Supporting information for

Visible-Light-Induced Photocatalyst-Free C-3 Functionalization of Indoles with Diethyl Bromomalonate

Guangmiao Gu,‡ Mengmeng Huang,‡ Jung Keun Kim, Jianye Zhang, Yabo Li* and Yangjie Wu*

College of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, P.R. China.

wyj@zzu.edu.cn, ybli@zzu.edu.cn

Contents

1. General Information

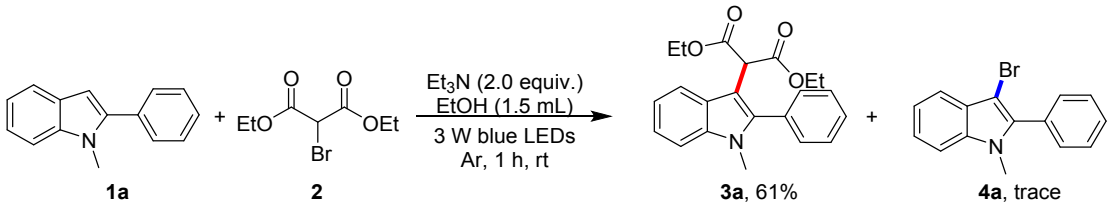
All reactions were performed using quartz tube. Commercial grade reagents (**1a** and **2**) and EtOH (OCEANPAK, GC ≥ 99.9%) were used without further purification except as indicated below. *N*-Methylindoles were synthesized from indoles according to the method in the literature.[1] 2-Arylindoles (**1b-1t**) were synthesized according to the method in the literature.[2] ^{1}H NMR and ^{13}C NMR spectral data of **1b-1u** are in accordance with those reported[2, 3] in the literature. Solvents were dried and degassed by standard methods[4] before they were used. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro^{+} and Digital Single Channel Adjustable Automatic Electronic Pipette Micropipette dPettee^{+} were purchased from Dragon Laboratory Instruments Limited. ^{1}H NMR spectra was recorded on a Bruker DPX-400 (400 MHz) spectrometer with deuteraterated chloroform as solution, the chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. ^{13}C NMR spectra was recorded at 100 MHz on Bruker DPX-400. The chemical shifts δ are reported relative to residual $CHCl_3$ (δ_C = 77.00 ppm). ^{19}F NMR spectra was recorded at 376.5 MHz on Bruker DPX-400, the chemical shifts δ are reported relative to $CFCl_3$ (δ = 0 ppm) as internal standard. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd = doublet of doublet, td = triplet of doublet. Coupling constants *J* are reported in Hertz (Hz). High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). The UV-Vis absorption spectra were recorded in DMF on a Perkin Elmer Lambda 35 spectrometer. The cyclic voltammetry (CV) was recorded in DMF by CHI650A. And the luminescence quenching experiment was recorded using a F-4500 FL spectrophotometer in EtOH. All reactions were carried out with photoreactor (Serial No: PEA12) which was purchased from LUOYANG JINFENG ELECTROMECHANICAL EQUIPMENT CO., LTD.

2. Experimental Procedures

2.1 General procedure for the synthesis of α-indolyl diethyl malonates

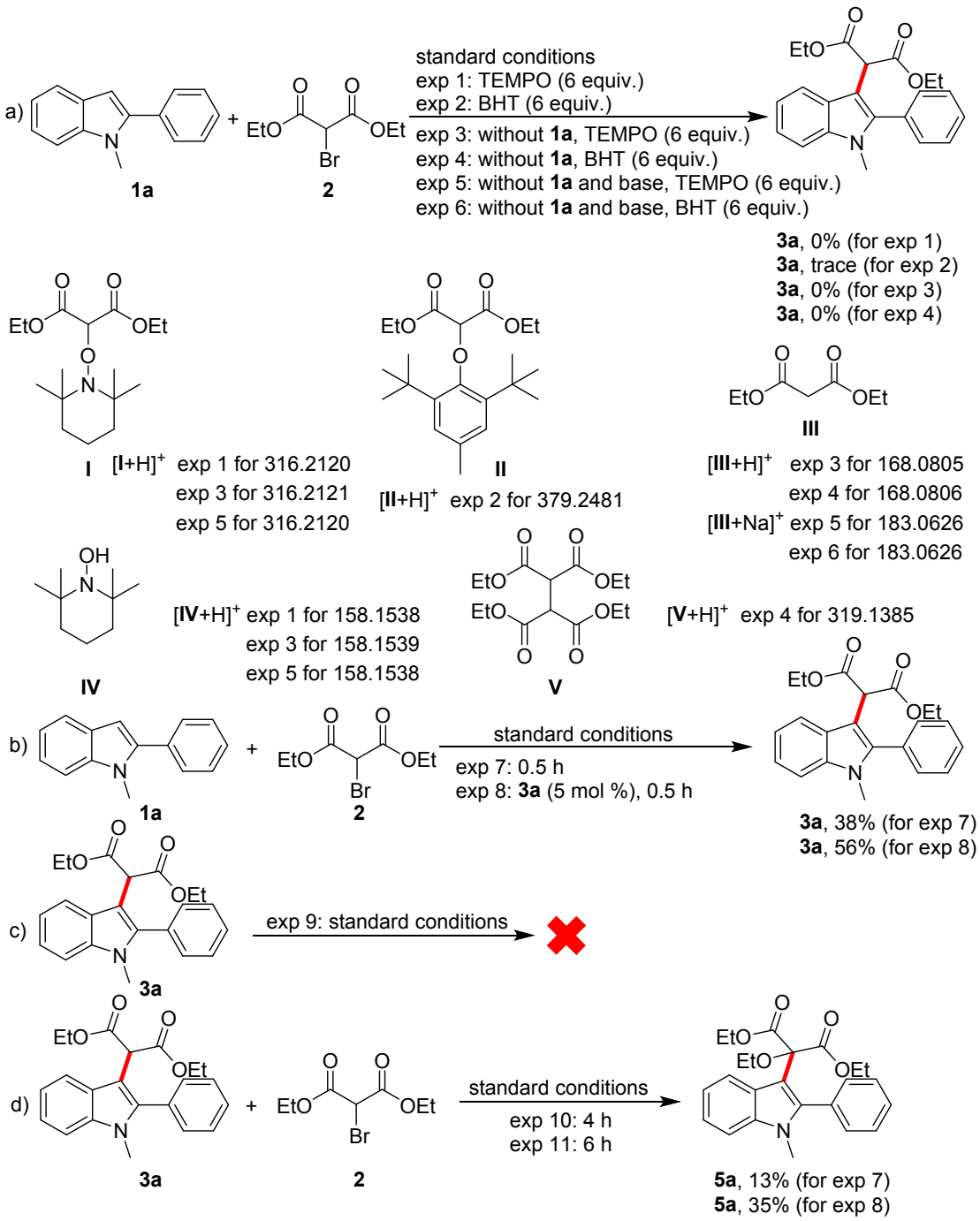
2-Substitutedindoles **1** (0.2 mmol), diethyl bromomalonate **2** (0.6 mmol, 3.0 equiv.) and $K_2HPO_4{\cdot}3H_2O$ (0.4 mmol, 2.0 equiv.) were combined in EtOH (1.5 mL) under Ar atmosphere. The mixture was stirred at room temperature under 3 W blue LED. After 1 hour, the reaction mixture was extracted with dichloromethane and saturated salt water, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Then, they were purified by chromatography on silica gel (elute: Ethyl acetate/Petroleum ether = 1/0-10/1, v/v) to give the desired product **3**.

2.2 Supplementary reaction with Et_3N instead of $K_2HPO_4{\cdot}3H_2O$



Scheme S1. Reaction conditions: **1a** (0.2 mmol), **2** (3.0 equiv.), Et_3N (2.0 equiv.), EtOH (1.5 mL), in a quartz tube under Ar at room temperature for 1 hour. Isolated yield.

3. Control Experiments



Scheme S2. Control experiments.

