Supporting Information

$HfCl_4$-Phosphoric acid catalytic reduction of in situ generated carbocations with hydrosilane: facile approaches to 2,4-dihydrocyclopent[*b*]indoles

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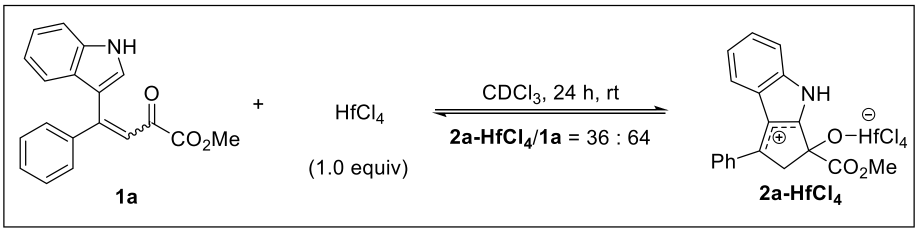
I. General Experimental Information and Materials

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 $CDCl_3$ or DMSO-d_6 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. 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, and mass spectra were obtained on a Brucker Microflex LRF with an ESI source. UV-vis absorption spectra were obtained on a Shimadzu UV-2600 spectrophotometer.

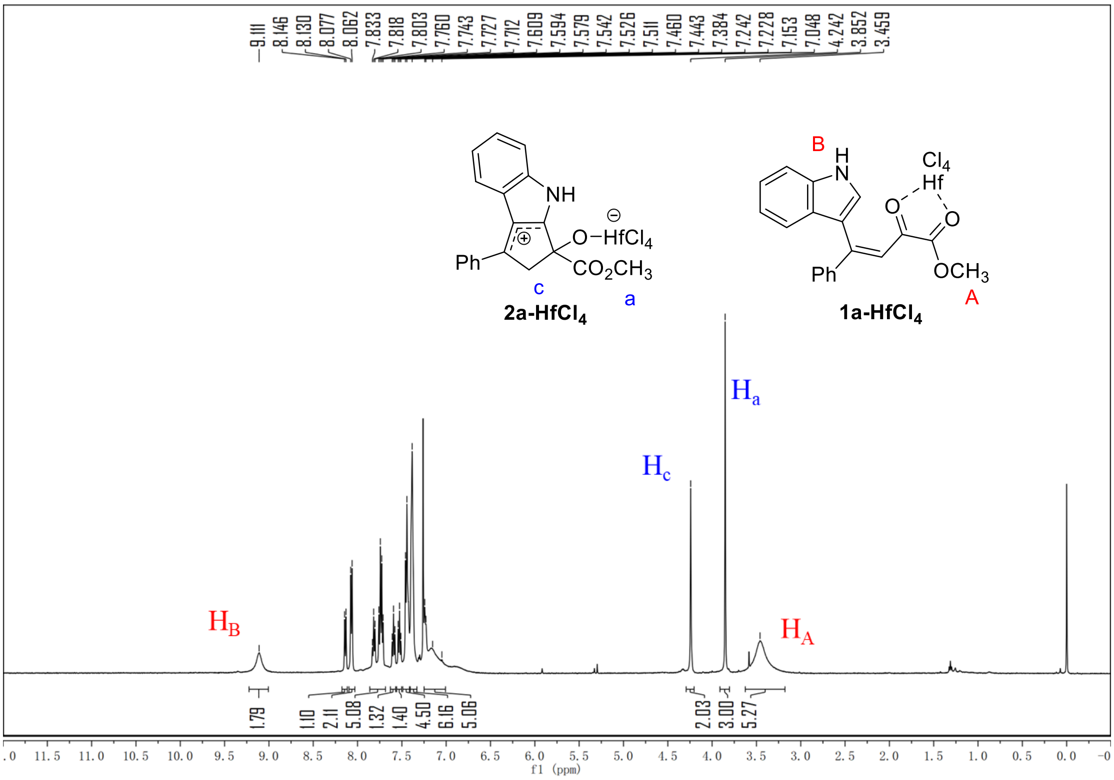
II. Synthesis and Examination of New Stabilized Carbocation

A) In situ generation of carbocation 2a-HfCl4

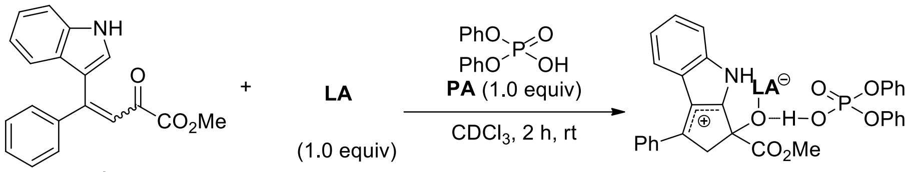


To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1a** (0.1 mmol, 1.0 equiv) and $HfCl_4$ (0.1 mmol, 1.0 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then $CDCl_3$ (1.0 mL, 0.1 M) was added under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h. After reaction, the solution was examined by ^1H NMR.

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



B) In situ generation of carbocation 2a-LA(PA)

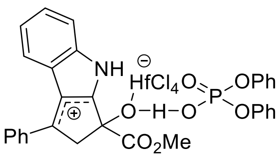


1a

2a-LA(PA)

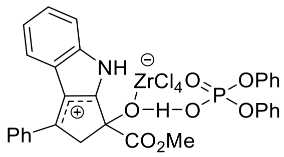
entry	Lewis acid (**LA**)	conv. (%)
1	$HfCl_4$	100
2	$ZrCl_4$	100
3	none	nr
4	$Hf(OTf)_4$	np
5	$Bi(OTf)_3$	nr
6	$InBr_3$	nr

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-indolyl β,γ-unsaturated-α-ketoester derivatives **1a** (0.1 mmol, 1.0 equiv), Lewis acid **LA** (0.1 mmol, 1.0 equiv) and diphenyl phosphate (0.1 mmol, 1.0 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then $CDCl_3$ (1.0 mL, 0.1 M) was added under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h. Through TLC (PE/EA = 3:2, v/v) detection, it was found that no reaction occurred or no product was observed when the reaction solution was added $Hf(OTf)_4$, $Bi(OTf)_3$ or $InBr_3$; when the reaction solution was added $HfCl_4$ or $ZrCl_4$, **1a** was completely consumed. The solution containing $HfCl_4$ and the solution containing $ZrCl_4$ were examined by ^1H NMR and ^{13}C NMR.



2a-$HfCl_4$(PA)

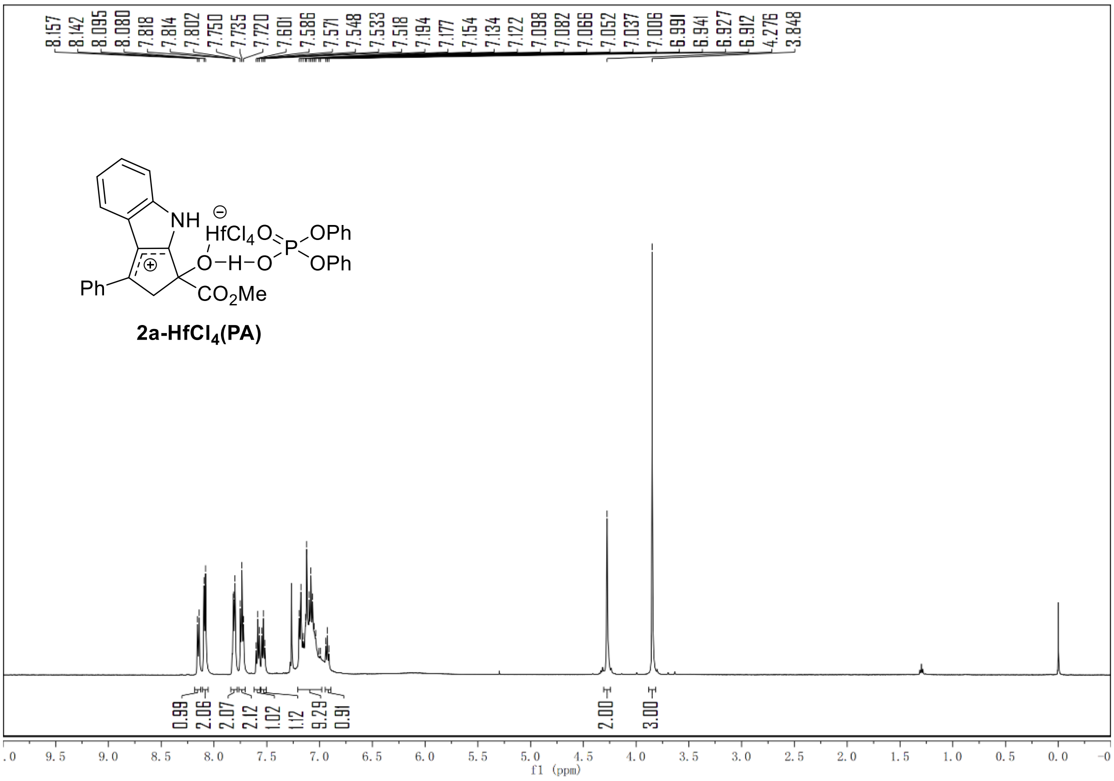
2a-$HfCl_4$(PA): ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.5 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 2H), 7.82 – 7.80 (m, 2H), 7.74 (t, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.19 – 6.99 (m, 9H), 6.93 (t, *J* = 7.0 Hz, 1H), 4.28 (s, 2H), 3.85 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.3, 178.7, 169.3, 150.02, 149.96, 147.01, 136.75, 133.6, 132.5, 131.5, 130.9, 130.2, 129.6, 129.4, 129.3, 128.2, 125.3, 125.1, 124.1, 121.2, 120.83, 120.79, 117.7, 74.4, 55.1, 54.2 ppm.



2a-ZrCl$_4$(PA)

2a-ZrCl$_4$(PA): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.83 – 7.79 (m, 2H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.59 – 7.52 (m, 2H), 7.19 – 6.91 (m, 10H), 4.34 – 4.24 (m, 2H), 3.83 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.1, 178.9, 169.4, 150.1, 150.0, 147.0, 136.9, 133.7, 132.4, 131.6, 130.9, 130.2, 129.6, 129.5, 129.4, 128.3, 125.3, 125.1, 124.2, 121.2, 120.9, 120.8, 117.7, 74.3, 55.1, 54.3 ppm.

^{1}H NMR (500 MHz, CDCl$_3$)



^{13}C NMR (126 MHz, CDCl$_3$)

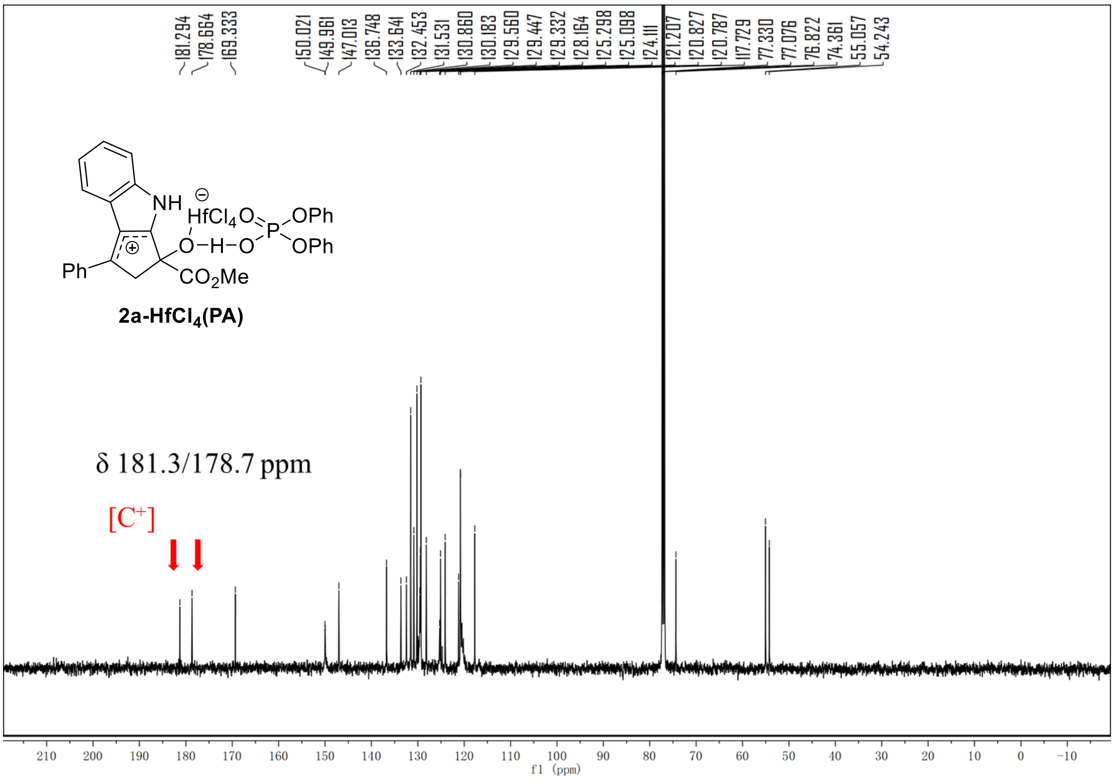
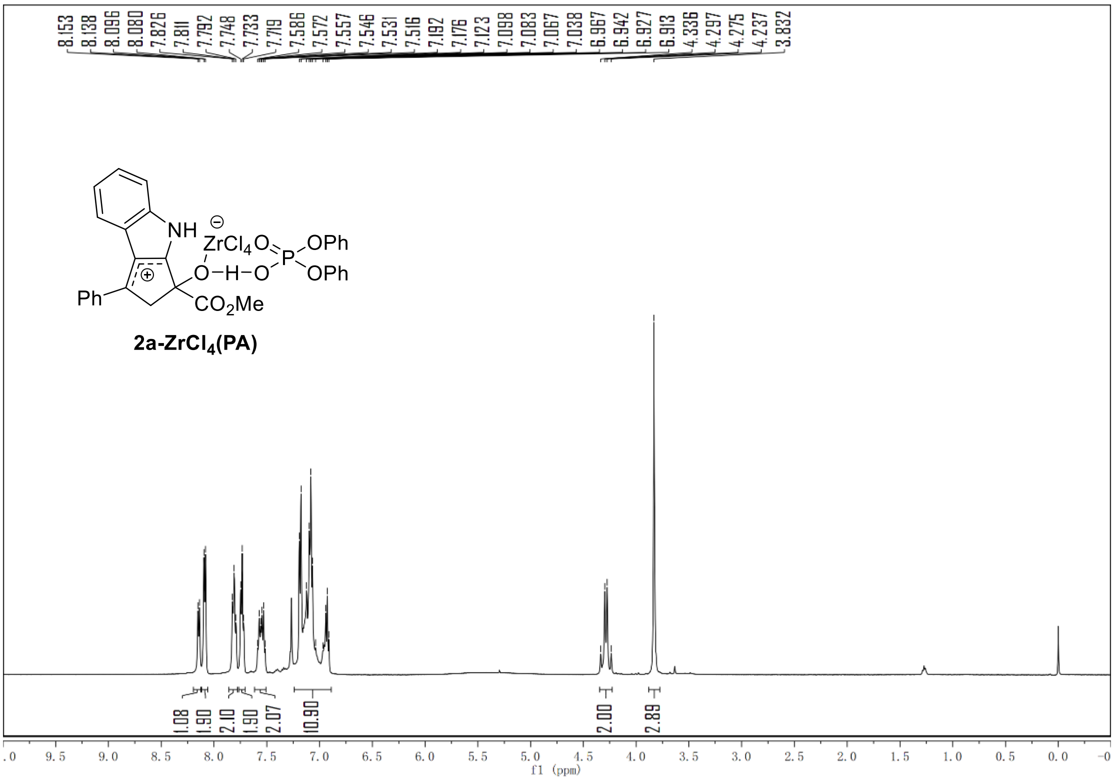


Figure S1. ^{1}H NMR and ^{13}C NMR for 2a-HfCl$_4$(PA)

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



^{13}C NMR (126 MHz, $CDCl_3$)

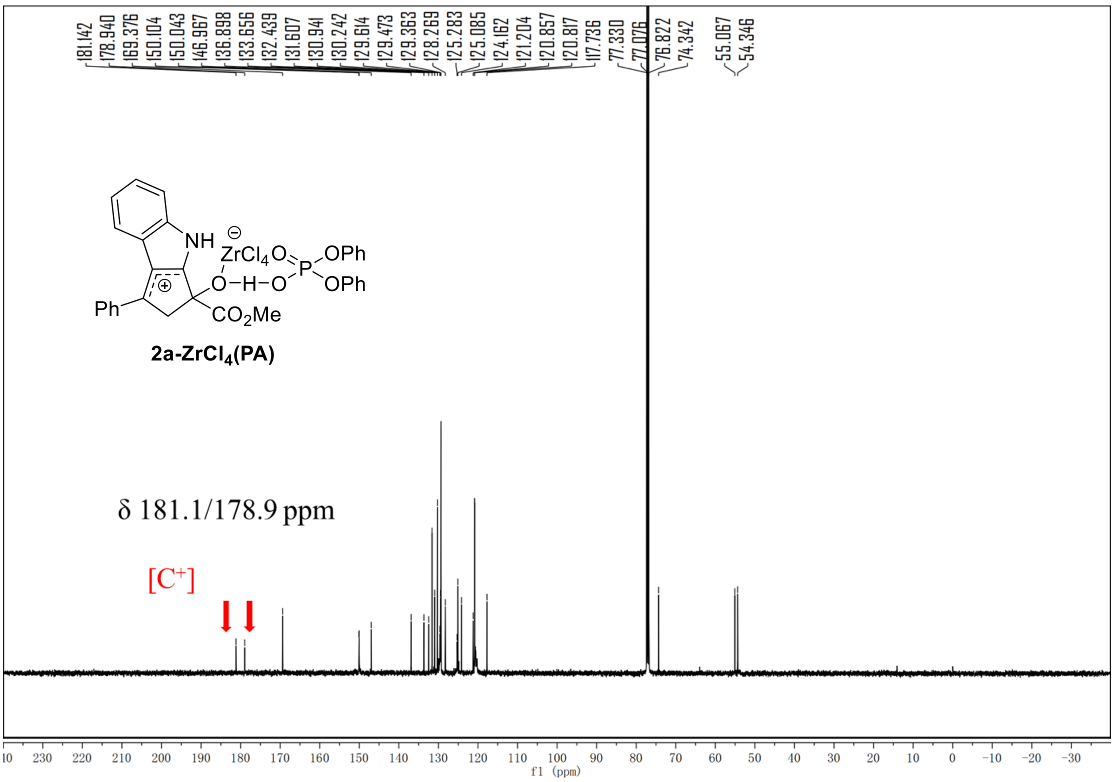


Figure S2. ^1H NMR and ^{13}C NMR for 2a-$ZrCl_4$(PA)

UV-vis absorption spectra: The UV/Vis absorption spectra of **1a** (0.05 mM), PA (0.05 mM) and **2a-HfCl$_4$(PA)** (0.05 mM) in $CHCl_3$ were recorded in 1 cm path quartz cuvettes by using the UV-2600 UV-Vis spectrophotometer, respectively.

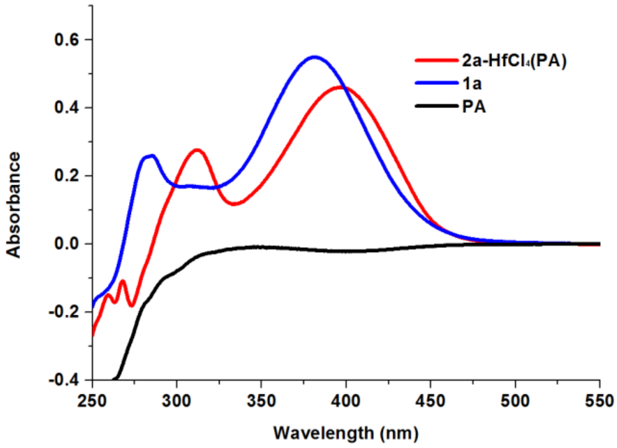


Figure S3. UV-vis absorption spectra of **1a**, **PA**, and **2a-HfCl$_4$(PA)** in $CHCl_3$

C) Hydride Reduction of in situ Generated Carbocation 2a-HfCl$_4$(PA) from 1a

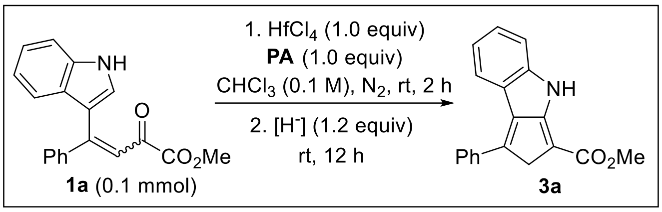
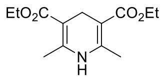


Table S1. Hydride Reduction of in situ Generated Carbocation 2a-HfCl$_4$(PA) from 1a[a]

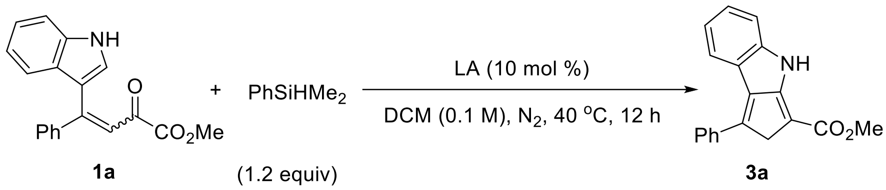
entry	[H$^-$]	N[b]	yield (%)[c]
1	NaBH$_4$	11.72	18
2		9.00	39
3	Et$_3$SiH	3.58	37
4	PhMe$_2$SiH	3.55	58

[a] All reactions were performed on a 0.10 mmol scale (based on α-keto ester **1a**) using HfCl$_4$ (0.1 mmol, 1.0 equiv) and **PA** (0.1 mmol, 1.0 equiv) in CHCl$_3$ (1.0 mL) under N$_2$ at room temperature for 2 h, and then different hydride [H$^-$] (0.12 mmol, 1.2 equiv) was added and stirred at room temperature for 12 h. [b] *N*ucleophilicity parameter (*N*) was predicted in http://pka.luoszgroup.com/ne_prediction. [c] Isolated yield.

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1a** (0.1 mmol, 1.0 equiv), HfCl$_4$ (0.1 mmol, 1.0 equiv) and diphenyl phosphate (0.1 mmol, 1.0 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then CHCl$_3$ (1.0 mL, 0.1 M) was added under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h. Then different hydride compounds (0.12 mmol, 1.2 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at room temperature for other 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 4:1, v/v) to give the desired product **3a**.

III. Optimization

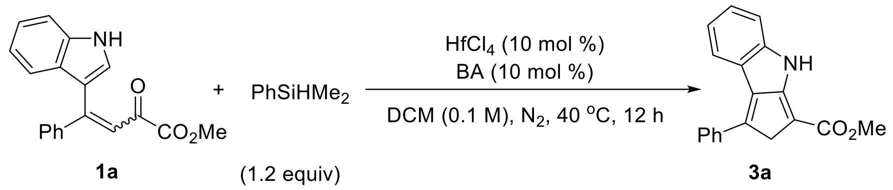
Table S2. Screening of Different Lewis Acids [a]



entry	Lewis acid (LA)	yield (%) [b]
1	none	NR
2	$Mg(OTf)_2$	NR
3	$Sc(OTf)_3$	NR
4	$Y(OTf)_3$	NR
5	ZrF_4	NR
6	$ZrCl_4$	28
7	$ZrBr_4$	29
8	$HfCl_4$	39
9	$Hf(OTf)_4$	NR
10	$FeBr_3$	NR
11	$FeCl_3$	NP
12	$Fe(OTf)_3$	NP
13	$Ni(OTf)_2$	NR
14	$Cu(OTf)_2$	NP
15	$Zn(OTf)_2$	NR
16	$InBr_3$	NR
17	$In(OTf)_3$	NR
18	$Bi(OTf)_3$	NR
19	$Yb(OTf)_3$	NR

[a] Reaction Conditions: **1a** (0.1 mmol), $PhSiHMe_2$ (1.2 equiv), Lewis acid (10 mol %), were added to DCM (1.0 mL) under N_2 for 12 h at 40 °C. Compound **1a** as a mixture (*E/Z* = 75:25) was determined by ^1H NMR. [b] Yields of isolated products. DCM = CH_2Cl_2, NR = No Reaction, NP = No Product.

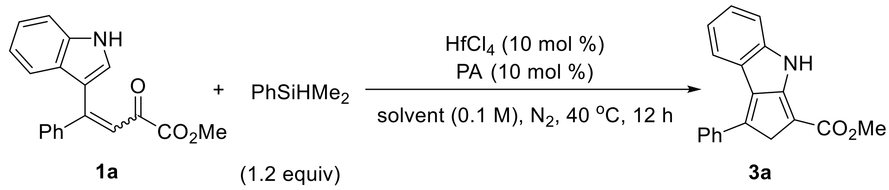
Table S3. Screening of Different Brønsted acid [a]



entry	Brønsted acid (BA)	yield (%) [b]
1	none	39
2	PA	90
3	TsOH	79
4	TFA	75
5	H_3PO_4	78

[a] Reaction Conditions: **1a** (0.1 mmol), $PhSiHMe_2$ (1.2 equiv), $HfCl_4$ (10 mol %), Brønsted acid (10 mol %), were added to DCM (1.0 mL) under N_2 for 12 h at 40 °C. Compound **1a** as a mixture (*E/Z* = 75:25) was determined by ^{1}H NMR. [b] Yields of isolated products. DCM = CH_2Cl_2, PA = diphenyl phosphate, NR = No Reaction, NP = No Product.

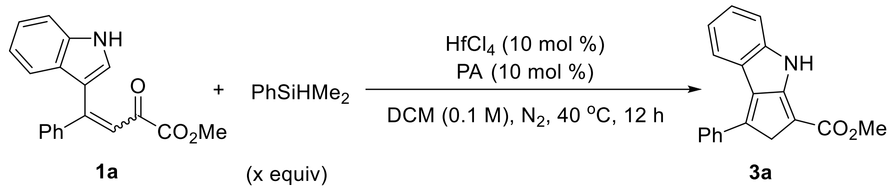
Table S4. Screening of Different Solvents [a]



entry	solvent	yield (%) [b]
1	DCM	90
2	$ClCH_2CH_2Cl$	69
3	$CHCl_3$	70
4	THF	17
5	MeCN	NP
6	Toluene	26
7	Acetone	23
8	Hexane	NR

[a] Reaction Conditions: **1a** (0.1 mmol), $PhSiHMe_2$ (1.2 equiv), $HfCl_4$ (10 mol %), PA (10 mol %), were added to solvent (1.0 mL) under N_2 for 12 h at 40 °C. Compound **1a** as a mixture (*E/Z* = 75:25) was determined by ^1H NMR. [b] Yields of isolated products. DCM = CH_2Cl_2, PA = diphenyl phosphate, NR = No Reaction, NP = No Product.

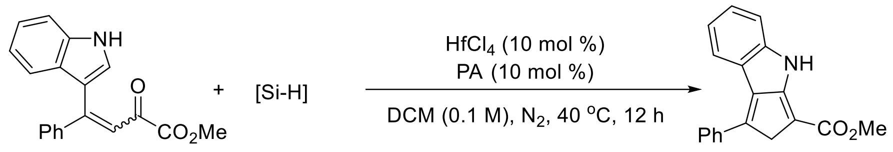
Table S5. Screening of Different Equivalent of $PhSiHMe_2$ [a]



entry	x	yield (%) [b]
1	1.2	90
2	1.5	88
3	2	82
4	3	79

[a] Reaction Conditions: **1a** (0.1 mmol), $PhSiHMe_2$ (x equiv), $HfCl_4$ (10 mol %), PA (10 mol %), were added to solvent (1.0 mL) under N_2 for 12 h at 40 °C. Compound **1a** as a mixture (*E/Z* = 75:25) was determined by ^1H NMR. [b] Yields of isolated products. DCM = CH_2Cl_2, PA = diphenyl phosphate, NR = No Reaction, NP = No Product.

Table S6. Screening of Different Silane [a]



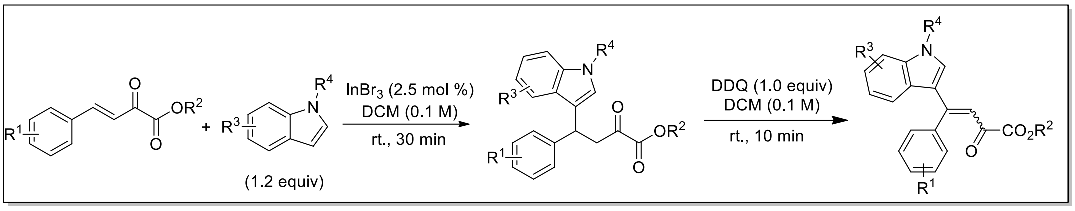
1a (1.2 equiv) **3a**

entry	[Si-H]	yield (%) [b]
1	$PhSiHMe_2$	90
2	Et_3SiH	26
3	TMDS	NP

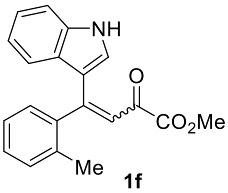
[a] Reaction Conditions: **1a** (0.1 mmol), [Si-H] (1.2 equiv), $HfCl_4$ (10 mol %), PA (10 mol %), were added to solvent (1.0 mL) under N_2 for 12 h at 40 °C. Compound **1a** as a mixture (*E/Z* = 75:25) was determined by ^1H NMR. [b] Yields of isolated products. DCM = CH_2Cl_2, PA = diphenyl phosphate, TMDS = 1,1,3,3 - Tetramethyldisilazane, NR = No Reaction, NP = No Product.

IV. Experimental Procedures and Characterization Data

A) One-pot synthesis of γ-indolyl β,γ-unsaturated α-keto esters

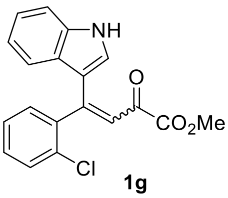


General procedure I: γ-Indolyl β,γ-unsaturated-α-ketoesters were prepared on slightly modified literature precedures.[1] β,γ-unsaturated-α-ketoester derivatives (4 mmol, 1.0 equiv) and indole derivatives (4.8 mmol, 1.2 equiv) were dissolved in DCM (40 mL, 0.1 M), then $InBr_3$ (0.1 mmol, 2.5 mol %) was added. The solution was stirred at room temperature for 30 min. Subsequently, DDQ (4 mmol, 1.0 equiv) was added. The solution was stirred at room temperature for 10 minutes. After reaction, purification of mixture by column chromatography on silica gel gave the desired product.



1f

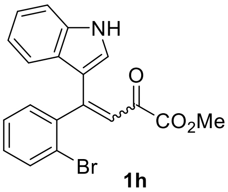
1f: Prepared according to the general procedure I above and obtained as yellow solid (0.64 g, 50% yield, *E/Z* > 25:1), eluent: DCM/EA = 30:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.99 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.21 (m, 4H), 7.18 – 7.13 (m, 2H), 7.11 (d, *J* = 7.0 Hz, 1H), 3.42 (s, 3H), 2.05 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO- d_6) δ 184.2, 164.8, 156.9, 138.4, 138.3, 136.2, 133.0, 130.1, 129.5, 128.8, 125.8, 125.0, 123.3, 122.1, 120.6, 116.2, 115.1, 113.4, 52.4, 19.5 ppm.



1g

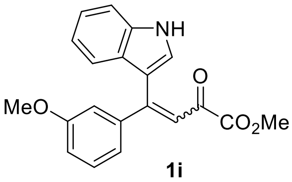
1g: Prepared according to the general procedure I above and obtained as yellow solid

(0.63 g, 46% yield, *E/Z* > 25:1), eluent: DCM/EA = 30:1; ^{1}H NMR (500 MHz, DMSO- d_6) δ 12.05 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.49 – 7.45 (m, 1H), 7.43 – 7.39 (m, 2H), 7.29 – 7.24 (m, 3H), 7.21 (t, *J* = 7.0 Hz, 1H), 3.64 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO- d_6) δ 181.3, 163.6, 152.9, 137.9, 137.7, 133.1, 131.7, 130.2, 129.6, 129.2, 126.9, 124.4, 123.0, 121.8, 120.1, 115.3, 113.7, 113.0, 52.3 ppm.



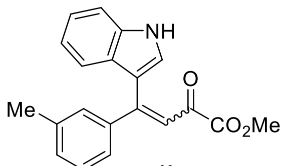
1h

1h: Prepared according to the general procedure I above and obtained as yellow solid (0.75 g, 49% yield, *E/Z* > 25:1), eluent: DCM/EA = 30:1; ^{1}H NMR (500 MHz, DMSO- d_6) δ 12.03 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.28 – 7.21 (m, 4H), 3.64(s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 181.1, 163.3, 154.5, 139.7, 137.9, 133.2, 132.3, 130.1, 129.7, 127.4, 124.4, 123.0, 121.8, 121.8, 120.2, 115.3, 113.3, 113.0, 52.3 ppm.



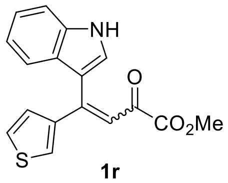
1i

1i: Prepared according to the general procedure I above and obtained as yellow solid (0.60 g, 45% yield, *E/Z* = 77:23), eluent: DCM/EA = 30:1; ^{1}H NMR (500 MHz, DMSO- d_6) δ 12.01 (s, 1H), 11.81 (s, 0.3H), 7.73 (d, *J* = 2.5 Hz, 0.3H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 0.3H), 7.37 – 7.32 (m, 2.2H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.19 – 7.13 (m, 1.3H), 7.09 – 7.01 (m, 3H), 6.93 (t, *J* = 7.5 Hz, 0.3H), 6.86 – 6.84 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 0.3H), 6.69 (s, 0.3H), 3.76 (s, 3H), 3.74 (s, 0.9H), 3.45 (s, 3H), 3.12 (s, 0.9H) ppm; ^{13}C NMR (126 MHz, DMSO- d_6) δ 185.3, 184.2, 164.6, 164.3, 159.8, 159.2, 157.0, 154.9, 141.3, 140.3, 138.2, 137.4, 133.6, 132.9, 130.1, 129.6, 126.5, 125.2, 123.3, 122.8, 122.4, 122.0, 120.9, 120.74, 120.66, 116.8, 116.5, 115.6, 115.4, 115.0, 114.7, 113.4, 112.6, 55.7, 55.6, 52.4, 52.1 ppm.



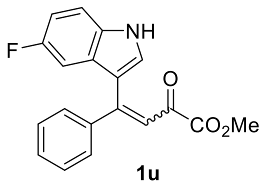
1j

1j: Prepared according to the general procedure I above and obtained as yellow solid (0.38 g, 30% yield, *E/Z* = 77:23), eluent: DCM/EA = 30:1; ^{1}H NMR (500 MHz, DMSO- d$_6$) δ 12.00 (s, 1H), 11.81 (s, 0.3H), 7.73 (s, 0.3H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 0.3H), 7.34 – 7.29 (m, 3.9H), 7.23 (t, *J* = 8.0 Hz, 1.3H), 7.18 – 7.13 (m, 1.3H), 7.12 – 7.07 (m, 2H), 6.99 (s, 1H), 6.91 (t, *J* = 7.5 Hz, 0.3H), 6.71 (d, *J* = 8.0 Hz, 0.3H), 6.64 (s, 0.3H), 3.41 (s, 3H), 3.12 (s, 0.9H), 2.34 (s, 3H), 2.31 (s, 0.9H) ppm; ^{13}C NMR (126 MHz, DMSO- d$_6$) δ 184.7, 184.0, 164.2, 163.9, 157.0, 155.0, 139.4, 138.4, 137.8, 137.7, 137.0, 136.9, 133.0, 132.4, 131.2, 130.2, 129.6, 129.3, 128.4, 127.8, 126.8, 126.4, 126.0, 124.7, 122.8, 122.3, 121.4, 120.2, 120.1, 120.0, 116.5, 115.0, 113.0, 112.8, 112.1, 51.8, 51.6, 20.9 ppm.



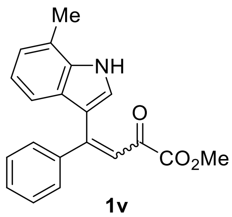
1r

1r: Prepared according to the general procedure I above and obtained as yellow solid (0.57 g, 46% yield, *E/Z* = 63:37), eluent: DCM/EA = 30:1; ^{1}H NMR (500 MHz, DMSO- d$_6$) δ 12.00 (s, 1H), 11.74 (s, 0.6H), 7.712 – 7.707 (m, 0.6H), 7.66 – 7.62 (m, 3.2H), 7.54 – 7.51 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 0.6H), 7.44 (d, *J* = 3.0 Hz, 1H), 7.35 (dd, *J* = 1.0, 5.0 Hz, 0.6H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1.6H), 7.07 (dd, *J* = 1.0, 5.0 Hz, 1H), 7.00 – 6.96 (m, 1.2H), 6.94 (s, 1H), 6.76 (s, 0.6H), 3.50 (s, 3H), 3.07 (s, 1.8H) ppm; ^{13}C NMR (126 MHz, DMSO- d$_6$) δ 185.8, 184.5, 164.6, 164.4, 151.5, 148.9, 142.0, 139.4, 138.2, 137.3, 133.0, 131.9, 130.0, 129.9, 128.8, 127.9, 127.8, 126.53, 126.48, 125.3, 123.3, 122.7, 121.9, 120.63, 120.55, 120.5, 119.7, 116.6, 116.3, 113.4, 113.3, 112.6, 52.5, 52.0 ppm.



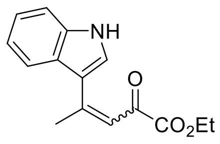
1u

1u: Prepared according to the general procedure I above and obtained as yellow solid (0.68 g, 53% yield, *E/Z* = 76:24), eluent: DCM/EA = 30:1; ^{1}H NMR (500 MHz, DMSO- d_6) δ 12.10 (s, 1H), 11.94 (s, 0.32H), 7.84 (s, 0.32H), 7.54 – 7.49 (m, 2.32H), 7.48 – 7.43 (m, 4.60H), 7.28 (d, *J* = 7.0 Hz, 2H), 7.09 – 7.05 (m, 1H), 7.03 – 6.99 (m, 1.32H), 6.98 (s, 1H), 6.70 (s, 0.32H), 6.31 – 6.29 (m, 0.32H), 3.44 (s, 3H), 3.24(s, 0.96H) ppm; ^{13}C NMR (126 MHz, DMSO- d_6) δ 184.0, 183.6, 164.1, 163.7, 158.1 (d, $^{1}J_{C\text{-}F}$ = 236.1 Hz), 157.2 (d, $^{1}J_{C\text{-}F}$ = 234.2 Hz), 156.3, 154.1, 139.4, 138.2, 134.2, 134.1, 134.0, 133.5, 130.6, 129.5, 129.0, 128.9, 128.7, 128.0, 126.5 (d, $^{3}J_{C\text{-}F}$ = 10.3 Hz), 125.2 (d, $^{3}J_{C\text{-}F}$ = 10.3 Hz), 119.8, 116.5 (d, $^{4}J_{C\text{-}F}$ = 4.4 Hz), 115.0, 114.0 (d, $^{3}J_{C\text{-}F}$ = 9.8 Hz), 113.4 (d,$^{3}J_{C\text{-}F}$ = 9.4 Hz), 112.9 (d, $^{4}J_{C\text{-}F}$ = 4.5 Hz), 110.8 (d,$^{3}J_{C\text{-}F}$ = 25.9 Hz), 110.5 (d, $^{2}J_{C\text{-}F}$ = 25.9 Hz), 105.2 (d, $^{2}J_{C\text{-}F}$ = 24.8 Hz), 104.9 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 52.0, 51.8 ppm; ^{19}F NMR (376 MHz, DMSO- d_6) δ -121.5, -123.0 ppm.



1v

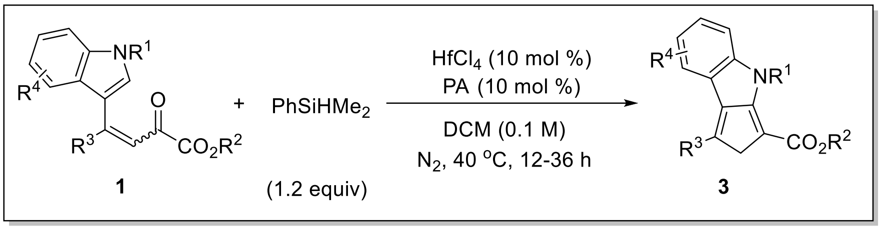
1v: Prepared according to the general procedure I above and obtained as yellow solid (0.64 g, 50% yield, *E/Z* = 76:24), eluent: DCM/EA = 30:1; ^{1}H NMR (500 MHz, DMSO- d_6) δ 11.98 (s, 1H), 11.79 (s, 0.31H), 7.71 (s, 0.31H), 7.47 – 7.40 (m, 4.55H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.20 (s, 1H), 7.05 – 7.02 (s, 3H), 6.91 (d, *J* = 6.5 Hz, 0.31H), 6.78 (t, *J* = 7.0 Hz, 0.31H), 6.63 (s, 0.31H), 6.48 (d, *J* = 8.0 Hz, 0.31H), 3.41 (s, 3H), 3.12 (s, 0.94H), 2.46 (s, 3.94H) ppm; ^{13}C NMR (126 MHz, DMSO- d_6) δ 184.2, 183.1, 163.7, 163.3, 156.4, 154.5, 138.9, 138.0, 136.6, 135.9, 132.0, 129.9, 129.0, 128.5, 128.4, 128.1, 127.4, 125.3, 124.1, 122.9, 122.2, 121.6, 121.1, 120.9, 119.8, 119.6, 117.2, 116.6, 114.4, 112.7, 51.4, 51.2, 16.1 ppm.



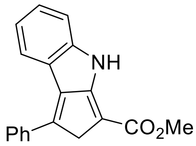
1w

1w: Prepared according to the general procedure I above and obtained as yellow solid (0.10 g, 10% yield, *E/Z* > 25:1), eluent: DCM/EA = 2:1; ^{1}H NMR (500 MHz, DMSO- d_6) δ 12.06 (s, 1H), 8.16 (d, *J* = 3.0 Hz, 1H), 7.96 – 7.94 (m, 1H), 7.51 (t, *J* = 4.5 Hz, 1H), 7.39 (s, 1H), 7.26 – 7.22 (m, 2H), 4.27 (q, *J* = 7.0 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (126 MHz, DMSO- d_6) δ 181.2, 163.3, 157.1, 137.8, 132.1, 124.2, 123.0, 121.6, 120.4, 117.2, 112.8, 112.6, 61.5, 18.8, 13.9 ppm.

B) Catalytic Reductive Nazarov Cyclization of γ-Indolyl β,γ-unsaturated-α-Keto Esters

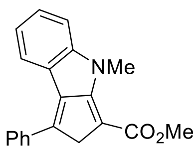


General procedure Ⅱ: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1** (0.15 mmol, 1.0 equiv), $HfCl_4$ (0.015 mmol, 10 mol %) and diphenyl phosphate (0.015 mmol, 10 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.5 mL, 0.1 M) and $PhSiHMe_2$ (0.18 mmol, 1.2 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 12-36 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 4:1, v/v) to give the desired product **3**.



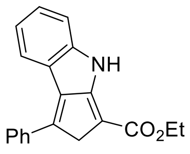
3a

3a: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (39.0 mg, 90% yield, M.P. = 230 - 233 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 10.50 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 3.95 (s, 2H), 3.72 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 163.9, 157.5, 152.0, 142.1, 136.1, 135.3, 129.3, 129.0, 128.4, 127.5, 122.8, 120.3, 119.7, 111.5, 93.9, 50.2, 44.9 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{19}H_{16}NO_2$ 290.1181, found 290.1180.



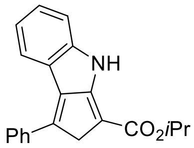
3b

3b: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (22.3 mg, 49% yield, M.P. = 212 - 215 °C), eluent: PE/EA = 6:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 7.89 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 4.02 (s, 2H), 3.91 (s, 3H), 3.70 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.8, 158.1, 153.2, 141.9, 136.9, 135.9, 129.0, 128.8, 128.3, 127.7, 122.6, 121.0, 120.5, 108.8, 94.7, 50.6, 47.4, 31.8 ppm; HRMS (ESI, quadrupole) *m/z* (M+H)$^+$ calcd. for $C_{20}H_{18}NO_2$ 304.1338, found 304.1330.



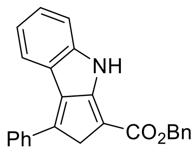
3c

3c: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (33.7 mg, 74% yield, M.P. = 200 - 203 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 10.40 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.95 (s, 2H), 1.30 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 163.2, 157.3, 152.1, 141.8, 136.1, 135.4, 129.3, 129.0, 128.3, 127.5, 122.7, 120.2, 119.8, 111.6, 94.3, 58.4, 44.9, 14.8 ppm; HRMS (ESI, quadrupole) *m/z* (M+Na)$^+$ calcd. for $C_{20}H_{17}NNaO_2$ 326.1157, found 326.1160.



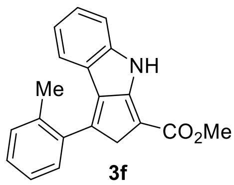
3d

3d: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (36.1 mg, 76% yield, M.P. = 171 - 174 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 10.26 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.08 – 5.03 (m, 1H), 3.93 (s, 2H), 1.31 (d, *J* = 6.0 Hz, 6H) ppm; ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 163.3, 157.1, 152.0, 141.6, 136.1, 135.4, 129.3, 128.9, 128.3, 127.5, 122.7, 120.2, 119.7, 111.6, 94.8, 65.3, 45.0, 22.1 ppm; HRMS (ESI, quadrupole) *m/z* (M+Na)$^+$ calcd for $C_{21}H_{19}NNaO_2$ 340.1313, found 340.1306.



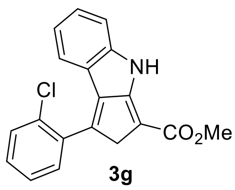
3e

3e: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (40.6 mg, 74% yield, M.P. = 195 - 197 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 10.59 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 5.27 (s, 2H), 4.00 (s, 2H) ppm; ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 163.3, 158.0, 152.0, 142.4, 137.8, 136.1, 135.3, 129.3, 129.0, 128.4, 128.3, 127.6, 127.5, 127.4, 122.8, 120.4, 119.8, 111.6, 93.7, 63.7, 44.9 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{25}H_{20}NO_2$ 366.1494, found 366.1489.



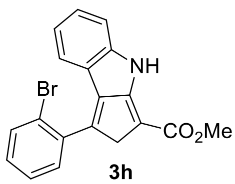
3f

3f: Prepared according to the general procedure Ⅱ above and obtained as brown solid (36.4 mg, 80% yield, M.P. = 118 – 120 °C), eluent: PE/EA = 6:1; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.83 (br,1H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.31 – 7.25 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 2H), 3.84 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.4, 157.8, 150.9, 142.8, 138.2, 136.0, 135.8, 130.8, 129.2, 129.0, 128.2, 125.8, 123.5, 121.0, 120.9, 110.7, 95.2, 50.8, 47.7, 20.5 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{20}H_{18}NO_2$ 304.1338, found 304.1341.



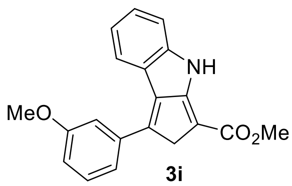
3g

3g: Prepared according to the general procedure Ⅱ above and obtained as brown solid (25.7 mg, 53% yield, M.P. = 125 - 127 °C), eluent: PE/EA = 6:1; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.83 (br,1H), 7.57 – 7.55 (m, 1H), 7.52 – 7.51 (m, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 4.05 (s, 2H), 3.84 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 155.4, 149.0, 137.4, 136.9, 133.0, 130.7, 128.8, 128.4, 127.32, 127.27, 124.7, 122.2, 118.8, 118.7, 108.7, 94.2, 48.8, 45.0 ppm; HRMS (ESI, quadrupole) *m/z* $(M+Na)^+$ calcd. for $C_{19}H_{14}ClNNaO_2$ 346.0611, found 346.0605.



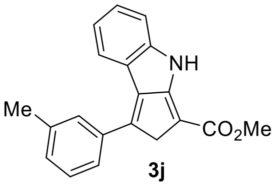
3h

3h: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (36.5 mg, 66% yield, M.P. = 127 - 131 °C), eluent: PE/EA = 5:1; ^1H NMR (500 MHz, DMSO-d_6) δ 10.52 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.20 – 7.16 (m, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 3.94 (s, 2H), 3.73 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 164.4, 156.8, 152.6, 139.9, 139.6, 137.1, 133.7, 131.6, 130.5, 129.9, 128.2, 124.0, 122.1, 120.7, 120.1, 111.9, 95.3, 50.8, 47.5 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ for $C_{19}H_{15}BrNO_2$ 368.0286, found 368.0287.



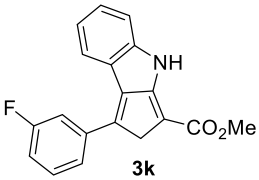
3i

3i: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (32.1 mg, 67% yield, M.P. = 181- 183 °C), eluent: PE/EA = 4:1; ^1H NMR (500 MHz, DMSO-d_6) δ 10.49 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.34 – 7.31 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 2H), 3.84 (s, 3H), 3.72 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.9, 159.6, 157.4, 152.1, 142.0, 136.7, 136.2, 130.0, 129.3, 122.7, 120.3, 120.0, 119.7, 114.3, 112.6, 111.6, 94.0, 55.2, 50.2, 45.0 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{20}H_{18}NO_3$ 320.1287, found 320.1285.



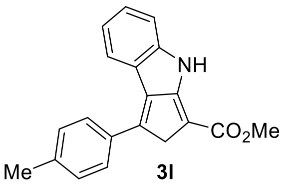
3j

3j: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (31.8 mg, 70% yield, M.P. = 192 - 195 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 10.50 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 5.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 3.93 (s, 2H), 3.72 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 163.7, 157.2, 151.7, 142.0, 137.9, 135.7, 135.0, 129.0, 128.8, 128.6, 127.8, 124.4, 122.4, 120.0, 119.6, 111.3, 93.5, 49.9, 44.6, 20.7 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{20}H_{18}NO_2$ 304.1340, found 304.1339.



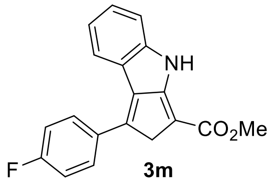
3k

3k: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (26.7 mg, 58% yield, M.P. = 207 - 212 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 10.53 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 3.96 (s, 2H), 3.72 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 163.6, 162.2 (d, $^{1}J_{C-F}$ = 244.4 Hz), 156.8, 152.0, 139.9, 137.4 (d, $^{3}J_{C-F}$ = 8.2 Hz), 136.7, 130.6 (d, $^{3}J_{C-F}$ = 8.7 Hz), 129.4, 123.4, 122.6, 120.0, 119.1, 114.7 (d, $^{2}J_{C-F}$ = 23.8 Hz), 113.7 (d, $^{2}J_{C-F}$ = 22.2 Hz), 111.4, 94.4, 50.0, 44.7 ppm; ^{19}F NMR (376 MHz, DMSO-d$_6$) δ -112.4 ppm; HRMS (ESI, quadrupole) *m/z* $(M+Na)^+$ calcd. for $C_{19}H_{14}FNNaO_2$ 330.0906, found 330.0911.



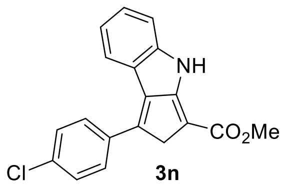
3l

3l: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (25.0 mg, 55% yield, M.P. = 215 - 220 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.30 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 2H), 3.71 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.8, 163.5, 157.8, 148.2, 143.9, 141.3, 138.4, 135.4, 135.0, 133.3, 128.5, 126.1, 125.7, 117.3, 99.2, 56.0, 50.7, 26.8 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{20}H_{18}NO_2$ 304.1338, found 304.1332.



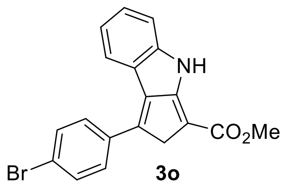
3m

3m: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (31.3 mg, 68% yield, M.P. = 222 - 225 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.50 (s, 1H), 7.85 – 7.83 (m, 3H), 7.36 – 7.31 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 3.93 (s, 2H), 3.71 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.6, 161.3 (d, $^1J_{C-F}$ = 247.2 Hz), 157.1, 151.8, 140.5, 135.6, 131.7 (d, $^4J_{C-F}$ = 3.0 Hz), 129.4 (d, $^3J_{C-F}$ = 8.3 Hz), 129.1, 122.4, 120.0, 119.4, 115.7 (d, $^2J_{C-F}$ = 21.7 Hz), 111.3, 93.6, 49.9, 44.8 ppm; ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.5 ppm; HRMS (ESI, quadrupole) *m/z* $(M+Na)^+$ calcd. for $C_{19}H_{14}FNNaO_2$ 330.0906, found 330.0904.



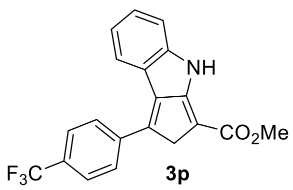
3n

3n: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (40.3 mg, 83% yield, M.P. = 233 - 238 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.50 (s, 1H), 7.86 – 7.81 (m, 3H), 7.56 – 7.55 (m, 2H), 7.33 (s, 1H), 7.20 (d, *J* = 6.0 Hz, 1H), 7.00 (s, 1H), 3.94 (s, 2H), 3.72 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.9, 157.2, 152.1, 140.3, 136.6, 134.2, 132.7, 129.5, 129.2, 129.0, 122.9, 120.2, 119.5, 111.6, 94.4, 50.2, 44.9 ppm; HRMS (ESI, quadrupole) *m/z* $(M+Na)^+$ calcd. for $C_{19}H_{14}ClNNaO_2$ 346.0611, found 346.0612.



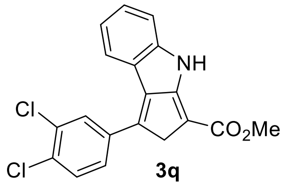
3o

3o: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (29.8 mg, 54% yield, M.P. = 247 - 255 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.52 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.73 (dd, *J* = 8.5 Hz, 26.0 Hz, 4H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 3.94 (s, 2H), 3.72 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.7, 157.0, 152.0, 140.1, 136.4, 134.3, 131.7, 129.4, 129.3, 122.7, 121.2, 120.1, 119.3, 111.4, 94.2, 50.0, 44.7 ppm; HRMS (ESI, quadrupole) *m/z* $(M+Na)^+$ calcd. for $C_{19}H_{14}BrNNaO_2$ 390.0106, found 390.0110.



3p

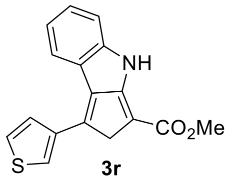
3p: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (42.3 mg, 79% yield, M.P. = 228 - 234 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.57 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 4.01 (s, 2H), 3.73 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.6, 156.7, 152.1, 139.1, 139.0, 137.7, 129.7, 127.8, 125.6 (q, J_{CF} = 2.8), 122.9, 120.1, 119.0, 111.4, 95.2, 50.1, 44.7 ppm; ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.1 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{20}H_{15}F_3NO_2$ 358.1055, found 358.1049.



3q

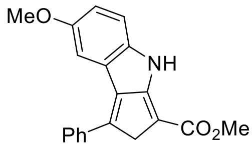
3q: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (48.9 mg, 91% yield, M.P. = 223 - 225 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.51 (s, 1H), 7.95 (s, 1H), 7.80 – 7.72 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 3.94 (s, 2H), 3.72 (s, 3H) ppm; ^{13}C NMR (126

MHz, DMSO-d6) δ 163.8, 156.9, 152.3, 138.5, 137.5, 135.9, 131.7, 131.0, 130.3, 129.8, 128.9, 127.5, 122.9, 120.3, 119.2, 111.7, 95.2, 50.3, 44.9 ppm; HRMS (ESI, quadrupole) *m/z* $(M+Na)^+$ calcd. for $C_{19}H_{13}Cl_2NNaO_2$ 358.0402, found 358.0401.



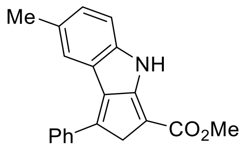
3r

3r: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (14.6 mg, 33% yield, M.P. = 233 - 236 °C), eluent: PE/EA = 5:1; ^{1}H NMR (500 MHz, DMSO-d6) δ 10.47 (s, 1H), 8.01 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.59 (d, *J* = 5.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 3.94 (s, 2H), 3.71 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d6) δ 169.2, 163.0, 157.0, 142.0, 141.9, 140.0, 134.3, 132.6, 130.2, 128.3, 125.6, 125.1, 116.7, 97.7, 55.4, 50.8 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{17}H_{14}NO_2S$ 296.0745, found 296.0743.



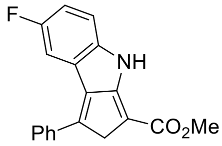
3s

3s: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (30.1 mg, 63% yield, M.P. = 220 - 224 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d6) δ 10.28 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.47 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.98 – 6.96 (m, 1H), 3.94 (s, 2H), 3.75 (s, 3H), 3.71 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d6) δ 163.7, 157.7, 153.3, 146.0, 142.3, 136.0, 135.1, 128.8, 128.2, 127.3, 120.1, 115.2, 111.6, 108.0, 93.1, 55.3, 49.9, 44.6 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{20}H_{18}NO_3$ 320.1287, found 320.1284.



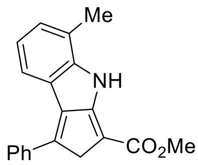
3t

3t: Prepared according to the general procedure Ⅱ above and obtained as yellow solid (26.8 mg, 59% yield, M.P. = 247 - 253 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 10.33 (s, 1H), 7.80 (d, *J* = 6.5 Hz, 2H), 7.66 (s, 1H), 7.52 (s, 2H), 7.39 (d, *J* = 5.5 Hz, 1H), 7.13 – 7.09 (m, 2H), 3.93 (s, 2H), 3.72 (s, 3H), 3.32 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 164.0, 157.7, 150.0, 141.9, 136.1, 135.4, 130.1, 129.0, 128.3, 127.5, 123.0, 119.9, 111.2, 93.5, 50.1, 44.9, 20.8 ppm; HRMS (ESI, quadrupole) *m/z* (M+H)$^+$ calcd. for $C_{20}H_{18}NO_2$ 304.1338, found 304.1345.



