Supporting Information

A Rapid Construction and Biological Evaluation of Densely Substituted Pyrrolo[1,2-*a*]indoles via $BF_3{\cdot}OEt_2$ Assisted Cascade Approach

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1. General Information

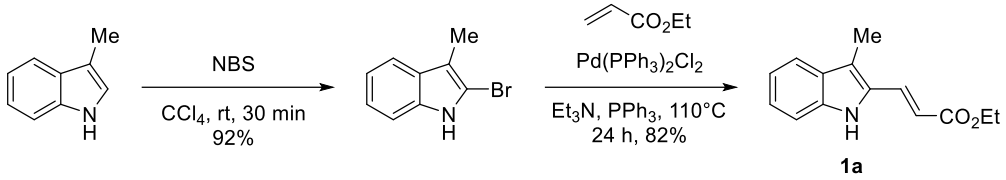
All reactions were carried out under nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. All the chemicals were purchased commercially, and used without further purification. All reactions were routinely carried out in oven-dried glassware under a nitrogen or argon atmosphere unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and an *p*-anisaldehyde stain, and heat as developing agents. Merck silica gel (particle sizes 100-200 and 230-400 mesh) was used for flash column chromatography. Yields refer to chromatographically pure material, unless otherwise stated.

^{1}H-NMR spectra were recorded at 500 MHz using a Make: Bruker High Perfomance Digital FT-NMR (Model: AVANCE III HD, AscendTM WB, 500 MHz Equipment control: Topspin 3.2 Features Standard operating procedure) whereas ^{13}C-NMR spectra were recorded at 126 MHz. Chemical shifts in the ^{1}H-NMR spectra are reported with reference to internal Me_4Si (TMS) (δ 0.00) in $CDCl_3$ and DMSO-d_6; in ^{13}C-NMR spectra they are reported with reference to TMS in $CDCl_3$. NMR spectra were processed and analyzed using Mnova software. The HRMS data were collected using a 6545 LC/Q-TOF HRMS.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dt = doublet of a triplet, m = multiplet, br = broad.

2. Preparation of Substrates

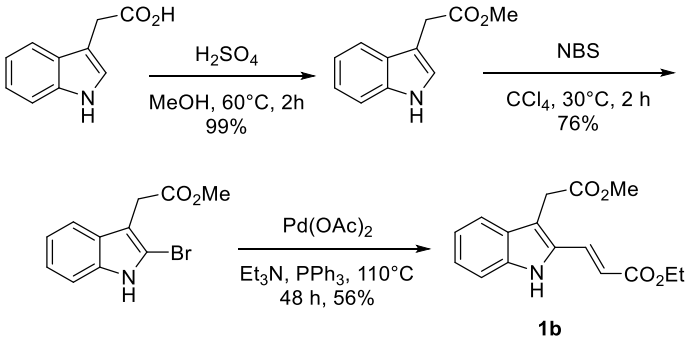
2.1 Ethyl (*E*)-3-(3-methyl-1H-indol-2-yl)acrylate 1a[1]



2-Bromo-3-methyl indole was synthesized according to the following modifications of literature methods[2]. To a solution of 3-methylindole (500 mg, 3.811 mmol) in CCl_4 (10 mL), NBS (*N*-brommosuccinimide; 746 mg, 4.192 mmol) was added in 200 mg portions. The mixture was stirred at room temperature for 30 min, filtered and. the filtrate was concentrated under reduced pressure. The purification of the residue on a silica gel column using EtOAc/hexane (1/9) as eluent gave the 2-bromo-3-methyl indole (737 mg, 3.506 mmol, 92%) as a white solid: R_f = 0.6 (EtOAc/hexane 1/4).

To 2-bromo-3-methyindole (737 mg, 3.506 mmol) in a 10 mL round bottom flask were added ethyl acrylate (0.47 mL, 4.382 mmol), Et_3N (0.62 mL, 4.382 mmol), Ph_3P (28 mg, 0.106 mmol), and $Pd(PPh_3)Cl_2$ (37 mg, 0.053 mmol), and the resulting mixture was stirred at 110°C for 24 h. The reaction was allowed to room temperature and extracted 3x with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The purification of the residue on a silica gel column using (EtOAc/hexane 2/23) as eluent gave the ester **1a** (659 mg, 2.875 mmol, 82%) as a yellow solid: R_f = 0.6 (EtOAc/hexane 1/4); The obtained NMR data agreement with the reported data.[1] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.27 (dd, *J* = 9.6, 5.3 Hz, 1H), 7.12 (dd, *J* = 11.0, 3.9 Hz, 1H), 6.16 (d, *J* = 15.9 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR**(126 MHz, CDCl3) δ 167.5, 137.5, 132.4, 130.1, 129.2, 125.2, 120.0 (2 x CH), 118.9, 113.9, 111.1, 60.7, 14.5, 9.1.

2.2 Ethyl (*E*)-3-(3-(2-methoxy-2-oxoethyl)-1*H*-indol-2-yl)acrylate 1b[3]



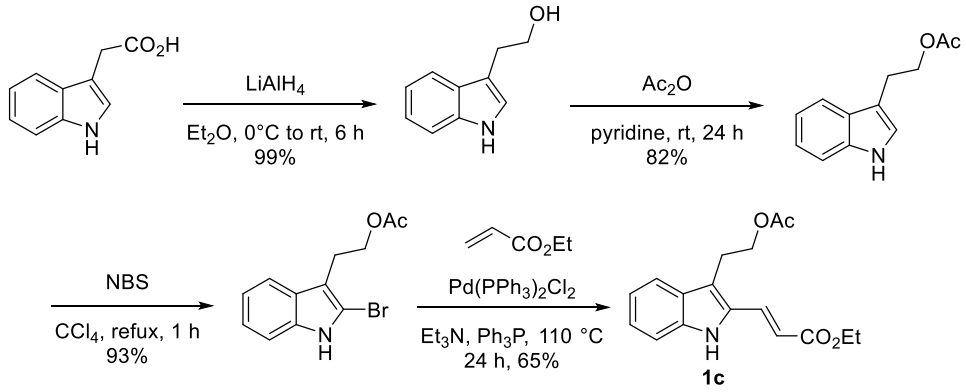
H_2SO_4 (98%) (0.2 mL) was added to a stirred solution of Indole-3-acetic acid (500 mg, 2.854 mmol) in CH_3OH (10 mL) at room temperature, and the mixture was then stirred for 2 h at 60 °C. TLC was used to monitor the reaction progress until

it was complete. A large amount of iced water was then added to the mixture. A saturated solution of Na_2CO_3 was used to neutralize the mixture until a white solid appeared. After filtering the mixed solution, methyl indole-3-acetate (535 mg, 2.827 mmol, 99%) was obtained as a white solid; R_f= 0.6 (EtOAc/hexane 3/7). Spectral data were in agreement with those reported.[4]

Methyl 2-(2-bromo-1H-indol-3-yl)acetate was synthesized according to the following modification of the literature method.[5] To a solution of methyl indole-3-acetate (100 mg, 0.528 mmol) in CCl_4 (3 mL), NBS (104 mg, 0.584 mmol) was added portion wise. The resulting mixture was warmed to 30°C and stirred for 2 h, filtered and. the filtrate was concentrated under reduced pressure. The purification of the residue on a silica gel column using EtOAc/hexane (2/8) as eluent gave the methyl 2-(2-bromo-1H-indol-3-yl)acetate (108 mg, 0.403 mmol, 76%) as a light-yellow solid: R_f = 0.7 (EtOAc/hexane 3/7).

To methyl 2-(2-bromo-1*H*-indol-3-yl)acetate (100 mg, 0.373 mmol) in a 10 mL round-bottom flask were added ethyl acrylate (0.05 mL, 0.470 mmol), Et_3N (0.07 mL, 0.502 mmol), Ph_3P (28 mg, 0.106 mmol), and $Pd(OAc)_2$ (1 mg, 0.004 mmol) and the mixture was stirred at 110°C for 48 h. The reaction was allowed to room temperature and extracted 3x with EtOAc (5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The purification of the residue on a silica gel column using EtOAc/hexane 1/4 as eluent gave the ethyl (*E*)-3-(3-(2-methoxy-2-oxoethyl)-1*H*-indol-2-yl)acrylate **1b** (60 mg, 0.209 mmol, 56%) as a yellow solid: R_f = 0.4 (EtOAc/hexane 1/4). Spectral data were in agreement with those reported.[3]

2.3 ethyl (*E*)-3-(3-(2-acetoxyethyl)-1*H*-indol-2-yl)acrylate 1c



Tryptophol was synthesized according to the following modification of the literature method.[6] To a dried 25 mL round-bottom flask containing solution of Indole-3-acetic acid (500 mg, 2.854 mmol) in Et_2O (10 mL) and chilled in an ice bath, was added portion wise $LiAlH_4$ (239 mg 6.298 mmol). It was allowed to stir at 0ºC for 10 minutes. The resulting mixture was warmed to rt and stirred for 6 h. After reaction completion was confirmed by TLC, the reaction mixture was quenched by the careful addition of water at 0°C. The mixture was stirred for 10 minutes until a white precipitate was observed, filtered by washing the precipitate with Et_2O, and the filtrate was evaporated. The residue was purified by silica gel flash

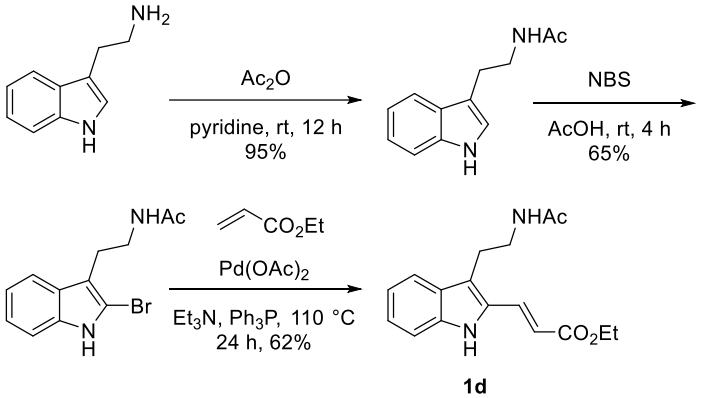
column chromatography to afford the corresponding tryptophol (455 mg, 2.823 mmol, 99%) as a brown solid: R_f=0.7 (EtOAc/hexane, 1/1). Spectral data were in agreement with those reported.[7]

To a solution of tryptophol (455 mg, 2.823 mmol) in pyridine (5 mL) dropwise Ac_2O (0.40 mL, 4.260 mmol) was added. The mixture was stirred at room temperature for 24h. The solution was poured into 20 mL H_2O and stirred for 20 min. The heterogeneous mixture was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel using EtOAc/hexanes (1/4) for elution provided the tryptophol ester (472 mg, 2.323 mmol 82%) as a colorless oil; R_f=0.5 (EtOAc/hexanes, 1/4); Spectral data were in agreement with those reported.[8]

To a solution of tryptophol ester (472 mg, 2.323 mmol) in CCl_4 (5 mL), NBS (455 mg, 2.555 mmol) portion wise was added. The mixture was reflux for 1h, filtrated and. the filtrate was concentrated under reduced pressure. The purification of the residue on a silica gel column using EtOAc/hexane (1/9) as eluent gave the 2-bromotryptophol ester (610 mg, 2.162 mmol, 93%) as a white solid: R_f = 0.5 (EtOAc/hexane 1/4).

To 2-bromotryptophol ester (610 mg, 2.162 mmol) in a 25 mL round-bottom flask, were added ethyl acrylate (0.58 mL, 5.405 mmol), Et_3N (0.60 mL, 4.324 mmol), Ph_3P (28 mg, 0.106 mmol), $Pd(PPh_3)Cl_2$ (46 mg, 0.065 mmol) and resulting mixture was stirred at 110°C for 24h. The reaction was allowed to room temperature and extracted 3x with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The purification of the residue on a silica gel column using EtOAc/hexane 1/4 as eluent gave the ethyl (*E*)-3-(3-(2-acetoxyethyl)-1*H*-indol-2-yl)acrylate **1c** (420 mg, 1.401 mmol, 65%) as a yellow solid: R_f = 0.4 (EtOAc/hexane 1/4); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.81 (d, *J* = 16.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.31 – 6.21 (m, 1H), 4.29 (dt, *J* = 14.0, 7.0 Hz, 4H), 3.21 (t, *J* = 6.9 Hz, 2H), 2.02 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 171.2, 167.2, 137.5, 132.1, 130.9, 128.5, 125.2, 120.4, 119.9, 118.4, 114.9, 111.3, 64.5, 60.8, 23.9, 21.1, 14.5; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NO_4$ 302.1387; Found 302.1391.

2.4 ethyl (*E*)-3-(3-(2-acetamidoethyl)-1H-indol-2-yl)acrylate 1d



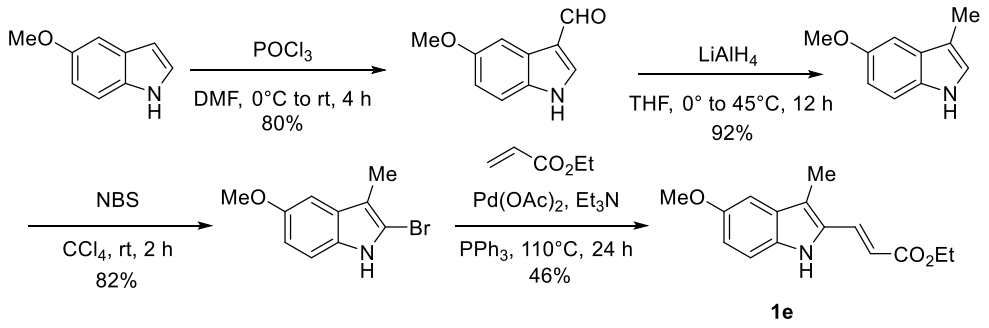
To a solution of tryptamine (200 mg, 1.248 mmol) in pyridine (5 mL) was added dropwise Ac_2O (0.18 mL, 1.872 mmol). The mixture was stirred at room temperature for 12 h. The solution was poured into 10 mL H_2O and stirred for 20 min. The heterogeneous mixture was separated and the aqueous layer was extracted with CH_2Cl_2 (4 x 10 mL). The combined

organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel using EtOAc/hexanes (4/1) for elution provided the acetamide (240 mg, 1.187 mmol 95%) as a colourless oil; R_f=0.5 (EtOAc/hexanes, 4/1); Spectral data were in agreement with those reported.[8]

To a solution of acetamide (240 mg, 1.187 mmol) in AcOH (5 mL) was added portion wise NBS (233 mg, 1.309 mmol). The mixture was stirred at room temperature for 4 h, filtrated and neutralized by aq. $NaHCO_3$ then the filtrate was concentrated under reduced pressure. The purification of the residue on a silica gel column using EtOAc/hexane (4/1) as eluent gave the 2-bromo tryptamine (217 mg, 0.772 mmol, 65%) as a white solid: R_f = 0.4 (EtOAc/hexane 4/1).

To 2-bromo tryptamine (217 mg, 0.772 mmol) in a 10 mL round bottom flask added ethyl acrylate (0.10 mL, 0.965 mmol), Et_3N (0.13 mL, 0.965 mmol), Ph_3P (13 mg, 0.049 mmol), $Pd(OAc)_2$ (6 mg, 0.027 mmol) and resulting mixture was stirred at 110°C for 24 h. The reaction was allowed to room temperature and extracted 3x with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The purification of the residue on a silica gel column using (EtOAc/hexane 9/1) as eluent gave the ethyl (*E*)-3-(3-(2-acetamidoethyl)-1H-indol-2-yl)acrylate **1d** (144 mg, 0.479 mmol, 62%) as a yellow solid: R_f = 0.5 (EtOAc/hexane 9/1); **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.41 (s, *J* = 29.2 Hz, 1H), 8.03 – 7.91 (m, 1H), 7.65 – 7.60 (m, 2H), 7.56 (d, *J* = 6.0 Hz, 1H), 7.35 – 7.00 (m, 2H), 6.54 (dd, *J* = 21.1, 12.2 Hz, 1H), 4.19 (q, *J* = 13.7, 6.8 Hz, 2H), 3.26 – 3.15 (m, 2H), 2.95 (t, *J* = 6.6 Hz, 2H), 1.75 (d, *J* = 11.1 Hz, 3H), 1.29 – 1.24 (t, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.0, 136.5, 127.7, 125.0, 122.4, 120.4, 120.1, 117.9, 112.5, 112.1, 110.9, 109.0, 39.8, 29.8, 24.8, 24.8, 23.2; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}N_2O_3$ 301.1547; Found 301.1549.

2.5 Ethyl (*E*)-3-(3-methyl-1H-indol-2-yl)acrylate 1e



5-methoxy-indole-3-carbaldehyde was synthesized according to the following modification of literature methods[9]. To a dried 25 mL round bottom flask containing solution of 5-methoxy indole (200 mg, 1.359 mmol) in DMF (5 mL) and chilled in an ice bath, $POCl_3$ (0.38 mL, 4.077 mmol) was added slowly, turning the mixture into a red solution. It was allowed to stir at 0ºC for 30 min. The resulting mixture was warmed to rt and stirred for 3.5h, until it turned into a yellow suspension. After reaction completion confirmed by TLC, the reaction mixture was quenched by adding crushed ice in a round bottom flask containing the crude, followed by the dropwise addition of 15% NaOH (8 mL), using an ice bath. The crude was mixed with EtOAc and extracted (3 x 20 mL). The combined organic layers were washed with water (3 x 10 mL), dried over Na_2SO_4, filtered and the solvent evaporated under reduced pressure to afford 5-methoxy-indole-3-carbaldehyde (190

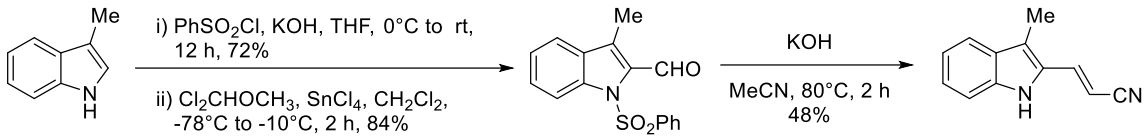
mg, 1.085 mmol, 80%) as a brown solid: R_f=0.2 (EtOAc/hexane, 1/1). The obtained product used in next step without further purification.

To a dried 25 mL round bottom flask containing solution of 5-methoxy indole-3-carbaldehyde (190 mg, 1.085 mmol) in THF (5 mL) and chilled in an ice bath, $LiAlH_4$ (83 mg, 2.170 mmol) was added portion wise. It was allowed to stir at 0ºC for 15 min. The resulting mixture was warmed to 45°C and stirred for 12 h. After reaction completion confirmed by TLC, the reaction mixture was quenched by adding crushed ice in round bottom flask containing the crude, using an ice bath. The crude was mixed with EtOAc and extracted (3 x 10 mL). The combined organic layers were washed with water (3 x 10 mL), dried over Na_2SO_4, filtered and the solvent evaporated under reduced pressure. The crude product purified by silica gel column by using EtOAc/hexane (1/4) as eluent gave 5-methoxy-3-methyl indole (161 mg, 0.999 mmol, 92%) as a white solid: R_f=0.5 (EtOAc/hexane, 1/4).

To a solution of 5-methoxy-3-methyl indole (161 mg, 0.999 mmol) in CCl_4 (4 mL) was added portions wise NBS (196 mg, 1.099 mmol). The mixture was stirred at room temperature for 2h, filtered and. the filtrate was concentrated under reduced pressure. The purification of the residue on a silica gel column using EtOAc/hexane (1/9) as eluent gave the 2-bromo-5-methoxy-3-methyl indole (197 mg, 0.820 mmol, 82%) as a white solid: R_f = 0.6 (EtOAc/hexane 1/4).

To 2-bromo-5-methoxy-3-methyindole (197 mg, 0.820 mmol) in a 5 mL round bottom flask added ethyl acrylate (0.11 mL, 1.024 mmol), Et_3N (0.15 mL, 1.024 mmol), Ph_3P (28 mg, 0.106 mmol), $Pd(OAc)_2$ (37 mg, 0.053 mmol) and resulting mixture was stirred at 110°C for 24h. The reaction was allowed to room temperature and extracted 3x with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The purification of the residue on a silica gel column using EtOAc/hexane (1/9) as eluent gave the ethyl (*E*)-3-(5-methoxy-3-methyl-1*H*-indol-2-yl)acrylate **1e** (98 mg, 0.378 mmol, 46%) as a yellow solid: R_f = 0.6 (EtOAc/hexane ¼); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.77 (d, *J* = 16.0 Hz, 1H), 7.52 (s, 1H), 7.30 – 7.21 (m, 1H), 6.97 (s, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 2.39 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 4H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 167.2, 150.7, 132.8, 132.1, 131.1, 129.0, 118.2, 115.7, 114.5, 111.2, 101.5, 60.7, 56.9, 14.5, 9.1; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}NO_3$ 260.1281; Found 260.1289.

2.6 (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylonitrile 1f



Indole-2-carbaldehyde was synthesized according to the following modification of literature method.[1]

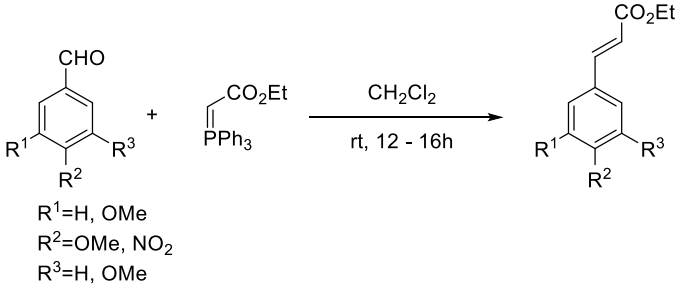
To a magnetically stirred solution of the 3-methyl indole (500 mg, 3.811 mmol) in THF (15 mL) was added KOH powder (321 mg, 5.720 mmol) followed by dropwise addition of $PhSO_2Cl$ (0.60 mL, 4.700 mmol) at 0°C, and the mixture was stirred magnetically for 12h at room temperature. Water (10 mL) was then added to the reaction mixture, which was then extracted with EtOAc (3×10 mL), washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and

purification of the residue on silica gel column using (EtOAc/hexane 1/4) as eluent furnished 3-methyl-1-(phenylsulfonyl)-1*H*-indole (742 mg, 2.735, 72%) as a white solid: R_f= 0.5 (EtOAc/hexane1/4).

To a magnetically stirred solution of the protected 3-methyl indole (500 mg, 1.843 mmol) in CH_2Cl_2(10 mL) was added dichloromethyl methyl ether (0.60 mL, 6.634 mmol) followed by dropwise addition of $SnCl_4$ (0.43 mL, 2.765 mmol) at −78 °C; the mixture was then warmed slowly to −10 °C over a period of 2 h. HCl (1.0 N, 10 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2. The organic layer was then washed with brine and dried over Na_2SO_4. Evaporation of the solvent and recrystallization of the crude product from CH_2Cl_2 furnished the Indole-2-carbaldehyde (466 mg, 1.556 mmol, 84%) as black solid: R_f= 0.5 (EtOAc/hexane 3/7);

To a magnetically stirred solution of the protected indole-2-carbaldehyde (200 mg, 0.668 mmol) in acetonitrile (5 mL) was added KOH powder (75 mg, 1.337 mmol) at rt, and the mixture was stirred magnetically for 2 h at 80°C. Water (5 mL) was then added to the reaction mixture, which was then extracted with EtOAc (3×10 mL), washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using (EtOAc/hexane 1/9) as eluent furnished (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylonitrile (59 mg, 0.322 mmol, 48%) as a white solid: R_f= 0.5 (EtOAc/hexane1/9); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 16.5 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.14 (ddd, *J* = 8.0, 5.9, 2.1 Hz, 1H), 5.47 (d, *J* = 16.5 Hz, 1H), 2.41 (s, 3H); **^{13}C{^{1}H} NMR**(101 MHz, $CDCl_3$) δ 137.8, 129.4, 129.0, 126.1, 125.8, 120.6, 120.4, 119.0, 111.3, 100.1, 90.9, 9.1; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}N_2$ 183.0917; Found 260.0944.

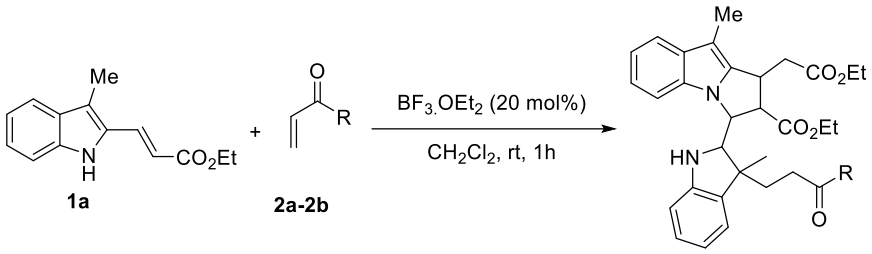
2.7 Cinnamate



Cinnamate **2e-2g** and **8'** was prepared following a previously reported methodology.[10] Ethyl (triphenylphosphoranylidene)acetate (1.5 equiv.) was added to a stirring mixture of the corresponding benzaldehyde (1.0 equiv.) in dichloromethane (5-10 mL) and the resulting solution was stirred at room temperature for 12-16 h. Water (5 mL) was then added to the reaction mixture, which was then extracted with EtOAc (3×10 mL) and, dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc/hexane (1/4) as eluent furnished cinnamate **2e-2g** and **8'** as a solid.

3. General procedure for synthesis of pyrrolo[1,2-*a*]indole (3a-3g, 4a-4f and 5a-5d)

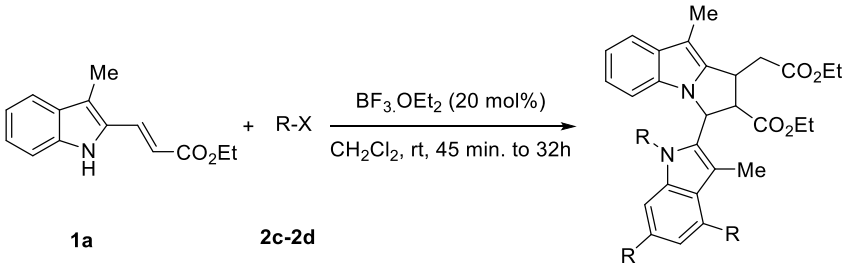
3.1 General procedure A



3a-3b, 77-85% yield, 96:4 *dr*

Under nitrogen atmosphere, an oven dried 10 mL round bottom flask, equipped with a magnetic stirring bar, was charged with compound ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (1.0 equiv.) and CH_2Cl_2(0.6 mL). To this solution was added dropwise $BF_3{\cdot}OEt_2$ (20 mol%) followed by addition of compound **2a** or **2b** (2.0 equiv.) at room temperature. Then the whole reaction mixture was allowed to stir for 1h at room temperature. After completion of the reaction (monitored by TLC), water (1 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (3×10 mL) and, dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc/hexane (3/7) as eluent furnished compound **3a** and **3b** with 85% and 77% respectively.

3.2 General procedure B

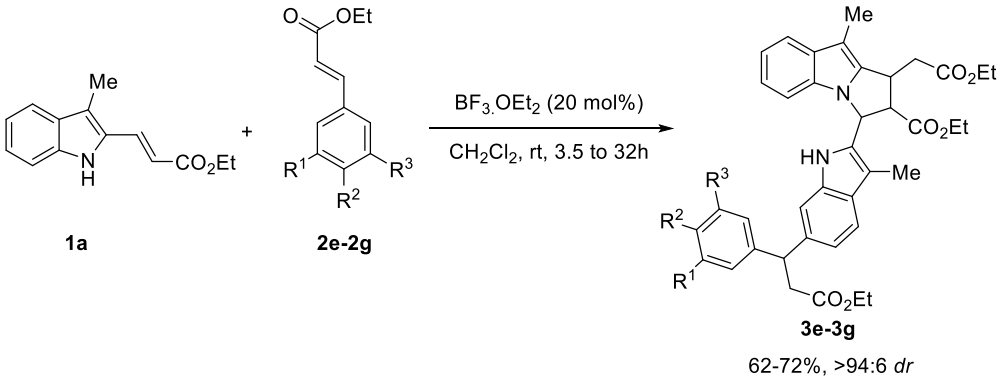


3c-3d

64-73% yield, >96:4 *dr*

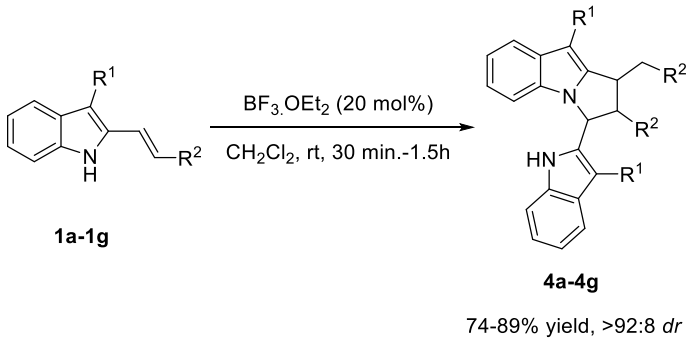
Under nitrogen atmosphere, an oven dried 10 mL round bottom flask, equipped with a magnetic stirring bar, was charged with compound ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (1.0 equiv.) and CH_2Cl_2(0.6 mL). To this solution was added dropwise $BF_3{\cdot}OEt_2$ (20 mol%) followed by addition of compound **2c** or **2d** (1.0 equiv.) at room temperature. Then the whole reaction mixture was allowed to stir for 45 minutes to 32h at room temperature. After completion of the reaction (monitored by TLC), water (1 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (3×10 mL) and, dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc/hexane as eluent furnished compound **3c-3d** (64-73%) as a solid.

3.3 General procedure C



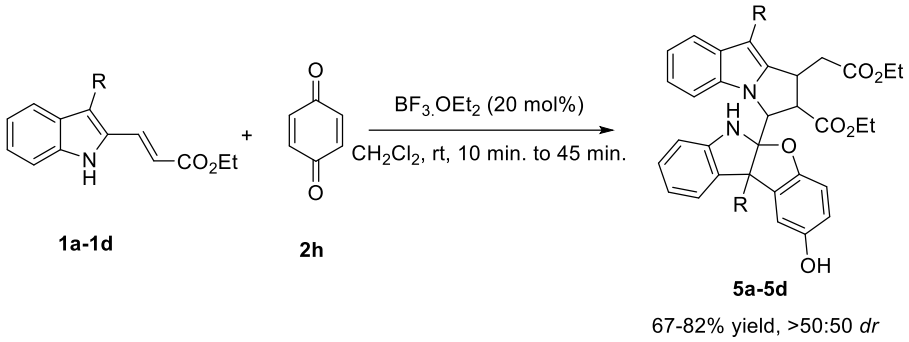
Under nitrogen atmosphere, an oven dried 10 mL round bottom flask, equipped with a magnetic stirring bar, was charged with compound ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (1.0 equiv.) and CH_2Cl_2(1.5 mL). To this solution was added dropwise $BF_3{\cdot}OEt_2$ (20 mol%) followed by addition of compound cinnamates **2e** or **2f** or **2g** (2.0 equiv.) at room temperature. Then the whole reaction mixture was allowed to stir for 3.5-32h at room temperature. After completion of the reaction (monitored by TLC), water (1 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (3×10 mL) and, dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc/hexane as eluent furnished compound **3e-3g** (62-72%) as a solid.

3.4 General procedure D



Under nitrogen atmosphere, an oven dried 10 mL round bottom flask, equipped with a magnetic stirring bar, was charged with compound (1.0 equiv.) and CH_2Cl_2(0.6 mL). To this solution was added $BF_3{\cdot}OEt_2$ (20 mol%) dropwise at room temperature, then stirring for 30 min to 1.5 h at room temperature. Water (5 mL) was then added to the reaction mixture, which was then extracted with CH_2Cl_2 (3×10 mL) and, dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc/hexane (1/4) as eluent furnished self-dimer **4a-4g** (74-89%) as a yellow solid.

3.5 General procedure E



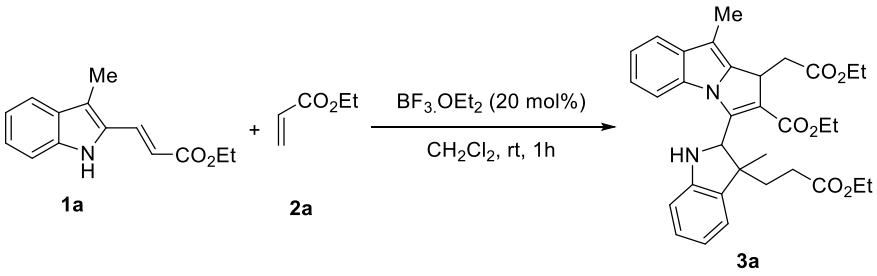
1a-1d **2h** **5a-5d**

67-82% yield, >50:50 *dr*

Under nitrogen atmosphere, an oven dried 10 mL round bottom flask, equipped with a magnetic stirring bar, was charged with compound **1a-1d** (1.0 equiv.) and CH_2Cl_2(0.6 mL). To this solution was added dropwise $BF_3{\cdot}OEt_2$ (20 mol%) followed by addition of 1,4-benzoqunone **2h** (1.5 equiv.) at room temperature. Then the whole reaction mixture was allowed to stir for 10-45 min. at room temperature. After completion of the reaction (monitored by TLC), water (1 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (3×10 mL) and, dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc/hexane as eluent furnished compound **5a-5d** (67-82%) as a solid.

4. Characterization of compounds 3a-3g

Synthesis of pyrrolo[1,2-*a*]indole 3a:

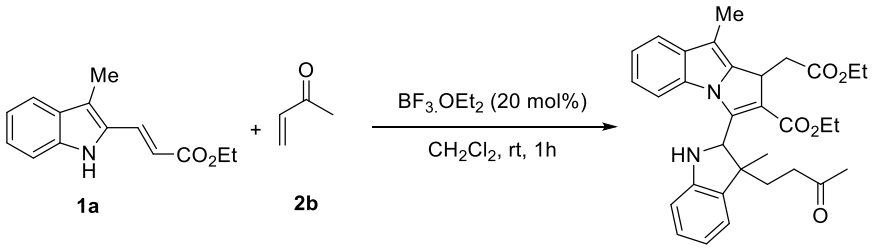


1a **2a** **3a**

85%, *dr* 96:4

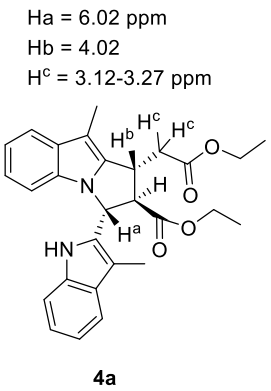
The title compound **3a** was prepared from ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (10 mg 0.044 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and ethyl acrylate **2a** (9.4 µL, 0.088 mmol, 2.0 equiv.) according to general procedure **A** with a reaction time of 1h. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (3/7) to furnish the title compound **3a** (11 mg 0.019 mmol, 85%) as a white solid; R_f=0.4 (EtOAc/hexane 3/7); m.p. 242°C; **IR** (neat): ν_{max}/cm^{-1} 3020, 2362, 1731, (C=O), 1215, 742, 667; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.91 (dd, *J* = 14.8, 7.4 Hz, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.26 (d, *J* = 7.8 Hz, 1H), 5.60 (d, *J* = 4.5 Hz, 1H), 4.26 – 4.20 (m, 4H), 4.06 – 4.02 (m, 3H), 3.50 (d, *J* = 17.9 Hz, 1H), 3.37 (d, *J* = 17.9 Hz, 1H), 2.47 (s, 3H), 2.31 – 2.23 (m, 1H), 2.19 – 2.11 (m, 2H), 1.96 – 1.84 (m, 1H), 1.52 (s, 3H), 1.34 – 1.25 (m, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 173.7, 173.1, 171.9, 156.4, 143.8, 138.1, 136.3, 131.3, 128.4, 128.2, 122.3, 122.2, 119.4, 119.0, 118.9, 111.2, 109.9, 107.5, 95.2, 61.5, 61.4, 61.1, 60.5, 55.81, 44.5, 35.2, 31.0, 30.4, 26.6, 14.4, 14.3, 14.3, 9.1; **HRMS** (ESI/Q-TOF) m/z: [M-H]$^+$ Calcd for $C_{33}H_{37}N_2O_6$ 527.2652; Found 527.2680.

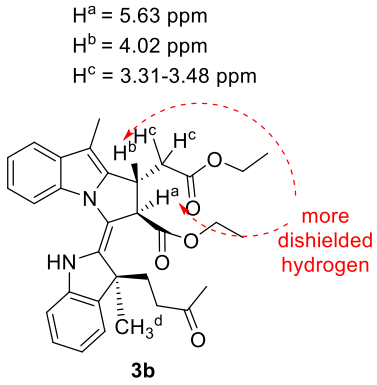
Synthesis of pyrrolo[1,2-*a*]indole 3b

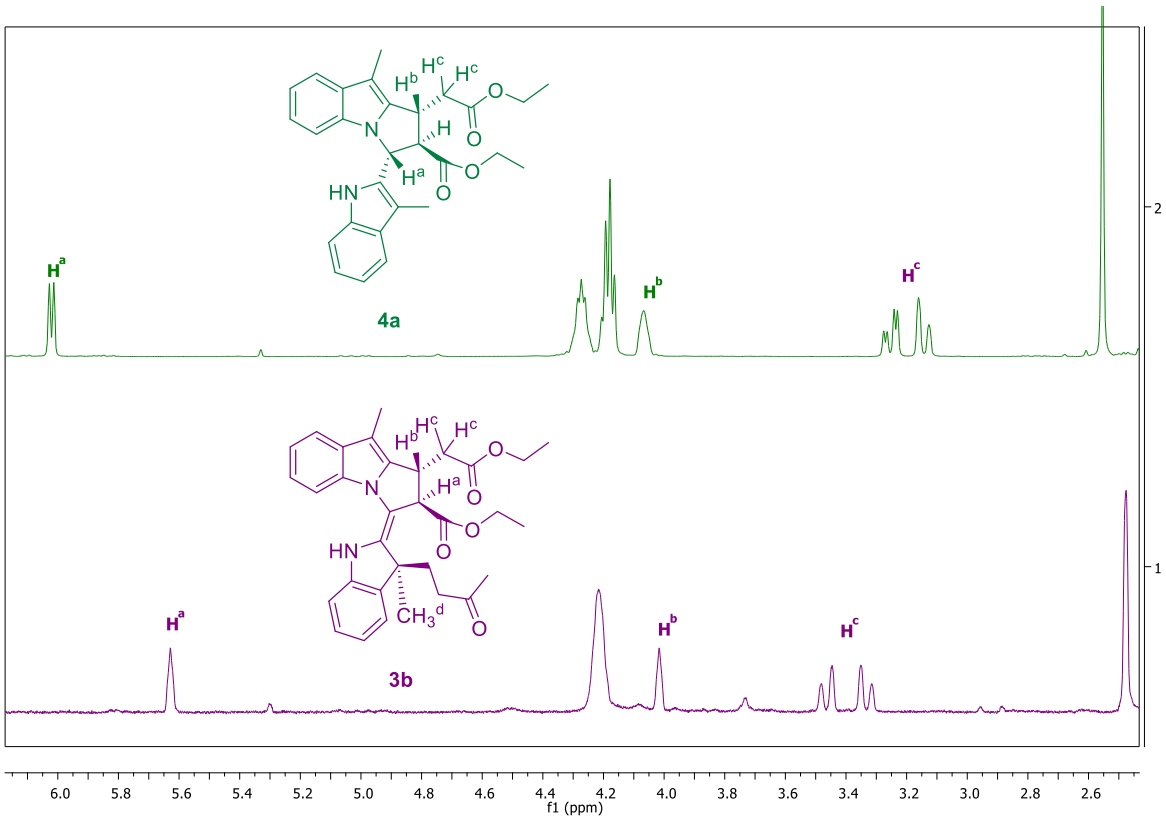


The title compound **3b**was prepared from ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (10 mg 0.044 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and methyl vinyl ketone **2b** (7.4 µL, 0.088 mmol, 2.0 equiv.) according to general procedure **A** with a reaction time of 1h. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (1/4) to furnish the title compound **3b** (9 mg 0.017 mmol, 77%) as a white solid; R_f=0.4 (EtOAc/hexane 1/4); m.p. 240°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.52 (d, *J* = 6.2 Hz, 1H), 7.36 (s, 1H), 7.10 (d, *J* = 37.5 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.67 (s, 1H), 6.29 (s, 1H), 5.63 (d, *J* = 4.5 Hz, CH^a), 4.22 (s, 4H), 4.02 (d, *J* = 4.5 Hz, CH^b), 3.46 (d, *J* = 17.9 Hz, CH^c), 3.33 (d, *J* = 18.0 Hz, CH^c), 2.48 (s, 3H), 2.35 (d, *J* = 10.7 Hz, 1H), 2.16 (d, *J* = 12.7 Hz, 1H), 2.03 (d, 5H), 1.50 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 208.8, 173.2, 171.9, 156.6, 143.8, 138.4, 136.4, 131.3, 128.4, 128.2, 122.3, 122.2, 119.4, 119.0, 118.9, 111.2, 109.9, 107.5, 95.2, 61.5, 61.4, 61.0, 55.7, 44.4, 39.5, 33.8, 31.0, 30.20, 26.8, 14.4, 14.4, 9.0; **HRMS** (ESI/Q-TOF) m/z: $[M-H]^+$ Calcd for $C_{32}H_{35}N_2O_5$ 527.2446; Found 527.2552. 1H NMR (500 MHz, CDCl3)

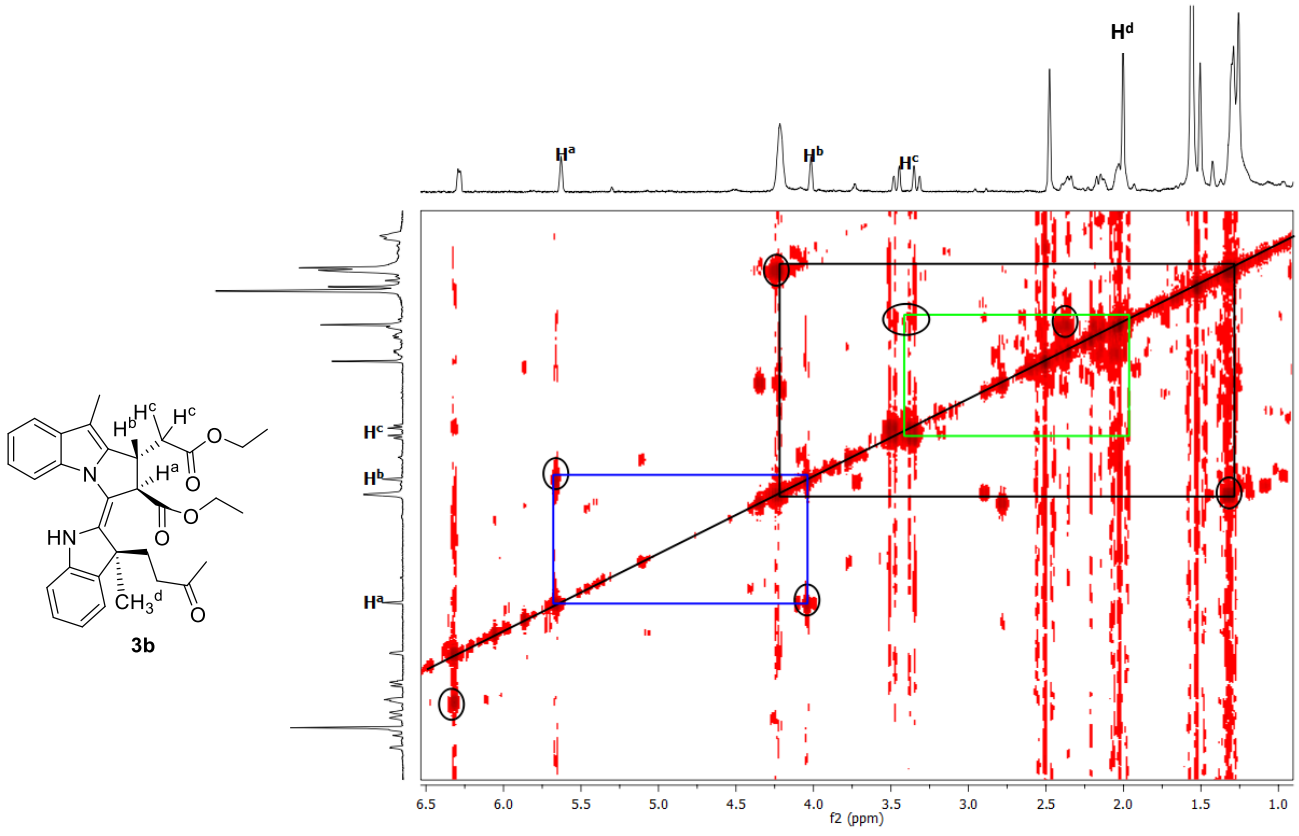
The examination of the chemical shift value and comparison of **4a** and **3b** was used to pinpoint the location of the double bond in a five-member ring. Additionally, determined structure supported by the 2D NMR (^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY).



