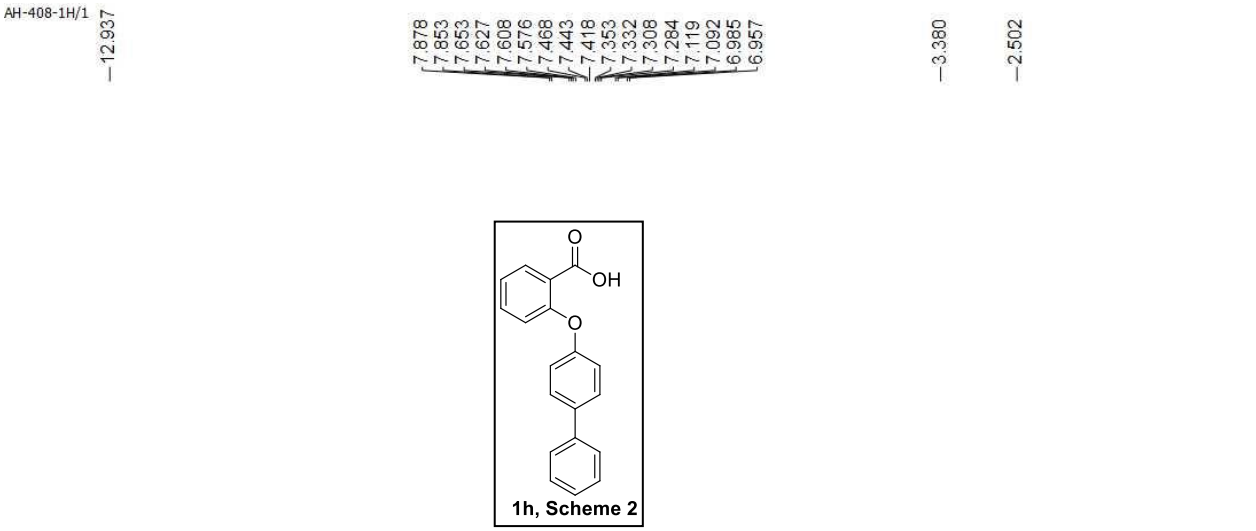

AH-370-C/1
167.06
156.44
155.54
150.34
133.43
131.33
123.78
123.12
120.03
119.23
115.18
55.58
40.33
40.06
39.78
39.50
39.22
38.94
38.67
OH
OMe
1e, Scheme 2
f1 (ppm)

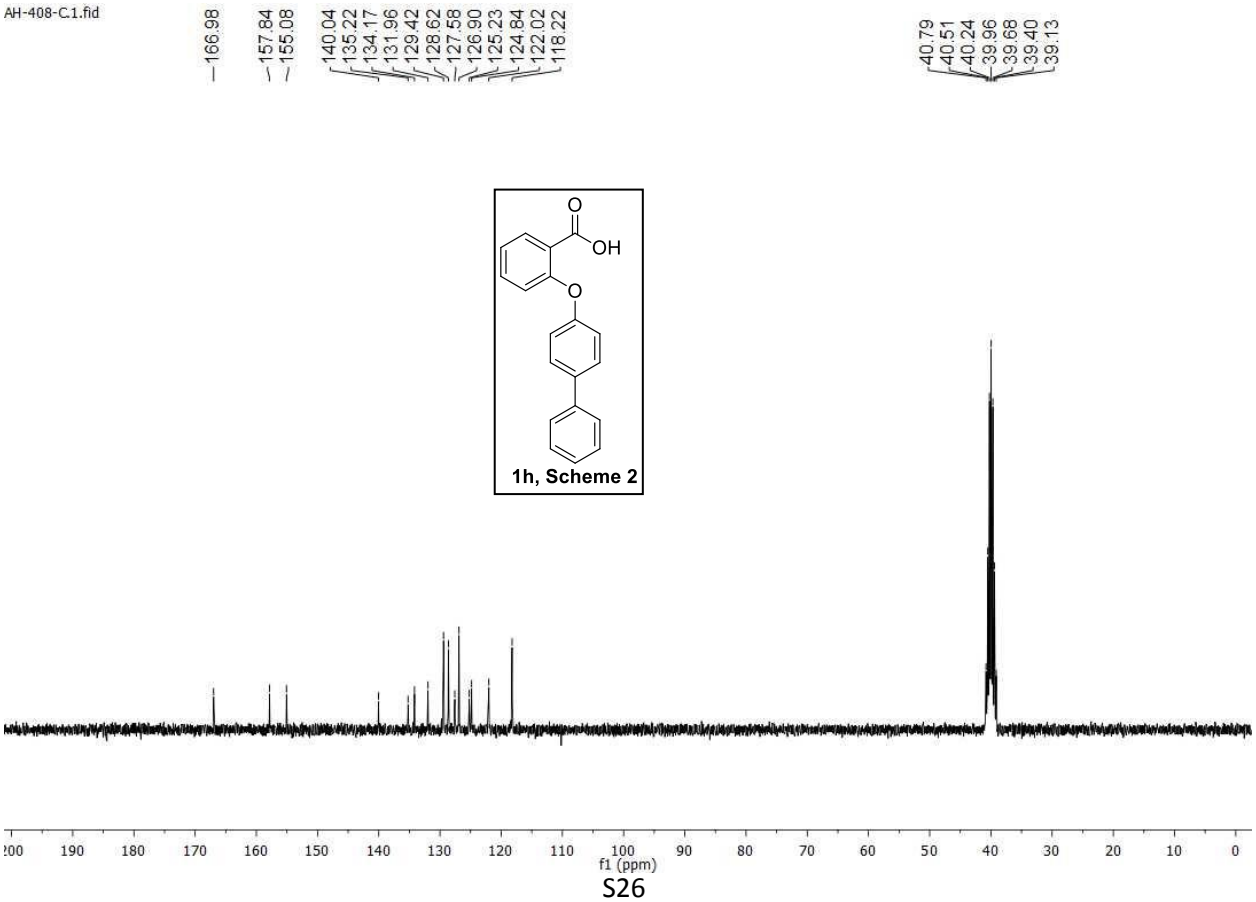

AH-382-1H/1
12.851
7.795
7.791
7.770
7.765
7.525
7.520
7.497
7.467
7.442
7.422
7.399
7.374
7.354
7.331
7.308
7.208
7.183
7.159
7.040
7.010
6.934
6.904
6.882
6.854
5.073
3.359
2.503
OH
O
1f, Scheme 2
0.71
1.03
6.37
1.10
2.11
3.08
2.00
f1 (ppm)

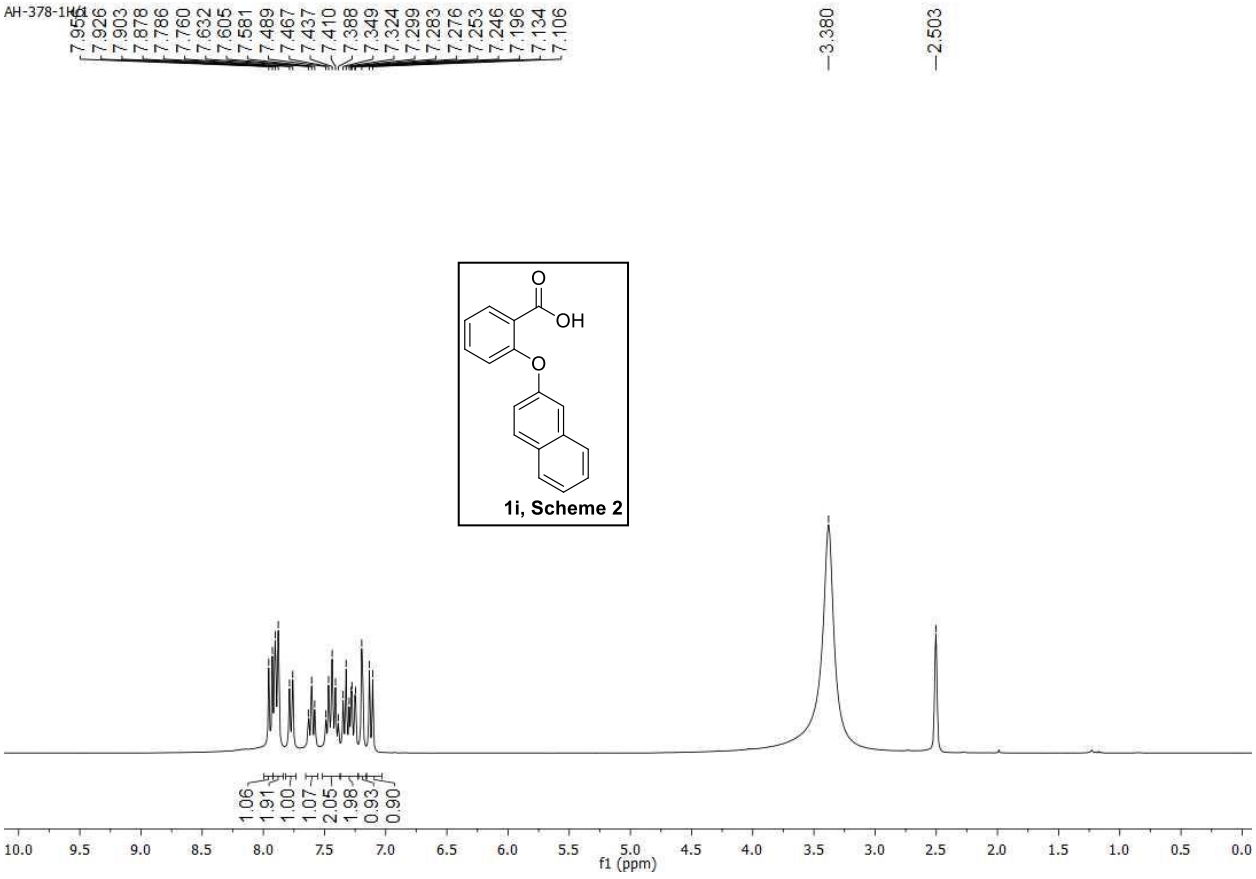

AH-382-C/1
166.85
156.26
154.48
150.44
137.12
133.32
131.26
128.49
127.90
127.77
123.71
123.03
119.86
119.23
115.99
69.70
40.36
40.09
39.81
39.53
39.25
38.97
38.70
OH
O
1f, Scheme 2
f1 (ppm)

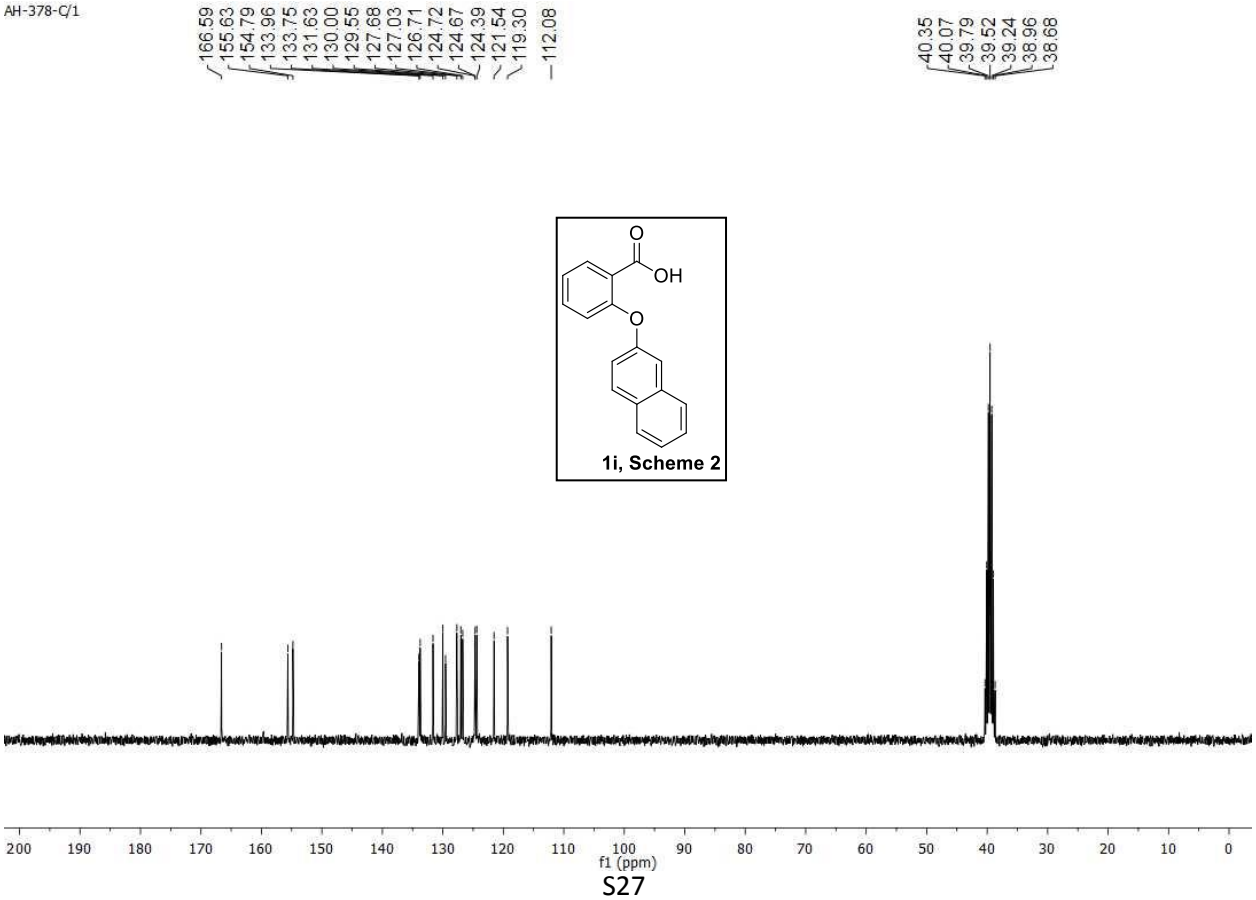

AH-390-1H/1
7.817
7.812
7.791
7.786
7.552
7.547
7.524
7.522
7.500
7.495
7.249
7.247
7.224
7.199
7.197
7.172
7.145
6.948
6.921
6.835
6.807
3.367
2.503
2.269
O
OH
O
CH3
1g, Scheme 2
1.00
1.05
1.08
2.02
1.06
2.00
3.05
f1 (ppm)

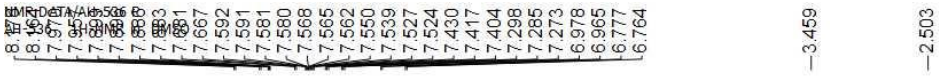

AH-390-C/1
166.72
155.48
155.04
133.40
132.12
131.31
130.30
124.25
123.53
120.27
117.98
40.36
40.09
39.81
39.53
39.25
38.97
38.70
20.26
O
OH
O
CH3
1g, Scheme 2
f1 (ppm)

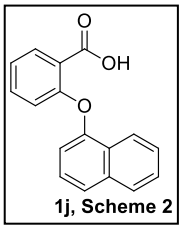

AH-408-1H/1
12.937
7.878
7.853
7.653
7.627
7.608
7.576
7.468
7.443
7.418
7.353
7.332
7.308
7.284
7.119
7.092
6.985
6.957
3.380
2.502
O
OH
O
1h, Scheme 2
0.64
1.05
5.15
2.09
2.05
1.05
2.00
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

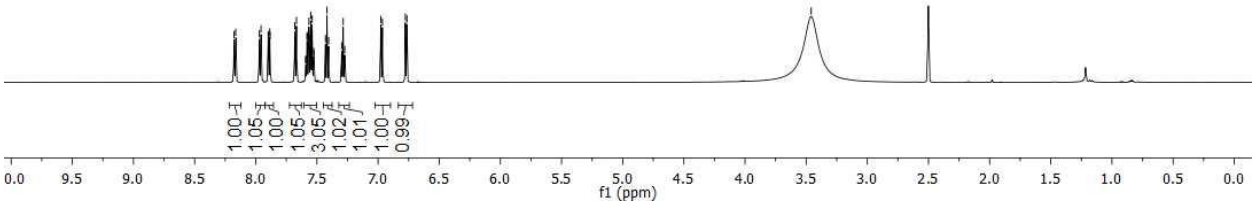

AH-408-C1.fid
166.98
157.84
155.08
140.04
135.22
134.17
131.96
129.42
128.62
127.58
126.90
125.23
124.84
122.02
118.22
40.79
40.51
40.24
39.96
39.68
39.40
39.13
O
OH
O
1h, Scheme 2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


AH-378-1H/1
7.950
7.926
7.903
7.878
7.786
7.760
7.632
7.605
7.581
7.489
7.467
7.437
7.410
7.388
7.349
7.324
7.299
7.283
7.276
7.253
7.246
7.196
7.134
7.106
3.380
2.503
O
OH
O
1i, Scheme 2
1.06
1.91
1.00
1.07
2.05
1.98
0.93
0.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

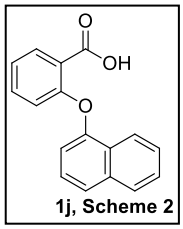

AH-378-C/1
166.59
155.63
154.79
133.96
133.75
131.63
130.00
129.55
127.68
127.03
126.71
124.72
124.67
124.39
121.54
119.30
112.08
40.35
40.07
39.79
39.52
39.24
38.96
38.68
O
OH
O
1i, Scheme 2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

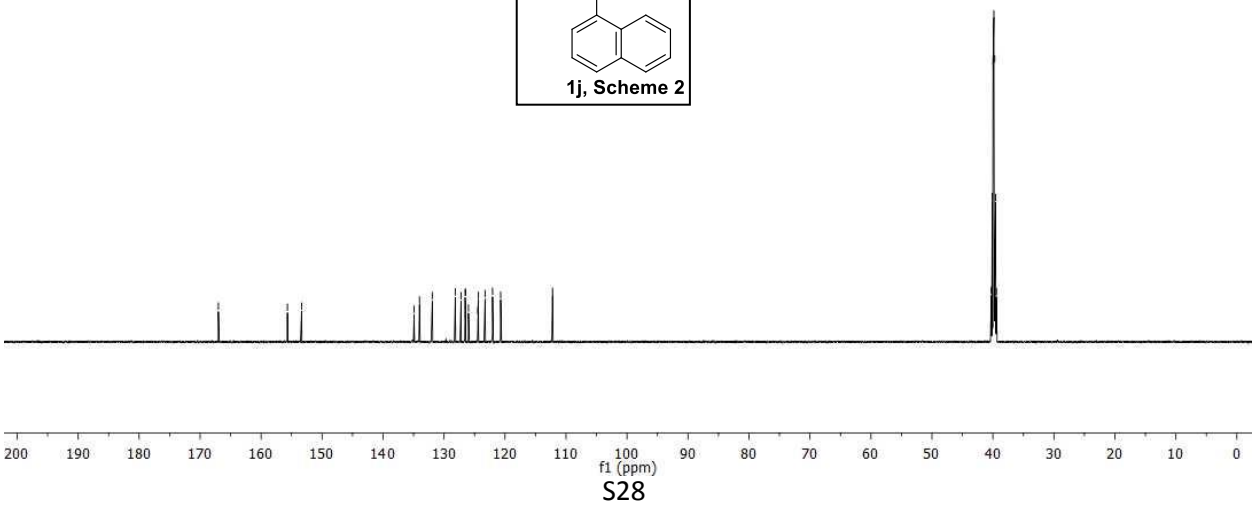

7.667
7.592
7.591
7.581
7.580
7.568
7.565
7.562
7.550
7.539
7.527
7.524
7.430
7.417
7.404
7.298
7.285
7.273
6.978
6.965
6.777
6.764
3.459
2.503

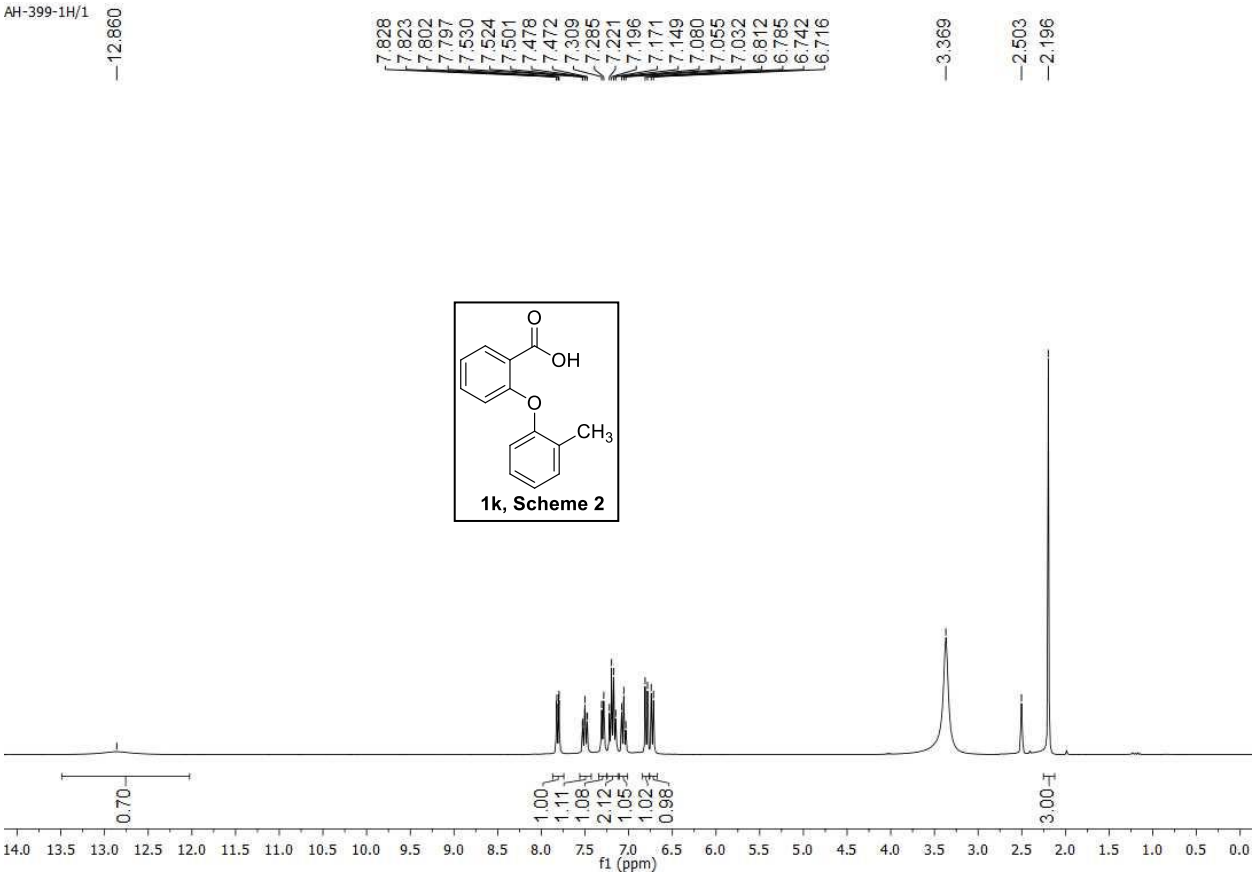

O
OH
O
1j, Scheme 2

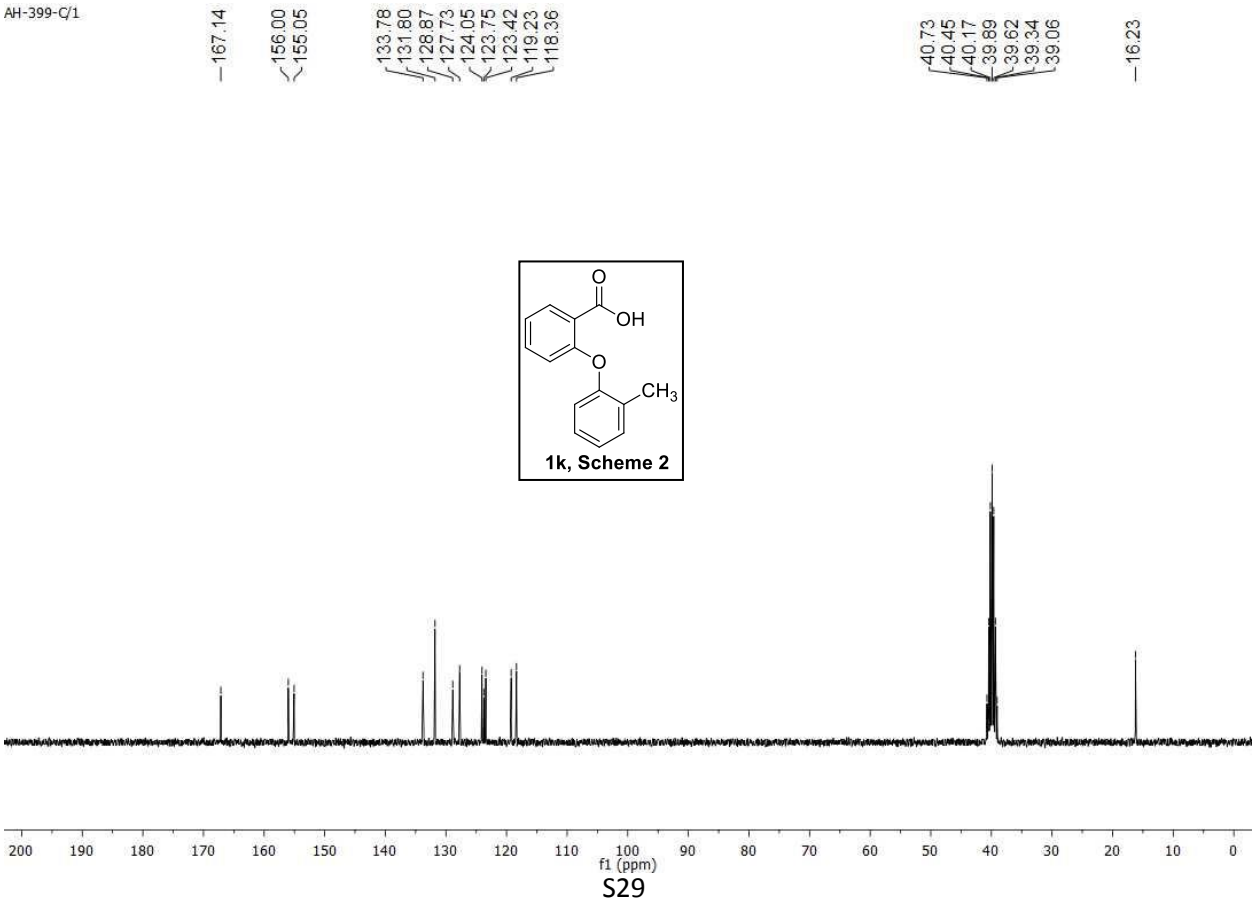

1.00
1.05
1.00
1.05
3.05
1.02
1.01
1.00
0.99
f1 (ppm)

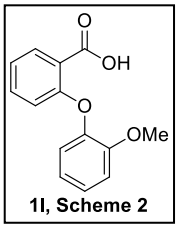

NMR DATA/AH-536 C
AH-536 13C-NMR in DMSO
167.00
155.68
153.36
134.92
134.03
131.93
128.16
127.22
126.54
126.46
126.00
124.48
124.37
123.27
122.05
120.72
112.21
40.26
40.12
39.98
39.85
39.71
39.57
39.43


