Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Effect of *ortho*-substitution on persulfate mediated decarboxylation and functionalization of arylacetic acids

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General considerations

Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. All reactions were performed in a screw capped vial. All reaction temperatures correspond to oil bath temperatures. The proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained using 400, 500 or 600 MHz and 100, 125 or 150 MHz respectively with Me_4Si as an internalstandard and are reported in δ units. Coupling constants (*J* values) are reported in hertz (Hz). Column chromatography was performed on silica gel (60-120 or 100-200 mesh). High resolution mass spectra (HRMS) was obtained using Electron Spray Ionization (ESI) technique and as TOF mass analyzer. All melting points were taken using a melting point apparatus equipped with a calibrated thermometer. New compounds were characterized by melting point, ^{1}H NMR, ^{13}C NMR, IR and HRMS data.

I. Experimental Procedure

General procedure for the synthesis of benzofuranone (3)

In an oven-dried screw capped vial equipped with a magnetic stir bar, a solution of 2-hydroxyphenylacetic acid (**1**) (0.5 mmol), $K_2S_2O_8$ (2 equiv) and DCE (2 mL) was heated at 80 ˚C for 12 h. After complete consumption of the starting material, monitored through TLC, the reaction mixture was extracted using dichloromethane. Organic layers were collected, washed with saturated solution of $NaHCO_3$; dried over Na_2SO_4, concentrated under reduced pressure, and purified using column chromatography (100–200 mesh silica, EtOAc: hexane = 3.0: 7.0) to obtain the desired product.

General procedure for the synthesis of 2-(2-hydroxyphenyl)-*N*-phenylacetamide derivatives(5a-5k)

In an oven-dried screw capped vial equipped with a magnetic stir bar, a solution of 2-hydroxyphenylacetic acid (**1**) (0.5 mmol), substituted aniline (**4a-4k**) (1 equiv), $K_2S_2O_8$ (2 equiv) and DCE (2 mL) was heated at 80 ˚C for 12 h. After complete consumption of the starting material, monitored through TLC, the reaction mixture was extracted using dichloromethane. Organic layers were collected, washed with saturated solution of $NaHCO_3$; dried over Na_2SO_4, concentrated under reduced pressure, and purified using column chromatography (100–200 mesh silica, EtOAc: hexane = 3.0: 7.0) to obtain the desired product.

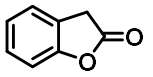
General procedure for the synthesis of 1-(2,6-dichlorophenyl)indolin-2-one (9)

In an oven-dried screw capped vial equipped with a magnetic stir bar, a solution of diclofenac (**7**) (0.5 mmol), $K_2S_2O_8$ (2 equiv) and DCE (2 mL) was heated at 80 ˚C for 12 h. After complete consumption of the starting material, monitored through TLC, the reaction mixture was extracted using dichloromethane. Organic layers were collected, washed with saturated solution of $NaHCO_3$; dried over Na_2SO_4, concentrated under reduced pressure, and purified using column chromatography (100–200 mesh silica, EtOAc: hexane = 3.0: 7.0) to obtain the desired product.

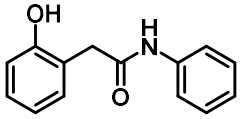
General procedure for the synthesis of isobenzofuranone (11)

In an oven-dried screw capped vial equipped with a magnetic stir bar, a solution of homophthalic acid (0.5 mmol), $K_2S_2O_8$ (2 equiv) and DCE (2 mL) was heated at 80 ˚C for 12 h. After complete consumption of the starting material, monitored through TLC, the reaction mixture was extracted using dichloromethane. Organic layers were collected, washed with saturated solution of $NaHCO_3$; dried over Na_2SO_4, concentrated under reduced pressure, and purified using column chromatography (100–200 mesh silica, EtOAc: hexane = 3.0: 7.0) to obtain the desired product.

