Supporting Information

Dual C(sp^3)-H Bond Functionalization of N-Heterocycles via Visible-Light Photocatalyzed Dehydrogenation/[2+2] Cycloaddition Sequential Reaction

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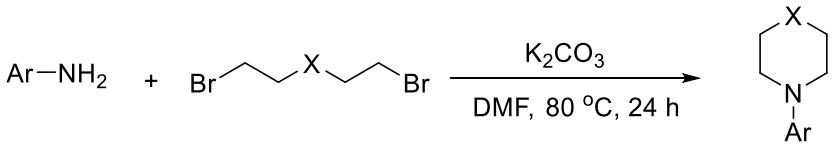
Supplementary Materials

1. General Information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in $CDCl_3$ as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q=quartet, m = multiplet, dd = doublet, dt = doublet of triplet, ddd = doublet of doublets of doublets), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. IR spectra were recorded using Nicolet NEXUS 670 FT-IR instrument and are reported in wavenumbers (cm^{-1}). HRMS were performed on a Bruker Apex II mass instrument (ESI). All the samples for Stern-Volmer bimolecular quenching studies were prepared in 1 cm quartz cuvettes, using spectrophotometric grade DCM that was freeze-pump-thaw degassed prior to use. A three-electrode setup was used, consisting of a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). All samples were prepared using spectrophotometric grade acetonitrile, which was degassed via purging with N_2 before 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was used as the supporting electrolyte; Bu_4NPF_6 was recrystallized twice from ethanol. Ferrocene was added as an internal standard. Data were acquired by cyclic voltammetry (CV), the scan rate for the CV measurements was 0.1 V/s. All photocatalytic reactions were performed under irradiation of a 23-W compact fluorescent light (CFL, 1-2 centimeters from either side of the vial).

2. Synthesis of Substrates

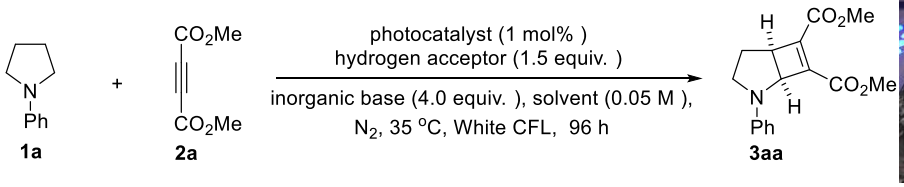
Cyclic amines were synthesized according to reported procedures with some modifications. [1-2]

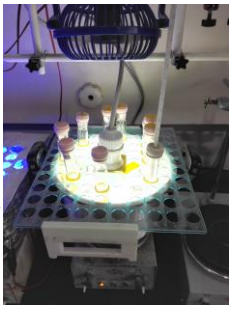


General Procedure: K_2CO_3 (1.52 g, 11 mmol, 1.1 equiv.) was weighed into an oven-dried 25 mL round-bottom flask with magnetic stirring and DMF (10 mL, 1.0 M) was then added. The appropriate aniline (10 mmol, 1.0 equiv.) was added into the reaction mixture *via* syringes. The reaction system was degassed (10 min) and backfilled with nitrogen. The corresponding dibromide (11 mmol, 1.1 equiv.) was added, and the reaction mixture was heated to 80 ℃ for 24 h. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and then diluted with EtOAc (20 mL) and H_2O (20 mL). The layers were separated, and the organic layer was extracted with 1 N HCl (3 x 10 mL). The acid layers were combined and adjusted to pH 8 with 1 N NaOH and then extracted with EtOAc (3 x 10 mL). The organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by flash chromatography.

3. Optimization Studies

3.1 Optimization of the reaction conditions



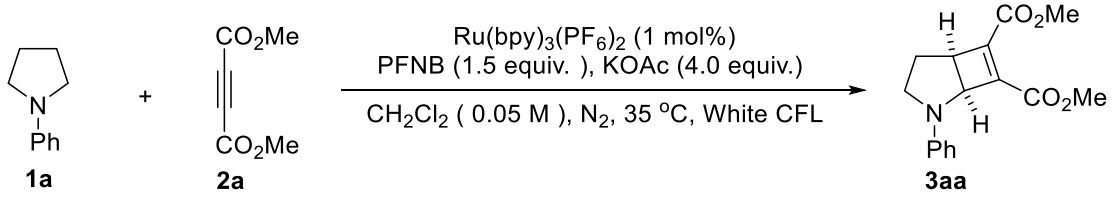


Entry	Photocatalyst	Base	Hydrogen acceptor	Solvent	Yield [a]
1	$Ru(bpy)_3(PF_6)_2$	KOAc	$PhNO_2$	DCM	70%
2	$Ir(ppy)_2(dtbbpy)PF_6$	KOAc	$PhNO_2$	DCM	59%
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	KOAc	$PhNO_2$	DCM	67%
4	$Ir(ppy)_3$	KOAc	$PhNO_2$	DCM	24%
5	$Ru(bpy)_3(PF_6)_2$	LiOAc	$PhNO_2$	DCM	48%
6	$Ru(bpy)_3(PF_6)_2$	NaOAc	$PhNO_2$	DCM	68%
7	$Ru(bpy)_3(PF_6)_2$	CsOAc	$PhNO_2$	DCM	52%
8	$Ru(bpy)_3(PF_6)_2$	KOH	$PhNO_2$	DCM	46%

9	$Ru(bpy)_3(PF_6)_2$	K_2CO_3	$PhNO_2$	DCM	11%
10	$Ru(bpy)_3(PF_6)_2$	K_3PO_4	$PhNO_2$	DCM	38%
11	$Ru(bpy)_3(PF_6)_2$	DBU	$PhNO_2$	DCM	Trace
12	$Ru(bpy)_3(PF_6)_2$	Et_3N	$PhNO_2$	DCM	8%
13	$Ru(bpy)_3(PF_6)_2$	Pyridine	$PhNO_2$	DCM	trace
14	$Ru(bpy)_3(PF_6)_2$	DABCO	$PhNO_2$	DCM	13%
15	$Ru(bpy)_3(PF_6)_2$	KOAc	Selectflour	DCM	trace
16	$Ru(bpy)_3(PF_6)_2$	KOAc	1,4-BQ	DCM	18%
17	$Ru(bpy)_3(PF_6)_2$	KOAc	$BrCCl_3$	DCM	trace
18	$Ru(bpy)_3(PF_6)_2$	KOAc	O_2 Ball	DCM	29%
19	$Ru(bpy)_3(PF_6)_2$	KOAc	$MeNO_2$	DCM	N.R.
20	$Ru(bpy)_3(PF_6)_2$	KOAc	$BrCF_2CO_2Et$	DCM	26%
21	$Ru(bpy)_3(PF_6)_2$	KOAc	$PhNO_2$	Toluene	26%
22	$Ru(bpy)_3(PF_6)_2$	KOAc	$PhNO_2$	DCE	60%
23	$Ru(bpy)_3(PF_6)_2$	KOAc	$PhNO_2$	$CHCl_3$	54%
24	$Ru(bpy)_3(PF_6)_2$	KOAc	$PhNO_2$	DME	N.R.

Table S1: Optimization Studies. The reaction was carried out with **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.3 mmol, 3.0 equiv.), photocatalyst (0.001 mmol, 1 mol%), base (0.4 mmol, 4.0 equiv.), hydrogen acceptor (0.15 mmol, 1.5 equiv.), solvent (0.05 M) at 35 ^{o}C under the irradiation of 23-W fluorescent light bulb. [a] Isolated yield.

3.2 Time-yield relationship curve.



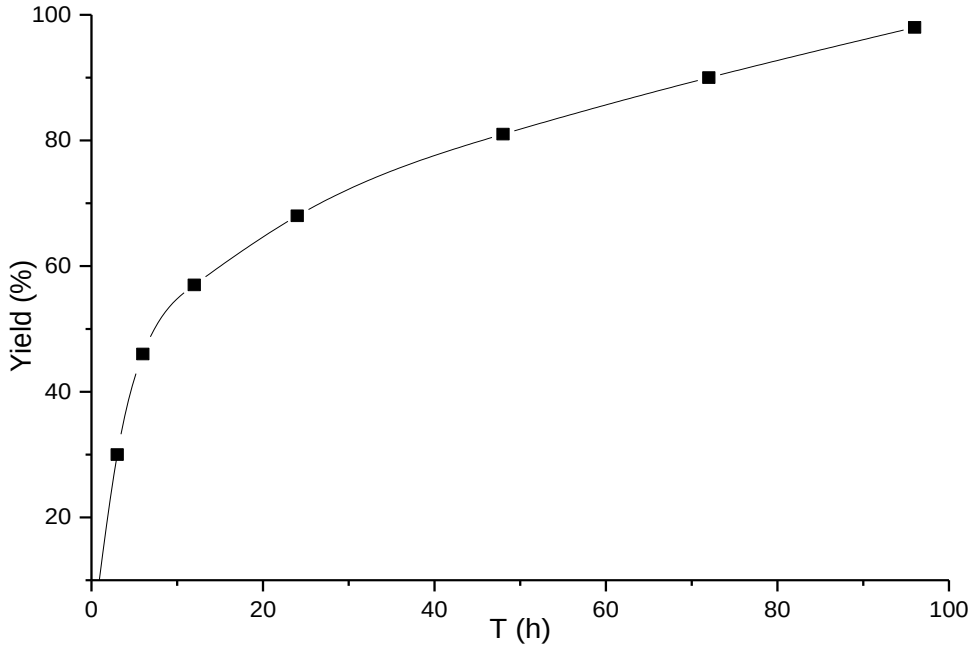
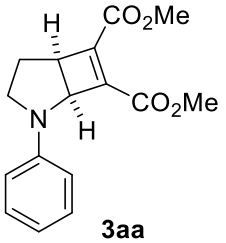


Figure S1: Time-yield relationship curve. The reaction was carried out with **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.3 mmol, 3.0 equiv.), photocatalyst (0.001 mmol, 1 mol%), base (0.4 mmol, 4.0 equiv.), hydrogen acceptor (0.15 mmol, 1.5 equiv.), and solvent (0.05 M) at 35 ^{o}C under the irradiation of a 23-W fluorescent light bulb. Seven parallel reactions were performed under the same conditions. After 3 h, 6 h, 12 h, 24 h, 48 h, 72 h, 96 h, the reaction mixtures were concentrated and purified by flash chromatography, respectively. Time-yield relationship curve was done in Origin.

4. Photocatalyzed Dehydrogenation/[2+2] Cycloaddition Reaction

General Procedure: $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%) and KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.) were weighed into an oven-dried 8 mL vial with a magnetic stirring bar, and then DCM (0.05 M, 2 mL) was added. The corresponding alkynester **2** (0.3 mmol, 3.0 equiv.), 1, 2, 3, 4, 5-pentafluoro-6- nitrobenzene (PFNB, 0.15 mmol, 18.8 μL, 1.5 equiv.) and amine (0.1 mmol, 1.0 equiv.) were successively added into the mixture *via* syringes. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a 23-W compact fluorescent light (CFL, 1-2 centimeters from the vial), allowing the temperature to rise due to its proximity to the lights. After 96 h, the crude mixture was concentrated and purified by flash chromatography (silica gel, mixtures of petroleum ether/ethyl acetate) to afford the pure product **3**.

Dimethyl 2-phenyl-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarbo-xylate (3aa)

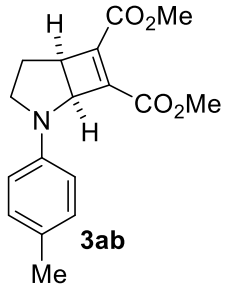


3aa

Following the general procedure: **1a** (14.7 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (18.8 μL, 0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05

M). Compound **3aa** was obtained as a yellow solid in 99% yield; mp= 106-108 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.15 (m, 2H), 6.89-6.80 (m, 2H), 6.75 (t, *J*=7.3 Hz, 1H), 5.10 (d, *J*=3.7 Hz, 1H), 3.79(s, 3H), 3.76-3.69 (m, 2H), 3.56 (s, 3H), 3.18 (td, *J*=10.4 Hz, *J*=6.1 Hz, 1H), 2.11 (dd, *J*=13.1 Hz, *J*=6.1 Hz, 1H), 1.99-1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 161.5, 146.3, 143.0, 141.2, 128.8, 118.1, 114.3, 60.3, 51.9, 51.7, 45.3, 45.2(9), 24.4; IR (KBr, cm^{-1}): 2949.7, 2842.4, 2360.3, 1713.5, 1640.7, 1597.7, 1502.0, 1431.5, 1360.8, 1291.3, 1236.1, 1174.7, 1123.6, 1077.5, 755.2, 690.8; HRMS (ESI) for $C_{16}H_{17}NO_4$ $[M+H]^+$ calcd. 288.1230, found 288.1228;

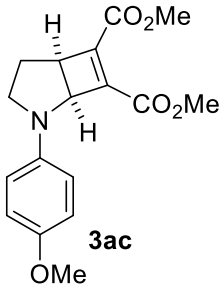
Dimethyl 2-(p-tolyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3ab).



Following the general procedure: **1b** (16.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ab** was obtained as a red solid in 88 % yield; mp= 55-57 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, *J*=8.4 Hz, 2H), 6.76 (d, *J*=8.5 Hz, 2H), 5.06 (d, *J*=3.7 Hz, 1H), 3.79(s, 3H), 3.74-3.67 (m, 2H), 3.56 (s, 3H), 3.15 (td, *J*=10.4 Hz, *J*=6.1 Hz, 1H), 3.24 (s, 3H), 2.11 (dd, *J*=13.0 Hz, *J*=6.1 Hz, 1H), 1.99-1.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 161.5, 144.1, 143.2, 141.0, 129.4, 127.3, 114.4, 60.6, 52.0, 51.8, 45.4, 45.3(6), 24.4, 20.3; IR (KBr, cm^{-1}): 2951.5, 2859.0, 1721.9, 1642.8, 1617.9, 1592.2, 1517.7, 1434.8, 1357.1, 1306.6, 1255.9, 1235.6, 1175.5, 1118.3, 1081.3, 965.1, 807.9, 756.1; HRMS (ESI) for $C_{17}H_{19}NO_4$ $[M+H]^+$ calcd. 302.1387, found 302.1382;

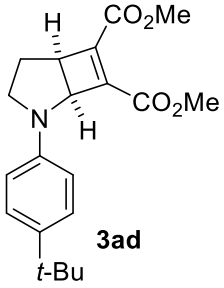
Dimethyl 2-(4-methoxyphenyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate

(3ac).



Following the general procedure: **1c** (17.7 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ac** was obtained as a red solid in 42 % yield; mp= 36-38 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 6.80 (s, 4H), 5.04 (d, *J*=3.7 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.70 (dd, *J*=7.9 Hz, *J*=3.7 Hz, 1H), 3.62 (dd, *J*=9.4 Hz, *J*=7.9 Hz, 1H), 3.55 (s, 3H), 3.15 (td, *J*=10.7 Hz, *J*=6.9 Hz, 1H), 2.08 (dd, *J*=13.2 Hz, *J*=6.1 Hz, 1H), 1.99-1.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 161.5, 152.5, 143.1, 140.9, 140.7, 115.7, 114.3, 61.1, 55.6, 52.0, 51.7, 45.7, 45.3, 24.5; IR (KBr, cm^{-1}): 2951.5, 2926.4, 2838.5, 1721.2, 1641.5, 1591.3, 1511.2, 1434.9, 1350.5, 1243.1, 1178.2, 1119.4, 1072.7, 1036.5, 963.0, 822.1, 756.4; HRMS (ESI) for $C_{16}H_{17}NO_5$ $[M+H]^+$ calcd. 318.1336, found 318.1333;

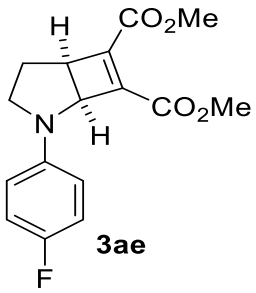
Dimethyl 2-(4-(tert-butyl)phenyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3ad).



Following the general procedure: **1d** (20.3 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (31.2 μL, 0.25 mmol, 2.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ad** was obtained as a red solid in 80 % yield; mp= 78-80 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.20 (m, 2H), 6.83-6.77 (m, 2H), 5.07 (d, *J*=3.8 Hz,

1H), 3.79 (s, 3H), 3.75-3.69 (m, 2H), 3.54 (s, 3H), 3.17 (td, *J*=10.5 Hz, *J*=6.2 Hz, 1H), 2.08 (dd, *J*=13.2 Hz, *J*=6.2 Hz, 1H), 1.99-1.84 (m, 1H), 1,27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 161.6, 144.0, 143.3, 141.1, 140.8, 125.6, 114.1, 60.6, 52.0, 51.7, 45.4(5), 45.4(3), 33.8, 31.5, 24.5; IR (KBr, cm^{-1}): 2954.9, 2867.7, 1779.8, 1726.1, 1637.1, 1612.6, 1587.9, 1517.7, 1435.5, 1352.7, 1274.6, 1234.5, 1174.5, 1114.7, 1070.7, 1017.8, 961.6, 824.3, 764.9; HRMS (ESI) for $C_{20}H_{25}NO_4$ $[M+H]^+$ calcd. 344.1856, found 344.1852;

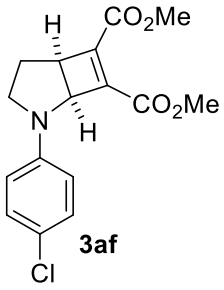
Dimethyl 2-(4-fluorophenyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3ae).



3ae

Following the general procedure: **1e** (16.5 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (31.2 μL, 0.25 mmol, 2.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ae** was obtained as a red solid in 86 % yield; mp= 88-90 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99-6.86 (m, 2H), 6.82-6.75 (m, 2H), 5.05 (d, *J*=3.8 Hz, 1H), 3.79 (s, 3H), 3.72 (dd, *J*=8.0 Hz, *J*=3.8 Hz, 1H), 3.72 (dd, *J*=9.5 Hz, *J*=8.0 Hz, 1H), 3.56 (s, 3H), 3.17 (td, *J*=10.9 Hz, *J*=6.0 Hz, 1H), 2.08 (dd, *J*=13.1 Hz, *J*=6.0 Hz, 1H), 1.99-1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 161.5, 157.3, 155.0, 142.8 (d, *J*=1.6 Hz), 142.1 (d, *J*=109.0 Hz), 115.4, 115.3 (d, *J*=30.0 Hz), 60.8, 52.0, 51.8, 45.8, 45.4, 24.5; IR (KBr, cm^{-1}): 2953.9, 2844.2, 1721.9, 1642.9, 1510.8, 1435.6, 1288.2, 1234.6, 1157.9, 1121.8, 1085.7, 965.4, 821.9, 764.9; HRMS (ESI) for $C_{16}H_{16}FNO_4$ $[M+H]^+$ calcd. 306.1136, found 306.1133;

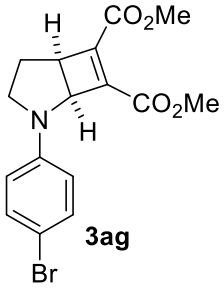
Dimethyl 2-(4-chlorophenyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3af).



3af

Following the general procedure: **1f** (18.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (31.2 μL, 0.25 mmol, 2.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3af** was obtained as a red solid in 85 % yield; mp= 84-86 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.17-7.13 (m, 2H), 6.81-6.72 (m, 2H), 5.05 (d, *J*=3.7 Hz, 1H), 3.80 (s, 3H), 3.75-3.72 (m, 1H), 3.71-3.65 (m, 1H), 3.59 (s, 3H), 3.17 (td, *J*=10.8 Hz, *J*=6.2 Hz, 1H), 2.11 (dd, *J*=13.3 Hz, *J*=6.1 Hz, 1H), 1.99-1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 161.5, 144.9, 142.4, 141.9, 128.7, 122.9, 115.4, 60.2, 52.1, 51.9, 45.6, 45.5, 24.4; IR (KBr, cm^{-1}): 2950.1, 2844.9, 1720.6, 1604.2, 1588.5, 1495.3, 1434.7, 1366.5, 1233.9, 1162.0, 1097.7, 1074.4, 1.15.0, 945.2, 822.1, 776.5, 739.6, 704.9; HRMS (ESI) for $C_{16}H_{16}ClNO_4$ $[M+Na]^+$ calcd. 344.0660, found 344.0655;

Dimethyl 2-(4-bromophenyl)-2-azabicyclo[3.2.0]hept-6-ene- 6,7-dicarboxylate (3ag).

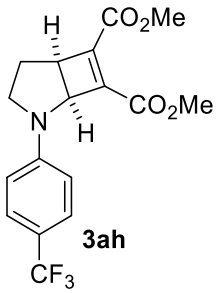


3ag

Following the general procedure: **1g** (22.6 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (31.2 μL, 0.25 mmol, 2.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ag** was obtained as a red solid in 78 % yield; mp= 88-90 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 2H), 6.76-6.68 (m, 2H), 5.04 (d, *J*=3.8 Hz,

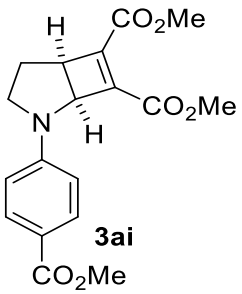
1H), 3.80 (s, 3H), 3.76-3.72 (m, 1H), 3.71-3.66 (m, 1H), 3.60 (s, 3H), 3.17 (td, *J*=10.3 Hz, *J*=6.1 Hz, 1H), 2.11 (dd, *J*=13.2 Hz, *J*=6.1 Hz, 1H), 1.99-1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 161.5, 145.3, 142.4, 142.0, 131.6, 115.9, 110.1, 60.0, 52.1, 51.9, 45.5, 24.4; IR (KBr, cm^{-1}): 2951.6, 2844.4, 2360.3, 1720.7, 1545.4, 1591.9, 1493.4, 1434.5, 1359.9, 1287.9, 1235.9, 1177.0, 1154.5, 1125.0, 1078.8, 964.1, 811.4, 757.4; HRMS (ESI) for $C_{16}H_{16}BrNO_4$ $[M+H]^+$ calcd. 366.0335, found 366.0335;

Dimethyl 2-(4-(trifluoromethyl)phenyl)-2-azabicyclo[3.2.0] hept-6-ene-6,7-dicarboxylate (3ah).



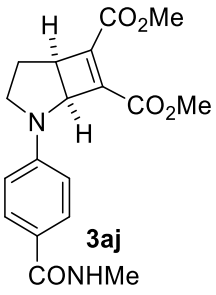
Following the general procedure: **1h** (21.5 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (37.5 μL, 0.3 mmol, 3.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ah** was obtained as a red solid in 67 % yield; mp= 90-92 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J*=8.8 Hz, 2H), 6.87 (d, *J*=8.8 Hz, 2H), 5.12 (d, *J*=3.7 Hz, 1H), 3.82 (s, 3H), 3.81-3.75 (m, 2H), 3.62 (s, 3H), 3.17 (td, *J*=10.5 Hz, *J*=6.3 Hz, 1H), 2.11 (dd, *J*=13.2 Hz, *J*=6.1 Hz, 1H), 2.02-1.90 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.7, 161.2, 148.6, 142.6, 141.8, 126.0 (q, *J*=3.7 Hz), 124.8 (q, *J*=267.0 Hz), 119.0 (q, *J*=32.4 Hz), 113.3, 59.5, 51.8, 51.6, 45.5 45.4, 24.2; IR (KBr, cm^{-1}): 2955.4, 2923.9, 2851.3, 2361.1, 1731.9, 1613.1, 1527.7, 1438.5, 1383.2, 1327.1, 1263.2, 1238.0, 1194.2, 1131.3, 1112.7, 1068.9, 983.9, 822.0, 761.3; HRMS (ESI) for $C_{17}H_{16}F_3NO_4$ $[M+H]^+$ calcd. 356.1104, found 356.1101;

Dimethyl 2-(4-(methoxycarbonyl)phenyl)-2-azabicyclo[3.2.0] hept-6-ene-6,7-dicarboxylate (3ai).



Following the general procedure: **1i** (20.5 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (37.5 μL, 0.3 mmol, 3.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ai** was obtained as a red solid in 84 % yield; mp= 108-110 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J*=9.0 Hz, 2H), 6.82 (d, *J*=9.0 Hz, 2H), 5.14 (d, *J*=3.8 Hz, 1H), 3.91-3.74 (m, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 3.61 (s, 3H), 3.30 (td, *J*=10.6 Hz, *J*=6.4 Hz, 1H), 2.16 (dd, *J*=13.3 Hz, *J*=6.4 Hz, 1H), 2.02-1.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 161.7, 161.4, 149.8, 142.7, 142.1, 131.0, 118.9, 113.0, 59.5, 52.1, 51.9, 51.6, 45.6, 45.5, 24.3; IR (KBr, cm^{-1}): 2953.2, 2922.9, 2851.1, 2370.7, 1707.2, 1603.9, 1519.7, 1458.6, 1434.6, 1375.9, 1283.1, 1236.3, 1180.7, 1108.9, 949.0, 912.5, 836.9, 770.0; HRMS (ESI) for $C_{18}H_{19}NO_6$ $[M+H]^+$ calcd. 346.1285, found 346.1283;

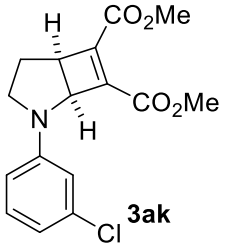
Dimethyl 2-(4-(methylcarbamoyl)phenyl)-2-azabicyclo[3.2.0] hept-6-ene-6,7-dicarboxylate (3aj).



Following the general procedure: **1j** (20.4 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (37.5 μL, 0.3 mmol, 3.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3aj** was obtained as a red solid in 71 % yield; mp= 161-163 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 2H), 6.85 (s, 2H), 6.12 (s,1H), 5.14 (s, 1H),

3.82 (s, 3H), 3.81-3.72 (m, 2H), 3.60 (s, 3H), 3.31 (s, 1H), 3.11 (s, 2H), 2.15 (d, *J*=9.3 Hz, 1H), 1.96 (s, 1H), 1.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 161.9, 161.4, 148.7, 142.5, 142.2, 128.0, 123.3, 113.3, 59.6, 52.1, 52.0, 45.6, 45.4, 26.7, 24.3; IR (KBr, cm^{-1}): 2952.6, 2924.3, 2851.0, 2410.0, 1720.2, 1639.4, 1605.9, 1551.4, 1509.6, 1434.9,1375.4, 1295.4, 1236.9, 1201.7, 1178.9, 1155.2, 1128.0, 1088.3, 1.41.0, 963.2, 833.8, 767.2; HRMS (ESI) for $C_{18}H_{20}N_2O_5$ $[M+H]^+$ calcd. 345.1445, found 345.1442;

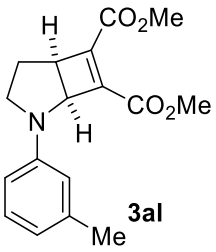
Dimethyl 2-(4-(methylcarbamoyl)phenyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3ak).



3ak

Following the general procedure: **1k** (18.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ak** was obtained as a red oil in 84 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (t, *J*=8.3 Hz, 1H), 6.84 (t, *J*=2.1 Hz, 1H), 6.76-6.72 (m, 1H), 6.72-6.67 (m, 1H), 5.05 (d, *J*=3.8 Hz, 1H), 3.81 (s, 3H), 3.77-3.69 (m, 2H), 3.63 (s, 3H), 3.17 (td, *J*=10.5 Hz, *J*=6.1 Hz, 1H), 2.11 (dd, *J*=13.3 Hz, *J*=6.1 Hz, 1H), 1.99-1.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 161.5, 147.4, 142.4, 142.3, 134.6, 129.8, 117.9, 114.3, 112.4, 60.0, 52.1, 51.9, 51.6, 45.6, 45.5, 24.3; IR (KBr, cm^{-1}): 2951.9, 2842.5, 2361.1, 1722.9, 1643.6, 1602.3, 1494.9, 1435.3, 1354.5, 1237.0, 1171.9, 1120.1, 1081.9, 1040.1, 960.8, 846.7, 772.7, 692.2; HRMS (ESI) for $C_{16}H_{16}ClNO_4$ $[M+H]^+$ calcd. 322.0841, found 322.0839;

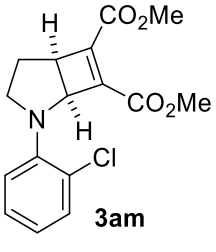
Dimethyl 2-(m-tolyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3al).



3al

Following the general procedure: **1l** (18.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (18.8 μL, 0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3al** was obtained as a red solid in 80 % yield; mp= 66-68 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.13-7.05 (m, 1H), 6.70-6.63 (m, 2H), 6.58 (d, *J*=7.6 Hz, 1H), 5.08 (d, *J*=3.7 Hz, 1H), 3.79 (s, 3H), 3.75-3.72 (m, 1H), 3.72-3.70 (m, 1H), 3.56 (s, 3H), 3.17 (td, *J*=10.3 Hz, *J*=6.1 Hz, 1H), 2.30 (s, 3H), 2.11 (dd, *J*=13.3 Hz, *J*=6.0 Hz, 1H), 1.98-1.87 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.4, 161.6, 146.4, 143.3, 141.1, 138.5, 128.7, 119.0, 115.1, 111.6, 60.4, 52.0, 51.7, 45.4(4), 45.3(9), 24.4, 21.7; IR (KBr, cm^{-1}): 2952.5, 2925.3, 2850.7, 2361.3, 1720.1, 1644.4, 1594.9,1563.0, 1489.2, 1434.7, 1360.7, 1288.4, 1235.8, 1197.2, 1180.6, 1154.4, 1121.4, 1094.4, 1040.8, 989.2, 840.3, 808.2, 760.4; HRMS (ESI) for $C_{17}H_{19}NO_4$ $[M+H]^+$ calcd. 302.1387, found 302.1382;

Dimethyl 2-(2-chlorophenyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7- dicarboxylate (3am).

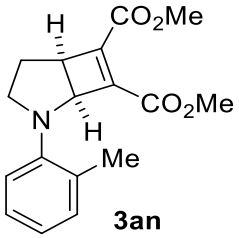


3am

Following the general procedure: **1m** (18.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (18.8 μL, 0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3am** was obtained as a yellow oil in 86 % yield; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.33 (m, 1H), 7.18-7.10 (m, 1H), 6.98-6.90 (m, 2H), 5.45 (d,

J=3.7 Hz, 1H), 3.82 (s, 3H), 3.67 (dd, *J*=7.6 Hz, *J*=3.5 Hz, 1H), 3.46-3.37 (m, 1H), 3.31 (s, 3H), 3.26 (dd, *J*=9.6 Hz, *J*=6.9 Hz, 1H), 2.05 (dd, *J*=12.9 Hz, *J*=5.4 Hz, 1H), 1.97-1.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 160.9, 144.2, 142.9, 141.1, 130.5, 127.0, 123.1, 120.6, 60.5, 52.1, 51.5, 46.3, 45.4, 24.1; IR (KBr, cm^{-1}): 2951.7, 2848.8, 2360.8, 1722.4, 1642.7, 1587.7, 1480.0, 1435.8, 1288.9, 1255.6, 1230.8, 1193.9, 1119.7, 1059.9, 1040.0, 967.1, 755.1, 700.9; HRMS (ESI) for $C_{16}H_{16}ClNO_4$ $[M+H]^+$ calcd. 322.0841, found 322.0833;

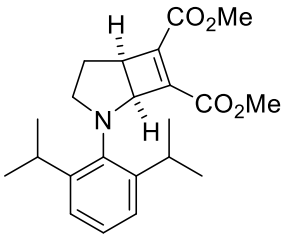
Dimethyl 2-(o-tolyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7- dicarboxylate (3an).



3an

Following the general procedure: **1n** (16.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (18.8 μL, 0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3an** was obtained as a red oil in 70 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J*=7.6 Hz, 1H), 7.07 (t, *J*=7.5 Hz, 1H), 6.96-6.86 (m, 2H), 4.81 (d, *J*=3.6 Hz, 1H), 3.81 (s, 3H), 3.67 (dd, *J*=7.9 Hz, *J*=3.6 Hz, 1H), 3.49-3.39 (m, 1H), 3.32 (s, 3H), 3.26 (dd, *J*=9.9 Hz, *J*=6.9 Hz, 1H), 2.37 (s, 3H), 2.05 (dd, *J*=12.8 Hz, *J*=5.3 Hz, 1H), 1.91-1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 161.3, 145.8, 142.0, 141.7, 131.2, 131.0, 126.0, 122.6, 119.1, 61.6, 52.0, 51.5, 46.6, 45.6, 24.4, 19.4; IR (KBr, cm^{-1}): 2952.6, 2925.5, 2853.1, 2360.3, 1725.2, 1696.9, 1593.7, 1492.7, 1435.7, 1381.3, 1349.1, 1257.3, 1226.1, 1191.1, 1117.6, 1067.7, 984.1, 945.2, 758.4; HRMS (ESI) for $C_{17}H_{19}NO_4$ $[M+H]^+$ calcd. 302.1387, found 302.1379;

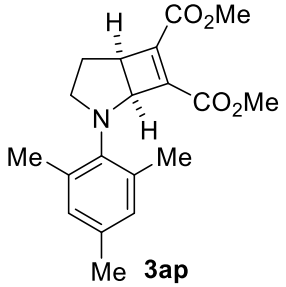
Dimethyl 2-(2,6-diisopropylphenyl)-2-azabicyclo[3.2.0] hept-6-ene-6,7-dicarboxylate (3ao).



3ao

Following the general procedure: **1o** (23.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (18.8 μL, 0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ao** was obtained as a yellow oil in 91 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.32 (t, *J*=7.9 Hz, 1H), 7.18 (d, *J*=7.8 Hz, 2H), 6.51 (t, *J*=7.3 Hz, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 3.62-3,58 (m, 2H), 3.04 (quint, *J*=6.8 Hz, 2H), 2.82-2.72 (m, 2H), 1.22 (d, *J*=6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 168.9, 147.8, 145.8, 144.1, 133.7, 128.8, 124.5, 95.6, 55.7, 52.0, 51.3, 29.4, 28.4, 24.4, 24.1; IR (KBr, cm^{-1}): 2961.6, 2926.6, 2869.7, 2364.9, 1726.9, 1698.4, 1604.9, 1435.6, 1346.5, 1240.5, 1203.8, 1114.3, 1067.2, 983.6, 804.9, 771.3;HRMS (ESI) for $C_{22}H_{29}NO_4$ $[M+H]^+$ calcd. 372.2169, found 372.2166;

Dimethyl 2-mesityl-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3ap).

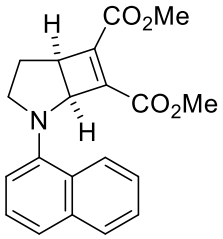


3ap

Following the general procedure: **1p** (18.9 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (6.2 μL, 0.05 mmol, 0.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ap** was obtained as a red solid in 68 % yield; mp= 138-140 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 1H), 6.90 (s, 2H), 6.50 (t, *J*=7.3 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 3.59-3.54 (m, 2H), 2.80-2.74 (m, 2H), 2.28 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 169.0, 147.6, 144.2, 137.7, 134.7, 134.0, 133.7,

129.5, 96.0, 54.1, 52.0, 51.3, 29.6, 20.8, 18.2; IR (KBr, cm^{-1}): 2951.5, 2924.8, 2855.2, 2364.9, 1726.8, 1696.1, 1594.4, 1484.1, 1435.5, 1388.3, 1348.4, 1257.3, 1214.6, 1156.6, 1116.4, 1067.7, 984.1, 851.0, 765.4; HRMS (ESI) for $C_{19}H_{23}NO_4$ $[M+H]^+$ calcd. 330.1700, found 330.1694;

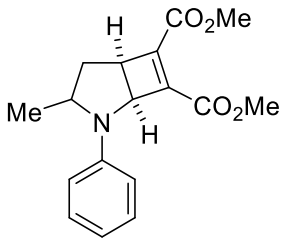
Dimethyl 2-(naphthalen-1-yl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3aq).



3aq

Following the general procedure: **1q** (19.7 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (18.8 μL, 0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3aq** was obtained as a red solid in 48 % yield; mp= 54-56 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J*=7.9 Hz, 1H), 7.86-7.79 (m, 1H), 7.56-7.43 (m, 3H), 7.32 (d, *J*=7.7 Hz, 1H), 7.01 (d, *J*=7.4 Hz, 1H), 5.05 (d, *J*=3.5 Hz, 1H), 3.83 (s, 3H), 3.74-3.68 (m, 1H), 3.65-3.53 (m, 1H), 3.34 (dd, *J*=10.1Hz, *J*=6.6 Hz, 1H), 3.17 (s, 3H), 2.10 (dd, *J*=12.8Hz, *J*=5.5 Hz, 1H), 2.06-1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 161.0, 144.3, 142.4, 141.4, 134.6, 128.8, 128.2, 125.8, 125.3, 125.2, 124.0, 123.4, 115.4, 64.3, 52.1, 51.4, 46.8, 45.6, 24.5; IR (KBr, cm^{-1}): 2951.4, 2924.9, 2852.3, 1723.1, 1697.2, 1597.6, 1508.5, 1435.5, 1395.7, 1349.1, 1349.1, 1247.1, 1230.8, 1193.4, 1108.8, 1064.1, 985.1, 801.8, 775.1; HRMS (ESI) for $C_{20}H_{19}NO_4$ $[M+H]^+$ calcd. 338.1387, found 338.1381;

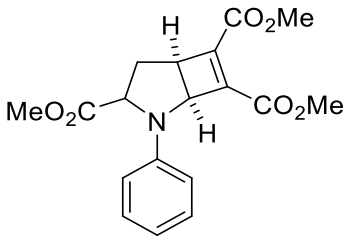
Dimethyl 3-methyl-2-phenyl-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3ar).



3ar

Following the general procedure: **1r** (16.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ar** was obtained as a red oil in 98 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) first diastereoisomer: δ 7.26-7.20 (m, 2H), 6.80 (d, *J*=8.0 Hz, 2H), 6.71 (t, *J*=7.1 Hz, 1H), 5.04 (d, *J*=4.0 Hz, 1H), 4.42 (quint, *J*=7.3 Hz, 1H), 3.83 (s, 3H), 3.79-3.77 (m, 1H), 3.73 (s, 3H), 2.23 (dt, *J*=13.5 Hz, *J*=9.1 Hz, 1H), 2.01 (d, *J*=13.7 Hz, 1H), 1.25 (d, *J*=6.7 Hz, 3H); second diastereoisomer: δ 7.26-7.20 (m, 2H), 6.98 (d, *J*=8.0 Hz, 2H), 6.89 (7, *J*=7.3 Hz, 1H), 5.03 (d, *J*=3.6 Hz, 1H), 3.78 (s, 3H), 3.76-3.70 (m, 1H), 3.58 (dd, *J*=7.6 Hz, *J*=3.2 Hz, 1H), 3.32 (s, 3H), 2.29 (ddd, *J*=13.2 Hz, *J*=5.6 Hz, *J*=0.9 Hz, 1H), 2.01 (td, *J*=13.1 Hz, *J*=8.5 Hz, 1H), 1.21 (d, *J*=5.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) first diastereoisomer: δ 162.3, 161.7, 146.9, 145.2, 144.5, 129.2, 116.6, 112.7, 60.7, 55.6, 52.1, 52.0, 45.9, 31.8, 21.2; second diastereoisomer: δ 162.0, 161.6, 146.2, 143.4, 141.8, 128.6, 121.0, 120.2, 66.3, 51.9, 51.6, 51.5, 42.9, 33.8, 18.6; IR (KBr, cm^{-1}): 2951.8, 2924.7, 2851.1, 2360.5, 1718.7, 1644.1, 1597.0, 1502.4, 1434.1, 1368.8, 1314.1, 1282.5, 1250.7, 1196.2, 1158.3, 1128.2, 1096.2, 1011.4, 948.8, 747.9; HRMS (ESI) for $C_{17}H_{19}NO_4$ $[M+H]^+$ calcd. 302.1387, found 302.1381;

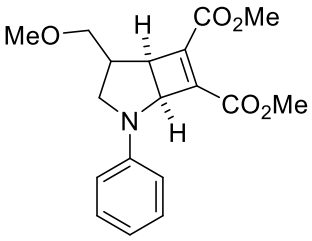
Trimethyl (3S)-2-phenyl-2-azabicyclo[3.2.0]hept-6- ene-3,6,7-tricarboxylate (3as).



