Supporting Information

Rh(III)-catalyzed Synthesis of Pyrazolo[1,2-*a*]cinnolines from Pyrazolidinones and Diazo compounds

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CONTENT

1. General Information

Reagents and Solvents: PE refers to petroleum ether b.p. 60-90 ^{o}C, EA refers to ethyl acetate, DCM refers to methylene dichloride and DCE refers to 1,2-dichloroethane. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

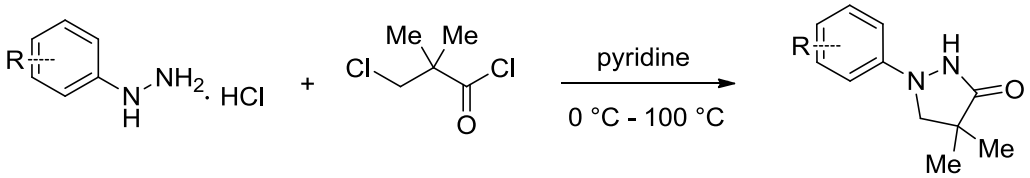
Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

Data collection: ^{1}H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using $CDCl_3$ as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.16 ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus.

2. General Procedure for the Preparation of Starting Materials

2.1 Preparation of 1-arylpyrazolidin-3-ones

Phenidones substrates were synthesized from the corresponding phenylhydrazine hydrochloride as shown in Scheme S1.



Scheme S1. Preparation of 1-arylpyrazolidin-3-ones

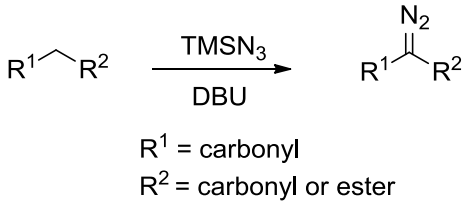
1a, 1b, 1d are commercially available, other phenidones were synthesized following a literature procedure.[1] To a solution of substituted phenylhydrazine hydrocholoride (5.0 mmol, 1.0 equiv.) in dry pyridine (25 mL, 0.5 M), then 3-chloro-2,2-dimethylpropionyl chloride (5.0 mmol, 1.0 equiv.) were added at 0 ^{o}C. The reaction was allowed to warm to room temperature in 4 hours and was heated to 100 ^{o}C for 8 hours. The mixture was cooled, diluted using 30 mL DCM, and neutralized to pH 2 using aqueous HCl (1 M). Then the combined organic phases were washed with brine and

[1] C. F. H. Allen, J. R. Jr. Byers, *US2772282*, 1956.

dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product which was purified by flash column chromatography to afford the desired compounds.

2.2 Preparation of Diazo Substrates

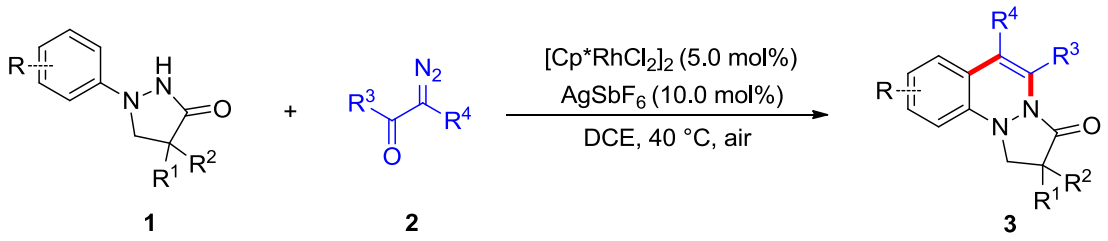
Diazo substrates were synthesized from the corresponding ketonic esters or 1,3 di-ketone as shown in Scheme S2.



Scheme S2. Preparation of Diazo Substrates

To a solution of ketonic ester or 1,3 di-ketone (5.0 mmol, 1.0 equiv.) in CH_3CN (10 mL), TsN_3 (6.0 mmol, 1.1 equiv.) was added. Then the reaction mixture was cooled to 0 °C and a solution of DBU (6.0 mmol, 1.1 equiv.) in 10 mL CH_3CN was added dropwise. Next, the reaction temperature was raised to room temperature. After stirring for 3 hours, the residue was extracted with EA for three times. The combined organic layers were washed with water and brine sequentially, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel to afford the corresponding product in 70-90% yields.

3. Experimental Procedures



Scheme S3. Synthesis of Pyrazolo[1,2-*a*]cinnolines

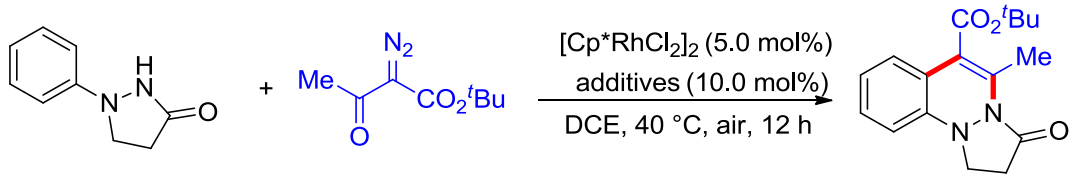
3.1 General Procedures

A sealed tube was charged with phenidone substrate **1** (0.2 mmol, 1.0 equiv.), $(RhCp^*Cl_2)_2$ (0.01 mmol, 5.0 mol%), $AgSbF_6$ (0.02 mmol, 0.1 equiv.), diazo **2** (0.32 mmol, 1.6 equiv.), 3 mL DCE. The reaction mixture was vigorously stirred at 40 °C (oil temperature) for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA (10 mL) and filtered through a plug of celite. The mixture was concentrated in *vacuo* and purified by flash chromatography on silica gel to afford the desired product **3**

3.2 Additional Condition Screening

Following the general procedure for Rh-catalyzed intramolecular coupling between pyrazolidinone and diazo compounds, additional condition screening of different additives, precatalyst to silver salt ratios and solvent are shown below.

Table S1. Screening of additives

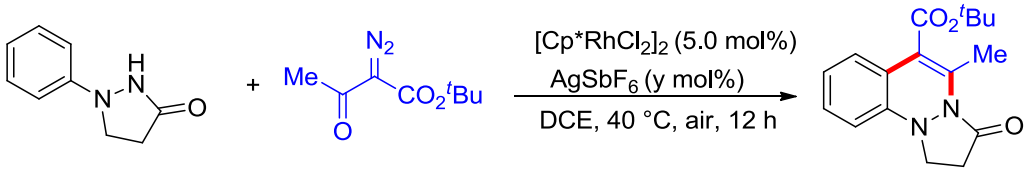


1a 1.0 equiv. **2a** 1.6 equiv. **3aa**

entry	additives	yield (%)[a]
1	$AgNTf_2$	68
2	$AgSbF_6$	84
3	$AgBF_4$	59
4	AgOTf	50
5	AgOAc	trace
6	CsOAc	0
7	NaOAc	0
8	HOAc	0
9	PivOH	0

[a]Isolated yields

Table S2. Screening [Rh]/Ag ratio

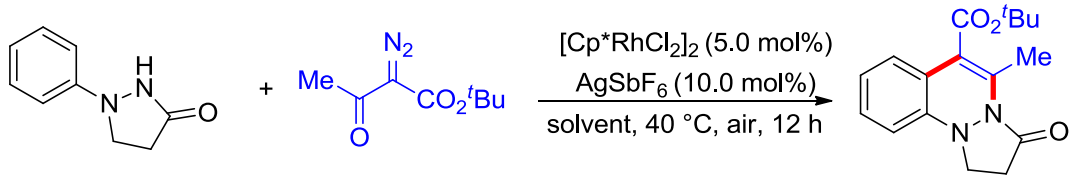


1a 1.0 equiv. **2a** 1.6 equiv. **3aa**

entry	y	yield (%)[a]
1	0%	0
2	5%	<5
3	7%	50
4	9%	75
5	10%	84
6	13%	78
7	15%	74
8	20%	70
9[b]	5%	80

[a]Isolated yields. [b]2.5 mmol% $[Cp^*RhCl_2]_2$) was used.

Table S3. Screening solvent



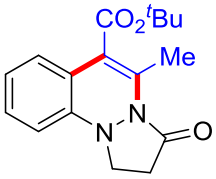
1a 1.0 equiv. **2a** 1.6 equiv. **3aa**

entry	solvent	yield (%)[a]
1	toluene	45
2	DCM	73
3	THF	49
4	EA	43
5	1,4-dioxane	20
6	acetone	41
7	CH_3CN	35
8	DMSO	0
9	^{t}AmylOH	<5
10	methanol	trace

[a]Isolated yields.

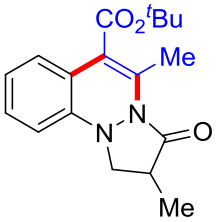
4. Characterization of the Titled Products

tert-butyl 5-methyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3aa)



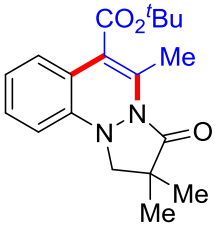
50.4 mg, 84% yield, R_f = 0.23 (PE/EA = 6:1), yellow solid, m. p. 84 - 85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (m, 1H), 6.98 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.86 (m, 1H), 6.46 (dd, *J* = 8.0, 1.1 Hz, 1H), 3.58 (t, *J* = 8.4 Hz, 2H), 2.71 (t, *J* = 8.4 Hz, 2H), 2.40 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 165.7, 146.5, 137.5, 128.7, 123.4, 122.8, 122.4, 118.3, 111.0, 82.2, 46.6, 31.7, 28.2, 15.8, 15.8 ppm. IR (KBr): 3455, 1702, 1639, 1400, 1367, 1332, 1224, 1158, 748, 619 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}N_2NaO_3^+$ 323.1372; Found 323.1366.

tert-butyl 2,5-dimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ba)



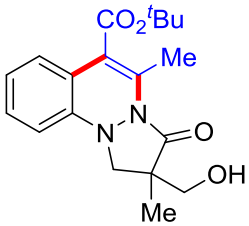
46.5 mg, 74% yield, R_f = 0.25 (PE/EA = 6:1), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (td, *J* = 7.7, 1.5 Hz, 1H), 6.90 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.76 (td, *J* = 7.6, 1.2 Hz, 1H), 6.39 (dd, *J* = 7.9, 1.1 Hz, 1H), 3.81 (t, *J* = 9.1 Hz, 1H), 2.95 (dd, *J* = 10.9, 9.4 Hz, 1H), 2.74 (m, 1H), 2.33 (s, 3H), 1.49 (s, 9H), 1.20 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 165.8, 146.4, 137.5, 128.7, 123.4, 122.8, 122.3, 118.0, 111.1, 82.2, 54.2, 37.1, 28.2, 15.8, 13.9 ppm. IR (KBr): 3453, 2976, 1706, 1637, 1492, 1452, 1382, 1368, 1334, 1227, 1161, 1146, 1015, 983, 845, 749, 685 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{22}N_2NaO_3^+$ 337.1528; Found 337.1518.

tert-butyl 2,2,5-trimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ca)



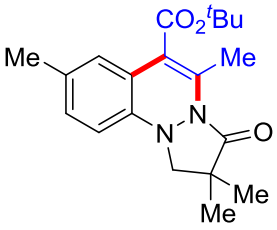
49.9 mg, 76% yield, R_f = 0.24 (PE/EA = 6:1), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (td, *J* = 7.7, 1.5 Hz, 1H), 6.97 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.84 (td, *J* = 7.6, 1.1 Hz, 1H), 6.44 (dd, *J* = 8.0, 1.1 Hz, 1H), 3.34 (s, 2H), 2.40 (s, 3H), 1.57 (s, 9H), 1.28 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 165.8, 146.5, 137.4, 128.6, 123.4, 122.7, 122.2, 117.9, 111.0, 82.2, 60.2, 41.4, 28.2, 23.1, 15.7 ppm. IR (KBr): 3435, 2974, 2931, 1718, 1624, 1493, 1452, 1389, 1368, 1334, 1275, 1227, 1152, 1016, 983, 843, 778, 749, 699, 655 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}N_2NaO_3^+$ 351.1685; Found 351.1677.

tert-butyl 2-(hydroxymethyl)-2,5-dimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3da)



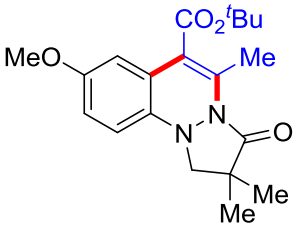
56.4 mg, 82% yield, R_f = 0.20 (PE/EA = 3:1), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (td, *J* = 7.7, 1.5 Hz, 1H), 6.88 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.77 (td, *J* = 7.5, 1.0 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 3.71 (dd, *J* = 11.1, 6.4 Hz, 1H), 3.60 – 3.43 (m, 2H), 3.29 (d, *J* = 9.5 Hz, 1H), 2.74 (t, *J* = 6.0 Hz, 1H), 2.31 (s, 3H), 1.50 (s, 9H), 1.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 165.7, 146.5, 136.7, 128.9, 123.4, 122.7, 122.0, 118.8, 111.2, 82.5, 65.4, 55.5, 47.2, 28.2, 18.9, 15.8 ppm. IR (KBr): 3449, 2924, 1701, 1452, 1399, 1335, 1229, 1153, 1051, 1017, 843, 748 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}N_2NaO_4^+$ 367.1634; Found 367.1629.

tert-butyl 2,2,5,8-tetramethbbyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ea)



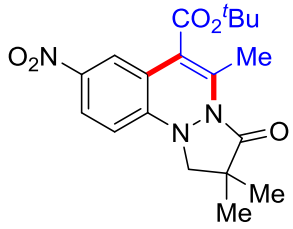
53.4 mg, 78% yield, R_f = 0.35 (PE/EA = 6:1), yellow solid, m. p. 63 - 64 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (d, *J* = 8.1 Hz, 1H), 6.81 (s, 1H), 6.37 (d, *J* = 8.0 Hz, 1H), 3.33 (s, 2H), 2.41 (s, 3H), 2.22 (s, 3H), 1.59 (d, *J* = 1.5 Hz, 9H), 1.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 165.9, 144.2, 137.3, 132.0, 128.8, 124.2, 122.1, 118.0, 111.0, 82.2, 60.4, 41.4, 28.2, 23.1, 20.8, 15.8 ppm. IR (KBr): 3435, 2973, 2930, 1705, 1629, 1499, 1459, 1389, 1368, 1333, 1273, 1236, 1151, 1025, 846, 807, 723, 675, 574 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}N_2NaO_3^+$ 365.1841; Found 365.1834.

tert-butyl 8-methoxy-2,2,5-trimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxate (3fa)



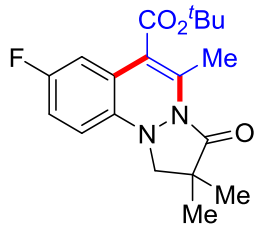
53.7 mg, 75% yield, R_f = 0.30 (PE/EA = 6:1), yellow solid, m. p. 90 - 91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (d, *J* = 2.7 Hz, 1H), 6.60 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.39 (d, *J* = 8.6 Hz, 1H), 3.73 (s, 3H), 3.31 (s, 2H), 2.42 (s, 3H), 1.58 (s, 9H), 1.28 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 165.7, 155.4, 140.0, 138.4, 123.5, 117.5, 112.4, 111.9, 110.3, 82.2, 60.6, 55.5, 41.5, 28.2, 23.1, 15.7 ppm. IR (KBr): 3467, 2973, 2932, 1718, 1612, 1498, 1461, 1389, 1368, 1335, 1217, 1151, 1069, 1036, 845, 804, 724, 679, 592 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}N_2NaO_4^+$ 381.1790; Found 381.1785.

tert-butyl 2,2,5-trimethyl-8-nitro-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ga)



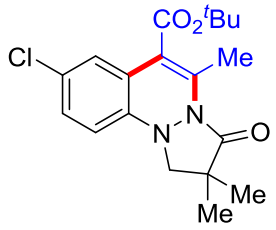
32.8 mg, 44% yield, R_f = 0.33 (PE/EA = 3:1), red solid, m. p. 168 - 169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.82 (d, *J* = 2.5 Hz, 1H), 6.36 (d, *J* = 8.8 Hz, 1H), 3.40 (s, 2H), 2.42 (s, 3H), 1.60 (s, 9H), 1.31 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 164.6, 151.5, 142.4, 140.4, 125.2, 122.3, 118.6, 115.4, 109.6, 83.2, 59.2, 41.2, 28.2, 23.2, 15.9 ppm. IR (KBr): 3449, 2974, 2921, 1720, 1708, 1655, 1638, 1580, 1512, 1396, 1333, 1305, 1227, 1149, 1095, 833, 751, 600 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}N_3O_5^+$ 374.1716; Found 374.1713.

tert-butyl 8-fluoro-2,2,5-trimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylae (3ha)



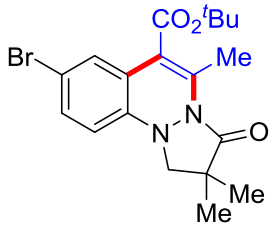
45.0 mg, 65% yield, R_f = 0.31 (PE/EA = 6:1), red oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 – 6.54 (m, 2H), 6.38 (dd, *J* = 8.8, 4.6 Hz, 1H), 3.32 (d, *J* = 1.4 Hz, 2H), 2.44 (s, 3H), 1.59 (s, 9H), 1.29 (d, *J* = 1.5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 165.3, 157.0, 142.5, 139.8, 124.1, 124.1, 116.6, 114.2, 113.9, 111.9, 111.8, 111.2, 110.9, 82.5, 60.4, 41.5, 28.2, 23.1, 15.8 ppm. IR (KBr): 3467, 2975, 2932, 1706, 1618, 1494, 1421, 1368, 1332, 1273, 1234, 1149, 1018, 845, 799, 724, 678 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{23}FN_2NaO_3^+$ 369.1590; Found 369.1582.

tert-butyl 8-chloro-2,2,5-trimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylae (3ia)



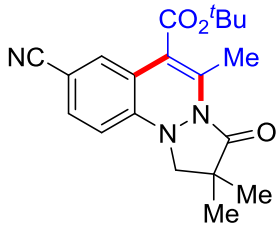
47.0 mg, 65% yield, R_f = 0.34 (PE/EA = 6:1), yellow solid, m. p. 68 - 69 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (m, 2H), 6.56 – 6.07 (m, 1H), 3.31 (d, *J* = 1.5 Hz, 2H), 2.42 (s, 3H), 1.59 (s, 9H), 1.29 (d, *J* = 1.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 165.2, 145.0, 139.6, 128.0, 127.9, 123.9, 123.5, 116.5, 112.1, 82.6, 60.1, 41.4, 28.2, 23.1, 15.8 ppm. IR (KBr): 3460, 2975, 1707, 1618, 1489, 1460, 1403, 1330, 1272, 1226, 1151, 1063, 1018, 968, 845, 806, 724, 674 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{23}ClN_2NaO_3^+$ 385.1295; Found 385.1288.

tert-butyl 8-bromo-2,2,5-trimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ja)



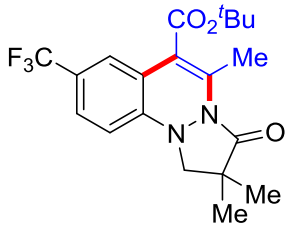
56.0 mg, 69% yield, R_f = 0.33 (PE/EA = 6:1), yellow solid, m. p. 65 - 66 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.06 (m, 2H), 6.30 (d, *J* = 8.3 Hz, 1H), 3.30 (d, *J* = 1.6 Hz, 2H), 2.42 (s, 3H), 1.58 (s, 9H), 1.28 (d, *J* = 1.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 165.2, /145.5, 139.6, 130.9, 126.3, 124.3, 116.3, 115.4, 112.4, 82.6, 60.0, 41.4, 28.2, 23.1, 15.8 ppm. IR (KBr): 3457, 2974, 1707, 1638, 1484, 1398, 1329, 1270, 1225, 1150, 1017, 844, 804, 663 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{23}BrN_2NaO_3^+$ 429.0790; Found 429.0785.

tert-butyl 8-cyano-2,2,5-trimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ka)



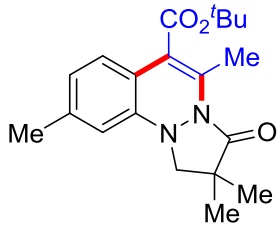
44.5 mg, 63% yield, R_f = 0.23 (PE/EA = 5:1), yellow solid, m. p. 133 - 134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.25 (m, 1H), 7.20 (s, 1H), 6.40 (d, *J* = 8.3 Hz, 1H), 3.36 (s, 2H), 2.42 (s, 3H), 1.60 (s, 9H), 1.31 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 164.8, 149.9, 140.1, 133.3, 126.3, 123.0, 115.6, 110.7, 105.4, 83.1, 59.3, 41.3, 28.2, 23.2, 15.9 ppm. IR (KBr): 3456, 2975, 2222, 1708, 1596, 1496, 1391, 1369, 1334, 1286, 1233, 1149, 1020, 887, 844, 814, 681 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{23}N_3NaO_3^+$ 376.1637; Found 376.1630.

tert-butyl 2,2,5-trimethyl-3-oxo-8-(trifluoromethyl)-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3la)



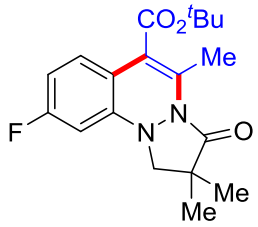
57.8 mg, 73% yield, R_f = 0.20 (PE/EA = 6:1), yellow solid, m. p. 68 - 69 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.11 (m, 2H), 6.45 (d, *J* = 8.3 Hz, 1H), 3.36 (s, 2H), 2.44 (s, 3H), 1.58 (s, 9H), 1.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 165.0, 149.3, 140.1, 125.8, 125.7, 125.7, 124.7, 124.3, 122.7, 120.5, 120.4, 116.3, 110.5, 82.7, 59.7, 41.3, 28.1, 23.1, 15.8 ppm. IR (KBr): 3463, 2976, 1719, 1611, 1391, 1369, 1329, 1279, 1227, 1150, 1120, 1086, 1019, 842, 812, 654 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{23}F_3N_2NaO_3^+$ 419.1558; Found 419.1553.

tert-butyl 2,2,5,9-tetramethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ma)



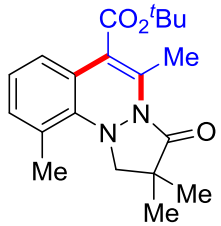
39.7 mg, 58% yield, R_f = 0.25 (PE/EA = 6:1), yellow solid, m. p. 94 - 95 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.29 (s, 1H), 3.35 (d, *J* = 1.4 Hz, 2H), 2.40 (s, 3H), 2.26 (s, 3H), 1.57 (s, 9H), 1.29 (d, *J* = 1.5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 165.9, 146.6, 138.8, 136.4, 123.4, 123.1, 119.4, 118.1, 112.0, 82.1, 60.3, 41.4, 28.2, 23.1, 21.6, 15.7 ppm. IR (KBr): 3434, 2974, 1718, 1612, 1508, 1459, 1389, 1368, 1333, 1280, 1229, 1152, 1030, 991, 847, 812 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}N_2NaO_3^+$ 365.1841; Found 365.1829.

tert-butyl 9-fluoro-2,2,5-trimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3na)



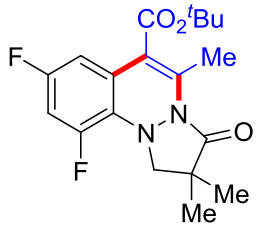
39.7 mg, 49% yield, R_f = 0.26 (PE/EA = 6:1), yellow solid, m. p. 150 - 151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (td, *J* = 8.4, 6.1 Hz, 1H), 6.59 (t, *J* = 9.4 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 3.35 (s, 2H), 2.39 (s, 3), 1.55 (s, 9H), 1.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 165.7, 158.6, 149.4, 138.4, 129.7, 129.6, 114.4, 110.6, 110.3, 106.9, 106.9, 82.1, 60.3, 41.4, 27.9, 23.1, 15.1 ppm. IR (KBr): 3464, 2977, 1712, 1697, 1612, 1583, 1469, 1392, 1340, 1249, 1237, 1154, 1094, 1028, 844, 792, 773, 734 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{23}FN_2NaO_3^+$ 369.1590; Found 369.1582.

tert-butyl 2,2,5,10-tetramethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3oa)



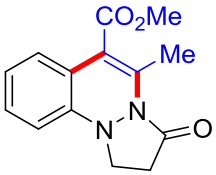
48.6 mg, 71% yield, R_f = 0.23 (PE/EA = 6:1), yellow solid, m. p. 48 - 49 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (m, 1H), 6.83 – 6.71 (m, 2H), 3.61 (s, 2H), 2.37 (s, 3H), 2.29 (s, 3H), 1.56 (s, 9H), 1.27 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 166.0, 147.9, 135.3, 133.1, 122.5, 122.1, 121.6, 121.6, 120.3, 82.2, 64.4, 40.2, 28.2, 22.7, 22.5, 16.1 ppm. IR (KBr): 3442, 2974, 1704, 1460, 1392, 1368, 1337, 1238, 1154, 1077, 1006, 846, 783, 739, 724 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}N_2NaO_3^+$ 365.1841; Found 365.1832.

tert-butyl 8,10-difluoro-2,2,5-trimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3pa)



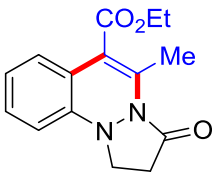
58.3 mg, 80% yield, R_f = 0.26 (PE/EA = 6:1), yellow solid, m. p. 80 - 81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 – 6.01 (m, 2H), 3.64 (dd, *J* = 4.6, 1.4 Hz, 2H), 2.41 (s, 3H), 1.57 (m, 9H), 1.26 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 165.3, 160.4, 157.2, 142.5, 139.8, 124.2, 124.1, 116.6, 114.1, 113.8, 111.9, 111.8, 111.2, 110.9, 82.5, 60.4, 41.5, 28.2, 23.1, 15.7 ppm. IR (KBr): 3448, 2975, 2362, 1709, 1616, 1444, 1390, 1349, 1323, 1278, 1252, 1151, 1137, 996, 844, 683, 573 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{22}F_2N_2NaO_3^+$ 387.1496; Found 387.1497.

methyl 5-methyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ab)



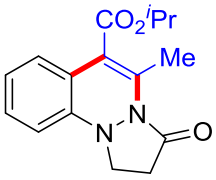
40.8 mg, 79% yield, R_f = 0.21 (PE/EA = 6:1), yellow solid, m. p. 94 - 95 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (td, *J* = 7.7, 1.5 Hz, 1H), 6.98 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.86 (td, *J* = 7.6, 1.1 Hz, 1H), 6.49 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.86 (s, 3H), 3.60 (t, *J* = 8.4 Hz, 2H), 2.74 (t, *J* = 8.4 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 167.0, 146.6, 140.2, 128.8, 123.9, 122.9, 122.2, 116.3, 111.0, 52.0, 46.6, 31.7, 16.1 ppm. IR (KBr): 3450, 1720, 1707, 1655, 1630, 1492, 1400, 1366, 1330, 1209, 1031, 898, 751, 671, 643 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{14}N_2NaO_3^+$ 281.0902; Found 281.0894.

ethyl 5-methyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ac)



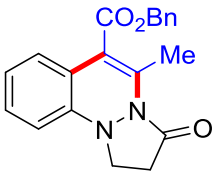
43.5 mg, 80% yield, R_f = 0.22 (PE/EA = 6:1), yellow solid, m. p. 47 - 48 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (td, *J* = 7.7, 1.5 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.85 (td, *J* = 7.6, 1.1 Hz, 1H), 6.57 – 6.39 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.59 (t, *J* = 8.4 Hz, 2H), 2.73 (t, *J* = 8.4 Hz, 2H), 2.43 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 166.5, 146.5, 139.5, 128.8, 123.7, 122.8, 122.2, 116.7, 111.0, 61.2, 46.6, 31.7, 16.0, 14.2 ppm. IR (KBr): 3458, 2980, 1707, 1620, 1451, 1360, 1330, 1205, 1098, 1032, 899, 751, 643 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{16}N_2NaO_3^+$ 295.1059; Found 295.1055.

isopropyl 5-methyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ad)