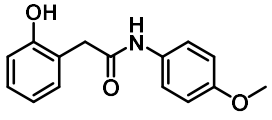
II. Characterization data of substrates:



Benzofuran-2(3*H*)-one (**3**)[1]: Pale yellow solid; yield 84% (56 mg) (for 0.5 mmol); ^{1}H NMR (500 MHz, DMSO-d_6): 7.32 (d, J = 7.3Hz, 1H), 7.27 (t,J = 7.7 Hz, 1H), 7.14-7.09 (m, 2H), 3.88 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 175.0, 154.6, 128.8, 125.3, 124.9, 124.3, 110.6, 33.1.



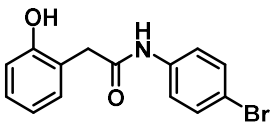
2-(2-Hydroxyphenyl)-*N*-phenylacetamide (**5a**): Off-white shiny solid; m. p. 172-173 ˚C, yield 85% (96 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, $CDCl_3$): 8.81 (s, 1H), 7.70 (bs, 1H), 7.47 (d, J = 7.6Hz, 2H), 7.34-7.26 (m, 2H), 7.19 (t,J = 7.4 Hz, 1H), 7.15-7.11 (m, 2H), 6.97 (d, J = 8.0 Hz, 1H), 6.88 (dt, J = 7.4, 1.0 Hz, 1H), 3.73 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.3, 155.6, 136.9, 130.6, 129.3, 129.0, 125.2, 121.1, 120.7, 120.3, 117.8, 41.9.HR-MS (ESI) $[M+Na]^+$: m/z calc. for $C_{14}H_{13}NNaO_2^+$ 250.0858 found 250.0853.



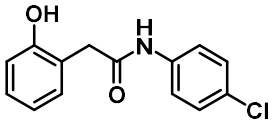
2-(2-Hydroxyphenyl)-*N*-(4-methoxyphenyl)acetamide **(5b):** Off-white shiny solid; mp: 141-142 ˚C; yield 84% (108 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 9.87 (s, 1H), 9.47 (s, 1H), 7.48 (d, J = 9.0 Hz, 2H), 7.10 (d, J = 7.3 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.83 (d,

J = 8.8 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 3.67 (s, 3H), 3.53 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 169.0, 155.3, 155.0, 132.5, 130.8, 127.6, 122.5, 120.5, 118.8, 114.9, 113.7, 55.1, 37.8.HR-MS (ESI) $[M+Na]^+$: *m*/*z* calc. for $C_{15}H_{15}NNaO_3^+$ 280.0944 found 280.0954.

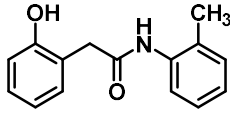
N-(4-Bromophenyl)-2-(2-hydroxyphenyl)acetamide (5c):Slight brown shiny solid; mp: 174-175 ˚C; yield 81% (123 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 10.16 (s, 1H), 9.45 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 1H), 6.75 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 3.55 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 169.6, 155.3, 138.7, 131.4, 130.9, 127.7, 122.2, 120.8, 118.7, 114.8, 114.4, 37.9.HR-MS (ESI) $[M+Na]^+$: *m*/*z* calc. for $C_{14}H_{12}BrNNaO_2^+$ 327.9944 found 327.9951.



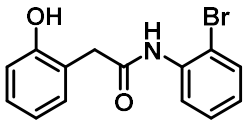
N-(4-Chlorophenyl)-2-(2-hydroxyphenyl)acetamide **(5d):** White shiny solid; mp: 144-145 ˚C; yield 79% (103 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 10.14 (s, 1H), 9.44 (s, 1H), 7.61-7.59 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.10-7.01 (m, 2H), 6.76-6.70 (m, 2H), 3.56 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 171.2, 156.9, 139.9, 132.5, 130.1, 129.3, 128.0, 123.9, 122.1, 120.3, 116.4, 39.4.HR-MS (ESI) $[M+Na]^+$: *m*/*z* calc. for $C_{14}H_{12}ClNNaO_2^+$ 284.0449 found 284.0454.



