Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Bioinspired Cyclization of in Situ Generated γ-Indolyl β,γ-Unsaturated α-Keto Esters via Oxidative Enamine Process: Facile Approaches to Pyrano[2,3-b]indoles

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I. General Experiment Information and Materials

All commercial reagents were used without further purification unless otherwise noted. Solvents were freshly dried according to *the purification handbook Purification of Laboratory Chemicals* before using. All of 4-alkoxy-substituted 3-(1H-indol-3-yl)-1,3-diphenylpropan-1-one **11**[1] and 4-(1H-indol-3-yl)-1,4-diphenyl butan-1,2-dione **14**[2] were prepared according to literature procedure. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker Avance 400 and 500MHz spectrometer. Tetramethylsilane (TMS) served as the internal standard for ^{1}H NMR, and $CDCl_3$ served as the internal standard for ^{13}C NMR. ^{1}H NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. Infrared Spectroscopy was conducted on Thermo Fisher Nicolet is10. The X-ray single-crystal diffraction was performed on Saturn 724+ instrument. High resolution mass spectra were obtained on an Ultima Global spectrometer with an ESI source.

II. Initial Exploration

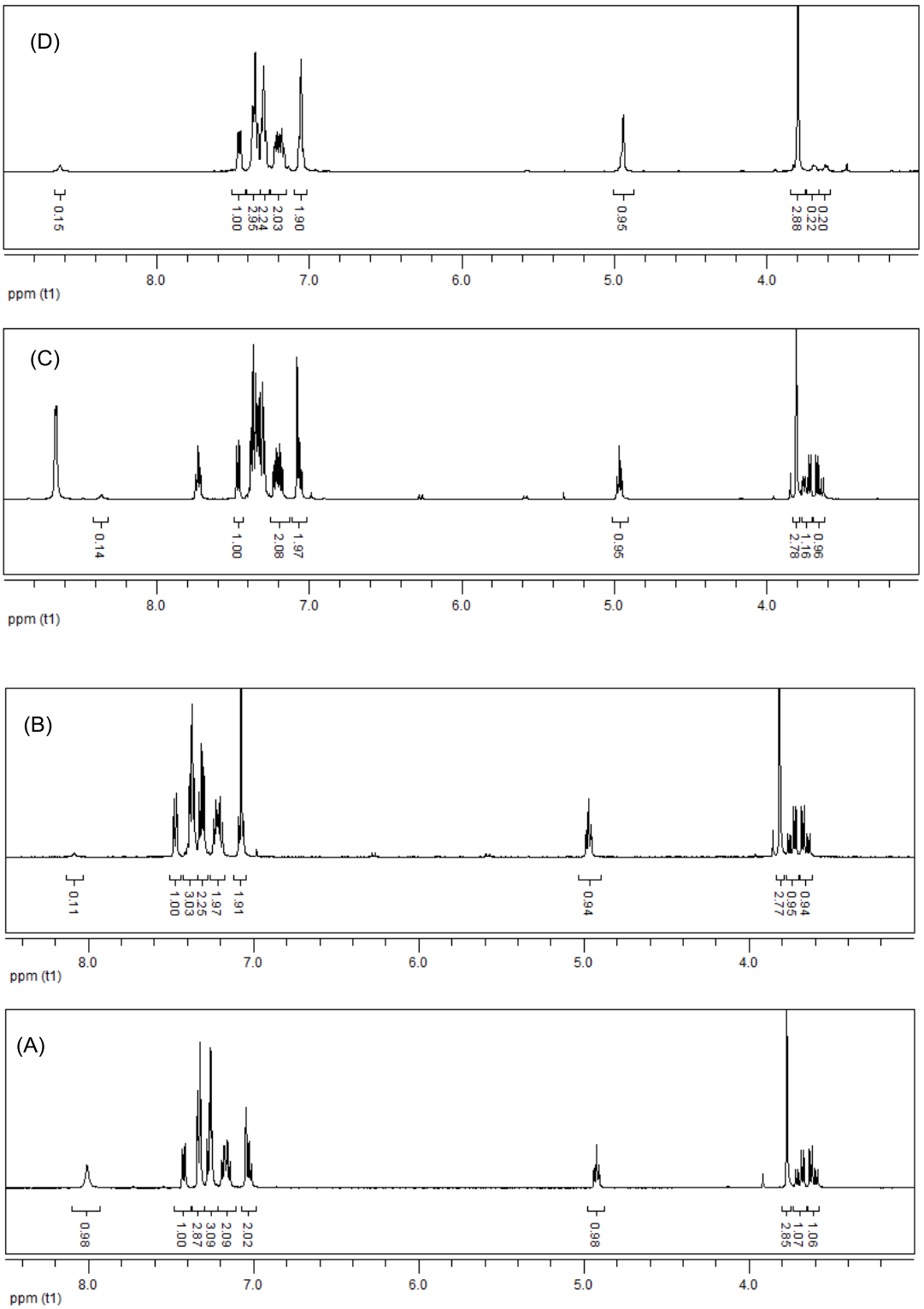
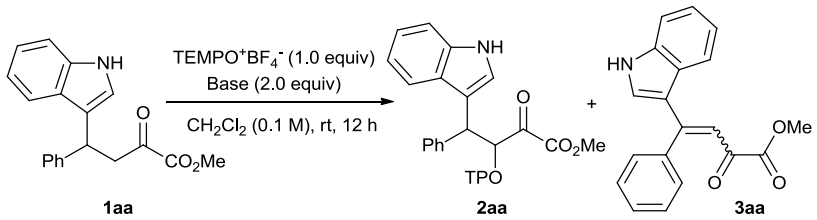


Figure S1. Deuterium-labelling Experiments in $CDCl_3$ (1.0 mL). (A) **1a** (0.1 mmol); (B) **1a** (0.1 mmol) and D_2O (10 equiv); (C) pyridine (0.1 mmol), **1a** (0.1 mmol) and D_2O (10 equiv); (D) DABCO (0.1 mmol), **1a** (0.1 mmol) and D_2O (10 equiv).

Regioselective oxidative test of γ-indolyl α-keto ester 1aa with $TEMPO^+BF_4^-$

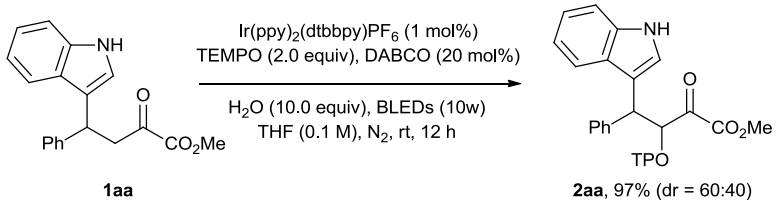


1aa **2aa** **3aa**

A) **Pyridine as a base**: To a solution of corresponding α-keto ester **1aa** (0.1 mmol) and pyridine (0.1 mmol) in DCM (1.0 mL), was added $TEMPO^+BF_4^-$ (0.1 mmol). After the mixture were stirred for 12 h, the mixture was diluted with DCM and washed with saturated sodium carbonate aqueous solution and saturated sodium chloride aqueous solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. The solution was stirred at room temperature. Purification of mixture by column chromatography on silica gel (DCM/EA = 30:1, v/v) gave the desired product **3aa** (28.1 mg, 92% yield).

B) DABCO as a base: To a solution of corresponding α-keto ester **1aa** (0.1 mmol) and DABCO (0.1 mmol) in DCM (1.0 mL), was added $TEMPO^+BF_4^-$ (0.1 mmol). After the mixture were stirred for 12 h, the mixture was diluted with DCM and washed with saturated sodium carbonate aqueous solution and saturated sodium chloride aqueous solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. The solution was stirred at room temperature. Purification of mixture by column chromatography on silica gel (DCM/EA = 30:1, v/v) gave the product **2aa** (10.2 mg, 22% yield) and **3aa** (6.1 mg, 20% yield), respectively.

Photocatalytic oxidative coupling reaction of γ-indolyl α-keto ester 1a with TEMPO



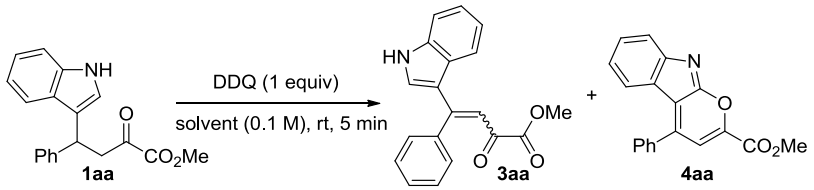
1aa **2aa**, 97% (dr = 60:40)

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **1aa** (0.1 mmol), TEMPO (0.2 mmol), DABCO (20 mol%) and $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (1.0 mL) and H_2O (18 μL, 10.0 equiv) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10w) for 12h at room temperature. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 8:1, v/v) gave the desired product *cis*-**2aa** (26.9 mg, 58%) and *trans*-**2aa** (18.0 mg, 39% yield). *cis*-**2aa**: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (br, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.19 – 7.11 (m, 3H), 6.91 (s, 1H), 6.07 (d, *J* = 10.0 Hz, 1H), 4.96 (d, *J* = 9.5 Hz, 1H), 3.57 (s, 3H), 1.43 – 1.19 (m, 6H), 1.12 (s, 3H), 1.01 (s, 3H), 0.95 (s, 3H), 0.45 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.3, 161.4, 140.0, 136.0, 129.0, 128.5, 127.9, 126.7, 123.4, 122.0, 119.9, 119.5, 116.6, 110.9, 84.3, 61.1, 59.9, 52.6, 43.6, 40.5, 40.2, 34.2, 33.7, 20.5, 20.0, 17.0 ppm; IR(KBr, cm^{-1}): 3409, 2941, 1741, 1618, 1543, 1282, 1256, 1133, 1069, 784, 745, 705, 632; HRMS (ESI) calcd for $C_{28}H_{34}N_2NaO_4^+$ $(M+Na)^+$ 485.2411, found 485.2423. *trans*-**2aa**: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (br, 1H), 7.38 (d, *J* = 8.0 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.22 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.0 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.87 (d, *J* = 10.5 Hz, 1H), 4.96 (d, *J* = 9.5 Hz, 1H), 3.60 (s, 3H), 1.47 – 1.20 (m, 6H), 1.07 (s, 6H), 0.94 (s, 3H), 0.63 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.3, 161.6, 140.7, 136.1, 129.5, 128.0, 127.0, 126.7, 122.8, 122.3, 119.5, 113.9, 111.0, 83.4, 61.2, 60.6, 52.6, 44.1, 40.6, 40.2, 34.0, 33.7, 20.7, 20.4, 20.0, 17.0

ppm; IR(KBr, cm^{-1}): 3415, 2931, 1730, 1619, 1454, 1378, 1281, 1223, 1033, 909, 735, 699; HRMS (ESI) calcd for $C_{28}H_{35}N_2O_4^+$ $(M+H)^+$ 463.2591, found 463.2587.

III. Optimization

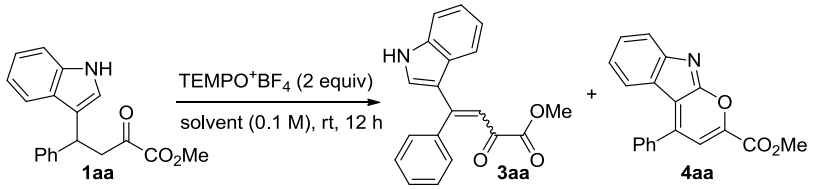
Table S1. Screening of Different Solvents in Oxidative Dehydrogenation of *α*-keto ester **1**[a]



entry	solvent	yield (**3aa**, %)[b]	*E*/*Z*[c]	yield (**4aa**, %)
1	**CH_2Cl_2 (DCM)**	**94**	**75:25**	**–**
2	1,2-$C_2H_4Cl_2$ (DCE)	93	75:25	–
3	Toluene	86	75:25	–
4	MeCN	74	75:25	–
5	THF	63	75:25	–
6	EtOH	76	4:1	–

[a] Reaction Conditions: **1aa** (0.1 mmol), DDQ (0.1 mmol), were added to solvent (1.0 mL) at room temperature for 5 h. [b] Isolated yield. [c] Determined by ^{1}H NMR.

Table S2. Screening of Different Solvents in Oxidative Intramolecular Cyclization of α-keto ester **1aa**[a]

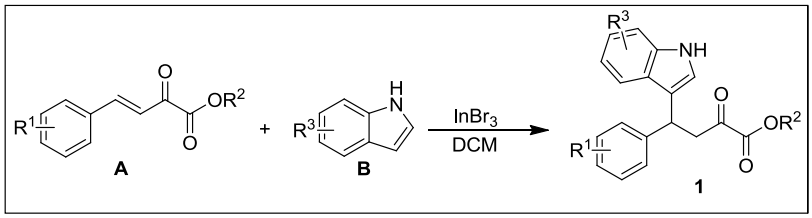


entry	solvent	yield (**3aa**, %)[b]	*E*/*Z*[c]	yield (**4aa**, %)[b]
1	CH_2Cl_2 (DCM)	7	68:32	75
2	1,2-$C_2H_4Cl_2$ (DCE)	14	68:32	57
3	toluene	27	68:32	23
4	MeCN	12	75:25	42
5	THF	34	68:32	trace
6	acetone	41	68:32	trace
7[d]	**DCM**	**–**	**–**	**78**

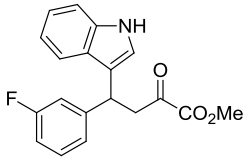
[a] Reaction Conditions: **1aa** (0.1 mmol), $TEMPO^+BF_4^-$ (0.2 mmol), were added to solvent (1.0 mL) at room temperature for 12 h. [b] Isolated yield. [c] Determined by ^1H NMR. [d] DDQ (0.1 mmol) and $TEMPO^+BF_4^-$ (0.15 mmol) at room temperature for 40 min.

IV. Experimental Procedures and Characterization Data

A) Synthesis of γ-indolyl α-keto ester 1:

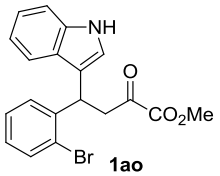


General procedure I: *β*,*γ*-unsaturated *α*-ketoester derivatives **A** (4 mmol) and indole derivatives **B** (4.8 mmol) were dissolved in 40 mL DCM, then $InBr_3$ (5mol%, 0.2 mmol) was added. The solution was stirred at room temperature for 2 hours. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1 to 3:1, v/v) gave the desired products **1**.



1al

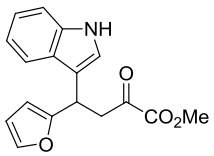
1al: Prepared according to the general procedure I above and obtained as light yellow solid (1.04g, 80%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.18 – 7.12 (m, 2H), 7.05 – 6.99 (m, 3H), 6.88 – 6.85 (m, 1H), 4.91 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H), 3.67 (dd, *J* = 7.0, 17.5 Hz, 1H), 3.58 (dd, *J* = 8.0, 17.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.2, 163.0 (d, *J* = 244.3 Hz), 161.2, 146.0 (d, *J* = 3.4 Hz), 136.6, 130.0 (d, *J* = 7.8 Hz), 126.3, 123.5, 122.5, 121.5, 119.7, 119.3, 117.7, 114.7 (d, *J* = 7.8 Hz), 113.6 (d, *J* = 21.1 Hz), 111.3, 53.0, 45.4, 37.4 ppm.



1ao

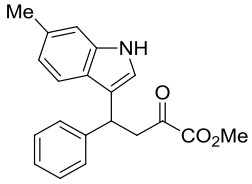
1ao: Prepared according to the general procedure I above and obtained as light yellow solid (1.09g, 71%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500

MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.10 (m, 3H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.98 (s, 1H), 5.41 (t, *J* = 7.5 Hz, 1H), 3.77 (s, 3H), 3.70 (dd, *J* = 9.0, 17.0 Hz, 1H), 3.42 (dd, *J* = 6.0, 17.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.2, 161.3, 142.2, 136.6, 133.1, 129.2, 128.3, 127.8, 126.5, 124.2, 122.4, 122.2, 120.0, 119.5, 116.9, 111.3, 53.1, 44.8, 37.0 ppm.



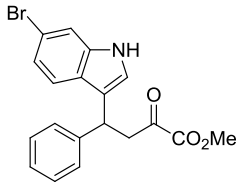
1ar

1ar: Prepared according to the general procedure I above and obtained as light red solid (0.70g, 59%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.10 – 7.07 (m, 2H), 6.26 – 6.25 (m, 1H), 6.05 (d, *J* = 3.0 Hz, 1H), 4.98 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H), 3.71 (dd, *J* = 7.5, 17.5 Hz, 1H), 3.59 (dd, *J* = 7.0, 17.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.2, 161.1, 155.8, 141.4, 136.4, 126.0, 122.3, 122.3, 119.6, 119.3, 115.5, 111.3, 110.2, 106.0, 53.0, 43.8, 31.7 ppm.



1ha

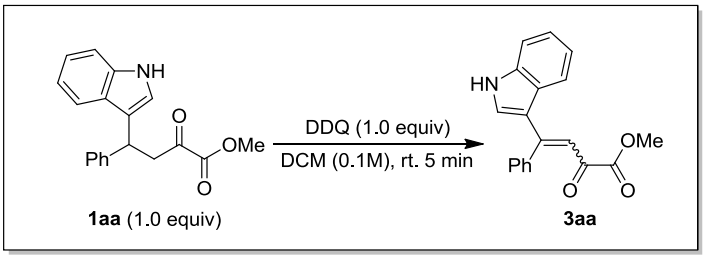
1ha: Prepared according to the general procedure I above and obtained as light yellow solid (0.91g, 71%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.32 – 7.27 (m, 3H), 7.25 – 7.24 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.89 (t, *J* = 7.5 Hz, 1H), 3.76 (s, 3H), 3.67 (dd, *J* = 7.0, 17.0 Hz, 1H), 3.58 (dd, *J* = 7.5, 17.0 Hz, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.0, 161.3, 143.3, 137.1, 132.1, 128.5, 127.8, 126.6, 124.3, 121.3, 121.0, 119.1, 118.1, 111.1, 52.9, 45.7, 37.8, 21.7 ppm.



1ja

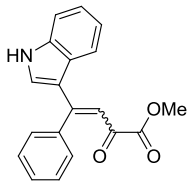
1ja: Prepared according to the general procedure I above and obtained as light yellow solid (1.19g, 77%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.06 (s, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.33 – 7.32 (m, 4H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.02 (dd, *J* = 1.5, 8.5 Hz, 1H), 4.69 (t, *J* = 7.5 Hz, 1H), 3.74 (s, 3H), 3.71 – 3.55 (m, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 192.1, 160.8, 144.1, 137.2, 128.2, 127.5, 126.1, 125.2, 123.1, 121.2, 120.4, 117.5, 113.9, 52.6, 44.9, 36.6 ppm.

B) Synthesis γ-indolyl β,γ-unsaturated α-keto esters 3aa:



Reaction procedure II: Compound **1aa** (0.2 mmol) and DDQ (0.2 mmol) was dissolved in DCM (2mL). The solution was stirred at room temperature for 5 minutes. Purification of mixture by column chromatography on silica gel (DCM/EA = 30:1, v/v) gave the desired product **3aa** (57.3 mg, 94% yield, *E*/*Z* = 75:25).

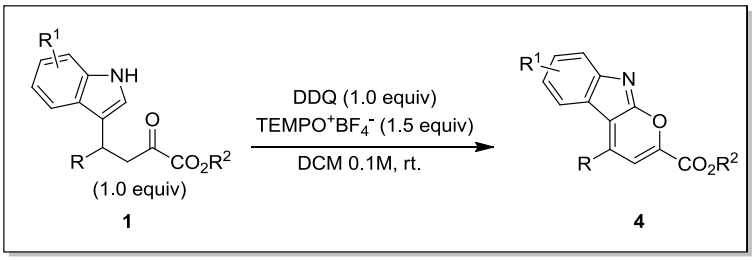
Large-scale Reaction: Compound **1aa** (3.9mmol, 1.20g) and DDQ (1.0 equiv, 885 mg) was dissolved in DCM (39 mL). After reaction, the mixture was diluted with DCM and washed with saturated sodium carbonate aqueous solution and saturated sodium chloride aqueous solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. Purification of mixture by column chromatography on silica gel (DCM /EA = 30:1, v/v) gave the desired product **3aa** (940mg, 79% yield, *E*/*Z* = 75:25, M.P. = 186 ^oC).



3aa

3aa: ^1H NMR (500 MHz, DMSO-d_6): δ 12.02 (br, 1H), 11.83 (br, 0.3H), 7.75 (s, 0.3H), 7.55 – 7.48 (m, 4H), 7.46 – 7.43 (m, 2.9H), 7.30 – 7.28 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.13 (m, 1.3H), 7.06 (s, 1H), 6.91 (t, *J* = 7.5 Hz, 0.3H), 6.69 (d, *J* = 8.0 Hz, 0.3H), 6.67 (s, 0.3H), 3.44 (s, 3H), 3.13 (s, 0.9H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 184.7, 183.6, 164.2, 163.8, 156.9, 154.8, 139.3, 138.5, 137.7, 137.0, 133.1, 132.5, 130.5, 129.5, 129.0, 128.8, 128.6, 127.9, 126.0, 124.7, 122.8, 122.3, 121.5, 120.2, 116.6, 114.8, 112.9, 112.1, 51.9, 51.6 ppm; IR (KBr, cm^{-1}): 3443, 3236, 2925, 2351, 1735, 1641, 1535, 1478, 1409, 1249, 1085, 743, 683, 589; HRMS (ESI) calcd for $C_{19}H_{16}NO_3^+$ $(M+H)^+$ 306.1130, found 306.1132.

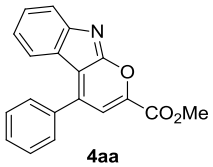
C) Synthesis of pyrano[2,3-b]indoles



General procedure III: Compound **1** (0.2 mmol), DDQ (0.2 mmol) and $TEMPO^{+}BF_4^{-}$ (0.3 mmol) was dissolved in DCM (2.0 mL). After reaction, the mixture was diluted with DCM and washed with saturated sodium carbonate aqueous solution and saturated sodium chloride aqueous solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. The solution was stirred at room temperature. Purification of mixture by column chromatography on silica gel (DCM/EA = 20:1, v/v) gave the desired product **4**.

Large-scale Reaction:

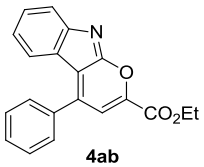
Compound **1aa** (3.6mmol, 1.10g), DDQ (1.0 eq., 817 mg) and $TEMPO^{+}BF_4^{-}$ (1.5 eq., 1.31g) was dissolved in DCM (36ml). After reaction, the mixture was diluted with DCM and washed with saturated sodium carbonate aqueous solution and saturated sodium chloride aqueous solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. Purification of mixture by column chromatography on silica gel (DCM/EA = 20:1, v/v) gave the desired product **4aa** (730mg, 66% yield).



4aa

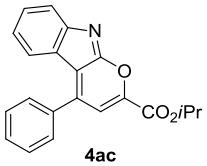
4aa: Prepared according to the general procedure III above and obtained as red solid (47.3mg, 78% yield, M.P. = 202 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 – 7.76 (m, 3H), 7.74 (d, *J* = 7.0 Hz, 1H), 7.67 (s, 1H), 7.65 – 7.62 (m, 3H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 160.6, 153.5, 143.9, 143.7, 135.3, 130.9, 130.6, 129.3, 128.5, 124.5, 123.2, 122.2, 119.9, 113.5, 53.3 ppm; IR (KBr, cm^{-1}): 3836, 3743, 2922, 1741, 1642, 1549, 1436, 1366, 1319, 1286, 1247, 1191, 1137, 1114, 935, 874, 760,

703, 565, 481, 437; HRMS (ESI) calcd for $C_{19}H_{14}NO_3^+$ $(M+H)^+$ 304.0973, found 304.0975.



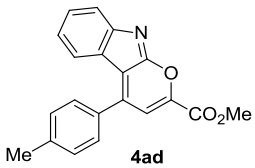
4ab

4ab: Prepared according to the general procedure III above and obtained as red solid (43.7mg, 69% yield, M.P. = 181 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 – 7.76 (m, 3H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.65 (s, 1H), 7.63 – 7.59 (m, 3H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 4.49 (q, *J* = 7.0 Hz, 2H), 1.46(d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 160.1, 153.5, 144.3, 143.8, 135.4, 130.8, 130.6, 129.2, 128.5, 124.3, 123.2, 122.1, 119.8, 113.2, 62.7, 14.2 ppm; IR (KBr, cm^{-1}): 2922, 2850, 1734, 1642, 1552, 1472, 1439, 1395, 1369, 1320, 1290, 1245, 1228, 1192, 1143, 1112, 1025, 757, 731, 704, 671; HRMS (ESI) calcd for $C_{20}H_{16}NO_3^+$ $(M+H)^+$ 318.1130, found 318.1130.



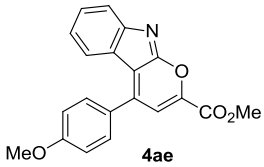
4ac

4ac: Prepared according to the general procedure III above and obtained as red solid (43.0mg, 65% yield, M.P. = 181 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 3H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.61 (m, 4H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.36 – 5.29 (m, 1H), 1.44(d, *J* = 6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3, 159.6, 153.5, 144.6, 143.9, 135.4, 130.8, 130.6, 129.2, 128.5, 124.2, 123.1, 122.1, 119.8, 113.1, 70.8, 21.8 ppm; IR (KBr, cm^{-1}): 2922, 2851, 1730, 1641, 1578, 1550, 1494, 1466, 1437, 1376, 1366, 1319, 1289, 1275, 1251, 1227, 1190, 1141, 1102, 758, 731, 705, 670; HRMS (ESI) calcd for $C_{21}H_{18}NO_3^+$ $(M+H)^+$ 332.1287, found 332.1288.



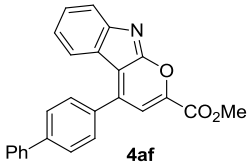
4ad

4ad: Prepared according to the general procedure III above and obtained as red solid (44.4mg, 70% yield, M.P. = 185 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.65 (s, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 4.03 (s, 3H), 2.51 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 160.6, 153.4, 143.9, 141.2, 132.4, 130.7, 129.9, 128.6, 124.1, 123.2, 122.3, 122.0, 119.8, 113.5, 53.2, 21.6 ppm; IR (KBr, cm^{-1}): 3425, 3059, 2921, 1719, 1639, 1543, 1434, 1370, 1297, 1255, 1230, 1191, 1124, 1018, 941, 895, 829, 757, 564, 517, 459, 427; HRMS (ESI) calcd for $C_{20}H_{16}NO_3^+$ $(M+H)^+$ 318.1130, found 318.1131.



4ae

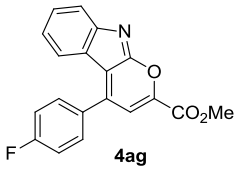
4ae: Prepared according to the general procedure III above and obtained as red solid (46.6mg, 70% yield, M.P. = 206 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.77 – 7.72 (m, 3H), 7.66 (s, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.15 – 7.12 (m, 3H), 4.03 (s, 3H), 3.95 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 161.7, 160.7, 153.3, 143.8, 143.7, 130.6, 130.4, 127.4, 123.5, 123.0, 122.3, 122.0, 119.8, 114.7, 113.5, 55.6, 53.2 ppm; IR (KBr, cm^{-1}): 2923, 1724, 1639, 1548, 1427, 1368, 1299, 1255, 1116, 1022, 838, 759, 566, 530, 474, 411; HRMS (ESI) calcd for $C_{20}H_{16}NO_4^+$ $(M+H)^+$ 334.1079, found 334.1076.



4af

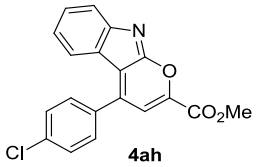
4af: Prepared according to the general procedure III above and obtained as red solid (54.6mg, 72% yield, M.P. = 235 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 – 7.85 (m, 5H), 7.75 – 7.70 (m, 4H), 7.55 – 7.50 (m, 3H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 160.6, 153.5, 144.0, 143.6, 143.4, 139.8, 134.1, 130.9, 129.1, 129.1, 128.2, 127.8, 127.2, 124.3, 123.2, 122.2, 119.9, 113.3, 53.3 ppm; IR (KBr, cm^{-1}): 2921, 2850,

1718, 1639, 1553, 1487, 1436, 1404, 1364, 1301, 1257, 1227, 1191, 1152, 1128, 1024, 1006, 875, 843, 786, 766, 754, 734, 724, 692, 672, 646; HRMS (ESI) calcd for $C_{25}H_{18}NO_3^+$ $(M+H)^+$ 380.1287, found 380.1284.



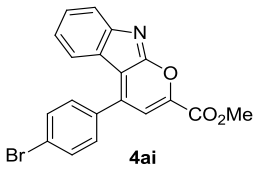
4ag

4ag: Prepared according to the general procedure III above and obtained as red solid (56.5mg, 67% yield, M.P. = 206 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 – 7.77 (m, 2H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.61 (s, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 8.5 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.1, 163.0 (d, *J* = 250.8 Hz), 159.5, 152.5, 143.0, 141.5, 130.3, 130.0, 129.7 (d, *J* = 8.3 Hz), 123.5, 121.6 (d, *J* = 89.5 Hz), 121.0, 118.9, 115.5 (d, *J* = 21.9 Hz), 112.2, 52.3 ppm; IR (KBr, cm^{-1}): 3112, 3065, 2923, 2853, 1729, 1642, 1602, 1548, 1509, 1430, 1365, 1320, 1290, 1251, 1225, 1189, 1162, 1116, 936, 860, 806, 761, 731, 674, 612, 545, 514, 460, 427; HRMS (ESI) calcd for $C_{19}H_{13}FNO_3^+$ $(M+H)^+$ 322.0879, found 322.0881.



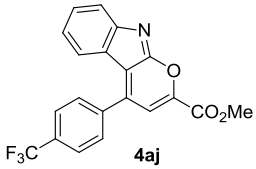
4ah

4ah: Prepared according to the general procedure III above and obtained as red solid (45.8mg, 68% yield, M.P. = 193 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.71 (m, 4H), 7.61 (d, *J* = 9.0 Hz, 3H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0, 160.5, 153.6, 144.0, 142.2, 136.9, 133.7, 131.1, 129.9, 129.6, 124.6, 123.1, 122.3, 121.9, 120.0, 113.0, 53.3 ppm; IR (KBr, cm^{-1}): 3057, 2953, 1735, 1644, 1556, 1438, 1269, 1139, 865, 851, 837, 735, 677, 566, 452; HRMS (ESI) calcd for $C_{19}H_{13}ClNO_3^+$ $(M+H)^+$ 338.0584, found 338.0583.



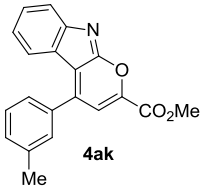
4ai

4ai: Prepared according to the general procedure III above and obtained as red solid (63.2mg, 83% yield, M.P. = 219 °C), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 – 7.71 (m, 4H), 7.66 – 7.64 (m, 2H), 7.60 – 7.59 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0, 160.5, 153.6, 144.1, 142.2, 134.2, 132.6, 131.2, 130.1, 125.2, 124.6, 123.1, 122.3, 121.9, 120.0, 112.9, 53.3 ppm; IR (KBr, cm^{-1}): 2919, 1743, 1642, 1547, 1434, 1358, 1286, 1245, 1189, 1116, 1068, 824, 758, 604, 563, 482, 419; HRMS (ESI) calcd for $C_{19}H_{13}BrNO_3^+$ $(M+H)^+$ 382.0079, found 382.0079.



4aj

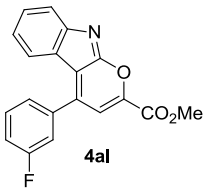
4aj: Prepared according to the general procedure III above and obtained as red solid (46.0mg, 62% yield, M.P. = 208 °C), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, 4H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9, 160.4, 153.8, 144.2, 141.6, 138.9, 132.5 (q, *J* = 33.4 Hz), 131.5, 129.0, 126.3, 125.2, 124.8, 123.1, 122.5, 121.7, 120.1, 112.7, 53.3 ppm; IR (KBr, cm^{-1}): 2921, 1734, 1645, 1555, 1439, 1428, 1412, 1382, 1325, 1290, 1276, 1254, 1230, 1193, 1171, 1122, 1065, 1018, 833; HRMS (ESI) calcd for $C_{20}H_{13}F_3NO_3^+$ $(M+H)^+$ 372.0848, found 372.0849.



4ak

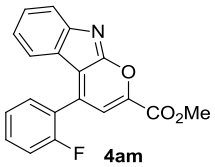
4ak: Prepared according to the general procedure III above and obtained as red solid (45.0mg, 71% yield, M.P. = 205 °C), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.58 – 7.48

(m, 4H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 4.03 (s, 3H), 2.49 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 160.6, 153.5, 144.0, 143.9, 139.2, 135.3, 131.4, 130.8, 129.1, 129.0, 125.7, 124.4, 123.2, 122.1, 119.8, 113.5, 53.2, 21.4 ppm; IR (KBr, cm^{-1}): 2920, 1748, 1646, 1603, 1553, 1442, 1429, 1366, 1321, 1295, 1275, 1255, 1192, 1136, 1117, 794, 780, 760, 707, 674; HRMS (ESI) calcd for $C_{20}H_{16}NO_3^+$ $(M+H)^+$ 318.1130, found 318.1136.



4al

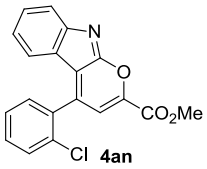
4al: Prepared according to the general procedure III above and obtained as red solid (50.7mg, 79% yield, M.P. = 204 °C), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (t, *J* = 7.5 Hz, 2H), 7.62 – 7.59 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0, 163.0 (d, *J* = 249.0 Hz), 160.4, 153.6, 144.0, 141.9, 137.4 (d, *J* = 7.8 Hz), 131.2, 131.1 (d, *J* = 8.3 Hz), 124.8, 124.3, 123.2, 122.4, 121.8, 120.0, 117.6 (d, *J* = 20.9 Hz), 115.6 (d, *J* = 22.5 Hz), 113.0, 53.3 ppm; IR (KBr, cm^{-1}): 2921, 1748, 1727, 1648, 1554, 1430, 1254, 1131, 801, 706; HRMS (ESI) calcd for $C_{19}H_{13}FNO_3^+$ $(M+H)^+$ 322.0879, found 322.0880.



4am

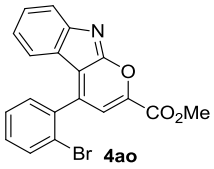
4am: Prepared according to the general procedure III above and obtained as red solid (48.8mg, 76% yield, M.P. = 226℃), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.66 (m, 3H), 7.63 – 7.59 (m, 1H), 7.55 – 7.51 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0, 160.5, 159.5 (d, *J* = 251.1 Hz), 153.7, 143.6, 137.4, 132.6 (d, *J* = 8.1 Hz), 131.2, 130.5, 126.3, 124.9 (d, *J* = 3.0 Hz), 123.4, 123.0 (d, *J* = 14.5 Hz), 122.4, 122.1, 119.9, 116.8 (d, *J* = 20.9 Hz), 113.6, 53.3 ppm; IR (KBr, cm^{-1}):

3087, 2933, 1729, 1639, 1555, 1435, 1370, 1240, 1114, 932, 864, 761, 538, 454; HRMS (ESI) calcd for $C_{19}H_{13}FNO_3^+$ $(M+H)^+$ 322.0879, found 322.0881.



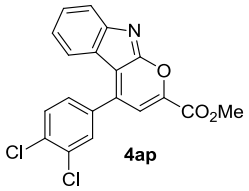
4an

4an: Prepared according to the general procedure III above and obtained as red solid (42.5mg, 63% yield, M.P. = 201℃), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz,1H), 7.66 – 7.63 (m, 2H), 7.56 – 7.48 (m, 4H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 160.5, 153.7, 143.6, 140.5, 134.0, 132.4, 131.4, 131.2, 130.6, 130.2, 127.4, 126.5, 123.5, 122.4, 122.1, 119.8, 113.7, 53.3 ppm; IR (KBr, cm^{-1}): 2934, 1729, 1640, 1555, 1430, 1367, 1269, 1115, 1048, 756, 678, 566; HRMS (ESI) calcd for $C_{19}H_{13}ClNO_3^+$ $(M+H)^+$ 338.0584, found 338.0583.



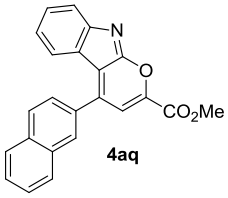
4ao

4ao: Prepared according to the general procedure III above and obtained as red solid (62.5mg, 82% yield, M.P. = 201 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.62 (s, 1H), 7.56 – 7.51 (m, 3H), 7.48 – 7.45 (m, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 160.5, 153.7, 143.6, 141.9, 136.0, 133.8, 131.4, 131.2, 130.1, 128.0, 126.3, 123.5, 122.4, 122.1, 121.5, 119.8, 113.7, 53.3 ppm; IR (KBr, cm^{-1}): 3842, 3741, 1728, 1642, 1554, 1431, 1371, 1269, 1117, 758, 617, 597; HRMS (ESI) calcd for $C_{19}H_{13}BrNO_3^+$ $(M+H)^+$ 382.0079, found 382.0081.



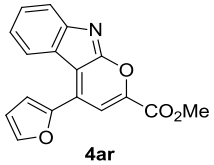
4ap

4ap: Prepared according to the general procedure III above and obtained as red solid (60.1mg, 88% yield, M.P. = 221 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.75 – 7.71 (m, 3H), 7.64 – 7.62 (m, 1H), 7.59 – 7.55 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9, 160.4, 153.8, 144.2, 140.6, 135.1, 135.1, 133.9, 131.5, 131.4, 130.3, 127.8, 125.0, 123.1, 122.6, 121.7, 120.2, 112.5, 53.4 ppm; IR (KBr, cm^{-1}): 3085, 2950, 1732, 1640, 1556, 1470, 1432, 1358, 1320, 1292, 1260, 1189, 1127, 1024, 939, 873, 830, 761, 678, 580, 516, 459, 427; HRMS (ESI) calcd for $C_{19}H_{12}Cl_2NO_3^+$ $(M+H)^+$ 372.0194, found 372.0193.