O
OH
O
1j, Scheme 2

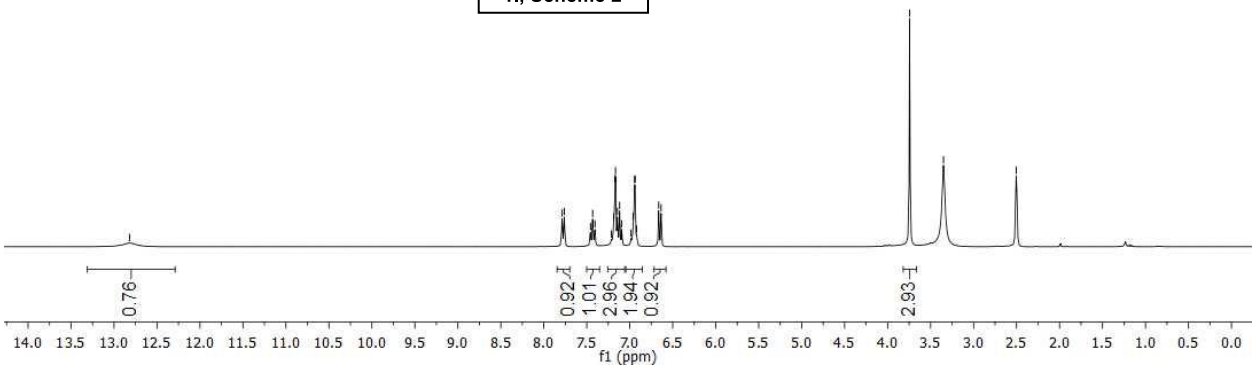

f1 (ppm)

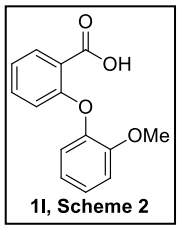

AH-399-1H/1
12.860
7.828
7.823
7.802
7.797
7.530
7.524
7.501
7.478
7.472
7.309
7.285
7.221
7.196
7.171
7.149
7.080
7.055
7.032
6.812
6.785
6.742
6.716
3.369
2.503
2.196
OH
O
CH3
1k, Scheme 2
0.70
1.00
1.11
1.08
2.12
1.05
1.02
0.98
3.00
f1 (ppm)


AH-399-C/1
167.14
156.00
155.05
133.78
131.80
128.87
127.73
124.05
123.75
123.42
119.23
118.36
40.73
40.45
40.17
39.89
39.62
39.34
39.06
16.23
OH
O
CH3
1k, Scheme 2
f1 (ppm)

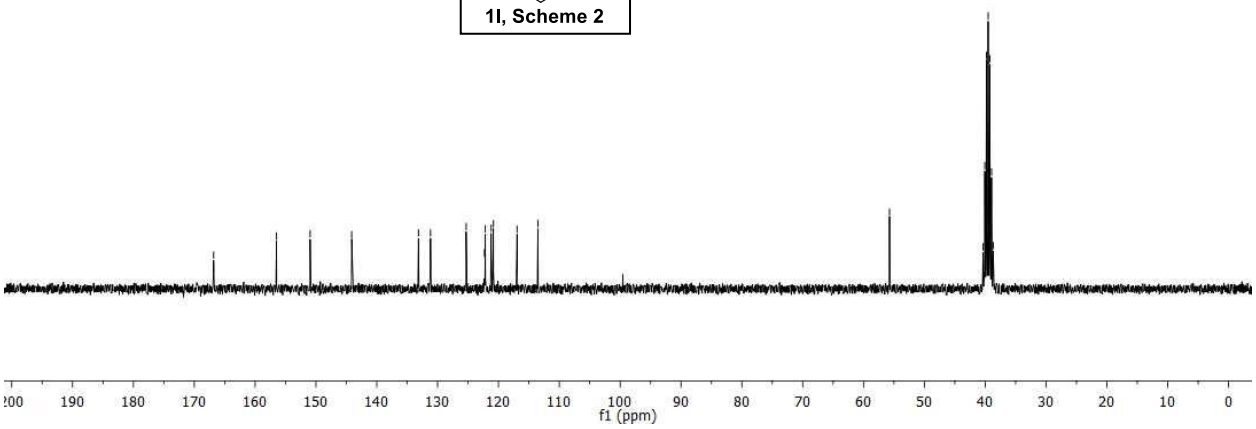


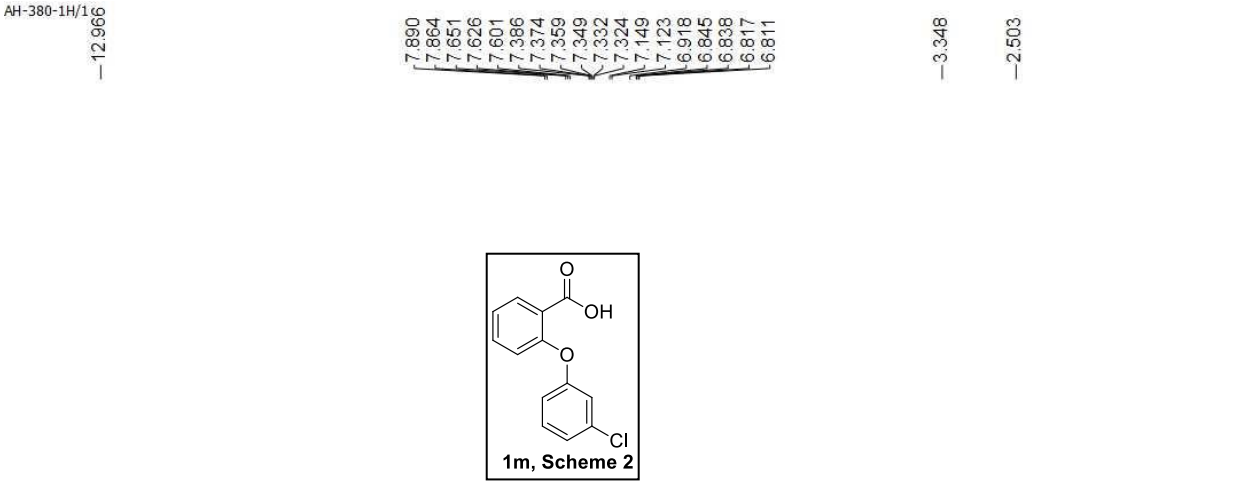
1l, Scheme 2

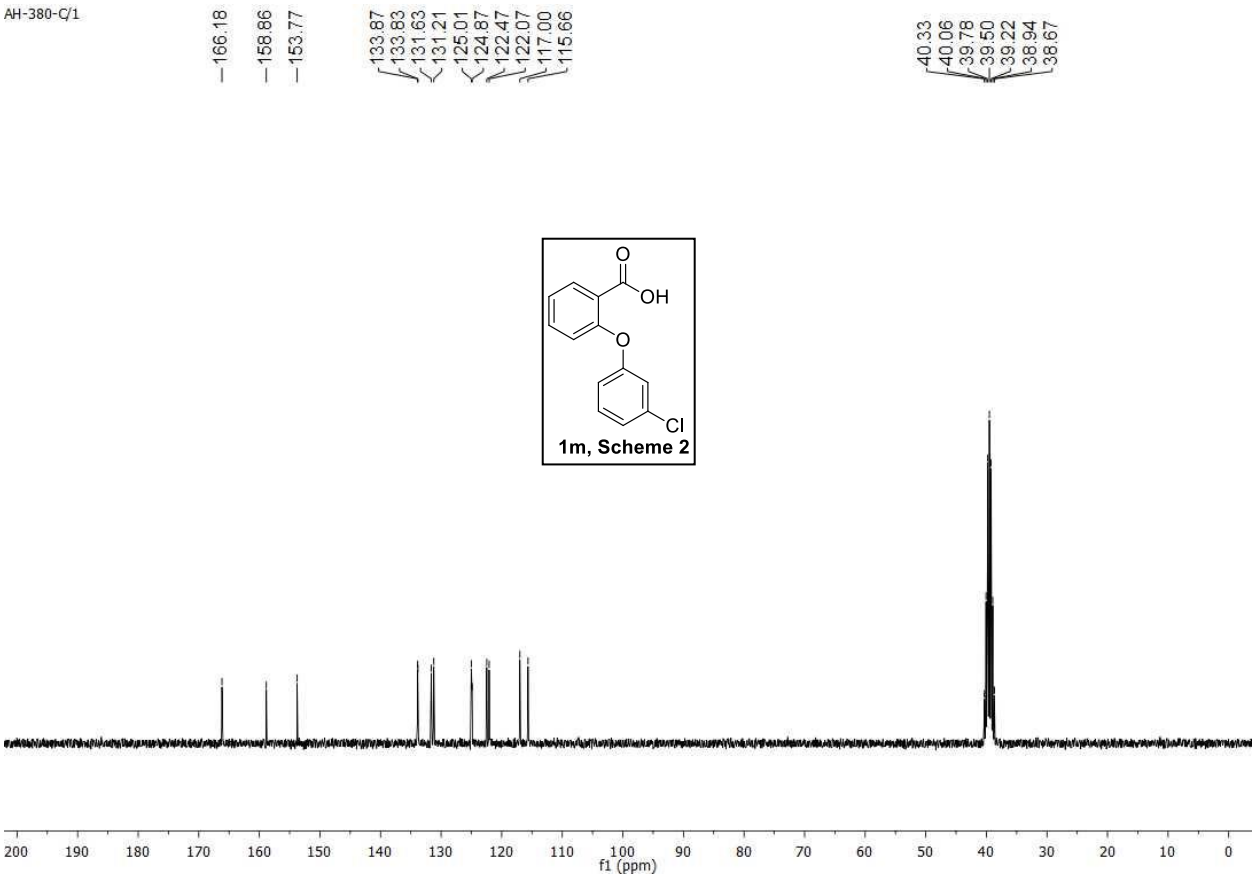




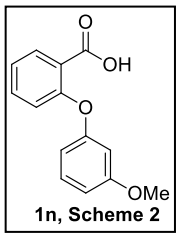
1l, Scheme 2



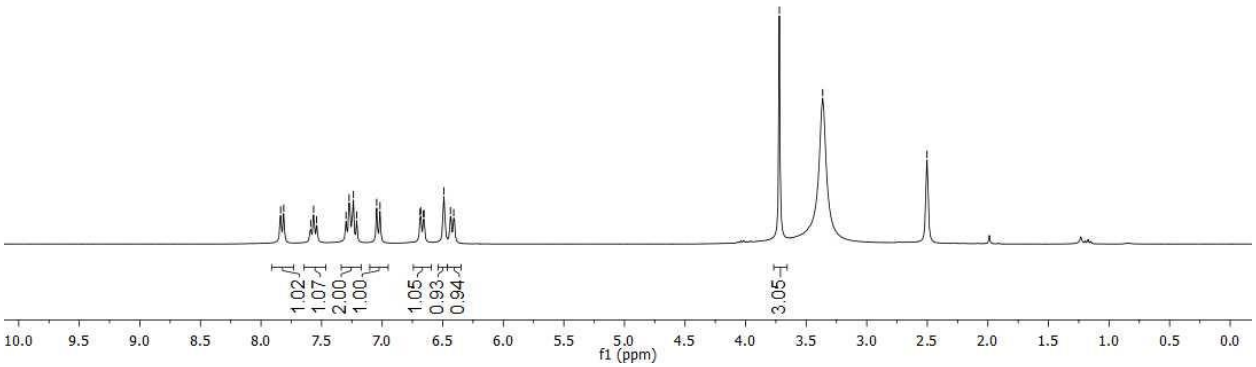

AH-380-1H/1
12.966
7.890
7.864
7.651
7.626
7.601
7.386
7.374
7.359
7.349
7.332
7.324
7.149
7.123
6.918
6.845
6.838
6.817
6.811
3.348
2.503
O
OH
O
Cl
1m, Scheme 2
0.78
1.03
1.07
2.07
2.00
0.94
1.01
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


AH-380-C/1
166.18
158.86
153.77
133.87
133.83
131.63
131.21
125.01
124.87
122.47
122.07
117.00
115.66
40.33
40.06
39.78
39.50
39.22
38.94
38.67
O
OH
O
Cl
1m, Scheme 2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

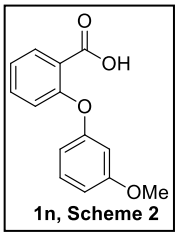
AH-383-1H/1



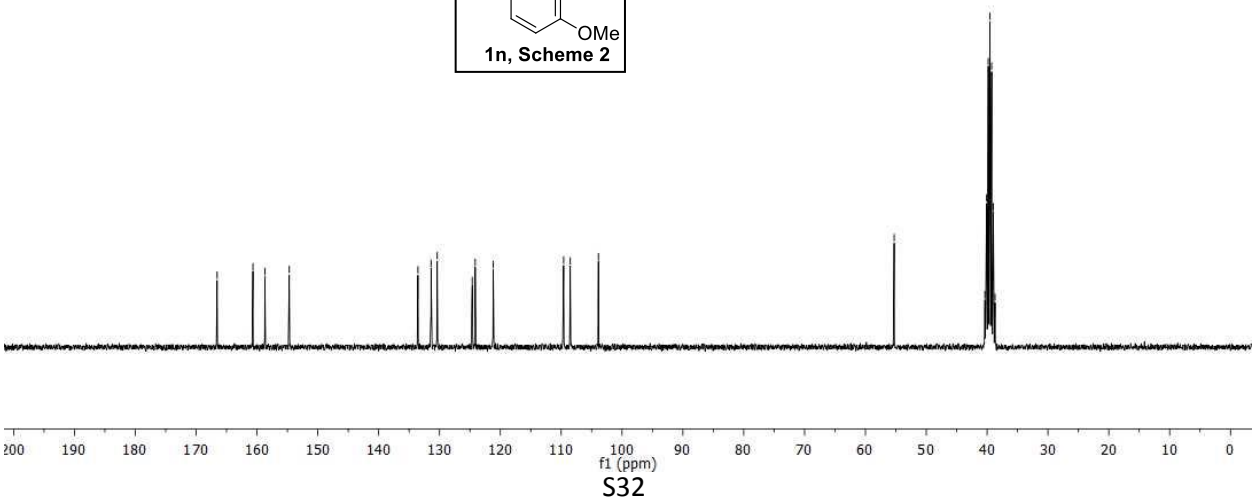
1n, Scheme 2



AH-383-C/1

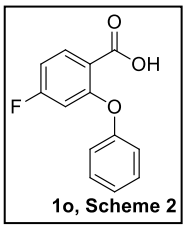


1n, Scheme 2

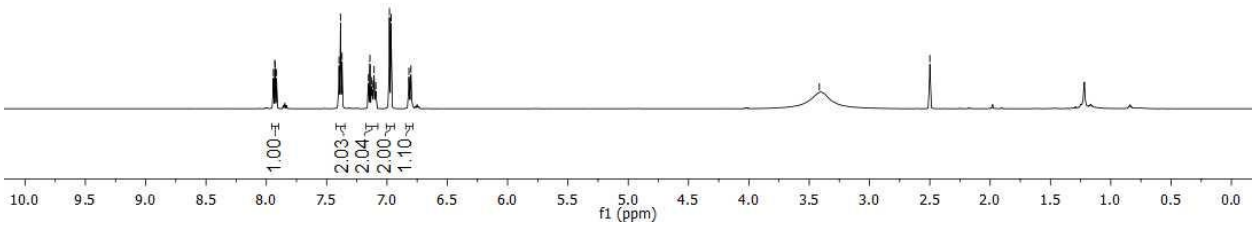


NMR DATA/AH-410 P
AH410 1H-NMR in DMSO

7.941
7.930
7.927
7.915
7.397
7.385
7.373
7.154
7.141
7.129
7.121
7.107
7.093
6.979
6.966
6.818
6.801
3.416
2.500

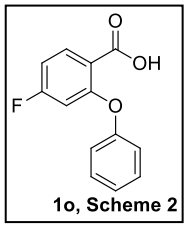


1o, Scheme 2

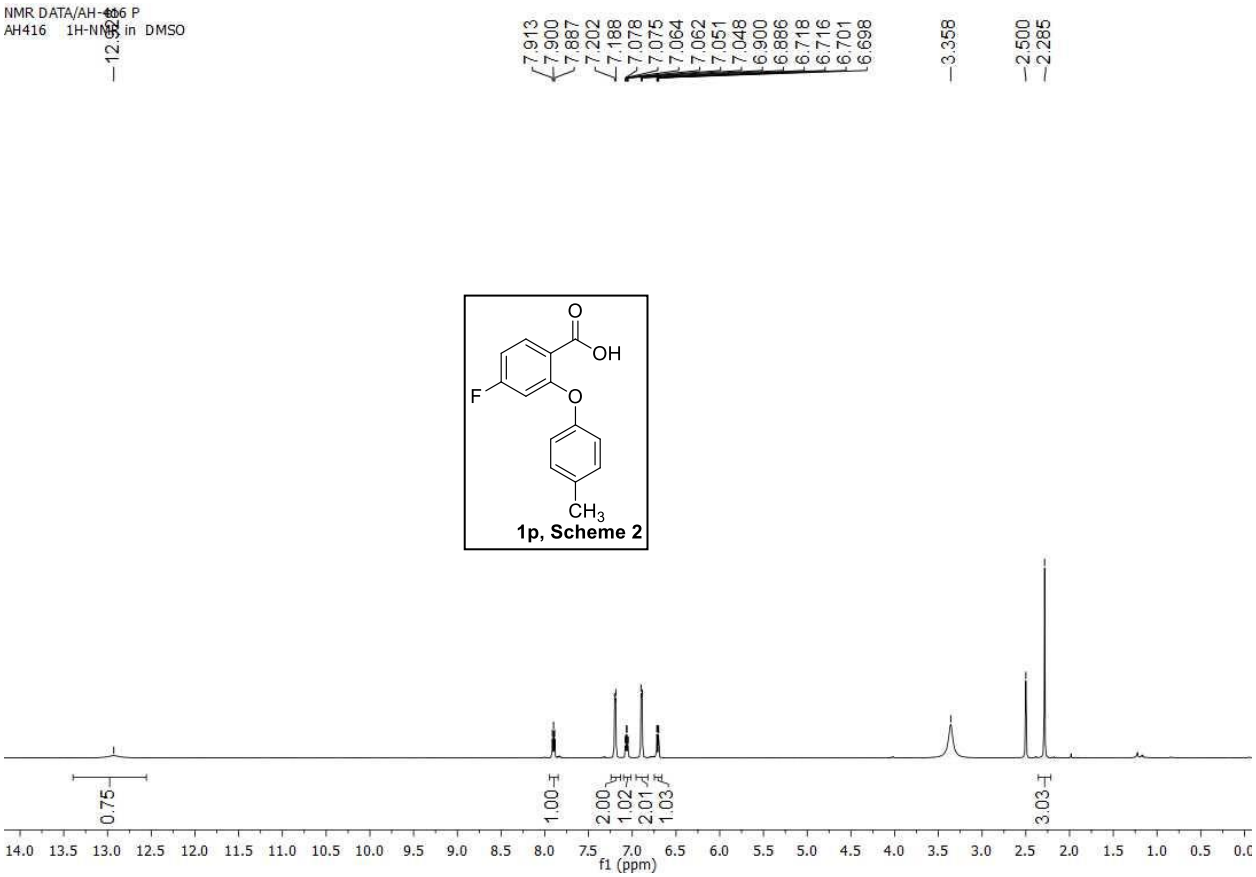


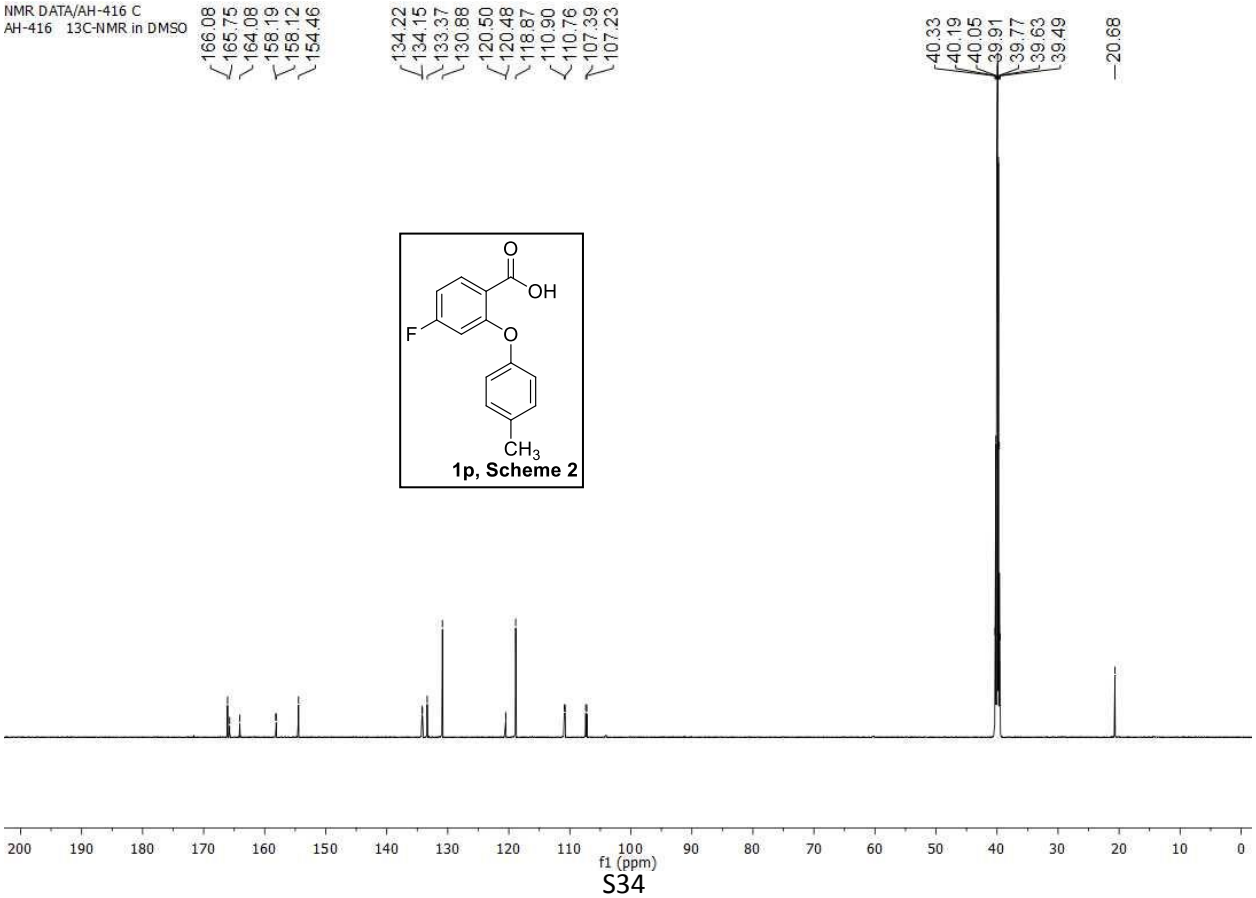
NMR DATA/AH-410 C
AH-410 13C-NMR in DMSO

165.97
165.80
164.13
157.53
157.46
157.02
134.30
134.23
130.47
124.01
120.93
120.91
118.51
111.45
111.30
108.29
108.12
40.31
40.17
40.03
39.89
39.75
39.61
39.47

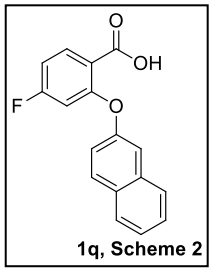


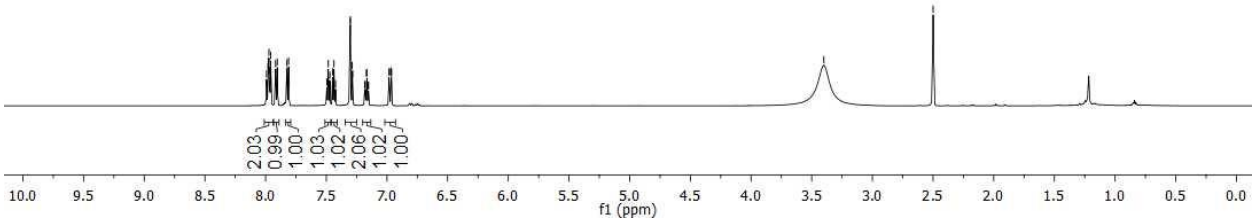
1o, Scheme 2

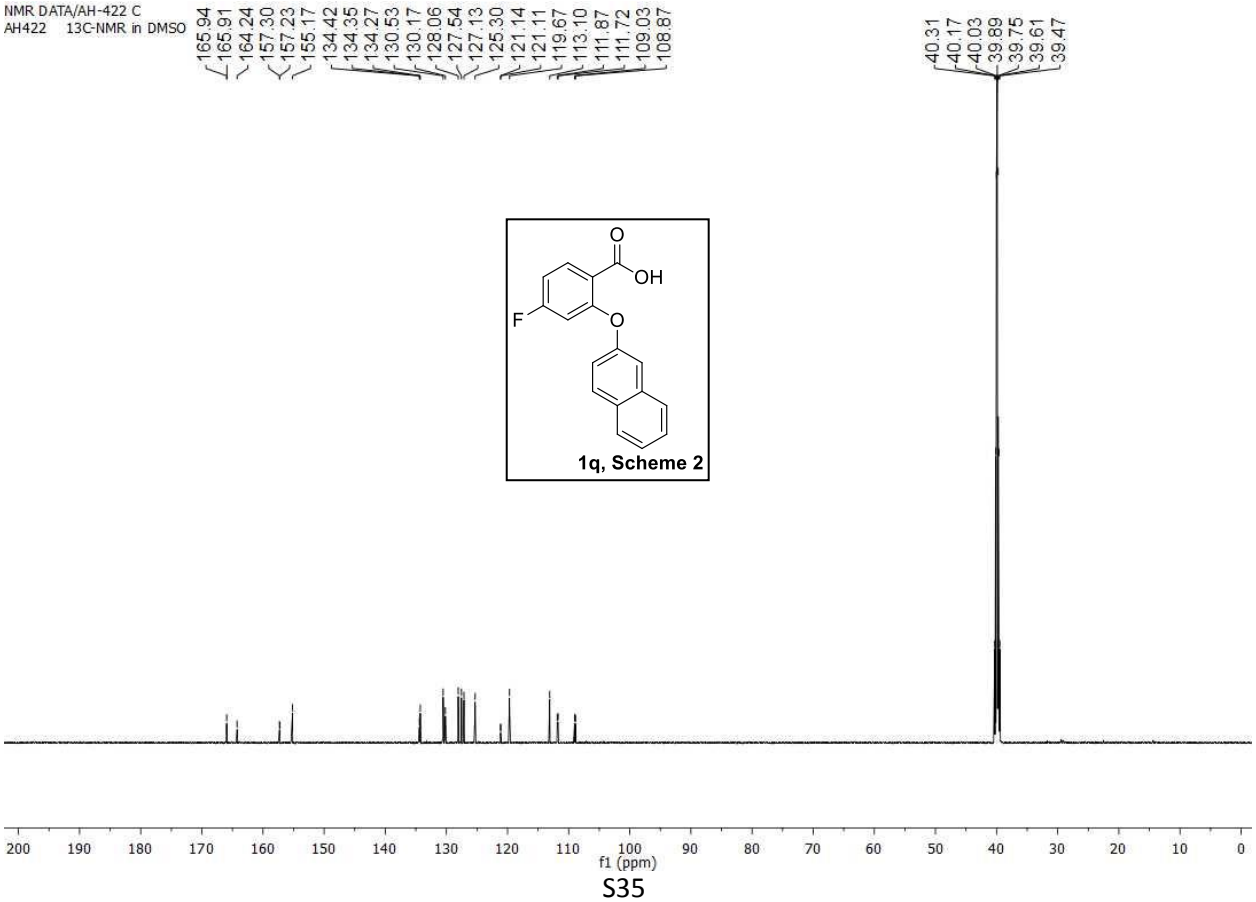

NMR DATA/AH-416 P
AH416 1H-NMR in DMSO
12.90
7.913
7.900
7.887
7.202
7.188
7.078
7.075
7.064
7.062
7.051
7.048
6.900
6.886
6.718
6.716
6.701
6.698
3.358
2.500
2.285
O
OH
F
O
CH3
1p, Scheme 2
0.75
1.00
2.00
1.02
2.01
1.03
3.03
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