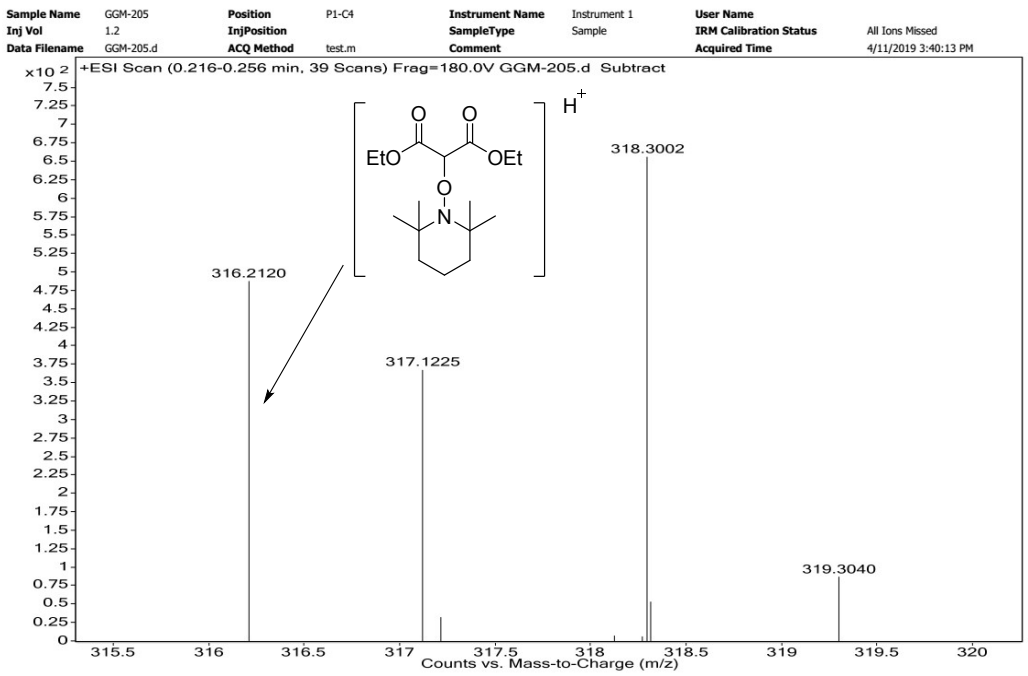


Figure S1. HRMS spectrum of compound [**I** + H]$^+$ for exp 1

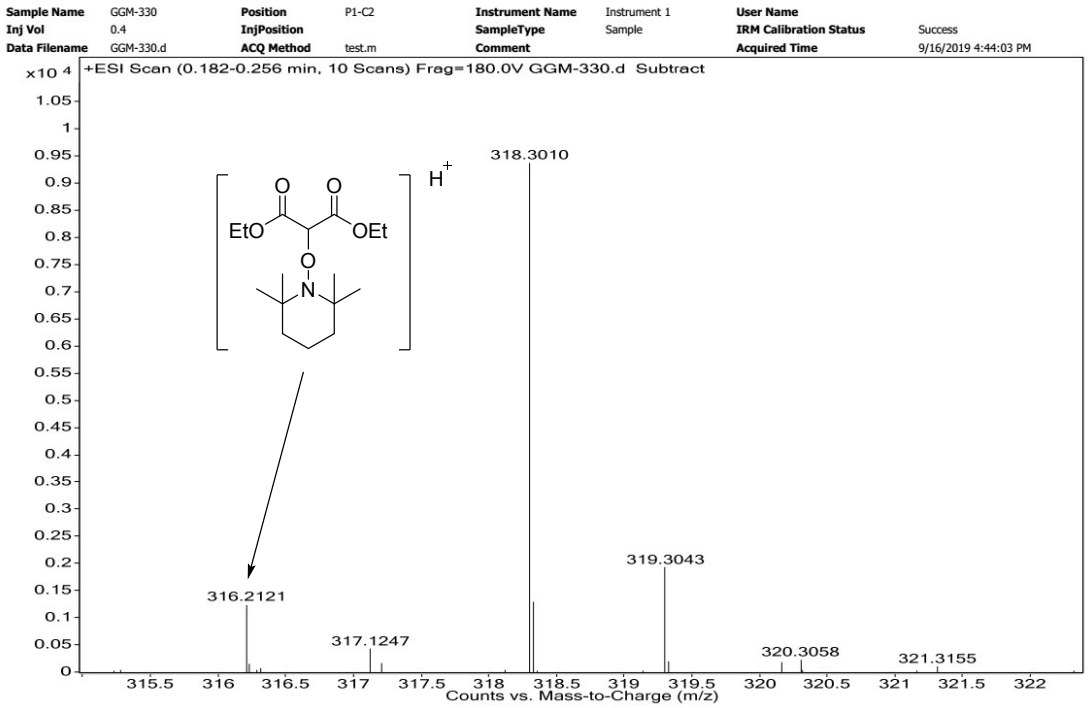


Figure S2. HRMS spectrum of compound [**I** + H]$^+$ for exp 3

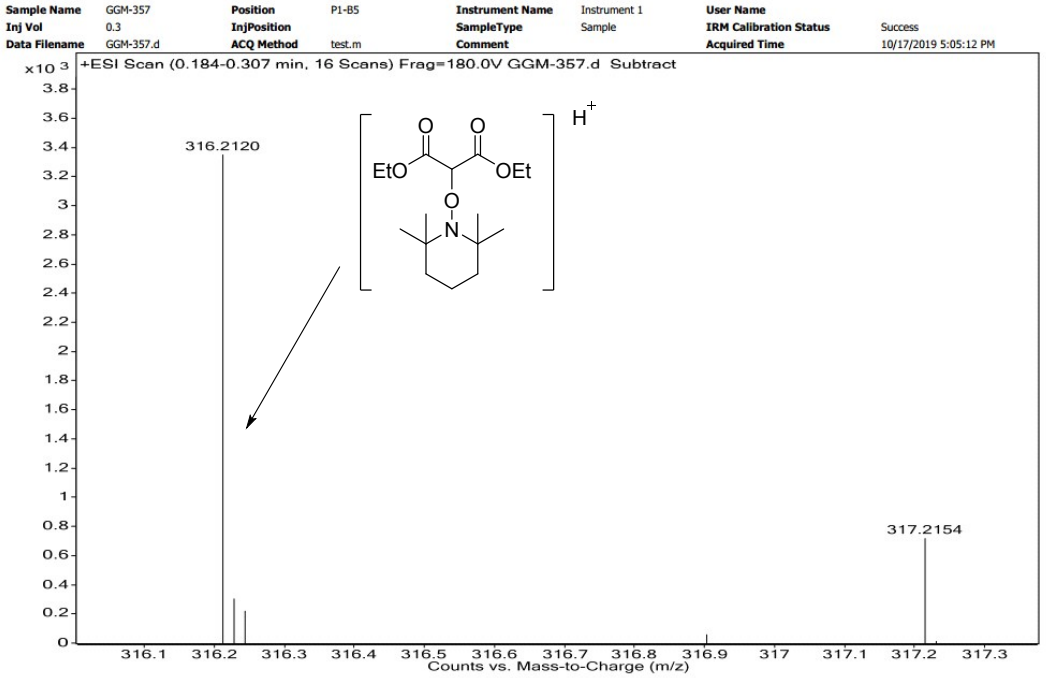


Figure S3. HRMS spectrum of compound [**I** + H]$^+$ for exp 5

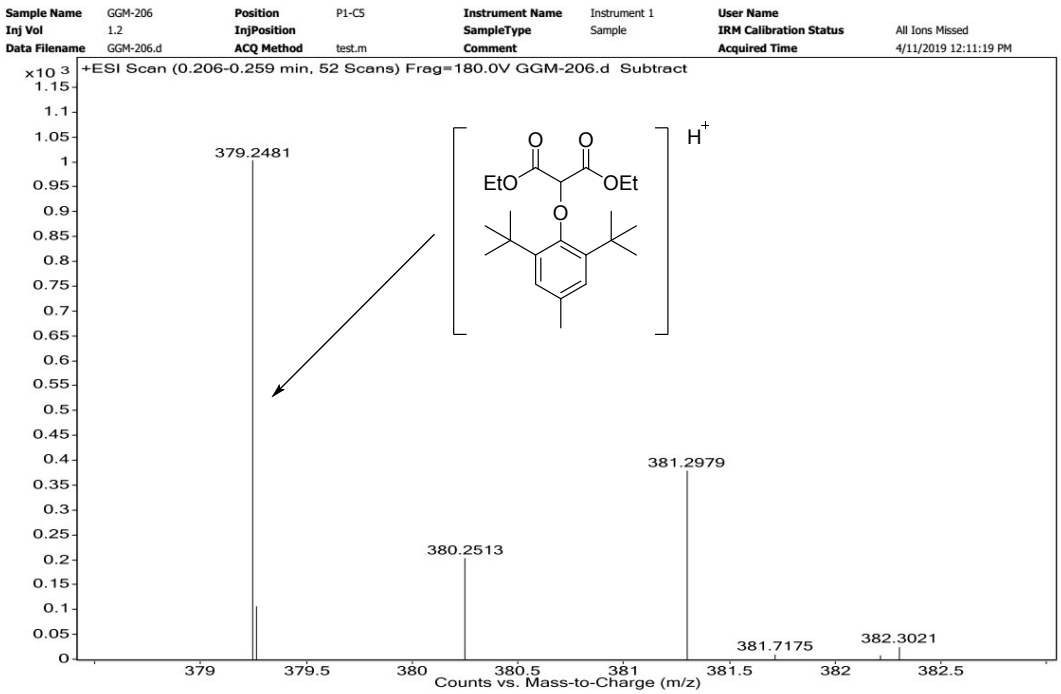


Figure S4. HRMS spectrum of compound [**II** + H]$^+$ for exp 2

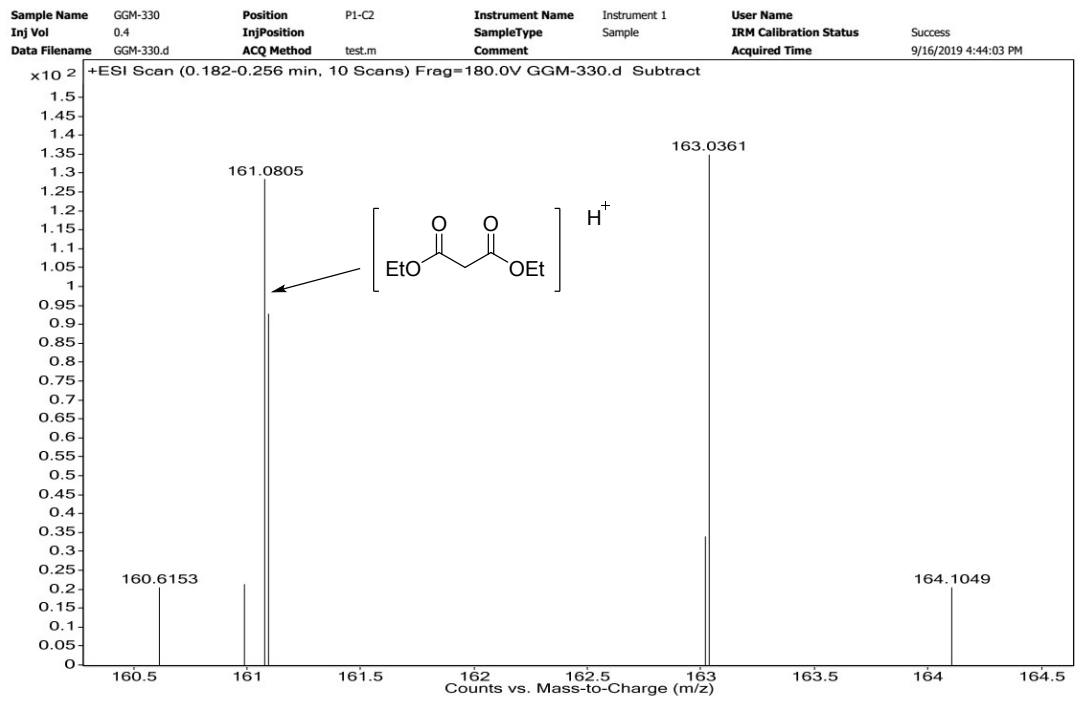


Figure S5. HRMS spectrum of compound [**III** + H]$^+$ for exp 3

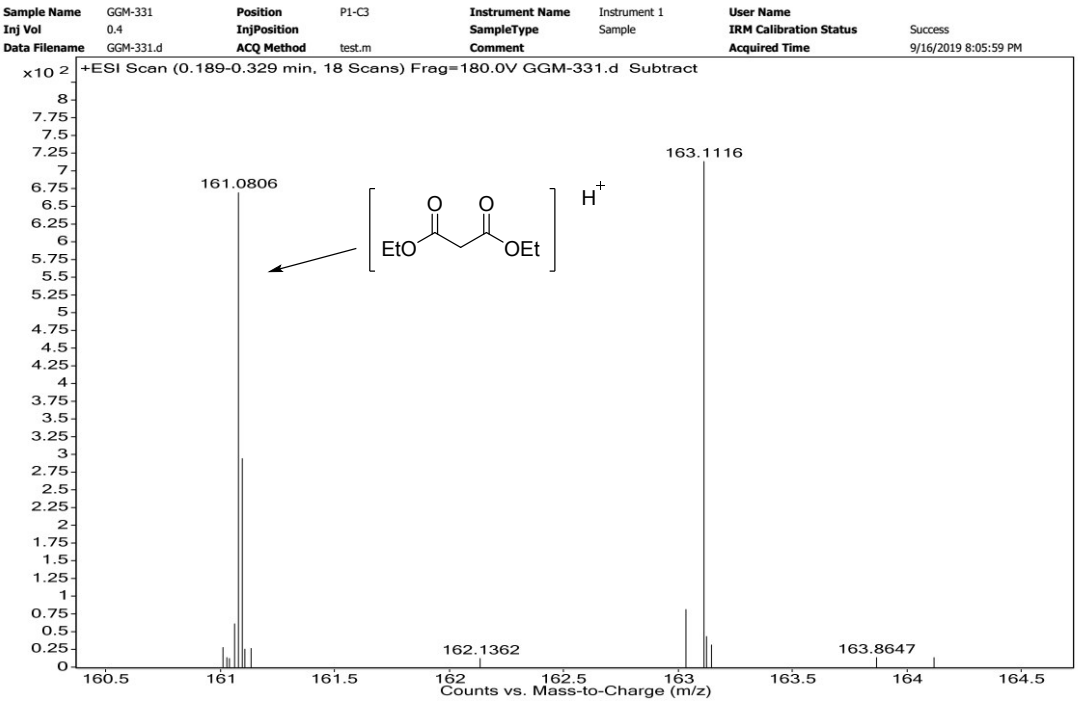


Figure S6. HRMS spectrum of compound [**III** + H]$^+$ for exp 4

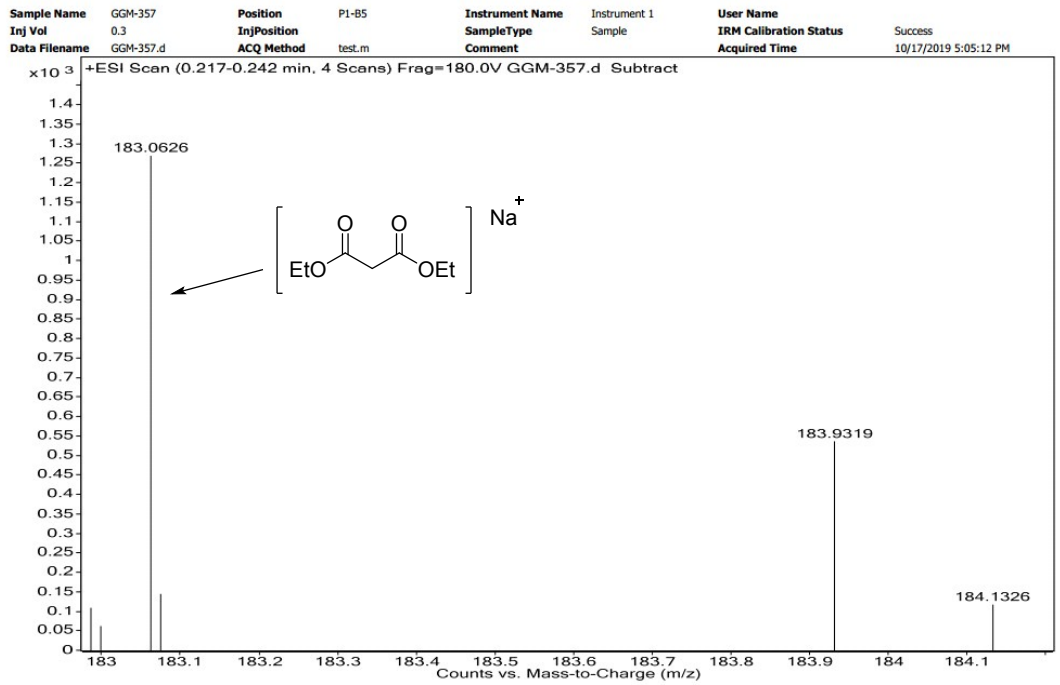


Figure S7. HRMS spectrum of compound [**III** + Na]$^+$ for exp 5

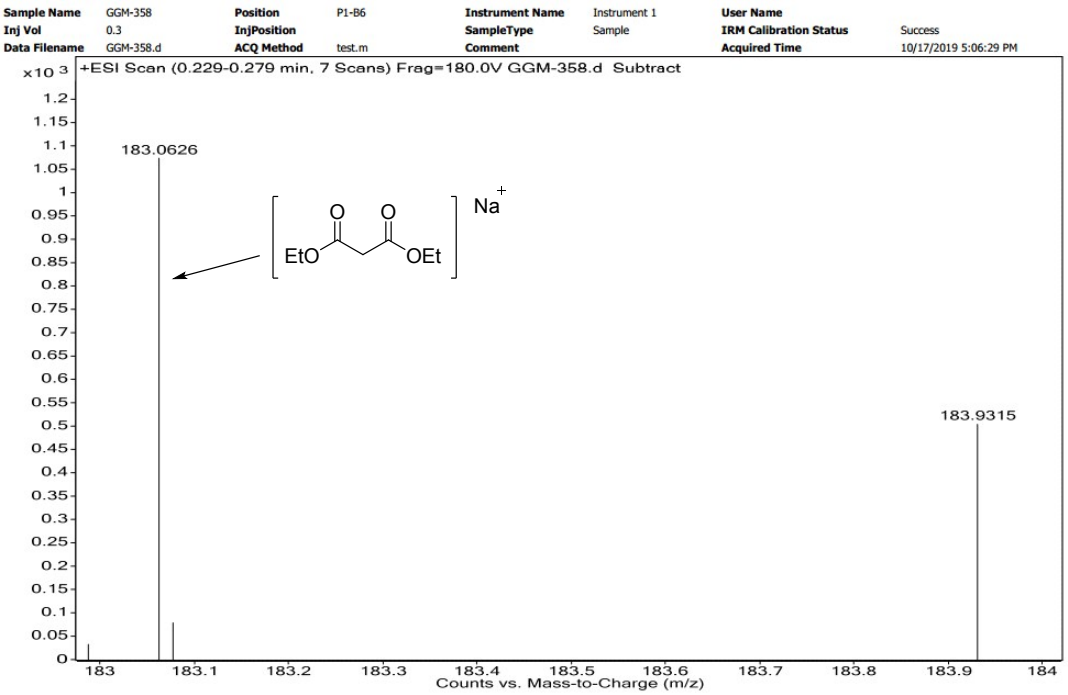


Figure S8. HRMS spectrum of compound [**III** + Na]$^+$ for exp 6

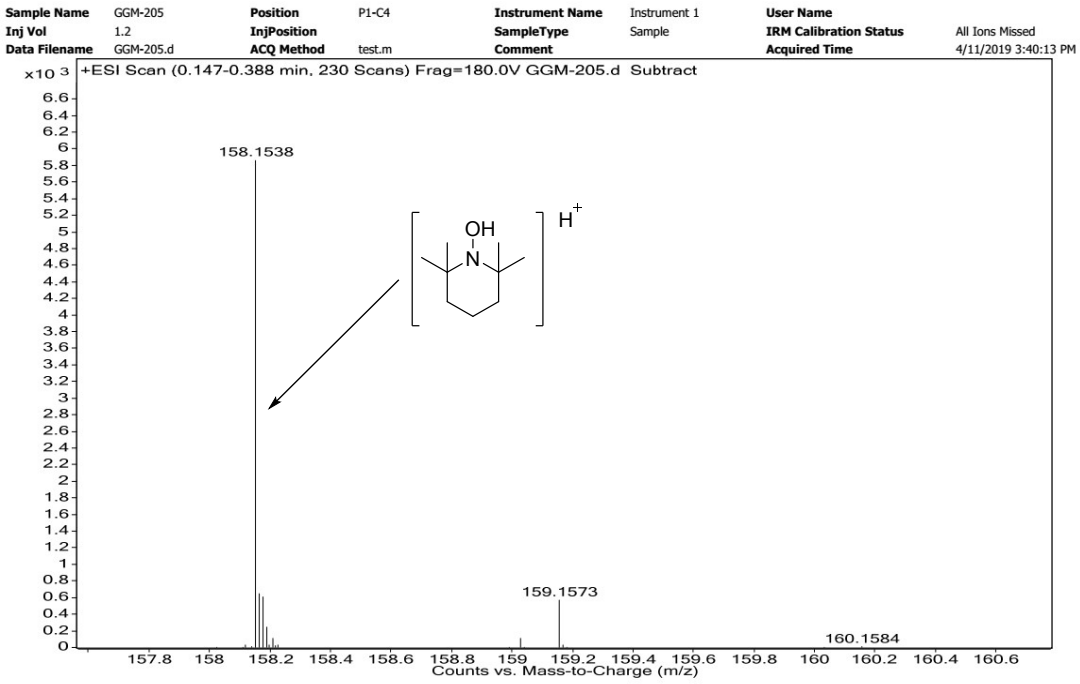


Figure S9. HRMS spectrum of compound [**IV** + H]$^+$ for exp 1

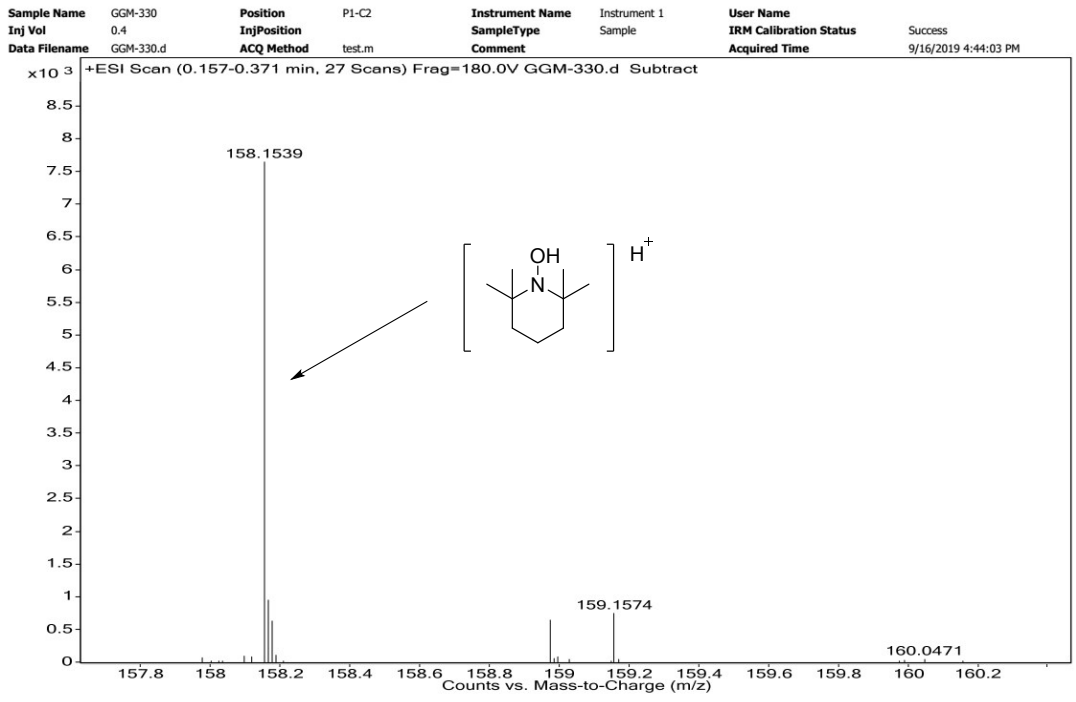


Figure S10. HRMS spectrum of compound [**IV** + H]$^+$ for exp 3

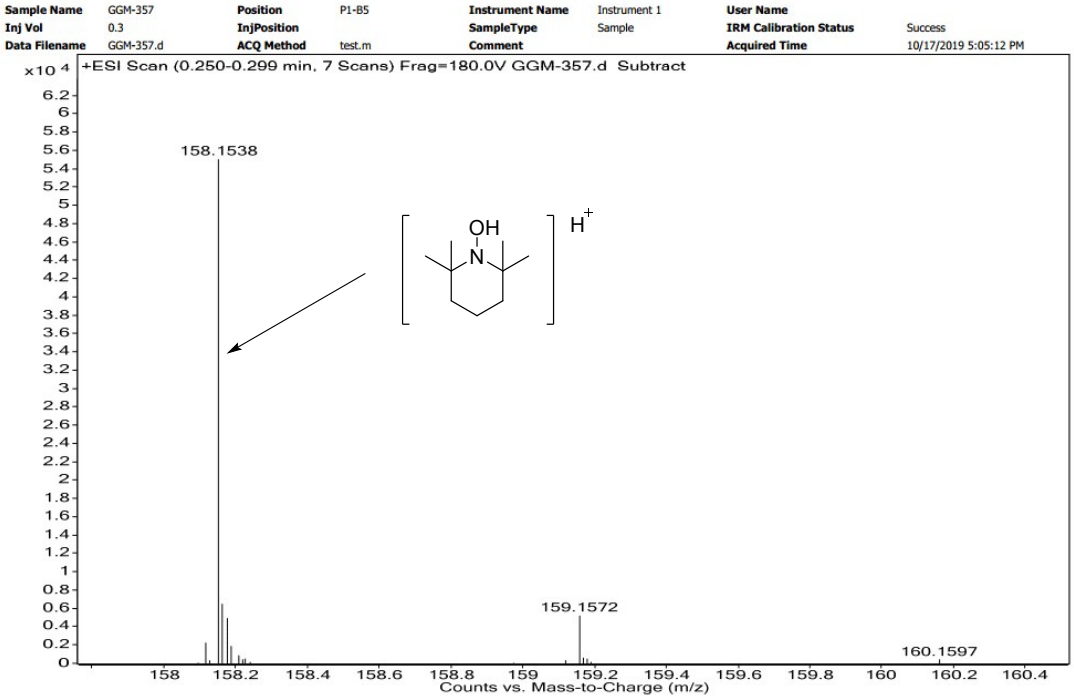


Figure S11. HRMS spectrum of compound [**IV** + H]$^+$ for exp 5

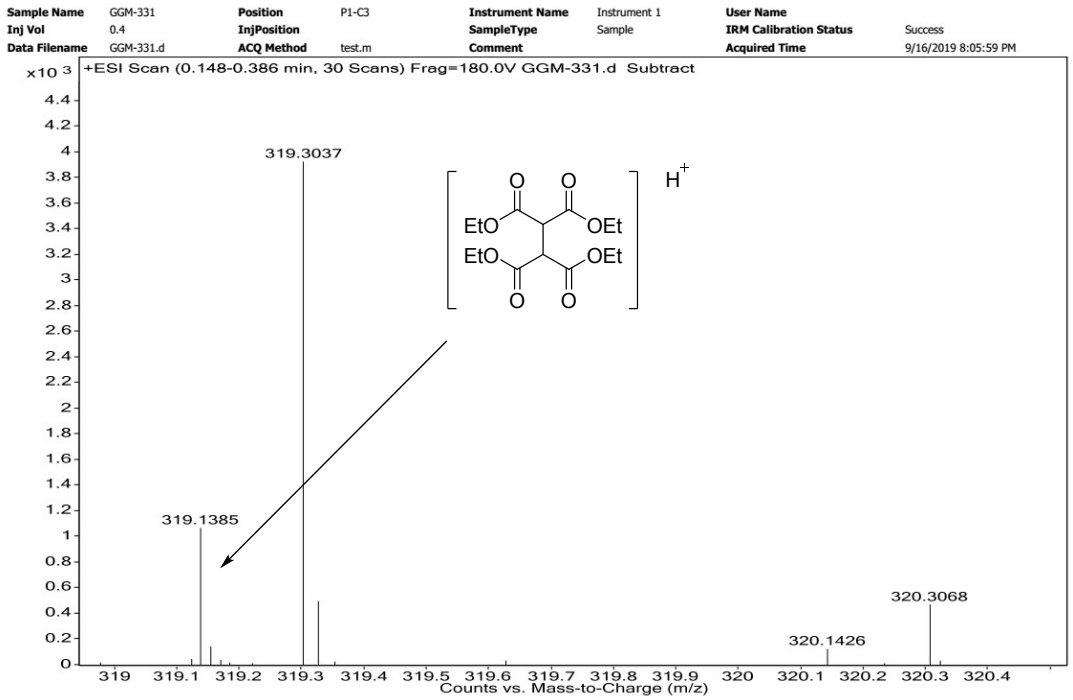


Figure S12. HRMS spectrum of compound [**V** + H]$^+$ for exp 4

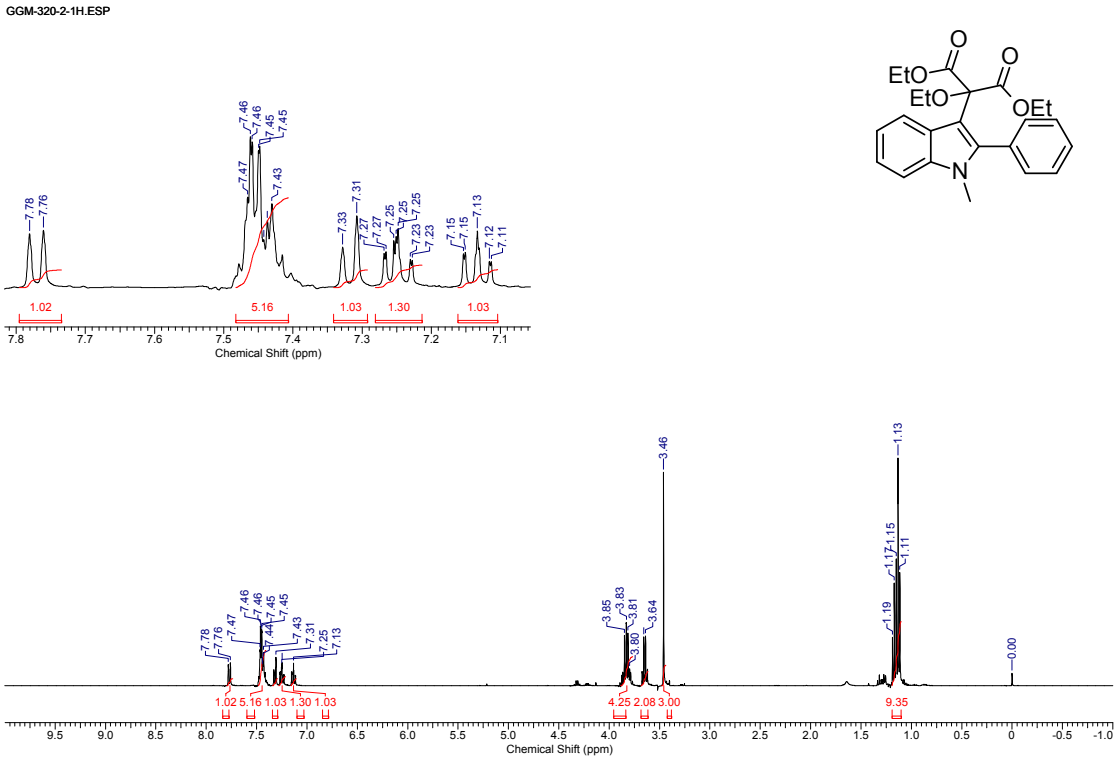


Figure S13. [1]H NMR spectrum of compound **5a**

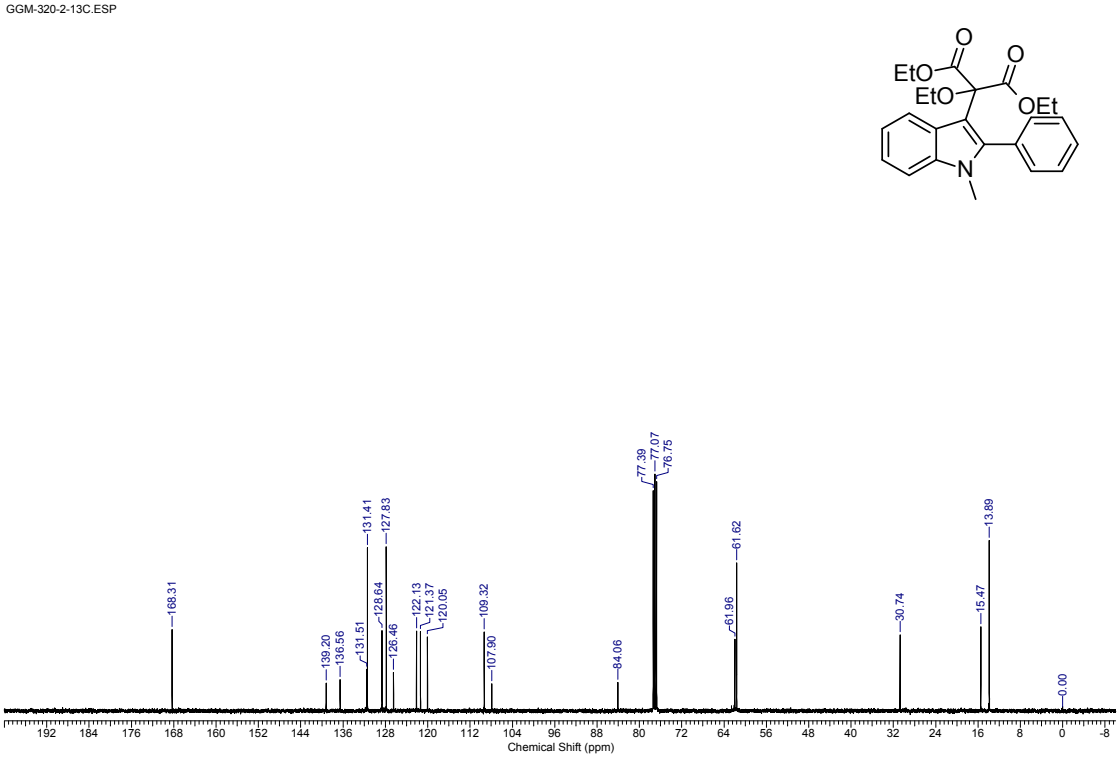


Figure S14. [13]C NMR spectrum of compound **5a**

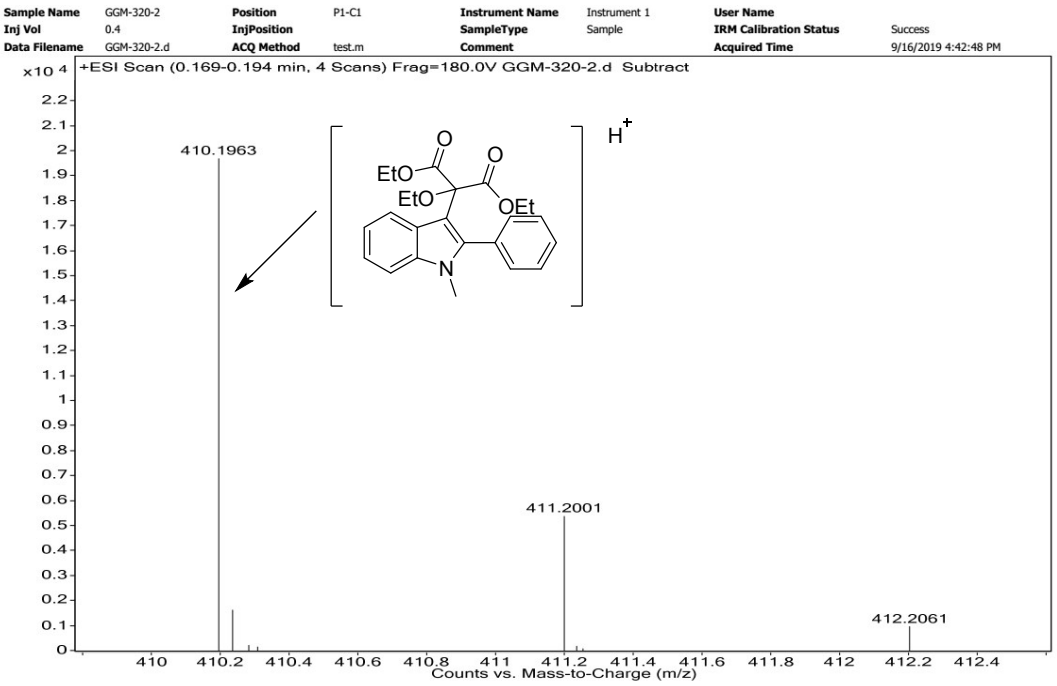


Figure S15. HRMS spectrum of compound [**5a** + H]$^+$

4. The UV-Vis Absorption Spectra, Luminescence Quenching Experiments, Cyclic Voltammetry and Data Processing

4.1 The UV-Vis absorption spectra

The UV-Vis absorption spectra were recorded in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 spectrometer.

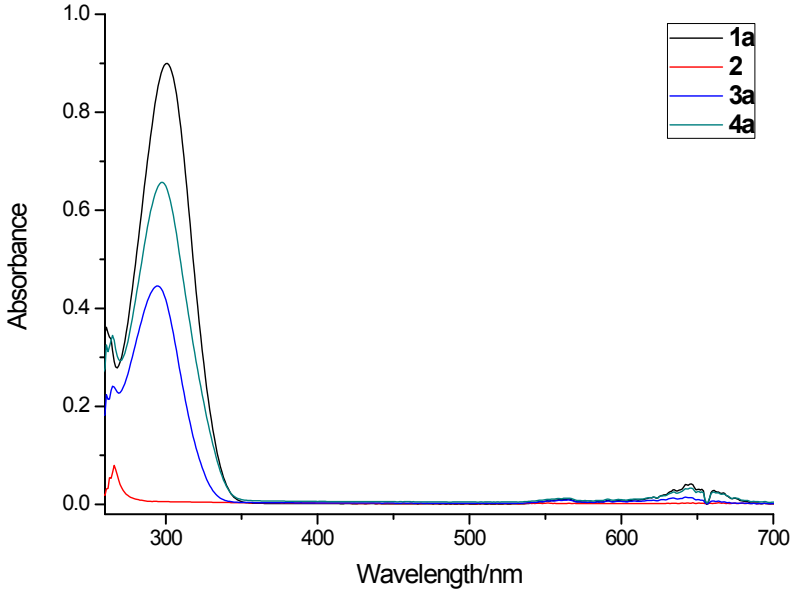


Figure S16. The UV-Vis absorption spectra of 1-methyl-2-phenylindole **1a** (λ_{max} = 355 nm), diethyl bromomalonate **2** (λ_{max} = 302 nm), **3a** (λ_{max} = 342 nm), **4a** (λ_{max} = 351 nm) in DMF (0.1 mM).

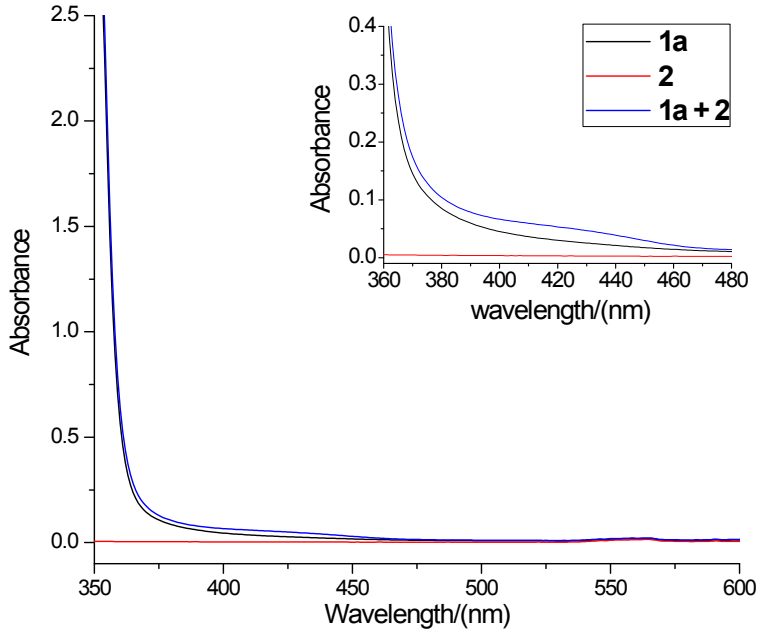


Figure S17. The UV-Vis absorption spectra of 1-methyl-2-phenylindole **1a** (0.13 M) and diethyl bromomalonate **2** (0.4 M) and mixture of **1a** (0.13 M) and **2** (0.4 M) in DMF

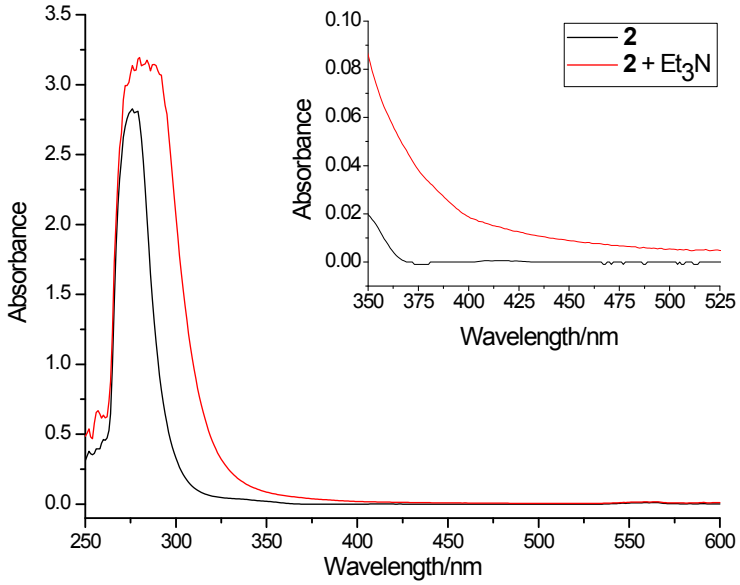


Figure S18. The UV-Vis absorption spectra of diethyl bromomalonate **2** (0.4 M) and mixture of **2** (0.4 M) and triethylamine (0.27 M) in DMF

4.2 Luminescence quenching experiments

Emission intensities were recorded using a F-4500 FL spectrophotometer. First, **3a** solution was excited at 311 nm and the emission/intensity at 378 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of **3a** and different concentration of diethyl bromomalonate **2** in EtOH in 10 mm path length quartz cuvette were collected.

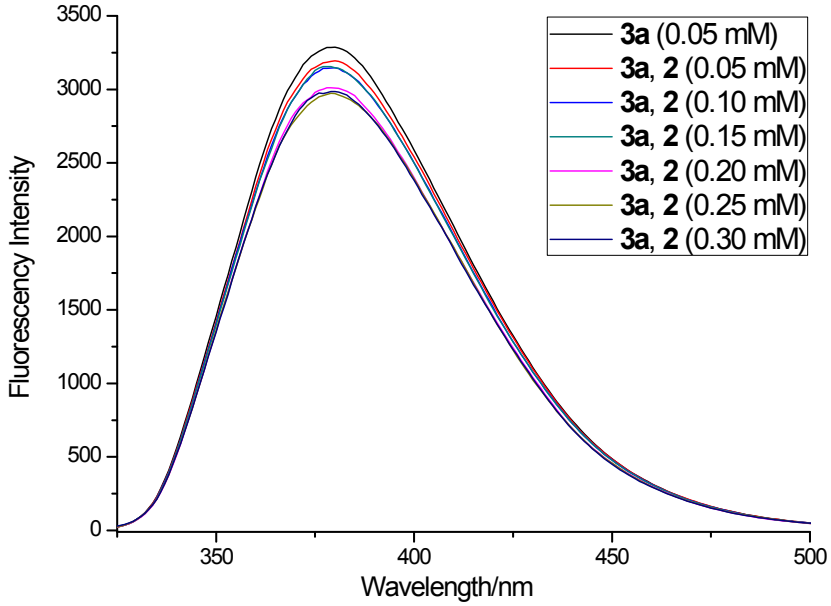


Figure S19. Luminescence quenching experiment of **3a** with **2**

4.3 Cyclic voltammetry

Cyclic voltammetry was measured under Ar balloon protection with conventional three-electrode system (Reference electrode: Ag/AgCl, working electrode: Glassy carbon, counter electrode: Pt wire, Supporting electrolyte: 0.1 M $TBAPF_6$ in DMF) at 50 mV/sec of scan rate.

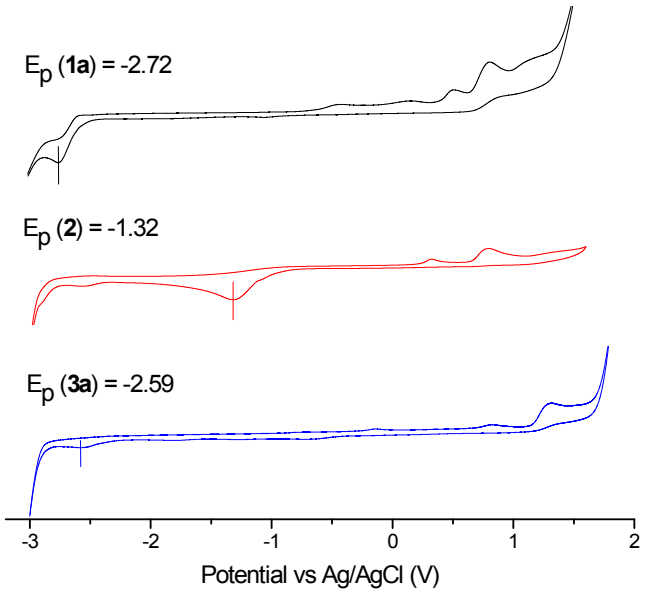


Figure S20. CV of reaction reagents (1 mM in DMF)

4.4 Data processing

We could see the reversible reduction waves of all the reagents. With these data in hand we calculated the excited redox potential, E_g by CV and UV absorption spectrometry theory.

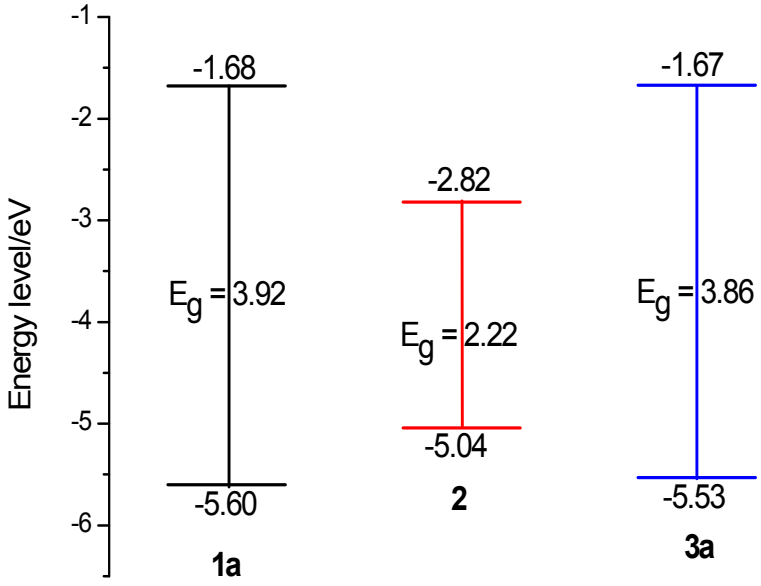


Figure S21. The E_{HOMO}, E_{LUMO} and E_g of different reagents

5. Characterization of EDA Complex

5.1 Stoichiometry of the EDA complex in solution

A Job's plot[5] was drawn to evaluate the stoichiometry of the EDA complex between the diethyl bromomalonate (**2**) and triethylamine in DMF. We measured the absorption at 430 nm in DMF solutions of triethylamine and **2** having a constant total concentration of 0.2 M but different donor/acceptor ratios. All the absorption spectra were recorded in 10 mm path length quartz cuvette using a Perkin Elmer Lambda 35 spectrometer. The absorbance values were plotted against the molar fraction (%) of diethyl bromomalonate (**2**). The maximum absorbance is obtained for a 1 : 1 mixture of triethylamine : **2**, indicating that this is the stoichiometry of the EDA complex in solution.

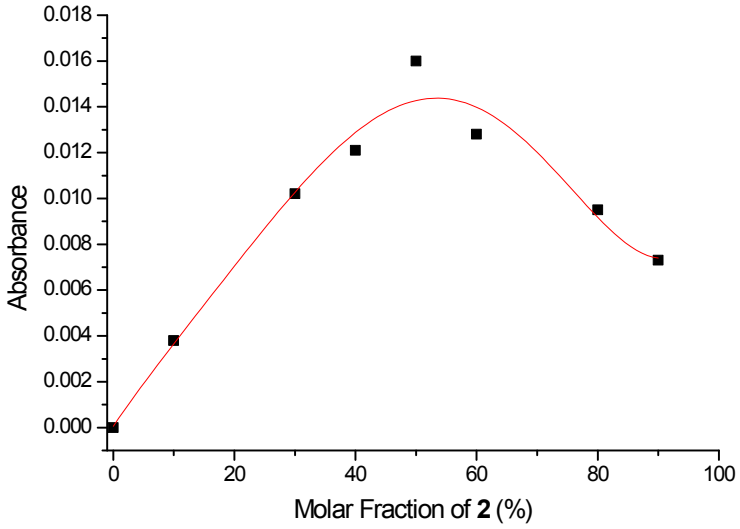


Figure S22. Job's plot in DMF

5.2 Determination of the association constant (K_{EDA})

The association constant of the EDA complex formed between diethyl bromomalonate (**2**) and 1-methyl-2-phenylindole (**1a**) was determined spectrophotometrically in DMF, employing the Benesi-Hildebrand methodology[6]. We measured the absorption at 430 nm of solutions with constant concentration of the diethyl bromomalonate (**2**, 0.05 M) but increased donor/acceptor ratios by adding excess of 1-methyl-2-phenylindole (**1a**). All the absorption spectra were recorded in 10 mm path length quartz cuvette using a Perkin Elmer Lambda 35 spectrometer. According to the methodology, a straight line is obtained when the reciprocal of the absorbance (A) is plotted against the reciprocal of the concentration of the partner in excess. The association constant (K_{EDA}), calculated dividing the intercept by the slope, is 2.4 ± 0.19 M^{-1} for the solution in DMF.

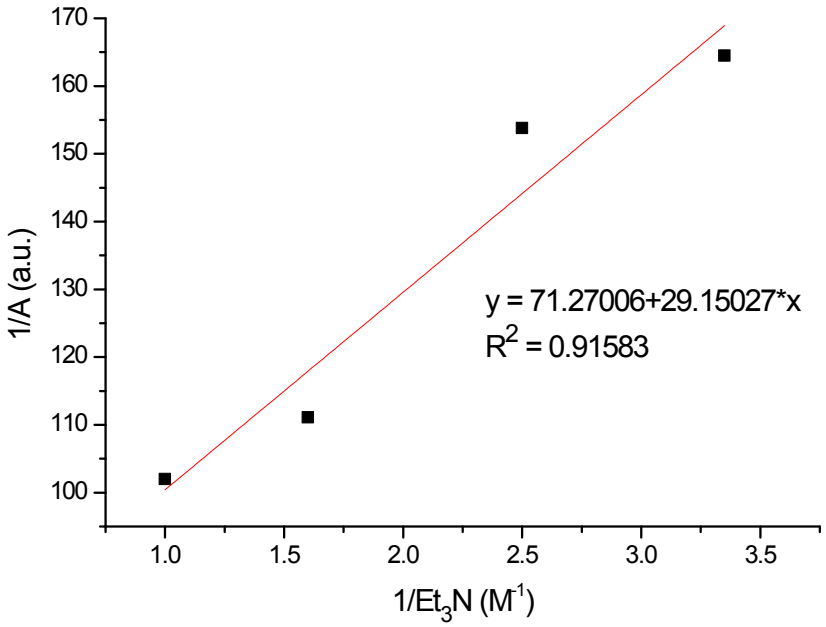


Figure S23. The Benesi-Hildebrand plot in DMF

6. Computational Details

All the calculations were conducted by using the Gaussian 16 program package.[7] The B3LYP[8] functional together with Becke-Johnson damping corrections[9] (abbreviated as B3LYP-D3BJ) and the 6-311+G(d,p) basis sets[10] were used for all the calculations. The polarizable continuum model (PCM)[11] was employed to consider the solvent effect of EtOH. The intrinsic reaction coordinate (IRC)[11] analysis was carried out to confirm that all the saddle point connected the correct reactant and product on the potential energy surface. With the help of Multiwfn 3.7-dew[12] and VMD version 1.9.3 programs[13], we drawn and analysed **TS** and intermediate **A1**, **A2**, **A3**, **A4**.

