Supporting Information for

Pd-Catalyzed Oxidative Annulation of Enamides with Diazabicyclic Olefins: A Rapid Access to Cyclopentene Fused 2-Pyrrolines

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1. General Methods

All chemicals were of the best grade commercially available and are used without further purification. All solvents were purified according to standard procedure; dry solvents were obtained according to the literature methods and stored over molecular sieves. Analytical thin layer chromatography was performed on glass plates coated with silica gel containing calcium sulfate binder. Gravity column chromatography was performed using neutral alumina and mixtures of hexane-ethyl acetate were used for elution.

Melting points were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AMX 500 spectrophotometer ($CDCl_3$ and CD_3CN, MeOD as solvents). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.25ppm) CD_3CN (1.94 ppm), MeOD (3.31 ppm). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quadret); dd (double doublet); m (multiplet). Coupling constants are reported as *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.03 ppm) CD_3CN (1.32 ppm), MeOD (49.0 ppm). Mass spectra were recorded under ESI/HRMS at 60,000 resolution using Thermo Scientific Exactive mass spectrometer. IR spectra were recorded on Bruker FT-IR spectrometer.

- *Most of the synthesized compounds bear an amide moiety and the ^{1}H & ^{13}C NMR of these compounds were broadened due to the presence of rotamers.* D. Hu, P. Grice, S. V. Ley *J. Org. Chem.,* 2012, **77**, 5198.
- *The enamides were prepared by following literature reports. (a*) R. B. Boar, J. F. Mc Ghie, M. Robinson, D. H. R. Barton, D. C. Horwell, R.V. Stick, *J. Chem. Soc., Perkin Trans. I,* 1975, 1237; (b) D. H. R. Barton, S. Z. Zard, *J. Chem. Soc., Perkin Trans. I*, 1985, 2191.

2. General procedure for the Pd-catalyzed oxidative annulation of enamides with diazabicyclic olefins

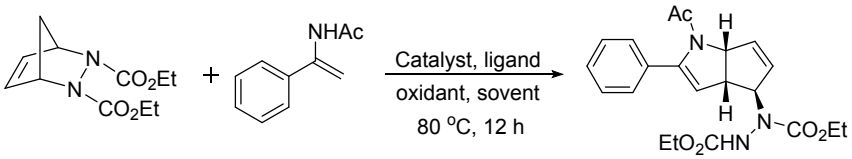
A mixture of azabicyclic olefin **1a** (100 mg, 0.399 mmol.), N-acetyl enamide **2a** (53 mg, 0.333 mmol) $Pd(OAc)_2$ (7 mg, 0.033), dppe (13 mg, 0.033 mmol), $Cu(OAc)_2$ (121 mg, 0.666 mmol) were weighed into a Schlenk tube and degassed for 10 minutes. Dry acetonitrile (2 mL) was added and the reaction mixture was purged with argon and allowed to stir at 80 ^{o}C for 12 hours. The solvent was evaporated in *vacuo* and the residue on column chromatography (activated neutral alumina) with hexane-ethylacetate mixtures yielded cyclopentene fused substituted 2-pyrrolines.

Optimization studies for suitable Pd-catalyzed oxidative annulation of enamide **2a** with diazabicyclic olefin **1a**

The interesting heteroannulation prompted us to optimize the reaction conditions (Table 1). From various solvents such as MeOH, CH_3CN, DMSO, DCE, DMF screened, CH_3CN was

found to be the best medium for the present transformation (Table 1, entries 1-5). Further experiments with different palladium salts proved $Pd(OAc)_2$ as the best choice for the catalyst precursor (Table 1, entries 6-8). It is noteworthy to mention that the reaction failed in the absence of either palladium catalyst or oxidant (Table 1, entries 9-10). From different phosphine ligands tested, dppe was found to be the best ligand furnishing the fused pyrroline in 65% yield (Table 1, entries 2, 12-14). The effect of different oxidants like $Cu(OAc)_2$, Ag_2CO_3 and O_2 was studied and better yield was obtained with $Cu(OAc)_2$ (Table 1, entries 12, 15-16). Finally, the use of 1.25 equivalents of alkene **1a** furnished the product in 71% yield.

Table 1: Optimization studies



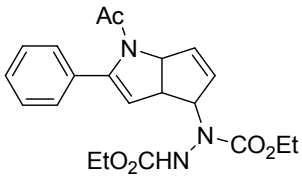
1a **2a** **3aa**

Entry	Catalyst	Oxidant	Ligand	Solvent	Yield (%)
1	$Pd(OAc)_2$	$Cu(OAc)_2$	PPh_3	MeOH	47
2	$Pd(OAc)_2$	$Cu(OAc)_2$	PPh_3	CH_3CN	62
3	$Pd(OAc)_2$	$Cu(OAc)_2$	PPh_3	DMSO	45
4	$Pd(OAc)_2$	$Cu(OAc)_2$	PPh_3	DCE	40
5	$Pd(OAc)_2$	$Cu(OAc)_2$	PPh_3	DMF	40
6	$PdCl_2$	$Cu(OAc)_2$	PPh_3	CH_3CN	38
7	$Pd(TFA)_2$	$Cu(OAc)_2$	PPh_3	CH_3CN	40
8	$Pd(PPh_3)_2Cl_2$	$Cu(OAc)_2$	PPh_3	CH_3CN	Trace
9	–	$Cu(OAc)_2$	PPh_3	CH_3CN	–
10	$Pd(OAc)_2$	–	PPh_3	CH_3CN	–
11	$Pd(OAc)_2$	$Cu(OAc)_2$	–	CH_3CN	48
12	$Pd(OAc)_2$	$Cu(OAc)_2$	dppe	CH_3CN	65
13	$Pd(OAc)_2$	$Cu(OAc)_2$	dppm	CH_3CN	48
14	$Pd(OAc)_2$	$Cu(OAc)_2$	dppf	CH_3CN	55
15	$Pd(OAc)_2$	Ag_2CO_3	dppe	CH_3CN	35
16	$Pd(OAc)_2$	O_2	dppe	CH_3CN	30
17[a]	**$Pd(OAc)_2$**	**$Cu(OAc)_2$**	**dppe**	**CH_3CN**	**71**

Reaction conditions: **1a** (1.0 equiv.), **2a** (1.0 equiv.), catalyst (10.0 mol %), oxidant (2.0 equiv.), ligand (10.0 mol %), solvent (2.0 mL), 12 h, 80 °C. [a] **1a** (1.25 equiv.)

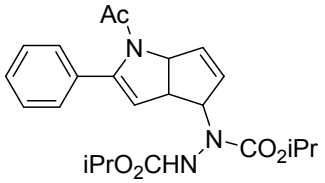
Characterisation of the products

Diethyl1-(1-acetyl-2-phenyl-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3aa**)



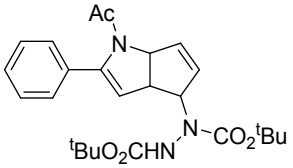
Yield: 94 mg, 71%; Colourless viscous liquid; R_f: 0.38 (hexane/ethyl acetate = 2:3). **IR (neat) ν_{max}:** 3284, 2982, 2935, 1709, 1654, 1519, 1386, 1319, 1257, 1224, 934, 762 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.48-7.14 (m, 6H), 6.11-6.08 (m, 1H), 5.88-5.77 (m, 1H), 5.44-5.32 (m, 2H), 5.15 (brs, 1H), 4.12-4.03 (m, 4H), 3.66-3.39 (m, 1H), 2.25 (s, 3H), 1.23 (t, *J* = 6.5 Hz, 6 H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.4, 157.7, 156.5, 142.9, 135.7, 135.1, 131.5, 129.4, 128.1, 117.8, 71.4, 69.7, 63.2, 62.6, 49.7, 24.7, 14.9, 14.8 ppm. **HRMS (ESI):** Calcd for $C_{21}H_{25}N_3O_5$, $(M+Na)^+$: 422.16919; Found: 422.16925.

Diisopropyl 1-(1-acetyl-2-phenyl-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3ba**)



Yield: 95 mg, 75%; Off white coloured solid; mp: 90-100 °C; R_f: 0.50 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3294, 2980, 2932, 2394, 1712, 1654, 1514, 1385, 1313, 1262, 1106, 946, 761 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.49-7.27 (m, 6H), 6.13-6.06 (m, 1H), 5.87-5.82 (m, 1H), 5.45-5.32 (m, 2H), 5.15- 5.11 (m, 1H), 4.85-4.84 (m, 2H), 3.67-3.40 (m, 1H), 2.37 (s, 3H), 1.22-1.19 (m, 12H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.6, 157.5, 156.0, 142.6, 135.1, 131.8, 129.3, 128.9, 128.4, 118.4, 71.4, 70.9, 70.2, 69.2, 49.9, 24.8, 22.3, 22.2 ppm. **HRMS (ESI):** Calcd for $C_{23}H_{29}N_3O_5$, $(M+Na)^+$: 450.20049; Found: 450.20062.

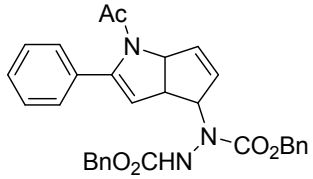
Di-*tert*-butyl 1-(1-acetyl-2-phenyl-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3ca**)



Yield: 83 mg, 68%; off white coloured solid; mp: 120-130 °C; R_f: 0.70 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3291, 3063, 3032, 2957, 1956, 1883, 1715, 1655, 1497, 1399, 1317, 1218, 1135, 1048, 737 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.32-7.06 (m, 6H),

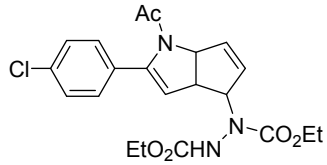
6.13-6.03 (m, 1H), 5.89-5.81 (m, 1H), 5.45-5.06 (m, 3H), 3.68-3.38 (m, 1H), 2.24 (s, 3H), 1.43 (s, 18H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.4, 156.9, 155.5, 142.9, 135.1, 131.8, 129.2, 128.3, 127.9, 118.6, 81.6, 81.2, 71.4, 68.5, 50.1, 28.4, 24.7 ppm. **HRMS (ESI):** Calcd for $C_{25}H_{33}N_3O_5$, $(M+H)^+$: 478.23179; Found: 478.23218.

Dibenzyl-1-(1-acetyl-2-phenyl-1,3a,4,6a-tetrahydrocyclo[b]pyrrol-4-yl)hydrazine1,2 dicarboxylate (**3da**)



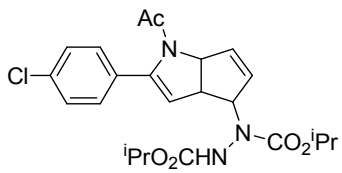
Yield: 74 mg, 65%; colourless viscous liquid; R_f: 0.57 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3311, 2978, 2933, 1706, 1627, 1485, 1450, 1257, 1164, 1050, 940, 861, 763 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.96-7.76 (m, 1H), 7.35-7.25 (m, 15H), 6.11-6.02 (m, 1H), 5.82-5.75 (m, 1H), 5.43-5.12 (m, 7H), 3.68-3.39 (m, 1H), 2.44 (s, 3H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.7, 157.7, 156.3, 142.8, 137.5, 136.1, 134.9, 131.1, 129.6, 129.1, 128.6, 117.8, 71.4, 70.0, 68.6, 67.8, 50.1, 24.5 ppm.
HRMS (ESI): Calcd for $C_{31}H_{29}N_3O_5$, $(M+H)^+$: 546.20049; Found: 546.20087.

Diethyl-1-(1-Acetyl-2-(4-chlorophenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3ab**)



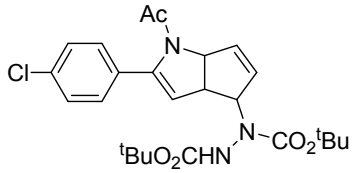
Yield: 104 mg, 72%; Pale yellow viscous liquid; R_f: 0.40 (hexane/ethyl acetate = 2:3). **IR (neat) ν_{max}:** 3294, 3059, 2982, 2935, 2347, 1708, 1655, 1589, 1490, 1382, 1226, 1174, 1093, 933, 826 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 7.31 (d, J = 5.5 Hz, 2H), 7.21 (d, J = 5.5 Hz, 2H), 6.55-6.40 (m, 1H), 6.15 (s, 1H), 5.84-5.64 (m, 2H), 5.30-5.18 (m, 2H), 4.21-4.17 (m, 4H), 3.62-3.35 (m, 1H), 1.69 (s, 3H), 1.30-1.25 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 168.9, 156.4, 155.4, 140.1, 134.6, 132.2, 128.7, 128.6, 118.0, 70.5, 68.5, 62.6, 62.1, 48.2, 24.9, 14.6, 14.4 ppm.
HRMS (ESI): Calcd for $C_{21}H_{24}ClN_3O_5$, $(M+Na)^+$: 456.1302; Found: 456.1295.

Diisopropyl-1-(1-Acetyl-2-(4-chlorophenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3bb**)



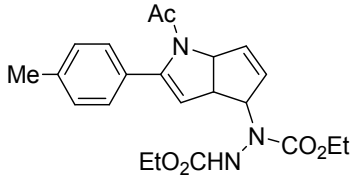
Yield: 92 mg, 67%; Yellow viscous liquid; R_f: 0.54 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3287, 2983, 2940, 1688, 1659, 1386, 1309, 1260, 1108, 1038, 825 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.31-7.24 (m, 5H), 6.12-6.07 (m, 1H), 5.87-5.82 (m, 1H), 5.37 (s, 2H), 5.14-5.08 (m, 1H), 4.86-4.83 (m, 2H), 3.70-3.43 (m, 1H),2.30 (s, 3H), 1.29-1.22 (m, 12H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 167.3, 157.5, 156.1, 136.7, 135.4, 133.8, 131.5, 130.6, 129.7, 129.3, 118.4, 71.4, 70.9, 70.8, 70.2, 55.1, 23.0, 22.2, 22.1 ppm.
HRMS (ESI): Calcd for $C_{23}H_{28}ClN_3O_5$, $(M+Na)^+$: 484.16152; Found: 484.16234.

Di-tert-butyl 1-(1-acetyl-2-(4-chlorophenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3cb**)



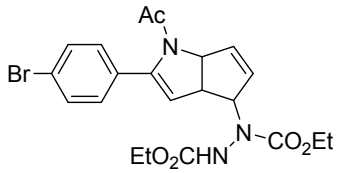
Yield: 85 mg, 65%; Pale yellow liquid; R_f: 0.66 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3298, 3045, 2976, 2943, 2347, 1698, 1655, 1584, 1492, 1382, 1226, 861 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.31-7.08(m, 5H), 6.11-6.05 (m, 1H), 5.88-5.80 (m, 1H), 5.49-5.36 (m, 2H), 5.11-5.10 (m, 1H), 3.72-3.47 (m, 1H), 2.30 (s, 3H), 1.43 (s, 15H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.4, 156.8, 155.5, 133.9, 132.0, 130.6, 130.5, 129.7, 129.4, 129.0, 118.3, 81.5, 81.2, 71.4, 68.2, 55.1, 28.6, 28.5, 23.0 ppm.
HRMS (ESI): Calcd for $C_{25}H_{32}ClN_3O_5$, $(M+Na)^+$: 512.19282; Found: 512.19362.

Diethyl1-(1-acetyl-2-(p-tolyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3ac**)



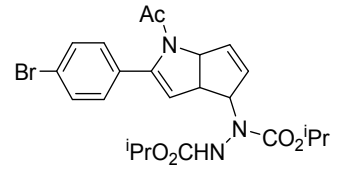
Yield: 76 mg, 55%; Colourless viscous liquid; R_f: 0.43 (hexane/ethyl acetate = 2:3). **IR (neat) ν_{max}:** 3293, 2982, 2934, 2873, 1710, 1656, 1511, 1406, 1317, 1257, 1099, 1061, 825, 760 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.39 (brs, 1H), 7.19-7.07 (m, 4H), 6.07-6.06 (m, 1H), 5.86-5.82 (m, 1H), 5.45-5.13 (m, 3H), 4.11-4.07 (m, 4H), 3.66-3.41 (m, 1H), 2.32 (s, 3H), 2.25 (s, 3H), 1.23-1.19 (m, 6H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.4, 157.8, 156.5, 142.5, 135.0, 132.1, 131.3, 129.9, 128.1, 126.6, 117.1, 71.4, 69.6, 63.2, 62.6, 50.0, 24.4, 21.3, 14.8 ppm.
HRMS (ESI): Calcd for $C_{22}H_{27}N_3O_5$, $(M+Na)^+$: 372.18451; Found: 372.18520.

Diethyl-1-(1-acetyl-2-(4-bromophenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine 1,2 dicarboxylate (**3ad**)



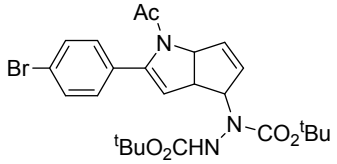
Yield: 119 mg, 75%; White solid; mp: 110-120°C R_f: 0.33 (hexane/ethyl acetate = 2:3). **IR (neat) ν_{max}:** 3294, 2982, 2938, 2309, 1711, 1630, 1387, 1264, 1167, 1035, 958, 800, 737 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.87-7.85 (m, 1H), 7.62-7.47 (m, 3H), 7.17 (s, 1H), 6.08 (s, 1H), 5.87-5.82 (m, 1H), 5.41-5.38 (m, 2H), 5.12-5.07 (m, 1H), 4.12-4.08 (m, 4H), 3.70-3.39 (m, 1H), 2.32 (s, 3H), 1.26-1.20 (m, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 170.5, 156.5, 135.6, 133.1, 132.4, 131.9, 129.5, 128.4, 67.2, 62.6, 62.2, 62.1, 55.7, 23.3, 14.4 ppm.
HRMS (ESI): Calcd for $C_{21}H_{24}BrN_3O_5$, $(M+Na)^+$: 500.07970; Found: 500.08072.

Diisopropyl-1-(1-acetyl-2-(4-bromophenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine 1,2 dicarboxylate (**3bd**)



Yield: 106 mg, 70%; White solid; mp: 110-120°C R_f: 0.55 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3294, 3064, 2982, 2938, 2309, 1711, 1630, 1387, 1264, 1167, 1035, 958, 800, 737 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.58-7.50 (m, 4H), 7.33-7.23 (m, 1H), 6.13-6.10 (m, 1H), 5.89-5.83 (m, 1H), 5.47- 5.38 (m, 2H), 5.16 (brs, 1H), 4.86-4.85 (m, 2H), 3.76-3.48 (m, 1H), 2.25 (s, 3H), 1.26-1.18 (m, 12H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.4, 157.5, 156.1, 141.6, 136.0, 134.6, 131.7, 129.7, 124.5, 119.5, 71.4, 70.8, 70.3, 61.0, 50.5, 24.0, 22.3, 22.2 ppm.
HRMS (ESI): Calcd **for** $C_{23}H_{28}BrN_3O_5$, $(M+Na)^+$: 528.11100; Found: 528.11010.

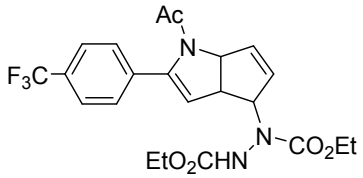
Di-*tert*-butyl -1-(1-acetyl-2-(4-bromophenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine 1,2 dicarboxylate (**3cd**)



Yield: 98 mg, 68%; Pale yellow solid; mp: 120-125 °C; R_f: 0.73 (hexane/ethyl acetate = 4:1). **IR (neat) ν_{max}:** 3294, 3059, 2982, 2935, 2347, 1708, 1655, 1589, 1490, 1382, 1226, 1174, 1093, 933, 826 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.87-7.82 (m, 2H), 7.67-7.63 (m, 2H), 7.29-7.04 (m, 1H), 6.35-6.31 (m, 1H), 5.93-5.70 (m, 2H), 5.23-4.97 (m, 2H), 3.39-3.20 (m, 1H), 2.26 (m, 3H), 1.41 (s, 18H). **^{13}C NMR (125 MHz, CD_3CN):** δ 170.5, 157.0, 155.3, 141.5, 137.2, 134.2, 132.8, 131.5, 131.4, 130.7, 129.0, 119.0, 81.8, 81.6, 69.9, 66.8, 55.2, 28.4, 23.0 ppm.

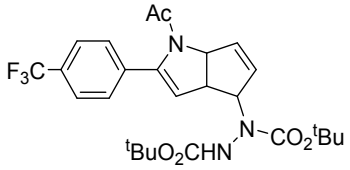
HRMS (ESI): Calcd for $C_{25}H_{32}BrN_3O_5$, $(M+H)^+$: 534.16036; Found: 534.15990

Di-ethyl-1-(1-acetyl-2-(4-(triflouromethyl)phenyl)-1,3a,4,6a tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3ae**)



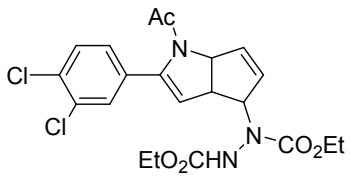
Yield: 110 mg, 71%; Pale yellow viscous liquid; R_f: 0.32 (hexane/ethyl acetate = 1:1 **IR (neat)** ν_{max}**:** 3307, 3069, 2976, 2933, 1708, 1652, 1484, 1391, 1328, 1262, 1167, 1071, 802, 760 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.57-7.48 (m, 4H), 7.31-7.17 (m, 1H), 6.11-6.10 (m, 1H), 5.87-5.83 (m, 1H), 5.47-5.14 (m, 3H), 4.11-4.08 (m, 4H), 3.74-3.48 (m, 1H), 2.27.(s, 3H), 1.24-1.18 (m, 6H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.7, 157.9, 156.6, 141.5, 136.0, 134.7, 131.8, 130.4, 126.4, 125.2, 124.2, 119.7, 71.5, 69.6, 63.3, 62.7, 51.1, 24.1, 14.8, 14.5 ppm.
HRMS (ESI): Calcd for $C_{22}H_{24}F_3N_3O_5$, $(M+Na)^+$: 467.16681; Found: 467.16754.

Di-tert-butyl-1-(1-acetyl-2-(4-(triflouromethyl)phenyl)-1,3a,4,6a tetrahydrocyclopenta[b] pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3ce**)



Yield: 89 mg, 63%; pale yellow solid; mp: 170-180 °C; R_f: 0.65 (hexane/ethyl acetate = 4:1). **IR (neat)** ν_{max}**:** 3306, 3049, 2965, 2944, 1698, 1654, 1456, 1371, 1368, 808 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.60-7.50(m, 4H), 7.19-7.09 (m, 1H), 6.18-6.09 (m, 1H), 5.89-5.82 (m, 1H), 5.47-5.39 (m, 2H), 5.16-5.09 (m, 1H), 3.74-3.46 (m, 1H), 2.29 (s, 3H), 1.43 (s, 18H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.4, 156.9, 155.3, 141.7, 136.2, 135.2, 132.0, 129.4, 126.4, 124.2, 119.8, 81.8, 81.3, 71.5, 68.6, 50.0, 28.4, 23.9 ppm.
HRMS (ESI): Calcd for $C_{26}H_{32}F_3N_3O_5$, $(M+Na)^+$: 546.21918; Found: 546.22032.

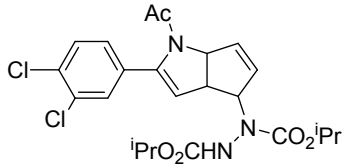
Diethyl-1-(1-acetyl-2-(3-nitrophenyl)-1,3a,4,6atetrahydrocyclopenta[b]pyrrol4-yl)hydrazine-1,2-dicarboxylate (**3af**)



Yield: 118 mg, 76%; Colourless viscous liquid; R_f: 0.40 (hexane/ethyl acetate = 2:3). **IR (neat)** ν_{max}**:** 3488, 3119, 3075, 3015, 2365, 2333, 1762, 1730, 1590, 1409, 1266, 1060 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.50-7.22 (m, 4H), 6.12-6.07 (m, 1H), 5.86-5.81 (m,

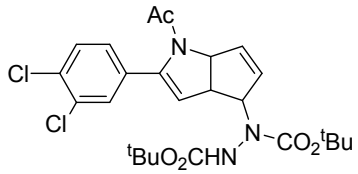
1H), 5.45-5.14 (m, 3H), 4.11-4.05 (m, 4H), 3.78-3.51 (m, 1H), 2.13 (s, 3H), 1.22 (t, *J* = 7.5Hz, 6H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 168.2, 157.9, 156.4, 139.7, 135.1, 134.2, 131.6, 130.3, 129.4, 128.7, 127.5, 118.7, 70.8, 69.5, 63.2, 62.6, 51.0, 23.3, 14.8 ppm.
HRMS (ESI): Calcd for $C_{21}H_{23}Cl_2N_2O_5$, $(M+Na)^+$: 490.09125; Found: 490.09133.

Diisopropyl-1-(1-acetyl-2-(3,4-dichlorophenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate **(3bf)**



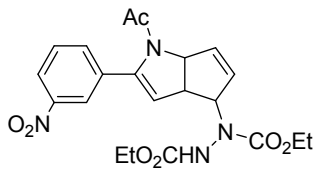
Yield: 106 mg, 72%; Colourless viscous liquid; R_f: 0.60 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3277, 3085, 2961, 2936, 2390, 1719, 1672, 1530, 1367, 1349, 1144, 1108, 1030, 942, 804 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.50-7.37 (m, 2H), 7.26-7.16 (m, 2H), 6.17-6.08 (m, 1H), 5.85-5.83 (m, 1H), 5.45-5.13 (m, 3H), 4.85 (s, 2H), 3.80-3.56 (m, 1H), 2.12 (s, 3H), 1.22 (s, 12H) ppm.**^{13}C NMR (125 MHz, CD_3CN):** δ 168.2, 157.5, 156.1, 139.7, 138.4, 136.2, 134.2, 132.6, 131.6, 129.4, 128.7, 127.5, 119.3, 70.9, 70.8, 70.2, 69.2, 51.2, 23.2, 22.3, 22.2 ppm.
HRMS (ESI): Calcd for $C_{23}H_{27}Cl_2N_3O_5$, $(M+Na)^+$: 518.12255; Found: 518.12344.

Di-*tert*-butyl 1-(1-acetyl-2-(3,4-dichlorophenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3cf**)



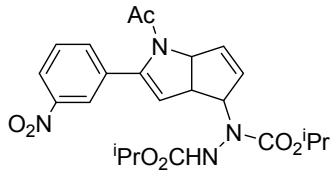
Yield: 94 mg, 67%; Colourless viscous liquid; R_f: 0.65 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3297, 3086, 2961, 2936, 2390, 1690, 1672, 1530, 1368, 1361, 1154, 1108, 1030, 944, 808 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.50-7.09 (m, 4H), 6.15-6.09 (m, 1H), 5.91-5.83 (m, 1H), 5.47-5.26 (m, 2H), 5.13-5.02 (m, 1H) 3.82-3.49 (m, 1H), 2.12 (s, 3H), 1.42 (m, 18H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 167.7, 156.8, 155.2, 139.6, 138.3, 135.0, 134.2, 133.4, 131.6, 129.1, 127.2, 119.3, 81.9, 81.3, 70.8, 68.5, 51.1, 28.1, 23.3 ppm.
HRMS (ESI): Calcd for $C_{25}H_{31}Cl_2N_3O_5$, $(M+Na)^+$: 546.15385; Found: 546.15445.

Diethyl-1-(1-acetyl-2-(3-nitrophenyl)-1,3a,4,6atetrahydrocyclopenta[b]pyrrol4-yl)hydrazine-1,2-dicarboxylate (**3ag**)



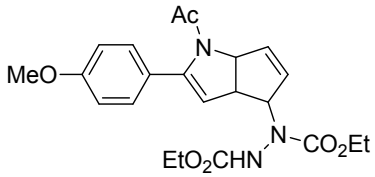
Yield: 123 mg, 83%; Pale yellow liquid; R_f: 0.30 (hexane/ethyl acetate = 2:3). **IR (neat) ν_{max}:** 3287, 3086, 2934, 1650, 1616, 1530, 1256, 810 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 8.11-8.04 (m, 2H), 7.64-7.34 (m, 3H), 6.17 (s, 1H), 5.91-5.85 (m, 1H), 5.55-5.41 (m, 2H), 5.17-5.10 (m, 1H), 4.12-4.08 (m, 4H), 3.77-3.52 (m, 1H), 2.29 (m, 3H), 1.24-1.21 (m, 6H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.4, 157.9, 156.4, 148.8, 136.8, 131.7, 129.6, 122.1, 120.3, 71.4, 69.1, 63.2, 62.6, 50.6, 23.9, 14.9, 14.8 ppm.
HRMS (ESI): Calcd for $C_{21}H_{24}N_4O_7$, $(M+Na)^+$: 467.15427; Found: 467.15365.

Diisopropyl-1-(1-acetyl-2-(3-nitrophenyl)-1,3a,4,6atetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3bg**)



Yield: 110 mg, 78%; Pale yellow solid; mp: 120-140 °C; R_f: 0.30 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3297, 3075, 2961, 2936, 2390, 1710, 1672, 1530, 1367, 1349, 1144, 1108, 1030, 942, 804 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 8.10-8.03 (m, 2H), 7.63-7.51 (m, 2H), 7.31 (brs, 1H), 6.16-6.12 (m, 1H), 5.89-5.84 (m, 1H), 5.55-5.17 (m, 3H), 4.86-4.85 (m, 2H), 3.77-3.52 (m, 1H), 2.31 (s, 3H), 1.23-1.18 (m, 12H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.6, 157.6, 156.0, 148.9, 141.2, 136.7, 133.9, 132.0, 130.0, 123.1, 122.2, 120.4, 71.5, 70.9, 70.3, 69.0, 51.1, 24.0, 22.3, 22.2 ppm.
HRMS (ESI): Calcd for $C_{23}H_{28}N_4O_7$, $(M+Na)^+$: 495.18557; Found: 495.18637.

Diethyl 1-(1-acetyl-2-(4-methoxyphenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine-1,2-dicarboxylate (**3ah**)



Yield: 57 mg, 40%; Pale yellow liquid; R_f: 0.43 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3297, 3117, 2961, 2601, 1700, 1655, 1530, 1252, 1057, 1030, 842, 680, 647 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.34-7.19 (m, 3H), 7.03-6.88 (m, 2H), 6.14-6.02 (m, 1H), 5.86-5.82 (m, 1H), 5.49-5.13 (m, 3H), 4.11-4.04 (m, 4H), 3.78 (s, 3H), 3.62-3.33 (m, 1H), 2.19 (s, 3H), 1.22 (t, J = 7 Hz, 6H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.4, 160.7, 157.6, 156.5, 142.4, 135.2, 131.4, 129.6, 128.1, 127.4, 116.5, 114.5, 71.2, 69.8, 63.2, 62.6, 56.0, 49.9, 24.7, 14.9, 14.8 ppm. **HRMS (ESI)**: Calcd for $C_{22}H_{27}N_3O_6$, $(M+H)^+$: 430.19781; Found: 430.19711.

3. General procedure for the Rh-catalyzed desymmetrization of diazabicycles with aromatic enamides

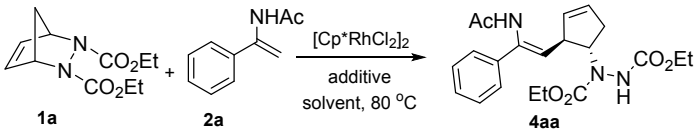
A mixture of azabicyclic olefin **1a** (50 mg, 0.208 mmol), N-acetyl enamide **2a** (34 mg, 0.208 mmol), $[RhCl_2Cp^*]_2$ (6 mg, 0.010 mmol), $Cu(OAc)_2.H_2O$ (83 mg, 0.416 mmol) were

weighed into a Schlenk tube and degassed for 10 minutes. Dry acetonitrile (2 mL) was added and the reaction mixture was purged with argon and allowed to stir at 80 ^{o}C for 12 hours. The solvent was evaporated in *vacuo* and the residue on activated neutral alumina column chromatography with hexane-ethylacetate mixtures yielded 3,4-*trans* disubstituted cyclopentene.

Optimization studies for suitable catalyst system for Rh-catalyzed C-N bond cleavage of alkene **1a** with enamide **2a**

Detailed optimization studies were carried out to find out the best condition for the transformation (Table 2). The solvent optimisation revealed acetonitrile as the most effective reaction medium. Use of other solvents such as DMSO, DMF, DCE, MeOH and xylene resulted in lower yields. The efficiency of various additives such as NaOAc, CsOAc, $Cu(OAc)_2.H_2O$ and AgOAc was tested, from which $Cu(OAc)_2.H_2O$ gave the highest yield. Among the additives tested, Ag_2CO_3 was found to be ineffective for the present transformation. Ultimately, **1a** (1 equiv.) and **2a** (1 equiv.) in the presence of $[RhCl_2Cp^*]_2$ (5.0 mol %) and $Cu(OAc)_2.H_2O$ (2.0 equiv.) in CH_3CN at 80 ^{o}C for 12 hour was found to be the optimal condition for the reaction.

Table 2: Optimization studies



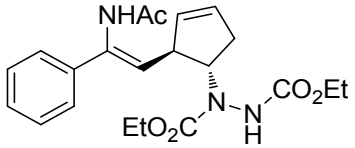
1a 2a 4aa

Entry	Catalyst	Additive	Solvent	Yield
1	$(RhCp^*Cl_2)_2$	$Cu(OAc)_2.H_2O$	DMF	40
2	,,	,,	MeOH	45
3	,,	,,	O-Xylene	15
4	,,	,,	DCE	45
5	,,	,,	DMSO	35
6	,,	,,	CH_3CN	88
[a]7	,,	,,	Toluene	52
[b]8	,,	,,	CH_3CN	50
9	,,	AgOAc	,,	65
10	,,	NaOAc	,,	58
11	,,	CsOAc	,,	46
12	,,	Ag_2CO_3	,,	Trace

Reaction Conditions: **1a** (1.0 equiv.), **2a** (1.0 equiv.), $(RhCp^*Cl_2)_2$ (5 mol %), $Cu(OAc)_2.H_2O$ (2.0 equiv.), solvent (2 mL), 80 ^{o}C, 12 h, [a]100 ^{o}C, [b]$Cu(OAc)_2.H_2O$ (1.0 equiv).

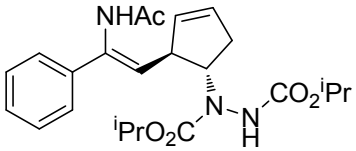
Characterisation of the products

Diethyl 1-((1S,2R)-2-((Z)-2-acetamido-2-phenylvinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4aa**)



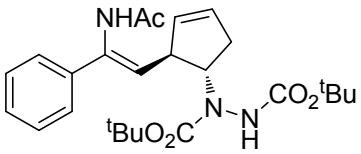
Yield: 73 mg, 88%; Colourless viscous liquid; R_f: 0.39 (hexane/ethyl acetate = 2:3). **IR (neat) ν_{max}:** 3284, 2979, 2856, 1708, 1498, 1265, 1106, 954, 813 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 9.06-9.79 (m, 1H), 7.45-7.14 (m, 6H), 5.77-5.71 (m, 1H), 5.53-5.38(m, 2H), 4.67-4.66 (m, 1H), 4.21-4.08 (m, 4H), 3.75 (s, 1H), 2.48 (brs, 2H), 2.09 (s, 3H), 1.32-1.00 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 169.6, 158.0, 156.0, 138.0, 136.3, 132.8, 132.1, 129.9, 128.7, 128.1, 127.6, 125.7, 124.0, 119.8, 65.2, 62.7, 62.4, 46.7, 34.4, 22.9, 14.4, 14.3 ppm.**HRMS (ESI):** Calcd for $C_{21}H_{27}N_3O_5$, $(M+H)^+$: 402.20290; Found: 402.20322.

Diisopropyl 1-((1S,2R)-2-((Z)-2-acetamido-2-phenylvinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4ba**)



Yield: 62 mg, 78%; Colourless viscous liquid; R_f: 0.51 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3286, 2981, 2933, 1710, 1514, 1408, 1273, 1108, 956, 819 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 9.04-8.81 (m, 1H), 7.39-7.37 (m, 2H), 7.28-7.26 (m, 2H), 7.22-7.20 (m, 1H), 6.57 (brss, 1H), 5.78-5.38 (m, 3H), 4.99-4.67 (m, 3H), 3.77 (s, 1H) 2.52-2.44 (m, 2H), 2.11 (s, 3H), 1.32-1.17 (m, 12H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 169.6, 158.2, 156.1, 136.9, 135.6, 133.2, 132.8, 128.8, 128.3, 127.0, 124.3, 71.1, 70.9, 65.2, 46.9, 34.4, 23.5, 23.3, 22.9 ppm. **HRMS (ESI):** Calcd for $C_{23}H_{31}N_3O_5$, $(M+Na)^+$: 452.21614; Found: 452.21500.

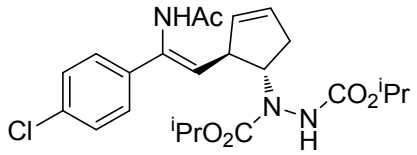
Di-tert-butyl 1-((1S,2R)-2-((Z)-2-acetamido-2-phenylvinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4ca**)



Yield: 58 mg, 75%; Off white coloured solid; mp: 165-175 °C; R_f: 0.70 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3292, 3056, 2979, 2932, 1702, 1686, 1448, 1285, 1100, 1054, 951, 860 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 9.20-8.98 (m, 1H), 7.48-7.40 (m, 2H), 7.29-7.26 (m, 2H), 7.23-7.20 (m, 1H), 6.34 (s, 1H), 5.81-5.74 (m, 1H), 5.58-5.57 (m, 1H), 5.36-

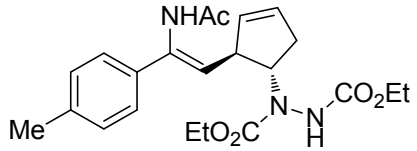
5.34 (m, 1H), 4.70-4.61 (m, 1H), 3.83-3.78 (m, 1H), 2.57-2.47 (m, 2H), 2.15 (s, 3H), 1.52 (s, 18H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** 169.7, 157.4, 154.8, 138.3, 136.4, 132.9, 128.9, 128.1, 127.4, 125.7, 124.2, 81.9, 81.8, 65.6, 47.4, 34.2, 28.2, 28.0, 23.1 ppm. **HRMS (ESI):** Calcd for $C_{25}H_{35}N_3O_5$, $(M+Na)^+$: 480.24744; Found: 480.24691

Diethyl-1-((1S,2R)-2-((Z)-2-acetamido-2-(4-chlorophenyl)vinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4ab**)



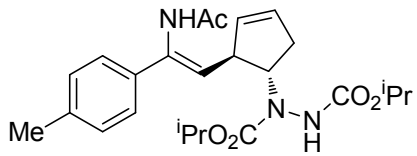
Yield: 64 mg, 74%; Yellow coloured liquid R_f: 0.58 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3284, 2982, 2936, 1706, 1679, 1468, 1373, 1252, 1107, 1044, 954, 829 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 9.25-9.02 (m, 1H), 7.30-7.28 (m, 2H), 7.22-7.21 (m, 2H), 7.15-7.11 (m, 1H), 5.71 (s, 1H), 5.51-5.32 (m, 2H), 4.97-4.65 (m, 3H), 3.73 (s, 1H), 2.48-2.43 (m, 2H), 2.09 (s, 3H), 1.31-0.88 (m, 12H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** 169.7, 157.7, 155.4, 135.5, 133.0, 132.4, 129.2, 128.9, 128.5, 128.3, 128.1, 127.0, 124.6, 70.4, 64.8, 47.0, 34.2, 22.8, 22.0 ppm. **HRMS (ESI):** Calcd for $C_{23}H_{30}ClN_3O_5$, $(M+Na)^+$: 486.17717; Found: 486.17688.

Diethyl-1-(1-acetyl-2-(4-bromophenyl)-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)hydrazine 1,2 dicarboxylate (**4ac**)



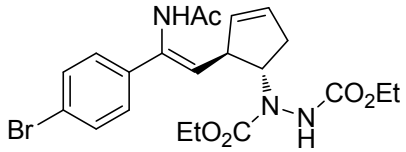
Yield: 62 mg, 72%; viscous liquid, 0.36 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3291, 2982, 2934, 1717, 1708, 1510, 1250, 1060, 951, 817 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 8.93-8.66 (m, 1H), 7.27-7.26 (m, 2H), 7.16-7.12 (m, 1H), 7.08-7.07 (m, 1H), 6.77 (s, 1H), 5.75-5.72 (m, 1H), 5.56-5.35 (m, 2H), 4.68-4.67 (m, 1H), 4.22-4.10 (m, 4H), 3.86-3.76 (m, 1H), 2.51 (s, 2H), 2.32 (s, 3H), 2.10 (s, 3H), 1.33-1.26 (m, 6H) ppm.**^{13}C NMR (125 MHz, $CDCl_3$):** δ 169.5, 157.9, 156.1, 137.0, 135.2, 133.0, 131.6, 128.8, 125.6, 65.2, 62.7, 60.4, 51.1, 34.4, 23.0, 21.2, 14.4, 14.2 ppm. **HRMS (ESI):** Calcd for $C_{22}H_{29}N_3O_5$, $(M+Na)^+$: 438.20049; Found: 438.19901

Diisopropyl 1-((1S,2R)-2-((Z)-2-acetamido-2-(p-tolyl)vinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4bc**)



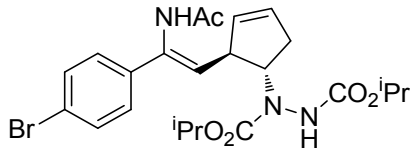
Yield: 58 mg, 70%; Colourless viscous liquid; R_f: 0.57 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3286, 2988, 2934, 1704, 1679, 1468, 1370, 1256, 1107, 1044, 952, 806. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 9.01-8.74 (m, 1H), 7.35-7.27 (m, 2H), 7.13-7.06 (m, 2H), 6.53 (brs, 1H), 5.78-5.72 (m, 1H), 5.57-5.33 (m, 2H), 5.00-4.69 (m, 3H), 3.76 (s, 1H), 2.52-2.51 (m, 2H), 2.32 (s, 3H), 2.11(s, 3H), 1.32-1.19 (m, 12H). **^{13}C NMR (125 MHz, CD_3CN):** δ 171.2, 155.8, 155.5, 136.9, 136.3, 129.1, 125.6, 122.5, 70.3, 64.9, 51.4, 34.4, 29.7, 23.0, 21.9, 21.2. **HRMS (ESI):** Calcd for $C_{24}H_{33}N_3O_5$, $(M+Na)^+$: 466.23179; Found: 466.23286.

Diethyl 1-((1S,2R)-2-((Z)-2-acetamido-2-(4-bromophenyl)vinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4ad**)



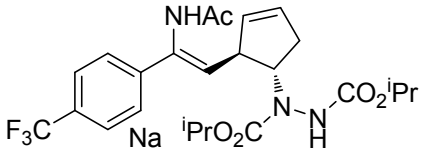
Yield: 84 mg, 84%; Pale yellow solid; mp: 120-125 °C; R_f: 0.33 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3283, 2982, 2934, 1710, 1676, 1587, 1327, 1097, 951, 827 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 9.22-8.90 (m, 1H), 7.41-7.39 (m, 2H), 7.27-7.25 (m, 2H), 6.83 (s, 1H), 5.74 (s, 1H), 5.54-5.29 (m, 2H), 4.70 (s, 1H), 4.29-4.10 (m, 4H), 3.76 (s, 1H), 2.50 (s, 2H), 2.12 (s, 3H), 1.33-1.01 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 169.9, 158.1, 155.8, 137.4, 135.7, 132.4, 131.2, 128.1, 129.1, 127.3, 124.4, 121.3, 65.1, 63.0, 46.8, 34.3, 22.9, 14.4 ppm. **HRMS (ESI):** Calcd for $C_{21}H_{26}BrN_3O_5$, $(M+Na)^+$: 502.09535; Found: 502.09413

Diisopropyl 1-((1S,2R)-2-((Z)-2-acetamido-2-(4-bromophenyl)vinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4bd**)



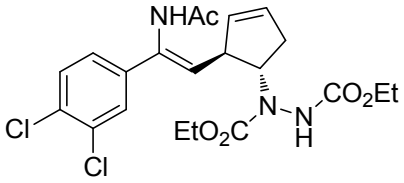
Yield: 69 mg, 73%; Pale yellow solid; mp: 170-175 °C R_f: 0.63 (hexane/ethyl acetate = 1:1 **IR (neat) ν_{max}:** 3286, 2981, 2933, 1708, 1676, 1516, 1489, 1387, 1255, 1107, 1045, 826 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 9.22-9.00 (m, 1H), 7.41-7.39 (m, 1H), 7.25-7.24 (m, 2H), 7.18-7.14 (m, 1H), 6.56-6.51 (m, 1H), 5.79-5.75 (m, 1H), 5.55-5.36 (m, 2H), 5.09-4.70 (m, 3H), 3.77 (s, 1H), 2.52-2.48 (m, 2H), 2.11 (s, 3H), 1.33-0.88 (m, 12H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 169.7, 158.0, 155.4, 137.2, 135.7, 132.7, 131.1, 129.0, 128.2,127.3, 124.4, 121.3, 70.6, 64.8, 46.6, 34.3, 22.8, 22.0, 21.8 ppm. **HRMS (ESI):** Calcd for $C_{23}H_{30}BrN_3O_5$, $(M+Na)^+$: 532.12665; Found: 532.12605.

Diisopropyl-1-((1S,2R)-2-((Z)-2-acetamido-2-(4-(trifluoromethyl)phenyl)vinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4be**)



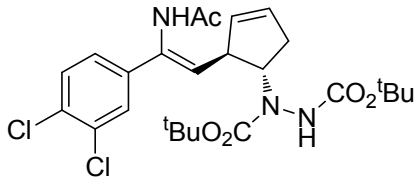
Yield: 83 mg, 76%; Pale yellow solid; mp; 140-150 ^{o}C R_f: 0.55 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3285, 2985, 2931, 1719, 1675, 1516, 1332, 1127, 1072, 952 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 9.29-9.10 (m, 1H), 7.61-7.27 (m, 4H), 6.94-6.75 (m, 1H), 5.83-5.74 (m, 1H), 5.56-5.40 (m, 2H), 5.00-4.71 (m, 3H), 3.78 (s, 1H), 2.56-2.48 (m, 2H), 2.13 (s, 3H), 1.33-1.13 (m, 12H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 169.8, 158.2, 155.4, 139.1, 135.5, 132.3, 130.6, 129.0, 128.4, 125.2, 124.0, 123.0, 122.4, 70.7, 69.9, 65.0, 47.1, 34.4, 22.9, 22.0, 21.9, 20.4 ppm. **HRMS (ESI):** Calcd for $C_{24}H_{30}F_3N_3O_5$, $(M+Na)^+$: 497.21376; Found: 497.21468.

Diethyl 1-((1S,2R)-2-((Z)-2-acetamido-2-(3,4-dichlorophenyl)vinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4af**)



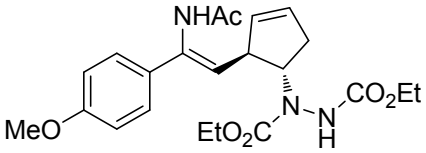
Yield: 83 mg, 85%; Pale yellow liquid; R_f: 0.35 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3284, 2984, 2933, 1719, 1585, 1519, 1472, 1271, 1061, 826 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 9.26 (brs,1H), 7.31-7.27 (m, 2H), 7.19-7.17 (m, 2H), 6.89 (s, 1H), 5.73 (s, 1H), 5.54 (s, 1H), 4.96-4.71 (m, 2H), 4.29-4.14 (m, 4H), 3.77 (s, 1H), 2.49 (s, 2H), 2.03 (s, 3H), 1.35-1.18 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 169.0, 158.2, 158.3, 136.8, 134.7, 134.4, 133.4, 132.6, 132.3, 131.6, 129.1, 126.7, 63.2, 62.8, 46.0, 34.3, 22.6, 14.4 ppm. **HRMS (ESI):** Calcd for $C_{21}H_{25}Cl_2N_3O_5$, $(M+Na)^+$: 492.10690; Found: 492.10760

Di-tert-butyl 1-((1S,2R)-2-((Z)-2-acetamido-2-(3,4-dichlorophenyl)vinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4cf**)



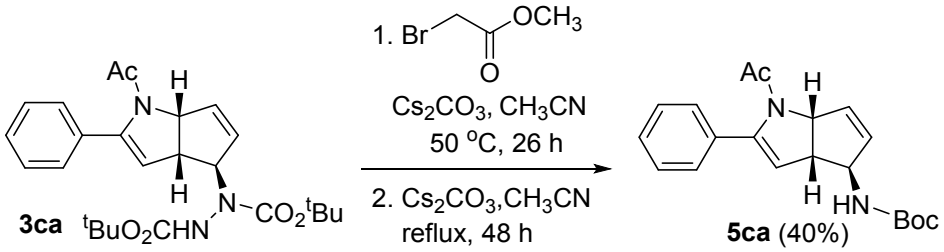
Yield: 69 mg, 78%; Pale yellow solid; mp; 160-170 ^{o}C, R_f: 0.75 (hexane/ethyl acetate = 2:3). **IR (neat) ν_{max}:** 3307, 3069, 2976, 2933, 1708, 1652, 1484, 1391, 1328, 1262, 1167, 1071, 802, 760 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 9.32 (s, 1H), 7.31-7.29 (m, 2H), 7.18-7.17 (m, 1H), 6.32 (s, 1H), 5.80-5.56 (m, 2H), 4.97 (d, J = 10.5 Hz, 1H), 4.79-4.62 (m, 1H), 3.77 (s, 1H), 2.66-2.49 (m, 2H), 2.08 (s, 3H), 1.53-1.46 (m, 18H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 169.1, 156.9, 154.8, 136.8, 134.0, 133.2, 132.7, 131.5, 129.2, 126.7, 125.2, 82.2, 81.9, 63.2, 46.6, 34.1, 29.2, 22.8 ppm. **HRMS (ESI):** Calcd for $C_{25}H_{33}Cl_2N_3O_5$, $(M+Na)^+$: 548.16950; Found: 548.17065.

Diethyl 1-((1S,2R)-2-((Z)-2-acetamido-2-(4-methoxyphenyl)vinyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate (**4ah**)

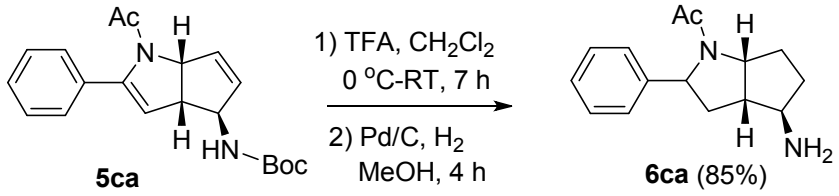


Yield: 61 mg, 68%; Viscous liquid R_f: 0.35 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3278, 2983, 2936, 1713, 1574, 1443, 1250, 1176, 1060, 1030, 833 cm^{-1}. **^{1}H NMR (500 MHz, $CDCl_3$, TMS):** δ 8.95-8.67 (m, 1H), 7.39-7.11 (m, 3H), 6.83-6.78 (m, 2H), 5.76-5.69 (m, 1H), 5.53-5.28 (m, 2H), 4.66 (s, 1H), 4.20-4.08 (m, 4H), 3.81-3.78 (m, 4H), 2.48 (s, 2H), 2.09 (s, 3H), 1.32-1.03 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 171.2, 159.2, 156.1, 136.0, 133.2, 130.6, 128.2, 126.5, 114.3, 63.0, 60.8, 55.1, 46.0, 34.4, 23.1, 21.2, 14.3 ppm. **HRMS (ESI):** Calcd for $C_{22}H_{29}N_3O_6$, $(M+Na)^+$: 454.19541; Found: 454.19651.

4. Typical procedure for the synthesis of pyrrolidine fused cyclopentyl amine derivative



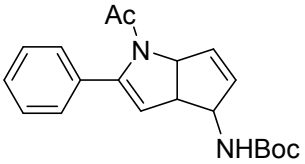
These transformations were done following reported procedures (S. Demerzhan, S. R. Gilbertson, *Tetrahedron Lett.* 2015, **56**, 3633). To a suspension of compound **3ca** (1 g, 0.002 mol) and Cs_2CO_3 (1.788 g, 0.005 mol) in CH_3CN (0.2 M) at 23 °C was added methyl bromoacetate (0.706 g, 0.004 mol). The mixture was heated to 50 °C until the starting material was consumed, as indicated by TLC. The reaction was quenched with saturated NH_4Cl (aq.), extracted with EtOAc, and the extracts were combined and washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography to afford alkylated compound (carbamate) as a viscous liquid which was used without further purification. To the solution of carbamate in CH_3CN (0.2 M) was added Cs_2CO_3 (1.955 g, 0.006 mol) and the mixture was heated at 82 °C until all starting material was consumed, as indicated by TLC. The reaction was quenched with saturated NH_4Cl (aq.), extracted with EtOAc, washed with brine and the combined extracts dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue purified by column chromatography (neutral alumina) give the desired –Boc protected amine **5ca** as a pale yellow solid (0.272 g, 40% yield).



To a solution of Boc-protected amine **5ca** (200 mg, 0.587 mmol) in anhydrous CH_2Cl_2 was added trifluoroacetic acid (1.726 mmol) at 0° C. The mixture was slowly warmed to room temperature and stirred until starting material was consumed, as indicated by TLC. The solvent was removed in *vacuo*, and the residue was dried under high vacuum. The crude product obtained was dissolved in 3 mL methanol and Pd/C (6 mg, 0.059) was added and stirred under hydrogen atmosphere (1 atm) for 4 hours. Reaction mixture was passed through celite and evaporated in *vacuo* to obtain the desired cyclopentyl amine **6ca** as a pale yellow liquid (122 mg, 85%).

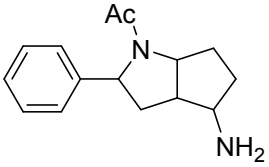
Characterisation of the products

Tert-butyl (1-acetyl-2-phenyl-1,3a,4,6a-tetrahydrocyclopenta[b]pyrrol-4-yl)carbamate **(5ca)**



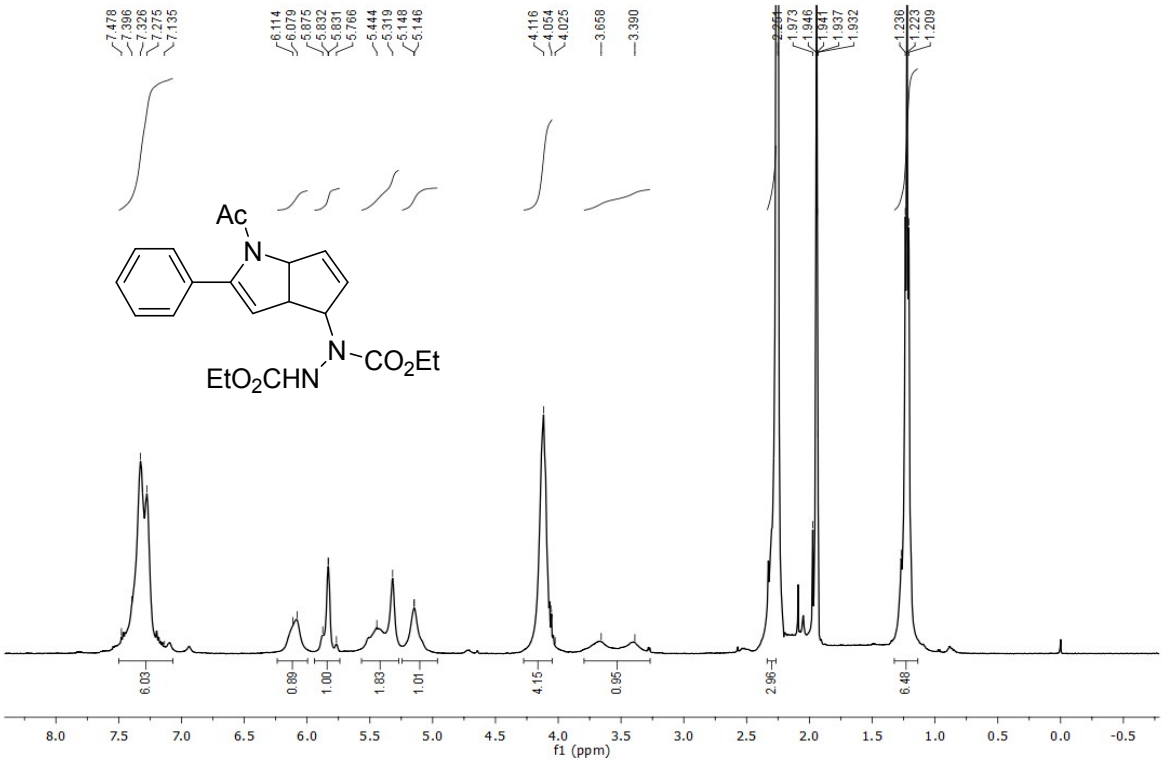
Yield: 272 mg, 40%; Pale yellow solid; mp: 110-120 °C; R_f; 0.35 (hexane/ethyl acetate = 1:1). **IR (neat) ν_{max}:** 3324, 3061, 2977, 1702, 1580, 1449, 1391, 1319, 1168, 1022 862 cm^{-1}. **^{1}H NMR (500 MHz, CD_3CN, TMS):** δ 7.37-7.25 (m, 5H), 6.01 (s, 1H), 5.93-5.91 (m, 1H), 5.48-5.47 (m, 2H), 5.32 (s, 1H), 4.50-4.49 (m, 1H), 3.33 (s, 1H), 2.20 (s, 3H), 1.44 (s, 9H) ppm. **^{13}C NMR (125 MHz, CD_3CN):** δ 169.4, 156.4, 142.6, 135.1, 133.8, 129.2, 128.7, 127.6, 118.9, 79.6, 71.2, 62.2, 52.8, 20.5, 24.3 ppm.
HRMS (ESI): Calcd for $C_{20}H_{24}N_2O_3$, $(M+Na)^+$: 363.16846 ; Found: 363.16859.

1-(4-amino-2-phenylhexahydrocyclopenta[b]pyrrol-1(2H)-yl)ethanone (**6ca**)

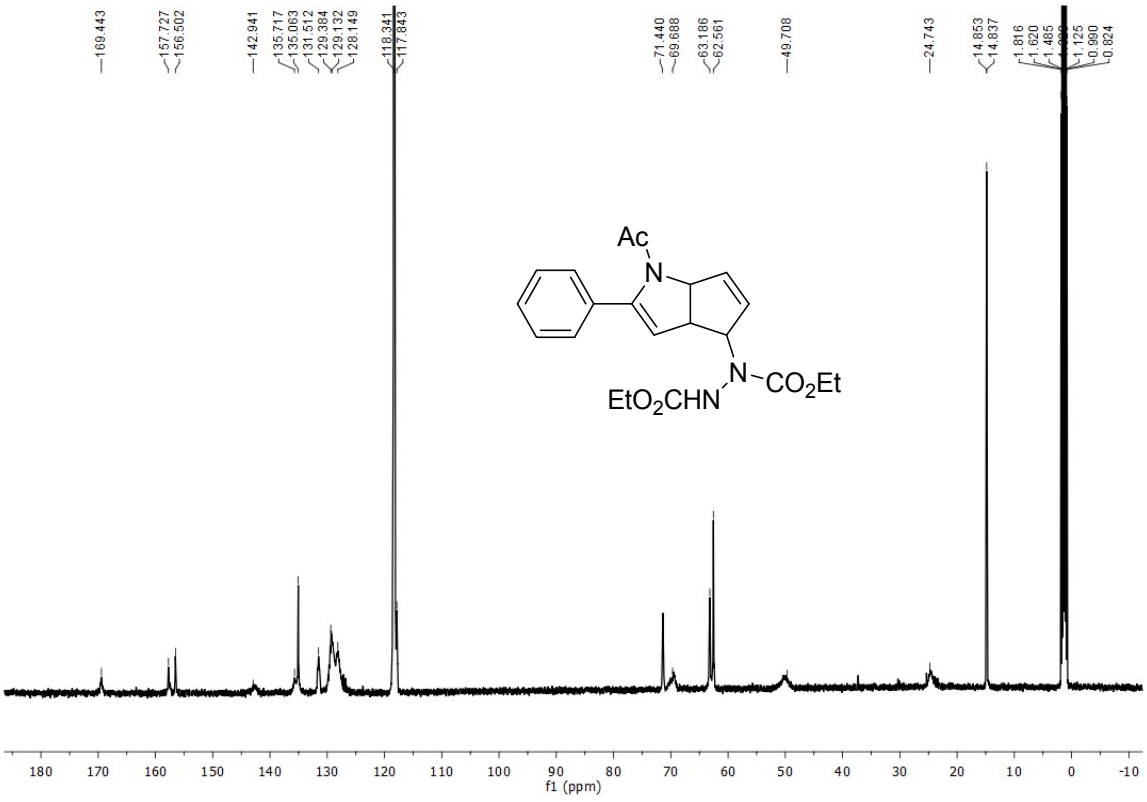


Yield: 122 mg, 85%; Pale yellow viscous liquid; **IR (neat) ν_{max}:** 3290, 2954, 2924, 2853, 1715, 1672, 1448, 1292, 1181, 1133 cm^{-1}. **^{1}H NMR (500 MHz, MeOD, TMS):** δ 8.01 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 4.52-4.51 (m, 1H), 3.51-3.50 (m, 1H), 3.43 (dd, J_1 = 6.5 Hz, J_2 = 23.5 Hz, 1H), 3.13 (dd, J_1 = 8 Hz, J_2 = 18.5 Hz, 1H), 2.76-2.74 (m, 1H), 2.36-2.14 (m, 3H), 1.88 (s, 3H), 1.72-1.71 (m, 2H) ppm. **^{13}C NMR (125 MHz, MeOD):** δ 171.8, 136.6, 133.3, 128.4, 127.8, 55.4, 51.7, 42.6, 37.1, 29.3, 28.1, 21.1 ppm. **HRMS (ESI):** Calcd for $C_{15}H_{20}N_2O$, $(M+H)^+$: 245.16539; Found: 245.16576.

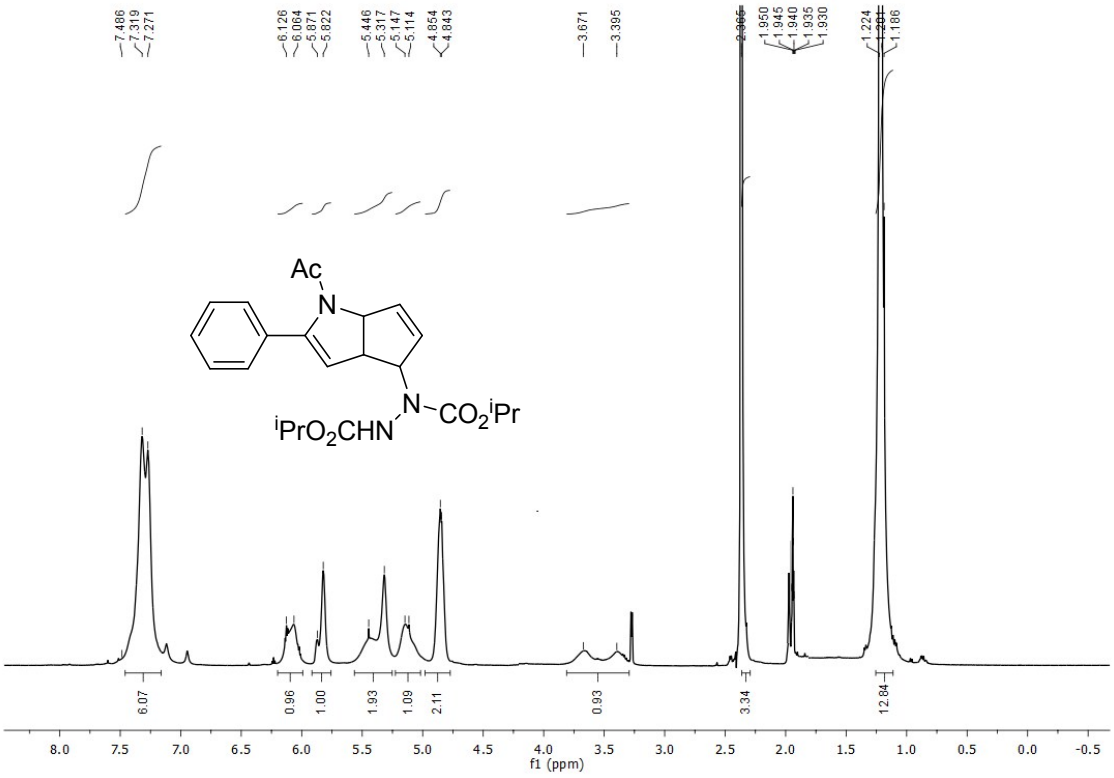
5. ^{1}H NMR & ^{13}C NMR Spectra



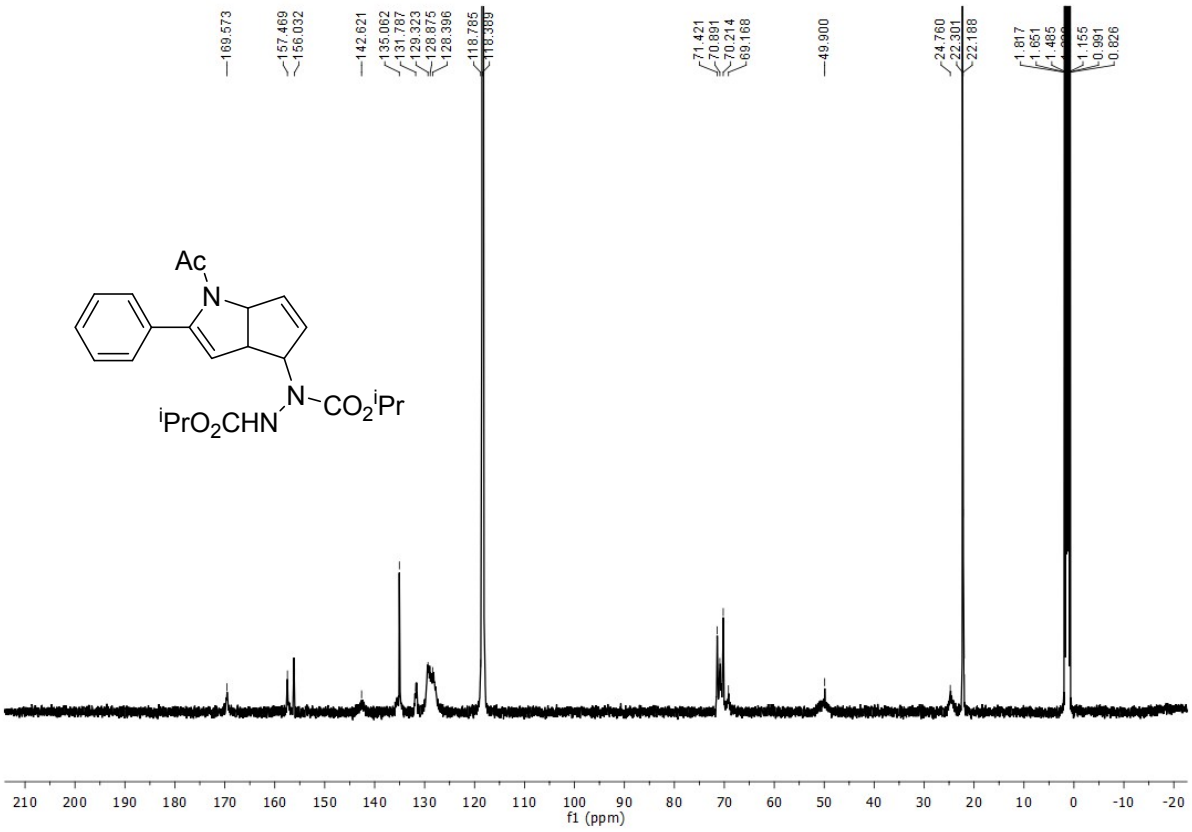
^{1}H NMR of **3aa**



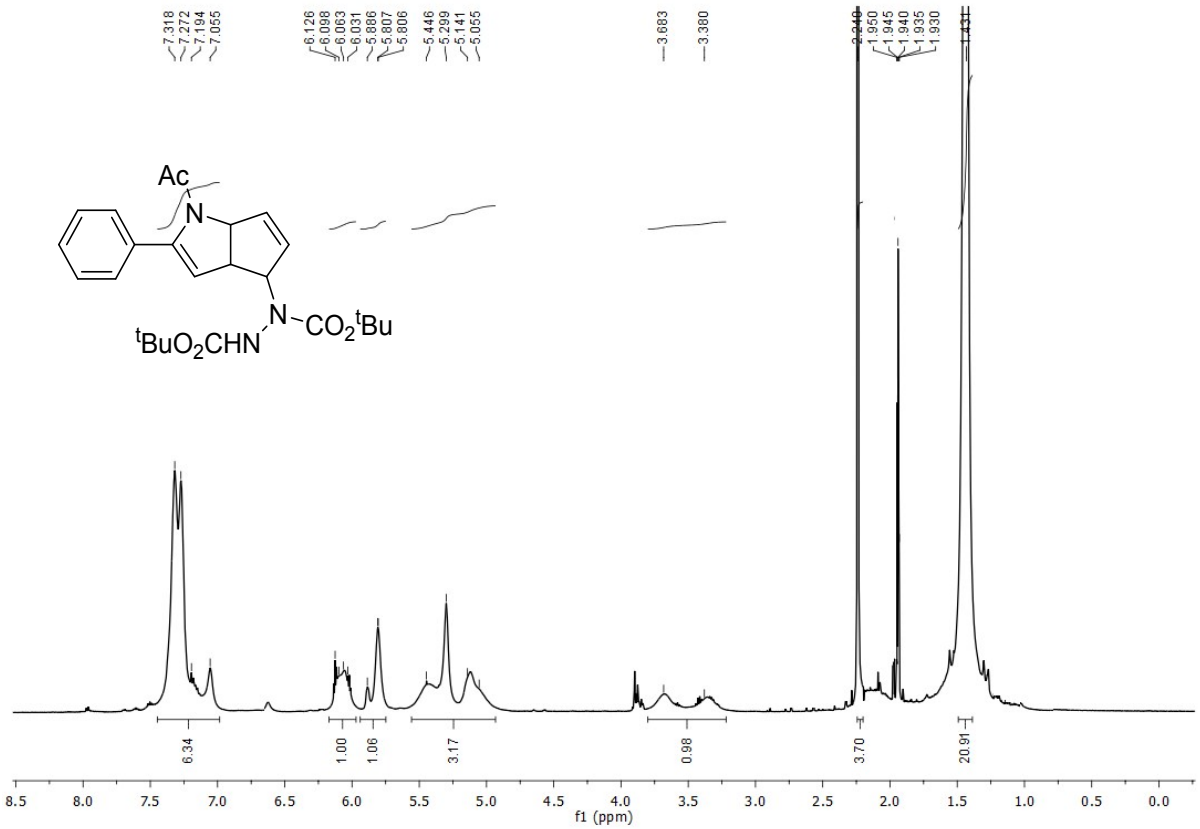
^{13}C NMR of **3aa**



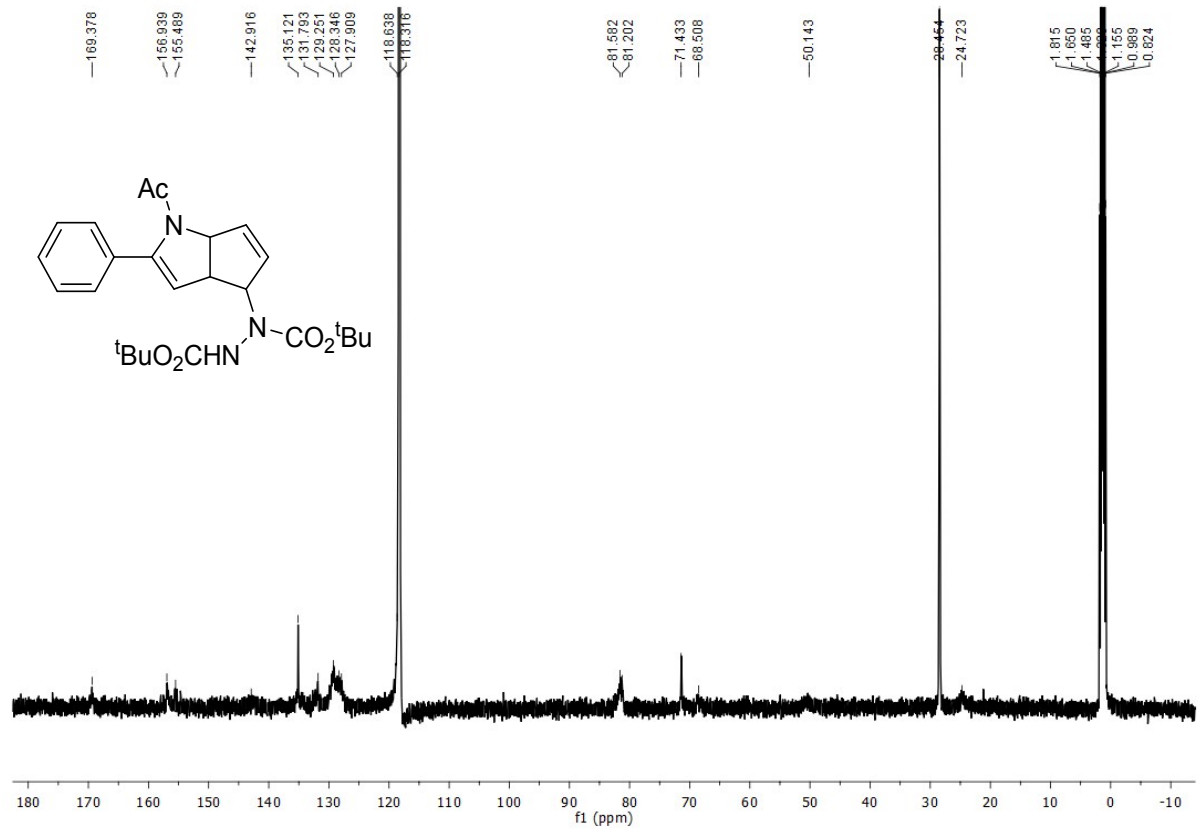
^{1}H NMR of **3ba**



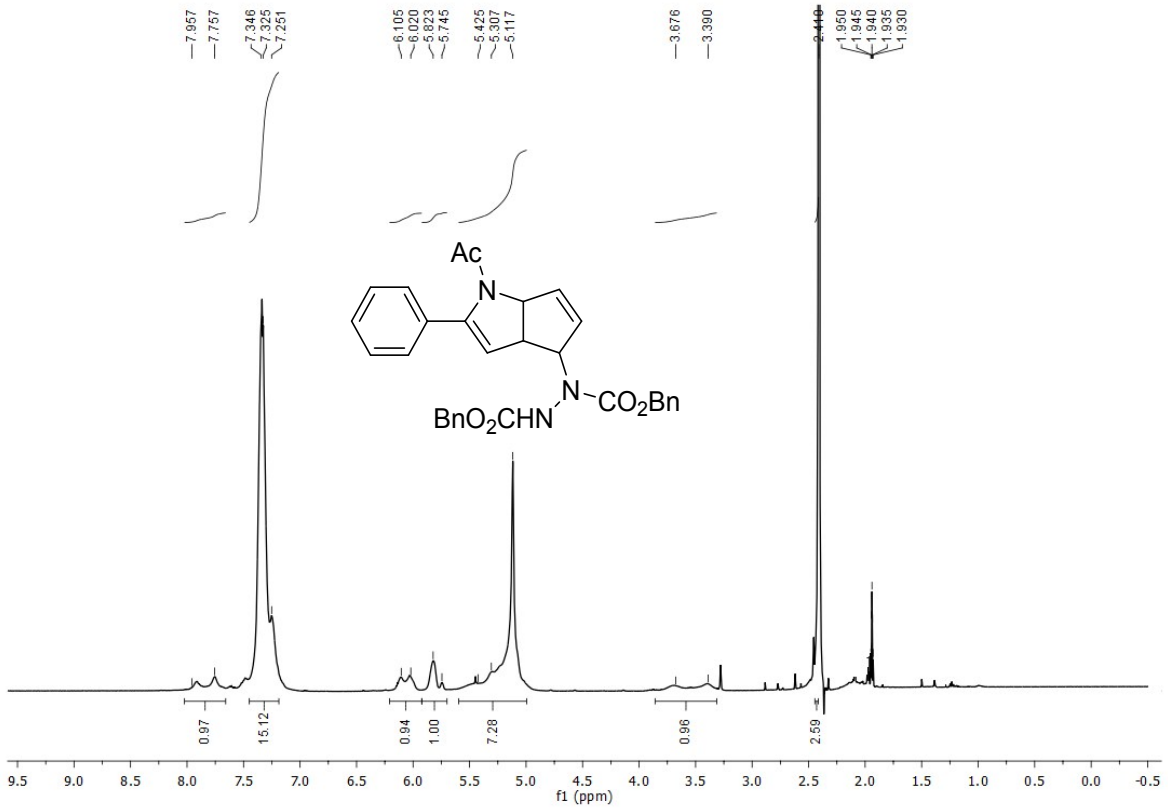
^{13}C NMR of **3ba**



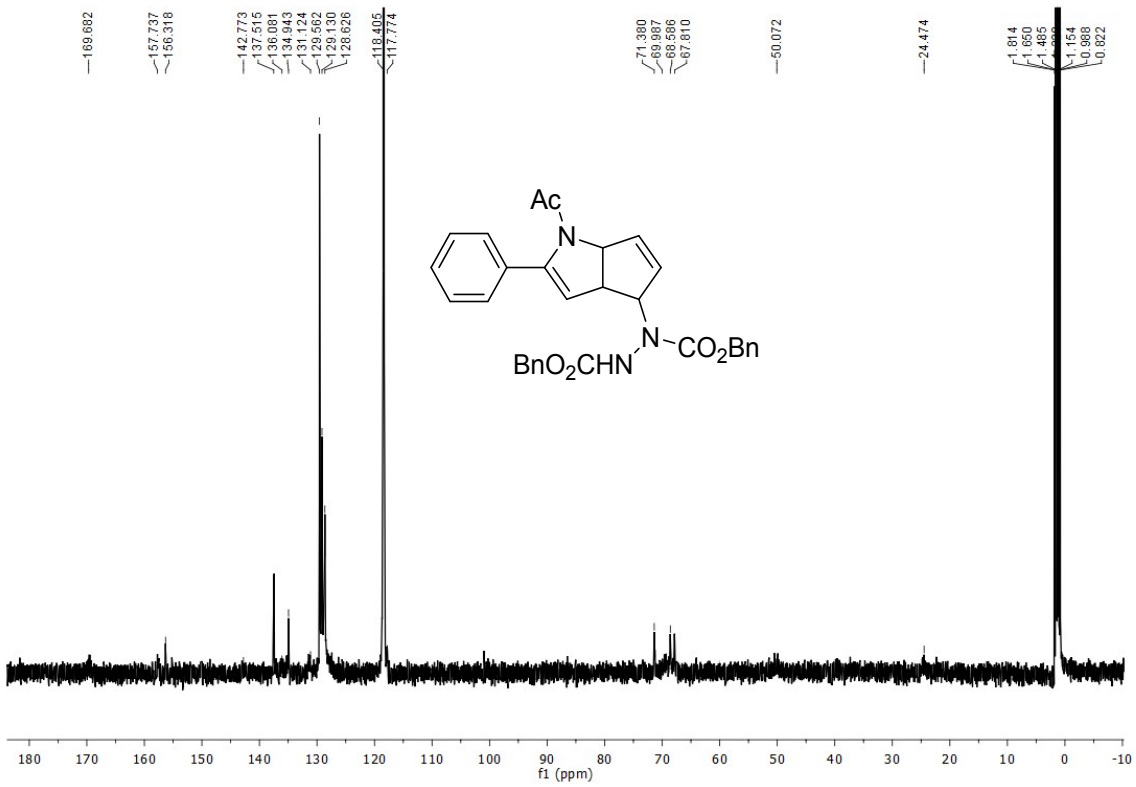
^{1}H NMR of **3ca**



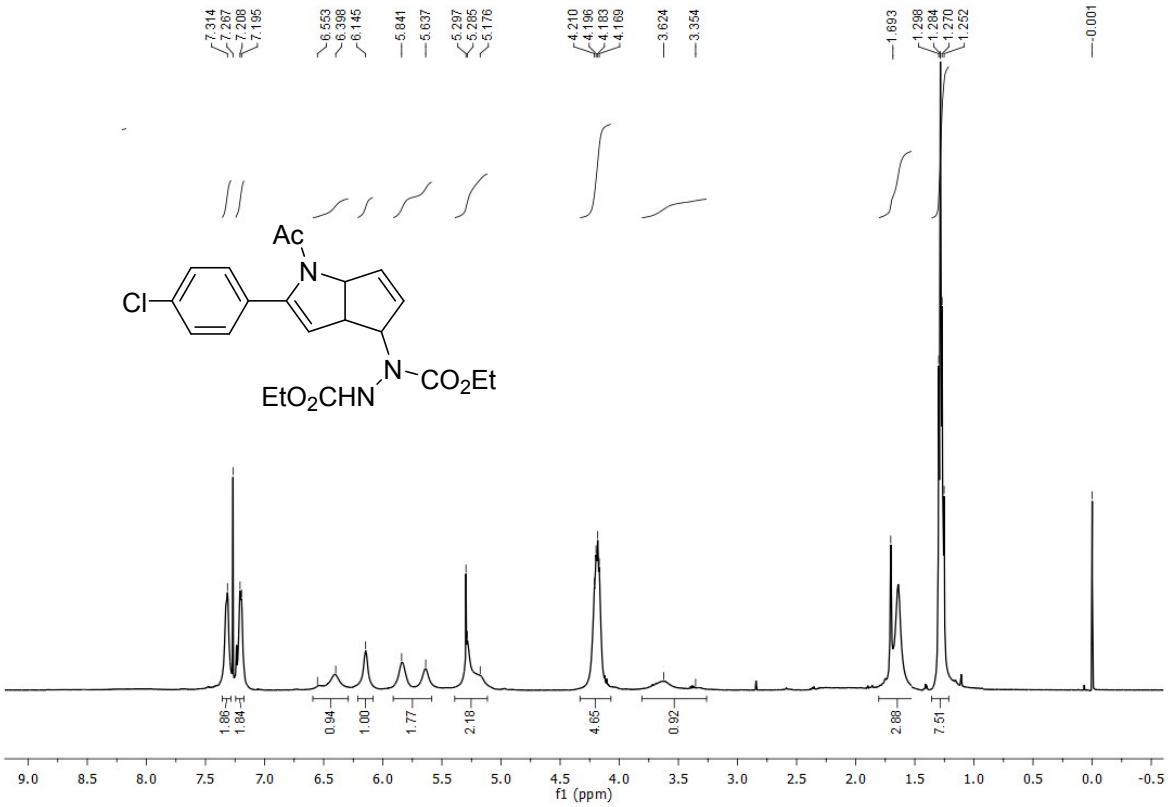
^{13}C NMR of **3ca**



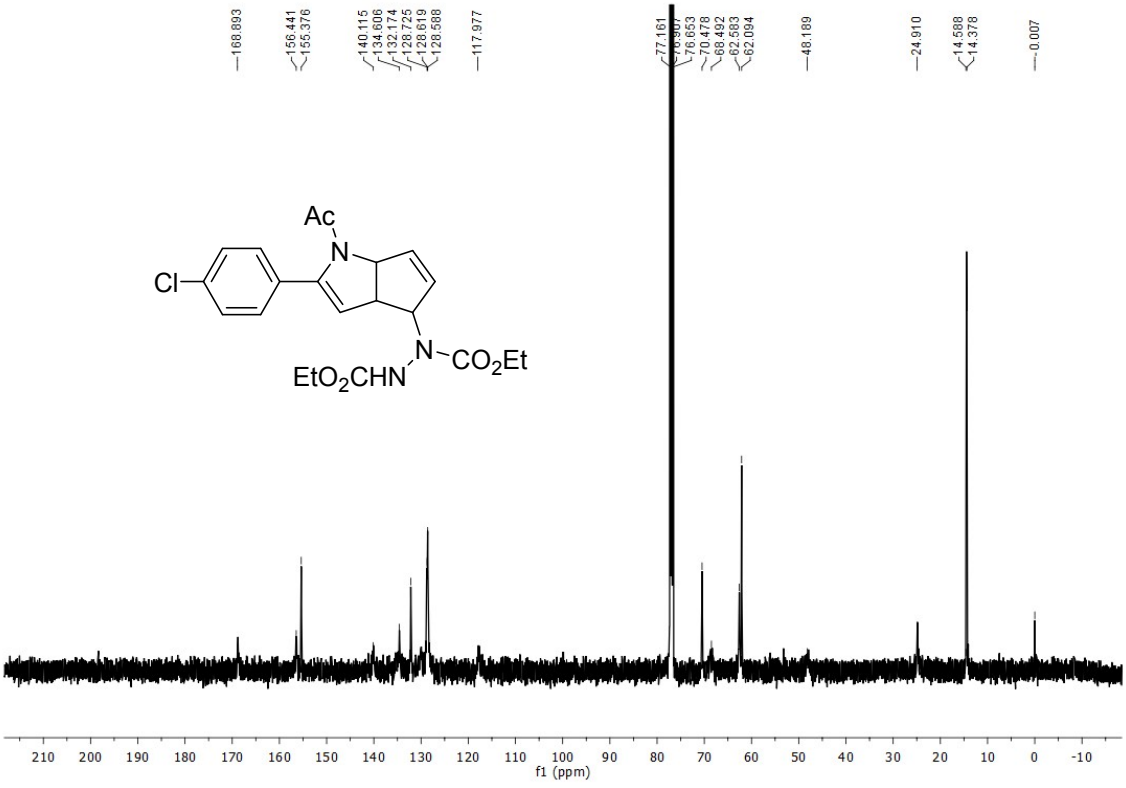
^{1}H NMR of **3da**



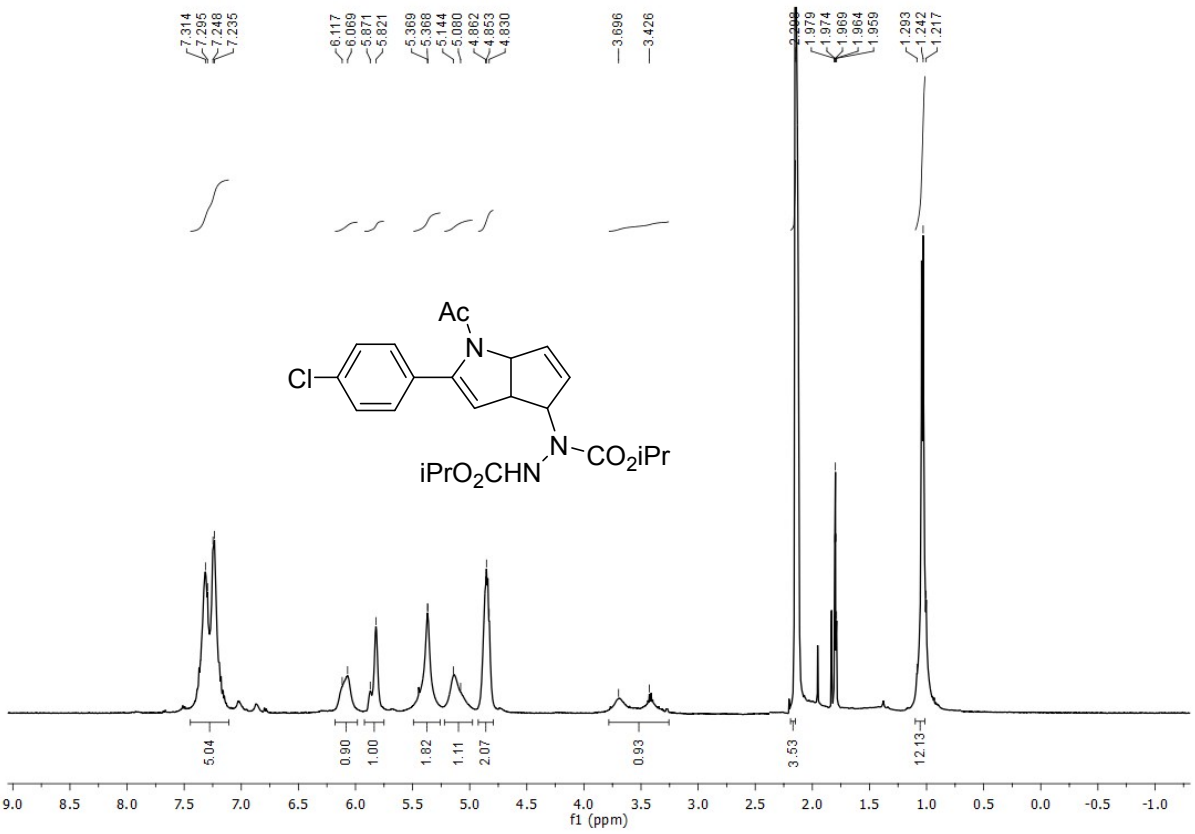
^{13}C NMR of **3da**



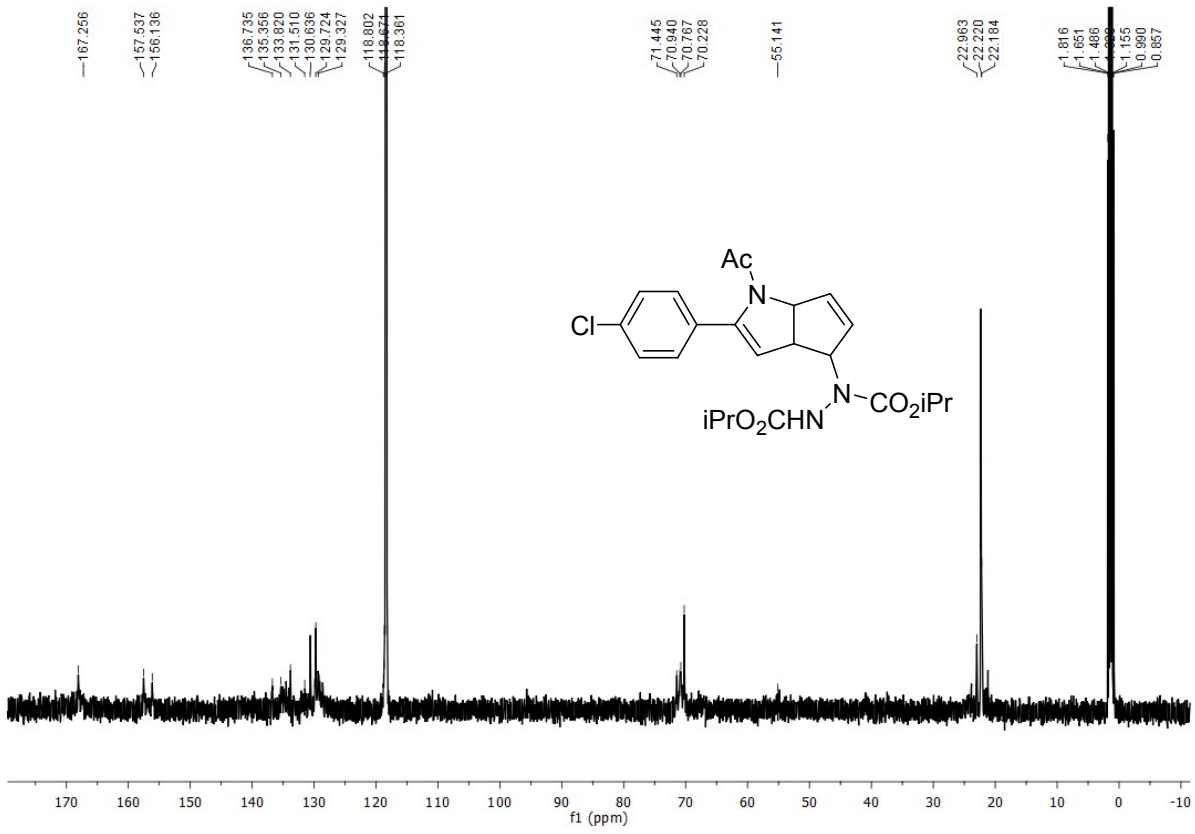
^{1}H NMR of **3ab**



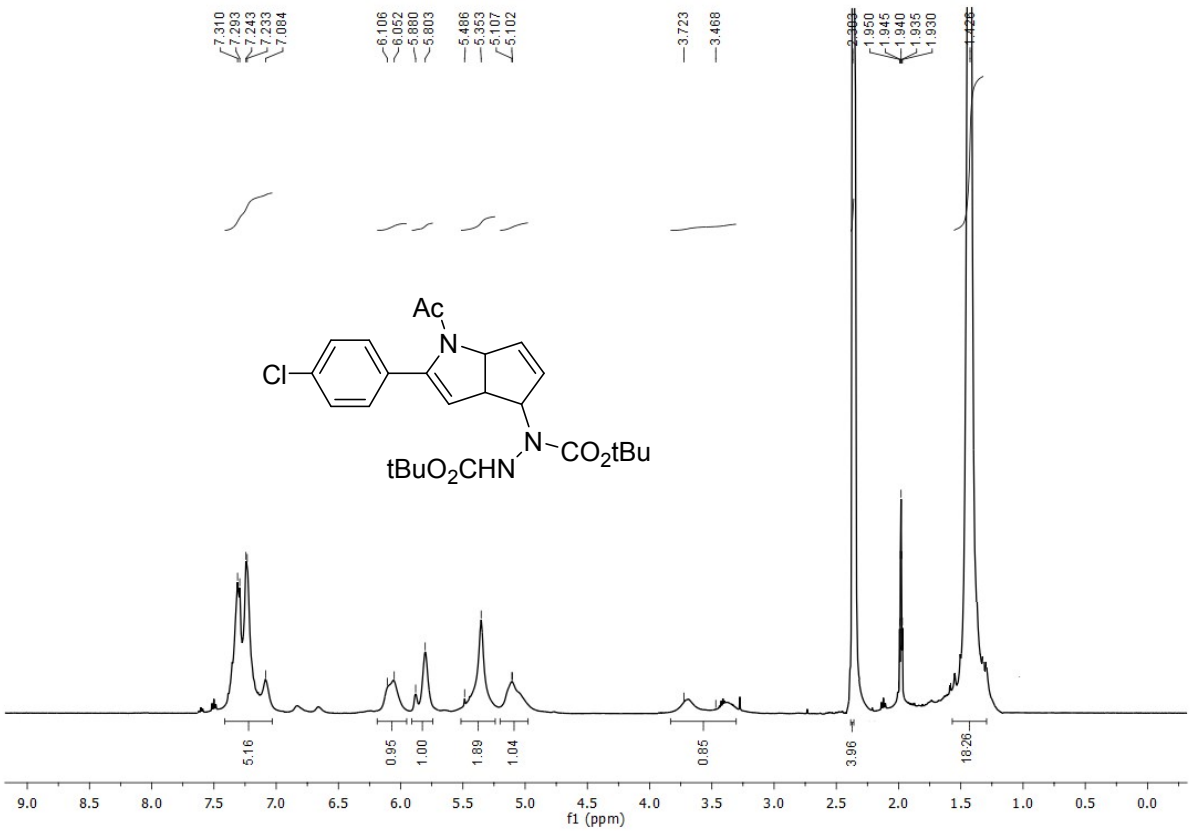
^{13}C NMR of **3ab**



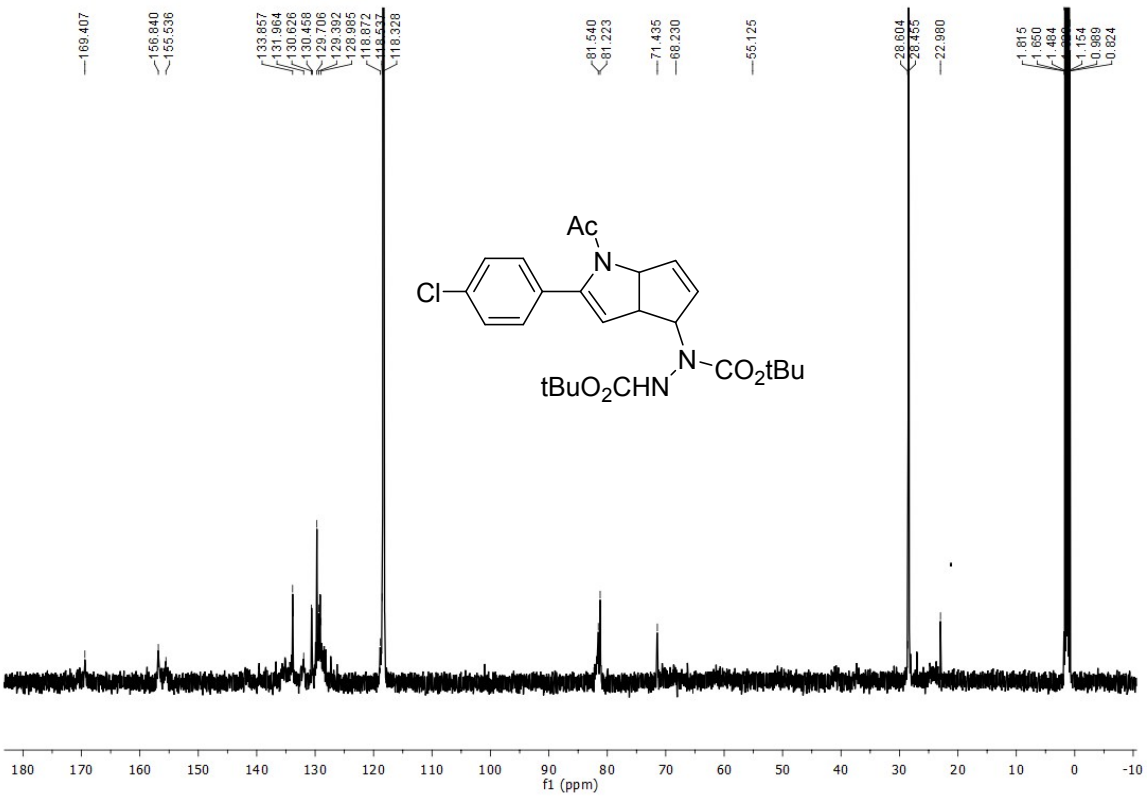
^{1}H NMR of **3bb**



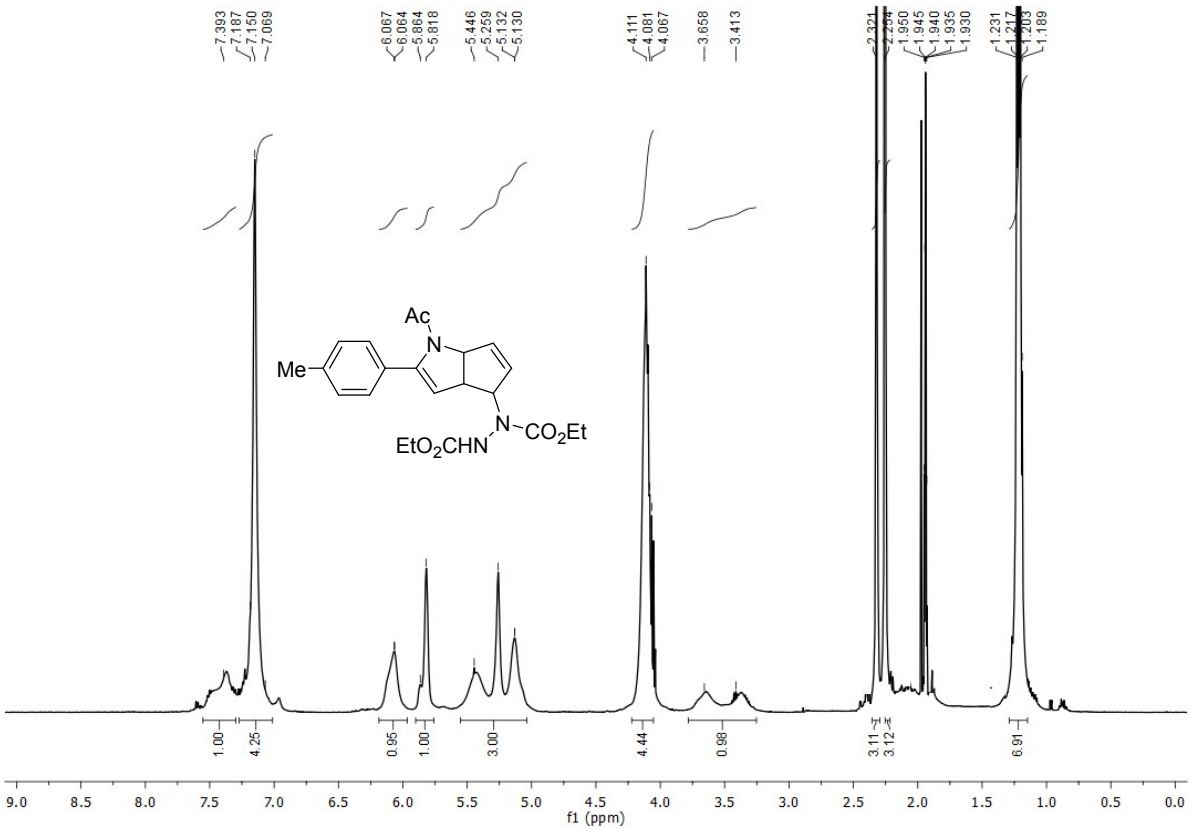
^{13}C NMR of **3bb**



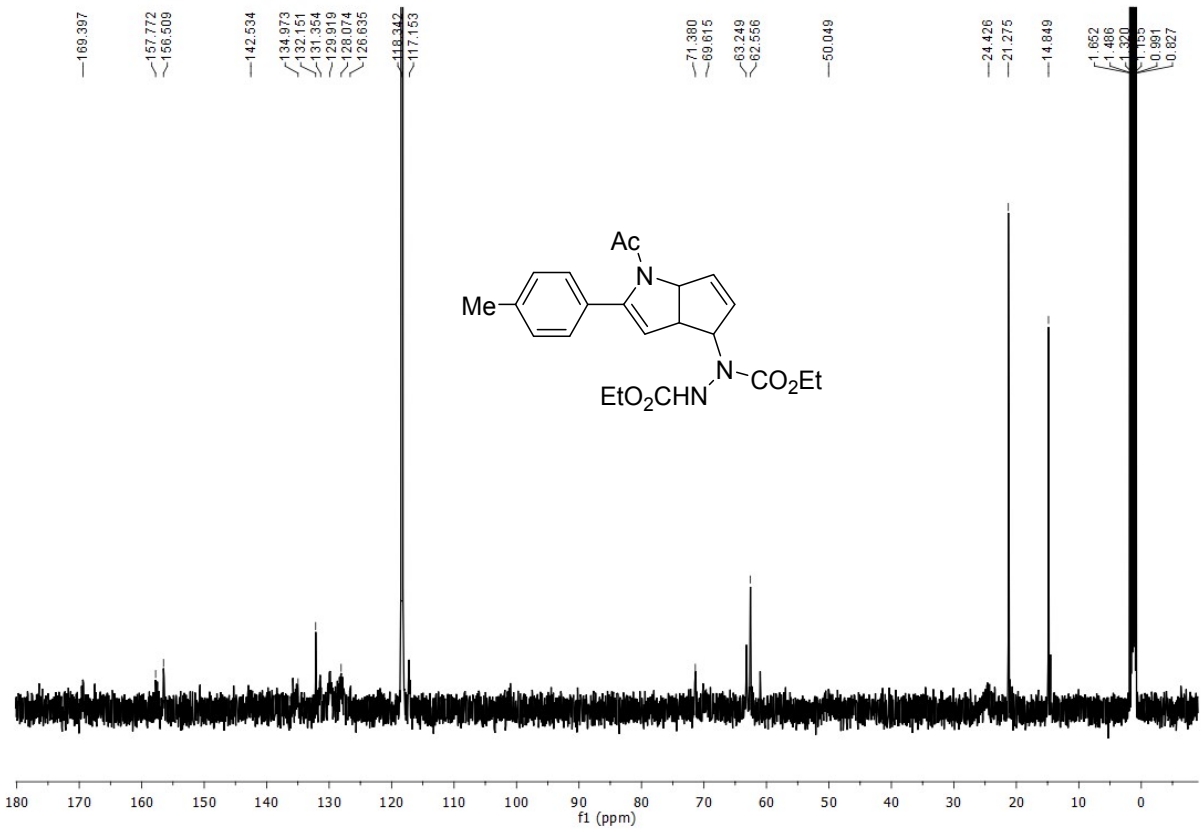
^{1}H NMR of **3cb**



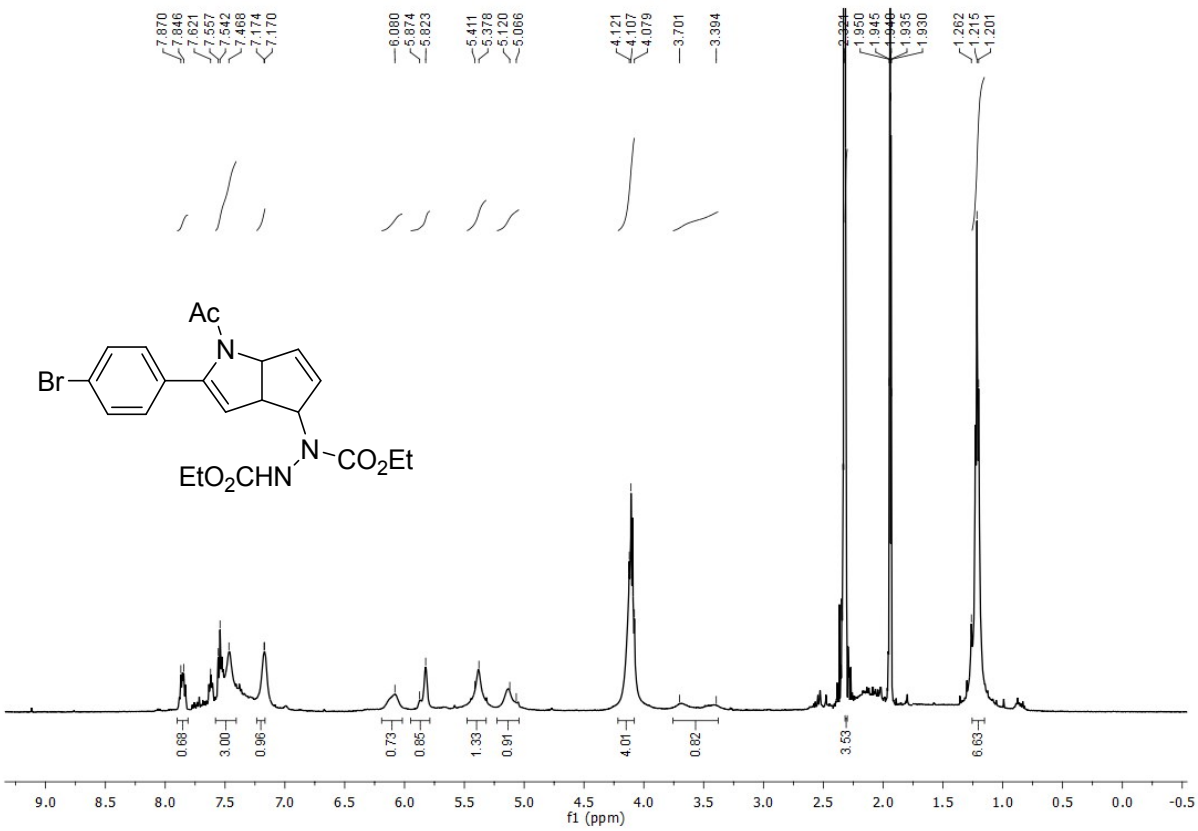
^{13}C NMR of **3cb**



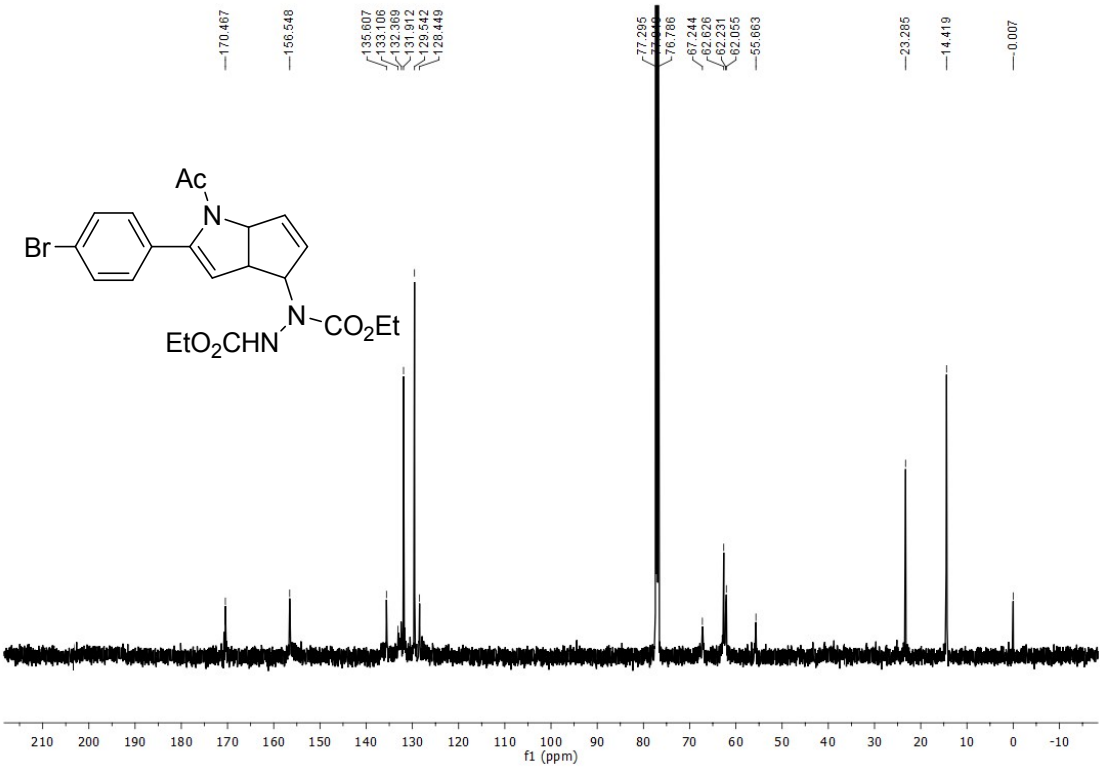
^{1}H NMR of **3ac**



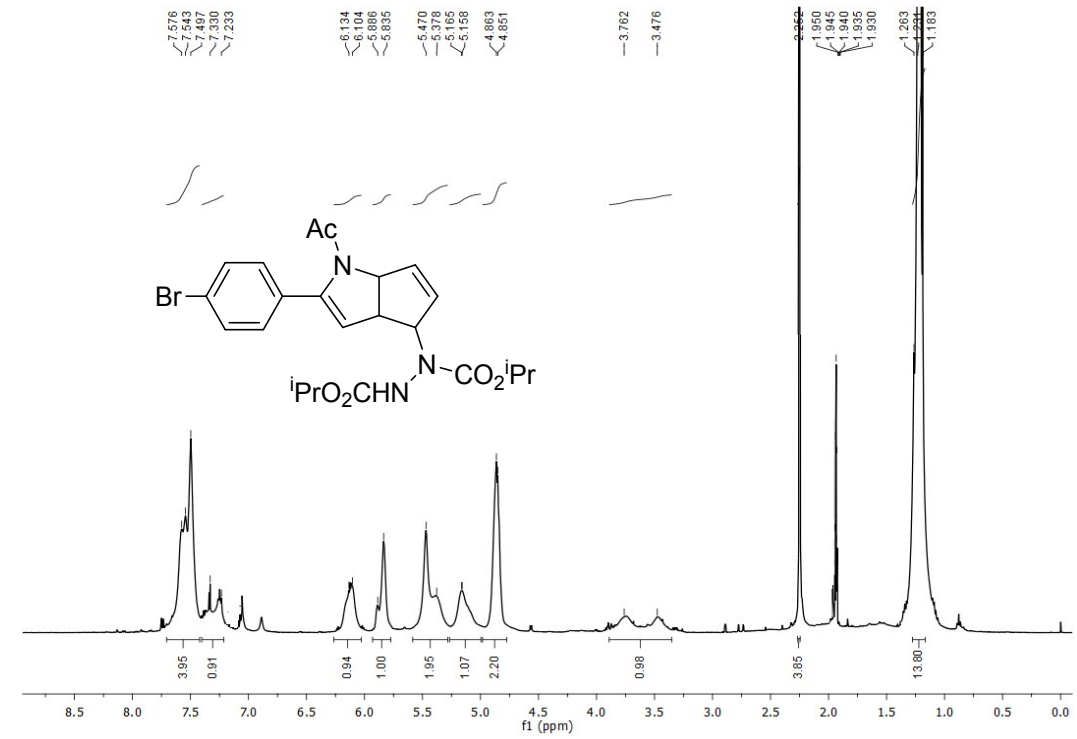
^{13}C NMR of **3ac**



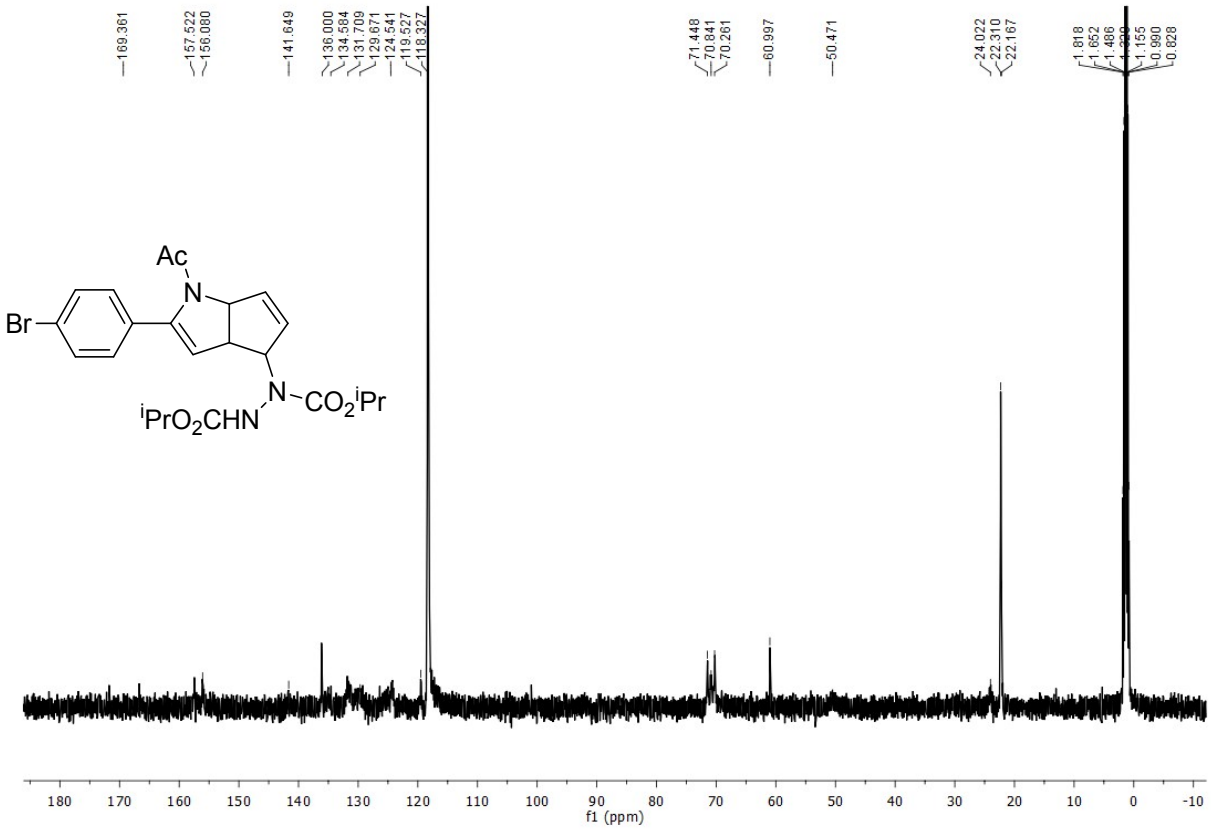
^{1}H NMR of **3ad**



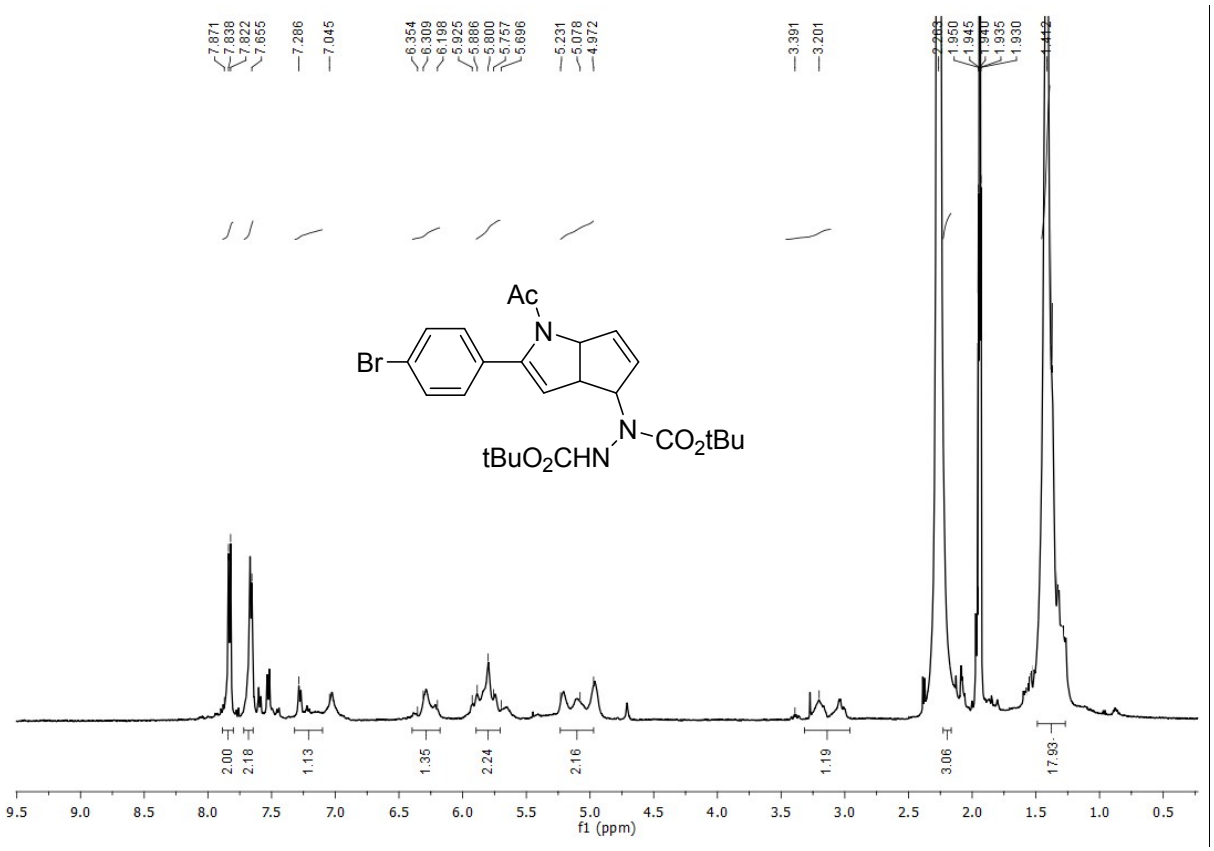
^{13}C NMR of **3ad**



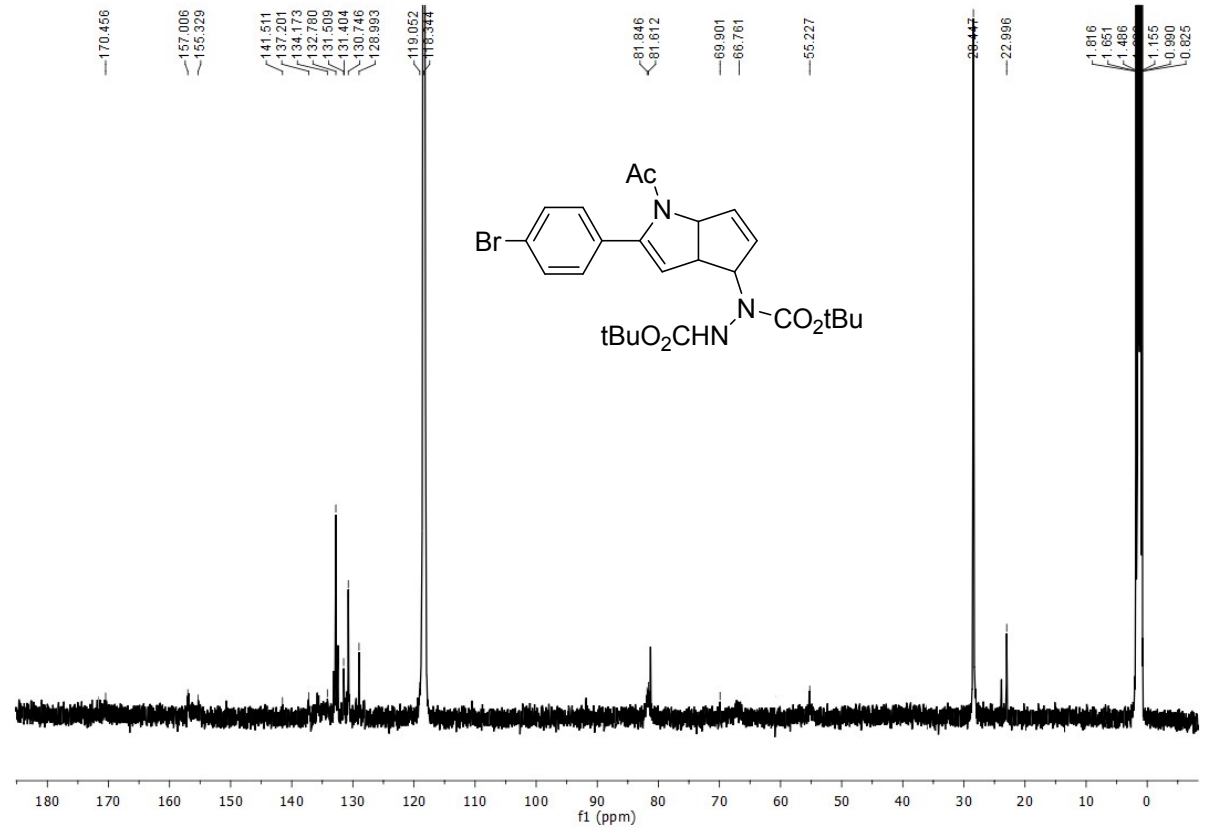
^{1}H NMR of **3bd**



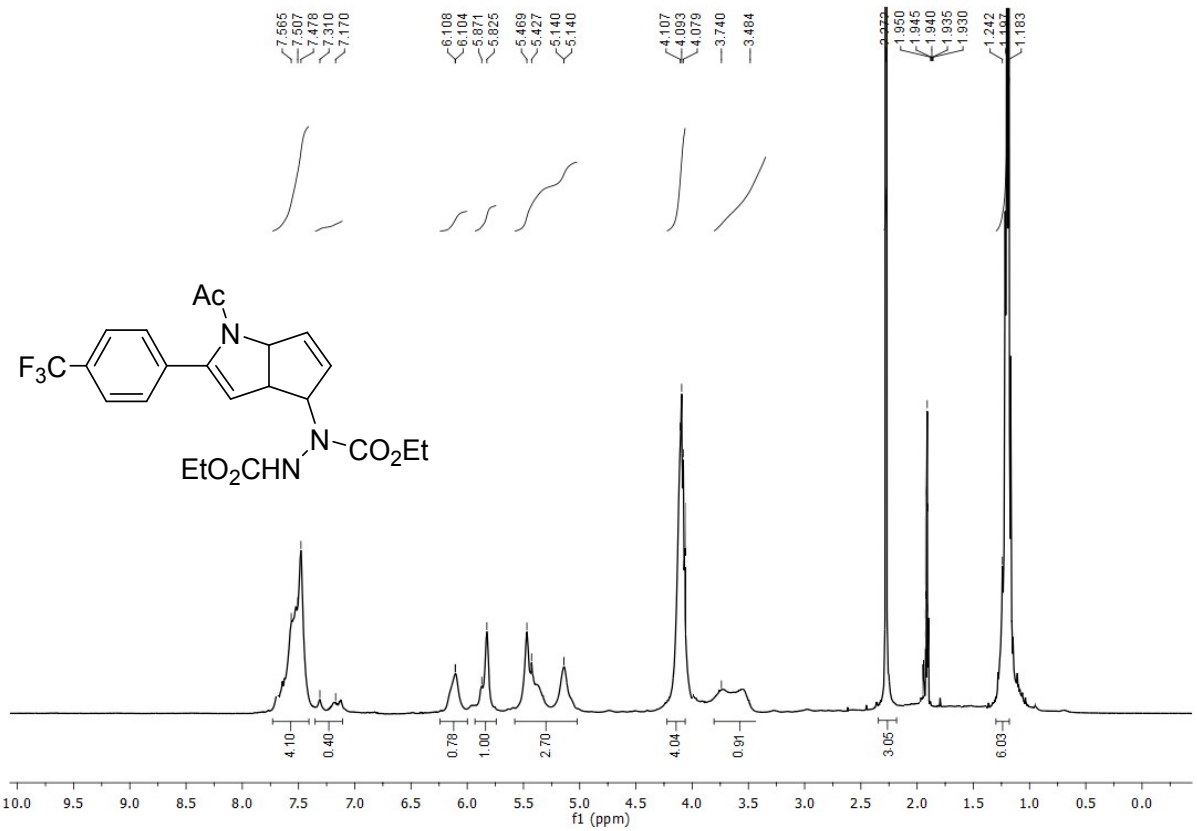
^{13}C NMR of **3bd**



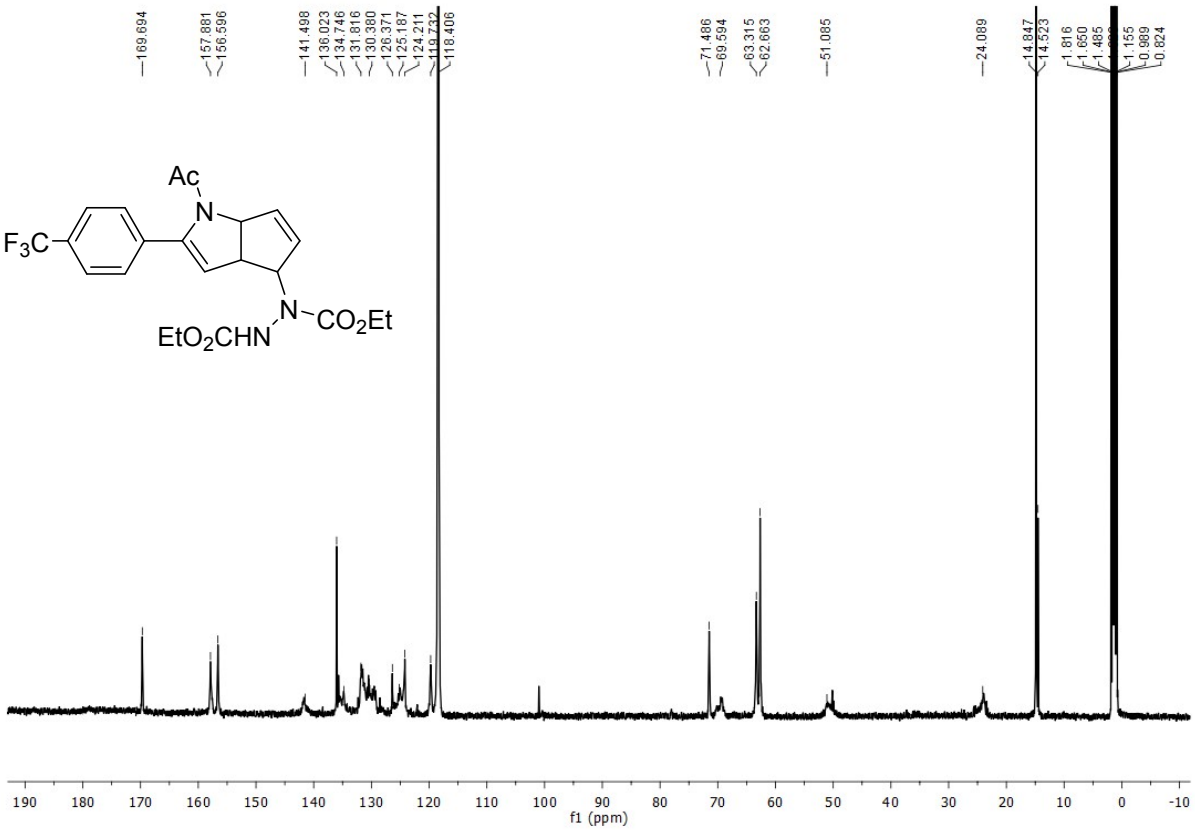
^{1}H NMR of **3cd**



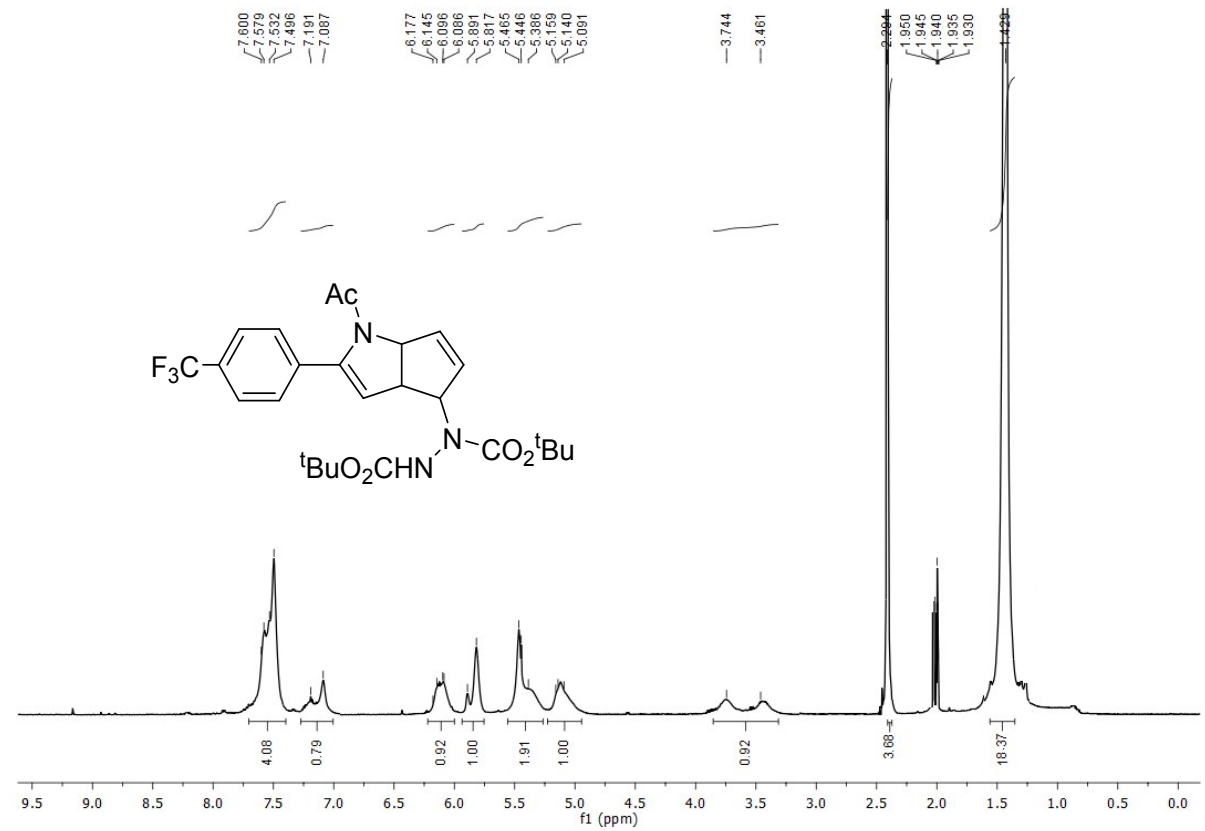
^{13}C NMR of **3cd**



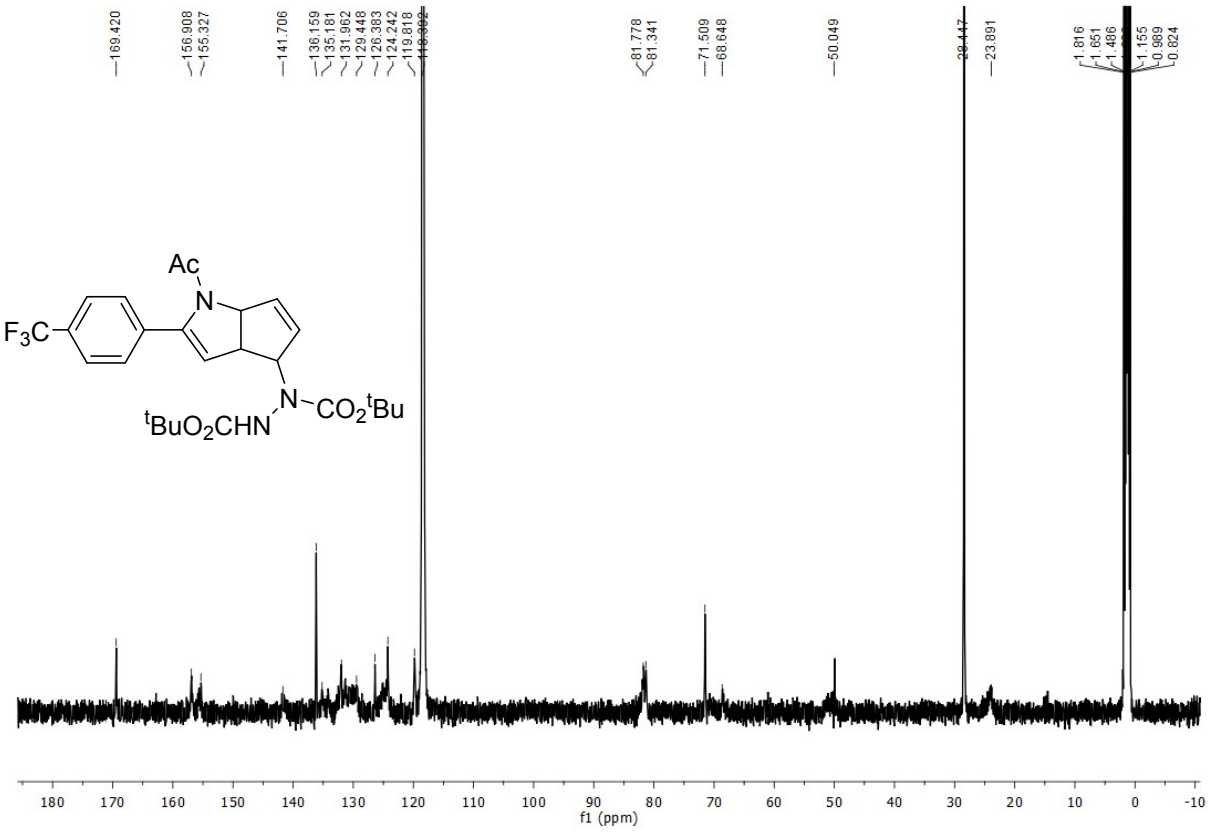
^{1}H NMR of **3ae**



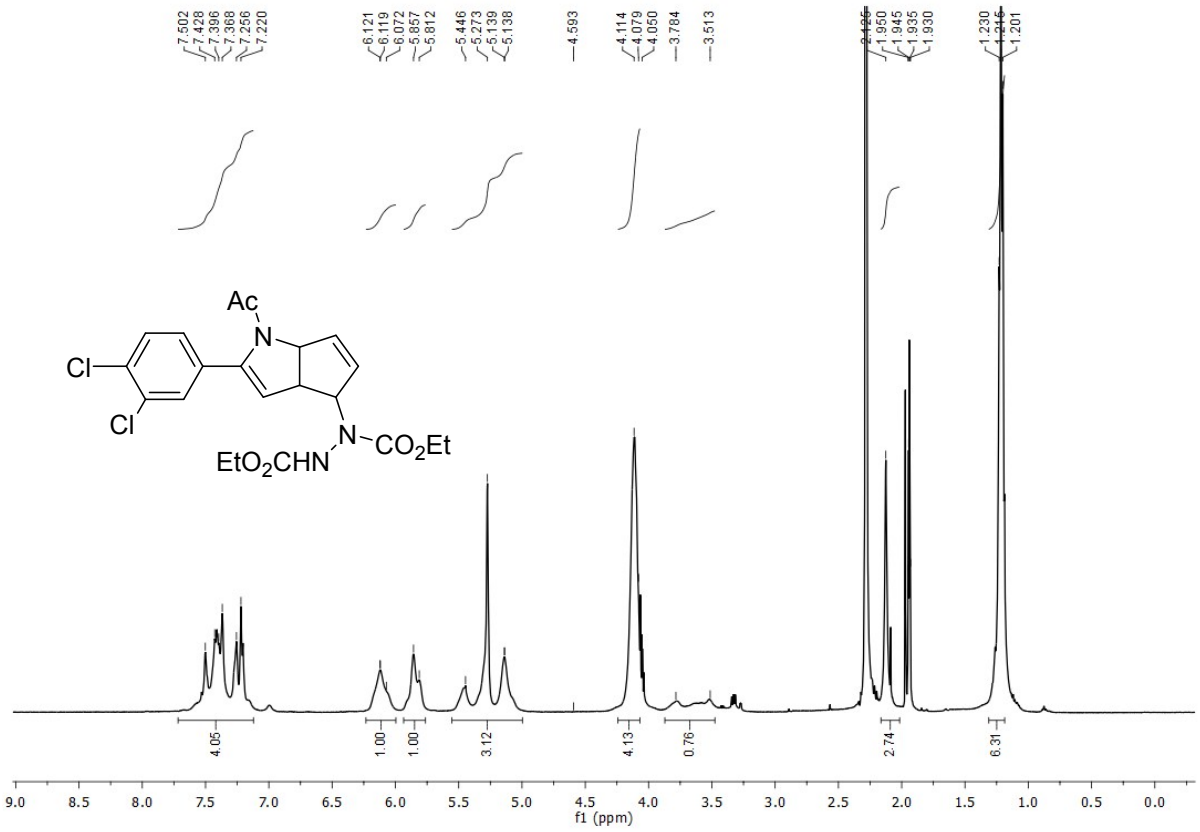
^{13}C NMR of **3ae**



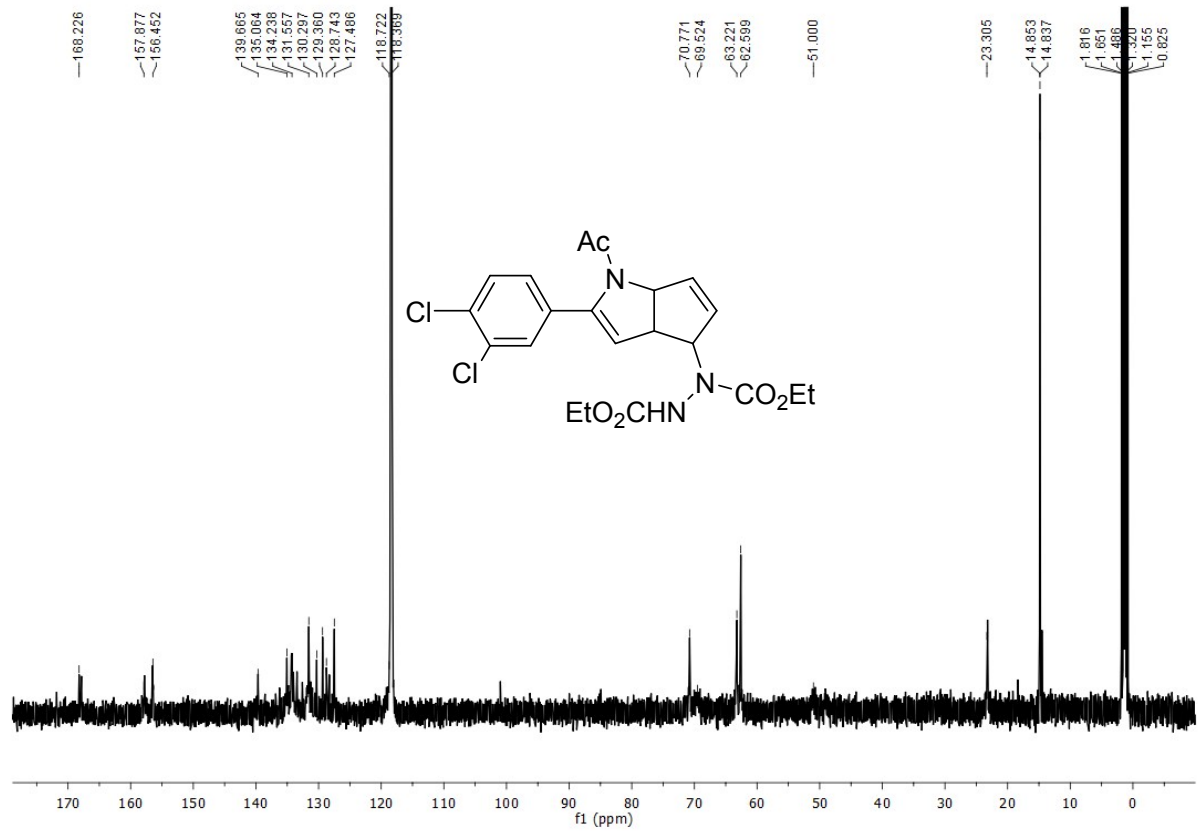
^{1}H NMR of **3ce**



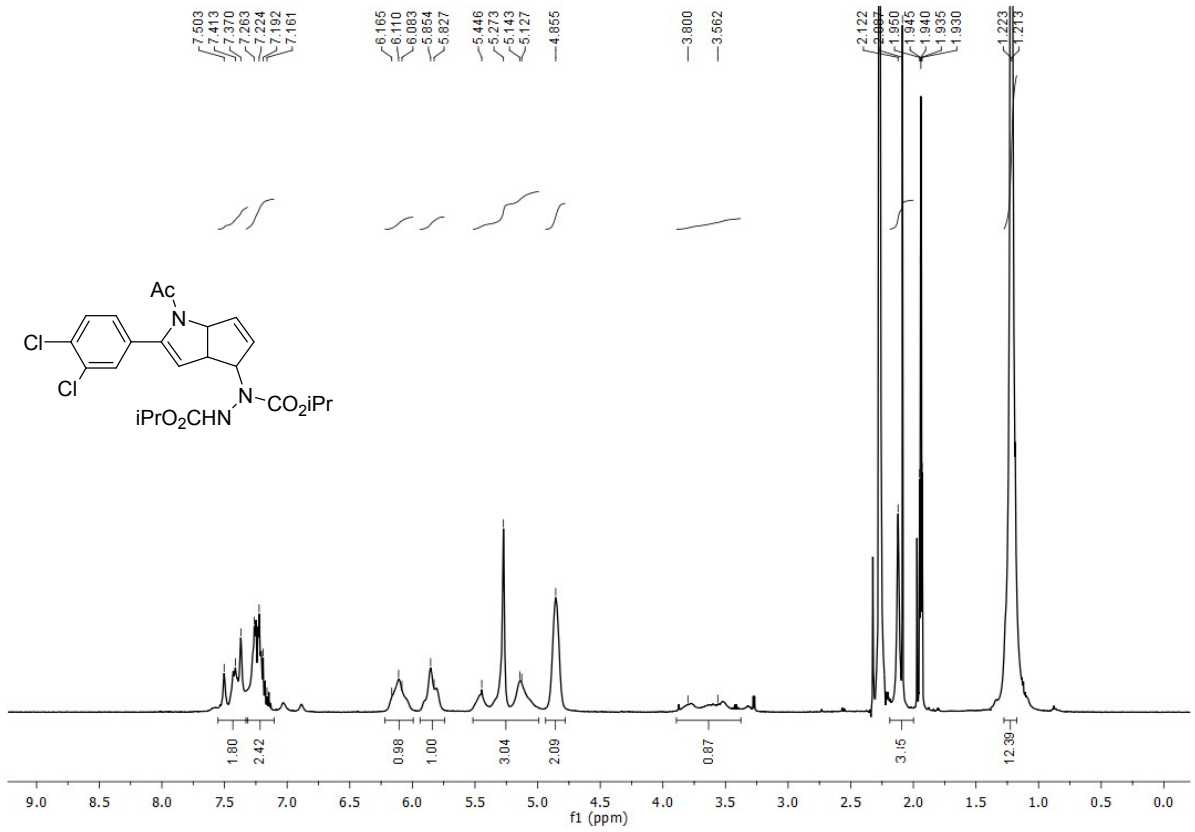
^{13}C NMR of **3ce**



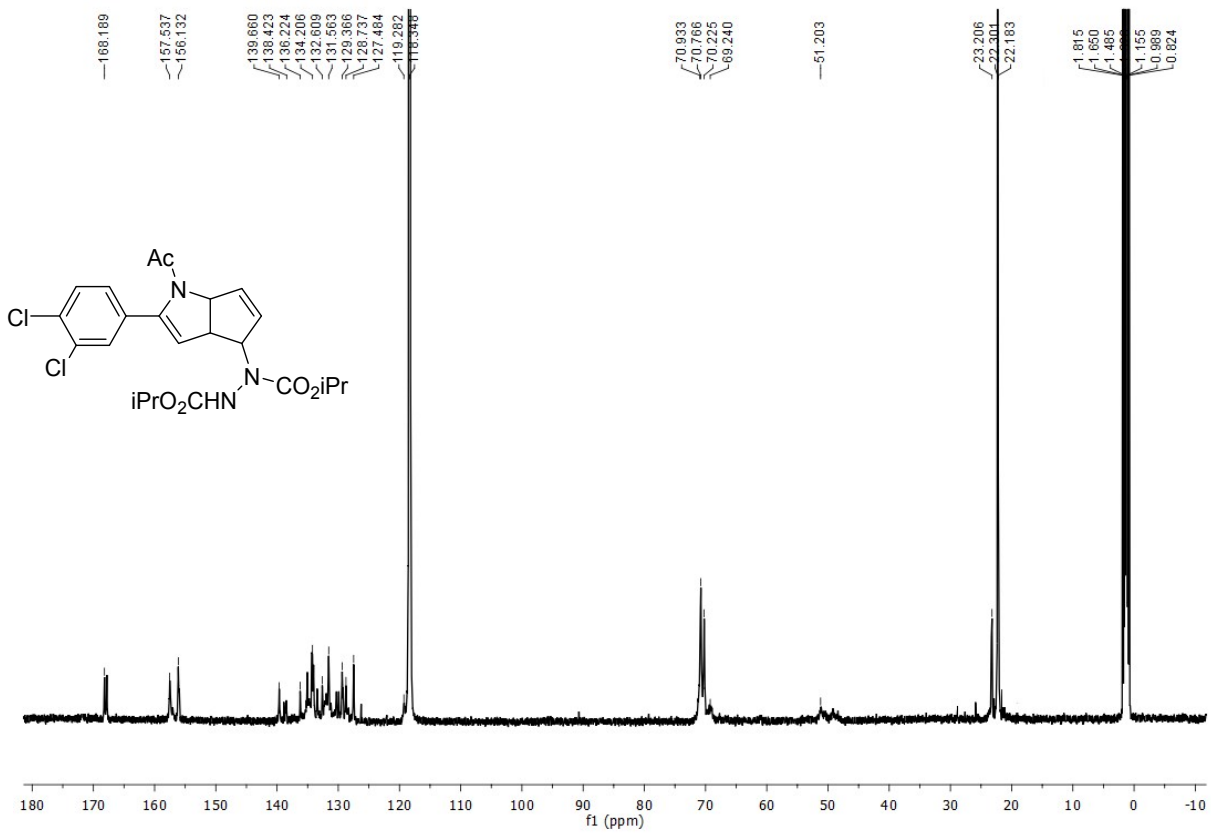
^{1}H NMR of **3af**



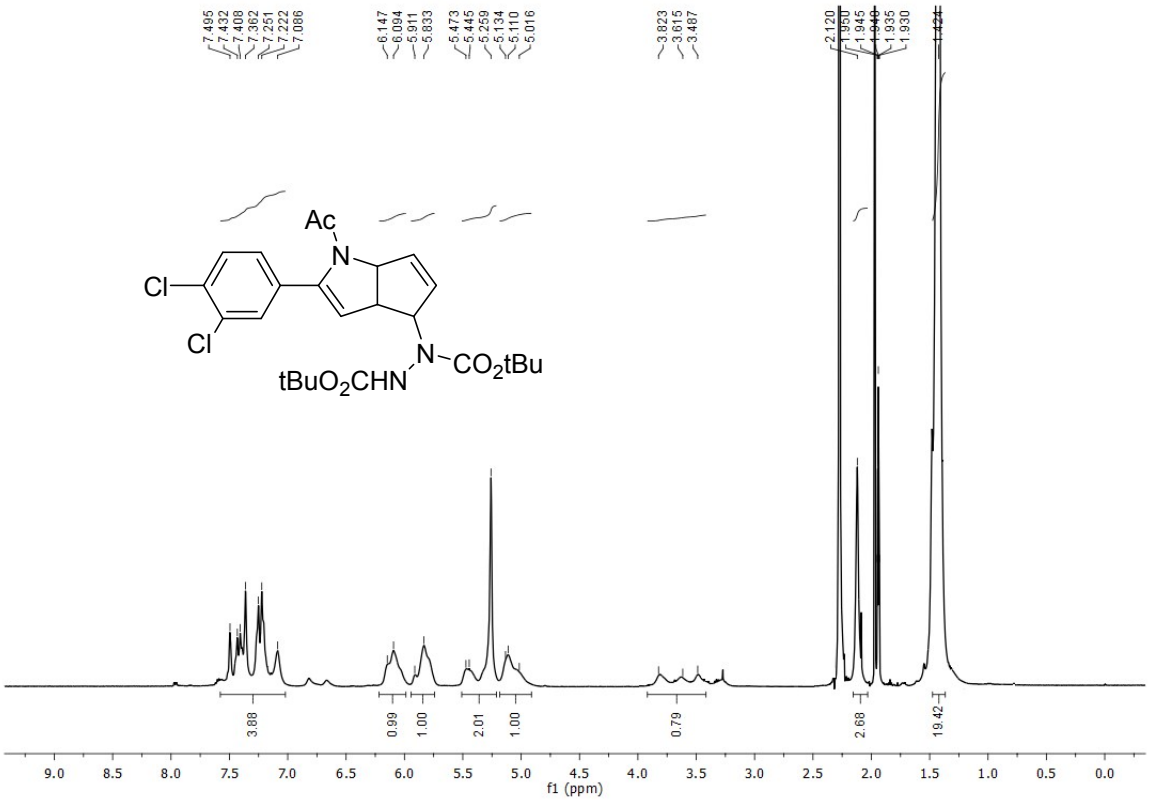
^{13}C NMR of **3af**



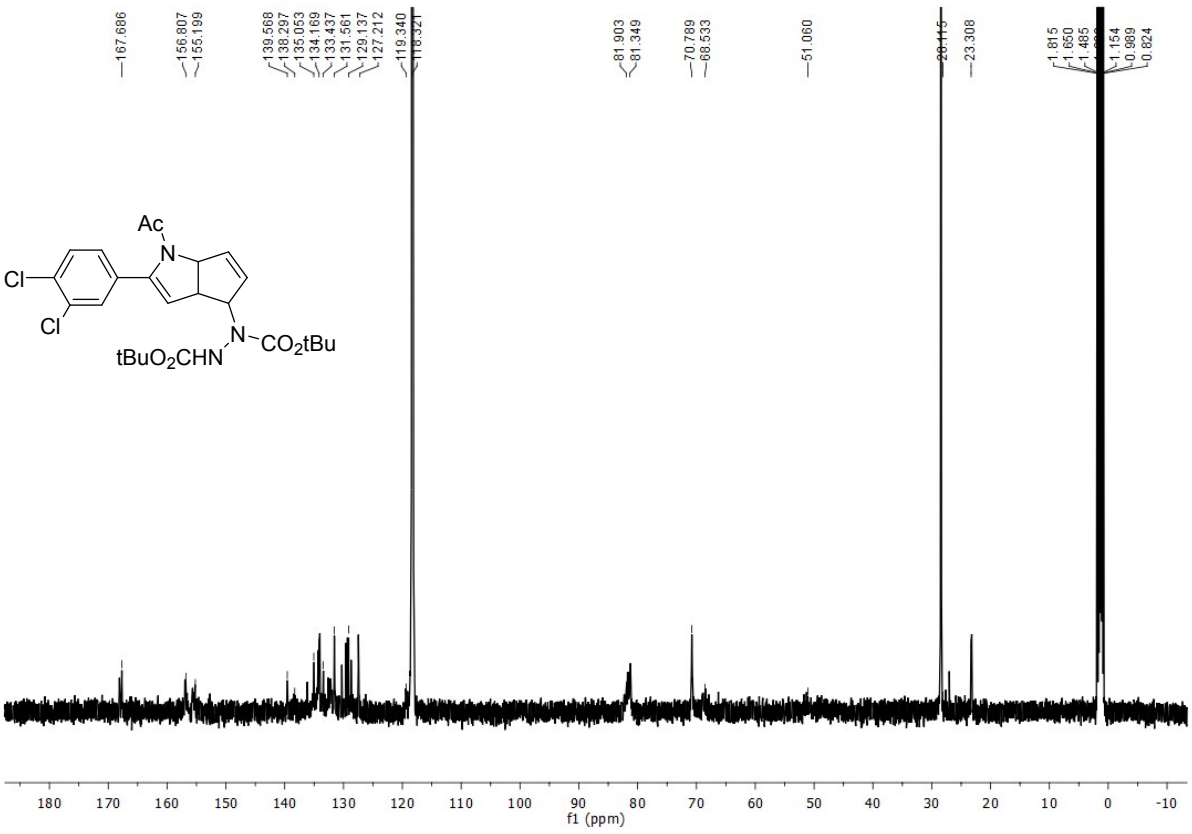
^{1}H NMR of **3bf**



^{13}C NMR of **3bf**



^{1}H NMR of **3cf**



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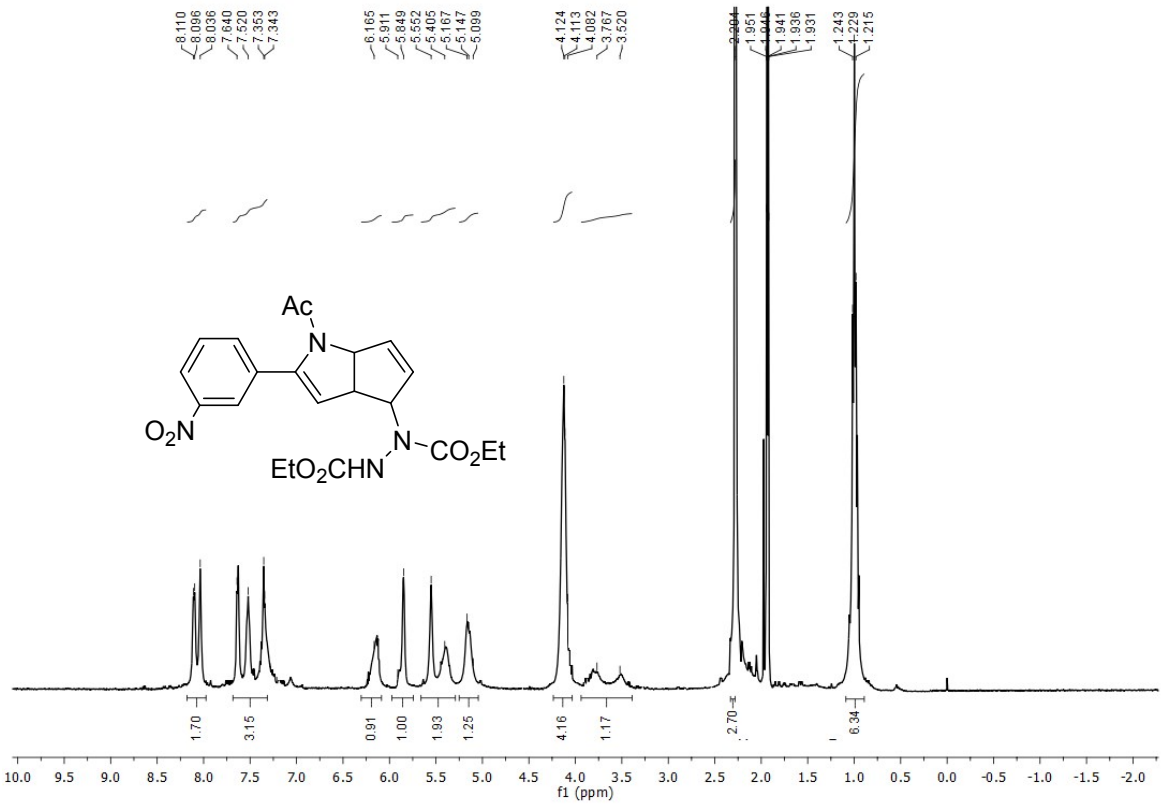
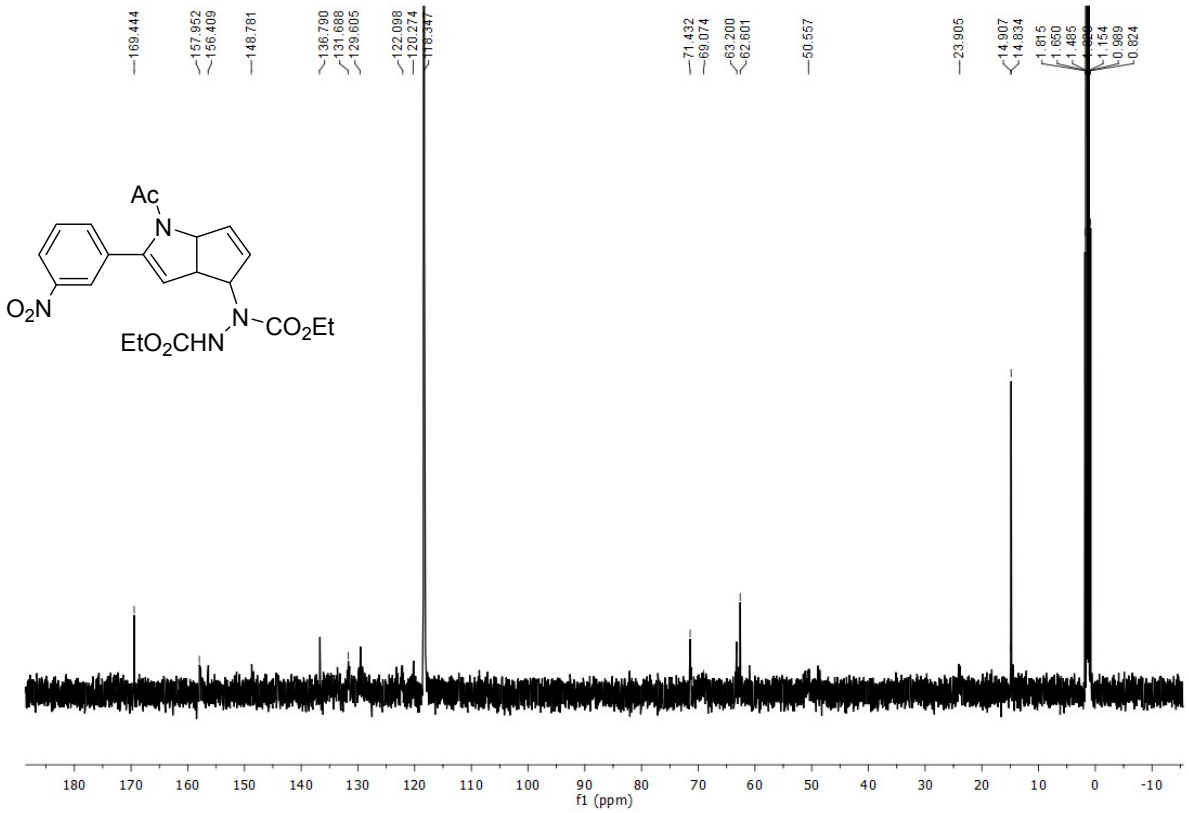
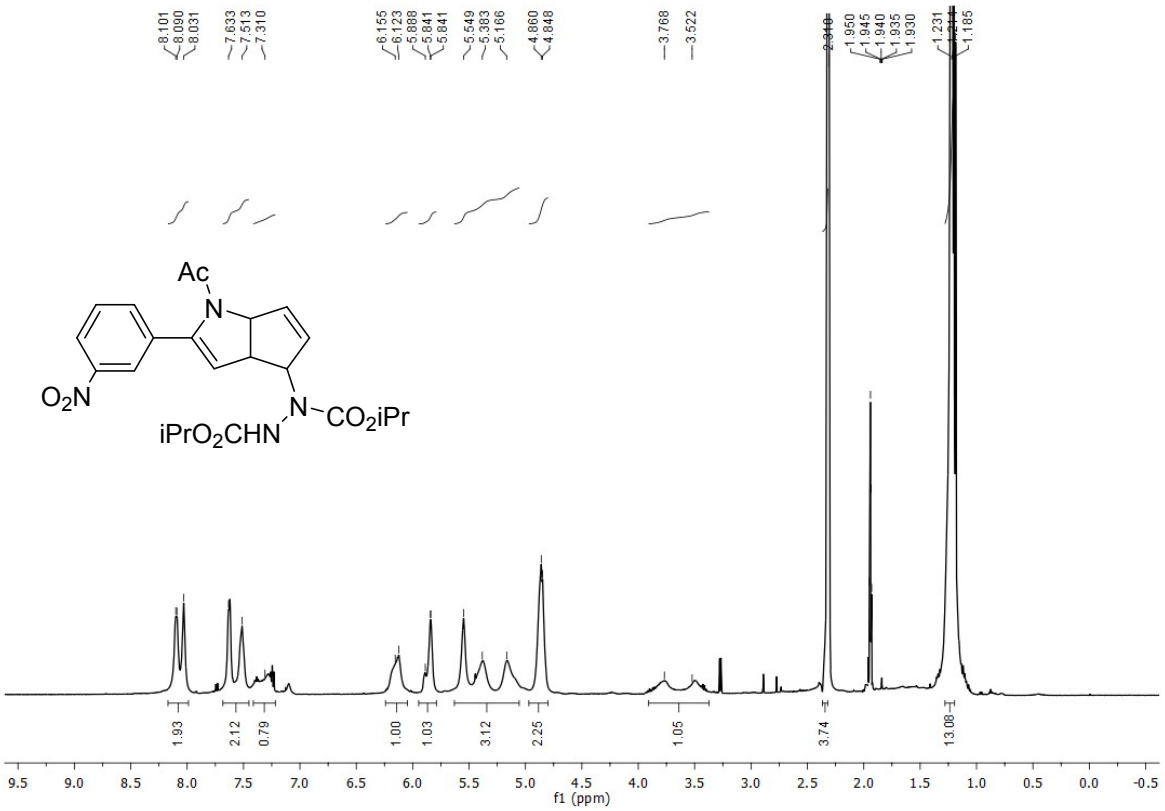


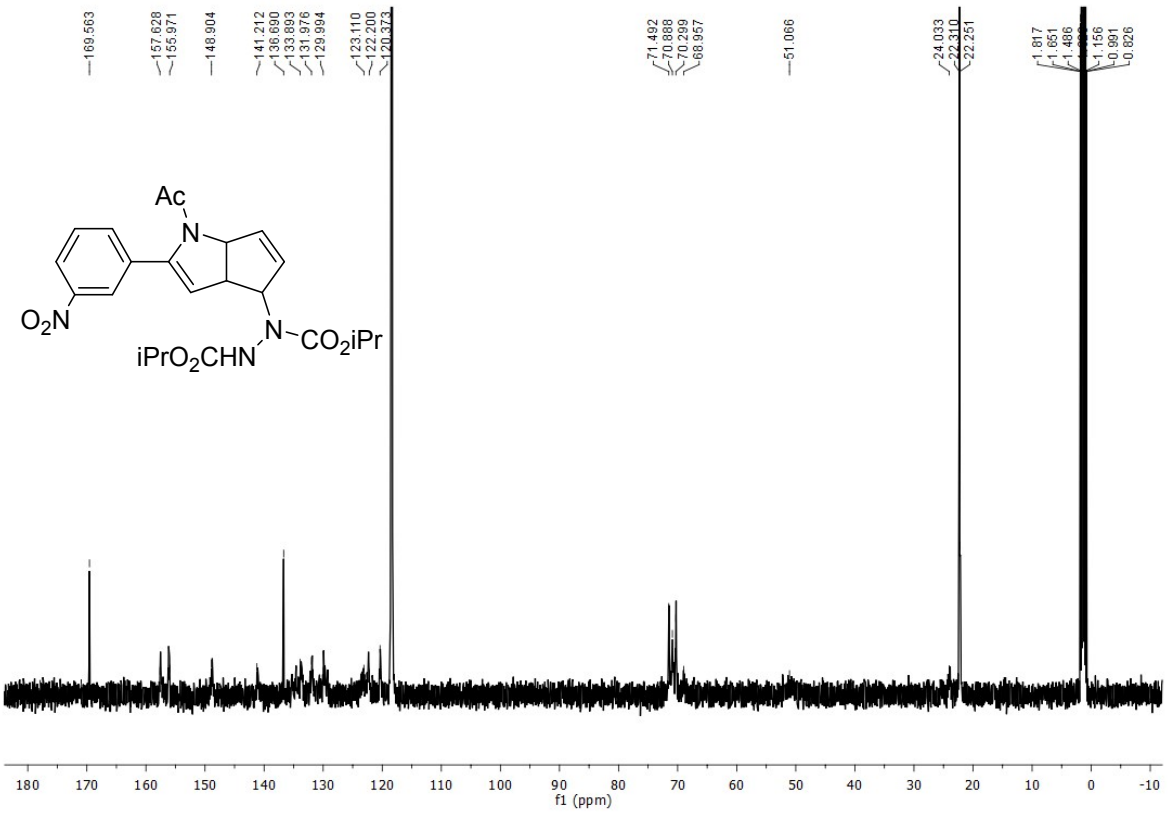
^{1}H NMR of **3ag**



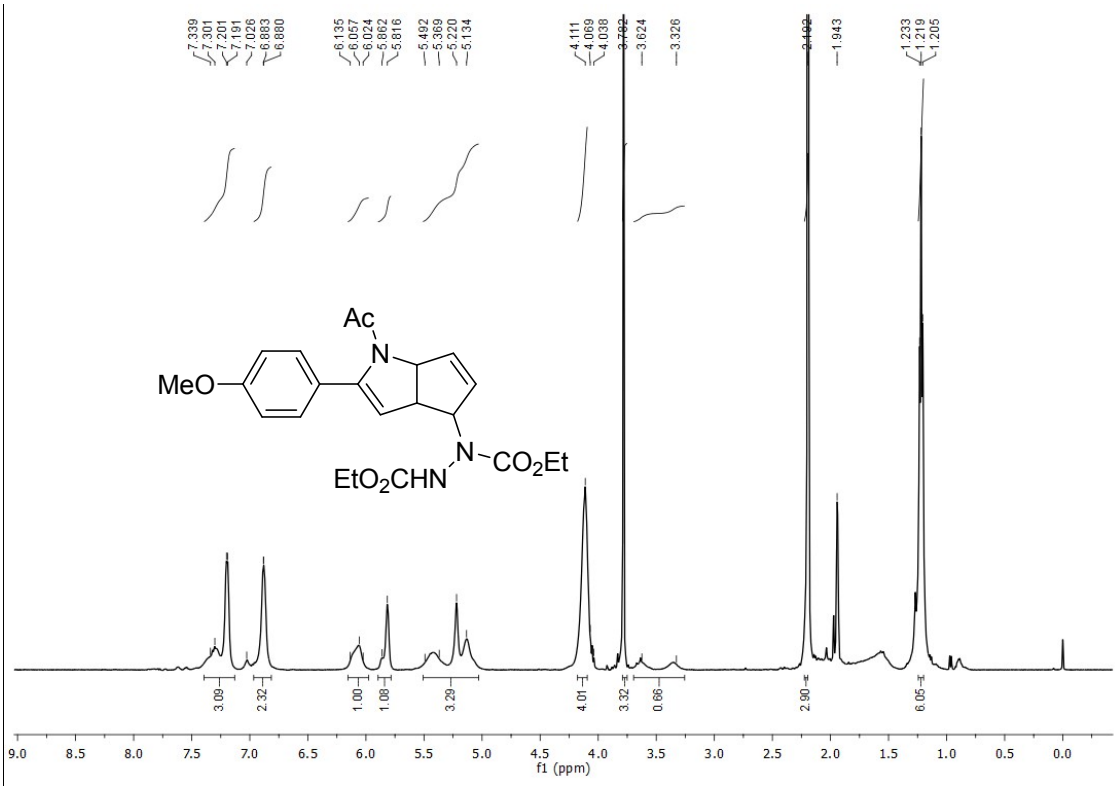
^{13}C NMR of **3ag**



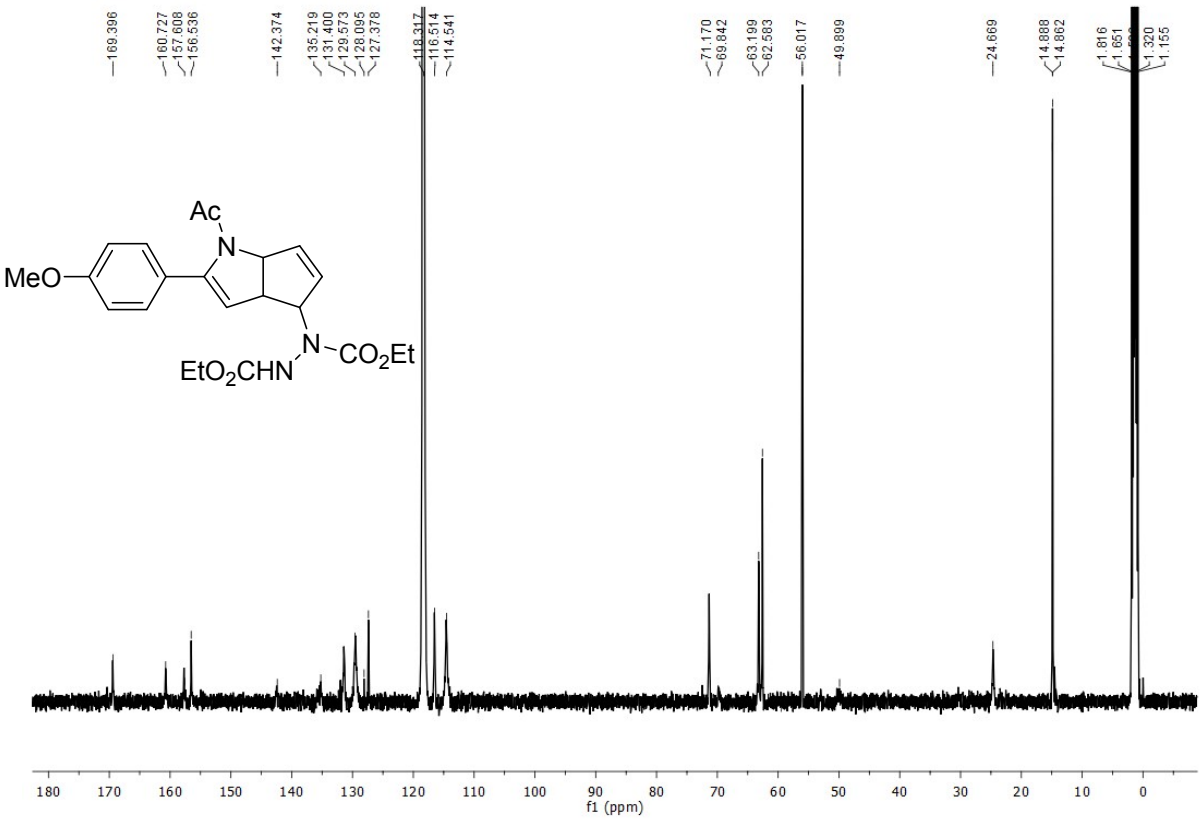
^{1}H NMR of **3bg**



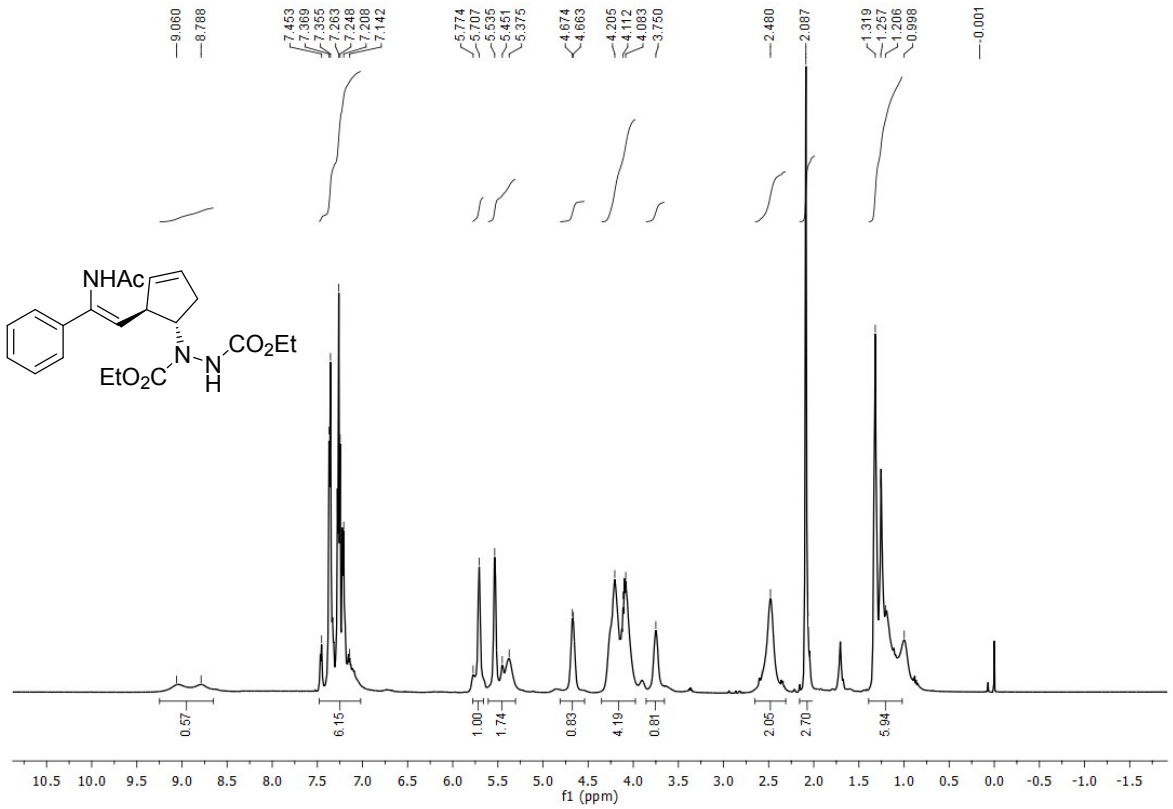
^{13}C NMR of **3bg**



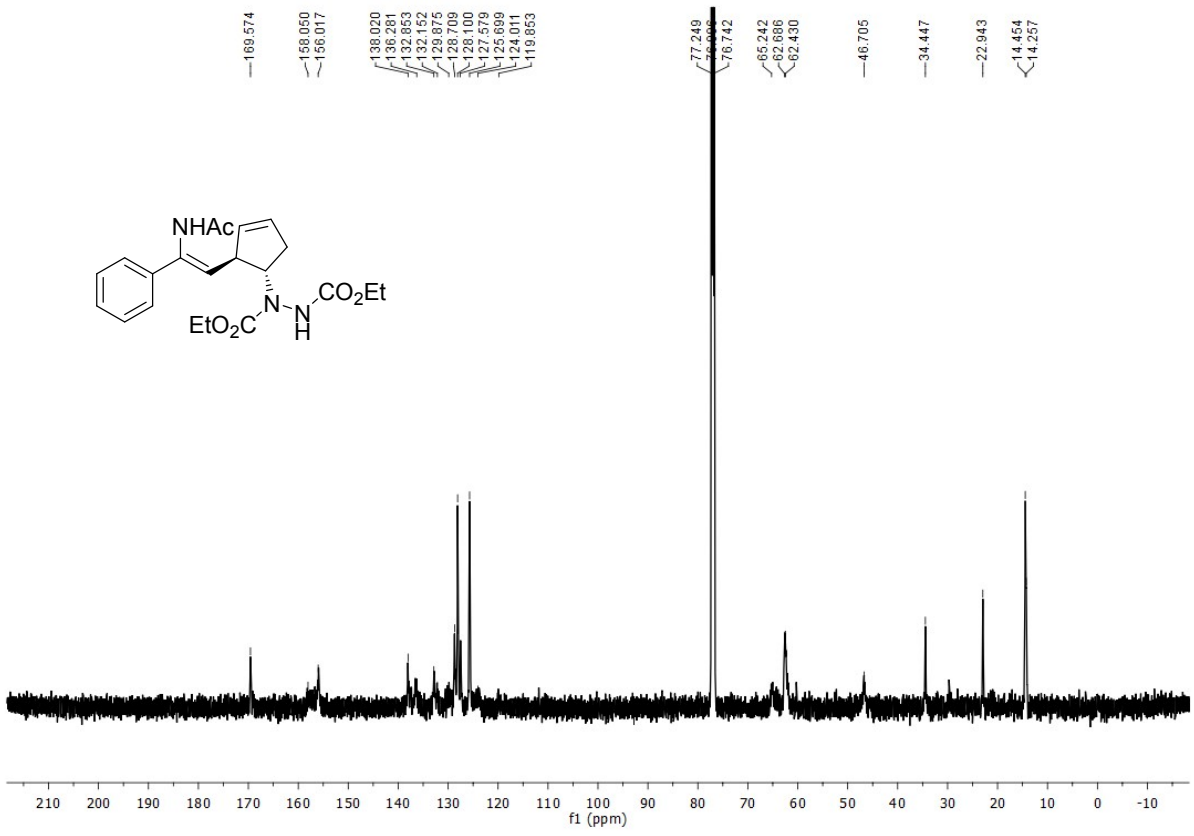
^{1}H NMR of **3ah**



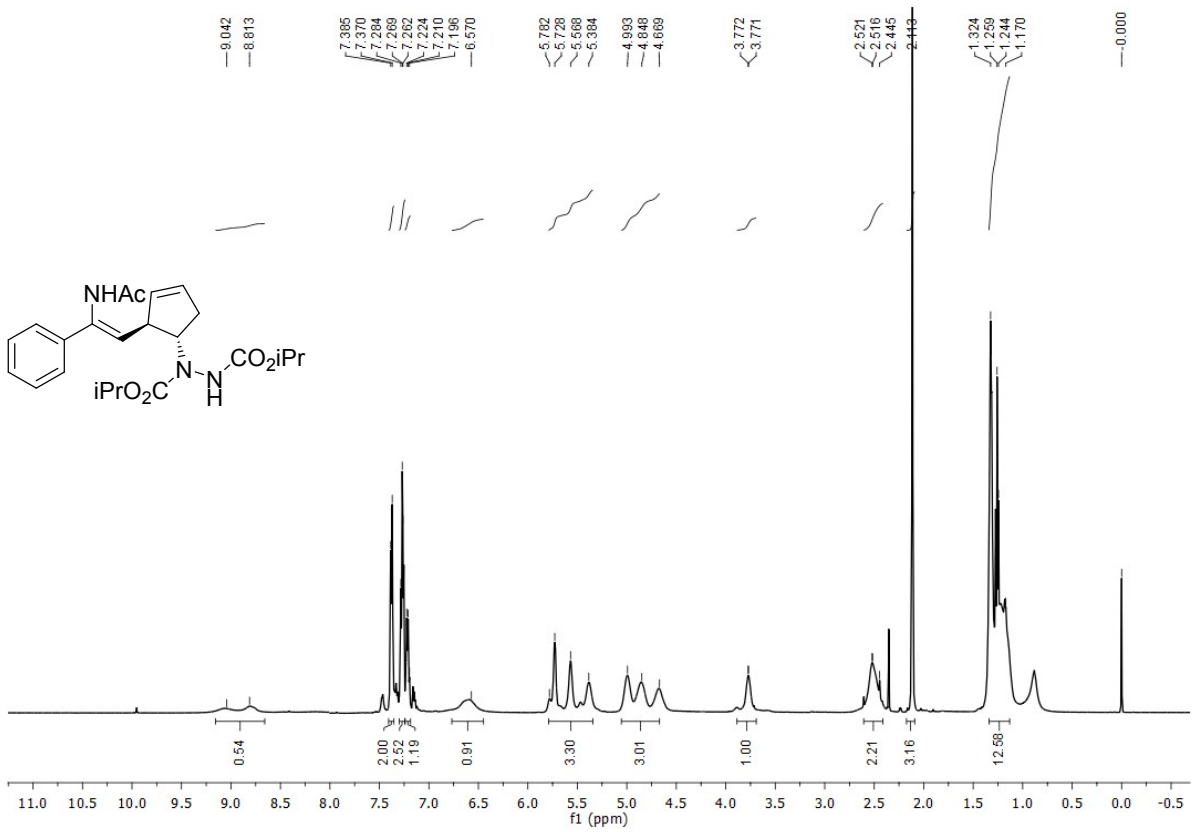
^{13}C NMR of **3ah**



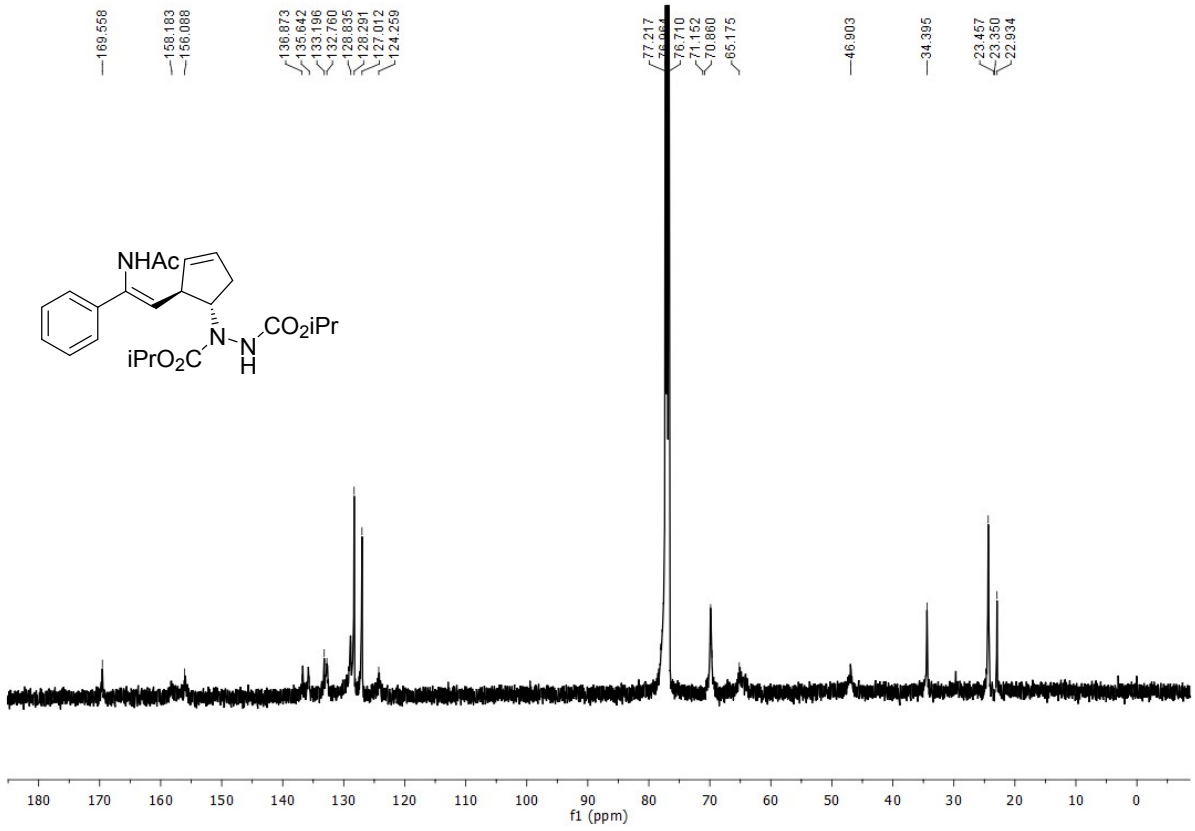
^{1}H NMR of **4aa**



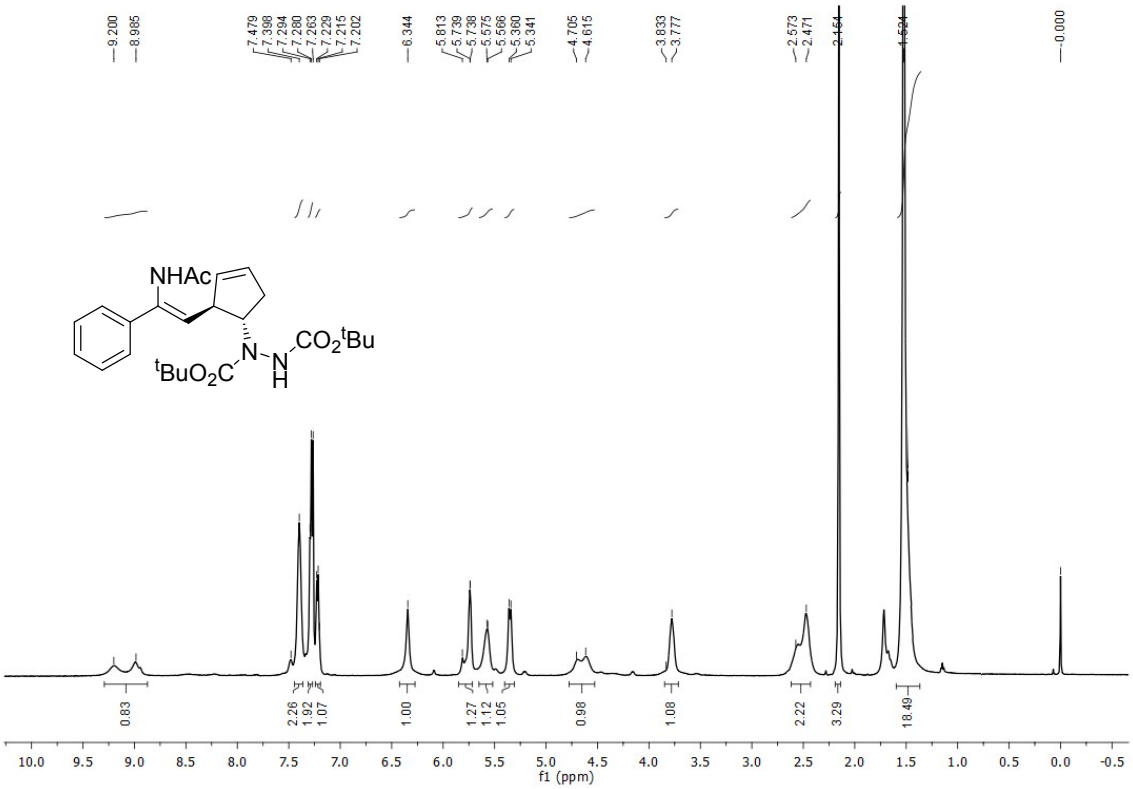
^{13}C NMR of **4aa**



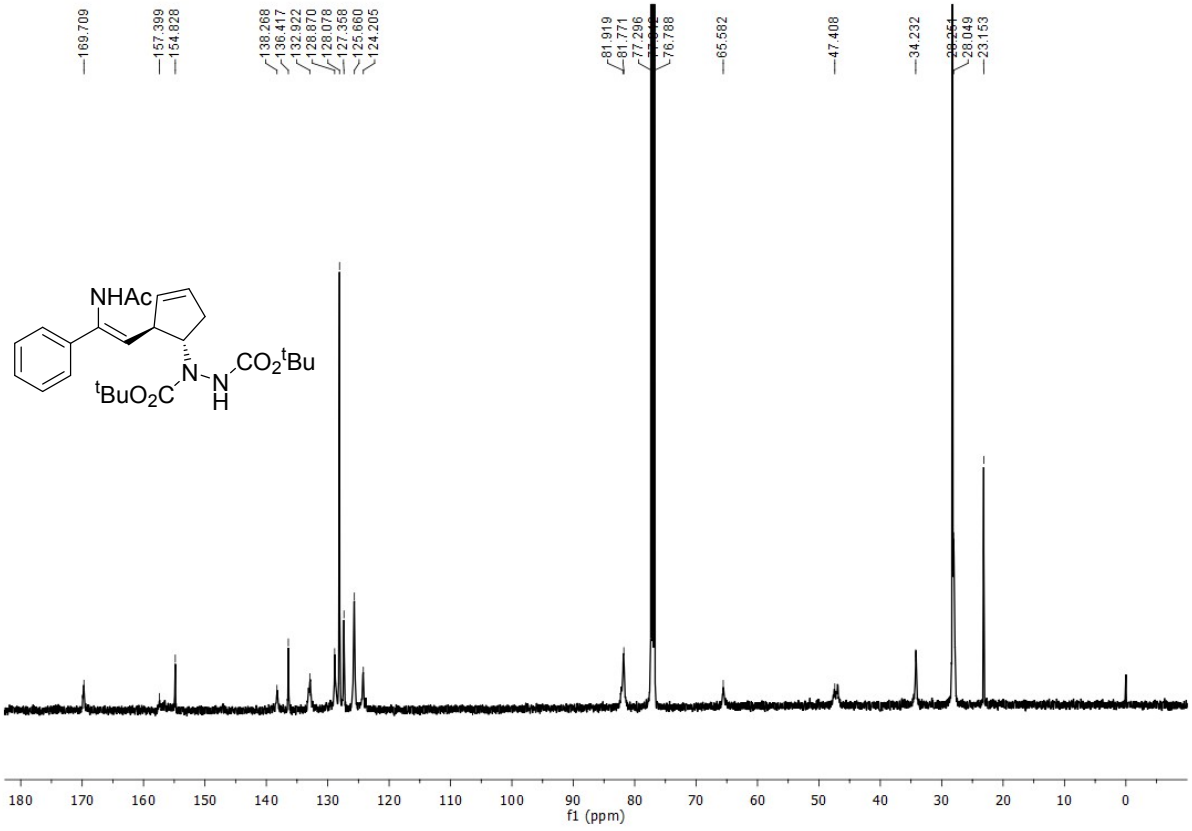
^{1}H NMR of **4ba**



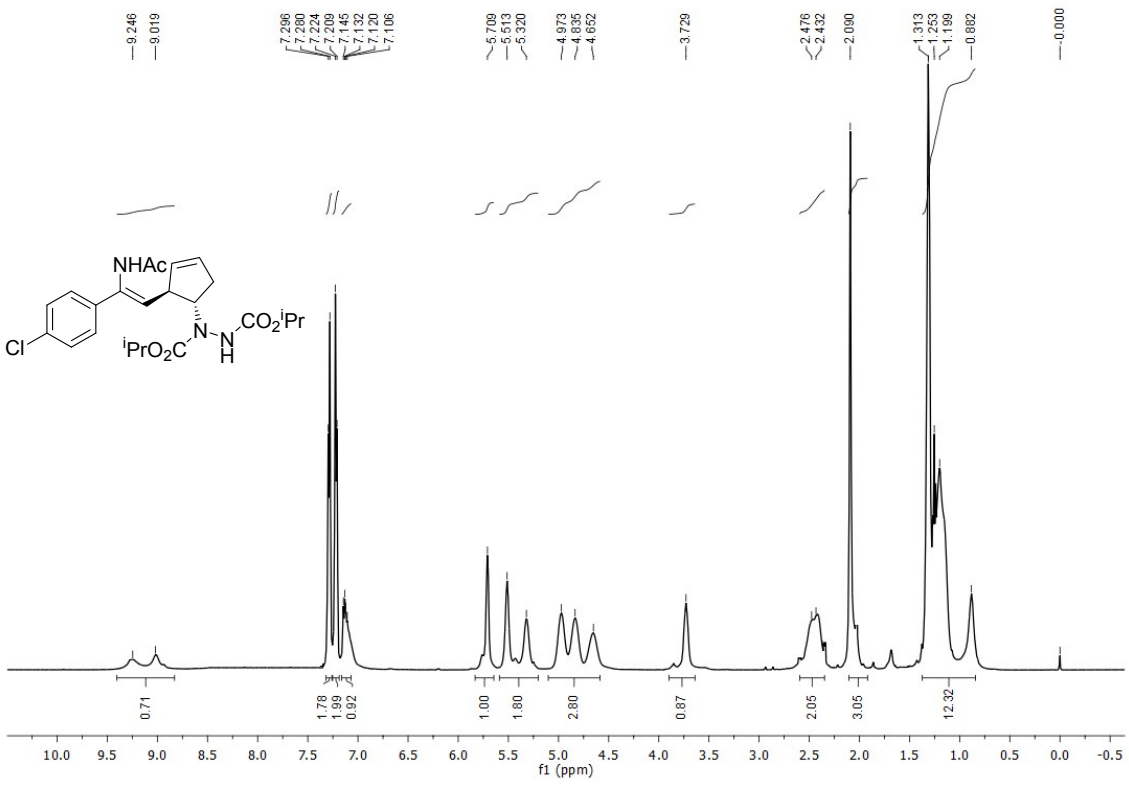
^{13}C NMR of **4ba**



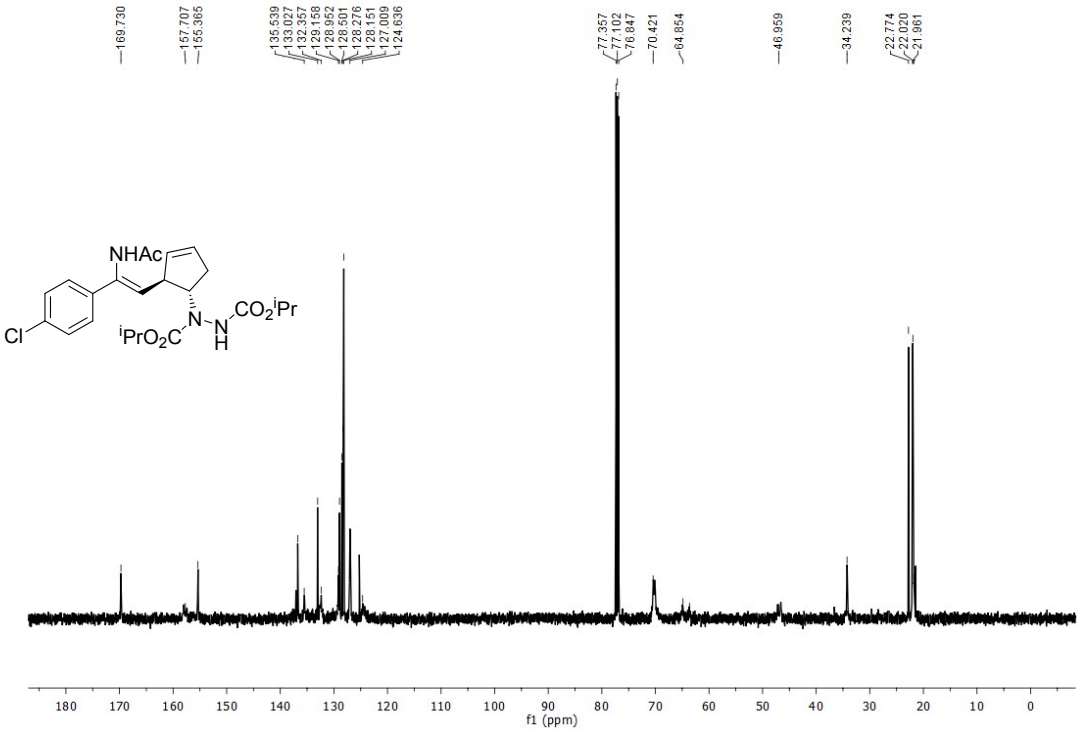
^{1}H NMR of **4ca**



^{13}C NMR of **4ca**



^{1}H NMR of **4ab**



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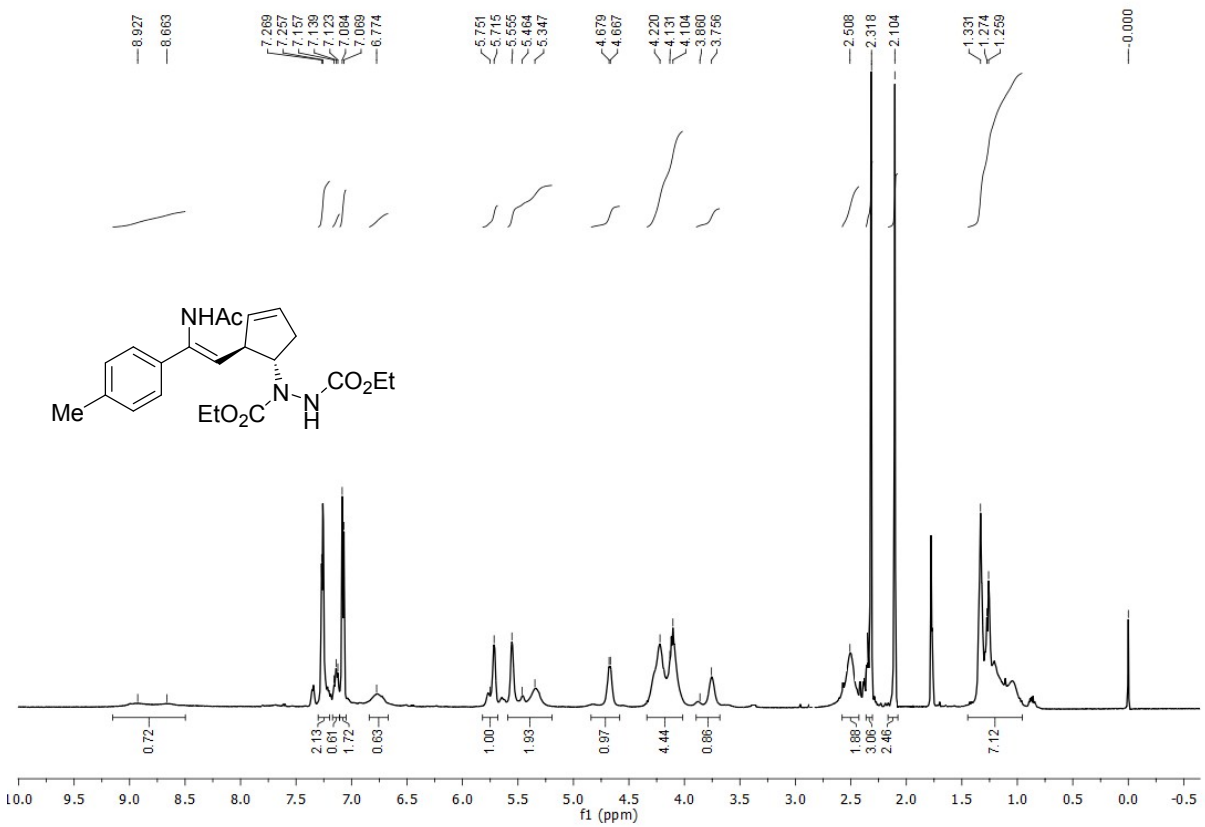
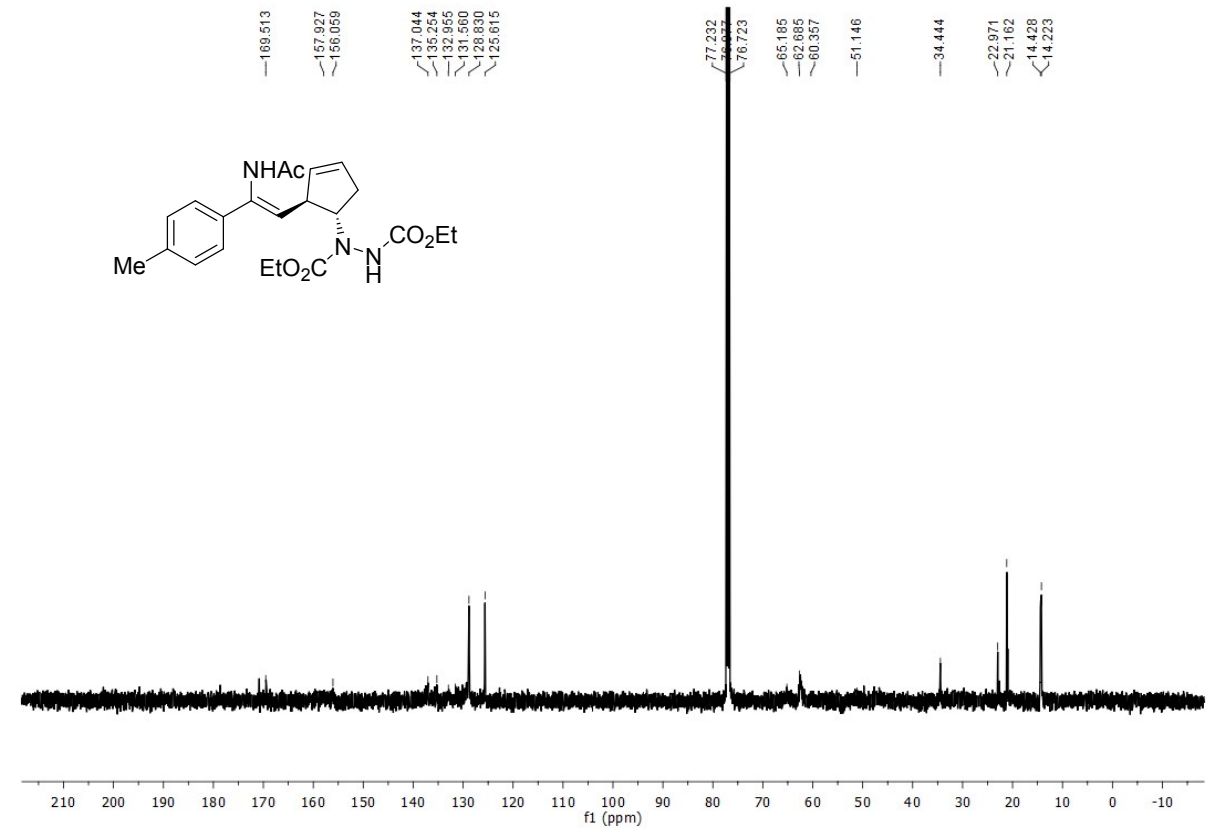
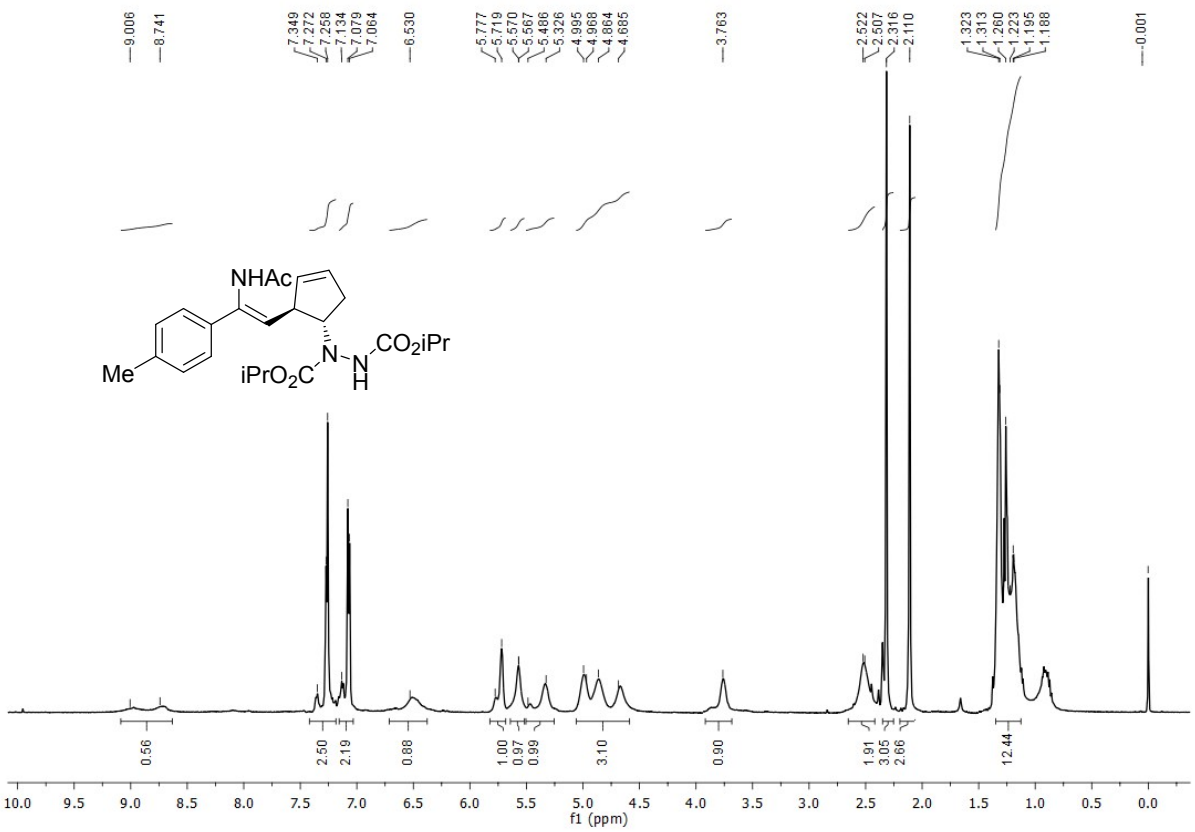


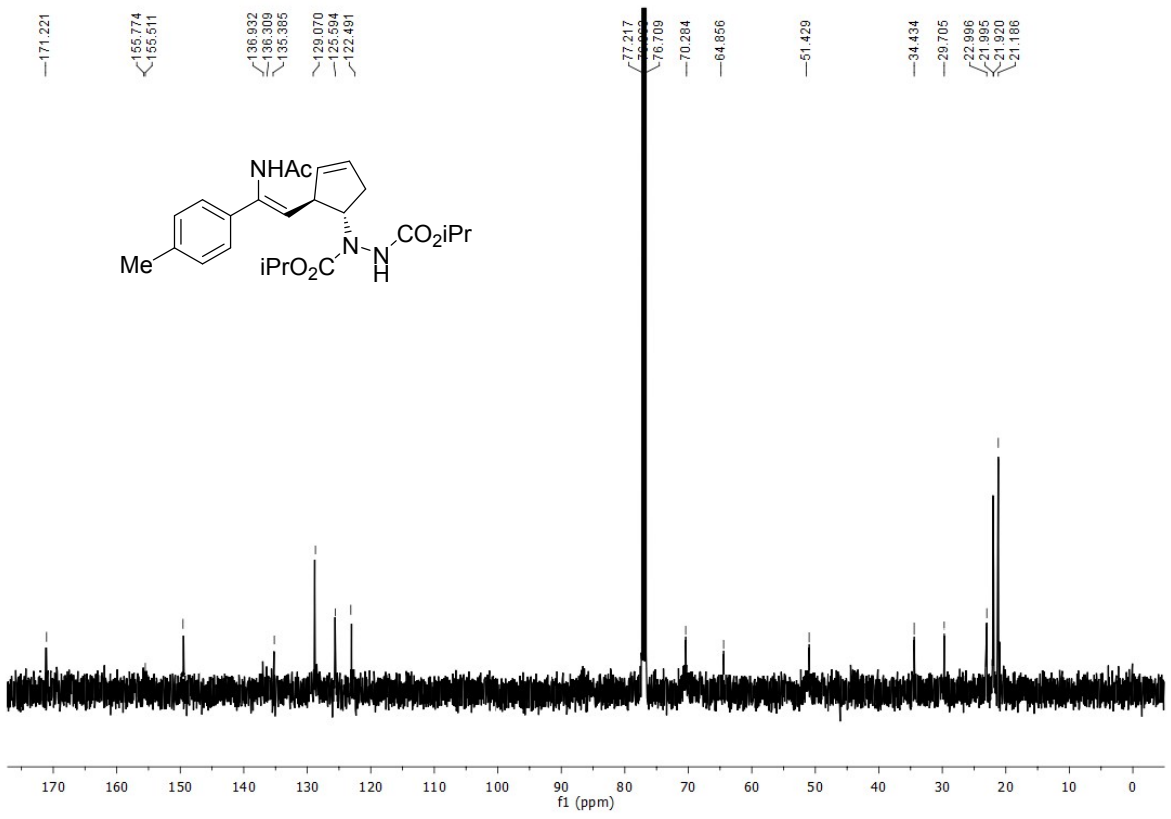
^{1}H NMR of **4ac**



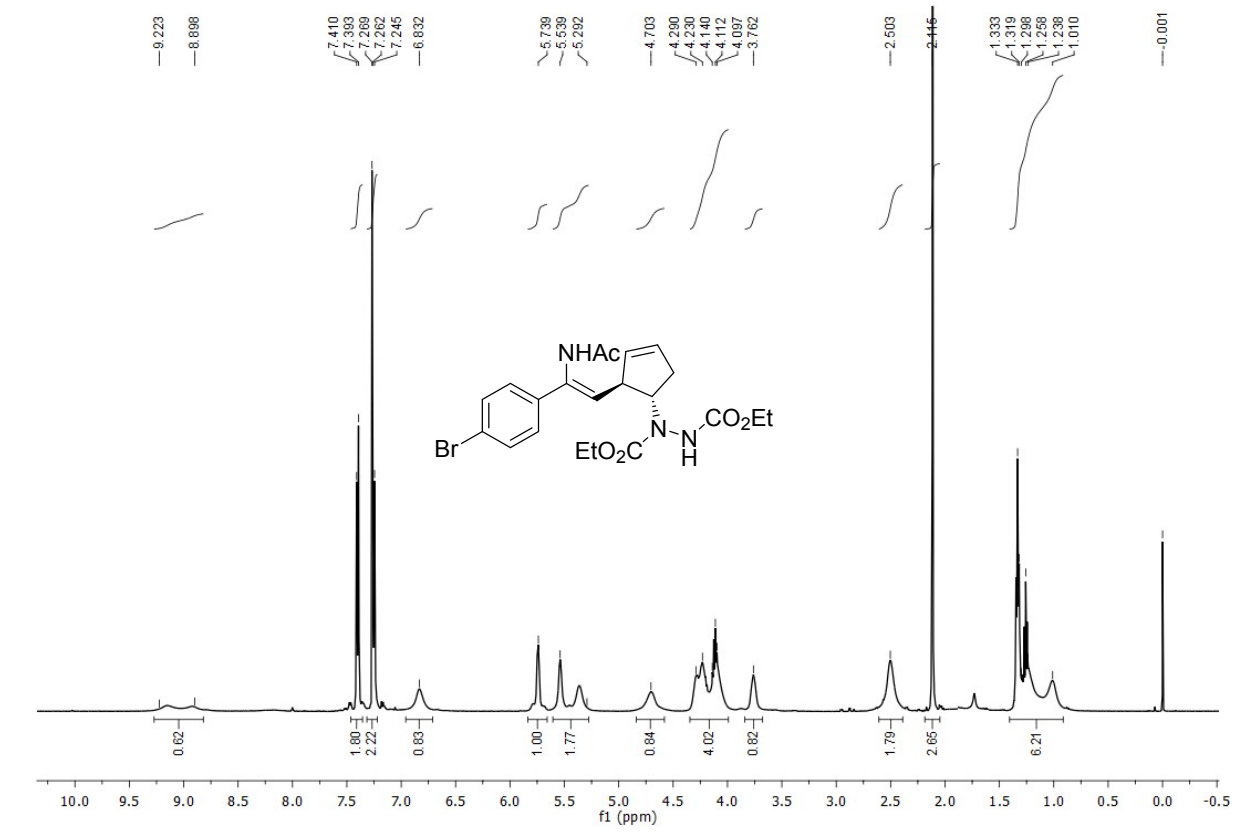
^{13}C NMR of **4ac**



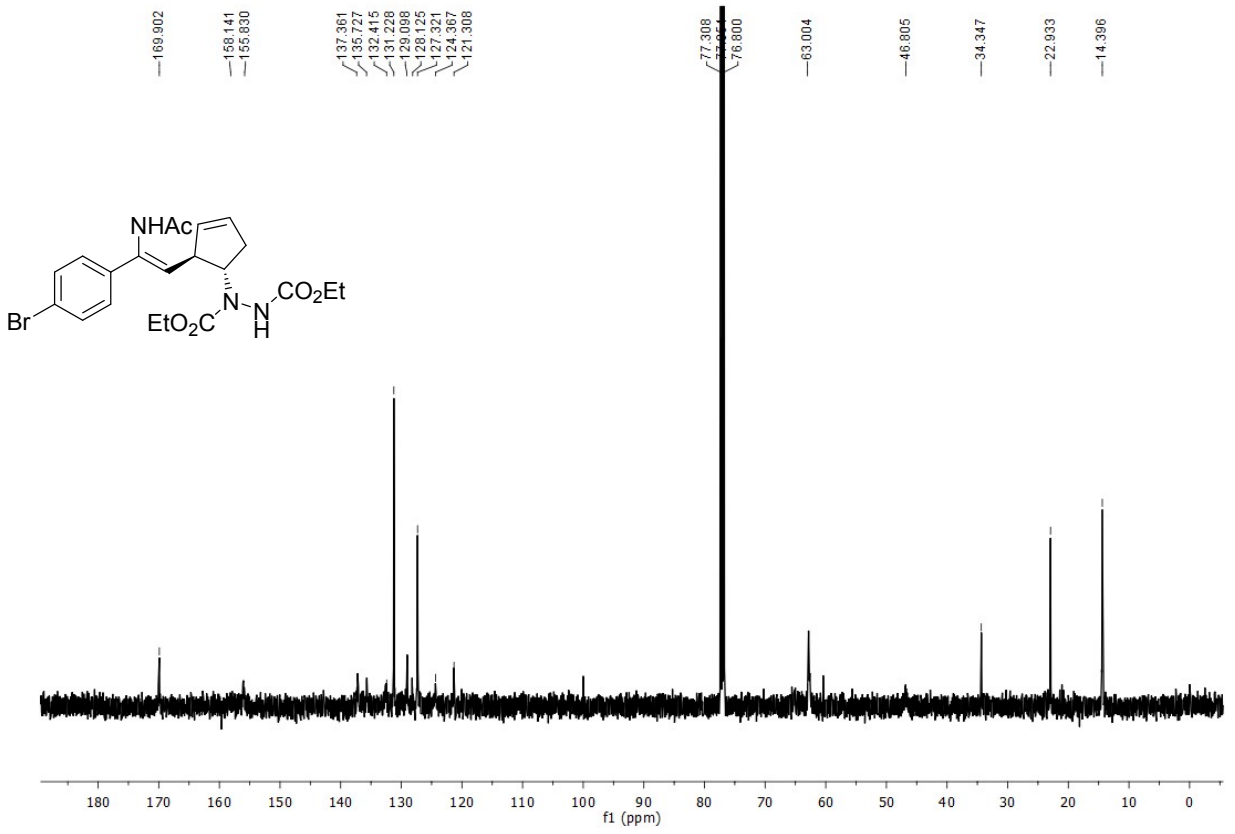
^{1}H NMR of **4bc**



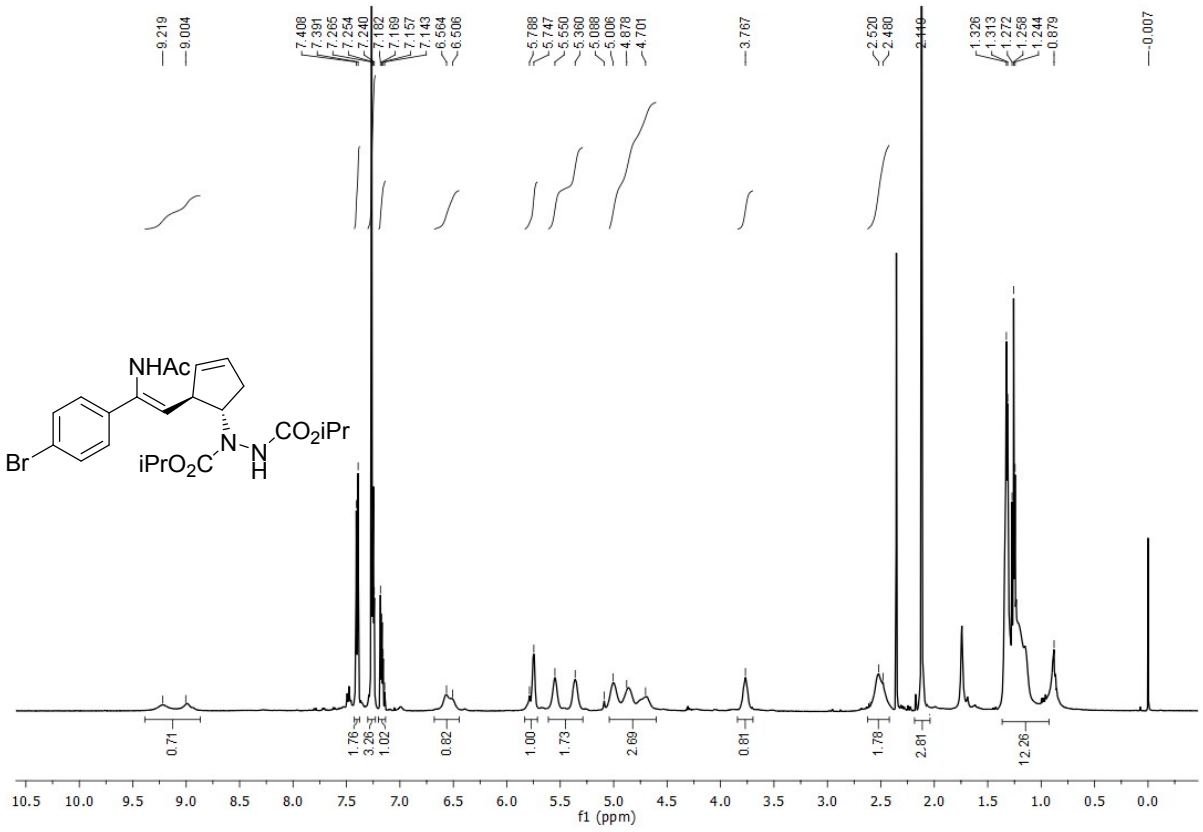
^{13}C NMR of **4bc**



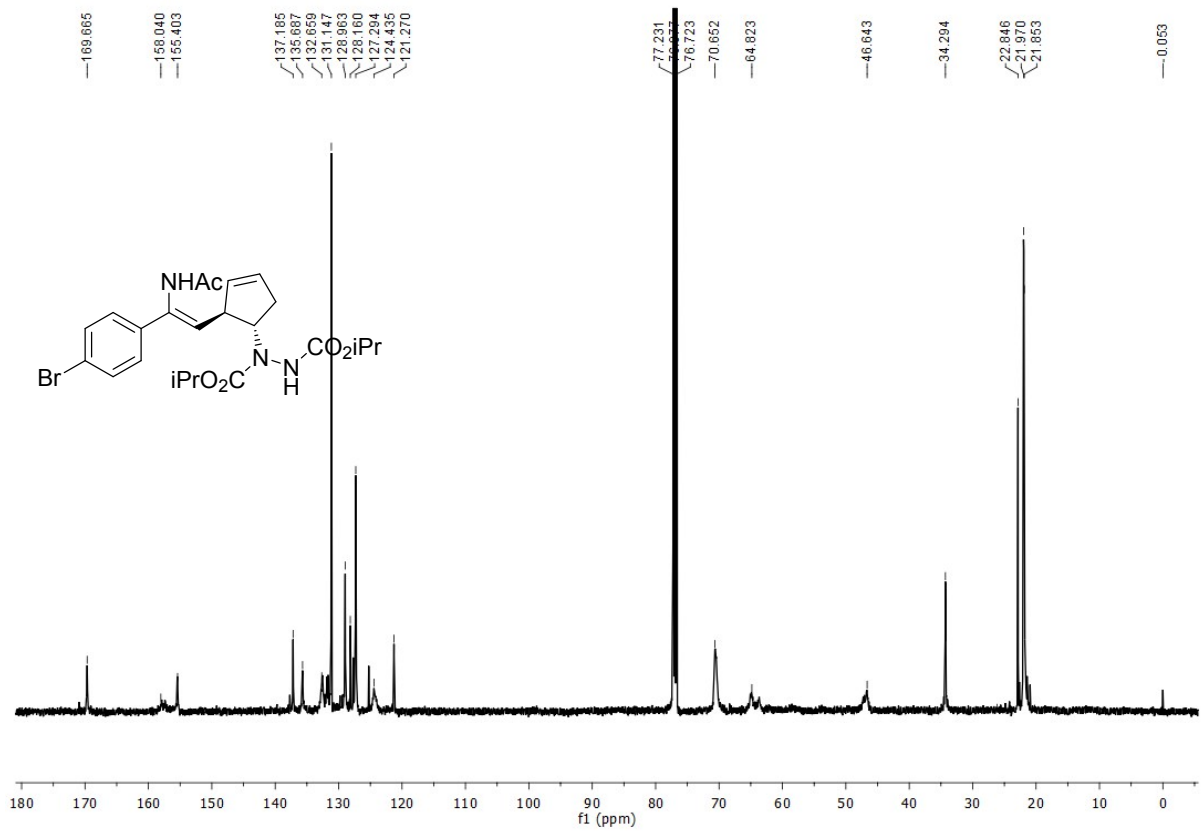
^{1}H NMR of **4ad**



^{13}C NMR of **4ad**



^{1}HNMR of **4bd**



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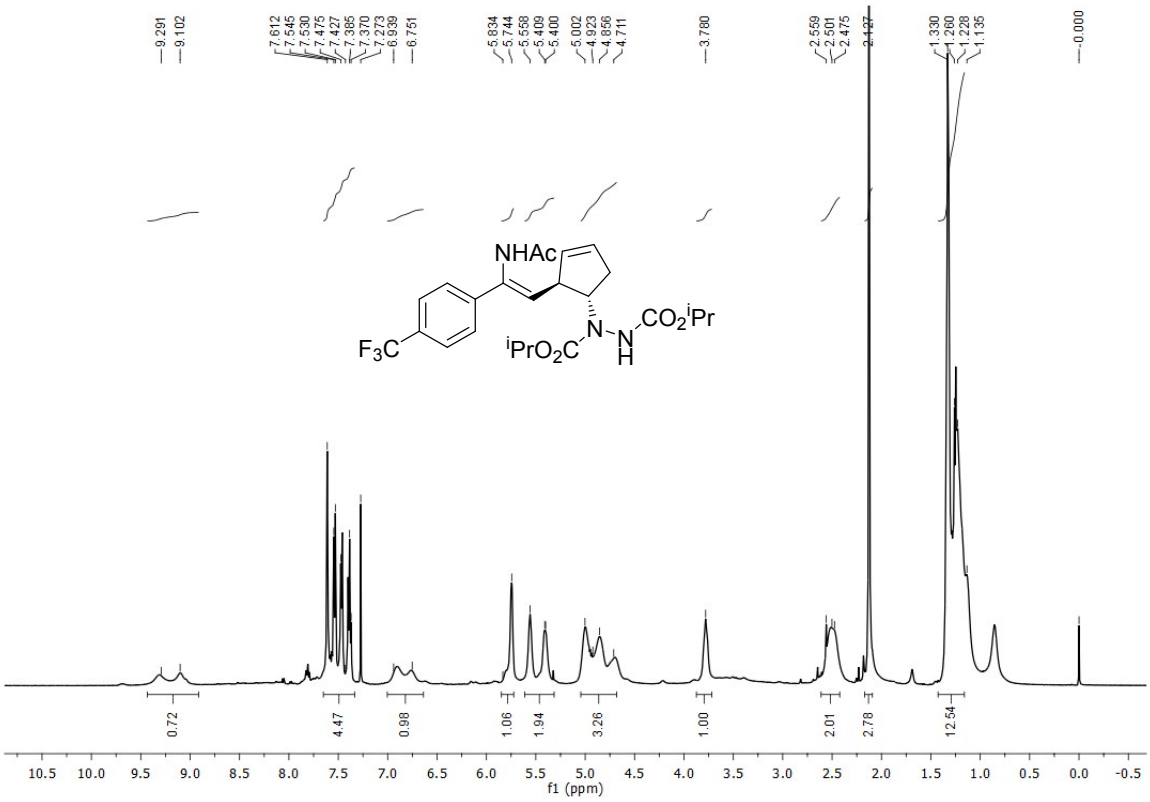
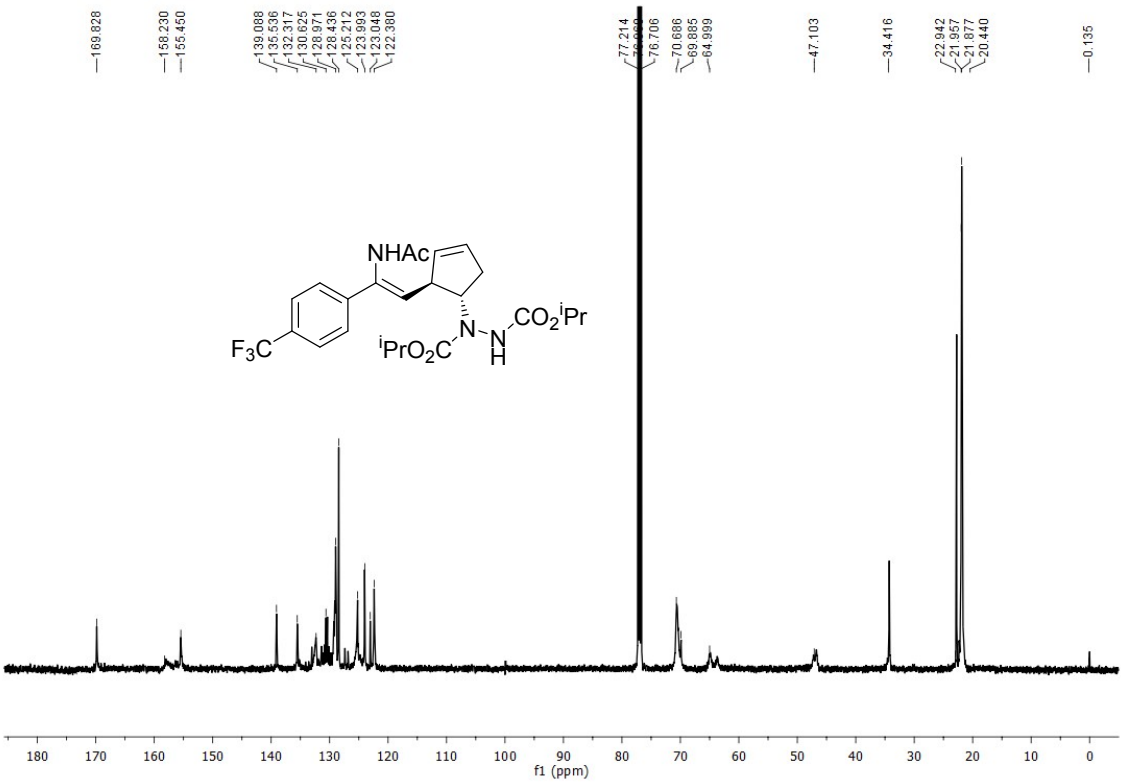


^{1}HNMR of **4be**



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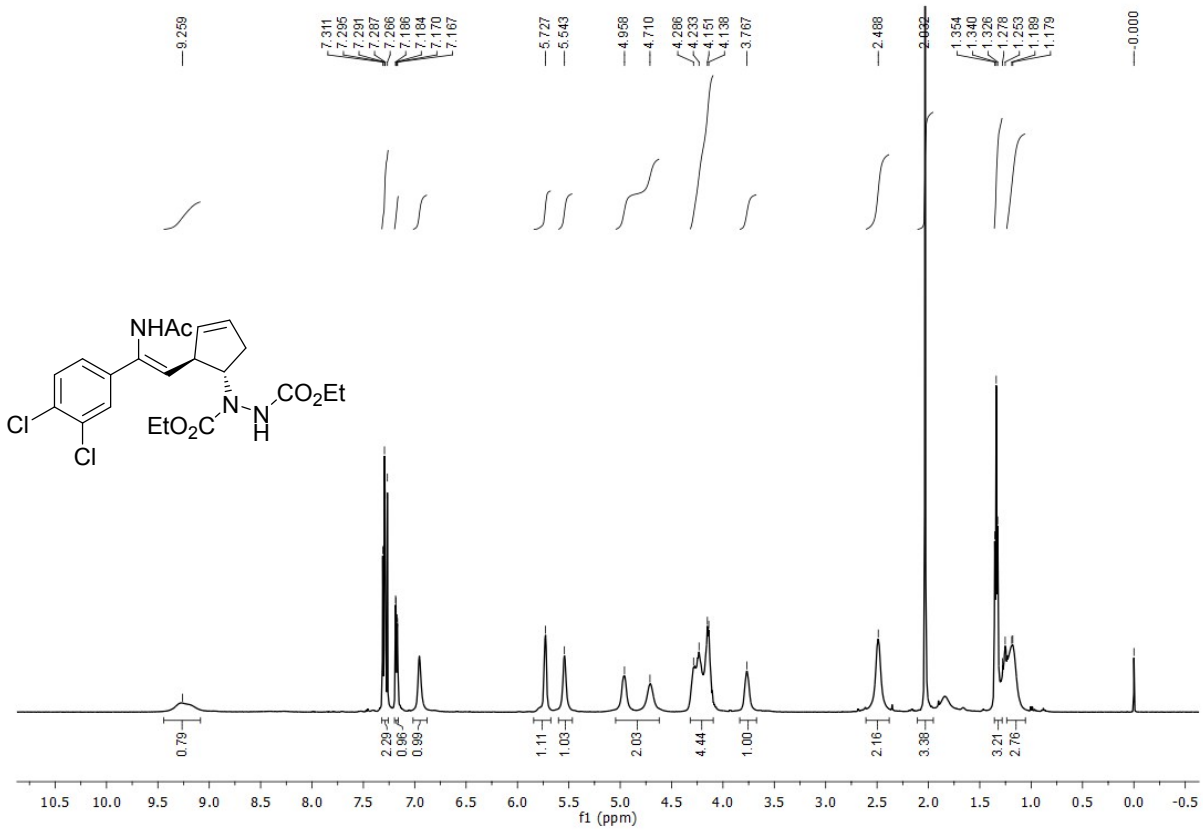

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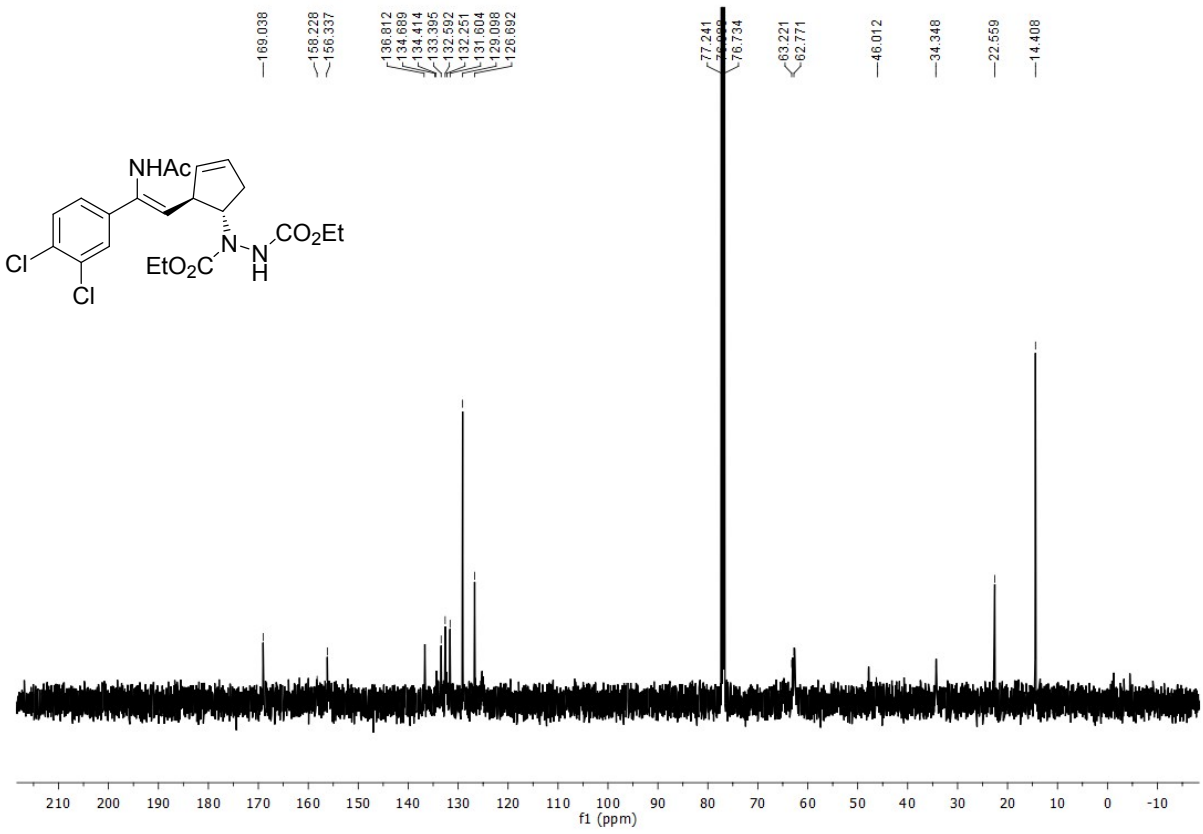

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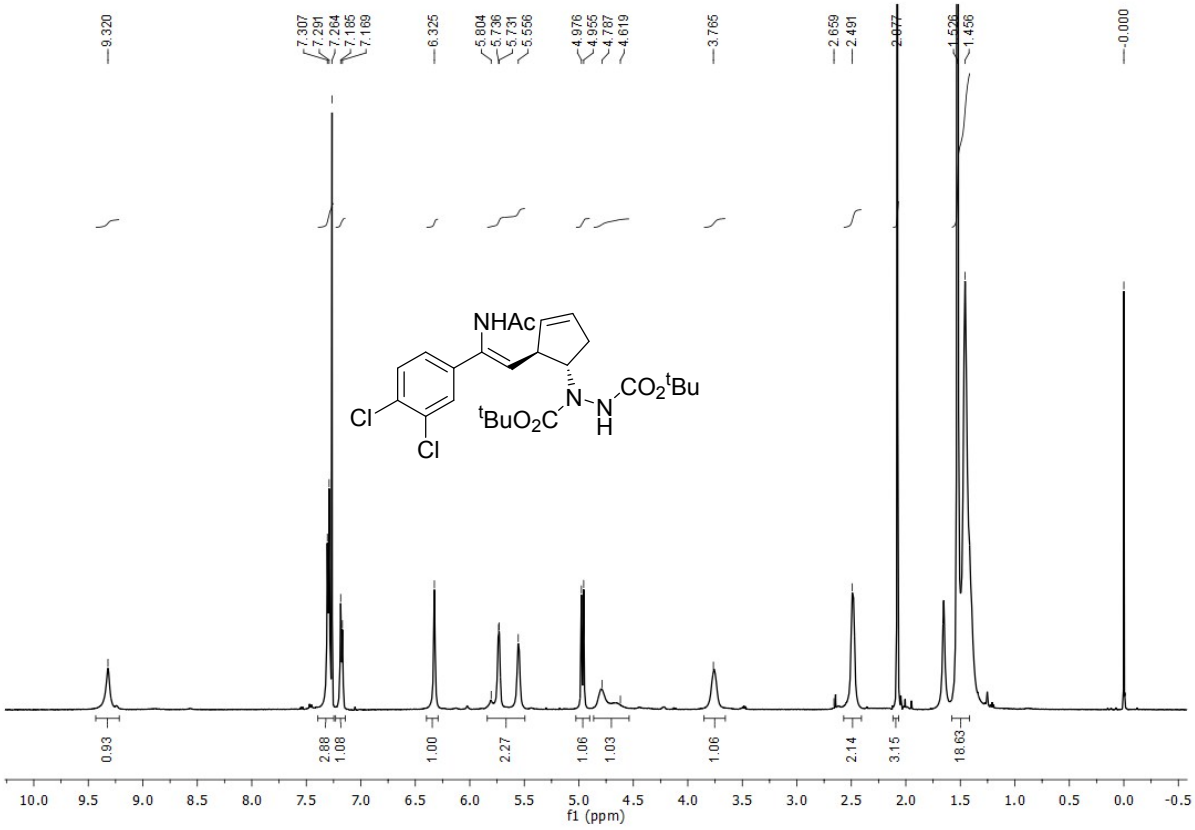

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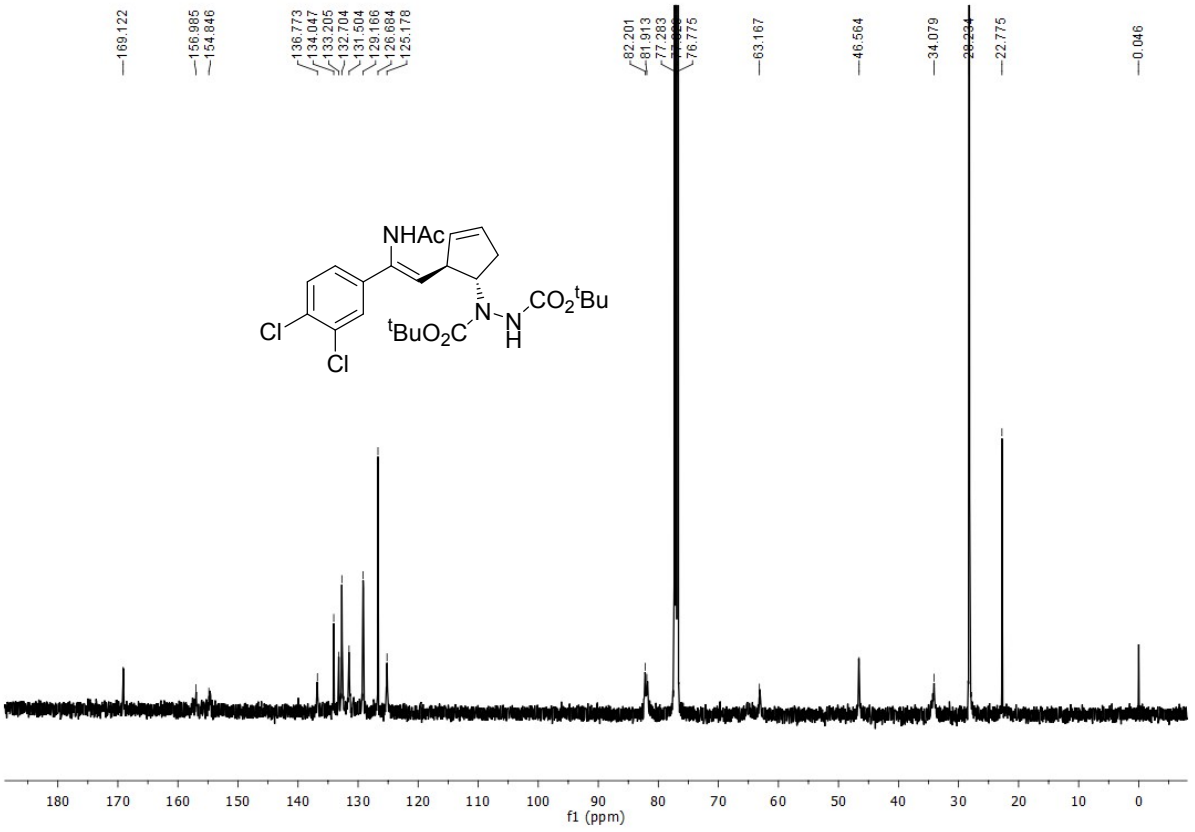
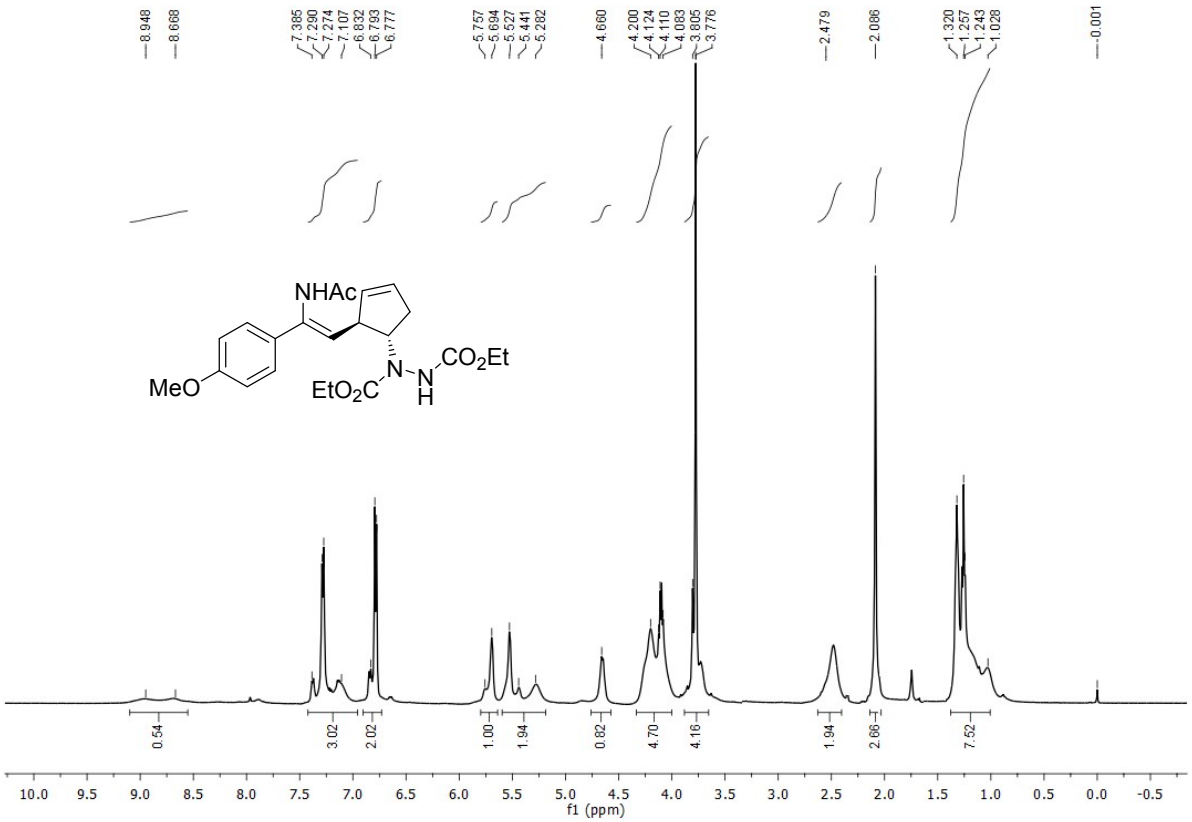
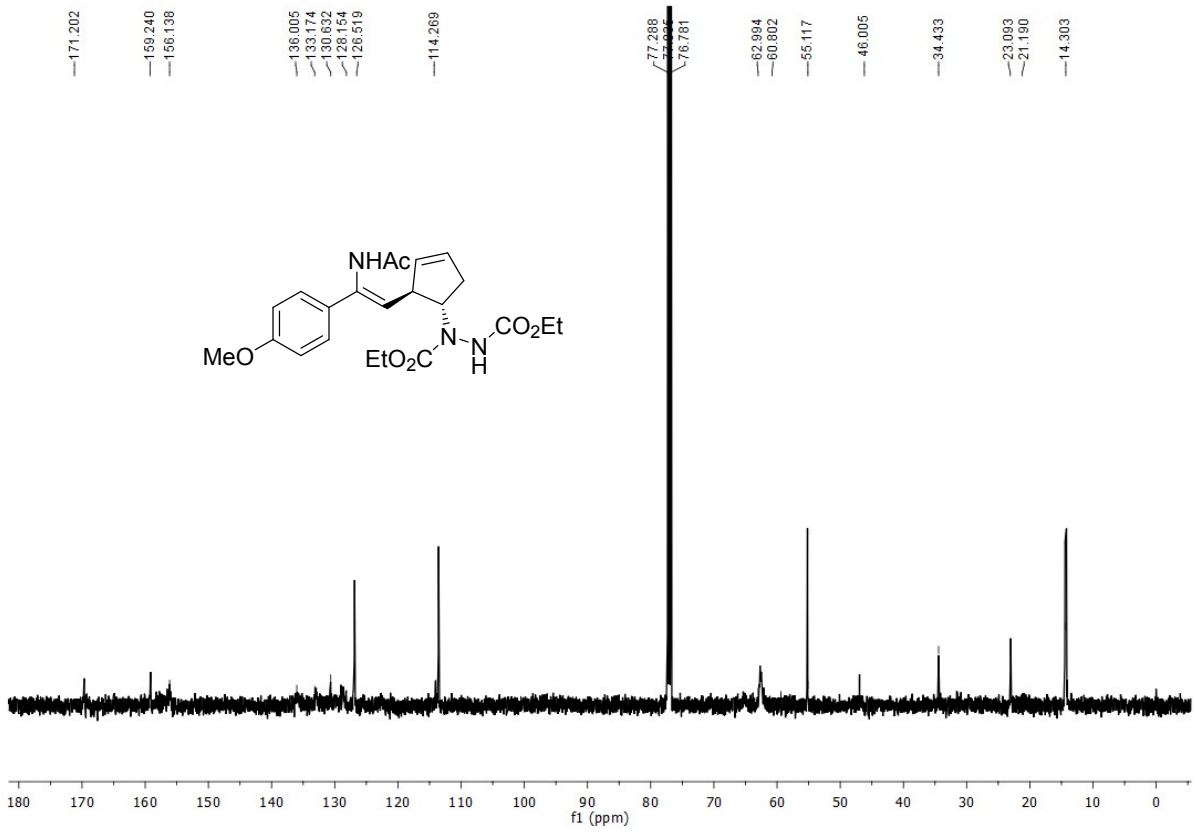


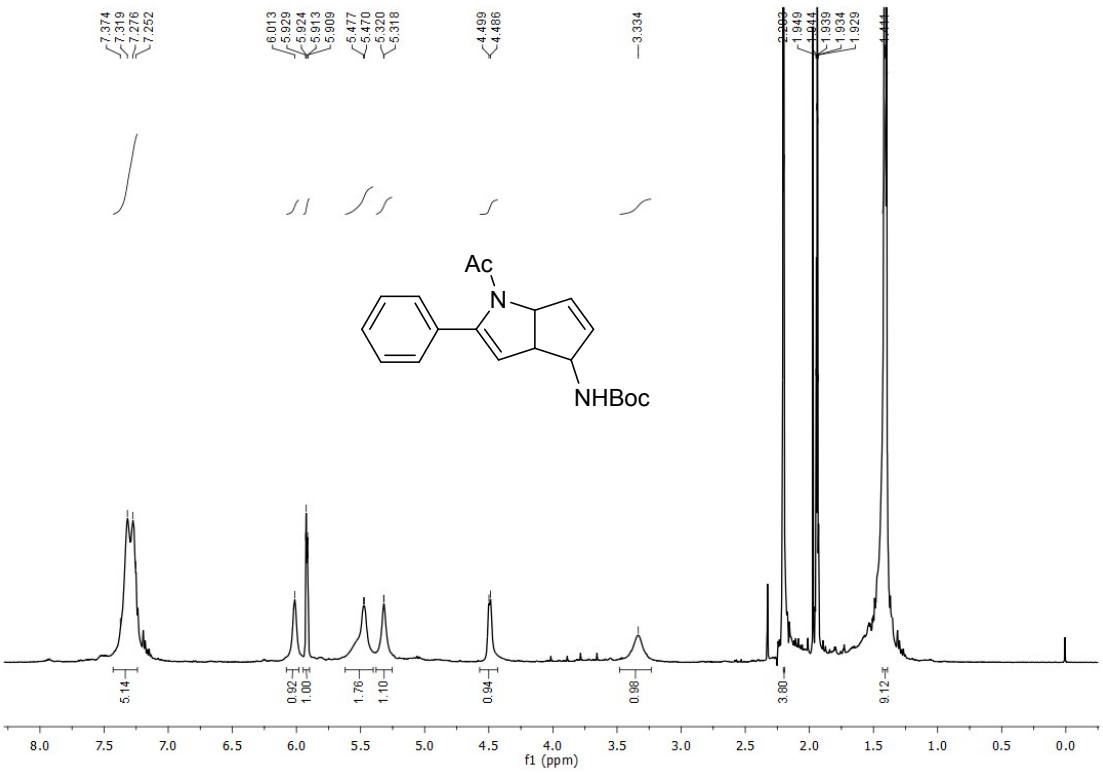
^{13}C NMR of **4cf**



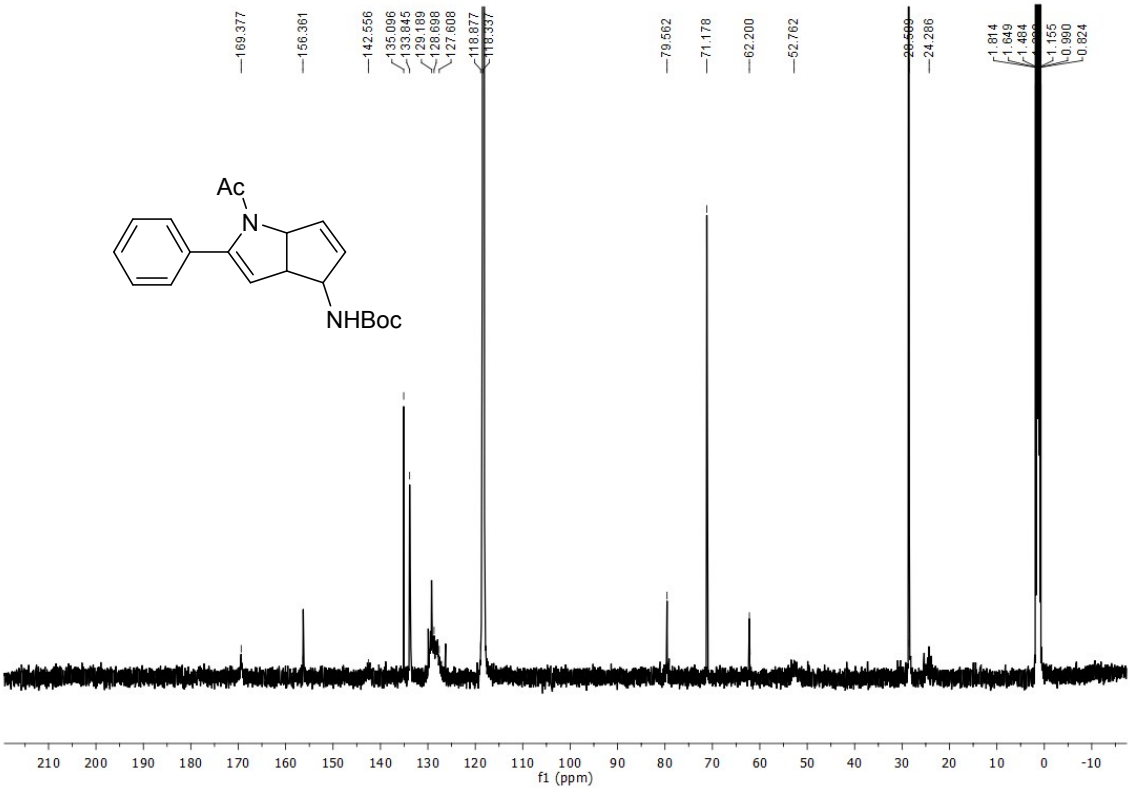
^{1}HNMR of **4ah**



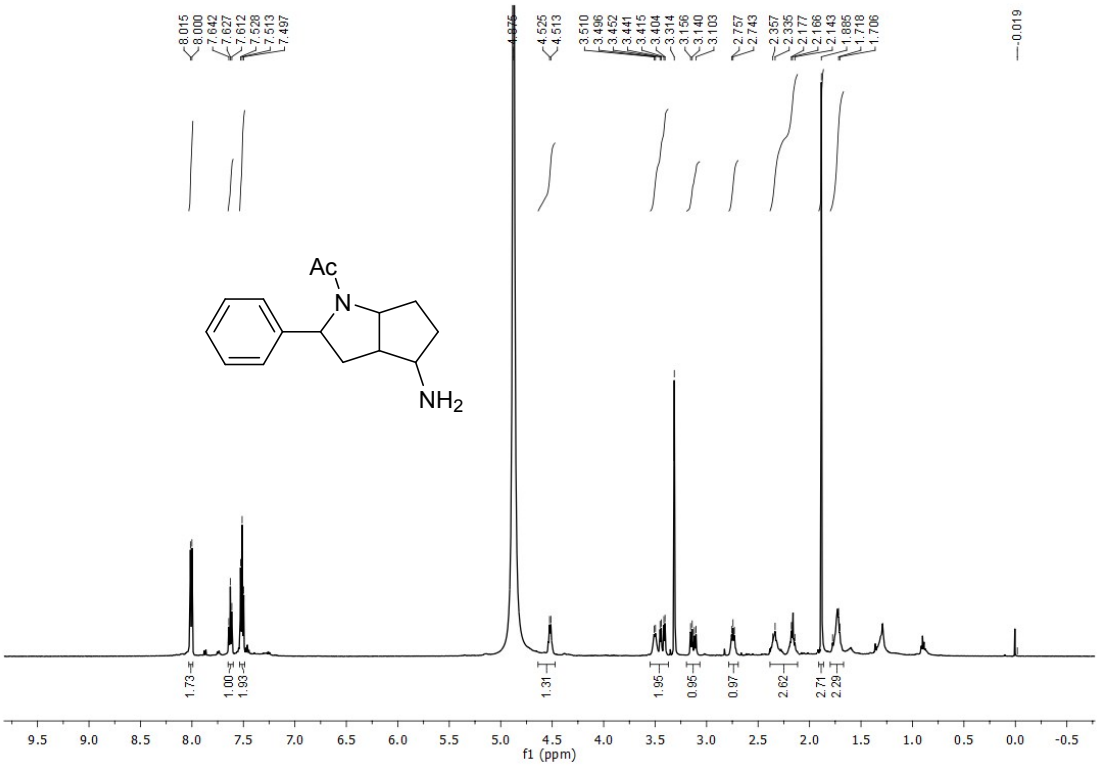
^{13}C NMR of **4ah**



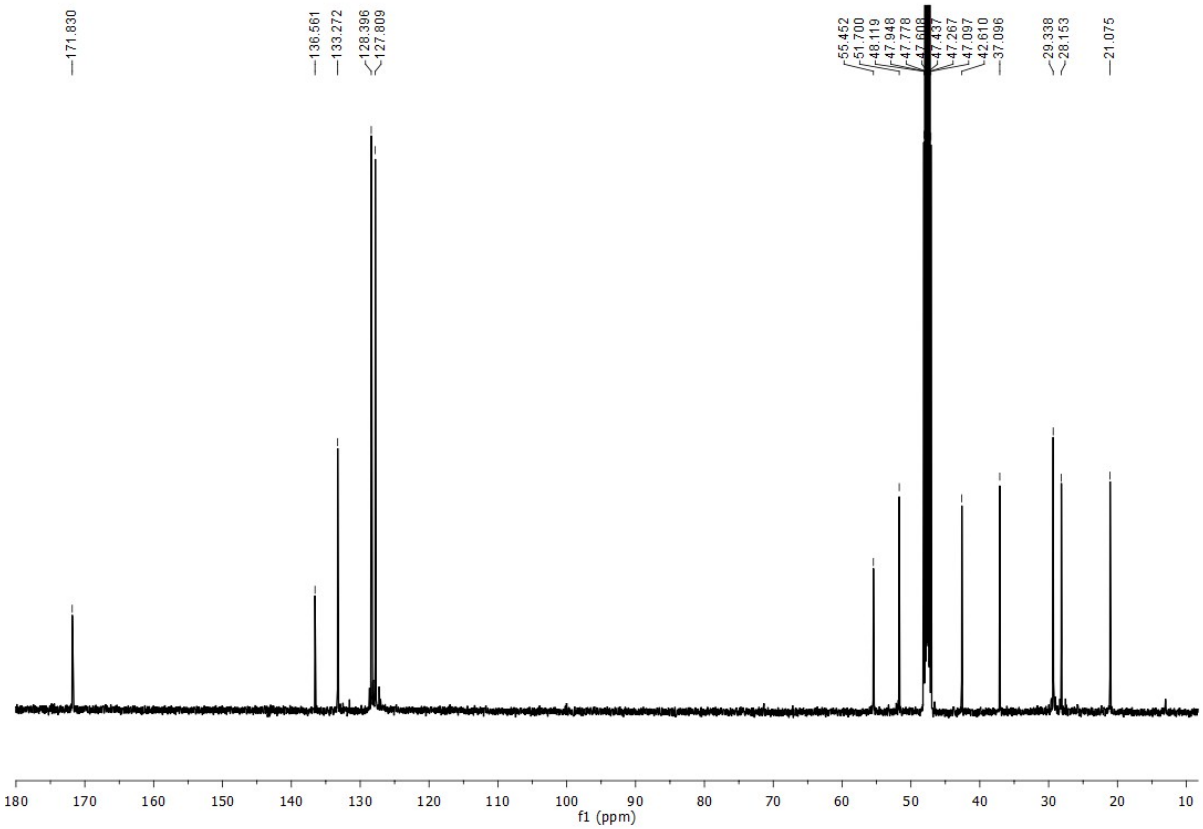
^{1}H NMR of **5ca**



^{13}C NMR of **5ca**

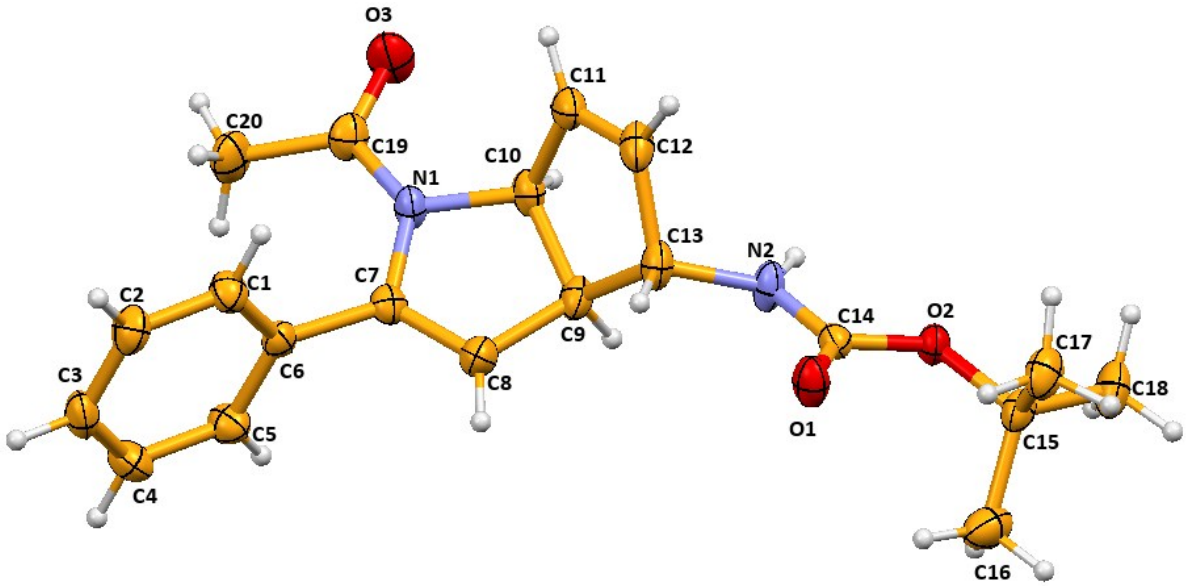


^{1}H NMR of **6ca**

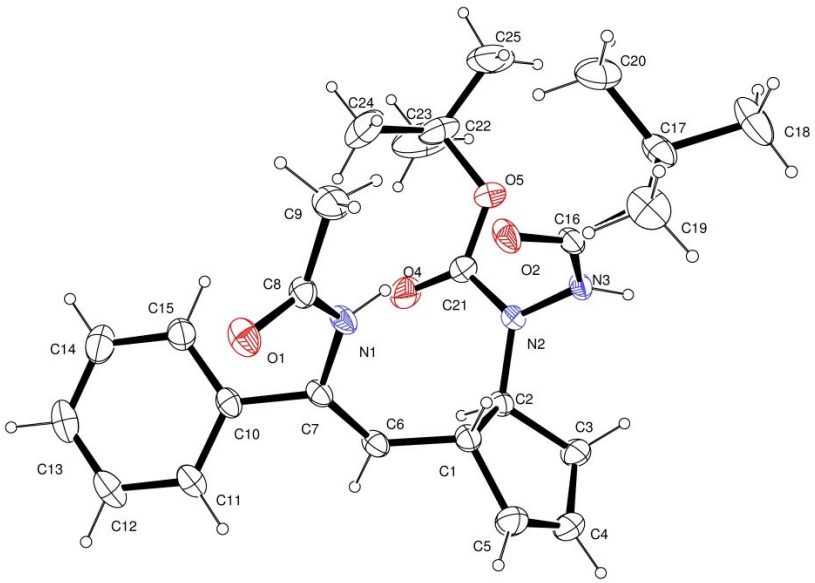


^{13}C NMR of **6ca**

6. **Single Crystal X-ray of 5ca & 4ca**



Single Crystal X-ray of **5ca** (CCDC 1511893)



Single Crystal X-ray of **4ca** (CCDC 1511896)