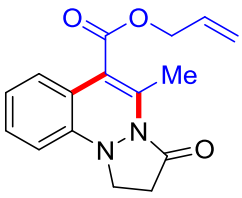
47.5 mg, 83% yield, R_f = 0.25 (PE/EA = 6:1), yellow solid, m. p. 90 - 91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.7 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.42 – 4.98 (m, 1H), 3.59 (t, *J* = 8.4 Hz, 2H), 2.72 (t, *J* = 8.4 Hz, 2H), 2.42 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 166.0, 146.5, 138.9, 128.8, 123.6, 122.8, 122.3, 117.1, 111.0, 69.0, 46.6, 31.7, 21.8, 16.0 ppm. IR (KBr): 3457, 2980, 1705, 1631, 1453, 1376, 1352, 1336, 1276, 1214, 1176, 1104, 1030, 900, 744, 670 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}N_2NaO_3^+$ 309.1215; Found 309.1209.

benzyl 5-methyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ae)



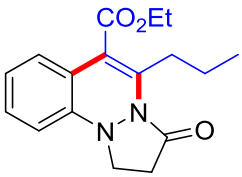
56.1 mg, 84% yield, R_f = 0.22 (PE/EA = 6:1), yellow solid, m. p. 83 - 84 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.26 (m, 5H), 7.13 – 6.99 (m, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 5.30 (s, 2H), 3.54 (t, *J* = 8.3 Hz, 2H), 2.69 (t, *J* = 8.3 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 166.3, 146.5, 140.2, 135.4, 128.8, 128.7, 128.6, 128.5, 123.8, 122.9, 122.2, 116.2, 111.1, 67.0, 46.6, 31.7, 16.2 ppm. IR (KBr): 3448, 1706, 1619, 1492, 1451, 1361, 1329, 1196, 1138, 1028, 895, 749, 695 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{18}N_2NaO_3^+$ 357.1215; Found 357.1207.

allyl 5-methyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3af)



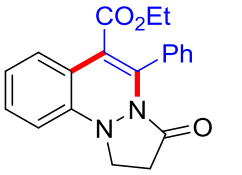
43.2 mg, 76% yield, R_f = 0.33 (PE/EA = 6:1), red solid, m. p. 49 - 50 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (td, *J* = 7.8, 1.5 Hz, 1H), 7.01 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.86 (td, *J* = 7.6, 1.1 Hz, 1H), 6.49 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.21 – 5.85 (m, 1H), 5.55 – 5.14 (m, 2H), 4.77 (dt, *J* = 5.8, 1.4 Hz, 2H), 3.60 (t, *J* = 8.4 Hz, 2H), 2.74 (t, *J* = 8.4 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 166.2, 146.6, 140.2, 131.6, 128.8, 123.9, 122.9, 122.2, 119.2, 116.3, 111.1, 65.8, 46.6, 31.7, 16.2 ppm. IR (KBr): 3434, 1707, 1618, 1580, 1493, 1451, 1357, 1328, 1273, 1199, 1029, 992, 935, 751, 672, 643, 567, 542 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{16}N_2NaO_3^+$ 307.1059; Found 307.1050.

ethyl 3-oxo-5-propyl-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ag)



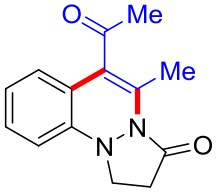
48.6 mg, 81% yield, R_f = 0.25 (PE/EA = 6:1), yellow solid, m. p. 59 - 60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 – 6.93 (m, 2H), 6.87 (m, 1H), 6.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.65 (t, *J* = 8.4 Hz, 2H), 2.91 – 2.79 (m, 2H), 2.73 (t, *J* = 8.3 Hz, 2H), 1.79 – 1.51 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 166.5, 146.6, 142.9, 128.9, 123.8, 122.8, 122.2, 117.5, 111.0, 61.2, 46.3, 31.7, 30.3, 22.2, 14.2, 13.7 ppm. IR (KBr): 3462, 2962, 1707, 1629, 1451, 1361, 1338, 1241, 1200, 1026, 910, 750, 568 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}N_2NaO_3^+$ 323.1372; Found 323.1366.

ethyl 3-oxo-5-phenyl-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (3ah)



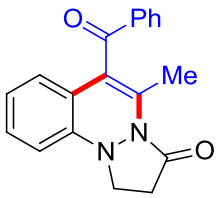
42.1 mg, 63% yield, R_f = 0.33 (PE/EA = 3:1), red solid, m. p. 79 - 80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.50 – 7.28 (m, 5H), 7.20 (td, *J* = 7.8, 1.5 Hz, 1H), 6.96 (td, *J* = 7.6, 1.1 Hz, 1H), 6.69 (dd, *J* = 8.1, 1.1 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.89 (t, *J* = 8.1 Hz, 2H), 2.69 (t, *J* = 8.1 Hz, 2H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 166.0, 146.1, 139.4, 132.5, 129.5, 128.4, 128.2, 124.5, 123.0, 122.6, 119.4, 111.2, 61.1, 45.7, 31.0, 13.5 ppm. IR (KBr): 3456, 2921, 1711, 1481, 1450, 1340, 1206, 1022, 919, 857, 754, 698, 547 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_3^+$ 335.1396; Found 335.1384.

6-acetyl-5-methyl-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (3ai)



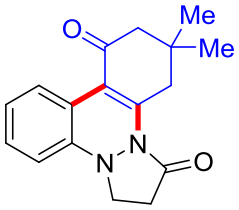
25.2 mg, 52% yield, R_f = 0.35 (PE/EA = 6:1), brown solid, m. p. 82 - 83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (td, *J* = 7.7, 1.4 Hz, 1H), 6.87 (td, *J* = 7.6, 1.1 Hz, 1H), 6.70 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.53 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.62 (t, *J* = 8.4 Hz, 2H), 2.76 (t, *J* = 8.4 Hz, 2H), 2.41 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.2, 167.0, 147.1, 135.9, 129.0, 124.7, 123.2, 123.0, 122.3, 111.3, 46.7, 31.7, 31.5, 15.7 ppm. IR (KBr): 3467, 2914, 1708, 1619, 1492, 1451, 1357, 1324, 1271, 1190, 1022, 960, 754, 559 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{14}N_2NaO_2^+$ 265.0953; Found 265.0950.

6-benzoyl-5-methyl-1H-pyrazolo[1,2-a]cinnolin-3(2H)-one (3aj)



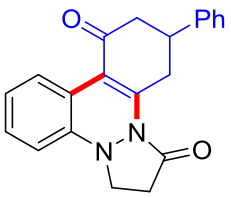
27.4 mg, 45% yield, R_f = 0.35 (PE/EA = 3:1), red solid, m. p. 131-132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.87 (m, 2H), 7.59 – 7.44 (m, 1H), 7.45 – 7.30 (m, 2H), 6.98 (td, *J* = 7.7, 1.5 Hz, 1H), 6.71 – 6.55 (m, 1H), 6.50 – 6.38 (m, 2H), 3.59 (t, *J* = 8.4 Hz, 2H), 2.72 (t, *J* = 8.4 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 195.4, 166.6, 146.3, 136.8, 135.6, 134.1, 129.6, 129.0, 128.9, 123.6, 122.9, 111.1, 77.5, 77.1, 76.6, 46.8, 31.8, 16.3. IR (KBr): 3475, 3413, 1712, 1662, 1616, 1496, 1449, 1401, 1368, 1326, 1224, 1177, 999, 964, 904, 756, 705, 670, 635, 568 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_2^+$ 305.1290; Found 305.1290

11,11-dimethyl-2,3,11,12-tetrahydro-1H-benzo[c]pyrazolo[1,2-a]cinnoline-1,9(10H)-dione (3ak)



38.4 mg, 68% yield, R_f = 0.23 (PE/EA = 3:1), red solid, m. p. 170 - 171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.12 (td, *J* = 7.7, 1.5 Hz, 1H), 6.94 (td, *J* = 7.7, 1.2 Hz, 1H), 6.49 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.60 (t, *J* = 8.3 Hz, 2H), 3.05 (s, 2H), 2.82 (t, *J* = 8.3 Hz, 2H), 2.38 (s, 2H), 1.13 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9, 167.7, 151.2, 146.4, 128.6, 126.2, 123.2, 121.0, 115.1, 111.0, 52.0, 47.2, 38.6, 32.2, 32.0, 28.3 ppm. IR (KBr): 3484, 2956, 2914, 1718, 1654, 1595, 1362, 1309, 1259, 1196, 1147, 1113, 901, 753, 545 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O_2^+$ 283.1447; Found 283.1442.

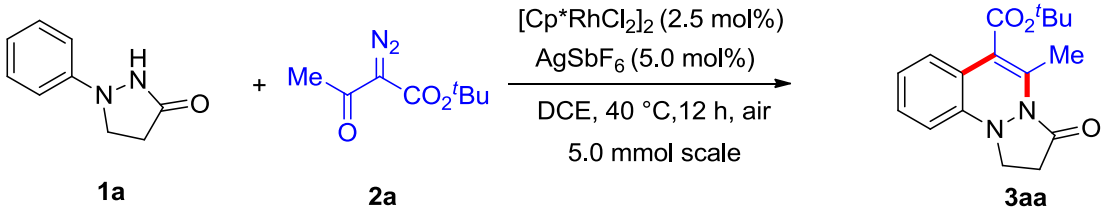
11-phenyl-2,3,11,12-tetrahydro-1H-benzo[c]pyrazolo[1,2-a]cinnoline-1,9(10H)-dione (3al)



35.7 mg, 54% yield, R_f = 0.22 (PE/EA = 3:1), red solid, m. p. 168 - 169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.22 (m, 5H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 3.90 (dd, *J* = 19.0, 4.5 Hz, 1H), 3.60 (m, 2H), 3.38 (m, 1H), 2.97 (m, 1H), 2.87 – 2.73 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 167.9, 152.3, 146.4, 142.3, 128.8, 128.8, 127.2, 126.8, 126.4, 123.4, 121.0, 115.8, 111.1, 47.1, 45.0, 38.6, 32.6, 32.0 ppm. IR (KBr): 3465, 2384, 1720, 1655, 1561, 1491, 1449, 1400, 1354, 1254, 1186, 1142, 904, 754, 700, 626 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}N_2O_2^+$ 331.1447; Found 331.1439.

5. Gram-scale Experiment and Further Transformations of Pyrazolo[1,2-*a*]cinnoline 3aa

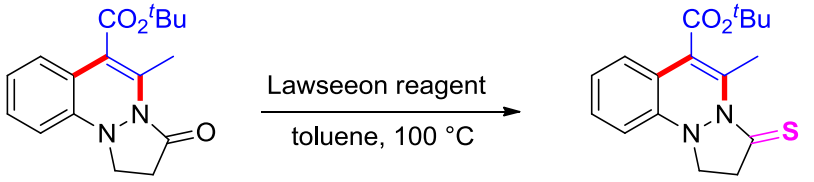
5.1 A gram scale experiment of 3aa



Scheme S4. Gram-Scale Synthesis

A sealed tube was charged with 1-phenylpyrazolidin-3-one **1a** (5.0 mmol, 811 mg), $(RhCp^*Cl_2)_2$ (0.125 mmol, 75 mg), $AgSbF_6$ (0.25 mmol, 88 mg), tert-butyl 2-diazo-3-oxobutanoate **2a** (8.0 mmol, 1.47g), 75 mL DCE. The reaction mixture was vigorously stirred at 40 °C (oil temperature) for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA (250 mL) and filtered through a plug of celite. The mixture was concentrated in *vacuo* and purified by flash chromatography on silica gel to afford the desired product **3aa** (1.24 g, 82% yield).

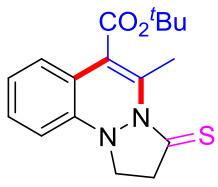
5.2 Further Transformations of 3aa



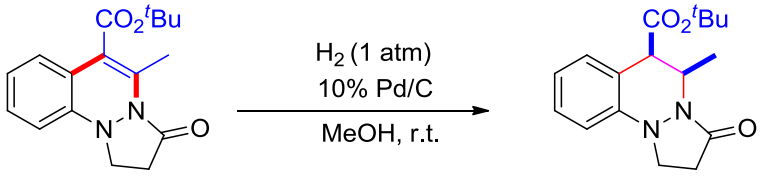
Scheme S5. Synthesis of the thioamide

A solution of **3aa** (60.0 mg, 0.2 mmol) and Lawesson reagent (60.6 mg, 0.15 mmol) in toluene (2.0 mL) was stirred and refluxed. After 12 hours, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford **4** in 60% yield.

tert-butyl 5-methyl-3-thioxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (4)



37.9 mg, 60% yield, R_f = 0.23 (PE/EA = 5:1), red solid, m. p. 106 - 107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (td, *J* = 7.7, 1.5 Hz, 1H), 7.08 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.93 (td, *J* = 7.6, 1.1 Hz, 1H), 6.66 – 6.52 (m, 1H), 3.78 (t, *J* = 8.7 Hz, 2H), 3.27 (t, *J* = 8.7 Hz, 2H), 2.68 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 146.5, 136.7, 129.5, 125.6, 124.5, 122.7, 121.2, 110.8, 83.1, 47.7, 45.0, 28.2, 18.0 ppm. IR (KBr): 3467, 2976, 2929, 1716, 1629, 1597, 1453, 1400, 1368, 1316, 1272, 1233, 1154, 1126, 1063, 1021, 975, 841, 748, 646 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_2S^+$ 317.1323; Found 317.1322.

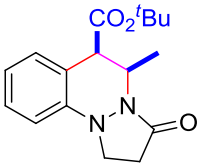


3aa **5** 85%

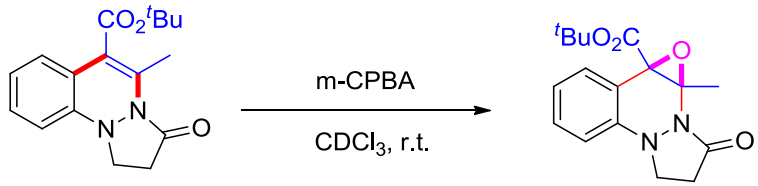
Scheme S6. Reduction of the C=C bond

A solution of **3aa** (60.0 mg, 0.2 mmol) in MeOH (2.0 mL) was added with 10% Pd/C (10 mg) in one portion. The mixture is stirred at room temperature under H_2 balloon (1 atm) for 24 hours and passed through a pad of celite, eluted with MeOH (10 mL). The mixture was concentrated under reduced pressure in *vacuo*. The residue was purified by silica gel column chromatography to afford **5** in 85% yield.

tert-butyl (5R,6R)-5-methyl-3-oxo-2,3,5,6-tetrahydro-1H-pyrazolo[1,2-a]cinnoline-6-carboxylate (5)



53.7 mg, 85% yield, R_f = 0.21 (PE/EA = 5:1), brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.12 (m, 2H), 6.94 (td, *J* = 7.6, 1.2 Hz, 1H), 6.85 – 6.64 (m, 1H), 5.04 – 4.71 (m, 1H), 4.24 – 3.86 (m, 2H), 3.41 (q, *J* = 9.6 Hz, 1H), 2.84 – 2.46 (m, 2H), 1.53 (s, 9H), 1.23 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 166.9, 145.4, 130.4, 127.9, 121.0, 118.5, 113.7, 81.8, 48.3, 46.3, 46.2, 31.3, 28.0, 14.4 ppm. IR (KBr): 3458, 2979, 1756, 1698, 1605, 1495, 1453, 1412, 1369, 1275, 119, 1147, 1063, 967, 914, 887, 754, 697, 557, 460 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{22}N_2NaO_3^+$ 325.1528; Found 325.1524.

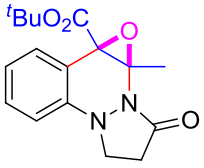


3aa **6** 60%

Scheme S7. Epoxidation reaction

A solution of **3aa** (60.0 mg, 0.2 mmol) in $CDCl_3$ (2 mL) was added m-CPBA (69.0 mg, 0.4 mmol) and the reaction mixture was stirred at room temperature for overnight. After completion of the reaction, the solvent was concentrated by evaporator in *vacuo*. The residue was purified by silica gel column chromatography to afford **6** in 60% yield.

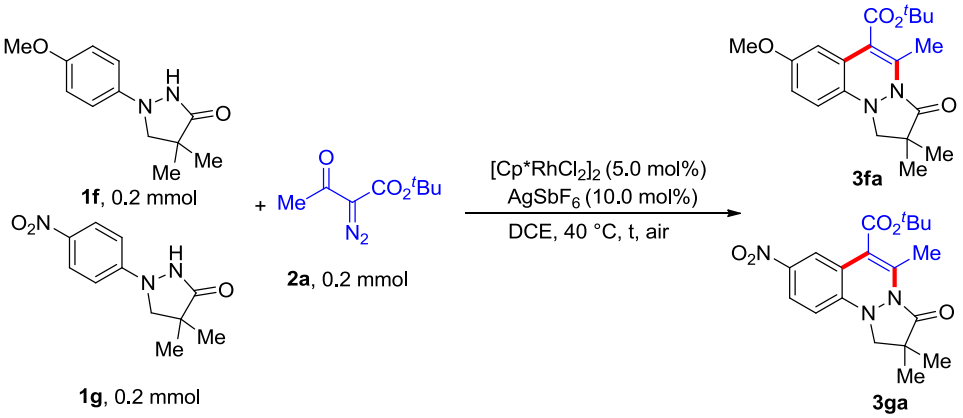
tert-butyl-(1aR,10bR)-1a-methyl-3-oxo-4,5-dihydro-3H-oxireno[2,3-c]pyrazolo[1,2-a]cinnoline-10b(1aH)-carboxylate (6)



37.9 mg, 60% yield, R_f = 0.35 (PE/EA = 6:1), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.52 (m, 1H), 7.42 (m, 1H), 7.32 – 7.13 (m, 1H), 7.00 – 6.74 (m, 1H), 4.51 (m, 1H), 3.77 (m, 1H), 2.38 (m, 1H), 2.25 (s, 3H), 2.11 – 1.85 (m, 1H), 1.54 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.4, 165.3, 159.8, 146.5, 130.5, 124.9, 124.5, 124.2, 111.5, 94.1, 84.8, 60.8, 34.9, 27.8, 19.6 ppm. IR (KBr): 3467, 2979, 1735, 1686, 1475, 1461, 1396, 1371, 1299, 1225, 1142, 1056, 943, 836, 803, 622 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_4^+$ 317.1501; Found 317.1501.

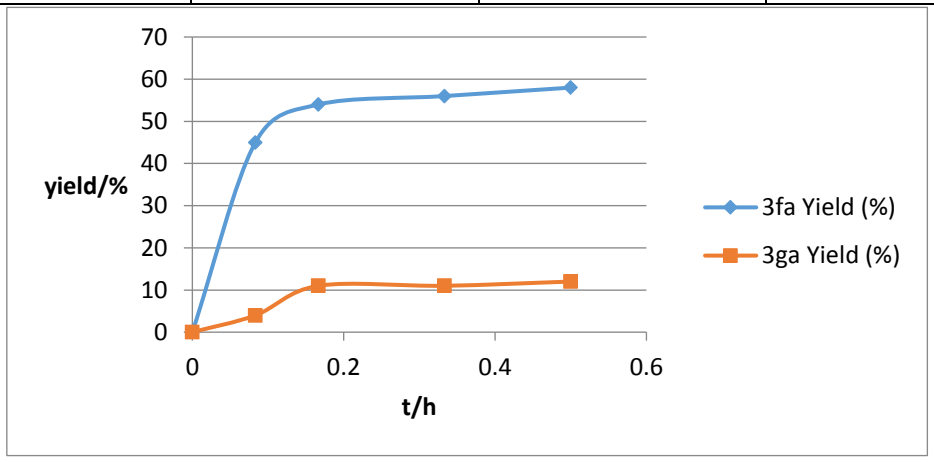
6. Mechanistic Experiments

6.1 Competitive Reaction



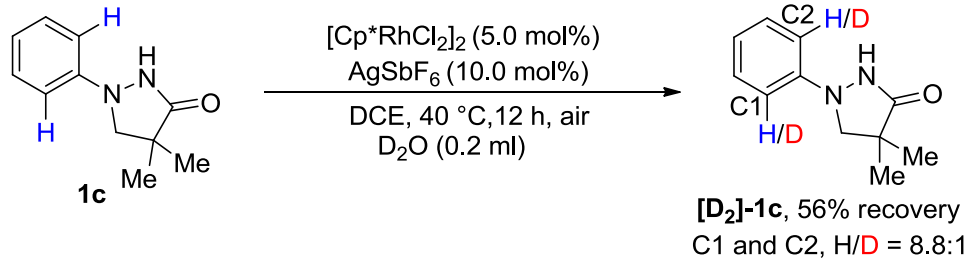
A sealed tube was charged with **1f** (0.2 mmol, 44 mg), **1g** (0.2 mmol, 47 mg), $(RhCp^*Cl_2)_2$ (0.01 mmol, 5.0 mol%), $AgSbF_6$ (0.02 mmol, 10.0 mol%), **2a** (0.2 mmol, 36.8 mg), 3 mL DCE. The reaction mixture was vigorously stirred at 40 °C (oil temperature). After cooling to room temperature, the reaction mixture was diluted with EA (20 mL) and filtered through a plug of celite. The mixture was concentrated in *vacuo* and the residue was purified by column chromatography to give **3fa** and **3ga**.

t	**3fa** Yield (%)	**3ga** Yield (%)	**3fa/3ga**
5 min	45	4	11.2
10 min	54	11	4.9
20 min	56	11	5.1
30 min	58	12	4.8
1 h	60	13	4.6
3 h	61	14	4.3
6 h	63	16	3.9
12 h	69	18	3.8



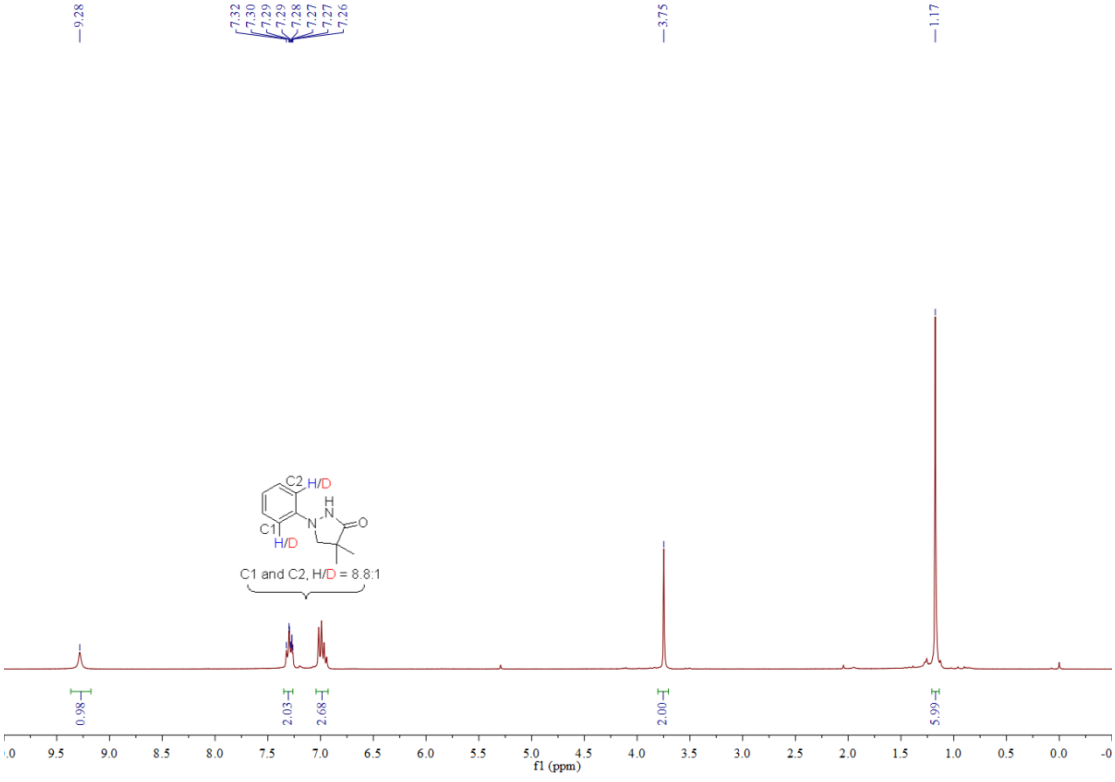
Scheme S8. Competitive Reaction

6.2 H/D exchange experiment

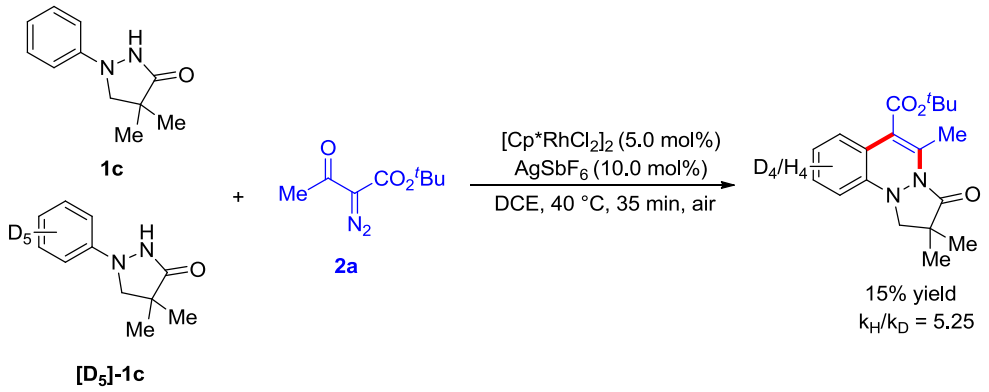


Scheme S9. H/D exchange experiment

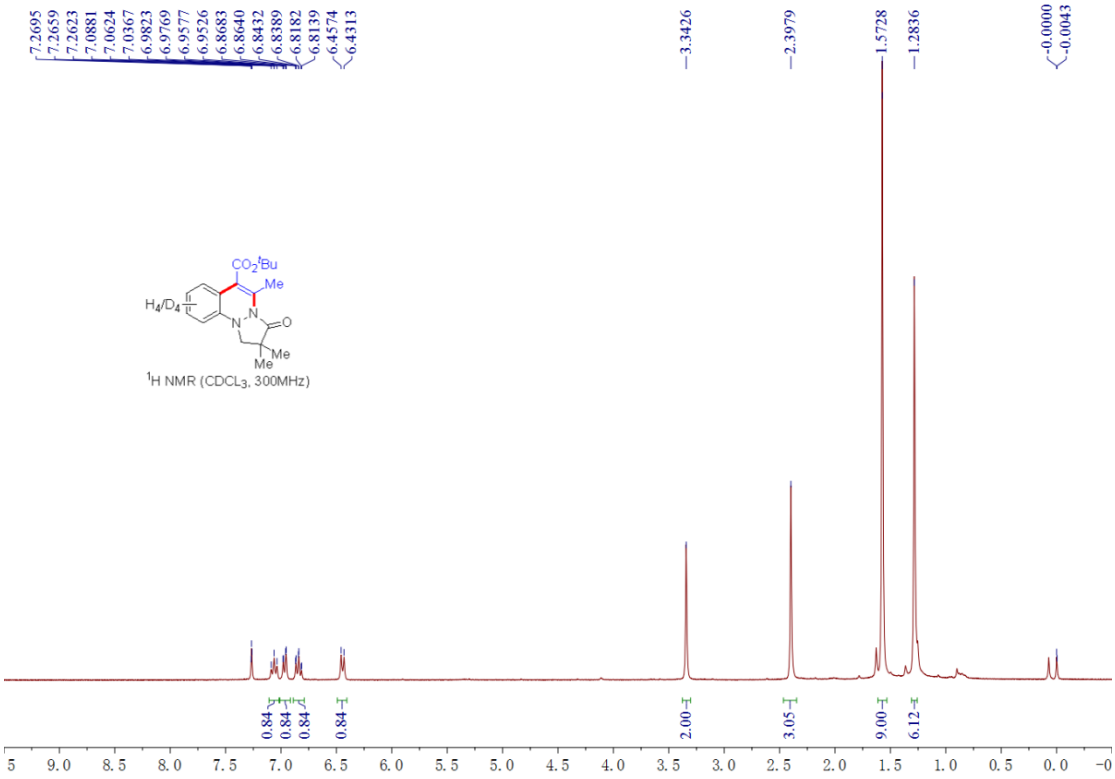
A sealed tube was charged with **1c** (0.2 mmol, 38 mg), $(RhCp^*Cl_2)_2$ (0.01 mmol, 5 mol%), $AgSbF_6$ (0.02 mmol, 10 mol%), 3 mL DCE and 0.2 mL D_2O. The reaction mixture was vigorously stirred at 40 °C (oil temperature) for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA (20 mL) and filtered through a plug of celite. The mixture was concentrated in *vacuo* and the residue was purified by column chromatography to give provide **[D_2]-1c**. The deuterated ratio was calculated from ^{1}H NMR analysis.