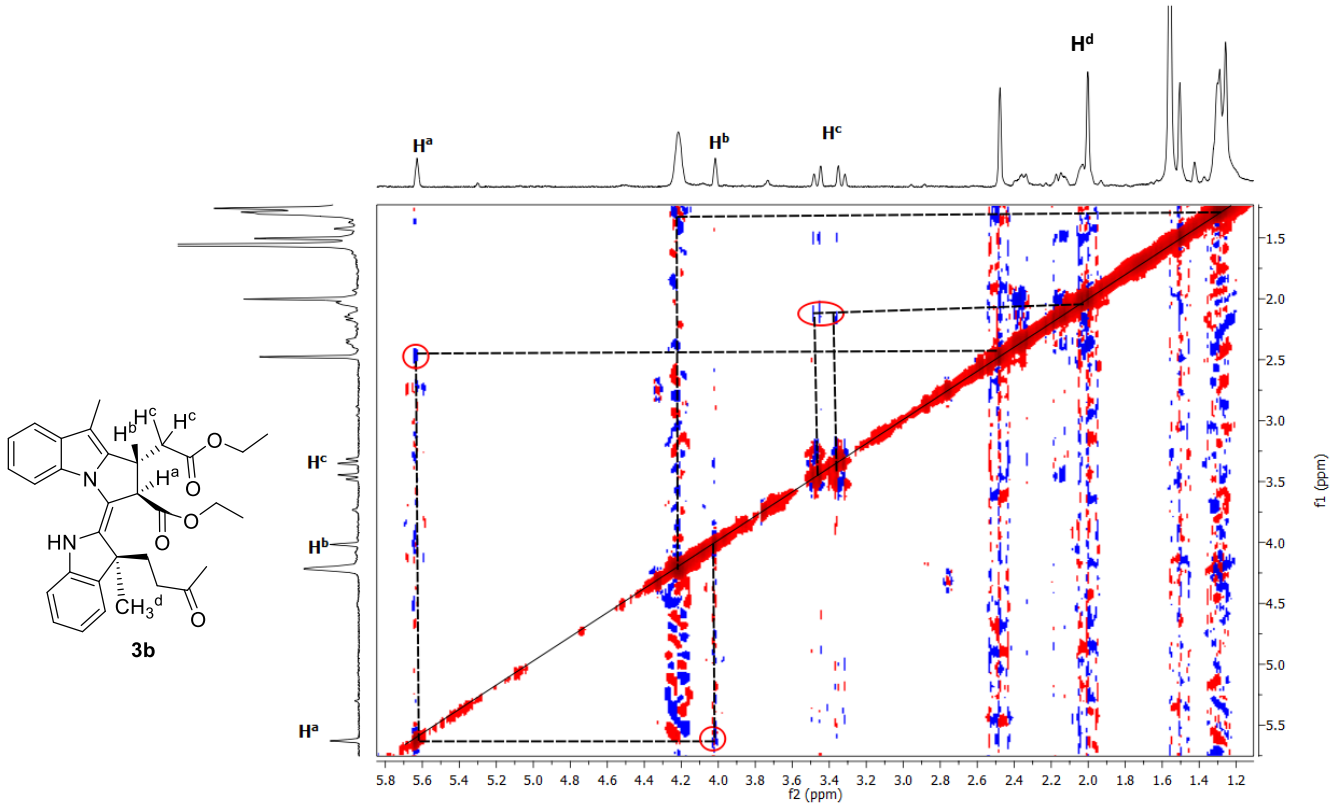




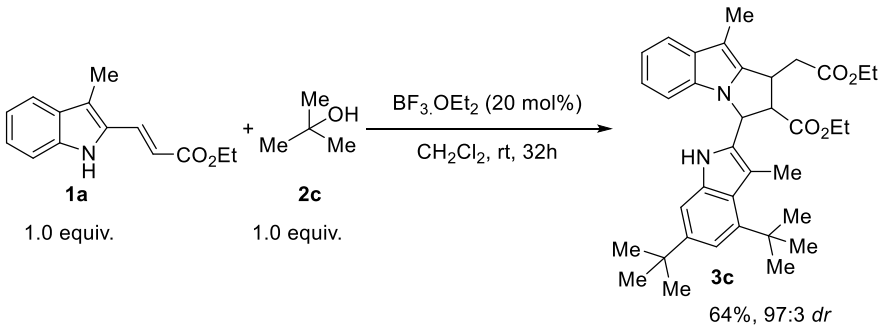
^{1}H–^{1} H COSY NMR spectrum of compound **3b**



^{1}H–^{1} H NOESY NMR spectrum of compound **3b**



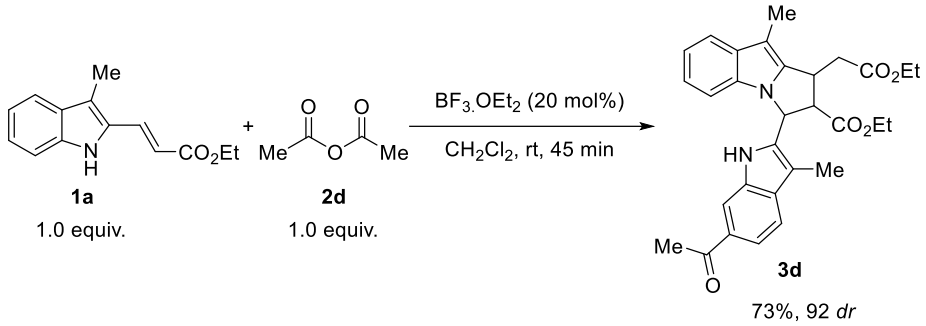
Synthesis of pyrrolo[1,2-*a*]indole 3c



The title compound **3c** was prepared from ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (10 mg 0.044 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and ^{t}BuOH (4.2 µL, 0.044 mmol, 1.0 equiv.) according to general procedure **B** with a reaction time of 32 h. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (1/4) to furnish the title compound **3c** (8 mg 0.014 mmol, 64%) as a yellow solid; R_f=0.3 (EtOAc/hexane 3/7);); m.p. 260°C **IR** (neat): ν_{max}/cm^{-1} 30320, 1731, 1527, 1215; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 1.8 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.98 (d, *J* = 7.4 Hz, 1H), 4.27 – 4.17 (m, 3H), 4.13 – 4.06 (m, 2H), 3.98 – 3.93 (m, 1H), 3.27 – 3.21 (m, 1H), 3.09 – 3.03 (m, 1H), 2.50 (s, 3H), 2.28 (s, 3H), 1.43 (s, 9H), 1.36 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.5, 172.2, 141.7, 139.6, 133.7, 133.2, 132.7, 132.2, 131.0, 129.1, 121.0, 119.1,

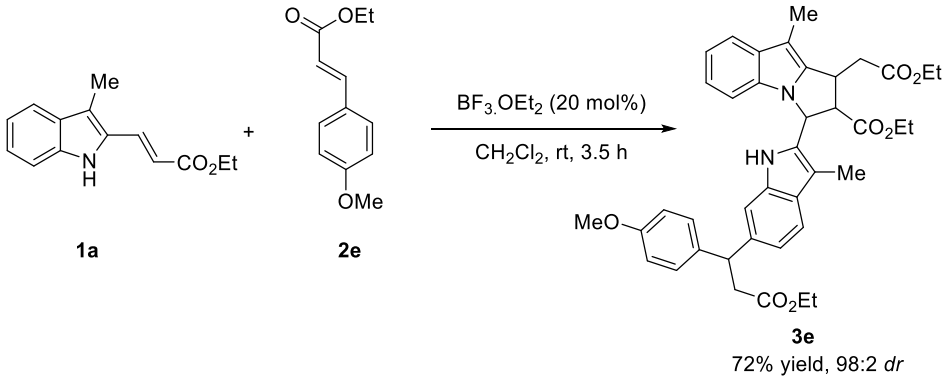
118.2, 117.6, 112.8, 110.4, 110.2, 101.4, 61.6, 61.0, 58.9, 54.7, 37.2, 35.8, 34.9, 34.7, 32.2, 30.2, 14.4, 14.2, 8.8, 8.5; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{36}H_{47}N_2O_4$ 571.3536; Found 571.3530.

Synthesis of pyrrolo[1,2-*a*]indole 3d



The title compound **3d** was prepared from ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (10 mg 0.044 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and acetic anhydride **2d** (4.2 µL, 0.044 mmol, 1.0 equiv.) according to general procedure **B** with a reaction time of 45 min. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (1/4) to furnish the title compound **3d** (8 mg 0.016 mmol, 73%) as a yellow solid; R_f=0.3 (EtOAc/hexane 3/7); m.p. 230°C; **IR** (neat): ν_{max}/cm^{-1} 3016, 2925, 2848, 1728, 1666, 1620, 1458, 1309, 1216, 1016; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.30 (s, 1H), 7.82 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 5.99 (d, *J* = 7.4 Hz, 1H), 4.23 (tdd, *J* = 15.2, 9.6, 5.8 Hz, 3H), 4.17 – 4.10 (m, 2H), 4.01 (s, 1H), 3.27 (dd, *J* = 17.3, 5.3 Hz, 1H), 3.09 (dd, *J* = 17.3, 3.1 Hz, 1H), 2.69 (s, 3H), 2.57 (s, 3H), 2.28 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 – 1.21 (m, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 198.5, 172.3, 172.1, 139.3, 139.1, 133.7, 133.4, 132.2, 129.4, 128.3, 123.0, 121.3, 121.2, 119.4, 118.6, 112.1, 111.2, 109.5, 101.7, 61.8, 61.2, 58.9, 54.3, 37.1, 35.6, 26.8, 14.4, 14.2, 8.7, 8.5; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_5$ 501.2389; Found 501.2387.

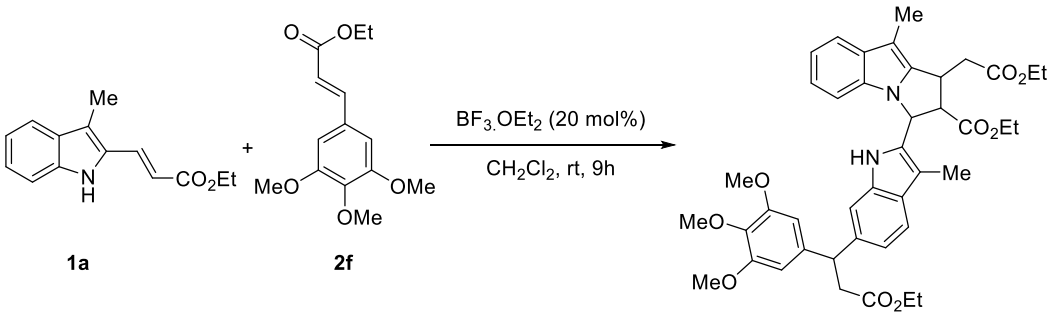
Synthesis of pyrrolo[1,2-*a*]indole 3e



The title compound **3e** was prepared from ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (50 mg 0.218 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and ethyl (*E*)-3-(4-methoxyphenyl)acrylate **2e** (90 mg, 0.436 mmol, 2.0 equiv.) according to general procedure **C** with a reaction time of 3.5h. The crude residue was purified by column chromatography on silica gel with an

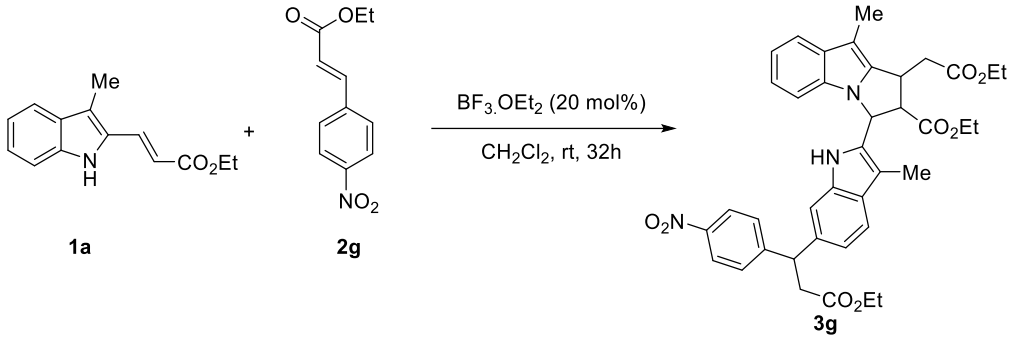
eluent of hexanes to EtOAc/hexanes (1/4) to furnish the title compound **3e** (52 mg 0.078 mmol, 72%) as a white solid; R_f=0.3 (EtOAc/hexane 1/4); m.p. 210°C **IR** (neat): ν_{max}/cm^{-1} 3020, 2362, 1716 (C=O), 1458, 1215, 752, 667; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.24 (dd, *J* = 8.5, 2.6 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.01 (t, *J* = 7.1 Hz, 2H), 6.88 (t, *J* = 7.8 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.71 – 6.64 (m, 1H), 5.94 (d, *J* = 7.2 Hz, 1H), 4.63 (t, *J* = 8.0 Hz, 1H), 4.25 – 4.19 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.09 – 3.97 (m, 4H), 3.77 (s, 3H), 3.18 (dd, *J* = 17.0, 5.8 Hz, 1H), 3.08 (dd, *J* = 6.0 Hz, 3H), 2.46 (s, *J* = 3.5 Hz, 3H), 2.28 (s, 3H), 1.29 (t, *J* = 6.8 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.4, 172.2, 172.0, 158.1, 139.5, 136.8, 135.1, 134.9, 133.7, 132.3, 131.9, 128.8, 127.1, 122.7, 121.1, 119.3, 118.5, 117.3, 113.9, 111.4, 110.3, 109.8, 101.6, 61.7, 61.0, 60.4, 59.4, 55.4, 54.7, 46.7, 46.6, 41.8, 37.3, 36.1, 14.4, 14.2, 8.7, 8.5; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{40}H_{45}N_2O_7$ 665.3221; Found 665.3266.

Synthesis of pyrrolo[1,2-*a*]indole 3f



The title compound **3f** was prepared from ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (50 mg 0.218 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and ethyl (*E*)-3-(3,4,5-trimethoxyphenyl)acrylate **2f** (116 mg, 0.436 mmol, 2.0 equiv.) according to general procedure **C** with a reaction time of 9h. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (1/4) to furnish the title compound **3f** (51 mg 0.070 mmol, 64%) as a white solid; R_f=0.3 (EtOAc/hexane 1/4); m.p. 240°C; **IR** (neat): ν_{max}/cm^{-1} 3020, 2933, 2364, 1718 (C=O), 1460, 1215, 744, 667; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.46 (s, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.88 (s, 1H), 6.67 (d, *J* = 6.9 Hz, 1H), 6.54 (s, 2H), 5.95 (s, 1H), 4.61 (s, 1H), 4.22 (s, 2H), 4.14 – 4.04 (m, 6H), 4.01 – 3.97 (m, 1H), 3.83 (s, 6H), 3.80 (s, 3H), 3.18 (d, *J* = 17.1 Hz, 1H), 3.09 (s, 3H), 2.46 (s, 3H), 2.28 (s, 3H), 2.08 – 1.99 (m, 1H), 1.22 (s, 3H), 1.13 (s, 3H), 0.84 (s, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.3, 172.2, 172.0, 153.2, 140.3, 139.5, 136.6, 135.2, 133.8, 132.4, 132.1, 131.1, 128.9, 125.2, 122.5, 121.1, 119.3, 118.5, 117.7, 111.4, 109.8, 105.1, 101.7, 61.7, 61.0, 61.0, 60.5, 59.4, 56.3, 54.7, 47.7, 41.9, 37.3, 36.0, 19.3, 14.4, 14.3, 14.3, 8.7, 8.5; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{42}H_{49}N_2O_9$ 725.3438; Found 725.3428.

Synthesis of pyrrolo[1,2-*a*]indole 3g

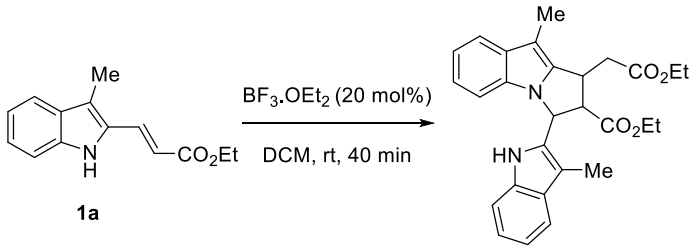


62% yield, 96:4 *dr*

The title compound **3g** was prepared from ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (50 mg 0.218 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and ethyl (*E*)-3-(4-nitrophenyl)acrylate **2g** (97 mg, 0.438 mmol, 2.0 equiv.) according to general procedure **C** with a reaction time of 30h. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (1/4) to furnish the title compound **3g** (46 mg 0.068 mmol, 62%) as a white solid; R_f=0.4 (EtOAc/hexane 1/4); m.p. 195°C;; **IR** (neat): ν_{max}/cm^{-1} 3020, 2362, 1731 (C=O), 1458, 1215, 744, 667; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.98 (d, *J* = 25.0 Hz, 1H), 7.50 (s, 1H), 7.47 (s, 1H), 7.23 (s, 1H), 7.16 – 6.98 (m, 5H), 6.89 (s, 1H), 6.67 (d, *J* = 15.0 Hz, 1H), 5.95 (s, 1H), 5.01 (s, 1H), 4.22 (s, 2H), 4.09 (d, *J* = 35.5 Hz, 4H), 4.00 (s, 1H), 3.20 (d, *J* = 17.4 Hz, 2H), 3.07 (d, *J* = 17.3 Hz, 1H), 2.47 (s, 2H), 2.35 (s, 3H), 2.28 (s, 3H), 1.25 (m, 6H), 1.10 (s, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.2, 172.1, 171.3, 139.5, 136.4, 135.4, 132.3, 129.6, 128.9, 122.6, 122.3, 121.3, 121.1, 119.3, 119.1, 118.5, 117.4, 117.2, 111.7, 110.7, 109.7, 107.3, 101.7, 61.7, 61.0, 60.5, 59.4, 54.6, 40.2, 39.0, 37.3, 36.0, 31.7, 22.8, 21.2, 14.3, 8.5; **HRMS** (ESI/Q-TOF) m/z: $[M+MeCN]^+$ Calcd for $C_{41}H_{44}N_4O_8$ 720.3159; Found 720.3201.

5. Characterization of compounds 4a-4f

Synthesis of self-dimer 4a

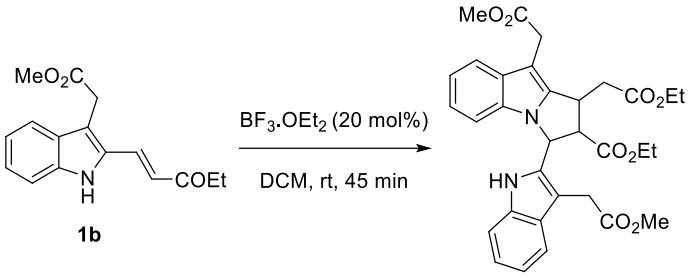


90% yield, 97:3 *dr*

The title compound **4a** was prepared from ethyl (*E)*-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (20 mg 0.087 mmol) and catalyst $BF_3{\cdot}OEt_2$ (20 mol%) according to general procedure **D** with a reaction time of 40 min. The crude residue was purified by column chromatography on silica gel with an eluent of EtOAc/hexanes (1/9) to furnish the title compound **4a** (18 mg 0.039 mmol, 90%) as a yellow solid; R_f=0.6 (EtOAc/hexane 1/4); m.p. 250°C; **IR** (neat): ν_{max}/cm^{-1} 3392, 2918, 2850, 1726 (C=O), 1458, 1215, 1180, 1029, 738, 667; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 4.9 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.02 (d, *J* = 7.4 Hz, 1H), 4.32 – 4.23 (m, 2H), 4.22 – 4.15 (m, 3H), 4.06 (s, 1H), 3.29 – 3.22 (m, 1H), 3.18 – 3.11 (m, 1H), 2.55 (s, 3H), 2.34 (s, 3H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.28 (d, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H}**

NMR(126 MHz, $CDCl_3$) δ 172.2, 172.0, 139.5, 136.4, 133.8, 132.4, 131.5, 128.8, 122.5, 121.2, 119.3, 119.2, 119.01, 118.5, 111.4, 110.4, 109.8, 101.7, 61.7, 61.0, 59.4, 54.7, 37.3, 36.1, 14.4, 14.3, 8.7, 8.5; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{31}N_2O_4$ 459.2289; Found 459.2331.

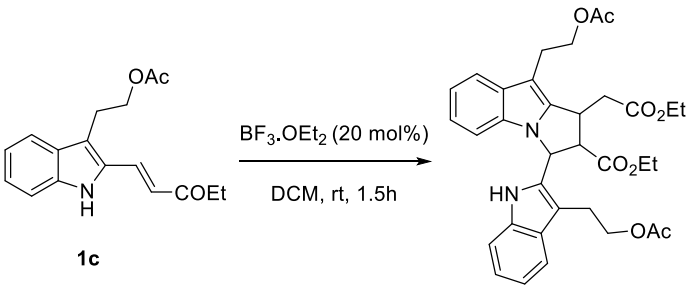
Synthesis of self-dimer 4b



74% yield, 97:3 *dr*

The title compound **4b** was prepared from ethyl (*E*)-3-(3-(2-methoxy-2-oxoethyl)-1*H*-indol-2-yl)acrylate **1b** (20 mg 0.070 mmol) and catalyst $BF_3{\cdot}OEt_2$ (20 mol%) according to general procedure **D** with a reaction time of 45 min. The crude residue was purified by column chromatography on silica gel with an eluent of EtOAc/hexanes (3/7) to furnish the title compound **4b** (15 mg 0.052 mmol, 74%) as a yellow solid; R_f=0.4 (EtOAc/hexane 3/7);); m.p. 220°C; **IR** (neat): ν_{max}/cm^{-1} 3012, 2923, 2846, 1728, 1600, 1514, 1216; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.65 – 7.61 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.16 (dt, *J* = 11.7, 3.7 Hz, 3H), 7.08 – 7.02 (m, 1H), 6.93 – 6.88 (m, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 6.15 (d, *J* = 9.0 Hz, 1H), 4.36 (dd, *J* = 14.9, 6.8 Hz, 1H), 4.18 – 4.05 (m, 6H), 4.00 (d, *J* = 16.2 Hz, 1H), 3.85 (d, *J* = 16.1 Hz, 1H), 3.80 (d, *J* = 2.4 Hz, 2H), 3.73 (s, 3H), 3.67 (s, 3H), 2.79 (t, *J* = 6.7 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.6, 172.0, 171.4, 169.9, 142.1, 136.1, 132.4, 132.3, 131.6, 128.2, 123.1, 122.1, 120.2, 120.1, 119.1, 118.9, 111.5, 110.5, 108.5, 100.2, 61.7, 61.0, 58.9, 54.7, 52.2, 52.0, 35.5, 35.5, 30.2, 29.8, 14.2, 14.2; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{35}N_2O_8$ 575.2393; Found 575.2413.

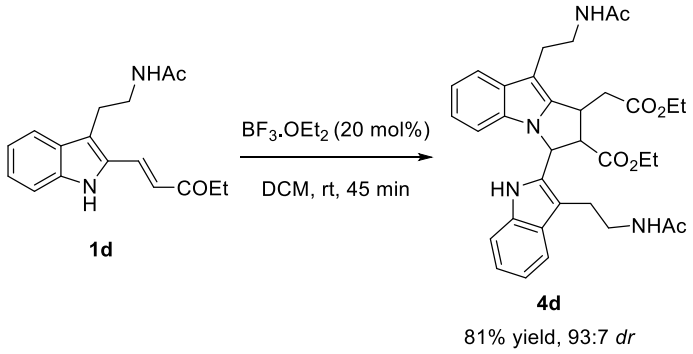
Synthesis of self-dimer 4c



79% yield, 92:8 *dr*

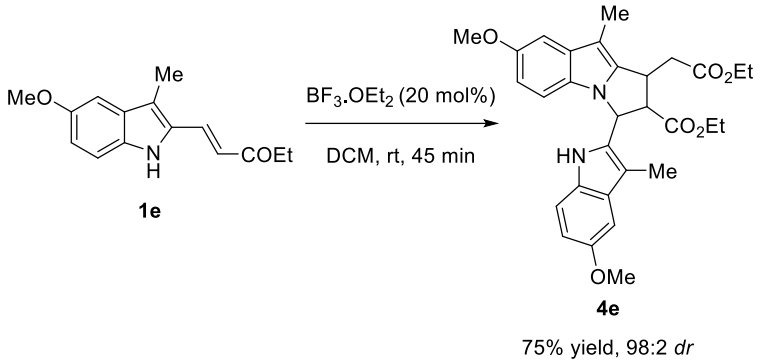
The title compound **4c** was prepared from ethyl (*E*)-3-(3-(2-acetoxyethyl)-1*H*-indol-2-yl)acrylate **1c** (20 mg 0.066 mmol) and catalyst $BF_3{\cdot}OEt_2$ (20 mol%) according to general procedure **D** with a reaction time of 1.5h. The crude residue was purified by column chromatography on silica gel with an eluent of EtOAc/hexanes (1/4) to furnish the title compound **4c** (16 mg 0.026 mmol, 79%) as a yellow solid; R_f=0.6 (EtOAc/hexane 3/7);); m.p. 205°C; **IR** (neat): ν_{max}/cm^{-1} 3020, 2933, 2844, 1735, 1456, 1365, 1213, 1024; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.04 (d, *J* = 7.3 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 2H), 4.28 – 4.22 (m, 4H), 4.16 – 4.12 (m, 2H), 4.12 – 4.08 (m, 1H), 4.04 – 4.00 (m, 1H), 3.40 (dt, *J* = 15.4, 7.8 Hz, 1H), 3.27 (ddd, *J* = 21.0, 16.0, 5.9 Hz, 2H), 3.14 (dd, *J* = 17.6, 3.4 Hz, 1H), 3.06 (t, *J* = 7.4 Hz, 2H), 2.07 (s, 3H), 1.99 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.0, 171.9, 171.3, 171.3, 140.8, 136.7, 136.4, 133.1, 132.7, 128.0, 122.7, 121.5, 119.8, 119.6, 119.2, 118.6, 111.6, 110.7, 110.1, 102.0, 64.9, 64.8, 61.9, 61.2, 59.4, 54.8, 37.5, 35.8, 23.9, 23.8, 21.3, 21.2, 14.4, 14.3; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{39}N_2O_8$ 603.2706; Found 603.2705.

Synthesis of self-dimer 4d



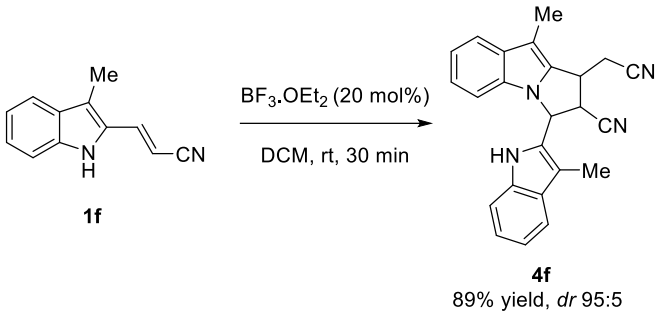
The title compound **4d** was prepared from ethyl (*E*)-3-(3-(2-acetamidoethyl)-1H-indol-2-yl)acrylate **1d** (20 mg 0.067 mmol) and catalyst $BF_3{\cdot}OEt_2$ (20 mol%) according to general procedure **D** with a reaction time of 45 min. The crude residue was purified by column chromatography on silica gel with an eluent of MeOH/DCM (0.2/9.8) to furnish the title compound **4d** (17 mg 0.028 mmol, 81%) as a yellow solid; R_f=0.2 (MeOH/DCM 0.2/9.8); m.p. 230°C **IR** (neat): ν_{max}/cm^{-1} 3022, 2920, 2856, 1731, 1222; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.69 – 7.63 (m, 2H), 7.56 (s, 1H), 7.47 (d, *J* = 6.7 Hz, 2H), 7.15 (dt, *J* = 14.3, 6.9 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.98 (d, *J* = 7.1 Hz, 1H), 4.24 (dd, *J* = 11.5, 6.9 Hz, 2H), 4.14 (dd, *J* = 14.2, 7.1 Hz, 3H), 4.00 (s, 1H), 3.68 (d, *J* = 4.8 Hz, 2H), 3.50 (d, *J* = 16.1 Hz, 2H), 3.34 (d, *J* = 16.5 Hz, 2H), 3.15 (d, *J* = 15.4 Hz, 2H), 2.96 (d, *J* = 5.6 Hz, 2H), 1.93 (d, *J* = 1.9 Hz, 6H), 1.30 (t, , 3H), 1.27 – 1.19 (t, 3H); **^{13}C{^{1}H} NMR**(126 MHz,) δ 172.4, 170.5, 140.5, 133.2, 132.5, 132.4, 132.30, 132.2, 128.7, 128.6, 122.9, 121.5, 119.9, 119.8, 119.3, 118.6, 112.0, 111.6, 109.9, 103.4, 61.3, 54.5, 40.6, 39.0, 37.3, 35.8, 33.4, 32.1, 26.9, 26.0, 24.3, 23.4, 14.3, 11.0; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{41}N_4O_6$ 601.3026; Found 601.3032.

Synthesis of self-dimer 4e



The title compound **4e** was prepared from ethyl (*E*)-3-(5-methoxy-3-methyl-1*H*-indol-2-yl)acrylate **1e** (20 mg 0.077 mmol) and catalyst $BF_3{\cdot}OEt_2$ (20 mol%) according to general procedure **D** with a reaction time of 45 min. The crude residue was purified by column chromatography on silica gel with an eluent of EtOAc/hexane (1/9) to furnish the title compound compound **4e** (15 mg 0.029 mmol, 75%) as a yellow solid; R_f=0.6 (EtOAc/hexane 1/4);); m.p. 240°C; **IR** (neat): ν_{max}/cm^{-1} 3016, 2918, 2848, 1739, 1456, 1213; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 7.06 – 7.03 (m, 1H), 6.91 (s, 1H), 6.82 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.54 (dd, *J* = 6.7, 4.5 Hz, 2H), 5.89 (d, *J* = 7.4 Hz, 1H), 4.22 (dd, *J* = 7.1, 3.1 Hz, 2H), 4.13 (d, *J* = 7.2 Hz, 2H), 3.97 (d, *J* = 9.0 Hz, 2H), 3.89 (d, *J* = 4.6 Hz, 3H), 3.80 (s, 3H), 3.20 – 3.03 (m, 2H), 2.44 (s, 3H), 2.25 (s, 3H), 1.26 (m, 6H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.2, 172.0, 154.2, 154.1, 140.4, 134.2, 132.4, 131.5, 129.2, 127.8, 112.6, 112.1, 110.9, 110.5, 110.1, 101.4, 101.2, 101.1, 61.6, 61.0, 59.6, 56.1, 56.1, 55.0, 37.5, 36.2, 14.4, 14.3, 8.7, 8.6; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{35}N_2O_6$ 519.2495; Found 519.2506.

Synthesis of self-dimer 4f

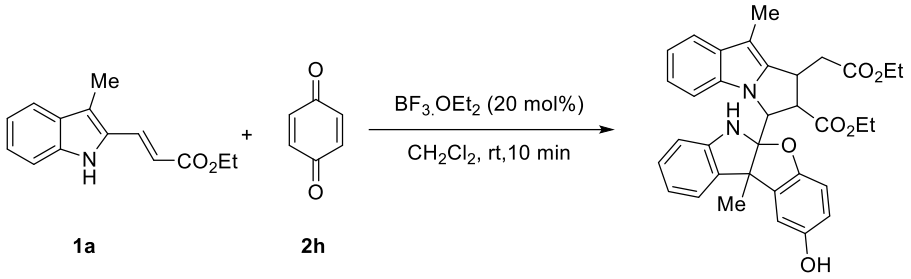


The title compound **4f** was prepared from (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylonitrile **1f** (20 mg 0.110 mmol) and catalyst $BF_3{\cdot}OEt_2$ (20 mol%) according to general procedure **D** with a reaction time of 30 min. The crude residue was purified by column chromatography on silica gel with an eluent of EtOAc/hexane (1/4) to furnish the title compound **4f** (18 mg 0.049 mmol, 89%) as a yellow solid; R_f=0.4 (EtOAc/hexane 1/4);); m.p. 190°C; **IR** (neat): ν_{max}/cm^{-1} 3012, 2985, 2898, 2310, 1448, 1377, 1232, 1041; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.17 (m, 3H), 7.12 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 5.88 (d, *J* = 8.4 Hz, 1H), 3.74 (t, *J* = 8.7 Hz, 1H), 3.32 (dd, *J* = 17.5, 4.9 Hz, 1H), 3.10 (dd, *J* = 17.5, 4.0 Hz, 1H), 2.76 (d, *J* = 6.4 Hz, 1H), 2.58 – 2.48 (m, 3H), 2.43 – 2.37 (m, 3H); **^{13}C{^{1}H} NMR**(101 MHz, $CDCl_3$) δ 136.5, 136.0, 125.5, 125.0, 123.7, 122.9, 120.6,

120.2, 120.0, 119.5, 119.4, 118.6, 116.4, 114.8, 113.9, 112.1, 111.7, 110.2, 44.9, 39.0, 32.1, 22.8, 21.2, 14.3.; **HRMS** (ESI/Q-TOF) m/z: $[M+H-CN]^+$ Calcd for $C_{23}H_{21}N_3$ 339.1735; Found 339.1727.

6. Characterization of compounds 5a-5d

Synthesis of substituted pyrrolo[1,2-a]indolyl furo[2,3-b]indole 5a

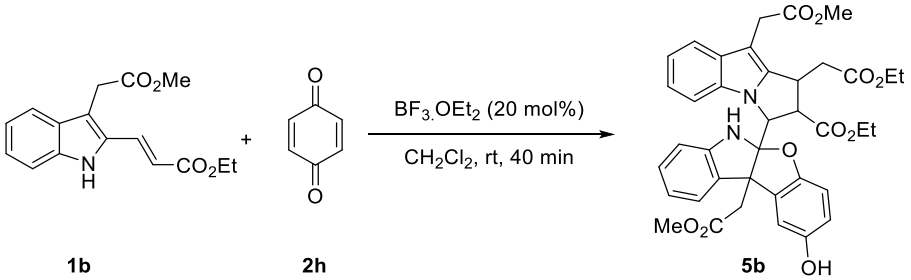


1a **2h** **5a**

82%yeld, 95:5 *dr*

The title compound **5a** was prepared from ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (10 mg 0.044 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and 1,4-benzoquinone **2h** (7 mg, 0.065 mmol, 1.5 equiv.) according to general procedure **E** with a reaction time of 10 min. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (2/3) to furnish the title compound **5a** (10 mg, 0.018 mmol, 82%) as a white solid; R_f=0.4 (EtOAc/hexane 2/3); m.p. 260°C; **IR** (neat): ν_{max}/cm^{-1} 3390, 2918, 2848, 1731 (C=O), 1494, 1309, 1218, 771; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 1H), 7.47 (s, 1H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.10 – 7.07 (m, 1H), 6.88 (d, *J* = 2.3 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 6.52 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.99 (d, *J* = 7.8 Hz, 1H), 5.92 (d, *J* = 3.4 Hz, 1H), 4.98 (s, 1H), 4.34 – 4.24 (m, 2H), 4.12 – 4.05 (m, 2H), 3.70 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.51 – 3.48 (m, 1H), 3.40 (td, *J* = 10.2, 4.3 Hz, 1H), 2.80 (dd, *J* = 17.8, 10.7 Hz, 1H), 2.59 (dd, *J* = 17.8, 4.3 Hz, 1H), 2.39 (s, 3H), 1.75 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.2, 171.3, 151.8, 150.1, 143.3, 137.3, 136.2, 133.7, 130.8, 129.1, 128.5, 122.6, 122.5, 119.9, 119.6, 118.94, 118.88, 114.7, 111.5, 111.2, 110.4, 110.0, 109.6, 66.0, 61.6, 61.0, 54.7, 54.1, 41.2, 31.9, 22.2, 14.2, 14.2, 8.8; **HRMS** (ESI/Q-TOF) m/z: $[M-2H]^+$ Calcd for $C_{34}H_{33}N_2O_6$ 565.2339; Found 565.2359.

Synthesis of substituted pyrrolo[1,2-a]indolyl furo[2,3-b]indole 5b



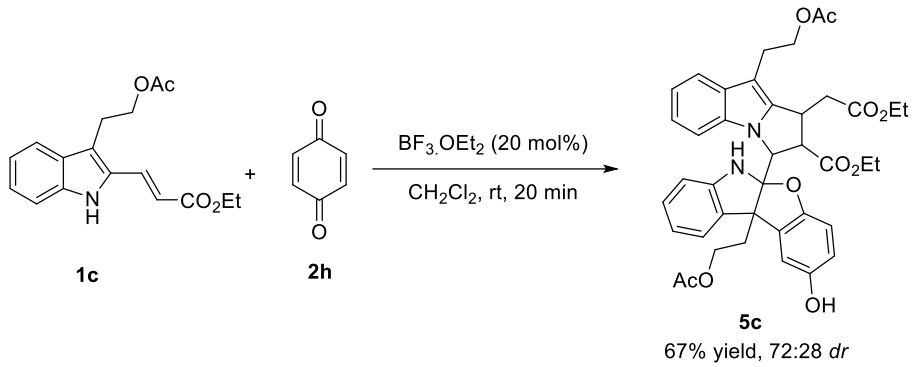
1b **2h** **5b**

84% yield, 95:5 *dr*

The title compound **5b** was prepared from ethyl (*E*)-3-(3-(2-methoxy-2-oxoethyl)-1H-indol-2-yl)acrylate **1b** (20 mg 0.070 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and 1,4-benzoquinone **2h** (11 mg, 0.102 mmol, 1.5 equiv.) according to general

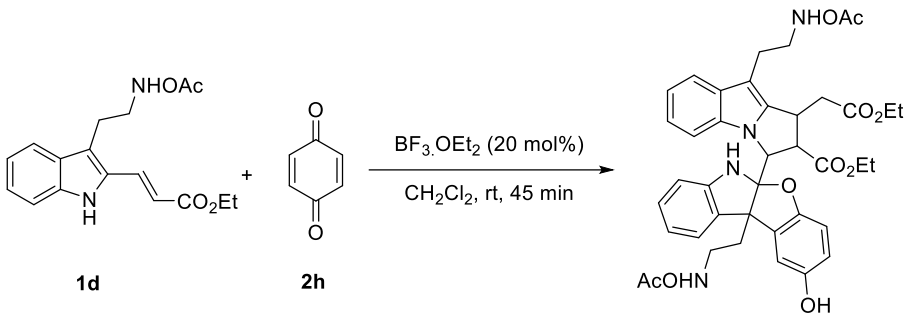
procedure **E** with a reaction time of 40 min. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (3/7) to furnish the title compound **5b** (20 mg, 0.029 mmol, 84%) as a white solid; R_f=0.7 (EtOAc/hexane 1/1);); m.p. 242°C; **IR** (neat): ν_{max}/cm^{-1} 3018, 1741, 1556, 1203, 1006; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.16 (ddd, *J* = 20.6, 11.5, 7.1 Hz, 3H), 6.93 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.62 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.29 (d, *J* = 7.9 Hz, 1H), 5.25 (d, *J* = 9.1 Hz, 1H), 4.17 – 4.05 (m, 3H), 4.00 – 3.93 (m, 3H), 3.85 – 3.78 (m, 1H), 3.64 (s, 3H), 3.51 (s, 3H), 3.31 (s, 2H), 2.88 – 2.82 (m, 1H), 2.77 – 2.70 (m, 1H), 2.05 (s, 1H), 1.21-1.17 (m, 6H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.3, 172.0, 171.2, 170.3, 151.1, 150.6, 147.7, 135.8, 135.2, 134.4, 131.7, 129.0, 129.0, 122.7, 122.5, 121.6, 119.9, 119.0, 115.6, 111.3, 111.0, 110.9, 110.0, 105.8, 61.6, 60.9, 59.8, 59.1, 57.9, 52.0, 43.6, 40.6, 34.4, 29.9, 24.8, 22.5, 14.2, 14.1; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{38}H_{39}N_2O_{10}$ 683.2599; Found 683.2607.

Synthesis of substituted pyrrolo[1,2-a]indolyl furo[2,3-b]indole 5c



The title compound **5c** was prepared from ethyl (*E*)-3-(3-(2-acetoxyethyl)-1*H*-indol-2-yl)acrylate **1c** (10 mg 0.033 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and 1,4-benzoquinone **2h** (5 mg, 0.050 mmol, 1.5 equiv.) according to general procedure **E** with a reaction time of 20 min. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (3/7) to furnish the title compound **5c** (8 mg, 0.011 mmol, 67%) as a white solid; R_f=0.7 (EtOAc/hexane 1/1);); m.p. 230°C; **IR** (neat): ν_{max}/cm^{-1} 3018, 2854, 2929, 1731, 1460, 1232, 1006; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 – 8.46 (m, 1H), 7.68 – 7.60 (m, 1H), 7.33 – 7.30 (m, 1H), 7.24 – 7.21 (m, 1H), 7.20 – 7.16 (m, 1H), 7.14 – 7.10 (m, 1H), 6.98 – 6.94 (m, 1H), 6.88 – 6.83 (m, 2H), 6.80 – 6.75 (m, 1H), 6.67 – 6.62 (m, 1H), 6.28 – 6.22 (m, 1H), 5.18 – 5.11 (m, 1H), 4.29 – 4.27 (m, 1H), 4.17 – 4.09 (m, 4H), 4.07 – 4.04 (m, 2H), 3.68 – 3.60 (m, 1H), 3.53 – 3.47 (m, 1H), 3.42 – 3.36 (m, 1H), 3.24 – 3.18 (m, 1H), 3.13 – 3.06 (m, 1H), 2.98 – 2.88 (m, 1H), 2.79 – 2.75 (m, 2H), 2.57 – 2.50 (m, 2H), 2.03 (s, 3H), 1.99 (s, 3H), 0.87-0.81 (m, 6H); **^{13}C{^{1}H} NMR**(101 MHz, $CDCl_3$) δ 171.4, 171.3 (2 x C), 170.9, 150.9, 150.6, 135.9, 134.2, 133.4, 132.5, 129.1, 129.0, 123.3, 122.5, 121.6, 119.7, 119.6, 119.2, 115.6, 111.3, 111.2, 110.4, 110.2, 109.0, 64.9, 61.8, 61.0, 60.0, 59.3, 58.4, 43.9, 39.0, 37.2, 34.0, 33.3, 32.1, 27.3, 26.9, 22.8, 14.3; **HRMS** (ESI/Q-TOF) m/z: $[M]^+$ Calcd for $C_{40}H_{42}N_2O_{10}$ 710.2839; Found 710.2817.