1a

Sum of electronic and zero-point Energies=			-634.176039
Sum of electronic and thermal Energies=			-634.163453
Sum of electronic and thermal Enthalpies=			-634.162509
Sum of electronic and thermal Free Energies=			-634.215499
C	-1.86451500	-0.94430500	-0.16239700
C	-1.84581500	0.46057800	0.06992200
C	-3.02079300	1.20936600	0.18224800
C	-4.22932300	0.53488500	0.04883700
C	-4.26952000	-0.85354100	-0.19047900
C	-3.10140900	-1.59627100	-0.29738600
C	-0.49929000	-1.36834100	-0.20471000
C	0.29151200	-0.25394500	-0.01199400
H	-2.99748000	2.27800000	0.35731900
H	-5.15769800	1.08866600	0.12644700
H	-5.23008000	-1.34548300	-0.29163900
H	-3.14105900	-2.66462700	-0.47880400
H	-0.13206700	-2.36367800	-0.39972800
C	-0.12098100	2.20516200	0.54481500
H	-0.15177100	2.89138700	-0.30545600
H	-0.79065700	2.57605600	1.32207100
H	0.88990000	2.18077100	0.94386700
C	1.75772500	-0.18588300	-0.02009300
C	2.44836200	0.81799300	-0.71690000
C	2.50038900	-1.17690900	0.64010400
C	3.84011200	0.83282100	-0.74452100
H	1.89615000	1.57502800	-1.25957400
C	3.89172800	-1.16395200	0.60499800
H	1.97849700	-1.95041200	1.19048900
C	4.56753800	-0.15664500	-0.08364400
H	4.35646700	1.61314500	-1.29135300
H	4.44875100	-1.93557600	1.12360600
H	5.65080200	-0.14363100	-0.10633500

N	-0.52772500	0.86204100	0.15947000

1a*

Sum of electronic and zero-point Energies=			-634.053453
Sum of electronic and thermal Energies=			-634.040548
Sum of electronic and thermal Enthalpies=			-634.039604
Sum of electronic and thermal Free Energies=			-634.092681
C	-1.84319000	-0.95412000	-0.04498200
C	-1.86139700	0.47718400	0.02129000
C	-3.03013400	1.20329600	0.00572300
C	-4.25043900	0.47650300	-0.06598900
C	-4.26295700	-0.92017700	-0.13129600
C	-3.07826900	-1.65459900	-0.12305100
C	-0.50846700	-1.34816300	-0.02868400
C	0.33003600	-0.15119200	0.03341900
H	-3.03851400	2.28471600	0.03589900
H	-5.18557600	1.02312200	-0.07260000
H	-5.21289900	-1.43841800	-0.18928800
H	-3.09025600	-2.73672000	-0.17108300
H	-0.13026800	-2.35450500	-0.10074400
C	-0.20082700	2.30450600	0.40795800
H	-0.05223600	2.89920900	-0.49665400
H	-1.02203700	2.73533900	0.97999900
H	0.70016000	2.33709000	1.01614200
C	1.74295300	-0.12343900	0.00319300
C	2.53562100	1.02362100	-0.35032200
C	2.46075900	-1.35001700	0.26702100
C	3.91117600	0.95522100	-0.38199000
H	2.05738600	1.94562000	-0.64592400
C	3.84037800	-1.38665600	0.24531500
H	1.91166200	-2.24623400	0.52385700
C	4.59340100	-0.24193000	-0.06727300
H	4.47646600	1.83535500	-0.66843100
H	4.34791100	-2.31850500	0.47119700
H	5.67543200	-0.28191300	-0.09152000
N	-0.52987000	0.92223100	0.09531000

2

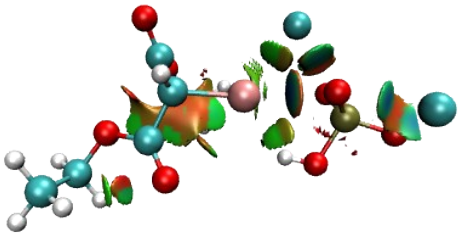
Sum of electronic and zero-point Energies=			-3148.461476
Sum of electronic and thermal Energies=			-3148.447380
Sum of electronic and thermal Enthalpies=			-3148.446436
Sum of electronic and thermal Free Energies=			-3148.505054
C	0.61633600	0.65089300	1.35747400
C	0.17095800	-0.63264000	0.64749300
H	-0.08355700	-1.33554900	1.43699600
C	-1.05986400	-0.50322000	-0.25220200
O	-1.91719800	0.32513900	0.34208100
O	0.90957500	1.74396600	0.65501800
C	-3.22300200	0.53023300	-0.29112300
H	-3.53220000	1.50707400	0.07448300
H	-3.07250000	0.57365000	-1.36902600
C	-4.19386200	-0.56119700	0.10917000
H	-5.17265700	-0.34382100	-0.32561400
H	-3.86641600	-1.53566900	-0.25663800
H	-4.30268500	-0.60465000	1.19461600
C	0.67259500	1.88644200	-0.77941500
H	-0.39128500	2.08084900	-0.91819900
H	0.95048500	0.96563900	-1.29017100
C	1.51651400	3.04578000	-1.25780200
H	2.57801800	2.84050800	-1.10750200
H	1.34086400	3.19962100	-2.32495200
H	1.25287100	3.96335700	-0.72872300
O	-1.23831500	-1.08487100	-1.29001700
O	0.73340900	0.66113100	2.56055900
Br	1.69717800	-1.45633400	-0.27794200

3a

Sum of electronic and zero-point Energies=			-1207.919103
Sum of electronic and thermal Energies=			-1207.893584
Sum of electronic and thermal Enthalpies=			-1207.892640
Sum of electronic and thermal Free Energies=			-1207.976084
C	2.18405100	-1.86902500	0.05701600
C	2.09047800	-0.60271200	0.69183600
C	3.21143200	-0.08546600	1.35991600
C	4.38338900	-0.83026700	1.37894200
C	4.45781500	-2.08385200	0.74028700
C	3.36260200	-2.62018200	0.07245200
C	0.09146100	-1.07896800	-0.27508600
C	0.75641000	-0.12052800	0.47059200
H	3.16951100	0.88123700	1.84930700
H	5.25680800	-0.44325400	1.89065900
H	5.38567200	-2.64282500	0.77227900
H	3.42490000	-3.58790100	-0.40966300
C	-1.29873500	-1.11639200	-0.75564400
C	-1.83535300	-0.04360800	-1.47925200
C	-2.10865600	-2.23602100	-0.50744100
C	-3.14803700	-0.09151800	-1.94353100
H	-1.21533000	0.81763600	-1.68472300
C	-3.41465600	-2.28503100	-0.98092700
H	-1.71661300	-3.06305000	0.07193500
C	-3.93947000	-1.21223500	-1.70202800
H	-3.54875100	0.74696900	-2.50119000
H	-4.02758500	-3.15500900	-0.77639200
H	-4.95889000	-1.24917500	-2.06771300
N	0.96349600	-2.14144800	-0.52321200
C	0.72195300	-3.29786800	-1.37397000
H	1.59984400	-3.47376600	-1.99697400
H	0.52180300	-4.19405700	-0.78137300
H	-0.12921300	-3.10478700	-2.02144500
C	0.30068500	1.21232800	0.99247000
H	0.80642800	1.37739800	1.94938300
C	-1.18097800	1.36077300	1.33538800
C	0.73524900	2.39937200	0.12670200
O	1.20102600	3.41666200	0.59013700
O	-1.88516200	2.25887700	0.93180400
O	0.55004300	2.17552200	-1.17365900
O	-1.56058900	0.43086400	2.21180000
C	0.94994600	3.21983900	-2.10798300
H	0.31282200	3.05349000	-2.97514000
H	0.71732300	4.18828700	-1.66678600

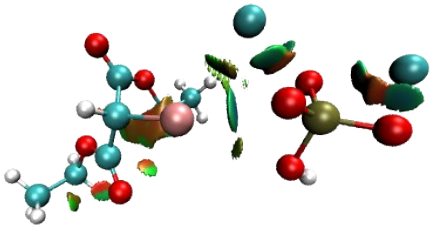
C	2.42004000	3.09130800	-2.45714900
H	2.68176300	3.84381300	-3.20537800
H	3.04706000	3.24905500	-1.57805000
H	2.63400500	2.10433500	-2.87270400
C	-2.91020100	0.53737800	2.75975700
H	-3.13442000	1.59337100	2.90779000
H	-2.83401900	0.04472100	3.72774700
C	-3.92956100	-0.13674900	1.86540400
H	-4.91683400	-0.05944200	2.32881600
H	-3.96962500	0.33653300	0.88436600
H	-3.69286500	-1.19230600	1.73056600

A1



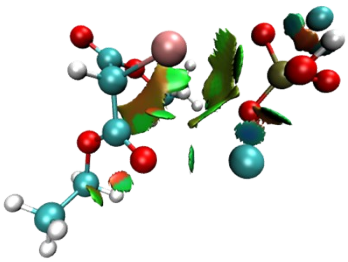
Sum of electronic and zero-point Energies=			-4991.641568
Sum of electronic and thermal Energies=			-4991.616226
Sum of electronic and thermal Enthalpies=			-4991.615282
Sum of electronic and thermal Free Energies=			-4991.703725
C	1.56782700	1.02399500	-1.40117600
C	1.44771405	-0.45016549	-0.83346115
H	1.62380700	-1.05236200	-1.69548400
C	2.42670000	-0.77443500	0.23364000
O	3.59100800	-0.15609400	0.00022500
O	1.48064000	2.07844300	-0.58290600
C	4.71430600	-0.46474700	0.88245500
H	5.34912000	0.41628900	0.80976900
H	4.33431300	-0.55686500	1.89936700
C	5.43355000	-1.71892400	0.42755600
H	6.30377800	-1.88555700	1.06755000
H	4.78464700	-2.59328700	0.49839200
H	5.78034500	-1.61487400	-0.60263400
C	1.40013200	1.97722600	0.86946000
H	2.41335600	1.82914200	1.24479600
H	0.77670500	1.12784600	1.14451800
C	0.80110000	3.26944300	1.37775700
H	-0.21238000	3.40217300	0.99457000
H	0.75710300	3.23997300	2.46905000
H	1.40948000	4.12567300	1.07964800
O	2.22400600	-1.55108900	1.13264500
O	1.71263700	1.21595400	-2.58915800
Br	-0.27096163	-0.70443375	-0.38593287
P	-4.06841434	-1.43613573	0.45305011
O	-2.59267368	-1.18944370	0.09379717
O	-4.40994284	-3.01979726	-0.09878623
O	-5.18316425	-0.51244102	-0.43808441
O	-4.37856025	-1.46044914	2.12434254
K	-5.20164448	1.98163882	-0.60903531
K	-2.79934601	-4.61894985	0.94939736
H	-4.07758035	-0.63828504	2.51811569

A2



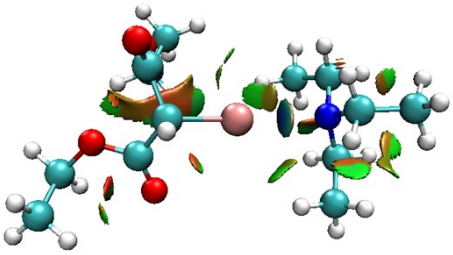
Sum of electronic and zero-point Energies=			-4991.639454
Sum of electronic and thermal Energies=			-4991.613949
Sum of electronic and thermal Enthalpies=			-4991.613005
Sum of electronic and thermal Free Energies=			-4991.702887
C	1.56782700	1.02399500	-1.40117600
C	1.43201600	-0.38957200	-0.85396100
H	1.62380700	-1.05236200	-1.69548400
C	2.42670000	-0.77443500	0.23364000
O	3.59100800	-0.15609400	0.00022500
O	1.48064000	2.07844300	-0.58290600
C	4.71430600	-0.46474700	0.88245500
H	5.34912000	0.41628900	0.80976900
H	4.33431300	-0.55686500	1.89936700
C	5.43355000	-1.71892400	0.42755600
H	6.30377800	-1.88555700	1.06755000
H	4.78464700	-2.59328700	0.49839200
H	5.78034500	-1.61487400	-0.60263400
C	1.40013200	1.97722600	0.86946000
H	2.41335600	1.82914200	1.24479600
H	0.77670500	1.12784600	1.14451800
C	0.80110000	3.26944300	1.37775700
H	-0.21238000	3.40217300	0.99457000
H	0.75710300	3.23997300	2.46905000
H	1.40948000	4.12567300	1.07964800
O	2.22400600	-1.55108900	1.13264500
O	1.71263700	1.21595400	-2.58915800
Br	-0.46285200	-0.74452000	-0.34628300
P	-4.10701900	-0.33254900	0.13573600
O	-4.19774100	0.25033900	-1.28544000
O	-3.65773500	0.98148400	1.13604100
H	-4.30062100	1.69156500	1.03290100
O	-2.92574484	-1.31989597	0.36197600
O	-5.46577596	-0.83935520	0.69998260
K	-3.28525848	-3.51262849	-1.15419485
K	-6.51061312	-2.66361567	-0.97825727

A3



Sum of electronic and zero-point Energies=			-4991.640489
Sum of electronic and thermal Energies=			-4991.615328
Sum of electronic and thermal Enthalpies=			-4991.614383
Sum of electronic and thermal Free Energies=			-4991.701267
C	2.96947917	1.63711844	1.61943053
C	2.96888138	1.43499740	3.19074309
H	3.65269323	0.62847219	3.32731244
C	3.41154480	2.62504935	3.95891919
O	4.36816944	3.28089027	3.29020157
O	2.27219034	2.63215083	1.06021072
C	5.01408490	4.40882992	3.95798912
H	5.37940622	5.02083557	3.13550148
H	4.25364522	4.95886135	4.51133109
C	6.14076219	3.93628677	4.85493184
H	6.64308118	4.80510925	5.28792005
H	5.76253010	3.31829385	5.67079257
H	6.87569645	3.36382801	4.28524138
C	1.57647370	3.66502439	1.81865912
H	2.31596322	4.41104232	2.11198718
H	1.12257393	3.22633895	2.70595535
C	0.52008247	4.25460976	0.91121402
H	-0.21238790	3.49644148	0.62791339
H	0.00023423	5.05731051	1.43956423
H	0.96970682	4.67063551	0.00739682
O	3.02238446	2.90745873	5.06403703
O	3.58003649	0.87515508	0.90127246
Br	1.35105775	0.80319993	3.64047487
P	-2.67021842	-0.77774266	4.94813079
O	-3.34999039	0.05097672	6.05215271
O	-3.68133405	-0.61995805	3.57630788
O	-2.69308983	-2.45852430	5.20200078
O	-1.15433901	-0.17728728	4.46692091
K	-1.80930196	-3.63919460	7.22064801
K	-3.96112100	1.80531465	3.03800351
H	-0.57762914	-0.11305723	5.23169554

A4



Sum of electronic and zero-point Energies=			-3440.799378
Sum of electronic and thermal Energies=			-3440.774036
Sum of electronic and thermal Enthalpies=			-3440.773092
Sum of electronic and thermal Free Energies=			-3440.859337
C	-1.90515000	1.07452400	1.45341600
C	-1.47778000	-0.29782500	0.95467900
H	-1.52603900	-0.96182200	1.81494300
C	-2.34385000	-0.91874300	-0.13300100
O	-3.59981300	-0.48330800	0.00167400
O	-1.99846500	2.10442300	0.60668700
C	-4.61309000	-1.03577900	-0.89696700
H	-5.38319600	-0.26721600	-0.91892400
H	-4.17027400	-1.13665400	-1.88717900
C	-5.14310700	-2.35424300	-0.37069000
H	-5.94135000	-2.70758900	-1.02824900
H	-4.35918800	-3.11282000	-0.34618600
H	-5.55444800	-2.23344800	0.63353200
C	-1.88334800	1.99467300	-0.84217000
H	-2.88375600	1.79852100	-1.22892100
H	-1.22428500	1.16921800	-1.10502700
C	-1.32517100	3.30357900	-1.35466900
H	-0.32362200	3.47853200	-0.95694300
H	-1.26280000	3.26606100	-2.44481800
H	-1.96954200	4.13892700	-1.07424300
O	-1.96726500	-1.71755800	-0.95382100
O	-2.11523700	1.26262000	2.63187500
Br	0.45948200	-0.25471800	0.45682400
N	3.16054900	-0.12631200	-0.15149400
C	3.75223100	-0.49175000	1.14668100
H	3.39512200	0.24399400	1.87234700
H	3.32886100	-1.45086800	1.45085300
C	5.28308500	-0.56788100	1.20448800
H	5.74930100	0.38840000	0.95719800
H	5.59521900	-0.83869300	2.21658800
H	5.67765800	-1.32461100	0.52207400

C	3.48062100	-1.05728900	-1.24380100
H	2.89362400	-0.75205900	-2.11106400
H	4.54025000	-0.96649300	-1.53616500
C	3.15769000	-2.51490400	-0.93015700
H	2.12198900	-2.62255600	-0.60049400
H	3.29247100	-3.11619700	-1.83248500
H	3.80908000	-2.92974000	-0.15829200
C	3.45205500	1.27148800	-0.50657000
H	3.23605600	1.87298400	0.38066600
H	4.52303900	1.40491000	-0.72915600
C	2.63201100	1.80517800	-1.67942200
H	2.80226600	2.88020100	-1.77819300
H	2.91087700	1.34176500	-2.62758900
H	1.56601800	1.64098300	-1.51486800

B

Sum of electronic and zero-point Energies=			-574.267217
Sum of electronic and thermal Energies=			-574.254550
Sum of electronic and thermal Enthalpies=			-574.253606
Sum of electronic and thermal Free Energies=			-574.308265
C	1.60795700	-1.15820000	-0.07973700
C	0.22639200	-1.14970200	-0.59763900
H	0.02246200	-1.77007300	-1.45988300
C	-0.88472900	-0.56974300	0.14484100
O	-2.03511500	-0.68288500	-0.53821900
O	2.23118700	-0.03052600	0.25088400
C	-3.23254000	-0.12204300	0.07431900
H	-4.04657000	-0.67335700	-0.39272300
H	-3.21005200	-0.34196500	1.14133900
C	-3.33656500	1.36772900	-0.19390700
H	-4.27409900	1.74320700	0.22396400
H	-2.51266000	1.91063600	0.27197700
H	-3.33426200	1.56893600	-1.26723400
C	1.66858200	1.27952500	-0.07594500
H	0.98981300	1.55588000	0.72899900
H	1.10481800	1.19898700	-1.00775600
C	2.82303100	2.24624000	-0.21021900
H	3.49294000	1.94780000	-1.01893400
H	2.43220400	3.24190900	-0.43335300
H	3.39291400	2.30171500	0.71946800
O	-0.78245300	-0.06431700	1.25077500
O	2.17509600	-2.22808400	0.05204200

C

Sum of electronic and zero-point Energies=			-1208.471247
Sum of electronic and thermal Energies=			-1208.445318
Sum of electronic and thermal Enthalpies=			-1208.444373
Sum of electronic and thermal Free Energies=			-1208.529713
C	1.97499700	-0.92223900	-0.31006300
C	1.83266900	-2.29228100	-0.03558000
C	2.94186300	-3.12416200	0.10879300
C	4.20816400	-2.55502800	-0.04988600
C	4.36174200	-1.20000200	-0.34607200
C	3.23644800	-0.37435300	-0.47423000
C	0.59638600	-0.29445500	-0.31105100
C	-0.30804000	-1.51174800	-0.25164200
H	2.83732600	-4.17647700	0.33847800
H	5.08458000	-3.18364400	0.05694700
H	5.35290400	-0.78309300	-0.47589200
H	3.35766900	0.67479400	-0.70991200
N	0.47940200	-2.63164500	0.01859600
C	0.04348100	-4.01711000	-0.09090900
H	0.83975500	-4.60541400	-0.54650000
H	-0.19493200	-4.44709100	0.88504800
H	-0.83534300	-4.07588200	-0.73001500
C	-1.72721000	-1.49822900	-0.38704700
C	-2.58884800	-2.42680200	0.25973200
C	-2.34751400	-0.49222500	-1.17823700
C	-3.96551100	-2.35198700	0.11205400
H	-2.17542200	-3.17598800	0.92010800
C	-3.72430500	-0.43015000	-1.31852700
H	-1.73249000	0.23281300	-1.69475000
C	-4.55210800	-1.35852000	-0.67832000
H	-4.59222300	-3.06694300	0.63372100
H	-4.15970600	0.34551400	-1.93886200
H	-5.62841100	-1.30472800	-0.78726700
H	0.41266000	0.33229600	-1.18482600
C	0.45342500	0.60402700	0.97434900
H	0.75399900	0.01163700	1.83705100
C	1.36057900	1.82907700	0.95340100
C	-0.97500200	1.05400900	1.26490800
O	-1.64337300	0.60878700	2.16972100
O	1.87871600	2.28264700	1.95071800
O	1.49895500	2.34714900	-0.26599300
O	-1.38260600	1.99991600	0.41784500
C	-2.74561400	2.48875800	0.57564200
H	-3.41425300	1.62790700	0.57836500

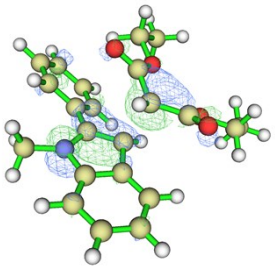
H	-2.81445300	2.99231700	1.54136900
C	2.29880300	3.55868800	-0.38833700
H	3.30049500	3.34714700	-0.01063500
H	1.84737900	4.32748900	0.24050300
C	2.30726900	3.94495600	-1.84984600
H	2.89861800	4.85426300	-1.97988800
H	2.75160200	3.15607900	-2.46036500
H	1.29422000	4.13914300	-2.20808300
C	-3.02300400	3.42238700	-0.58009500
H	-4.03871200	3.81509800	-0.49273800
H	-2.32753800	4.26432700	-0.58128500
H	-2.93908500	2.89628300	-1.53330800

D

Sum of electronic and zero-point Energies=			-1208.333914
Sum of electronic and thermal Energies=			-1208.308389
Sum of electronic and thermal Enthalpies=			-1208.307445
Sum of electronic and thermal Free Energies=			-1208.391112
C	2.06717900	-0.79453700	-0.22912600
C	1.98602100	-2.18172800	-0.11564400
C	3.09242800	-3.01015500	-0.02864700
C	4.34127300	-2.38731900	-0.06514700
C	4.44924000	-1.00089400	-0.19039400
C	3.31352500	-0.18883000	-0.27289000
C	0.65999700	-0.24553100	-0.24217900
C	-0.17539100	-1.51059600	-0.23885700
H	3.00576100	-4.08395900	0.06427100
H	5.23638300	-2.99246900	0.00077100
H	5.43035200	-0.54435100	-0.22684600
H	3.41499300	0.88123000	-0.38000500
N	0.60830800	-2.55940700	-0.14317800
C	0.21051400	-3.97038700	-0.17681600
H	0.88254300	-4.49397400	-0.85348300
H	0.29201900	-4.39366000	0.82401100
H	-0.80988500	-4.04984200	-0.53647300
C	-1.62404200	-1.54812600	-0.34582000
C	-2.40611000	-2.34821600	0.50434300
C	-2.24829800	-0.73757500	-1.30944700
C	-3.78881400	-2.33584700	0.38617300
H	-1.93841600	-2.93639900	1.28229400
C	-3.63061400	-0.75472800	-1.43754700
H	-1.65347200	-0.12071800	-1.96947400
C	-4.40169000	-1.54822400	-0.58858300
H	-4.38874000	-2.93665700	1.05774800
H	-4.10623900	-0.14534600	-2.19543600
H	-5.48073300	-1.54766300	-0.68195300
H	0.43982900	0.34249900	-1.13608500
C	0.38692100	0.63269600	1.01856300
H	0.69891200	0.08646500	1.90677600
C	1.17639300	1.94409600	1.00078100
C	-1.08819900	0.98899600	1.23869900
O	-1.73879500	0.57174600	2.16583200
O	1.50020600	2.51389600	2.01625400
O	1.41126700	2.38030200	-0.23140200
O	-1.52970500	1.82267800	0.30200000
C	-2.91843300	2.26643300	0.40531800
H	-3.55168900	1.38041100	0.44789100

H	-3.02220700	2.81847900	1.34018700
C	2.06872100	3.67911200	-0.36920000
H	3.03483100	3.62443400	0.13424100
H	1.45118200	4.42000800	0.13971900
C	2.20287300	3.95721500	-1.84810300
H	2.68971700	4.92493500	-1.98821700
H	2.81044900	3.19340600	-2.33768700
H	1.22331900	3.99217900	-2.32896900
C	-3.20610300	3.12236200	-0.80546800
H	-4.23868100	3.47548400	-0.75852400
H	-2.54629200	3.99162000	-0.83657800
H	-3.08022400	2.55146000	-1.72746700

TS



Sum of electronic and zero-point Energies=			-1208.457859
Sum of electronic and thermal Energies=			-1208.431918
Sum of electronic and thermal Enthalpies=			-1208.430974
Sum of electronic and thermal Free Energies=			-1208.517730
C	2.23884300	-0.43903500	-0.47780800
C	2.39635200	-1.78736800	-0.09154900
C	3.65381500	-2.34861000	0.12134600
C	4.76513300	-1.53205700	-0.08704700
C	4.62560100	-0.19774900	-0.49286600
C	3.36077600	0.35923400	-0.68308800
C	0.79791500	-0.16938900	-0.52153500
C	0.16971200	-1.45817000	-0.37001100
H	3.77513000	-3.37709700	0.43556300
H	5.75633200	-1.94212800	0.06643900
H	5.50940700	0.40728000	-0.65466300
H	3.25624900	1.39384000	-0.98469500
N	1.13684400	-2.38257200	-0.01651600
C	0.95640400	-3.81747200	0.15039300
H	1.83274700	-4.33108300	-0.24295800
H	0.83105300	-4.08524000	1.20213200
H	0.08377800	-4.14550400	-0.40969100
C	-1.24736400	-1.74141000	-0.51990900
C	-1.93925500	-2.65864100	0.29494000
C	-1.98048800	-1.04673700	-1.50336700
C	-3.29893500	-2.88463500	0.11573400
H	-1.42400400	-3.16145800	1.10128600
C	-3.33850500	-1.27642200	-1.67792000
H	-1.47467100	-0.33386100	-2.14197300
C	-4.00641000	-2.20078700	-0.87323700
H	-3.81166800	-3.58646600	0.76297100
H	-3.87774000	-0.73455600	-2.44583600
H	-5.06655300	-2.37803100	-1.00852500
H	0.37022700	0.57107700	-1.18334200
C	0.48524400	0.90448600	1.15036400
H	1.12400100	0.39651000	1.86204700

C	1.03414900	2.22958500	0.80971200
C	-0.93119300	0.69773900	1.49895900
O	-1.27954700	-0.09515700	2.36082400
O	2.05386400	2.67927200	1.31210800
O	0.36119300	2.86504300	-0.16470100
O	-1.80142900	1.39652200	0.75542000
C	-3.21015000	1.15627500	1.00491000
H	-3.40605100	0.09132200	0.87857200
H	-3.43217200	1.42976000	2.03834400
C	0.85238900	4.16960000	-0.56357400
H	1.88480700	4.06634800	-0.90294300
H	0.84372300	4.82588400	0.30885500
C	-0.05731600	4.67530100	-1.66194200
H	0.27941000	5.66181000	-1.98948700
H	-0.04040900	4.00329600	-2.52289800
H	-1.08635800	4.76309300	-1.30677500
C	-3.98963100	1.99479600	0.01659200
H	-5.06004400	1.83678400	0.16931000
H	-3.77617100	3.05784300	0.14886000
H	-3.74409000	1.71192300	-1.00877800

B-anione

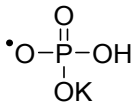
Sum of electronic and zero-point Energies=			-574.443488
Sum of electronic and thermal Energies=			-574.431070
Sum of electronic and thermal Enthalpies=			-574.430126
Sum of electronic and thermal Free Energies=			-574.483915
C	1.55027000	-1.20859800	-0.05948900
C	0.15675300	-1.25253300	-0.30199700
H	-0.17709500	-2.11876300	-0.85774200
C	-0.85974000	-0.44336600	0.25804000
O	-2.11015200	-0.82059000	-0.23903400
O	2.16385600	-0.05351900	0.39813600
C	-3.25029800	-0.08276000	0.22756500
H	-4.09089400	-0.77201000	0.12628600
H	-3.12044400	0.16143900	1.28291200
C	-3.48310800	1.17618200	-0.59475100
H	-4.38851000	1.68597000	-0.25185000
H	-2.64141900	1.86396300	-0.49346900
H	-3.60929100	0.92980400	-1.65231200
C	1.75031900	1.24502400	-0.07741800
H	1.07173000	1.68915600	0.64893100
H	1.20066900	1.11964500	-1.01385400
C	2.99353700	2.09168900	-0.27936300
H	3.65435100	1.65135100	-1.03031600
H	2.70795300	3.09321200	-0.61481800
H	3.55122200	2.19374600	0.65531900
O	-0.78818000	0.46114400	1.09740800
O	2.32139200	-2.16845300	-0.23583500

III

Sum of electronic and zero-point Energies=			-574.916055
Sum of electronic and thermal Energies=			-574.903243
Sum of electronic and thermal Enthalpies=			-574.902299
Sum of electronic and thermal Free Energies=			-574.958443
C	-1.13965000	-1.01701500	-0.76035300
C	-0.34472700	-1.65176000	0.36664700
H	-0.91745300	-1.70322800	1.29358800
H	-0.11339400	-2.67458800	0.06792500
C	0.97687700	-0.96817500	0.68133200
O	1.69116200	-1.29981500	1.59856900
O	-1.17236600	-1.49264000	-1.87339200
O	1.24929800	0.01613900	-0.17604500
O	-1.83802100	0.10074100	-0.51320300
C	2.49510500	0.75146100	0.01715500
H	3.32191200	0.05045000	-0.10498100
H	2.50794100	1.13237000	1.03904900
C	2.52504800	1.86082100	-1.00876800
H	1.68042300	2.53963300	-0.87401200
H	3.44827900	2.43324800	-0.89293600
H	2.49547100	1.45765000	-2.02300600
C	-1.84819000	0.73576900	0.79732700
H	-2.28013000	0.04356400	1.52251200
H	-0.82317200	0.97293900	1.08497500
C	-2.68069000	1.99278300	0.67805700
H	-3.70219400	1.75543700	0.37476000
H	-2.71586700	2.49525500	1.64744500
H	-2.24503100	2.67856400	-0.05112500