NMR DATA/AH-416 C
AH-416 13C-NMR in DMSO
166.08
165.75
164.08
158.19
158.12
154.46
134.22
134.15
133.37
130.88
120.50
120.48
118.87
110.90
110.76
107.39
107.23
40.33
40.19
40.05
39.91
39.77
39.63
39.49
20.68
O
OH
F
O
CH3
1p, Scheme 2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.824
7.810
7.495
7.484
7.470
7.448
7.436
7.423
7.303
7.301
7.286
7.282
7.184
7.180
7.169
7.166
7.156
7.152
6.983
6.979
6.966
6.962
3.400
2.499

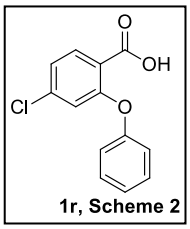

O
OH
F
O
1q, Scheme 2


2.03
0.99
1.00
1.03
1.02
2.06
1.02
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

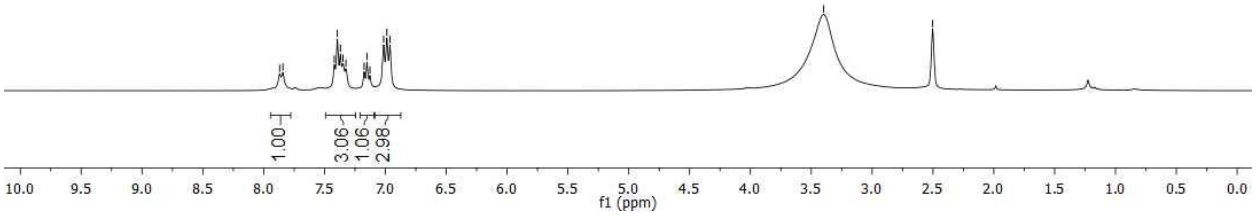

NMR DATA/AH-422 C
AH422 13C-NMR in DMSO
165.94
165.91
164.24
157.30
157.23
155.17
134.42
134.35
134.27
130.53
130.17
128.06
127.54
127.13
125.30
121.14
121.11
119.67
113.10
111.87
111.72
109.03
108.87
40.31
40.17
40.03
39.89
39.75
39.61
39.47
O
OH
F
O
1q, Scheme 2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

AH-396-1H/1

7.869
7.842
7.420
7.395
7.369
7.349
7.324
7.175
7.151
7.127
7.014
6.988
6.962
3.398
2.503

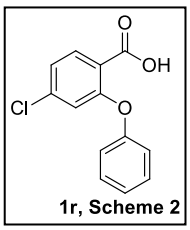


1r, Scheme 2



AH-396-C/1

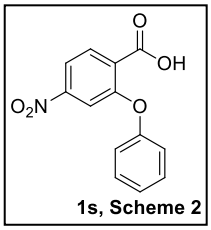
157.01
156.69
156.65
137.83
133.81
130.52
124.41
124.09
120.72
118.61
99.96
40.73
40.46
40.18
39.90
39.62
39.34
39.07



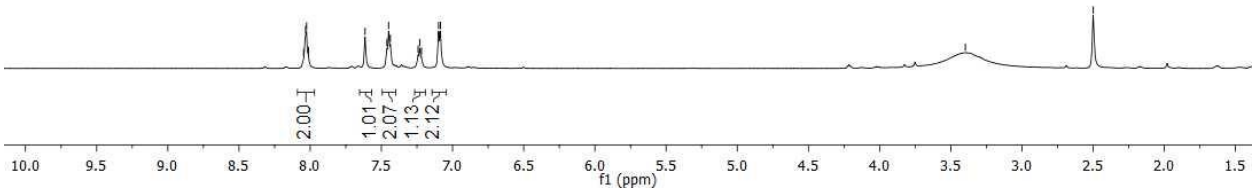
1r, Scheme 2

NMR DATA/AH-524 P
AH-574 1H-NMR in DMSO

8.046
8.032
8.025
8.012
7.615
7.461
7.449
7.437
7.242
7.230
7.219
7.098
7.085
3.397
2.499

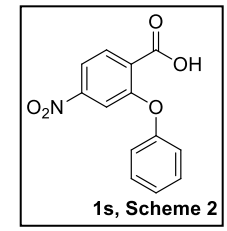


1s, Scheme 2



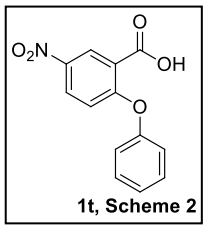
NMR DATA/AH-524 C
AH-574 13C-NMR in DMSO

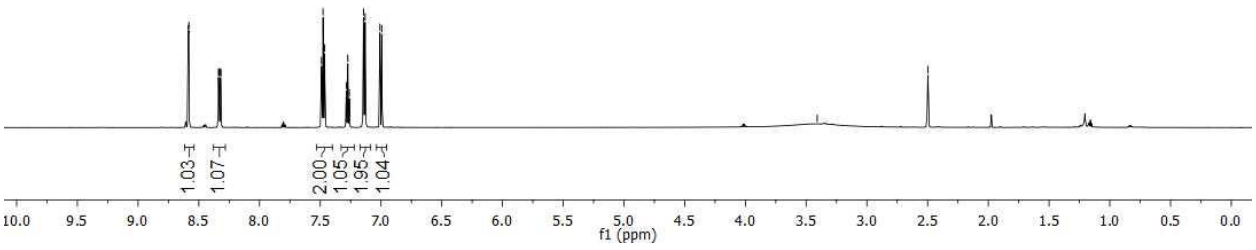
165.98
156.21
155.91
150.19
132.64
130.78
130.57
124.94
119.36
118.50
114.29
40.31
40.17
40.04
39.90
39.76
39.62
39.48



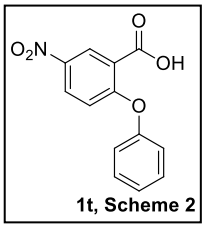
1s, Scheme 2

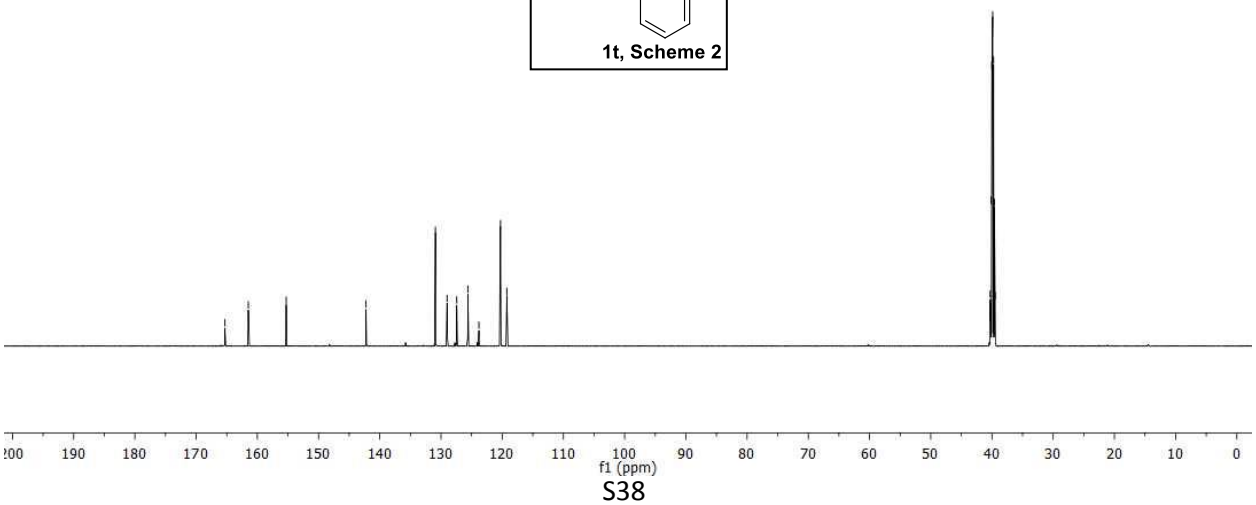

NMR DATA/AH-418 P
AH418 1H-NMR in
8.347
8.342
8.338
8.333
8.323
8.318
7.490
7.477
7.464
7.286
7.273
7.261
7.144
7.131
7.009
6.994
3.409
2.498

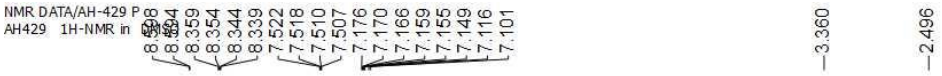

O2N
O
OH
O
1t, Scheme 2

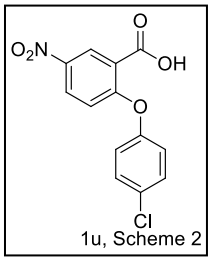

1.03
1.07
2.00
1.05
1.95
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

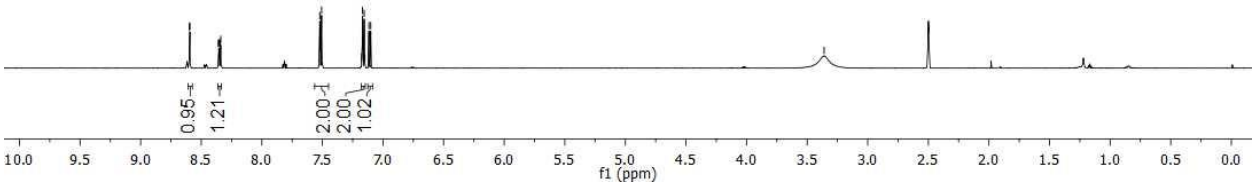

NMR DATA/AH-418 C
AH418 13C-NMR in DMSO
165.30
161.47
155.29
142.26
130.91
129.00
127.43
125.61
123.81
120.28
119.25
40.30
40.16
40.02
39.88
39.74
39.60
39.46


O2N
O
OH
O
1t, Scheme 2

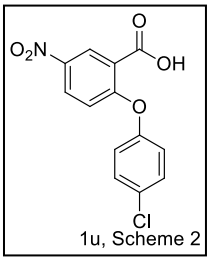

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NMR DATA/AH-429 P
AH429 1H-NMR in DMSO
8.359
8.354
8.344
8.339
7.522
7.518
7.510
7.507
7.176
7.170
7.166
7.159
7.155
7.149
7.116
7.101
3.360
2.496

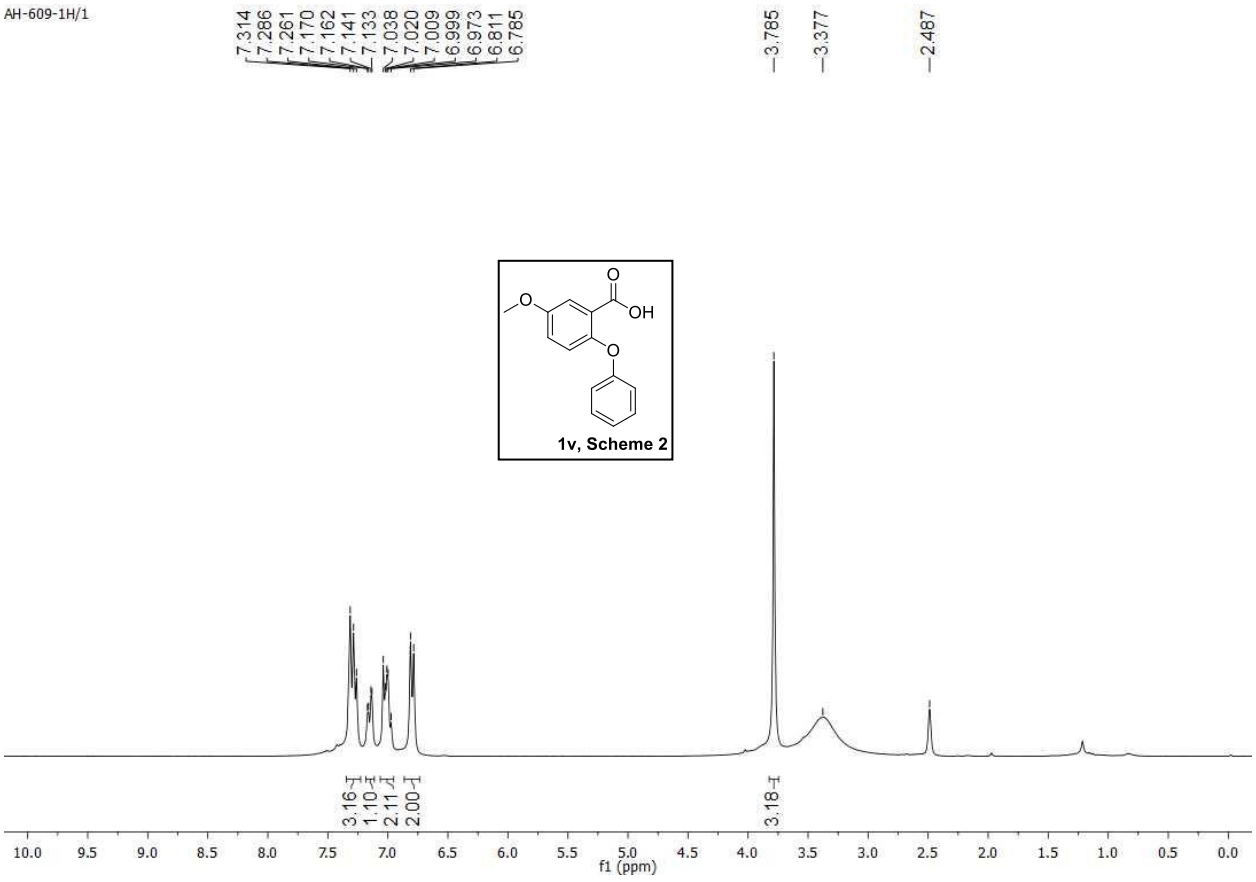

O
O2N
OH
O
Cl
1u, Scheme 2

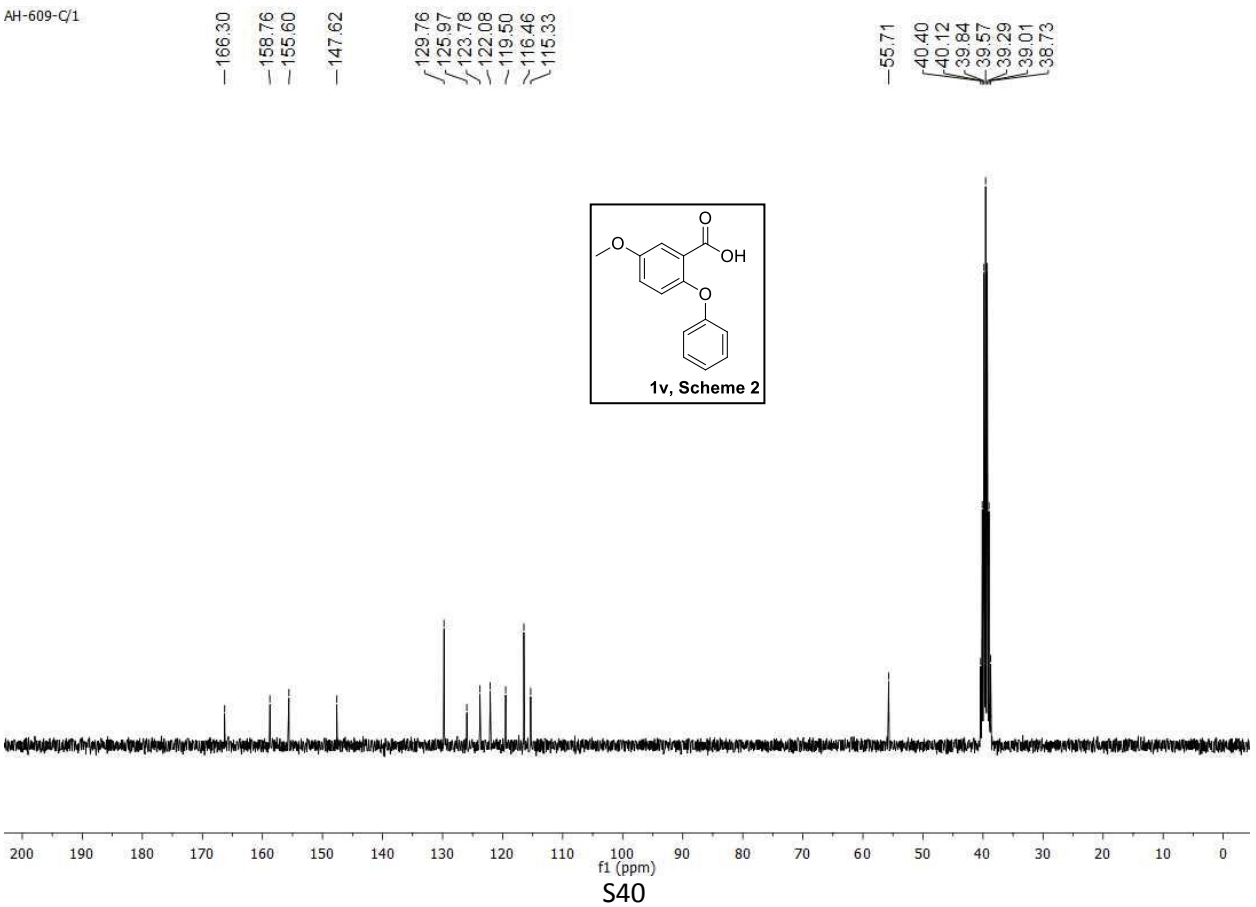

0.95
1.21
2.00
2.00
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

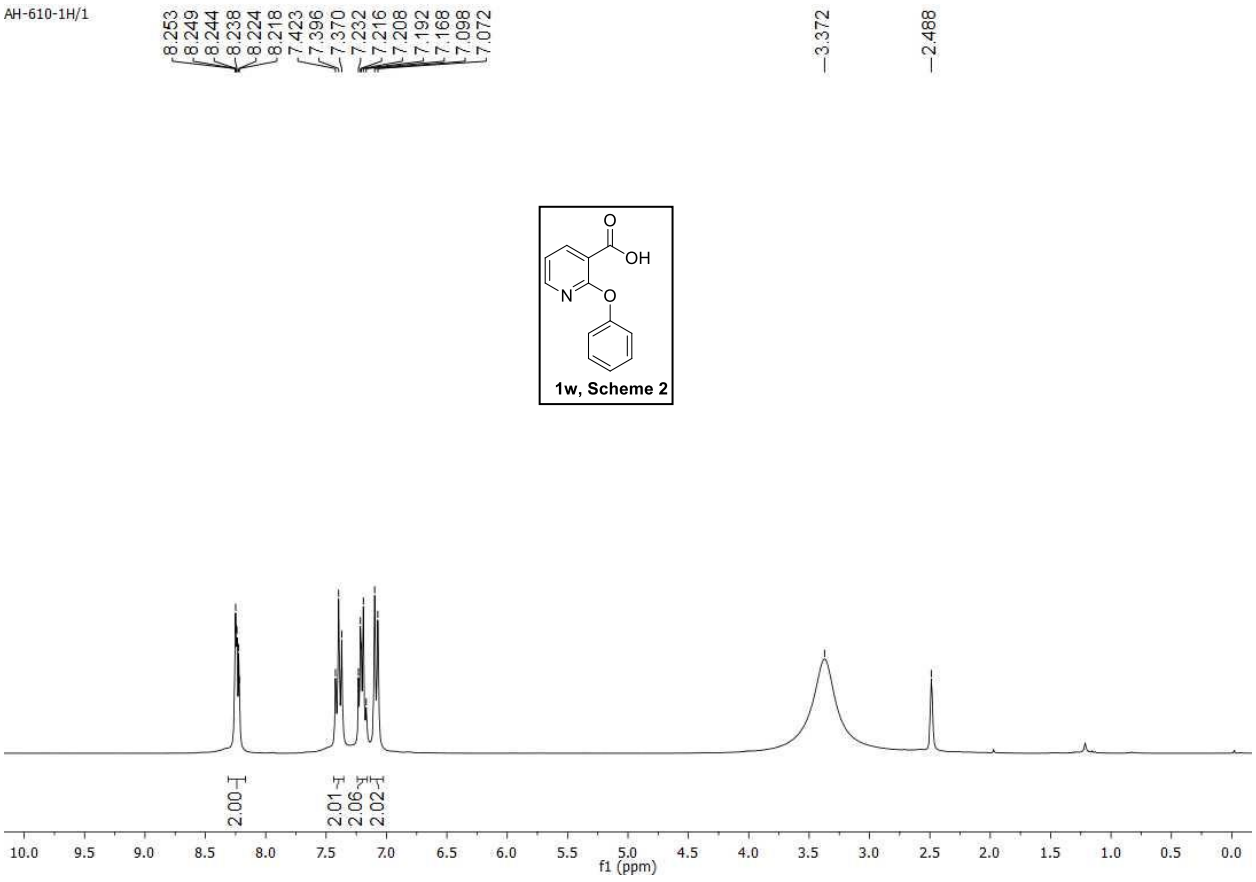

NMR DATA/AH-429 C
AH429 13C-NMR in DMSO
165.13
160.88
154.49
142.74
130.71
129.32
129.12
127.48
124.12
121.83
120.08
40.32
40.18
40.05
39.91
39.77
39.63
39.49


O
O2N
OH
O
Cl
1u, Scheme 2

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

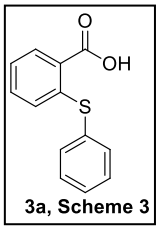

AH-609-1H/1
7.314
7.286
7.261
7.170
7.162
7.141
7.133
7.038
7.020
7.009
6.999
6.973
6.811
6.785
3.785
3.377
2.487
1v, Scheme 2
3.16
1.10
2.11
2.00
3.18
f1 (ppm)


AH-609-C/1
166.30
158.76
155.60
147.62
129.76
125.97
123.78
122.08
119.50
116.46
115.33
55.71
40.40
40.12
39.84
39.57
39.29
39.01
38.73
1v, Scheme 2
f1 (ppm)

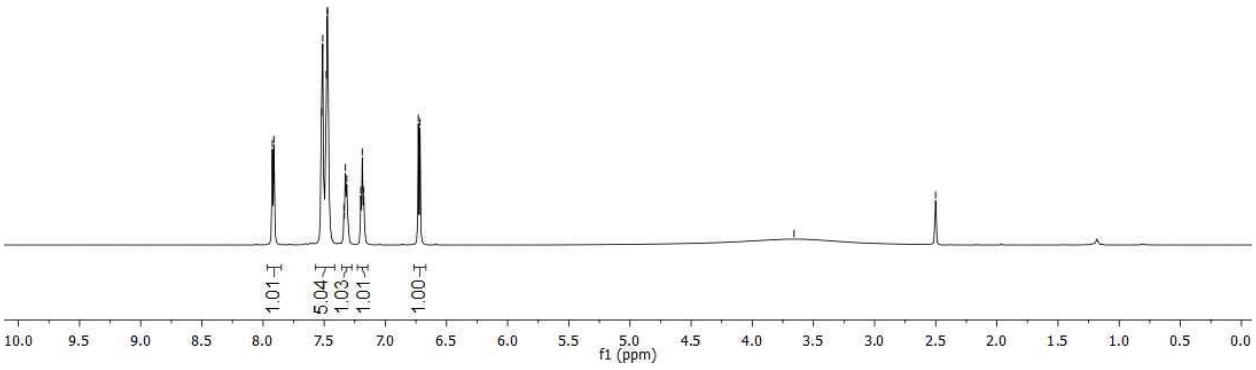

AH-610-1H/1
8.253
8.249
8.244
8.238
8.224
8.218
7.423
7.396
7.370
7.232
7.216
7.208
7.192
7.168
7.098
7.072
3.372
2.488
1w, Scheme 2
2.00
2.01
2.06
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
AH-610-C/1
165.93
160.89
153.94
150.57
141.61
129.68
124.62
121.48
119.02
116.39
40.35
40.08
39.80
39.52
39.24
38.96
38.69
1w, Scheme 2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

NMR DATA/AH-546-H
AH-546 1H-NMR in DMSO

7.524
7.511
7.502
7.512
7.483
7.474
7.473
7.339
7.327
7.315
7.201
7.189
7.177
6.731
6.717
3.659
2.501

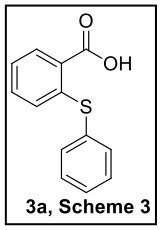


3a, Scheme 3

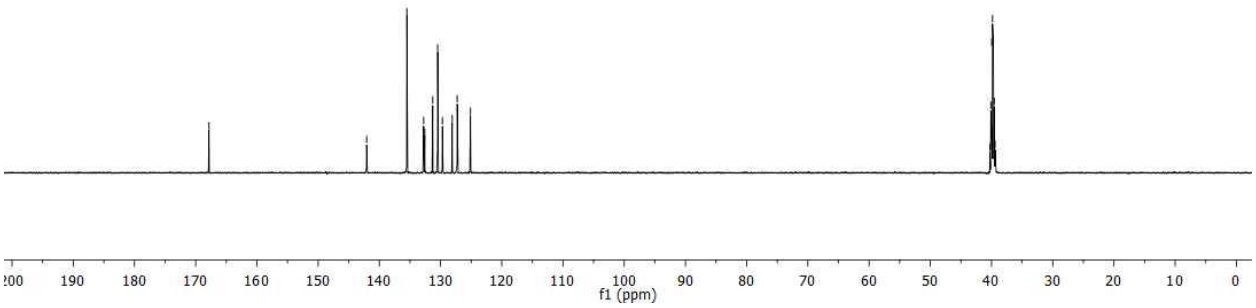


NMR DATA/AH-546 P
AH-546 13C-NMR in DMSO

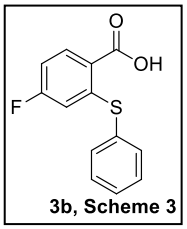
167.83
142.07
135.50
132.76
132.58
131.28
130.47
129.70
128.10
127.28
125.11
40.25
40.11
39.97
39.83
39.69
39.55
39.42