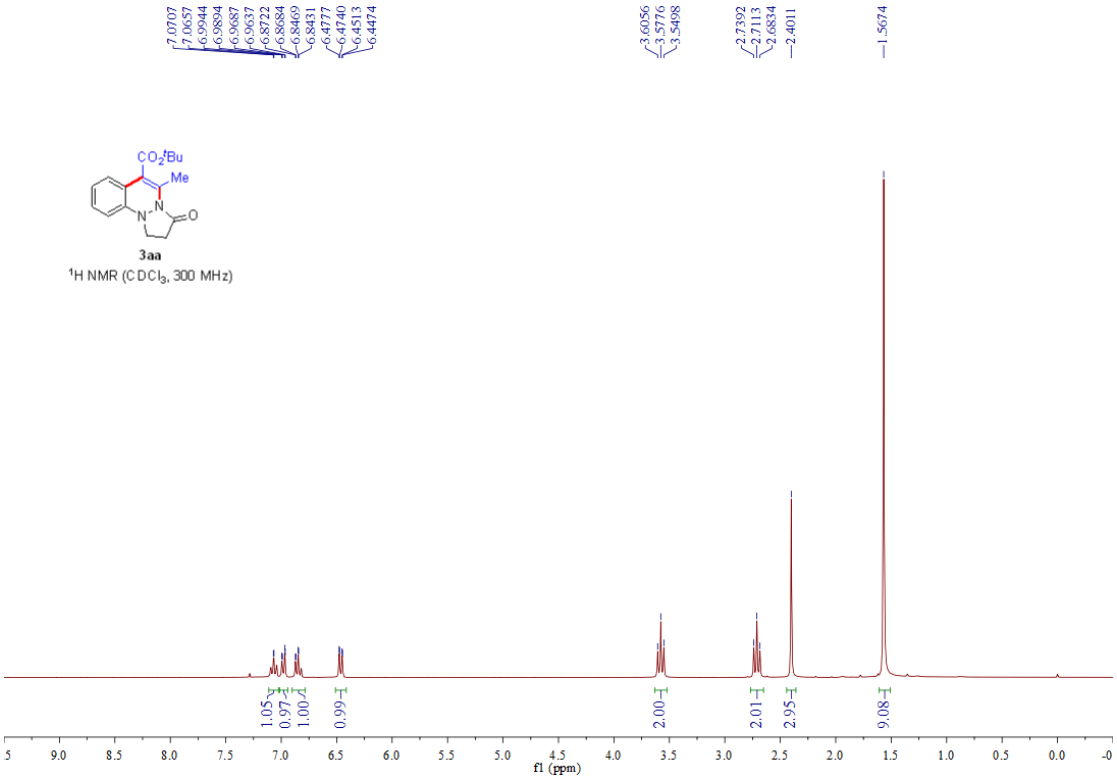
6.3 kinetic isotope effect

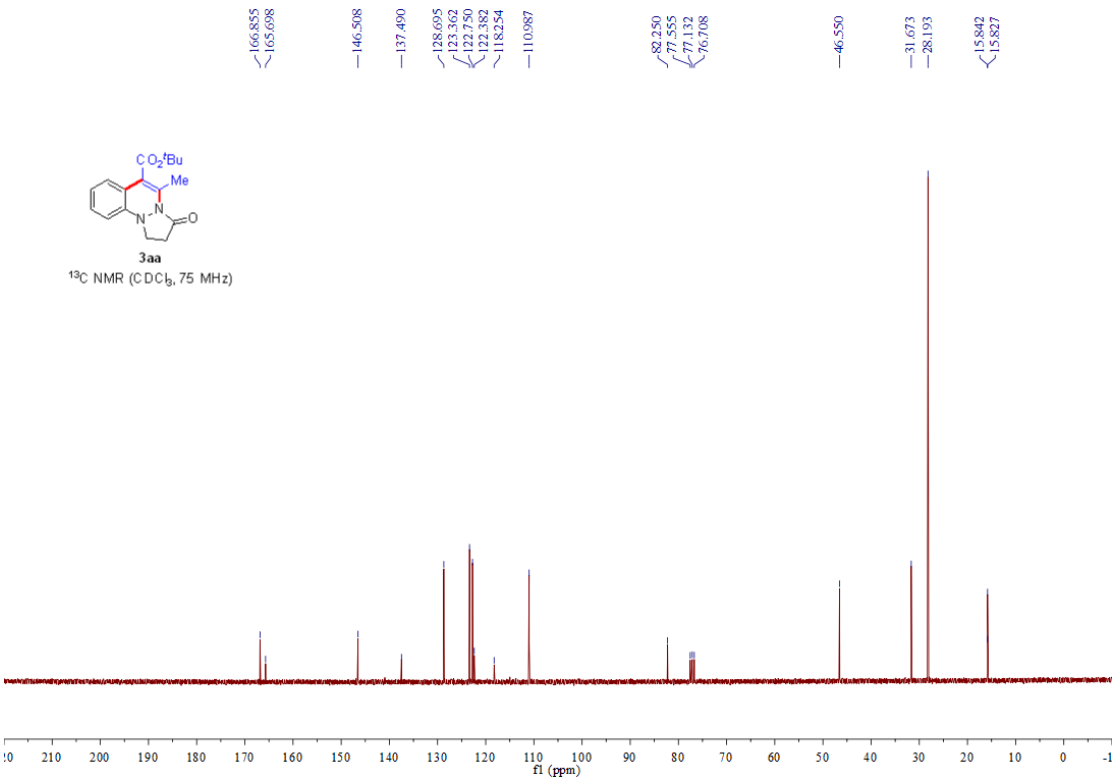


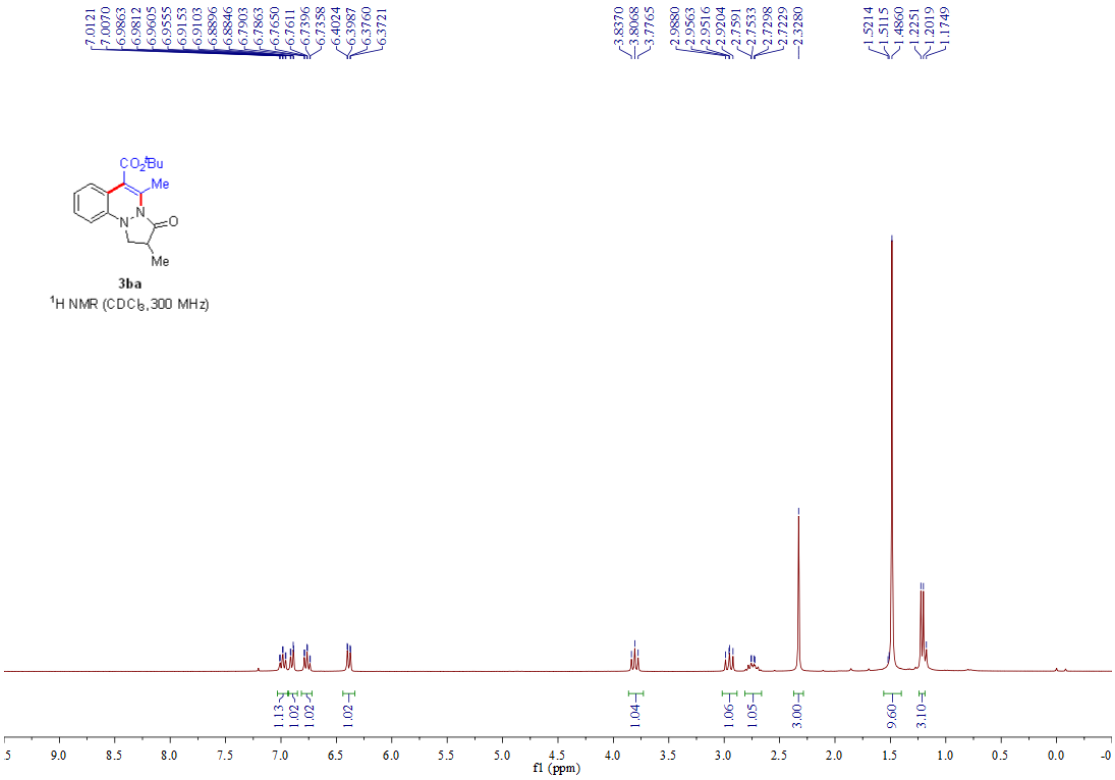
A sealed tube was charged with **1c** (0.2 mmol, 38 mg), **[D_5]-1c** (0.2 mmol, 39 mg), $(RhCp^*Cl_2)_2$ (0.01 mmol, 5.0 mol%), $AgSbF_6$ (0.02 mmol, 10.0 mol%), **2a** (0.32 mmol, 59 mg), 3 mL DCE. The reaction mixture was vigorously stirred at 40 °C (oil temperature) for 35 minutes. After cooling to room temperature, the reaction mixture was diluted with EA (20 mL) and filtered through a plug of celite. The mixture was concentrated in *vacuo* and the residue was purified by column chromatography. The k_H/k_D value was was calculate from ^{1}HNMR analysis.



7. Copies of ^{1}H NMR and ^{13}C NMR Spectra of the Titled Compounds

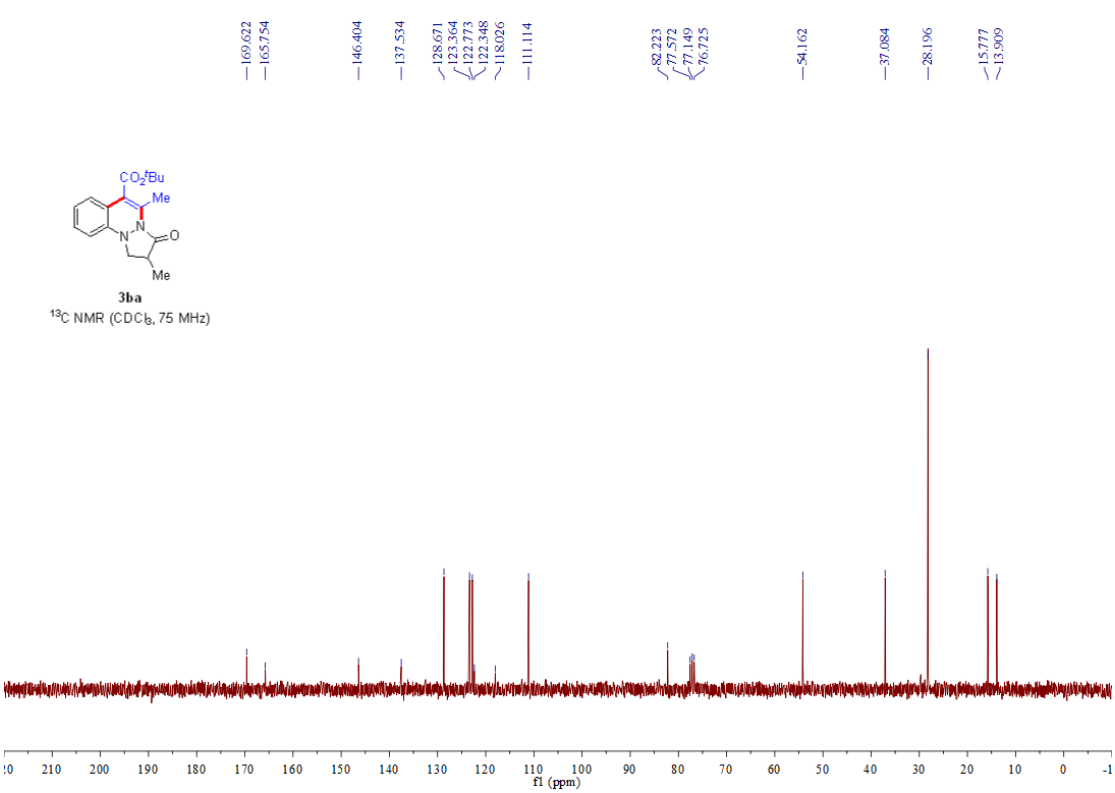






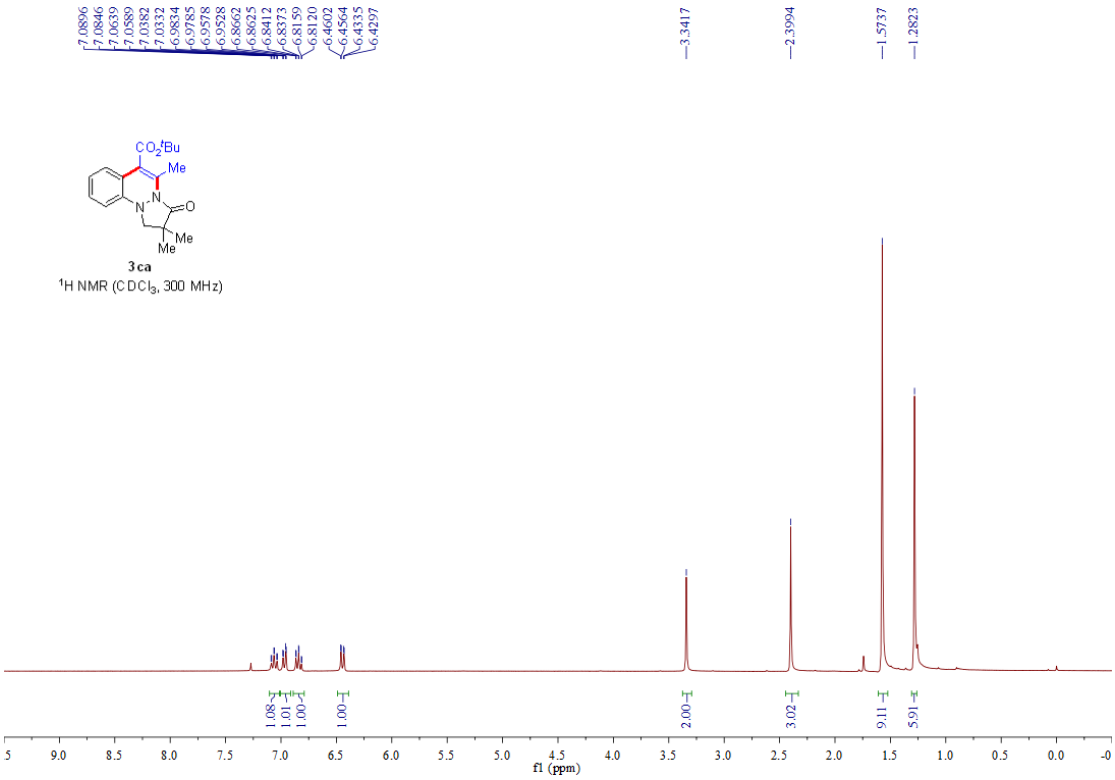
3ba

^{1}H NMR ($CDCl_3$, 300 MHz)



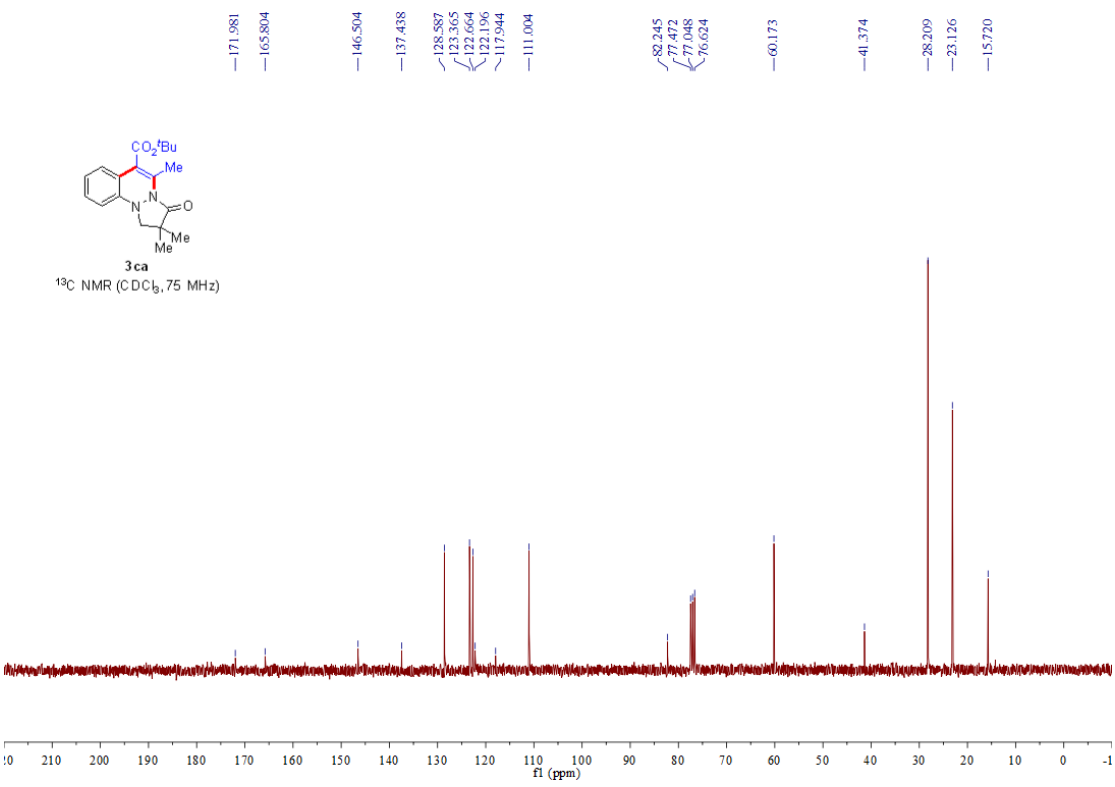
3ba

^{13}C NMR ($CDCl_3$, 75 MHz)



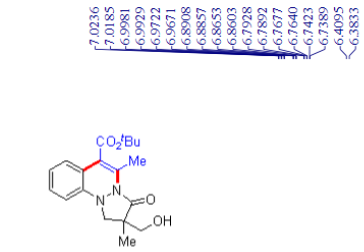
3ca

^{1}H NMR ($CDCl_3$, 300 MHz)



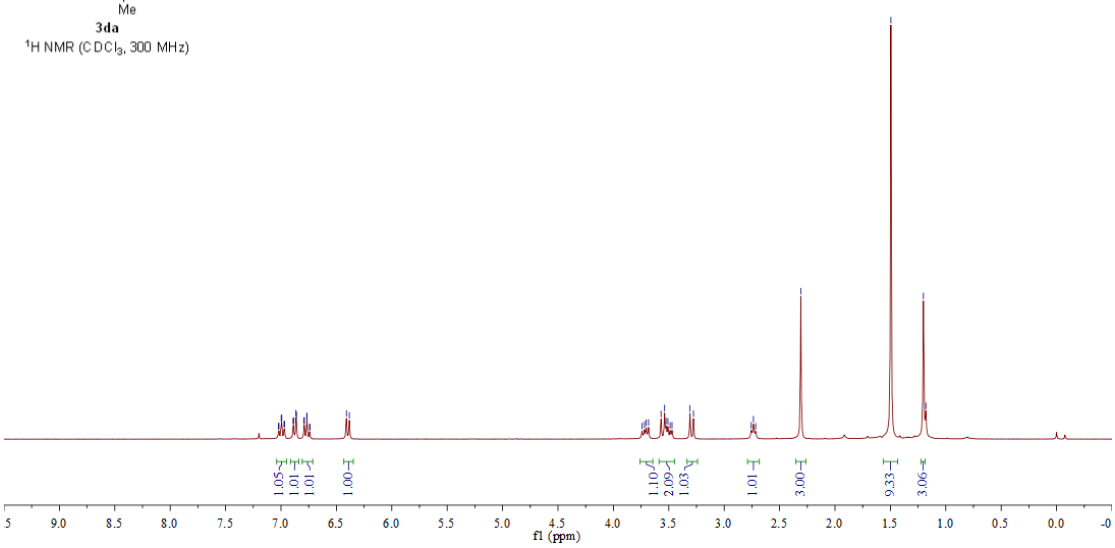
3ca

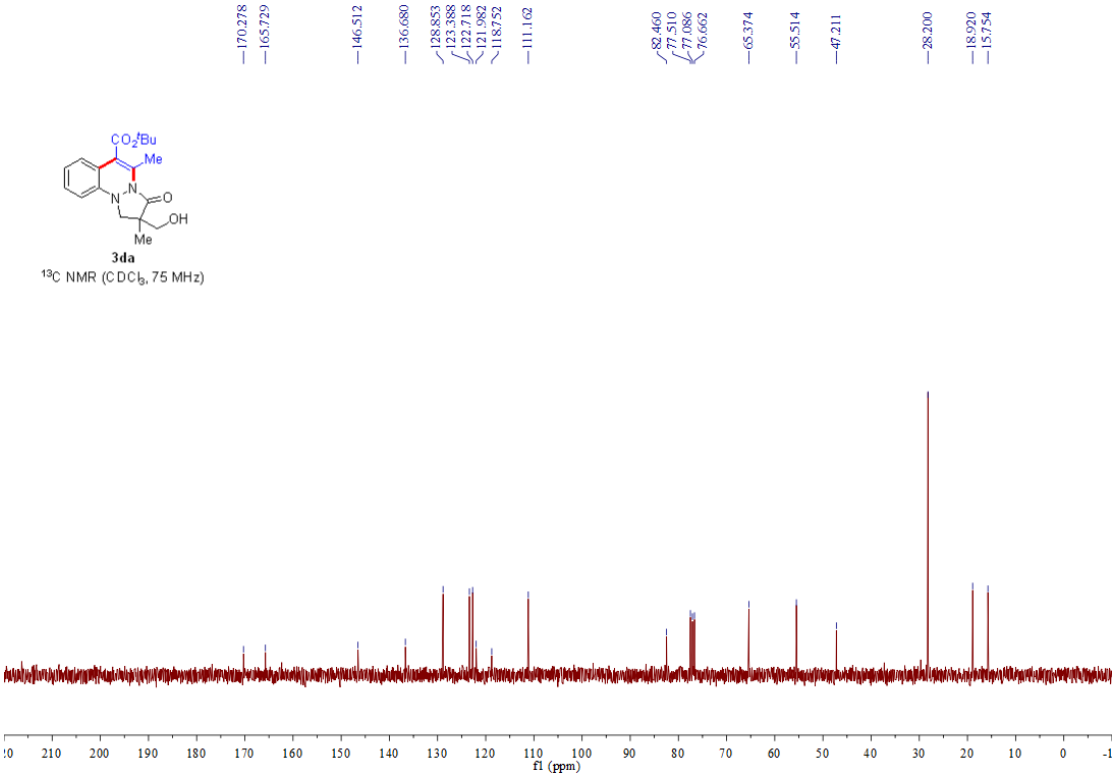
^{13}C NMR ($CDCl_3$, 75 MHz)



3da

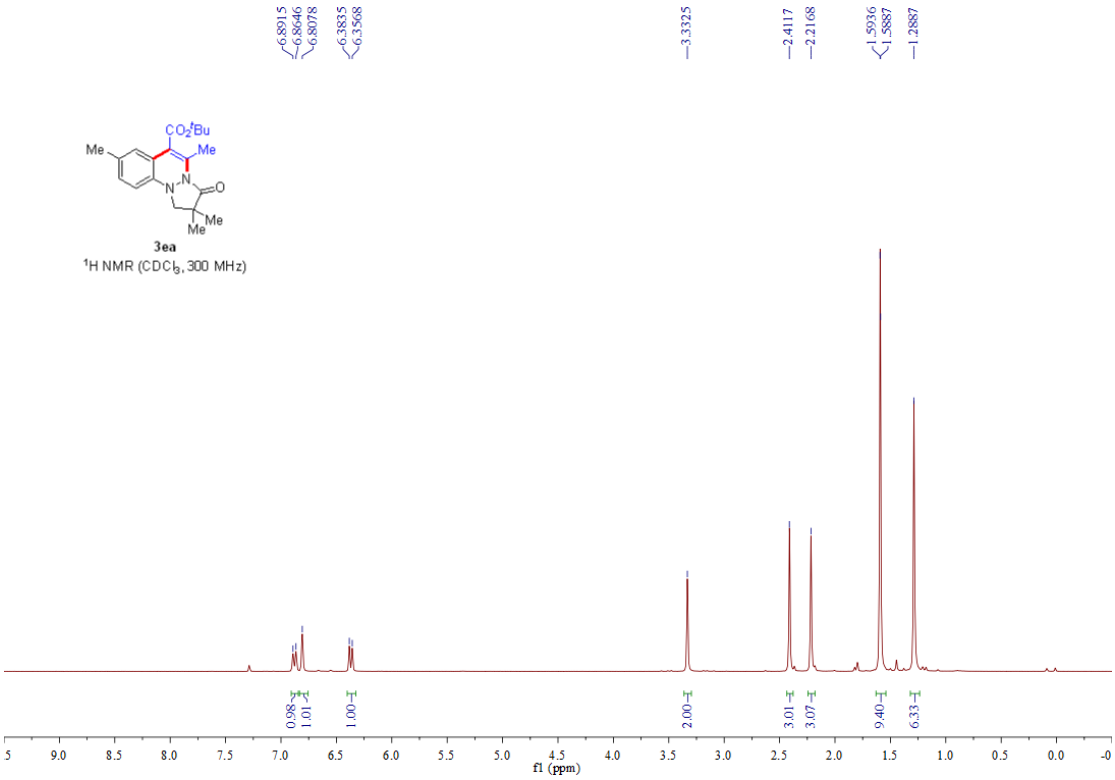
^{1}H NMR ($CDCl_3$, 300 MHz)





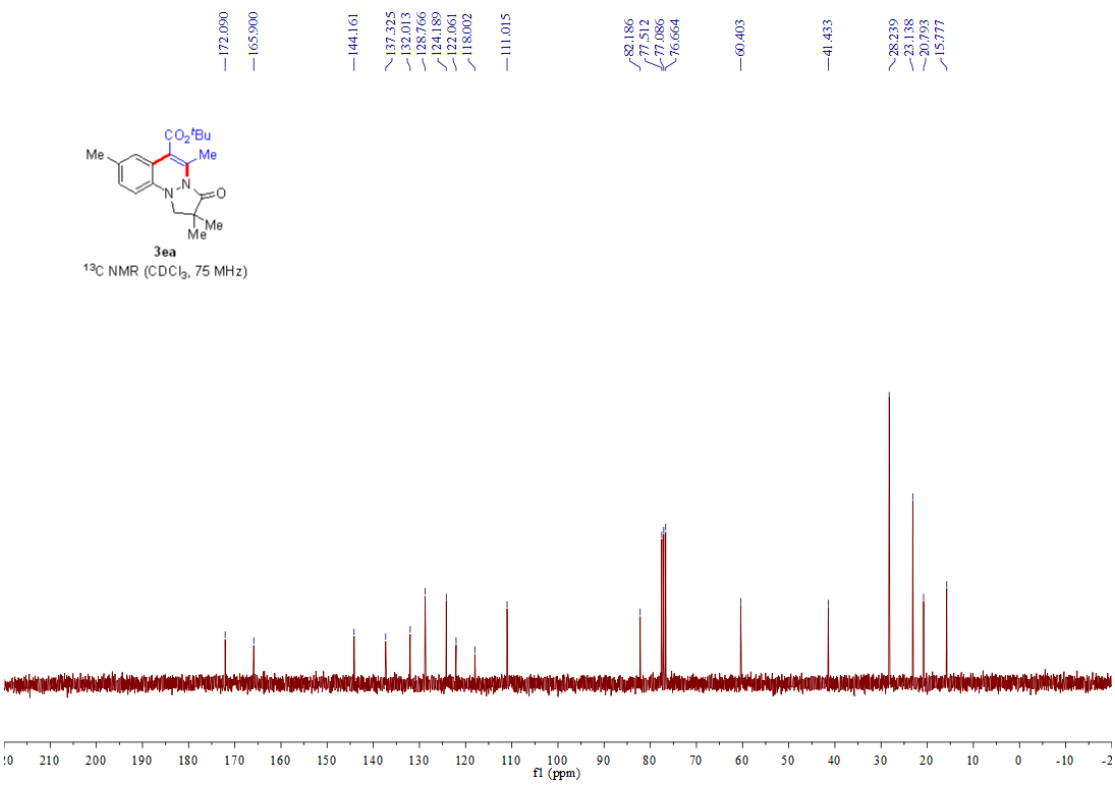
3da

^{13}C NMR ($CDCl_3$, 75 MHz)



