Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photocatalytic Redox-Neutral Reaction of γ-Indolyl α-Keto Esters

Man Wang,[a] Ming Li,[a] Long Zhang,[*b] Ran Song,[a] Daoshan Yang,[a] and Jian Lv[*a]

[a]Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science & Technology, Qingdao, 266042, China

[b]Center of Basic Molecular Science, Department of Chemistry, Tsinghua University, Beijing 100084, China

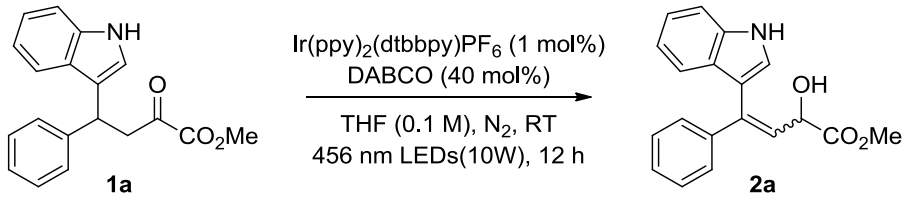
TABLE OF CONTENTS **PAGE**

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. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker Avance 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. Optimization

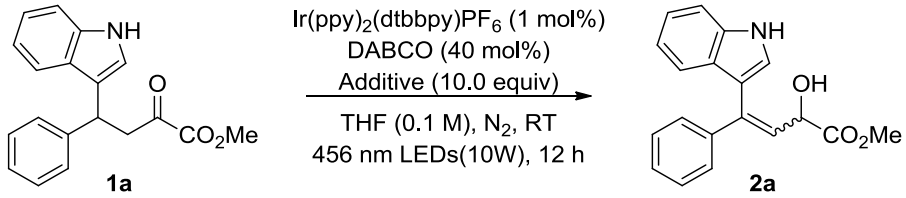
Table S1. Screening of different bases in the redox-neutral reaction of *α*-keto ester **1a** [a]



entry	base	yield (%])[b]	*Z*/*E*[c]
1	none	NR	–
2	DIPEA	NP	–
3	quinine	trace	–
4	quinuclidine	31	85:15
5	DABCO	39	80:20
6	Et_3N	trace	–
7	Morpholine	trace	–
8	N1,N1-diethylethane-1,2-diamine	trace	–
9	Na_3PO_4	NR	–
10	Na_2CO_3	NR	–

[a] Reaction Conditions: **1a** (0.1 mmol), base (40 mol%), and $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%) were added to THF (1.0 mL) as solvent at room temperature for 12 h. [b] Isolated yield. [c] Determined by ^1H NMR. NR = No reaction, NP = No product, DIPEA = Diisopropylethylamine.

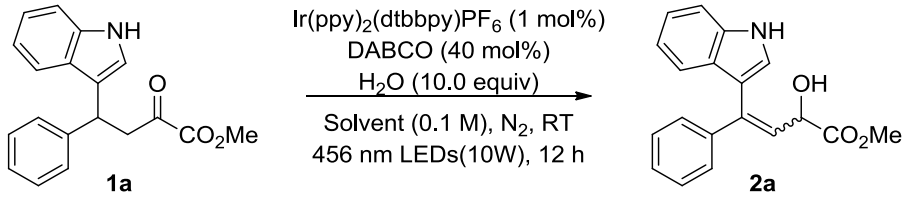
Table S2. Screening of different additives in the redox-neutral reaction of α-keto ester **1a** [a]



entry	additive	yield [%][b]	*Z*/*E*[c]
1	none	39	80:20
2	H_2O	72	77:23
3	MeOH	49	77:23
4	EtOH	52	77:23
5	*i*PrOH	39	77:23
6[d]	H_2O	58	73:27
7[e]	H_2O	67	75:25
8[f]	H_2O	47	73:27

[a] Reaction Conditions: **1a** (0.1 mmol), Additive (1.0 mmol), DABCO (40 mol%), and $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%) were added to THF (1.0 mL) as solvent at room temperature for 12 h. [b] Isolated yield. [c] Determined by ^1H NMR. [d] H_2O (5.0 equiv). [e] H_2O (20.0 equiv). [f] H_2O (0.1 mL).

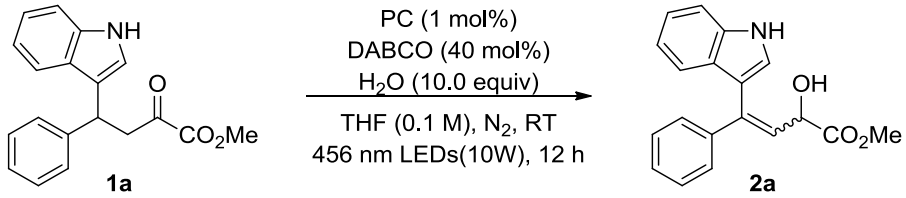
Table S3. Screening of different solvents in the redox-neutral reaction of α-keto ester **1a** [a]



entry	solvent	yield [%][b]	*Z*/*E*[c]
1	THF	72	77:23
2	DCM	Trace	–
3	Toluene	NR	–
4	MeCN	Trace	–
5	Acetone	NR	–
6	Et_2O	NR	–
7	THP	43	73:27
8	Dioxane	62	75:25
9	DME	51	83:17

[a] Reaction Conditions: **1a** (0.1 mmol), H_2O (1.0 mmol), DABCO (40 mol%), and $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%) were added to solvent (1.0 mL) at room temperature for 12 h. [b] Isolated yield. [c] Determined by ^1H NMR. DCM = dichloromethane, THP = tetrahydro-2H-pyran, DME = 1,2-dimethoxyethane.

Table S4. Screening of different photocatalysts in the redox-neutral reaction of α-keto ester **1a** [a]

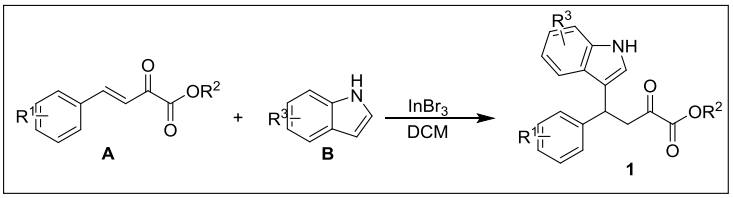


entry	PC	Yield [%][b]	*Z*/*E*[c]
1	None	NR	–
2	Acr-MesBF_4	NR	–
3	Eosin Y	NR	–
4	$Ir(ppy)_3$	NR	–
5	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	NR	–
6	$Ir[df(CF_3)ppy)_2(dtbpy)]PF_6$	20	72:28
7	$Ir(ppy)_2(dtbbpy)PF_6$	72	77:23
8[d]	$Ir(ppy)_2(dtbbpy)PF_6$	Trace	–
9[e]	$Ir(ppy)_2(dtbbpy)PF_6$	Trace	–
10[f]	$Ir(ppy)_2(dtbbpy)PF_6$	NR	–

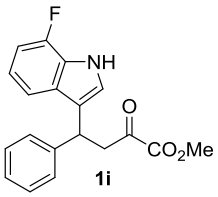
[a] Reaction Conditions: **1a** (0.1 mmol), H_2O (1.0 mmol), DABCO (40 mol%), and $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%) were added to solvent (1.0 mL) at room temperature for 12 h. [b] Isolated yield. [c] Determined by ^1H NMR. [d] CFL as light source. [e] In the air. [f] In the black.

III. Experimental Procedures and Characterization Data

A) Synthesis of γ-Indolyl α-Keto Esters 1:

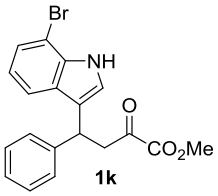


General procedure I: *β*, *γ*-unsaturated *α*-ketoester derivatives **A** (4 mmol) and indole derivatives **B** (4.8 mmol) were dissolved in DCM (40 mL), then $InBr_3$ (2.5 mol%, 0.1 mmol) was added. The solution was stirred at room temperature for 2 hours. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1 to 3:1, v/v) gave the desired products **1**.



1i

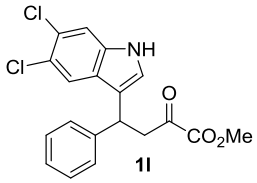
1i: Prepared according to the general procedure I above and obtained as light yellow solid (1.27g, 98%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, DMSO) δ 11.41 (s, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.87 – 6.85 (m, 2H), 4.70 (t, *J* = 7.0 Hz, 1H), 3.78 – 3.73 (m, 1H), 3.74 (s, 3H), 3.60 (dd, *J* = 7.5, 18.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 192.1, 160.8, 149.1 (d, *J* = 243.2Hz), 144.2, 130.2 (d, *J* = 5.8Hz), 128.2, 127.6, 126.1, 123.6 (d, *J* = 13.0Hz), 123.2, 118.6(d, *J* = 5.9Hz), 118.3, 114.9, 105.9 (d, *J* = 16.0Hz), 52.6, 44.9, 36.7 ppm.



1k

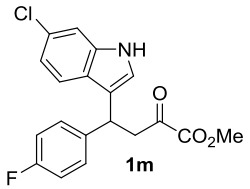
1k: Prepared according to the general procedure I above and obtained as light yellow solid (1.48g, 96%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500

MHz, DMSO) δ 11.15 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.35 (d, *J* =7.5 Hz, 2H), 7.26 – 7.23 (m, 3H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 4.70 (t, *J* = 7.0 Hz, 1H), 3.79 – 3.71 (m, 1H), 3.74 (s, 3H), 3.59 (dd, *J* = 7.0, 18.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 192.6, 161.4, 144.6, 135.0, 128.7, 128.4, 128.1, 126.6, 124.1, 123.9, 120.3, 119.1, 118.7, 104.6, 53.1, 45.4, 37.3 ppm.



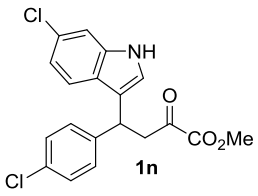
1l

1l: Prepared according to the general procedure I above and obtained as light yellow solid (1.05g, 70%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.45 (s, 1H), 7.42 (s, 1H), 7.29 (d, J = 4.5 Hz, 4H), 7.23 – 7.20 (m, 1H), 7.08 (s, 1H), 4.83 (t, J = 7.5 Hz, 1H), 3.81 (s, 3H), 3.65 (dd, J = 8.0, 17.5 Hz, 1H), 3.57 (dd, J = 7.0, 17.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 161.2, 142.5, 135.3, 128.8, 127.6, 127.0, 126.3, 126.2, 123.7, 123.3, 120.4, 118.1, 112.7, 53.1, 45.5, 37.4 ppm.



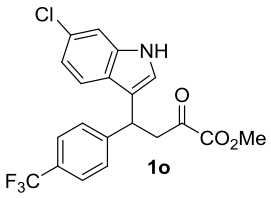
1m

1m: Prepared according to the general procedure I above and obtained as light yellow solid (1.02g, 71%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.32 (d, *J* =1.5 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.04 (d, *J* =2.0 Hz, 1H), 7.00 – 6.93 (m, 3H), 4.88 (t, *J* = 7.5 Hz, 1H), 3.80 (s, 3H), 3.64 (dd, *J* = 7.0, 17.0 Hz, 1H), 3.55 (dd, *J* = 8.0, 17.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 161.6 (d, *J* = 245.6Hz), 161.2, 138.6, 136.9, 129.2 (d, *J* = 7.6Hz), 128.5, 124.9, 121.9, 120.3 (d, *J* = 28.2Hz), 118.4, 115.4 (d, *J* = 21.3Hz), 111.2, 53.1, 45.6, 36.8 ppm.



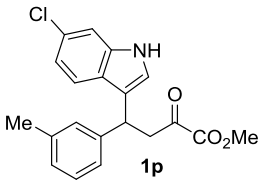
1n

1n: Prepared according to the general procedure I above and obtained as light yellow solid (1.16g, 77%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.32 (d, *J* =1.0 Hz, 1H), 7.25 – 7.23 (m, 5H), 7.05 (s, 1H), 7.00 – 6.98 (m, 1H), 4.85 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.64 (dd, *J* = 7.5, 17.0 Hz, 1H), 3.55 (dd, *J* = 8.0, 17.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 161.1, 141.4, 136.9, 132.5, 129.1, 128.8, 128.0, 124.8, 122.0, 120.5, 120.2, 118.1, 111.2, 53.1, 45.3, 36.9 ppm.



1o

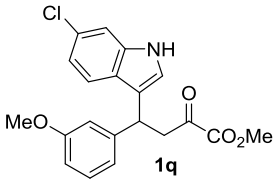
1o: Prepared according to the general procedure I above and obtained as light yellow solid (1.13g, 69%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 1.5 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 7.01 – 6.99 (m, 1H), 4.94 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.69 (dd, *J* = 8.0, 17.5 Hz, 1H), 3.60 (dd, *J* = 7.5, 17.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 161.1, 147.0, 136.9, 128.6, 128.1, 125.6, 125.2, 124.8, 121.1 (q, *J* = 256.2 Hz), 120.6, 117.7, 111.2, 53.2, 45.2, 37.2 ppm.



1p

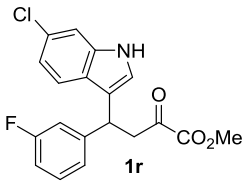
1p: Prepared according to the general procedure I above and obtained as light yellow solid (0.64g, 45%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.25 – 7.28 (m, 2H), 7.18 – 7.14 (m, 2H), 7.09 – 7.06 (m, 2H), 7.01 (s, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 4.83 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H), 3.64 (dd,

J = 7.5, 17.5 Hz, 1H), 3.55 (dd, *J* = 7.5, 17.0 Hz, 1H), 2.28 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 160.8, 139.4, 136.4, 135.8, 128.8, 128.0, 127.8, 127.0, 124.5, 124.2, 121.5, 119.8, 118.2, 110.6, 52.3, 45.1, 36.7, 20.5 ppm.



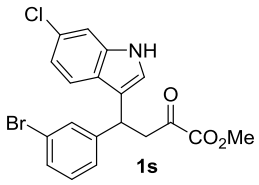
1q

1q: Prepared according to the general procedure I above and obtained as light yellow solid (1.19g, 80%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, DMSO) δ 11.05 (s, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.34 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.89 (m, 3H), 6.72 – 6.70 (m, 1H), 4.67 (t, *J* = 7.5 Hz, 1H), 3.74 (s, 3H), 3.73 – 3.70 (m, 1H), 3.69 (s, 3H), 3.57 (dd, *J* = 7.0, 18.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 192.1, 160.9, 159.1, 145.8, 136.7, 129.2, 125.8, 125.0, 123.2, 120.0, 119.8, 118.6, 117.4, 113.6, 111.1, 110.9, 54.9, 52.6, 44.8, 36.6 ppm.



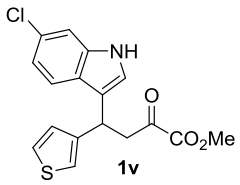
1r

1r: Prepared according to the general procedure I above and obtained as light yellow solid (1.12g, 78%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.33 (s, 1H), 7.28 – 7.21 (m, 2H), 7.10 (d, *J* =7.5 Hz, 1H), 7.06 (s, 1H), 7.01 – 6.96 (m, 2H), 6.88 (t, *J* = 8.0 Hz, 1H), 4.88 (t, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 3.66 (dd, *J* = 7.5, 17.5 Hz, 1H), 3.56 (dd, *J* = 8.0, 17.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 163.0 (d, *J* = 246.7Hz), 161.1, 145.6 (d, *J* = 6.8Hz), 136.9, 130.1 (d, *J* = 8.2Hz), 128.5, 124.9, 123.4, 122.0, 120.5, 120.1, 117.9, 114.7 (d, *J* = 21.8Hz), 113.7 (d, *J* = 21.3Hz), 111.2, 53.1, 45.3, 37.2 ppm.



1s

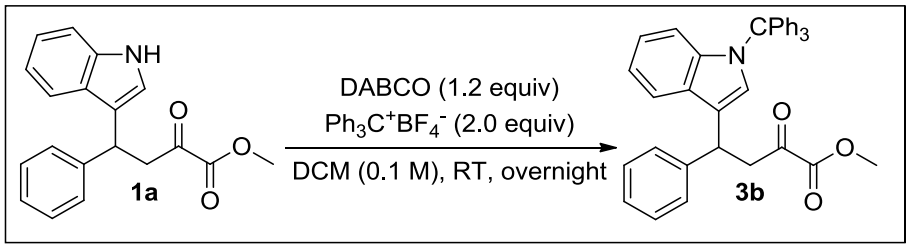
1s: Prepared according to the general procedure I above and obtained as white solid (1.35g, 80%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, DMSO) δ 11.10 (s, 1H), 7.54 (s, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.39 – 7.26 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 4.70 (t, *J* = 7.5 Hz, 1H), 3.77 – 3.72 (m, 4H), 3.61 (dd, *J* = 7.5, 17.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 192.3, 161.2, 147.7, 137.1, 130.9, 130.8, 129.5, 127.3, 126.5, 125.3, 123.9, 122.0, 120.4, 119.3, 117.4, 111.5, 53.1, 45.1, 36.6 ppm.



1v

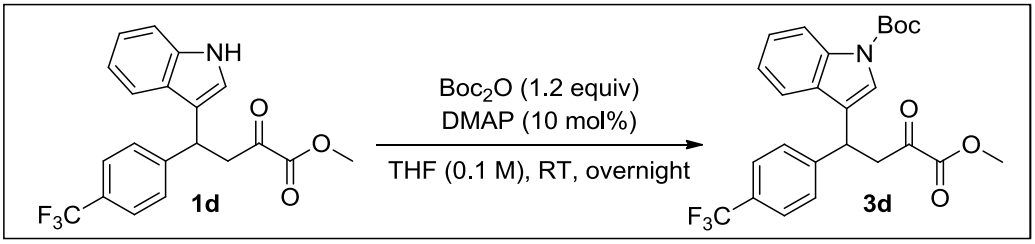
1v: Prepared according to the general procedure I above and obtained as light yellow solid (0.63g, 45%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, DMSO) δ 11.04 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.30 – 7.26 (m, 2H), 7.01 (d, *J* = 5.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 7.5 Hz, 1H), 3.73 (s, 3H), 3.71 – 3.58 (m, 2H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 192.1, 160.8, 144.9, 136.7, 127.7, 125.8, 124.8, 123.3, 120.5, 120.0, 118.6, 117.2, 111.0, 52.6, 44.8, 32.1 ppm.

B) Synthesis of γ-*N*-CPh_3 Indolyl α-Keto Ester 3b



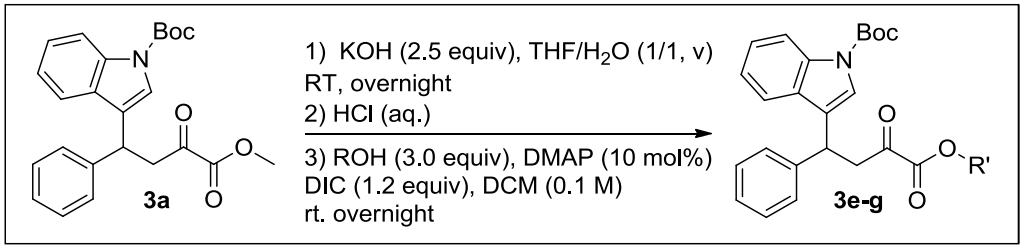
Reaction procedure II: γ-Indolyl α-keto ester **1a** (2 mmol) and $Ph_3C^+BF_4^-$ (4 mmol) were dissolved in DCM (20 mL), then DABCO (2.4 mmol) was added. The solution was stirred at room temperature overnight. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 10:1, v/v) gave the desired products **3b** (white solid, 0.66 g, 60%); ^{d1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 15H), 7.19 – 7.15 (m, 6H), 6.95 (s, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.72 (t, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 8.5 Hz, 1H), 4.86 (t, *J* = 7.0 Hz, 1H), 3.70 (s, 3H), 3.53 (dd, *J* = 7.5 Hz, *J* = 16.5 Hz, 1H), 3.45 (dd, *J* = 7.5 Hz, *J* = 16.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 161.3, 143.3, 142.7, 137.9, 130.1, 128.5, 127.8, 127.7, 127.4, 126.9, 126.5, 121.1, 119.4, 119.2, 116.1, 116.0, 75.6, 52.8, 45.6, 38.0 ppm.

C) Synthesis of γ-*N*-Boc Indolyl α-Keto Ester 3d

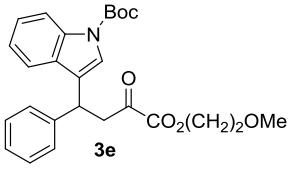


Reaction procedure III: γ-Indolyl α-keto ester **1d** (2 mmol) was dissolved in 20 mL THF, then Boc_2O (2.4 mmol) and DMAP (0.2 mmol) were added. The reaction mixture was stirred at room temperature overnight. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography (eluent: PE/EA = 12:1, v/v) on silica gel gave the desired product 3d (colorless oil, 523 mg, 55% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 3H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.89 (t, *J* = 7.5 Hz, 1H), 3.83 (s, 3H), 3.70 (dd, *J* = 6.5 Hz, *J* = 18.0 Hz, 1H), 3.62 (dd, *J* = 8.5 Hz, *J* = 18.0 Hz, 1H), 1.69 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 161.0, 149.7, 146.1, 135.7, 129.4, 129.2, 128.3, 125.7 (q, *J* = 3.75 Hz), 124.8, 124.1 (q, *J* = 261.8 Hz), 122.7, 122.6, 121.8, 119.4, 115.4, 84.1, 53.2, 44.8, 37.0, 28.2 ppm.

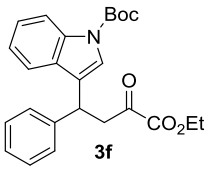
D) Synthesis of γ-*N*-Boc Indolyl α-Keto Esters 4e-g:



General procedure IV: γ-*N*-Boc indolyl α-keto **3a** (1 mmol) was dissolved in mixed solvent (10 mL, THF/H_2O = 1:1, v/v), then KOH (2.5 mmol) was added. The reaction mixture was stirred at room temperature overnight. After reaction, the organic solvent was evaporated under reduced pressure and the water solvent was treated by hydrochloric acid (3 M, until pH 1) and extracted with DCM (2 × 30 mL). The organic layers were dried (Na_2SO_4), evaporated under reduced pressure and gave a yellow solid acid. To a solution of acid in DCM (10 mL) was added corresponding alcohol (3 mmol), DMAP (0.1 mmol) and DIC (N,N'-Diisopropylcarbodiimide, 1.2 mmol). The reaction mixture was stirred at room temperature overnight. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel gave the desired product.

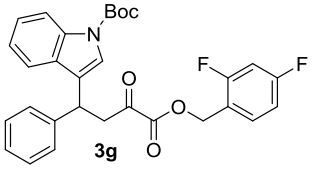


3e: Prepared according to the general procedure IV above and obtained as white solid (0.18g, 40%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.49 (s, 1H), 7.33 – 7.32 (m, 3H), 7.28 – 7.24 (m, 3H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 4.83 (t, *J* = 7.5 Hz, 1H), 4.37 – 4.30 (m, 2H), 3.67 (dd, *J* = 7.0 Hz, *J* = 17.5 Hz, 1H), 3.63 – 3.56 (m, 3H), 3.35 (s, 3H), 1.68 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9, 160.7, 149.8, 142.0, 135.7, 129.6, 128.7, 127.9, 126.9, 124.5, 122.7, 122.5, 119.7, 115.3, 83.8, 69.7, 65.2, 59.0, 45.2, 37.3, 28.2 ppm.



3f

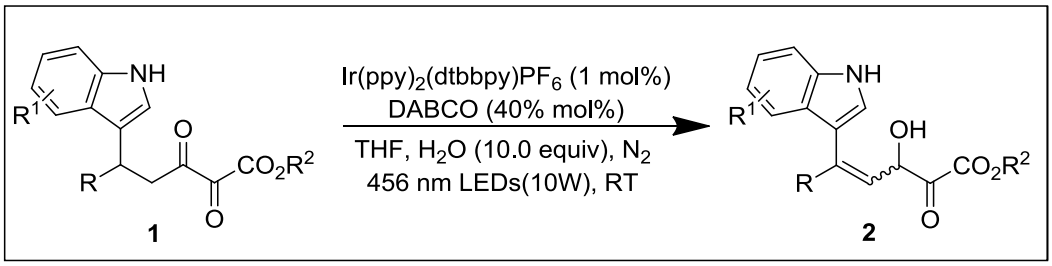
3f: Prepared according to the general procedure IV above and obtained as red oil (0.19g, 45%), eluent: petroleum ether/ethyl acetate (12:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.50 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 3H), 7.28 – 7.24 (m, 3H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 4.82 (t, *J* = 7.5 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.66 (dd, *J* = 7.0 Hz, *J* = 17.5 Hz, 1H), 3.58 (dd, *J* = 7.5 Hz, *J* = 17.0 Hz, 1H), 1.68 (s, 9H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 160.8, 149.8, 142.0, 135.7, 129.6, 128.7, 127.9, 126.9, 124.5 122.7, 122.5, 119.7, 115.2, 83.8, 62.6, 45.1, 37.4, 28.2, 13.9 ppm.



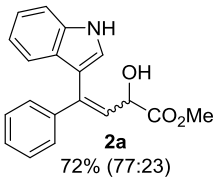
3g

3g: Prepared according to the general procedure IV above and obtained as colorless oil (0.16g, 31%), eluent: petroleum ether/ethyl acetate (10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.48 (s, 1H), 7.35 – 7.29 (m, 4H), 7.25 (t, *J* = 7.5 Hz, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.87 – 6.80 (m, 2H), 5.22 (dd, *J* = 12.5 Hz, *J* = 15 Hz, 2H), 4.80 (t, *J* = 7.5 Hz, 1H), 3.65 (dd, *J* = 7.0 Hz, *J* = 17.5 Hz, 1H), 3.58 (dd, *J* = 8.0 Hz, *J* = 17.5 Hz, 1H), 1.67 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 163.5 (dd, *J* = 12.0, 249.5 Hz), 161.4 (dd, *J* = 12.6, 250.6 Hz), 160.4, 149.8, 141.9, 135.7, 132.2 (dd, *J* = 4.8, 10.0 Hz), 129.5, 128.7, 127.8, 127.0, 124.6, 122.6, 122.5, 119.6, 117.8 (dd, *J* = 4.0, 14.7 Hz), 115.3, 111.6 (dd, *J* = 3.7, 21.3 Hz), 104.2 (t, *J* = 25.3 Hz), 83.8, 61.3 (d, *J* = 3.8 Hz), 45.2, 37.4, 28.2 ppm.

E) Synthesis of 4-indolyl substituted 2-hydroxy-3-enoic acid esters 2:



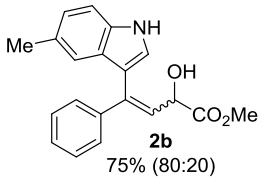
General procedure V: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-indolyl α-keto ester **1** (0.2 mmol), DABCO (0.08 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and H_2O (36 μL) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10W) at room temperature for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel gave the desired product **2**.



2a
72% (77:23)

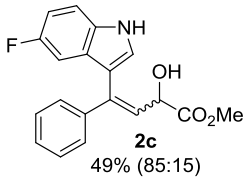
2a: Prepared according to the general procedure V above and obtained as light yellow solid (44.2mg, 72% yield, *Z/E* = 77:23, M.P. = 124 – 130 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.20 (s, 0.3H), 7.59 (d, *J* = 2.0 Hz, 1.3H), 7.44 – 7.43 (m, 0.6H), 7.40 – 7.35 (m, 4.2H), 7.29 – 7.28 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 0.3H), 7.17 (d, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 0.3H), 6.98 – 6.93 (m, 2H), 6.88 (d, *J* = 2.5 Hz, 0.3H), 6.15 (d, *J* = 10.0 Hz, 0.3H), 6.00 (d, *J* = 9.5 Hz, 1H), 5.01 (d, *J* = 9.0 Hz, 1H), 4.78 (d, *J* = 9.5 Hz, 0.3H), 3.82 (s, 0.9H), 3.81 (s, 3H), 3.04 (s, 1H), 2.97 (s, 0.3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 174.8, 141.9, 141.3, 141.1, 139.3, 136.8, 136.2, 129.9, 128.2, 128.1, 128.0, 127.8, 127.8, 127.1, 125.7, 125.6, 124.0, 122.6, 122.4, 120.9, 120.7, 120.6, 120.5, 120.0, 118.7, 113.5, 111.4, 111.1, 69.0, 68.9, 52.9 ppm; IR(KBr, cm^{-1}): 3477, 2922, 1725, 1458, 1441, 1416, 1246, 1101, 1056, 822, 750, 658; HRMS (ESI) calcd for $C_{19}H_{17}NNaO_3^+$ $(M + Na)^+$ 330.1106,

found 330.1105.



2b
75% (80:20)

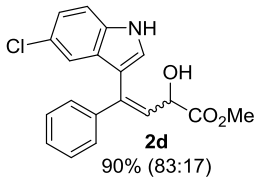
2b: Prepared according to the general procedure V above for 36 h and obtained as light yellow solid (48.2mg, 75% yield, *Z/E* = 80:20, M.P. = 140 – 145 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.12 (s, 0.25H), 7.50 (d, *J* = 1.5 Hz, 1H), 7.45 – 7.42 (m, 0.75H), 7.39 – 7.38 (m, 2.75H), 7.29 – 7.28 (m, 4H), 7.24 (s, 0.25H), 7.02 (d, *J* = 8.5 Hz, 0.25H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.79 (m, 1.25H), 6.15 (d, *J* = 10.0 Hz, 0.25H), 6.00 (d, *J* = 9.5 Hz, 1H), 4.99 (dd, *J* = 4.5 Hz, *J* = 9.0 Hz, 1H), 4.78 (dd, *J* = 4.5 Hz, *J* = 9.5 Hz, 0.25H), 3.82 (s, 0.75H), 3.80 (s, 3H), 3.05 (d, *J* = 4.5 Hz, 1H), 3.00 (d, *J* = 5.0 Hz, 0.25H), 2.42 (s, 0.75H), 2.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.5, 174.4, 140.7, 140.6, 138.9, 134.0, 129.4, 128.7, 127.7, 127.6, 127.5, 127.3, 126.9, 125.6, 125.3, 123.7, 123.5, 119.9, 119.7, 117.6, 112.4, 110.6, 110.3, 68.5, 52.4, 21.2, 21.0 ppm; IR(KBr, cm^{-1}): 3470, 3284, 2952, 1726, 1622, 1536, 1484, 1445, 1337, 1272, 1218, 1111, 1069, 977, 752, 700; HRMS (ESI) calcd for $C_{20}H_{19}NNaO_3^+$ $(M + Na)^+$ 344.1263, found 344.1260.



2c
49% (85:15)

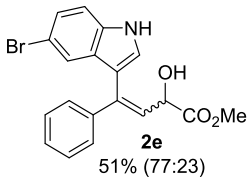
2c: Prepared according to the general procedure V above and obtained as light yellow solid (31.9mg, 49% yield, *Z/E* = 85:15, M.P. = 126 – 128 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.27 (s, 0.17H), 7.61 (s, 1H), 7.40 – 7.38 (m, 0.85H), 7.36 – 7.34 (m, 2H), 7.31 – 7.28 (m, 4H), 7.16 – 7.14 (m, 0.17H), 6.94 – 6.93 (m, 0.34H), 6.92 – 6.88 (m, 1H), 6.61 – 6.59 (m, 1H), 6.04 (d, *J* = 10.0 Hz, 0.17H), 5.98 (d, *J* = 10.0 Hz, 1H), 5.98 (d, *J* = 14.5 Hz, 1H), 5.78 (d, *J* = 14.5 Hz, 0.17H), 3.83 (s, 0.51H), 3.81 (s, 3H), 3.11 (s, 1H), 3.08 (s, 0.17H) ppm; ^{13}C

NMR (125 MHz, $CDCl_3$) δ 174.7, 157.8 (d, *J* = 235.9 Hz), 140.8 (d, *J* = 17.0 Hz), 132.7, 129.8, 128.3, 128.2, 127.8, 127.3, 124.2, 120.6, 113.6, 111.8 (d, *J* = 9.7 Hz), 110.9 (d, *J* = 26.6 Hz), 105.8 (d, *J* = 24.1 Hz), 68.9, 68.8, 53.0 ppm; IR(KBr, cm^{-1}): 3434, 3259, 1726, 1611, 1493, 1330, 1238, 1201, 1168, 1030, 880, 765, 696; HRMS (ESI) calcd for $C_{19}H_{16}FNNaO_3^+$ $(M + Na)^+$ 348.1012, found 348.1009.



2d
90% (83:17)

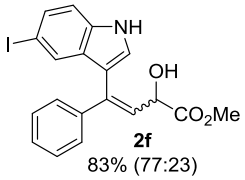
2d: Prepared according to the general procedure V above and obtained as light yellow solid (61.4mg, 90% yield, *Z/E* = 83:17, M.P. = 88 – 90 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^1H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.37 (s, 0.20H), 7.52 (s, 1.20H), 7.38 (s, 1H), 7.34 – 7.33 (m, 2H), 7.29 – 7.27 (m, 3.4H), 7.25 – 7.23 (m, 0.80H), 7.14 – 7.12 (m, 0.20H), 7.11 – 7.09 (m, 1H), 6.98 (s, 1H), 6.86 (s, 0.20H), 6.07 (d, *J* = 10.0 Hz, 0.20H), 6.02 (d, *J* = 10.0 Hz, 1H), 4.93 (dd, *J* = 4.0 Hz, *J* = 9.5 Hz, 1H), 4.79 (dd, *J* = 3.5 Hz, *J* = 10.0 Hz, 0.20H), 3.83 (s, 0.60H), 3.79 (s, 3H), 3.16 (d, *J* = 4.5 Hz, 1H), 3.13 (d, *J* = 4.0 Hz, 0.20H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 140.8, 140.5, 134.6, 129.8, 128.4, 127.6, 126.8, 125.7, 124.5, 122.8, 120.9, 120.2, 113.1, 112.2, 69.0, 53.0 ppm; IR(KBr, cm^{-1}): 3442, 3138, 1723, 1622, 1541, 1451, 1223, 1066, 866, 798, 732; HRMS (ESI) calcd for $C_{19}H_{16}ClNNaO_3^+$ $(M + Na)^+$ 364.0716, found 364.0718.



2e
51% (77:23)

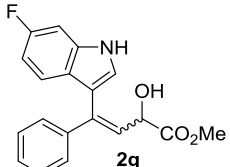
2e: Prepared according to the general procedure V above and obtained as light yellow solid (39.3mg, 51% yield, *Z/E* = 77:23, M.P. = 128 – 130 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.33 (s, 0.30H), 7.68 (s, 0.30H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.39 (s, 1.60H), 7.34 – 7.33 (m, 2.90H), 7.25 (s, 2H), 7.22 – 7.20 (m, 0.60H), 7.16 (s, 1H), 6.85 (d, *J* = 2.0 Hz, 0.30H), 6.07 (d, *J* = 10.0

Hz, 0.30H), 6.03 (d, *J* = 9.5 Hz, 1H), 4.90 (d, *J* = 10.5 Hz, 1H), 4.78 (d, *J* = 10.0 Hz, 0.30H), 3.84 (s, 0.90H), 3.81 (s, 3H), 3.11 (s, 1.30H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 174.6, 141.4, 140.7, 140.4, 138.9, 135.4, 134.8, 129.8, 128.9, 128.4, 128.3, 128.2, 128.0, 127.6, 127.1, 126.5, 125.4, 125.3, 124.7, 123.3, 121.0, 118.4, 113.9, 113.3, 112.9, 112.6, 68.9, 68.8, 53.0 ppm; IR(KBr, cm^{-1}): 3464, 3024, 1732, 1621, 1536, 1446, 1266, 1214, 1070, 864, 799, 731, 698; HRMS (ESI) calcd for $C_{19}H_{16}BrNNaO_3^+$ $(M + Na)^+$ 408.0211, found 408.0203.



2f
83% (77:23)

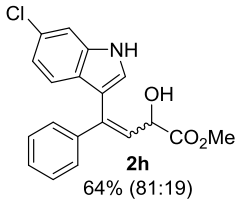
2f: Prepared according to the general procedure V above for 15 h and obtained as light yellow solid (71.9mg, 83% yield, *Z/E* = 77:23, M.P. = 127 – 129 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.31 (s, 0.30H), 7.90 (s, 0.30H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.42 (s, 0.30H), 7.41 – 7.39 (m, 3.20H), 7.34 – 7.33 (m, 2H), 7.30 – 7.28 (m, 3.30H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 0.30H), 6.81 (d, *J* = 2.0 Hz, 0.30H), 6.07 – 6.03 (m, 1.30H), 4.89 (d, *J* = 9.0 Hz, 1H), 4.78 (d, *J* = 9.5 Hz, 0.30H), 3.85 (s, 0.90H), 3.82 (s, 3H), 3.11 (s, 1 H), 3.08 (s, 0.30 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 140.7, 140.3, 135.2, 130.8, 129.8, 129.6, 128.4, 128.0, 127.6, 126.1, 124.7, 121.1, 113.4, 113.2, 112.8, 83.6, 68.9, 68.8, 53.1 ppm; IR(KBr, cm^{-1}): 3416, 2951, 1731, 1625, 1445, 1241, 1102, 1061, 879, 797, 699; HRMS (ESI) calcd for $C_{19}H_{16}INNaO_3^+$ $(M + Na)^+$ 456.0073, found 456.0069.



2g
38% (96:4)

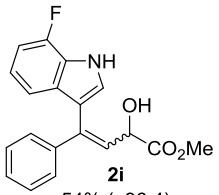
2g: Prepared according to the general procedure V above and obtained as light yellow solid (20.2mg, 38% yield, *Z/E* = 96:4, M.P. = 118 – 122 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.54 (s, 1H), 7.34

(s, 2H), 7.28 (s, 3H), 7.05 (d, *J* = 4.0 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.69 (t, *J* = 8.5 Hz, 1H), 6.00 (d, *J* = 9.5 Hz, 1H), 5.00 (d, *J* = 9.5 Hz, 1H), 3.80 (s, 3H), 3.63 (s, 0.13H), 3.18 (s, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 159.3 (d, *J* = 239.1 Hz), 140.4, 140.1, 135.5 (d, *J* = 12.2 Hz), 127.6, 127.5, 127.1, 125.2 (d, *J* = 3.0 Hz), 123.5, 123.0, 120.9 (d, *J* = 10.0 Hz), 112.8, 108.1 (d, *J* = 24.4 Hz), 96.8 (d, *J* = 26.3 Hz), 68.3, 52.3 ppm; IR(KBr, cm^{-1}): 3470, 3321, 2957, 1709, 1620, 1541, 1277, 1142, 1055, 800, 784; HRMS (ESI) calcd for $C_{19}H_{16}FNNaO_3^+$ $(M + Na)^+$ 348.1012, found 348.1016.



2h
64% (81:19)

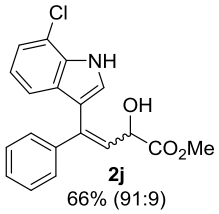
2h: Prepared according to the general procedure V above and obtained as light yellow solid (43.7mg, 64% yield, *Z/E* = 81:19, M.P. = 116 – 120 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, DMSO) δ 11.51 (s, 1H), 11.39 (s, 0.23H), 8.31 (s, 0.23H), 7.63 (s, 1H), 7.48 (s, 1H), 7.45 – 7.40 (m, 0.69H), 7.33 – 7.31 (s, 3.69H), 7.27 – 7.26 (m, 2H), 7.03 – 7.01 (m, 0.46H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.08 (d, *J* = 9.5 Hz, 0.23H), 5.97 (d, *J* = 9.0 Hz, 1H), 5.79 (d, *J* = 5.5 Hz, 1H), 5.73 (d, *J* = 6.0 Hz, 0.23H), 4.78 – 4.74 (m, 1H), 4.50 – 4.47 (m, 0.23H), 3.67 (s, 3.69H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 173.3, 141.2, 137.9, 136.7, 129.3, 128.3, 127.9, 127.4, 127.3, 126.1, 125.8, 125.3, 120.9, 119.3, 111.7, 111.4, 68.6, 51.8 ppm; IR(KBr, cm^{-1}): 3408, 2952, 1732, 1614, 1450, 1402, 1245, 1102, 1060, 805; HRMS (ESI) calcd for $C_{19}H_{16}ClNNaO_3^+$ $(M + Na)^+$ 364.0716, found 364.0711.



2i
54% (>96:4)

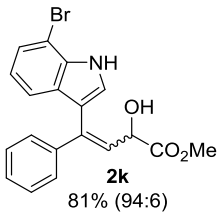
2i: Prepared according to the general procedure V above and obtained as light yellow solid (35.1mg, 54% yield, *Z/E* > 96:4, M.P. = 132 – 134 °C), eluent: petroleum

ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, DMSO) δ 11.91 (s, 1H), 7.63 (s, 1H), 7.31 (s, 3H), 7.28 – 7.26 (m, 2H), 6.92 – 6.88 (m, 1H), 6.81 – 6.77 (m, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.99 (d, *J* = 9.5 Hz, 1H), 5.81 (s, 1H), 4.76 (d, *J* = 9.0 Hz, 1H), 3.67 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 173.8, 149.7 (d, *J* = 244.1 Hz), 141.6, 138.6, 130.9 (d, *J* = 5.3 Hz), 128.8, 128.3, 127.8, 126.4, 124.7 (d, *J* = 13.2 Hz), 119.8 (d, *J* = 6.0 Hz), 116.4, 113.1, 106.6 (d, *J* = 15.9 Hz), 79.6, 69.1, 52.3 ppm; IR(KBr, cm^{-1}): 3399, 3026, 2952, 1729, 1641, 1579, 1496, 1445, 1237, 1043, 784, 701; HRMS (ESI) calcd for $C_{19}H_{16}FNNaO_3^+$ $(M + Na)^+$ 348.1012, found 348.1015.



2j
66% (91:9)

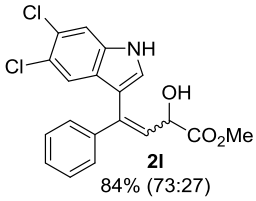
2j: Prepared according to the general procedure V above and obtained as light yellow solid (45.0mg, 66% yield, *Z/E* = 91:9, M.P. = 118 – 121 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.64 (s,1H), 7.35 – 7.29 (m, 6H), 6.88 (s, 2H), 6.02 (d, *J* = 8.0 Hz, 1H), 4.96 (s, 1H), 3.81 (s, 3H), 3.64 (s, 0.30H), 3.08 (s,1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 141.4, 141.0, 140.4, 138.9, 133.6, 129.8, 128.6, 128.3, 128.2, 128.2, 127.8, 126.1, 125.7, 124.7, 121.7, 120.8, 119.5, 116.6, 114.6, 68.9, 68.8, 53.0; IR(KBr, cm^{-1}): 3429, 3227, 1727, 1612, 1437, 1340, 1207, 1037, 877, 783, 739; HRMS (ESI) calcd for $C_{19}H_{16}ClNNaO_3^+$ $(M + Na)^+$ 364.0716, found 364.0710.



2k
81% (94:6)

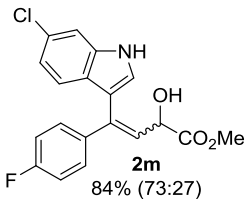
2k: Prepared according to the general procedure V above and obtained as light yellow solid (62.4mg, 81% yield, *Z/E* = 94:6, M.P. = 134 – 137 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.65 (s,1H), 7.35 –

7.29 (m, 6H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.82 (t, *J* = 7.0 Hz, 1H), 6.02 (d, *J* = 9.5 Hz, 1H), 4.97 (d, *J* = 9.0 Hz, 1H), 3.81 (s, 3H), 3.64 (s, 0.20H), 3.11 (s,1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 140.9, 140.5, 135.0, 129.8, 128.3, 128.2, 127.8, 126.1, 124.7, 124.7, 121.2, 120.1, 114.7, 104.7, 68.9, 53.0 ppm; IR(KBr, cm^{-1}): 3444, 3241, 1726, 1612, 1435, 1299, 1206, 1035, 971, 852, 821, 781; HRMS (ESI) calcd for $C_{19}H_{16}BrNNaO_3^+$ $(M + Na)^+$ 408.0211, found 408.0204.



2l
84% (73:27)

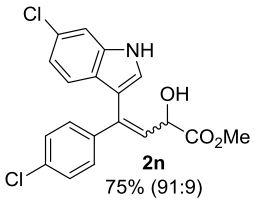
2l: Prepared according to the general procedure V above and obtained as light yellow solid (63.0mg, 84% yield, *Z/E* = 73:27, M.P. = 102 – 104 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.32 (s, 0.37H), 7.56 (s, 1.37H), 7.50 (s, 1H), 7.45 (s, 0.37H), 7.39 (s, 1.85H), 7.32 – 7.31 (m, 5H), 7.07 (s, 1H), 6.92 (d, *J* = 2.0 Hz, 0.37H), 6.05 – 6.02 (m, 1.37H), 4.89 (d, *J* = 9.5 Hz, 1H), 4.78 (d, *J* = 9.5 Hz, 0.37H), 3.85 (s, 1.11H), 3.82 (s, 3H), 3.12 (s, 1.37 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 172.9, 139.3, 138.9, 138.3, 133.9, 133.3, 128.1, 126.8, 126.5, 126.0, 125.6, 125.4, 124.8, 123.3, 122.5, 120.1, 119.7, 111.6, 111.2, 111.0, 67.2, 67.1, 51.4; IR(KBr, cm^{-1}): 3344, 2953, 1733, 1624, 1449, 1247, 1208, 1106, 762, 731, 701, 661, 569; HRMS (ESI) calcd for $C_{19}H_{15}Cl_2NNaO_3^+$ $(M + Na)^+$ 398.0327, found 398.0323.



2m
84% (73:27)

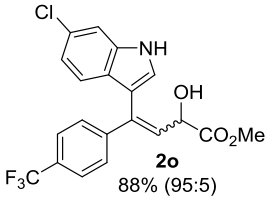
2m: Prepared according to the general procedure V above and obtained as light yellow solid (60.4mg, 84% yield, *Z/E* = 73:27, M.P. = 142 – 145 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.31 (s, 0.37H), 7.57 (s, 1H), 7.38 – 7.37 (m, 2H), 7.35 (s, 0.37H), 7.32 – 7.29 (m, 2.11H), 7.10 – 7.04 (m, 1.11H), 6.97 (t, *J* = 8.5 Hz, 2H), 6.93 – 6.89 (m, 1.37H), 6.83 (d, *J* = 8.5 Hz, 1H),

6.06 (d, *J* = 10.0 Hz, 0.37H), 5.94 (d, *J* = 9.5 Hz, 1H), 4.95 (d, *J* = 9.0 Hz, 1H), 4.75 (d, *J* = 10.0 Hz, 0.37H), 3.84 (s, 1.11H), 3.81 (s, 3H), 3.13 (s, 1.37 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 172.3, 160.6 (d, *J* = 248.3 Hz), 138.2, 137.3, 135.0, 134.8, 134.4, 132.5 (d, *J* = 3.5 Hz), 129.3 (d, *J* = 7.8 Hz), 127.2, 127.2, 126.3, 124.0, 123.6, 123.3, 121.9, 119.4, 119.2, 119.1, 119.0, 118.6, 116.5, 113.0, 112.9, 111.2, 109.2, 109.0, 66.6, 68.5, 50.8 ppm; IR(KBr, cm^{-1}): 3414, 2954, 1733, 1602, 1506, 1452, 1224, 1158, 1062, 803, 732, 649; HRMS (ESI) calcd for $C_{19}H_{15}ClFNNaO_3^+$ $(M + Na)^+$ 382.0622, found 382.0611.



2n
75% (91:9)

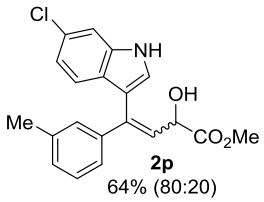
2n: Prepared according to the general procedure V above and obtained as light yellow solid (56.3mg, 75% yield, *Z/E* = 91:9, M.P. = 152 – 154 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.28 (s, 0.1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.39 (s, 1H), 7.37 – 7.36 (m, 0.4H), 7.28 – 7.22 (m, 4H), 7.06 (d, *J* = 9.0 Hz, 0.1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 2.0 Hz, 0.1H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.08 (d, *J* = 10.0 Hz, 0.1H), 5.98 (d, *J* = 9.5 Hz, 1H), 4.96 (d, *J* = 9.0 Hz, 1H), 4.74 (d, *J* = 9.5 Hz, 0.1H), 3.84 (s, 0.3H), 3.82 (s, 3H), 3.13 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 139.4, 139.4, 136.6, 134.1, 131.2, 129.0, 128.5, 126.3, 125.5, 124.7, 121.6, 120.9, 113.1, 111.2, 68.8, 53.1 ppm; IR(KBr, cm^{-1}): 3372, 2953, 1728, 1617, 1488, 1452, 1261, 1212, 1092, 1050, 830, 809, 757, 667; HRMS (ESI) calcd for $C_{19}H_{15}Cl_2NNaO_3^+$ $(M + Na)^+$ 398.0327, found 398.0320.



2o
88% (95:5)

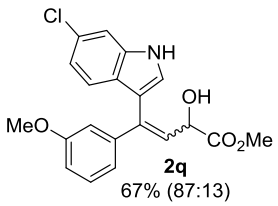
2o: Prepared according to the general procedure V above for 15 h and obtained as light yellow solid (72.0mg, 88% yield, *Z/E* = 95:5, M.P. = 186 – 189 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.61 (d,

J = 2.5 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 1H), 6.94 (dd, *J* = 1.5 Hz, *J* = 8.5 Hz, 1H), 6.06 (d, *J* = 9.5 Hz, 1H), 4.98 (dd, *J* = 5.0 Hz, *J* = 9.5 Hz, 1H), 3.84 (s, 3H), 3.12 (d, *J* = 5.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 175.8, 147.9, 139.4, 139.3, 130.9, 130.7, 130.4, 129.0, 128.0, 127.8, 127.0 (q, *J* = 270.4 Hz), 123.4, 122.3, 114.2, 113.6, 71.2, 54.6 ppm; IR(KBr, cm^{-1}): 3375, 2962, 1728, 1616, 1453, 1413, 1327, 1264, 1111, 1067, 841, 791; HRMS (ESI) calcd for $C_{20}H_{15}ClF_3NNaO_3^+$ (M + Na)$^+$ 432.0590, found 432.0577.



2p
64% (80:20)

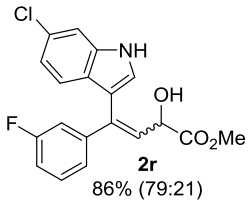
2p: Prepared according to the general procedure V above and obtained as light yellow solid (45.5mg, 64% yield, *Z/E* = 80:20, M.P. = 124 – 130 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.23 (s, 0.25H), 7.56 (s, 1H), 7.38 (s, 1H), 7.34 (s, 0.25H), 7.30 (d, *J* = 7.5 Hz, 0.5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 0.5H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 0.5H), 6.92 – 6.87 (m, 2.25H), 6.05 (d, *J* = 10.0 Hz, 0.25H), 5.97 (d, *J* = 9.5 Hz, 1H), 4.96 (d, *J* = 9.5 Hz, 1H), 4.81 (d, *J* = 10.0 Hz, 0.25H), 3.83 (s, 0.75H), 3.81 (s, 3H), 3.07 (s, 1 H), 3.02 (s, 0.25 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 173.1, 138.7, 136.4, 134.9, 128.0, 127.3, 127.2, 126.7, 126.0, 124.5, 124.1, 122.0, 120.1, 119.9, 119.4, 119.0, 117.4, 112.1, 109.6, 109.4, 67.3, 67.1, 51.3, 19.6, 19.5 ppm; IR(KBr, cm^{-1}): 3367, 3024, 1728, 1609, 1538, 1452, 1260, 1050, 906, 820, 808, 733, 648; HRMS (ESI) calcd for $C_{20}H_{18}ClNNaO_3^+$ (M + Na)$^+$ 378.0873, found 378.0867.



2q
67% (87:13)

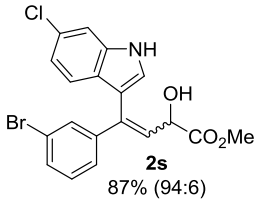
2q: Prepared according to the general procedure V above and obtained as light yellow solid (49.7mg, 67% yield, *Z/E* = 87:13, M.P. = 117 – 120 °C), eluent: petroleum

ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, DMSO) δ 11.50 (s, 1H), 11.40 (s, 0.15H), 8.31 (s, 0.15H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.47 (s, 1H), 7.45 (s, 0.15H), 7.35 – 7.33 (m, 0.45H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 0.15H), 7.03 (d, *J* = 9.5 Hz, 0.15H), 6.98 – 6.97 (m, 0.15H), 6.88 (t, *J* = 8.5 Hz, 2H), 6.82 – 6.79 (m, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.06 (d, *J* = 10.0 Hz, 0.15H), 5.99 (d, *J* = 9.0 Hz, 1H), 5.78 (d, *J* = 5.5 Hz, 1H), 5.72 (d, *J* = 6.0 Hz, 0.15H), 4.76 – 4.73 (m, 1H), 4.53 – 4.50 (m, 0.15H), 3.76 (s, 0.3H), 3.70 (s, 3H), 3.67 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 173.8, 159.7, 143.2, 138.2, 137.1, 129.8, 127.8, 126.6, 126.5, 125.8, 121.4, 120.3, 120.0, 113.6, 113.4, 112.2, 111.8, 69.1, 55.5, 52.3 ppm; IR(KBr, cm^{-1}): 3419, 2954, 1729, 1597, 1537, 1453, 1233, 1041, 981, 853, 780, 702, 629; HRMS (ESI) calcd for $C_{20}H_{18}ClNNaO_4^+$ $(M + Na)^+$ 394.0822, found 394.0814.



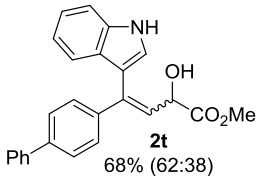
2r
86% (79:21)

2r: Prepared according to the general procedure V above and obtained as light yellow solid (61.8mg, 86% yield, *Z/E* = 79:21, M.P. = 121 – 125 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.31 (s, 0.27H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.42 – 7.39 (m, 1.27H), 7.36 – 7.34 (m, 0.51H), 7.25 – 7.20 (m, 1.27H), 7.13 (d, *J* = 7.5 Hz, 1.27H), 7.10 – 7.06 (m, 0.51H), 7.04 – 7.00 (m, 2H), 6.93 (dd, *J* = 1.5 Hz, *J* = 8.5 Hz, 1H), 6.89 – 6.88 (m, 1H), 6.86 (s, 0.27H), 6.08 (d, *J* = 10.0 Hz, 0.27H), 6.01 (d, *J* = 10.0 Hz, 1H), 4.95 (d, *J* = 9.0 Hz, 1H), 4.76 (d, *J* = 10.0 Hz, 0.27H), 3.84 (s, 0.81H), 3.81 (s, 3H), 3.15 (s, 1H), 3.11 (s, 0.27H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 162.8 (d, *J* = 246.1 Hz), 143.4 (d, *J* = 6.9 Hz), 139.5, 136.6, 129.72(d, *J* = 7.7 Hz), 128.5, 126.3, 125.9, 125.5, 125.3, 123.4, 121.5, 121.4, 120.9, 115.0 (d, *J* = 21.2 Hz), 114.6 (d, *J* = 22.2 Hz), 113.0, 111.4, 111.2, 68.8, 68.6, 53.1 ppm; IR(KBr, cm^{-1}): 3416, 2953, 1733, 1612, 1484, 1438, 1264, 1227, 1062, 907, 812, 699; HRMS (ESI) calcd for $C_{19}H_{15}ClFNNaO_3^+$ $(M + Na)^+$ 382.0622, found 382.0614.



2s
87% (94:6)

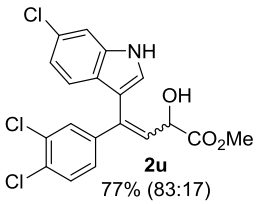
2s: Prepared according to the general procedure V above for 10 h and obtained as light yellow solid (72.9mg, 87% yield, *Z/E* = 94:6, M.P. = 98 – 100 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, DMSO) δ 11.56 (s, 1H), 8.31 (s, 0.18H), 7.63 (s, 1H), 7.52 – 7.49 (m, 2H), 7.39 (s, 1H), 7.31 – 7.25 (m, 2H), 6.91 – 6.89 (m, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.03 (d, *J* = 9.5 Hz, 1H), 5.82 (d, *J* = 6.0 Hz, 1H), 4.75 – 4.72 (m, 1H), 3.86 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 173.1, 143.7, 136.7, 136.4, 130.6, 130.5, 129.7, 127.6, 127.2, 126.4, 126.2, 125.1, 121.7, 120.7, 119.5, 111.5, 111.0, 68.5, 51.9 ppm; IR(KBr, cm^{-1}): 3417, 2952, 1727, 1617, 1558, 1452, 1330, 1231, 1063, 978, 805, 696; HRMS (ESI) calcd for $C_{19}H_{15}BrClNNaO_3^+$ (M + Na)$^+$ 441.9822, found 441.9814.