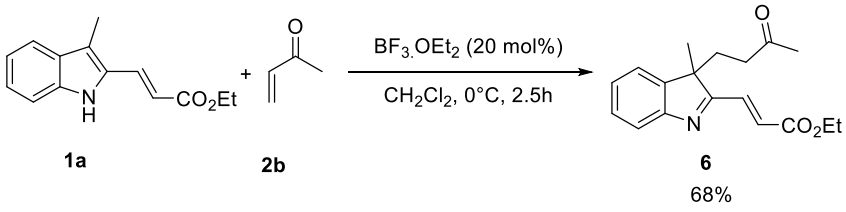
Synthesis of substituted pyrrolo[1,2-a]indolyl furo[2,3-b]indole 5d



The title compound **5d** was prepared from ethyl (*E*)-3-(3-(2-acetamidoethyl)-1H-indol-2-yl)acrylate **1d** (20 mg 0.066 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and 1,4-benzoquinone **2h** (11 mg, 0.099 mmol, 1.5 equiv.) according to general procedure **E** with a reaction time of 45 min. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to MeOH/DCM (0.5/9.5) to furnish the title compound **5d** (19 mg, 0.026 mmol, 78%) as a yellow solid; R_f=0.3 (MeOH/DCM 0.5/9.5);); m.p. 210°C; **IR** (neat): ν_{max}/cm^{-1} 3020, 2923, 1762, 1515, 1213, 763; **^{1}H NMR** (500 MHz, $CDCl_3$, rotamers) δ 7.70 – 7.63 (m, 3H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.47 (td, *J* = 7.6, 2.8 Hz, 3H), 7.19 (s, 1H), 7.11 (t, *J* = 6.8 Hz, 1H), 6.96 (dd, *J* = 15.4, 13.5 Hz, 1H), 6.86 (d, *J* = 12.8 Hz, 1H), 6.73 (s, 1H), 6.69 – 6.52 (m, 3H), 6.38 (dd, *J* = 15.5, 2.7 Hz, 1H), 6.04 – 5.74 (m, 1H) (OH), 4.23 (dd, *J* = 14.3, 7.1 Hz, 2H), 4.13 (tt, *J* = 11.3, 5.6 Hz, 3H), 3.76 – 3.47 (m, 3H), 3.21 – 2.86 (m, 3H), 2.69 – 2.57 (m, 2H), 2.21 (d, *J* = 9.9 Hz, 1H), 2.09 (s, 2H), 2.04 (s, 1H), 1.88 (t, *J* = 11.3 Hz, 3H), 0.88-0.82 (m, 6H); **^{13}C{^{1}H} NMR**(126 MHz, rotamers) δ 172.5, 171.3, 170.6, 170.6, 135.3, 134.0, 133.6, 132.5, 132.2, 129.0, 128.9, 128.8, 125.3, 125.1, 124.1, 123.6, 122.7, 122.6, 122.1, 119.8, 119.2, 119.2, 119.1, 115.8, 114.2, 112.3, 111.3, 111.3, 110.6, 110.5, 110.4, 110.0, 61.8, 61.3, 61.1, 60.5, 58.9, 43.4, 39.0, 37.5, 37.2, 36.8, 36.7, 35.2, 34.5, 34.2, 33.9, 33.7, 33.6, 33.5, 33.3, 32.8, 32.3, 32.0, 31.7, 31.5, 30.4, 30.3, 30.0, 29.0, 27.2, 26.8, 26.5, 26.0, 23.85, 23.79, 23.5, 23.3, 22.8, 21.1, 14.2, 14.0, 11.5, 11.0; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{40}H_{45}N_4O_8$ 709.3237; Found 709.3235.

7. Controlled experiments

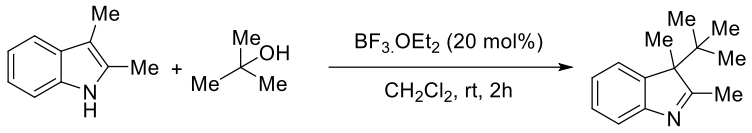
Synthesis of compound 6



Under nitrogen atmosphere, an oven dried 10 mL round bottom flask, equipped with a magnetic stirring bar, was charged with ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1a** (10 mg 0.044 mmol, 1.0 equiv.) and CH_2Cl_2(0.6 mL). To this solution was added dropwise $BF_3{\cdot}OEt_2$ (20 mol%) followed by addition of methyl vinyl ketone **2b** (5.9 µL, 0.066 mmol, 1.5 equiv.) at 0°C. Then the whole reaction mixture was allowed to stir for 2.5h at 0°C. After completion of the reaction (monitored by TLC), water (1 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (3×10 mL) and, dried

over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc/hexane (1/9) as eluent furnished compound **6** (9 mg, 0.030 mmol, 68%) as a solid. *Rf* = 0.4 (EtOAc/hexane 2/8); m.p. 180°C **IR** (neat): ν_{max}/cm^{-1} 3020, 2933, 2362, 1716 (C=O), 1460, 1369, 1215, 744, 667; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 15.9 Hz, 1H), 7.39 (s, 1H), 7.29 (d, *J* = 26.0 Hz, 2H), 6.85 (d, *J* = 16.3 Hz, 1H), 4.29 (d, *J* = 4.5 Hz, 2H), 2.37 – 2.21 (m, 2H), 2.07 – 1.93 (m, 1H), 1.86 (s, 3H), 1.84 – 1.78 (m, 1H), 1.45 (s, 3H), 1.34 (d, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR**(126 MHz, CDCl3) δ 207.5, 180.0, 166.1, 154.3, 144.5, 134.8, 128.6, 127.5, 127.0, 122.1, 121.8, 61.3, 56.6, 38.1, 30.8, 29.8, 23.1, 14.4; **HRMS** (ESI/Q-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{21}NO_3$ 299.1521; Found 299.1549.

Synthesis of compound 7

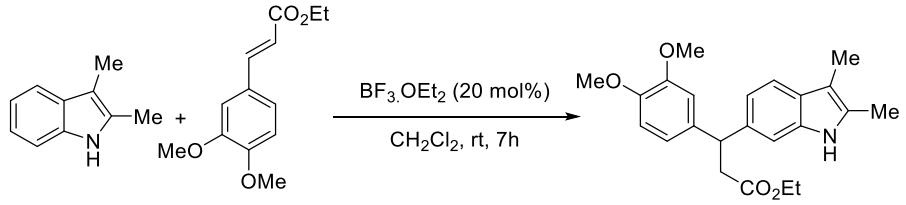


7' **2c** **7**

69%

The title compound **7** was prepared from 2,3-dimethyl indole **7'** (50 mg 0.344 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and ^{t}-BuOH **2c** (3.2 µL, 0.344 mmol, 1.0 equiv.) according to general procedure **A** with a reaction time of 2h. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (1/19) to furnish the title compound **7** (48 mg, 0.238 mmol, 69%) as a white solid; R_f=0.4 (EtOAc/hexane 1/9); m.p. 160°C; **IR** (neat): ν_{max}/cm^{-1} 3028, 1764, 1679, 1514, 1020; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.29 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 (td, *J* = 7.5, 1.1 Hz, 1H), 2.36 (s, 3H), 1.29 (s, 3H), 0.97 (s, 9H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 187.3, 154.6, 144.2, 127.6, 124.4, 124.3, 119.7, 64.1, 34.9, 26.8, 20.1, 17.3; **HRMS** (ESI/Q-TOF) m/z: $[M-C_4H_9]^+$ Calcd for C_9H_8N 130.0657; Found 130.0652.

Synthesis of compound 8



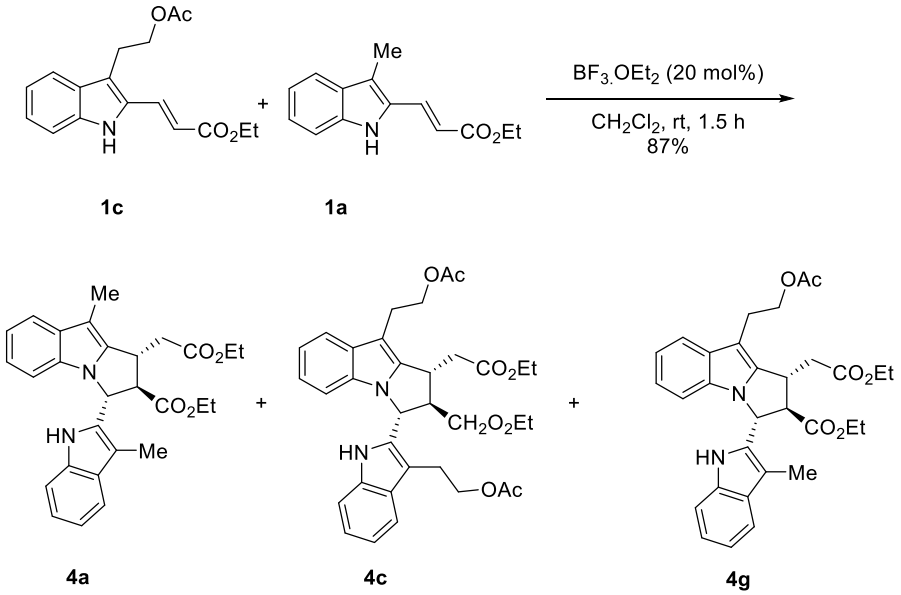
7' **8'** **8**

66%

The title compound **8** was prepared from 2,3-dimethyl indole **7'** (50 mg 0.344 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and ethyl (*E*)-3-(3,4-dimethoxyphenyl)acrylate **8'** (81 mg, 0.344 mmol, 1.0 equiv.) according to general procedure **A** with a reaction time of 7h. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (1/19) to furnish the title compound **8** (87 mg, 0.228 mmol, 66%) as a yellow solid; R_f=0.4 (EtOAc/hexane 1/9); m.p. 230°C **IR** (neat): ν_{max}/cm^{-1} 3014, 2912, 2852, 1724, 1514, 1452, 1211, 1143, 1035; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.08 (s, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.79 (dd, *J* = 22.4, 8.4 Hz, 3H), 4.59 (t, *J* = 7.9 Hz, 1H), 4.06 – 4.01 (m, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 3.06 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 2.18 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.3, 149.1, 147.7, 137.2, 137.0, 135.5, 130.8, 128.3, 119.6, 119.3,

118.1, 111.7, 111.3, 109.2, 107.1, 60.5, 56.0, 56.0, 47.0, 41.8, 14.3, 11.6, 8.55; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO_4$ 382.2018; Found 382.2011.

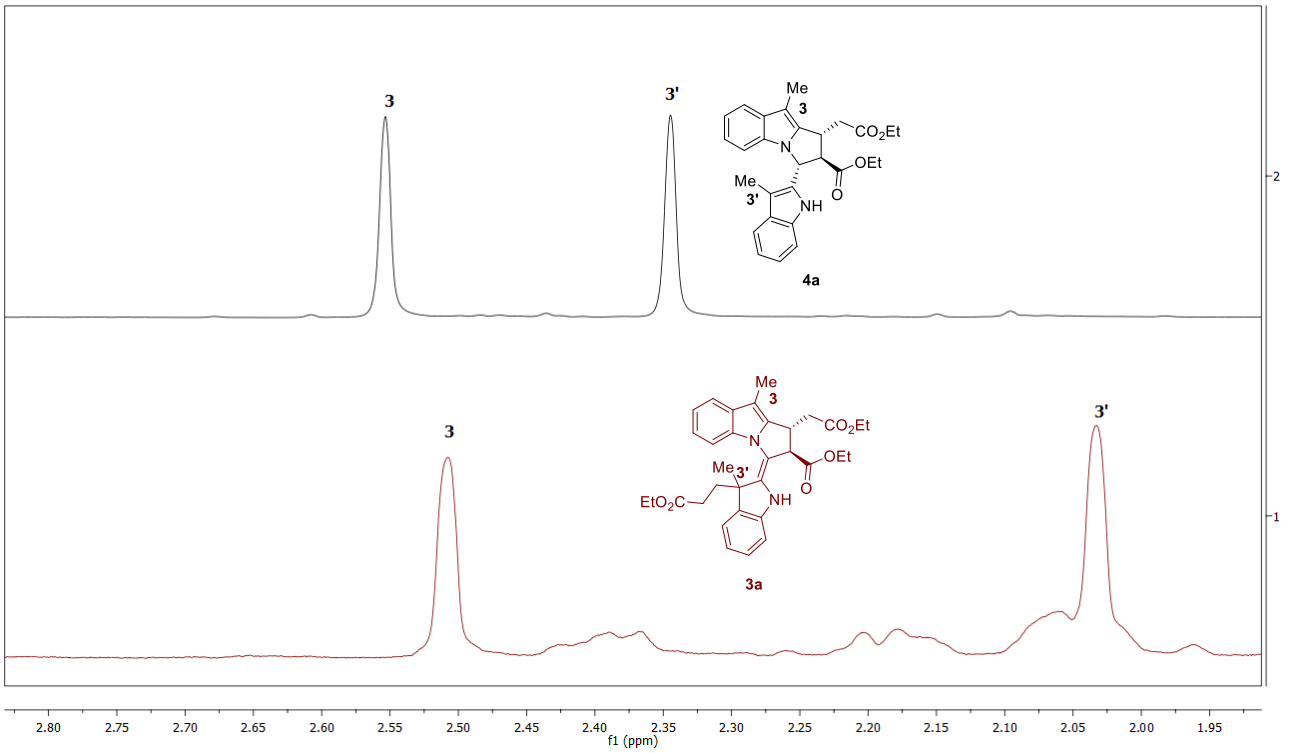
Synthesis of compound 4g: cross-dimerization

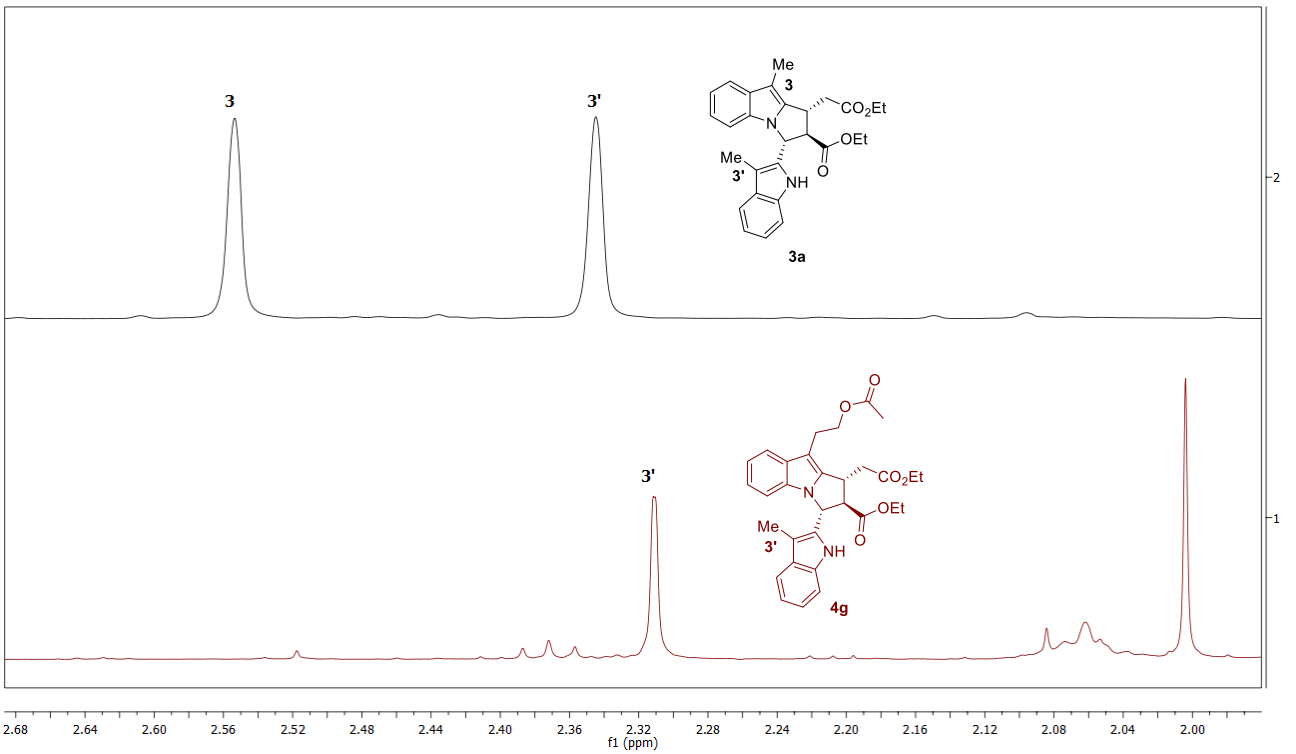


Under nitrogen atmosphere, an oven dried 10 mL round bottom flask, equipped with a magnetic stirring bar, was charged with ethyl (*E*)-3-(3-(2-acetoxyethyl)-1*H*-indol-2-yl)acrylate **1a** (10 mg 0.044 mmol, 1.0 equiv.) and ethyl (*E*)-3-(3-methyl-1*H*-indol-2-yl)acrylate **1c** (13 mg 0.044 mmol, 1.0 equiv.) and CH_2Cl_2(1.0 mL). To this solution was added dropwise $BF_3{\cdot}OEt_2$ (20 mol%) at rt. Then the whole reaction mixture was allowed to stir for 1.5h at rt. After completion of the reaction (monitored by TLC), water (1 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (3×10 mL) and, dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc/hexane (1/9) as eluent furnished compound **4a** (8 mg, 0.017 mmol, 39%), compound **4c** (8 mg, 0.013 mmol, 30%) and compound **4g** (4 mg, 0.008 mmol, 18%); *Rf* = 0.4 (EtOAc/hexane 2/8); m.p. 225°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.18 – 7.12 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.86 (dd, *J* = 11.2, 4.0 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.02 (d, *J* = 7.4 Hz, 1H), 4.42 (dt, *J* = 6.6, 4.4 Hz, 2H), 4.24 (qd, *J* = 7.1, 2.8 Hz, 2H), 4.13 (dtd, *J* = 10.3, 7.4, 2.7 Hz, 3H), 3.99 (t, *J* = 8.0 Hz, 1H), 3.38 (s, 1H), 3.29 – 3.19 (m, 2H), 3.09 (dd, *J* = 17.3, 3.4 Hz, 1H), 2.29 (s, 3H), 1.98 (s, 3H), 1.33 – 1.20 (m, 6H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 172.1, 172.0, 171.4, 139.5, 136.4, 135.4, 132.9, 125.2, 122.6, 122.0, 121.2, 119.6, 119.4, 119.2, 119.1, 118.5, 111.6, 110.6, 109.9, 101.7, 64.9, 61.8, 59.6, 54.6, 41.8, 37.4, 32.3, 26.5, 23.8, 22.8, 14.4; **HRMS-ESI**: m/z $[M+H]^+$ Calcd for $C_{31}H_{35}N_2O_6$ 531.2490; Found: 531.2494.

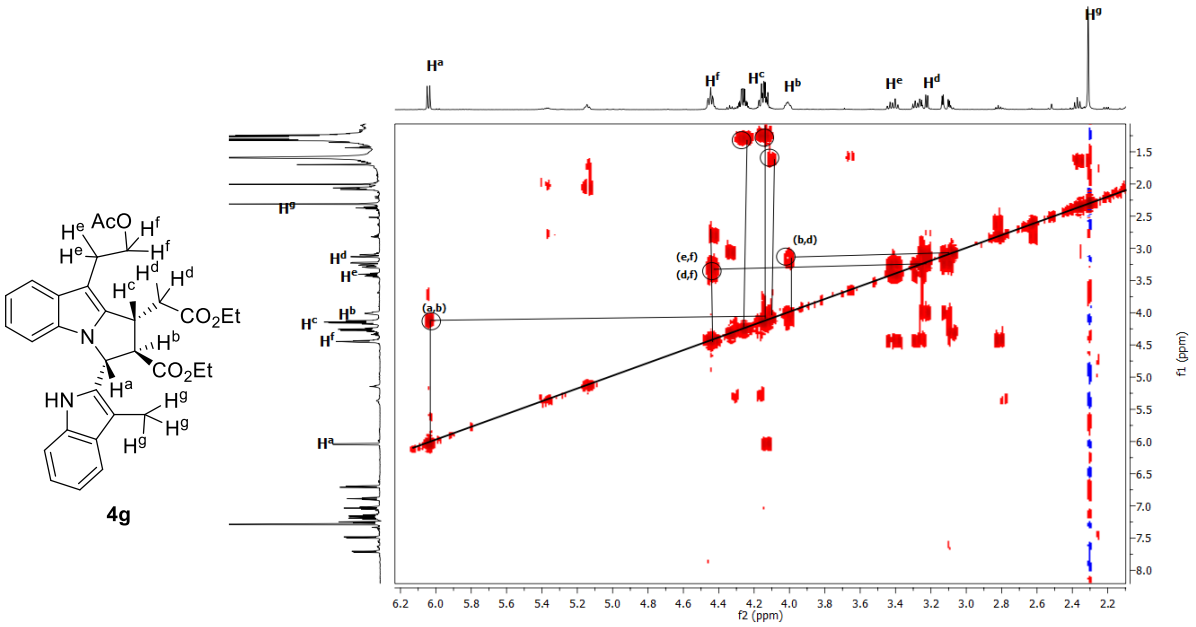
The substitute alkyl chain on pyrrolo[1,2-a]indole core and methyl group (3 and 3') on indole ring of hetero dimer determined by the comparison of the following ^{1}H NMR data of **3a, 4a** and **4g** and ^{1}H–^{1} H COSY and NOESY NMR of **4g**.

[1]HNMR comparison of **3a**, **4a** and **4g:**

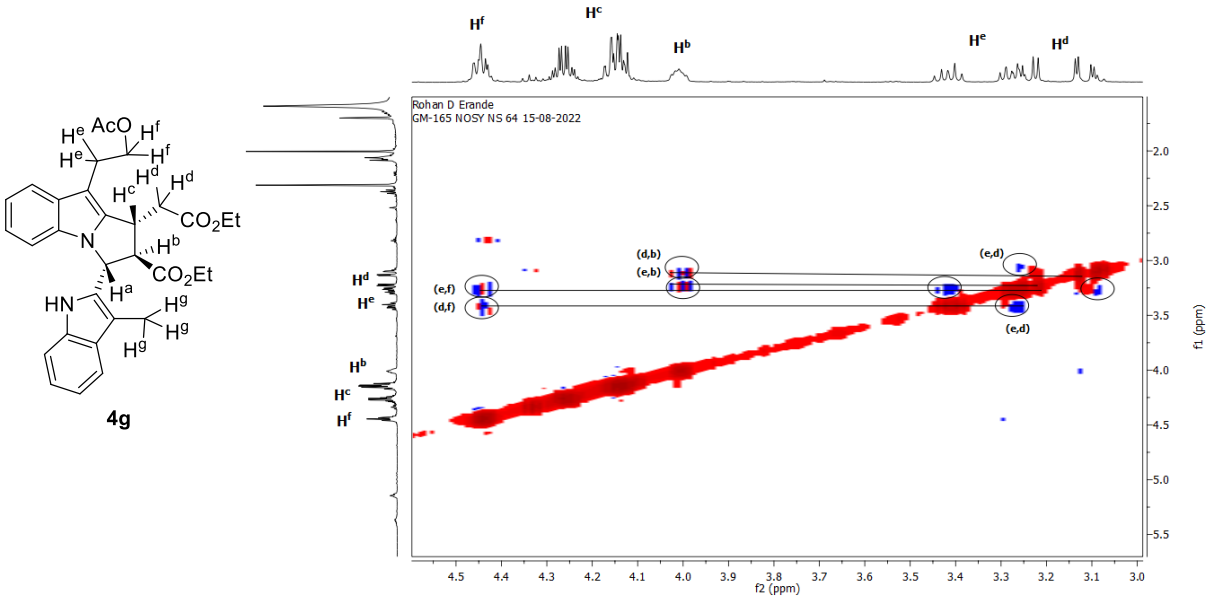




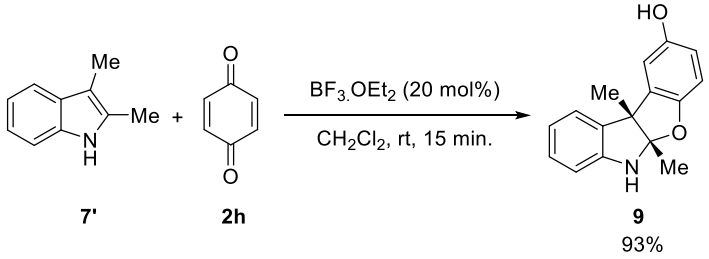
^{1}H–^{1} H COSY NMR spectrum of compound **4g**



^{1}H–^{1} H NOESY NMR spectrum of compound **4g**



Synthesis of compound 9[11]



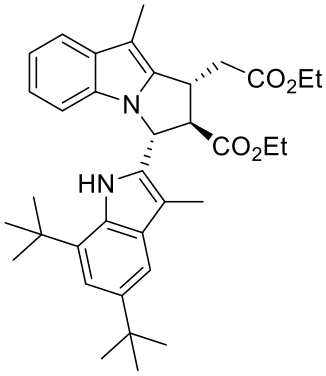
7' **2h** **9**

93%

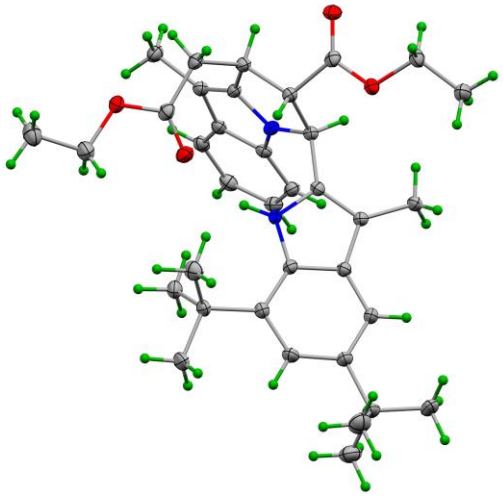
The title compound **9** was prepared from 2,3-dimethyl indole **7'** (50 mg 0.344 mmol, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (20 mol%) and 1,4-benzoquinone **2h** (56 mg, 0.516 mmol, 1.5 equiv.) according to general procedure **E** with a reaction time of 15 minutes. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to EtOAc/hexanes (1/4) to furnish the title compound **9** (81 mg, 0.320 mmol, 93%) as a white solid; R_f=0.2 (EtOAc/hexane 2/3); Spectral data were in agreement with those reported[11]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 6.52 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.90 (d, *J* = 125.0 Hz, 2H), 1.65 (s, 3H), 1.56 (s, 3H); **^{13}C{^{1}H} NMR**(126 MHz, $CDCl_3$) δ 151.6, 150.1, 146.5, 134.7, 133.7, 128.2, 123.0, 119.9, 116.3, 114.6, 110.7, 109.8, 109.2, 57.1, 21.2, 21.0.

8. Single Crystal X-Ray Analysis

8.1 X-ray crystallographic data of compound 3c



3c



X-ray crystal structure of **3c**

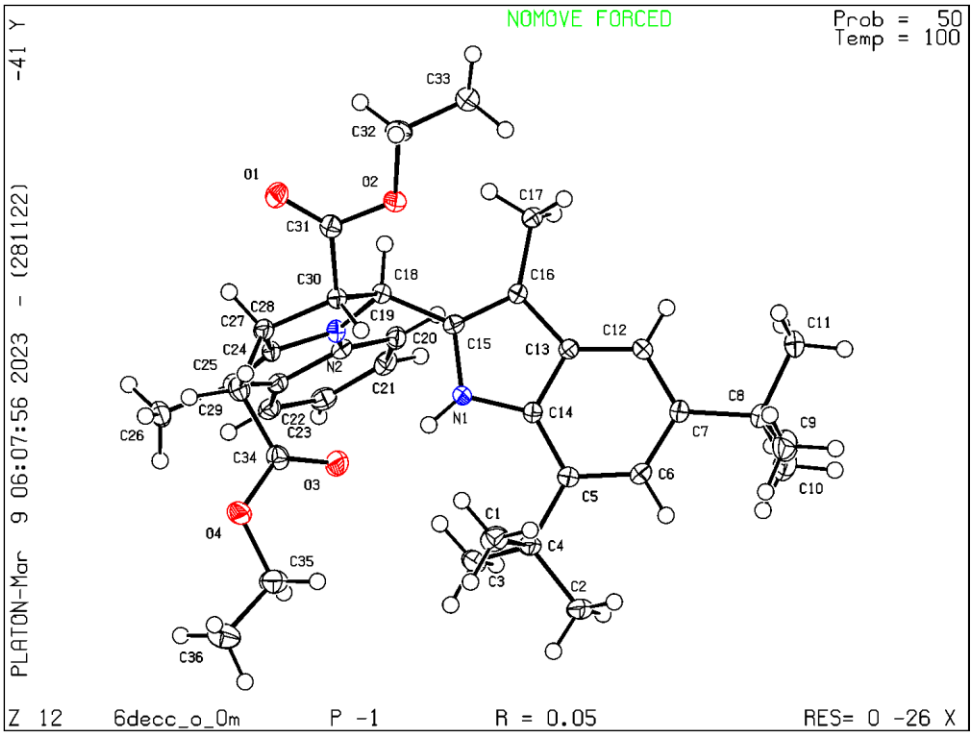


Figure S1 Crystal data and structure refinement for compound **3c**

Table S1. Data Collection and Structure Refinement Parameters for Compound **3c**

Empirical formula	$C_{36}H_{46}N_2O_4$
Formula weight	570.75
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	8.3075(3)
b /Å	10.5823(3)
c /Å	19.6489(7)
α /deg	98.1600(10)

β/deg	91.3010(10)
γ/deg	111.1680(10)
Volume/Å^3	1589.39(9)
Z	2
ρ_{calc}g/cm^3	1.193
μ/mm^{-1}	0.077
F(000)	616.0
Crystal size/mm^3	0.5 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073
2Θ range for data collection/°	4.182 to 56.922
Index ranges	-10 ≤ h ≤ 11, -14 ≤ k ≤ 14, -26 ≤ l ≤ 26
Reflections collected	27606
Independent reflections	7957 [R_{int} = 0.0402, R_{sigma} = 0.0455]
Data/restraints/parameters	7957/0/389
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0507, wR_2 = 0.1179
Final R indexes [all data]	R_1 = 0.0745, wR_2 = 0.1312
Largest diff. peak/hole / e Å^{-3}	0.38/-0.27

$^a R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^b wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 6decc_o_0m

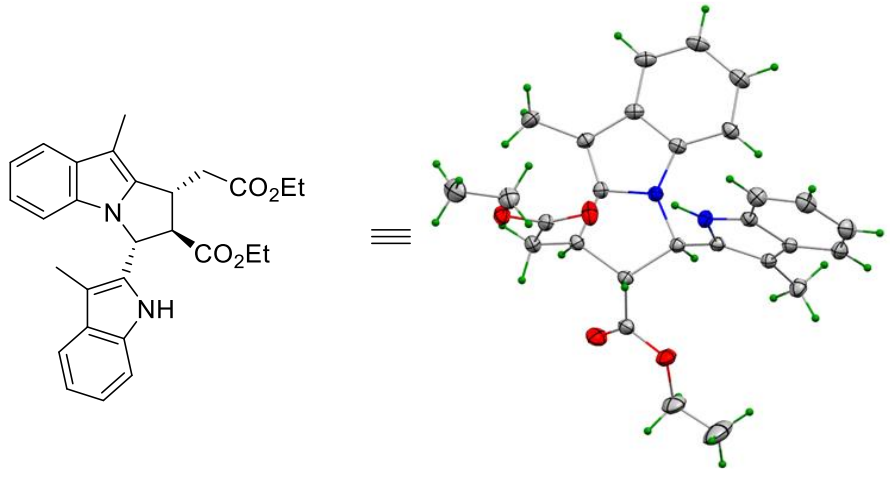
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 6decc_o_0m

```
Bond precision:   C-C = 0.0021 A           Wavelength=0.71073

Cell:           a=8.3075(3)        b=10.5823(3)      c=19.6489(7)
                alpha=98.160(1)    beta=91.301(1)    gamma=111.168(1)
Temperature:    100 K

                 Calculated                 Reported
Volume           1589.39(9)                 1589.39(9)
Space group      P -1                       P -1
Hall group       -P 1                       -P 1
Moiety formula   C36 H46 N2 O4              C36 H46 N2 O4
Sum formula      C36 H46 N2 O4              C36 H46 N2 O4
Mr               570.75                     570.75
Dx,g cm-3        1.193                      1.193
Z                2                          2
Mu (mm-1)        0.077                      0.077
F000             616.0                      616.0
F000'            616.26
h,k,lmax         11,14,26                   11,14,26
Nref             8017                       7957
Tmin,Tmax        0.982,0.992                0.686,0.746
Tmin'            0.962

Correction method= # Reported T Limits: Tmin=0.686 Tmax=0.746
AbsCorr = EMPIRICAL

Data completeness= 0.993            Theta(max)= 28.461

R(reflections)= 0.0507( 5953)                    wR2(reflections)=
                                                 0.1312( 7957)
S = 1.032                  Npar= 389
```

8.2 X-ray crystallographic data of compound 4a



4a X-ray crystal structure of **4a**

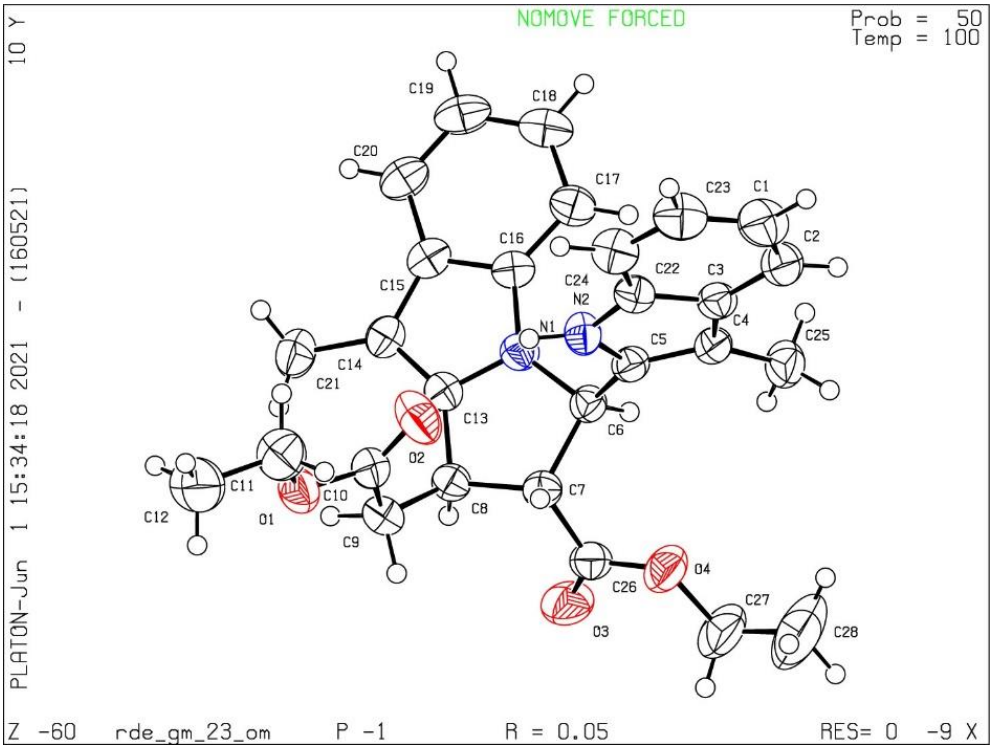


Figure S2. Crystal data and structure refinement for compound **4a**

Table S2. Data Collection and Structure Refinement Parameters for Compound **4a**

Emperical formula	$C_{28}H_{30}N_2O_4$
Formula weight	458.54
Crystal color, habit	colorless, block
T / K	100(2)
Crystal system	Triclinic
Space group	P-1 (no. 14)
a/Å	8.3294(19)
b/Å	9.907(2)
c/Å	16.337(4)
α/°	75.760(3)
β/°	78.824(3)
γ/°	69.309(3)
V/Å^3	1213.9(5)
Z	2
D_c/g cm^{-3}	1.255
μ/mm^{-1}	0.084
Reflections measured	30389
Unique reflections/R_{int}	5317/ 0.1345
$R(F)$ [$I > 2\sigma(I)$]	3728
$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	$R_1 = 0.0486^a$ $wR_2 = 0.1193^b$
$R_1{}^a$, $wR_2{}^b$ (all data)	$R_1 = 0.0743^a$ $wR_2 = 0.1345^b$
GOF on F^2	1.032

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) rde_gm_23_om

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: rde_gm_23_om

```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71073

Cell:          a=8.3294(19)       b=9.907(2)        c=16.337(4)
               alpha=75.760(3)    beta=78.824(3)    gamma=69.309(3)
Temperature:   100 K
```