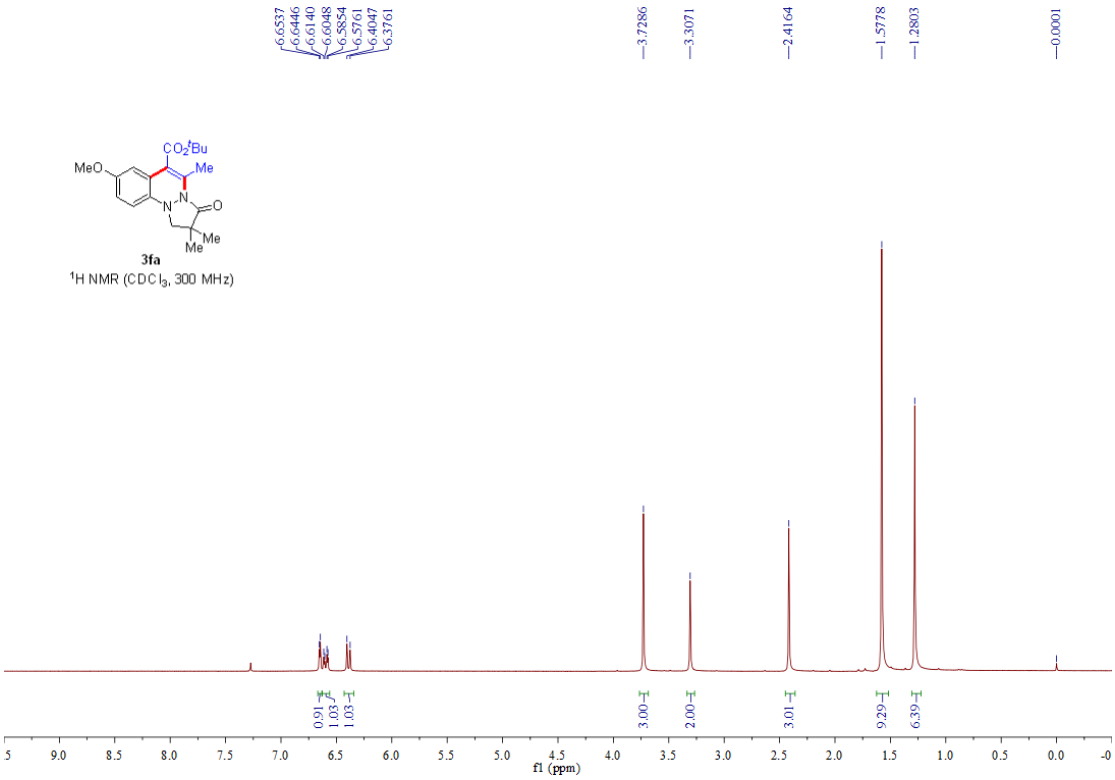
3ea

^{1}H NMR ($CDCl_3$, 300 MHz)



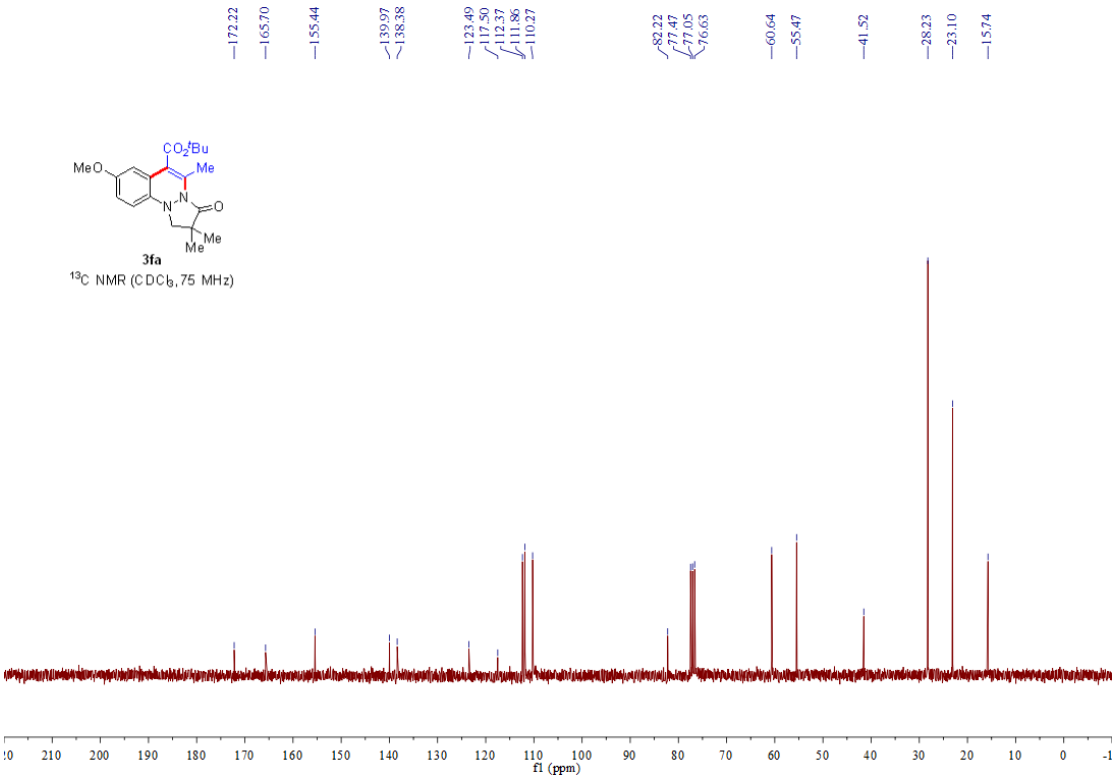
3ea

^{13}C NMR ($CDCl_3$, 75 MHz)



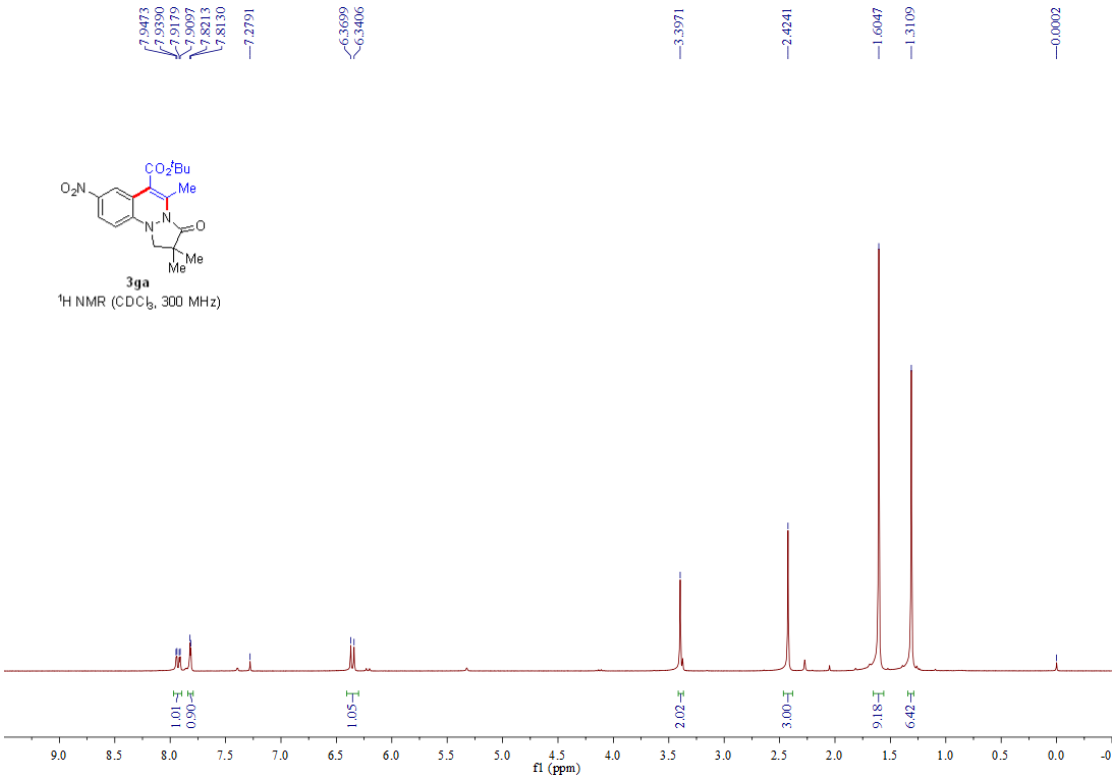
3fa

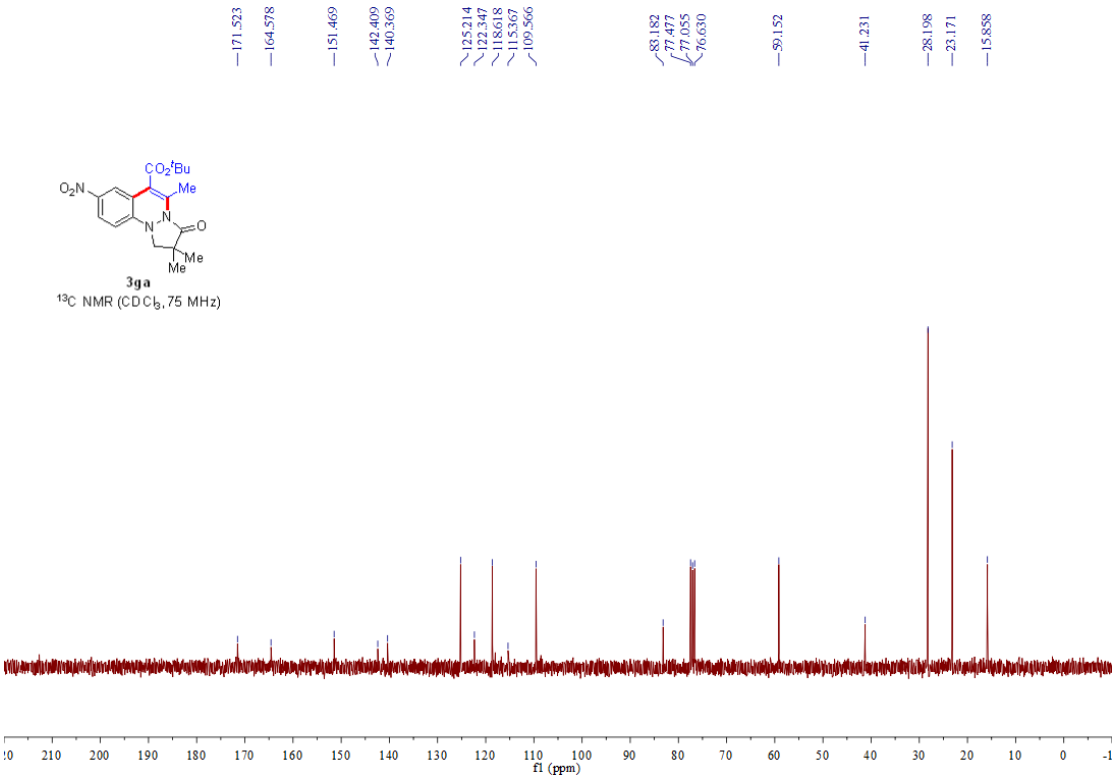
^{1}H NMR ($CDCl_3$, 300 MHz)

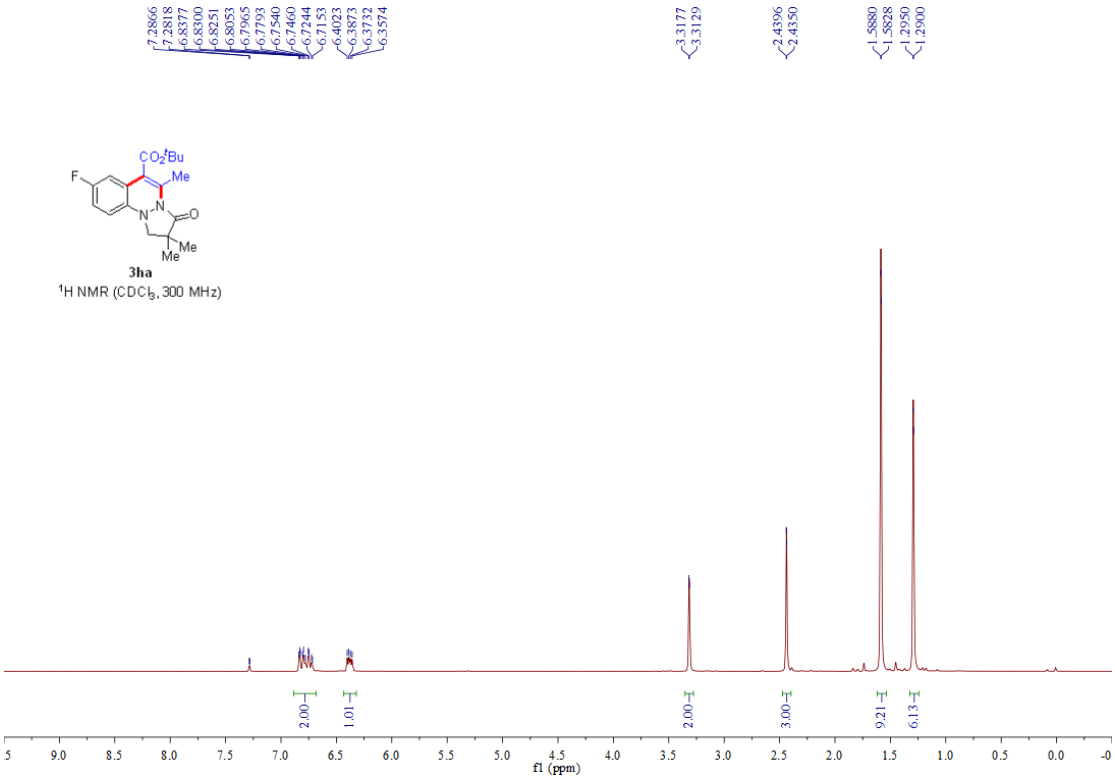


3fa

^{13}C NMR ($CDCl_3$, 75 MHz)


7.9473
7.9390
7.9179
7.9097
7.8213
7.8130
7.2791
6.3699
6.3406
3.3971
2.4241
1.6047
1.3109
0.0002
CO2tBu
Me
O2N
N
N
O
Me
Me
3ga
1H NMR (CDCl3, 300 MHz)
1.01
0.90
1.05
2.02
3.00
9.18
6.42
f1 (ppm)


171.523
164.578
151.469
142.409
140.369
125.214
122.347
118.618
115.367
109.566
83.182
77.477
77.055
76.630
59.152
41.231
28.198
23.171
15.858
CO2tBu
Me
O2N
N
N
O
Me
Me
3ga
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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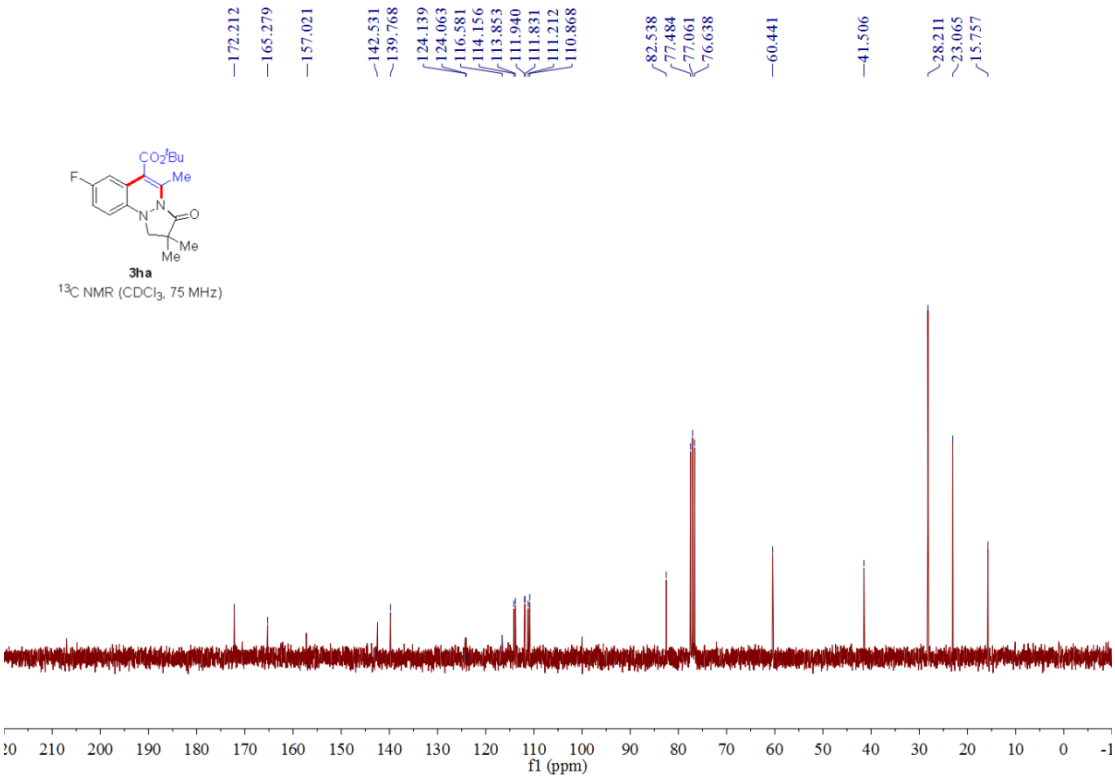
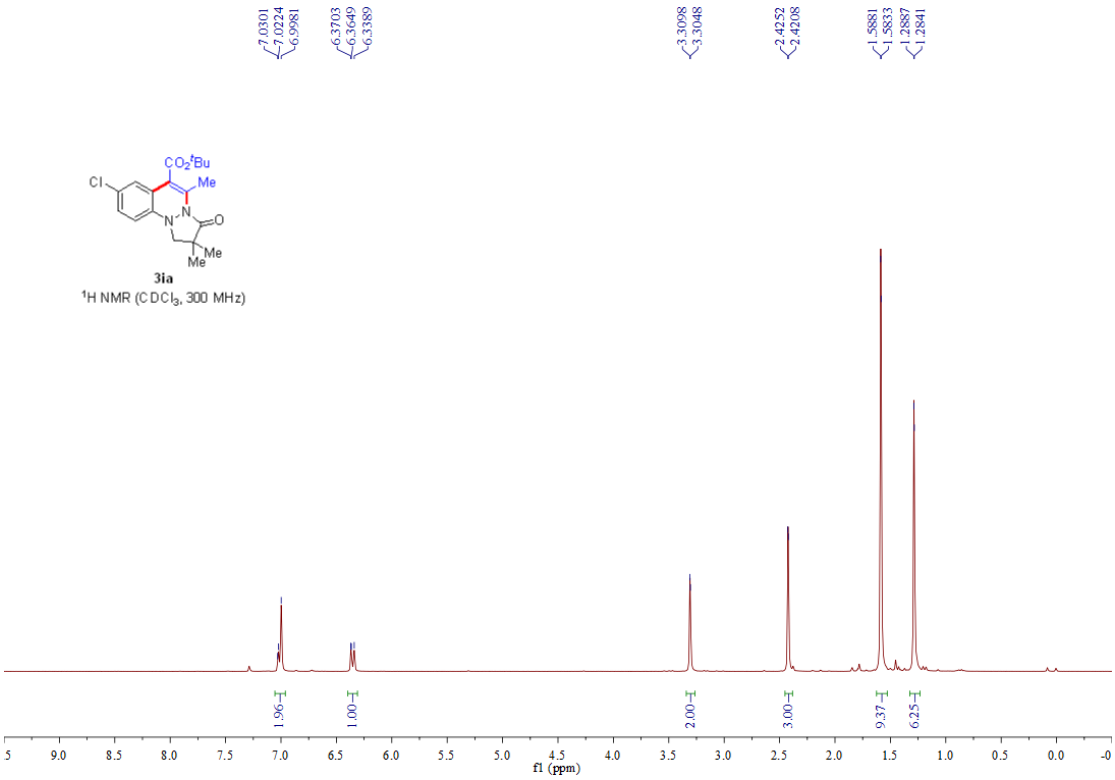
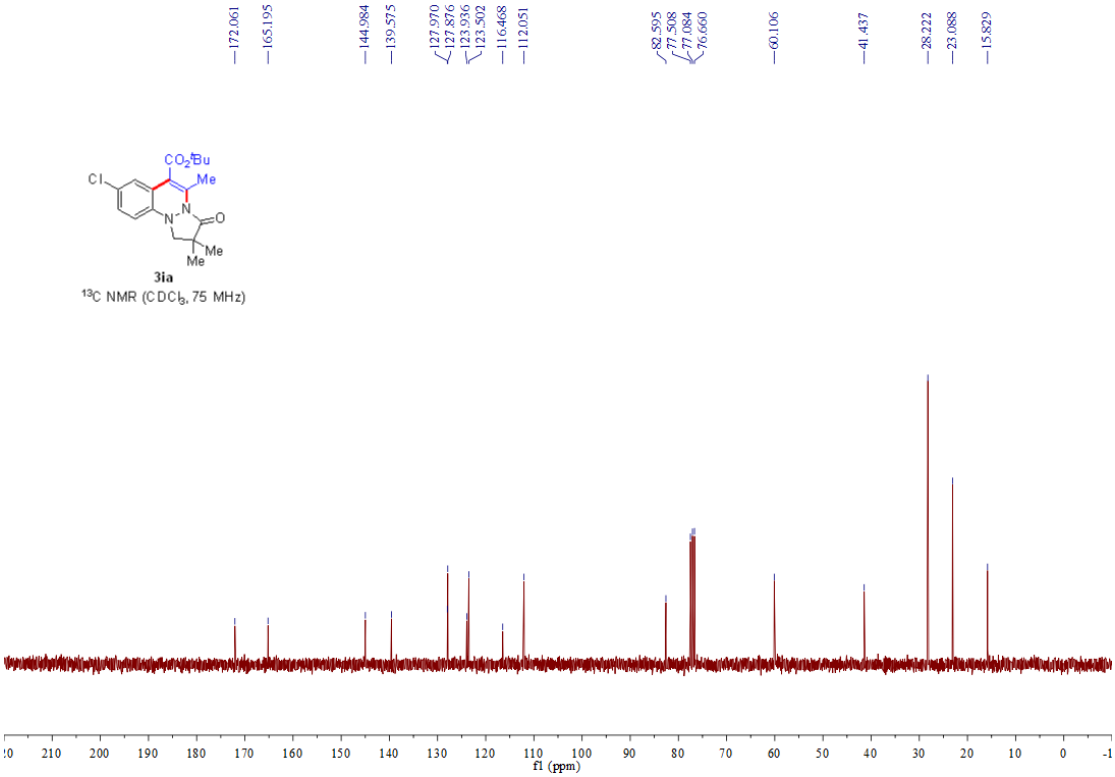
7.2818
6.8377
6.8300
6.8251
6.8053
6.7965
6.7793
6.7540
6.7460
6.7244
6.7153
6.4023
6.3873
6.3732
6.3574
3.3177
3.3129
2.4396
2.4350
1.5880
1.5828
1.2950
1.2900
CO2tBu
Me
F
N
N
O
Me
3ha
1H NMR (CDCl3, 300 MHz)
2.00
1.01
2.00
3.00
9.21
6.13
f1 (ppm)