2-(2-Hydroxyphenyl)-*N*-(*o*-tolyl)acetamide **(5e):** Orangish-brown solid; mp: 153-154 ˚C; yield 84% (101 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 9.63 (s, 1H), 9.23 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.05-7.00 (m, 2H) 6.79 (d, *J* = 7.9 Hz, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 3.58 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 169.3, 155.1, 136.3, 130.8, 130.7, 130.1, 127.6, 125.8, 124.7, 124.2, 122.4, 118.8, 114.8, 37.7, 17.5. HR-MS (ESI) $[M+Na]^+$: *m*/*z* calc. for $C_{15}H_{15}NNaO_2^+$ 264.0995 found 264.1005.

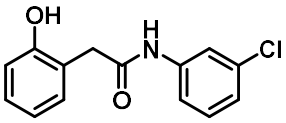


N-(2-Bromophenyl)-2-(2-hydroxyphenyl)acetamide **(5f):**Black viscous liquid; yield 71% (108 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 9.75 (s, 1H), 9.17 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.58 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.31 (dt, *J* = 8.4, 1.3 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.07-7.02 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.74 (dt, *J* = 7.3, 0.9 Hz, 1H), 3.61

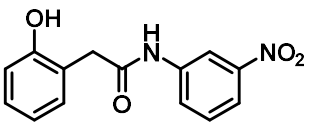


(s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 170.0, 155.6, 136.6, 132.9, 131.3, 128.6, 128.5, 126.5, 125.1, 122.2, 119.5, 115.4, 38.5.HR-MS (ESI) $[M+Na]^+$: *m*/*z* calc. for $C_{14}H_{12}BrNNaO_2^+$ 327.9944 found 327.9949.

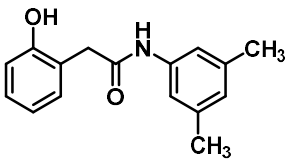
N-(3-Chlorophenyl)-2-(2-hydroxyphenyl)acetamide **(5g):** Black viscous liquid; yield 75% (98 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 10.21 (s, 1H), 9.45 (s, 1H), 7.79 (s, 1H), 7.42-7.41 (m, 1H), 7.28 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.05-7.01 (m, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 6.70 (dt, *J* = 7.3, 0.8 Hz, 1H), 3.55 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 171.4, 156.8, 142.4, 134.6, 132.5, 131.9, 129.3, 124.2, 123.7, 120.3, 119.9, 118.8, 116.3, 39.4.HR-MS (ESI) $[M+Na]^+$: *m*/*z* calc. for $C_{14}H_{12}ClNNaO_2^+$ 284.0449 found 284.0451.



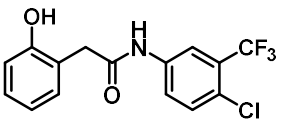
2-(2-Hydroxyphenyl)-*N*-(3-nitrophenyl)acetamide **(5h):**Yellowish-brown shiny solid; mp: 178-180 ˚C; yield 81% (110 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 10.53 (s, 1H), 9.47 (s, 1H), 8.62 (s, 1H), 7.89-7.88 (m, 1H), 7.86-7.84 (m, 1H), 7.56 (dt, *J* = 8.2, 0.7 Hz, 1H), 7.10 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.04 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.76 (dd, *J* = 7.9, 0.7 Hz, 1H), 6.71 (dt, *J* = 7.3, 0.6 Hz, 1H), 3.60 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 170.2, 155.3, 147.9, 140.4, 131.0, 130.1, 127.8, 124.9, 122.0, 118.7, 117.5, 114.7, 113.0, 37.9.HR-MS (ESI) $[M+Na]^+$: *m*/*z* calc. for $C_{14}H_{12}N_2NaO_4^+$ 295.0689 found 295.0698.



N-(3,5-Dimethylphenyl)-2-(2-hydroxyphenyl)acetamide **(5i):**Dark yellow viscous liquid; yield 87% (111 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 9.86 (s, 1H), 9.48 (s, 1H), 7.22 (s, 2H), 7.11 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.05 (dt, *J* = 7.6, 1.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.66 (s, 1H), 3.56 (s, 2H), 2.21 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 170.9, 156.7, 140.6, 139.0, 132.2, 129.1, 126.0, 124.0, 120.2, 118.3, 116.3, 39.4, 22.5. HR-MS (ESI) $[M+Na]^+$: *m*/*z* calc. for $C_{16}H_{17}NNaO_2^+$ 278.1151 found 278.1156.