3as

Following the general procedure: **1s** (20.5 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3as** was obtained as a yellow oil in 49 % yield; ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.22-7.14 (m, 2H), 6.82 (t, *J*=7.3 Hz, 1H), 6.86-6.80 (m, 2H), 4.00-3.93 (m, 1H), 3,87 (s, 3H), 3.81 (3.81), 3.74-3.69 (m, 1H), 3.55 (s, 3H), 3.33-3.25 (m, 1H), 2.15-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 161.4, 161.2, 145.4, 141.9, 141.2, 128.7, 119.7, 115.9, 71.5, 53.8, 53.1, 52.1, 51.9, 49.0, 23.9; IR (KBr, cm^{-1}): 2953.7, 2924.2, 2851.3, 2360.5, 1721.8, 1646.8, 1599.7, 1502.3, 1434.7, 1250.9, 1195.5, 1143.6, 1074.4, 1033.5, 948.7, 913.2, 877.4, 753.2; HRMS (ESI) for $C_{18}H_{19}NO_6$ $[M+H]^+$ calcd. 346.1285, found 346.1277;

Dimethyl 4-(methoxymethyl)-2-phenyl-2-azabicyclo [3.2.0]hept-6-ene-6,7-dicarboxylate (3at).

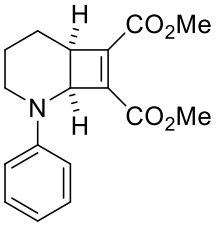


3at

Following the general procedure: **1t** (19.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (37.5 μL, 0.3 mmol, 3.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3at** was obtained as a yellow oil in 65 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) fisrt diastereoisomer: δ 7.23-7.16 (m, 2H), 6.83 (d, *J*=7.9 Hz, 2H), 6.75 (t, *J*=7.3 Hz, 1H), 4.95 (s, 1H), 3.80 (s, 3H), 3.78-3.73 (m, 2H), 3.60 (d, *J*=9.7 Hz, 1H),

3.55 (s, 3H), 3.37 (s, 3H), 3.21 (td, *J*=10.3 Hz, *J*=6.1 Hz, 1H), 2.09 (dd, *J*=13.2 Hz, *J*=5.9 Hz, 1H), 1.79 (m, 1H); second diastereoisomer: δ 7.21 (t, *J*=8.0 Hz, 2H), 6.84 (d, *J*=8.3 Hz, 2H), 6.75 (t, *J*=7.1 Hz, 1H), 5.09 (d, *J*=3.8 Hz, 1H), 3.80 (s, 3H), 3.67 (d, *J*=10.5 Hz, 1H), 3.58 (s, 3H), 3.49 (d, *J*=3.8 Hz, 1H), 3.36 (s, 3H), 3.34-3.27 (m, 3H), 2.01 (dd, *J*=14.2 Hz, *J*=7.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) fisrt diastereoisomer: δ 162.3, 161.3, 146.4, 142.2, 141.5, 128.8, 118.2, 114.4, 72.9, 63.2, 59.3, 57.6, 51.9, 51.7, 45.8, 26.6; second diastereoisomer: δ 162.3, 161.4, 146.4, 143.4, 141.3, 128.9, 118.1, 114.2, 73.0, 59.8, 58.7, 52.1, 51.8, 47.8, 47.4, 36.7; IR (KBr, cm^{-1}): 2952.4, 2927.1, 2850.5, 2361.7, 1722.5, 1646.2, 1598.8, 1503.7, 1435.4, 1360.7, 1250.3, 1221.1, 1123.4, 1035.0, 995.3, 957.1, 753.3, 692.0; HRMS (ESI) for $C_{18}H_{21}NO_5$ $[M+H]^+$ calcd. 332.1492, found 332.1486;

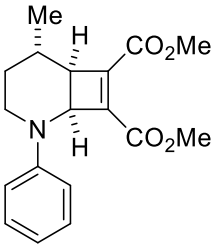
Dimethyl 2-phenyl-2-azabicyclo[4.2.0]oct-7-ene-7,8- dicarboxylate (3au).



3au

Following the general procedure: **1u** (16.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3au** was obtained as a yellow oil in 88 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.38 (t, *J*=8.0 Hz, 2H), 7.23-7.15 (m, 3H), 6.53 (dd, *J*=9.3 Hz, *J*=7.8 Hz, 1H), 4.26 (m, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 3.67-3.60 (m, 1H), 2.58-2.42 (m, 2H), 1.86-1.71 (m, 1H), 1.28-1.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 169.0, 146.8, 146.6, 136.3, 133.2, 129.6, 125.1, 121.8, 97.3, 52.0, 51.6, 46.3, 25.1, 17.8; IR (KBr, cm^{-1}): 2951.1, 2925.2, 2844.9, 2371.7, 1720.2, 1699.7, 1582.4, 1493.9, 1457.2, 14337, 1374.2, 1315.8, 1246.5, 1215.4, 1191.4, 1087.4, 1049.2, 1017.5, 945.0, 778.2, 762.4, 698.6; HRMS (ESI) for $C_{17}H_{19}NO_4$ $[M+H]^+$ calcd. 302.1387, found 302.1382;

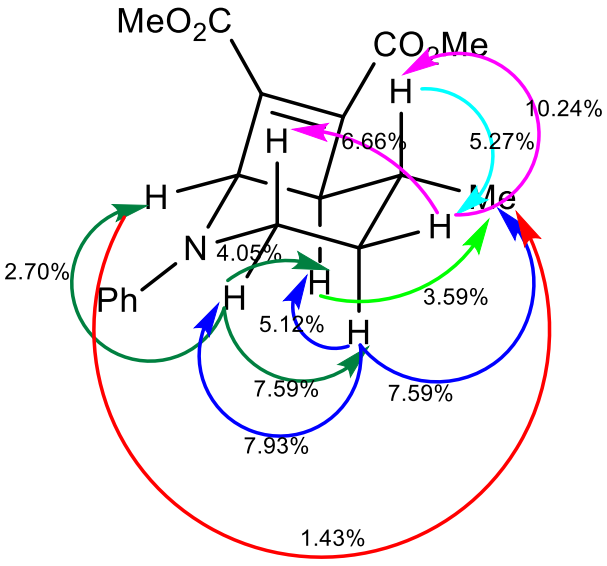
Dimethyl 5-methyl-2-phenyl-2-azabicyclo[4.2.0]oct-7-ene-7,8-dicarboxylate (3av).



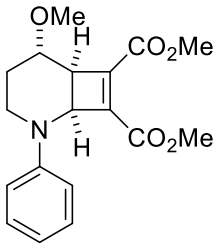
3av

Following the general procedure: **1v** (17.5 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3av** was obtained as a yellow oil in 75 % yield; ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.86 (s, 1H), 7.37 (t, *J*=8.5 Hz, 2H), 7.23-7.14 (m, 3H), 6.20 (d, *J*=9.4 Hz, 1H), 4.16 (ddd, *J*=14.9 Hz, *J*=12.2 Hz, *J*=2.8 Hz, 1H), 3.79 (s, 3H), 3.68 (s, 3H), 3.65 (d, *J*=3.4 Hz, 1H), 2.79-2.65 (m, 1H), 1.84-1.71 (m, 1H), 1.18 (d, *J*=6.5 Hz, 3H), 0.99 (t, *J*=12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 169.1, 146.7, 146.1, 142.7, 131.0, 129.5, 125.1, 121.6, 97.8, 52.0, 51.5, 47.2, 31.2, 27.2, 20.4; IR (KBr, cm^{-1}): 2949.1, 2925.3, 2853.2, 2384.8, 1719.1, 1698.5, 1607.9, 1579.3, 1493.9, 1457.6, 1433.8, 1374.3, 1326.5, 1263.1, 1231.7, 1180.8, 1106.9, 1072.6, 941.9, 893.2, 762.4, 698.2; HRMS (ESI) for $C_{18}H_{21}NO_4$ $[M+H]^+$ calcd. 316.1543, found 316.1536;

NOE assignments for compound 3av:



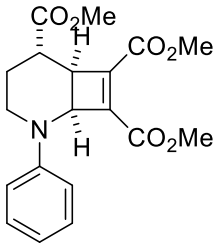
Dimethyl 5-methoxy-2-phenyl-2-azabicyclo[4.2.0]oct-7-ene-7,8-dicarboxylate (3aw).



3aw

Following the general procedure: **1w** (19.1 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3aw** was obtained as a red oil in 62 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.39 (t, *J*=7.9 Hz, 2H), 7.25-7.14 (m, 3H), 6.36 (d, *J*=7.6 Hz, 1H), 4.36-4.23 (m, 1H), 4.13-4.03 (m, 1H), 3.80 (s, 3H), 3.77-3.70 (m, 1H), 3.69 (s, 3H), 3.40 (s, 3H), 2.20-2.07 (m, 1H),1.34-1.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 168.1, 146.7, 146.4, 139.6, 132.1, 129.7, 125.5, 121.8, 97.4, 77.2, 57.5, 52.2, 51.6, 46.7, 25.5; IR (KBr, cm^{-1}): 2950.5, 2925.3, 2853.4, 1721.9, 1699.9, 1581.9, 1494.2, 1458.5, 1434.5, 1375.0, 1307.8, 1243.6, 1218.0, 1191.2, 1105.7, 1073.7, 1032.4, 953.2, 762.4, 698.8; HRMS (ESI) for $C_{18}H_{21}NO_5$ $[M+H]^+$ calcd. 332.1492, found 332.1483;

Trimethyl 2-phenyl-2-azabicyclo[4.2.0]oct-7-ene-5,7,8- tricarboxylate (3ax).

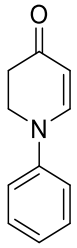


3ax

Following the general procedure: **1x** (21.9 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05

M). Compound **3ax** was obtained as a yellow oil in 50 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.43-7.36 (m, 2H), 7.24-7.17 (m, 3H), 6.55 (d, *J*=9.3 Hz, 1H), 4.22 (ddd, *J*=14.9 Hz, *J*=12.3 Hz, *J*=2.8 Hz, 1H), 3.80 (s, 3H), 3.75-3.70 (m, 4H), 3.68 (s, 3H), 3.67-3.61 (m,1H), 2.17-2.05 (m, 1H), 1.43 (t, *J*=13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 169.0, 168.3, 146.6, 146.5, 133.5, 133.3, 129.7, 125.6, 121.8, 97.4, 52.2, 51.6, 46.4, 42.9, 22.3; IR (KBr, cm^{-1}): 2951.9, 2924.8, 2852.3, 2365.2, 1722.2, 1581.0, 1494.9, 1435.0, 1374.8, 1244.8, 1205.4, 1087.8, 1063.6, 1032.8, 1009.7, 947.8, 762.4, 698.3; HRMS (ESI) for $C_{19}H_{21}NO_6$ $[M+H]^+$ calcd. 360.1442, found 360.1433;

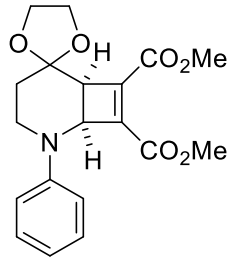
1-phenyl-2,3-dihydropyridin-4(1H)-one (3ay).



3ay

Following the general procedure: **1y** (17.5 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ay** was obtained as a yellow solid in 90 % yield; mp= 76-78 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J*=7.4 Hz, 1H), 7.39 (t, *J*=8.0 Hz, 2H), 7.16 (t, *J*=7.4 Hz, 1H), 7.10 (d, *J*=7.7 Hz, 2H), 5.23 (d, *J*=7.7 Hz, 1H), 4.01 (t, *J*=7.4 Hz, 2H), 2.27 (t, *J*=7.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$):δ191.9, 149.6, 145.1, 129.6, 124.4, 118.2, 102.1, 47.6, 35.9; IR (KBr, cm^{-1}): 2956.9, 2924.4, 2851.7, 2360.2, 1730.2, 1648.1, 1576.2, 1493.9, 1313.6, 1277.3, 1217.6, 1177.8, 1107.7, 1035.7, 800.7, 758.9, 694.2; HRMS (ESI) for $C_{11}H_{11}NO$ $[M+H]^+$ calcd. 174.0913, found 174.0909;

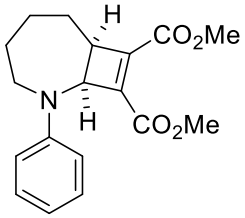
Dimethyl 5-phenyl-5-azaspiro[bicyclo[4.2.0]octane-2,2'-[1,3] dioxolan]-7-ene-7,8-dicarboxylate (3az).



3az

Following the general procedure: **1z** (21.9 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3az** was obtained as a yellow oil in 70 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.37 (t, *J*=7.7 Hz, 2H), 7.26-7.18 (m, 3H), 6.17 (s, 1H), 4.19 (d, *J*=12.8 Hz, 1H), 3.97-3.83 (m, 5H), 3.79 (s, 3H), 3.68 (s, 3H), 1.93-1.83 (m, 1H), 1.63 (d, *J*=14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 169.3, 147.1, 146.4, 135.2, 133.7, 129.4, 125.7, 123.3, 108.9, 96.7, 65.1, 63.1, 52.3, 51.4, 46.6, 27.2; IR (KBr, cm^{-1}): 2948.8, 2922.2, 1720.2, 1686.1, 1610.2, 1579.8, 1492.8, 1433.2, 1378.5, 1314.4, 1243.7, 1208.3, 1134.7, 1093.5, 1069.0, 1047.5, 948.1, 782.0, 762.4, 736.2, 697.9; HRMS (ESI) for $C_{19}H_{21}NO_6$ $[M+H]^+$ calcd. 360.1442, found 360.1435;

Dimethyl 2-phenyl-2-azabicyclo[5.2.0]non-8-ene-8,9- dicarboxylate (3ba).

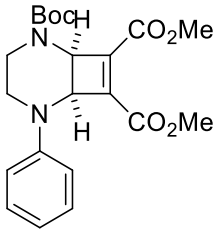


3ba

Following the general procedure: **1ba** (17.5 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3ba** was obtained as a yellow oil in 89 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.42-7.33 (m, 2H), 7.21-7.11 (m, 3H), 7.06 (dd, *J*=10.6 Hz, *J*=6.4 Hz, 1H), 4.50-4.39 (m, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.59 (dt, *J*=15.8 Hz, *J*=4.2 Hz, 1H), 2.51-2.38 (m, 1H), 2.36-2.23 (m, 1H), 1.98-1.78 (m, 3H), 1.74-1.63

(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 168.6, 146.1, 144.8, 129.5, 129.4, 124.6, 120.7, 98.0, 52.1, 51.6, 44.2, 27.9(0), 27.8(9), 22.8; IR (KBr, cm^{-1}): 2948.5, 2926.7, 2856.3, 2360.3, 1717.3, 1610.7, 1582.9, 1494.8, 1459.5, 1433.9, 1379.5, 1252.8, 1222.7, 1189.2, 1117.7, 1093.6, 1056.5, 1024.6, 946.2, 890.6, 799.3, 760.7, 697.1; HRMS (ESI) for $C_{18}H_{21}NO_4$ $[M+H]^+$ calcd. 316.1543, found 316.1535;

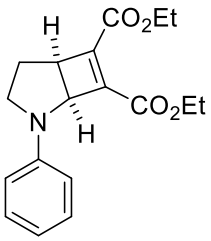
2-(tert-butyl) 7,8-dimethyl 5-phenyl-2,5-diazabicyclo[4.2.0]oct-7-ene-2,7,8-tricarboxylate (3bb)



3bb

Following the general procedure: **1bb** (26.5 mg, 0.1 mmol, 1.0 equiv.), **2a** (36.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (50.0 μL, 0.4 mmol, 4.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3bb** was obtained as a red oil in 51 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.50-7.27 (m, 3H), 7.15 (t, *J*=7.6 Hz, 1H), 7.10 (d, *J*=7.6 Hz, 2H), 4.15-3.83 (m, 3H), 3.77 (s, 3H), 3.74-3.67 (m, 4H), 1.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 168.6, 153.2, 147.0, 144.0, 134.5, 129.4, 124.5, 120.7, 118.7, 102.8, 82.2, 51.9, 51.5, 46.7, 39.4, 27.9; IR (KBr, cm^{-1}): 2979.9, 2950.0, 2253.0, 1705.7, 1632.9, 1584.8, 1495.0, 1434.8, 1368.3, 1250.4, 1150.3, 1100.5, 1053.0, 913.8, 835.6, 732.8, 696.5; HRMS (ESI) for $C_{21}H_{26}N_2O_6$ $[M+H]^+$ calcd. 403.1864 , found 403.1858;

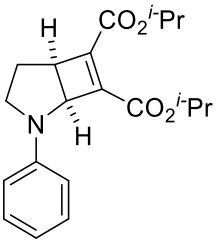
Diethyl 2-phenyl-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3bc)



3bc

Following the general procedure: **1a** (14.7 mg, 0.1 mmol, 1.0 equiv.), **2b** (48.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3bc** was obtained as a red oil in 80 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.16 (m, 2H), 6.84 (d, *J*=7.9 Hz, 2H), 6.75 (t, *J*=7.3 Hz, 1H), 5.10 (d, *J*=3.7 Hz, 1H), 4.24 (q, *J*=7.1 Hz, 2H), 4.06-3.97 (m, 2H), 3.76-3.68 (m, 2H), 3.20 (td, *J*=10.5 Hz, *J*=6.0 Hz, 1H), 3.20 (dd, *J*=13.2 Hz, *J*=6.1 Hz, 1H), 1.99-1.86 (m, 1H), 1.30 (t, *J*=7.2 Hz, 3H), 1.05 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 161.3, 146.5, 143.3, 141.1, 128.9, 118.1, 114.4, 61.0, 60.9, 60.3, 45.4, 45.3, 24.9, 14.1, 13.7; IR (KBr, cm^{-1}): 2957.6, 2927.1, 2850.3, 2360.7, 1718.4, 1637.9, 1598.0, 1500.8, 1473.8, 1367.2, 1256.0, 1233.5, 1176.1, 1115.3, 1036.7, 956.2, 849.1, 752.7, 691.3; HRMS (ESI) for $C_{18}H_{21}NO_4$ $[M+H]^+$ calcd. 316.1543 , found 316.1835;

Diisopropyl 2-phenyl-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3bd)

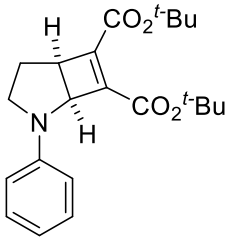


3bd

Following the general procedure: **1a** (14.7 mg, 0.1 mmol, 1.0 equiv.), **2c** (61.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3bd** was obtained as a red oil in 78 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.14 (m, 2H), 6.83 (d, *J*=7.9 Hz, 2H), 6.74 (t, *J*=7.4 Hz, 1H),

5.13-5.06 (m, 2H), 4.88 (quint, *J*=6.2 Hz, 1H), 3.74-3.66 (m, 2H), 3.21 (td, *J*=10.6 Hz, *J*=6.0 Hz, 1H), 3.20 (dd, *J*=13.1 Hz, *J*=6.1 Hz, 1H), 1.99-1.86 (m, 1H), 1.29 (d, *J*=1.1 Hz, 3H), 1.27 (d, *J*=1.1 Hz, 3H), 1.07 (d, *J*=6.2 Hz, 3H), 0.95 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 160.9, 146.7, 143.6, 140.2, 128.9, 118.0, 114.4, 68.7, 68.6(8), 60.4, 45.4, 45.2, 24.5, 21.7(8), 21.7(6), 21.4, 21.2; IR (KBr, cm^{-1}): 2979.1, 2935.3, 2873.2, 2360.4, 1712.5, 1640.2, 1598.3, 1502.2, 1468.0, 1371.5, 1267.9, 1235.4, 1178.4, 1105.7, 1033.9, 958.5, 913.9, 836.8, 752.7, 691.2; HRMS (ESI) for $C_{20}H_{25}NO_4$ $[M+H]^+$ calcd. 344.1856, found 344.1850;

Di-tert-butyl 2-phenyl-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (3be)

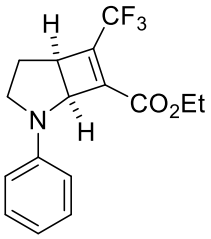


3be

Following the general procedure: **1a** (14.7 mg, 0.1 mmol, 1.0 equiv.), **2d** (67.8mg, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3be** was obtained as a red solid in 62 % yield; mp= 54-56 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.15 (m, 2H), 6.83 (d, *J*=8.0 Hz, 2H), 6.74 (t, *J*=7.3 Hz, 1H), 5.03 (d, *J*=3.6 Hz, 1H), 3.71-3.61 (m, 2H), 3.21 (dd, *J*=10.5 Hz, *J*=6.1 Hz, 1H), 2.10 (dd, *J*=13.1 Hz, *J*=6.1 Hz, 1H), 1.95-1.84 (m, 1H), 1.49 (s, 9H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 160.7, 146.8, 144.1, 139.5, 129.0, 118.0, 114.5, 82.0, 81.8, 60.3, 45.3, 45.0, 28.1, 27.7, 24.5; IR (KBr, cm^{-1}): 2976.9, 2930.6, 2867.9, 2365.1, 1711.8, 1643.3, 1599.6, 1503.5, 1477.1, 1457.1, 1367.9, 1311.1, 1257.2, 1151.4, 1121.5, 1085.1, 1032.7, 957.9, 841.0, 751.7, 690.8; HRMS (ESI) for $C_{22}H_{29}NO_4$ $[M+H]^+$ calcd. 372.2169, found 372.2161;

Ethyl 2-phenyl-6-(trifluoromethyl)-2-azabicyclo[3.2.0]hept-6-ene-7-carboxylate

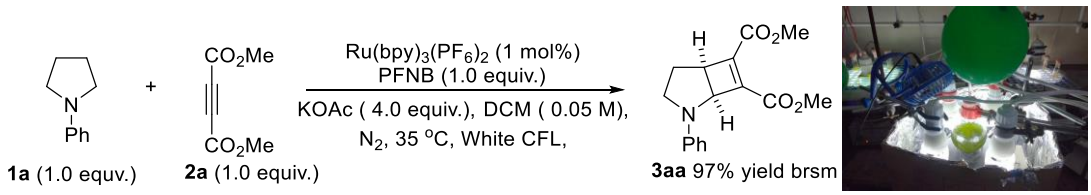
(3bf)



3bf

Following the general procedure: **1a** (14.7 mg, 0.1 mmol, 1.0 equiv.), **2d** (43.0 μL, 0.3 mmol, 3.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%), KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.), PFNB (25.0 μL, 0.2 mmol, 2.0 equiv.), CH_2Cl_2 (2.0 mL, 0.05 M). Compound **3bf** was obtained as a yellow oil in 57 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.17 (m, 2H), 6.88 (d, *J*=8.0 Hz, 2H), 6.77 (t, *J*=7.3 Hz, 1H), 7.16-7.10 (m, 1H), 4.11-3.96 (m, 2H), 3.79-3.70 (m, 2H), 3.21 (td, *J*=10.6 Hz, *J*=6.0 Hz, 1H), 2.10 (dd, *J*=13.2 Hz, *J*=5.9 Hz, 1H), 1.99-1.86 (m, 1H), 1.08 (d, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 146.0, 140.9 (q, *J*=37.7 Hz), 139.6 (q, *J*=5.0 Hz), 128.9, 119.1 (q, *J*=271.5 Hz), 118.3, 114.4, 61.2, 60.0, 45.0, 44.8 (q, *J*=1.8 Hz), 24.3, 13.6; IR (KBr, cm^{-1}): 2956.9, 2925.3, 2854.6, 2360.7, 1730.5, 1599.9, 1503.9, 1460.3, 1368.9, 1288.3, 1239.4, 1222.5, 1173.7, 1132.6, 1024.9, 953.5, 877.0, 750.7, 690.9; HRMS (ESI) for $C_{16}H_{16}F_3NO_2$ $[M+H]^+$ calcd. 312.1206, found 312.1200;

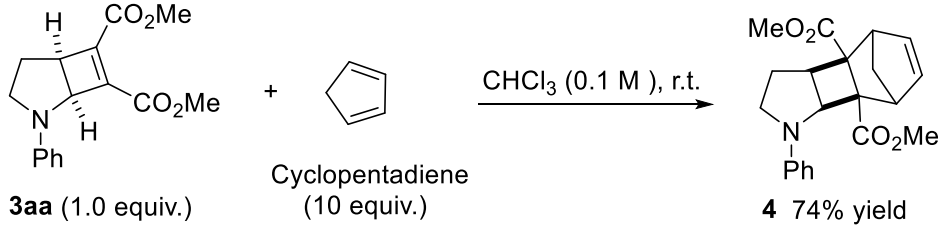
5. The Gram Scale Reaction



General Procedure: $Ru(bpy)_3(PF_6)_2$ (85.0 mg, 0.1mmol, 1 mol%) and KOAc (3.92 g, 40 mmol, 4.0 equiv.) were weighed into an oven-dried 250 mL flask with a balloon and degassed CH_2Cl_2 (200 mL) was added. Dimethyl acetylenedicarboxylate **2a** (DMAD, 3.6 mL, 30 mmol, 3.0 equiv.), 1,2,3,4,5-pentafluoro-6-nitrobenzene (PFNB,

1.25 mL, 10 mmol, 1.0 equiv.) and N-Ph pyrrolidine **1a** (1.47g, 10 mmol, 1.0 equiv.) were successively added into the mixture via syringes. The reaction mixture was then purged with N_2 for 30 minutes. The vial was then sealed and placed among four 23-W compact fluorescent lights (CFL, 1-2 centimeters from either side of the vial), allowing the temperature to rise due to its proximity to the lights. After 4 days, the crude mixture was concentrated and purified by flash chromatography (silica gel, mixtures of petroleum ether/ethyl acetate) to afford 1.75 g pure product **3a** and the recovered starting material **1a**. The recovered starting material **1a** was poured into the secondary reaction mixture with the similar procedure: $Ru(bpy)_3(PF_6)_2$ (34 mg, 0.04mmol, 1 mol%) and KOAc (1.568 g, 16 mmol, 4.0 equiv.) were weighed into an oven-dried 250 mL flask with a balloon and degassed CH_2Cl_2 (50 mL) was added. Dimethyl acetylenedicarboxylate **2a** (DMAD, 1.4 mL, 12 mmol, 3.0 equiv.), 1,2,3,4,5- pentafluoro-6-nitrobenzene (PFNB, 0.5 mL, 4 mmol, 1.0 equiv.) and N-Ph pyrrolidine **1a** (0.588 g, 4 mmol, 1.0 equiv.) were successively added into the mixture via syringes. The reaction mixture was then purged with N_2 for 30 minutes. The vial was sealed and placed among four 23-W compact fluorescent lights (CFL, 1-2 centimeter from either side of the vial), allowing the temperature to rise due to its proximity to the lights. After 4 days, the crude mixture was concentrated and purified by flash chromatography (silica gel, mixtures of petroleum ether/ethyl acetate) to afford 0.70 g pure product **3aa** and 0.18 g recovered starting material **1a**. After two visible light irradiation processes, the product **3aa** was obtained in 97% total yield based on consumed starting material.

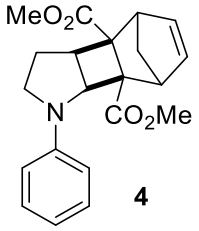
6. Transformations of Product 3aa



To a solution of **3aa** (57.4 mg, 0.2 mmol, 1.0 equiv.) in $CHCl_3$ (2.0 mL) was added

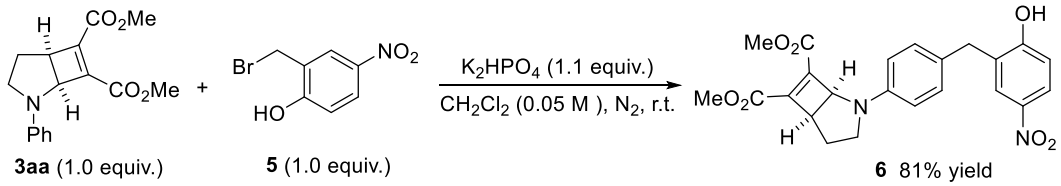
cyclopentadiene (0.83 mL, 2mmol, 10 equiv.) and stirred at 0 ℃ for 30 min. After being stirred at room temperature for 12 h, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give product **4** (52.2 mg, 0.15 mmol, yield: 74%) as a red solid. mp= 108-110 ^{o}C;

Dimethyl 1-phenyl-2,3,3a,4,7,7b-hexahydro-1H-4,7-methanobenzo[3,4]cyclobuta [1,2-b]pyrrole-3b,7a-dicarboxylate



4

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (dd, *J*=8.6 Hz, *J*=7.4 Hz, 2H), 6.75-6.68 (m, 1H), 6.63 (t, *J*=7.4 Hz, 1H), 6.60-6.52 (m, 1H), 6.40 (d, *J*=7.9 Hz, 2H), 7.11 (d, *J*=7.4 Hz, 1H), 6.78 (t, *J*=7.4 Hz, 1H), 7.76-6.64 (m, 4H), 4.44 (d, *J*=9.1 Hz, 1H), 3.66 (d, *J*=8.0 Hz, 1H), 3.46 (dd, *J*=9.1 Hz, *J*=3.0 Hz, 1H), 3.37-3.28 (m, 1H), 2.87 (d, *J*=9.1 Hz, 1H), 2.81-2.70 (m, 1H), 2.46 (dt, *J*=10.1 Hz, *J*=7.0 Hz, 1H), 2.29-2.10 (m, 3H), 2.03-1.92 (m, 1H), 1.84-1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 171.2, 145.9, 138.4, 137.2, 129.1, 116.1, 112.1, 64.1, 60.2, 58.9, 53.4, 52.6, 51.5, 51.4, 49.4, 48.8, 43.3, 26.5; IR (KBr, cm^{-1}): 2950.6, 2924.6, 2868.4, 2360.6, 1722.6, 1598.3, 1503.8, 1458.0, 1433.2, 1369.4, 1270.6, 1245.2, 1193.4, 1113.0, 1084.0, 1051.9, 996.4, 912.8, 747.4, 691.4; HRMS (ESI) for $C_{21}H_{23}NO_4$ $[M+H]^+$ calcd. 354.1701, found 354.1700;



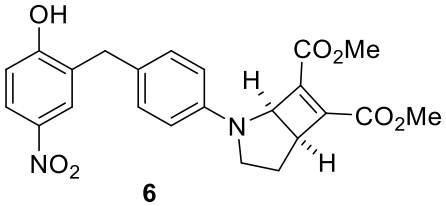
3aa (1.0 equiv.) **5** (1.0 equiv.) **6** 81% yield

To a solution of **3aa** (28.7 mg, 0.1 mmol, 1.0 equiv.) in CH_2Cl_2 (1.0 mL) was added 2-(bromomethyl)-4-nitrophenol **5** (23.2 mg, 0.1 mmol, 1.0 equiv.) under nitrogen atmosphere. After being stirred at room temperature for 28 h, the solvent was

evaporated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give product **6** (35.5 mg, 0.081 mmol, yield: 81%) as a red oil;

dimethyl

2-(4-(2-hydroxy-5-nitrobenzyl)phenyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate

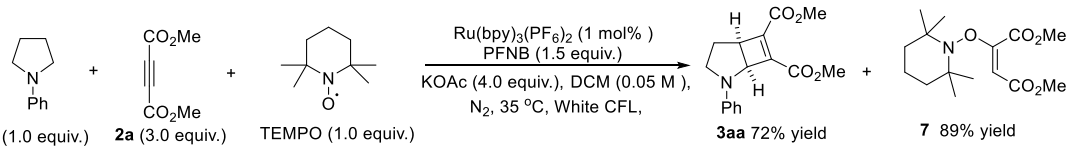


6

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.02 (m, 2H), 7.08 (d, *J*=8.3 Hz, 2H), 6.91-6.79 (m, 3H), 5.84 (s, 1H), 5.07 (d, *J*=3.6 Hz, 1H), 3.94 (s, 2H), 3.80 (s, 3H), 3.75-3.69 (m, 2H), 3.55 (s, 3H), 3.28-3.16 (m,1H), 2.11 (dd, *J*=13.3 Hz, *J*=6.1 Hz, 1H), 2.01-1.91 (m,1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 161.5, 160.2, 144.4, 142.4, 141.8, 140.9, 129.4, 129.0, 126.2, 123.8, 115.4, 115.1, 60.8, 52.2, 52.0, 45.7, 45.4, 34.9, 24.3; IR (KBr, cm^{-1}): 3318.3, 2952.3, 2925.9, 2852.8, 2361.9, 1720.5, 1590.4, 1519.3, 1436.7, 1338.5, 1284.0, 1227.1, 1126.5, 1079.4, 917.3, 826.9, 751.2, 736.1, 641.5; HRMS (ESI) for $C_{23}H_{22}N_2O_7$ $[M+H]^+$ calcd. 439.1503, found 439.1500;

7. Mechanistic Investigations

7.1 TEMPO-trapping experiments

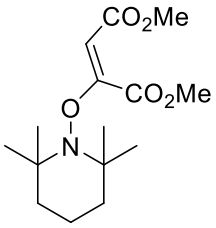


1a (1.0 equiv.) **2a** (3.0 equiv.) TEMPO (1.0 equiv.) **3aa** 72% yield **7** 89% yield

$Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001mmol, 1 mol%), TEMPO (15.6 mg, 0.1 mmol, 1.0 equiv.) and KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.) were weighed into an oven-dried 8 mL vial and DCM (2 mL) was then added. Dimethyl acetylenedicarboxylate **2a** (DMAD, 36 μL, 0.3 mmol, 3.0 equiv.), 1,2,3,4,5-pentafluoro-6-nitrobenzene (PFNB, 18.8 μL, 0.15 mmol, 1.5 equiv.) and N-Ph pyrrolidine **1a** (14.5 μL, 0.1 mmol, 1.0 equiv.) were successively added into the mixture via syringes. The reaction mixture

was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a 23-W compact fluorescent light (CFL, 1-2 centimeter from the vial), allowing the temperature to rise due to its proximity to the lights. After 96 h, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the product **3aa** (20.7 mg, 72% yield) and product **7** (26.5mg, 89% yield) as a red solid, mp= 111-113 ^{o}C.

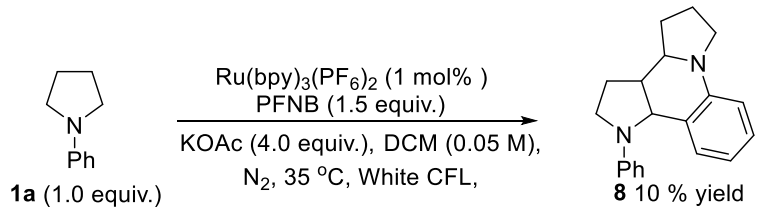
Dimethyl 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)maleate



7

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (s, 1H), 3.91 (s, 3H), 3.68 (s, 3H), 1.69-1.54 (m, 5H), 1.44-1.36 (m, 1H), 1.17 (s, 6H), 1.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 165.5, 163.6, 95.5, 61.4, 52.8, 51.3, 39.6, 31.8, 20.4, 16.7; IR (KBr, cm^{-1}): 2979.7, 2953.1, 2361.9, 1755.0, 1718.7, 1640.4, 1437.7, 1348.9, 1304.0, 1242.3, 1200.4, 1165.7, 1125.5, 1027.8, 973.3, 935.1, 898.4, 870.2, 849.6, 814.7, 772.2, 744.6, 710.7, 632.4, 566.1; HRMS (ESI) for $C_{15}H_{25}NO_5$ $[M+H]^+$ calcd. 300.1805, found 300.1800;

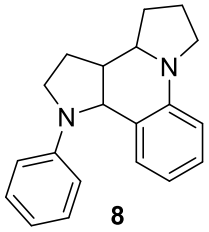
7.2 Iminium and enamine process



$Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.002mmol, 1 mol%) and KOAc (78.4 mg, 0.8 mmol, 4.0 equiv.) were weighed into an oven-dried 8 mL vial and DCM (2 mL) was then added. 1,2,3,4,5-pentafluoro-6-nitrobenzene (PFNB, 100 μL, 0.4 mmol, 2.0 equiv.) and N-Ph pyrrolidine **1a** (29.0 μL, 0.2 mmol, 1.0 equiv.) were successively added into the

mixture via syringes. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a 23-W compact fluorescent light (CFL, 1-2 centimeters from the vial), allowing the temperature to rise due to its proximity to the light. After 96 h, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the product **8** (2.9 mg, 10% yield) as a white solid. mp= 150-152 ^{o}C;

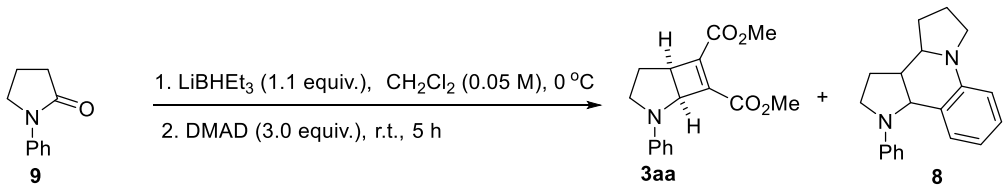
1-phenyl-2,3,3a,3b,4,5,6,11b-octahydro-1H-dipyrrolo[1,2-a:3',2'-c]quinoline



8

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.15 (m, 3H), 7.11 (d, *J*=7.4 Hz, 1H), 6.78 (t, *J*=7.4 Hz, 1H), 7.76-6.64 (m, 4H), 4.44 (d, *J*=9.1 Hz, 1H), 3.66 (d, *J*=8.0 Hz, 1H), 3.46 (dd, *J*=9.1 Hz, *J*=3.0 Hz, 1H), 3.37-3.28 (m, 1H), 2.87 (d, *J*=9.1 Hz, 1H), 2.81-2.70 (m, 1H), 2.46 (dt, *J*=10.1 Hz, *J*=7.0 Hz, 1H), 2.29-2.10 (m, 3H), 2.03-1.92 (m, 1H), 1.84-1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 165.5, 163.6, 95.5, 61.4, 52.8, 51.3, 39.6, 31.8, 20.4, 16.7; IR (KBr, cm^{-1}): 2920.5, 2850.2, 2360.5, 1968.7, 1735.4, 1700.3, 1508.8, 1459.0, 1376.4, 1305.5, 1195.3, 1076.5, 949.1, 912.7, 878.1, 765.9； HRMS (ESI) for $C_{20}H_{22}N_2$ $[M+H]^+$ calcd. 291.1856, found 291.1849;

7.3 [2+2] cycloaddition process



1-phenylpyrrolidin-2-one **9** (80.6 mg, 0.1 mmol, 1.0 equiv.) was weighed into an oven-dried 8 mL vial and CH_2Cl_2 (2 mL) was then added. The reaction mixture was stirred at 0 ^{o}C for 30 min, and then $LiBHEt_3$ (0.11 mmol, 1.1equiv.) was added into this system via a syringe. After stirring at 0 ^{o}C for 5 min, dimethyl

acetylenedicarboxylate **2a** (DMAD, 36 μL, 0.3 mmol, 3.0 equiv.) was added. And then the reaction mixture was stirred at room temperature for 5 h under dark or irradiation with a 23-W compact fluorescent light. Finally, the solvent was evaporated and the residue was subjected to a flash silica gel chromatography (petroleum ether/ethyl acetate = 50:1 to 4:1) to afford the product **8** and **3aa**, respectively.

8. Light-Dark Interval Reaction

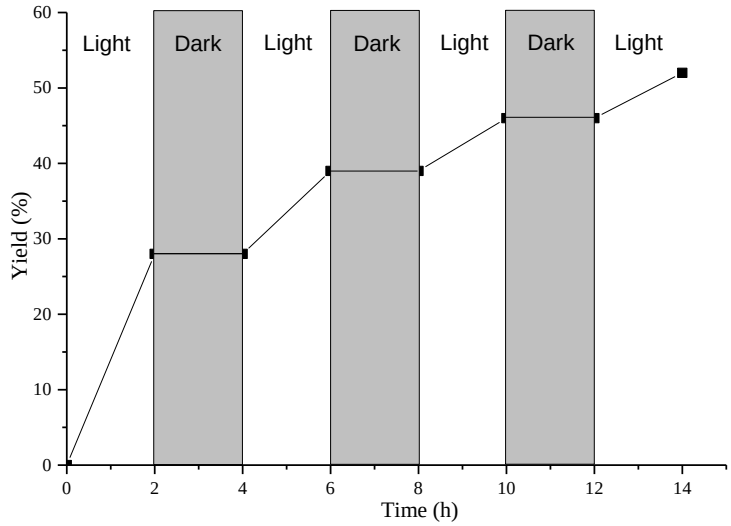


Figure S2: light on-off experiment. The light-dark interval experiments were performed according the general catalysis procedure with 0.4 mmol N-phenylpyrrolidine **1a** in 4 mL CH_2Cl_2. The yield of product **3aa** was determined by flash chromatography (silica gel, petroleum ether/ethyl acetate= 4:1) of an aliquot (0.5 mL) from the reaction mixture. An aliquot was taken out of the reaction system via syringes every 2 h. The whole process was performed under nitrogen balloon.

9. Cyclic Voltammetry

Cyclic voltammetry was carried out on a 25 ml Cell Stand and a CHI660E Electrochemical Analyzer using a glassy carbon electrode as the working electrode and a platinum wire cathode as the counter electrode at r.t. in acetonitrile containing

0.1 M Bu_4NBF_4. Potentials were referred to a saturated calomel electrode (SCE). Before each experiment the surface of the anode was polished and followed by thorough rinsing with distilled water.

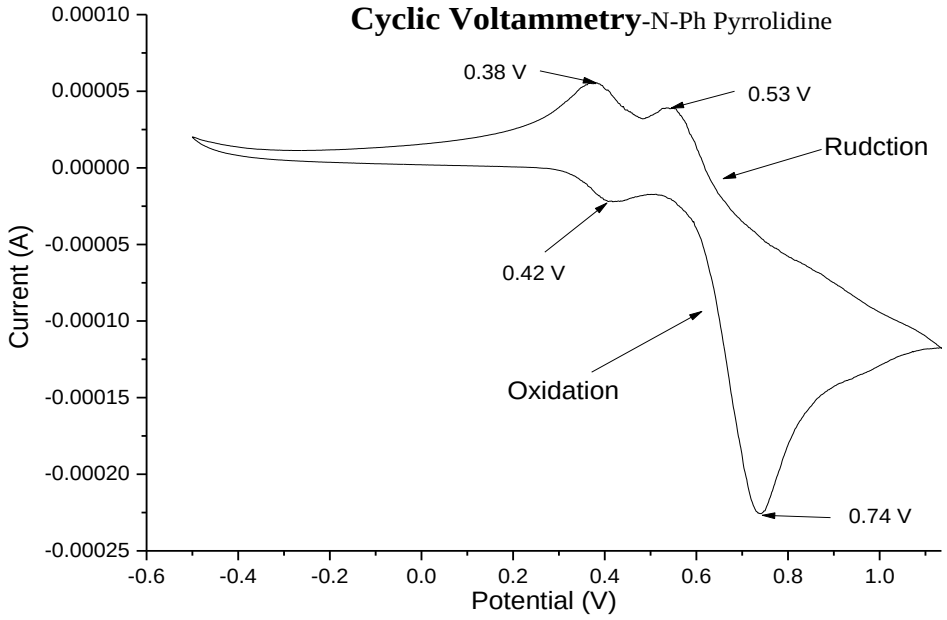


Figure S2: Cyclic voltammetry of N-Ph pyrrolidine (0.01 M) in acetonitrile containing 0.1 M Bu_4NBF_4. The result indicated that the oxidative potential of N-Ph pyrrolidine was 0.74 V.

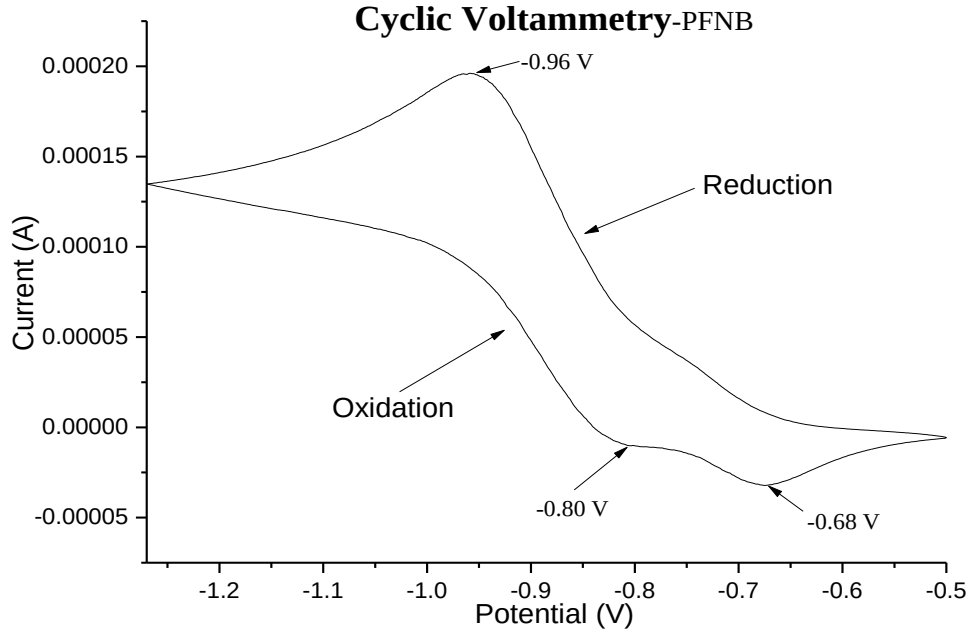


Figure S3: Cyclic voltammetry of PFNB (0.01 M) in acetonitrile containing 0.1 M Bu_4NBF_4. The result indicated that the oxidative potential of PFNB was -0.96 V.

10. Luminescence Quenching Experiments

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Rigorously purged (with nitrogen) solutions of each component were prepared prior to each set of experiments. Luminescence quenching experiments were run with dichloromethane as the solvent. The solutions were irradiated at 452 nm and the luminescence was measured from 500 nm to 800 nm (emission maximum is at 623 nm). The concentration of $Ru(bpy)_3(PF_6)_2$ stock solution was 0.1 mM in CH_2Cl_2. The concentrations of the quencher stock solution were 2.4 mM, 6 mM, 12 mM, 18 mM, and 24 mM in CH_2Cl_2, respectively. For each quenching experiment, l mL of the quencher stock solution was added to a solution (2 mL) of $Ru(bpy)_3(PF_6)_2$ stock solution in a 10.0 mm quartz cuvette. After being stirred with a thin glass rod, the emission spectrum was collected. Linear regression of I_0/I against concentration is done in Origin.

Experiment 7.1: $Ru(bpy)_3(PF_6)_2$ Emission Quenching by N-Ph pyrrolidine

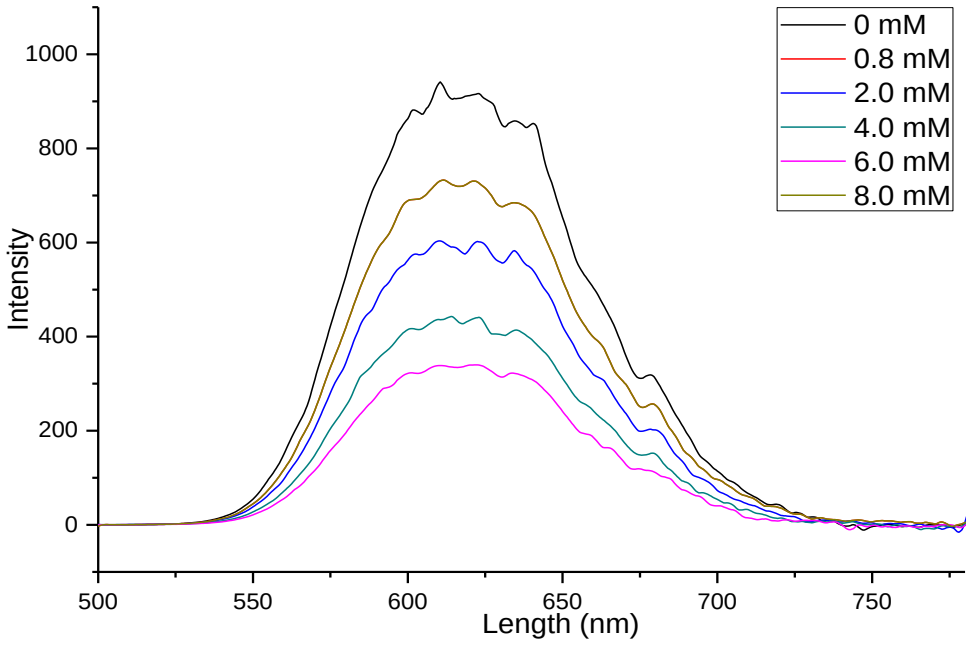


Figure S4: Fluorescence quenching data with $Ru(bpy)_3(PF_6)_2$ and variable N-Ph pyrrolidine.

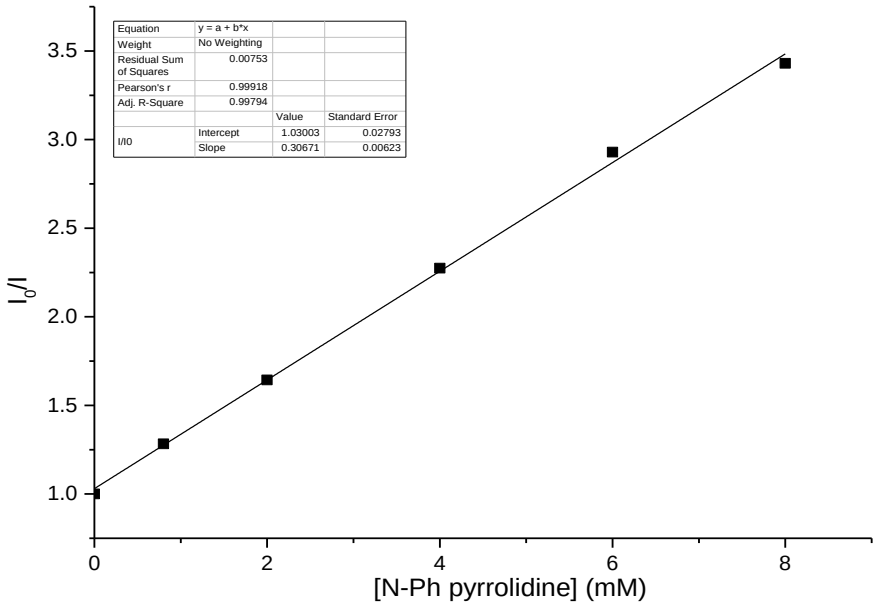


Figure S5: Stern-Volmer plot of $Ru(bpy)_3(PF_6)_2$ and variable N-Ph pyrrolidine (the intensity data was collected at 623 nm).

Experiment 7.2: $Ru(bpy)_3(PF_6)_2$ Emission Quenching by PFNB

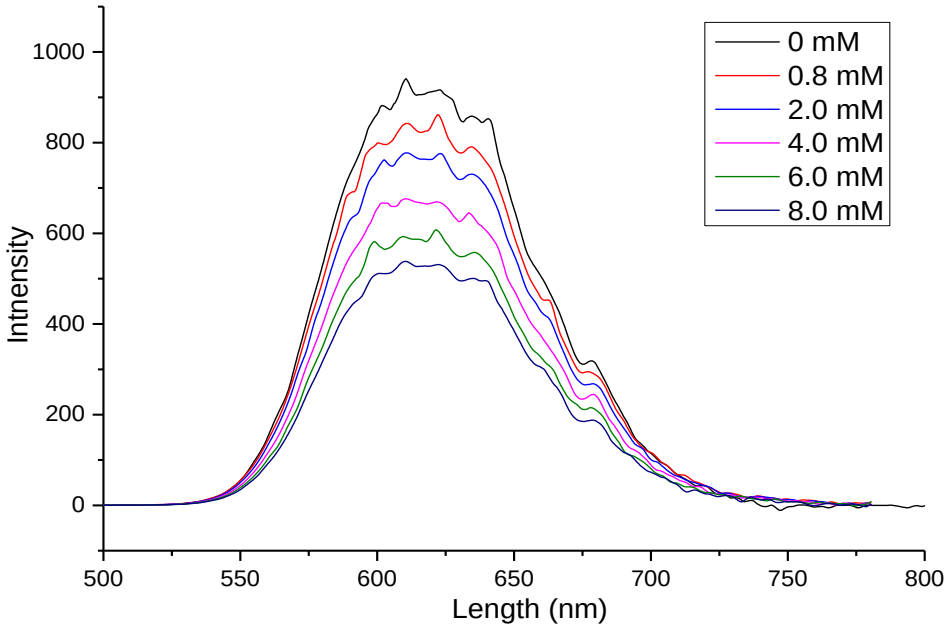


Figure S6: Fluorescence quenching data with $Ru(bpy)_3(PF_6)_2$ and variable PFNB.

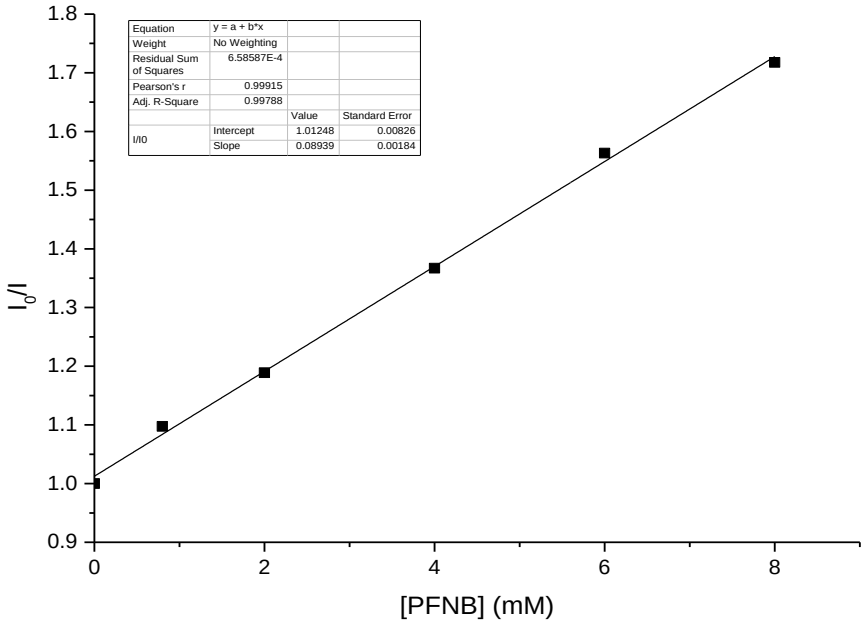


Figure S7: Stern-Volmer plot of $Ru(bpy)_3(PF_6)_2$ and variable PFNB (the intensity data was collected at 623 nm).

Experiment 7.3: $Ru(bpy)_3(PF_6)_2$ Emission Quenching by DMAD

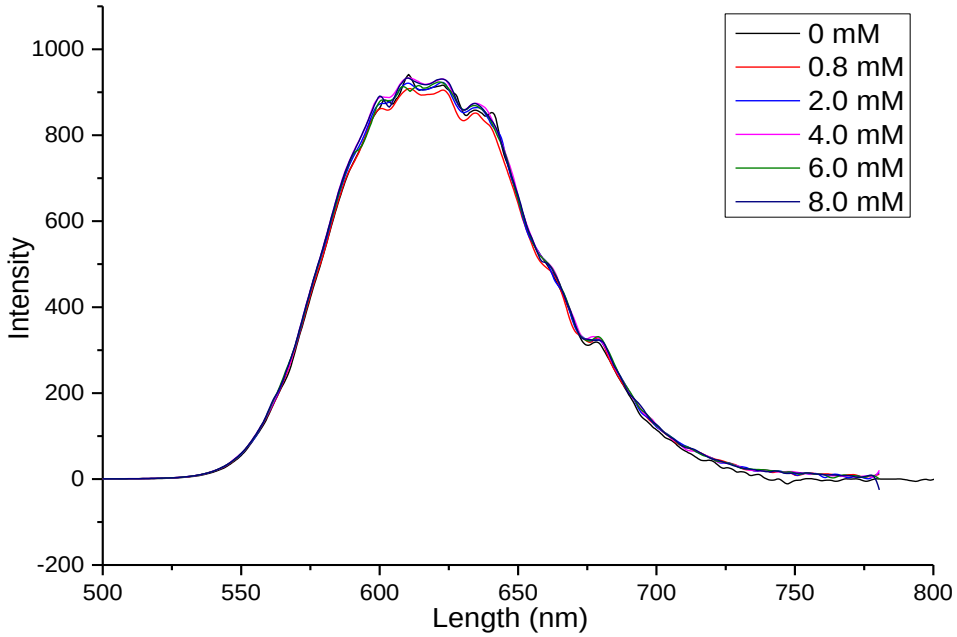


Figure S8: Fluorescence quenching data with $Ru(bpy)_3(PF_6)_2$ and variable DMAD.

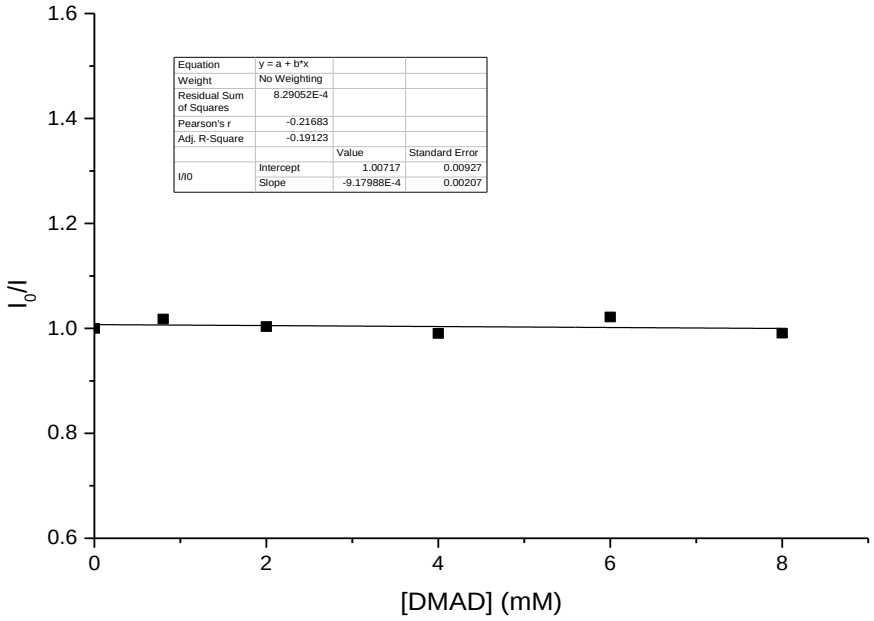
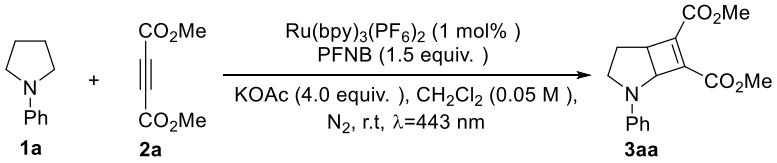


Figure S9: Stern-Volmer plot of $Ru(bpy)_3(PF_6)_2$ and variable DMAD (the intensity data was collected at 623 nm).

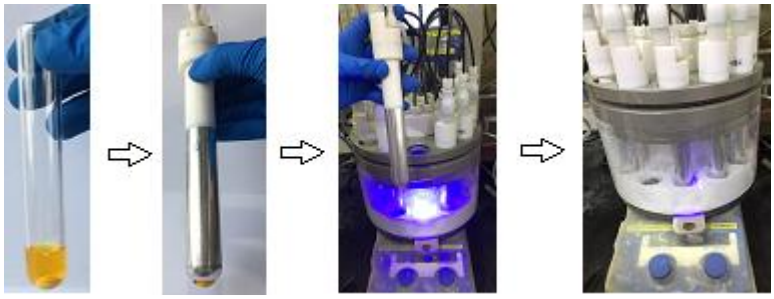
11. Determination of the Quantum Yield[3]



Step I: Reaction setup under standard conditions in a quartz tube

$Ru(bpy)_3(PF_6)_2$ (0.85 mg, 0.001 mmol, 1 mol%) and KOAc (39.2 mg, 0.4 mmol, 4.0 equiv.) were weighed into an oven-dried 8 mL quartz vial with a magnetic stirring bar, and then DCM (0.05 M, 2 mL) was added. Dimethyl acetylenedicarboxylate **2a** (0.3 mmol, 3.0 equiv.), 1, 2, 3, 4, 5-pentafluoro-6- nitrobenzene (PFNB, 0.15 mmol, 18.8 μL, 1.5 equiv.) and N-phenyl pyrrolidine **1a** (0.1 mmol, 1.0 equiv.) were successively added into the mixture via syringes. The reaction mixture was degassed by three cycles of freeze-pump-thaw.

Step II: Irradiating the mixture with 440-445 nm LEDs



The sample was irradiated in Parallel Light Reactor (WP-TEC-1020) (the diameter of hole was 15 mm with intensity of 1916.1 mW cm^{-2}) for 18000 s (5.0 h).

Step III: Determining the reaction yield with ^{1}H NMR

After irradiation, the yield of the product formed was determined by ^{1}H NMR based on a 1,3,5-trimethoxybenzene standard.

Step IV: Determining the absorbance of the catalyst in the reaction

The absorbance of $Ru(bpy)_3(PF_6)_2$ in CH_2Cl_2 was measured at the reaction concentration of 5.0×10^{-4} M and at a substantially diluted concentration of 5.0×10^{-6} M. The absorbance of the catalyst at 443 nm in a 5.0×10^{-4} M solution is >3 indicating that the fraction of light absorbed is >0.999.

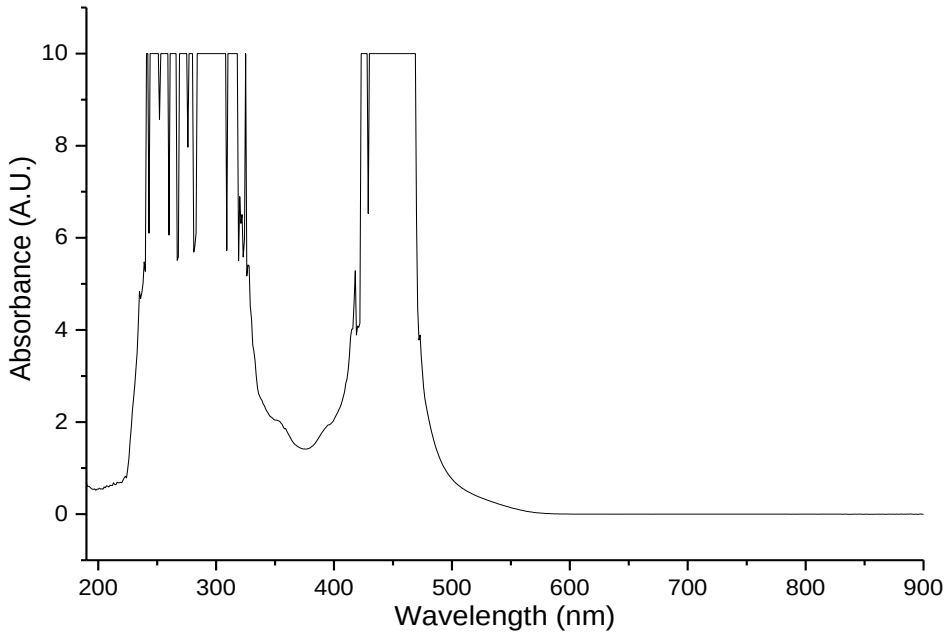


Figure S10. Absorbance of a 5.0×10^{-4} M solution of $Ru(bpy)_3(PF_6)_2$ in CH_2Cl_2.

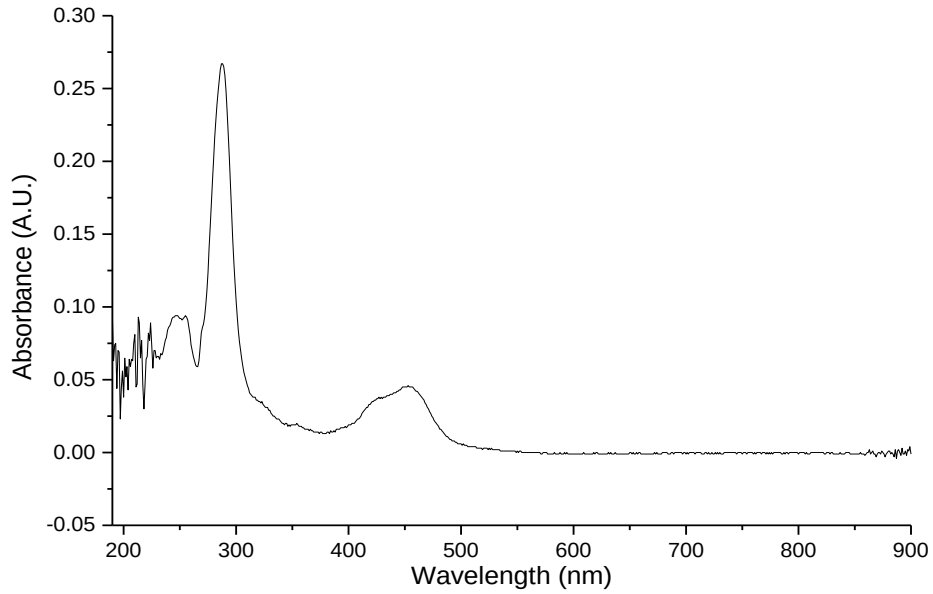


Figure S11. Absorbance of a 5.0 $\times 10^{-6}$ M solution of $Ru(bpy)_3(PF_6)_2$ in CH_2Cl_2

Step V: Calculating the quantum yield as follows

$$\Phi = \frac{n_{\mathbf{3aa}} N_A / t}{f\, P\lambda / hc}$$

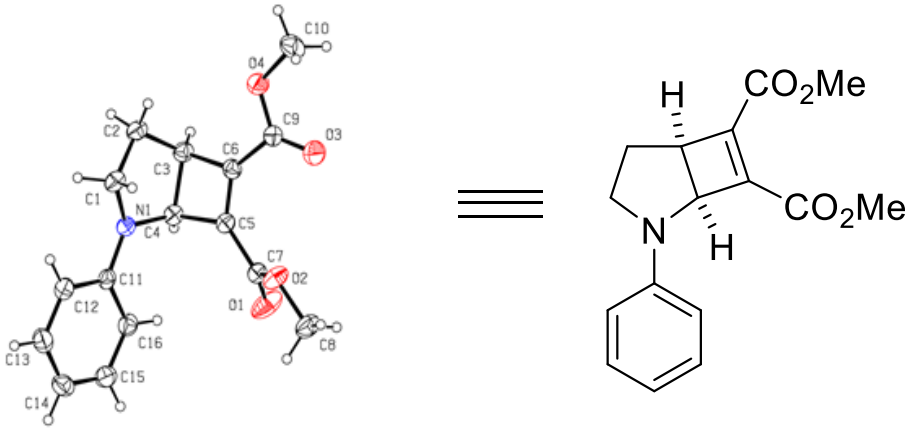
$n_{\mathbf{3aa}}$: the mole number of the product **3aa**; t: the reaction time (18000 s, 5.0 h); N_A: 6.02×10^{23}/mol; f: $1\text{-}10^{-A}$>0.999 (443 nm, A>3); P: P=E*S (E: illumination intensity, E=1916.1 mW/cm^2; S: the area irradiated S= 1.77 cm^2); λ: wavelength (λ= 4.43×10^{-7} m); h: planck constant (h=6.626×10^{-34} J*s); c: velocity of light (c=3×10^8 m/s).

ϕ = Mole number for the product/Mole number photons absorbed = 0.0158;

This result revealed that the main pathway of this reaction was not a photo-initiated radical chain process, but a photocatalyzed process.

12. X-Ray Crystallographic Data of 3aa:

The crystal structure **3aa** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1568396.



Bond precision:	C-C = 0.0041 A	Wavelength=0.71073	
Cell:	a=11.9369(6)	b=12.8573(6)	c=9.3580(4)
	alpha=90	beta=97.283(5)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	1424.64(12)	1424.65(12)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C16 H17 N O4	C16 H17 N O4	
Sum formula	C16 H17 N O4	C16 H17 N O4	
Mr	287.31	287.30	
Dx,g cm-3	1.339	1.340	
Z	4	4	
Mu (mm-1)	0.097	0.097	
F000	608.0	608.0	
F000’	608.32		
h,k,lmax	14,15,11	14,15,11	
Nref	2804	2797	
Tmin,Tmax	0.974, 0.977	0.892, 1.000	
Tmin’	0.974		
Correction method= # Reported T Limits: Tmin=0.892 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.998		Theta(max)= 26.006	
R(reflections)= 0.0651(1627)		wR2(reflections)= 0.1701(2797)	
S = 1.063		Npar= 192	

Table S2: X-Ray Crystallographic Data of 3aa.

13. Computational Experiment

(1) PES analysis

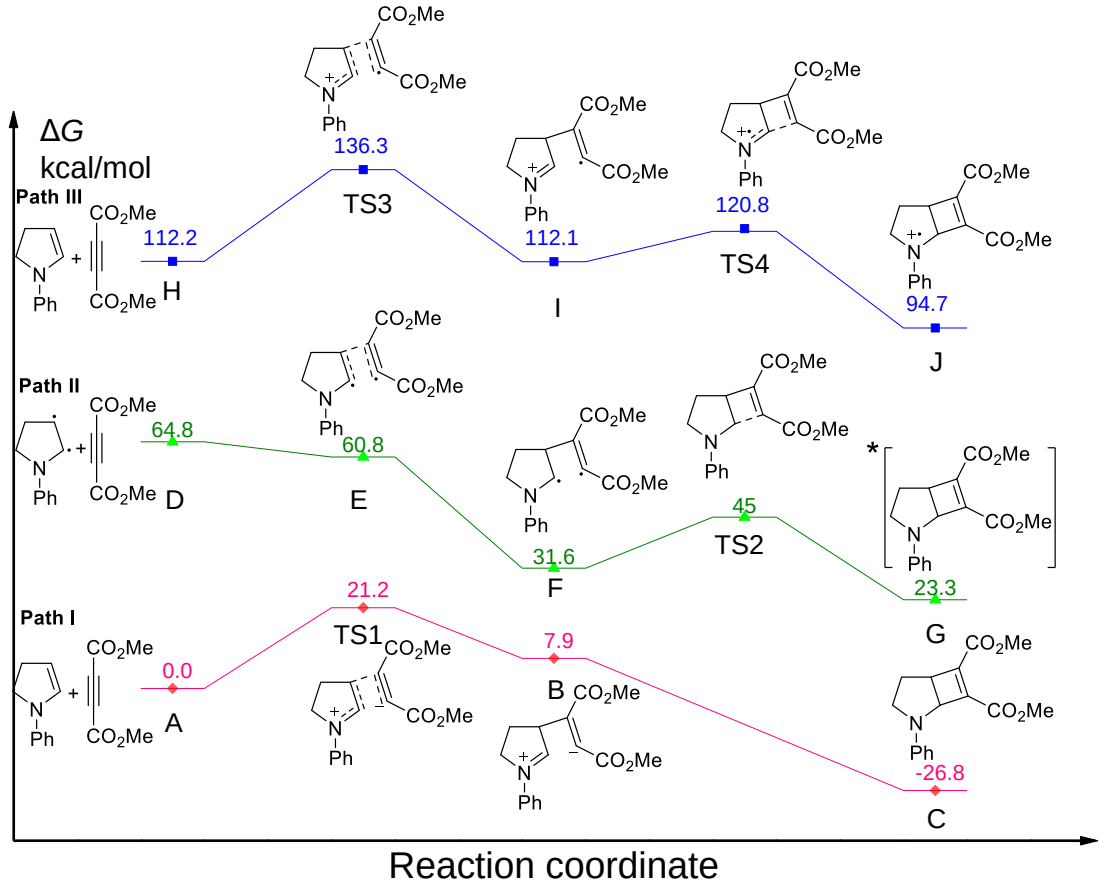


Figure S10: Analysis of the reaction pathway. Quantum mechanical calculations were performed using Gaussian 09 (Revision C.02 [4]). All geometries and single point energies were calculated with M06-2x/6-31G(d) and SMD solvation model for dichloromethane. (ε=8.9)

All energies are given in Hartree

A1

C	0.47409100	0.04457000	0.03746400
C	1.15890100	-1.18433500	-0.01972400
C	2.54953600	-1.21869500	-0.05171600
C	3.29868000	-0.04538600	-0.02967700
C	2.62420100	1.17450300	0.02822300
C	1.23731800	1.22974700	0.06396300
H	0.60306100	-2.11503000	-0.04274600
H	3.04870800	-2.18289300	-0.09793900

H	4.38302900	-0.07803000	-0.05542700
H	3.18522100	2.10490000	0.05077000
H	0.74924100	2.19612500	0.12370200
N	-0.90656400	0.06478700	0.08335800
C	-1.73748600	1.17840800	-0.06708800
C	-3.03134400	0.85080700	-0.10283800
H	-1.30354500	2.16717400	-0.13720500
H	-3.85096200	1.55094900	-0.19297500
C	-3.18445200	-0.64354000	0.06824200
H	-3.64949900	-0.88814700	1.03091100
H	-3.80163000	-1.10134100	-0.71069700
C	-1.72581300	-1.15309900	0.00172300
H	-1.47869600	-1.83410500	0.82124200
H	-1.52077600	-1.67099400	-0.94458300

0 imaginary frequencies
Zero-point Energies -442.042764
Thermal Energies -442.033757
Thermal Free Energies -442.077649

A2

C	0.59922500	0.19818400	0.06440500
C	-0.59922100	0.19810700	-0.06443300
C	2.04379100	0.24540000	0.27696700
O	2.56587000	0.96783600	1.08896500
O	2.67277400	-0.59785000	-0.53123700
C	-2.04379700	0.24547000	-0.27688000
O	-2.56587300	0.96829400	-1.08854100
O	-2.67276000	-0.59816600	0.53092500
C	4.10325700	-0.61976300	-0.39103300
H	4.45545300	-1.35275400	-1.11425800
H	4.51635200	0.36673500	-0.61104500
H	4.37612200	-0.91697900	0.62338200
C	-4.10326700	-0.61985600	0.39088000
H	-4.45547400	-1.35286900	1.11408300
H	-4.51620300	0.36667400	0.61103500
H	-4.37627400	-0.91697500	-0.62352500

0 imaginary frequencies
Zero-point Energies -532.750825
Thermal Energies -532.740175
Thermal Free Energies -532.788628

TS1

C	5.24140000	0.06957600	0.00625000
C	4.57528600	-0.50888900	1.08251000
C	3.24976700	-0.91897300	0.96274700
C	2.57239700	-0.74672700	-0.25039300
C	3.24702600	-0.18226300	-1.34307900
C	4.56791000	0.22537800	-1.20519400
H	6.27344600	0.39009400	0.10559600
H	5.08381200	-0.64315000	2.03248800
H	2.74602000	-1.35773100	1.81676300
H	2.75196300	-0.06699400	-2.30119100
H	5.07555900	0.66460200	-2.05882600
N	1.22504400	-1.13563800	-0.35375500
C	0.34370900	-0.71154200	-1.28256500
C	-0.96286800	-0.99397600	-0.92927100
H	0.67560700	-0.12697200	-2.12989100
H	-1.76456100	-0.94892500	-1.65592100
C	-2.74161100	0.63807700	0.49839100
C	-1.51975300	0.61246500	0.20465300
C	-0.32355300	1.39152800	0.61536500
O	-0.03206500	1.60007300	1.77038500
O	0.37648900	1.86006600	-0.41943300
C	1.54120900	2.62234300	-0.07369400
H	2.02929900	2.86059700	-1.01782700
H	1.24831100	3.53869500	0.44429200
H	2.20550700	2.03660800	0.56578100
C	-4.01335000	0.00119300	0.33484000
O	-4.40732100	-0.94953800	0.98816300
O	-4.76068400	0.60415700	-0.61211800
C	-6.06004000	0.04258200	-0.80276400
H	-6.53057900	0.64461100	-1.57982300
H	-5.99018900	-0.99935300	-1.12535700
H	-6.64303000	0.09537300	0.11996600
C	0.50339100	-1.82327400	0.74261600
H	0.45744900	-1.15426200	1.61070200
H	1.03372300	-2.73456400	1.02543300
C	-0.89001500	-2.06963800	0.14438300
H	-1.68046300	-1.99024000	0.89287400
H	-0.94396700	-3.06413100	-0.31352300

1 imaginary frequencies(-487.94)

Zero-point Energies -441.927020

Thermal Energies -441.917858

Thermal Free Energies -441.962556

B

C	4.90261100	0.08940600	-0.21017800
C	4.27160300	-0.10515500	1.01612900
C	2.95096900	-0.54166200	1.06826000
C	2.27264700	-0.78067300	-0.12523300
C	2.89865400	-0.61364300	-1.36041400
C	4.21477700	-0.16864500	-1.39545100
H	5.93160500	0.43292600	-0.24368400
H	4.80272000	0.09129300	1.94183500
H	2.45310300	-0.65995100	2.02334100
H	2.37692700	-0.84155900	-2.28407200
H	4.70587400	-0.03559900	-2.35395600
N	0.89733100	-1.17048600	-0.06513600
C	0.00765900	-0.93915800	-0.96889900
C	-1.35620800	-1.30105500	-0.52720800
H	0.25808400	-0.42439100	-1.89035200
H	-1.91987200	-1.79214800	-1.32294000
C	-2.07790500	0.01180500	-0.13221500
C	-1.52776700	1.14295200	0.32388300
C	-0.15866600	1.44541100	0.54810900
O	0.44702200	1.39459300	1.62184200
O	0.45598500	1.96176500	-0.57186300
C	1.69014200	2.63356400	-0.33808100
H	2.42300600	1.98340200	0.14585000
H	2.05566000	2.93724900	-1.32076000
H	1.53628900	3.52014900	0.28582200
C	-3.55381500	-0.15994100	-0.26064000
O	-4.08764300	-1.19693200	-0.61514500
O	-4.26661100	0.92982700	0.05887800
C	-5.68031400	0.77828000	-0.04707700
H	-6.10485800	1.73557900	0.25515900
H	-5.96983000	0.54522400	-1.07511000
H	-6.03670600	-0.01653400	0.61352100
C	0.29477200	-1.76224400	1.16603400
H	0.22738200	-0.95186000	1.89833600
H	0.94786100	-2.55496000	1.53320100
C	-1.06910500	-2.23772000	0.66554400
H	-1.83594300	-2.16340100	1.43793900
H	-1.00296500	-3.27517100	0.32675300

0 imaginary frequencies

Zero-point Energies -974.712123

Thermal Energies -974.786493

Thermal Free Energies -974.853716

C			
C	4.54184700	0.42954900	0.66044700
C	4.03178800	-0.59302000	1.45537800
C	2.85785500	-1.25694500	1.10737900
C	2.16480000	-0.91293100	-0.06635100
C	2.68690500	0.12103900	-0.86590100
C	3.85577200	0.77809600	-0.50258300
H	5.45283500	0.94815200	0.94147100
H	4.54629000	-0.87940100	2.36854300
H	2.48184600	-2.04185300	1.75432200
H	2.17268800	0.41816000	-1.77267800
H	4.23107000	1.57398400	-1.14035000
N	1.00351600	-1.58761100	-0.45348600
C	0.01980100	-0.88687700	-1.26438500
C	-1.29682100	-1.72078800	-1.14702000
H	0.38033800	-0.65630000	-2.26857100
H	-1.77817700	-2.00542000	-2.08494900
C	-1.86968000	-0.49684800	-0.46622700
C	-0.74593000	0.22983200	-0.54857500
C	-0.32947400	1.55695300	-0.02813300
O	-0.57668100	1.97175300	1.07896900
O	0.39360900	2.21747400	-0.93652200
C	0.97387000	3.44469100	-0.48192900
H	1.57703600	3.81158000	-1.31134600
H	0.19296300	4.16583000	-0.22997100
H	1.60021400	3.26219800	0.39463100
C	-3.22228600	-0.27218400	0.08700400
O	-4.03419400	-1.16038900	0.22529500
O	-3.43541800	1.00425000	0.40344200
C	-4.71406500	1.28710600	0.98273200
H	-4.71586000	2.35699800	1.18534300
H	-5.51386100	1.02942500	0.28458600
H	-4.84208600	0.72393500	1.91002300
C	0.30239100	-2.43445600	0.51616400
H	0.03223800	-1.86621200	1.41997400
H	0.93699200	-3.27029200	0.82088400
C	-0.94152500	-2.90227400	-0.24274700
H	-1.75776600	-3.18227200	0.42765100
H	-0.69137700	-3.76560200	-0.86615400

0 imaginary frequencies

Zero-point Energies -974.860559

Thermal Energies -974.841625
Thermal Free Energies -974.908954

D

C	-0.47224200	0.02737800	-0.02133700
C	-1.15993700	-1.20047100	-0.02814300
C	-2.54958400	-1.22383500	-0.00074800
C	-3.28767700	-0.04133900	0.02575800
C	-2.60867500	1.17651400	0.01103000
C	-1.22058800	1.22093200	-0.01979400
H	-0.61292800	-2.13591100	-0.06056500
H	-3.05937600	-2.18325200	-0.00550700
H	-4.37244200	-0.06824100	0.04561000
H	-3.16560200	2.10939500	0.01277800
H	-0.70957200	2.17613600	-0.06669800
N	0.91337700	0.07517400	-0.01728500
C	1.66710100	1.24151200	0.05045900
C	3.07987500	0.83325400	-0.14453100
H	1.33548700	2.01322200	0.74558000
H	3.66007200	1.21511500	-0.98241900
C	3.16347200	-0.61762500	0.22901500
H	3.94144100	-1.16752500	-0.30441700
H	3.33531300	-0.73975400	1.30728400
C	1.74793400	-1.13331600	-0.10941500
H	1.70205300	-1.55335800	-1.12128300
H	1.39382800	-1.89006400	0.59687700

0 imaginary frequencies
Zero-point Energies -441.938981
Thermal Energies -441.929856
Thermal Free Energies -441.974388

E

C	-5.24196900	-0.21090500	0.48184900
C	-4.81063400	-0.64805900	-0.76897500
C	-3.47222400	-0.95318800	-0.98876300
C	-2.54805600	-0.82152900	0.05716500
C	-2.97444700	-0.36045800	1.31281700
C	-4.31664000	-0.06673300	1.51516900
H	-6.28805900	0.02572200	0.64811800
H	-5.51982500	-0.75644900	-1.58361800
H	-3.15460800	-1.29702900	-1.96638600
H	-2.25694800	-0.18844000	2.10585800

H	-4.63831500	0.29356800	2.48738700
N	-1.19526500	-1.12053600	-0.16495600
C	-0.24672800	-1.25201400	0.78979000
C	1.02565200	-1.26043300	0.21038300
H	-0.49927200	-1.26770500	1.83847500
H	1.91629400	-1.52973300	0.76331800
C	1.53704800	0.88338100	0.07717800
C	2.80490900	0.86552100	0.05676200
C	4.07924500	0.27410200	-0.13873500
O	4.79973000	0.42875000	-1.11847300
O	4.46380200	-0.45171900	0.94885000
C	5.76618700	-1.02354400	0.85355200
H	6.52690200	-0.24526900	0.74816600
H	5.91846600	-1.57080600	1.78412800
H	5.83353500	-1.70593300	0.00178900
C	0.31244500	1.58701000	0.28679600
O	-0.39266000	1.46659300	1.28461000
O	-0.09243600	2.27005900	-0.81789400
C	-1.39387000	2.84324900	-0.71766400
H	-1.56945200	3.34734500	-1.66834600
H	-2.15120100	2.06938900	-0.55625700
H	-1.44228600	3.56400100	0.10307700
C	-0.59805600	-1.14841800	-1.51842300
H	-0.69761900	-0.15053500	-1.95945600
H	-1.12143300	-1.87136400	-2.14651100
C	0.86168800	-1.53797100	-1.25893500
H	1.56438800	-0.99121400	-1.88918900
H	1.01148400	-2.61132400	-1.43239500

1 imaginary frequency (-397.09)

Zero-point Energies -974.716264

Thermal Energies -974.695715

Thermal Free Energies -974.769397

F

C	4.82271500	0.15820000	-0.02990100
C	4.16159200	-0.14888800	1.15951700
C	2.86165500	-0.64177000	1.14898700
C	2.18985300	-0.83582100	-0.07181800
C	2.86347700	-0.54104200	-1.27277800
C	4.16203300	-0.04783200	-1.24099800
H	5.83706800	0.54354400	-0.01327800
H	4.65938600	0.00200900	2.11334300
H	2.35738100	-0.85126000	2.08613800

H	2.37666900	-0.71752900	-2.22564800
H	4.66561400	0.17126000	-2.17860900
N	0.87948600	-1.28589100	-0.08981500
C	0.02485500	-1.21899300	-1.18129000
C	-1.37417900	-1.44104300	-0.68786100
H	0.25777200	-0.51175000	-1.97003500
H	-2.02498200	-1.93143700	-1.41672700
C	-2.04868700	-0.13413000	-0.27046600
C	-1.38344800	0.93490100	0.10378300
C	-0.08159800	1.50595000	0.41024200
O	0.35183400	1.58112400	1.54219500
O	0.53779000	1.98062000	-0.67262500
C	1.79468800	2.62760500	-0.41887300
H	2.22757400	2.81892600	-1.39965300
H	1.62521900	3.56797400	0.11255500
H	2.44730100	1.98177500	0.17204500
C	-3.54770100	-0.14739000	-0.22720300
O	-4.20507000	-1.13076700	-0.47955700
O	-4.06628500	1.03035000	0.12448400
C	-5.49621900	1.07427300	0.20015800
H	-5.74392100	2.09613500	0.48341300
H	-5.93580000	0.83135800	-0.76984200
H	-5.85963800	0.37076700	0.95266100
C	0.19516200	-1.79140400	1.10622400
H	0.03500900	-0.97079900	1.81798200
H	0.79636800	-2.56234200	1.59677000
C	-1.12546500	-2.33115700	0.54800100
H	-1.93681200	-2.29016700	1.27834500
H	-0.99915500	-3.36661000	0.21892000

0 imaginary frequencies

Zero-point Energies -974.766724

Thermal Energies -974.747225

Thermal Free Energies -974.815843

TS2

C	4.99553700	0.26457900	0.71926100
C	4.78275600	-1.11072300	0.63566900
C	3.53453400	-1.60952500	0.28005200
C	2.49789100	-0.71593600	0.00462500
C	2.69421000	0.66245800	0.09594400
C	3.95093600	1.14541300	0.44907700
H	5.97173600	0.64671100	1.00087400
H	5.59262200	-1.80266700	0.84392700
H	3.37768400	-2.67986400	0.19888300

H	1.86656300	1.34393900	-0.08113300
H	4.10627700	2.21716700	0.52548600
N	1.21882400	-1.21861500	-0.37356200
C	0.37338500	-0.60155200	-1.17027900
C	-0.93497300	-1.36922400	-1.27351500
H	0.72953700	0.17758100	-1.83882000
H	-1.26458000	-1.49177000	-2.31065100
C	-1.81254800	-0.44693500	-0.46002100
C	-1.05302400	0.68384800	-0.17523700
C	-1.09923000	2.10262000	-0.18720500
O	-2.09333900	2.78256100	0.03866900
O	0.12394600	2.66594200	-0.42136000
C	0.15172400	4.08948700	-0.37012500
H	1.17903400	4.37481000	-0.59942000
H	-0.53014800	4.52100200	-1.10747200
H	-0.12433500	4.44945700	0.62470000
C	-3.08515300	-0.85804000	0.04004700
O	-3.65244000	-1.91000800	-0.25904300
O	-3.63575700	0.04154400	0.89891000
C	-4.91086200	-0.32169100	1.40976500
H	-5.20118000	0.48161400	2.08813500
H	-5.64711300	-0.41195500	0.60562000
H	-4.86348800	-1.27003800	1.95311400
C	0.57894400	-2.36182200	0.32321900
H	0.25510800	-2.00153100	1.30622200
H	1.29588900	-3.17109000	0.45550900
C	-0.58455800	-2.70995000	-0.60187900
H	-1.43946700	-3.12339900	-0.06643800
H	-0.25260100	-3.42803300	-1.35739100

1 imaginary frequency (-231.96)

Zero-point Energies -974.744111

Thermal Energies -974.724740

Thermal Free Energies -974.794538

G

C	4.92651500	0.03259600	0.31356700
C	4.34801600	-0.85020400	1.23714600
C	3.03789600	-1.25044200	1.09493600
C	2.25550200	-0.76198900	0.00580900
C	2.85372800	0.14982900	-0.91700000
C	4.16951200	0.52660200	-0.75602400
H	5.96171100	0.33602400	0.43076800
H	4.93255200	-1.21998200	2.07285300

H	2.59968200	-1.91877500	1.82507600
H	2.27352600	0.55472200	-1.73430700
H	4.61655000	1.21469200	-1.46554400
N	0.97553500	-1.15880700	-0.15098600
C	0.01574300	-0.58482100	-1.11057700
C	-1.21092800	-1.54582400	-1.08415700
H	0.50357900	-0.37806200	-2.06315500
H	-1.55536500	-1.87889400	-2.06744800
C	-1.98888900	-0.41236400	-0.45538300
C	-0.88354400	0.46767600	-0.47815200
C	-0.55471200	1.78422900	-0.05802200
O	-1.27635000	2.62141400	0.47339200
O	0.77260200	2.05411900	-0.32551100
C	1.21826700	3.33921000	0.07529800
H	2.28306700	3.37834900	-0.16293200
H	0.68926700	4.13008700	-0.46507400
H	1.07375700	3.49291400	1.14888600
C	-3.35345400	-0.44826100	-0.06751500
O	-4.07908700	-1.44341300	-0.17410400
O	-3.81978000	0.72453100	0.44977100
C	-5.18544100	0.70255700	0.83334500
H	-5.40735600	1.70079300	1.21397000
H	-5.83471100	0.47751100	-0.01845400
H	-5.36769100	-0.04081900	1.61568800
C	0.29924100	-2.14857300	0.71191100
H	-0.08281600	-1.62210300	1.59358800
H	1.00670100	-2.91204600	1.03353700
C	-0.81632600	-2.70846300	-0.17053800
H	-1.65944400	-3.06374400	0.42565200
H	-0.42758900	-3.54277500	-0.76245300

0 imaginary frequencies

Zero-point Energies -974.779675

Thermal Energies -974.760402

Thermal Free Energies -974.829226

H

C	0.48933200	0.05032100	-0.00610900
C	1.14443200	-1.19183800	-0.04144400
C	2.53107900	-1.23580900	-0.03544600
C	3.27394000	-0.05684300	0.00553800
C	2.62015700	1.17636600	0.04212700
C	1.23638000	1.24139700	0.03790100

H	0.57857100	-2.11505600	-0.08151700
H	3.03235500	-2.19749500	-0.06487600
H	4.35834400	-0.09676400	0.01092900
H	3.19348800	2.09668400	0.07830500
H	0.75153300	2.20927800	0.08165000
N	-0.90908100	0.07854000	-0.01096700
C	-1.69748400	1.17824500	-0.06636200
C	-3.02226000	0.83749900	-0.03662800
H	-1.27730200	2.17173500	-0.13325900
H	-3.83714300	1.54858800	-0.07450500
C	-3.17699200	-0.63913900	0.05217100
H	-3.71165900	-0.92121000	0.96635400
H	-3.75983400	-1.02569900	-0.79107700
C	-1.73191900	-1.15222800	0.04415700
H	-1.46252300	-1.70903900	0.94440800
H	-1.50224600	-1.75862500	-0.83507900

0 imaginary frequencies

Zero-point Energies -441.864372

Thermal Energies -441.855744

Thermal Free Energies -441.898809

TS3

C	-4.74660800	0.17824500	0.49813600
C	-4.37947500	-0.55070900	-0.63056400
C	-3.09155300	-1.06209100	-0.75299000
C	-2.16823900	-0.83935300	0.27225500
C	-2.52061200	-0.08708900	1.39929200
C	-3.81341200	0.40831200	1.50893000
H	-5.75272500	0.57498000	0.58691100
H	-5.09747500	-0.72741600	-1.42450600
H	-2.82573000	-1.63371900	-1.63439300
H	-1.79362100	0.13793700	2.17186600
H	-4.08432100	0.99177000	2.38256700
N	-0.84318600	-1.34236500	0.14007700
C	0.05116600	-1.43884700	1.09871300
C	1.32984400	-1.75417700	0.57644200
H	-0.18843600	-1.20753000	2.12978600
H	2.15363700	-2.05884400	1.20908900
C	2.10904500	0.20041500	0.18329200
C	1.22538400	1.03946400	-0.02627300
C	-0.04127200	1.75247400	-0.09329000
O	-0.46098800	2.43256500	0.81288000
O	-0.65378700	1.53950700	-1.25517400
C	-1.92014000	2.20734600	-1.41003300

H	-1.76666900	3.28854000	-1.41223500
H	-2.30868100	1.87304000	-2.37016700
H	-2.59536800	1.92860600	-0.59788400
C	3.56925100	-0.08370300	0.14472400
O	4.05343200	-1.18675800	0.09790800
O	4.24308700	1.05557900	0.15159700
C	5.67516600	0.91799100	0.08659300
H	6.06089800	1.93529700	0.08792800
H	6.03532200	0.36753300	0.95770100
H	5.96058600	0.39723100	-0.82919700
C	-0.27622500	-1.74137300	-1.17741900
H	-0.28070000	-0.85566200	-1.81926500
H	-0.90535300	-2.51427600	-1.61896400
C	1.12856900	-2.24542200	-0.82871400
H	1.88894300	-1.89504400	-1.52914100
H	1.16270500	-3.34193100	-0.82290000

1 imaginary frequency (-606.42)
Zero-point Energies -974.600241
Thermal Energies -974.580713
Thermal Free Energies -974.649067

I

C	-4.85182300	0.07317400	0.01435200
C	-4.18341300	-0.19587300	-1.17628600
C	-2.87221700	-0.66236900	-1.15692100
C	-2.23987900	-0.85311800	0.07157900
C	-2.90264400	-0.60106000	1.27443200
C	-4.21037000	-0.13502900	1.23570300
H	-5.87380400	0.43734400	-0.00579500
H	-4.67697200	-0.04134200	-2.13002100
H	-2.35648000	-0.85322900	-2.09113600
H	-2.42441200	-0.77532400	2.23216000
H	-4.73086200	0.06047800	2.16737200
N	-0.86208800	-1.25745500	0.07445200
C	-0.03436500	-1.13200400	1.05249900
C	1.36851900	-1.42451600	0.63738500
H	-0.33614500	-0.73998400	2.01838400
H	1.93937300	-1.94078700	1.41196500
C	2.05511800	-0.09075800	0.32805700
C	1.42577200	1.05066400	0.16606600
C	0.11243900	1.67652600	0.31239000
O	-0.37939200	1.91154000	1.39607500
O	-0.45573600	1.94053000	-0.85977900
C	-1.73785500	2.59253300	-0.78271400

H	-1.61112000	3.60485100	-0.39289300
H	-2.11153000	2.61984500	-1.80448700
H	-2.41420000	2.03033200	-0.13492400
C	3.54069300	-0.20285800	0.13535700
O	4.12891000	-1.25246700	0.24482800
O	4.10118000	0.96158200	-0.16495900
C	5.52410200	0.92846000	-0.36087800
H	5.80925100	1.95354200	-0.59010700
H	6.02000700	0.58555000	0.54930500
H	5.77338700	0.26565700	-1.19205900
C	-0.18800900	-1.75816400	-1.16485100
H	-0.09255500	-0.90770000	-1.84662800
H	-0.81400000	-2.52722800	-1.61690600
C	1.15144800	-2.26511600	-0.63580500
H	1.95369600	-2.14222300	-1.36416900
H	1.07618700	-3.32003300	-0.36272500

0 imaginary frequencies

Zero-point Energies -974.639042

Thermal Energies -974.619893

Thermal Free Energies -974.687650

TS4

C	-4.85822600	0.39706800	-0.05562600
C	-4.55325700	-0.73203100	-0.81140600
C	-3.29561800	-1.31863300	-0.72730900
C	-2.34109100	-0.76796700	0.13222400
C	-2.63525700	0.37448900	0.88774900
C	-3.89616600	0.94666100	0.79197300
H	-5.83998300	0.85315600	-0.13153800
H	-5.29537300	-1.16322400	-1.47497600
H	-3.07738900	-2.20123400	-1.31627700
H	-1.88845000	0.83308900	1.52812300
H	-4.12267500	1.83447600	1.37322100
N	-1.04982900	-1.35771300	0.21488900
C	-0.17277000	-1.12355500	1.16837200
C	1.16375100	-1.78950000	0.87164700
H	-0.47967600	-0.72308500	2.12985600
H	1.61399700	-2.29000200	1.73183700
C	1.88925800	-0.53109900	0.46620300
C	1.01791700	0.45364400	0.49825000
C	0.61814300	1.84388500	0.26727200
O	1.02139700	2.77701500	0.91731900
O	-0.29202600	1.89318900	-0.70056500

C	-0.88243000	3.18473300	-0.92670400
H	-1.66325900	3.02131900	-1.66705000
H	-1.30718800	3.56915800	0.00314500
H	-0.13100200	3.87953100	-1.30684100
C	3.32422300	-0.49362200	0.05260800
O	4.01961200	-1.48004300	0.05411000
O	3.69835500	0.72672300	-0.30469600
C	5.07146100	0.85982800	-0.70947500
H	5.19940100	1.90969500	-0.96615700
H	5.73209900	0.58428300	0.11492200
H	5.27074600	0.22484600	-1.57497700
C	-0.44916400	-2.13033000	-0.90798900
H	-0.26375100	-1.42198500	-1.72147700
H	-1.14835900	-2.89334600	-1.24506200
C	0.82070000	-2.72761500	-0.29523200
H	1.63030300	-2.79855400	-1.02337500
H	0.61180700	-3.72493800	0.09770100

1 imaginary frequency (-647.84)

Zero-point Energies -974.622998

Thermal Energies -974.603565

Thermal Free Energies -974.673664

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C	-4.94279500	0.15978000	-0.24924700
C	-4.41803300	-0.75532900	-1.17752100
C	-3.12337000	-1.20134000	-1.06110600
C	-2.29852900	-0.72753000	0.00809900
C	-2.84395800	0.21528300	0.93840400
C	-4.14506300	0.63793600	0.80164400
H	-5.96818000	0.50003700	-0.34694600
H	-5.03621300	-1.11127200	-1.99441900
H	-2.72611600	-1.89452300	-1.79137800
H	-2.23595500	0.60081900	1.74551800
H	-4.55433200	1.34649700	1.51328900
N	-1.03282400	-1.16417700	0.13311600
C	-0.05288600	-0.64405800	1.08929700
C	1.15104900	-1.63422900	1.04833200
H	-0.49520200	-0.40637500	2.05502600
H	1.50906700	-1.98938400	2.01588300
C	1.93145900	-0.48297800	0.45665300
C	0.89685800	0.37394800	0.46734100
C	0.64354100	1.76915500	0.03377500
O	1.45697500	2.52567900	-0.43301800
O	-0.64551900	2.06433800	0.23535700

C	-1.04408800	3.38945100	-0.14099700
H	-2.11114600	3.44689100	0.06938300
H	-0.49706500	4.12784900	0.44911300
H	-0.85376100	3.55395900	-1.20350400
C	3.36013100	-0.48919000	0.05302100
O	4.02170700	-1.50195500	0.10465900
O	3.79797500	0.69368500	-0.34950000
C	5.17778500	0.74014600	-0.74045000
H	5.36005200	1.76842600	-1.04739700
H	5.81763100	0.47370800	0.10368200
H	5.35826500	0.05350200	-1.57028500
C	-0.38874700	-2.15607300	-0.75684700
H	-0.01569600	-1.62419600	-1.63950000
H	-1.11290200	-2.90471700	-1.07364900
C	0.73529000	-2.75260200	0.09255100
H	1.56131100	-3.10631900	-0.52738900
H	0.34905300	-3.59387200	0.67308400

0 imaginary frequencies

Zero-point Energies -974.666074

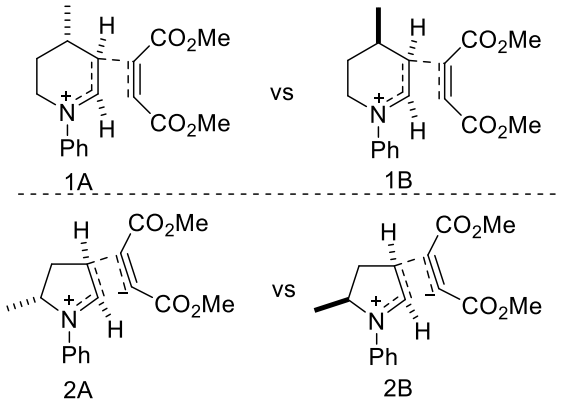
Thermal Energies -974.646943

Thermal Free Energies -974.715289

(2) Calculation of diastereoselectivity.

We have investigated the diastereoselectivity of the reaction with DFT calculation. The geometry of all the species was optimized with the B3LYP method and 6-31G(d) basis set. Frequency analysis was performed under the same level in order to obtain the thermal correction to Gibbs free energy. The solvent effect was taken into consideration by using the M06/6-311++G(d,p) level and SMD solvation model for dichloromethane (ε=8.9).

Cartesian coordinates of calculated structures



	G(Hartree)	$\Delta\Delta G^{\ddagger}$(kcal/mol)	d.r.[a]	Experimental d.r.
1A	-1053.396157	5.2	6538:1	>20:1
1B	-1053.387932			
2A	-1014.130035	0.2	1.4:1	2.7:1
2B	-1014.129758			

A the d.r. was calculated by $\frac{[A]}{[B]} = e^{-\frac{\Delta\Delta G}{RT}}$

All energies are given in Hartree

1A

C	3.04906300	-1.02325700	-1.15245100
C	4.30487000	-0.81751200	-1.72221600
C	5.22029100	0.05315900	-1.12908900
C	4.87210000	0.71558700	0.04950200
C	3.62496500	0.50800500	0.63556300
C	2.70168300	-0.35713500	0.03104400
N	1.42064000	-0.57087800	0.61427300
C	0.71864700	0.43673500	1.16904300
C	-0.59945600	0.31905000	1.61275000
C	-0.08328000	-2.13563500	1.76555800
C	0.79671500	-1.90621800	0.53354400
C	-2.05867800	0.22267100	-0.86898200
C	-1.51963900	1.03324800	-0.06194900
C	-1.33295000	2.49175200	0.01963400
O	-0.59147800	3.07474300	0.79351900
O	-2.10083400	3.13581700	-0.88336700
C	-1.97162500	4.56568500	-0.88094000
C	-2.25072500	-1.09007400	-1.36406600
O	-1.39840000	-1.74339900	-1.96654500

O	-3.51497400	-1.55612200	-1.14049300
C	-3.77280700	-2.86736000	-1.65469800
H	2.32972400	-1.67211000	-1.64104000
H	4.56015100	-1.33275700	-2.64404600
H	6.19611100	0.21201200	-1.57867300
H	5.57987100	1.38626300	0.52882300
H	3.37718300	0.99578400	1.57321500
H	1.18573700	1.41386700	1.14948900
H	-0.92290800	1.14123400	2.24396600
H	-0.53537600	-3.13148800	1.69425800
H	0.55539600	-2.13411700	2.65977700
H	1.60347500	-2.64277700	0.49315900
H	0.20767400	-1.98268000	-0.39148700
H	-2.25324500	4.97810300	0.09196700
H	-0.94360100	4.86214800	-1.10712300
H	-2.65151000	4.91689500	-1.65779600
H	-3.63677900	-2.89579300	-2.73968400
H	-3.10813900	-3.60847000	-1.19967300
H	-4.81105300	-3.08161200	-1.39627500
C	-1.17585900	-1.05963700	1.90630800
H	-1.95581000	-1.27321700	1.16385400
C	-1.83383000	-1.10468500	3.29306600
H	-2.63934200	-0.36541400	3.36769400
H	-2.26772900	-2.09232400	3.48941300
H	-1.10572800	-0.89199700	4.08563800

1 imaginary frequency(-255.59)
Correction to Gibbs free energies 0.308084
Gibbs free energy -1053.396157

1B

C	2.74354900	0.66472500	1.05701400

C	3.90629800	0.44824200	1.79644500
C	4.90352500	-0.40518700	1.31865300
C	4.73693400	-1.04765600	0.09052700
C	3.58528700	-0.82817600	-0.66549400
C	2.59004400	0.02589700	-0.17935300
N	1.40287400	0.25092500	-0.94640500
C	0.59416500	-0.76625500	-1.28786300
C	-0.69257500	-0.59442000	-1.80354800
C	-1.04301000	0.70260700	-2.53729500
C	0.14304000	1.70020500	-2.48526900
C	0.95499900	1.63455200	-1.18662200
C	-1.74124200	0.12336000	0.85727500
C	-1.55602800	-0.83065500	0.04571600
C	-1.72757800	-2.29570200	0.12747400
O	-1.16934700	-3.12280500	-0.57409900
O	-2.59195500	-2.63180400	1.10670500
C	-2.78886400	-4.04273200	1.28541100
C	-1.56332200	1.43379100	1.34185200
O	-0.51500700	1.88887400	1.80778300
O	-2.70932300	2.17747200	1.27166800
C	-2.59807700	3.50999000	1.78561000
H	1.93793700	1.27962400	1.44847400
H	4.02305700	0.93674600	2.75990400
H	5.80458800	-0.57159100	1.90233000
H	5.50909800	-1.71124900	-0.28885600
H	3.45987700	-1.30241300	-1.63475100
H	0.93891800	-1.75948800	-1.02123400
H	-1.12205300	-1.50128200	-2.21514700
H	-1.14060200	0.40260700	-3.59072600
H	-0.21412900	2.72735600	-2.62202500
H	0.82759100	1.48887800	-3.31613800
H	1.85075400	2.25743100	-1.26589700
H	0.38354200	1.98704700	-0.32042800
H	-3.18241200	-4.49758900	0.37212900
H	-1.84840700	-4.53453800	1.54913500
H	-3.50894900	-4.13146200	2.09949300
H	-2.32940000	3.49699200	2.84575700
H	-1.84307100	4.08417000	1.24003600
H	-3.58449900	3.95594000	1.64914200
C	-2.39192800	1.33998000	-2.16359300
H	-2.64091600	2.12111500	-2.89235200
H	-3.19376500	0.59411600	-2.18209500
H	-2.39352000	1.79182200	-1.17001600

1 imaginary frequency(-256.85)

Correction to Gibbs free energies	0.308464
Gibbs free energy	-1053.387932

2A

C	-4.87279300	-0.08855400	-1.36765300
C	-4.61685500	0.91824700	-0.43458700
C	-3.43103700	0.91863200	0.29679400
C	-2.47405800	-0.08509600	0.08389400
C	-2.72797300	-1.09603000	-0.85470600
C	-3.92484500	-1.09324500	-1.56941900
H	-5.80221900	-0.09104900	-1.92946300
H	-5.35021000	1.70095700	-0.26065100
H	-3.25346100	1.68220900	1.04849000
H	-1.97965100	-1.85702300	-1.04997900
H	-4.10774600	-1.87682200	-2.29946900
N	-1.26054200	-0.07344700	0.81308200
C	-0.51901300	1.02806500	1.05951400
C	0.74470300	0.74038900	1.55834500
H	-0.89182500	2.00096100	0.76802700
H	1.29848400	1.47435600	2.12936500
C	2.29535800	-0.21466600	-0.65223300
C	1.89709600	0.87332300	-0.15433200
C	2.09060500	2.29470800	-0.49241900
O	2.81202900	2.69012300	-1.38267000
O	1.37895200	3.14325900	0.30085200
C	1.55741700	4.53473000	-0.00515700
H	0.94237600	5.07428400	0.71645100
H	2.60799600	4.81918600	0.09602400
H	1.23163000	4.74968200	-1.02643500
C	2.29435200	-1.62052400	-0.81195300
O	1.38631200	-2.26656300	-1.33467300
O	3.43840400	-2.19966200	-0.34239600
C	3.50928800	-3.61965800	-0.51575200
H	4.47415700	-3.91459500	-0.10044700
H	2.69678500	-4.12427500	0.01648000
H	3.45251200	-3.88698800	-1.57484600
C	0.72305300	-0.72737900	1.94738700
H	1.64182900	-1.25119400	1.66743300
H	0.59908600	-0.83374200	3.03357800
C	-0.51241700	-1.30731400	1.20402800
H	-0.18628900	-1.81151000	0.28617500
C	-1.36166400	-2.25281200	2.05038900
H	-1.70170700	-1.75779300	2.96704200

H	-2.23992200	-2.61236300	1.50575800
H	-0.76090800	-3.12431400	2.33313900

1 imaginary frequency(-280.06)

Correction to Gibbs free energies 0.278314

Gibbs free energy -1014.130035

2B

C	-5.18219000	-0.23400000	-1.16569000
C	-4.92650900	-1.12730700	-0.12370500
C	-3.69591800	-1.12243300	0.52970300
C	-2.69618000	-0.21815300	0.13737300
C	-2.94626700	0.66616000	-0.92415400
C	-4.18576500	0.66112100	-1.55974000
H	-6.14313400	-0.24219700	-1.67138000
H	-5.69199400	-1.83106100	0.19130600
H	-3.51831000	-1.80759300	1.35198600
H	-2.16029600	1.33048600	-1.26927300
H	-4.36361500	1.34835500	-2.38219600
N	-1.45777500	-0.18487300	0.81604700
C	-0.71379000	0.92213900	1.00804100
C	0.54764500	0.66943600	1.54255100
H	-1.10326700	1.88743000	0.71354400
H	1.01494700	1.41812100	2.17051000
C	2.37673600	-0.11042100	-0.44837300
C	1.81228200	0.91589600	0.01740300
C	1.94765100	2.35640400	-0.28060400
O	2.73309800	2.82172700	-1.07734800
O	1.09352000	3.14033200	0.43941900
C	1.21619600	4.54762400	0.18341000
H	0.48704300	5.02915300	0.83663700
H	2.22701600	4.89377900	0.41418200
H	1.00023300	4.76945600	-0.86522800
C	2.72889300	-1.42709700	-0.80980200
O	2.16679900	-2.09247400	-1.67598700
O	3.80551800	-1.88635600	-0.10038600
C	4.24536100	-3.19836000	-0.46906100
H	5.10113800	-3.40890900	0.17452700
H	3.45605300	-3.93909800	-0.30740800
H	4.54345500	-3.23025500	-1.52105600
C	0.55170100	-0.79682100	1.95341000
H	1.40966700	-1.32424700	1.51922000
H	0.61670500	-0.90231800	3.04107400
C	-0.78876900	-1.38322300	1.41451500

H	-1.41508100	-1.72635400	2.24785600
C	-0.61618400	-2.51876900	0.40627800
H	-1.57795400	-2.85818400	0.00973400
H	0.02361800	-2.22157100	-0.42982200
H	-0.14262800	-3.36989000	0.90854500

1 imaginary frequency(-280.16)

Correction to Gibbs free energies 0.278561

Gibbs free energy -1014.129758

14. References

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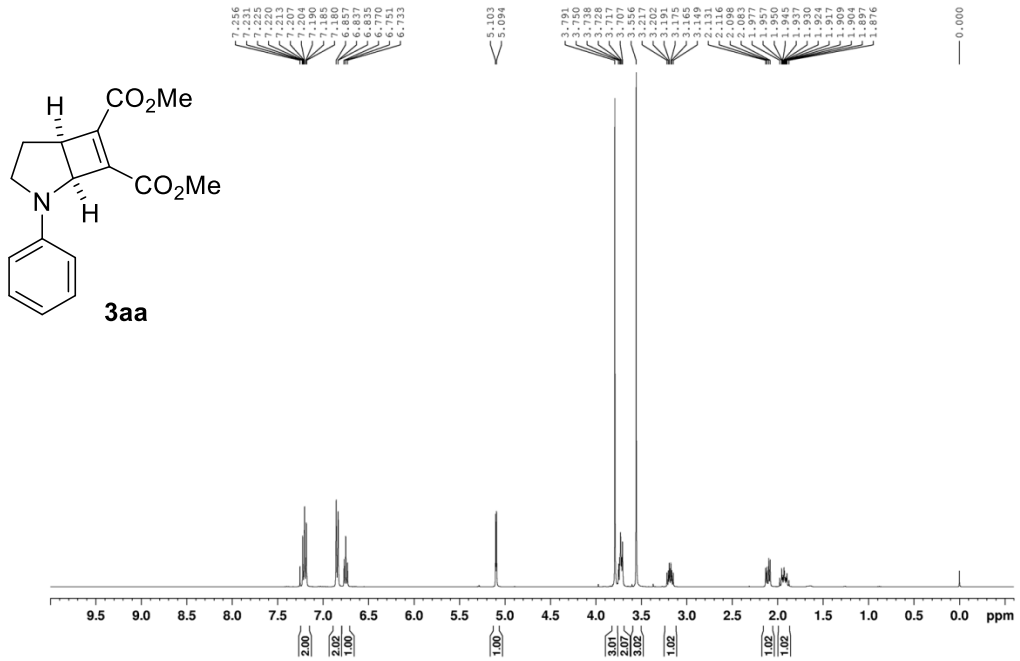
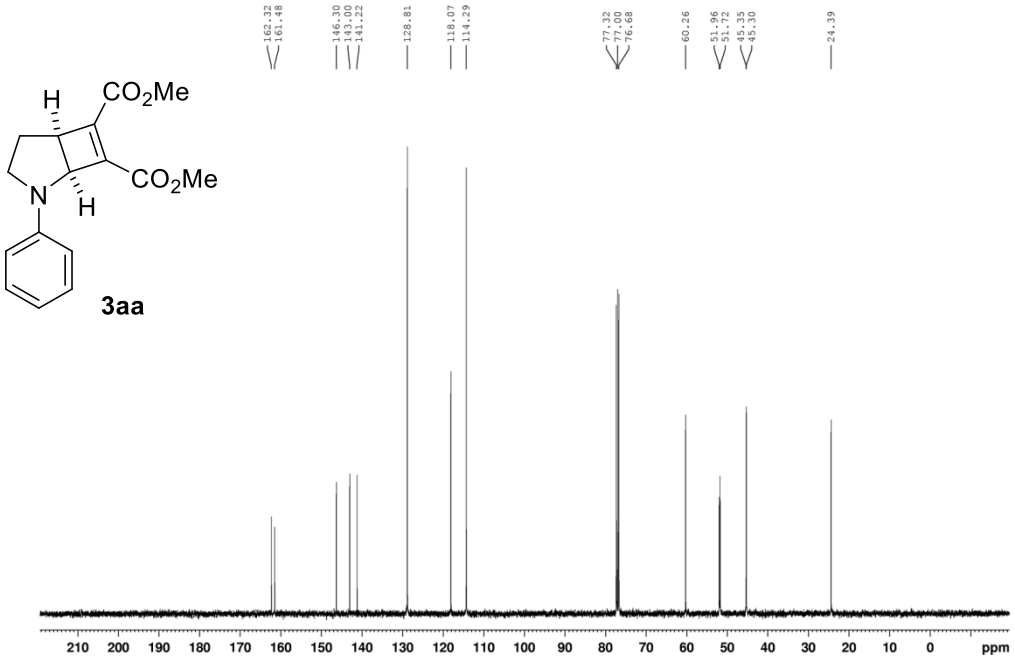
15. NMR Spectra

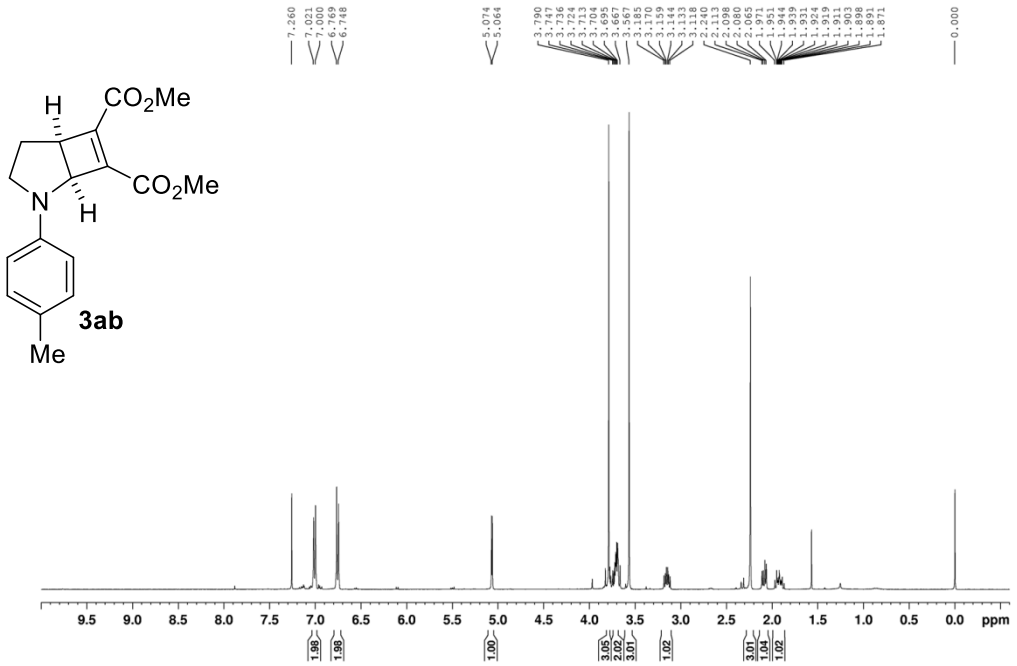
^{1}H NMR of **3aa** in $CDCl_3$



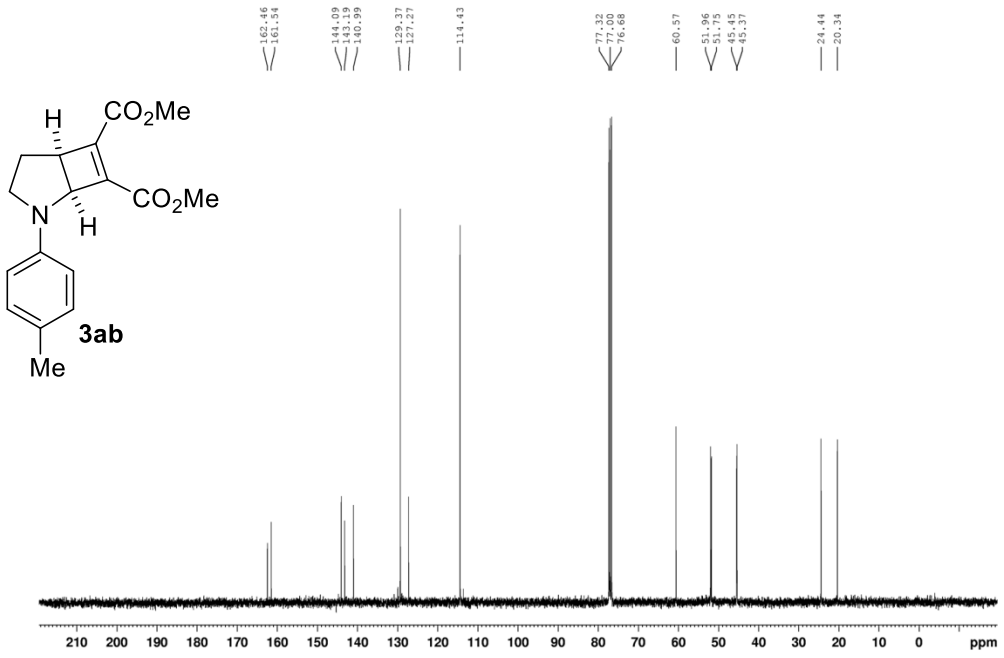
^{13}C NMR of **3aa** in $CDCl_3$



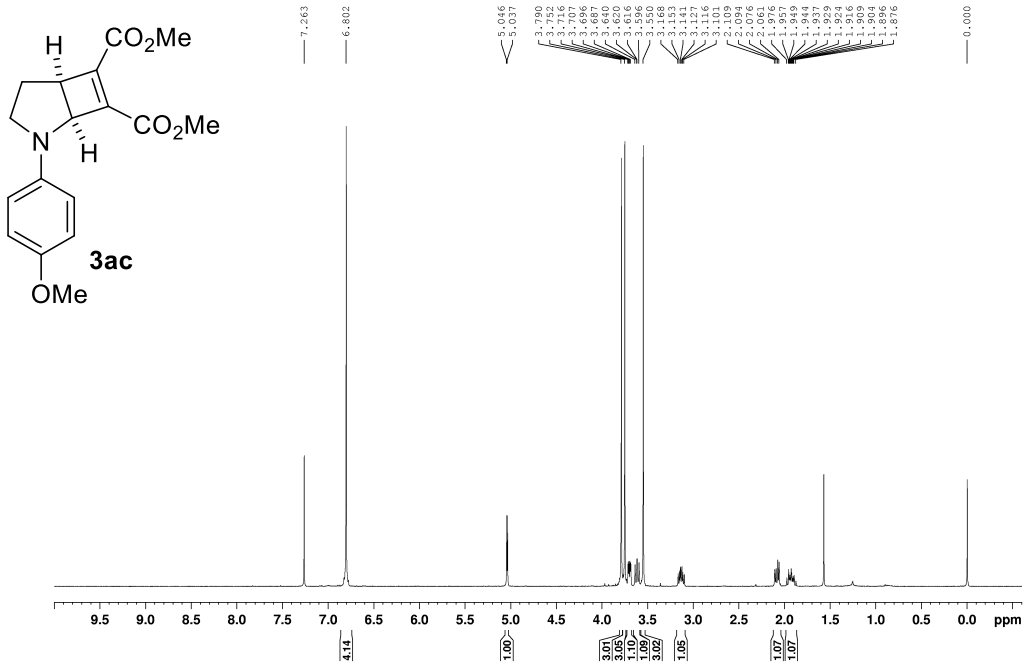
^{1}H NMR of **3ab** in $CDCl_3$



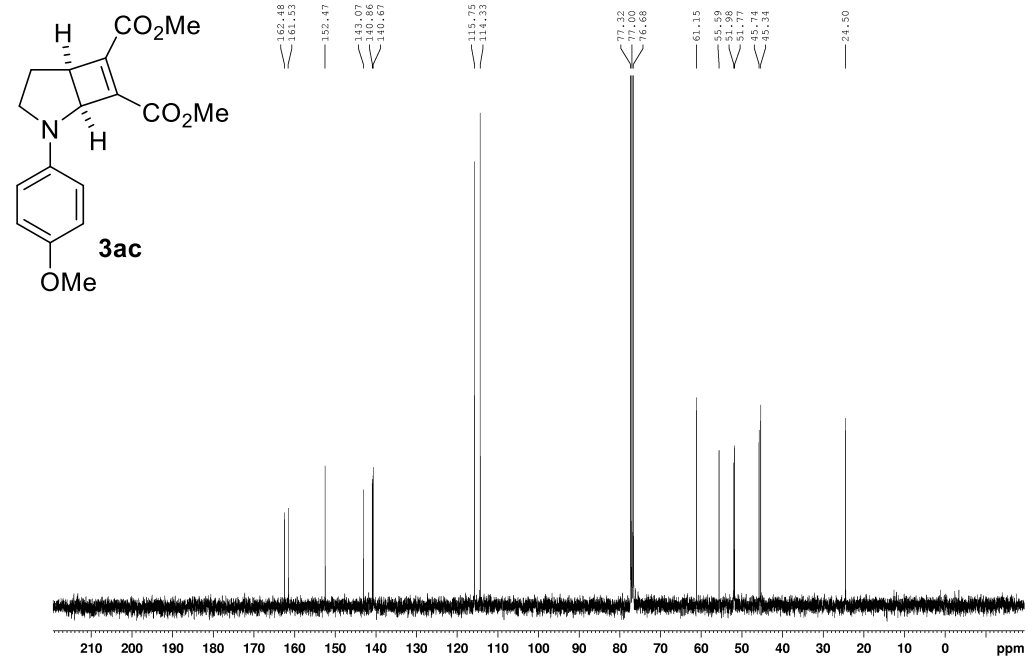
^{13}C NMR of **3ab** in $CDCl_3$



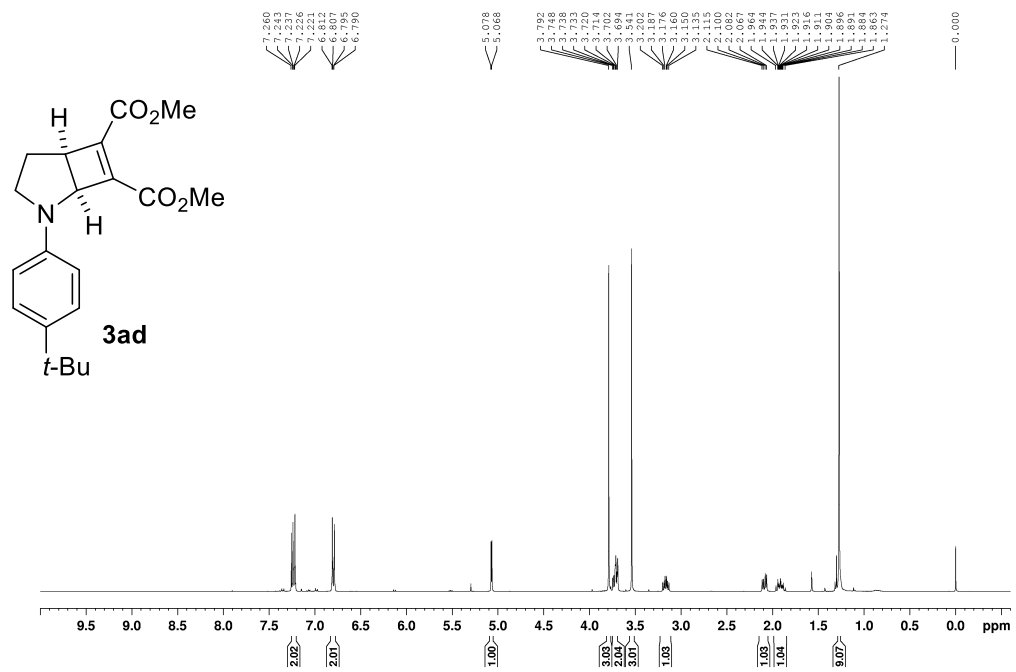
^{1}H NMR of **3ac** in $CDCl_3$



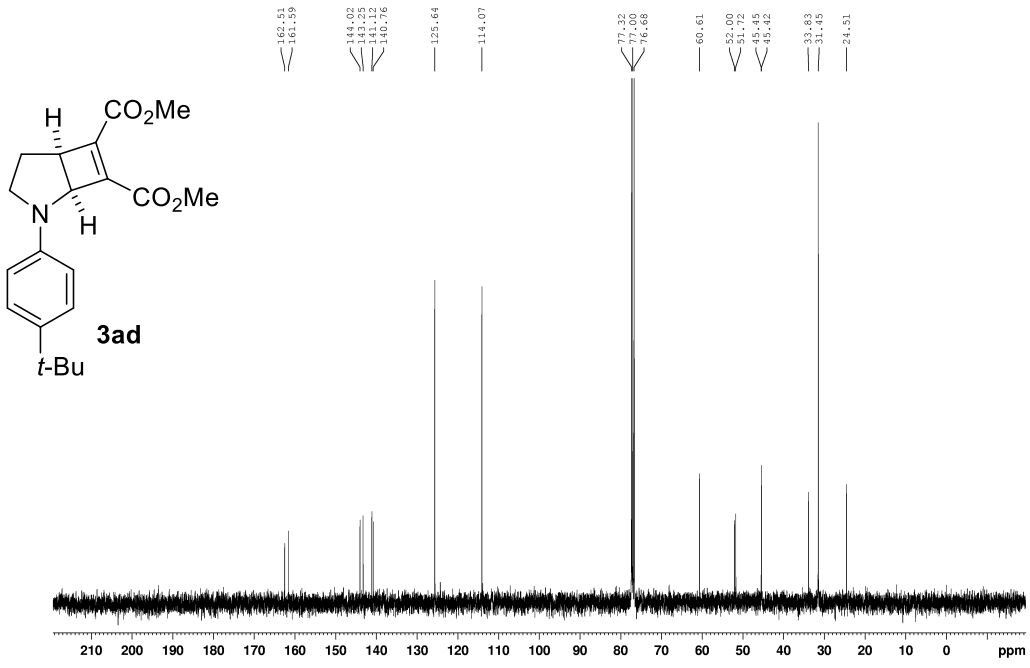
^{13}C NMR of **3ac** in $CDCl_3$



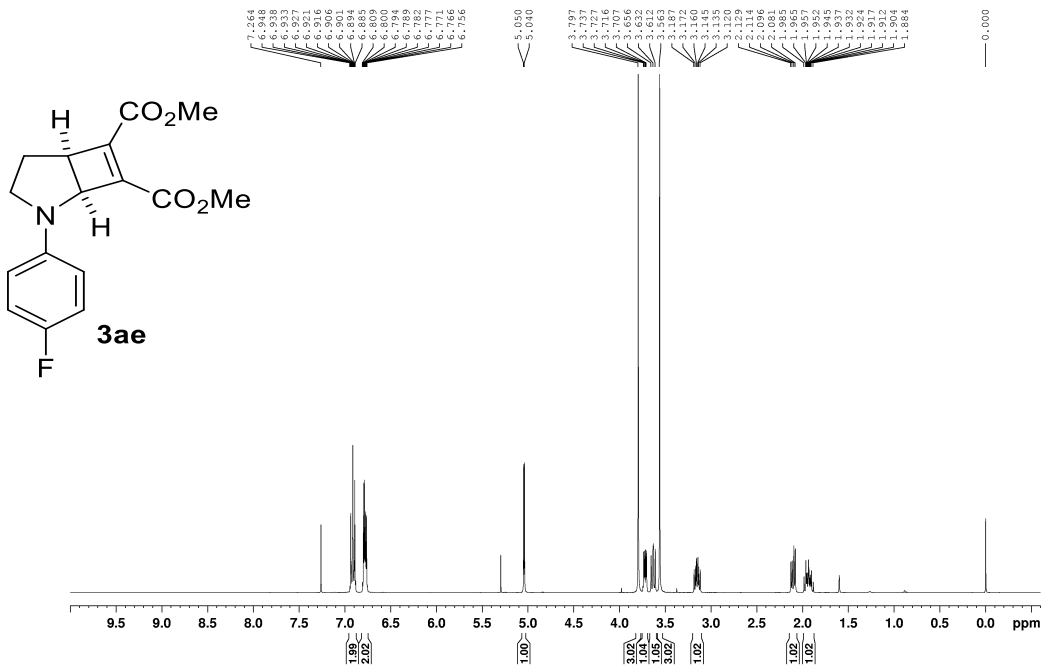
^{1}H NMR of **3ad** in $CDCl_3$



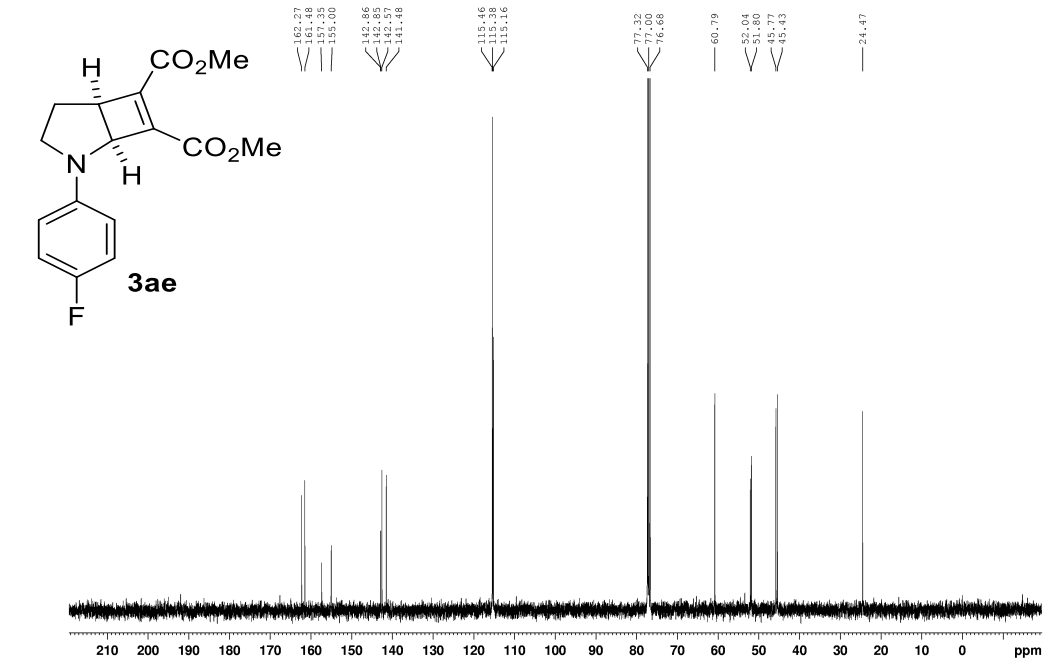
^{13}C NMR of **3ad** in $CDCl_3$



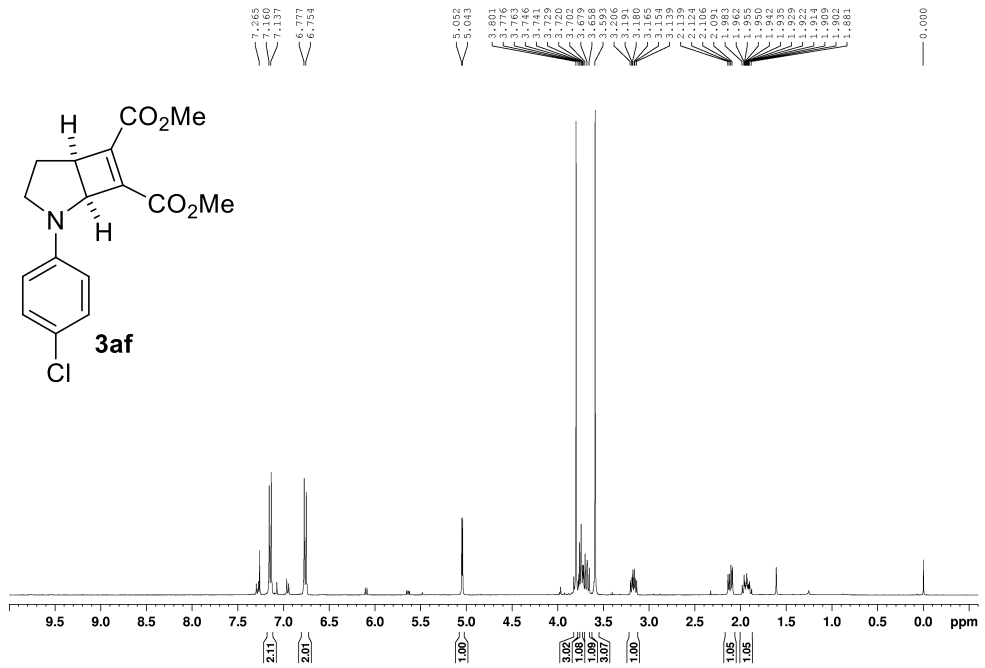
^{1}H NMR of **3ae** in $CDCl_3$



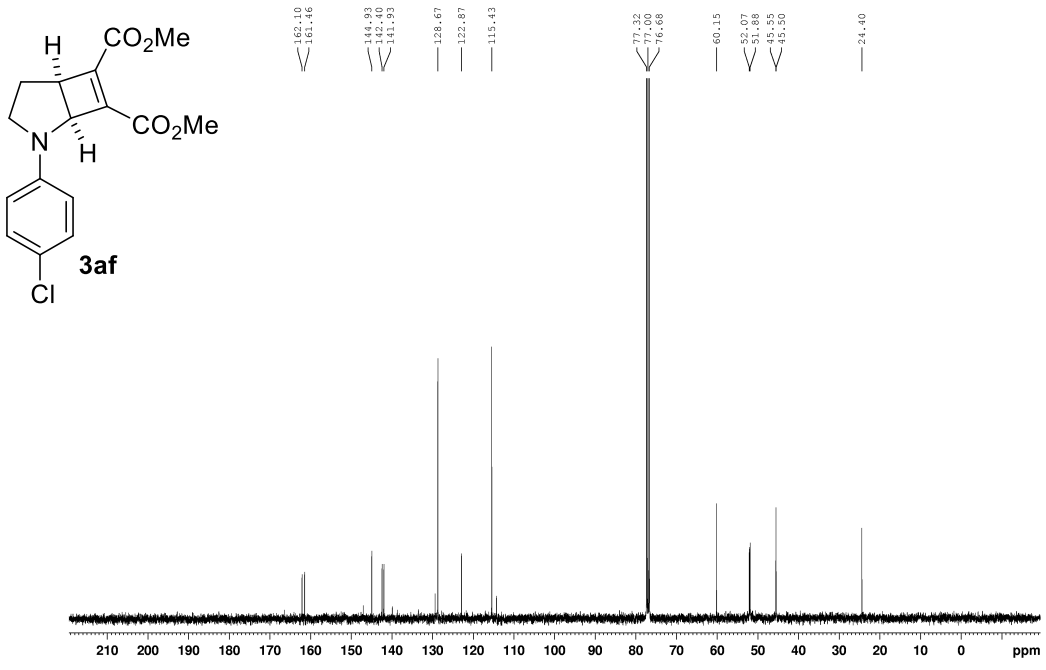
^{13}C NMR of **3ae** in $CDCl_3$



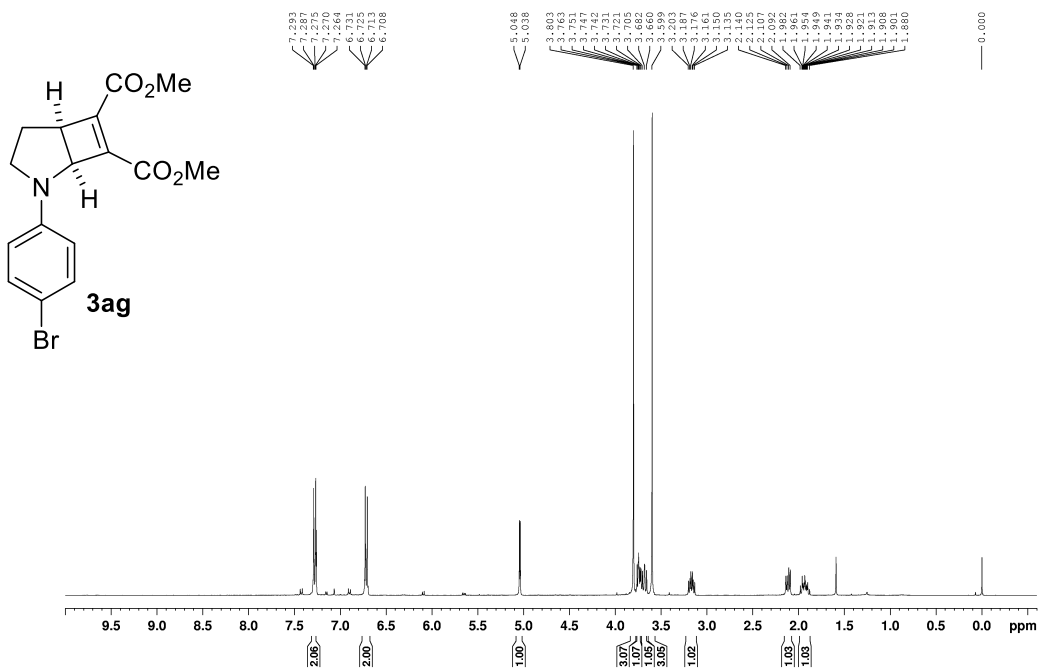
^{1}H NMR of **3af** in $CDCl_3$



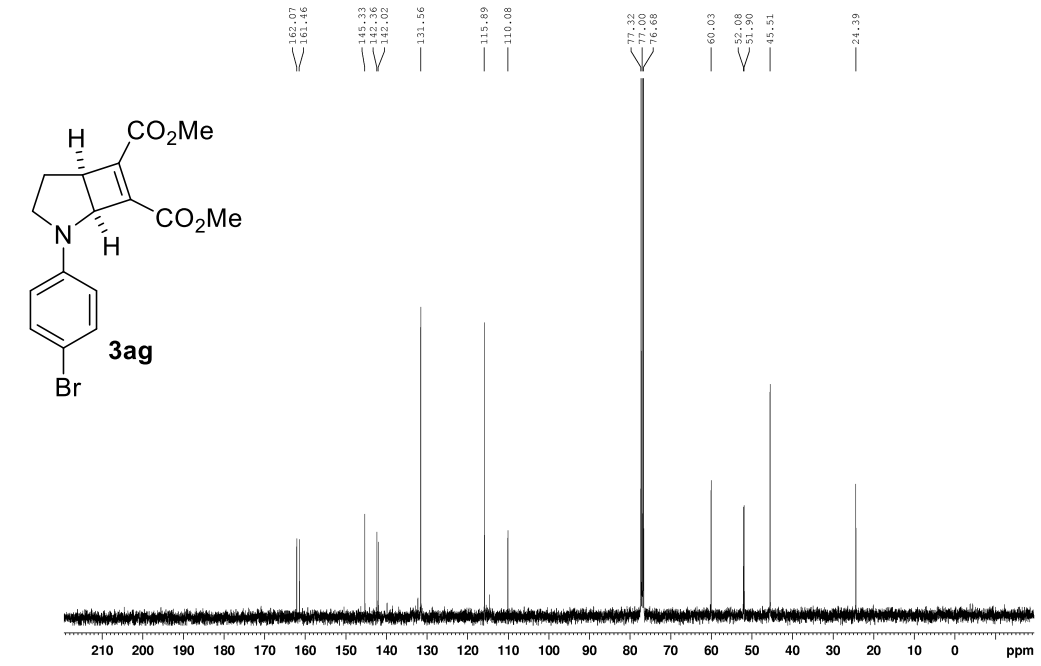
^{13}C NMR of **3af** in $CDCl_3$



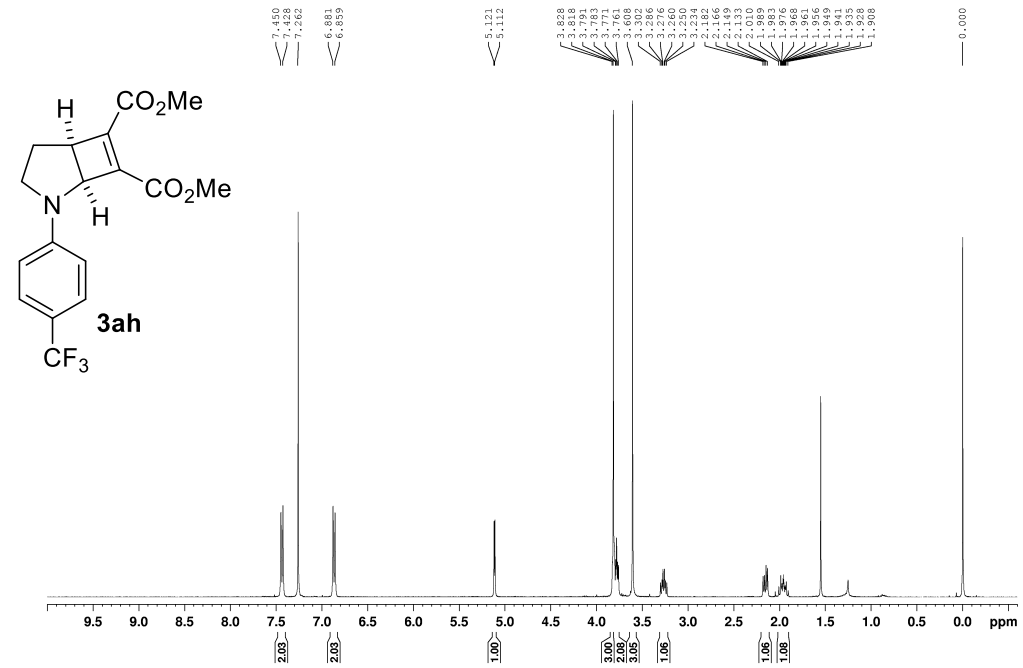
^{1}H NMR of **3ag** in $CDCl_3$



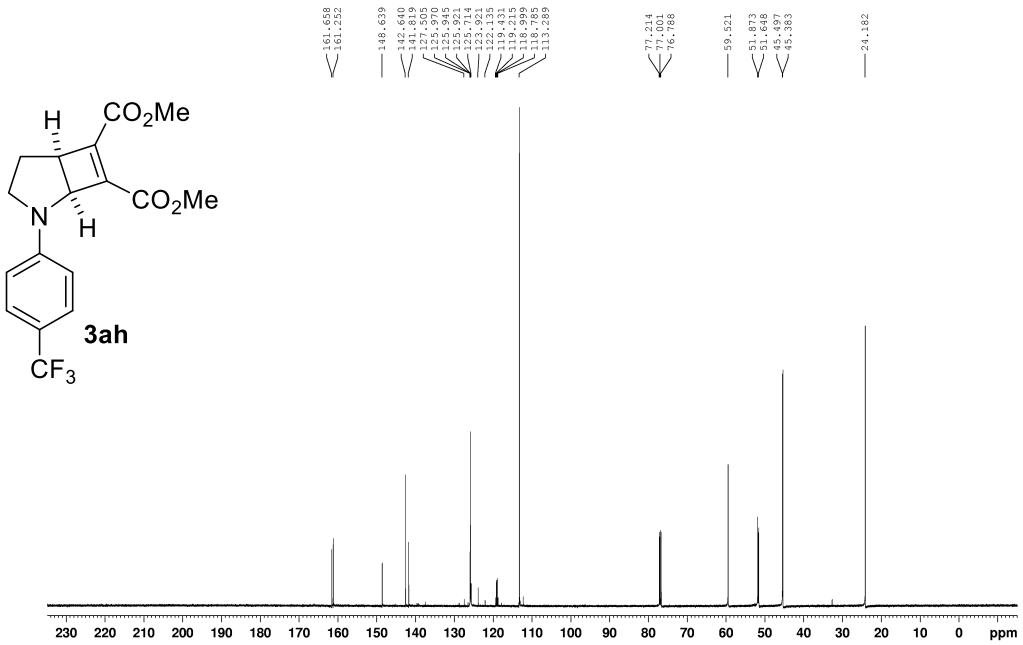
^{13}C NMR of **3ag** in $CDCl_3$



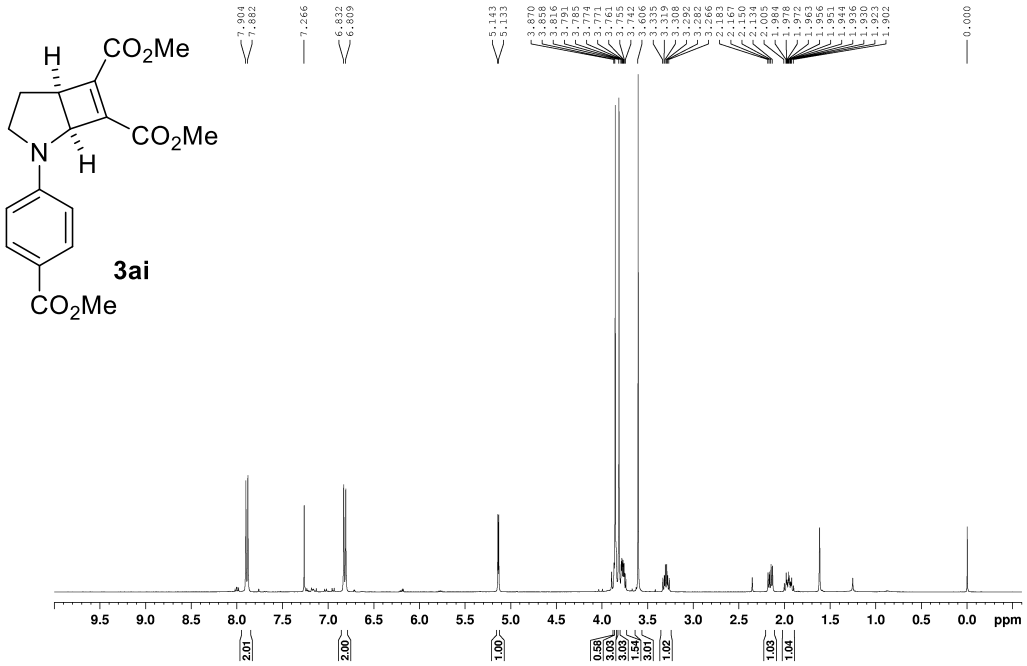
^{1}H NMR of **3ah** in $CDCl_3$



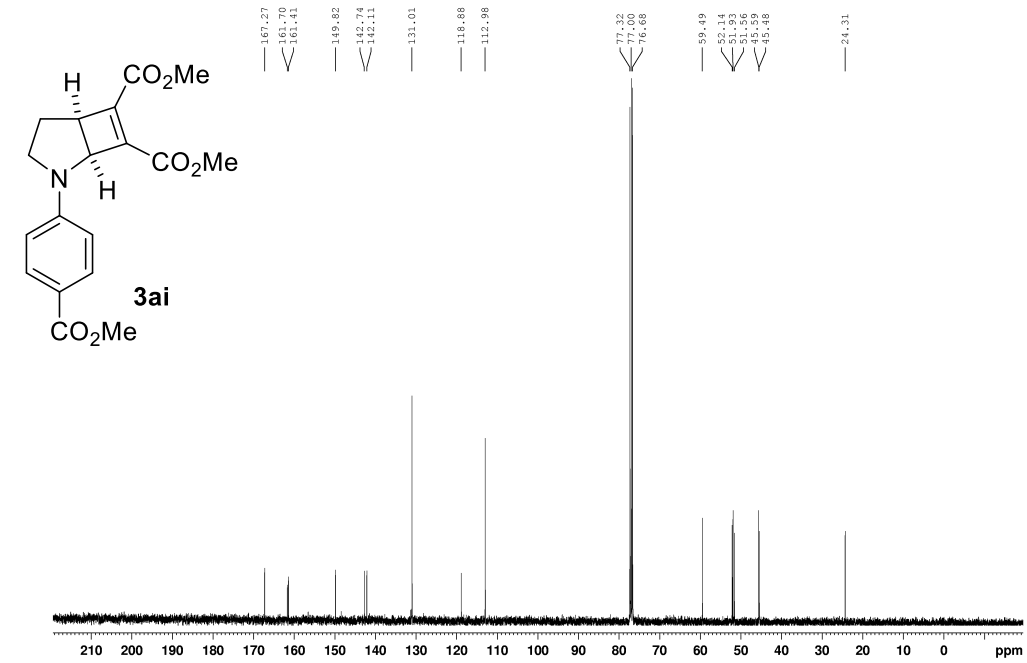
^{13}C NMR of **3ah** in $CDCl_3$



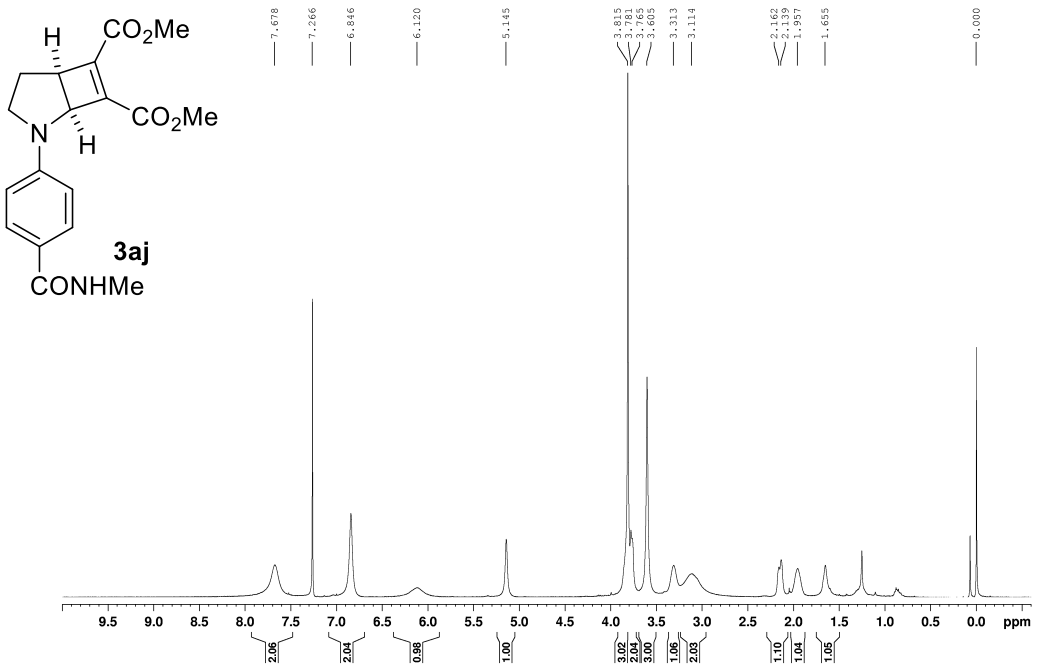
^{1}H NMR of **3ai** in $CDCl_3$



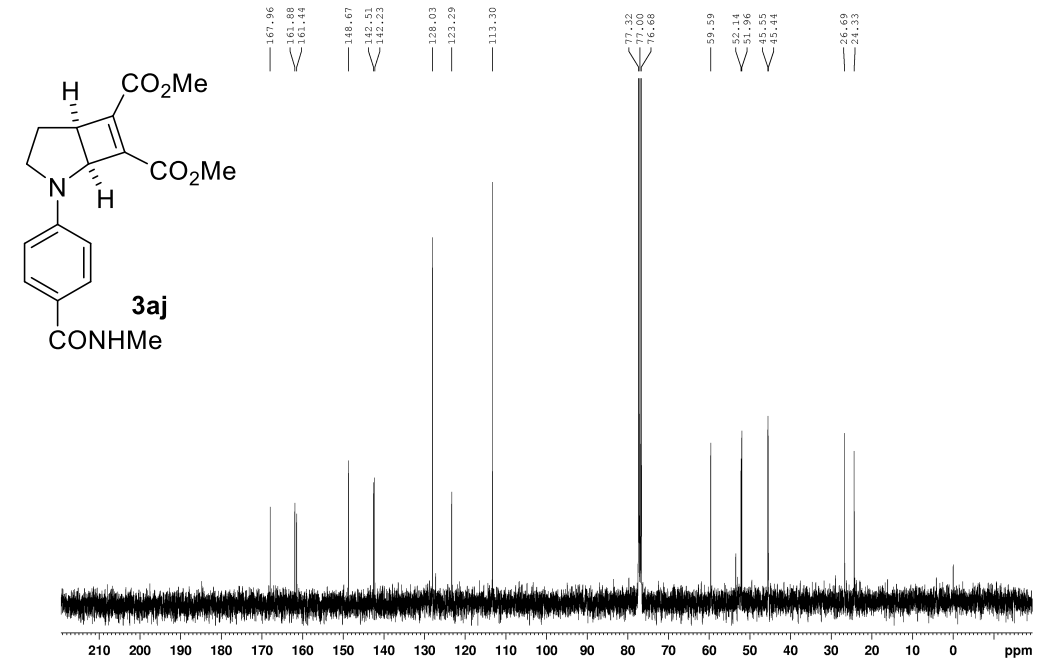
^{13}C NMR of **3ai** in $CDCl_3$



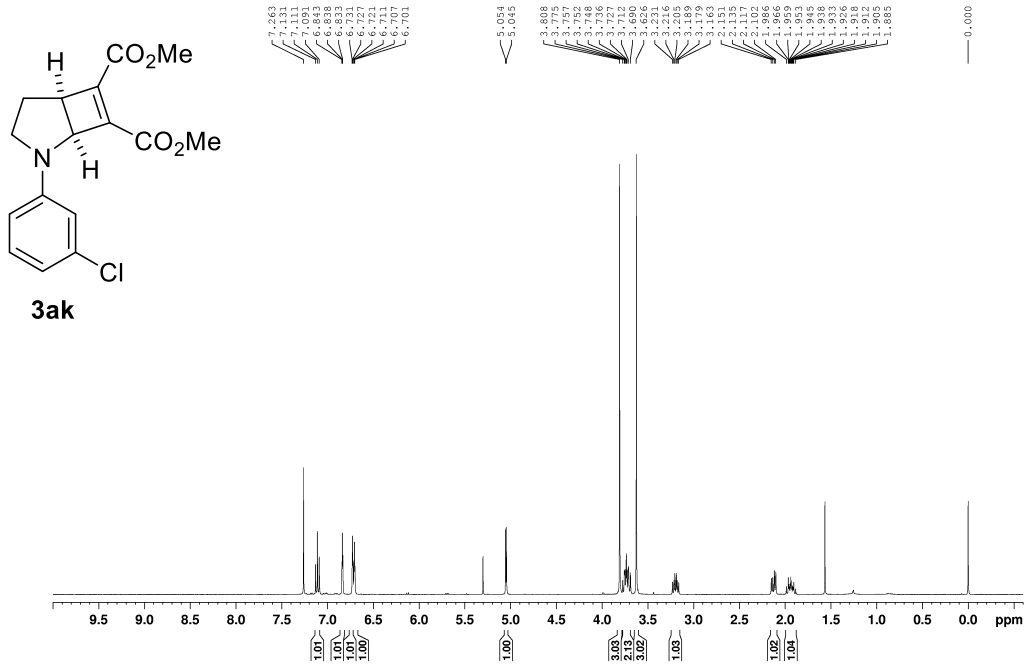
^{1}H NMR of **3aj** in $CDCl_3$



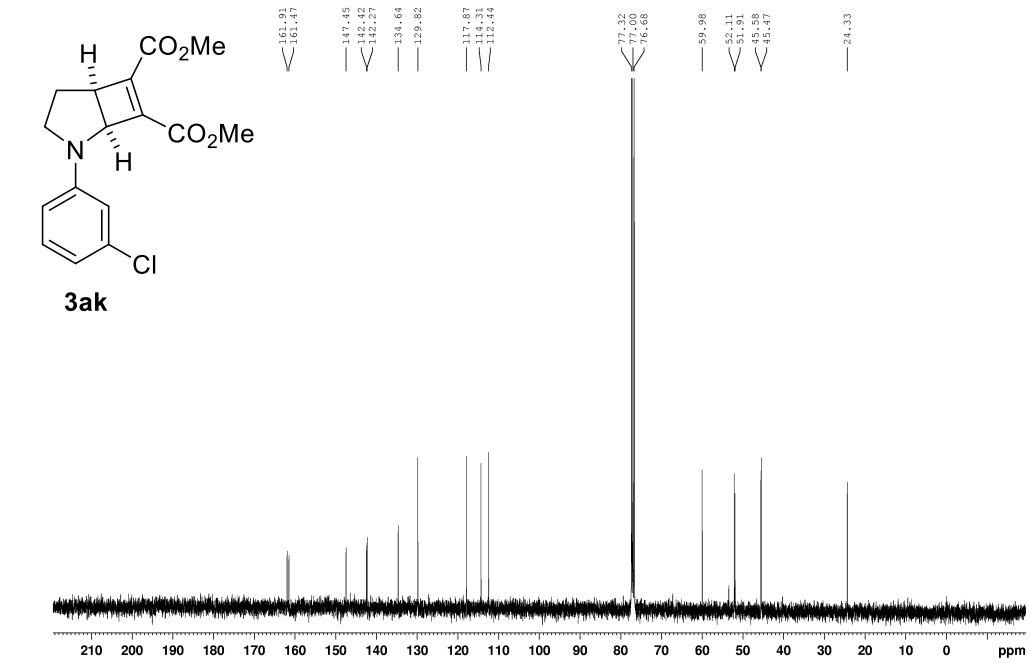
^{13}C NMR of **3aj** in $CDCl_3$



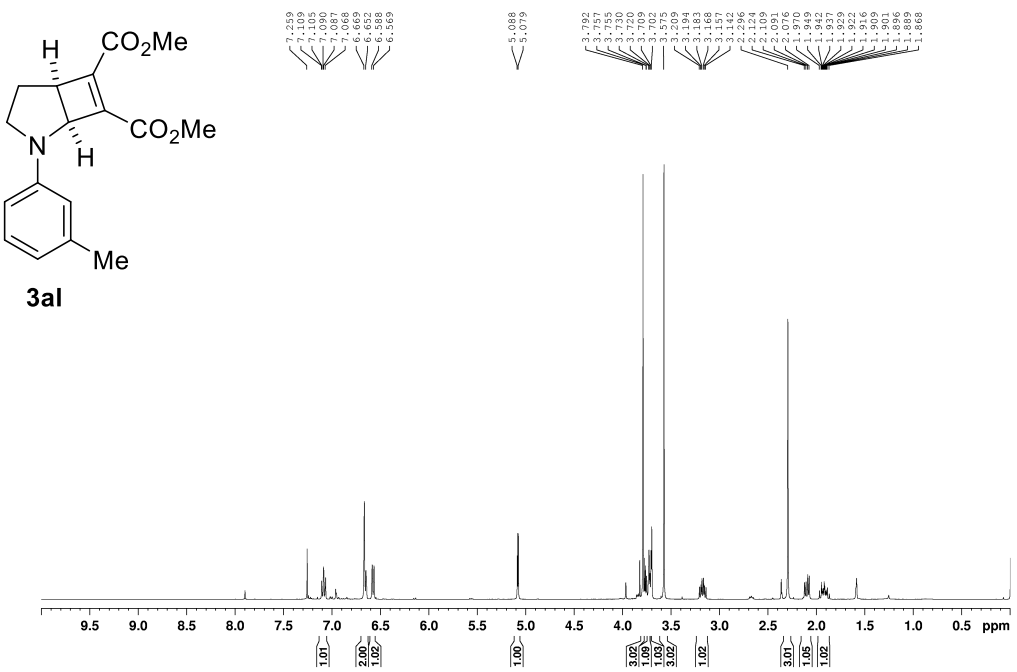
^{1}H NMR of **3ak** in $CDCl_3$



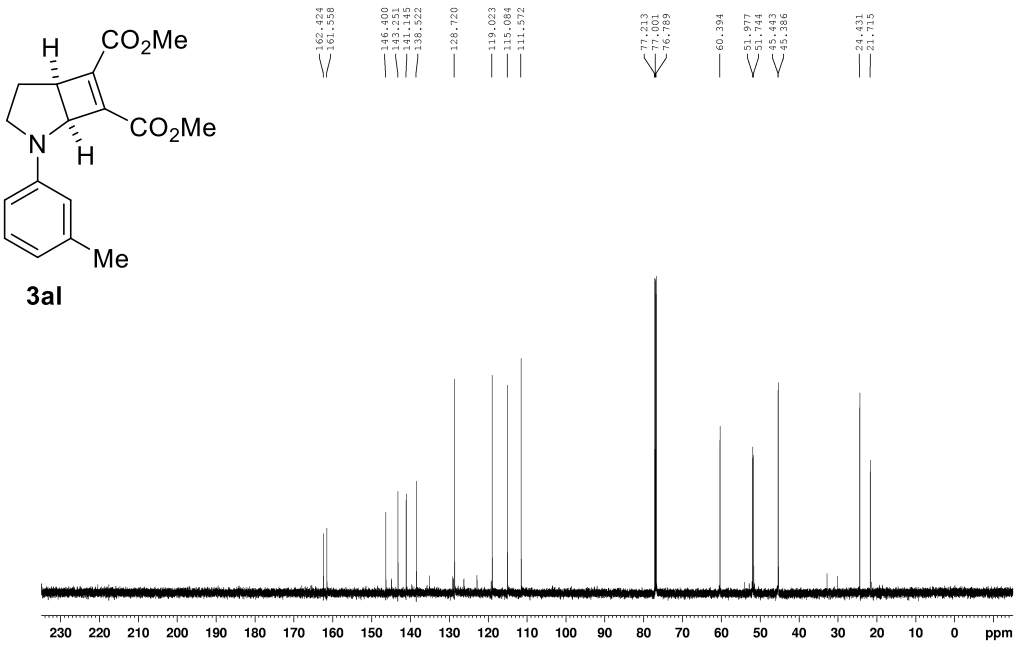
^{13}C NMR of **3ak** in $CDCl_3$



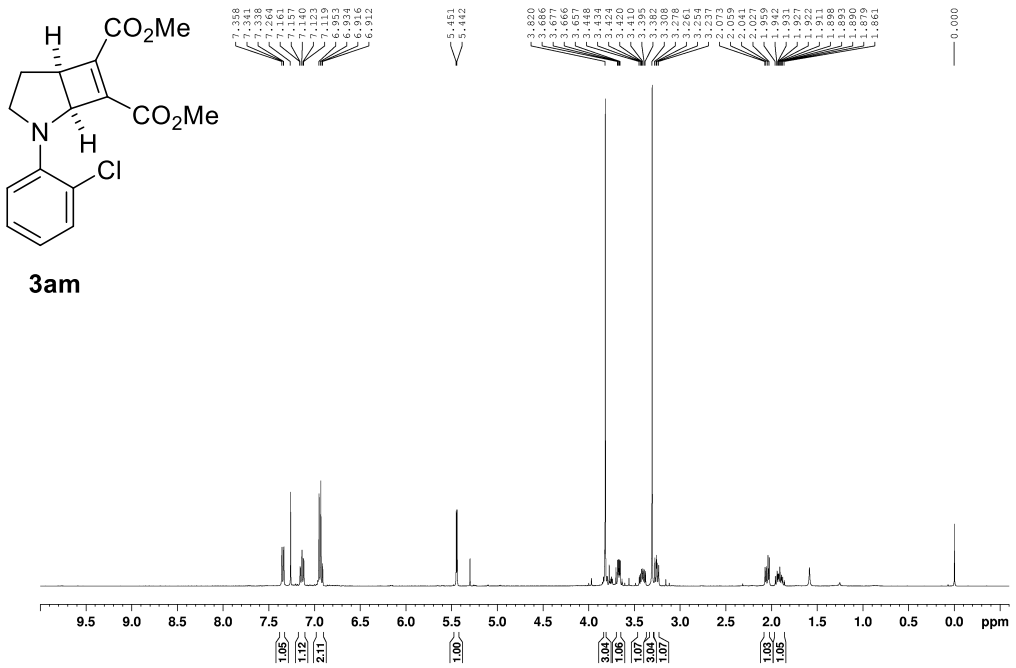
^{1}H NMR of **3al** in $CDCl_3$



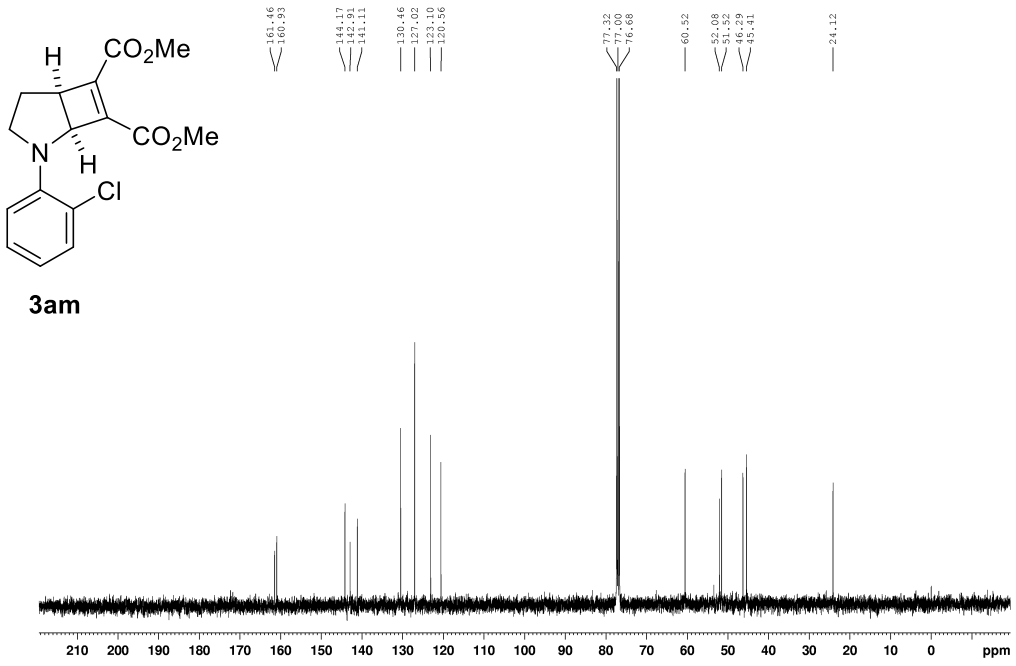
^{13}C NMR of **3al** in $CDCl_3$



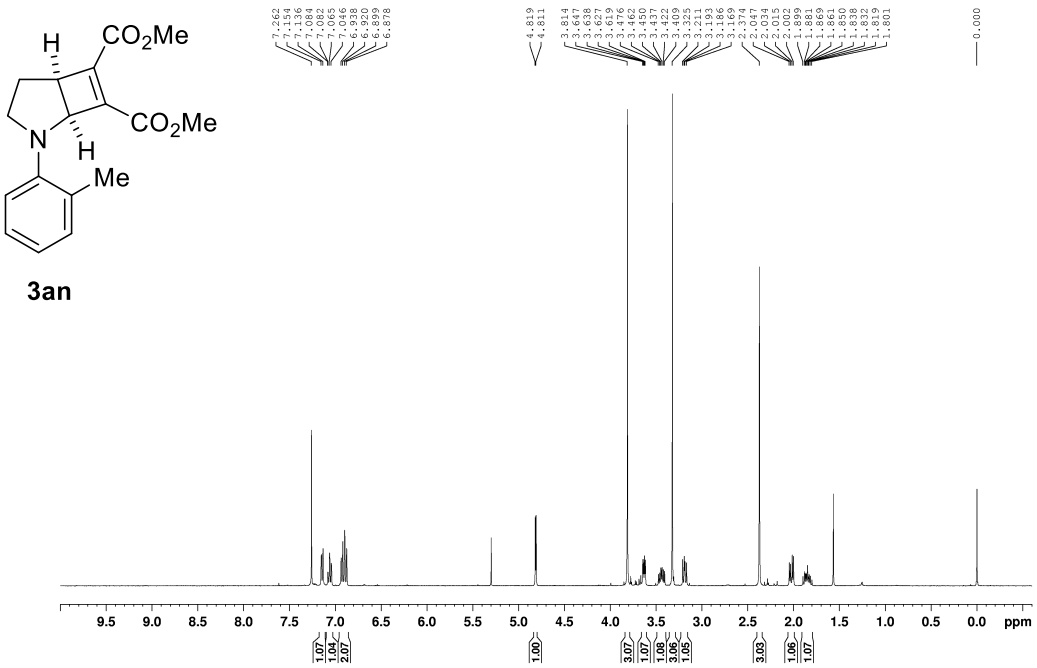
^{1}H NMR of **3am** in $CDCl_3$



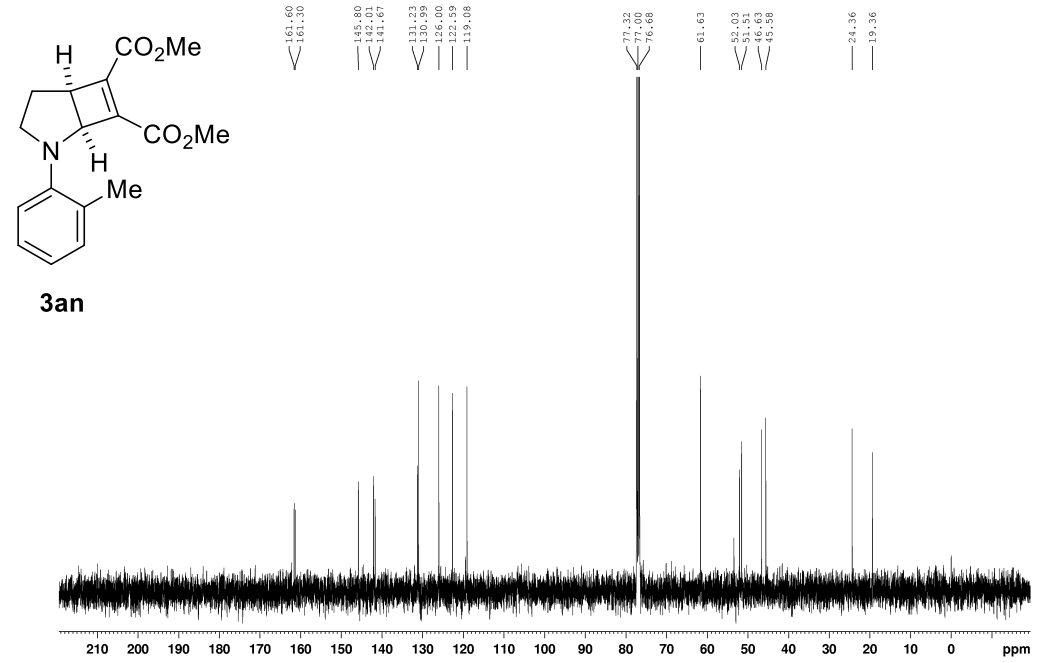
^{13}C NMR of **3am** in $CDCl_3$



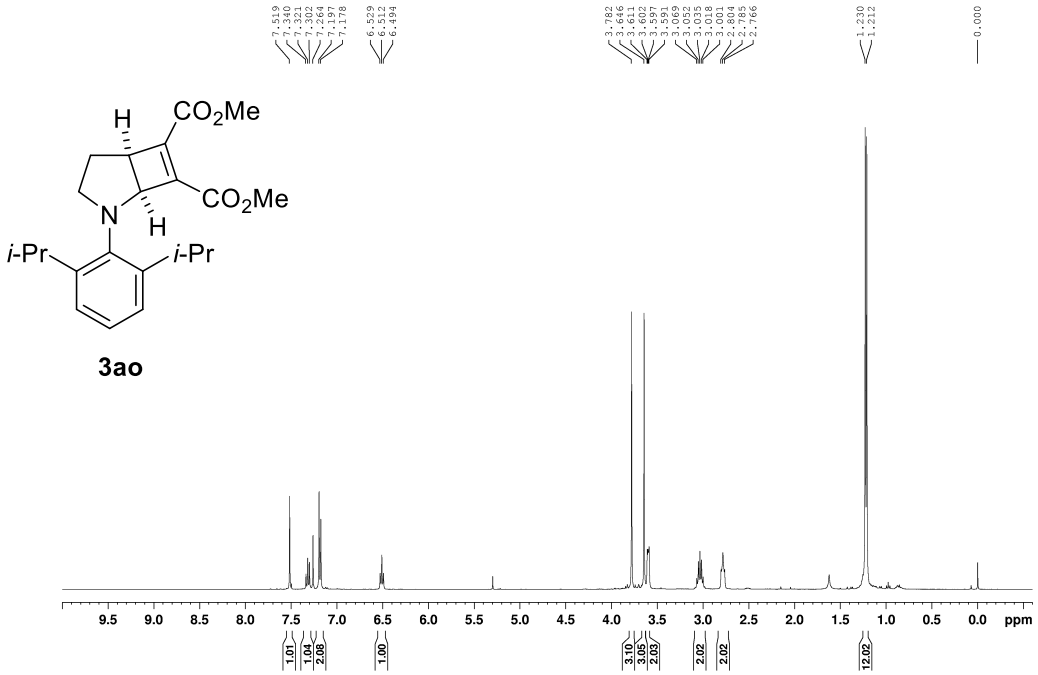
^{1}H NMR of **3an** in $CDCl_3$



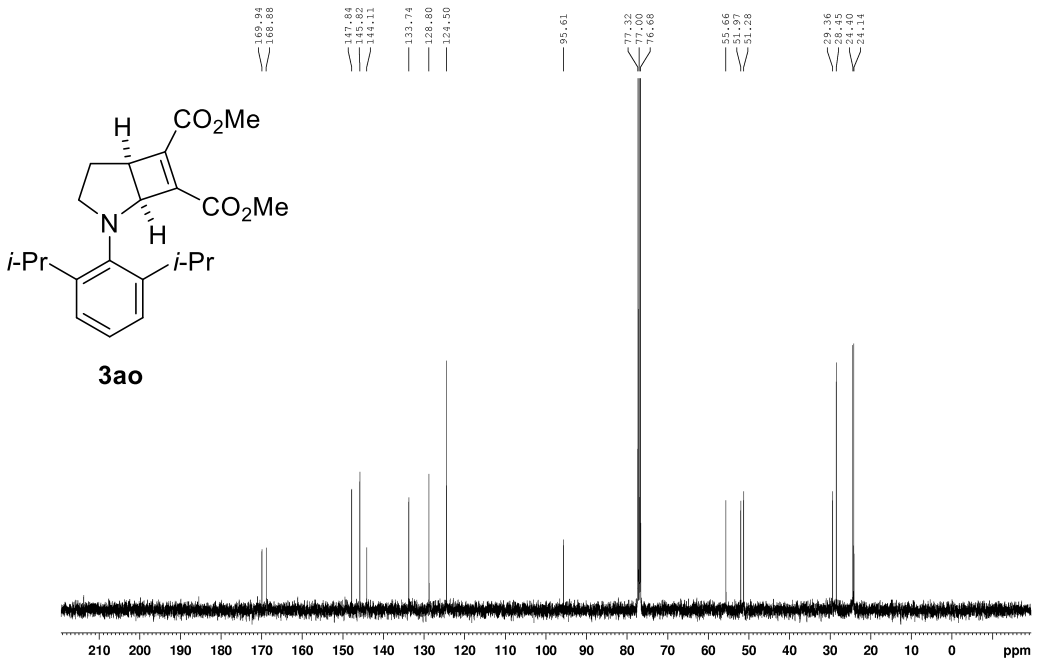
^{13}C NMR of **3an** in $CDCl_3$



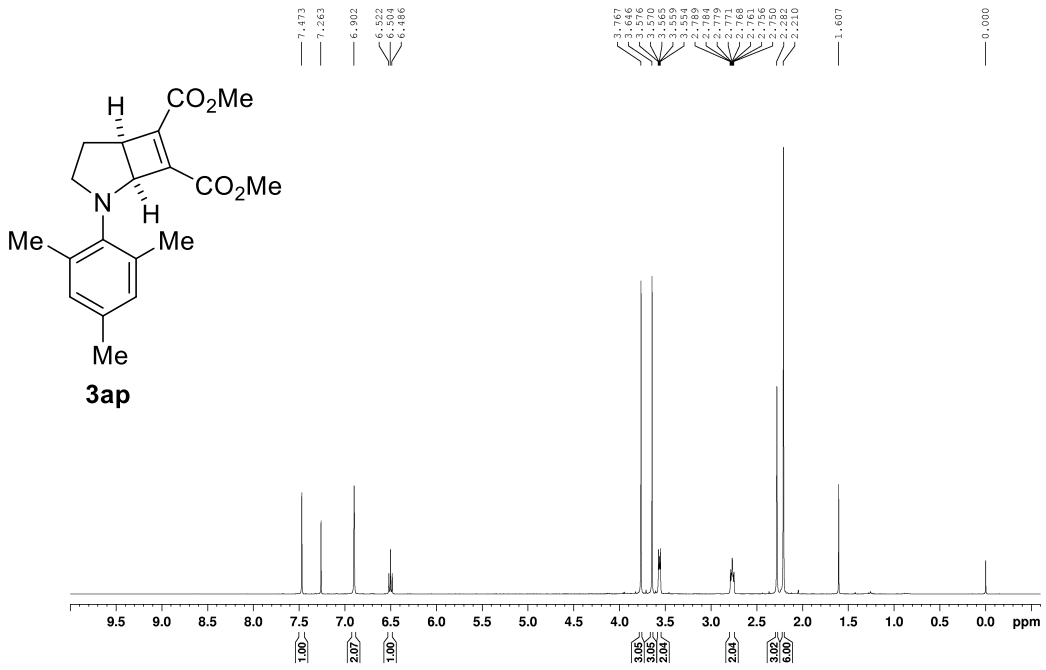
^{1}H NMR of **3ao** in $CDCl_3$



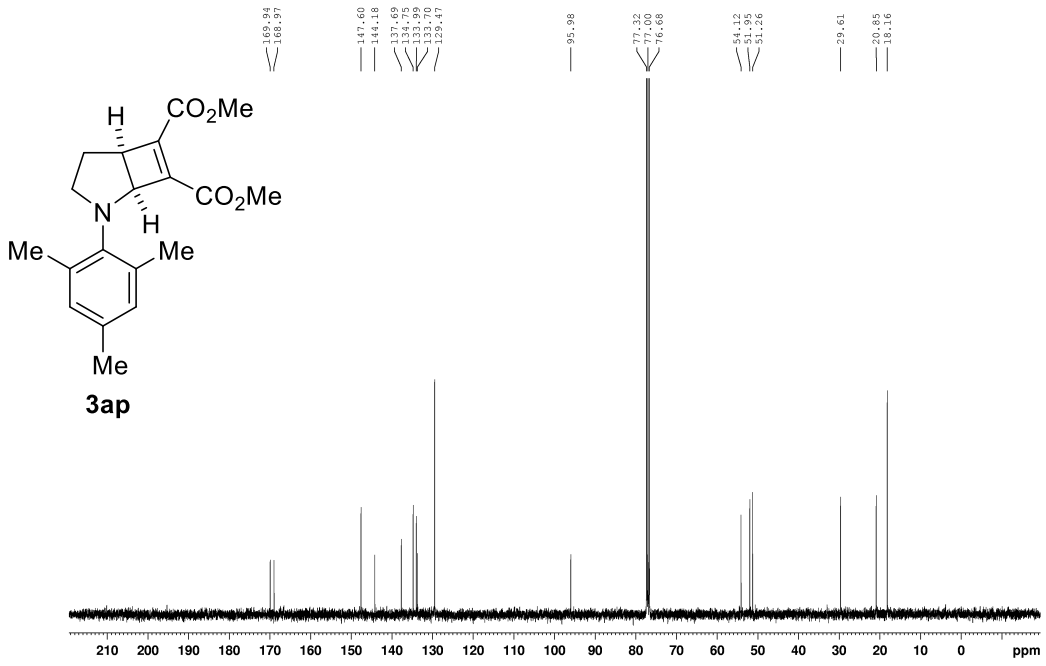
^{13}C NMR of **3ao** in $CDCl_3$



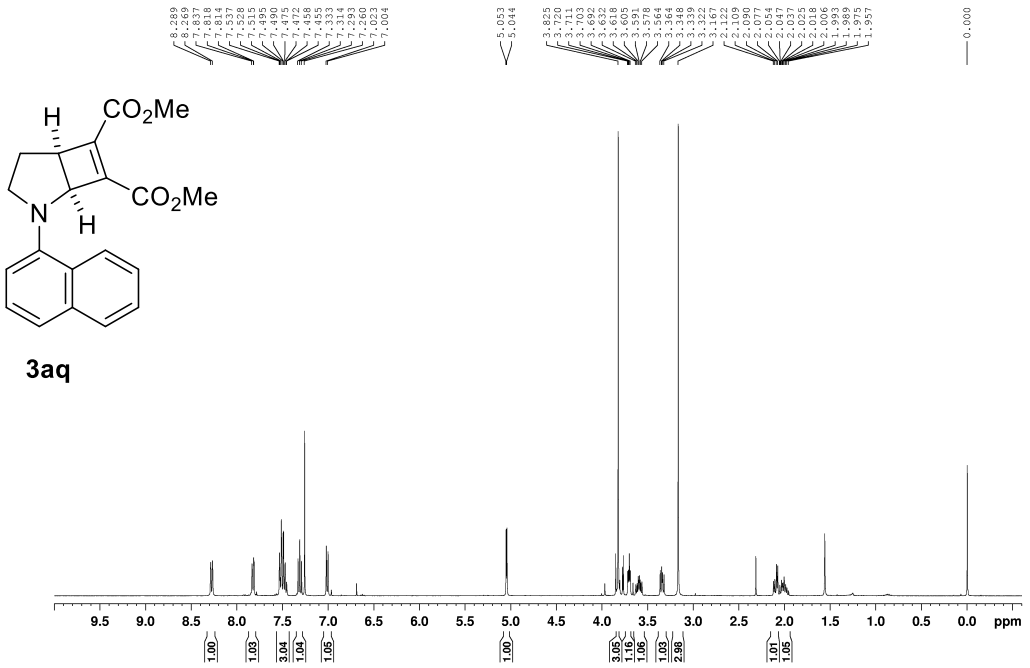
^{1}H NMR of **3ap** in $CDCl_3$



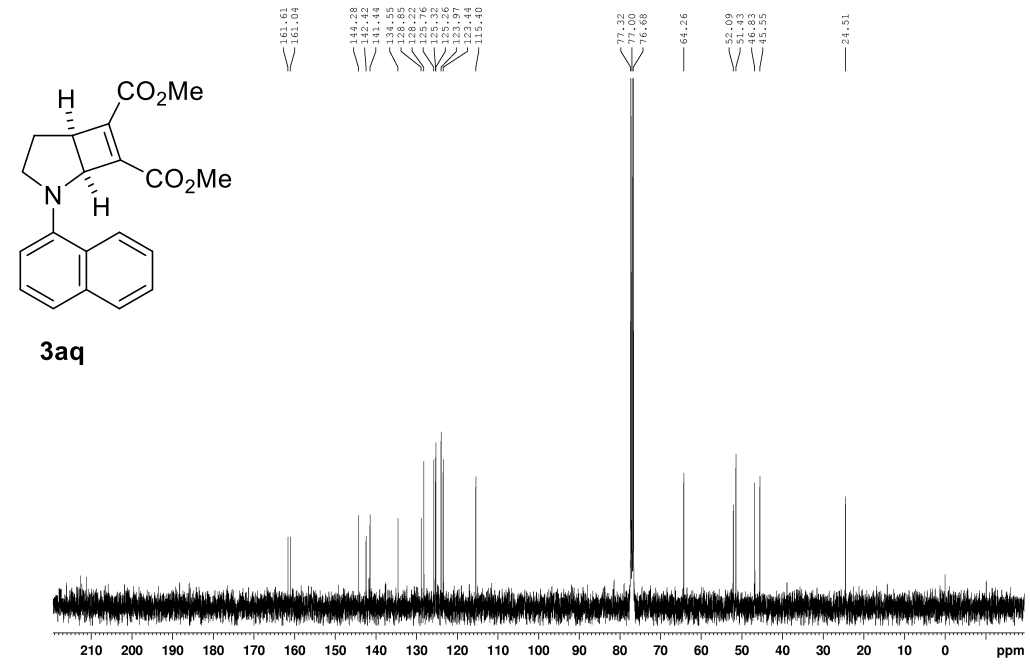
^{13}C NMR of **3ap** in $CDCl_3$



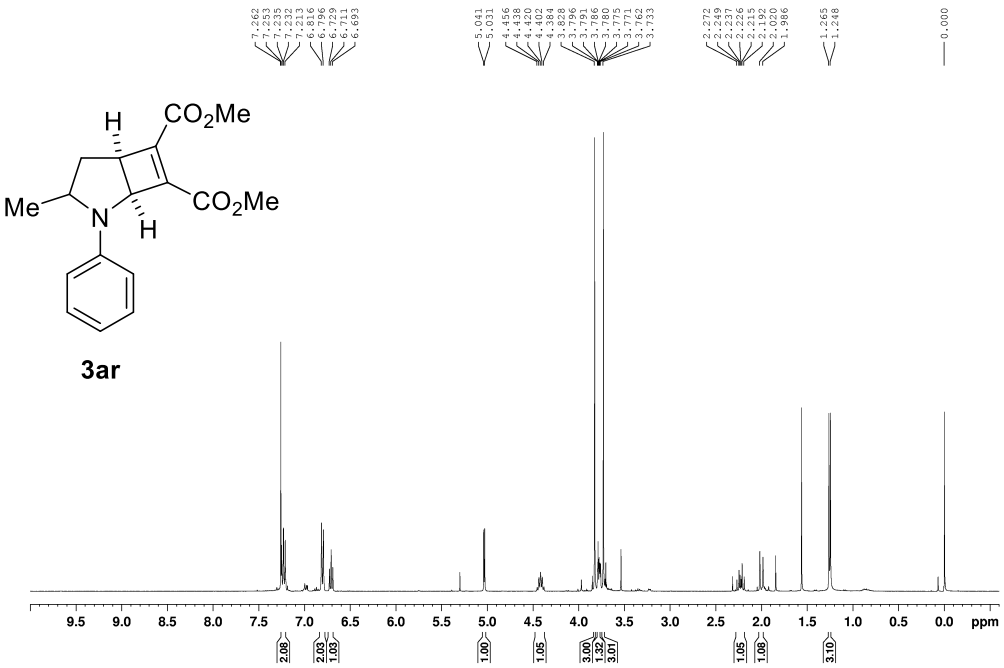
^{1}H NMR of **3aq** in $CDCl_3$



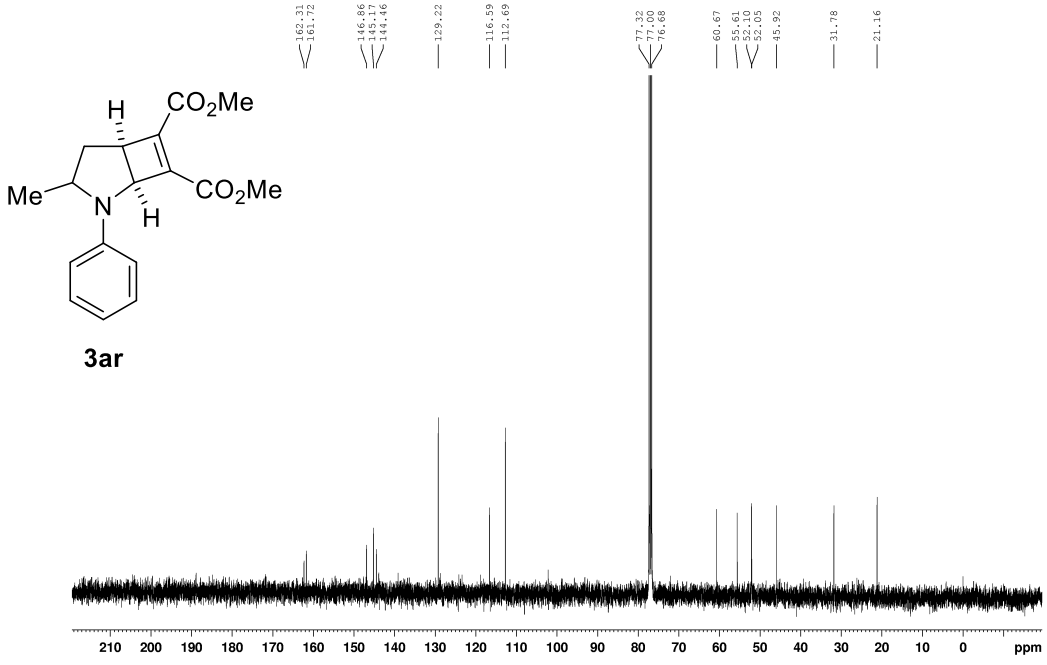
^{13}C NMR of **3aq** in $CDCl_3$



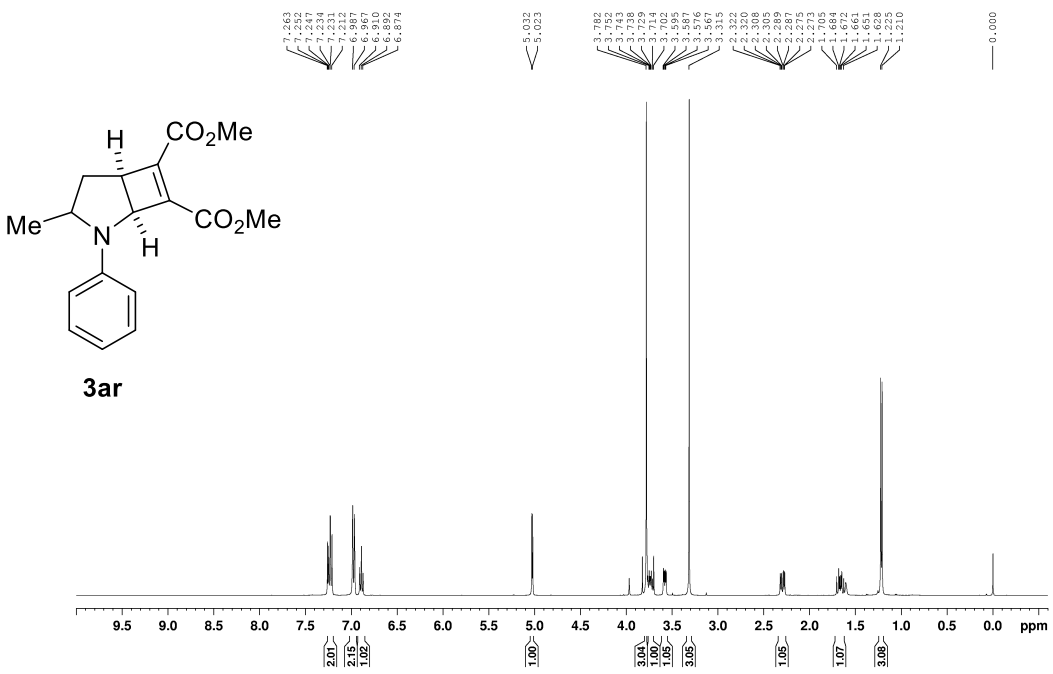
^{1}H NMR of **3ar** in $CDCl_3$ (first diastereoisomer)



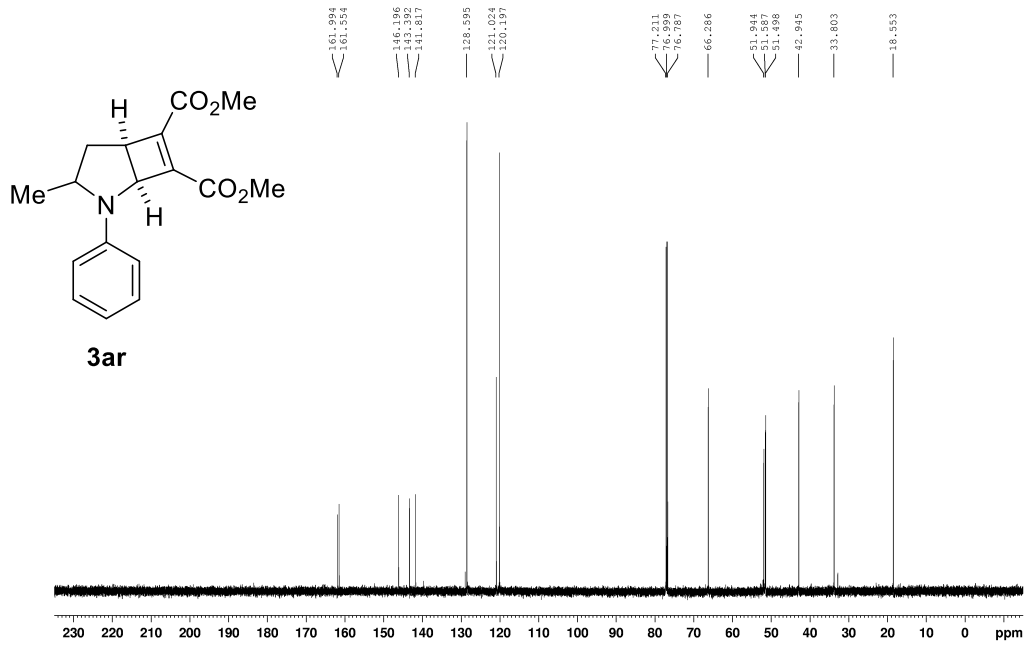
^{13}C NMR of **3ar** in $CDCl_3$ (first diastereoisomer)



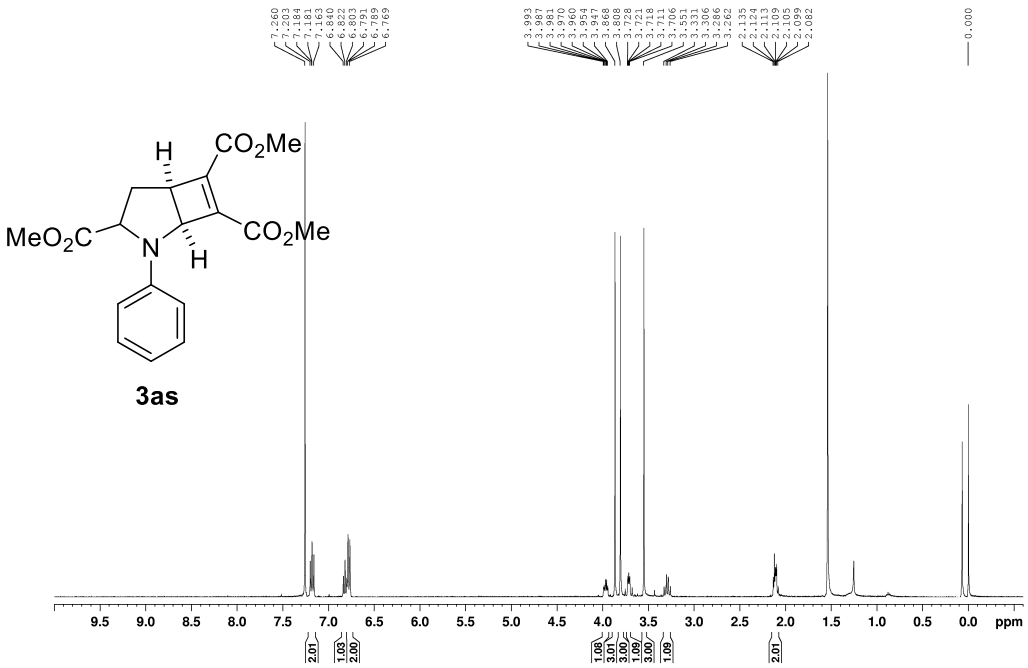
^{1}H NMR of **3ar** in $CDCl_3$ (second diastereoisomer)



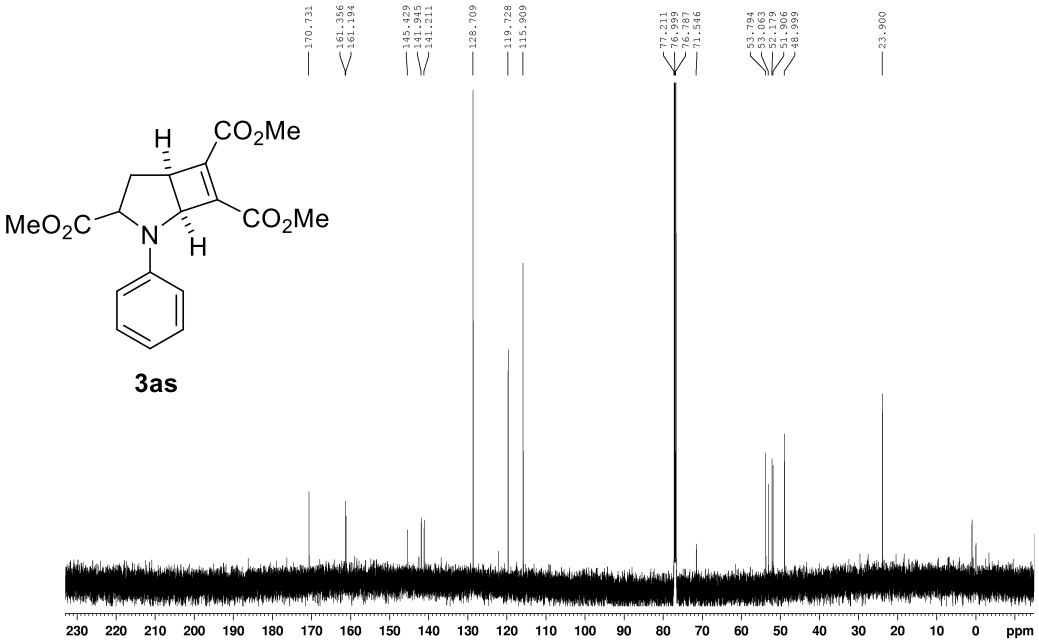
^{13}C NMR of **3ar** in $CDCl_3$ (second diastereoisomer)



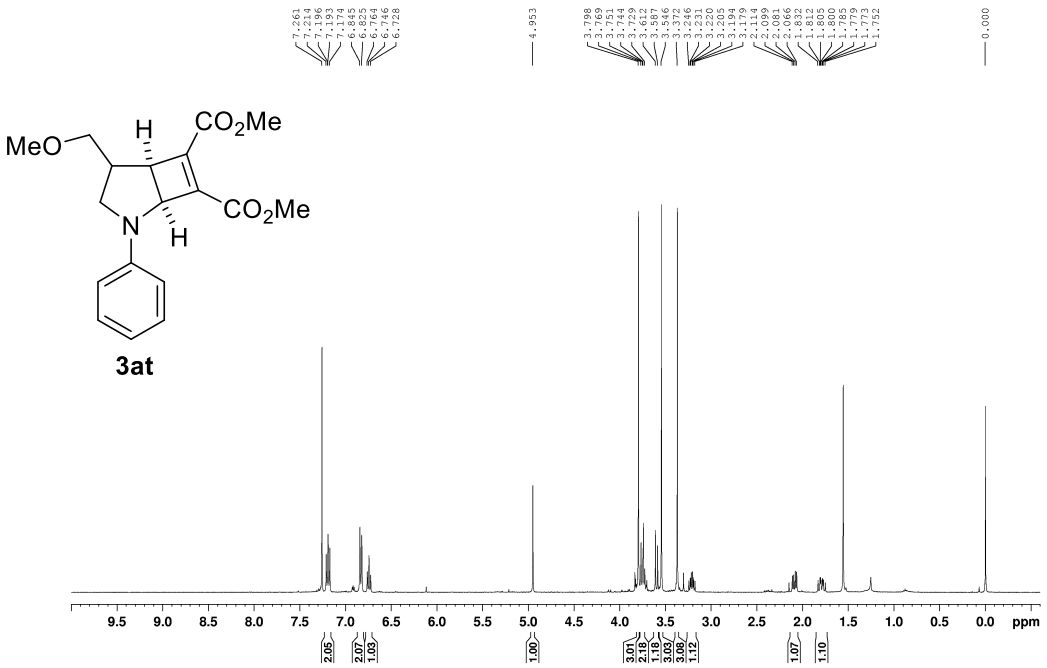
^{1}H NMR of **3as** in $CDCl_3$



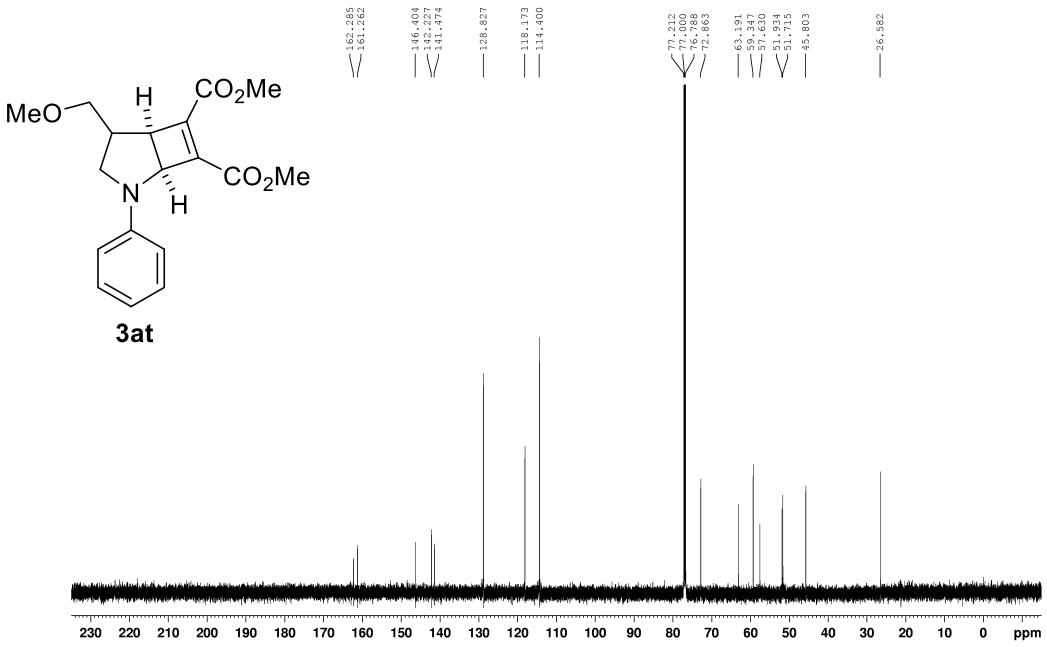
^{13}C NMR of **3as** in $CDCl_3$



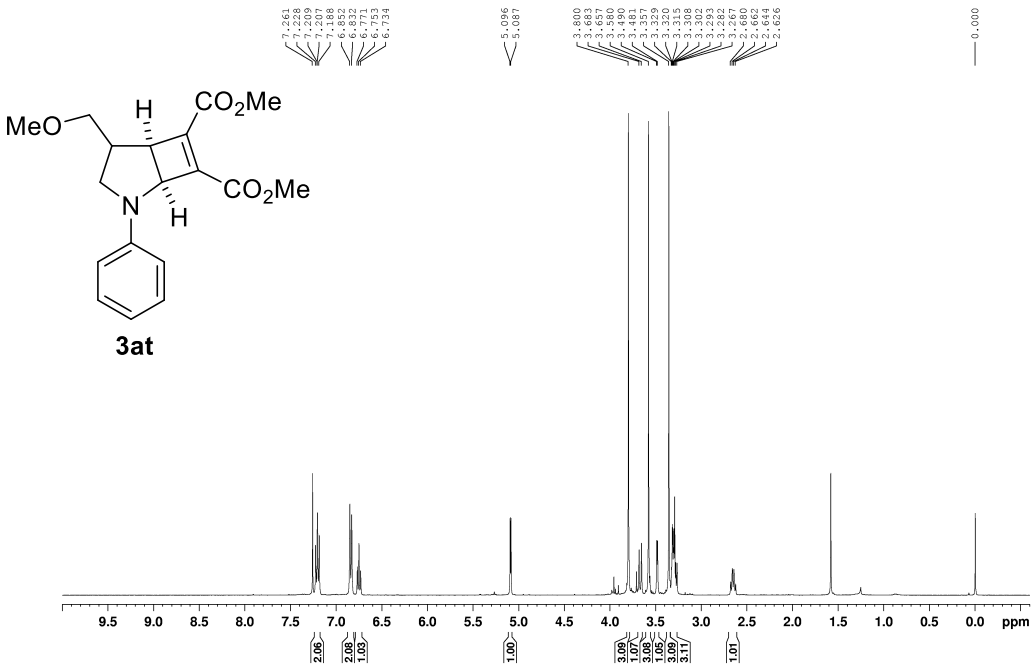
^{1}H NMR of **3at** in $CDCl_3$ (first diastereoisomer)



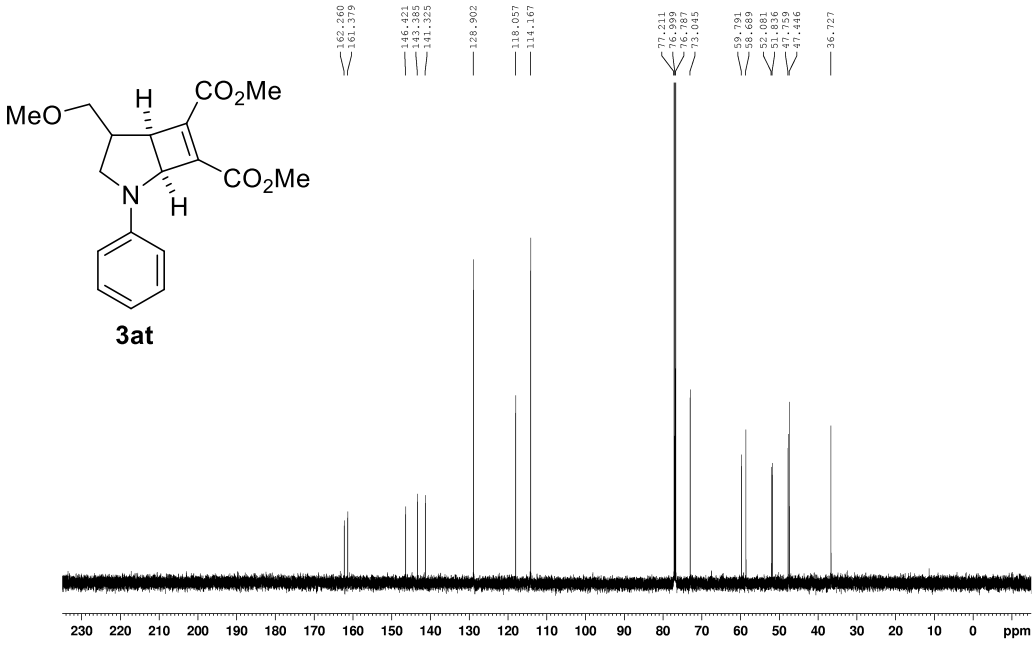
^{13}C NMR of **3at** in $CDCl_3$ (first diastereoisomer)



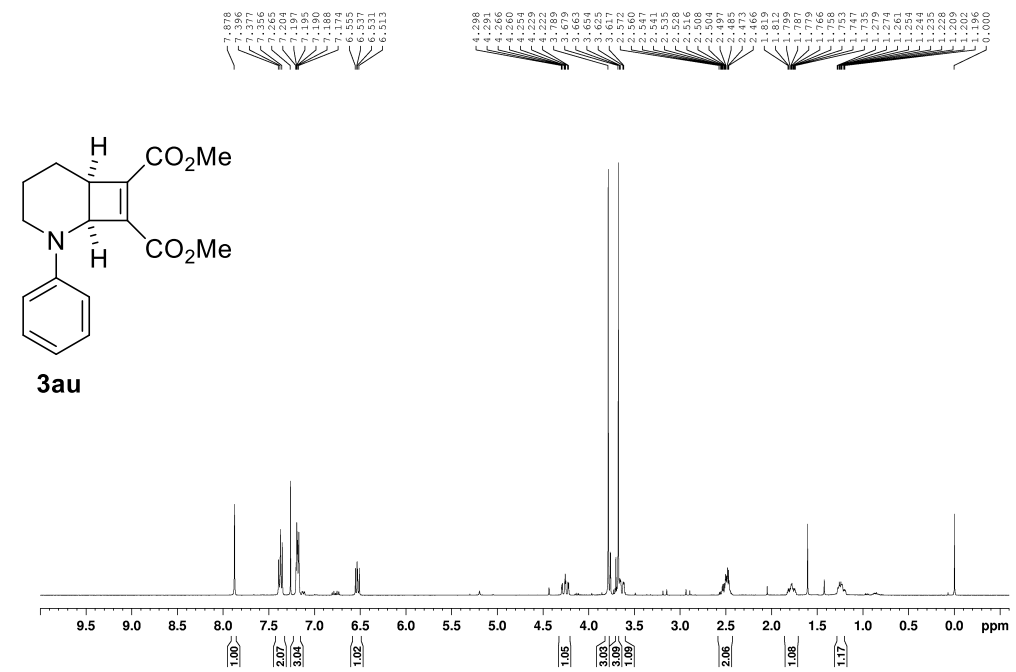
^{1}H NMR of **3at** in $CDCl_3$ (second diastereoisomer)



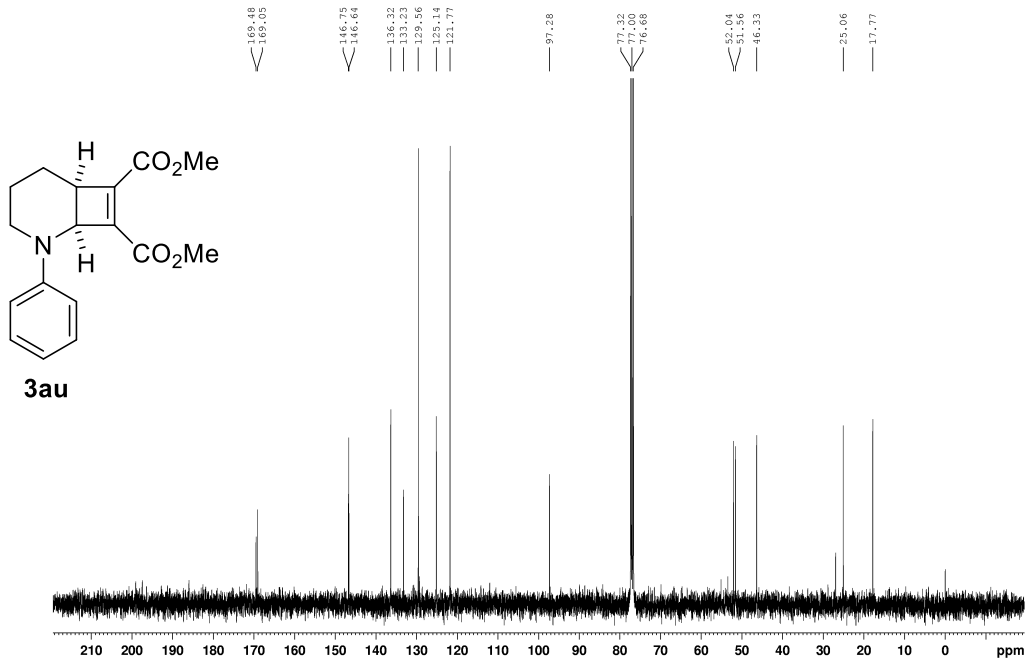
^{13}C NMR of **3at** in $CDCl_3$ (second diastereoisomer)