4aq

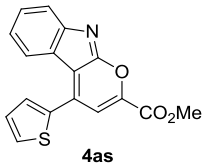
4aq: Prepared according to the general procedure III above and obtained as red solid (60.7 mg, 86% yield, M.P. = 238 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.07 (d, *J* = 7.0 Hz, 1H), 7.97 (t, *J* = 8.5Hz, 1H), 7.84 – 7.74 (m, 4H), 7.66 – 7.61 (m, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 160.6, 153.6, 144.0, 143.7, 134.1, 133.1, 132.6, 130.9, 129.2, 128.7, 128.0, 127.9, 127.3, 125.3, 124.6, 123.2, 122.2, 119.9, 113.5, 53.3 ppm; IR (KBr, cm^{-1}): 3053, 2957, 2361, 1734, 1637, 1552, 1433, 1368, 1280, 1257, 1226, 1191, 1141, 1116, 1008, 934, 869, 819, 759, 676, 544, 493, 437, 404; HRMS (ESI) calcd for $C_{23}H_{16}NO_3^+$ $(M+H)^+$ 354.1130, found 354.1128.



4ar

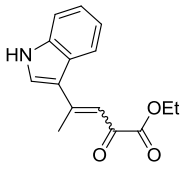
4ar: Prepared according to the general procedure III above and obtained as red solid (50.4mg, 86% yield, M.P. = 232 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.68 (d, *J* = 7.5 Hz, 1H), 7.93 (s, 1H), 7.78 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 5.6 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.77 – 6.77 (m, 1H), 4.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.5, 160.6, 153.3, 150.1,

146.7, 143.6, 130.6, 129.1, 125.3, 122.5, 119.7, 116.8, 113.4, 109.1, 53.3 ppm; IR (KBr, cm^{-1}): 3136, 2920, 2850, 1741, 1634, 1572, 1546, 1427, 1362, 1264, 1152, 756, 701; HRMS (ESI) calcd for $C_{17}H_{12}NO_4^+$ $(M+H)^+$ 294.0766, found 294.0769.



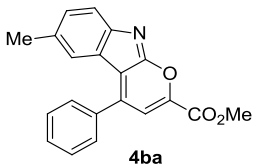
4as

4as: Prepared according to the general procedure III above and obtained as red solid (45.7mg, 74% yield, M.P. = 228 ^oC), eluent: DCM/EA = 20:1; ^1H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 3.0 Hz, 1H), 7.73 – 7.72 (m, 2H), 7.69 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 9.0 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 4.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 160.5, 153.3, 143.6, 137.1, 136.5, 131.0, 130.8, 130.6, 128.6, 123.1, 122.2, 119.9, 113.3, 53.3 ppm; IR (KBr, cm^{-1}): 2920, 1727, 1632, 1553, 1416, 1369, 1280, 1252, 1203, 1136, 1114, 1002, 758, 721, 677, 611, 506, 440; HRMS (ESI) calcd for $C_{17}H_{12}NO_3S^+$ $(M+H)^+$ 310.0538, found 310.0543.



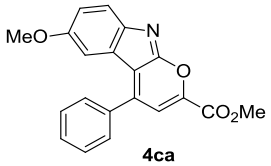
3at

3at: Prepared according to the general procedure III above and obtained as yellow solid (39.1 mg, 70% yield, *E/Z* = 90:10, M.P. = 175 ^oC), eluent: DCM/EA = 30:1; ^1H NMR (500 MHz, DMSO-d_6): δ 12.06 (br, 1H), 8.16 (d, *J* = 3.0 Hz, 1H), 7.96 – 7.94 (m, 1H), 7.51 (t, *J* = 4.5 Hz, 1H), 7.39 (s, 1H), 7.26 – 7.22 (m, 2H), 4.27 (q, *J* = 7.0 Hz, 2H), 2.69 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 181.2, 163.3, 157.1, 137.8, 132.1, 124.2, 122.7, 121.6, 120.4, 117.2, 112.8, 112.6, 61.5, 18.8, 13.9 ppm; IR (KBr, cm^{-1}): 3420, 3207, 2919, 1723, 1646, 1578, 1541, 1478, 1490, 1249, 1093, 1021, 737, 609, 570, 491; HRMS (ESI) calcd for $C_{15}H_{15}NNaO_3^+$ $(M+Na)^+$ 280.0950, found 280.0953.



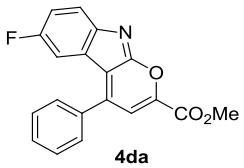
4ba

4ba: Prepared according to the general procedure III above and obtained as red solid (39.3mg, 62% yield, M.P. = 229 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 – 7.76 (m, 2H), 7.62 – 7.60 (m, 5H), 7.56 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 160.7, 151.5, 143.8, 143.3, 135.5, 132.1, 131.6, 130.6, 129.2, 128.5, 124.5, 123.3, 122.2, 119.4, 113.4, 53.2, 21.5 ppm; IR (KBr, cm^{-1}): 2920, 2853, 1719, 1642, 1554, 1493, 1438, 1364, 1303, 1248, 1161, 1113, 1031, 942, 866, 814, 757, 694, 663, 612, 541, 472, 432; HRMS (ESI) calcd for $C_{20}H_{16}NO_3^+$ $(M+H)^+$ 318.1130, found 318.1132.



4ca

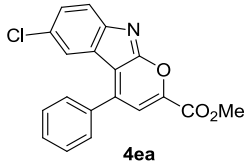
4ca: Prepared according to the general procedure III above and obtained as red solid (60.6mg, 91% yield, M.P. = 220 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 6.5 Hz, 2H), 7.62 – 7.58 (m, 5H), 7.28 (s, 1H), 7.14 – 7.12 (m, 1H), 4.03 (s, 3H), 3.71 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.2, 160.6, 155.3, 147.7, 144.0, 143.7, 135.2, 130.7, 129.2, 128.5, 124.7, 122.6, 120.2, 118.1, 113.0, 107.7, 55.7, 53.2 ppm; IR (KBr, cm^{-1}): 3017, 2950, 1723, 1642, 1565, 1471, 1433, 1366, 1299, 1279, 1200, 1163, 1124, 1028, 952, 851, 814, 760, 704, 660, 611, 540, 512, 428, 403; HRMS (ESI) calcd for $C_{20}H_{16}NO_4^+$ $(M+H)^+$ 334.1079, found 334.1083.



4da

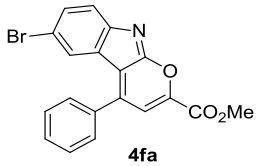
4da: Prepared according to the general procedure III above and obtained as red solid (27.6mg, 43% yield, M.P. = 239 ºC), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 – 7.74 (m, 2H), 7.67 – 7.62 (m, 5H), 7.45 – 7.43 (m, 1H), 7.27 – 7.23

(m, 1H), 4.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9, 160.4, 158.6 (d, *J* = 237.6 Hz), 149.6, 145.1, 144.5, 134.9, 131.0, 129.5, 128.4, 124.2, 122.5 (d, *J* = 9.6 Hz), 120.6 (d, *J* = 8.3 Hz), 118.2 (d, *J* = 24.3 Hz), 113.1, 109.4 (d, *J* = 25.4 Hz), 53.3 ppm; IR (KBr, cm^{-1}): 2922, 2853, 1722, 1644, 1564, 1465, 1428, 1366, 1307, 1261, 1157, 1120, 864, 812, 757, 701, 658, 613, 538, 474, 453, 406; HRMS (ESI) calcd for $C_{19}H_{13}FNO_3^+$ $(M+H)^+$ 322.0879, found 322.0880.



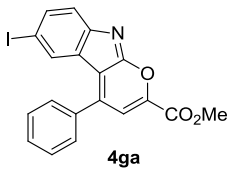
4ea

4ea: Prepared according to the general procedure III above and obtained as red solid (35.0mg, 52% yield, M.P. = 266 °C), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 – 7.73 (m, 3H), 7.68 – 7.65 (m, 5H), 7.50 – 7.48 (m, 1H), 4.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 160.4, 151.8, 145.4, 144.6, 134.9, 131.1, 130.8, 129.5, 128.4, 127.5, 123.6, 123.2, 122.8, 120.9, 113.4, 53.4 ppm; IR (KBr, cm^-): 2929, 1715, 1639, 1545, 1429, 1363, 1300, 1249, 1114, 862, 756, 691, 603, 532, 442; HRMS (ESI) calcd for $C_{19}H_{13}ClNO_3^+$ $(M+H)^+$ 338.0584, found 338.0586.



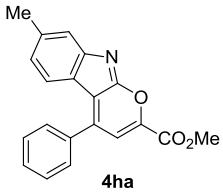
4fa

4fa: Prepared according to the general procedure III above and obtained as red solid (31.2mg, 41% yield, M.P. = 259 °C), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.77 – 7.75 (m, 2H), 7.69 (s, 1H), 7.66 – 7.61 (m, 5H), 4.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 160.4, 151.8, 145.4, 144.6, 134.9, 131.1, 130.8, 129.5, 128.4, 127.5, 123.6, 123.2, 122.8, 120.9, 113.4, 53.4 ppm; IR (KBr, cm^{-1}): 3802, 3690, 3649, 3327, 2955, 2549, 2192, 1942, 1718, 1645, 1552, 1460, 1434, 1363, 1297, 1255, 1192, 1125, 1014, 852, 819, 788, 759, 694, 622, 600; HRMS (ESI) calcd for $C_{19}H_{13}BrNO_3^+$ $(M+H)^+$ 382.0079, found 382.0081.



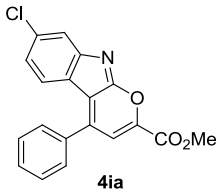
4ga

4ga: Prepared according to the general procedure III above and obtained as red solid (53.2mg, 62% yield, M.P. = 270 °C), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 1.5 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.69 (s, 1H), 7.64 – 7.62 (m, 4H), 7.26 – 7.24 (m, 1H), 4.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7, 160.4, 154.5, 144.6, 144.4, 135.0, 130.9, 129.4, 128.5, 125.3, 124.8, 124.1, 123.7, 123.0, 120.9, 113.7, 53.4 ppm; IR (KBr, cm^{-1}): 2926, 1713, 1637, 1539, 1424, 1360, 1296, 1249, 1110, 758, 687, 592, 534; HRMS (ESI) calcd for $C_{19}H_{13}INO_3^+$ $(M+H)^+$ 429.9935, found 429.9939.



4ha

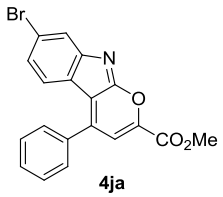
4ha: Prepared according to the general procedure III above and obtained as red solid (45.6mg, 72% yield, M.P. = 235 °C), eluent: DCM/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 – 7.75 (m, 2H), 7.66 – 7.59 (m, 5H), 7.52 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 3H), 2.49 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5, 159.7, 152.9, 142.4, 141.3, 140.9, 134.5, 129.5, 128.2, 127.5, 123.5, 122.4, 121.9, 119.2, 118.6, 112.5, 52.2, 21.4 ppm; IR (KBr, cm^{-1}): 2922, 1716, 1643, 1551, 1442, 1358, 1302, 1242, 1124, 1021, 944, 869, 763, 703, 571, 512, 419; HRMS (ESI) calcd for $C_{20}H_{16}NO_3^+$ $(M+H)^+$ 318.1130, found 318.1134.



4ia

4ia: Prepared according to the general procedure III above and obtained as red solid (44.5mg, 66% yield, M.P. = 242 °C), eluent: dichloromethane/ethyl acetate (20:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 – 7.75 (m, 2H), 7.69 – 7.67 (m, 3H), 7.64 – 7.62 (m, 3H), 7.09 – 7.07 (m, 1H), 4.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9,

160.4, 154.4, 144.3, 144.2, 136.5, 135.0, 130.9, 129.4, 128.5, 123.9, 123.6, 122.5, 120.5, 120.0, 113.6, 53.3 ppm; IR (KBr, cm^{-1}): 2924, 2117, 1735, 1638, 1544, 1429, 1357, 1246, 1125, 1063, 767, 705, 612, 482, 425; HRMS (ESI) calcd for $C_{19}H_{13}ClNO_3^+$ $(M+H)^+$ 338.0584, found 338.0587.



4ja

4ja: Prepared according to the general procedure III above and obtained as red solid (42.7mg, 56% yield, M.P. = 246 ºC), eluent: DCM/EA = 20:1; ^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.76 – 7.74 (m, 2H), 7.69 (s, 1H), 7.64 – 7.62 (m, 4H), 7.26 – 7.24 (m, 1H), 4.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 160.4, 152.2, 145.4, 144.6, 134.8, 133.5, 131.2, 129.5, 128.4, 125.7, 123.8, 123.5, 121.3, 115.0, 113.5, 53.4 ppm; IR (KBr, cm^{-1}): 3045, 2929, 1732, 1636, 1537, 1417, 1355, 1241, 1122, 1050, 933, 869, 760, 701, 541; HRMS (ESI) calcd for $C_{19}H_{13}BrNO_3^+$ $(M+H)^+$ 382.0079, found 382.0077.

V. Cyclic Voltammetry (CV) Experiments

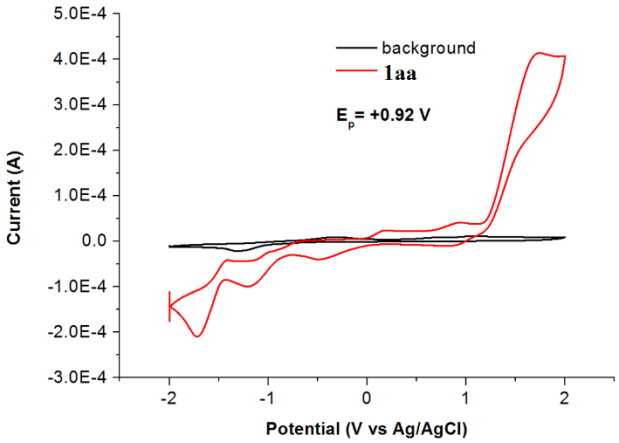


Figure S2. Cyclic voltammograms of **1aa** (2×10^{-2} M) in electrolyte solution (0.02 M nBu$_4$NPF$_6$ in CH$_3$CN) using a glassy carbon working electrode, Pt wire and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate.

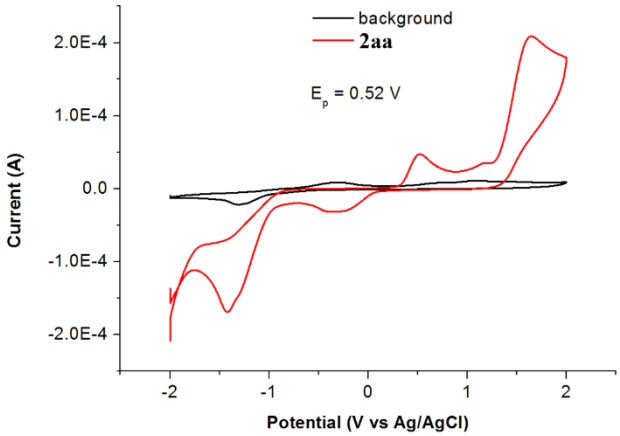


Figure S3. Cyclic voltammograms of **2aa** (2×10^{-2} M) in electrolyte solution (0.02 M nBu$_4$NPF$_6$ in CH$_3$CN) using a glassy carbon working electrode, Pt wire and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate.

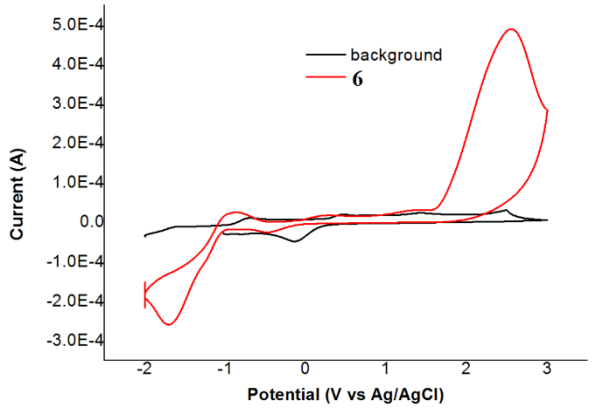


Figure S4. Cyclic voltammograms of **6** (2×10^{-2} M) in electrolyte solution (0.03 M nBu$_4$NPF$_6$ in CH$_3$CN) using a glassy carbon working electrode, Pt wire and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate.

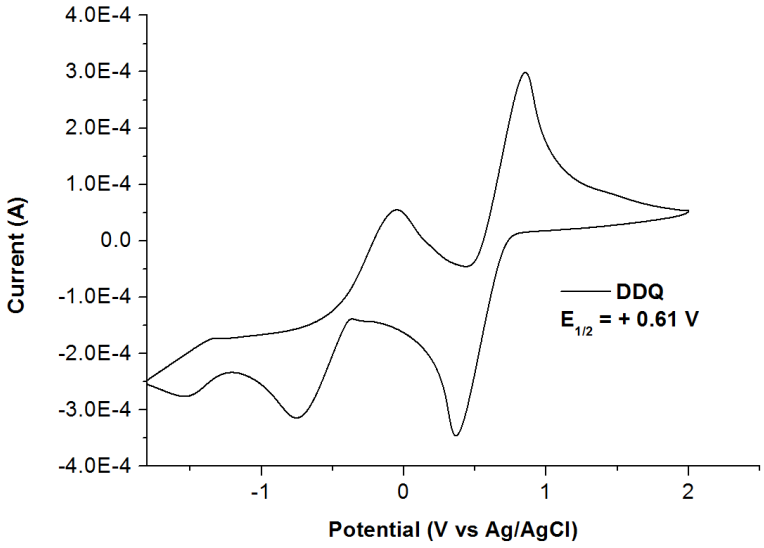


Figure S5. Cyclic voltammograms of **DDQ** (2×10^{-2} M) in electrolyte solution (0.03 M nBu$_4$NPF$_6$ in CH$_3$CN) using a glassy carbon working electrode, Pt wire and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate.

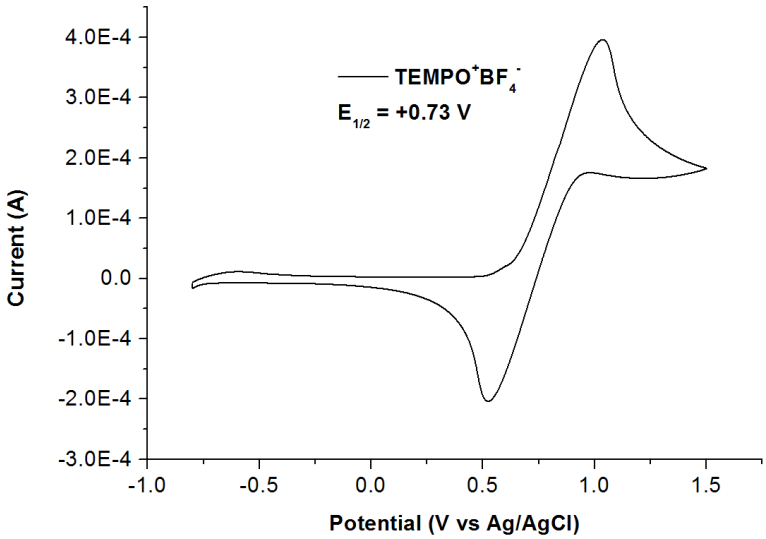
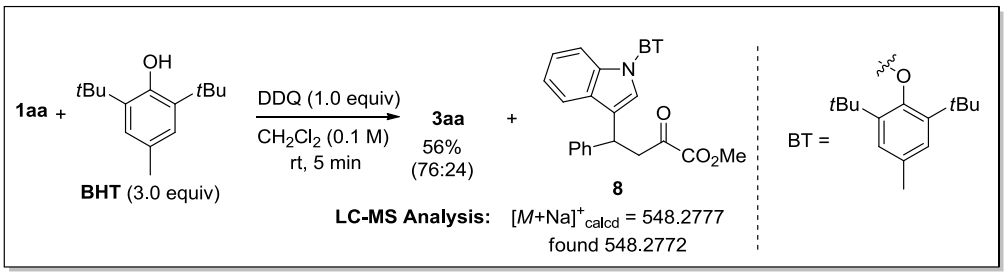
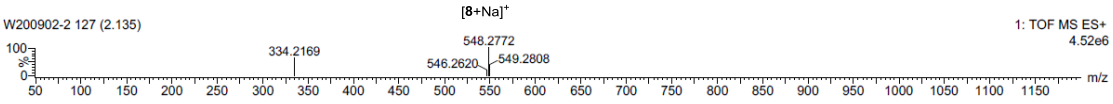


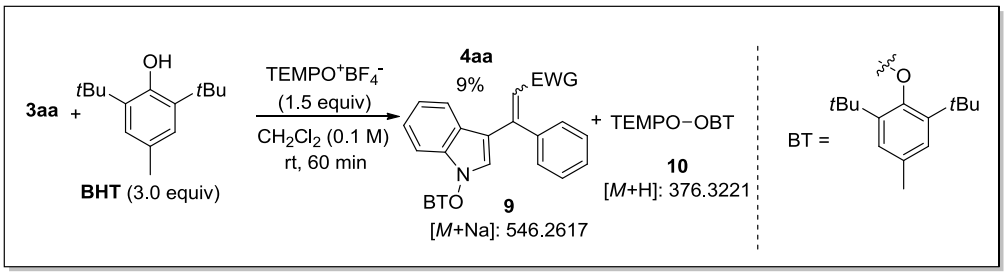
Figure S6. Cyclic voltammograms of $TEMPO^{+}BF_4^{-}$ (2×10^{-2} M) in electrolyte solution (0.02 M nBu$_4$NPF$_6$ in CH_3CN) using a glassy carbon working electrode, Pt wire and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate.

VI. Radical Trapping Experiments

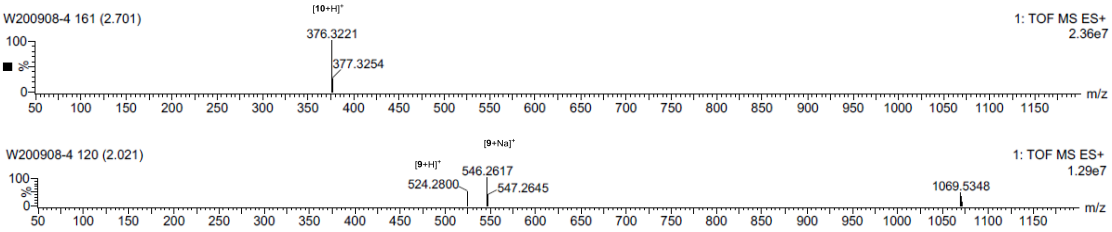


A) BHT as radical trapping regent in the reaction of 1aa: Compound **1aa** (0.1 mmol), DDQ (0.1 mmol) and BHT (0.3 mmol) was dissolved in DCM (1.0 ml). The solution was stirred at room temperature for 5 minutes, quenched with CH_3CN. The mixture was analyzed by LC-MS. The product **3aa** was obtained in 56% yield and with 76:24 *E*/Z value.

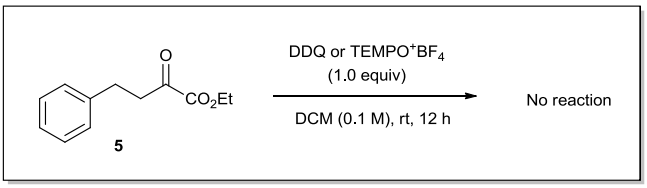




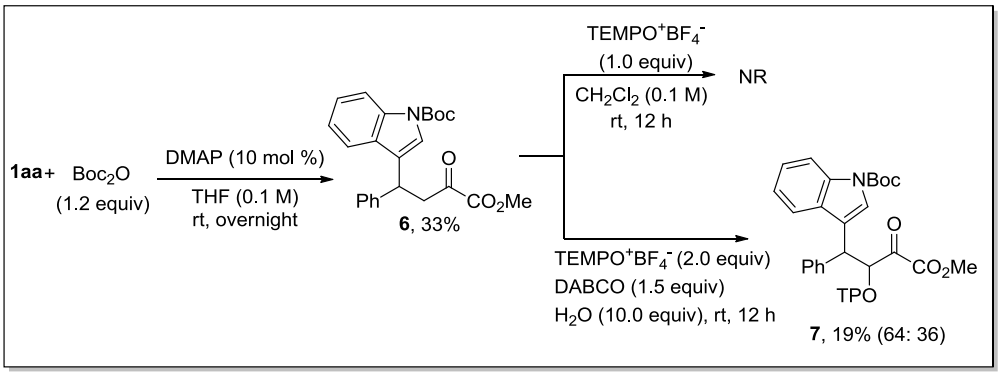
B) BHT as radical trapping regent in the reaction of 3aa: Compound **3aa** (0.1 mmol), $TEMPO^{+}BF_4^{-}$ (0.15 mmol) and BHT (0.3 mmol) was dissolved in DCM (1.0 ml). The solution was stirred at room temperature for 60 minutes, quenched with CH_3CN. The mixture was analyzed by LC-MS. The product **4aa** was obtained in 9% yield.



VII. Control Experiments

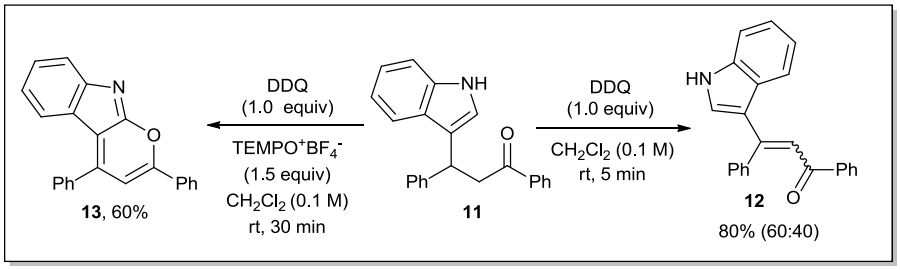


A) Oxidative reaction of ethyl 2-oxo-4-phenylbutanoate 5: Compound **5** (0.1 mmol), DDQ (0.1 mmol) or $TEMPO^{+}BF_4^{-}$ (0.1 mmol) as an oxidant was dissolved in DCM (1.0 mL). The solution was stirred at room temperature for 12 h. No reaction was observed.



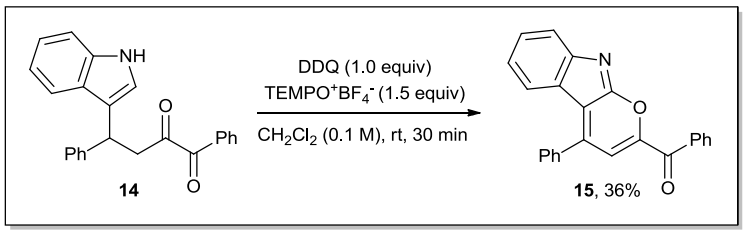
B) Synthesis and oxidative reaction of *N*-Boc indolyl derivative 6： To a solution of THF (10 mL) were added **1aa** (1 mmol, 307 mg), Boc_2O (1.2 mmol, 262 mg) and DMAP (0.1 mmol, 12 mg). The reaction mixture was stirred at room temperature for overnight. The reaction mixture was stirred at room temperature overnight. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography (eluent: PE/EA = 12:1, v/v) on silica gel gave the desired product **6** (light yellow oil**,** 135 mg, 33% yield),; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.50 (s, 1H), 7.32 (d, *J* = 7.0 Hz, 3H), 7.27 – 7.24 (m, 3H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 4.82 (t, *J* = 7.5 Hz, 1H), 3.80 (s, 3H), 3.67 (dd, J = 7.0, 17.5 Hz, 1H), 3.59 (dd, J = 8.0, 17.5 Hz, 1H), 1.67 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.0, 161.2, 149.8, 142.0, 135.7, 129.5, 128.7, 127.9, 127.0, 124.6, 122.7, 122.5, 119.7, 115.3, 83.8, 53.0, 45.2, 37.4, 28.2 ppm. Compound **6** (0.1 mmol), $TEMPO^{+}BF_4^{-}$ (0.10 mmol) was dissolved in DCM (1.0 ml). The solution was stirred

at room temperature for 12 h, but the reaction didn't work. Compound **6** (0.1 mmol), $TEMPO^+BF_4^-$ (0.2 mmol), H_2O (1.0 mmol) and DABCO (0.15 mmol) was dissolved in DCM (1.0 mL). The solution was stirred at room temperature for 12 h. Purification of mixture by column chromatography on silica gel (eluent: PE/EA = 10:1, v/v) gave the desired product **7** (light yellow oil**,** 10.7 mg, 19% yield, dr = 59:41). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 – 8.05 (m, 1.7H), 7.82 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 0.7H), 7.52 (s, 1H), 7.37 (d, *J* = 7.0 Hz, 3.4H), 7.25 (d, *J* = 7.0 Hz, 4.8H), 7.22 – 7.18 (m, 3.4H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.09 (d, *J* = 9.5 Hz, 0.7H), 5.96 (d, *J* = 10.0 Hz, 1H), 4.84 – 4.79 (m, 1.7H), 3.75 (s, 3H), 3.74 (s, 2.1H), 1.68 (s, 9H), 1.65 (s, 6.3H), 1.49 – 1.44 (m, 2.8H), 1.38 – 1.36 (m, 4H), 1.32 – 1.28 (m, 3.4H), 1.17 (s, 2.1H), 1.11 (s, 3H), 1.04 (s, 3H), 0.99 (s, 4.2H), 0.94 (s, 3H), 0.59 (s, 5.1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.6, 195.0, 161.7, 161.7, 149.8, 139.3, 138.8, 129.4, 128.9, 128.7, 128.2, 127.2, 127.0, 124.5, 124.3, 124.2, 123.5, 122.4, 122.4, 120.1, 119.7, 115.0, 114.9, 83.6, 83.0, 61.6, 61.3, 60.2, 60.1, 52.8, 52.8, 43.8, 43.4, 40.6, 40.5, 40.1, 40.1, 34.0, 33.8, 28.2, 20.7, 20.3, 20.0, 17.0, 17.0 ppm; IR(KBr, cm^{-1}): 2933, 1731, 1453, 1371, 1255, 1156, 1075, 733, 700; HRMS (ESI) calcd for $C_{33}H_{43}N_2O_6^+$ $(M+H)^+$ 563.3116, found 563.3118.



C) Oxidative reaction of 3-(1H-indol-3-yl)-1,3-diphenylpropan-1-one 11: Compound **11** (0.2 mmol) and DDQ (0.2 mmol) was dissolved in DCM (2.0 mL). The solution was stirred at room temperature for 5 minutes. Purification of mixture by column chromatography on silica gel (DCM/EA = 30:1, v/v) gave the desired product **12** (yellow solid, 51.7mg, 80% yield, *E/Z* = 60:40, M.P. = 189 °C); ^{1}H NMR (500 MHz, DMSO) δ 11.74 (s, 1H), 11.42 (s, 0.66H), 7.92 – 7.90 (m, 2H), 7.88 (d, *J* = 8.0 Hz, 1.32H), 7.57 – 7.40 (m, 10.30H), 7.38 – 7.34 (m, 5.30H), 7.27 – 7.23 (m, 3H),

7.19 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 0.66H), 6.99 (s, 0.66H), 6.81 (t, *J* = 7.5 Hz, 0.66H), 6.68 (d, *J* = 8.0 Hz, 0.66H) ppm; ^{13}C NMR (125 MHz, DMSO) δ major: 189.9, 151.5, 140.4, 139.2, 137.4, 132.1, 130.4, 129.0, 128.6, 128.5, 127.9, 127.7, 125.0, 122.2, 120.7, 120.2, 117.1, 116.8, 112.5 ppm; minor: 191.5, 147.9, 141.8, 138.3, 136.2, 132.2, 129.5, 129.2, 128.4, 128.3, 128.1, 127.7, 126.4, 121.9, 121.3, 119.9, 119.3, 112.9, 111.8 ppm; IR(KBr, cm^{-}): 3442, 3223, 2927, 1631, 1541, 1491, 1434, 1341, 1225, 1135, 1028, 842, 700, 595, 419; HRMS (ESI) calcd for $C_{23}H_{17}NNaO^{+}$ $(M+Na)^{+}$ 346.1202, found 346.1211. Compound **11** (0.2 mmol), DDQ (0.2 mmol) and $TEMPO^{+}BF_4^{-}$ (0.3 mmol) was dissolved in DCM (2.0 mL). After reaction, the mixture was diluted with DCM and washed with saturated sodium carbonate aqueous solution and saturated sodium chloride aqueous solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. The solution was stirred at room temperature. Purification of mixture by column chromatography on silica gel (DCM/EA = 20:1, v/v) gave the desired product **13** (red solid, 38.5mg, 60% yield, M.P. = 228 °C), which is a known compound.[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 6.5 Hz, 2H), 7.79 (d, *J* = 6.5 Hz, 2H), 7.72(t, *J* = 9.0 Hz, 2H), 7.63 – 7.58 (m, 3H), 7.52 – 7.45 (m, 4H), 7.16 (s, 1H), 7.08(t, *J* = 7.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.3, 154.0, 150.2, 144.6, 134.5, 129.7, 128.9, 128.2, 127.1, 127.1, 126.4, 124.0, 120.6, 120.3, 119.4, 117.3, 117.2, 102.7 ppm.



D) Oxidative reaction of 4-(1H-indol-3-yl)-1,4-diphenylbutan-1,2-dione 14: Compound **14** (0.2 mmol), DDQ (0.2 mmol) and $TEMPO^{+}BF_4^{-}$ (0.3 mmol) was dissolved in DCM (2.0 mL). After reaction, the mixture was diluted with DCM and washed with saturated sodium carbonate aqueous solution and saturated sodium chloride aqueous solution. The organic layer was dried over $MgSO_4$, filtered and

concentrated under vacuum. The solution was stirred at room temperature. Purification of mixture by column chromatography on silica gel (DCM) gave the desired product **15** (red solid, 25.8 mg, 36% yield, M.P. = 182 ^{o}C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.83 – 7.80 (m, 3H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.63 (m, 5H), 7.58 – 7.53 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 163.9, 153.5, 150.9, 144.5, 135.5, 135.3, 133.8, 131.0, 130.7, 130.3, 129.3, 128.7, 128.6, 124.1, 123.3, 122.3, 119.8, 113.4 ppm; IR (KBr, cm^{-1}): 1627, 1551, 525; HRMS (ESI) calcd for $C_{24}H_{16}NO_2^+$ $(M+H)^+$ 350.1181, found 350.1181.