2t
68% (62:38)

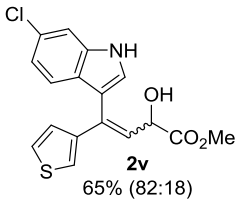
2t: Prepared according to the general procedure V above for 36 h and obtained as light yellow solid (52.1mg, 68% yield, *Z/E* = 63:38, M.P. = 127 – 129 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.22 (s, 0.62H), 7.63 (t, *J* = 8.0 Hz, 3H), 7.59 (d, *J* = 7.0 Hz, 3H), 7.53 – 7.50 (m, 3.10H), 7.48 – 7.40 (m, 6H), 7.38 – 7.32 (m, 2.48H), 7.23 – 7.17 (m, 1.86H), 7.12 (t, *J* = 7.5 Hz, 0.62H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.94 (br, 0.62H), 6.17 (d, *J* = 10.0 Hz, 0.62H), 6.06 (d, *J* = 9.5 Hz, 1H), 5.02 (d, *J* = 9.0 Hz, 1H), 4.86 (d, *J* = 10.0 Hz, 0.62H), 3.84 (s, 1.86H), 3.81 (s, 3H), 3.07 (br, 1.62 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 174.8, 141.6, 140.8, 140.7, 140.6, 140.2, 138.3, 130.4, 128.8, 128.2, 127.4, 127.1, 127.0, 126.9, 126.8, 125.7, 124.1, 122.6, 122.4, 121.0, 120.8, 120.7, 120.6, 120.0, 118.7, 113.3, 111.5, 111.2, 69.0, 68.9, 53.0 ppm; IR(KBr, cm^{-1}): 3411, 3028, 1732, 1618, 1242, 840, 745, 697; HRMS (ESI) calcd for $C_{25}H_{21}NNaO_3^+$ (M + Na)$^+$ 406.1419,

found 406.1408.



2u
77% (83:17)

2u: Prepared according to the general procedure V above for 15 h and obtained as light yellow solid (63.0mg, 77% yield, *Z/E* = 83:17, M.P. = 131 – 133 °C), eluent: petroleum ether/ethyl acetate = 3:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.27 (s, 0.21H), 7.57 (s, 1H), 7.54 (s, 0.211H), 7.44 –7.45 (m, 1.42H), 7.41 (s, 1H), 7.37 (s, 0.21H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.29 (s, 0.21H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.89 – 6.87(m, 1.21H), 6.09 (d, *J* = 9.5 Hz, 0.21H), 5.99 (d, *J* = 9.5 Hz, 1H), 4.93 (d, *J* = 9.0 Hz, 1H), 4.71 (d, *J* = 10.0 Hz, 0.21H), 3.85 (s, 0.63H), 3.83 (s, 3H), 3.11 (br, 1.21 H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 173.1, 173.0, 141.8, 139.6, 137.4, 136.8, 136.7, 135.5, 131.1, 130.9, 130.5, 130.5, 130.3, 129.7, 129.3, 128.8, 128.1, 127.8, 127.6, 127.6, 126.4, 126.3, 124.9, 123.5, 122.9, 120.8, 120.7, 120.1, 119.7, 116.0, 111.7, 111.5, 110.6, 68.5, 68.3, 51.9, 51.9 ppm; IR(KBr, cm^{-1}): 3417, 2954, 1730, 1620, 1454, 1248, 1134, 1065, 1029, 975, 907, 825, 803, 765, 613; HRMS (ESI) calcd for $C_{19}H_{14}Cl_3NNaO_3^+$ $(M + Na)^+$ 431.9937, found 431.9924.

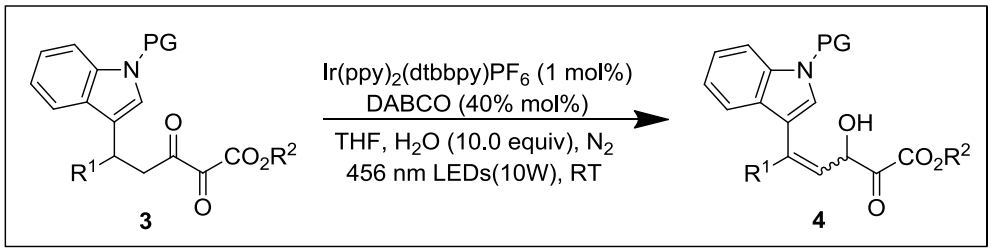


2v
65% (82:18)

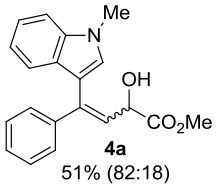
2v: Prepared according to the general procedure V above and obtained as light yellow solid (45.1mg, 65% yield, *Z/E* = 82:18, M.P. = 134 – 137 °C), eluent: petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.29 (s, 0.22H), 7.51 (s, 0.22H), 7.48 (s, 1H), 7.40 (s, 1H), 7.35 (s, 0.22H), 7.33 – 7.31 (m, 0.44H), 7.19 (d, *J* = 5.0 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.07 – 7.03 (m, 2H), 6.99 – 6.98 (m, 1.22H), 6.08 (d, *J* = 9.5 Hz, 1H), 6.01 (d, *J* = 9.5 Hz, 0.22H), 4.98 (d, *J* = 9.5 Hz, 0.22H), 4.89 (d, *J* = 9.5 Hz, 1H), 3.86 (s, 0.66H), 3.79 (s, 3H), 3.07 (br, 1H) ppm; ^{13}C NMR (125 MHz,

$CDCl_3$) δ 174.6, 142.6, 139.1, 137.0, 136.4, 136.0, 134.7, 129.5, 128.4, 126.2, 125.7, 125.6, 125.4, 125.3, 125.3, 124.0, 123.5, 121.6, 121.4, 121.1, 120.8, 113.5, 111.3, 111.1, 68.8, 68.7, 53.1, 53.0 ppm; IR(KBr, cm^{-1}): 3413, 3106, 1731, 1614, 1536, 1451, 1227, 1061, 907, 803, 786, 731; HRMS (ESI) calcd for $C_{17}H_{14}ClNNaO_3S^+$ $(M + Na)^+$ 370.0281, found 370.0274.

F) Synthesis of 4-*N*-protected indolyl substituted 2-hydroxy-3-enoic acid esters 4:

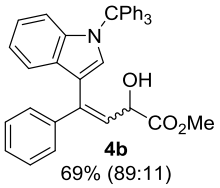


General procedure VI: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-*N*-protecting group indolyl α-keto ester **3** (0.2 mmol), DABCO (0.08 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and H_2O (36 μL) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10W) at room temperature. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel gave the desired product.



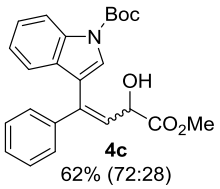
4a
51% (82:18)

4a: Prepared according to the general procedure VI above for 36 h and obtained as light yellow solid (34.9mg, 51% yield, *Z/E* = 82:18, M.P. = 104 – 106 °C), eluent: petroleum ether/ethyl acetate = 8:1; ^{1}H NMR (500 MHz, DMSO) δ 7.44 – 7.41 (m, 5H), 7.34 (d, *J* = 6.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 6.10 (d, *J* = 9.5 Hz, 1H), 5.75 (d, *J* = 6.0 Hz, 1H), 4.50 – 4.47 (m, 1H), 3.72 (s, 3H), 3.66 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 173.6, 139.3, 139.2, 137.3, 130.2, 129.3, 128.1, 127.6, 125.3, 121.7, 121.3, 119.9, 119.7, 115.8, 110.2, 68.5, 51.7, 32.4 ppm; IR (KBr, cm^{-1}): 3052, 1724, 1664, 1558, 1517, 1382, 1283, 1071, 747, 697, 639, 572; HRMS (ESI) calcd for $C_{20}H_{17}NNaO_3^+$ $(M + Na)^+$ 342.1106, found 342.1103.



4b
69% (89:11)

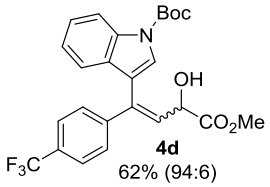
4b: Prepared according to the general procedure VI above for 36 h and obtained as colorless oil (78.9mg, 69% yield, *Z/E* = 89:11), eluent: petroleum ether/ethyl acetate = 8:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.40 – 7.39 (m, 2.39H), 7.31 – 7.28 (m, 17H), 7.25 – 7.23 (m, 2.21H), 6.90 – 6.87 (m, 0.39H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.79 – 6.72 (m, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 0.13H), 6.00 (d, *J* = 10.0 Hz, 0.13H), 5.89 (d, *J* = 9.5 Hz, 1H), 4.99 (d, *J* = 9.0 Hz, 1H), 4.79 (d, *J* = 10.0 Hz, 0.13H), 3.80 (s, 0.39H), 3.53 (s, 3H), 3.03 (br, 1.13H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 142.6, 141.2, 140.5, 137.6, 131.0, 130.1, 129.1, 128.2, 127.9, 127.8, 127.5, 124.0, 121.1, 120.9, 119.6, 116.0, 111.7, 75.8, 68.7, 52.9 ppm; IR(KBr, cm^{-1}): 3453, 2951, 1734, 1599, 1539, 1491, 1446, 1379, 1308, 1224, 745, 700; HRMS (ESI) calcd for $C_{38}H_{31}NNaO_3^+$ $(M + Na)^+$ 572.2202, found 572.2205.



4c
62% (72:28)

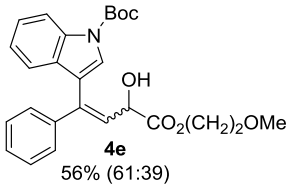
4c: Prepared according to the general procedure VI above for 12 h and obtained as light yellow oil (53.3mg, 62% yield, *Z/E* = 72:28), eluent: petroleum ether/ethyl acetate = 6:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.13 (m, 1.39H), 7.93 (s, 1H), 7.44 – 7.41 (m, 1.39H), 7.40 – 7.37 (m, 2.78H), 7.34 – 7.28 (m, 4.17H), 7.15 (t, *J* = 8.0 Hz, 0.78H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.13 (d, *J* = 10.0 Hz, 0.39H), 6.09 (d, *J* = 9.0 Hz, 1H), 4.99 (q, *J* = 5.0 Hz, 1H), 4.84 (q, *J* = 5.0 Hz, 0.39H), 3.84 (s, 1.17H), 3.83 (s, 3H), 3.13 (d, *J* = 5.5 Hz, 1H), 3.07 (d, *J* = 5.5 Hz, 0.39H), 1.71 (s, 9H), 1.65 (s, 3.47H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 174.5, 149.6, 140.5, 140.1, 139.1, 138.2, 130.0, 129.7, 128.7, 128.5, 128.4, 128.3, 128.3, 128.1, 127.5, 126.4, 126.2, 124.6, 123.7, 122.9, 122.7, 122.5, 121.1, 120.7, 117.5, 115.3, 115.1, 84.1, 84.0, 68.8, 68.5, 53.0, 28.2, 28.2 ppm; IR(KBr, cm^{-1}): 3443, 2977, 1735, 1453, 1382, 1310,

1251, 1075, 766, 748, 700, 587; HRMS (ESI) calcd for $C_{24}H_{25}NNaO_5^+$ $(M + Na)^+$ 430.1630, found 430.1626.



4d
62% (94:6)

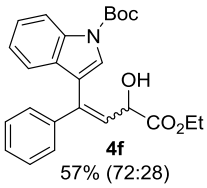
4d: Prepared according to the general procedure VI above for 12 h and obtained as light yellow oil (61.8mg, 62% yield, *Z/E* = 94:6), eluent: petroleum ether/ethyl acetate = 6:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.0 Hz, 1H), 7.95 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.15 (d, *J* = 9.5 Hz, 1H), 4.99 (dd, *J* = 3.0 Hz, *J* = 9.5 Hz, 1H), 3.85 (s, 3H), 3.65 (s, 0.2H), 4.17 (d, *J* = 4.0 Hz, 1H), 1.71 (s, 9H), 1.69 (s, 0.59H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.2, 149.5, 143.6, 137.9, 135.5, 130.3, 130.1, 129.6, 128.3, 128.0, 127.8, 125.4 (q, *J* = 3.4 Hz), 123.8 (q, *J* = 251.4 Hz), 116.7, 115.3, 84.2, 68.6, 53.2, 28.2 ppm; IR(KBr, cm^{-1}): 3226, 2986, 1714, 1659, 1646, 1551, 1403, 1251, 1067, 540, 405; HRMS (ESI) calcd for $C_{25}H_{24}F_3NNaO_5^+$ $(M + Na)^+$ 498.1504, found 498.1502.



4e
56% (61:39)

4e: Prepared according to the general procedure VI above for 12 h and obtained as colorless oil (53.1mg, 56% yield, *Z/E* = 61:39), eluent: petroleum ether/ethyl acetate = 4:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.5 Hz, 1.64H), 7.96 (s, 0.64H), 7.46 – 7.44 (m, 2.28H), 7.40 – 7.36 (m, 5.92H), 7.31 – 7.25 (m, 3.64H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 0.64H), 6.99 (d, *J* = 9.0 Hz, 0.64H), 6.14 (d, *J* = 10.0 Hz, 1H), 6.11 (d, *J* = 9.5 Hz, 0.64H), 4.97 (d, *J* = 9.5 Hz, 0.64H), 4.84 (d, *J* = 9.5 Hz, 1H), 4.40 – 4.32 (m,3.28H), 3.65 – 3.61 (m,3.28H), 3.39 (s, 3H), 3.36 (s, 1.92H), 3.15 (br, 0.64H), 3.11 (br, 1H), 1.71 (s, 5.77H), 1.65 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 173.9, 149.6, 140.4, 140.3, 139.1, 138.3, 135.9, 135.4, 129.8, 128.7, 128.3, 128.3, 128.1,

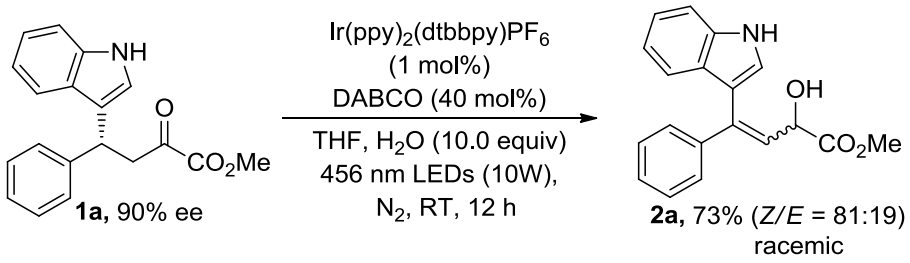
127.5, 126.3, 125.7, 124.5, 124.5, 123.9, 122.9, 122.7, 122.6, 121.0, 120.7, 117.6, 115.3, 115.1, 84.1, 84.0, 70.2, 70.1, 68.9, 68.6, 65.0, 64.9, 59.0, 59.0, 28.2, 28.2 ppm; IR(KBr, cm^{-1}): 3384, 2973, 2901, 1734, 1452, 1382, 1250, 1053, 880, 748; HRMS (ESI) calcd for $C_{26}H_{29}NNaO_6^+$ $(M + Na)^+$ 474.1893, found 474.1881.



4f
57% (72:28)

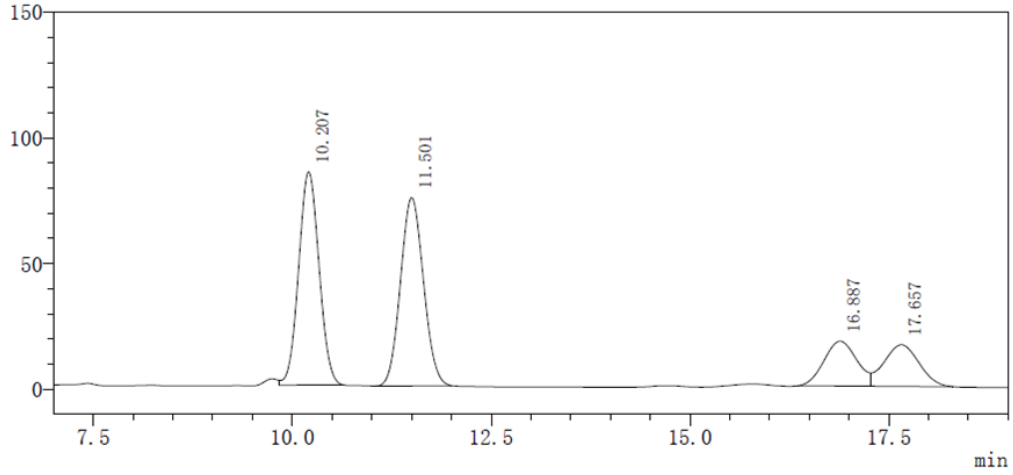
4f: Prepared according to the general procedure VI above for 12 h and obtained as light yellow oil (50.6mg, 57% yield, *Z/E* = 72:28), eluent: petroleum ether/ethyl acetate = 6:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1.38H), 7.92 (s, 0.38H), 7.45 – 7.43 (m, 2H), 7.40 – 7.35 (m, 4.9H), 7.31 – 7.28 (m, 3H), 7.15 (t, *J* = 8.0 Hz, 1.38H), 7.06 (t, *J* = 8.0 Hz, 0.38H), 6.99 (d, *J* = 8.0 Hz, 0.38H), 6.12 (d, *J* = 10.0 Hz, 1H), 6.10 (d, *J* = 10.0 Hz, 0.38H), 4.94 (d, *J* = 9.0 Hz, 0.38H), 4.80 (d, *J* = 9.0 Hz, 1H), 4.31 – 4.25 (m, 2.76H), 3.15 (br, 0.38H), 3.09 (br, 1H), 1.70 (s, 3.45H), 1.65 (s, 9H), 1.34 (t, *J* = 7.0 Hz, 4.15H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 174.1, 149.6, 140.3, 138.9, 138.3, 135.9, 129.8, 128.7, 128.4, 128.3, 128.1, 127.5, 126.5, 124.5, 124.0, 122.9, 122.7, 122.6, 121.1, 120.7, 117.6, 115.3, 115.1, 84.1, 68.9, 68.6, 62.3, 62.2, 28.2, 28.2, 14.2 ppm; IR(KBr, cm^{-1}): 3361, 2973, 1731, 1633, 1454, 1384, 1154, 1049, 881; HRMS (ESI) calcd for $C_{25}H_{27}NNaO_5^+$ $(M + Na)^+$ 444.1787, found 444.1778.

G) Enantioselective Synthesis of Allyl Alcohol 2a with *R*-1a



Reaction procedure VII: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added (*R)*-γ-indolyl α-ketoesters **1a** (0.2 mmol, 90% ee),[1] DABCO (0.08 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and D_2O (36 μL) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10W) for 4h at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 3:1, v/v) gave the desired product **2a** (44.8 mg, 73% yield, 0% *ee*). HPLC analysis: Daicel Chiralpak AD-H, hexane/*iso*-propanol = 80:20, flow rate = 1.0 mL/min, λ = 245nm, major isomer *Z*-**2a:** tR (major) = 10.2 min, tR (minor) = 11.5 min; minor isomer *E*-**2a**: tR (major) = 16.9 min, tR (minor) = 17.7 min.

*Chiral HPLC spectrum of racemic **2a***

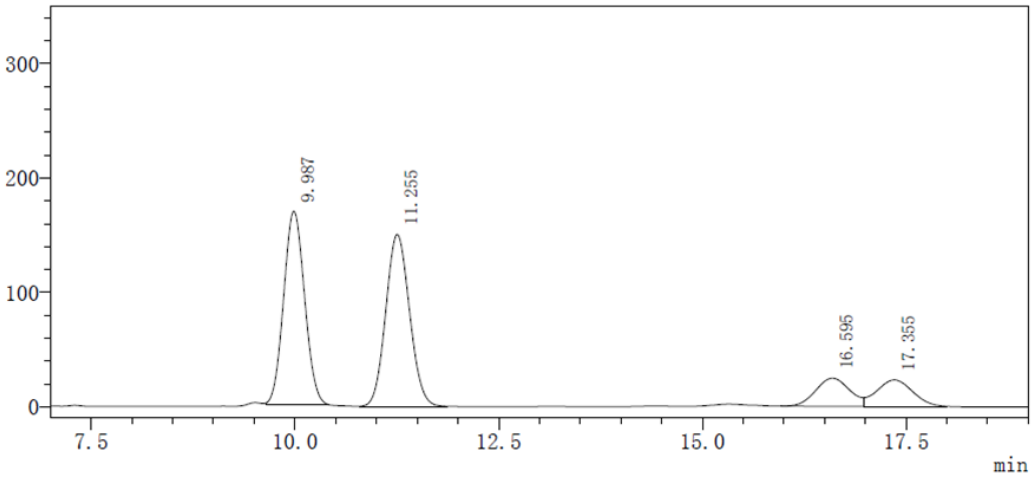


〈Peak Results〉

Ch1 254nm

Index	Time/min	Area	Area%	Height	Height%
1	10.207	1519212	37.519	84868	43.704
2	11.501	1507468	37.229	74910	38.576
3	16.887	515896	12.741	17848	9.191
4	17.657	506575	12.511	16562	8.529

*Chiral HPLC spectrum of chiral **2a***

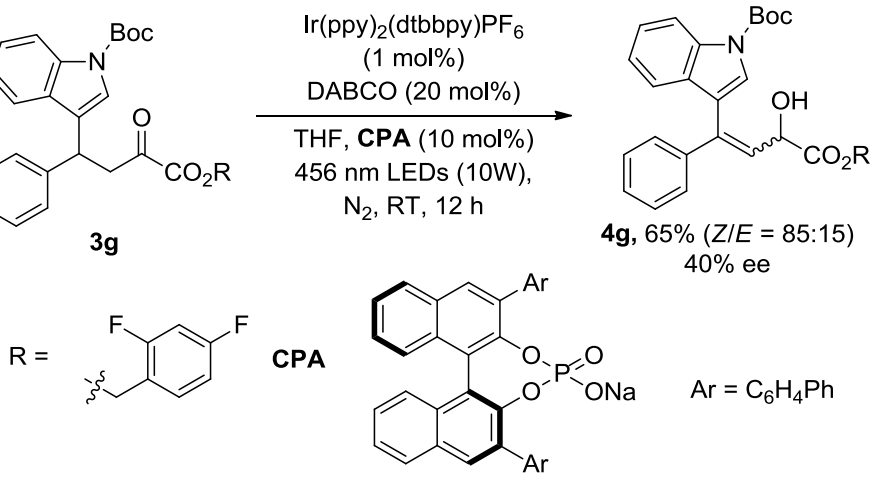


〈Peak Results〉

Ch1 254nm

Index	Time/min	Area	Area%	Height	Height%
1	9.987	3022926	40.326	169141	46.088
2	11.255	3054803	40.751	150179	40.921
3	16.595	710293	9.475	24566	6.694
4	17.355	708160	9.447	23114	6.298

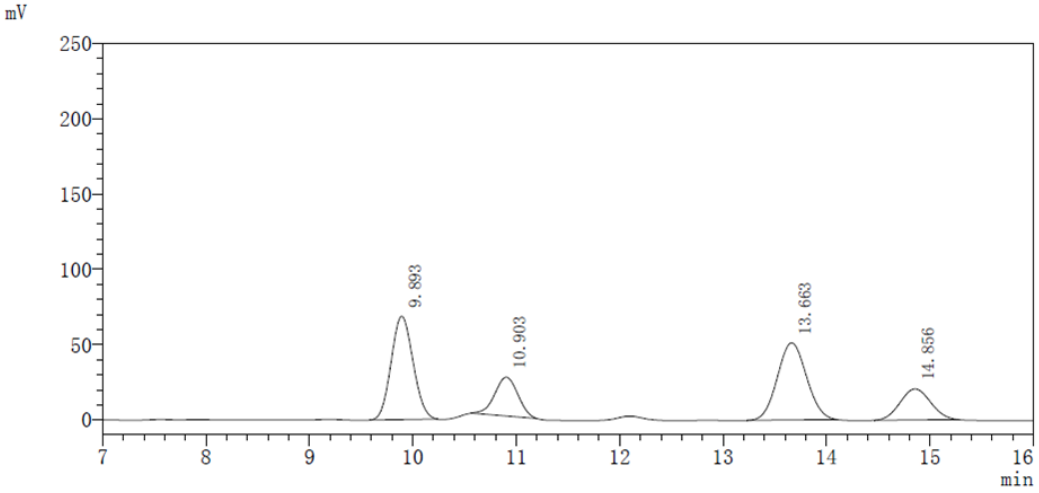
H) Asymmetric Catalytic Redox-neutral of *γ-N*-Boc-indolyl *α*-Ketoester 3g



Reaction procedure VIII: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added *γ-N*-Boc indolyl *α*-ketoesters **3g** (0.1 mmol), CPA (0.01 mmol), DABCO (0.02 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.001 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (1.0 mL) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10W) for 12h at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 6:1, v/v) gave the desired product **4g** (colorless oil, 33.7 mg, 65% yield, *Z/E* = 85:15, 40% *ee* for *Z*-**4g**,). $[\alpha]_D^{25}$ = -16.4 (c = 0.24, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.39 – 7.33 (m, 4H), 7.31 – 7.27 (m, 3.54H), 7.13 (t, *J* = 7.5 Hz, 0.36H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.89 – 6.81 (m, 2.36H), 6.08 (d, *J* = 9.5 Hz, 1H), 5.32 – 5.22 (m, 2.36H), 4.97 (dd, *J* = 4.5 Hz, *J* = 9.5 Hz, 1H), 4.83 (dd, *J* = 4.5 Hz, *J* = 10.0 Hz, 0.18H), 3.05 (d, *J* = 5.0 Hz, 1H), 3.01 (d, *J* = 5.5 Hz, 0.18H), 1.67 (s, 9H), 1.64 (s, 1.62H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, for major isomer) δ 173.7, 163.3 (dd, *J* = 11.5, 249.5 Hz), 161.2 (dd, *J* = 11.0, 250.1 Hz), 149.6, 140.2, 139.4, 131.8 (dd, *J* = 5.1, 9.9 Hz), 130.0, 129.6, 128.4, 128.3, 127.4, 125.9, 124.5, 122.7, 120.9, 118.4 (dd, *J* = 3.8, 14.8 Hz), 117.5, 115.1, 111.5 (dd, *J* = 3.6, 21.1 Hz), 104.2 (t, *J* = 25.3 Hz), 84.1, 69.0, 61.1 (d, *J* = 3.8 Hz), 29.7, 28.2 ppm; IR (KBr, cm^{-1}): 3386, 2924, 1735, 1623, 1507, 1453, 1383, 1249, 1156, 1071, 851, 748; HRMS (ESI) calcd for $C_{30}H_{27}F_2NNaO_5^+$ $(M + Na)^+$ 542.1755, found 542.1756; HPLC analysis: Daicel Chiralpak AD-H, hexane/*iso*-propanol = 88:12, flow rate = 0.8 mL/min, λ = 245nm, major isomer *Z*-**4g:**

tR (minor) = 9.7 min, tR (major) = 13.6 min; minor isomer *E*-**4g**: tR (minor) = 10.8 min, tR (major) = 14.9 min.

*Chiral HPLC spectrum of racemic **4g***

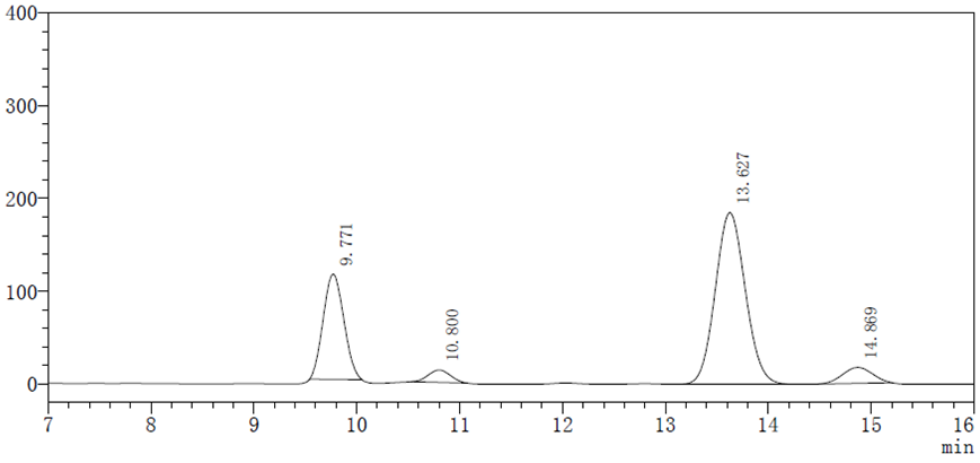


〈Peak Results〉

Ch1 254nm

Index	Time/min	Area	Area%	Height	Height%
1	9.893	1012745	35.589	68716	41.299
2	10.903	402495	14.144	25767	15.486
3	13.663	1007442	35.402	51297	30.830
4	14.856	423021	14.865	20605	12.384

*Chiral HPLC spectrum of chiral **4g***

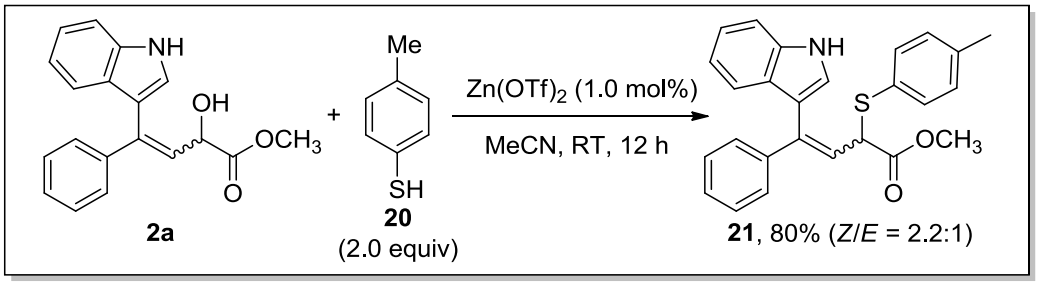


〈Peak Results〉

Ch1 254nm

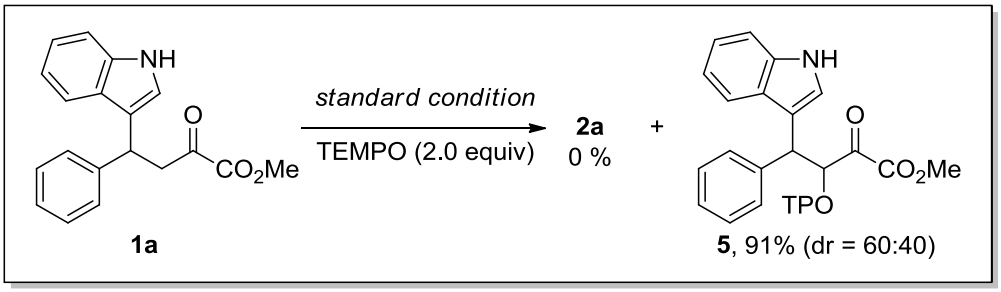
Index	Time/min	Area	Area%	Height	Height%
1	9.771	1581702	26.956	113358	34.489
2	10.800	199226	3.395	13293	4.045
3	13.627	3739363	63.727	184791	56.223
4	14.869	347450	5.921	17232	5.243

I) Transformation of 2a



To a 10 mL tube equipped with a magnetic stir bar was added 4-indoyl substituted 2-hydroxy-3-enoic acid esters **2a** (0.1 mmol), 4-methylbenzenethiol **20** (0.2 mmol), and $Zn(OTf)_2$ (0.001 mmol). Then anhydrous MeCN (1.0 mL) was added. After that, the reaction mixture was stirred for 12h at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 8:1, v/v) gave the desired product **21** (light yellow oil, 33.0 mg, 80% yield, *Z/E* = 2.2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 0.45H), 8.13 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 0.45H), 7.35 (s, 0.45H), 7.33 – 7.32 (m, 3.9H), 7.30 – 7.27 (m, 2.9H), 7.24 – 7.18 (m, 4.9H), 7.15 (d, *J* = 7.5 Hz, 0.45H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.95 – 6.92 (m, 1.45H), 6.85 (d, *J* = 8.0 Hz, 0.45H), 6.80 (d, *J* = 2.5 Hz, 1H), 6.31 (d, *J* = 11.0 Hz, 1H), 6.19 (d, *J* = 10.5 Hz, 0.45H), 4.76 (d, *J* = 10.5 Hz, 0.45H), 4.46 (d, *J* = 11.0 Hz, 1H), 3.69 (s, 3H), 3.69 (s, 1.35H), 2.31 (s, 3H), 2.25 (s, 1.35H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 171.1, 141.4, 139.8, 139.3, 138.7, 138.7, 136.8, 136.1, 134.8, 134.0, 129.7, 129.6, 129.5, 128.7, 128.1, 127.8, 127.6, 127.6, 125.4, 125.3, 124.7, 122.6, 122.5, 122.3, 120.8, 120.5, 119.8, 119.0, 118.4, 113.6, 111.3, 111.0, 52.5, 52.4, 51.4, 51.3, 21.2, 21.2 ppm; IR(KBr, cm^{-1}): 3403, 3055, 2951, 2248, 2128, 1729, 1616, 1530, 1491, 1432, 1261, 1154, 1102, 1017, 909, 811, 738, 703, 503; HRMS (ESI) calcd for $C_{26}H_{23}NNaO_2S^+$ $(M + Na)^+$ 436.1347, found 436.1340.

IV. Radical Trapping Experiments

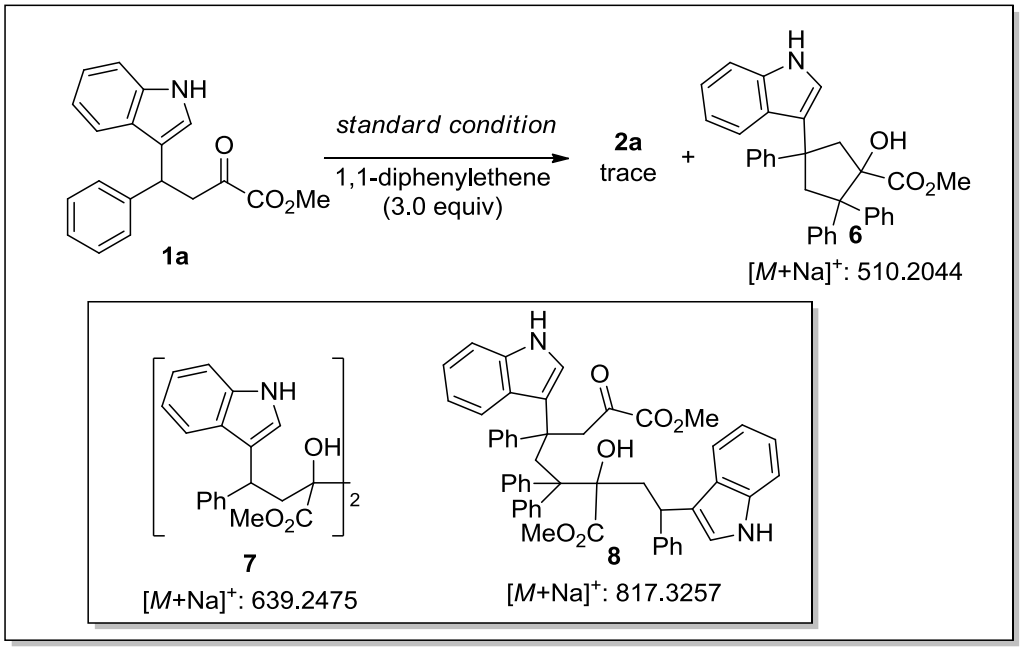


A) TEMPO as a radical trapping reagent: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-indolyl α-keto ester **1a** (0.2 mmol), DABCO (0.08 mmol), TEMPO (0.4 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and H_2O (36 μL) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10W) for 12 h 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 trapping product **5** (42.2 mg, 91%). The product **2a** was not detected.

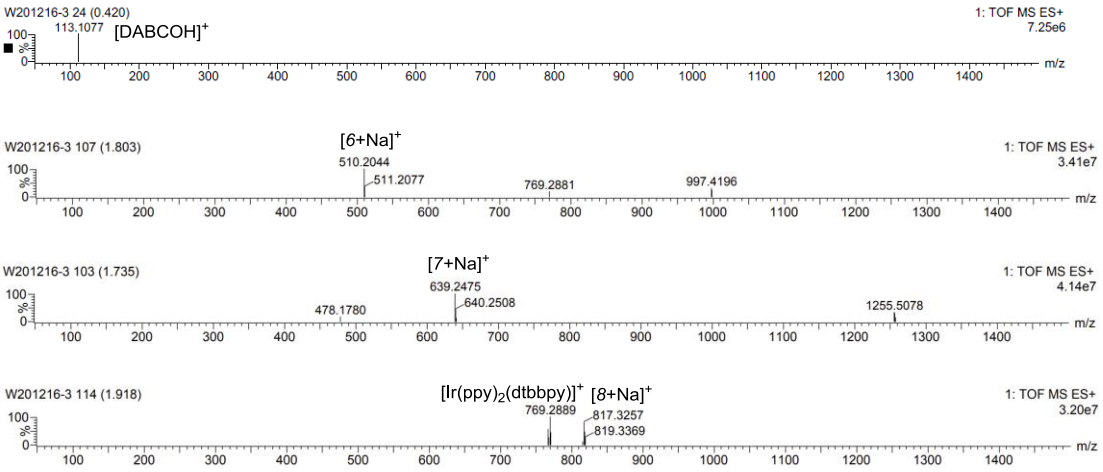
***cis*-5**: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (br, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.19 – 7.11 (m, 3H), 6.91 (s, 1H), 6.07 (d, *J* = 10.0 Hz, 1H), 4.96 (d, *J* = 9.5 Hz, 1H), 3.57 (s, 3H), 1.43 – 1.19 (m, 6H), 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.

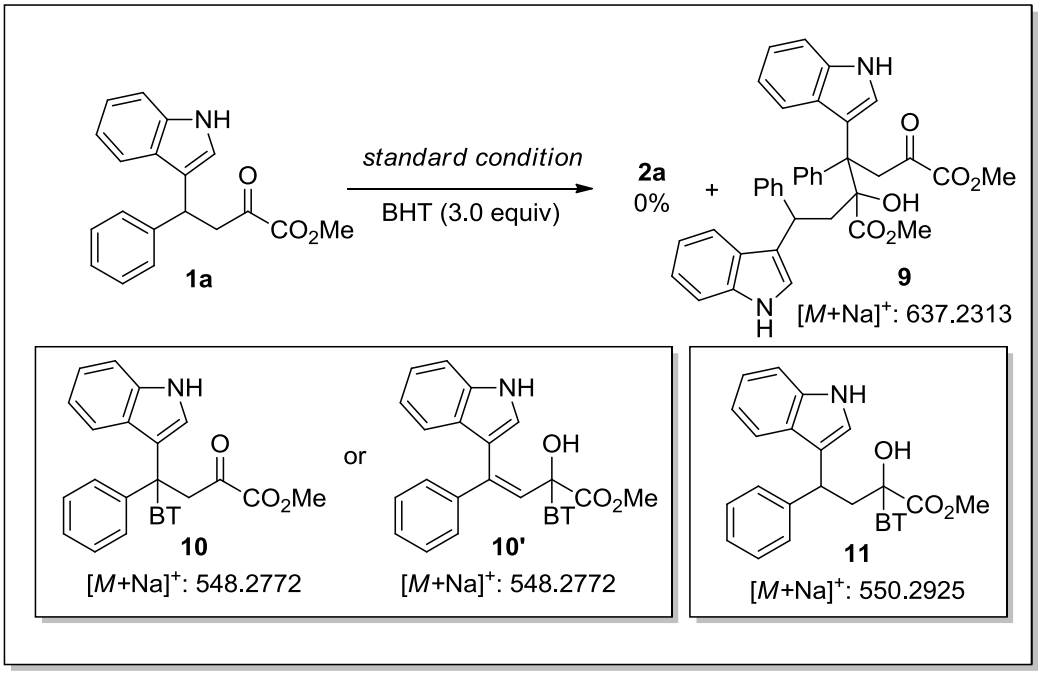
***trans*-5**: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (br, 1H), 7.38 (d, *J* = 8.0 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.22 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.0 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.87 (d, *J* = 10.5 Hz, 1H), 4.96 (d, *J* = 9.5 Hz, 1H), 3.60 (s, 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.

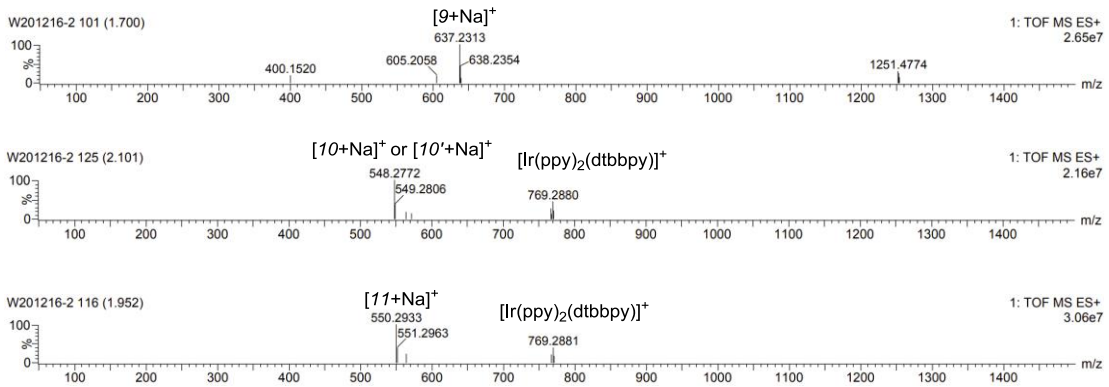


B) 1,1-Diphenylethene as a radical trapping reagent: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-indolyl α-keto ester **1a** (0.2 mmol), DABCO (0.08 mmol), 1,1-diphenylethene (0.6 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and H_2O (36 μL) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10W) for 12 h at room temperature. After reaction, the mixture was analyzed by LC-MS. Trace **2a** can be detected.

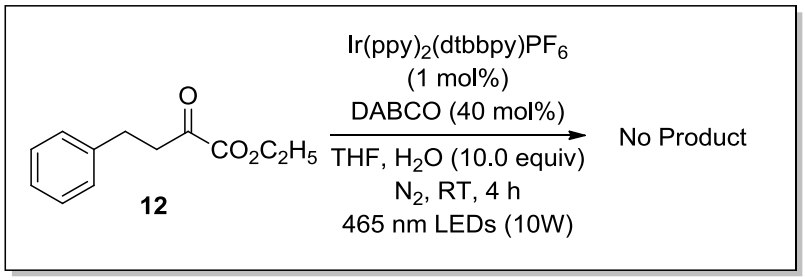




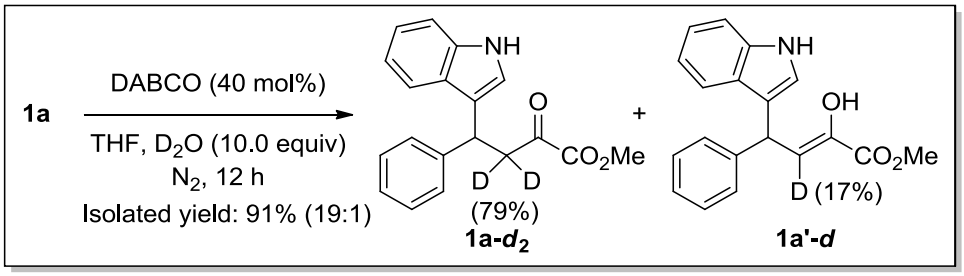
C) BHT as a radical trapping reagent: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-indolyl α-keto ester **1a** (0.2 mmol), DABCO (0.08 mmol), BHT (0.6 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and H_2O (36 μL) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10W) for 12 h at room temperature. After reaction, the mixture was analyzed by LC-MS. The product **2a** was not detected.



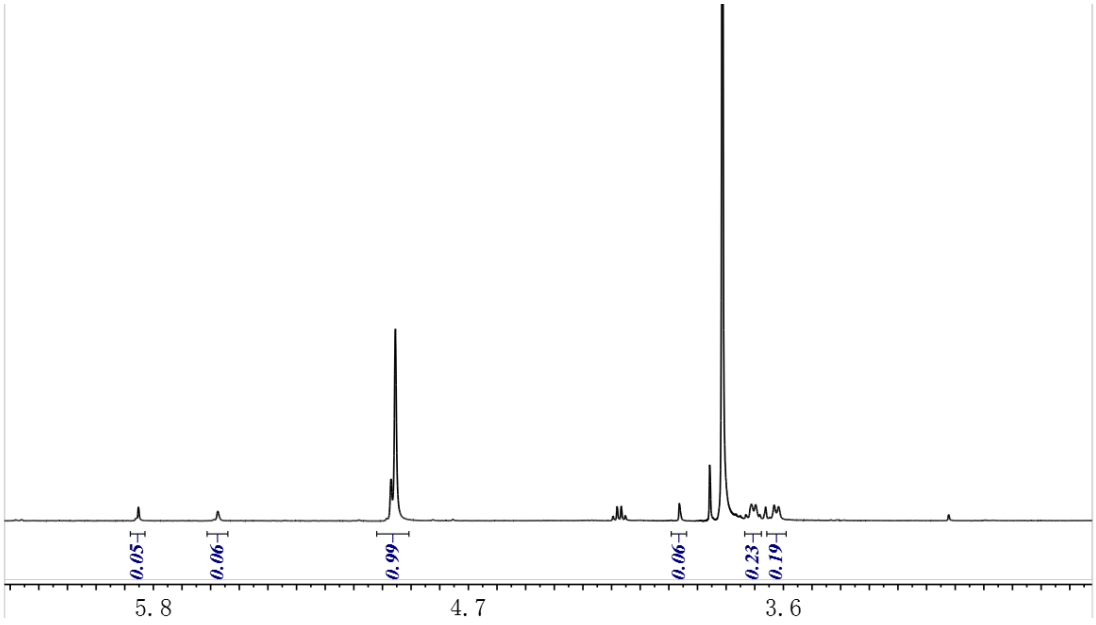
V. Control Experiments

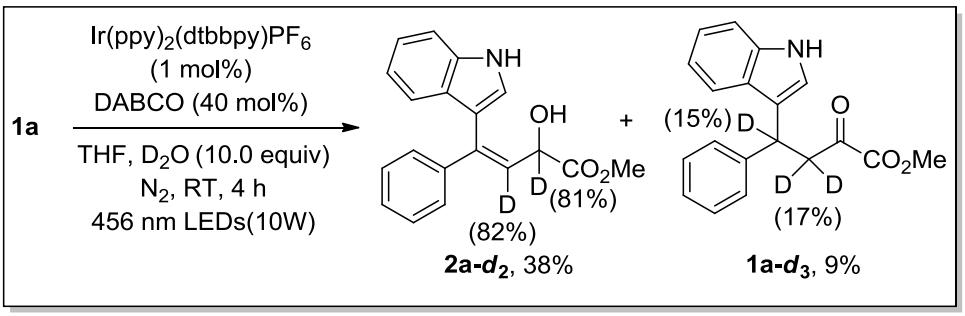


A) Compound 12 as a reaction substrate: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added α-keto ester **12** (0.2 mmol), DABCO (0.08 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and H_2O (36 μL) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10W) for 4 h at room temperature. After reaction, α-keto ester **12** was consumed completely, but primary allyl alcohol wasn't observed.

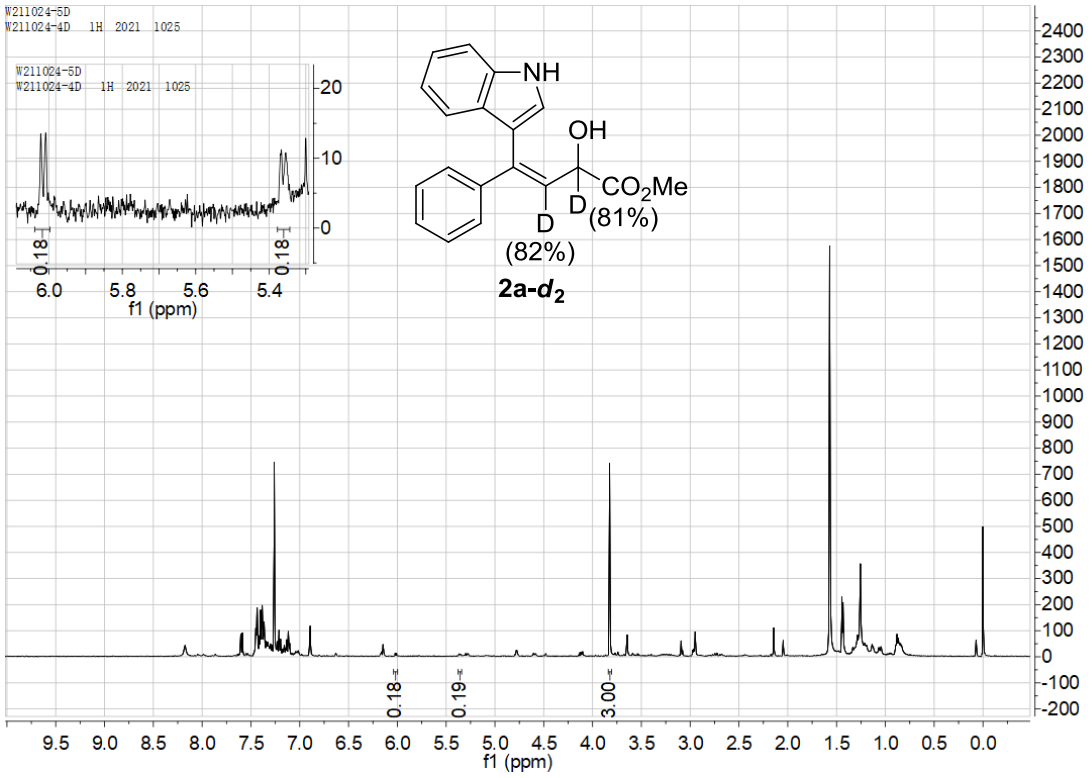


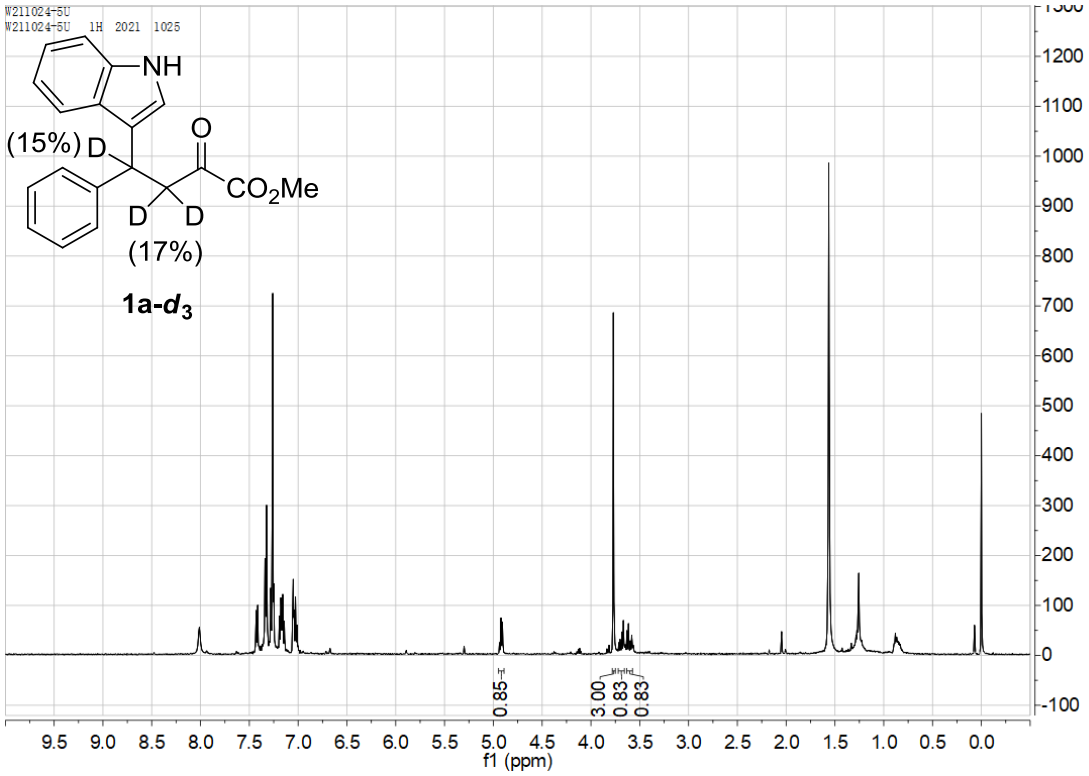
B) Deuterium experiment of α-ketoester 1a: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-indolyl α-keto ester **1a** (0.2 mmol) and DABCO (0.08 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and D_2O (36 μL) was added. After that, the reaction mixture was stirred for 4 h at room temperature. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 3:1, v/v) gave the desired product **1a-*d*$_2$/1a'-*d*$_1$** (55.9 mg, 91%, 19:1). Compound **1a-*d*$_2$/1a'-*d*** was analyzed by ^{1}H NMR.

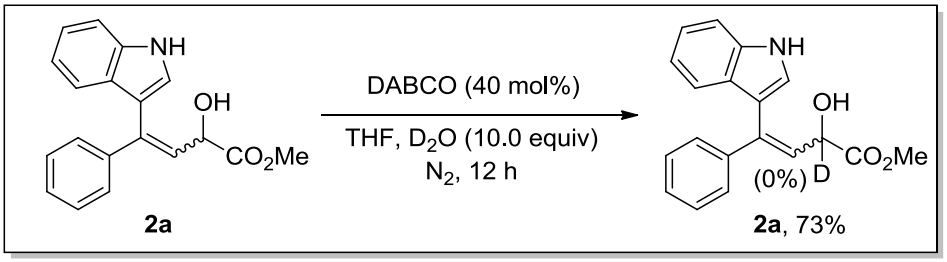




C) D_2O as an additive under the standard condition: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-indolyl α-keto ester **1a** (0.2 mmol), DABCO (0.08 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and D_2O (36 μL) was added. After that, the reaction mixture was irradiated by blue LEDs (456nm, 10W) for 4 h at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 4:1, v/v) gave the desired product **2a-*d*$_2$** (23.3 mg, 38%) and **1a-*d*$_3$** (5.5 mg, 9%). Compound **2a-*d*$_2$** and **1a-*d*$_3$** was analyzed by ^{1}H NMR.

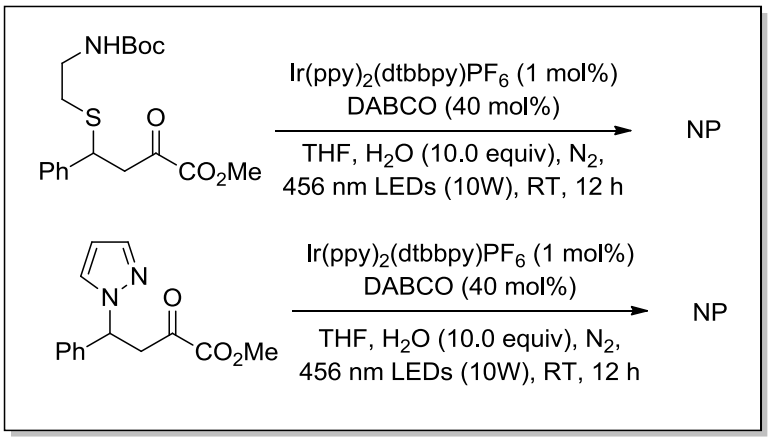



W211024-5U
W211024-5U 1H 2021 1025
NH
O
(15%) D
CO2Me
D D
(17%)
1a-d3
0.85
3.00
0.83
0.83
f1 (ppm)



D) Deuterium experiment of allyl alcohol 2a: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 4-indolyl substituted 2-hydroxy -3-enoic acid esters **2a** (0.2 mmol) and DABCO (0.08 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (2.0 mL) and D_2O (36 μL) was added. After that, the reaction mixture was stirred for 12 h at room temperature. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 4:1, v/v) gave the desired product **2a** (44.8 mg, 73%), which wasn't deuterated.

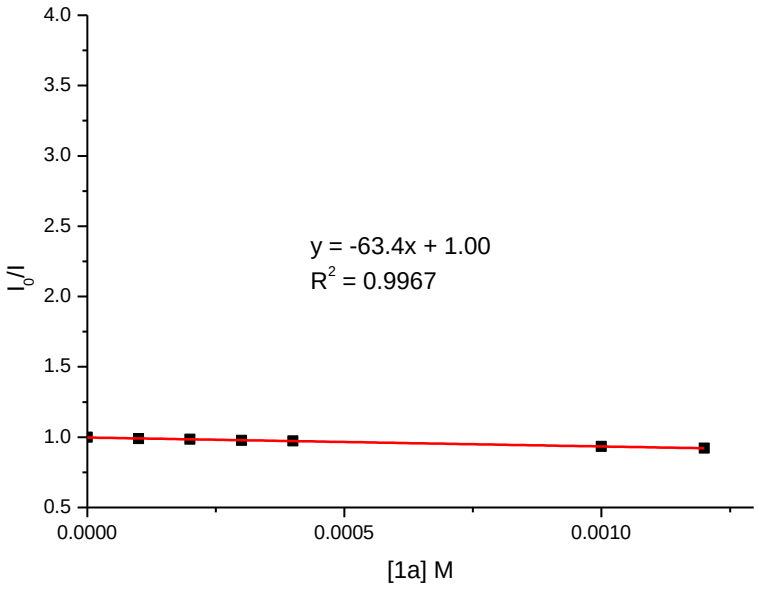
E) No reaction scope of the substrate:

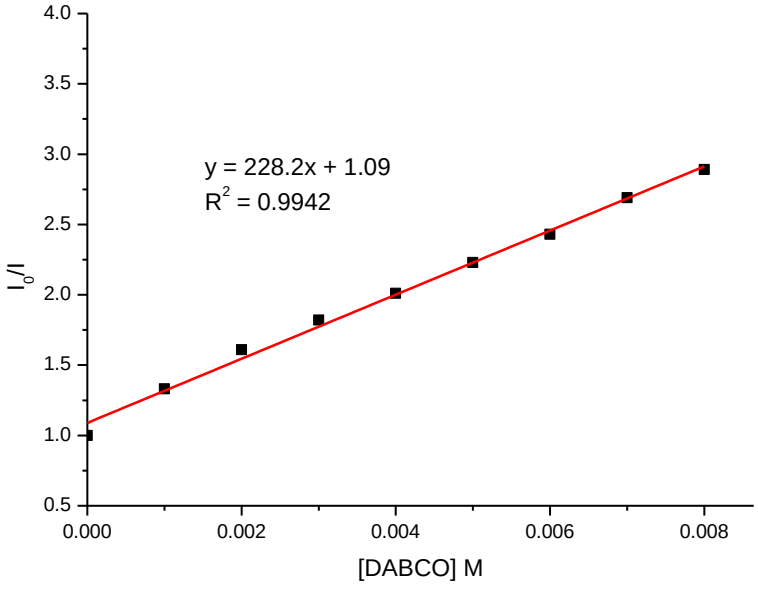


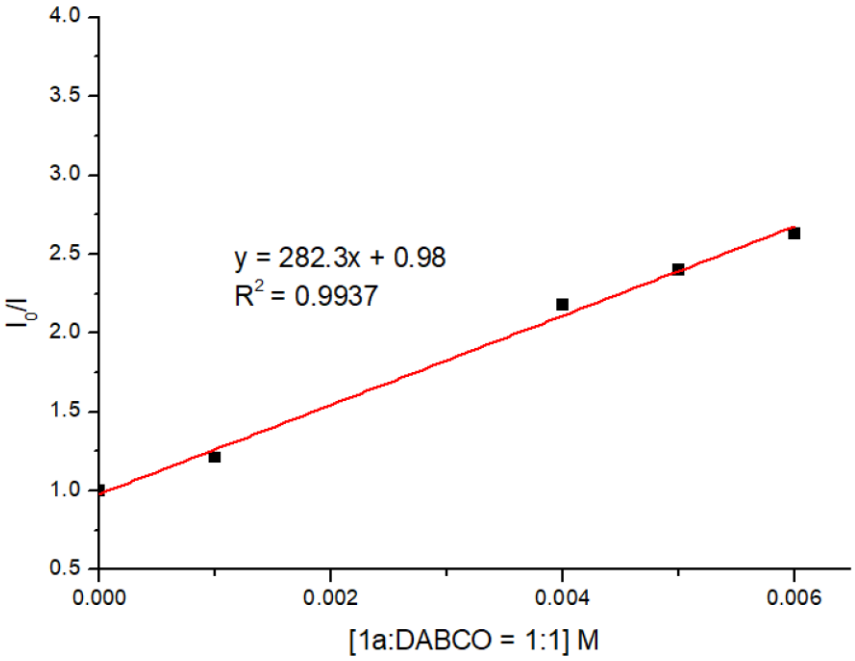
Scheme S1. No reaction scope of the other substrates

VI. Stern-Volmer Quenching Studies

Emission intensities were recorded using a PerkinElmer LS-55 luminescence spectrometer. All solutions of $Ir(ppy)_2(dtbbpy)]PF_6$ (2×10^{-6} M) containing variable amounts of the quencher in dry THF were exited at 450 nm and the emission intensity at 560 nm were observed.






4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
I_0/I
y = 282.3x + 0.98
R^2 = 0.9937
0.000
0.002
0.004
0.006
[1a:DABCO = 1:1] M

VII. X-ray Structure

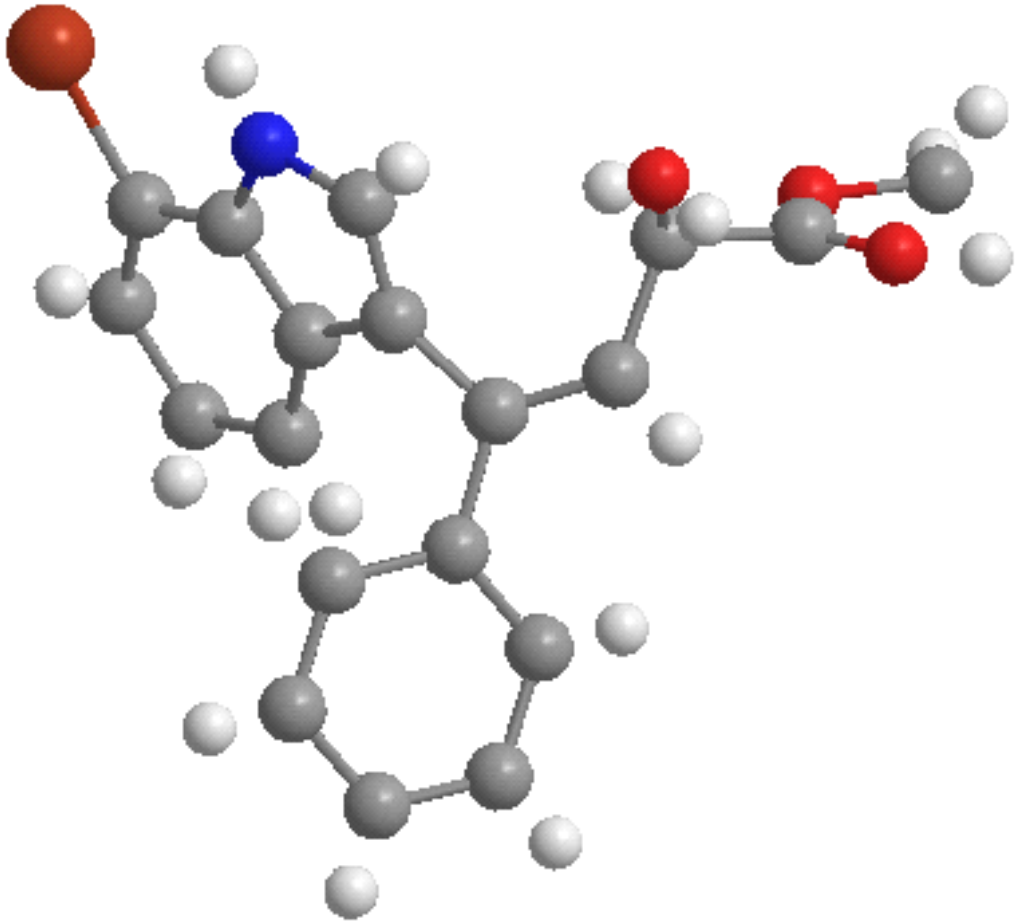


Fig. S1. X-ray structure of compound **2k** (CCDC 2044653)

VIII. Computational Data

DFT calculations were performed with Gaussian 09. [2] Geometry optimizations were computed at M06-2X/def2-SVP level of theory [3,4] and solvation (THF) with SMD model. [5] Frequency analysis was performed at the same level to provide correction to thermodynamic functions and confirm the nature of optimized structures (minima and transition states featured zero or one imaginary frequency, respectively). Single point energies were computed at M06-2X/def2-TZVPP level of theory and solvation (THF) with SMD model. Molecular structures were visualized with CYLview [6] or Multiwfn.[7]

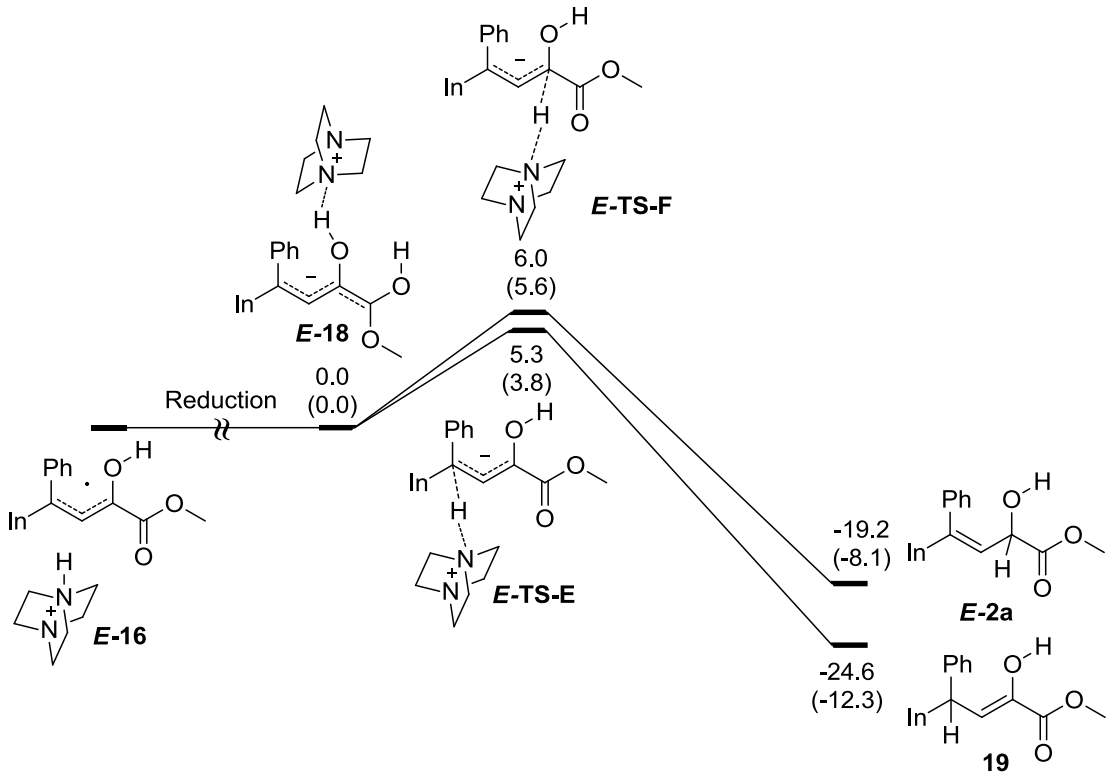


Fig. S2 The reaction profile of *E*-16

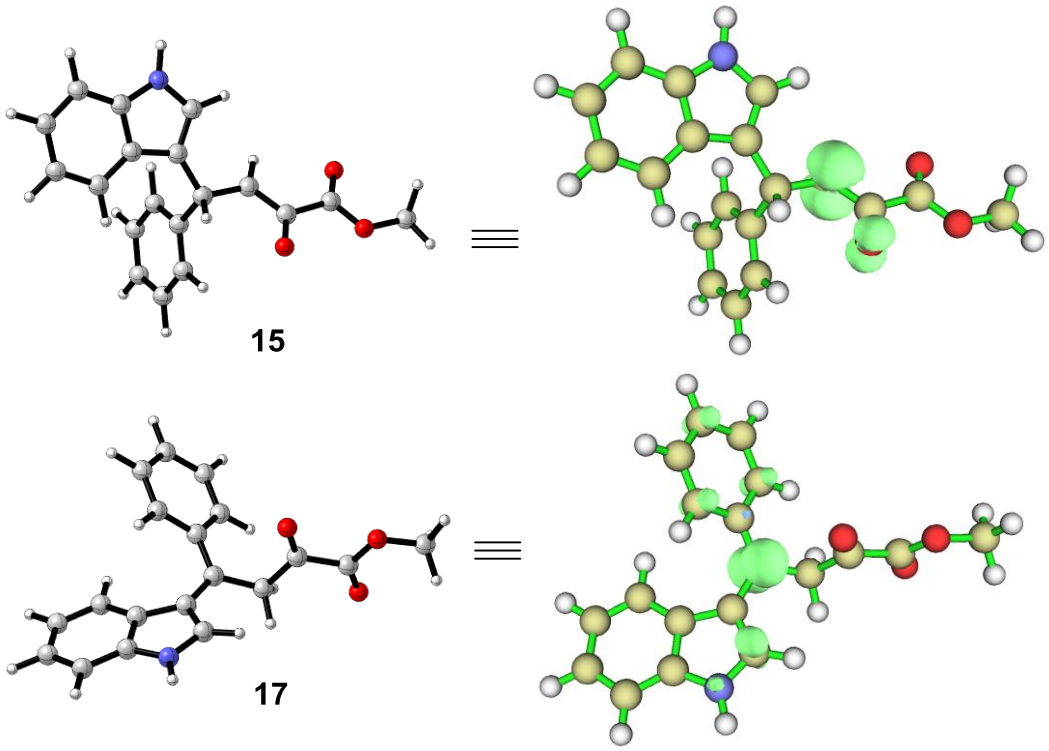


Fig. S3 The spin delocalized intermediate **15** and **17**.

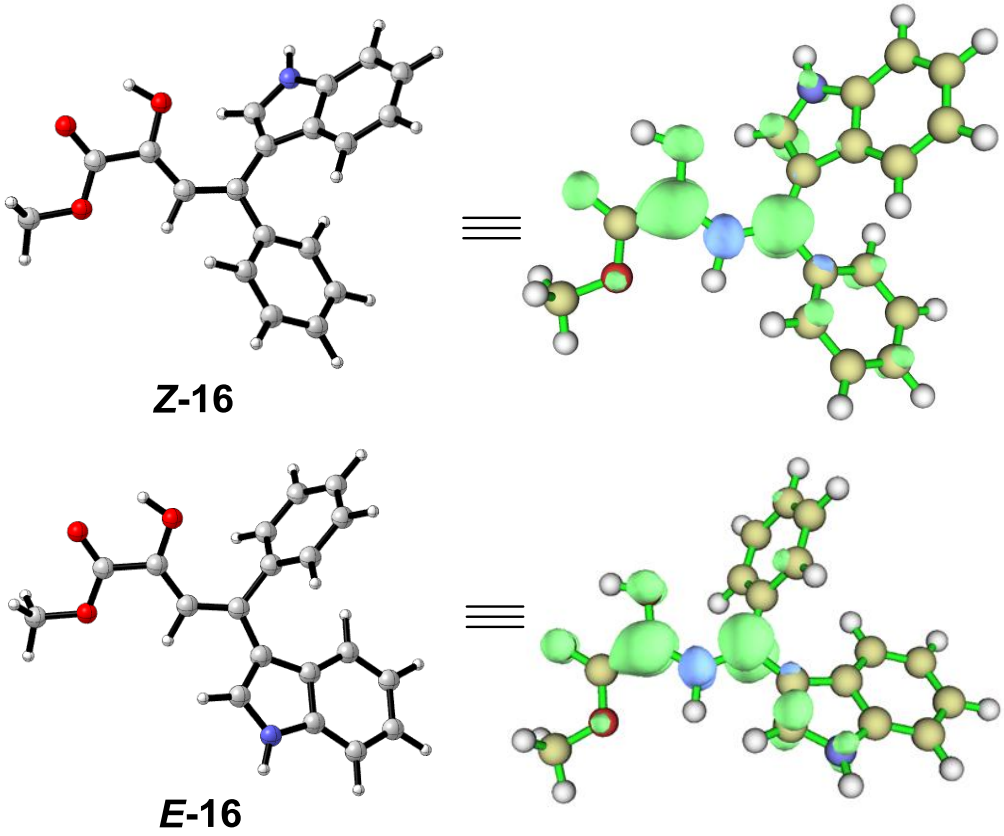


Fig. S4 The spin delocalized intermediate ***Z*-16** and ***E*-16**.

The DABCO radical cation participated reaction profile were also investigated, extremely high activation energy (33.5 kcal/mol) was found for the direct β-H abstraction process. The energy barrier forγ-H abstraction was 24.9 kcal/mol, slightly higher than the DABCO assisted enolate formation. However, the following β-H abstraction was very difficult, with an activation barrier of 36.2 kcal/mol. These results indicated that the DABCO radical cation participated reaction was infeasible.

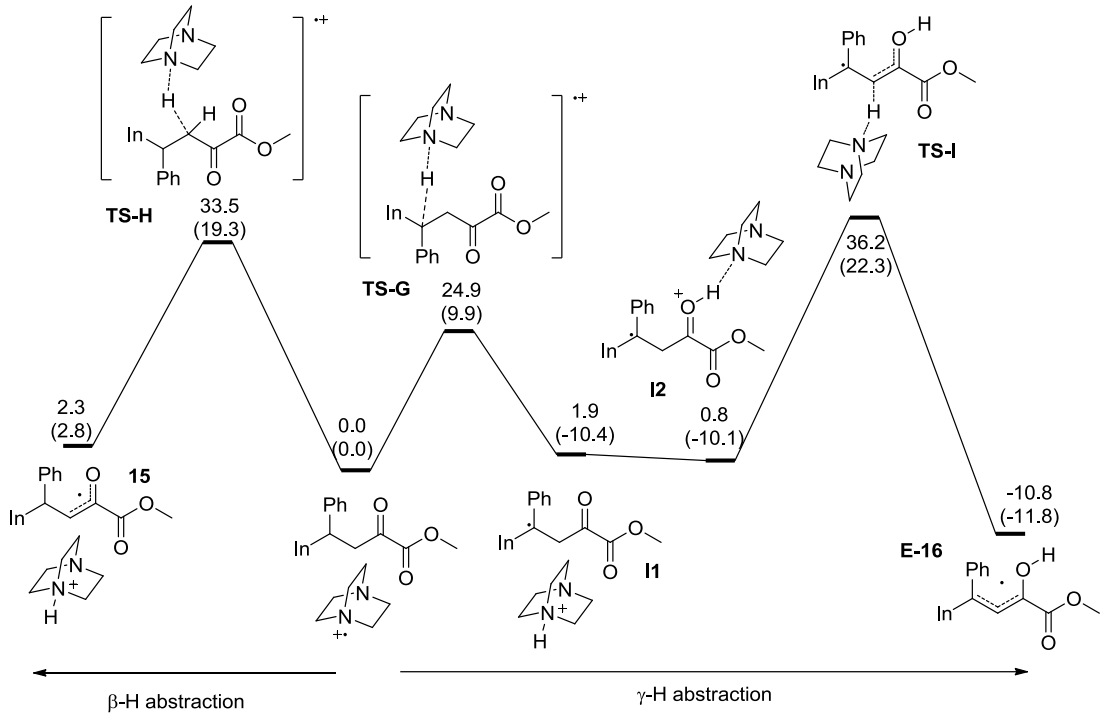


Fig. S5 The DABCO radical cation participated H-abstraction

Table S5. The energies of intermediates and transition states

Species	Electronic energies	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Free Energy
1a	-1014.695268	0.323829	0.343426	0.34437	0.273654
DABCO	-345.3158514	0.184643	0.190894	0.191839	0.15424
DABCO-RC[a]	-345.1289441	0.184606	0.19096	0.191904	0.153415
enol_**TS-A**	-1359.99381	0.506041	0.533179	0.534123	0.445632
13	-1014.69257	0.323987	0.343705	0.344649	0.272954
14	-1359.827604	0.510412	0.538189	0.539133	0.445876
15	-1014.045856	0.311108	0.330664	0.331608	0.259506
Z-**TS-B**	-1359.807984	0.506239	0.533205	0.534149	0.447001
E-**TS-B**	-1359.80664	0.505901	0.532946	0.53389	0.446435
TS-C	-1013.99638	0.305779	0.324843	0.325787	0.255678
TS-D	-1014.000137	0.30656	0.325846	0.32679	0.256244
Z-**16**	-1014.069366	0.312121	0.331323	0.332268	0.262715
E-**16**	-1014.069398	0.311605	0.330884	0.331828	0.262193
17	-1014.054527	0.310343	0.329933	0.330878	0.259256
DABCO-H^+	-345.7765282	0.200038	0.206417	0.207361	0.169371
Z-**TS-G**	-1359.797413	0.506104	0.533247	0.534191	0.445923
Z-**18**	-1359.992661	0.509275	0.536772	0.537717	0.447664
Z-**TS-E**	-1359.979903	0.505422	0.532666	0.53361	0.445766
Z-**TS-F**	-1359.979392	0.505618	0.532957	0.533901	0.445556
Z-**2a**	-1014.686572	0.323727	0.343526	0.34447	0.273511
E-**18**	-1359.99018	0.50935	0.536842	0.537786	0.448142
E-**TS-E**	-1359.979447	0.505115	0.532202	0.533146	0.445917
E-**TS-F**	-1359.977059	0.50515	0.532628	0.533572	0.444547
E-**2a**	-1014.686018	0.324262	0.343842	0.344786	0.274926
TS-G	-1359.806055	0.506291	0.53296	0.533901	0.448602
TS-H	-1359.791211	0.506338	0.53309	0.534032	0.447505
TS-I	-1359.785613	0.505414	0.53234	0.533286	0.446177
I1	-1359.845374	0.512461	0.5399	0.540845	0.45129
I2	-1359.845106	0.512545	0.5402	0.541139	0.449313

[a] DABCO-RC: DABCO radical cation.

Coordinates of the intermediates and transition states:

1) **1a**

C 2.47916700 0.06896200 -0.63874300

C 3.82663800 -0.02089600 0.11313900

O 2.32580000 -0.51867800 -1.67402200

O 4.76531200 -0.58464400 -0.62054800

O 3.97426000 0.38201000 1.23655400

C 6.04900100 -0.70512100 -0.00974100

H 6.70355200 -1.16486300 -0.75628200

H 6.43149400 0.28470300 0.27413100

H 5.98982000 -1.33828600 0.88584100

C 1.44866400 0.95833700 0.00678100

H 1.72708900 1.98777300 -0.28413900

H 1.55139400 0.92379900 1.10086000

C 0.01954100 0.65099300 -0.44707700

H 0.04130800 0.57319700 -1.54643400

C -0.89894500 1.81370700 -0.09664200

C -1.49798300 1.91837000 1.16354100

C -1.11641500 2.83265300 -1.03131900

C -2.29410500 3.01885600 1.48229800

H -1.34501000 1.12498200 1.89930000

C -1.91215000 3.93414700 -0.71576000

H -0.65676700 2.75725000 -2.02059800

C -2.50383100 4.03022300 0.54404500

H -2.75666500 3.08547000 2.46901700

H -2.07337800 4.71746100 -1.45890500

H -3.12948000 4.88920100 0.79343600

C -1.77618300 -2.50907800 0.51628900

C -1.72372900 -1.29363100 -0.21450400

C -2.80920300 -0.94053400 -1.03891600

C -3.89576000 -1.79879600 -1.11848500

C -3.92558600 -3.00677400 -0.38725900

C -2.87410600 -3.37824800 0.43707700

C 0.16479800 -1.50156200 0.99093000

C -0.46628700 -0.66311300 0.10273500

H -2.79358700 -0.00530100 -1.60352600

H -4.74479100 -1.53950400 -1.75343300

H -4.79550900 -3.66087800 -0.47043300

H -2.89666100 -4.30977200 1.00498200

H -0.36483500 -3.37229600 1.84792300

H 1.13269700 -1.39959100 1.47916600

N -0.61497400 -2.60483000 1.23612600

2) **DABCO**

C 0.77837600 -0.52102800 -1.27491600

C -0.77945400 -0.51813700 -1.27537100

C -0.77917500 -0.84526800 1.08676700

C 0.77846000 -0.84449500 1.08791300

H -1.17871900 0.11228200 -2.08429000

H 1.18045600 0.10584100 -2.08517500

H 1.17669200 -1.53764600 -1.41255300

H 1.17917800 -1.85990800 0.94862600

H -1.17866500 -1.86066600 0.94377900

H -1.18061900 -0.46116000 2.03674200

H 1.17800700 -0.45697000 2.03728000

H -1.18163300 -1.53285000 -1.41597100

C 0.77946400 1.36407100 0.18649800

H 1.18168100 1.75216800 1.13457000

H 1.17906300 1.99128600 -0.62471900

C -0.77781500 1.36478600 0.18894700

H -1.17914500 1.99464600 -0.61942900

H -1.17666100 1.75045200 1.13939000

N 1.27258400 -0.00060500 0.00001600

N -1.27240800 0.00102700 0.00037300

3) **DABCO-RC**

C -0.81375900 -0.03045400 1.36882400

C 0.81685800 -0.02695100 1.36704500

C 0.81777000 -1.16912800 -0.70990200

C -0.81369000 -1.17297500 -0.70811800

H 1.17363100 0.86498500 1.89322000

H -1.17331800 0.85999900 1.89559800

H -1.16870900 -0.94445000 1.85762700

H -1.16826100 -2.07505400 -0.19760500

H 1.17772500 -2.06941800 -0.19999200

H 1.17430700 -1.13561200 -1.74505100

H -1.17244500 -1.14112900 -1.74255800

H 1.17682700 -0.93945600 1.85494100

C -0.81938900 1.19785000 -0.65851100

H -1.17833600 1.20852100 -1.69348300

H -1.17796100 2.07543000 -0.10946000

C 0.81224100 1.20179400 -0.66002600

H 1.16752900 2.08095200 -0.11137600

H 1.16934300 1.21453900 -1.69562000

N -1.21736200 -0.00286900 0.00114100

N 1.21728800 0.00285100 -0.00144200

4) **TS-A**

C 0.76378500 -1.96652100 -0.54948600

C 1.62891200 -2.96543700 0.25901200

O 0.71119100 -2.10292800 -1.77303100

O 2.51556300 -3.59468900 -0.51049200

O 1.52791500 -3.17020500 1.44315200

C 3.35784800 -4.52746300 0.15248300

H 4.02677000 -4.94073200 -0.60969100

H 3.94369400 -4.03046000 0.93915400

H 2.76451700 -5.33117300 0.60996100

C 0.20064800 -0.93418500 0.24302700

H 1.44973800 -0.00117000 0.12306900

H 0.17133500 -1.13181400 1.31982400

C -0.96235800 -0.14351700 -0.33092600

H -0.84164800 -0.16291500 -1.42736200

C -0.92468700 1.31694200 0.09708400

C -1.05716500 1.66920900 1.44700500

C -0.72945700 2.33693900 -0.84019600

C -0.97689700 3.00115300 1.84937900

H -1.22617800 0.88499600 2.19005400

C -0.64867300 3.67426900 -0.44299400

H -0.64710400 2.07860400 -1.89962300

C -0.76721400 4.01015400 0.90509600

H -1.08094500 3.25603000 2.90608600

H -0.49894000 4.45529600 -1.19139600

H -0.70707900 5.05362300 1.21998500

C -4.54872000 -1.21409000 0.21845400

C -3.61489700 -0.26149900 -0.27454300

C -4.10264300 0.90621300 -0.89422500

C -5.47313800 1.08942300 -1.00558900

C -6.38106300 0.12900300 -0.50870500

C -5.93477200 -1.03037100 0.10734600

C -2.49059600 -1.98174400 0.64311900

C -2.29501200 -0.77817400 0.00866100

H -3.41101200 1.65800100 -1.27915900

H -5.86066400 1.99139600 -1.48267900

H -7.45392000 0.30311100 -0.61090300

H -6.63315900 -1.77518900 0.49304200

H -4.22985100 -3.07100600 1.19651900

H -1.75002400 -2.68607900 1.01627600

N -3.83302400 -2.24389900 0.76733400

C 4.89935600 0.46473900 0.20667600

C 3.55642200 -0.30373400 0.31763800

C 2.49044800 1.79968400 0.91342700

C 3.83641400 2.54286400 0.69215800

H 3.48898600 -1.13576500 -0.39813100

H 5.57849300 -0.04654400 -0.48896800

H 5.39633800 0.52097200 1.18472600

H 4.39001500 2.63015900 1.63702700

H 2.38152100 1.41404800 1.93625200

H 1.61944500 2.42750800 0.68250600

H 3.65771100 3.55768800 0.31083300

H 3.37164800 -0.69632300 1.32714000

C 3.97736400 1.77035000 -1.56276500

H 3.86654800 2.79331300 -1.94772200

H 4.60537800 1.21010300 -2.26899700

C 2.58817200 1.09411000 -1.40785300

H 2.46083700 0.21440400 -2.05247100

H 1.76256500 1.79021100 -1.60039900

N 4.66215000 1.82274800 -0.27360000

N 2.45875800 0.63863500 -0.00397500

5) **13**

C -2.56362800 -0.37476400 0.79932000

C -3.92869500 -0.77302000 0.33998600

O -2.52344900 -0.03590200 2.10412500

O -4.00852500 -1.11217900 -0.93400500

O -4.86173800 -0.77754900 1.10929700

C -5.29712300 -1.51278300 -1.39777200

H -5.17936700 -1.74848200 -2.45970200

H -5.64241900 -2.39833900 -0.84768200

H -6.02290100 -0.69907700 -1.26852100

C -1.49165200 -0.35458800 -0.00295000

H -1.63271100 -0.61983700 -1.05215800

C -0.12173800 0.07179000 0.45358000

H -0.13476200 0.11345100 1.55403900

C 0.13328000 1.49828000 -0.03353500

C 0.72660200 1.75948200 -1.27263500

C -0.28116600 2.57584600 0.75837200

C 0.90710000 3.07258500 -1.70913200

H 1.05829500 0.92604100 -1.89678600

C -0.09994000 3.88843400 0.32468300

H -0.75523100 2.37787700 1.72341600

C 0.49674000 4.14111600 -0.91149400

H 1.37643000 3.26051100 -2.67686800

H -0.42240600 4.71842400 0.95645000

H 0.64299100 5.16810300 -1.25111500

C 2.98399100 -1.91382200 -0.29516400

C 2.35967500 -0.76769400 0.26341300

C 3.15475600 0.20623400 0.89756900

C 4.52665200 0.01308900 0.96035700

C 5.12815100 -1.13476700 0.39889400

C 4.37155700 -2.10943100 -0.23409500

C 0.78192300 -2.08411300 -0.65737400

C 0.94415700 -0.89859400 0.01834800

H 2.69627700 1.09894300 1.32955700

H 5.15598800 0.75904000 1.44885200

H 6.21106600 -1.25634800 0.46300100

H 4.83443700 -2.99626200 -0.67011100

H 2.14161800 -3.57868500 -1.31140500

H -0.13010100 -2.55527100 -1.01783500

N 1.99877400 -2.69095300 -0.84513100

H -3.42278200 -0.14807100 2.45522500

6) **14**

C -0.64927300 0.84750800 -0.65483500

C -1.62853200 1.56764100 -1.52395000

O -1.22153500 0.02579100 0.24617600

O -1.08710900 2.36993600 -2.42009700

O -2.82202000 1.40159100 -1.39296600

C -1.99091200 3.08043000 -3.26553500

H -1.37041400 3.69323900 -3.92634800

H -2.59741100 2.37946400 -3.85438600

H -2.65144300 3.72047800 -2.66568300

C 0.67680400 1.00833300 -0.76577200

H 1.04945900 1.70250200 -1.52114500

C 1.67976300 0.30712000 0.11082200

H 1.12305800 -0.30879000 0.83391200

C 2.45030700 1.35685900 0.91185200

C 3.61540100 1.94514700 0.40896600

C 1.96146000 1.78177200 2.15248100

C 4.27983300 2.93565700 1.13222000

H 4.01113800 1.61609800 -0.55489900

C 2.62598500 2.76983800 2.87914500

H 1.04852500 1.33132600 2.55169500

C 3.78864700 3.35019600 2.37026900

H 5.19012400 3.38195400 0.72716700

H 2.23642400 3.08725100 3.84848500

H 4.31189100 4.12174000 2.93800500

C 4.24949500 -2.07678200 -1.25335100

C 3.64356900 -1.41315300 -0.15435400

C 4.13350700 -1.64553500 1.14474400

C 5.19263400 -2.52485300 1.31264100

C 5.77995700 -3.17775000 0.20647000

C 5.32161300 -2.96546200 -1.08510600

C 2.60111000 -0.78812000 -2.04970800

C 2.58795600 -0.58992900 -0.69018700

H 3.68653800 -1.13862900 2.00317000

H 5.58448400 -2.71525300 2.31337800

H 6.61268700 -3.86383900 0.37183200

H 5.77712900 -3.46768600 -1.94010600

H 3.79982000 -1.98880100 -3.32801300

H 1.96079700 -0.35822700 -2.81720500

N 3.59243800 -1.67611800 -2.38699900

C -6.01852300 -1.74182600 -0.49559300

C -4.50356700 -1.18844500 -0.72123500

C -4.88870100 0.50402300 0.89450400

C -6.39565300 -0.05789800 1.13412200

H -3.85448600 -2.02777900 -0.99590400

H -6.03822500 -2.82179000 -0.67841600

H -6.70036700 -1.21275100 -1.17053400

H -7.08021300 0.44079100 0.43957600

H -4.89694900 1.24501900 0.08824500

H -4.52124500 0.94616900 1.82738900

H -6.68705100 0.12189500 2.17456800

H -4.50664100 -0.42309700 -1.50451600

C -5.51646000 -2.16606800 1.78585800

H -5.82738300 -1.96554100 2.81703900

H -5.53250300 -3.23972300 1.56983700

C -4.00638200 -1.59793700 1.56242900

H -3.35466300 -2.42606100 1.26230000

H -3.65375300 -1.14247800 2.49452200

N -6.34079000 -1.45703200 0.86387400

N -4.08355700 -0.61850700 0.52237700

H -2.19089700 0.07096500 0.15500200

7) **15**

C 2.57834000 -0.47082600 -0.59782500

C 3.85945200 -0.91379300 0.12265900

O 2.60734200 -0.13432600 -1.77732300

O 4.91292200 -0.86762700 -0.67048700

O 3.88208100 -1.25948400 1.27526100

C 6.15324500 -1.25437000 -0.08378500

H 6.90682500 -1.17141200 -0.87293200

H 6.40546300 -0.58838500 0.75267400

H 6.09994900 -2.28860600 0.28229600

C 1.39324600 -0.48297400 0.20329500

H 1.47229000 -0.74902200 1.25885900

C 0.08380800 -0.04330100 -0.35582100

H 0.16735100 -0.05994900 -1.45372200

C -0.09098700 1.42556100 0.05244300

C -0.72129300 1.77752600 1.25026200

C 0.42986600 2.43300400 -0.76744700

C -0.84087200 3.11830600 1.61519600

H -1.13203300 0.99657700 1.89451000

C 0.30760100 3.77348400 -0.40337800

H 0.93645500 2.15894400 -1.69631400

C -0.32957400 4.11958700 0.78900900

H -1.34253600 3.38152200 2.54830500

H 0.71016600 4.55044900 -1.05590000

H -0.42835100 5.16873800 1.07318800

C -3.17186000 -1.78661000 0.32120800

C -2.43680700 -0.74265900 -0.29844100

C -3.11540300 0.20043400 -1.09334400

C -4.48705500 0.07534100 -1.25206600

C -5.20090800 -0.97269800 -0.62945900

C -4.55975200 -1.91339400 0.16222000

C -1.02011400 -2.03000000 0.88955300

C -1.05755100 -0.91987300 0.08049300

H -2.56911200 1.01596100 -1.57332400

H -5.02900900 0.79755300 -1.86491300

H -6.28067600 -1.04172800 -0.77372200

H -5.11001000 -2.72184700 0.64644000

H -2.51641800 -3.36922900 1.57828500

H -0.17268100 -2.50599600 1.37895000

N -2.28239000 -2.54836300 1.03272400

8) ***Z*-TS-B**

C 2.39601200 -0.56094900 -0.88997000

C 3.87020000 -0.78372100 -1.03668700

O 1.89351300 0.23054600 -1.85635000

O 4.40429200 -1.56395300 -0.12150900

O 4.47337000 -0.26422500 -1.94656700

C 5.80794600 -1.80953600 -0.23638500

H 6.06817700 -2.47325400 0.59309000

H 6.03167100 -2.29306100 -1.19615100

H 6.36688900 -0.86778000 -0.16146800

C 1.66678700 -1.08384400 0.11124300

H 2.20969900 -1.67853700 0.84697300

C 0.19997100 -0.87626700 0.31572200

H 0.08706400 0.32428600 0.31929200

C -0.23081500 -1.24726000 1.71681000

C -1.15618800 -2.26421600 1.97986900

C 0.35816700 -0.57339100 2.79784500

C -1.49048700 -2.59071200 3.29440200

H -1.61202200 -2.81007100 1.15231500

C 0.02300600 -0.89754300 4.11048100

H 1.08868800 0.21712600 2.59966000

C -0.90674900 -1.90820100 4.36180100

H -2.20854400 -3.39039400 3.48428400

H 0.48920100 -0.36253900 4.93955200

H -1.17168200 -2.16668000 5.38835300

C -2.49886100 -1.55401600 -2.18580700

C -2.11704900 -1.08958300 -0.90257600

C -3.11039600 -0.57545900 -0.04797800

C -4.42396700 -0.52844400 -0.49548300

C -4.77643700 -0.99237300 -1.77934800

C -3.82140500 -1.51390600 -2.64071800

C -0.28891600 -1.84319600 -2.00610700

C -0.68265700 -1.28194300 -0.79886300

H -2.86074400 -0.23444300 0.95833200

H -5.20158800 -0.13470400 0.16095000

H -5.81862600 -0.94573400 -2.09900200

H -4.08676900 -1.87890700 -3.63380300

H -1.33184300 -2.41568900 -3.74587400

H 0.70522900 -2.14393400 -2.32826800

N -1.36113600 -2.00537000 -2.81810900

C -0.71082400 3.76342500 -1.14403100

C -0.63998900 2.18688800 -1.01633600

C 1.26846500 2.47605700 0.42899800

C 1.09382900 4.04809000 0.37061500

H -1.64076100 1.73850800 -1.05842300

H -1.74033200 4.06540800 -1.37357800

H -0.05061700 4.10322800 -1.95200800

H 1.72843800 4.45702900 -0.42558400

H 1.89325600 2.11611600 -0.39573300

H 1.69578200 2.15724900 1.38842300

H 1.39153900 4.49408100 1.32801100

H -0.00435800 1.74107100 -1.79064100

C -1.12621800 3.90179200 1.18826500

H -0.84292100 4.41059900 2.11824200

H -2.17601000 4.12849100 0.96366300

C -0.94233400 2.33770000 1.36208500

H -1.90238900 1.81620800 1.27148700

H -0.48029200 2.09546100 2.32674700

N -0.29139600 4.36582000 0.10280200

N -0.06111500 1.89777200 0.28892300

H 2.63344000 0.46802400 -2.44582000

9) ***E*-TS-B**

C -2.55926600 0.76755700 -0.13980200

C -3.91130900 0.99897900 -0.73720500

O -2.61001700 0.27562100 1.11009400

O -3.89394700 1.49936300 -1.95532200

O -4.90801400 0.72720200 -0.11063100

C -5.16680800 1.71555400 -2.56885700

H -4.96122700 2.15295200 -3.55015600

H -5.70130000 0.76281300 -2.67992300

H -5.77040200 2.40365600 -1.96318600

C -1.40553100 0.98202200 -0.79219000

H -1.46920400 1.35350400 -1.81566300

C -0.06846400 0.76183300 -0.16215600

H -0.17886100 -0.34196400 0.37274800

C 0.23199800 1.73192300 0.96776800

C 0.68576800 3.01835000 0.64491300

C 0.07161500 1.38440800 2.31097200

C 0.98700900 3.93394500 1.64978900

H 0.81376300 3.29539200 -0.40439700

C 0.37837000 2.30121500 3.31892600

H -0.29745400 0.39173400 2.57175800

C 0.83940100 3.57507100 2.99155600

H 1.34205900 4.93148800 1.38493700

H 0.25528800 2.01584100 4.36504100

H 1.08191700 4.28966100 3.77990700

C 3.09533700 0.19285800 -2.05516600

C 2.46051000 0.57803100 -0.84927900

C 3.26065700 0.87106300 0.27130000

C 4.64130500 0.77731800 0.14865300

C 5.24702400 0.40164500 -1.06611300

C 4.48352400 0.10214400 -2.18684800

C 0.89093000 0.14109200 -2.43644200

C 1.03014800 0.55033300 -1.10617000

H 2.81260700 1.16734300 1.22058300

H 5.27135000 1.00314800 1.01023200

H 6.33485200 0.34387900 -1.12762700

H 4.94300700 -0.19342700 -3.13085000

H 2.26928400 -0.33986900 -3.94954800

H -0.01699700 -0.00551000 -3.01814400

N 2.10605800 -0.06399700 -2.98564700

C -1.17594400 -3.91425700 -0.29317300

C -1.21804700 -2.34268800 -0.33030700

C -0.67541100 -2.22447300 2.01249800

C -0.78071800 -3.79486400 2.04825500

H -0.93012800 -1.94655700 -1.31584400

H -0.78835200 -4.30852600 -1.24162400

H -2.18967600 -4.30604000 -0.13942100

H -1.82262000 -4.10008100 2.21026600

H -1.63644500 -1.74199800 2.22488000

H 0.08100500 -1.85854500 2.71813900

H -0.16891200 -4.18964300 2.86963500

H -2.21025200 -1.96055500 -0.06019500

C 1.04650900 -3.91988400 0.53620500

H 1.68313300 -4.22296800 1.37748300

H 1.42006000 -4.40170200 -0.37652600

C 1.08303100 -2.35466000 0.37107000

H 1.34807600 -2.06866400 -0.65614900

H 1.78818600 -1.88635200 1.07003900

N -0.31487500 -4.34994300 0.79036800

N -0.26084700 -1.85554900 0.65892400

H -3.54911800 0.22282700 1.36578700

10) **TS-C**

C -2.48806300 -0.56712300 0.19058400

C -3.82362500 -0.93829600 -0.39855400

O -2.38935000 -0.09514700 1.37389700

O -4.83504200 -0.57510400 0.37300200

O -3.93629100 -1.50658400 -1.45355800

C -6.13539500 -0.89866300 -0.11188100

H -6.84492200 -0.50195300 0.62084000

H -6.30608100 -0.43773300 -1.09408600

H -6.25154500 -1.98739700 -0.20094100

C -1.30624300 -0.73830900 -0.52298900

H -1.22010800 -1.34619200 -1.42428400

C -0.18737500 -0.12801900 0.19968700

H -1.02021000 -0.09656300 1.25098900

C 0.00089800 1.36484700 0.15898500

C -0.56687000 2.15518000 -0.84802600

C 0.77366400 1.98859600 1.15167300

C -0.35819000 3.53562000 -0.86728400

H -1.15948300 1.67980700 -1.63231700

C 0.98621400 3.36287400 1.12816600

H 1.21440400 1.37946000 1.94505700

C 0.42055200 4.14349500 0.11593200

H -0.80117800 4.13651800 -1.66388400

H 1.59192800 3.83128700 1.90623900

H 0.58679000 5.22197400 0.09684400

C 3.13631500 -1.85695800 0.16328700

C 2.39774400 -0.67089700 -0.08465700

C 3.07023100 0.43903200 -0.63356300

C 4.43007700 0.34062100 -0.89098400

C 5.14502800 -0.84360500 -0.61667200

C 4.50964600 -1.95831600 -0.09018400

C 1.01094600 -2.27738800 0.71059700

C 1.02242800 -0.95669800 0.28125500

H 2.53399900 1.36171900 -0.85839300

H 4.95787000 1.19548800 -1.31713800

H 6.21497000 -0.88538000 -0.82796400

H 5.05253600 -2.88235200 0.11452100

H 2.51187300 -3.74736100 0.91832800

H 0.17047300 -2.86322800 1.07919100

N 2.26089400 -2.80276600 0.64686200

11) **TS-D**

C -2.69955400 -0.09747200 -0.09022400

C -3.85299600 -1.05116300 0.21171200

O -2.91859200 1.04873200 -0.47649200

O -5.02983000 -0.49136600 -0.03224300

O -3.72027400 -2.18253900 0.61274300

C -6.16781500 -1.30923400 0.20735700

H -7.04319100 -0.70584000 -0.05387500

H -6.13421200 -2.21420800 -0.41507100

H -6.21661500 -1.60692200 1.26407900

C -1.40637600 -0.70392000 0.12245900

H -1.39586800 -1.78085000 0.29650900

C -0.09121900 -0.07399500 -0.02681600

H -0.72177100 -0.30086300 1.13190500

C 0.08582100 1.39528800 -0.11593900

C 0.97794500 1.92188000 -1.06382600

C -0.58540400 2.28271100 0.74134600

C 1.18802300 3.29636200 -1.15475200

H 1.50797200 1.24485200 -1.73641600

C -0.36580300 3.65316900 0.65524800

H -1.27640500 1.89262000 1.49191000

C 0.52067100 4.16744700 -0.29442100

H 1.88113300 3.68721100 -1.90189500

H -0.88927700 4.32637100 1.33643700

H 0.69167600 5.24334100 -0.35918900

C 3.15698500 -1.88300100 -0.25516400

C 2.43450000 -0.73808500 0.16468800

C 3.11704600 0.28163000 0.85515300

C 4.47653200 0.13686100 1.08849500

C 5.17754800 -1.00691600 0.65074300

C 4.53066000 -2.03194200 -0.02240300

C 1.02415500 -2.18776800 -0.85754100

C 1.05696900 -0.94975600 -0.23652700

H 2.58602800 1.17001900 1.20219500

H 5.01638800 0.92111400 1.62182200

H 6.24760300 -1.08766200 0.84948600

H 5.06539900 -2.92276000 -0.35564800

H 2.50550000 -3.63099500 -1.28073300

H 0.18139900 -2.70341600 -1.31403100

N 2.26824100 -2.73474400 -0.86958100

12) ***Z*-16**

C -2.34014500 -0.98995100 -0.11620600

C -3.81208100 -0.98432100 -0.22191100

O -1.81095300 -2.20568000 -0.30632400

O -4.39120800 0.19442400 -0.03039400

O -4.41982800 -2.00778500 -0.47105600

C -5.81129400 0.21919900 -0.13346500

H -6.11585100 1.24660500 0.08929100

H -6.13059400 -0.05854600 -1.14724600

H -6.26140800 -0.47512000 0.58864500

C -1.60767100 0.16969600 0.11090500

H -2.23241700 1.06183600 0.16862300

C -0.22645900 0.36488000 0.23443800

H -2.56042000 -2.80080200 -0.49378000

C 0.27587500 1.75621600 0.22152800

C -0.35701400 2.75369700 -0.54377400

C 1.39789100 2.12480700 0.98874400

C 0.10959100 4.06604700 -0.53788300

H -1.20907500 2.48906700 -1.17277200

C 1.86040800 3.43740300 0.99623900

H 1.90148700 1.36910900 1.59431100

C 1.21968900 4.41535400 0.23244000

H -0.39206200 4.81984200 -1.14763600

H 2.72681700 3.70053900 1.60605300

H 1.58601900 5.44341800 0.23506600

C 2.62615500 -2.03111400 0.35063300

C 2.07504400 -0.81796500 -0.13394500

C 2.83929400 -0.03528600 -1.02014000

C 4.10885900 -0.46771800 -1.37572800

C 4.64047400 -1.67289000 -0.87001200

C 3.90754400 -2.47138000 -0.00462900

C 0.56724700 -1.84361600 1.20311400

C 0.73819600 -0.71180700 0.42424700

H 2.43882200 0.89617200 -1.42474300

H 4.70926700 0.13328600 -2.06093700

H 5.64294200 -1.98427100 -1.16908900

H 4.30674400 -3.40982500 0.38378300

H 1.80407800 -3.49481000 1.65783600

H -0.29458700 -2.13894600 1.79602200

N 1.68379000 -2.61896000 1.16159900

13) ***E*-16**

C -2.70900800 0.13400900 0.13082200

C -4.00310700 -0.54020000 -0.07530600

O -2.83340000 1.42495300 0.46372400

O -3.92688800 -1.82212300 -0.41626400

O -5.04953000 0.06319700 0.06555300

C -5.16850500 -2.48759600 -0.62326600

H -4.92221400 -3.51849100 -0.89680700

H -5.77238200 -2.47495100 0.29436400

H -5.73323600 -2.00546000 -1.43261200

C -1.49172700 -0.52972800 0.02525000

H -1.59039800 -1.59995600 -0.16203200

C -0.19324700 -0.02890700 0.16807000

H -3.78969700 1.61105800 0.49045200

C 0.12809100 1.41544700 0.16947100

C -0.39481700 2.27428800 -0.81016600

C 1.01704600 1.94370600 1.12039400

C -0.03499200 3.61902100 -0.84102300

H -1.07955600 1.87290900 -1.55986700

C 1.36480300 3.29217800 1.09870000

H 1.43600500 1.28303600 1.88274100

C 0.84413700 4.13376700 0.11430100

H -0.44040500 4.27117900 -1.61696000

H 2.05089200 3.68738000 1.85020700

H 1.12369900 5.18871100 0.08988900

C 2.95986300 -2.02003100 0.22625300

C 2.29422000 -0.81293200 -0.10821100

C 3.02224600 0.19622800 -0.76930800

C 4.36489300 -0.01430300 -1.04683400

C 5.00872000 -1.21660400 -0.68561400

C 4.31650200 -2.23587600 -0.05018800

C 0.82687000 -2.23911000 0.86241300

C 0.90953900 -0.96915300 0.30872100

H 2.53922200 1.12954300 -1.06251800

H 4.93508400 0.76375500 -1.55725200

H 6.06724800 -1.34913800 -0.91608000

H 4.80360700 -3.17389500 0.22082100

H 2.23654300 -3.78149700 1.17509100

H -0.02890800 -2.73070000 1.32094700

N 2.03912600 -2.85527400 0.81266300

14) **17**

C 2.42220300 -0.52558900 0.23183000

C 3.80956400 -0.94457400 -0.30590400

O 2.27860900 -0.23871700 1.38692700

O 4.71479500 -1.00384100 0.65021900

O 4.00959300 -1.18546400 -1.46678800

C 6.03018700 -1.37991300 0.24500800

H 6.64390900 -1.37597000 1.15088900

H 6.02051700 -2.38268200 -0.20293700

H 6.42567700 -0.66144100 -0.48559500

C 1.32399000 -0.54709900 -0.80842100

H 1.19616200 -1.60125100 -1.10516900

C 0.02842400 0.05347100 -0.34904500

H 1.71773900 -0.05920200 -1.71481900

C -0.03329500 1.48444600 -0.13028600

C -0.98835100 2.05882500 0.74533800

C 0.90169300 2.36617000 -0.72690500

C -1.02609600 3.42757900 0.97825500

H -1.68884400 1.40856500 1.26994200

C 0.85668900 3.73590300 -0.49151400

H 1.66694500 1.97780200 -1.40058200

C -0.10994500 4.28099600 0.35658400

H -1.77061600 3.83324900 1.66629600

H 1.58595300 4.38720500 -0.97740900

H -0.14072000 5.35589600 0.54142400

C -3.11248400 -1.87584600 0.21704300

C -2.50279100 -0.65331100 -0.16389700

C -3.32900500 0.39308700 -0.61687300

C -4.70395700 0.21006300 -0.63734400

C -5.28676100 -1.00517600 -0.22101900

C -4.50091800 -2.06474100 0.20406900

C -0.90131700 -2.16167400 0.37418300

C -1.06103600 -0.84399200 -0.04671100

H -2.89730500 1.33707600 -0.95237100

H -5.34841200 1.01957300 -0.98409800

H -6.37226700 -1.11617200 -0.24286900

H -4.93955000 -3.01522500 0.51225900

H -2.25334100 -3.71306800 0.85596600

H 0.01676200 -2.70335300 0.59294200

N -2.11247700 -2.75979400 0.54098900

15) DABCO-H^+

C -12.81997500 -2.08832800 10.51498700

C -12.23611200 -0.68354200 10.81148700

C -14.46464600 0.30980600 10.50101200

C -14.95230800 -1.10188100 10.08663400

H -11.39355000 -0.70496600 11.51227100

H -12.30210800 -2.85143200 11.11027200

H -12.68589700 -2.33503100 9.45395800

H -14.77972000 -1.26783000 9.01544100

H -14.08185100 0.89795500 9.65916500

H -15.23012400 0.89005900 11.02952600

H -16.02886700 -1.19887200 10.27655500

H -11.94147900 -0.14112600 9.90544300

C -14.42987300 -1.91608100 12.26875900

H -15.50546100 -1.92680200 12.48746300

H -13.96122200 -2.74169700 12.81953600

C -13.80542000 -0.56536700 12.70323400

H -12.93175100 -0.68508600 13.35431500

H -14.52452100 0.10750500 13.18382300

N -14.24002900 -2.12614800 10.83947300

N -13.32717600 0.11660300 11.45716700

H -12.95089700 1.03776900 11.70863500

16) ***Z*-TS-G**

C -1.34818600 0.86885400 -1.26786800

C -1.93935800 2.18838000 -1.73184700

O -1.71250700 -0.14569400 -2.12068700

O -1.58203900 3.22146800 -0.99752200

O -2.72000300 2.22419600 -2.65016100

C -2.15844400 4.48379200 -1.34972500

H -1.90030900 4.74322700 -2.38423200

H -3.25011700 4.44292500 -1.24221100

H -1.73384000 5.21500000 -0.65603600

C 0.02077300 0.90815200 -0.73467800

H 0.26809800 1.88005600 -0.30195700

C 0.92413100 -0.09894600 -0.55631900

H -1.98096800 0.68517400 -0.25318600

C 2.14011700 0.18574200 0.25877000

C 3.36162600 -0.43078600 -0.05899500

C 2.09697700 1.05849800 1.35854800

C 4.50742400 -0.16591300 0.68650200

H 3.41095500 -1.11635000 -0.90689100

C 3.24238900 1.31781800 2.10790900

H 1.15124000 1.52250500 1.64580700

C 4.45239000 0.70858100 1.77300700

H 5.44962000 -0.64672900 0.41817900

H 3.18791600 1.99269200 2.96381100

H 5.34942000 0.91057000 2.36076000

C 0.82694100 -3.75649600 -1.23950700

C 1.03103100 -2.68121500 -0.33898600

C 1.33125600 -2.96613200 1.00660200

C 1.42468000 -4.29235800 1.40498500

C 1.22647500 -5.34707700 0.48854300

C 0.92459800 -5.09616100 -0.84217900

C 0.50561300 -1.85573600 -2.37663700

C 0.80981900 -1.46130700 -1.08796400

H 1.49631300 -2.15821300 1.72317200

H 1.66155700 -4.52752000 2.44397500

H 1.31115900 -6.37892700 0.83344900

H 0.76485500 -5.90756300 -1.55370700

H 0.35440900 -3.74128400 -3.31543900

H 0.28378300 -1.24016300 -3.24351000

N 0.52117800 -3.21260500 -2.46605000

C -2.77955300 -2.31322100 1.92938200

C -1.98143600 -1.35341800 0.95013500

C -4.07243800 -0.50484700 0.12570400

C -4.84549600 -1.45440700 1.13440800

H -1.01978100 -1.05076600 1.38687100

H -2.17754900 -2.50600800 2.82587900

H -2.98499800 -3.26366300 1.42154100

H -5.06255700 -2.41152900 0.64454000

H -3.86423200 -1.01540200 -0.82253900

H -4.63073900 0.42084300 -0.06135100

H -5.78848800 -0.98113800 1.43486200

H -1.81007200 -1.82168400 -0.02781100

C -3.76611100 -0.43223700 2.98450800

H -4.71486300 0.02318700 3.29393000

H -3.14991700 -0.61995400 3.87239100

C -3.00051700 0.55390500 2.00284400

H -2.01983900 0.83441700 2.40681600

H -3.59330700 1.45422200 1.80076900

N -4.02301300 -1.67879300 2.30127800

N -2.80765600 -0.17293800 0.76045800

H -2.40641400 0.21639000 -2.70081200

17) ***Z*-18**

C -2.00354000 1.12616200 -1.03938300

C -3.27212400 1.62516500 -0.96762900

O -1.90869900 -0.09711800 -1.65520500

O -3.55982600 2.84510700 -0.51532400

O -4.31588800 0.91174900 -1.40784900

C -4.83626200 3.02883400 0.08296100

H -5.64264700 2.88520000 -0.64838500

H -4.97911600 2.33575900 0.92658000

H -4.85595400 4.05990900 0.45186600

C -0.88635300 1.84233600 -0.46875200

H -1.19532100 2.73666000 0.07900600

C 0.44822200 1.56598000 -0.48001600

H -1.51580500 -0.74738600 -0.98250200

C 1.35470300 2.40945200 0.34849200

C 2.64559200 2.73885900 -0.09968600

C 0.95385000 2.88917600 1.60729100

C 3.49175400 3.53428100 0.66997400

H 2.98324700 2.36792800 -1.06992600

C 1.79981400 3.68568300 2.37782700

H -0.02813700 2.61096800 1.99613500

C 3.07338000 4.01373500 1.91310600

H 4.48700700 3.78325500 0.29608900

H 1.46519400 4.04013700 3.35495100

H 3.73885500 4.63184500 2.51850900

C 2.39321100 -1.30515300 -1.88261100

C 2.11757000 -0.41729700 -0.80930400

C 2.79443500 -0.60156800 0.41245400

C 3.70352500 -1.64346700 0.52980300

C 3.96352400 -2.51161800 -0.55290900

C 3.31529100 -2.35468500 -1.76958400

C 0.80294400 0.11564900 -2.55994800

C 1.08025900 0.48679800 -1.26172700

H 2.60127800 0.06253100 1.25809500

H 4.23062400 -1.79515600 1.47347000

H 4.68755600 -3.31917000 -0.43050100

H 3.50756500 -3.02736900 -2.60712900

H 1.56459000 -1.39391500 -3.83797600

H 0.07880900 0.54020600 -3.24981800

N 1.57944300 -0.94853400 -2.92793900

C -0.67524300 -2.22849400 2.62069600

C -0.76397100 -1.15962500 1.49582300

C -0.37584000 -2.92568600 -0.08372800

C -0.45552100 -3.99808000 1.03910000

H -1.46209600 -0.34904900 1.75470300

H -1.21537500 -1.90216100 3.52167700

H 0.37162000 -2.41288000 2.90478700

H 0.54903300 -4.25455000 1.40651500

H 0.64530000 -2.53458700 -0.19735200

H -0.69547700 -3.32554900 -1.05767200

H -0.92415800 -4.92401200 0.67387400

H 0.21401100 -0.70502200 1.28488400

C -2.62231100 -3.25624900 1.70578700

H -3.08115700 -4.22132500 1.44505300

H -3.19277100 -2.83134800 2.54491000

C -2.61977300 -2.29207800 0.48719400

H -3.27812700 -1.42341400 0.64354200

H -2.94888800 -2.79919300 -0.43219200

N -1.25111400 -3.48986600 2.15631000

N -1.25258400 -1.79767200 0.26378300

H -3.92736800 0.07761400 -1.73062500

18) ***Z*-TS-E**

C 0.72235900 -1.95605300 0.11151300

C 0.83292700 -3.34215100 0.57423600

O 0.94630000 -1.81357000 -1.22947200

O 0.60694900 -3.53137000 1.87757200

O 1.11290800 -4.25098600 -0.18658000

C 0.71808000 -4.86878400 2.34153800

H -0.01238700 -5.52032200 1.84183000

H 1.72740600 -5.26335900 2.15949600

H 0.51711000 -4.83890300 3.41765300

C 0.38357100 -0.91908500 0.92383300

H 0.17040000 -1.21477400 1.95356300

C 0.22477500 0.47422200 0.55352800

H -1.03186900 0.29141100 -0.21836500

C -0.26767300 1.39923600 1.60485800

C 0.03134100 2.77928800 1.60028600

C -1.13134800 0.94986300 2.63128300

C -0.50030000 3.64775000 2.55173200

H 0.70307100 3.17508400 0.83735500

C -1.65716700 1.81896000 3.58440200

H -1.40922300 -0.10491100 2.68056000

C -1.35240100 3.18119200 3.55376700

H -0.23678000 4.70738800 2.51144200

H -2.32118300 1.42495900 4.35740800

H -1.76813700 3.86422100 4.29629400

C 3.13051500 1.54202200 -1.58366300

C 2.61617100 0.82448200 -0.47138100

C 3.51164600 0.12240500 0.35728800

C 4.86636700 0.14665100 0.05951400

C 5.35538000 0.86156900 -1.05597900

C 4.49968100 1.56734700 -1.88881100

C 0.91321100 1.83253100 -1.53048200

C 1.18278100 1.01595500 -0.45540600

H 3.14051400 -0.43027300 1.22295800

H 5.56991300 -0.39336200 0.69589300

H 6.42694700 0.86102200 -1.26489600

H 4.87456700 2.12596900 -2.74845200

H 2.13030300 2.74077000 -3.02264900

H -0.04086700 2.23157500 -1.87170600

N 2.07067100 2.14794400 -2.20412500

C -3.26148800 -0.68487900 -2.82234700

C -1.88721100 -0.31092700 -2.20775500

C -2.90280400 1.35682800 -0.76848600

C -4.20122000 1.12813300 -1.58689300

H -1.16530400 -1.13894400 -2.19559200

H -3.33409400 -1.76870300 -2.99052700

H -3.39807400 -0.18516800 -3.79150200

H -4.18089200 1.70457000 -2.52248500

H -2.28144700 2.16398500 -1.17978500

H -3.10530700 1.58630900 0.28685400

H -5.07949700 1.45190000 -1.01142000

H -1.42211800 0.53639900 -2.72859600

C -4.26225800 -1.08019300 -0.69666400

H -5.02383200 -0.71195300 0.00507900

H -4.49555700 -2.12872800 -0.92806300

C -2.84249800 -0.96517600 -0.08227700

H -2.26103400 -1.88954000 -0.19641900

H -2.86275300 -0.69997000 0.98297100

N -4.34206000 -0.28736400 -1.92107900

N -2.11384100 0.10470800 -0.80434700

H 1.20287300 -2.69337600 -1.55000400

19) ***Z*-TS-F**

C -1.34069300 0.80073700 -1.29821100

C -1.98613200 2.04325400 -1.71316500

O -1.72712500 -0.27607300 -2.11819100

O -1.61803700 3.13361600 -1.01995900

O -2.85872200 2.07887500 -2.56622300

C -2.29656700 4.33591400 -1.34523800

H -2.15121000 4.59755800 -2.40232100

H -3.37459600 4.24582100 -1.14962500

H -1.86692400 5.11573900 -0.70716900

C -0.00212900 0.85284400 -0.73771800

H 0.20815500 1.83713400 -0.30976600

C 0.95173100 -0.10206300 -0.54740300

H -2.05008400 0.44905600 -0.13087300

C 2.16068200 0.23627500 0.25592500

C 3.39881900 -0.37191100 -0.02121200

C 2.11479700 1.15476900 1.32141400

C 4.53951900 -0.06240600 0.71705000

H 3.46398500 -1.09506800 -0.83668600

C 3.25571400 1.46796500 2.05776700

H 1.16342800 1.61734900 1.59200700

C 4.47737800 0.86139800 1.76123200

H 5.48659600 -0.54797100 0.47277300

H 3.18560800 2.18241700 2.88068100

H 5.36936300 1.10042500 2.34287000

C 0.93596300 -3.77998600 -1.23749500

C 1.10895800 -2.69574100 -0.33627800

C 1.41032200 -2.97383400 1.01107700

C 1.53155700 -4.29602000 1.41609900

C 1.36124600 -5.35773900 0.50118800

C 1.06186800 -5.11618300 -0.83215400

C 0.61282900 -1.87848100 -2.37329800

C 0.88838500 -1.47688500 -1.08597600

H 1.54879400 -2.15823800 1.72509700

H 1.76607000 -4.52270600 2.45776400

H 1.46632400 -6.38704000 0.84903100

H 0.92646200 -5.93420500 -1.54176800

H 0.46771800 -3.77730000 -3.31017500

H 0.37659600 -1.26555200 -3.23806900

N 0.63585100 -3.24577600 -2.46445900

C -3.10593100 -2.40676800 1.77040300

C -2.19460900 -1.58389800 0.81930200

C -4.12842700 -0.25952100 0.20520800

C -4.99815100 -1.06886000 1.20514600

H -1.16628000 -1.49985800 1.19577900

H -2.52375500 -2.81446500 2.60836300

H -3.56544900 -3.25137500 1.23845300

H -5.46665600 -1.92791000 0.70536400

H -4.08105600 -0.71600900 -0.79176100

H -4.47526300 0.77705500 0.09093600

H -5.79966300 -0.44288400 1.62151100

H -2.14789900 -1.98798600 -0.20066700

C -3.58633200 -0.42769600 3.01905700

H -4.39781900 0.17290500 3.45291400

H -2.97455100 -0.81463700 3.84561800

C -2.72286200 0.43038800 2.05180300

H -1.67445500 0.49503400 2.37369700

H -3.11174900 1.45115500 1.93281000

N -4.17098000 -1.55949800 2.30420500

N -2.74699800 -0.21534300 0.72669200

H -2.35161400 0.11362200 -2.75185200

20) ***Z*-2a**

C 2.41471500 -0.30729000 -1.31525200

C 3.43031000 -0.61079100 -0.21407500

O 1.80387300 -1.47113500 -1.76182900

O 4.26379900 0.40139000 -0.01519200

O 3.44593800 -1.63515000 0.41792400

C 5.21574800 0.23998400 1.03485200

H 4.70641000 0.08973900 1.99624500

H 5.86763000 -0.62015300 0.83184600

H 5.80474300 1.16196900 1.06064900

C 1.49304200 0.80052200 -0.83634400

H 1.87768300 1.81043700 -1.00284600

C 0.28524700 0.67100900 -0.25244200

H 2.98928900 0.10194600 -2.16053900

C -0.53760100 1.88953200 0.01704600

C -1.34881000 1.95839600 1.16034500

C -0.52893700 2.98314300 -0.86206600

C -2.10680100 3.09600500 1.42976600

H -1.37618400 1.11182700 1.84958700

C -1.29028700 4.11987900 -0.59431300

H 0.06312400 2.93223600 -1.77804100

C -2.08036400 4.18194600 0.55402300

H -2.72446500 3.13244600 2.32911800

H -1.27596400 4.95698300 -1.29486100

H -2.68025000 5.06984200 0.76166000

C -1.77965700 -2.34149100 0.54010700

C -1.63197300 -1.09604100 -0.12134700

C -2.69826200 -0.59659200 -0.89255600

C -3.86484500 -1.33989400 -0.97830200

C -3.99248000 -2.57891000 -0.31134800

C -2.95859500 -3.09710300 0.45264300

C 0.26824700 -1.56343400 1.00327100

C -0.30253200 -0.61609800 0.17797200

H -2.60442100 0.36000900 -1.41133300

H -4.70120700 -0.96650700 -1.57162000

H -4.92507200 -3.13916100 -0.40019700

H -3.05390000 -4.05459100 0.96725800

H -0.42696300 -3.40484500 1.78896200

H 1.24922900 -1.56910800 1.47434300

N -0.60975800 -2.59273800 1.21054600

H 1.45273900 -1.94137400 -0.99315600

21) ***E*-18**

C 1.22785500 1.85309700 0.91109300

C 1.87447500 3.05522400 0.84410000

O 1.93927000 0.86795000 1.54960700

O 1.32115900 4.16574500 0.36055700

O 3.11711800 3.18630100 1.31968100

C 2.19611100 5.19333200 -0.08475800

H 2.77706200 5.60973500 0.74897000

H 2.88448800 4.81987300 -0.85795400

H 1.55680700 5.97375400 -0.51112900

C -0.07680700 1.67325500 0.32041800

H -0.39170100 2.54005600 -0.26750900

C -0.93462000 0.61129700 0.32030300

H 2.06481200 0.10266500 0.89154900

C -0.78386800 -0.61572900 1.14544600

C -1.16733300 -1.86713600 0.62862500

C -0.31924200 -0.56780100 2.47045200

C -1.06654200 -3.02737800 1.39373500

H -1.55509000 -1.92647500 -0.39106300

C -0.21263300 -1.72878400 3.23482100

H -0.04650300 0.39388900 2.90374000

C -0.58148700 -2.96465800 2.70095600

H -1.37003600 -3.98549400 0.96677000

H 0.14966100 -1.66464100 4.26289800

H -0.50559600 -3.87106700 3.30459900

C -4.21848800 0.51257200 -1.48718000

C -3.46207100 0.24608100 -0.31513800

C -4.11850400 -0.29649200 0.80725600

C -5.47719100 -0.56361000 0.72818900

C -6.20722000 -0.29839600 -0.45099800

C -5.59267000 0.24338200 -1.56943800

C -2.10490200 1.12622900 -1.88599100

C -2.09932700 0.65485300 -0.58965600

H -3.56558900 -0.50387300 1.72575300

H -5.99411100 -0.98631400 1.59157700

H -7.27555100 -0.52070900 -0.48095100

H -6.15336000 0.45648300 -2.48116100

H -3.62017100 1.31808900 -3.35973600

H -1.27359000 1.50307000 -2.47916600

N -3.36550700 1.04813000 -2.41701000

C 2.39731100 -1.83238600 -2.56622900

C 1.75063000 -0.87637400 -1.52332200

C 2.55969400 -2.31731700 0.22132000

C 3.26880700 -3.21638400 -0.83101400

H 1.74722500 0.16799100 -1.87071900

H 2.65705700 -1.29321700 -3.48908100

H 1.70810500 -2.64543000 -2.83771900

H 2.61963700 -4.04801200 -1.14183900

H 1.52305900 -2.63430300 0.40633000

H 3.08874700 -2.32155000 1.18559200

H 4.19373300 -3.65013800 -0.42306700

H 0.71222900 -1.15684100 -1.29518800

C 4.53988000 -1.36229500 -1.63196000

H 5.47377000 -1.81941900 -1.27356400

H 4.77987300 -0.77327400 -2.52928000

C 3.89755200 -0.47137800 -0.53247300

H 3.85000300 0.58704100 -0.83070500

H 4.45557500 -0.52791400 0.41381400

N 3.61291700 -2.42627000 -2.01268500

N 2.52538100 -0.93386200 -0.27512100

H 3.34309200 2.30083400 1.66184700

22) ***E*-TS-E**

C -1.63638800 -1.88972800 0.54076200

C -2.42938200 -3.07184100 0.19517400

O -2.28609400 -1.04413200 1.40044600

O -1.84559800 -3.93198400 -0.64099800

O -3.54819600 -3.23958800 0.64752900

C -2.61281300 -5.07350200 -0.99682200

H -2.89561100 -5.64796800 -0.10408300

H -3.52501900 -4.78074000 -1.53561100

H -1.97511300 -5.68286600 -1.64587900

C -0.42688800 -1.59839200 -0.00844100

H -0.09341300 -2.32233900 -0.75725800

C 0.39522400 -0.41454700 0.17522600

H -0.56703200 0.62162700 -0.24130000

C 0.64371100 0.15087800 1.52703300

C 1.28678700 1.40209500 1.64998500

C 0.27106600 -0.49504300 2.72110400

C 1.54133300 1.97585900 2.89176700

H 1.60103900 1.92622200 0.74319600

C 0.52383300 0.08177100 3.96599400

H -0.21199900 -1.47084600 2.67006000

C 1.15764400 1.32077200 4.06516300

H 2.04515200 2.94367000 2.94584400

H 0.22829400 -0.45276100 4.87182600

H 1.35369800 1.76844100 5.04113200

C 3.58655300 -0.26672200 -1.83686400

C 2.94718300 -0.35520500 -0.56982100

C 3.74855500 -0.50541600 0.58017200

C 5.12815800 -0.54405100 0.44319400

C 5.74030300 -0.43711200 -0.82497200

C 4.98218500 -0.30036700 -1.97751000

C 1.37840700 -0.17775300 -2.17126600

C 1.51686700 -0.28980600 -0.80384600

H 3.28765500 -0.59513600 1.56543100

H 5.75460900 -0.66066000 1.32941000

H 6.82908600 -0.46668000 -0.89905000

H 5.44938300 -0.22455200 -2.96107900

H 2.76390600 -0.09575800 -3.78553500

H 0.46616500 -0.11714600 -2.76321300

N 2.60736800 -0.16786900 -2.78776600

C -3.45249500 1.93704600 -1.84553500

C -2.48881200 0.84318900 -1.31597000

C -0.76706500 2.54665700 -1.40387100

C -1.81580300 3.66016000 -1.66921900

H -2.98054200 0.15435500 -0.61691500

H -4.49430900 1.67180600 -1.61731600

H -3.36451000 2.04756800 -2.93581900

H -1.85545500 3.90253300 -2.74038100

H -0.43627000 2.05995300 -2.33077000

H 0.12082000 2.91901200 -0.87547100

H -1.55587900 4.57938100 -1.12522300

H -2.02885900 0.25508400 -2.12293400

C -3.13095700 3.06436400 0.22846300

H -3.02944700 4.05250600 0.69867700

H -4.10081900 2.64566600 0.53325900

C -1.96468000 2.13751000 0.66050100

H -2.27781400 1.32551100 1.32914800

H -1.15170300 2.69354600 1.14514500

N -3.13693600 3.22229200 -1.22543600

N -1.40263700 1.51017200 -0.55998300

H -3.12662000 -1.48083800 1.61879200

23) ***E*-TS-F**

C -1.34203700 0.79246800 -1.30148900

C -2.13304200 1.87139500 -1.87817300

O -1.53400200 -0.42021800 -1.98528100

O -1.93364900 3.08142200 -1.32638000

O -2.97782200 1.68111000 -2.73968200

C -2.76498800 4.12504900 -1.80669300

H -2.62524700 4.27597800 -2.88611100

H -3.82527200 3.90538500 -1.61662200

H -2.46965000 5.03020500 -1.26484100

C -0.05876300 1.07897500 -0.68622300

H -0.03593300 2.08779800 -0.26197200

C 1.01906200 0.29178600 -0.40796500

H -2.08544500 0.47217900 -0.13344500

C 1.23575900 -1.07651800 -0.94992000

C 1.64181400 -2.11578900 -0.09528500

C 1.10858500 -1.36148700 -2.31880300

C 1.89457500 -3.39623200 -0.58469800

H 1.76473900 -1.90962600 0.97092300

C 1.36692300 -2.63958900 -2.81168300

H 0.80813800 -0.56298800 -2.99710600

C 1.75971300 -3.66379400 -1.94802100

H 2.20404900 -4.18767000 0.10093800

H 1.26804200 -2.83631800 -3.88123800

H 1.96637100 -4.66294200 -2.33628600

C 4.05608600 1.28709300 1.55739600

C 3.48401000 0.59599700 0.45559500

C 4.34002900 -0.07529000 -0.44098700

C 5.70794600 -0.04819800 -0.21473900

C 6.25285400 0.63878800 0.89244800

C 5.43967000 1.31473300 1.78887600

C 1.83828000 1.56360900 1.65245400

C 2.04959000 0.79174100 0.52878000

H 3.93130300 -0.60796000 -1.30185100

H 6.37845500 -0.56512800 -0.90347600

H 7.33393700 0.63927400 1.04360900

H 5.85588100 1.85117600 2.64326200

H 3.13731800 2.41358200 3.10412900

H 0.89972100 1.91781700 2.07427600

N 3.03163900 1.86514200 2.25907300

C -2.90103900 -2.28605700 2.00030300

C -2.01252600 -1.42843400 1.05740800

C -4.04323300 -0.53456000 0.08268100

C -4.89709100 -1.33809000 1.09935600

H -1.06914400 -1.12598600 1.53309700

H -2.36912900 -2.51429600 2.93415300

H -3.16853800 -3.23926600 1.52355500

H -5.19073600 -2.30861600 0.67649800

H -3.80349000 -1.10426900 -0.82367300

H -4.52283300 0.40610100 -0.22159800

H -5.81448900 -0.79154500 1.35846200

H -1.77281900 -1.92869000 0.11006600

C -3.80635000 -0.28623700 2.94153700

H -4.74017600 0.21449200 3.23237900

H -3.22731900 -0.47721900 3.85569600

C -2.99569700 0.59565900 1.95063700

H -2.01828800 0.89048900 2.35602000

H -3.53750900 1.50557600 1.65785600

N -4.13274900 -1.56817100 2.32287500

N -2.75759900 -0.19396600 0.72837500

H -2.15818800 -0.20894300 -2.69822500

24) ***E*-2a**

C -2.71526200 -0.66101700 -1.08313600

C -3.50256200 -0.84468800 0.21313300

O -2.90166800 0.62351200 -1.57884400

O -3.56049900 -2.11141400 0.59443800

O -3.98602700 0.07360400 0.82396500

C -4.21428400 -2.37159800 1.83609200

H -3.69628200 -1.85745400 2.65689000

H -5.25858400 -2.03423700 1.79946600

H -4.17315600 -3.45498300 1.98417500

C -1.27774600 -1.09738700 -0.86354800

H -1.12647000 -2.17914000 -0.92037700

C -0.19559500 -0.32109500 -0.65477100

H -3.14900700 -1.37086500 -1.80746100

C -0.26017900 1.15125100 -0.41612500

C 0.52509400 2.02712200 -1.17752400

C -1.04789100 1.67522900 0.61742200

C 0.49748500 3.39832800 -0.93277700

H 1.16117100 1.62466400 -1.96925600

C -1.07181500 3.04828900 0.86614100

H -1.63601900 1.00111600 1.24410300

C -0.30132400 3.91384500 0.08984900

H 1.10707800 4.06884100 -1.54145000

H -1.69028400 3.44039900 1.67572200

H -0.31669400 4.98749400 0.28544000

C 3.36459300 -1.39128800 -0.22237200

C 2.30080300 -0.52264300 0.13768800

C 2.52959300 0.45508100 1.12751200

C 3.78450900 0.53863000 1.71097300

C 4.82859900 -0.33317800 1.33288200

C 4.63453800 -1.30808200 0.36679800

C 1.58275300 -1.96266600 -1.44739300

C 1.15691000 -0.91224200 -0.66053500

H 1.73239100 1.13664200 1.43018500

H 3.97054800 1.29305900 2.47736400

H 5.80524100 -0.23864700 1.81115700

H 5.43611000 -1.98745500 0.07248300

H 3.43648300 -2.96684900 -1.64694800

H 1.03361600 -2.51425800 -2.20802100

N 2.89127400 -2.24947500 -1.18268100

H -2.99881800 1.22104100 -0.82302400

25) **TS-G**

C 2.56376700 -0.68444800 -0.30410000

C 4.02078100 -1.16661200 -0.12157600

O 2.29082200 0.11217000 -1.16193800

O 4.82980200 -0.63062300 -1.00983700

O 4.34025200 -1.93683800 0.74307300

C 6.20431900 -1.00833000 -0.91184900

H 6.72354800 -0.49082300 -1.72382700

H 6.61346600 -0.70100500 0.05986300

H 6.30990800 -2.09563100 -1.02234400

C 1.59638900 -1.26876100 0.68545200

H 1.96804800 -0.97093900 1.68052900

H 1.70452600 -2.36752100 0.67347600

C 0.12934800 -0.86934600 0.53232300

H 0.13265500 0.36590800 0.38997100

C -0.61234500 -1.04818400 1.83636400

C -1.56838000 -2.05643800 2.01516500

C -0.28480300 -0.23010600 2.92829100

C -2.19625800 -2.22539300 3.24906700

H -1.81937400 -2.71603900 1.18248500

C -0.91454300 -0.39474100 4.15953200

H 0.47746300 0.54594700 2.80751800

C -1.87711600 -1.39279100 4.32173300

H -2.93671900 -3.01750600 3.37321900

H -0.65135700 0.25432700 4.99646300

H -2.37152400 -1.52584600 5.28553600

C -2.06939200 -1.66876300 -2.37693000

C -1.93660700 -1.15619900 -1.06461200

C -3.07377600 -0.61388700 -0.43822300

C -4.27700400 -0.58944000 -1.13170900

C -4.37873600 -1.10336000 -2.43905100

C -3.27708100 -1.65438500 -3.07980500

C 0.07128200 -1.93235400 -1.78717700

C -0.54054700 -1.32711100 -0.68562800

H -3.02216700 -0.23182400 0.58221000

H -5.16367300 -0.17182500 -0.65233700

H -5.33941900 -1.07258800 -2.95536500

H -3.34562200 -2.05873200 -4.09058000

H -0.62842600 -2.57502400 -3.66195900

H 1.10395700 -2.24850800 -1.91890300

N -0.82979400 -2.13462500 -2.76925100

C -1.14514800 2.36060300 0.95105800

C -1.40543500 3.84611300 0.50407500

C 0.93980800 4.11132700 0.27504800

C 1.21125300 2.58191200 0.51798500

H -2.36577100 3.91986000 -0.02331400

H -2.01637000 1.72314000 0.76022400

H -0.88310000 2.30311200 2.01424300

H 1.44793500 2.37485300 1.57036300

H 0.92763500 4.65294900 1.23013200

H 1.73558300 4.53103700 -0.35390800

H 2.02382800 2.21701800 -0.11988300

H -1.44131700 4.49617200 1.38808100

C -0.29907500 1.97531500 -1.26928100

H 0.49991700 1.46836200 -1.82304700

H -1.25378100 1.46945000 -1.46474100

C -0.37632800 3.50839000 -1.60823200

H -1.30525000 3.71976000 -2.15371200

H 0.47374700 3.80101600 -2.23871300

N -0.01437000 1.86245500 0.16343200

N -0.34320500 4.28433400 -0.38126600

26) **TS-H**

C -0.48211700 2.01564300 -0.56746100

C -1.21414900 3.11659900 0.22934900

O -0.17433900 2.18686600 -1.71997300

O -1.34862600 4.21984900 -0.46758300

O -1.60978200 2.94428500 1.35366300

C -2.01081300 5.30589400 0.18620900

H -2.03308400 6.12728800 -0.53563000

H -3.03155100 5.01417400 0.46697800

H -1.45587200 5.60122300 1.08651200

C -0.23609400 0.75844800 0.18198800

H -1.38497300 0.11149800 -0.01464500

H -0.31698700 0.85712400 1.27283300

C 0.89625600 -0.10919600 -0.31948700

H 0.87018900 -0.08828500 -1.42139700

C 0.72095900 -1.55298400 0.12956000

C 0.80080300 -1.89299000 1.48533500

C 0.44086000 -2.55391400 -0.80539200

C 0.58701000 -3.20638700 1.89922100

H 1.03858900 -1.11982700 2.22094400

C 0.22969500 -3.87216500 -0.39355100

H 0.39895900 -2.30117200 -1.86824300

C 0.29656200 -4.19949900 0.96032600

H 0.65232200 -3.45892900 2.95917900

H 0.02188900 -4.64611900 -1.13476500

H 0.13565500 -5.22936000 1.28387800

C 4.46817000 0.85232500 0.36425900

C 3.51783900 0.01940800 -0.28087900

C 3.96802500 -1.01155300 -1.12690000

C 5.33222000 -1.17963600 -1.30646800

C 6.26263800 -0.33936500 -0.65598400

C 5.84882400 0.68235700 0.18456500

C 2.42937000 1.54076100 0.97889200

C 2.21492000 0.48019300 0.12842800

H 3.25388200 -1.66800000 -1.62884900

H 5.69776000 -1.97319200 -1.96019300

H 7.33015900 -0.49835600 -0.81875800

H 6.56631700 1.33297300 0.68696100

H 4.18861300 2.49043500 1.68861300

H 1.71500500 2.17614300 1.50087800

N 3.77433100 1.76302400 1.11751900

C -4.97855800 -0.04636800 0.02063700

C -3.55094200 0.61089100 0.13254600

C -2.66892500 -1.52292600 0.89172600

C -4.12112700 -2.12800300 0.76385900

H -3.40887200 1.38638300 -0.63216900

H -5.54927500 0.45382700 -0.77139600

H -5.50957300 0.07249000 0.97303200

H -4.65401900 -2.00448500 1.71451200

H -2.49508600 -1.08123500 1.88049600

H -1.89821800 -2.27278400 0.67504900

H -4.04717800 -3.19783600 0.53307400

H -3.36389700 1.03016400 1.12801900

C -4.16598000 -1.62447500 -1.55269500

H -4.08596300 -2.69387900 -1.78394500

H -4.73341200 -1.12793600 -2.34951900

C -2.71773200 -0.99864500 -1.47175000

H -2.58880500 -0.17865300 -2.18834400

H -1.94071800 -1.75615100 -1.62215000

N -4.84772800 -1.45310100 -0.28913000

N -2.57177200 -0.45735300 -0.11521900

27) **TS-I**

C 1.01218100 2.26218400 0.75256100

C 2.35688900 2.79036000 0.61858600

O 0.29498600 2.82090200 1.72981200

O 3.02252400 2.32387600 -0.43831000

O 2.80068400 3.61018500 1.40502000

C 4.34598600 2.82113000 -0.61031600

H 4.72168200 2.38842500 -1.54332200

H 4.33864400 3.91709500 -0.68032200

H 4.98537700 2.52073600 0.23156500

C 0.37531000 1.36172400 -0.21475600

H 1.21997600 0.40846300 -0.41453300

H 0.33265900 1.84893800 -1.20086300

C -0.85260000 0.67822600 0.15847000

H 0.89111500 3.43713600 2.20095400

C -0.83195900 -0.26603200 1.30482000

C -1.29936600 -1.57240900 1.05210500

C -0.23723000 -0.00304500 2.55083100

C -1.16313400 -2.58041300 2.00002900

H -1.74621500 -1.80661700 0.08436100

C -0.12353400 -1.01181800 3.50618900

H 0.10638800 0.99675700 2.79783800

C -0.57351700 -2.30239900 3.23429000

H -1.51601900 -3.58728400 1.77146500

H 0.32689000 -0.78237800 4.47314900

H -0.46807100 -3.08941900 3.98300200

C -4.11603900 0.62240700 -1.56719500

C -3.37724500 0.29002100 -0.41197700

C -4.07085500 -0.26668200 0.67560600

C -5.43470200 -0.50442100 0.55190700

C -6.13380300 -0.19715900 -0.62865400

C -5.48283800 0.38261900 -1.70865800

C -2.03218700 1.34130100 -1.94333800

C -1.99905000 0.73790600 -0.66110300

H -3.56266900 -0.50436000 1.60910000

H -5.97545500 -0.93933900 1.39375800

H -7.20322200 -0.40308000 -0.69125800

H -6.01237000 0.65129400 -2.62341200

H -3.51475200 1.59102800 -3.37989500

H -1.23223800 1.81807000 -2.50570500

N -3.24768500 1.23976100 -2.46214700

C 1.22292200 -1.59780000 -1.58748700

C 1.90800700 -2.97559900 -1.79493600

C 3.97384700 -1.80255400 -1.88872200

C 3.33852100 -0.46701100 -1.41123600

H 1.36241500 -3.76795500 -1.26243100

H 0.23568200 -1.69939200 -1.11604600

H 1.09514900 -1.05422700 -2.53538400

H 3.12178700 0.21664700 -2.24382200

H 3.90861500 -1.90386100 -2.98168500

H 5.03668600 -1.84349800 -1.61127500

H 3.99026500 0.05672300 -0.70100000

H 1.93045800 -3.24051200 -2.86147600

C 2.37919600 -1.50822800 0.52969100

H 2.89993400 -0.82415200 1.21545800

H 1.42610700 -1.79796700 0.99334600

C 3.23993300 -2.75143200 0.16893700

H 2.82280200 -3.65548700 0.63497100

H 4.27267400 -2.63529500 0.52728500

N 2.07534700 -0.77122500 -0.71250400

N 3.27401800 -2.93159900 -1.28104400

28) **I1**

C 2.48427500 -0.69558900 0.21704800

C 3.95542700 -1.08491600 -0.03540800

O 1.96852600 0.17225400 -0.44229900

O 4.56809900 -0.21401300 -0.80758600

O 4.44463300 -2.07719000 0.43202600

C 5.93521900 -0.49822800 -1.11491000

H 6.28417900 0.32455500 -1.74555300

H 6.52872600 -0.55165100 -0.19260400

H 6.01266500 -1.45177600 -1.65388500

C 1.79422300 -1.44733200 1.32549400

H 2.21593700 -1.04644200 2.26467400

H 2.13961100 -2.49038700 1.29688600

C 0.29636400 -1.32853100 1.28663900

H 0.13731200 1.10051200 -0.17370000

C -0.33214200 -0.31440900 2.11465200

C -1.64231400 -0.46546100 2.62759400

C 0.37862200 0.85233400 2.49154000

C -2.21642700 0.50892500 3.43594400

H -2.19508600 -1.38087600 2.41201100

C -0.20175200 1.82531500 3.29996400

H 1.39889500 1.01000000 2.13357800

C -1.50659500 1.66644500 3.77174100

H -3.22490700 0.35715400 3.82573600

H 0.37252200 2.71522900 3.56619500

H -1.95945800 2.42576600 4.41104200

C -1.84262600 -3.26178900 -1.08224300

C -1.72748700 -2.14117100 -0.21905100

C -2.80478400 -1.23255900 -0.18836100

C -3.92797600 -1.47070000 -0.96949100

C -4.01939600 -2.60847500 -1.79523000

C -2.97623700 -3.51755600 -1.86299100

C 0.18441300 -3.36763700 -0.15293700

C -0.39836100 -2.21819700 0.39787400

H -2.77746500 -0.34900800 0.44716500

H -4.76037200 -0.76569600 -0.93660300

H -4.92016600 -2.77502400 -2.38819300

H -3.02272700 -4.39921200 -2.50399500

H -0.47739700 -4.82996400 -1.51963100

H 1.16541900 -3.80117900 0.02543500

N -0.67279900 -3.97612100 -1.00780500

C -1.57476900 2.30514500 -0.19415300

C -1.92436600 3.67206800 -0.83571300

C 0.35448300 4.28034100 -1.18607800

C 0.75515500 3.06503900 -0.31436100

H -2.91358800 3.61986200 -1.30837500

H -2.23376600 1.50031700 -0.54026700

H -1.56872600 2.32461000 0.90389300

H 0.64820700 3.25683300 0.76084200

H 0.27990800 5.18068500 -0.56271700

H 1.11150200 4.46386100 -1.96016900

H 1.76820500 2.69879800 -0.51723800

H -1.95315200 4.46116300 -0.07256300

C -0.18396500 1.69444800 -2.12062200

H 0.85995800 1.50567900 -2.39813000

H -0.77096300 0.78423700 -2.29521700

C -0.78303500 2.94805600 -2.80406300

H -1.77182300 2.72262200 -3.22576300

H -0.13159300 3.27549800 -3.62466600

N -0.19331800 1.95505800 -0.64647300

N -0.92639900 4.03135300 -1.83751900

29) **I2**

C -0.44082500 1.45180800 -0.72154600

C -1.62056700 2.21262600 -1.37121200

O -0.72214200 0.44544400 -0.12314800

O -1.24679000 3.29098600 -2.01444600

O -2.75107100 1.81002100 -1.26574800

C -2.27577400 4.05490500 -2.65755800

H -1.76956700 4.88988300 -3.14972100

H -2.79692500 3.43235400 -3.39602200

H -2.99107400 4.42405900 -1.91148200

C 0.94482500 2.02255800 -0.86313100

H 0.91517600 3.03119600 -0.41634800

H 1.10202000 2.20520300 -1.93918800

C 2.01735900 1.15865300 -0.26764900

H -2.72029400 0.06376500 -0.10128000

C 2.46699600 1.43367600 1.08146100

C 3.76664000 1.07640300 1.51593500

C 1.64345400 2.12508200 2.00205900

C 4.20478600 1.37891700 2.79900800

H 4.44285400 0.57812800 0.81960200

C 2.08594000 2.42014200 3.28680200

H 0.63120600 2.41617500 1.71485900

C 3.36827100 2.04865200 3.69719600

H 5.21634500 1.09929200 3.10002600

H 1.42204600 2.94387400 3.97731800

H 3.71502500 2.28542000 4.70429900

C 3.35478600 -1.94195800 -1.84002900

C 3.03199600 -1.23023600 -0.65723100

C 3.17518500 -1.88996800 0.57885000

C 3.66181100 -3.18894100 0.60020600

C 4.00567100 -3.86232900 -0.59038900

C 3.85059400 -3.25226600 -1.82514800

C 2.56085100 0.05218700 -2.46618000

C 2.52705000 0.07582100 -1.07224100

H 2.90596200 -1.39225800 1.51076400

H 3.77912100 -3.70192500 1.55627100

H 4.39061000 -4.88227600 -0.53874600

H 4.09553900 -3.77029300 -2.75365700

H 3.19932300 -1.37722300 -3.88411900

H 2.28291000 0.82684400 -3.17739600

N 3.06029700 -1.13215400 -2.91000200

C -2.74854000 -1.55466600 1.18975400

C -3.83151700 -2.53907600 1.70095300

C -5.50055200 -0.83870800 1.54626500

C -4.47185500 0.18206200 0.99517300

H -3.58330900 -3.56695400 1.40575700

H -1.95234900 -2.04663400 0.61905000

H -2.29333100 -0.95994300 1.99046100

H -3.96027200 0.74453800 1.78554700

H -5.53655100 -0.78971500 2.64224400

H -6.50370600 -0.61277100 1.16160100

H -4.90340100 0.88880800 0.27656800

H -3.88882500 -2.50575700 2.79661500

C -4.03423700 -1.32954300 -0.88689900

H -4.45491000 -0.57626400 -1.56329400

H -3.21742900 -1.85311100 -1.39817300

C -5.10215600 -2.29093300 -0.30538600

H -4.87508300 -3.32727400 -0.58773800

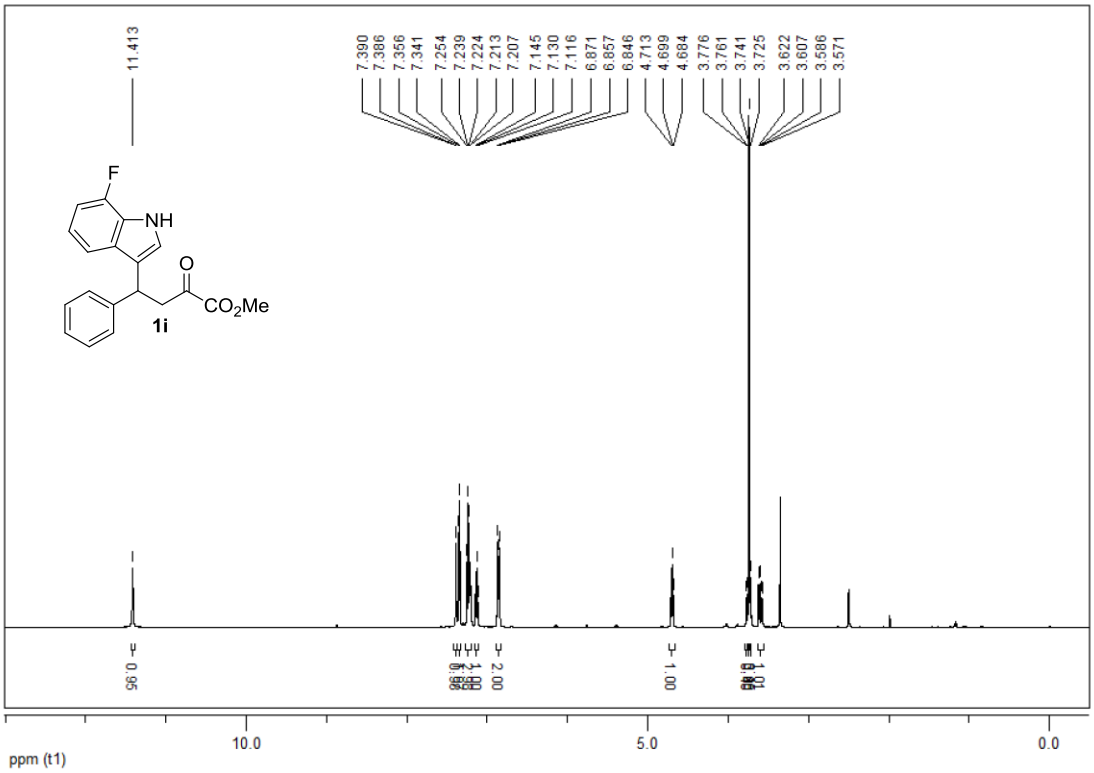
H -6.09553600 -2.04083200 -0.69988800

N -3.42598900 -0.59600100 0.26480700

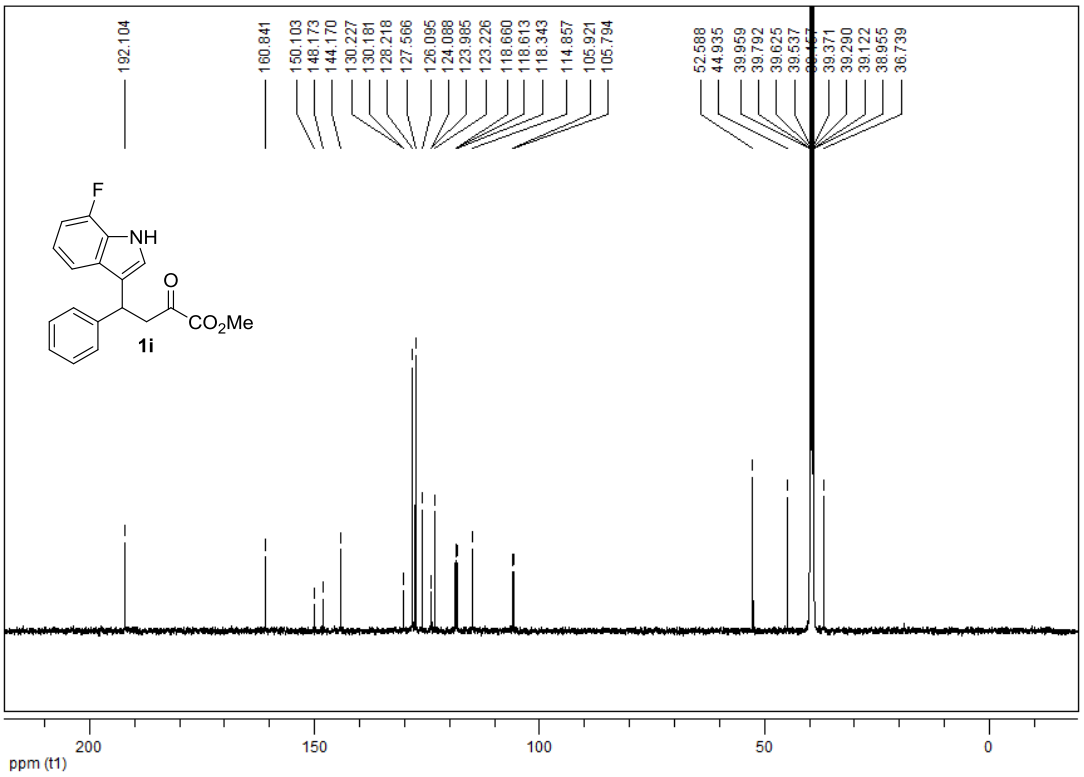
N -5.13586000 -2.19291100 1.14865800

IX. NMR Spectrum

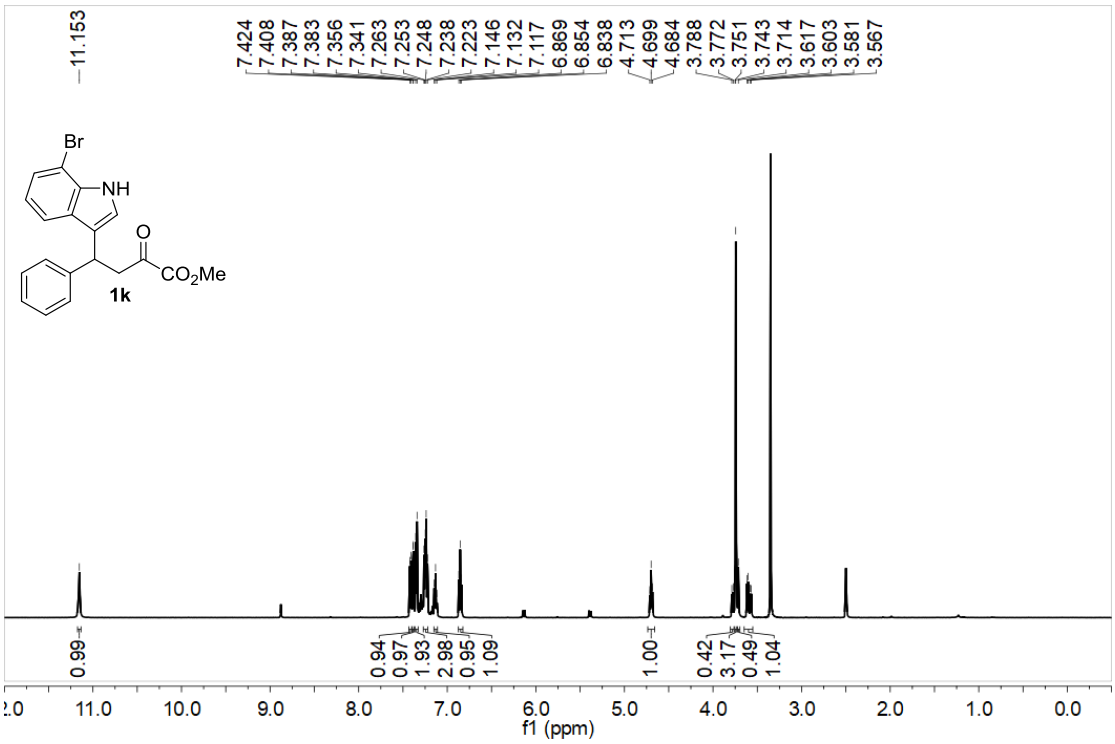
^{1}H NMR (500 MHz, DMSO-d_6)



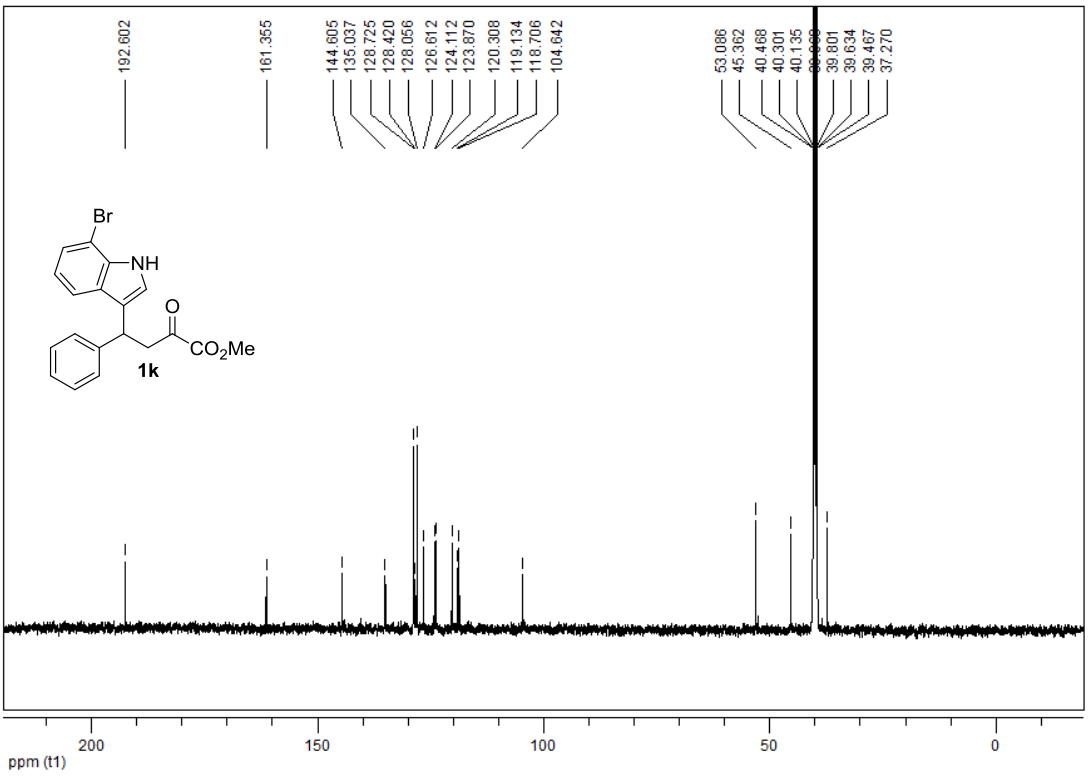
^{13}C NMR (125 MHz, DMSO-d_6)



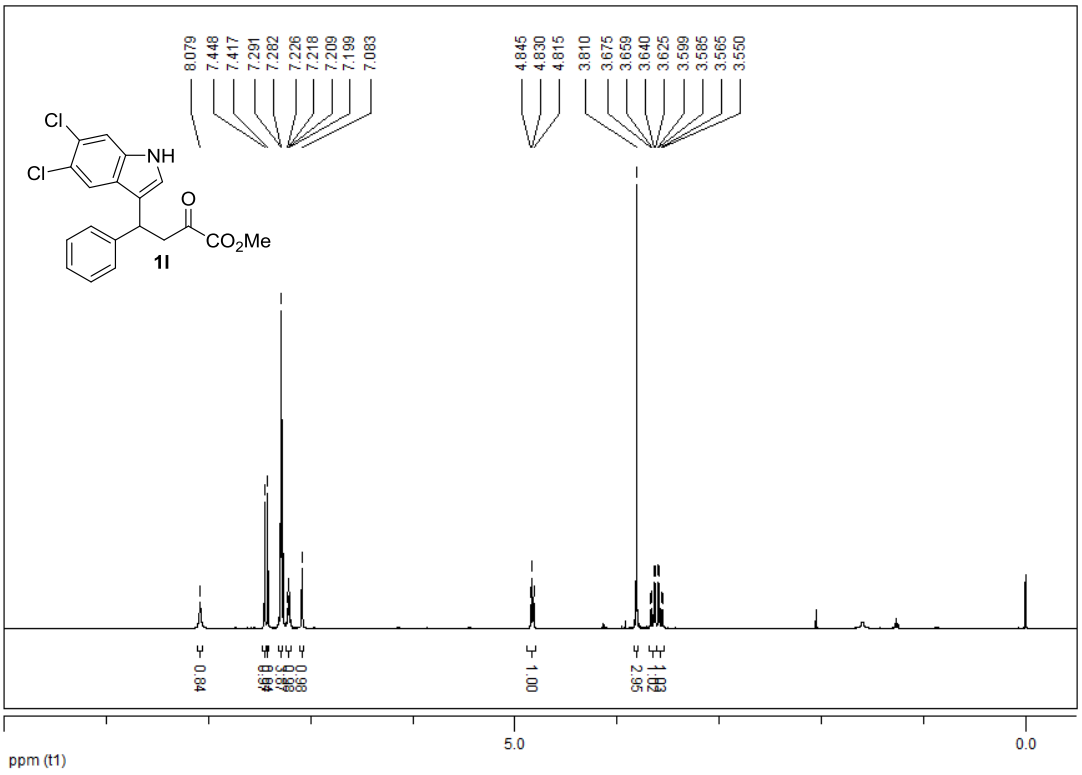
^{1}H NMR (500 MHz, DMSO-d$_6$)



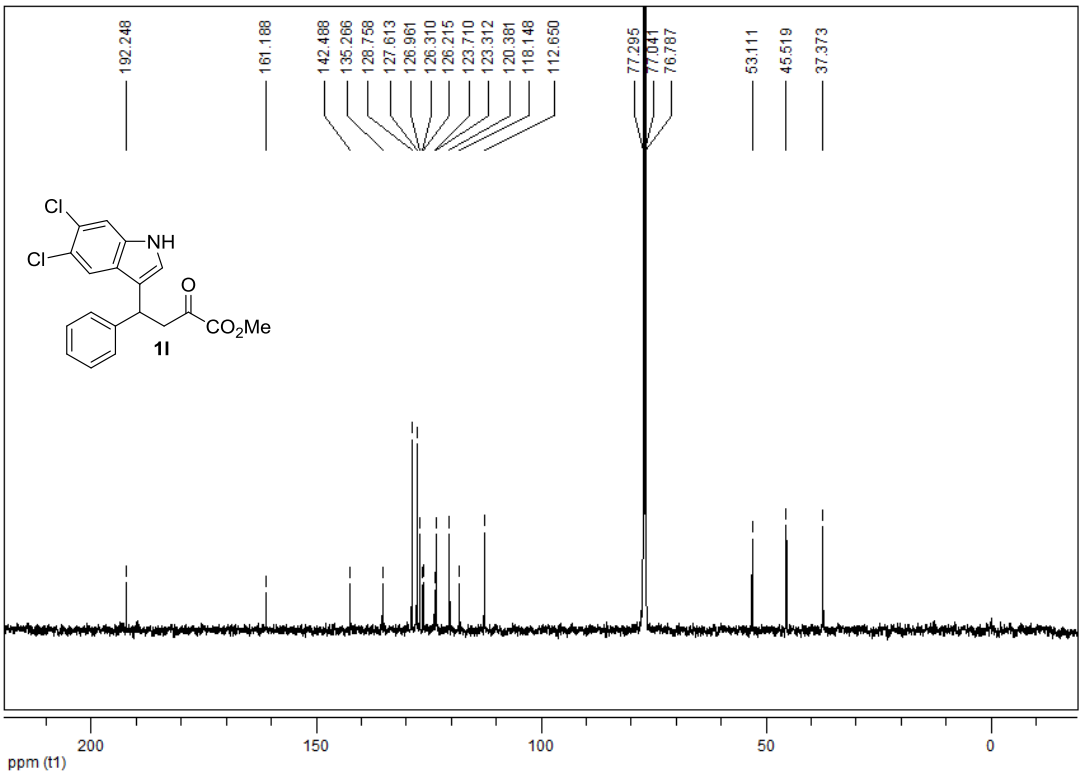
^{13}C NMR (125 MHz, DMSO-d$_6$)



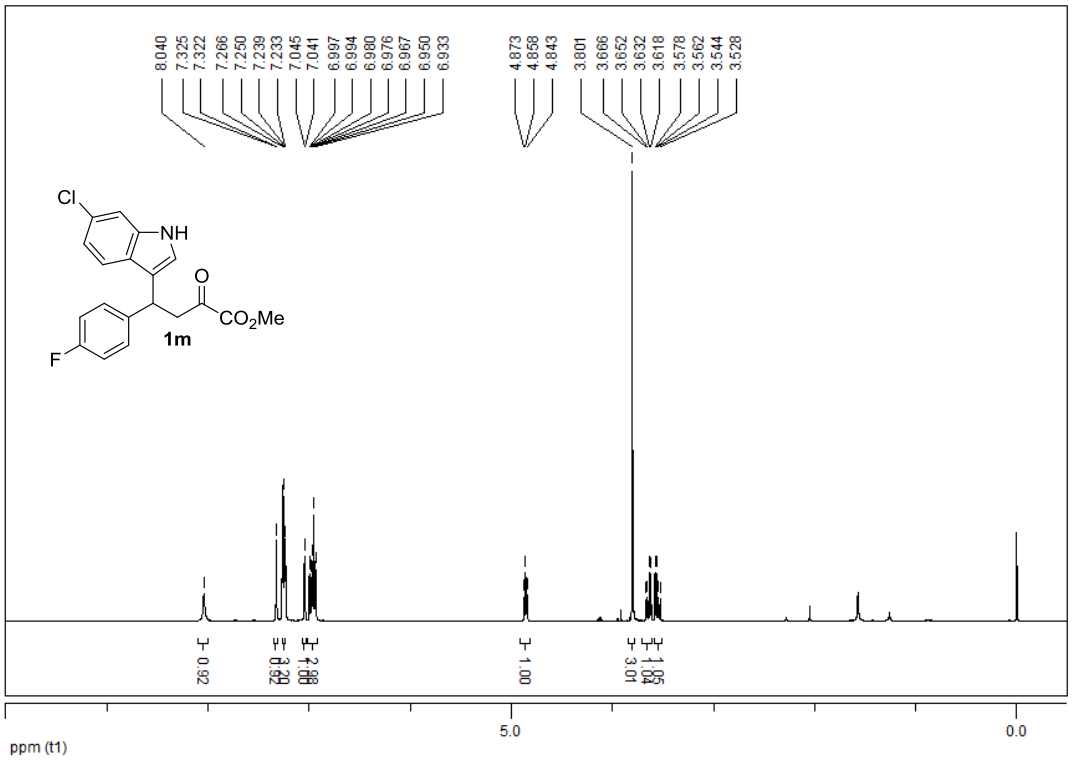
^{1}H NMR (500 MHz, $CDCl_3$)



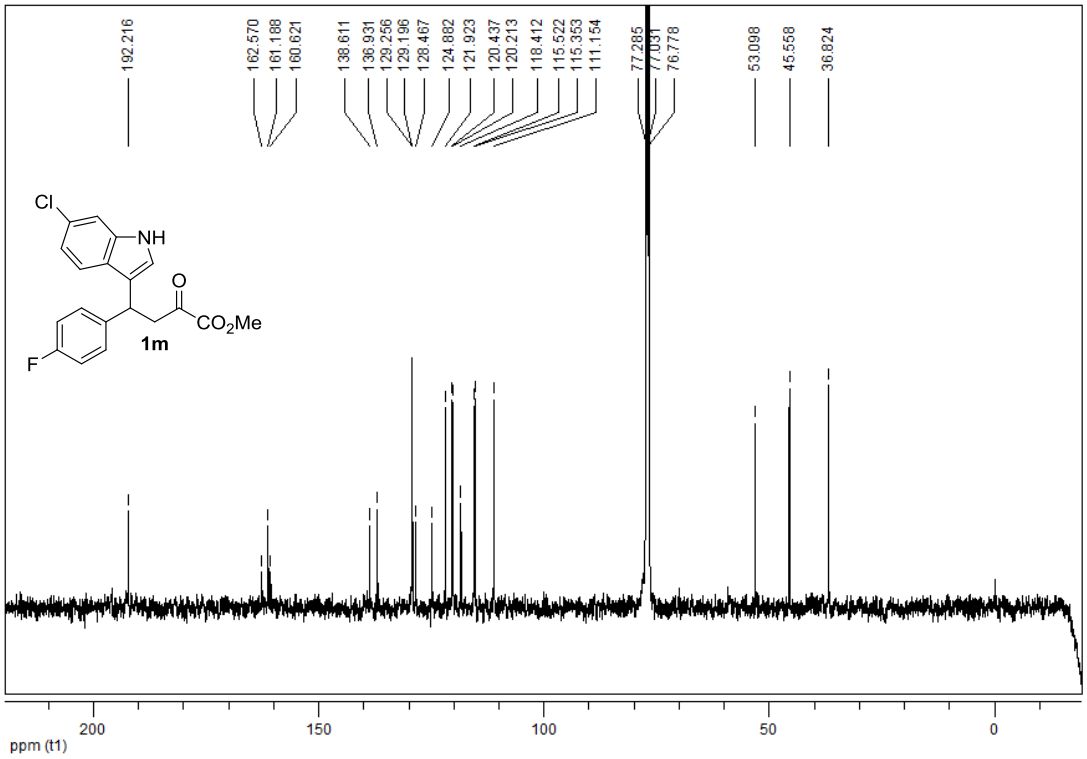
^{13}C NMR (125 MHz, $CDCl_3$)