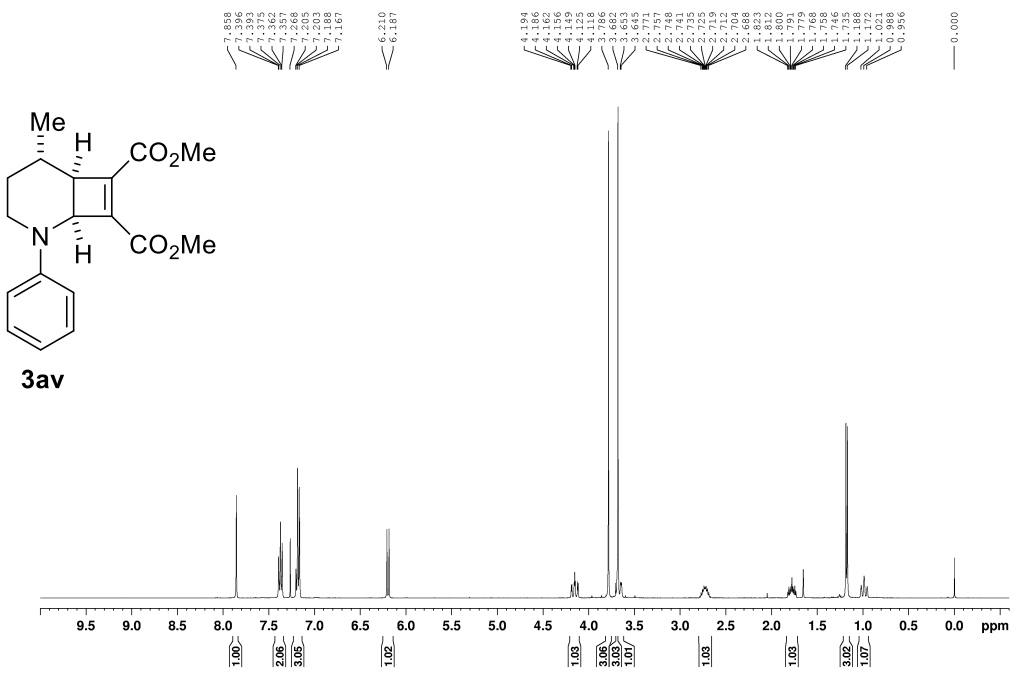
^{1}H NMR of **3au** in $CDCl_3$



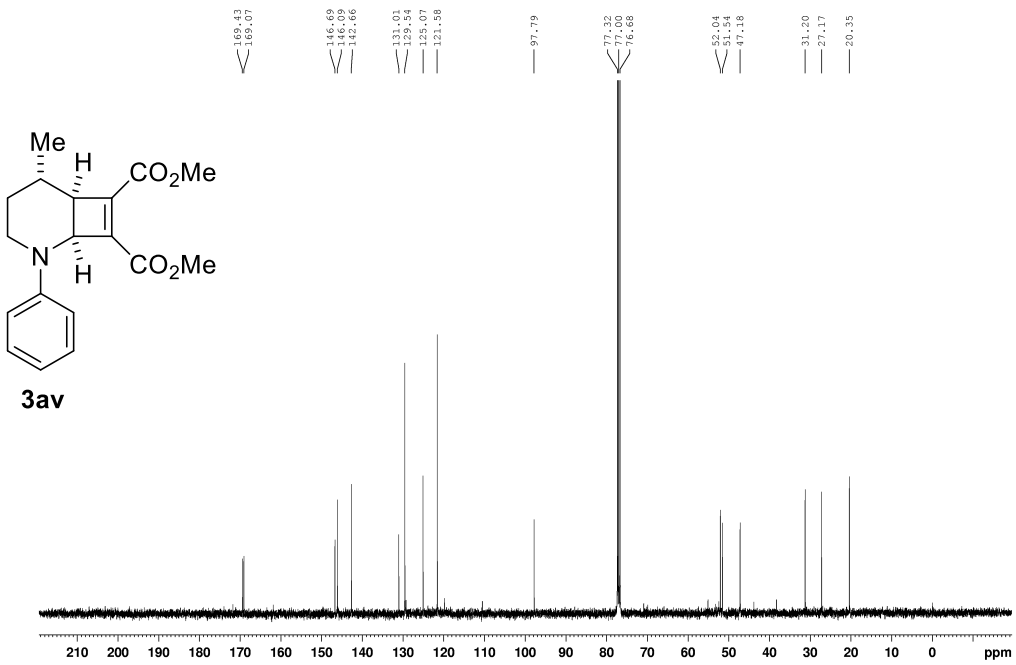
^{13}C NMR of **3au** in $CDCl_3$



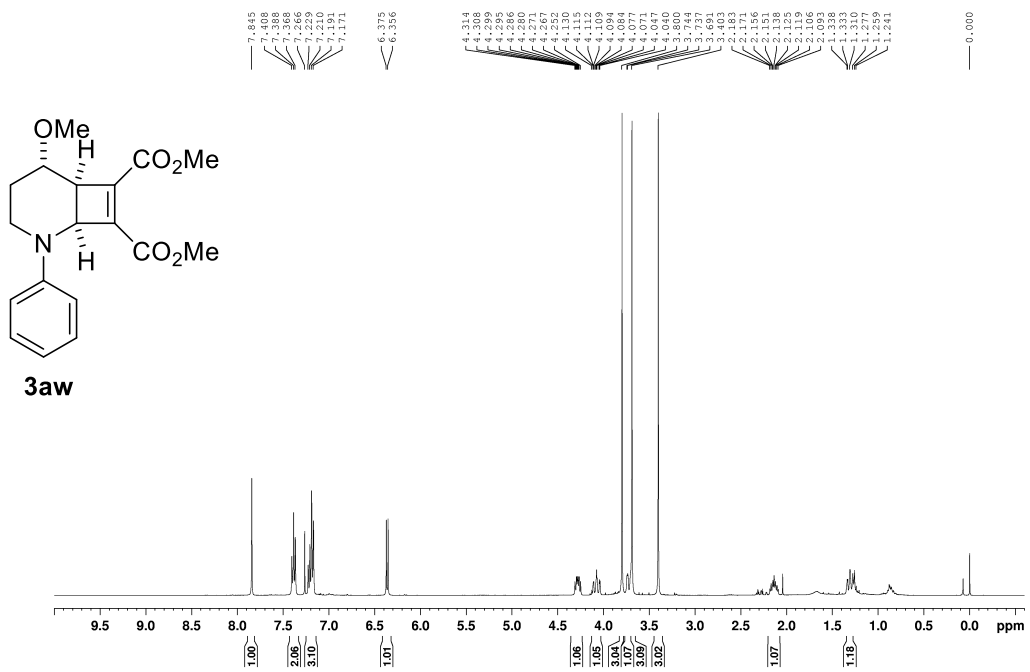
^{1}H NMR of **3av** in $CDCl_3$



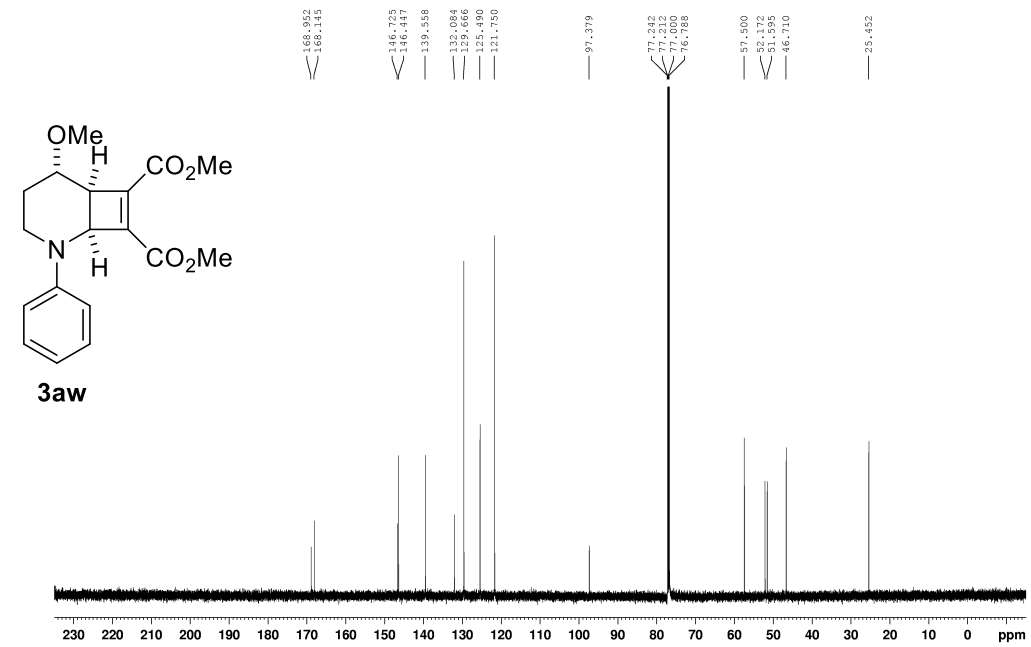
^{13}C NMR of **3av** in $CDCl_3$



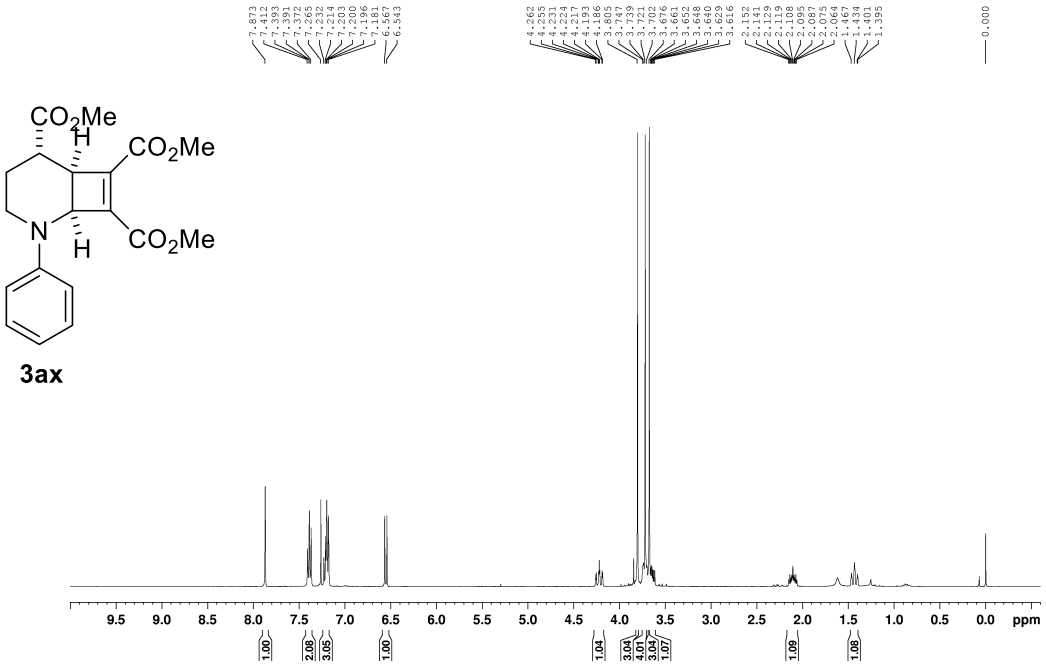
^{1}H NMR of **3aw** in $CDCl_3$



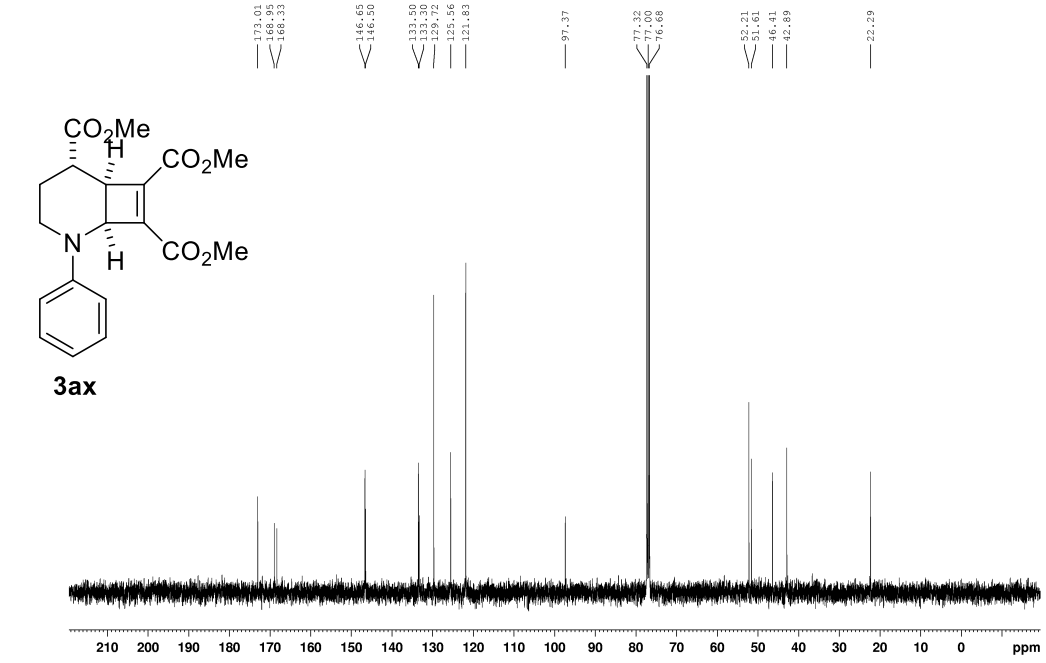
^{13}C NMR of **3aw** in $CDCl_3$



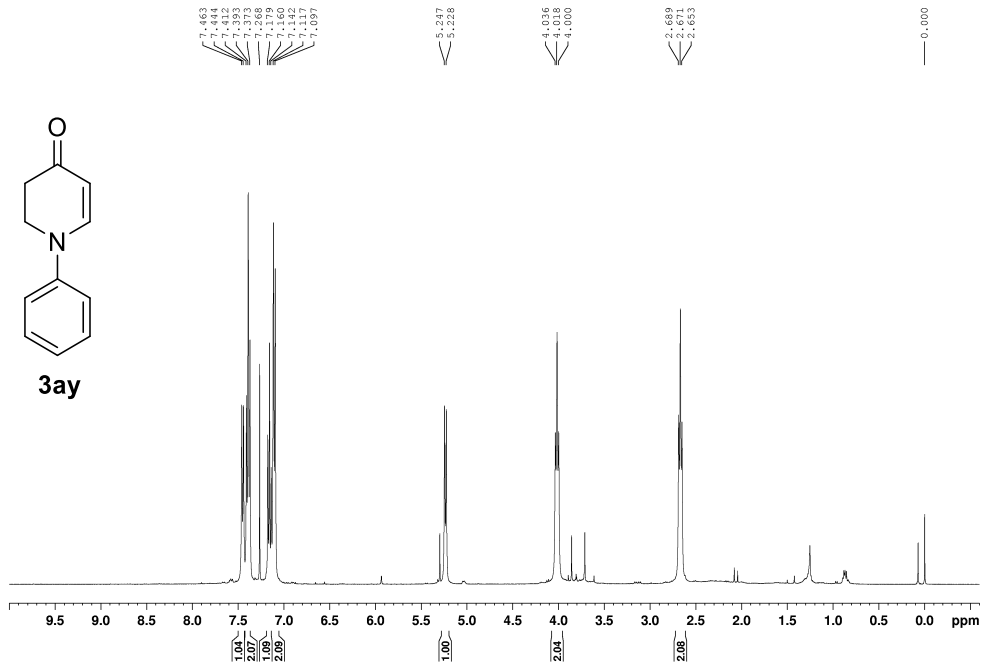
^{1}H NMR of **3ax** in $CDCl_3$



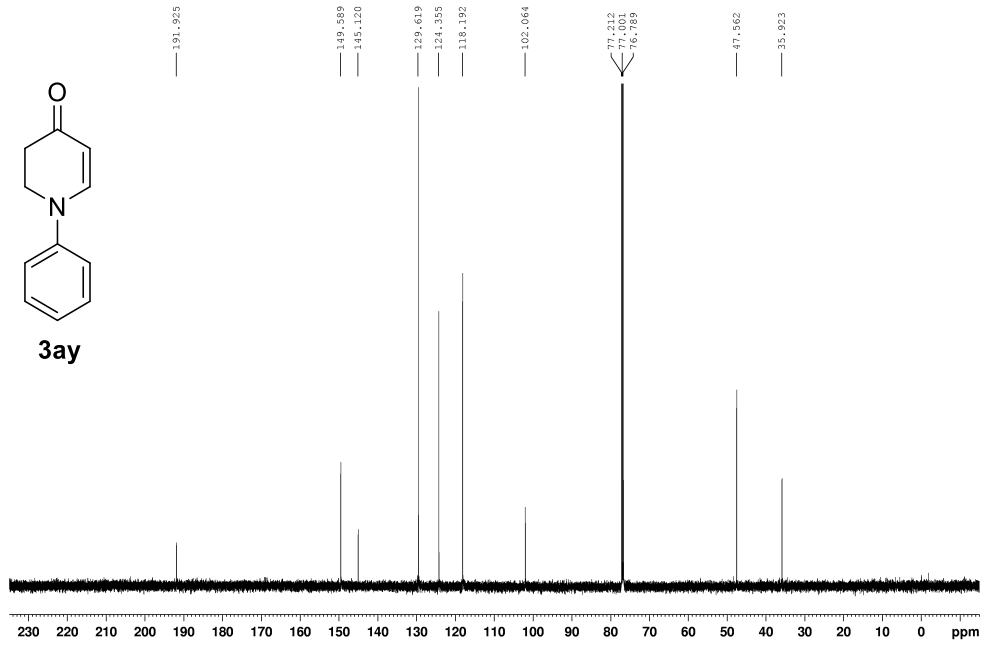
^{13}C NMR of **3ax** in $CDCl_3$



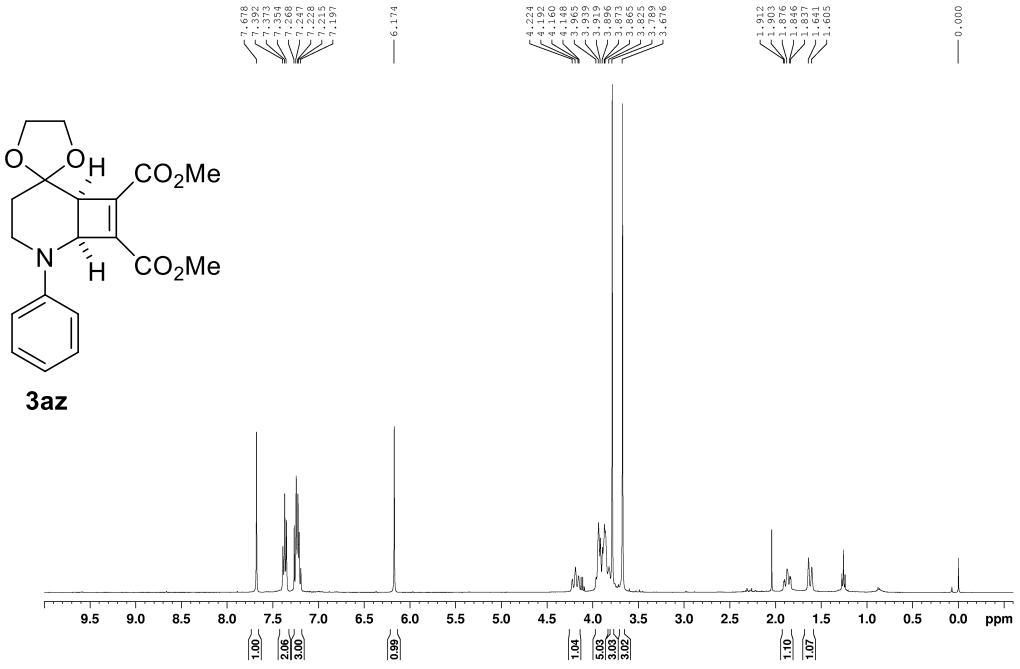
^{1}H NMR of **3ay** in $CDCl_3$



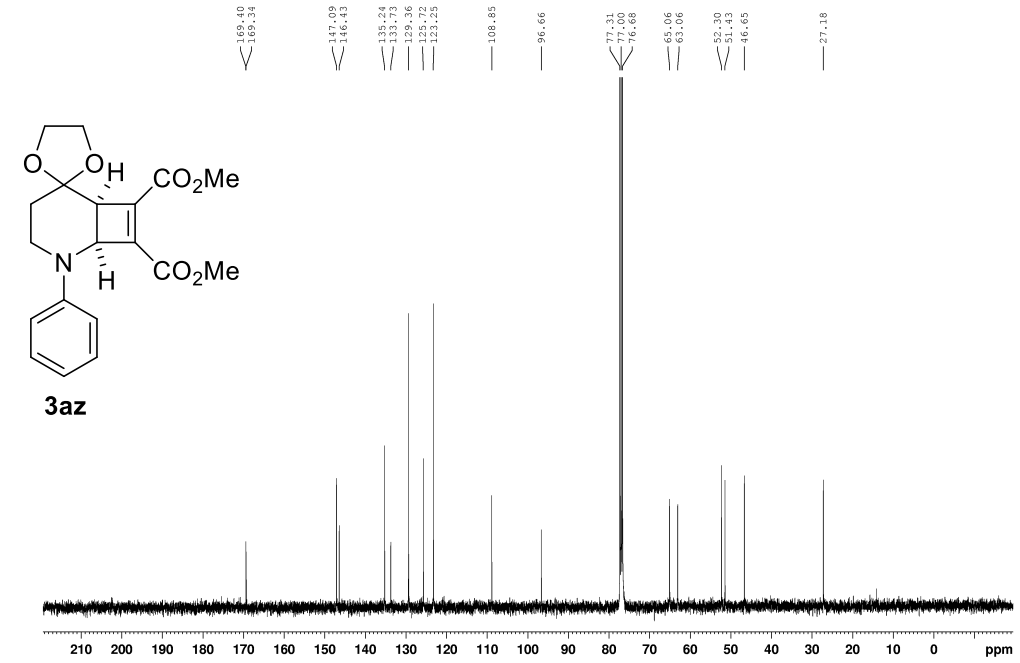
^{13}C NMR of **3ay** in $CDCl_3$



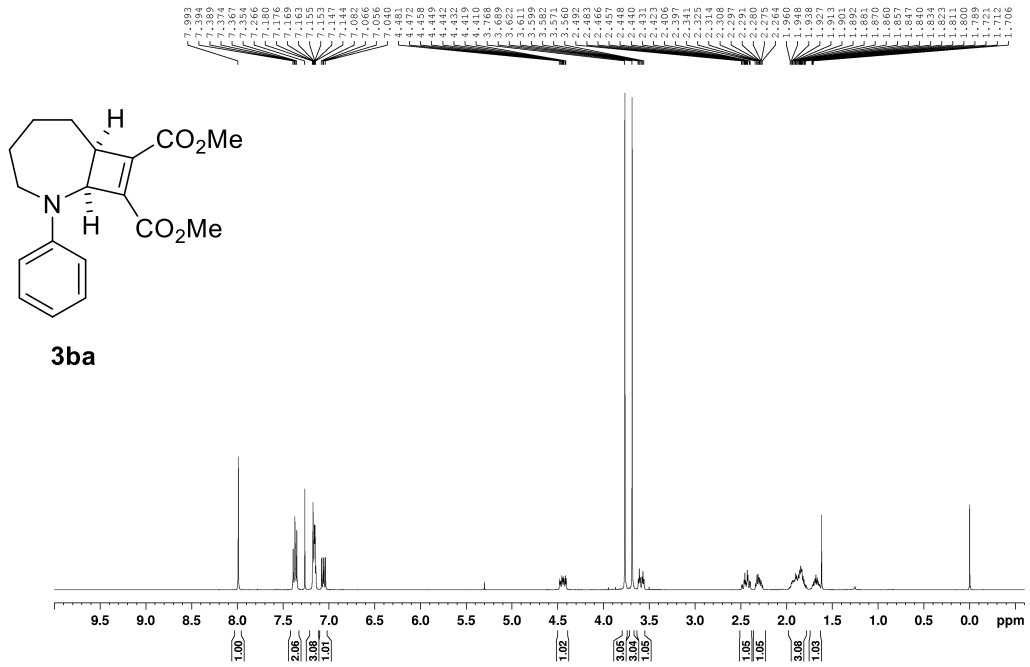
^{1}H NMR of **3az** in $CDCl_3$



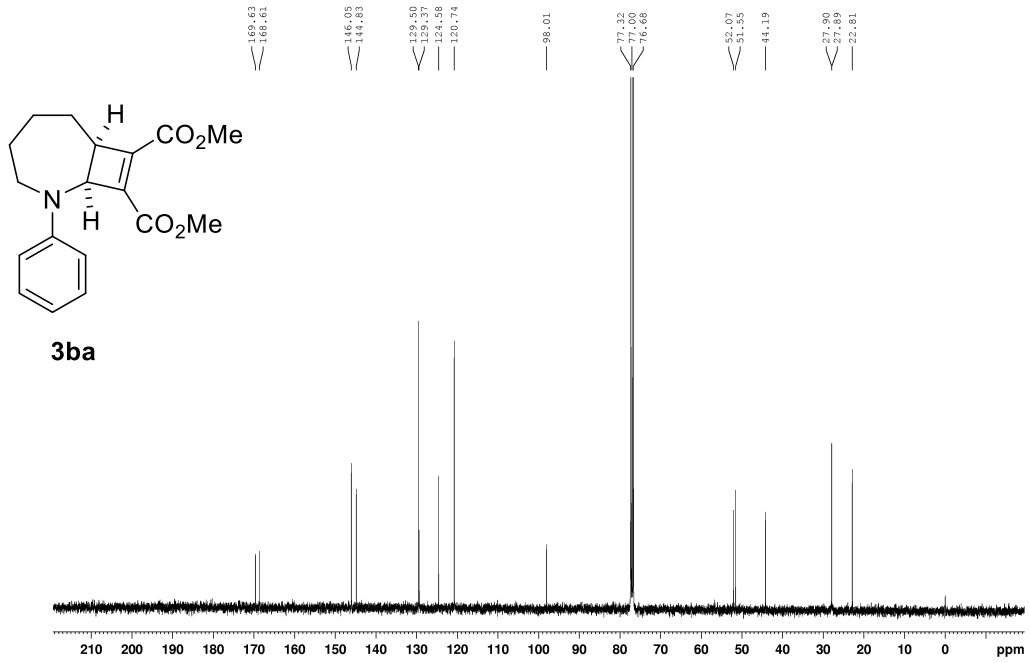
^{13}C NMR of **3az** in $CDCl_3$



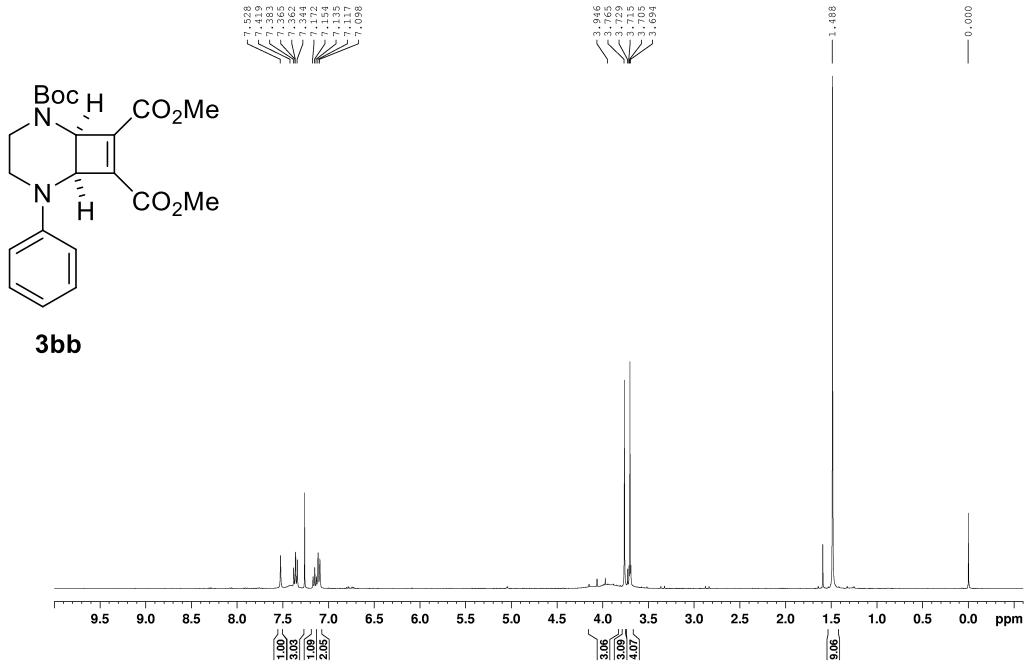
^{1}H NMR of **3ba** in $CDCl_3$



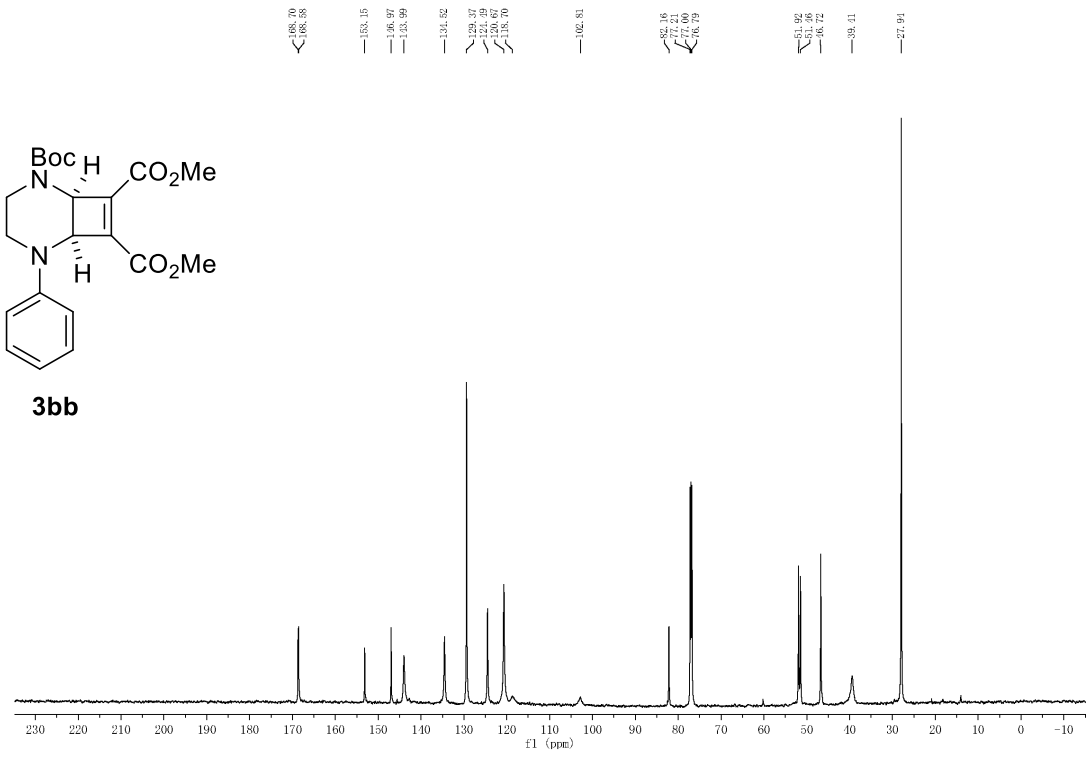
^{13}C NMR of **3ba** in $CDCl_3$



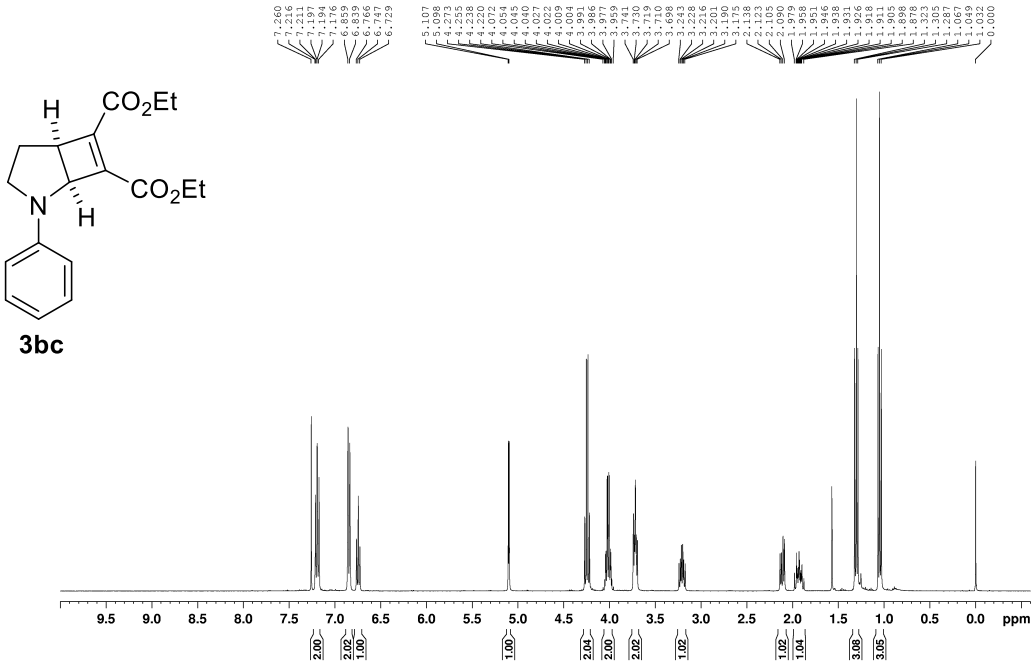
^{1}H NMR of **3bb** in $CDCl_3$



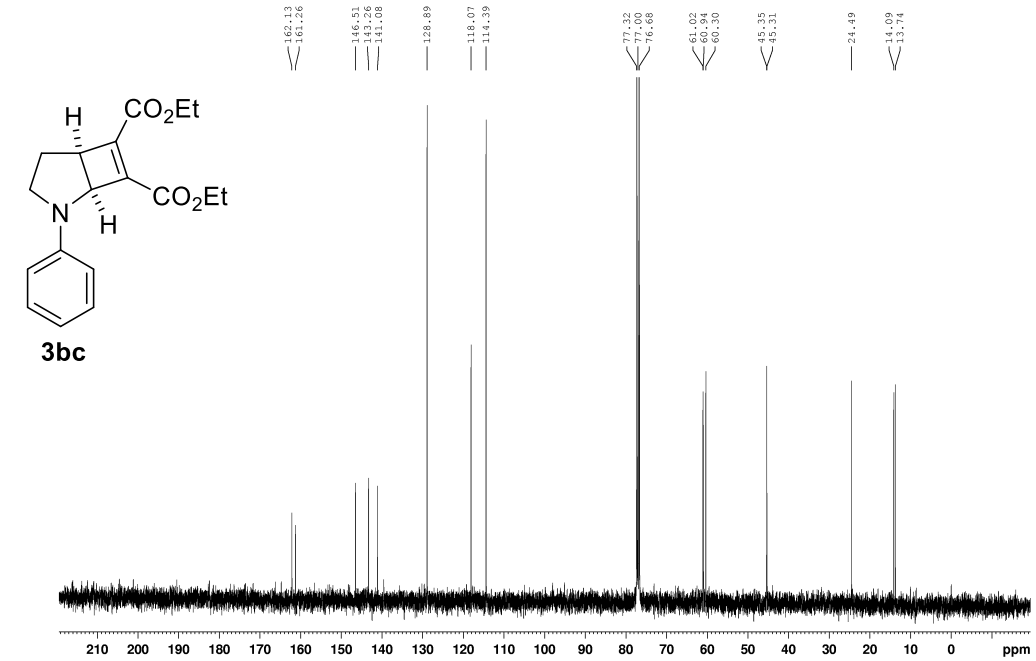
^{13}C NMR of **3bb** in $CDCl_3$



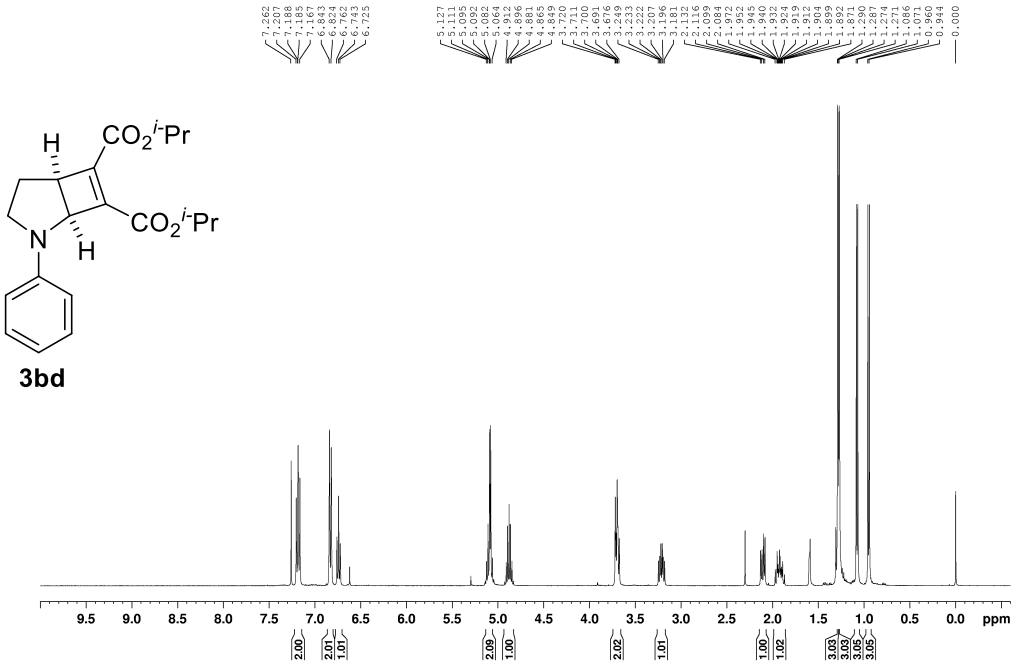
^{1}H NMR of **3bc** in $CDCl_3$



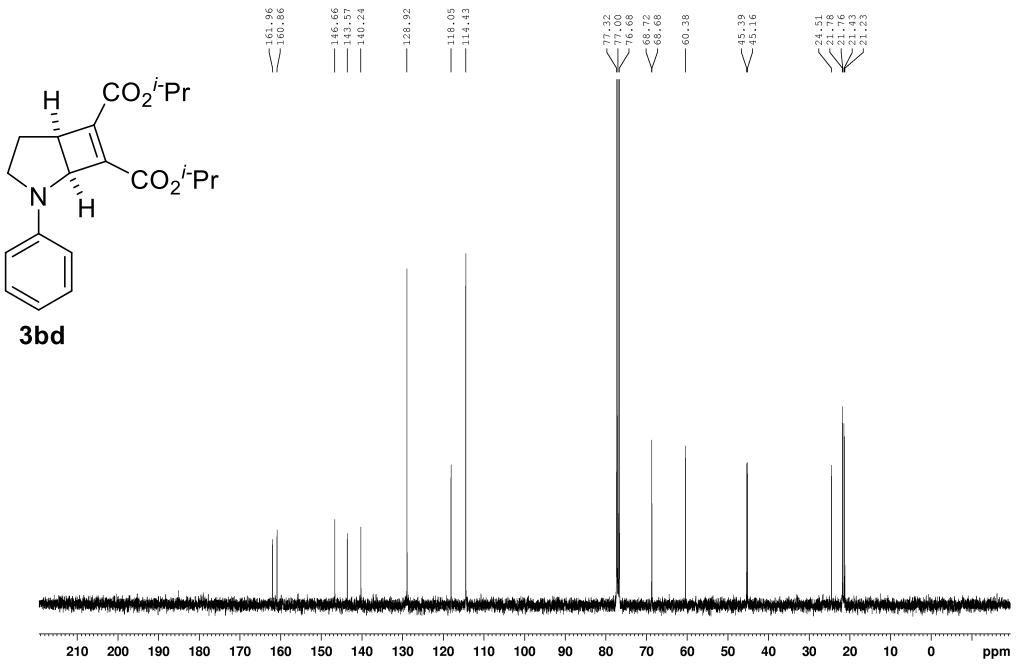
^{13}C NMR of **3bc** in $CDCl_3$



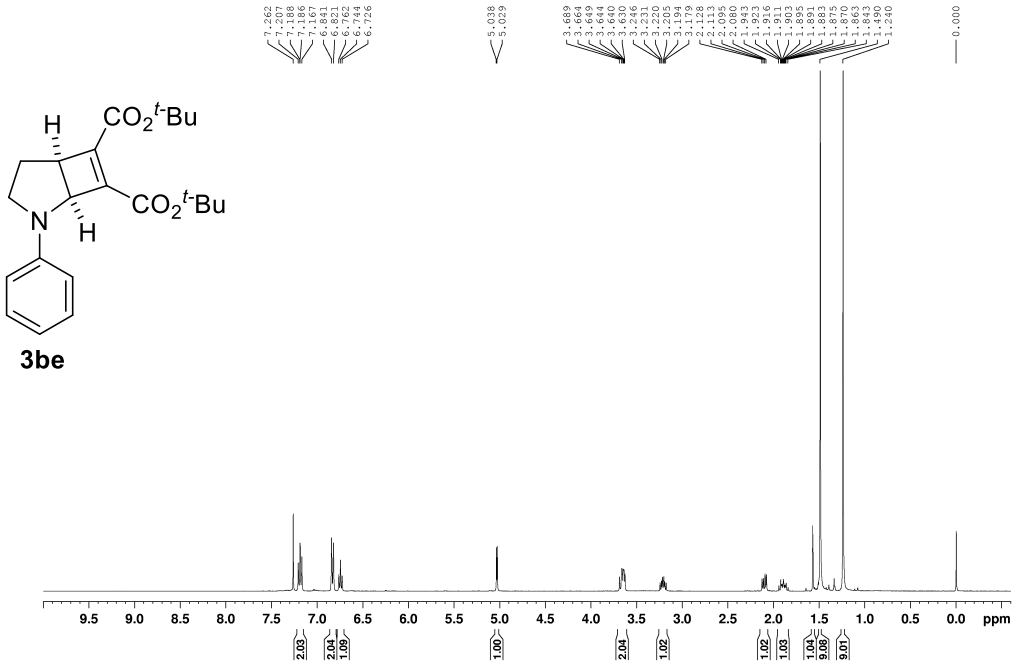
^{1}H NMR of **3bd** in $CDCl_3$



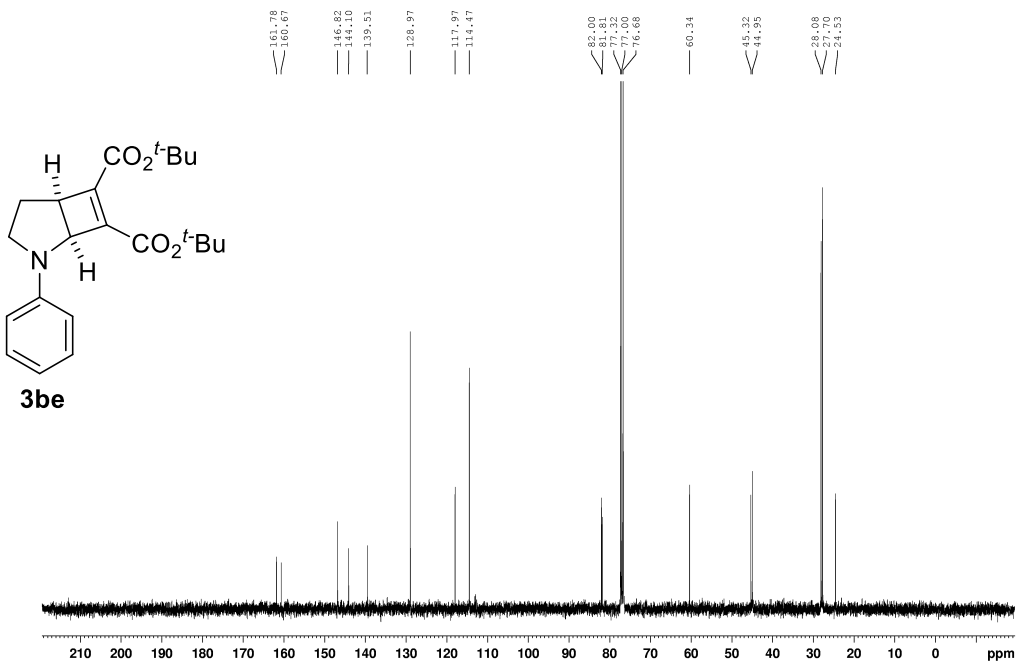
^{13}C NMR of **3bd** in $CDCl_3$



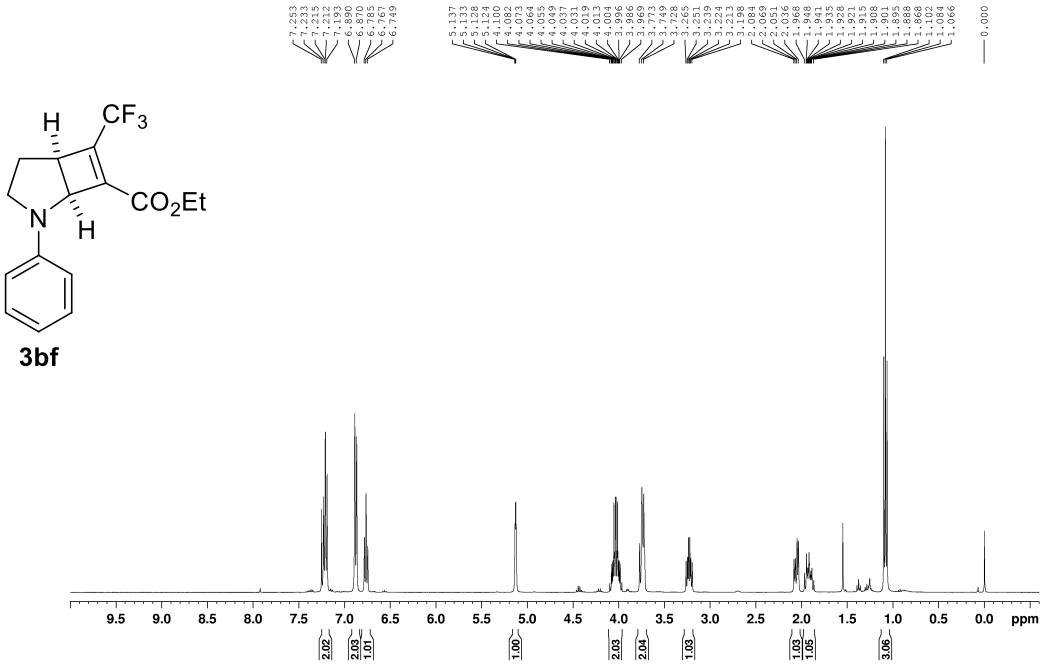
^{1}H NMR of **3be** in $CDCl_3$



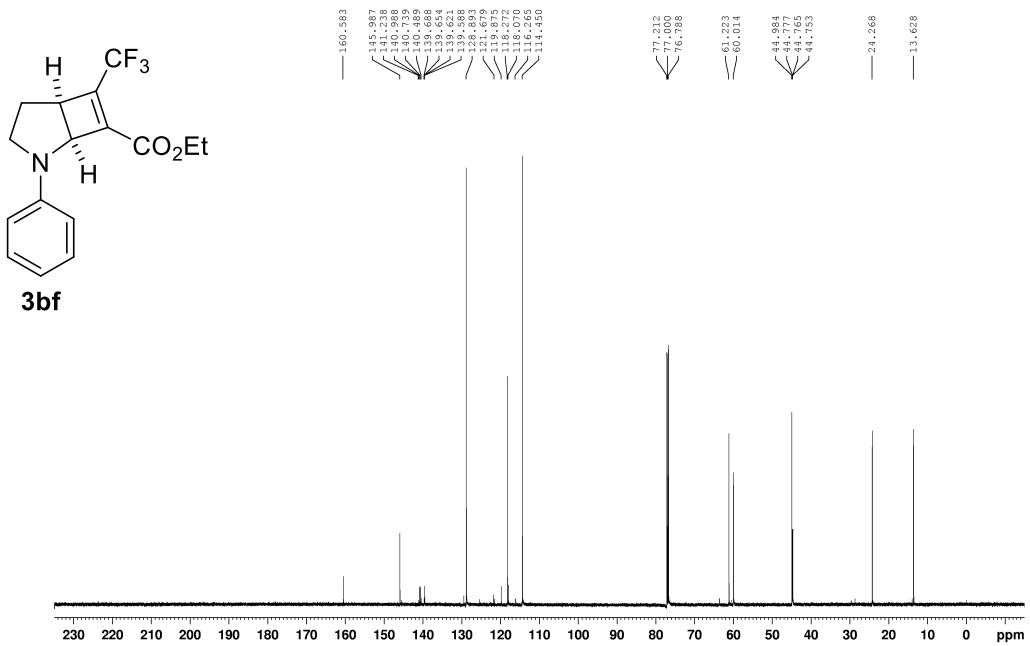
^{13}C NMR of **3be** in $CDCl_3$



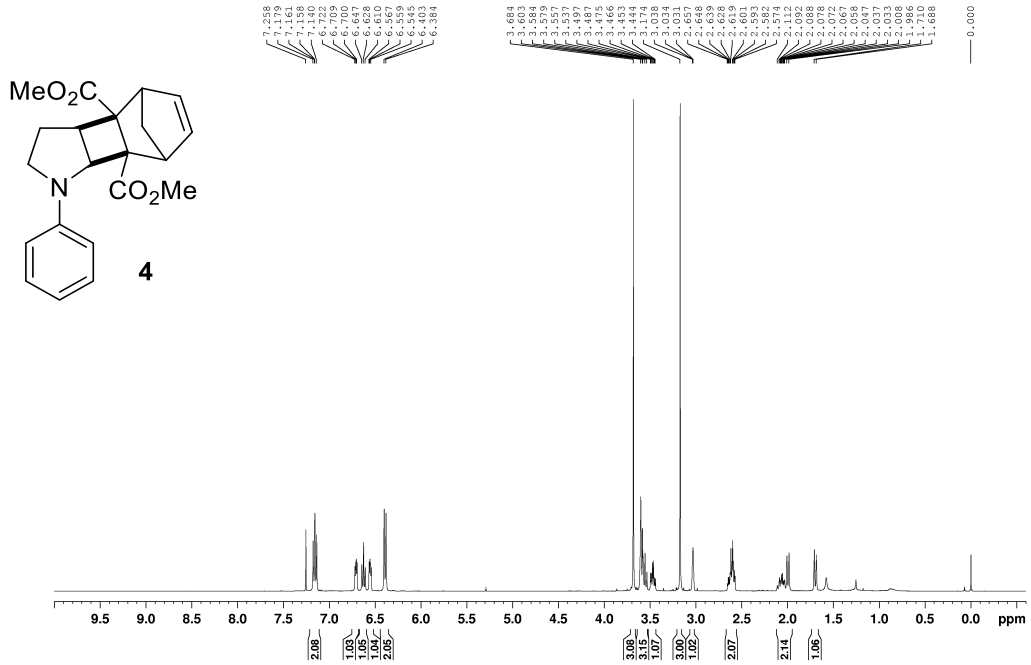
^{1}H NMR of **3bf** in $CDCl_3$



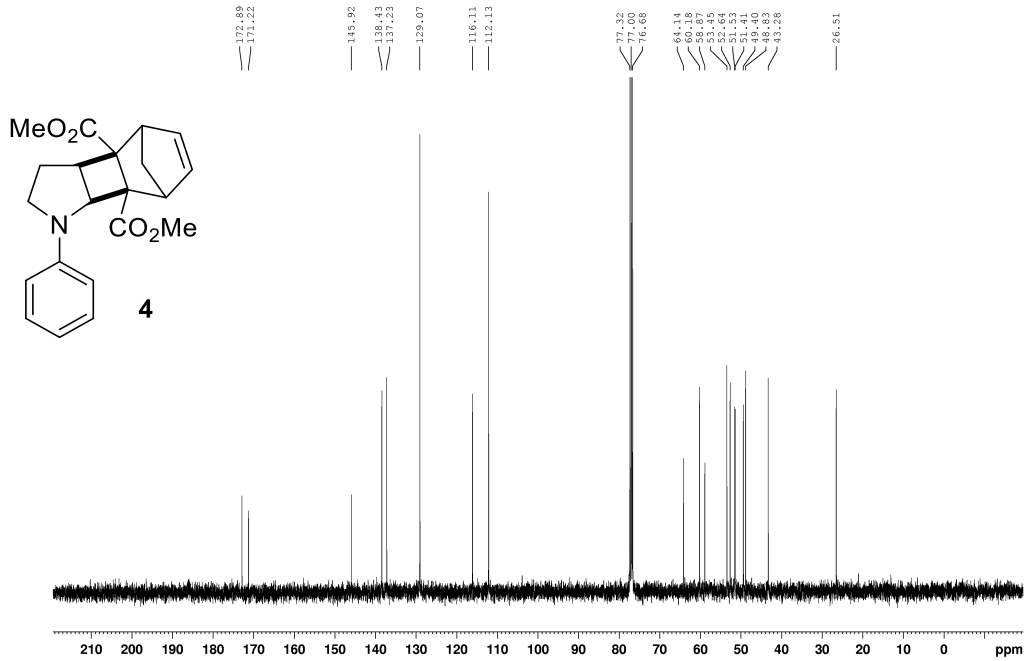
^{13}C NMR of **3bf** in $CDCl_3$



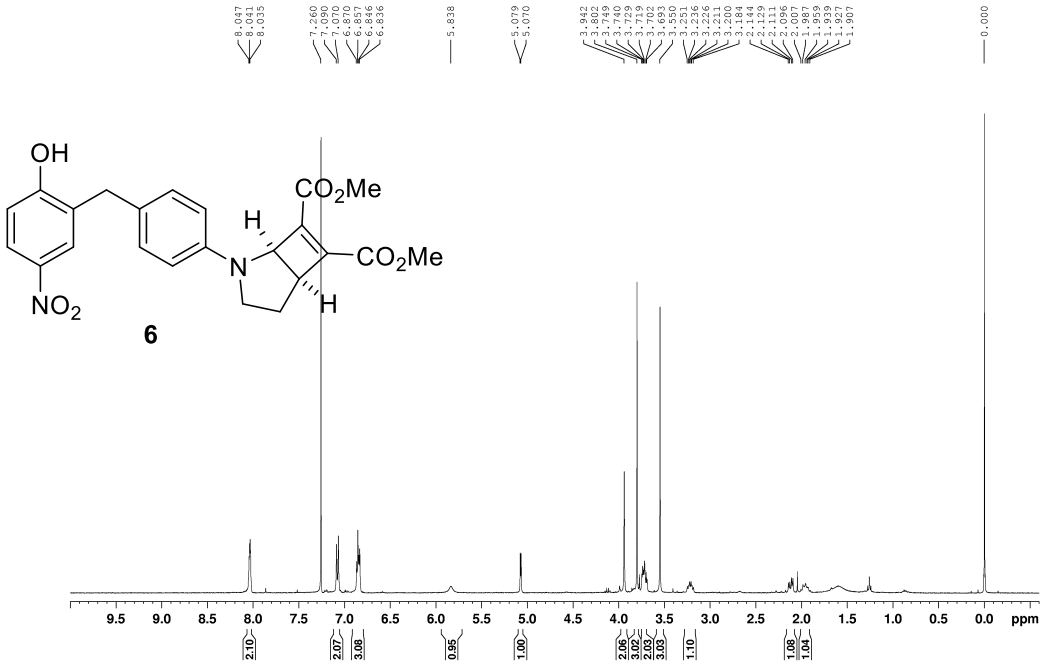
^{1}H NMR of **4** in $CDCl_3$



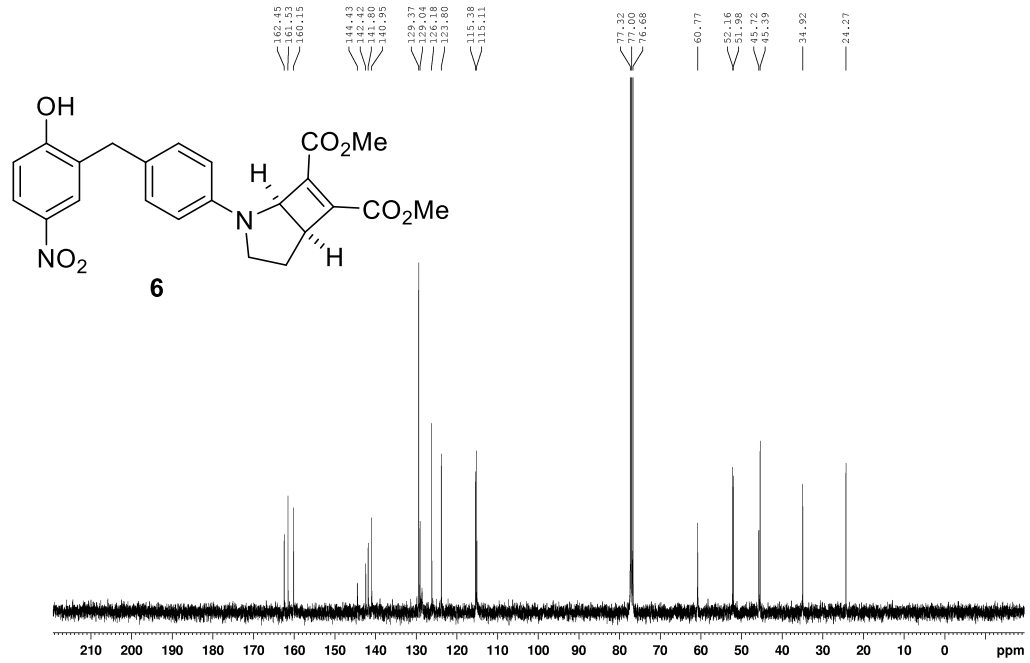
^{13}C NMR of **4** in $CDCl_3$



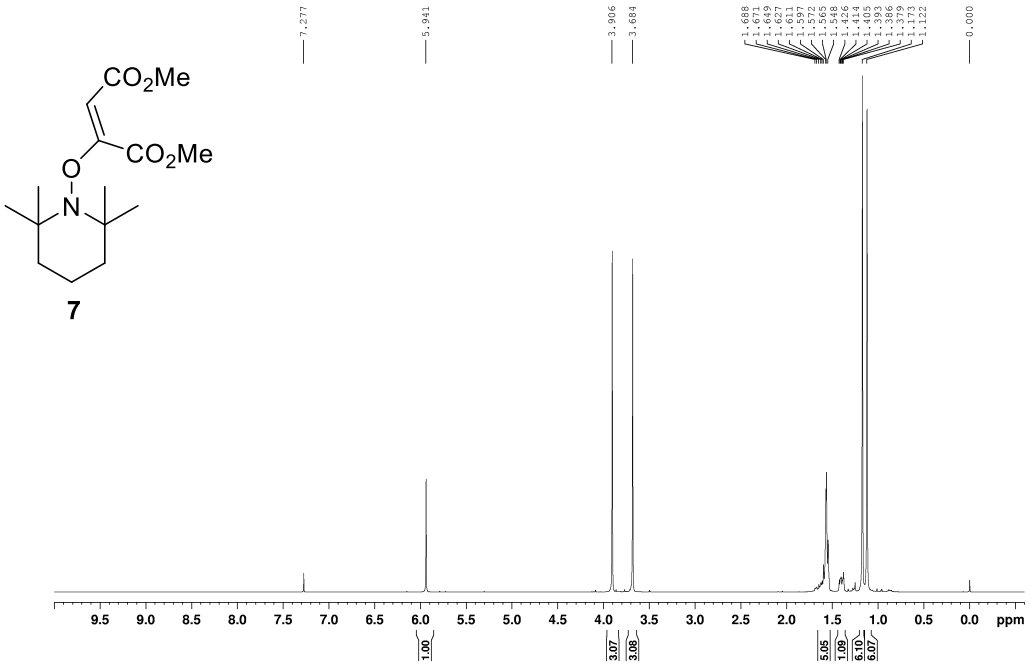
^{1}H NMR of **6** in $CDCl_3$



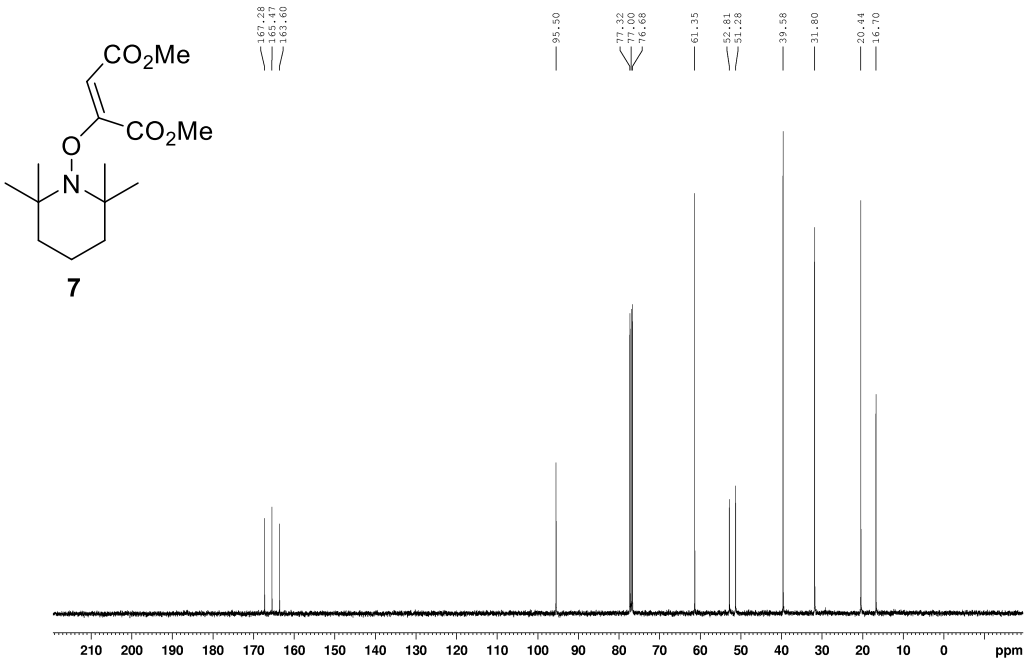
^{13}C NMR of **6** in $CDCl_3$



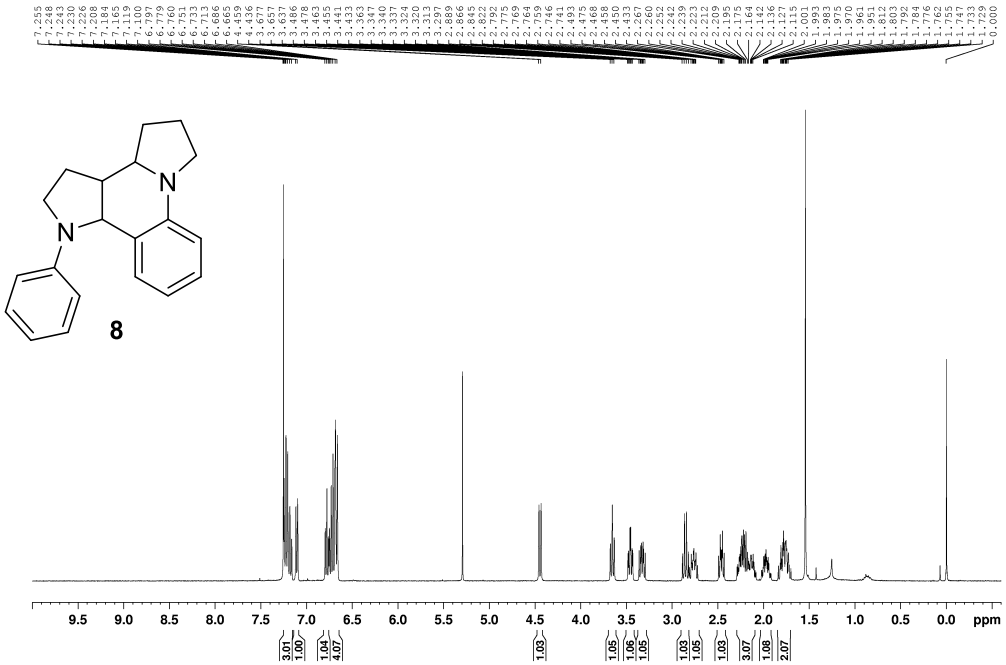
^{1}H NMR of **7** in $CDCl_3$



^{13}C NMR of **7** in $CDCl_3$



^{1}H NMR of **8** in $CDCl_3$



^{13}C NMR of **8** in $CDCl_3$