172.212
165.279
157.021
142.531
139.768
124.139
124.063
116.581
114.156
113.853
111.940
111.831
111.212
110.868
82.538
77.484
77.061
76.638
60.441
41.506
28.211
23.065
15.757
CO2tBu
Me
F
N
N
O
Me
Me
3ha
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.0301
7.0224
6.9981
6.3703
6.3649
6.3389
3.3098
3.3048
2.4252
2.4208
1.5881
1.5833
1.2887
1.2841
CO2tBu
Cl
Me
O
N
Me
Me
3ia
1H NMR (CDCl3, 300 MHz)
1.96
1.00
2.00
3.00
9.37
6.25
f1 (ppm)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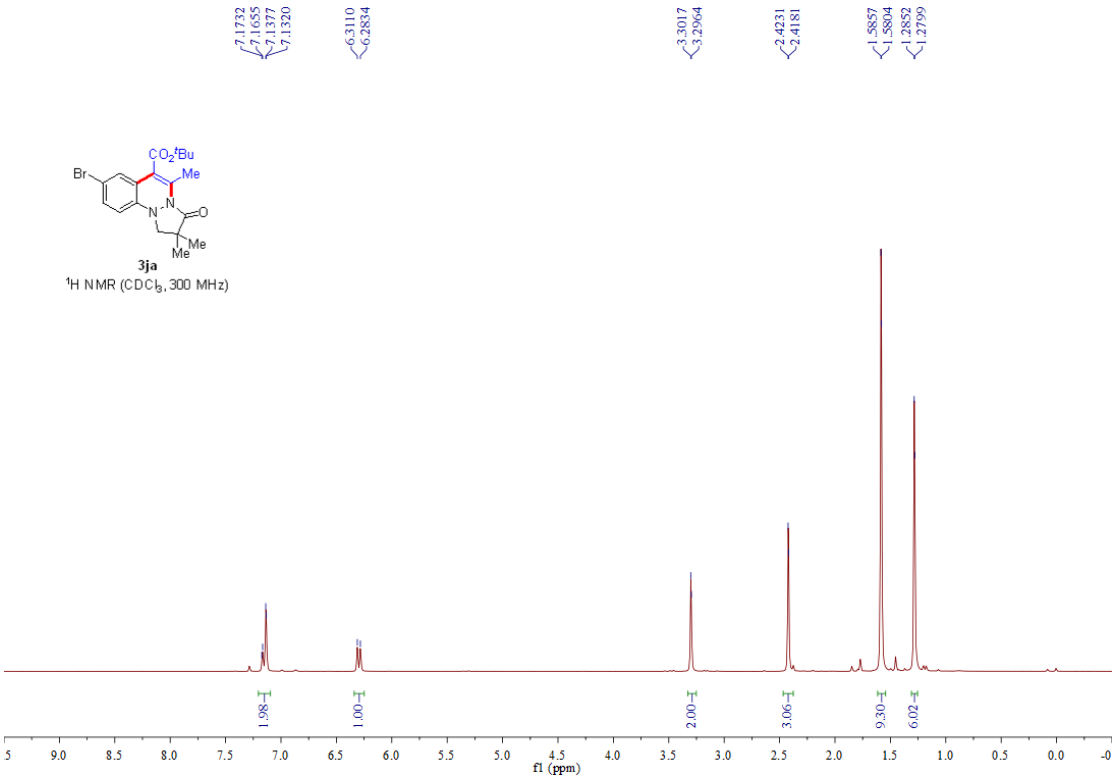
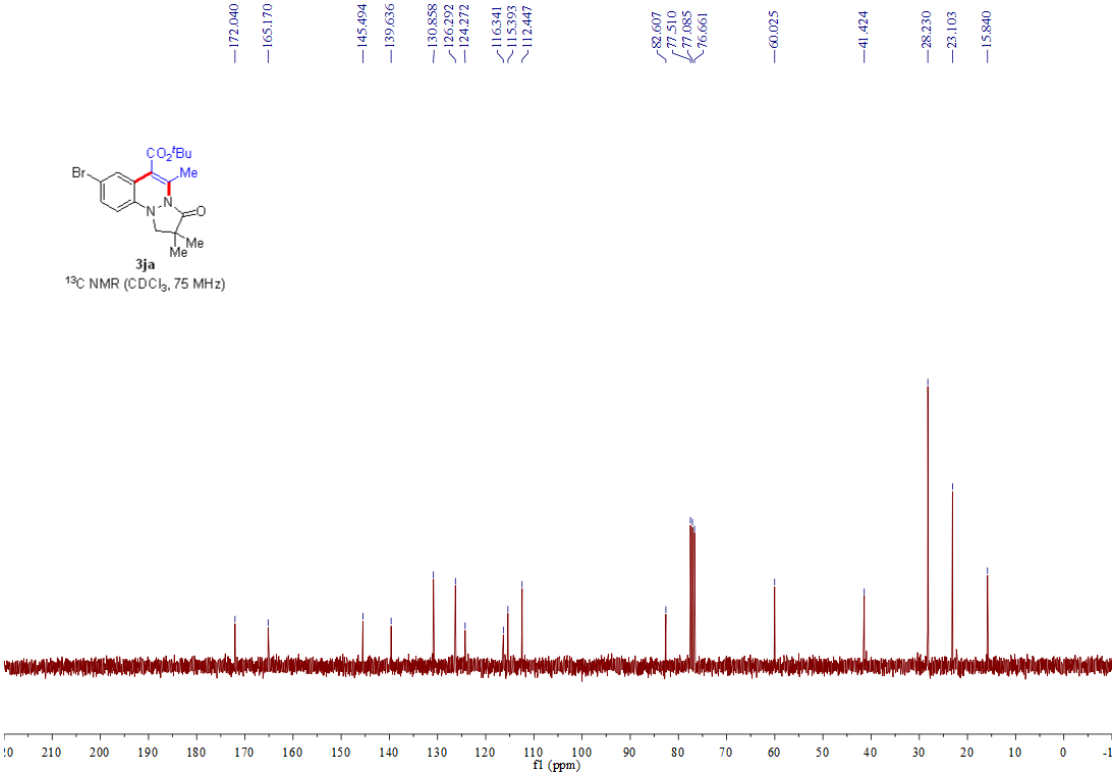
165.195
144.984
139.575
127.970
127.876
123.936
123.502
116.468
112.051
82.595
77.508
77.084
76.660
60.106
41.437
28.222
23.088
15.829
CO2tBu
Cl
Me
O
N
Me
Me
3ia
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.1732
7.1655
7.1377
7.1320
6.3110
6.2834
3.3017
3.2964
2.4231
2.4181
1.5857
1.5804
1.2852
1.2799
Br
CO2tBu
Me
N
N
O
Me
Me
3ja
1H NMR (CDCl3, 300 MHz)
1.98
1.00
2.00
3.06
9.30
6.02
f1 (ppm)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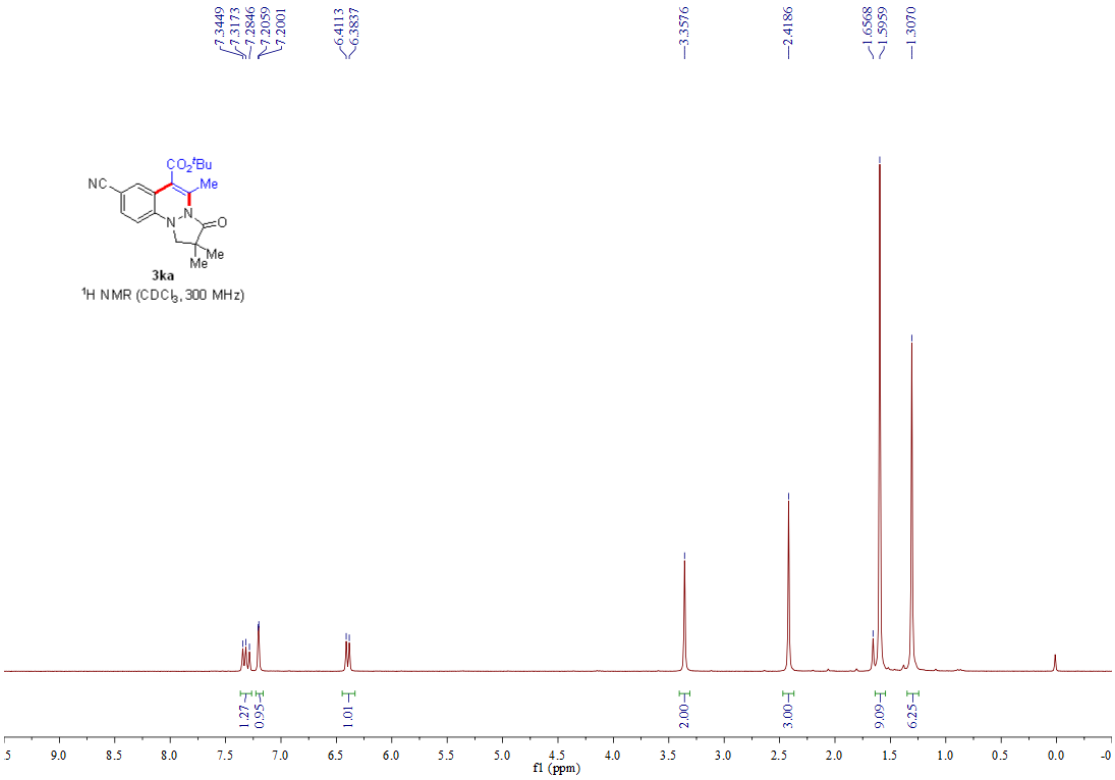
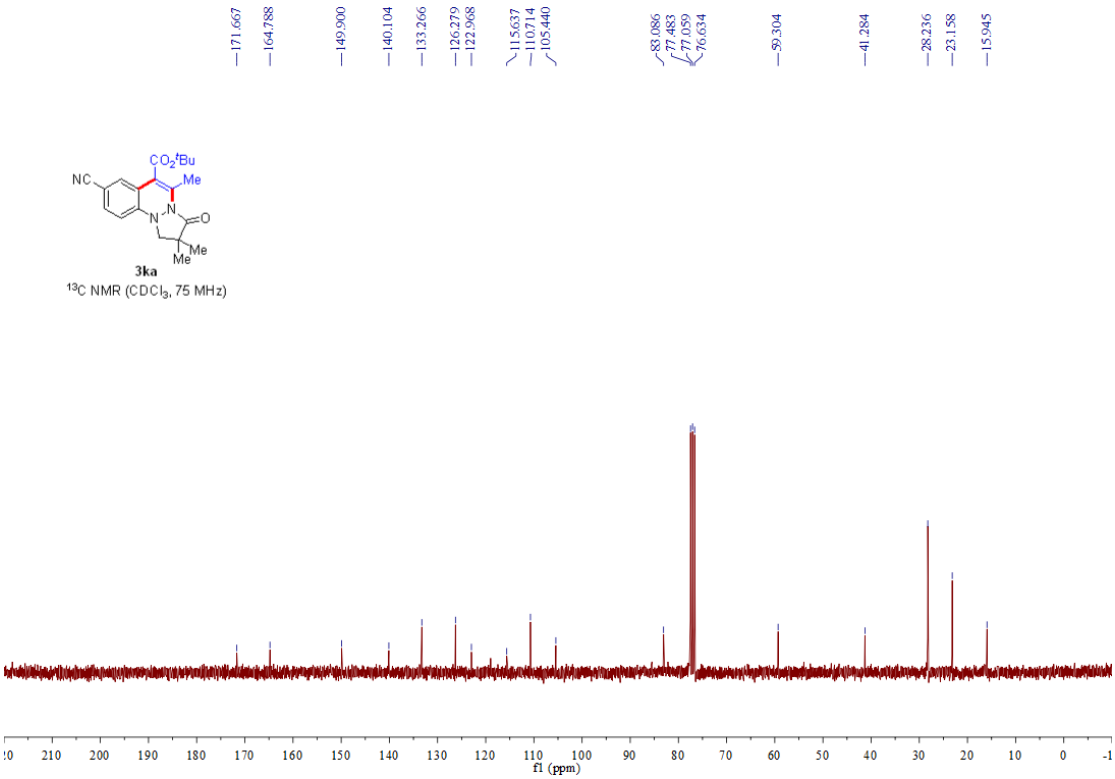
145.494
139.636
130.858
126.292
124.272
116.341
115.393
112.447
82.607
77.510
77.085
76.661
60.025
41.424
28.230
23.103
15.840
Br
CO2tBu
Me
N
N
O
Me
Me
3ja
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.3449
7.3173
7.2846
7.2059
7.2001
6.4113
6.3837
3.3576
2.4186
1.6568
1.5959
1.3070
CO2tBu
Me
NC
N
N
O
Me
Me
3ka
1H NMR (CDCl3, 300 MHz)
1.27
0.95
1.01
2.00
3.00
9.09
6.25
f1 (ppm)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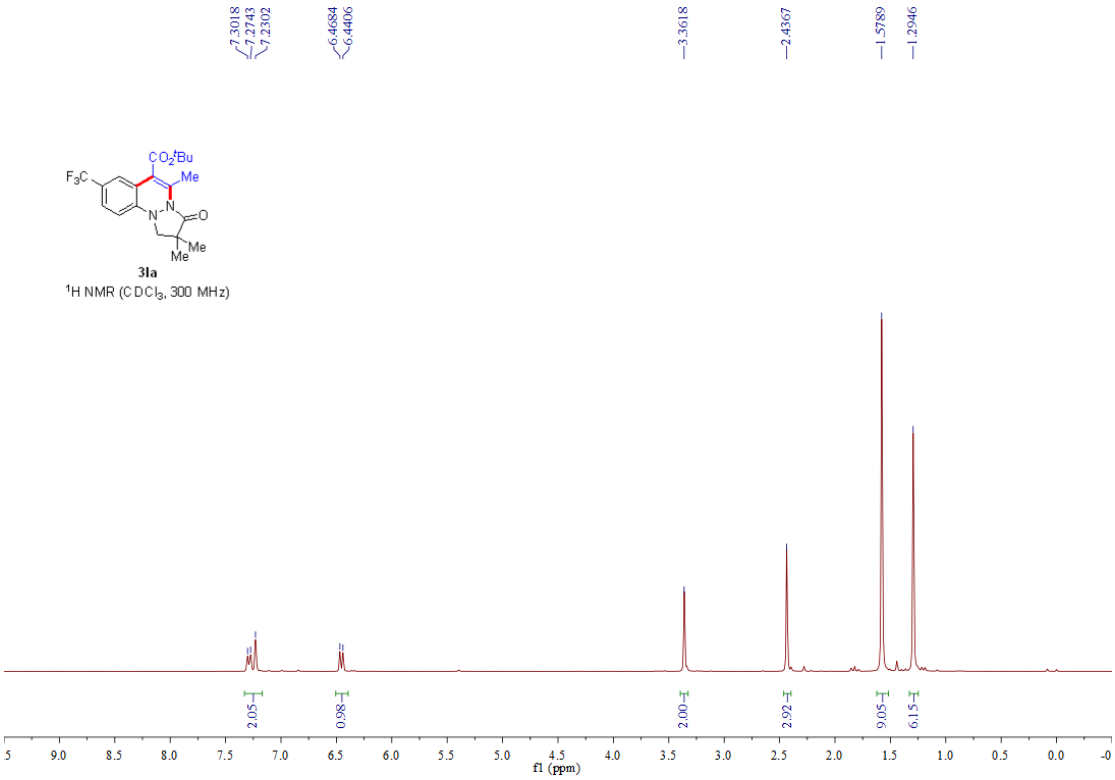
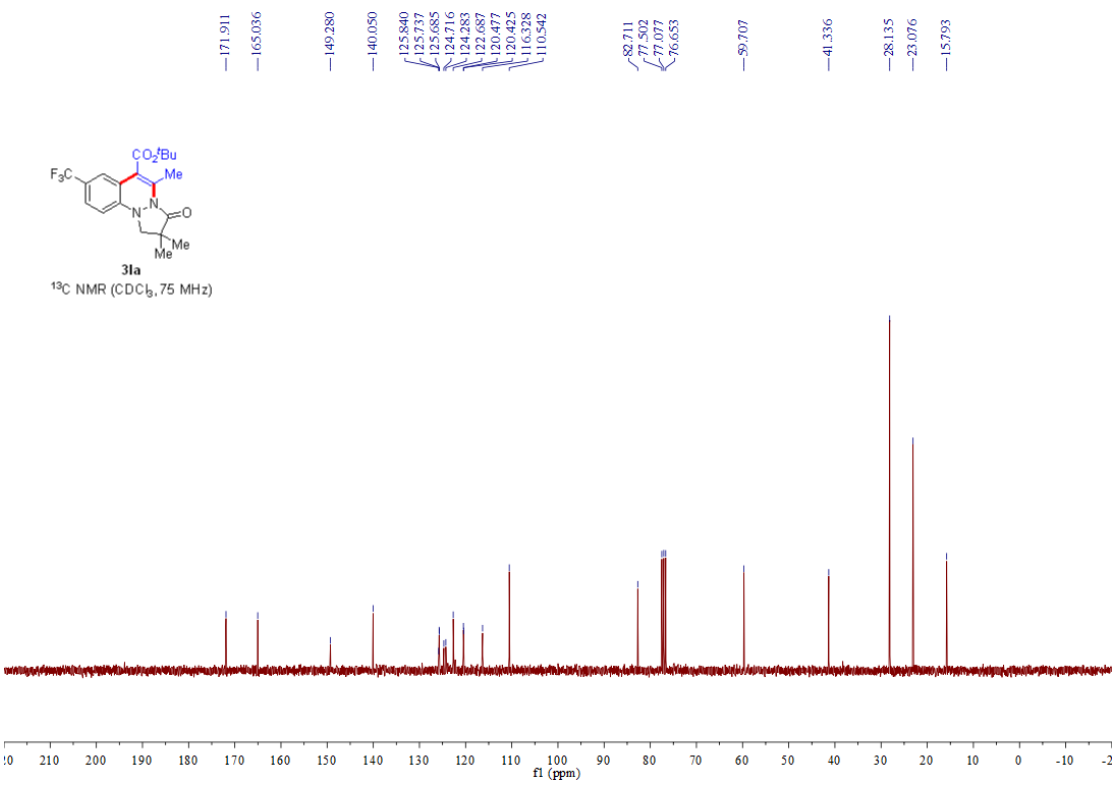
164.788
149.900
140.104
133.266
126.279
122.968
115.637
110.714
105.440
83.086
77.483
77.059
76.634
59.304
41.284
28.236
23.158
15.945
CO2tBu
Me
NC
N
N
O
Me
Me
3ka
13C NMR (CDCl3, 75 MHz)
f1 (ppm)



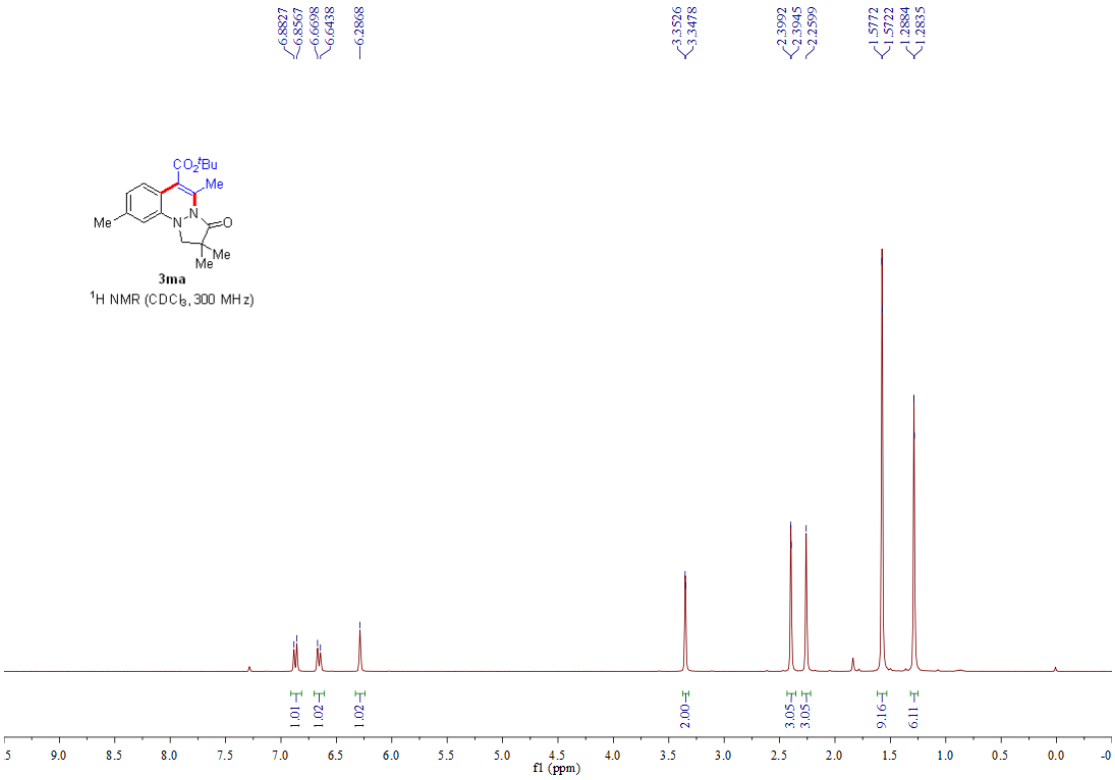
3la

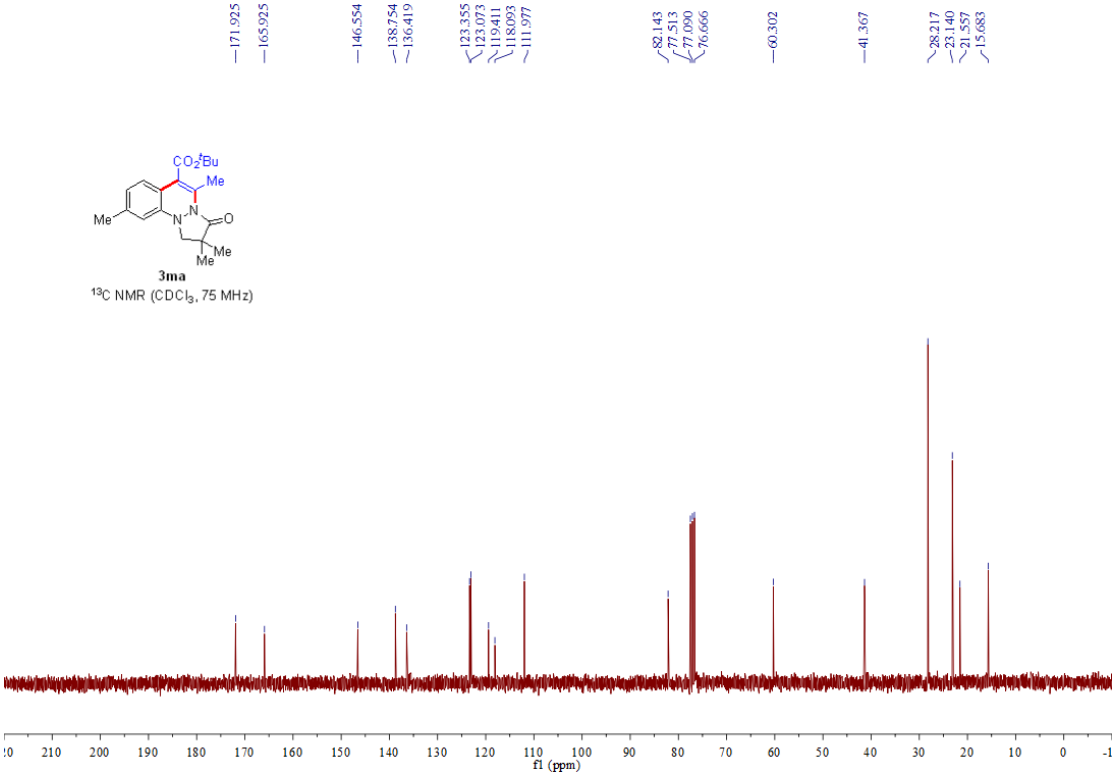
^{1}H NMR ($CDCl_3$, 300 MHz)

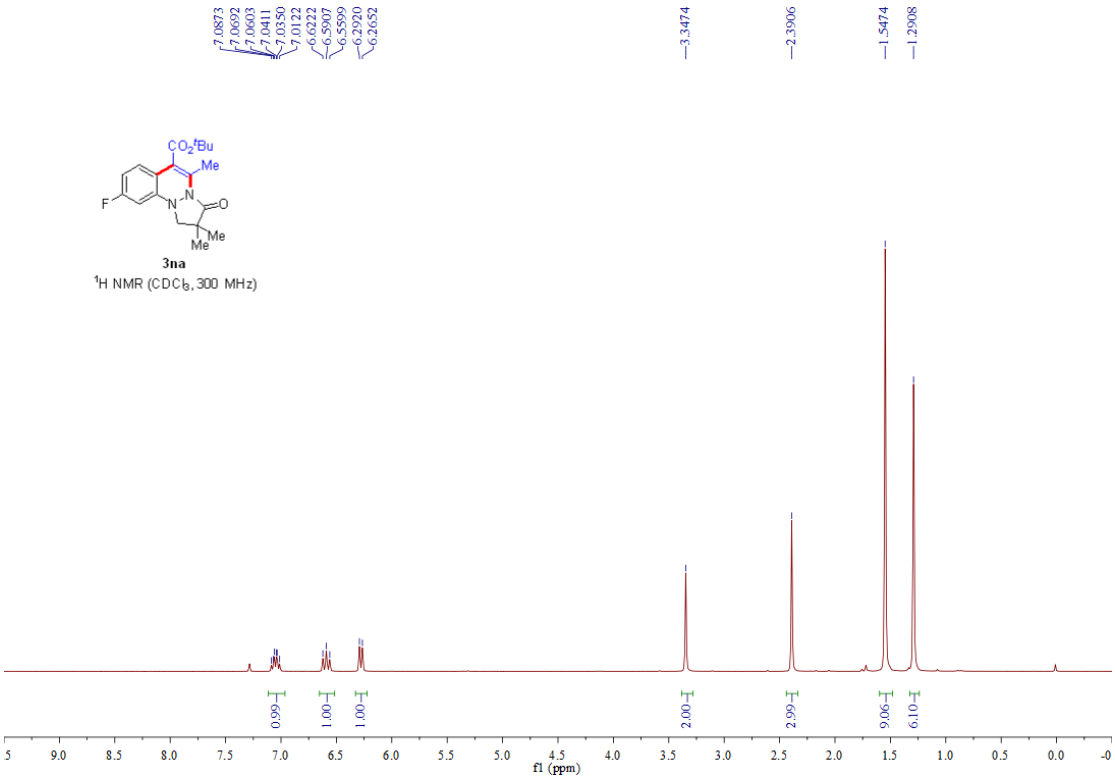


3la

^{13}C NMR ($CDCl_3$, 75 MHz)

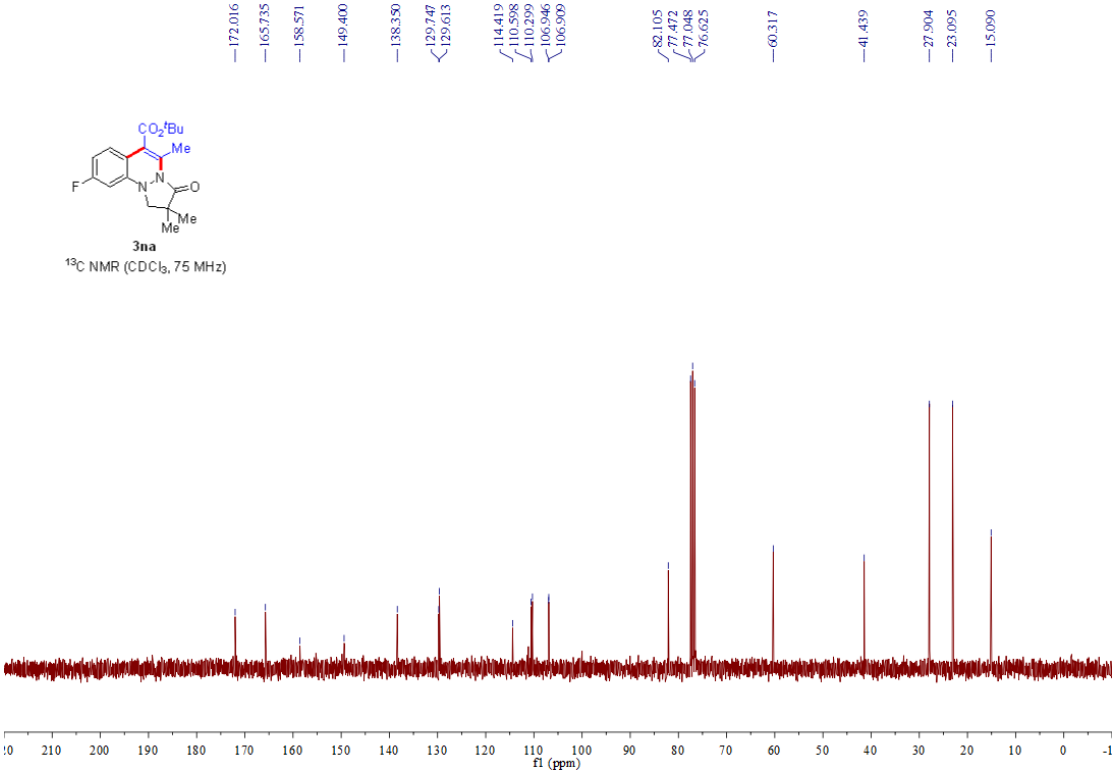

6.8827
6.8567
6.6698
6.6438
6.2868
3.3526
3.3478
2.3992
2.3945
2.2599
1.5772
1.5722
1.2884
1.2835
CO2tBu
Me
Me
N
N
O
Me
Me
3ma
1H NMR (CDCl3, 300 MHz)
1.01
1.02
1.02
2.00
3.05
3.05
9.16
6.11
f1 (ppm)


171.925
165.925
146.554
138.754
136.419
123.355
123.073
119.411
118.093
111.977
82.143
77.513
77.090
76.666
60.302
41.367
28.217
23.140
21.557
15.683
CO2tBu
Me
Me
N
N
O
Me
Me
3ma
13C NMR (CDCl3, 75 MHz)
f1 (ppm)



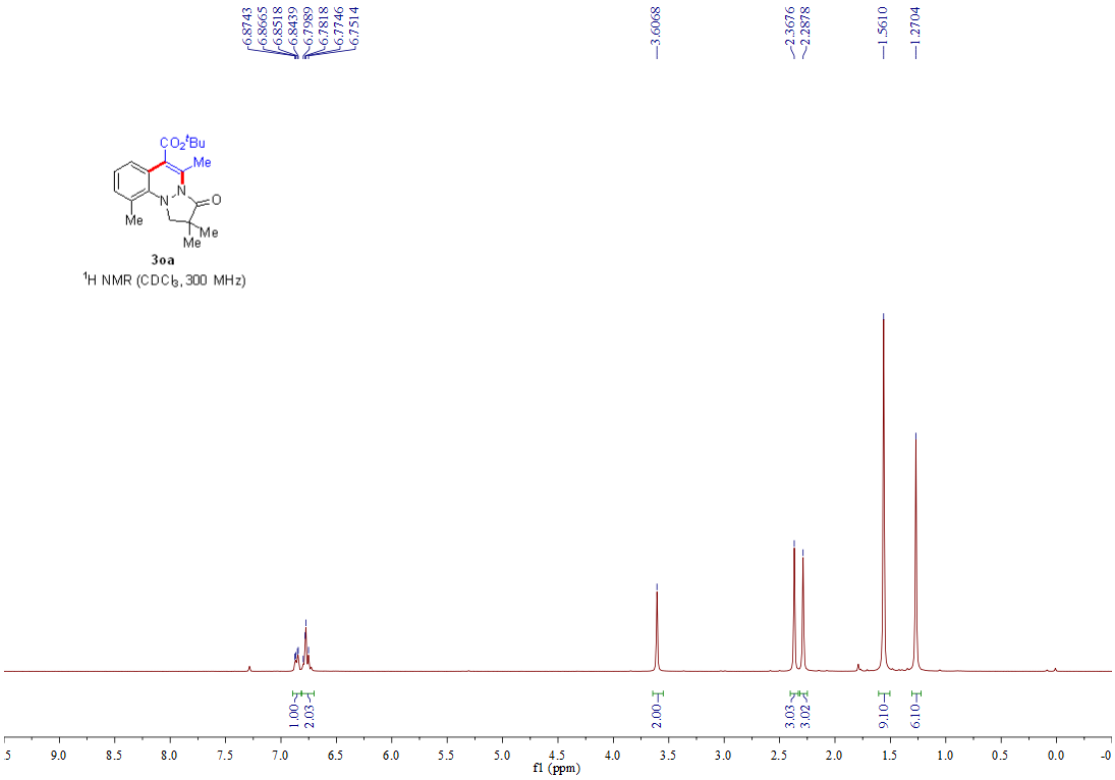
3na

^{1}H NMR ($CDCl_3$, 300 MHz)