3u

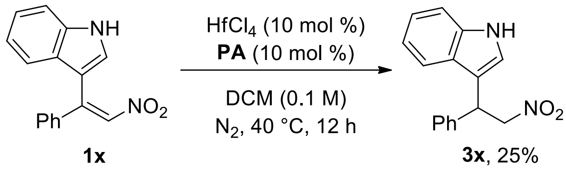
3u: Prepared according to the general procedure II above and obtained as yellow solid (16.6 mg, 36% yield, M.P. = 245 - 251 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 10.51 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.60 – 7.58 (m, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 1H), 7.22 – 7.16 (m, 2H), 3.98 (s, 2H), 3.72 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 164.3, 158.1, 157.3 (d, $^1J_{C\text{-}F}$ = 264.0 Hz), 148.9, 144.1, 136.0 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 135.5, 129.6, 129.2, 128.1, 121.0 (d, $^3J_{C\text{-}F}$ = 9.6 Hz), 116.5 (d, $^2J_{C\text{-}F}$ = 24.6 Hz), 112.5 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 109.8 (d, $^2J_{C\text{-}F}$ = 25.3 Hz), 94.6, 50.7, 45.5 ppm; ^{19}F NMR (376 MHz, DMSO-d$_6$) δ -123.2 ppm; HRMS (ESI, quadrupole) *m/z* (M+H)$^+$ calcd. for $C_{19}H_{15}FNO_2$ 308.1087, found 308.1090.



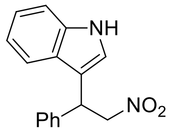
3v

3v: Prepared according to the general procedure II above and obtained as yellow solid (36.0 mg, 79% yield, M.P. = 208 - 210 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 9.90 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 3.96 (s, 2H), 3.73 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 163.9, 157.3, 150.5, 141.6, 136.6, 135.4, 130.6, 128.9, 128.3, 127.5, 121.0, 120.4, 120.1, 119.6, 94.8, 50.2, 45.2, 17.0 ppm; HRMS (ESI, quadrupole) *m/z* (M+H)$^+$ calcd. for $C_{20}H_{18}NO_2$ 304.1338, found 304.1333.

Failed substrates:

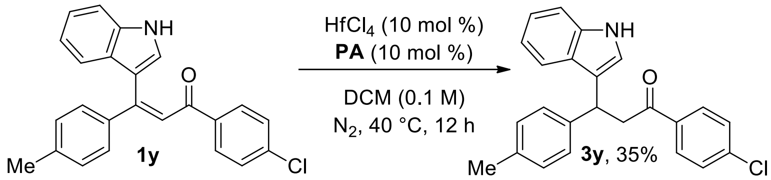


Compound **1x** is a known compound prepared according to literature precedures.[13]

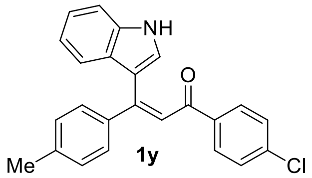


3x

3x: Prepared according to the general procedure Ⅱ above and obtained as white solid (10.0 mg, 25% yield), eluent: PE/EA = 6:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.37 – 7.30 (m, 5H), 7.27 – 7.24 (m, 1H), 7.21 – 7.18 (m, 1H), 7.09 – 7.06 (m, 1H), 7.04 – 7.03 (m, 1H), 5.19 (t, *J* = 8.0 Hz, 1H), 5.07 (dd, *J* = 12.5, 7.5 Hz, 1H), 4.94 (dd, *J* = 12.5, 8.5 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3, 136.5, 129.0, 127.8, 127.6, 126.1, 122.7, 121.7, 120.0, 119.0, 114.4, 111.5, 79.6, 41.6 ppm.

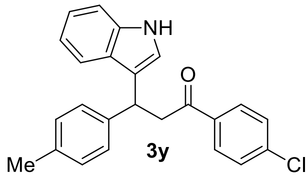


1y was prepared according to literature precedures.[1]



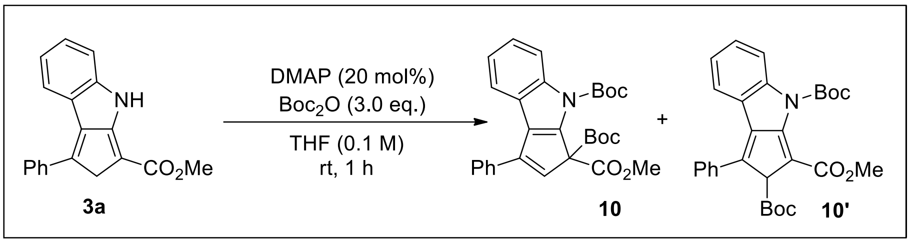
1y

1y: Yellow solid (0.76 g, 2.04 mmol, 50% yield, *E/Z* = 77:23), eluent: DCM; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.76 (s, 1H), 11.44 (s, 0.33H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 0.66H), 7.52 – 7.49 (m, 4.33H), 7.40 (d, *J* = 8.0 Hz, 0.33H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 3.0 Hz, 1H), 7.22 – 7.17 (m, 1.66H), 7.14 – 7.10 (m, 4.33H), 7.08 (d, *J* = 7.5 Hz, 0.66H), 7.04 (t, *J* = 7.5 Hz, 0.33H), 6.92 (s, 0.33H), 6.84 (t, *J* = 8.0 Hz, 0.33H), 6.72 (d, *J* = 8.0 Hz, 0.33H), 2.35 (s, 1H), 2.33 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 190.9, 189.4, 152.7, 149.2, 139.5, 139.2, 138.5, 137.9, 137.7, 137.6, 137.3, 137.2, 136.8, 131.2, 130.40, 130.37, 130.3, 129.7, 129.5, 129.2, 129.0, 128.9, 128.7, 126.9, 125.6, 122.8, 121.9, 121.22, 121.16, 120.7, 120.5, 119.9, 117.7, 116.9, 113.6, 113.0, 112.3, 21.38, 21.36 ppm.

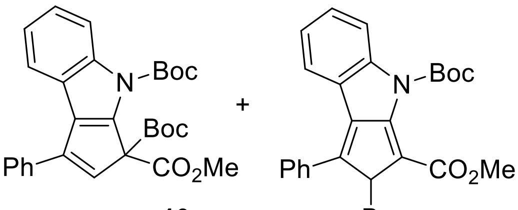


3y: Prepared according to the general procedure Ⅱ above and obtained as white solid (19.6 mg, 35% yield), eluent: PE/EA = 6:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.86 – 7.83 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.13 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.03 – 7.00 (m, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 5.00 (t, *J* = 7.5 Hz, 1H), 3.75 (dd, *J* = 16.5, 6.5 Hz, 1H), 3.66 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.27 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 141.0, 139.4, 136.7, 135.9, 135.5, 129.6, 129.2, 128.9, 127.6, 126.6, 122.2, 121.3, 119.5, 119.5, 119.4, 111.1, 45.2, 37.9, 21.0 ppm.

(C) **Transformations of 2,4-dihydrocyclo-pent[b]indole 3a**

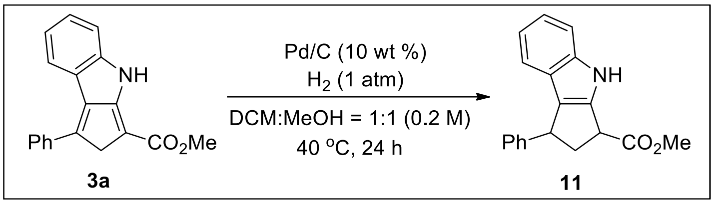


To a 10 mL tube equipped with a magnetic stir bar was added 2,4-dihydrocyclo-pent[b]indole **3a** (1 mmol, 1.0 equiv) and DMAP (0.2 mmol, 20 mol %). Then, THF (10.0 mL, 0.1 M) and Boc_2O (3.0 mmol, 3.0 equiv) was added. The reaction mixture was stirred at room temperature for 1 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel to give the mixture of product **10** and **10'**.

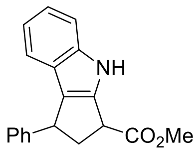


10 **10'**

10 and **10'**: Yellow foam solid (330 mg, 67% yield, **10**/**10'** = 88:12, M.P. = 57 - 60 ℃), eluent: PE/EA = 10:1; ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 0.14H), 7.75 – 7.73 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.60 (m, 0.28H), 7.51 – 7.48 (m, 2.42H), 7.44 – 7.41 (m, 1.14H), 7.35 – 7.30 (m, 1.14H), 7.26 – 7.23 (m, 1.14H), 6.20 (s, 1H), 5.01 (s, 0.14H), 3.73 (s, 0.42H), 3.69 (s, 3H), 1.70 (s, 1.26H), 1.66 (s, 9H), 1.37 (s, 9H), 1.36 (s, 1.26H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 166.2, 163.9, 162.9, 149.4, 149.2, 144.44, 144.0, 140.10, 139.96, 134.7, 134.5, 128.9, 128.7, 128.61, 128.58, 127.9, 127.8, 127.7, 127.6, 125.2, 124.6, 124.0, 123.7, 123.5, 123.3, 123.0, 120.0, 119.6, 116.4, 116.2, 85.3, 84.8, 82.5, 80.7, 67.4, 53.8, 52.8, 52.5, 28.2, 28.1, 28.0, 27.8 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{29}H_{32}NO_6$ 490.2230, found 490.2226.

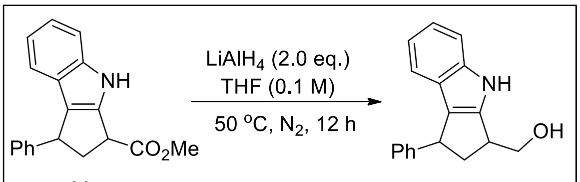


To an oven-dried 10 mL round-bottom flask equipped with a stir bar was added 2,4-dihydrocyclo-pent[b]indole **3a** (0.4 mmol, 1.0 equiv) and Pd/C (10 wt % of Pd). The flask was evacuated and backfilled with H_2 for three times. Then, DCM (1.0 mL) and MeOH (1.0 mL) was added via a syringe. The flask was equipped with a H_2 balloon (1 atm), and the mixture was stirred at 40 °C for 24 h. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under vacuum and purified by column chromatography on silica gel to give the desired product **3ab**.

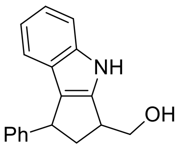


11

11: Yellow solid (90 mg, 77% yield, dr = 62:38, M.P. = 125 - 130 °C), eluent: PE/EA = 6:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.19 (s, 0.61H), 7.35 (d, *J* = 8.0 Hz, 1.61H), 7.30 – 7.27 (m, 4.83H), 7.24 – 7.19 (m, 3.83H), 7.15 – 7.12 (m, 2.61H), 7.02 – 6.96 (m, 1.61H), 4.62 (t, *J* = 6.5 Hz, 0.61H), 4.44 (t, *J* = 6.5 Hz, 1H), 4.25 – 4.23 (m, 0.61H), 4.19 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 1.83H), 3.41 – 3.36 (m, 0.61H), 3.29 – 3.23 (m, 1H), 2.67 – 2.61 (m, 1.61H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.70, 172.67, 145.2, 144.7, 141.3, 139.82, 139.75, 128.50, 128.47, 127.5, 127.3, 126.4, 126.3, 124.1, 122.9, 122.5, 121.7, 121.6, 119.9, 119.8, 119.3, 119.2, 111.8, 52.3, 44.1, 43.9, 43.8, 43.44, 43.39, 43.2 ppm; HRMS (ESI) calcd for $C_{19}H_{18}NO_2^+$ $(M+H)^+$ 292.1338, found 292.1336.

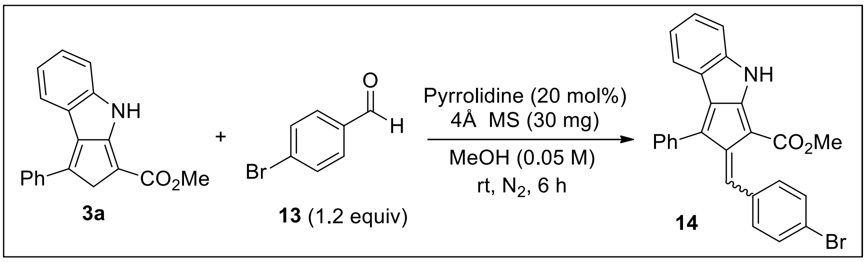


To a 10 mL Schlenk tube equipped with a magnetic stir bar was added compounds **11** (0.1 mmol, 1.0 equiv) and $LiAlH_4$ (0.2 mmol, 2.0 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous THF (1.0 mL, 0.1 M) was added under nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel to give the desired product **12**.

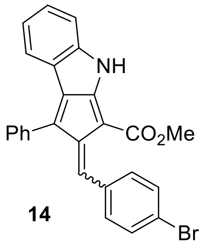


12

12: Brown oil (16 mg, 61% yield, dr = 71:29), eluent: PE/EA = 2:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.27 (s, 0.4H), 7.34 (d, J = 8.0 Hz, 1.4H), 7.29 – 7.25 (m, 4.2H), 7.22 – 7.17 (m, 2.8H), 7.14 – 7.09 (m, 2.8H), 7.01 – 6.96 (m, 1.4H), 4.54 – 4.52 (m, 0.4H), 4.50 – 4.47 (m, 1H), 3.97 – 3.91 (m, 1.4H), 3.69 – 3.63 (m, 1.4H), 3.62 – 3.56 (m, 0.4H), 3.54 – 3.48 (m, 1H), 3.12 – 3.06 (m, 1H), 2.72 – 2.66 (m, 0.4H), 2.53 – 2.48 (m, 0.4H), 1.92 – 1.87 (m, 1H), 1.73 (s, 1.4H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 146.0, 145.5, 141.07, 140.98, 128.5, 127.4, 127.3, 126.2, 126.1, 124.21, 124.18, 121.7, 121.1, 121.02, 120.99, 119.7, 119.6, 119.01, 118.99, 111.7, 111.6, 67.0, 66.5, 44.0, 43.5, 43.12, 43.09, 41.6, 41.2 ppm; HRMS (ESI) calcd for $C_{18}H_{18}NO^+$ $(M+H)^+$ 264.1388, found 264.1386.

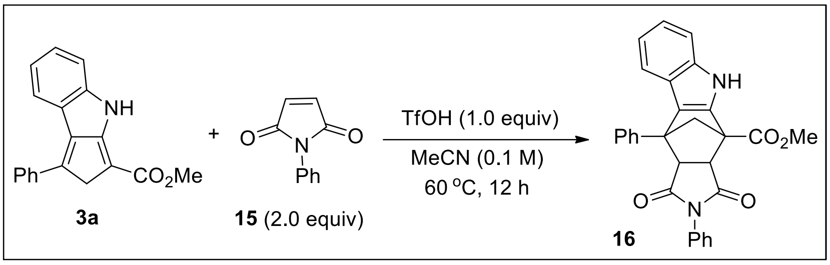


Synthesis of 14: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added compounds **3a** (0.1 mmol, 1.0 equiv), 4-bromobenzaldehyde (0.12 mmol, 1.2 equiv) and 4Å molecular sieve (30 mg). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then, pyrrolidine (0.02 mmol, 0.2 equiv) was dissolved in anhydrous MeOH (2.0 mL, 0.05 M), the solution was added to the tube under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 6 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel to give the desired product **14**.

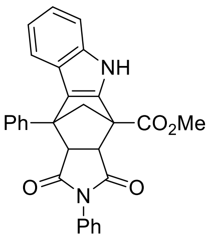


14

14: Brown solid (30.2 mg, 66% yield, dr = 89:11, M.P. = 179 – 182 ℃), eluent: PE/EA = 6:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 0.12H), 8.28 (s, 1H), 7.58 (d, *J* = 7.0 Hz, 2H), 7.54 – 7.49 (m, 3.12H), 7.47 – 7.44 (m, 3H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.18 – 7.15 (m, 0.36H), 7.12 – 7.07 (m, 1.48H), 7.01 (d, *J* = 8.0 Hz, 1.24H), 6.97 (d, *J* = 8.0 Hz, 0.12H), 6.90 (t, *J* = 7.5 Hz, 1.24H), 6.84 (t, *J* = 7.5 Hz, 0.12H), 3.89 (s, 0.36H), 3.47 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 163.0, 149.6, 149.2, 144.14, 144.08, 139.8, 138.7, 138.6, 136.7, 135.7, 135.1, 134.4, 133.9, 133.2, 132.4, 130.6, 130.4, 130.3, 129.5, 129.1, 128.6, 128.4, 128.0, 127.0, 123.4, 123.0, 122.6, 122.0, 121.60, 121.57, 121.4, 111.3, 111.1, 91.3, 89.5, 50.7, 50.4 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{26}H_{19}NO_2$ 456.0599, found 456.0594.



Synthesis of 16: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added compounds **3a** (0.1 mmol, 1.0 equiv) and N-phenylmaleimide **15** (0.2 mmol, 2.0 equiv). Then, TfOH (0.1 mmol, 1.0 equiv) was dissolved in MeCN (2.0 mL, 0.05 M), the solution was added to the tube. The reaction mixture was stirred at 60 ℃ for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel to give the desired product **16**.

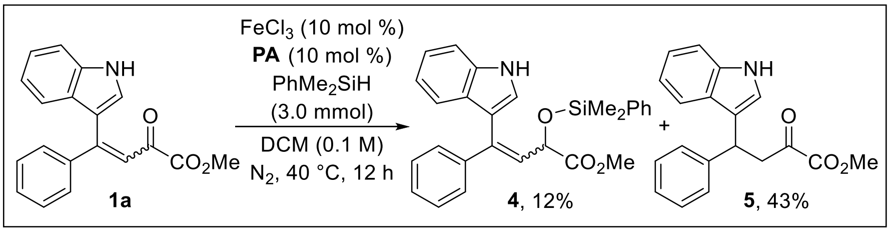


16

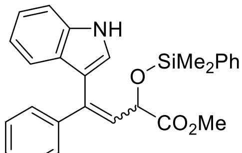
16: White solid (15.5 mg, 32% yield, M.P. = 235 – 237 ℃), eluent: PE/EA = 3:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.46 (s, 1H), 7.92 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.14 – 7.07 (m, 3H), 7.03 (t, *J* = 8.0, 2H), 6.97 – 6.94 (m, 1H), 5.81 (dd, *J* = 8.0, 1.5 Hz, 2H), 4.42 (d, *J* = 7.5 Hz, 1H), 4.32 (d, *J* = 7.5 Hz, 1H), 3.90 (s, 3H), 2.70 (d, *J* = 8.0 Hz, 1H), 2.61 (d, *J* = 8.5 Hz, 1H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 174.6, 174.1, 170.7, 141.6, 140.9, 139.5, 131.9, 129.0, 128.6, 128.34, 128.28, 127.7, 126.8, 122.9, 121.7, 120.7, 120.0, 119.3, 113.3, 64.8, 60.6, 58.9, 54.1, 53.1, 52.0 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{29}H_{23}N_2O_4$ 463.1658, found 463.1663.

V. Control Reaction

A) The reduction of 1a with binary acid complex of $FeCl_3$/PA as catalyst

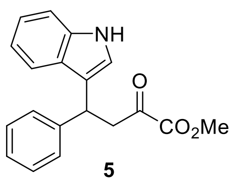


To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1a** (0.2 mmol, 1.0 equiv), $FeCl_3$ (0.02 mmol, 10 mol %) and diphenyl phosphate (0.02 mmol, 10 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (2.0 mL, 0.1 M) and $PhSiHMe_2$ (0.6 mmol, 3.0 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 10:1 to 3:1, v/v) to give the 1,2-adduct **4** (brown oil, 10.6 mg, 12% yield) and 1,4-adduct **5** (light yellow solid, 26.4 mg, 43% yield).



4

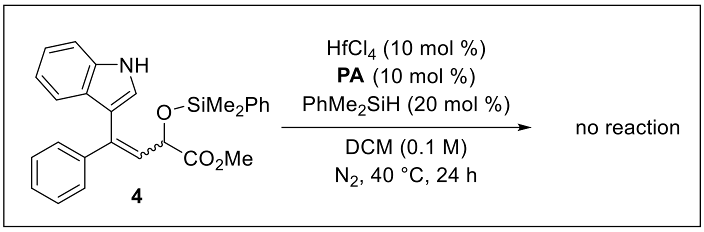
4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.51 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.27 – 7.23 (m, 4H), 7.21 – 7.19 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.82 (s, 1H), 6.54 (d, *J* = 10.0 Hz, 1H), 5.37 (d, *J* = 10.0 Hz, 1H), 3.66 (s, 3H), 0.46 (s, 3H), 0.45 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 143.7, 140.2, 138.2, 137.3, 134.1, 130.3, 129.1, 128.8, 128.4, 127.4, 127.1, 125.6, 122.8, 122.7, 120.5, 120.1, 118.8, 111.7, 52.6, 39.8, 0.0, -0.2 ppm; HRMS (ESI, quadrupole) *m/z* $(M+H)^+$ calcd. for $C_{27}H_{28}NO_3Si$ 442.1838, found 442.1842.



5

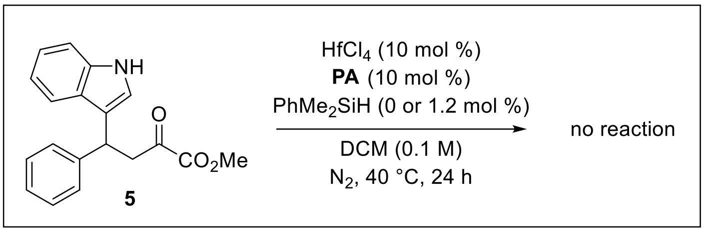
5: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 3H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.03 – 7.00 (m, 2H), 4.91 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 3H), 3.68 (dd, *J* = 17.0, 7.0 Hz, 1H), 3.60 (dd, *J* = 17.0, 8.0 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7, 161.4, 143.2, 136.6, 128.6, 127.8, 126.7, 126.4, 122.3, 121.6, 119.6, 119.4, 118.3, 111.2, 53.0, 45.7, 37.8 ppm.

B) The reduction of 1,2-adduct 4 under standard conditions



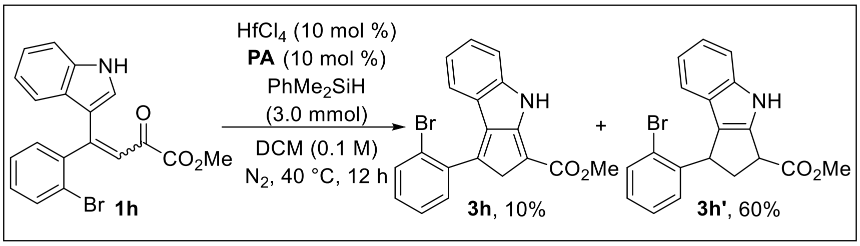
To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 1,2-adduct compound **4** (0.05 mmol, 1.0 equiv), $HfCl_4$ (0.005 mmol, 10 mol %) and diphenyl phosphate (0.005 mmol, 10 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (0.5 mL, 0.1 M) and $PhSiHMe_2$ (0.01 mmol, 20 mol %) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 ° C for 24 h. No reaction was observed.

C) The reduction of 1,4-adduct 5 under standard conditions

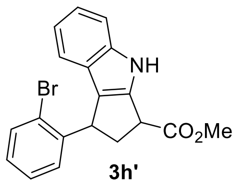


To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 1,4-adduct compound **5** (0.1 mmol, 1.0 equiv), $HfCl_4$ (0.01 mmol, 10 mol %) and diphenyl phosphate (0.01 mmol, 10 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.0 mL, 0.1 M) and $PhSiHMe_2$ (0 or 0.12 mmol, 120 mol %) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 24 h. No reaction was observed.

D) The reduction of 1h with excessive $PhMe_2SiH$ as reductant



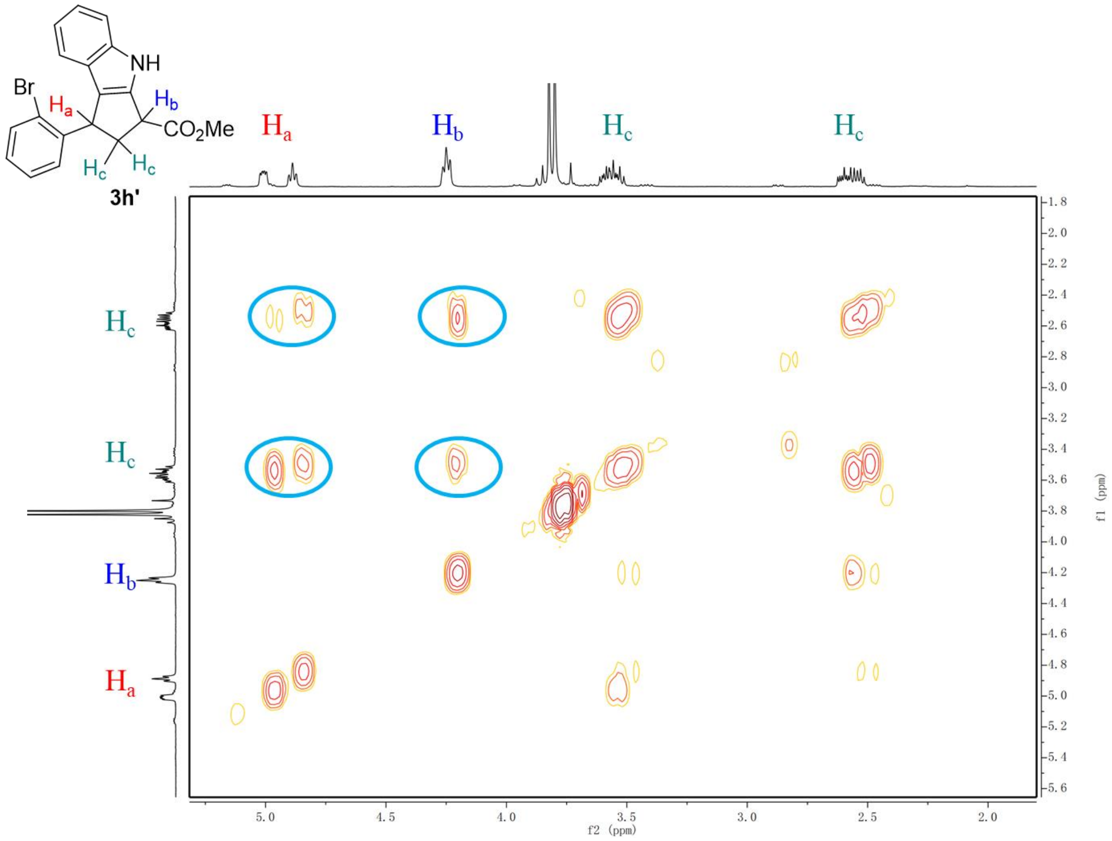
To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1h** (0.2 mmol, 1.0 equiv), $HfCl_4$ (0.02 mmol, 10 mol %) and diphenyl phosphate (0.02 mmol, 10 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (2.0 mL, 0.1 M) and $PhSiHMe_2$ (0.6 mmol, 3.0 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 ℃ for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 6:1 to 4:1, v/v) to give the desired product **3h** (yellow solid ,7.4 mg, 10% yield) and **3h**′ (light yellow oil, 44.4 mg, 60% yield).



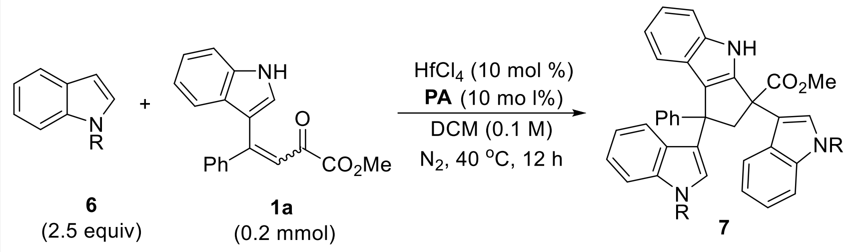
3h'

3h′: ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.61 – 7.59 (m, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.23 – 7.14 (m, 6H), 7.10 – 7.00 (m, 5H), 6.95 – 6.93 (m, 1H), 4.98 – 4.95 (m, 1H), 4.84 (t, *J* = 7.0 Hz, 1H), 4.21 (t, *J* = 7.0 Hz, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 3.57 – 3.47 (m, 2H), 2.58 – 2.47 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.60, 172.58, 144.0, 143.6, 141.38, 141.35, 140.4, 140.3, 132.9, 132.6, 128.9, 128.3, 128.0, 127.9, 127.7, 127.5, 124.4, 124.1, 124.0, 123.9, 121.82, 121.77, 121.4, 121.2, 120.0, 119.9, 119.4, 119.3, 111.84, 111.83, 52.4, 52.3, 43.9, 43.6, 43.1, 43.0, 41.8, 41.3 ppm; HRMS (ESI, quadrupole) *m/z* $(M+Na)^+$ calcd. for $C_{19}H_{16}BrNNaO_2$ 392.0262, found 392.0259.

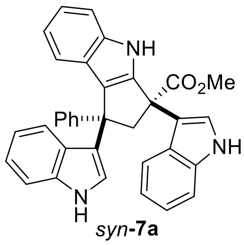
H-HCOSY for 1,2,3,4-tetrahydrocyclopenta[*b*]indole 3h′



E) Carbocation capture experiment

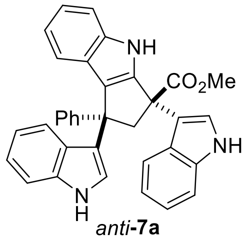


Aromatic nucleophile: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1a** (0.2 mmol, 1.0 equiv), $HfCl_4$ (0.02 mmol, 10 mol %), diphenyl phosphate (0.02 mmol, 10 mol %) and indole derivatives **6** (0.5 mmol, 2.5 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (2.0 mL, 0.1 M) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel to give the bisindole adducts **7**.



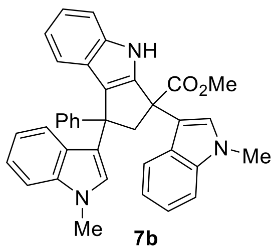
syn-**7a**

syn-**7a**: Light yellow solid (36.5 mg, 35% yield, M.P. = 150 - 158 °C), eluent: DCM/PE = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.55 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.39 – 7.36 (m, 4H), 7.25 – 7.16 (m, 3H), 7.13 – 7.07 (m, 5H), 7.05 – 6.95 (m, 4H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 22.5 Hz, 2H), 4.31 (d, *J* = 13.5 Hz, 1H), 3.75 (d, *J* = 13.5 Hz, 1H), 3.62 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 147.9, 141.2, 140.6, 136.9, 136.6, 128.1, 127.6, 126.4, 126.3, 125.9, 125.1, 124.0, 123.3, 122.7, 122.4, 122.2, 121.9, 121.6, 121.4, 120.2, 120.1, 119. 7, 119.0, 117.7, 112.1, 111.5, 111.0, 58.5, 53.3, 52.8, 50.9 ppm; HRMS (ESI, quadrupole) *m/z* $(M+Na)^+$ calcd. for $C_{35}H_{27}N_3NaO_2$ 544.2001, found 544.2001.



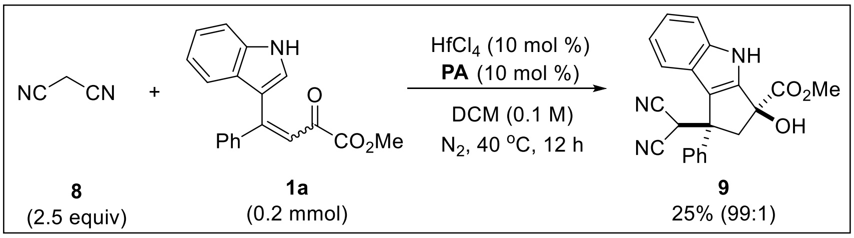
anti-**7a**

anti-**7a**: Light yellow solid (41.4 mg, 40% yield, M.P. = 161 - 167 °C), eluent: DCM/PE = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.78 (d, *J* = 13.5 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.23 (m, 5H), 7.21 – 7.18 (m, 1H), 7.14 – 7.08 (m, 4H), 7.01 – 6.98 (m, 4H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 33.0 Hz, 2H), 4.32 (d, *J* = 13.5 Hz, 1H), 3.86 (d, *J* = 14.0 Hz, 1H), 3.45 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 147.0, 141.1, 140.5, 137.2, 136.8, 127.8, 127.6, 126.9, 126.5, 125.7, 125.2, 124.0, 123.6, 123.3, 122.52, 122.46, 121.8, 121.7, 121.4, 120.1, 119.99, 119.95, 119.8, 119.2, 117.7, 112.1, 111.6, 111.1, 57.5, 53.5, 52.5, 51.0 ppm; HRMS (ESI, quadrupole) *m/z* $(M+Na)^+$ calcd. for $C_{35}H_{27}N_3NaO_2$ 544.2001, found 544.2010.

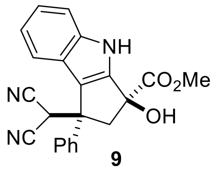


7b

7b: Light yellow solid (88.0 mg, 80% yield, *anti*/*syn* = 74:26, M.P. = 130 - 140 °C), eluent: PE/EA = 4:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.32 (s, 0.35H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 0.35H), 7.43 (d, *J* = 7.5 Hz, 0.7H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1.35H), 7.29 – 7.21 (m, 5.7H), 7.19 (d, *J* = 8.5 Hz, 0.7H), 7.15 (t, *J* = 7.5 Hz, 2.7H), 7.11 – 7.06 (m, 3.05H), 7.04 – 6.97 (m, 5.05H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 0.35H), 6.74 (s, 1H), 6.73 (s, 0.35H), 6.67 (s, 1H), 6.56 (s, 0.35H), 4.39 (d, *J* = 13.5 Hz, 0.35H), 4.30 (d, *J* = 13.5 Hz, 1H), 3.83 (d, *J* = 13.5 Hz, 1H), 3.74 (d, *J* = 13.5 Hz, 0.35H), 3.65 (s, 4.05H), 3.61 (s, 3H), 3.60 (s, 1.05H), 3.52 (s, 3H), 3.51 (s, 1.05H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 173.8, 147.8, 147.2, 141.2, 141.1, 140.62, 140.57, 137.9, 137.7, 137.6, 137.5, 128.0, 127.9, 127.74, 127.69, 127.6, 127.3, 126.9, 126.8, 126.7, 126.6, 125.8, 125.72, 125.68, 125.5, 124.2, 124.1, 122.1, 122.0, 121.7, 121.54, 121.46, 121.23, 121.17, 120.14, 120.67, 119.99, 119.96, 119.62, 119.56, 118.6, 118.5, 116.3, 116.1, 112.1, 112.0, 109.5, 109.4, 109.1, 109.0, 59.1, 58.0, 53.4, 53.3, 52.7, 52.4, 51.0, 50.9, 32.7, 32.5 ppm; HRMS (ESI) $(M+Na)^+$ calcd. for $C_{37}H_{31}N_3NaO_2$ 572.2314, found 572.2311.



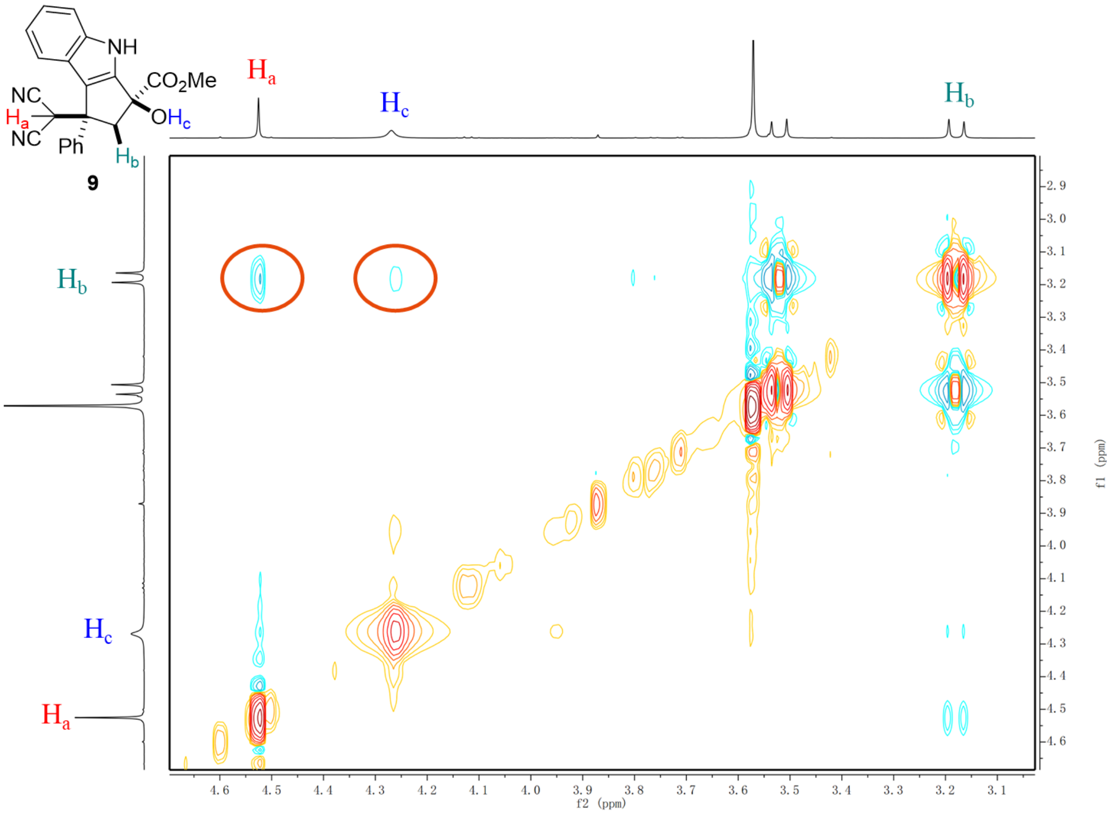
C-nucleophile: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1a** (0.2 mmol, 1.0 equiv), $HfCl_4$ (0.02 mmol, 10 mol %), diphenyl phosphate (0.02 mmol, 10 mol %) and malononitrile **8** (0.5 mmol, 2.5 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (2.0 mL, 0.1 M) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 ℃ for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel to give the mono-malononitrile adduct **9**.



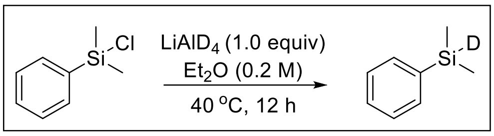
9

9: Yellow solid (18.6 mg, 25% yield, dr = 99:1, M.P. = 99 - 102 °C), eluent: DCM/EA = 10:1; ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 7.0 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.29 – 7.25 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 4.53 (s, 1H), 4.27 (br, 1H), 3.57 (s, 3H), 3.52 (d, J = 14.5 Hz, 1H), 3.18 (d, J = 14.5 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 141.9, 141.8, 140.8, 129.1, 128.4, 126.9, 123.9, 122.8, 122.2, 121.6, 121.4, 112.90, 112.88, 112.8, 77.1, 58.2, 54.9, 53.6, 35.7 ppm; HRMS (ESI, quadrupole) m/z $(M+Na)^+$ calcd. for $C_{22}H_{17}N_3NaO_3$ 394.1168, found 394.1169.

NOESY for mono-malononitrile adduct 9



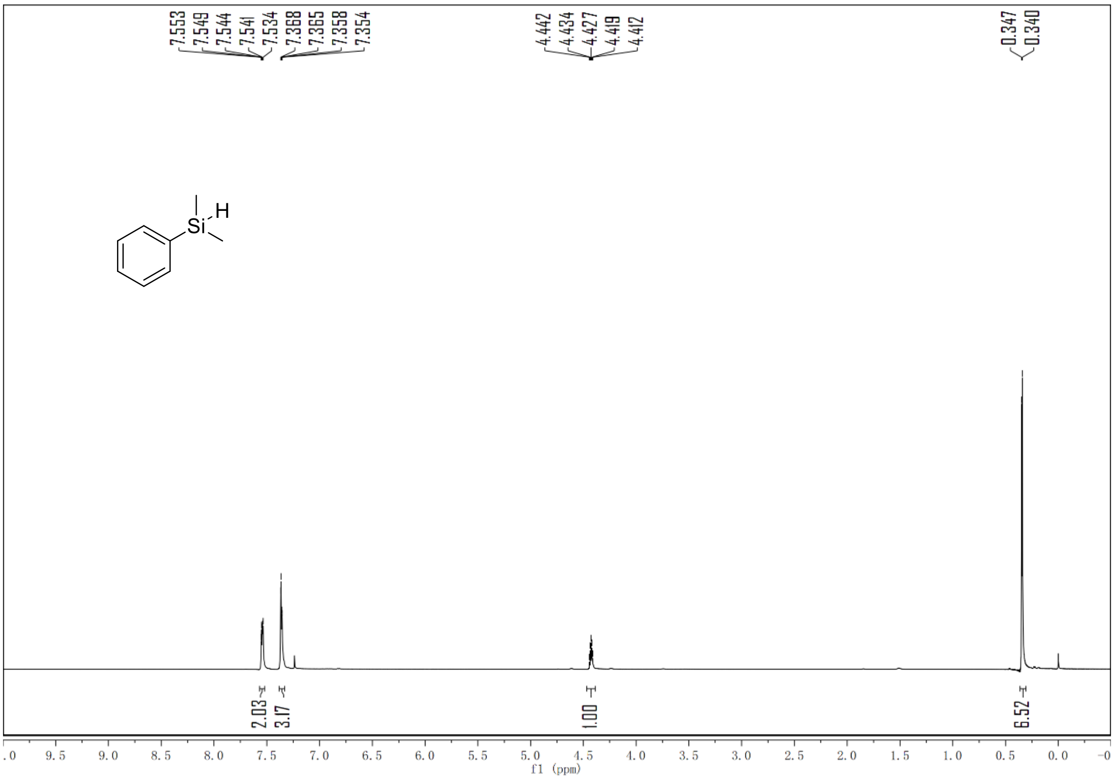
VI. Deuterium-labelling Experiments



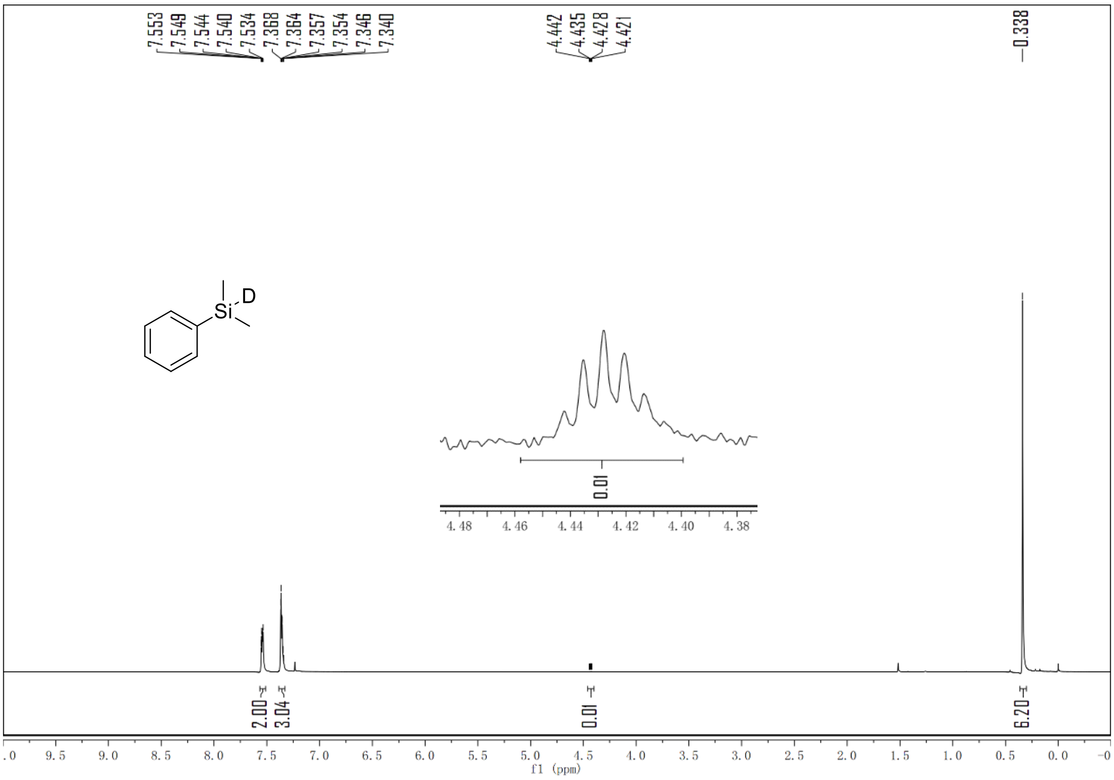
A) Synthesis of deuterated dimethylphenylsilane: $PhSiDMe_2$ were prepared on slightly modified literature precedures.[2] $LiAlD_4$ (5 mmol, 1.0 equiv) was dissolved in diethyl ether (10 mL, 0.2 M), then $PhMe_2SiCl$ (15 mmol, 3.0 equiv) was added dropwise under nitrogen atmosphere. The reaction mixture was stirred at 40 ℃ for 10 h and cooled down to room temperature. Then, the reaction was quenched by adding aqueous solution of sodium hydroxide (15 mL, 10 wt%) into the crude reaction mixture, which was subsequently extracted by diethyl ether for three times. The combined organic layers were dried over Na_2SO_4, evaporated under reduced pressure, and purified by column chromatography on silica gel (eluent: PE) to give $PhMe_2SiD$ (colorless liquid, 1.55g, 75% yield, 99% D). $PhSiDMe_2$ was analyzed by ^1H NMR.

$PhSiDMe_2$: ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.53 (m, 2H), 7.37 – 7.34 (m, 3H), 0.34 (s, 6H) ppm.

^{1}H NMR (500 MHz, CDCl$_3$)



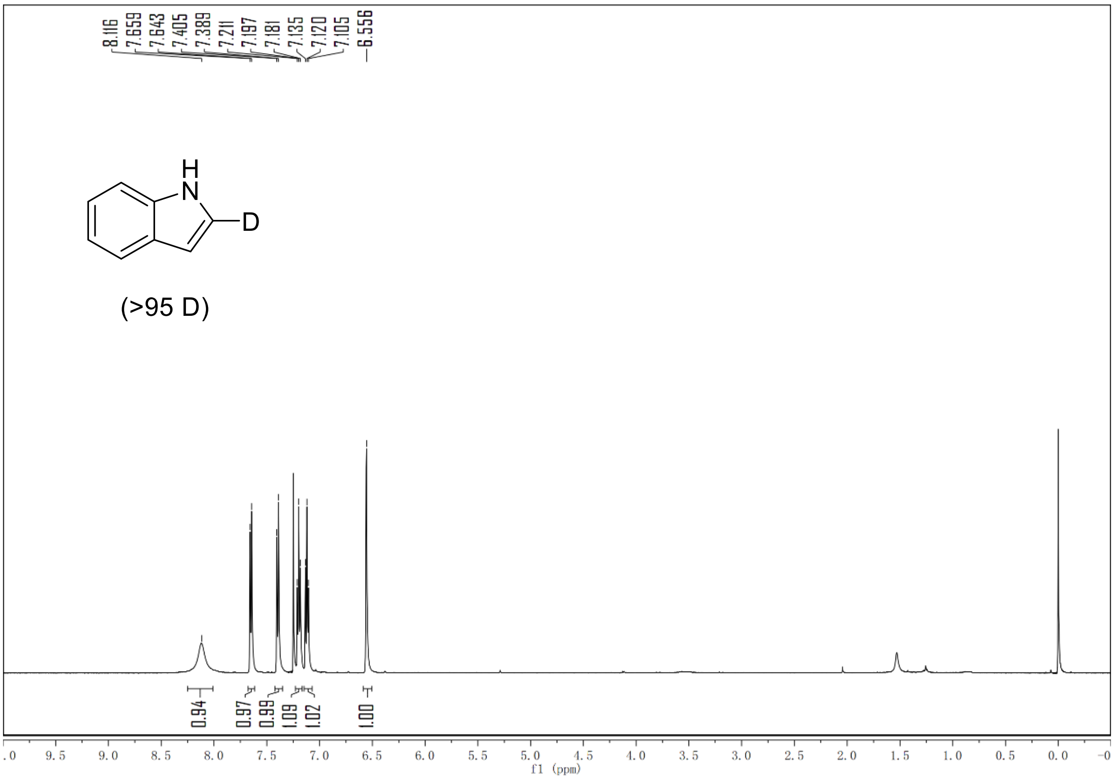
^{1}H NMR (500 MHz, CDCl$_3$)

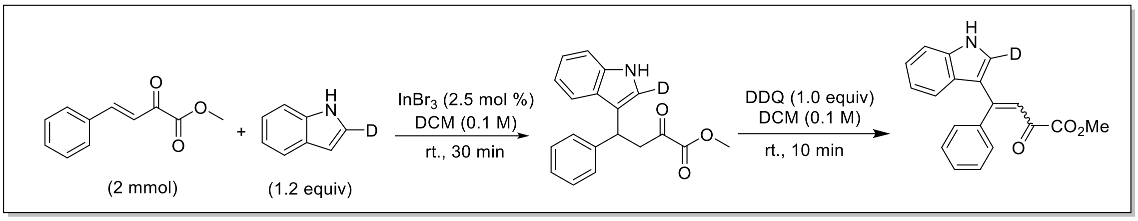


B) Synthesis of deuterated indole: Deuterated Indole were prepared according to literature precedures.[3] Deuterated indole was analyzed by ^{1}H NMR.

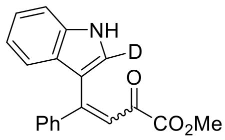
Deuterated indole: Off-white solid (502 mg, 4.25 mmol, 85% yield, > 95% D); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.56 (s, 1H) ppm.

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





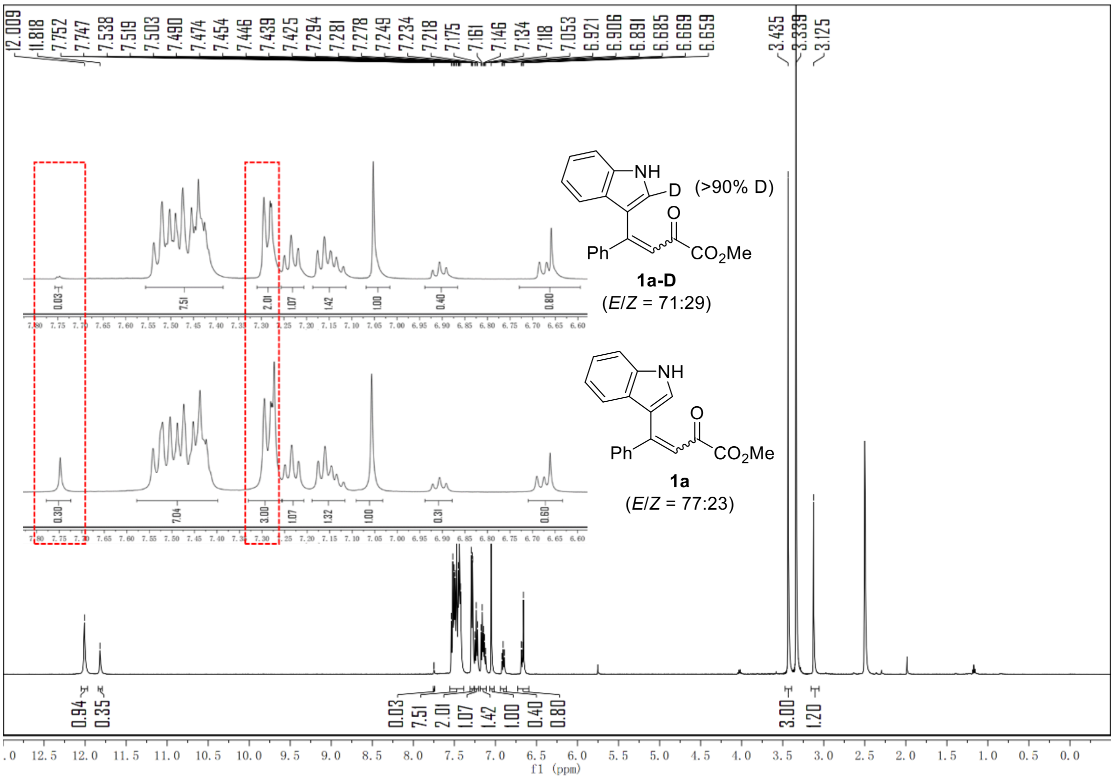
C) One-pot synthesis of deuterated *γ*-indolyl *β,γ*-unsaturated *α*-keto esters: β,γ-unsaturated-α-ketoester derivatives (2 mmol, 1.0 equiv) and deuterated indole (2.4 mmol, 1.2 equiv) were dissolved in DCM (20 mL, 0.1 M), then $InBr_3$ (0.05 mmol, 2.5 mol %) was added. The solution was stirred at room temperature for 30 min. Subsequently, DDQ (2 mmol, 1.0 equiv) was added. The solution was stirred at room temperature for 10 minutes. After reaction, purification of mixture by column chromatography on silica gel (eluent: DCM/EA = 30:1, v/v) gave the deuterated *γ*-indolyl *β,γ*-unsaturated *α*-keto esters **1a[D]**. Deuterated *γ*-indolyl *β,γ*-unsaturated *α*-keto esters was analyzed by ^1H NMR.

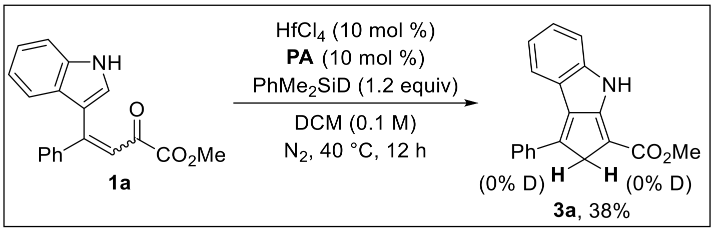


1a[D]

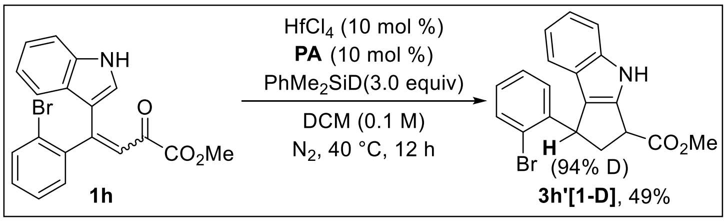
1a[D]: Yellow solid (459 mg, 75% yield, *E/Z* = 71:29, > 90% D); ^1H NMR (500 MHz, DMSO-d_6) δ 12.01 (s, 1H), 11.82 (s, 0.4H), 7.54 – 7.43 (m, 7.4H), 7.29 – 7.28 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.12 (m, 1.4H), 7.05 (s, 1H), 6.91 (t, *J* = 7.5 Hz, 0.4H), 6.69 – 6.66 (m, 0.8H), 3.44 (s, 3H), 3.13 (s, 1.2H) ppm.

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



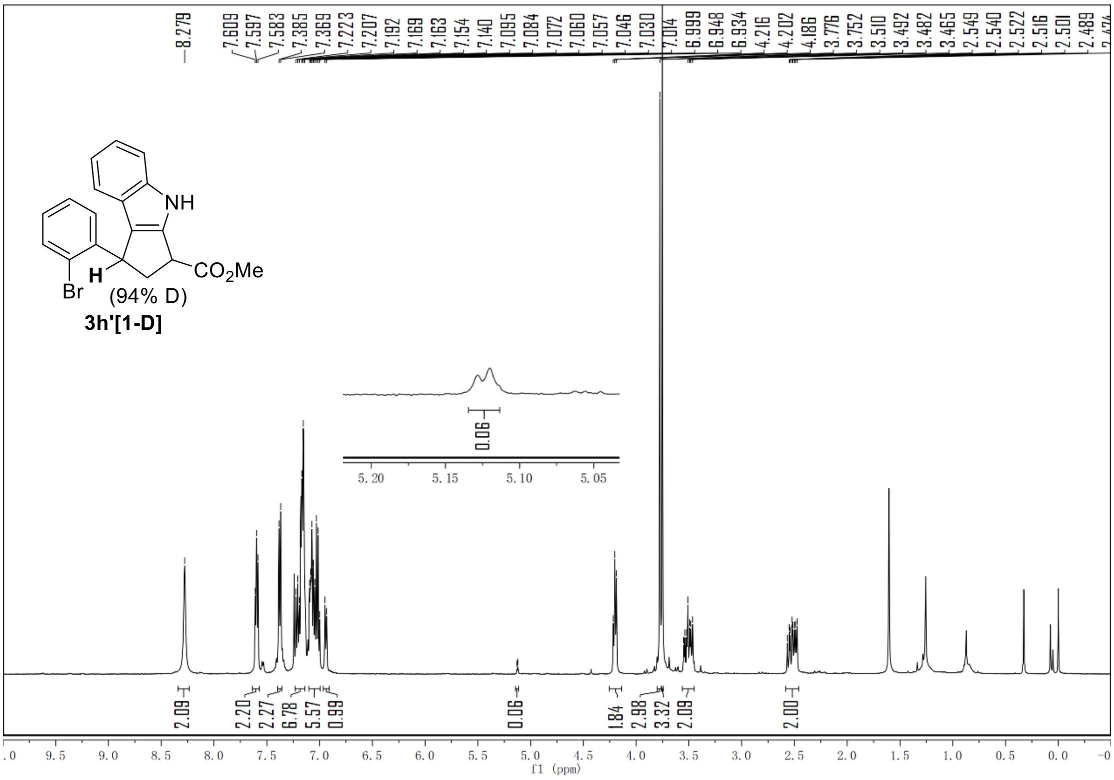


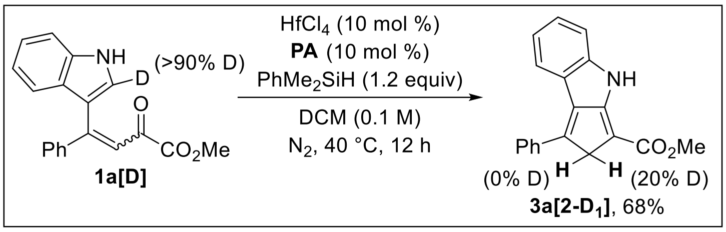
D) $PhMe_2SiD$ replaces $PhMe_2SiH$ as reducing reagent under standard conditions: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1a** (0.15 mmol, 1.0 equiv), $HfCl_4$ (0.015 mmol, 10 mol %) and diphenyl phosphate (0.015 mmol, 10 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.5 mL, 0.1 M) and $PhSiDMe_2$ (0.18 mmol, 1.2 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 4:1, v/v) to give the desired product **3a** (16.5 mg, 38% yield). Through NMR testing, it was found that compound **3a** was not deuterated.