	Calculated	Reported
Volume	1213.9(5)	1213.9(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C28 H30 N2 O4	C28 H30 N2 O4
Sum formula	C28 H30 N2 O4	C28 H30 N2 O4
Mr	458.54	458.54
Dx,g cm-3	1.255	1.254
Z	2	2
Mu (mm-1)	0.084	0.084
F000	488.0	488.0
F000'	488.22	
h,k,lmax	10,12,20	10,12,20
Nref	5337	5317
Tmin,Tmax	0.995,0.997	0.660,0.746
Tmin'	0.992	

```
Correction method= # Reported T Limits: Tmin=0.660 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 27.055

R(reflections)= 0.0486( 3728)     wR2(reflections)= 0.1345( 5317)

S = 1.032                 Npar= 319
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

9. Biological Evaluation

Table S3. *In silico* MptpB binding affinity prediction of synthesized of Pyrrolo[1,2-a]indole derivatives. MptpB binding affinity prediction of one previously reported MptpB inhibitor (OMTS) was also considered as the positive control.

Name of Ligands	Binding Free Energy (Kcal/Mol)	pK_d(-logK_d)	MM/PB(GB)SA Free Energy (Kcal/Mol)
3a	-8.6	7.62	-43.32
3b	-9.2	6.71	-42.59
3c	-8.7	7.74	-44.59
3d	-8.9	7.19	-43.28
3e	-9.6	8.93	-59.12
3f	-9.0	9.96	-58.44
3g	-9.9	9.09	-59.61
4a	-8.4	6.85	-35.15
4b	-8.4	7.17	-45.76
4c	-8.6	7.09	-50.68
4d	-9.0	7.92	-54.79
4e	-8.6	7.59	-41.57
4f	-9.5	5.53	-23.13
4g	-9.5	7.54	-50.41
5a	-10.3	7.85	-38.86
5b	-9.4	8.24	-52.77
5c	-8.6	8.91	-48.1
5d	-9.8	8.54	-51.86
6	-6.3	4.81	-20.76
7	-6.7	3.47	-22.22
8	-7.6	6.06	-31.71
9	-8.0	4.67	-18.45
OMTS (Positive Control)	-9.2	5.99	-44.45

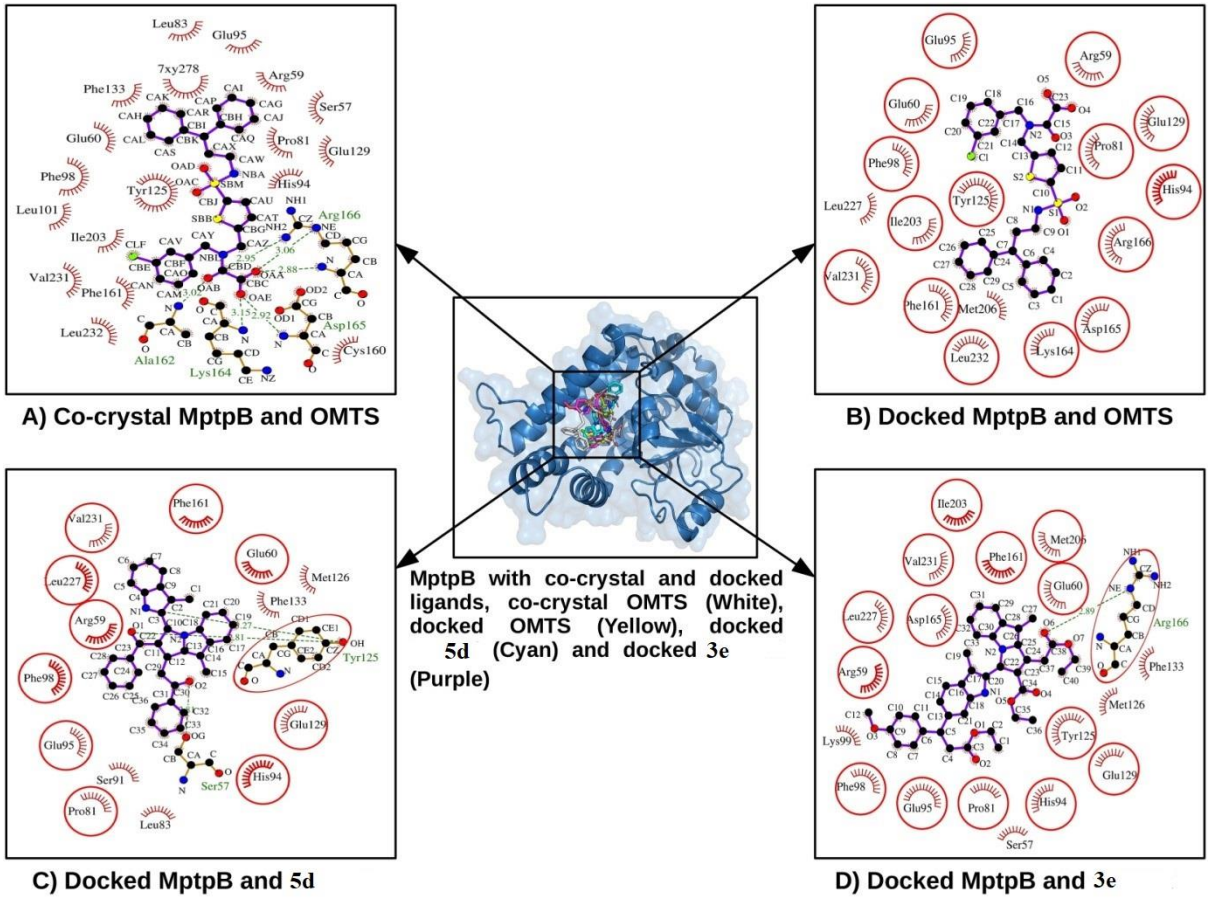


Figure S3. Fidelity of the docking experiment and comparative MptpB binding profiles of synthesized Pyrrolo[1,2-a]indole derivatives (5d, 3e) along with prior reported MptpB substrate competitive inhibitor, OMTS. The central figure represents the structural glimpse of MptpB with bound ligands (**5d**, **3e** and OMTS). The boxed figures (A,B,C,D) represent 2D interaction profile of MptpB bound (co-crystallized or docked) ligands with the active site amino acids residues. The encircled amino acid residues in Figure S3.B, Figure S3.C and Figure S3.D represent the engagement of identical active site amino acid residues of MptpB which arepreviously found to interact with co-crystallized ligand OMTS Figure A The engagement of identical sets of amino acids in FigA and Fig S3.B for the same ligand OMTS which is either co-crystallized (Figure S3 A) or blind docked (Figure S3.B) justifies the fidelity of docking experiment. Likewise, the engagement of similar sets of amino acids in Figure S3 C and Figure.S3 D as compared with Figure.S3 A suggests that the synthesized Pyrrolo[1,2-a]indole derivatives **5d**, and **3e** may also act as substrate competitive inhibitor of MptpB. Spiked arches represent the hydrophobic interactions while the green dotted line represent the formation of hydrogen bonds.

Methodology:

2D structure of the all molecules in the library from pyrrolo indole derivatives were drawn using a freely available online tool named ChemDraw from PerkinElmer Informatics (https://chemdrawdirect.perkinelmer.cloud/js/sample/index.html) followed by the conversion into 3D SDF format using open babel software.[12] Further these ligands were converted into PDB followed by conversion into PDBQT format by using PyMol (The PyMOL Molecular Graphics System, Version 1.2r3pre, Schrödinger, LLC) and AutoDock Tools 1.5.6.[13] Mycobacterial protein tyrosine phosphatase B (MptpB) 3D structure (PDB ID: 2OZ5)[14] was downloaded from protein data bank RCSB website[15] and associated ligands and water molecules were removed using PyMol. The AutodockVina was used for molecular docking and AutoDock Tools 1.5.6 for protein and ligand preparation for docking. The Kollman charges and polar hydrogen were added followed by converting to PDBQT format. In order to perform blind docking grid box was prepared to cover up whole protein, box size of 1Å with spacing 54x66x56. Post docking, the binding affinity of the best pose of the ligands out of nine possible binding sites was calculated using online server KDEEP.[16] The interaction profile of ligand with protein and binding poses were analyzed by using PyMol and Ligplot.[17] To study the stability of the bound ligand with the MptpB protein we have performed the

molecular dynamic simulation (MD simulation) study. Alone MptpB and MptpB docked with ligands (**5d** and **3e**) were simulated to understand the stability behavior of the protein in physiologically simulated conditions in presence of ligands. All the MD simulation was perform using NAMD 2.14 software.[18] VMD (visual Molecular Dynamics was used to protein and ligand preparation and results analysis.[19] Best pose of the ligand, post docking study by autodokvina and protein PDBQT format was used as a complex for simulation file preparation. modeler tools[20] was used to generate force field and topology files of ligands such as ligandrm.psf and ligandrm.pdb. The ligand and protein structure complex were solvated with a boundary of 5Åcubic cell and langevin dynamics were applied to generate isothermal–isobaric ensemble environment for simulation. The simulation was performed for 30ns with a 2 femto second time step per cycles. The energy minimization of the system was done for 1000 steps and the steps for dcd, xst, and restart frequency was set to 5000 steps and output energy to 50 steps. To study the change in conformation of the alone protein and protein with ligands RMSD profile was analyzed using VMD tools. Since Molecular Mechanics/Poison Boltzmann Surface area and Molecular Mechanics/Generalized Born surface area are the two well evaluated methods for ranking docked poses hence to be double sure and increase the probability of the prediction and scoring function we have done the free energy calculation based on MM/PB(GB)SA method. Here we have applied fastDRH, a web server to re-score the docked poses that apply AmberTools17 for free energy calculation. Here, we have chosen ff19SB force field for receptor and GAFF2 for ligand and we consider the score of GB8 method due to higher success rate.[21] All the data are plotted using origin software (Origin, Version 2022. OriginLab Corporation, Northampton, MA, USA.).

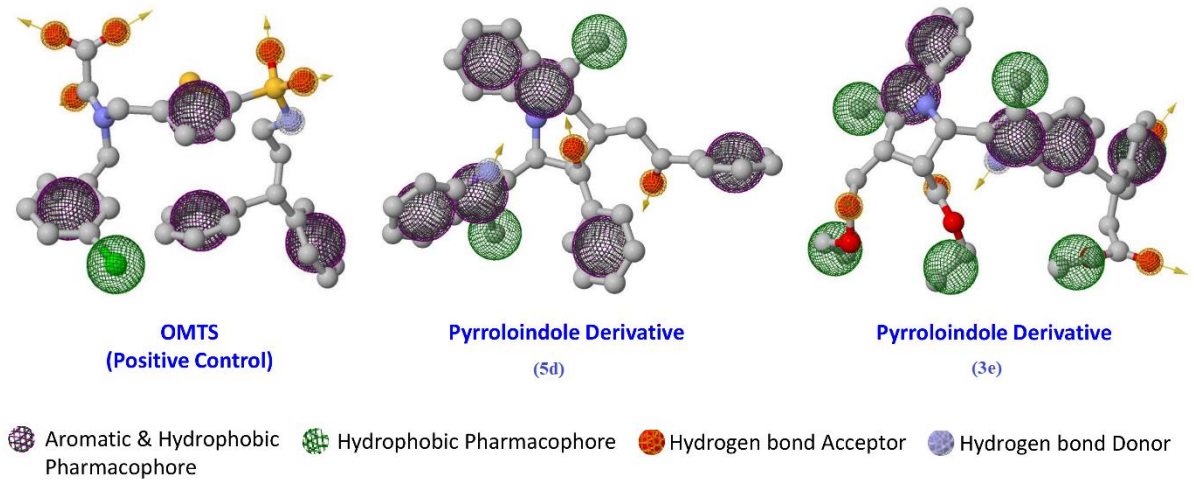


Figure S4. Pictorial view of similarity in pharmacophore of control ligand (OMTS) and pyrroloindole derivatives

OMTS is potentially binding at the active site of MptpB and considered as a potential inhibitor of this mycobacterial drug target protein. Our synthesized pyrroloindole derivatives have the similar pharmacophore as OMTS so it gives a hunch that these molecules may also bind and inhibit MptpB. Taking pharmacophoric similarity in consideration, using *in silico* approaches we have extended our study to screen these derivatives as potential lead molecules against MptpB.

10. Computational Details

In order to gain an understanding of the mechanism behind the novel $BF_3.OEt_2$ catalyzed cascade reaction, we propose a reaction as depicted in Scheme 2. Initially, the formation of product **3a'** was expected over the reaction between the indole ester **1a** and ethyl acrylate **2a**. However, the experiment resulted in the formation of a self-dimerized intermediate **4a**, eventually producing the product **3a**. To understand the reaction mechanism and to know the reason behind the formation of **3a** instead of anticipated product **3a'**, density functional theory (DFT) electronic structure calculations were carried out. Geometry optimization was performed at the B3LYP/def2-SVP level of theory followed by single point calculations for the optimized structures at B3LYP/def2-TZVP were completed using ORCA package.[22–26] Solvation effects were also considered throughout the calculations using the CPCM (Conductor-like Polarizable Continuum Model) implicit model.[27]As seen in Figure S5, the barrier height for TS 1 is 43.8 kcal/mol and the energy of **3a'** is 5.6 kcal/mol below the reactants. This shows that the formation of **3a'** is neither kinetically nor thermodynamically favoured. Hence, the potential energy profile presenting the detailed mechanism for the formation of self-dimerization adduct **4a** and its reaction with ethyl acrylate **2a** to give substituted pyrrolo[1,2-*a*]indoles **3a** was computed and provided in Figures 2 and SI-3, respectively. The transition state (1a-TS 1) for the formation of self-dimer **4a** has a barrier height of 33.4 kcal/mol leading to the formation of a stable intermediate 1a-IM 1 followed by the keto-enol tautomerism.

It was anticipated that the indole ester **1a** under $BF_3.OEt_2$ conditions generates an unstable intermediate **A**, which subsequently undergoes [3+2] cycloaddition with another molecule of indole ester **1a** to generate self-dimerized adduct **4a** . Notably, the self-dimerization adduct **4a** was found to be highly stable, which lies at 36.9 kcal/mol below the reactants. Further reaction of self-dimer **4a** with ethyl acrylate **2a** led to the formation of **3a** with 12.6 kcal/mol of energy above the reactants. In addition, cross dimerization product **4g** (Figure S6) has also been observed in the experiments where an unstable **1c'** intermediate on reaction with **1a** undergoes [3+2] cycloaddition similar tso the self-dimerization reaction process. Both the reactions follow a similar reaction mechanism approach, where there is a formation of five-membered ring. The energies for each transition state as well as the intermediates follows almost identical trend.