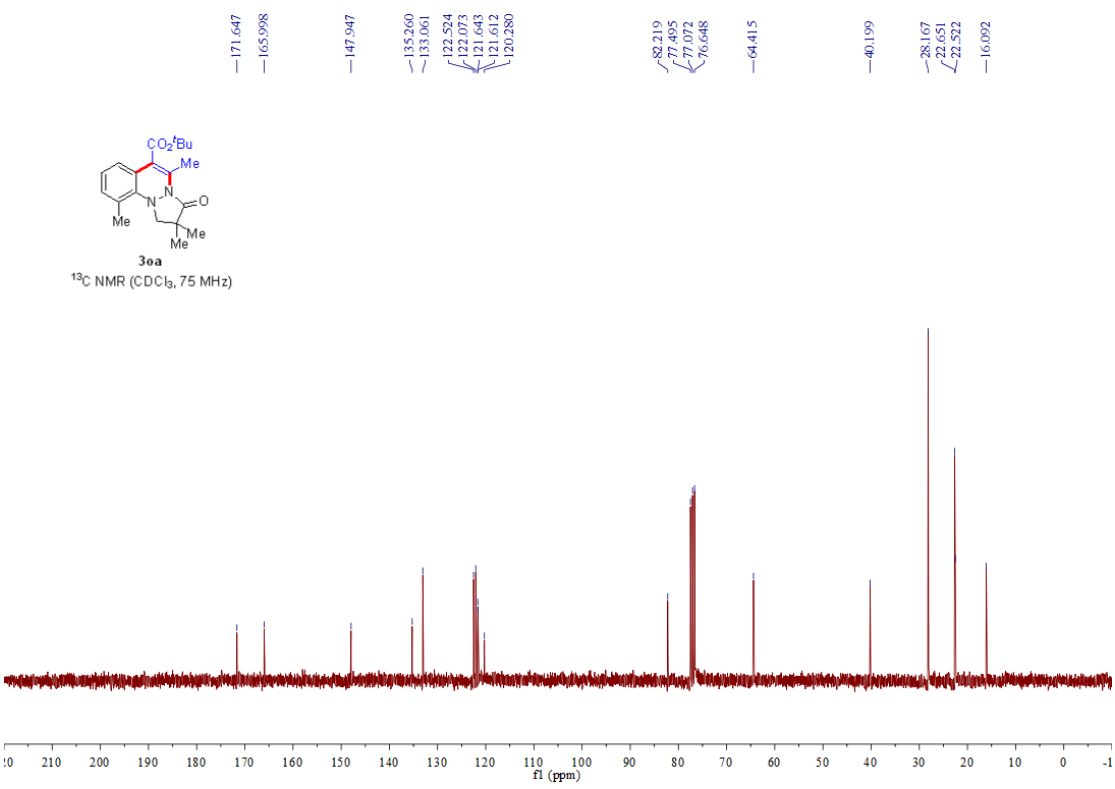
3na

^{13}C NMR ($CDCl_3$, 75 MHz)



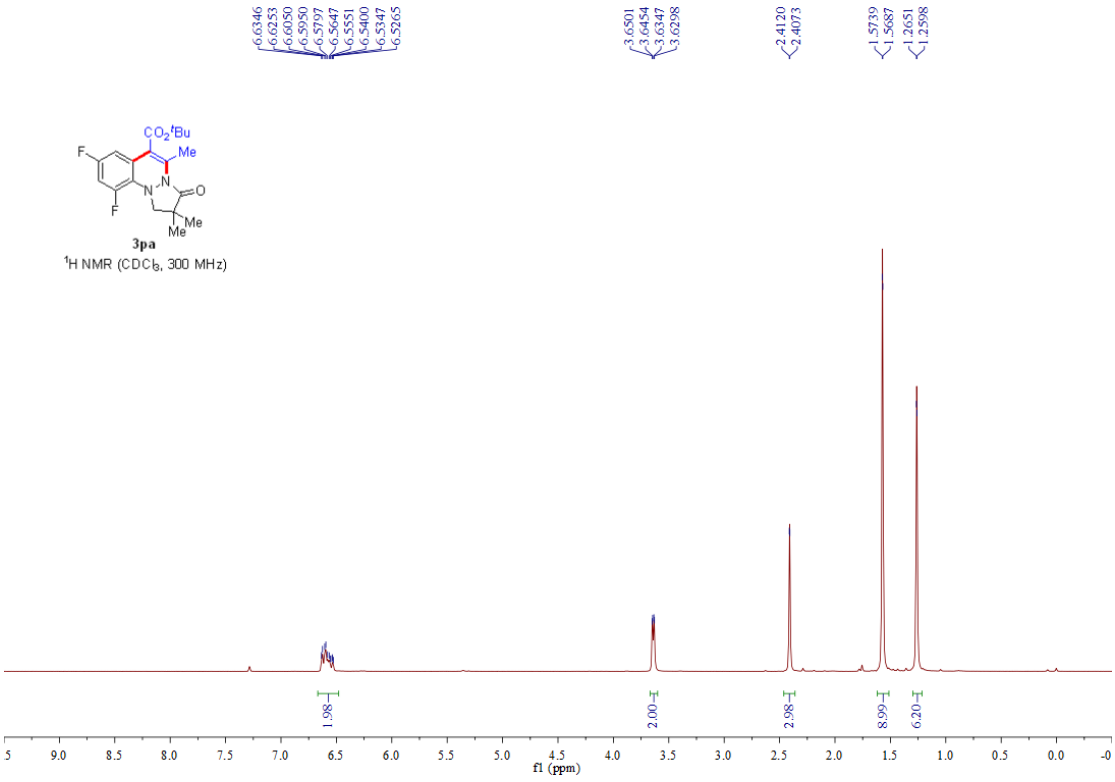
3oa

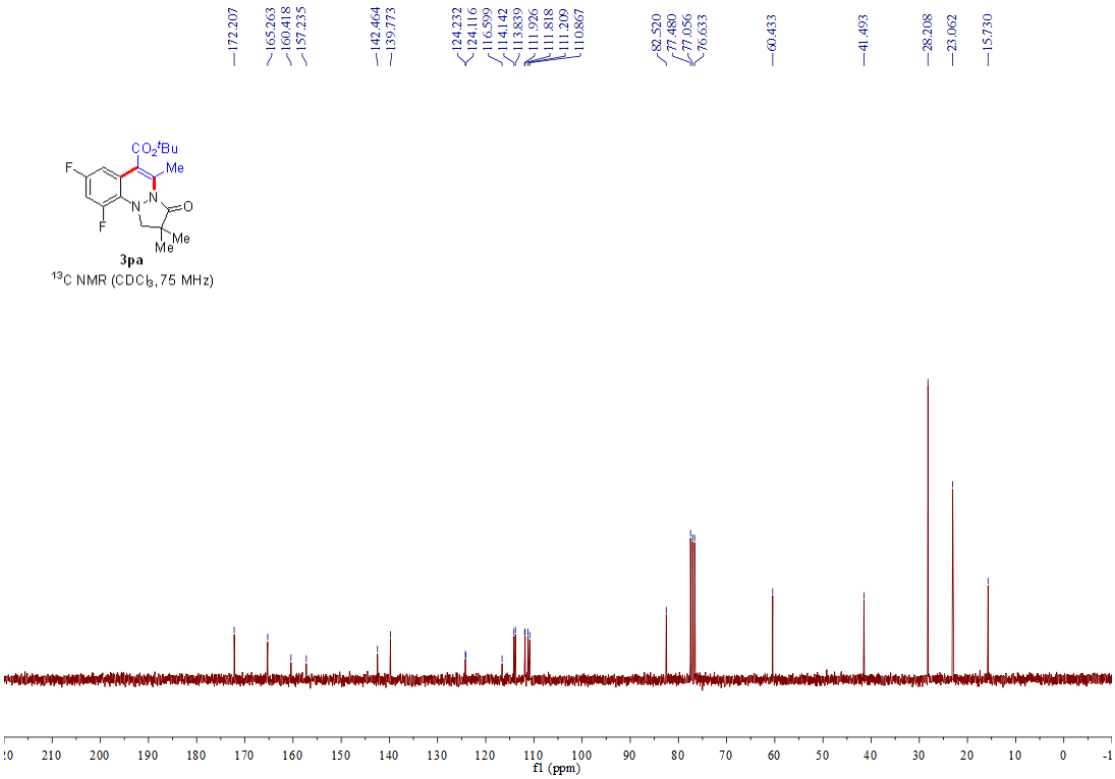
^{1}H NMR ($CDCl_3$, 300 MHz)

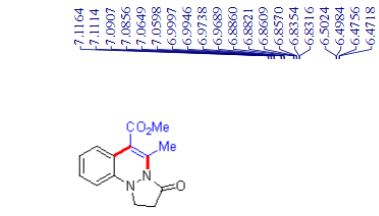


3oa

^{13}C NMR ($CDCl_3$, 75 MHz)

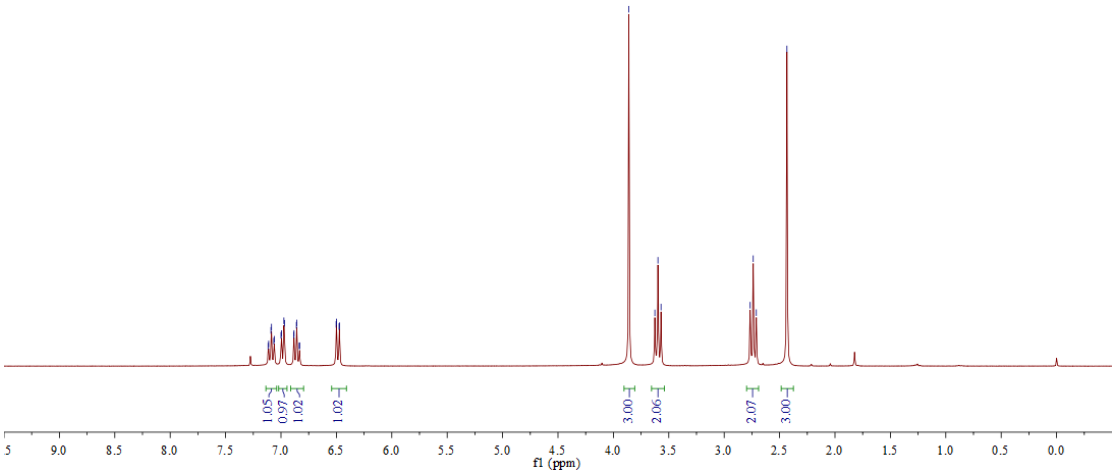

6.6346
6.6253
6.6050
6.5950
6.5797
6.5647
6.5551
6.5400
6.5347
6.5265
3.6501
3.6454
3.6347
3.6298
2.4120
2.4073
1.5739
1.5687
1.2651
1.2598
CO2tBu
Me
F
N
O
F
Me
Me
3pa
1H NMR (CDCl3, 300 MHz)
1.98
2.00
2.98
8.99
6.20
f1 (ppm)

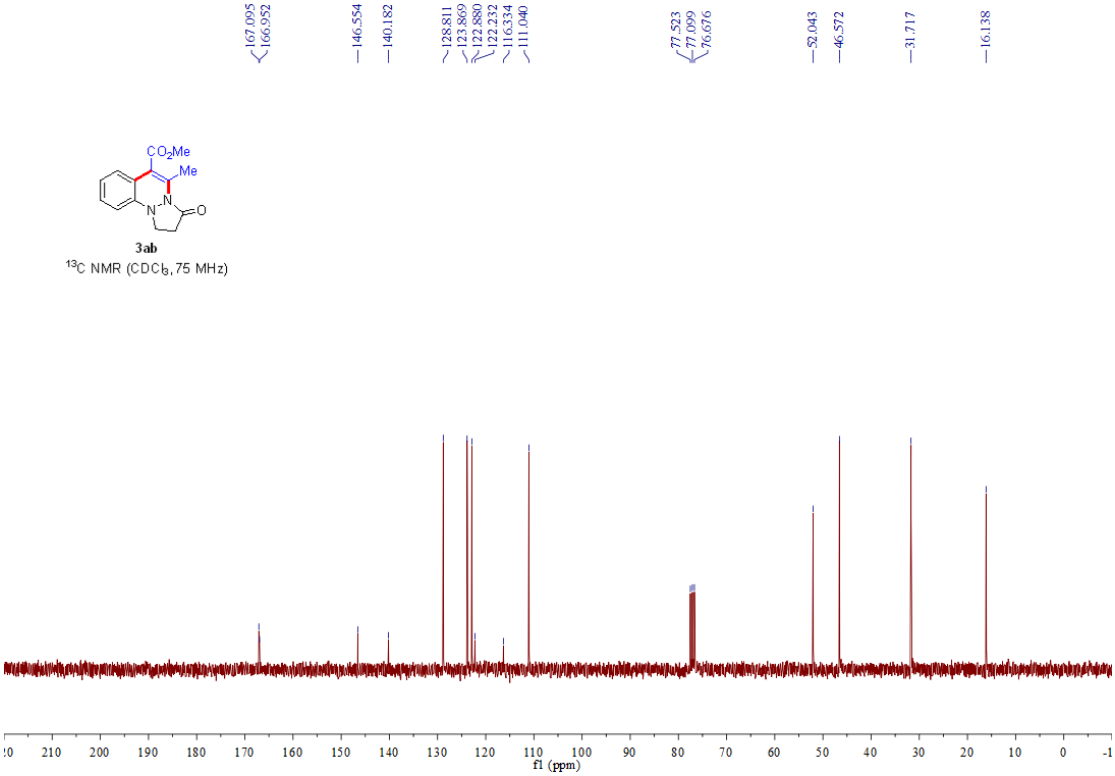

172.207
165.263
160.418
157.235
142.464
139.773
124.232
124.116
116.599
114.142
113.839
111.926
111.818
111.209
110.867
82.520
77.480
77.056
76.633
60.433
41.493
28.208
23.062
15.730
CO2tBu
Me
F
N
O
F
Me
Me
3pa
13C NMR (CDCl3, 75 MHz)
f1 (ppm)



3ab

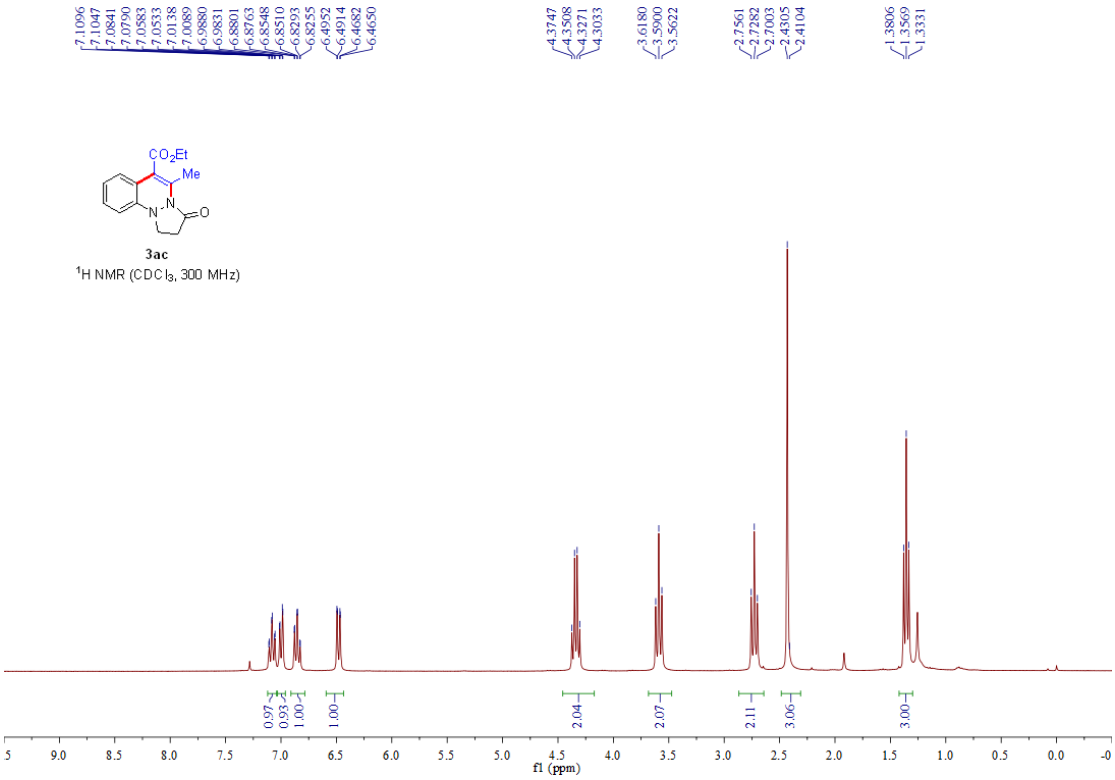
^{1}H NMR ($CDCl_3$, 300 MHz)





3ab

^{13}C NMR ($CDCl_3$, 75 MHz)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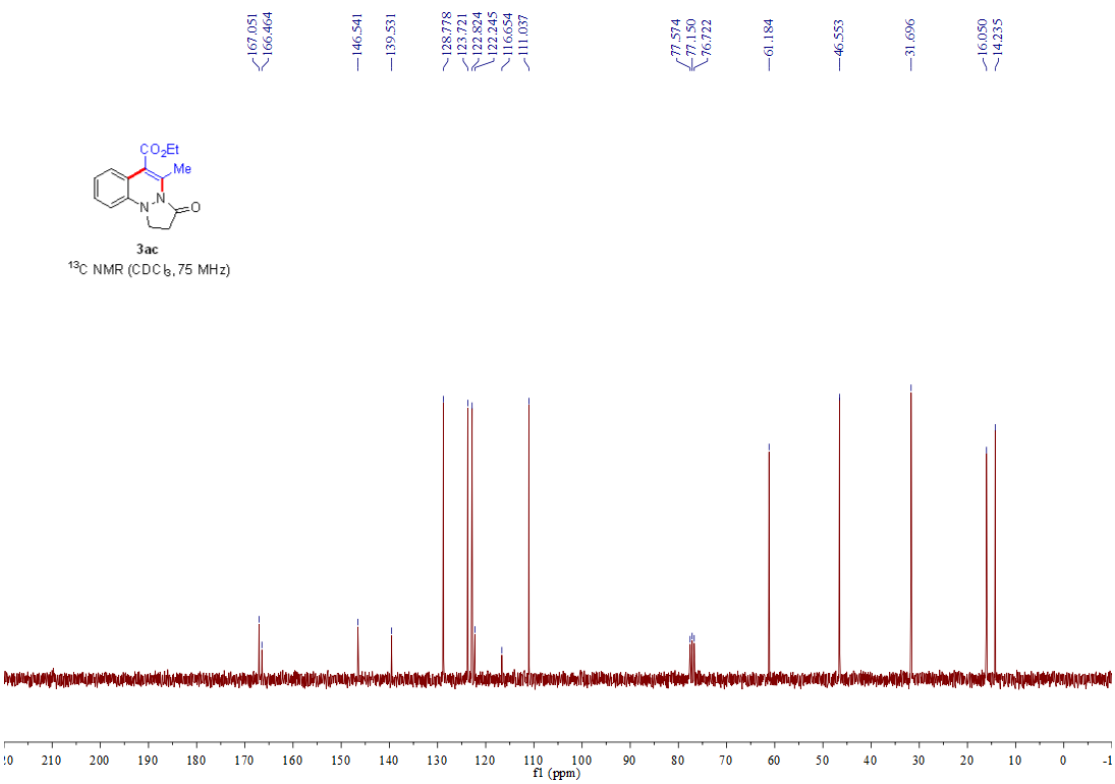
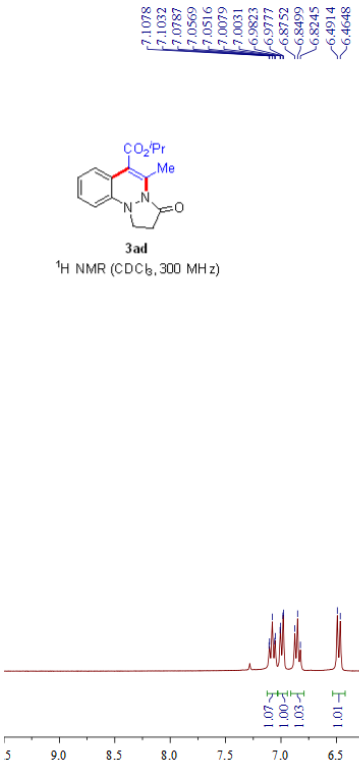
7.1047
7.0841
7.0790
7.0583
7.0533
7.0138
7.0089
6.9880
6.9831
6.8801
6.8763
6.8548
6.8510
6.8293
6.8255
6.4952
6.4914
6.4682
6.4650
4.3747
4.3508
4.3271
4.3033
3.6180
3.5900
3.5622
2.7561
2.7282
2.7003
2.4305
2.4104
1.3806
1.3569
1.3331
CO2Et
Me
N
N
O
3ac
1H NMR (CDCl3, 300 MHz)
0.97
0.93
1.00
1.00
2.04
2.07
2.11
3.06
3.00
f1 (ppm)


167.051
166.464
146.541
139.531
128.778
123.721
122.824
122.245
116.654
111.037
77.574
77.150
76.722
61.184
46.553
31.696
16.050
14.235
CO2Et
Me
N
N
O
3ac
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.1078
7.1032
7.0787
7.0569
7.0516
7.0079
7.0031
6.9823
6.9777
6.8752
6.8499
6.8245
6.4914
6.4648
5.2516
5.2307
5.2099
3.6182
3.5904
3.5625
2.7526
2.7248
2.6969
2.4190
1.3543
1.3334
CO2iPr
Me
N
N
O
3ad
1H NMR (CDCl3, 300 MHz)
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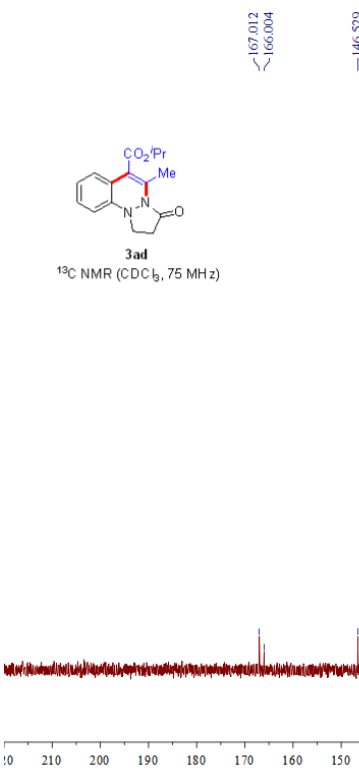
1.00
1.03
1.01
1.01
2.08
2.06
3.00
6.14
f1 (ppm)


167.012
166.004
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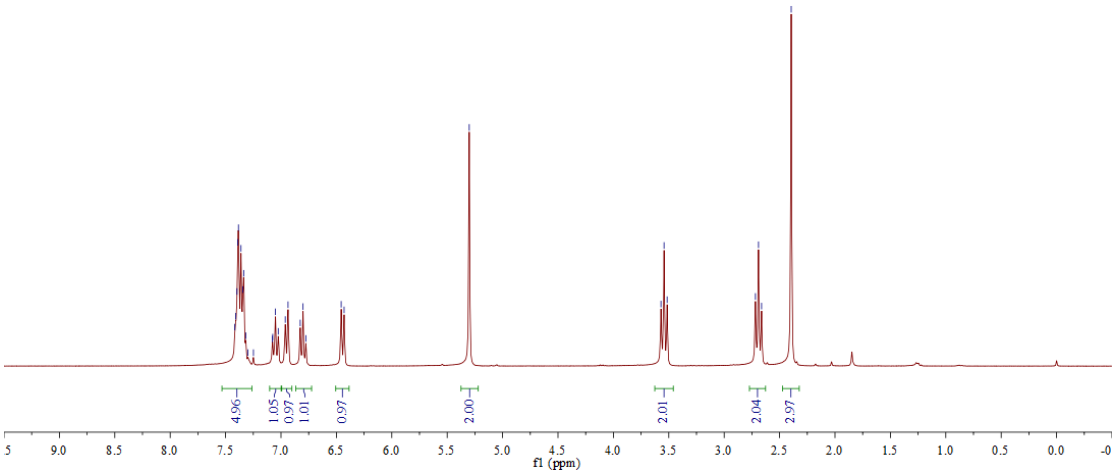
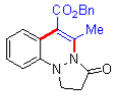
128.773
123.596
122.834
122.303
117.064
111.041
77.560
77.137
76.710
68.987
46.556
31.703
21.844
15.962
CO2iPr
Me
N
N
O
3ad
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

3ae

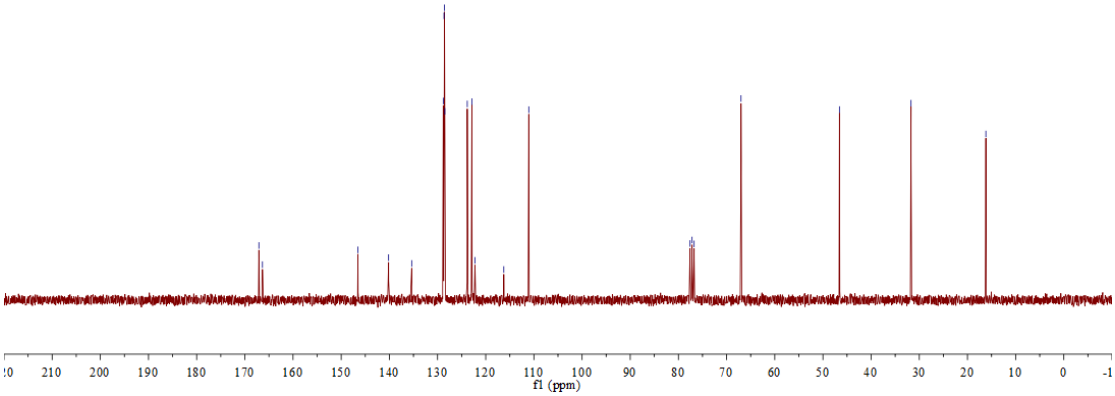
^{1}H NMR ($CDCl_3$, 300 MHz)

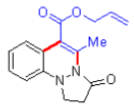




3ae

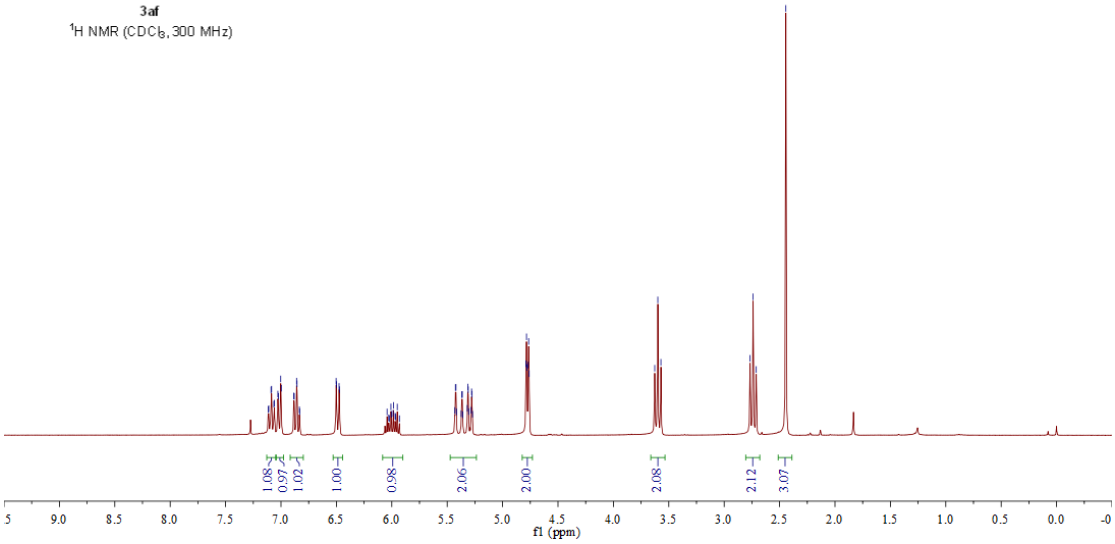
^{13}C NMR ($CDCl_3$, 75 MHz)