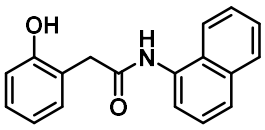


N-(4-chloro-3-(trifluoromethyl)phenyl)-2-(2-hydroxyphenyl)acetamide **(5j):** White solid; mp: 176-177 ˚C; yield 81% (133 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 10.45 (s, 1H), 9.44 (s, 1H), 8.19 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.76 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 3.58 (s, 2H); ^{13}C



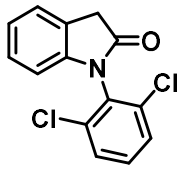
NMR (150 MHz, DMSO-d_6): δ 171.8, 156.9, 140.4, 133.6, 132.6, 129.4, 125.2, 125.1, 123.5, 120.3, 119.15, 119.11, 116.3, 39.4. HR-MS (ESI) $[M+Na]^+$: *m/z* calc. for $C_{15}H_{11}ClF_3NNaO_2^+$ 352.0323 found 352.0327.

2-(2-hydroxyphenyl)-*N*-(naphthalene-1-yl)acetamide **(5k):**White solid; mp: 130-131 ˚C; yield

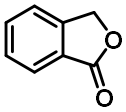


79% (109 mg) (for 0.5 mmol); ^{1}H NMR (600 MHz, DMSO-d_6): 9.94 (s, 1H), 9.62 (s, 1H), 8.06-8.05 (m, 1H), 7.90-7.89 (m, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.51-7.49 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.05 (dt, *J* = 7.9, 1.3 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 3.73 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 171.8, 157.0, 135.3, 132.6, 129.7, 129.3, 127.5, 127.4, 127.1, 126.7, 124.3, 124.2, 122.9, 120.5, 116.6, 39.5. HR-MS (ESI) $[M+Na]^+$: *m/z* calc. for $C_{18}H_{15}NNaO_2^+$ 300.0995 found 300.1002.

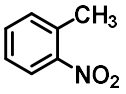
1-(2,6-dichlorophenyl)indolin-2-one **(9):** Dark yellow viscous liquid; yield 68% (94 mg) (for



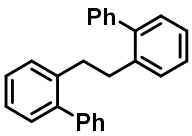
0.5 mmol); ^{1}H NMR (500 MHz, DMSO-d_6): 7.71 (d, *J* = 8.0Hz, 2H), 7.59-7.56 (m, 1H), 7.34 (dd, *J* = 7.3, 0.5 Hz, 1H), 7.17 (t, *J* = 6.5 Hz, 1H), 7.05 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 3.85 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 173.7, 143.3, 134.9, 132.4, 130.4, 129.9, 128.3, 125.5, 125.1, 123.3, 109.0, 35.6.HR-MS (ESI) $[M+Na]^+$: *m/z* calc. for $C_{14}H_9Cl_2NNaO^+$ 299.9953 found 299.9958.



Isobenzofuran-1(3*H*)-one (**11**)[2]: white solid; yield 95% (64 mg) (for 0.5 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96-7.95 (m, 1H), 7.71-7.69 (m, 1H), 7.58-7.52 (m, 2H), 5.35 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 146.5, 134.0, 129.0, 125.8, 125.7, 122.1, 69.6.



2-Nitrotoluene (**15**)[1]Colorless liquid; yield 21% (16 mg) (for 0.5 mmol);^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.7 Hz, 1H), 7.49 (t,*J* =7.5 Hz, 1H), 7.34-7.31 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 133.6, 133.0, 132.8, 126.9, 124.7, 20.5.

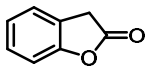


1,2-Di([1,1'-biphenyl]-2-yl)ethane(**20**)[3]: white solid; yield 45% (75 mg) (for 0.5 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 6H), 7.21-7.15 (m, 10H), 6.99 (s, 2H), 2.74 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 141.7, 139.1, 129.9, 129.2, 129.1, 128.0, 127.3, 126.7, 125.7, 34.8.

III.References

1. The data matches with that of the commercial sample obtained from Sigma Aldrich.
2. A. Cowell andJ. K. Stille, *J. Am. Chem. Soc*. 1980, **102**, 4193.
3. J. K. Laha, U.Gulati, Saima;T. Schulte and M. Breugst, *J. Org. Chem.* 2022, **87**, 6638.

^{1}H NMR (500 MHz, DMSO-d_6)



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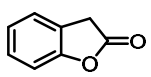
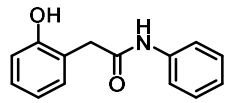
^{13}C NMR (125 MHz, DMSO-d_6)



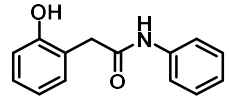
3

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



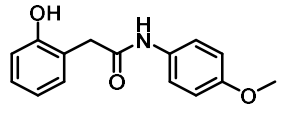
5a

^{13}C NMR (150 MHz, $CDCl_3$)



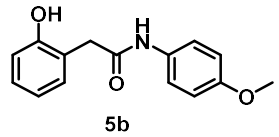
5a

^{1}H NMR (600 MHz, DMSO-d_6)



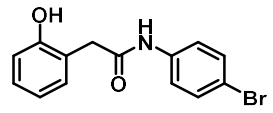
5b

^{13}C NMR (150 MHz, DMSO-d_6)



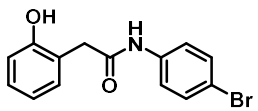
5b

^{1}H NMR (600 MHz, DMSO-d_6)



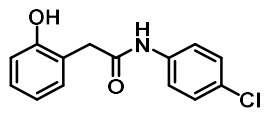
5c

^{13}C NMR (150 MHz, DMSO-d_6)



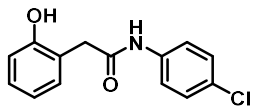
5c

^{1}H NMR (600 MHz, DMSO-d_6)



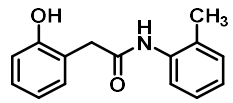
5d

^{13}C NMR (150 MHz, DMSO-d_6)



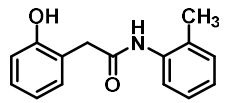
5d

^{1}H NMR (600 MHz, DMSO-d_6)



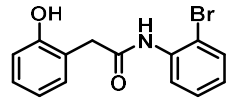
5e

^{13}C NMR (150 MHz, DMSO-d_6)



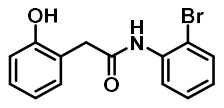
5e

^{1}H NMR (600 MHz, DMSO-d_6)



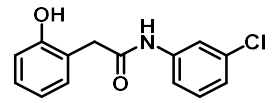
5f

^{13}C NMR (150 MHz, DMSO-d_6)



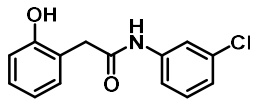
5f

^{1}H NMR (600 MHz, DMSO-d_6)



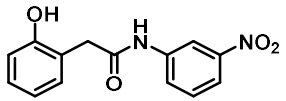
5g

^{13}C NMR (150 MHz, DMSO-d_6)



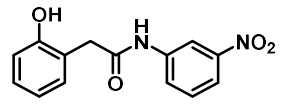
5g

^{1}H NMR (600 MHz, DMSO-d_6)



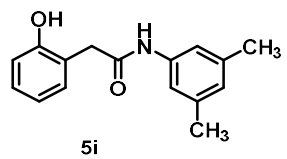
5h

^{13}C NMR (150 MHz, DMSO-d_6)



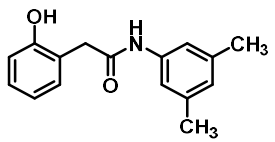
5h

^{1}H NMR (600 MHz, DMSO-d_6)



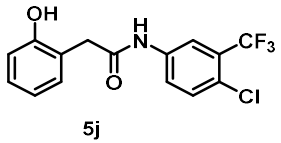
5i

^{13}C NMR (150 MHz, DMSO-d_6)