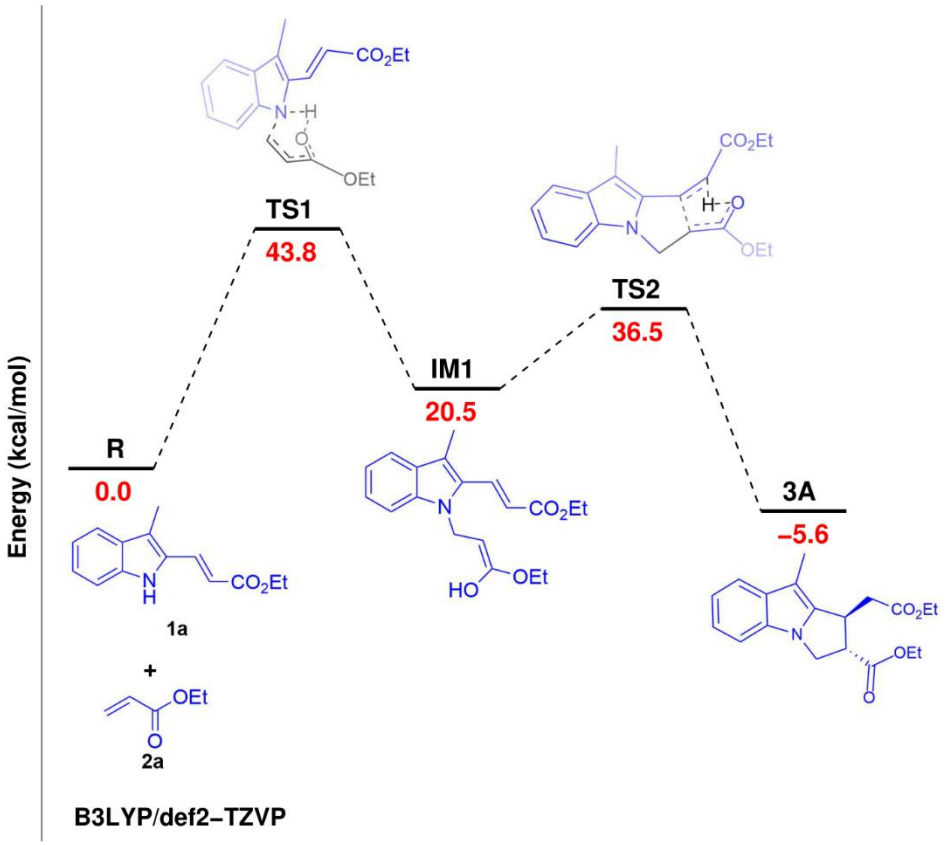


Figure S5. Potential energy profile for the expected product (**3A)**. Energies are in kcal/mol.

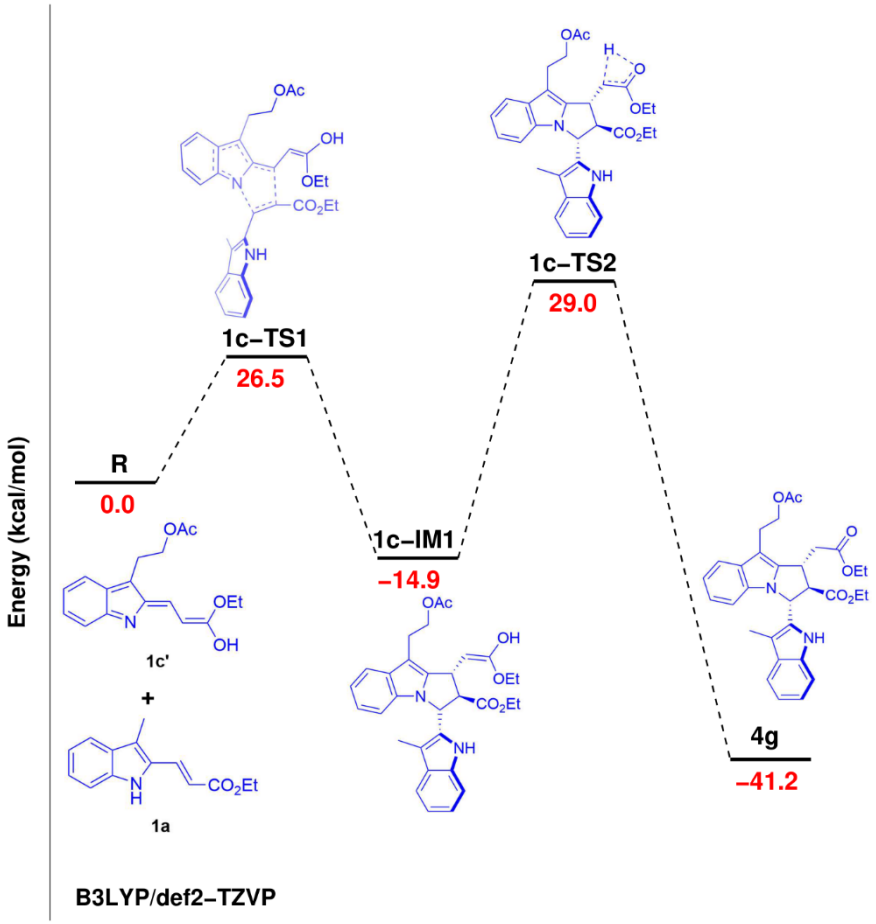


Figure S6. Potential energy profile for cross-dimerization (**4g**). Energies are in kcal/mol.

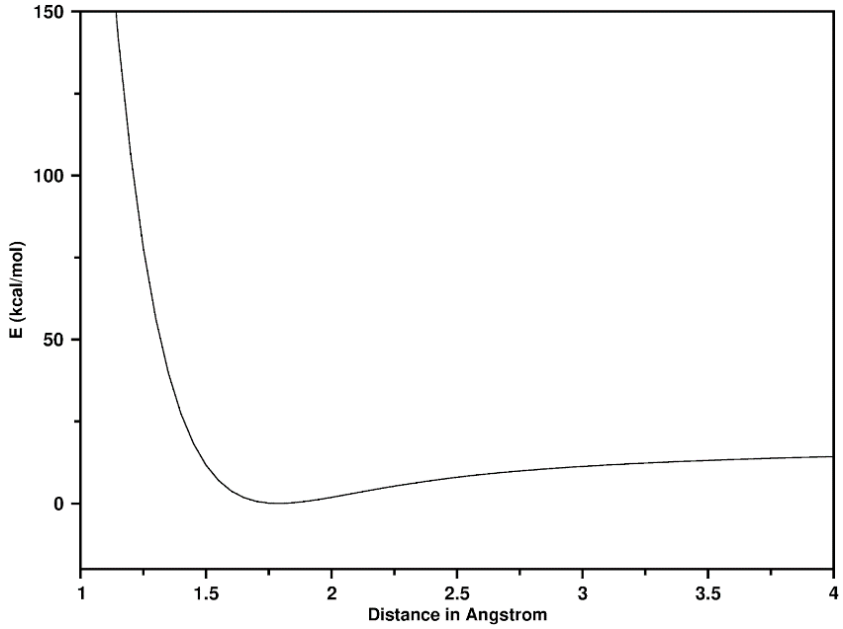


Figure S7. TS-Scan graph from addition of ethyl acrylate **2a** on dimer **4a** to the formation of molecule **3a**.

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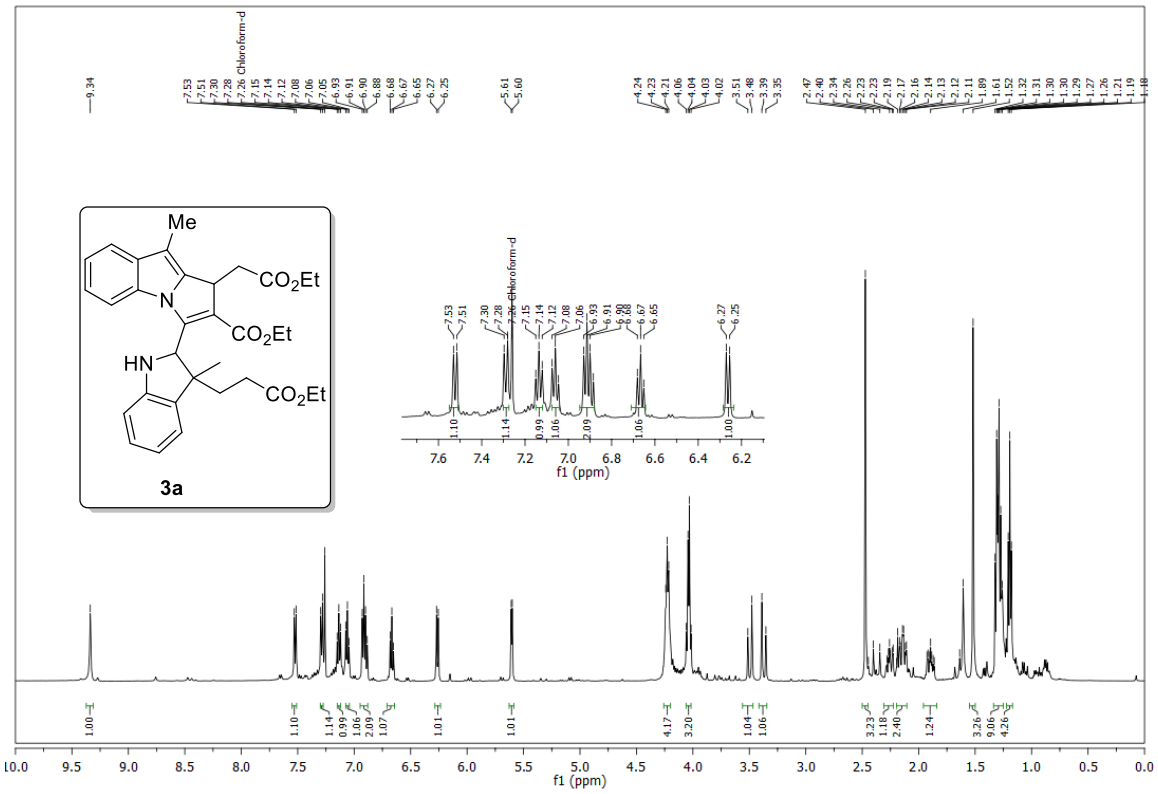
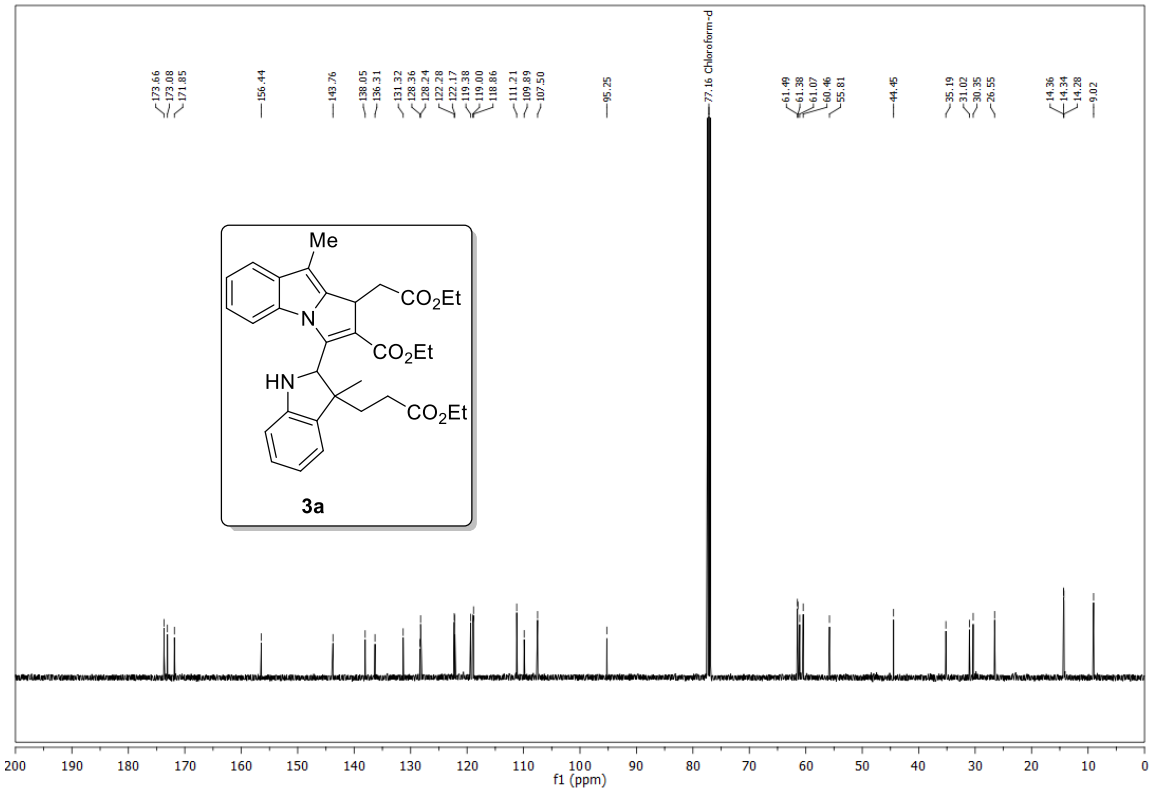
11. NMR spectra of new compounds 3a-3g, 4a-4f, 5a-5d and 6-9

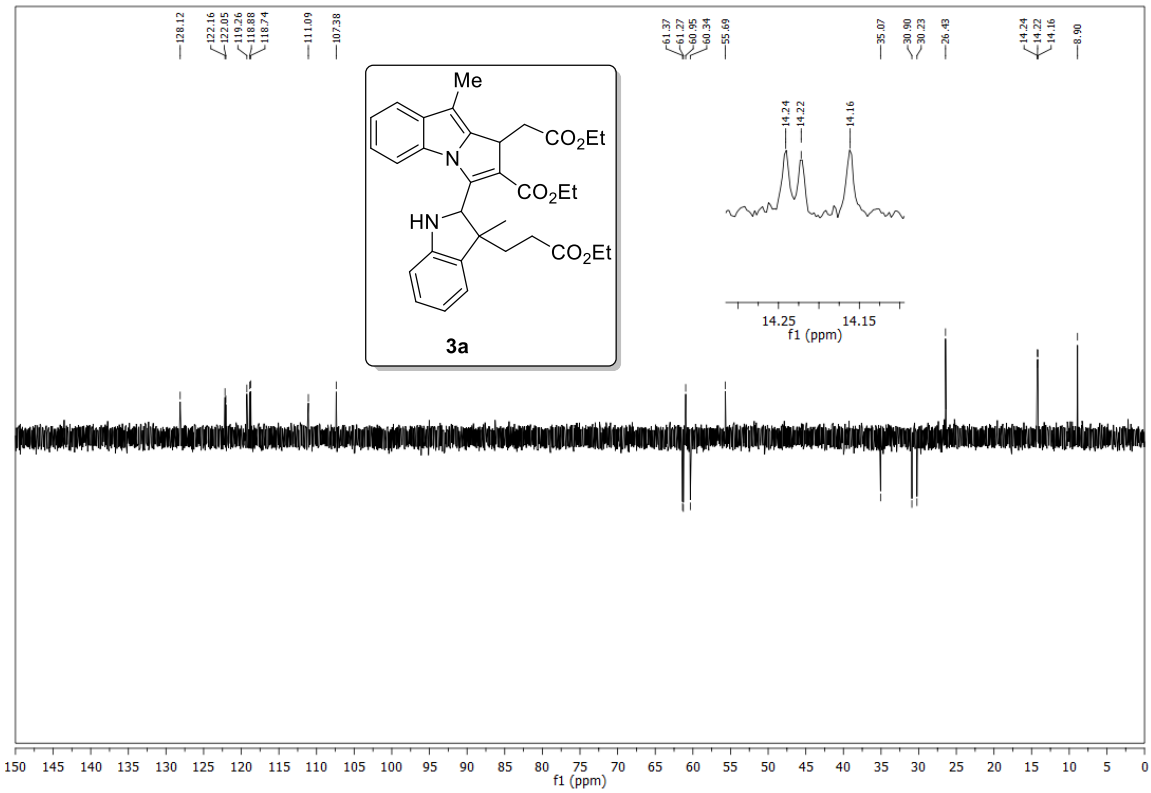
^{1}H NMR (500 MHz, $CDCl_3$) of 3a



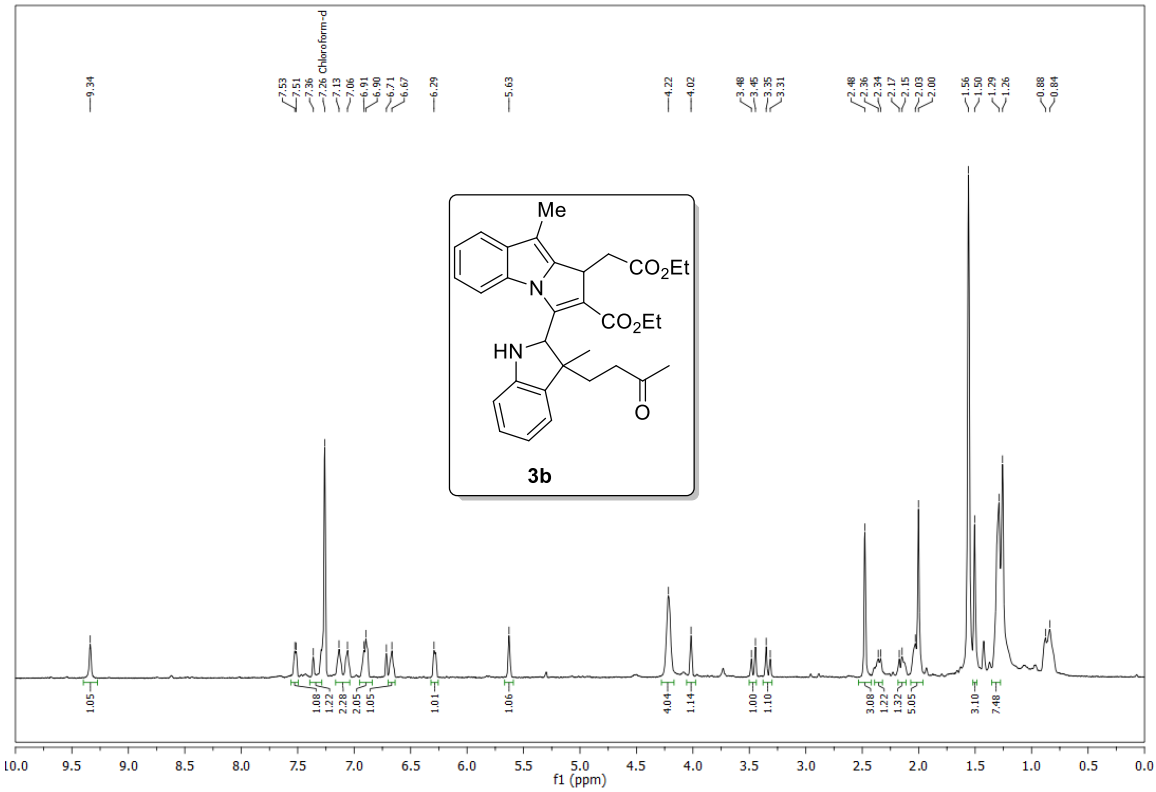
^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$) of 3a



DEPT of 3a



^{1}H NMR (500 MHz, $CDCl_3$) of 3b



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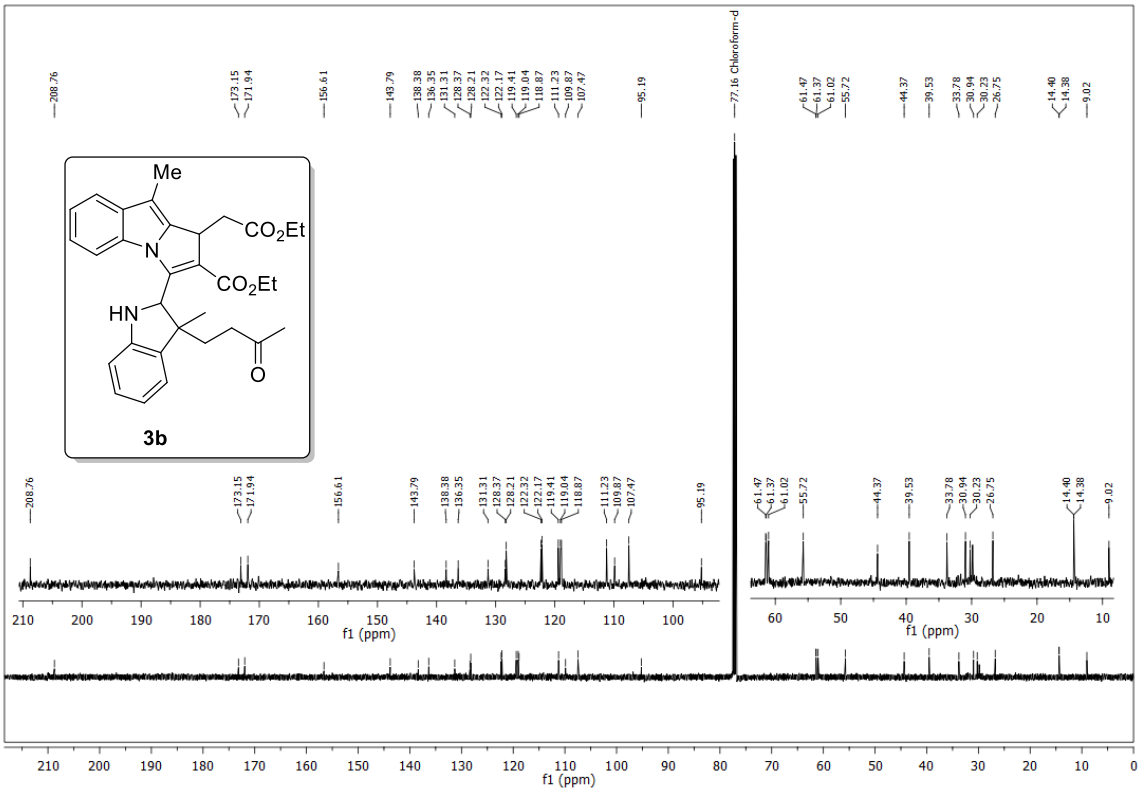

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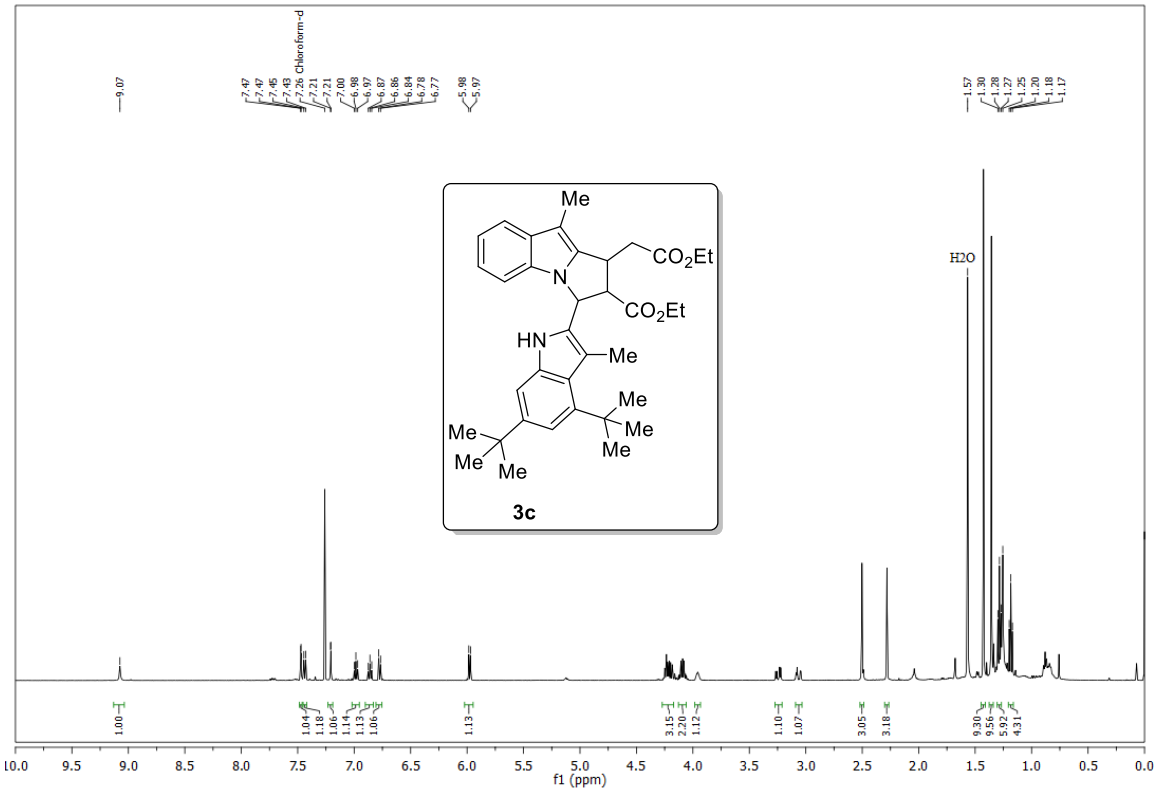

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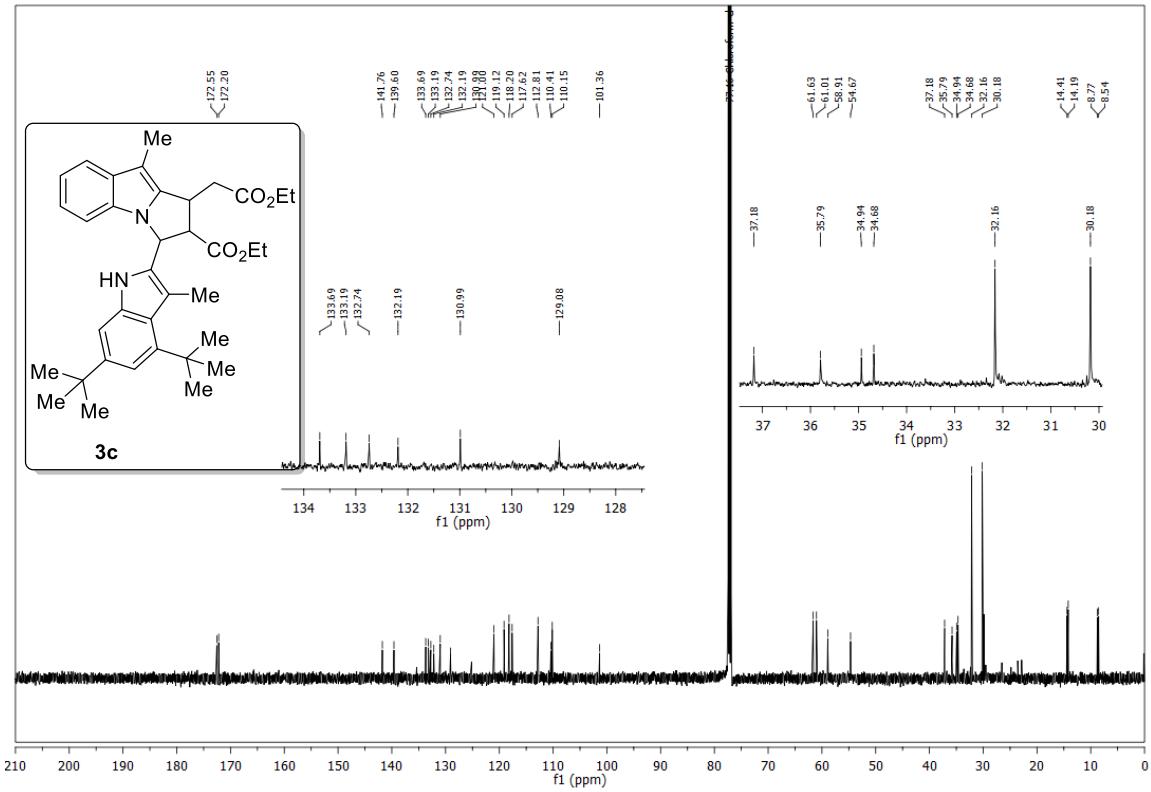
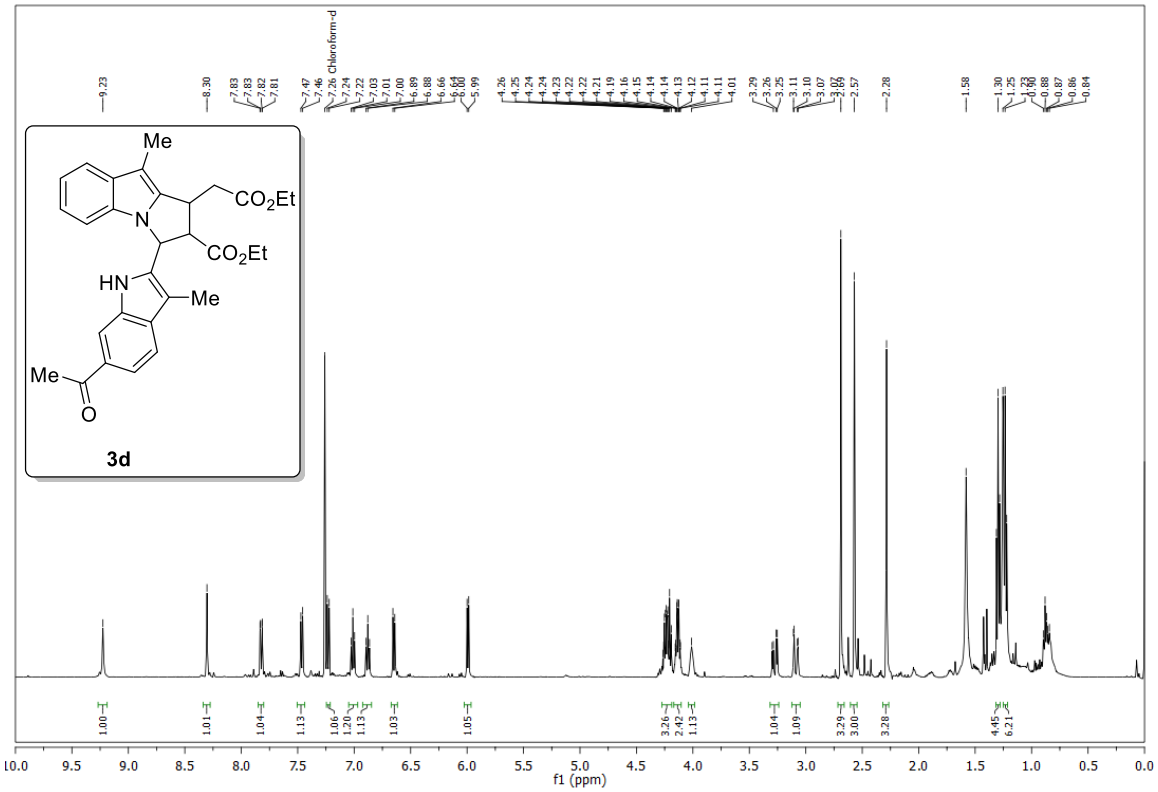


^{1}H NMR (500 MHz, $CDCl_3$) of 3d



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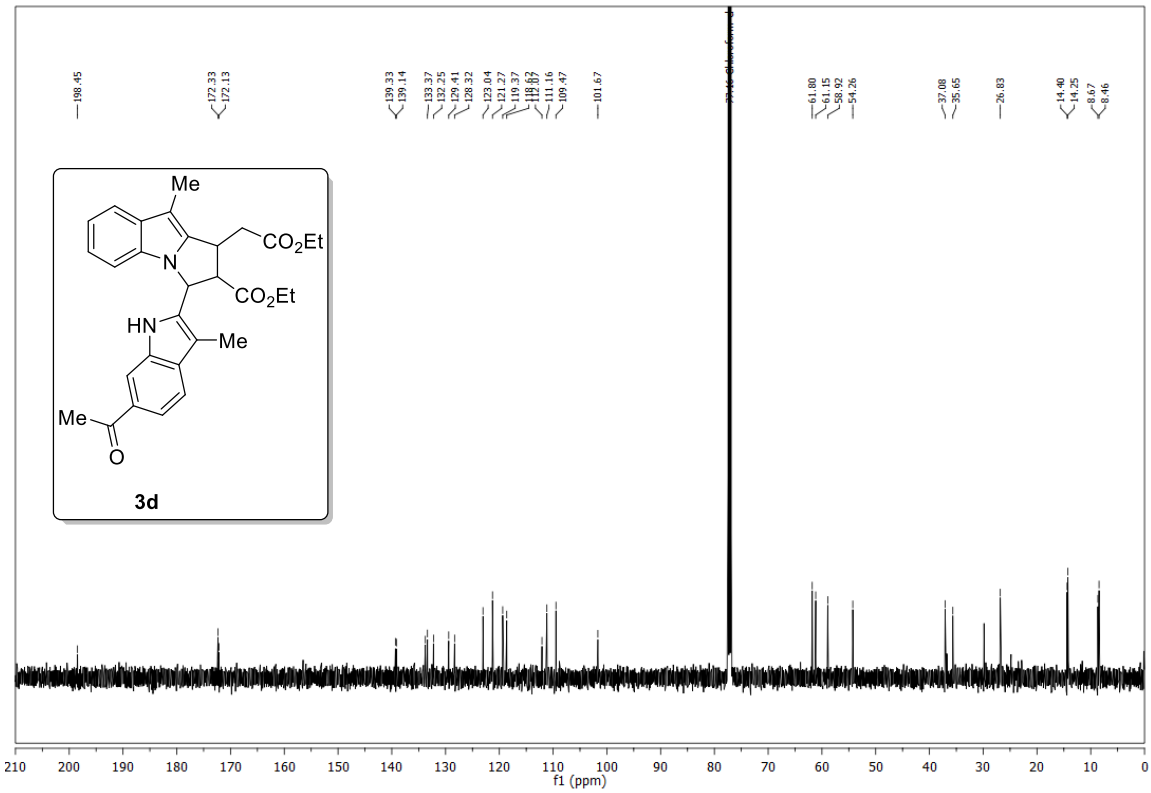
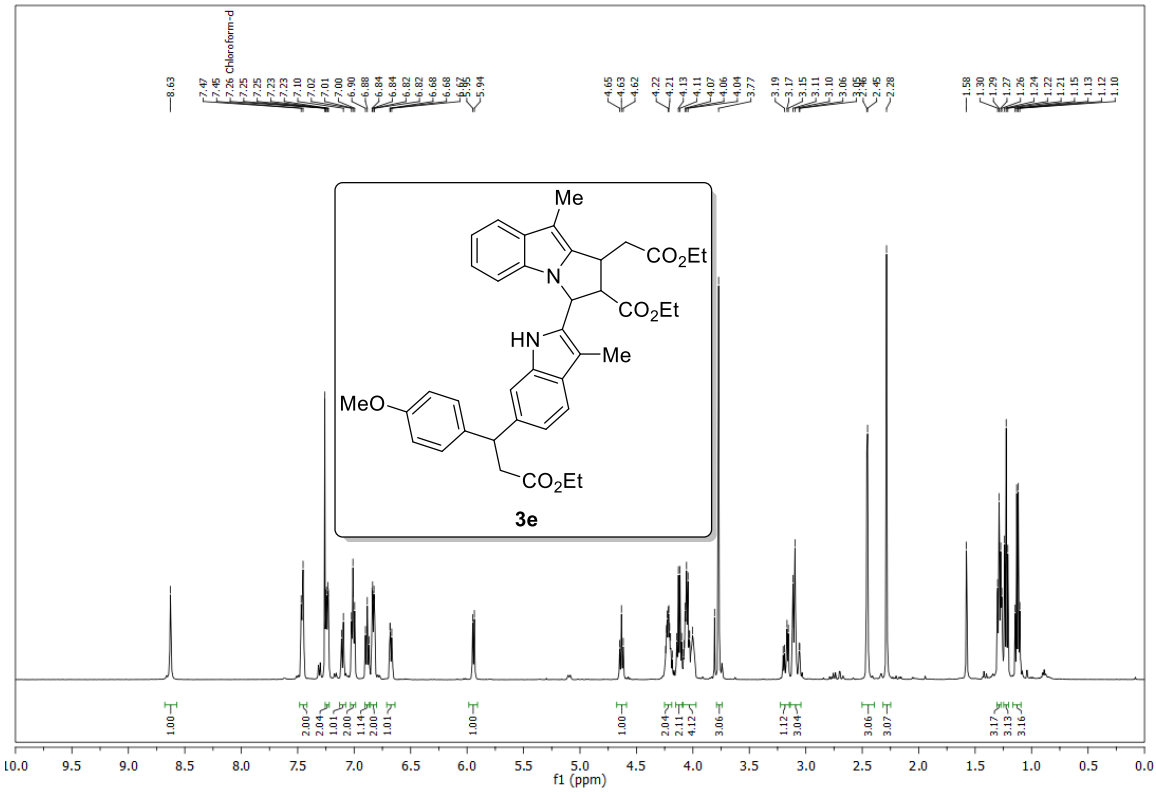
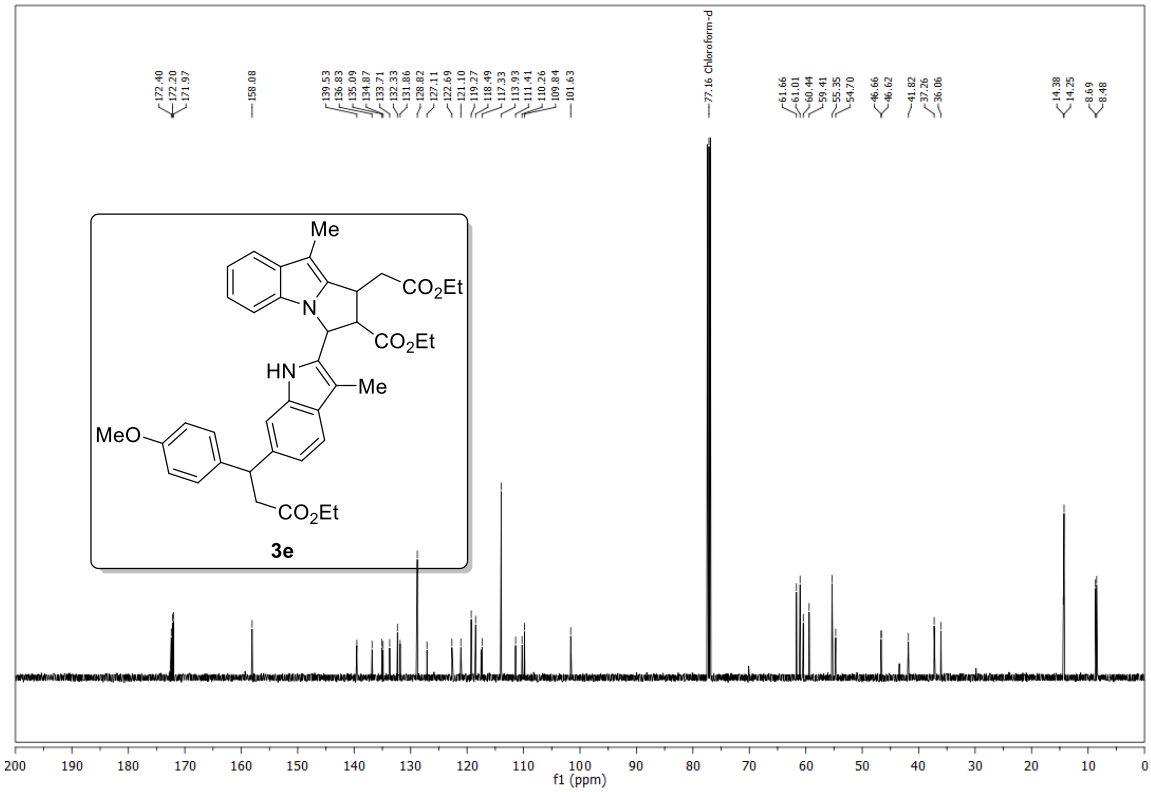


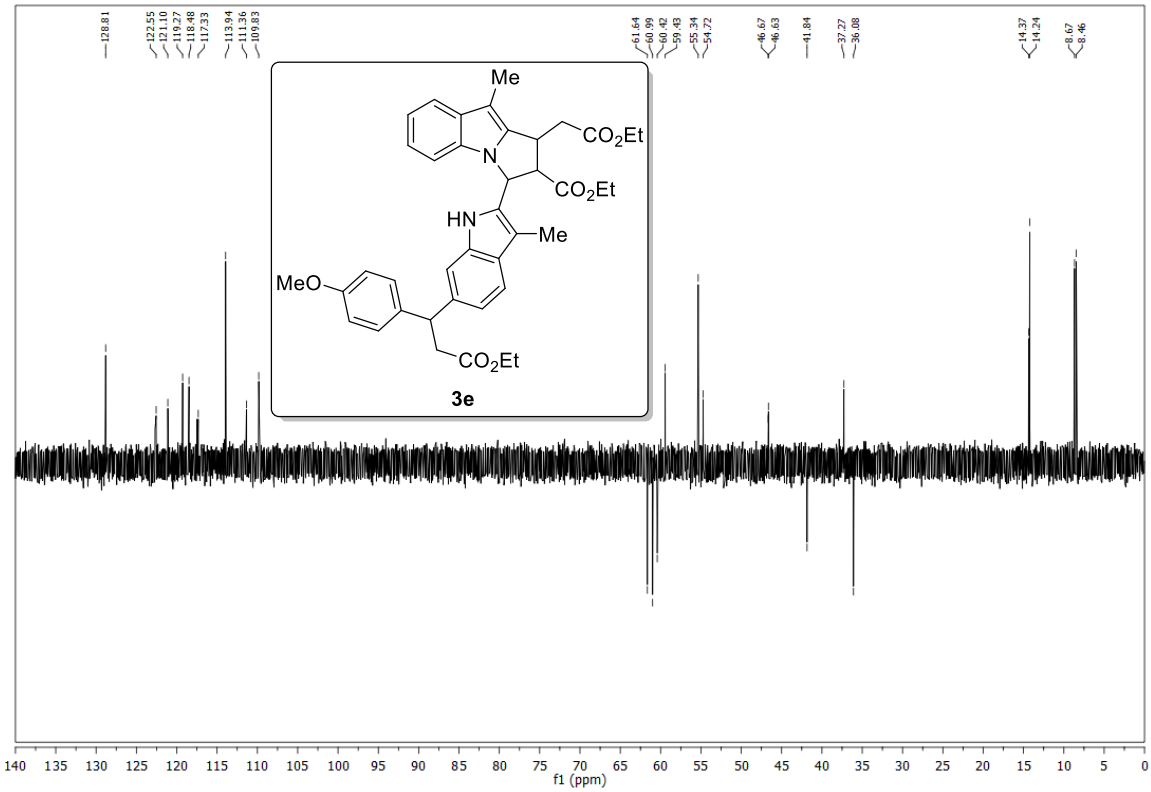
^{1}H NMR (500 MHz, $CDCl_3$) of 3e



$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 3e



DEPT of 3e



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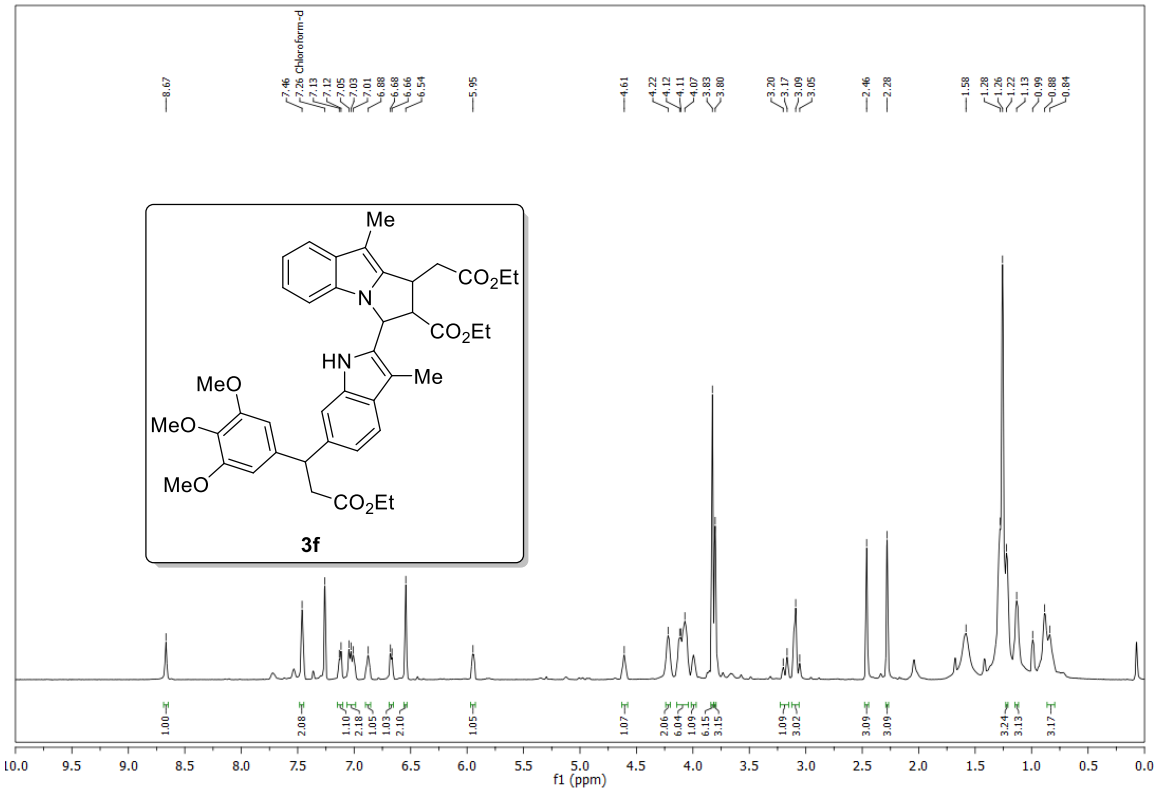
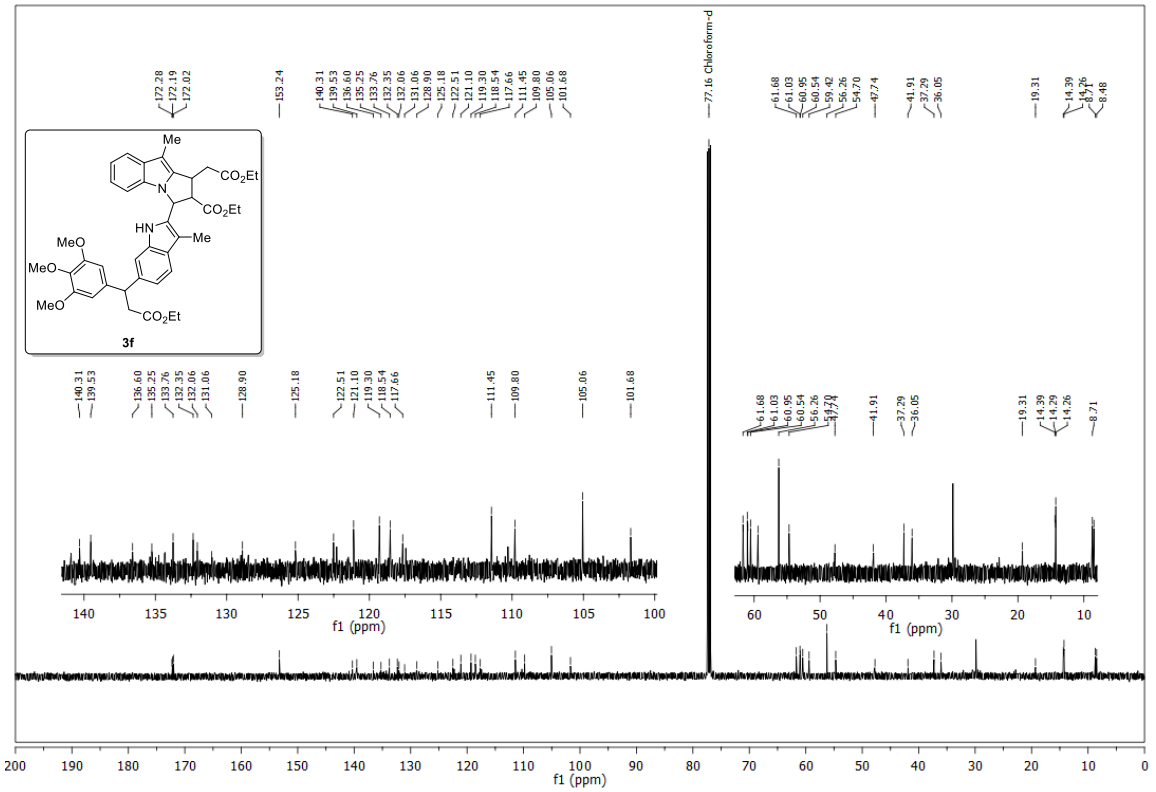
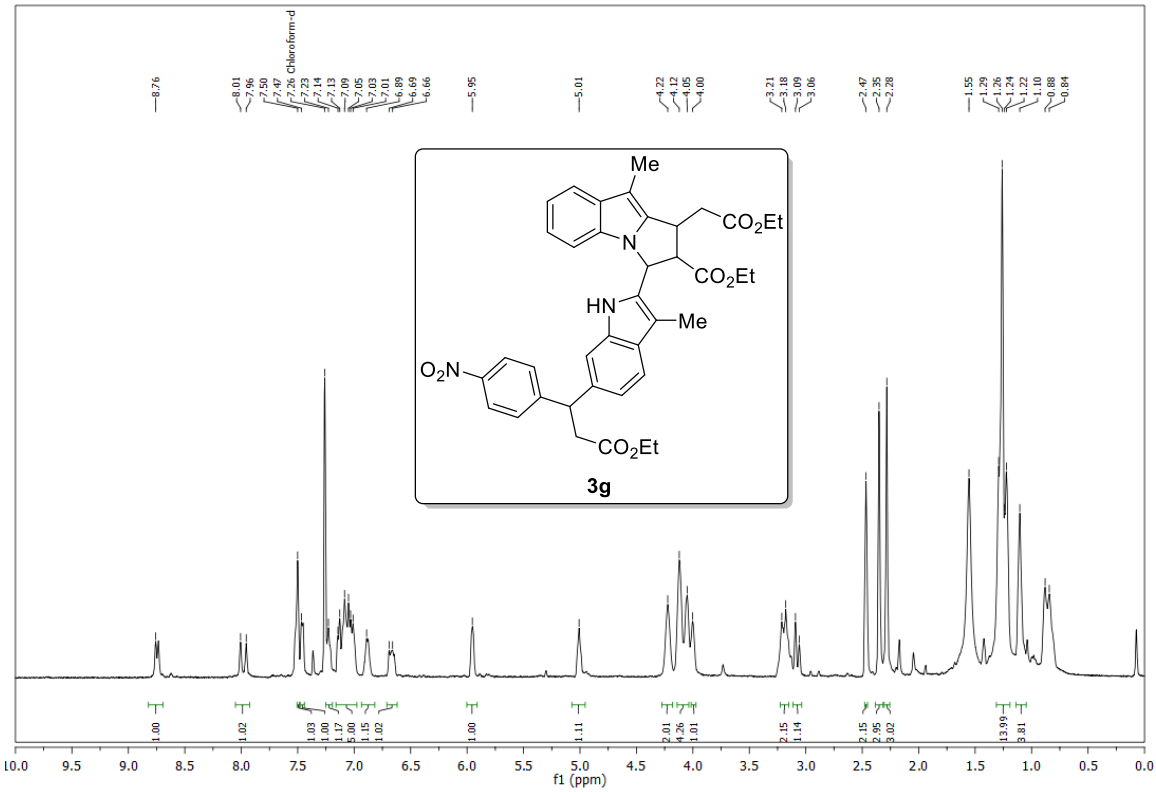


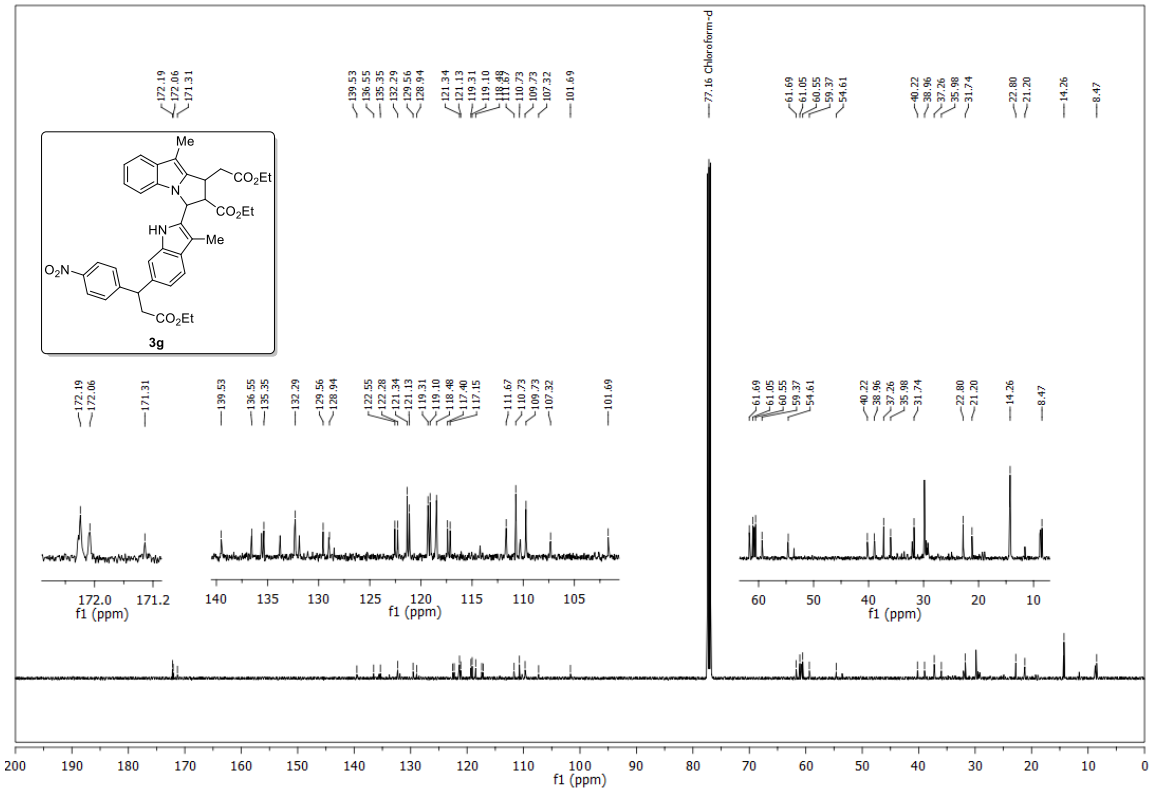
^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$) of 3f



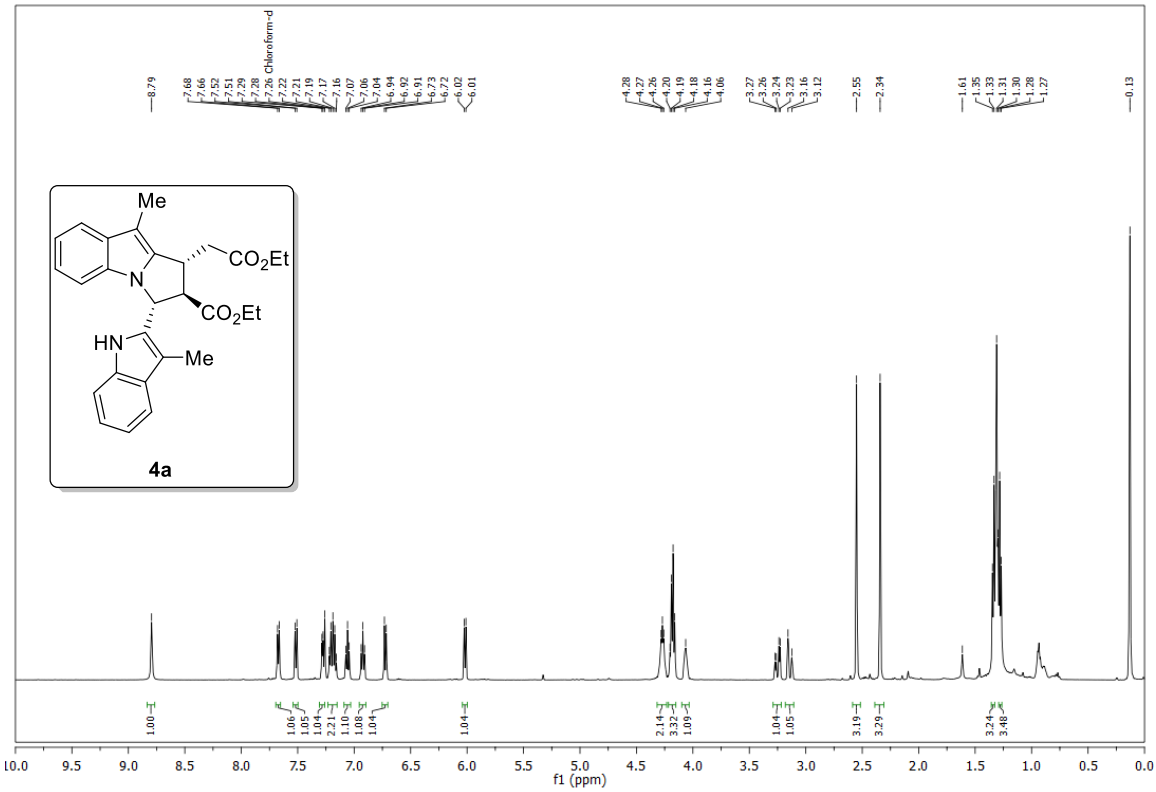
^{1}H NMR (500 MHz, $CDCl_3$) of 3g



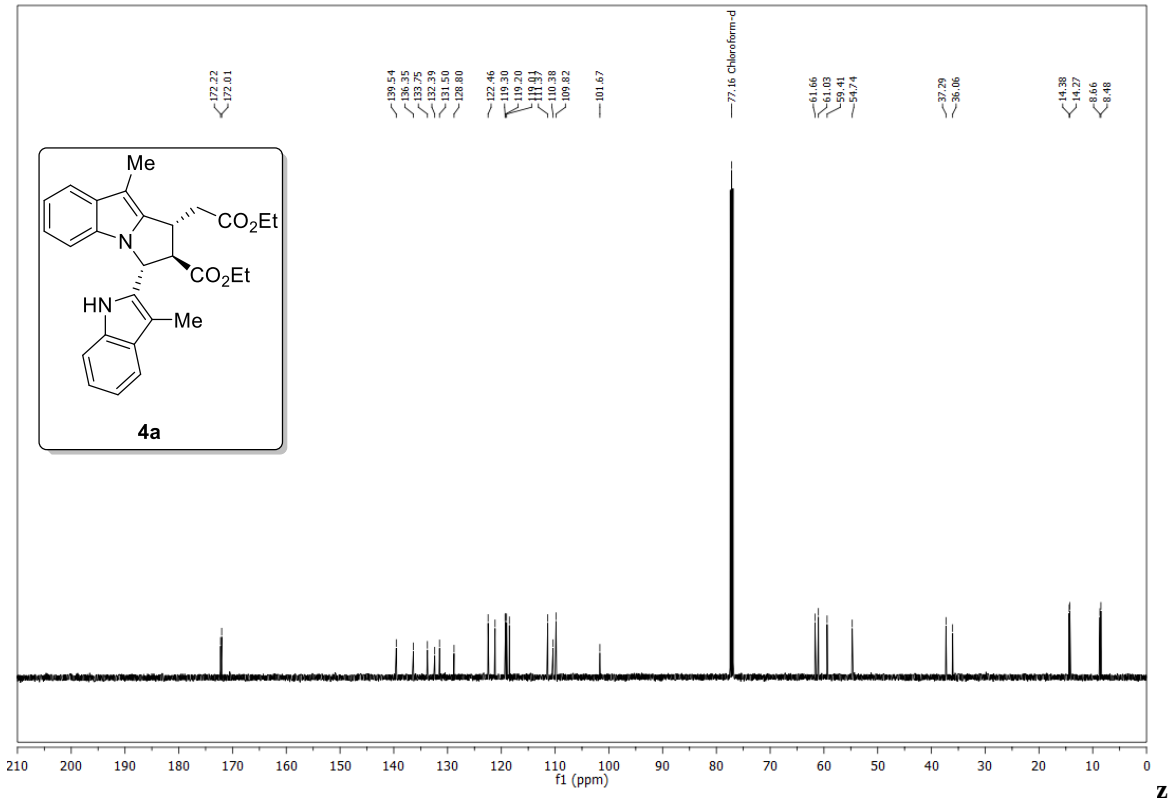
^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$) of 3g



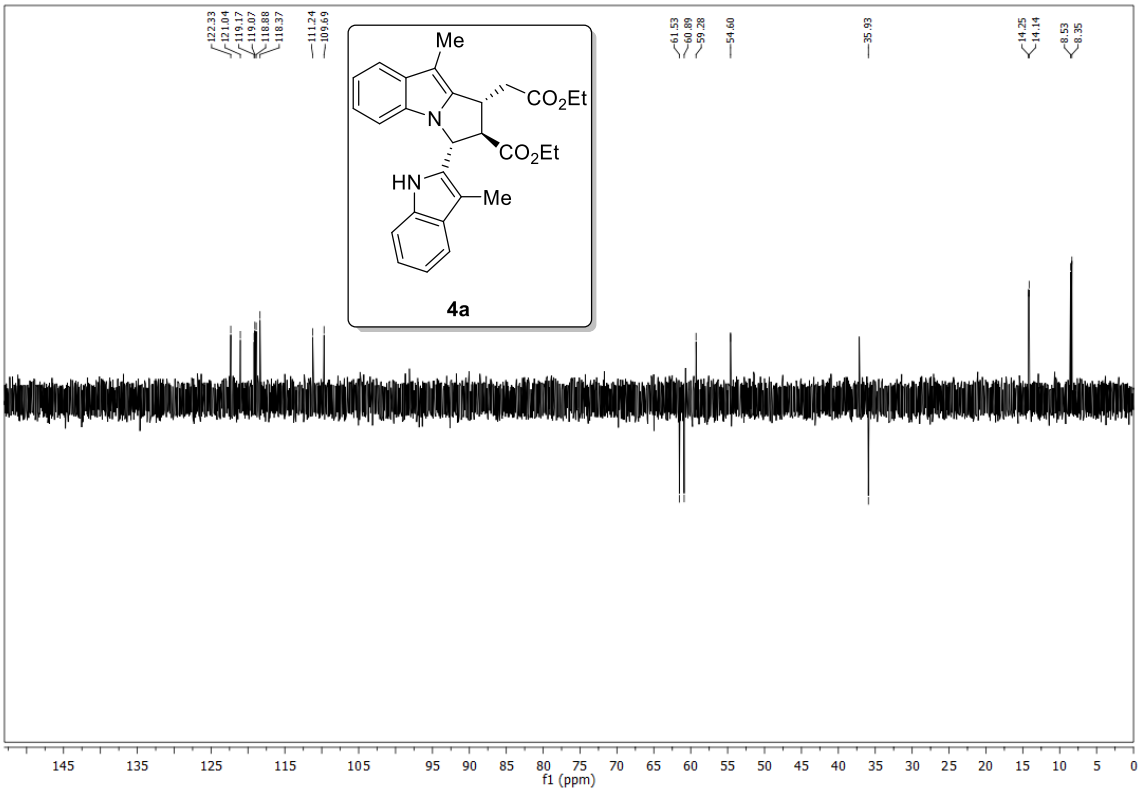
^{1}H NMR (500 MHz, $CDCl_3$) of 4a



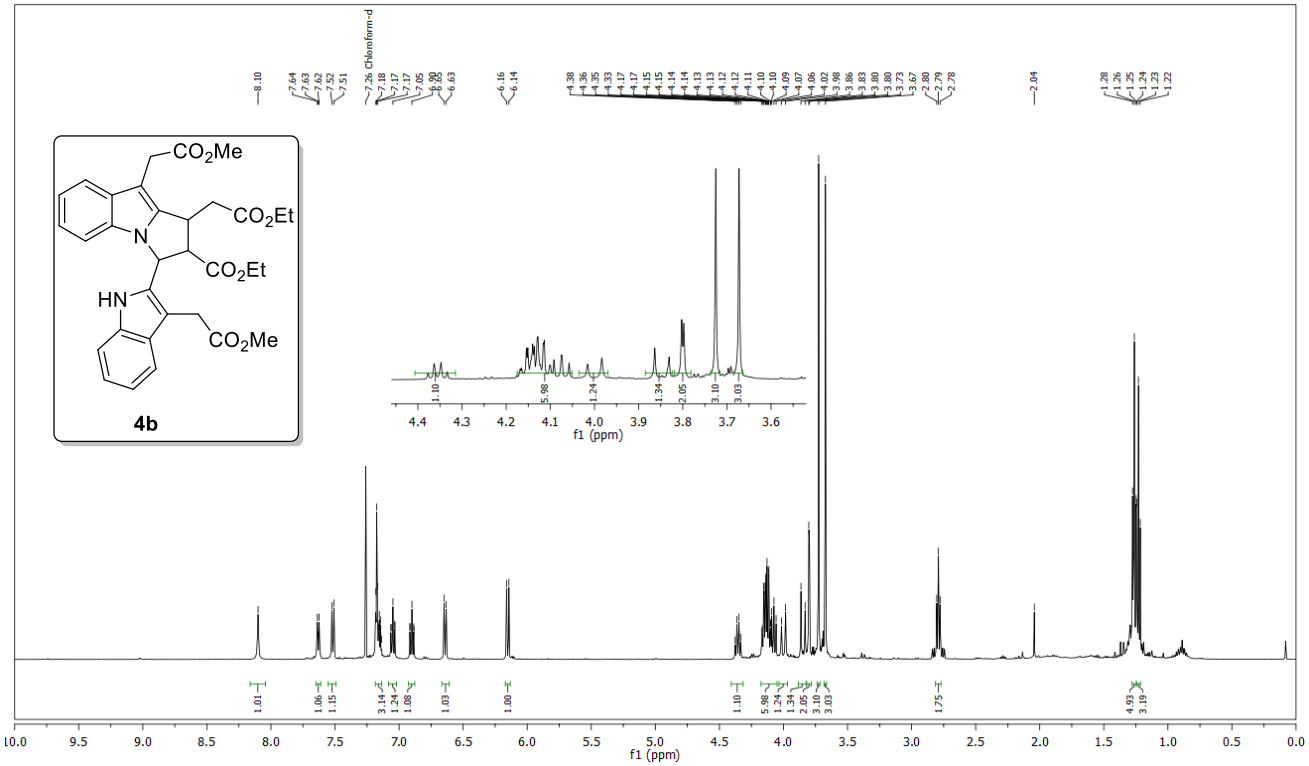
^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$) of 4a



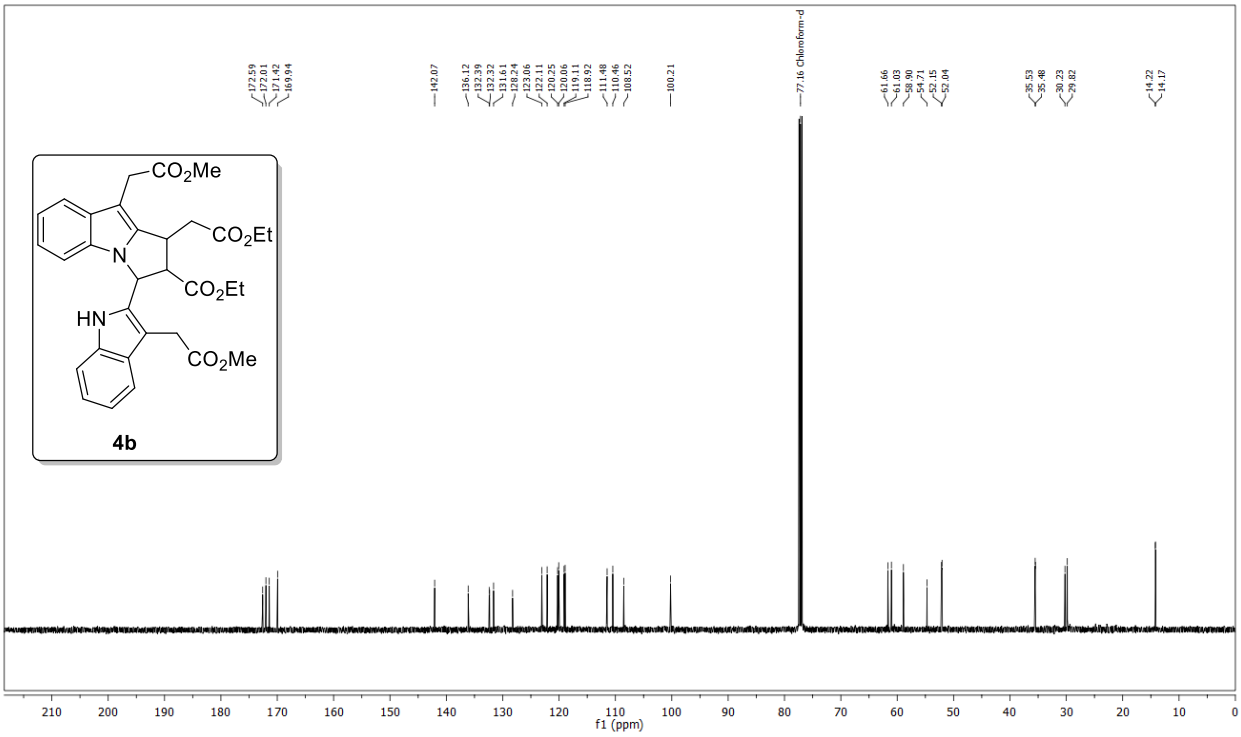
DEPT of 4a



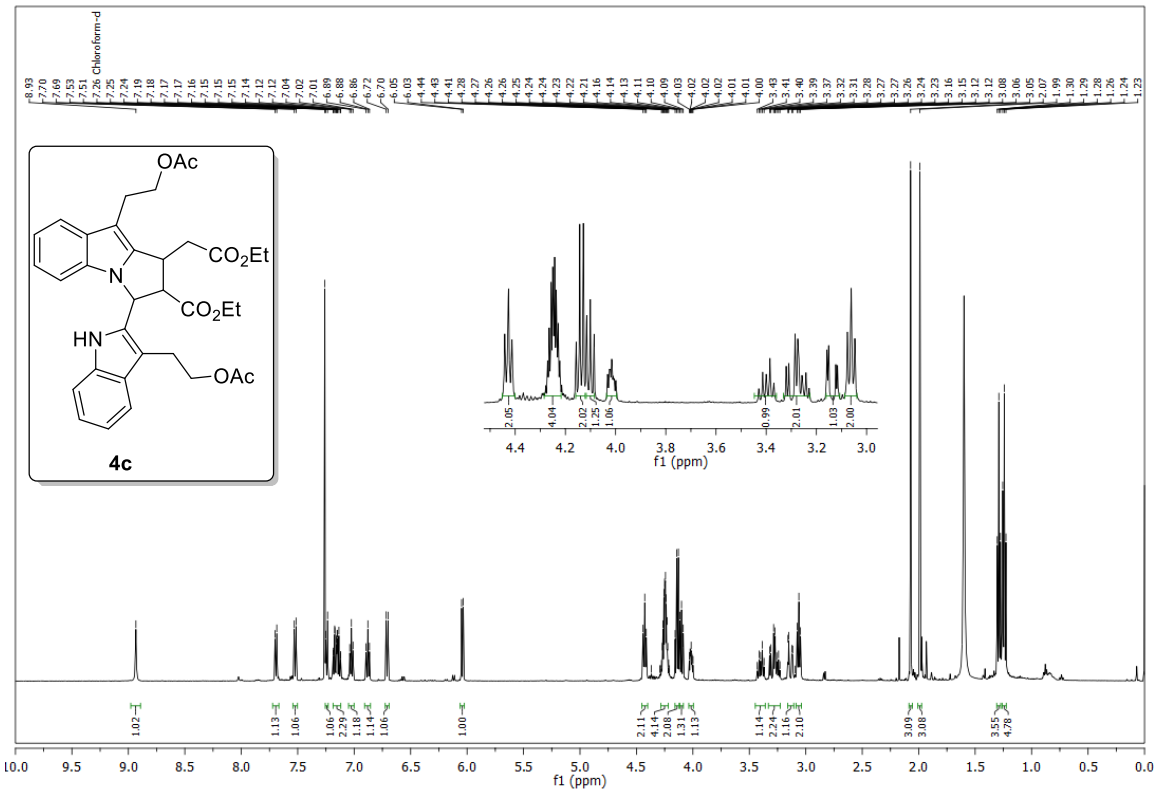
^{1}H NMR (500 MHz, $CDCl_3$) of 4b



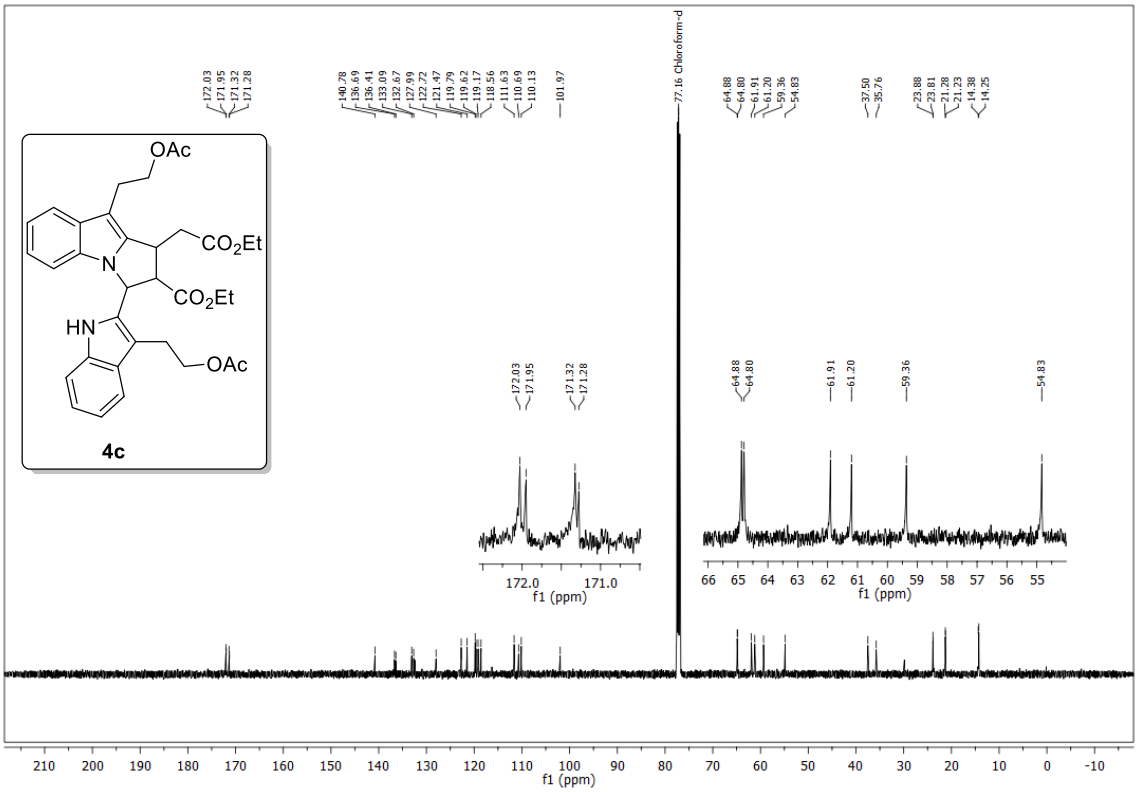
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 4b



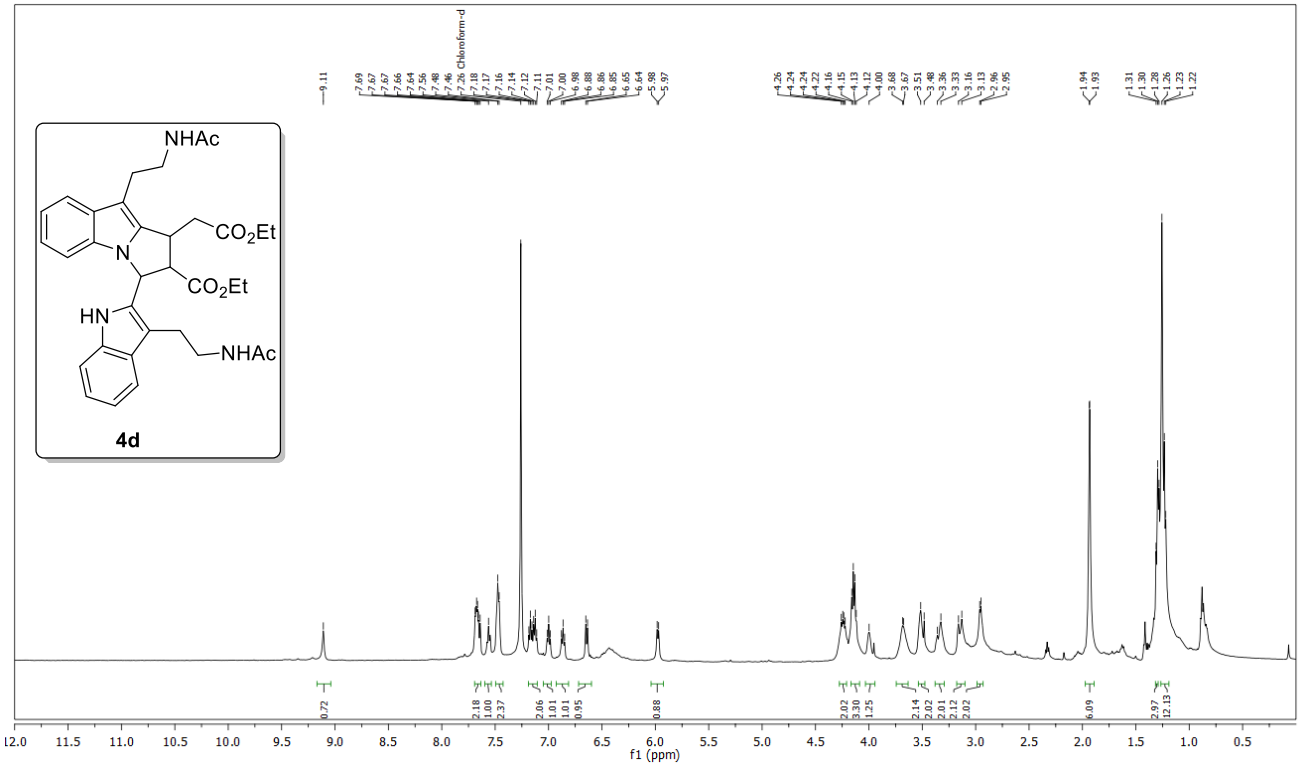
^{1}H NMR (500 MHz, $CDCl_3$) of 4c



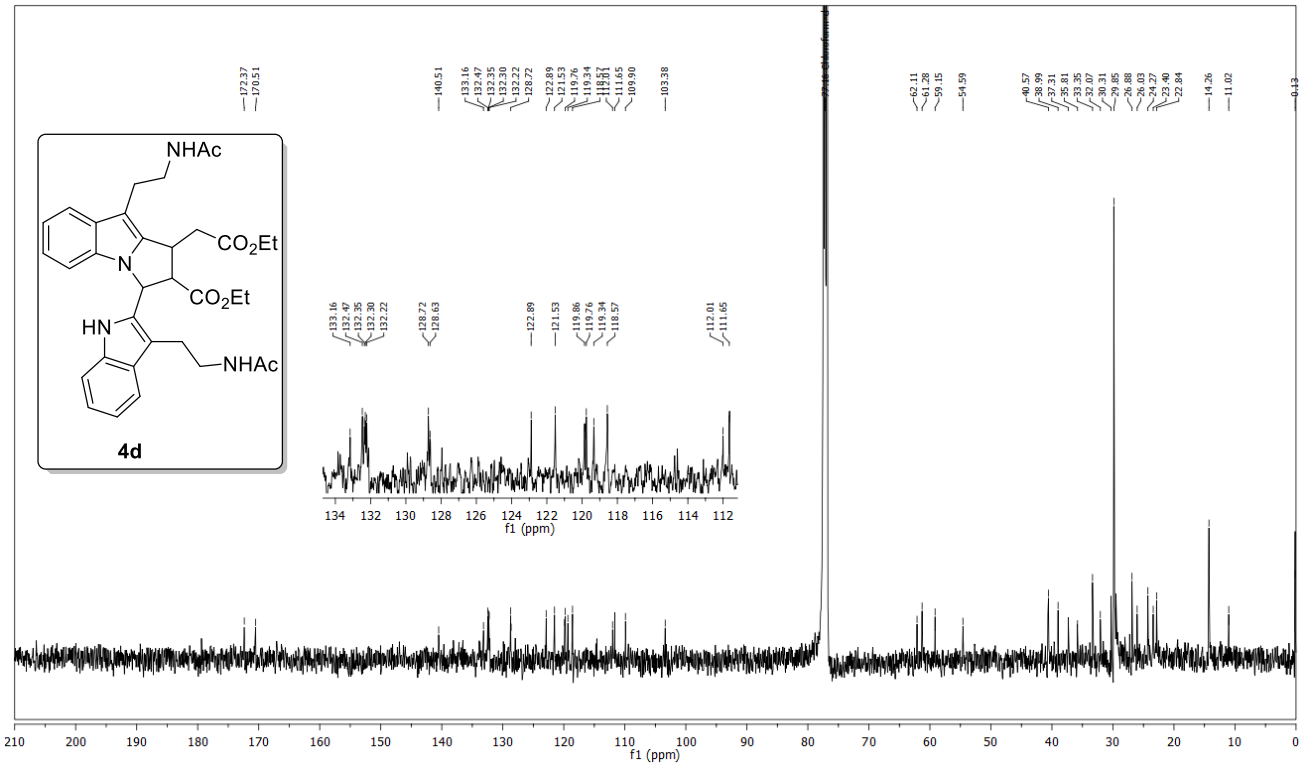
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 4c



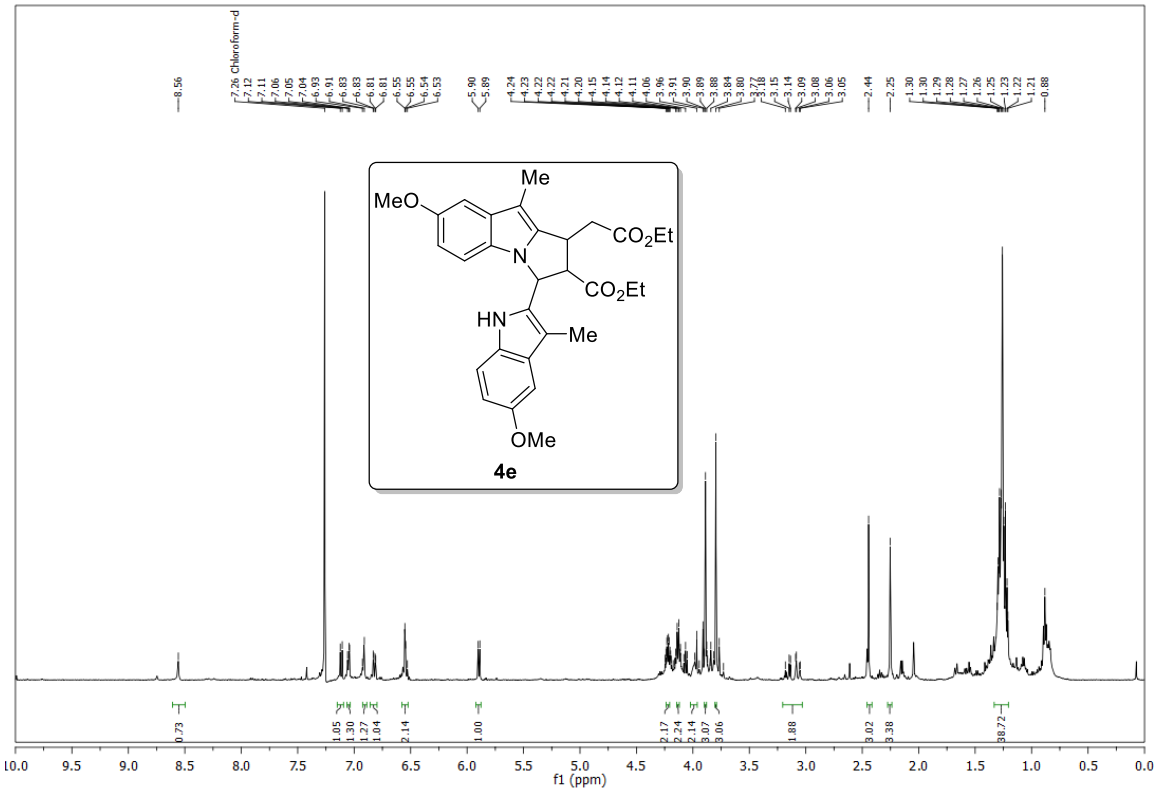
^{1}H NMR (500 MHz, $CDCl_3$) of 4d



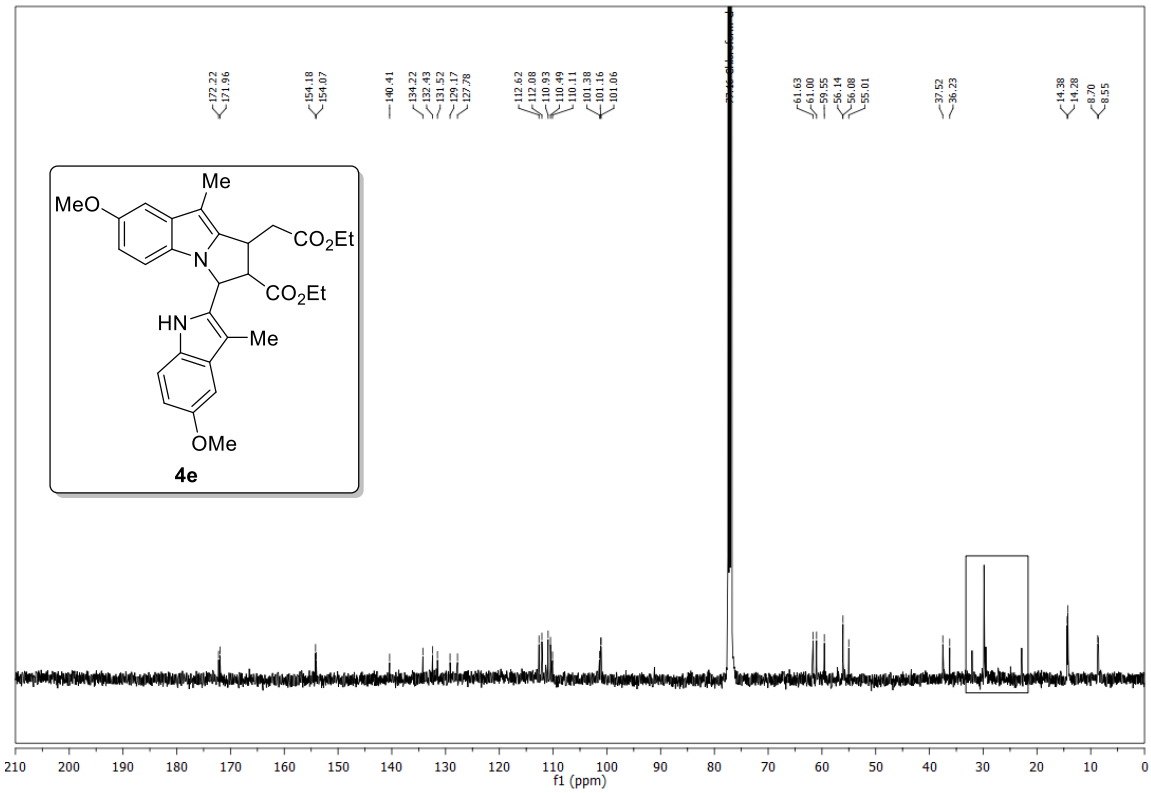
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 4d



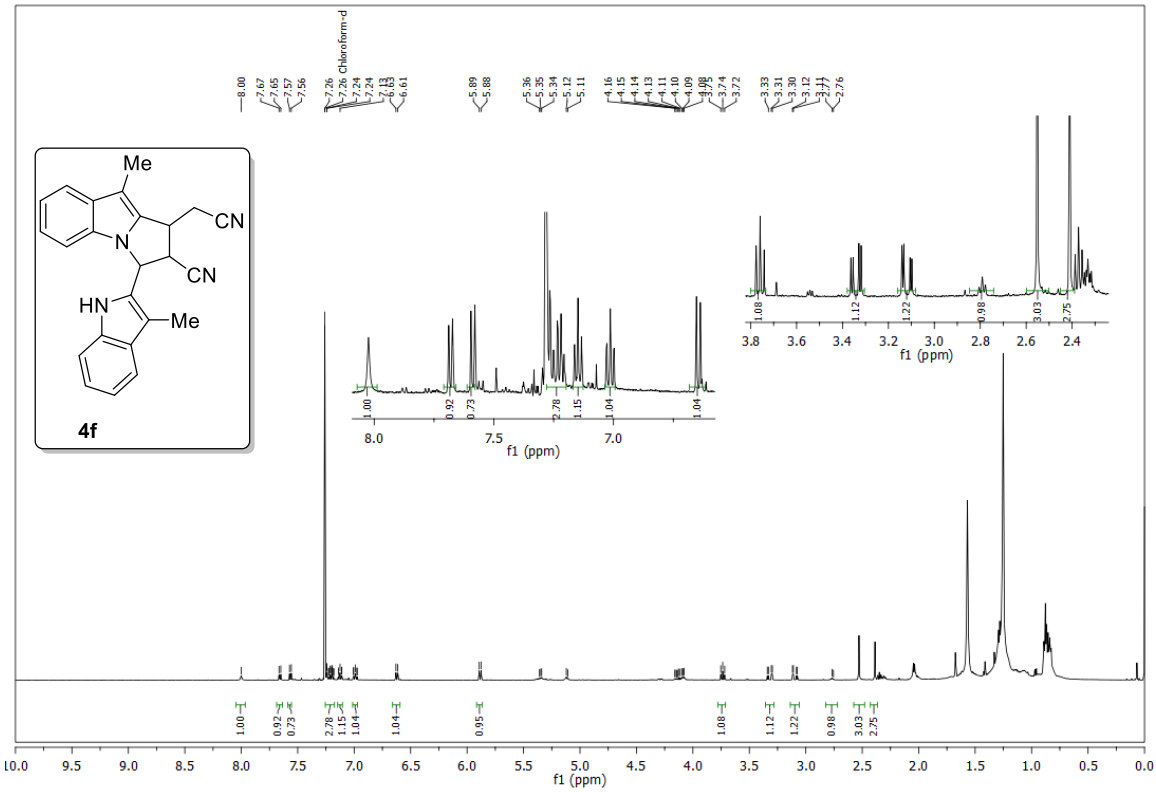
^{1}H NMR (500 MHz, $CDCl_3$) of 4e



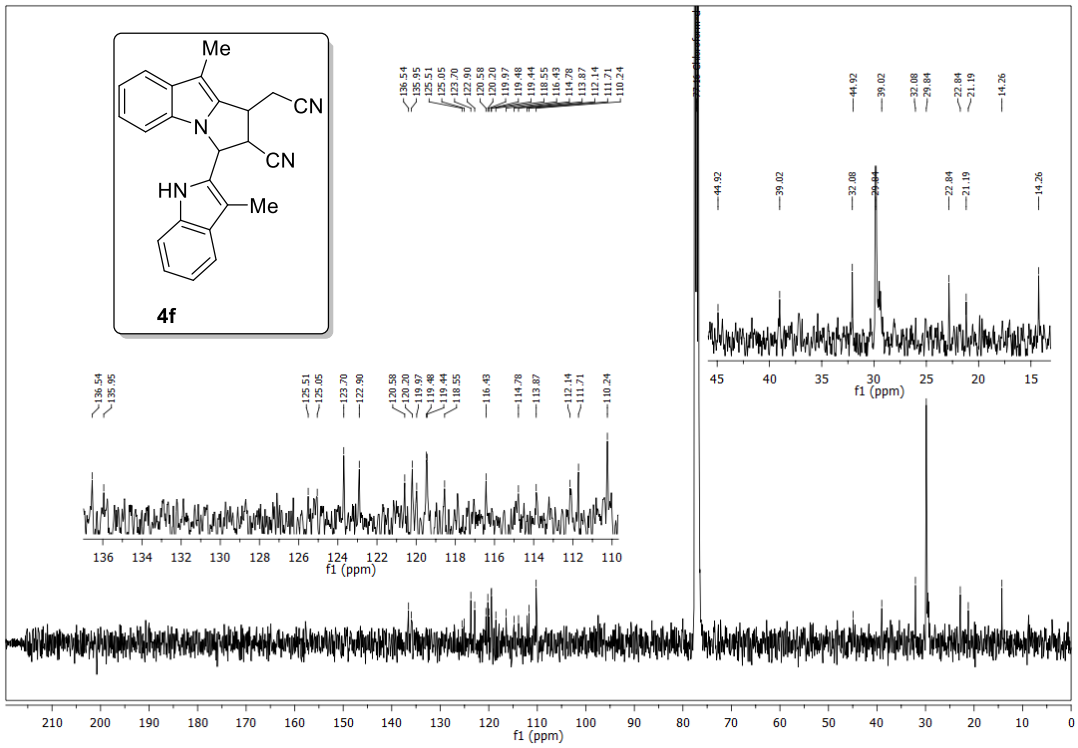
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 4e



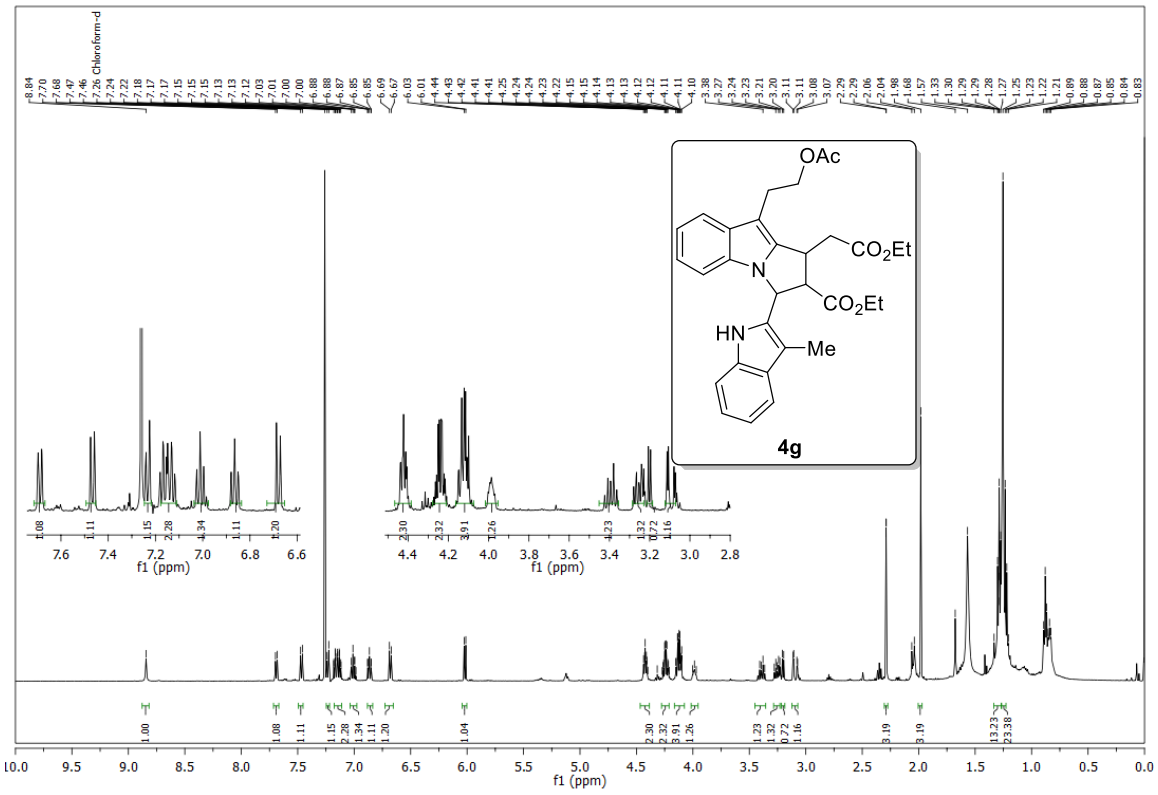
^{1}H NMR (500 MHz, $CDCl_3$) of 4f



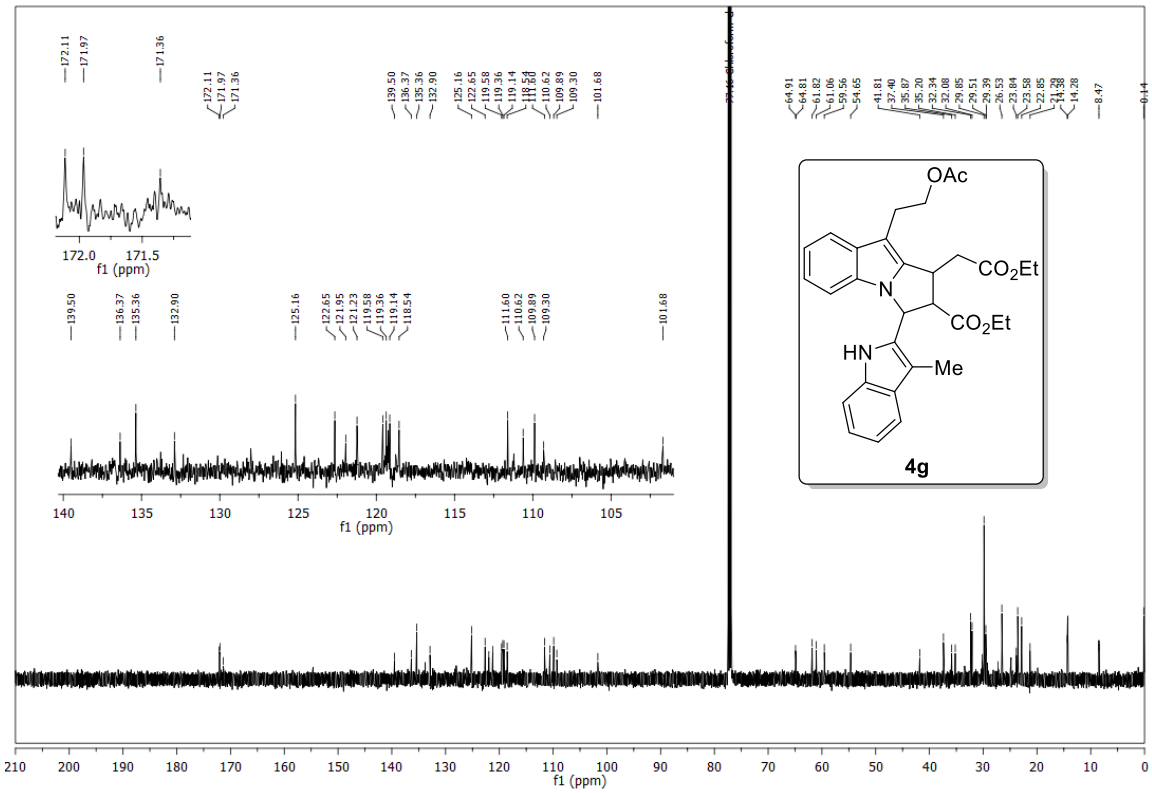
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 4f



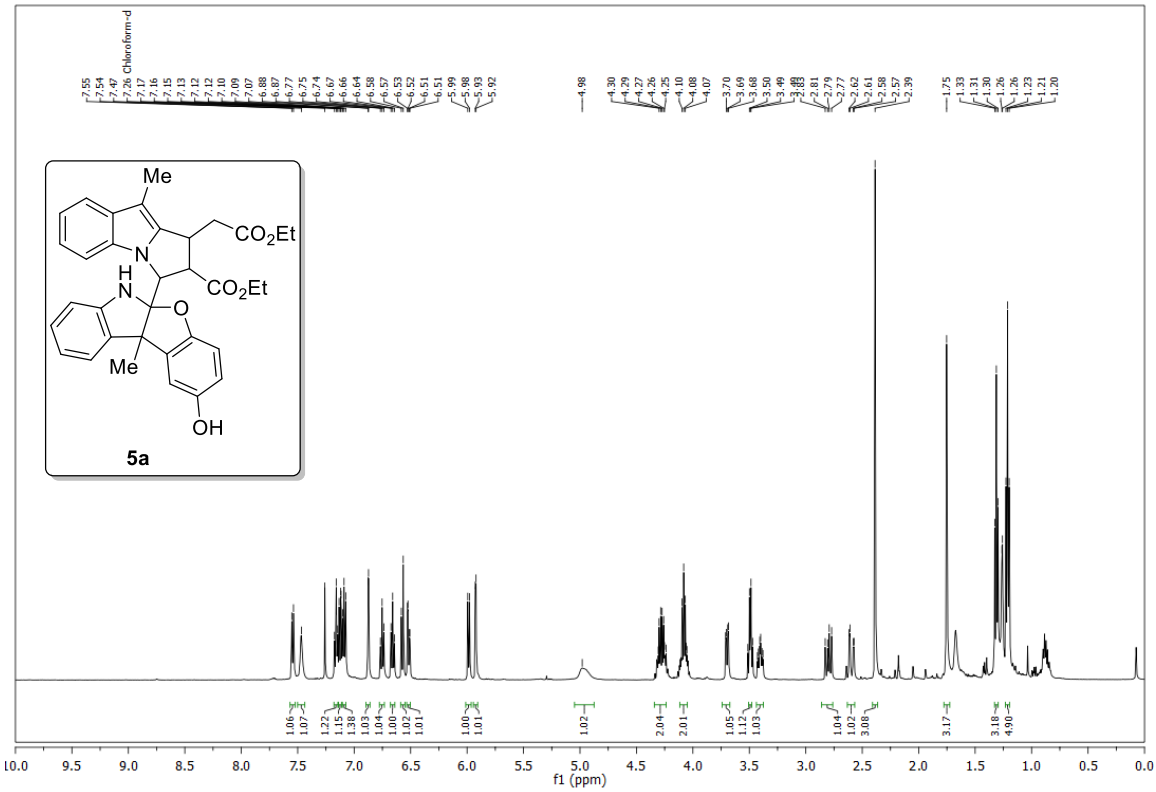
^{1}H NMR (500 MHz, $CDCl_3$) of 4g



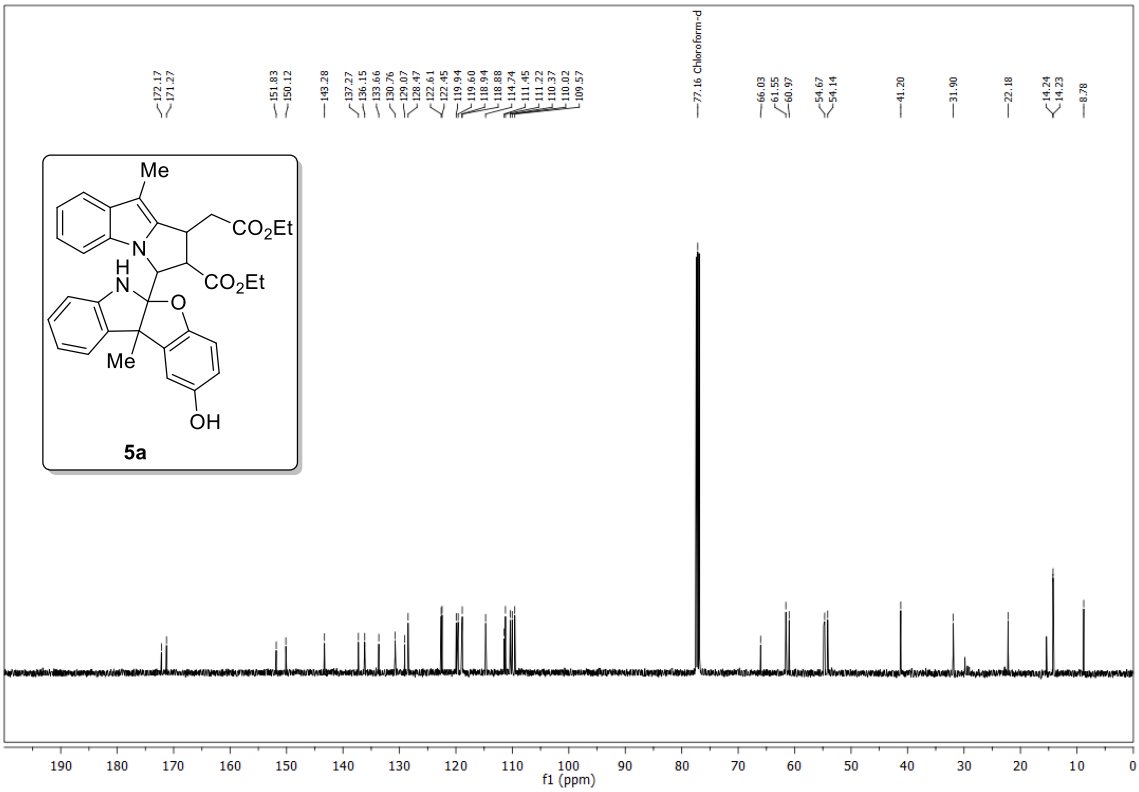
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 4g



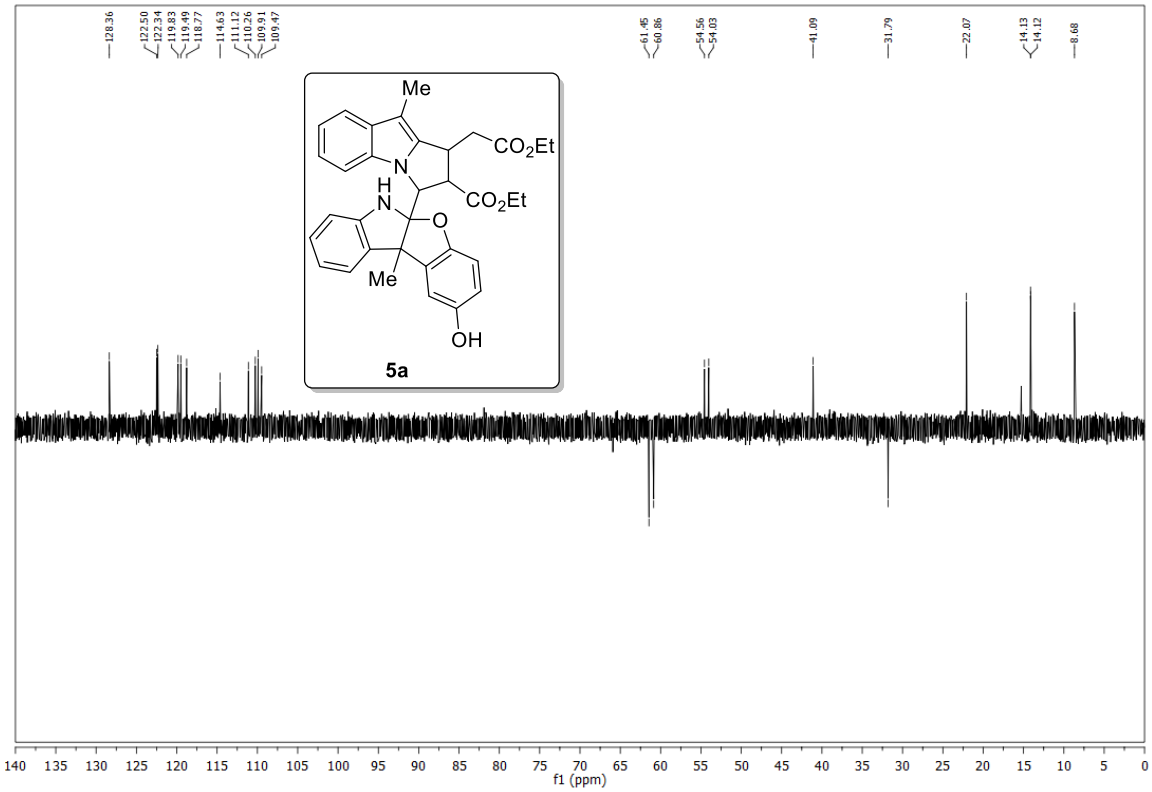
^{1}H NMR (500 MHz, $CDCl_3$) of 5a



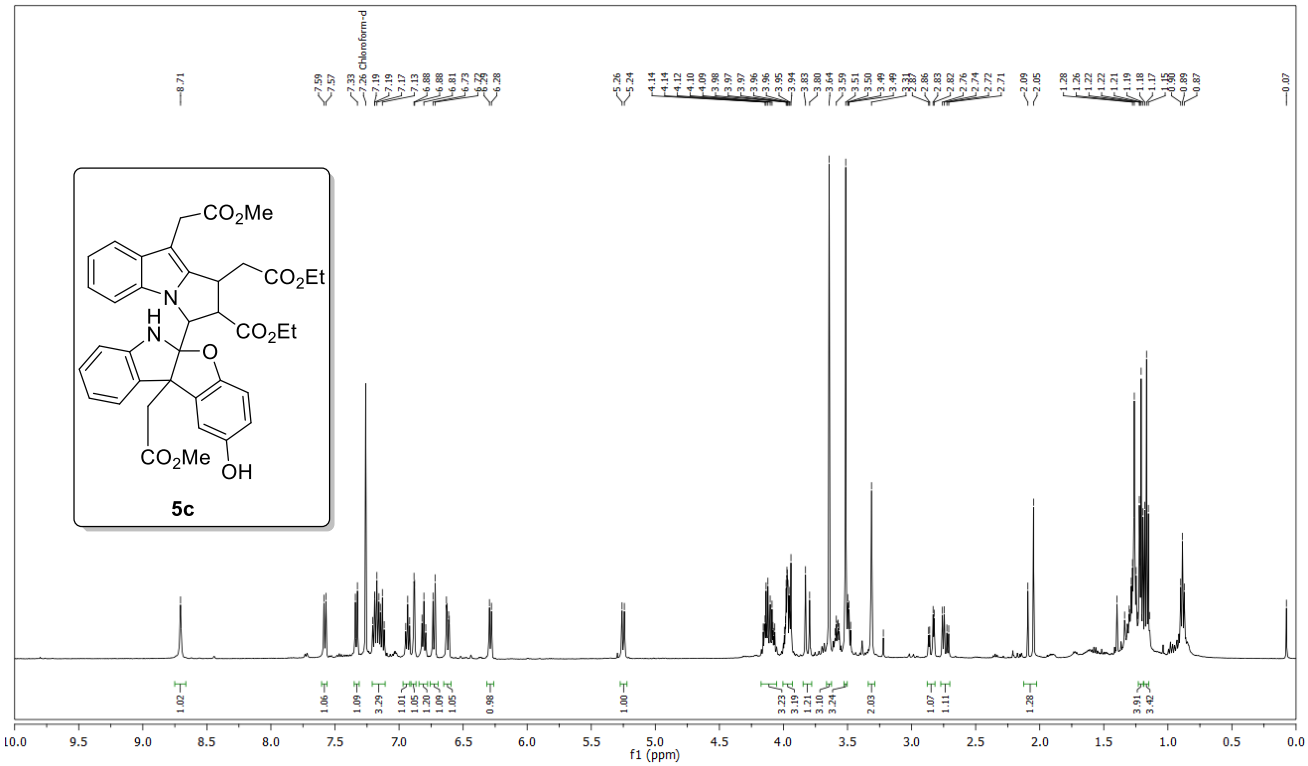
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 5a



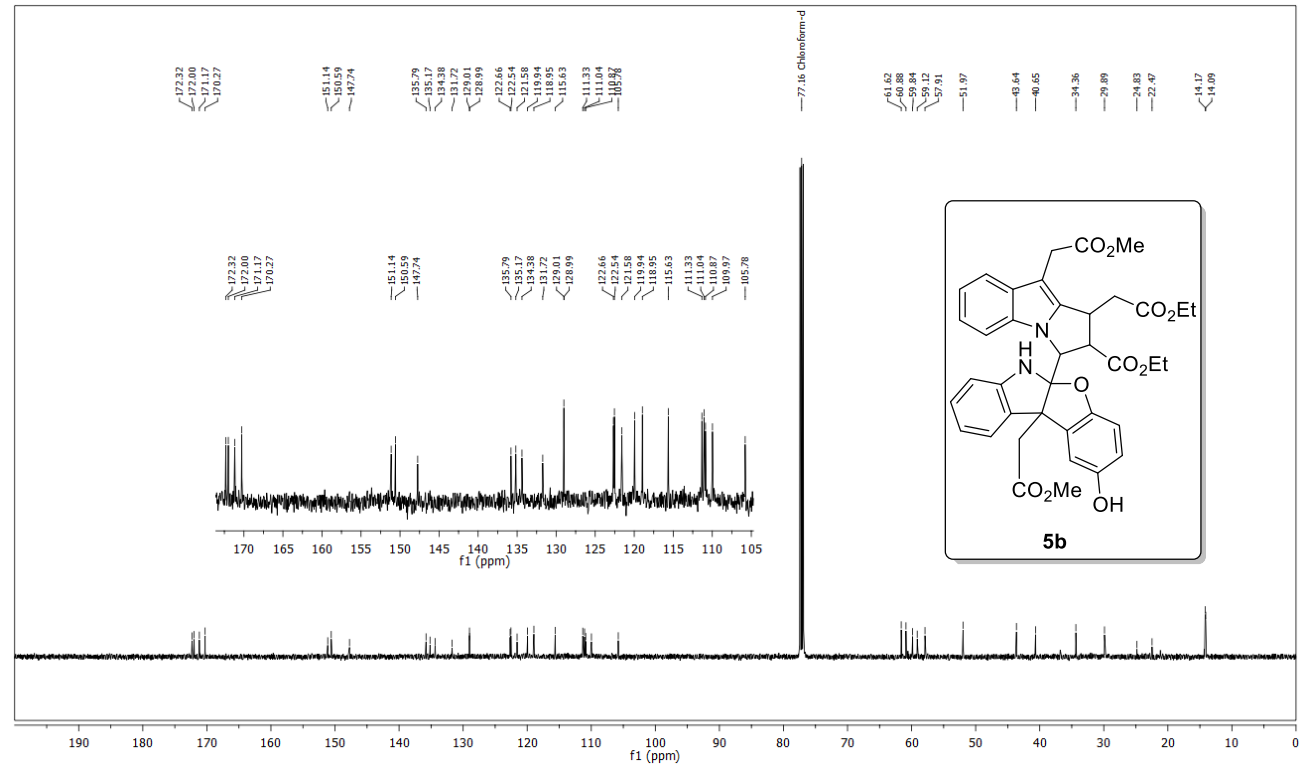
DEPT of 5a



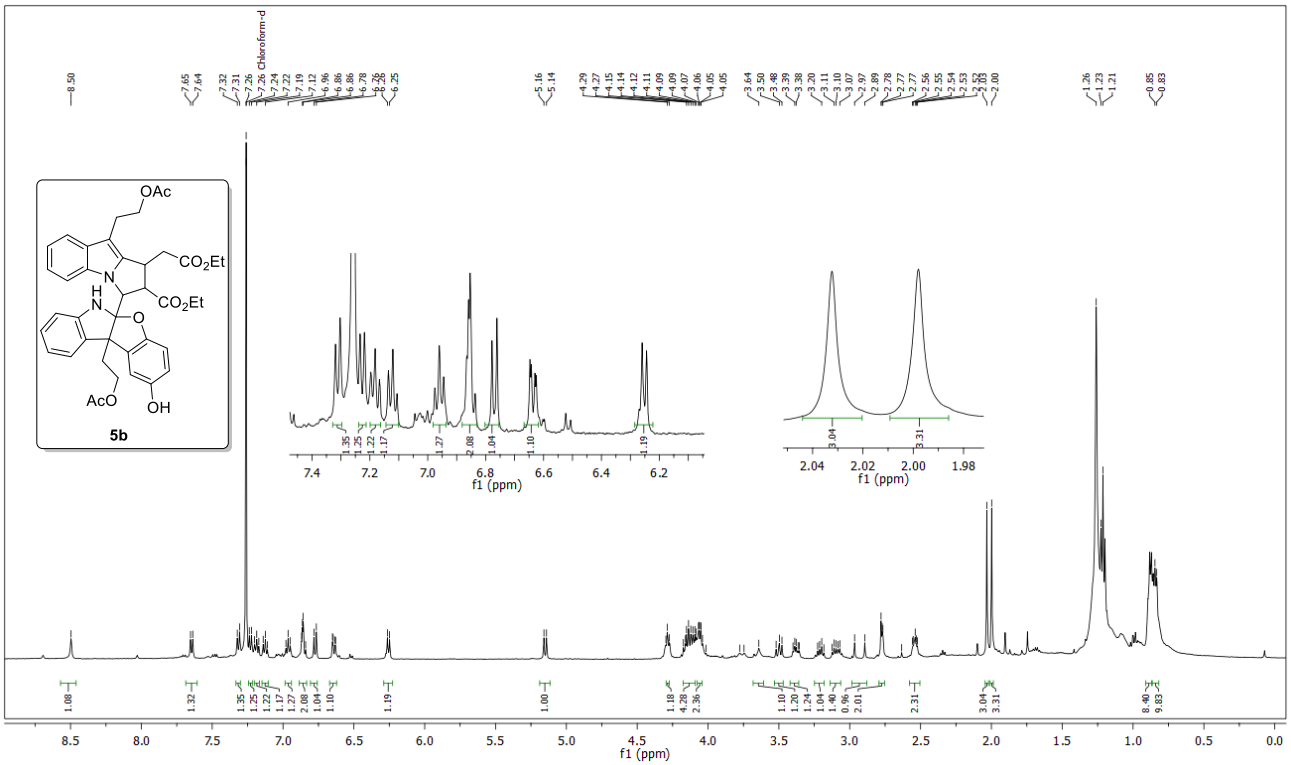
^{1}H NMR (500 MHz, $CDCl_3$) of 5b



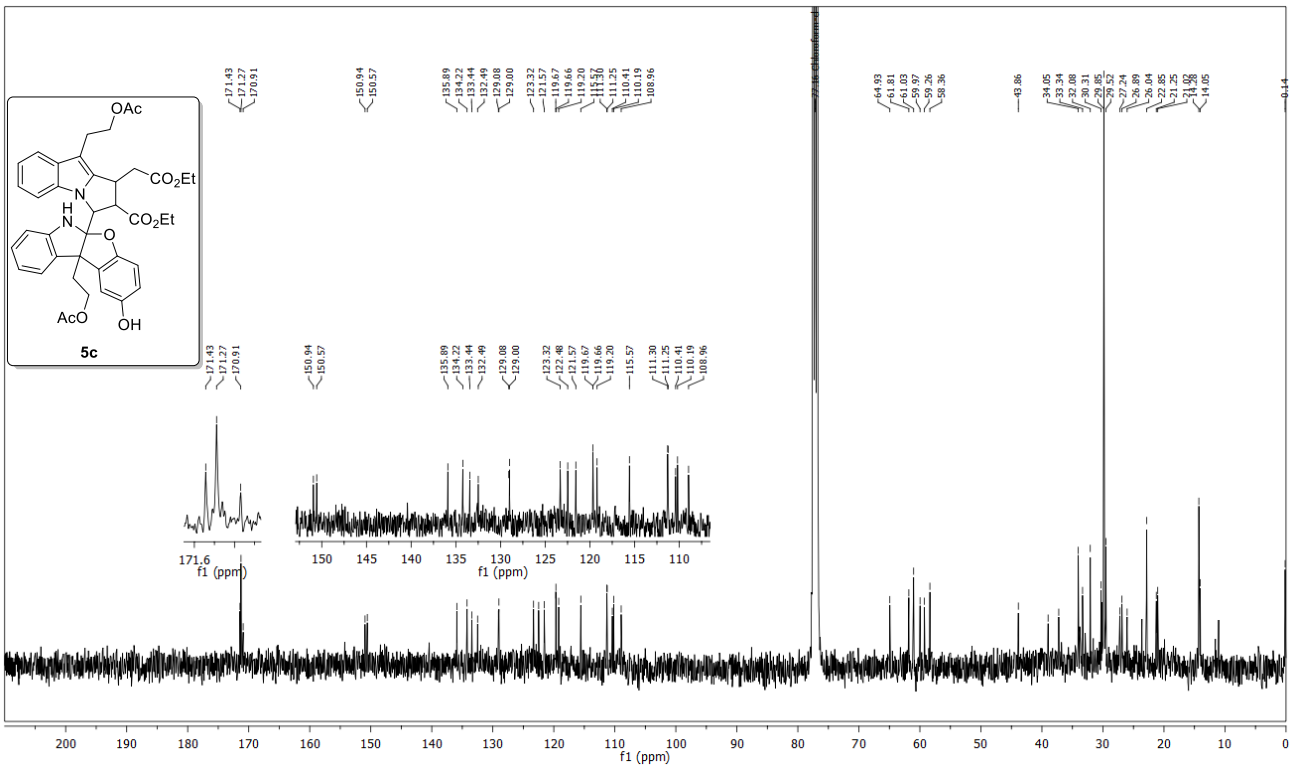
^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$) of 5b



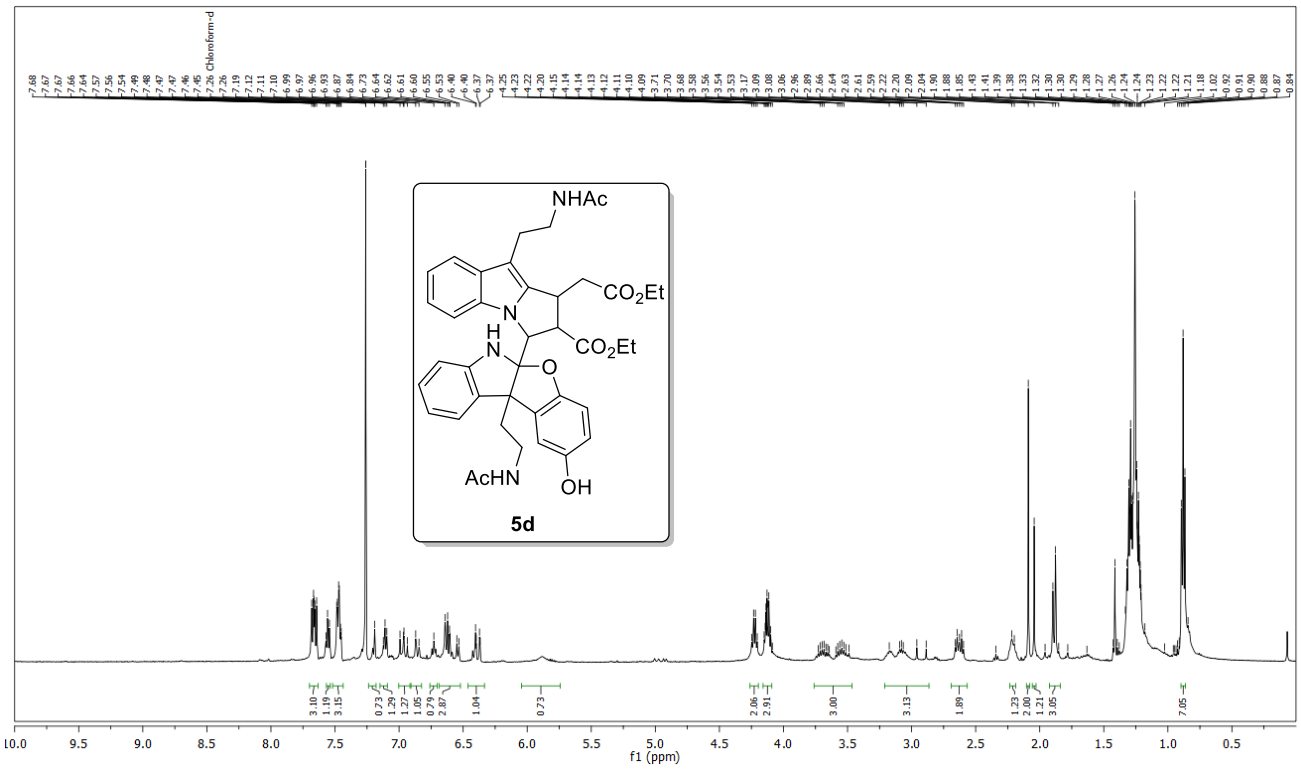
^{1}H NMR (500 MHz, $CDCl_3$) of 5c



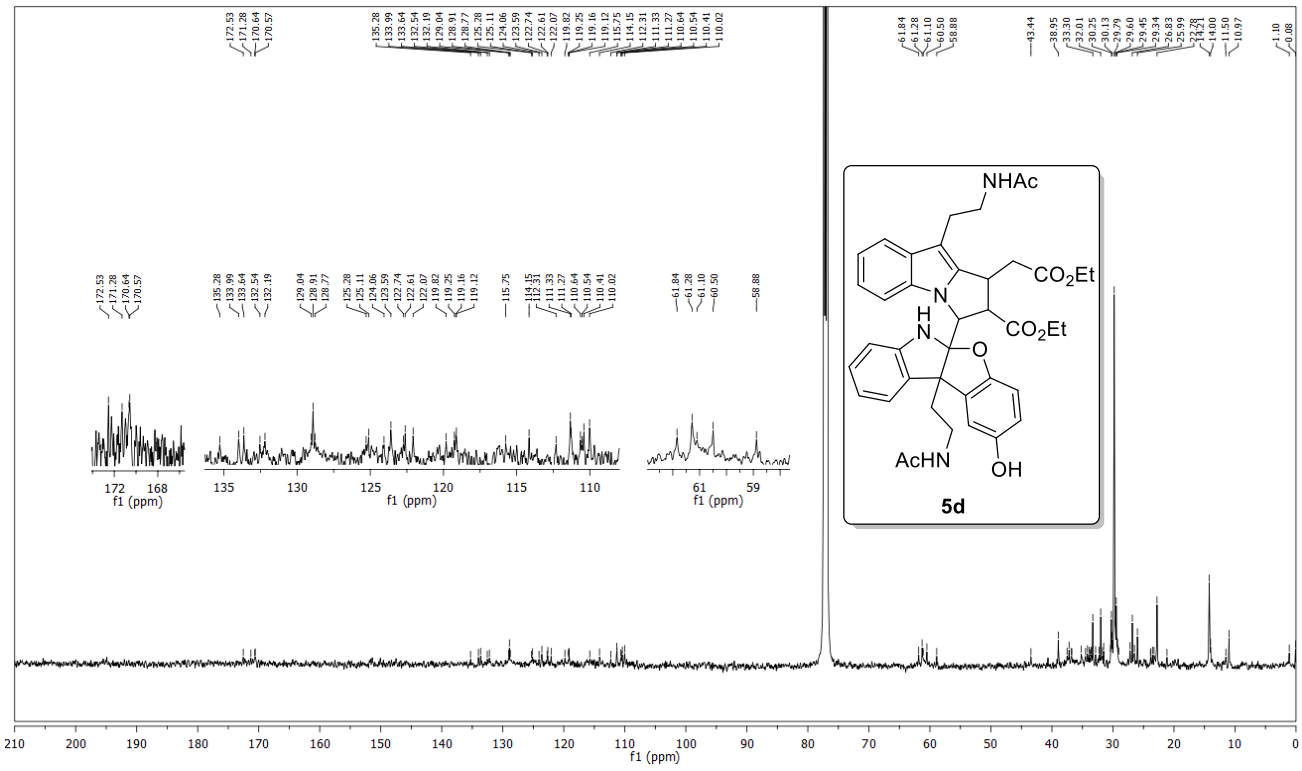
^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$) of 5c



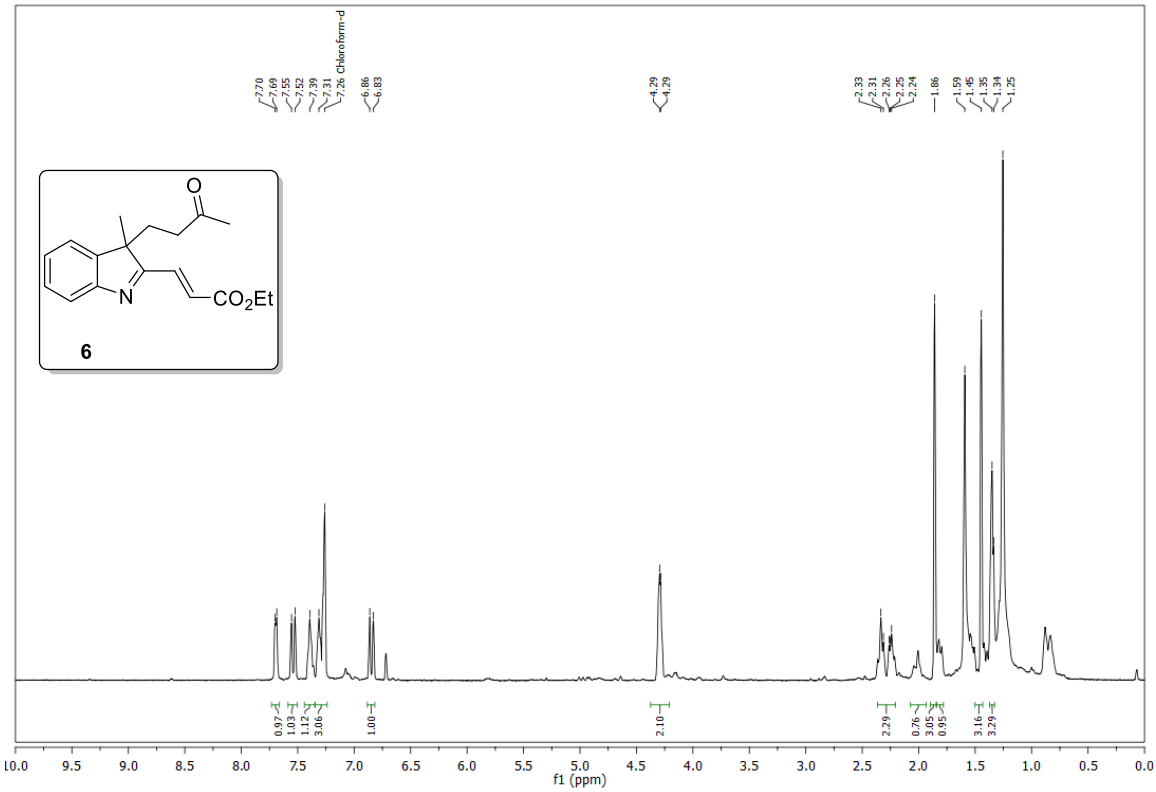
^{1}H NMR (500 MHz, $CDCl_3$) of 5d



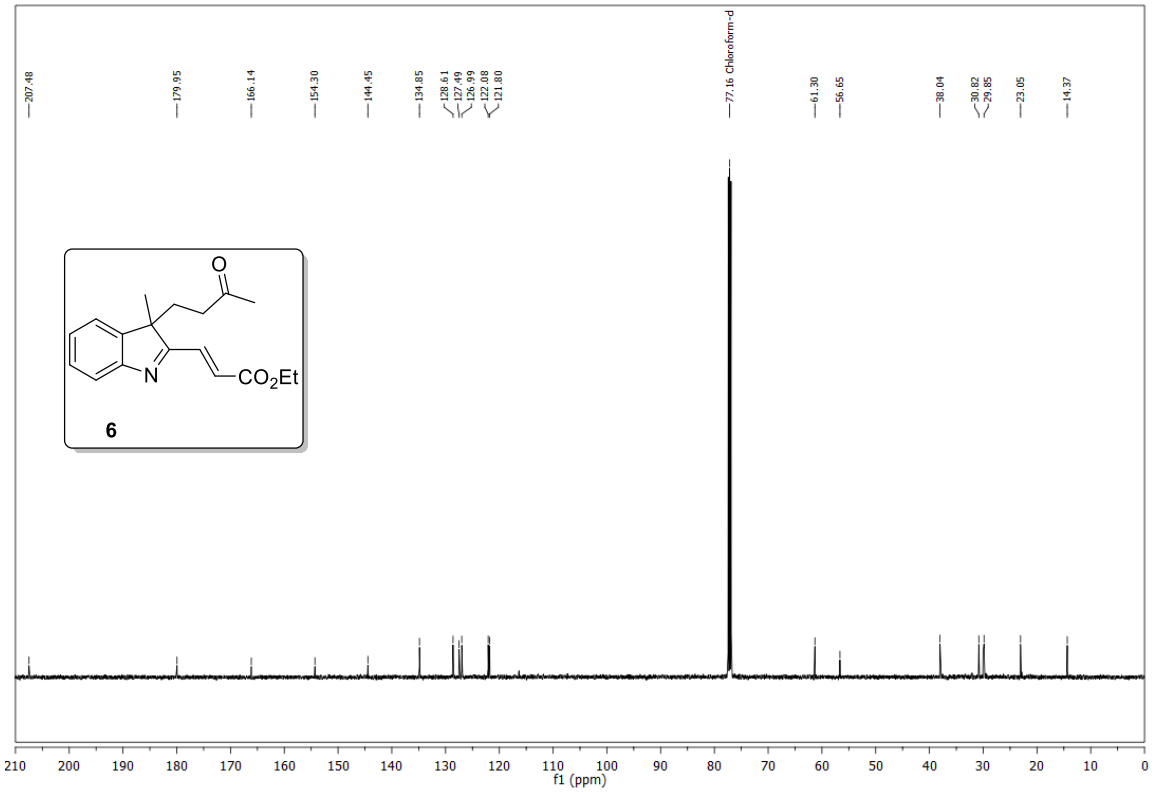
^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$) of 5d



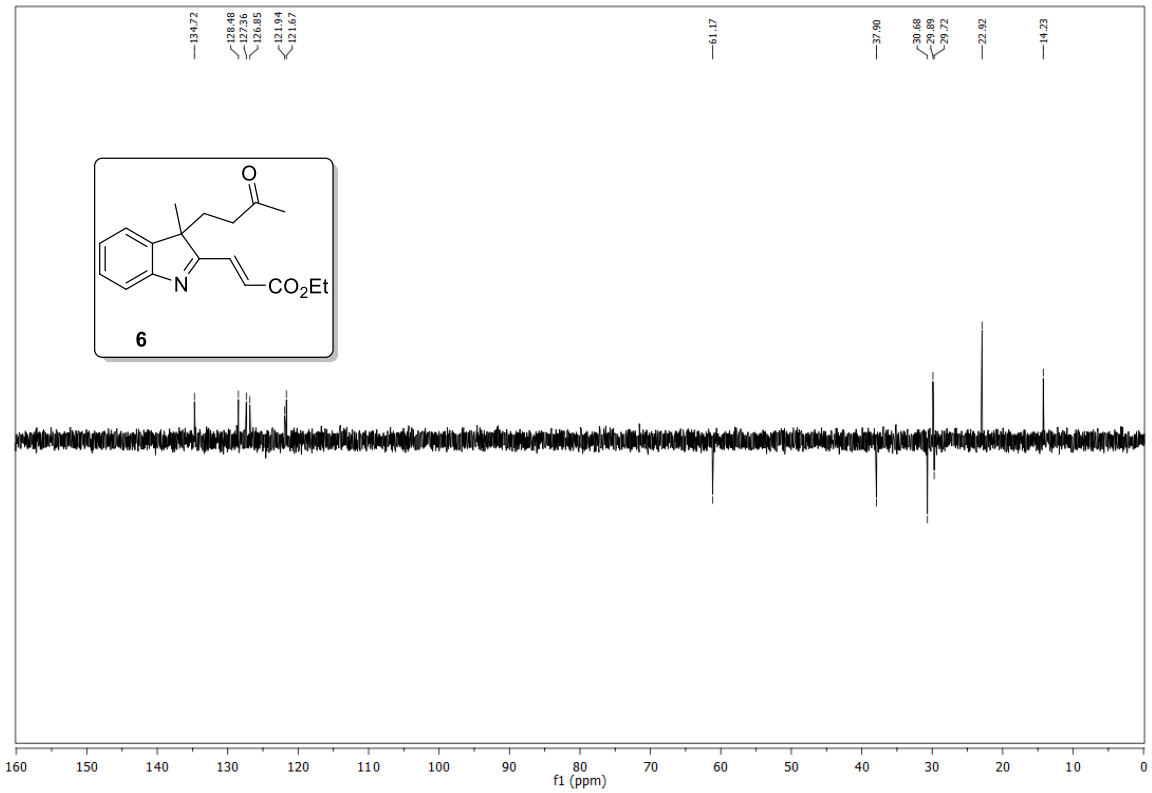
^{1}H NMR (500 MHz, $CDCl_3$) of 6



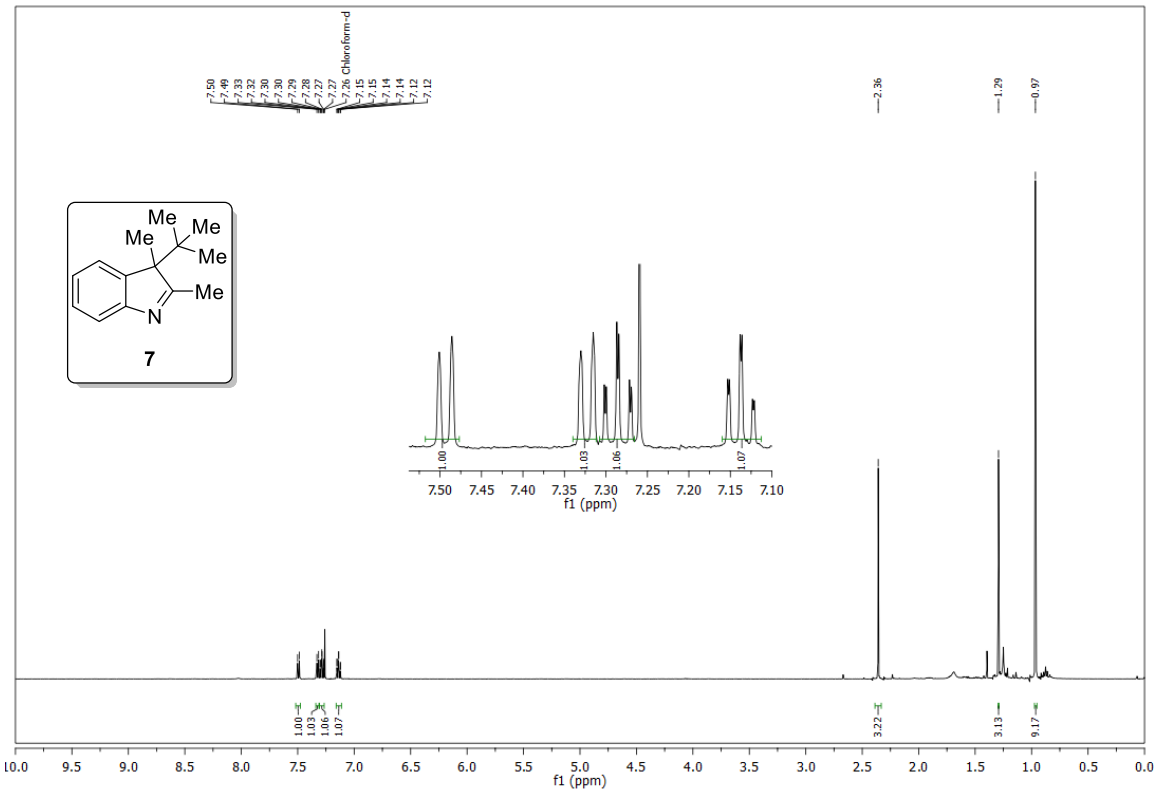
^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$) of 6



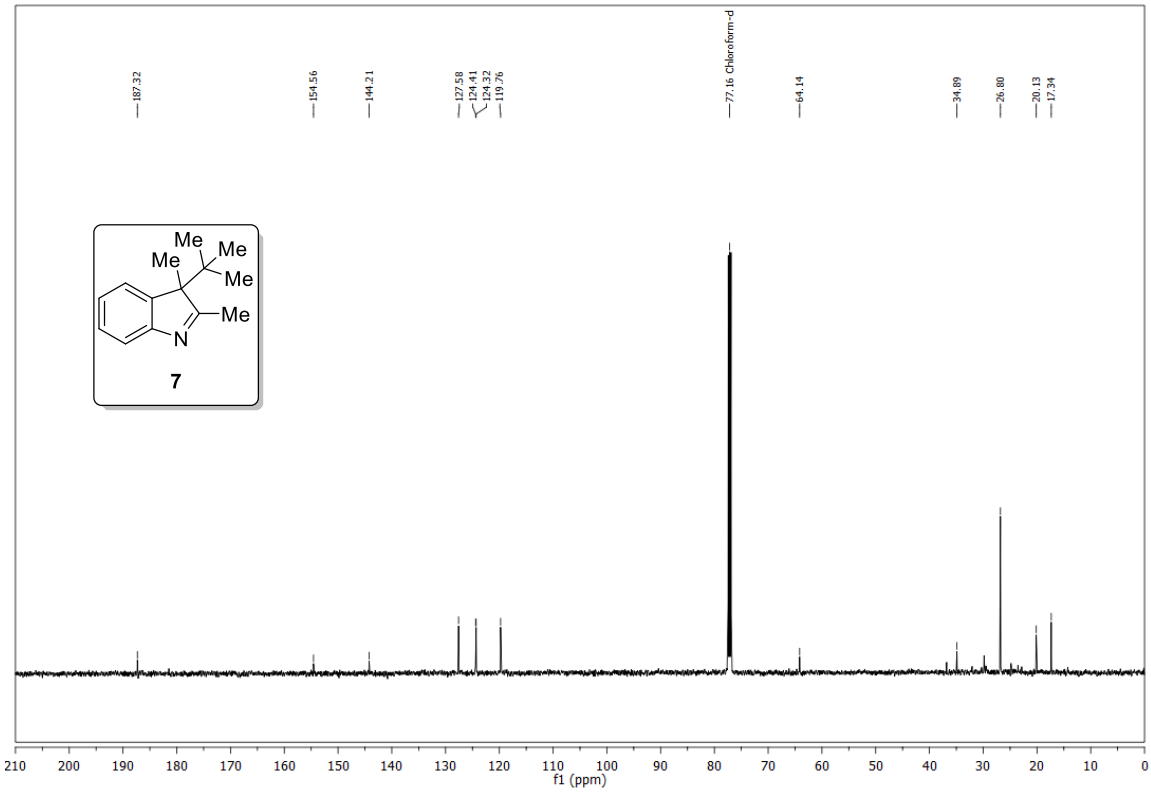
DRPT of 6



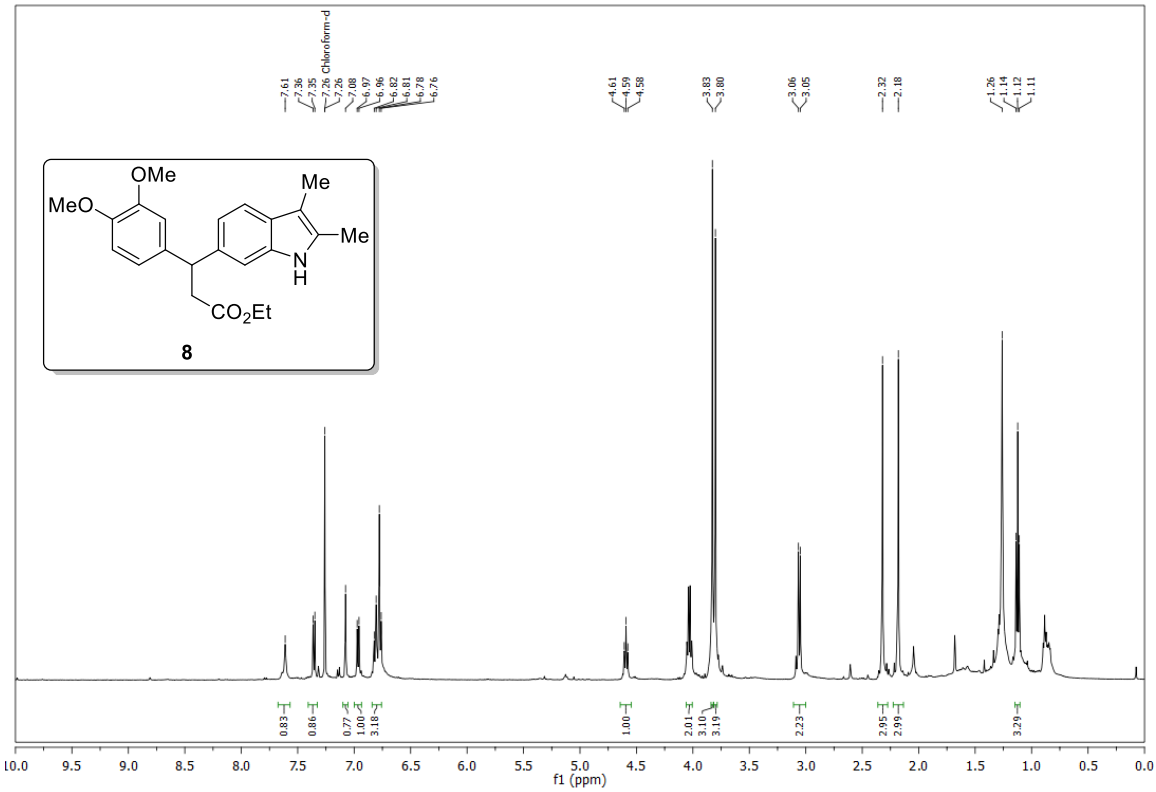
^{1}H NMR (500 MHz, $CDCl_3$) of 7



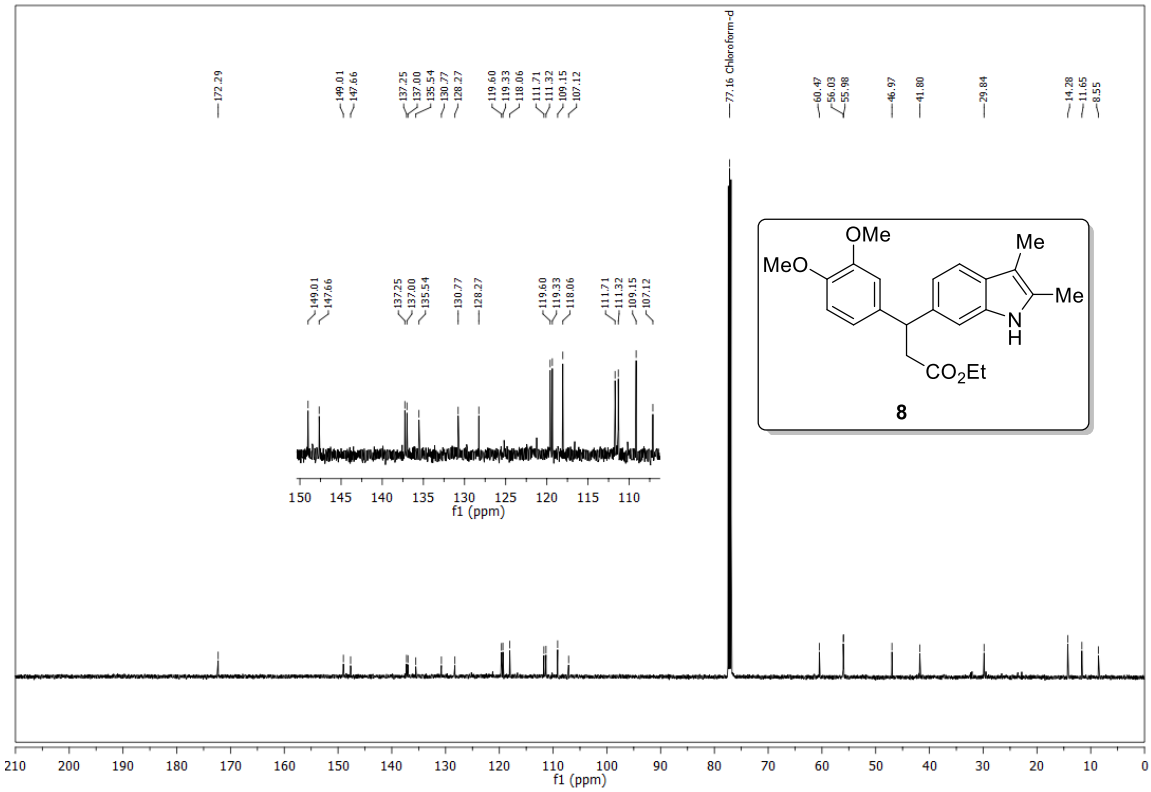
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 7



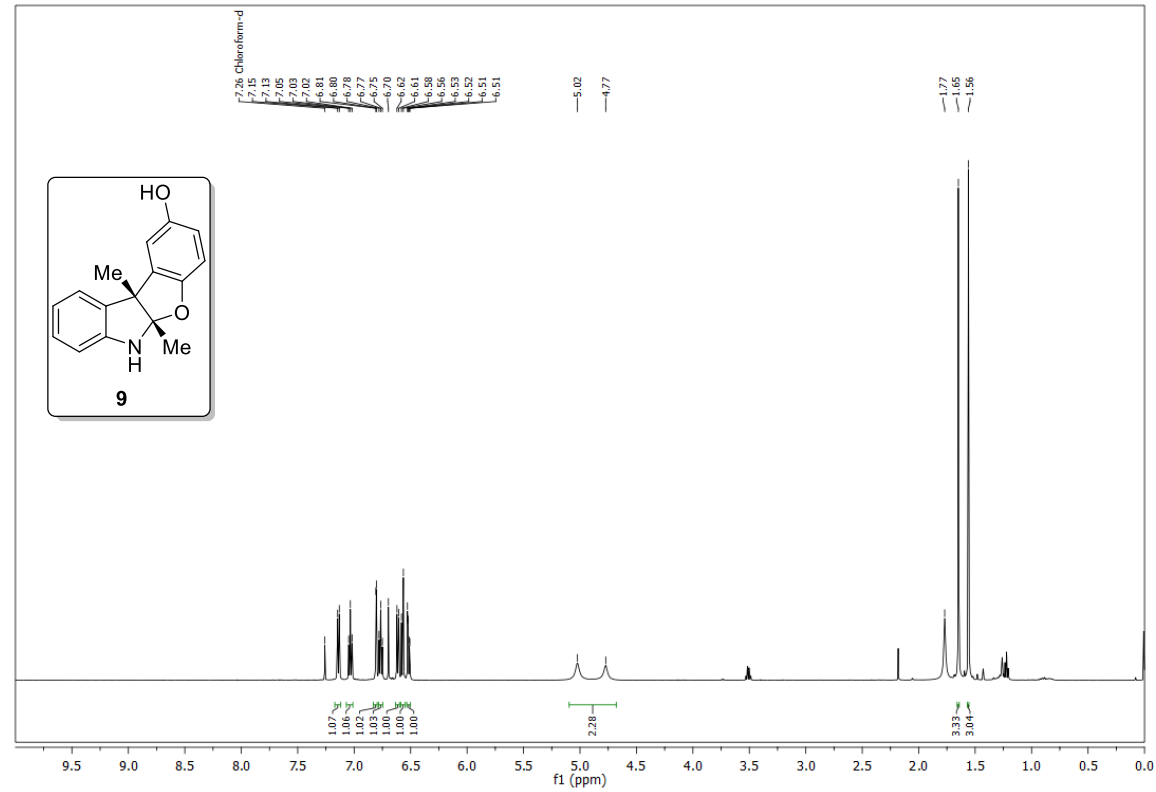
^{1}H NMR (500 MHz, $CDCl_3$) of 8



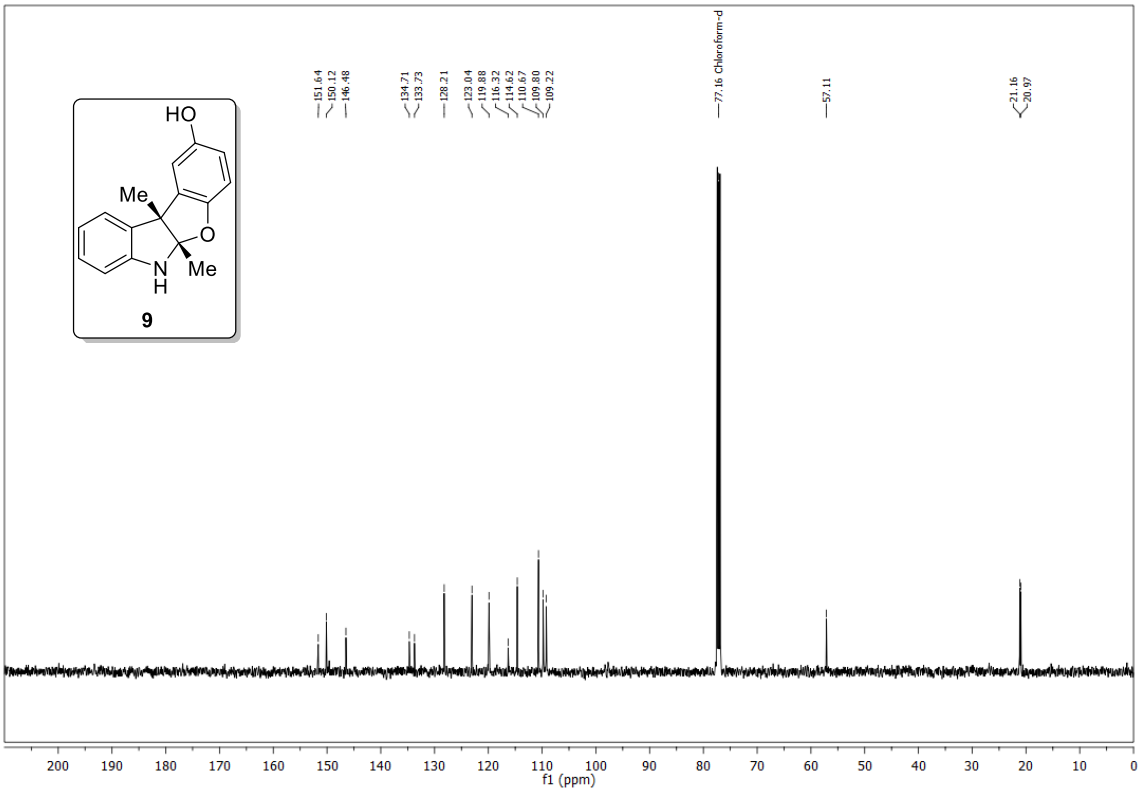
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 8



^{1}H NMR (500 MHz, $CDCl_3$) of 9



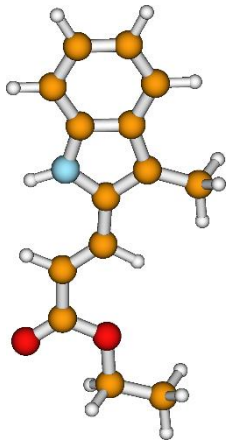
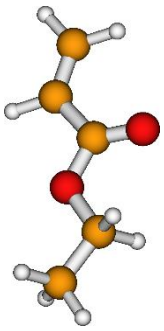
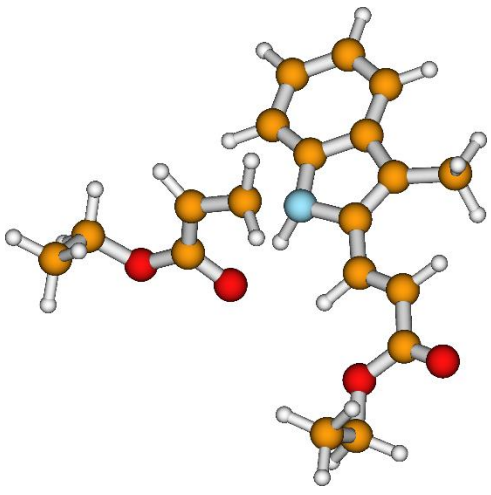
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) of 9

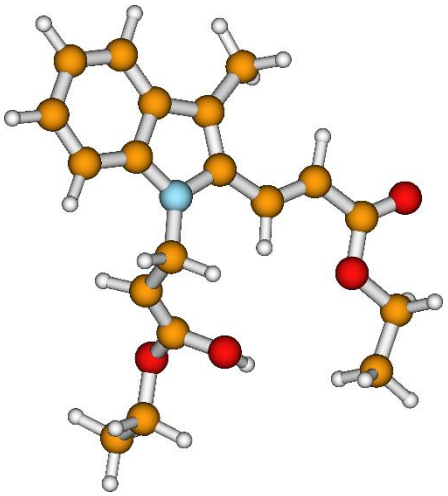
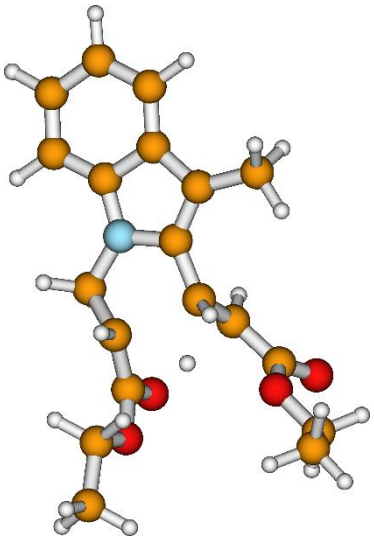
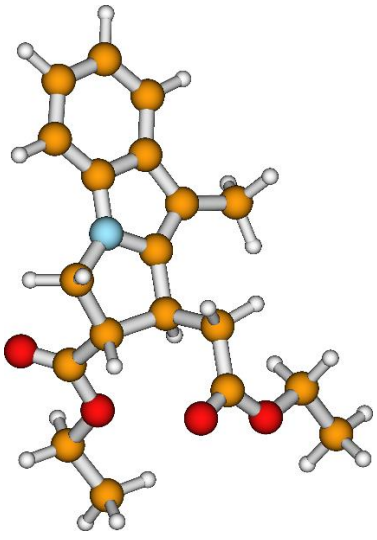


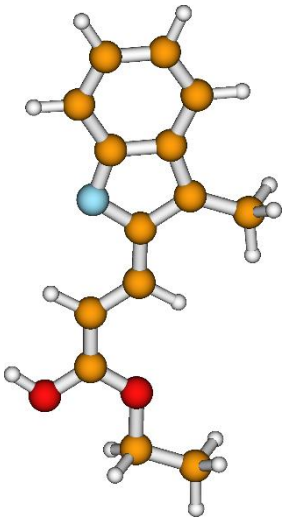
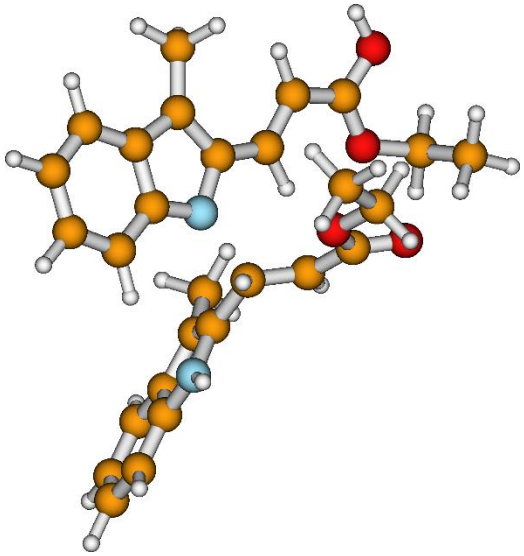
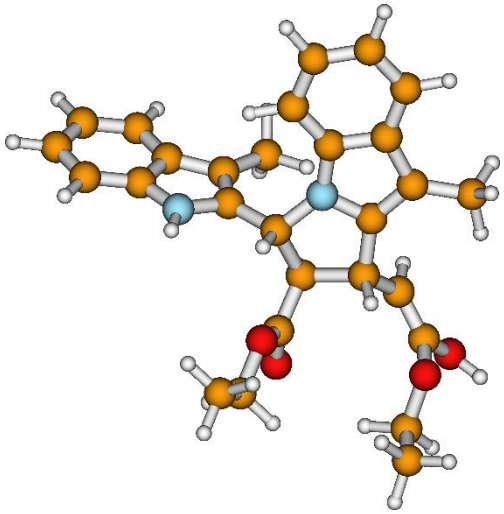
12. COMPUTATIONAL DETAILS-SUPPLEMENTARY DATA

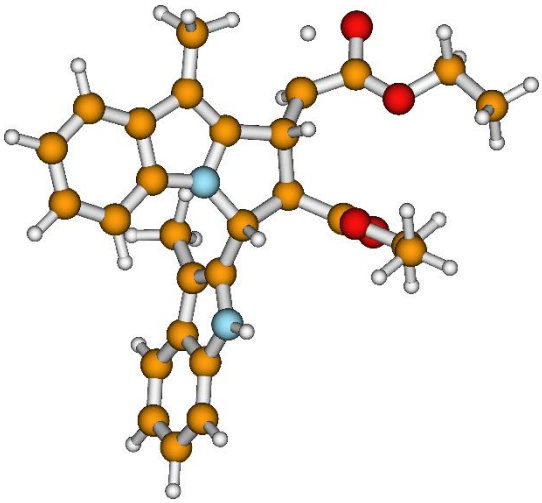
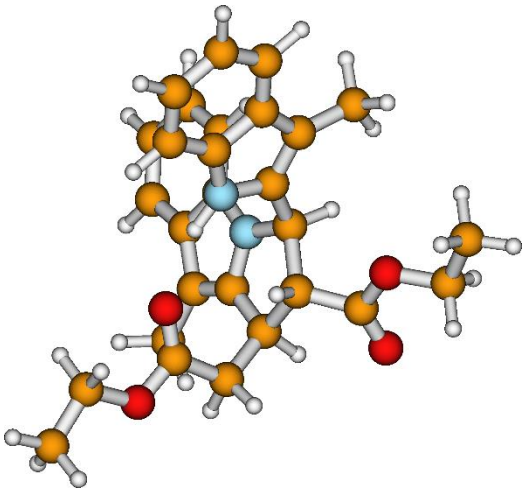
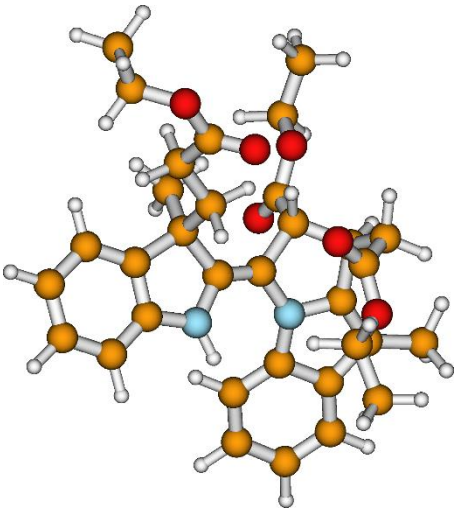
Computational Studies at B3LYP/def2-SVP level of theory.

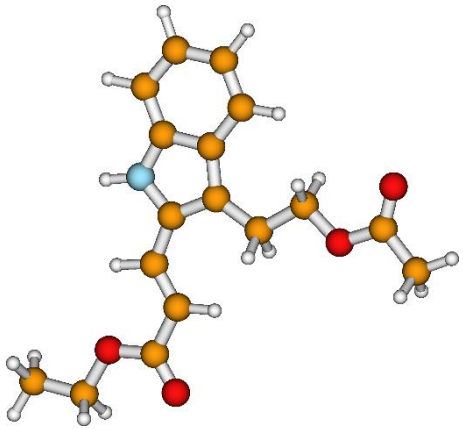
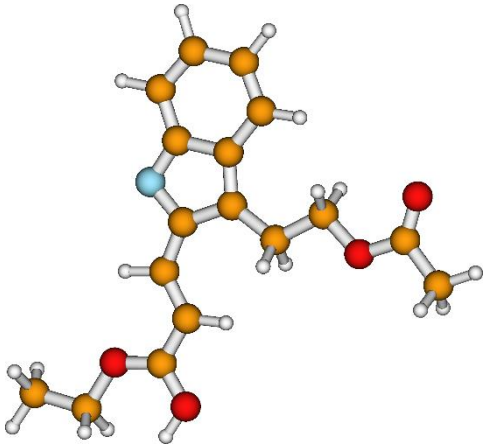
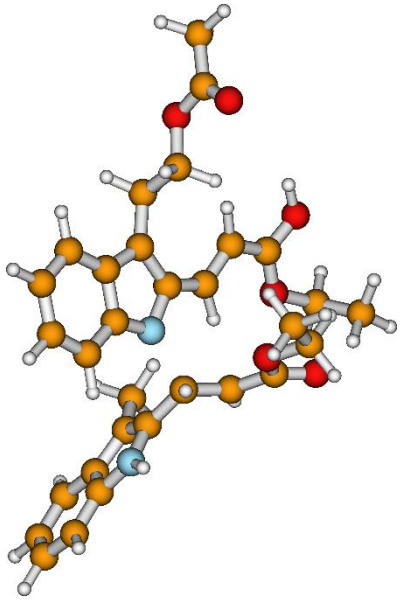
All the equilibrium points were optimized using B3LYP/def2-SVP level of DFT theory. The transition states were identified by normal mode frequency analysis. Intrinsic reaction coordinates (IRC) calculations also confirmed the transition states reported in the present work.

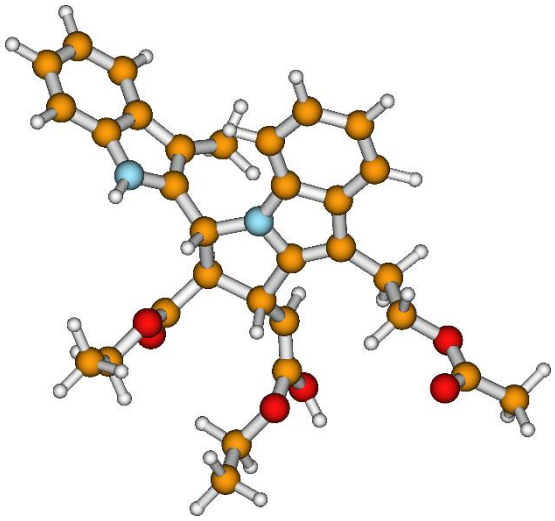
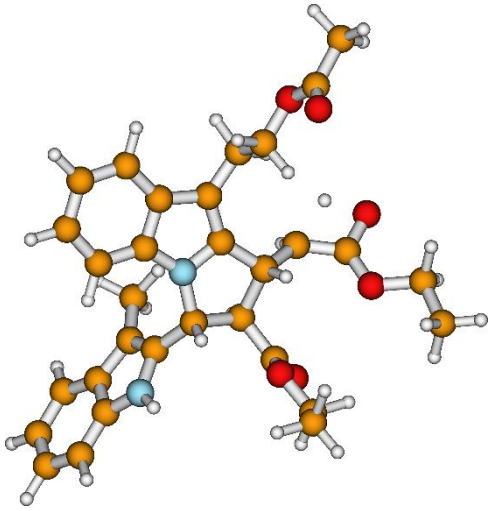
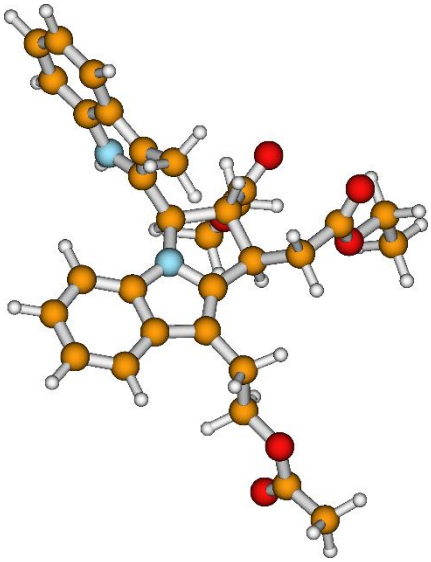
S.No.	Structure notation	Structures in 3D
1.	1a	
2.	2a	
3.	TS1	

4.	IM1	
5.	TS2	
6.	3A	

7.	A	
8.	1a-TS1	
9.	1a-IM1	

10.	1a-TS2	
11.	4a	
12.	3a	

13.	1c	
14.	1c’	
15.	1c-TS1	

16.	1c-IM1	
17.	1c-TS2	
18.	4g	

Cartesian coordinates of all the stationary points. Energy is in hartree and frequency corresponding to transition state in cm^{-1}:

1. 1a
Energy= -746.770929.

CARTESIAN COORDINATES (ANGSTROMS)

C	-0.749874	2.670948	-0.003148
C	0.678601	2.703785	-0.003585
C	1.339346	3.952356	-0.006149
C	0.578651	5.116514	-0.008211
C	-0.837251	5.061861	-0.007805
C	-1.518463	3.847475	-0.005306
H	2.431837	4.001474	-0.006496
H	1.075282	6.090495	-0.010195
H	-1.407823	5.994792	-0.009494
H	-2.610663	3.808223	-0.004995
C	1.136641	1.343123	-0.001086
C	-0.009580	0.539064	0.000882
N	-1.134628	1.357395	-0.000424
H	-2.094303	1.033315	0.000277
C	2.568703	0.905255	-0.000530
H	2.671398	-0.189039	0.001665
H	3.102535	1.290482	-0.886632
H	3.102927	1.294035	0.883785
C	-0.076290	-0.898565	0.003953
C	-1.196081	-1.665172	0.007583
C	-1.187018	-3.137035	0.010548
O	-2.198389	-3.817577	0.014710
O	0.050248	-3.671481	0.007847
C	0.151486	-5.107667	0.010111
C	1.620958	-5.474983	0.006234
H	1.729899	-6.570921	0.007794
H	2.124832	-5.079438	-0.889973
H	2.130339	-5.076347	0.897947
H	-0.371929	-5.504040	-0.875446
H	-0.366511	-5.500898	0.900242
H	-2.202049	-1.237015	0.008914
H	0.889356	-1.409756	0.003354

2. 2a
Energy =-345.341202

CARTESIAN COORDINATES (ANGSTROMS)

C	-0.278541	3.036240	-0.000128

C	-0.676906	1.758838	0.000106
C	0.305327	0.640718	0.000332
O	1.514147	0.763066	0.000035
O	-0.318421	-0.547321	0.000208
C	0.504594	-1.731943	0.000044
C	-0.410337	-2.938511	-0.000069
H	-0.998763	3.858881	-0.000269
H	0.786850	3.286875	-0.000172
H	-1.734479	1.480655	0.000156
H	0.192375	-3.860216	-0.000194
H	-1.053744	-2.946558	0.893951
H	-1.053799	-2.946350	-0.894052
H	1.156591	-1.709394	-0.888347
H	1.156645	-1.709600	0.888401

3. TS1

Energy = -1092.048103.

Imaginary Frequency = -324.33

CARTESIAN COORDINATES (ANGSTROMS)

C	-1.419664	2.237288	0.039266
C	-2.645814	1.559458	-0.353149
C	-2.295796	0.294453	-0.872317
N	-0.880907	0.126133	-0.756328
C	-0.372861	1.386250	-0.239773
C	-3.993042	1.950512	-0.324467
C	-4.954724	1.065073	-0.818141
C	-4.584585	-0.187812	-1.338019
C	-3.243402	-0.592800	-1.376916
C	1.059375	1.550233	-0.159178
C	1.740537	2.542541	0.464188
C	3.213972	2.647448	0.465240
O	3.823351	1.675427	-0.237387
C	5.265768	1.667164	-0.284708
C	5.859952	0.910957	0.891736
C	-1.345380	3.624340	0.590614
O	3.812785	3.533198	1.048034
C	-0.423030	-1.249804	0.166579
C	-0.579194	-2.446735	-0.634746
C	-0.008565	-2.395746	-1.911867
O	-0.046227	-3.428964	-2.797603
C	-0.498410	-4.729491	-2.404650
C	0.553251	-5.512038	-1.631473
O	0.519344	-1.332725	-2.368067
H	-6.009410	1.351957	-0.807654

H	-5.355062	-0.858087	-1.727639
H	-2.955236	-1.557931	-1.792806
H	-4.285123	2.926743	0.069936
H	-1.050208	3.617824	1.654081
H	-0.595921	4.228592	0.053385
H	-2.315736	4.134393	0.514844
H	1.648957	0.787671	-0.677047
H	1.248777	3.333175	1.030651
H	0.610274	-0.938150	0.367649
H	-1.033006	-1.191060	1.076131
H	6.955113	0.857117	0.781142
H	5.635885	1.418510	1.842528
H	5.467009	-0.117199	0.937693
H	5.509948	1.176240	-1.237666
H	5.626616	2.705595	-0.315326
H	1.483199	-5.593313	-2.216926
H	0.786386	-5.029594	-0.670165
H	0.185324	-6.530532	-1.425645
H	-1.440351	-4.652574	-1.836081
H	-0.732712	-5.239354	-3.351921
H	-1.276823	-3.223931	-0.326124
H	-0.335419	-0.253615	-1.630154

