Supporting Information

Blue LED induced solvent free multicomponent reaction among aryl diazoacetates, pyridine derivatives and maleimides: Direct eco-friendly synthesis of densely functionalized Itaconimides

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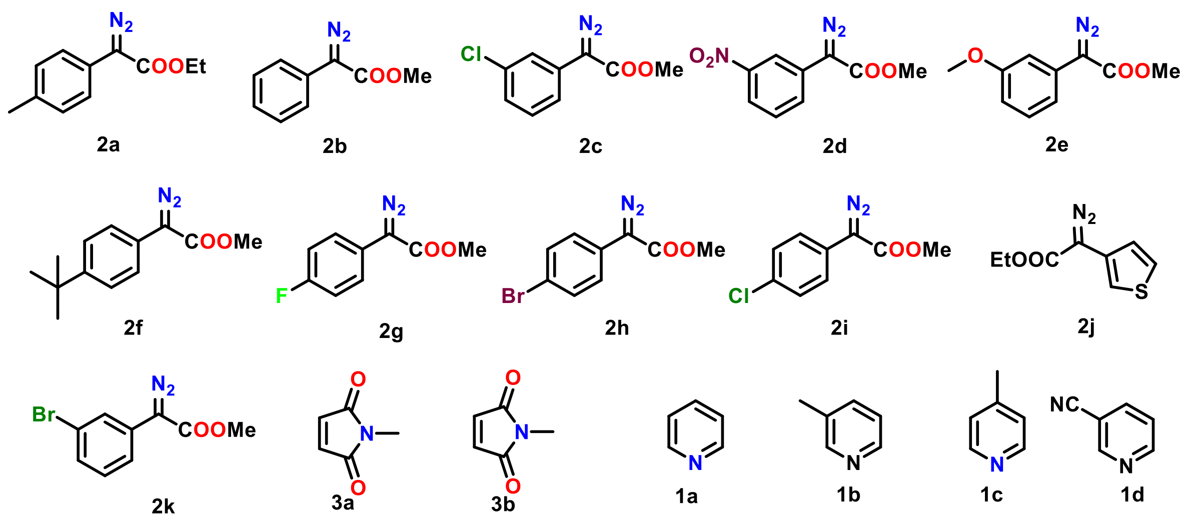
Content

1. General experimental Procedure:

All blue light reactions were carried out under air as specified unless otherwise mentioned. Photochemical Reactor Aldrich® Micro Photochemical Reactor, blue LED lights (ALDKIT001-1EA). LED light is IP68 double density 12V DC water proof blue light with spectral range of 435-445 nm with wall plug power supply 500mA with 5-6 watts. The irradiation vessel material is borosilicate glass. The distance of irradiation vessel from light source is 2 cm. Reactions were monitored through TLC by visualising in UV detector. All purifications were done in silica gel (100-200 mesh size) column chromatography. All ^{1}H and ^{13}C NMR spectra were recorded taking tetramethylsilane (TMS) as an internal standard at ambient temperature unless otherwise indicated with Bruker 400 MHz instruments at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR spectroscopy. Splitting patterns are designated as singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), quintet (quin) doublet of doublets (dd) and triplet of doublets (td). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Ultra-performance liquid chromatography (UPLC) was carried out using an Agilent 6540 accurate–mass Q-TOF LC/MS (Agilent Technologies, U.S.A.). Liquid chromatographic separations ware performed at room temperature of 25 °C, using a UPLC C18 analytical column. MS analyses were performed under the following operation parameters: dry gas temperature 350 °C, dry gas (N_2) flow rate 10 L/min, nebulizer pressure 30 psi, Vcap 4000 and fragmentor voltage 100 V. Mass spectra were acquired in the positive ion mode by scanning from 100 to 1500 in the mass to charge ratio (m/z). The mobile phase composition used for UHPLC–QTOF MS comprised of H_2O (A) and ACN (B), with optimized linear gradient elution. The injection volume was 5 µL. The flow rate was set at 0.3 mL/min. Accurate mass analysis calibration was carried out by ESI-low concentration tuning mix solution provided by Agilent technologies, U.S.A. The accuracy error threshold was set at 5 ppm.

2. Synthetic Procedure

2.1 Synthesis of aryl diazo esters (2a-i):

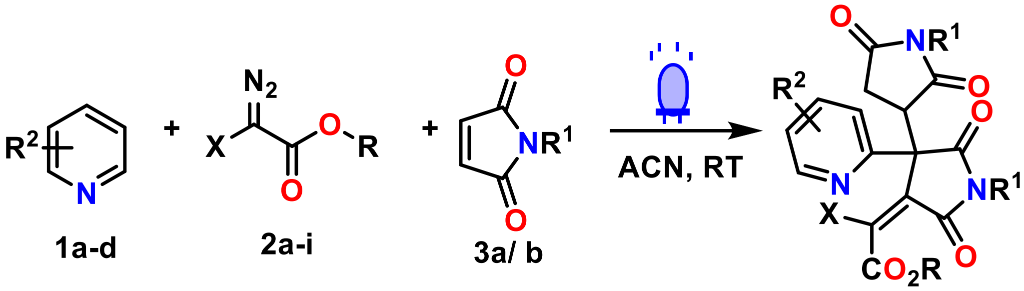


Scheme S1: Structures of aryl diazoesters, N-alkyl maleimides, pyridines used in this study.

All aryl diazo acetates were prepared by reported procedure. Aryl acetates (1 equivalent, 5 mmol) were dissolved in acetonitrile (10ml) in a clean oven dried round bottom flask, added DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) (1.2equivalent, 6 mmol), stirred for 10 minutes, pABSA (4-Acetamidobenzenesulfonyl azide) (1.2 equivalent, 6 mmol) was added, stirred for 4 hours in dark and r.t; after completion acetonitrile was removed under vacuum, diluted with ethyl acetate (25ml), washed with water and organic layer was dried with brine and sodium sulphate, purified with column chromatography in silica gel (100-200 mesh size) with 5% ethyl acetate in hexane to yield ~98%.[1]

2.2 Synthesis of itaconimides (6a-v)

2.2.1 General procedure



In an oven dried vial differently substituted aryl diazo acetates, **2** (1 equiv., 0.19 mmol) was taken; pyridine or substituted pyridines (**1a-d**) (3equiv., 0.57 mmol) were added to it and stirred in presence of blue light for 30 minute. Then N-alkyl maleimides, **3** (2 equiv., 0.38 mmol) were added into the reaction mixture and continued stirring for 10 h. Reaction quenched with saturated $CuSO_4$ aqueous solution (2 ml) and extracted with DCM (3 × 5 ml). Purification done by column chromatography using silica gel (100/200 mess size), eluted with ethyl acetate in hexane (20-40%). In all cases, inseparable mixture of diastereoisomers obtained except **6a, 6i, 6n, 6p**; d.r. were determined by relative integration in 1H NMR spectrum, only data for major diastereoisomer reported.

2.2.2 Scale up Synthesis:

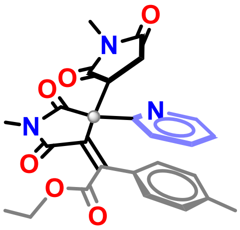
In an oven dried 100 ml beaker tolyl diazo acetate, **2a** (1 equiv., 1 g, 4.9 mmol) was taken with pyridine **1a** (3 equiv., 1.18 ml, 14.7 mmol) and stirred in presence of blue light for 30 minute. Then N-methyl maleimide, **3a** (2 equiv., 1.09 g, 9.8 mmol) was added into the reaction mixture and continued stirring for 15 h. Reaction quenched with saturated $CuSO_4$ aqueous solution (5ml), resulted mixture was extracted with DCM (3 × 30 ml). Recrystallization of the organic mixture afforded 1.9 g of **6a** (83% yield).

2.2.3 Synthesis of 5l under argon:

In a double neck 25 ml oven dried flask **2j** (0.19 mmol**,** 37.3 mg) was taken with **1a** (3 equiv., 0.57 mmol, 46 μl), and **3a** (2 equiv., 0.38 mmol, 42.2 mg) and closed with argon filled balloon after backfilling with argon. The reaction mixture was irradiated with blue light for 10 h. Reaction was quenched with $CuSO_4$ aqueous solution and extracted with DCM (3 × 5 ml). Immediate purification was done by column chromatography using silica gel (100/200 mess size), eluted with ethyl acetate in hexane (20-40%) to afford **5l** (oily mass, 22.6 g, 32%) and thereafter NMR recorded immediately.

2.2.4 Characterization data:

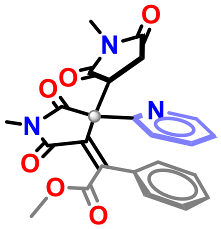
Ethyl (Z)-2-(1,1'-dimethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)-2-(p-tolyl)acetate, 6a:



6a

Crystalline colourless solid (78.6 mg, 87%, d.r ~ 95:5); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.27-8.25 (m, 1H), 7.56 (td, J = 7.8, 1.7 Hz, 1H), 7.18-7.15 (m, 1H), 6.97 (d, J = 7.6 Hz, 2H), 6.75 (d, J = 8.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 4.32-4.26 (m, 2H), 3.87-3.83 (m ,1H), 3.24 (dd, J = 18.6, 5.6 Hz, 1H), 3.15 (s, 3H), 2.99-2.92 (m, 4H), 2.32 (s, 3H), 1.31 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.8, 175.8, 175.7, 167.7, 167.5, 156.8, 148.9, 143.1, 139.1, 136.9, 131.4, 129.3, 129.1, 127.4, 123.0, 122.3, 62.1, 57.6, 44.3, 33.7, 25.4, 25.0, 21.4, 14.0; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{25}N_3O_6$ $[M+H]^+$ 476.1816, found 476.1833.

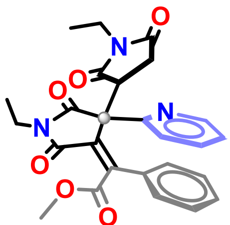
Methyl (Z)-2-(1,1'-dimethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)-2-phenylacetate, 6b:



6b

Colourless oil (68.0 mg, 80%, d.r ~ 82:18); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 8.23 (d, J = 4.0 Hz, 1H), 7.55 (t, J = 7.0 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.16 (t, J = 7.8 Hz, 3H), 6.73 (t, J = 7.8 Hz, 3H), 3.89-3.84 (m, 4H), 3.22-3.20 (m, 1H), 3.15 (s, 3H), 2.96-2.91 (m, 4H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.8, 175.8, 175.5, 167.8, 167.7, 156.5, 149.0, 142.4, 137.0, 132.0, 129.2, 128.5, 127.5, 123.1, 122.3, 57.5, 53.1, 44.5, 33.5, 29.4, 27.3, 25.5, 25.1 ; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{21}N_3O_6$ $[M+H]^+$ 448.1503, found 448.1500.

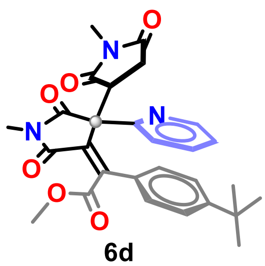
Methyl (Z)-2-(1,1'-diethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)-2-phenylacetate, 6c:



6c

Colourless oil (75.9 mg, 84%, d.r ~ 90:10); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.21-8.19 (m,1H), 7.30-7.28 (m, 1H), 7.17-7.13 (m, 3H), 6.75-6.71 (m, 3H), 3.87-3.84 (m, 3H), 3.71 (q, J = 7.2 Hz, 2H), 3.53 (q, J = 7.2 Hz, 2H), 3.21 (dd, J = 18.6, 5.0 Hz, 1H), 2.92 (dd, J = 18.8, 9.2 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.5, 175.6, 175.1, 167.9, 167.4, 156.6, 148.9, 142.2, 136.9, 132.2, 129.0, 128.4, 127.5, 123.0, 122.3, 57.3, 53.1, 44.4, 34.5, 33.9, 33.6, 13.1, 13.0. HRMS (ESI-TOF) m/z calcd for $C_{26}H_{25}N_3O_6$ $[M+H]^+$ 476.1816, found 476.1819.

Methyl (Z)-2-(4-(tert-butyl)phenyl)-2-(1,1'-dimethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6d:

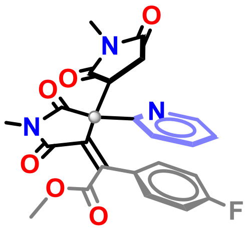


6d

Colourless oil (83.2 mg, 87%, d.r ~ 95:5); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.19-8.17 (m, 1H), 7.53-7.48 (m, 1H), 7.17-7.11 (m, 3H), 6.70-6.66 (m, 3H), 3.96-3.93 (m, 1H), 3.85 (s, 3H), 3.25 (dd, J = 18.6, 5.8 Hz, 1H), 3.15 (s, 3H), 2.98-2.94 (m, 4H), 1.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.8, 175.9, 175.6, 168.0, 167.7, 156.4, 152.3, 148.9, 142.7, 136.8, 132.1, 129.1, 127.1, 125.4, 122.9, 122.3, 57.6, 53.1, 44.9, 34.8, 33.6, 31.3, 31.2, 29.8, 25.5, 25.1. HRMS (ESI-TOF) m/z calcd for $C_{28}H_{29}N_3O_6$ $[M+H]^+$ 504.2129, found 504.2130.

Methyl (Z)-2-(1,1'-dimethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)-2-(4-fluorophenyl)acetate, 6e:

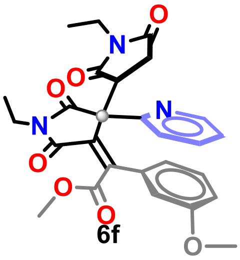
Colourless oil (78.7 mg, 89%, d.r ~ 90:10); 1H NMR (CDCl3, 400 MHz) δH 8.26 (d, J = 3.2 Hz, 1H), 7.59 (dd, J = 7.6 Hz, 1H), 7.20-7.17 (m, 1H), 6.88-6.84 (m, 2H), 6.79 (d, J = 8.0 Hz, 2H), 6.73-6.70 (m, 2H), 3.84-3.79 (m, 4H), 3.22-3.19 (m, 1H), 3.14 (s, 3H), 3.04-2.95; 13C NMR (CDCl3, 100 MHz) δC 176.7, 175.6, 175.2, 167.6, 167.4, 162.9 (d, *J* = 248.0 Hz), 156.2, 148.8, 141.3, 137.0, 136.9, 132.4, 129.4 (d, *J* = 8.0 Hz), 127.7 (d, *J* = 3Hz), 123.1, 122.1, 115.5 (d, *J* = 22 Hz), 57.4, 53.0, 44.3, 33.6, 25.4, 24.9; 19F NMR (478 MHz) δ -111.63; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{20}FN_3O_6$ [M+H]+ 466.1409, found 466.1411.



6e

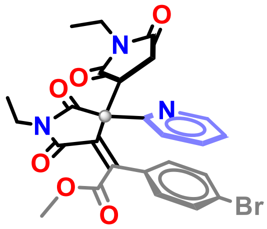
Methyl (Z)-2-(1,1'-diethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)-2-(3-methoxyphenyl)acetate, 6f:

Colourless oil (77.8 mg, 81%, d.r ~ 80:20); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.25-8.23 (m, 1H), 7.55 (td, *J* = 7.7, 2.8 Hz, 1H), 7.17-7.10 (m, 2H), 6.83-6.80 (m, 1H), 6.75-6.72 (m, 1H), 6.44-6.41 (m, 1H), 6.17-6.16 (m, 1H), 3.94-3.90 (m, 1H), 3.85 (s, 3H), 3.71 (q, *J* = 7.33 Hz, 2H), 3.63 (s, 3H), 3.55-3.51 (m, 2H), 3.22 (dd, *J* = 18.4, 5.2 Hz, 1H), 2.93 (dd, *J* = 18.8, 9.2 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.5, 175.6, 175.1, 167.8, 167.4, 159.4, 156.6, 149.0, 142.0, 136.9, 133.3, 129.6, 123.0, 122.3, 119.8, 114.9, 112.8, 57.4, 55.3, 53.1, 44.4, 34.5, 33.9, 33.6, 13.1, 13.0. HRMS (ESI-TOF) m/z calcd for $C_{27}H_{27}N_3O_7$ $[M+H]^+$ 506.1922, found 506.1929.



Methyl (Z)-2-(4-bromophenyl)-2-(1,1'-diethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6g:

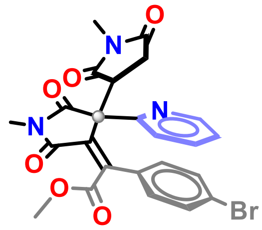
Colourless oil (94.8 mg, 90%, d.r ~ 95:5); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.25-8.23 (m, 1H), 7.60 (td, *J* = 7.8, 1.7 Hz, 1H), 7.31-7.29 (m, 2H), 7.20-7.17 (m, 1H), 6.82-6.79 (1H), 6.66-6.60 (m, 2H), 3.84 (s, 3H), 3.84-3.80 (m, 1H), 3.71 (q, *J* = 7.2 Hz, 2H), 3.52 (q, *J* = 7.2 Hz, 2H), 3.21 (dd, *J* = 18.8, 5.2 Hz, 1H), 2.96 (dd, *J* = 18.8, 9.2 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 177.2, 176.3, 174.6, 167.8, 167.4, 152.5, 145.5, 142.6, 139.8, 132.0, 131.8, 130.9, 128.5, 128.3, 126.7, 123.1, 57.8, 53.1, 47.3, 33.8, 25.1, 24.9, 18.8; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{24}BrN_3O_6$ $[M+H]^+$ 554.0921, found 554.0929.



6g

Methyl (Z)-2-(4-bromophenyl)-2-(1,1'-dimethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6h:

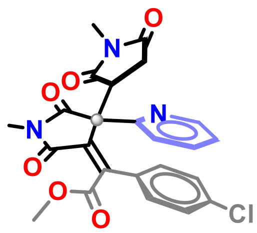
Colourless oil (92.0 mg, 92%, d.r ~ 80:20); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.27-8.25 (m, 1H), 7.61 (td, *J* = 7.7, 1.9 Hz, 1H), 7.32-7.30 (m, 2H), 7.22-7.19 (m, 1H), 6.83-6.80 (m, 1H), 6.71 (s, 1H), 6.63-6.61 (m, 2H), 3.85 (s, 3H), 3.84-3.82 (m, 1H), 3.24 (dd, *J* = 18.6, 5.4 Hz, 1H), 3.16 (s, 3H), 3.02-2.97 (m, 1H), 2.96 (s, 3H), ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.8, 175.7, 167.5, 156.3, 149.1, 141.2, 137.2, 132.5, 131.7, 130.9, 129.2, 123.7, 123.3, 122.3, 57.6, 53.3, 44.5, 33.5, 25.6, 25.1 . HRMS (ESI-TOF) m/z calcd for $C_{24}H_{20}BrN_3O_6$ $[M+H]^+$ 526.0608, found 526.0601.



6h

Methyl (Z)-2-(4-chlorophenyl)-2-(1,1'-dimethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6i:

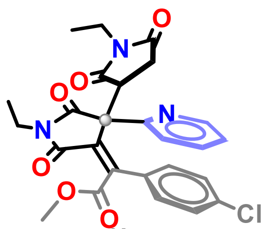
Colourless oil (76.0 mg, 83%, d.r ~ 95:5); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.28-8.26 (m, 1H), 7.61 (td, J = 7.7, 1.7 Hz, 1H), 7.22-7.18 (m, 1H), 7.16-7.14 (m, 2H), 3.85-3.81 (m, 4H), 3.24 (dd, J = 18.8, 5.2, 1H), 3.16 (s, 3H), 2.99-2.96 (m, 4H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.8, 175.7, 175.2, 167.6, 167.4, 156.3, 149.0, 141.2, 137.2, 135.5, 130.4, 129.0, 128.8, 123.3, 122.3, 57.5, 53.2, 44.5, 33.5, 29.8, 25.6, 25.1, 22.8, 14.2 ; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{20}ClN_3O_6$ $[M+H]^+$ 482.1113, found 482.1119.



6i

Methyl (Z)-2-(4-chlorophenyl)-2-(1,1'-diethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6j:

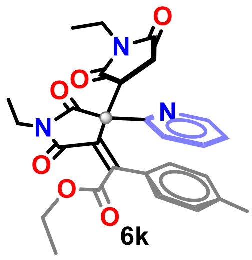
Colourless oil (76.5 mg, 79%, d.r ~ 80:20); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.24-8.22 (m, 1H), 7.59 (td, J = 7.8, 1.7 Hz, 1H), 7.19-7.16 (m, 1H), 7.15-7.12 (m, 1H), 6.81-6.78 (m,1H), 6.68-6.66 (2H), 3.84 (s, 3H), 3.82-3.79 (m, 1H), 3.70 (q, J = 7.2 Hz, 2H), 3.51 (q, J = 7.1 Hz, 2H), 3.20 (dd, J = 18.8, 4.8 Hz, 1H), 2.95 (dd, J = 18.6, 9 Hz, 1H), 1.21 (t, J = 7.0 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.5, 175.5, 174.9, 167.6, 167.1, 156.4, 148.9, 141.0, 137.2, 135.4, 132.8, 130.5, 128.9, 128.7, 123.2, 122.3, 57.3, 53.2, 44.4, 34.5, 33.9, 33.5, 13.1, 13.0. ; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{24}ClN_3O_6$ $[M+H]^+$ 510.1426, found 510.1429.



6j

Ethyl (Z)-2-(1,1'-diethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)-2-(p-tolyl)acetate, 6k:

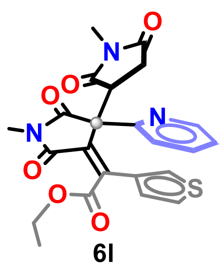
Colourless oil (84.2 mg, 88%, d.r ~ 80:20); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.24-8.22 (m, 1H), 7.56 (td, J = 7.7, 1.9 Hz, 1H), 7.29-7.27 (m, 1H), 6.97-6.94 (m, 3H), 6.64-6.61 (m, 2H), 4.32-4.27 (m, 2H), 3.74-3.68 (m, 2H), 3.53-3.51 (m, 2H), 3.22 (dd, J = 18.8, 5.2 Hz, 1H), 2.93 (dd, J = 18.4, 9.2 Hz, 1H), 2.32 (s, 3H), 1.21 (t, J = 7.2 Hz, 6H), 1.11 (t, J = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.5, 175.8, 175.3, 174.1, 167.6, 167.4, 157.6, 156.9, 149.6, 148.9, 138.0, 136.9, 129.8, 129.1, 127.4, 127.1, 123.3, 123.0, 122.3, 62.3, 62.1, 57.4, 44.2, 35.0, 34.4, 33.9, 33.7, 21.5, 14.1,13.0; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{29}N_3O_6$ $[M+H]^+$ 504.2129, found 504.2129.



6k

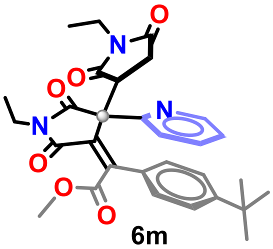
Ethyl (Z)-2-(1,1'-dimethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)-2-(thiophen-3-yl)acetate, 6l:

Colourless oil (84 mg, 95%, d.r ~ 95:5); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.40-8.38 (m, 1H), 7.61 (td, J = 7.7, 1.7 Hz, 1H), 7.22-7.19 (m, 2H), 6.88 (d, J = 8.0 Hz, 1H), 6.62-6.61 (m, 1H), 4.35 (q, J =7.2 Hz. 2H), 3.93-3.89 (m, 1H), 3.35 (dd, J = 18.8, 5.6 Hz, 1H), 3.14-3.08 (m, 4H), 2.94 (s, 3H), 1.34 (t, J = 7.0, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.8, 175.9, 175.5, 167.2, 156.7, 149.1, 137.2, 131.7.130.0, 127.3, 126.4, 125.9, 123.3, 122.2, 62.3, 57.6, 44.0, 33.9, 29.5, 27.4, 25.5, 25.1, 14.1. ; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{21}N_3O_6S$ $[M+H]^+$ 468.1224, found 468.1220.



6l

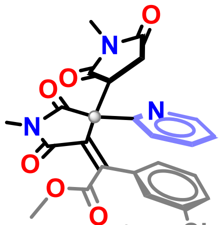
Methyl (Z)-2-(4-(tert-butyl)phenyl)-2-(1,1'-diethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6m:



6m

Colourless oil (83.0 mg, 83%), d.r ~ 95:5; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.15 (d, J = 4.8 Hz, 1H), 7.49 (t, J = 6.8 Hz, 1H), 7.15-7.09 (m, 3H), 6.69-6.65 (m, 3H), 3.95-3.91 (M, 1H), 3.84 (s, 3H), 3.70 (q, J = 7.1 Hz, 2H), 3.52 (q, J = 7.1 Hz, 2H), 3.21 (dd, J = 18.8, 4.8 Hz, 1H), 2.95 (dd, J = 18.6, 9 Hz, 1H), 1.29 (s, 9H), 1.21 (t, J = 7.0 Hz, 3H), 1.12 (t, J = 7.0 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 175.7, 175.1, 168.1, 167.4, 156.5, 152.2, 148.8, 142.5, 136.8, 132.4, 129.2, 127.1,126.8, 126.1, 125.3, 122.8, 122.3, 57.4, 53.1, 44.8, 34.8, 34.4, 33.9, 33.6, 31.3, 31.2, 13.1, 13.0 ; HRMS (ESI-TOF) m/z calcd for $C_{30}H_{33}N_3O_6$ $[M+H]^+$ 532.2442, found 532.2447.

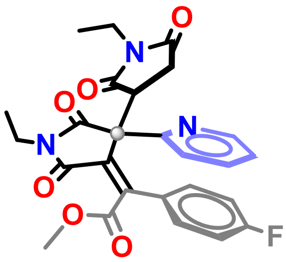
Methyl (Z)-2-(3-chlorophenyl)-2-(1,1'-dimethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6n:



6n

Colourless oil (74.2 mg, 81%, d.r ~ 80:20); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.28-8.26 (m, 1H), 7.63 (td, J = 7.7 Hz, 1.73 Hz, 1H), 7.30-7.27 (m, 1H), 7.24-7.21 (m, 1H), 7.17 (t, J = 7.8, 1H), 6.86-6.80 (m, 2H), 6.42 (t, J = 2.0 Hz, 1H), 3.86 (s, 3H), 3.82-3.78 (m, 1H), 3.25 (dd, J = 18.8, 5.6 Hz, 1H) 3.16 (s, 3H), 3.02-2.96 (m, 4H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 180.4, 176.6, 175.5,169.2, 167.2, 156.1, 149.0, 144.7, 140.6, 137.1, 133.5, 132.6, 129.7, 129.3, 127.6, 125.5, 123.3, 122.2, 53.1, 44.3, 33.4, 25.4. HRMS (ESI-TOF) m/z calcd for $C_{24}H_{20}ClN_3O_6$ $[M+H]^+$ 482.1113, found 482.1109.

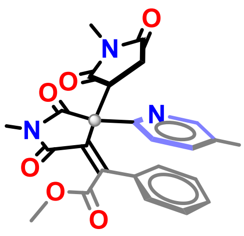
Methyl (Z)-2-(1,1'-diethyl-2,2',5,5'-tetraoxo-3-(pyridin-2-yl)-[3,3'-bipyrrolidin]-4-ylidene)-2-(4-fluorophenyl)acetate, 6o:



6o

Colourless oil (79.7 mg, 85%, d.r ~ 82:18); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.24-8.23 (m, 1H), 7.60 (td, J = 7.8, 1.9 Hz, 1H), 7.19-7.16 (m, 1H), 6.88-6.84 (m, 2H), 6.81-6.78 (m, 1H), 6.73-6.69 (m, 2H), 3.85 (s, 3H), 3.83-3.78 (m, 1H), 3.71 (q, J = 7.2 Hz, 2H), 3.54 (q, J = 7.2 Hz, 2H), 3.21 (dd, J = 18.8, 5.2 Hz, 1H), 3.21 (dd, J = 18.8, 9.2 Hz, 1H), 1.22 (t, J = 6.0 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.5, 175.6, 174.9, 167.8, 167.2, 163.1 (d, J = 248.6 Hz), 156.4, 148.9, 141.3, 137.1, 135.8, 129.5 (d, J = 8.4 Hz), 123.1, 122.3, 115.7 (d, J = 21.8 Hz), 57.3, 53.2, 50.5, 44.4, 34.5, 33.9, 33.9, 13.1, 12.9; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{24}FN_3O_6$ $[M+H]^+$ 494.1722, found 494.1720.

Methyl (Z)-2-(1,1'-dimethyl-3-(5-methylpyridin-2-yl)-2,2',5,5'-tetraoxo-[3,3'-bipyrrolidin]-4-ylidene)-2-phenylacetate, 6p:

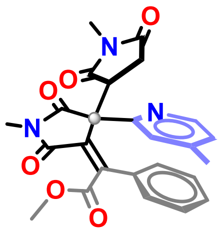


6p

Colourless oil (69.3 mg, 79%, d.r ~ 75:25); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.78-7.77 (m, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.18-7.14 (m, 1H), 7.05-6.97 (m, 3H), 6.66-6.64 (m, 2H), 4.19 (t, J = 7.0 Hz, 1H), 3.85 (s, 3H), 3.11-3.09 (m, 4H), 2.99-2.96 (m, 1H), 2.95 (s, 3H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 177.2, 176.3, 174.6, 167.8, 167.4, 152.5, 145.5, 142.6, 139.8, 132.0, 131.8, 130.9, 128.5, 128.3, 126.7, 123.1, 57.8, 53.1, 47.3, 33.8, 25.1, 24.9, 18.8; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{23}N_3O_6$ $[M+H]^+$ 462.1660, found 462.1669.

Methyl (Z)-2-(1,1'-dimethyl-3-(4-methylpyridin-2-yl)-2,2',5,5'-tetraoxo-[3,3'-bipyrrolidin]-4-ylidene)-2-phenylacetate, 6q:

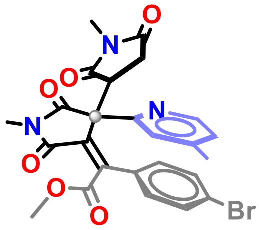
Colourless oil (74.5 mg, 85%, d.r ~ 95:5); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.10 (d, J = 4.0 Hz, 1H), 7.33-7.29 (m, 1H), 7.19 (t, J = 6.0 Hz, 2H), 6.98 (d, J = 4.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 2H), 6.43 (s, 1H), 3.85 (s ,3H), 3.22 (dd, J = 16.0, 4.0 Hz, 1H), 3.16 (s, 3H), 2.96 (s, 3H), 2.90 (dd, J = 12.0, 8 Hz, 1H), 2.25 (s, 3H), 2.0 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.87, 175.82, 148.81, 148.26, 132.02, 129.15, 128.43, 127.59, 124.18, 122.98, 57.36, 53.16, 44.50, 33.58, 29.85, 29.47, 25.53, 25.10, 21.24; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{23}N_3O_6$ $[M+H]^+$ 462.1660, found 462.1663.



6q

Methyl (Z)-2-(4-bromophenyl)-2-(1,1'-dimethyl-3-(4-methylpyridin-2-yl)-2,2',5,5'-tetraoxo-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6r:

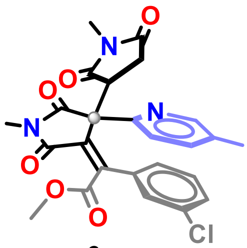
Colourless oil (74.1 mg, 73%, d.r ~ 85:15); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.12 (d, J = 4.0 Hz, 1H), 7.47 (dd, J = 16.0, 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.01 (s ,1H), 6.63 (d, J = 8.0 Hz, 1H), 6.51 (s, 1H), 3.85 (s ,3H), 3.69 (dd, J = 30.0, 6 Hz, 1H), 3.16 (s, 3H), 2.95 (s, 3H), 2.71 (d, J = 16.0 Hz, 1H), 2.41 (d, J = 28.0 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.84, 175.68, 175.42, 167.53, 156.05, 148.84, 148.52, 140.99, 132.47, 131.66, 130.95, 129.29, 124.33, 123.67, 122.95, 57.41, 53.26, 44.61, 33.50, 29.84, 29.47, 25.57, 25.10, 22.84, 21.27, 14.27; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{22}BrN_3O_6$ $[M+H]^+$ 540.0765, found 540.0768.



6r

Methyl (Z)-2-(3-chlorophenyl)-2-(1,1'-dimethyl-3-(5-methylpyridin-2-yl)-2,2',5,5'-tetraoxo-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6s:

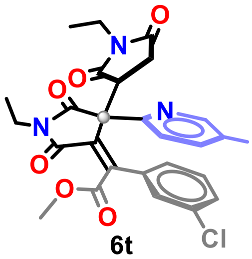
Colourless oil (67.8 mg, 72%, d.r ~ 70:30); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.87-7.85 (m, 1H), 7.45-7.42 (m, 1H), 7.18-7.15 (m, 1H), 7.10-7.08 (m, 1H), 7.07-7.05 (m, 1H), 6.78-6.76 (m, 1H), 6.37-6.36 (m, 1H), 4.15-4.12 (m, 1H), 3.87 (s, 3H), 3.15-3.10 (m, 4H), 3.00-2.95 (m, 4H), 2.11 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.0, 174.3, 167.2, 152.1, 145.5, 139.8, 132.0, 129.6, 128.9, 126.6, 125.1, 123.5, 57.6, 53.2, 47.1, 33.7, 29.7, 25.0, 24.9, 18.7 ; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{22}ClN_3O_6$ $[M+H]^+$ 496.1270, found 496.1269.



6s

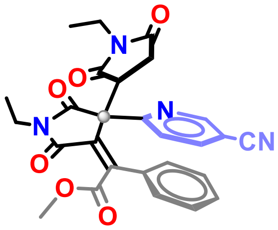
Methyl (Z)-2-(3-chlorophenyl)-2-(1,1'-diethyl-3-(5-methylpyridin-2-yl)-2,2',5,5'-tetraoxo-[3,3'-bipyrrolidin]-4-ylidene)acetate, 6t:

Colourless oil (77.7, 78%, d.r ~ 65:35); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.85-7.83 (m, 1H), 7.44-7.41 (m, 1H), 7.17-7.14 (m, 1H), 7.09-7.05 (m, 2H), 6.80-6.77 (m, 1H), 6.38-6.37 (m, 1H), 4.12 (t, J = 7.0 Hz, 1H), 3.86 (s, 3H), 3.70-3.64 (m, 2H), 3.55-3.49 (m, 2H), 3.09 (d, J = 6.8 Hz, 2H), 2.14 (s, 3H), 1.21-1.17 (m, 3H), 1.14-1.10 (m, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 176.8, 176.0, 174.1, 167.4, 166.8, 152.3, 145.6, 140.5, 139.8, 134.3, 133.5, 132.3, 129.7, 128.9, 126.7, 125.3, 123.5, 100.1, 57.7, 53.3, 47.2, 34.3, 33.8, 29.8, 18.9, 13.2, 12.6 ; HRMS (ESI-TOF) m/z calcd for $C_{27}H_{26}ClN_3O_6$ $[M+H]^+$ 524.1583, found 524.1588.