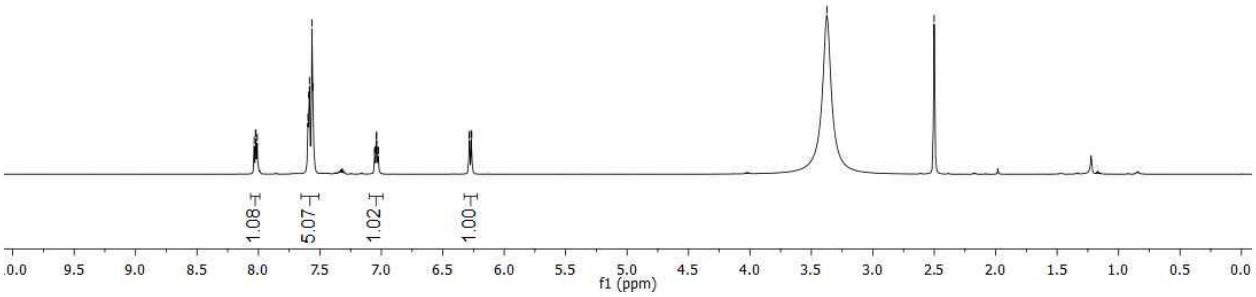


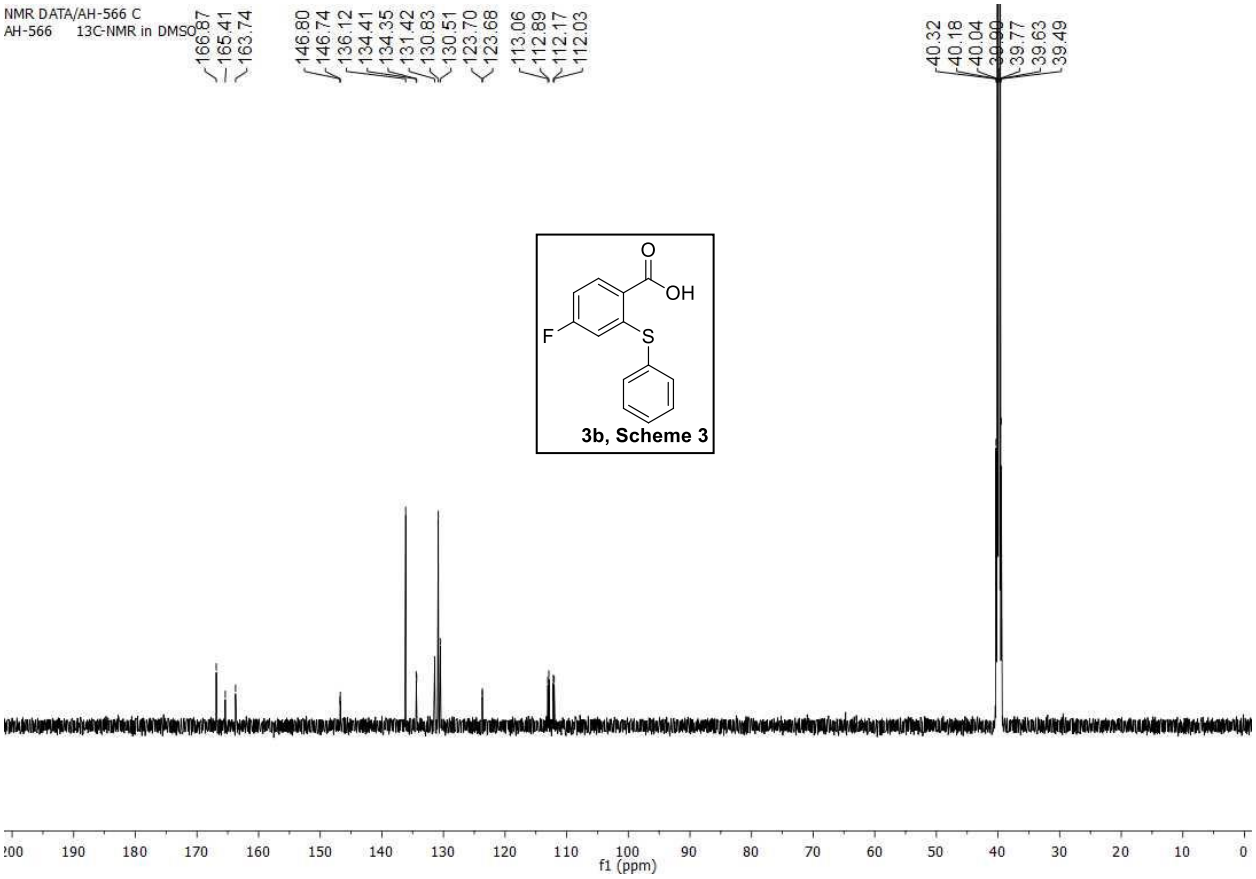
3a, Scheme 3

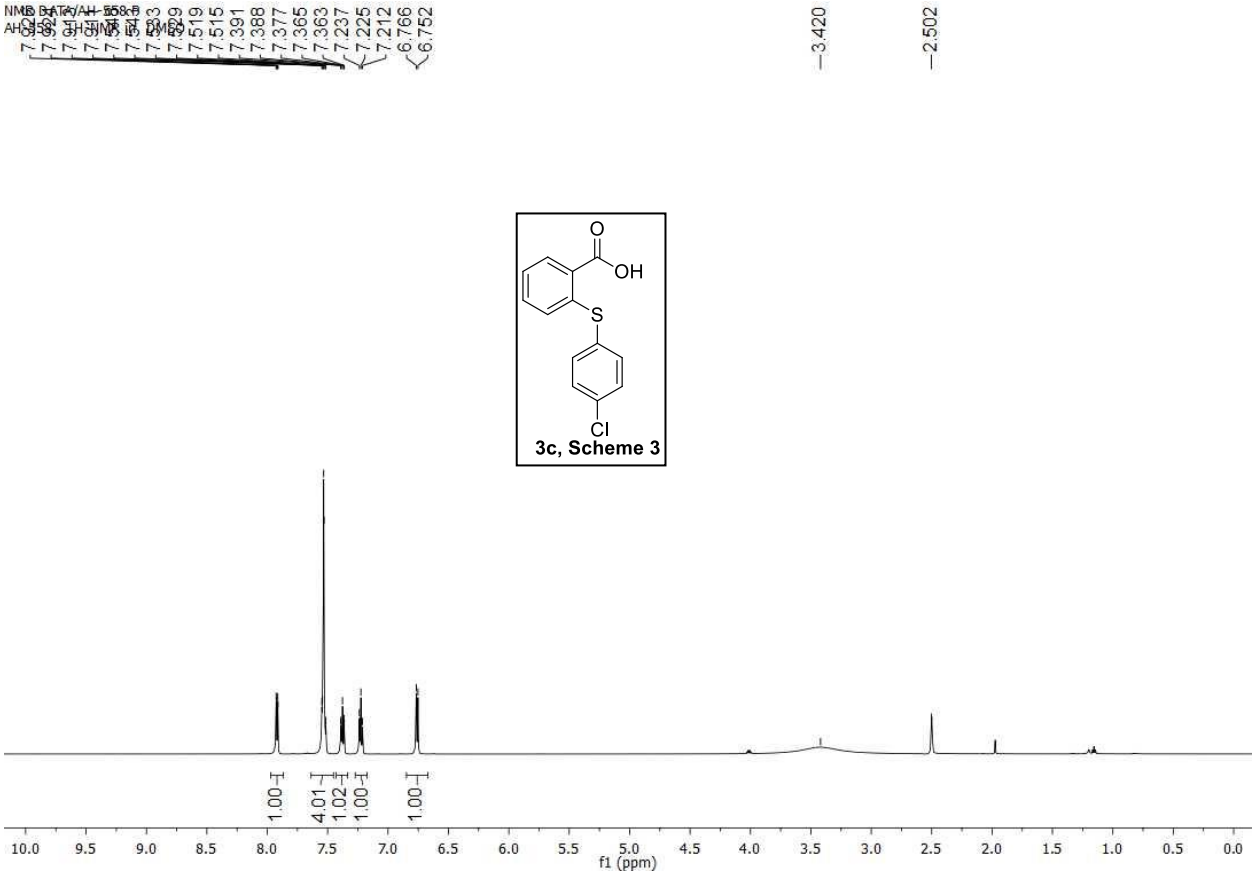


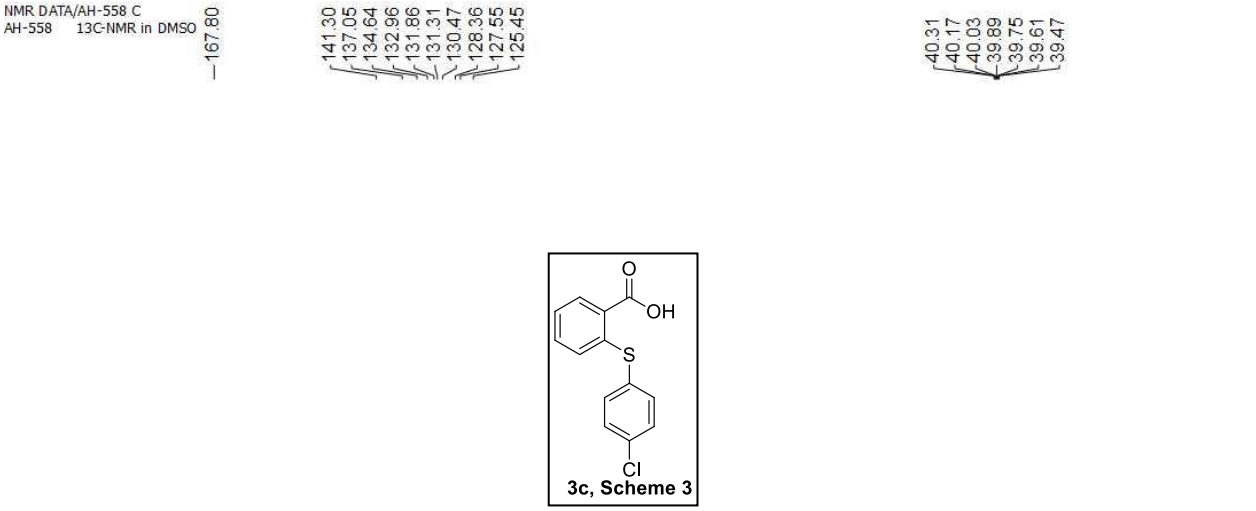

NMR DATA/AH-566 P
AH-566 1H-NMR in DMSO
8.035
8.024
8.020
8.010
7.597
7.591
7.585
7.565
7.557
7.055
7.052
7.041
7.038
7.028
7.024
6.286
6.282
6.268
6.265
3.374
2.501

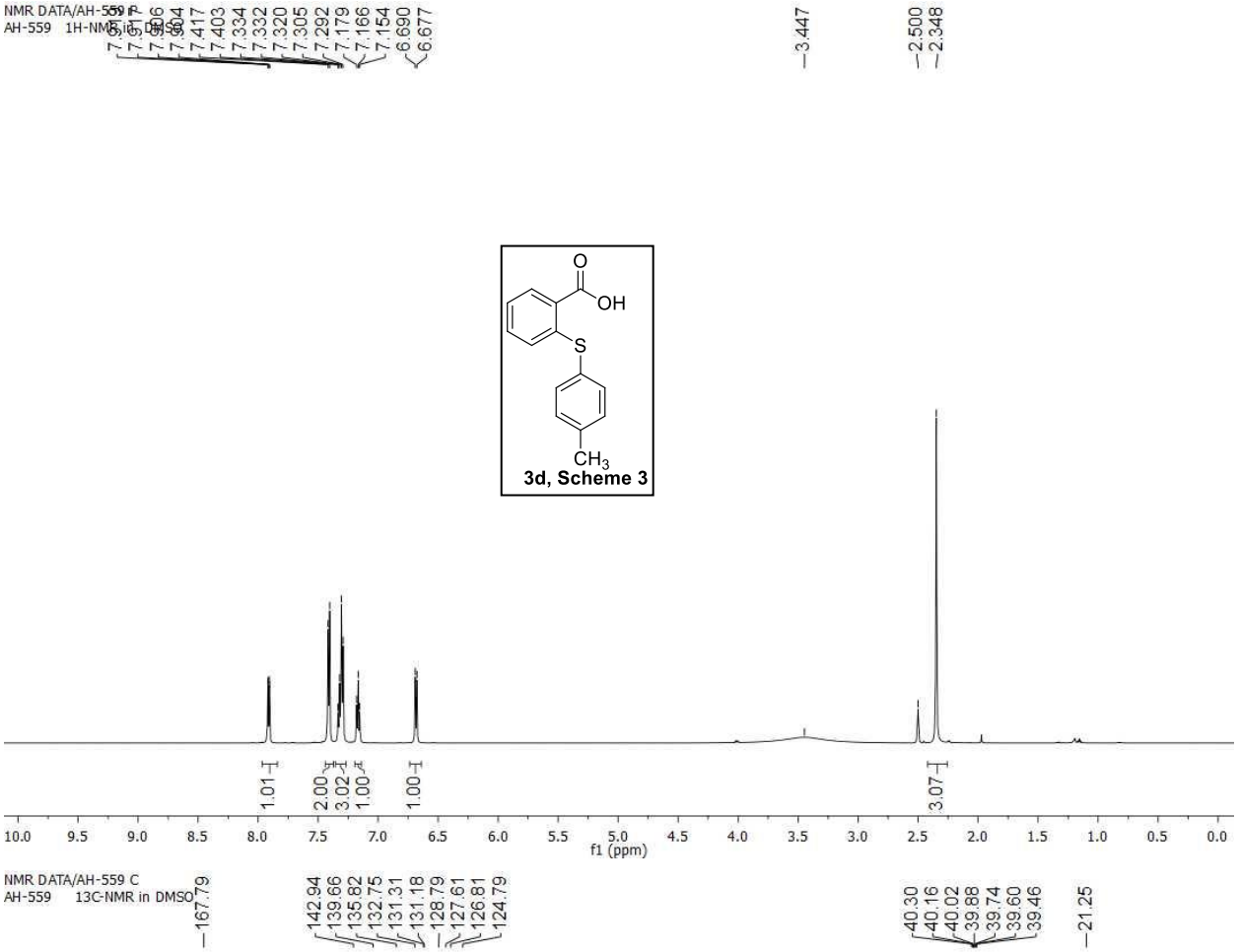

O
OH
F
S
3b, Scheme 3

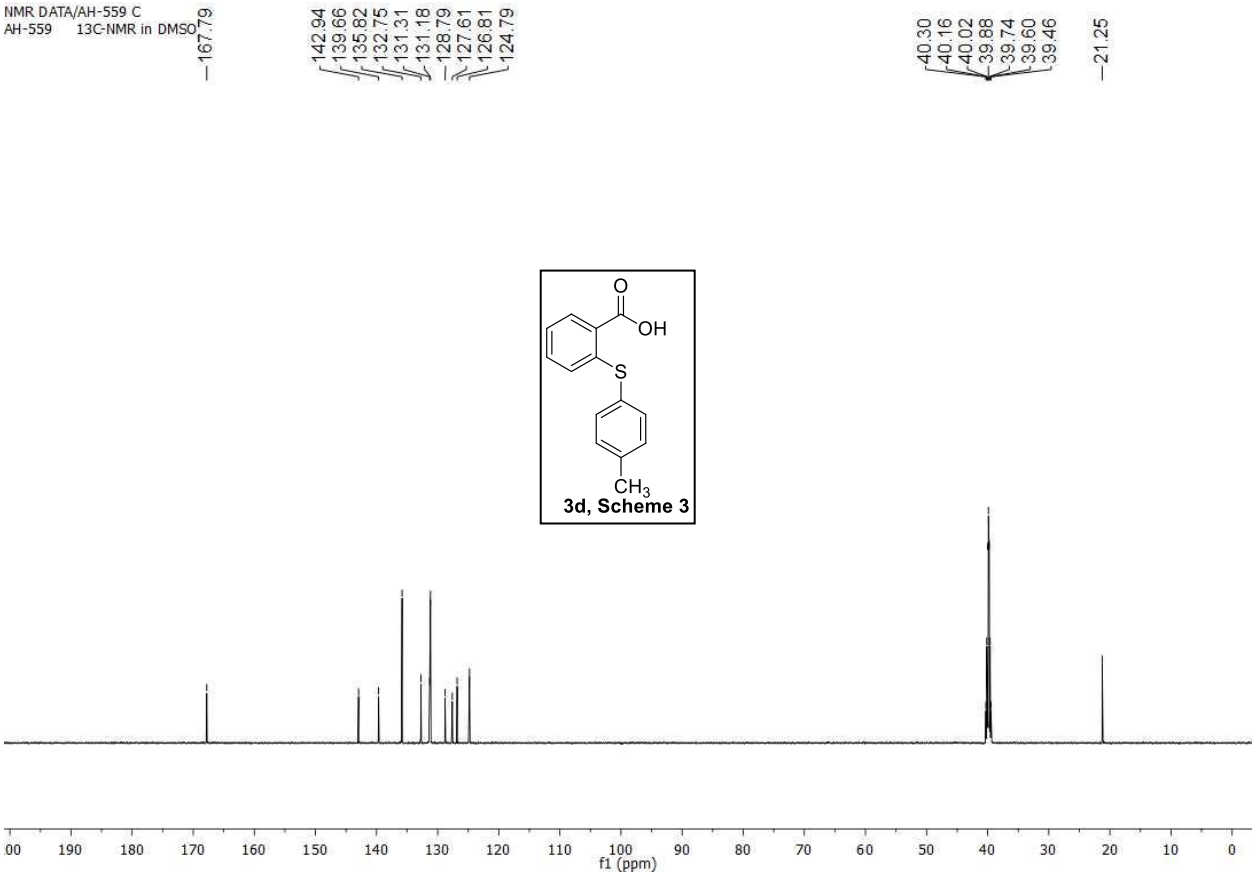

1.08
5.07
1.02
1.00
f1 (ppm)


NMR DATA/AH-566 C
AH-566 13C-NMR in DMSO
166.87
165.41
163.74
146.80
146.74
136.12
134.41
134.35
131.42
130.83
130.51
123.70
123.68
113.06
112.89
112.17
112.03
40.32
40.18
40.04
39.77
39.63
39.49
O
OH
F
S
3b, Scheme 3
f1 (ppm)

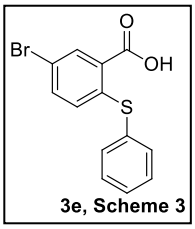

7.543
7.539
7.519
7.515
7.391
7.388
7.377
7.365
7.363
7.237
7.225
7.212
6.766
6.752
3.420
2.502
O
OH
S
Cl
3c, Scheme 3
1.00
4.01
1.02
1.00
1.00
f1 (ppm)

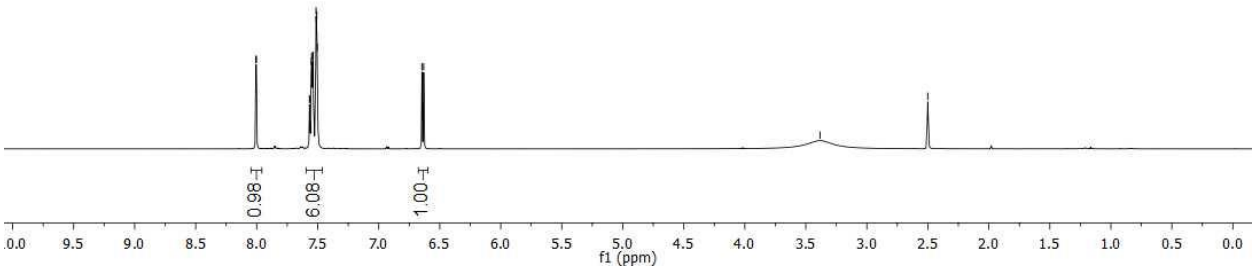

NMR DATA/AH-558 C
AH-558 13C-NMR in DMSO
167.80
141.30
137.05
134.64
132.96
131.86
131.31
130.47
128.36
127.55
125.45
40.31
40.17
40.03
39.89
39.75
39.61
39.47
O
OH
S
Cl
3c, Scheme 3
f1 (ppm)

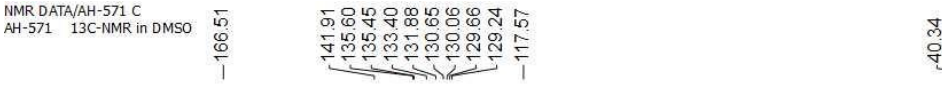

NMR DATA/AH-559 F
AH-559 1H-NMR in DMSO
7.917
7.906
7.904
7.417
7.403
7.334
7.332
7.320
7.305
7.292
7.179
7.166
7.154
6.690
6.677
3.447
2.500
2.348
O
OH
S
CH3
3d, Scheme 3
1.01
2.00
3.02
1.00
1.00
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

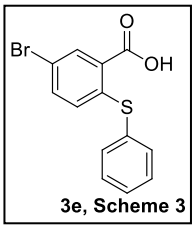

NMR DATA/AH-559 C
AH-559 13C-NMR in DMSO
167.79
142.94
139.66
135.82
132.75
131.31
131.18
128.79
127.61
126.81
124.79
40.30
40.16
40.02
39.88
39.74
39.60
39.46
21.25
O
OH
S
CH3
3d, Scheme 3
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

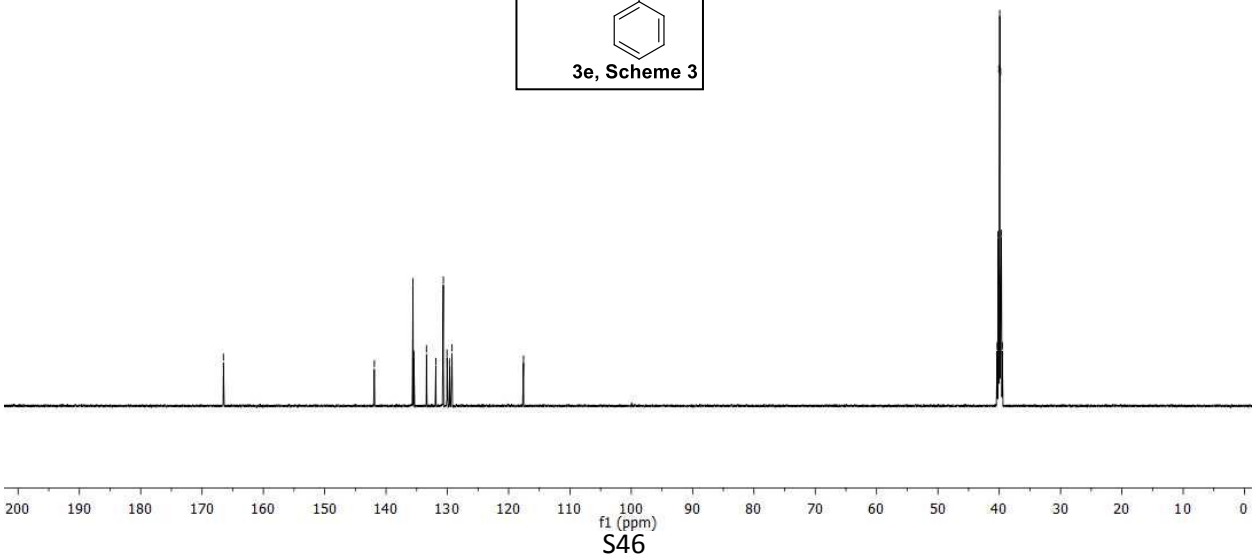

NMR DATA/AH-571 P
AH-571 1H-NMR in DMSO
8.007
8.003
7.568
7.564
7.553
7.549
7.541
7.537
7.514
7.508
7.503
6.646
6.631
3.384
2.500


Br
O
OH
S
3e, Scheme 3

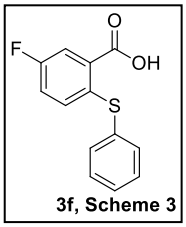

0.98
6.08
1.00
f1 (ppm)

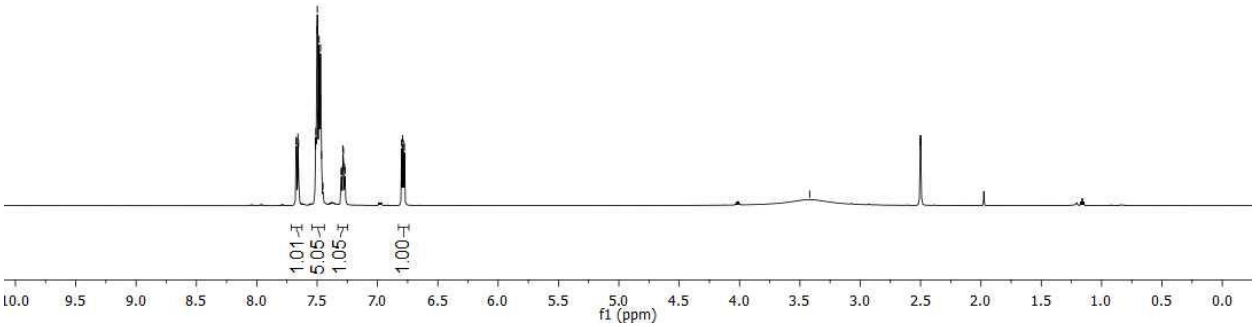

NMR DATA/AH-571 C
AH-571 13C-NMR in DMSO
166.51
141.91
135.60
135.45
133.40
131.88
130.65
130.06
129.66
129.24
117.57
40.34
40.20
40.06
39.92
39.78
39.64
39.50


Br
O
OH
S
3e, Scheme 3

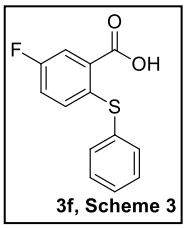

f1 (ppm)

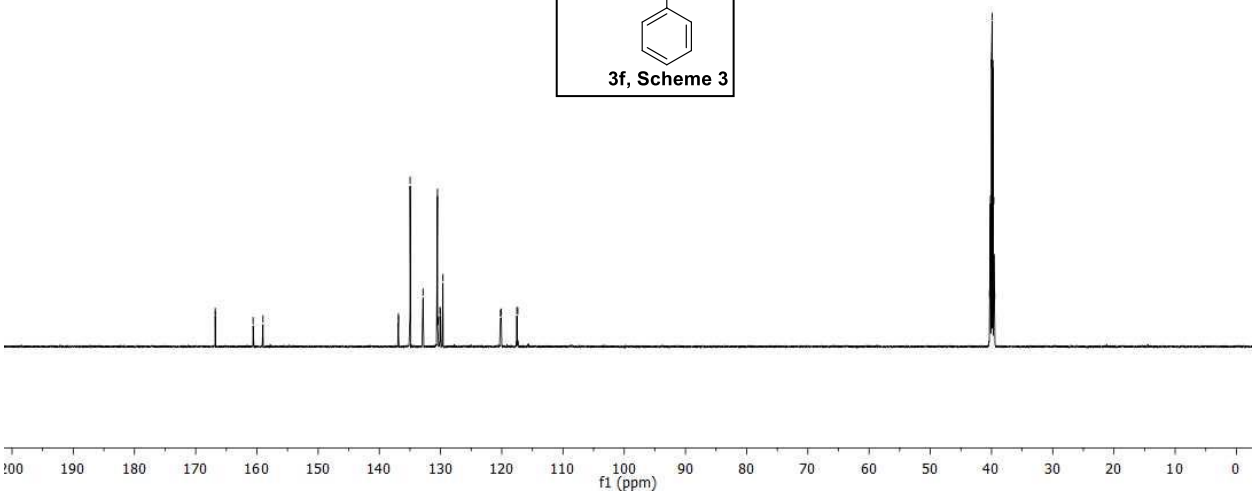

7.493
7.489
7.484
7.472
7.464
7.287
7.282
7.273
6.791
6.785
6.776
3.419
2.503


F
O
OH
S
3f, Scheme 3

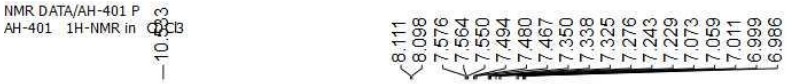

1.01
5.05
1.05
1.00
f1 (ppm)

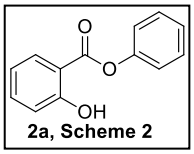

NMR DATA/AH-574 C
AH-574 13C-NMR in DMSO
166.79
160.63
159.01
136.89
136.87
134.98
132.87
130.50
130.45
130.40
130.09
130.04
129.61
120.22
120.07
117.54
117.39
40.32
40.18
40.04
39.90
39.76
39.62
39.48


F
O
OH
S
3f, Scheme 3

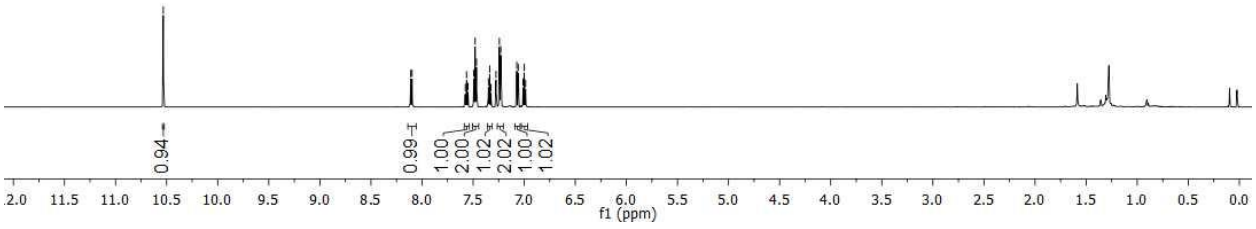

f1 (ppm)

NMR DATA/AH-401 P
AH-401 1H-NMR in CDCl3

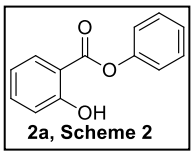




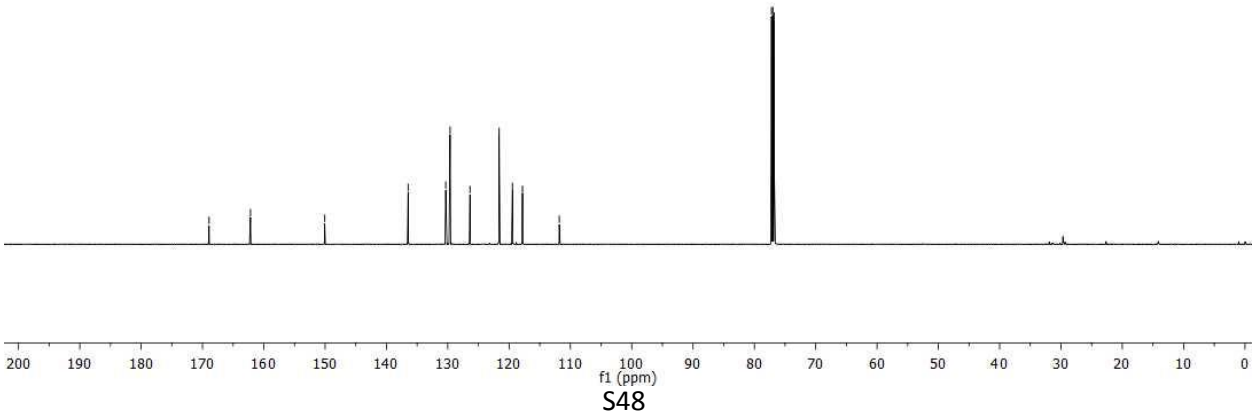
2a, Scheme 2



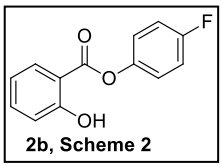
NMR DATA/AH-401 C
AH-401 13C-NMR in CDCl3

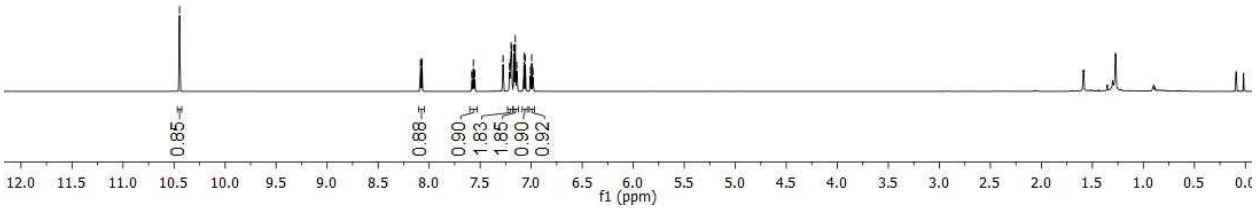


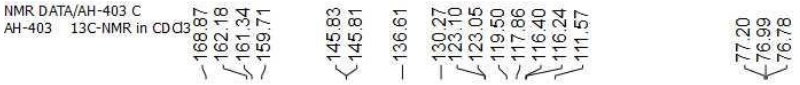
2a, Scheme 2

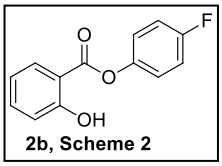


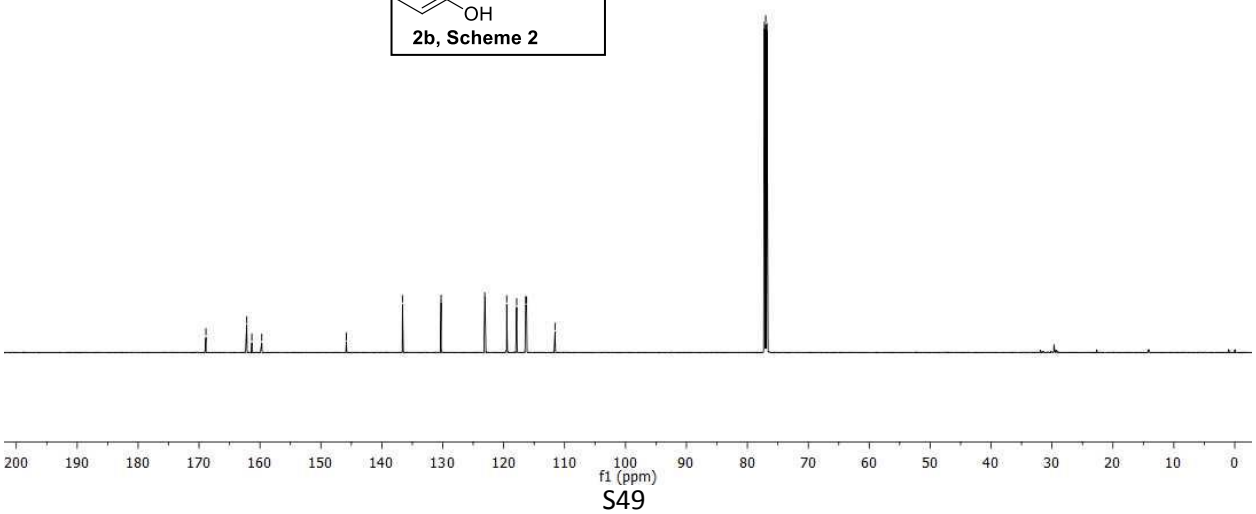

NMR DATA/AH-403 P
AH-403 1H-NMR in CDCl3
10.47
8.084
8.082
8.071
8.069
7.581
7.579
7.567
7.555
7.553
7.276
7.213
7.205
7.202
7.198
7.190
7.169
7.156
7.141
7.071
7.057
7.008
6.995
6.982


O
O
F
OH
2b, Scheme 2

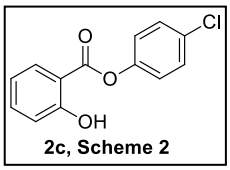

0.85
0.88
0.90
1.83
1.85
0.90
0.92
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


NMR DATA/AH-403 C
AH-403 13C-NMR in CDCl3
168.87
162.18
161.34
159.71
145.83
145.81
136.61
130.27
123.10
123.05
119.50
117.86
116.40
116.24
111.57
77.20
76.99
76.78

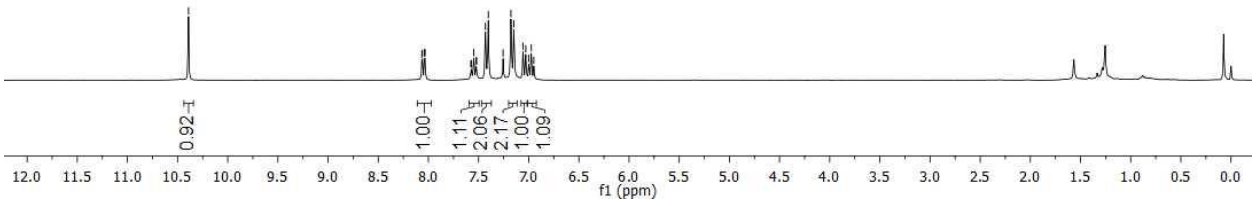

O
O
F
OH
2b, Scheme 2


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

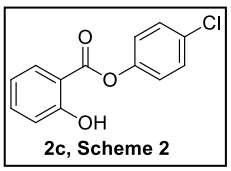
AH-398-1H/1



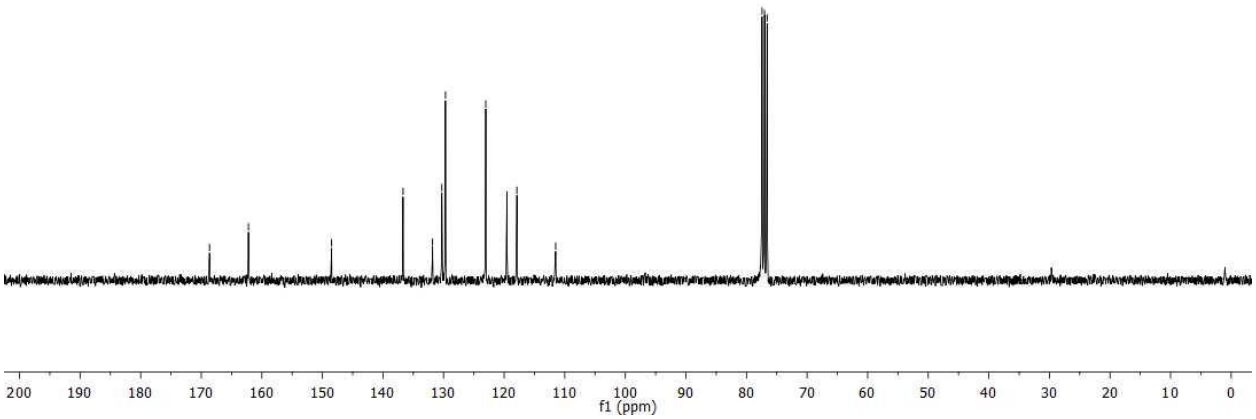
2c, Scheme 2



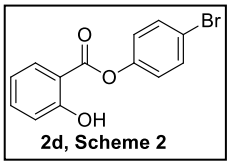
AH-398-C.1.fid

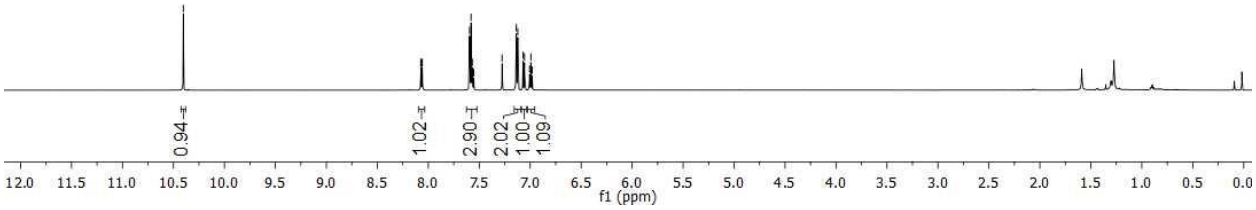


2c, Scheme 2

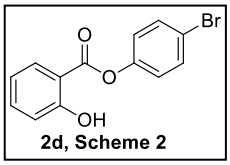


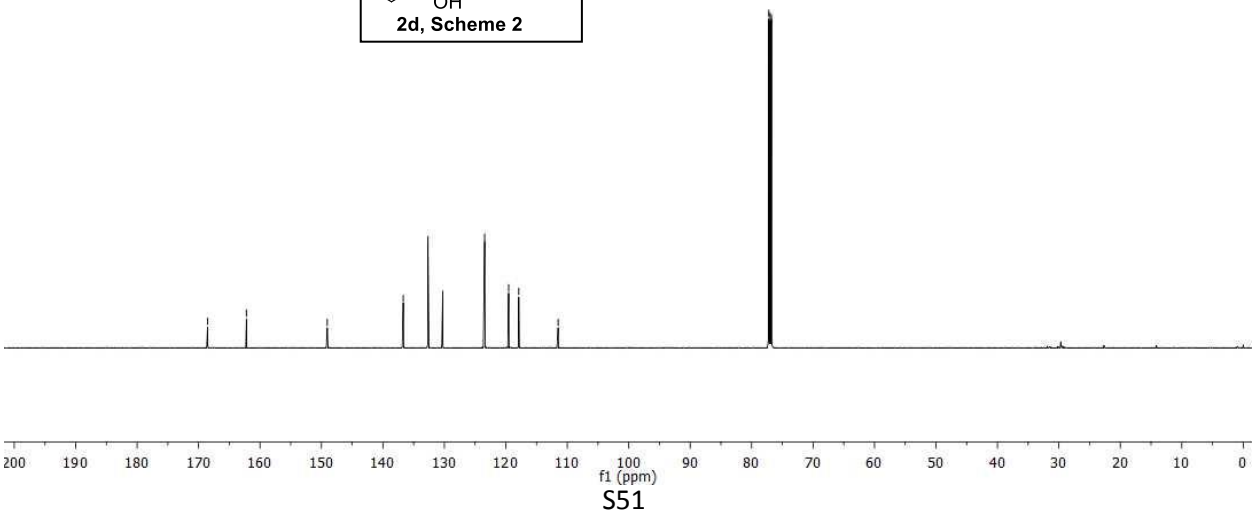

NMR DATA/AH-406 P
AH-406 1H-NMR in CDCl3
10.403
8.074
8.072
8.060
8.059
7.595
7.580
7.568
7.556
7.554
7.276
7.137
7.122
7.070
7.056
7.006
6.994
6.981


Br
O
O
OH
2d, Scheme 2


0.94
1.02
2.90
2.02
1.00
1.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


NMR DATA/AH-406 C
AH-406 13C-NMR in CDCl3
168.54
162.21
149.06
136.69
132.67
130.28
123.44
119.54
117.89
111.48
77.21
76.99
76.78

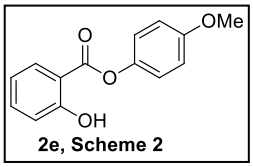

Br
O
O
OH
2d, Scheme 2


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

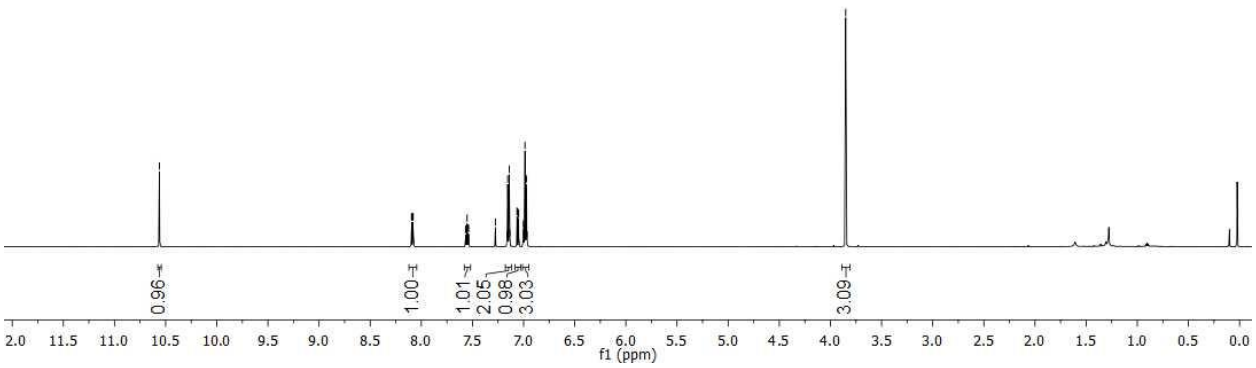
NMR DATA/AH-371 P
AH-371 1H-NMR in CDCl3

10.851

8.096
8.093
8.083
8.080
7.567
7.565
7.553
7.541
7.539
7.276
7.161
7.155
7.152
7.144
7.140
7.134
7.064
7.063
7.050
7.049
7.001
6.999
6.992
6.987
6.983
6.975
6.971
6.965
3.851

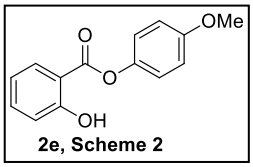


2e, Scheme 2

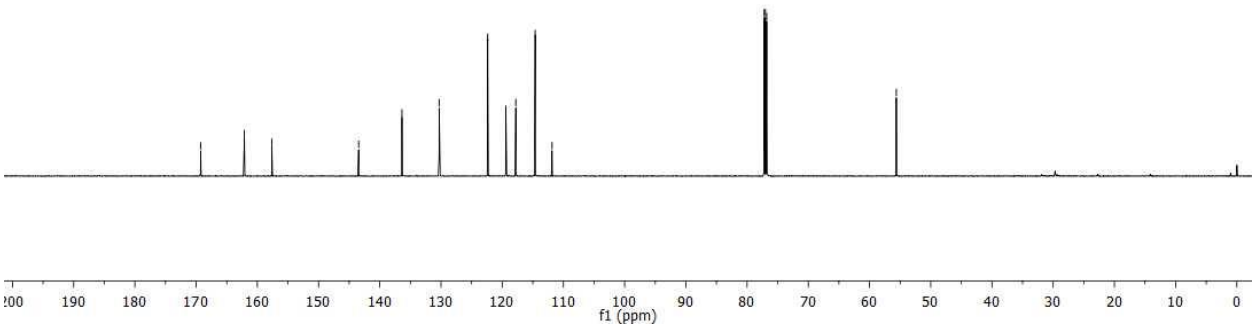


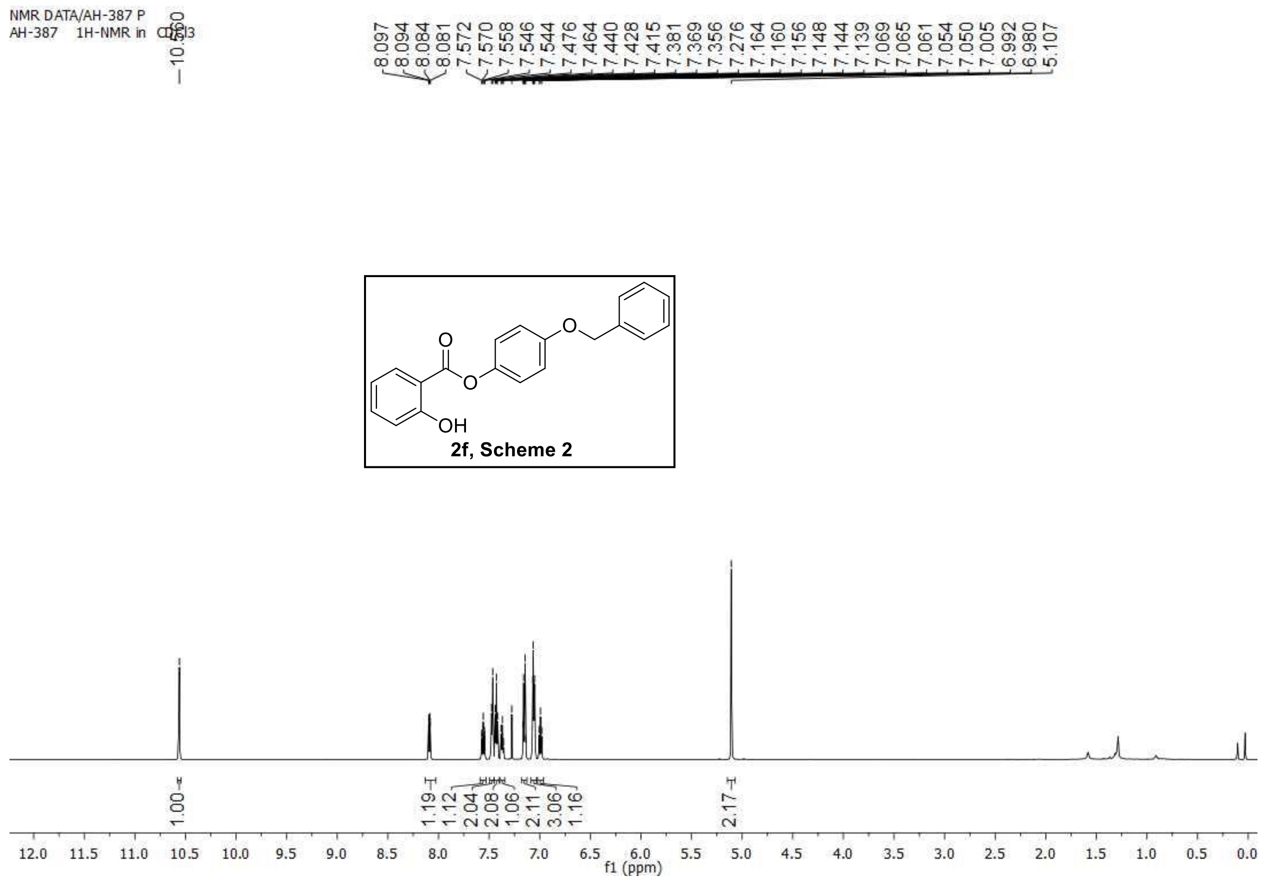
NMR DATA/AH-371 C
AH-371 13C-NMR in CDCl3

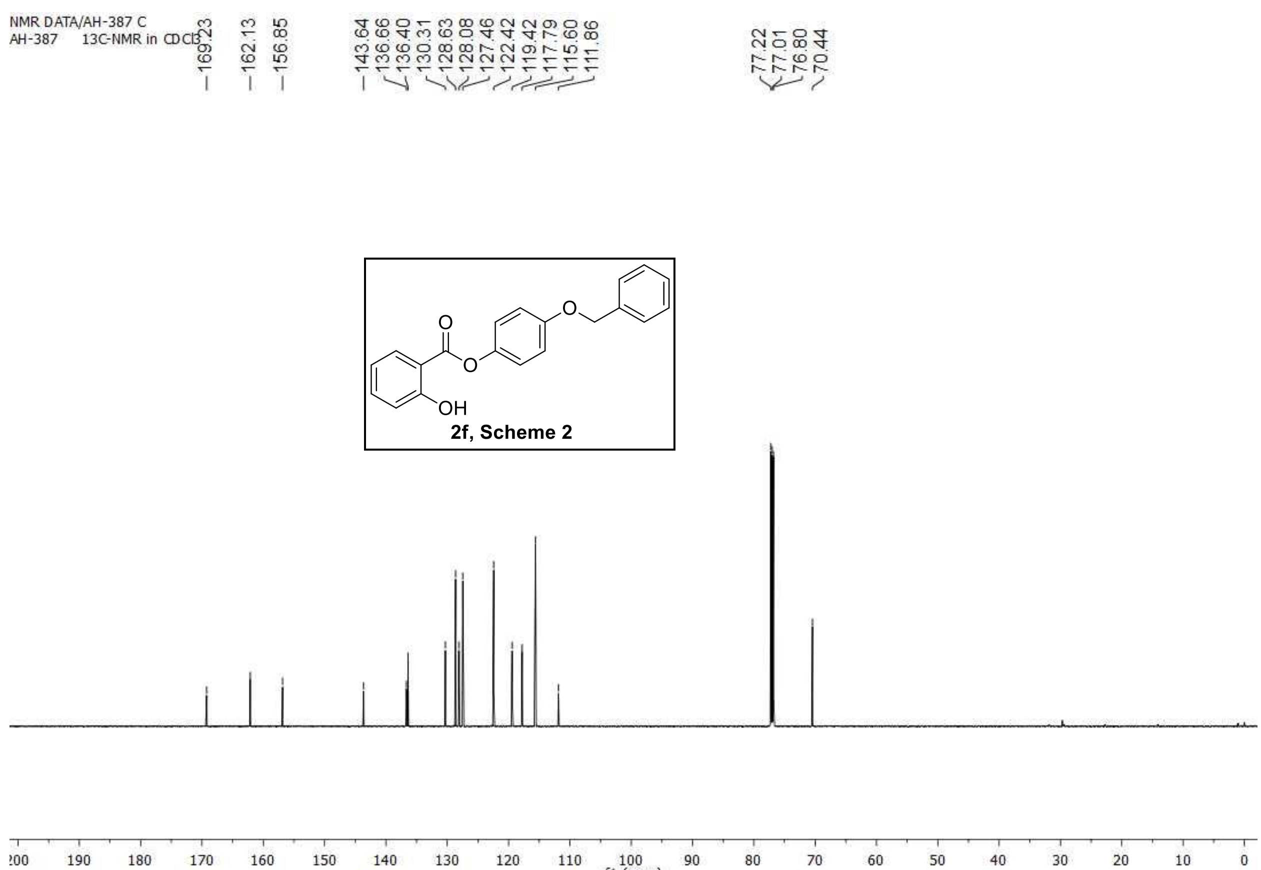
169.27
162.11
157.63
143.45
136.38
130.30
122.37
119.41
117.78
114.61
111.86
77.22
77.01
76.79
55.62



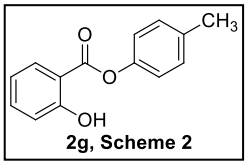
2e, Scheme 2

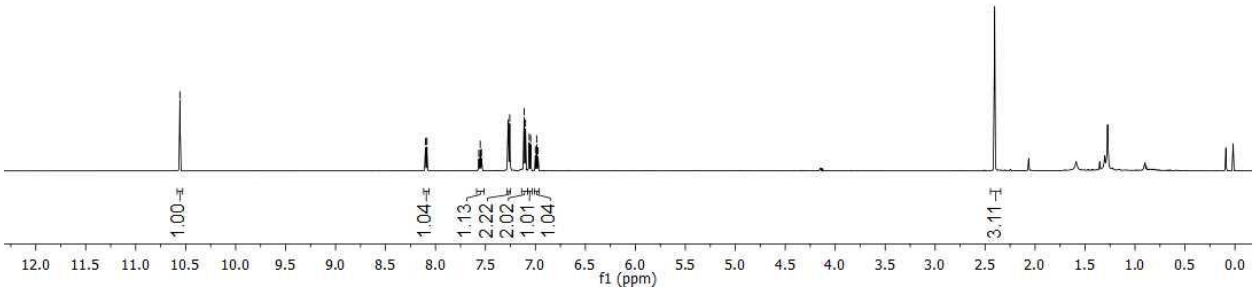



NMR DATA/AH-387 P
AH-387 1H-NMR in CDCl3
10.560
8.097
8.094
8.084
8.081
7.572
7.570
7.558
7.546
7.544
7.476
7.464
7.440
7.428
7.415
7.381
7.369
7.356
7.276
7.164
7.160
7.156
7.148
7.144
7.139
7.069
7.065
7.061
7.054
7.050
7.005
6.992
6.980
5.107
O
O
O
OH
2f, Scheme 2
1.00
1.19
1.12
2.04
2.08
1.06
2.11
3.06
1.16
2.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

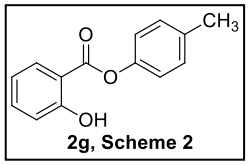

NMR DATA/AH-387 C
AH-387 13C-NMR in CDCl3
169.23
162.13
156.85
143.64
136.66
136.40
130.31
128.63
128.08
127.46
122.42
119.42
117.79
115.60
111.86
77.22
77.01
76.80
70.44
O
O
O
OH
2f, Scheme 2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NMR DATA/AH-394 P
AH-394 1H-NMR in CDCl3
10.557
8.099
8.086
7.566
7.552
7.540
7.275
7.271
7.257
7.113
7.099
7.062
7.048
7.000
6.987
6.975
2.405

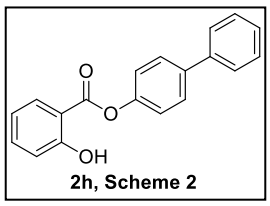

CH3
O
O
OH
2g, Scheme 2


1.00
1.04
1.13
2.22
2.02
1.01
1.04
3.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

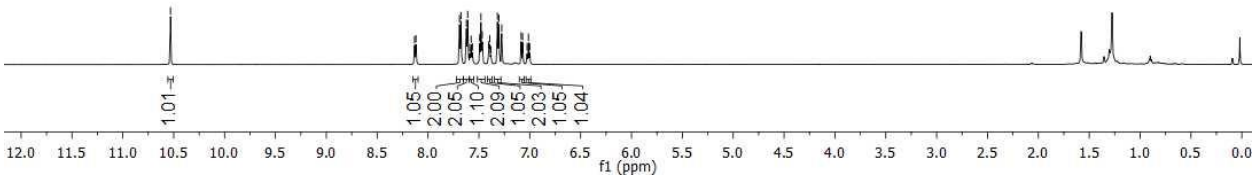

NMR DATA/AH-394 C
AH-394 13C-NMR in CDCl3
169.13
162.12
147.80
136.37
136.10
130.32
130.12
121.26
119.40
117.77
111.89
77.20
76.99
76.78
20.90