4. IM1

Energy = -1092.088756.

CARTESIAN COORDINATES (ANGSTROMS)

C	-5.712515	1.223484	-0.890399
C	-5.531981	-0.120526	-0.477338
C	-4.296728	-0.586615	-0.039164
C	-3.222379	0.324144	-0.014869
C	-3.384497	1.681249	-0.432549
C	-4.654036	2.122488	-0.872311
N	-1.917095	0.146712	0.369080
C	-1.224913	1.355859	0.195102
C	-2.114034	2.324793	-0.294811
C	-1.823742	3.755699	-0.631449
C	0.182126	1.448761	0.504553
C	0.954665	2.566620	0.507494
C	-1.352634	-1.129066	0.822737
C	-0.699379	-1.928409	-0.270456
C	0.601264	-2.269981	-0.274500

O	1.178564	-2.874160	-1.338070
O	1.417502	-2.018032	0.783732
C	1.808038	-4.154719	-1.111334
C	2.343799	-4.656718	-2.435271
C	2.389485	2.578346	0.835423
O	3.053004	3.599795	0.892158
O	2.914878	1.358754	1.071519
C	4.701987	-0.149625	1.587509
C	4.309621	1.304149	1.426212
H	-6.699372	1.551364	-1.228126
H	-6.382323	-0.807586	-0.506279
H	-4.171667	-1.626789	0.268521
H	-4.800898	3.157469	-1.192986
H	-1.558672	4.348925	0.261285
H	-0.981816	3.849486	-1.338317
H	-2.700538	4.232427	-1.093307
H	0.684125	0.513991	0.766904
H	0.560254	3.557068	0.286070
H	-0.639895	-0.935599	1.635257
H	-2.184761	-1.693057	1.271806
H	-1.304516	-2.250515	-1.120808
H	2.319920	-1.849455	0.464876
H	2.618820	-4.049234	-0.370730
H	1.054677	-4.846679	-0.693764
H	2.826985	-5.636422	-2.295629
H	1.531046	-4.770418	-3.169889
H	3.089839	-3.957582	-2.845438
H	5.761589	-0.218536	1.879648
H	4.096850	-0.639595	2.366740
H	4.572117	-0.700962	0.641971
H	4.898686	1.801363	0.638759
H	4.461997	1.873366	2.358118

5. TS2

Energy = -1092.054107.

Imaginary Frequency = -669.89

CARTESIAN COORDINATES (ANGSTROMS)

C	0.221703	-1.048855	0.480693
C	0.760736	0.935296	-0.078369
C	-0.665825	1.360853	-0.045004
N	-1.605782	0.352666	-0.135011

C	-1.131010	-1.019381	-0.202464
C	-1.287459	2.594930	0.017397
C	-2.705318	2.317782	-0.040015
C	-2.867296	0.898583	-0.139386
C	-3.855508	3.132364	-0.011086
C	-5.113244	2.534901	-0.082035
C	-5.249687	1.131180	-0.182095
C	-4.132835	0.295708	-0.213218
C	-0.643705	3.945371	0.121251
C	1.458943	0.977590	-1.315996
C	2.905390	1.211569	-1.402224
O	3.537161	1.046381	-0.214670
C	4.963268	1.234871	-0.189624
C	5.413892	1.238819	1.256828
C	1.310924	-1.730942	-0.091635
O	2.285798	-2.324141	0.584405
C	2.153597	-2.611014	1.994321
C	3.236704	-3.598914	2.373696
O	3.503870	1.500493	-2.424821
O	1.533622	-1.639843	-1.363389
H	-6.011048	3.159095	-0.062239
H	-6.249330	0.691238	-0.238441
H	-4.242074	-0.788601	-0.294424
H	-3.762277	4.219746	0.064333
H	-0.847636	4.565637	-0.769695
H	-1.022476	4.508817	0.991856
H	0.448849	3.864306	0.224685
H	1.353755	1.127818	0.820610
H	0.907744	1.243490	-2.223563
H	-1.843869	-1.675789	0.322226
H	-1.059843	-1.365985	-1.247465
H	0.171256	-1.019413	1.571918
H	5.440306	0.421595	-0.762478
H	5.210049	2.181075	-0.696414
H	6.507710	1.358656	1.305962
H	5.148481	0.293944	1.757320
H	4.950946	2.070910	1.811434
H	1.149022	-3.022995	2.183573
H	2.254400	-1.667594	2.555632
H	4.237581	-3.187774	2.170419
H	3.122909	-4.540319	1.813945
H	3.166646	-3.823480	3.449360
H	1.475347	-0.575029	-1.592847

6. 3A

Energy= -1092.133290.

CARTESIAN COORDINATES (ANGSTROMS)

C	-5.706444	0.776096	0.346357
C	-5.625136	-0.531739	0.877879
C	-4.394114	-1.157696	1.074598
C	-3.238168	-0.441123	0.727965
C	-3.295451	0.887065	0.188725
C	-4.557377	1.486741	0.000892
N	-1.909939	-0.778543	0.795593
C	-1.139331	0.270846	0.337357
C	-1.937525	1.326630	-0.056612
C	-1.514585	2.648445	-0.626550
C	-1.149587	-1.925997	1.261175
C	0.272580	-1.626826	0.733664
C	0.320439	-0.078902	0.451223
C	1.029447	0.721259	1.580659
C	2.504357	0.371436	1.680964
O	2.898488	-0.590224	2.306912
O	3.408132	1.114274	1.021741
C	4.346045	2.817902	-0.366353
C	3.076141	2.313337	0.287771
C	0.614627	-2.445524	-0.507534
O	-0.088444	-3.293715	-1.010800
O	1.829654	-2.124794	-0.965418
C	3.730136	-2.345155	-2.403616
C	2.327937	-2.839514	-2.119919
H	-6.689120	1.235243	0.206019
H	-6.544580	-1.062793	1.140010
H	-4.331529	-2.168777	1.484736
H	-4.634429	2.498033	-0.409253
H	-0.425519	2.690604	-0.781618
H	-1.996558	2.843575	-1.600548
H	-1.788356	3.489671	0.034849
H	-1.165967	-1.991721	2.362281
H	-1.543255	-2.865367	0.847292
H	1.036657	-1.886955	1.481768
H	0.848016	0.119373	-0.493592
H	0.871124	1.793826	1.411727
H	0.574941	0.461899	2.548208
H	4.131175	3.740427	-0.928061
H	5.114336	3.042262	0.389982
H	4.750907	2.070653	-1.066716
H	2.308858	2.086560	-0.469400
H	2.667215	3.062345	0.985386
H	4.139105	-2.875792	-3.277666
H	3.733113	-1.265648	-2.622592
H	4.394267	-2.529709	-1.544637

H	2.307179	-3.918515	-1.899261
H	1.646112	-2.658506	-2.966232

7. A

Energy = -746.712482.

CARTESIAN COORDINATES (ANGSTROMS)

C	-0.772330	2.534171	-0.039792
C	0.682299	2.670898	-0.007211
C	1.279956	3.965361	0.009063
C	0.463499	5.076988	-0.005686
C	-0.965759	4.944270	-0.037098
C	-1.582595	3.710796	-0.053927
H	2.368921	4.073919	0.032838
H	0.900334	6.079596	0.006408
H	-1.575181	5.853240	-0.047833
H	-2.672438	3.619319	-0.077819
C	1.188293	1.363905	0.000397
C	0.010141	0.523115	-0.028138
N	-1.165371	1.255808	-0.052529
C	2.626621	0.946042	0.029754
H	2.745386	-0.147558	0.028337
H	3.179607	1.339362	-0.841837
H	3.142051	1.333161	0.926765
C	0.014747	-0.878180	-0.032798
C	-1.134903	-1.673278	-0.066117
C	-1.098321	-3.066508	-0.071437
O	-2.180627	-3.824611	-0.108036
O	0.037938	-3.720150	-0.039888
C	0.063661	-5.174625	-0.045401
C	1.512413	-5.604440	-0.001121
H	1.563391	-6.704287	-0.004110
H	2.063115	-5.229627	-0.877759
H	2.006150	-5.237001	0.911811
H	-0.444778	-5.526539	-0.955992
H	-0.501324	-5.534051	0.828149
H	-2.113809	-1.189773	-0.092333
H	0.984443	-1.383761	-0.009660
H	-2.988452	-3.282610	-0.132631

8. 1a-TS1

Energy = -1493.440604.

Imaginary Frequency = -291.66

CARTESIAN COORDINATES (ANGSTROMS)

N	-0.993036	0.553288	0.109184
C	-0.297029	1.761675	0.042575
C	1.063335	1.793205	-0.332138
C	-1.175460	2.855858	0.326939
C	-2.437378	2.274884	0.572675
C	-2.269921	0.844088	0.445197
C	-3.709337	2.818106	0.901117
C	-4.766839	1.957305	1.119664
C	-4.590000	0.545022	1.015089
C	-3.371052	-0.021511	0.685722
C	-0.866552	4.320255	0.311253
C	1.944922	2.868304	-0.330768
C	3.293099	2.681434	-0.689864
O	3.714036	1.527727	-1.120275
C	5.134890	1.220343	-1.277675
C	5.752358	0.835548	0.053035
O	4.197199	3.632968	-0.611532
H	-5.753304	2.353015	1.375352
H	-5.448895	-0.108060	1.195116
H	-3.269950	-1.103271	0.598165
H	-3.845294	3.900313	0.981038
H	1.665422	3.869174	-0.003152
H	6.771638	0.456226	-0.122401
H	5.820600	1.700956	0.730066
H	5.157447	0.048007	0.540586
H	5.131031	0.379128	-1.982240
H	5.632554	2.079734	-1.746880
H	3.815179	4.466863	-0.285196
H	1.483205	0.836695	-0.641181
H	1.740133	-1.471884	-0.346087
C	1.128200	-1.202321	0.516918
C	1.842698	-0.889133	1.706950
O	1.028752	-0.497725	2.752425
C	1.659462	-0.227390	4.003838
C	0.602274	0.272365	4.970484
H	1.057786	0.491141	5.949552
H	-0.187237	-0.482128	5.119060

H	0.130618	1.194999	4.595202
H	2.144592	-1.144141	4.384082
H	2.459939	0.519120	3.864512
O	3.068335	-0.941597	1.869371
C	-0.287722	-1.141787	0.394433
H	-0.812927	-1.246223	1.349049
C	-0.909020	-1.979648	-0.670983
N	-1.748967	-3.019450	-0.287885
H	-1.950741	-3.269749	0.673517
C	-2.164086	-3.719371	-1.394990
C	-2.992776	-4.845501	-1.510147
H	-3.425161	-5.321440	-0.625910
C	-3.246017	-5.334033	-2.792268
H	-3.888669	-6.210369	-2.915521
C	-2.686829	-4.715983	-3.934602
C	-1.861352	-3.598809	-3.816385
H	-1.432495	-3.130473	-4.707146
H	-2.906581	-5.124733	-4.925032
C	-1.583202	-3.084136	-2.532956
C	-0.786672	-1.980615	-2.052448
C	-0.011156	-1.037504	-2.922808
H	0.778820	-1.563567	-3.488014
H	0.471330	-0.244011	-2.338602
H	-0.662804	-0.551778	-3.670620
H	-0.409570	4.634049	-0.642720
H	-1.780512	4.914914	0.453324
H	-0.161310	4.601628	1.112933

9. 1a-IM1

Energy = -1493.509746.

CARTESIAN COORDINATES (ANGSTROMS)

C	-4.337247	2.512642	-0.940371
C	-4.656759	1.148449	-0.773503
C	-3.603155	0.216580	-0.533317
C	-2.258718	0.613871	-0.454271
C	-1.975251	1.968208	-0.621806
C	-3.004230	2.909229	-0.863321
N	-4.179454	-1.023611	-0.415186
C	-5.554667	-0.917323	-0.563160
C	-5.895214	0.407550	-0.787191
C	-6.398169	-2.159276	-0.442182
N	-7.336022	-2.373248	-1.542396

C	-8.566930	-2.872854	-1.158993
C	-8.631372	-3.008793	0.342831
C	-7.361090	-2.173087	0.784949
C	-9.336517	-3.167597	-2.265561
C	-8.506086	-2.840479	-3.406666
C	-7.247026	-2.361790	-2.915967
C	-8.705955	-2.918327	-4.799573
C	-7.674029	-2.539684	-5.657959
C	-6.436382	-2.082239	-5.152178
C	-6.205900	-1.986369	-3.779032
C	-9.907083	-2.551826	0.987125
C	-10.545427	-3.220855	1.965512
O	-10.176269	-4.461720	2.363984
C	-9.892000	-4.648548	3.770528
C	-9.420505	-6.072891	3.970820
C	-6.784850	-2.703458	2.080444
O	-5.905262	-3.695092	1.893955
C	-5.333573	-4.318332	3.067639
C	-4.284159	-5.308725	2.610290
C	-7.255439	1.002097	-1.010467
O	-11.610620	-2.680750	2.608808
O	-7.126439	-2.309719	3.175937
H	-7.820179	-2.600153	-6.740178
H	-5.642615	-1.798233	-5.848842
H	-5.247635	-1.635325	-3.391054
H	-9.657497	-3.277401	-5.202657
H	-5.716312	-3.023732	-0.376045
H	-7.692455	-1.147042	0.993002
H	-8.461057	-4.065939	0.609934
H	-10.337784	-1.599454	0.667888
H	-3.683153	-1.889480	-0.236762
H	-1.464592	-0.114036	-0.267990
H	-0.937986	2.310231	-0.565785
H	-2.744241	3.963900	-0.990137
H	-5.124978	3.248319	-1.126620
H	-3.836995	-5.801968	3.487553
H	-4.724779	-6.085699	1.965868
H	-3.479945	-4.804101	2.051820
H	-4.908441	-3.531801	3.710292
H	-6.143803	-4.808867	3.630674
H	-9.216049	-6.250209	5.038384
H	-10.189495	-6.789854	3.641806
H	-8.496112	-6.267076	3.403932
H	-9.118307	-3.920697	4.069575

H	-10.799616	-4.448466	4.364477
H	-8.042901	0.237600	-1.056687