VIII. X-ray Structure

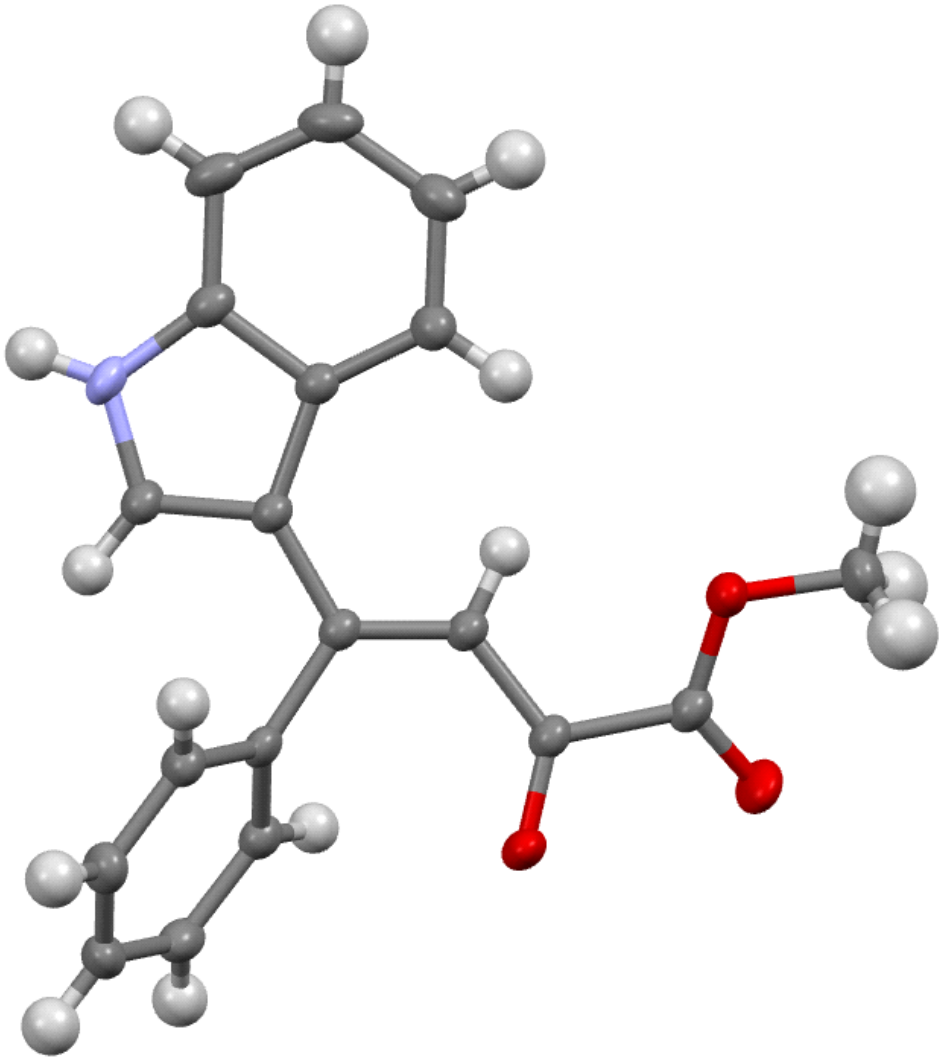


Figure S6. X-ray structure of compound 3aa (CCDC 2050910)

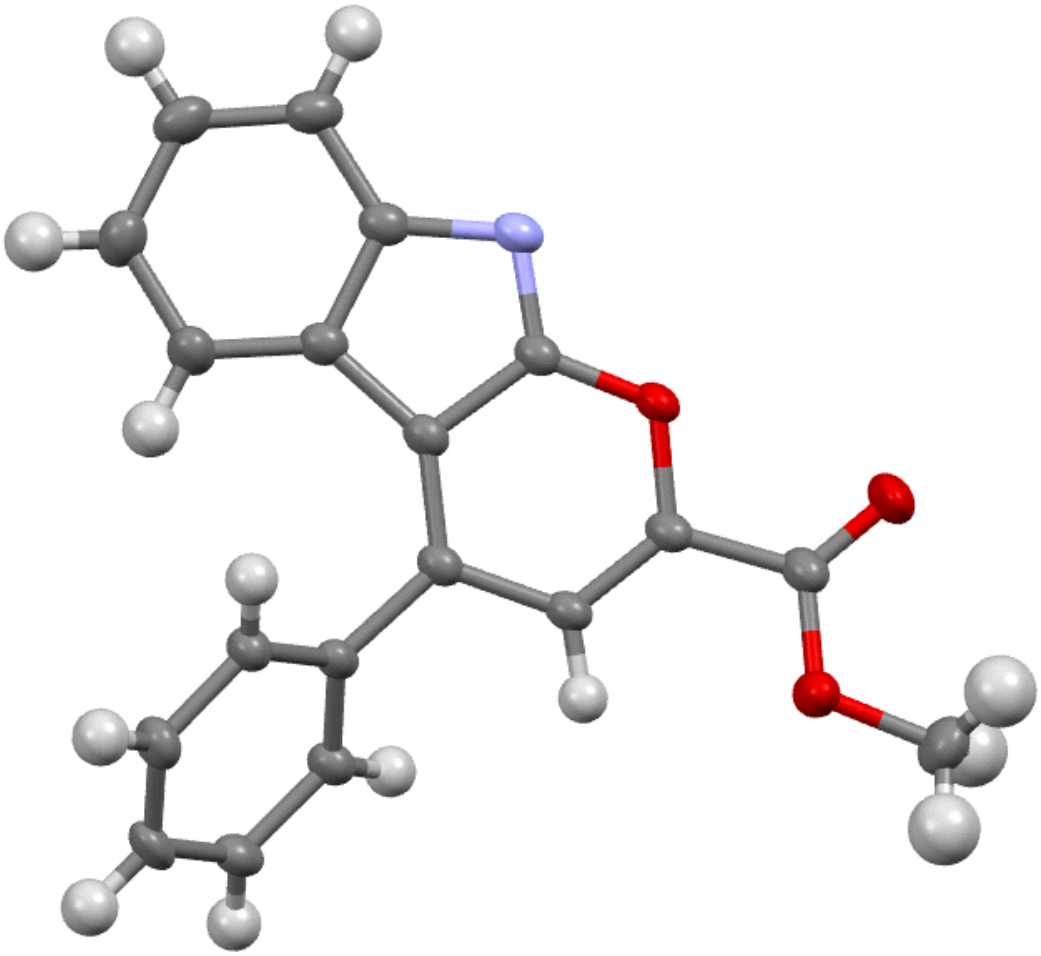
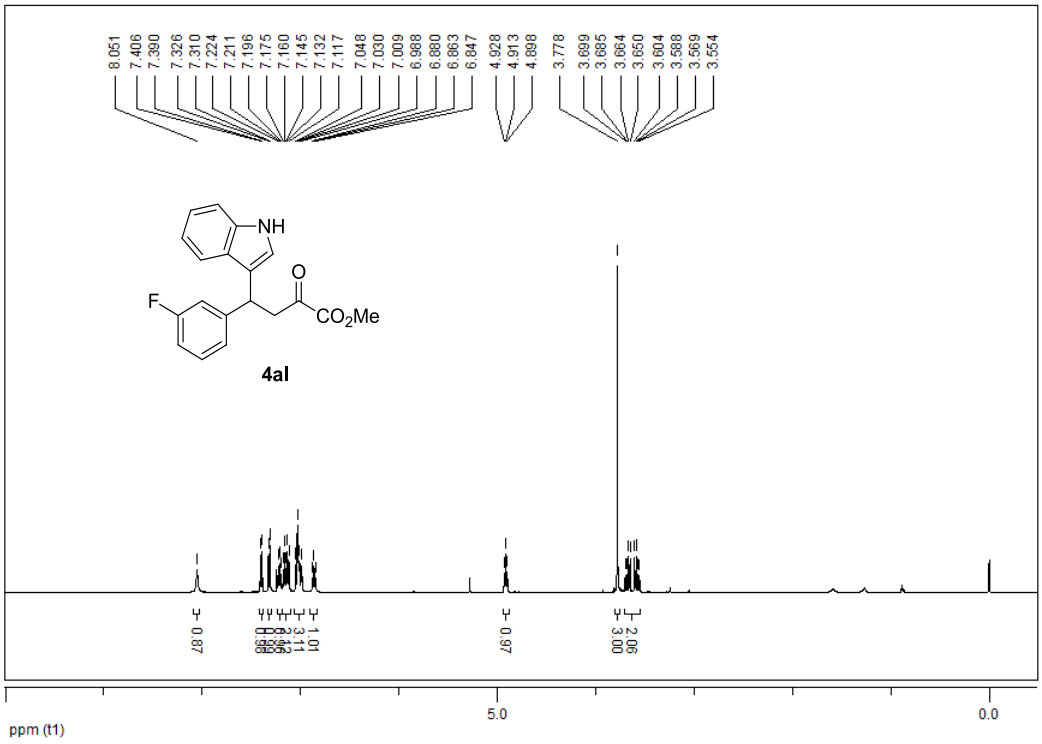


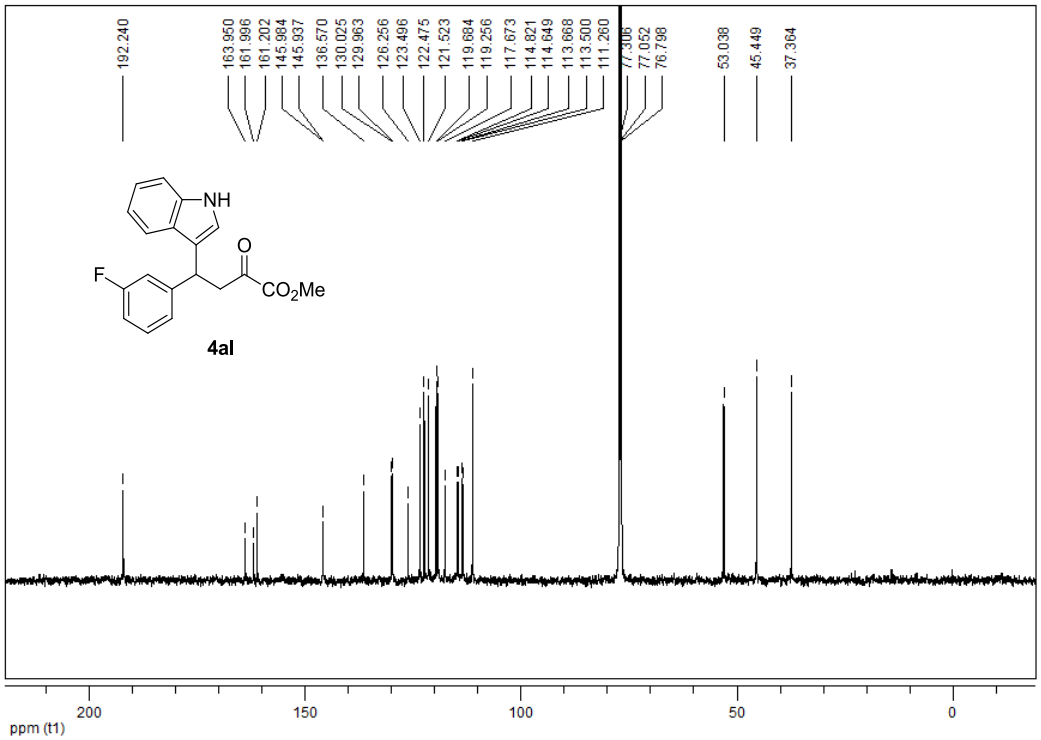
Figure S7. X-ray Structure of Compound **4aa (CCDC 2040081)**

IX. NMR Spectrum

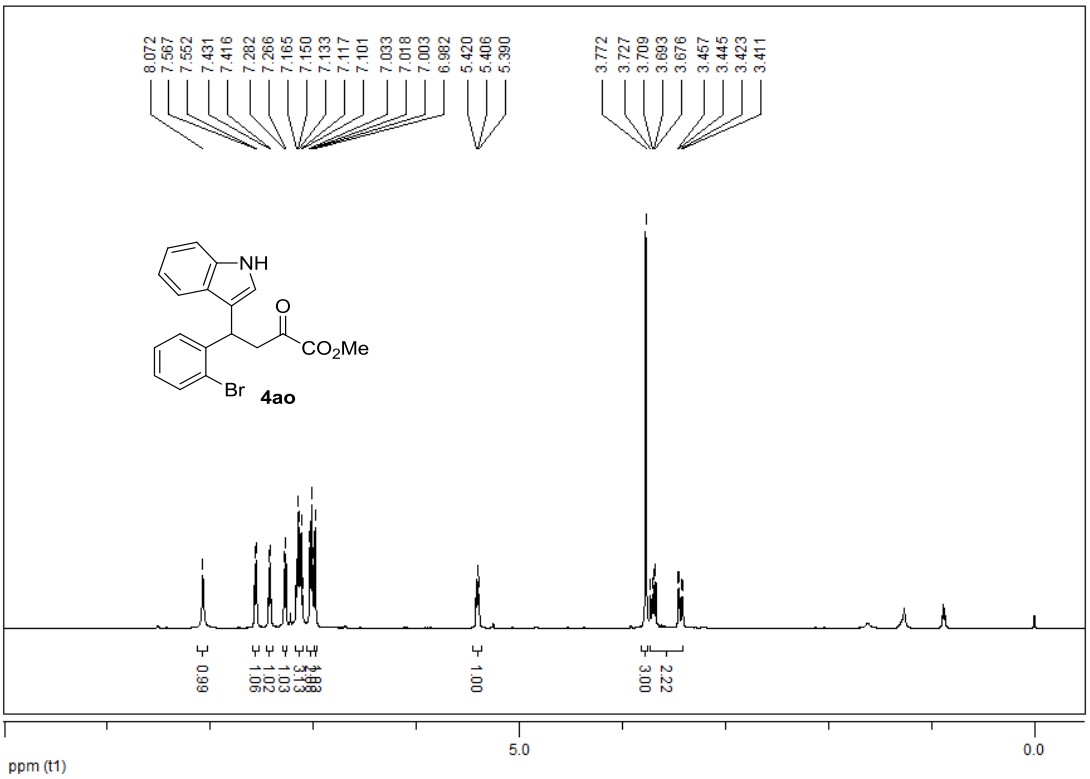
4al: ^{1}H NMR (500 MHz, $CDCl_3$)



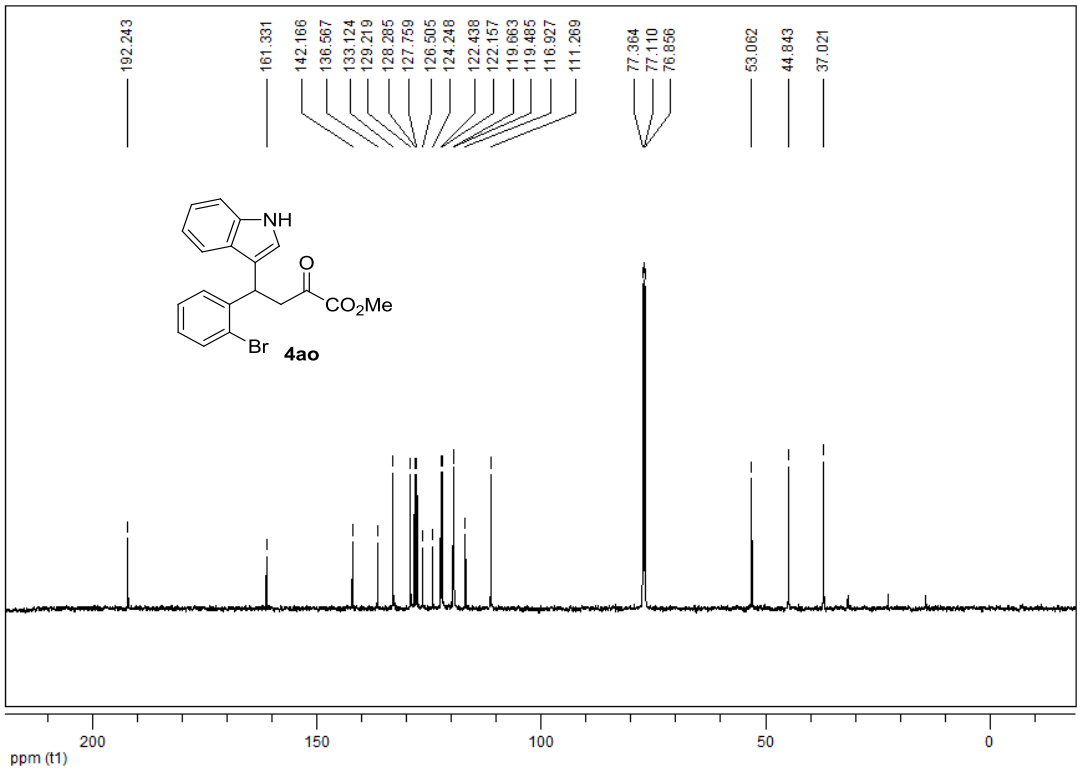
4al: ^{13}C NMR (125 MHz, $CDCl_3$)



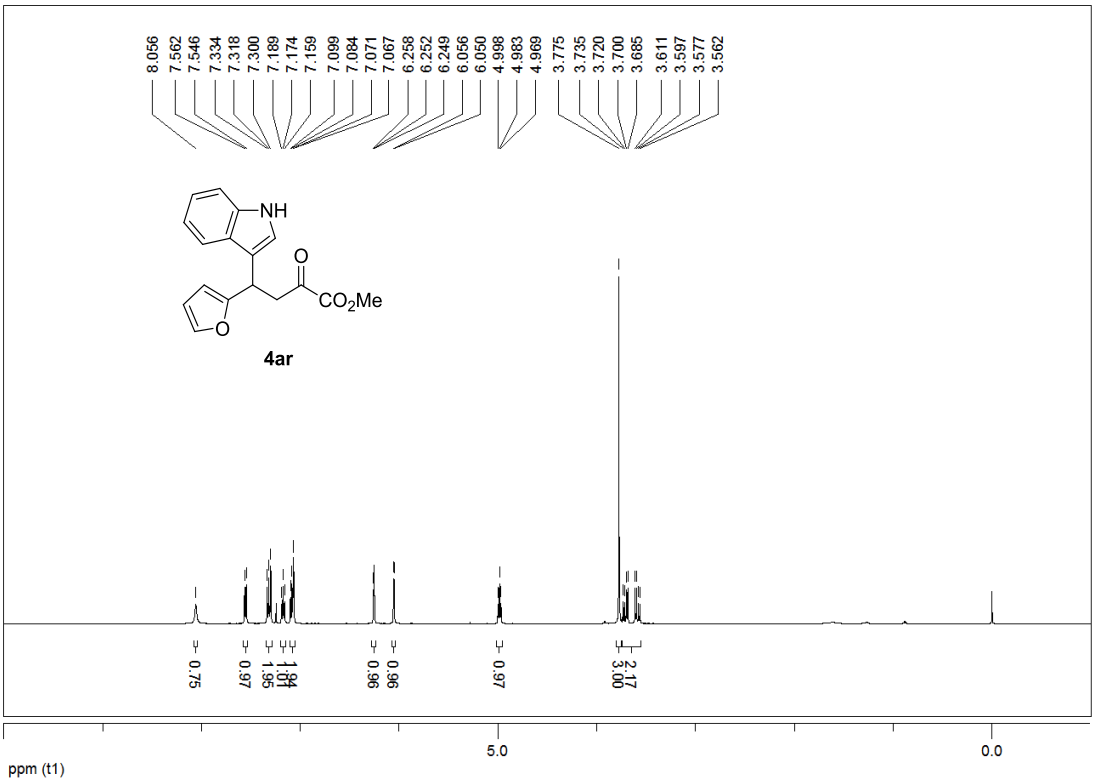
4ao: ^{1}H NMR (500 MHz, $CDCl_3$)



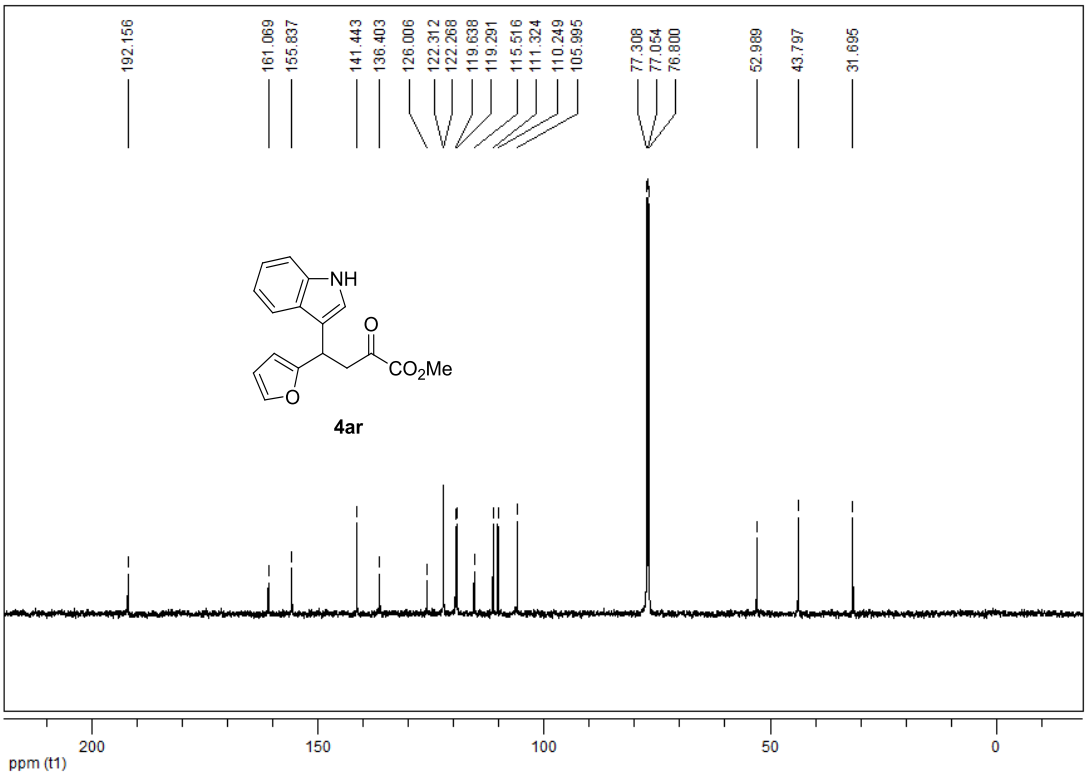
4ao: ^{13}C NMR (125 MHz, $CDCl_3$)



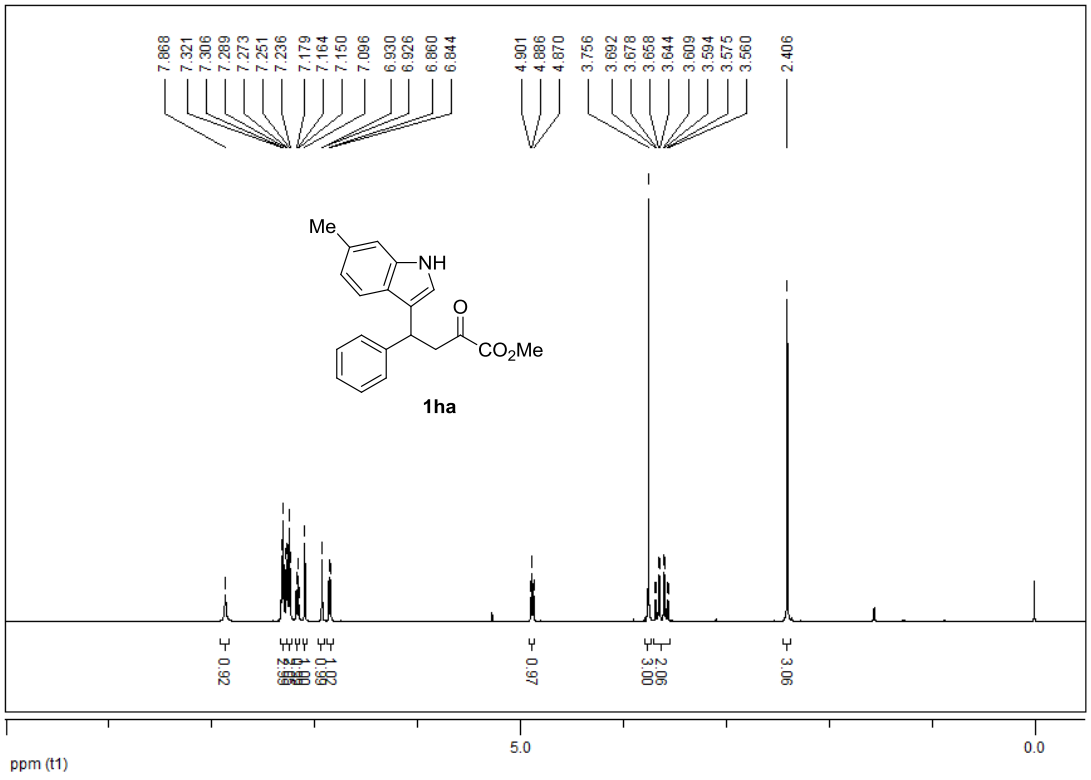
4ar: ^{1}H NMR (500 MHz, $CDCl_3$)



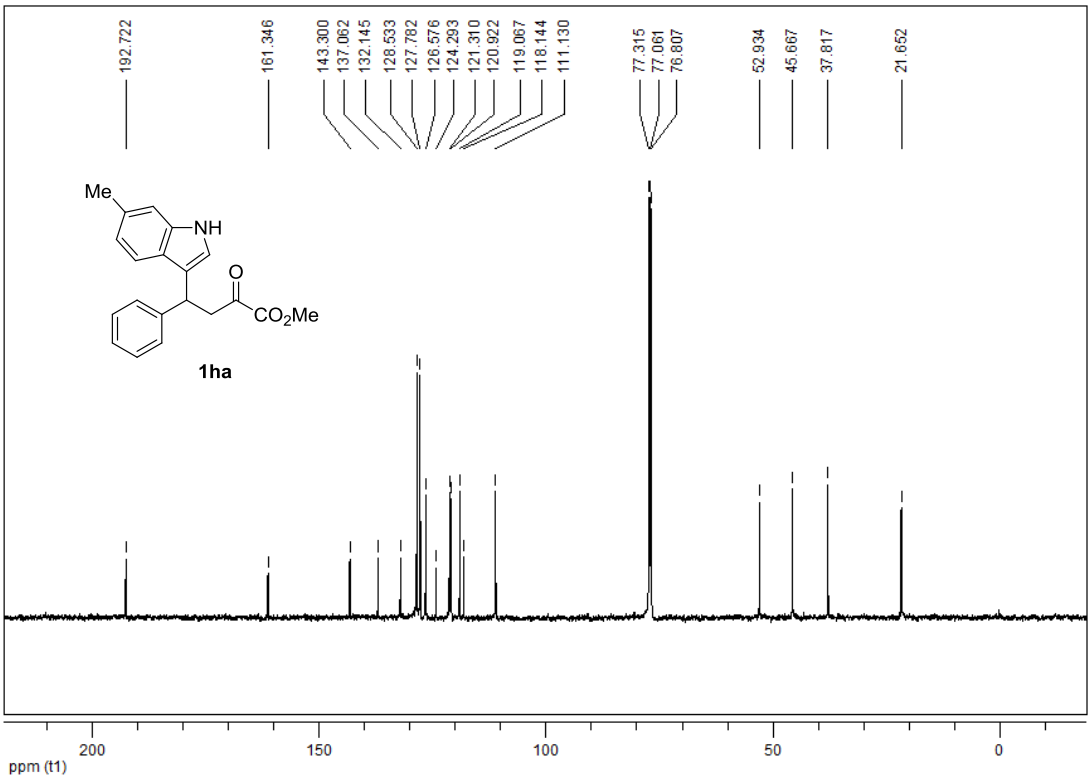
4ar: ^{13}C NMR (125 MHz, $CDCl_3$)



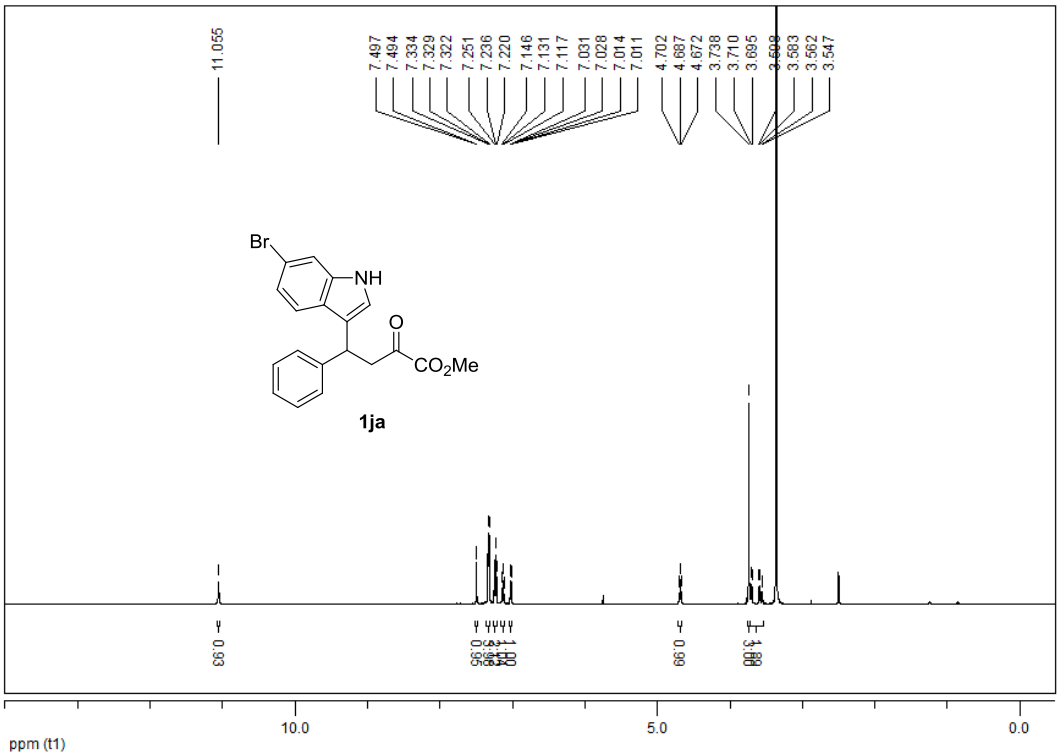
1ha: ^{1}H NMR (500 MHz, $CDCl_3$)



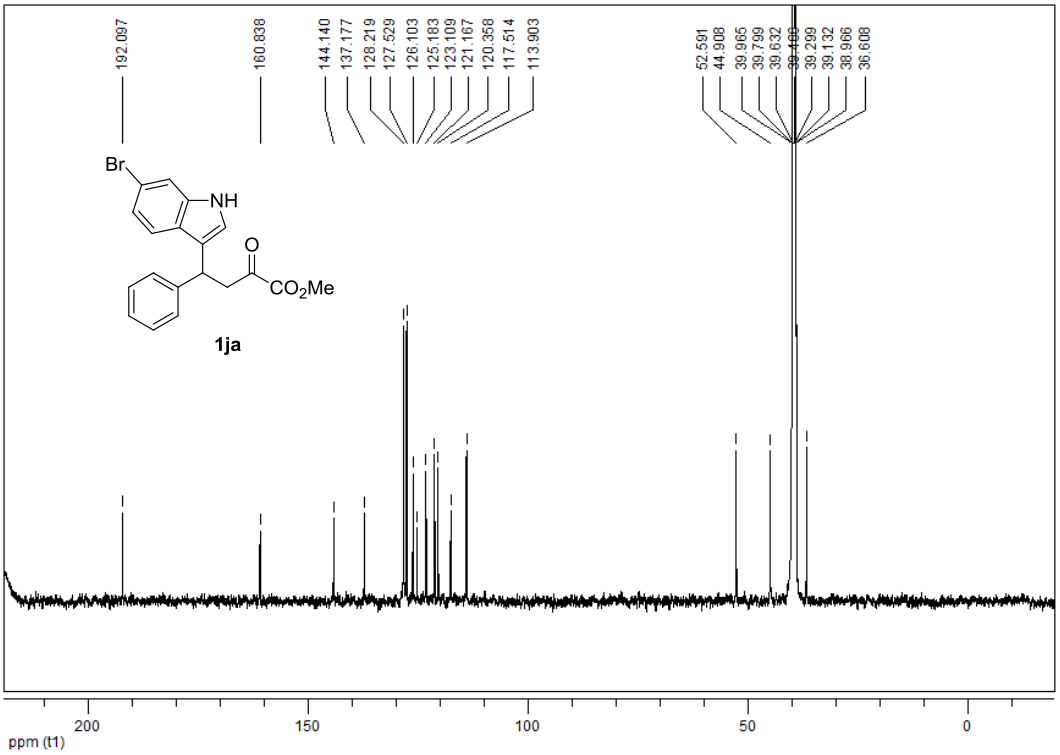
1ha: ^{13}C NMR (125 MHz, $CDCl_3$)



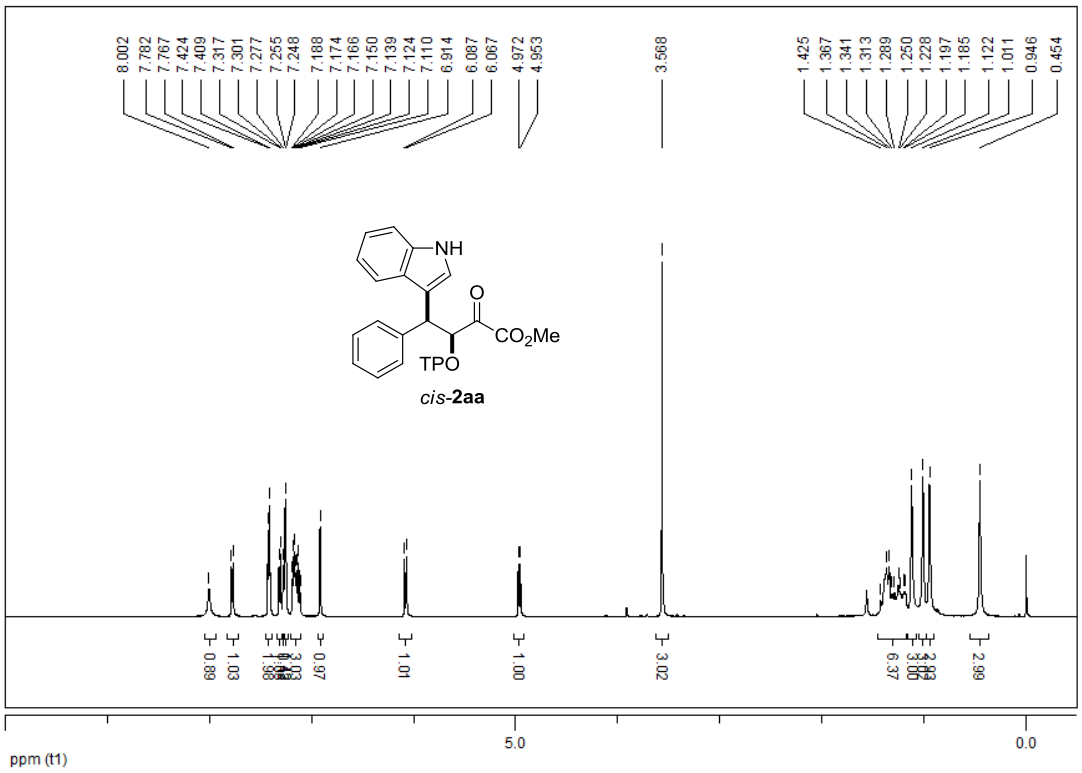
1ja: ^{1}H NMR (500 MHz, $CDCl_3$)



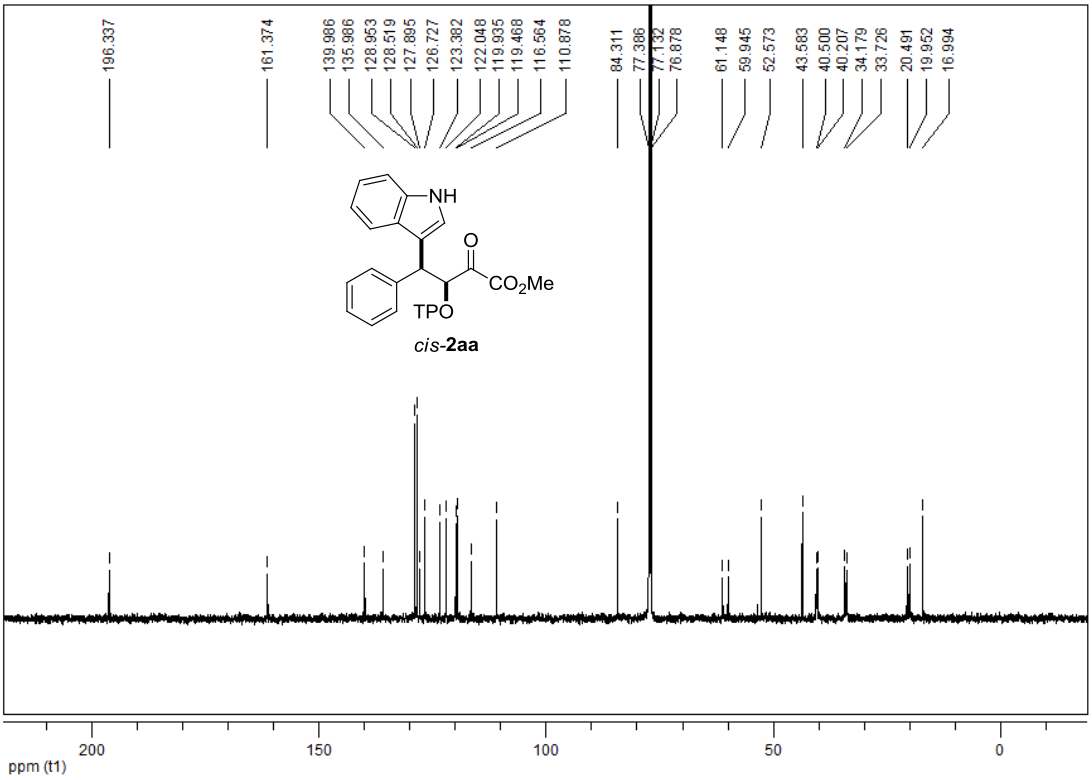
1ja: ^{13}C NMR (125 MHz, $CDCl_3$)



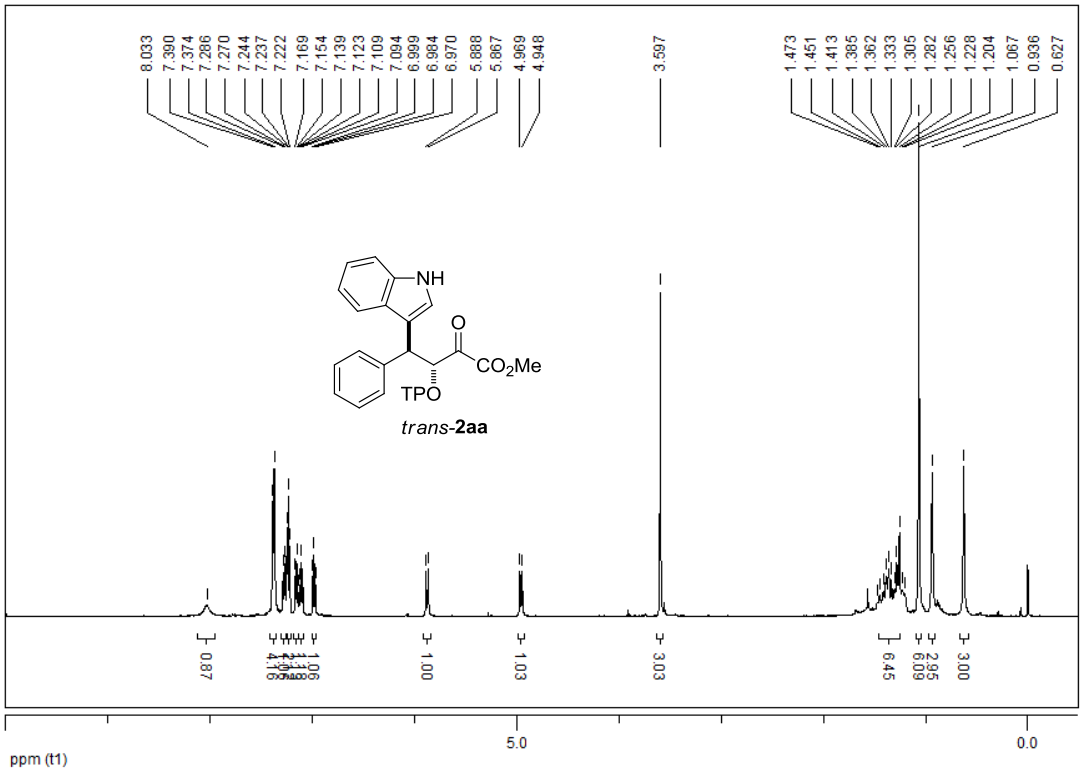
cis-2aa: ^{1}H NMR (500 MHz, $CDCl_3$)

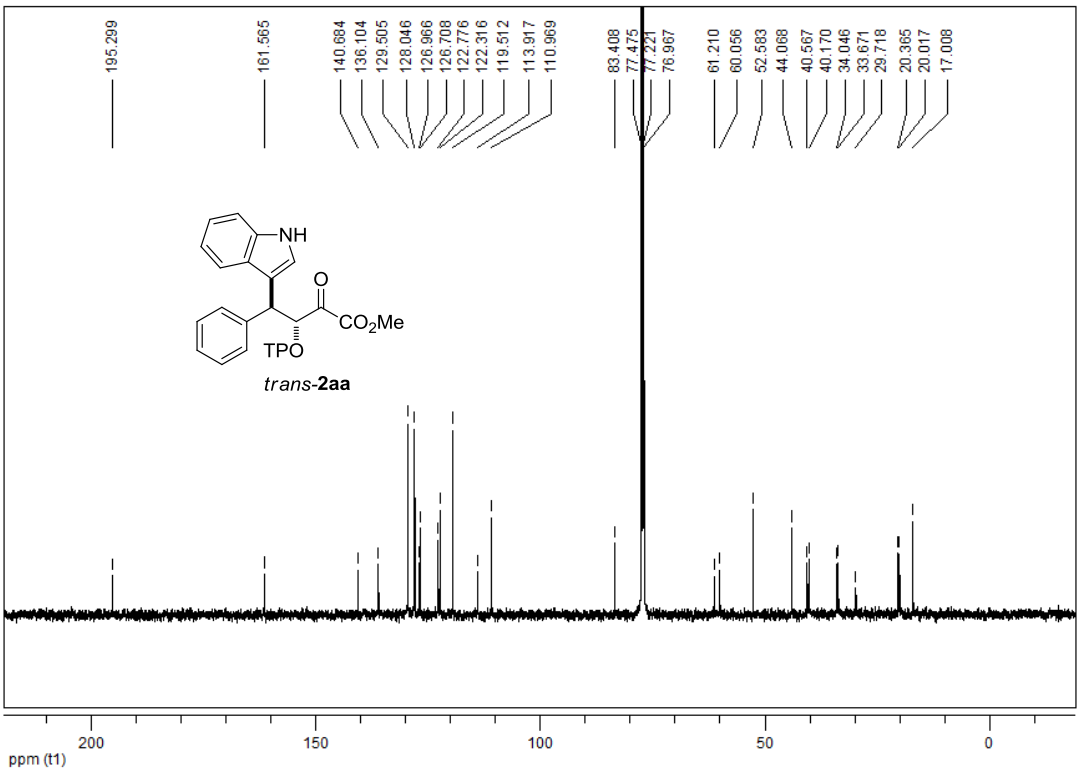


cis-2aa: ^{13}C NMR (125 MHz, $CDCl_3$)