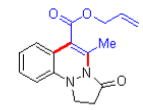




3af

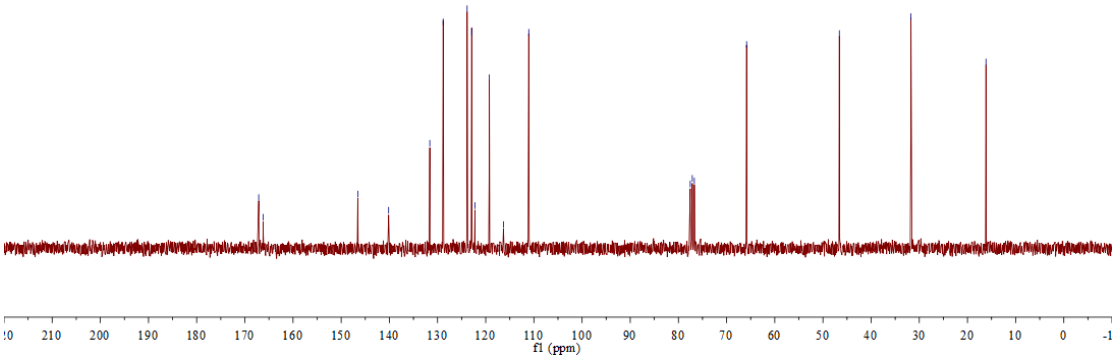
^{1}H NMR ($CDCl_3$, 300 MHz)

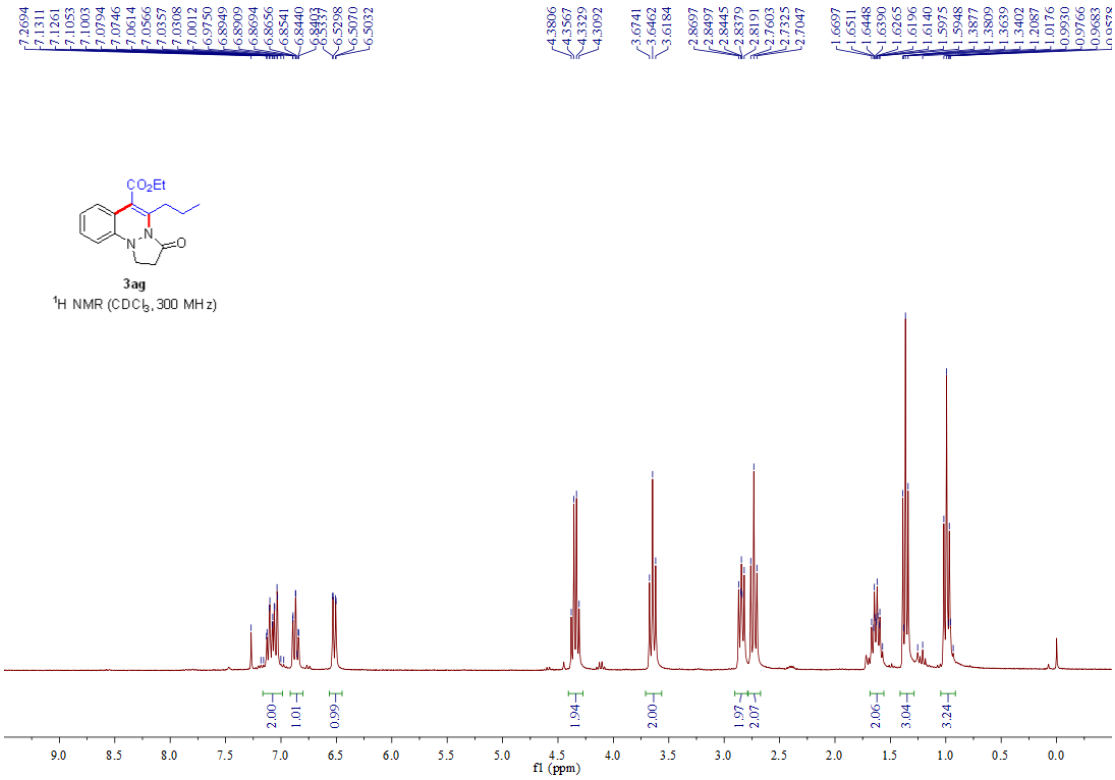




3af

^{13}C NMR ($CDCl_3$, 75 MHz)




7.2694
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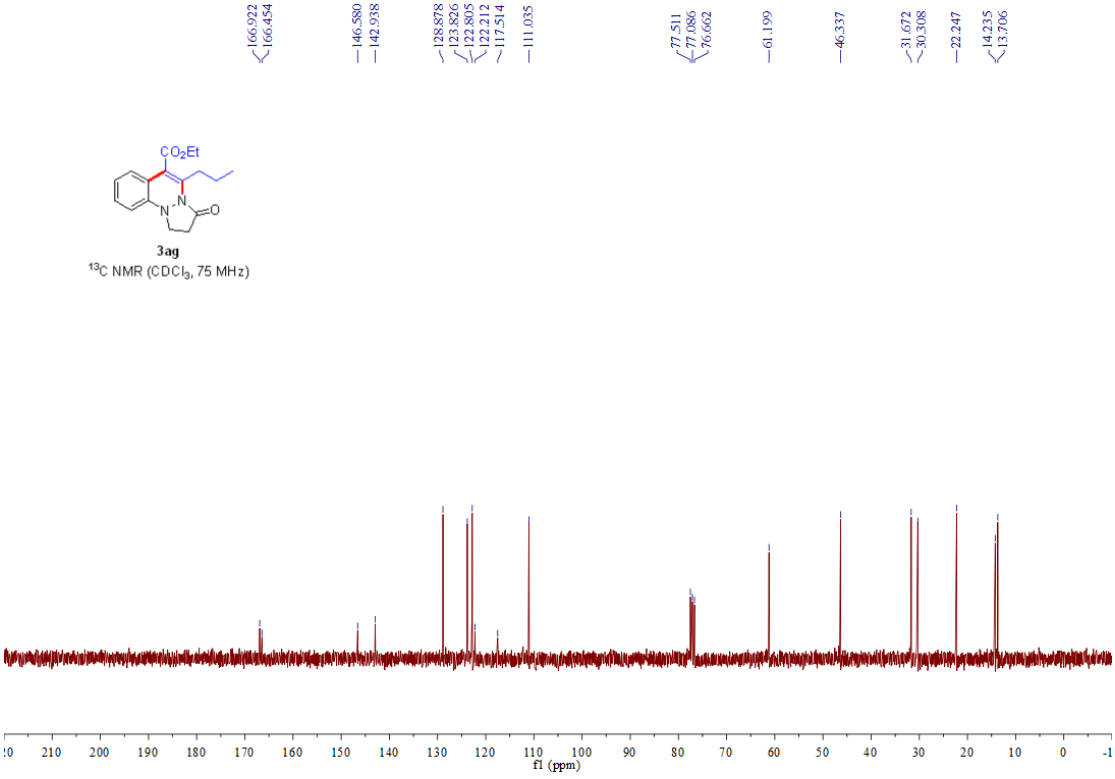
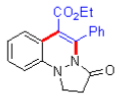
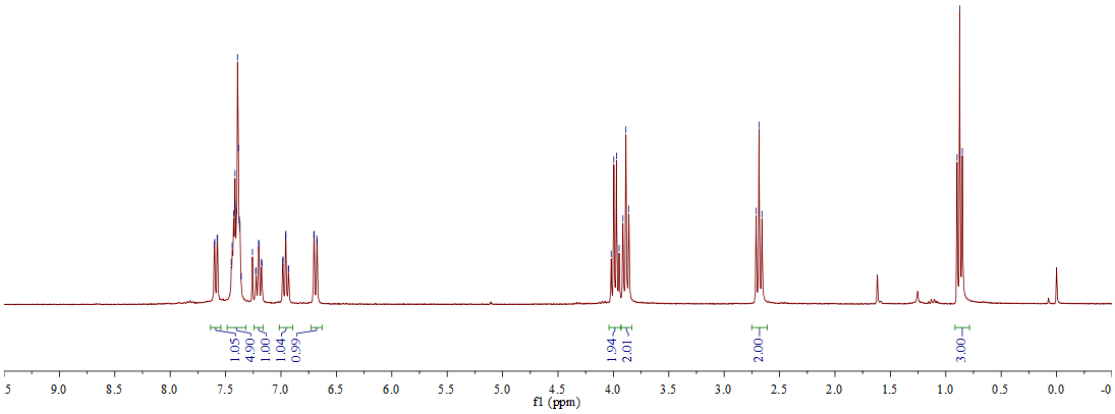
7.1261
7.1053
7.1003
7.0794
7.0746
7.0614
7.0566
7.0357
7.0308
7.0012
6.9750
6.8949
6.8909
6.8694
6.8656
6.8541
6.8440
6.5298
6.5070
6.5032
4.3806
4.3567
4.3329
4.3092
3.6741
3.6462
3.6184
2.8697
2.8497
2.8445
2.8379
2.8191
2.7603
2.7325
2.7047
1.6697
1.6511
1.6448
1.6390
1.6265
1.6196
1.6140
1.5975
1.5948
1.3877
1.3809
1.3639
1.3402
1.2087
1.0176
0.9930
0.9766
0.9683
CO2Et
N
N
O
3ag
1H NMR (CDCl3, 300 MHz)
2.00
1.01
0.99
1.94
2.00
1.97
2.07
2.06
3.04
3.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

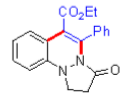

166.922
166.454
146.580
142.938
128.878
123.826
122.805
122.212
117.514
111.035
77.511
77.086
76.662
61.199
46.337
31.672
30.308
22.247
14.235
13.706
CO2Et
N
N
O
3ag
13C NMR (CDCl3, 75 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



3ah

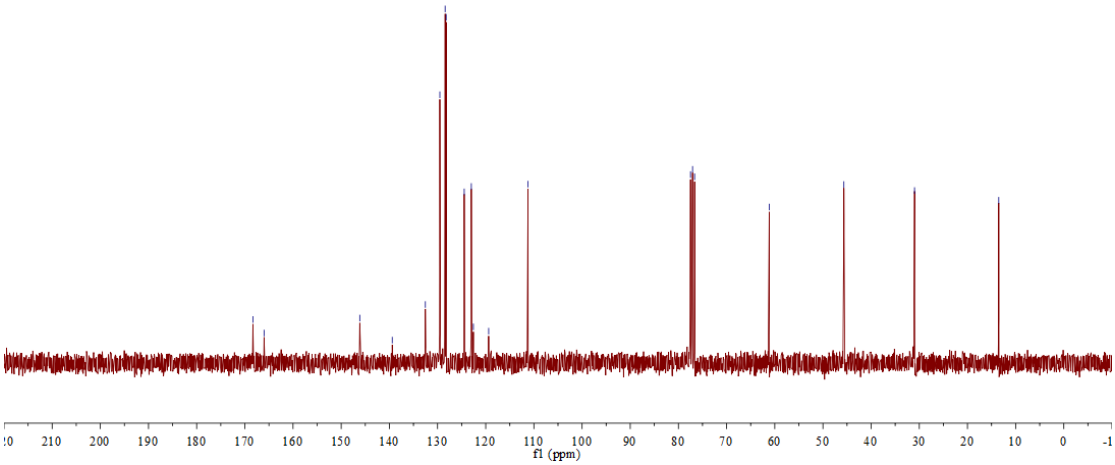
^{1}H NMR ($CDCl_3$, 300 MHz)

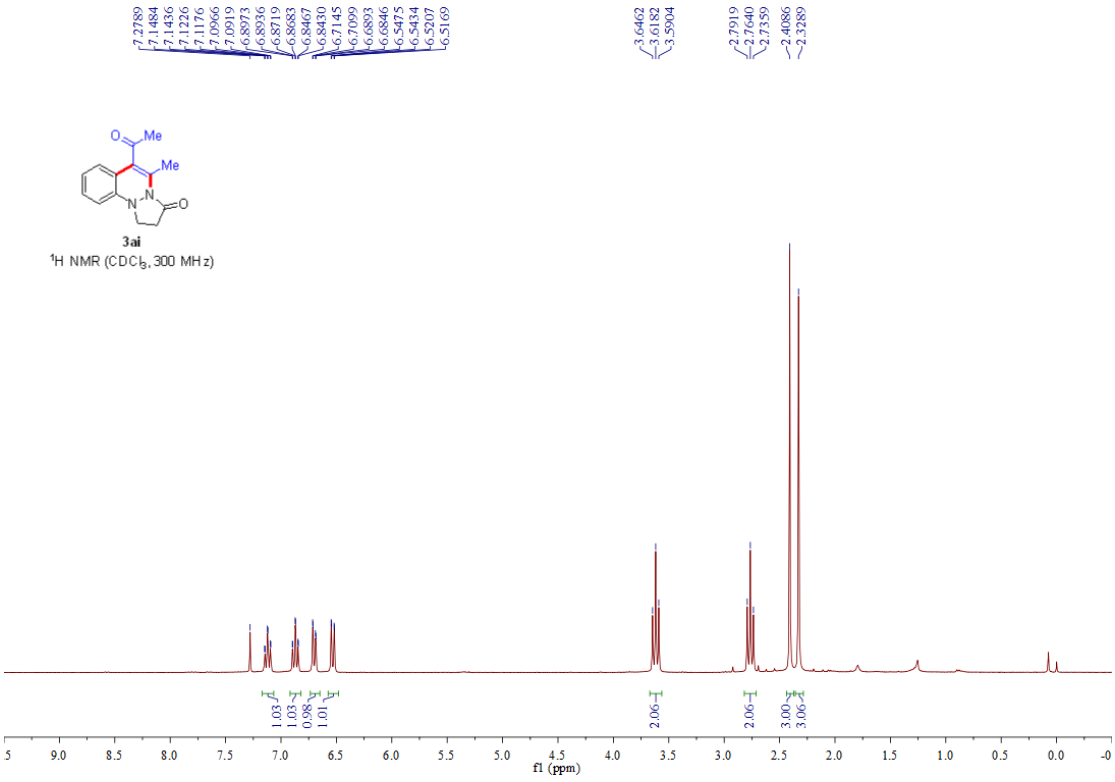


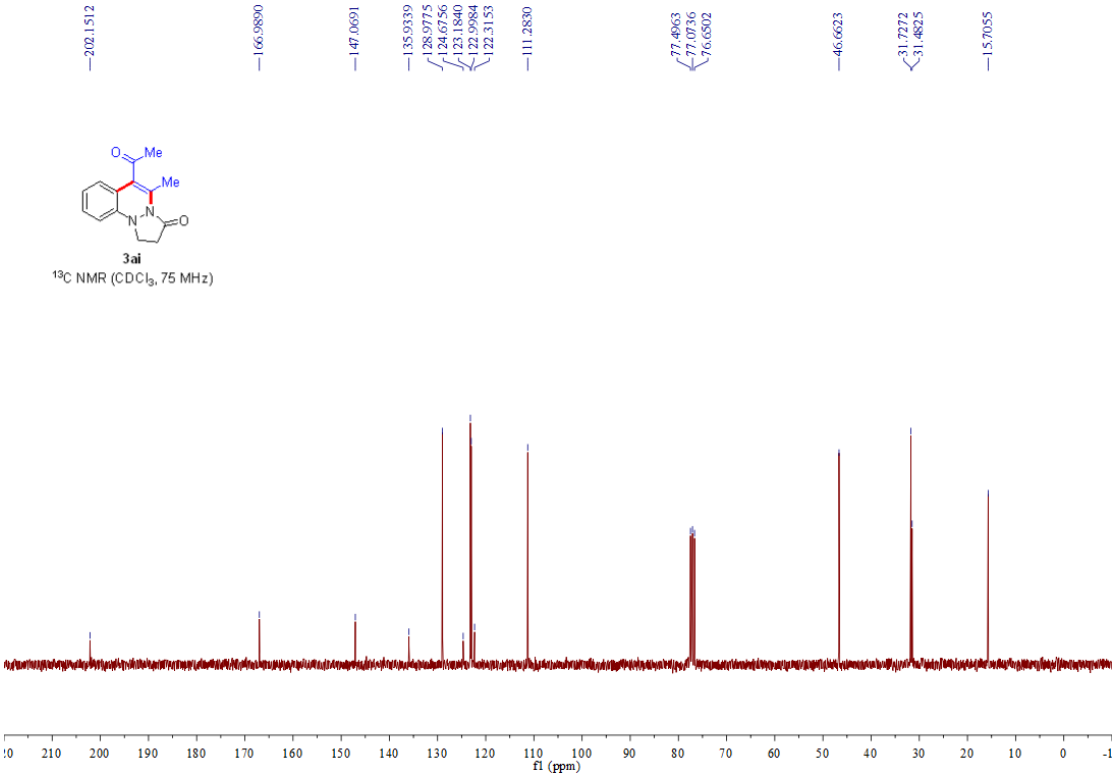


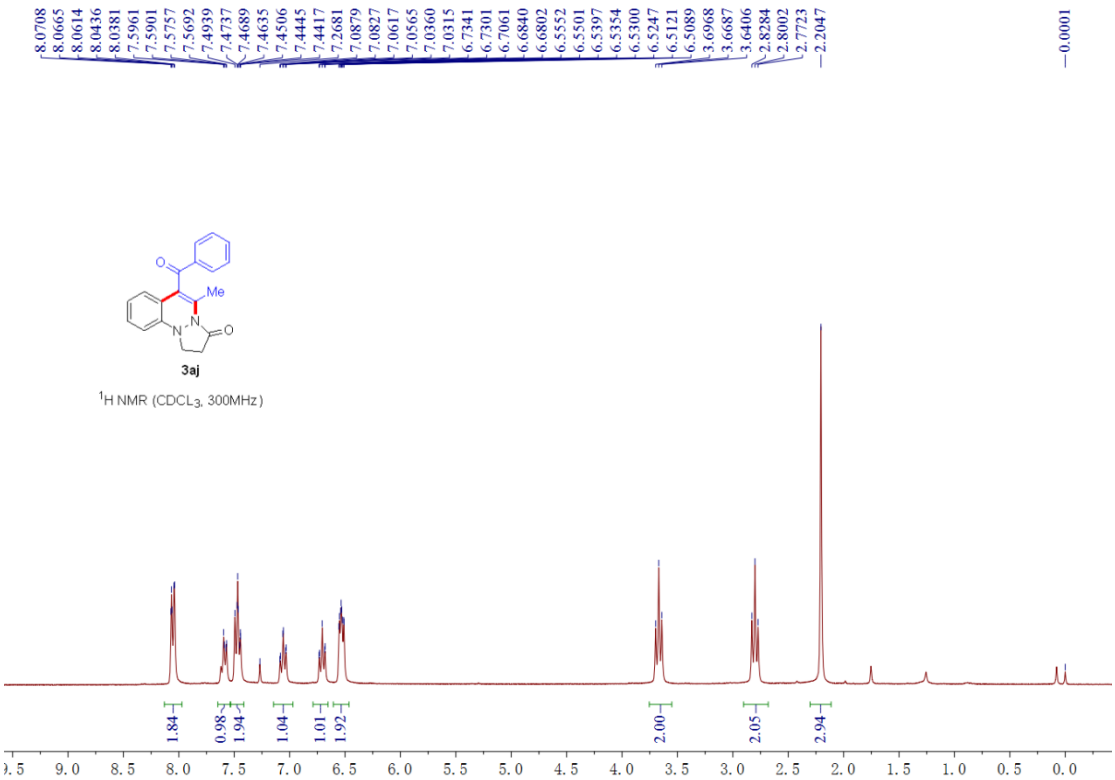
3ah

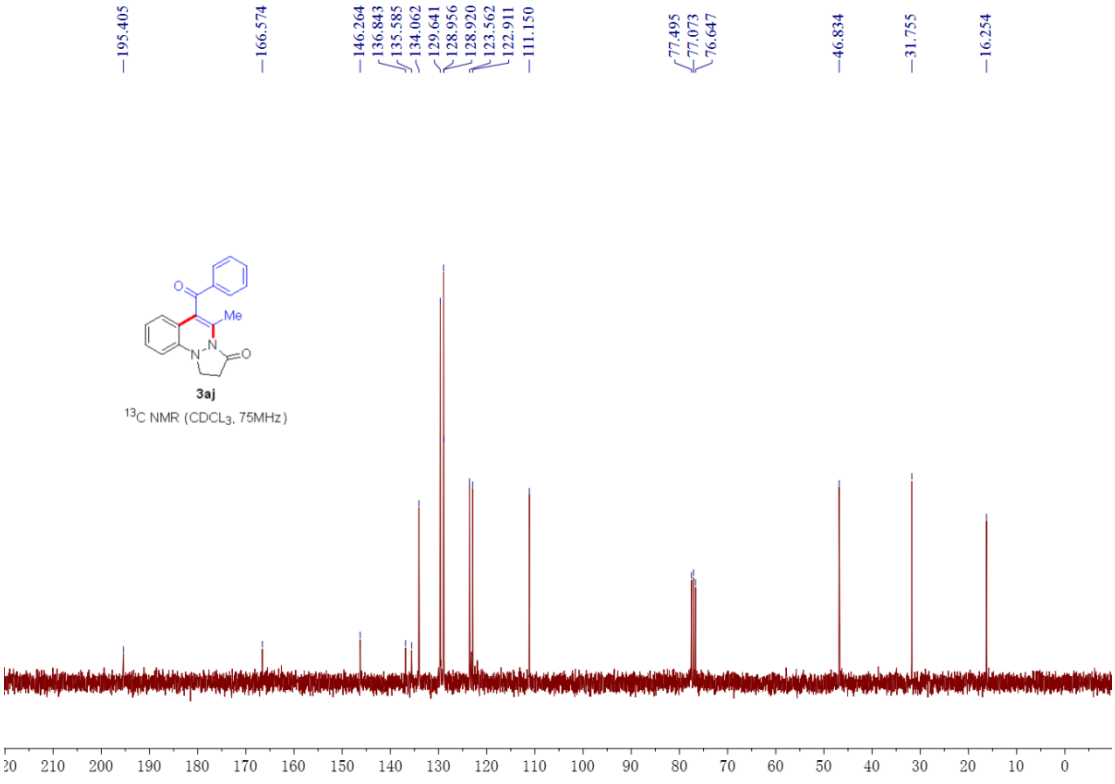
^{13}C NMR ($CDCl_3$, 75 MHz)

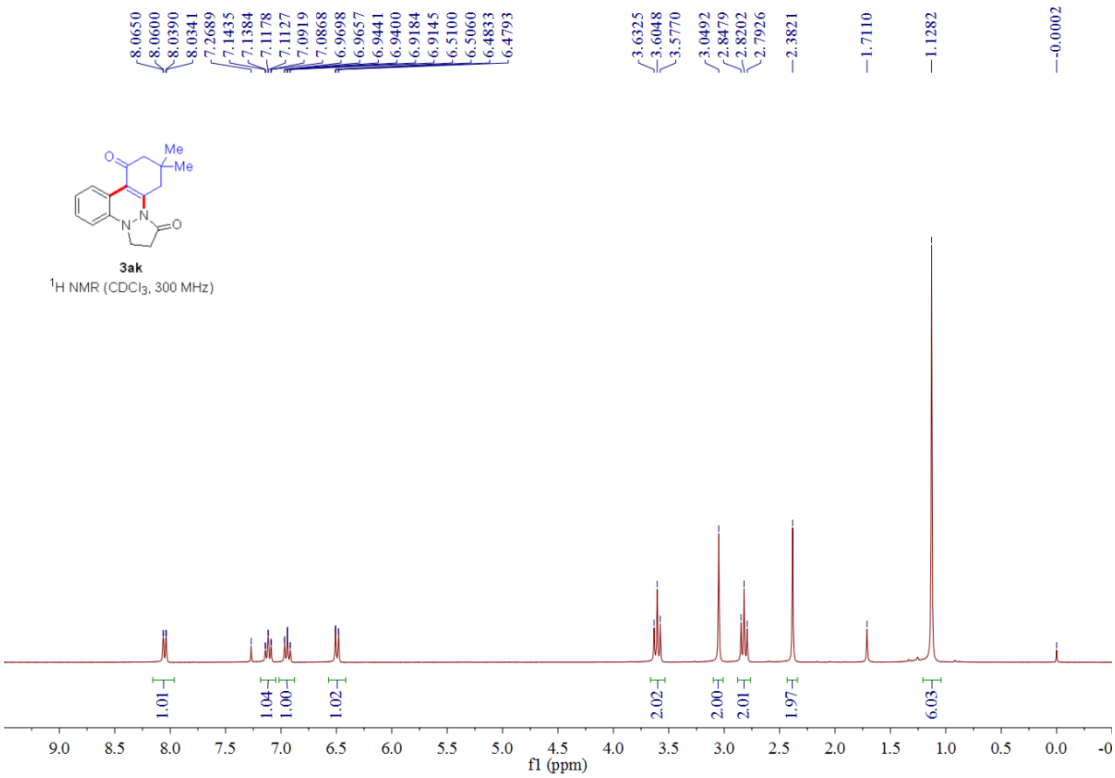


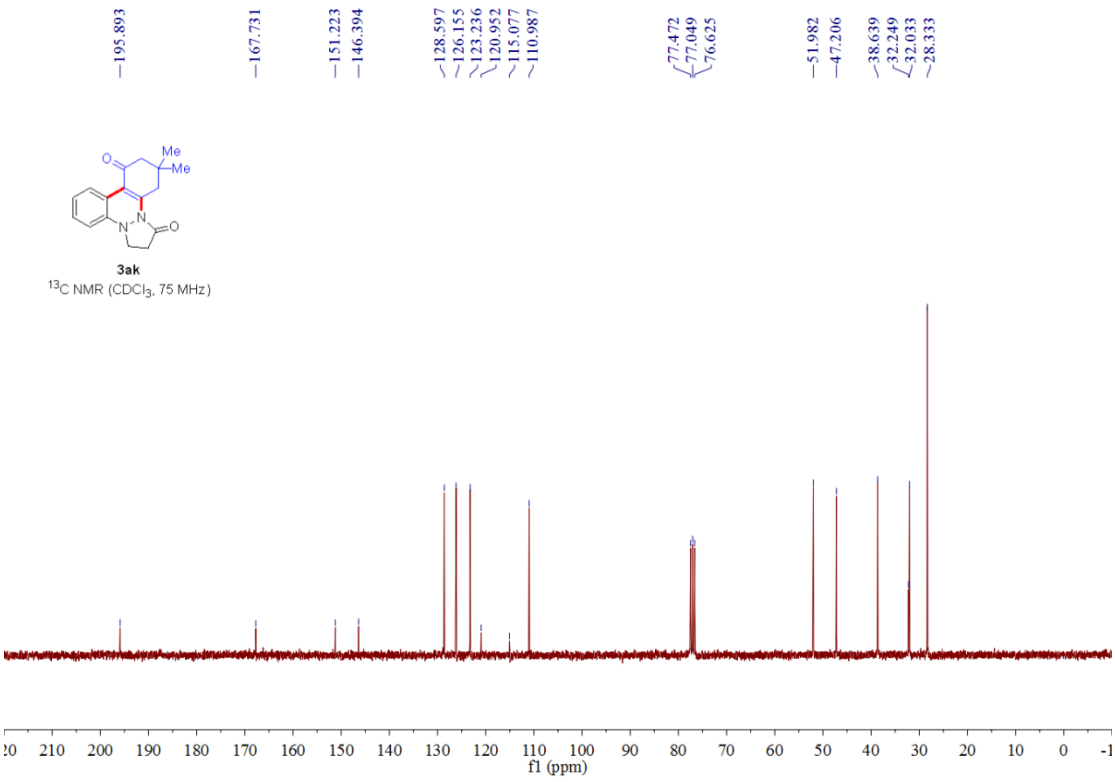

7.2789
7.1484
7.1436
7.1226
7.1176
7.0966
7.0919
6.8973
6.8936
6.8719
6.8683
6.8467
6.8430
6.7145
6.7099
6.6893
6.6846
6.5475
6.5434
6.5207
6.5169
3.6462
3.6182
3.5904
2.7919
2.7640
2.7359
2.4086
2.3289
Me
Me
O
N
N
O
3ai
1H NMR (CDCl3, 300 MHz)
1.03
1.03
0.98
1.01
2.06
2.06
3.00
3.06
f1 (ppm)