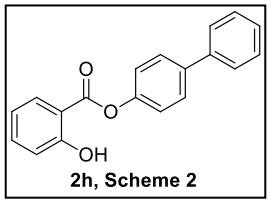

CH3
O
O
OH
2g, Scheme 2

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

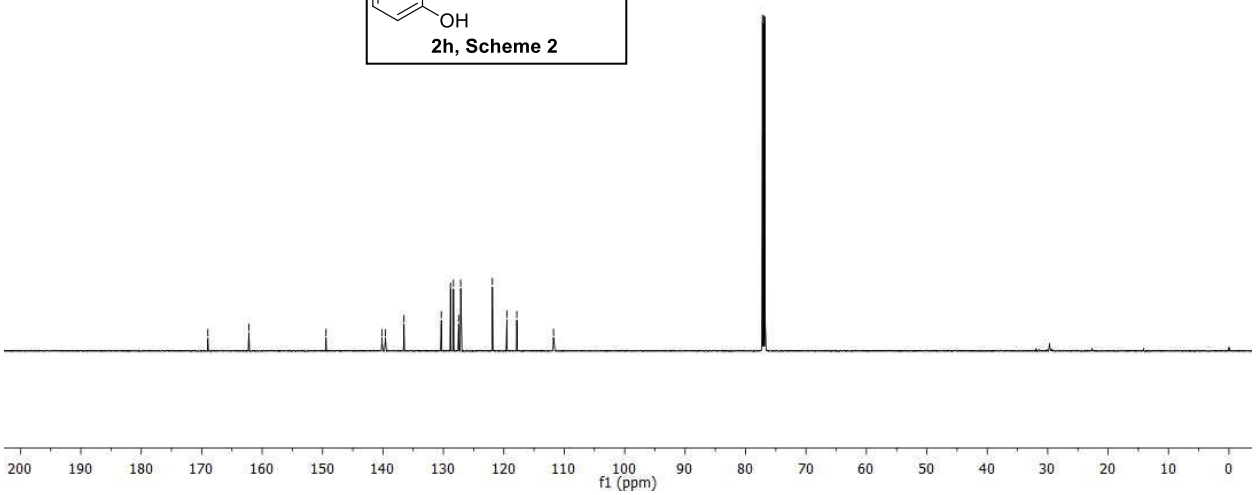


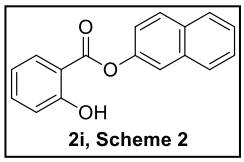
2h, Scheme 2



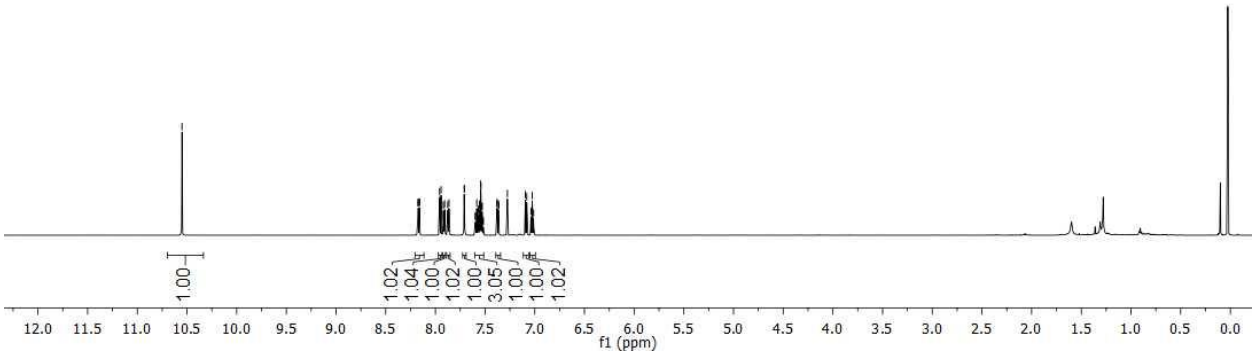


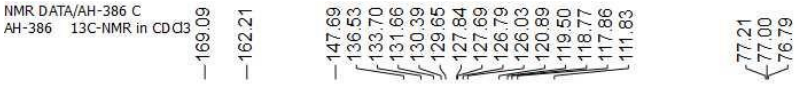
2h, Scheme 2

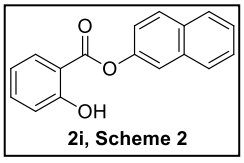




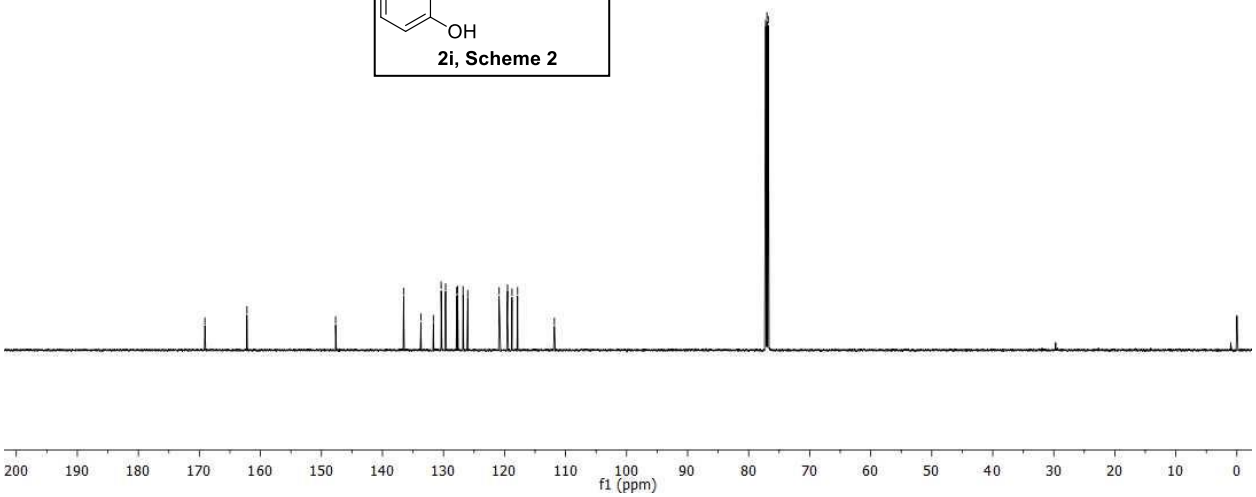
2i, Scheme 2



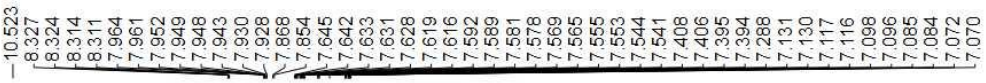


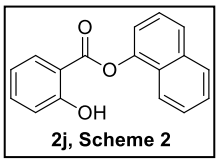


2i, Scheme 2

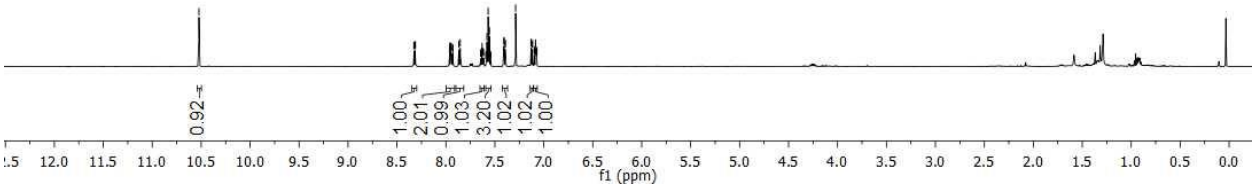


NMR DATA/AH-526 P

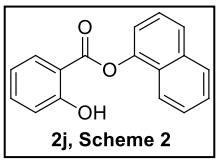




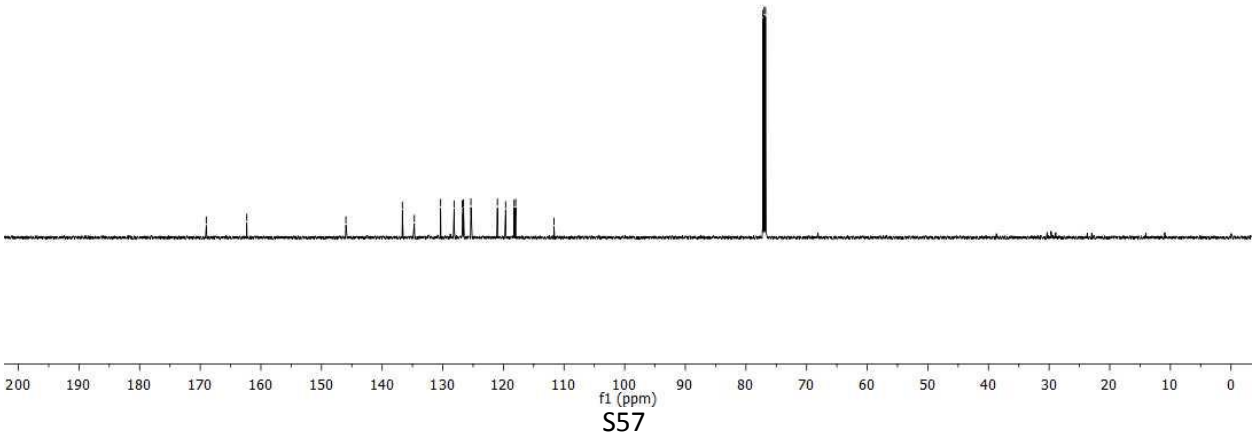
2j, Scheme 2



NMR DATA/AH-526 C

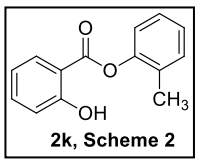


2j, Scheme 2

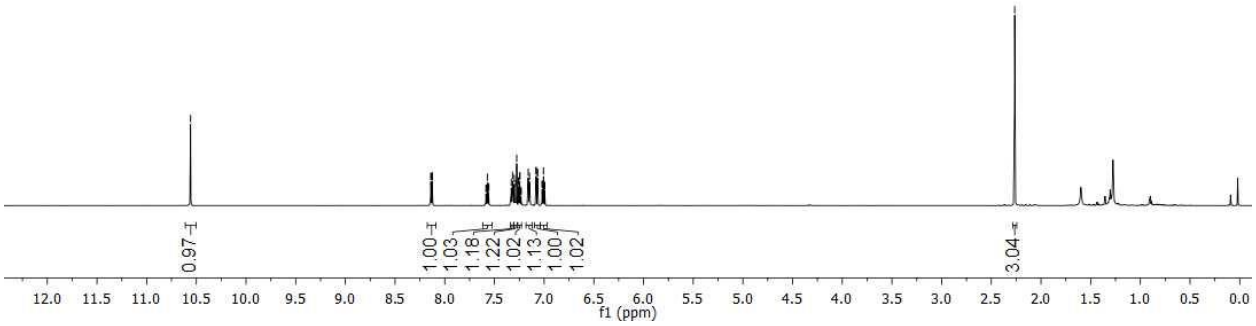


NMR DATA/AH-395 P
AH-395 1H-NMR in CDCl3

10.558
8.140
8.137
8.127
8.124
7.586
7.583
7.571
7.559
7.557
7.330
7.318
7.311
7.300
7.287
7.276
7.258
7.256
7.245
7.244
7.233
7.231
7.160
7.147
7.081
7.080
7.067
7.066
7.020
7.019
7.007
6.995
6.993
2.264

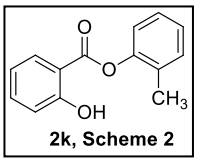


2k, Scheme 2

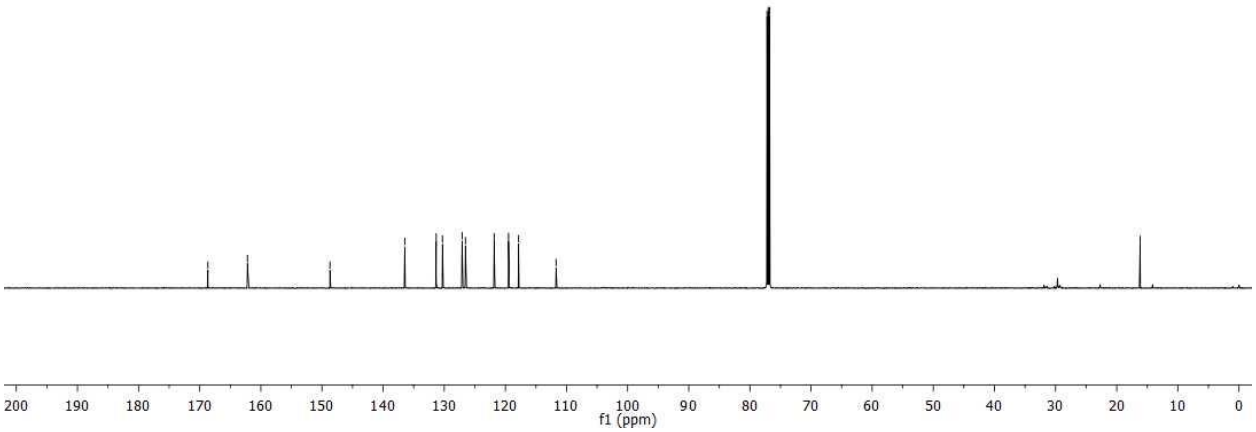


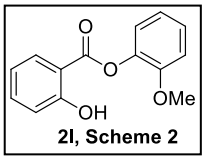
NMR DATA/AH-395 C
AH-395 13C-NMR in CDCl3

168.66
162.19
148.69
136.45
131.32
130.29
130.26
127.08
126.53
121.84
119.48
117.84
111.71
77.20
76.99
76.78
16.16

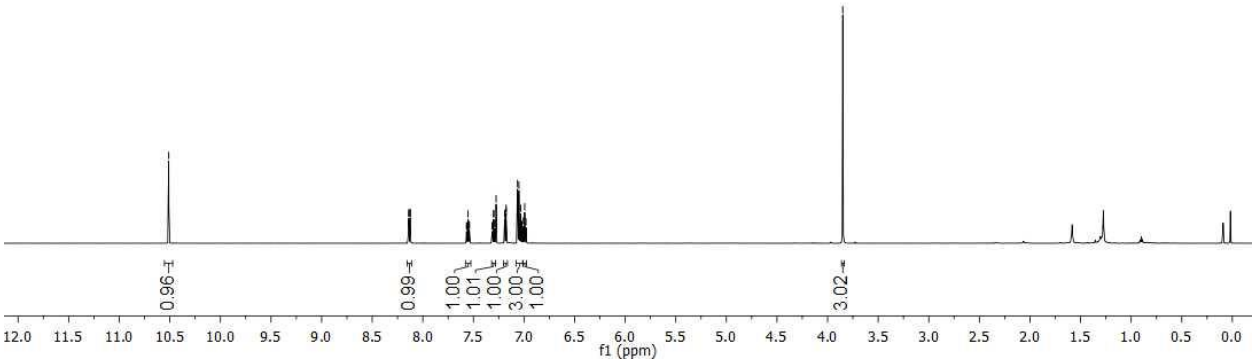


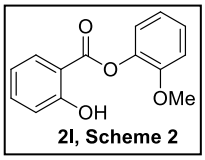
2k, Scheme 2



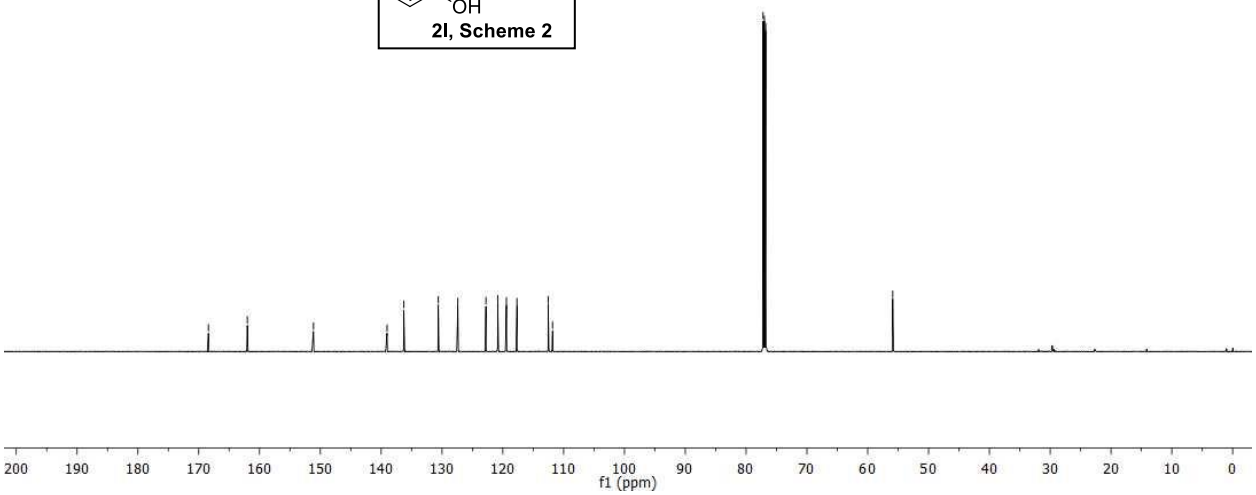


2l, Scheme 2

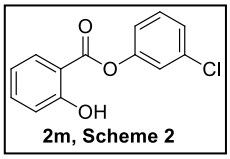


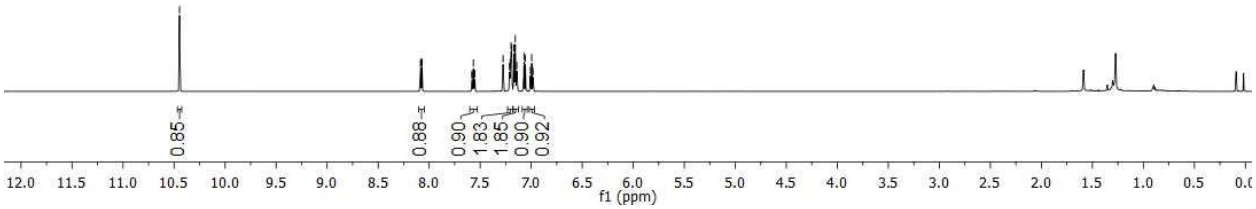


2l, Scheme 2

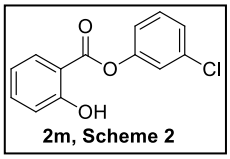


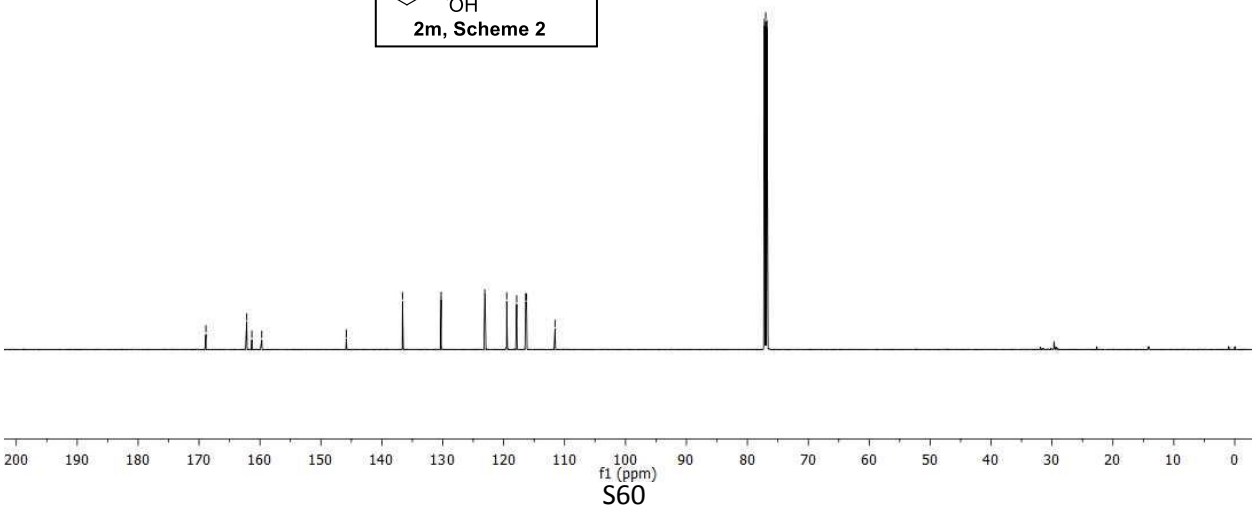

NMR DATA/AH-403 P
AH-403 1H-NMR in CDCl3
10.447
8.084
8.082
8.071
8.069
7.581
7.579
7.567
7.555
7.553
7.276
7.213
7.205
7.202
7.198
7.190
7.169
7.156
7.141
7.071
7.057
7.008
6.995
6.982


O
O
Cl
OH
2m, Scheme 2

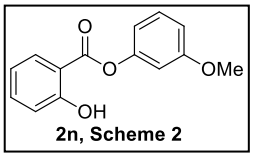

0.85
0.88
0.90
1.83
1.85
0.90
0.92
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


NMR DATA/AH-403 C
AH-403 13C-NMR in CDCl3
168.87
162.18
161.34
159.71
145.83
145.81
136.61
130.27
123.10
123.05
119.50
117.86
116.40
116.24
111.57
77.20
76.99
76.78

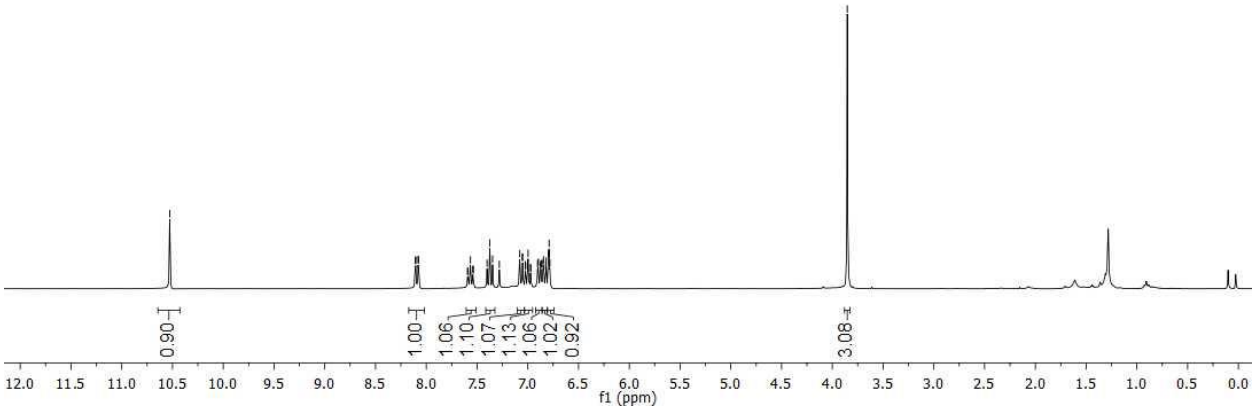

O
O
Cl
OH
2m, Scheme 2


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

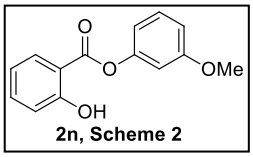
AH-400-1H/1



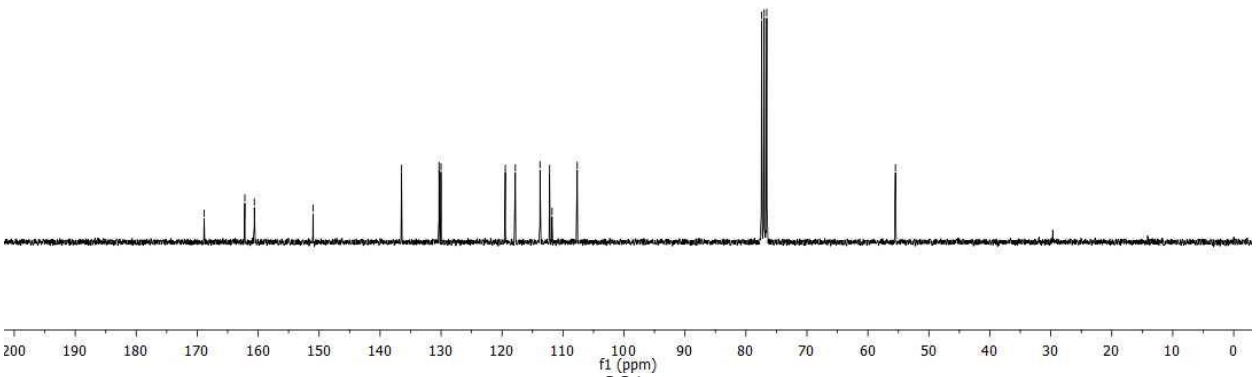
2n, Scheme 2



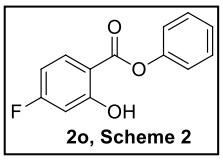
AH-400-C/1

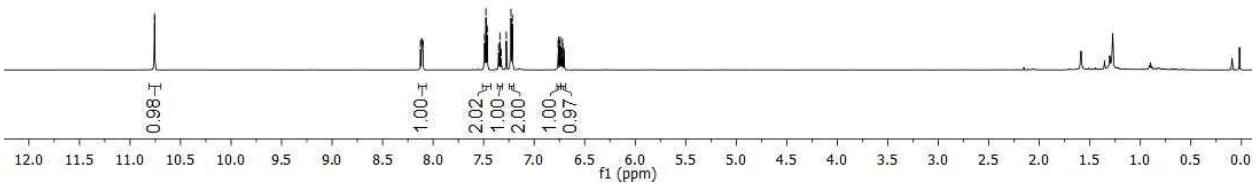


2n, Scheme 2

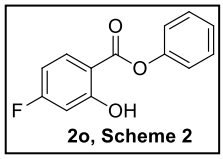


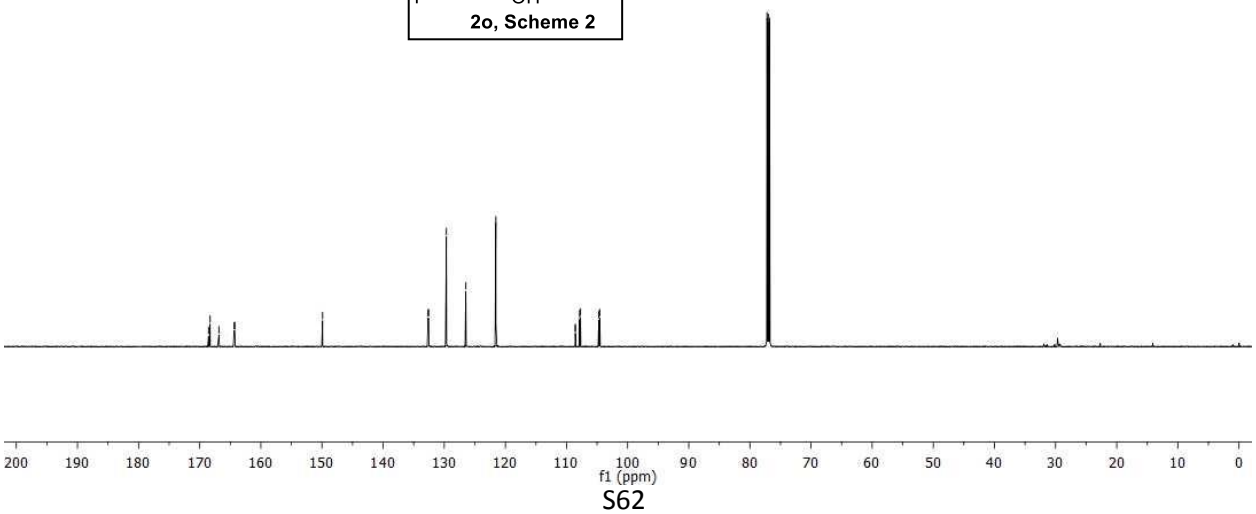

NMR DATA/AH-412 F
AH412 1H-NMR in CDCl3
10.757
10.725
8.125
8.114
8.110
8.099
7.491
7.477
7.464
7.352
7.339
7.327
7.276
7.229
7.216
6.763
6.759
6.746
6.742
6.734
6.730
6.720
6.716
6.706
6.702