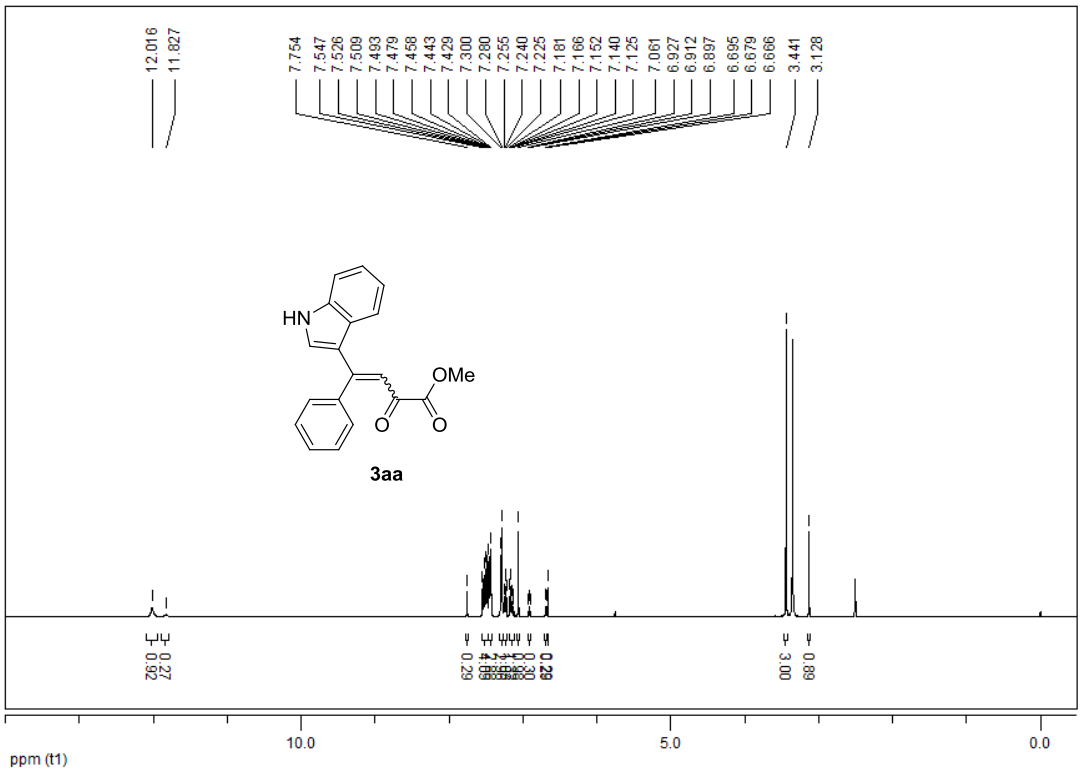


***trans*-2aa: ^{1}H NMR (500 MHz, $CDCl_3$)**

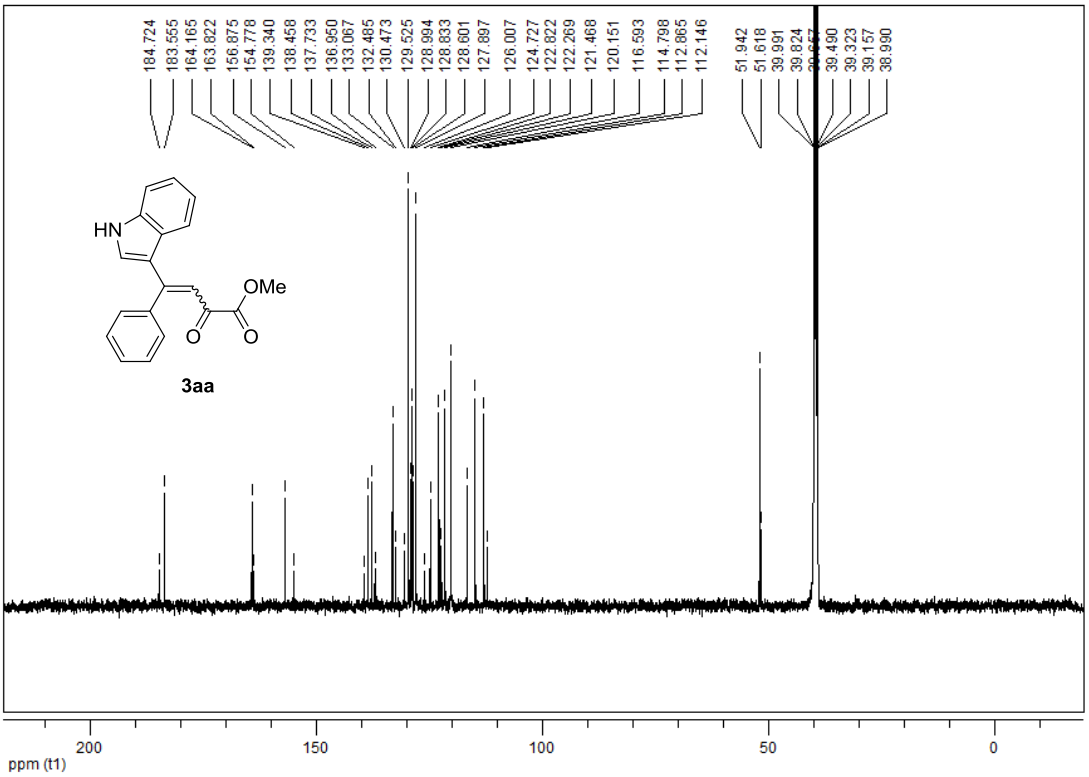




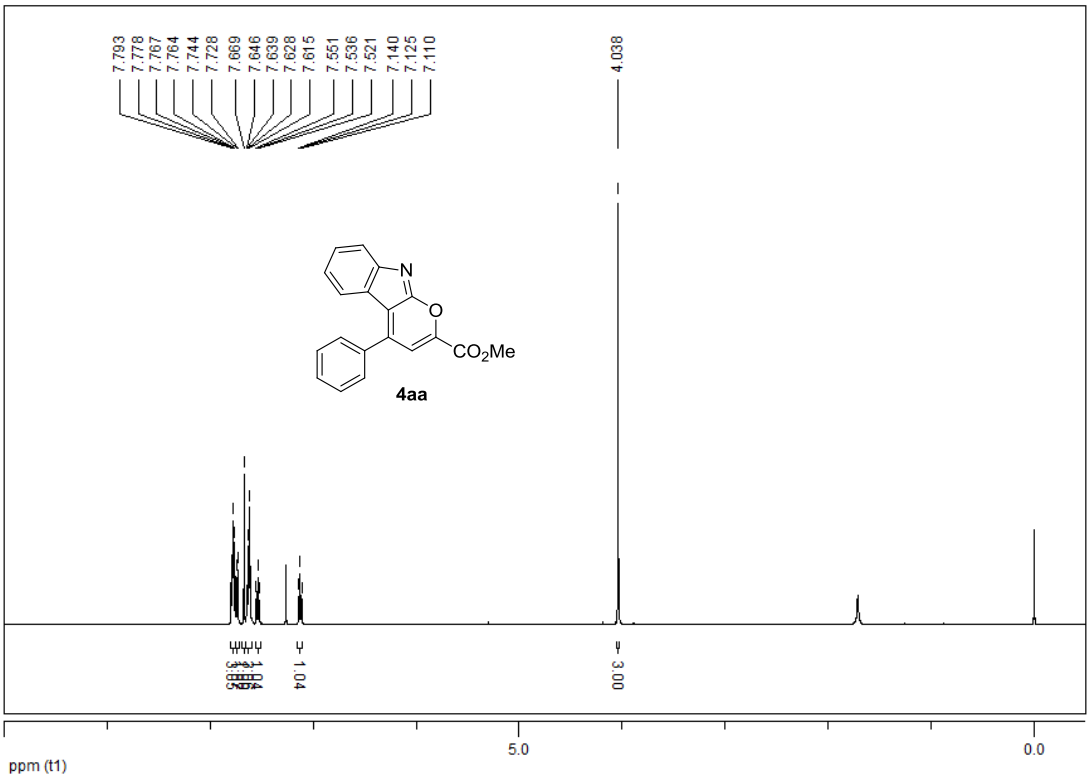
3aa: ^{1}H NMR (500 MHz, DMSO-d$_6$)



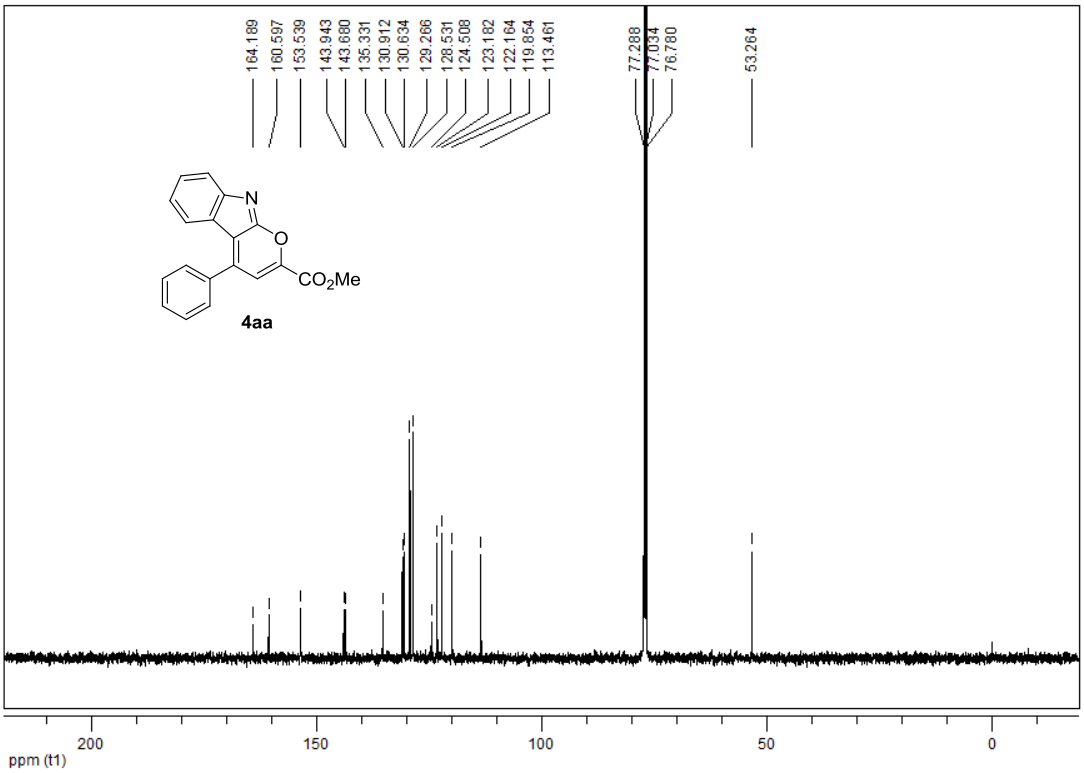
3aa: ^{13}C NMR (125 MHz, DMSO-d$_6$)



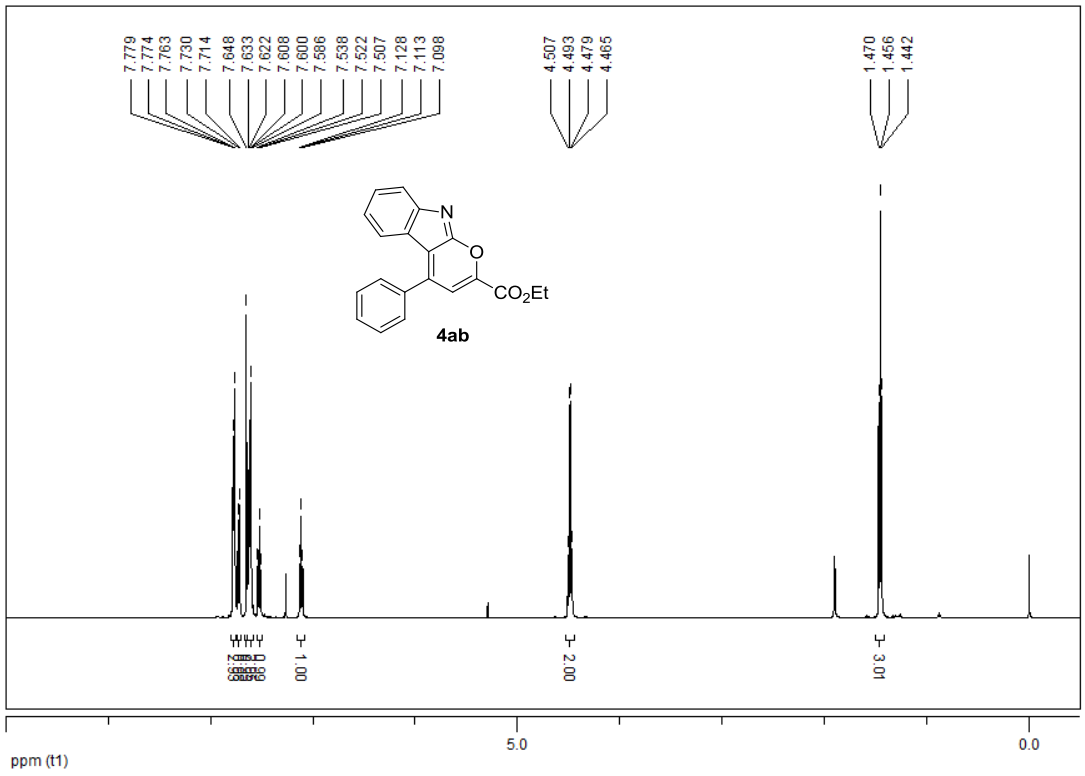
4aa: ^{1}H NMR (500 MHz, $CDCl_3$)



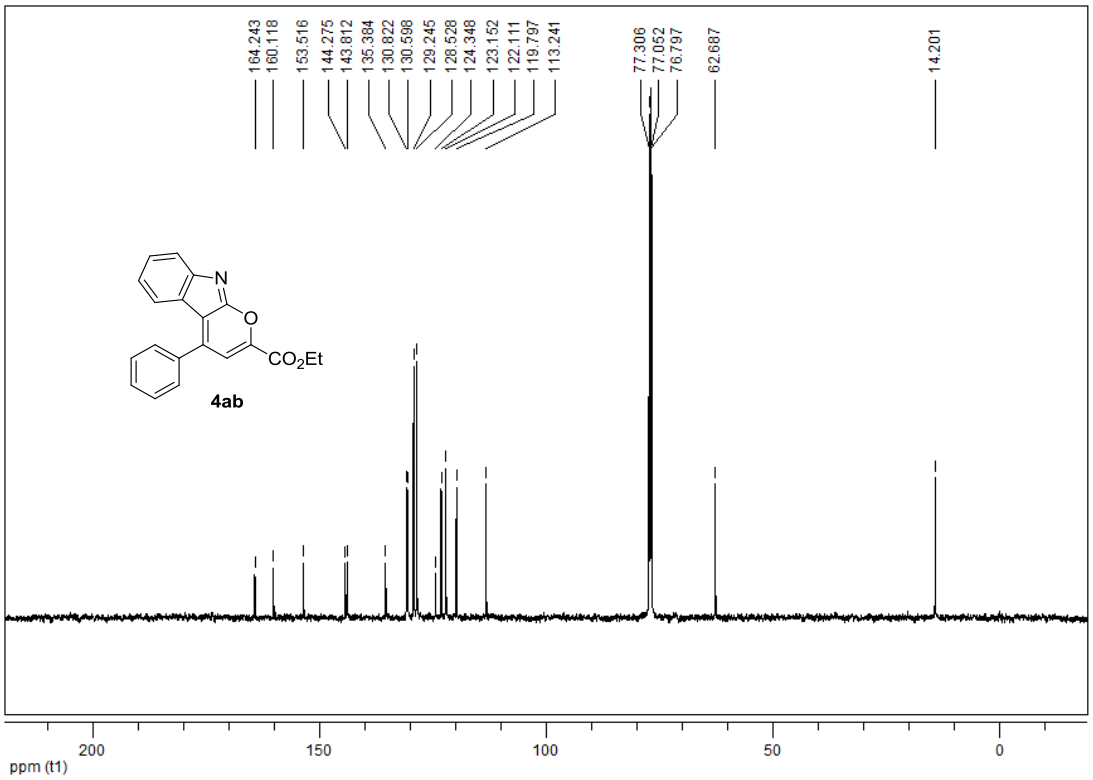
4aa: ^{13}C NMR (125 MHz, $CDCl_3$)



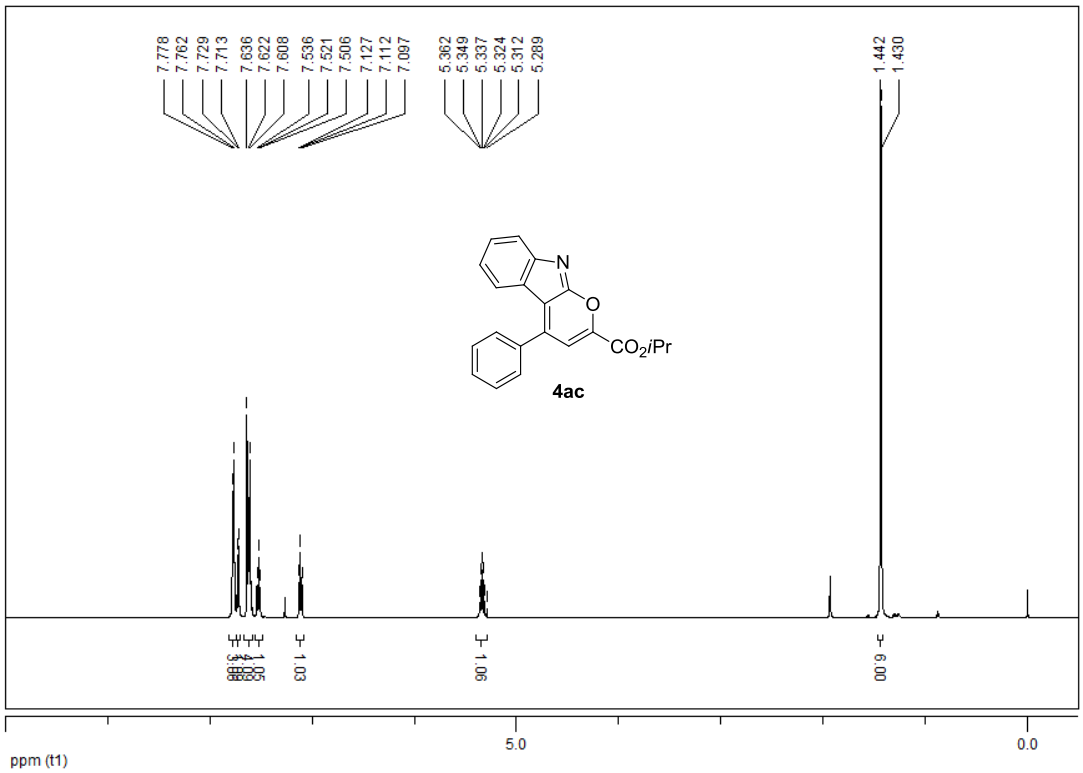
4ab: ^{1}H NMR (500 MHz, $CDCl_3$)



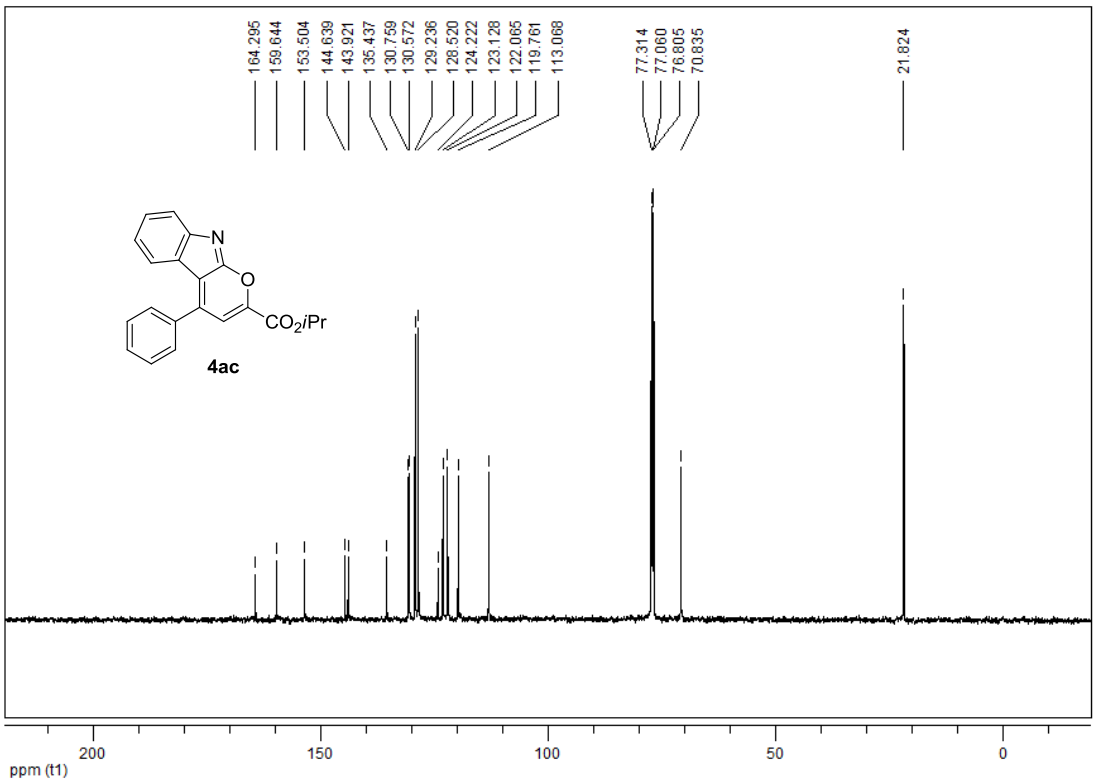
4ab: ^{13}C NMR (125 MHz, $CDCl_3$)



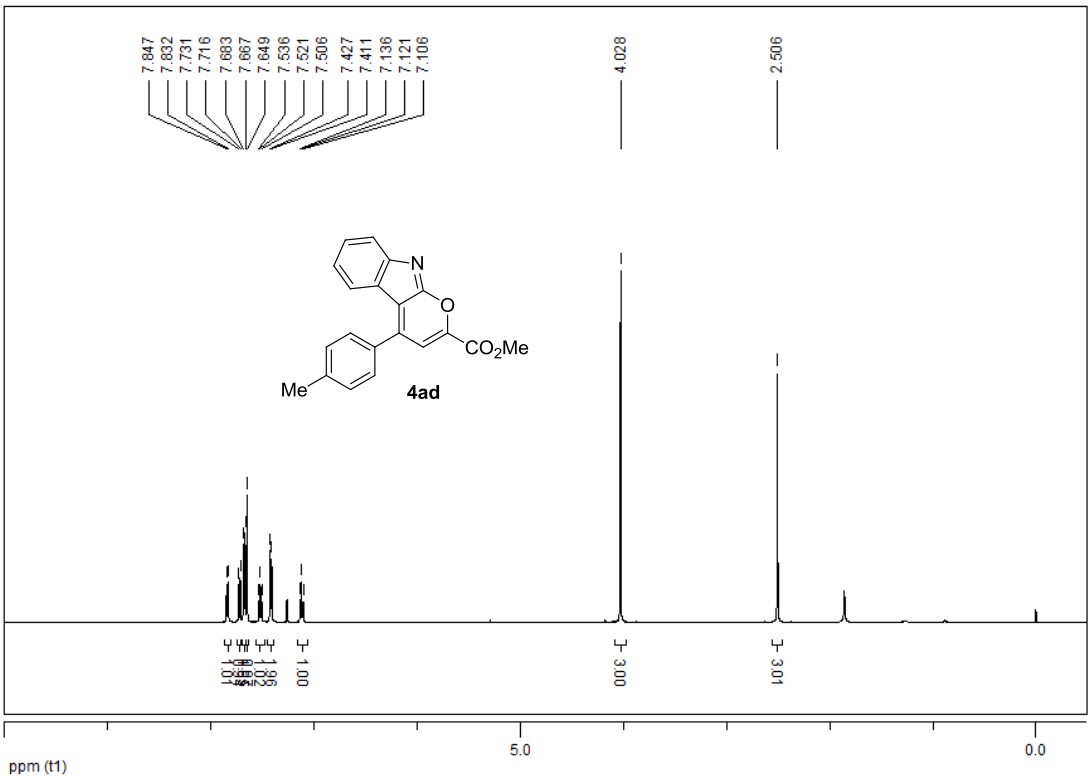
4ac: ^{1}H NMR (500 MHz, $CDCl_3$)



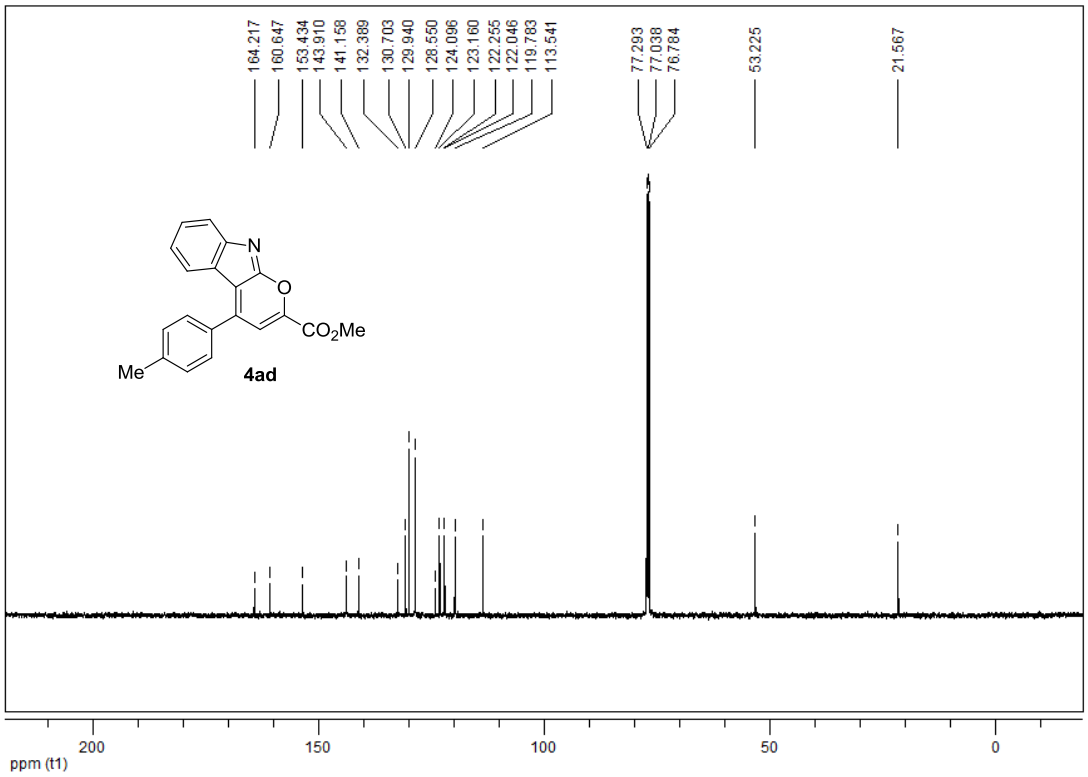
4ac: ^{13}C NMR (125 MHz, $CDCl_3$)



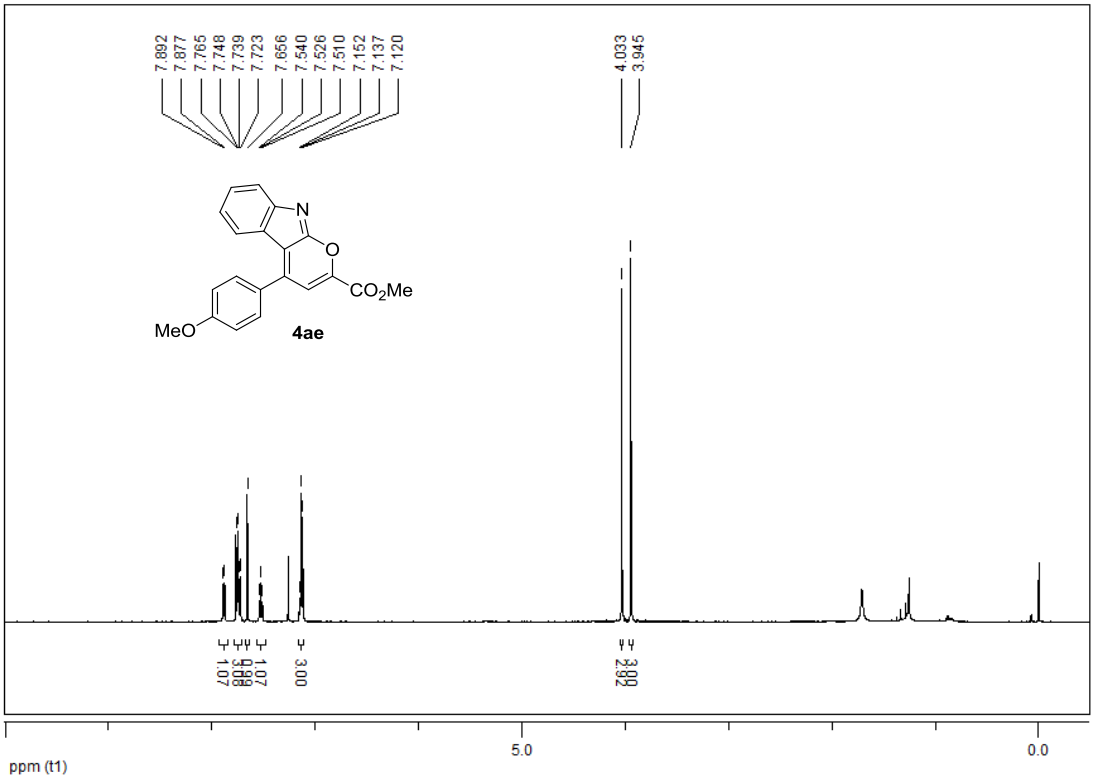
4ad: ^{1}H NMR (500 MHz, $CDCl_3$)



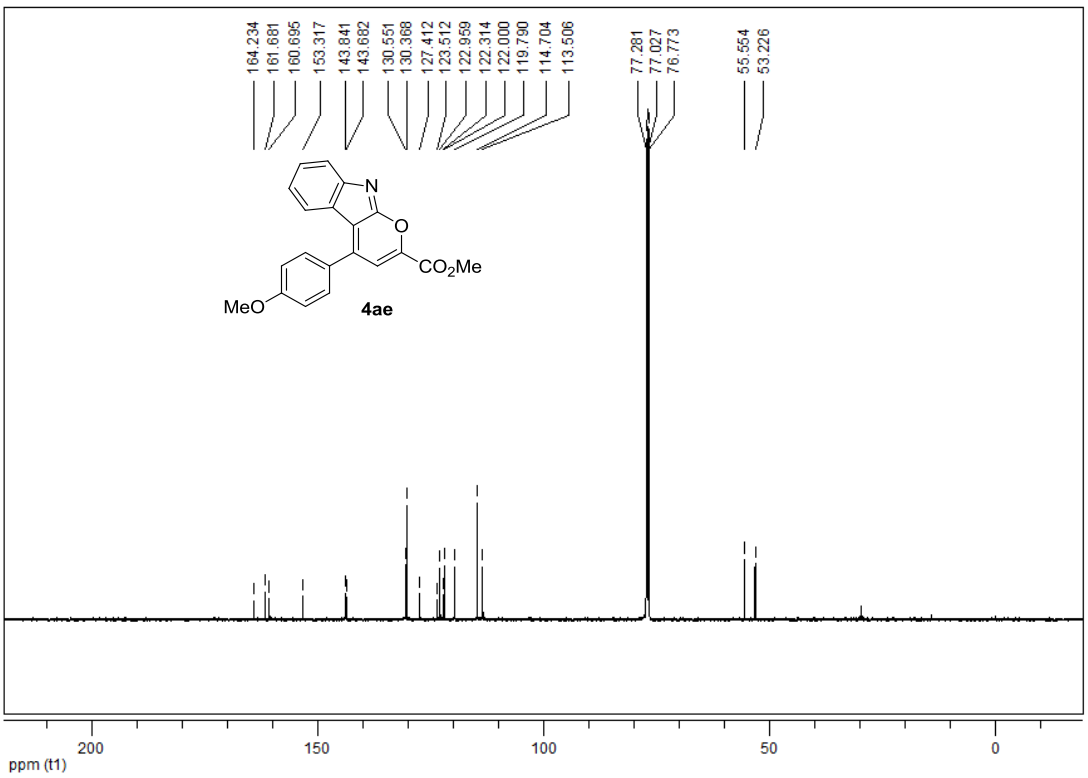
4ad: ^{13}C NMR (125 MHz, $CDCl_3$)



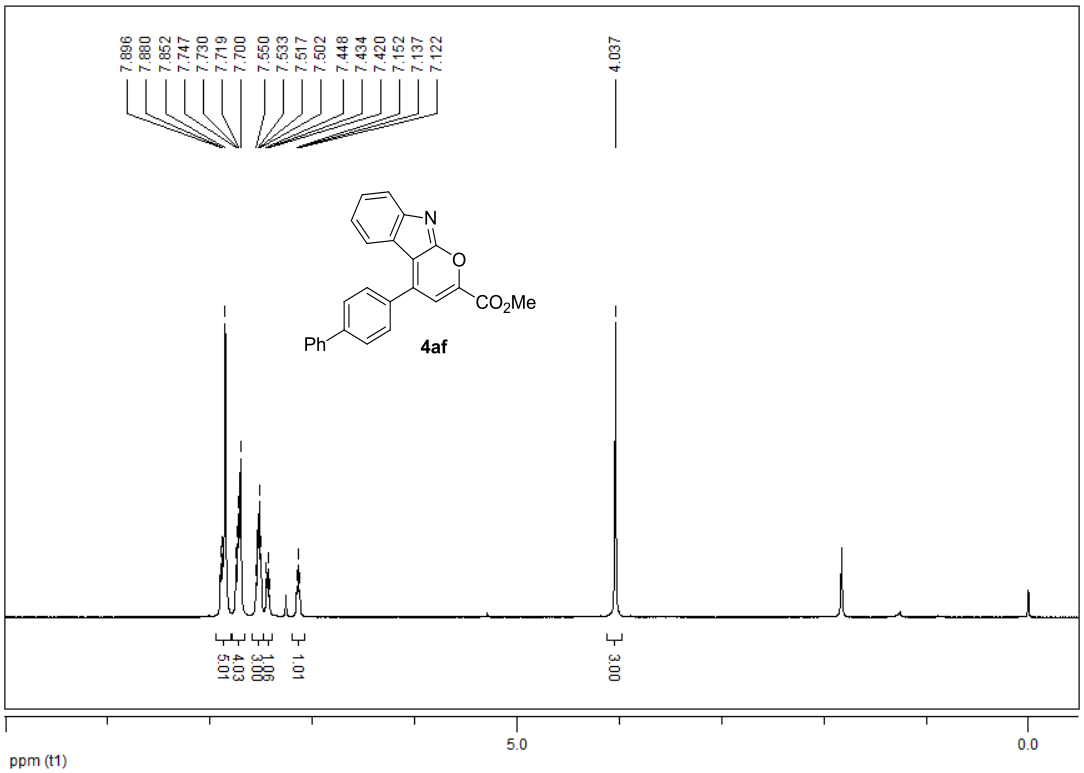
4ae: ^{1}H NMR (500 MHz, $CDCl_3$)



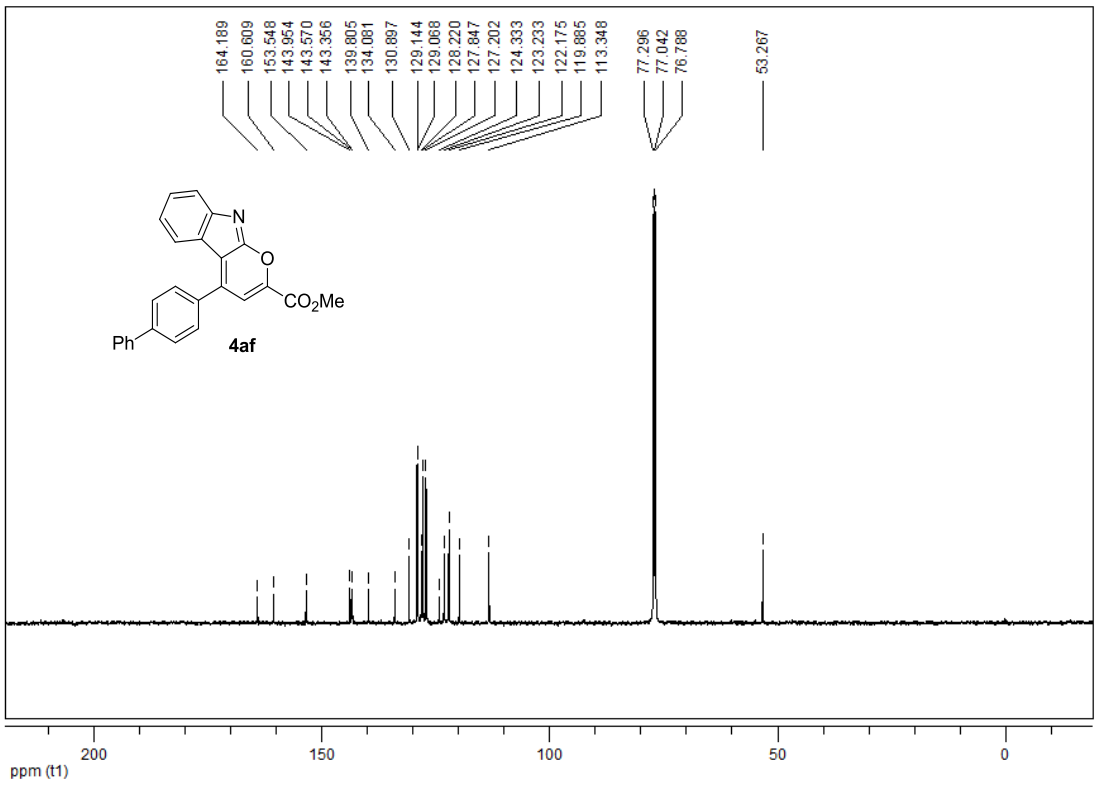
4ae: ^{13}C NMR (125 MHz, $CDCl_3$)