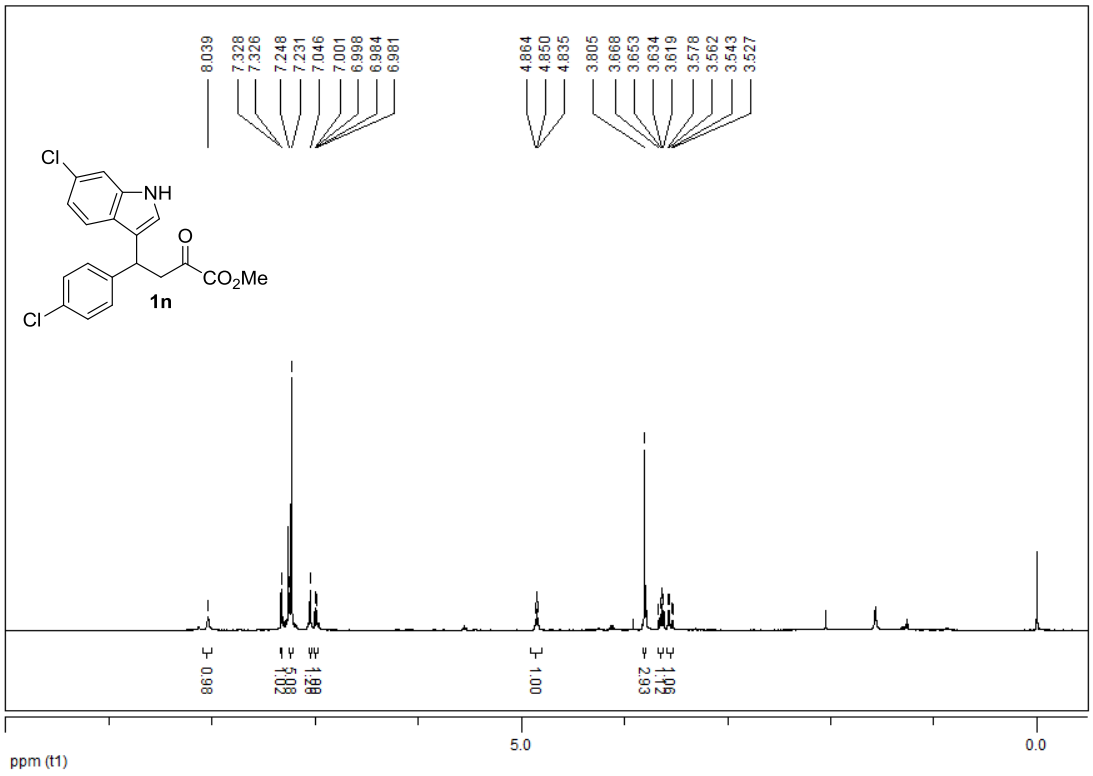
^{1}H NMR (500 MHz, $CDCl_3$)



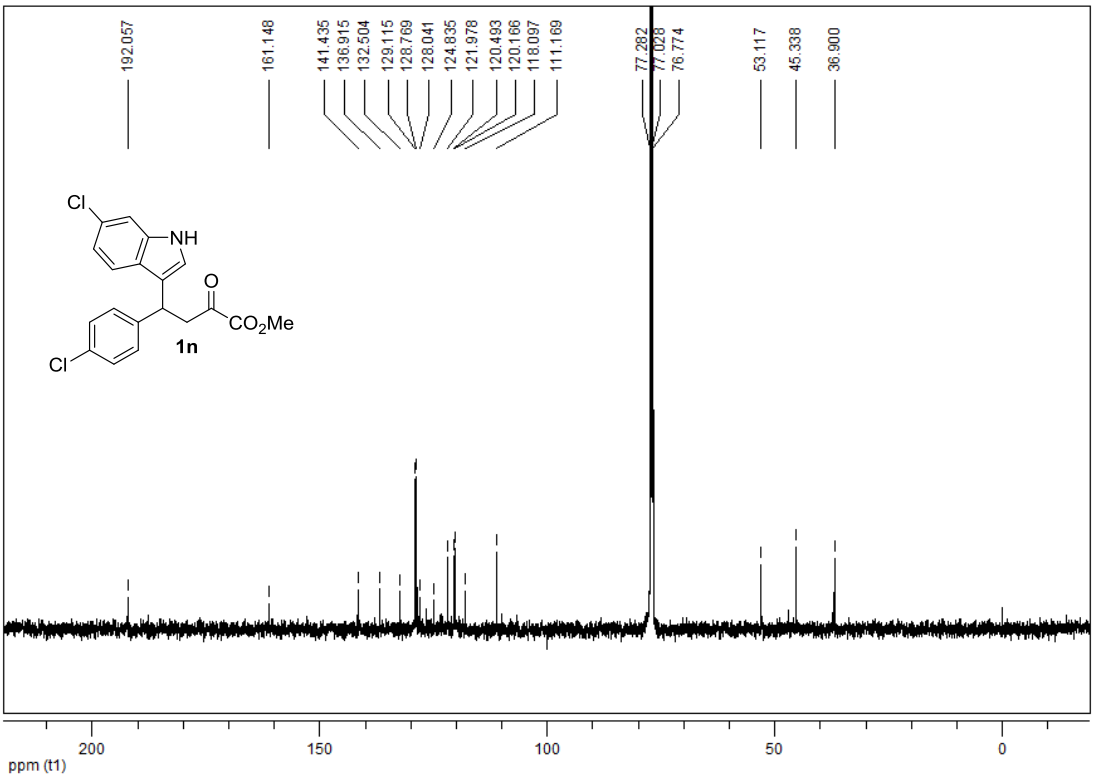
^{13}C NMR (125 MHz, $CDCl_3$)



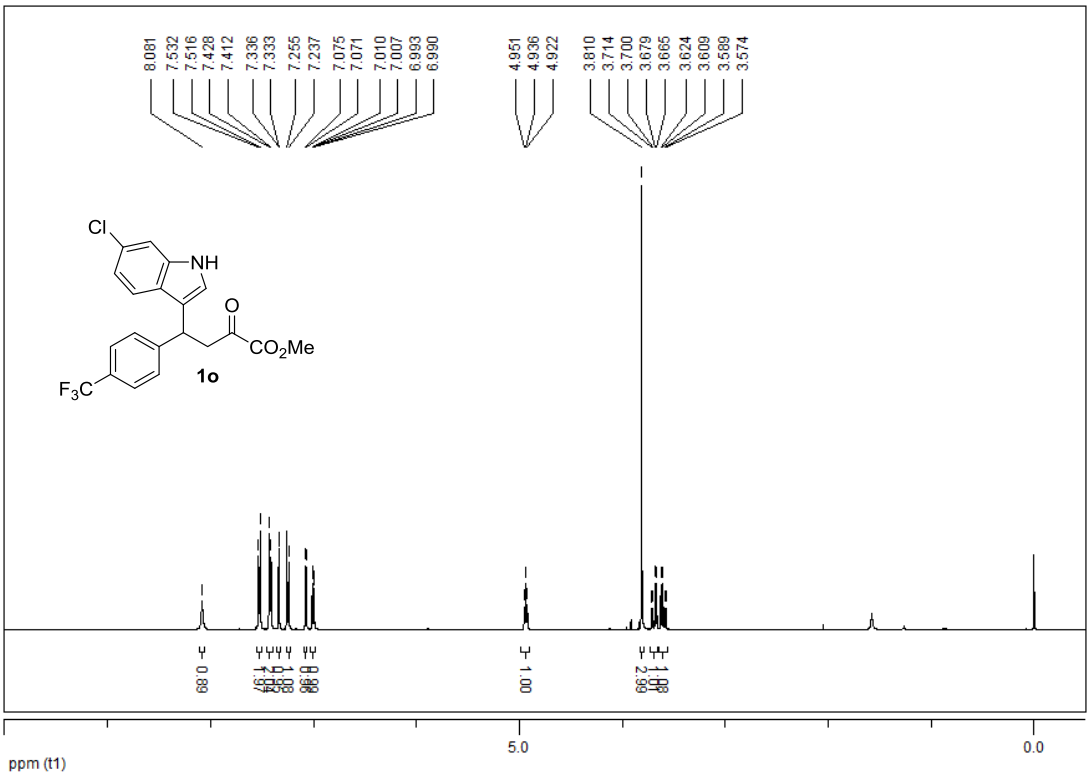
^{1}H NMR (500 MHz, $CDCl_3$)



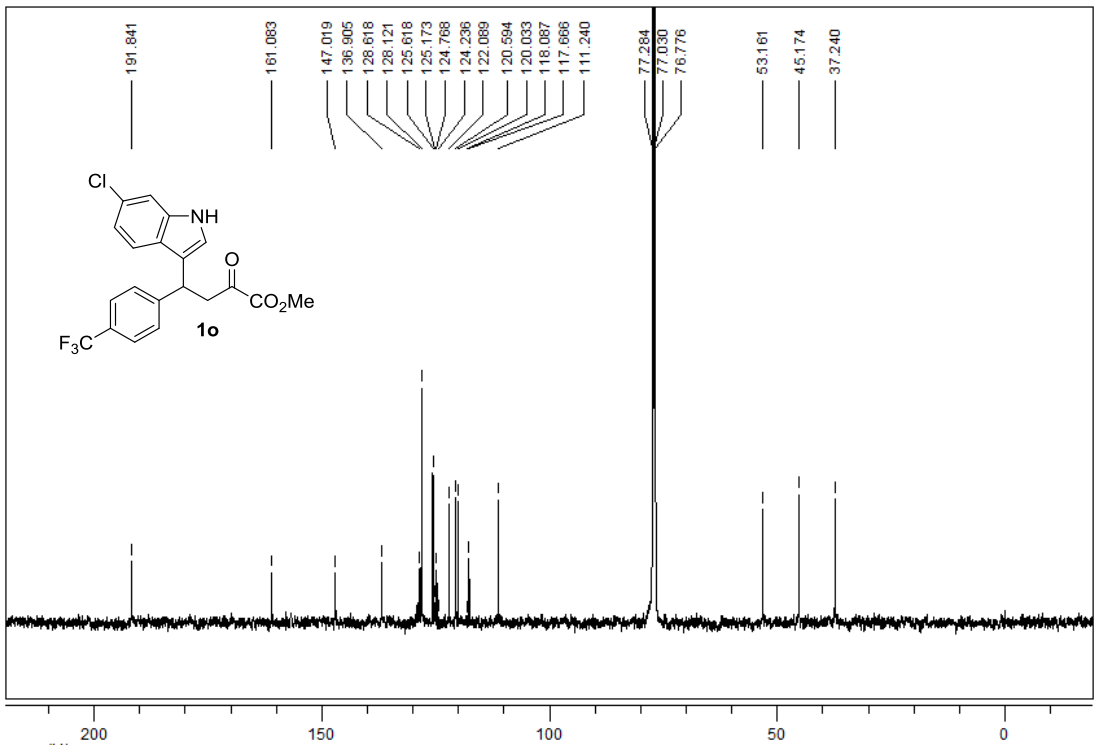
^{13}C NMR (125 MHz, $CDCl_3$)



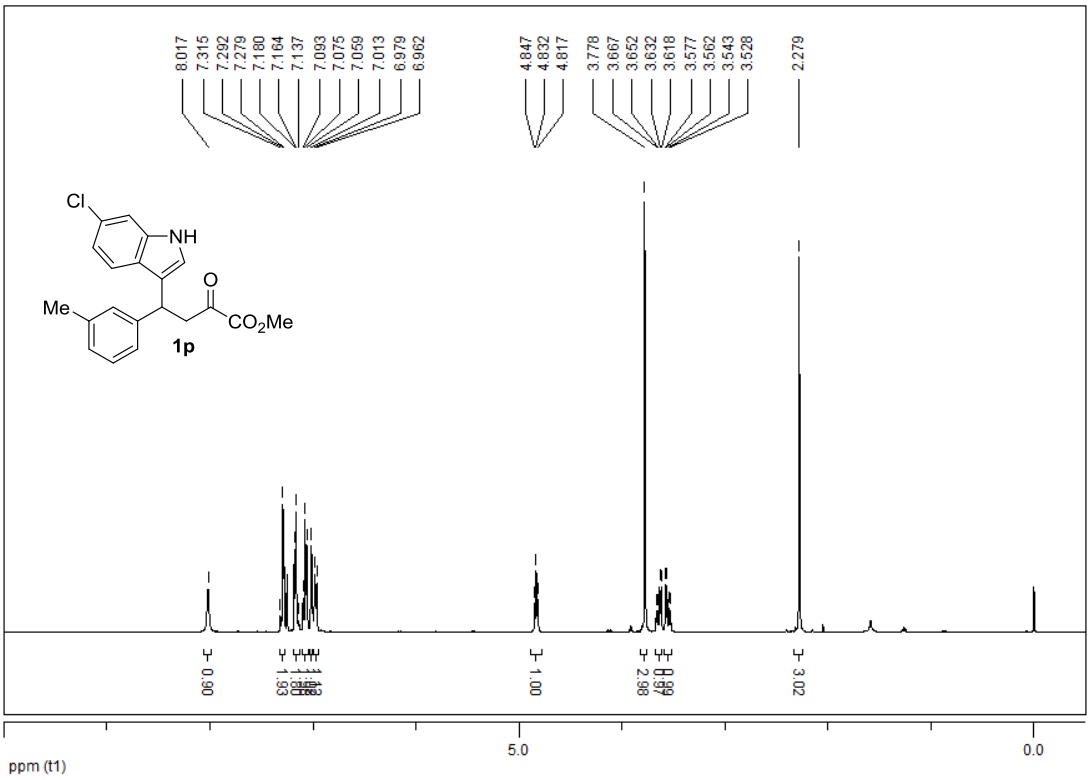
^{1}H NMR (500 MHz, $CDCl_3$)



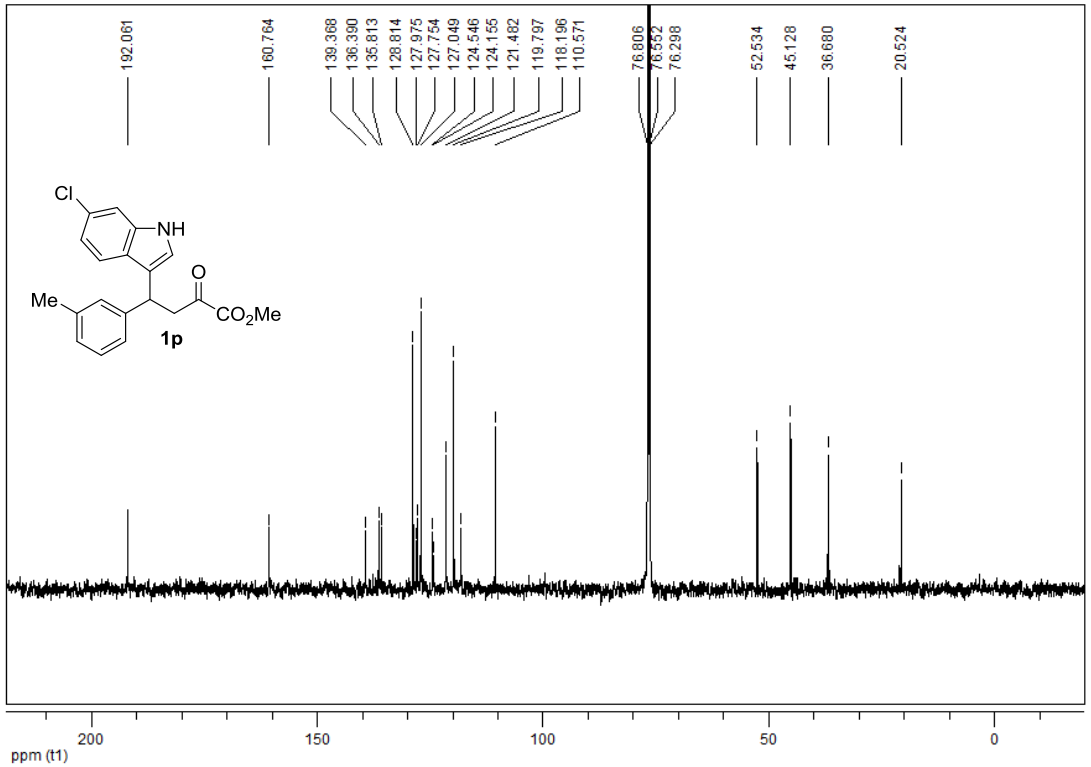
^{13}C NMR (125 MHz, $CDCl_3$)



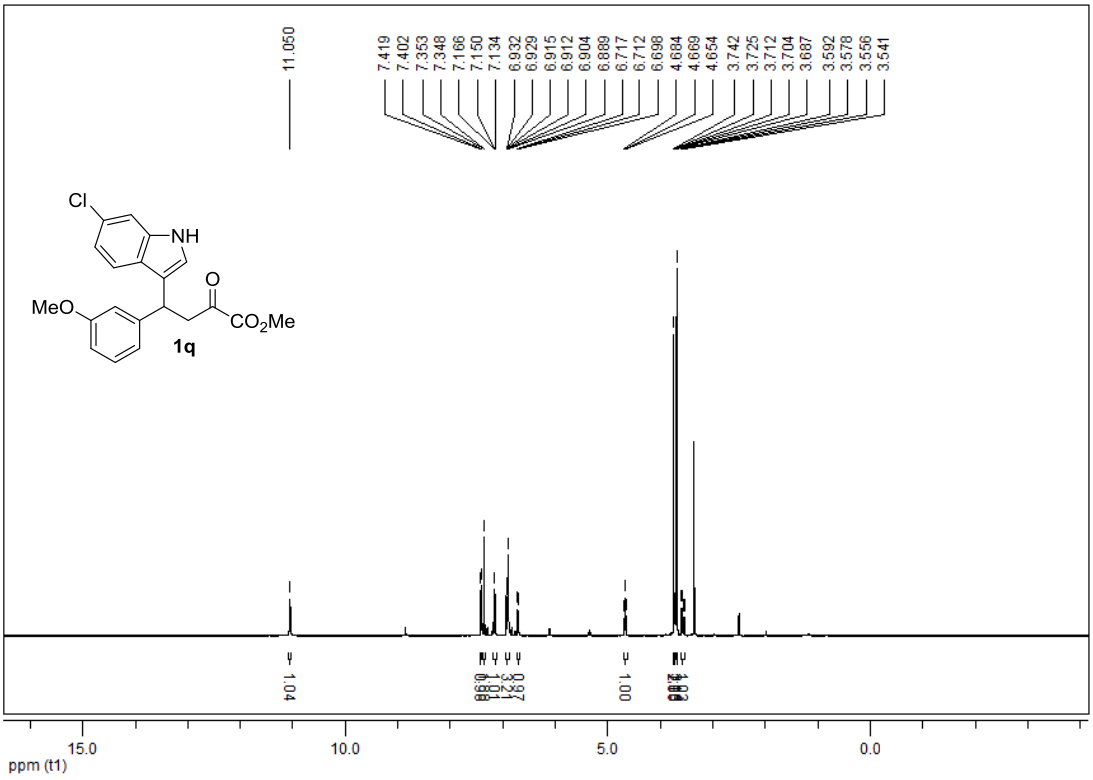
^{1}H NMR (500 MHz, $CDCl_3$)



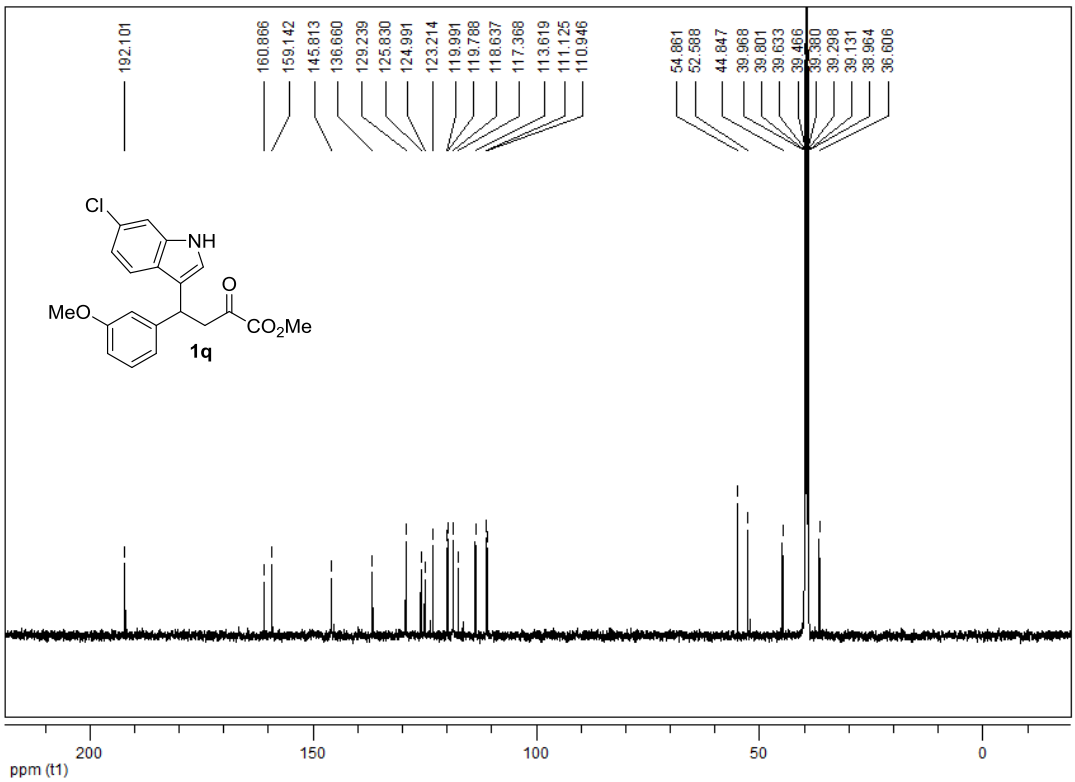
^{13}C NMR (125 MHz, $CDCl_3$)



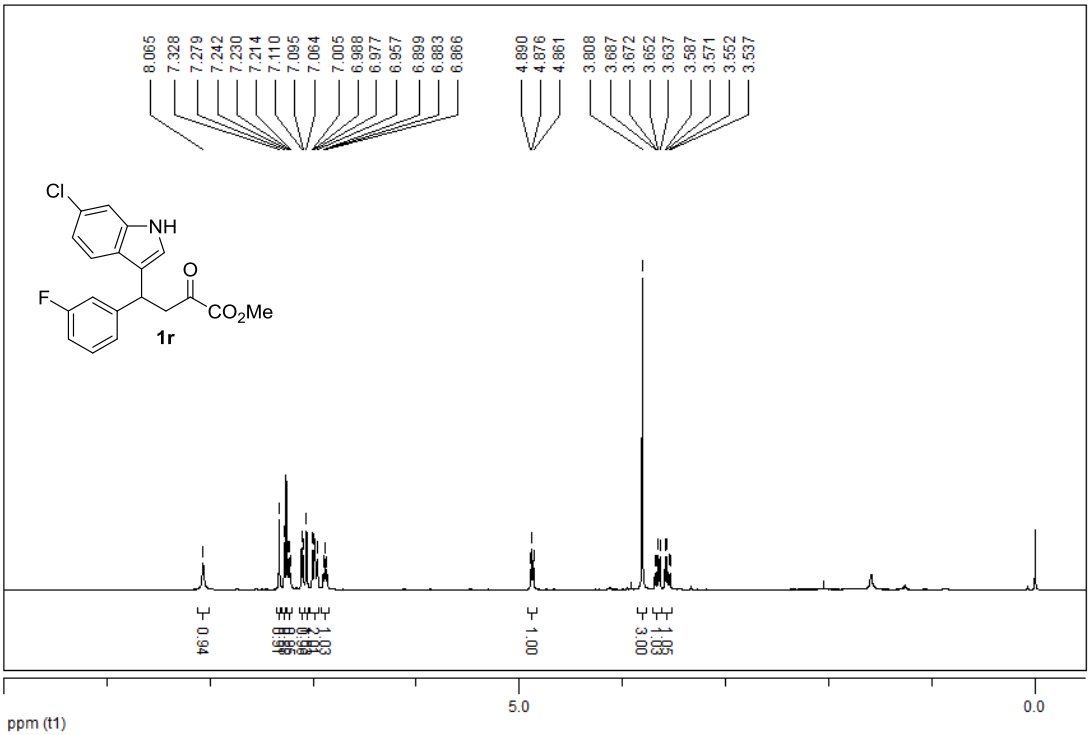
^{1}H NMR (500 MHz, DMSO-d_6)



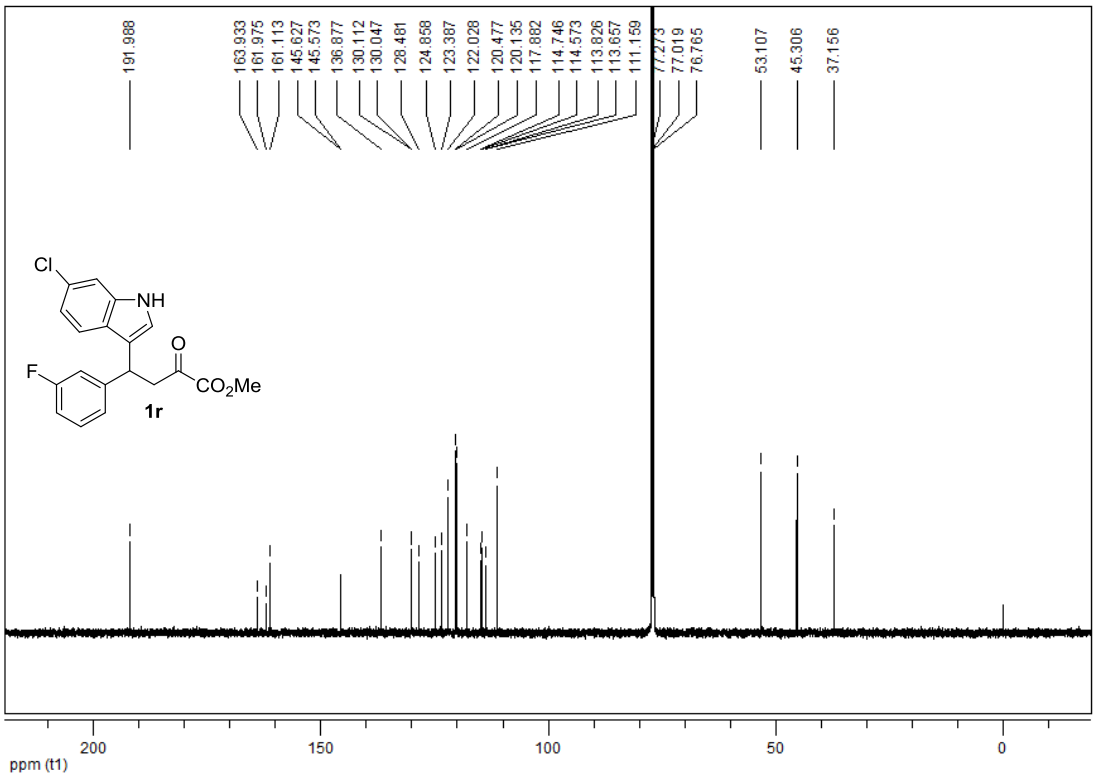
^{13}C NMR (125 MHz, DMSO-d_6)



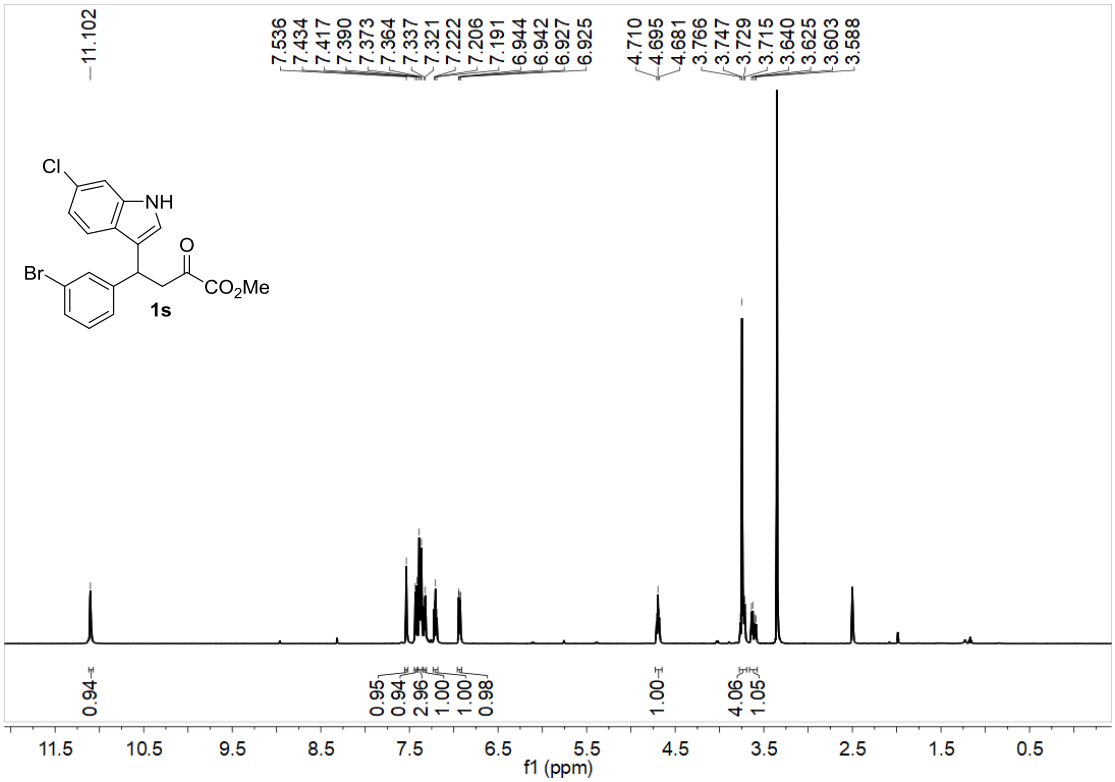
^{1}H NMR (500 MHz, $CDCl_3$)



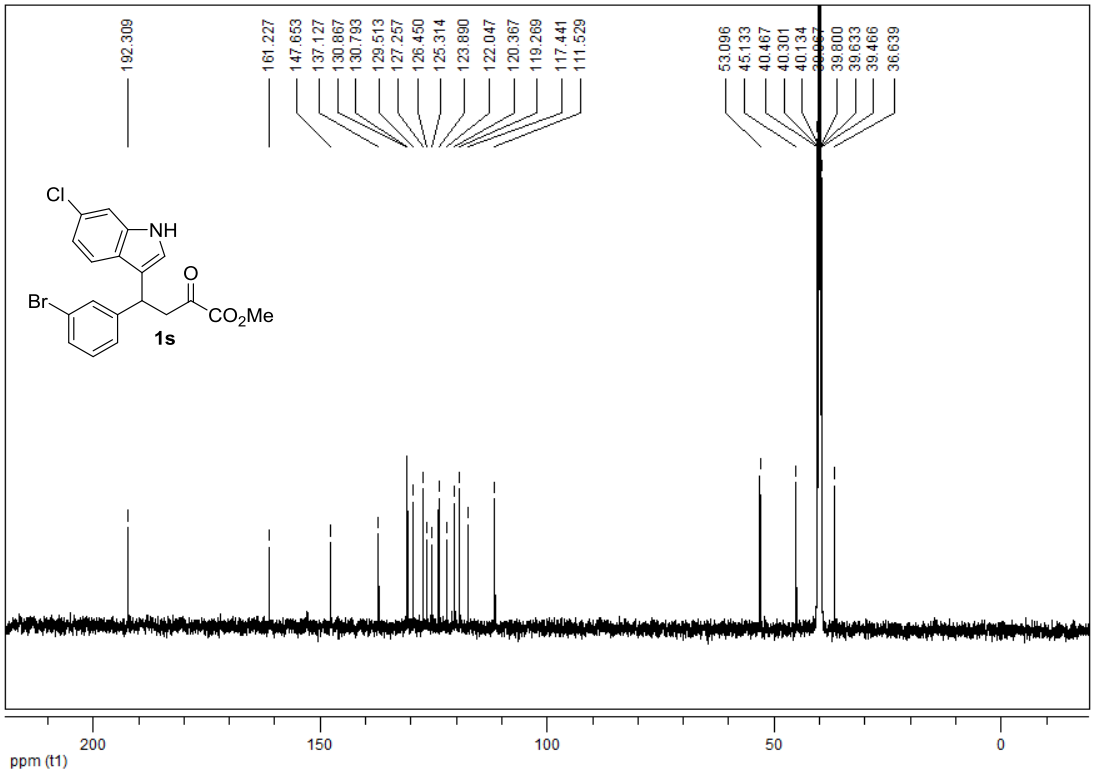
^{13}C NMR (125 MHz, $CDCl_3$)



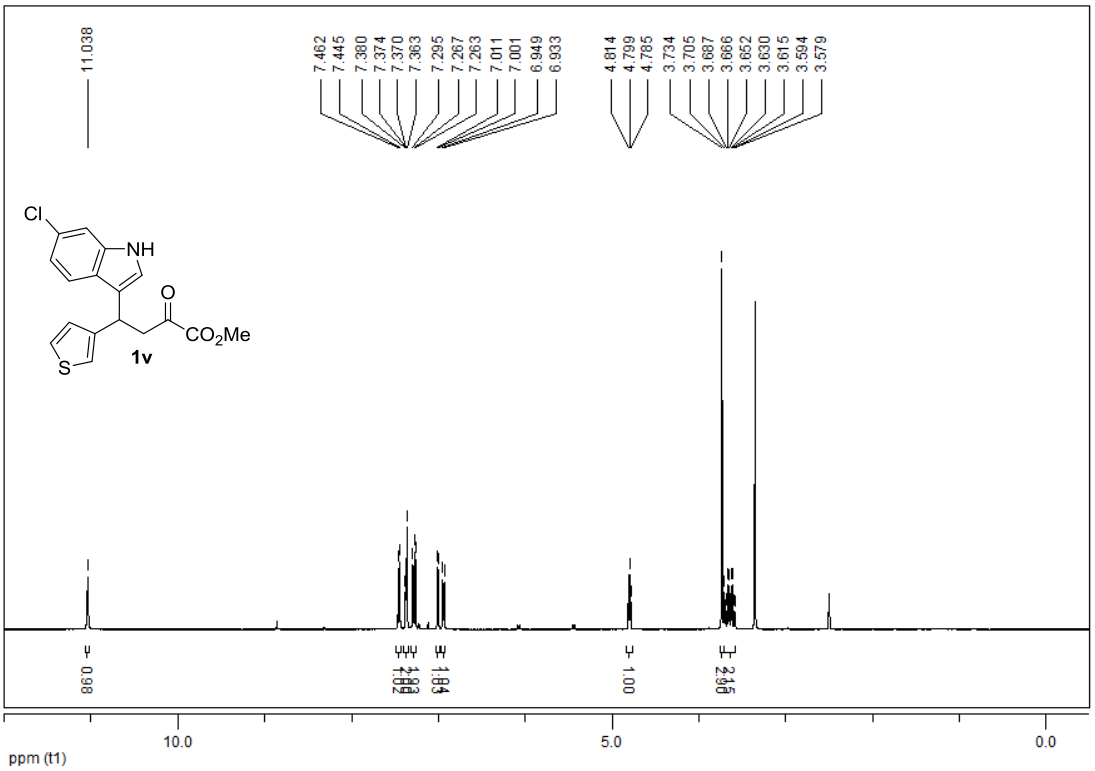
^{1}H NMR (500 MHz, DMSO-d_6)



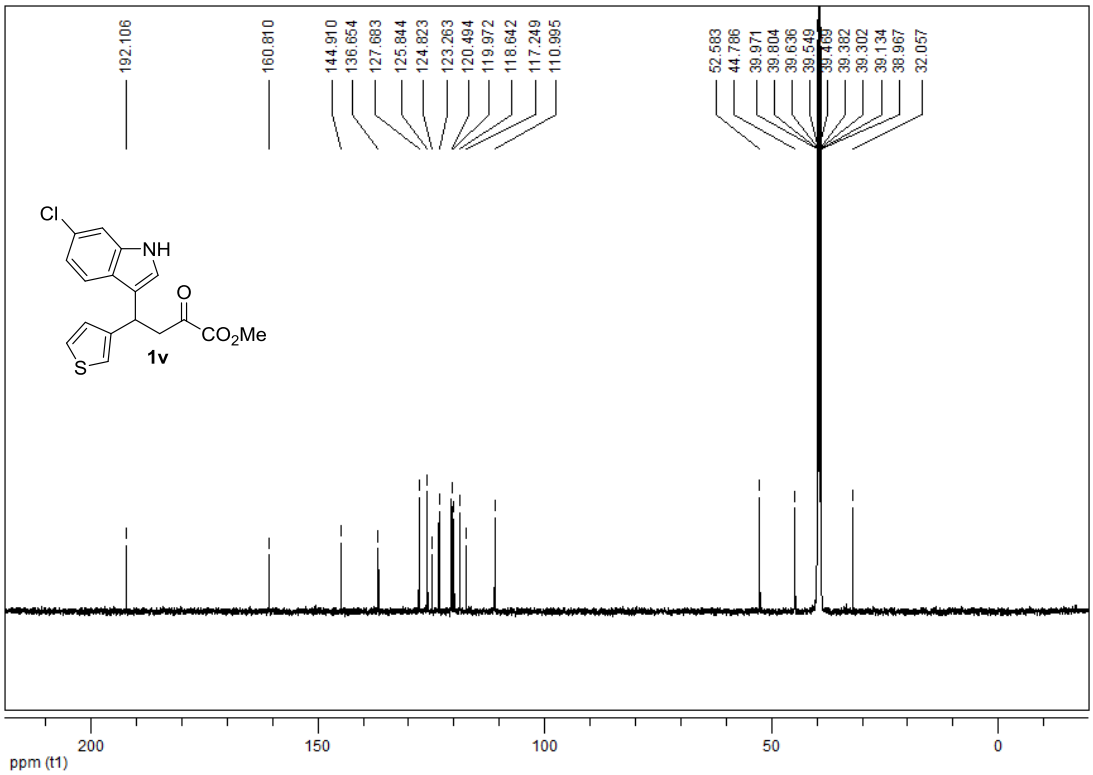
^{13}C NMR (125 MHz, DMSO-d_6)



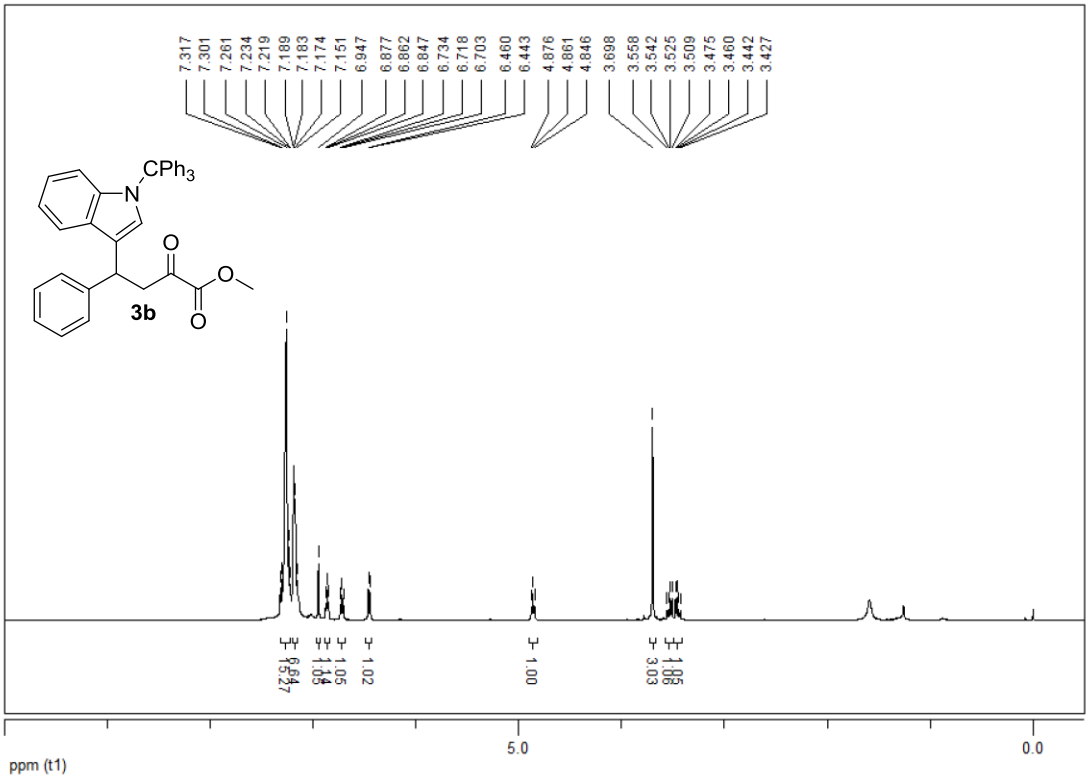
^{1}H NMR (500 MHz, DMSO-d_6)



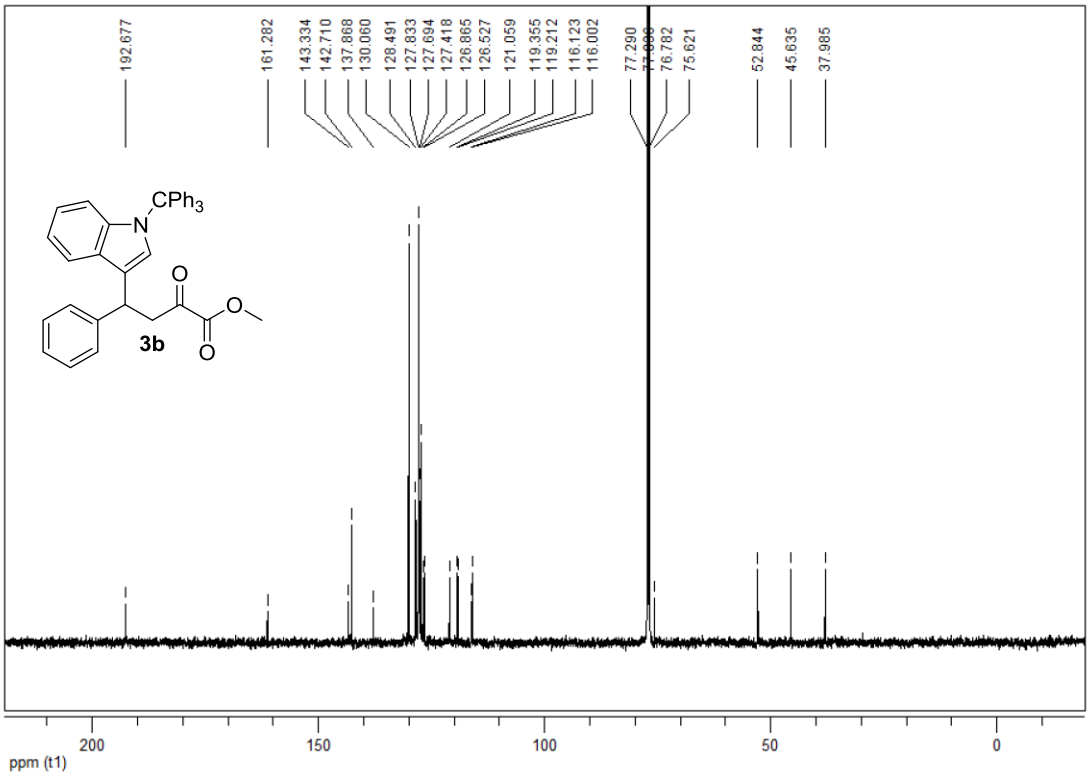
^{13}C NMR (125 MHz, DMSO-d_6)



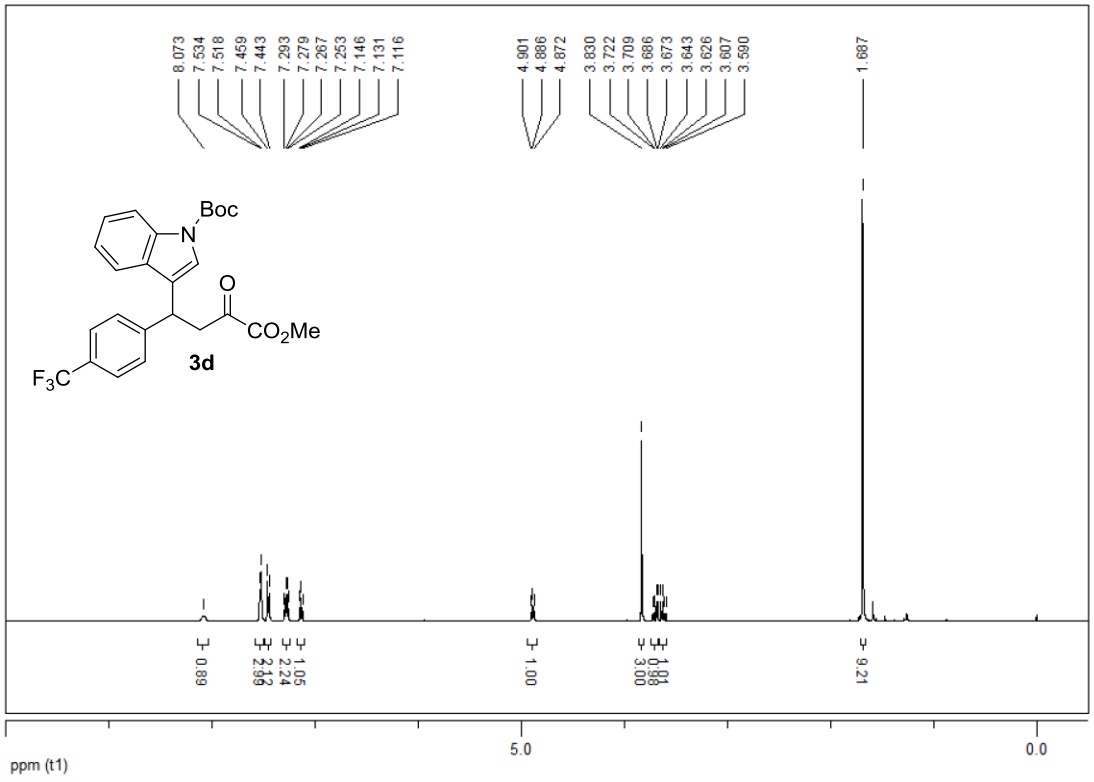
^{1}H NMR (500 MHz, $CDCl_3$)



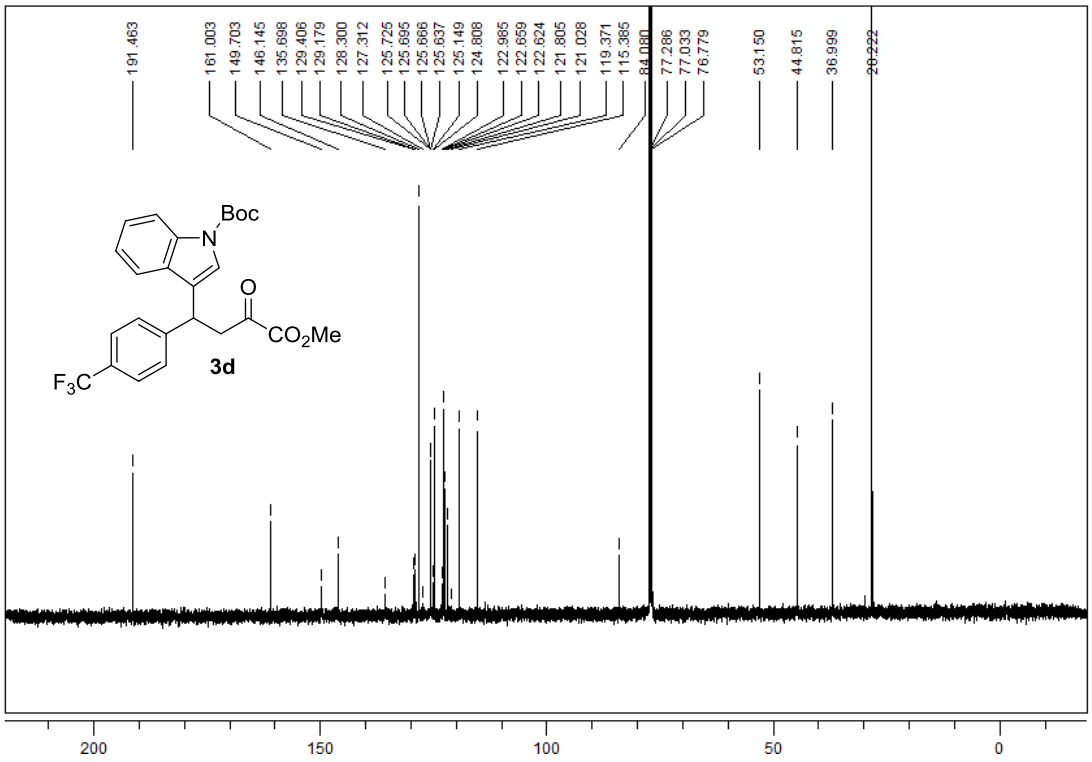
^{13}C NMR (125 MHz, $CDCl_3$)



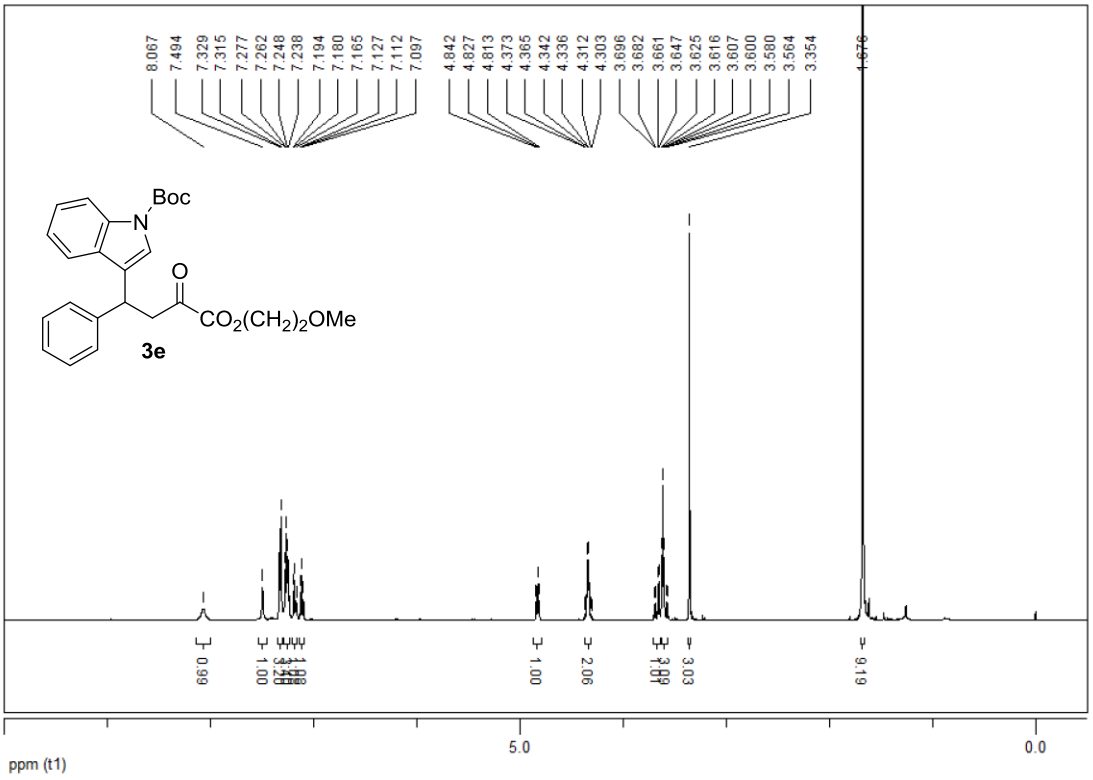
^{1}H NMR (500 MHz, $CDCl_3$)



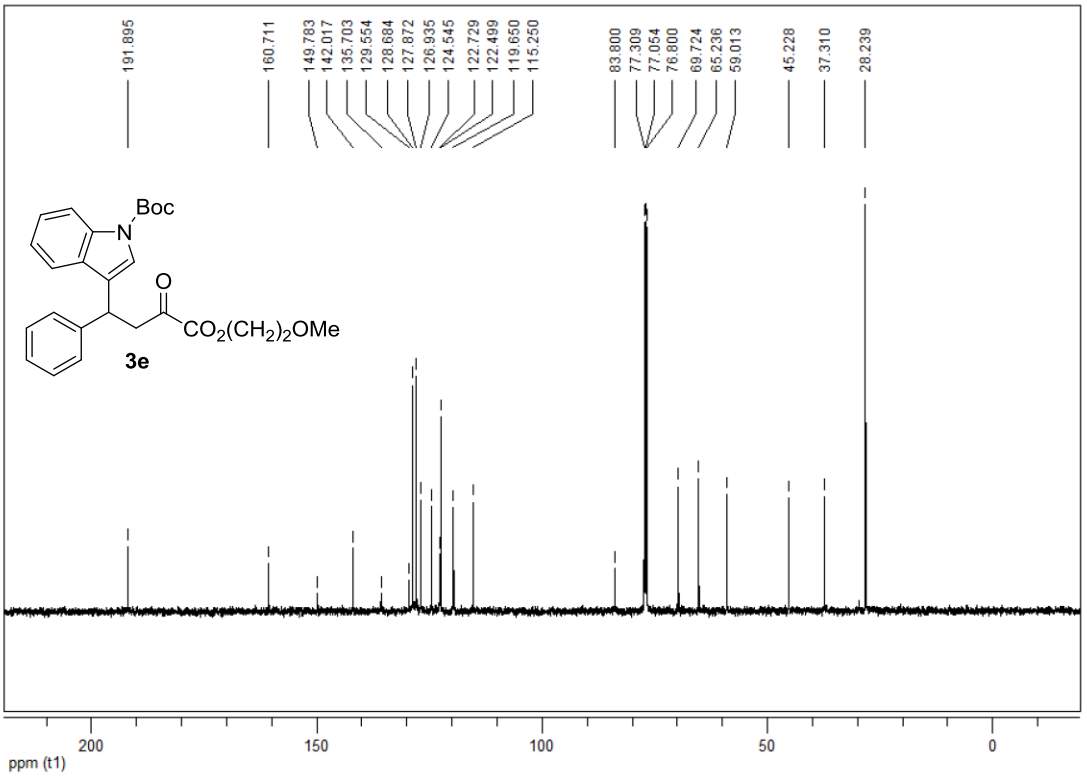
^{13}C NMR (125 MHz, $CDCl_3$)



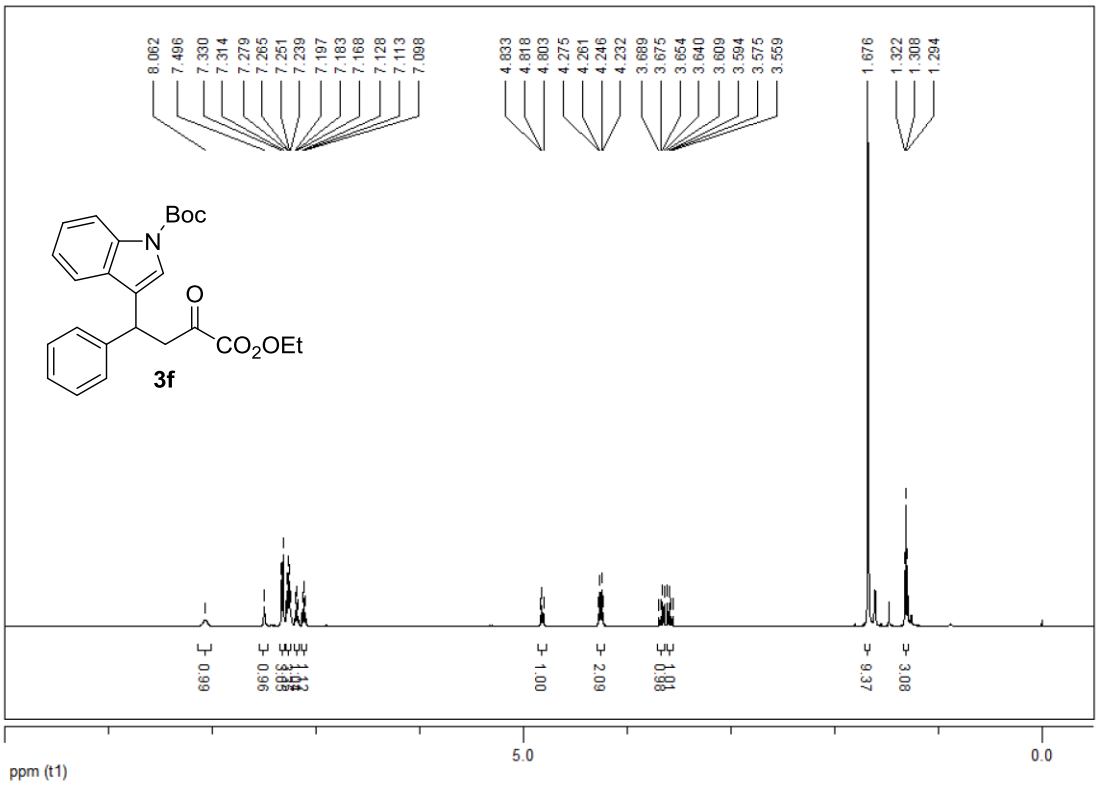
^{1}H NMR (500 MHz, $CDCl_3$)



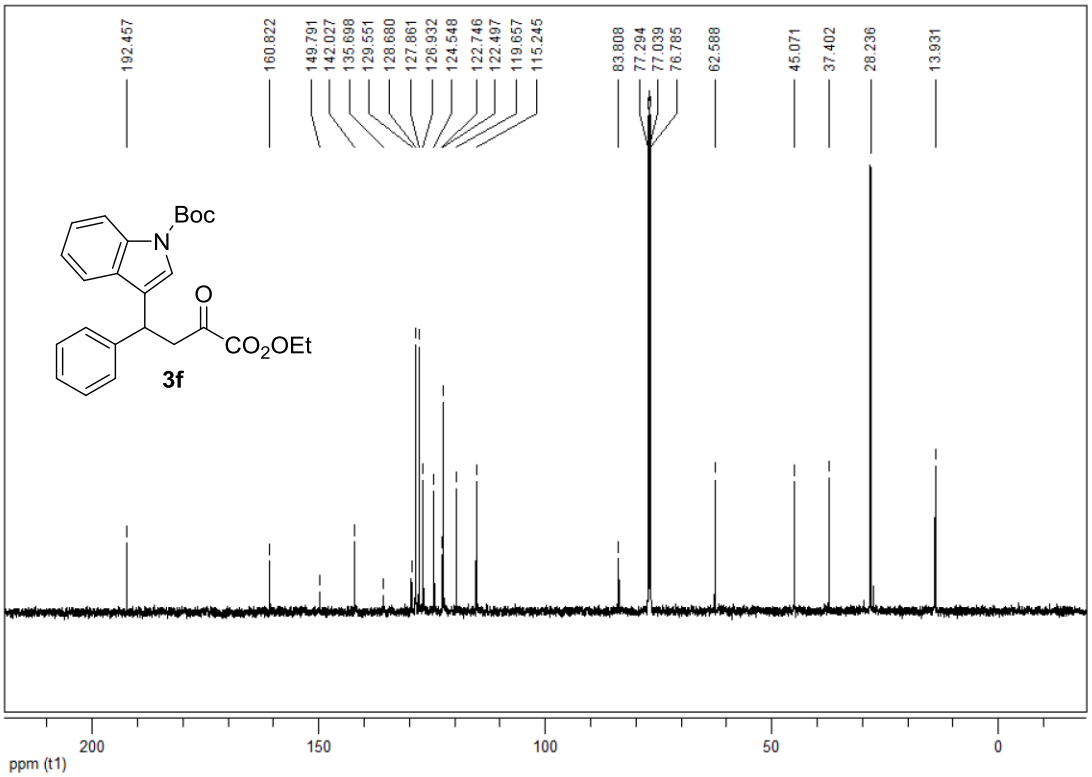
^{13}C NMR (125 MHz, $CDCl_3$)



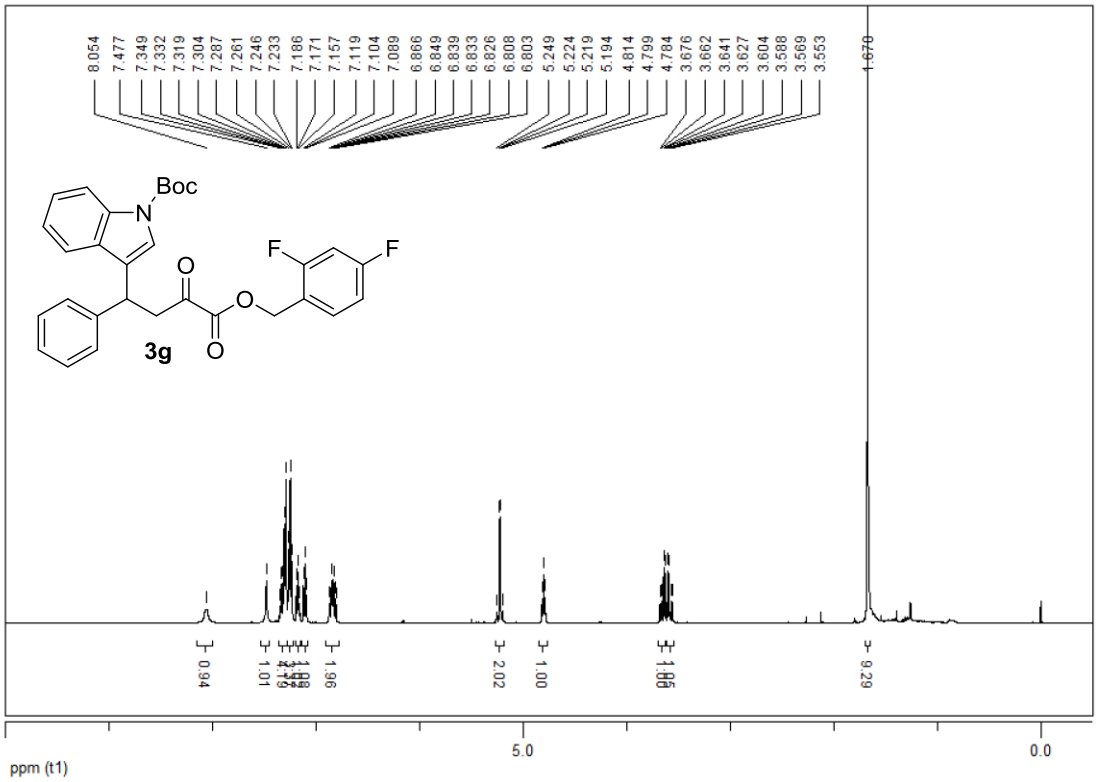
^{1}H NMR (500 MHz, $CDCl_3$)



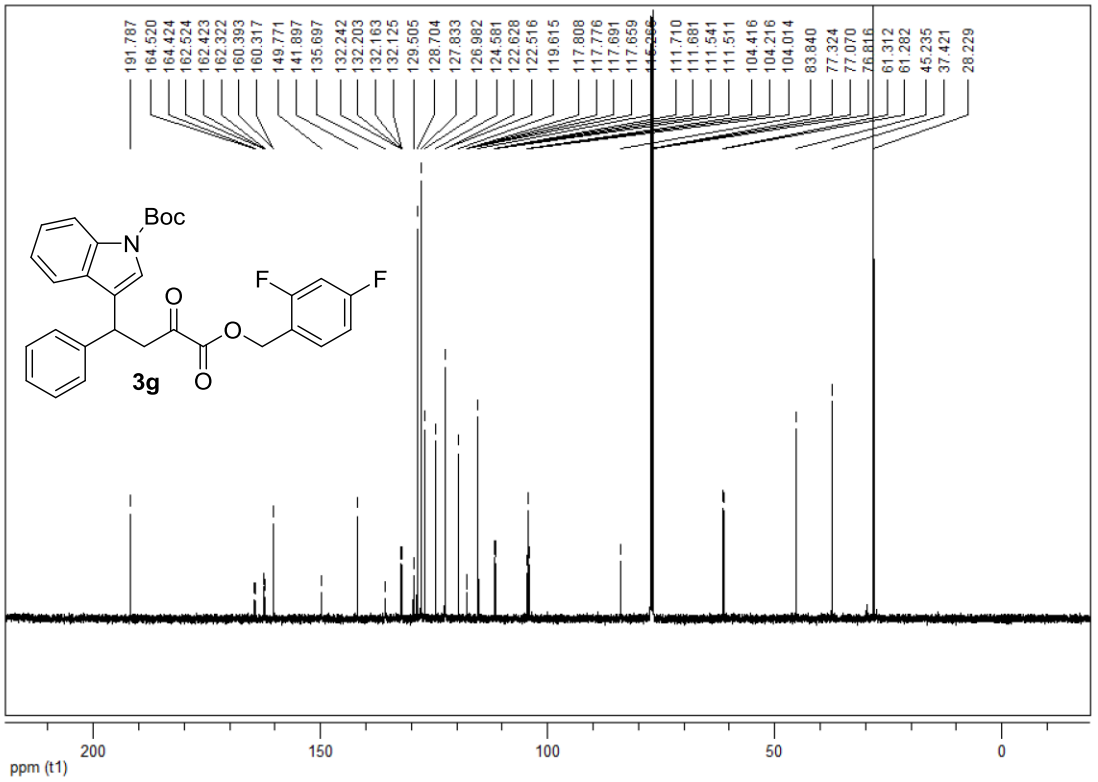
^{13}C NMR (125 MHz, $CDCl_3$)



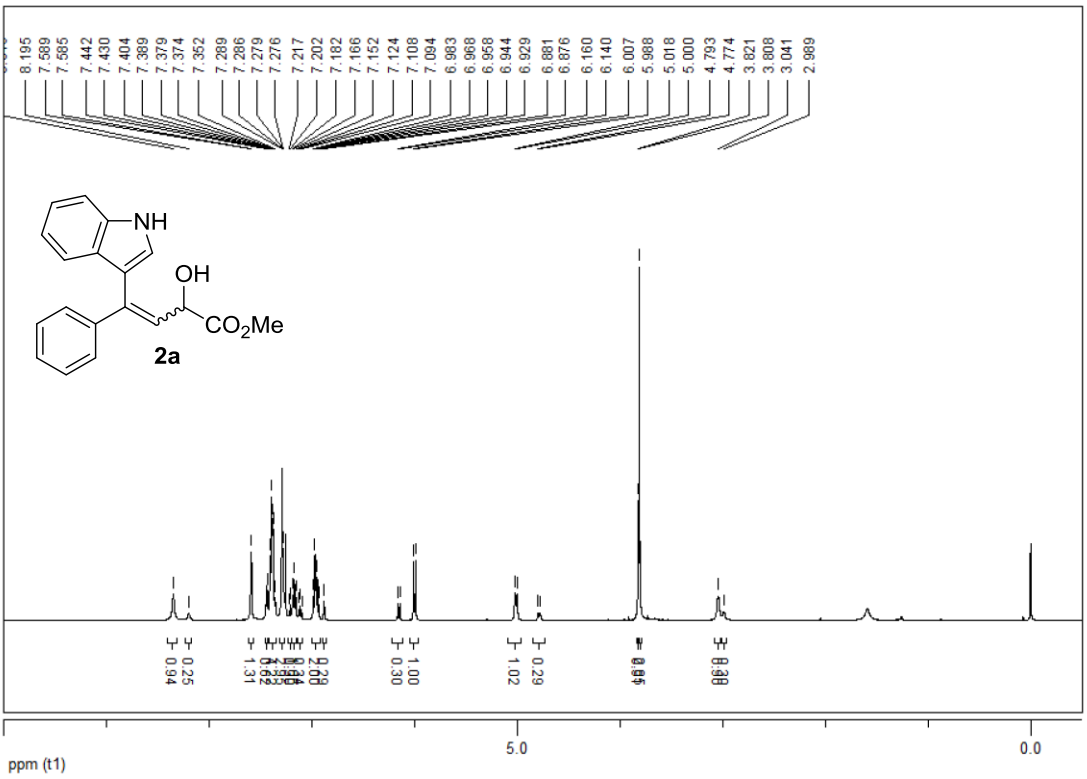
^{1}H NMR (500 MHz, $CDCl_3$)



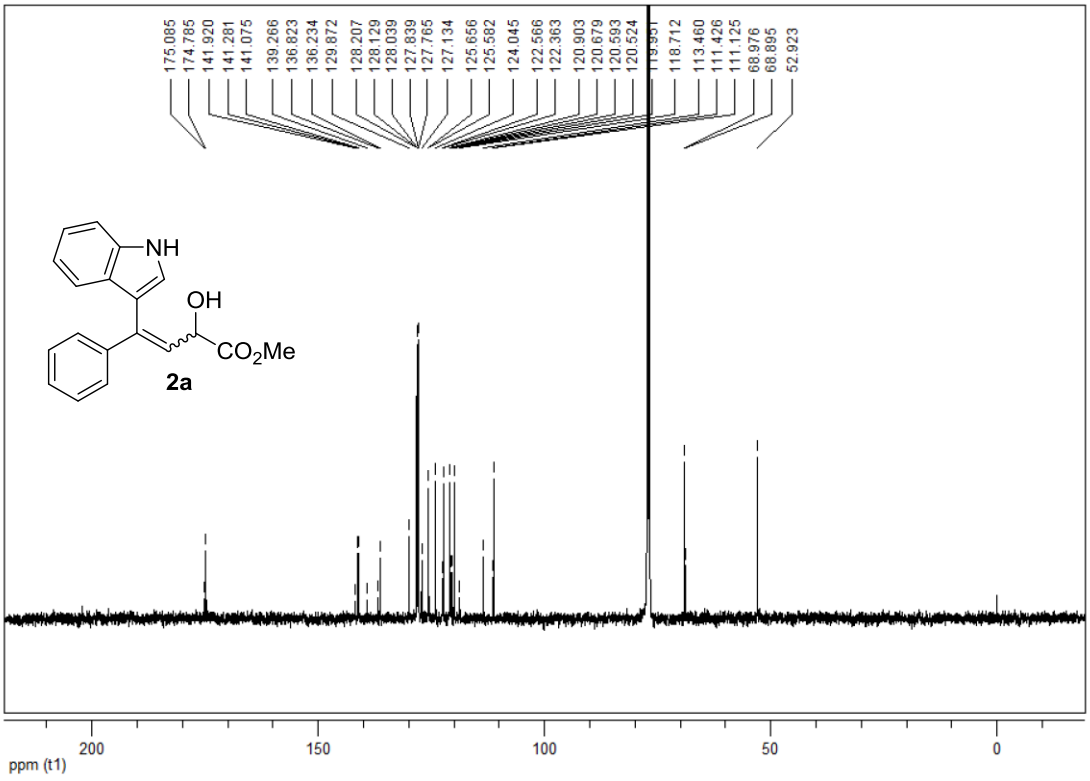
^{13}C NMR (125 MHz, $CDCl_3$)



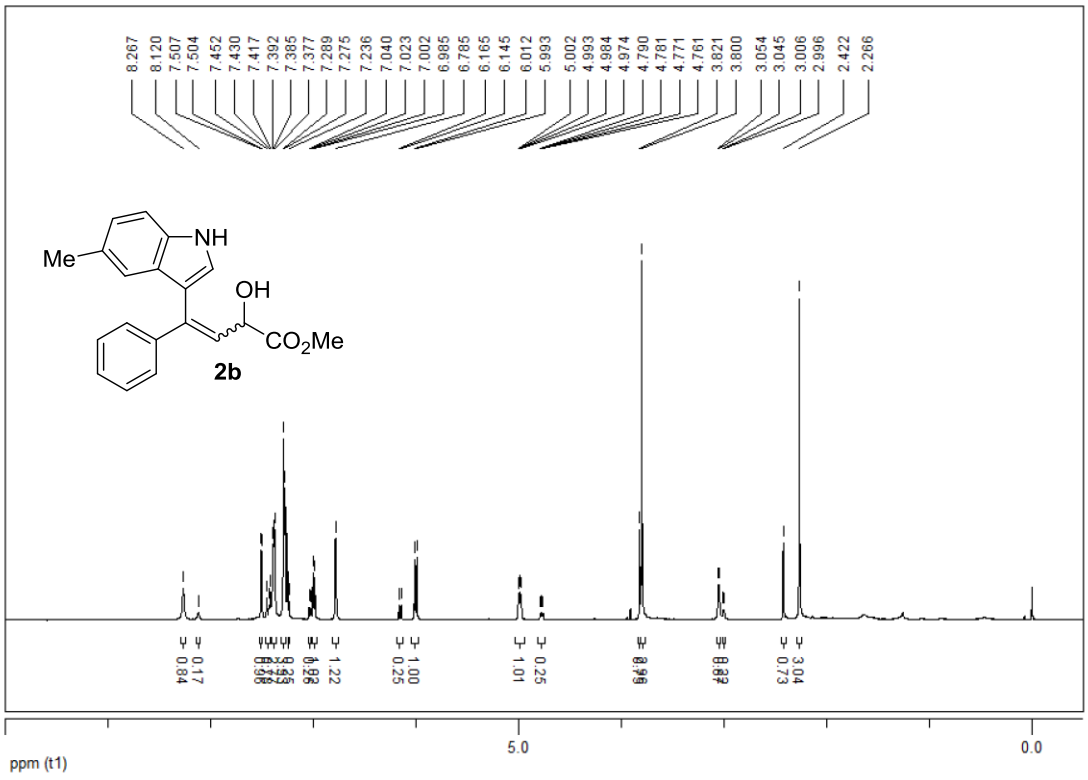
^{1}H NMR (500 MHz, $CDCl_3$)



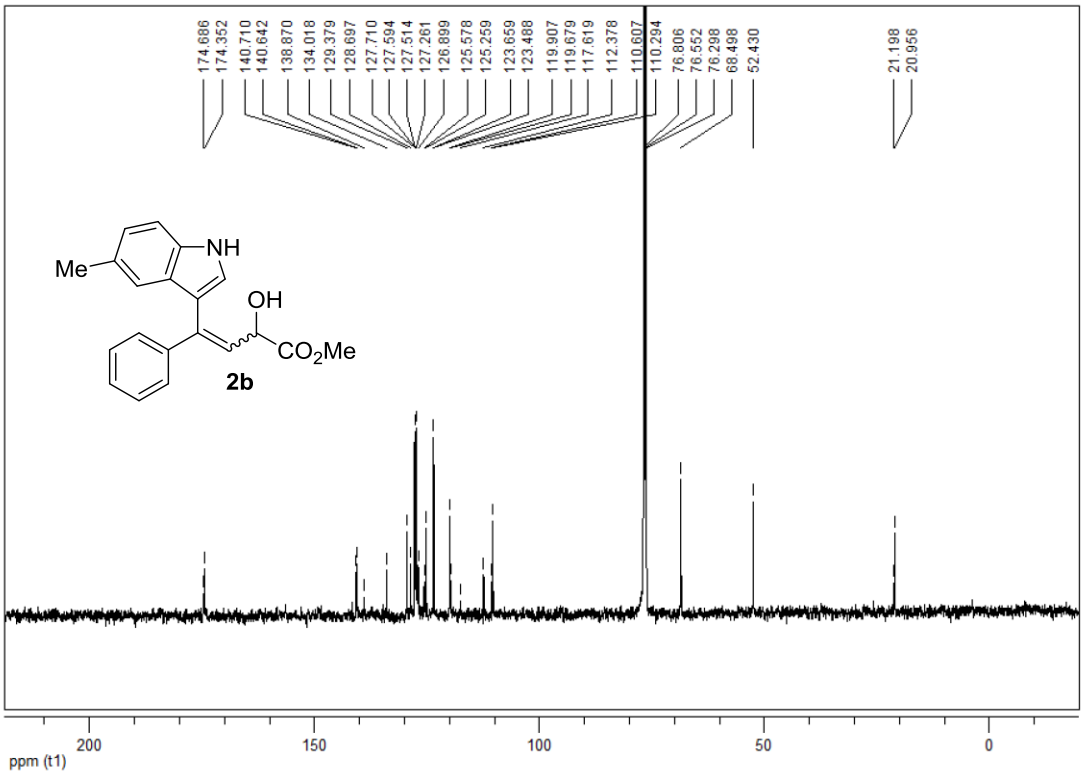
^{13}C NMR (125 MHz, $CDCl_3$)



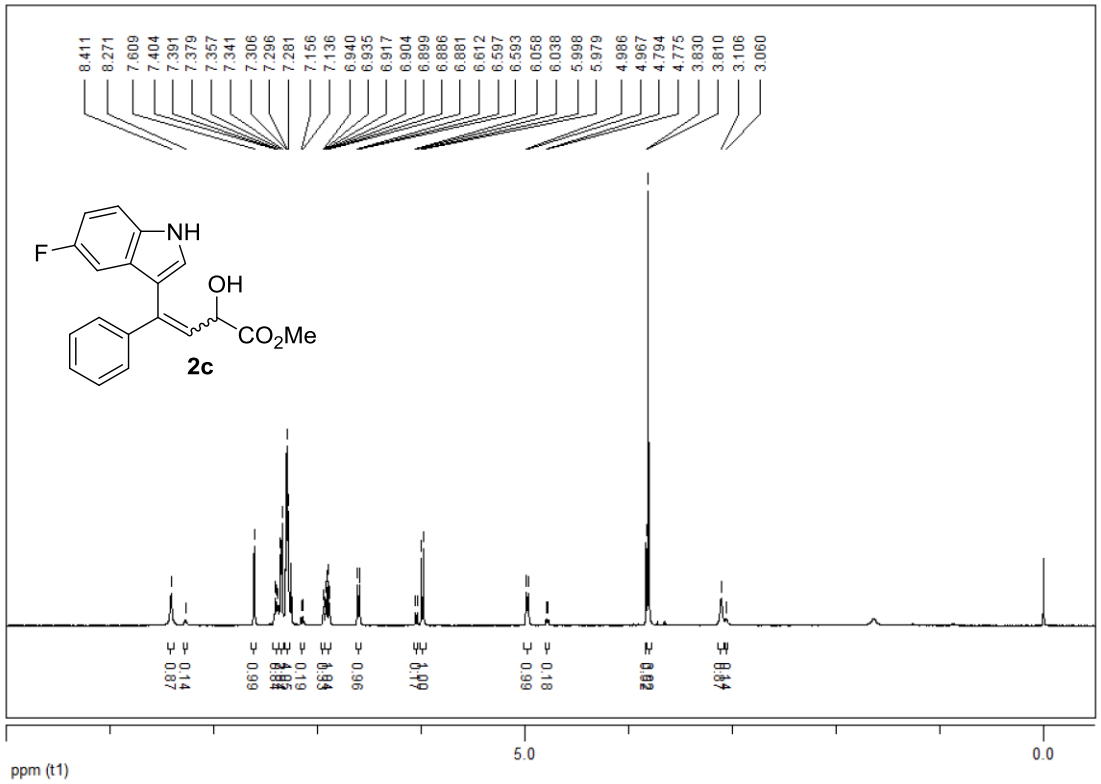
^{1}H NMR (500 MHz, $CDCl_3$)



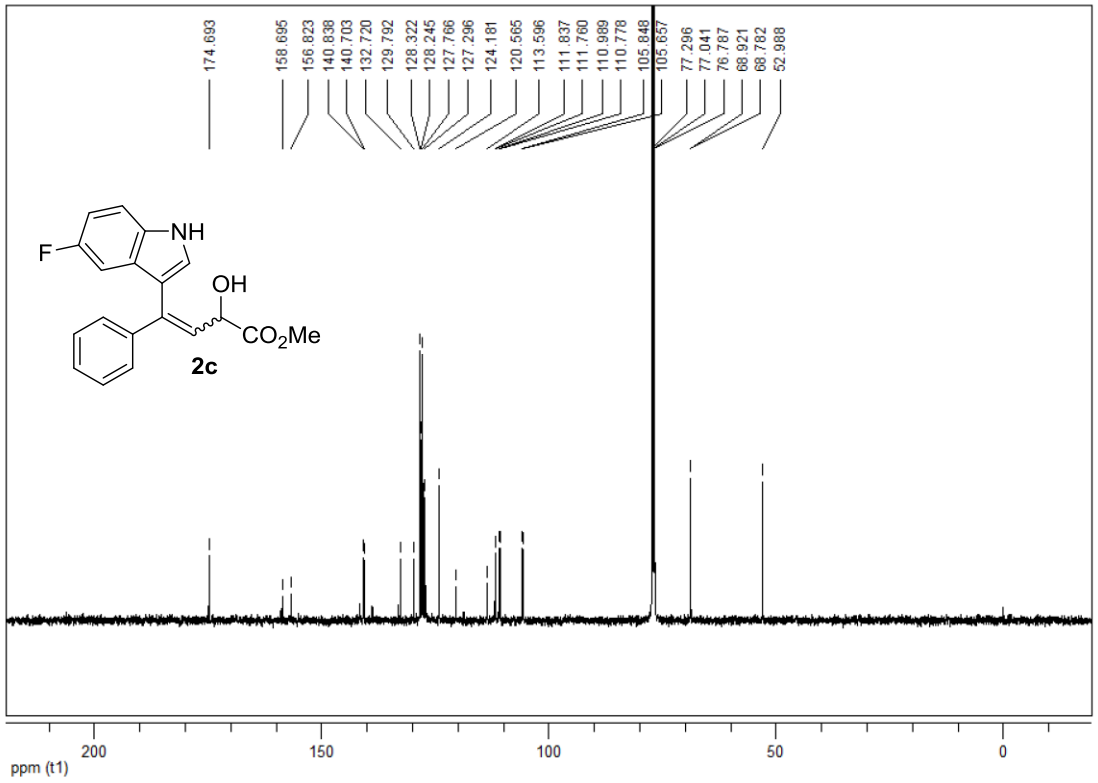
^{13}C NMR (125 MHz, $CDCl_3$)



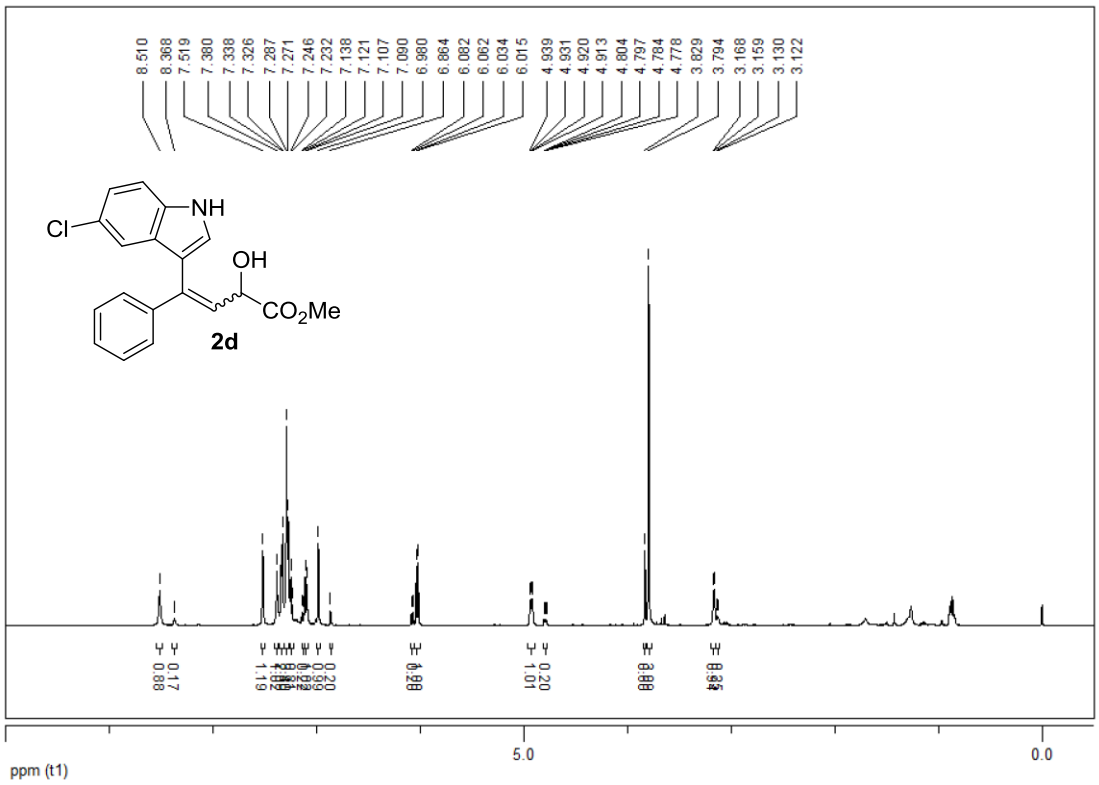
^{1}H NMR (500 MHz, $CDCl_3$)



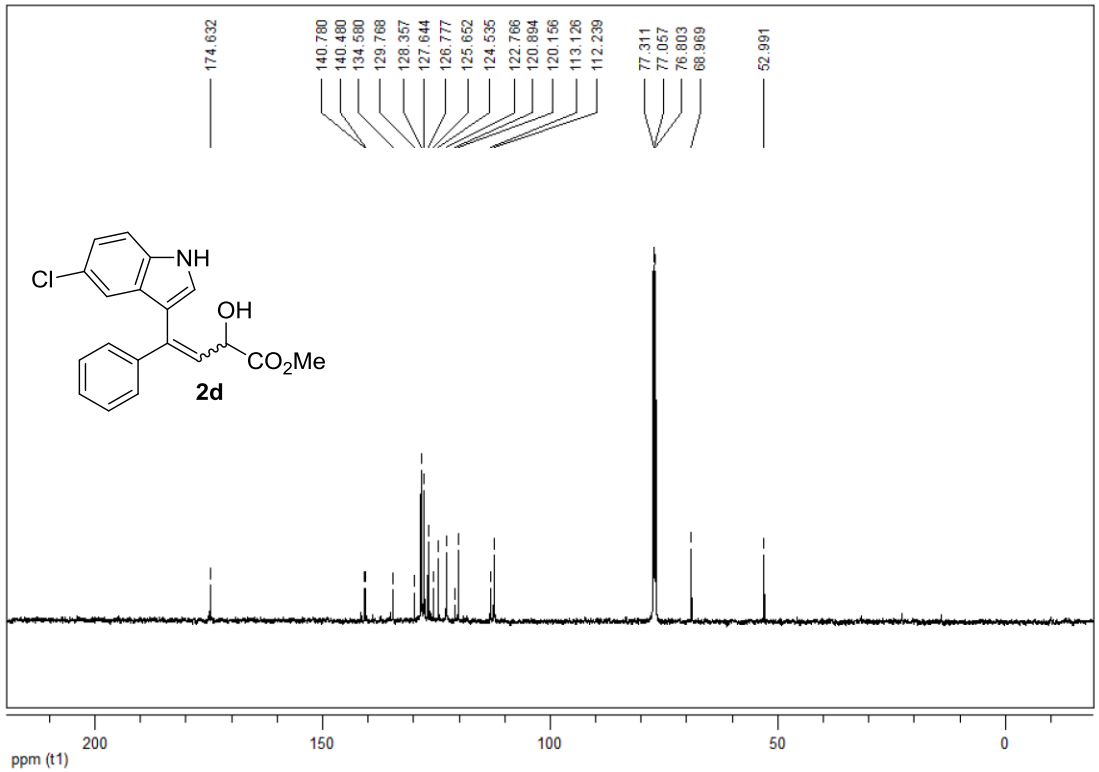
^{13}C NMR (125 MHz, $CDCl_3$)



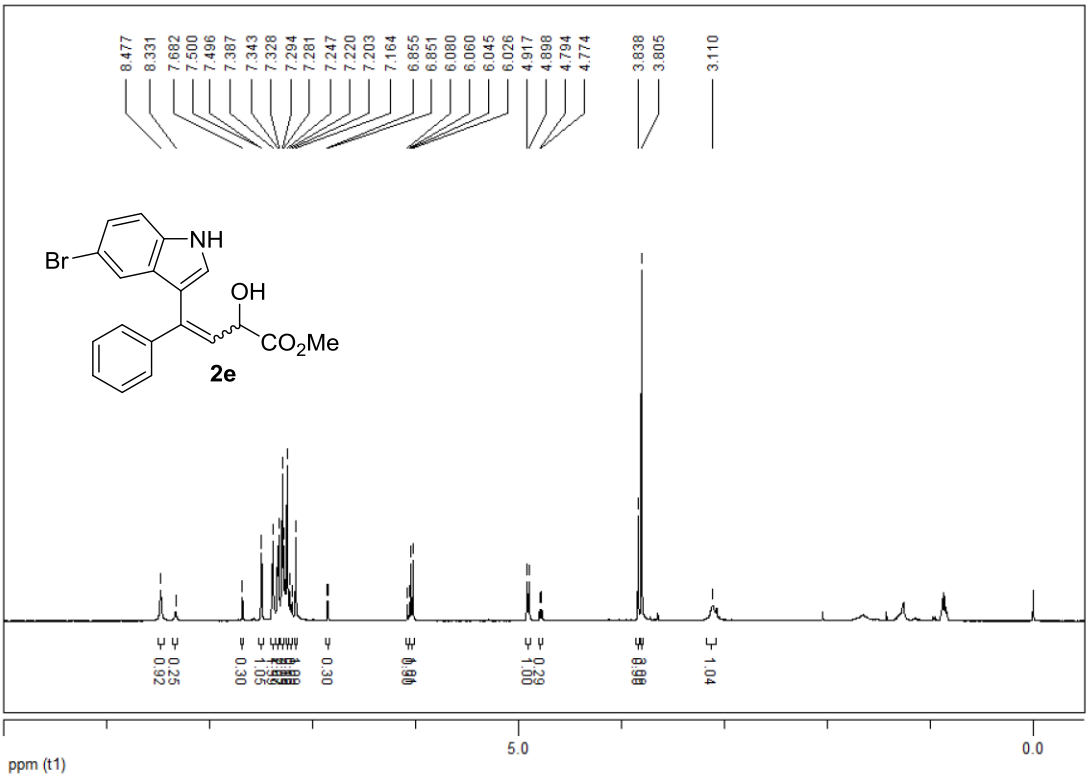
^{1}H NMR (500 MHz, $CDCl_3$)



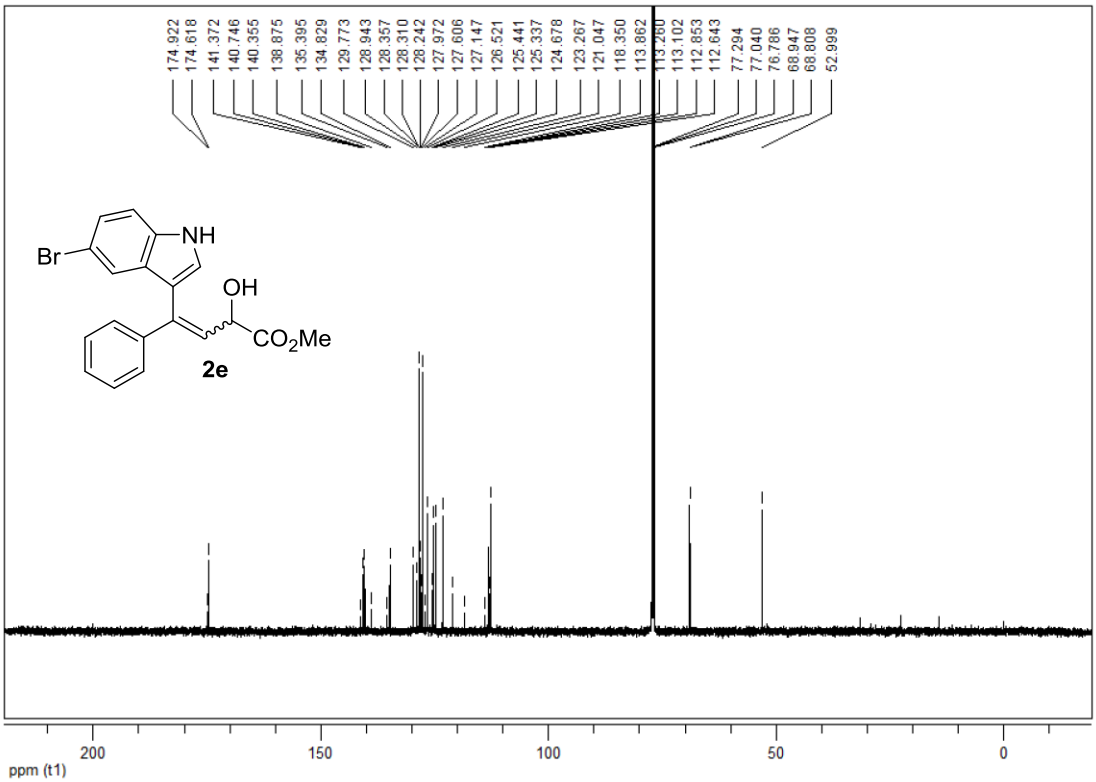
^{13}C NMR (125 MHz, $CDCl_3$)



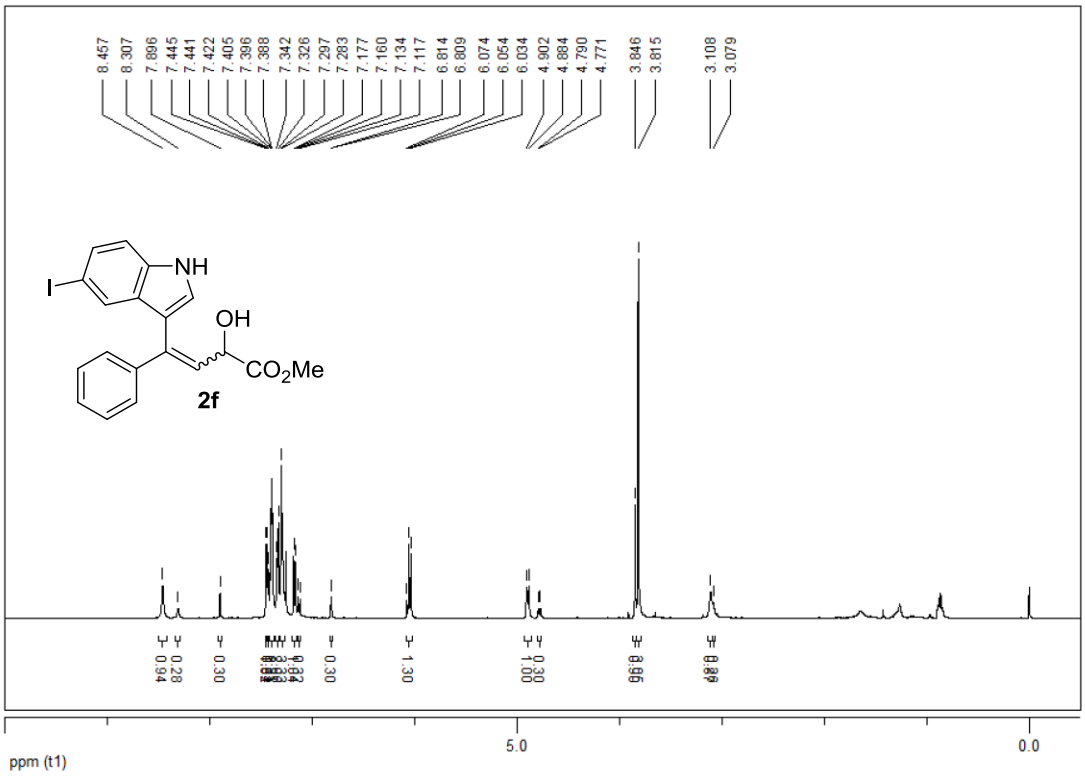
^{1}H NMR (500 MHz, $CDCl_3$)



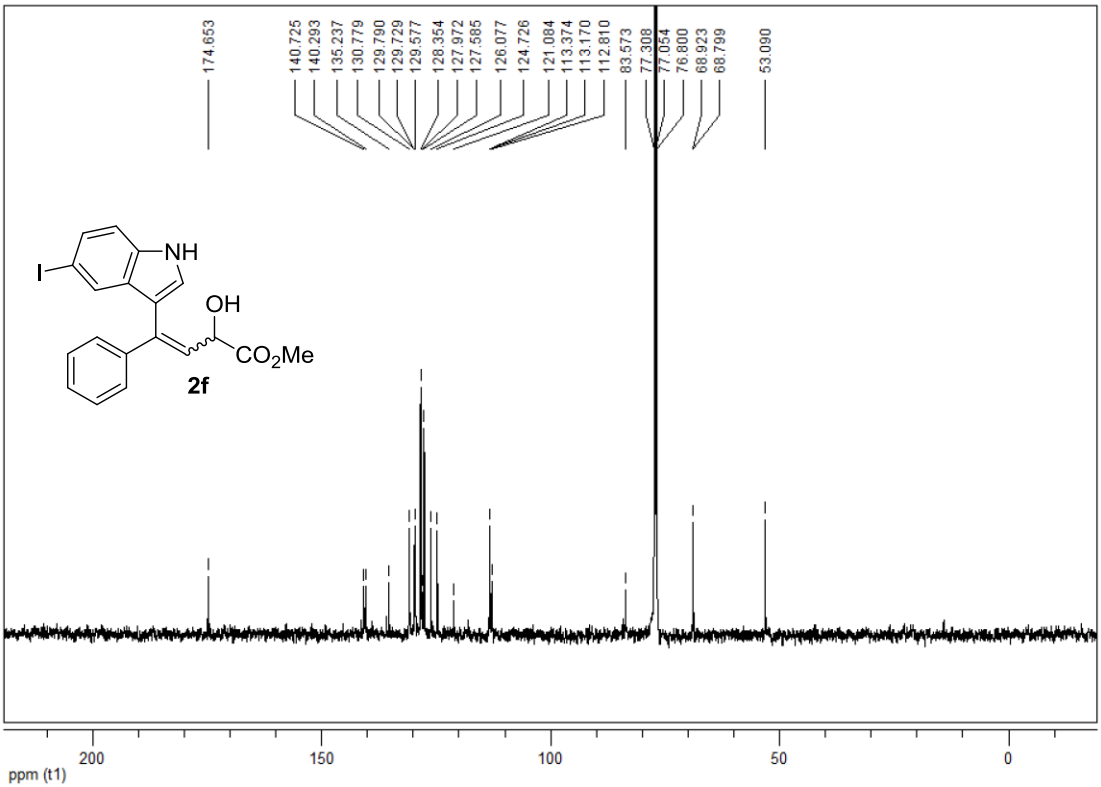
^{13}C NMR (125 MHz, $CDCl_3$)



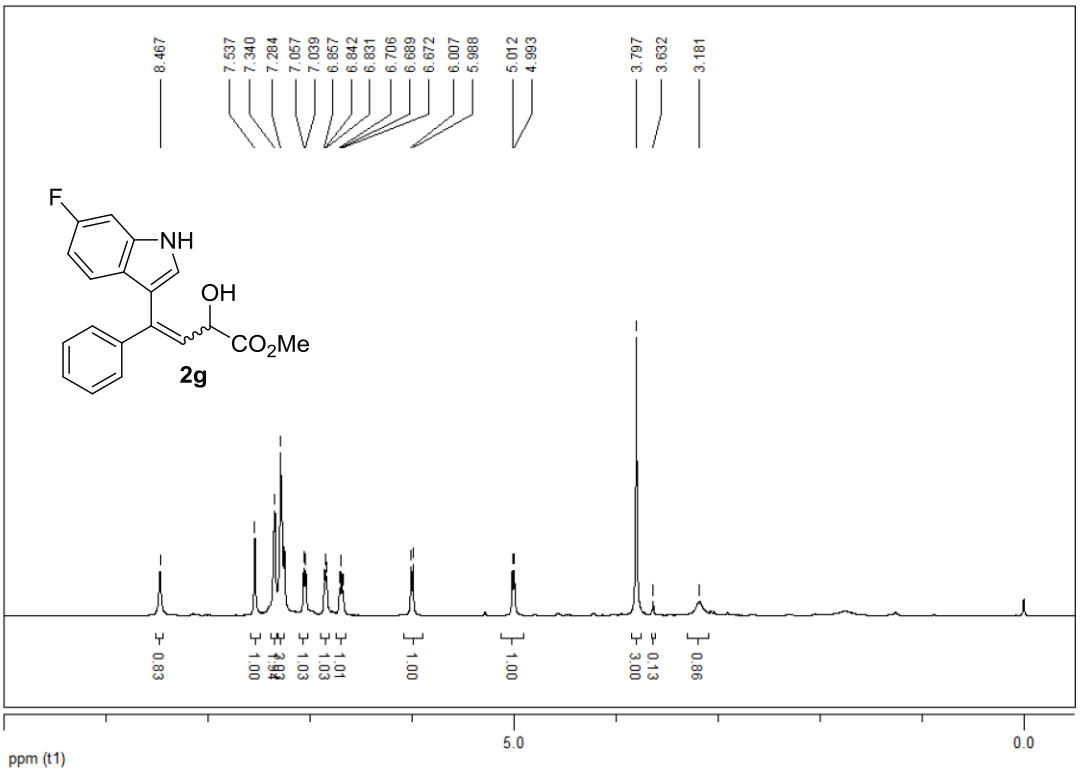
^{1}H NMR (500 MHz, $CDCl_3$)



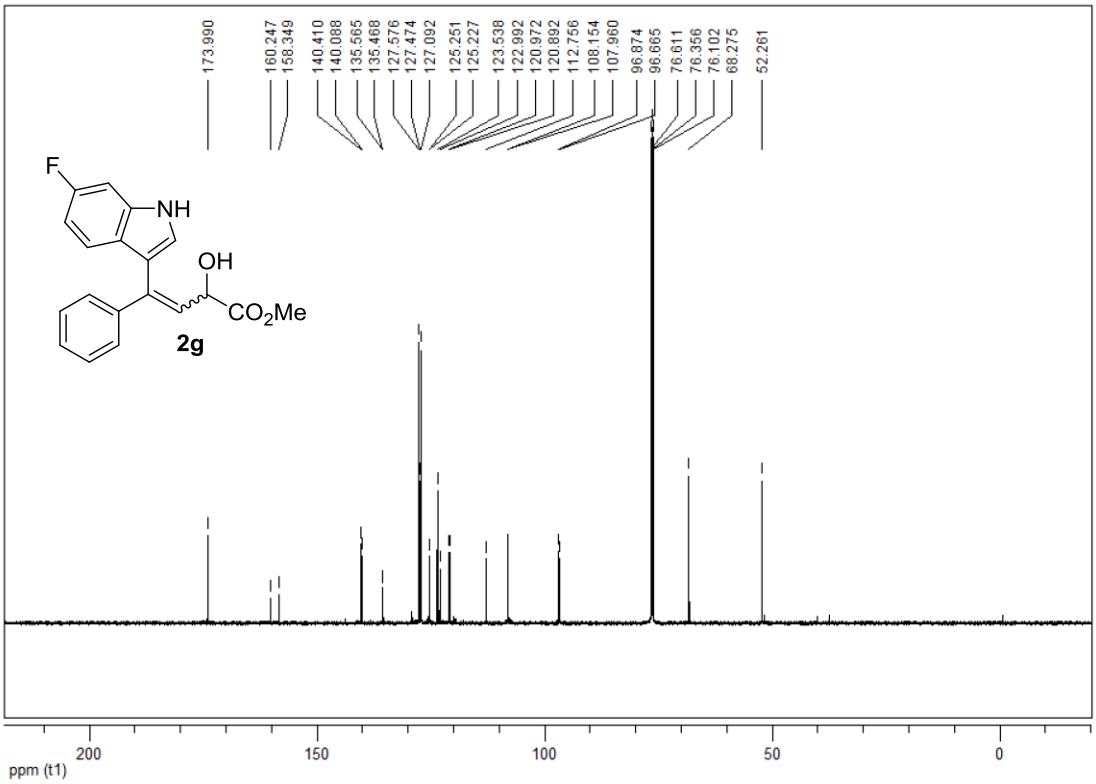
^{13}C NMR (125 MHz, $CDCl_3$)



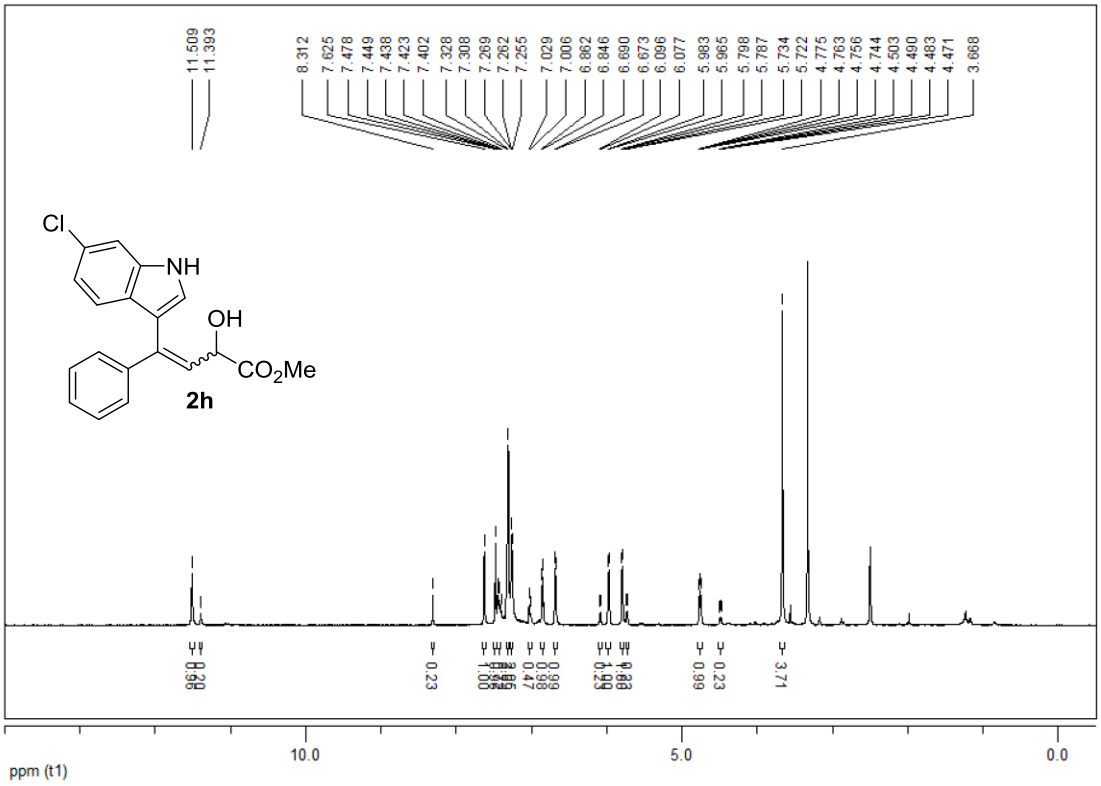
^{1}H NMR (500 MHz, $CDCl_3$)



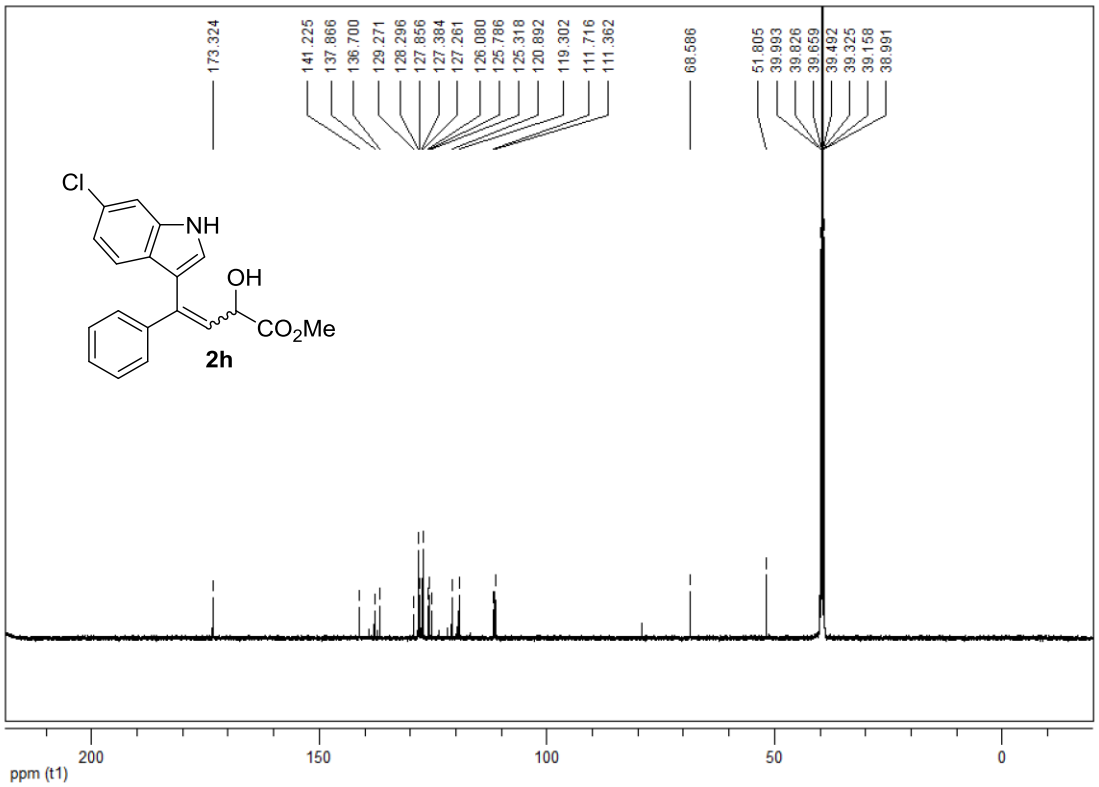
^{13}C NMR (125 MHz, $CDCl_3$)



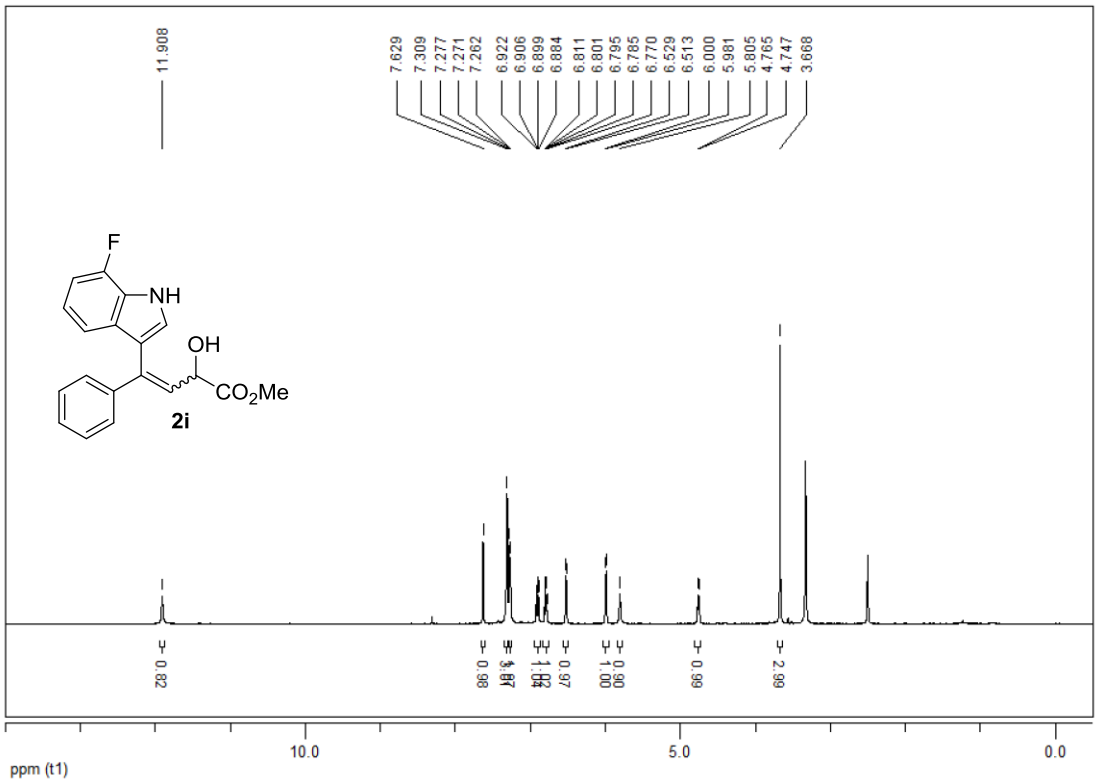
^{1}H NMR (500 MHz, DMSO-d_6)



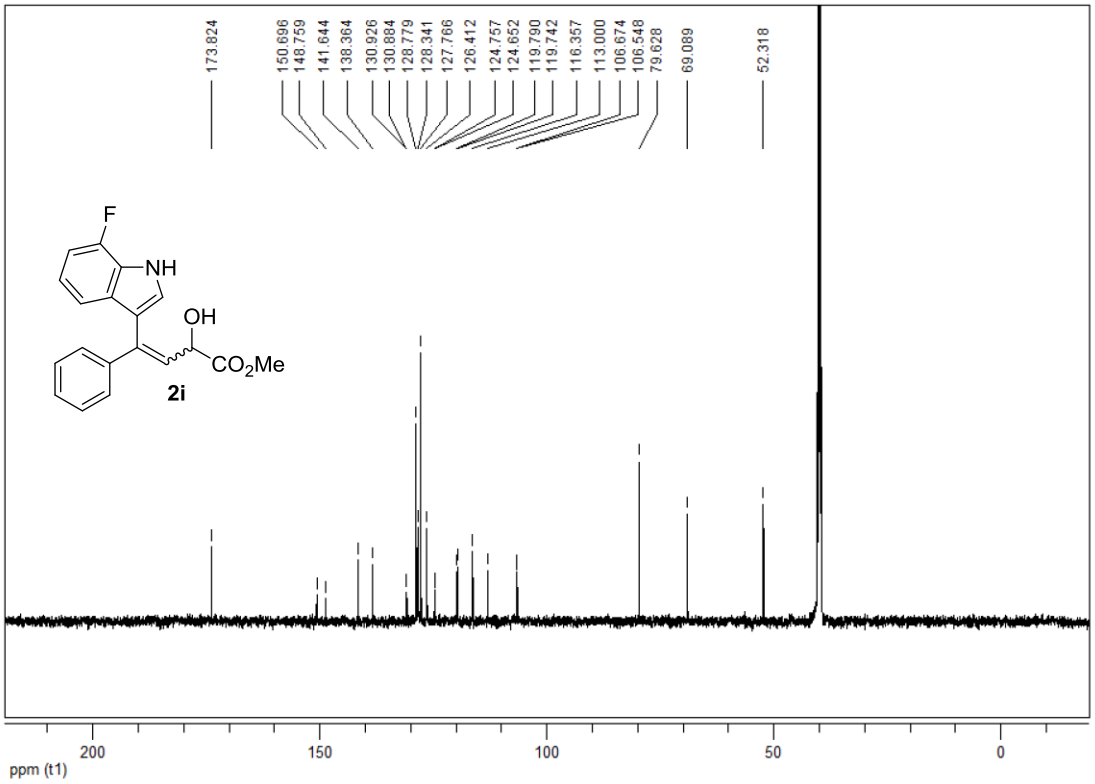
^{13}C NMR (125 MHz, DMSO-d_6)



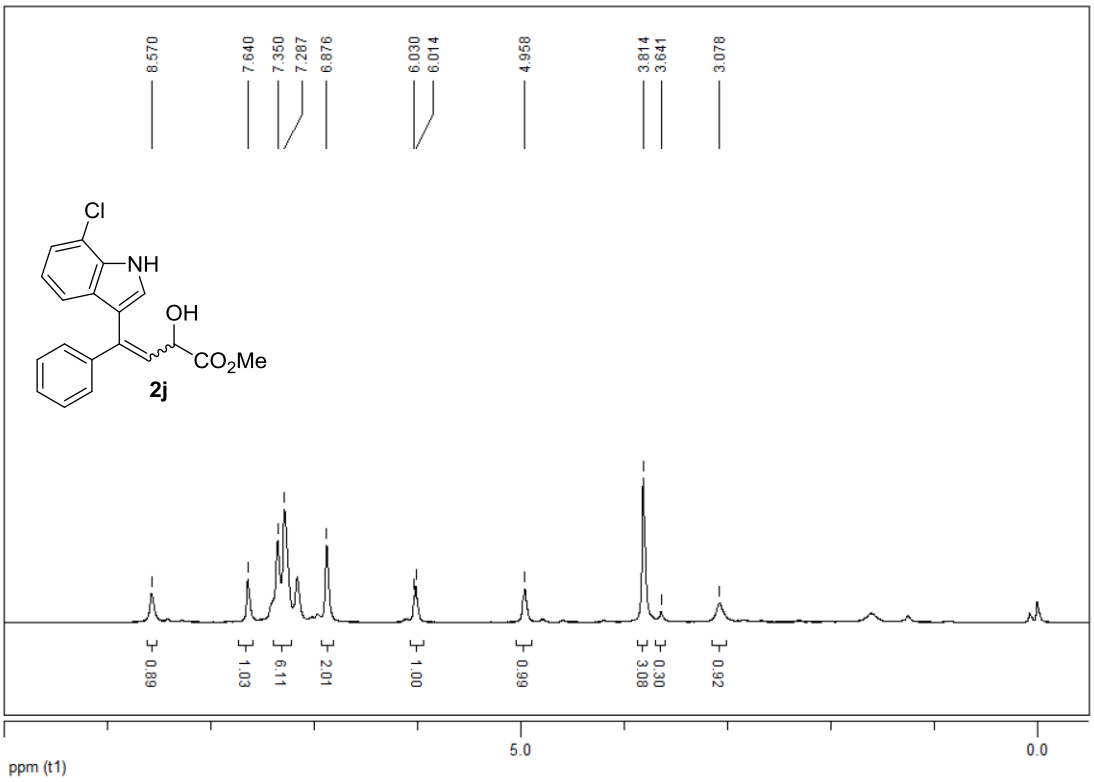
^{1}H NMR (500 MHz, DMSO-d_6)



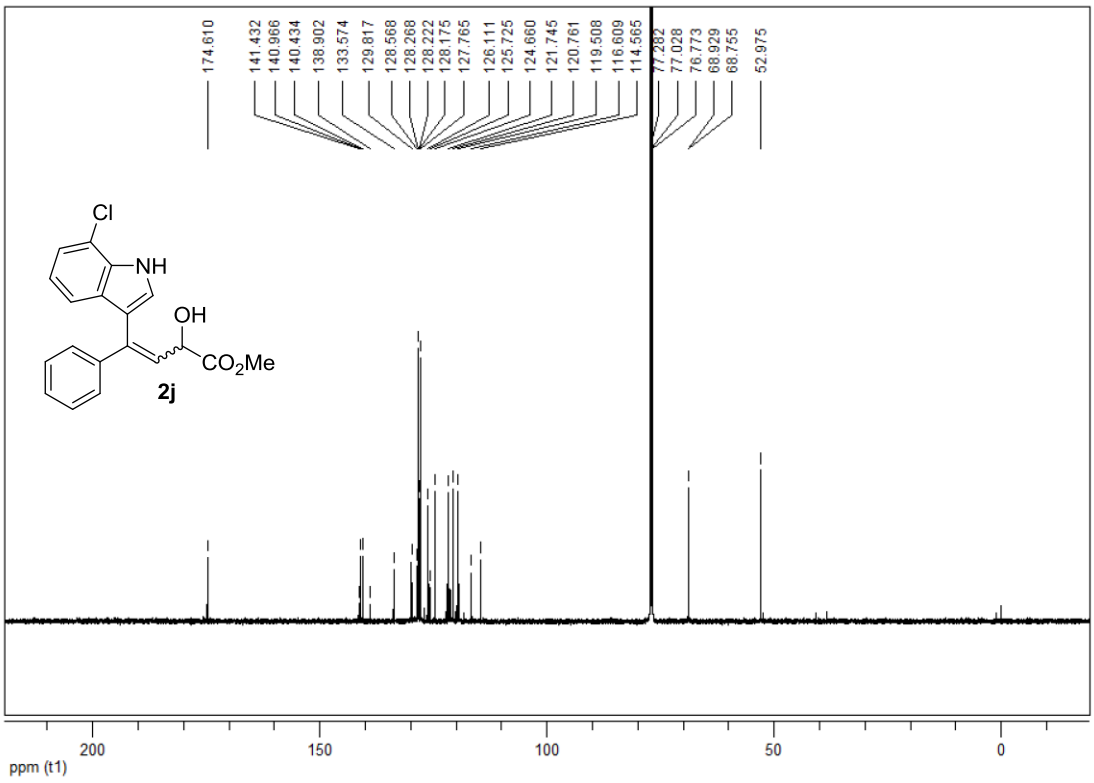
^{13}C NMR (125 MHz, DMSO-d_6)



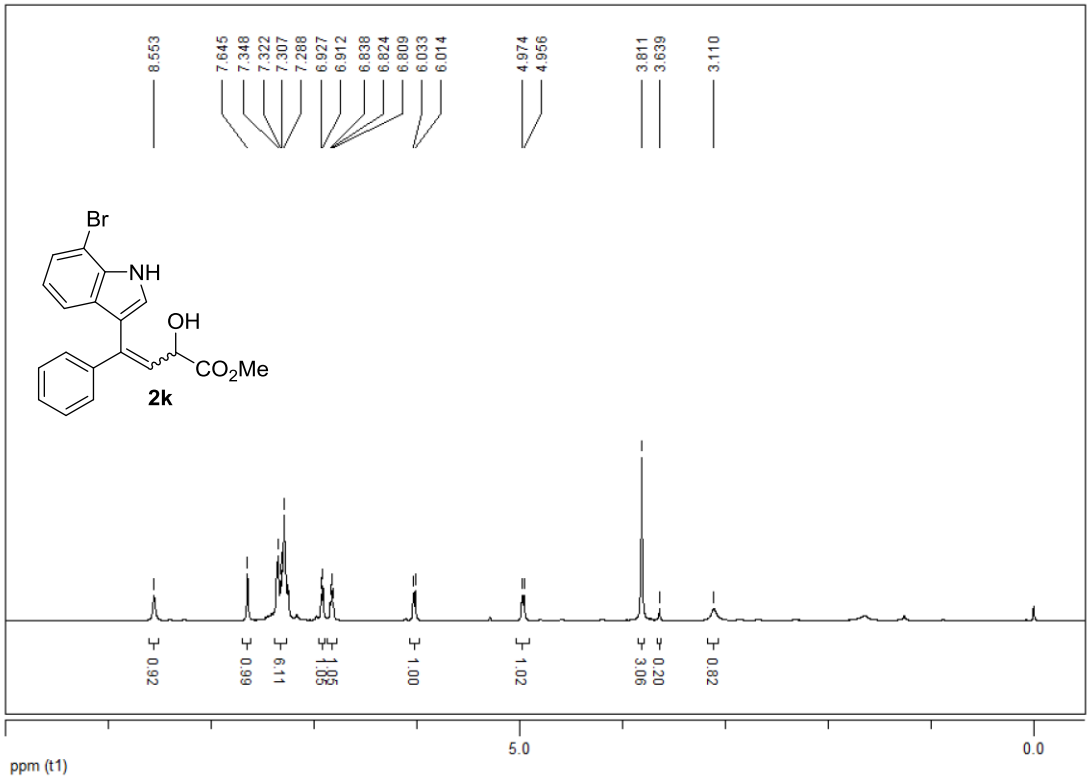
^{1}H NMR (500 MHz, $CDCl_3$)



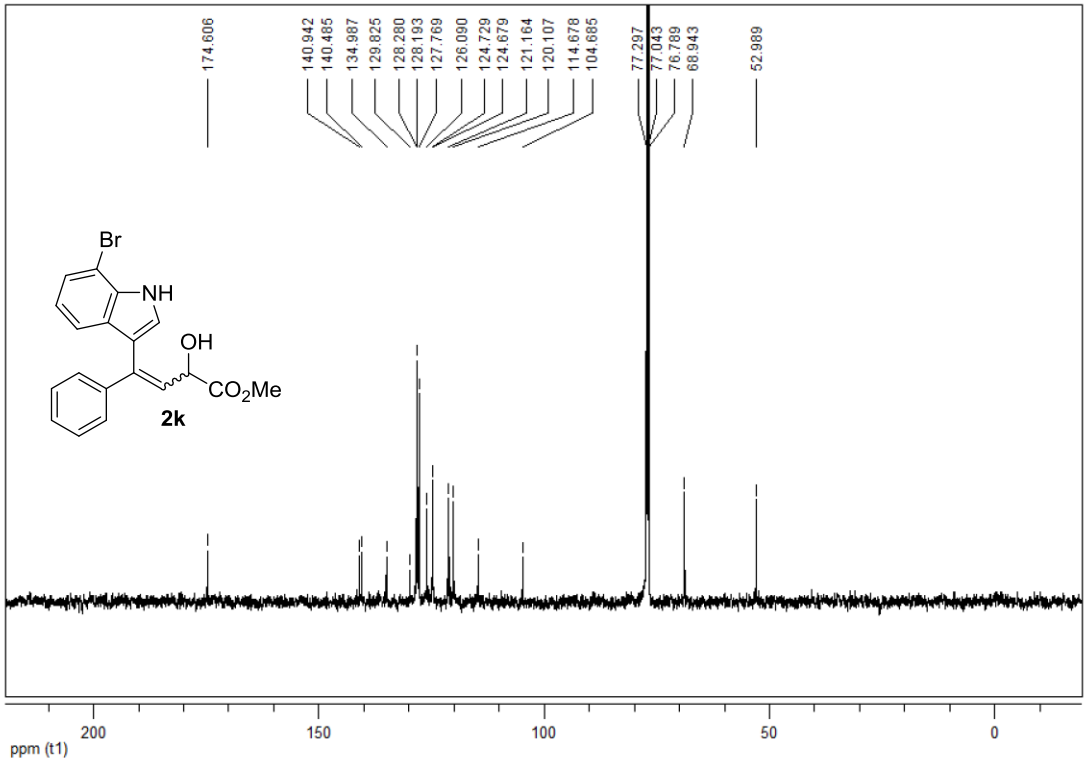
^{13}C NMR (125 MHz, $CDCl_3$)



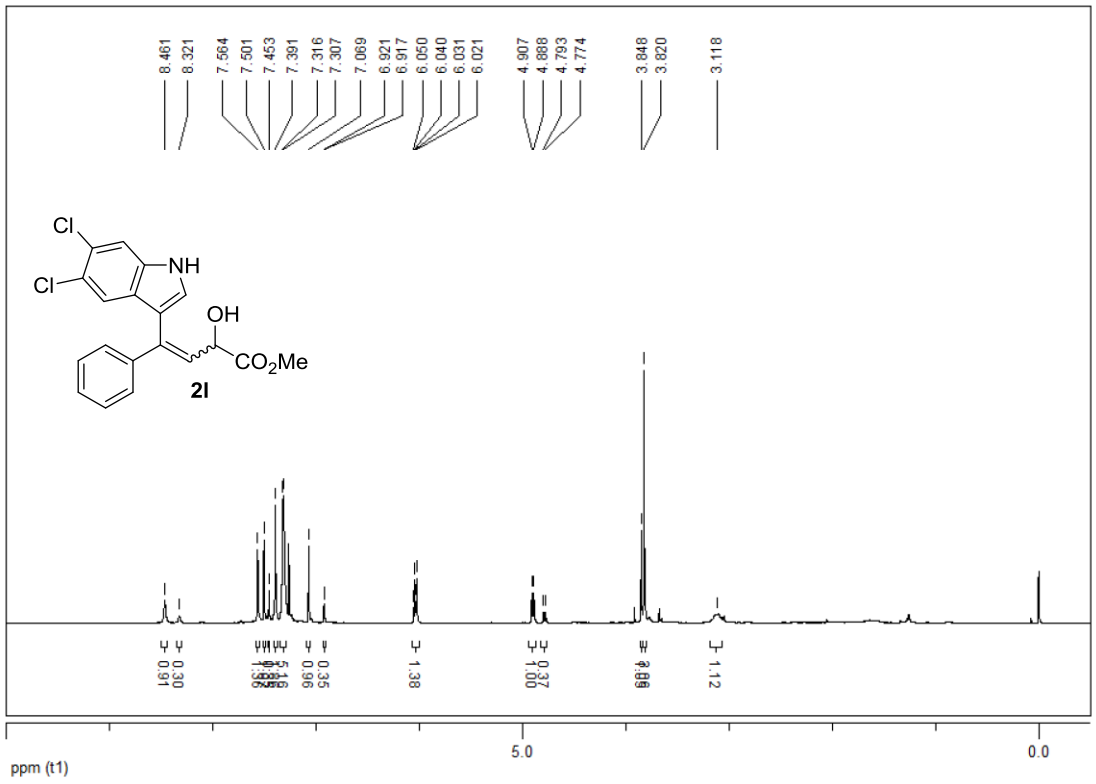
^{1}H NMR (500 MHz, $CDCl_3$)



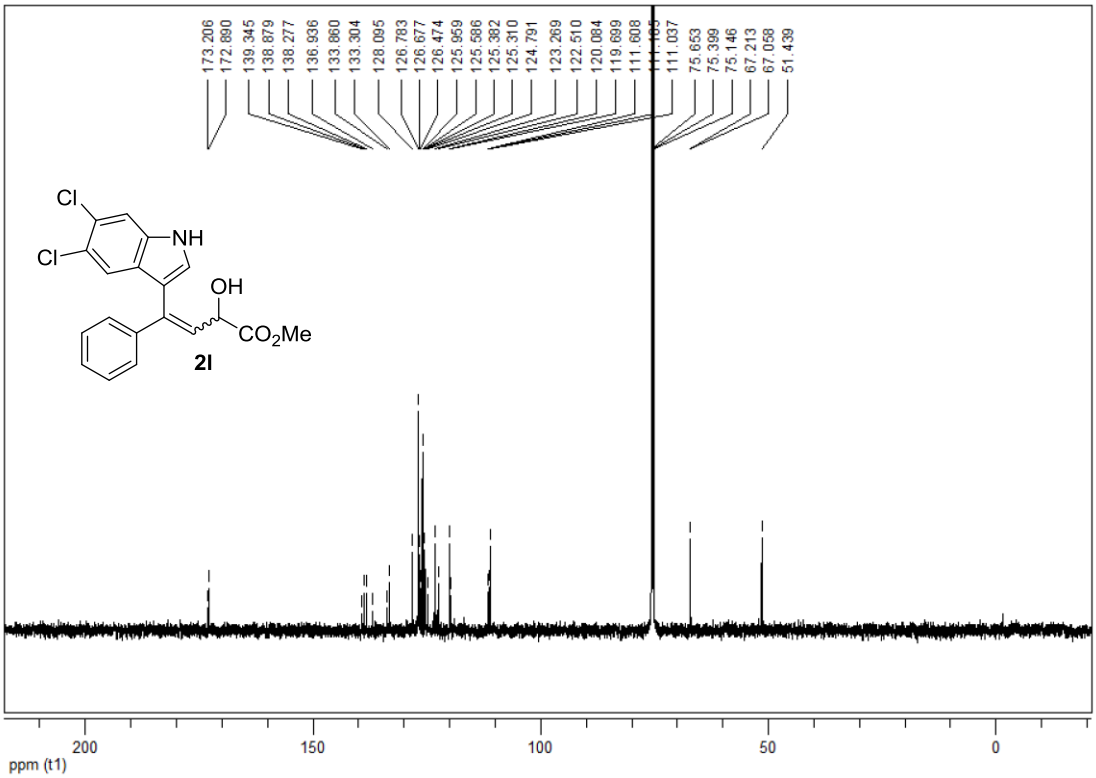
^{13}C NMR (125 MHz, $CDCl_3$)



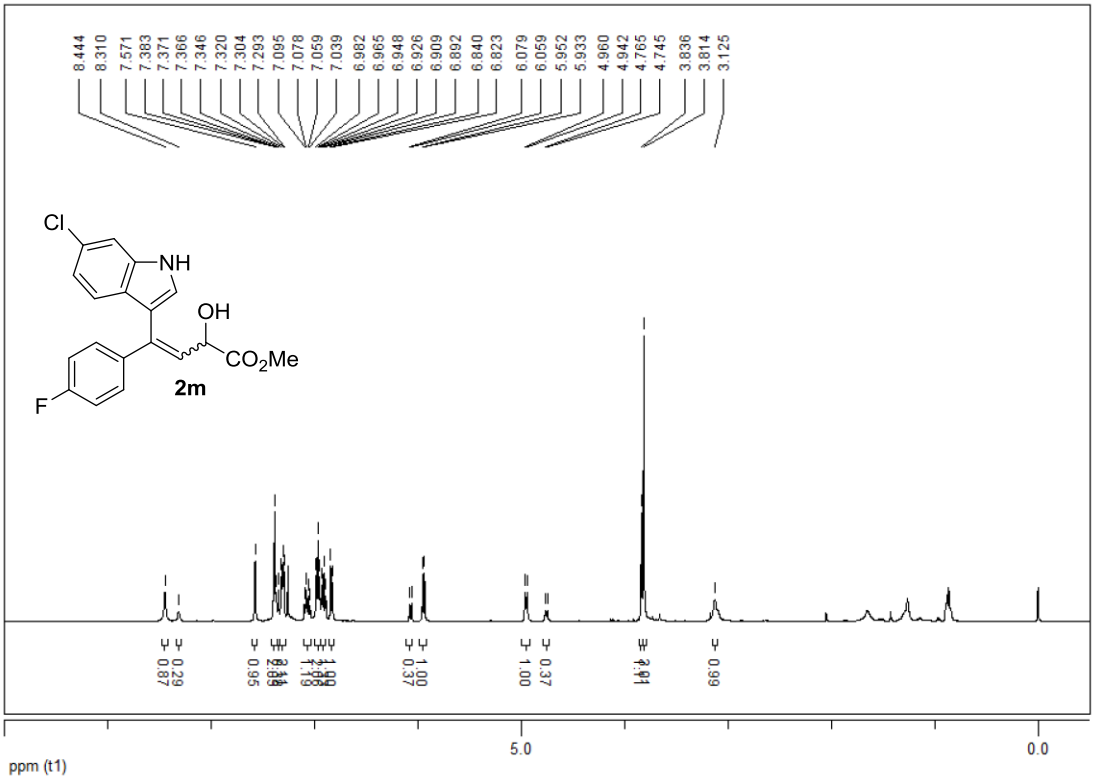
^{1}H NMR (500 MHz, $CDCl_3$)



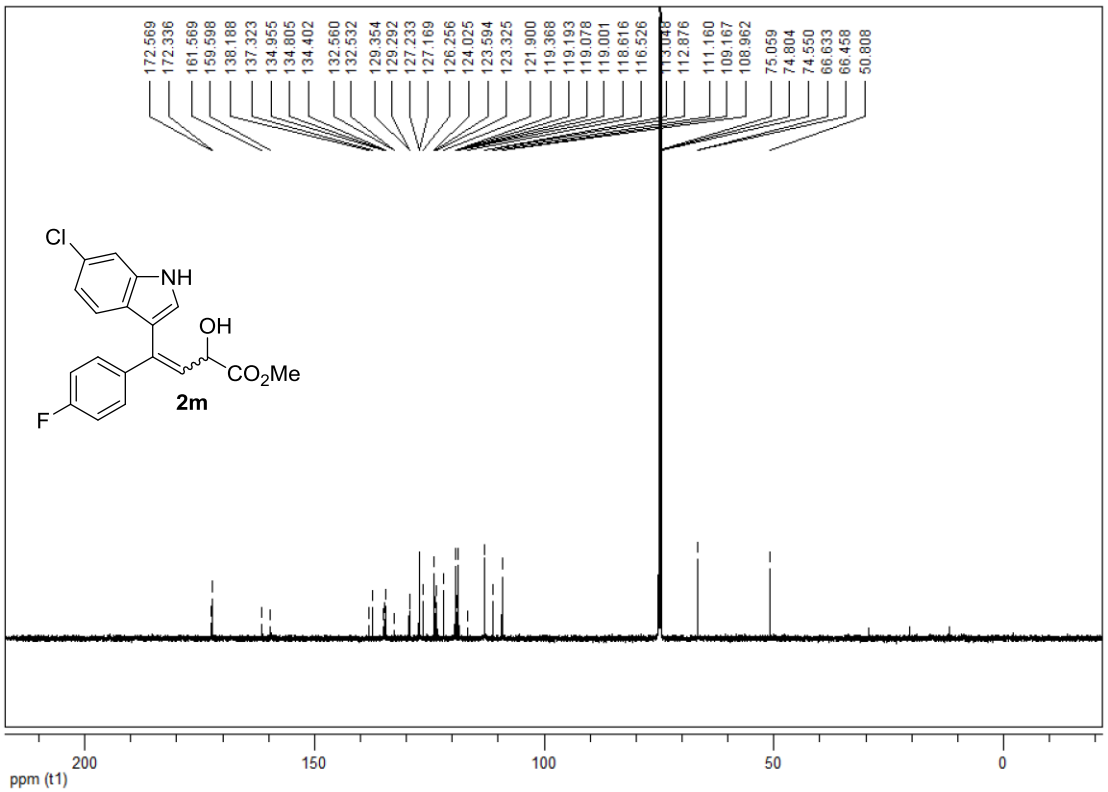
^{13}C NMR (125 MHz, $CDCl_3$)



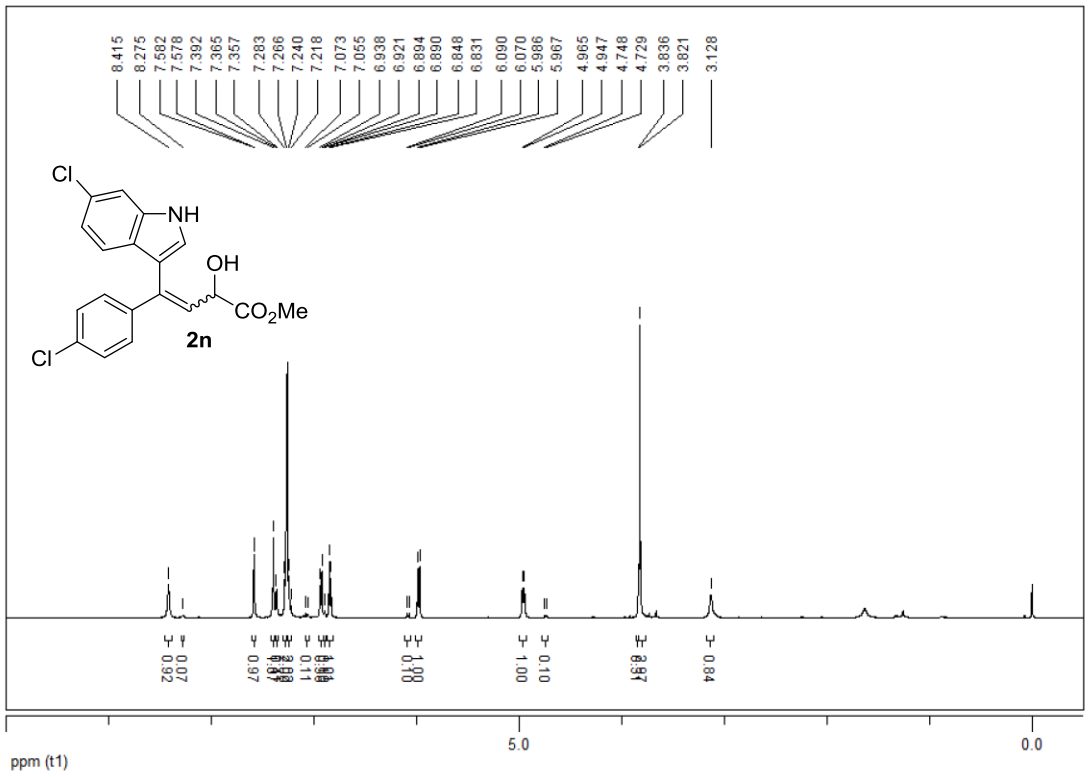
^{1}H NMR (500 MHz, $CDCl_3$)



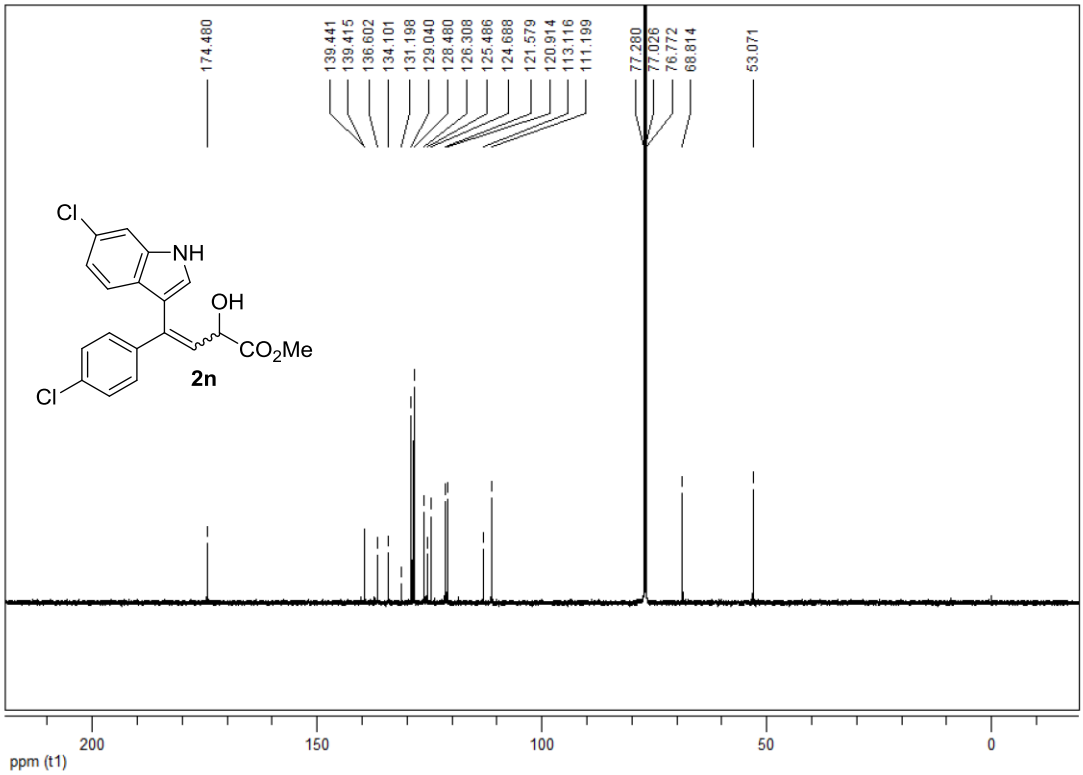
^{13}C NMR (125 MHz, $CDCl_3$)



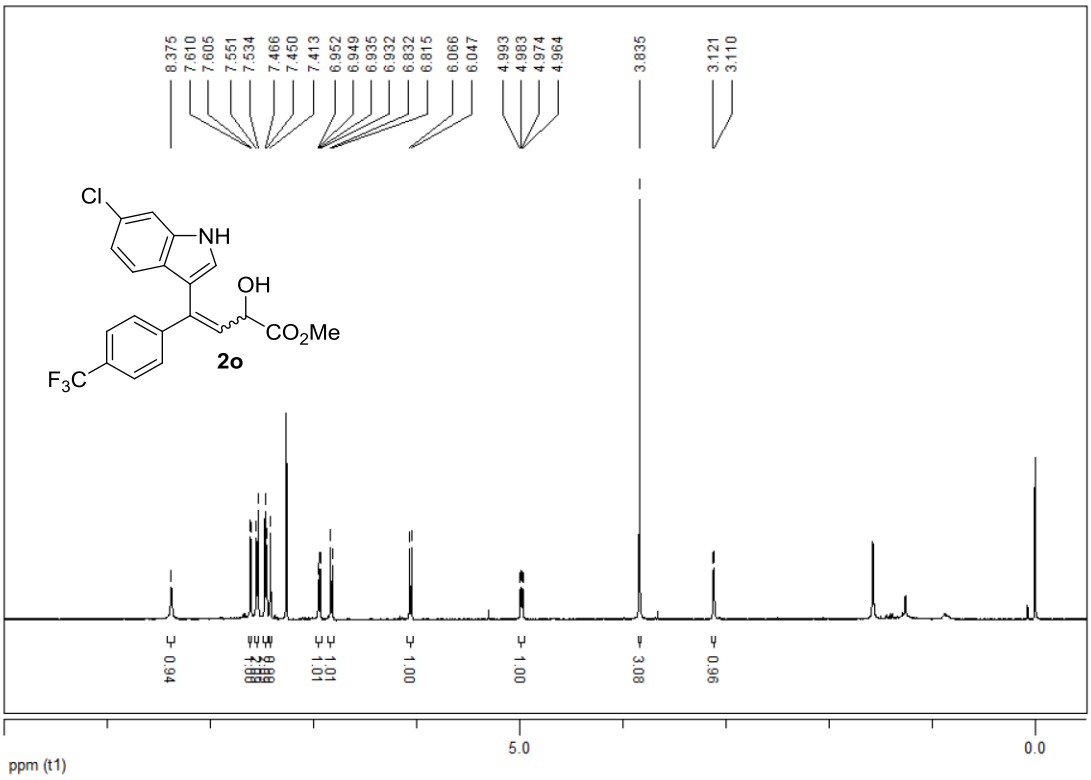
^{1}H NMR (500 MHz, $CDCl_3$)



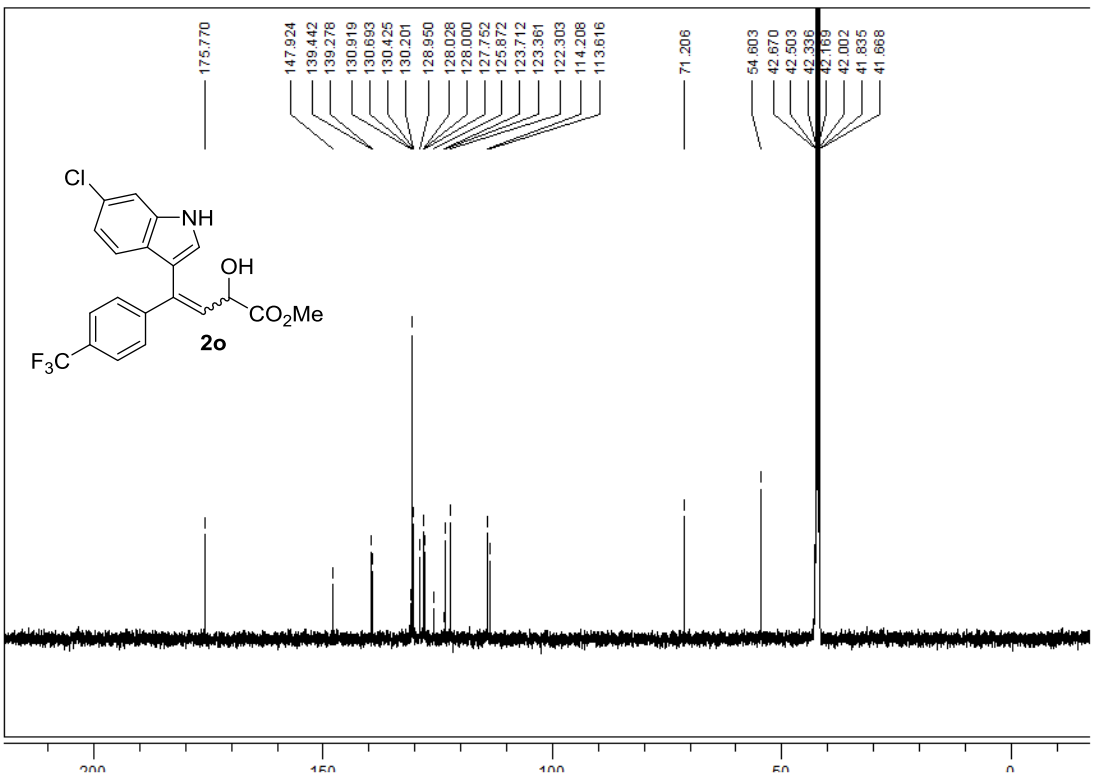
^{13}C NMR (125 MHz, $CDCl_3$)



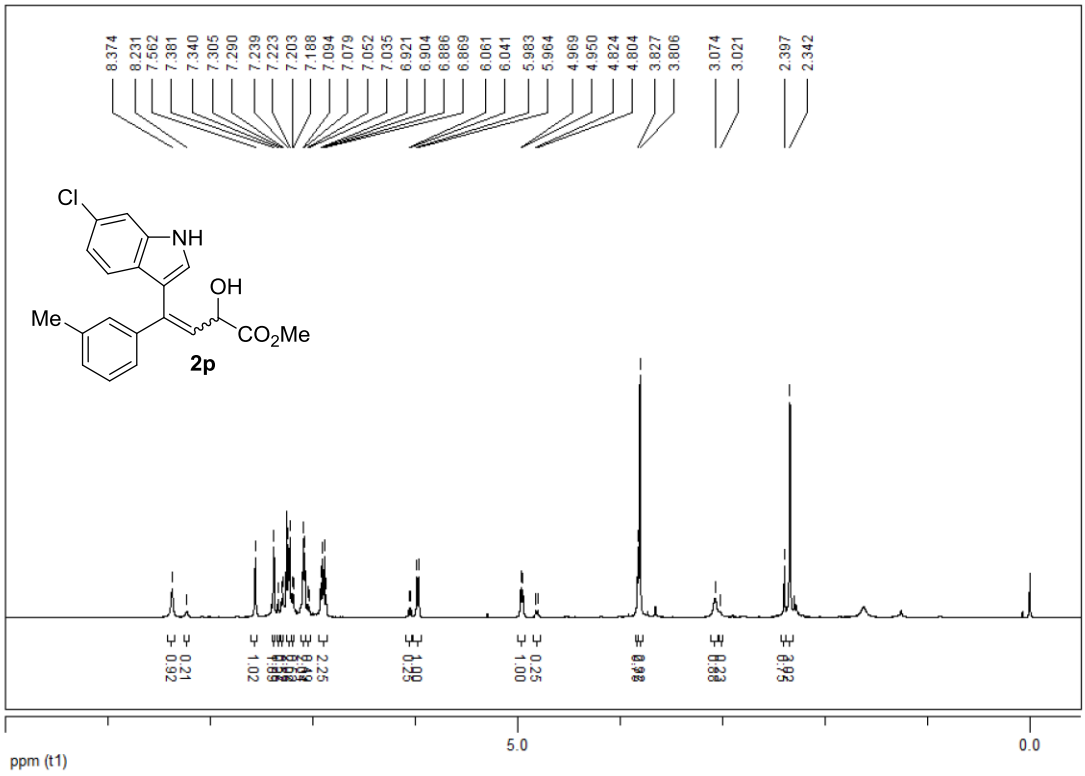
^{1}H NMR (500 MHz, $CDCl_3$)



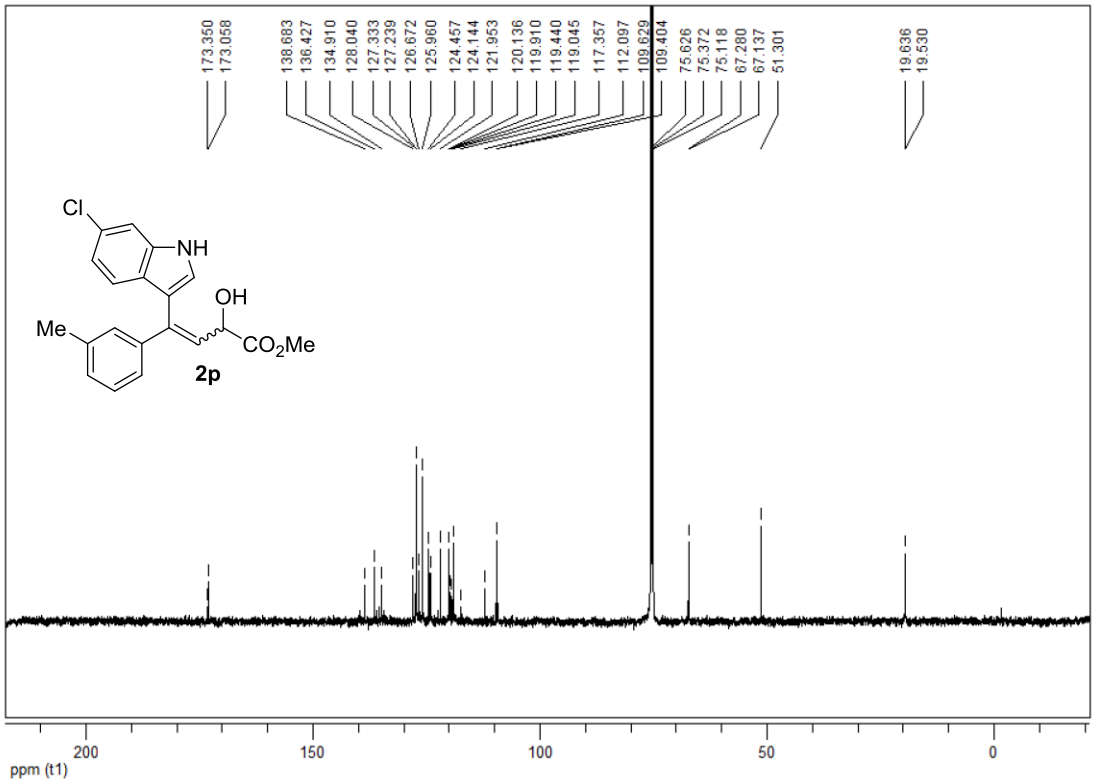
^{13}C NMR (125 MHz, DMSO-d_6)



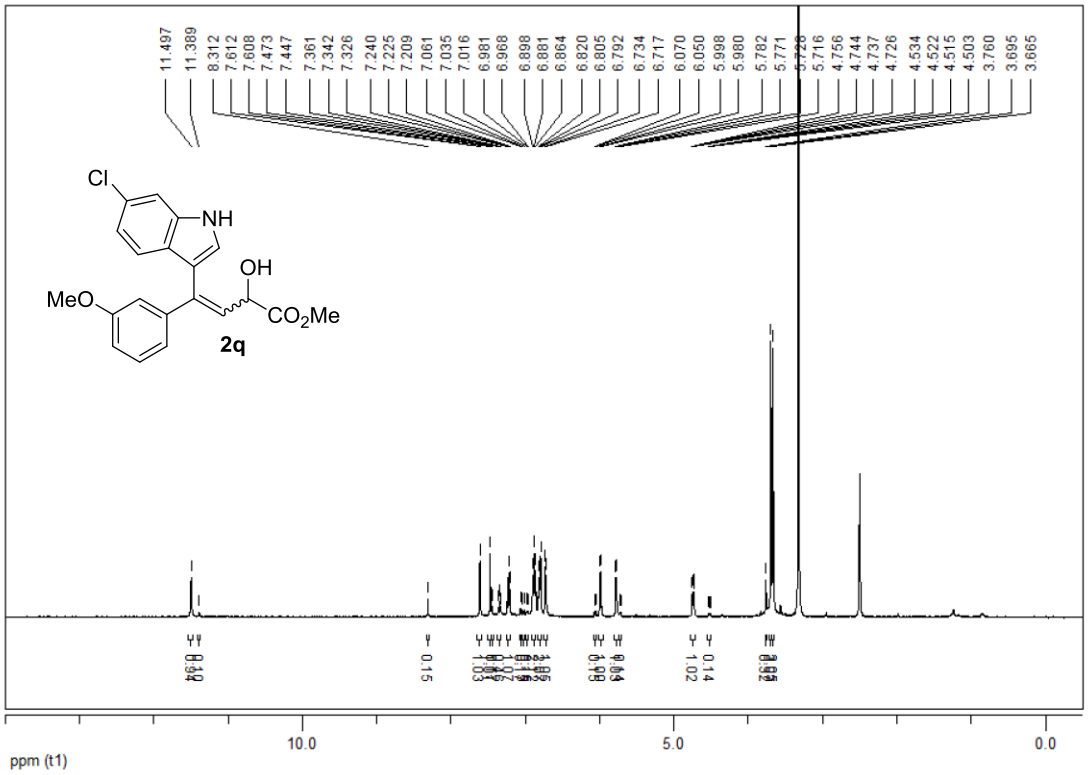
^{1}H NMR (500 MHz, $CDCl_3$)



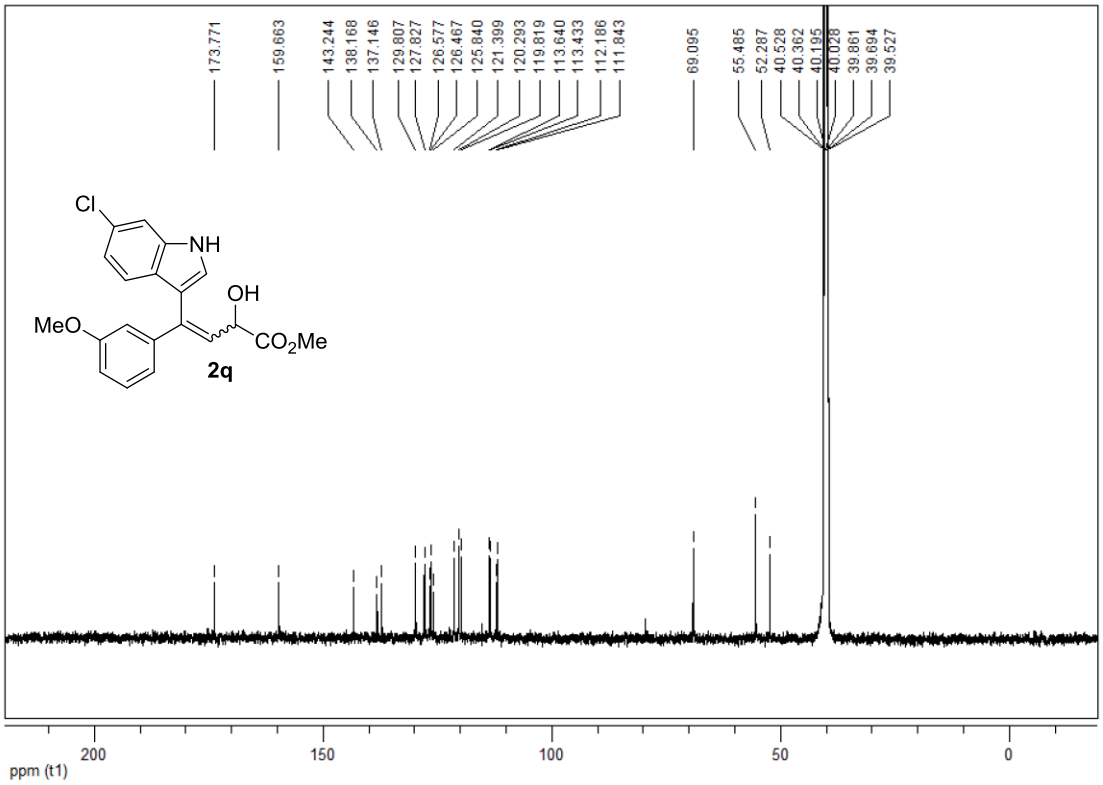
^{13}C NMR (125 MHz, $CDCl_3$)



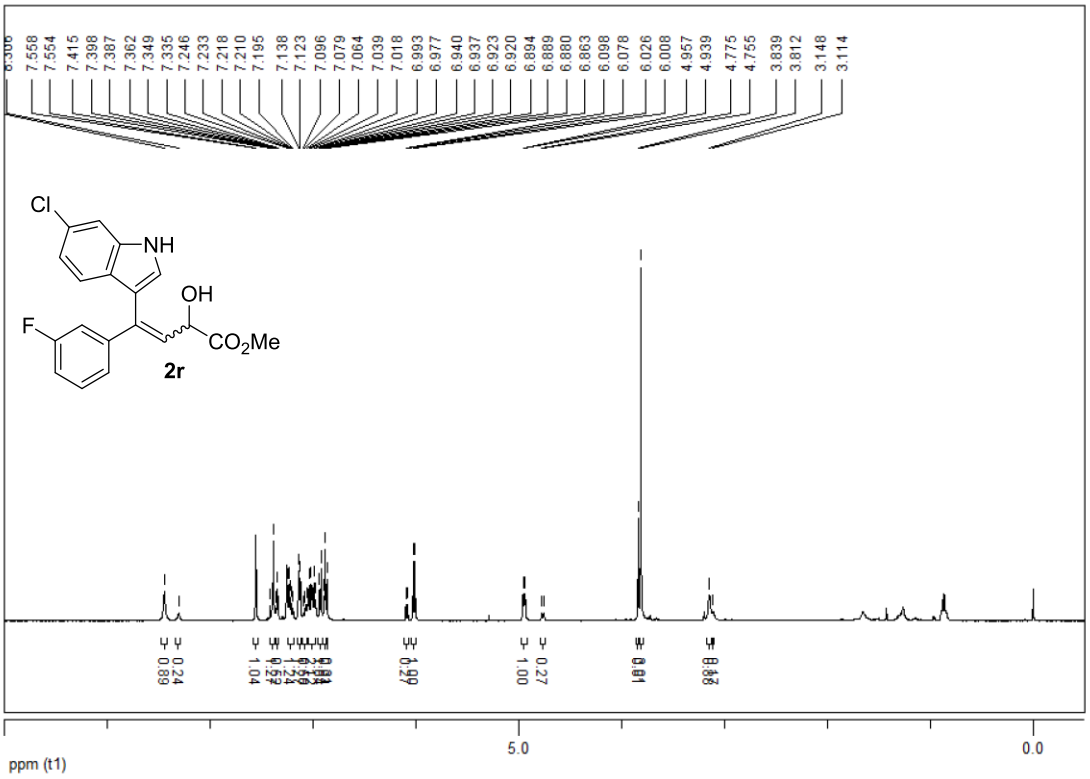
^{1}H NMR (500 MHz, DMSO-d_6)



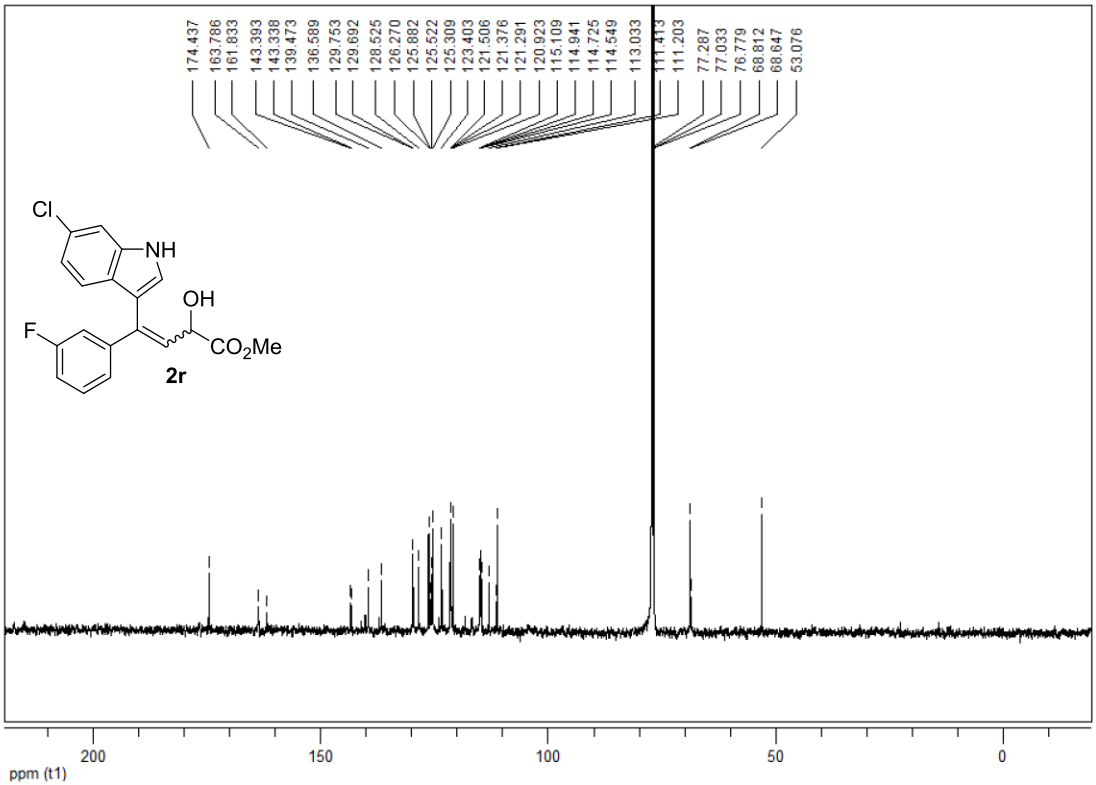
^{13}C NMR (125 MHz, DMSO-d_6)



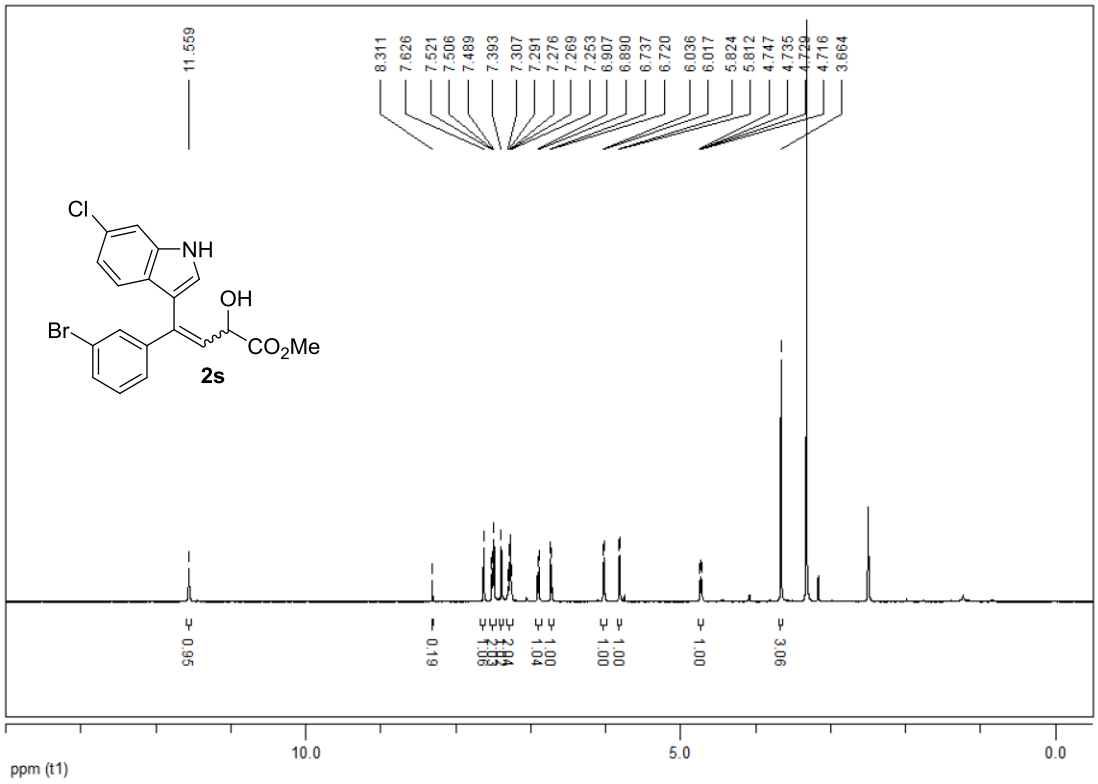
^{1}H NMR (500 MHz, $CDCl_3$)



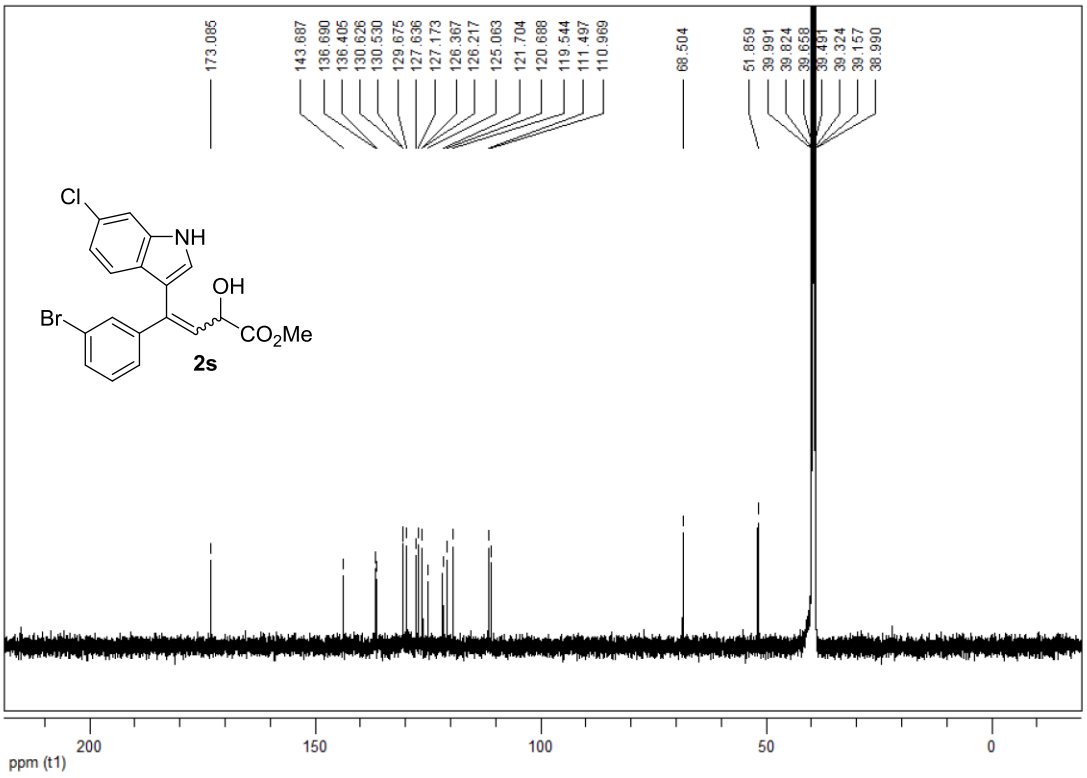
^{13}C NMR (125 MHz, $CDCl_3$)



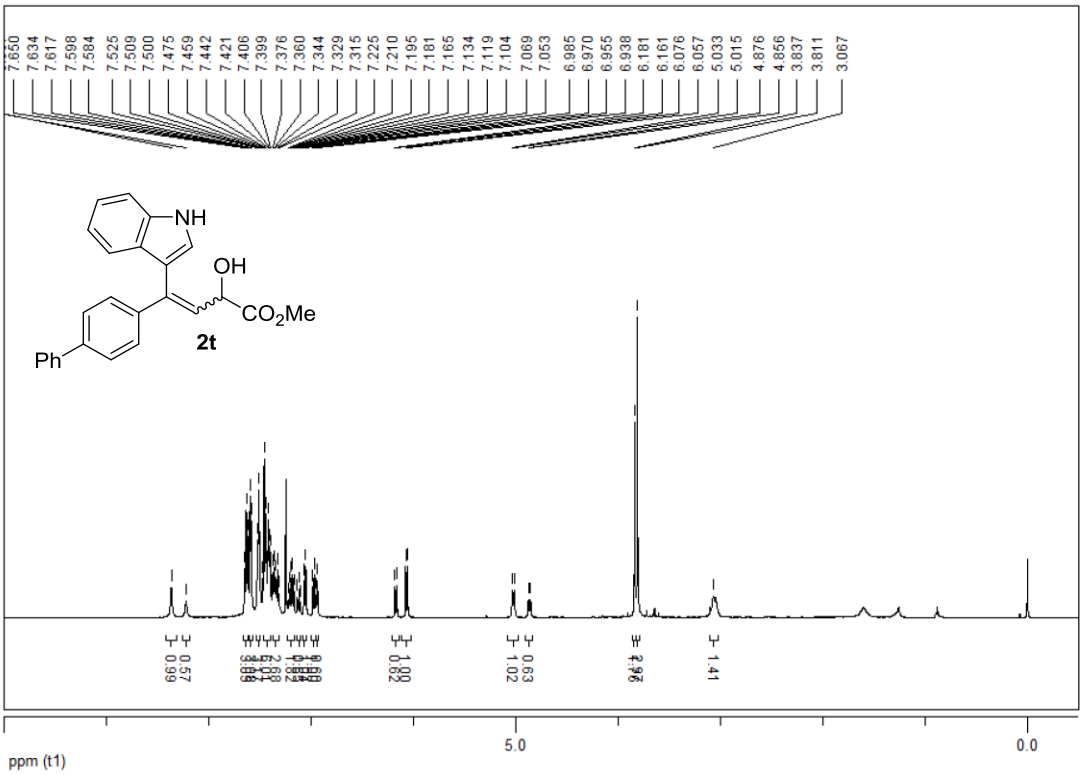
^{1}H NMR (500 MHz, DMSO-d_6)



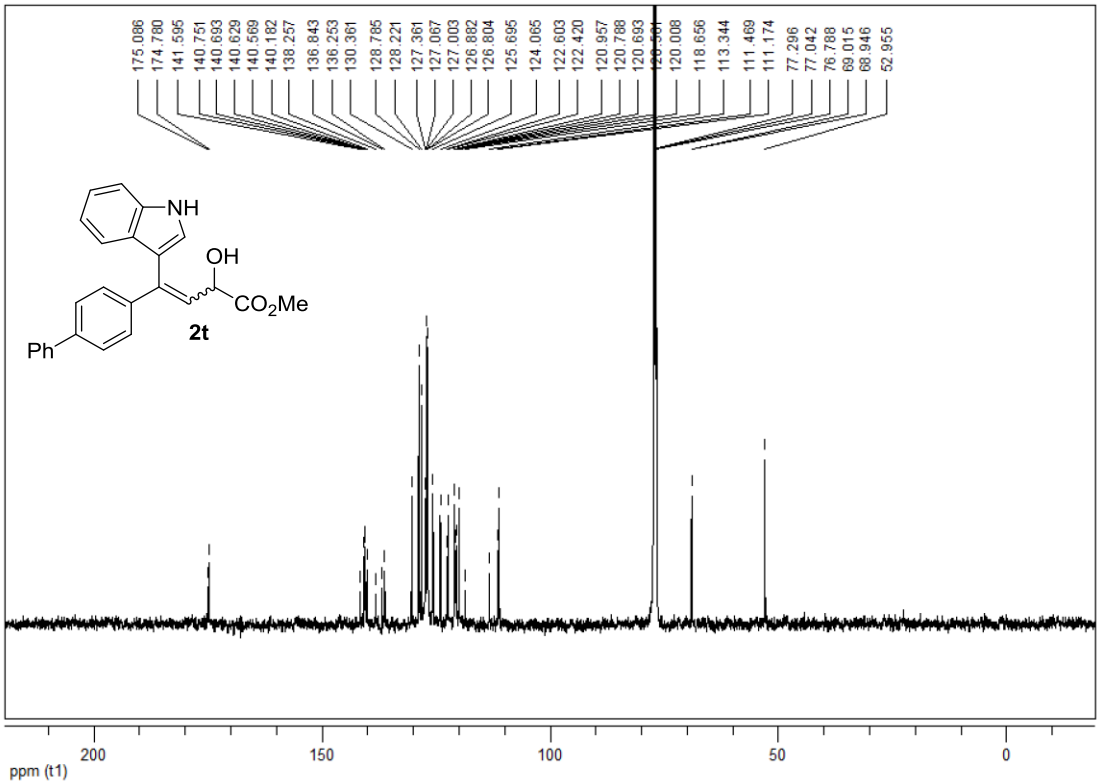
^{13}C NMR (125 MHz, DMSO-d_6)



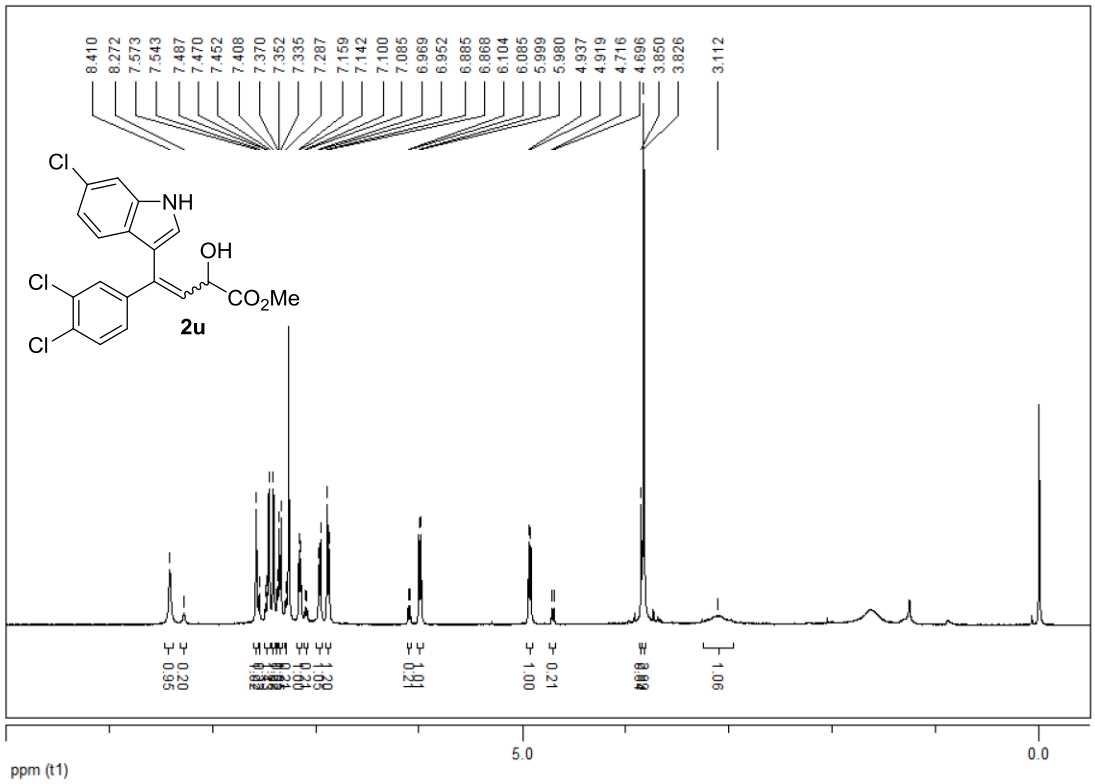
^{1}H NMR (500 MHz, $CDCl_3$)



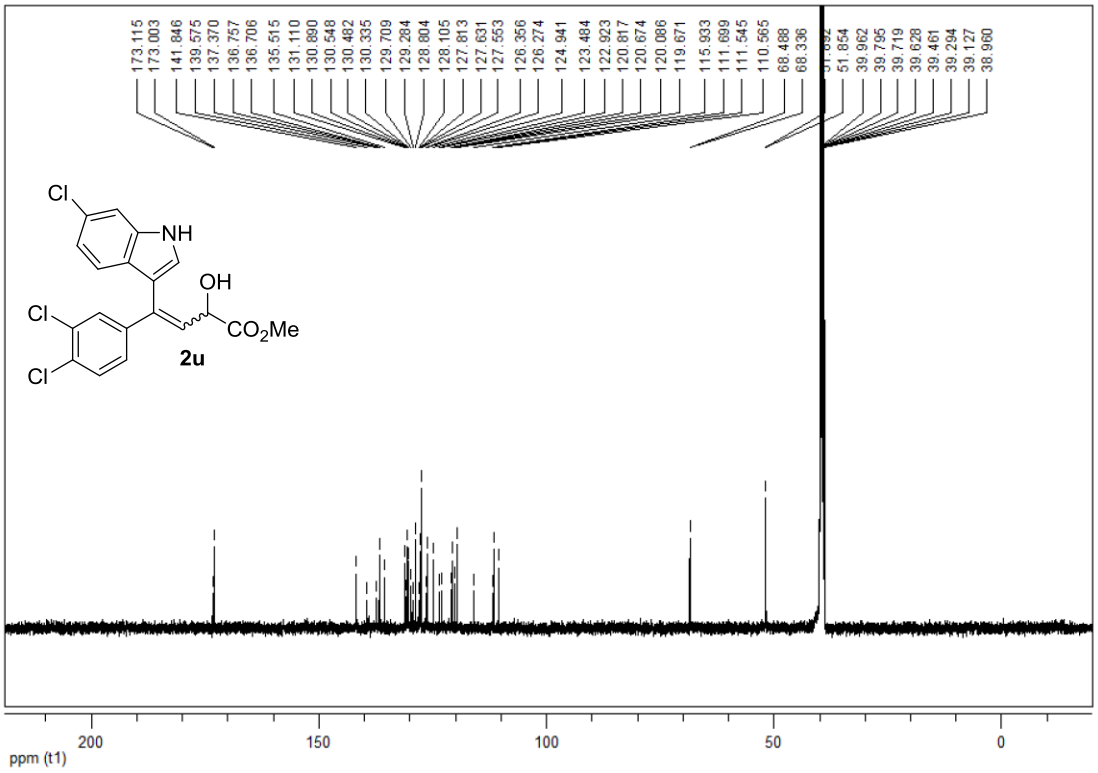
^{13}C NMR (125 MHz, $CDCl_3$)



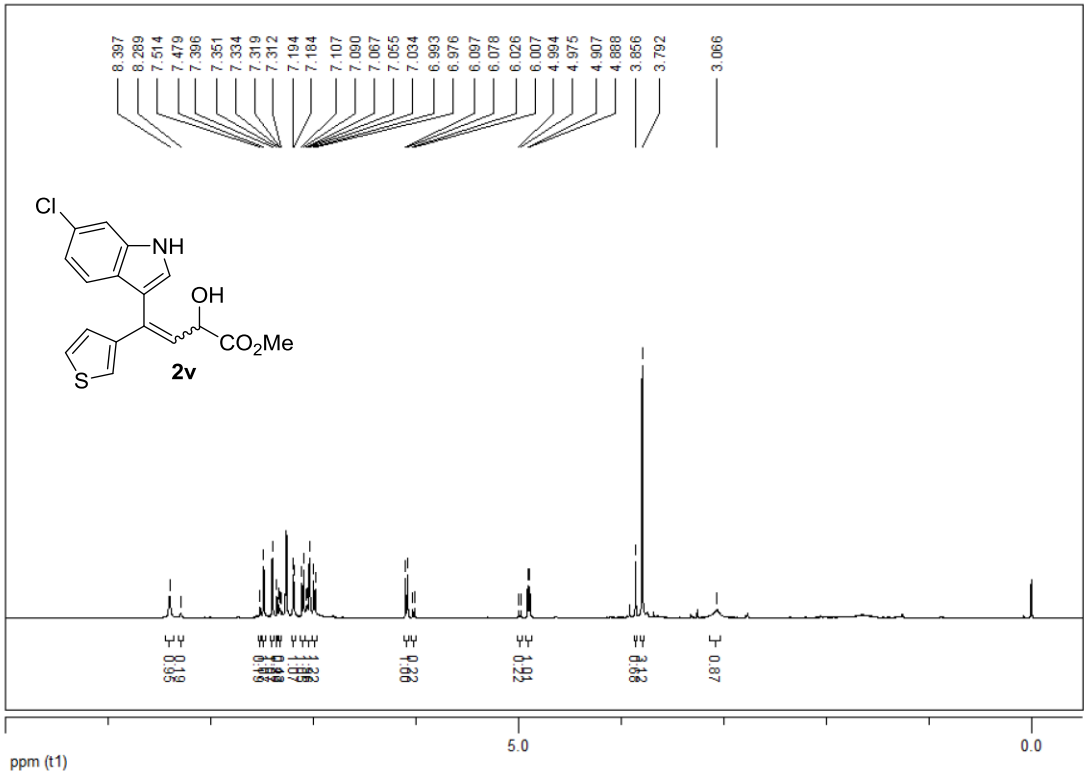
^{1}H NMR (500 MHz, $CDCl_3$)



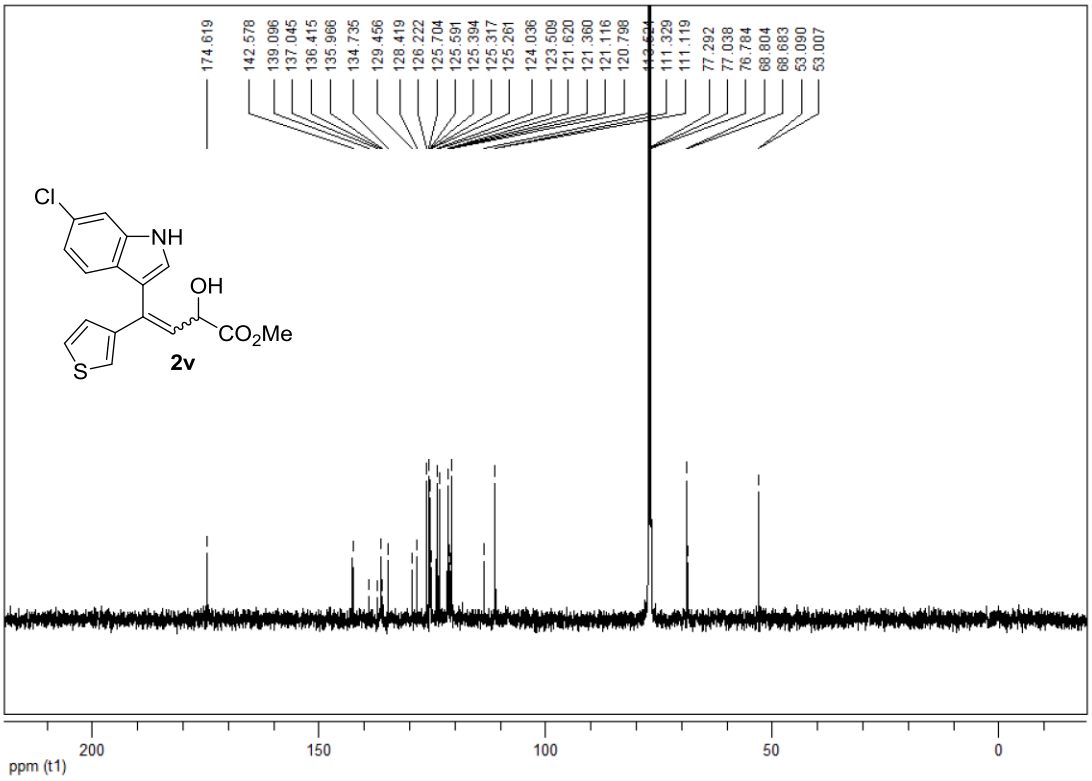
^{13}C NMR (125 MHz, DMSO-d_6)



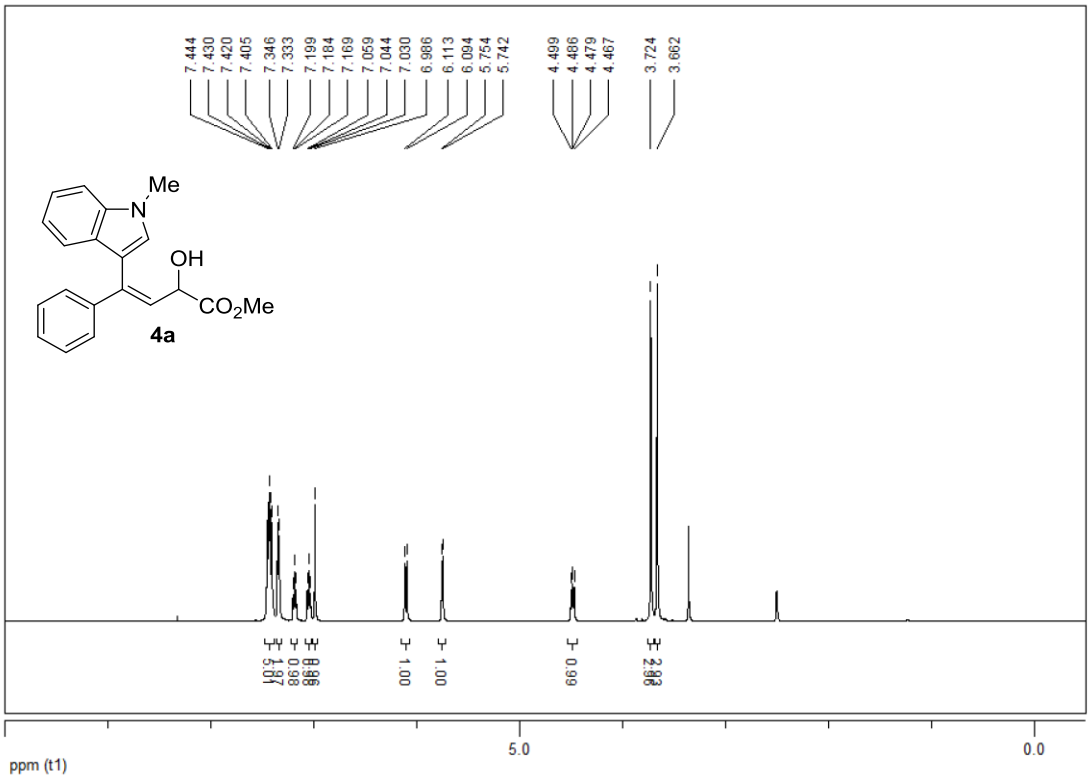
^{1}H NMR (500 MHz, $CDCl_3$)



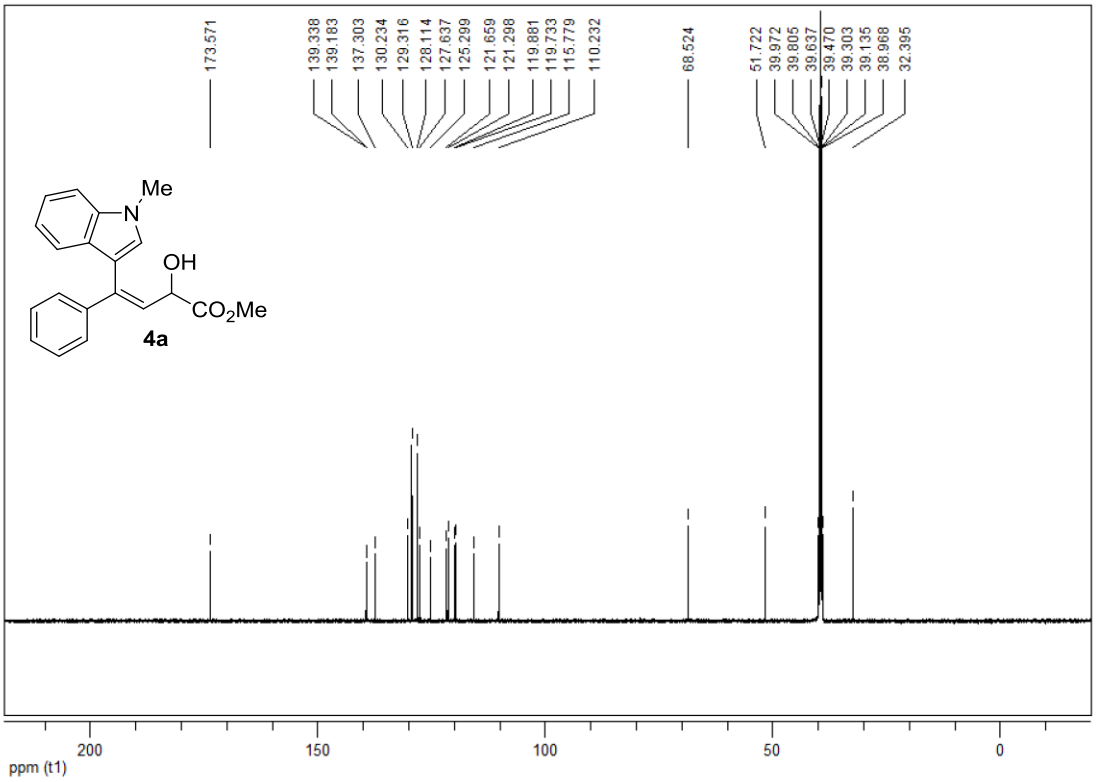
^{13}C NMR (125 MHz, $CDCl_3$)



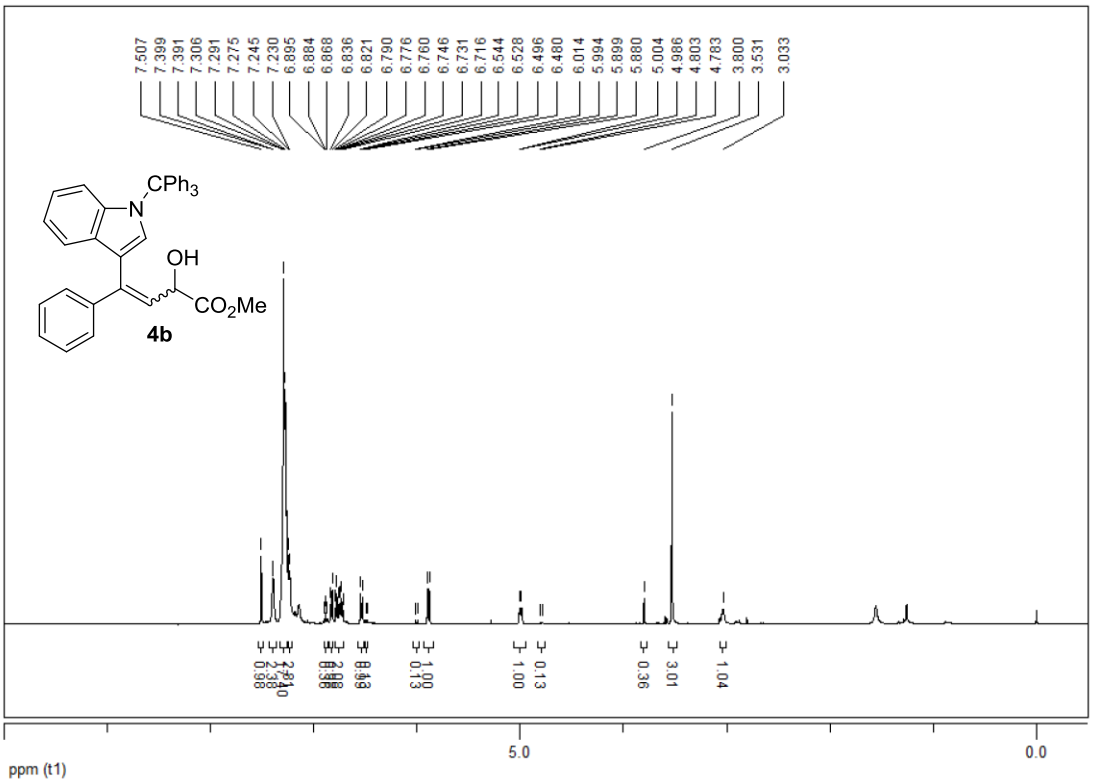
^{1}H NMR (500 MHz, DMSO-d_6)



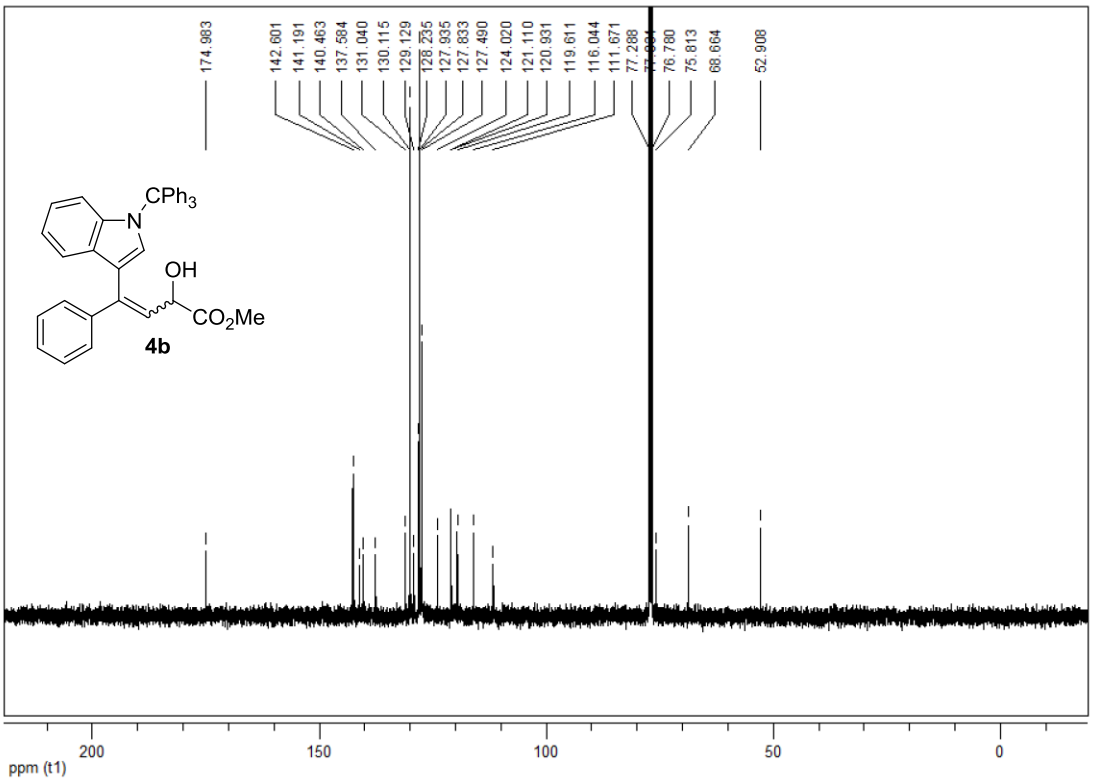
^{13}C NMR (125 MHz, DMSO-d_6)



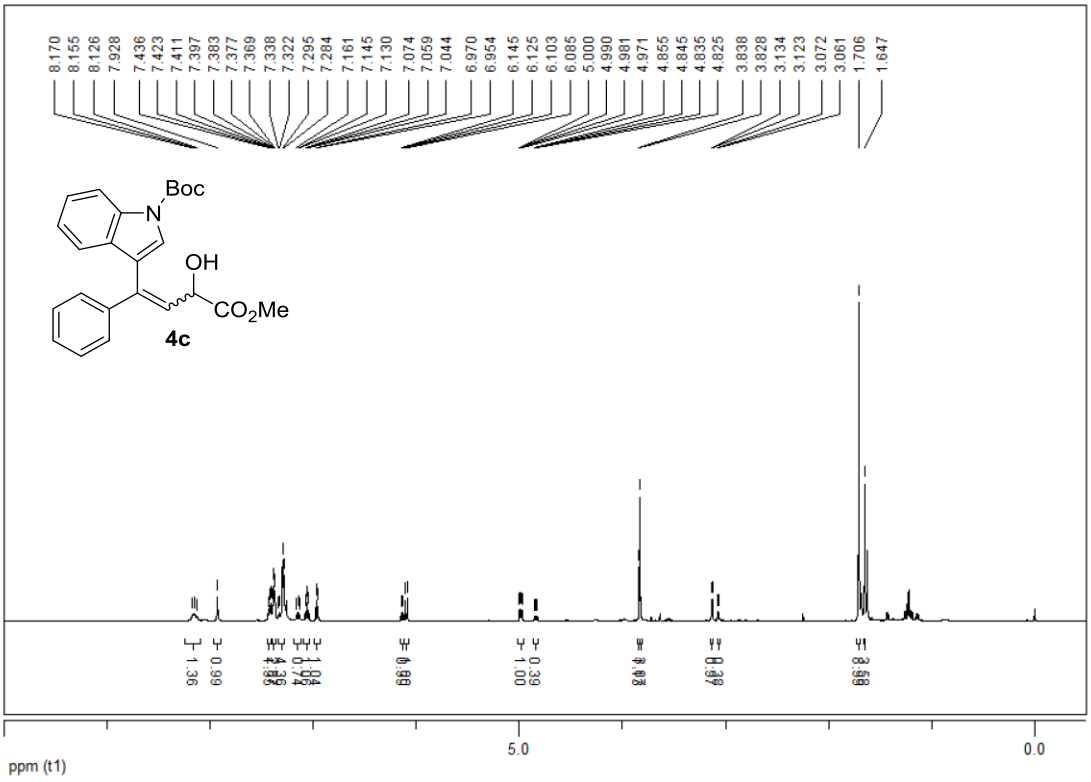
^{1}H NMR (500 MHz, $CDCl_3$)



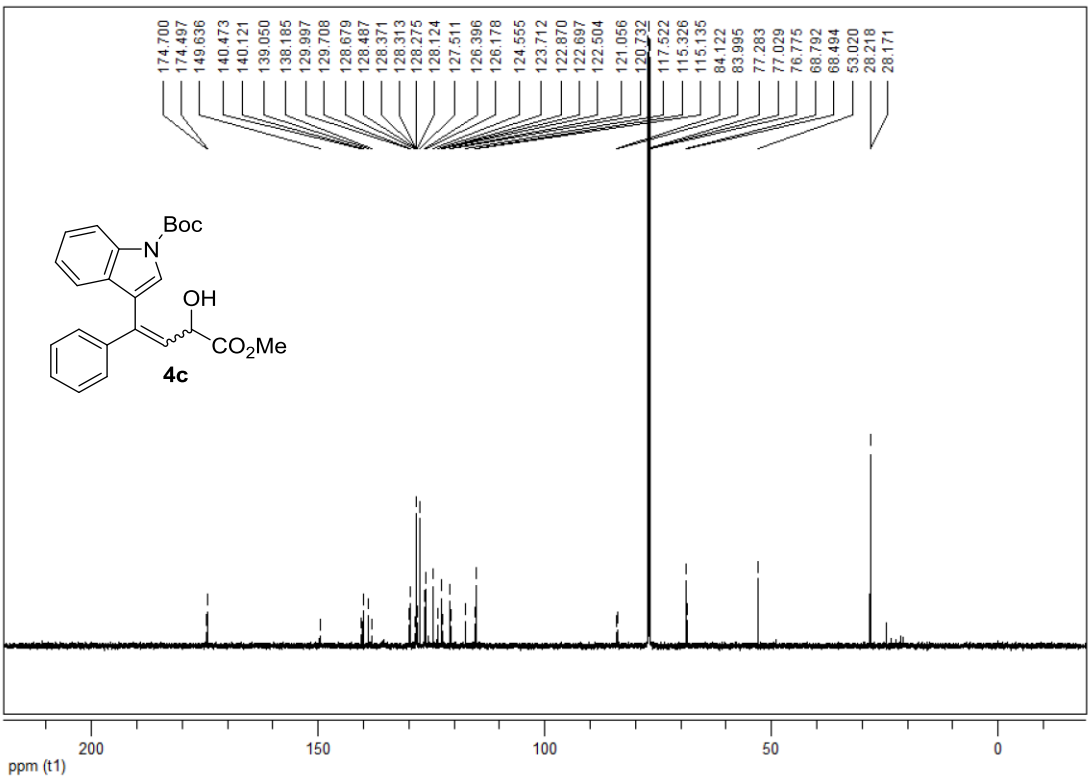
^{13}C NMR (125 MHz, $CDCl_3$)



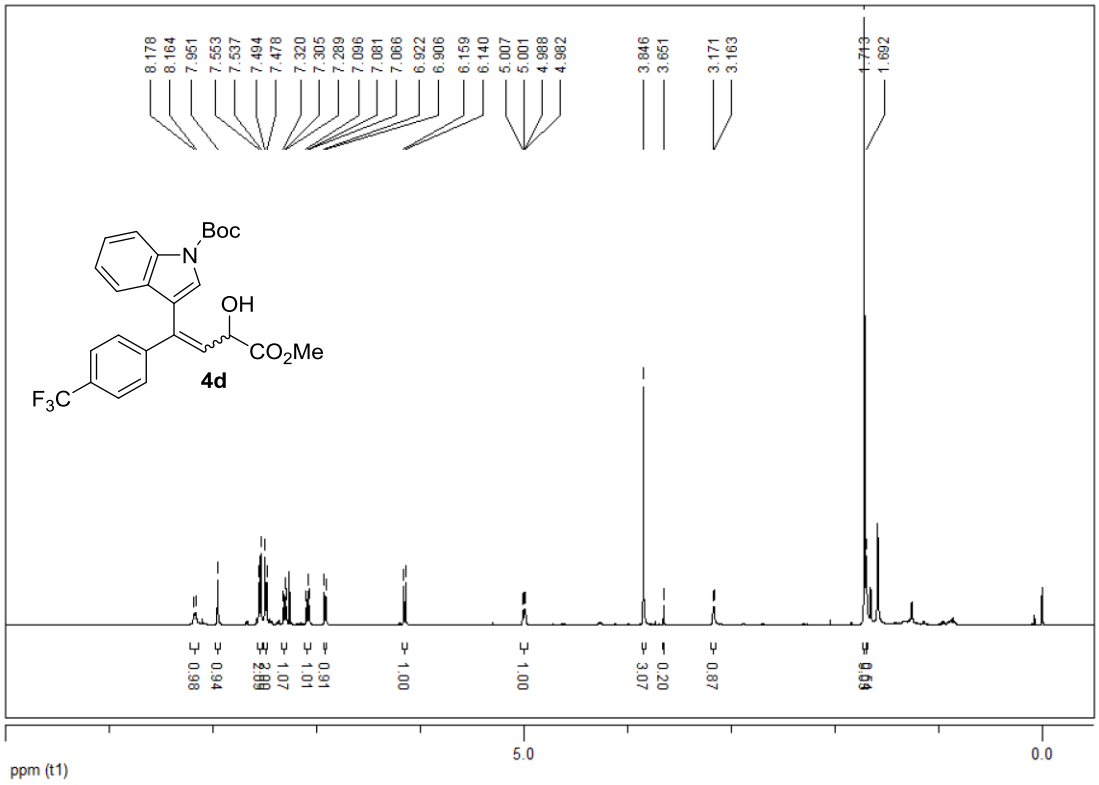
^{1}H NMR (500 MHz, $CDCl_3$)



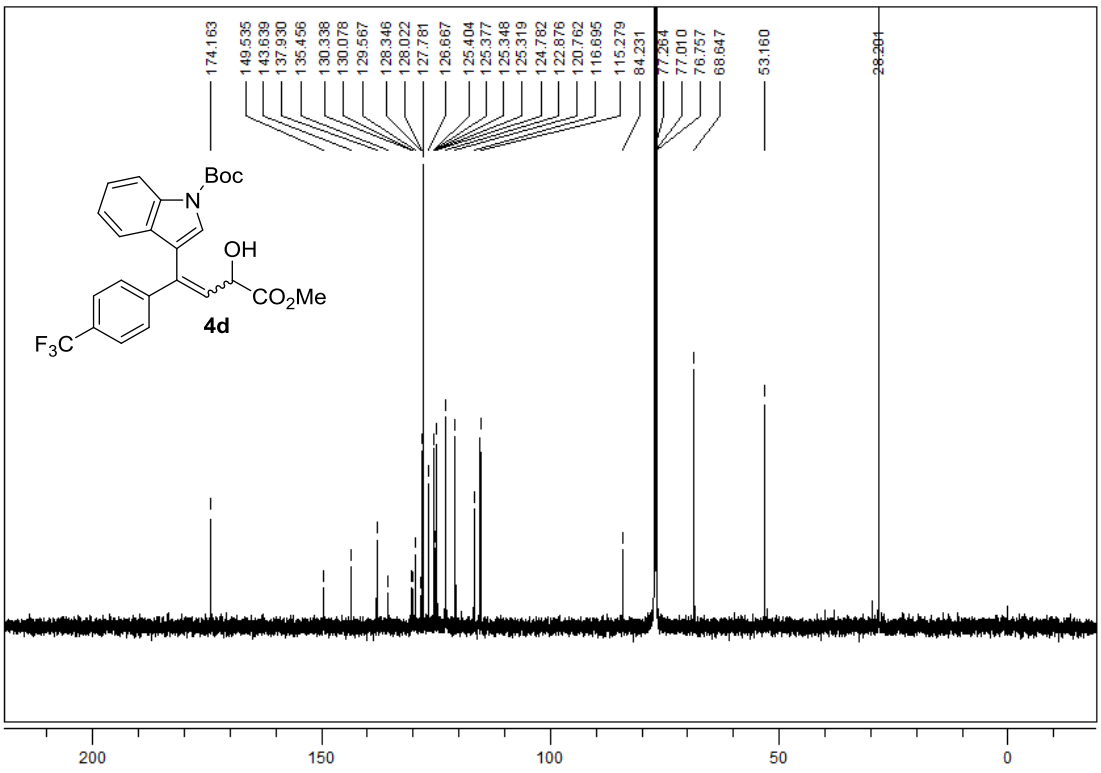
^{13}C NMR (125 MHz, $CDCl_3$)



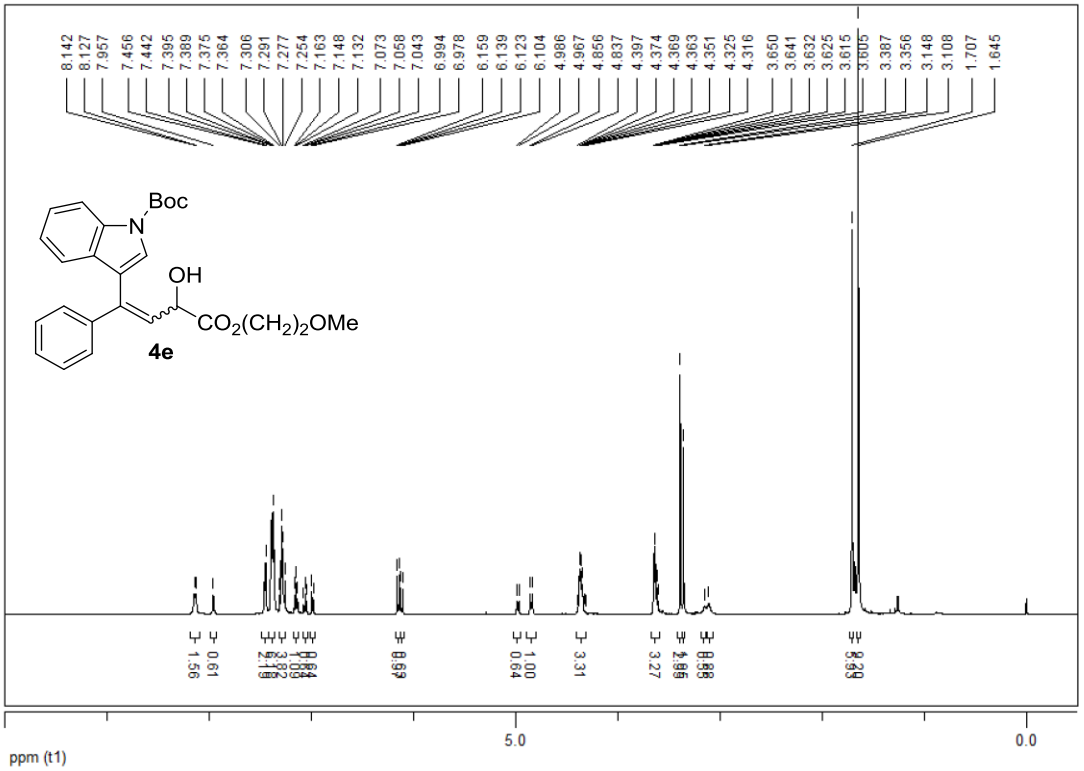
^{1}H NMR (500 MHz, $CDCl_3$)



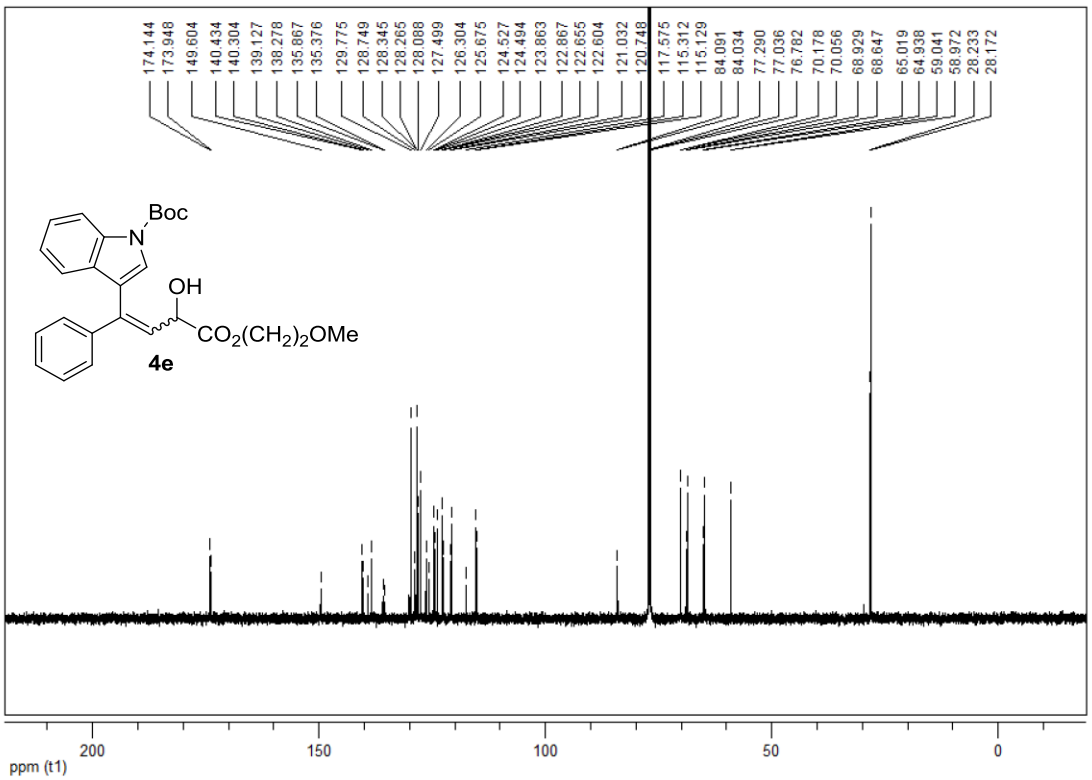
^{13}C NMR (125 MHz, $CDCl_3$)



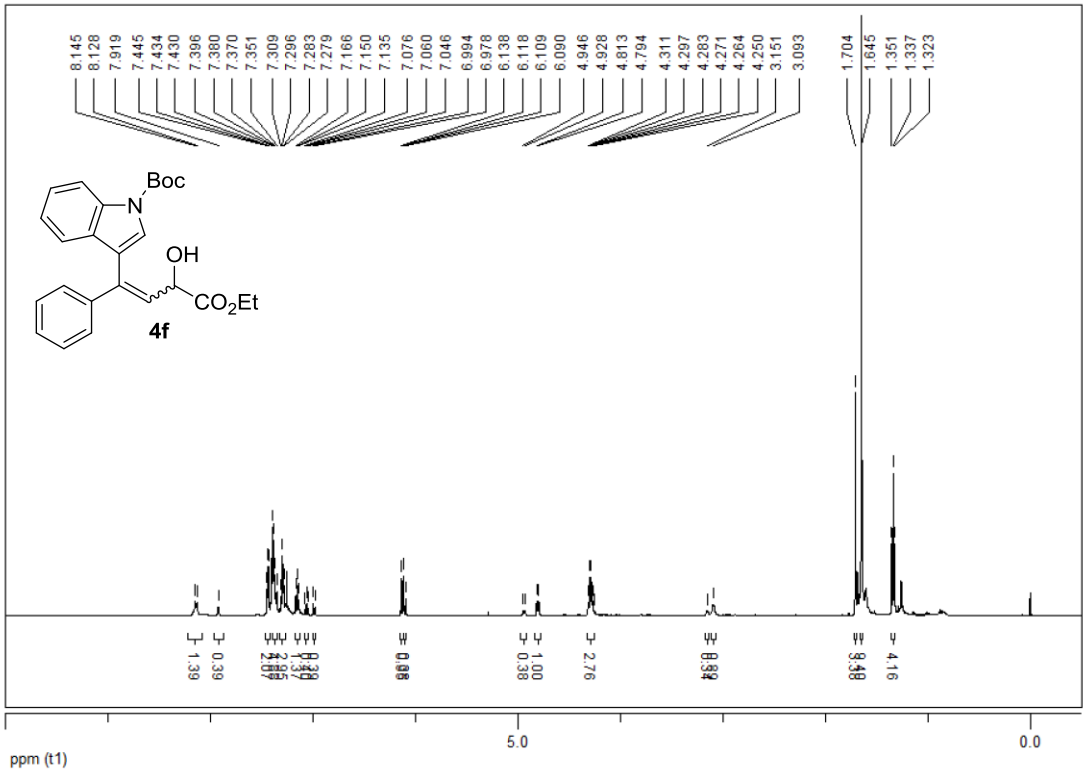
^{1}H NMR (500 MHz, $CDCl_3$)



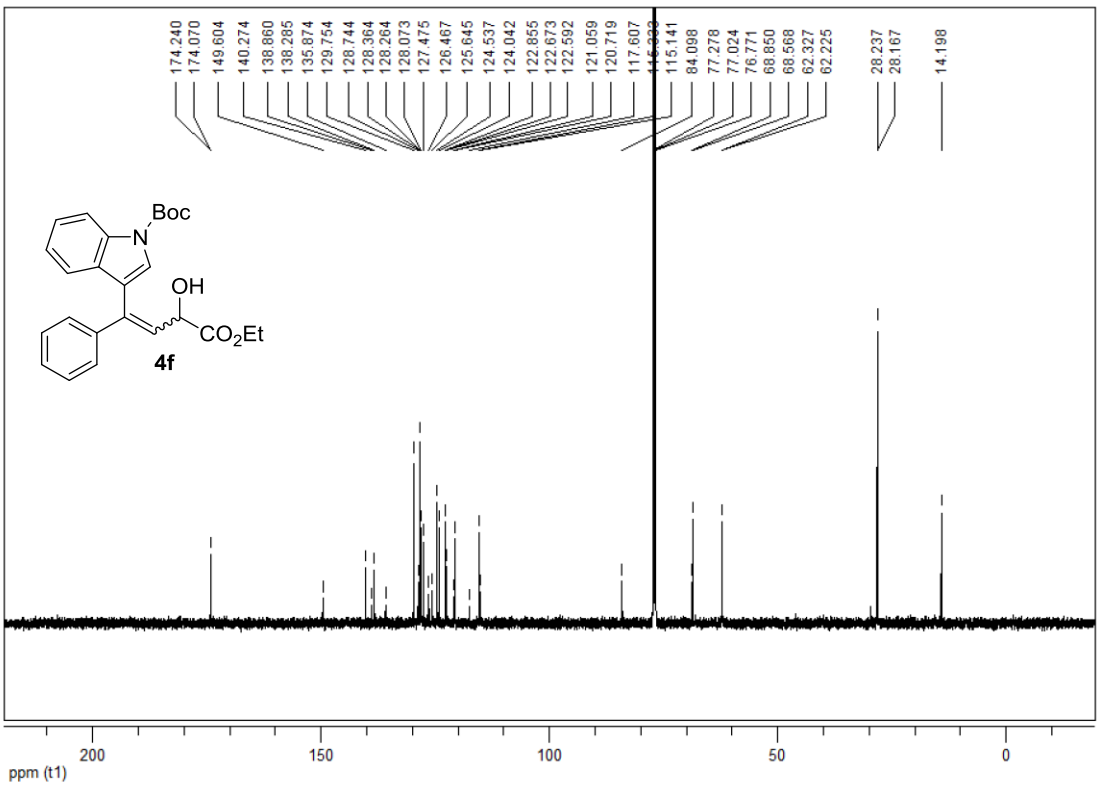
^{13}C NMR (125 MHz, $CDCl_3$)



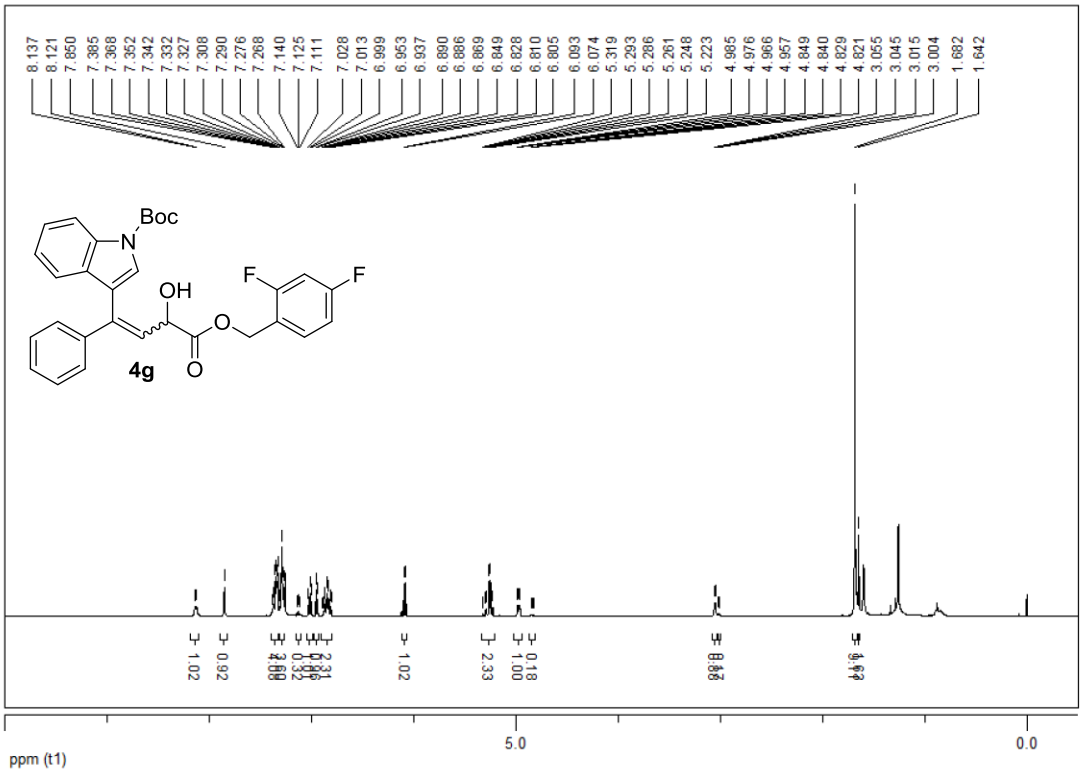
^{1}H NMR (500 MHz, $CDCl_3$)



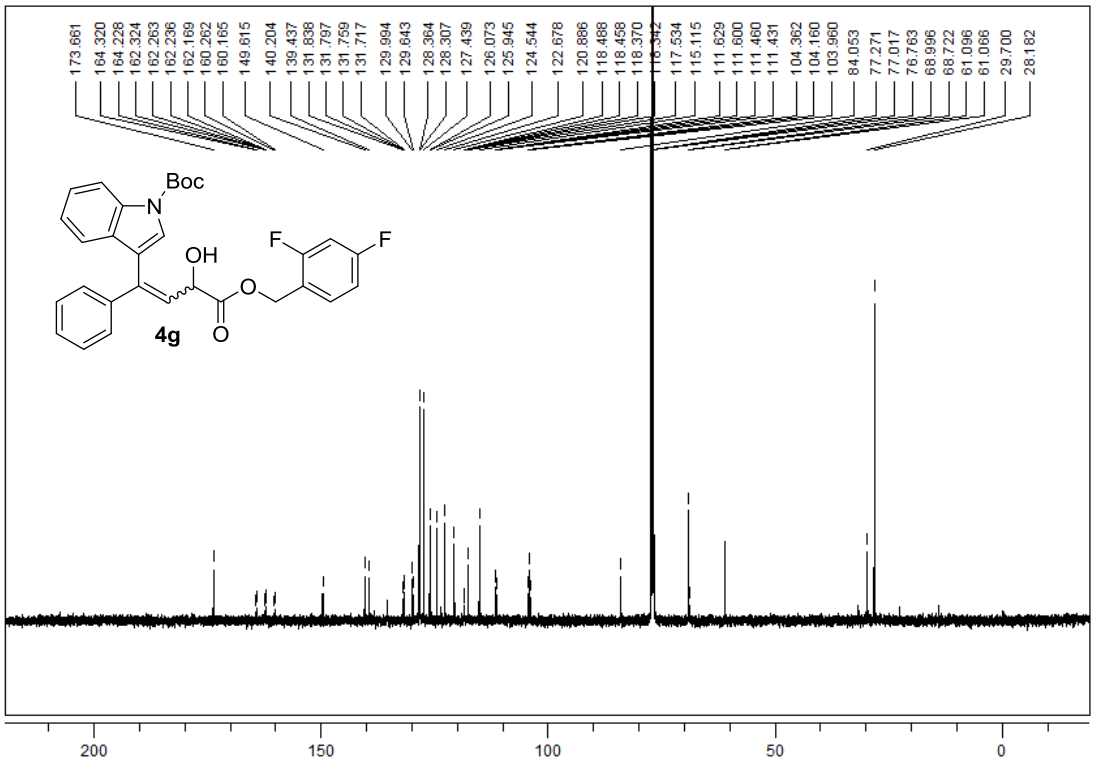
^{13}C NMR (125 MHz, $CDCl_3$)



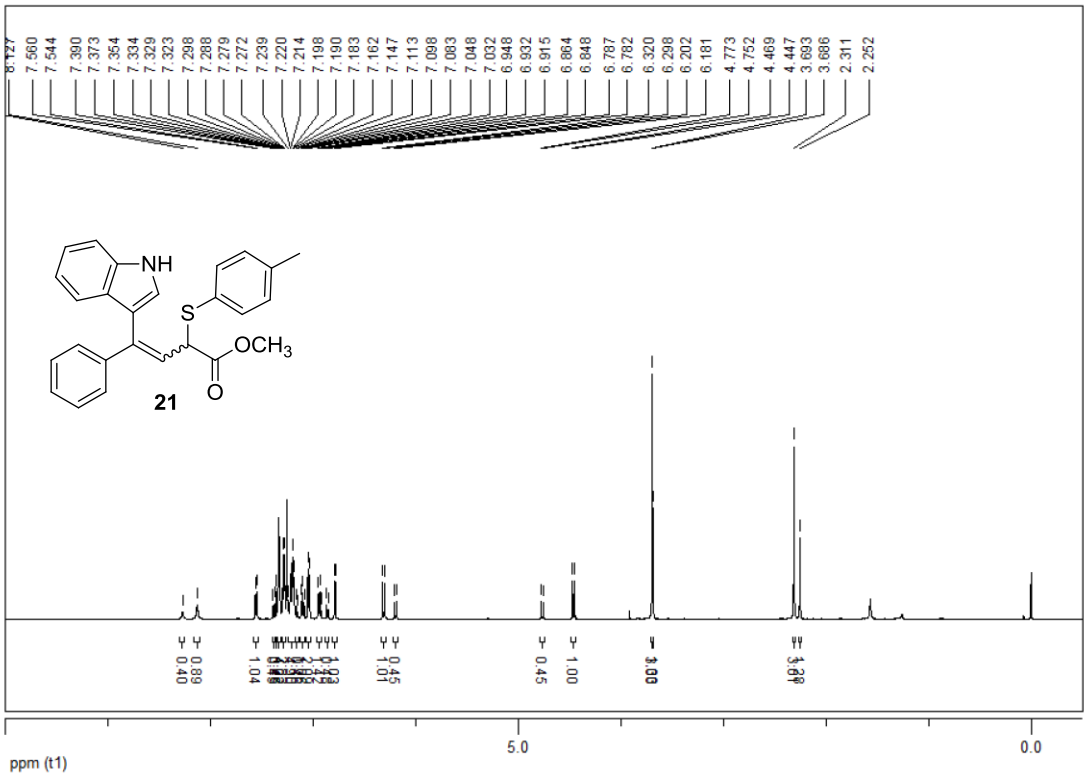
^{1}H NMR (500 MHz, $CDCl_3$)



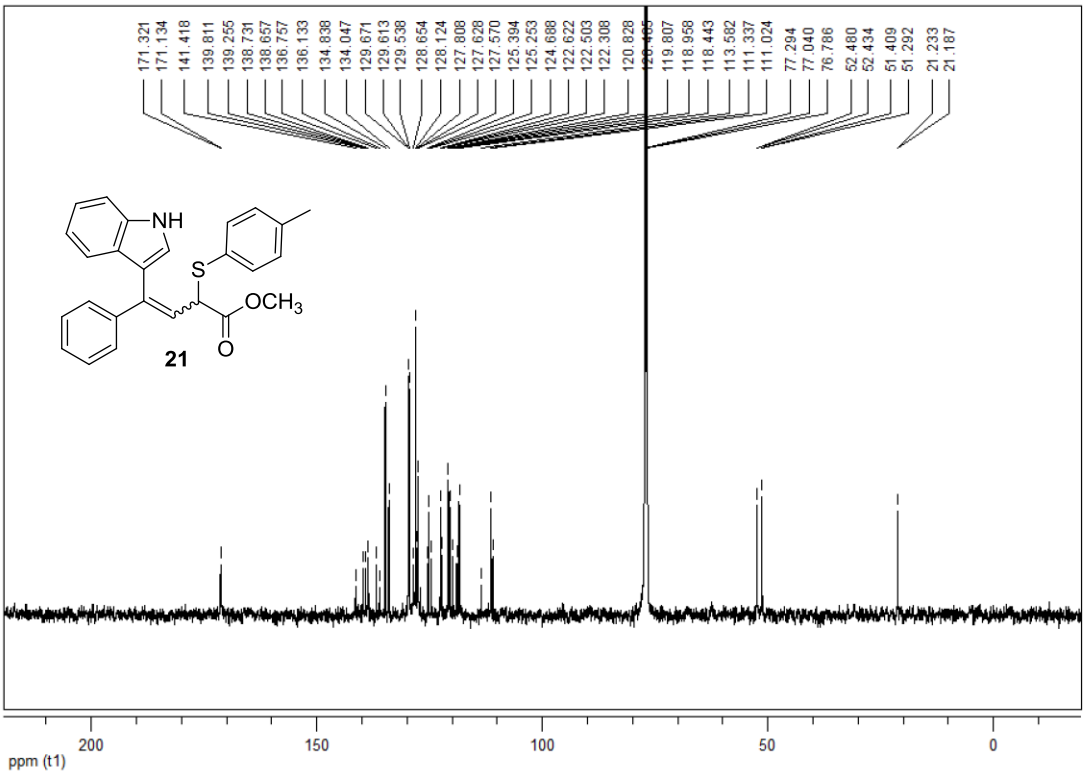
^{13}C NMR (125 MHz, $CDCl_3$)



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



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



X. Reference

(1) J. Lv. Q. Zhang, X. Zhong, S. Luo, *J. Am. Soc. Chem.,* 2015, **137**, 15576.

(2) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr. J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision E.01, Gaussian, Inc., Wallingford CT, 2009.

(3) Y. Zhao, D. Truhlar, *Theor. Chem. Acc.,* 2008, **120**, 215.

(4) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.,* 2005, **7**, 3297.

(5) A. V. Marenich, C. J. Cramer, D. G. J. Truhlar, *Phys. Chem. B.,* 2009, **113**, 6378.

(6) CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke, 2009.

(7) T. Lu, F. Chen, *J. Comput. Chem.,* 2012, **33**, 580.