H	-7.523036	1.710577	-0.206728
H	-7.290573	1.569763	-1.956486
H	-12.212663	-3.389142	2.891170
C	-10.726014	-3.731608	-2.311663
H	-11.139046	-3.857547	-1.300251
H	-11.413697	-3.077443	-2.876192
H	-10.748829	-4.717208	-2.809773

10. 1a-TS2
Energy = -1493.440850.
Imaginary Frequency = -2041.00

CARTESIAN COORDINATES (ANGSTROMS)

C	-6.184165	-2.014077	-3.747223
C	-7.233412	-2.375440	-2.875775
C	-8.486761	-2.771637	-3.431160
C	-8.708770	-2.816123	-4.816967
C	-7.653131	-2.453604	-5.651506
C	-6.402255	-2.055690	-5.122386
N	-9.321421	-3.060689	-2.380655
C	-8.649969	-2.868393	-1.181844
C	-7.355286	-2.445408	-1.439416
C	-9.373728	-3.139555	0.110234
N	-9.322748	-2.050904	1.080959
C	-9.206856	-2.460052	2.398027
C	-9.103964	-3.966788	2.463168
C	-8.796993	-4.322749	0.955459
C	-9.303421	-1.375958	3.247616
C	-9.512108	-0.229781	2.386031
C	-9.539082	-0.692693	1.030372
C	-9.691497	1.145470	2.637161
C	-9.901200	2.011831	1.564390
C	-9.936638	1.531225	0.236116
C	-9.755583	0.177098	-0.049651
C	-9.245750	-1.345511	4.746469
C	-8.110883	-4.500111	3.471367
C	-8.217596	-5.797146	4.072788
O	-8.874978	-6.825607	3.616505
C	-9.051817	-7.989261	4.482224
C	-9.895953	-8.999578	3.740410

C	-9.311229	-5.681600	0.524521
O	-10.650812	-5.732453	0.511687
C	-11.272969	-6.977967	0.123158
C	-12.772330	-6.770175	0.109746
C	-6.268087	-2.105754	-0.461849
O	-7.640905	-5.799961	5.226795
O	-8.604059	-6.620337	0.229774
H	-10.044996	3.079888	1.750978
H	-10.110709	2.232341	-0.585022
H	-9.787754	-0.191096	-1.076918
H	-9.673155	1.527377	3.662119
H	-10.428184	-3.357965	-0.133924
H	-7.707265	-4.351851	0.825988
H	-10.105608	-4.366260	2.706367
H	-7.057200	-4.273528	3.243824
H	-10.285491	-3.363869	-2.461640
H	-9.675560	-3.123211	-5.224536
H	-7.794169	-2.476319	-6.735783
H	-5.596585	-1.777658	-5.807634
H	-5.213324	-1.705725	-3.348763
H	-13.271573	-7.706863	-0.184057
H	-13.141864	-6.480313	1.106057
H	-13.057184	-5.987422	-0.610999
H	-10.887224	-7.270095	-0.866339
H	-10.972228	-7.756775	0.841483
H	-10.043462	-9.885162	4.377956
H	-10.884605	-8.584791	3.489571
H	-9.398923	-9.321169	2.812090
H	-8.054559	-8.384285	4.724442
H	-9.524393	-7.644978	5.415095
H	-6.607042	-2.177112	0.580578
H	-5.397775	-2.775303	-0.578922
H	-5.898820	-1.077417	-0.619395
H	-7.699713	-4.580209	4.940946
H	-9.029080	-2.341761	5.156758
H	-8.464232	-0.654466	5.108978
H	-10.199608	-0.998527	5.182709

11. 4a

Energy = -1493.560792.

CARTESIAN COORDINATES (ANGSTROMS)

C	-0.156825	-2.461602	3.394360
C	-0.029705	-2.309835	2.004117
C	0.208652	-3.422898	1.142064
C	0.321343	-4.712277	1.701816
C	0.195589	-4.864340	3.081366
C	-0.042399	-3.748651	3.918171
N	-0.095419	-1.186441	1.218887
C	0.087727	-1.542991	-0.107446
C	0.281045	-2.911180	-0.206724
C	0.517161	-3.734859	-1.437578
C	0.053393	-0.493634	-1.180961
N	1.073209	0.541539	-1.014679
C	0.624016	1.844443	-1.094678
C	-0.867642	1.867328	-1.296410
C	-1.271552	0.366224	-1.207497
C	1.682183	2.727641	-1.021776
C	2.863332	1.899107	-0.892909
C	2.445790	0.528611	-0.904003
C	3.362644	-0.530191	-0.819552
C	4.716620	-0.207287	-0.716329
C	5.150549	1.137163	-0.697318
C	4.238274	2.188575	-0.784302
C	-2.212789	-0.069552	-2.320426
O	-2.545928	-1.356650	-2.185805
C	-3.434702	-1.928612	-3.174490
C	-3.688048	-3.372431	-2.797190
C	-1.656730	2.792685	-0.356268
C	-1.427909	2.584157	1.127218
O	-0.904964	1.612137	1.640141
C	1.662614	4.227271	-1.079064
O	-1.898549	3.608063	1.837641
C	-1.800505	3.532105	3.280684
C	-2.411193	4.791050	3.857148
O	-2.624395	0.641709	-3.210673
H	-0.281503	-0.233918	1.534369
H	0.281290	-5.859114	3.527537
H	0.504996	-5.581152	1.063015
H	0.200074	-0.996671	-2.150080
H	-1.809903	0.179494	-0.267831
H	-1.090906	2.212958	-2.319058
H	-1.445069	3.848819	-0.581764
H	-2.739367	2.668563	-0.537418
H	-0.738716	3.424898	3.553240
H	-2.325907	2.625021	3.619421

H	-1.875700	5.687174	3.506268
H	-2.348866	4.759783	4.956189
H	-3.471580	4.882308	3.573756
H	3.029398	-1.569839	-0.833244
H	5.454629	-1.011574	-0.648909
H	6.219463	1.353410	-0.614708
H	4.586027	3.225724	-0.772071
H	2.351130	4.607879	-1.853496
H	1.981115	4.681489	-0.123599
H	0.659976	4.615491	-1.311739
H	-0.137833	-3.898873	4.997330
H	-0.340480	-1.599270	4.040558
H	0.571245	-3.118273	-2.346718
H	-0.287693	-4.475867	-1.588390
H	1.460754	-4.303339	-1.365499
H	-2.960944	-1.837739	-4.165070
H	-2.749157	-3.947948	-2.780331
H	-4.362190	-3.832925	-3.536296
H	-4.161304	-3.444541	-1.805374
H	-4.363775	-1.337183	-3.192962

12. 3a

Energy = -1838.886960.

CARTESIAN COORDINATES (ANGSTROMS)

C	0.116534	-5.752868	0.857795
C	-0.305012	-4.480657	0.429145
C	0.307677	-3.310595	0.991254
C	1.266107	-3.414285	2.014803
C	1.657811	-4.691789	2.420398
C	1.100581	-5.851039	1.841174
N	-0.298951	-2.220246	0.389046
C	-1.309672	-2.679540	-0.451514
C	-1.345174	-4.052108	-0.481940
C	-2.086693	-1.516414	-1.000773
C	-1.652394	-0.357785	-0.017684
C	-0.290390	-0.798213	0.494418
C	0.782418	-0.026369	0.800448
N	2.074890	-0.512088	0.999606
C	2.902053	0.432672	1.587030
C	2.205265	1.650766	1.703308
C	0.827422	1.509477	1.040477

C	2.817566	2.732612	2.327766
C	4.135814	2.602706	2.806671
C	4.823023	1.393486	2.654398
C	4.214172	0.285567	2.044908
C	0.820128	2.236858	-0.343472
C	0.973158	3.757297	-0.294159
C	0.901575	4.394186	-1.669038
O	1.096846	5.724697	-1.757538
C	1.390136	6.557603	-0.618610
C	1.525838	7.983707	-1.113165
C	-0.306764	2.005891	1.956353
C	-1.848929	-1.210040	-2.503965
C	-0.410463	-0.914349	-2.872914
O	0.293784	-2.032435	-3.089274
C	1.699787	-1.890495	-3.393281
C	2.267265	-3.272552	-3.638075
C	-2.696677	-0.251032	1.092355
O	-2.681846	-0.870249	2.132573
C	-2.272837	-4.936070	-1.259771
O	-3.669610	0.602370	0.748362
C	-4.775951	0.759914	1.667182
C	-5.753045	1.744231	1.060673
O	0.063701	0.198915	-2.956434
O	0.673149	3.782063	-2.688216
H	4.619522	3.449094	3.300728
H	2.285431	3.678255	2.459701
H	-1.623071	0.599888	-0.548863
H	-3.167819	-1.702876	-0.908443
H	-2.194623	-2.077830	-3.085250
H	-2.451674	-0.335151	-2.787320
H	2.192217	-1.388740	-2.544624
H	1.806120	-1.237631	-4.274076
H	2.147937	-3.911772	-2.749155
H	3.341868	-3.195895	-3.866759
H	1.767253	-3.760315	-4.489777
H	1.678709	-2.533257	2.506411
H	2.403355	-4.790730	3.214244
H	1.431730	-6.835815	2.182134
H	-0.334973	-6.654152	0.433263
H	-2.743749	-5.695540	-0.612427
H	-1.742868	-5.484026	-2.059169
H	-3.077126	-4.354282	-1.735537
H	5.847432	1.300825	3.026384
H	4.742172	-0.666014	1.945957

H	-5.235489	-0.227228	1.834632
H	-5.279277	2.725472	0.899758
H	-6.607956	1.881526	1.741234
H	-6.136074	1.377588	0.095190
H	1.754842	8.650372	-0.267077
H	0.590900	8.326887	-1.583322
H	2.339361	8.066620	-1.850872
H	2.324088	6.215367	-0.143452
H	0.577419	6.472626	0.121328
H	-0.112283	1.994085	-0.872744
H	1.626665	1.816591	-0.963952
H	0.189367	4.224193	0.326878
H	-1.274700	2.023057	1.432974
H	-0.106995	3.031822	2.301394
H	-0.401677	1.364277	2.844728
H	-4.380355	1.111870	2.633254
H	2.358163	-1.465424	0.814388
H	1.929315	4.047911	0.169078

13. 1c

Energy = -1013.621493.

CARTESIAN COORDINATES (ANGSTROMS)

C	-4.656484	-1.489571	-0.000040
C	-4.350139	-2.873247	-0.000122
C	-3.032984	-3.312369	-0.000165
C	-2.019424	-2.337030	-0.000127
C	-2.295431	-0.929945	-0.000044
C	-3.656741	-0.526021	-0.000002
N	-0.666370	-2.494809	-0.000157
C	-0.040043	-1.255037	-0.000096
C	-1.023637	-0.252202	-0.000026
C	-0.711407	1.222890	0.000045
C	1.402284	-1.218866	-0.000116
C	2.233896	-0.146348	-0.000048
C	-1.901819	2.168260	0.000089
C	3.704086	-0.256205	-0.000079
O	4.447645	0.709257	0.000004
O	4.157799	-1.524161	-0.000206
C	5.859125	-3.205741	-0.000380
C	5.585168	-1.716200	-0.000240
O	-1.365918	3.504004	0.000146

O	-3.448222	4.347798	0.000133
C	-2.248880	4.518182	0.000173
C	-1.552835	5.854849	0.000212
H	-5.703519	-1.174974	-0.000007
H	-5.163411	-3.604144	-0.000150
H	-2.784285	-4.376623	-0.000228
H	-3.938052	0.526905	0.000061
H	-0.180804	-3.385217	-0.000216
H	-0.088747	1.468777	0.879168
H	-0.088748	1.468859	-0.879055
H	1.879304	-2.204980	-0.000194
H	1.878399	0.882939	0.000039
H	-2.535568	2.038927	-0.890505
H	-2.535563	2.038851	0.890676
H	6.946151	-3.382709	-0.000407
H	5.431533	-3.686753	0.893684
H	5.431515	-3.686588	-0.894523
H	6.011717	-1.220917	-0.887932
H	6.011739	-1.221079	0.887532
H	-2.296089	6.661433	0.000179
H	-0.905506	5.938930	0.887319
H	-0.905412	5.938939	-0.886825

14. 1c’

Energy = -1013.557853.

CARTESIAN COORDINATES (ANGSTROMS)

C	-4.619314	-1.496313	-0.000009
C	-4.283323	-2.892463	-0.000122
C	-2.972859	-3.310301	-0.000183
C	-1.932506	-2.329308	-0.000132
C	-2.266200	-0.901187	-0.000013
C	-3.648229	-0.519576	0.000044
N	-0.618777	-2.547150	-0.000180
C	-0.039457	-1.284497	-0.000086
C	-1.033496	-0.226396	0.000014
C	-0.717606	1.246320	0.000103
C	1.361831	-1.221262	-0.000094
C	2.225454	-0.121293	0.000047
C	-1.907762	2.191356	0.000114
C	3.613233	-0.277141	0.000024
O	4.365264	0.809106	0.000227

O	4.156283	-1.474528	-0.000198
C	5.841342	-3.174480	-0.000553
C	5.592612	-1.682578	-0.000215
O	-1.376001	3.530752	0.000156
O	-3.459750	4.371861	0.000052
C	-2.260283	4.542606	0.000151
C	-1.566535	5.880972	0.000088
H	-5.674575	-1.208585	0.000036
H	-5.092315	-3.629201	-0.000160
H	-2.708823	-4.371746	-0.000269
H	-3.950386	0.528736	0.000131
H	-0.094967	1.495598	0.879118
H	-0.094920	1.495685	-0.878855
H	1.833368	-2.209474	-0.000215
H	1.876259	0.908953	0.000215
H	-2.541645	2.060708	-0.890148
H	-2.541666	2.060664	0.890354
H	6.926469	-3.359073	-0.000566
H	5.407293	-3.644056	0.895188
H	5.407342	-3.643642	-0.896534
H	6.017267	-1.206253	-0.900211
H	6.017224	-1.206666	0.900020
H	-2.311020	6.686460	0.000016
H	-0.919525	5.966441	0.887307
H	-0.919471	5.966334	-0.887104