6t

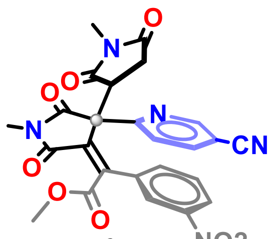
Methyl (Z)-2-(3-(5-cyanopyridin-2-yl)-1,1'-diethyl-2,2',5,5'-tetraoxo-[3,3'-bipyrrolidin]-4-ylidene)-2-phenylacetate, 6u:



6u

Colourless oil (64.7 mg, 68%, d.r ~ 60:40); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.12-8.11 (m, 1H), 7.92 (dd, J = 7.8, 1.8 Hz, 1H), 7.34-7.30 (m, 1H), 7.23-7.21 (m, 1H), 7.21-7.17 (m, 2H), 7.06 (t, J = 7.6 Hz, 2H), 6.78-6.70 (m, 2H), 4.16-4.12 (m, 1H), 3.88 (s, 3H), 3.71-3.68 (m, 2H), 3.55-3.52 (m, 2H), 3.09-3.04 (m, 1H), 2.95-2.88 (m, 1H), 1.22-121 (m, 2H), 1.13-1.11 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 175.0, 167.2, 166.5, 151.2, 141.9, 140.1, 132.1, 129.4, 128.7, 128.5, 127.2, 126.9, 122.6, 57.9, 53.2, 44.9, 34.8, 34.0, 33.3, 13.2, 13.1, 12.5; HRMS (ESI-TOF) m/z calcd for $C_{27}H_{24}N_4O_6$ $[M+H]^+$ 501.1789, found 501.1770.

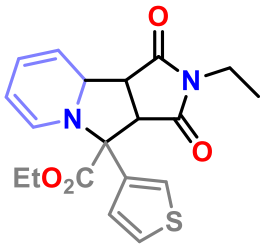
Methyl (Z)-2-(3-(5-cyanopyridin-2-yl)-1,1'-dimethyl-2,2',5,5'-tetraoxo-[3,3'-bipyrrolidin]-4-ylidene)-2-(3-nitrophenyl)acetate, 6v:



6v

Colourless oil (68.8 mg, 70%, d.r ~ 62:38); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.20-8.18 (m, 2H), 8.10 (s, 1H), 7.60-7.58 (m, 2H), 7.55-7.52 (m, 2H), 4.60 (d, J = 8.0 Hz, 1H), 4.19 (d, J = 8.0 Hz, 1H), 3.79 (s, 3H), 3.66-3.64 (m, 1H), 2.71 (s, 3H), 2.46 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 173.4, 173.3, 172.0, 171.2, 148.2, 138.5, 133.0, 129.1, 123.7, 121.8, 88.0, 60.9, 54.2, 50.3, 29.8, 25.3, 18.9; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}N_5O_8$ $[M+H]^+$ 518.1306, found 518.1310.

Ethyl 2-ethyl-1,3-dioxo-4-(thiophen-3-yl)-2,3,3a,4,9a,9b-hexahydro-1H-pyrrolo[3,4-a]indolizine-4-carboxylate, 5l :



5l

Oily mass (22.6 mg, 32%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.41-8.40 (m, 1H), 7.48-7.45 (m, 1H), 7.09-7.07 (m, 2H), 6.94 (s, 1H), 6.83-6.72 (m, 2H) 4.65-4.64 (m, 1H), 4.24-4.22 (m, 2H), 4.16-4.15 (m, 1H), 3.98-3.95 (m, 1H), 3.63-3.59 (m, 2H), 1.28-1.25 (m , 3H), 1.22-1.19 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 177.6, 176.2, 171.9, 156.1, 149.7, 136.6, 135.8, 127.2, 126.4, 124.4, 122.6, 122.5, 61.7, 51.8, 49.9, 45.2, 34.3, 14.2, 12.9; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{20}N_2O_4S$ $[M+H]^+$ 373.1217, found 373.1211.

3. HRMS Data:

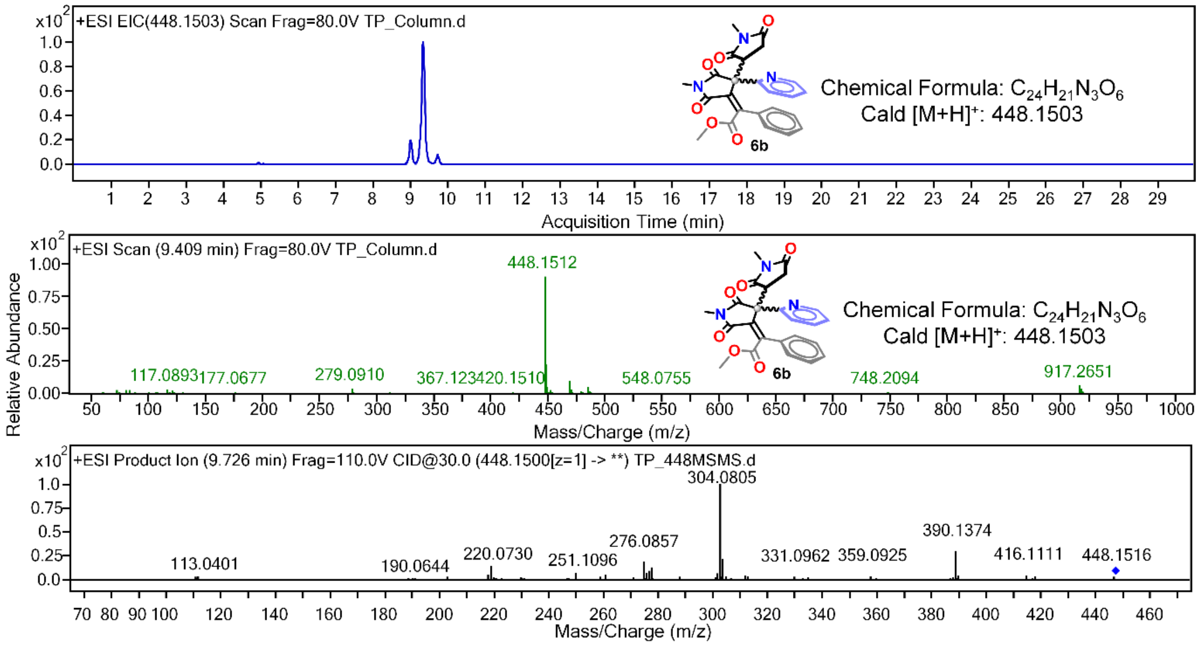


Figure S1: EIC/ESI-HRMS chromatogram of the (**6b**) obtained from the reaction mixture when phenyl diazoacetate (**2b**) treated with pyridine (**1a**), then treated with N-methylmaleimide (**3a**), finally irradiate with blue LED. Also showing the ESI/LCMS/MSMS plausible fragmentation pattern of (**6b**).

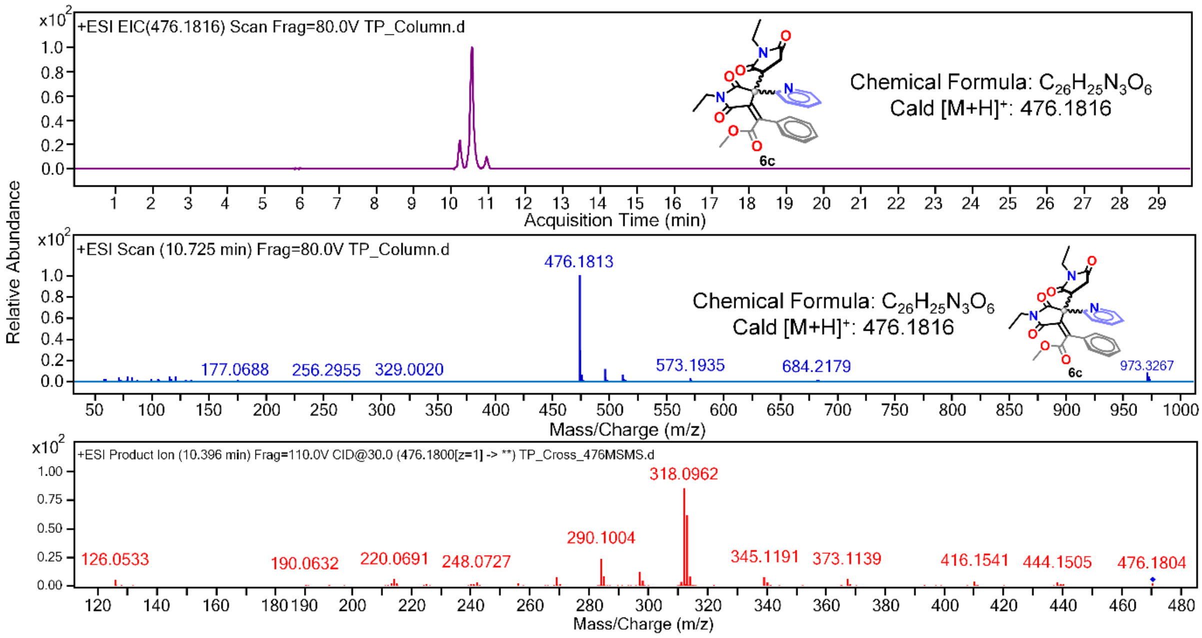


Figure S2: EIC/ESI-HRMS chromatogram of the (**6b**) obtained from the reaction mixture when phenyl diazoacetate (**2b**) treated with pyridine (**1a**), then treated with) N-ethylmaleimide(**3b**), finally irradiate with blue LED. Also showing the ESI/LCMS/MSMS plausible fragmentation pattern of (**6c**).

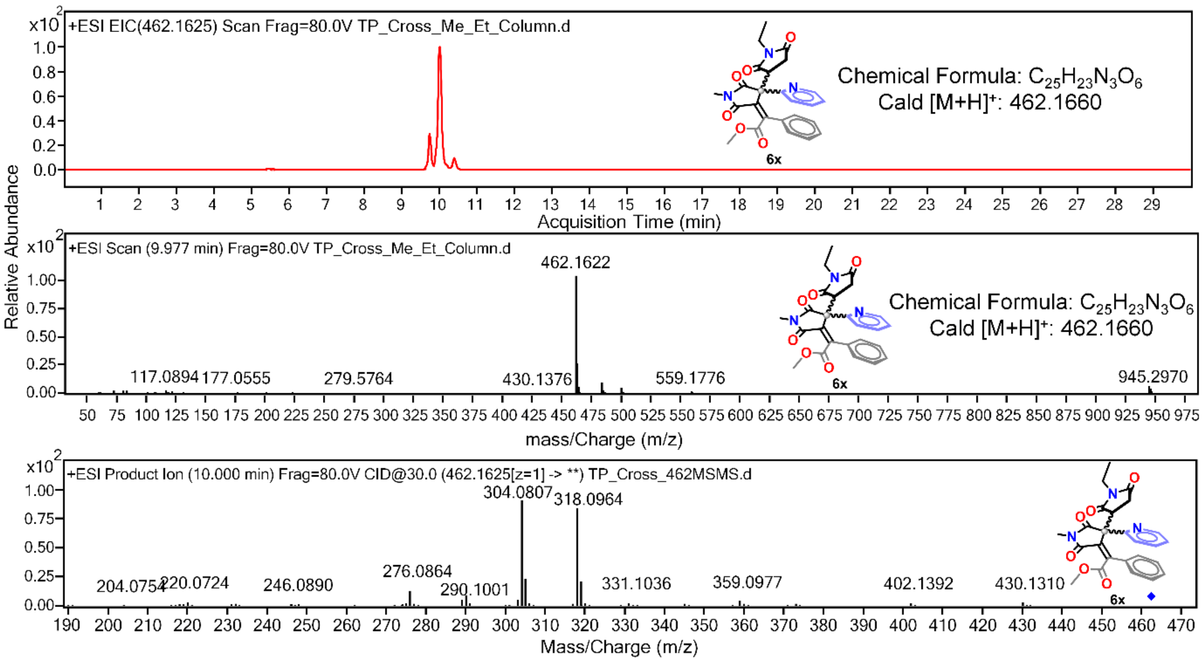


Figure S3: EIC/ESI-HRMS chromatogram of the (**6b**) obtained from the reaction mixture when phenyl diazoacetate (**2b**) treated with pyridine (**1a**), then treated with N-methylmaleimide (**3a**) N-ethylmaleimide(**3b**), finally irradiate with blue LED. Also showing the ESI/LCMS/MSMS plausible fragmentation pattern of (**6x**).

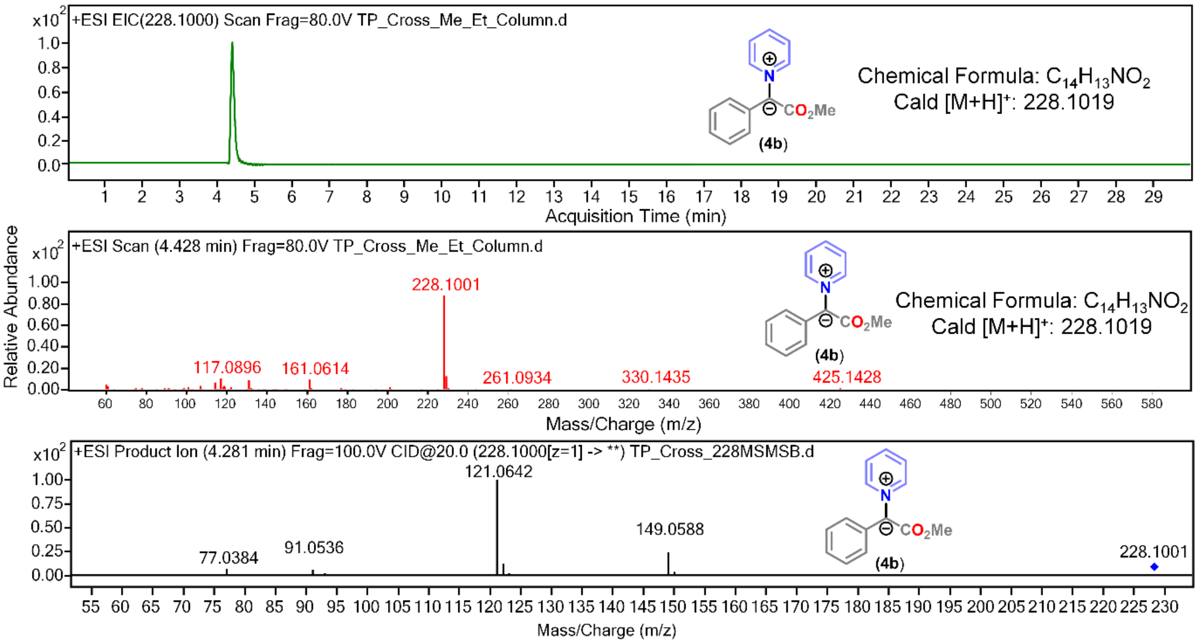


Figure S4: EIC/ESI-HRMS chromatogram of the (**6b**) obtained from the reaction mixture when phenyl diazoacetate (**2b**) treated with pyridine (**1a**), finally irradiate with blue LED. Also showing the ESI/LCMS/MSMS plausible fragmentation pattern of (**4b**).

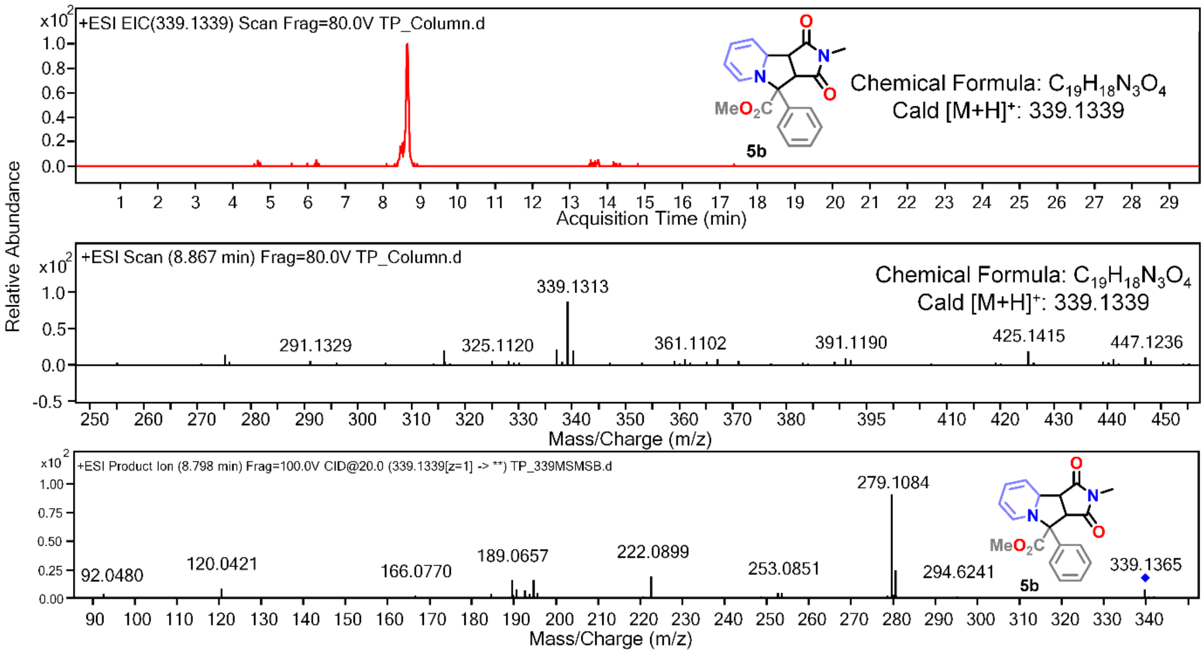


Figure S5: EIC/ESI-HRMS chromatogram of the (**6b**) obtained from the reaction mixture when phenyl diazoacetate (**2b**) treated with pyridine (**1a**), then finally treated with N-methylmaleimide (**3a**)), finally irradiate with blue LED. Also showing the ESI/LCMS/MSMS plausible fragmentation pattern of (**5b**).

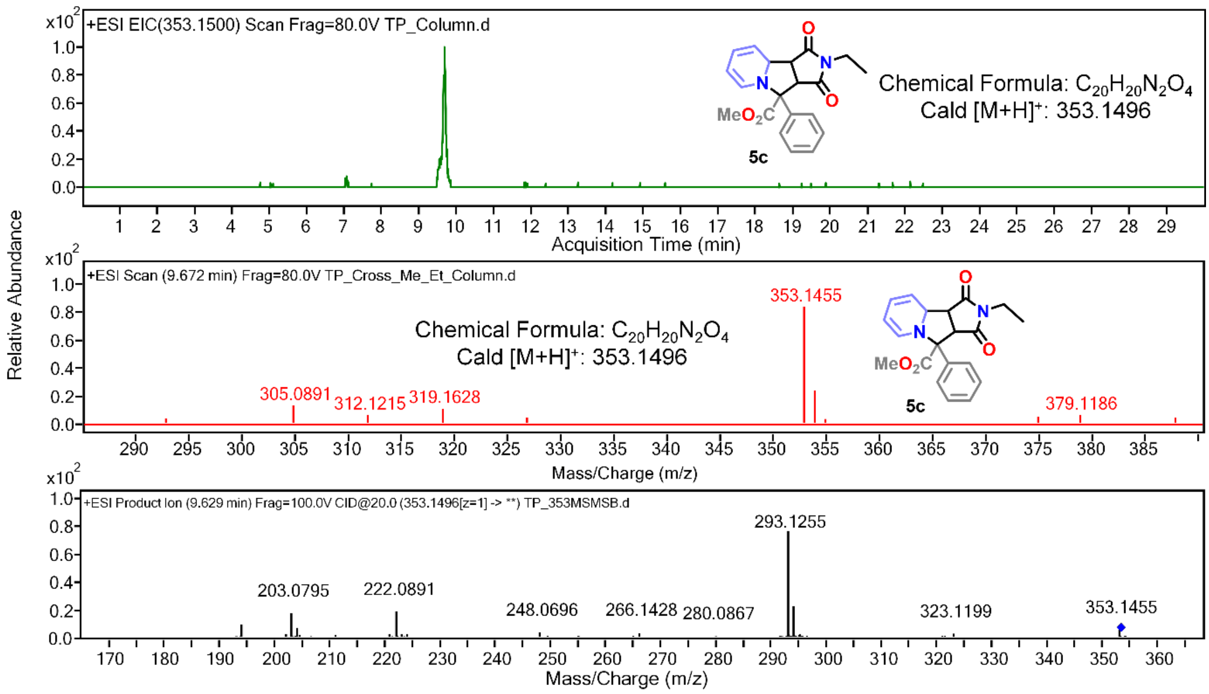


Figure S6: EIC/ESI-HRMS chromatogram of the (**6b**) obtained from the reaction mixture when phenyl diazoacetate (**2b**) treated with pyridine (**1a**), then finally treated with N-methylmaleimide (**3a**) N-ethylmaleimide(**3b**), finally irradiate with blue LED. Also showing the ESI/LCMS/MSMS plausible fragmentation pattern of (**5c**).

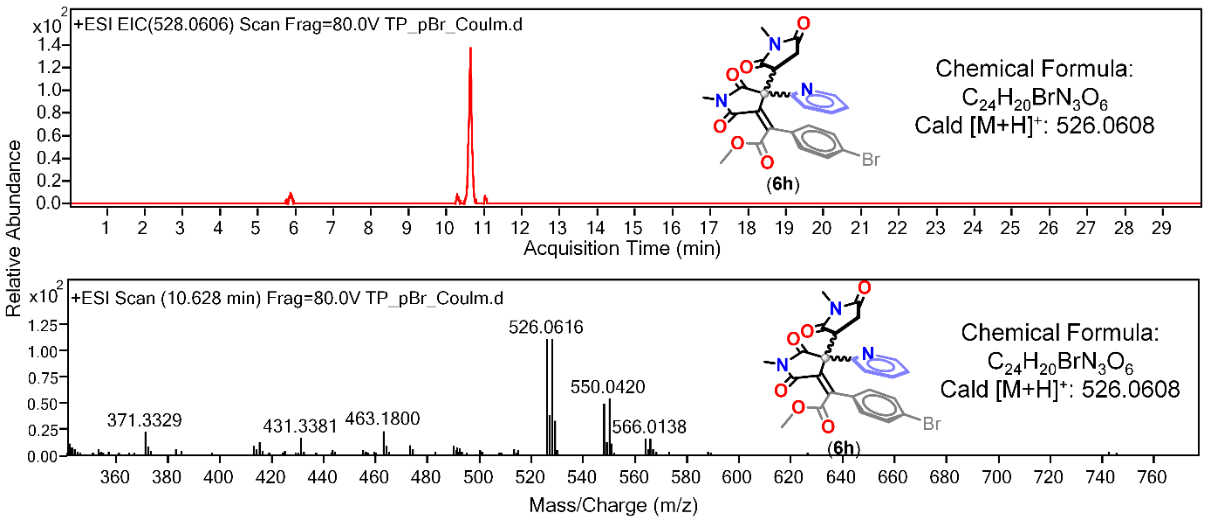


Figure S7: (A) EIC/ESI-HRMS chromatogram of the (**6b**) obtained from the reaction mixture when 4-bromo phenyl diazoacetate (**2h**) treated with pyridine (**1a**), then treated with N-methylmaleimide (**3a**), finally irradiate with blue LED. Also showing the ESI/LCMS/MSMS plausible fragmentation pattern of (**6h**).

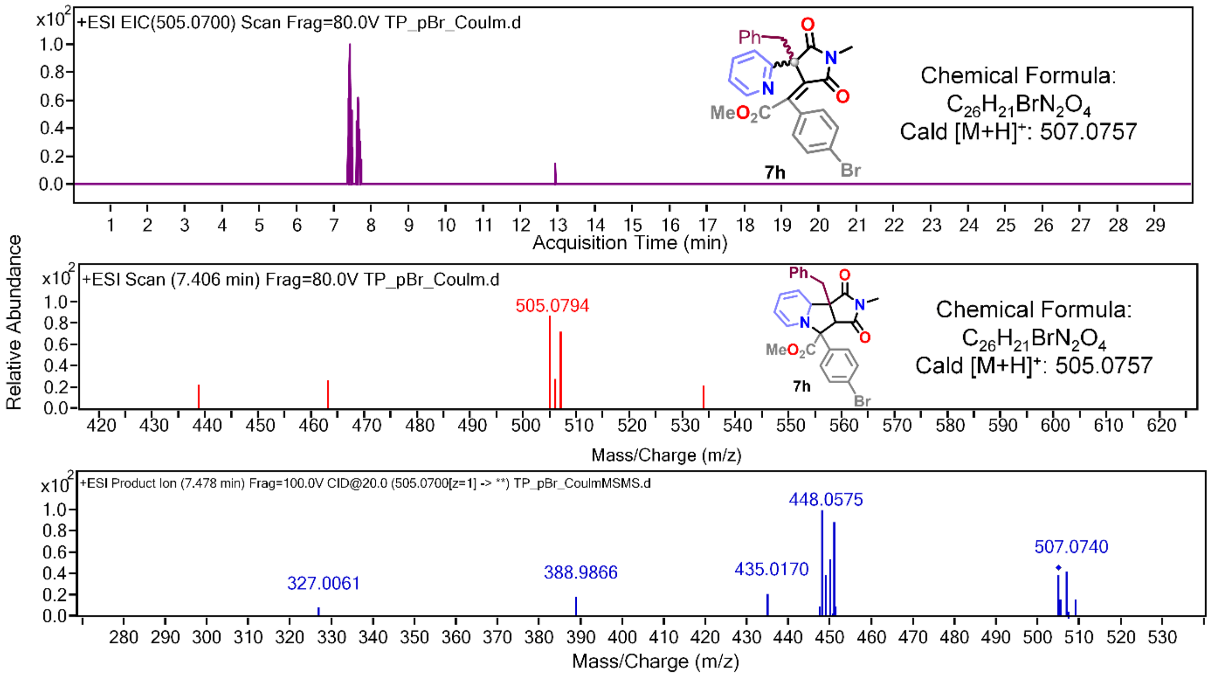


Figure S8: (A) EIC/ESI-HRMS chromatogram of the (**6b**) obtained from the reaction mixture when 4-bromophenyl diazoacetate (**2h**) treated with pyridine, then treated with N-methylmaleimide (**3a**) benzyl bromide, finally irradiate with blue LED. Also showing the the ESI/LCMS/MSMS plausible fragmentation pattern of (**7h**).

4. DFT Calculations:

All the calculations are performed by using B3LYP[2] level of theory as implemented in the Gaussians 09 package.[3] For geometry optimizations, 6-311++G (2d, p) basis set was used for all atoms. Frequency calculations of all the optimized structures were performed to ensure that the optimized structures were the local energy minima without any imaginary frequency, and to obtain zero-point corrections and the Gibbs free energies. Transition states were obtained using Berny optimization algorithm implemented in Gaussian 09 and were in each case verified the presence of a single imaginary vibrational frequency associated with the desired reaction coordinate. Moreover, solvent plays a crucial role on the blue LED mediated multicomponent reaction. Therefore, the solvent effect has been considered in self-consistent reaction field method (SCRF)[4] First, all the compound has been optimized B3LYP/6-311++G(2d,p) by SCRF model using acetonitrile (ACN) as a solvent. Furthermore, dispersion correction factor D3 has been implemented in the all calculation for more precise results.[5] All the compounds has been optimized by using different functional using same 6-311++G(2d,p) basis set. Whereas natural bond orbital calculations were performed in 6-311++G (2d, p). The NBO Version 3.1 program implemented in Gaussian 03 was used to perform NPA. All the HOMO and LUMO visualisation files were generated from FCHK file by the help of chemcraft software. The NBO Version 3.1 program implemented in Gaussian 09 was used to perform NPA[6] Frequency calculations were performed at the optimization level of basis set to confirm the nature of stationary points, and to obtain zero-point corrections and the Gibbs free energies.

The reaction free energies (ΔG) (the Gibbs free energies i.e., the term of the sum of electronic and thermal free energies) are calculated using the following equation.

$$\Delta G = G_{product} - G_{reactant}$$

Similarly, transition state energy calculated as follows

$$\Delta G^{\ddagger} = G_{transition\ state} - G_{reactant}$$

Where $G_{product}$ and $G_{reactant}$ are the total energies of products and reactants respectively.

Table S1: Optimized Energy of the Reactants, Products, and Transition States of Blue LED mediated multicomponent reaction between phenyl diazoacetate (**2b**) with N-methylmaleimide (**3a**), pyridine (**1a**) by considering the Z conformer.

	B3LYP(PCM)/6-311++ G (2d, p) Empirical dispersion GD3 [E^h], in Pyridine A.U.	Thermal correction to Gibbs Free Energy	Relative Energy (kcal mol^{-1})	Imaginary Frequency
1a	-248.3678676	0.061745 A.U.	–	–
2b	-607.8723681	0.168777 A.U.		
1a+**2b**	-856.2402367	0.230522 A.U.		
carbene	-498.2914184	0.109166 A.U.		
Nitrogen (**N_2**)	-109.563792	0.007911 A.U.		
1a+carbene	-746.659286	0.170911 A.U.	-	
1a+carbene+N_2	-856.223078	0.178822 A.U.	+10.76	
[Ylide]‡_reverse	-746.668989	0.147891 A.U.	-6.08	
[Ylide]‡	-746.6438051	0.189499 A.U.	+15.80	-243.4324
Ylide (**4**)	-746.7382358	0.195465 A.U.	-43.45	
(**3a**)	-398.8992285	0.101862 A.U.		
[TS2]‡_reverse	-1145.647453	0.147891 A.U.	-6.26	
[TS2]‡	-1145.602125	0.254789 A.U.	+28.44	-453.1248
[TS1]‡_forward	-1145.604158	0.241789 A.U.	-1.27	
Cycloaddition (**3a**+**4**)	-1145.6374643	0.297327 A.U.		
[3+2] adduct (**5b**)	-1145.580765	0.264308 A.U.	35.58	–
(½)O_2	-75.1873828			
Water (H_2O)	-76.461212	0.245789 A.U.		
B	-1144.415849	0.262972 A.U.	-68.34	–
(C)	-1143.975489	0.248971 A.U.		
Lewis base **1a**	-248.3678676	0.061745 A.U.		
Hpyridine+ H**1a**(+)	-248.8101003		-1.17	
C + **3a**	- 1542.8747175	0.278546 A.U.	-13.7	
9	-1542.895151	0.291867 A.U.	-12.82	
[TOPTS3]‡	-1542.857915	0.002882 A.U.	23.36	-576.2631
[BottomTS3]‡	-1542.857748	0.245897 A.U.	23.47	-580.2186
12	-1619.309133		6.27	
13	-1619.308397	0.007585 A.U.	0.46	
[TOPTS4]‡	-1619.284578	0.124589 A.U.	14.94	-1248.1245
[BottomTS4]‡	-1619.284815		14.79	-1178.1245
Hydroxide(-OH)	-75.9596430	0.298928 A.U.		
16	-1619.357161	0.027485 A.U.	-45.54	
17	-1619.342182	0.124581 A.U.	-35.99	

6b	-1543.398160	0.215486 A.U.		
6b'	-1543.382539	0.245879 A.U.		

Table S2: Optimized Energy of the Reactants, Products, and Transition States of Blue LED mediated multicomponent reaction between phenyl diazoacetate (**2b**) with N-methylmaleimide (**3a**), pyridine (**1a**) by considering the E conformer.

	B3LYP(PCM)/6-311++ G (2d, p) Empirical dispersion GD3 [E^h], in Pyridine A.U.	Thermal correction to Gibbs Free Energy	Relative Energy (kcal mol^{-1})	Imaginary Frequency
1a	-248.3678676	0.061745 A.U.	–	–
2b	-607.8723681	0.168777 A.U.		
1a+2b	-856.2402367	0.230522 A.U.		
carbene	-498.2914184	0.109166 A.U.		
Nitrogen (**N_2**)	-109.563792	0.007911 A.U.		
1a+carbene	-746.659286	0.170911 A.U.	-	
1a+carbene+N_2	-856.223078	0.178822 A.U.	+10.76	
[Ylide]‡_reverse	-746.668989	0.147891 A.U.	-6.08	
[Ylide]‡	-746.6438051	0.189499 A.U.	+15.80	-243.4324
Ylide (**4**)	-746.7382358	0.195465 A.U.	-43.45	
(**3a**)	-398.8992285	0.101862 A.U.	0	
[TS2]A‡_reverse	-1145.646549	0.214581 A.U.	-5.70055	-496.2458
[TS2]A‡	-1145.602125	0.201458 A.U.	27.87604	
[TS1]A‡_forward	-1145.605012	0.224589 A.U.	-1.81137	–
Cycloadduct (**5b**)	-1145.580765	0.262972 A.U.	15.2151	–
(½)O_2	-75.1873828			
Water (H_2O)	-76.461212	0.245789 A.U.		
B	-1144.415849	0.012410 A.U.	0	–
(c)	-1143.975489	0.278546 A.U.	0	
Lewis base **1a**	-248.3678676	0.061745 A.U.		
Hpyridine+ H**1a**(+)	-248.8101003		-1.17	
C + 3a	- -1542.8747175	0.291867 A.U.	-13.7	
[TOPTS3]A‡ reverse	-1542.889748	0.145891 A.U.	-9.43172	-609.2145
[TOPTS3]A‡	-1542.858749	0.147859 A.U.	19.45217	-601.1245
[BottomTS3]A‡	-1542.858215	0.124589 A.U.	19.78751	
Water (H_2O)	-76.461212	0.145897 A.U.	0	
[TOPTS3]A‡+H_2O	-1619.319961		0	
[BottomTS3]A‡+ H_2O	-1619.319427		0	
[TOPTS3]A‡_forward	-1619.291458	0.201245 A.U.	17.88597	
[TOPTS4]A‡_reverse= [Bottom TS4]A‡_reverse	-1619.28489	0.124589 A.U.	4.121413	-1121.1245
[TOPTS4]A‡	-1619.259778		15.75777	-1045.8457
[BottomTS4] ‡	-1619.259875	0.298928 A.U.	15.6974	
Hydroxide(-OH)	-75.959643	0.027485 A.U.	0	
[TOPTS4]‡_forward	-1619.364589	0.214589 A.U.	-65.7696	
[Bottom TS4]‡_forward	-1619.36758	0.174895 A.U.	-67.5862	

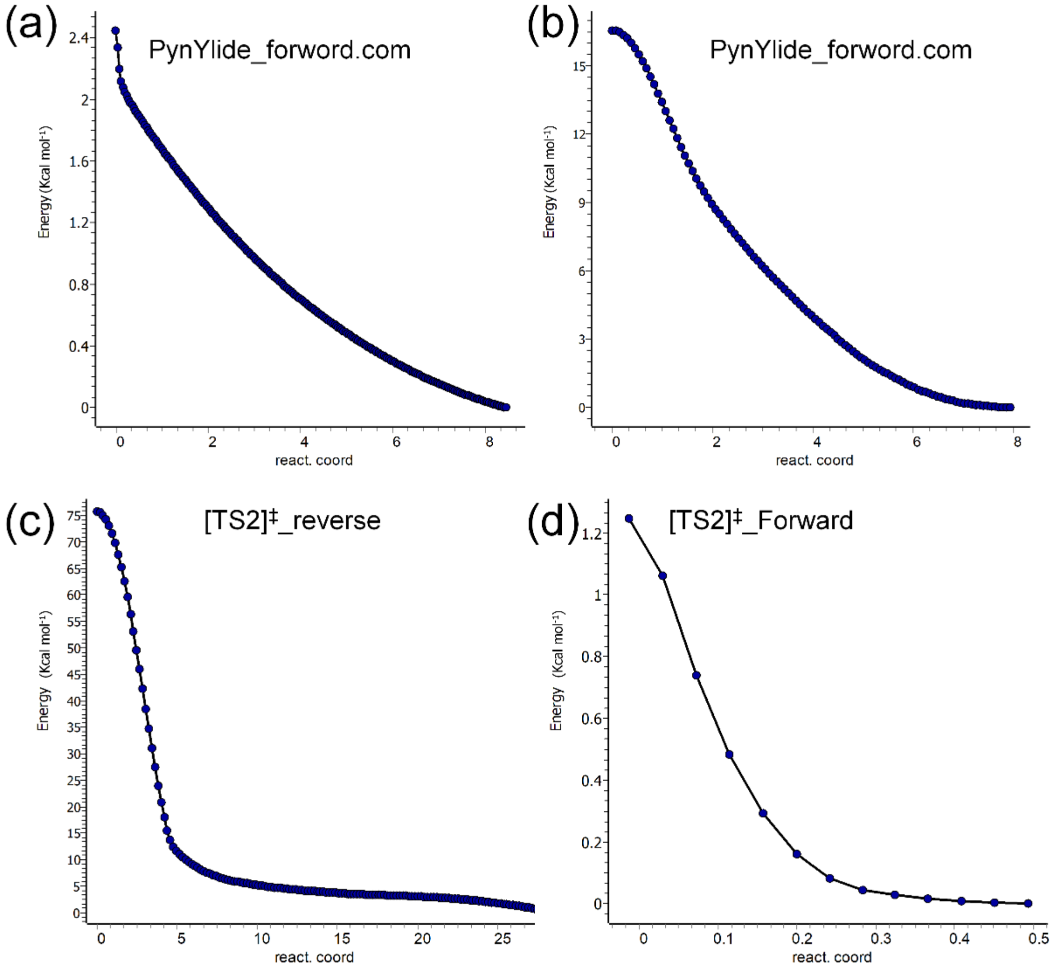


Figure S9: Intrinsic reaction coordinate calculation for (a and b)TS1 and (c and d) TS2

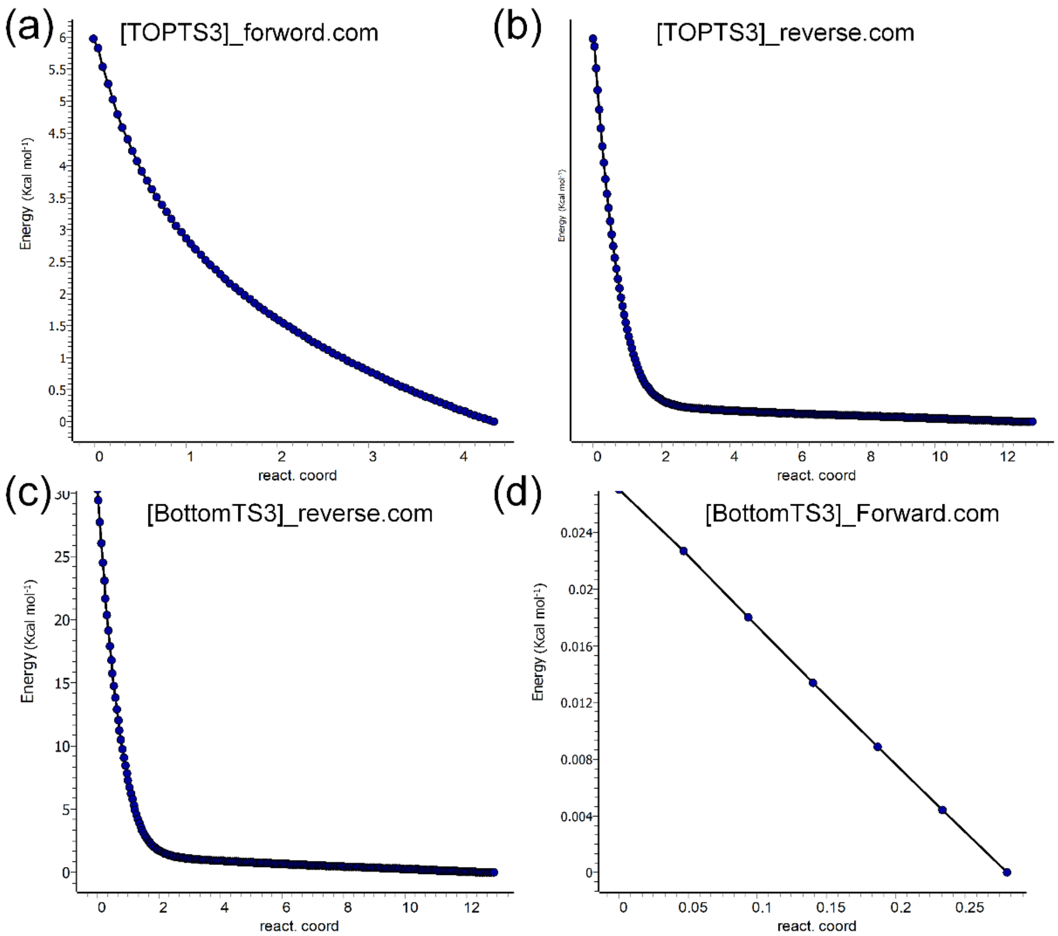


Figure S10: Intrinsic reaction coordinate calculation for (a and b) [TOPTS3] and (c and d) [BottomTS3]

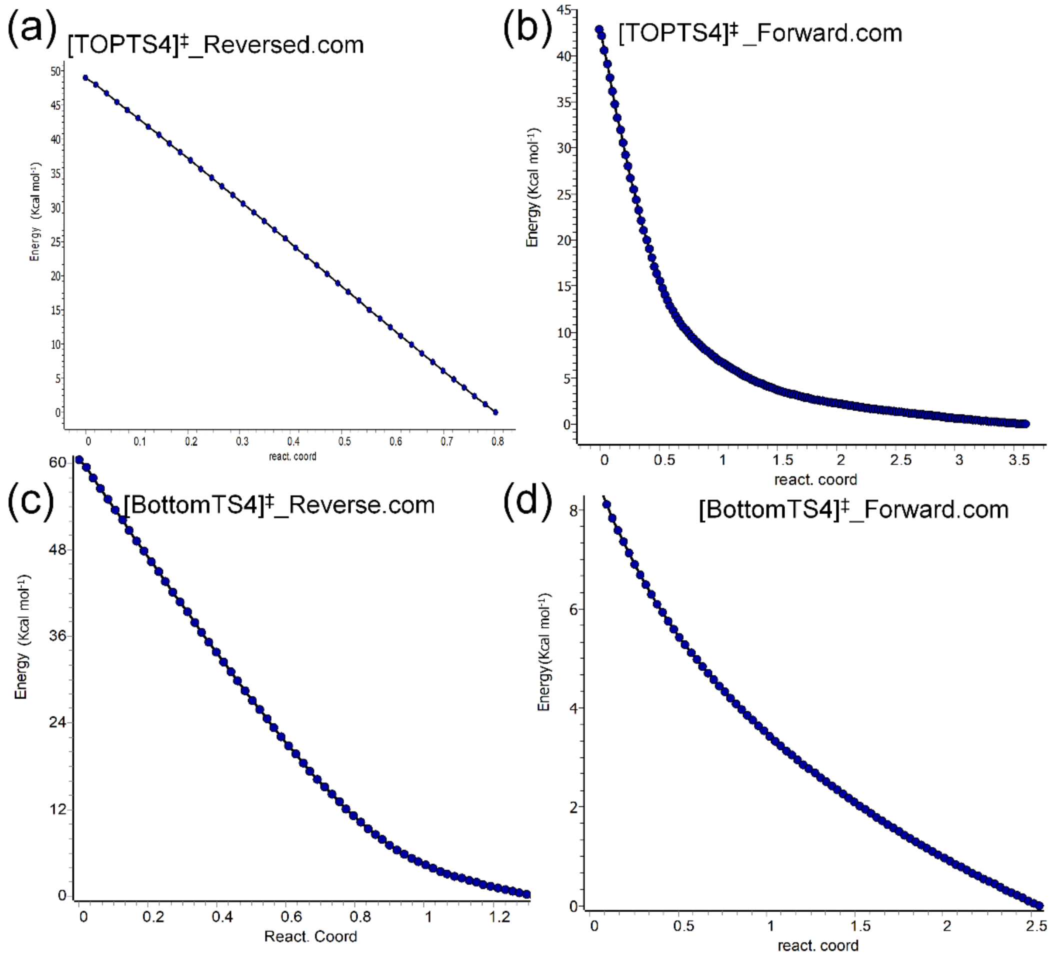


Figure S11: Intrinsic reaction coordinate calculation for (a and b) [TOPTS4] and (c and d) [BottomTS4]

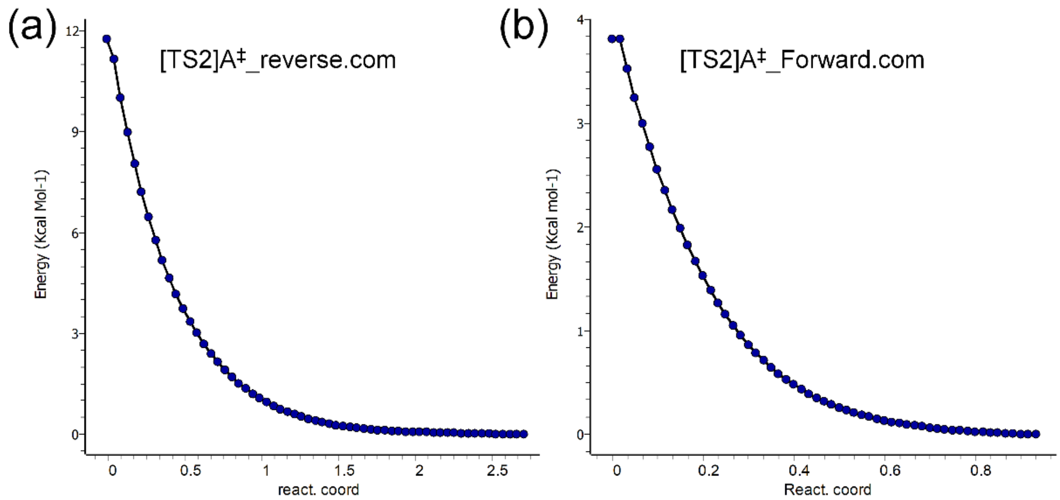


Figure S12: Intrinsic reaction coordinate calculation for (a and b) [TS2]A.

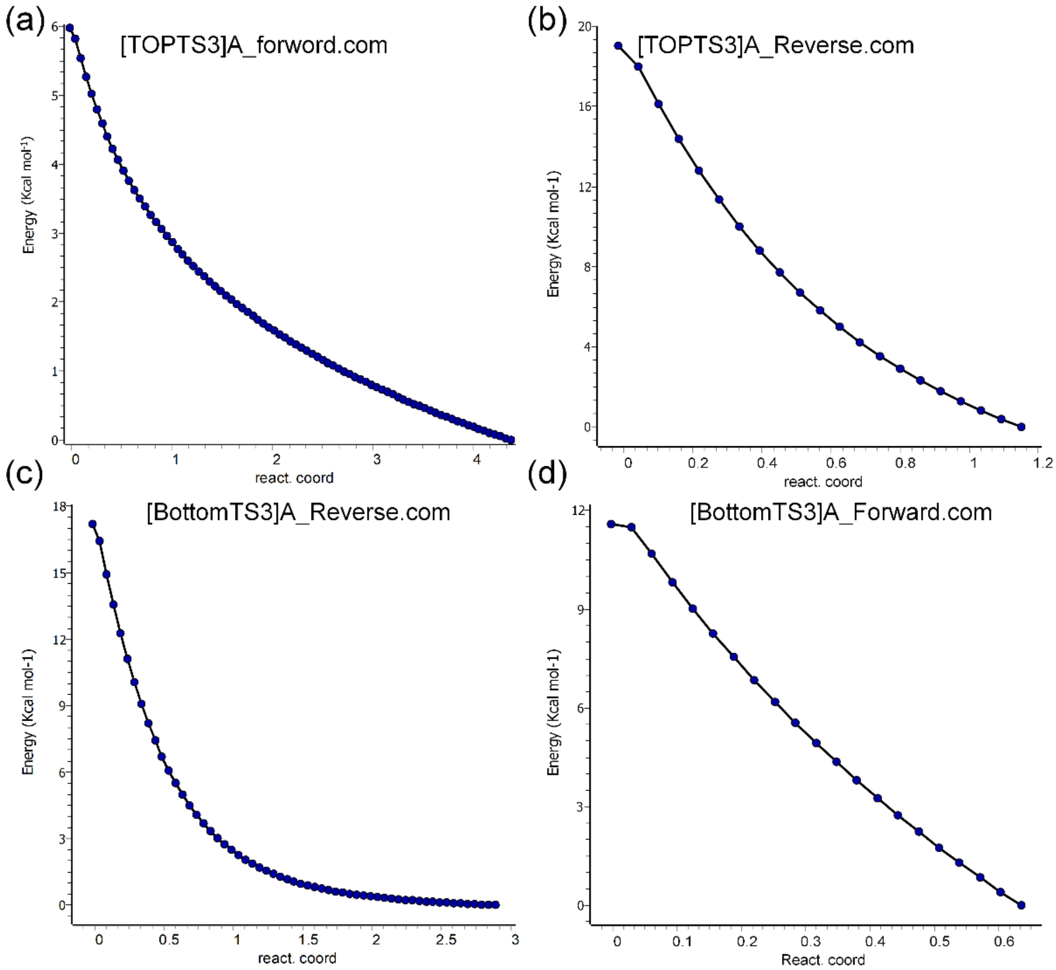


Figure S13 Intrinsic reaction coordinate calculation for (a and b) [TOPTS3] and (c and d) [BottomTS3]

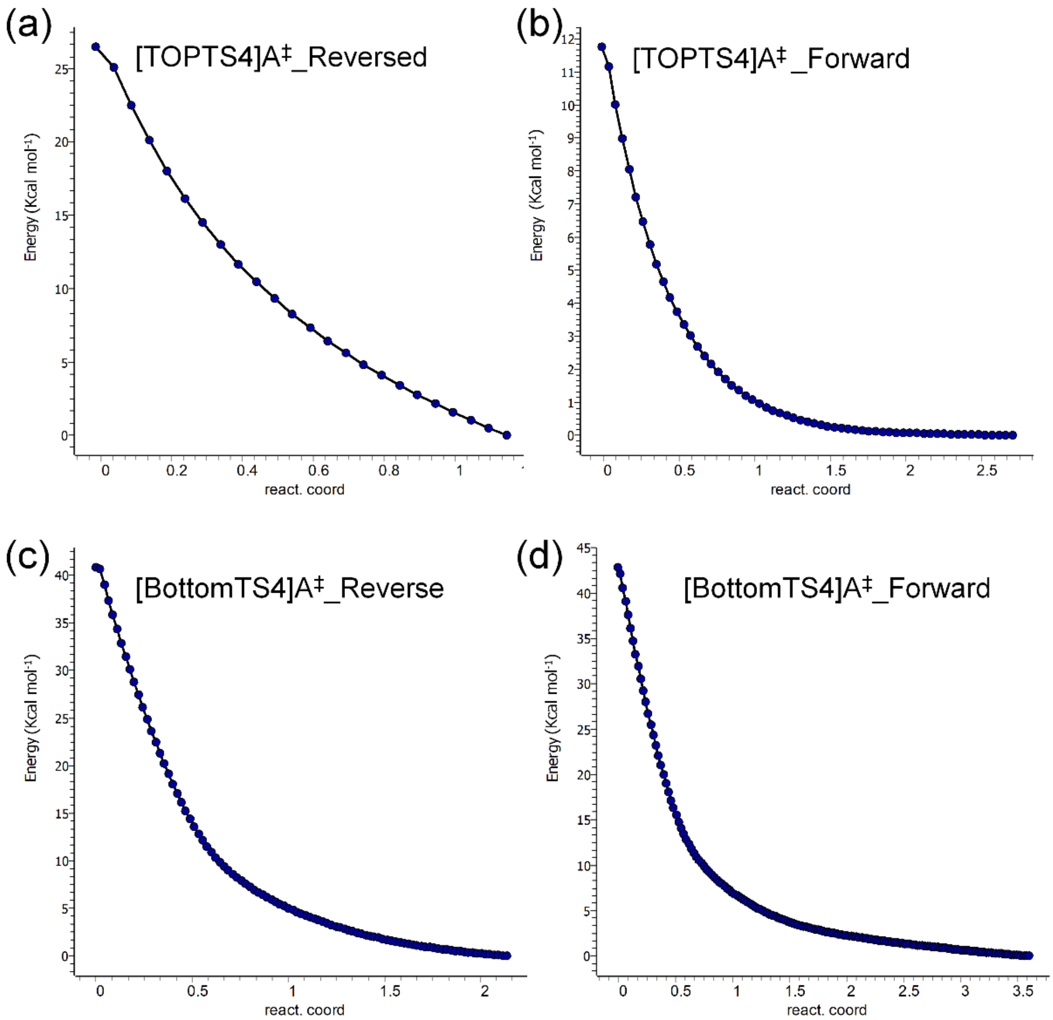


Figure S14 Intrinsic reaction coordinate calculation for (a and b) [TOPTS4]A and (c and d) [BottomTS4]A

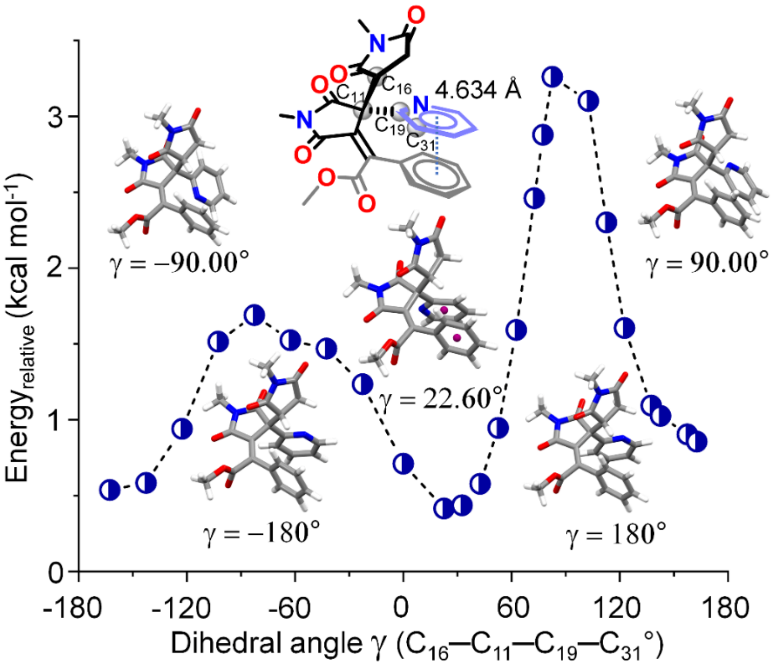


Figure S15: Variation of relative stabilization energy of **6b** for the change in the C_{16}-C_{11}-C_{19}-C_{31} dihedral angle. The single-point energies were calculated using B3LYP(PCM)/6-311++G(d,p) level of theory in water as a solvent with dispersion correction D3.

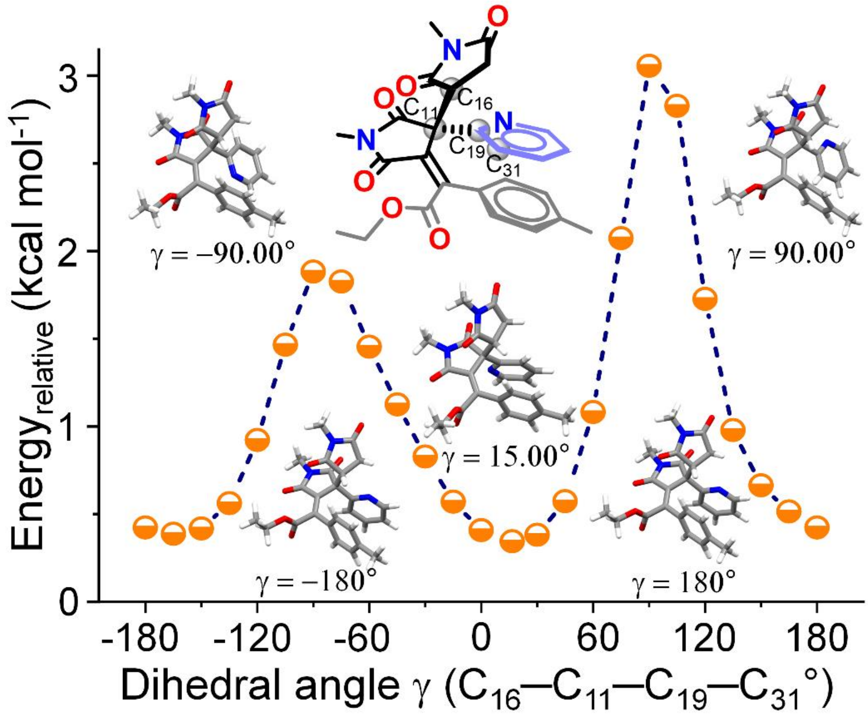
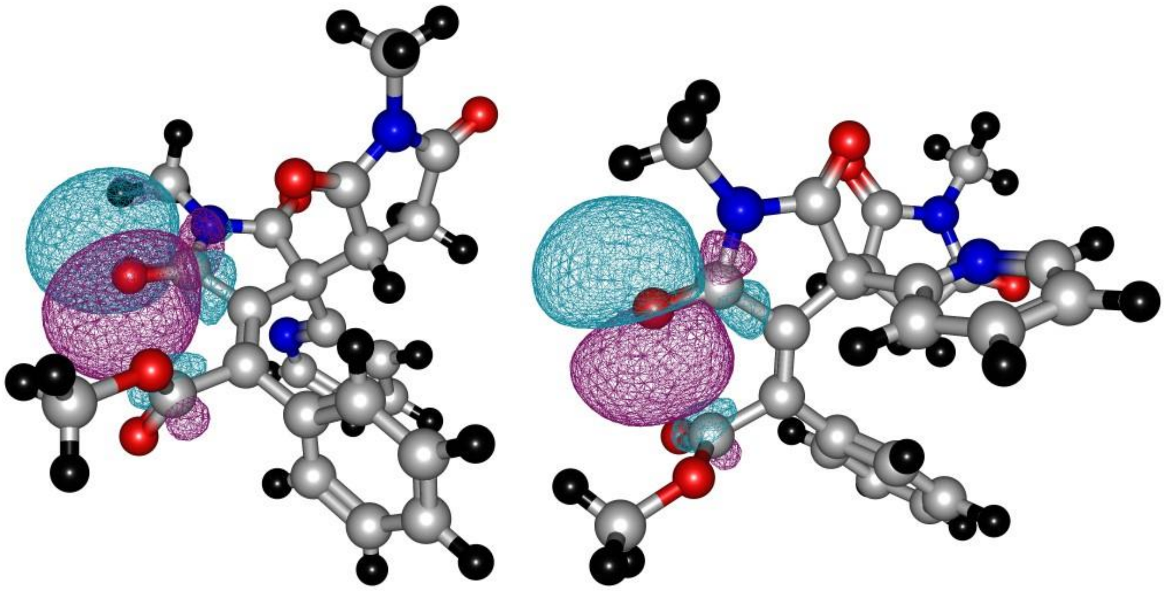


Figure S16: Variation of relative stabilization energy of **6a** for the change in the C_{16}-C_{11}-C_{19}-C_{31} dihedral angle. The single-point energies were calculated using B3LYP(PCM)/6-311++G(d,p) level of theory in water as a solvent with dispersion correction D3.



6b **6b'**

Figure S17: N-π* intraction stabilizing the Z conformer in 6b and 6b'

```
Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis 6b

     Threshold for printing:   0.50 kcal/mol

                                                                    E(2)  E(j)-E(i) F(i,j)
    Donor NBO (i)                         Acceptor NBO (j)        kcal/mol   a.u.    a.u.
==============================================================================================


108. LP (   2) O   3          /976. BD*(   1) N   5 - C  13           28.22  0.69  0.126
108. LP (   2) O   3          /982. BD*(   2) O   7 - C  26            2.88  0.28  0.026
108. LP (   2) O   3          /989. BD*(   1) C  10 - C  13           17.93  0.71  0.103
```

```
Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis 6b'

     Threshold for printing:   0.50 kcal/mol

                                                                    E(2)  E(j)-E(i) F(i,j)
    Donor NBO (i)                         Acceptor NBO (j)        kcal/mol   a.u.    a.u.
==============================================================================================

106. LP (   2) O   2         /973. BD*(   1) N   4 - C   9          27.53     0.70     0.126
106. LP (   2) O   2         /976. BD*(   2) O   5 - C  18           3.02     0.28     0.026
106. LP (   2) O   2         /978. BD*(   1) C   6 - C   9          18.26     0.71     0.104
```

5. Single-crystal XRD analysis:

Single crystal data collections and corrections with D8 Venture Bruker AXS single-crystal X-ray diffractometer equipped with CMOS PHOTON 100 detector having monochromatized microfocus sources (Mo-Kα = 0.71073 Å). Single crystals of **6a** (CCDC 2110512) suitable for X-ray diffraction study were obtained from the slow evaporation process. The structure solution and refinement were performed by using the SHELX program implemented in APEX3.[8-10] The non-H atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters. All the hydrogen atoms were placed at the hybridized positions and refined using a riding model with appropriate HFIX commands. The molecular structures were drawn by ORTEP.[11]

Table S3: Crystallographic data for **6a**

CCDC No	2110512	**Radiation (λ)/A°**	0.71073
Lattice	Orthorhombic	**ρ/ (g cm^{-3})**	1.309
Formula	$C_{26}H_{25}N_3O_6$	**μ (Mo K$_α$) mm^{-1}**	0.094
Formula Weight	475.49	**θ$_{max}$/deg**	26.379
Space Group	*P b c a*	**Collected reflections**	50005
a/ A°	12.6825(3)	**Unique reflections**	4921
b/ A°	14.3250(4)	**No of parameters**	297
c/ A°	26.5675(6)	**R$_1$ [I> 2σI]**	0.1071
α/ °	90	**wR$_2$ [I> 2σI]**	0.0554
β/ °	90	**R$_1$ [all data]**	0.0228
γ/ °	90	**wR$_2$ [all data]**	0.3348
V/ A°^{3}	4826.7(2)	**R$_{int}$ [all data]**	0.1499
Z	8	**GOF**	1.068

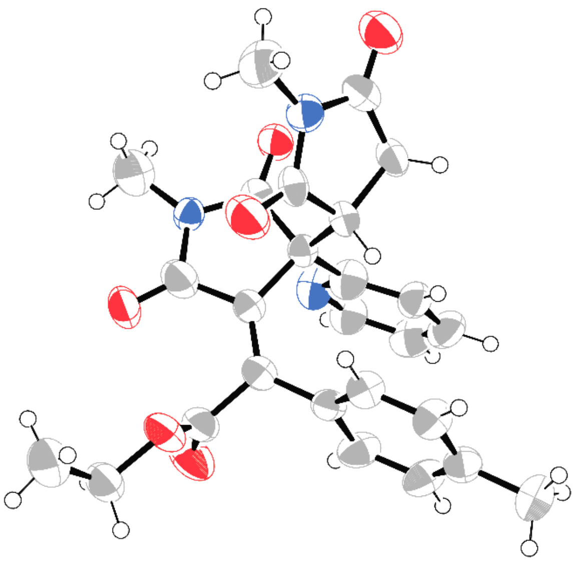
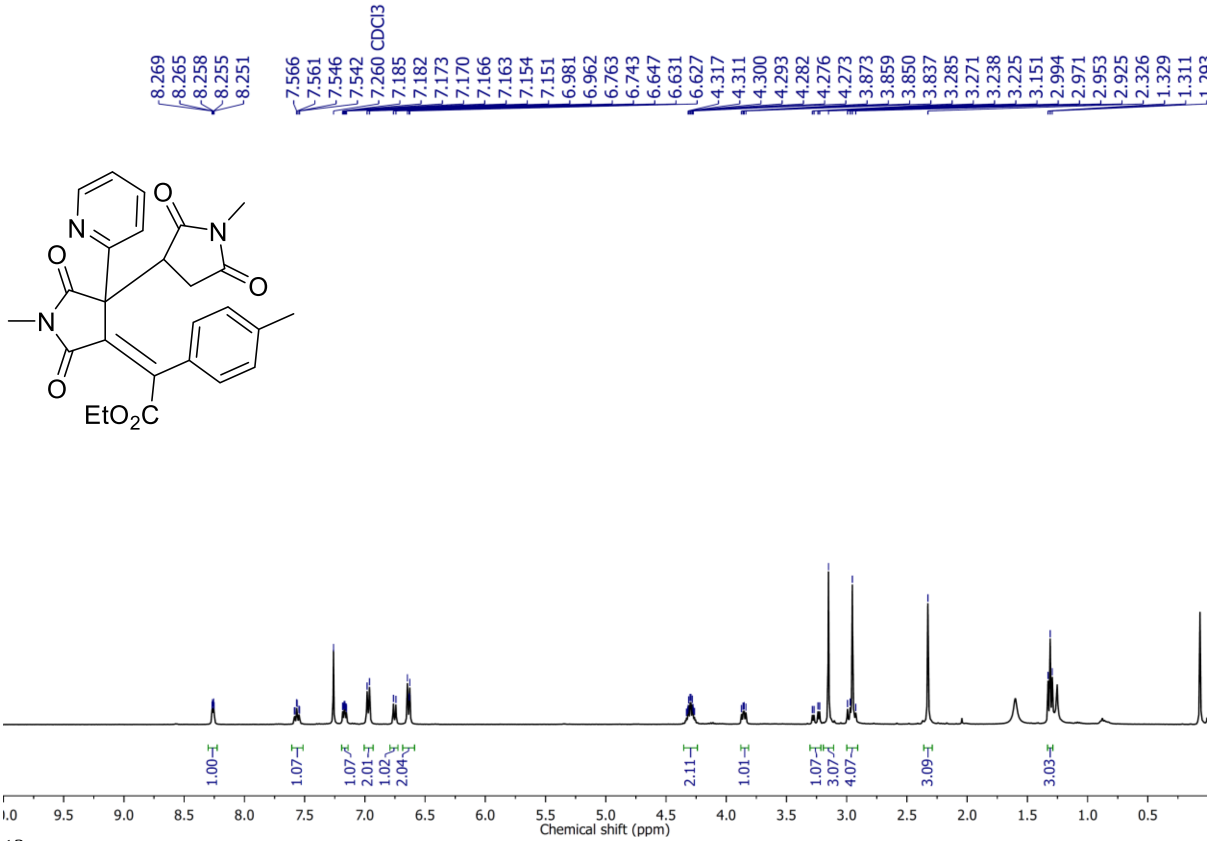


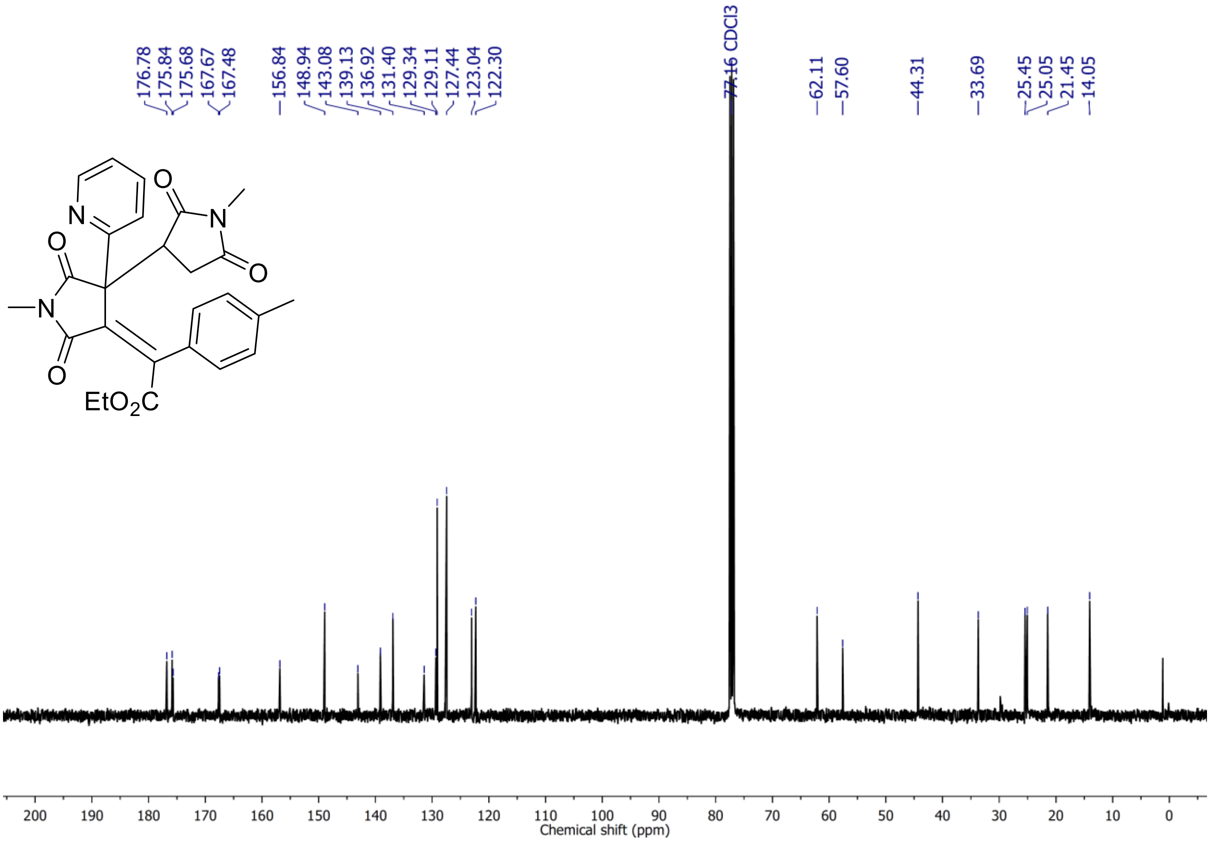
Figure S18: ORTEP diagram of **6a**

6. NMR Spectra:

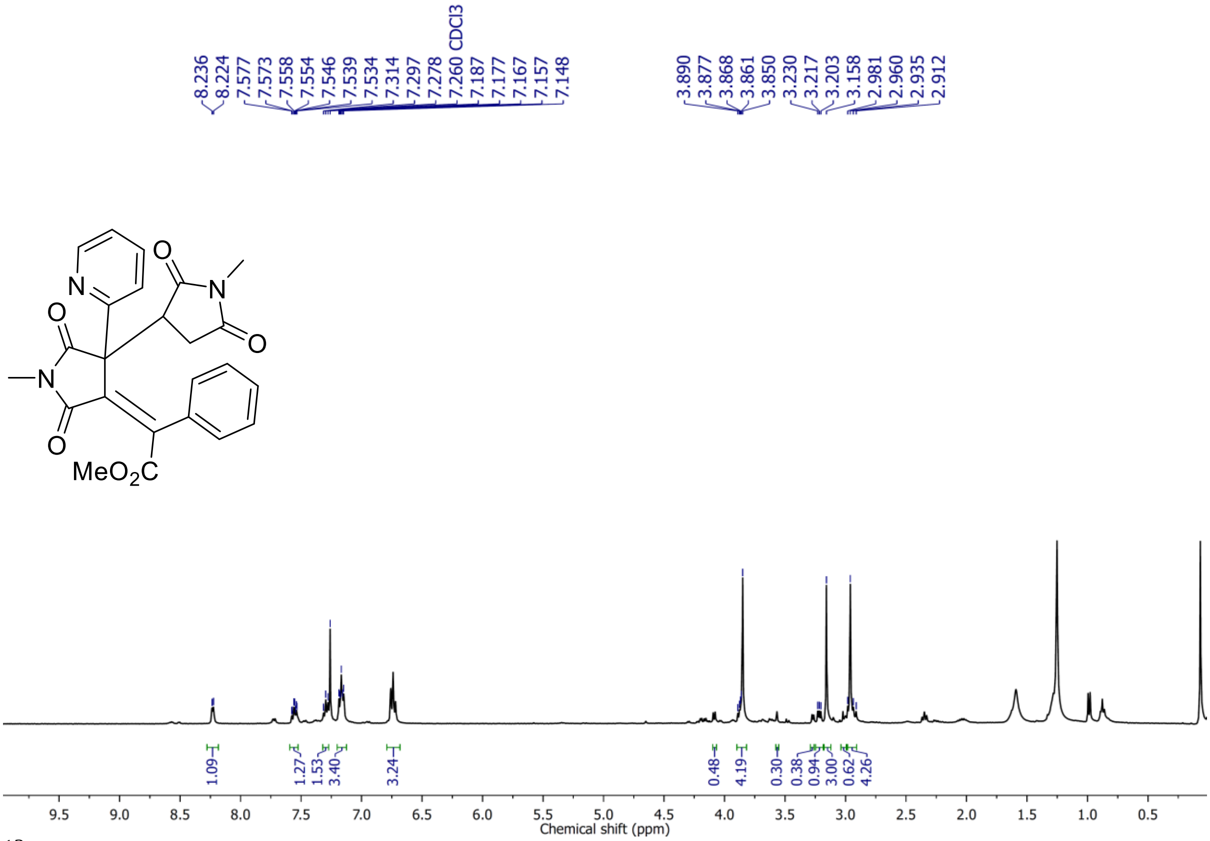
^{1}H NMR (400 MHz) of **6a** in $CDCl_3$



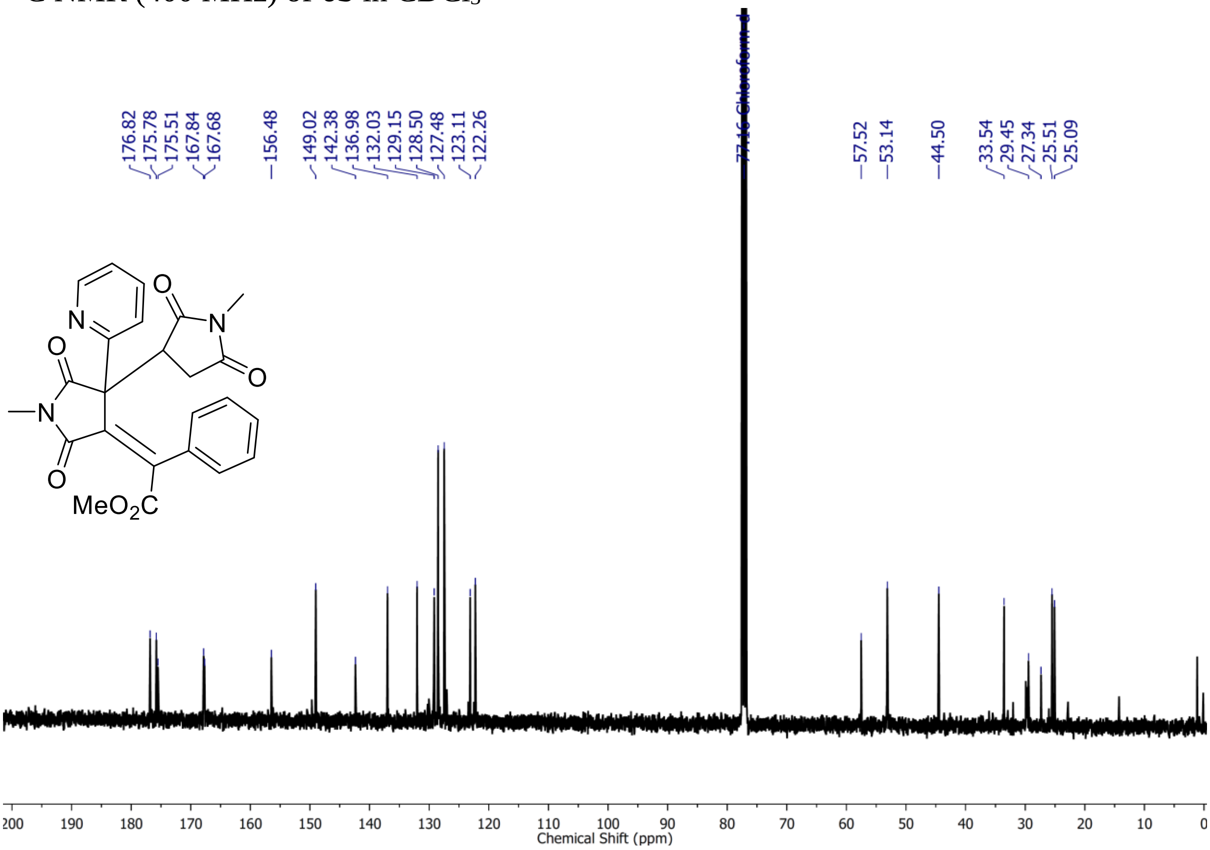
^{13}C NMR (400 MHz) of **6a** in $CDCl_3$



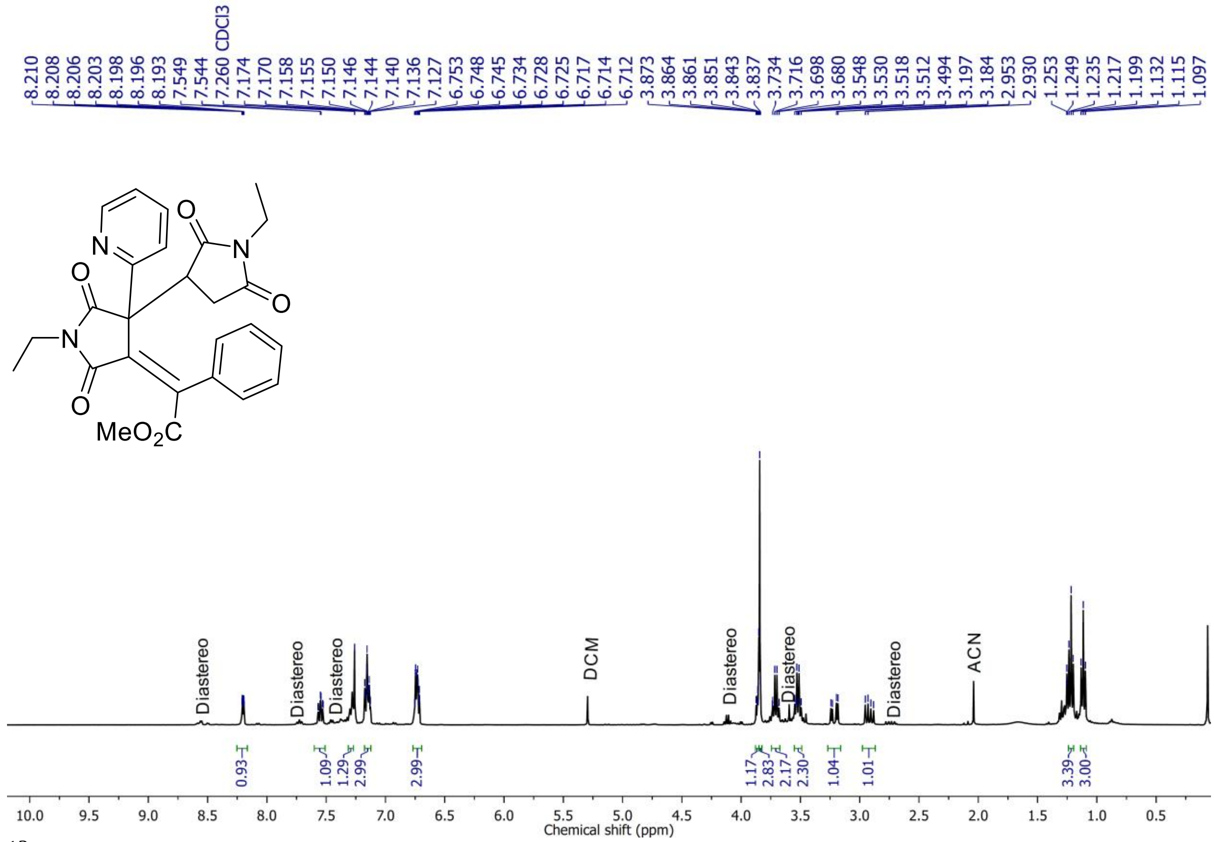
[1]H NMR (400 MHz) of **6b** in $CDCl_3$



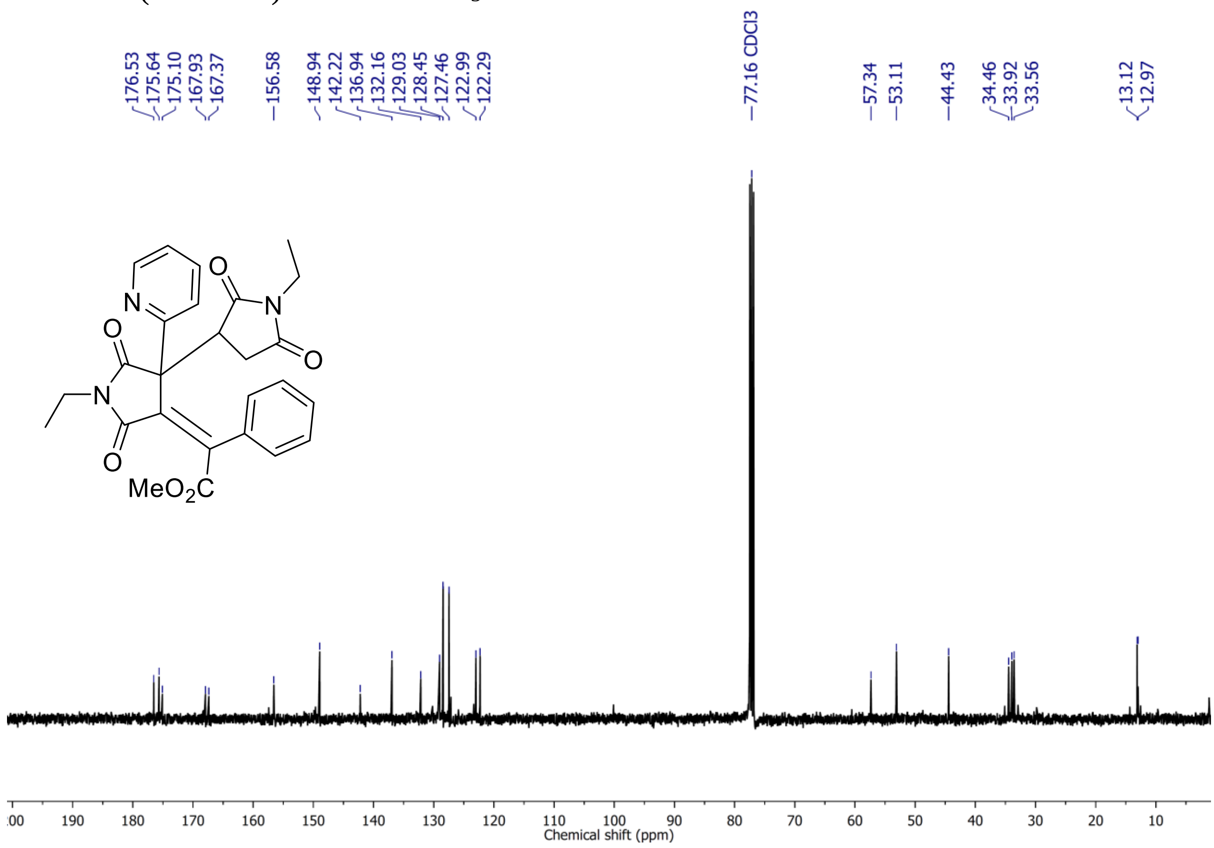
[13]C NMR (400 MHz) of **6b** in $CDCl_3$



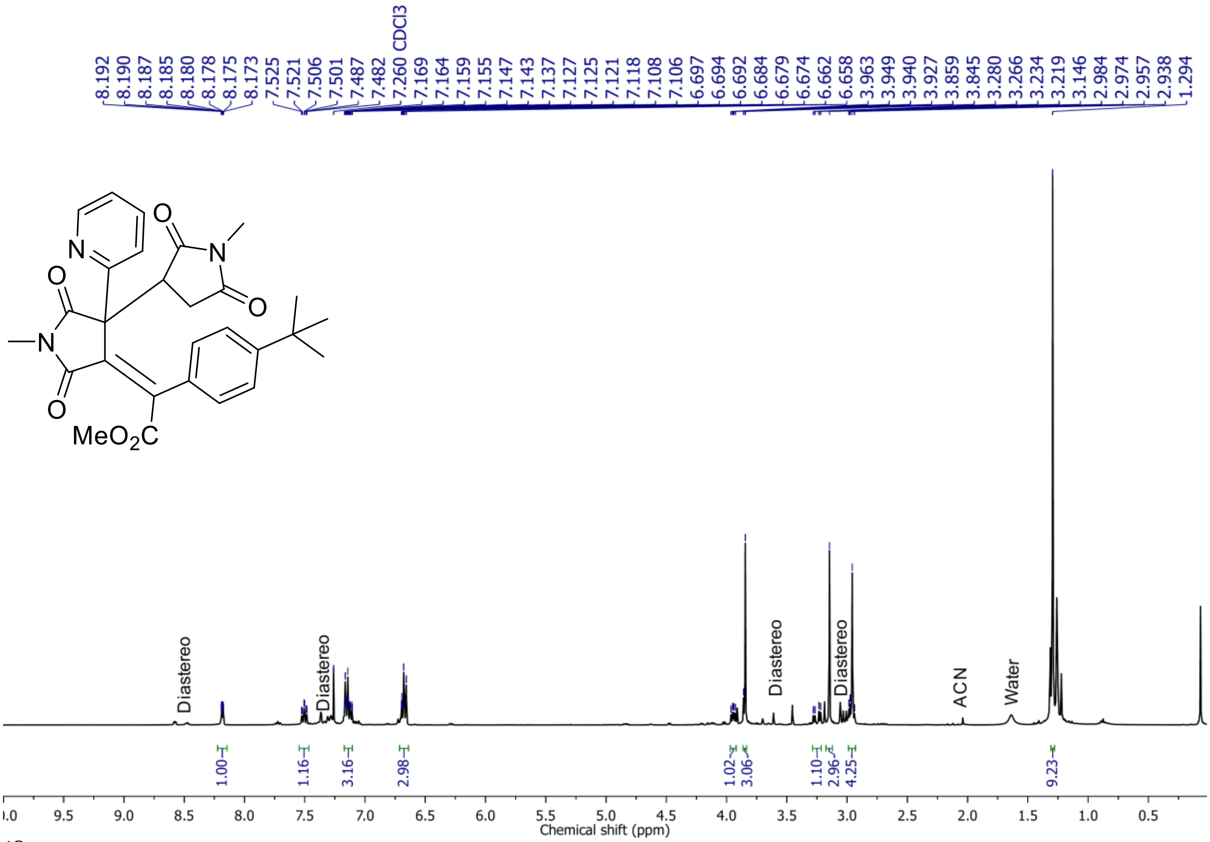
^{1}H NMR (400 MHz) of **6c** in $CDCl_3$



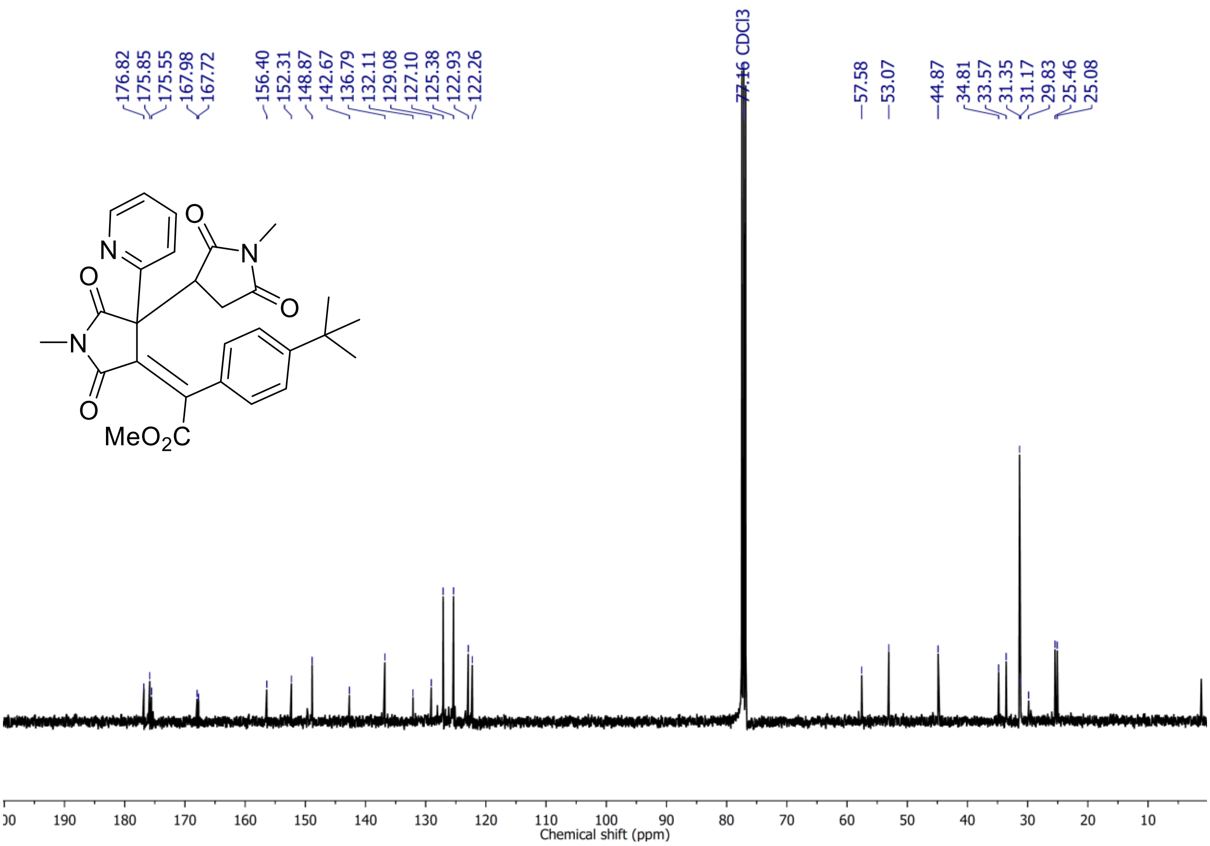
^{13}C NMR (400 MHz) of **6c** in $CDCl_3$



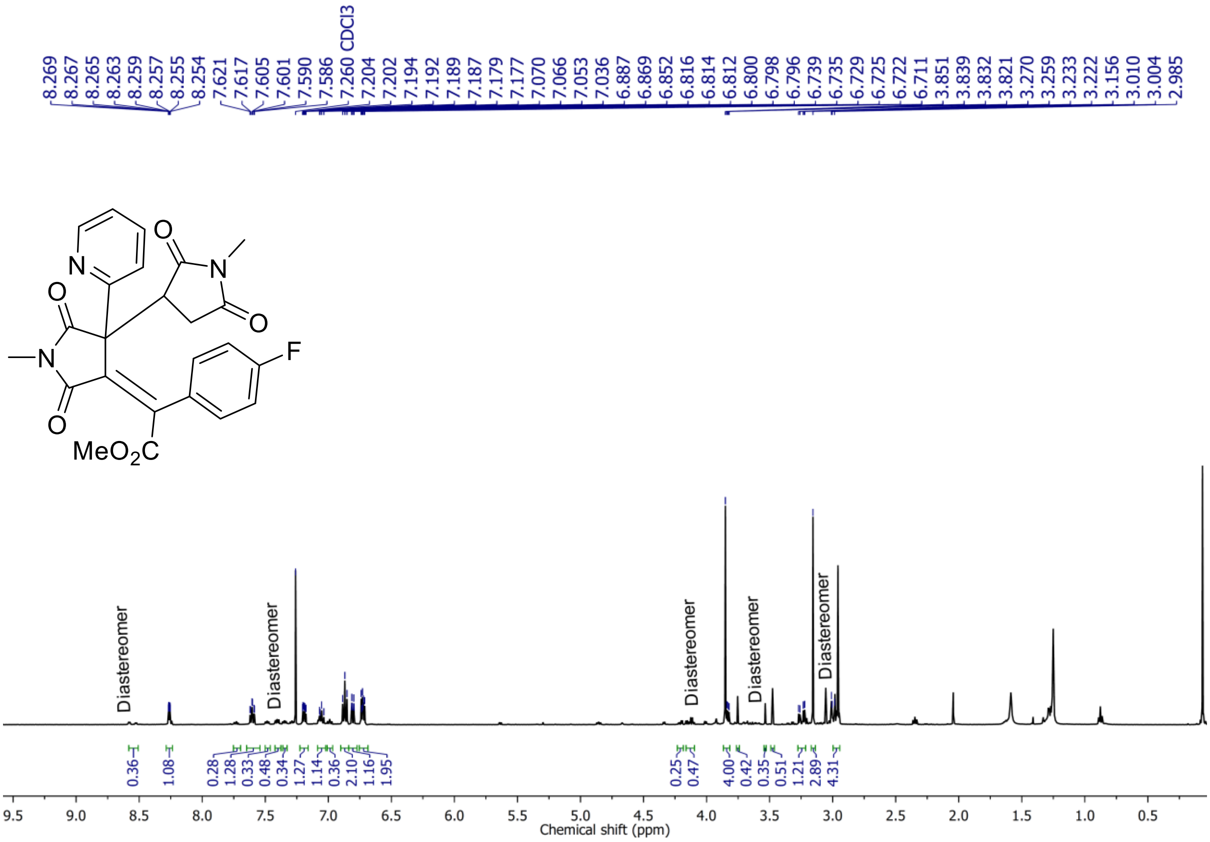
^{1}H NMR (400 MHz) of **6d** in $CDCl_3$



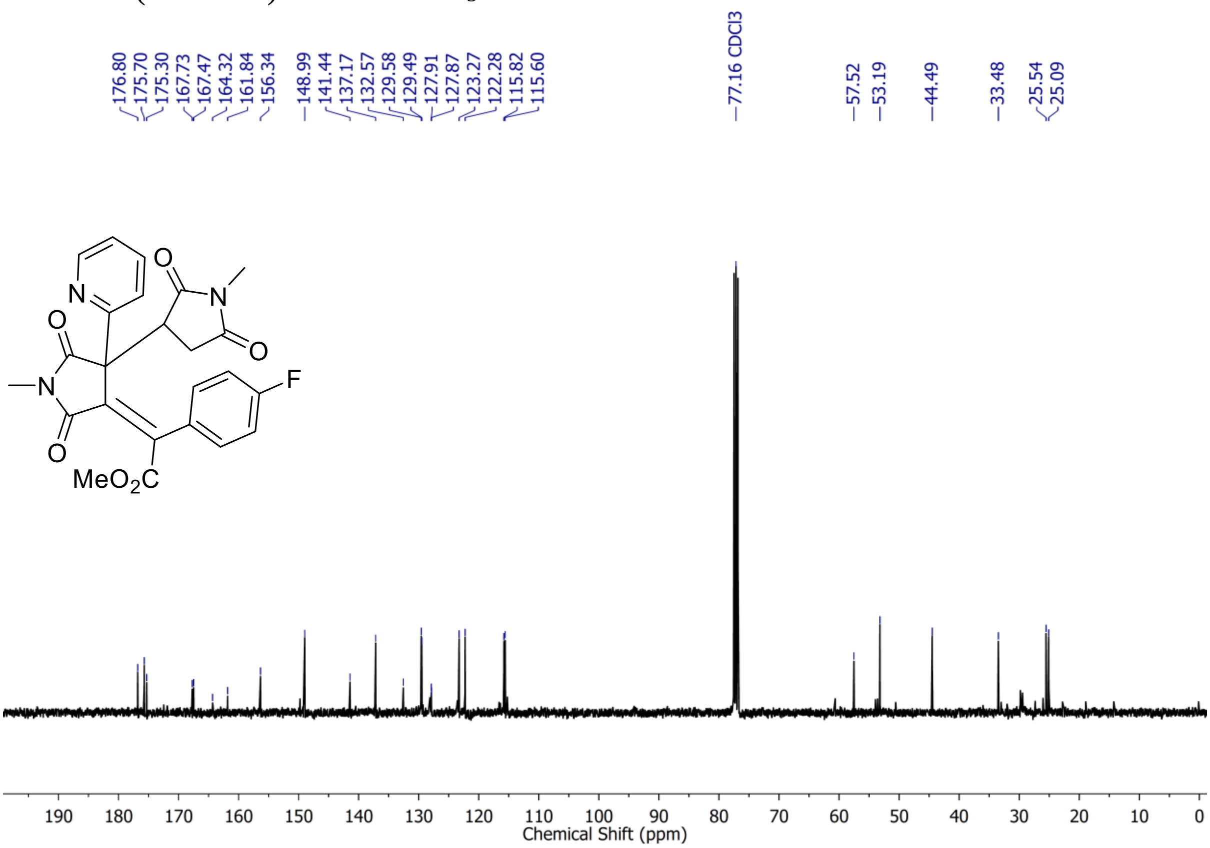
^{13}C NMR (400 MHz) of **6d** in $CDCl_3$



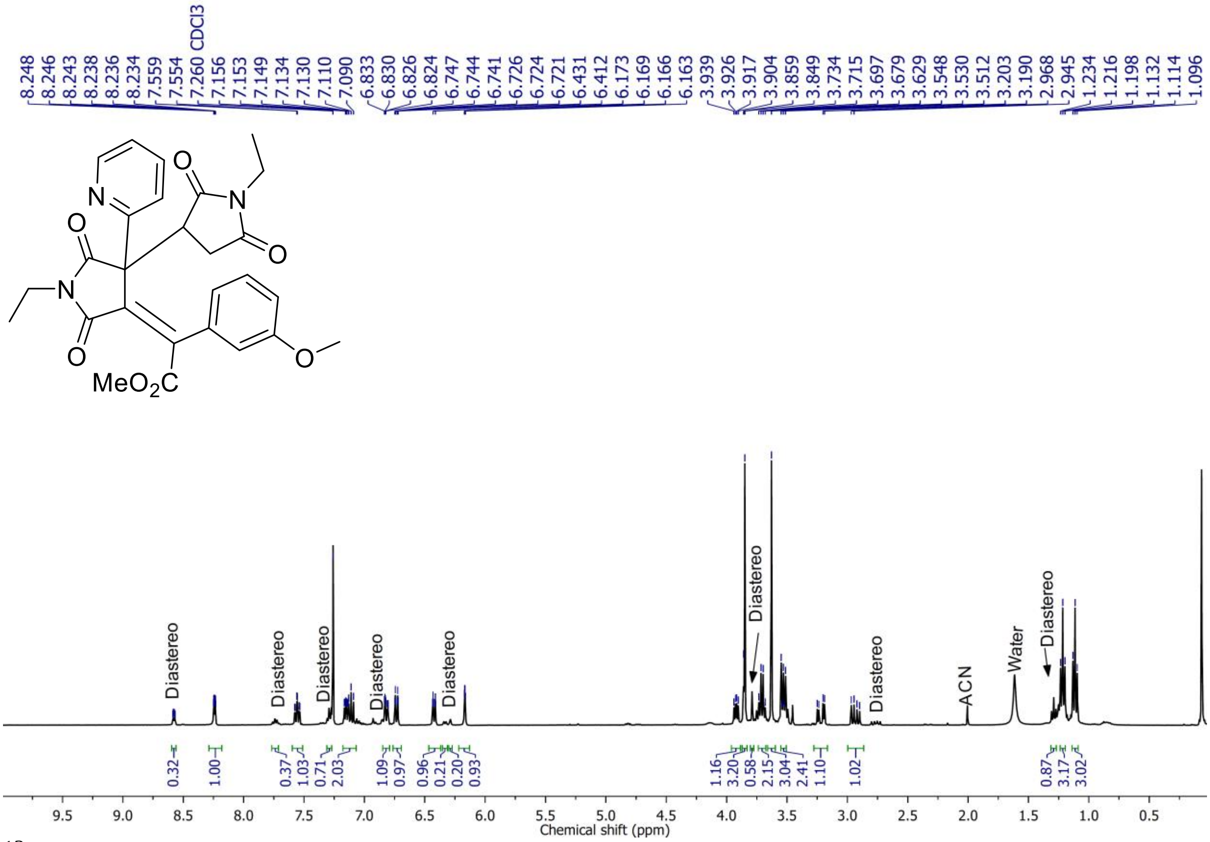
^{1}H NMR (400 MHz) of **6e** in $CDCl_3$



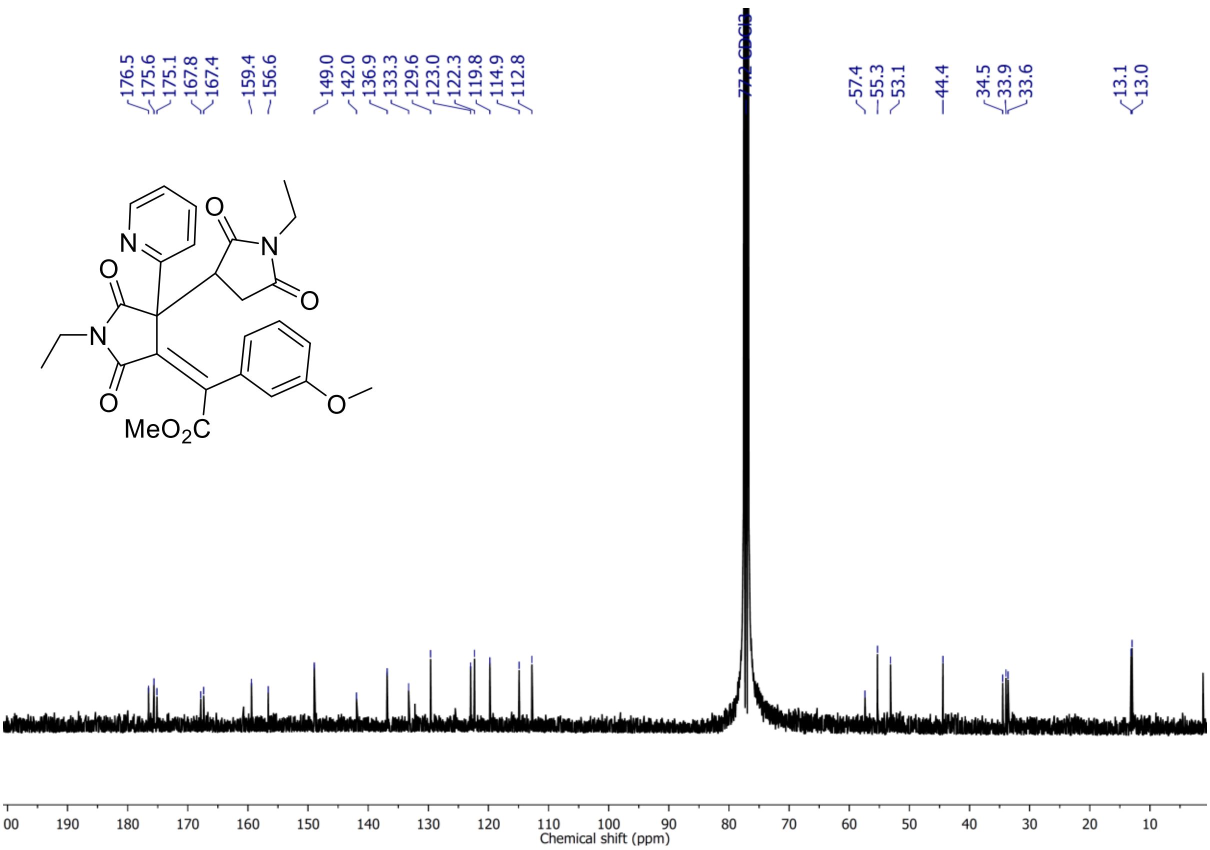
^{13}C NMR (400 MHz) of **6e** in $CDCl_3$



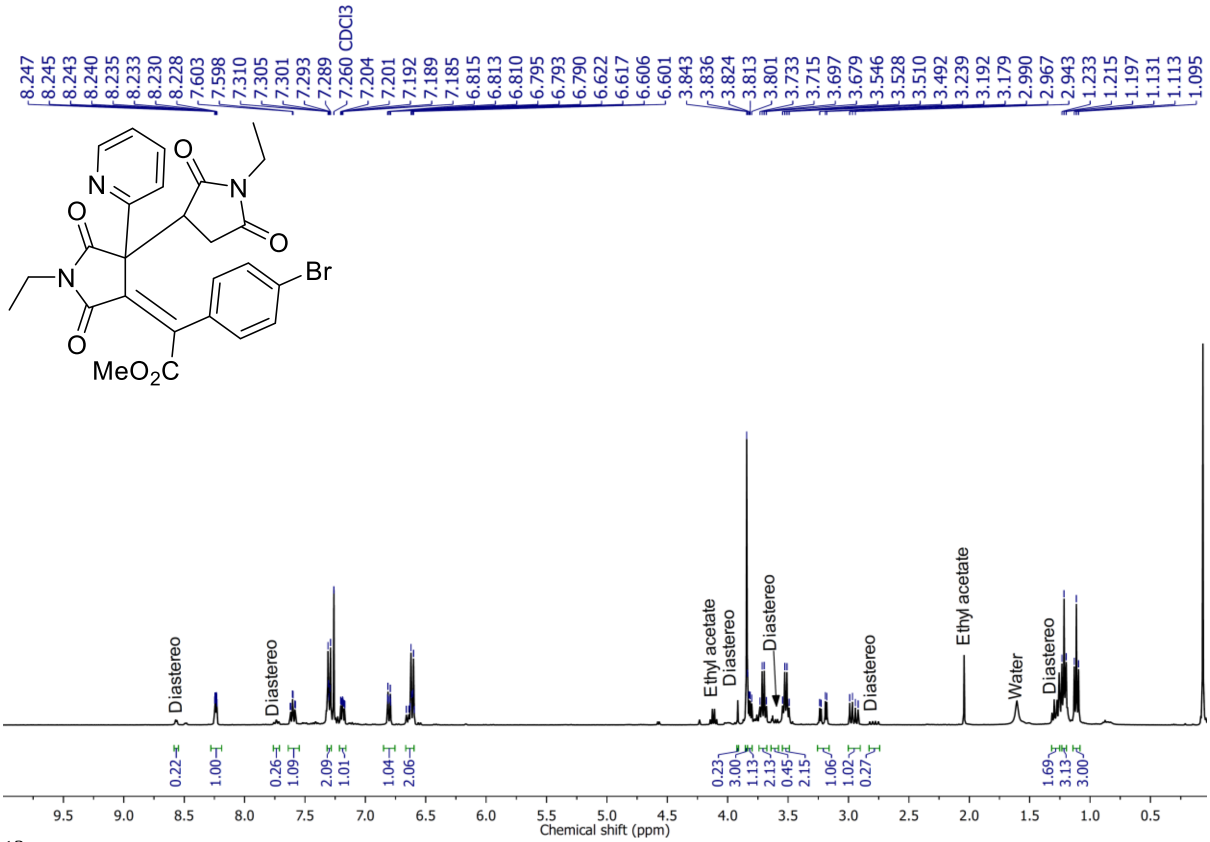
^{1}H NMR (400 MHz) of **6f** in $CDCl_3$



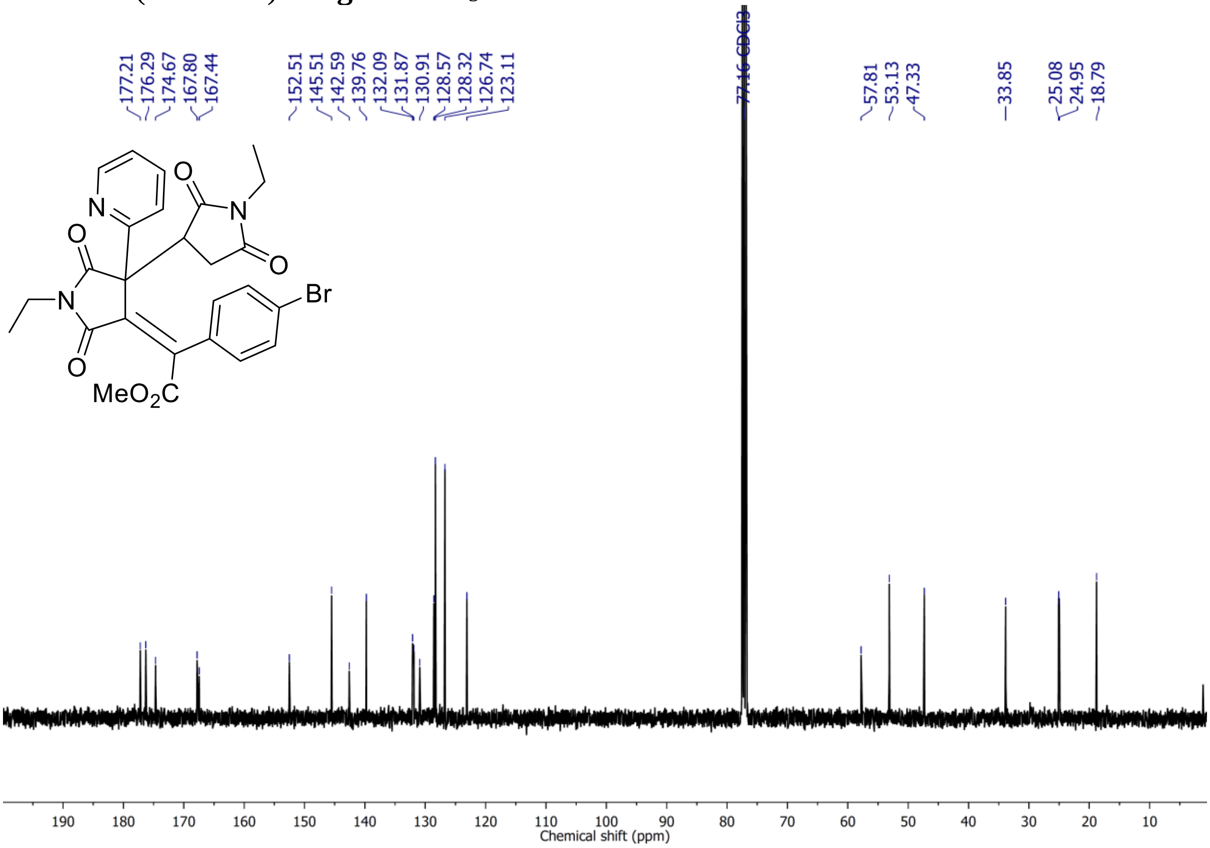
^{13}C NMR (400 MHz) of **6f** in $CDCl_3$



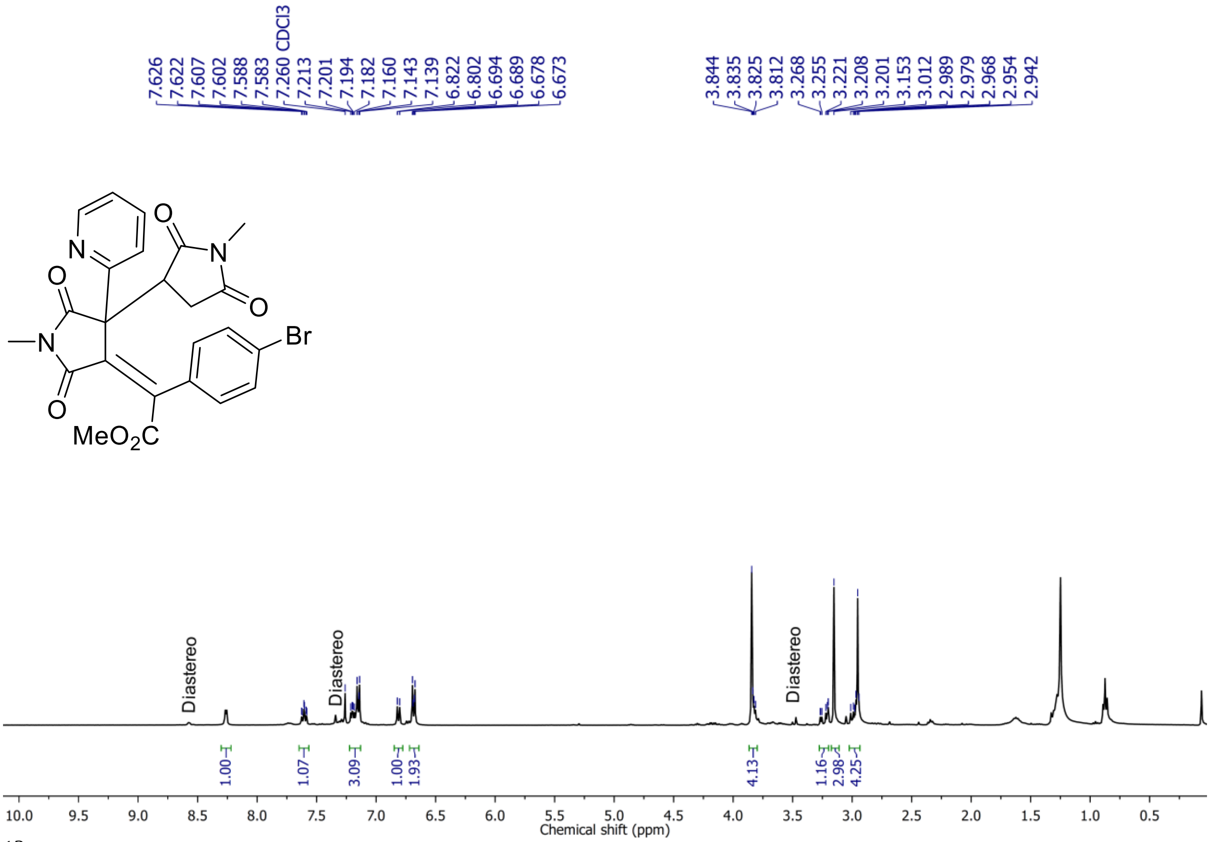
^{1}H NMR (400 MHz) of **6g** in $CDCl_3$



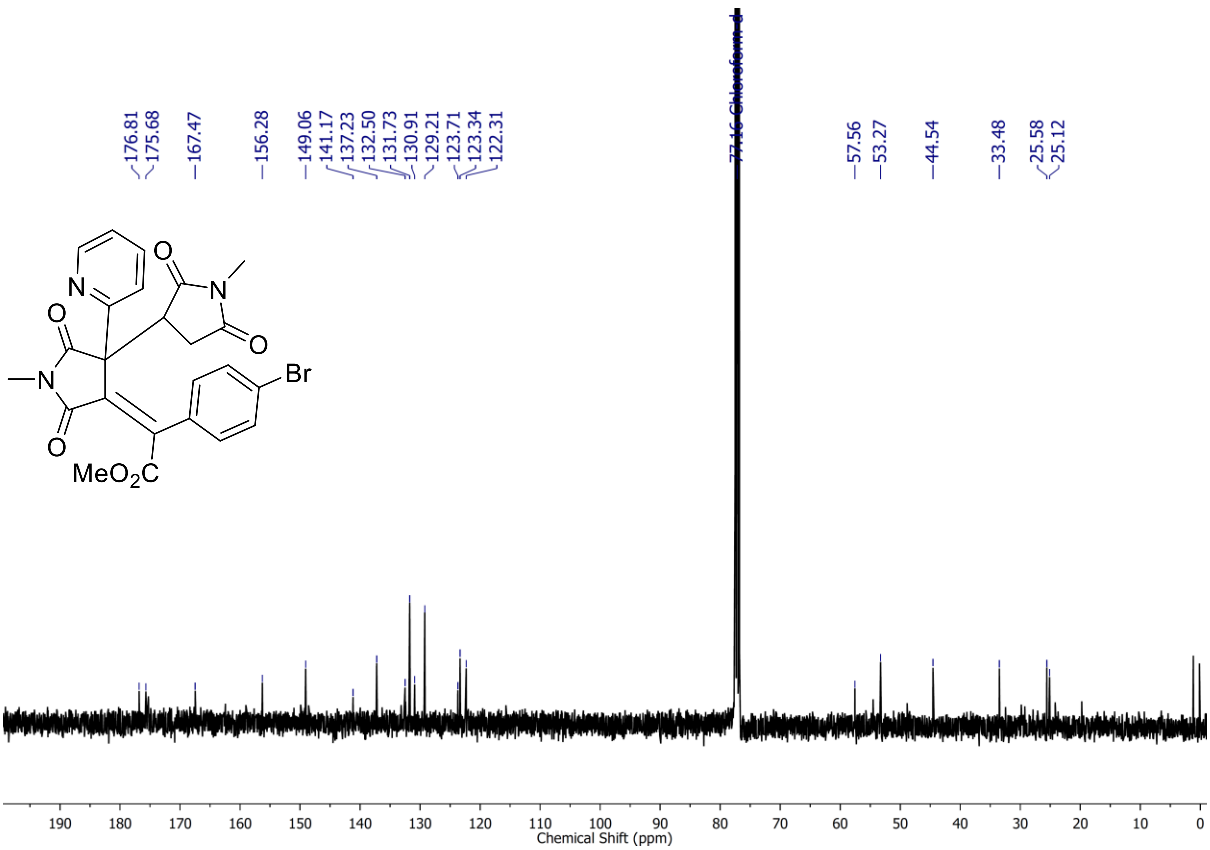
^{13}C NMR (400 MHz) of **6g** in $CDCl_3$



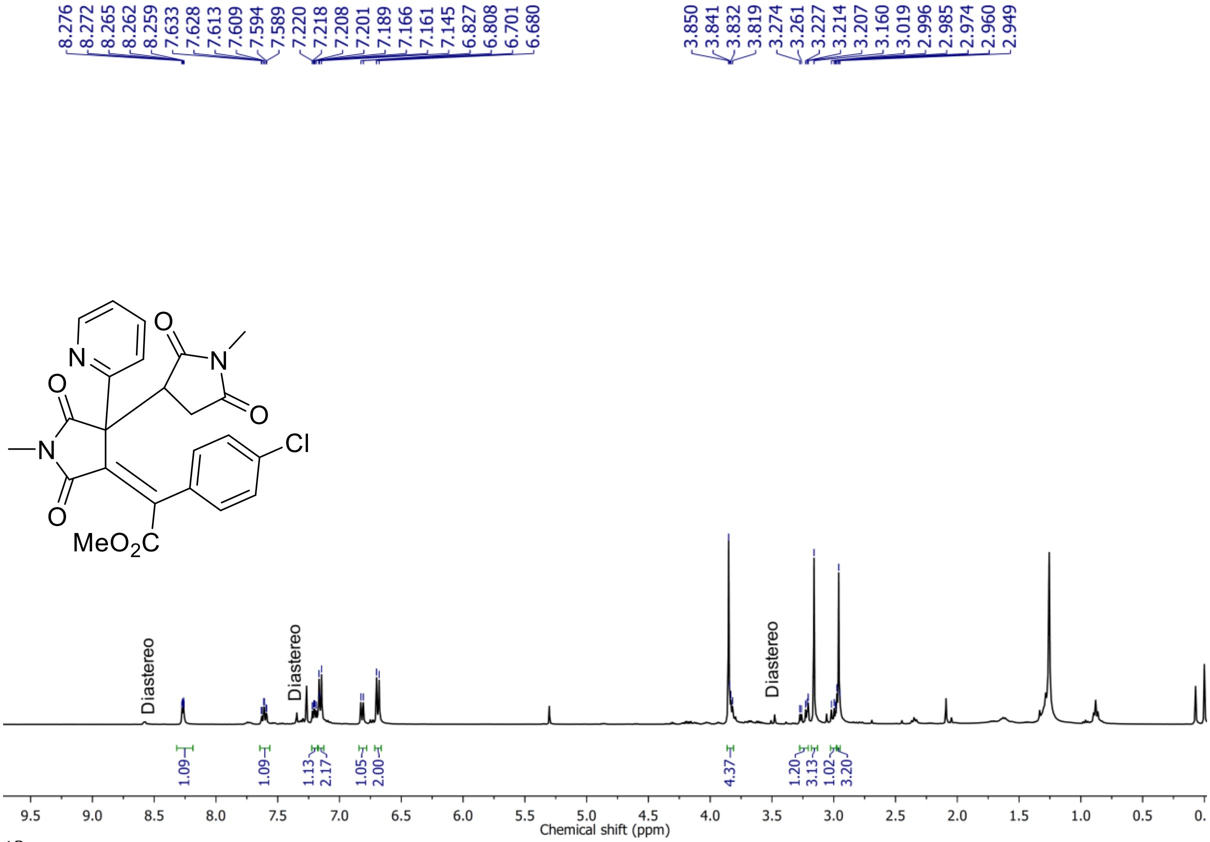
^{1}H NMR (400 MHz) of **6h** in $CDCl_3$



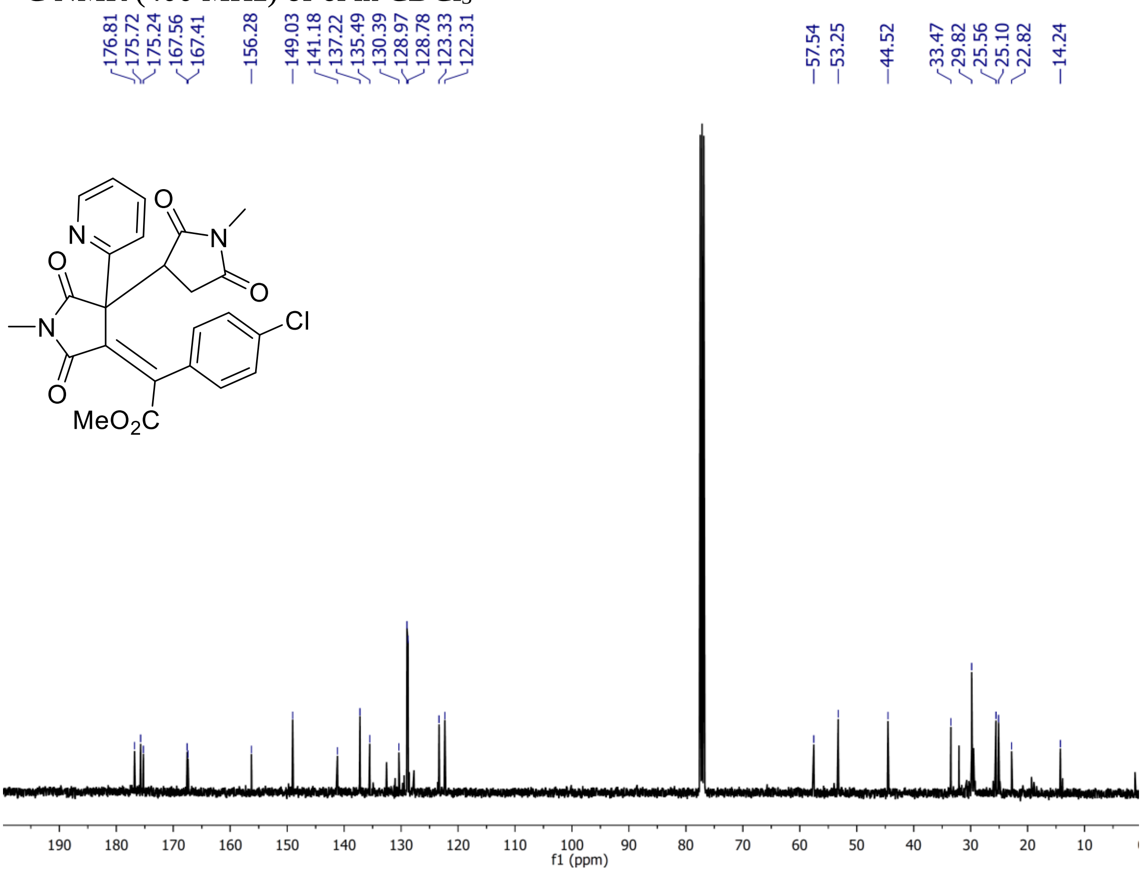
^{13}C NMR (400 MHz) of **6h** in $CDCl_3$



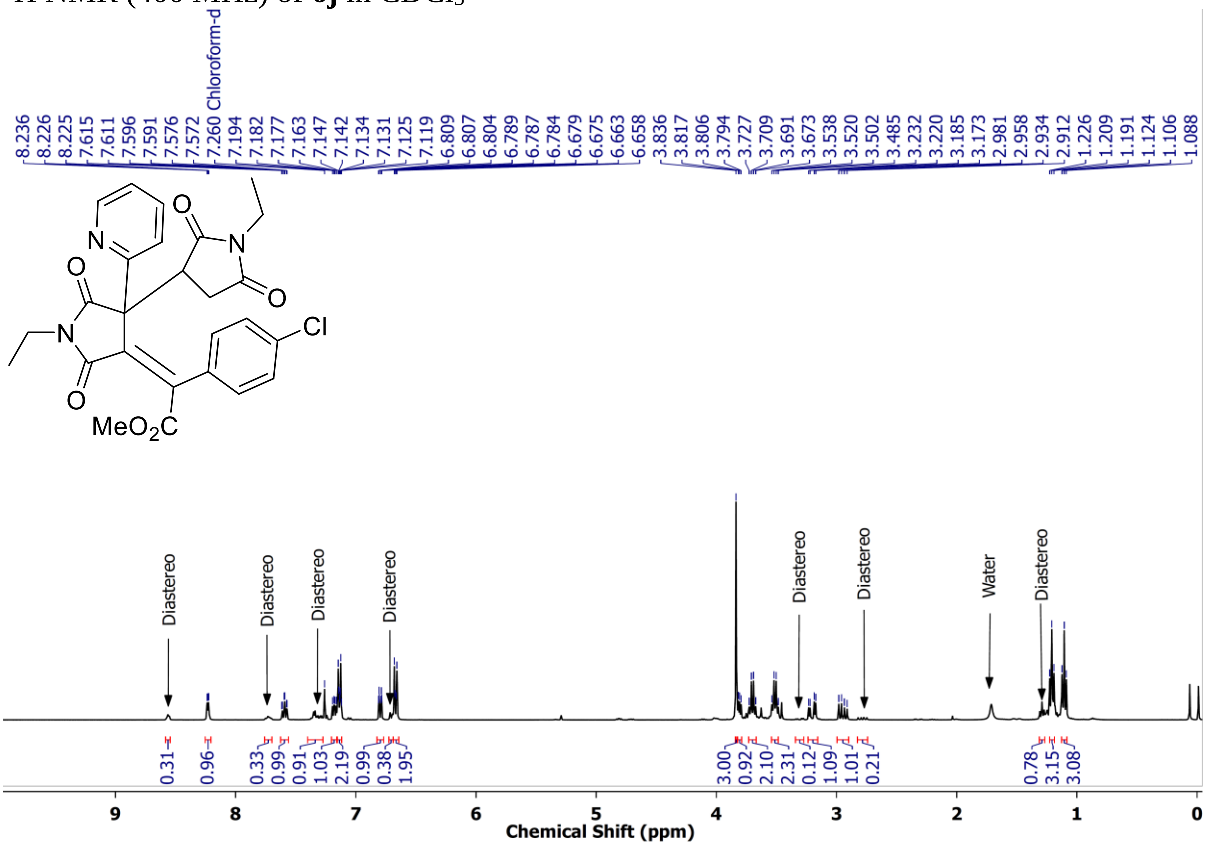
^{1}H NMR (400 MHz) of **6i** in $CDCl_3$



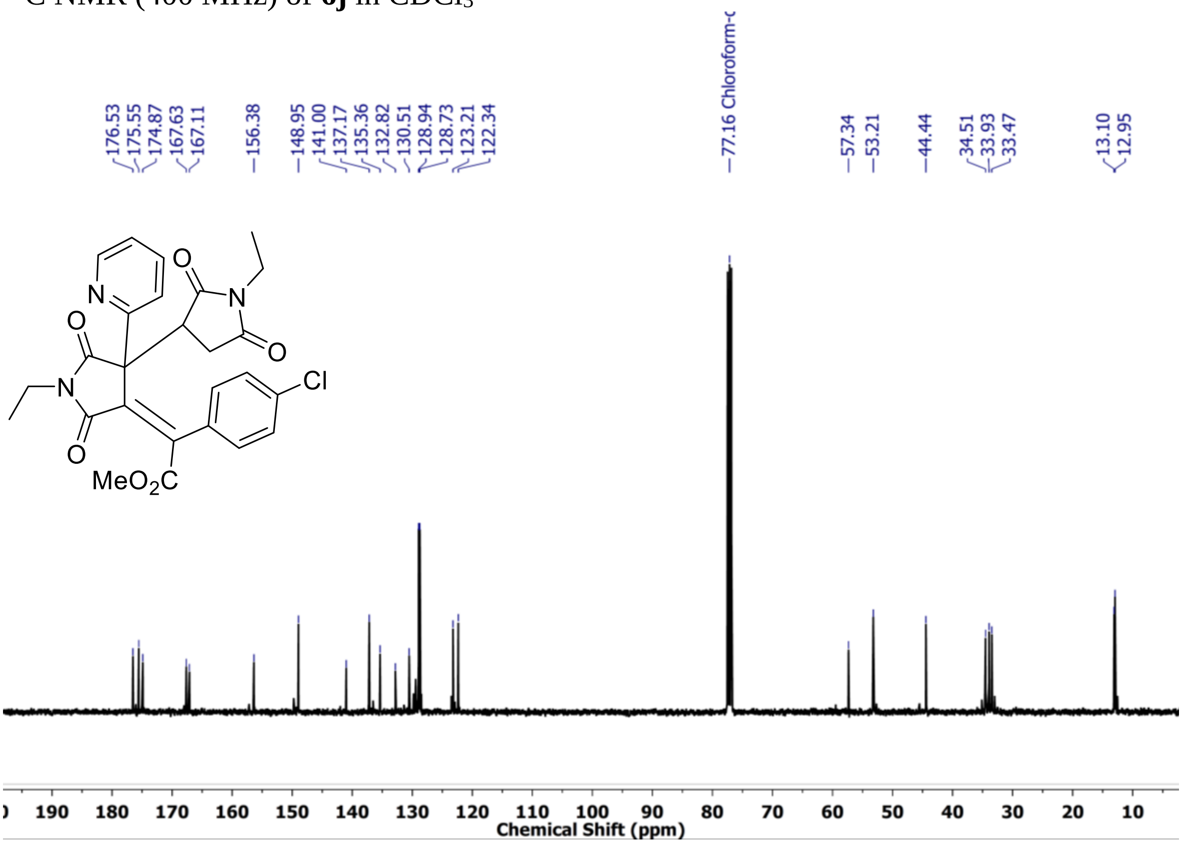
^{13}C NMR (400 MHz) of **6i** in $CDCl_3$



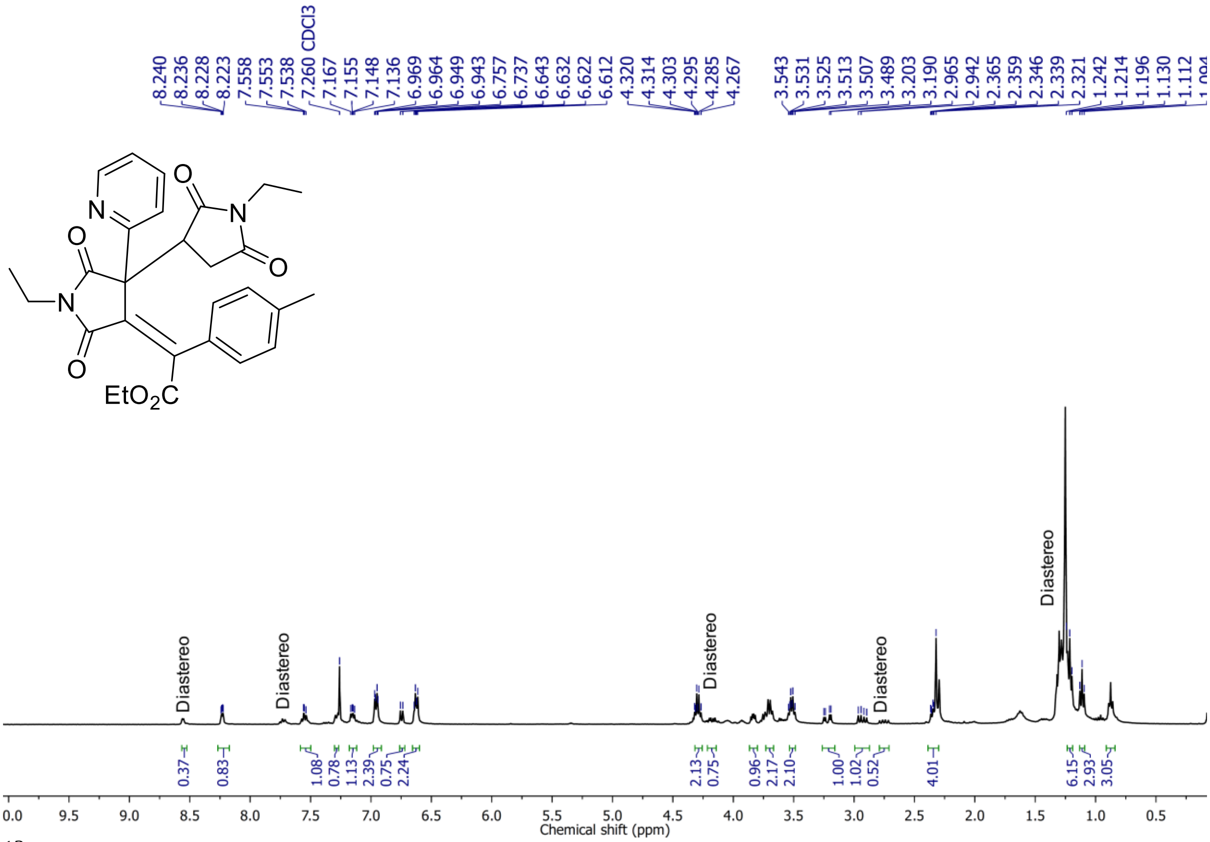
[1]H NMR (400 MHz) of **6j** in $CDCl_3$



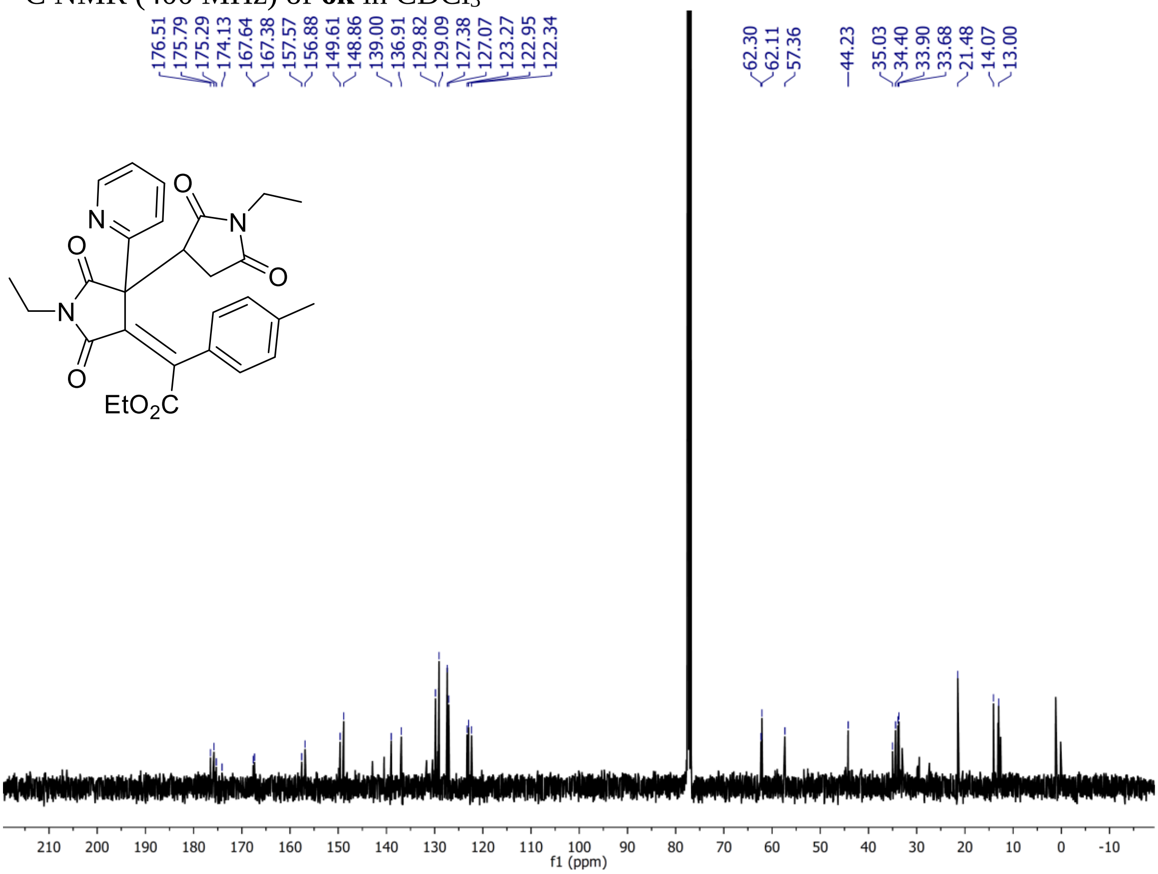
[13]C NMR (400 MHz) of **6j** in $CDCl_3$



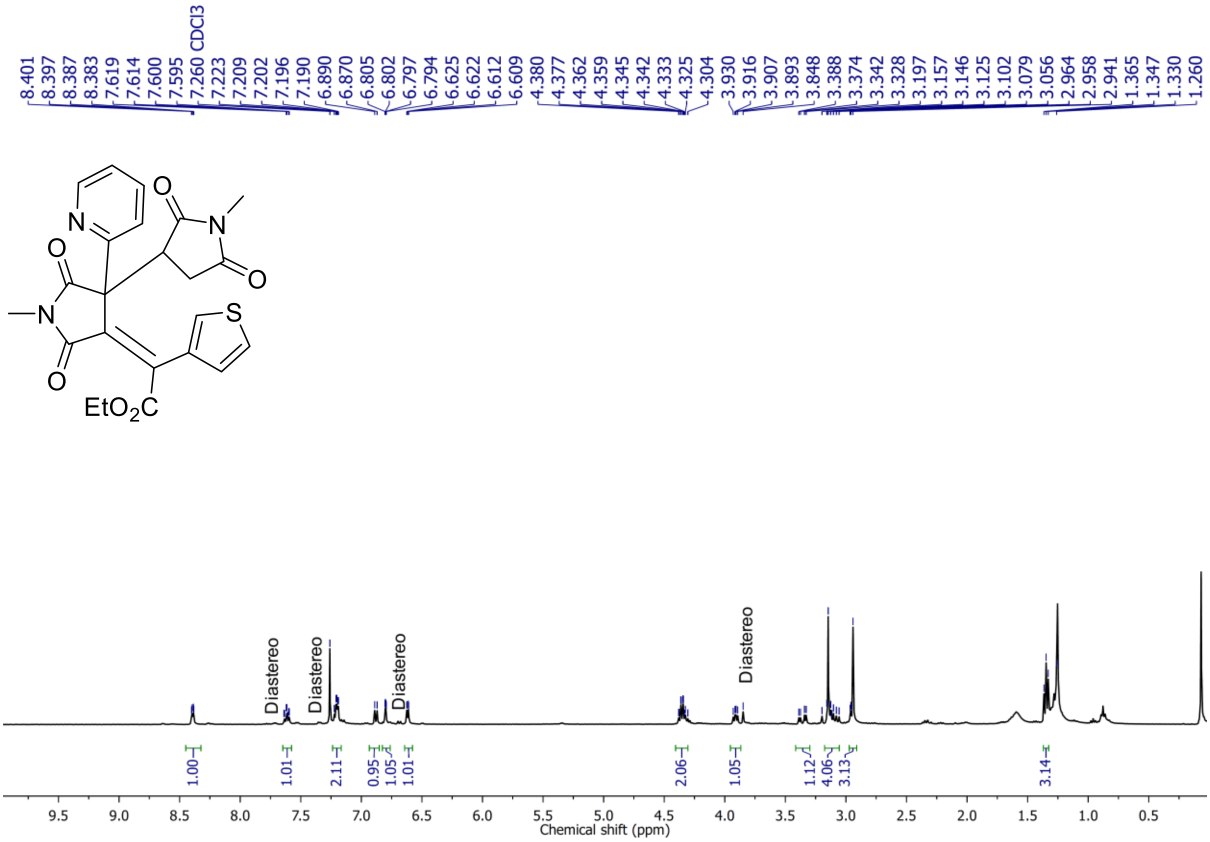
[1]H NMR (400 MHz) of **6k** in $CDCl_3$



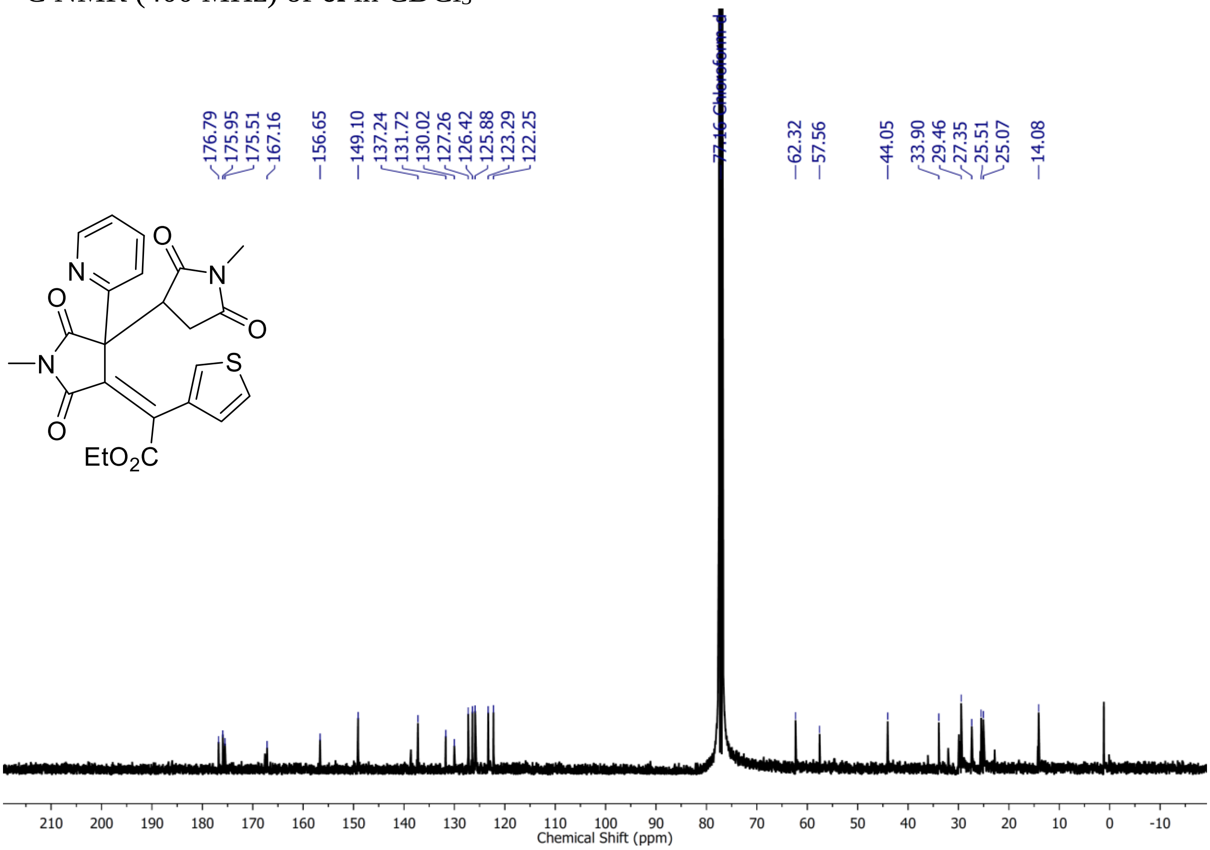
[13]C NMR (400 MHz) of **6k** in $CDCl_3$



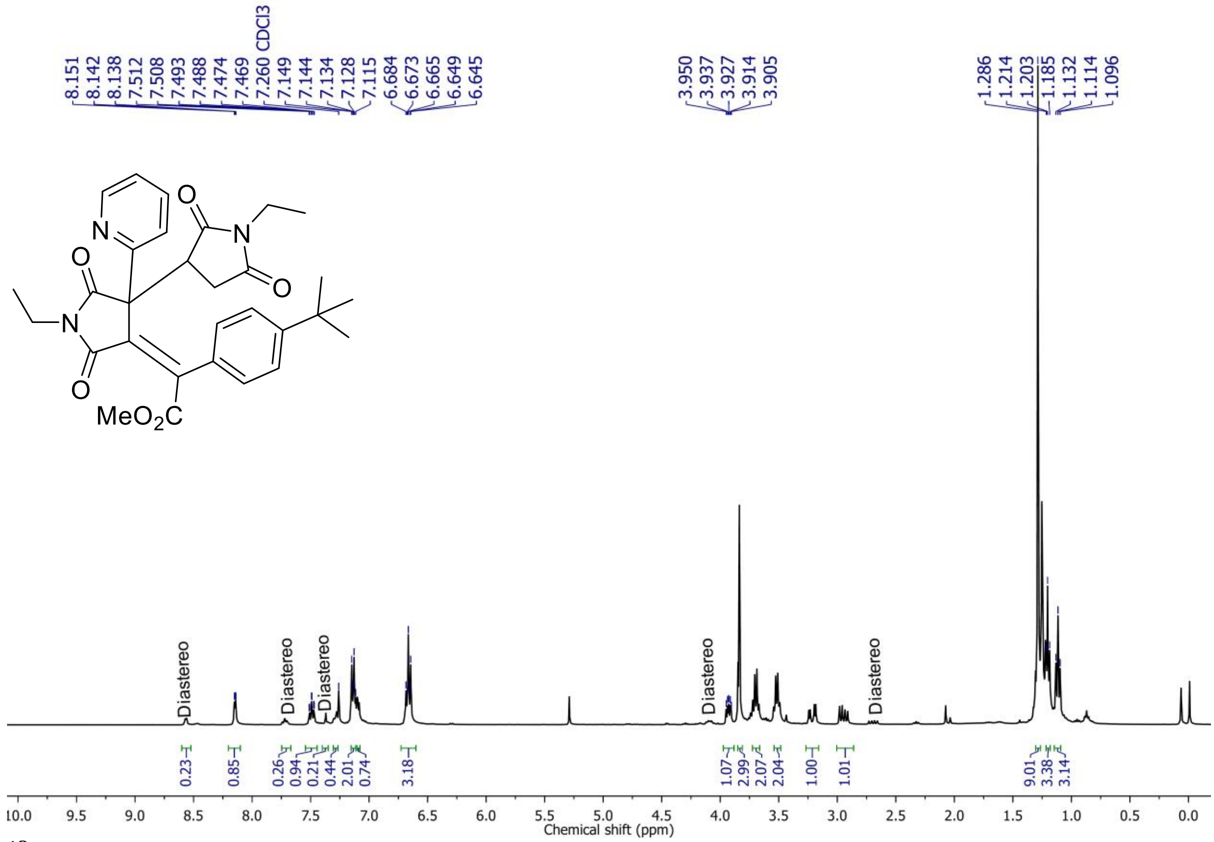
^{1}H NMR (400 MHz) of **6l** in $CDCl_3$



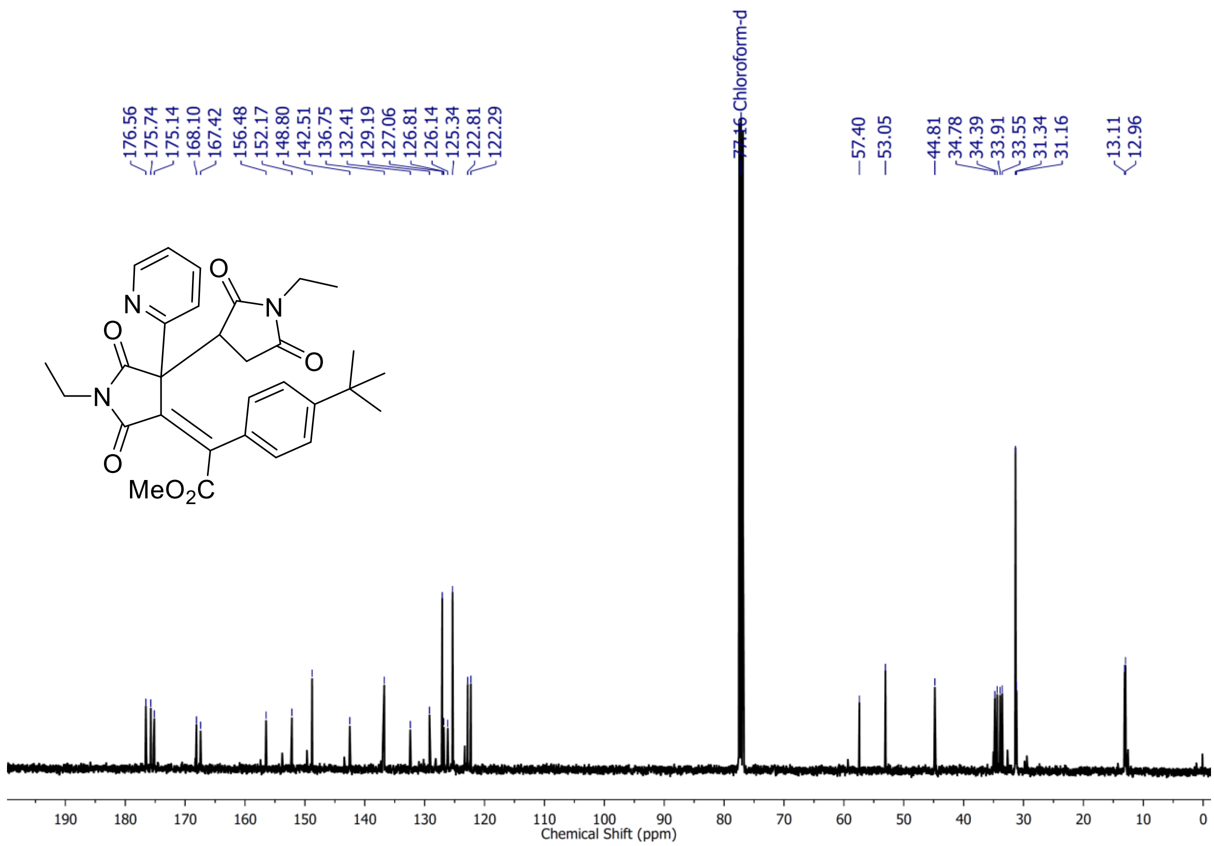
^{13}C NMR (400 MHz) of **6l** in $CDCl_3$



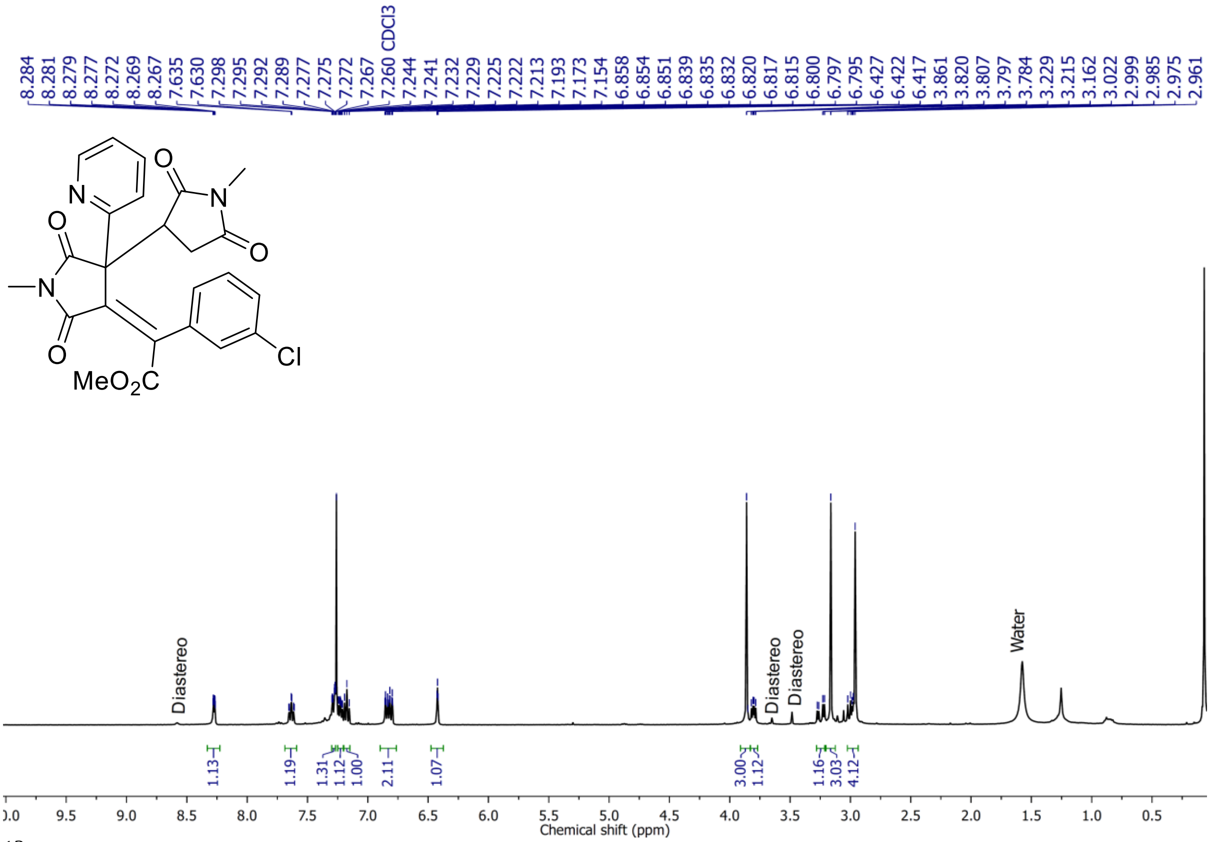
[1]H NMR (400 MHz) of **6m** in $CDCl_3$



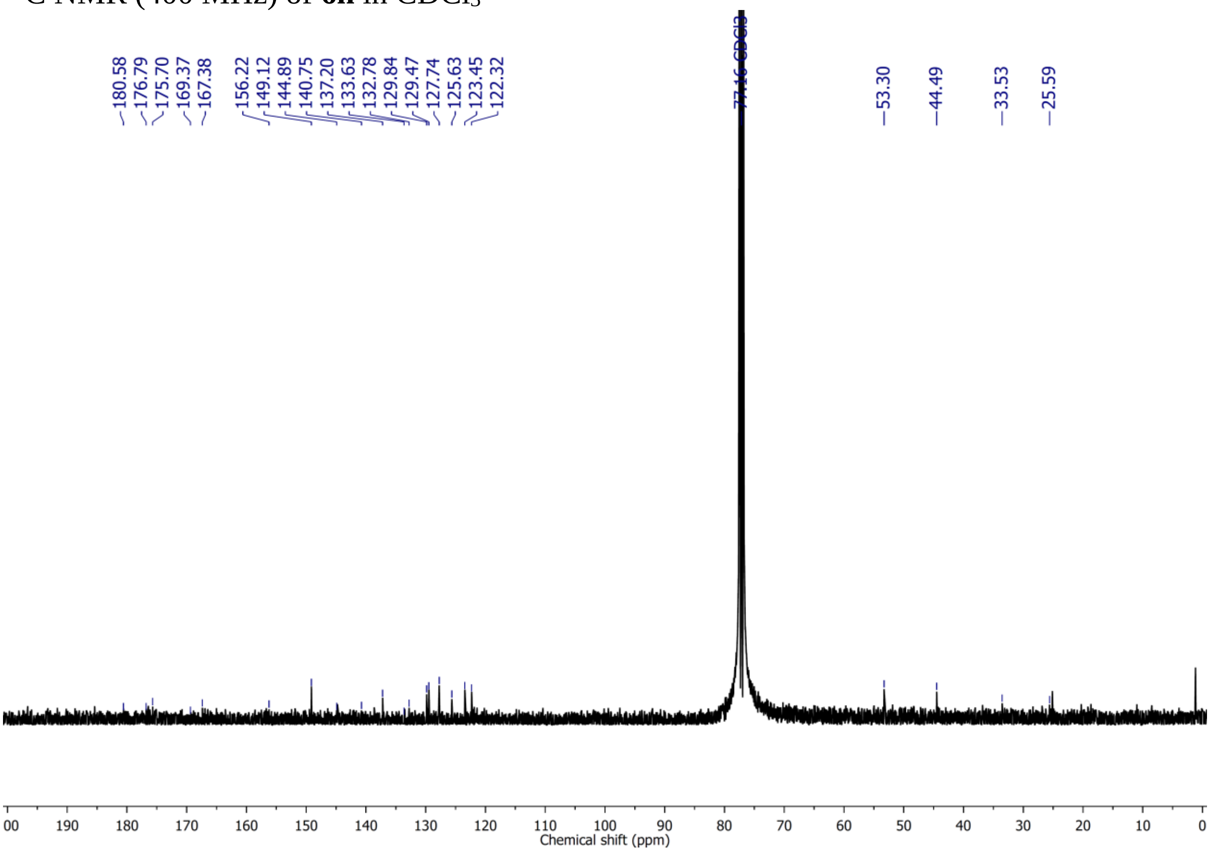
[13]C NMR (400 MHz) of **6m** in $CDCl_3$



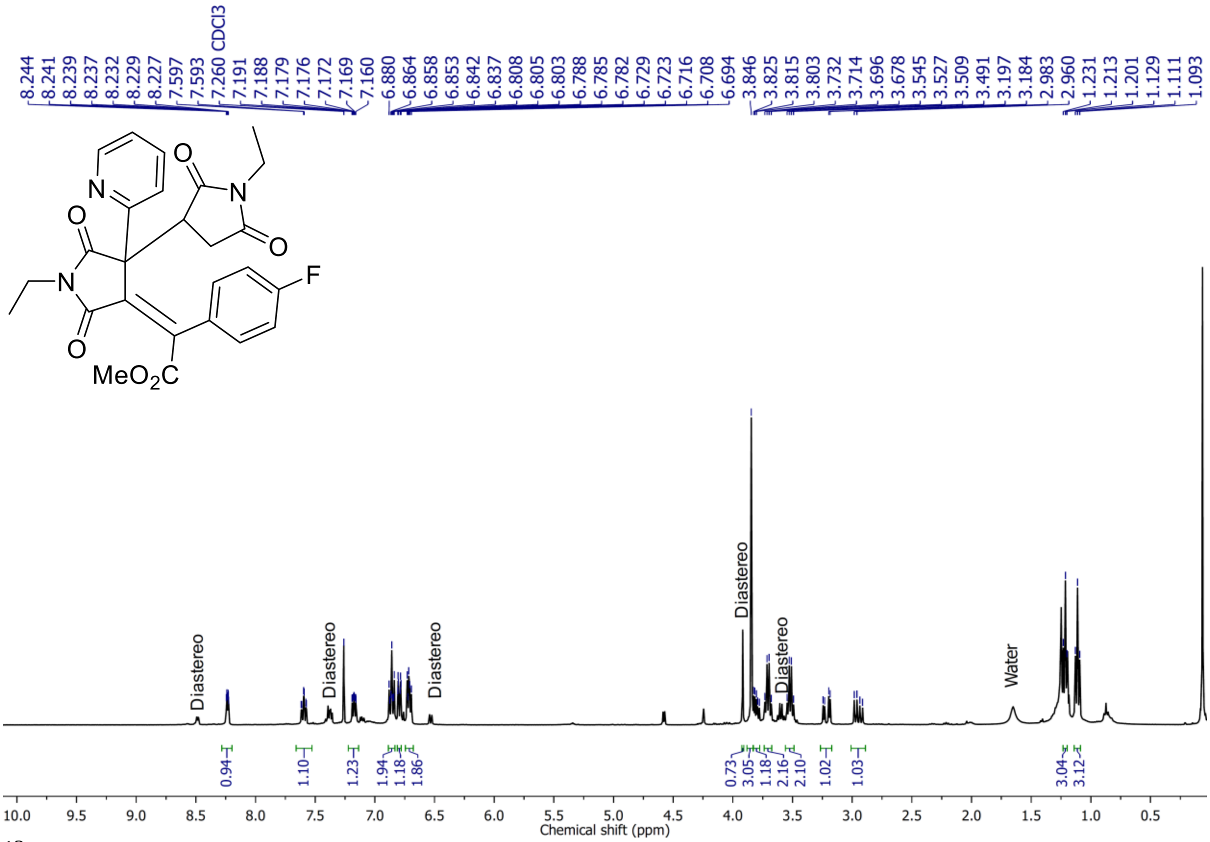
[1]H NMR (400 MHz) of **6n** in $CDCl_3$



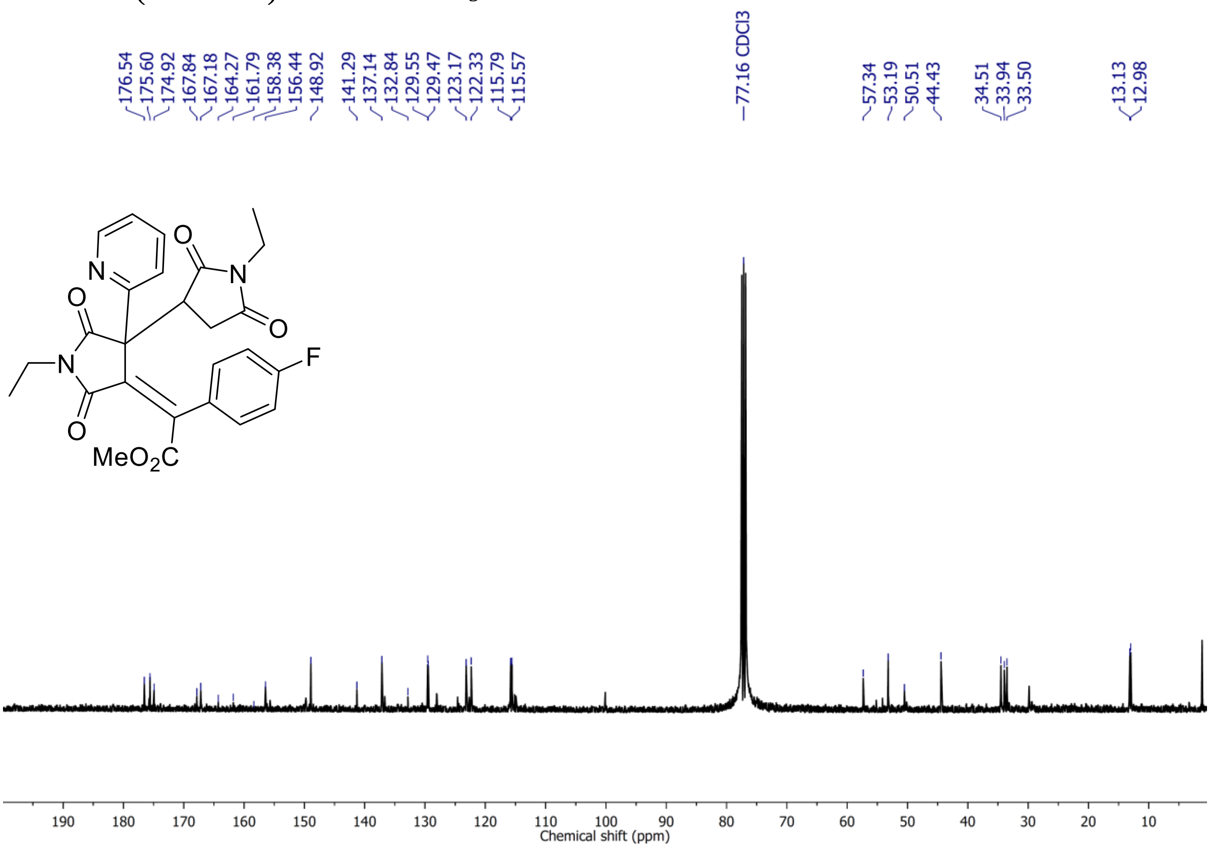
[13]C NMR (400 MHz) of **6n** in $CDCl_3$



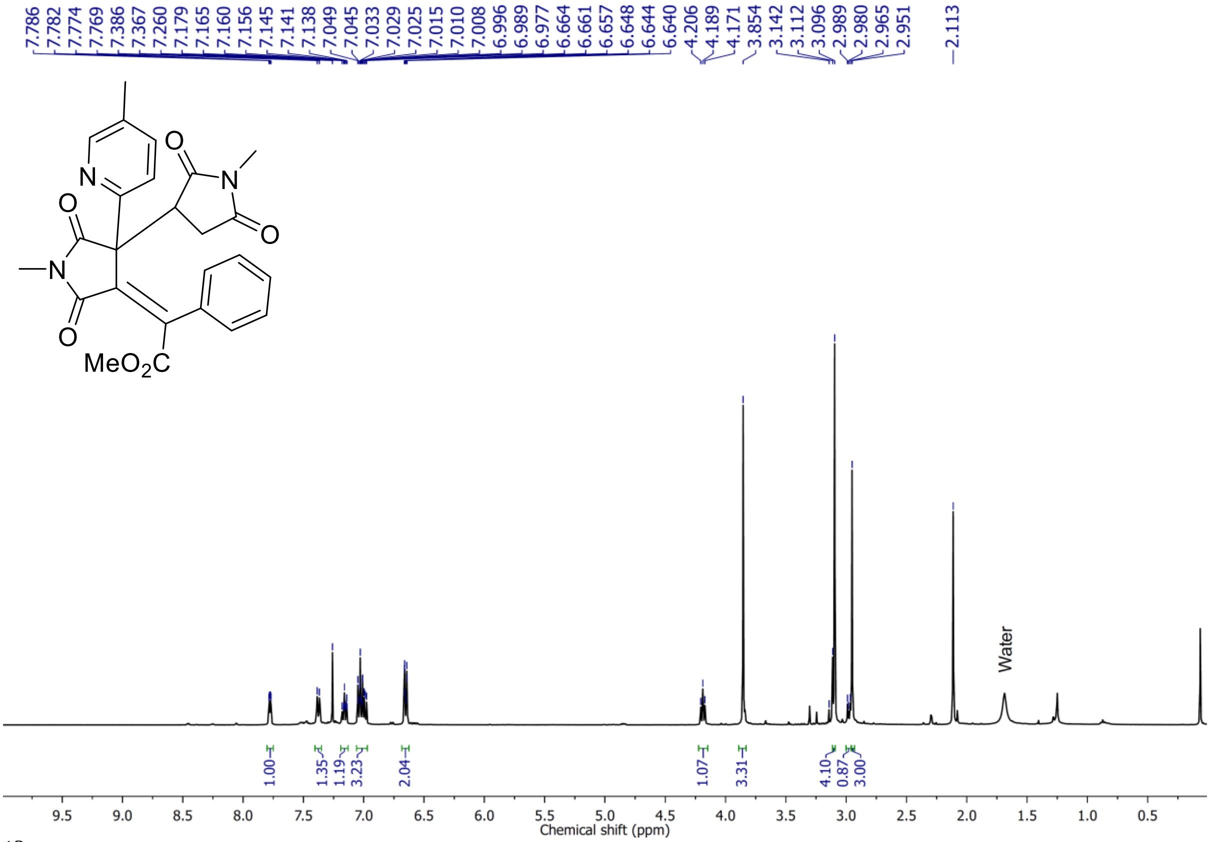
^{1}H NMR (400 MHz) of **6o** in $CDCl_3$



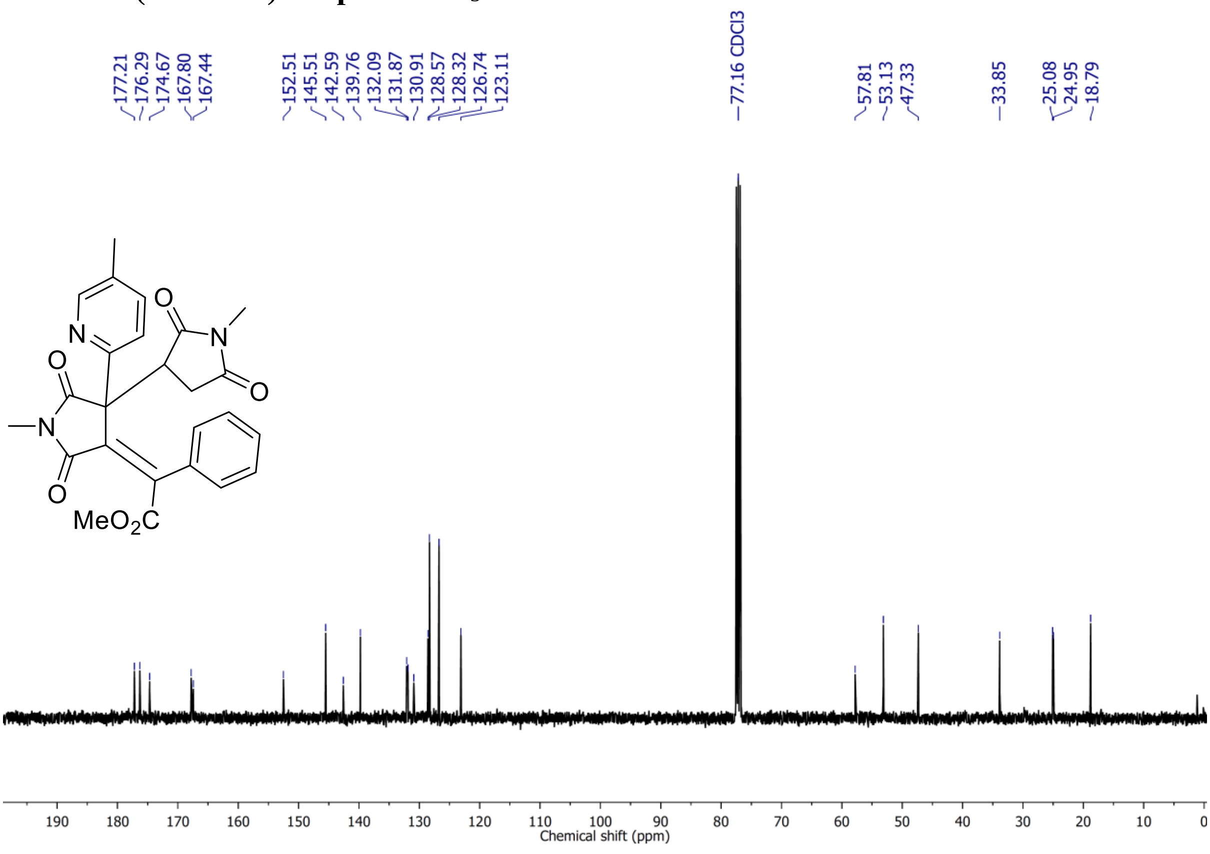
^{13}C NMR (400 MHz) of **6o** in $CDCl_3$



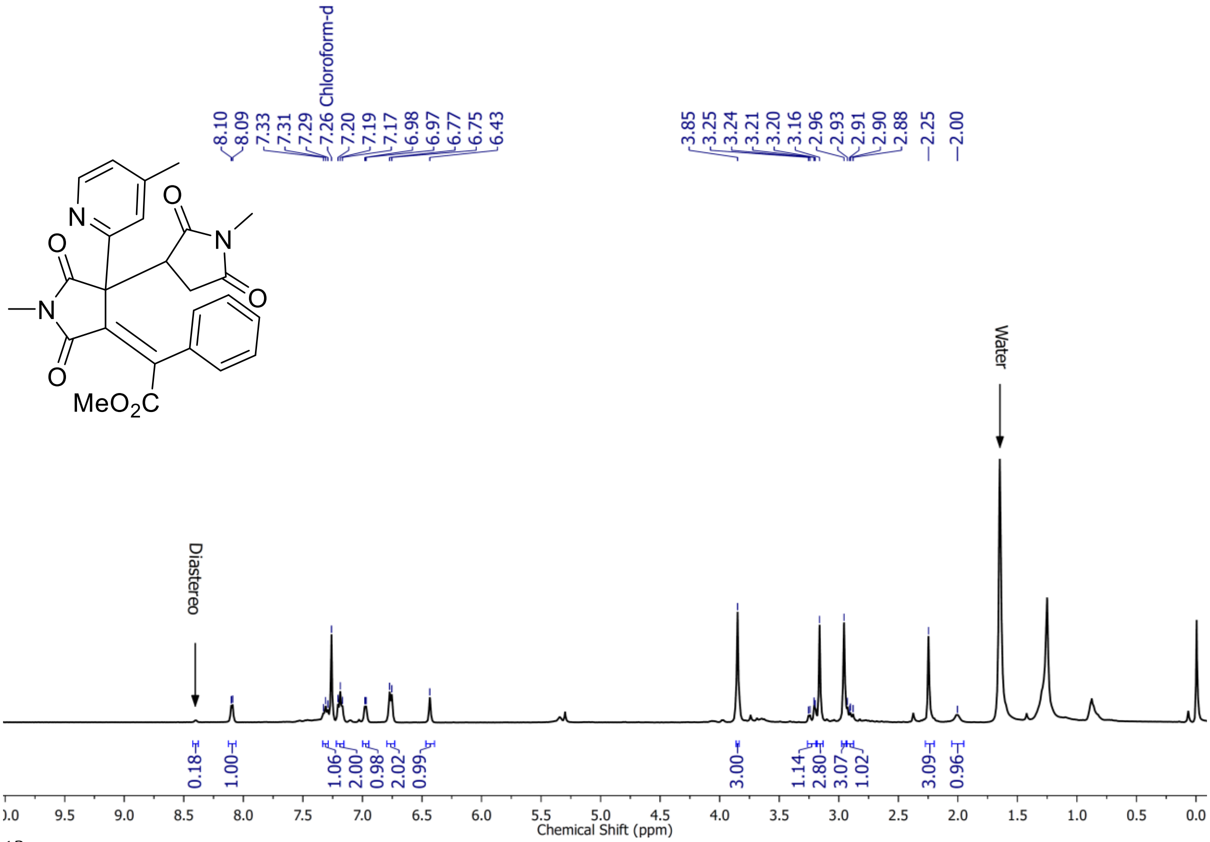
^{1}H NMR (400 MHz) of **6p** in $CDCl_3$



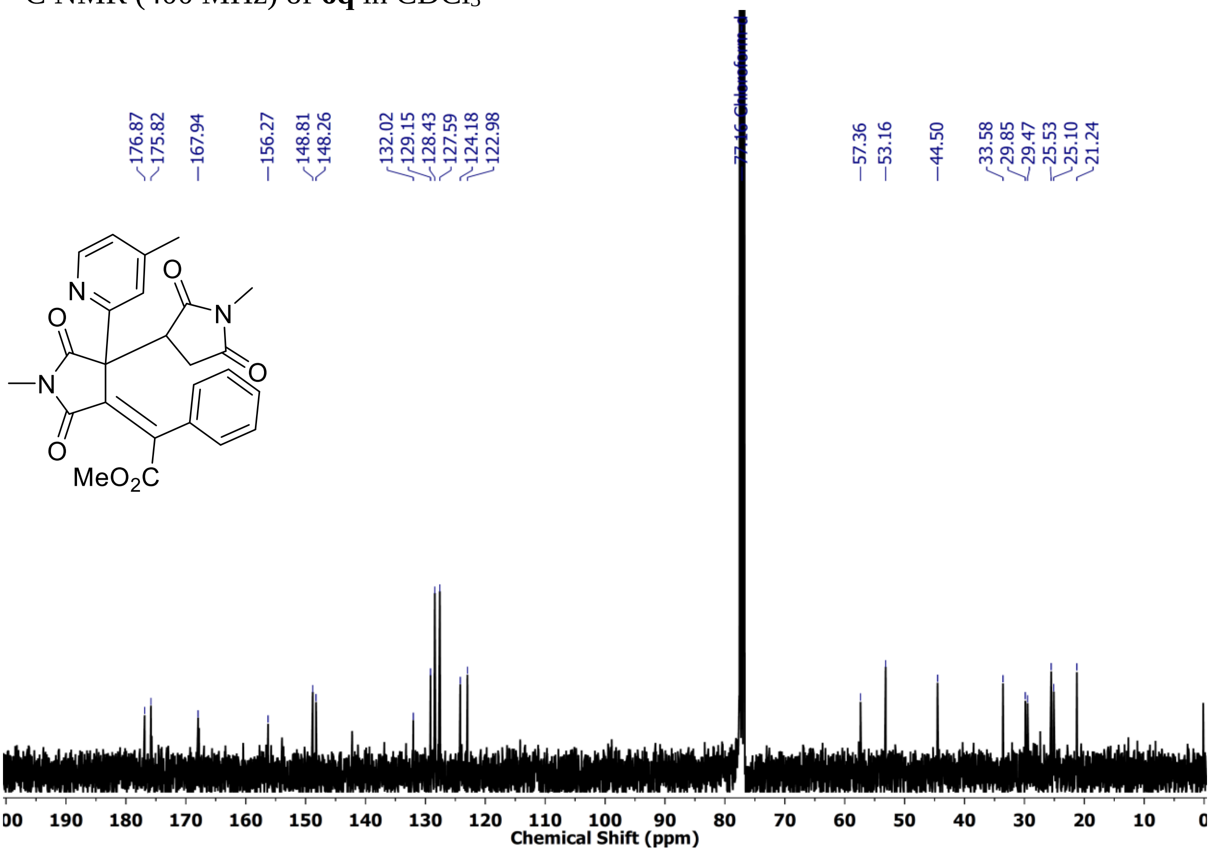
^{13}C NMR (400 MHz) of **6p** in $CDCl_3$



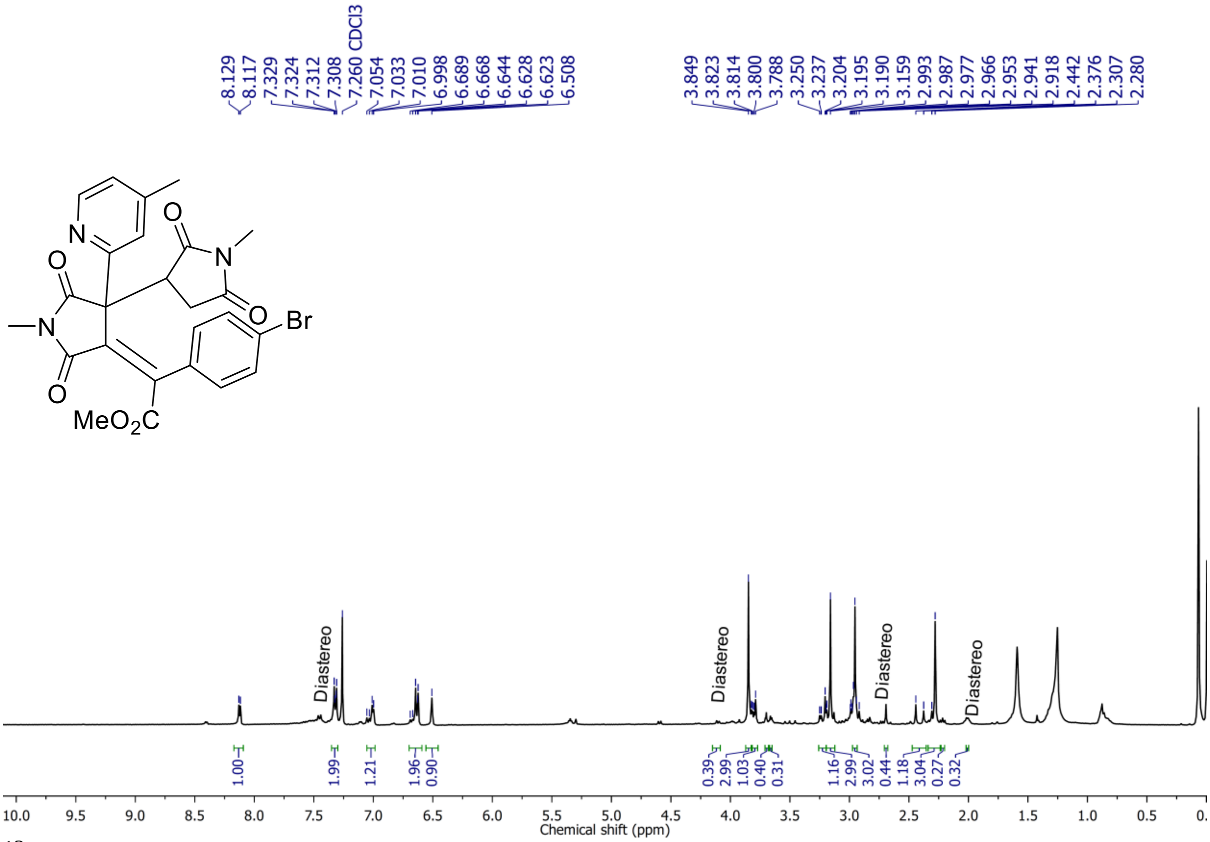
^{1}H NMR (400 MHz) of **6q** in $CDCl_3$



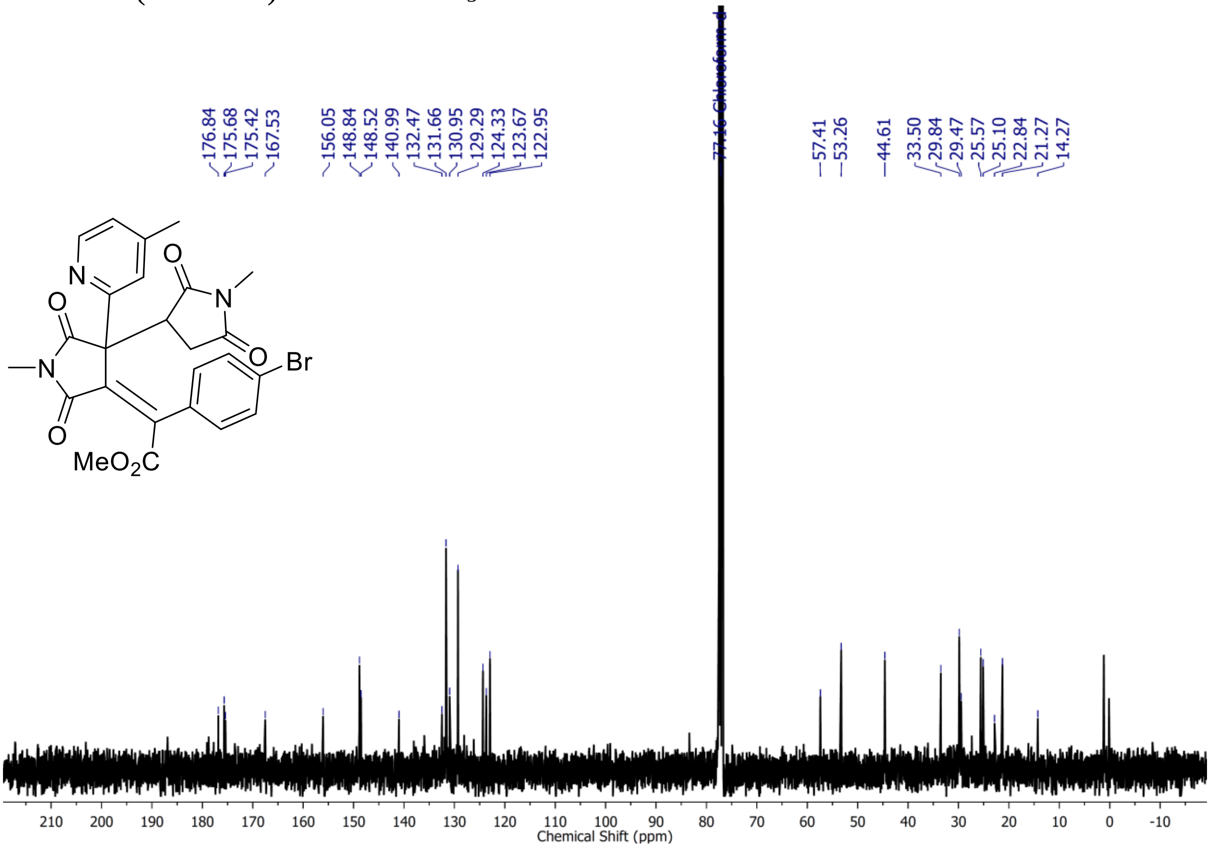
^{13}C NMR (400 MHz) of **6q** in $CDCl_3$



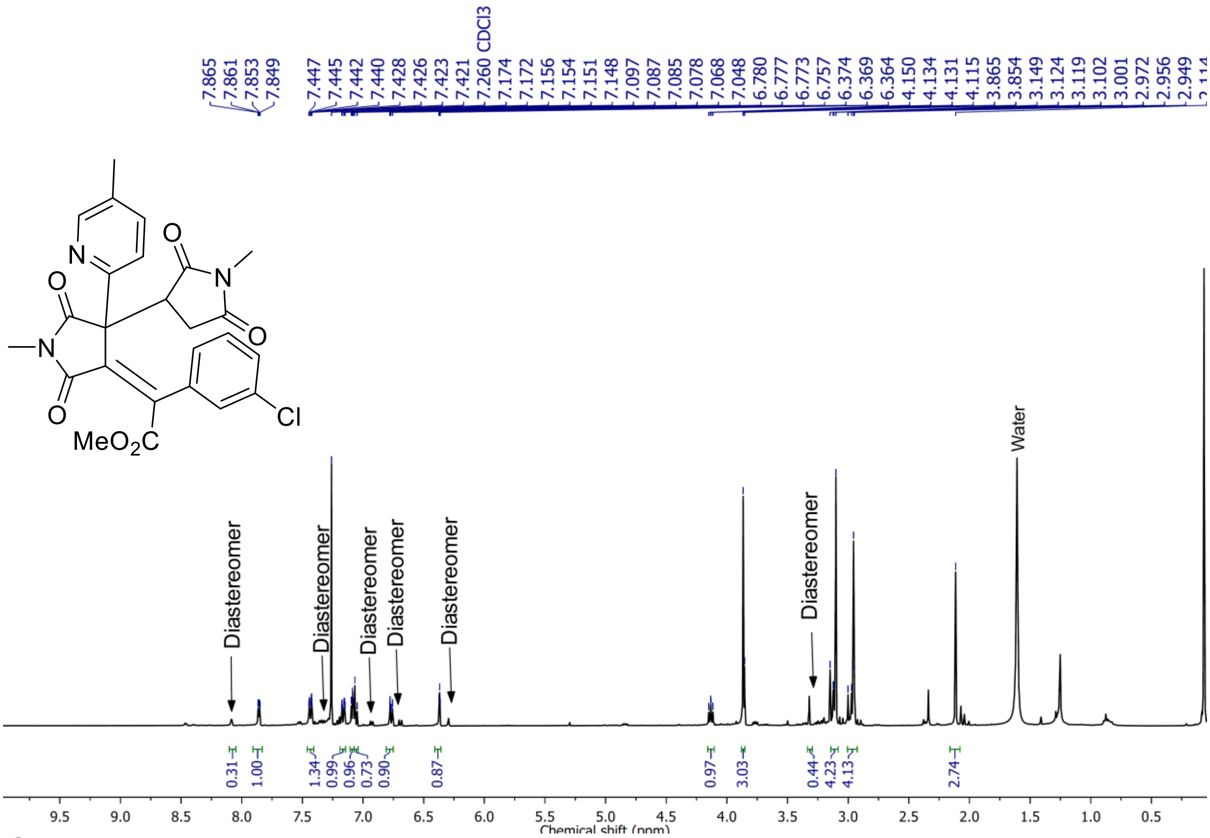
^{1}H NMR (400 MHz) of **6r** in $CDCl_3$



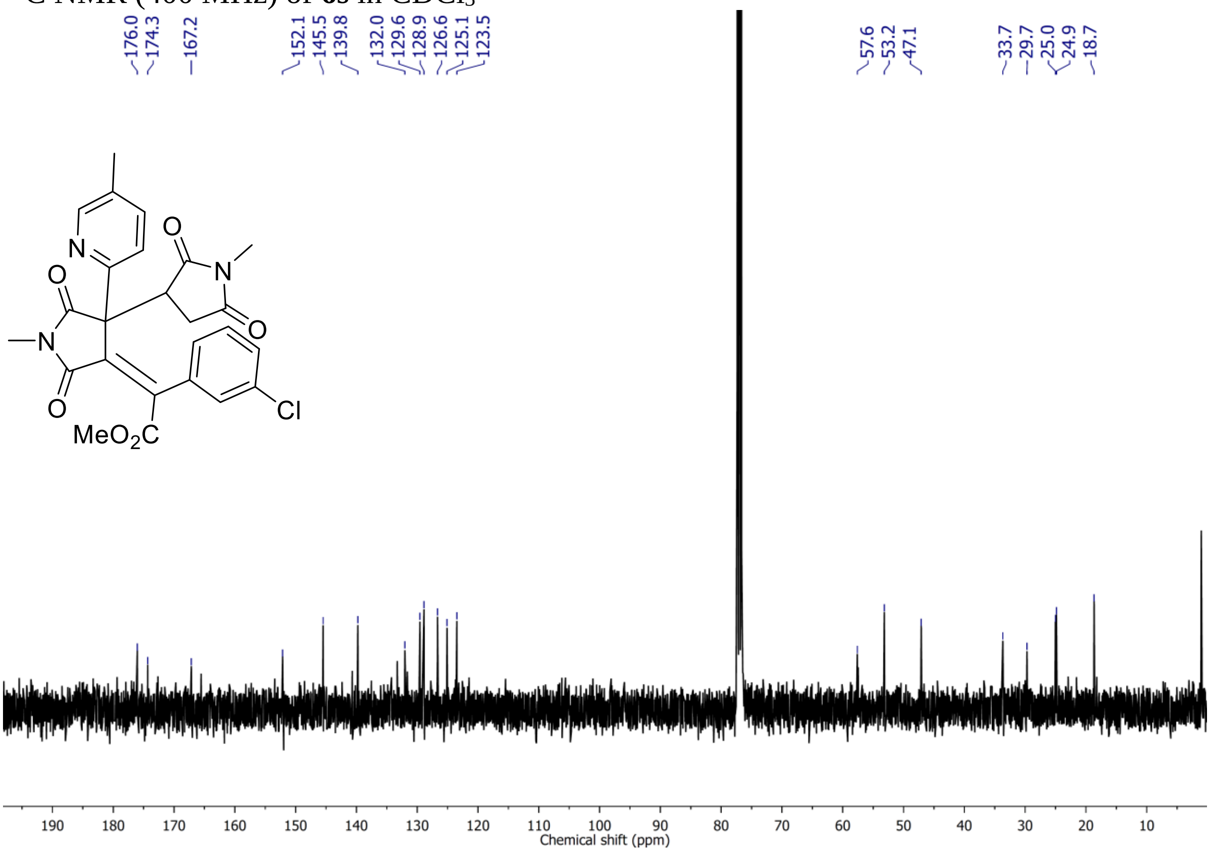
^{13}C NMR (400 MHz) of **6r** in $CDCl_3$



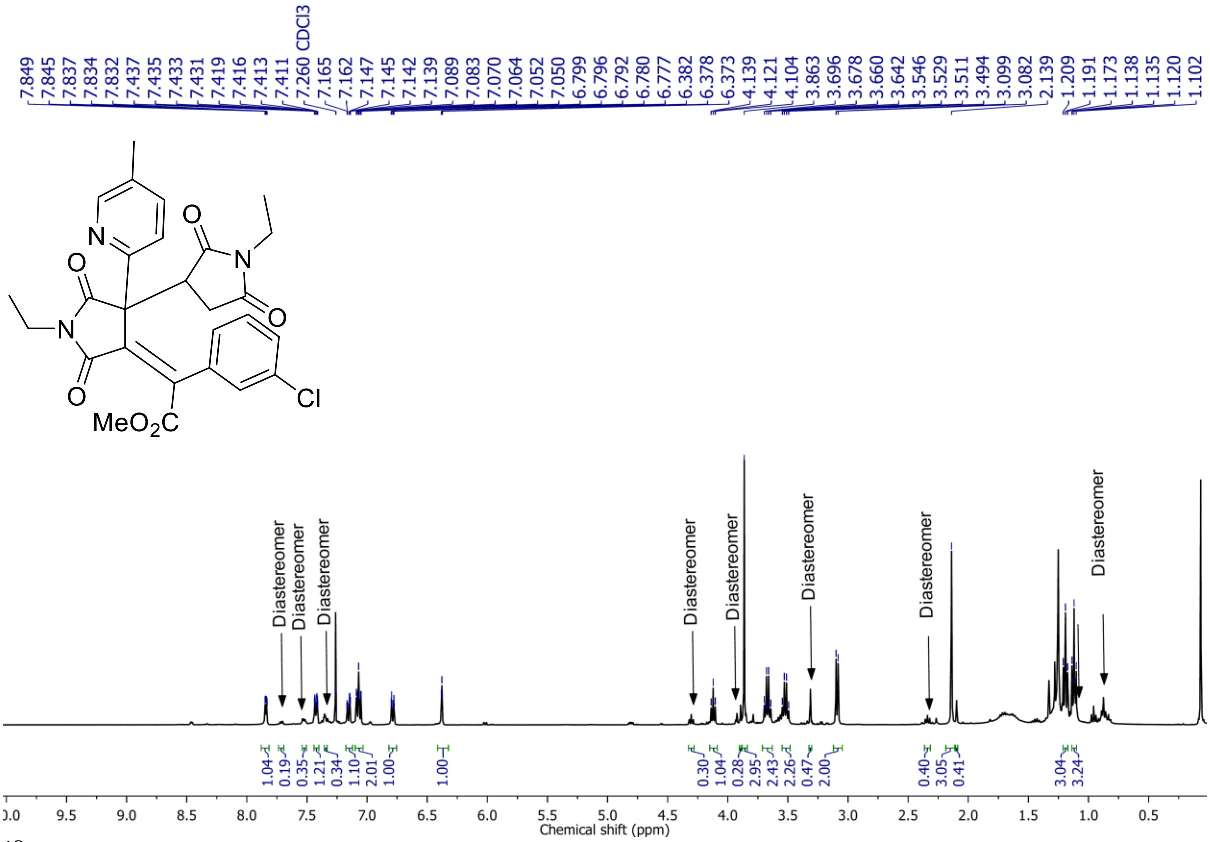
[1]H NMR (400 MHz) of **6s** in CDCl3



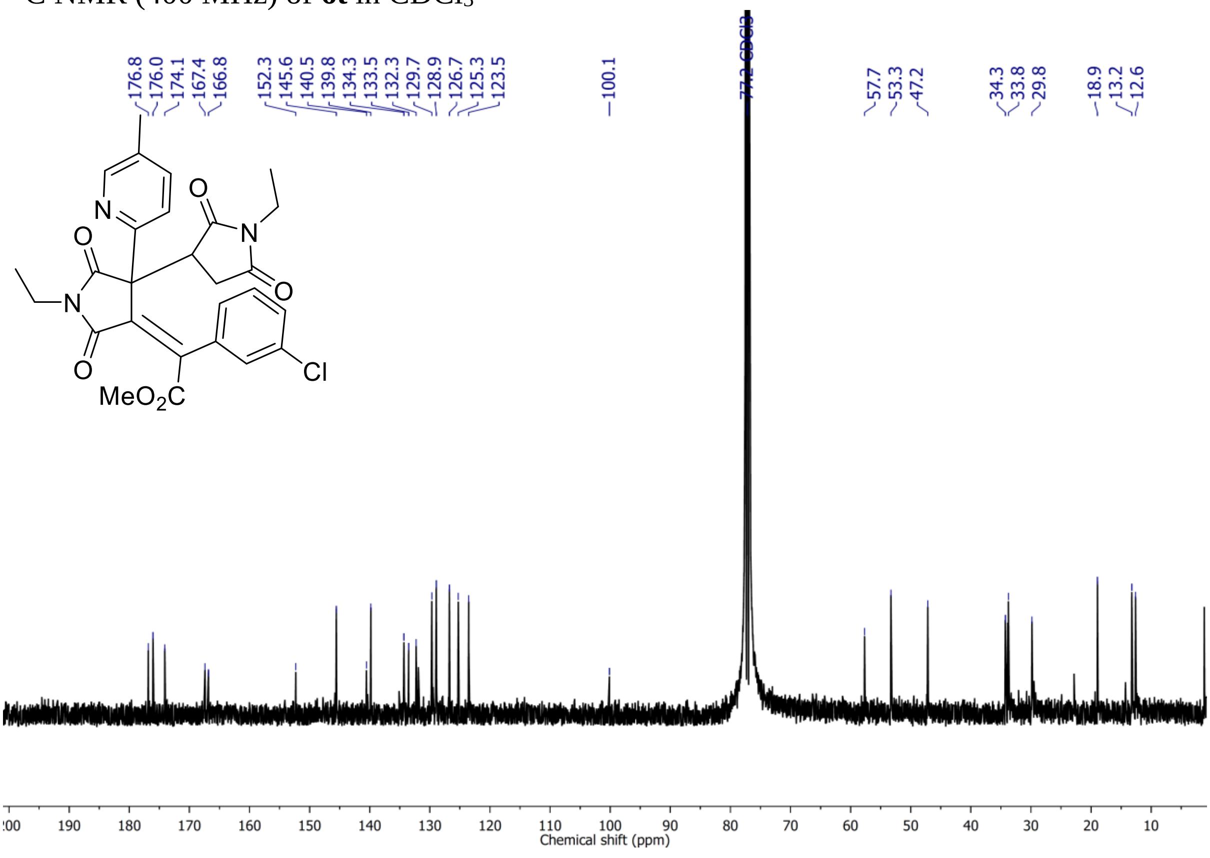
[13]C NMR (400 MHz) of **6s** in $CDCl_3$



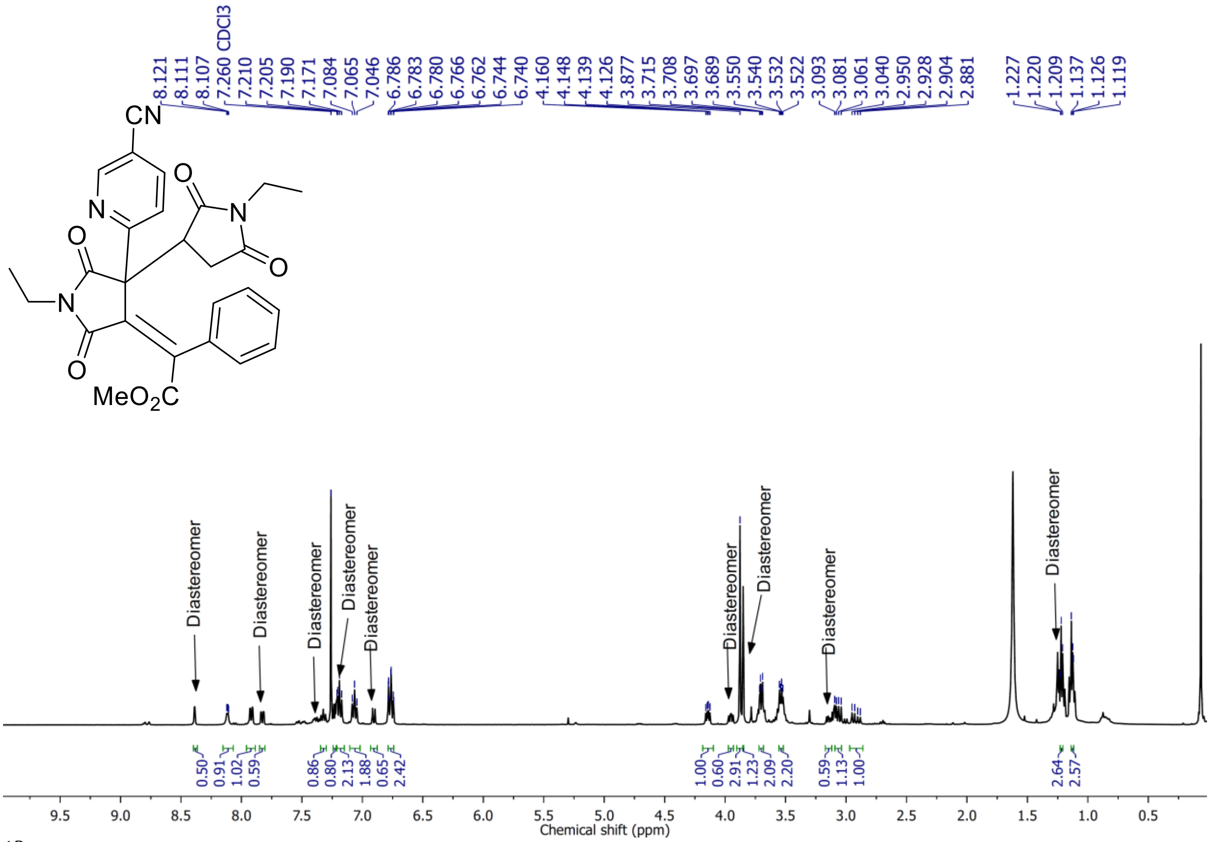
^{1}H NMR (400 MHz) of **6t** in $CDCl_3$



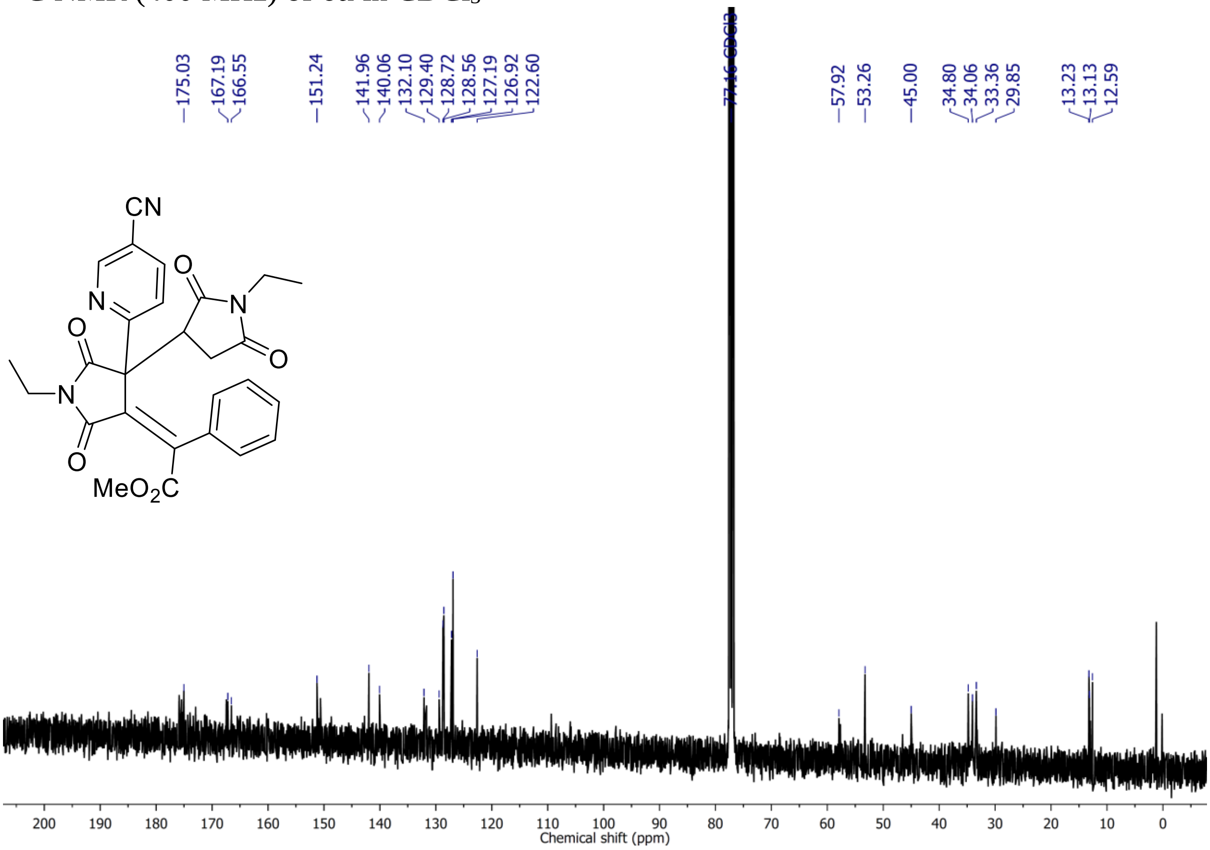
^{13}C NMR (400 MHz) of **6t** in $CDCl_3$



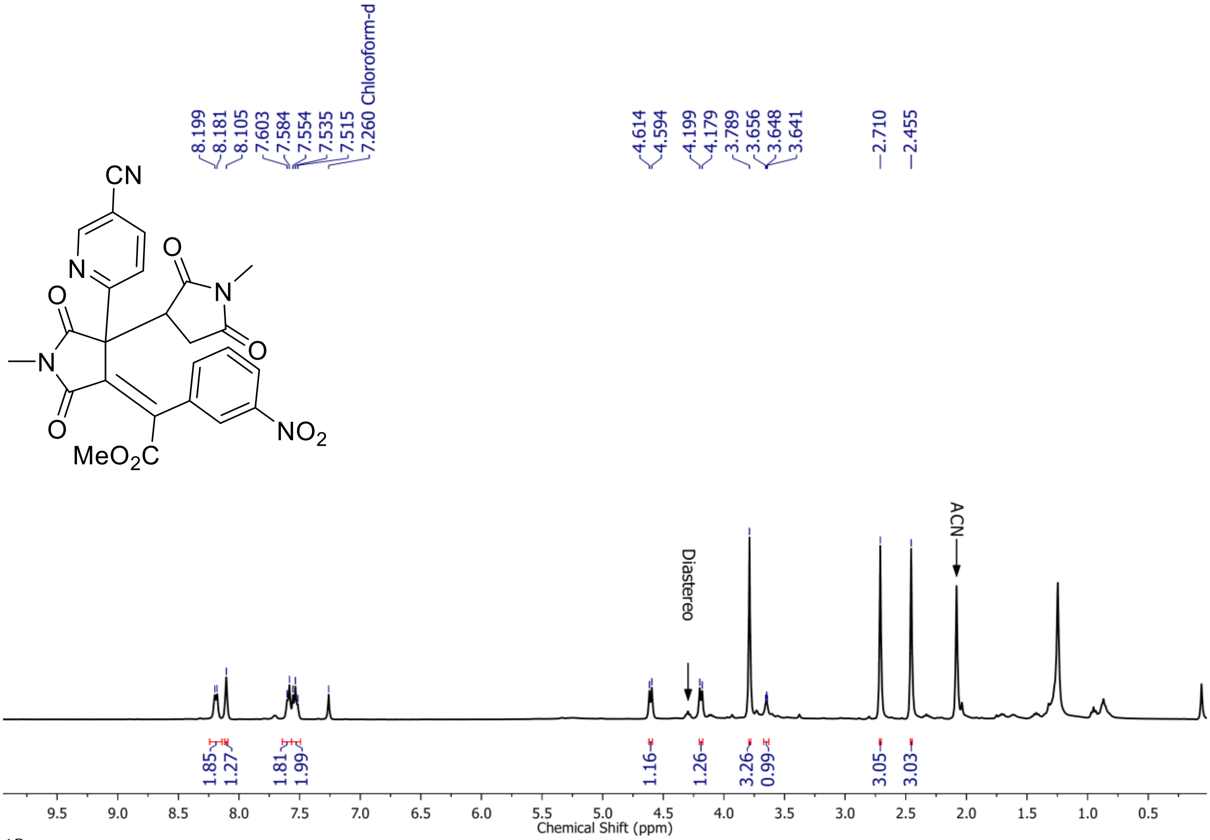
[1]H NMR (400 MHz) of **6u** in $CDCl_3$



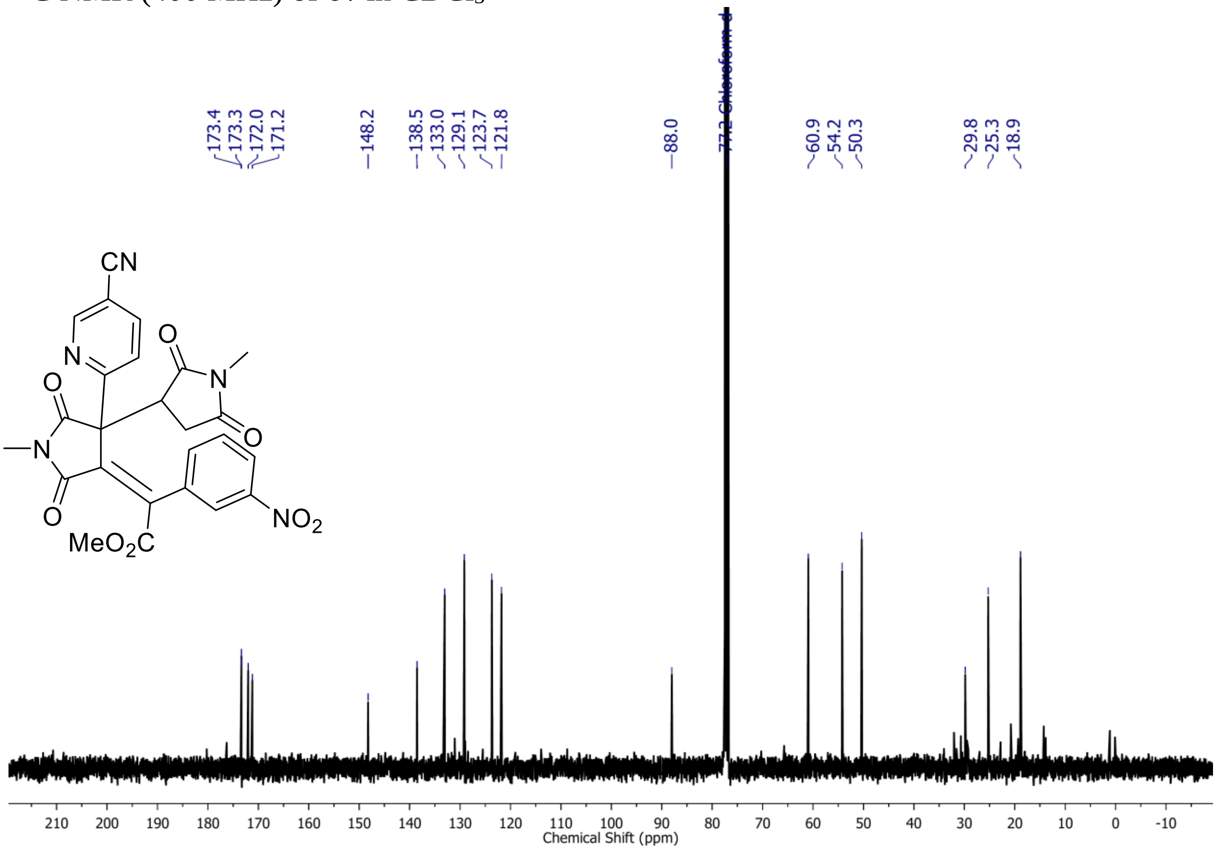
[13]C NMR (400 MHz) of **6u** in $CDCl_3$



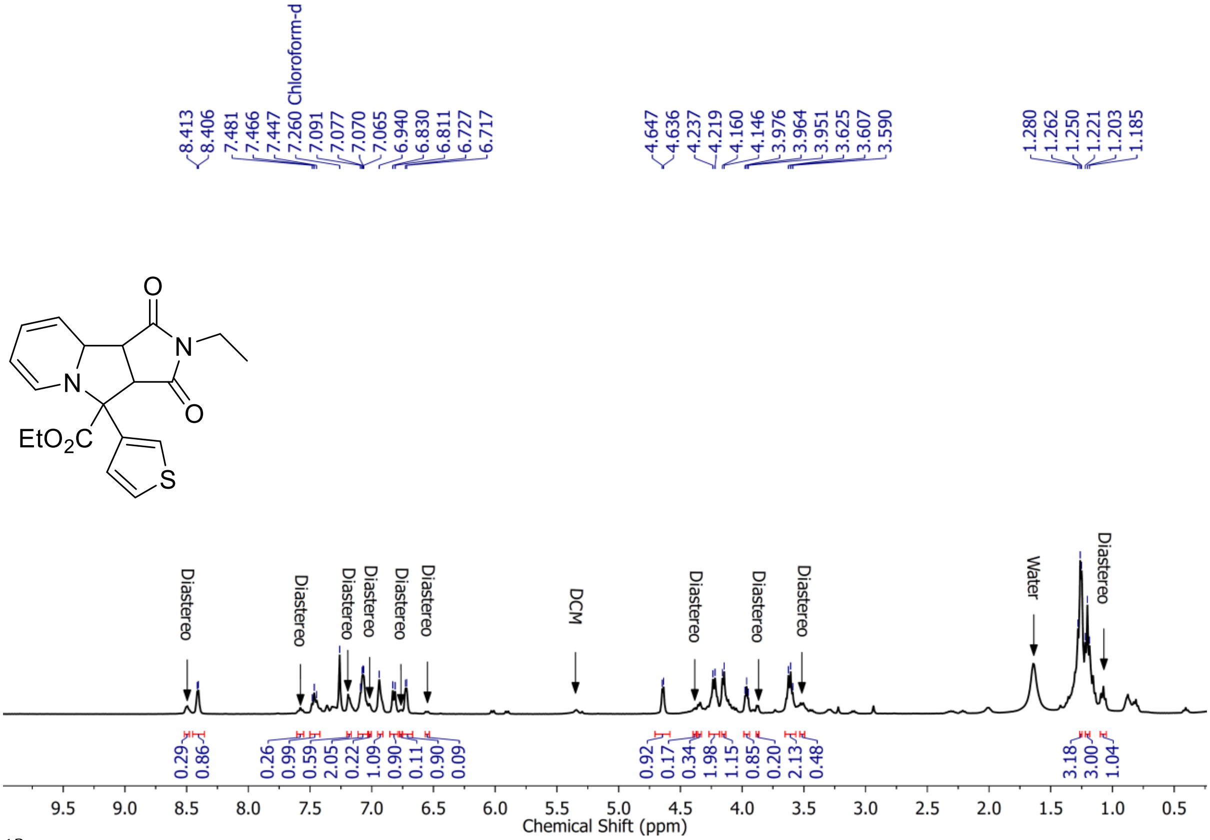
[1]H NMR (400 MHz) of **6v** in $CDCl_3$



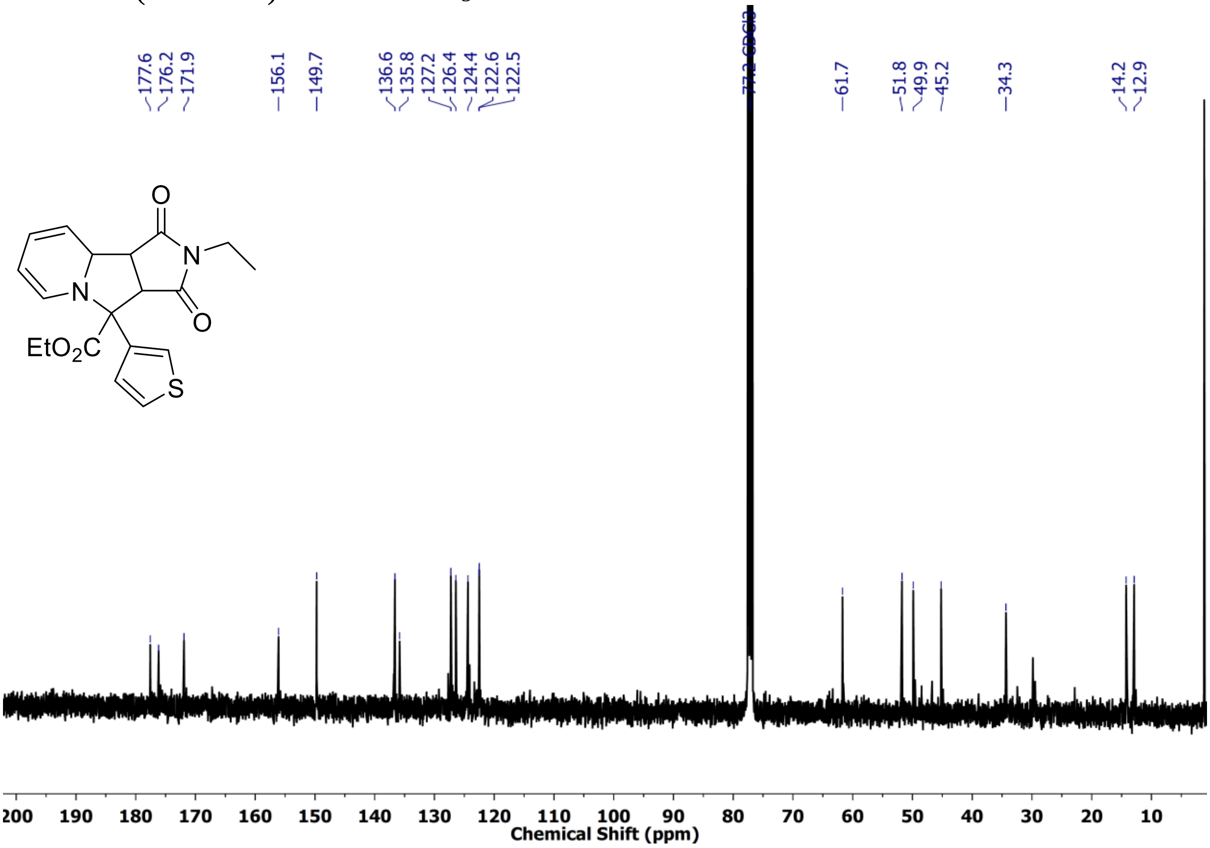
[13]C NMR (400 MHz) of **6v** in $CDCl_3$



^{1}H NMR (400 MHz) of **5l** in $CDCl_3$



^{13}C NMR (400 MHz) of **5l** in $CDCl_3$



7. Optimized Geometries:

(1a)			
6	0.000000000	0.000000000	-1.380608000
6	0.000000000	1.195130000	-0.670555000
6	0.000000000	1.142977000	0.719816000
7	0.000000000	0.000000000	1.415993000
6	0.000000000	-1.142977000	0.719816000
6	0.000000000	-1.195130000	-0.670555000
1	0.000000000	0.000000000	-2.463884000
1	0.000000000	2.151180000	-1.178594000
1	0.000000000	2.059842000	1.300815000
1	0.000000000	-2.059842000	1.300815000
1	0.000000000	-2.151180000	-1.178594000

(2b)			
6	2.125882000	1.492536000	0.174264000
6	0.874492000	0.913912000	0.198656000
6	0.717220000	-0.487106000	-0.006717000
6	1.882829000	-1.267224000	-0.234802000
6	3.134083000	-0.681753000	-0.262821000
6	3.252155000	0.694350000	-0.057222000
1	2.242057000	2.557387000	0.330413000
1	-0.002136000	1.524589000	0.376714000
1	1.761265000	-2.331943000	-0.388081000
1	4.018032000	-1.280617000	-0.439850000
1	4.233349000	1.153722000	-0.077020000
6	-0.531965000	-1.138054000	-0.015927000
6	-1.735648000	-0.416201000	0.268770000
8	-2.159778000	-0.334884000	1.418035000
8	-2.387269000	0.046668000	-0.812365000
6	-3.693624000	0.621943000	-0.572952000
1	-4.067089000	0.901706000	-1.553862000
1	-4.351050000	-0.112456000	-0.108854000
1	-3.610599000	1.498923000	0.067686000

(4b)			
7	-0.958199000	-0.548836000	0.010422000
6	-1.769455000	-0.724736000	-1.056028000
6	-1.097874000	-1.338258000	1.101294000
6	-2.762761000	-1.682756000	-1.048002000
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6	-2.053122000	-2.329267000	1.148476000
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6	-2.908112000	-2.503687000	0.063447000
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1	-2.133190000	-2.941554000	2.035474000
1	-3.673132000	-3.268537000	0.085378000
6	1.435607000	0.045692000	-0.034087000
6	2.519933000	0.928350000	0.189010000
6	1.768768000	-1.303835000	-0.302740000
6	3.833821000	0.481907000	0.151029000
1	2.311761000	1.968255000	0.388597000
6	3.087230000	-1.739184000	-0.333201000
1	0.988721000	-2.028329000	-0.501079000
6	4.138595000	-0.854275000	-0.106620000
1	4.633843000	1.192180000	0.331110000
1	3.292265000	-2.783107000	-0.544101000
1	5.166389000	-1.195301000	-0.131709000
6	-0.407793000	1.819778000	0.016096000
6	0.056892000	0.488336000	-0.004926000
8	0.276003000	2.850479000	-0.025355000
8	-1.789875000	1.908775000	0.111286000
6	-2.328815000	3.233800000	0.087057000
1	-2.069844000	3.747607000	-0.840150000
1	-3.408195000	3.112167000	0.155127000
1	-1.966185000	3.822659000	0.930954000

[TS1]‡			
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6	-1.994615000	-0.602613000	-0.887970000
6	-0.896114000	-1.552442000	0.981270000
6	-2.972015000	-1.584873000	-0.835252000
1	-1.978245000	0.174591000	-1.642873000
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1	-0.073099000	-1.464305000	1.682321000
6	-2.897124000	-2.598351000	0.128839000
1	-3.768949000	-1.565497000	-1.575299000
1	-1.725309000	-3.330897000	1.812092000
1	-3.645135000	-3.387064000	0.168987000
6	1.436104000	0.059638000	-0.046929000
6	2.484727000	0.888578000	0.436833000
6	1.813833000	-1.203559000	-0.583957000
6	3.820147000	0.475803000	0.384806000
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1	3.395628000	-2.588115000	-1.046550000
1	5.210956000	-1.096601000	-0.175587000
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6	0.031981000	0.477539000	-0.019066000
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6	-2.400649000	3.261776000	0.061251000
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1	-1.652556000	4.006780000	-0.228686000
1	-3.169753000	3.171491000	-0.717418000

(6b)				(6b')			
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8	2.632205000	2.713772000	-0.725261000	7	0.473001000	-3.031995000	-0.152922000
7	-1.110231000	1.596229000	2.039691000	8	3.814088000	0.012849000	-1.811981000
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8	3.581852000	1.612082000	0.998370000	6	-0.397257000	-0.812994000	0.065994000
7	-0.007842000	-1.538781000	2.517170000	6	-0.689023000	-2.342960000	0.125427000
8	-4.818313000	-1.083566000	-1.859998000	6	1.578965000	-2.210612000	-0.297068000
6	0.463822000	0.740437000	0.559324000	6	1.956245000	0.221714000	-0.316818000
6	-0.700792000	-0.257679000	0.590237000	6	1.612857000	1.666432000	-0.263577000
6	-1.660435000	0.415107000	1.602107000	6	1.275236000	2.291788000	0.938653000
6	0.129671000	1.864578000	1.477241000	1	1.267751000	1.725851000	1.858532000
6	-2.024476000	0.888009000	-1.304164000	6	0.541492000	-4.485739000	-0.169300000
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6	-1.438410000	-0.424311000	-0.772377000	1	-0.339409000	-4.874639000	-0.674953000
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6	2.112021000	-0.379665000	-1.003484000	6	3.404742000	-0.012670000	-0.675401000
6	-0.236569000	-1.590237000	1.199147000	6	0.954348000	4.380002000	-0.226466000
6	1.721310000	-0.361036000	-2.345796000	6	0.944319000	3.642666000	0.953698000
1	1.051030000	0.411801000	-2.701383000	1	0.676373000	4.116287000	1.890119000
6	-1.772775000	2.469740000	2.997440000	6	1.658840000	2.419576000	-1.441479000
1	-1.072337000	3.251468000	3.277895000	1	1.940482000	1.940795000	-2.370661000
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1	-2.661790000	2.914111000	2.549771000	1	1.335156000	4.336294000	-2.343394000
6	2.708110000	1.732610000	0.172002000	6	5.580298000	-0.292217000	0.189944000
6	3.097388000	-2.292018000	-2.789308000	1	5.753839000	-1.216527000	-0.359308000
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6	0.653529000	-3.841132000	2.475007000	1	-1.135512000	1.839799000	-0.109924000
1	1.001362000	-4.707987000	3.021494000	7	-2.120569000	0.114504000	1.512758000
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1	3.434427000	4.423804000	-1.456894000	1	-5.424213000	0.723403000	-1.670305000
1	3.475923000	-3.035999000	-3.479700000	1	-4.939328000	-0.667957000	-2.676674000

(B)				(5b)			
6	1.346113000	2.317400000	0.922150000	6	1.406885000	2.204360000	1.110916000
6	1.115930000	3.631717000	0.685515000	6	1.217556000	3.516951000	0.818912000
6	-0.146138000	4.014657000	0.084393000	6	0.040337000	3.891141000	0.060659000
6	-1.178098000	3.158857000	0.013140000	6	-1.010257000	3.057108000	-0.042258000
1	2.322014000	1.931166000	1.184782000	1	2.358994000	1.809322000	1.441769000

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1	-0.223485000	4.992120000	-0.379378000	1	0.057785000	4.824059000	-0.492485000
1	-2.096965000	3.393515000	-0.508560000	1	-1.856452000	3.257078000	-0.687788000
6	-1.542909000	-1.527147000	-0.655533000	6	-1.529884000	-1.309624000	-1.004029000
6	-3.037382000	0.212457000	-0.376698000	6	-3.016171000	0.404806000	-0.383941000
7	-2.867071000	-1.096334000	-0.827258000	7	-2.843248000	-0.808931000	-1.059449000
8	-1.110381000	-2.602595000	-0.996933000	8	-1.179900000	-2.369168000	-1.465478000
8	-4.076038000	0.835551000	-0.407454000	8	-4.024889000	1.072672000	-0.425767000
6	-3.920212000	-1.890444000	-1.438702000	6	-3.917775000	-1.455962000	-1.799654000
1	-4.724041000	-2.071690000	-0.725208000	1	-4.770590000	-1.628411000	-1.144192000
1	-4.322885000	-1.377607000	-2.311944000	1	-4.229581000	-0.830876000	-2.636461000
1	-3.486198000	-2.839486000	-1.743796000	1	-3.542650000	-2.405694000	-2.171877000
6	-1.696833000	0.635207000	0.120823000	6	-1.752623000	0.582784000	0.424833000
6	0.540923000	-0.040903000	0.491401000	6	0.552091000	-0.101680000	0.448694000
6	-0.843843000	-0.372422000	-0.013391000	6	-0.727781000	-0.170391000	-0.409064000
7	0.344410000	1.394557000	0.791045000	7	0.390307000	1.302194000	0.931528000
6	-1.072977000	1.840677000	0.742384000	6	-1.005312000	1.844388000	0.848046000
1	-1.465801000	1.951642000	1.769951000	1	-1.313729000	2.133496000	1.861857000
6	1.638138000	-0.292619000	-0.554026000	6	1.823161000	-0.327612000	-0.373863000
6	2.708469000	-1.155467000	-0.326794000	6	2.660910000	-1.420545000	-0.152491000
6	1.550602000	0.368962000	-1.782106000	6	2.137779000	0.558674000	-1.409706000
6	3.673416000	-1.357841000	-1.311267000	6	3.783067000	-1.629495000	-0.950680000
1	2.810733000	-1.678883000	0.615270000	1	2.453179000	-2.125911000	0.641646000
6	2.512194000	0.167334000	-2.763471000	6	3.258139000	0.351973000	-2.204444000
1	0.729626000	1.051190000	-1.968281000	1	1.511651000	1.423423000	-1.592271000
6	3.577961000	-0.699325000	-2.531037000	6	4.085937000	-0.744947000	-1.978460000
1	4.500100000	-2.030505000	-1.117876000	1	4.418957000	-2.486030000	-0.762683000
1	2.430173000	0.687961000	-3.709891000	1	3.485835000	1.051327000	-2.999846000
1	4.329037000	-0.856568000	-3.295639000	1	4.960491000	-0.905078000	-2.597289000
6	0.858664000	-0.799080000	1.812655000	6	0.537268000	-1.031059000	1.687911000
8	1.523725000	-0.329719000	2.702010000	8	1.166301000	-0.802557000	2.692065000
8	0.316048000	-2.013950000	1.829095000	8	-0.240176000	-2.099415000	1.513035000
6	0.562820000	-2.819499000	3.008172000	6	-0.318226000	-3.033418000	2.617808000
1	0.035953000	-3.751967000	2.831965000	1	-0.993253000	-3.815194000	2.283982000
1	1.630984000	-2.995347000	3.121910000	1	0.668487000	-3.440413000	2.830566000
1	0.172034000	-2.314512000	3.889414000	1	-0.712268000	-2.531771000	3.499650000
				1	-1.948940000	0.000386000	1.333498000
				1	-0.506424000	0.450417000	-1.284891000

(3a)				(H_2)			
6	1.139175000	0.204031000	-0.000598000	1	0.000000000	0.000000000	0.372276000
6	-1.139264000	0.203691000	-0.000615000	1	0.000000000	0.000000000	-0.372276000
7	0.000085000	-0.592244000	-0.008828000				
6	0.664479000	1.626516000	0.001656000				
6	-0.664980000	1.626316000	0.001719000				
1	1.348537000	2.461215000	0.002131000				
1	-1.349294000	2.460805000	0.002212000				
8	2.281307000	-0.202832000	0.001395000				
8	-2.281290000	-0.203452000	0.001381000				
6	0.000392000	-2.044528000	0.003595000				
1	-0.890991000	-2.398194000	-0.510172000				
1	0.889094000	-2.398124000	-0.514866000				
1	0.003117000	-2.425880000	1.025745000				

[TS2]$S_0^‡$				(C)			
6	-4.713505000	1.606382000	-1.057085000	6	-0.684441000	1.073175000	-0.108908000
6	-4.473559000	2.921103000	-0.798770000	6	-0.948733000	-0.287374000	-0.078014000
6	-3.347285000	3.255349000	0.048666000	6	0.626050000	1.646585000	-0.452490000
6	-2.336841000	2.382416000	0.208115000	6	1.092430000	2.823302000	0.156000000
1	-5.668988000	1.268363000	-1.429835000	6	1.451098000	1.046242000	-1.416987000
1	-5.211103000	3.664003000	-1.068434000	6	2.333437000	3.358898000	-0.164442000
1	-3.425223000	4.131742000	0.683927000	1	0.479457000	3.315853000	0.901331000
1	-1.645603000	2.414008000	1.040340000	6	2.690211000	1.581513000	-1.741913000
6	-1.763511000	-1.886164000	1.133366000	1	1.113432000	0.144266000	-1.911360000
6	-0.293577000	-0.165723000	0.468710000	6	3.144836000	2.739391000	-1.113461000
7	-0.410951000	-1.373992000	1.151513000	1	2.672050000	4.260940000	0.332748000
8	-2.052052000	-2.970255000	1.577470000	1	3.304922000	1.092696000	-2.489329000
8	0.686112000	0.534606000	0.526861000	1	4.114444000	3.154660000	-1.361614000
6	0.688374000	-1.985138000	1.865186000	6	-1.760480000	2.034767000	0.179274000
1	0.791783000	-1.558464000	2.862470000	8	-1.953463000	3.091432000	-0.404488000
1	0.493555000	-3.054315000	1.942711000	8	-2.502209000	1.672942000	1.256408000
1	1.637910000	-1.803896000	1.289285000	6	-3.695491000	2.436762000	1.484930000
6	-1.457410788	-0.074256510	-0.388855474	1	-4.160920000	2.000122000	2.365508000
6	-3.969770615	-0.655004831	-0.366775412	1	-3.458962000	3.485951000	1.663391000
6	-2.549815651	-0.788783831	0.686644175	1	-4.362945000	2.354898000	0.625831000
7	-3.735594000	0.673573000	-0.882732000	7	-2.266200000	-2.172541000	-0.378165000
6	-2.387196946	1.301390172	-0.776919289	6	-2.343409000	-0.807920000	-0.380792000
1	-2.162917946	1.657943172	-1.787352289	6	-0.920296000	-2.602823000	-0.187817000
6	-5.251638615	-0.910547831	0.427236588	8	-3.346433000	-0.177135000	-0.690696000
6	-6.487454615	-0.822741831	-0.220244412	8	-0.627040000	-3.800656000	-0.173651000
6	-5.219092615	-1.314575831	1.760625588	6	-3.364593000	-3.043628000	-0.736130000
6	-7.669984615	-1.070302831	0.466870588	1	-3.019632000	-4.071375000	-0.648222000
1	-6.527533615	-0.595855831	-1.278264412	1	-4.210292000	-2.885341000	-0.065839000
6	-6.402853615	-1.571453831	2.446703588	1	-3.692421000	-2.856403000	-1.761496000
1	-4.280358615	-1.437974831	2.279946588	6	1.282497000	-1.504119000	0.409118000
6	-7.631203615	-1.439340831	1.808160588	6	2.129278000	-2.516941000	-0.083216000
1	-8.618222615	-0.988770831	-0.050235412	6	3.457902000	-2.548927000	0.302769000
1	-6.359719615	-1.881482831	3.483759588	1	1.731788000	-3.254552000	-0.765565000
1	-8.550087615	-1.635945831	2.347012588	6	3.034864000	-0.614839000	1.624400000
6	-3.964925615	-1.695474831	-1.512046412	6	3.935814000	-1.573370000	1.175932000
8	-4.191835615	-1.425817831	-2.667276412	1	4.118755000	-3.318201000	-0.080473000
8	-3.719183615	-2.918370831	-1.026000412	1	3.364013000	0.160983000	2.310814000
6	-3.704576615	-4.041434831	-1.937302412	1	4.968889000	-1.554225000	1.499086000
1	-4.725039615	-4.268606831	-2.247502412	7	1.750653000	-0.570313000	1.267801000
1	-3.090408615	-3.829829831	-2.808207412	6	-0.114407000	-1.427853000	0.007940000
1	-3.295962615	-4.864245831	-1.357975412				
1	-1.287312788	-0.691477510	-1.283406474				
1	-2.707998651	-0.124131831	1.544214175				

[TOPTS3]$S_0^‡$				[BottomTS3]$S_0^‡$			
8	3.033390080	-0.007966529	1.414401563	8	2.004907851	2.391958597	1.373303552
8	0.787033312	-1.895714266	-1.662750809	8	-2.187098194	3.015468298	-0.511530298
8	-0.680080808	-2.475576839	2.295650811	8	-4.046498552	0.808227851	0.380851000
8	-2.836065280	-2.473103976	-0.130231339	7	-0.050012806	3.020299552	0.355954149
7	1.351176590	-1.440911883	1.995680503	8	-3.816685000	0.606820000	-1.935574851
7	2.855583664	-0.939463439	-1.869798472	6	-0.952323298	0.931072403	-0.119796657
8	-3.525409147	-1.244615087	1.625675060	6	0.469202492	0.714778464	0.363669315
7	0.403789821	1.697150431	2.498068907	6	0.980598403	2.127518613	0.692457238
8	4.636881460	0.515577216	-1.898025990	6	-1.190380851	2.380007895	-0.108349597
6	-0.441336512	-0.557154540	0.817339932	6	-1.943164702	0.059147702	-0.450856448
6	0.380317244	0.370950633	0.702742568	6	-1.825408000	-1.434874000	-0.634609000
6	1.873082740	-0.347146298	1.356472815	6	-2.357100851	-2.315890000	0.339137000
6	-0.012528138	-1.611486258	1.777586334	1	-2.784495597	-1.913150000	1.255717552
6	1.517640913	-0.941840489	-1.529921449	6	0.154836298	4.440769194	0.480416149
6	-1.675825890	-0.481614180	0.317757617	1	1.001150403	4.726875685	-0.153869298

6	1.156625644	0.430793534	-0.945477570	1	0.409386254	4.677488238	1.521730000
1	0.294104323	0.800201703	-1.495942881	1	-0.742861044	4.986092508	0.179038702
6	-2.148002314	0.566494213	-0.626942770	6	-3.336668552	0.552412000	-0.782229149
6	0.517100337	1.726431738	1.165932936	6	-1.756561000	-4.228179149	-1.050069000
6	-2.340505077	0.268018285	-1.977638220	6	-2.308231851	-3.709762851	0.140826851
1	-2.143681990	-0.732799082	-2.339348006	1	-2.692215298	-4.381971702	0.903986851
6	2.149139908	-2.290426704	2.865552248	6	-1.296189149	-1.965885000	-1.840556702
1	2.961257353	-2.734350301	2.292379025	1	-0.918924702	-1.292581000	-2.603558552
1	1.495853807	-3.062475251	3.260480904	6	-1.259084149	-3.360980851	-2.043573702
1	2.569862707	-1.706042140	3.685004036	1	-0.852175552	-3.764037552	-2.969385552
6	-2.763219729	-1.450453570	0.712739847	6	-5.424739597	1.319289149	0.208843000
6	-3.004001798	2.550492287	-2.391314214	1	-5.385262448	2.304219149	-0.266383000
6	2.346996056	1.305268537	-1.046329735	1	-6.011158448	0.624341149	-0.402578000
1	2.840635875	2.108879489	-0.369782662	1	-5.825855149	1.383912149	1.220514149
6	0.367875644	2.895944107	0.430500379	1	-1.727767702	-5.304906149	-1.205964000
1	0.427910913	2.897769003	-0.646876469	6	0.696538895	-0.346639270	1.451471536
6	-2.758094821	1.260973835	-2.856793314	6	-0.323375149	-0.616470895	2.392399403
1	-2.889682734	1.027132434	-3.906202223	6	2.286603403	-1.450804552	2.808618000
6	-2.414958138	1.854639090	-0.159852102	6	-0.047817851	-1.467159851	3.478335149
1	-2.281357071	2.082811431	0.889423722	1	-1.325333448	-0.221056387	2.238011806
6	-2.839035416	2.842841947	-1.040910908	6	1.282707851	-1.854712641	3.713927105
1	-3.033395315	3.842182313	-0.671412762	1	3.312547298	-1.820847928	2.889705835
6	3.476896213	0.319468373	-1.693760766	1	-0.864333956	-1.864019226	4.092029133
6	0.092112904	4.078678742	1.106996030	1	1.500111790	-2.659390032	4.444710177
1	-0.033156908	5.002081212	0.555759485	6	1.350169254	0.142899448	-1.065499149
6	0.135775641	2.833881583	3.138507326	6	1.808696149	-1.272862552	-1.089184851
1	0.047470938	2.768283743	4.217844488	1	0.619295597	0.411484298	-1.838671492
6	-0.027869336	4.053253471	2.488349948	1	1.190250702	-2.140066403	-0.904821895
1	-0.243786952	4.949996441	3.054142409	7	2.024470403	-0.622499044	1.749407105
6	3.533652132	-2.117362016	-2.387897378	6	2.627625000	0.974905000	-1.303655149
1	3.504759640	-2.913001234	-1.644743783	7	3.677057000	0.108199851	-1.305432000
1	4.564215528	-1.848156376	-2.604530921	6	3.198938000	-1.323976000	-1.165603851
1	3.039387642	-2.457287192	-3.297304620	8	4.065342149	-2.277278149	-1.168469000
6	-3.872783288	-3.441978850	0.124596319	8	2.694740851	2.236147851	-1.521456851
1	-3.715559121	-3.903011155	1.098697165	6	5.075645149	0.477759000	-1.492731000
1	-4.850490483	-2.963412591	0.093675147	1	5.230046000	0.988725000	-2.453962000
1	-3.781234722	-4.179477030	-0.667244347	1	5.419614000	1.144224000	-0.688510000
1	-3.327000634	3.322848561	-3.078685062	1	5.659175149	-0.448278000	-1.473689000

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