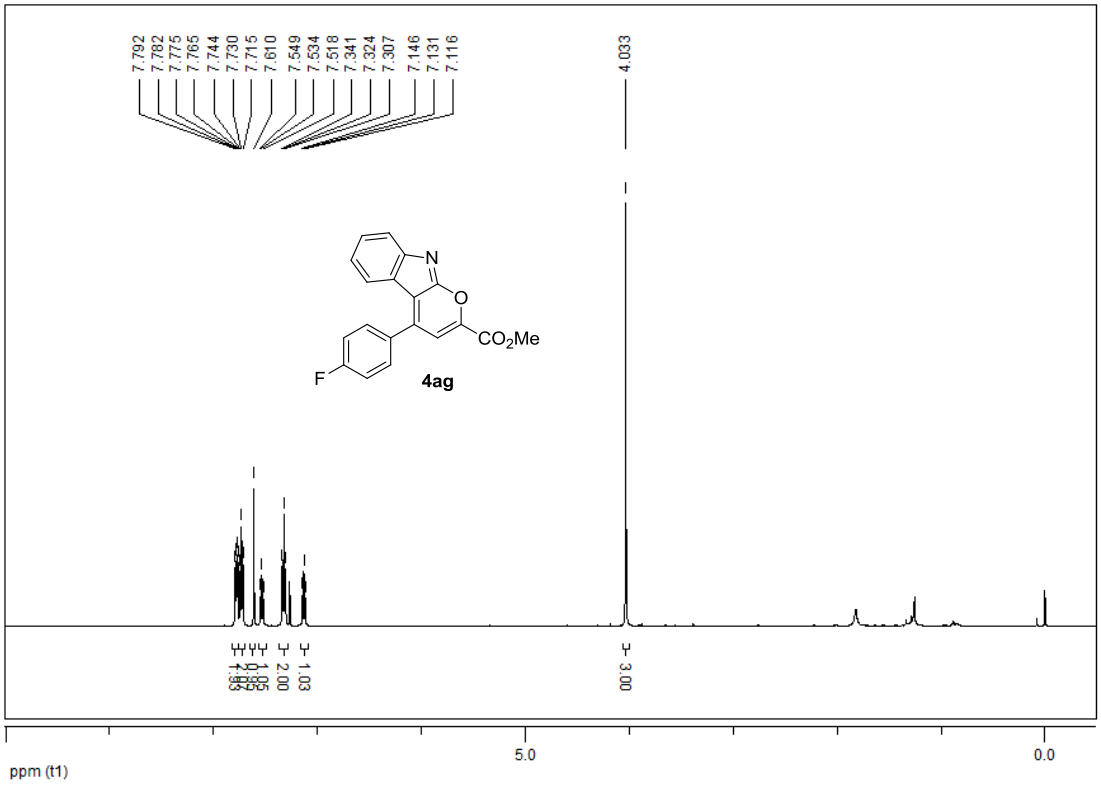
4af: ^{1}H NMR (500 MHz, $CDCl_3$)



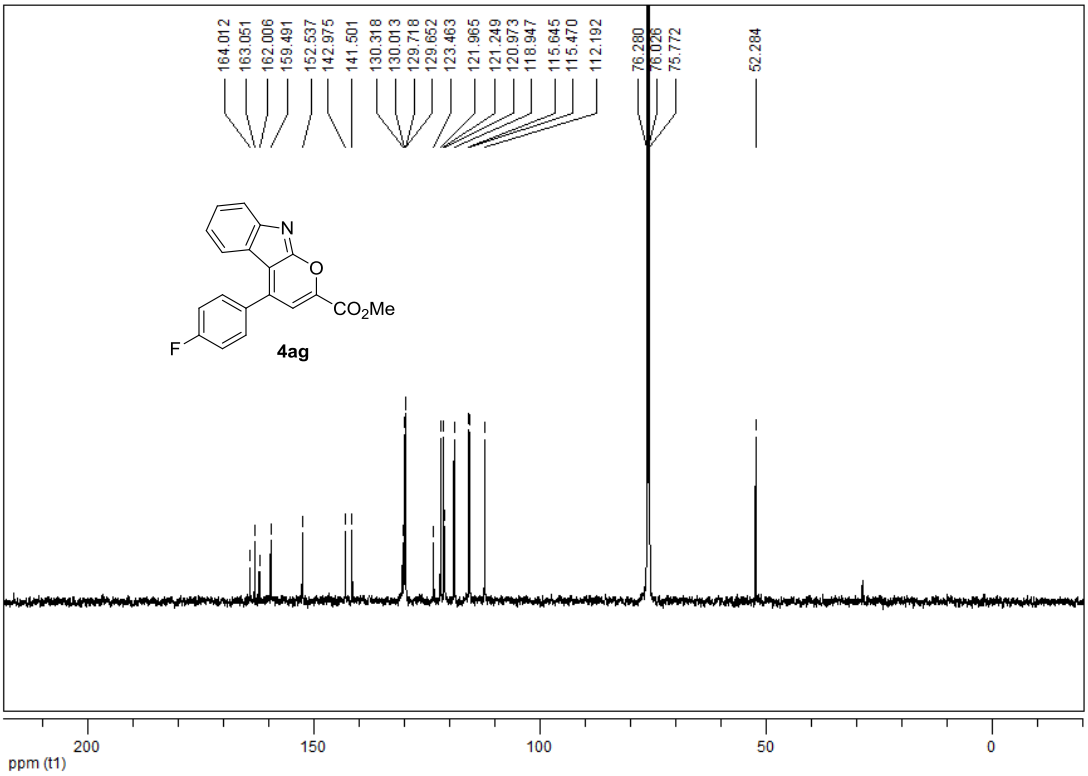
4af: ^{13}C NMR (125 MHz, $CDCl_3$)



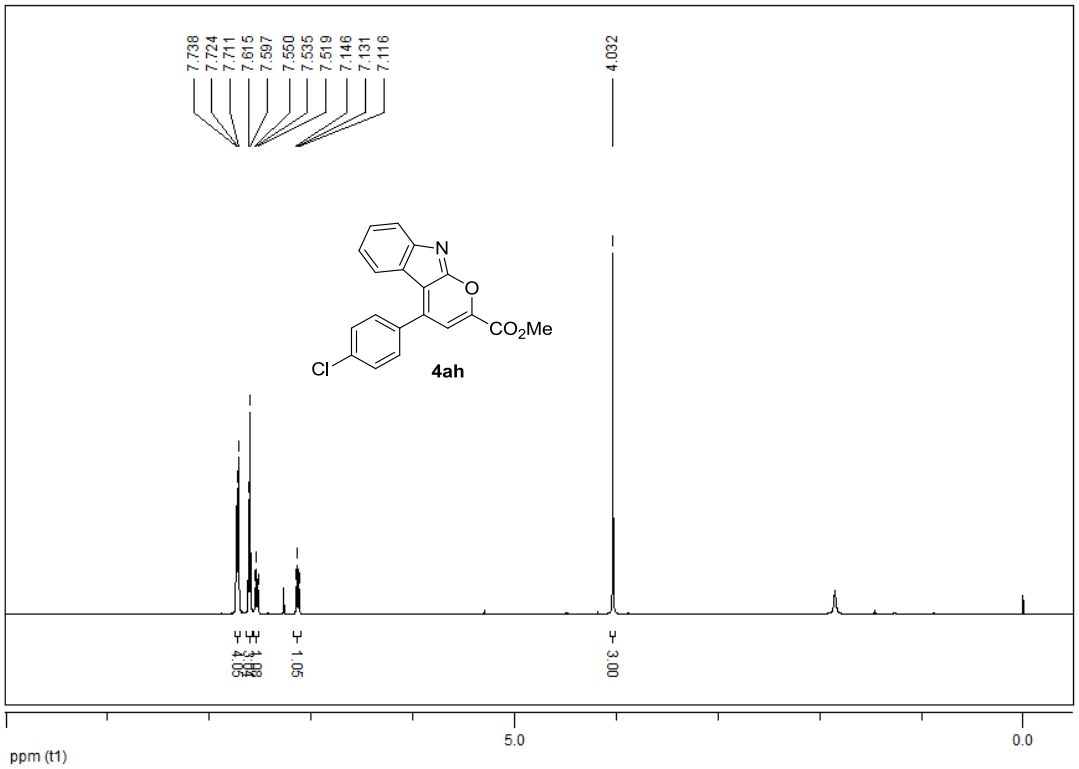
4ag: ^{1}H NMR (500 MHz, $CDCl_3$)



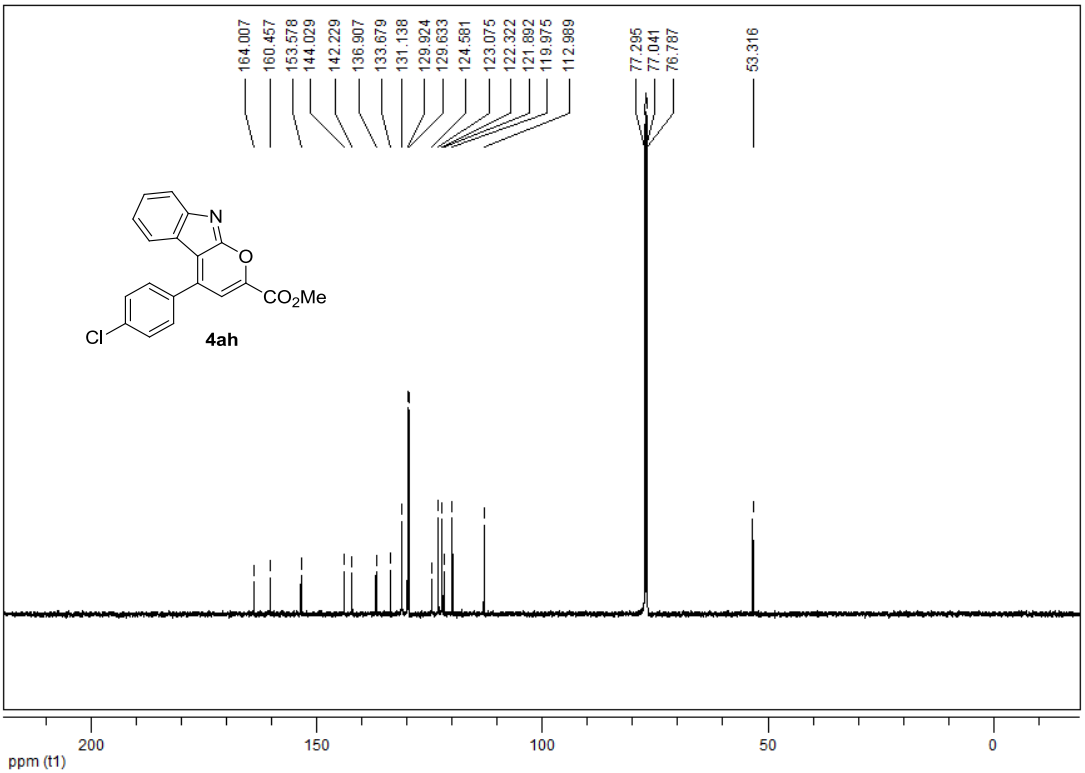
4ag: ^{13}C NMR (125 MHz, $CDCl_3$)



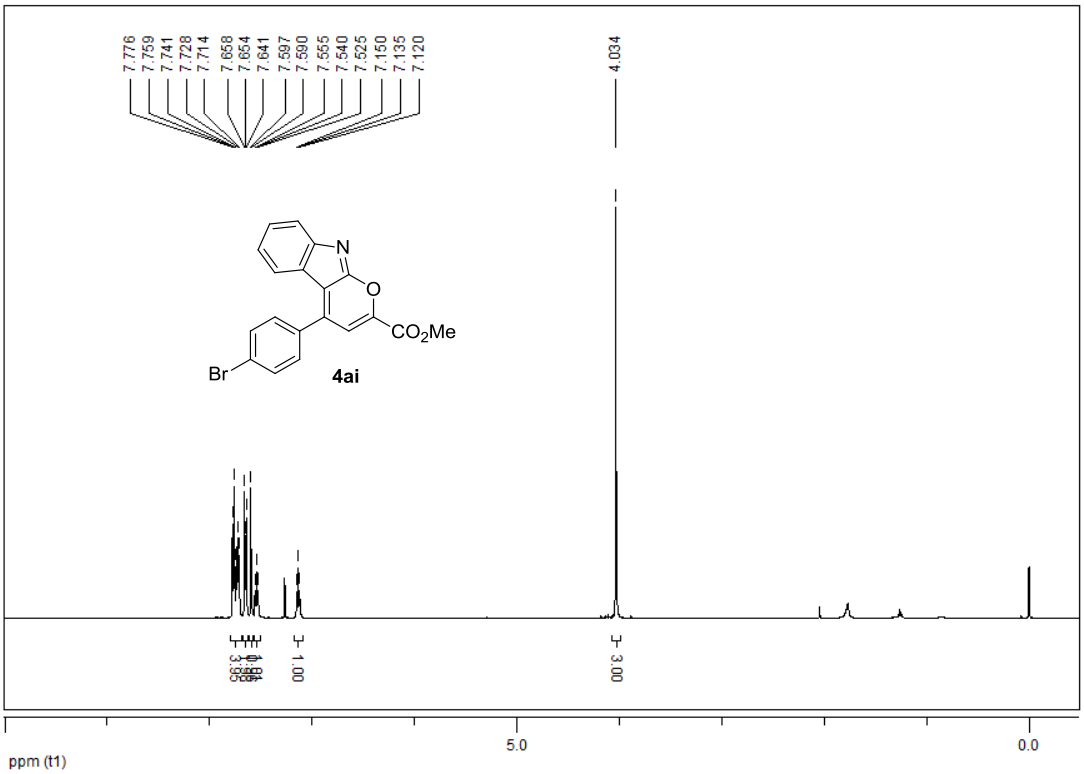
4ah: ^{1}H NMR (500 MHz, $CDCl_3$)



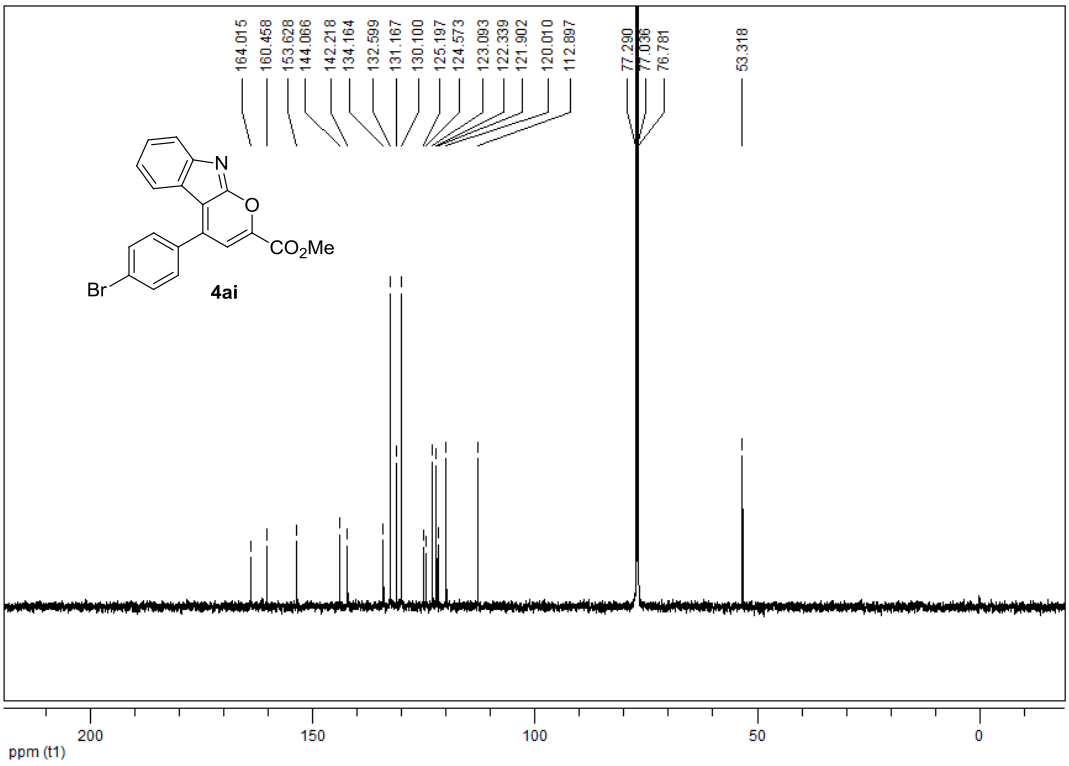
4ah: ^{13}C NMR (125 MHz, $CDCl_3$)



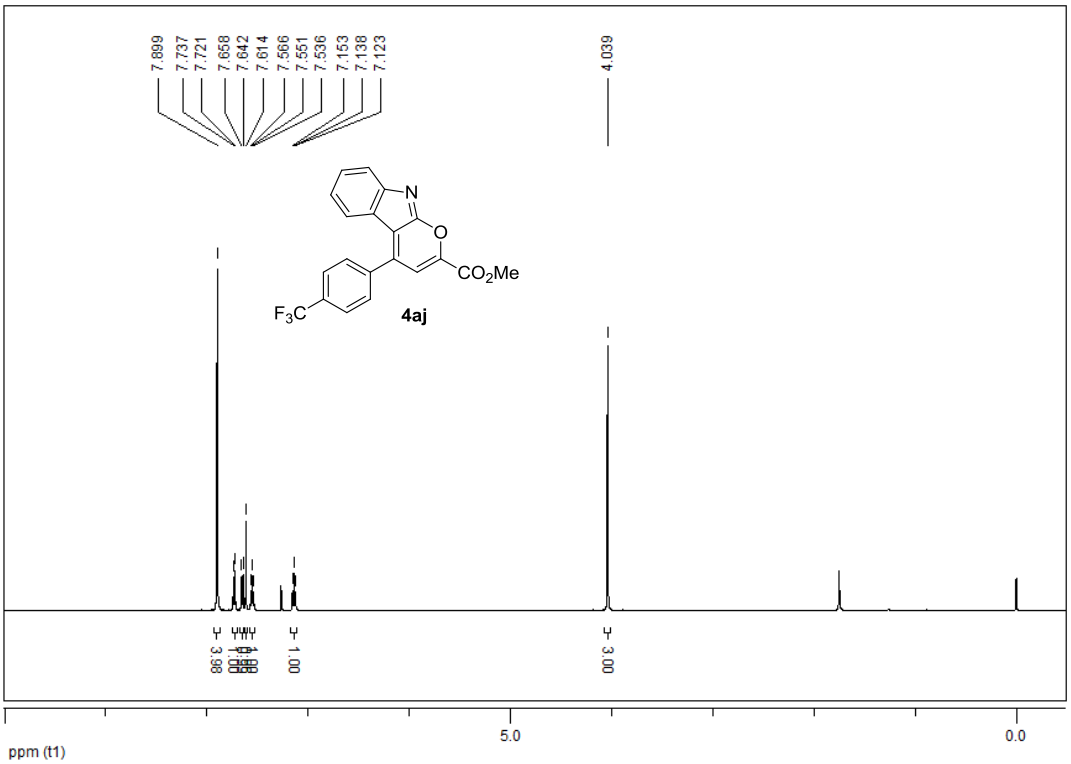
4ai: ^{1}H NMR (500 MHz, $CDCl_3$)



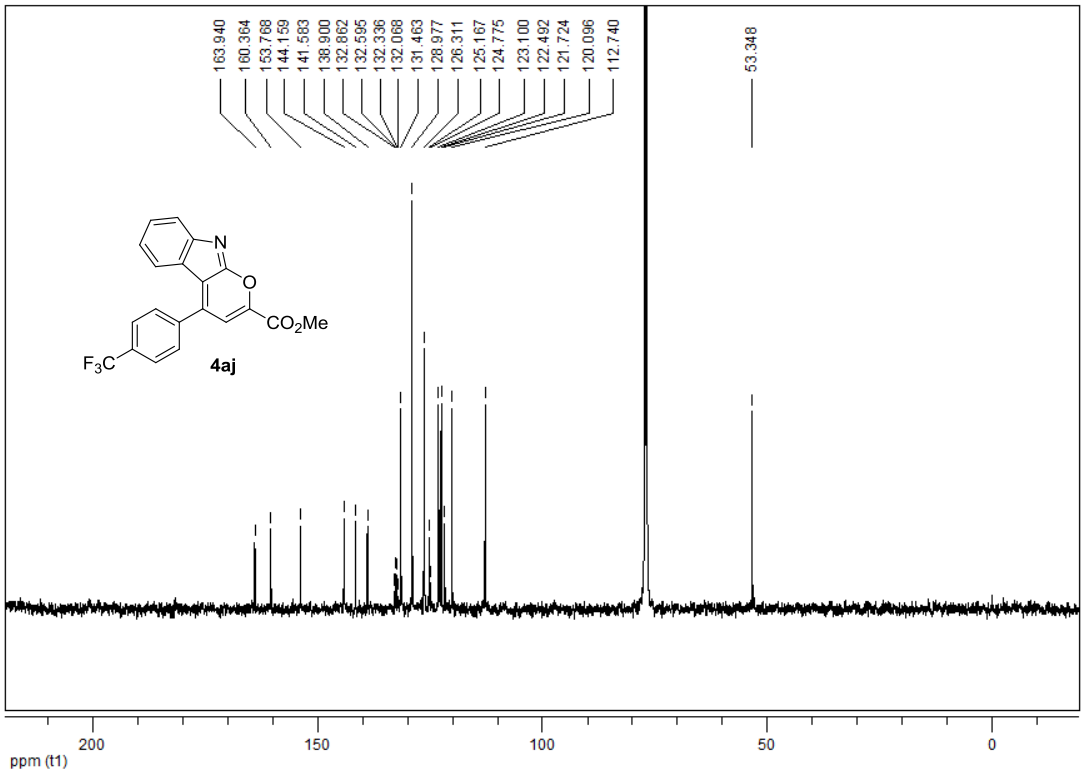
4ai: ^{13}C NMR (125 MHz, $CDCl_3$)



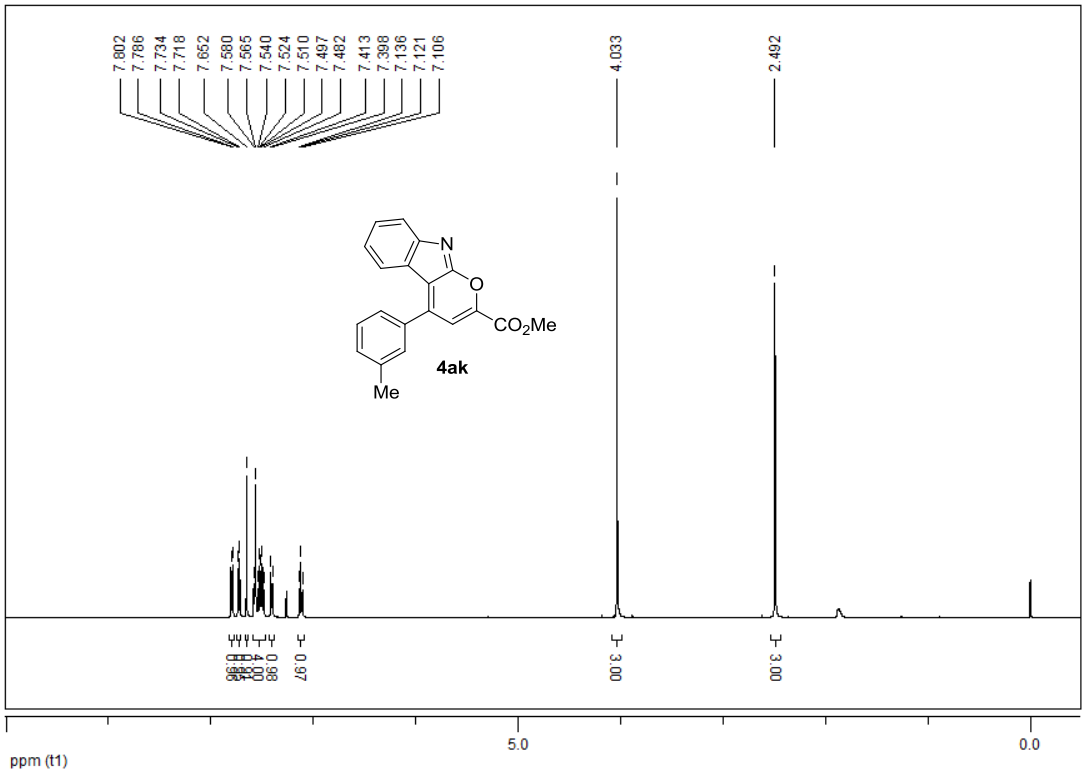
4aj: ^{1}H NMR (500 MHz, $CDCl_3$)



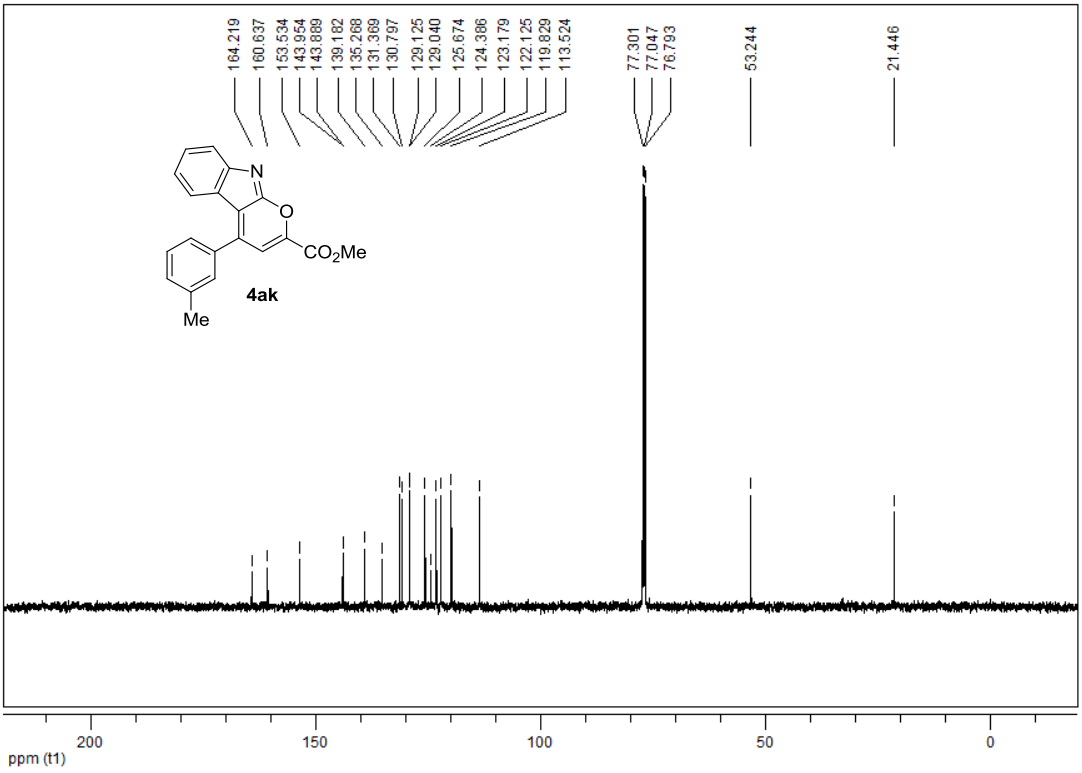
4aj: ^{13}C NMR (125 MHz, $CDCl_3$)



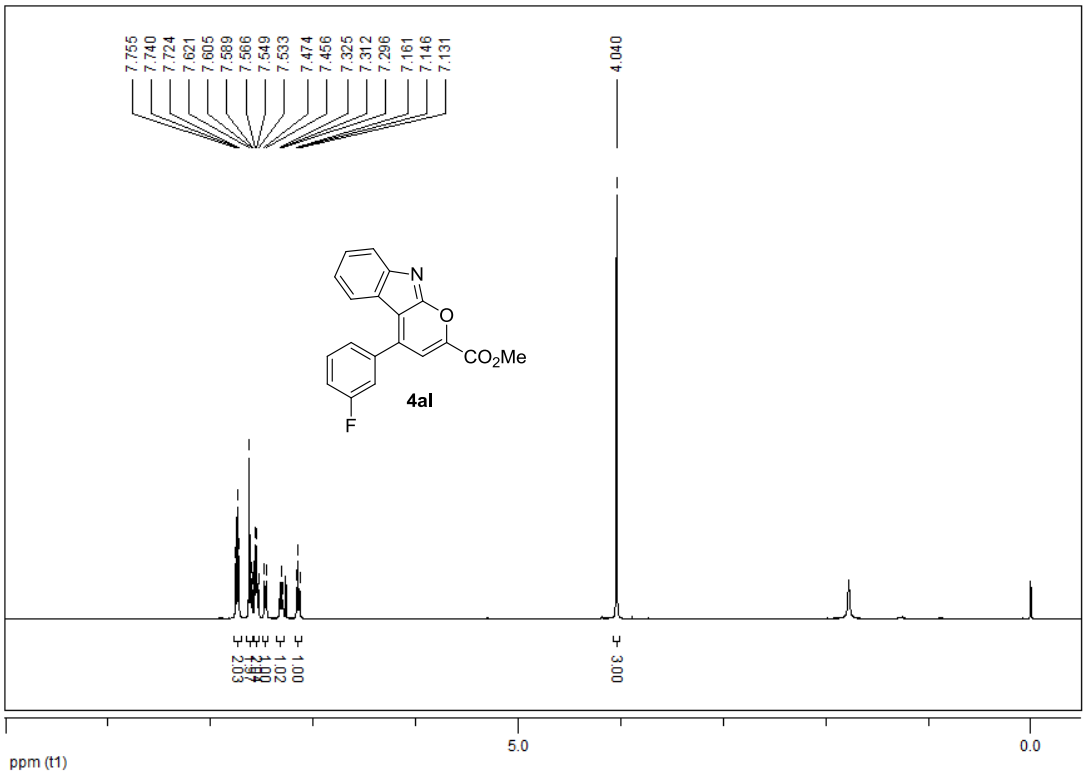
4ak: ^{1}H NMR (500 MHz, $CDCl_3$)



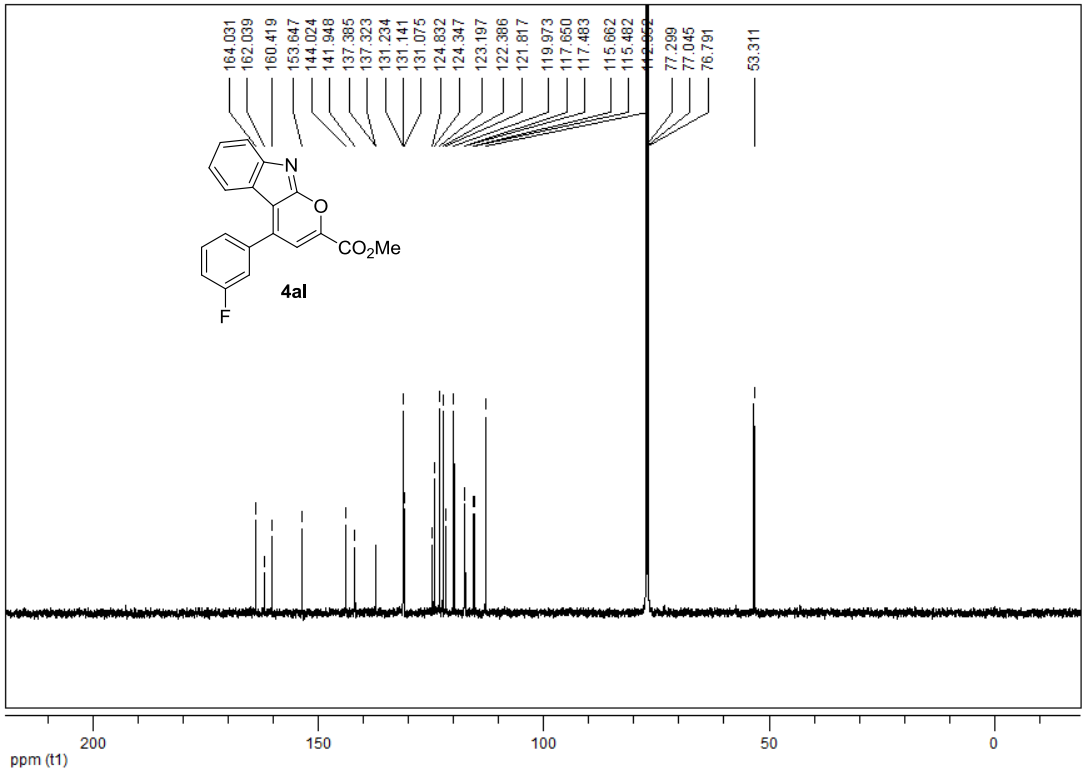
4ak: ^{13}C NMR (125 MHz, $CDCl_3$)



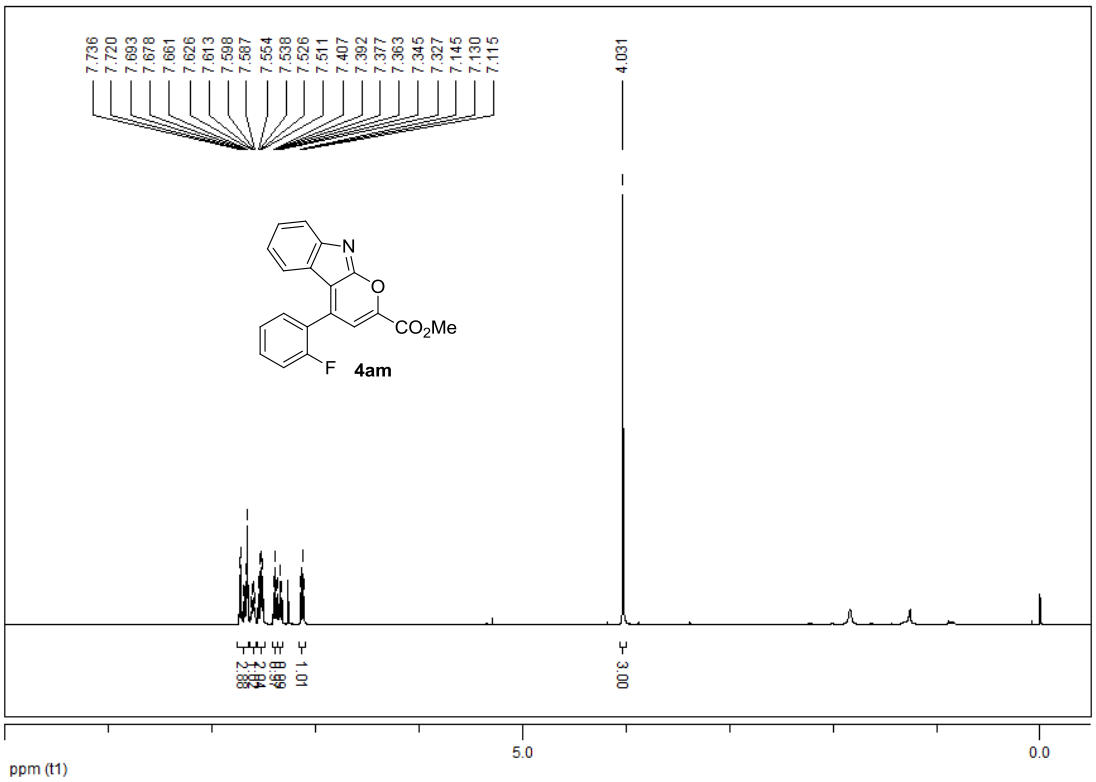
4al: ^{1}H NMR (500 MHz, $CDCl_3$)



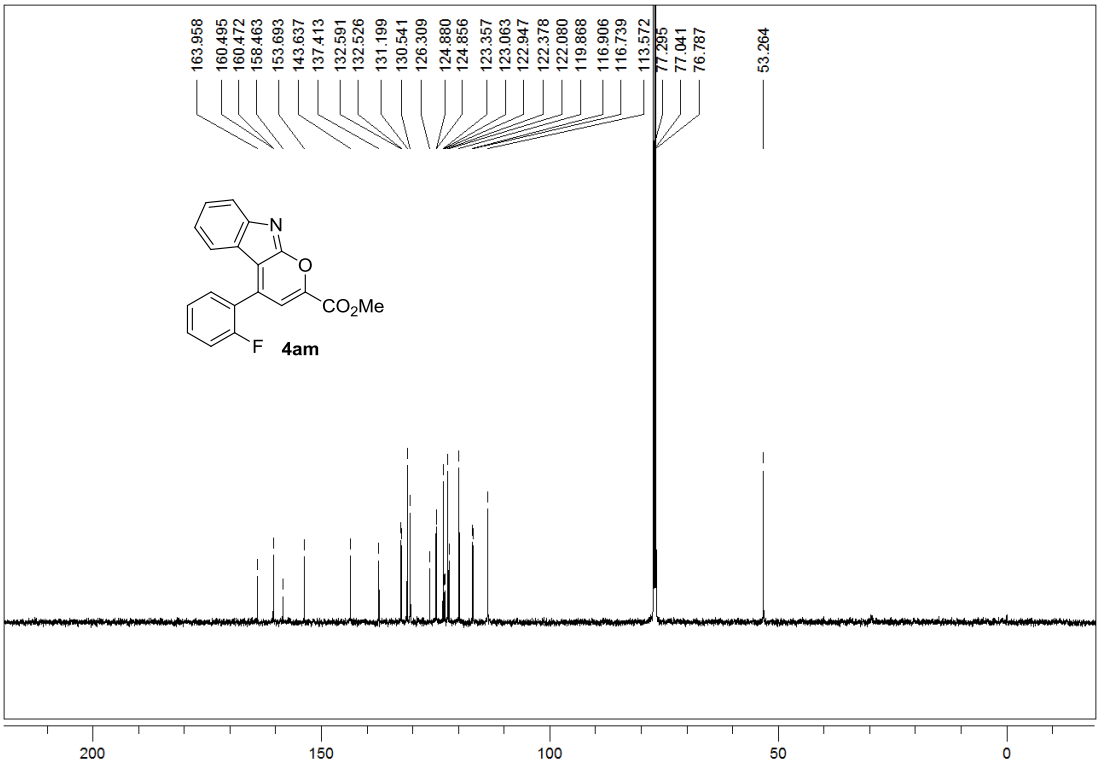
4al: ^{13}C NMR (125 MHz, $CDCl_3$)