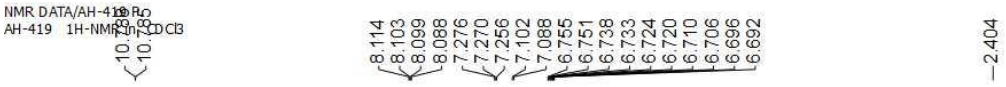

O
O
F
OH
2o, Scheme 2

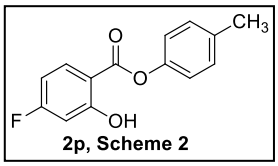

0.98
1.00
2.02
1.00
2.00
1.00
0.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


NMR DATA/AH-412 C
AH412 13C-NMR in CDCl3
168.56
168.31
166.86
164.36
164.27
149.90
132.64
132.56
129.65
126.47
121.56
108.57
108.55
107.86
107.71
104.72
104.56
77.20
76.99
76.78

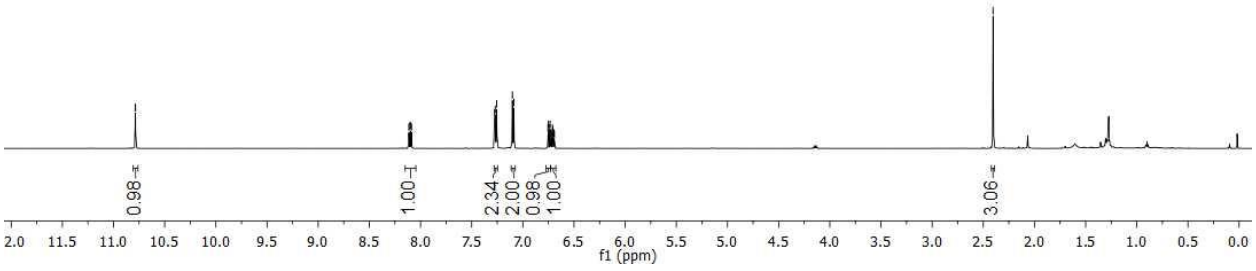

O
O
F
OH
2o, Scheme 2

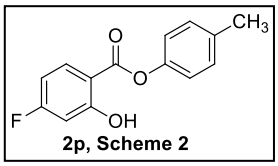

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



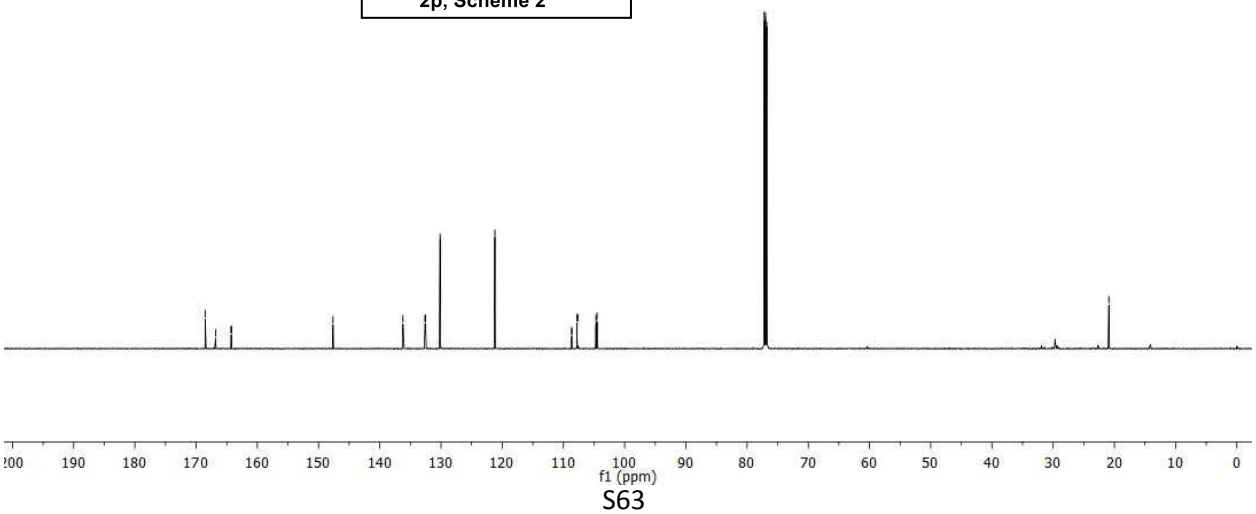


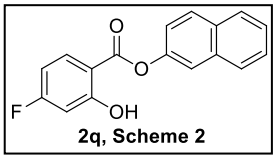
2p, Scheme 2



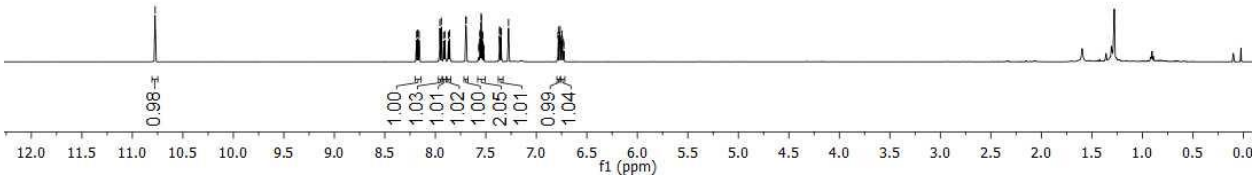


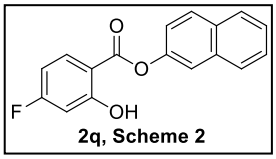
2p, Scheme 2



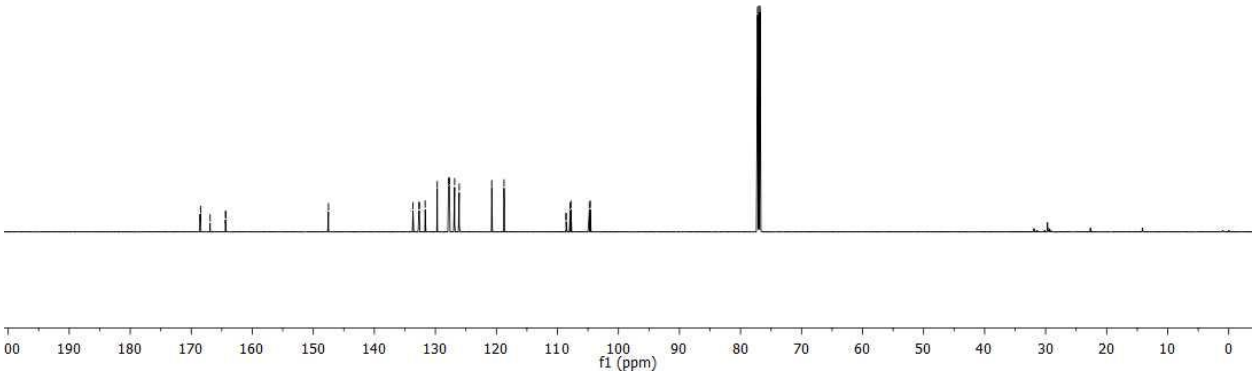


2q, Scheme 2

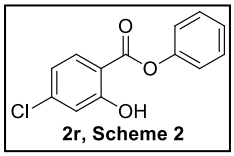


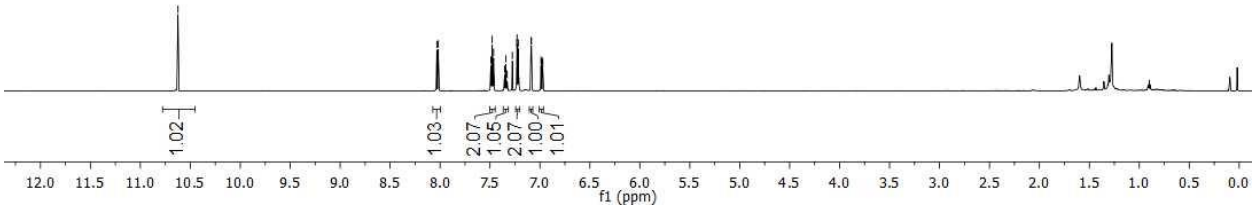


2q, Scheme 2

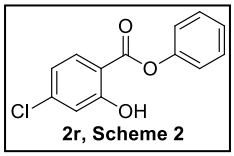


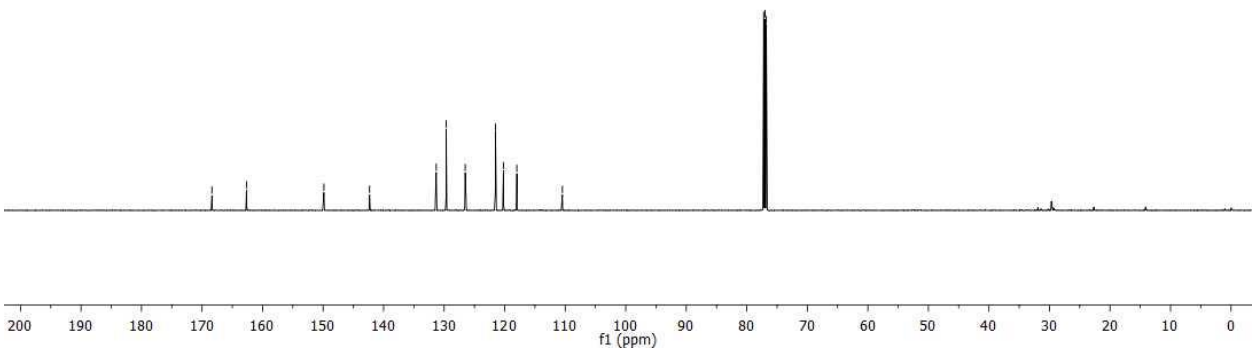

NMR DATA/AH-397 P
AH-397 1H-NMR in CDCl3
10.624
8.032
8.017
7.491
7.488
7.478
7.465
7.461
7.353
7.341
7.328
7.276
7.231
7.229
7.217
7.211
7.089
7.085
6.989
6.986
6.975
6.972

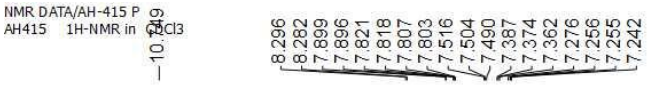

O
O
Cl
OH
2r, Scheme 2

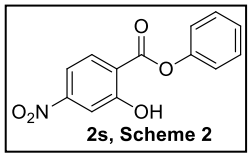

1.02
1.03
2.07
1.05
2.07
1.00
1.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

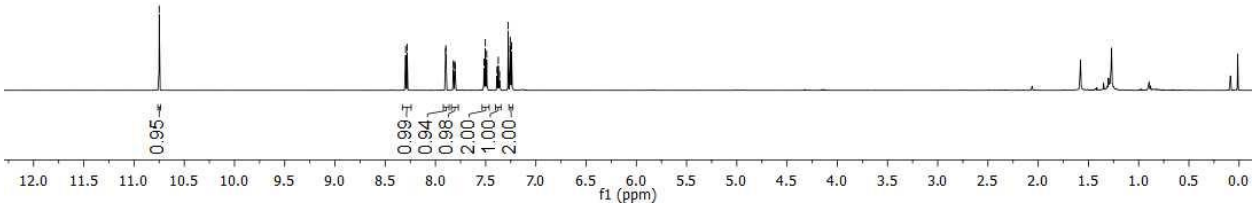

NMR DATA/AH-397 C
AH-397 13C-NMR in CDCl3
168.37
162.66
149.86
142.32
131.31
129.67
126.52
121.52
120.21
117.99
110.47
77.21
77.00
76.78

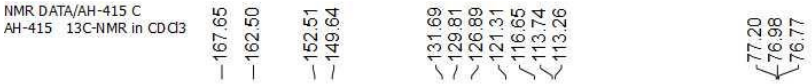

O
O
Cl
OH
2r, Scheme 2

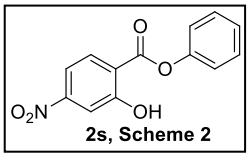

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

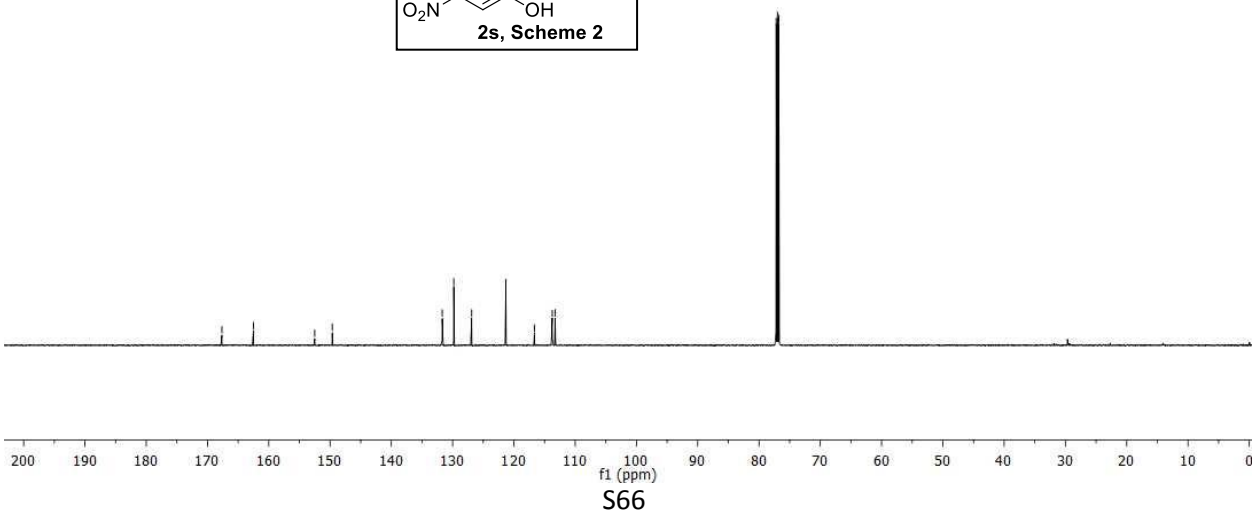

NMR DATA/AH-415 P
AH415 1H-NMR in CDCl3
10.729
8.296
8.282
7.899
7.896
7.821
7.818
7.807
7.803
7.516
7.504
7.490
7.387
7.374
7.362
7.276
7.256
7.255
7.242

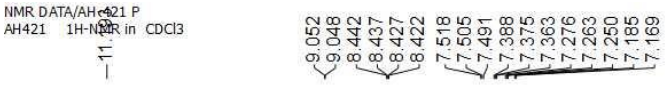

O
O
O2N
OH
2s, Scheme 2

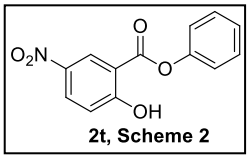

0.95
0.99
0.94
0.98
2.00
1.00
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

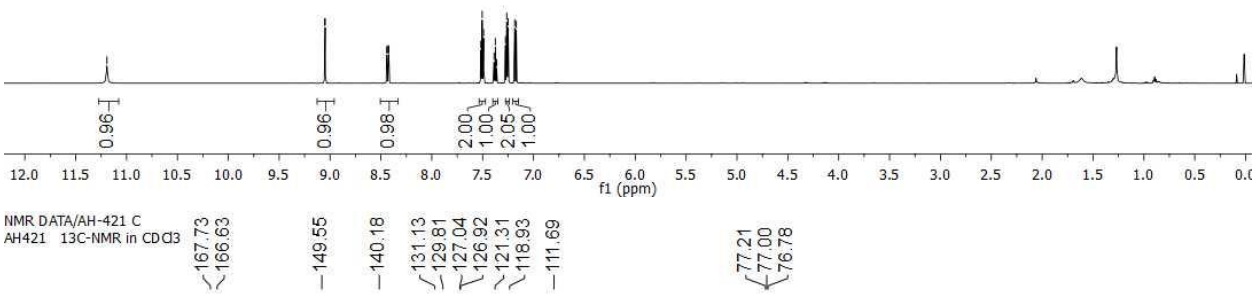

NMR DATA/AH-415 C
AH-415 13C-NMR in CDCl3
167.65
162.50
152.51
149.64
131.69
129.81
126.89
121.31
116.65
113.74
113.26
77.20
76.98
76.77


O
O
O2N
OH
2s, Scheme 2

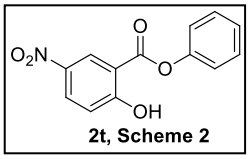

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

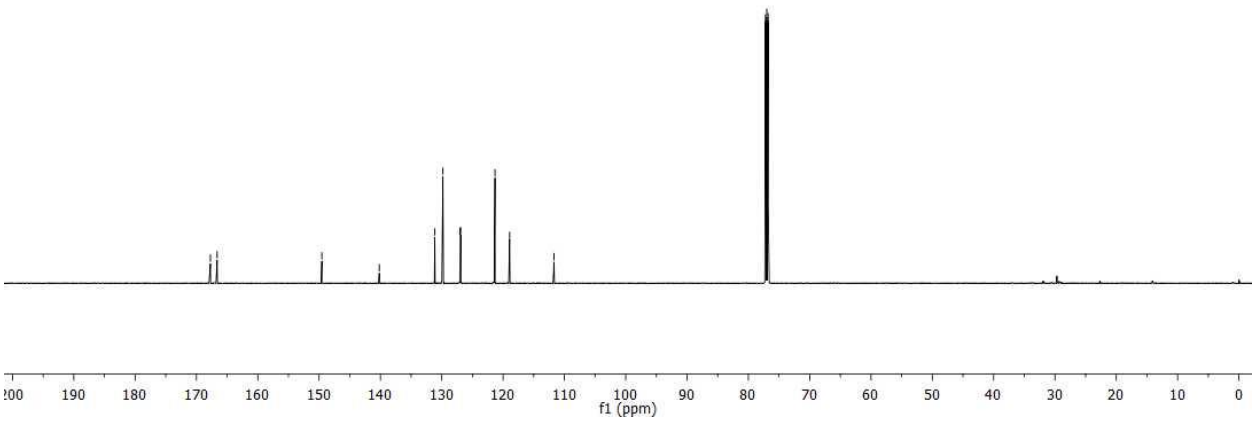

NMR DATA/AH-421 P
AH421 1H-NMR in CDCl3
11.
9.052
9.048
8.442
8.437
8.427
8.422
7.518
7.505
7.491
7.388
7.375
7.363
7.276
7.263
7.250
7.185
7.169

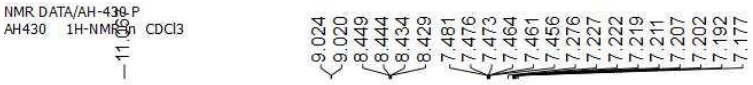

O
O2N
O
OH
2t, Scheme 2

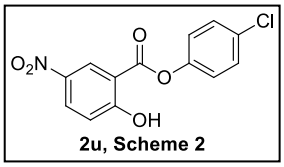

0.96
0.96
0.98
2.00
1.00
2.05
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

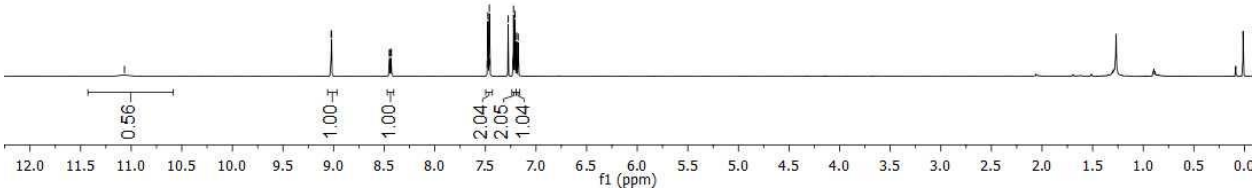
NMR DATA/AH-421 C
AH421 13C-NMR in CDCl3
167.73
166.63
149.55
140.18
131.13
129.81
127.04
126.92
121.31
118.93
111.69
77.21
77.00
76.78

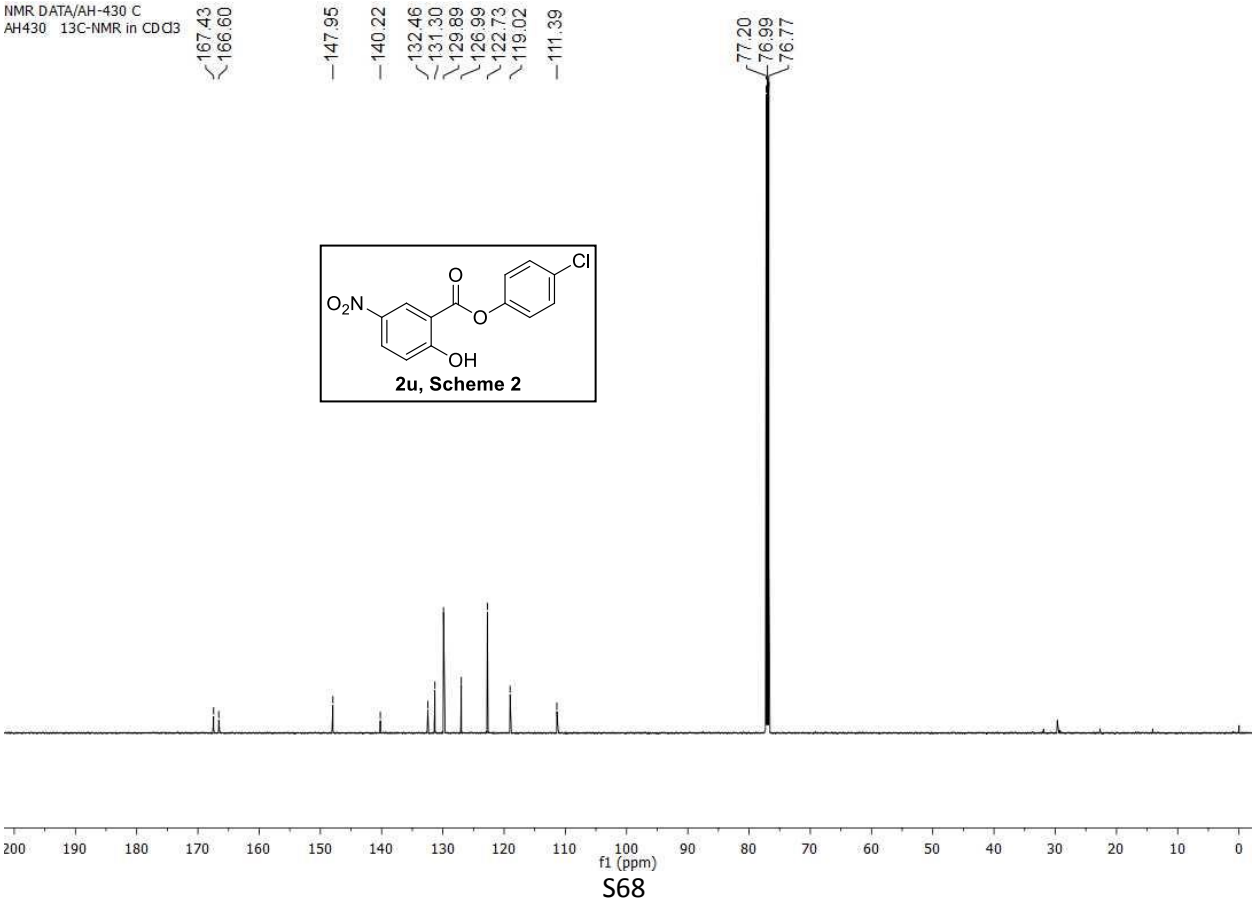

O
O2N
O
OH
2t, Scheme 2

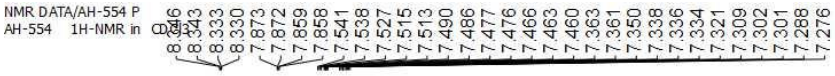

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

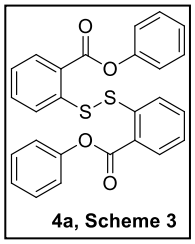

NMR DATA/AH-430 P
AH430 1H-NMR in CDCl3
11.056
9.024
9.020
8.449
8.444
8.434
8.429
7.481
7.476
7.473
7.464
7.461
7.456
7.276
7.227
7.222
7.219
7.211
7.207
7.202
7.192
7.177

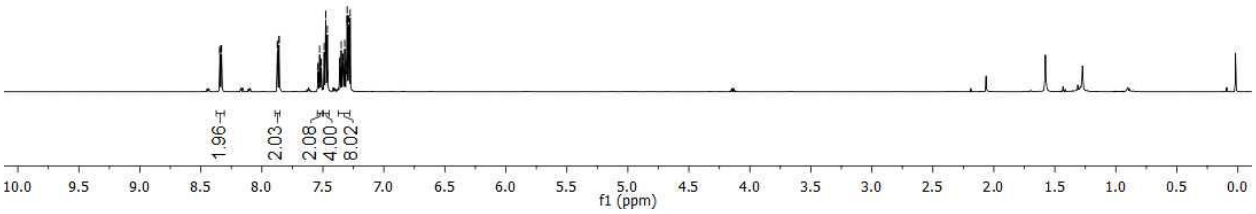

O2N
O
O
Cl
OH
2u, Scheme 2

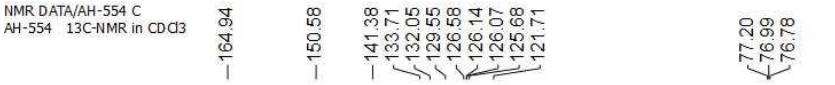

0.56
1.00
1.00
2.04
2.05
1.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

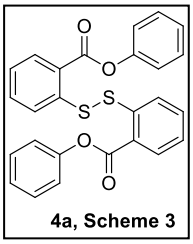

NMR DATA/AH-430 C
AH430 13C-NMR in CDCl3
167.43
166.60
147.95
140.22
132.46
131.30
129.89
126.99
122.73
119.02
111.39
77.20
76.99
76.77
O2N
O
O
Cl
OH
2u, Scheme 2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

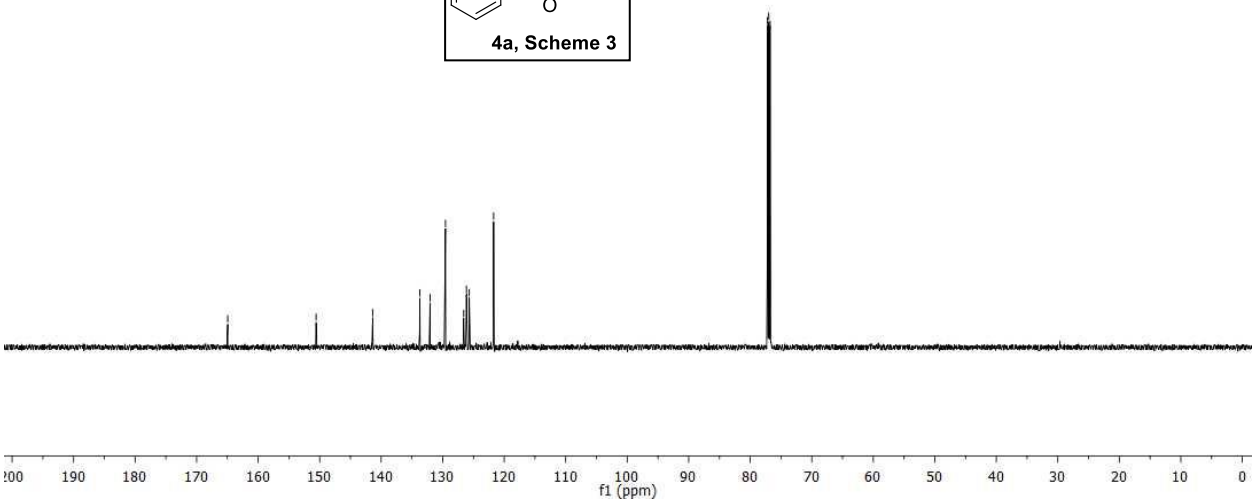

NMR DATA/AH-554 P
AH-554 1H-NMR in CDCl3
8.346
8.343
8.333
8.330
7.873
7.872
7.859
7.858
7.541
7.538
7.527
7.515
7.513
7.490
7.486
7.477
7.476
7.466
7.463
7.460
7.363
7.361
7.350
7.338
7.336
7.334
7.321
7.309
7.302
7.301
7.288
7.276