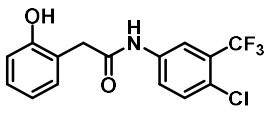
5i

^{1}H NMR (600 MHz, DMSO-d_6)



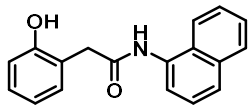
5j

^{13}C NMR (150 MHz, DMSO-d_6)

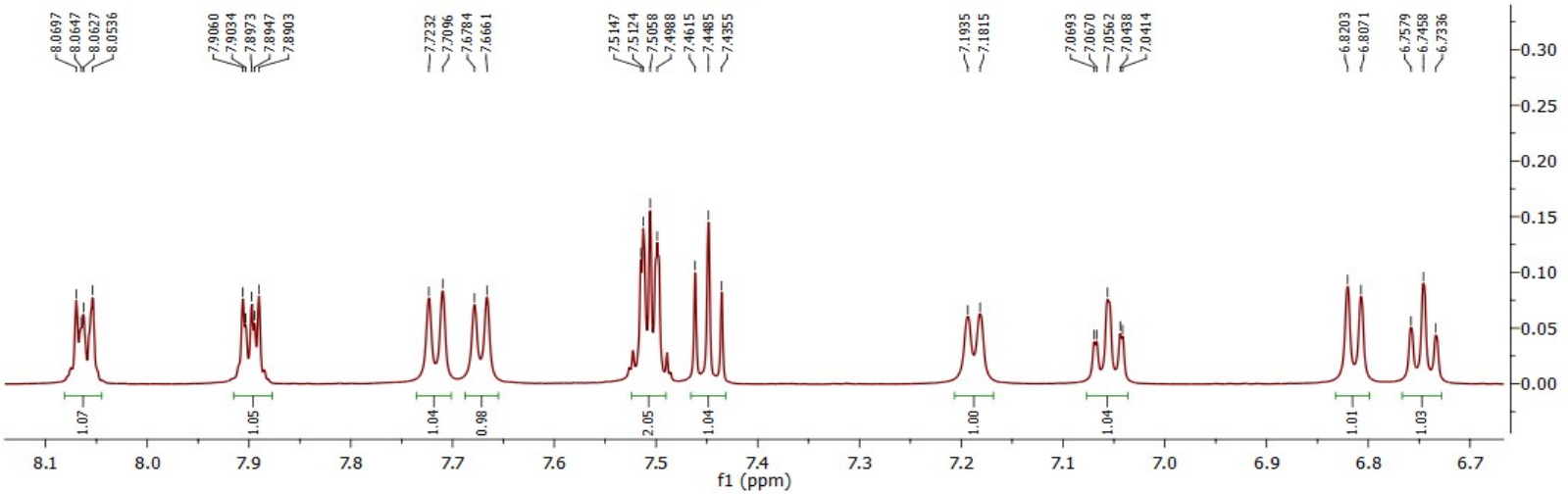


5j

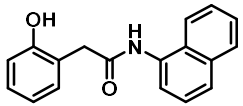
^{1}H NMR (600 MHz, DMSO-d_6)



5k

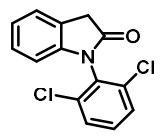


^{13}C NMR (150 MHz, DMSO-d_6)



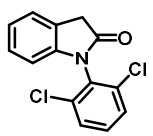
5k

^{1}H NMR (500 MHz, DMSO-d_6)



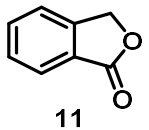
9

^{13}C NMR (125 MHz, DMSO-d_6)



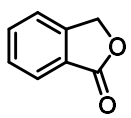
9

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



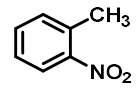
11

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



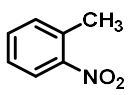
11

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



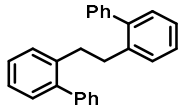
15

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



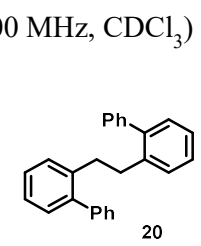
15

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



20

^{13}C NMR (100 MHz, $CDCl_3$)



20