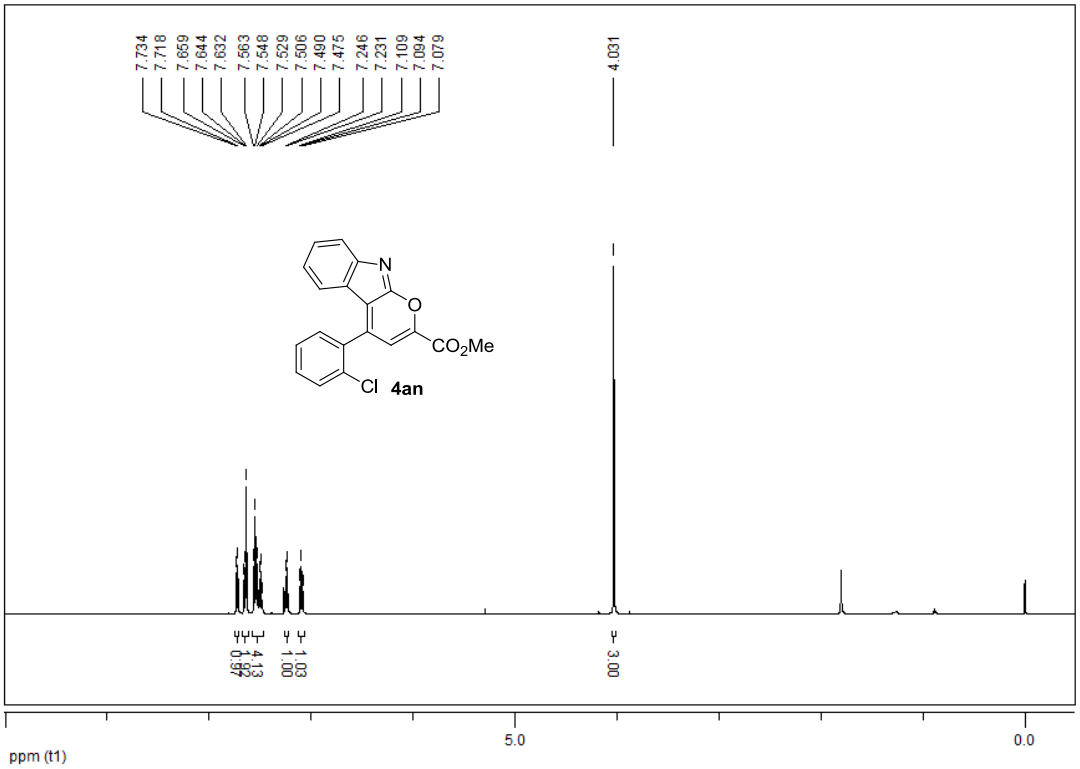
4am: ^{1}H NMR (500 MHz, $CDCl_3$)



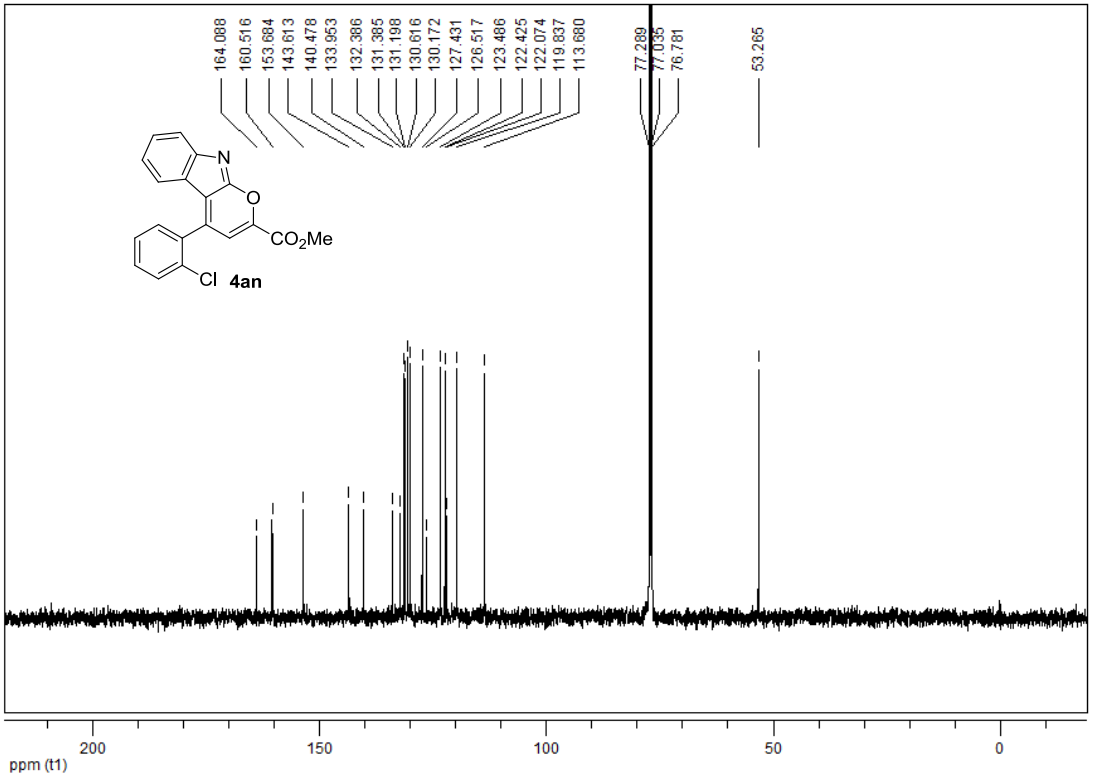
4am: ^{13}C NMR (125 MHz, $CDCl_3$)



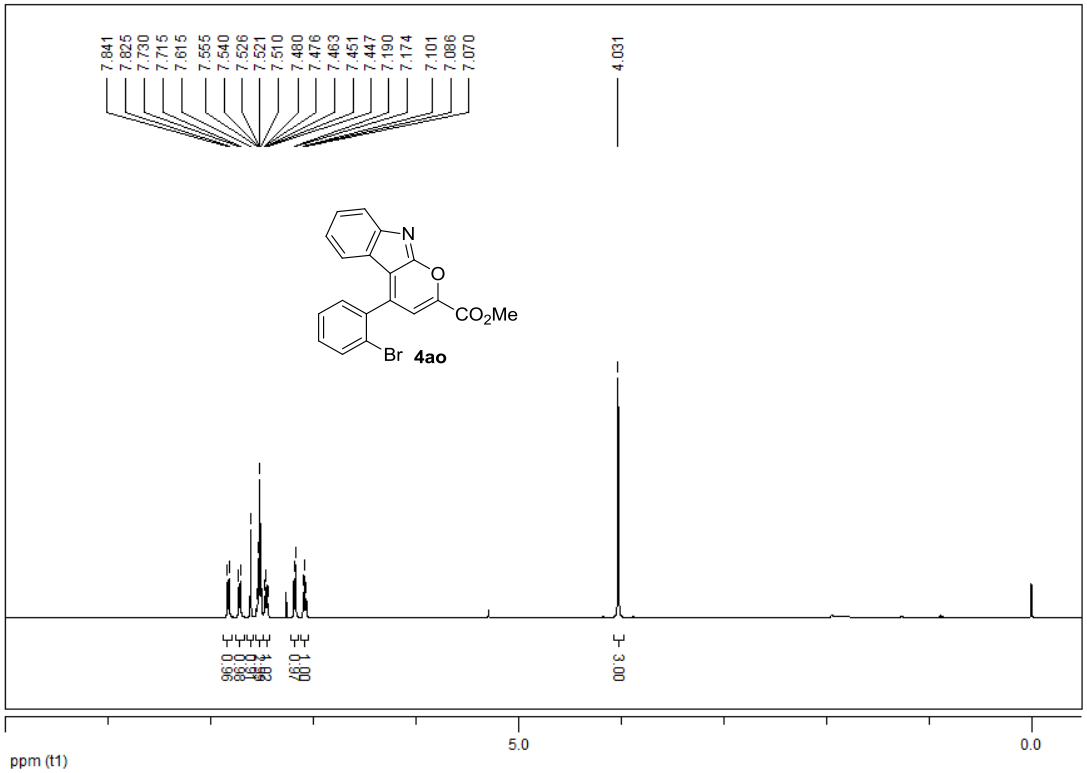
4an: ^{1}H NMR (500 MHz, $CDCl_3$)



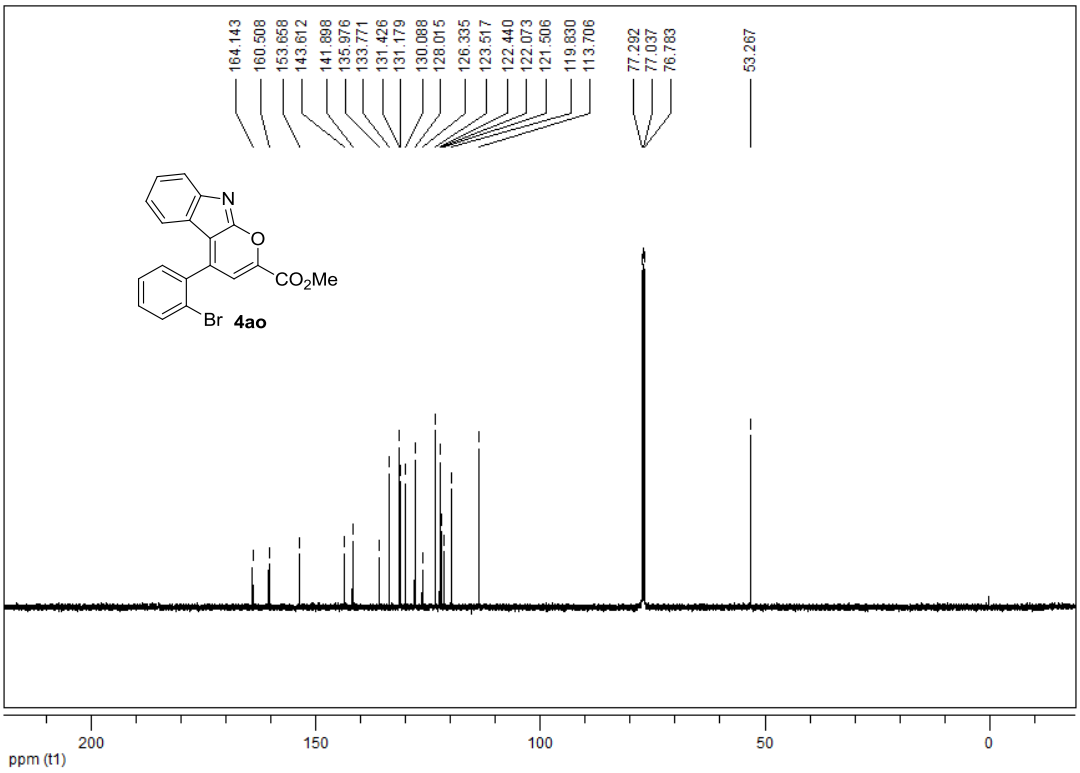
4an: ^{13}C NMR (125 MHz, $CDCl_3$)



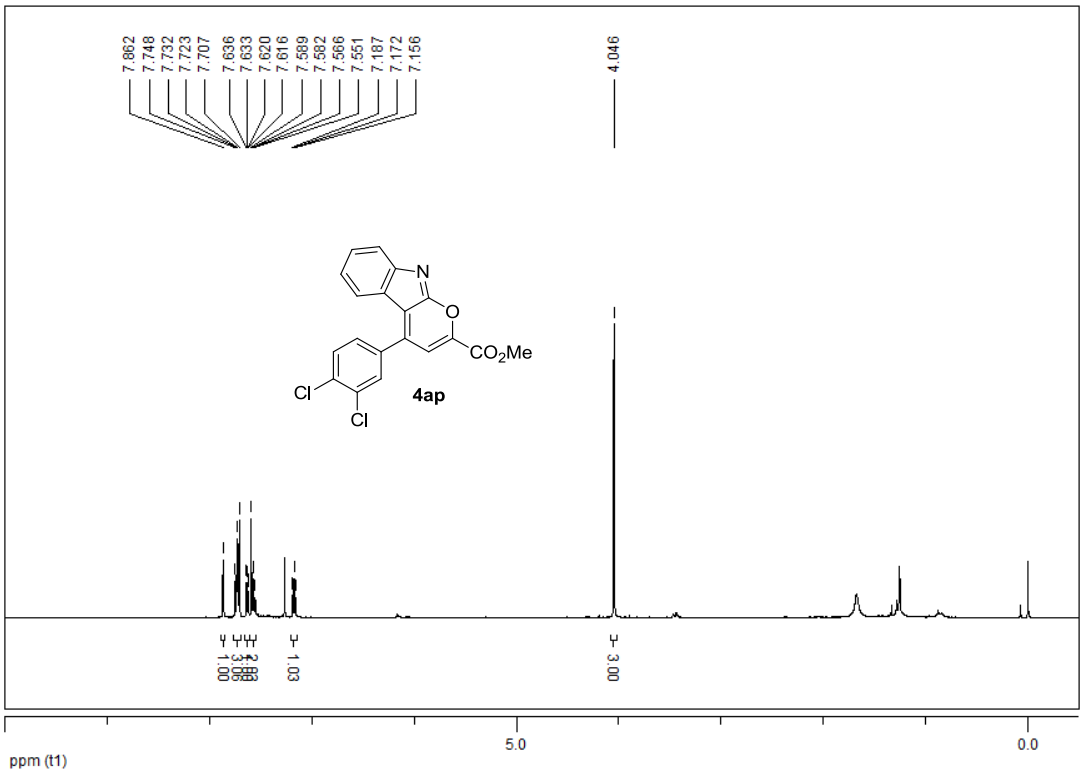
4ao: ^{1}H NMR (500 MHz, $CDCl_3$)



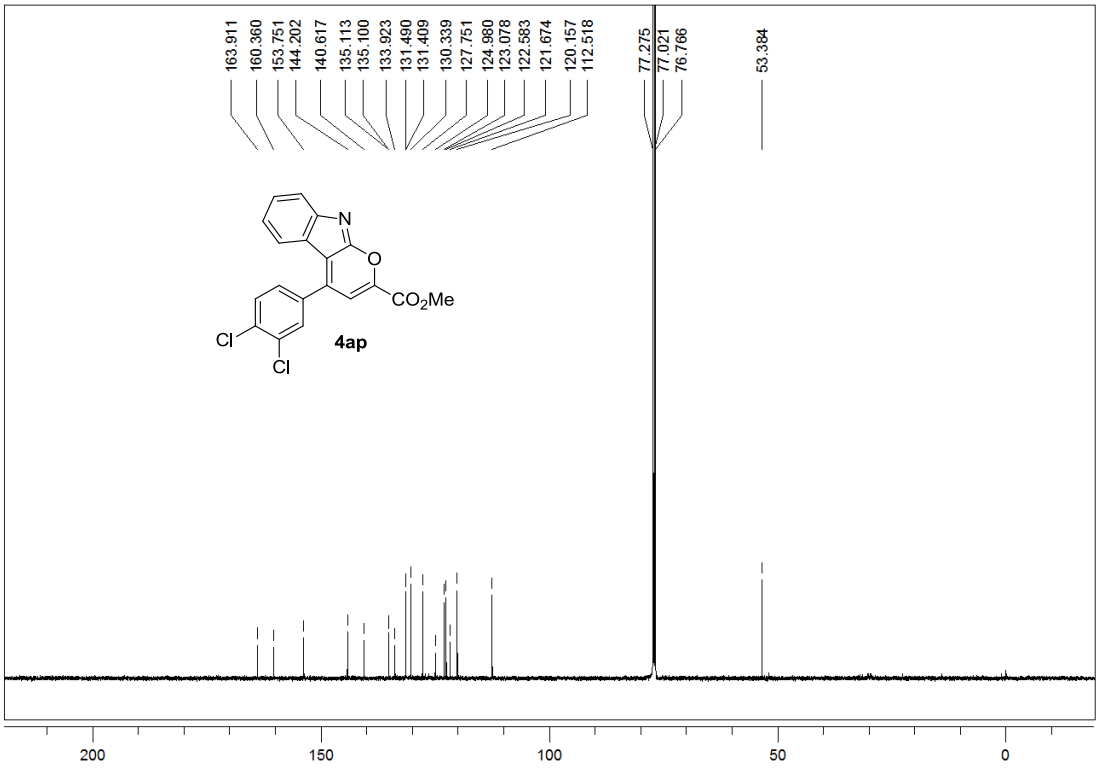
4ao: ^{13}C NMR (125 MHz, $CDCl_3$)



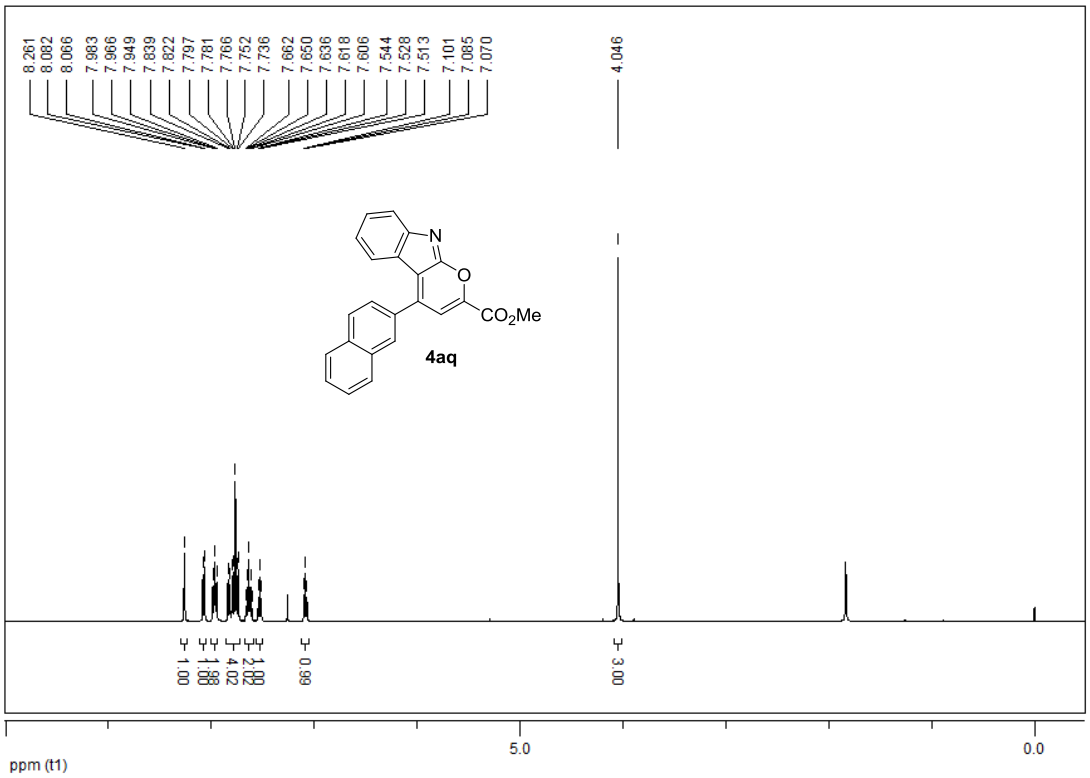
4ap: ^{1}H NMR (500 MHz, $CDCl_3$)



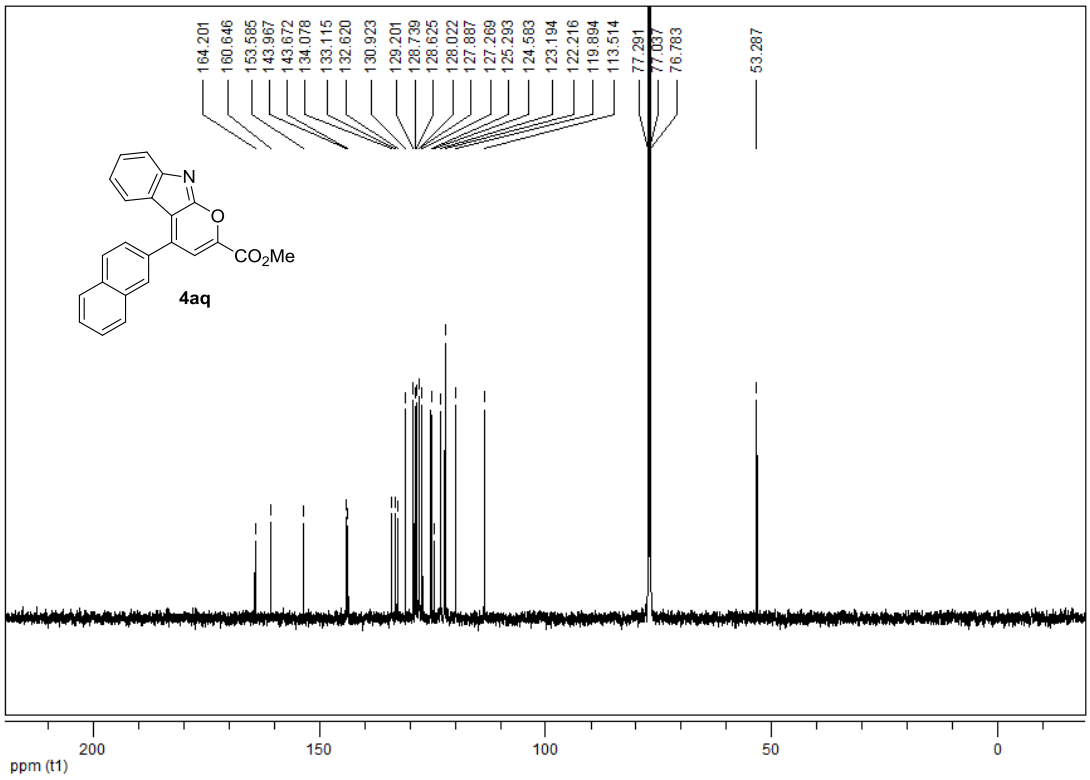
4ap: ^{13}C NMR (125 MHz, $CDCl_3$)



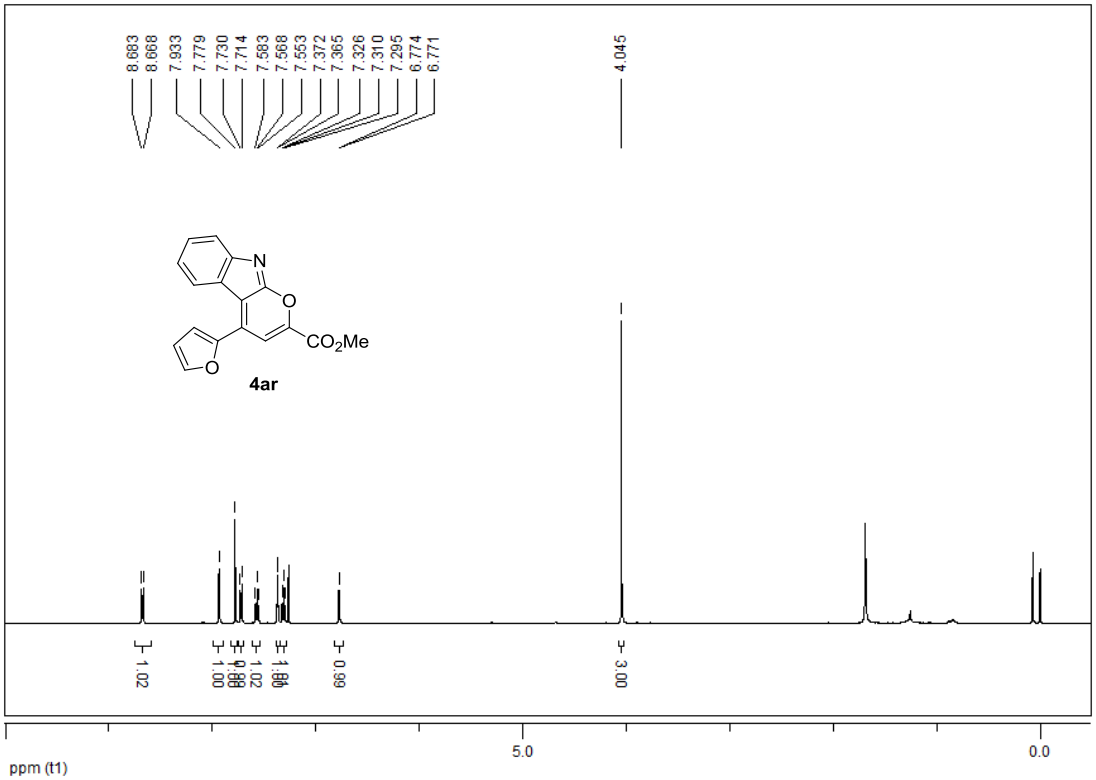
4aq: ^{1}H NMR (500 MHz, $CDCl_3$)



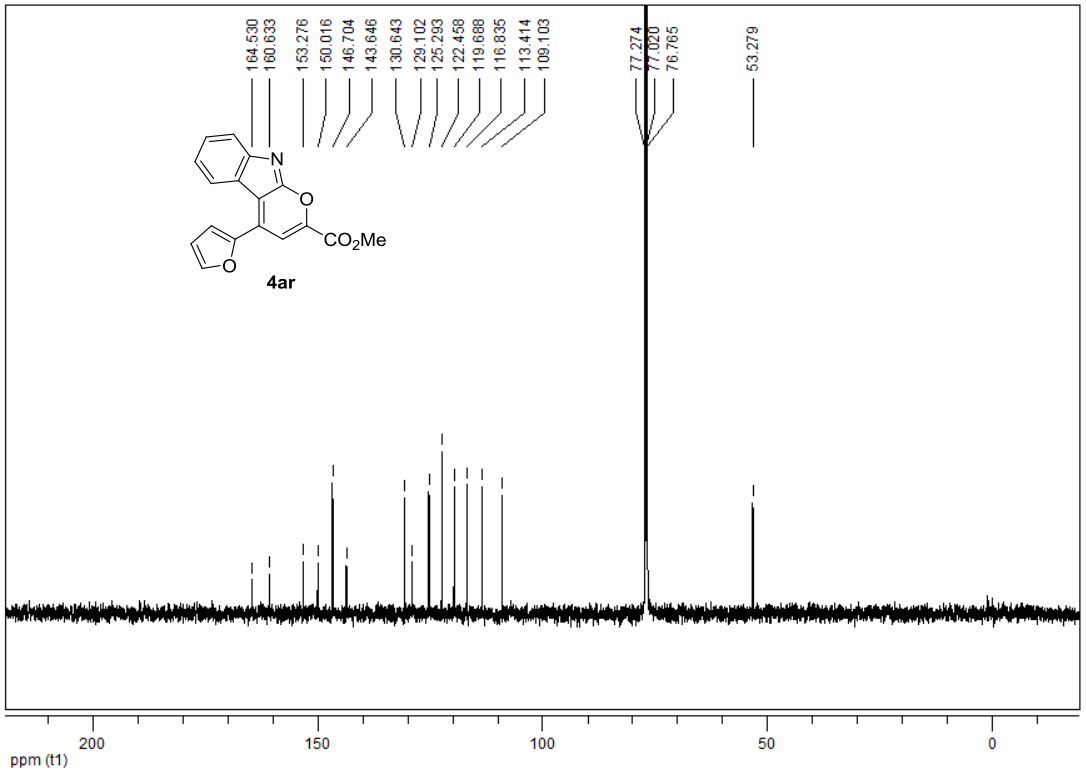
4aq: ^{13}C NMR (125 MHz, $CDCl_3$)



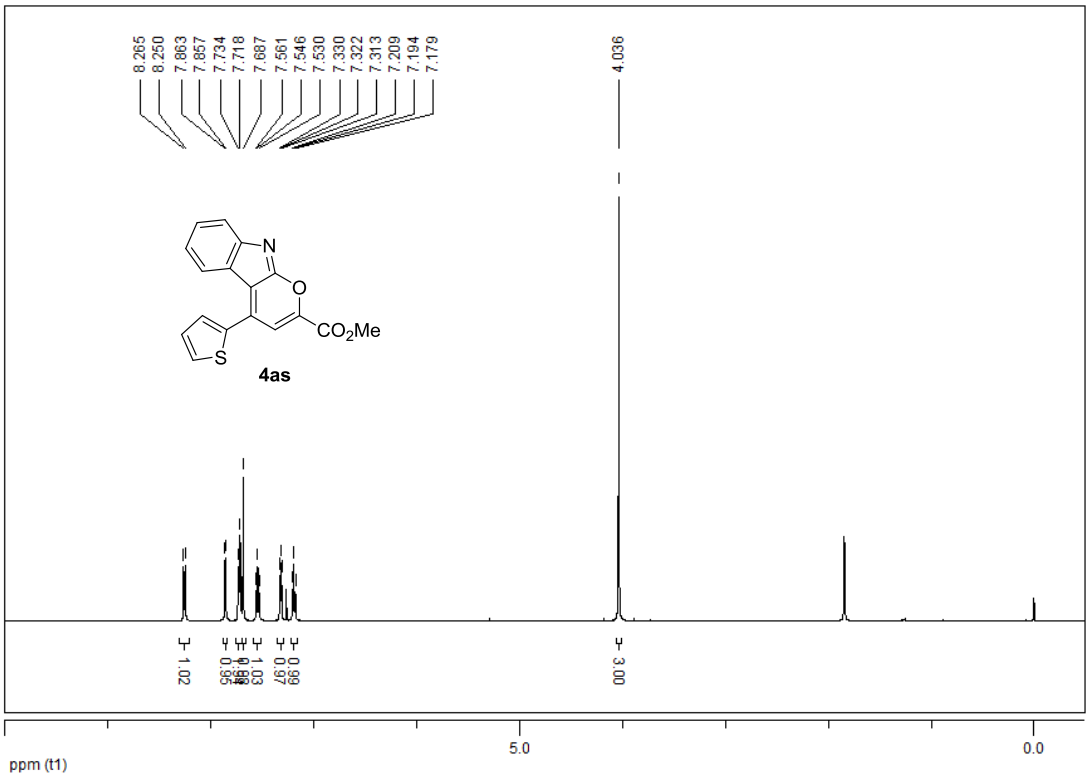
4ar: ^{1}H NMR (500 MHz, $CDCl_3$)



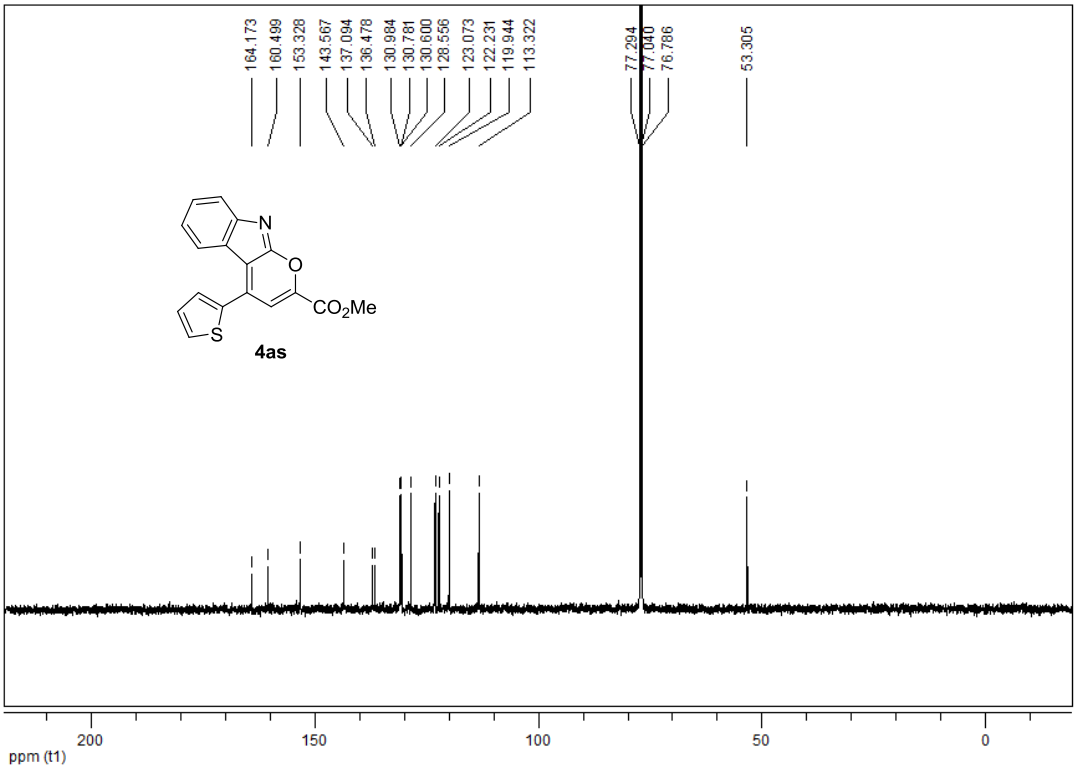
4ar: ^{13}C NMR (125 MHz, $CDCl_3$)



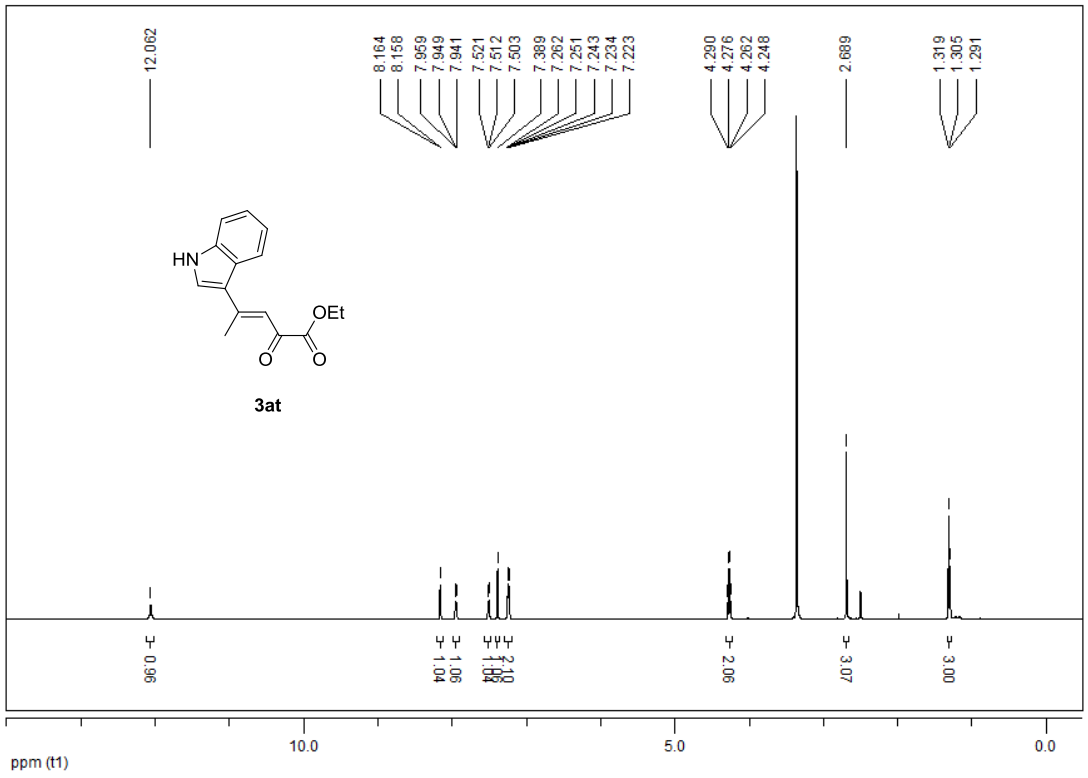
4as: ^{1}H NMR (500 MHz, $CDCl_3$)



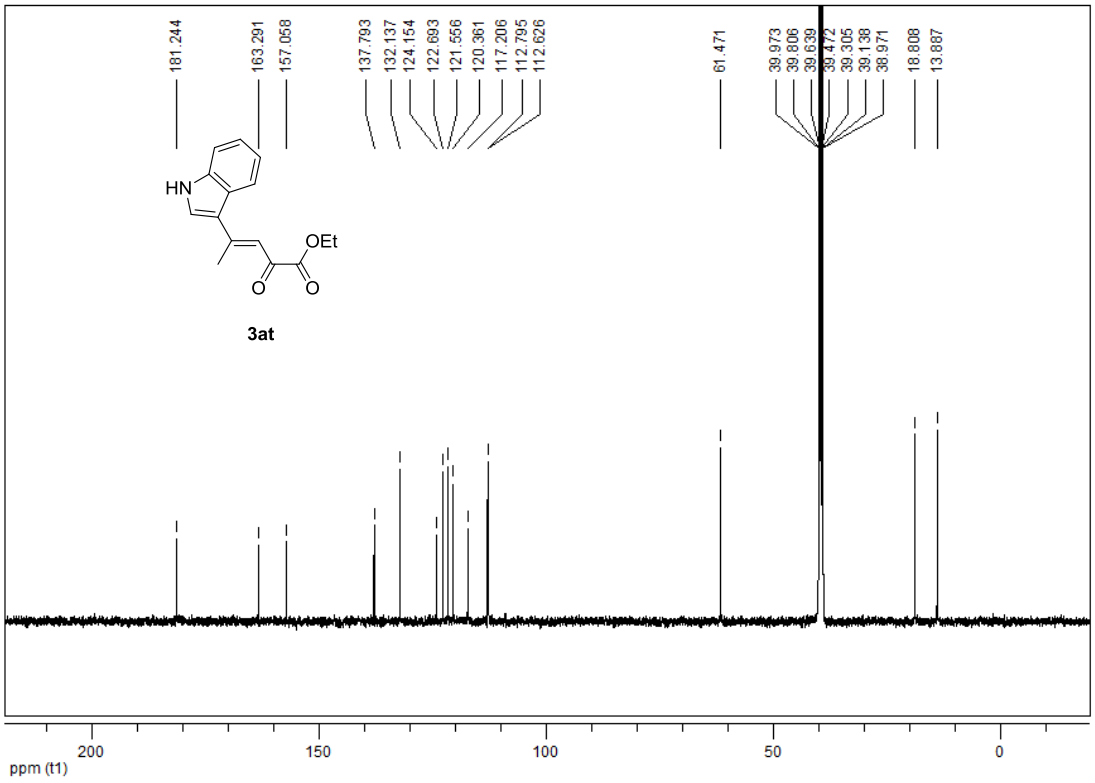
4as: ^{13}C NMR (125 MHz, $CDCl_3$)