E) Excessive $PhMe_2SiD$ to reduce 1h under catalytic conditions: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1h** (0.15 mmol, 1.0 equiv), $HfCl_4$ (0.015 mmol, 10 mol %) and diphenyl phosphate (0.015 mmol, 10 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.5 mL, 0.1 M) and $PhSiDMe_2$ (0.45 mmol, 3.0 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 6:1, v/v) to give the desired product **3h'-D** (26.7 mg, 49% yield). Through NMR testing, it was found that the deuterated ratio of compound **3h'[1-D]** is 94%.

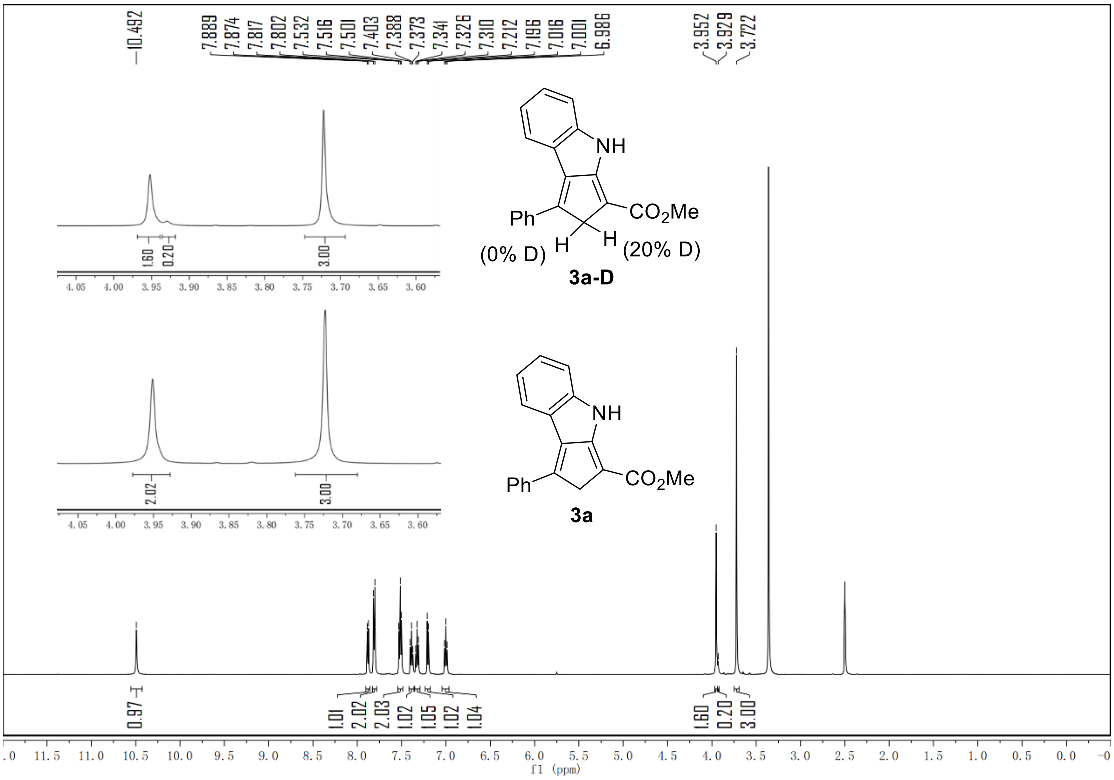
^1H NMR (500 MHz, $CDCl_3$)

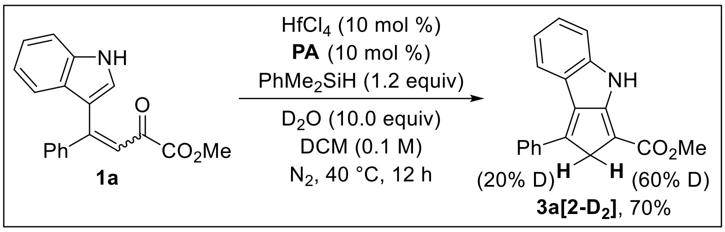




F) 1a[D] replaces 1a as substrate under standard conditions: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added deuterated γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1a[D]** (0.15 mmol, 1.0 equiv), $HfCl_4$ (0.015 mmol, 10 mol %) and diphenyl phosphate (0.015 mmol, 10 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.5 mL, 0.1 M) and $PhSiHMe_2$ (0.18 mmol, 1.2 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 ℃ for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 4:1, v/v) to give the desired product **3a[2-D$_1$]** (29.5 mg, 68% yield). Through NMR testing, it was found that the deuterated ratio of compound **3a[2-D$_1$]** is 20%.

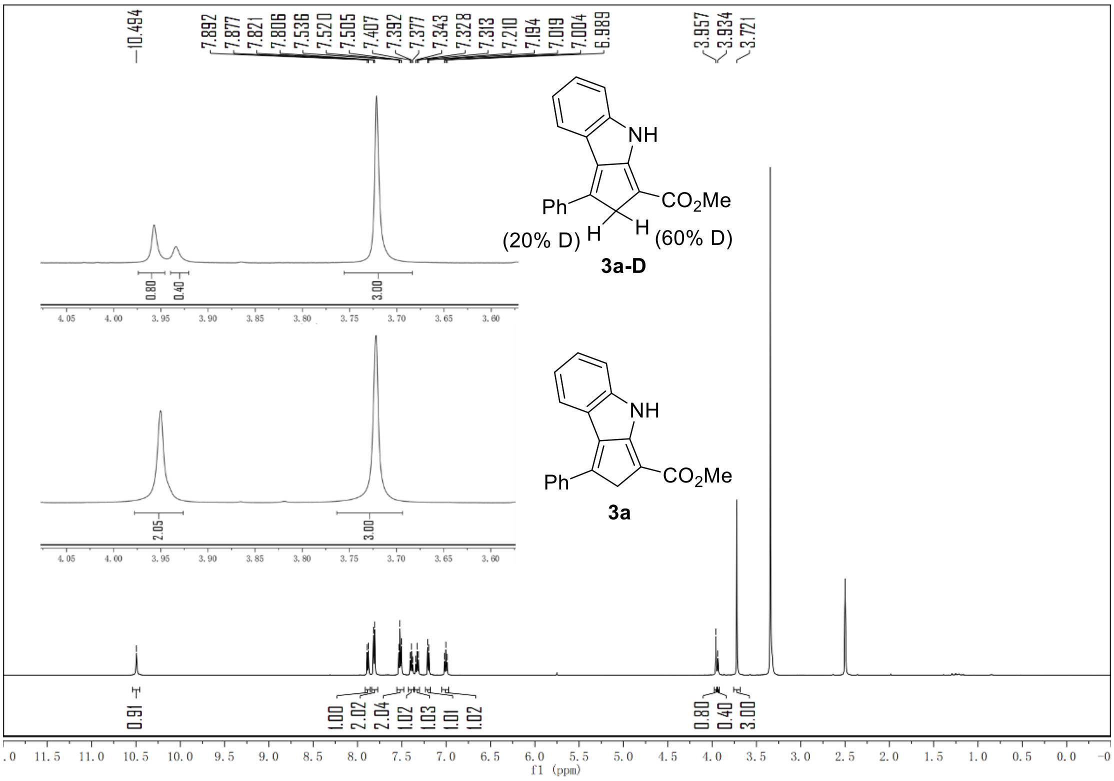
^{1}H NMR (500 MHz, DMSO-d_6)





G) Add additional deuterium water under standard conditions: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added γ-Indolyl β,γ-unsaturated-α-ketoester derivatives **1a** (0.15 mmol, 1.0 equiv), $HfCl_4$ (0.015 mmol, 10 mol %) and diphenyl phosphate (0.015 mmol, 10 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.5 mL, 0.1 M), D_2O (1.5 mmol, 10.0 equiv) and $PhSiHMe_2$ (0.18 mmol, 1.2 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 12 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 4:1, v/v) to give the desired product **3a[2-D₂]** (30.5 mg, 70% yield). Through NMR testing, it was found that the deuterated ratio of compound **3a[2-D₂]** is 60%.

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



VII. UV-vis Spectra of $Hf(OTf)_4$/PA/1a

UV-vis absorption spectra: The UV/Vis absorption spectra of the reaction of **1a** (0.1 mmol), **PA** (0.1 mmol) and **$Hf(OTf)_4$** (0.1 mmol) in $CHCl_3$ (2.0 mL) stirring for 5 min and 120 min were recorded in 1 cm path quartz cuvettes by using the UV-2600 UV-Vis spectrophotometer, respectively.

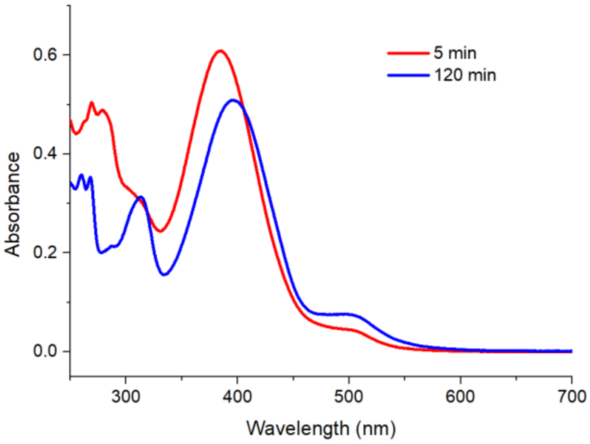


Figure S4. UV-vis spectra of $Hf(OTf)_4$/**PA**/**1a** (1:1:1, 0.05 M)

VIII. X-ray Structure

The crystal was cultivated from EtOH/DCM (1:1) with volatilization method.

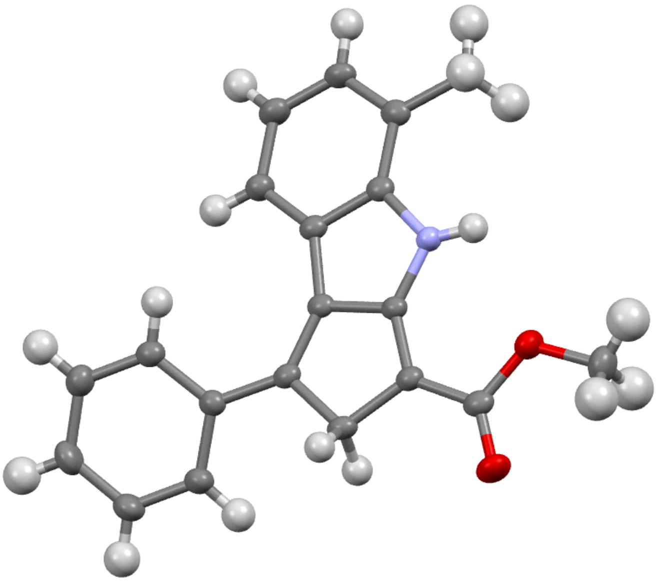


Figure S5. X-ray structure of compound **3v** (CCDC 2251334)

Table S7 Crystal data and structure refinement for **3v**

Empirical formula	$C_{20}H_{17}NO_2$	
Formula weight	303.35	
Temperature/K	293(2) K	
Crystal system	Triclinic	
Space group	P-1	
a/Å	7.5526(9)	
b/Å	10.6072(14)	
c/Å	10.6696(14)	
α/°	77.765(3)	
β/°	84.820(4)	
γ/°	69.886(2)	
Volume/Å3	784.26(17)	
Z	2	
ρcalc mg/m^3	1.285	
μ/mm^{-1}	0.083	
F(000)	320	
Crystal size/mm^3	0.30 x 0.07 x 0.04	
Radiation	radiation_wavelength	0.71073
	radiation_type	MoK\a
	radiation_source	'fine-focus sealed tube'
	radiation_monochromator	graphite
2Θ range for data collection/°	1.95 to 25.00	
Index ranges	-8<=h<=8, -12<=k<=11, -11<=l<=12	
Reflections collected	3795	
Independent reflections	2685 [R(int) = 0.0403]	
Data/restraints/parameters	2685 / 0 / 210	
Goodness-of-fit on F^2	0.970	
Final R indexes [I>=2σ (I)]	R1 = 0.0785, wR2 = 0.1980	
Final R indexes [all data]	R1 = 0.1176, wR2 = 0.2228	
Largest diff. peak/hole / e Å^{-3}	0.223 / -0.460	

The crystal was cultivated from acetone/CH_3OH (2:1) with volatilization method.

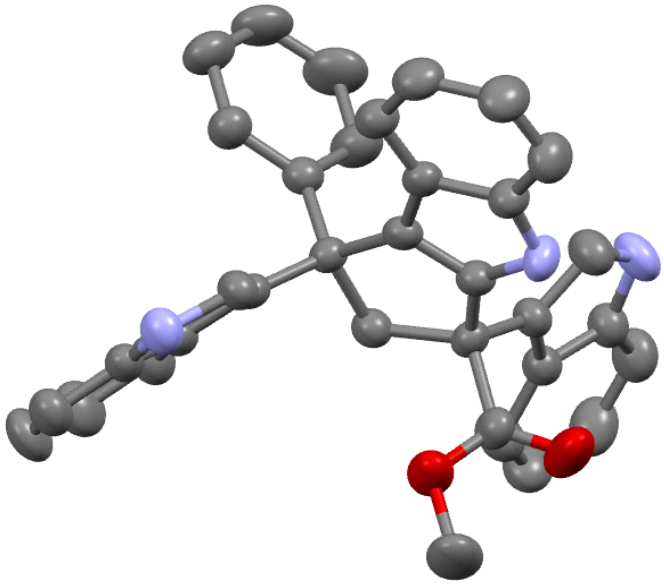


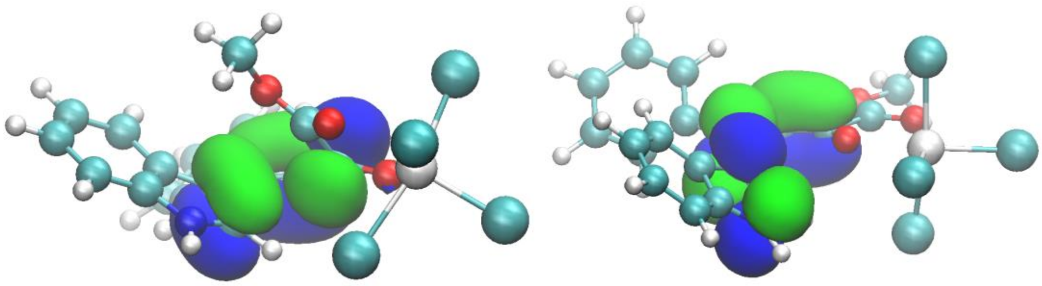
Figure S6. X-ray structure of compound *anti*-**7a** (CCDC 2323814)

Table S8 Crystal data and structure refinement for *anti*-**7a**

Empirical formula	$C_{38}H_{33}N_3O_3$
Formula weight	579.67
Temperature/K	298(2) K
Crystal system	Monoclinic
Space group	C2/c
a/Å	20.385(2)
b/Å	8.8207(9)
c/Å	33.720(3)
α/°	90
β/°	98.974(3)
γ/°	90
Volume/Å^3	5988.9(10)
Z	8
ρcalcg/cm^3	1.286
μ/mm^{-1}	0.082
F(000)	2448
Crystal size/mm^3	0.48 x 0.17 x 0.13
Radiation	MoKα(λ = 0.71073)
2Θ range for data collection/°	2.19 to 25.01
Index ranges	-18<=h<=24, -10<=k<=10, -39<=l<=40
Reflections collected	13983
Independent reflections	5241 [R(int) = 0.0837]
Data/restraints/parameters	5241/0/ 401
Goodness-of-fit on F2 0.985	1.047
Final R indexes [I>=2σ (I)]	R1 = 0.0667, wR2 = 0.1177
Final R indexes [all data]	R1 = 0.1397, wR2 = 0.1370
Largest diff. peak/hole / e Å^{-3}	0.361/-0.210

IX. Computational Data

The computations were performed using Gaussian16 program.[4] Initial geometry and transition structure optimizations were performed with the B3LYP functional[5] using def2-svp basis set[6] for all atoms except Hf atom. The SDD pseudopotentials and basis sets were, instead, employed for Hf atom.[7] SMD solvation model was used to account for the solvent dichloromethane.[8] Single point calculations were also carried out using B3LYP density functional with def2-tzvp basis set for H, C, O, N, Si, Cl and P atom[9], the SDD basis and pseudopotentials[7] with an added f function with exponent 0.874 was used for Hf. Dispersion corrections[10] (EmpiricalDispersion=D3BJ in the Gaussian package) were also enclosed during the geometry optimization and single point calculations. The molecular orbitals were generated with Multiwfn[11] and VMD[12].



s-E-sub_HfCl$_4$ **s-Z-sub_HfCl$_4$**

Figure S7. The molecular orbitals of pericyclic substrates (E and Z form)

Table S9. The energetic table for the key intermediates and transition states

Name	Lowest Imaginary Frequency	Electronic energies	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Free Energy	Zero-point Energies
PA		-1106.68303	0.21043	0.225373	0.226317	0.165082	-1106.47
PA anion		-1106.22249	0.199166	0.213386	0.214331	0.155357	-1106.02
1a		-1013.96972	0.297358	0.316844	0.317788	0.246364	-1013.67
s-Z-sub_HfCl4		-2903.34034	0.304719	0.332977	0.333921	0.241549	-2903.04
s-E-sub_HfCl4		-2903.3367	0.30408	0.332396	0.33334	0.2409	-2903.03
TS1	-258.341	-2903.31267	0.303294	0.330709	0.331653	0.242617	-2903.01
TS1'	-369.069	-2903.29853	0.302765	0.33048	0.331424	0.241211	-2903
Int1		-2903.31581	0.304464	0.332152	0.333097	0.243217	-2903.01
Int1'		-2903.30985	0.304681	0.332396	0.33334	0.242549	-2903.01
Int2		-4010.02798	0.516513	0.560489	0.561433	0.430198	-4009.51
TS2	-1202.75	-4010.0117	0.510208	0.553611	0.554555	0.426572	-4009.5
Int3		-4010.02882	0.516274	0.560109	0.561053	0.432198	-4009.51
TS3	-1245.08	-4010.01984	0.510191	0.553496	0.554441	0.427292	-4009.51
Int4		-4010.05515	0.51817	0.561849	0.562793	0.433655	-4009.54
Int4'		-2903.34253	0.305723	0.333268	0.334212	0.244763	-2903.04
PhMe$_2$SiH		-601.794086	0.172618	0.182934	0.183878	0.136264	-601.621
Int4'+PhMe$_2$SiH		-3505.1498	0.480226	0.519905	0.520849	0.403141	-3504.67
TS4	-466.007	-3505.13135	0.477696	0.516781	0.517725	0.402757	-3504.65
Int5		-3505.19294	0.484472	0.523114	0.524058	0.410845	-3504.71
TS5	-243.134	-3505.17513	0.482294	0.520816	0.52176	0.409207	-3504.69
Int6+PhMe$_2$SiOHfCl$_4$		-3505.20809	0.481859	0.521447	0.522391	0.407321	-3504.73
PhMe$_2$SiOH		-677.114686	0.178017	0.189937	0.190881	0.139913	-676.937
Int6		-2045.39385	0.506253	0.540356	0.541301	0.434562	-2044.89
TS6	-453.849	-2045.38701	0.501851	0.535194	0.536138	0.433015	-2044.89
3a		-938.72297	0.293746	0.311463	0.312408	0.247254	-938.429

The coordinates of intermediates and transition states:

1) PA

0 1

P	-0.07452100	1.41955500	0.37391200
O	-0.32593000	1.19905000	1.81696300
O	-0.61051100	2.80430900	-0.23047700
H	-0.87994600	3.42243100	0.47342700
O	1.45655600	1.44978900	-0.13803800
O	-0.66325400	0.29541400	-0.63080400
C	2.31128100	0.35325900	-0.08990900
C	3.17880000	0.18470600	-1.17002000
C	2.32581600	-0.52461500	0.99771600
C	4.07872500	-0.88383800	-1.16036600
H	3.13650800	0.88945700	-2.00255100
C	3.22597100	-1.59468700	0.98861000
H	1.64557400	-0.36575600	1.83557700
C	4.10355100	-1.77776300	-0.08433000
H	4.76100600	-1.01913300	-2.00307900
H	3.24095700	-2.28581900	1.83489300
H	4.80598200	-2.61434100	-0.08194300
C	-1.89720300	-0.31386000	-0.41415600
C	-3.07475200	0.38467500	-0.68523100
C	-1.91747400	-1.63186800	0.04087800
C	-4.30085100	-0.25979700	-0.49667000
H	-3.02189100	1.41498300	-1.04166800
C	-3.14970700	-2.26608000	0.22176900
H	-0.97442300	-2.14177200	0.24691700
C	-4.34138100	-1.58307000	-0.04497200
H	-5.22872300	0.27753900	-0.70715400
H	-3.17663400	-3.29918400	0.57646700
H	-5.30213700	-2.08260500	0.09936900

2) PA anion

P	-0.09240500	1.55498200	0.24897300
O	-0.16916600	1.25680600	1.71797900
O	-0.63295400	2.80096600	-0.37862200
O	1.47690800	1.40187600	-0.32261800
O	-0.65752700	0.19159200	-0.58882300
C	2.30673500	0.34117800	-0.12454200
C	3.41133900	0.23846500	-0.98544200
C	2.11739900	-0.62364700	0.87967800
C	4.31519800	-0.81651000	-0.84740100
H	3.53972400	0.99787200	-1.76011900
C	3.02755900	-1.67720800	1.00276200

H	1.26992400	-0.51794500	1.55690100
C	4.12812500	-1.78475700	0.14584900
H	5.17029400	-0.88348600	-1.52568800
H	2.87189600	-2.42328000	1.78719100
H	4.83371000	-2.61238300	0.25179500
C	-1.90181200	-0.31226200	-0.38266300
C	-3.02407600	0.51271600	-0.19460600
C	-2.05768200	-1.70672400	-0.38822500
C	-4.28302300	-0.06312700	-0.00797700
H	-2.88985800	1.59582500	-0.20944100
C	-3.32334700	-2.27021700	-0.21115800
H	-1.17207500	-2.32998800	-0.53079800
C	-4.44313900	-1.45338300	-0.01583900
H	-5.15044200	0.58621800	0.13972000
H	-3.43326300	-3.35817600	-0.21830200
H	-5.43156100	-1.89643800	0.12819800

3) 1a

C	-2.68325300	-0.04742300	0.06123500
C	-3.91410500	-0.96796500	-0.14524200
O	-2.86257300	1.14003300	0.28416500
O	-5.05192900	-0.28966800	-0.04509400
O	-3.84668000	-2.15598000	-0.37321700
C	-6.25914800	-1.03843600	-0.22496300
H	-7.08274000	-0.32418500	-0.10468900
H	-6.29080700	-1.48858400	-1.22885500
H	-6.33668200	-1.83773100	0.52765900
C	-1.41828800	-0.75857300	-0.02784600
H	-1.50669800	-1.83535100	-0.16957300
C	-0.16552500	-0.21126500	0.09946800
C	0.06688700	1.25913600	0.15471000
C	-0.25129400	2.07537600	-0.94129800
C	0.67816600	1.83236300	1.27986300
C	0.04274400	3.43900700	-0.91455800
H	-0.72027000	1.63100600	-1.82157800
C	0.95244000	3.20159000	1.31513500
H	0.94053500	1.19918000	2.13037200
C	0.64221500	4.00728900	0.21553800
H	-0.19928400	4.06309900	-1.77852900
H	1.41984300	3.63862800	2.20108200
H	0.86798500	5.07639200	0.23729900
C	3.16511900	-1.89993700	0.12301100
C	2.40232300	-0.71906900	-0.11315100
C	3.07526000	0.42653500	-0.58375000

C	4.45297600	0.36889700	-0.78055900
C	5.18604200	-0.80941800	-0.52366100
C	4.54985700	-1.96249400	-0.07141500
C	1.02200700	-2.39664600	0.57451300
C	1.01395500	-1.05600300	0.18208300
H	2.53199300	1.34687200	-0.79443800
H	4.97854900	1.25607700	-1.14240800
H	6.26643600	-0.81876700	-0.68701500
H	5.10390300	-2.88370800	0.12176400
H	2.55331400	-3.82715100	0.80904200
H	0.19447800	-3.02019000	0.90650700
N	2.28837400	-2.88406300	0.54169200

4) s-Z-sub_$HfCl_4$

C	-0.02663100	1.32350600	-0.16630700
C	1.07841500	2.35725600	-0.19405400
O	0.43911600	0.15553200	0.08959700
O	0.76015700	3.60161400	-0.35614400
O	2.24075800	1.94772800	-0.07572200
C	1.82852000	4.58147000	-0.41265300
H	1.33216400	5.54514100	-0.56575200
H	2.38519600	4.57196400	0.53410800
H	2.49857700	4.34582900	-1.25040800
C	-1.33961700	1.69672200	-0.39557400
H	-1.50563700	2.76640000	-0.51812000
C	-2.49709400	0.86496100	-0.34952700
C	-3.78357700	1.54888200	-0.11429600
C	-3.87899600	2.60024600	0.81899300
C	-4.92799700	1.18142700	-0.85053500
C	-5.09587400	3.24801200	1.02884700
H	-3.00130300	2.88516800	1.40260100
C	-6.13530000	1.84815700	-0.65562700
H	-4.85690300	0.38319700	-1.59099300
C	-6.22455200	2.87644700	0.29011700
H	-5.16453800	4.04660400	1.77100900
H	-7.01174000	1.56609500	-1.24346000
H	-7.17507900	3.39148300	0.44887500
C	-2.93195400	-2.80381400	-0.49973700
C	-3.41884000	-1.55482700	-0.03735900
C	-4.55136500	-1.54710700	0.79123100
C	-5.16782400	-2.76135700	1.10035300
C	-4.67547700	-3.98345600	0.60697400
C	-3.53712700	-4.02277500	-0.20014800
C	-1.48846600	-1.25299100	-1.25016400

C	-2.47598300	-0.53709500	-0.52154300
H	-4.95023500	-0.61499900	1.19025700
H	-6.05288700	-2.76128900	1.74070600
H	-5.18367900	-4.91491600	0.86614100
H	-3.12905100	-4.96373200	-0.57363700
H	-1.22174900	-3.26507400	-1.71581400
H	-0.62990200	-0.87455700	-1.79853800
N	-1.77527100	-2.55225600	-1.24351500
Hf	2.53187800	-0.32868100	0.13274800
Cl	4.93891700	-0.01947900	-0.00882600
Cl	2.20433600	-2.71699100	0.34517800
Cl	2.27044000	-0.33548600	-2.34496500
Cl	2.45552200	0.11916500	2.55296300

5) s-E-sub_HfCl$_4$

C	-0.12017000	0.99644600	0.05124800
C	-0.04225600	-0.27466900	0.89496100
O	1.04444700	1.41881100	-0.24507500
O	-1.04393200	-0.60093500	1.64533700
O	1.04780400	-0.86208800	0.91308200
C	-0.92983000	-1.78656300	2.47226000
H	-1.90315400	-1.89245000	2.96147800
H	-0.71330400	-2.65746000	1.83992700
H	-0.12963200	-1.64272000	3.21097800
C	-1.30265800	1.68738300	-0.25337900
H	-1.19149100	2.75685500	-0.44916700
C	-2.55804000	1.07316000	-0.38311700
C	-3.78888500	1.86052200	-0.25500900
C	-3.82611000	2.99358000	0.58428100
C	-4.94696500	1.50996800	-0.97990700
C	-4.99250000	3.74661500	0.70251600
H	-2.94180200	3.26360500	1.16491100
C	-6.10838700	2.26974100	-0.86487100
H	-4.92295400	0.64911000	-1.64961700
C	-6.13503900	3.38717300	-0.02168600
H	-5.01381300	4.61462200	1.36524000
H	-6.99638700	1.99458700	-1.43834200
H	-7.04842400	3.97984100	0.07003500
C	-2.95739300	-2.59499800	-0.72498000
C	-3.49142600	-1.36975300	-0.24093200
C	-4.61573900	-1.40465700	0.60212400
C	-5.18188200	-2.63958200	0.91056400
C	-4.64494200	-3.84041000	0.40136800
C	-3.51928400	-3.83692900	-0.42115100

C	-1.59432200	-0.96866300	-1.46486800
C	-2.59426000	-0.32087800	-0.70078900
H	-5.04108000	-0.48450400	1.00424300
H	-6.06012900	-2.68023700	1.55878800
H	-5.11524700	-4.79143800	0.66158300
H	-3.08654800	-4.76235800	-0.80559700
H	-1.27304700	-2.97035100	-1.99863700
H	-0.79329900	-0.53222200	-2.05806300
N	-1.82316400	-2.29417300	-1.47377400
Hf	2.84343100	0.18063100	-0.05690000
Cl	4.25562200	-1.70835800	0.50352000
Cl	4.30191500	1.71810600	-1.20695900
Cl	3.08973800	1.22771800	2.15784900
Cl	1.99857300	-0.90583800	-2.12400400

6) TS1

C	0.35550800	-0.64402400	-0.17550300
C	0.12396900	0.28872000	1.01402700
O	-0.79705600	-1.06225900	-0.64288100
O	1.15022900	0.68339000	1.69503600
O	-1.03729200	0.64328200	1.23535800
C	0.94992200	1.65345100	2.75580600
H	1.95407800	1.89457000	3.11900900
H	0.45414700	2.54540100	2.35131000
H	0.34053800	1.20400100	3.55111400
C	1.48297900	-1.59514600	-0.14523100
H	1.28084200	-2.65322600	0.03381800
C	2.71967800	-1.05644100	-0.40498000
C	4.01230200	-1.73874200	-0.26107700
C	4.15758000	-2.82591400	0.62164800
C	5.12328600	-1.31970100	-1.01673600
C	5.38491300	-3.47641800	0.74240900
H	3.30946400	-3.14819100	1.22927600
C	6.34997600	-1.97252100	-0.89285700
H	5.01771000	-0.48882300	-1.71753400
C	6.48374000	-3.05169400	-0.01321900
H	5.48757900	-4.31478500	1.43527400
H	7.20349700	-1.64118600	-1.48882800
H	7.44510000	-3.56152100	0.08544300
C	2.15744000	2.56340100	-0.65252100
C	3.15507100	1.54648600	-0.43625700
C	4.38288200	1.89228600	0.18392200
C	4.59636900	3.21083000	0.53114300
C	3.60573600	4.20428500	0.28926900

C	2.38479800	3.90316700	-0.29103500
C	1.21180700	0.61583500	-1.29939900
C	2.54815300	0.32173200	-0.79624600
H	5.13958200	1.12967200	0.36973100
H	5.53735600	3.50523300	0.99988900
H	3.81588400	5.23701300	0.57763700
H	1.62315100	4.66577400	-0.46014400
H	0.20713000	2.48225400	-1.50424500
H	0.81609400	0.15244900	-2.20706000
N	1.03344000	1.99027400	-1.17020500
Hf	-2.68540900	-0.30910400	-0.07945500
Cl	-4.30725700	1.07329400	1.11703400
Cl	-3.99948300	-1.54789400	-1.68651800
Cl	-2.74398800	-2.04832200	1.67239000
Cl	-2.19400700	1.58657300	-1.64887900

7) TS1'

C	-0.52081400	-1.01317500	0.54408800
C	0.48920700	-1.87333100	1.28321100
O	0.09642800	-0.16000800	-0.23330200
O	0.01204400	-2.78385600	2.07167900
O	1.69169400	-1.66906400	1.09151500
C	0.94738500	-3.64725400	2.76980500
H	0.32878700	-4.34919900	3.33813800
H	1.57416100	-4.17558800	2.03903100
H	1.57218000	-3.04140500	3.43986000
C	-1.81390700	-1.63663200	0.16814600
H	-1.85870000	-2.68375600	-0.13954100
C	-2.88120500	-0.78670100	0.25573800
C	-4.23290600	-0.99356900	-0.27287700
C	-4.47242400	-1.93914100	-1.28909100
C	-5.31440000	-0.24760700	0.23321700
C	-5.76242400	-2.13630900	-1.77861200
H	-3.63881300	-2.50465800	-1.71043900
C	-6.60356500	-0.44448200	-0.26236500
H	-5.14245200	0.48266900	1.02695600
C	-6.83097200	-1.38986200	-1.26765500
H	-5.93513400	-2.86842200	-2.57088000
H	-7.43461200	0.13952100	0.13983600
H	-7.84042100	-1.54259500	-1.65704100
C	-1.29569400	2.33881500	1.33223300
C	-2.40911400	1.77313100	0.61695000
C	-3.10292000	2.56177600	-0.33675900
C	-2.69602200	3.86612800	-0.52811400

C	-1.59610100	4.40885500	0.19643200
C	-0.88231200	3.66541100	1.12155100
C	-1.38260800	0.17545100	1.92876300
C	-2.44109800	0.40549500	0.96467200
H	-3.93932700	2.13895300	-0.89495000
H	-3.21578400	4.49872100	-1.25042300
H	-1.30265100	5.44419200	0.00752700
H	-0.02710700	4.07861800	1.65754700
H	0.06173100	1.51803600	2.72865300
H	-1.42692500	-0.55959900	2.73409600
N	-0.75722700	1.38042300	2.14268300
Hf	2.20215800	-0.02674900	-0.46299700
Cl	4.57973200	-0.56737200	-0.26842500
Cl	2.11391200	1.83378500	-2.00098900
Cl	2.39067600	1.38683000	1.58550900
Cl	1.93805100	-1.82565800	-2.14353900

8) Int1

C	-0.37920700	0.43412200	-0.21400300
C	-0.07067900	-0.25141000	1.13229800
O	0.79292500	0.83933500	-0.75125200
O	-1.08274200	-0.62413100	1.85053100
O	1.10697100	-0.44896200	1.42837400
C	-0.82762500	-1.36667600	3.07121000
H	-1.81531500	-1.58191500	3.49184700
H	-0.29275100	-2.29482600	2.82912000
H	-0.23295100	-0.75017500	3.75824200
C	-1.44411700	1.49818200	-0.11617900
H	-1.17479100	2.52490200	0.13726500
C	-2.70740400	1.03421000	-0.37329500
C	-3.96819200	1.78104600	-0.25971300
C	-4.07224300	2.88592600	0.60572300
C	-5.08483200	1.40897100	-1.03017700
C	-5.26696000	3.59925900	0.69706500
H	-3.21825600	3.17349100	1.22244800
C	-6.27852700	2.12615300	-0.93717100
H	-5.01057300	0.56390600	-1.71803900
C	-6.37283200	3.22161200	-0.07307200
H	-5.33825000	4.45069900	1.37788700
H	-7.13719500	1.83103000	-1.54471300
H	-7.30851100	3.78081300	0.00198100
C	-2.22664200	-2.61155900	-0.53470200
C	-3.23525000	-1.57001100	-0.42589500
C	-4.54595800	-1.90045100	0.02465800

C	-4.82868000	-3.21559200	0.30556200
C	-3.83137800	-4.23065600	0.16189200
C	-2.54132900	-3.95690400	-0.24666500
C	-1.18105500	-0.67121100	-1.09237300
C	-2.58012500	-0.36956500	-0.70300000
H	-5.30160800	-1.12180100	0.12878400
H	-5.82677700	-3.50223200	0.64161300
H	-4.10459200	-5.26374600	0.39053800
H	-1.78688100	-4.73902600	-0.34134300
H	-0.19320400	-2.58922900	-1.12640200
H	-0.93332300	-0.38200600	-2.12634300
N	-1.03955900	-2.07542900	-0.88190900
Hf	2.67717100	0.29826400	-0.12841700
Cl	4.37128600	-0.80031100	1.27682500
Cl	3.93139200	1.19570500	-1.99623400
Cl	2.78637000	2.34294900	1.26058100
Cl	2.22368800	-1.92948800	-1.23986100

9) Int1'

C	-0.44584400	-0.63552900	0.78372400
C	0.55177900	-1.40070900	1.65779300
O	0.25941500	-0.07182300	-0.25007500
O	0.05563000	-2.04177000	2.67116200
O	1.74745300	-1.38453100	1.36242600
C	0.96117700	-2.79246800	3.52157400
H	0.32939900	-3.24941200	4.29018200
H	1.47176400	-3.56088100	2.92594200
H	1.69439300	-2.10915400	3.97086600
C	-1.60385900	-1.51157400	0.31437300
H	-1.44675400	-2.53982000	-0.01488200
C	-2.79097600	-0.83602100	0.28242600
C	-4.07472500	-1.31530500	-0.25070700
C	-4.11284200	-2.32235000	-1.23319500
C	-5.28585700	-0.78520200	0.22962300
C	-5.33438600	-2.78575700	-1.72045000
H	-3.18029000	-2.72772300	-1.63102200
C	-6.50698500	-1.25265300	-0.25900100
H	-5.26897300	-0.01230400	1.00109700
C	-6.53437000	-2.25328000	-1.23509500
H	-5.35076300	-3.56164600	-2.48947200
H	-7.44037600	-0.83530400	0.12584800
H	-7.48999200	-2.61644300	-1.62071300
C	-1.67822200	2.60680400	0.90152500
C	-2.82803300	1.81265800	0.46896000

C	-3.87345700	2.43382000	-0.28179500
C	-3.77221700	3.77246100	-0.55724700
C	-2.64045000	4.53676800	-0.11508500
C	-1.60033500	3.98750200	0.60081800
C	-1.24602500	0.47997700	1.56689400
C	-2.52129200	0.49991300	0.79004000
H	-4.72746000	1.84501300	-0.61689300
H	-4.55625100	4.27760500	-1.12399700
H	-2.60578500	5.60013200	-0.36467800
H	-0.74047800	4.57750600	0.92025400
H	0.17065000	2.11438100	1.77346700
H	-1.42004900	0.14476400	2.60470700
N	-0.78281900	1.83538000	1.52648500
Hf	2.28892100	-0.06554500	-0.48113100
Cl	4.65454800	-0.57011300	-0.00265500
Cl	2.37285100	1.49126100	-2.33845300
Cl	2.42212800	1.74774300	1.29745700
Cl	2.12458500	-2.13503700	-1.83010400

10) Int2

C	0.19596900	-1.24251300	-0.32570900
C	-0.32988000	-2.68075100	-0.21947000
O	-0.84836700	-0.46486300	-0.75167600
O	0.54303100	-3.60461700	0.01754000
O	-1.54439300	-2.87114400	-0.30569100
C	0.07547100	-4.96120900	0.24433900
H	0.97848300	-5.54858000	0.43918700
H	-0.59723100	-4.97445200	1.11223600
H	-0.44533900	-5.32382700	-0.65163900
C	1.45755000	-1.09112200	-1.13784800
H	1.40547200	-0.94674800	-2.21782700
C	2.59728000	-1.13618900	-0.38090000
C	3.98551800	-1.09318200	-0.85936400
C	4.30083500	-1.44513300	-2.18518800
C	5.01817900	-0.67227100	-0.00284500
C	5.61874900	-1.38634000	-2.63613000
H	3.51203500	-1.78464500	-2.85945200
C	6.33695000	-0.62063500	-0.45531400
H	4.78405600	-0.35814500	1.01562800
C	6.64132800	-0.97899900	-1.77142000
H	5.85148800	-1.66776900	-3.66571400
H	7.12781100	-0.28560600	0.21958500
H	7.67398200	-0.93813100	-2.12594600
C	1.34038700	-2.15558500	2.93512200

C	2.54517100	-2.02937600	2.13157800
C	3.73479400	-2.70075400	2.53822300
C	3.71477200	-3.41649400	3.71118000
C	2.52916300	-3.49593000	4.50711800
C	1.34665500	-2.88360800	4.14464700
C	0.76601100	-0.88576900	1.14083600
C	2.17609400	-1.30173500	0.99804100
H	4.63704500	-2.63437400	1.93035500
H	4.61306300	-3.93425400	4.05227300
H	2.56372300	-4.07060300	5.43592700
H	0.44498900	-2.96006100	4.75380300
H	-0.60544100	-1.35536500	2.73685800
H	0.64212300	0.22288600	1.18683700
N	0.30943300	-1.53701600	2.32537300
Hf	-2.87420500	-1.03284400	-0.73334200
Cl	-4.83379800	-2.46730000	-0.46040000
Cl	-3.73932100	1.17643700	-1.18143400
Cl	-2.63780300	-1.67669100	-3.10574200
Cl	-2.78811100	-0.68408100	1.75351700
P	0.18209600	2.72491700	-0.37070900
O	0.49296100	2.04574100	0.92043700
O	-0.07554400	1.80643400	-1.62950100
H	-0.42764600	0.89665900	-1.34880000
O	-1.09704700	3.70424100	-0.32971600
O	1.32735200	3.75425400	-0.87904300
C	-1.51290800	4.33862700	0.83873500
C	-0.76913900	5.39674600	1.36269400
C	-2.69663700	3.90811100	1.43757200
C	-1.22754900	6.03708200	2.51786100
H	0.15051400	5.71020800	0.86508600
C	-3.14538600	4.55957400	2.58994400
H	-3.24509300	3.07358700	0.99762500
C	-2.41375300	5.62194000	3.13231500
H	-0.65330000	6.86719500	2.93644900
H	-4.07192900	4.23029100	3.06648800
H	-2.76848400	6.12679700	4.03390100
C	2.64007000	3.31463500	-1.05009200
C	3.01981000	2.75245600	-2.26983400
C	3.55021600	3.47316400	-0.00431500
C	4.34940600	2.35931300	-2.44889400
H	2.27767800	2.63354800	-3.06056300
C	4.87736700	3.07969400	-0.19767100
H	3.21188800	3.90262000	0.94027400
C	5.27942300	2.52717400	-1.41825400

H	4.65809400	1.91884500	-3.39947700
H	5.59961300	3.20347500	0.61288900
H	6.31580700	2.21851100	-1.56387500

11) TS2

C	-0.08016100	-1.37637100	-0.15651900
C	-0.86467600	-2.60789400	0.31516900
O	-0.99843700	-0.54472000	-0.78677500
O	-0.17993900	-3.58099900	0.81827200
O	-2.09756800	-2.59423500	0.23950000
C	-0.89511600	-4.72186700	1.36035300
H	-1.54510700	-4.38872600	2.18047700
H	-1.48960100	-5.19410400	0.56693100
H	-0.11960400	-5.40186400	1.72726000
C	1.11745800	-1.72925800	-1.01959600
H	0.99689600	-1.90052900	-2.08946200
C	2.28585300	-1.70909600	-0.31793400
C	3.63281400	-1.98732600	-0.83658400
C	3.81447700	-2.80989200	-1.96462000
C	4.76114000	-1.40179300	-0.23581300
C	5.09217300	-3.04191100	-2.47251800
H	2.94924300	-3.28264900	-2.43394800
C	6.03957300	-1.64062300	-0.74241700
H	4.63489200	-0.72782000	0.61251400
C	6.20972400	-2.46138700	-1.86063400
H	5.21891200	-3.68677200	-3.34537800
H	6.90490300	-1.17257500	-0.26782200
H	7.21064300	-2.64920100	-2.25664700
C	1.26239200	-1.22590600	3.22968200
C	2.39704000	-1.54233900	2.39356400
C	3.59190100	-2.01109100	2.99670700
C	3.64483300	-2.10926000	4.37322800
C	2.53135700	-1.74626400	5.18179600
C	1.34150600	-1.29969200	4.63517700
C	0.63337900	-0.81680200	1.10999000
C	1.95913200	-1.33262600	1.06223600
H	4.44979800	-2.28618100	2.38308400
H	4.55586300	-2.46665400	4.85768000
H	2.62001000	-1.83010300	6.26772700
H	0.48663100	-1.03041400	5.25786900
H	-0.66636800	-0.46683100	2.77652900
H	0.79971300	0.54724900	0.79117800
N	0.20482200	-0.87995100	2.44613800
Hf	-3.10365600	-0.73531500	-0.63115200

Cl	-5.28013000	-1.64942200	-0.01567400
Cl	-3.54700800	1.42967300	-1.59689600
Cl	-3.08691200	-1.95158500	-2.77543600
Cl	-2.82413900	0.19053500	1.69818500
P	0.57212800	2.32743200	-0.80675100
O	0.92880800	1.69985100	0.54844000
O	0.12631300	1.32860800	-1.90741600
H	-0.39970100	0.49650300	-1.50443300
O	-0.57497400	3.42020100	-0.66588600
O	1.80341000	3.17287400	-1.37677300
C	-0.70663700	4.25984500	0.45223300
C	-0.06161300	5.49427800	0.44719200
C	-1.50644900	3.84012400	1.51272900
C	-0.23164900	6.34062200	1.54733800
H	0.55538900	5.78056900	-0.40618800
C	-1.66594200	4.69766300	2.60505700
H	-1.98591400	2.86015500	1.47992100
C	-1.03195100	5.94496500	2.62420600
H	0.26427500	7.31399800	1.55880100
H	-2.29127300	4.38525100	3.44473400
H	-1.16251600	6.61089500	3.48028300
C	3.07773000	2.60751400	-1.54952200
C	3.31285400	1.75412000	-2.62714400
C	4.07982200	2.95406000	-0.64626300
C	4.60118300	1.24275600	-2.80589000
H	2.50019600	1.50305200	-3.31003500
C	5.36534100	2.44060400	-0.84281500
H	3.84717000	3.61811600	0.18809000
C	5.62690100	1.58830400	-1.92043100
H	4.80067600	0.56669700	-3.64014700
H	6.16371900	2.70762000	-0.14659900
H	6.63068400	1.18534900	-2.06689300

12) Int3

C	-0.54284200	1.23705700	0.66191400
C	-1.57691200	2.19218900	1.26191600
O	-1.30652000	0.19466800	0.07143200
O	-1.11104400	3.22223100	1.88087100
O	-2.78389000	1.95355600	1.13326300
C	-2.05092600	4.17247400	2.45155300
H	-1.43165100	4.95905000	2.89402600
H	-2.69150200	4.57546400	1.65591800
H	-2.65726200	3.67081800	3.21746500
C	0.44510600	0.77562000	1.74209700

H	0.11051800	0.22727500	2.62242100
C	1.70047200	1.26898800	1.49025800
C	2.88540900	1.03726400	2.33030800
C	2.77073500	0.97252100	3.73141000
C	4.14161700	0.81818000	1.73610900
C	3.89054700	0.70384100	4.51854100
H	1.80198600	1.15334800	4.20159400
C	5.25700500	0.53806200	2.52633500
H	4.23800300	0.83010200	0.65127400
C	5.13580500	0.48483300	3.91846300
H	3.79244300	0.66728500	5.60607300
H	6.22203600	0.35575200	2.04883400
H	6.01133500	0.27201700	4.53671800
C	1.53829500	3.08158100	-1.80537600
C	2.45485700	2.74667500	-0.74727600
C	3.79085000	3.18182300	-0.85229400
C	4.18321500	3.89241500	-1.98179200
C	3.27183100	4.18573000	-3.02080000
C	1.94015700	3.78785400	-2.94528800
C	0.38701100	1.94788200	-0.28727500
C	1.67616100	1.99869100	0.20775000
H	4.50882700	2.96490800	-0.06121900
H	5.21857600	4.23018300	-2.07005100
H	3.61628200	4.74078400	-3.89655100
H	1.22835000	4.01825900	-3.74062400
H	-0.55486800	2.63960400	-2.05537700
H	1.40764400	-0.86526100	1.03242300
N	0.28177300	2.58915400	-1.47785500
Hf	-3.53136900	0.22573500	-0.09311400
Cl	-5.85307900	0.85975600	0.03668900
Cl	-3.48417100	-1.75458100	-1.46104600
Cl	-3.54143900	-0.96532900	2.05393600
Cl	-3.08138100	1.79006100	-1.98255400
P	1.44875000	-1.79098200	-0.95243400
O	1.76928100	-1.68154500	0.59848500
O	0.17655100	-1.13122900	-1.39838700
H	-0.71122000	-0.38892700	-0.55292600
O	2.66783100	-1.21467400	-1.80250100
O	1.54021100	-3.36326800	-1.24238200
C	4.01660800	-1.15212100	-1.45000700
C	4.63817500	-2.15459300	-0.70562300
C	4.71146600	-0.02627300	-1.88978600
C	5.99048400	-2.00633800	-0.38243200
H	4.08321400	-3.03440100	-0.37919500

C	6.06347700	0.10378000	-1.56488300
H	4.18686100	0.73613100	-2.46584300
C	6.70487300	-0.88166100	-0.80655800
H	6.48519200	-2.78172200	0.20687400
H	6.61146700	0.98743200	-1.89979400
H	7.76067100	-0.77455100	-0.54818800
C	0.69543900	-4.29633700	-0.61877200
C	-0.68997500	-4.13327300	-0.63955800
C	1.29852200	-5.39370100	-0.00742400
C	-1.48759500	-5.09660900	-0.01461200
H	-1.13915300	-3.27202200	-1.13358200
C	0.48668400	-6.35356800	0.60373800
H	2.38584900	-5.48766500	-0.01514600
C	-0.90460600	-6.20555200	0.60622100
H	-2.57298000	-4.97213600	-0.02123000
H	0.94838300	-7.21899700	1.08489300
H	-1.53390500	-6.95590900	1.09007900

13) TS3

C	0.11221500	-1.44541200	-0.41247700
C	-0.58565600	-2.76783800	-0.75661200
O	-0.90538900	-0.52709300	-0.13140400
O	0.17598900	-3.77185400	-1.04402000
O	-1.81960900	-2.81618700	-0.75230500
C	-0.44984100	-5.04055600	-1.37088200
H	0.37781300	-5.73140800	-1.56060600
H	-1.05828900	-5.37957800	-0.52178900
H	-1.07482400	-4.92118800	-2.26601100
C	1.08486100	-1.05978900	-1.55514400
H	0.79805200	-1.24049300	-2.59596400
C	2.41411000	-1.22175700	-1.09910200
C	3.58969800	-1.04823700	-1.95234800
C	3.56651000	-1.45528600	-3.30110000
C	4.74116300	-0.41545800	-1.44630500
C	4.68024200	-1.25444300	-4.11446700
H	2.68105500	-1.95165800	-3.70191900
C	5.84412500	-0.19669700	-2.27015300
H	4.75164400	-0.05098000	-0.42043000
C	5.81988100	-0.62333100	-3.60208700
H	4.66005600	-1.58906600	-5.15405300
H	6.72445100	0.31247100	-1.87166800
H	6.68892000	-0.46059500	-4.24414300
C	2.27963800	-1.79562200	2.58574200
C	3.22112800	-1.62611500	1.51634200

C	4.59220500	-1.64675200	1.82416200
C	4.98578800	-1.80717100	3.15134400
C	4.04021700	-1.94789700	4.18697800
C	2.67250800	-1.94838100	3.91710900
C	1.08710100	-1.60543900	0.72501900
C	2.41431500	-1.47700400	0.31953100
H	5.34271800	-1.54288200	1.04091400
H	6.05061800	-1.82223000	3.39499000
H	4.38347100	-2.06571000	5.21734300
H	1.93196300	-2.06723600	4.71039400
H	0.11105800	-1.86840000	2.56782600
H	-0.44526700	0.66738900	0.31794100
N	0.98810300	-1.77862000	2.05184700
Hf	-2.96779100	-1.00084500	0.02004400
Cl	-5.03693700	-2.28835000	-0.01615800
Cl	-3.54752200	1.14183800	0.95568200
Cl	-3.20961100	-0.32094200	-2.33806700
Cl	-2.35790200	-1.99181400	2.25940300
P	0.55024100	2.42337000	-0.60823100
O	-0.01029600	1.61831100	0.59310200
O	1.09965200	1.56917600	-1.75963300
H	1.09619400	0.41348300	-1.64948800
O	-0.53218700	3.40647700	-1.23092800
O	1.66962400	3.42126300	-0.04805900
C	-1.57185400	4.04526000	-0.53986200
C	-2.83809900	3.97704500	-1.11458700
C	-1.33435500	4.73027600	0.65037600
C	-3.90106100	4.61788200	-0.47466900
H	-2.98070800	3.41385700	-2.03812200
C	-2.41124200	5.35723700	1.28492000
H	-0.32951200	4.77745100	1.07323400
C	-3.69180300	5.30437300	0.72596900
H	-4.90059300	4.56573500	-0.91226500
H	-2.24133900	5.89291100	2.22177300
H	-4.52784200	5.79685400	1.22753600
C	2.90460800	2.94890900	0.43045800
C	4.04189900	3.20676100	-0.33128900
C	2.96625600	2.27344300	1.64919600
C	5.28247400	2.77885800	0.15034800
H	3.94559300	3.73118100	-1.28332900
C	4.21264600	1.84218800	2.11229400
H	2.05472100	2.08824300	2.21842600
C	5.36937600	2.09526800	1.36773700
H	6.18292700	2.97635900	-0.43550700

H	4.27521500	1.30321200	3.05945500
H	6.33945000	1.75380700	1.73553700

14) Int4

C	-0.03783500	-1.62362700	0.48460200
C	0.74282600	-2.88168500	0.89012500
O	0.89849500	-0.63547100	0.21522300
O	0.03872500	-3.93075900	1.16793400
O	1.97273500	-2.83473400	0.93423800
C	0.73397300	-5.14636800	1.55689400
H	-0.05269500	-5.88833700	1.72675200
H	1.40324000	-5.46072800	0.74497900
H	1.30570100	-4.96174800	2.47601600
C	-1.09357500	-1.23525800	1.57338600
H	-1.04795900	-1.86482500	2.47446200
C	-2.45433100	-1.32619800	0.92297000
C	-3.65496100	-1.01128200	1.66009300
C	-3.59016800	-0.12593900	2.76205800
C	-4.90110000	-1.57536300	1.30405600
C	-4.74446200	0.19234200	3.47084700
H	-2.64642200	0.35663200	3.01673000
C	-6.04604800	-1.26624300	2.02995400
H	-4.95480100	-2.29285200	0.48595000
C	-5.97095900	-0.37737300	3.11031300
H	-4.69064100	0.89490000	4.30512100
H	-7.00138000	-1.72036000	1.75865500
H	-6.87367600	-0.12844200	3.67338500
C	-1.96988400	-2.03660200	-2.65798500
C	-3.00574400	-1.82854300	-1.69872700
C	-4.32765000	-1.74849900	-2.15156300
C	-4.58114800	-1.88282800	-3.51968700
C	-3.54203200	-2.09378800	-4.44060100
C	-2.21099800	-2.17211500	-4.02069800
C	-0.93838500	-1.86252300	-0.69669700
C	-2.32074600	-1.70473500	-0.41219100
H	-5.14987600	-1.57212400	-1.46038500
H	-5.61019500	-1.81820200	-3.87957500
H	-3.77464800	-2.19496000	-5.50287400
H	-1.39319700	-2.32624300	-4.72657800
H	0.20228000	-2.12070200	-2.41514800
H	0.31890300	0.75205200	-0.13825000
N	-0.72938000	-2.04986000	-1.98624800
Hf	2.97155300	-0.91661000	0.13304500
Cl	5.12666000	-2.05949700	0.26584600

Cl	3.45032500	1.21223700	-0.88420000
Cl	3.10892900	-0.15462600	2.47029600
Cl	2.52677500	-2.07011500	-2.09037500
P	-0.57605500	2.50813100	0.86342700
O	-0.11506200	1.63885800	-0.37586900
O	-0.89656200	1.79236800	2.12700000
H	-0.88639000	-0.19984700	1.89296100
O	0.53020100	3.64840600	1.11823700
O	-1.79549900	3.39068700	0.24933300
C	1.33249600	4.27326600	0.17059200
C	2.68551700	4.40645000	0.48341400
C	0.81003600	4.77520200	-1.02299800
C	3.53237200	5.05506200	-0.41753300
H	3.05901900	3.98876300	1.41978900
C	1.67162000	5.41277800	-1.92110100
H	-0.25301500	4.67307500	-1.24225100
C	3.03034100	5.55580200	-1.62354800
H	4.59369200	5.15702500	-0.17863700
H	1.27082900	5.80393000	-2.85946800
H	3.69685300	6.05594800	-2.32995900
C	-2.98481600	2.77400000	-0.13777800
C	-4.03398000	2.68784400	0.77743800
C	-3.10764000	2.27715500	-1.43707200
C	-5.23630000	2.09775700	0.37676000
H	-3.89717700	3.07593000	1.78767100
C	-4.31449600	1.68963700	-1.82540200
H	-2.26320100	2.34965400	-2.12370000
C	-5.37901800	1.59891500	-0.92160500
H	-6.06022900	2.02004500	1.08893200
H	-4.41869900	1.29521100	-2.83809700
H	-6.31904600	1.13494800	-1.22871000

15) Int4'

C	0.39622900	-0.38754200	0.02176500
C	-0.14608500	-0.64797800	1.44540700
O	-0.68295900	-0.27164900	-0.81067800
O	0.73271600	-0.84973500	2.37619600
O	-1.36365700	-0.64780600	1.62014700
C	0.26342200	-1.09724300	3.72786700
H	1.16832800	-1.22476400	4.33092300
H	-0.34914900	-2.00866400	3.74188400
H	-0.32326100	-0.23674300	4.07647700
C	1.44146400	-1.48744400	-0.37597500
H	1.23346200	-1.75097900	-1.42529600

C	2.81173200	-0.84808800	-0.26916900
C	4.02022200	-1.63454100	-0.34238800
C	3.98852700	-2.93744700	-0.89390600
C	5.24401900	-1.13779000	0.16234400
C	5.15044800	-3.69900000	-0.96571700
H	3.05544100	-3.34174500	-1.28815800
C	6.39831700	-1.91072800	0.10370300
H	5.27074900	-0.16014000	0.64065100
C	6.35602800	-3.18845400	-0.46860400
H	5.11944200	-4.69696700	-1.40783200
H	7.33450700	-1.52206000	0.50970800
H	7.26518100	-3.79224400	-0.51988900
C	2.30859600	2.79714500	-0.02213600
C	3.34947000	1.82700400	-0.13898400
C	4.66537100	2.28022100	-0.29659000
C	4.90844800	3.65711200	-0.31429300
C	3.86579100	4.58729500	-0.17971500
C	2.53990900	4.16754700	-0.03550900
C	1.28615700	0.82539900	0.02363100
C	2.67052400	0.52971600	-0.11172500
H	5.49437500	1.58304700	-0.41311600
H	5.93289100	4.01507900	-0.43682600
H	4.09023900	5.65601200	-0.19449100
H	1.71785100	4.87952900	0.05558100
H	0.13796100	2.55030300	0.15648300
N	1.07226700	2.12455300	0.07984000
Hf	-2.64729200	-0.13985800	-0.26246000
Cl	-4.58398400	-0.05227500	1.25328400
Cl	-3.55524500	0.46972900	-2.42390400
Cl	-2.12820200	2.26239400	0.42298300
Cl	-2.90954400	-2.58346300	-0.52362100
H	1.35939200	-2.40791200	0.21817800

16) $PhMe_2SiH$

Si	-1.65489900	-0.19042700	-0.36966200
C	0.22032400	-0.04771900	-0.17725300
C	0.83494300	1.14500200	0.24707900
C	1.04760900	-1.15951400	-0.43207700
C	2.22186300	1.22553900	0.41483800
H	0.22651000	2.03030400	0.45175000
C	2.43328800	-1.08555000	-0.26690700
H	0.60524000	-2.10268400	-0.76920400
C	3.02381600	0.10972700	0.15845700
H	2.67747700	2.16280400	0.74551900

H	3.05547700	-1.96083100	-0.47222000
H	4.10761200	0.17078300	0.28776500
C	-2.34867400	-1.31784700	0.97138400
H	-2.15999000	-0.88875300	1.97001700
H	-1.87872900	-2.31470600	0.93694300
H	-3.43780400	-1.44984700	0.85542600
C	-2.46312600	1.50647400	-0.29706500
H	-2.05762500	2.18439200	-1.06601200
H	-2.31150300	1.97581500	0.68936800
H	-3.55031000	1.41924700	-0.46133900
H	-1.92803200	-0.81721700	-1.70348500

17) Int4'+PhMe$_2$SiH

C	-0.45112700	-1.21988700	-0.08017800
C	-1.54137600	-2.21796800	0.36503800
O	-1.08286800	-0.05782600	-0.43321500
O	-1.14336700	-3.40364900	0.70422200
O	-2.71275900	-1.84245900	0.37396100
C	-2.13961400	-4.37085000	1.12932600
H	-1.57804300	-5.27833100	1.37388300
H	-2.84532000	-4.55548200	0.30842000
H	-2.67041100	-3.98748400	2.01106900
C	0.45520800	-1.85734600	-1.19272500
H	0.61915300	-1.06626100	-1.94225400
C	1.77463700	-2.20669300	-0.53616600
C	2.77578800	-2.99541800	-1.21413300
C	2.74101400	-3.13098700	-2.62222500
C	3.78750600	-3.66607800	-0.48861500
C	3.70928500	-3.88278900	-3.28009800
H	1.96783100	-2.62367300	-3.20070600
C	4.74155100	-4.43076200	-1.15102000
H	3.79148000	-3.61839100	0.59973700
C	4.71048400	-4.53255100	-2.54768600
H	3.68507400	-3.96670100	-4.36855600
H	5.51051000	-4.95530200	-0.57999000
H	5.46568800	-5.12737900	-3.06694300
C	1.90981500	-0.37220800	2.65343100
C	2.71761800	-1.19529900	1.81190100
C	4.07433100	-1.34041400	2.12613000
C	4.57941900	-0.68652400	3.25438800
C	3.75747400	0.10588200	4.07176000
C	2.40100500	0.27862700	3.77911500
C	0.57393400	-1.02145500	1.00140800
C	1.83401400	-1.61894000	0.72492500

H	4.73711100	-1.94100600	1.50405500
H	5.63749800	-0.79359000	3.50261600
H	4.18353400	0.60205500	4.94638300
H	1.75453600	0.90549200	4.39541300
H	-0.19204300	0.21908600	2.47870500
N	0.60701800	-0.31617700	2.11420200
Hf	-3.05043700	0.40701300	-0.16174000
Cl	-5.38205100	0.04213900	0.53365400
Cl	-2.94361100	2.76625200	-0.69326300
Cl	-2.45145800	0.74859600	2.29675600
Cl	-3.55011600	-0.36140400	-2.45908800
H	-0.00640600	-2.71126400	-1.70674000
Si	1.51793300	2.25440700	-0.65215400
H	1.89166700	0.82574100	-0.43899900
C	3.15527200	3.19622000	-0.77392000
C	3.38816100	4.17662900	-1.75570000
C	4.18126700	2.94266600	0.15819300
C	4.59674600	4.88063800	-1.80519400
H	2.61587300	4.39849900	-2.49787300
C	5.39060000	3.64174600	0.11489300
H	4.03725500	2.18299300	0.93354500
C	5.60046100	4.61468100	-0.86911300
H	4.75514200	5.63873800	-2.57704400
H	6.17280700	3.42740700	0.84826300
H	6.54543600	5.16313800	-0.90618600
C	0.57571500	2.87931500	0.85163100
H	1.21437200	2.84596300	1.74989200
H	-0.32922600	2.28679700	1.04380100
H	0.26939800	3.92750300	0.69630100
C	0.53405100	2.41619800	-2.24297900
H	1.14129500	2.12768100	-3.11711100
H	0.17984500	3.44883700	-2.39521600
H	-0.34728300	1.75953400	-2.19948500

18) TS4

C	-0.60480300	0.71603500	1.11308900
C	-1.80142600	1.15174700	1.96329300
O	-1.08180000	-0.16407700	0.15856600
O	-1.55803500	1.95945200	2.94861700
O	-2.92170500	0.72478200	1.67748500
C	-2.67085900	2.39432300	3.77197000
H	-2.23712400	3.07219900	4.51437600
H	-3.13054900	1.52331100	4.25811500
H	-3.40939800	2.91567600	3.14828200

C	0.54903400	0.09493400	1.95853800
H	0.41146900	-0.98805900	2.05963900
C	1.83437000	0.49663900	1.22736300
C	3.15537100	0.13221500	1.77672200
C	3.41151400	-1.18965400	2.18716200
C	4.16925800	1.09667400	1.90219200
C	4.66121000	-1.54272100	2.68771700
H	2.63204600	-1.94789900	2.08882400
C	5.41797300	0.74239000	2.41637300
H	3.97214100	2.13079100	1.62172700
C	5.67034800	-0.57782300	2.79827400
H	4.85492600	-2.57586800	2.98385700
H	6.19707200	1.50161000	2.51502300
H	6.65296300	-0.85763800	3.18531000
C	0.95620600	3.29556700	-1.04406800
C	2.08413700	2.61817400	-0.47991200
C	3.36587300	2.93112100	-0.96209800
C	3.49387800	3.89634400	-1.96133200
C	2.36945700	4.56107500	-2.48716700
C	1.08219300	4.27002000	-2.03445900
C	0.13998700	1.83887000	0.42631400
C	1.52799300	1.68789500	0.48622300
H	4.24953200	2.42673500	-0.57119400
H	4.48724100	4.14170000	-2.34379900
H	2.50534500	5.31403600	-3.26680100
H	0.20377000	4.77213300	-2.44420300
H	-1.16327700	2.96898000	-0.76915000
N	-0.20758300	2.78535500	-0.45811700
Hf	-3.02806700	-0.58971400	-0.24433900
Cl	-5.48051300	-0.54784500	0.01969400
Cl	-2.63047800	-1.82964700	-2.29282500
Cl	-3.17256500	1.66443600	-1.39144500
Cl	-2.87936500	-2.55320700	1.26976900
H	0.58889800	0.53867300	2.96501400
Si	1.70923800	-1.51092900	-1.09046700
H	1.75318100	-0.56413300	0.17943600
C	3.53903400	-1.87207500	-1.20523200
C	4.06420500	-3.14648800	-0.91700300
C	4.44000000	-0.82071900	-1.46929400
C	5.44429000	-3.36425100	-0.89658500
H	3.39059800	-3.98025600	-0.70283600
C	5.81919000	-1.03303500	-1.43901300
H	4.06171700	0.18075700	-1.69093300
C	6.32319500	-2.30624600	-1.14997400

H	5.83591000	-4.36048400	-0.67602200
H	6.50379400	-0.20458100	-1.63742900
H	7.40288700	-2.47396900	-1.12313400
C	1.04317400	-0.37233100	-2.40829300
H	0.81716800	-0.95326600	-3.31878300
H	1.77282700	0.40949800	-2.66740700
H	0.11398000	0.10012600	-2.06049000
C	0.67556000	-2.98672300	-0.62081400
H	1.18478400	-3.60295100	0.13633200
H	0.48546300	-3.61386300	-1.50859800
H	-0.29297700	-2.66482700	-0.21493000

19) Int5

C	-0.28851200	0.49250000	-0.11142400
C	0.34851400	1.78911400	0.37266200
O	0.80231200	-0.40962000	-0.44391800
O	-0.48868300	2.70047600	0.73552800
O	1.57356300	1.95600300	0.39733800
C	0.01915700	3.98518100	1.18222000
H	-0.87043500	4.58190600	1.40682500
H	0.60941400	4.44477000	0.37848000
H	0.63600900	3.84213400	2.07929000
C	-1.24333500	0.82437900	-1.31777300
H	-0.94753100	0.20367500	-2.16994700
C	-2.72731000	0.53632600	-0.87845000
C	-3.62670600	1.75226100	-1.01407000
C	-4.32754000	1.96577100	-2.21027400
C	-3.75101400	2.69569200	0.01683000
C	-5.12660000	3.10024500	-2.37953200
H	-4.24547900	1.23069500	-3.01602300
C	-4.55103700	3.82977800	-0.14841900
H	-3.21808400	2.53729200	0.95604900
C	-5.24002100	4.03763900	-1.34794900
H	-5.66633600	3.25008000	-3.31824500
H	-4.64052600	4.55331100	0.66624700
H	-5.86737800	4.92337800	-1.47584600
C	-2.37163600	-0.93669600	2.59599100
C	-3.32387600	-0.55710300	1.58737900
C	-4.69098200	-0.81540400	1.80267500
C	-5.08038300	-1.42781100	2.98965000
C	-4.12939800	-1.79028500	3.97128200
C	-2.76900200	-1.55320400	3.79001000
C	-1.24218800	-0.05259500	0.89552400
C	-2.55411200	0.00427200	0.51349700

H	-5.42863300	-0.54040100	1.04571300
H	-6.13797100	-1.63444700	3.17071800
H	-4.46921400	-2.26930300	4.89289000
H	-2.03532100	-1.83848800	4.54702400
H	-0.22842600	-0.75442800	2.63963200
N	-1.10401000	-0.60874700	2.14516200
Hf	2.99777700	0.30632300	0.06645700
Cl	4.77208900	1.75728900	0.77916500
Cl	4.24012300	-1.73712800	-0.27658100
Cl	2.30083900	-0.34734000	2.36203200
Cl	3.01608800	1.00040200	-2.27826000
H	-1.11961900	1.86806900	-1.63201600
Si	0.49233200	-2.10603700	-0.98291400
H	-3.13569400	-0.24980100	-1.53056700
C	-1.30388400	-2.42388800	-1.41911000
C	-1.76523500	-2.27976300	-2.74221800
C	-2.19260400	-2.94734000	-0.46185300
C	-3.07423900	-2.62274600	-3.09127400
H	-1.09864700	-1.89190600	-3.51633300
C	-3.50197700	-3.29066700	-0.80475100
H	-1.86691200	-3.08018800	0.57155500
C	-3.94641500	-3.12560400	-2.12037800
H	-3.41346400	-2.49824800	-4.12261800
H	-4.17799300	-3.68208900	-0.04105300
H	-4.97143400	-3.39243700	-2.39009100
C	0.97482100	-3.18613400	0.45527200
H	0.74251900	-4.23165400	0.19118500
H	0.40793700	-2.92763400	1.36152900
H	2.04718000	-3.12170200	0.68137700
C	1.52305000	-2.31978400	-2.51891900
H	1.30196200	-3.31966900	-2.92950100
H	2.60074700	-2.26611700	-2.32127900
H	1.27065600	-1.57074900	-3.28444500

20) TS5

C	0.47546300	0.85793600	0.16909700
C	-0.44534600	2.04554700	0.06071000
O	-0.99527400	-0.51450000	0.41706400
O	0.22513200	3.12082200	-0.21832300
O	-1.65756200	2.05182300	0.25448300
C	-0.49835100	4.37935600	-0.31683300
H	0.26057000	5.12495700	-0.57337700
H	-0.96645500	4.60680000	0.65003100
H	-1.25956400	4.30011800	-1.10411200

C	1.37693800	0.83300200	1.39712300
H	0.95004100	0.16110500	2.15415500
C	2.79002800	0.35711500	0.91565600
C	3.89348200	1.37844300	1.15099000
C	5.01388800	1.03111800	1.91561500
C	3.81950500	2.66613300	0.59743600
C	6.04505700	1.95327700	2.12692600
H	5.07843100	0.02918100	2.34762600
C	4.84598500	3.58814500	0.80925300
H	2.95068300	2.94782600	-0.00273300
C	5.96365200	3.23380800	1.57448200
H	6.91351700	1.66798500	2.72602900
H	4.77573400	4.58792700	0.37322800
H	6.76802600	3.95527700	1.73787000
C	2.24086100	-0.32987200	-2.75986900
C	3.22145400	-0.36807900	-1.70029600
C	4.53227500	-0.82138400	-1.97424800
C	4.83387100	-1.23076700	-3.26152000
C	3.85413500	-1.19416000	-4.28862300
C	2.55794400	-0.74929000	-4.06040300
C	1.23447200	0.37863300	-0.91280600
C	2.54729300	0.06835400	-0.53318600
H	5.27954000	-0.85063100	-1.17935300
H	5.83775800	-1.58888300	-3.49907200
H	4.13029600	-1.52644400	-5.29233400
H	1.81269200	-0.72532000	-4.85737500
H	0.15423100	0.20036700	-2.73810700
N	1.05065900	0.14602100	-2.25531700
Hf	-2.94979200	0.23974700	0.05328200
Cl	-4.76080500	1.85325200	-0.33242900
Cl	-4.19294400	-1.79402200	-0.39779700
Cl	-2.21767200	0.45338200	-2.36521300
Cl	-3.30520600	0.28865500	2.48724300
H	1.41538100	1.83249400	1.85338000
Si	-0.57004900	-2.19069200	0.51732200
H	3.07745300	-0.56332600	1.43770800
C	1.19223700	-2.48048700	1.12647000
C	1.50044700	-2.41466000	2.50010000
C	2.19994900	-2.92058300	0.24859000
C	2.77212600	-2.74652200	2.97487900
H	0.73668200	-2.09992100	3.21645900
C	3.47347900	-3.25849000	0.71621400
H	1.99680400	-2.99756200	-0.82117600
C	3.76363800	-3.16751500	2.08080200

H	2.99011900	-2.68082600	4.04380000
H	4.24050500	-3.59035700	0.01220900
H	4.75873600	-3.42939700	2.44935900
C	-0.74686400	-2.92998300	-1.19196100
H	-0.42982800	-3.98590600	-1.18314200
H	-0.13614000	-2.39129200	-1.93246700
H	-1.79536500	-2.89324200	-1.52131400
C	-1.67854500	-3.00027600	1.79243200
H	-1.32142800	-4.03231600	1.94985800
H	-2.72911100	-3.04268000	1.47682600
H	-1.62837400	-2.46966300	2.75577400

21) Int6+PhMe$_2$SiOHfCl$_4$

C	-1.44028200	-1.18536800	0.54884000
C	-0.13651200	-1.86648400	0.64768400
O	1.82393200	1.19929600	0.05985000
O	-0.16792600	-2.97229400	1.33900200
O	0.86939900	-1.44053400	0.08382800
C	1.06182700	-3.73228500	1.45545800
H	0.79352700	-4.63805900	2.00881300
H	1.80750300	-3.13816900	1.99935000
H	1.44168400	-3.97241600	0.45370700
C	-2.75048500	-1.77034100	0.99410800
H	-2.72670100	-2.06090000	2.05459700
C	-3.83041200	-0.67907900	0.68822000
C	-5.07843500	-1.17079400	-0.02052000
C	-6.30151600	-1.23368100	0.65849800
C	-5.01792700	-1.58151600	-1.36122900
C	-7.44899400	-1.70169300	0.00975200
H	-6.35513700	-0.91388700	1.70247700
C	-6.16266300	-2.04848200	-2.00944300
H	-4.06894000	-1.53329800	-1.90165100
C	-7.38210900	-2.10957400	-1.32502200
H	-8.39761200	-1.74577400	0.55046600
H	-6.10362300	-2.36496400	-3.05372600
H	-8.27811900	-2.47411300	-1.83330800
C	-1.85376900	1.91455200	-1.19004500
C	-3.19684100	1.53659700	-0.77329500
C	-4.30987800	2.34427700	-1.14236500
C	-4.07273300	3.47596000	-1.88808700
C	-2.74785500	3.82479600	-2.28820700
C	-1.63358400	3.06580100	-1.95643600
C	-1.64252800	0.02571800	-0.05530100
C	-3.05145600	0.35615900	-0.04893600

H	-5.31731700	2.05824700	-0.83651300
H	-4.90066200	4.11966900	-2.19004300
H	-2.60667700	4.72780100	-2.88715200
H	-0.63073100	3.34347800	-2.28161300
H	0.07437000	1.05925200	-0.80367600
N	-0.94891800	0.99479200	-0.72877500
Hf	2.73946100	-0.42118300	-0.66298500
Cl	3.43531400	-2.71669200	-1.43182100
Cl	4.74612300	0.74556000	-1.41326700
Cl	1.44734200	-0.14235400	-2.79066900
Cl	3.62996600	-0.98234300	1.61651400
H	-2.95243800	-2.69130600	0.42103000
Si	1.54014400	2.29069400	1.30490600
H	-4.13633700	-0.23000200	1.64855500
C	0.12269700	1.54291600	2.30963300
C	0.29328600	0.29090700	2.93279300
C	-1.14566300	2.14376500	2.38470100
C	-0.76292300	-0.33564300	3.60397400
H	1.26328200	-0.21129700	2.88258400
C	-2.20659800	1.52356900	3.05690500
H	-1.32134700	3.10954900	1.90361300
C	-2.01639400	0.28318600	3.67068000
H	-0.60736800	-1.31028100	4.07350400
H	-3.18317900	2.01262300	3.09957700
H	-2.84169900	-0.20372300	4.19601700
C	1.02120100	3.93269000	0.56652000
H	0.87628800	4.69039300	1.35489900
H	0.08832000	3.86121500	-0.01170300
H	1.81085800	4.29918600	-0.11097600
C	3.07627300	2.51167000	2.34980300
H	2.89958000	3.26217900	3.13888800
H	3.91339300	2.86159100	1.72221000
H	3.38206300	1.56655700	2.82130300

22) $PhMe_2SiOH$

Si	-1.47110300	-0.05413700	-0.00001000
C	0.40880500	-0.01757900	0.00002800
C	1.10163100	1.20860600	0.00006000
C	1.16499700	-1.20407000	0.00001100
C	2.49887200	1.25011300	0.00004100
H	0.54556700	2.15186300	0.00008200
C	2.56330600	-1.16865300	0.00000200
H	0.64847700	-2.16727500	0.00000800
C	3.23301300	0.05889500	0.00001400

H	3.01756600	2.21259100	0.00005600
H	3.13284800	-2.10209500	-0.00001500
H	4.32589400	0.08830800	0.00000900
C	-2.14253200	0.79017200	1.53708600
H	-1.83113100	1.84826300	1.56771200
H	-1.77032000	0.30056700	2.45229100
H	-3.24582600	0.76703500	1.55872700
C	-2.14219600	0.78942900	-1.53765600
H	-1.76850400	0.30046100	-2.45259900
H	-1.83201700	1.84789400	-1.56777000
H	-3.24543800	0.76499600	-1.56037500
O	-1.83948700	-1.69709500	0.00054100
H	-2.78115000	-1.91940300	0.00016900

23) Int6

C	-0.62516100	0.60542600	2.05936900
C	0.02017800	0.32187000	3.36655100
O	0.92100000	1.24156200	3.69120500
O	-0.30162700	-0.62016600	4.05877500
C	1.67774600	1.00204400	4.88263200
H	1.01490600	0.91439200	5.75614800
H	2.34693500	1.86305300	4.99701200
H	2.26420000	0.07706800	4.77532700
C	-0.45601600	1.82685700	1.21338600
H	0.60079300	2.04438600	1.01240900
C	-1.25861700	1.53550600	-0.10000600
C	-1.99719800	2.70722300	-0.70186100
C	-1.40836100	3.44727300	-1.73689700
C	-3.25832200	3.09442100	-0.22273900
C	-2.06607300	4.55283000	-2.28429200
H	-0.42620300	3.15028400	-2.11406200
C	-3.91827100	4.19721100	-0.77042400
H	-3.72850900	2.52640400	0.58436000
C	-3.32363300	4.92993100	-1.80354500
H	-1.59528000	5.11904400	-3.09194800
H	-4.90131100	4.48602200	-0.38967500
H	-3.84030000	5.79178600	-2.23325100
C	-3.20667800	-1.55946800	0.81523600
C	-3.08756500	-0.51222500	-0.18043900
C	-3.93597900	-0.52198100	-1.31646300
C	-4.86890200	-1.53261300	-1.43337600
C	-4.97453700	-2.54683200	-0.44168100
C	-4.15758200	-2.58169600	0.67957400
C	-1.61005800	-0.18778900	1.51669000

C	-2.06340400	0.33813200	0.27481200
H	-3.84526700	0.26072800	-2.07124900
H	-5.53719000	-1.56389600	-2.29605600
H	-5.72525500	-3.33027000	-0.57143000
H	-4.24694600	-3.37039500	1.42814400
H	-2.14873400	-1.91244800	2.64330900
N	-2.29078100	-1.34342500	1.81478900
H	-0.88514600	2.69219800	1.74967300
H	-0.48390600	1.18778500	-0.80994700
P	2.03034100	-0.50624800	0.19345700
O	1.66593900	0.64602800	-0.69957600
O	1.35584800	-0.74841600	1.52439700
O	1.95571000	-1.93810300	-0.67312700
O	3.65596900	-0.52667500	0.49689200
C	0.72354500	-2.37715500	-1.09641600
C	0.16391400	-1.86793800	-2.27506800
C	0.04307300	-3.34322100	-0.34630500
C	-1.07244200	-2.34935300	-2.71351400
H	0.70450000	-1.09701400	-2.82597900
C	-1.19179800	-3.81886800	-0.79477200
H	0.49315300	-3.70353100	0.58027900
C	-1.75153600	-3.32688000	-1.97868400
H	-1.51116700	-1.95256100	-3.63252600
H	-1.72379300	-4.57473000	-0.21205600
H	-2.72098700	-3.69446000	-2.32030300
C	4.61503500	-0.08839700	-0.37965300
C	4.59105400	-0.41187800	-1.74295300
C	5.66261700	0.67919200	0.14335500
C	5.61816400	0.04203900	-2.57464800
H	3.77943000	-1.02322400	-2.13735200
C	6.68829700	1.12045800	-0.69619300
H	5.65646600	0.91928600	1.20870200
C	6.66970900	0.80775300	-2.05977400
H	5.59573500	-0.21192400	-3.63772100
H	7.50423400	1.71763700	-0.28072900
H	7.47010000	1.15700400	-2.71638200

24) TS6

C	-1.15288600	2.21664200	0.35980800
C	-0.38325400	3.46926400	0.40507300
O	-0.55990100	4.21250900	-0.68603200
O	0.33405000	3.77435300	1.33973500
C	0.21607700	5.41119300	-0.78369000
H	0.00928400	6.08075000	0.06444500

H	-0.07830900	5.88769000	-1.72632800
H	1.28970600	5.17018600	-0.80164800
C	-2.02929400	1.72905800	-0.75359100
H	-1.57151100	1.90873400	-1.73951800
C	-2.25690600	0.23236500	-0.44048300
C	-3.39702100	-0.54738000	-1.02121600
C	-3.23643600	-1.92143100	-1.27060700
C	-4.62755400	0.05331600	-1.32937500
C	-4.28498300	-2.67917000	-1.79581800
H	-2.27364900	-2.39359900	-1.06305800
C	-5.67527900	-0.70440500	-1.86133900
H	-4.77438800	1.11961500	-1.14658000
C	-5.51008700	-2.07277600	-2.09317000
H	-4.14085500	-3.74605700	-1.98424700
H	-6.62749700	-0.22013000	-2.09263700
H	-6.33003900	-2.66341100	-2.50909000
C	-0.91372100	-0.21362300	2.99873500
C	-1.71375000	-0.86057100	1.98916900
C	-2.18770200	-2.17371700	2.20182700
C	-1.86977800	-2.81034100	3.39132500
C	-1.08702300	-2.15560100	4.37240200
C	-0.60086500	-0.86214900	4.19646500
C	-1.09094900	1.25470700	1.33084800
C	-1.82211000	0.06995900	0.91929200
H	-2.78795200	-2.66898300	1.43775500
H	-2.22197700	-3.82637900	3.57905700
H	-0.85208300	-2.68485200	5.29929300
H	0.01072500	-0.37467300	4.95673900
H	0.07237700	1.69079200	3.05272100
N	-0.55415100	1.05258900	2.57360200
H	-2.98735700	2.27941100	-0.74058800
H	-1.23279100	-0.22113300	-0.97772400
P	0.92660800	0.51670100	-2.09327000
O	-0.01641400	-0.60147200	-1.62023800
O	0.44554600	1.62631900	-2.95722100
O	1.63902700	1.20590700	-0.75861100
O	2.21277300	-0.20156100	-2.82987400
C	2.01363500	0.65694100	0.44116800
C	1.75276700	-0.66657300	0.82061900
C	2.68791700	1.51873700	1.31721500
C	2.17764100	-1.11625000	2.07302100
H	1.21779800	-1.32944500	0.14537500
C	3.09901600	1.05799900	2.56850100
H	2.86630500	2.54800700	1.00434900

C	2.84805400	-0.26401000	2.95453800
H	1.96850800	-2.14911300	2.36140000
H	3.62236300	1.73864800	3.24514800
H	3.17116900	-0.62502400	3.93368900
C	2.95214200	-1.20884800	-2.24463000
C	4.19102000	-0.89604800	-1.67864800
C	2.46841000	-2.52048200	-2.23150000
C	4.94894600	-1.90780500	-1.08386000
H	4.53639400	0.13915800	-1.69742300
C	3.23330800	-3.52494000	-1.63285800
H	1.49295100	-2.73027700	-2.67195400
C	4.47154700	-3.22258700	-1.05491800
H	5.91426500	-1.66415100	-0.63319700
H	2.85658200	-4.55082900	-1.61566300
H	5.06397400	-4.01084900	-0.58436600

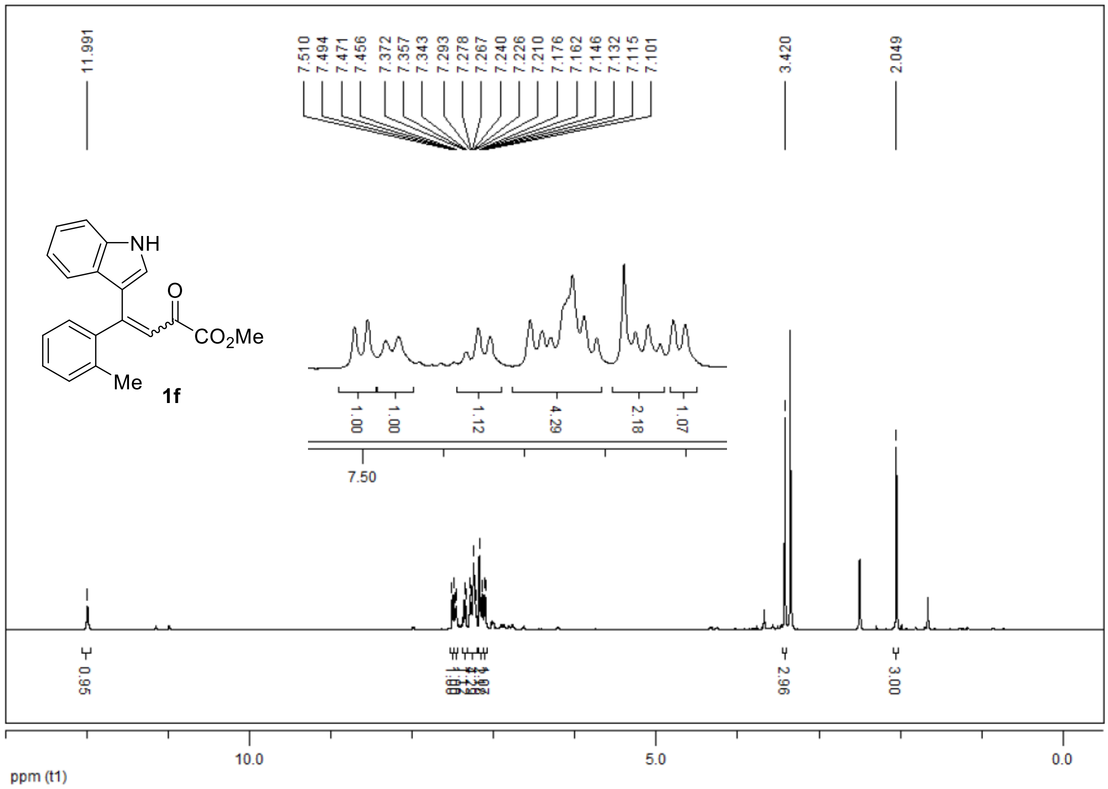
25) **3a**

C	-1.56757600	-1.27320600	0.03203900
C	-2.83885800	-1.95467800	0.04035300
O	-3.88045300	-1.07410800	0.08045500
O	-3.00892300	-3.16229400	0.01584100
C	-5.18741600	-1.64141300	0.09357800
H	-5.88962200	-0.79824100	0.13079000
H	-5.33287400	-2.28657200	0.97432700
H	-5.37149600	-2.23958900	-0.81278900
C	-0.21980100	-1.94966400	-0.01174800
H	-0.11047900	-2.57814000	-0.91446500
C	0.80033600	-0.82309700	-0.00454600
C	2.24042000	-1.07254100	0.01221400
C	2.76949800	-2.27396300	-0.50777400
C	3.14044900	-0.14414000	0.57744300
C	4.14211200	-2.52061800	-0.48800400
H	2.09941600	-3.01456800	-0.94769500
C	4.51205600	-0.39468500	0.59979900
H	2.75390600	0.76536200	1.03680600
C	5.02163400	-1.58129500	0.06123400
H	4.52886300	-3.45325500	-0.90637400
H	5.18733300	0.33758900	1.04954500
H	6.09670500	-1.77630900	0.07627900
C	-1.12356600	2.32073000	-0.01852300
C	0.22026800	1.82890400	-0.04245800
C	1.27173500	2.74763500	-0.13803400
C	0.98738400	4.11767400	-0.19173800
C	-0.33642900	4.57695000	-0.14921600

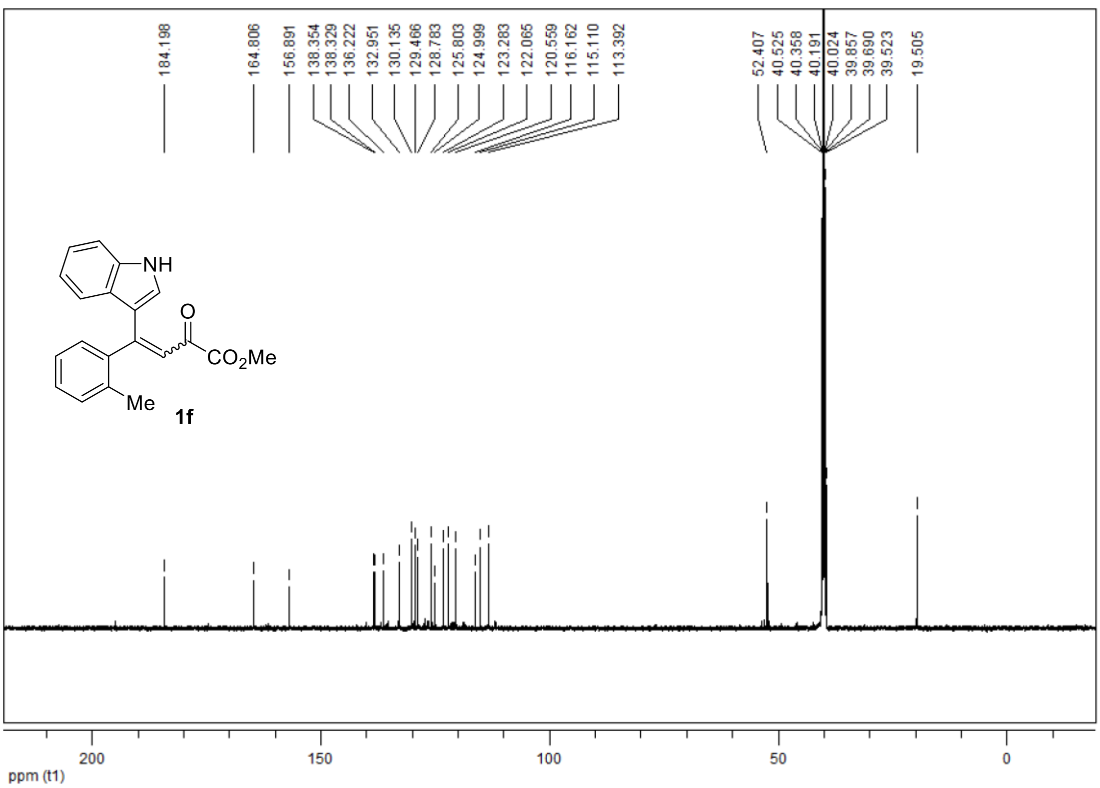
C	-1.41125800	3.68312800	-0.06407200
C	-1.32457600	0.07841500	0.03592700
C	0.11090300	0.36955900	0.00927100
H	2.30618100	2.40693800	-0.18047400
H	1.80746700	4.83520700	-0.26717400
H	-0.53772000	5.65046400	-0.18729500
H	-2.44366600	4.03803500	-0.04119700
H	-3.03034900	1.32376100	0.03580900
N	-2.01951800	1.24980100	0.03797100
H	-0.05591900	-2.63025500	0.84327400

X. NMR Spectra

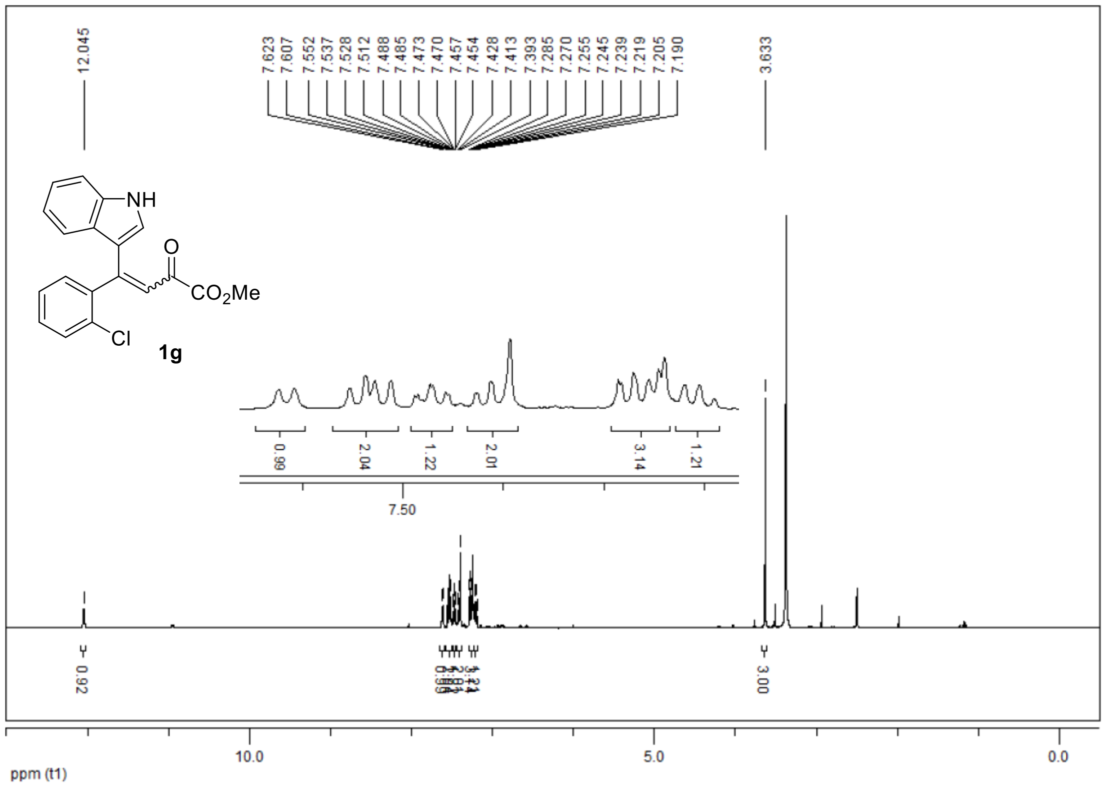
^{1}H NMR (500 MHz, DMSO-d$_6$)



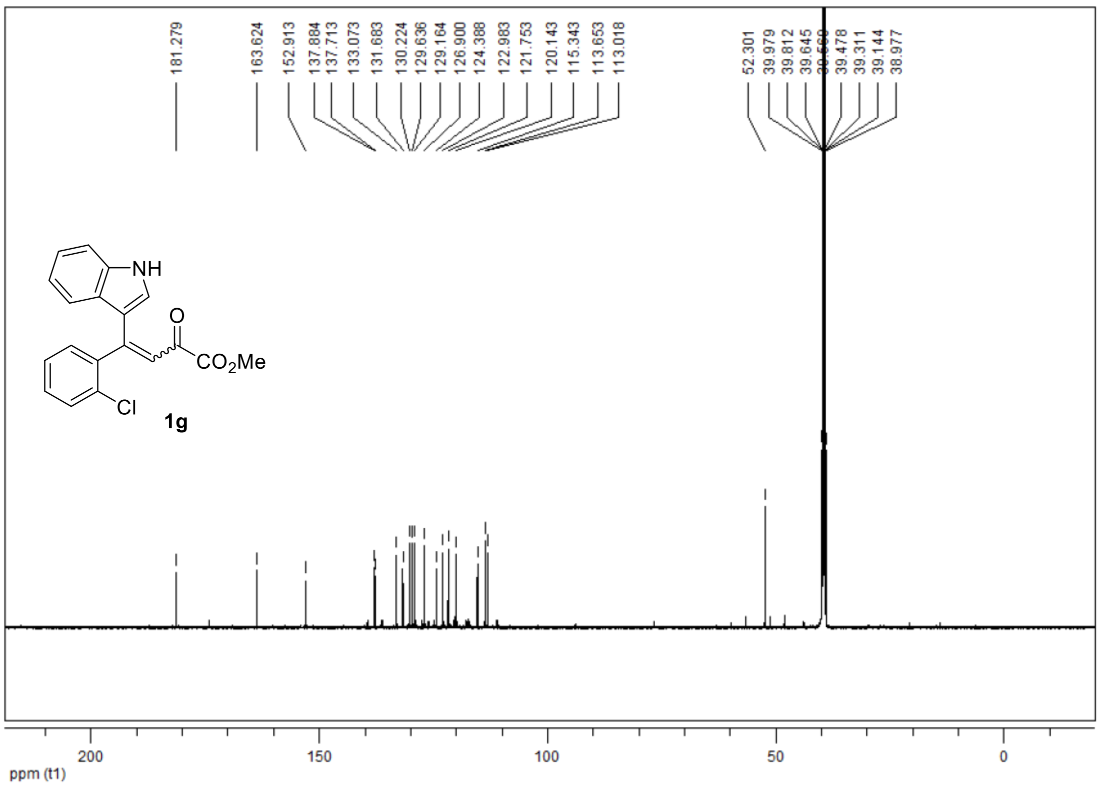
^{13}C{H} NMR (126 MHz, DMSO-d$_6$)



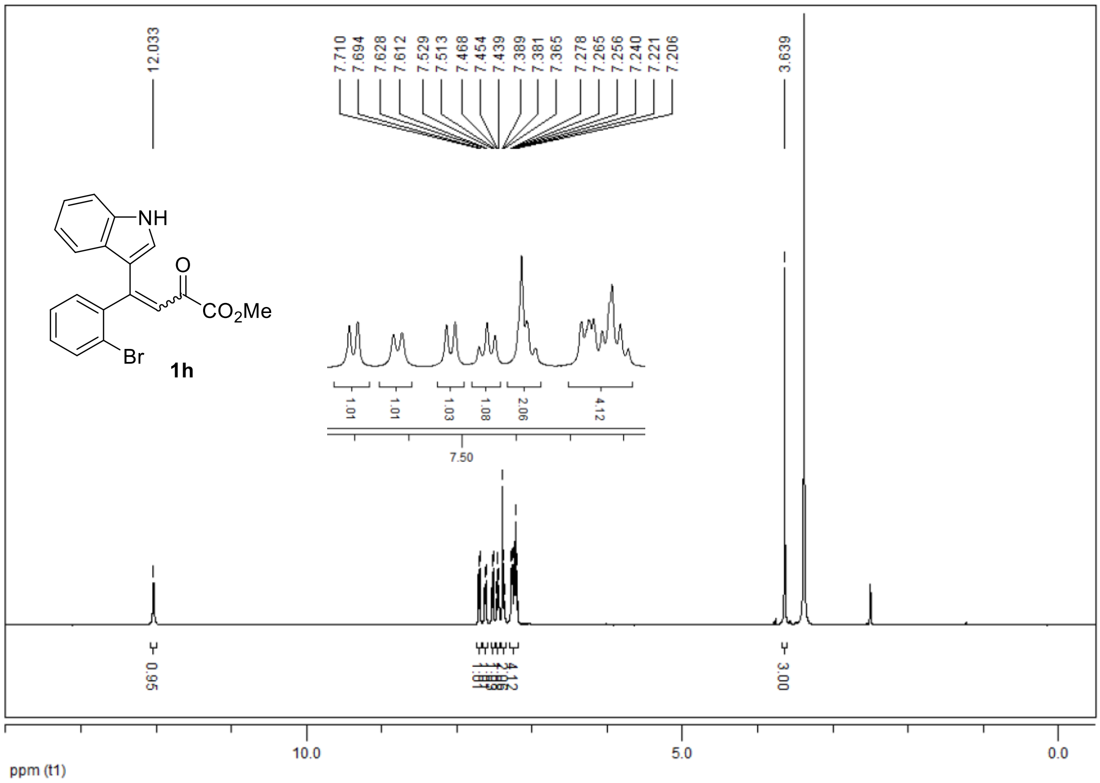
^{1}H NMR (500 MHz, DMSO-d$_6$)



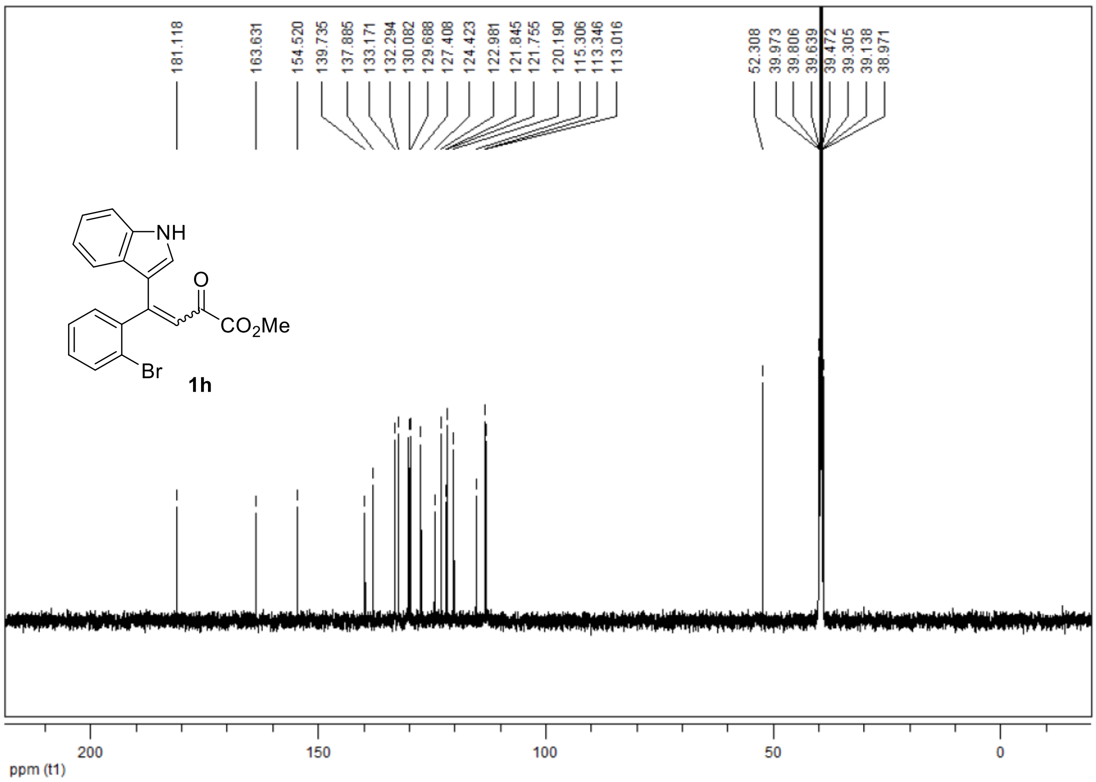
^{13}C{H} NMR (126 MHz, DMSO-d$_6$)



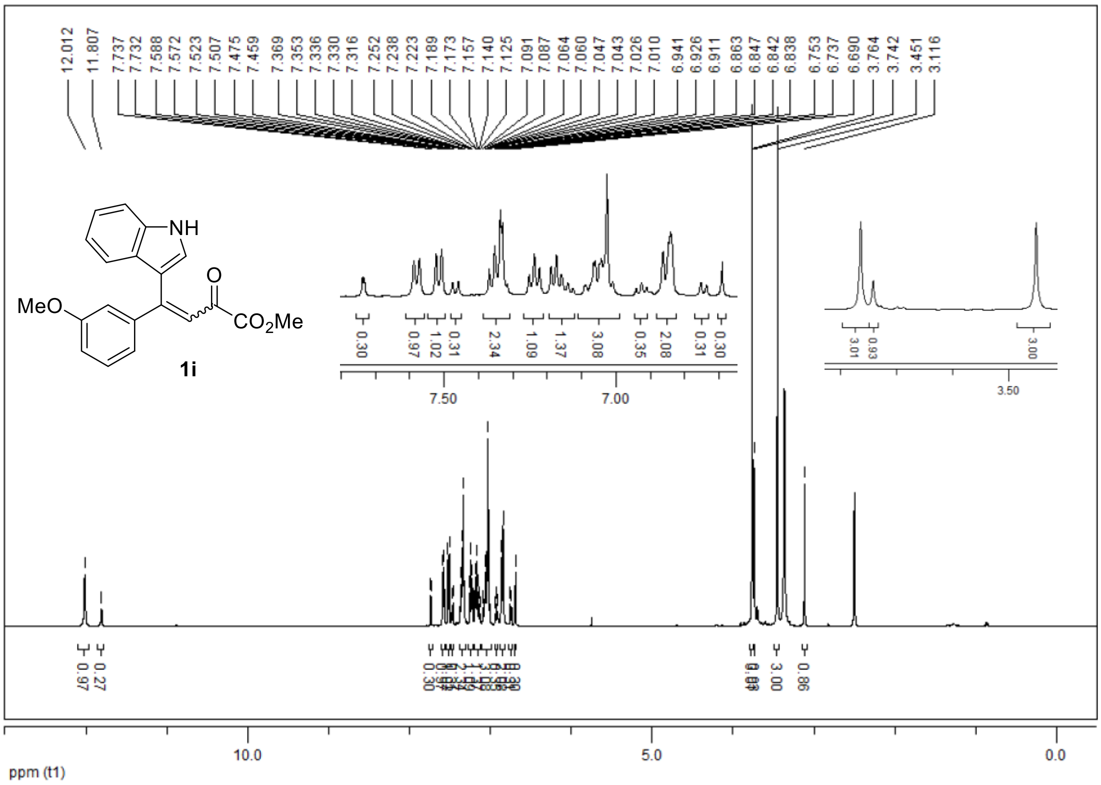
^{1}H NMR (500 MHz, DMSO-d$_6$)



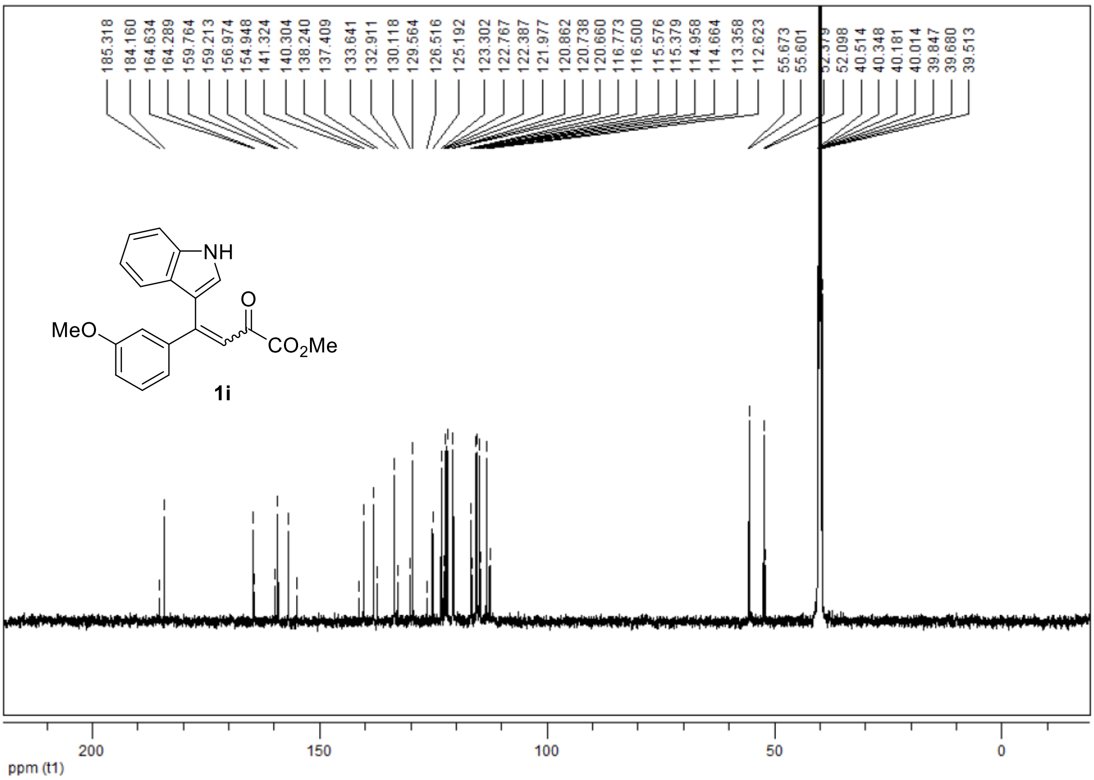
^{13}C{H} NMR (126 MHz, DMSO-d$_6$)



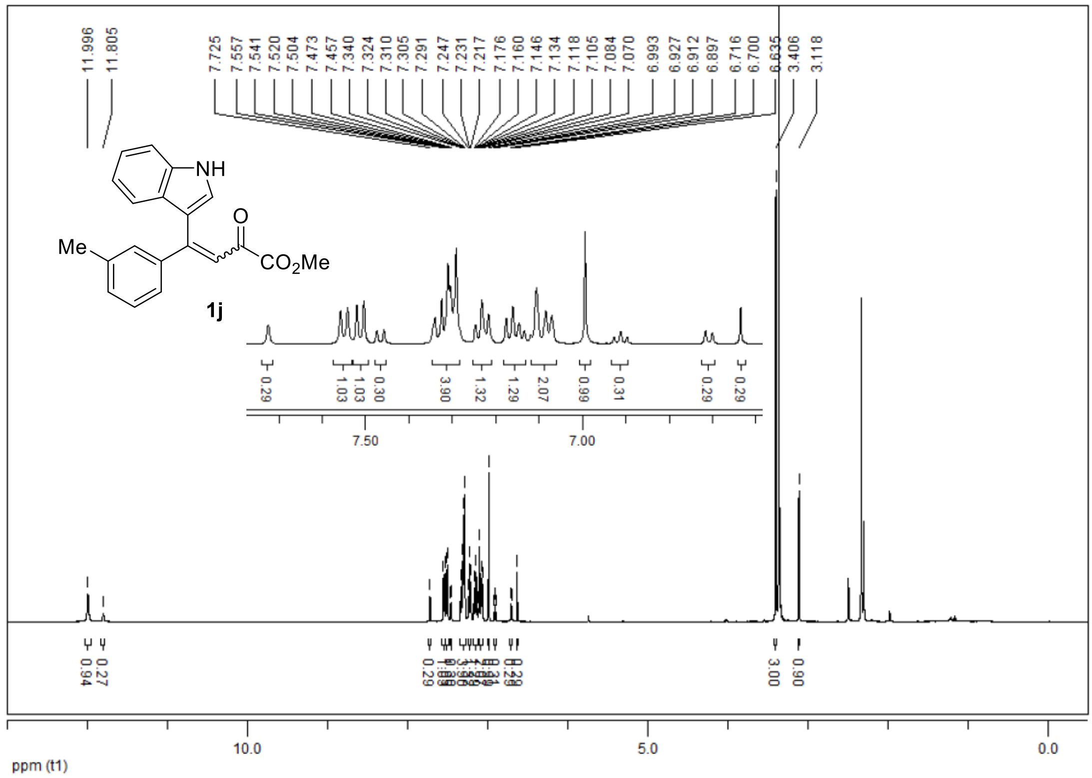
^{1}H NMR (500 MHz, DMSO-d_6)



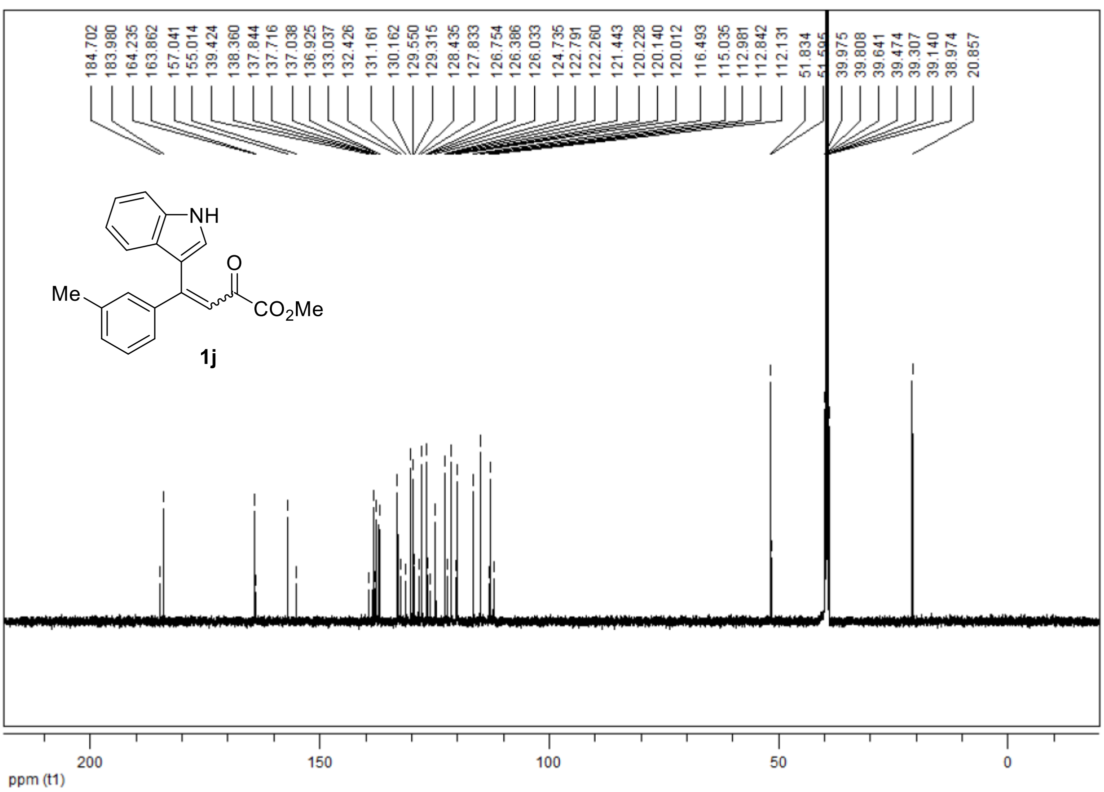
$^{13}C\{H\}$ NMR (126 MHz, DMSO-d_6)



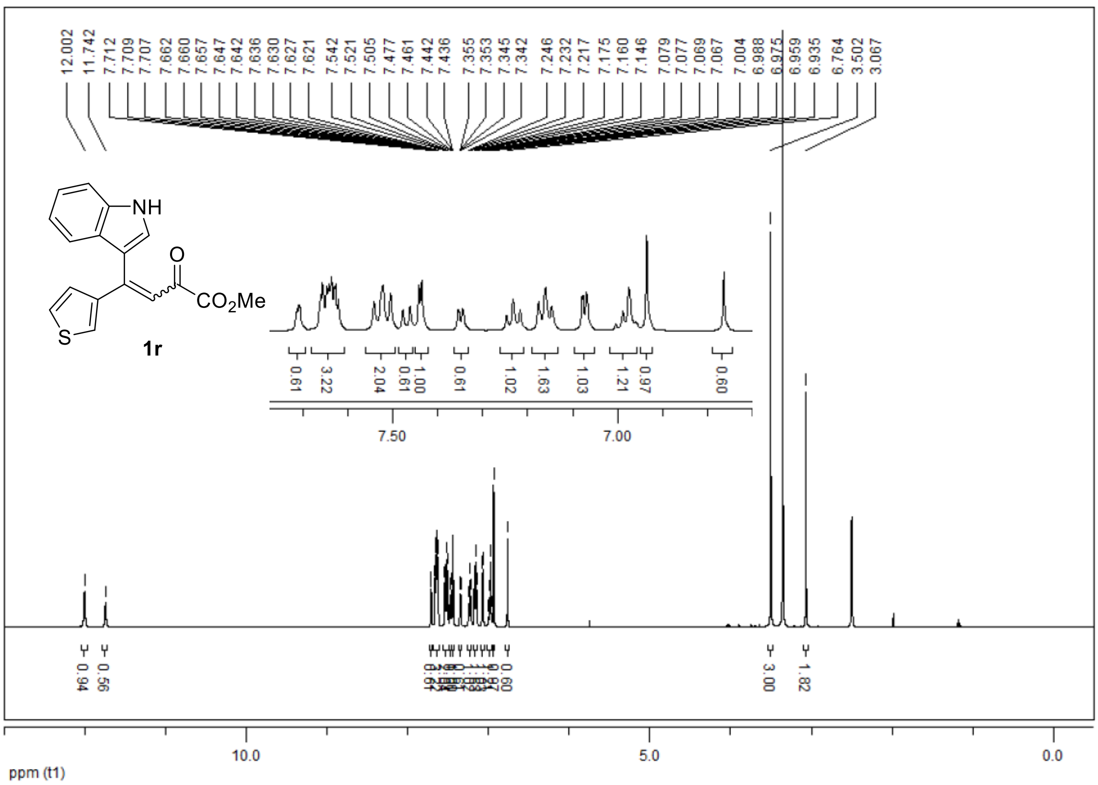
^{1}H NMR (500 MHz, DMSO-d$_6$)



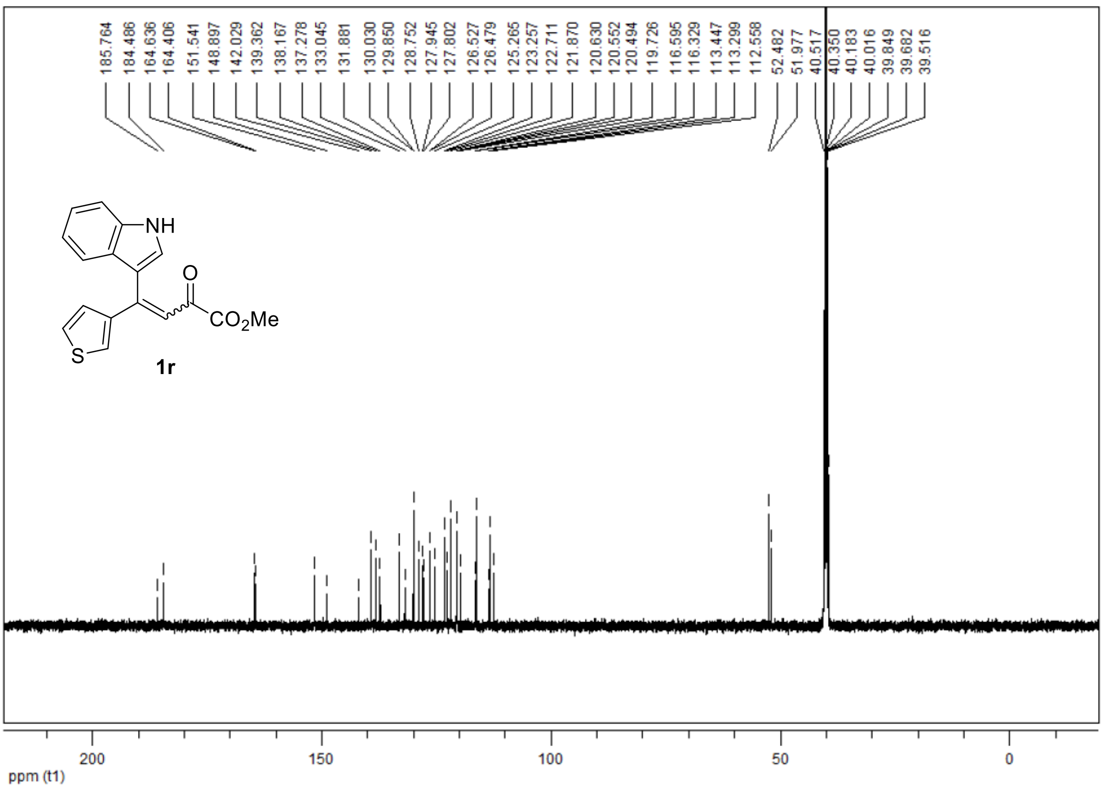
^{13}C{H} NMR (126 MHz, DMSO-d$_6$)



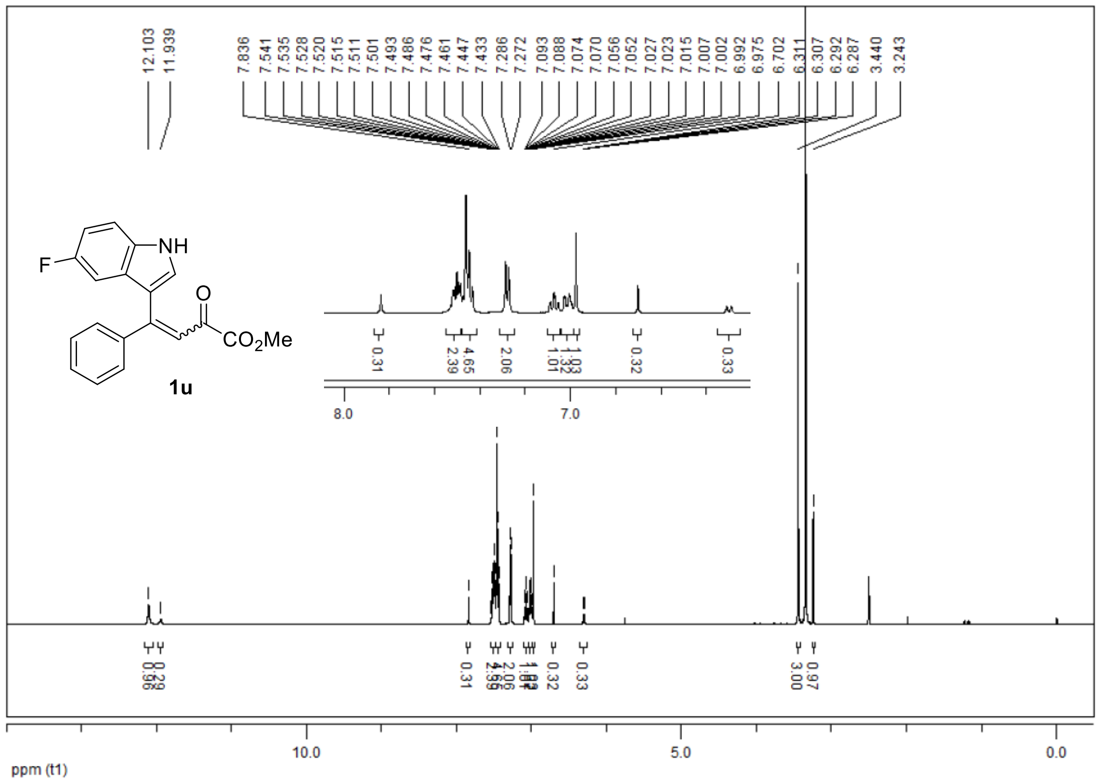
[1]H NMR (500 MHz, DMSO-d$_6$)



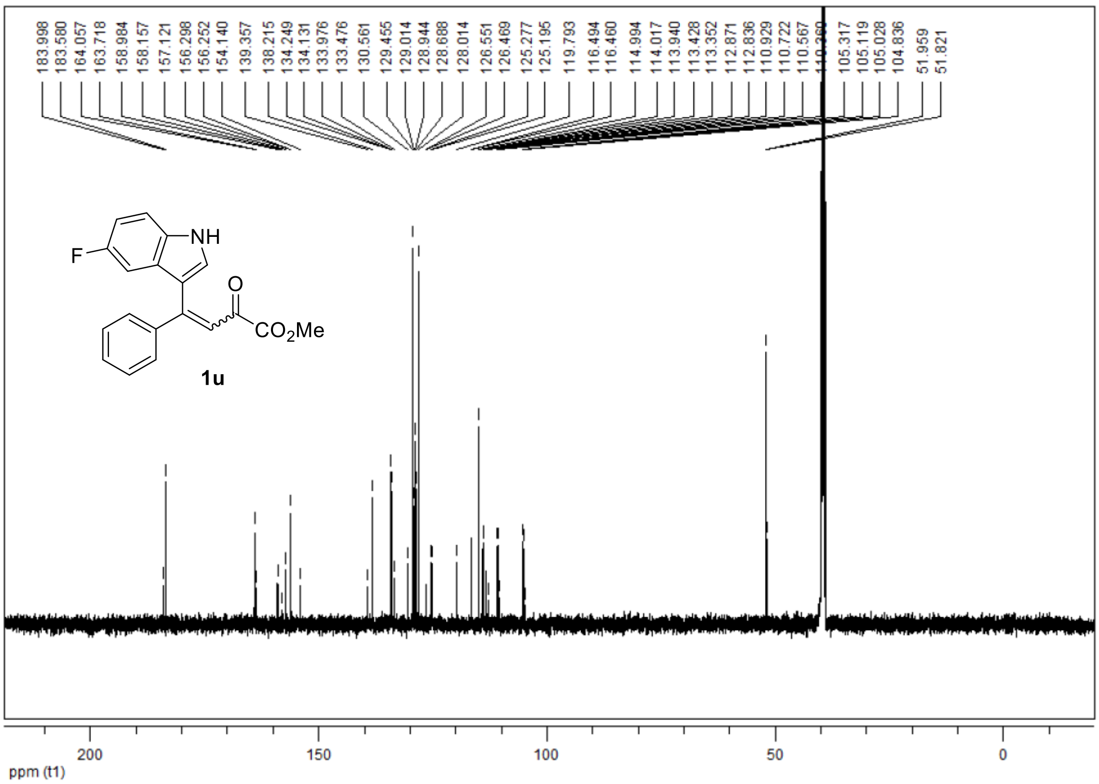
[13]C{H} NMR (126 MHz, DMSO-d$_6$)



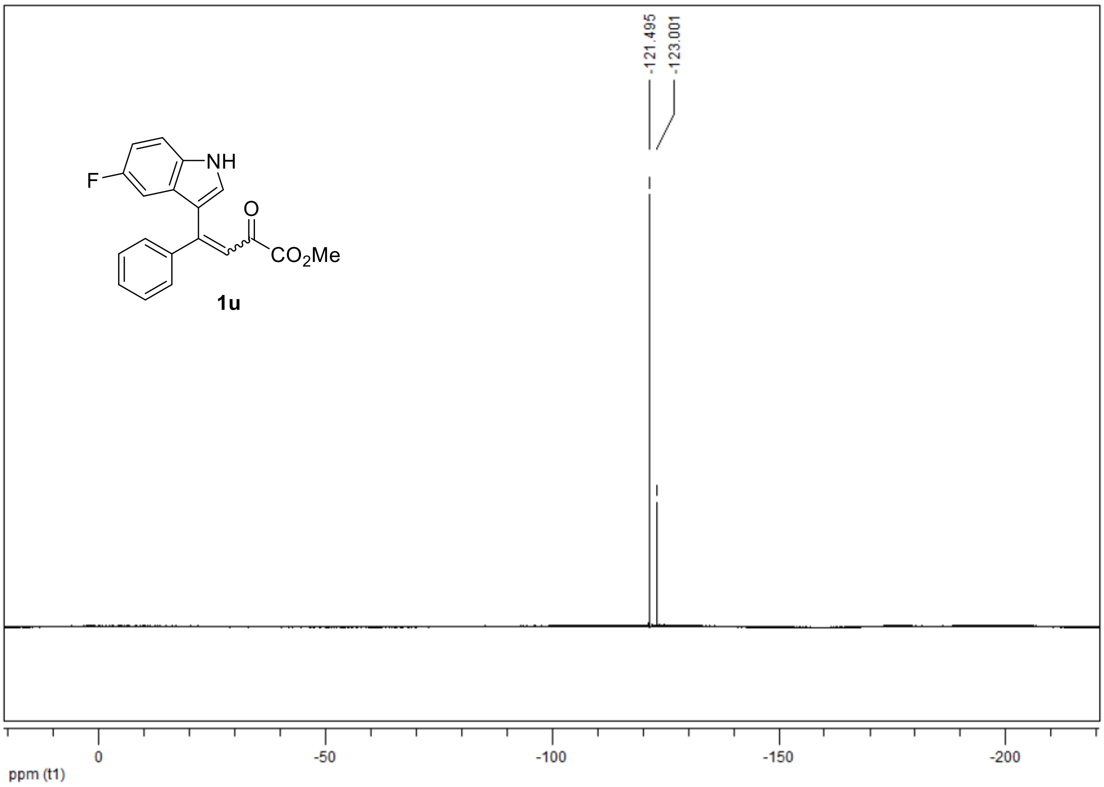
[1]H NMR (500 MHz, DMSO-d6)



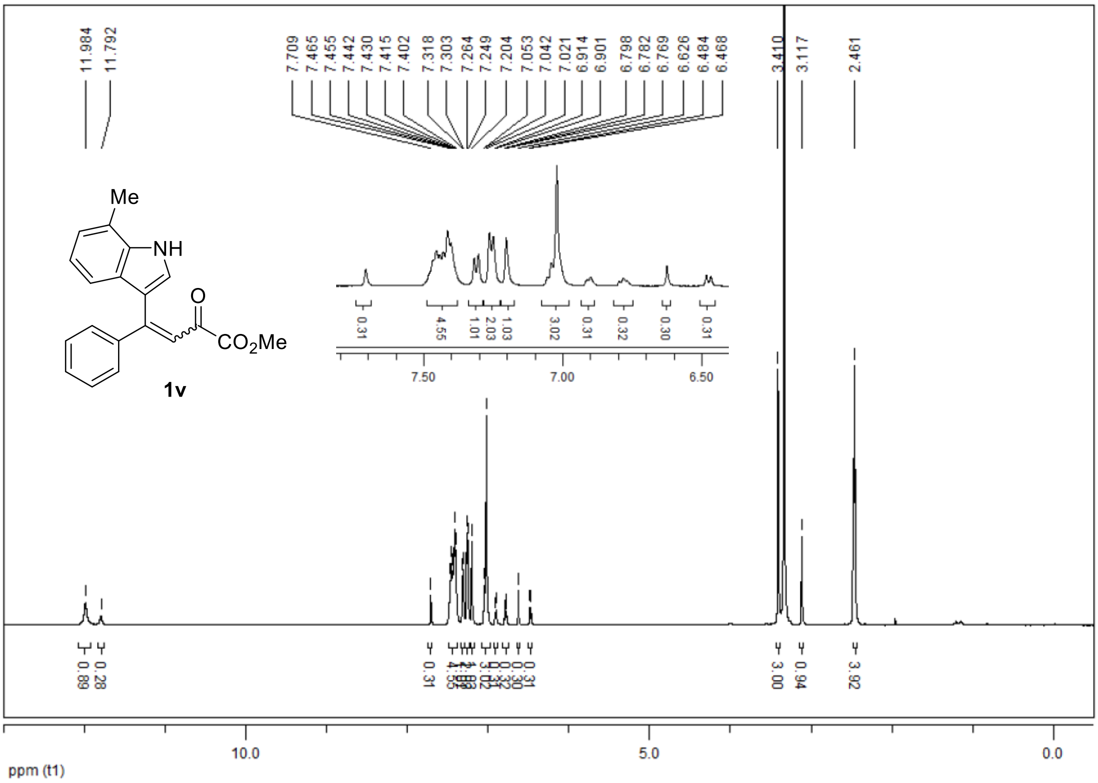
[13]C{H} NMR (126 MHz, DMSO-d6)



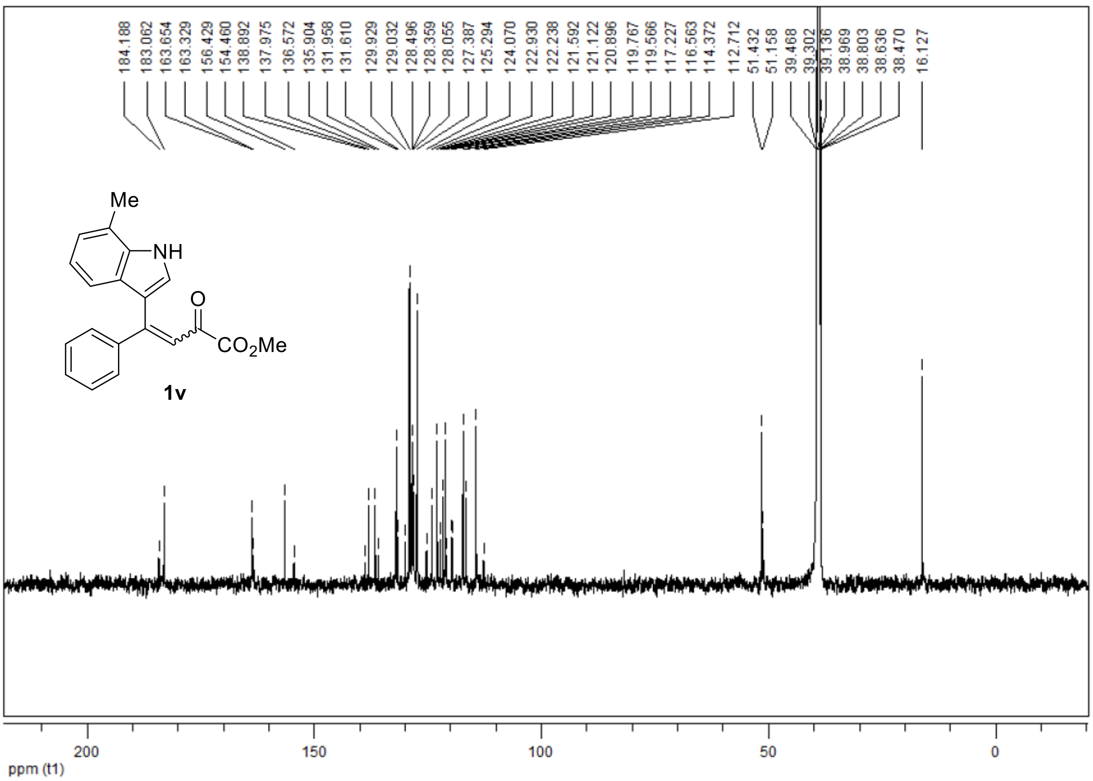
^{19}F NMR (376 MHz, DMSO-d$_6$)



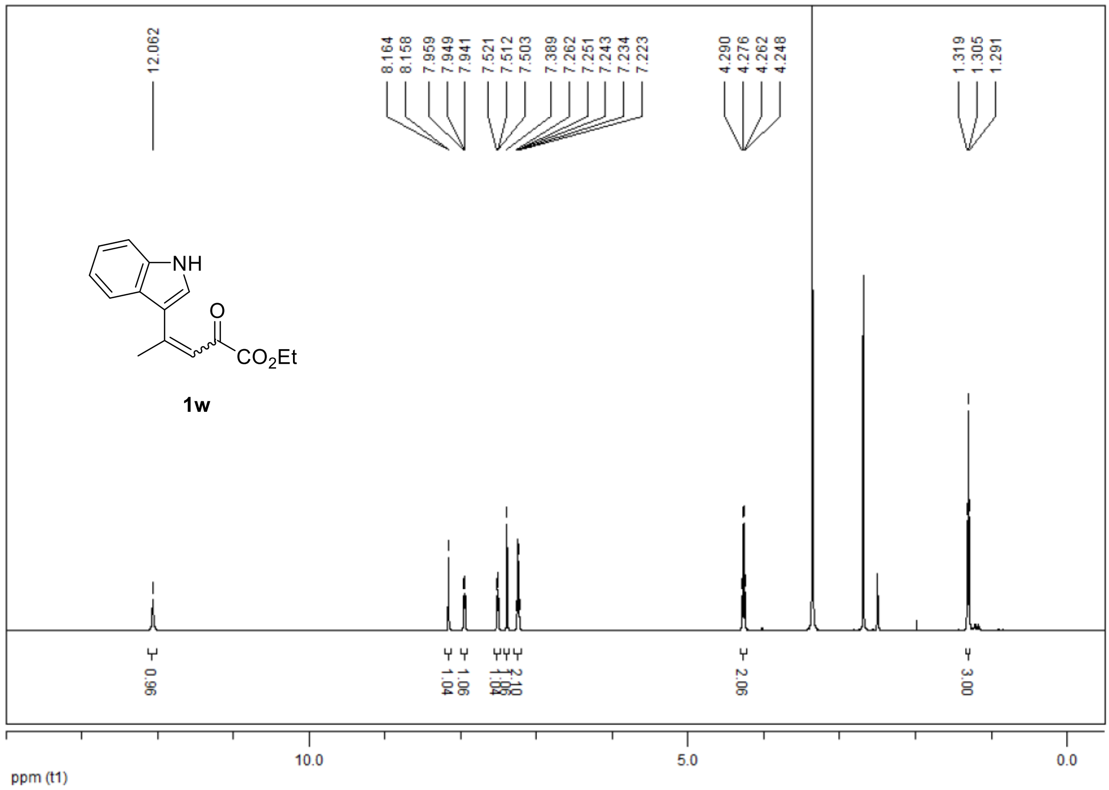
^{1}H NMR (500 MHz, DMSO-d$_6$)



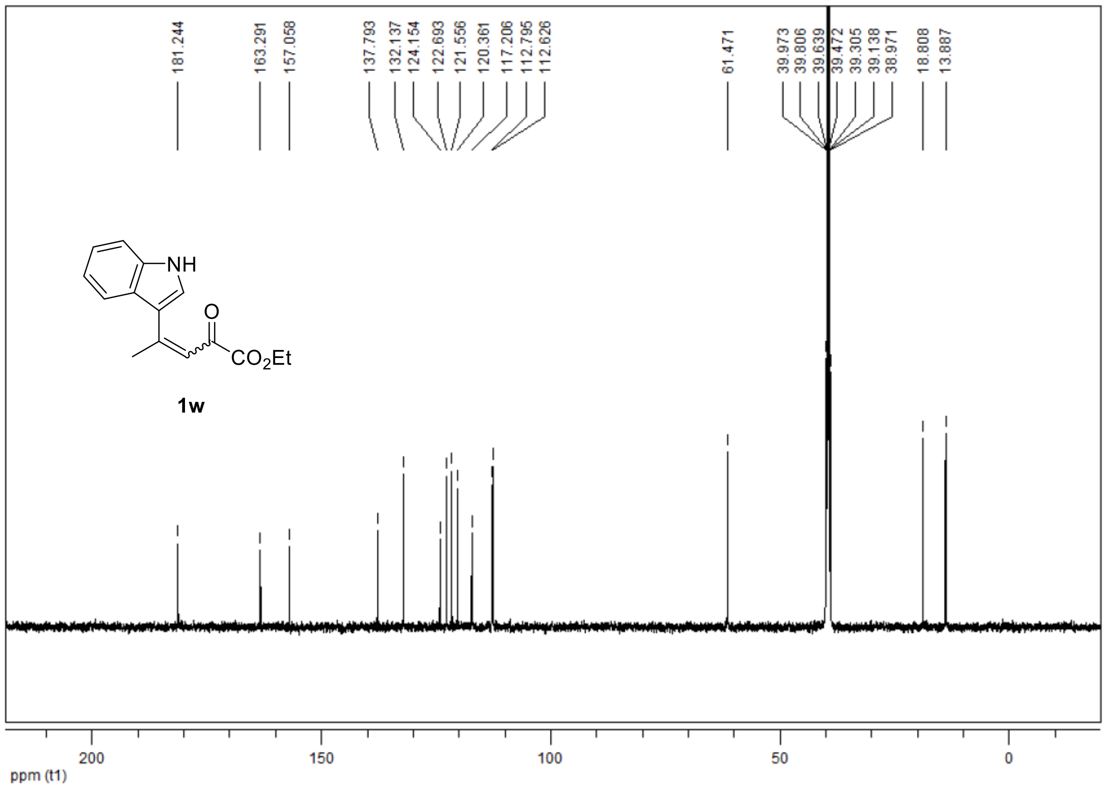
^{13}C{H} NMR (126 MHz, DMSO-d$_6$)



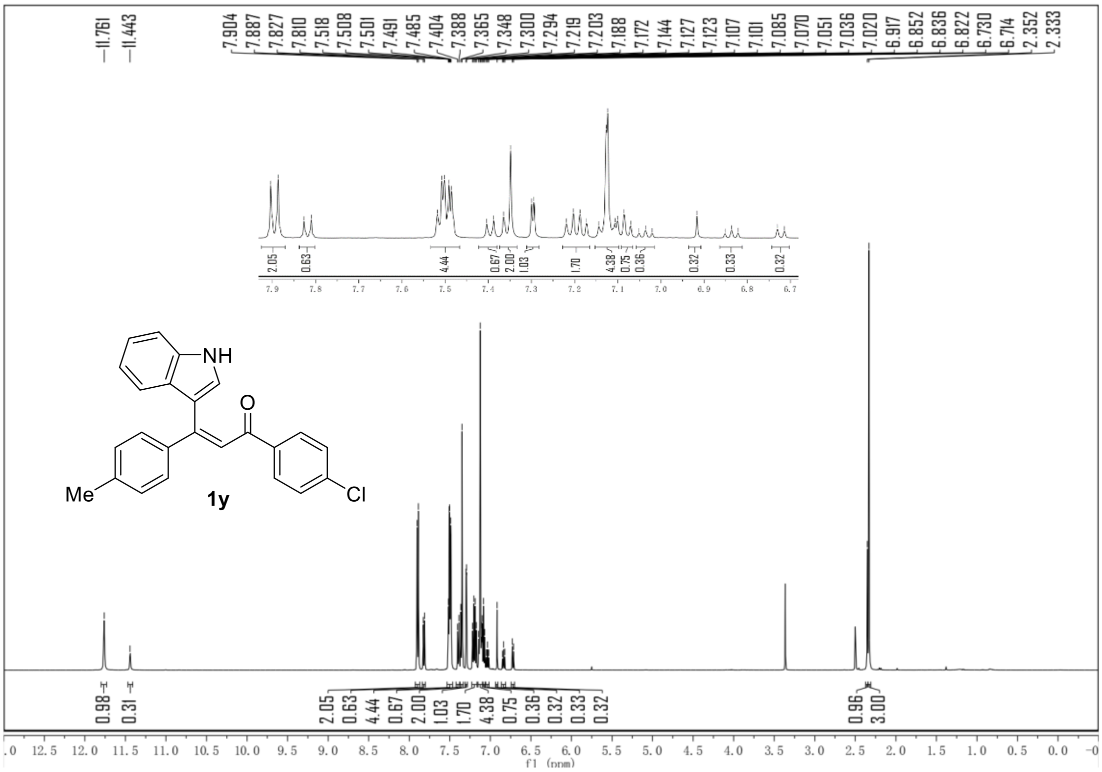
^{1}H NMR (500 MHz, DMSO-d$_6$)



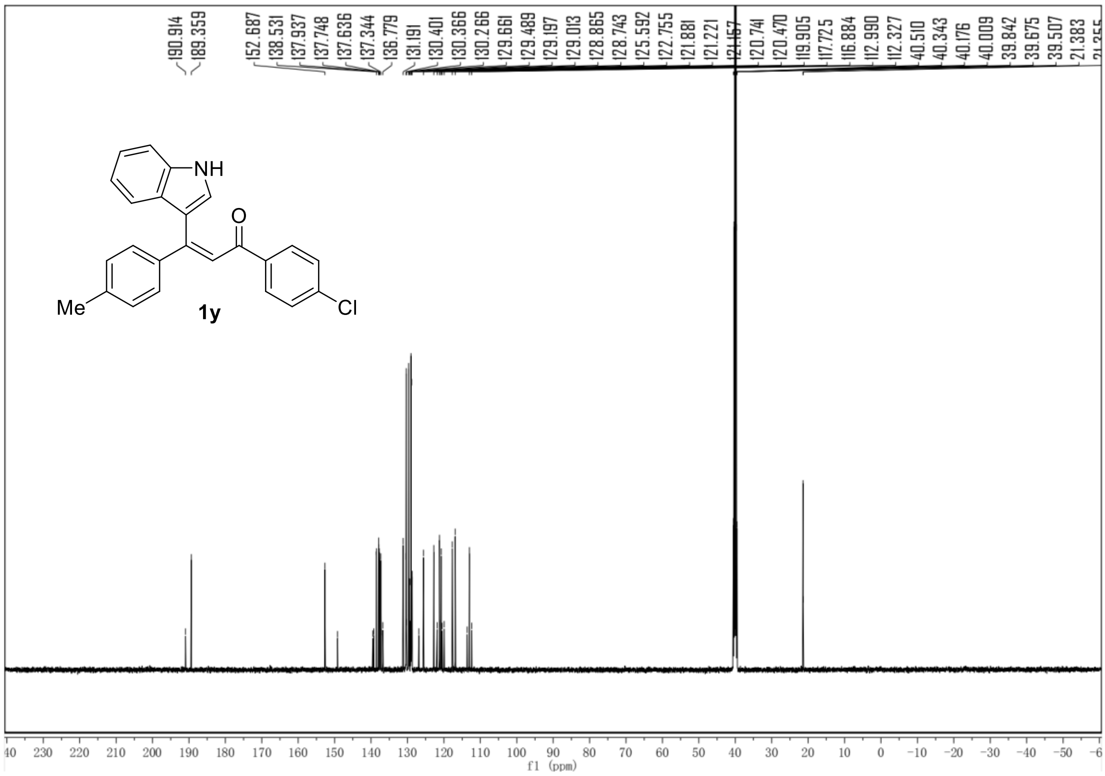
$^{13}C\{H\}$ NMR (126 MHz, DMSO-d$_6$)



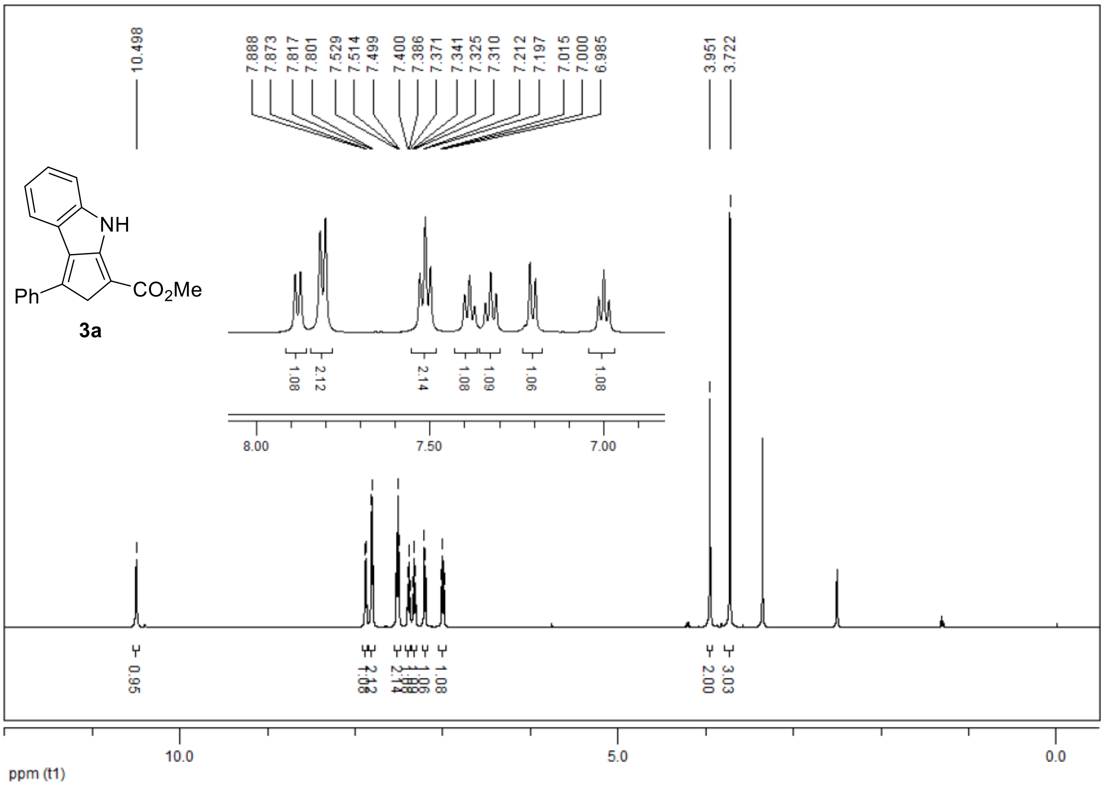
^{1}H NMR (500 MHz, DMSO-d$_6$)



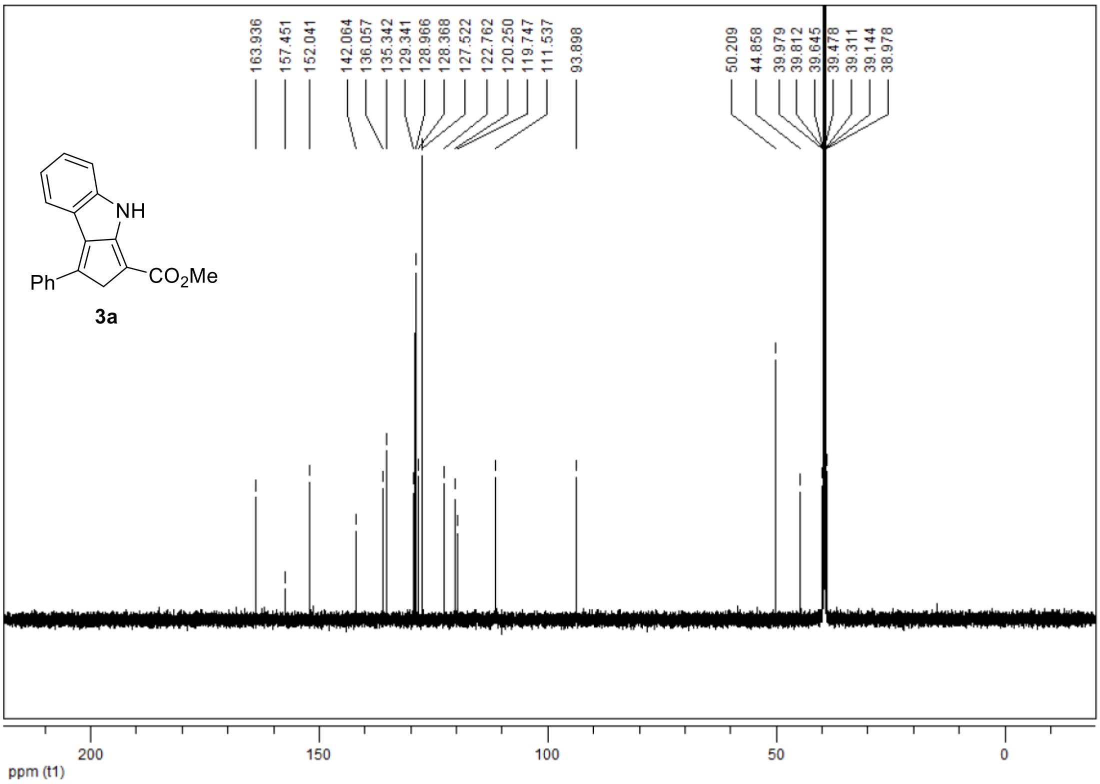
^{13}C{H} NMR (126 MHz, DMSO-d$_6$)



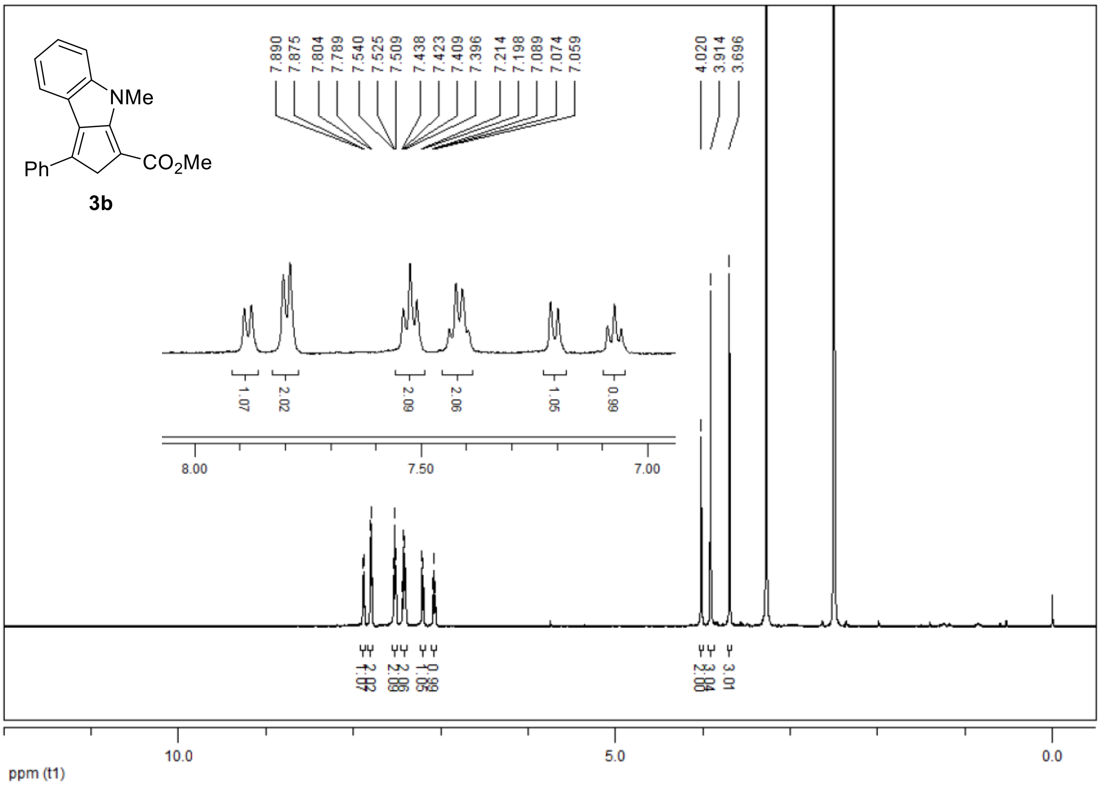
^1H NMR (500 MHz, DMSO-d_6)



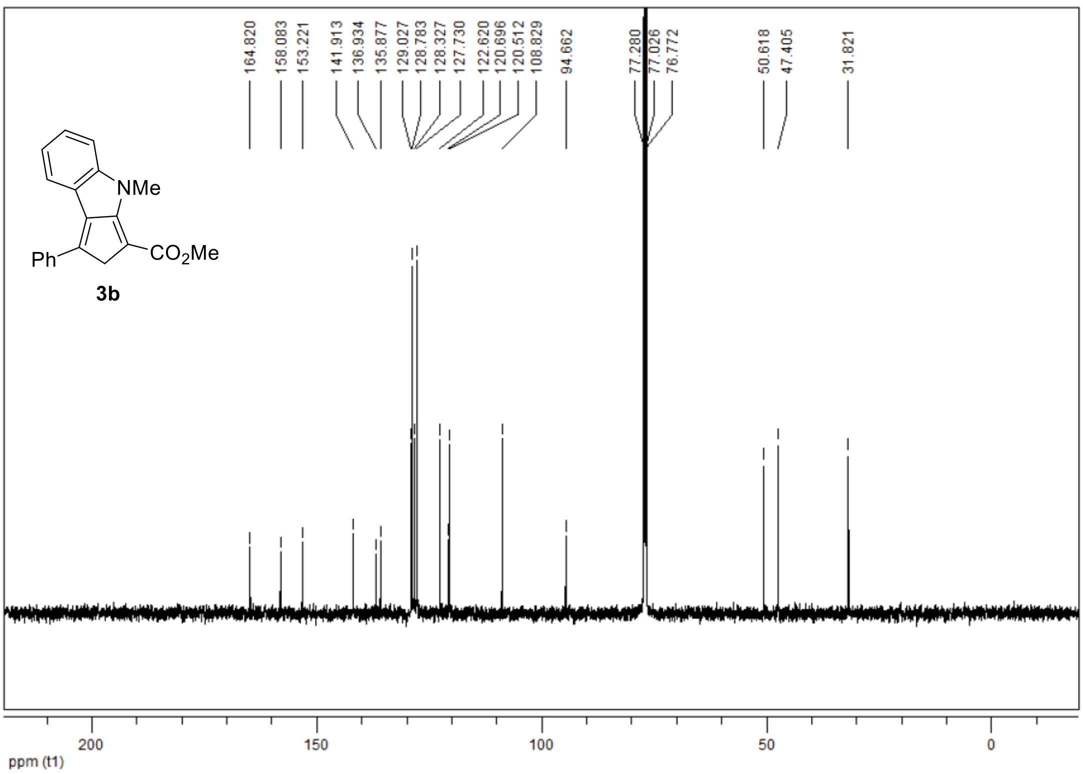
$^{13}C\{H\}$ NMR (126 MHz, DMSO-d_6)



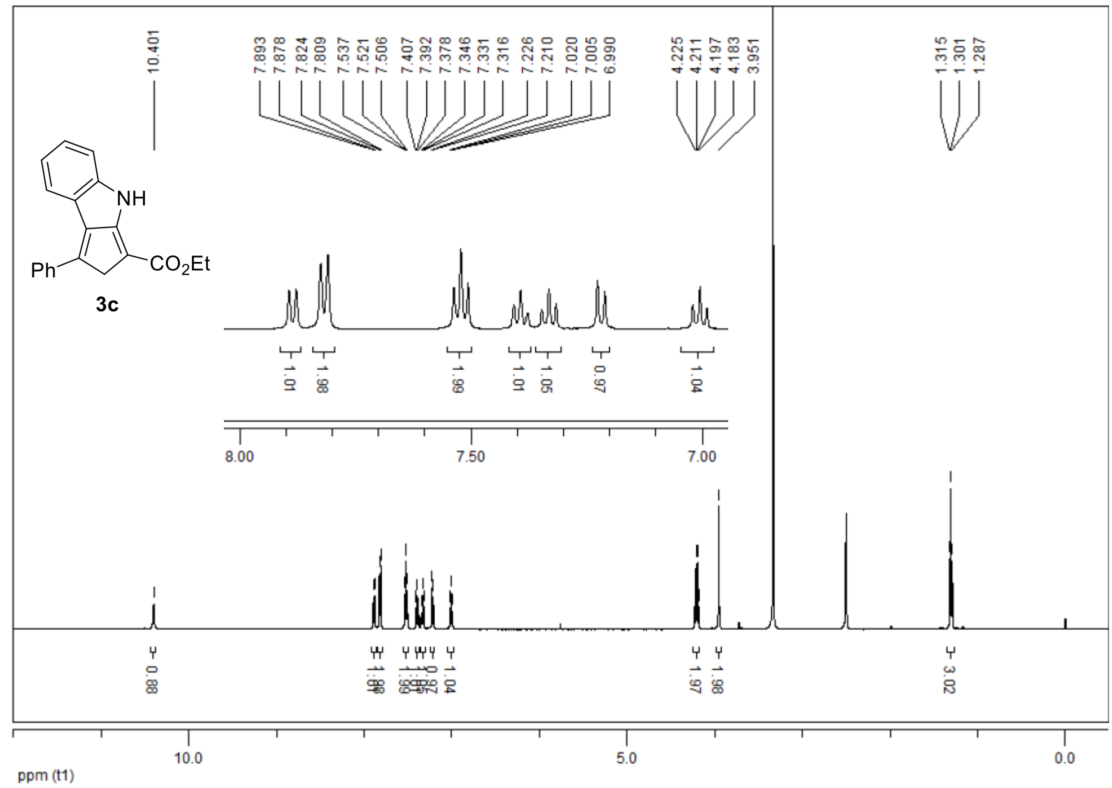
^{1}H NMR (500 MHz, DMSO-d_6)



^{13}C{H} NMR (126 MHz, $CDCl_3$)



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



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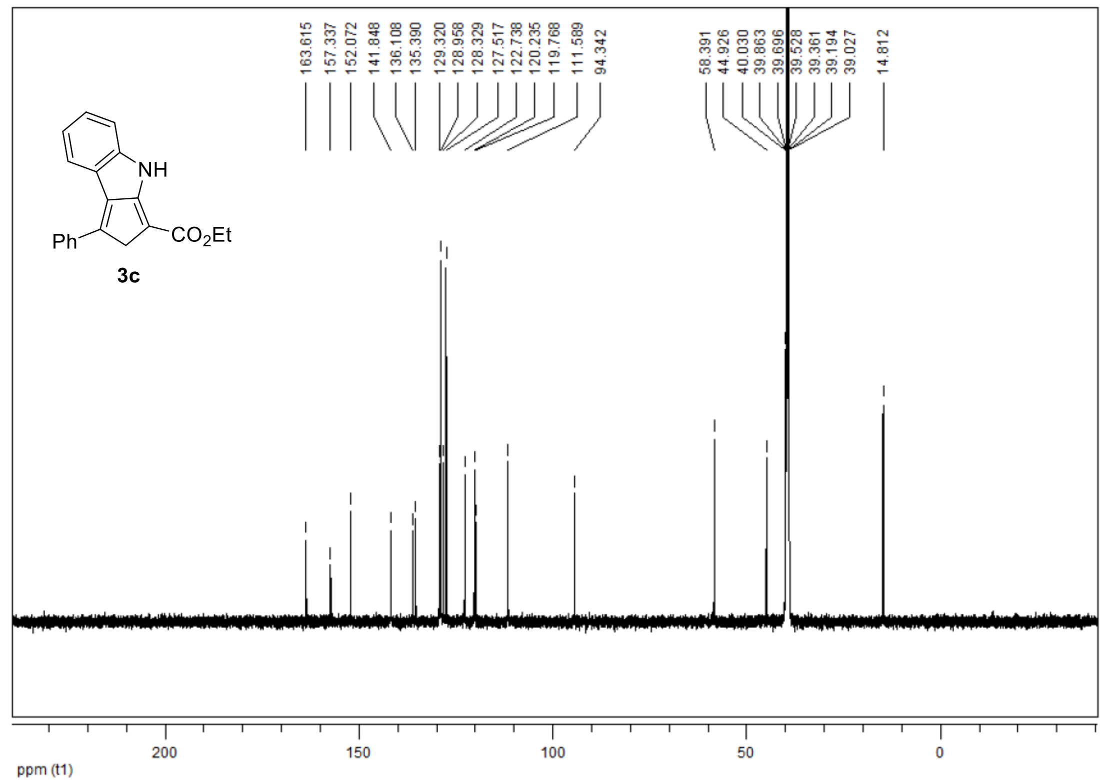
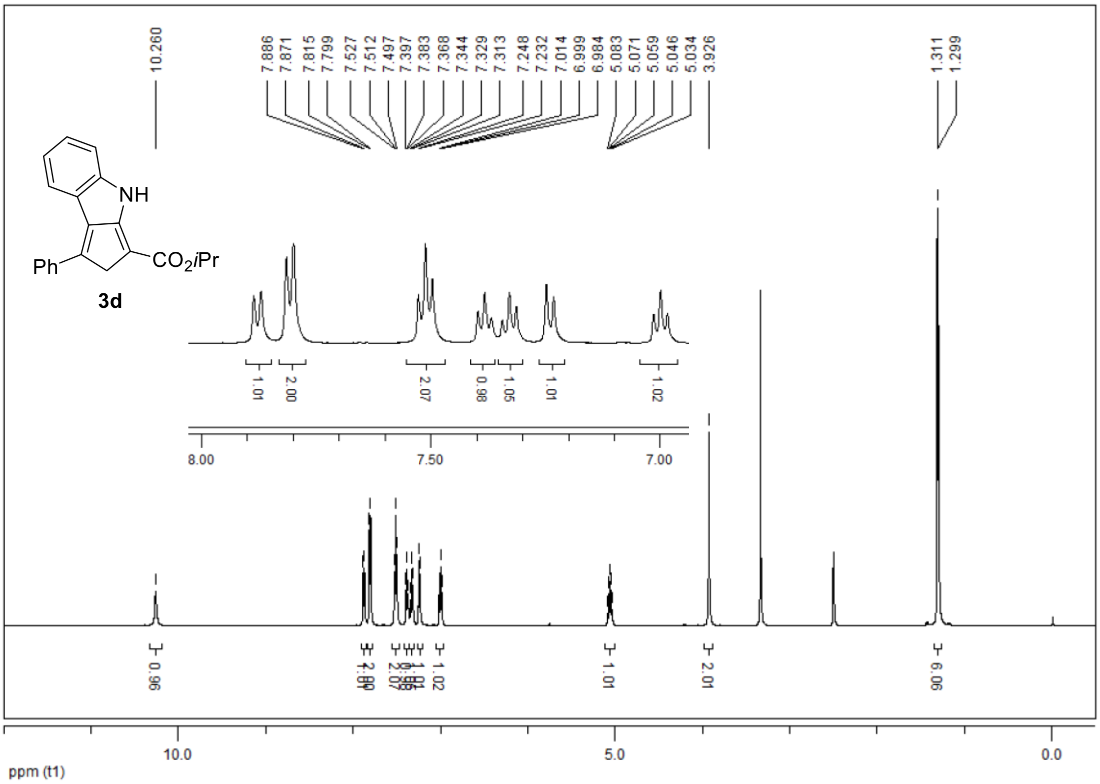


^{1}H NMR (500 MHz, DMSO-d$_6$)



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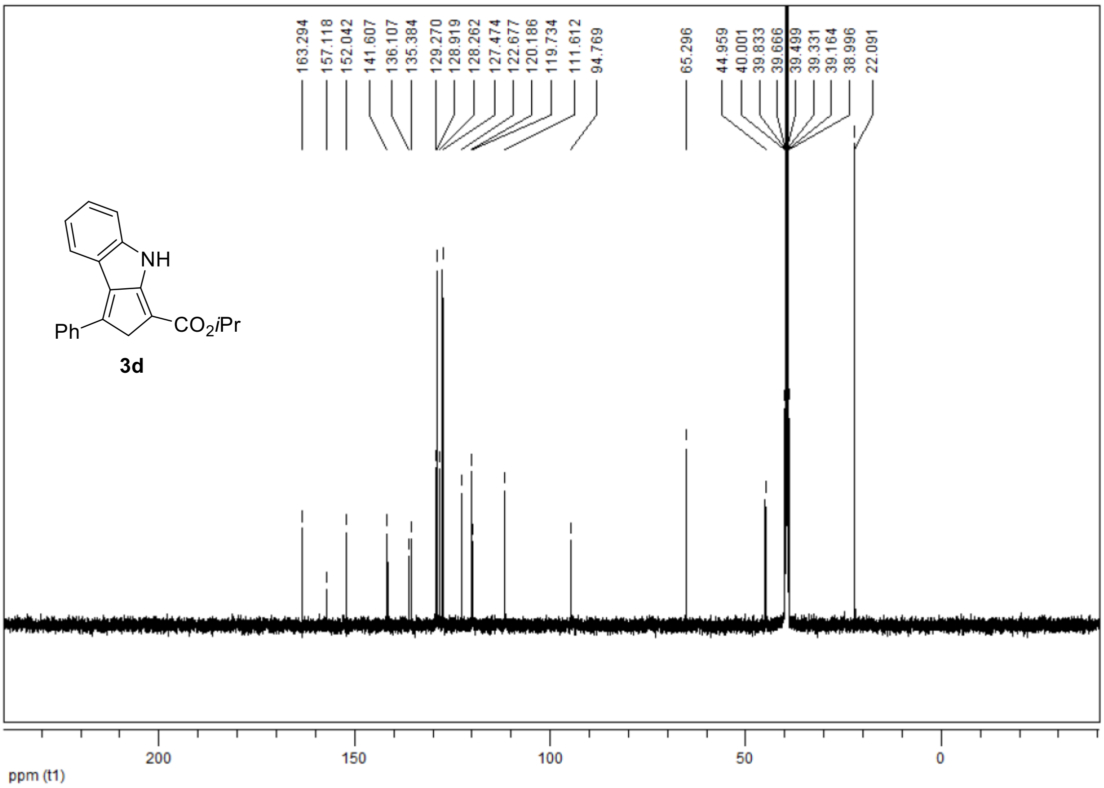
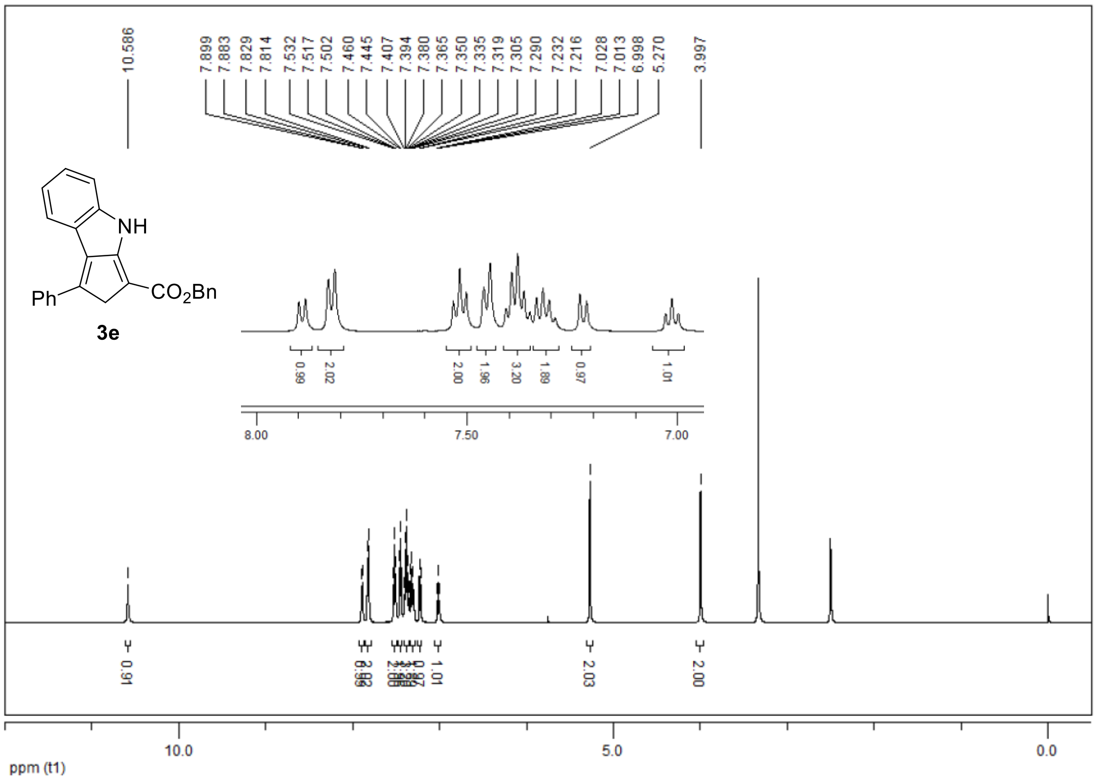
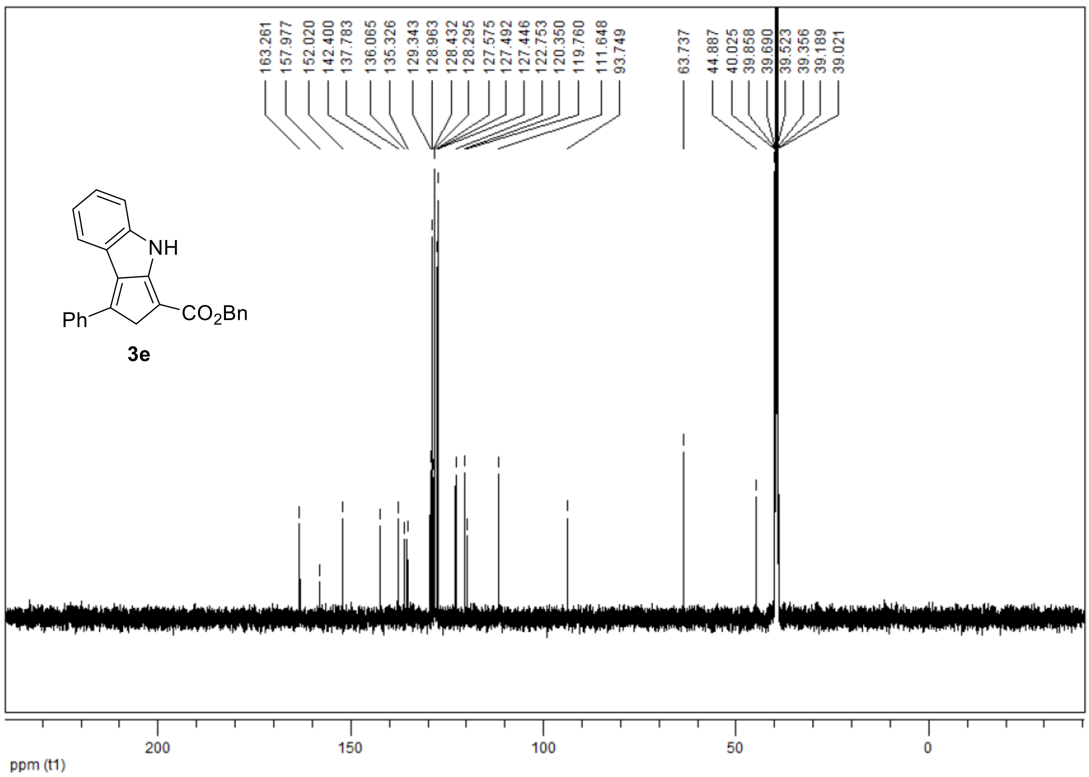


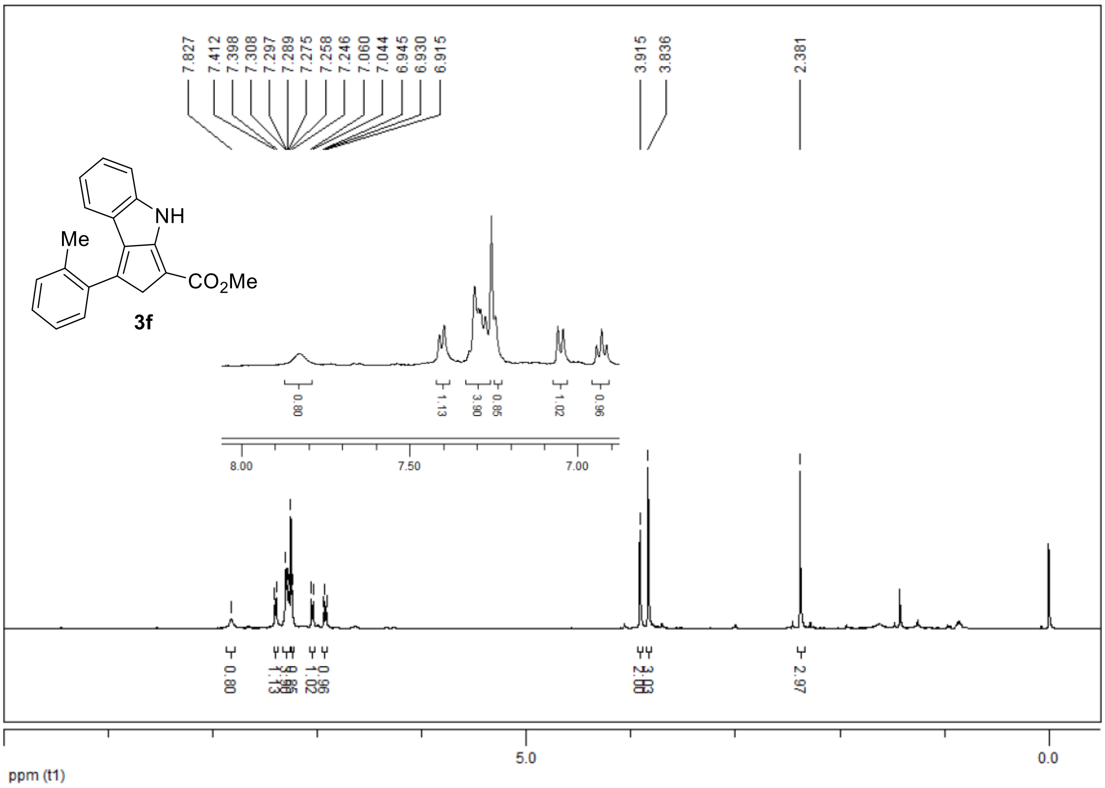
[1]H NMR (500 MHz, DMSO-d$_6$)



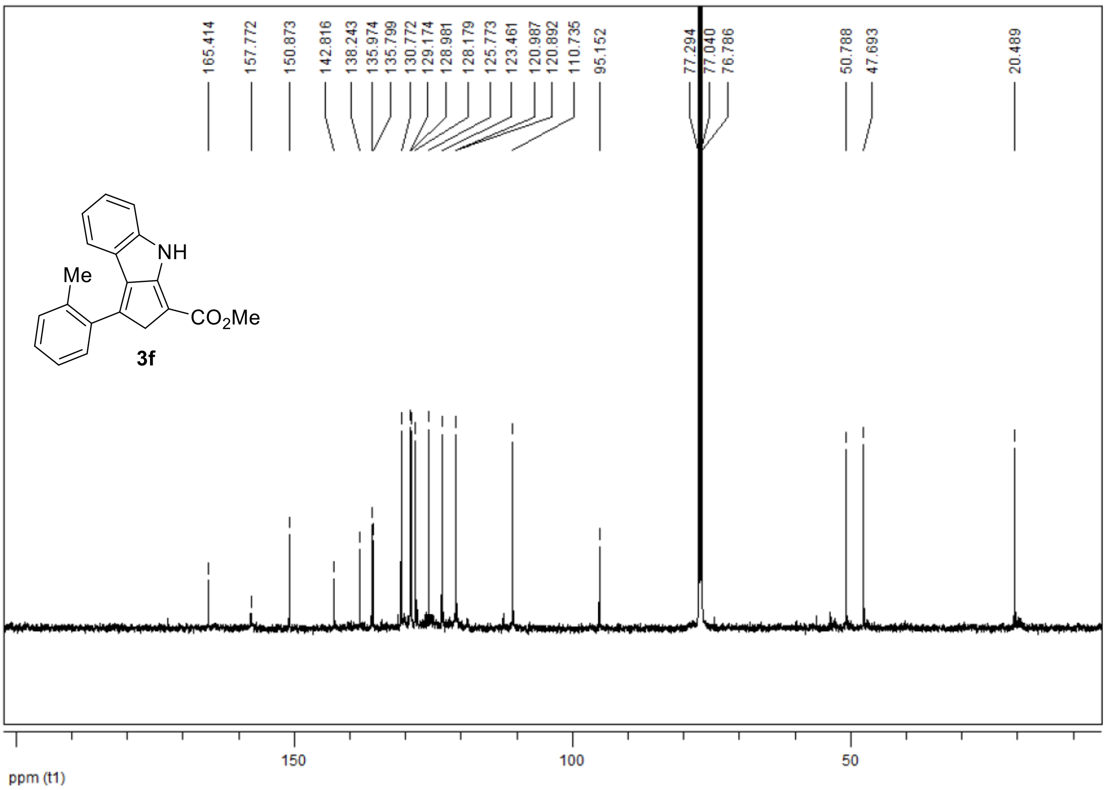
[13]C{H} NMR (126 MHz, DMSO-d$_6$)



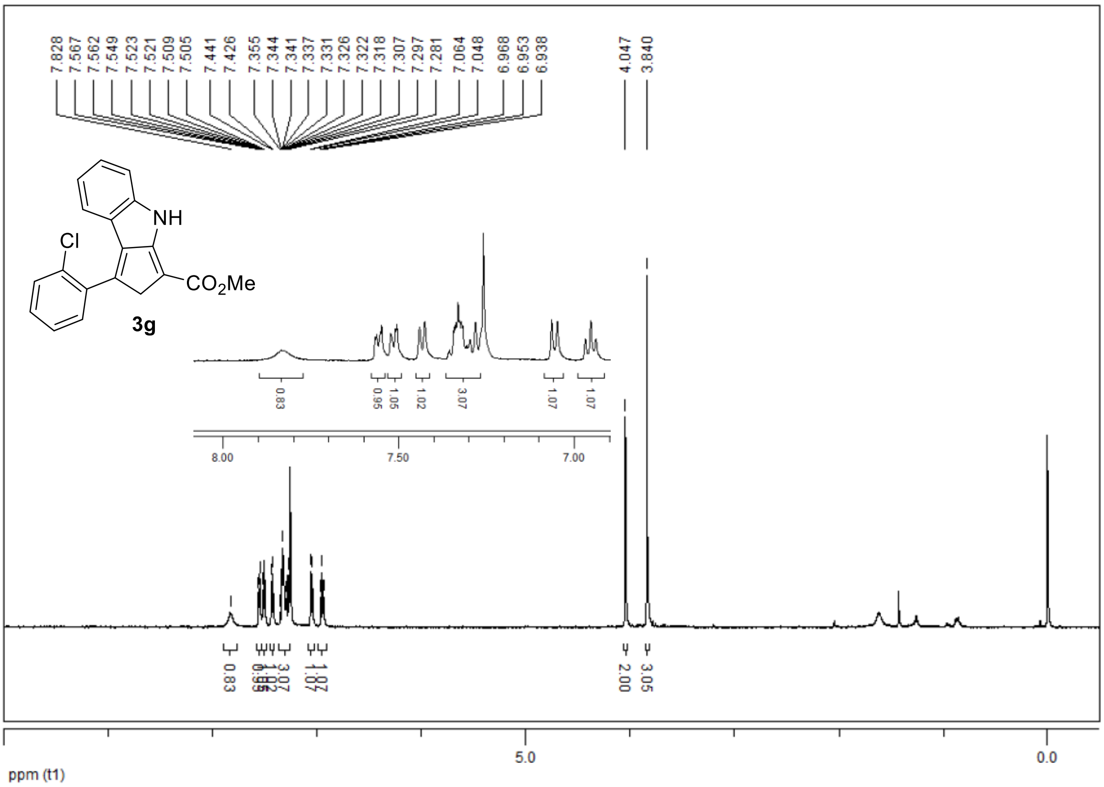
^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$)



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



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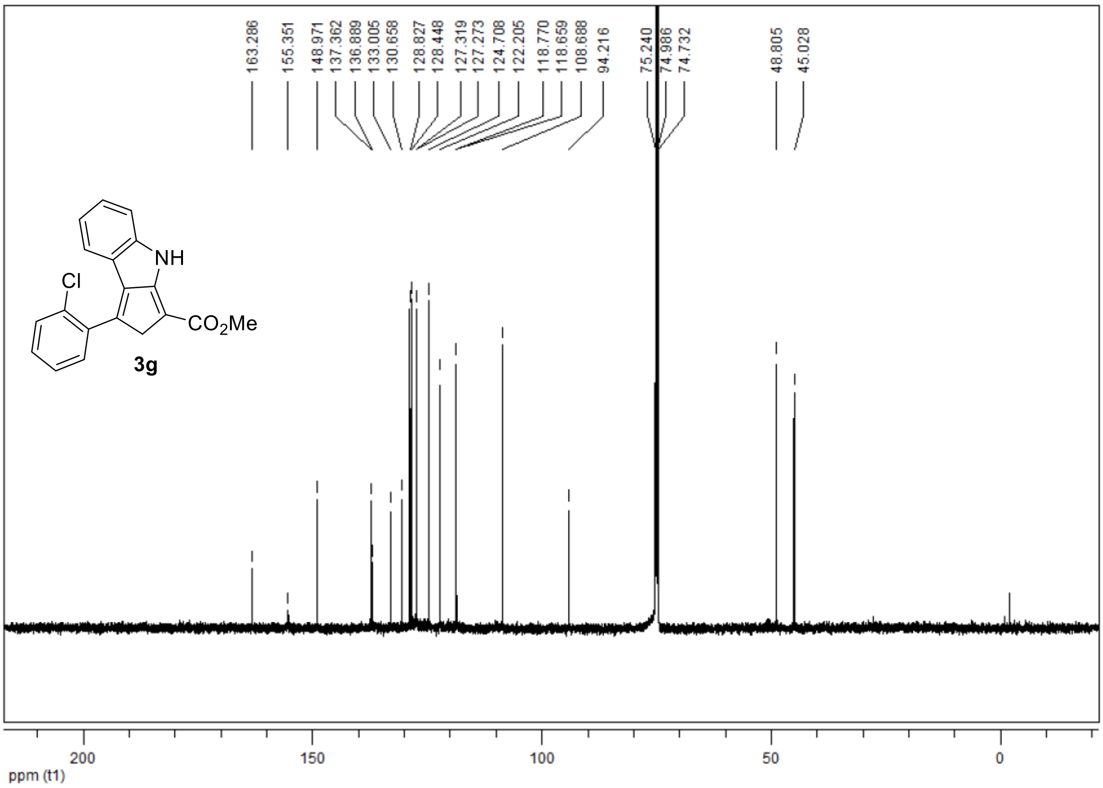
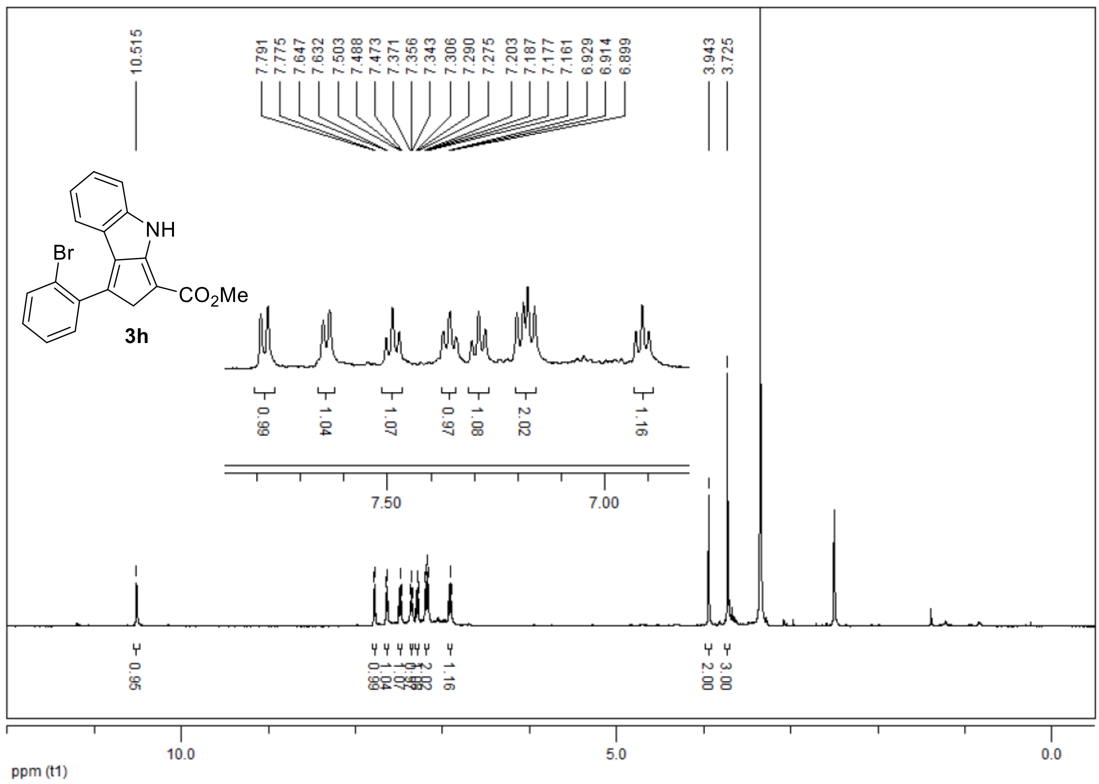


^{1}H NMR (500 MHz, DMSO-d$_6$)



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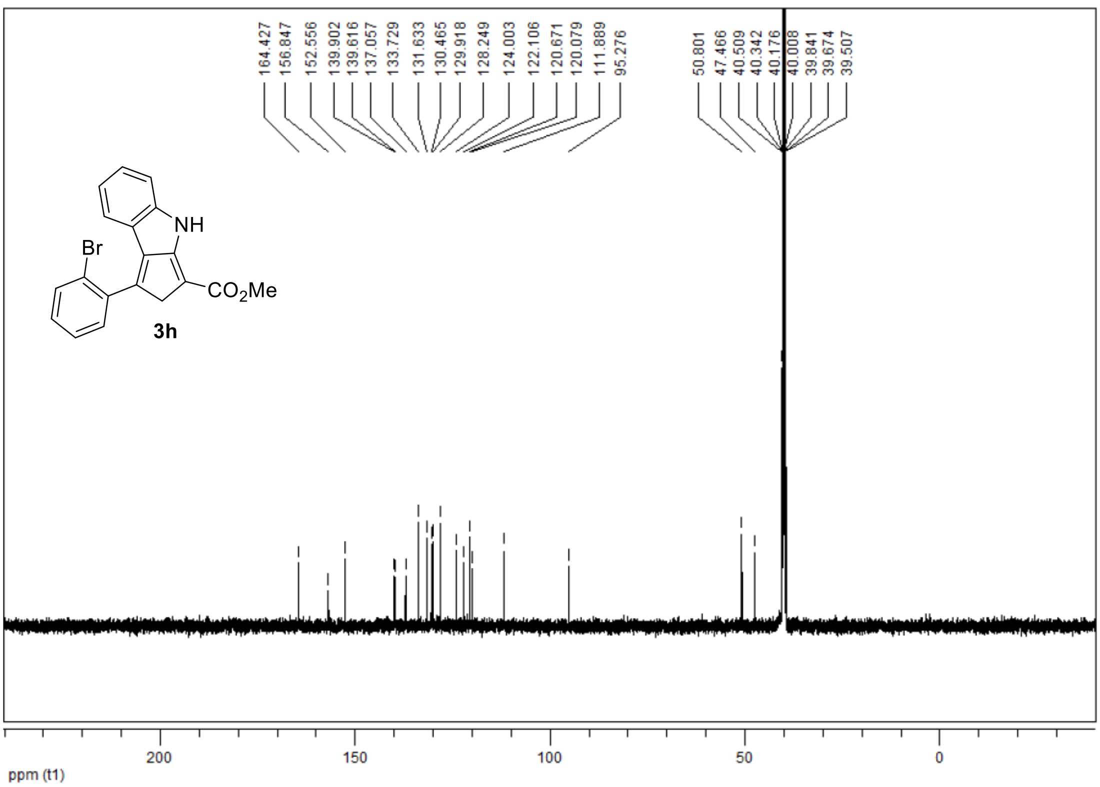

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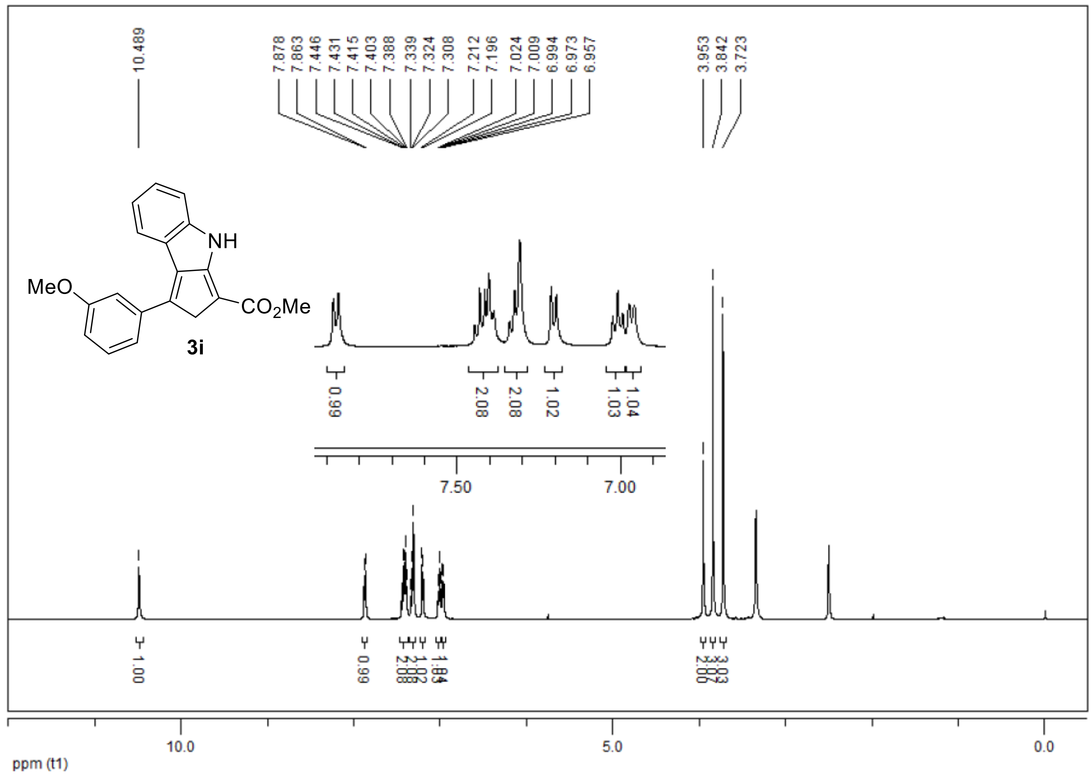

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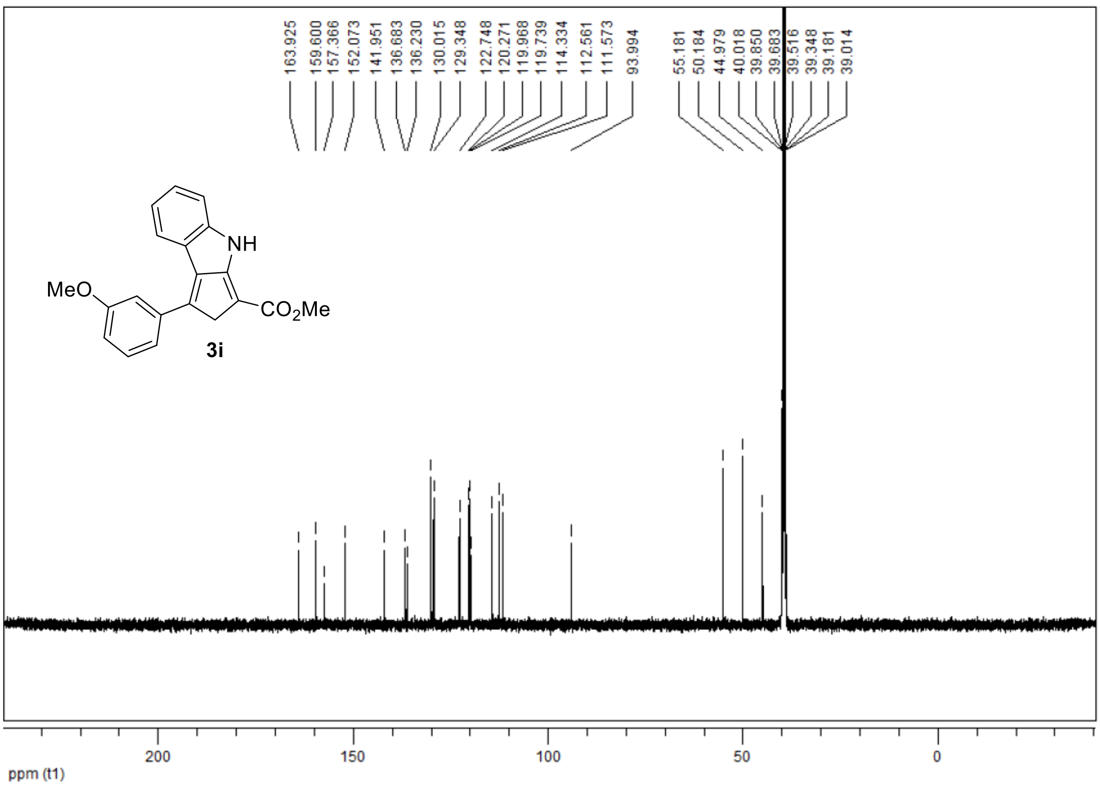

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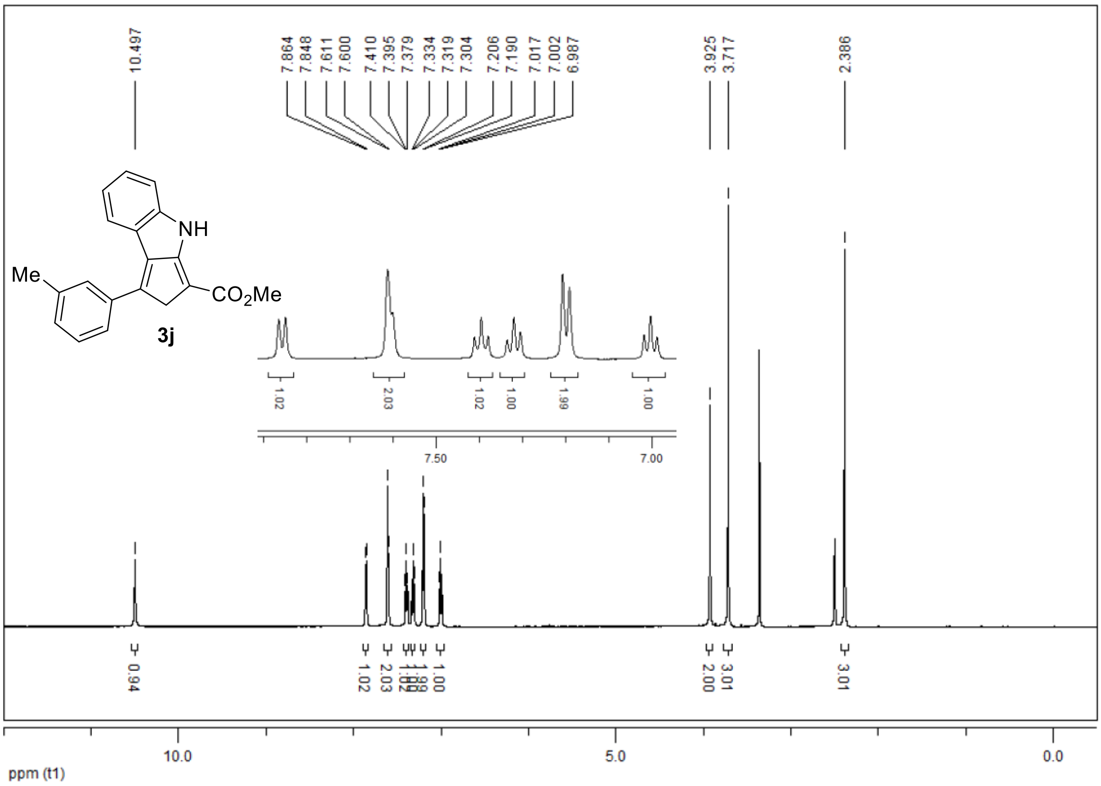
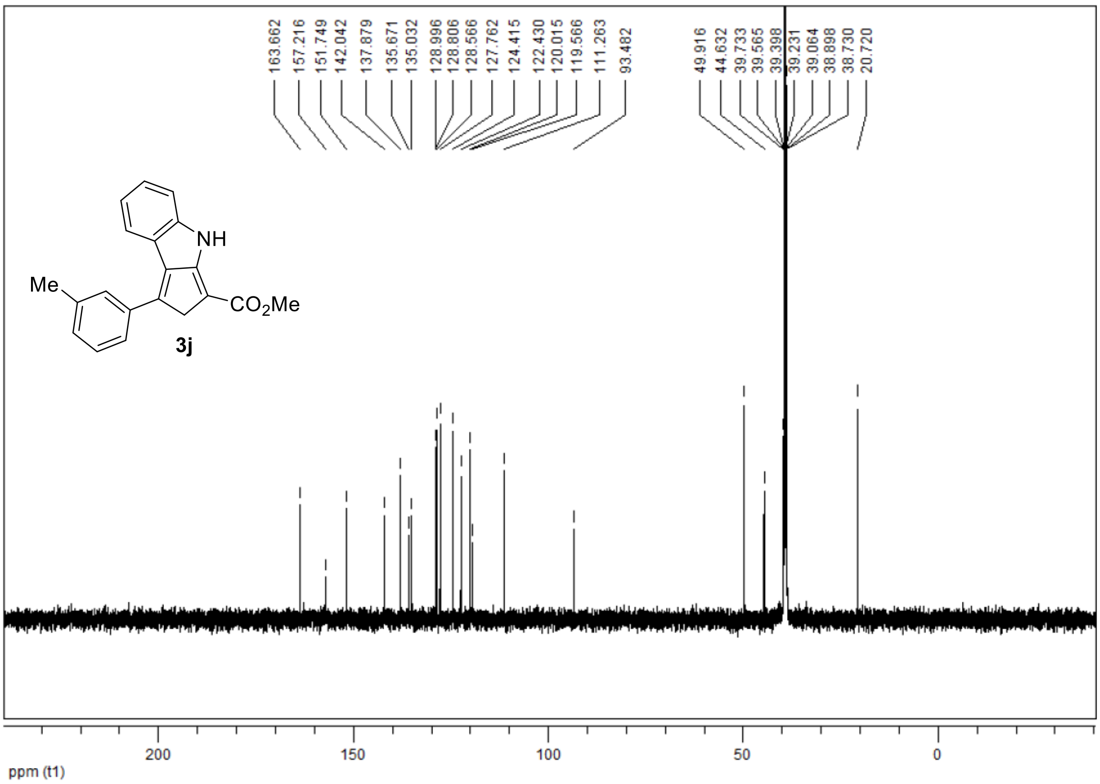


$^{13}C\{H\}$ NMR (126 MHz, DMSO-d_6)



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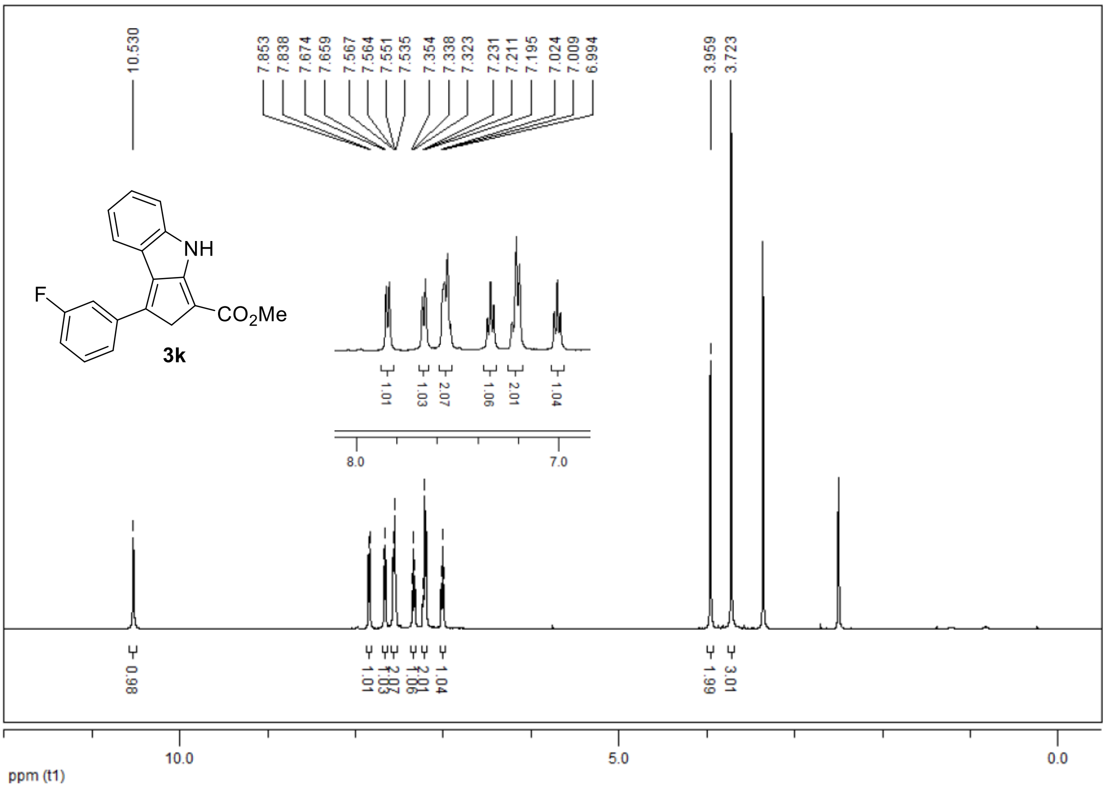

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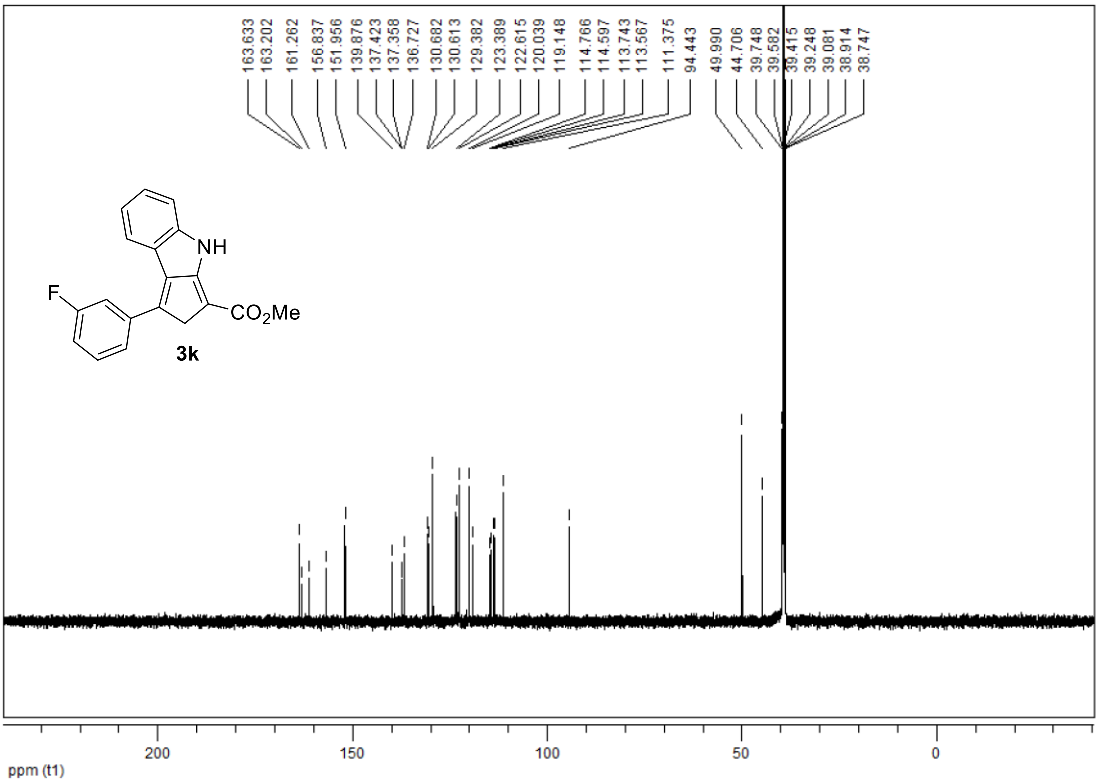
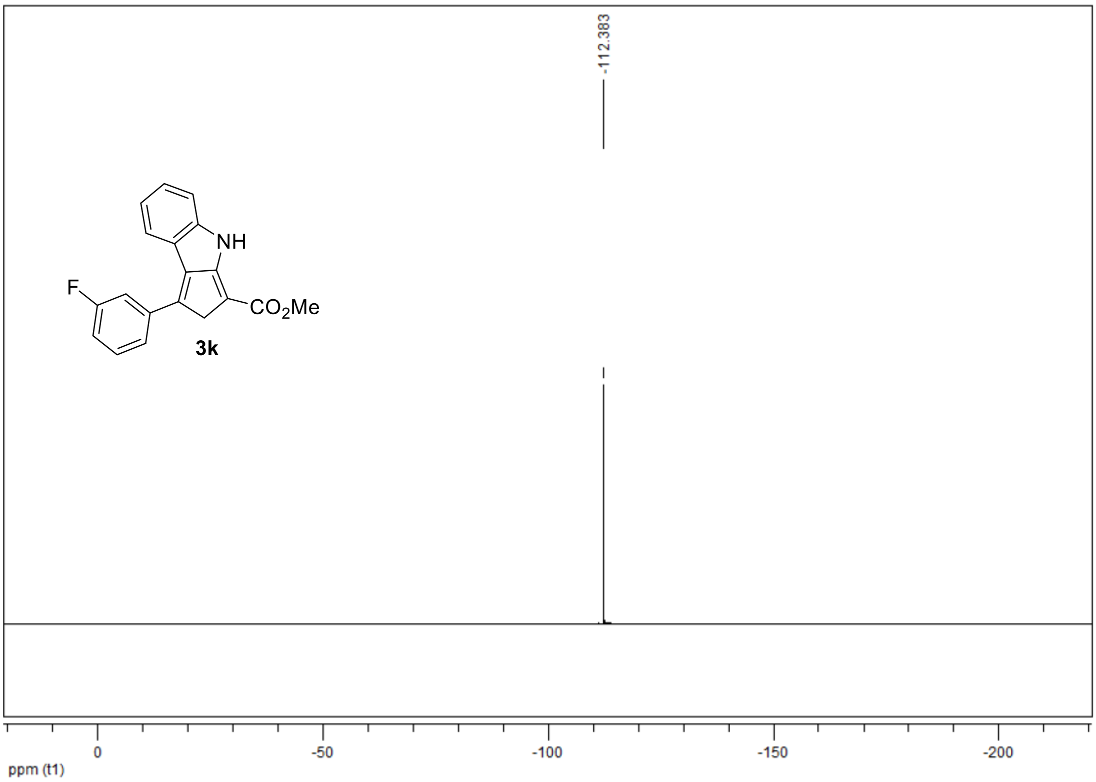
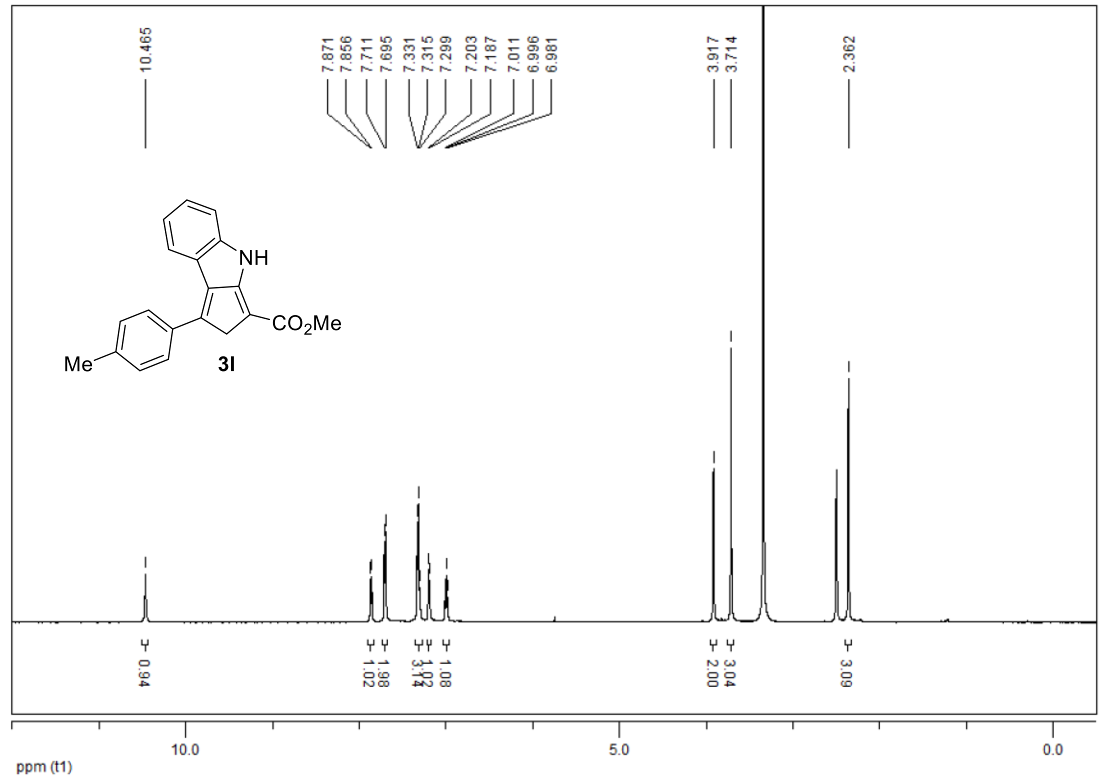


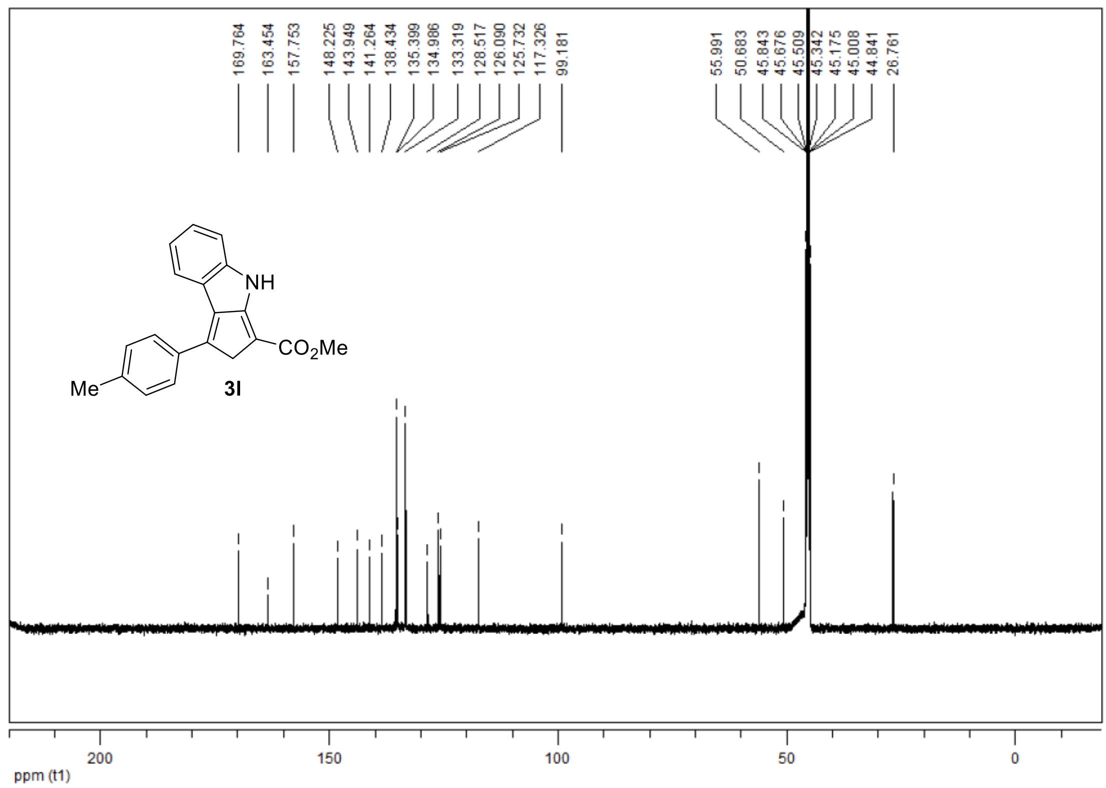
^{19}F NMR (376 MHz, DMSO-d$_6$)



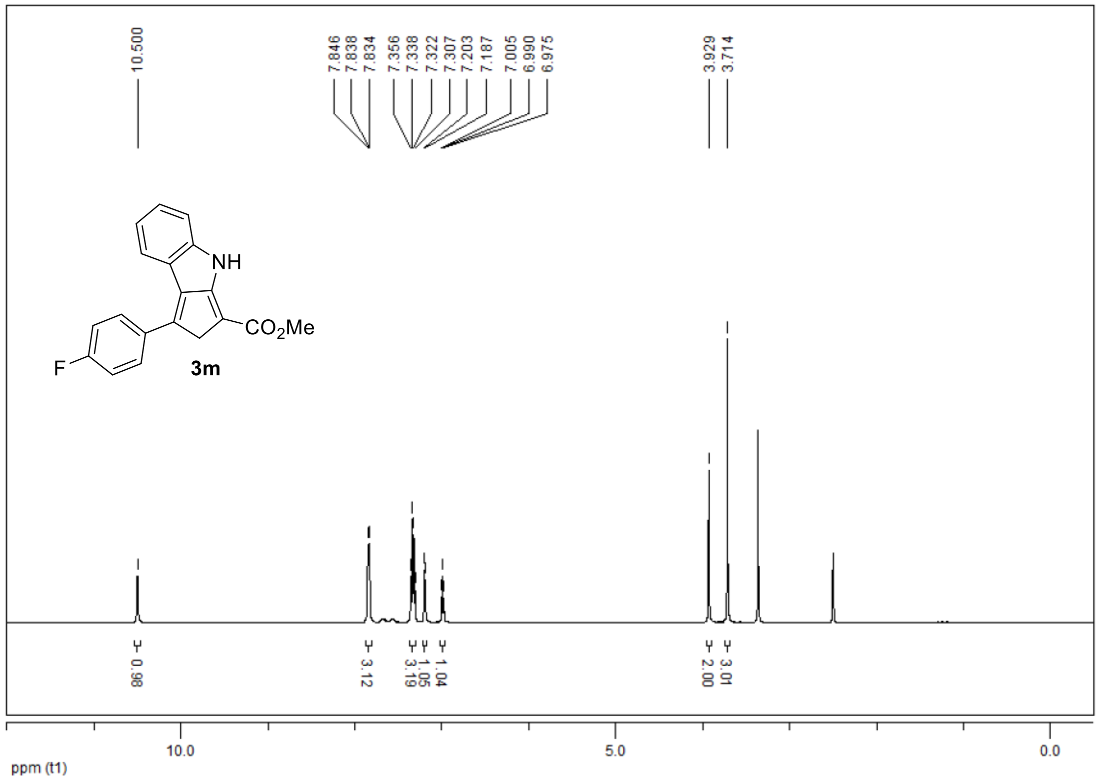
^{1}H NMR (500 MHz, DMSO-d$_6$)



^{13}C{H} NMR (126 MHz, DMSO-d$_6$)



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



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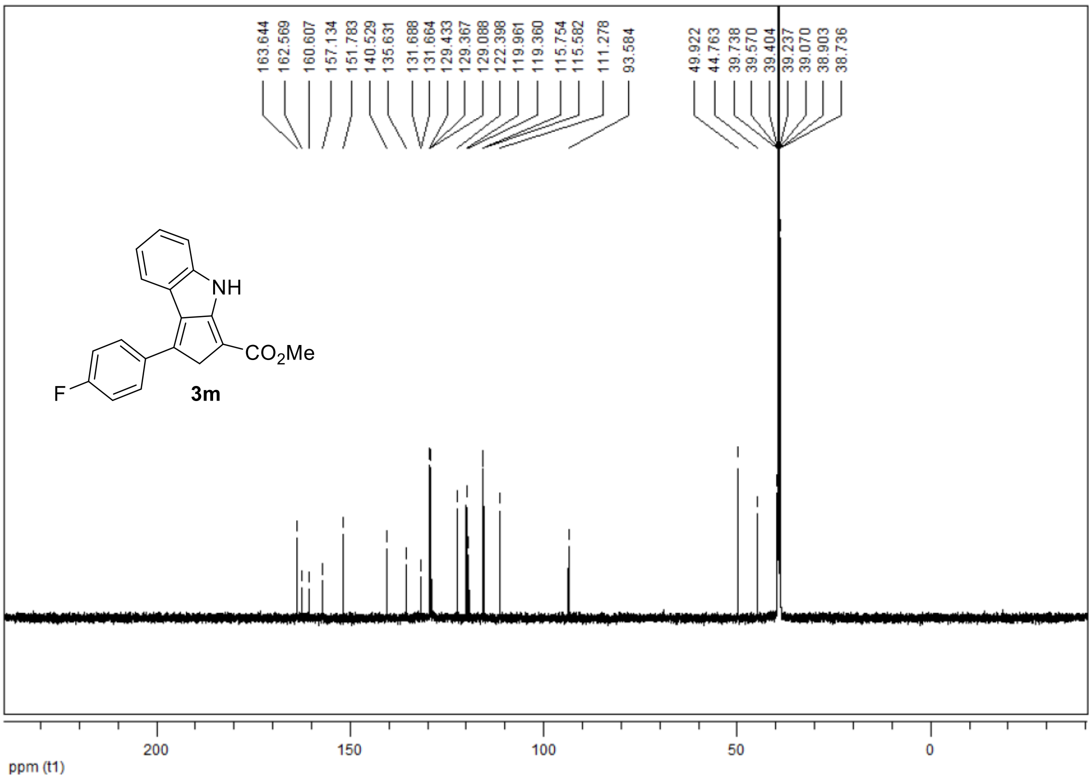

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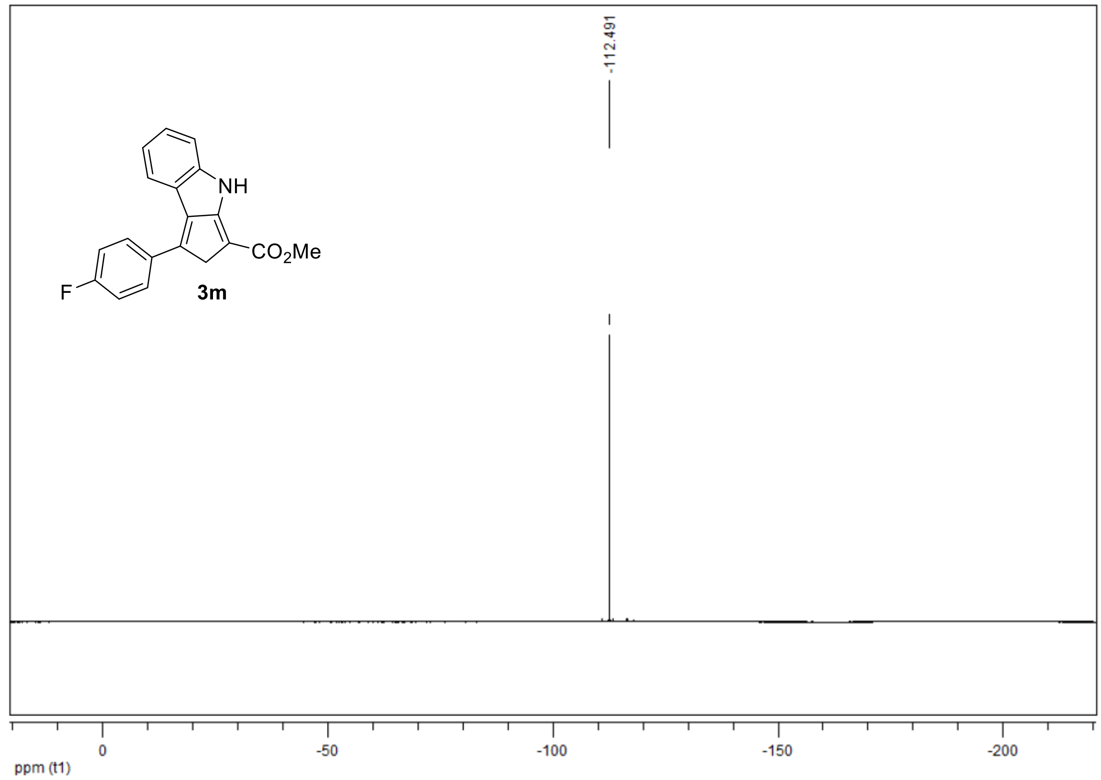

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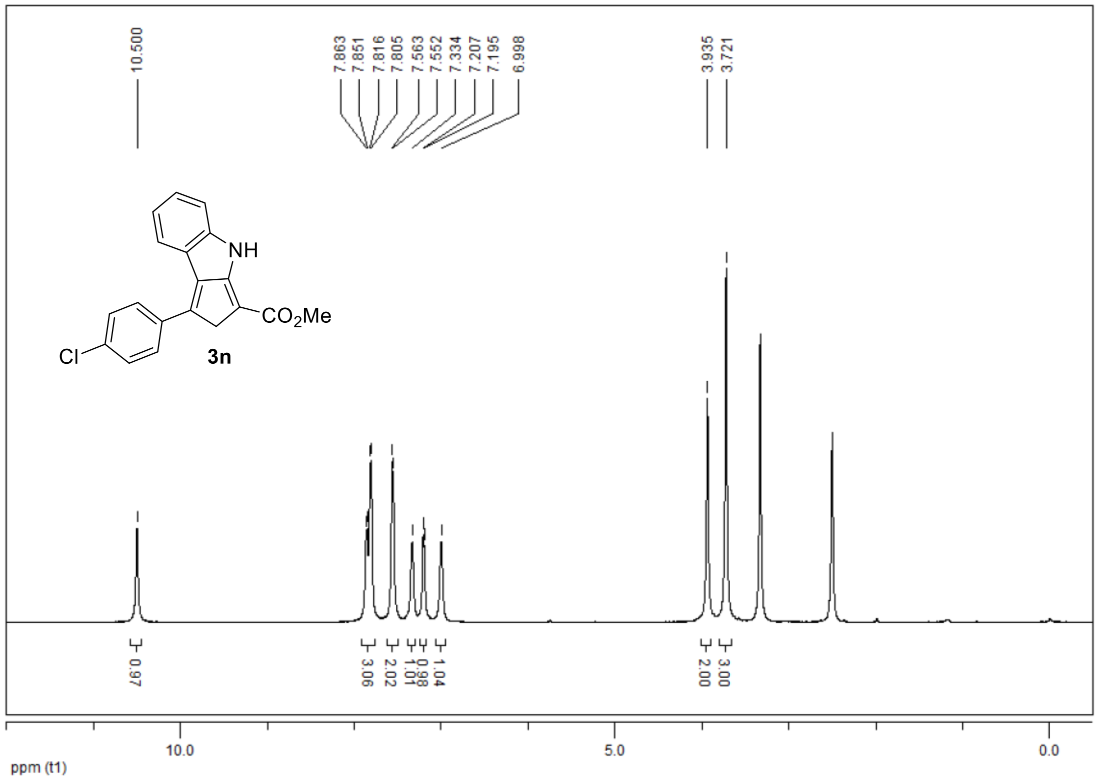

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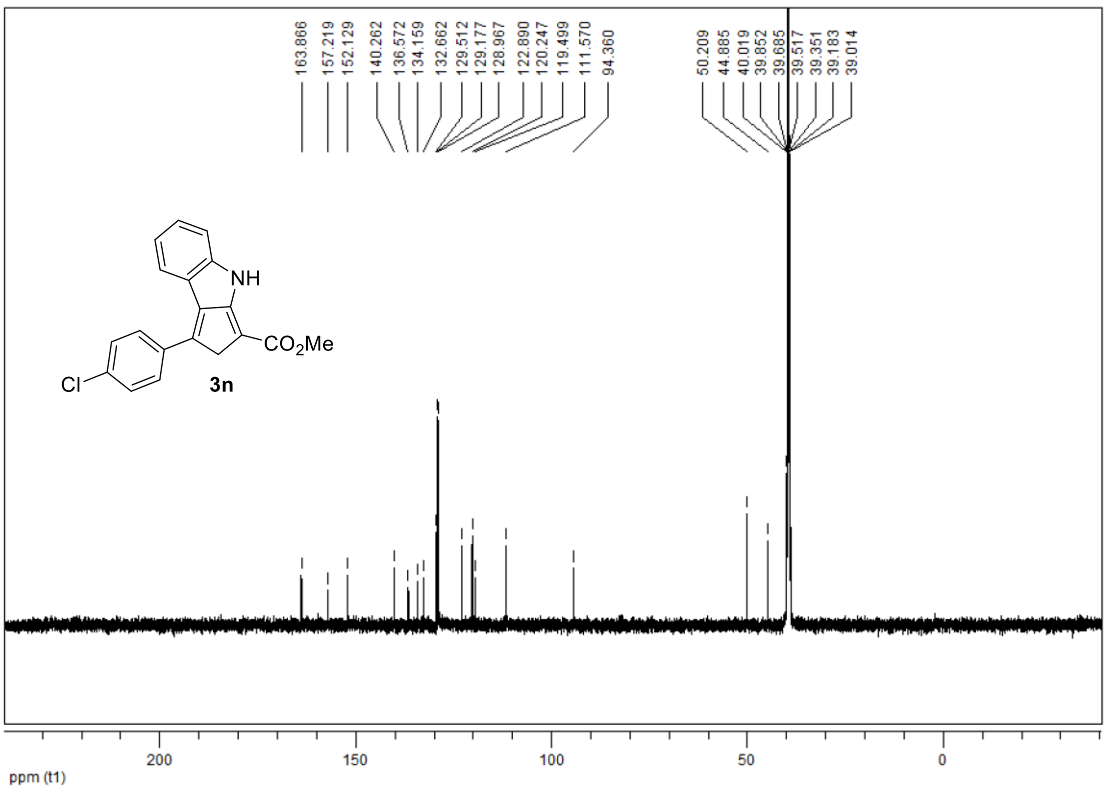
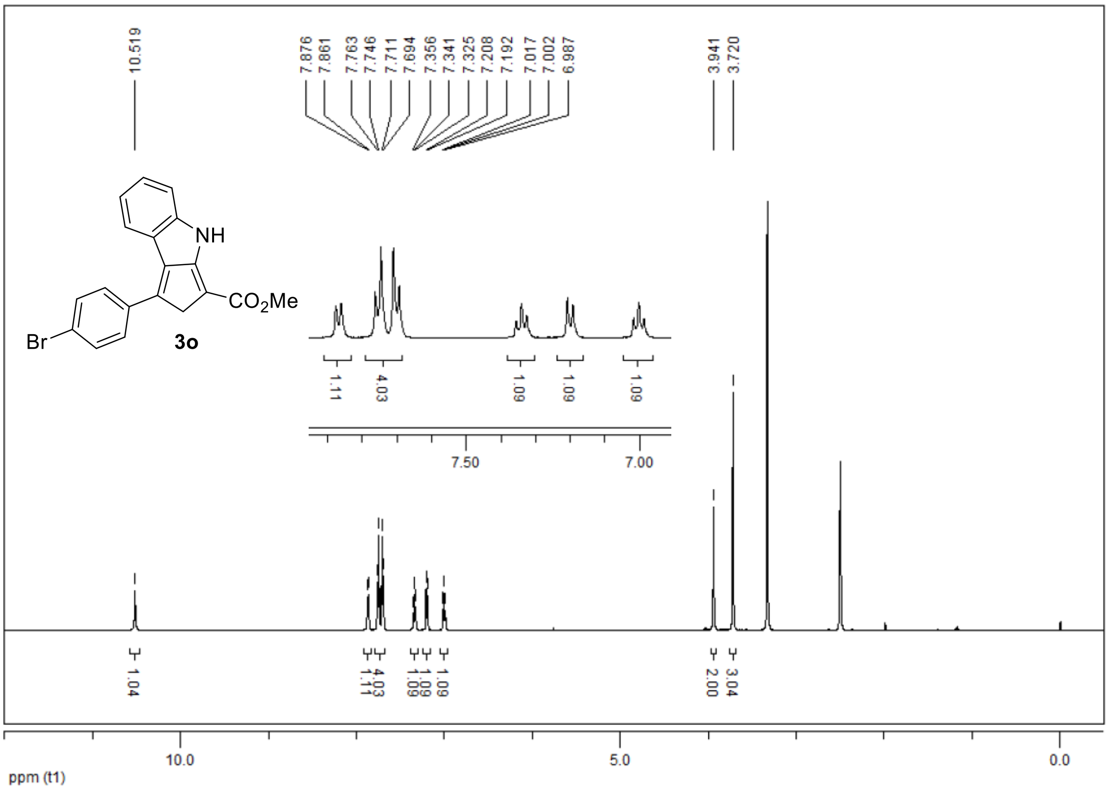


^{1}H NMR (500 MHz, DMSO-d$_6$)



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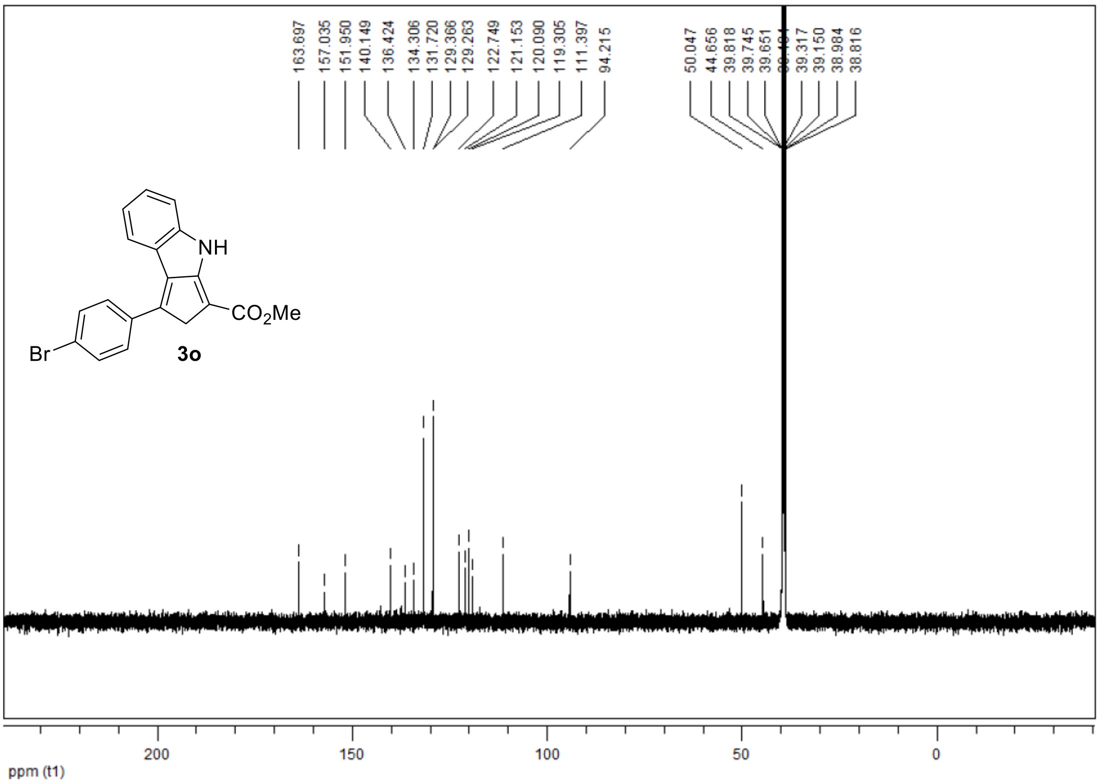