H	5.320871	0.630775	0.000235

15. 1c-TS1
Energy = -1760.297510.
Imaginary Frequency = -294.92.

CARTESIAN COORDINATES (ANGSTROMS)

N	-0.976536	-0.296452	-0.150932
C	-0.269952	0.897133	-0.289265
C	1.104574	0.878831	-0.630446
C	-1.152514	2.011448	-0.135583
C	-2.427627	1.457551	0.110779
C	-2.265288	0.022546	0.112389
C	-3.706829	2.033690	0.335910
C	-4.778567	1.198816	0.586368
C	-4.607599	-0.217051	0.613255

C	-3.380366	-0.814839	0.383108
C	-0.862105	3.479460	-0.263214
C	-0.501522	4.123844	1.075121
O	-0.268773	5.522790	0.833572
C	0.041538	6.288061	1.895572
C	0.230220	7.730061	1.500694
C	2.026371	1.915609	-0.620255
C	3.371454	1.676434	-0.970473
O	3.749288	0.509337	-1.398269
C	5.159458	0.153588	-1.564562
C	5.784339	-0.215627	-0.232996
O	4.308524	2.592201	-0.882284
O	0.142559	5.845791	3.018485
H	-5.771641	1.619027	0.766023
H	-5.477426	-0.848951	0.814667
H	-3.284445	-1.900228	0.391923
H	-3.836954	3.119378	0.314387
H	-1.753281	3.994111	-0.657892
H	-0.050417	3.665773	-0.983554
H	1.791585	2.925209	-0.283513
H	-1.318651	4.009446	1.804616
H	0.402331	3.676453	1.519108
H	6.785469	-0.637910	-0.414451
H	5.896666	0.665538	0.416962
H	5.169379	-0.965460	0.287832
H	5.118202	-0.704038	-2.247797
H	5.674819	0.986084	-2.062505
H	0.560493	8.313379	2.368908
H	0.967449	7.807609	0.686828
H	-0.721350	8.135325	1.120641
H	3.957555	3.439221	-0.554336
H	1.494174	-0.098551	-0.913675
H	1.724975	-2.376583	-0.499368
C	1.122674	-2.054227	0.352247
C	1.849637	-1.714565	1.528110
O	1.051302	-1.271678	2.564021
C	1.697082	-0.981759	3.803794
C	0.653628	-0.455541	4.771120
H	1.121294	-0.218528	5.740126
H	-0.137994	-1.202476	4.944410
H	0.182785	0.461561	4.381660
H	2.179552	-1.894558	4.196233
H	2.501798	-0.244448	3.641034
O	3.074509	-1.788236	1.685973

C	-0.293914	-1.979734	0.234768
H	-0.813209	-2.020828	1.197375
C	-0.935065	-2.870697	-0.774251
N	-1.802711	-3.860423	-0.326066
H	-2.008147	-4.045938	0.649224
C	-2.242103	-4.614410	-1.387303
C	-3.107824	-5.717418	-1.431175
H	-3.552380	-6.122985	-0.518378
C	-3.382432	-6.274800	-2.680277
H	-4.054645	-7.134828	-2.748342
C	-2.807800	-5.746739	-3.859561
C	-1.945098	-4.652800	-3.811992
H	-1.504142	-4.255161	-4.730768
H	-3.045068	-6.207911	-4.822547
C	-1.645974	-4.068842	-2.563264
C	-0.815930	-2.961701	-2.152972
C	-0.009245	-2.100835	-3.078358
H	0.434697	-1.243384	-2.556923
H	-0.629568	-1.706229	-3.902042
H	0.814718	-2.667930	-3.547654

16. 1c-IM1

Energy = -1760.368897.

CARTESIAN COORDINATES (ANGSTROMS)

C	-4.370153	2.520241	-0.917281
C	-4.671326	1.150090	-0.765666
C	-3.601072	0.222756	-0.590785
C	-2.257620	0.630197	-0.561320
C	-1.992414	1.990072	-0.712327
C	-3.038332	2.926918	-0.889192
C	-5.903407	0.398848	-0.741982
C	-5.543056	-0.927266	-0.560251
N	-4.161830	-1.024587	-0.473996
C	-6.369726	-2.179199	-0.432041
N	-7.339983	-2.387605	-1.507102
C	-8.551602	-2.900170	-1.092795
C	-8.556876	-3.084127	0.404738
C	-7.295028	-2.225210	0.822627
C	-9.366530	-3.151955	-2.178929
C	-8.581068	-2.787971	-3.341420
C	-7.305259	-2.323651	-2.882360

C	-8.834939	-2.809528	-4.727960
C	-7.838541	-2.391875	-5.609148
C	-6.582946	-1.950038	-5.134390
C	-6.299372	-1.908889	-3.769020
C	-10.758102	-3.721606	-2.179510
C	-10.776971	-5.238708	-2.346140
O	-12.155998	-5.656425	-2.367771
C	-12.409086	-6.972690	-2.449511
C	-13.891508	-7.247504	-2.467683
C	-6.671125	-2.756086	2.095629
O	-5.761030	-3.711644	1.873091
C	-5.138242	-4.331094	3.022776
C	-4.045504	-5.253206	2.525882
C	-9.823368	-2.694875	1.107459
C	-10.407196	-3.427804	2.074525
O	-9.978437	-4.667721	2.409896
C	-9.632752	-4.894740	3.797359
C	-9.081630	-6.298951	3.921091
C	-7.276071	0.986613	-0.896554
O	-7.003180	-2.392933	3.204386
O	-11.471777	-2.956803	2.769700
O	-11.537508	-7.812855	-2.502321
H	-8.027179	-2.409138	-6.686263
H	-5.818060	-1.634880	-5.849600
H	-5.328172	-1.569252	-3.404002
H	-9.800068	-3.155817	-5.109085
H	-11.271939	-3.471068	-1.238027
H	-11.348908	-3.276013	-2.997755
H	-5.678303	-3.037618	-0.401220
H	-7.643192	-1.208849	1.050477
H	-8.341491	-4.143318	0.627886
H	-10.295494	-1.745629	0.842360
H	-10.289258	-5.552507	-3.283166
H	-10.258491	-5.741326	-1.514114
H	-3.651643	-1.889630	-0.335004
H	-1.450471	-0.094447	-0.425024
H	-0.956427	2.339953	-0.694043
H	-2.792344	3.986219	-1.004700
H	-5.171027	3.252632	-1.053717
H	-3.558979	-5.742601	3.384137
H	-4.455097	-6.036960	1.869341
H	-3.278270	-4.693246	1.968149
H	-4.745565	-3.538476	3.678220
H	-5.912293	-4.878045	3.584839

H	-8.828892	-6.508096	4.972416
H	-9.824165	-7.041889	3.589114
H	-8.170325	-6.419670	3.314271
H	-8.886280	-4.139563	4.097847
H	-10.526500	-4.765014	4.430260
H	-14.070200	-8.328880	-2.510658
H	-14.363164	-6.821859	-1.568152
H	-14.349941	-6.756710	-3.340811
H	-8.060227	0.217738	-0.923633
H	-7.514010	1.678378	-0.069321
H	-7.354902	1.570951	-1.829657
H	-12.030660	-3.700212	3.050635

17. 1c-TS2
Energy = -1760.300090.
Imaginary Frequency = -2047.64

CARTESIAN COORDINATES (ANGSTROMS)

C	-6.330905	-1.802690	-3.833126
C	-7.316651	-2.247336	-2.938330
C	-8.593976	-2.717731	-3.384784
C	-8.871238	-2.715300	-4.767011
C	-7.894854	-2.268831	-5.656526
C	-6.636849	-1.820916	-5.194187
N	-7.327825	-2.339826	-1.564568
C	-8.526033	-2.877689	-1.137980
C	-9.355582	-3.115808	-2.217317
C	-8.485149	-3.106072	0.355265
C	-7.244867	-2.220647	0.763395
C	-6.338137	-2.150096	-0.505434
C	-5.513318	-0.896589	-0.622760
C	-5.874760	0.431725	-0.784807
C	-4.643236	1.184153	-0.798307
C	-3.572265	0.255294	-0.636462
N	-4.131955	-0.994044	-0.537323
C	-2.229144	0.663177	-0.601043
C	-1.964927	2.025316	-0.732085
C	-3.011535	2.963832	-0.895364
C	-4.343061	2.556603	-0.929688
C	-7.248195	1.020460	-0.927523
C	-9.764004	-2.814969	1.105609
C	-10.175184	-3.549425	2.265404

O	-11.458700	-3.509647	2.384745
C	-6.548766	-2.713618	2.014594
O	-6.652704	-2.190088	3.102393
C	-10.738631	-3.705996	-2.221651
C	-10.733798	-5.222531	-2.393084
O	-12.106230	-5.661190	-2.428700
C	-12.339413	-6.980083	-2.524338
O	-11.455512	-7.807620	-2.573242
C	-13.817389	-7.275772	-2.565404
O	-5.826922	-3.820103	1.792189
C	-5.156560	-4.422043	2.922990
C	-4.396729	-5.633926	2.428267
O	-9.419437	-4.262674	3.051686
C	-10.057051	-5.139435	4.031742
C	-8.977581	-5.956409	4.702843
H	-8.101341	-2.268009	-6.730509
H	-5.887793	-1.482966	-5.915727
H	-5.357763	-1.458534	-3.477766
H	-9.838289	-3.066231	-5.138884
H	-11.256369	-3.465024	-1.280387
H	-11.332385	-3.267819	-3.041674
H	-5.646355	-3.009937	-0.499772
H	-7.611140	-1.211154	0.992979
H	-8.212896	-4.164511	0.524217
H	-9.998917	-1.745888	1.226144
H	-10.233388	-5.526226	-3.326785
H	-10.214884	-5.720686	-1.558485
H	-3.620698	-1.860633	-0.412407
H	-1.421525	-0.062790	-0.474920
H	-0.929222	2.375688	-0.708378
H	-2.766366	4.024920	-0.995076
H	-5.144485	3.290328	-1.055325
H	-3.877384	-6.113363	3.272814
H	-5.078854	-6.372681	1.978563
H	-3.643247	-5.349328	1.676946
H	-4.489028	-3.671722	3.375511
H	-5.916070	-4.689501	3.674368
H	-9.442643	-6.640463	5.429727
H	-8.421088	-6.559004	3.968215
H	-8.270090	-5.308921	5.243745
H	-10.599857	-4.505153	4.747738
H	-10.789177	-5.763633	3.496878
H	-13.980324	-8.359987	-2.598520
H	-14.312430	-6.844804	-1.681272

H	-14.265238	-6.803188	-3.454098
H	-8.031765	0.251220	-0.957517
H	-7.481942	1.704435	-0.092663
H	-7.332021	1.613422	-1.854756
H	-11.261773	-3.072544	1.220044

18. 4g

Energy = -1760.411631.

CARTESIAN COORDINATES (ANGSTROMS)

C	-4.630114	2.596615	-0.669676
C	-4.872802	1.205713	-0.605421
C	-3.824541	0.292980	-0.490342
C	-2.519230	0.806494	-0.438141
C	-2.250269	2.211762	-0.485416
C	-3.333737	3.105246	-0.610512
N	-1.296890	0.179184	-0.341904
C	-0.289412	1.120629	-0.284419
C	-0.815866	2.394844	-0.383447
C	-0.100368	3.717335	-0.335125
C	-0.870491	-1.189868	-0.069006
C	0.682384	-1.075589	-0.243357
C	1.041077	0.443574	-0.071959
C	2.148359	0.914998	-1.034513
C	-0.046626	4.303107	1.074090
C	-1.521240	-2.241415	-0.927847
N	-2.103765	-3.340858	-0.314555
C	-2.608765	-4.189071	-1.268031
C	-2.341059	-3.599865	-2.539657
C	-1.644790	-2.357979	-2.303411
C	-3.277745	-5.416992	-1.139606
C	-3.682375	-6.056040	-2.309934
C	-3.428369	-5.489257	-3.581703
C	-2.763937	-4.271599	-3.706330
C	1.467260	-1.986231	0.687105
O	2.351211	-2.730804	0.321624
O	1.083956	-1.858885	1.961461
C	1.098728	-2.419027	4.292245
C	1.767627	-2.658772	2.956070
C	3.461861	0.172087	-0.891361
O	4.057252	-0.354038	-1.805114

O	3.901717	0.177115	0.374881
C	5.500943	-0.268793	2.102730
C	5.136433	-0.521828	0.655558
O	0.633429	5.570221	0.994005
O	0.434655	5.851433	3.214452
C	0.814416	6.253647	2.136672
C	1.536455	7.554117	1.891835
C	-1.172384	-1.413988	-3.370698
H	-5.476224	3.283037	-0.763860
H	-5.901361	0.836810	-0.647277
H	-4.013414	-0.781089	-0.440560
H	-3.160852	4.184374	-0.654568
H	0.930895	3.622685	-0.709307
H	-0.607212	4.443163	-0.993101
H	-1.094429	-1.428875	0.984589
H	0.944537	-1.387114	-1.263276
H	1.377616	0.625198	0.962484
H	2.357999	1.980796	-0.845954
H	1.824077	0.813995	-2.079568
H	-1.056001	4.458527	1.487612
H	0.498905	3.640768	1.765262
H	-2.143249	-3.490551	0.687455
H	-3.473055	-5.853690	-0.156689
H	-4.206094	-7.013873	-2.244503
H	-3.759870	-6.020059	-4.478533
H	-2.571256	-3.843329	-4.694168
H	1.607364	-3.011266	5.068984
H	1.152905	-1.356744	4.577981
H	0.040237	-2.722430	4.265918
H	1.716048	-3.715203	2.650026
H	2.829154	-2.364479	2.967628
H	6.443881	-0.785323	2.341511
H	5.638538	0.807240	2.293466
H	4.720220	-0.647577	2.781112
H	4.977484	-1.592474	0.450546
H	5.912346	-0.156628	-0.034988
H	1.682252	8.084285	2.840934
H	2.510028	7.358097	1.415831
H	0.953030	8.179562	1.197851
H	-0.755397	-0.487032	-2.953880
H	-0.394316	-1.876557	-4.003251
H	-1.999787	-1.131048	-4.044099