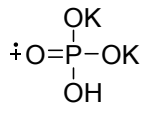
K_2HPO_4

Sum of electronic and zero-point Energies=			-1843.168590
Sum of electronic and thermal Energies=			-1843.159364
Sum of electronic and thermal Enthalpies=			-1843.158420
Sum of electronic and thermal Free Energies=			-1843.205478
P	3.02730200	0.98618500	-0.05468800
O	3.19753800	-0.39536000	0.63423200
O	2.09200100	1.93131200	0.97569000
H	2.59944300	2.16635500	1.76060000
O	2.16505700	0.89176600	-1.32373400
O	4.37933000	1.70473700	-0.19630800
K	1.84255600	-1.82912900	-1.11799400
K	5.83354500	-0.20751400	0.95718000



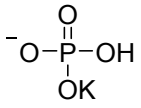
(**$KHPO_4$·**)

Sum of electronic and zero-point Energies=			-1243.060487
Sum of electronic and thermal Energies=			-1243.052875
Sum of electronic and thermal Enthalpies=			-1243.051931
Sum of electronic and thermal Free Energies=			-1243.094859
P	-0.13825792	0.94817854	-0.21603893
O	0.09023146	-0.63932274	0.37703128
O	0.32995249	2.07655444	0.98047553
H	1.25584659	1.94645717	1.19817901
O	-1.78750679	1.17991430	-0.60382326
O	0.69998528	1.14828141	-1.44962323
K	2.68466390	-1.00386613	0.98705459



(**K_2HPO_4**·+)

Sum of electronic and zero-point Energies=			-1842.941727
Sum of electronic and thermal Energies=			-1842.931402
Sum of electronic and thermal Enthalpies=			-1842.930458
Sum of electronic and thermal Free Energies=			-1842.983607
P	-0.13825792	0.94817854	-0.21603893
O	0.09023146	-0.63932274	0.37703128
O	0.32995249	2.07655444	0.98047553
H	1.25584659	1.94645717	1.19817901
O	-1.78750679	1.17991430	-0.60382326
O	0.69998528	1.14828141	-1.44962323
K	2.68466390	-1.00386613	0.98705459
K	-1.98231242	2.55618946	-2.90686851



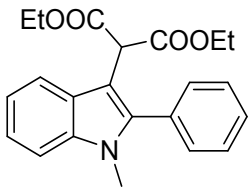
(**$KHPO_4^-$**)

Sum of electronic and zero-point Energies=			-1243.259438
Sum of electronic and thermal Energies=			-1243.252268
Sum of electronic and thermal Enthalpies=			-1243.251324
Sum of electronic and thermal Free Energies=			-1243.292128
P	-0.11178239	0.76830822	-0.33698095
O	0.09148210	-0.62388789	0.63491080
O	0.31779997	2.15837582	0.56150170
H	1.23520562	2.09099750	0.83614153
O	-1.74591120	0.88832583	-0.82618315
O	0.76934574	0.66456579	-1.55241246
K	2.66212918	-0.81268753	1.40447450

KH_2PO_4

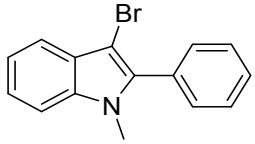
Sum of electronic and zero-point Energies=			-1243.713913
Sum of electronic and thermal Energies=			-1243.706008
Sum of electronic and thermal Enthalpies=			-1243.705064
Sum of electronic and thermal Free Energies=			-1243.748799
P	1.03349442	-0.02029189	0.11596816
O	1.46897675	-0.48447894	1.47577473
O	-0.41482948	0.24999786	-0.21627161
O	1.92246696	1.33117553	-0.21100166
H	1.62351359	1.77587104	-1.01384763
O	1.54171776	-1.08543161	-1.03939683
H	2.41631138	-1.44150001	-0.83933482
K	-2.93099459	-0.00632082	0.00214858

7. Characterization Data



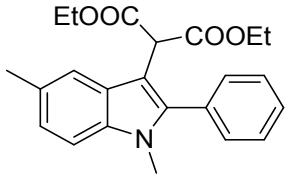
diethyl 2-(1-methyl-2-phenyl-1*H*-indol-3-yl)malonate (3a)

White solid (59.3 mg, 87%), mp. 89.9-90.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.95 Hz, 1H), 7.53-7.45 (m, 5H), 7.34 (d, J = 8.19 Hz, 1H), 7.26 (t, J = 7.09 Hz, 1H), 7.16 (t, J = 7.21 Hz, 1H), 4.74 (s, 1H), 4.20-4.12 (m, 4H), 3.59 (s, 3H), 1.23 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 140.2, 137.3, 131.0, 130.7, 128.7, 128.6, 126.4, 122.1, 121.2, 120.0, 109.5, 105.0, 61.5, 50.3, 31.0, 14.1. HRMS (ESI) calcd. for $C_{22}H_{24}NO_4$ $(M+H)^+$: 366.1700, found: 366.1704.



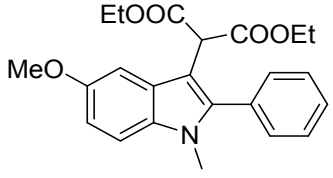
3-bromo-1-methyl-2-phenyl-1*H*-indole (4a)

Gray solid (1.7 mg, 3%), mp. 61.5-61.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.82 Hz, 1H), 7.54-7.44 (m, 5H), 7.36-7.28 (m, 2H), 7.23 (td, J_1 = 7.34 Hz, J_2 = 1.10 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 136.8, 130.7, 130.4, 128.7, 128.5, 127.2, 122.9, 120.6, 119.4, 109.7, 90.1, 31.7. HRMS (ESI) calcd. for $C_{15}H_{13}BrN$ $(M+H)^+$: 286.0226, found: 286.0225.



diethyl 2-(1,5-dimethyl-2-phenyl-1*H*-indol-3-yl)malonate (3b)

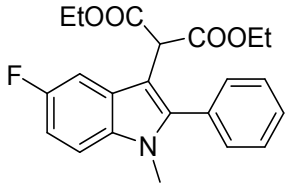
Yellow liquid (64.7mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.52-7.43 (m, 5H), 7.22 (d, J = 8.44 Hz, 1H), 7.08 (d, J = 8.44 Hz, 1H), 4.71 (s, 1H), 4.21-4.11 (m, 4H), 3.55 (s, 3H), 2.47 (s, 3H), 1.23 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 140.2, 135.7, 131.0, 130.9, 129.1, 128.6, 128.5, 126.6, 123.7, 120.7, 109.6, 104.4, 61.5, 50.3, 31.0, 21.7, 14.1. HRMS (ESI) calcd. for $C_{23}H_{26}NO_4$ $(M+H)^+$: 380.1856, found: 380.1855.



diethyl 2-(5-methoxy-1-methyl-2-phenyl-1*H*-indol-3-yl)malonate (3c)

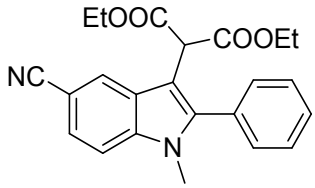
Yellow solid (47.0 mg, 59%), mp. 61.3-62.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.42 (m, 5H), 7.26 (d, J = 2.45 Hz, 1H), 7.23 (d, J = 8.80 Hz, 1H), 6.92 (dd, J_1 = 8.80 Hz, J_2 = 2.45 Hz,

1H), 4.71 (s, 1H), 4.16 (q, J = 7.09 Hz, 4H), 3.86 (s, 3H), 3.55 (s, 3H), 1.23 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 154.3, 140.7, 132.7, 130.9, 130.8, 128.7, 128.6, 126.7, 112.5, 110.2, 104.6, 102.9, 61.5, 55.9, 50.3, 31.1, 14.2. HRMS (ESI) calcd. for $C_{23}H_{26}NO_5$ $(M+H)^+$: 396.1805, found: 396.1803.



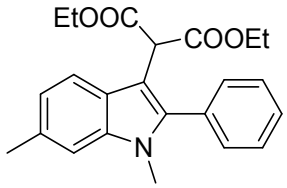
diethyl 2-(5-fluoro-1-methyl-2-phenyl-1*H*-indol-3-yl)malonate (3d)

Yellow solid (37.6mg, 49%), mp. 64.5-65.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.43 (m, 6H), 7.26-7.23 (m, 1H), 7.00 (td, J_1 = 9.05 Hz, J_2 = 2.57 Hz, 1H), 4.68(s, 1H), 4.22-4.14 (m, 4H), 3.57 (s, 3H), 1.24 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 158.0 (d, ^1J = 234.0 Hz), 141.8, 133.9, 130.9, 130.4, 128.9, 128.7, 126.6 (d, ^3J = 10.3 Hz), 110.5 (d, ^2J = 26.4 Hz), 110.1 (d, ^3J = 9.5 Hz), 106.2 (d, ^2J = 24.2 Hz), 105.0 (d, ^4J = 5.1 Hz), 61.6, 50.2, 31.2, 14.1. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -124.1. HRMS (ESI) calcd. for $C_{22}H_{23}FNO_4$ $(M+H)^+$: 384.1606, found: 384.1605.



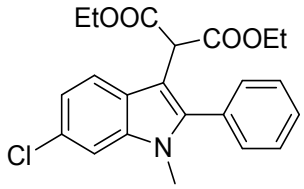
diethyl 2-(5-cyano-1-methyl-2-phenyl-1*H*-indol-3-yl)malonate (3e)

Yellow solid (15.7 mg, 20%), mp. 92.4-93.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.55-7.52 (m, 3H), 7.49 (dd, J_1 = 8.56 Hz, J_2 = 1.59 Hz, 1H), 7.45-7.43 (m, 2H), 7.39 (d, J = 8.56 Hz, 1H), 4.70 (s, 1H), 4.23-4.15 (m, 4H), 3.62 (s, 3H), 1.26 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 142.5, 138.8, 130.8, 129.6, 129.5, 128.9, 127.2, 126.1, 125.0, 120.9, 110.4, 106.1, 103.1, 61.9, 50.1, 31.3, 14.1. HRMS (ESI) calcd. for $C_{23}H_{23}N_2O_4$ $(M+H)^+$: 391.1652, found: 391.1653.



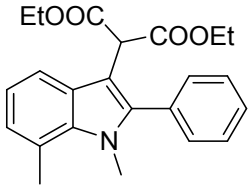
diethyl 2-(1,6-dimethyl-2-phenyl-1*H*-indol-3-yl)malonate (3f)

White solid (64.2 mg, 85%), mp. 113.8-114.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.19 Hz, 1H), 7.50-7.42 (m, 5H), 7.12 (s, 1H), 6.99 (d, J = 8.19 Hz, 1H), 4.71 (s, 1H), 4.21-4.09 (m, 4H), 3.54 (s, 3H), 2.49 (s, 3H), 1.22 (d, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 139.6, 137.7, 131.9, 131.0, 130.9, 128.6, 128.6, 124.3, 121.7, 120.9, 109.5, 104.9, 61.5, 50.3, 30.9, 21.9, 14.1. HRMS (ESI) calcd. for $C_{23}H_{26}NO_4$ $(M+H)^+$: 380.1856, found: 380.1858.



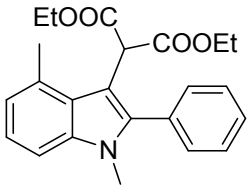
diethyl 2-(6-chloro-1-methyl-2-phenyl-1*H*-indol-3-yl)malonate (3g)

Yellow solid (58.5mg, 73%), mp. 77.5-77.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.56 Hz, 1H), 7.54-7.48 (m, 3H), 7.44-7.42 (m, 2H), 7.34 (d, J = 1.83 Hz, 1H), 7.13 (dd, J_1 = 8.56 Hz, J_2 = 1.71 Hz, 1H), 4.69 (s, 1H), 4.21-4.13 (m, 4H), 3.54 (s, 3H), 1.22 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 140.9, 137.8, 130.9, 130.2, 129.0, 128.7, 128.0, 124.9, 122.2, 120.6, 109.6, 105.2, 61.6, 50.1, 31.1, 14.1. HRMS (ESI) calcd. for $C_{22}H_{23}ClNO_6$ $(M+H)^+$: 400.1310, found: 400.1308.



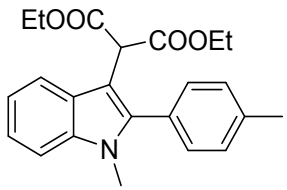
diethyl 2-(1,7-dimethyl-2-phenyl-1*H*-indol-3-yl)malonate (3h)

White solid (59.6 mg, 85%), mp. 118.2-119.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 7.95 Hz, 1H), 7.51-7.42 (m, 5H), 7.01 (t, J = 7.82 Hz, 1H), 6.94 (d, J = 7.09 Hz, 1H), 4.68 (s, 1H), 4.17-4.10 (m, 4H), 3.79 (d, J = 1.10 Hz, 3H), 2.78 (s, 3H), 1.21 (td, J_1 = 7.09 Hz, J_2 = 1.59 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 141.2, 136.3, 131.2, 131.0, 128.7, 128.5, 127.2, 125.1, 121.2, 120.0, 119.0, 105.3, 61.4, 50.3, 34.4, 20.4, 14.1. HRMS (ESI) calcd. for $C_{23}H_{26}NO_4$ $(M+H)^+$: 380.1856, found: 380.1857.



diethyl 2-(1,4-dimethyl-2-phenyl-1*H*-indol-3-yl)malonate (3i)

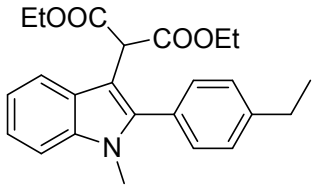
White solid (54.7 mg, 66%), mp. 105.4-106.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.43 (m, 5H), 7.19-7.11 (m, 2H), 5.19 (s, 1H), 4.04-3.92 (m, 4H), 3.49 (s, 3H), 2.65 (s, 3H), 1.17 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 140.1, 137.3, 131.5, 131.2, 130.2, 128.8, 128.1, 125.7, 122.4, 122.0, 107.6, 105.4, 61.4, 51.0, 31.0, 20.7, 14.0. HRMS (ESI) calcd. for $C_{23}H_{26}NO_4$ $(M+H)^+$: 380.1856, found: 380.1858.



diethyl 2-(1-methyl-2-(*p*-tolyl)-1*H*-indol-3-yl)malonate (3j)

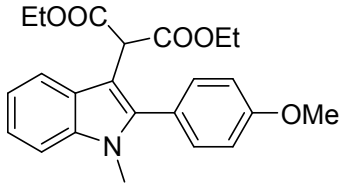
Yellow solid (54.6 mg, 87%), mp. 115.9-117.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.95 Hz, 1H), 7.35-7.30 (m, 5H), 7.24 (td, J_1 = 8.19 Hz, J_2 = 1.10 Hz, 1H), 7.15 (td, J_1 = 6.97 Hz, J_2 = 0.98 Hz, 1H), 4.73 (s, 1H), 4.20-4.12 (m, 4H), 3.58 (s, 3H), 2.44 (s, 3H), 1.22 (t,

J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 140.3, 138.6, 137.2, 130.8, 129.3, 127.6, 126.4, 121.9, 121.1, 119.9, 109.4, 104.8, 61.4, 50.3, 30.9, 21.4, 14.1. HRMS (ESI) calcd. for $C_{23}H_{26}NO_4$ $(M+H)^+$: 380.1856, found: 380.1857.



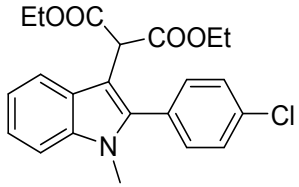
diethyl 2-(2-(4-ethylphenyl)-1-methyl-1*H*-indol-3-yl)malonate (3k)

Yellow solid (61.4 mg, 78%), mp. 77.4-78.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.95 Hz, 1H), 7.38-7.32 (m, 5H), 7.24 (t, *J* = 7.09 Hz, 1H), 7.15 (t, *J* = 7.09 Hz, 1H), 4.75 (s, 1H), 4.22-4.10 (m, 4H), 3.58 (s, 3H), 2.74 (q, *J* = 7.58 Hz, 2H), 1.31 (t, *J* = 7.58 Hz, 3H), 1.23 (t, *J* = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 144.8, 140.4, 137.2, 130.9, 128.1, 127.8, 126.3, 121.9, 121.1, 119.8, 109.4, 104.8, 61.4, 50.3, 31.0, 28.7, 15.4, 14.1. HRMS (ESI) calcd. for $C_{24}H_{28}NO_4$ $(M+H)^+$: 394.2013, found: 394.2015.



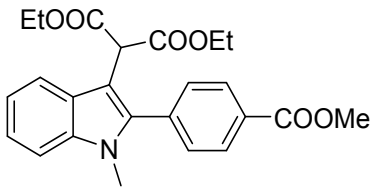
diethyl 2-(2-(4-methoxyphenyl)-1-methyl-1*H*-indol-3-yl)malonate (3l)

Yellow solid (52.3 mg, 66%), mp. 114.7-117.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.95 Hz, 1H), 7.37 (d, *J* = 8.80 Hz, 2H), 7.32 (d, *J* = 8.07 Hz, 1H), 7.24 (t, *J* = 8.07 Hz, 1H), 7.15 (t, *J* = 8.07 Hz, 1H), 7.03 (d, *J* = 8.80 Hz, 2H), 4.73 (s, 1H), 4.22-4.10 (m, 4H), 3.88 (s, 3H), 3.57 (s, 3H), 1.23 (t, *J* = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 160.0, 140.1, 137.1, 132.2, 126.4, 122.8, 121.9, 121.0, 119.9, 114.0, 109.4, 104.8, 61.5, 55.4, 50.4, 30.9, 14.1. HRMS (ESI) calcd. for $C_{23}H_{26}NO_5$ $(M+H)^+$: 396.1805, found: 396.1807.



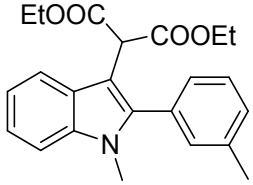
diethyl 2-(2-(4-chlorophenyl)-1-methyl-1*H*-indol-3-yl)malonate (3m)

Yellow solid (51.1 mg, 64%), mp. 132.6-115.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.95 Hz, 1H), 7.50-7.39 (m, 4H), 7.33 (d, *J* = 8.19 Hz, 1H), 7.26 (t, *J* = 6.97 Hz, 1H), 7.17 (t, *J* = 6.97 Hz, 1H), 4.69 (s, 1H), 4.23-4.10 (m, 4H), 3.57 (s, 3H), 1.23 (t, *J* = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 138.8, 137.3, 135.0, 132.3, 129.2, 128.9, 126.3, 122.4, 121.2, 120.1, 109.5, 105.4, 61.6, 50.2, 31.0, 14.1. HRMS (ESI) calcd. for $C_{22}H_{23}ClNO_4$ $(M+H)^+$: 400.1310, found: 400.1311.



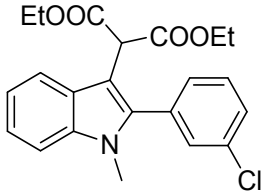
diethyl 2-(2-(4-(methoxycarbonyl)phenyl)-1-methyl-1*H*-indol-3-yl)malonate (3n)

Yellow solid (59.7 mg, 70%), mp. 96.1-97.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.07 Hz, 2H), 7.80 (d, J = 8.68 Hz, 1H), 7.56 (d, J = 7.95 Hz, 2H), 7.35 (d, J = 8.19 Hz, 1H), 7.27 (td, J_1 = 8.19 Hz, J_2 = 1.10 Hz, 1H), 7.17 (t, J = 7.09 Hz, 1H), 4.71 (s, 1H), 4.20-4.11 (m, 4H), 3.96 (s, 3H), 3.59 (s, 3H), 1.22 (s, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 166.7, 138.9, 137.6, 135.4, 131.0, 130.3, 129.8, 126.4, 122.6, 121.3, 120.2, 109.6, 105.7, 61.6, 52.4, 50.2, 31.1, 14.1. HRMS (ESI) calcd. for $C_{24}H_{26}NO_6$ $(M+H)^+$: 424.1755, found: 424.1757.



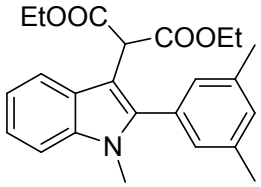
diethyl 2-(1-methyl-2-(*m*-tolyl)-1*H*-indol-3-yl)malonate (3o)

Yellow solid (58.6 mg, 77%), mp. 78.1-78.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.95 Hz, 1H), 7.39 (t, J = 7.89 Hz, 1H), 7.33 (d, J = 8.07 Hz, 1H), 7.28-7.23 (m, 4H), 7.16 (t, J = 7.95 Hz, 1H), 4.74 (s, 1H), 4.21-4.13 (m, 4H), 3.58 (s, 3H), 2.43 (s, 3H), 1.23 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 140.4, 138.3, 137.2, 131.6, 130.6, 129.5, 128.4, 128.0, 126.4, 122.0, 121.2, 119.9, 109.5, 104.9, 61.5, 50.3, 31.0, 21.5, 14.1. HRMS (ESI) calcd. for $C_{23}H_{26}NO_4$ $(M+H)^+$: 380.1856, found: 380.1857.



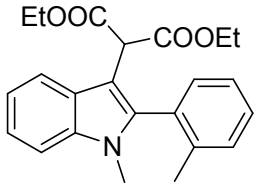
diethyl 2-(2-(3-chlorophenyl)-1-methyl-*1H*-indol-3-yl)malonate (3p)

Yellow solid (55.2 mg, 69%), mp. 84.7-85.6°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.95 Hz, 1H), 7.49-7.45 (m, 3H), 7.37-7.33 (m, 2H), 7.27 (td, J_1 = 7.43 Hz, J_2 = 1.10 Hz, 1H), 7.17 (td, J_1 = 8.01 Hz, J_2 = 1.04 Hz, 1H), 4.71 (s, 1H), 4.21-4.13 (m, 4H), 3.59 (s, 3H), 1.24 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 138.5, 137.3, 134.5, 132.5, 131.0, 129.9, 129.2, 128.9, 126.3, 122.5, 121.3, 120.2, 109.6, 105.6, 61.6, 50.1, 31.1, 14.1. HRMS (ESI) calcd. for $C_{22}H_{23}ClNO_4$ $(M+H)^+$: 400.1310, found: 400.1312.



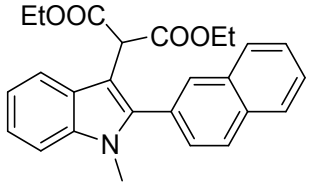
diethyl 2-(2-(3,5-dimethylphenyl)-1-methyl-1*H*-indol-3-yl)malonate (3r)

Yellow solid (69.0 mg, 88%), mp. 111.9-112.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.82 Hz, 1H), 7.32 (d, J = 8.19 Hz, 1H), 7.24 (t, J = 7.09 Hz, 1H), 7.15 (t, J = 7.82 Hz, 1H), 7.09 (s, 1H), 7.06 (s, 2H), 4.75 (s, 1H), 4.21-4.13 (m, 4H), 3.58 (s, 3H), 2.39 (s, 6H), 1.24 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 140.6, 138.1, 137.2, 130.5, 130.4, 128.7, 126.4, 121.9, 121.2, 119.9, 109.4, 104.8, 61.5, 50.3, 31.0, 21.4, 14.1. HRMS (ESI) calcd. for $C_{24}H_{28}NO_4$ $(M+H)^+$: 394.2013, found: 394.2015.



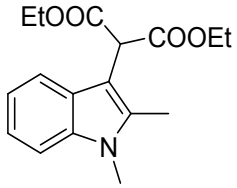
diethyl 2-(1-methyl-2-(*o*-tolyl)-1*H*-indol-3-yl)malonate (3s)

Yellow oil (31.1 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.07 Hz, 1H), 7.42-7.23 (m, 6H), 7.17 (t, J = 7.09 Hz, 1H), 4.49 (s, 1H), 4.17-4.09 (m, 4H), 3.44 (s, 3H), 2.09 (s, 3H), 1.22 (t, J = 7.09 Hz, 3H), 1.18 (t, J = 7.21 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 168.7, 139.8, 139.2, 137.1, 131.6, 130.3, 130.1, 129.5, 126.4, 125.9, 121.8, 121.1, 119.9, 109.3, 104.9, 61.4, 61.4, 50.3, 30.3, 19.7, 14.1. HRMS (ESI) calcd. for $C_{23}H_{26}NO_4$ $(M+H)^+$: 380.1856, found: 380.1859.



diethyl 2-(1-methyl-2-(naphthalen-2-yl)-1*H*-indol-3-yl)malonate (3t)

White solid (44.3 mg, 53%), mp. 129.6-130.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.90 (m, 4H), 7.84 (d, J = 7.95 Hz, 1H), 7.57-7.52 (m, 3H), 7.36 (d, J = 8.19 Hz, 1H), 7.27 (td, J_1 = 8.19 Hz, J_2 = 1.10 Hz, 1H), 7.19 (td, J_1 = 6.97 Hz, J_2 = 0.98 Hz, 1H), 4.81 (s, 1H), 4.20-4.12 (m, 4H), 3.62 (s, 3H),1.22 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 140.2, 137.4, 133.1, 133.1, 130.7, 128.4, 128.3, 128.1, 127.9, 127.0, 126.8, 126.5, 122.2, 121.3, 120.1, 109.5, 105.4, 61.6, 50.3, 31.2, 14.1. HRMS (ESI) calcd. for $C_{26}H_{26}NO_4$ $(M+H)^+$: 416.1856, found: 416.1858.



diethyl 2-(1,2-dimethyl-1*H*-indol-3-yl)malonate (3u)

Yellow solid (21.5 mg, 35%), mp. 78.0-78.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.95 Hz, 1H), 7.24 (d, J = 8.07 Hz, 1H), 7.15 (td, J_1 = 7.52 Hz, J_2 = 1.22 Hz, 1H), 7.09 (td, J_1 = 8.01 Hz, J_2 = 1.22 Hz, 1H), 4.89 (s, 1H), 4.23-4.16 (m, 4H), 3.65 (s, 3H), 2.41 (s, 3H), 1.25 (t, J = 7.09 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 136.6, 135.4, 126.8, 121.0, 119.5, 119.1, 108.8, 103.1, 61.6, 49.7, 29.7, 14.1, 10.9. HRMS (ESI) calcd. for $C_{17}H_{22}NO_4$ $(M+H)^+$: 304.1543, found: 304.1544.

8. References

(1) W. G. Tobias, G. D. Constantin and S. Armido, *Org. Lett.*, 2015, **17**, 254.

(2) (a) S. D. Yang, C. L. Sun, Z. Fang, B. J. Li, Y. Z. Li and Z. J. Shi, *Angew. Chem. Int. Ed.*, 2008, **47**, 1473; (b) J. L. Zhao, Y. H. Zhang and K. Cheng, *J. Org. Chem.*, 2008, **73**, 7428.

(3) (a) M. Y. Wu, J. Y. Luo, F. H. Xiao, S. F. Zhang, G. J. Deng and H. A. Luo, *Adv. Synth. Catal.*, 2012, **354**, 335; (b) M. F. Ibad, D. S. Zinad, M. Hussain, A. Ali, A. Villinger and P. Langer, *Tetrahedron*, 2013, **69**, 7492; (c) N. K. Dolla, C, Chen, J. Larkins-Ford, R. Rajamuthiah, S. Jagadeesan, A. L. Conery, F. M. Ausubel, E. Mylonakis, J. B. Bremner, K. Lewis and M. J. Kelso, *Aust. J. Chem.*, 2014, **67**, 1471; (d) L. Omann and M. Oestreich, *Organometallics*, 2017, **36**, 767; (e) P. H. Ni, J. Tan, W. Q. Zhao, H. W. Huang, F. H. Xiao and G. J. Deng, *Org. Lett.*, 2019, **21**, 3518; (f) K. Hisler, A. G. J. Commeureuc, S. Z. Zhou and J. A. Murphy, *Tetrahedron Lett.*, 2009, **50**, 3290.

(4) (a) D. R. Burfield, K. H. Lee and R. H. Smithers, *J. Org. Chem.*, 1977, **42**, 3060; (b) D. R. Burfield and R. H. Smithers, *J. Org. Chem.*, 1978, **43**, 3966.

(5) P. Job, *Ann. Chem.*, 1928, **9**, 113.

(6) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.

(7) Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

(8) (a) A. D. Becke*, J. Chem. Phys.*, 1993, **98**, 5648; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623; (c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

(9) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.

(10) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.

(11) M. Cossi, V. Barone, R. Cammi and J. Tomasi, *Chem. Phys. Lett.*, 1996, **255**, 327.

(12) (a) T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580; (b) E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498.

(13) W. Humphrey, A. Dalke and K. Schluten, *J. Molec. Graphics*, 1996, **14**, 33.

9. ^{1}H, ^{13}C and ^{19}F NMR Spectra

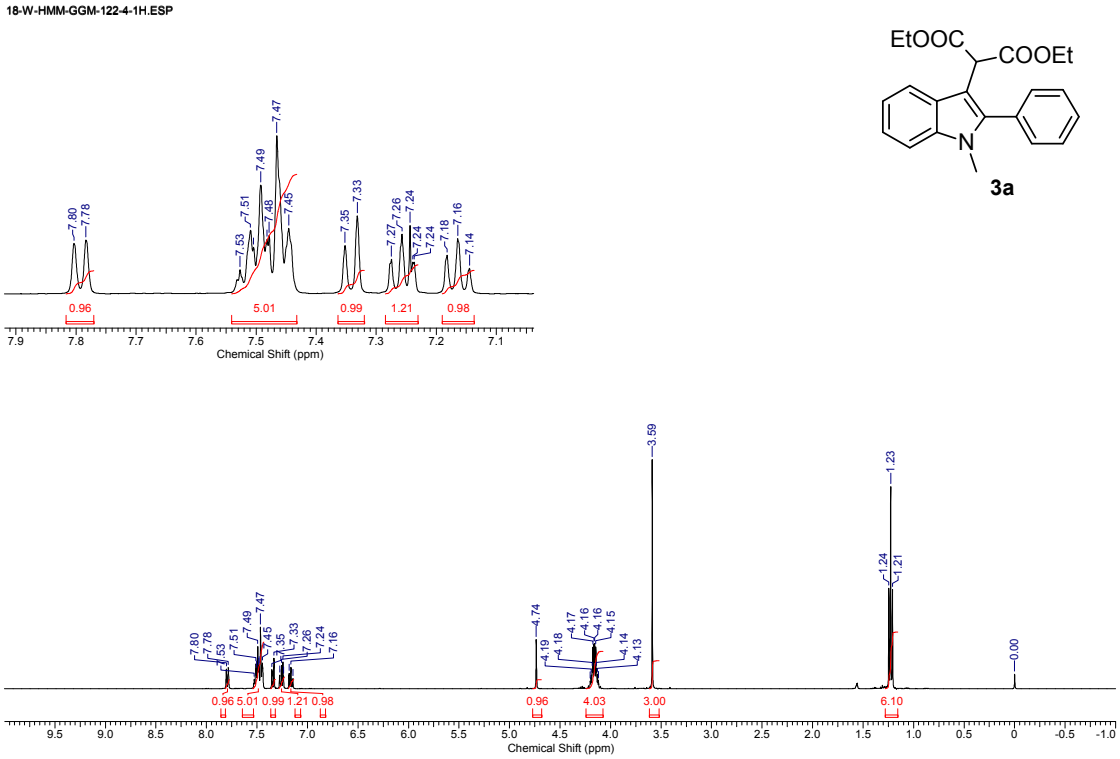


Figure S24. ^{1}H NMR spectrum of compound **3a**

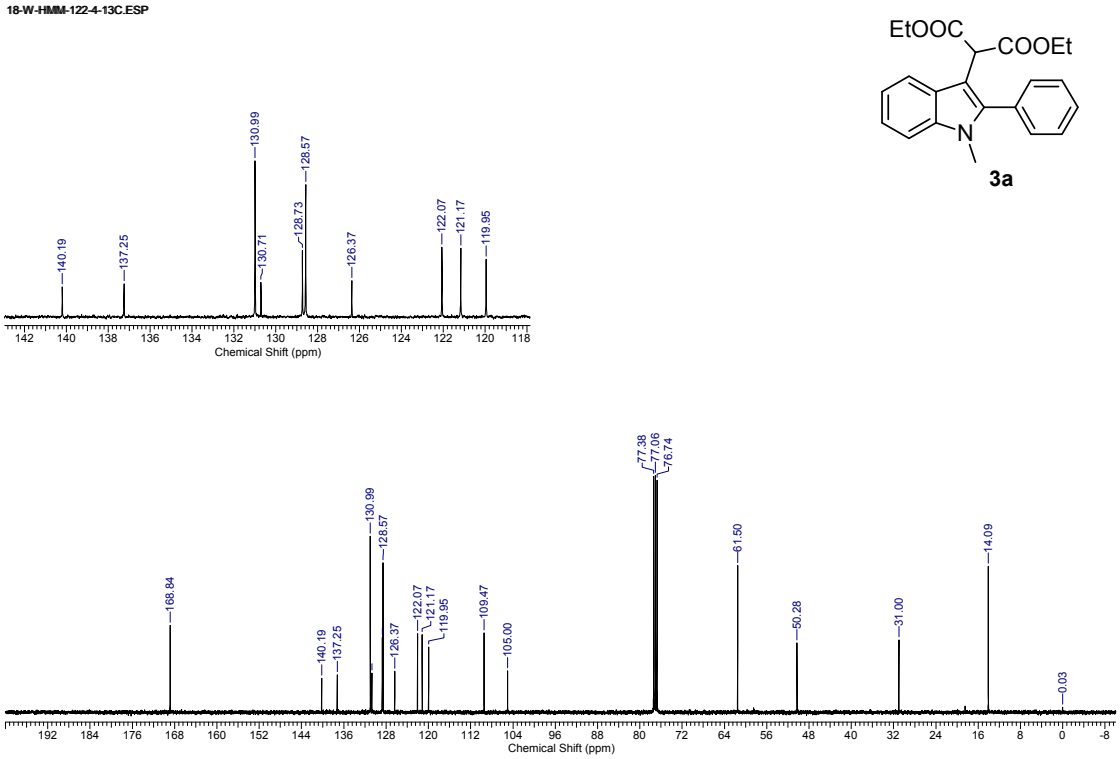


Figure S25. ^{13}C NMR spectrum of compound **3a**

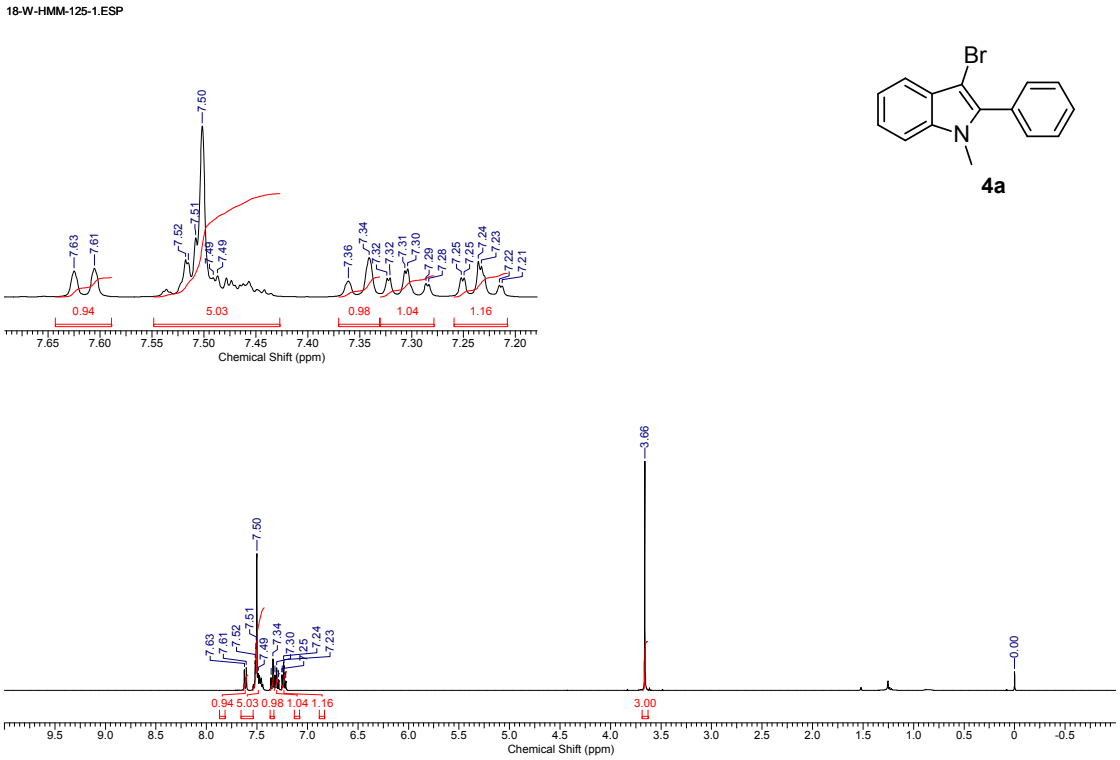


Figure S26. ^{1}H NMR spectrum of compound **4a**

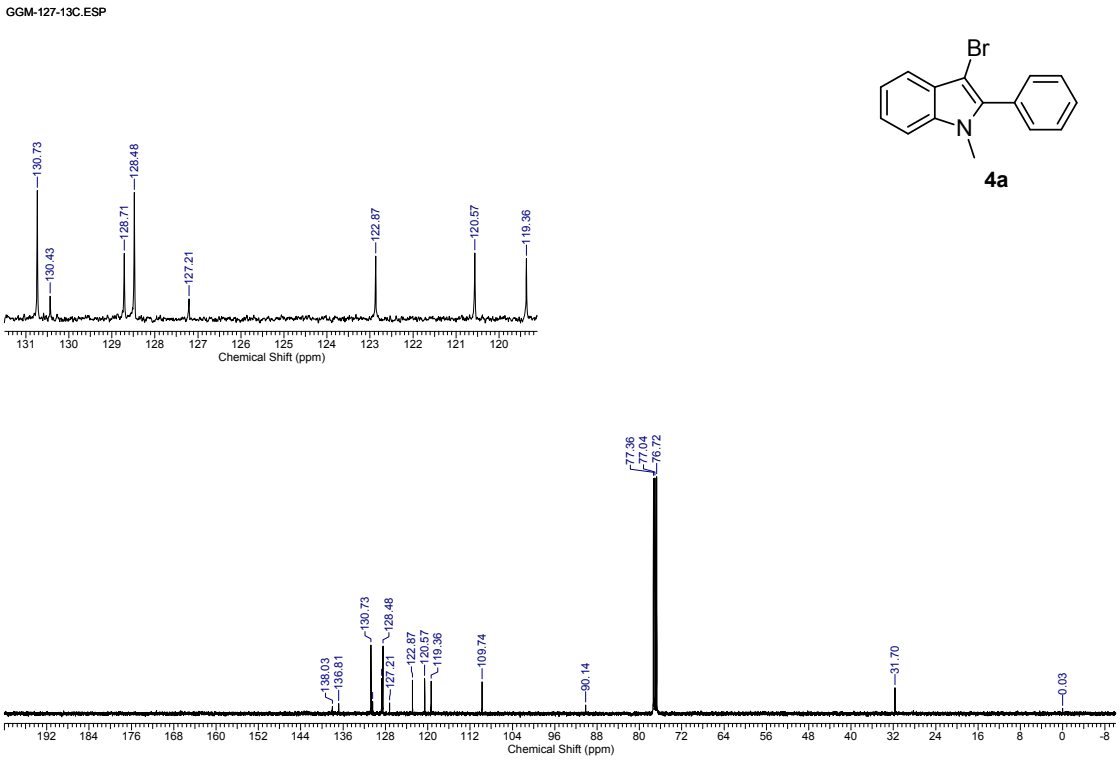


Figure S27. ^{13}C NMR spectrum of compound **4a**

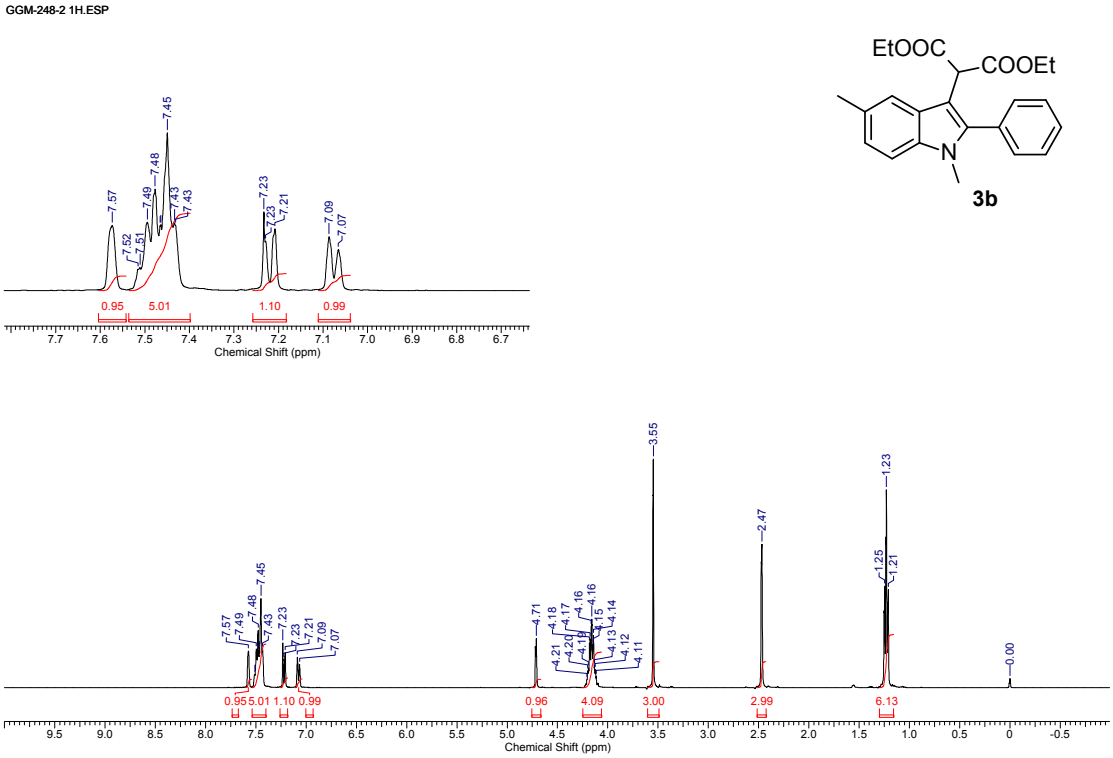


Figure S28. ^{1}H NMR spectrum of compound **3b**

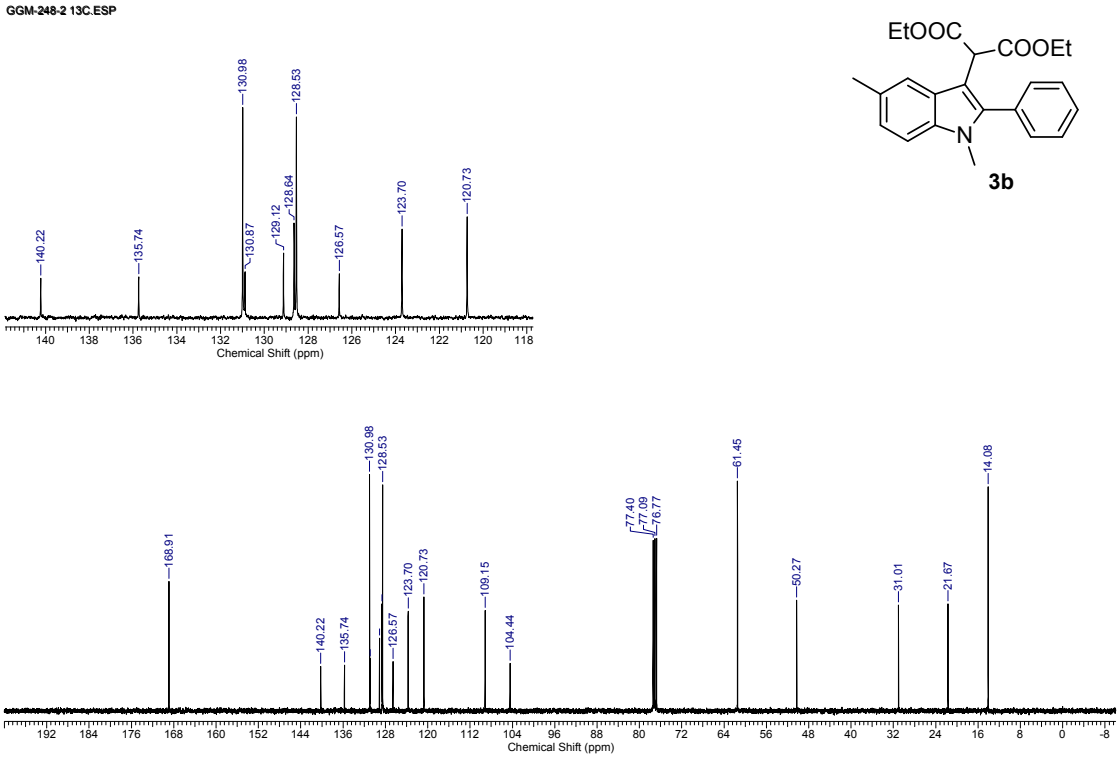


Figure S29. ^{13}C NMR spectrum of compound **3b**

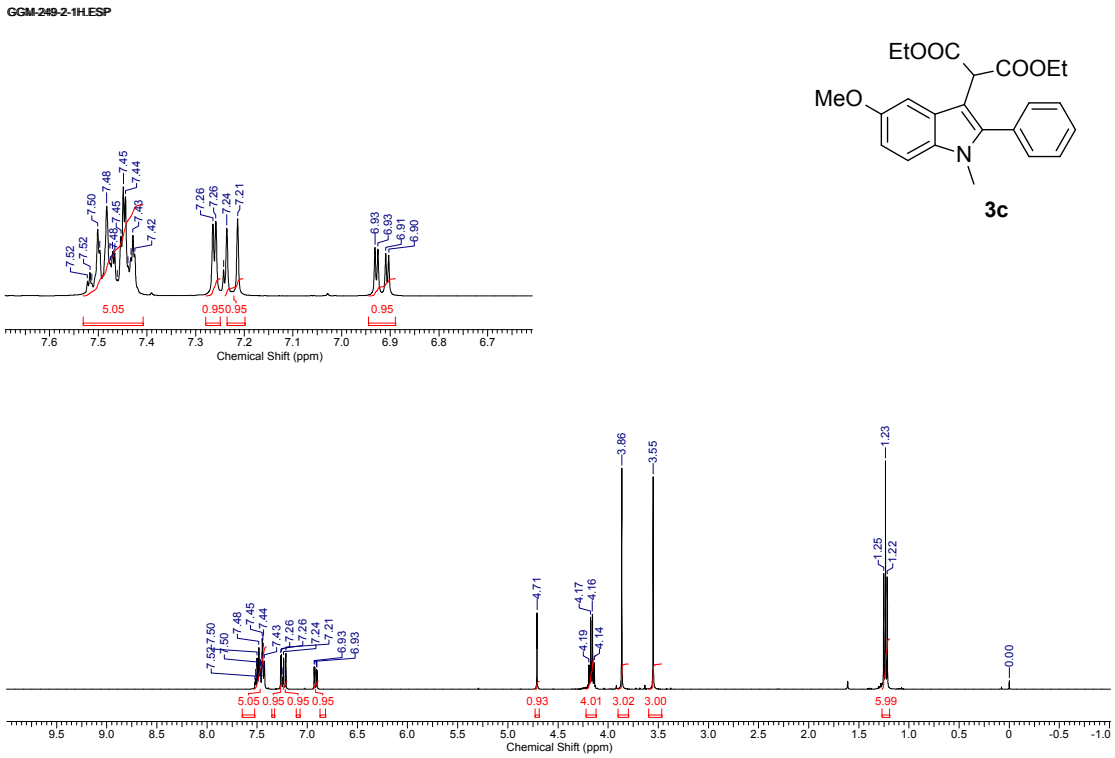


Figure S30. ^{1}H NMR spectrum of compound **3c**

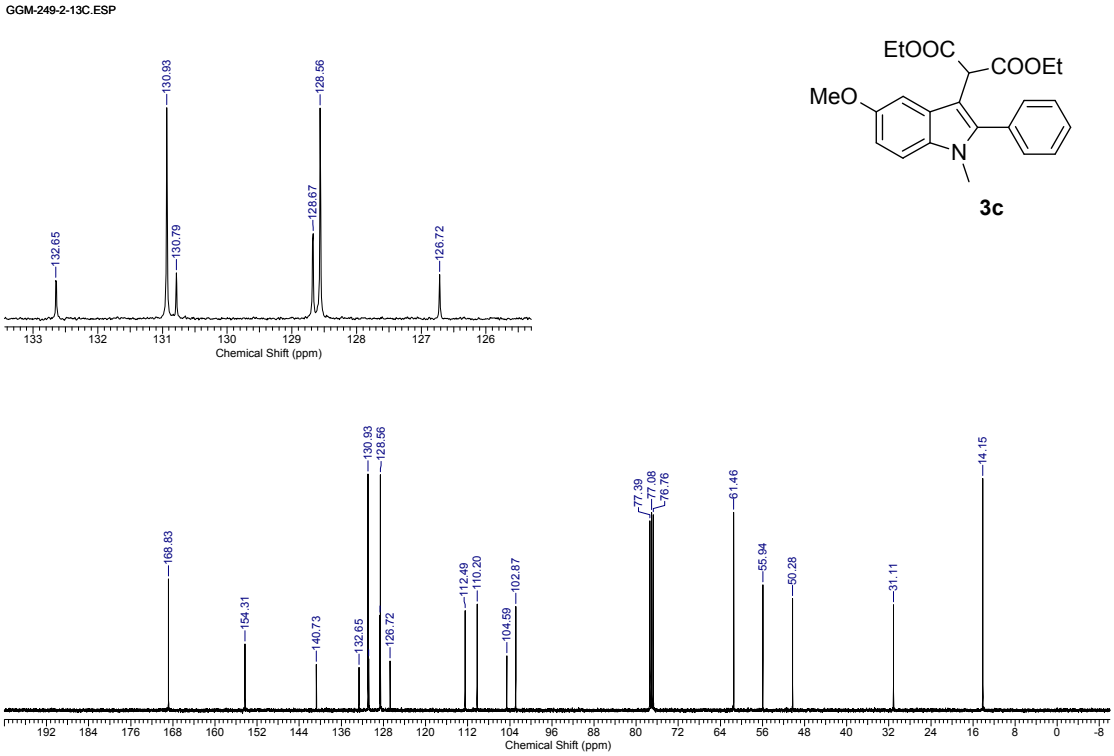


Figure S31. ^{13}C NMR spectrum of compound **3c**

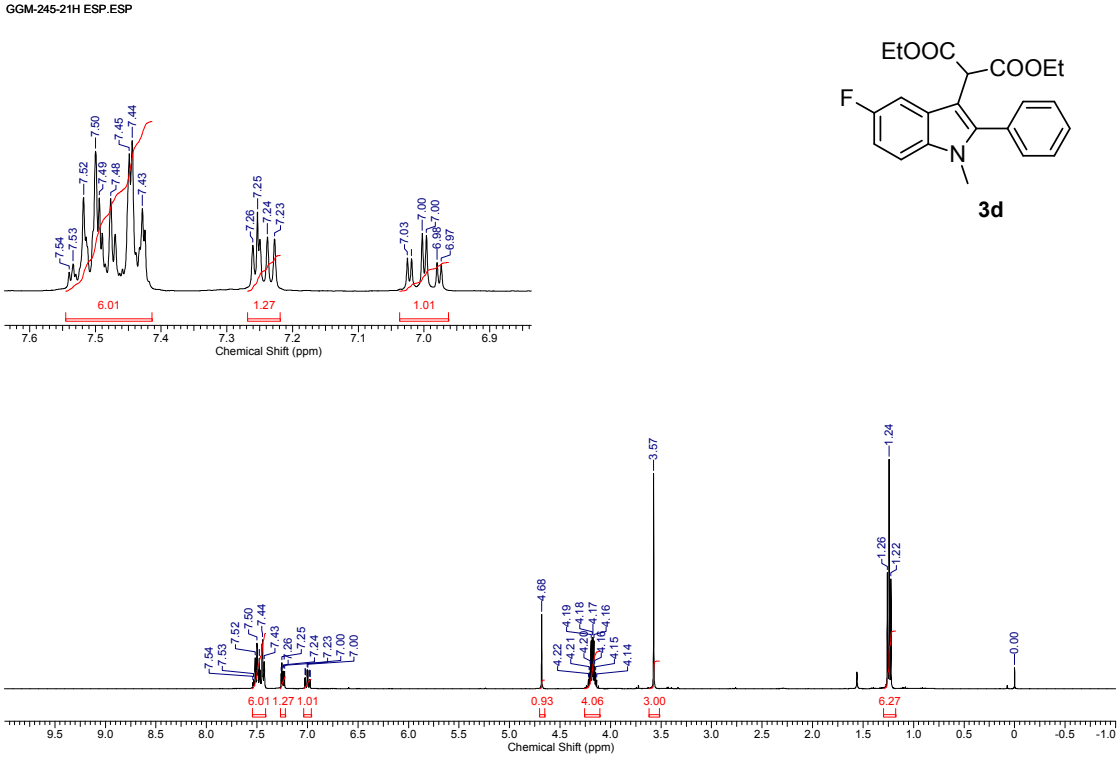


Figure S32. ^{1}H NMR spectrum of compound **3d**

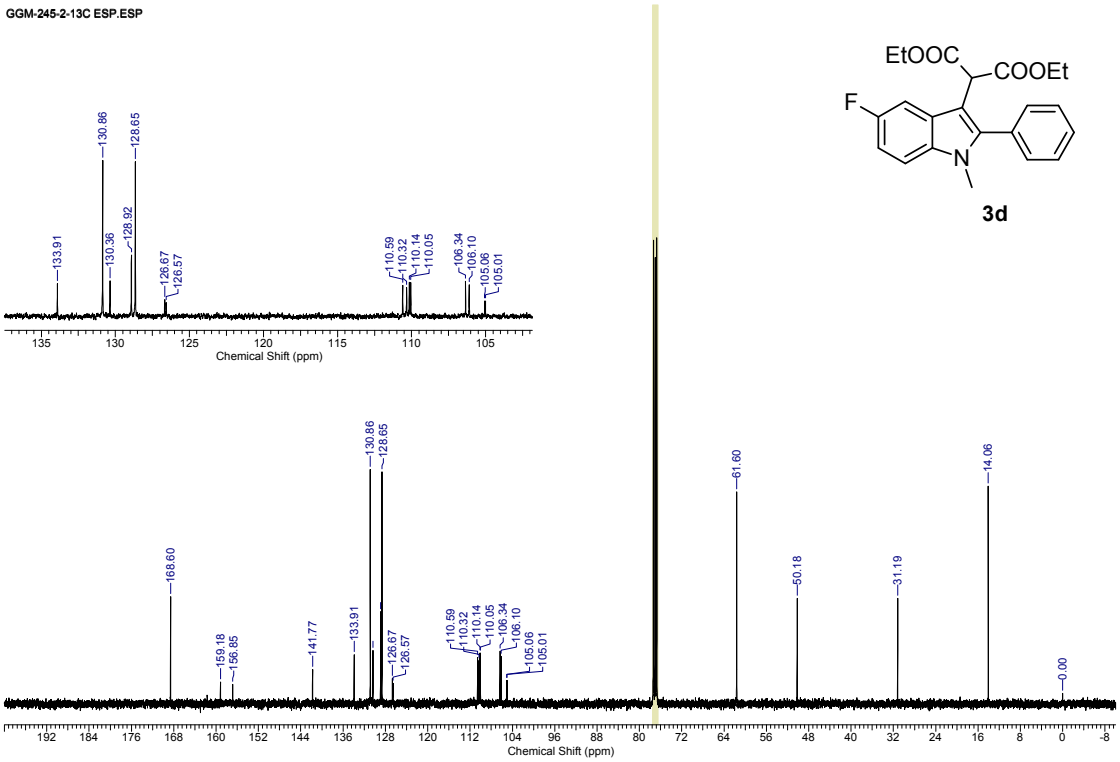


Figure S33. ^{13}C NMR spectrum of compound **3d**

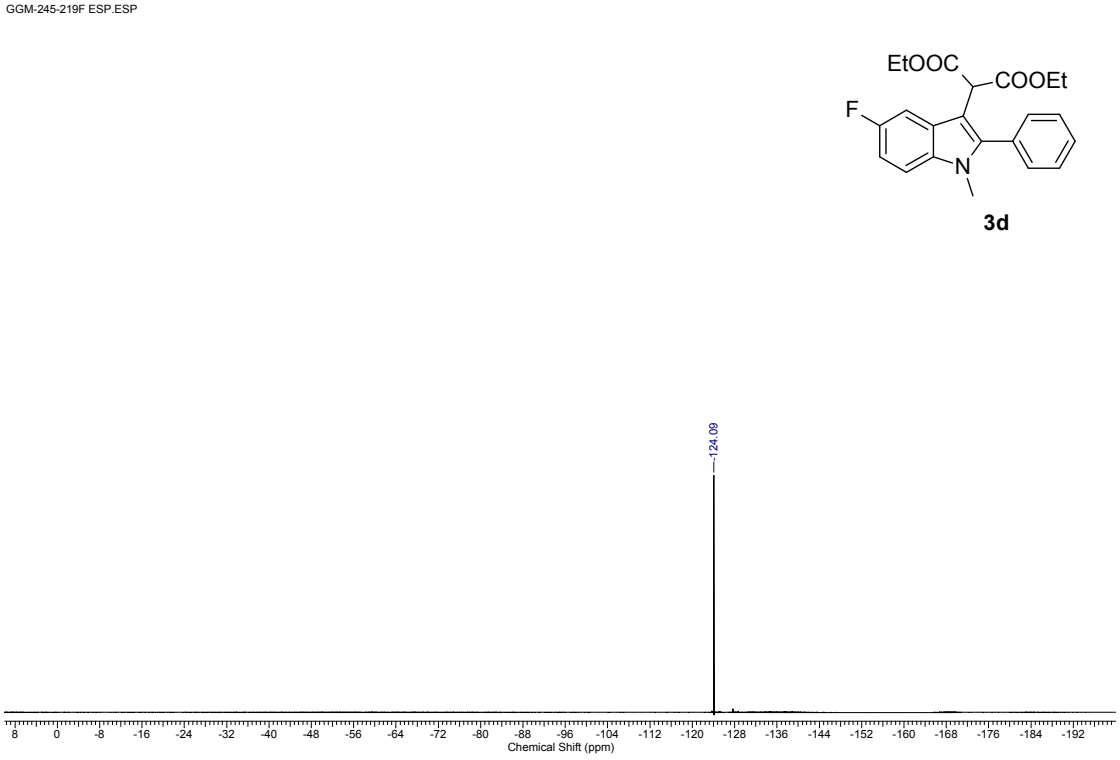


Figure S34. ^{19}F NMR spectrum of compound **3d**

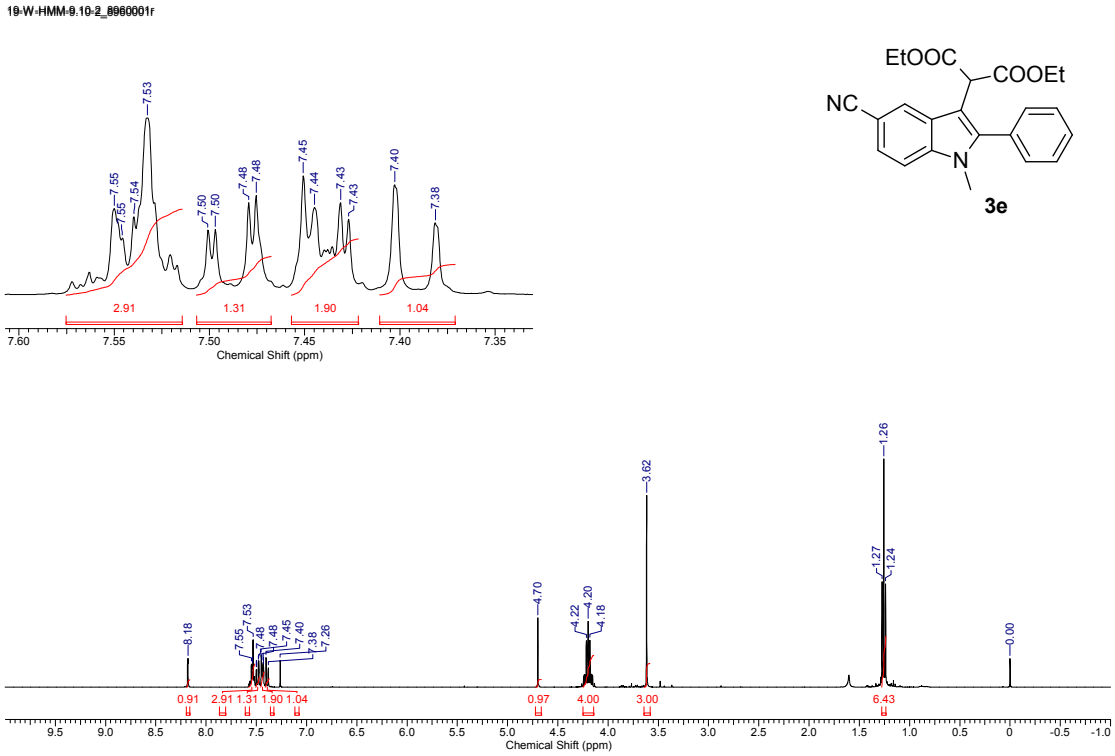


Figure S35. ^{1}H NMR spectrum of compound **3e**

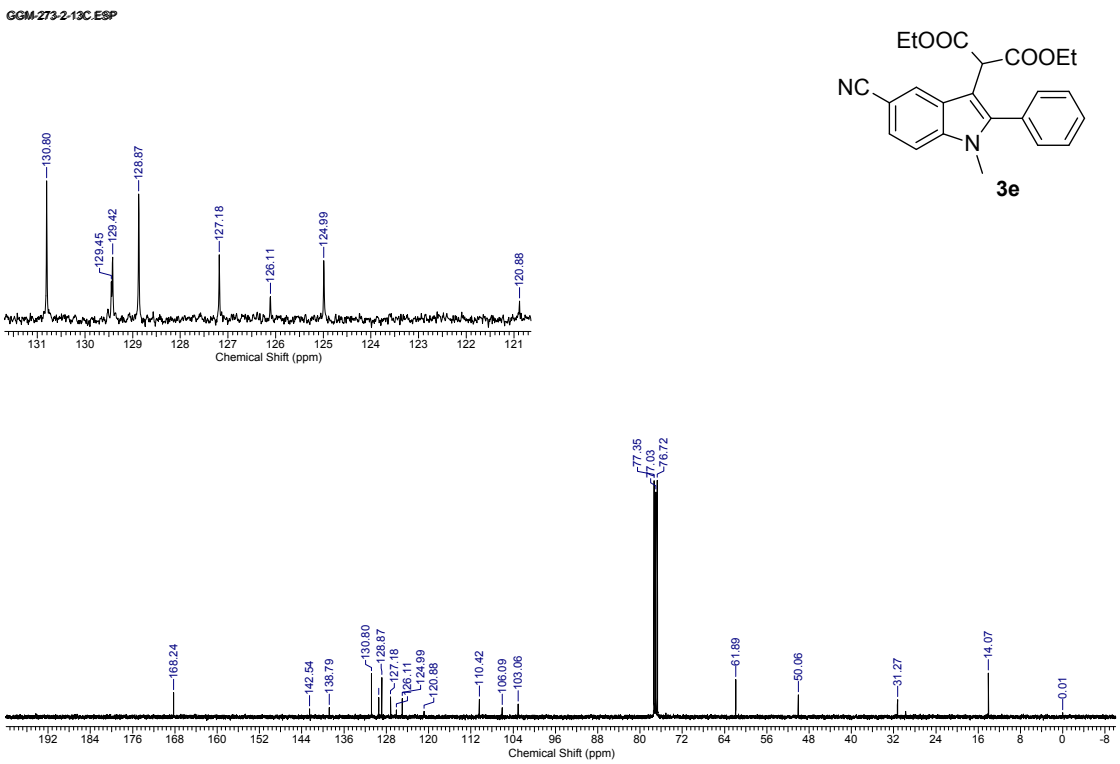


Figure S36. ^{13}C NMR spectrum of compound **3e**

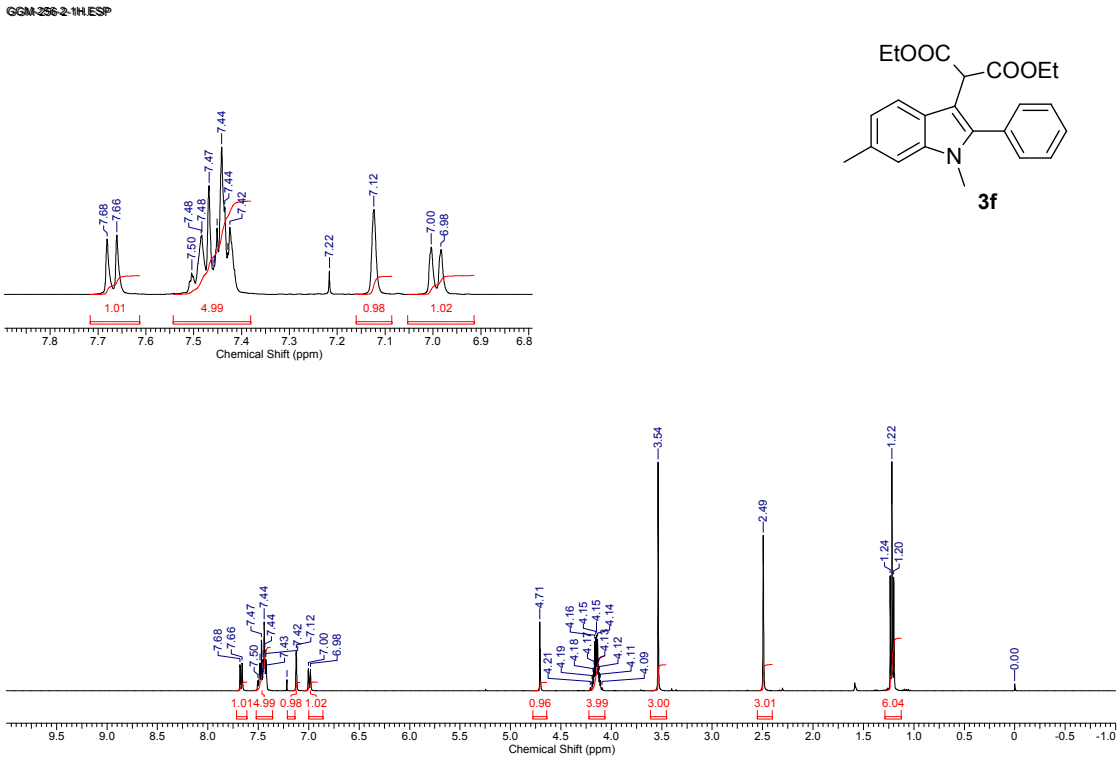


Figure S37. ^{1}H NMR spectrum of compound **3f**

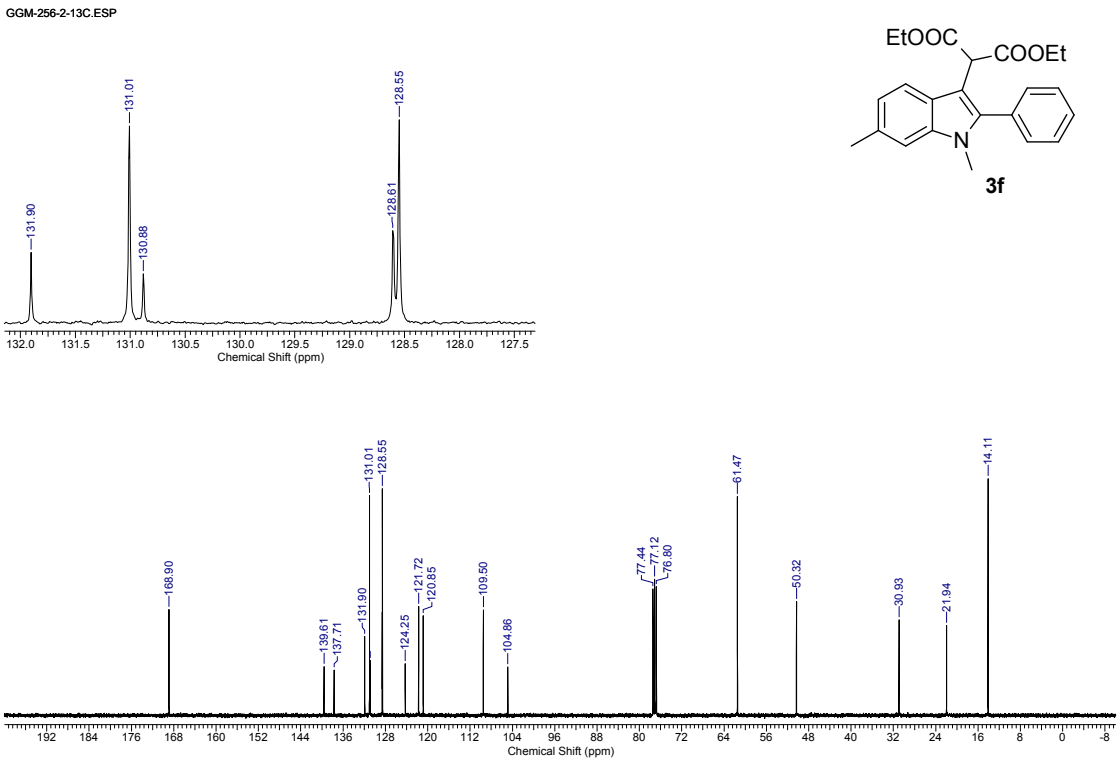


Figure S38. ^{13}C NMR spectrum of compound **3f**

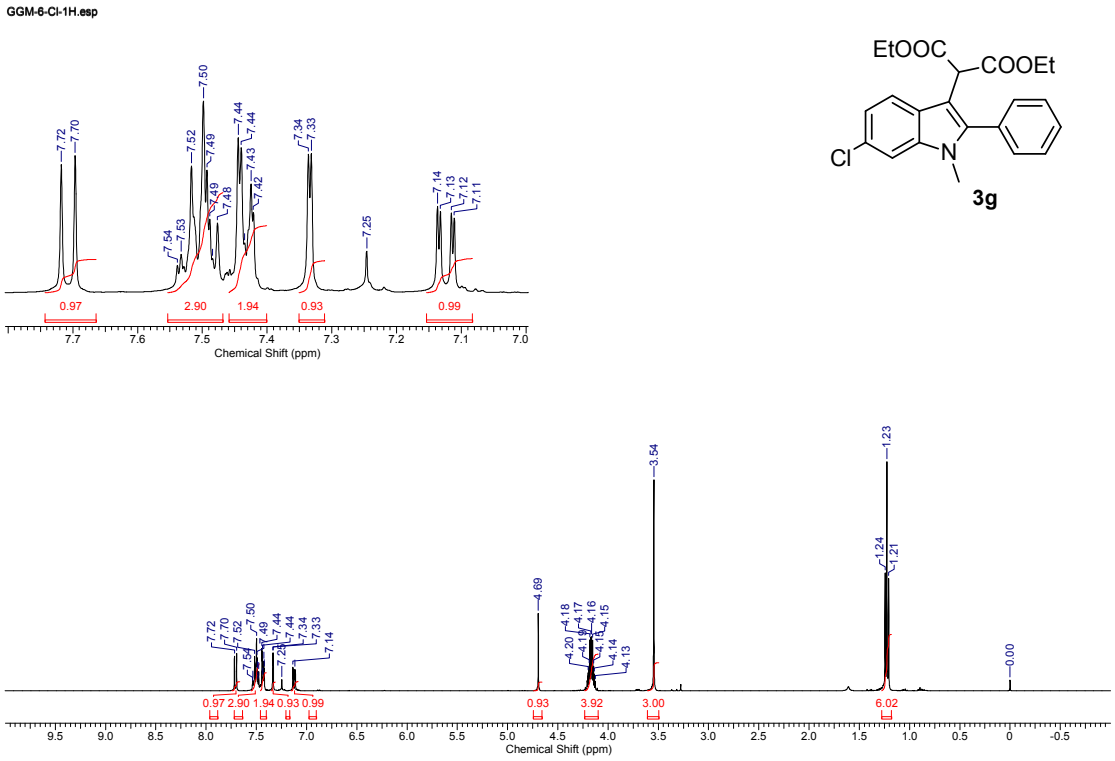


Figure S39. ^{1}H NMR spectrum of compound **3g**

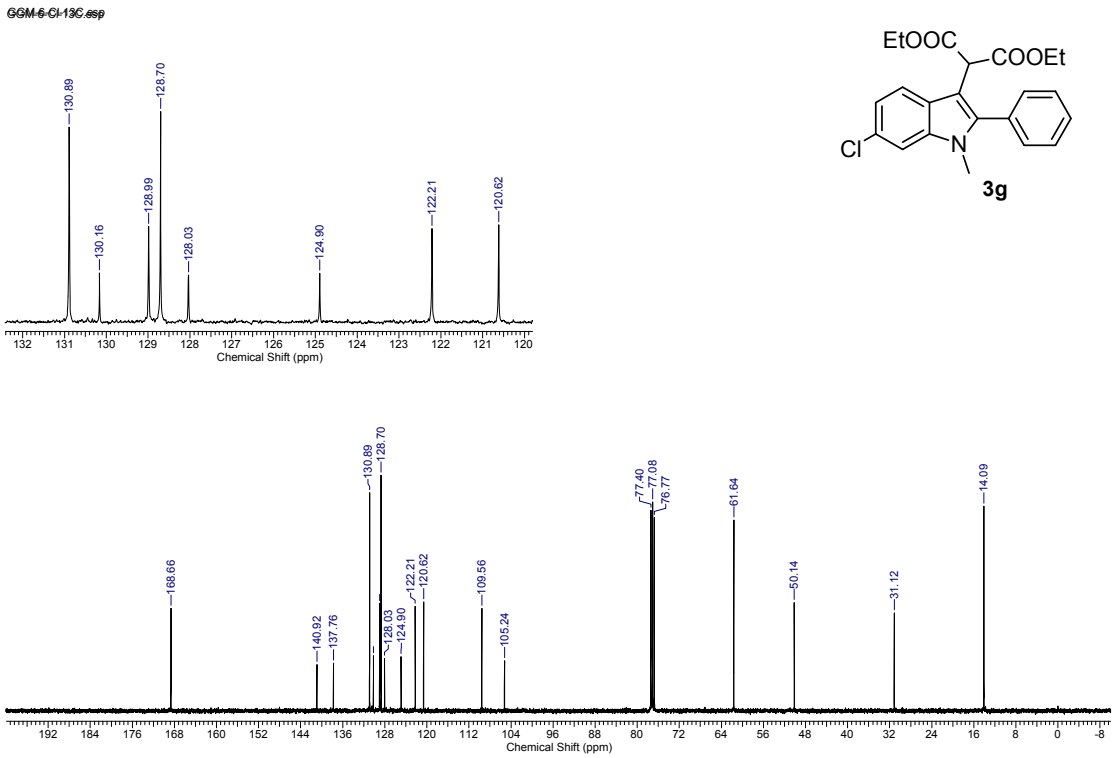


Figure S40. ^{13}C NMR spectrum of compound **3g**

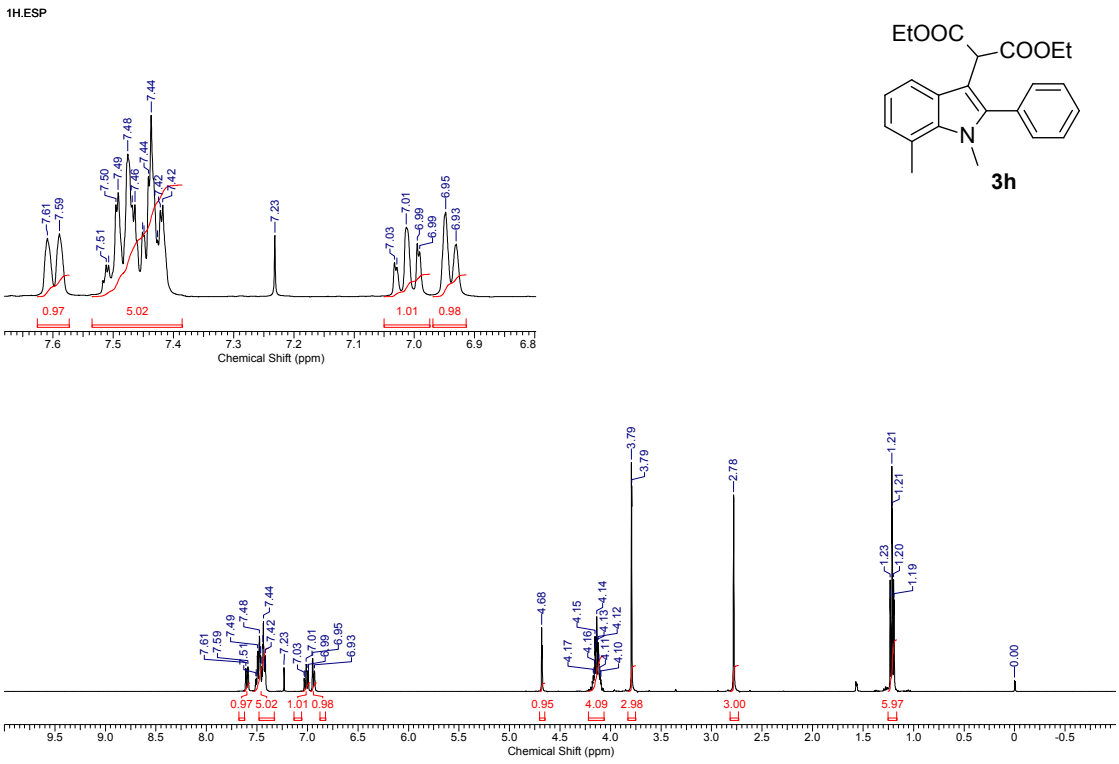


Figure S41. ^{1}H NMR spectrum of compound **3h**

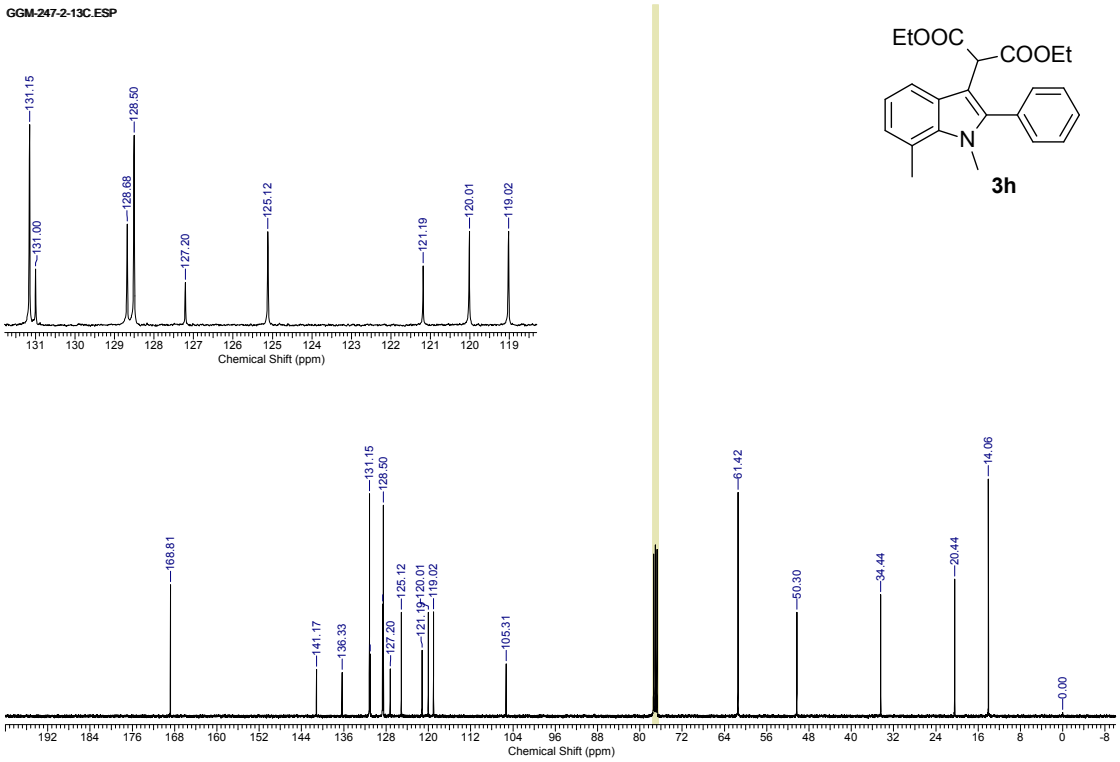


Figure S42. ^{13}C NMR spectrum of compound **3h**

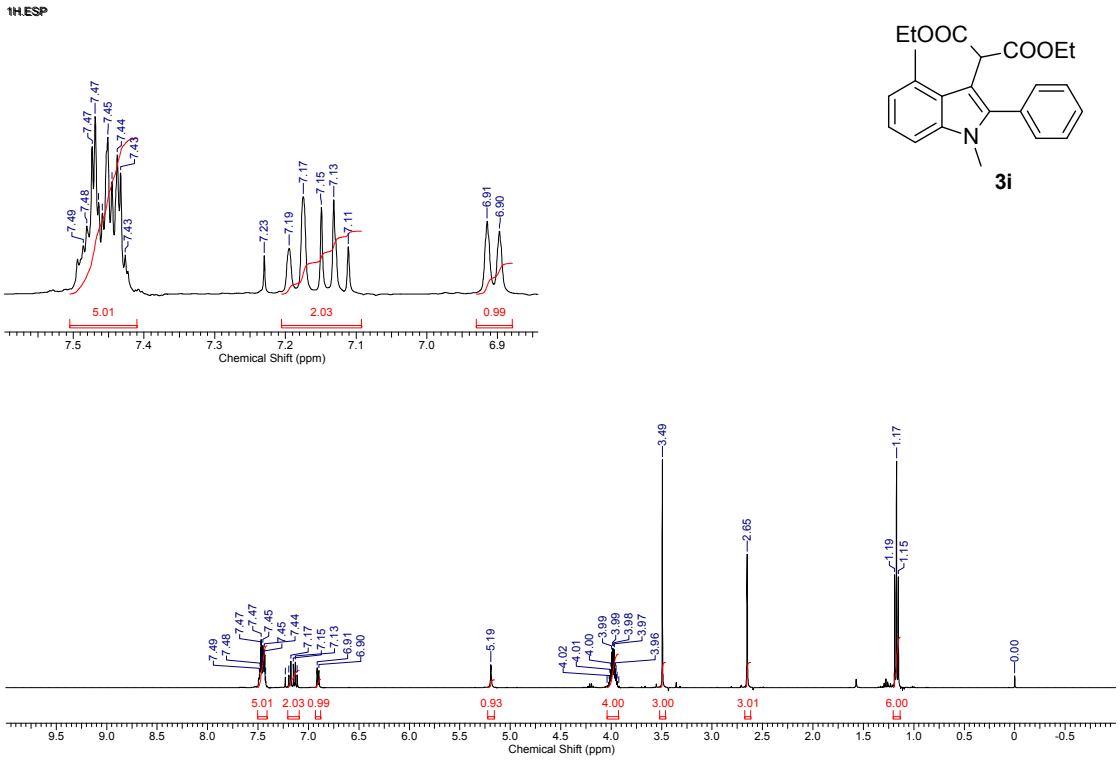


Figure S43. ^{1}H NMR spectrum of compound **3i**

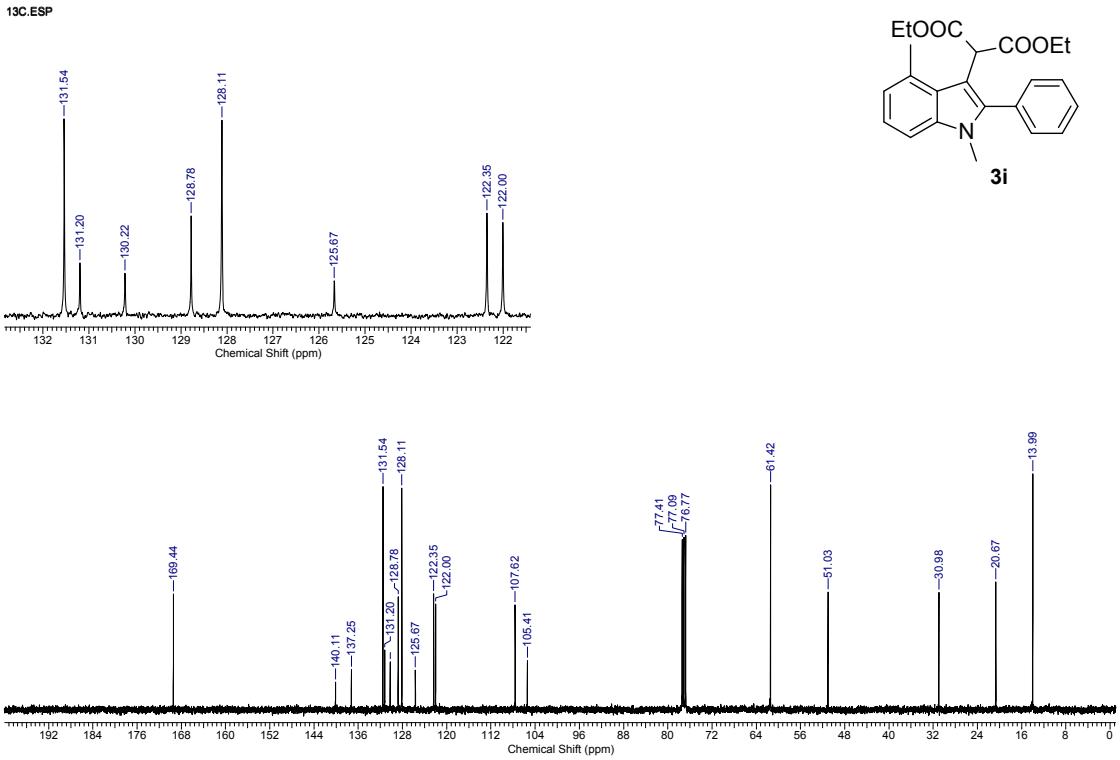


Figure S44. ^{13}C NMR spectrum of compound **3i**

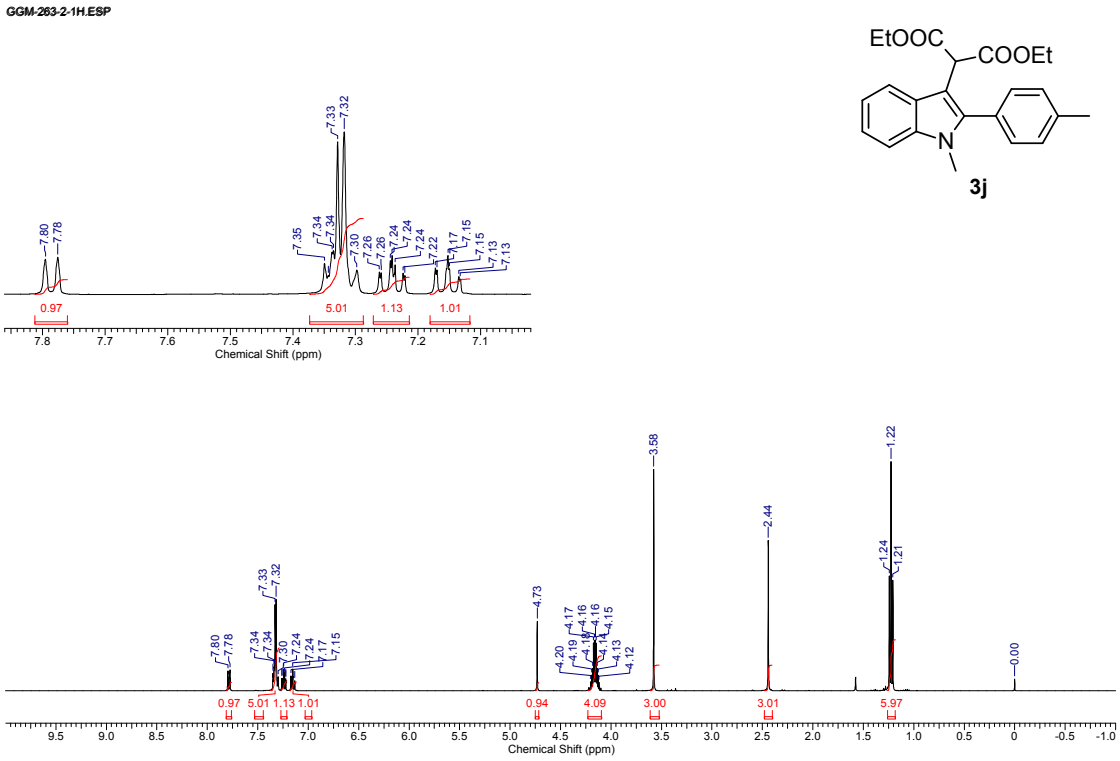


Figure S45. ^{1}H NMR spectrum of compound **3j**

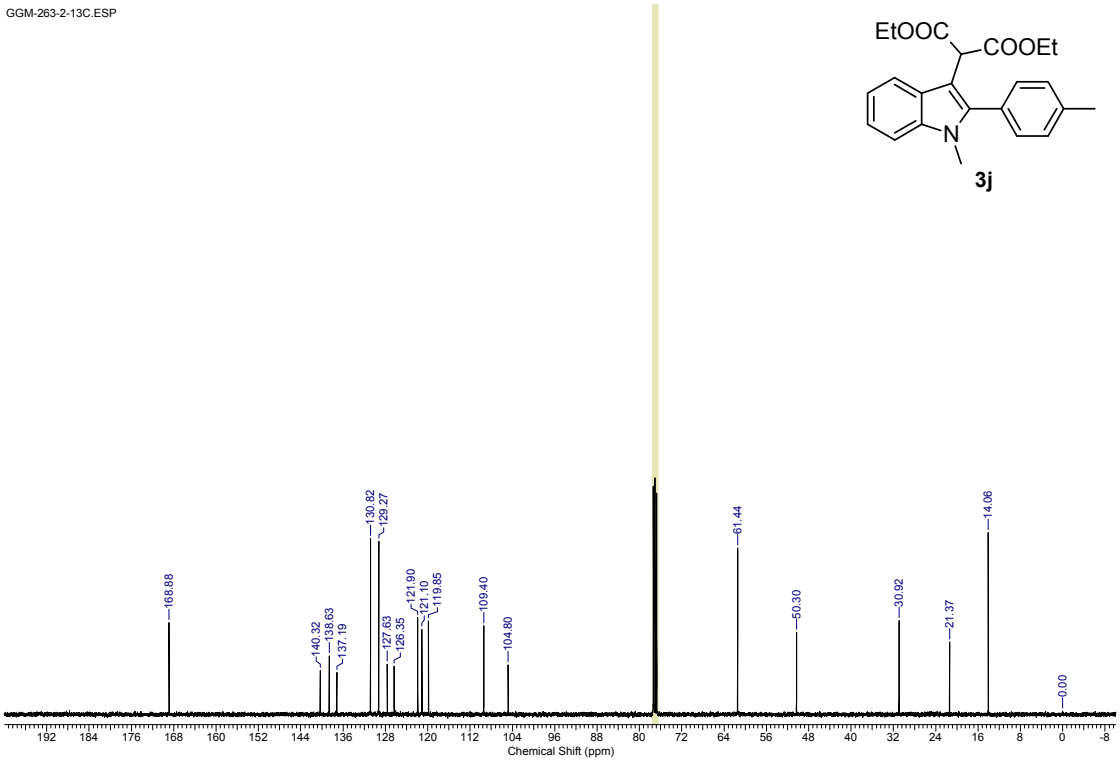


Figure S46. ^{13}C NMR spectrum of compound **3j**

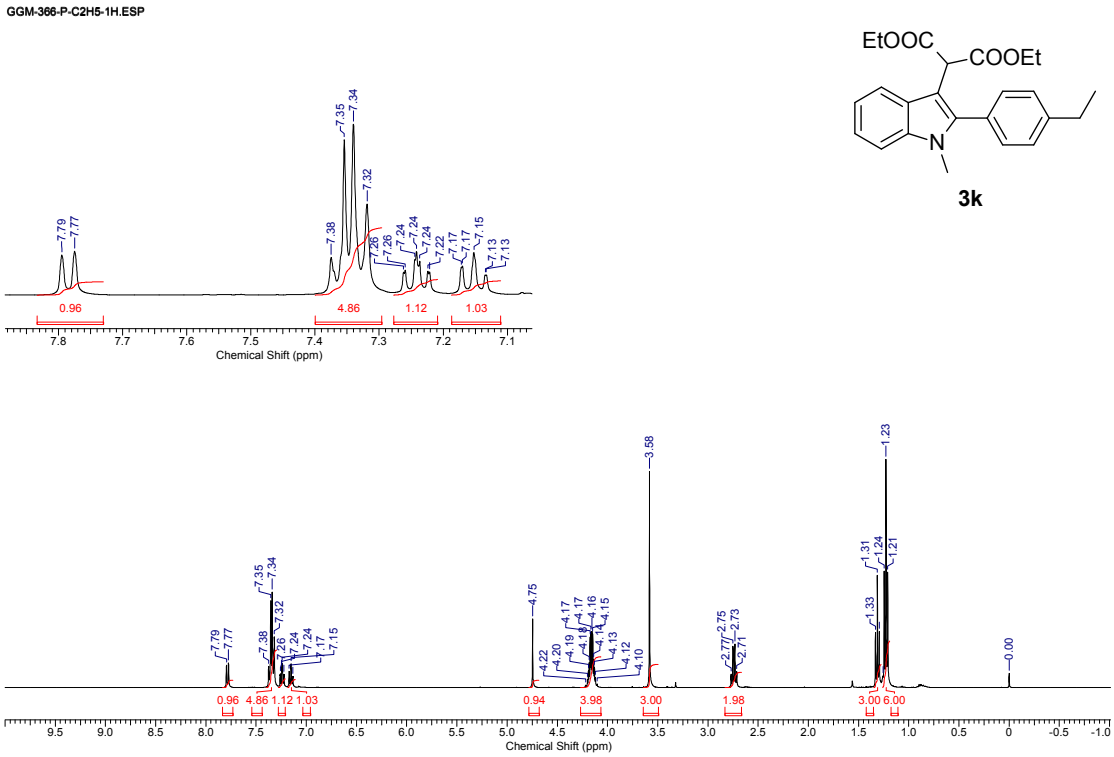


Figure S47. ^{1}H NMR spectrum of compound **3k**

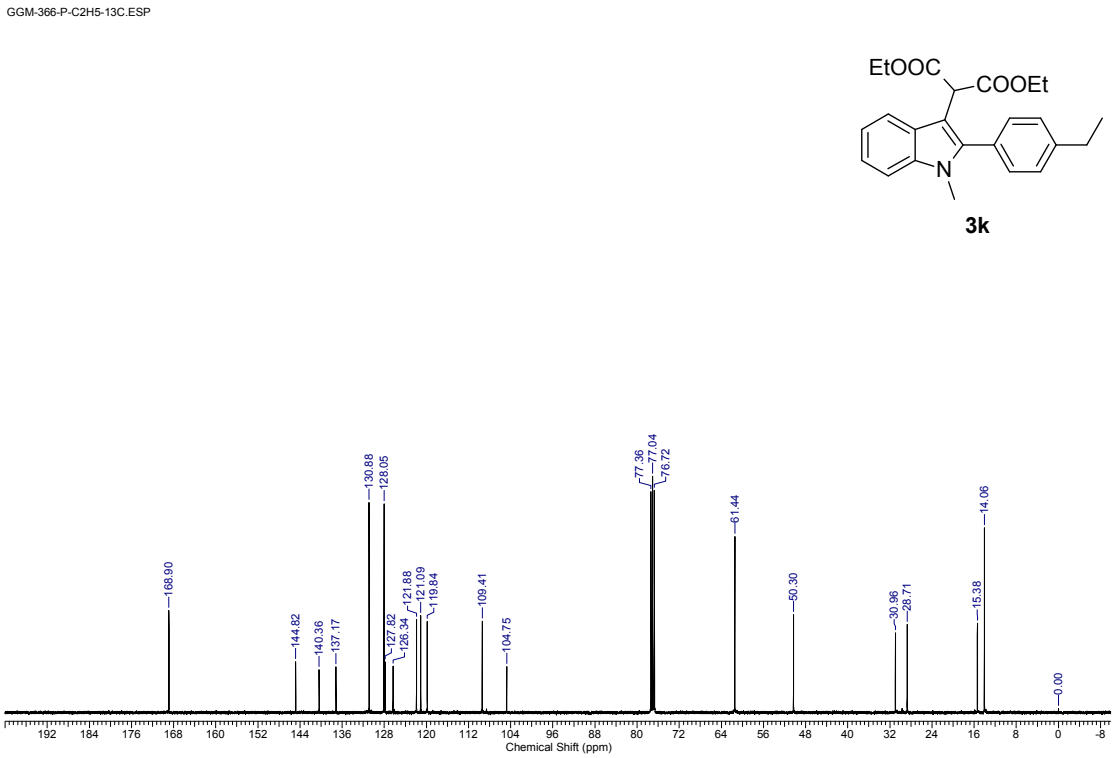


Figure S48. ^{13}C NMR spectrum of compound **3j**

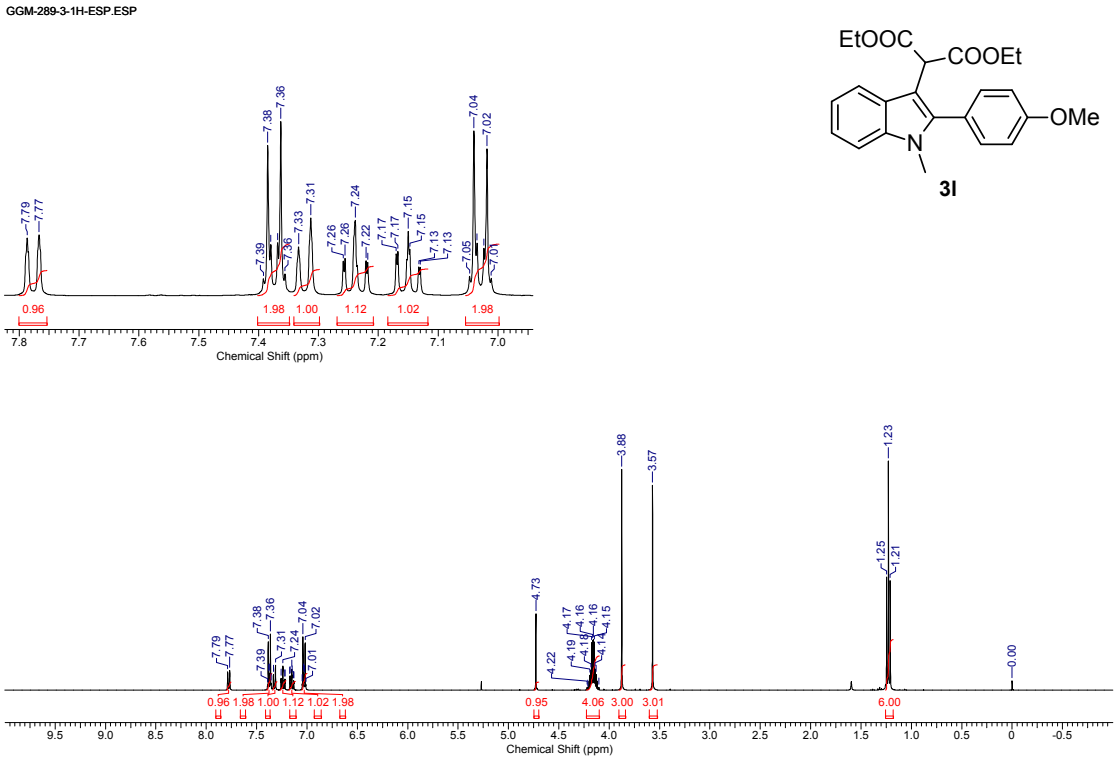


Figure S49. ^{13}H NMR spectrum of compound **3l**

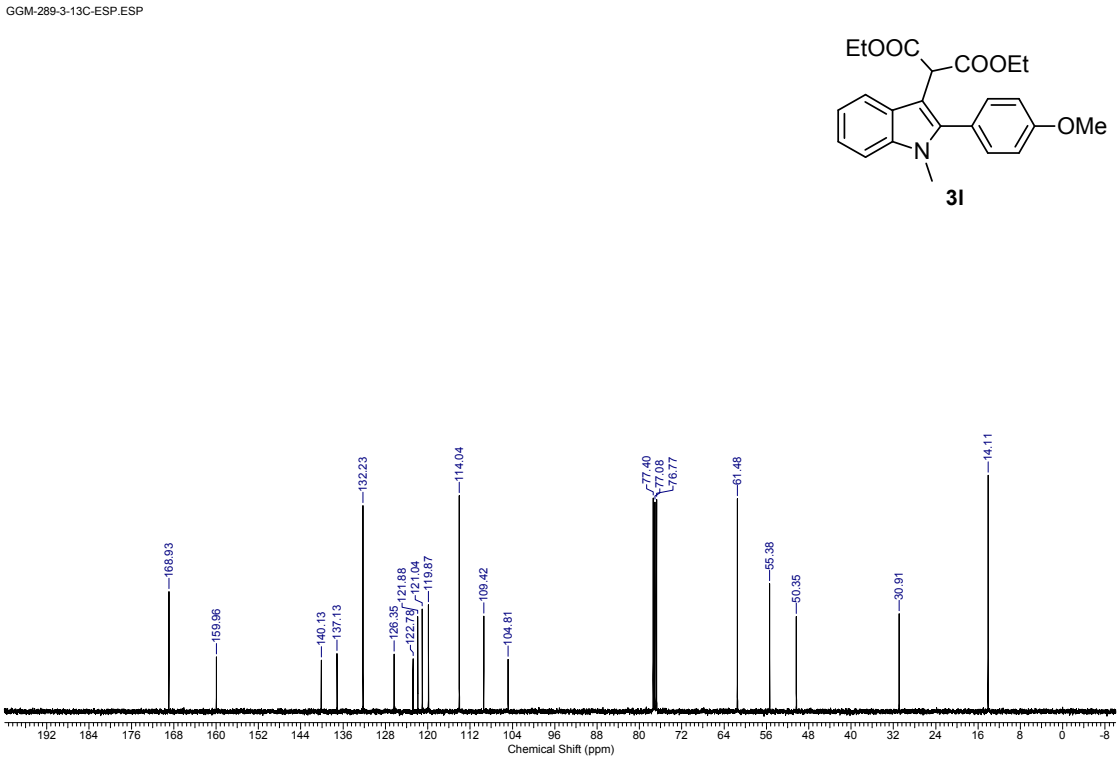


Figure S50. ^{13}C NMR spectrum of compound **3l**

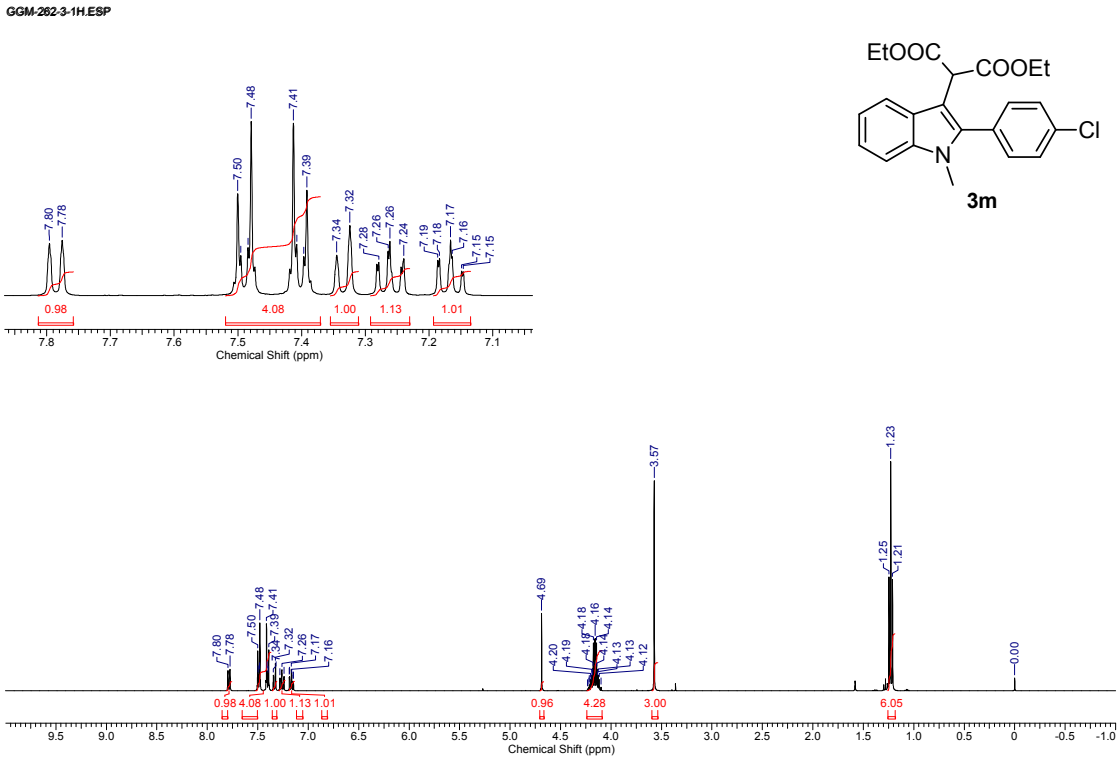


Figure S51. ^{1}H NMR spectrum of compound **3m**

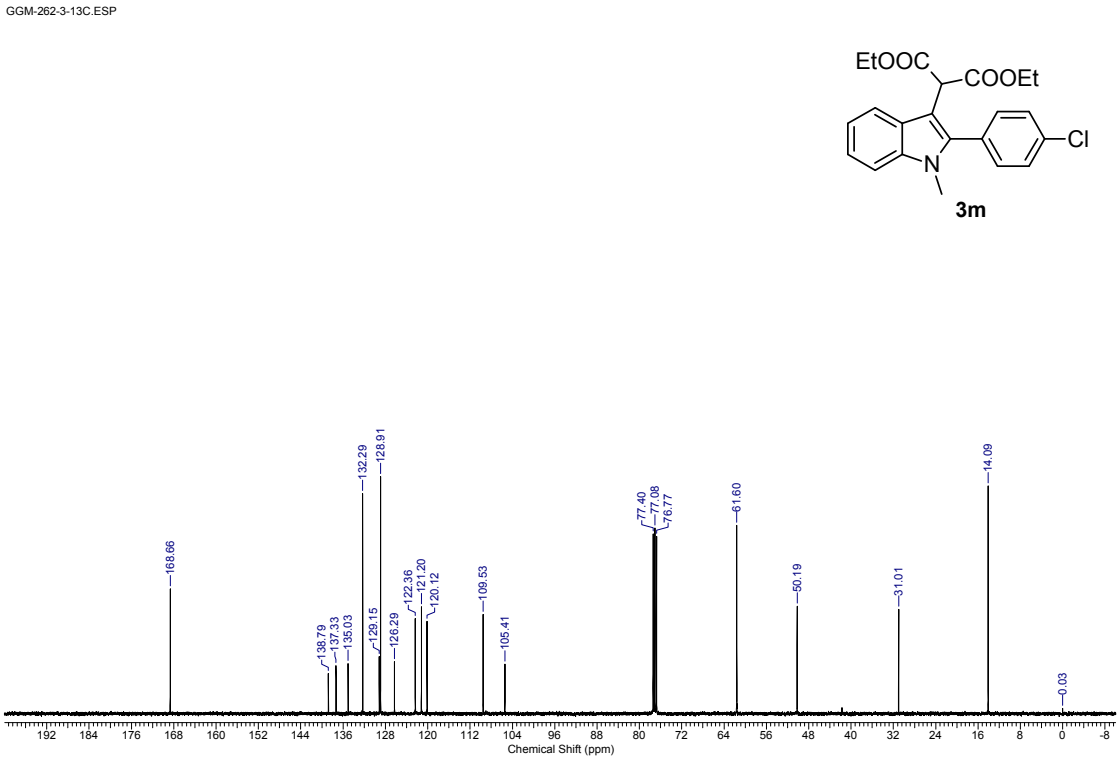


Figure S52. ^{13}C NMR spectrum of compound **3m**

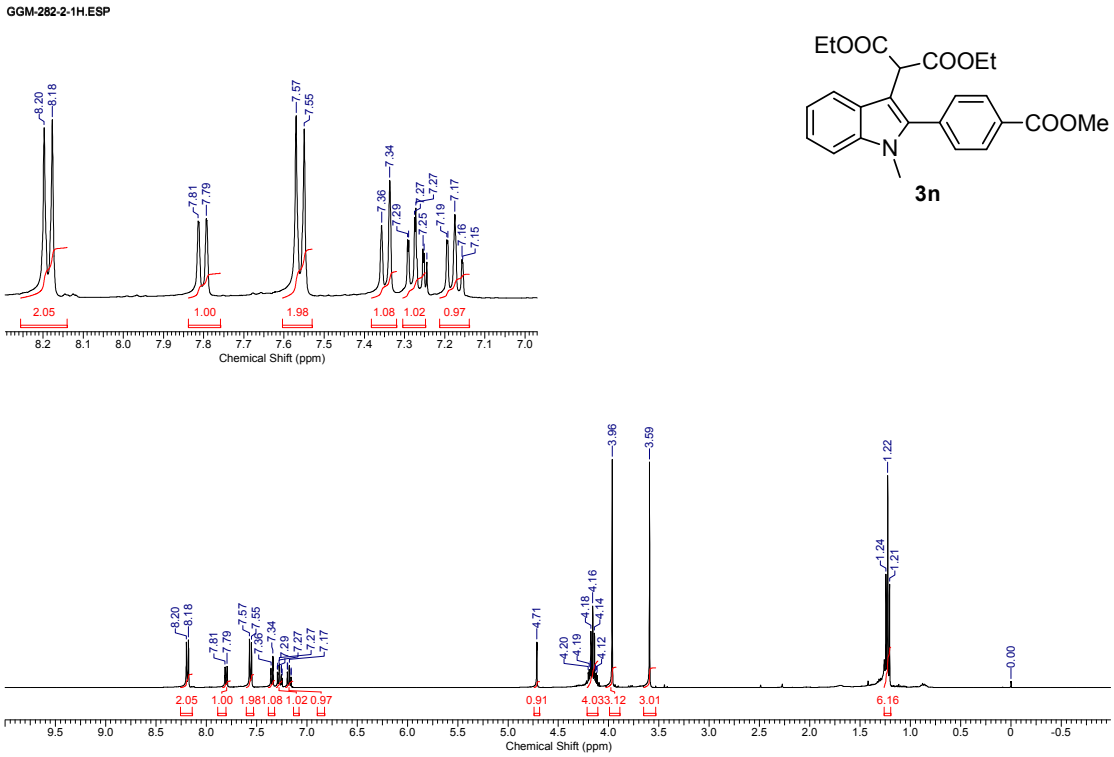


Figure S53. ^{1}H NMR spectrum of compound **3n**

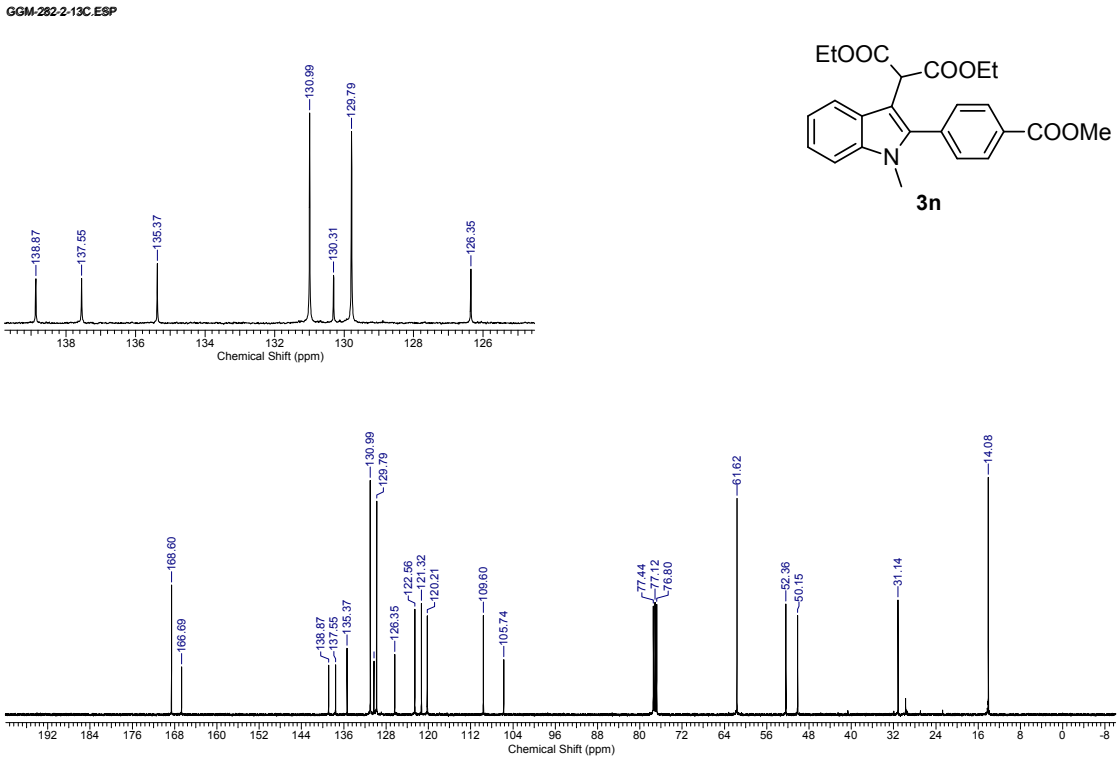


Figure S54. ^{13}C NMR spectrum of compound **3n**

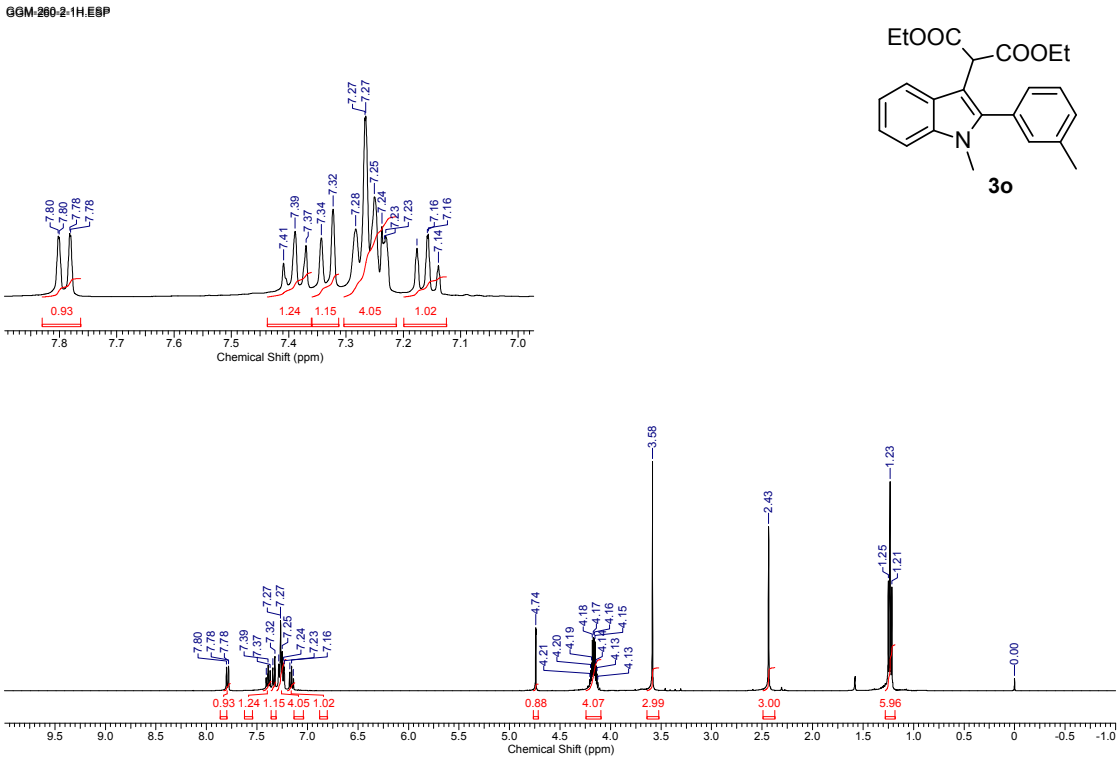


Figure S55. ^{1}H NMR spectrum of compound **3o**

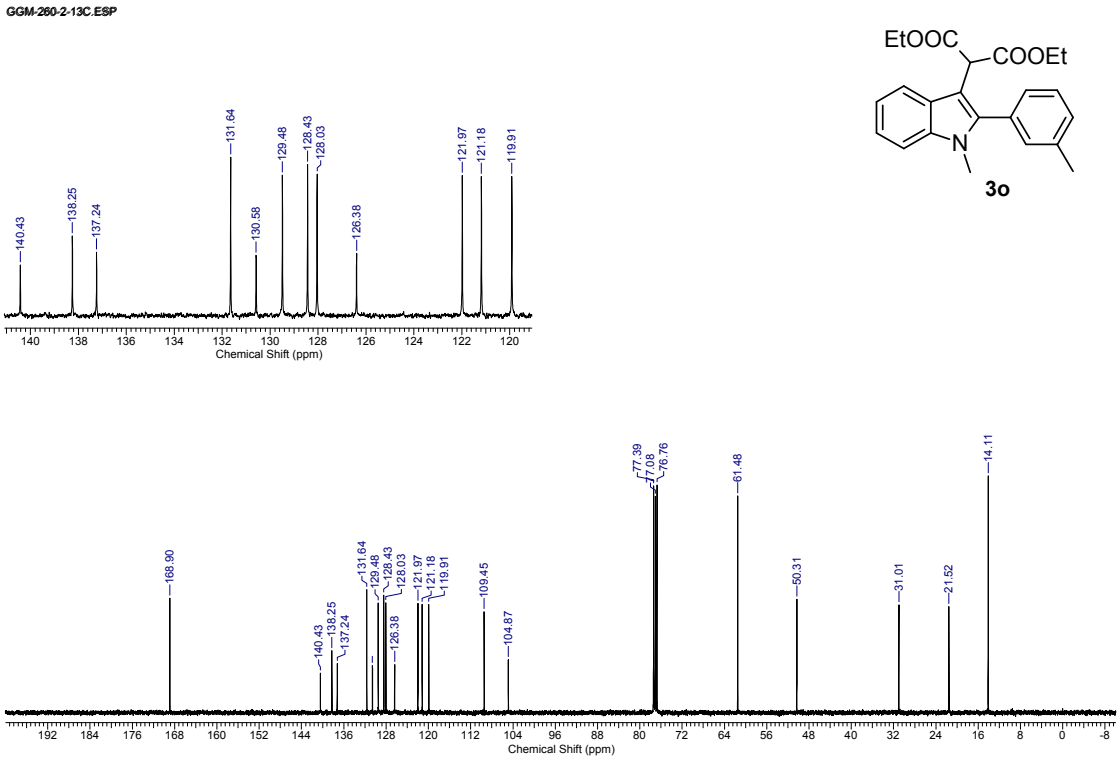


Figure S56. ^{13}C NMR spectrum of compound **3o**

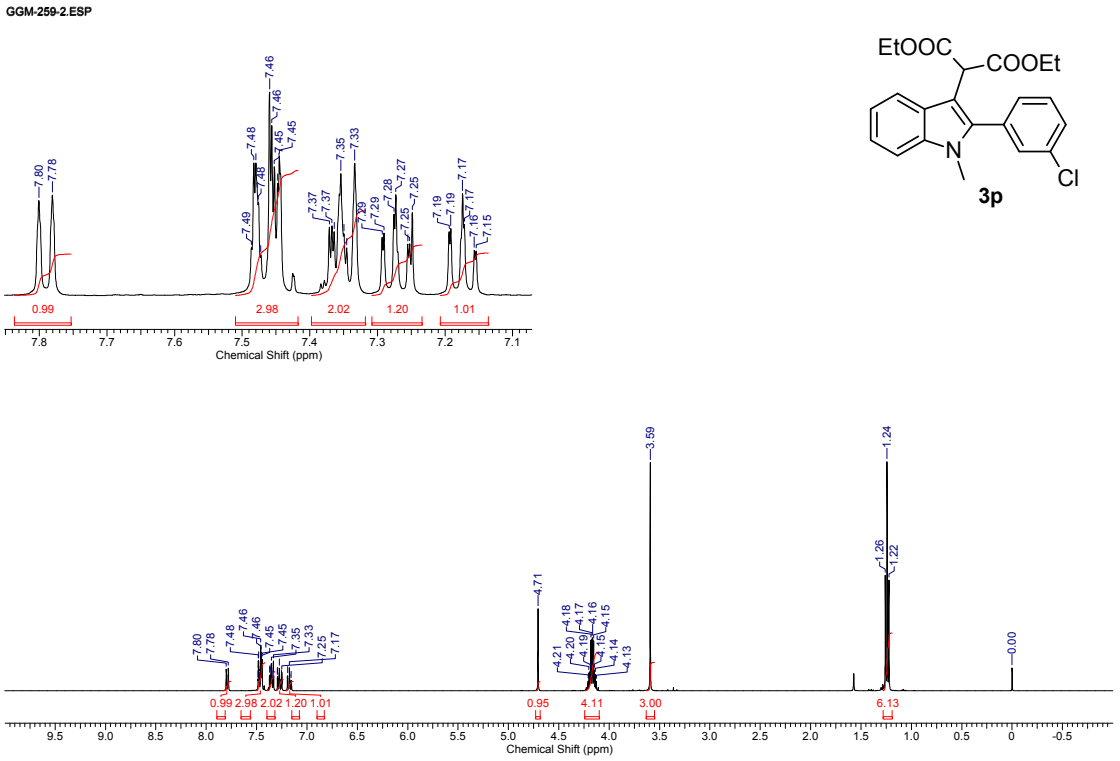


Figure S57. ^{1}H NMR spectrum of compound **3p**

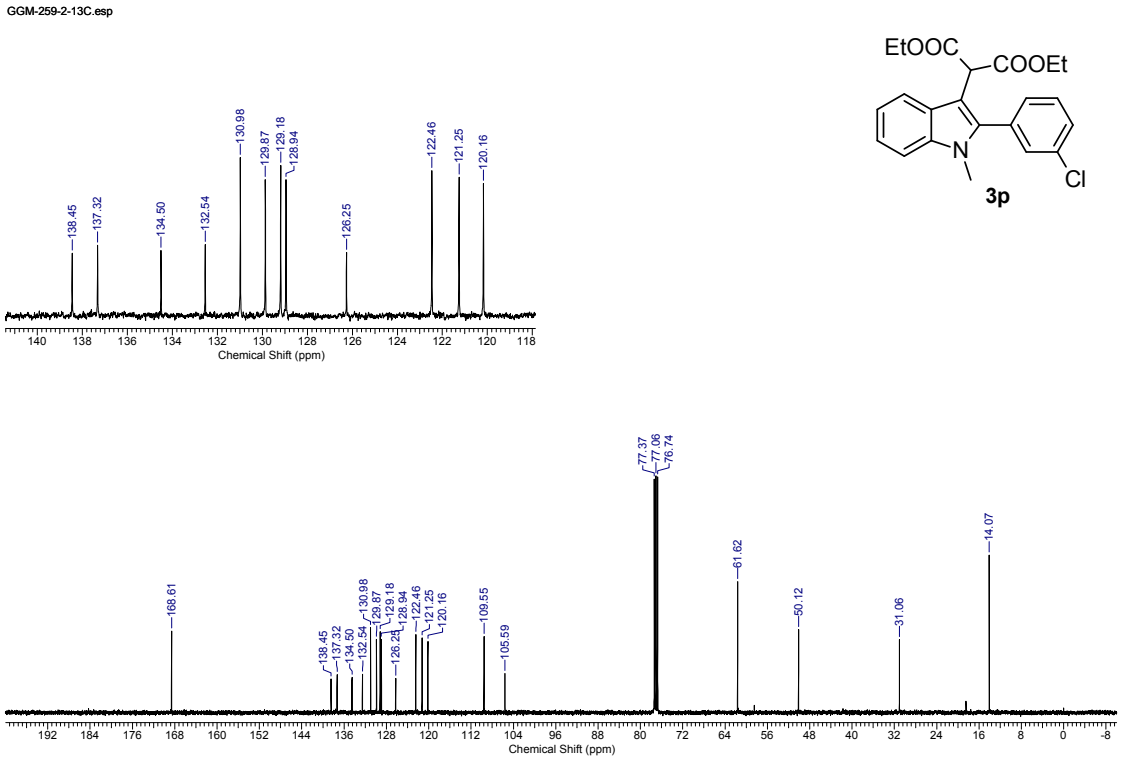


Figure S58. ^{13}C NMR spectrum of compound **3p**

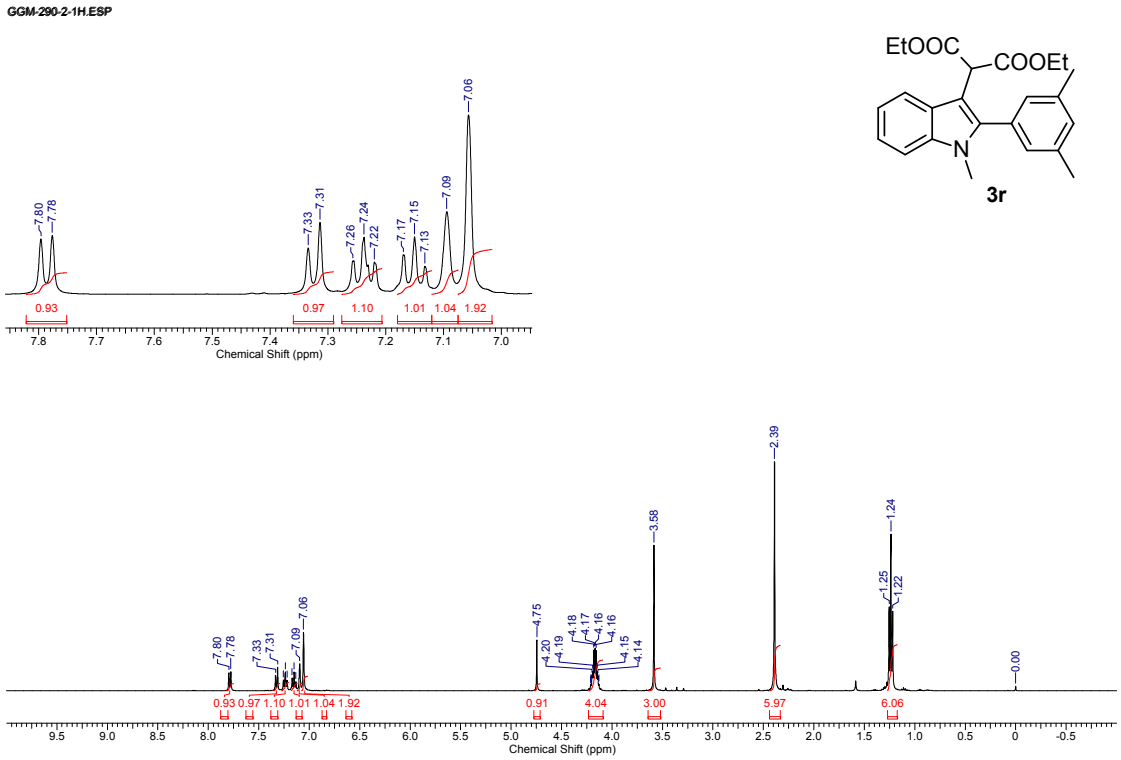


Figure S59. ^{1}H NMR spectrum of compound **3r**

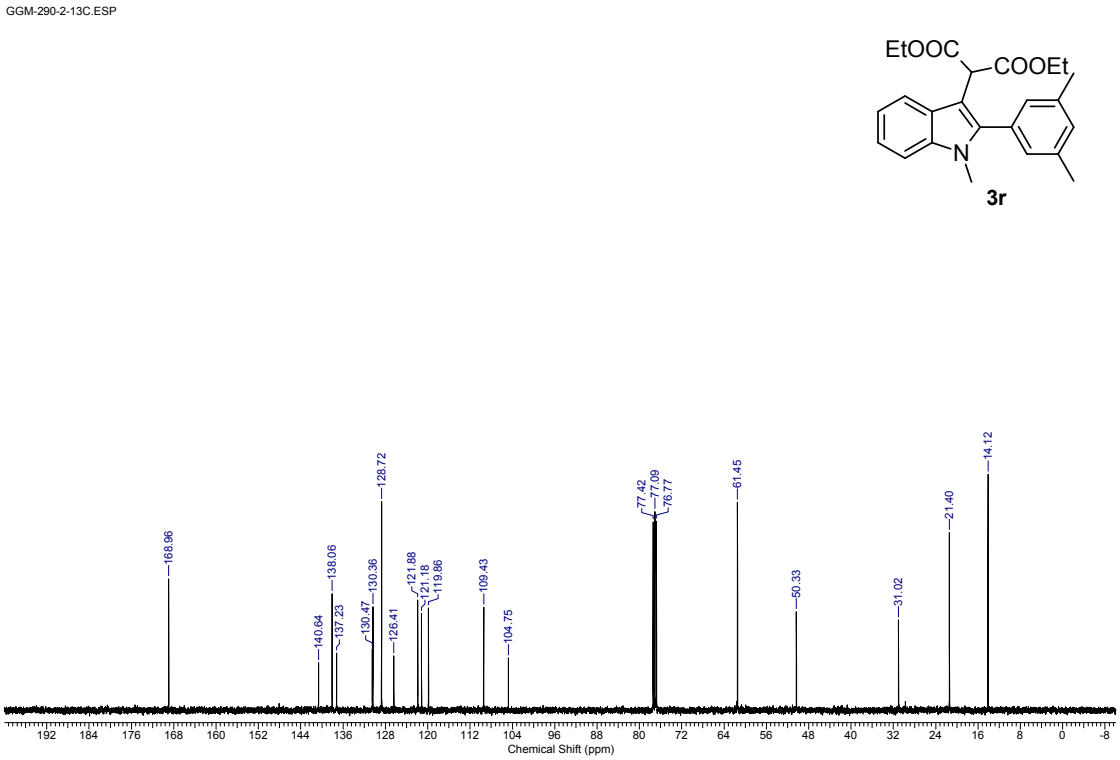


Figure S60. ^{13}C NMR spectrum of compound **3r**

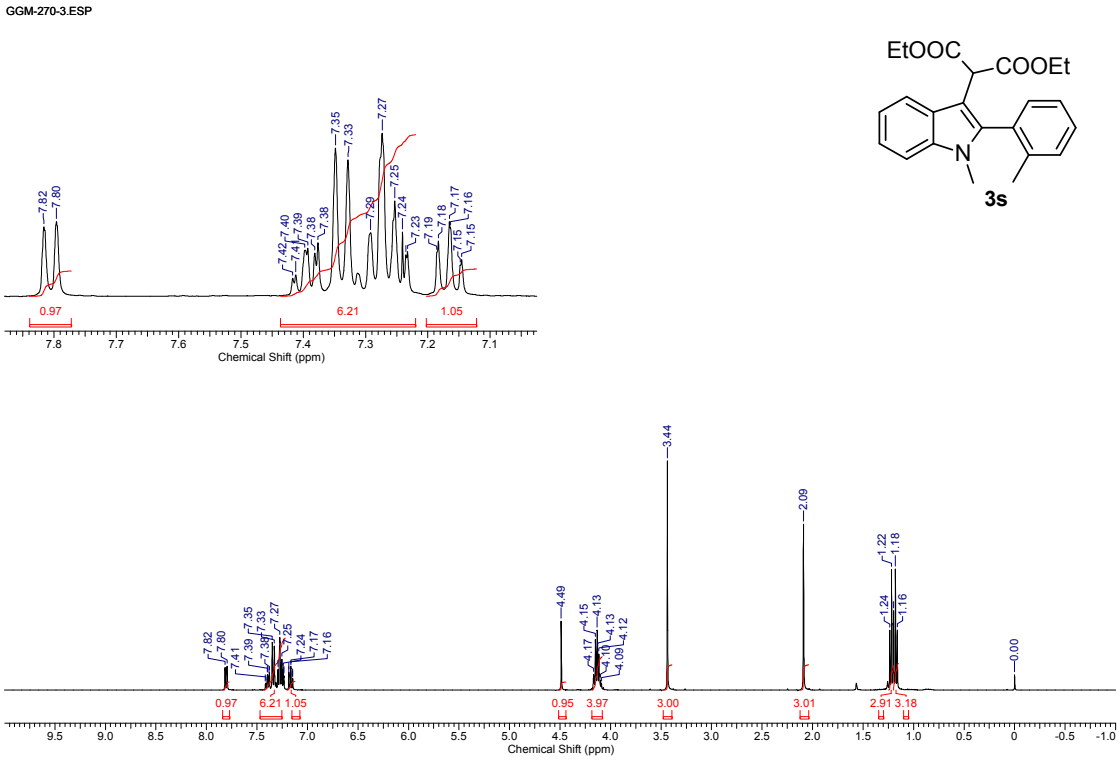


Figure S61. ^{1}H NMR spectrum of compound **3s**

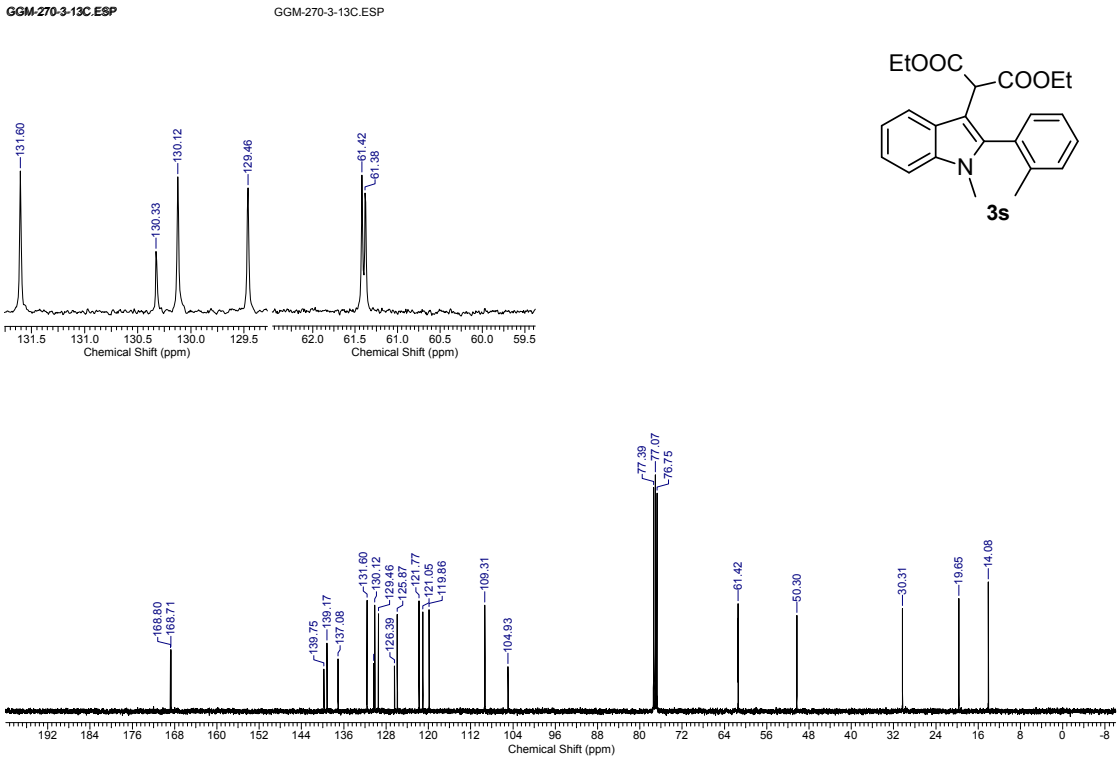


Figure S62. ^{13}C NMR spectrum of compound **3s**

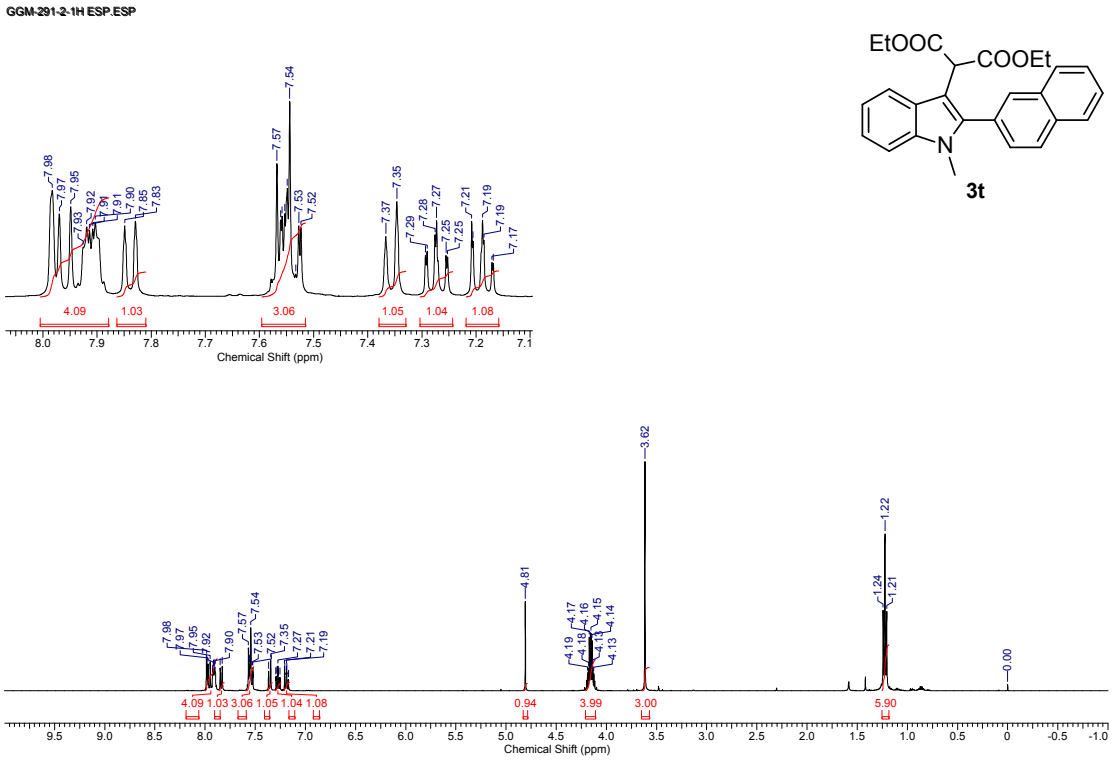


Figure S63. ^{1}H NMR spectrum of compound **3t**