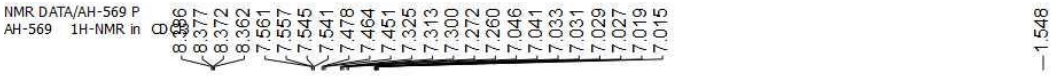

4a, Scheme 3

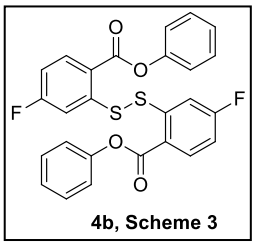

1.96
2.03
2.08
4.00
8.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

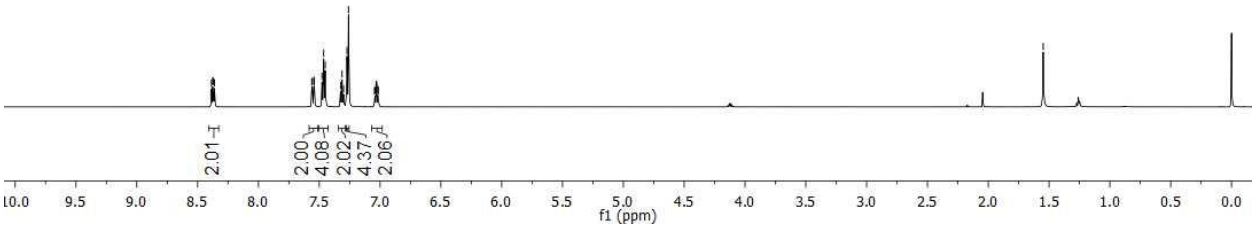

NMR DATA/AH-554 C
AH-554 13C-NMR in CDCl3
164.94
150.58
141.38
133.71
132.05
129.55
126.58
126.14
126.07
125.68
121.71
77.20
76.99
76.78

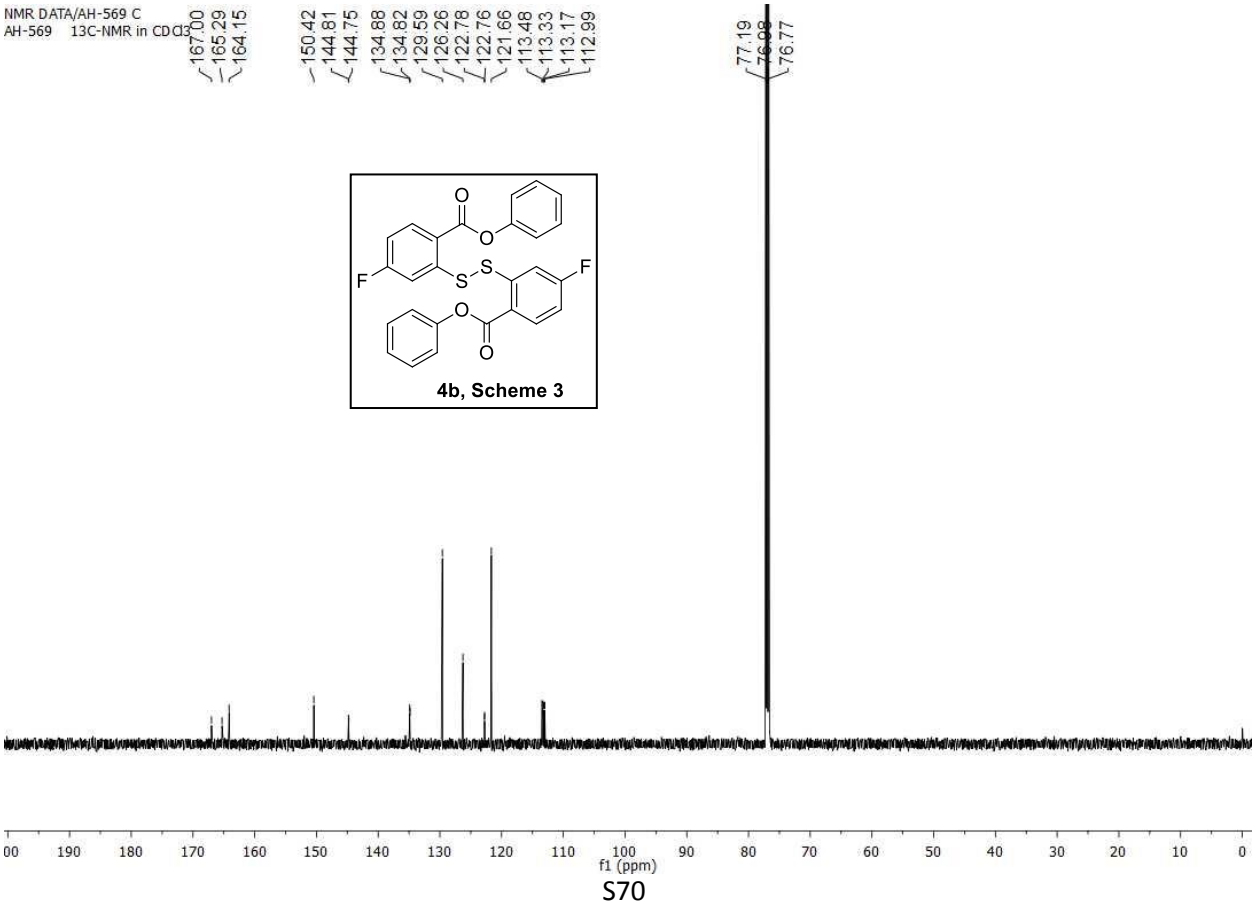

4a, Scheme 3


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NMR DATA/AH-569 P
AH-569 1H-NMR in CDCl3
8.396
8.377
8.372
8.362
7.561
7.557
7.545
7.541
7.478
7.464
7.451
7.325
7.313
7.300
7.272
7.260
7.046
7.041
7.033
7.031
7.029
7.027
7.019
7.015
1.548

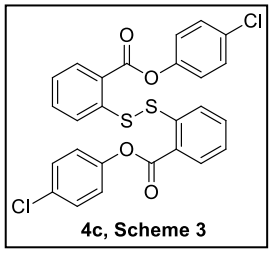

O
O
S
S
F
F
O
O
4b, Scheme 3


2.01
2.00
4.08
2.02
4.37
2.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

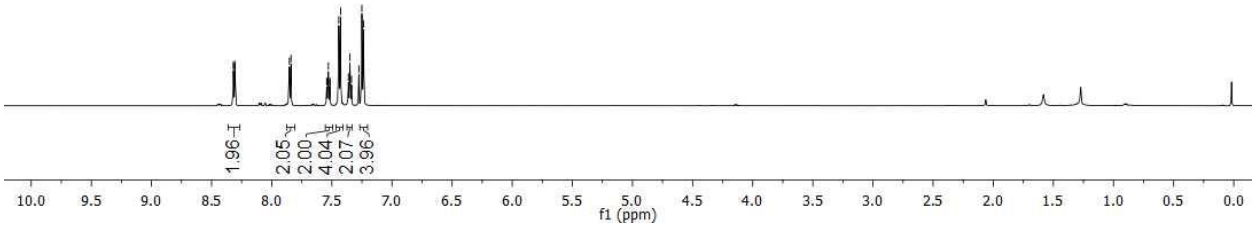

NMR DATA/AH-569 C
AH-569 13C-NMR in CDCl3
167.00
165.29
164.15
150.42
144.81
144.75
134.88
134.82
129.59
126.26
122.78
122.76
121.66
113.48
113.33
113.17
112.99
77.19
76.98
76.77
O
O
S
S
F
F
O
O
4b, Scheme 3
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

NMR DATA/AH-564 P
AH-564 1H-NMR in CDCl3

8.319
8.317
8.306
8.304
7.853
7.839
7.543
7.541
7.529
7.517
7.515
7.442
7.427
7.362
7.350
7.337
7.276
7.250
7.236

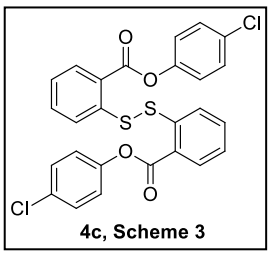


4c, Scheme 3

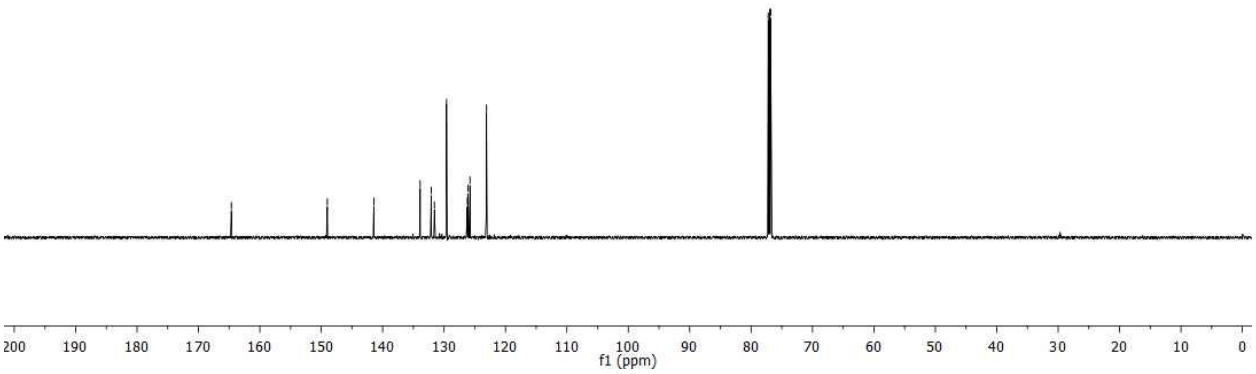


NMR DATA/AH-564 C
AH-564 13C-NMR in CDCl3

164.63
149.01
141.43
133.90
132.09
131.57
129.60
126.21
126.09
125.78
123.09
77.21
77.00
76.78

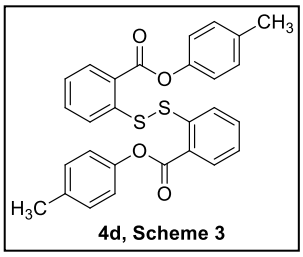


4c, Scheme 3

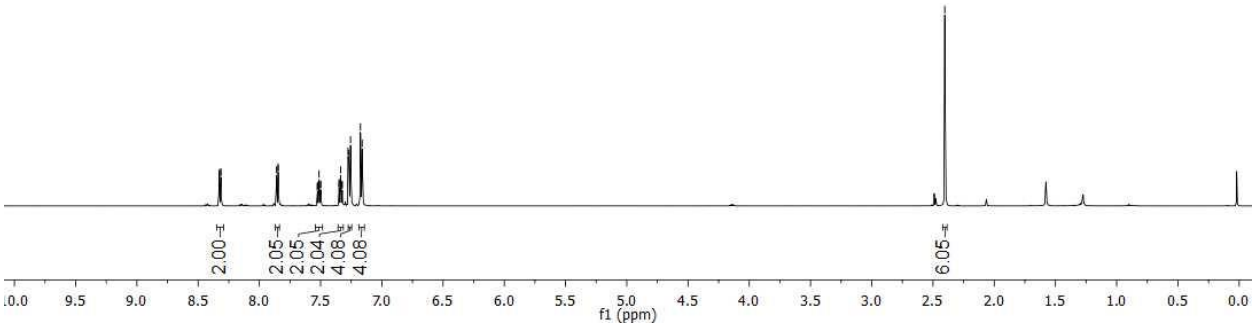


NMR DATA/AH-565 P
AH-565 1H-NMR in CDCl3

8.329
8.327
8.316
8.314
7.860
7.847
7.846
7.527
7.525
7.513
7.501
7.499
7.350
7.349
7.336
7.325
7.323
7.276
7.269
7.255
7.175
7.160
2.404

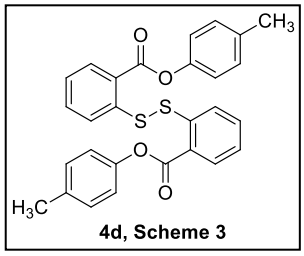


4d, Scheme 3

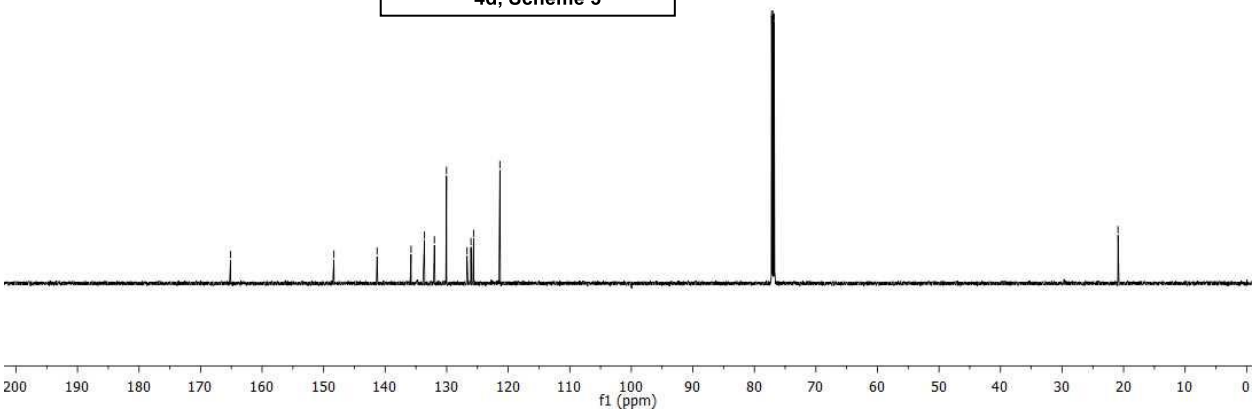


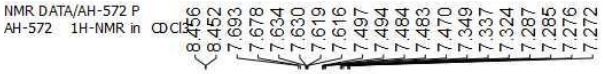
NMR DATA/AH-565 C
AH-565 13C-NMR in CDCl3

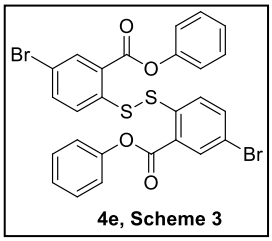
165.13
148.34
141.32
135.80
133.62
132.00
130.03
126.69
126.06
125.63
121.35
77.20
76.99
76.78
20.90



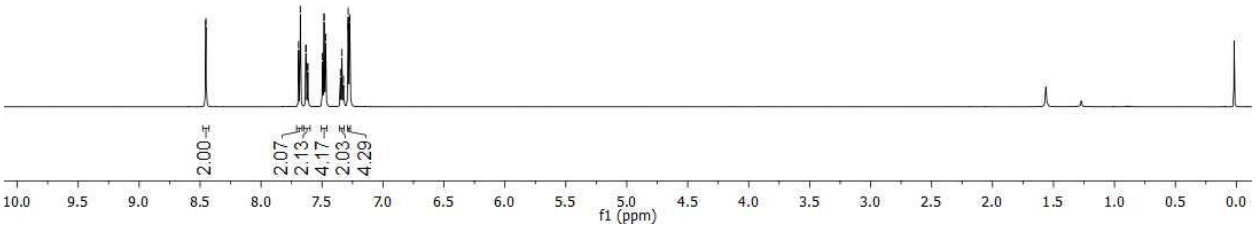
4d, Scheme 3

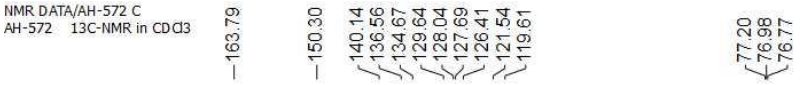


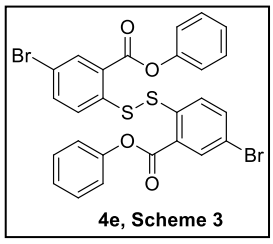




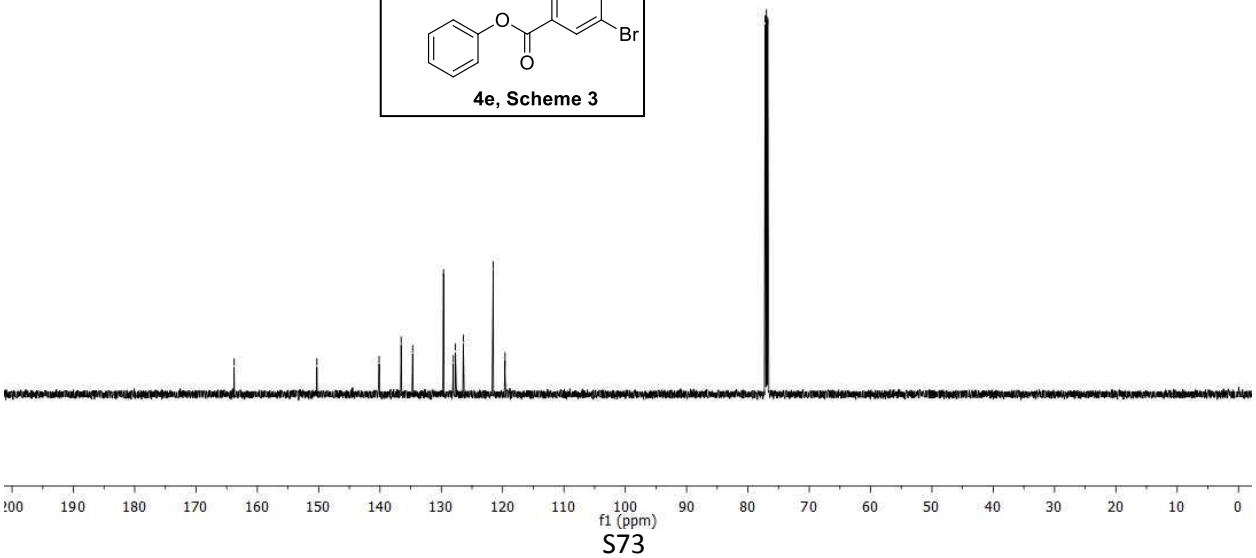
4e, Scheme 3

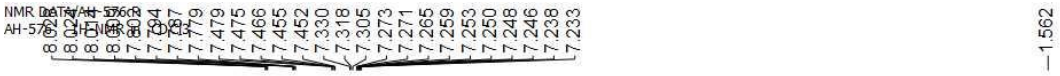


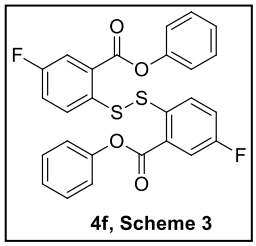




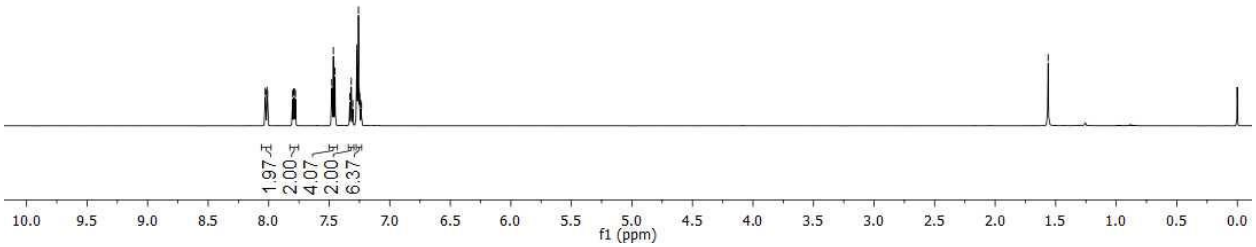
4e, Scheme 3

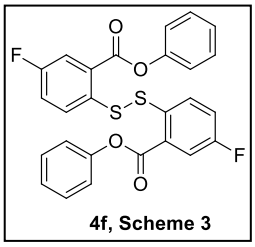




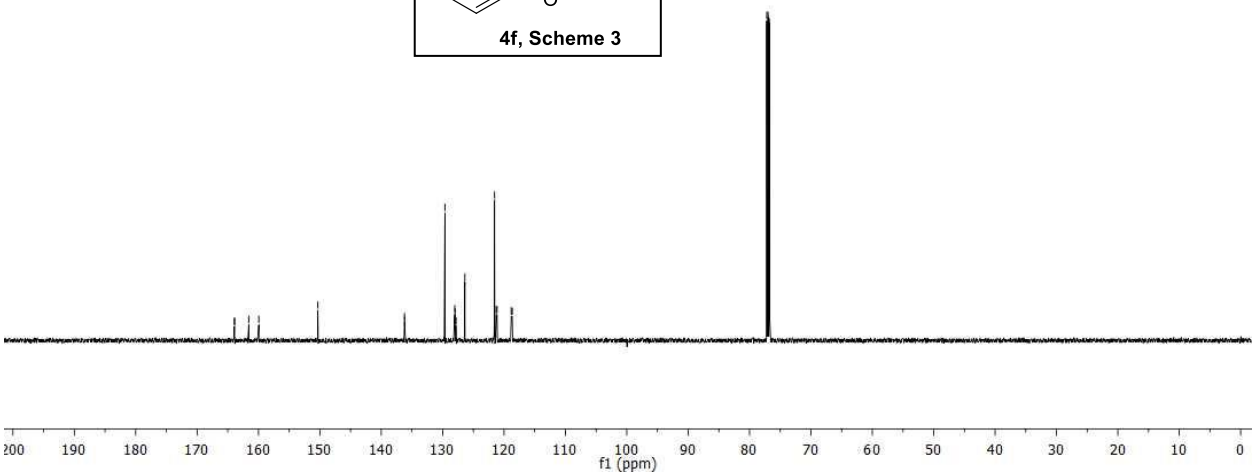


4f, Scheme 3



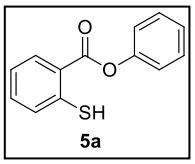


4f, Scheme 3

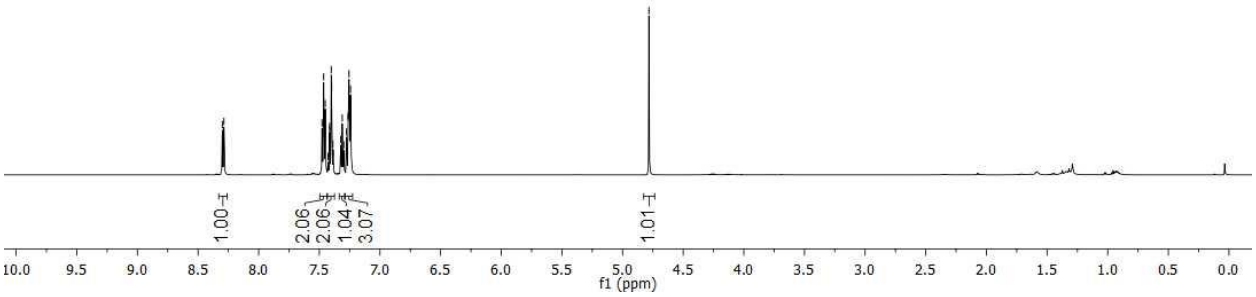


NMR DATA/AH-584 P
AH-584 1H-NMR in CDCl3

8.300
8.287
7.478
7.464
7.451
7.429
7.426
7.415
7.413
7.402
7.398
7.388
7.386
7.323
7.311
7.298
7.276
7.273
7.262
7.259
7.255
7.252
7.249
7.243
4.782

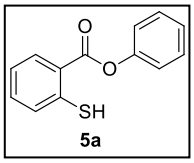


5a

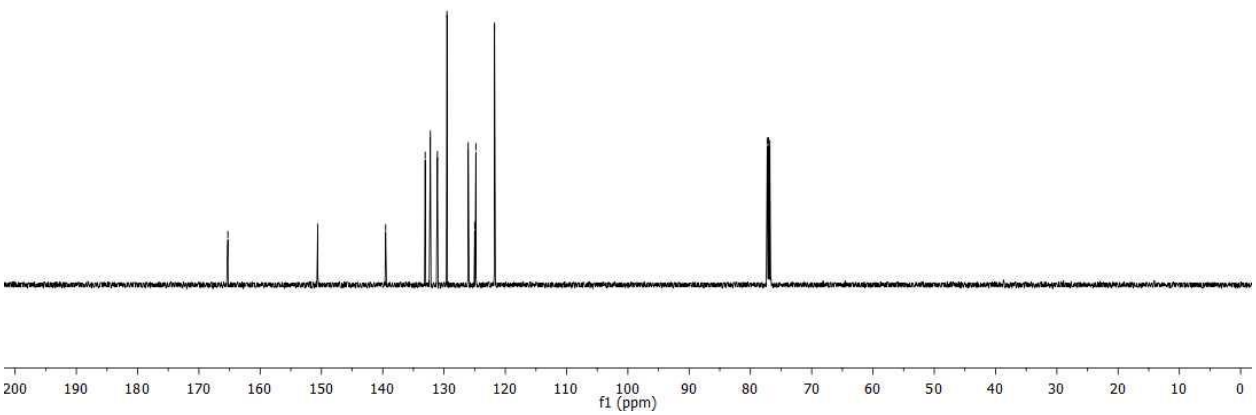


NMR DATA/AH-584 C
AH-584 13C-NMR in CDCl3

165.28
150.62
139.53
133.08
132.23
131.08
129.52
126.05
125.00
124.80
121.76
77.26
77.05
76.83



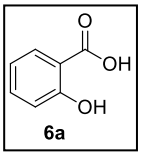
5a



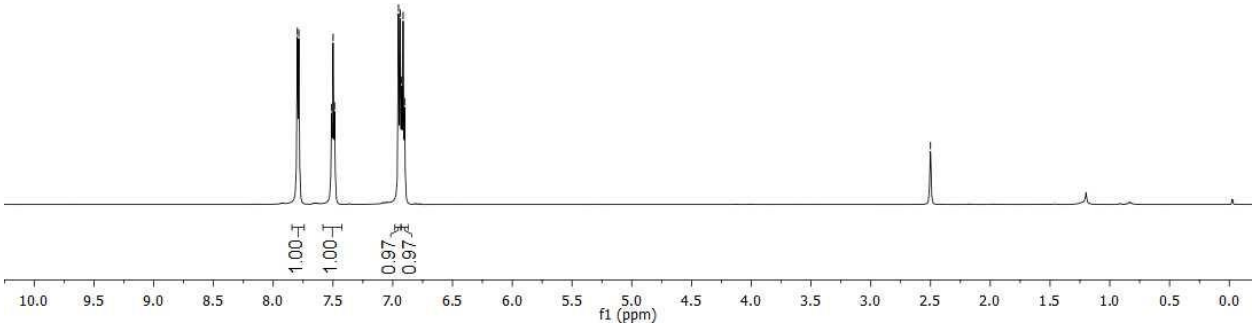
NMR DATA/AH-583 P
AH-583 1H-NMR in DMSO

7.798
7.786
7.512
7.499
7.487
6.952
6.938
6.926
6.913
6.901

2.501



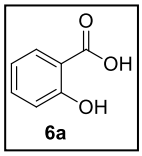
6a



NMR DATA/AH-583 C
AH-583 13C-NMR in DMSO

172.67
161.56
136.06
130.68
119.58
117.50
113.29

40.30
40.16
40.02
39.88
39.74
39.61
39.47



6a