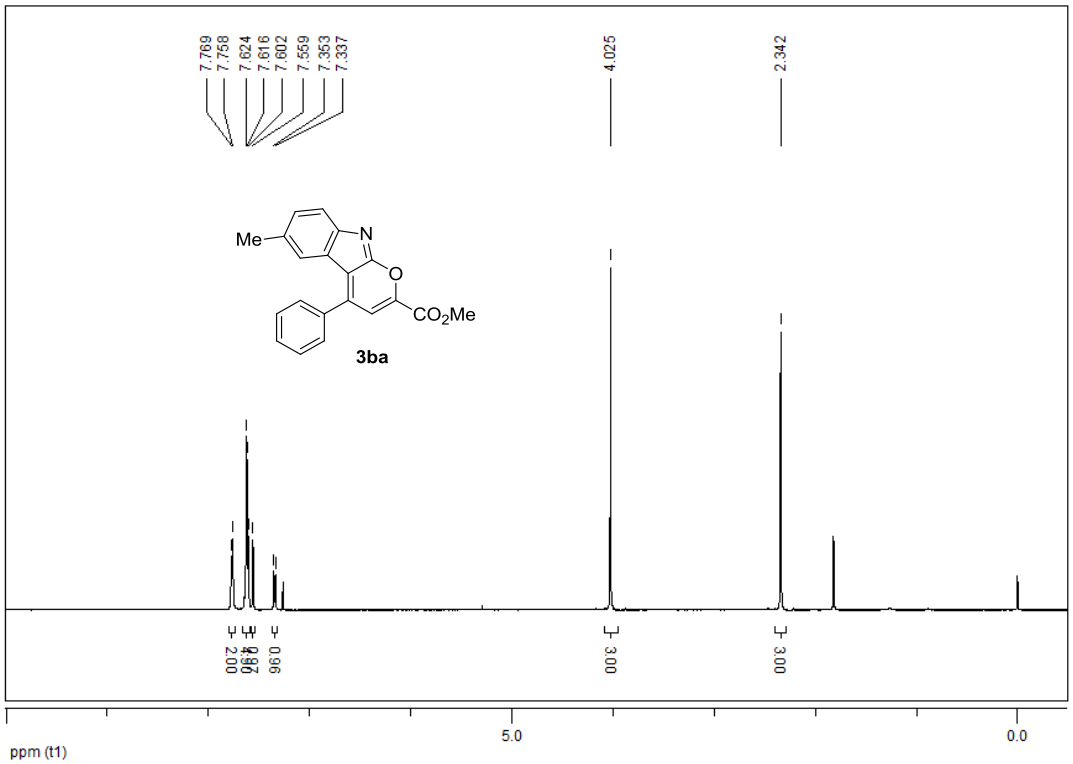
3at: ^{1}H NMR (500 MHz, DMSO-d$_6$)



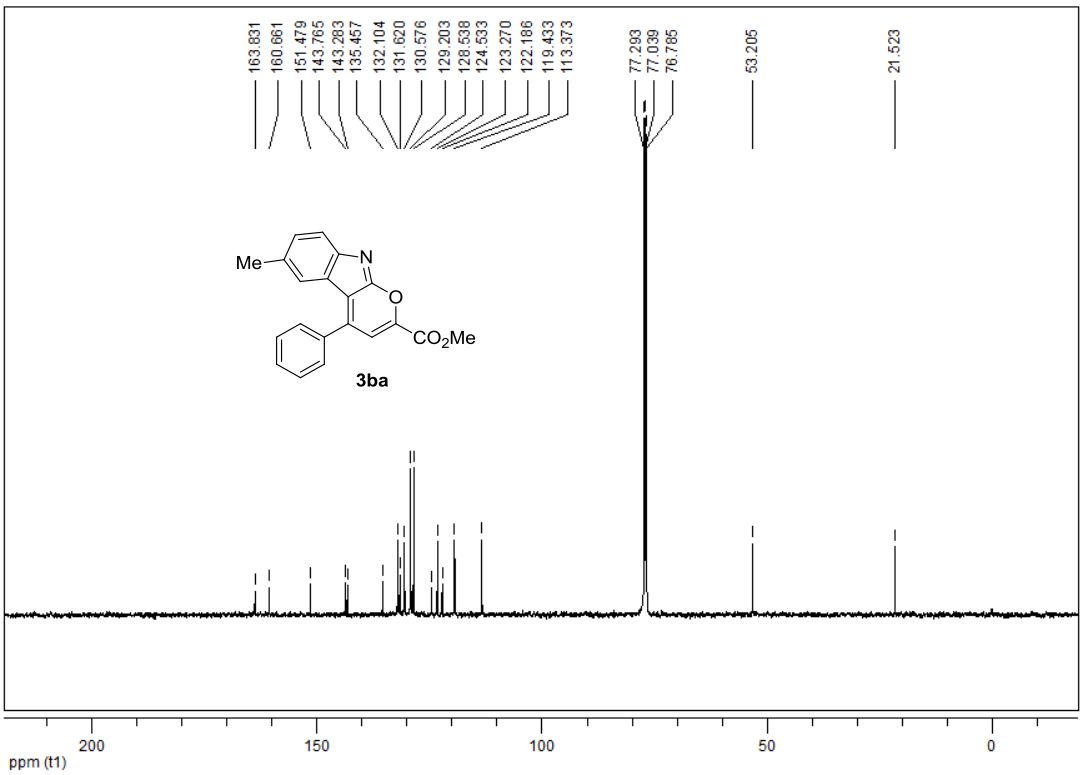
3at: ^{13}C NMR (125 MHz, DMSO-d$_6$)



4ba: ^{1}H NMR (500 MHz, $CDCl_3$)



4ba: ^{13}C NMR (125 MHz, $CDCl_3$)



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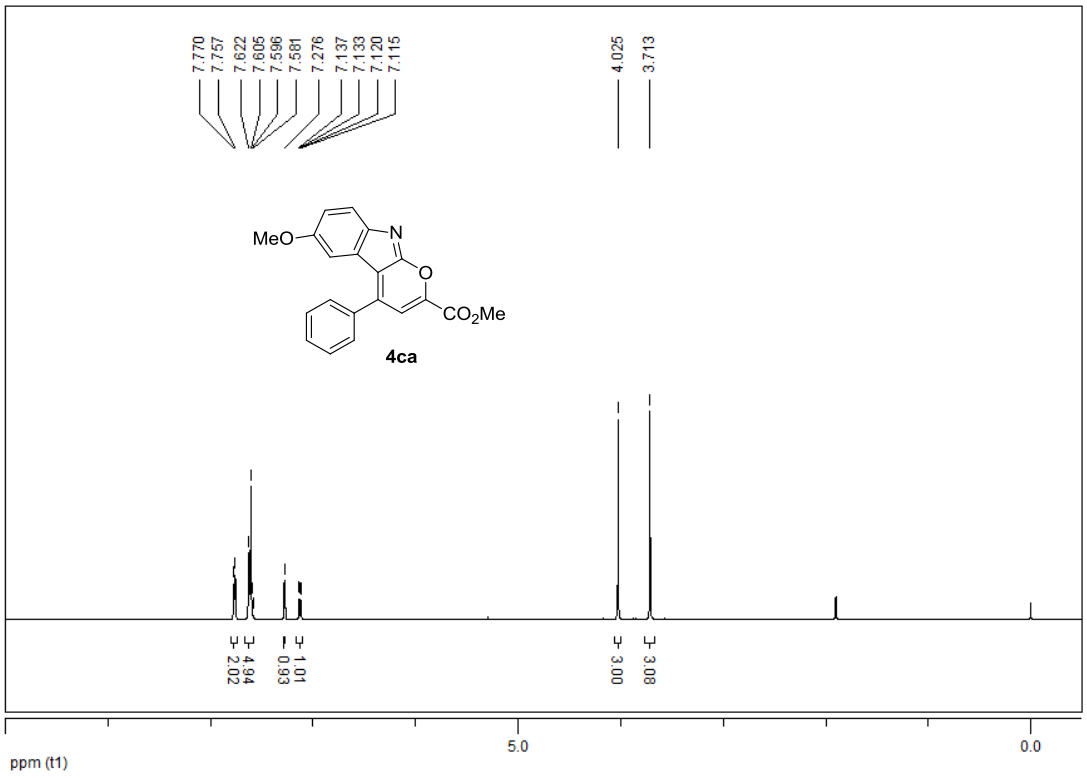
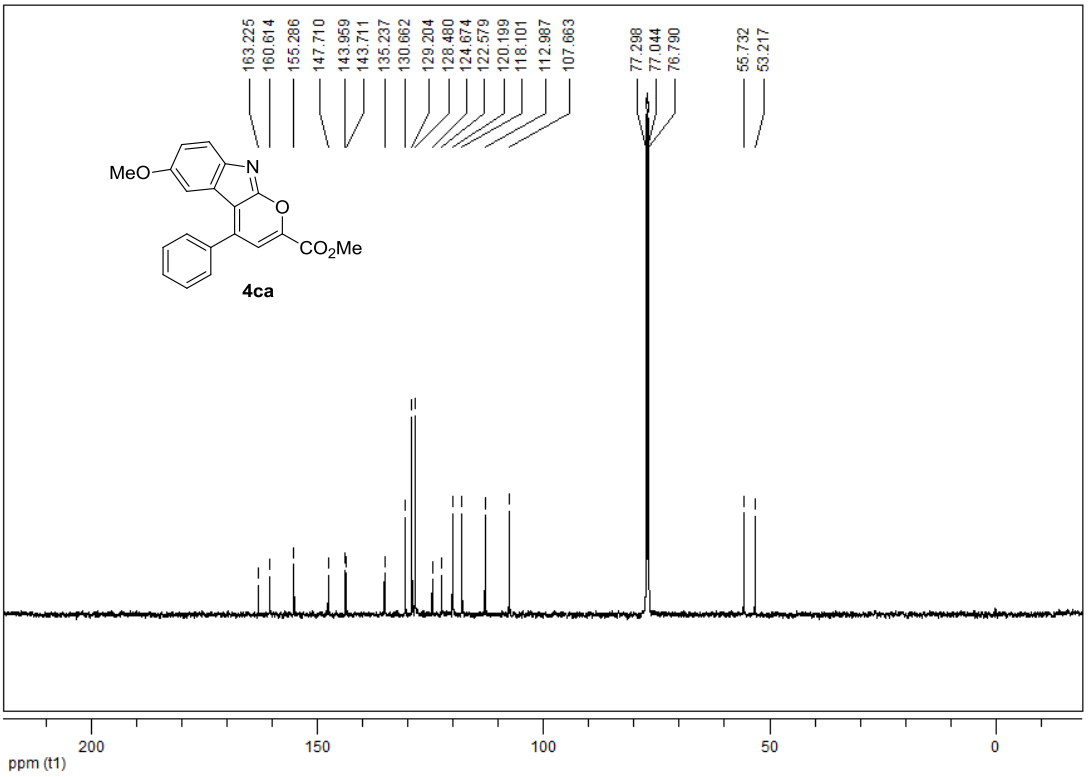
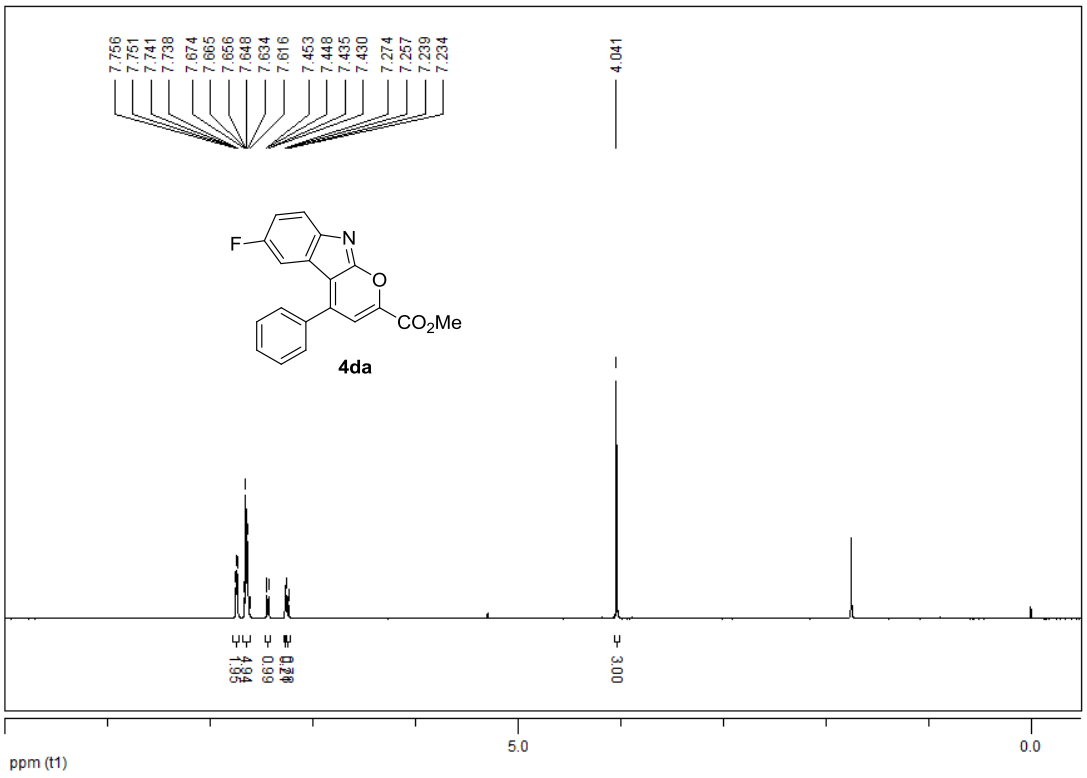


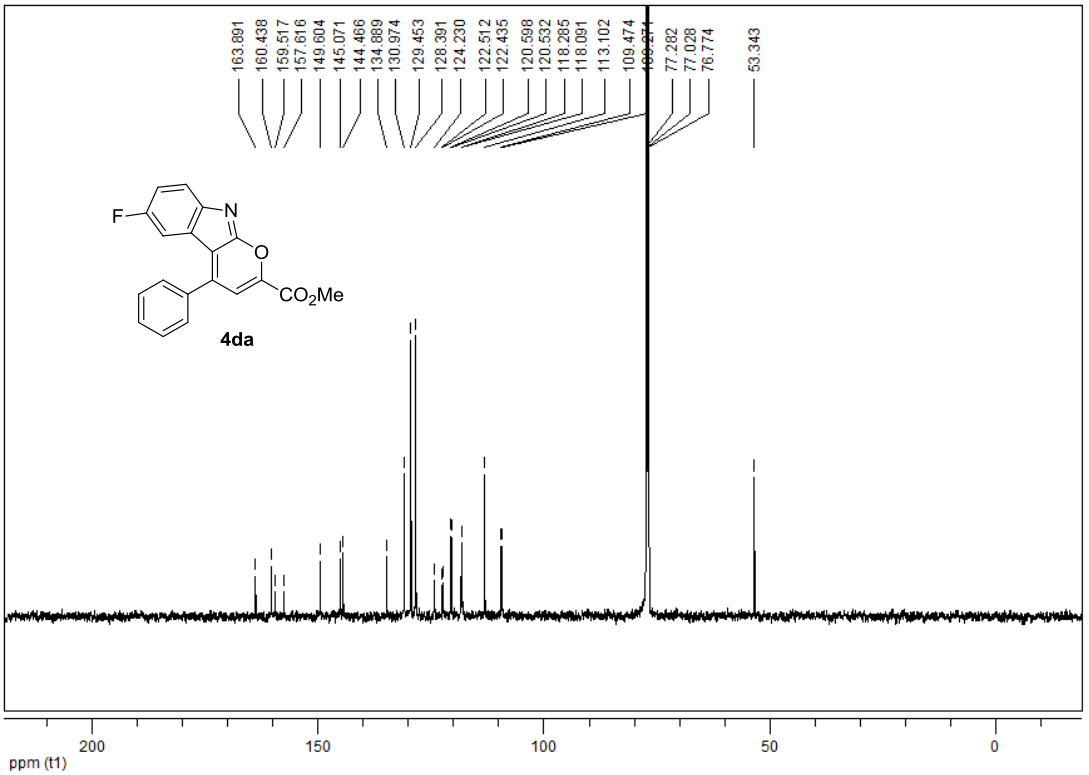
4ca: ^{13}C NMR (125 MHz, $CDCl_3$)



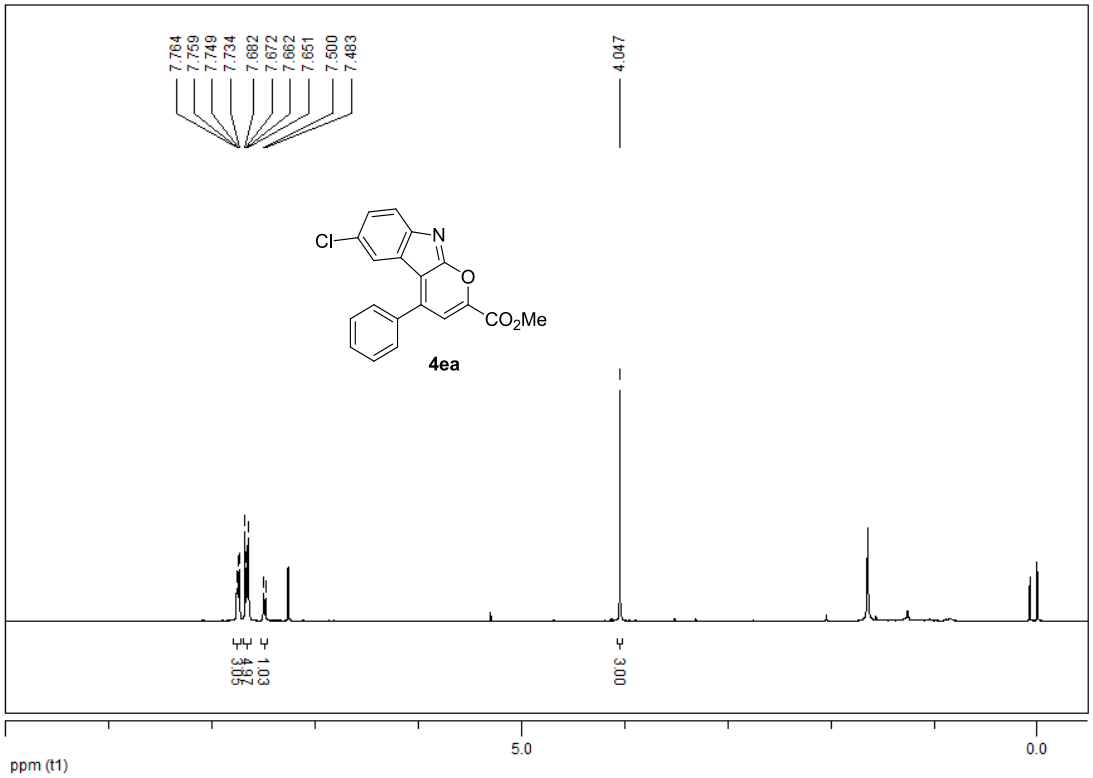
4da: ^{1}H NMR (500 MHz, $CDCl_3$)



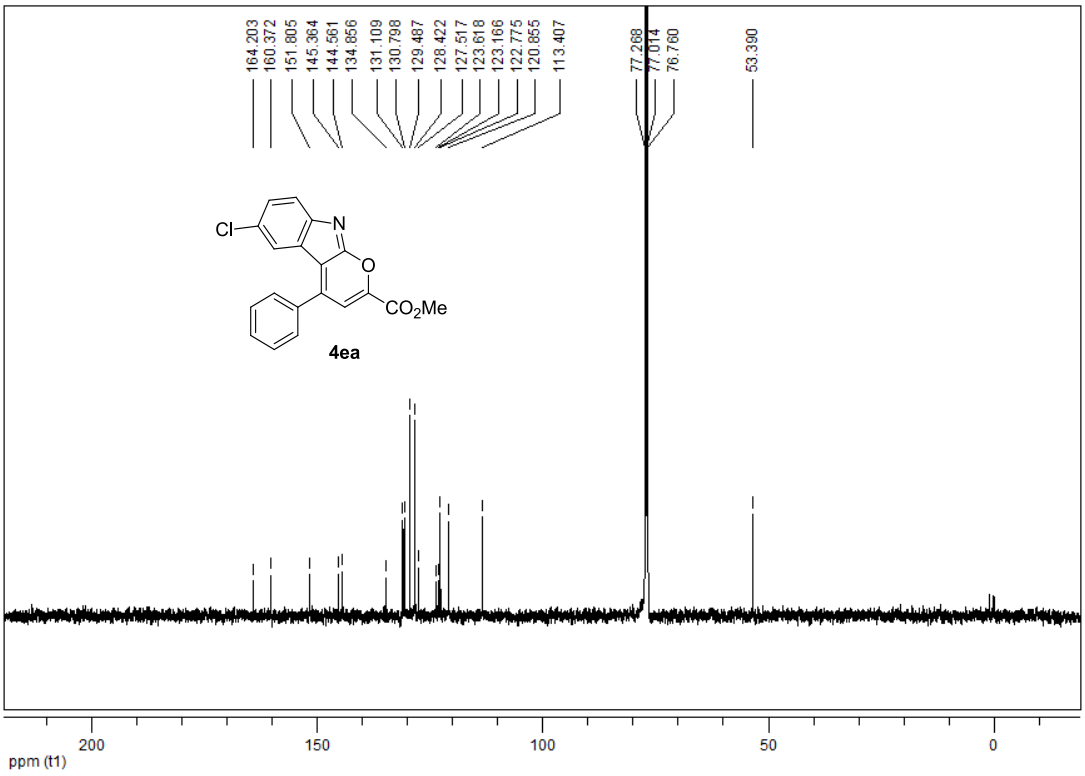
4da: ^{13}C NMR (125 MHz, $CDCl_3$)



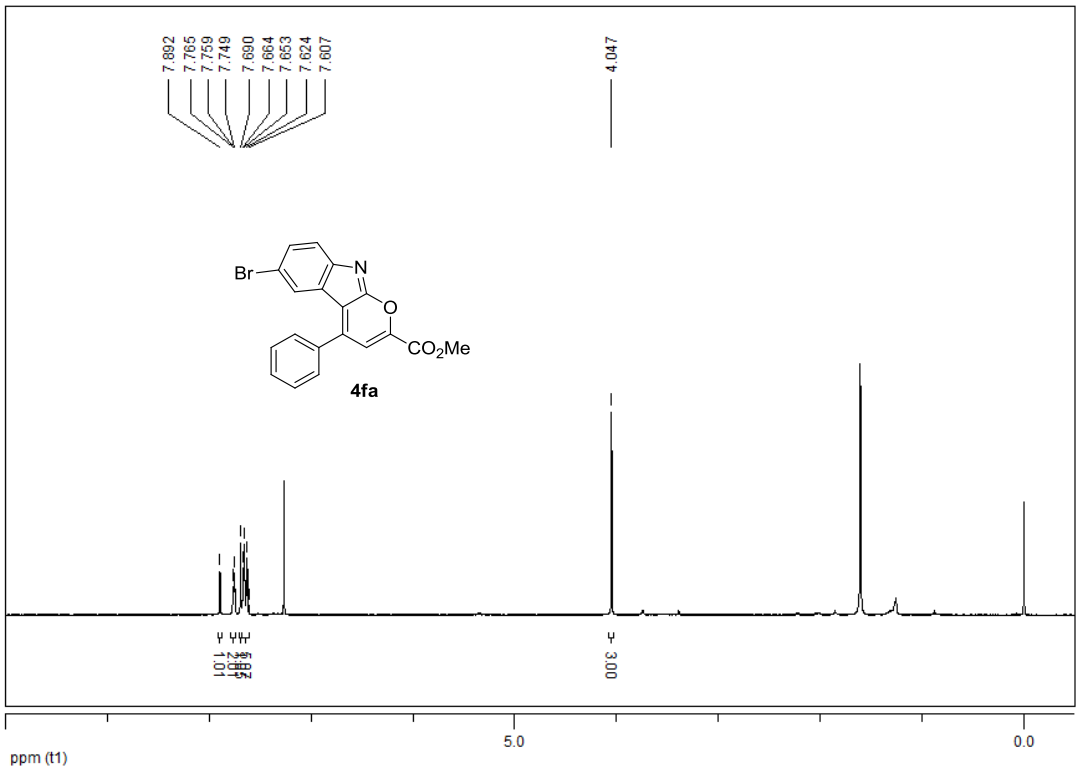
4ea: ^{1}H NMR (500 MHz, $CDCl_3$)



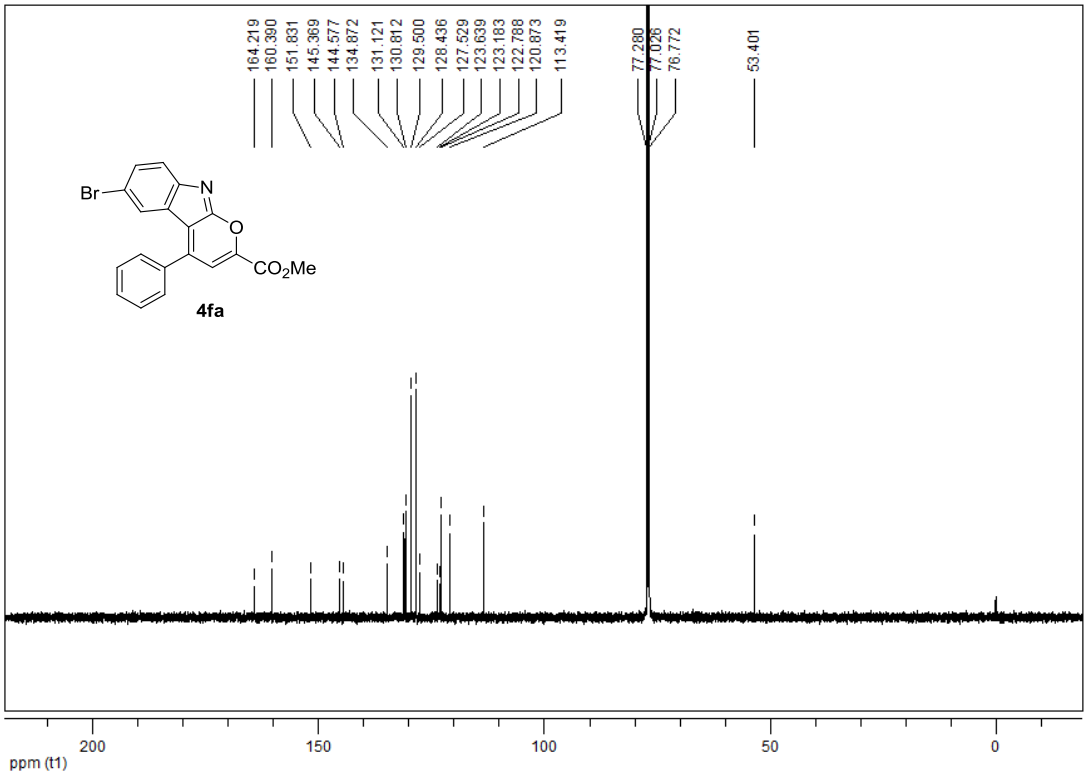
4ea: ^{13}C NMR (125 MHz, $CDCl_3$)



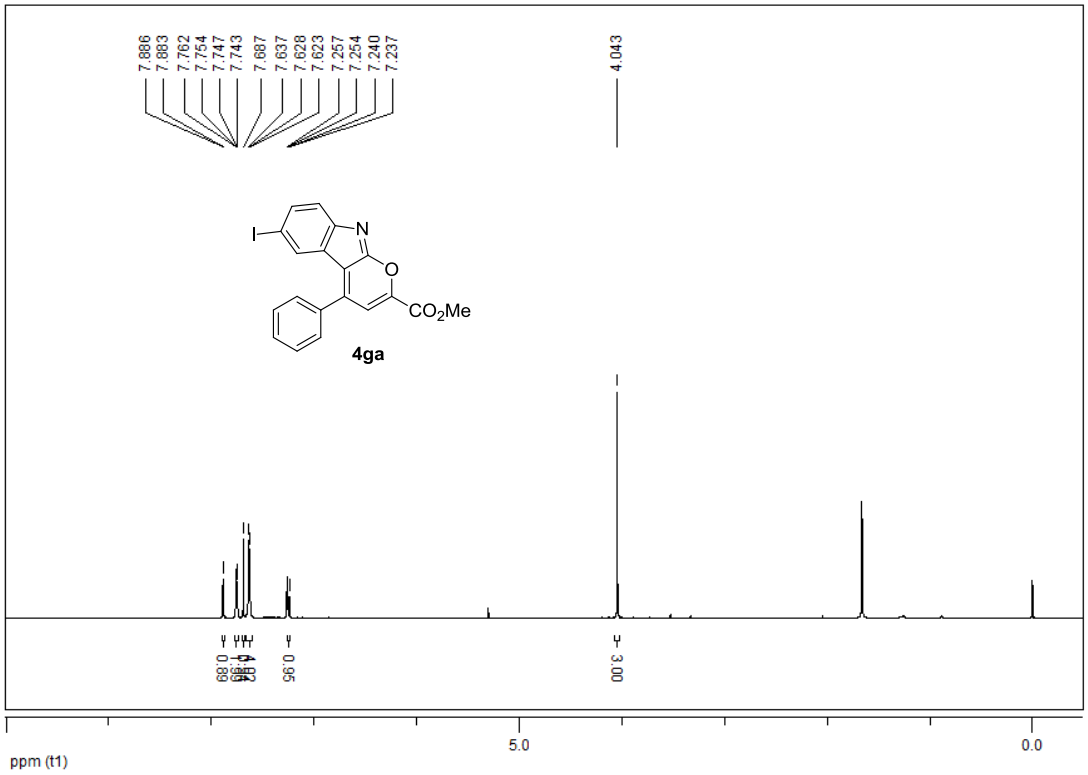
4fa: ^{1}H NMR (500 MHz, $CDCl_3$)



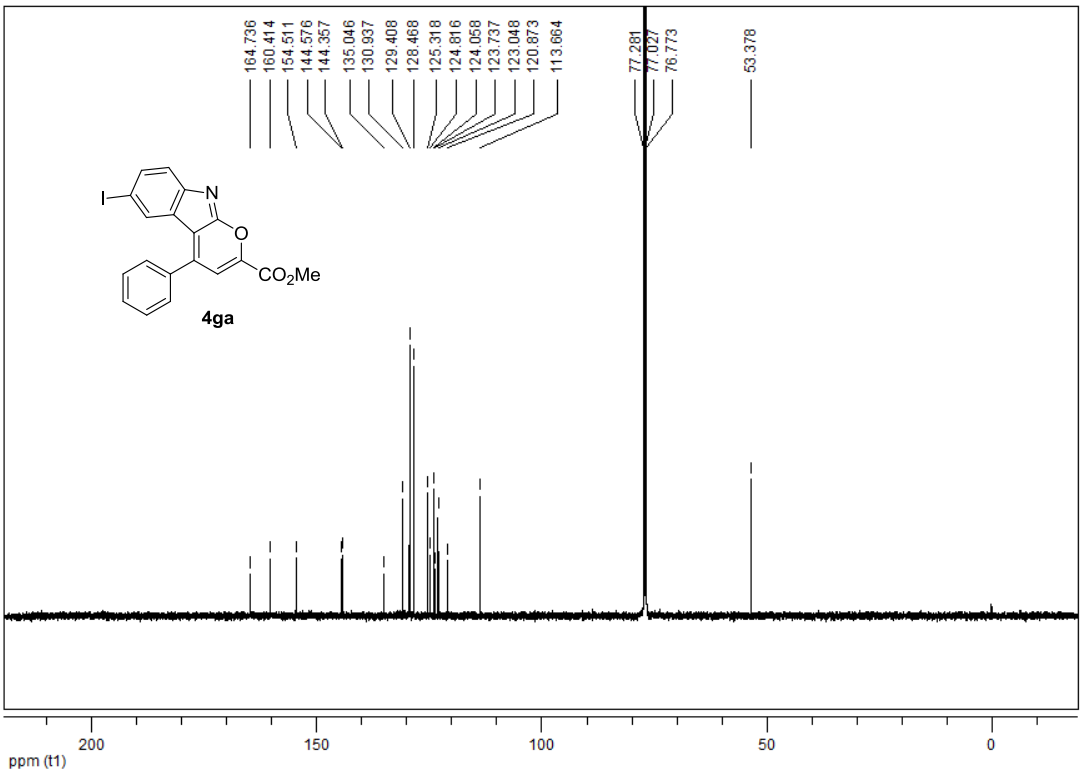
4fa: ^{13}C NMR (125 MHz, $CDCl_3$)



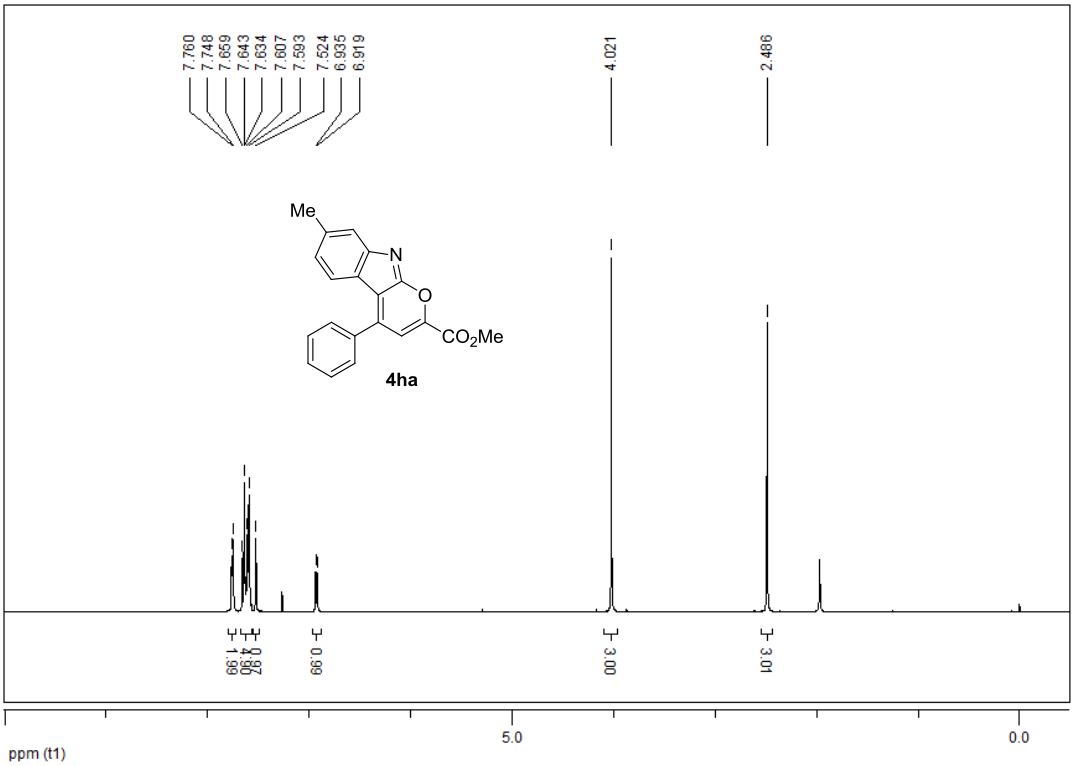
4ga: ^{1}H NMR (500 MHz, $CDCl_3$)



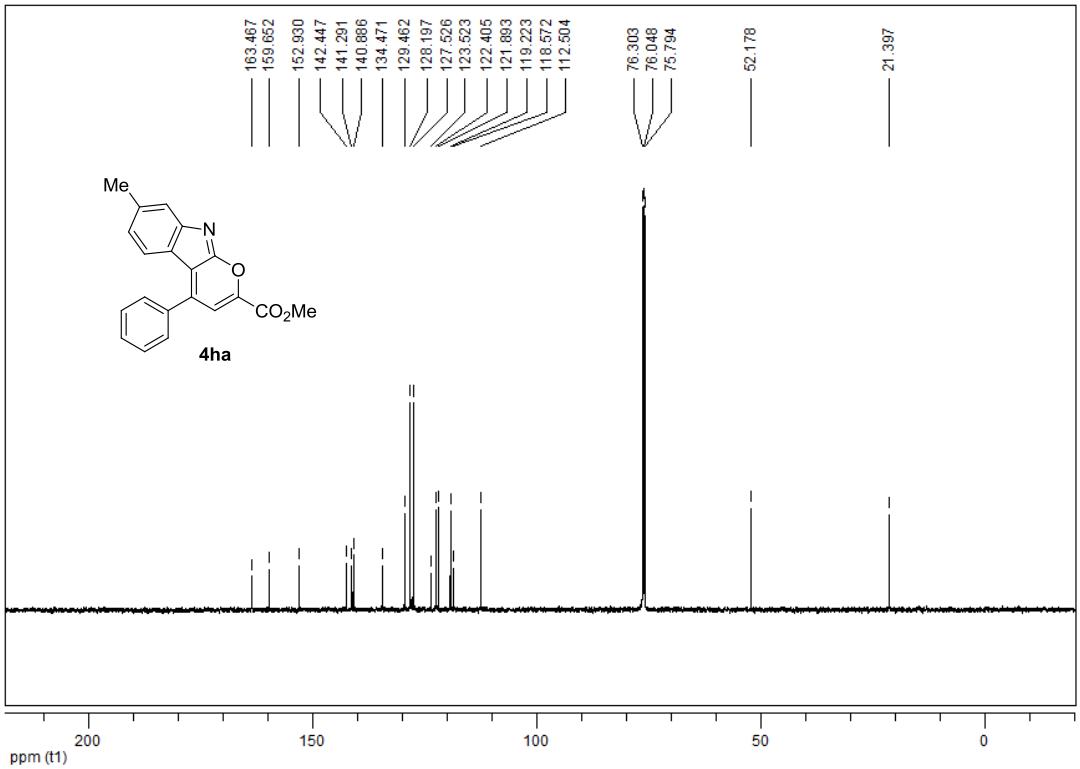
4ga: ^{13}C NMR (125 MHz, $CDCl_3$)



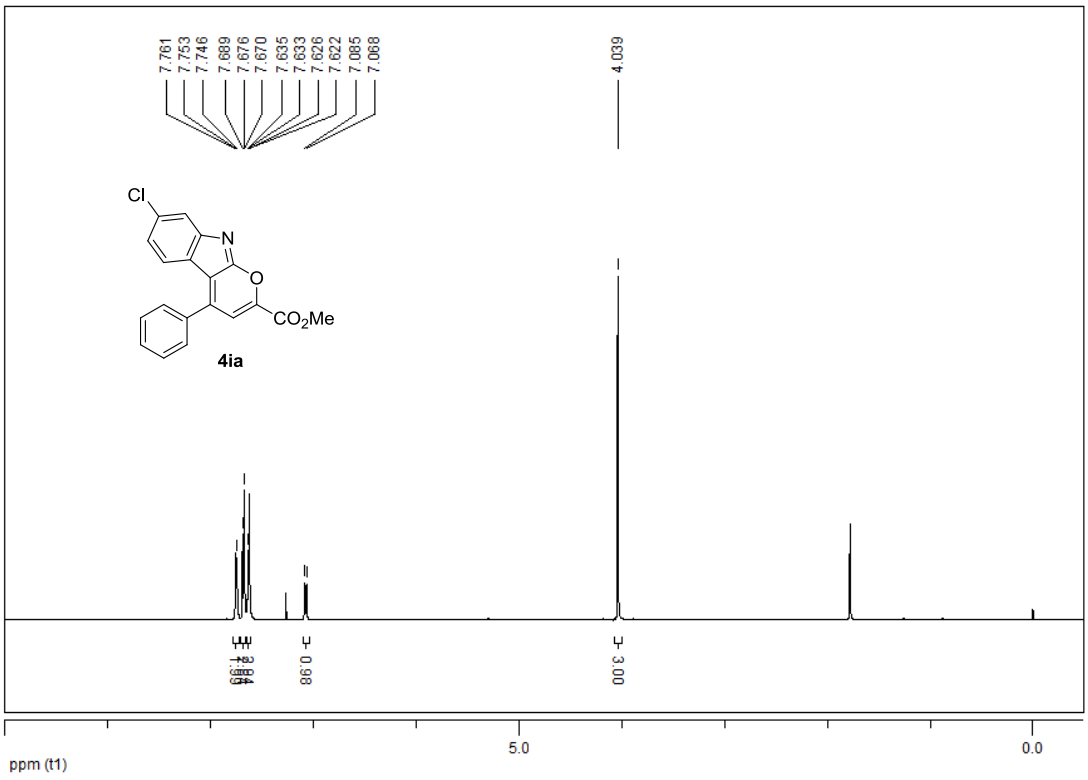
4ha: ^{1}H NMR (500 MHz, $CDCl_3$)



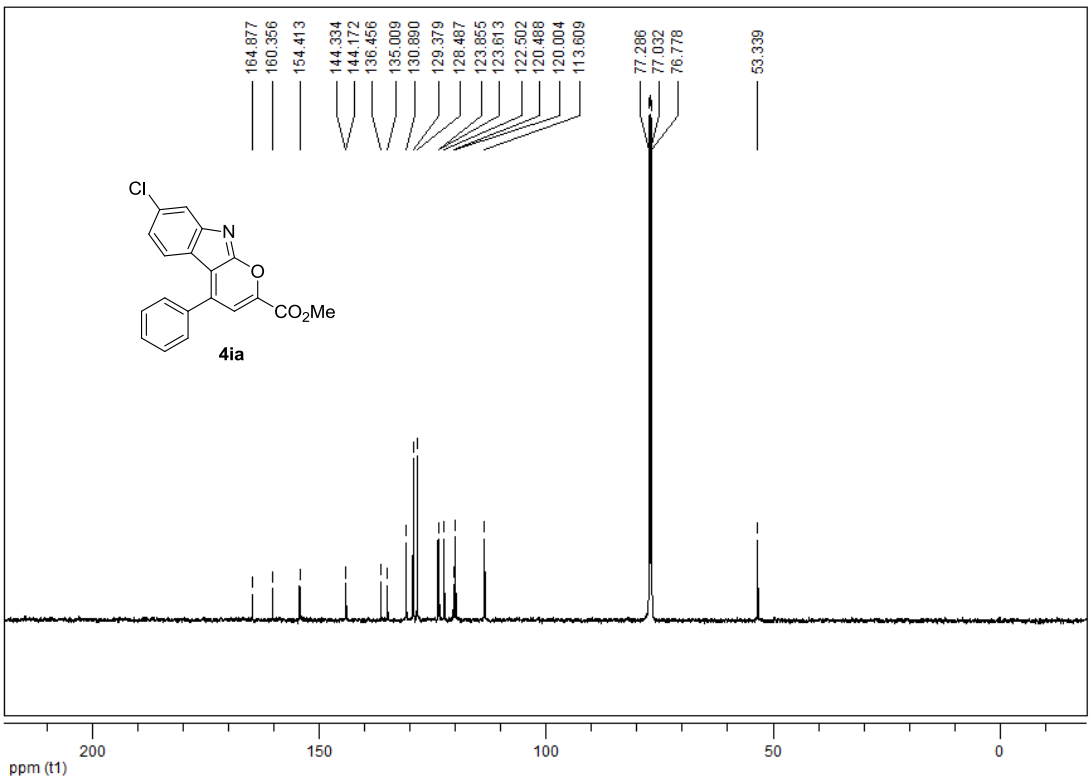
4ha: ^{13}C NMR (125 MHz, $CDCl_3$)



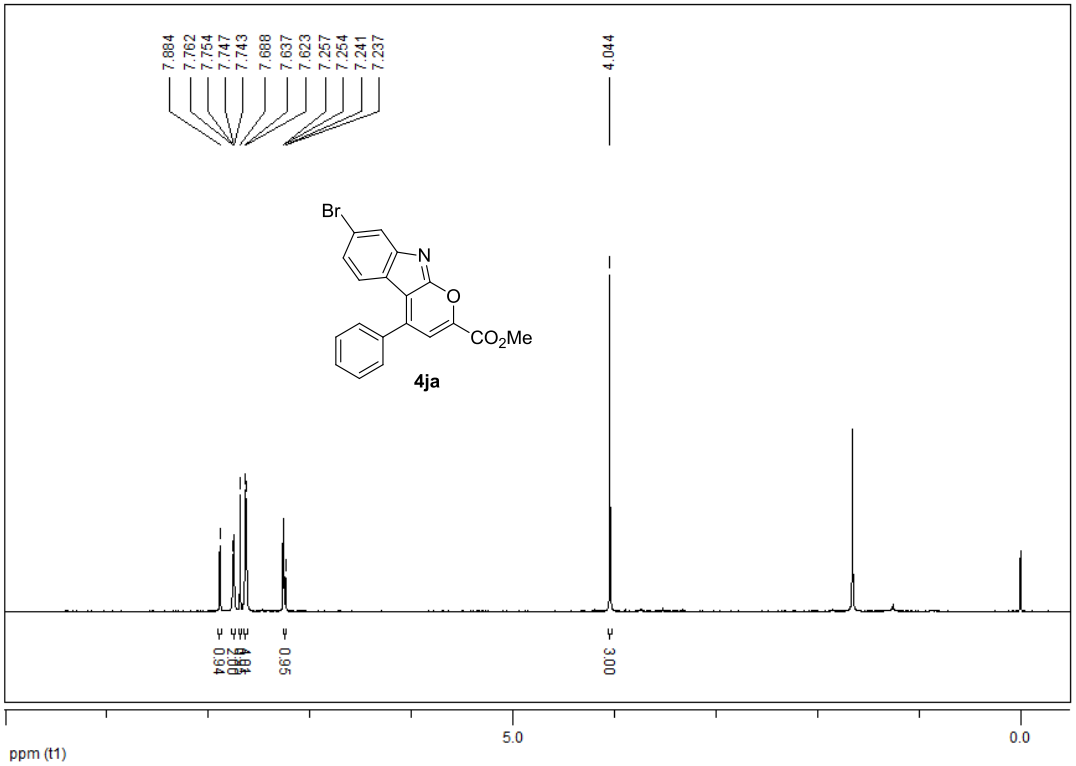
4ia: ^{1}H NMR (500 MHz, $CDCl_3$)



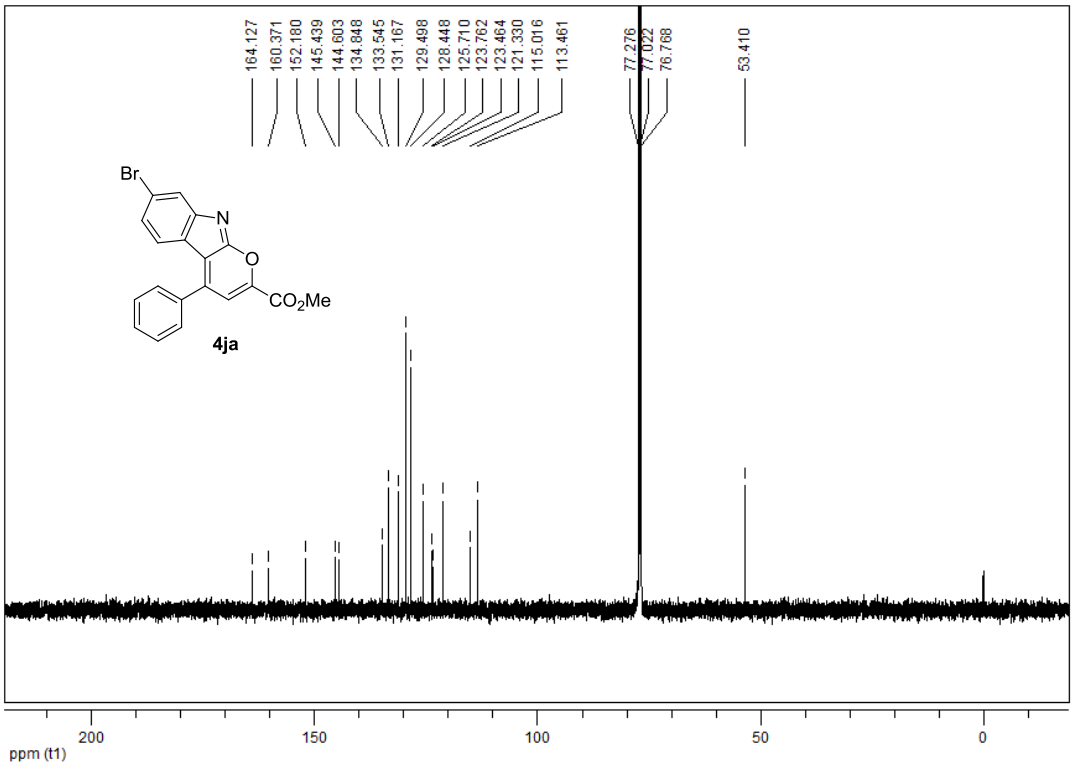
4ia: ^{13}C NMR (125 MHz, $CDCl_3$)



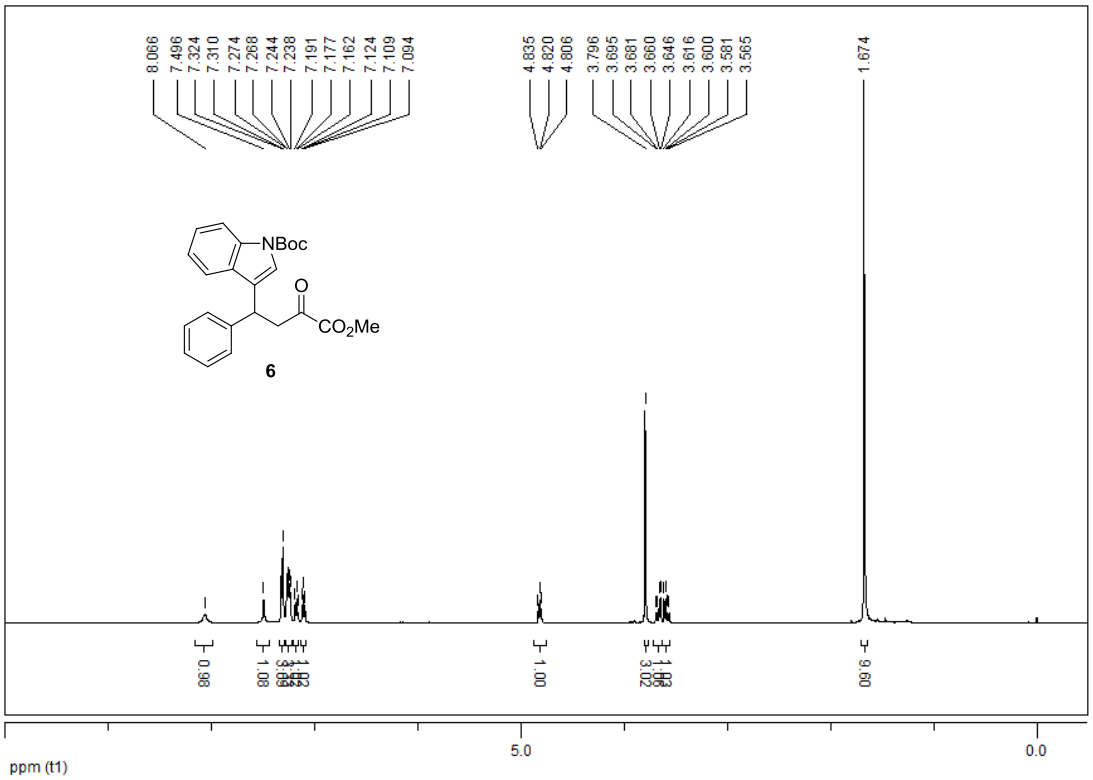
4ja: ^{1}H NMR (500 MHz, $CDCl_3$)



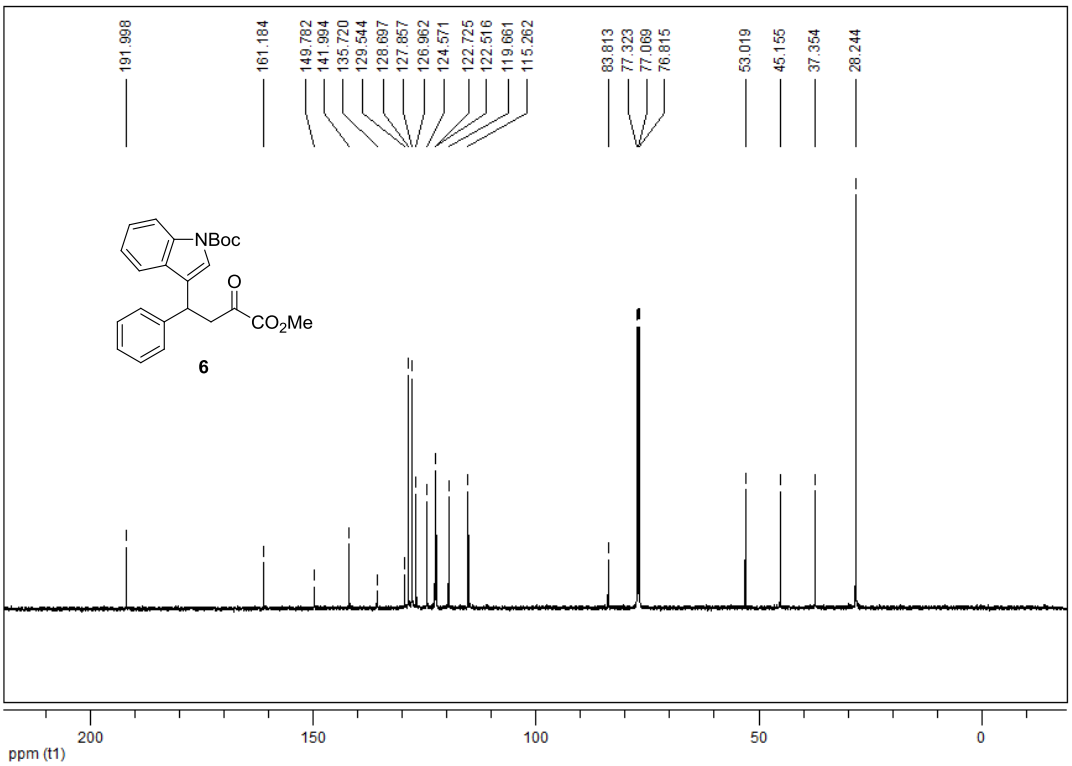
4ja: ^{13}C NMR (125 MHz, $CDCl_3$)



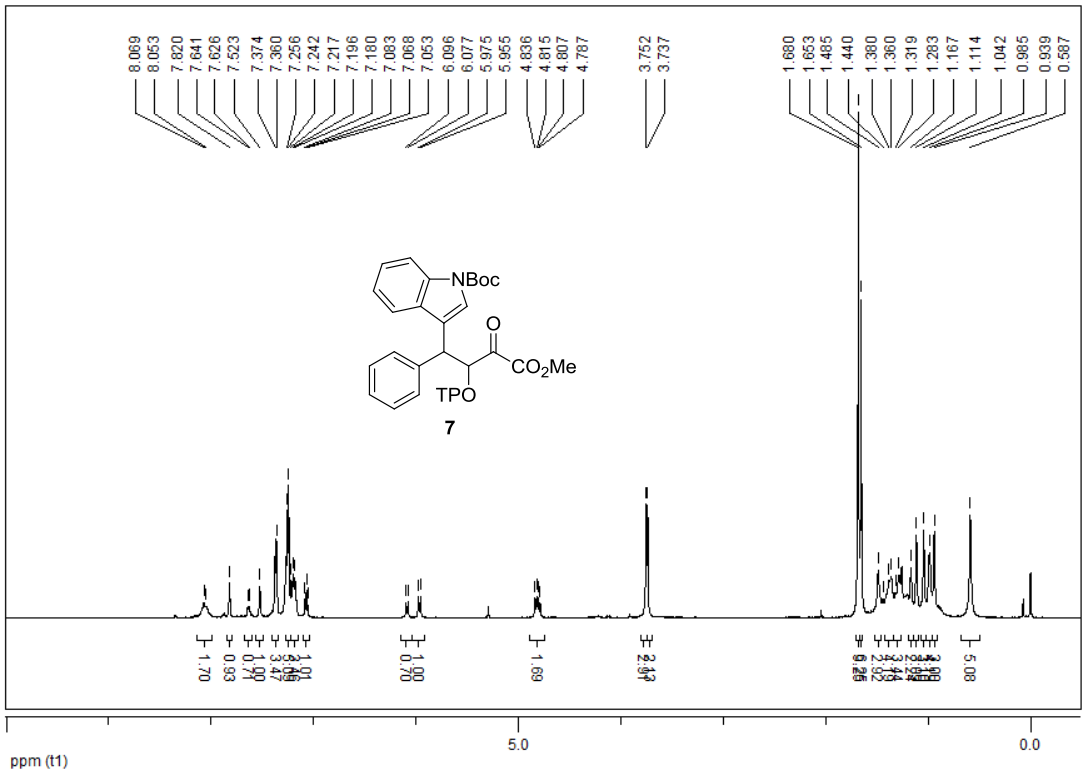
6: ^{1}H NMR (500 MHz, $CDCl_3$)

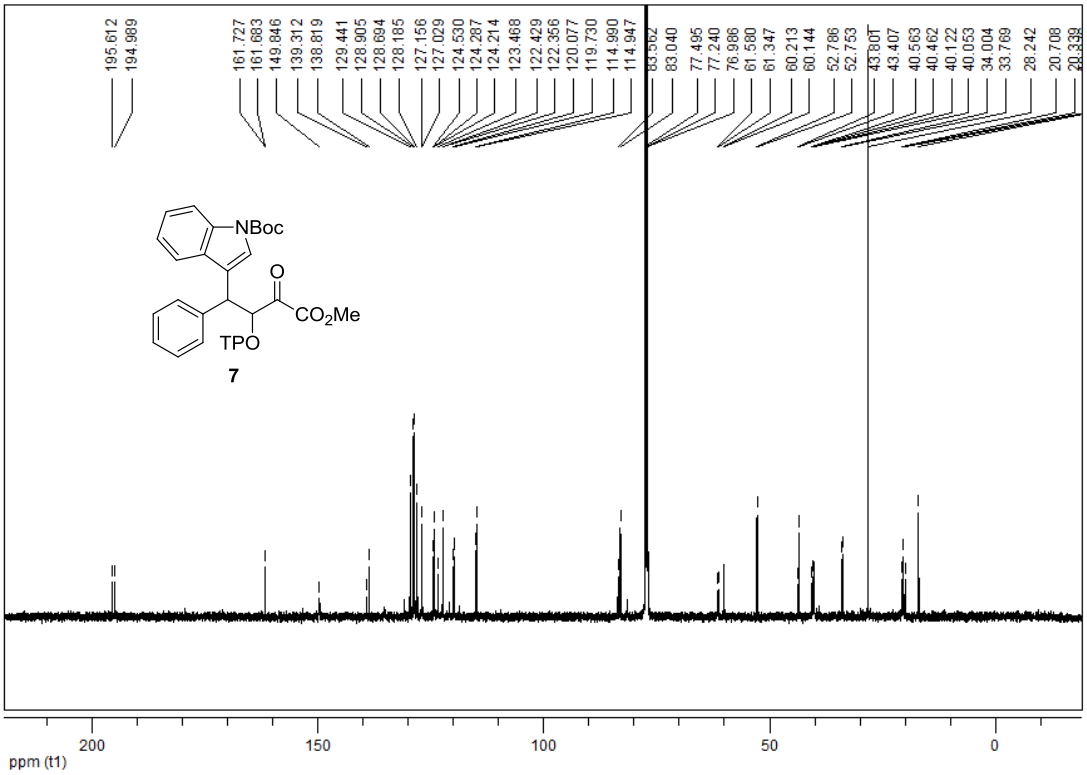


6: ^{13}C NMR (125 MHz, $CDCl_3$)

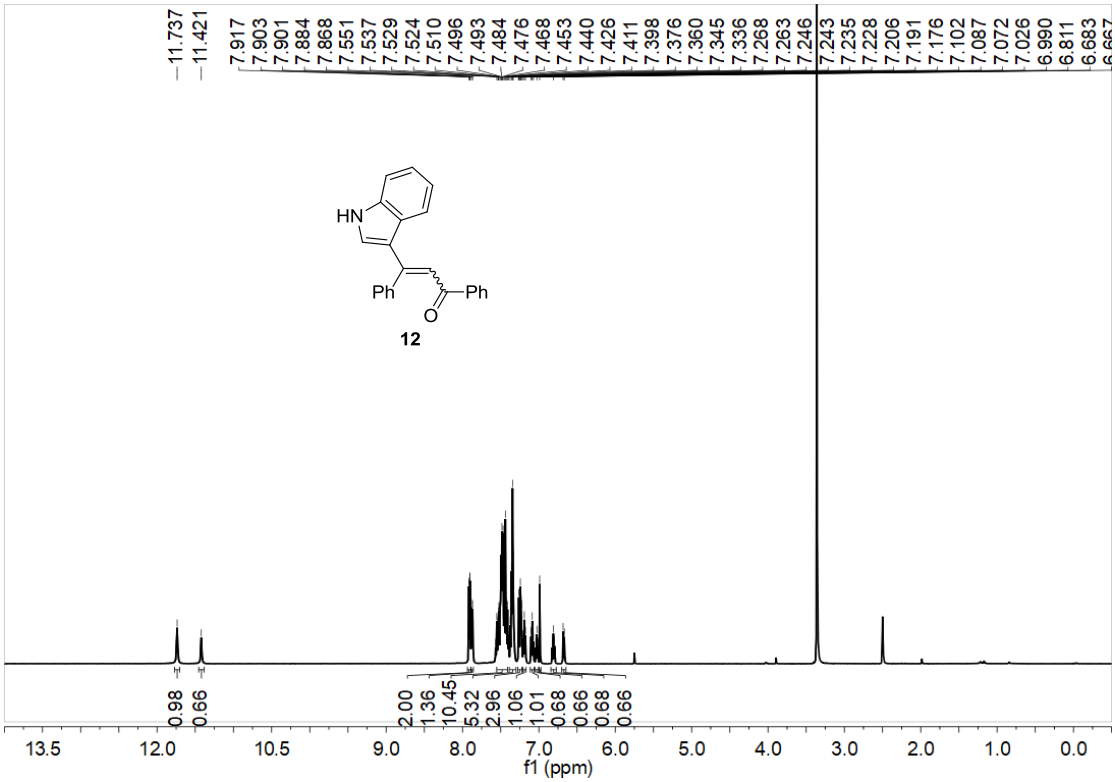


7: ^{1}H NMR (500 MHz, $CDCl_3$)

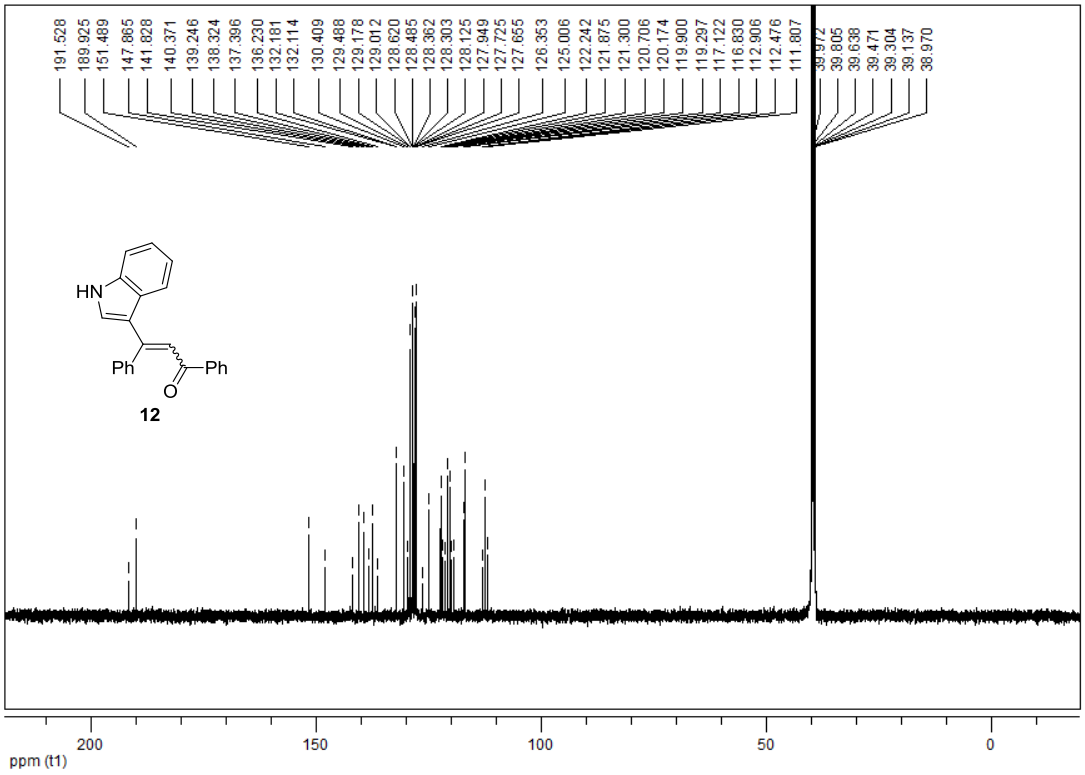




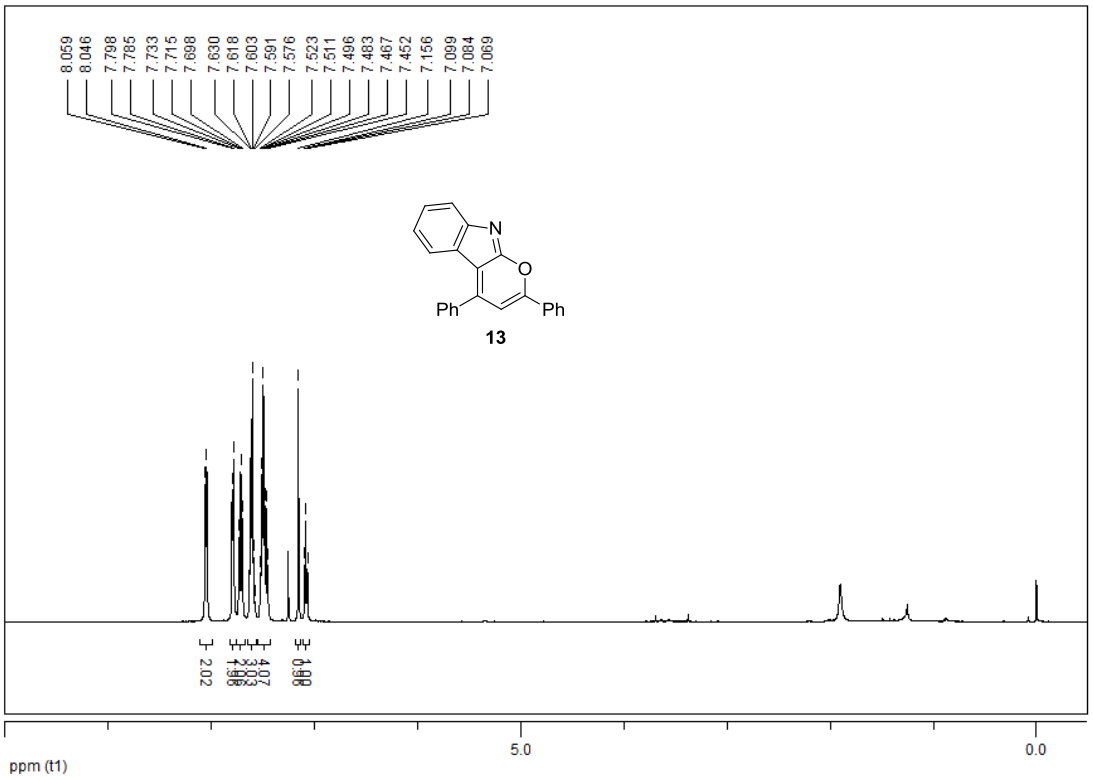
12: ^{1}H NMR (500 MHz, DMSO-d$_6$)



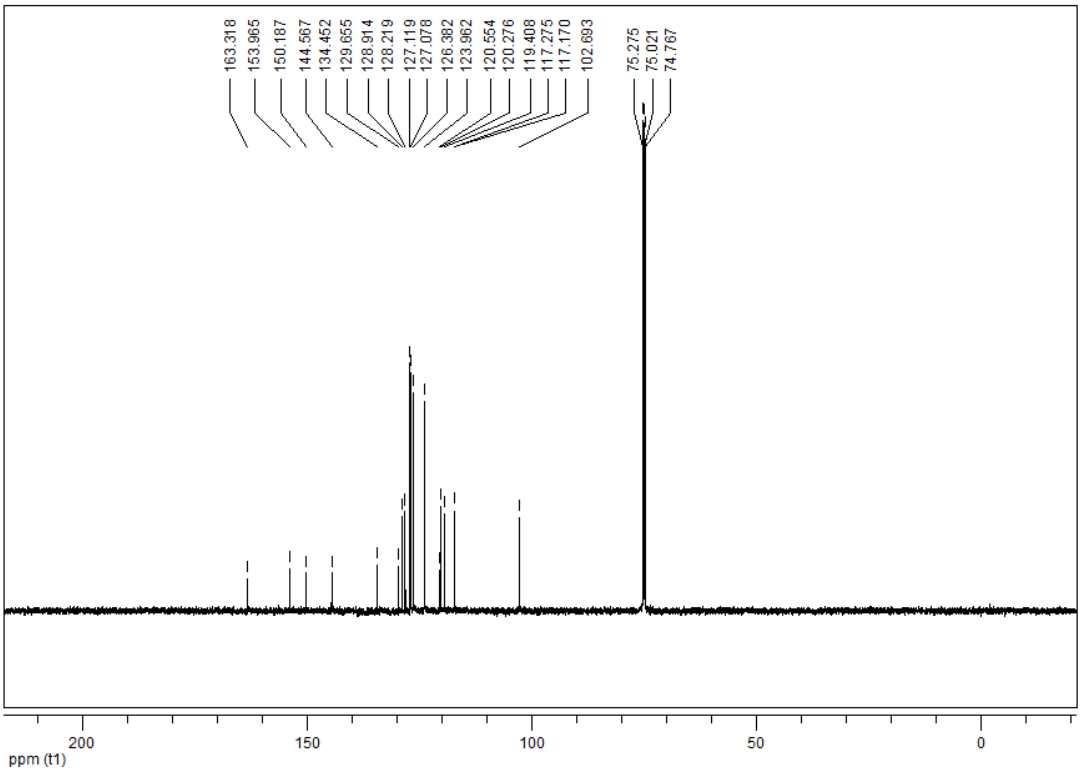
12: ^{13}C NMR (125 MHz, DMSO-d$_6$)



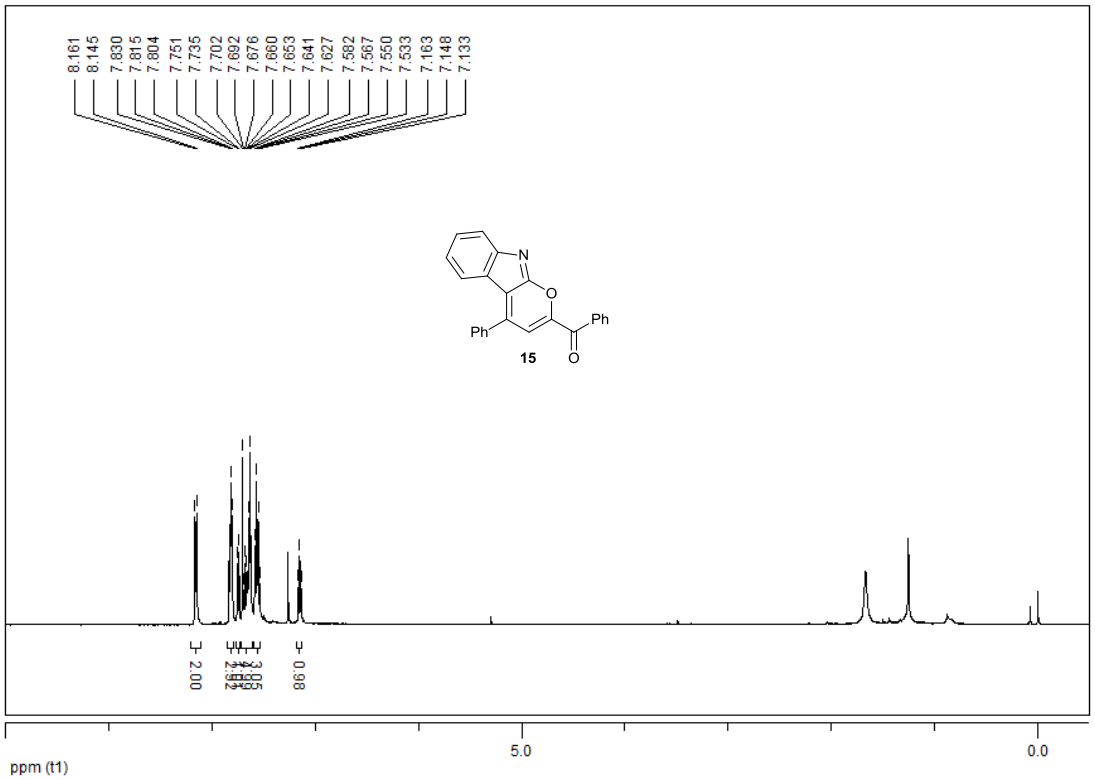
13: ^{1}H NMR (500 MHz, $CDCl_3$)



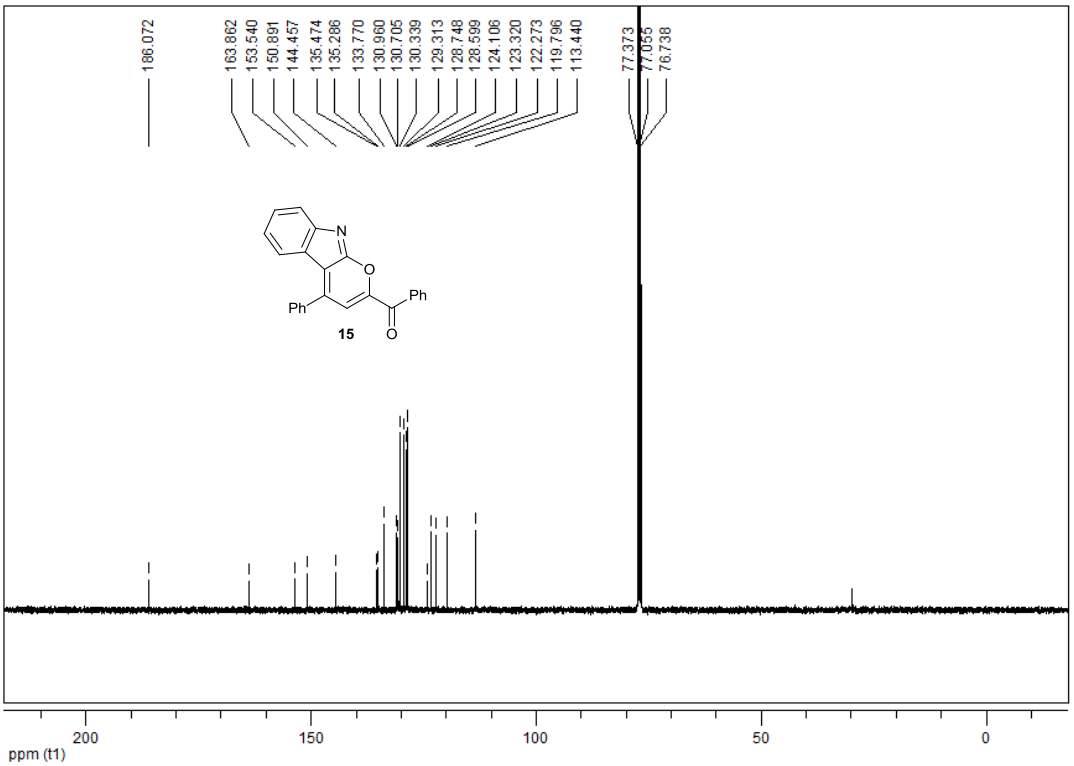
13: ^{13}C NMR (125 MHz, $CDCl_3$)



15: ^{1}H NMR (500 MHz, $CDCl_3$)



15: ^{13}C NMR (100 MHz, $CDCl_3$)



IX. Reference

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