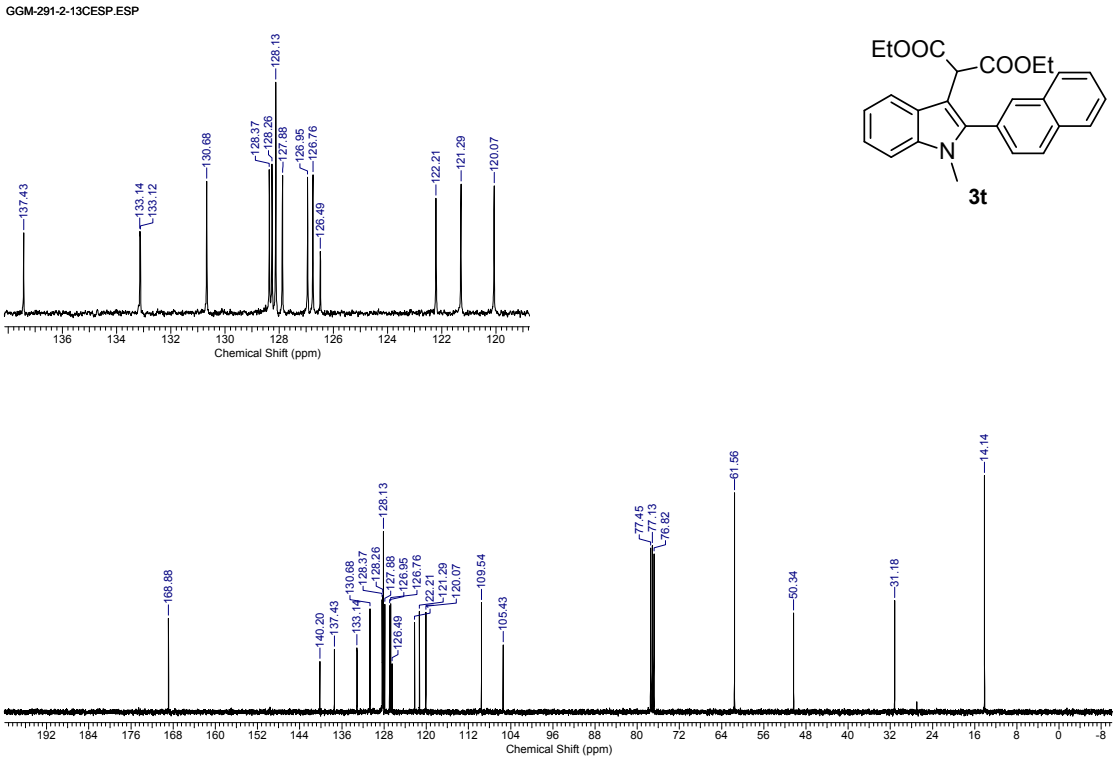


Figure S64. ^{13}C NMR spectrum of compound **3t**

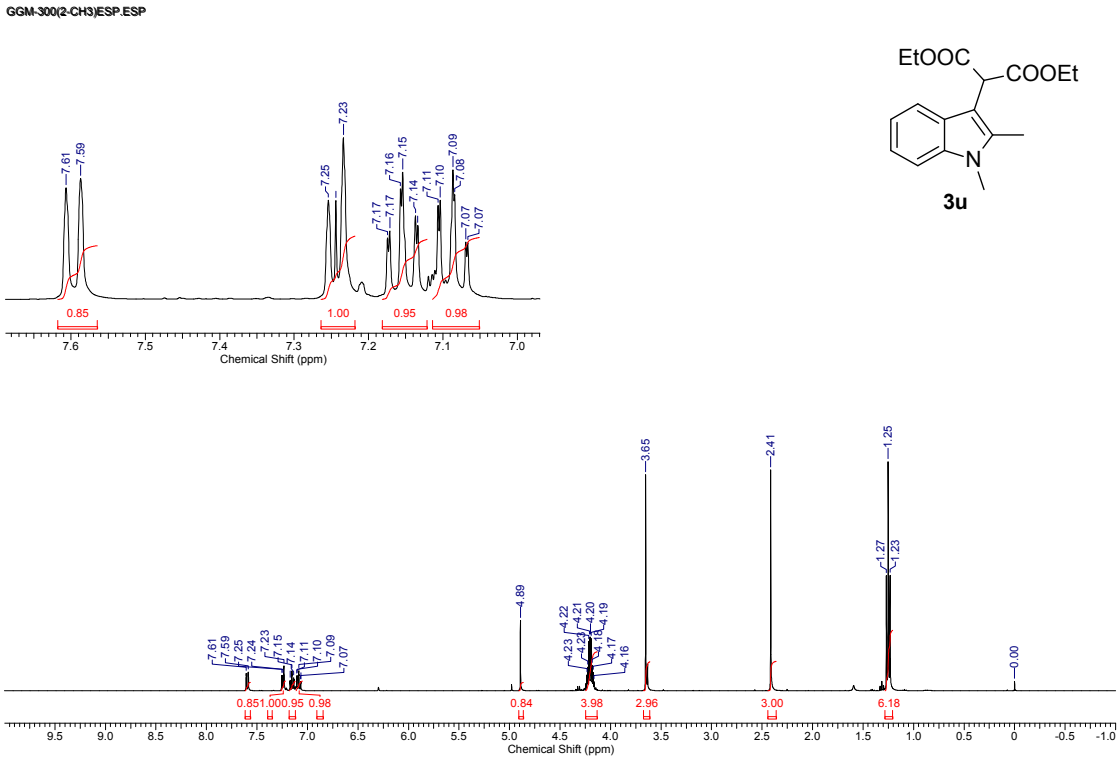


Figure S65. ^{1}H NMR spectrum of compound **3u**

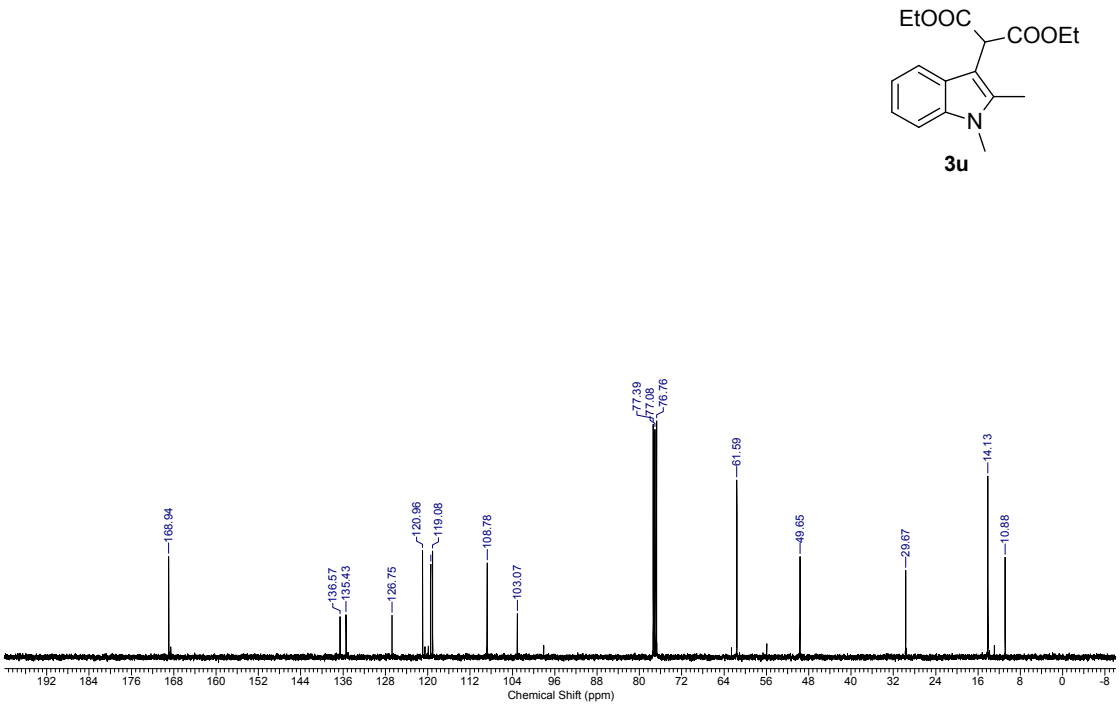


Figure S66. ^{13}C NMR spectrum of compound **3u**

10. Determination of Structure of 3a

The structure of **3a** was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **1923193**.

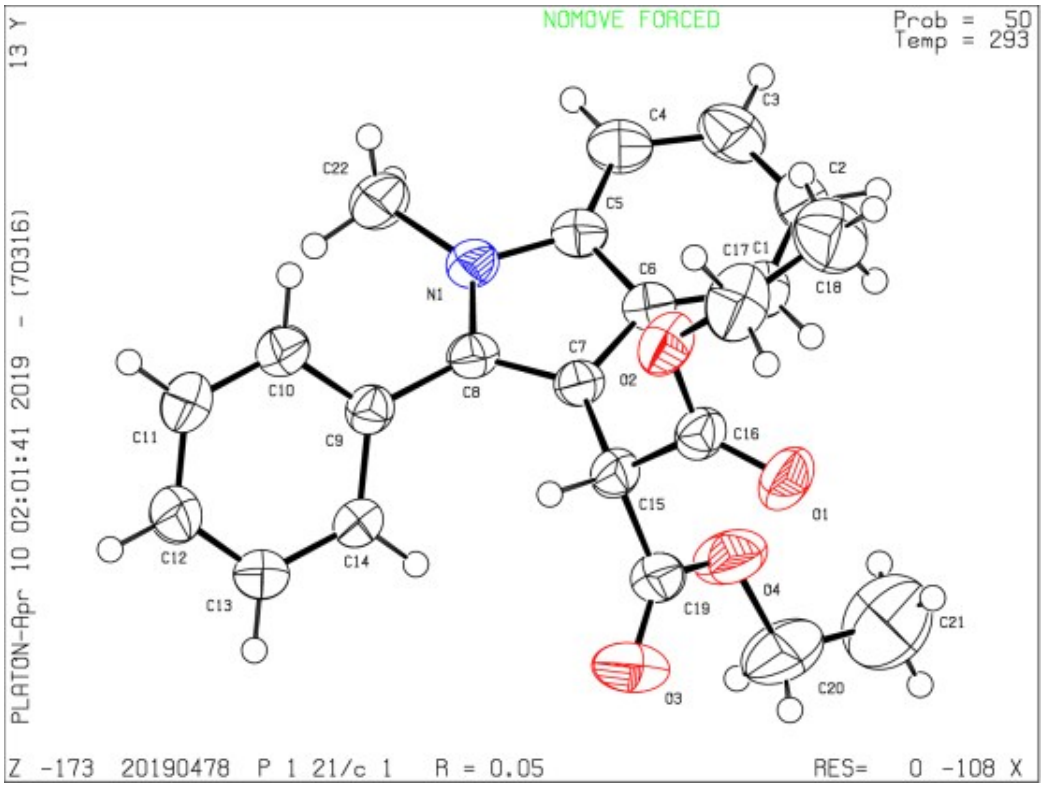


Table 1 Crystal data and structure refinement for 3a

Identification code	20190478
Empirical formula	$C_{22}H_{23}NO_4$
Formula weight	365.41
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.2745(8)
b/Å	7.8001(2)
c/Å	24.2247(14)
α/°	90
β/°	129.278(10)
γ/°	90
Volume/Å^3	1941.6(3)
Z	4
ρ_{calc}g/cm^3	1.250

μ/mm^{-1}	0.697
F(000)	776.0
Crystal size/mm^3	0.17 × 0.14 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.76 to 134.144
Index ranges	$-10 \leq h \leq 15$, $-7 \leq k \leq 9$, $-28 \leq l \leq 25$
Reflections collected	7250
Independent reflections	3471 [R_{int} = 0.0268, R_{sigma} = 0.0315]
Data/restraints/parameters	3471/0/247
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0490, wR_2 = 0.1250
Final R indexes [all data]	R_1 = 0.0630, wR_2 = 0.1387
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.23