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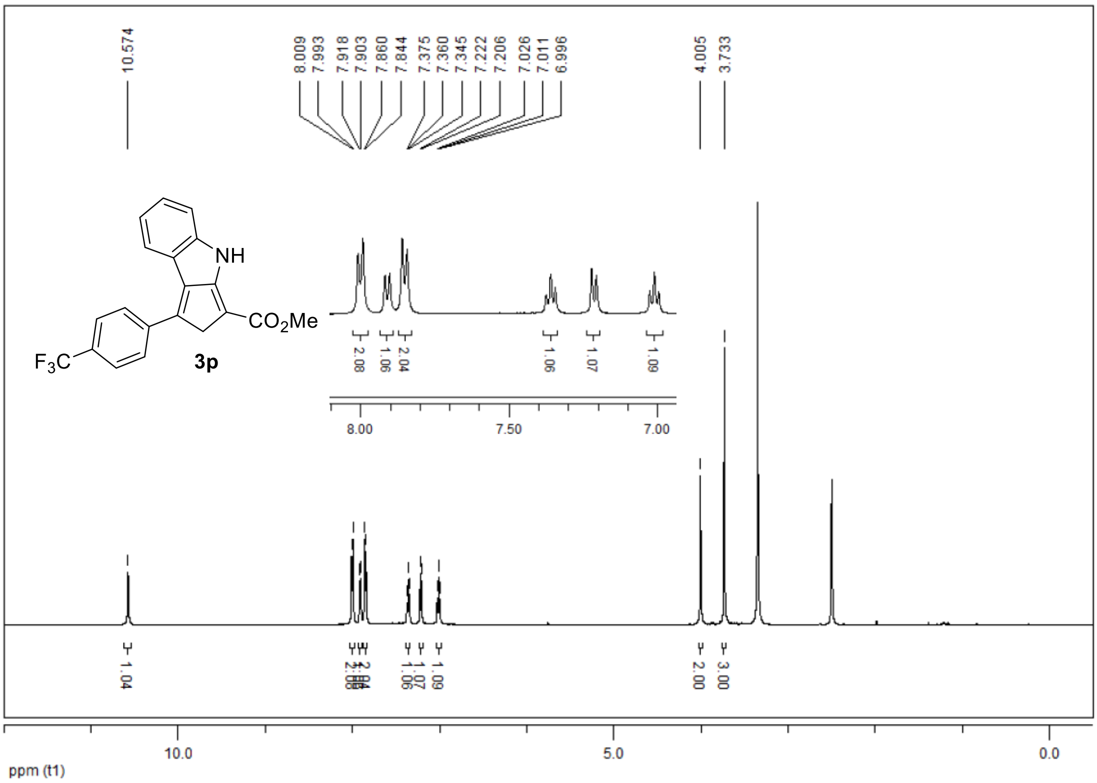

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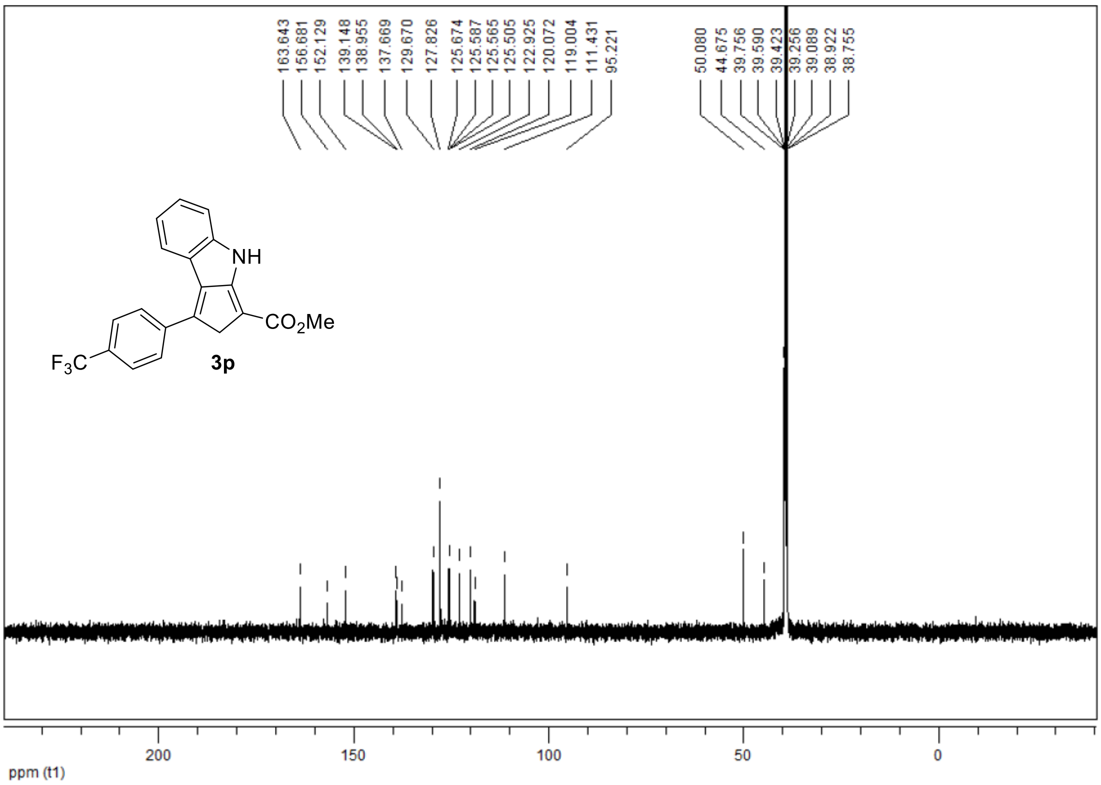

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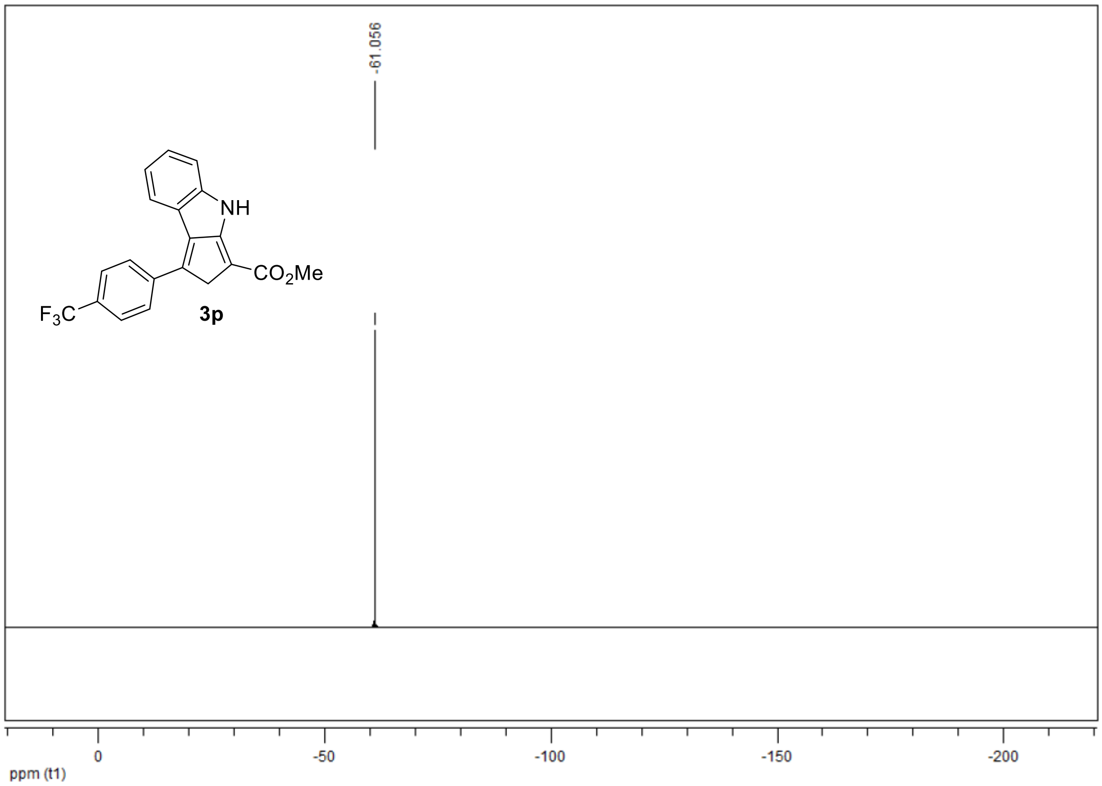

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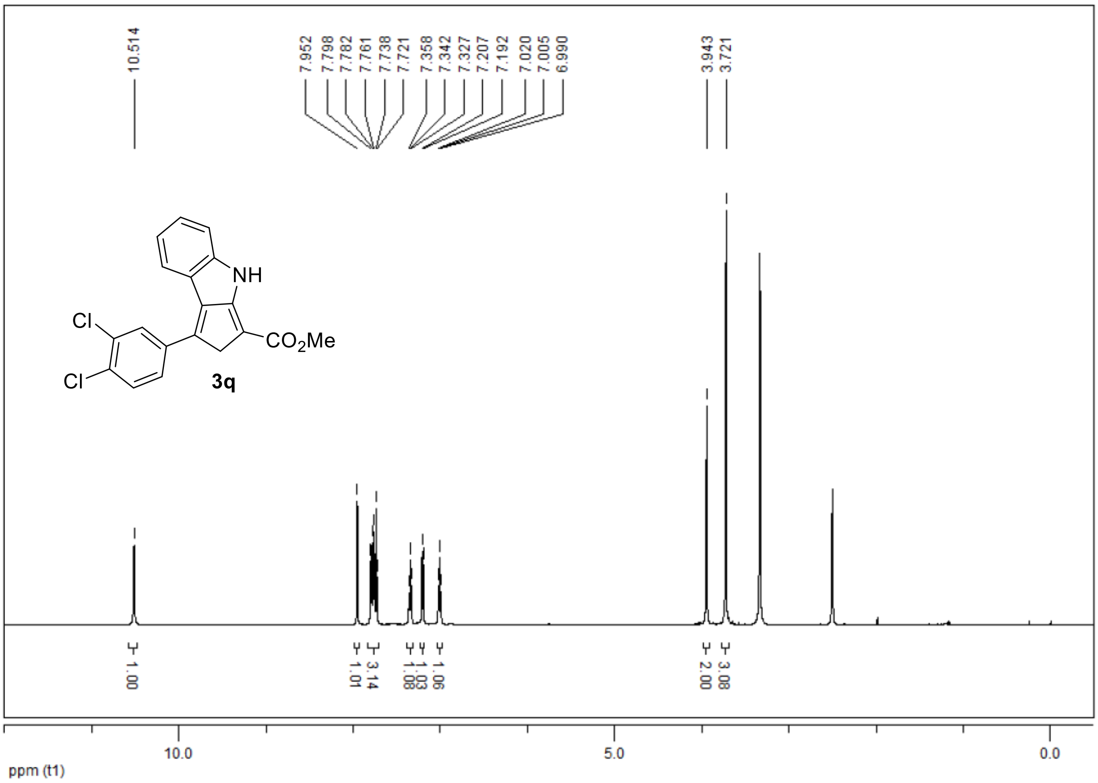

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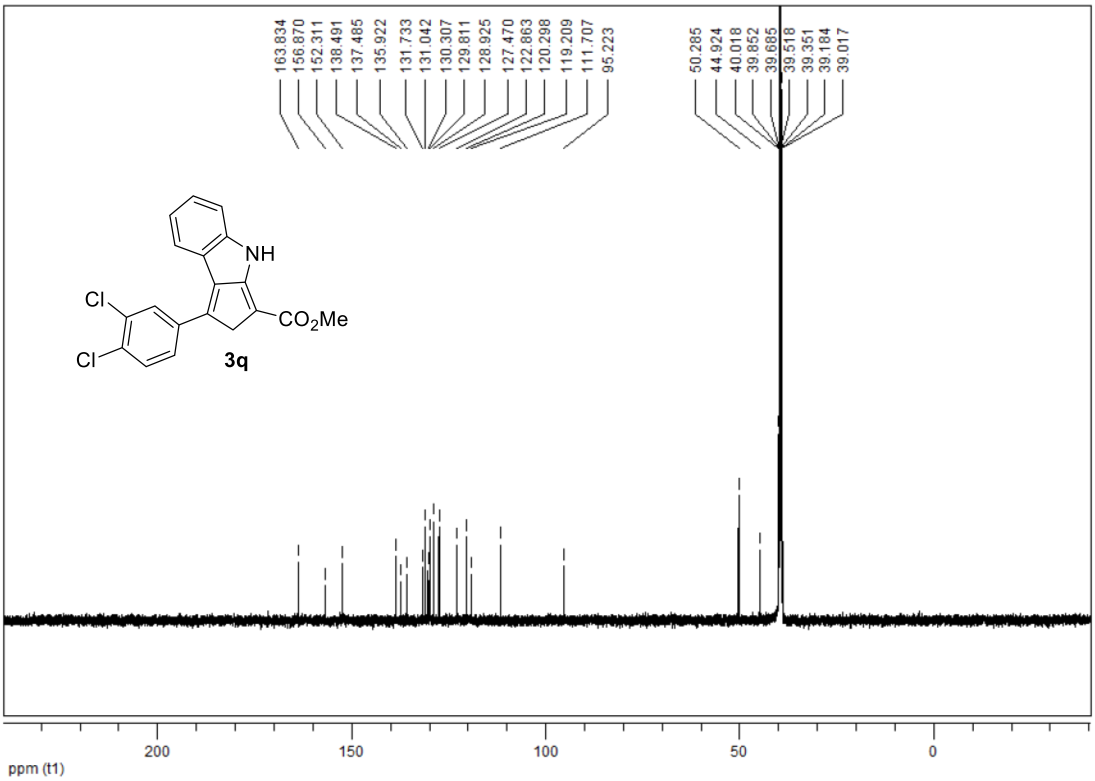

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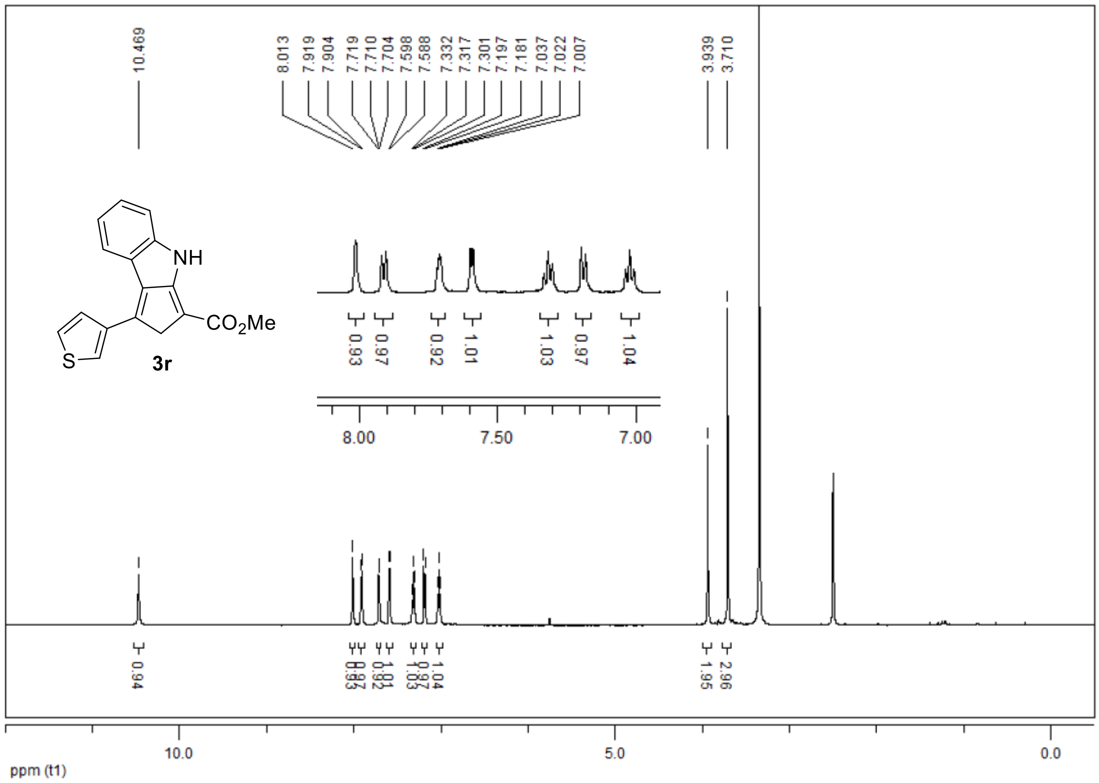

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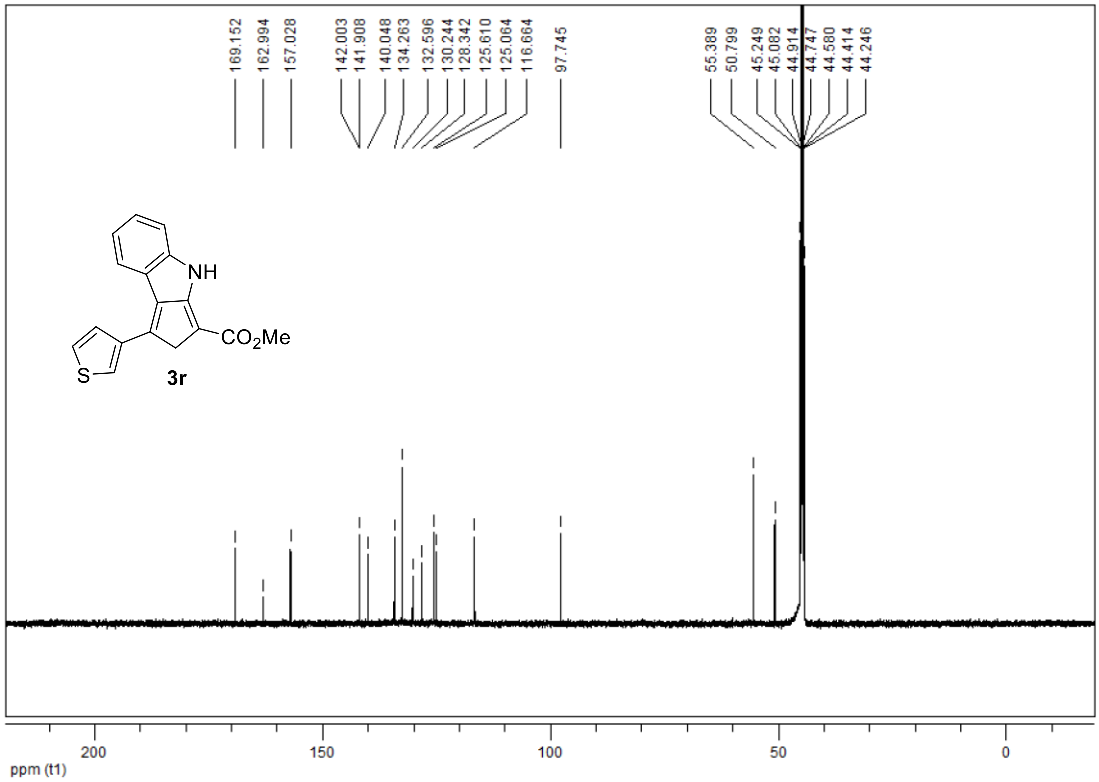
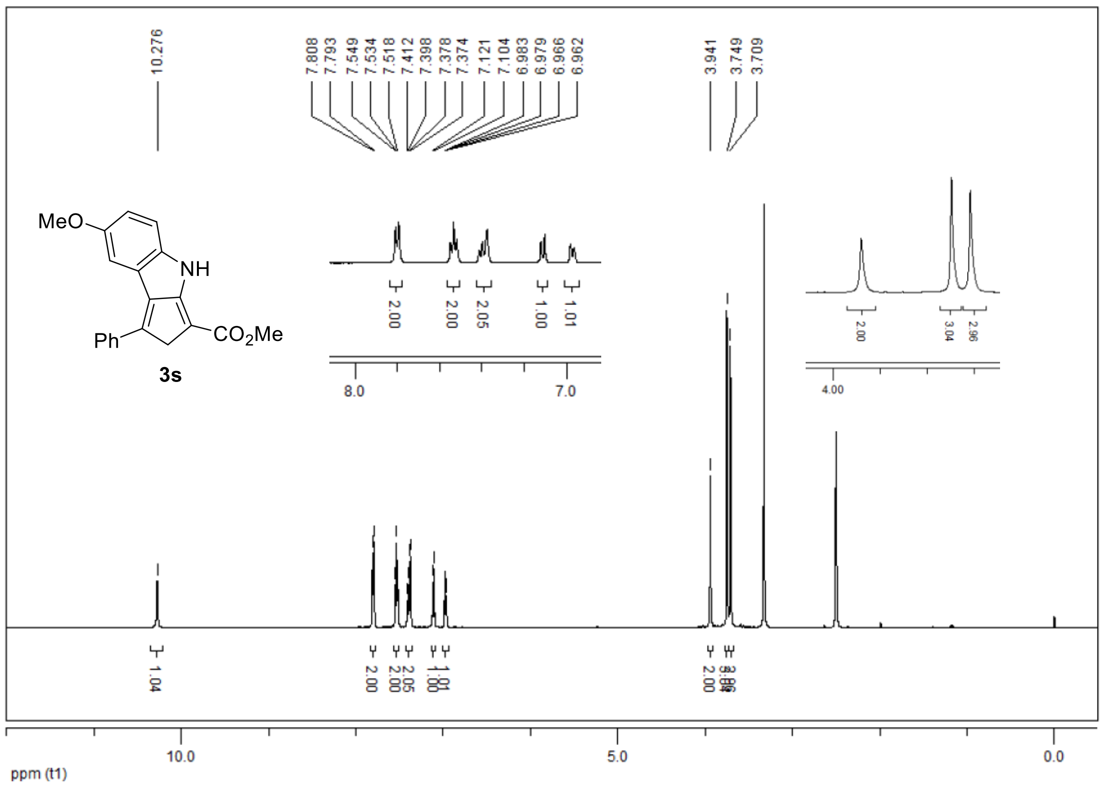


^{1}H NMR (500 MHz, DMSO-d$_6$)



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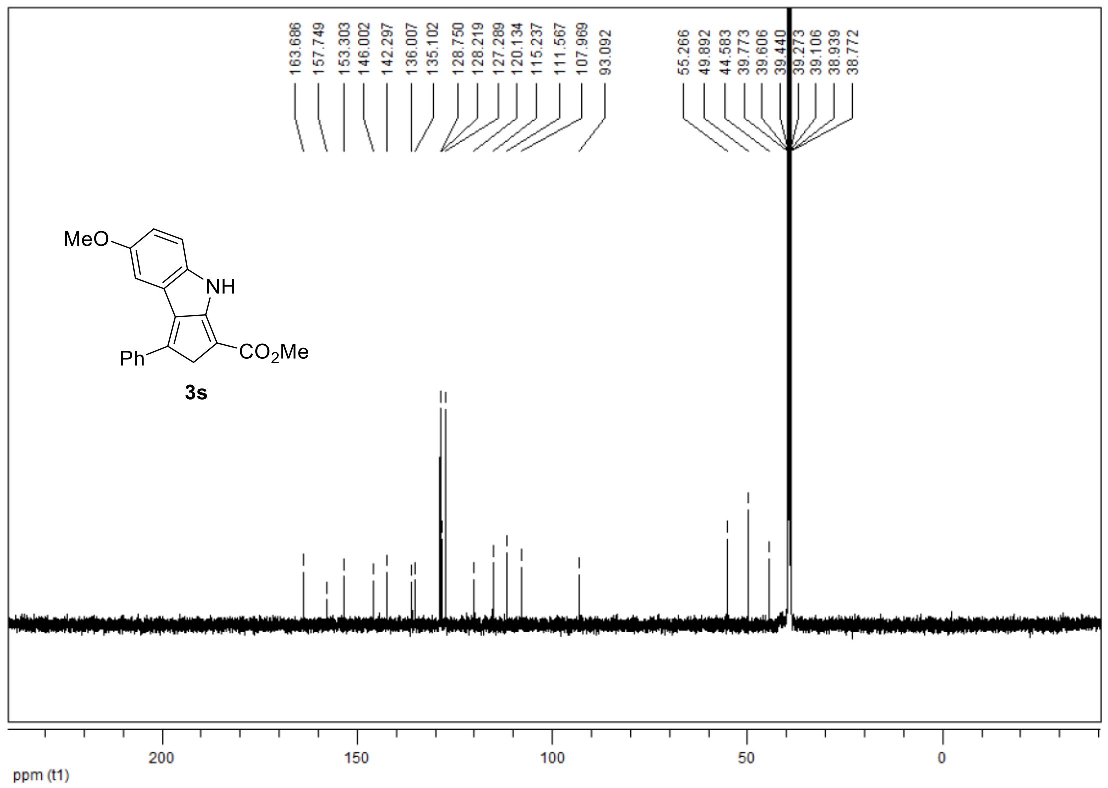

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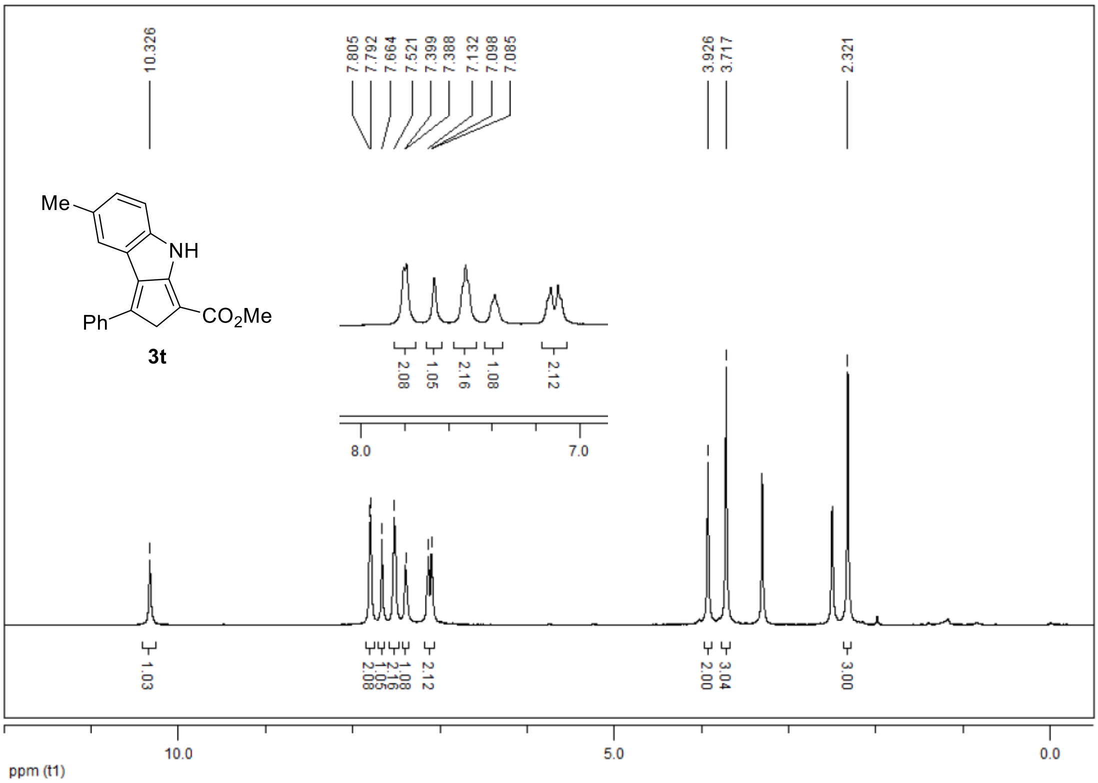
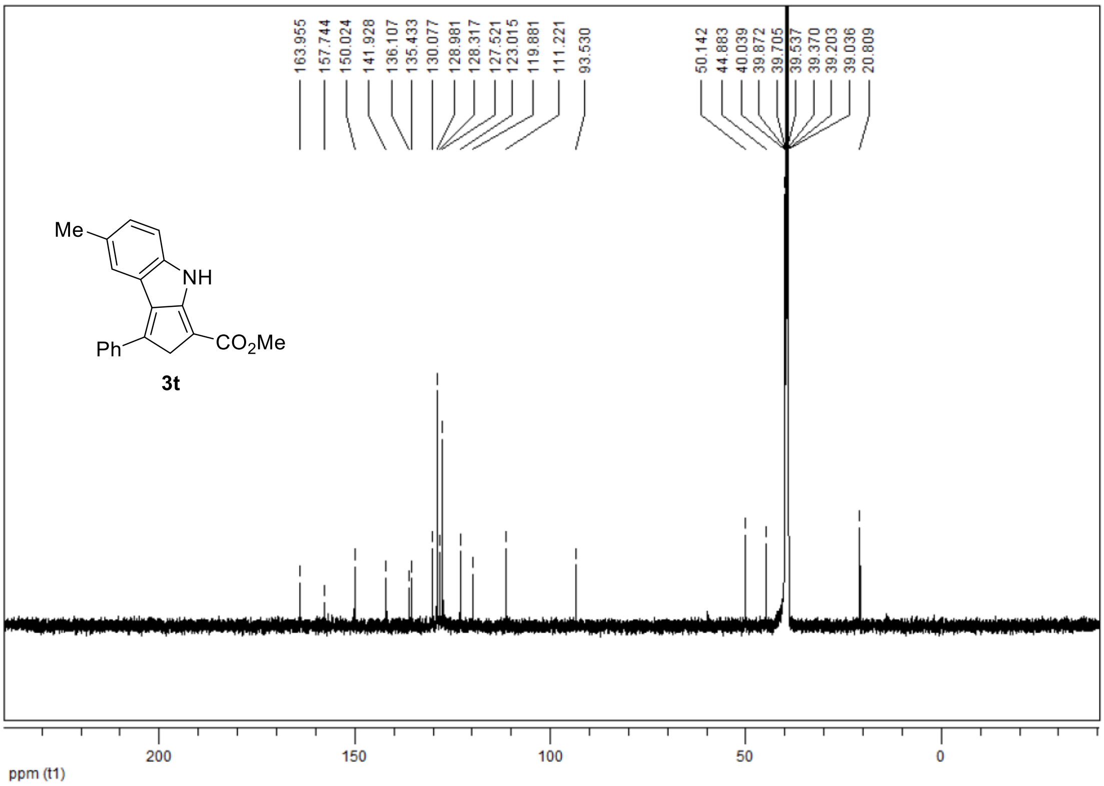
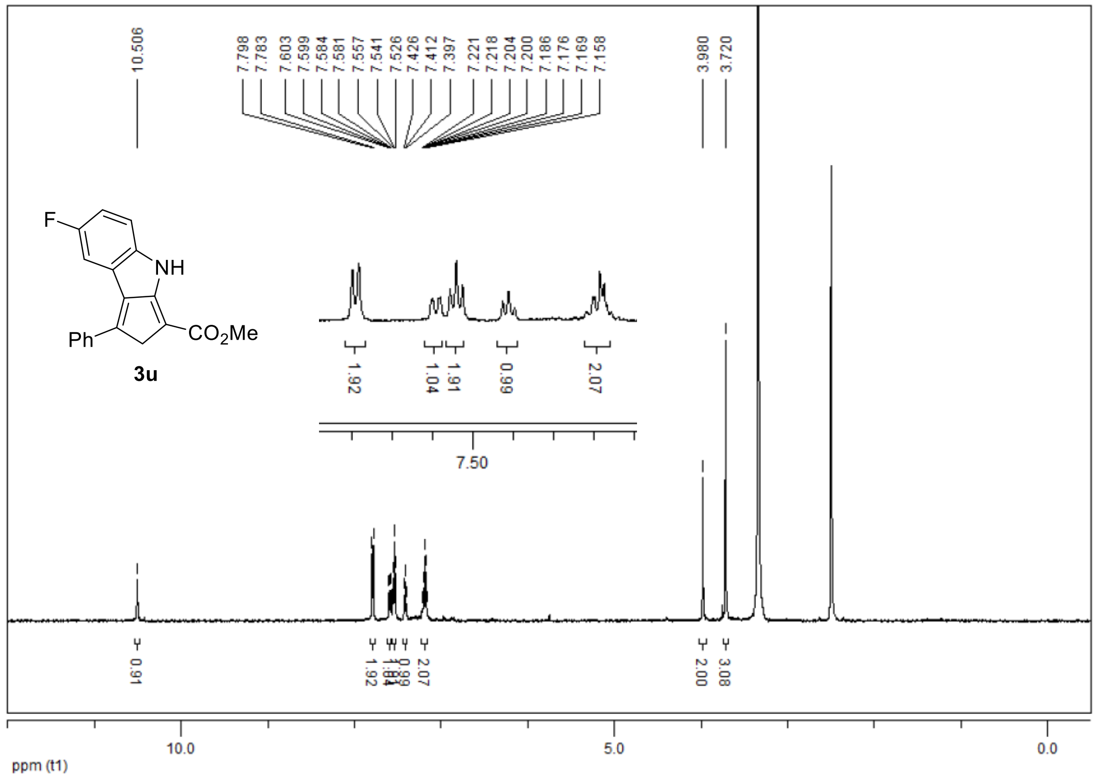


$^{13}C\{H\}$ NMR (126 MHz, DMSO-d_6)



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



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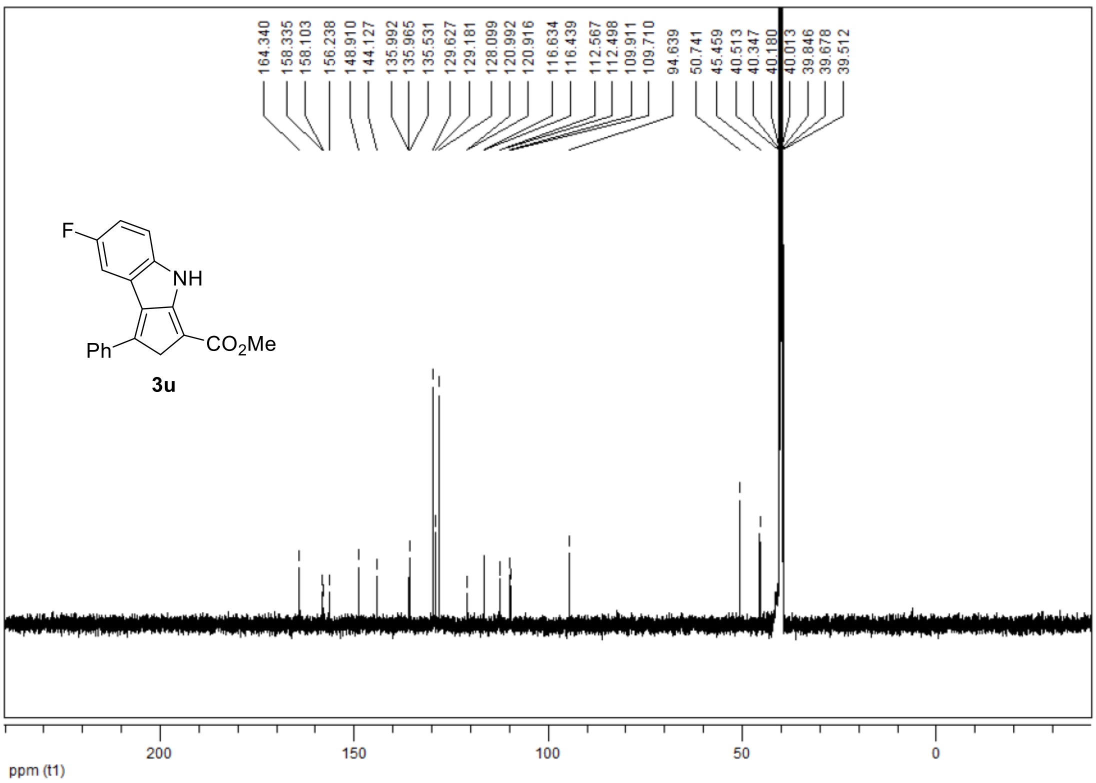

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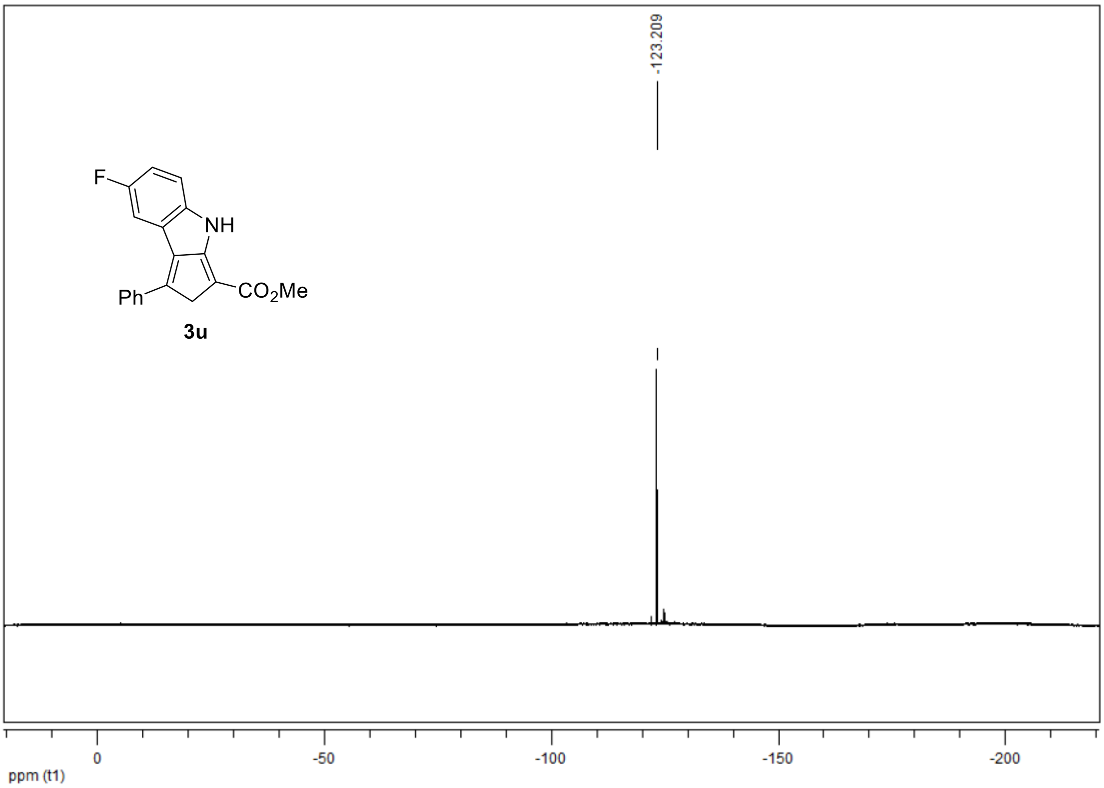
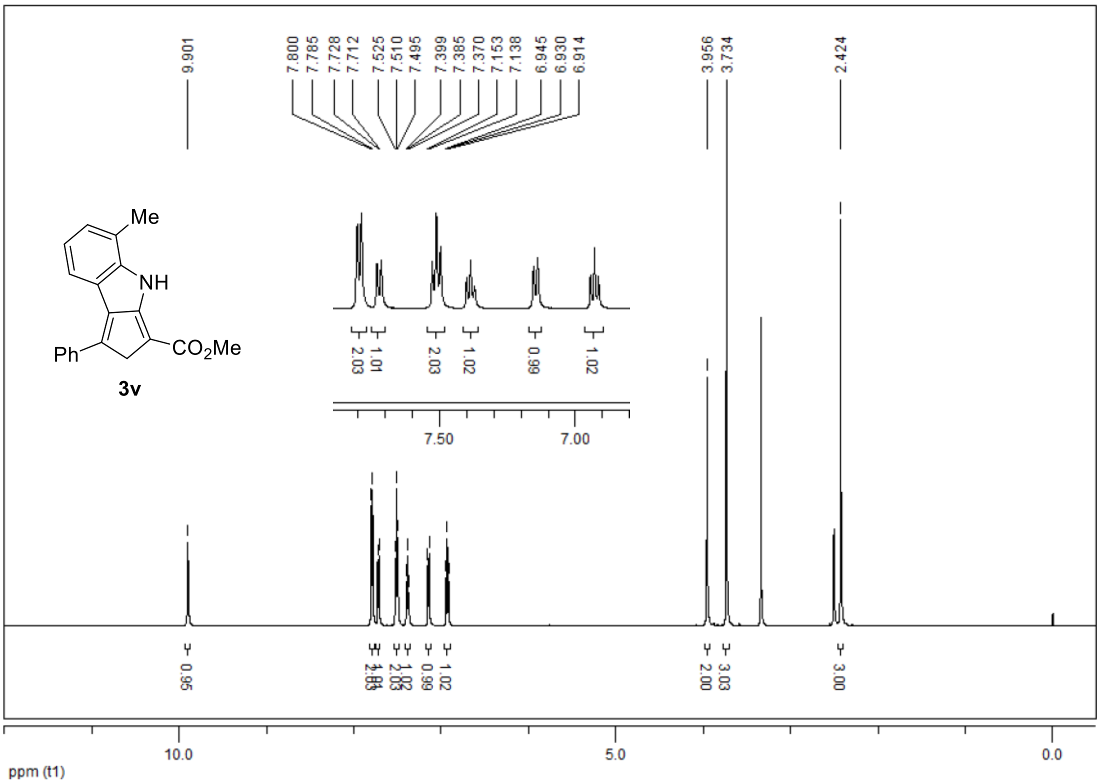
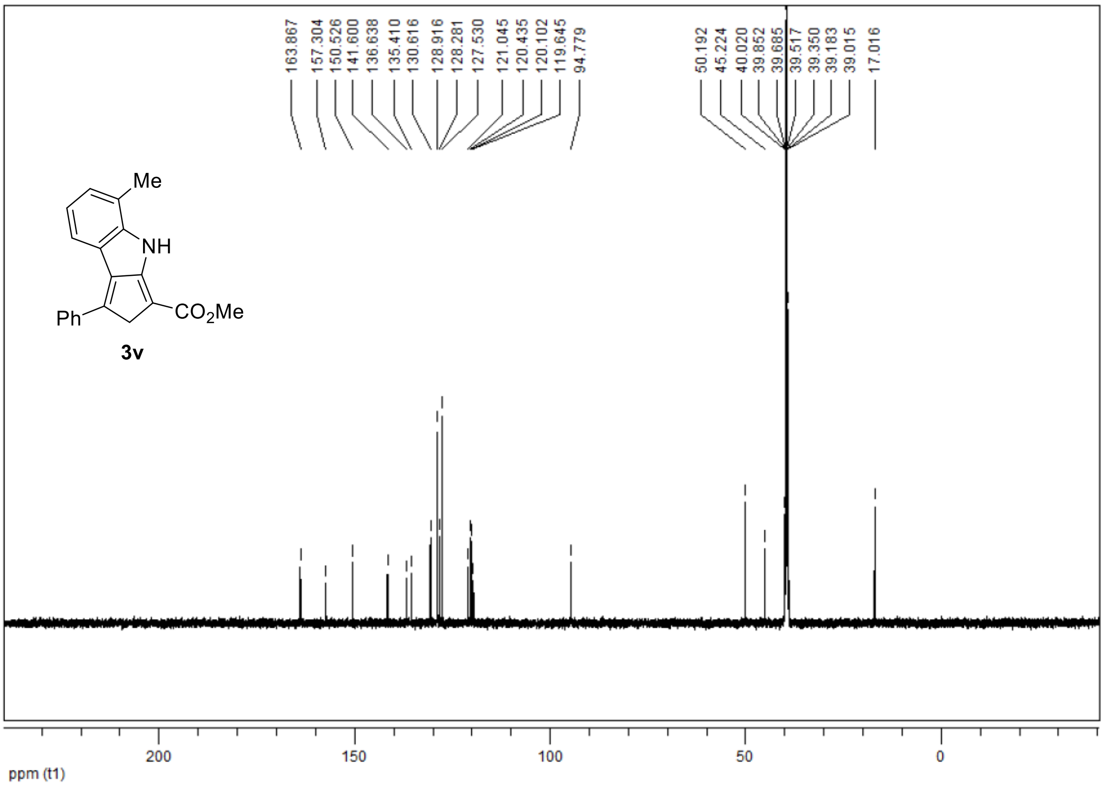


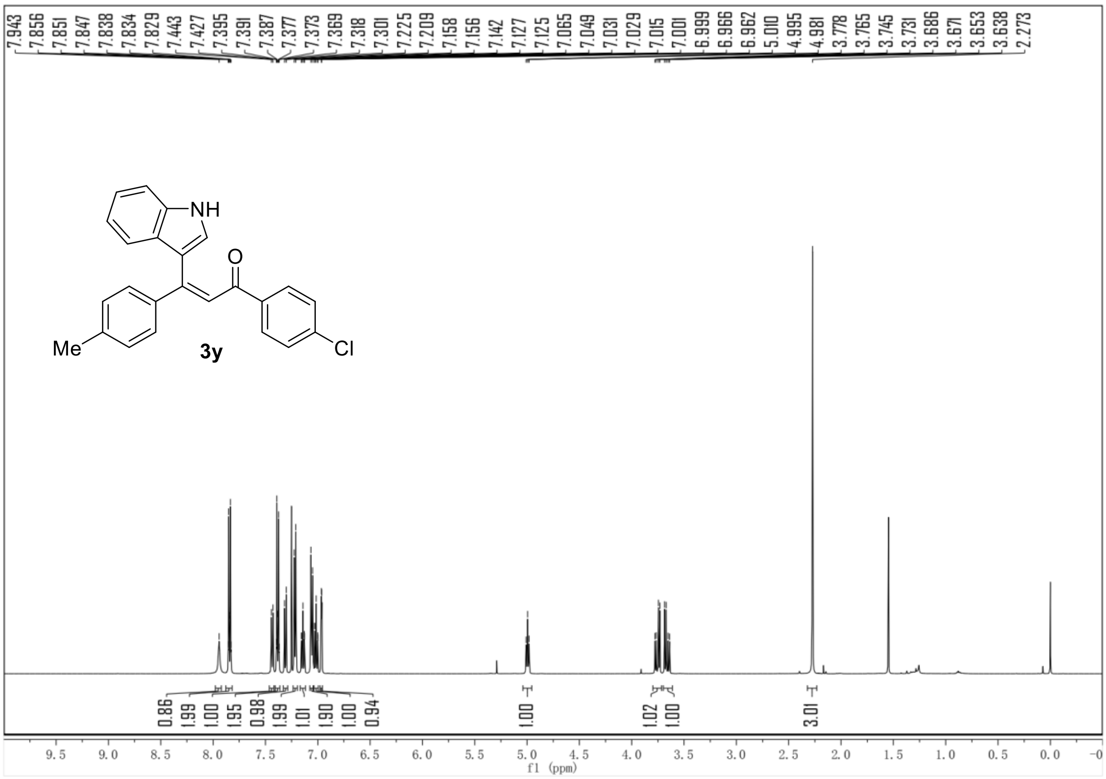
[1]H NMR (500 MHz, DMSO-d$_6$)



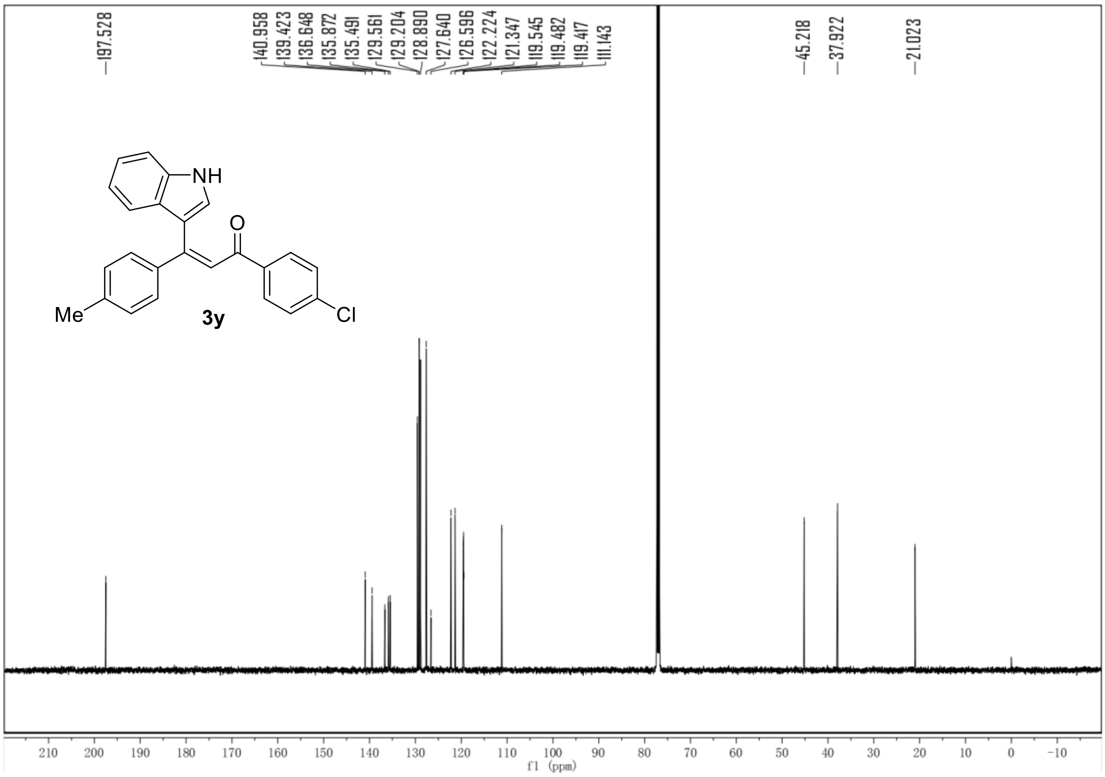
[13]C{H} NMR (126 MHz, DMSO-d$_6$)



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



$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$)



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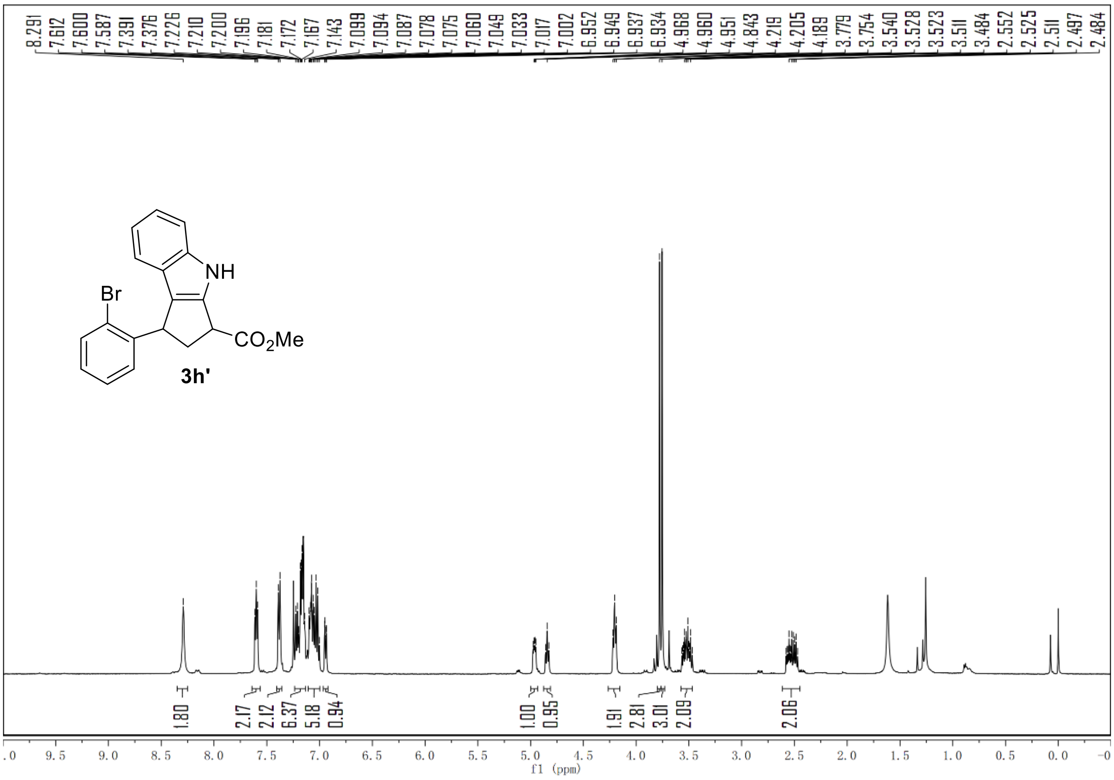

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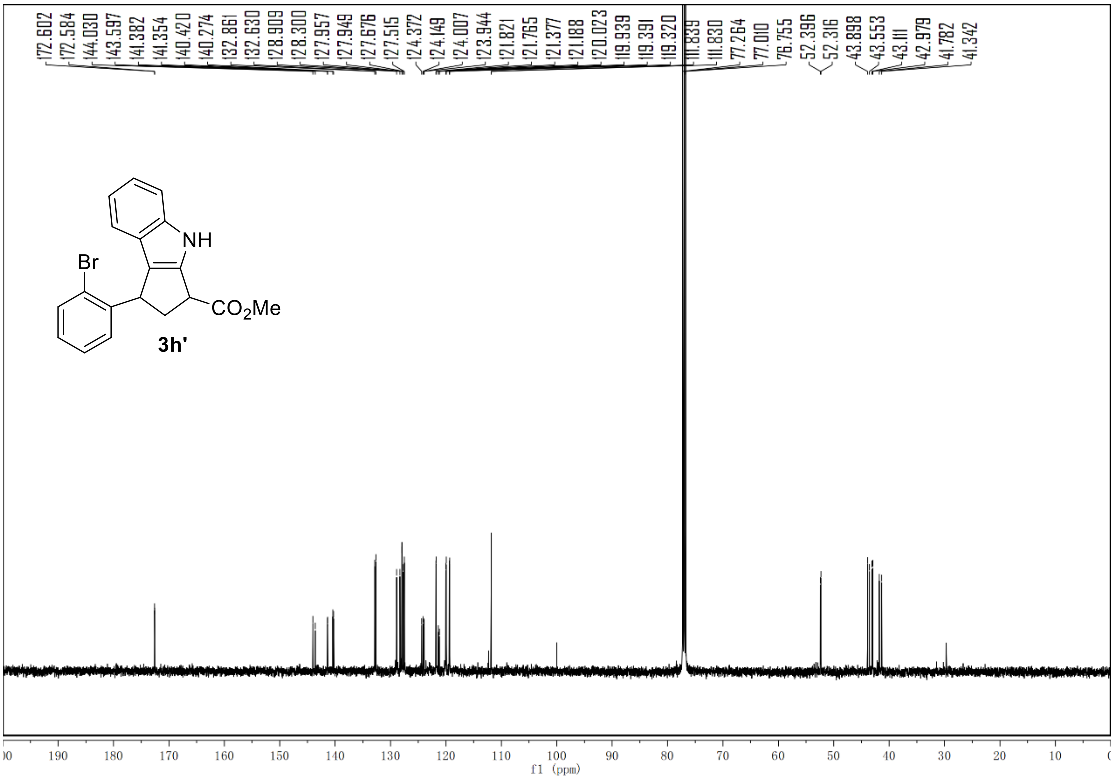

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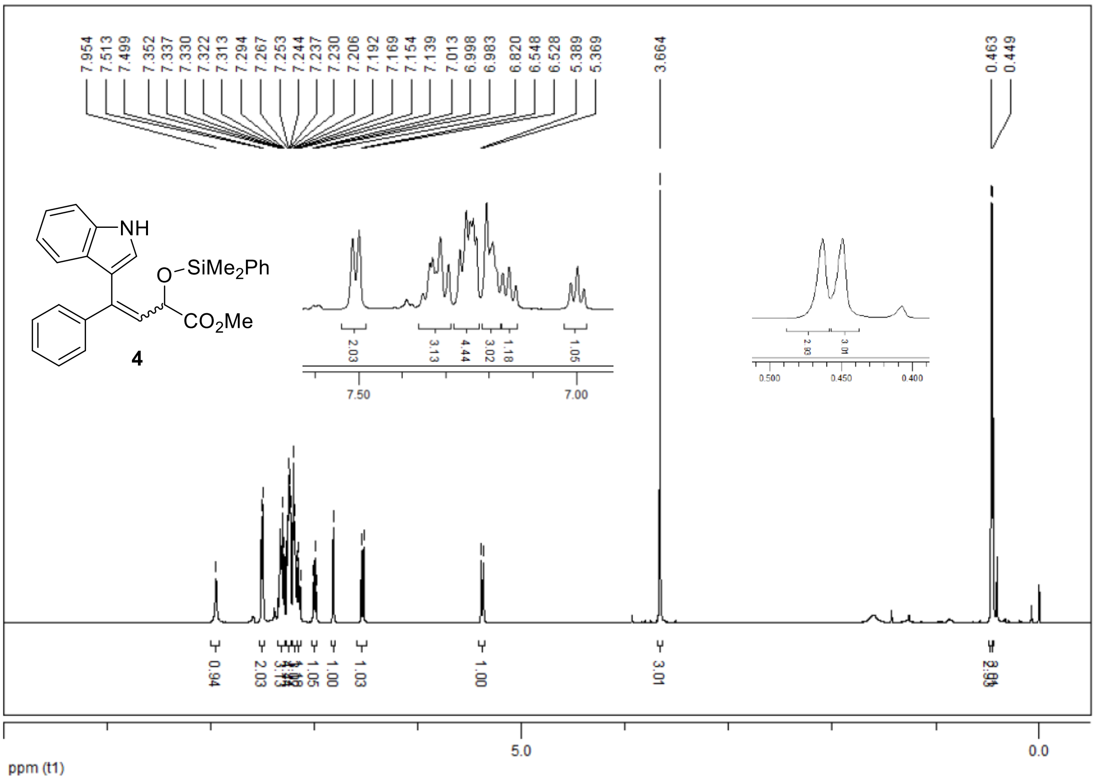

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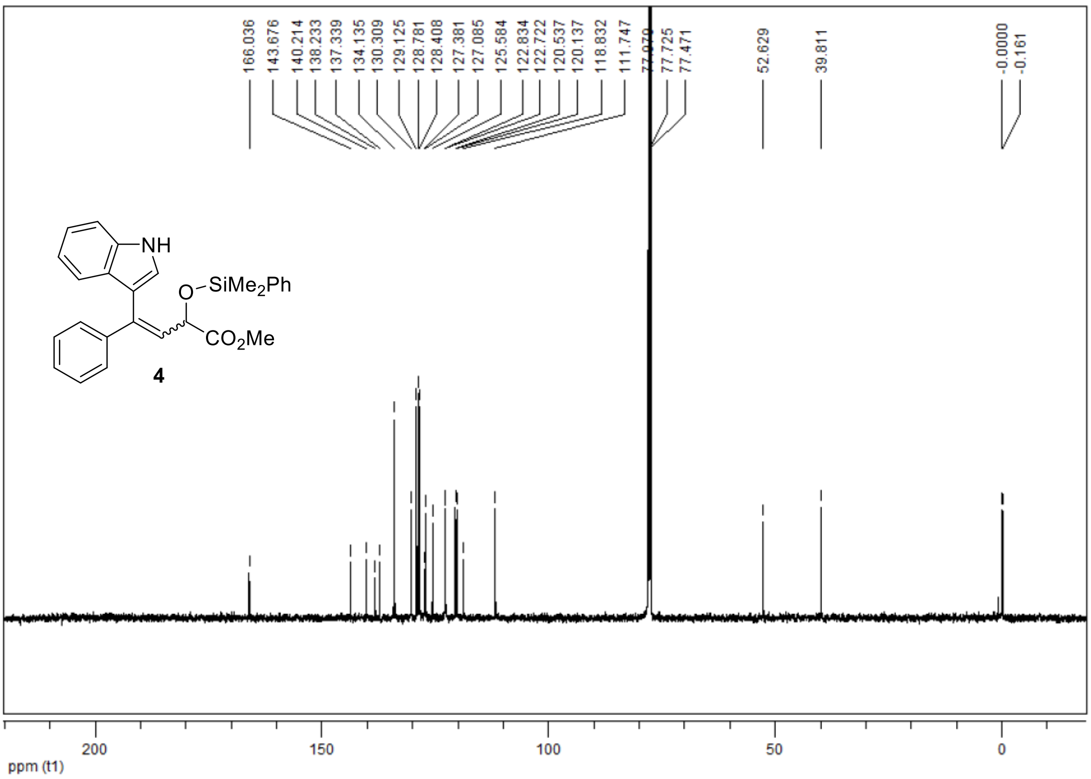

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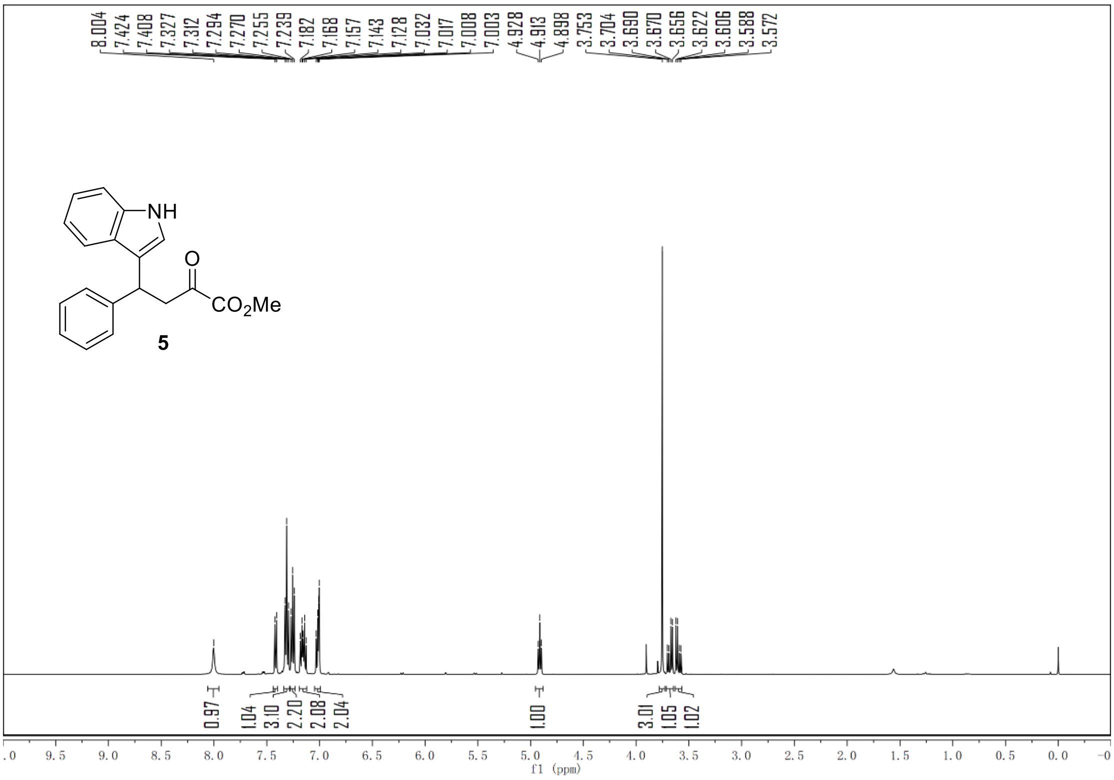

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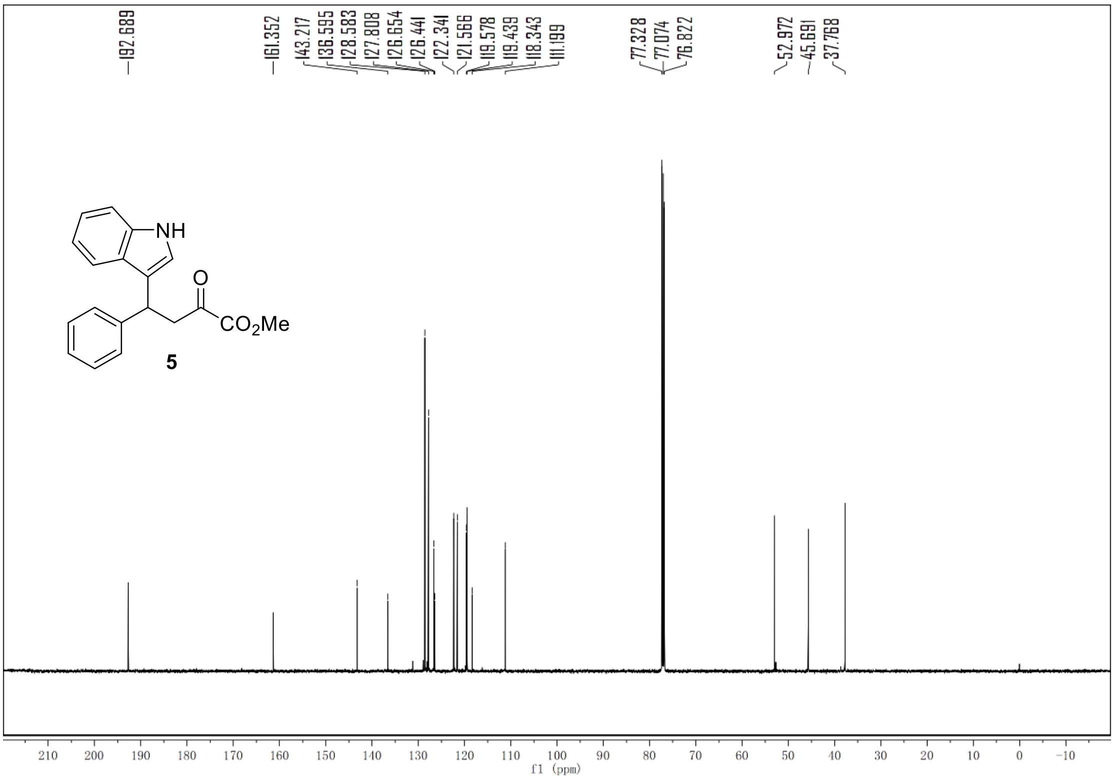
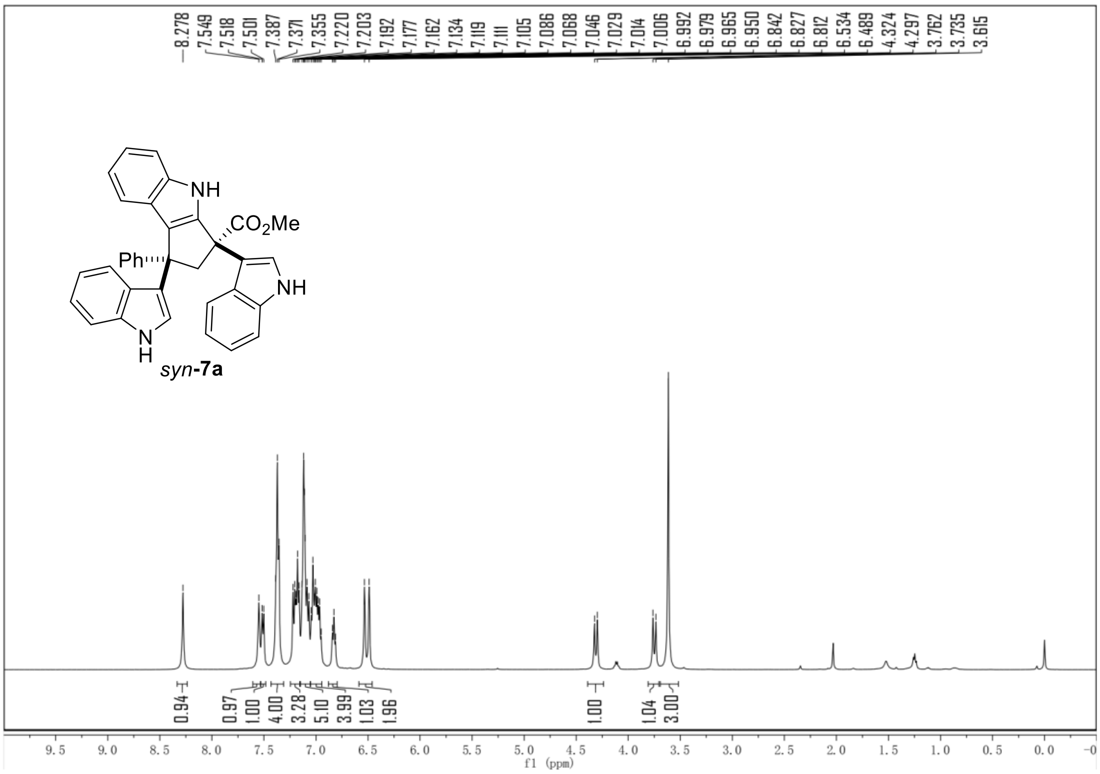
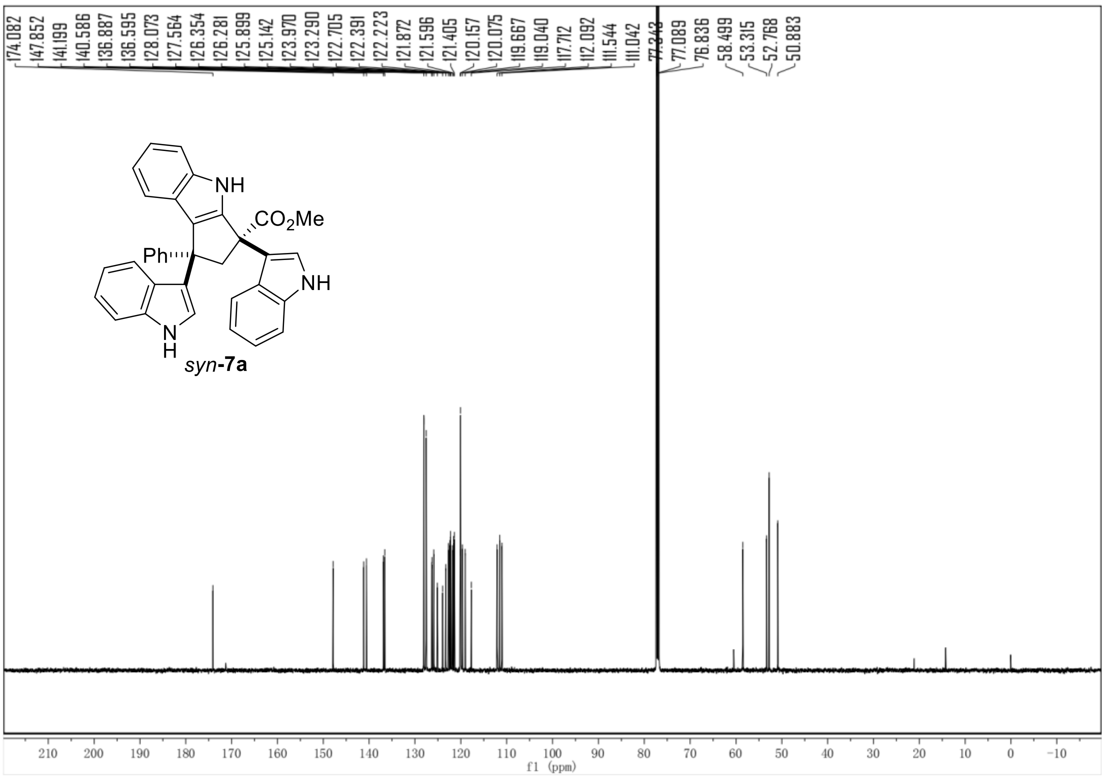


^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{H} NMR (126 MHz, $CDCl_3$)



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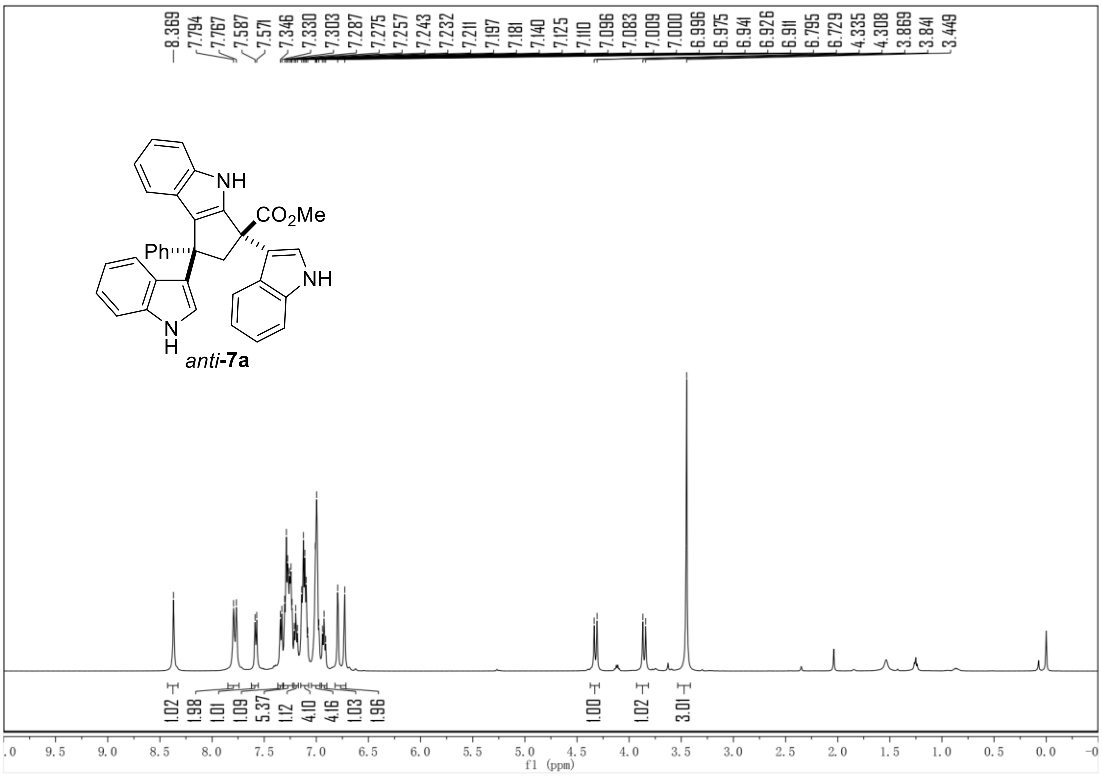
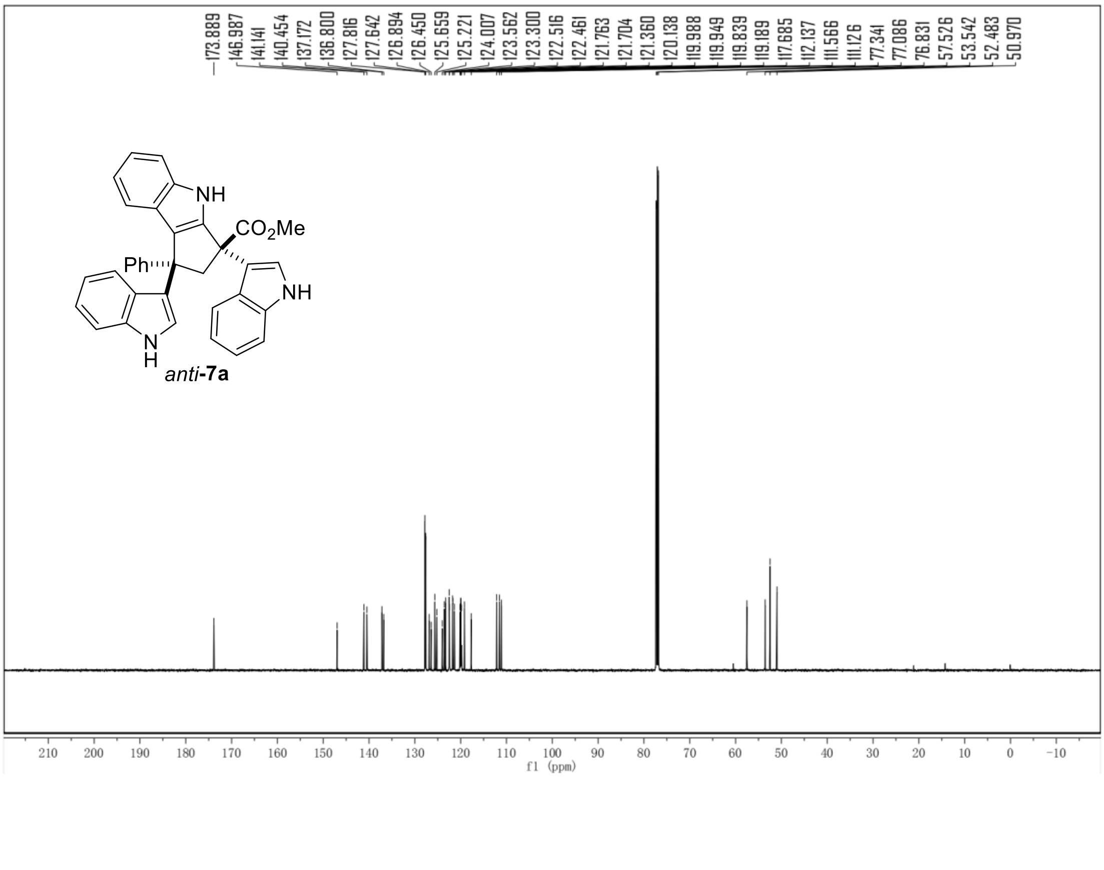
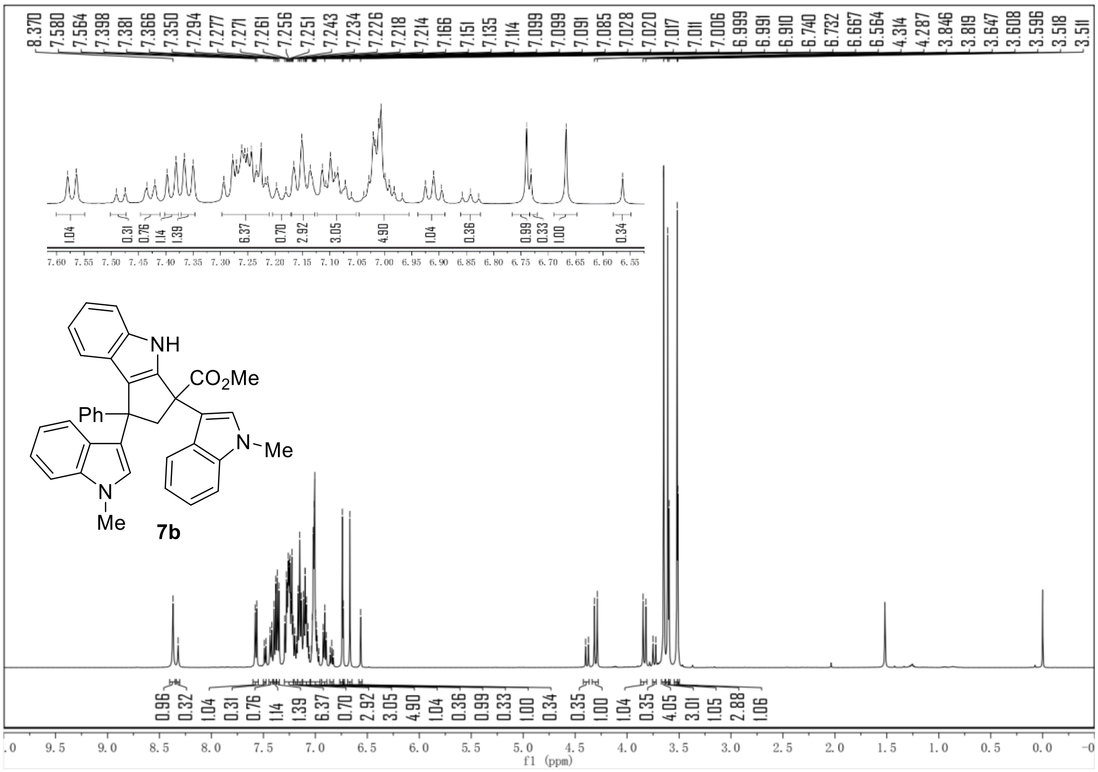


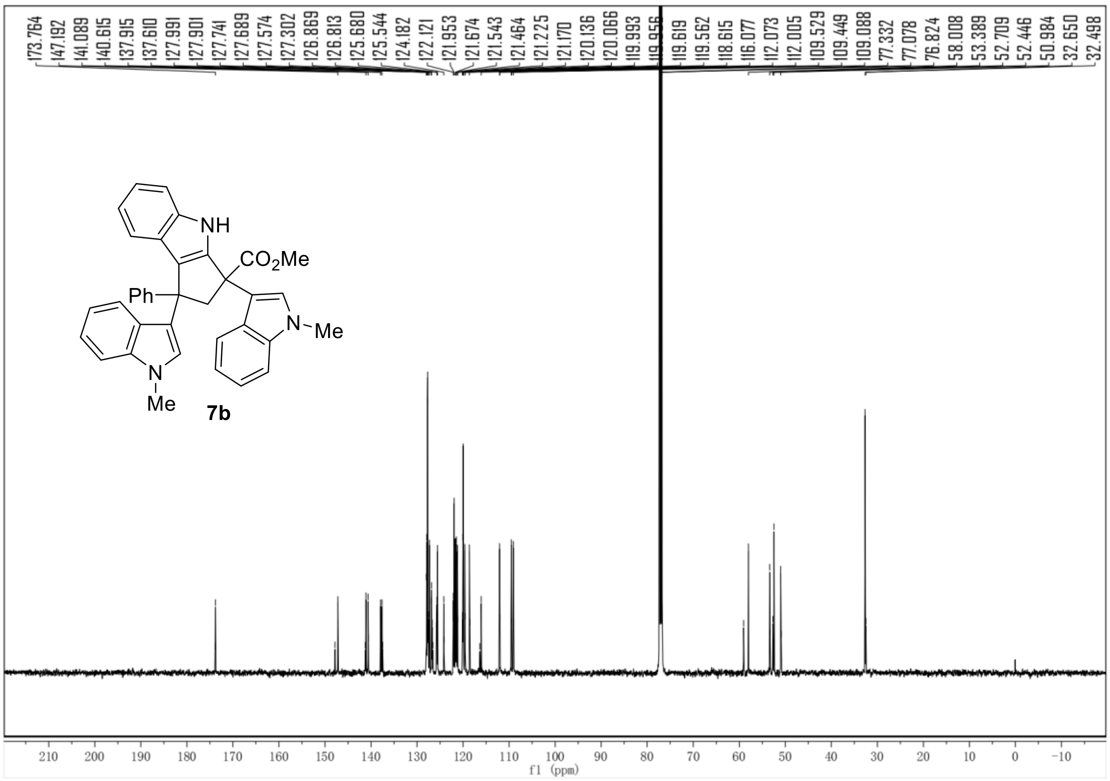
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$)



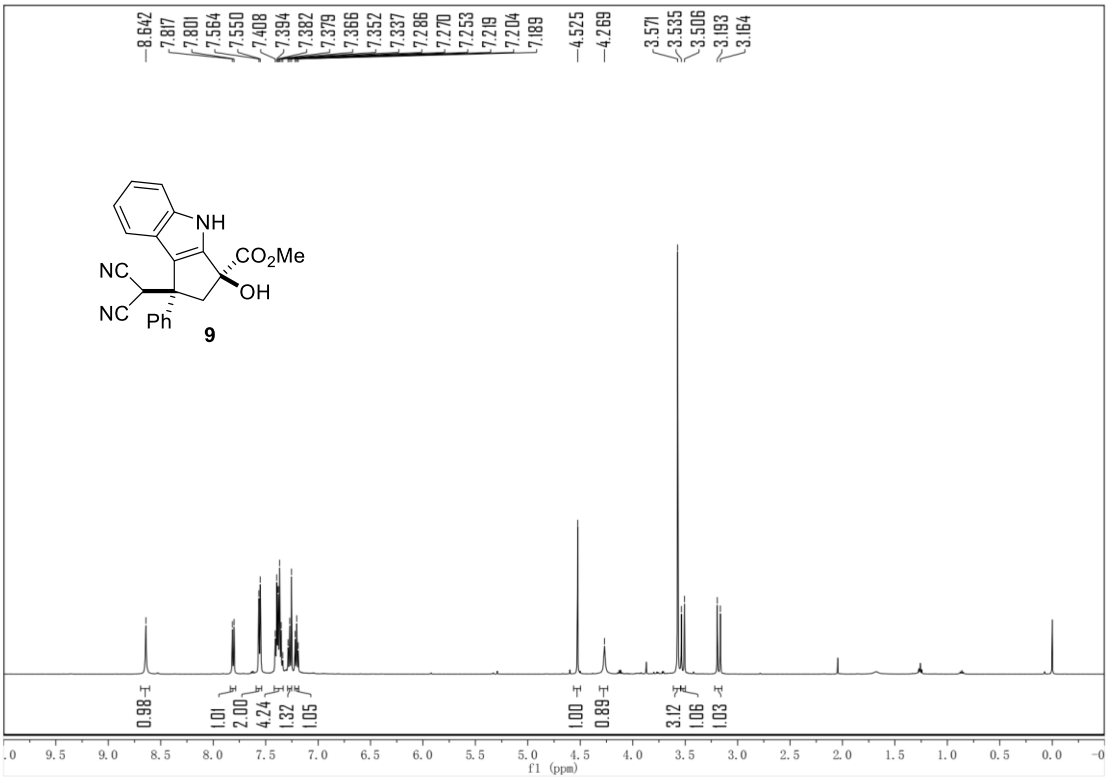
^{1}H NMR (500 MHz, CDCl$_3$)



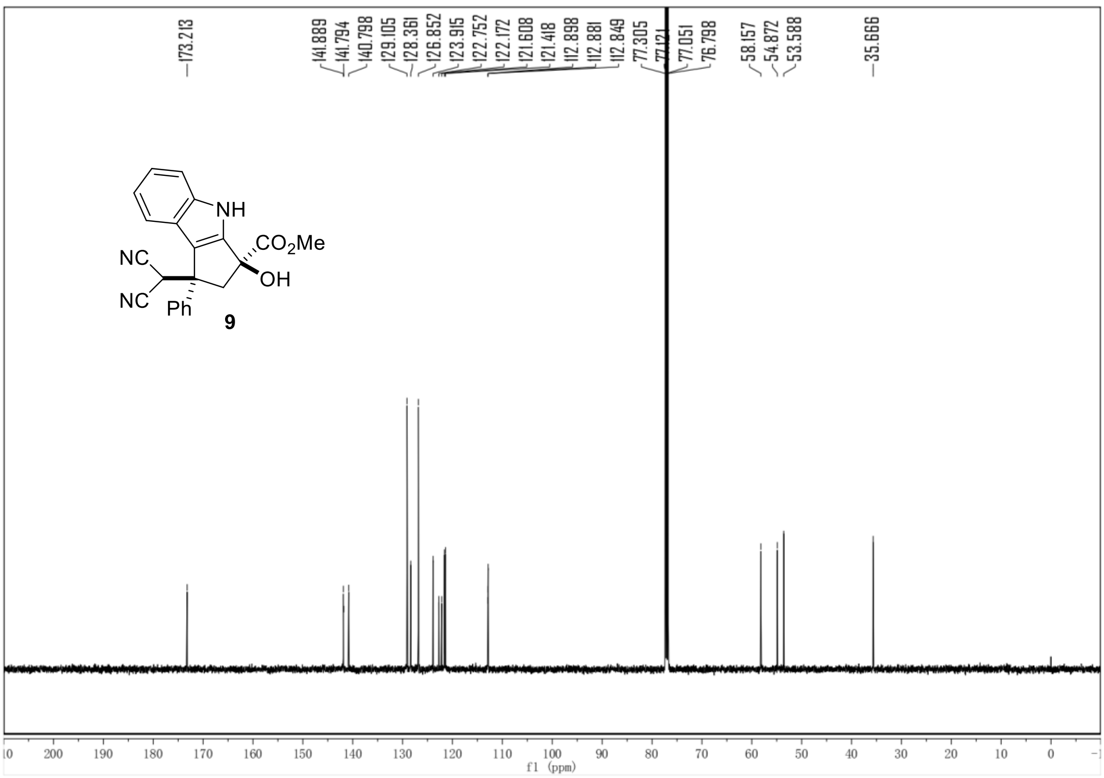
^{13}C{H} NMR (126 MHz, CDCl$_3$)



[1]H NMR (500 MHz, $CDCl_3$)



[13]C{H} NMR (126 MHz, $CDCl_3$)



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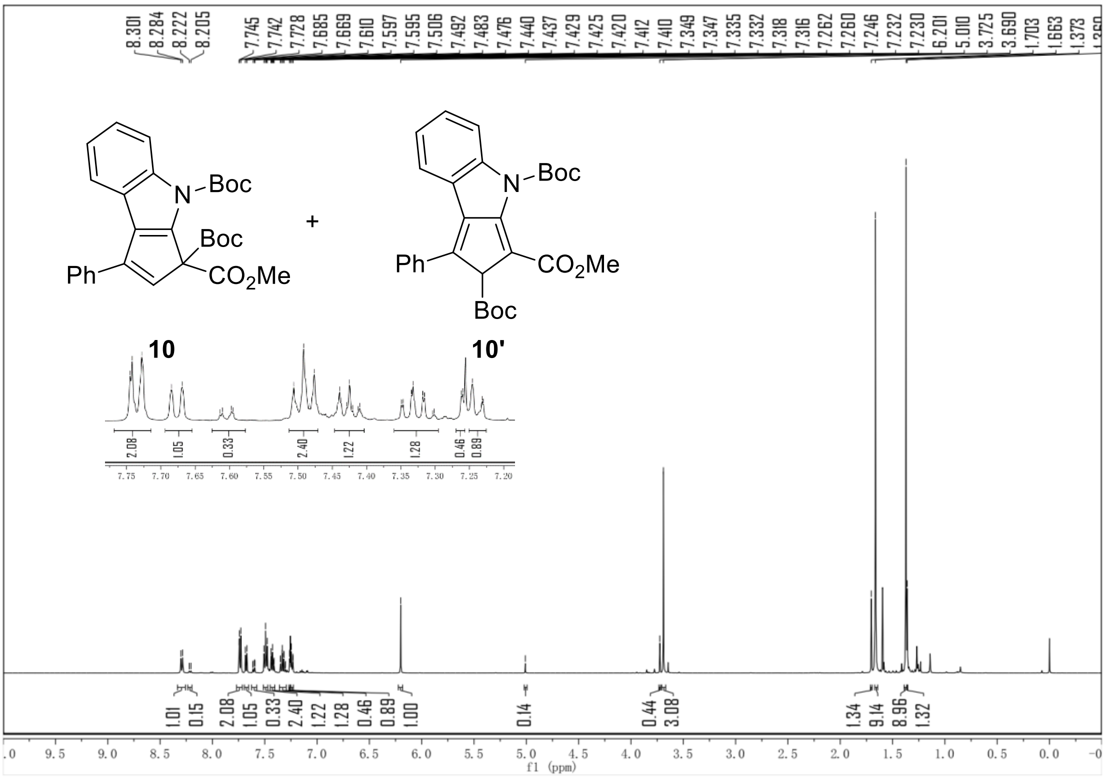

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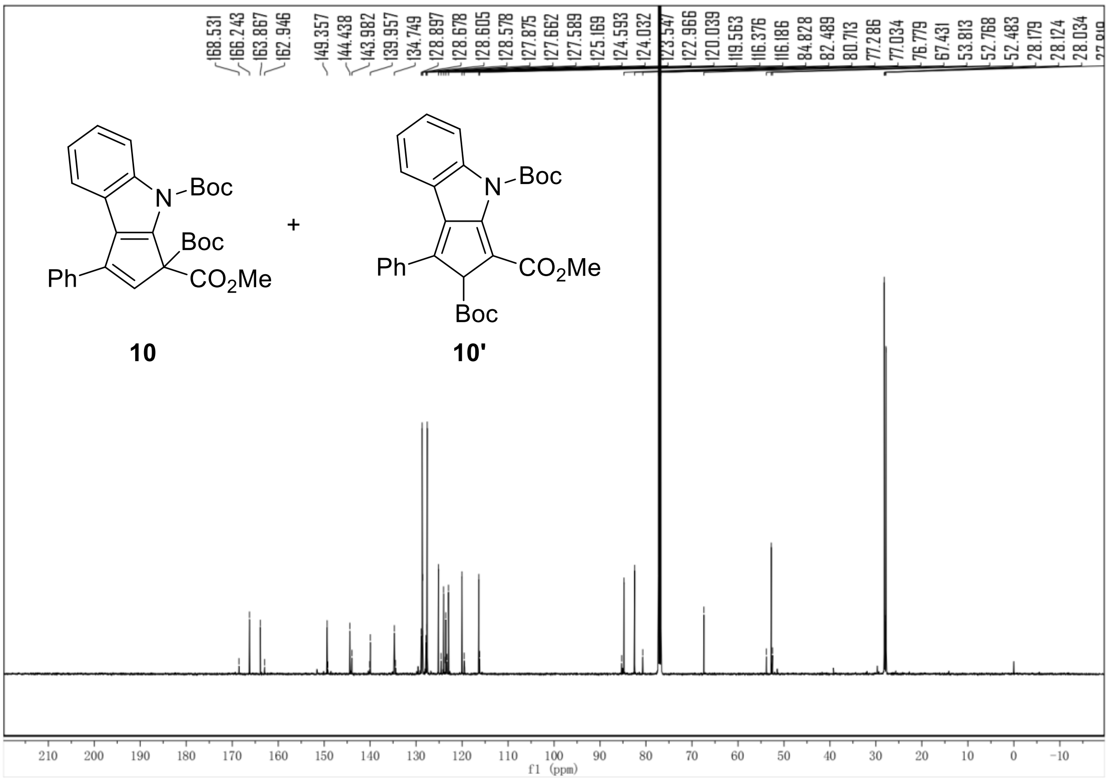
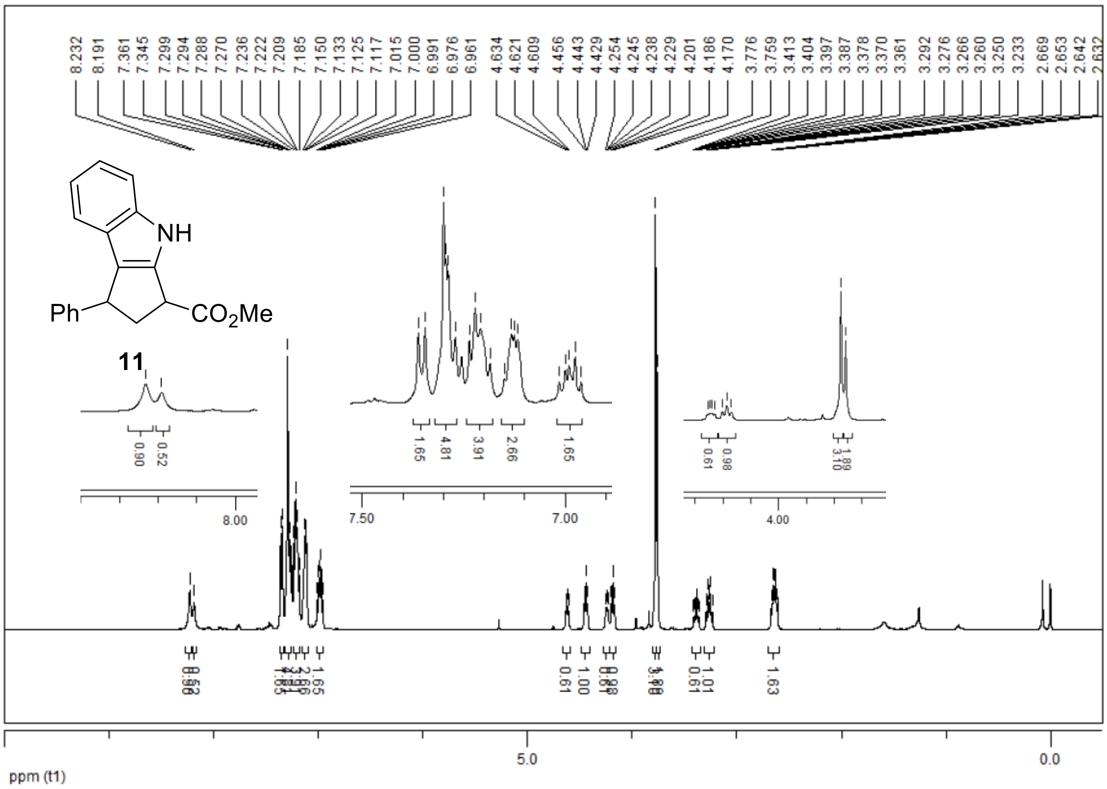
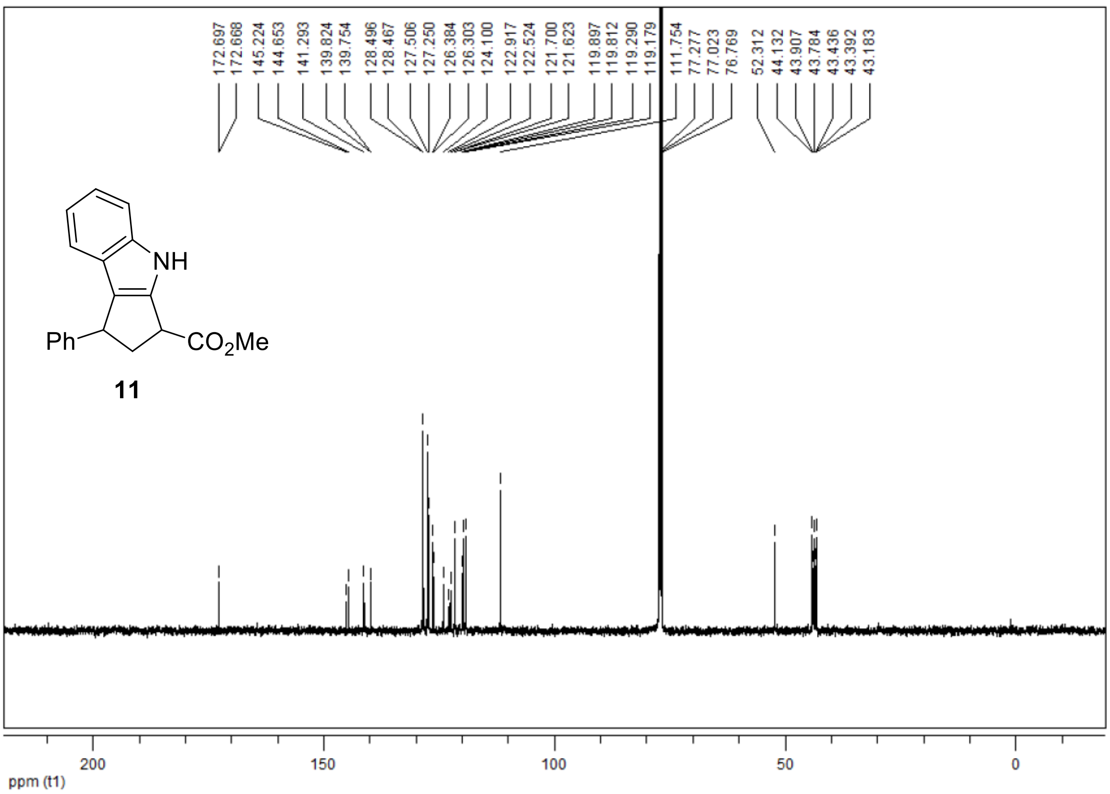


[1]H NMR (500 MHz, $CDCl_3$)



[13]C{H} NMR (126 MHz, $CDCl_3$)



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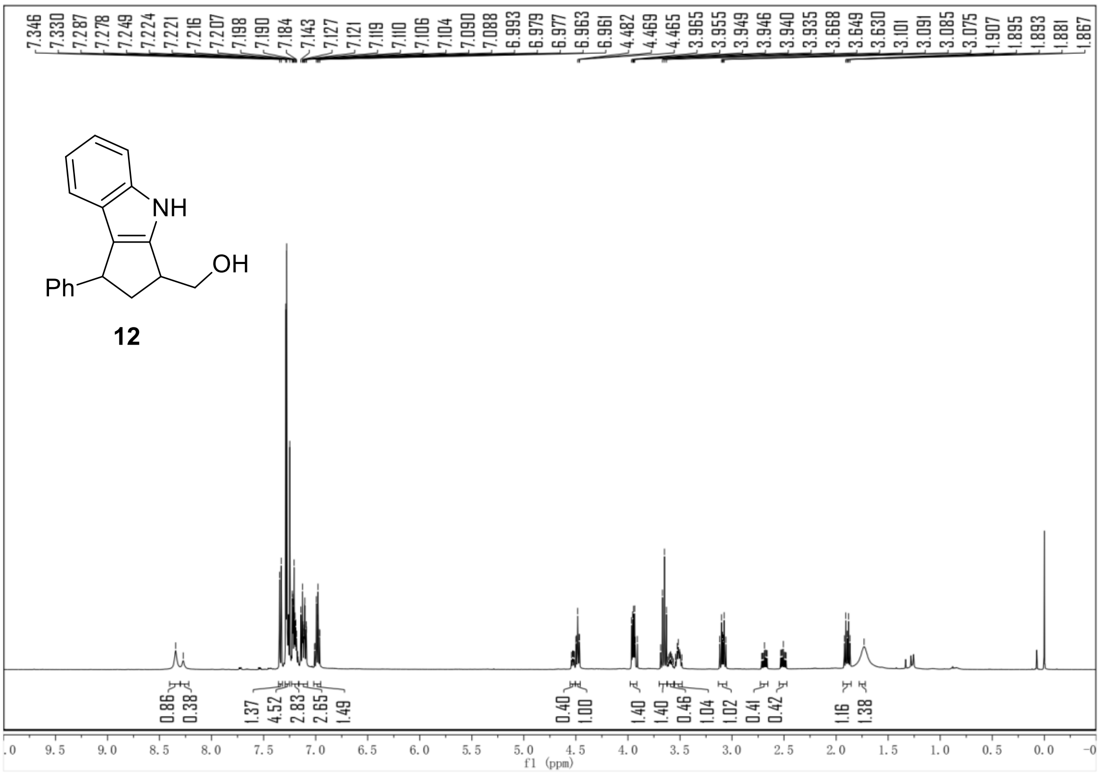

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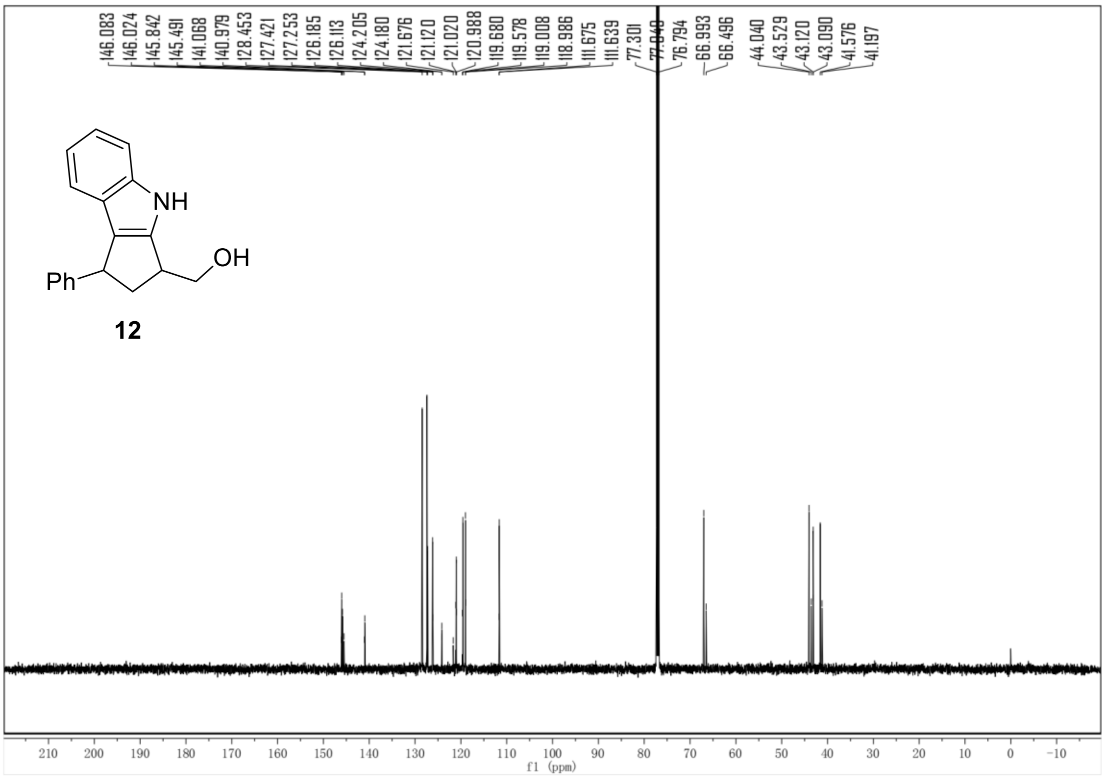

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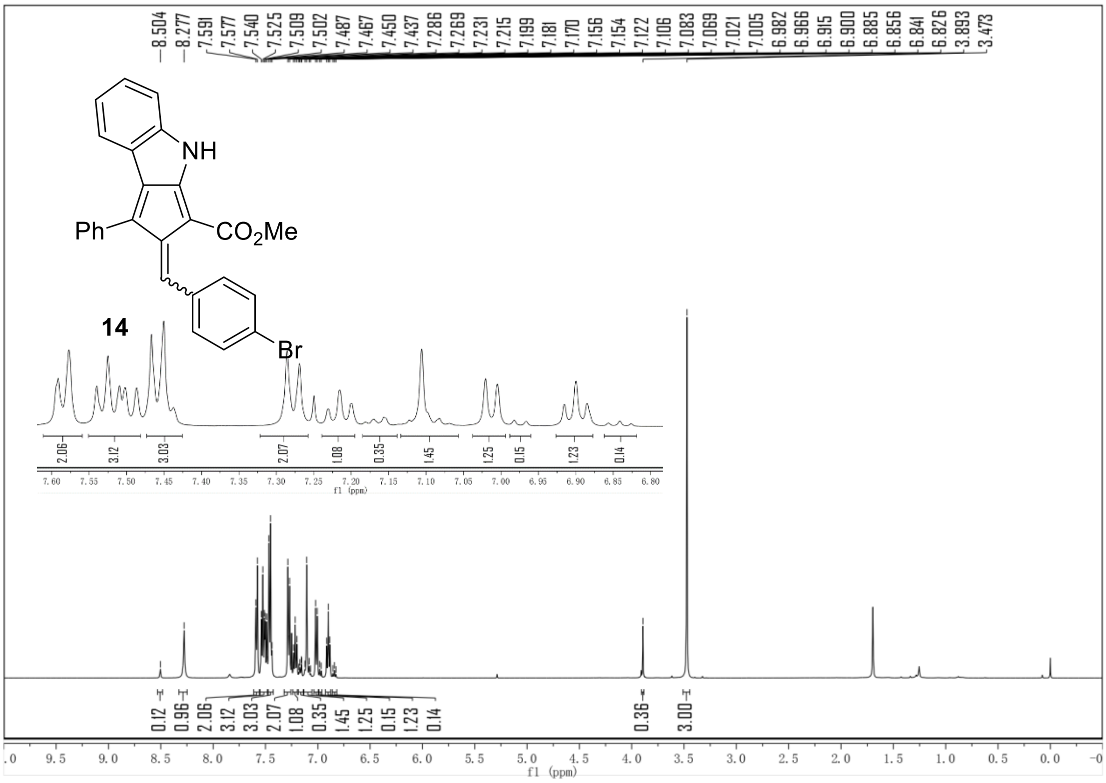

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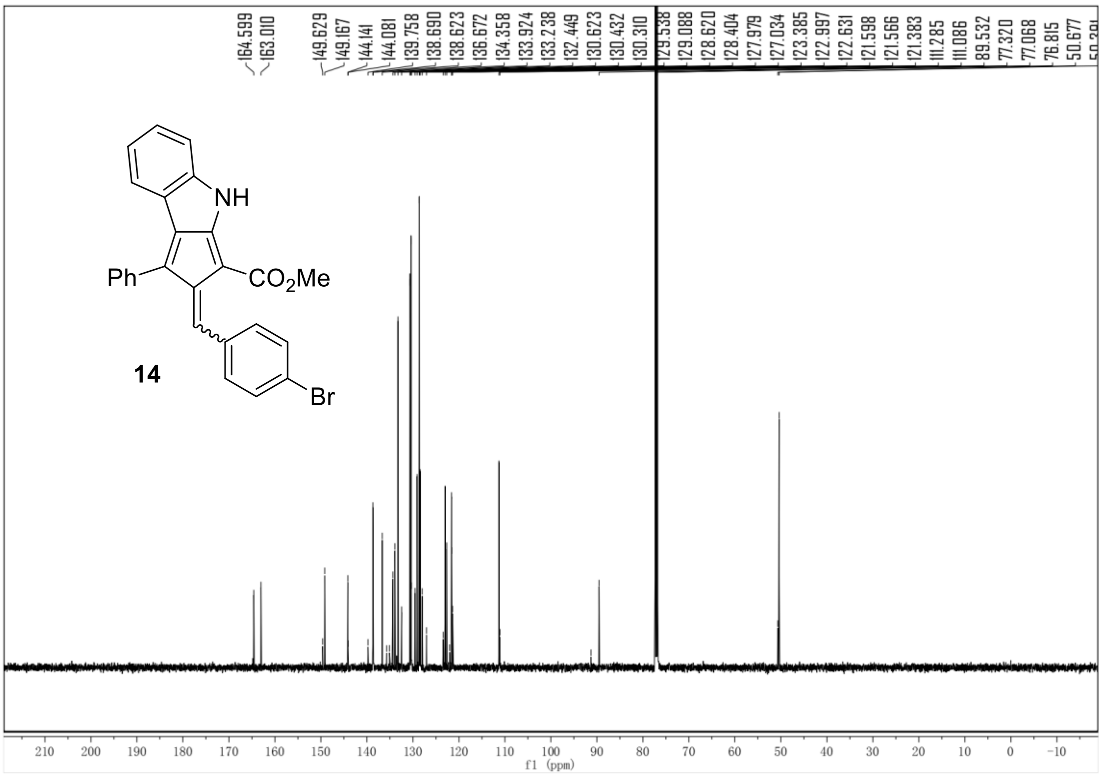
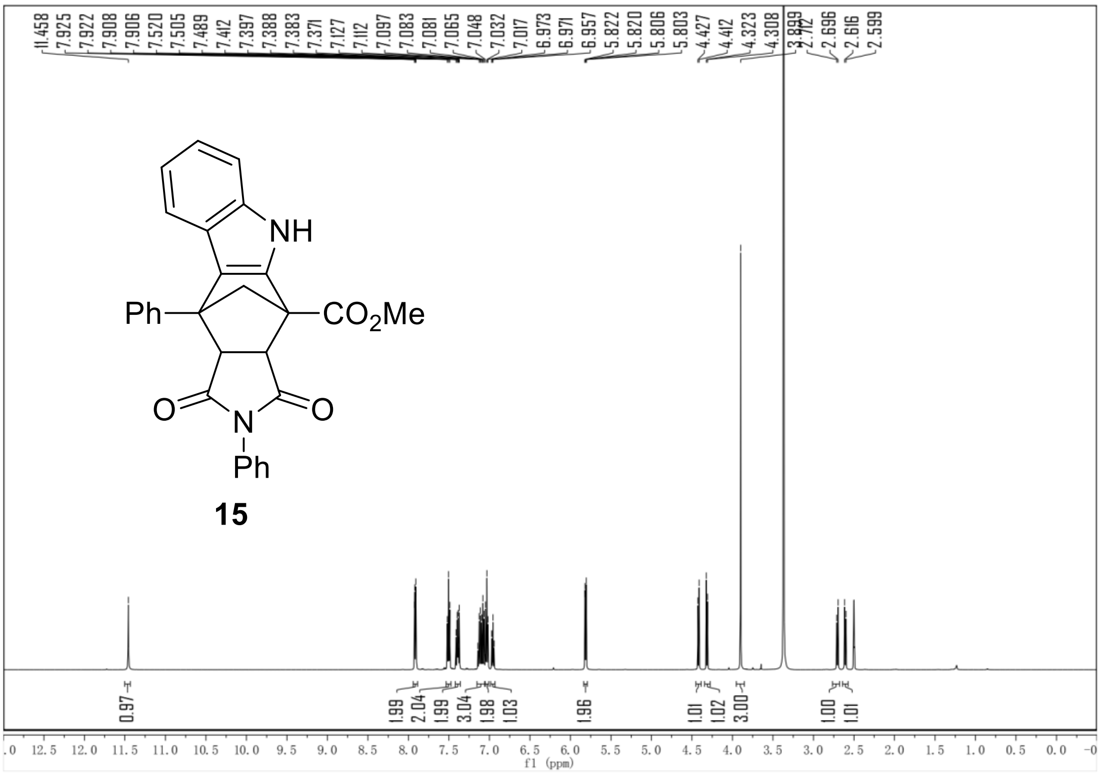
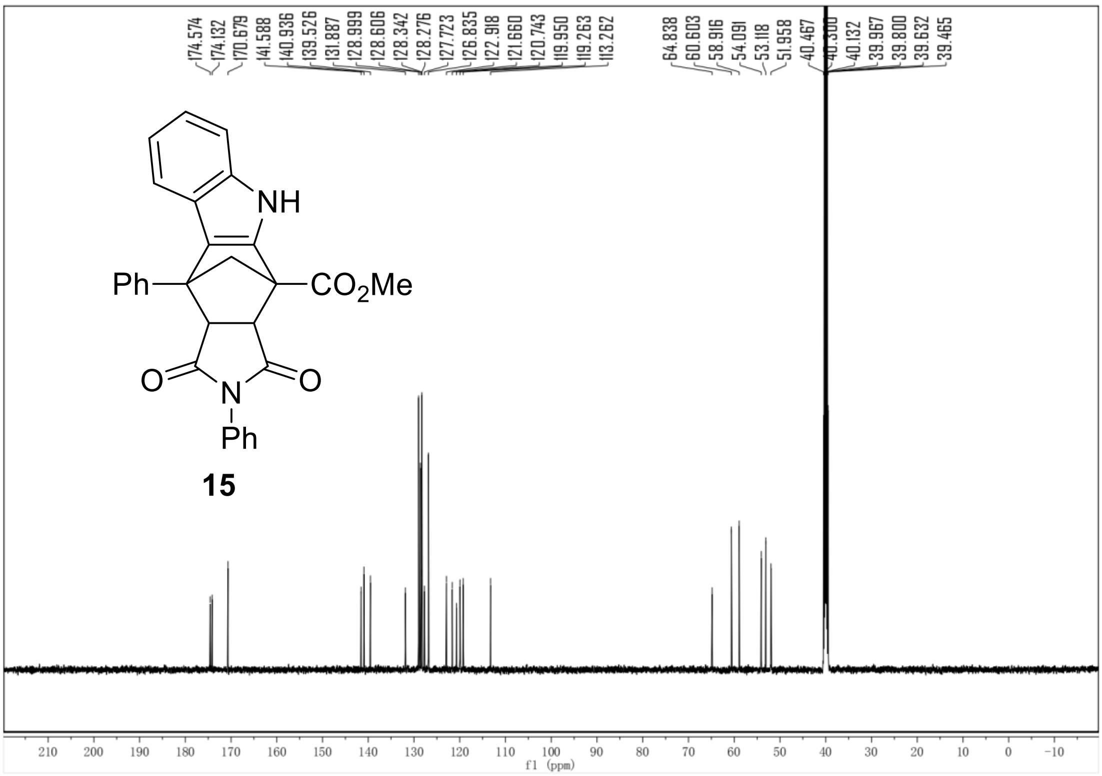


^{1}H NMR (500 MHz, DMSO-d_6)



$^{13}C\{H\}$ NMR (126 MHz, DMSO-d_6)



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