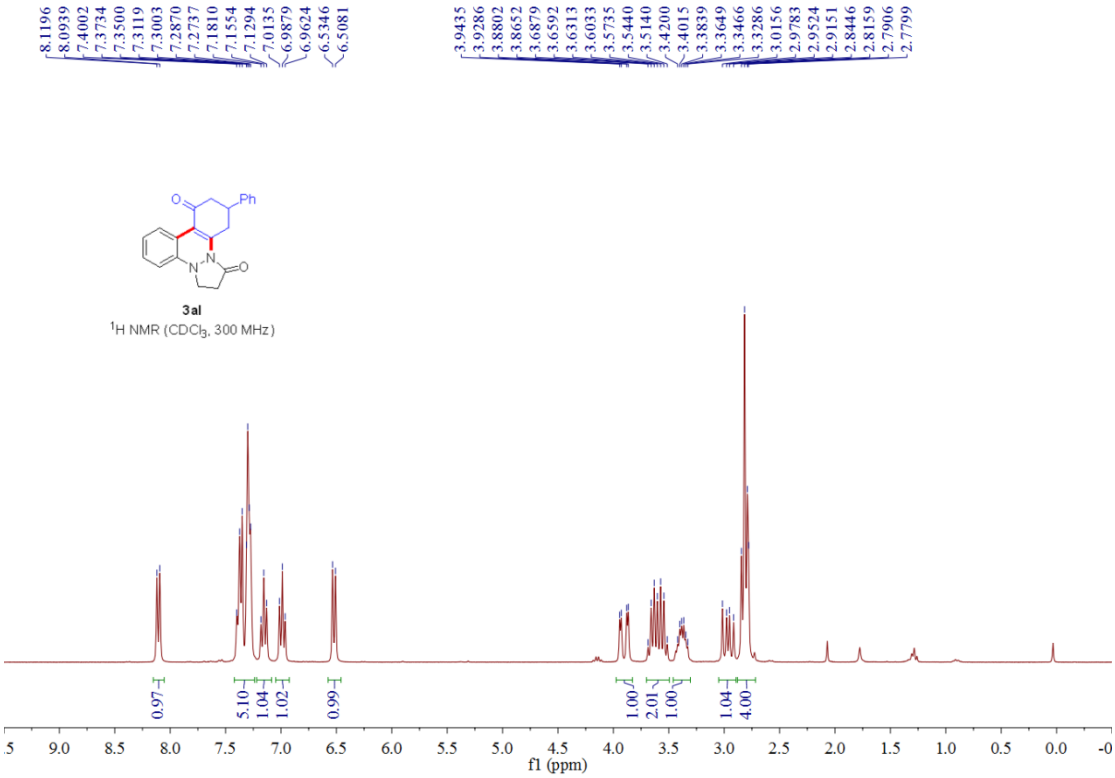

202.1512
166.9890
147.0691
135.9339
128.9775
124.6756
123.1840
122.9984
122.3153
111.2830
77.4963
77.0736
76.6502
46.6623
31.7272
31.4825
15.7055
Me
Me
O
N
N
O
3ai
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

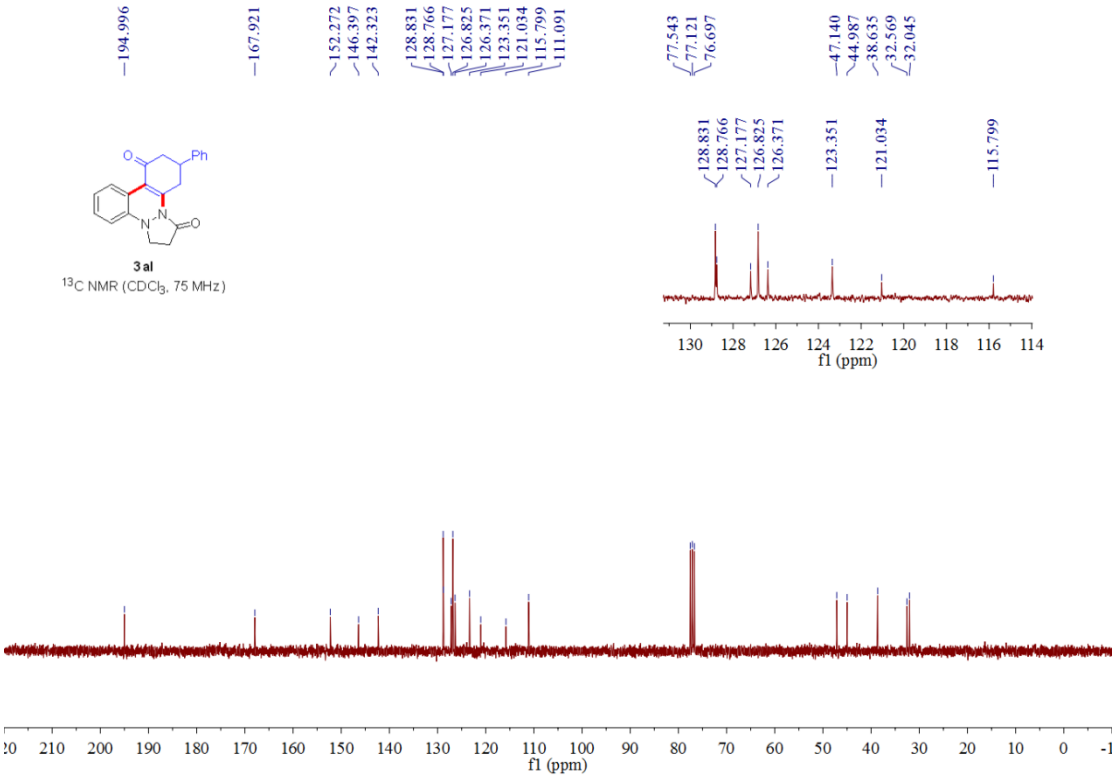

8.0708
8.0665
8.0614
8.0436
8.0381
7.5961
7.5901
7.5757
7.5692
7.4939
7.4737
7.4689
7.4635
7.4506
7.4445
7.4417
7.2681
7.0879
7.0827
7.0617
7.0565
7.0360
7.0315
6.7341
6.7301
6.7061
6.6840
6.6802
6.5552
6.5501
6.5397
6.5354
6.5300
6.5247
6.5121
6.5089
3.6968
3.6687
3.6406
2.8284
2.8002
2.7723
2.2047
0.0001
O
Me
N
N
O
3aj
1H NMR (CDCL3, 300MHz)
1.84
0.98
1.94
1.04
1.01
1.92
2.00
2.05
2.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

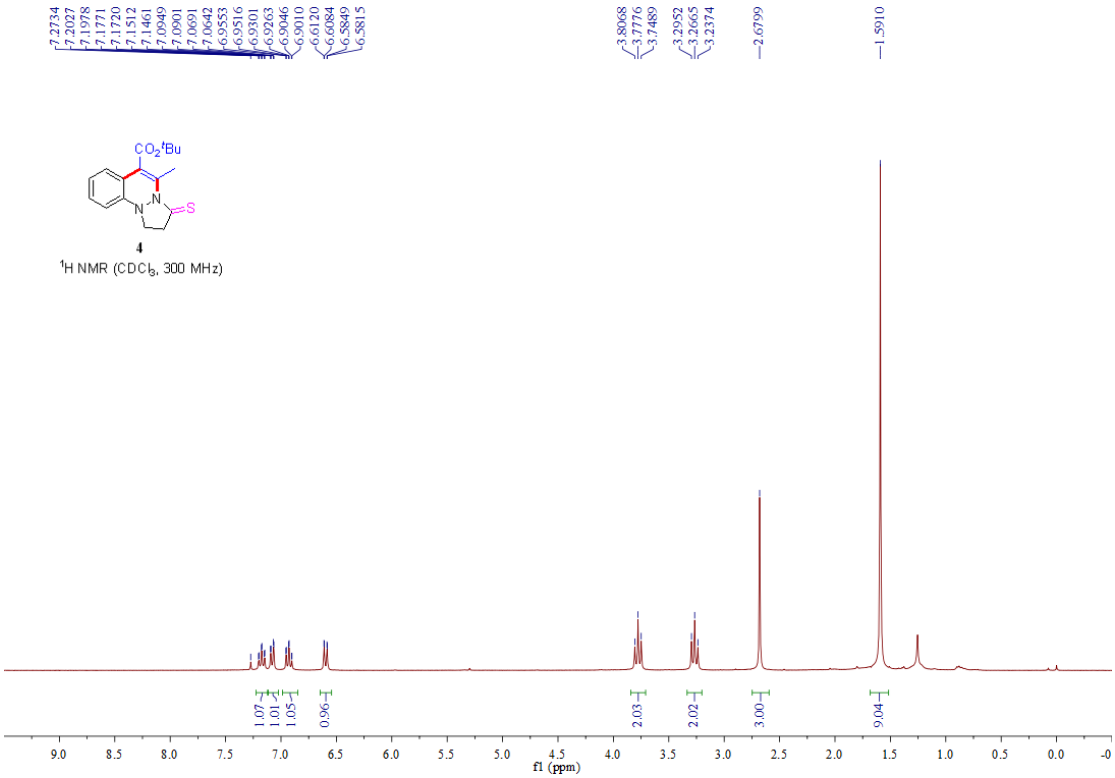

195.405
166.574
146.264
136.843
135.585
134.062
129.641
128.956
128.920
123.562
122.911
111.150
77.495
77.073
76.647
46.834
31.755
16.254
O
Me
N
N
O
3aj
13C NMR (CDCL3, 75MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

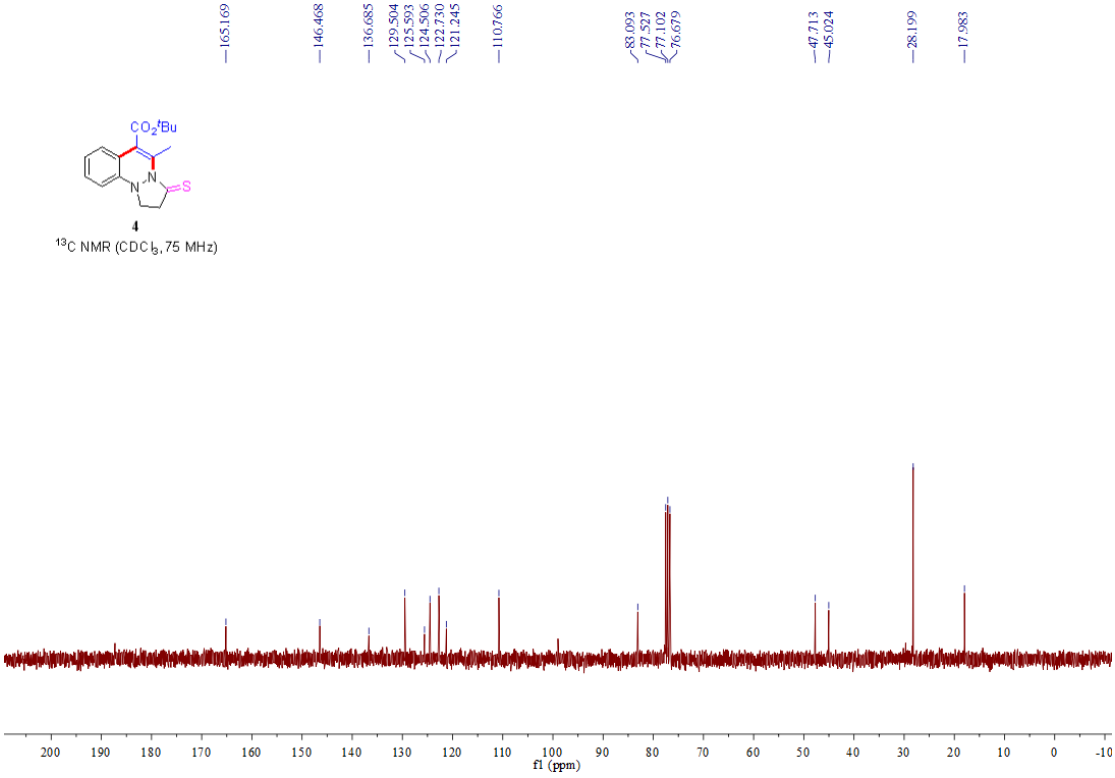

8.0650
8.0600
8.0390
8.0341
7.2689
7.1435
7.1384
7.1178
7.1127
7.0919
7.0868
6.9698
6.9657
6.9441
6.9400
6.9184
6.9145
6.5100
6.5060
6.4833
6.4793
3.6325
3.6048
3.5770
3.0492
2.8479
2.8202
2.7926
2.3821
1.7110
1.1282
-0.0002
Me
Me
O
N
N
O
3ak
1H NMR (CDCl3, 300 MHz)
1.01
1.04
1.00
1.02
2.02
2.00
2.01
1.97
6.03
f1 (ppm)

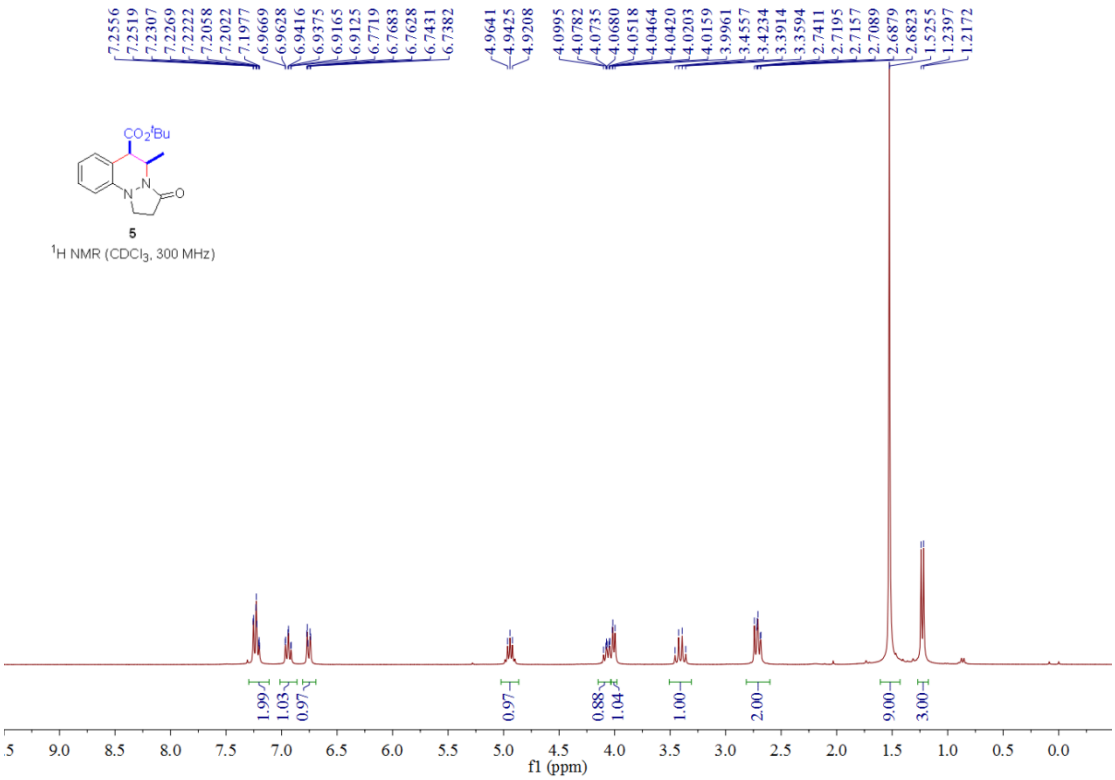

195.893
167.731
151.223
146.394
128.597
126.155
123.236
120.952
115.077
110.987
77.472
77.049
76.625
51.982
47.206
38.639
32.249
32.033
28.333
Me
Me
O
N
N
O
3ak
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

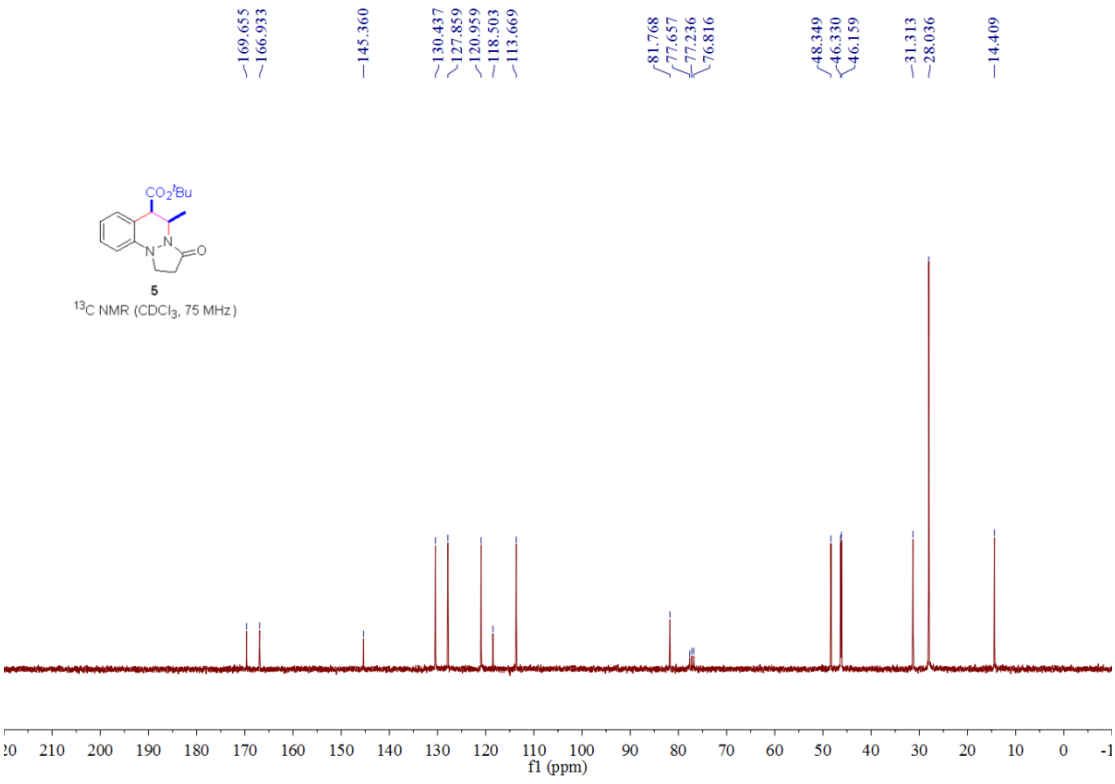

8.1196
8.0939
7.4002
7.3734
7.3500
7.3119
7.3003
7.2870
7.2737
7.1810
7.1554
7.1294
7.0135
6.9879
6.9624
6.5346
6.5081
3.9435
3.9286
3.8802
3.8652
3.6879
3.6592
3.6313
3.6033
3.5735
3.5440
3.5140
3.4200
3.4015
3.3839
3.3649
3.3466
3.3286
3.0156
2.9783
2.9524
2.9151
2.8446
2.8159
2.7906
2.7799
Ph
O
N
N
O
3al
1H NMR (CDCl3, 300 MHz)
0.97
5.10
1.04
1.02
0.99
1.00
2.01
1.00
1.04
4.00
f1 (ppm)

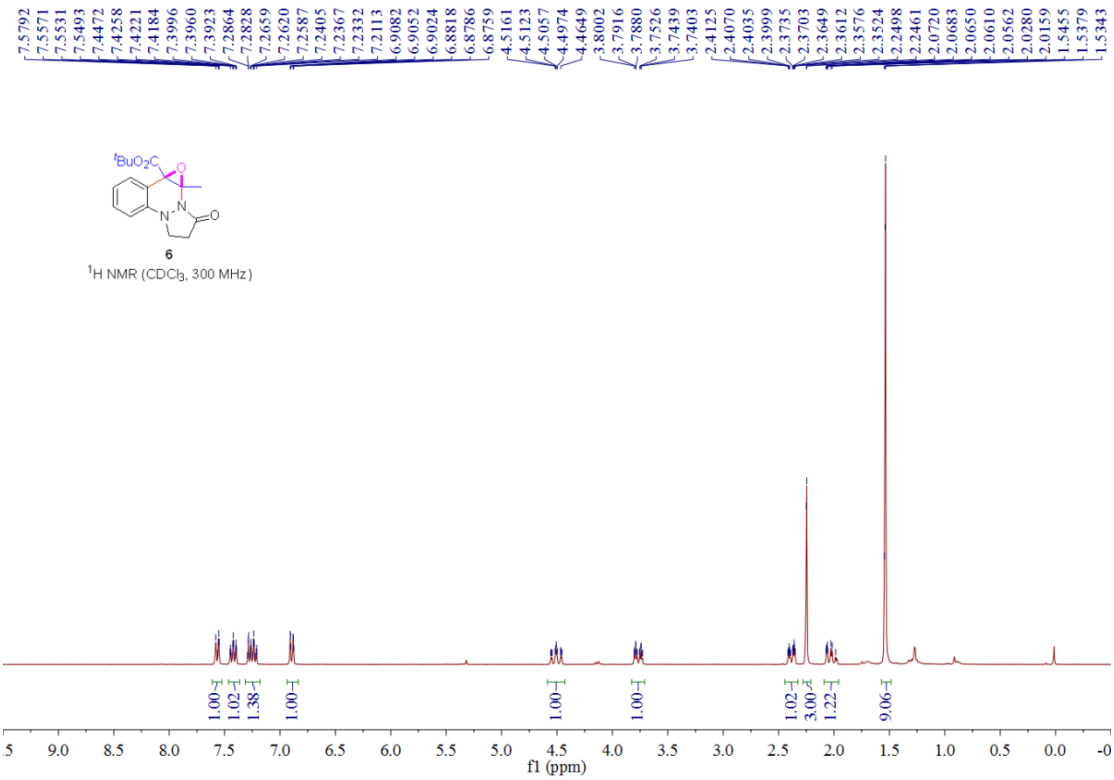

194.996
167.921
152.272
146.397
142.323
128.831
128.766
127.177
126.825
126.371
123.351
121.034
115.799
111.091
77.543
77.121
76.697
47.140
44.987
38.635
32.569
32.045
Ph
O
N
N
O
3al
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

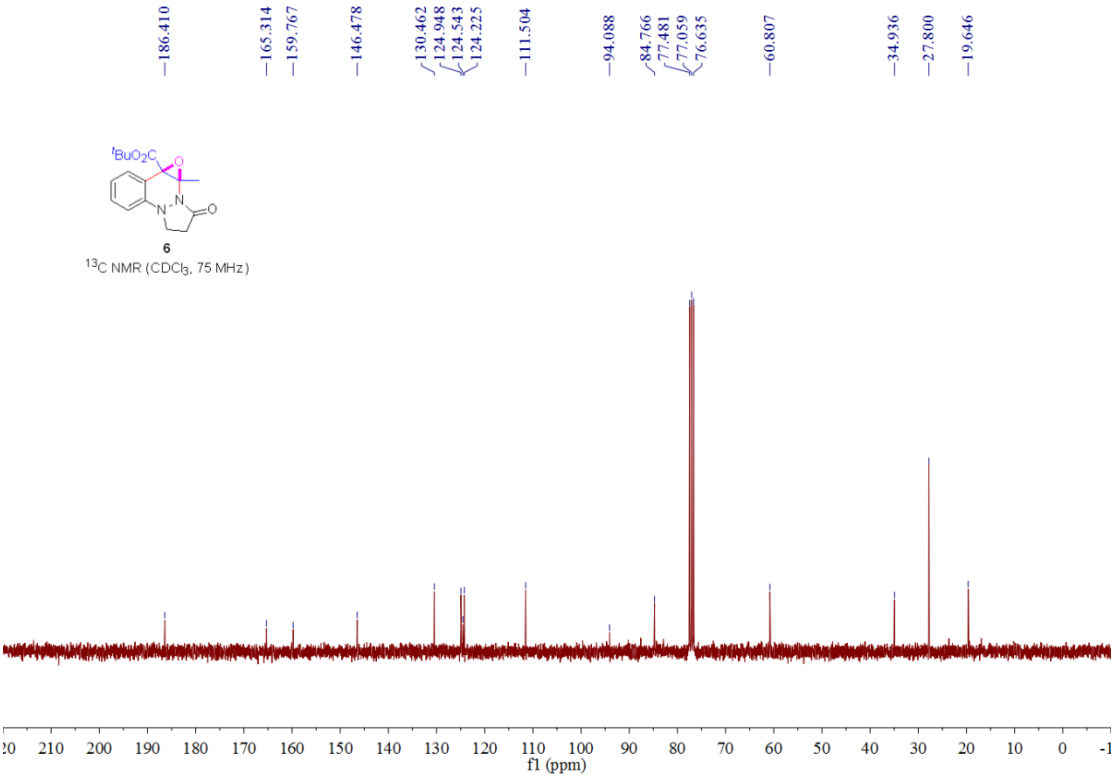

7.2734
7.2027
7.1978
7.1771
7.1720
7.1512
7.1461
7.0949
7.0901
7.0691
7.0642
6.9553
6.9516
6.9301
6.9263
6.9046
6.9010
6.6120
6.6084
6.5849
6.5815
3.8068
3.7776
3.7489
3.2952
3.2665
3.2374
2.6799
1.5910
CO2tBu
N
N
S
4
1H NMR (CDCl3, 300 MHz)
1.07
1.01
1.05
0.96
2.03
2.02
3.00
9.04
f1 (ppm)


165.169
146.468
136.685
129.504
125.593
124.506
122.730
121.245
110.766
83.093
77.527
77.102
76.679
47.713
45.024
28.199
17.983
CO2tBu
N
N
S
4
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.2556
7.2519
7.2307
7.2269
7.2222
7.2058
7.2022
7.1977
6.9669
6.9628
6.9416
6.9375
6.9165
6.9125
6.7719
6.7683
6.7628
6.7431
6.7382
4.9641
4.9425
4.9208
4.0995
4.0782
4.0735
4.0680
4.0518
4.0464
4.0420
4.0203
4.0159
3.9961
3.4557
3.4234
3.3914
3.3594
2.7411
2.7195
2.7157
2.7089
2.6879
2.6823
1.5255
1.2397
1.2172
CO2tBu
O
5
1H NMR (CDCl3, 300 MHz)
1.99
1.03
0.97
0.97
0.88
1.04
1.00
2.00
9.00
3.00
f1 (ppm)


169.655
166.933
145.360
130.437
127.859
120.959
118.503
113.669
81.768
77.657
77.236
76.816
48.349
46.330
46.159
31.313
28.036
14.409
CO2tBu
O
5
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.5792
7.5571
7.5531
7.5493
7.4472
7.4258
7.4221
7.4184
7.3996
7.3960
7.3923
7.2864
7.2828
7.2659
7.2620
7.2587
7.2405
7.2367
7.2332
7.2113
6.9082
6.9052
6.9024
6.8818
6.8786
6.8759
4.5161
4.5123
4.5057
4.4974
4.4649
3.8002
3.7916
3.7880
3.7526
3.7439
3.7403
2.4125
2.4070
2.4035
2.3999
2.3735
2.3703
2.3649
2.3612
2.3576
2.3524
2.2498
2.2461
2.0720
2.0683
2.0650
2.0610
2.0562
2.0280
2.0159
1.5455
1.5379
1.5343
tBuO2C
O
N
N
O
6
1H NMR (CDCl3, 300 MHz)
1.00
1.02
1.38
1.00
1.00
1.00
1.02
3.00
1.22
9.06
f1 (ppm)


186.410
165.314
159.767
146.478
130.462
124.948
124.543
124.225
111.504
94.088
84.766
77.481
77.059
76.635
60.807
34.936
27.800
19.646
tBuO2C
O
N
N
O
6
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

8. HMBC analysis

We determined the regioselectivity from HMBC analysis. We found that the 5-methyl group of the product was weakly related to the carbonyl group, but strongly related to the carbon atoms at 5- and 6-positions. It indicated that the product was **3aj** rather than **3aj'**. The results are shown as below: