Syntheses of highly functionalized cyclobutenes via [2+1+1] cycloadditions of isocyanides and an unprecedented ring expansion

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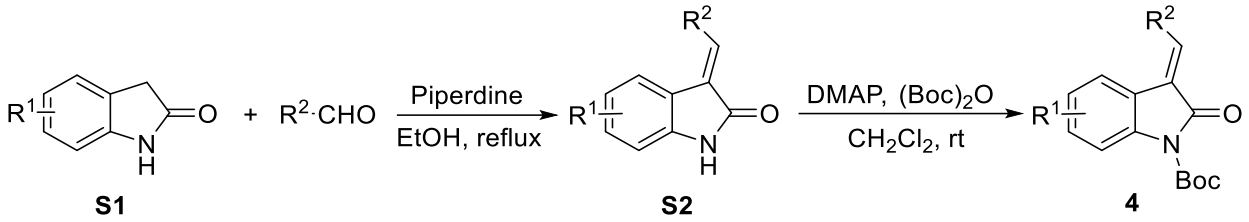
Contents

1. General information

Reactions were carried out using commercial reagents in over-dried apparatus. Et_2O was dried over powdered Na and distilled under nitrogen just before use. ^1H NMR spectra were recorded on commercial instruments (400 MHz and 600 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 ppm; DMSO-d_6, δ = 2.50 ppm). Spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR data were collected on commercial instruments (101 MHz and 151 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ= 77.0 ppm; DMSO-d_6, δ = 39.5 ppm). ^{19}F NMR data were collected on commercial instruments (376 MHz and 565 MHz) with complete proton decoupling. Melting points (m. p.) were measured on the electrothermal digital melting point apparatus. HRMS was recorded on a commercial apparatus (ESI Source). All isocyanides **1**[1] and alkylidene malonates **2**[2] were prepared according to the literature.

2. Preparing of 3-methyleneoxindoles 4.



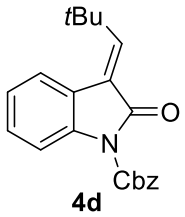
S1 S2 4

S1 to S2: The aldehyde (1.2 equiv.) was added to a solution of **S1** (1.0 equiv., 133 mg) in EtOH (5 mL), finally piperidine (10 mol%) was added. The reaction was refluxed for 24 h, then it was cooled to room temperature and the solvent was removed under reduced pressure. The product **S2** was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4/1).

S2 to 4: The **S2** was dissolved in CH_2Cl_2 (5 mL), and DMAP (5 mol%) was added. Then $(Boc)_2O$ (1.1 equiv.) was added. The reaction mixture was stirred at room temperature for 1 h. After the reaction was completed, the solvent was removed under reduced pressure and the product **4** was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30/1).

3-methyleneoxindoles **4a**,[3a] **4b**,[3b] **4c**,[3c] **4f**,[3d] and **4g**,[3a] are known compounds.

Benzyl (*E*)-3-(2,2-dimethylpropylidene)-2-oxoindoline-1-carboxylate 4d



4d

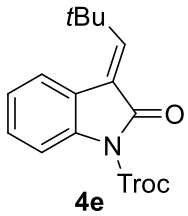
Yellow solid. R_f = 0.4 (PE:EA = 30:1), m.p. 89–91 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.73 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.16 (td, *J* = 7.7, 1.2 Hz, 1H), 5.43 (s, 2H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.6, 150.8, 139.6, 135.1, 129.0, 128.5, 128.2, 127.8, 126.0, 125.2, 123.9, 121.0, 115.1, 68.3, 32.7, 29.0.

HRMS (ESI–TOF) calcd for $C_{21}H_{22}NO_3^+$ ([M+H$^+$]) = 336.1594, Found 336.1597.

2,2,2-trichloroethyl (*E*)-3-(2,2-dimethylpropylidene)-2-oxoindoline-1-carboxylate 4e



4e

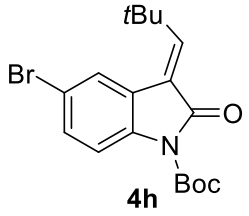
Yellow solid. R_f = 0.4 (PE:EA = 30:1), m.p. 77–78 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.23 (td, *J* = 7.9, 1.7 Hz, 1H), 5.03 (d, *J* = 2.2 Hz, 2H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 155.4, 149.4, 138.9, 129.2, 126.2, 124.9, 124.4, 121.3, 115.3, 94.2, 75.6, 32.8, 29.0.

HRMS (ESI–TOF) calcd for $C_{16}H_{17}Cl_3NO_3^+$ ([M+H$^+$]) = 376.0269, Found 376.0268.

Tert-butyl (*E*)-5-bromo-3-(2,2-dimethylpropylidene)-2-oxoindoline-1-carboxylate 4h



4h

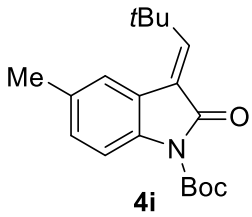
Yellow yield R_f = 0.4 (PE:EA = 30:1), m.p. 60–62 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.42 (dt, *J* = 8.8, 2.0 Hz, 1H), 7.27 (d, *J* = 1.8 Hz, 1H), 1.62 (s, 9H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 156.1, 149.2, 139.0, 131.6, 128.7, 124.6, 122.9, 116.7, 116.6, 84.4, 33.0, 29.2, 28.1.

HRMS (ESI–TOF) calcd for $C_{18}H_{22}BrNNaO_3^+$ ([M+Na$^+$]) = 402.0675, Found 402.0671.

Tert-butyl (*E*)-3-(2,2-dimethylpropylidene)-5-methyl-2-oxoindoline-1 carboxylate 4i



4i

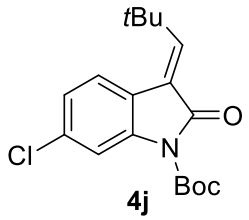
Yellow solid. R_f = 0.4 (PE:EA = 30:1), m.p. 62–64 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.20 (s, 1H), 7.11 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.37 (s, 3H), 1.62 (s, 9H), 1.38 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 153.9, 149.4, 137.8, 133.0, 129.5, 126.6, 125.6, 120.9, 114.7, 83.8, 32.7, 29.1, 28.1, 21.3.

HRMS (ESI–TOF) calcd for $C_{19}H_{25}NNaO_3^+$ ([M+Na$^+$]) = 338.1727, Found 338.1722.

Tert-butyl (*E*)-6-chloro-3-(2,2-dimethylpropylidene)-2-oxoindoline-1-carboxylate 4j



4j

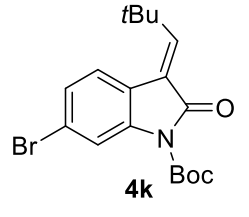
Yellow solid. R_f = 0.4 (PE:EA = 30:1), m.p. 105–107 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.23 (s, 1H), 7.13 (dt, *J* = 8.3, 2.1 Hz, 1H), 1.63 (s, 9H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.8, 149.1, 140.9, 135.0, 126.6, 124.7, 123.7, 119.4, 115.7, 84.5, 32.8, 29.1, 28.0.

HRMS (ESI–TOF) calcd for $C_{18}H_{22}ClNNaO_3^+$ ([M+Na$^+$]) = 358.1180, Found 358.1178.

Tert-butyl (*E*)-6-bromo-3-(2,2-dimethylpropylidene)-2-oxoindoline-1-carboxylate 4k



4k

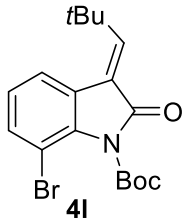
Yellow solid. R_f = 0.4 (PE:EA = 30:1), m.p. 128–129 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.33 (dt, *J* = 8.3, 1.3 Hz, 1H), 7.28 (s, 1H), 1.66 (s, 9H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 155.1, 149.1, 141.0, 126.9, 126.7, 124.8, 123.1, 119.9, 118.5, 84.5, 32.9, 29.1, 28.1.

HRMS (ESI–TOF) calcd for $C_{18}H_{22}BrNNaO_3^+$ ([M+Na$^+$]) = 402.0675, Found 402.0673.

Tert-butyl (*E*)-7-bromo-3-(2,2-dimethylpropylidene)-2-oxoindoline-1-carboxylate 4l



4l

Yellow solid. R_f = 0.4 (PE:EA = 30:1), m.p. 51–52 ℃.

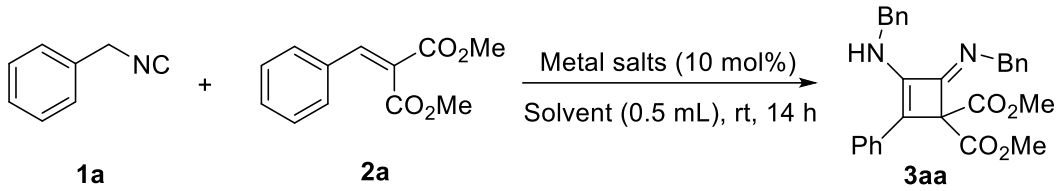
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.25 (s, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 1.64 (s, 9H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 156.0, 148.3, 139.1, 133.6, 125.4, 125.1, 124.5, 124.2, 106.9, 85.2, 32.9, 29.1, 27.7.

HRMS (ESI–TOF) calcd for $C_{18}H_{23}BrNO_3^+$ ([M+H$^+$]) = 380.0856, Found 380.0854.

3. Optimization of reaction conditions

Table 1. Screening of reaction conditions for cycloaddition between isocyanide and alkylidene malonate

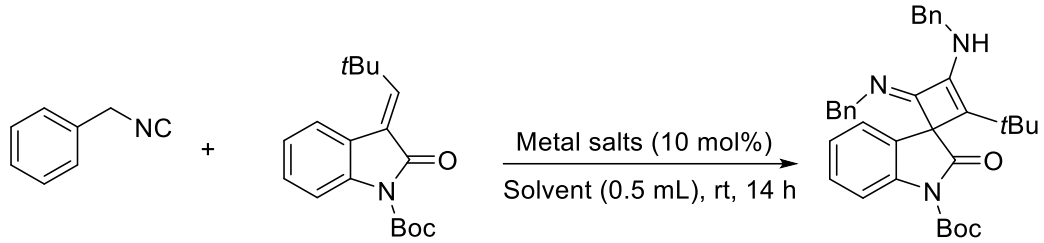


1a **2a** **3aa**

Entry[a]	Metal salts	Solvent	**1a**:**2a**	Yield (%)[b] **3aa**
1	–	EtOAc	2:1	0
2	$La(OTf)_3$	EtOAc	2:1	74
3	$Yb(OTf)_3$	EtOAc	2:1	44
4	$Mg(OTf)_2$	EtOAc	2:1	42
5	$Fe(OTf)_3$	EtOAc	2:1	0
6	$Ni(OTf)_2$	EtOAc	2:1	0
7	$Cu(OTf)_2$	EtOAc	2:1	0
8	$Zn(OTf)_2$	EtOAc	2:1	19
9	AgOTf	EtOAc	2:1	0
10	$Al(OTf)_3$	EtOAc	2:1	0
11	$In(OTf)_3$	EtOAc	2:1	20
12	$Y(OTf)_3$	EtOAc	2:1	82
13	$Y(OTf)_3$	$CHCl_3$	2:1	63
14	$Y(OTf)_3$	$ClCH_2CH_2Cl$	2:1	76
15	$Y(OTf)_3$	THF	2:1	67
16	$Y(OTf)_3$	Toluene	2:1	0
17	$Y(OTf)_3$	CH_2Cl_2	2:1	77
18	$Y(OTf)_3$	1,4-Dioxane	2:1	14
19	$Y(OTf)_3$	CH_3CN	2:1	7
20	$Y(OTf)_3$	Et_2O	2:1	88
21	$Y(OTf)_3$	Et_2O	3:1	72
22	$Y(OTf)_3$	Et_2O	4:1	51
23	$Y(OTf)_3$	Et_2O	3:2	82

[a]Unless otherwise noted, the reactions were performed with metal salts (10 mol%), **1a** (0.2 mmol) and **2a** (0.10 mmol) in indicated solvent (0.5 mL) at rt for 14 h. [b]The yield of isolated product for **3aa**.

Table 2. Screening of reaction conditions for cycloaddition between isocyanide and 3-methyleneoxindole



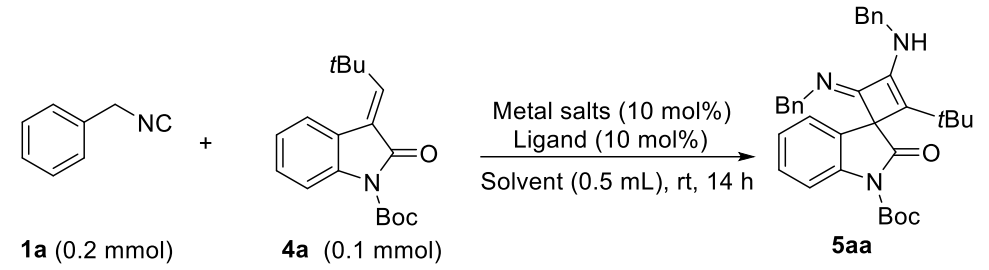
1a (0.2 mmol) **4a** (0.2 mmol) **5aa**

Entry[a]	Catalyst	Solvent	Yield (%)[b] **5aa**
1	-	Et_2O	N.D.
2	$Cu(OTf)_2$	Et_2O	N.D.
3	$Sc(OTf)_3$	Et_2O	40
4	$La(OTf)_3$	Et_2O	83
5	$Zn(OTf)_2$	Et_2O	17
6	$Mg(OTf)_2$	Et_2O	49
7	$Y(OTf)_3$	Et_2O	71
8	$Yb(OTf)_3$	Et_2O	62
9	$Bi(OTf)_3$	Et_2O	N.D.
10	$Fe(OTf)_3$	Et_2O	N.D.
11	$Pr(OTf)_3$	Et_2O	67
12	$Ni(OTf)_2$	Et_2O	N.D.
13	$Tm(OTf)_3$	Et_2O	21
14	$Gd(OTf)_3$	Et_2O	48
15	$Tb(OTf)_3$	Et_2O	49
16	$La(OTf)_3$	$CHCl_3$	65
17	$La(OTf)_3$	Toluene	69
18	$La(OTf)_3$	THF	52
19	$La(OTf)_3$	EtOAc	49
20	$La(OTf)_3$	CH_3CN	45
21	$La(OTf)_3$	1,4-Dioxane	51
22	$La(OTf)_3$	CH_2Cl_2	62
23	$La(OTf)_3$	$ClCH_2CH_2Cl$	62

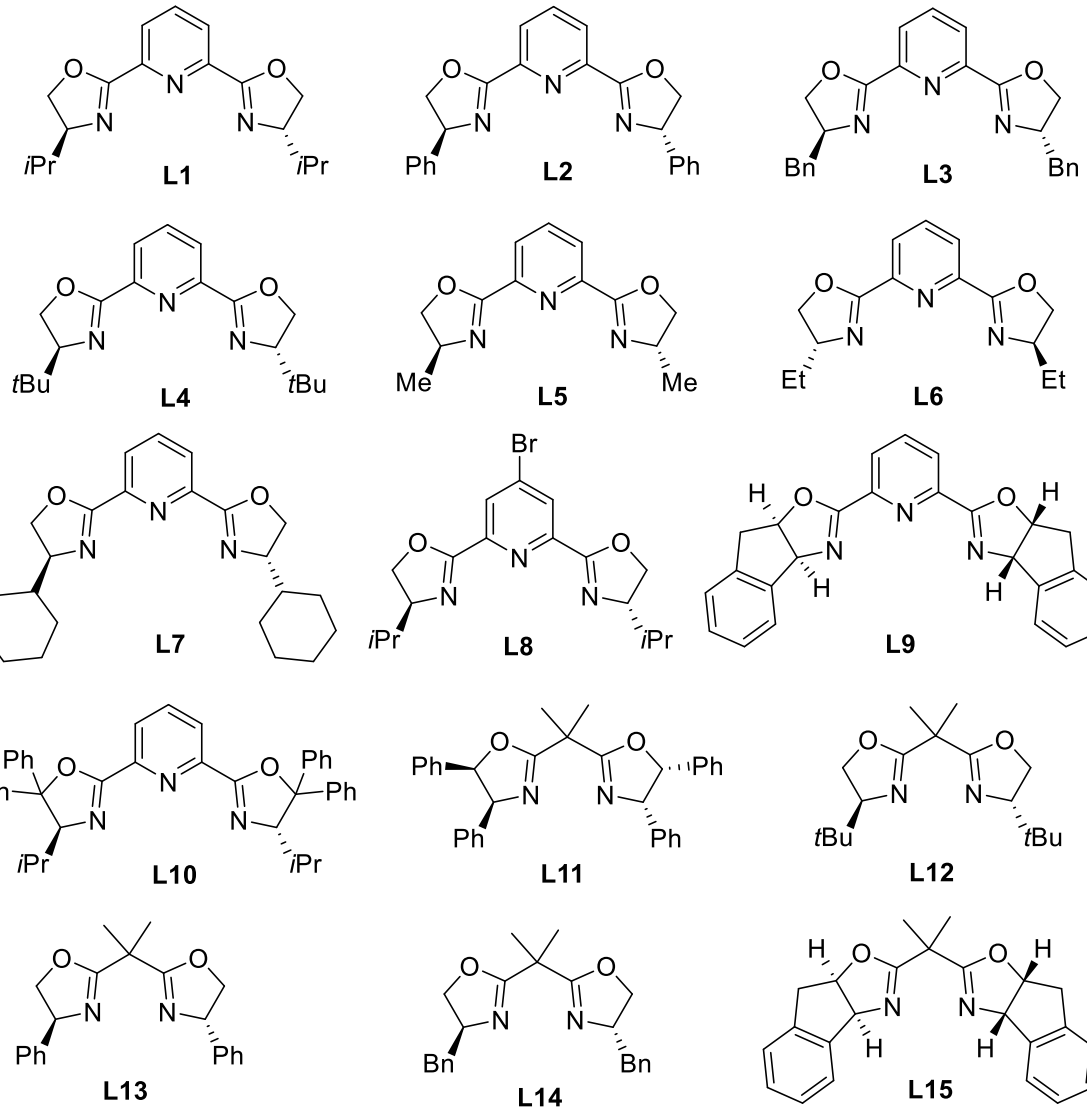
[a]Unless otherwise noted, the reactions were performed with metal salts (10 mol%), **1a** (0.2 mmol) and **4a** (0.10 mmol) in indicated solvent (0.5 mL) at rt for 14 h. [b]The yield of isolated product for **5aa**.

4. Catalytic enantioselective variant

Table 3. Screening of reaction conditions for catalytic enantioselective cycloaddition between isocyanide and 3- methyleneoxindole



1a (0.2 mmol) **4a** (0.1 mmol) **5aa**



Entry[a]	Metal salts	Ligand	Solvents	Yield (%)[b] **5aa**	*ee*[c] **(5aa)**
1	$Y(OTf)_3$	**L1**	Et_2O	65	51
2	$Pr(OTf)_3$	**L1**	Et_2O	60	17
3	$La(OTf)_3$	**L1**	Et_2O	64	23
4	$Yb(OTf)_3$	**L1**	Et_2O	65	68
5	$Gd(OTf)_3$	**L1**	Et_2O	49	45

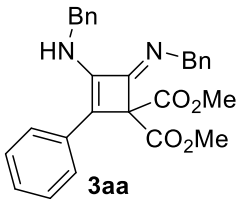
6	$Yb(OTf)_3$	**L2**	Et_2O	59	30
7	$Yb(OTf)_3$	**L3**	Et_2O	65	19
8	$Yb(OTf)_3$	**L4**	Et_2O	58	20
9	$Yb(OTf)_3$	**L5**	Et_2O	71	14
10	$Yb(OTf)_3$	**L6**	Et_2O	81	36
11	$Yb(OTf)_3$	**L7**	Et_2O	60	45
12	$Yb(OTf)_3$	**L8**	Et_2O	68	30
13	$Yb(OTf)_3$	**L9**	Et_2O	66	15
14	$Yb(OTf)_3$	**L10**	Et_2O	62	0
15	$Yb(OTf)_3$	**L11**	Et_2O	71	0
16	$Yb(OTf)_3$	**L12**	Et_2O	61	0
17	$Yb(OTf)_3$	**L13**	Et_2O	70	0
18	$Yb(OTf)_3$	**L14**	Et_2O	64	0
19	$Yb(OTf)_3$	**L15**	Et_2O	66	0
20	$Yb(OTf)_3$	**L1**	Toluene	70	43
21	$Yb(OTf)_3$	**L1**	THF	50	55
22	$Yb(OTf)_3$	**L1**	EtOAc	47	60
23	$Yb(OTf)_3$	**L1**	CH_3CN	38	20
24	$Yb(OTf)_3$	**L1**	1,4-Dioxane	44	51
25	$Yb(OTf)_3$	**L1**	CH_2Cl_2	50	45
26	$Yb(OTf)_3$	**L1**	$CHCl_3$	61	46
27	$Yb(OTf)_3$	**L1**	$ClCH_2CH_2Cl$	51	39
28[d]	$Yb(OTf)_3$	**L1**	Et_2O	63	56
29[e]	$Yb(OTf)_3$	**L1**	Et_2O	60	61
30[f]	$Yb(OTf)_3$	**L1**	Et_2O	59	57
31[g]	$Yb(OTf)_3$	**L1**	Et_2O	59	65
32[h]	$Yb(OTf)_3$	**L1**	Et_2O	58	74
33[i]	$Yb(OTf)_3$	**L1**	Et_2O	54	72
34[j]	$Yb(OTf)_3$	**L1**	Et_2O	61	66
35[k]	$Yb(OTf)_3$	**L1**	Et_2O	59	61

[a]Unless otherwise noted, the reactions were performed with metal salts (10 mol%), Ligand (10 mol%), **4a** (0.10 mmol) and **1a** (0.20 mmol) in Et_2O (0.5 mL) at rt for 14 h. [b]The yield of isolated product for the **5aa**. [c]*ee* (**5aa**) determined by chiral HPLC analysis. [d]at 0 ℃. [e]at -5 ℃. [f]at -10 ℃. [g]at -20 ℃. [h] with $Yb(OTf)_3$ (20 mol%) and **L1** (10 mol%). [i] with $Yb(OTf)_3$ (15 mol%) and **L1** (10 mol%). [j] with $Yb(OTf)_3$ (10 mol%) and **L1** (15 mol%). [k] with $Yb(OTf)_3$ (10 mol%) and **L1** (20 mol%).

5. General procedure and spectral data of products 3

A dry reaction tube was charged with isocyanides **1** (0.2 mmol, 2 equiv.), $Y(OTf)_3$ (10 mol%) and alkylidene malonates **2** (0.1 mmol, 1 equiv.), Et_2O (0.5 mL) was added. The reaction mixture continued stirring at rt for 14 h. The residue was directly purified by flash chromatography on silica gel using petroleum ether/ethyl acetate= 10/1 as eluent to afford the desired products **3**.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3aa



3aa

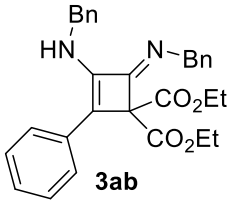
The reaction was run at rt for 14 h, affording product **3aa** in 88% yield (39.8 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 113–114 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 3H), 7.35 – 7.31 (m, 5H), 7.31 – 7.30 (m, 2H), 7.29 – 7.25 (m, 3H), 7.24 – 7.18 (m, 2H), 4.88 (d, *J* = 6.3 Hz, 2H), 4.80 (s, 2H), 4.60 (t, *J* = 6.4 Hz, 1H), 3.70 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 150.8, 145.7, 139.7, 139.6, 132.5, 128.6, 128.6 128.2, 127.6, 127.4, 127.4, 126.8, 126.5, 126.2, 118.8, 68.7, 55.7, 52.7, 48.8.

HRMS (ESI–TOF) calcd for $C_{28}H_{27}N_2O_4^+$ ([M+H$^+$]) = 455.1966, Found 455.1962.

Diethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ab



3ab

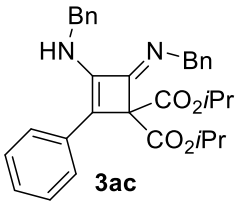
The reaction was run at rt for 14 h, affording product **3ab** in 80% yield (38.4 mg) as a yellow solid. R_f = 0.3 (PE:EA = 4:1), m.p. 80–81 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.35 – 7.33 (m, 3H), 7.33 – 7.30 (m, 3H), 7.30 – 7.26 (m, 5H), 7.24 – 7.16 (m, 2H), 4.88 (d, *J* = 6.4 Hz, 2H), 4.82 (s, 2H), 4.60 (t, *J* = 6.4 Hz, 1H), 4.18 (m, 4H), 1.15 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 151.1, 145.6, 139.8, 139.8, 132.6, 128.6, 128.4, 128.2, 127.6, 127.4, 127.4, 126.7, 126.5, 126.4, 119.1, 69.3, 61.7, 55.7, 48.7, 13.9.

HRMS (ESI-TOF) calcd for $C_{30}H_{31}N_2O_4^+$ ([M+H$^+$]) = 483.2279, Found 483.2278.

Diisopropyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ac



3ac

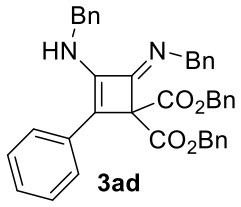
The reaction was run at rt for 14 h, affording product **3ac** in 73% yield (37.2 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 142–144 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.34 – 7.29 (m, 4H), 7.29 – 7.26 (m, 5H), 7.26 – 7.13 (m, 2H), 5.14 – 5.01 (m, 2H), 4.86 (d, *J* = 6.4 Hz, 2H), 4.81 (s, 2H), 4.59 (t, *J* = 6.4 Hz, 1H), 1.15 (d, *J* = 6.3 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 151.3, 145.6, 140.0, 139.9, 132.7, 128.6, 128.3, 128.2, 127.5, 127.4, 127.3, 126.7, 126.6, 126.4, 119.4, 69.8, 69.3, 55.8, 48.7, 21.5, 21.4.

HRMS (ESI–TOF) calcd for $C_{32}H_{35}N_2O_4^+$ ([M+H$^+$]) = 511.2592, Found 511.2590.

Dibenzyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ad



3ad

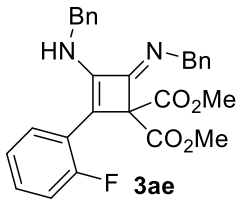
The reaction was run at rt for 14 h, affording product **3ad** in 71% yield (42.8 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 130–132 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 3H), 7.30 – 7.26 (m, 6H), 7.26 – 7.22 (m, 6H), 7.22 – 7.16 (m, 4H), 7.14 (s, 3H), 7.13 (s, 3H), 5.14 (q, *J* =12.4 Hz, 4H), 4.84 (d, *J* = 6.3 Hz, 2H), 4.64 (s, 2H), 4.60 (t, *J* = 6.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 150.5, 145.7, 139.7, 139.6, 135.2, 132.5, 128.6, 128.5, 128.4, 128.2, 128.1, 128.1, 127.5, 127.4, 127.3, 126.8, 126.4, 126.4, 118.7, 69.4, 67.4, 55.7, 48.7.

HRMS (ESI–TOF) calcd for $C_{40}H_{35}N_2O_4^+$ ([M+H$^+$]) = 607.2592, Found 607.2589.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(2-fluorophenyl)cyclobut-2-ene-1,1-dicarboxylate 3ae



3ae

The reaction was run at rt for 14 h, affording product **3ae** in 70% yield (33.3 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 110–112 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dt, *J* = 13.1, 7.4 Hz, 5H), 7.31 – 7.26 (m, 4H), 7.25 (s, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.02 (dd, *J* = 12.6, 8.4 Hz, 1H), 5.10 (dt, *J* = 10.3, 6.5 Hz, 1H), 4.94 (d, *J* = 6.4 Hz, 2H), 4.79 (s, 2H), 3.69 (s, 6H).

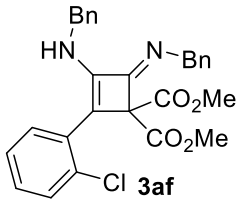
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 159.0 (*J* = 163.6 Hz), 150.8, 146.4, 139.9, 139.6, 128.6, 128.2, 128.1 (*J* = 5.1 Hz), 127.8 (*J* = 4.0 Hz), 127.4, 127.4, 127.2, 126.5, 124.5 (*J* = 2.0 Hz),120.4 (*J* = 11.1 Hz), 115.5 (*J* = 16.2 Hz), 111.7, 68.2, 55.7, 52.7, 48.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ −110.75.

HRMS (ESI–TOF) calcd for $C_{28}H_{26}FN_2O_4^+$ ([M+H$^+$]) = 473.1872, Found 473.1871.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(2-chlorophenyl)cyclobut-2-ene-1,1-dicarboxylate 3af

The reaction was run at rt for 14 h, affording product **3af** in 62% yield (30.1 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 100–102 ℃.



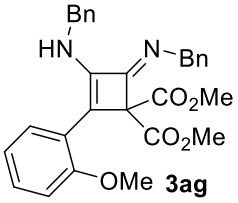
3af

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 1H), 7.34 – 7.30 (m, 4H), 7.30 – 7.26 (m, 3H), 7.25 – 7.22 (m, 4H), 7.21 – 7.17 (m, 2H), 4.79 (s, 2H), 4.74 (t, *J* = 6.2 Hz, 1H), 4.53 (d, *J* = 6.2 Hz, 2H), 3.70 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.8, 147.3, 139.5, 139.0, 132.9, 131.9, 130.0, 129.7, 128.8, 128.5, 128.3, 127.6, 127.5, 127.3, 126.7, 126.5, 114.7, 70.3, 55.7, 52.7, 47.9.

HRMS (ESI–TOF) calcd for $C_{28}H_{26}ClN_2O_4^+$ ([M+H$^+$]) = 489.1576, Found 489.1574.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(2-methoxyphenyl)cyclobut-2-ene-1,1-dicarboxylate 3ag



3ag

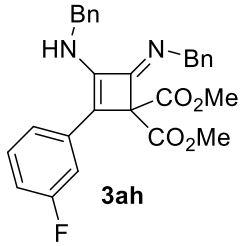
The reaction was run at rt for 14 h, affording product **3ag** in 66% yield (33.8 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 95–96 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.31 – 7.26 (m, 5H), 7.23 – 7.19 (m, 2H), 7.19 – 7.14 (m, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 5.44 (t, *J* = 6.4 Hz, 1H), 4.93 (d, *J* = 6.4 Hz, 2H), 4.78 (s, 2H), 3.75 (s, 3H), 3.67 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 155.6, 151.2, 146.0, 140.6, 139.9, 128.5, 128.1, 128.1, 127.8, 127.3, 127.1, 126.4, 122.3, 121.3, 115.2, 111.3, 68.2, 55.6, 55.6, 52.6, 48.3.

HRMS (ESI–TOF) calcd for $C_{29}H_{29}N_2O_5^+$ ([M+H$^+$]) = 485.2071, Found 485.2068.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(3-fluorophenyl)cyclobut-2-ene-1,1-dicarboxylate 3ah



3ah

The reaction was run at rt for 14 h, affording product **3ah** in 80% yield (37.9 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 130–131 ℃.

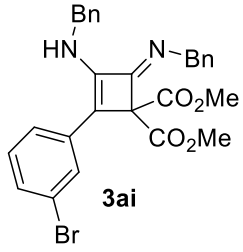
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 5H), 7.30 – 7.26 (m, 4H), 7.25 – 7.21 (m, 1H), 7.08 (d, *J* = 7.91 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.89 (td, *J* = 8.4, 2.5 Hz, 1H), 4.88 (d, *J* = 6.2 Hz, 2H), 4.82 (s, 2H), 4.68 (t, *J* = 6.1 Hz, 1H), 3.72 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 162.8 (*J* = 246.6 Hz),150.6, 146.3, 139.5, 139.3, 134.6 (*J* = 8.2 Hz), 130.1 (*J* = 8.7 Hz), 128.6, 128.2, 127.6, 127.5, 127.4, 126.6, 121.9 (*J* = 2.8 Hz), 117.1 (*J* = 2.9 Hz), 113.6 (*J* = 21.5 Hz), 112.7 (*J* = 22.7 Hz), 68.9, 55.7, 52.7, 48.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ –112.38.

HRMS (ESI-TOF) calcd for $C_{28}H_{26}FN_2O_4^+$ ([M+H$^+$]) = 473.1832, Found 473.1872.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(3-bromophenyl)cyclobut-2-ene-1,1-dicarbox ylate 3ai



3ai

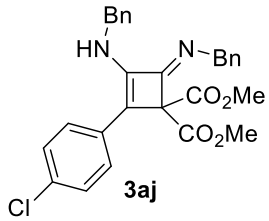
The reaction was run at rt for 14 h, affording product **3ai** in 71% yield (37.8 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 127–128 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 1.7 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.33 – 7.28 (m, 4H), 7.28 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 7.22 – 7.16 (m, 2H), 4.87 (d, *J* = 6.3 Hz, 2H), 4.80 (s, 2H), 4.66 (t, *J* = 6.4 Hz, 1H), 3.71 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 150.5, 146.4, 139.5, 139.3, 134.6, 130.1, 129.5, 128.8, 128.7, 128.2, 127.6, 127.5, 127.4, 126.6, 124.7, 122.7, 116.6, 68.9, 55.7, 52.8, 48.8.

HRMS (ESI–TOF) calcd for $C_{28}H_{26}BrN_2O_4^+$ ([M+H$^+$]) = 533.1071, Found 533.1072.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(4-chlorophenyl)cyclobut-2-ene-1,1-dicarbox ylate 3aj



3aj

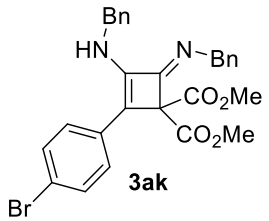
The reaction was run at rt for 14 h, affording product **3aj** in 65% yield (31.8 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 150–151 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 4H), 7.33 – 7.29 (m, 3H), 7.29–7.26 (m, 4H), 7.25 (s, 2H), 7.22 (s, 1H), 4.86 (d, *J* = 6.3 Hz, 2H), 4.79 (s, 2H), 4.57 (t, *J* = 5.2, 6.2 Hz, 1H), 3.70 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 150.5, 145.9, 139.6, 139.4, 132.3, 131.0, 128.8, 128.7, 128.2, 127.6, 127.5, 127.4, 127.4, 126.6, 117.5, 68.9, 55.7, 52.7, 48.8.

HRMS (ESI–TOF) calcd for $C_{28}H_{26}ClN_2O_4^+$ ([M+H$^+$]) = 489.1576, Found 489.1578.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(4-bromophenyl)cyclobut-2-ene-1,1-dicarbox ylate 3ak



3ak

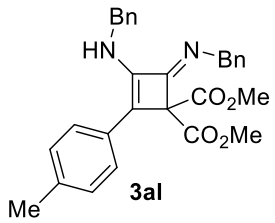
The reaction was run at rt for 14 h, affording product **3ak** in 71% yield (37.9 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 150–151 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.38 – 7.33 (m, 4H), 7.33 – 7.26 (m, 5H), 7.25 – 7.19 (m, 1H), 7.17 (dt, *J* = 8.6, 2.4 Hz, 2H), 4.86 (d, *J* = 6.3 Hz, 2H), 4.79 (s, 2H), 4.57 (t, *J* = 6.3 Hz, 1H), 3.70 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 150.5, 146.0, 139.5, 139.3, 131.7, 131.4, 128.7, 128.2, 127.6, 127.5, 127.4, 126.6, 120.5, 117.4, 68.8, 55.7, 52.8, 48.8.

HRMS (ESI–TOF) calcd for $C_{28}H_{26}BrN_2O_4^+$ ([M+H$^+$]) = 533.1071, Found 533.1066.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(p-tolyl)cyclobut-2-ene-1,1-dicarboxylate 3al



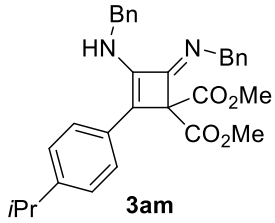
The reaction was run at rt for 14 h, affording product **3al** in 72% yield (33.6 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 144–145 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 3H), 7.34 – 7.29 (m, 3H), 7.29 – 7.26 (m, 3H), 7.26 – 7.18 (m, 3H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.86 (d, *J* = 6.3 Hz, 2H), 4.78 (s, 2H), 4.51 (t, *J* = 6.4 Hz, 1H), 3.69 (s, 6H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 150.9, 145.1, 139.8, 139.8, 136.9, 129.7, 129.4, 128.6, 128.2, 127.6, 127.4, 127.4, 126.5, 126.2, 119.3, 68.7, 55.6, 52.6, 48.8, 21.3.

HRMS (ESI–TOF) calcd for $C_{28}H_{26}BrN_2O_4^+$ ([M+H$^+$]) = 469.2122, Found 469.2118.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(4-isopropylphenyl)cyclobut-2-ene-1,1-dicarboxylate 3am



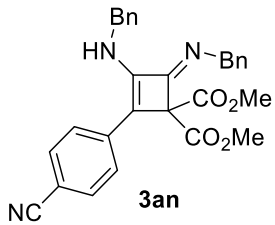
The reaction was run at rt for 14 h, affording product **3am** in 70% yield (34.6 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 136–138 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.35 (m, 3H), 7.35 – 7.30 (m, 3H), 7.30-7.26 (m, 4H), 7.26 – 7.16 (m, 4H), 4.88 (d, *J* = 6.3 Hz, 2H), 4.80 (s, 2H), 4.57 (t, *J* = 6.4 Hz, 1H), 3.70 (s, 6H), 2.99 – 2.80 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 150.9, 147.8, 145.1, 139.8, 130.0, 128.6, 128.2, 128.2, 127.6, 127.4, 127.4, 126.7, 126.5, 126.2, 119.3, 68.7, 55.6, 52.6, 48.8, 33.9, 23.8.

HRMS (ESI–TOF) calcd for $C_{29}H_{26}N_3O_4^+$ ([M+H$^+$]) = 497.2435, Found 497.2427.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(4-cyanophenyl)cyclobut-2-ene-1,1-dicarboxylate 3an



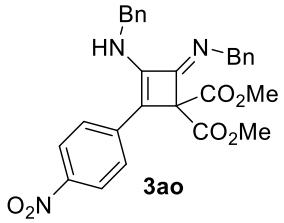
The reaction was run at rt for 14 h, affording product **3an** in 80% yield (38.3 mg) as a yellow solid. R_f = 0.3 (PE:EA = 4:1), m.p. 157–159 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.35 (t, *J* = 4.3 Hz, 5H), 7.34 – 7.29 (m, 4H), 7.27 (s, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 4.92 (d, *J* = 6.2 Hz, 2H), 4.82 (s, 3H), 3.71 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 150.3, 147.7, 139.2, 138.8, 137.0, 132.3, 128.8, 128.3, 127.7, 127.6, 127.4, 126.7, 126.1, 119.0, 115.6, 109.0, 68.8, 55.9, 52.9, 48.9.

HRMS (ESI–TOF) calcd for $C_{29}H_{26}N_3O_4^+$ ([M+H$^+$]) = 480.1918, Found 480.1917.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(4-nitrophenyl)cyclobut-2-ene-1,1-dicarbox ylate 3ao



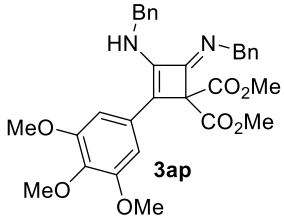
The reaction was run at rt for 14 h, affording product **3ao** in 86% yield (43.1 mg) as a yellow solid. R_f = 0.3 (PE:EA = 4:1), m.p. 140–142 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)) δ 8.19 – 8.13 (m, 2H), 7.42 – 7.34 (m, 6H), 7.34 – 7.26 (m, 5H), 7.26 – 7.20 (m, 1H), 4.99 – 4.90 (m, 3H), 4.84 (s, 2H), 3.72 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 150.3, 148.2, 145.1, 139.1, 139.0, 138.7, 128.8, 128.3, 127.8, 127.7, 127.4, 126.8, 126.0, 124.1, 115.2, 68.9, 56.0, 52.9, 49.0.

HRMS (ESI–TOF) calcd for $C_{28}H_{26}N_3O_6^+$ ([M+H$^+$]) = 500.1817, Found 500.1812.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(3,4,5-trimethoxyphenyl)cyclobut-2-ene-1,1-dicarboxylate 3ap



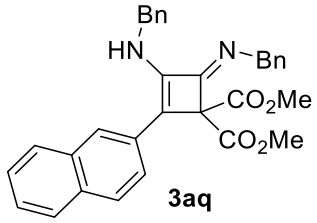
The reaction was run at rt for 14 h, affording product **3ap** in 86% yield (45.2 mg) as a yellow solid. R_f = 0.3 (PE:EA = 4:1), m.p. 100–101 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 5H), 7.30 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 6.61 (s, 2H), 4.83 (d, *J* = 6.5 Hz, 2H), 4.78 (s, 2H), 4.63 (t, *J* = 6.6 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 6H), 3.71 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 153.2, 150.5, 145.3, 139.5, 139.5, 137.5, 128.5, 128.1, 128.0, 127.3, 127.3, 127.1, 126.5, 119.3, 104.1, 69.0, 60.8, 56.0, 55.5, 52.6, 48.5.

HRMS (ESI–TOF) calcd for $C_{31}H_{33}N_2O_7^+$ ([M+H$^+$]) = 545.2283, Found 545.2282.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(naphthalen-2-yl)cyclobut-2-ene-1,1-dicarbo xylate 3aq



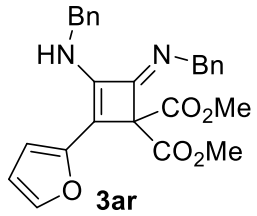
The reaction was run at rt for 14 h, affording product **3aq** in 90% yield (45.6 mg) as a yellow solid. R_f = 0.3 (PE:EA = 4:1), m.p. 88–90 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 4H), 7.52 – 7.44 (m, 3H), 7.44 – 7.41 (m, 2H), 7.40 – 7.35 (m, 2H), 7.35 – 7.30 (m, 5H), 7.28 – 7.24 (m, 1H), 4.95 (d, *J* = 6.0 Hz, 2H), 4.87 (s, 2H), 4.83 (t, *J* = 6.0 Hz, 1H), 3.73 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$)) δ 169.6, 150.8, 145.9, 139.6, 139.6, 133.4, 132.0, 130.0, 128.6, 128.2, 128.2, 128.0, 127.6, 127.6, 127.4, 126.5, 126.4, 126.0, 125.1, 124.1, 118.8, 68.8, 55.7, 52.7, 48.8.

HRMS (ESI–TOF) calcd for $C_{32}H_{29}N_2O_4^+$ ([M+H$^+$]) =505.2122, Found 505.2121.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(furan-2-yl)cyclobut-2-ene-1,1-dicarboxylate 3ar



3ar

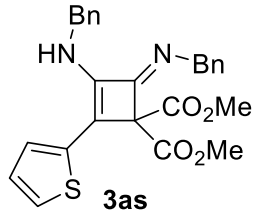
The reaction was run at rt for 14 h, affording product **3ar** in 60% yield (26.6 mg) as a green solid. R_f = 0.3 (PE:EA = 4:1), m.p. 116–118 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.29 (s, 1H), 7.26 (d, *J* = 6.9 Hz, 4H), 7.20 (t, *J* = 7.1 Hz, 1H), 6.41 (d, *J* = 1.7 Hz, 1H), 6.33 (d, *J* = 3.4 Hz, 1H), 4.92 (t, *J* = 6.5 Hz, 1H), 4.83 (d, *J* = 6.4 Hz, 2H), 4.78 (s, 2H), 3.70 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 150.2, 148.4, 143.3, 142.5, 139.7, 139.5, 128.6, 128.2, 127.7, 127.5, 127.4, 126.6, 111.8, 108.5, 107.8, 67.8, 55.7, 52.7, 48.6.

HRMS (ESI–TOF) calcd for $C_{26}H_{25}N_2O_5^+$ ([M+H$^+$]) = 445.1758, Found 445.1757.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-(thiophen-2-yl)cyclobut-2-ene-1,1-dicarboxylate 3as



3as

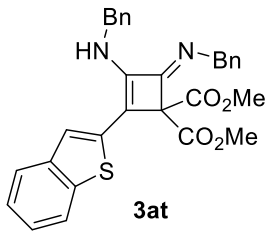
The reaction was run at rt for 14 h, affording product **3as** in 60% yield (27.6 mg) as a red solid. R_f = 0.3 (PE:EA = 4:1), m.p. 107–109 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.31 – 7.26 (m, 6H), 7.24 – 7.20 (m, 1H), 7.07 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 4.8, 3.6 Hz, 1H), 4.89 (d, *J* = 6.4 Hz, 2H), 4.80 (s, 2H), 4.44 (t, *J* = 6.4 Hz, 1H), 3.71 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 150.3, 143.7, 139.7, 139.5, 134.6, 128.6, 128.2, 127.7, 127.5, 127.4, 127.4, 126.5, 124.9, 124.6, 113.5, 69.2, 55.7, 52.7, 48.7.

HRMS (ESI–TOF) calcd for $C_{26}H_{25}N_2O_4S^+$ ([M+H$^+$]) = 461.1530, Found 461.1527.

Dimethyl (*E*)-2-(benzo[b]thiophen-2-yl)-3-(benzylamino)-4-(benzylimino)cyclobut-2-ene-1,1-dicarboxylate 3at



3at

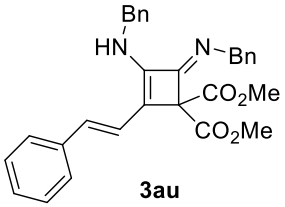
The reaction was run at rt for 14 h, affording product **3at** in 68% yield (34.1 mg) as a yellow solid. R_f = 0.3 (PE:EA = 4:1), m.p. 144–145 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 8.8 Hz, 2H), 7.43 – 7.33 (m, 5H), 7.33 – 7.27 (m, 6H), 7.26 – 7.18 (m, 2H), 4.95 (d, *J* = 6.3 Hz, 2H), 4.83 (s, 2H), 4.66 (t, *J* = 6.3 Hz, 1H), 3.74 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 150.3, 145.4, 139.9, 139.6, 139.3, 139.2, 134.1, 128.7, 128.2, 127.6, 127.5, 127.4, 126.6, 124.8, 124.3, 123.7, 121.9, 120.7, 113.0, 69.2, 55.9, 52.8, 48.8.

HRMS (ESI–TOF) calcd for $C_{30}H_{27}N_2O_4S^+$ ([M+H$^+$]) = 511.1687, Found 511.1684.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-((E)-styryl)cyclobut-2-ene-1,1-dicarboxylate 3au



3au

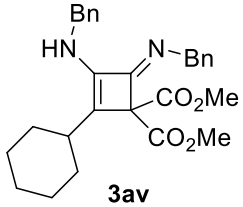
\The reaction was run at 35℃ for 14 h, affording product **3au** in 62% yield (29.9 mg) as a yellow solid. R_f = 0.3 (PE:EA = 4:1), m.p. 120-122 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)δ 7.42 – 7.37 (m, 4H), 7.33 (s, 1H), 7.31 (m, 3H), 7.30 – 7.26 (m, 5H), 7.25 – 7.17 (m, 2H), 6.73 (dd, 77.2, 15.6 Hz, 2H), 4.91 (t, *J* = 6.0 Hz, 1H), 4.76 (s, 2H), 4.62 (d, *J* =6.0 Hz, 2H), 3.76 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$).δ 169.1, 150.6, 145.3, 139.4, 138.1, 137.4, 130.1, 128.8, 128.5, 128.3, 127.7, 127.7, 127.5, 127.4, 126.7, 126.4, 119.2, 117.9, 68.8, 55.7, 52.7, 48.5.

HRMS (ESI–TOF) calcd for $C_{30}H_{29}N_2O_4^+$ ([M+H$^+$]) = 481.2122, Found 481.2122.

Dimethyl (*E*)-3-(benzylamino)-4-(benzylimino)-2-cyclohexylcyclobut-2-ene-1,1-dicarboxylate 3av



3av

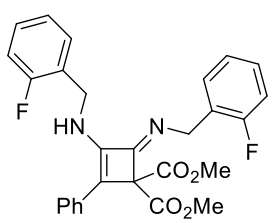
The reaction was run at rt for 14 h, affording product **3av** in 68% yield (31.3 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 90–92 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 5H), 7.28 (t, *J* = 7.4 Hz, 3H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.63 (s, 2H), 4.57 (d, *J* = 5.2 Hz, 2H), 4.17 (s, 1H), 3.70 (s, 6H), 2.46 (t, *J* = 11.9 Hz, 1H), 1.75 (s, 1H), 1.69 (s, 1H), 1.63 (d, *J* = 10.8 Hz, 1H), 1.39 – 1.29 (m, 3H), 1.24 – 1.08 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 151.3, 146.1, 139.8, 139.7, 128.5, 128.2, 127.6, 127.5, 127.4, 127.3, 126.5, 68.5, 55.3, 52.4, 48.5, 38.1, 30.8, 26.2, 25.8.

HRMS (ESI–TOF) calcd for $C_{28}H_{33}N_2O_4^+$ ([M+H$^+$]) = 461.2435, Found 461.2434.

Dimethyl (*E*)-3-((2-fluorobenzyl)amino)-4-((2-fluorobenzyl)imino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ba



3ba

The reaction was run at rt for 14 h, affording product **3ba** in 72% yield (35.3 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 116–117 ℃.

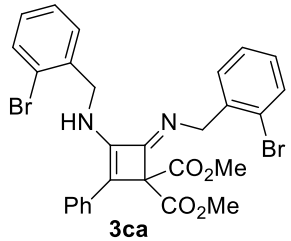
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (td, *J* = 7.6, 1.8 Hz, 1H), 7.37 – 7.27 (m, 5H), 7.26 – 7.17 (m, 3H), 7.11 – 7.01 (m, 4H), 4.91 (d, *J* = 6.6 Hz, 2H), 4.82 (s, 2H), 4.68 (t, *J* = 6.6 Hz, 1H), 3.70 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.3, 161.0 (*J* = 246.1 Hz), 150.4 (*J* = 244.6 Hz), 151.4, 145.4, 132.4, 130.0 (*J* = 4.5 Hz),129.5 (*J* = 4.5 Hz), 129.1 (*J* = 7.6 Hz), 128.6, 128.2 (*J* = 7.6 Hz), 127.0, 126.8 (*J* = 7.6 Hz), 126.7 (*J* = 7.6 Hz), 126.2, 124.2 (*J* = 3.0 Hz), 123.9 (*J* = 3.0 Hz), 119.5, 115.2 (*J* = 60.4 Hz), 115.0 (*J* = 60.4 Hz), 68.7, 52.7, 49.1, 42.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ −118.95, −119.16.

HRMS (ESI–TOF) calcd for $C_{28}H_{25}F_2N_2O_4^+$ ([M+H$^+$]) = 491.1777, Found 491.1776.

Dimethyl (*E*)-3-((2-bromobenzyl)amino)-4-((2-bromobenzyl)imino)-2-phenylcyclobut-2-ene-1, 1-dicarboxylate 3ca



3ca

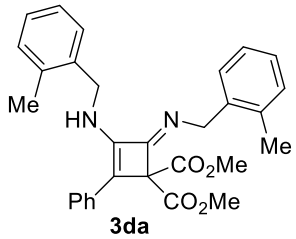
The reaction was run at rt for 14 h, affording product **3ca** in 79% yield (48.4 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 125–127 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.50 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.37 – 7.30 (m, 5H), 7.29 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 7.23 – 7.19 (m, 1H), 7.16 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.13 – 7.09 (m, 1H), 4.97 (s, 3H), 4.83 (s, 2H), 3.67 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 151.5, 145.2, 139.0, 138.8, 132.7, 132.3, 132.2, 130.0, 129.0, 129.0, 128.7, 128.0, 127.6, 127.2, 127.0, 126.2, 123.5, 123.0, 119.6, 68.7, 55.4, 52.7, 48.6.

HRMS (ESI–TOF) calcd for $C_{28}H_{25}Br_2N_2O_4^+$ ([M+H$^+$]) = 613.0156, Found 613.0156.

Dimethyl (*E*)-3-((2-methylbenzyl)amino)-4-((2-methylbenzyl)imino)-2-phenylcyclobut-2-ene-1, 1-dicarboxylate 3da



3da

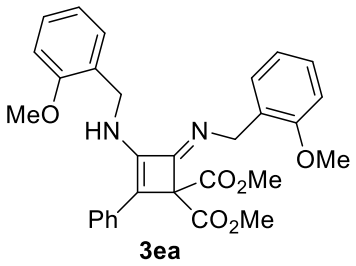
The reaction was run at rt for 14 h, affording product **3da** in 74% yield (35.5 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 142–143 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 3H), 7.32 – 7.29 (m, 2H), 7.24 – 7.20 (m, 2H), 7.20 – 7.17 (m, 3H), 7.17 – 7.11 (m, 4H), 4.89 (d, *J* = 6.1 Hz, 2H), 4.75 (s, 2H), 4.46 (t, *J* = 6.1 Hz, 1H), 3.68 (s, 6H), 2.36 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 150.6, 145.8, 137.8, 137.2, 136.4, 135.8, 132.6, 130.5, 129.8, 128.6, 128.0, 127.6, 127.4, 126.7, 126.6, 126.1, 125.8, 118.4, 68.8, 53.6, 52.6, 47.0, 19.1, 19.0.

HRMS (ESI–TOF) calcd for $C_{30}H_{31}N_2O_4^+$ ([M+H$^+$]) = 483.2279, Found 483.2279.

Dimethyl (*E*)-3-((2-methoxybenzyl)amino)-4-((2-methoxybenzyl)imino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ea



3ea

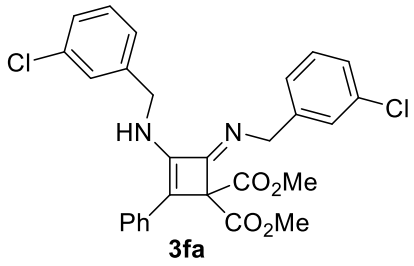
The reaction was run at rt for 14 h, affording product **3ea** in 82% yield (42.0mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 91–93 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 7.29 – 7.21 (m, 3H), 7.21 – 7.14 (m, 1H), 6.96 – 6.84 (m, 4H), 4.97 (t, *J* = 6.5 Hz, 1H), 4.86 (d, *J* = 6.5 Hz, 2H), 4.80 (s, 2H), 3.86 (d, *J* = 5.6 Hz, 6H), 3.64 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 157.5, 156.7, 151.1, 146.2, 132.8, 129.6, 128.6, 128.5, 128.3, 128.2, 127.9, 127.4, 126.4, 126.0, 120.5, 120.3, 118.3, 110.2, 109.9, 68.7, 55.3, 55.2, 52.5, 50.2, 44.6.

HRMS (ESI–TOF) calcd for $C_{30}H_{31}N_2O_6^+$ ([M+H$^+$]) = 515.2177, Found 515.2175.

Dimethyl (*E*)-3-((3-chlorobenzyl)amino)-4-((3-chlorobenzyl)imino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3fa



3fa

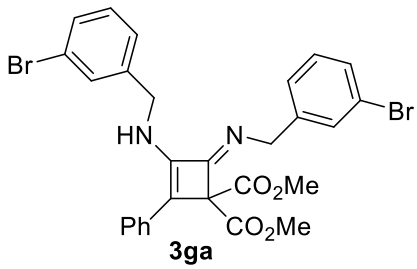
The reaction was run at rt for 14 h, affording product **3fa** in 74% yield (38.8 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 55–57 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 6H), 7.25 (s, 2H), 7.24 – 7.16 (m, 4H), 7.12 (d, *J* = 7.3 Hz, 1H), 4.85 (d, *J* = 6.5 Hz, 2H), 4.75 (s, 2H), 4.67 (t, *J* = 6.6 Hz, 1H), 3.71 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.3, 151.3, 145.2, 141.8, 141.6, 134.5, 134.1, 132.2, 129.9, 129.5, 128.7, 127.5, 127.5, 127.1, 126.7, 126.2, 125.5, 119.6, 68.6, 55.1, 52.8, 48.0.

HRMS (ESI–TOF) calcd for $C_{28}H_{25}Cl_2N_2O_4^+$ ([M+H$^+$]) = 523.1186, Found 523.1185.

Dimethyl (*E*)-3-((3-bromobenzyl)amino)-4-((3-bromobenzyl)imino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ga



3ga

The reaction was run at rt for 14 h, affording product **3ga** in 82% yield (50.0 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 86–88 ℃.

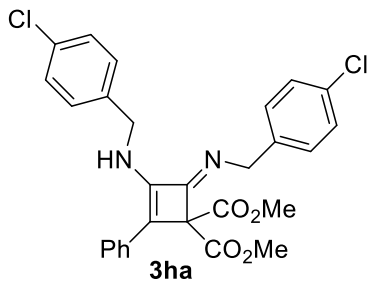
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.31 (d, *J* = 6.9 Hz, 2H), 7.27 (d, *J* = 8.0

Hz, 1H), 7.24 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 4.84 (d, *J* = 6.5 Hz, 2H), 4.75 (s, 2H), 4.68 (t, *J* = 6.6 Hz, 1H), 3.72 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 151.4, 145.2, 142.1, 141.9, 132.3, 130.6, 130.5, 130.5, 130.3, 129.9, 129.8, 128.8, 127.2, 126.3, 126.1, 122.8, 122.4, 119.6, 68.7, 55.1, 52.9, 48.1.

HRMS (ESI–TOF) calcd for $C_{28}H_{25}Br_2N_2O_4^+$ ([M+H$^+$]) = 613.0156, Found 613.0158.

Dimethyl (*E*)-3-((4-chlorobenzyl)amino)-4-((4-chlorobenzyl)imino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ha



3ha

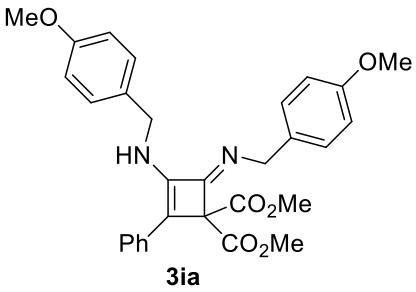
The reaction was run at rt for 14 h, affording product **3ha** in 78% yield (46.6 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 90–92 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 5H), 7.29 – 7.26 (m, 5H), 7.24 – 7.19 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 4.82 (d, *J* = 6.5 Hz, 2H), 4.73 (s, 2H), 4.64 (t, *J* = 6.6 Hz, 1H), 3.70 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 151.1, 145.3, 138.2, 138.1, 133.2, 132.3, 132.3, 128.8, 128.7, 128.7, 128.3, 127.1, 126.2, 119.5, 68.7, 55.0, 52.7, 48.0.

HRMS (ESI–TOF) calcd for $C_{28}H_{25}Cl_2N_2O_4^+$ ([M+H$^+$]) = 523.1186, Found 523.1181.

Dimethyl (*E*)-3-((4-methoxybenzyl)amino)-4-((4-methoxybenzyl)imino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ia



3ia

The reaction was run at rt for 14 h, affording product **3ia** in 83% yield (42.8 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 93–95 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.16 (m, 3H), 6.86 (dd, *J* = 8.5, 1.7 Hz, 4H), 4.78 (d, *J* = 6.2 Hz, 2H), 4.73 (s, 2H), 4.55 (t, *J* = 6.2 Hz, 1H), 3.80 (d, *J* = 3.6 Hz, 6H), 3.72 (s, 6H).

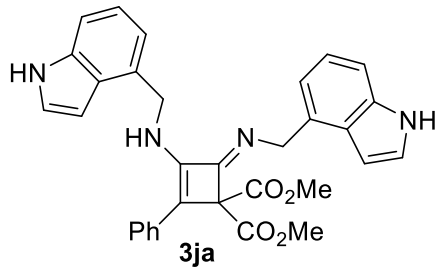
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 158.9, 158.3, 150.5, 145.7, 132.5, 131.8, 131.7, 129.0, 128.7, 128.6, 128.6, 126.7, 126.1, 118.5, 113.9, 113.6, 68.7, 55.2, 55.2, 55.2, 52.7, 48.3.

HRMS (ESI–TOF) calcd for $C_{30}H_{31}N_2O_6^+$ ([M+H$^+$]) = 515.2177, Found 515.2159.

Dimethyl (*E*)-3-(((1H-indol-4-yl)methyl)amino)-4-(((1H-indol-4-yl)methyl)imino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ja

The reaction was run at rt for 14 h, affording product **3ja** in 90% yield (48.0 mg) as a yellow solid.

R_f = 0.3 (PE:EA = 2:1), m.p. 92–94 ℃.



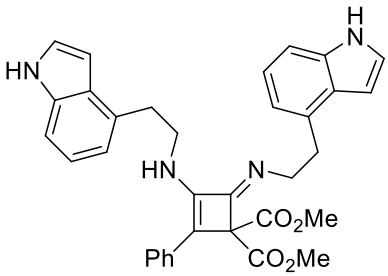
3ja

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 46.7 Hz, 2H), 7.35 – 7.27 (m, 5H), 7.24 (s, 1H), 7.18 – 7.14 (m, 1H), 7.14 – 7.10 (m, 3H), 7.10 – 7.05 (m, 3H), 6.70 – 6.66 (m, 1H), 6.64 – 6.58 (m, 1H), 5.14 (dd, *J* = 8.8, 2.4 Hz, 4H), 4.62 (t, *J* = 5.9 Hz, 1H), 3.70 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 150.7, 146.1, 135.9, 135.7, 132.7, 131.5, 130.8, 128.5, 126.5, 126.1, 124.3, 123.8, 121.9, 121.8, 118.9, 118.3, 117.9, 110.7, 109.7, 101.2, 100.7, 68.8, 54.1, 52.7, 47.4.

HRMS (ESI–TOF) calcd for $C_{32}H_{29}N_4O_4^+$ ([M+H$^+$]) = 533.2184, Found 533.2185.

Dimethyl (*E*)-3-((2-(1H-indol-4-yl)ethyl)amino)-4-((2-(1H-indol-4-yl)ethyl)imino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3ka



3ka

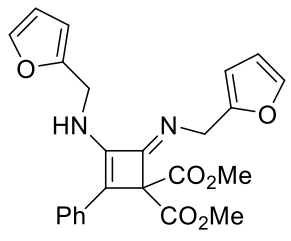
The reaction was run at rt for 14 h, affording product **3ka** in 74% yield (41.5 mg) as a white solid. R_f = 0.3 (PE:EA = 2:1), m.p. 69–71 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 31.7 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.26 – 7.23 (m, 2H), 7.20 – 7.16 (m, 3H), 7.16 – 7.14 (m, 1H), 7.14 – 7.10 (m, 3H), 7.04 (d, *J* = 7.1 Hz, 1H), 6.95 (d, *J* = 7.1 Hz, 1H), 6.70 – 6.64 (m, 2H), 4.41 (t, *J* = 6.5 Hz, 1H), 4.03 – 3.94 (m, 4H), 3.69 (s, 6H), 3.30 (t, *J* = 7.8 Hz, 2H), 3.18 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 149.9, 146.0, 135.8, 135.7, 132.6, 132.3, 130.8, 128.4, 127.5, 126.3, 125.9, 124.0, 123.7, 122.0, 122.0, 119.9, 119.6, 118.1, 109.6, 109.1, 101.0, 100.8, 68.4, 53.3, 52.6, 45.3, 35.1, 34.8.

HRMS (ESI–TOF) calcd for $C_{34}H_{33}N_4O_4^+$ ([M+H$^+$]) = 561.2497, Found 561.2501.

Dimethyl (*E*)-3-((furan-2-ylmethyl)amino)-4-((furan-2-ylmethyl)imino)-2-phenylcyclobut-2-ene-1,1-dicarboxylate 3la



3la

The reaction was run at 50℃ for 20 h, affording product **3la** in 46% yield (20.1 mg) as a white solid. R_f = 0.3 (PE:EA = 4:1), m.p. 121–123 ℃.

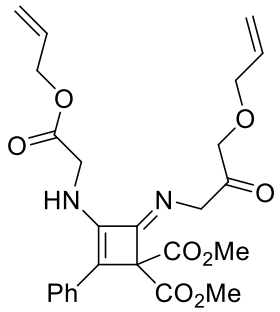
^{1}H NMR (600 MHz, $CDCl_3$)δ 7.39 – 7.30 (m, 6H), 7.23 – 7.18 (m, 1H), 6.33 (dd, *J* = 2.8, 1.9 Hz, 1H), 6.29 (dd, *J* = 2.9, 1.9 Hz, 1H), 6.19 (dd, *J* = 7.5,

3.1 Hz, 2H), 4.77 (d, *J* = 6.3 Hz, 2H), 4.75 (s, 2H), 4.59 (t, *J* = 6.3 Hz, 1H), 3.75 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$)δ 169.3, 152.9, 152.5, 151.6, 145.1, 142.1, 141.7, 132.2, 128.6, 127.1, 126.4, 119.9, 110.4, 110.2, 107.3, 106.5, 68.8, 52.8, 49.2, 41.6.

HRMS (ESI–TOF) calcd for $C_{24}H_{23}N_2O_6^+$ ([M+H$^+$]) = 435.1551, Found 435.1549.

Dimethyl (*E*)-3-((2-(allyloxy)-2-oxoethyl)amino)-4-((2-oxo-3-(vinyloxy)propyl)imino)-2-phenyl cyclobut-2-ene-1,1-dicarboxylate 3ma



3ma

The reaction was run at rt for 14 h, affording product **3ma** in 60% yield (29.6 mg) as a white solid. R_f = 0.3 (PE:EA = 2:1), m.p. 90–92 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.3 Hz, 4H), 7.25 – 7.20 (m, 1H), 5.99 – 5.86 (m, 2H), 5.38 – 5.35 (m, 1H), 5.33 – 5.31 (m, 1H), 5.27 – 5.26 (m, 1H), 5.25 – 5.23 (m, 1H), 4.83 (t, *J* = 5.5 Hz, 1H), 4.69 – 4.64 (m, 4H), 4.49 (d, *J* = 5.5 Hz, 2H), 4.42 (s, 2H), 3.74 (s, 6H).

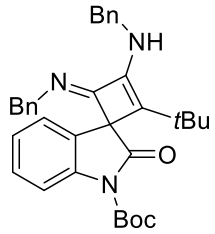
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 169.7, 169.0, 153.1, 144.1, 131.9, 131.5, 128.6, 127.3, 126.5, 120.7, 118.8, 118.4, 68.7, 66.0, 65.4, 53.4, 52.9, 46.0.

HRMS (ESI–TOF) calcd for $C_{24}H_{27}N_2O_8^+$ ([M+H$^+$]) = 471.1762, Found 471.1762.

6. General procedure and spectral data of products 5

A dry reaction tube was charged with isocyanides **1** (0.2 mmol, 2 equiv.), $La(OTf)_3$ (10 mol%) and 3-methyleneoxindoles **4** (0.1 mmol, 1 equiv.), Et_2O (0.5 mL) was added. The reaction mixture continued stirring at rt for 14 h. The residue was directly purified by flash chromatography on silica gel using petroleum ether/ethyl acetate= 5/1 as eluent to afford the desired products **5aa**.

Tert-butyl-3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5aa



5aa

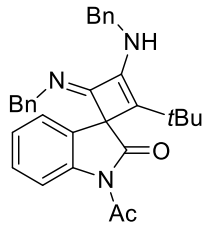
The reaction was run at rt for 14 h, affording product **5aa** in 83% yield (44.5 mg) as a yellow solid. R_f = 0.5 (PE:EA = 5:1), m.p. 120–121 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.18 (m, 3H), 7.15 (d, *J* = 7.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 4.76 (ddd, *J* = 35.0, 14.7, 6.1 Hz, 2H), 4.08 (d, *J* = 14.2 Hz, 1H), 4.02 (t, *J* = 6.0 Hz, 1H), 3.83 (d, *J* = 14.2 Hz, 1H), 1.64 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 154.5, 149.5, 146.1, 140.5, 139.0, 138.3, 132.9, 128.7, 128.5, 128.2, 128.0, 127.7, 127.6, 127.1, 126.5, 124.4, 123.5, 115.2, 84.2, 65.6, 55.6, 49.0, 34.4, 29.2, 28.1.

HRMS (ESI–TOF) calcd for $C_{34}H_{38}N_3O_3^+$([M+H$^+$]) = 536.2908, Found 536.2901.

1'-acetyl-3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)spiro[cyclobutane-1,3'-indolin]-2-en-2'-one 5ab



5ab

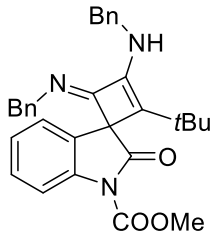
The reaction was run at rt for 14 h, affording product **5ab** in 79% yield (37.7 mg) as a yellow solid. R_f = 0.5 (PE:EA = 5:1), m.p. 98–100 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.36 – 7.34 (m, 1H), 7.33 – 7.27 (m, 1H), 7.22 – 7.10 (m, 5H), 6.92 – 6.85 (m, 2H), 4.87 – 4.70 (m, 2H), 4.06 (t, *J* = 6.1 Hz, 1H), 3.97 (d, *J* = 14.3 Hz, 1H), 3.87 (d, *J* = 15.6 Hz 1H), 2.61 (s, 3H), 0.99 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 171.2, 154.5, 146.3, 140.5, 138.9, 138.8, 132.8, 129.0, 128.6, 128.5, 128.1, 127.6, 127.4, 127.3, 126.6, 125.3, 123.4, 116.9, 65.7, 55.3, 49.0, 34.6, 29.2, 26.6.

HRMS (ESI–TOF) calcd for $C_{32}H_{32}N_3O_2^+$([M+H$^+$]) = 478.2490, Found 478.2491.

Methyl-3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ac



5ac

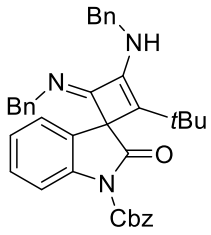
The reaction was run at rt for 14 h, affording product **5ac** in 83% yield (41.0 mg) as a yellow solid. R_f = 0.4 (PE:EA = 5:1), m.p. 103–105 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.38 – 7.33 (m, 3H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.19 – 7.11 (m, 5H), 6.91 – 6.83 (m, 2H), 4.76 (qd, *J* = 14.8, 6.6 Hz, 2H), 4.10 (d, *J* = 14.4 Hz, 1H), 4.05 (t, *J* = 6.2, 1H), 4.03 (s, 3H), 3.79 (d, *J* = 14.4 Hz, 1H), 1.00 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.1, 154.1, 151.8, 146.3, 140.6, 138.9, 138.2, 132.9, 128.9, 128.6, 128.3, 128.0, 127.6, 127.5, 127.2, 126.5, 124.8, 123.6, 115.3, 65.6, 55.5, 53.9, 49.0, 34.5, 29.2.

HRMS (ESI–TOF) calcd for $C_{31}H_{32}N_3O_3^+$([M+H$^+$]) = 494.2439, Found 494.2436.

Benzyl-3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ad



5ad

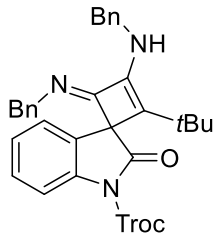
The reaction was run at rt for 14 h, affording product **5ad** in 74% yield (42.2 mg) as a yellow solid. R_f = 0.4 (PE:EA = 5:1), m.p. 118–120 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.43 – 7.27 (m, 9H), 7.21 – 7.10 (m, 5H), 6.93 – 6.86 (m, 2H), 5.54 – 5.41 (m, 2H), 4.77 (qd, *J* = 14.6, 6.6 Hz, 2H), 4.07 (d, *J* = 9.7 Hz, 1H), 4.05 – 4.01 (m, 1H), 3.81 (d, *J* = 14.3 Hz, 1H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 154.2, 151.1, 146.3, 140.5, 138.9, 138.3, 135.1, 132.8, 129.0, 128.7, 128.6, 128.4, 128.3, 128.1, 127.8, 127.7, 127.6, 127.2, 126.6, 124.9, 123.6, 115.4, 68.5, 65.6, 55.7, 49.1, 34.6, 29.3.

HRMS (ESI–TOF) calcd for $C_{37}H_{36}N_3O_3^+$([M+H$^+$]) = 570.2752, Found 570.2747.

2,2,2-trichloroethyl-3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ae



5ae

The reaction was run at rt for 14 h, affording product **5ae** in 87% yield (53.1 mg) as a yellow solid. R_f = 0.5 (PE:EA = 5:1), m.p. 102–103 ℃.

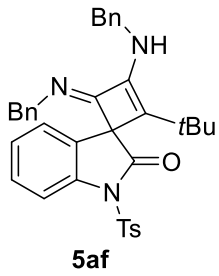
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.38 – 7.37 (m, 2H), 7.37 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.23 – 7.17 (m, 2H), 7.17 – 7.11 (m, 3H), 6.94 – 6.86 (m, 2H), 5.07 (s, 2H), 4.76 (ddd, *J* = 36.4, 14.8, 6.5 Hz, 2H), 4.07 (d, *J* = 14.3 Hz, 2H), 3.83 (d, *J* = 14.3 Hz,1H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 153.8, 149.6, 146.4, 140.4, 138.7, 137.6, 132.6, 129.1, 128.6,

128.4, 128.1, 127.6, 127.6, 127.2, 126.6, 125.3, 123.8, 115.5, 94.3, 75.5, 65.4, 55.7, 49.0, 34.6, 29.2.

HRMS (ESI–TOF) calcd for $C_{32}H_{31}Cl_3N_3O_3^+$([M+H$^+$]) = 610.1426, Found 610.1426.

3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-1'-tosylspiro[cyclobutane-1,3'-indolin]-2-en-2'-one 5af



5af

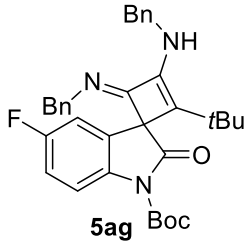
The reaction was run at rt for 14 h, affording product **5af** in 76% yield (44.8 mg) as a yellow solid. R_f = 0.4 (PE:EA = 5:1), m.p. 137–138 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.93 (m, 2H), 7.39 – 7.36 (m, 1H), 7.36 – 7.33 (m, 4H), 7.28 (m, 1H), 7.17 – 7.09 (m, 7H), 6.74 – 6.62 (m, 2H), 4.75 – 4.63 (m, 2H), 4.01 (t, *J* = 6.6 Hz, 1H), 3.43 (d, *J* = 14.5 Hz, 1H), 3.32 (d, *J* = 14.5 Hz, 1H), 2.28 (s, 3H), 0.91 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.0, 153.5, 146.2, 145.5, 140.4, 138.6, 138.0, 134.8, 132.6, 129.6, 129.2, 128.5, 128.4, 127.9, 127.7, 127.5, 127.4, 127.1, 126.5, 124.8, 123.9, 113.9, 65.2, 55.4, 48.9, 34.4, 29.0, 21.5.

HRMS (ESI–TOF) calcd for $C_{36}H_{36}N_3O_3S^+$([M+H$^+$]) = 590.2472, Found 590.2476.

Tert-buty-3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-5'-fluoro-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ag



5ag

The reaction was run at rt for 14 h, affording product **5ag** in 81% yield (44.9 mg) as a yellow solid. R_f = 0.4 (PE:EA = 5:1), m.p. 87–88 ℃.

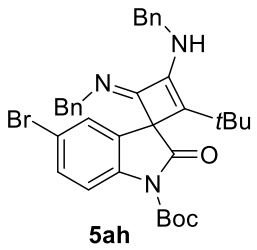
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (q, *J* = 4.4 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 7.21 – 7.13 (m, 3H), 7.01 (td, *J* = 8.9, 2.8 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.85 (dd, *J* = 7.6, 2.8 Hz, 1H), 4.74 (ddd, *J* = 40.5, 14.7, 6.7 Hz, 2H), 4.07 (d, *J* = 14.2 Hz, 1H), 4.02 (t, *J* = 6.6 Hz, 1H), 3.82 (d, *J* = 14.2 Hz, 1H), 1.62 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 160.1 (*J* = 246.1 Hz), 153.6, 149.5, 146.4, 140.4, 138.7, 134.6, 132.5, 130.5 (*J* = 8.0 Hz), 128.6, 128.1, 127.6, 127.3, 126.7, 116.6 (*J* = 7.7 Hz), 115.3 (*J* = 23.2 Hz), 110.8 (*J* = 24.5 Hz), 84.4, 65.8, 55.7, 49.0, 34.5, 29.2, 28.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.7.

HRMS (ESI–TOF) calcd for $C_{34}H_{37}FN_3O_3^+$([M+H$^+$]) = 554.2814, Found 554.2813.

Tert-butyl-3-(benzylamino)-4-(benzylimino)-5'-bromo-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ah



5ah

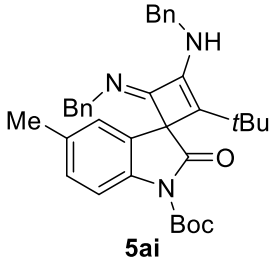
The reaction was run at rt for 14 h, affording product **5ah** in 83% yield (51.0 mg) as a yellow solid. R_f = 0.4 (PE:EA = 5:1), m.p. 162–163 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 1H), 7.43 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.37 (s, 2H), 7.37 – 7.36 (m, 2H), 7.33 – 7.28 (m, 1H), 7.22 (d, *J* = 2.1 Hz, 1H), 7.21 – 7.14 (m, 3H), 6.94 – 6.86 (m, 2H), 4.74 (ddd, *J* = 30.2, 14.6, 6.8 Hz, 2H), 4.08 (d, *J* = 14.0 Hz, 1H), 4.03 (t, *J* = 6.5 Hz, 1H), 3.82 (d, *J* = 14.0 Hz, 1H), 1.62 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 153.5, 149.3, 146.5, 140.3, 138.6, 137.7, 132.5, 131.6, 130.7, 128.6, 128.1, 127.6, 127.6, 127.3, 126.7, 126.5, 117.6, 116.9, 84.6, 65.4, 55.8, 49.0, 34.5, 29.2, 28.1.

HRMS (ESI–TOF) calcd for $C_{34}H_{37}BrN_3O_3^+$([M+H$^+$]) = 614.2013, Found 614.2010.

Tert-butyl-3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-5'-methyl-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ai



5ai

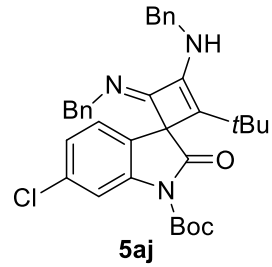
The reaction was run at rt for 14 h, affording product **5ai** in 70% yield (38.5 mg) as a yellow solid. R_f = 0.5 (PE:EA = 5:1), m.p. 70–71 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.37 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.19 – 7.12 (m, 3H), 7.12 – 7.09 (m, 1H), 6.93 – 6.88 (m, 3H), 4.74 (qd, *J* = 14.7, 6.4 Hz, 2H), 4.09 (d, *J* = 14.1 Hz, 1H), 3.99 (t, *J* = 6.6 Hz, 1H), 3.79 (d, *J* = 14.1 Hz, 1H), 2.28 (s, 3H), 1.63 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 154.7, 149.6, 146.1, 140.5, 139.0, 136.3, 134.0, 133.3, 129.2, 128.5, 128.2, 127.9, 127.7, 127.7, 127.2, 126.5, 124.1, 115.0, 84.0, 65.6, 55.7, 49.0, 34.5, 29.2, 28.1, 21.0.

HRMS (ESI–TOF) calcd for $C_{35}H_{40}N_3O_3^+$([M+H$^+$]) = 550.3065, Found 550.3063.

Tert-butyl-3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-6'-chloro-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5aj



5aj

The reaction was run at rt for 14 h, affording product **5aj** in 82% yield (46.7 mg) as a yellow solid. R_f = 0.3 (PE:EA = 5:1), m.p. 73–74 ℃.

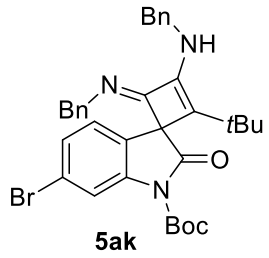
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 1H), 7.44 (dt, *J* = 8.7, 1.6 Hz, 1H), 7.37 (d, *J* = 5.9 Hz, 4H), 7.31 (dq, *J* = 6.2, 2.9 Hz, 1H), 7.23 (s, 1H), 7.19 (dt, *J* = 14.4, 6.8 Hz, 3H), 6.92 (d, *J* = 7.4 Hz, 2H), 4.79 – 4.70 (m, 2H),

4.09 (d, *J* = 14.1 Hz, 1H), 4.06 (d, *J* = 6.7 Hz, 1H), 3.83 (d, *J* = 14.1 Hz, 1H), 1.63 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.7, 153.9, 149.3, 146.3, 140.4, 139.5, 138.8, 134.4, 132.4, 128.6, 128.1, 127.6, 127.2, 126.7, 126.6, 124.5, 124.3, 116.0, 84.7, 65.2, 55.7, 49.0, 34.5, 29.2, 28.0.

HRMS (ESI–TOF) calcd for $C_{34}H_{37}ClN_3O_3^+$([M+H$^+$]) = 570.2518, Found 570.2517.

Tert-butyl-3-(benzylamino)-4-(benzylimino)-6'-bromo-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ak



5ak

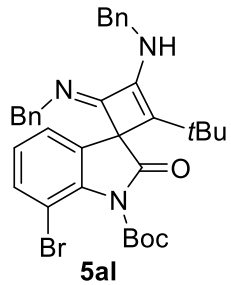
The reaction was run at rt for 14 h, affording product **5ak** in 80% yield (49.2 mg) as a yellow solid. R_f = 0.3 (PE:EA = 5:1), m.p. 89–91 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.7 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.37 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 7.24 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.17 – 7.13 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.96 – 6.91 (m, 2H), 4.74 (qd, *J* = 14.7, 6.5 Hz, 2H), 4.06 (d, *J* = 14.3 Hz, 1H), 4.02 (t, *J* = 6.5 Hz, 1H), 3.82 (d, *J* = 14.3 Hz, 1H), 1.62 (s, 9H), 0.99 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.6, 153.7, 149.3, 146.3, 140.4, 139.6, 138.7, 132.4, 128.6, 128.1, 127.6, 127.4, 127.3, 127.2, 126.6, 124.7, 122.2, 118.7, 84.8, 65.3, 55.7, 49.0, 34.5, 29.2, 28.0.

HRMS (ESI–TOF) calcd for $C_{34}H_{37}BrN_3O_3^+$([M+H$^+$]) = 614.2013, Found 614.2011.

Tert-butyl-3-(benzylamino)-4-(benzylimino)-7'-bromo-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5al



5al

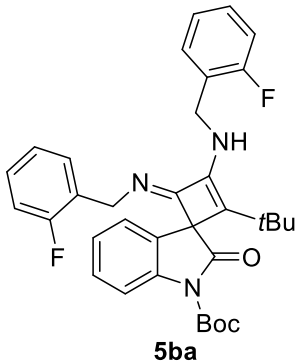
The reaction was run at rt for 14 h, affording product **5al** in 82% yield (50.4 mg) as a yellow solid. R_f = 0.3 (PE:EA = 5:1), m.p. 103–105 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.42 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 7.21 – 7.11 (m, 3H), 7.09 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.00 – 6.93 (m, 3H), 4.83 – 4.70 (m, 2H), 4.11 (d, *J* = 14.4 Hz, 1H), 4.06 (t, *J* = 6.7 Hz, 1H), 3.87 (d, *J* = 14.4 Hz, 1H), 1.59 (s, 9H), 1.02 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 153.6, 148.3, 146.1, 140.4, 138.8, 137.7, 133.2, 132.2, 131.9, 128.5, 128.0, 127.5, 127.5, 127.2, 126.5, 125.3, 122.5, 106.9, 85.2, 66.1, 55.8, 48.9, 34.4, 29.1, 27.6.

HRMS (ESI–TOF) calcd for $C_{34}H_{37}BrN_3O_3^+$([M+H$^+$]) = 614.2013, Found 614.2014.

Tert-butyl-2-(tert-butyl)-3-((2-fluorobenzyl)amino)-4-((2-fluorobenzyl)imino)-2'-oxospiro [cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ba



5ba

The reaction was run at rt for 14 h, affording product **5ba** in 65% yield (37.2 mg) as a yellow solid. R_f = 0.3 (PE:EA = 5:1), m.p. 91–92 ℃.

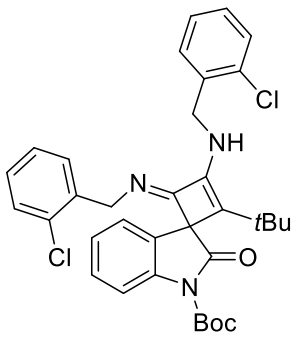
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.42 (td, *J* = 7.6, 1.5 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.15 – 7.11 (m, 1H), 7.10 – 7.04 (m, 3H), 7.03 – 7.01 (m, 1H), 7.00 – 6.96 (m, 2H), 6.92 – 6.85 (m, 1H), 4.84 (dd, *J* = 15.0, 7.5 Hz, 1H), 4.70 (dd, *J* = 15.0, 6.3 Hz, 1H), 4.14 (t, *J* = 6.9 Hz, 1H), 4.07 (d, *J* = 14.5 Hz, 1H), 3.91 (d, *J* = 14.9 Hz, 1H), 1.62 (s, 9H), 0.98 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.9, 161.4 (d, *J* = 133.1 Hz, 1C), 159.8(d, *J* = 134.0 Hz, 1C), 155.2, 149.4, 145.9, 138.7, 134.3, 130.3 (d, *J* = 4.7 Hz, 1C), 129.8 (d, *J* = 4.4 Hz, 1C), 128.9(d, *J* = 8.2 Hz, 1C), 128.8, 128.1 (d, *J* = 8.0 Hz, 1C), 127.8, 127.4 (d, *J* = 14.5 Hz, 1C), 126.1 (d, *J* = 14.7 Hz, 1C), 124.3, 124.1(d, *J* = 3.5 Hz, 1C), 123.7, 123.1 (d, *J* = 3.0 Hz, 1C), 123.4, 115.2, 115.0, 114.6 (d, *J* = 21.5 Hz, 1C), 84.1, 65.4, 48.4(d, *J* = 3.0 Hz, 1C), 43.1 (d, *J* = 3.0 Hz, 1C), 34.4, 29.1, 28.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -119.04, -119.65.

HRMS (ESI–TOF) calcd for $C_{34}H_{36}F_2N_3O_3^+$([M+H$^+$]) = 572.2720, Found 572.2720.

Tert-butyl-2-(tert-butyl)-3-((2-chlorobenzyl)amino)-4-((2-chlorobenzyl)imino)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ca



5ca

The reaction was run at rt for 14 h, affording product **5ca** in 77% yield (46.6 mg) as a yellow solid. R_f = 0.3 (PE:EA = 5:1), m.p. 91–93 ℃.

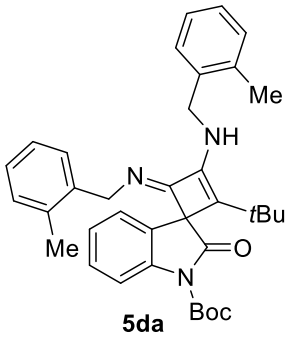
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.50 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.39 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.21 – 7.19 (m, 1H), 7.15 – 7.07 (m, 3H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.5 Hz, 1H), 4.88 (dd, *J* = 15.1, 7.5 Hz, 1H), 4.75 (dd, *J* = 15.1, 6.5 Hz, 1H), 4.39 (t, *J* = 7.0 Hz, 1H), 4.10 (d, *J* = 16.0 Hz, 1H), 3.93 (d, *J* = 16.0 Hz, 1H), 1.61 (s, 9H), 0.98 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 155.4, 149.4, 145.8, 138.8, 137.7, 136.8, 134.3, 133.3, 132.7, 130.3, 129.4, 129.1, 128.8, 128.7, 128.6, 127.8, 127.7, 127.0, 126.5, 124.2, 123.3, 115.2, 84.1, 65.5, 52.2, 46.7, 34.4, 29.1, 28.1.

HRMS (ESI–TOF) calcd for $C_{34}H_{36}Cl_2N_3O_3^+$([M+H$^+$]) = 604.2129, Found 604.2132.

Tert-butyl-2-(tert-butyl)-3-((2-methylbenzyl)amino)-4-((2-methylbenzyl)imino)-2'-oxospiro[c

yclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5da



5da

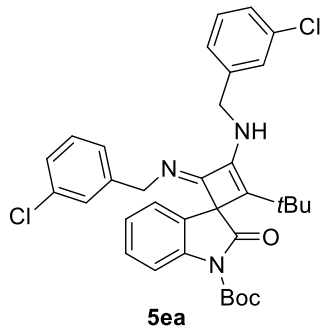
The reaction was run at rt for 14 h, affording product **5da** in 69% yield (38.9 mg) as a yellow solid. R_f = 0.5(PE:EA = 5:1), m.p. 81–83 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.32 (td, *J* = 7.8, 1.4 Hz, 1H), 7.25 – 7.16 (m, 4H), 7.12 (td, *J* = 7.5, 1.1 Hz, 1H), 7.06 (td, *J* = 7.3, 1.4 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.77 (d, *J* = 7.5 Hz, 1H), 4.87 (dd, *J* = 14.6, 6.8 Hz, 1H), 4.71 (dd, *J* = 14.6, 5.7 Hz, 1H), 4.06 (d, *J* = 14.9 Hz, 1H), 3.89 (t, *J* = 6.3 Hz, 1H), 3.75 (d, *J* = 14.9 Hz, 1H), 2.39 (s, 3H), 2.04 (s, 3H), 1.65 (s, 9H), 1.03 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 154.2, 149.5, 146.1, 138.7, 138.1, 137.2, 136.4, 135.9, 131.6, 130.4, 129.7, 128.7, 128.3, 127.9, 127.9, 127.3, 126.6, 126.0, 125.6, 124.4, 123.6, 115.1, 84.2, 65.6, 53.2, 47.0, 34.4, 29.3, 28.1, 19.1, 18.8.

HRMS (ESI–TOF) calcd for $C_{36}H_{42}N_3O_3^+$([M+H$^+$]) = 564.3221, Found 564.3224.

Tert-butyl-2-(tert-butyl)-3-((3-chlorobenzyl)amino)-4-((3-chlorobenzyl)imino)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ea



5ea

The reaction was run at rt for 14 h, affording product **5ea** in 72% yield (43.7mg) as a yellow solid. R_f = 0.4(PE:EA = 5:1), m.p. 88–89 ℃.

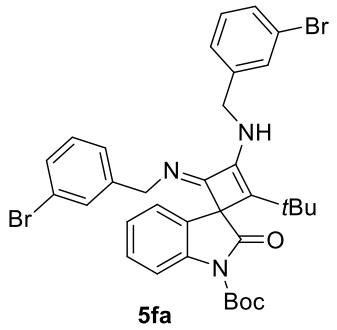
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.37 (s, 1H), 7.35 – 7.31 (m, 1H), 7.31 – 7.24 (m, 3H), 7.16 – 7.05 (m, 4H), 6.80 (s, 1H), 6.78 (dt, *J* = 7.0, 1.7 Hz, 1H), 4.79 (dd, *J* = 15.2, 7.2 Hz, 1H), 4.64 (dd, *J* = 15.2, 6.2 Hz, 1H), 4.08 – 4.00 (m, 2H), 3.72 (d, *J* = 14.4 Hz, 1H), 1.64 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 155.0, 149.5, 145.7, 142.7, 140.8, 138.7, 134.4, 133.9, 133.8, 129.9, 129.3, 129.0, 127.8, 127.7, 127.5, 127.3, 126.7, 125.8, 125.6, 124.5, 123.6, 115.3, 84.4, 65.5, 55.0, 48.3, 34.5, 29.1, 28.1.

HRMS (ESI–TOF) calcd for $C_{34}H_{36}Cl_2N_3O_3^+$([M+H$^+$]) = 604.2129, Found 604.2130.

Tert-butyl-3-((3-bromobenzyl)amino)-4-((3-bromobenzyl)imino)-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5fa

The reaction was run at rt for 14 h, affording product **5fa** in 67% yield (46.5 mg) as a yellow solid. R_f = 0.4 (PE:EA = 5:1), m.p. 62–64 ℃.



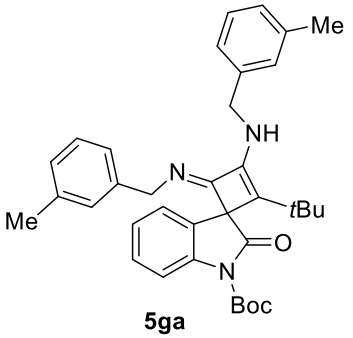
5fa

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.53 (s, 1H), 7.41 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 7.15 – 7.10 (m, 2H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.93 (s, 1H), 6.82 (dt, *J* = 7.6, 1.3 Hz, 1H), 4.79 (dd, *J* = 15.2, 7.3 Hz, 1H), 4.62 (dd, *J* = 15.2, 6.2 Hz, 1H), 4.08 – 4.01 (m, 2H), 3.70 (d, *J* = 14.3 Hz, 1H), 1.64 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.0, 155.0, 149.4, 145.6, 142.9, 141.1, 138.6, 133.9, 130.6, 130.4, 130.2, 129.7, 129.6, 129.0, 127.7, 126.3, 126.1, 124.6, 123.6, 122.6, 122.1, 115.3, 84.4, 65.4, 55.0, 48.2, 34.5, 29.1, 28.1.

HRMS (ESI–TOF) calcd for $C_{34}H_{36}Br_2N_3O_3^+$([M+H$^+$]) = 694.1098, Found 694.1100.

Tert-butyl-2-(tert-butyl)-3-((3-methylbenzyl)amino)-4-((3-methylbenzyl)imino)-2'-oxospiro [cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ga



5ga

The reaction was run at rt for 14 h, affording product **5ga** in 81% yield (45.7 mg) as a yellow solid. R_f = 0.5 (PE:EA = 5:1), m.p. 75–76 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.27 – 7.24 (m, 1H), 7.22 – 7.16 (m, 3H), 7.14 – 7.09 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 4.70 (ddd, *J* = 48.2, 14.6, 6.9 Hz, 2H), 4.07 (d, *J* = 14.0 Hz, 1H), 3.97 (t, *J* = 6.5 Hz, 1H), 3.76 (d, *J* = 14.0 Hz, 1H), 2.35 (s, 3H), 2.23 (s, 3H), 1.64 (s, 9H), 1.00 (s, 9H).

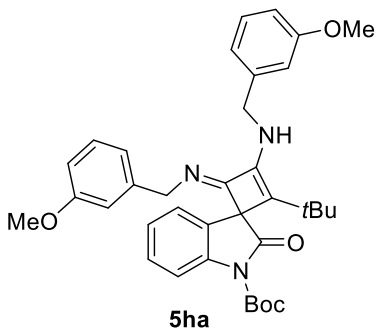
^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 154.3, 149.6, 146.3, 140.5, 138.8, 138.7, 138.1, 137.5, 132.9, 128.7, 128.6, 128.4, 128.4, 128.3, 127.9, 127.9, 127.3, 124.9, 124.6, 124.3, 123.6, 115.2, 84.2, 65.6, 55.8, 49.0, 34.4, 29.2, 28.1, 21.4, 21.3.

HRMS (ESI–TOF) calcd for $C_{36}H_{42}N_3O_3^+$([M+H$^+$]) = 564.3221, Found 564.3284.

Tert-butyl-2-(tert-butyl)-3-((3-methoxybenzyl)amino)-4-((3-methoxybenzyl)imino)-2'-oxospiro [cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ha

The reaction was run at rt for 14 h, affording product **5ha** in 71% yield (44.7 mg) as a yellow solid. R_f = 0.5(PE:EA = 5:1), m.p. 78–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.32 (td, *J* = 7.8, 1.5 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.21 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.12 (td, *J* = 7.4, 1.0 Hz, 1H), 7.07 (t, *J* = 8.1 Hz, 1H), 7.00 – 6.92



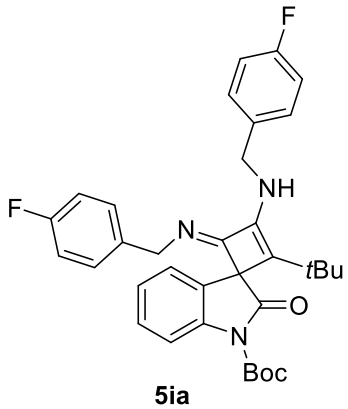
5ha

(m, 2H), 6.85 – 6.79 (m, 1H), 6.72 – 6.66 (m, 1H), 6.54 – 6.47 (m, 2H), 4.81 – 4.66 (m, 2H), 4.08 – 3.98 (m, 2H), 3.81 (s, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 1.63 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 159.9, 159.5, 154.7, 149.6, 146.2, 142.4, 140.6, 138.8, 133.1, 129.6, 129.0, 128.8, 128.3, 124.4, 123.6, 120.1, 119.7, 115.3, 113.2, 112.9, 112.7, 112.6, 84.3, 65.6, 55.7, 55.2, 55.1, 49.0, 34.5, 29.2, 28.1.

HRMS (ESI–TOF) calcd for $C_{36}H_{42}N_3O_5^+$([M+H$^+$]) = 596.3119, Found 596.3118.

Tert-butyl-2-(tert-butyl)-3-((4-fluorobenzyl)amino)-4-((4-fluorobenzyl)imino)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ia



5ia

The reaction was run at rt for 14 h, affording product **5ia** in 80% yield (45.8 mg) as a yellow solid. R_f = 0.3 (PE:EA = 5:1), m.p. 84–85 °C.

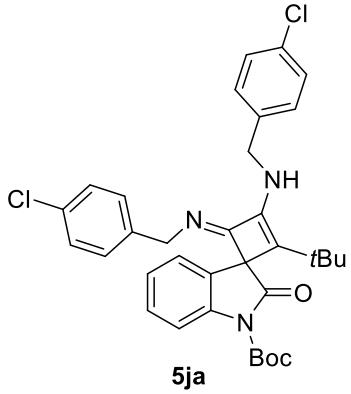
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.17 – 7.09 (m, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 7.1 Hz, 4H), 4.69 (d, *J* = 6.6 Hz, 2H), 4.00 (dd, *J* = 14.2, 1.0 Hz, 1H), 3.98 (d, *J* = 6.6 Hz, 1H), 3.77 (d, *J* = 13.9 Hz, 1H), 1.63 (s, 9H), 0.99 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 162.7 (d, *J* = 55.8 Hz, 1C), 161.1 (d, *J* = 54.4 Hz, 1C), 154.7, 149.5, 145.9, 138.7, 136.3, 136.3, 134.6, 134.6, 133.5, 129.2, 129.2, 129.2, 129.1, 128.9, 128.0, 124.4, 123.5, 115.4, 115.3, 114.8, 114.7, 84.3, 65.5, 54.9, 48.2, 34.5, 29.1, 28.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.56, -116.49.

HRMS (ESI–TOF) calcd for $C_{34}H_{36}F_2N_3O_3^+$([M+H$^+$]) = 572.2720, Found 572.2719.

Tert-butyl-2-(tert-butyl)-3-((4-chlorobenzyl)amino)-4-((4-chlorobenzyl)imino)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ja



5ja

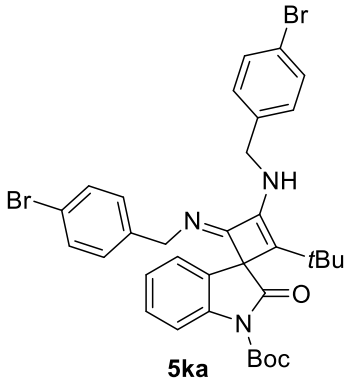
The reaction was run at rt for 14 h, affording product **5ja** in 85% yield (43.7 mg) as a yellow solid. R_f = 0.4(PE:EA = 5:1), m.p. 88–91 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.15 – 7.08 (m, 4H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.70 (d, *J* = 6.6 Hz, 2H), 4.04 – 4.01 (m, 1H), 3.99 (d, *J* = 14.5 Hz, 1H), 3.75 (d, *J* = 14.3 Hz, 1H), 1.63 (s, 9H), 0.99 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.1, 154.8, 149.4, 145.7, 139.1, 138.7, 137.3, 133.5, 132.9, 132.3, 129.0, 128.9, 128.8, 128.7, 128.1, 127.9, 124.5, 123.5, 115.3, 84.4, 65.5, 54.9, 48.1, 34.5, 29.1, 28.1.

HRMS (ESI–TOF) calcd for $C_{34}H_{36}Cl_2N_3O_3^+$([M+H$^+$]) = 604.2129, Found 604.2130.

Tert-butyl-3-((4-bromobenzyl)amino)-4-((4-bromobenzyl)imino)-2-(tert-butyl)-2'-oxospiro [cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ka



5ka

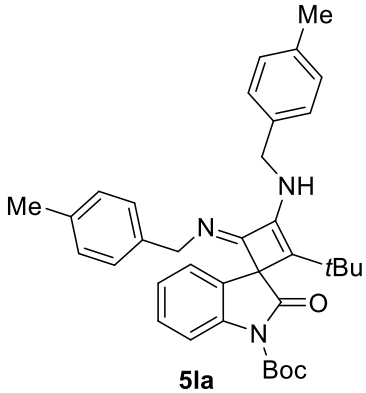
The reaction was run at rt for 14 h, affording product **5ka** in 76% yield (52.7 mg) as a yellow solid. R_f = 0.4(PE:EA = 5:1), m.p. 92–93 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.28 – 7.23 (m, 4H), 7.15 – 7.08 (m, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 4.68 (d, *J* = 6.6 Hz, 2H), 4.02 (t, *J* = 6.7 Hz, 1H), 3.97 (d, *J* = 14.3 Hz, 1H), 3.73 (d, *J* = 14.3 Hz, 1H), 1.63 (s, 9H), 0.99 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 154.8, 149.4, 145.7, 139.6, 138.7, 137.9, 133.5, 131.6, 131.0, 129.3, 129.2, 128.9, 127.9, 124.5, 123.5, 121.0, 120.4, 115.3, 84.4, 65.5, 54.9, 48.2, 34.5, 29.1, 28.1.

HRMS (ESI–TOF) calcd for $C_{34}H_{36}Br_2N_3O_3^+$([M+H$^+$]) = 694.1098, Found 694.1104.

Tert-butyl-2-(tert-butyl)-3-((4-methylbenzyl)amino)-4-((4-methylbenzyl)imino)-2'-oxospiro [cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5la



5la

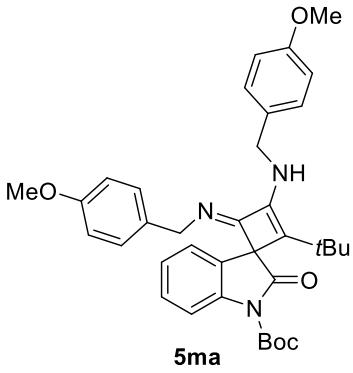
The reaction was run at rt for 14 h, affording product **5la** in 87% yield (48.9 mg) as a yellow solid. R_f = 0.5(PE:EA = 5:1), m.p. 82–84 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.30 – 7.26 (m, 2H), 7.22 – 7.10 (m, 4H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 7.9 Hz, 2H), 4.78 – 4.61 (m, 2H), 4.03 (d, *J* = 14.1 Hz, 1H), 3.94 (t, *J* = 6.4 Hz, 1H), 3.78 (d, *J* = 14.1 Hz, 1H), 2.37 (s, 3H), 2.27 (s, 3H), 1.64 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 154.3, 149.6, 146.3, 138.8, 137.6, 136.8, 136.1, 136.0, 132.6, 129.2, 128.8, 128.7, 128.4, 127.8, 127.7, 124.4, 123.6, 115.2, 84.2, 65.7, 55.5, 48.9, 34.5, 29.3, 28.1, 21.2, 21.1.

HRMS (ESI–TOF) calcd for $C_{36}H_{42}N_3O_3^+$([M+H$^+$]) = 564.3221, Found 564.3224.

Tert-butyl-2-(tert-butyl)-3-((4-methoxybenzyl)amino)-4-((4-methoxybenzyl)imino)-2'-oxospiro [cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ma



5ma

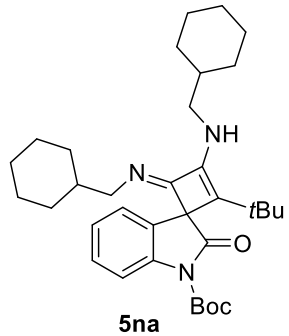
The reaction was run at rt for 14 h, affording product **5ma** in 85% yield (50.6 mg) as a yellow solid. R_f = 0.5 (PE:EA = 5:1), m.p. 99–100 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.24 (td, *J* = 7.8, 1.4 Hz, 1H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.92 – 6.87 (m, 3H), 6.82 (td, *J* = 7.4, 1.1 Hz, 1H), 6.71 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.72 (dd, *J* = 14.4, 7.9 Hz, 1H), 4.59 (dd, *J* = 14.3, 5.7 Hz, 1H), 4.46 – 4.41 (m, 1H), 4.07 (d, *J* = 15.0 Hz, 1H), 3.87 (s, 3H), 3.85 (d, *J* = 15.0 Hz, 1H), 3.67 (s, 3H), 1.60 (s, 9H), 0.94 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.0, 157.5, 156.7, 154.6, 149.6, 147.0, 138.7, 134.1, 130.0, 129.0, 128.5, 128.4, 128.4, 128.3, 127.7, 127.5, 124.1, 123.4, 120.5, 120.2, 115.0, 110.0, 109.9, 83.9, 65.5, 55.2, 49.8, 45.2, 34.3, 29.1, 28.1.

HRMS (ESI-TOF) calcd for $C_{36}H_{42}N_3O_5^+$([M+H$^+$]) = 596.3119, Found 596.3117.

Tert-butyl-2-(tert-butyl)-3-((cyclohexylmethyl)amino)-4-((cyclohexylmethyl)imino)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5na



5na

The reaction was run at rt for 14 h, affording product **5na** in 79% yield (43.9 mg) as a yellow solid. R_f = 0.5 (PE:EA = 5:1), m.p. 138–140 ℃.

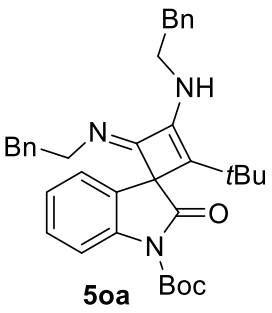
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.75 (m, 1H), 7.32 – 7.22 (m, 1H), 7.22 – 7.15 (m, 1H), 7.13 – 7.07 (m, 1H), 3.80 – 3.70 (m, 1H), 3.35 – 3.27 (m, 2H), 2.58 – 2.46 (m, 2H), 1.83 – 1.70 (m, 5H), 1.69 – 1.60 (m, 9H), 1.56 – 1.49 (m, 3H), 1.48 – 1.36 (m, 3H), 1.29 – 1.21 (m, 3H), 1.19 – 1.05 (m, 4H), 1.01 – 0.92 (m, 10H), 0.64 (dq, *J* = 78.0, 12.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 153.4, 149.7, 146.6, 138.6, 129.8, 129.0, 128.3, 124.1, 123.4, 114.9, 83.8, 65.7, 58.3, 53.4, 51.0, 39.6, 39.1, 34.2, 31.1, 31.0, 30.5, 29.2, 28.1, 26.6, 26.5, 26.0, 26.0, 25.9, 25.9.

HRMS (ESI–TOF) calcd for $C_{34}H_{50}N_3O_3^+$([M+H$^+$]) = 548.3847, Found 548.3847.

Tert-butyl-2-(tert-butyl)-2'-oxo-3-(phenethylamino)-4-(phenethylimino)spiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5oa

The reaction was run at rt for 14 h, affording product **5oa** in 66% yield (37.2 mg) as a yellow solid. R_f = 0.5 (PE:EA = 5:1), m.p. 121–123 ℃.



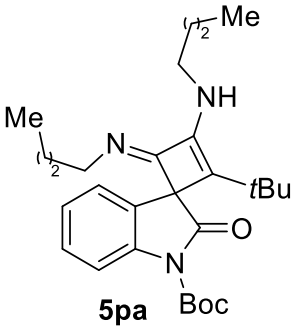
5oa

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.31 (m, 3H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.17 (t, *J* = 7.0 Hz, 2H), 7.15 – 7.10 (m, 3H), 6.84 (d, *J* = 7.2 Hz, 2H), 3.83 – 3.76 (m, 1H), 3.75 – 3.69 (m, 2H), 3.14 – 3.08 (m, 1H), 2.93 – 2.89 (m, 2H), 2.88 – 2.85 (m, 1H), 2.70 – 2.63 (m, 1H), 2.46 (ddd, *J* = 16.3, 10.1, 6.3 Hz, 1H), 1.64 (s, 9H), 0.92 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 154.3, 149.4, 146.0, 139.8, 139.3, 138.7, 132.3, 129.2, 128.8, 128.6, 128.5, 128.5, 128.1, 126.3, 125.8, 124.4, 123.5, 115.2, 84.1, 65.3, 54.1, 45.8, 37.7, 36.9, 34.4, 29.0, 28.1.

HRMS (ESI–TOF) calcd for $C_{36}H_{42}N_3O_3^+$([M+H$^+$]) = 564.3221, Found 564.3223.

Tert-butyl-2-(tert-butyl)-3-(butylamino)-4-(butylimino)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5pa



5pa

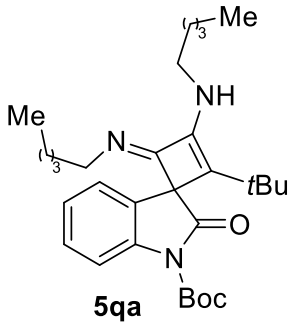
The reaction was run at rt for 14 h, affording product **5pa** in 84% yield (39.3 mg) as a yellow solid. R_f = 0.6 (PE:EA = 5:1), m.p. 108–109 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.22 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.14 – 7.10 (m, 1H), 3.63 (t, *J* = 6.3 Hz, 1H), 3.51 – 3.44 (m, 2H), 2.78 – 2.71 (m, 1H), 2.68 – 2.62 (m, 1H), 1.63 (s, 9H), 1.60 – 1.43 (m, 3H), 1.39 (h, *J* = 7.4 Hz, 2H), 1.35 – 1.06 (m, 4H), 1.06 – 1.00 (m, 3H), 0.98 (s, 9H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.67 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 153.7, 149.7, 146.6, 138.7, 130.9, 128.9, 128.4, 124.2, 123.4, 115.0, 83.9, 65.6, 51.6, 44.7, 34.2, 33.6, 32.4, 29.3, 28.1, 20.3, 19.8, 13.8, 13.6.

HRMS (ESI–TOF) calcd for $C_{28}H_{42}N_3O_3^+$([M+H$^+$]) = 468.3221, Found 468.3212.

Tert-butyl-2-(tert-butyl)-2'-oxo-3-(pentylamino)-4-(pentylimino)spiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5qa



5qa

The reaction was run at rt for 14 h, affording product **5qa** in 73% yield (36.2 mg) as a yellow solid. R_f = 0.6 (PE:EA = 5:1), m.p. 111–113 ℃.

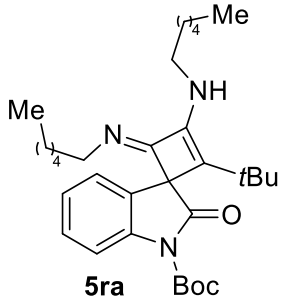
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.28 (td, *J* = 7.8, 1.4 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.11 (td, *J* = 7.5, 1.0 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 1H), 3.46 (q, *J* = 6.8 Hz, 2H), 2.76 (ddd, *J* = 11.9, 7.6, 6.7 Hz, 1H), 2.66 – 2.60 (m, 1H), 1.63 (s, 9H), 1.60 – 1.52 (m, 2H), 1.43 –

1.15 (m, 8H), 1.13 – 1.00 (m, 4H), 0.99 (s, 9H), 0.98 – 0.94 (m, 2H), 0.93 – 0.89 (m, 3H), 0.75 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 153.7, 149.7, 146.6, 138.7, 130.9, 128.9, 128.4, 124.1, 123.4, 115.0, 83.9, 65.6, 52.0, 45.0, 34.2, 31.2, 30.0, 29.5, 29.3, 28.8, 28.1, 22.4, 22.2, 14.0, 13.9.

HRMS (ESI–TOF) calcd for $C_{30}H_{46}N_3O_3^+$([M+H$^+$]) = 496.3534, Found 496.3527.

Tert-butyl-2-(tert-butyl)-3-(hexylamino)-4-(hexylimino)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ra



5ra

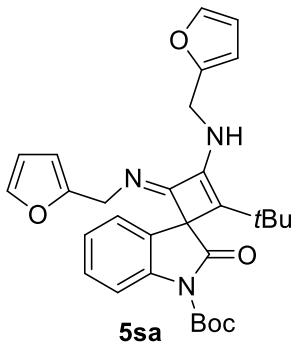
The reaction was run at rt for 14 h, affording product **5ra** in 72% yield (37.8 mg) as a yellow solid. R_f = 0.6 (PE:EA = 5:1), m.p. 117–118 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.24 – 7.21 (m, 1H), 7.11 (td, *J* = 7.5, 1.0 Hz, 1H), 3.67 – 3.61 (m, 1H), 3.49 – 3.43 (m, 2H), 2.80 – 2.74 (m, 1H), 2.67 – 2.59 (m, 1H), 1.63 (s, 9H), 1.59 – 1.52 (m, 2H), 1.46 – 1.23 (m, 10H), 1.21 – 1.11 (m, 4H), 1.07 – 0.99 (m, 4H), 0.99 (s, 9H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.79 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 153.7, 149.7, 146.6, 138.7, 131.0, 128.9, 128.4, 124.1, 123.4, 115.0, 83.9, 65.6, 52.0, 45.1, 34.3, 31.6, 31.5, 31.4, 30.3, 29.3, 28.1, 26.9, 26.3, 22.6, 22.5, 14.0, 13.9.

HRMS (ESI–TOF) calcd for $C_{32}H_{50}N_3O_3^+$([M+H$^+$]) = 524.3847, Found 524.3842.

Tert-butyl-2-(tert-butyl)-3-((furan-2-ylmethyl)amino)-4-((furan-2-ylmethyl)imino)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5sa



5sa

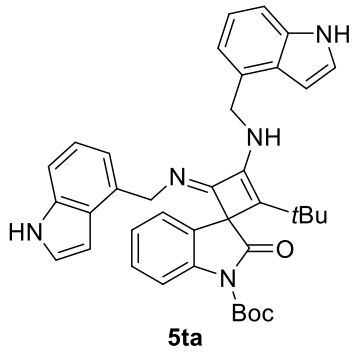
The reaction was run at rt for 14 h, affording product **5sa** in 51% yield (26.3 mg) as a yellow solid. R_f = 0.3 (PE:EA = 4:1), m.p. 68–69 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.32 (td, *J* = 7.9, 1.5 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.18 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.14 (td, *J* = 7.4, 1.0 Hz, 1H), 6.34 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.25 – 6.22 (m, 1H), 6.19 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.82 – 5.78(m, 1H), 4.77 (dd, *J* = 15.4, 7.4 Hz, 1H), 4.56 (dd, *J* = 15.5, 5.6 Hz, 1H), 4.02 (t, *J* = 7.7 Hz, 1H), 4.00 (s, 1H), 3.79 (d, *J* = 14.8 Hz, 1H), 1.64 (s, 9H), 0.98 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 155.6, 153.6, 152.2, 149.5, 145.9, 141.9, 141.5, 138.7, 135.1, 128.9, 127.8, 124.4, 123.7, 115.2, 110.3, 110.1, 107.0, 106.6, 84.3, 65.4, 48.5, 42.0, 34.5, 29.1, 28.1.

HRMS (ESI–TOF) calcd for $C_{30}H_{34}N_3O_5^+$([M+H$^+$]) = 516.2493, Found 516.2491.

Tert-butyl-3-(((1H-indol-4-yl)methyl)amino)-4-(((1H-indol-4-yl)methyl)imino)-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ta



5ta

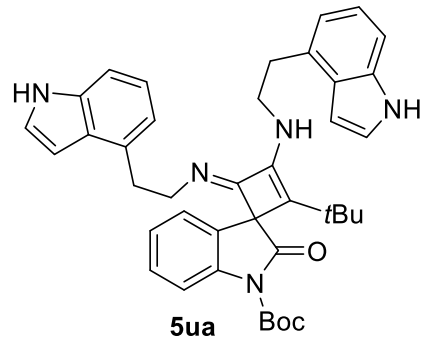
The reaction was run at rt for 14 h, affording product **5ta** in 73% yield (44.8 mg) as a yellow solid. R_f = 0.4 (PE:EA = 2:1), m.p. 99–100 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.16 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.26 – 7.24 (m, 1H), 7.20 – 7.06 (m, 5H), 7.02 – 6.99 (m, 1H), 6.99 – 6.94 (m, 1H), 6.70 – 6.61 (m, 2H), 6.37 – 6.33 (m, 1H), 5.09 – 4.96 (m, 2H), 4.41 (d, *J* = 14.6 Hz, 1H), 4.13 (d, *J* = 14.7 Hz, 1H), 4.04 (t, *J* = 6.0 Hz, 1H), 1.65 (s, 9H), 0.98 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 154.3, 149.6, 146.7, 138.8, 136.0, 135.7, 131.9, 131.9, 131.0, 128.7, 128.7, 126.6, 126.6, 124.5, 124.4, 123.8, 123.7, 121.8, 121.8, 118.8, 118.7, 115.2, 110.5, 109.8, 101.1, 100.9, 84.3, 65.9, 53.8, 53.5, 47.7, 34.5, 29.3, 28.2.

HRMS (ESI–TOF) calcd for $C_{38}H_{40}N_5O_3^+$([M+H$^+$]) = 614.3126, Found 614.3129.

Tert-butyl-3-((2-(1H-indol-4-yl)ethyl)amino)-4-((2-(1H-indol-4-yl)ethyl)imino)-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 5ua



5ua

The reaction was run at rt for 14 h, affording product **5ua** in 84% yield (55.2 mg) as a yellow solid. R_f = 0.4 (PE:EA = 2:1), m.p. 98–99 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.25 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.25 – 7.11 (m, 5H), 7.07 – 7.03 (m, 2H), 7.03 – 6.97 (m, 1H), 6.75 – 6.71 (m, 1H), 6.56 (d, *J* =

7.7 Hz, 1H), 6.31 – 6.25 (m, 1H), 3.98 – 3.90 (m, 2H), 3.78 (t, *J* = 6.6 Hz, 1H), 3.28 (td, *J* = 10.9, 4.8 Hz, 1H), 3.22 (t, *J* = 6.5 Hz, 2H), 3.15 – 2.97 (m, 2H), 2.87 – 2.77 (m, 1H), 1.63 (s, 9H), 0.88 (s, 9H).

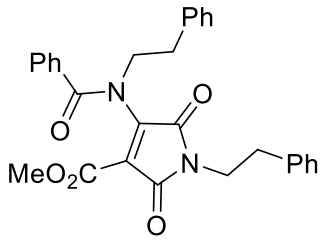
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 154.2, 149.5, 146.3, 138.7, 136.0, 135.6, 132.2, 131.9, 131.3, 128.7, 128.6, 127.6, 127.4, 124.4, 124.1, 123.7, 123.6, 122.0, 121.9, 120.2, 119.5, 115.3, 109.6, 109.1, 101.1, 100.9, 84.2, 65.4, 53.5, 45.2, 35.4, 34.6, 34.5, 29.1, 28.2.

HRMS (ESI–TOF) calcd for $C_{40}H_{44}N_5O_3^+$([M+H$^+$]) = 642.3439, Found 642.3442.

7. General procedure and spectral data of products 6

A dry reaction tube was charged with isocyanide **1** (0.2 mmol, 2 equiv.) $Y(OTf)_3$ (10 mol%) and alkylidene malonates **2** (0.1 mmol, 1 equiv.), Et_2O (0.5 mL) was added. The reaction mixture continued stirring at rt for 14 h. The residue was directly purified by flash chromatography on silica gel using petroleum ether/ethyl acetate= 10/1 as eluent to afford the desired products **3**. Then **3** was smoothly transformed through a second silica gel column chromatography by using petroleum ether/ethyl acetate = 8/1 as the eluent, thus affording the desired products **6.**

Methyl 2,5-dioxo-1-phenethyl-4-(N-phenethylbenzamido)-2,5-dihydro-1H-pyrrole-3-carboxy late 6a



6a

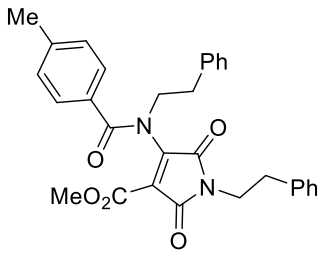
The reaction was run at rt, affording product **6a** in 40% yield (19.3 mg) as a yellow solid. R_f = 0.2 (PE:EA = 2:1), m.p. 109–110℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 3H), 7.34 – 7.26 (m, 4H), 7.25 – 7.11 (m, 8H), 4.33 (t, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.63 (t, *J* = 7.3 Hz 2H), 3.05 (t, *J* = 7.1 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 165.2, 165.0, 160.2, 149.2, 138.1, 137.4, 134.3, 132.0, 129.4, 128.7, 128.6, 128.6, 128.4, 128.3, 126.9, 126.8, 114.7, 52.3, 51.2, 39.4, 35.5, 34.1.

HRMS (ESI–TOF) calcd for $C_{29}H_{27}N_2O_5^+$ ([M+H$^+$]) = 483.1915, Found 483.1965.

Methyl 4-(4-methyl-N-phenethylbenzamido)-2,5-dioxo-1-phenethyl-2,5-dihydro-1H-pyrrole-3-carboxylate 6b



6b

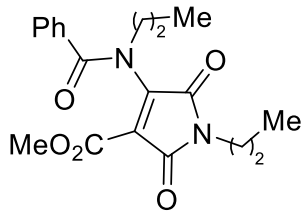
The reaction was run at rt, affording product **6b** in 54% yield (26.8 mg) as a yellow solid. R_f = 0.2 (PE:EA = 2:1), m.p. 112–114 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 7.24 – 7.17 (m, 5H), 7.17 – 7.13 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 2H) , 4.32 (t, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.63 (t, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 165.3, 165.1, 160.2, 149.4, 142.8, 138.1, 137.5, 131.4, 129.4, 129.1, 128.7, 128.7, 128.6, 128.4, 126.8, 126.8, 114.2, 52.3, 51.1, 39.4, 35.6, 34.2, 21.5.

HRMS (ESI–TOF) calcd for $C_{30}H_{29}N_2O_5^+$ ([M+H$^+$]) = 497.2071, Found 497.2073.

Methyl 1-butyl-4-(N-butylbenzamido)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carboxylate 6c



6c

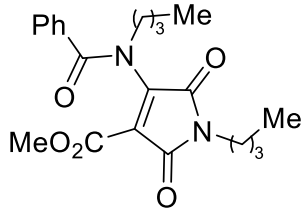
The reaction was run at rt, affording product **6c** in 41% yield (15.8 mg) as a yellow solid. R_f = 0.2 (PE:EA = 2:1), m.p. 80–82 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)δ 7.52 – 7.47 (m, 2H), 7.46 – 7.39 (m, 1H), 7.37 – 7.27 (m, 2H), 4.02 (t, *J* = 7.6, 2H), 3.81 (s, 3H), 3.46 (t, *J* = 7.0 Hz, 2H), 1.76 – 1.57 (m, 3H), 1.52 – 1.26 (m, 6H), 1.20 – 1.03 (m, 3H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 165.6, 165.6, 160.4, 149.3, 135.3, 131.8, 128.6, 128.4, 115.6, 52.5, 49.7, 38.2, 30.8, 30.1, 20.0, 19.6, 13.6, 13.4.

HRMS (ESI–TOF) calcd for $C_{21}H_{27}N_2O_5^+$ ([M+H$^+$]) = 387.1915, Found. 387.1916.

Methyl 2,5-dioxo-1-pentyl-4-(N-pentylbenzamido)-2,5-dihydro-1H-pyrrole-3-carboxylate 6d



6d

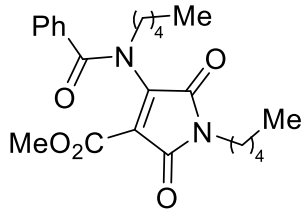
The reaction was run at rt, affording product **6d** in 49% yield (20.3 mg) as a yellow solid. R_f = 0.2 (PE:EA = 2:1), m.p. 90–91 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.45 – 7.40 (m, 1H), 7.36 – 7.30 (m, 2H), 4.01 (t, *J* = 7.6 Hz 2H), 3.80 (s, 3H), 3.45 (t, *J* = 7.1 Hz, 2H), 1.76 – 1.64 (m, 2H), 1.50 – 1.40 (m, 2H), 1.36 – 1.27 (m, 7H), 1.25 – 1.20 (m, 1H), 1.14 – 1.05 (m, 2H), 0.90 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 165.6, 165.6, 160.4, 149.3, 135.2, 131.9, 128.6, 128.4, 115.6, 52.5, 49.9, 38.5, 28.9, 28.5, 28.4, 27.7, 22.2, 22.1, 13.9, 13.8.

HRMS (ESI–TOF) calcd for $C_{23}H_{31}N_2O_5^+$ ([M+H$^+$]) = 415.2228, Found 415.2224.

Methyl 1-hexyl-4-(N-hexylbenzamido)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carboxylate 6e



6e

The reaction at rt , affording product **6e** in 50% yield (22.1 mg) as a yellow solid. R_f = 0.3 (PE:EA = 2:1), m.p. 108–110 ℃.

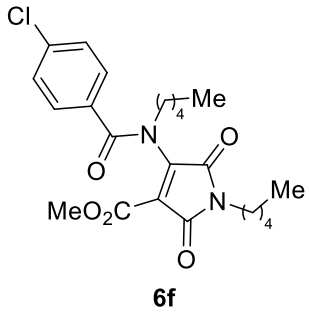
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.45 – 7.40 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 4.04 – 3.98 (m, 2H), 3.80 (s, 3H), 3.45 (t, *J* = 7.1 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.50 – 1.41 (m, 2H), 1.38 – 1.28 (m, 6H), 1.26 – 1.21 (m, 4H), 1.17 – 1.09 (m, 2H), 0.90 – 0.84 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 165.6, 165.6, 160.4, 149.3, 135.2, 131.9, 128.6, 128.4, 115.6, 52.5, 49.9, 38.5, 31.3, 31.2, 28.7, 28.0, 26.4, 26.1, 22.5, 22.4, 13.9, 13.9.

HRMS (ESI–TOF) calcd for $C_{25}H_{35}N_2O_5^+$ ([M+H$^+$]) = 443.2541, Found 443.2537.

Methyl 4-(4-chloro-N-hexylbenzamido)-1-hexyl-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-car

boxylate 6f



6f

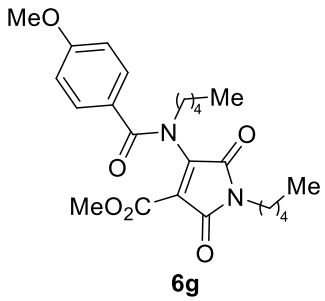
The reaction was run at rt, affording product **6f** in 35% yield (16.7 mg) as a yellow solid. R_f = 0.2 (PE:EA = 2:1), m.p. 120–121 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 3.98 (t, *J* = 7.6 Hz 2H), 3.82 (s, 3H), 3.46 (t, *J* = 7.0 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.50 – 1.41 (m, 3H), 1.37 (d, *J* = 3.6 Hz, 1H), 1.34 – 1.27 (m, 8H), 1.17 – 1.08 (m, 3H), 0.89 – 0.85 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$)δ 170.0, 165.5, 165.4, 160.4, 149.1, 138.2, 133.8, 129.9, 128.8, 115.7, 52.6, 50.1, 38.6, 31.3, 31.1, 28.6, 28.0, 26.4, 26.1, 22.4, 22.4, 13.9, 13.9.

HRMS (ESI–TOF) calcd for $C_{25}H_{34}ClN_2O_5^+$ ([M+H$^+$]) = 477.2151, Found 477.2148.

Methyl 1-hexyl-4-(N-hexyl-4-methoxybenzamido)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbo xylate 6g



6g

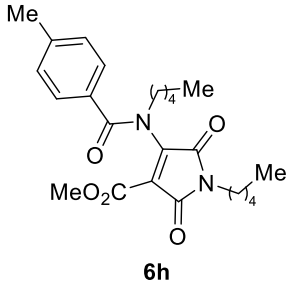
The reaction was run at rt, affording product **6g** in 52% yield (24.4 mg) as a yellow solid. R_f = 0.2 (PE:EA = 2:1), m.p. 98–100 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dt, *J* = 8.8, 2.0 Hz, 2H), 6.87 – 6.80 (m, 2H), 4.02 (t, *J* = 7.6 Hz 2H), 3.82 (d, *J* = 4.0 Hz, 6H), 3.48 (t, *J* = 7.1 Hz, 2H), 1.75 – 1.67 (m, 2H), 1.53 – 1.44 (m, 3H), 1.41 – 1.38 (m, 1H), 1.31 (s, 7H), 1.26 – 1.21 (m, 3H), 1.20 – 1.12 (m, 2H), 0.92 – 0.85 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$)δ 170.8, 165.9, 165.7, 162.6, 160.5, 149.8, 130.7, 127.5, 113.8, 55.4, 52.4, 50.0, 38.5, 31.3, 31.2, 29.7, 28.7, 28.1, 26.4, 26.1, 22.5, 22.4, 13.9, 13.9.

HRMS (ESI–TOF) calcd for $C_{26}H_{37}N_2O_6^+$ ([M+H$^+$]) = 473.2647, Found 473.2642.

Methyl 1-hexyl-4-(N-hexyl-4-methylbenzamido)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carboxyl ate 6h



6h

The reaction was run at rt, affording product **6h** in 55% yield (23.4 mg) as a yellow solid. R_f = 0.2 (PE:EA = 2:1), m.p 100–102 ℃.

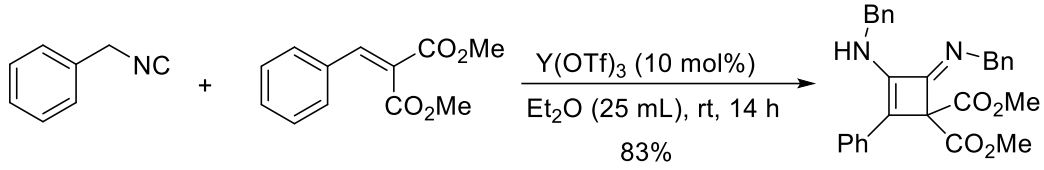
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.00 (t, 7.7 Hz, 2H), 3.79 (s, 3H), 3.46 (t, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.72 – 1.64 (m, 2H), 1.50 – 1.41 (m, 3H), 1.35 – 1.28 (m, 6H), 1.25 – 1.20 (m, 3H), 1.17 – 1.10 (m, 2H), 0.89 – 0.85 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 165.7, 160.4, 149.5, 142.6, 132.4, 129.1, 128.6, 115.0, 52.4, 49.9, 38.5, 31.3, 31.2, 28.7, 28.1, 26.4, 26.1, 22.5, 22.4, 21.5, 13.9, 13.9.

HRMS (ESI−TOF) calcd for $C_{26}H_{37}N_2O_5^+$ ([M+H$^+$]) = 457.2697, Found 457.2694.

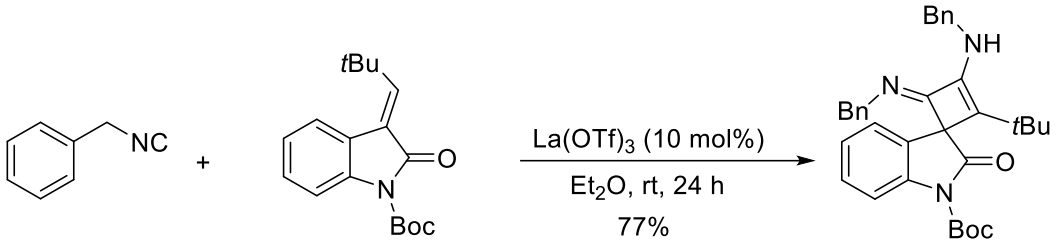
8. Experimental procedure for the scale-up reaction and transformations of the products

a) Scale-up of the reaction



1a (10 mmol) **2a** (5 mmol) **3aa**

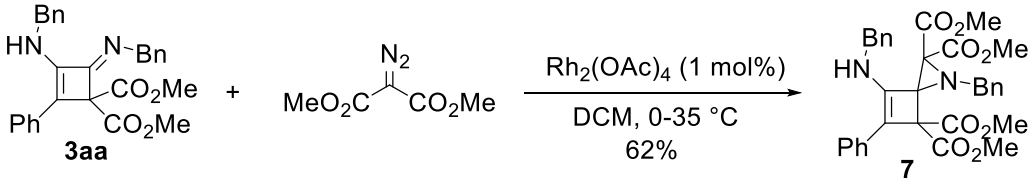
Procedure: The **1a** (10 mmol, 1.17 g), **2a** (5 mmol, 1.10 g) and $Y(OTf)_3$ (10 mol%) was added into a dry round bottle, then anhydrous ether (25 mL) was added. The reaction mixture was stirred at room temperature for 14 h. TLC monitored that the reaction was complete. The solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography to obtain product **3aa** in 83% yield (petroleum ether/ethyl acetate=10:1).



1a (8 mmol) **4a** (4 mmol) **5aa**

Procedure: The **1a** (8 mmol, 0.93 g), **4a** (4 mmol, 1.20 g) and $La(OTf)_3$ (10 mol%) was added into a dry round bottle, then anhydrous ether (20 mL) was added. The reaction mixture was stirred at room temperature for 24 h. TLC monitored that the reaction was complete. The solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography to obtain product **5aa** in 77% yield (petroleum ether/ethyl acetate=5:1).

b) [2+1] cycloaddition reaction

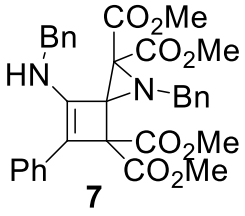


3aa **7**

Procedure: To a dry reaction tube was added **3aa** (0.1 mmol, 45 mg) and rhodium acetate dimer (1 mol%, 0.4 mg), then CH_2Cl_2 (0.5 mL) was added. The reaction mixture was stirred at 0 °C for 10 minutes under N_2. Next, a solution of dimethyl diazomalonate (0.2 mmol, 31.6 mg) in CH_2Cl_2 (0.5 ml) was dropped into the reaction mixture, the reaction mixture was stirred at 35 °C for 20 h. After the starting material was consumed, saturated $NaHCO_3$ aqueous solution was added to quench the reaction, the residue was diluted with ethyl acetate, washed with water, dried over anhydrous Na_2SO_4, and the solvent was removed in

vacuo. The crude product was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as eluent to afford the desired product **7** in 62% yield.

Tetramethyl 1-benzyl-6-(benzylamino)-5-phenyl-1-azaspiro[2.3]hex-5-ene-2,2,4,4-tetracar boxylate 7



7

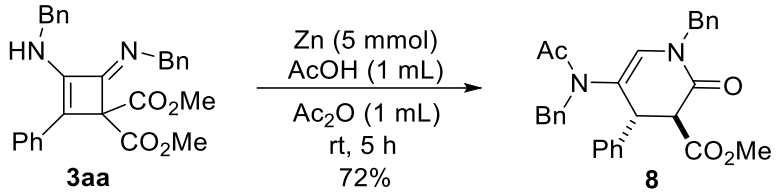
The reaction was run at 35 ℃ for 20 h, affording product **7** in 62% yield (36.1 mg) as a white solid. R_f = 0.3 (PE:EA = 3:1), m.p. 79–81 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.20 – 7.15 (m, 5H), 7.15 – 7.08 (m, 3H), 7.03 (d, *J* = 6.1 Hz, 2H), 6.30 (s, 1H), 4.77 (s, 2H), 4.61 (s, 2H), 3.63 (d, *J* = 1.9 Hz, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 167.5, 151.7, 145.5, 139.6, 136.9, 131.8, 128.7, 128.1, 127.8, 127.7, 127.2, 127.0, 126.6, 126.5, 124.4, 69.7, 64.1, 55.3, 52.6, 51.9.

HRMS (ESI–TOF) calcd for $C_{33}H_{33}N_2O_8^+$ ([M+H$^+$]) = 585.2232, Found 585.2232.

c) Reductive ring expansion reaction

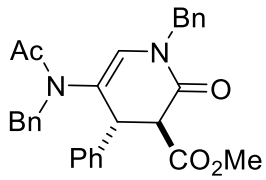


3aa
(0.1 mmol)

8

Procedure: To a dry round-bottom flask was added **3aa** (0.1 mmol, 45 mg) under nitrogen, then AcOH (1 mL) and Ac_2O (1 mL) was added. Next, activated Zn powder (5 mmol, 32.6 mg) was slowly added to the reaction mixture. The reaction mixture was stirred at room temperature for 5 hours. The reaction was monitored by TLC, after the starting material was competed, the precipitate was filtered out and the solvent was removed under reduced pressure. Saturated $NaHCO_3$ aqueous solution was added to the mixture to adjust the pH of the solution to 8.0-9.0. The solution was then diluted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as eluent to afford the product **8** in 72% yield.

Methyl 6-(N-benzylacetamido)-5-(benzylamino)-2-oxo-4-phenyl-5,6-dihydro-2H-pyran-3-car boxylate 8



8

The reaction was run at rt for 5 h, affording product **8** in 72% yield (33.7 mg) as a white solid. R_f = 0.4 (PE:EA = 3:1), m.p. 68–70 °C.

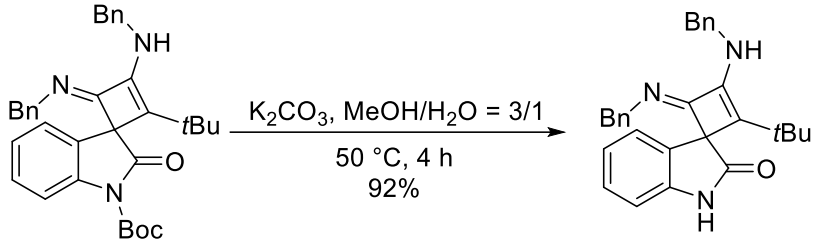
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 6H), 7.21 – 7.16 (m, 5H), 7.08 – 7.02 (m, 2H), 6.96 – 6.89 (m, 2H), 5.43 (d, *J* = 1.8 Hz, 1H), 4.85 (d, *J* = 15.5 Hz,

1H), 4.64 (d, *J* = 15.4 Hz, 1H), 4.55 (d, *J* = 14.0 Hz, 1H), 4.33 – 4.30 (m, 1H), 3.83 (s, 3H), 3.68 (d, *J* = 3.1 Hz, 1H), 3.51 (d, *J* = 14.0 Hz, 1H), 1.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 169.4, 168.7, 145.1, 139.7, 136.8, 134.5, 129.3, 128.9, 128.7, 128.4, 128.2, 128.0, 127.3, 127.1, 126.9, 107.6, 56.3, 53.3, 50.5, 44.8, 44.4, 21.6.

HRMS (ESI-TOF) calcd for $C_{29}H_{29}N_2O_4^+$ ([M+H$^+$]) = 469.2122, Found 469.2121.

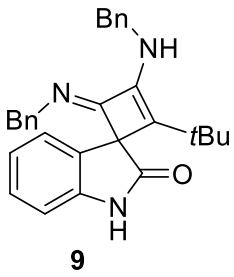
d) Deprotection reaction



5aa **9**

Procedure: The **5aa** (0.1 mmol, 53.5 mg), potassium carbonate (0.25 mmol, 34.5 mg) and methanol/water = 3/1 (1 mL) was added to a round bottom flask. After the reaction mixture was stirred at 50 ℃ for 4 h, the solution was concentrated under reduced pressure. The crude product was purified by column chromatography with petroleum ether/ethyl acetate = 2/1 as eluent to afford the product **9** in 92% yield.

3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)spiro[cyclobutane-1,3'-indolin]-2-en-2'-one 9



9

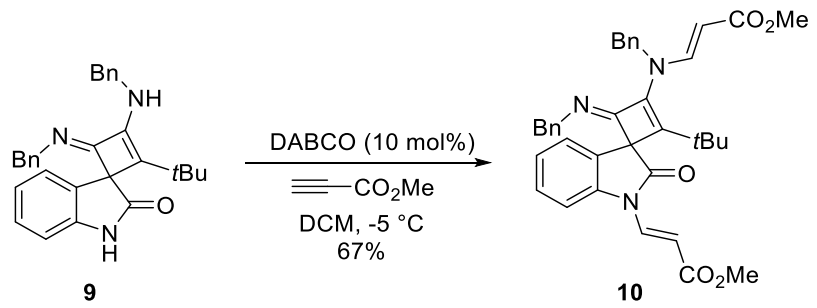
Yellow solid. R_f = 0.3 (PE:EA = 2:1), m.p. 151–152 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.49 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.24 (td, *J* = 7.7, 1.3 Hz, 1H), 7.15 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.13 – 7.06 (m, 3H), 7.00 (td, *J* = 7.5, 1.0 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.95 – 6.92 (m, 2H), 4.87 (dd, *J* = 14.7, 7.2 Hz, 1H), 4.68 (dd, *J* = 14.7, 5.8 Hz, 1H), 4.07 (dd, *J* = 14.5, 3.1 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.86 (dd, *J* = 14.3, 2.4 Hz, 1H), 1.02 (d, *J* = 2.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 180.1, 155.1, 145.5, 140.6, 140.0, 139.2, 133.0, 129.6, 128.5, 127.9, 127.6, 127.6, 127.1, 126.4, 123.9, 122.4, 110.4, 65.6, 55.3, 49.0, 34.7, 29.1.

HRMS (ESI–TOF) calcd for $C_{29}H_{30}N_3O^+$([M+H$^+$]) = 436.2384, Found 436.2380.

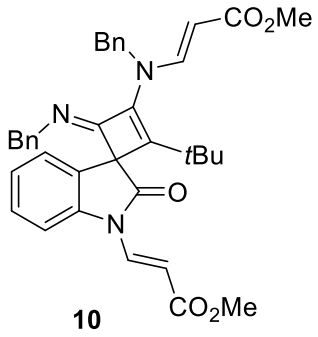
e) Addition reaction



9 **10**

Procedure: The compound **9** (0.1 mmol, 43.6 mg) was dissolved in CH_2Cl_2 (1 mL). DABCO (0.01 mmol, 1.2 mg) was added, the reaction mixture was cooled down to -5 ℃. Then methyl propionate (0.25 mmol, 21 mg) was slowly added, the reaction mixture continued to stir at -5 ℃ for 0.5 h. The solution was concentrated under reduced pressure. The crude product was purified by column chromatography with petroleum ether/ethyl acetate = 4/1 as eluent to afford the product **10** in 67% yield.

methyl-3-(-3-(benzyl(-3-methoxy-3-oxoprop-1-en-1-yl)amino)-4-(benzylimino)-2-(tert-butyl)-2'-oxospiro[cyclobutane-1,3'-indolin]-2-en-1'-yl)acrylate 10



10

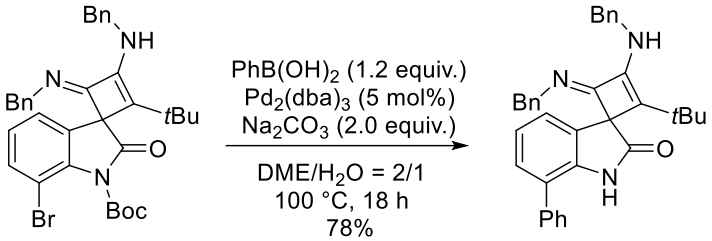
Yellow solid. R_f = 0.2 (PE:EA = 4:1), m.p. 121−123 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 14.5 Hz, 1H), 7.58 (d, *J* = 12.2 Hz, 1H), 7.42 – 7.33 (m, 5H), 7.32 – 7.26 (m, 2H), 7.21 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.18 – 7.10 (m, 4H), 6.90 – 6.86 (m, 2H), 6.78 (d, *J* = 14.5 Hz, 1H), 5.67 (d, *J* = 12.2 Hz, 1H), 4.85 – 4.68 (ddd, *J* = 35.1, 14.8, 6.8 Hz, 2H), 4.07 (t, *J* = 6.5 Hz, 1H), 4.00 (d, *J* = 14.3 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 1H), 3.74 (s, 3H), 0.98 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 168.2, 166.3, 157.3, 154.1, 146.2, 140.5, 139.4, 138.8, 134.1, 132.8, 129.1, 128.9, 128.5, 128.0, 127.5, 127.2, 126.6, 124.5, 124.3, 110.3, 105.7, 104.0, 64.9, 55.5, 51.5, 49.0, 34.5, 29.1.

HRMS (ESI–TOF) calcd for $C_{37}H_{38}N_3O_5^+$([M+H$^+$]) = 604.2806, Found 604.2806.

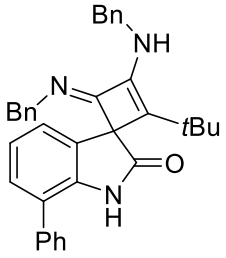
f) Suzuki coupling reaction



5am **11**

Procedure: A dry reaction tube was charged with **5am** (0.1 mmol, 61.4 mg), sodium carbonate (0.2 mmol, 21.2 mg), $Pd_2(dba)_3$ (5 mol%, 4.6 mg) and phenylboronic acid (0.12 mmol, 14.6 mg) under nitrogen. After adding ethylene glycol dimethyl ether/H_2O (2.3 mL, 2/1), the reaction mixture was placed at 100 °C and stirred for 18 h. The solution was concentrated under reduced pressure. The crude product was purified by column chromatography with petroleum ether/ethyl acetate = 2/1 as eluent to afford the product **11** in 78% yield.

3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-7'-phenylspiro[cyclobutane-1,3'-indolin]-2-en-2'-one 11



11

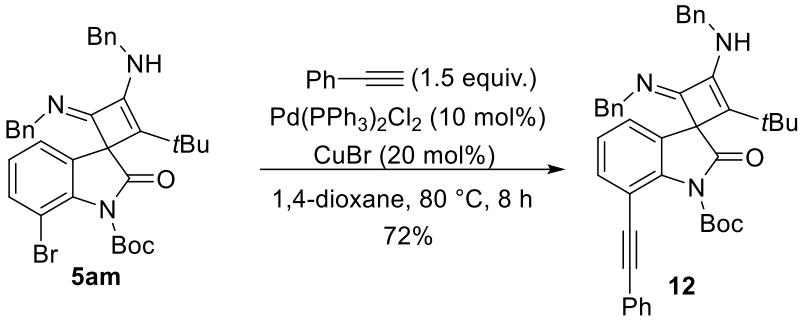
Yellow solid. R_f = 0.3 (PE:EA = 2:1), m.p. 109–111 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.52 – 7.45 (m, 4H), 7.42 – 7.34 (m, 5H), 7.33 – 7.27 (m , 2H), 7.19 – 7.12 (m, 4H), 7.08 (t, J = 7.5 Hz, 1H), 7.00 – 6.96 (m, 2H), 4.86 (dd, J = 14.6, 6.9 Hz, 1H), 4.71 (dd, J = 14.7, 5.7 Hz, 1H), 4.17 (d, J = 14.4 Hz, 1H), 4.03 (t, J = 6.4 Hz, 1H), 3.94 (d, J = 14.4 Hz, 1H), 1.07 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 155.0, 145.6, 140.6, 139.3, 137.4, 137.0, 132.8, 130.1, 129.2, 128.8, 128.5, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.1, 126.5, 124.2, 123.1, 122.9, 65.7, 55.3, 49.0, 34.7, 29.2.

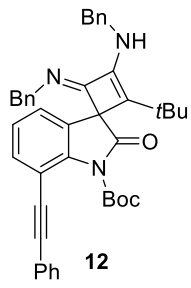
HRMS (ESI–TOF) calcd for $C_{35}H_{34}N_3O^+$([M+H$^+$]) = 512.2697, Found 512.2696.

g) Sonogashira coupling reaction



Procedure: A dry reaction tube was charged with **5am** (0.1 mmol, 61.4 mg), phenylacetylene (0.15 mmol, 15.3 mg), bis (triphenylphosphine) palladium dichloride (0.01 mmol, 7.0 mg) and copper bromide (0.02 mmol, 3 mg) under nitrogen. The 1,4-dioxane (1 mL) was added. Then the reaction mixture was stirred at 80 ℃ for 8 h. The solution was concentrated under reduced pressure. The crude product was purified by column chromatography with petroleum ether/ethyl acetate = 4/1 as eluent to afford the product **12** in 72% yield.

tert-butyl -3-(benzylamino)-4-(benzylimino)-2-(tert-butyl)-2'-oxo-7'-(phenylethynyl)spiro [cyclobutane-1,3'-indolin]-2-ene-1'-carboxylate 12



12

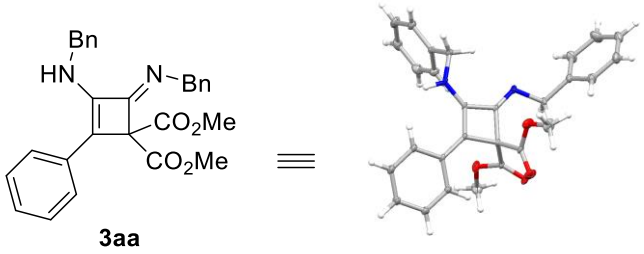
Brown solid. R_f = 0.4 (PE:EA = 5:1), m.p. 87–88 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.32 (m, 5H), 7.31 – 7.27 (m, 2H), 7.26 (s, 1H), 7.18 – 7.11 (m, 4H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.96 (d, *J* = 7.9 Hz, 3H), 4.80 – 4.71 (m, 2H), 4.09 (d, *J* = 14.4 Hz, 1H), 4.02 (t, *J* = 6.6 Hz, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 1.58 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 153.7, 148.4, 146.2, 140.4, 138.9, 137.8, 133.3, 132.3, 132.0, 128.6, 128.0, 127.6, 127.5, 127.2, 126.5, 125.3, 122.5, 107.0, 85.3, 66.1, 55.9, 49.0, 34.5, 29.2, 27.7.

HRMS (ESI–TOF) calcd for $C_{42}H_{42}N_3O_3^+$([M+H$^+$]) =636.3221, Found 636.3215.

9. X-ray crystallographic data of 3aa, 5aa and 6a



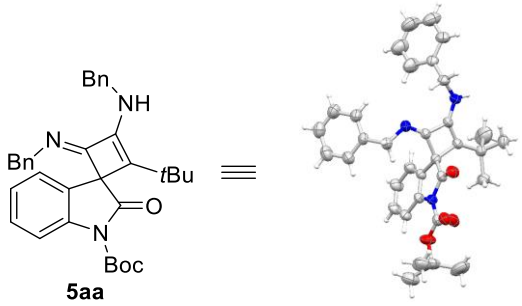
3aa ≡ CCDC 2299398

The single crystal for compound **3aa** was obtained by vaporization of a mixture solvent of Petroleum ether and ethyl acetate (v/v = 2:1). The data were collected on a Xcalibur Eos diffractometer equipped with MoKα X-ray sources (λ =1.54178 Å).

X-ray derived ORTEP of **3aa** with thermal ellipsoids shown at the 30% probability level.

Structure deposited at the Cambridge Crystallographic Data Centre. CCDC 2299398 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures/.

Empirical formula	$C_{28}H_{26}N_2O_4$
Formula weight	454.51
Temperature/K	173(2)
Crystal system	orthorhombic
Space group	Pna2(1)
a/Å	21.1225(6)
b/Å	13.4659(3)
c/Å	8.2008(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2332.58(10)
Z	4
ρ_{calc}g/cm^3	1.294
μ/mm^{-1}	0.702
F(000)	960
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	CuK\a (λ = 1.54178)
2Θ range for data collection/°	7.786 to 136.542
Index ranges	-23 ≤ h ≤ 25, -14 ≤ k ≤ 16, -8≤ l ≤ 9
Reflections collected	11968
Independent reflections	3457 [R_{int} = 0.0729, R_{sigma} = 0.0671]
Data/restraints/parameters	3457/2/313
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0727, wR_2 = 0.1559
Final R indexes [all data]	R_1 = 0.0841, wR_2 = 0.1657
Largest diff. peak/hole/e Å^{-3}	0.32/-0.34



5aa

CCDC 2335282

The single crystal for compound **5aa** was obtained by vaporization of a mixture solvent of ethyl acetate and petroleum ether (v/v = 1:10). The data were collected on a Xcalibur Eos diffractometer equipped with MoKα X-ray sources (λ = 1.54178 Å).

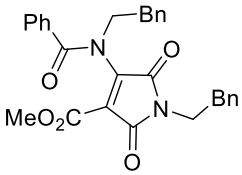
X-ray derived ORTEP of **5aa** with thermal ellipsoids shown at the 30% probability level.

Structure deposited at the Cambridge Crystallographic Data Centre. CCDC 2335282 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures/.

Crystal data and structure refinement for CCDC 2335282

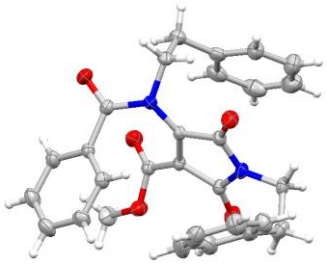
Empirical formula	$C_{34}H_{37}N_3O_3$
Formula weight	536.66
Temperature/K	290.00
Crystal system	Monoclinic
Space group	P121/c1
a/Å	12.9218(6)
b/Å	9.7348(5)
c/Å	24.6695(12)
α/°	90
β/°	91.204(3)
γ/°	90
Volume/Å^3	3102.5(3)
Z	4
ρcalcg/cm^3	1.147
μ/mm^{-1}	0.582
F(000)	1144.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 1.54178)
2Θ range for `1data collection/°	6.842 to 136.806
Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 9, -29 ≤ l ≤ 29
Reflections collected	5652
Independent reflections	22284 [Rint = 0.1247, Rsigma = 0.1063]
Data/restraints/parameters	5652/78/395
Goodness-of-fit on F^2	1.142
Final R indexes [I>=2σ (I)]	R^1 = 0.0973, wR^2 = 0.2789
Final R indexes [all data]	R^1 = 0.2098, wR^2 = 0.3638

Largest diff. peak/hole/e $Å^{-3}$	0.34/-0.34



6a

≡



CCDC 2335281

The single crystal for compound **6a** was obtained by vaporization of a mixture solvent of petroleum ether and ethyl acetate (v/v = 2:1). The data were collected on a Xcalibur Eos diffractometer equipped with MoKα X-ray sources (λ =0.71073 Å).

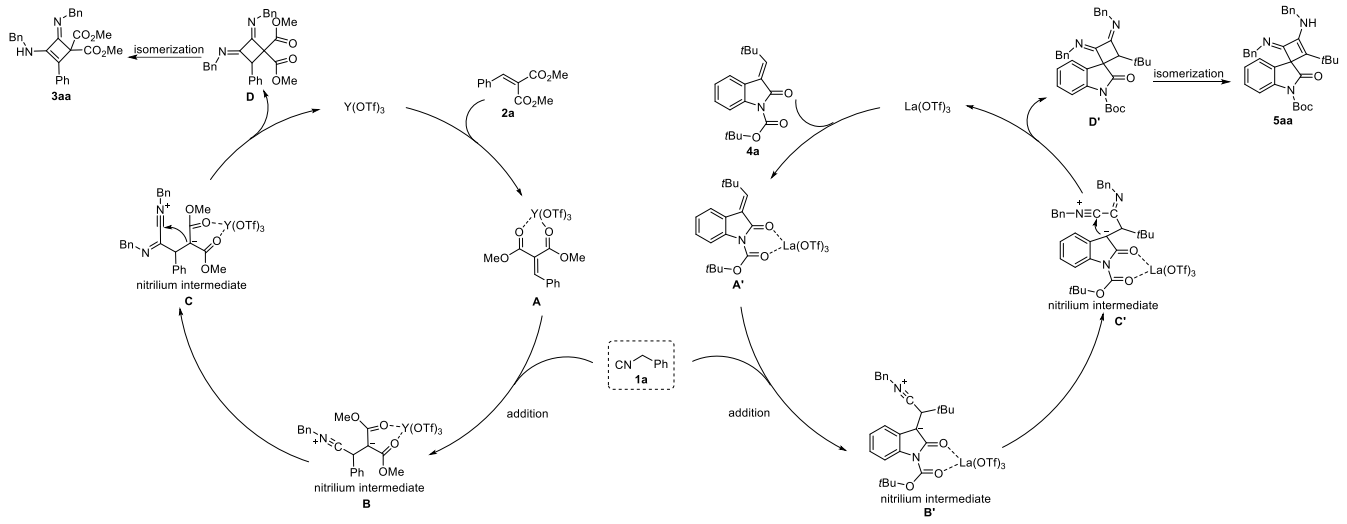
X-ray derived ORTEP of **6a** with thermal ellipsoids shown at the 30% probability level.

Structure deposited at the Cambridge Crystallographic Data Centre. CCDC 2335281 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures/.

Empirical formula	$C_{29}H_{26}N_2O_5$
Formula weight	482.52
Temperature/K	293.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	36.7020(16)
b/Å	8.5520(4)
c/Å	15.8388(8)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	4971.4(4)
Z	8
$\rho_{calc}g/cm^3$	1.289
μ/mm^{-1}	0.089
F(000)	2032.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.128 to 52.736
Index ranges	$-45 \le h \le 45$, $-10 \le k \le 7$, $-11 \le l \le 19$
Reflections collected	15777
Independent reflections	5077 [R_{int} = 0.0422, R_{sigma} = 0.0587]
Data/restraints/parameters	5077/0/326
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0616, wR_2 = 0.1214

Final R indexes [all data]	$R_1 = 0.1076$, $wR_2 = 0.1468$
Largest diff. peak/hole/e $Å^{-3}$	0.19/-0.24

10. A plausible mechanism



Based on the X-ray single crystal structure of the product **3aa** and previous reports, we proposed a possible reaction mechanism for the [2+1+1] cycloaddition of isocyanide with alkylidene malonate. Initially, the strong bidentate coordination of the two ester groups to the yttrium metal center activated the carbon–carbon double bond of alkylene malonate **2a**, generating intermediate **A**. Nitrilium intermediate **B** is generated by Ugi-type nucleophilic attack of the isocyanide **1a**. Then the intermediate **B** was attacked by a second isocyanide **1a**, giving rise to the nitrilium intermediate **C**. Next, intramolecular trapping of the nitrilium intermediate by the α-anion of the alkylene malonate occurred to afford the cyclobutane derivatives and regenerated the catalyst. Finally, imine-enamine isomerization occurs smoothly, affording desired product **3aa**.

The mechanism of the [2+1+1] cycloaddition of isocyanide with 3-alkenyl-oxindole was similar with the above mechanism.

11. Quantum chemical calculations

The exchange and correlation electronic effects are considered by employing the density functional theory (DFT)[4] at the M06-2X-D3 level,[5] which included Grimme's zero-damping D3-dispersion correction.[6] The ultrafine grid (99,590), having 99 radial shells and 590 angular points per shell, is used to evaluate the numerical integration accuracy. Geometry optimizations are performed with the double-zeta basis set 6-31G(d,p) in the ethyl acetate medium while using Truhlar's SMD solvation model.[7] The temperature is set to 298.15 K for thermochemistry analysis. Based on the optimized structures, the electronic energy (E_{electron}) and solvation free energy (ΔG_{solv}) are calculated at the same level of theory. The harmonic vibrational frequencies are analyzed after the geometry optimizations to characterize the nature of the stationary point as a minimum with all positive frequencies or as a transition state with only one imaginary frequency and to provide the zero-point energy (E_{ZPE}), total entropy (S_{tot}) and thermal correction to enthalpy (H_{corr}) at the same theoretical level. The Gibbs free energies of free substrates (G_i) are defined as reference-point. In addition, the intrinsic reaction coordinate (IRC)[8] calculations are carried out to verify the transition state (TS) associated with the correct reactant complexes (RC), intermediates (IM) and product complexes (PC) at the same level of theory. All calculations were carried out with Gaussian 16 program.[9]

$$G = E_{\text{electron}} + \Delta G_{\text{solv}} + E_{\text{ZPE}} + H_{\text{corr}} - TS_{\text{tot}} \qquad (1)$$

$$\Delta G = G - \sum_i G_i \qquad (2)$$

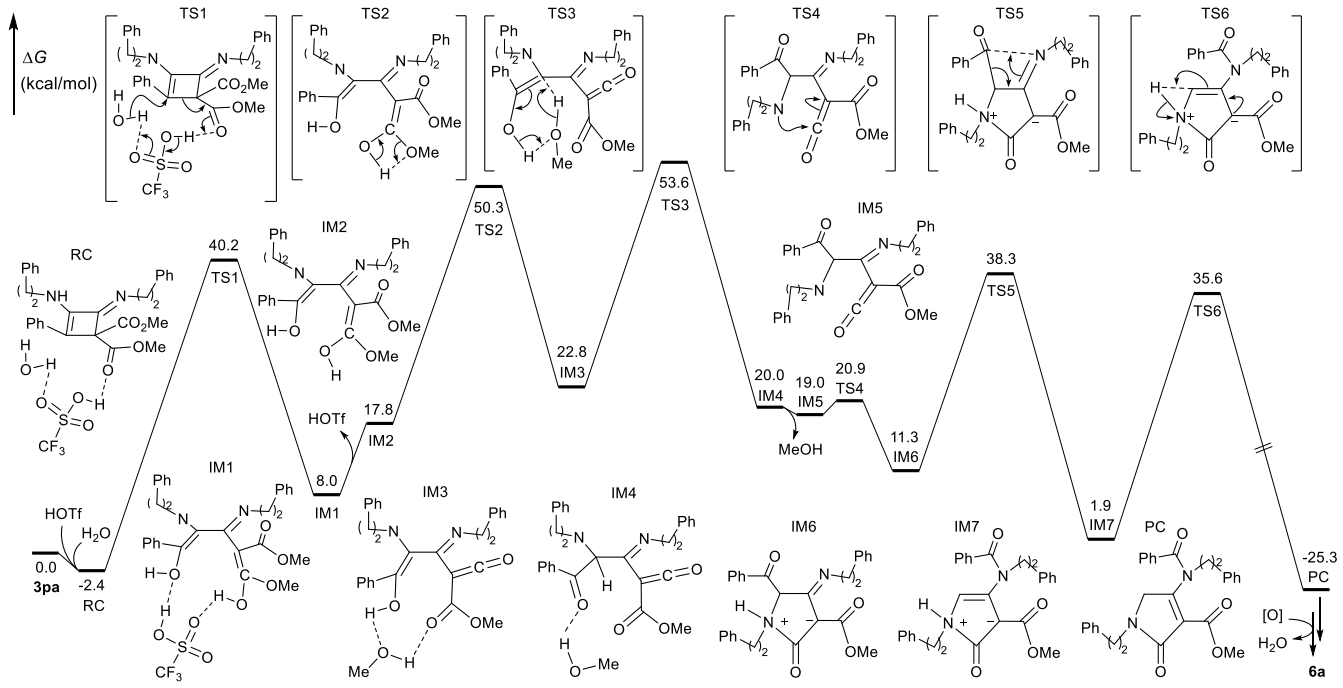


Figure 1. Relative energy profiles (kcal/mol) of reaction pathways at the M06-2X-D3/6-31G(d,p)/SMD(Ethyl acetate) theoretical level.

Cartesian coordinate for theoretical calculation

3pa

C	-0.08715900	-0.95943300	0.05991600
C	-1.52469200	-0.95624600	-0.47322400
C	-1.39612000	0.24563100	-1.11409400
C	0.00818100	0.38633400	-0.71688400
N	0.86720500	1.28645900	-0.91317100
N	-2.15876000	1.12142100	-1.82105200
H	-1.66870100	1.99623800	-1.97922300
C	2.19904800	1.10492900	-0.35470600
H	2.26804200	0.21845300	0.28968800
H	2.43777300	1.98682700	0.25137900
C	-3.57854600	1.29170400	-1.52146700
H	-3.95432000	2.05941000	-2.20302600
H	-4.11194100	0.36365000	-1.74309100
C	3.22341800	0.97824000	-1.48954000
H	3.21487400	1.89577600	-2.08614400
H	2.90710100	0.14960000	-2.12992600
C	4.60089000	0.70935300	-0.93849400
C	4.94241500	-0.58211500	-0.52113900
C	5.53654800	1.73454000	-0.78365000
C	6.19306100	-0.84296800	0.03113700
H	4.21324400	-1.38140000	-0.63799700
C	6.79036400	1.47667800	-0.23163300
H	5.28053100	2.74193100	-1.10304000
C	7.12184400	0.18714700	0.17703000
H	6.44584800	-1.85129700	0.34539100
H	7.50885700	2.28363900	-0.12276400
H	8.09883200	-0.01536200	0.60500500
C	-2.58738800	-1.94030400	-0.30382100
C	-2.67915100	-2.71078000	0.86544900
C	-3.52577300	-2.15173200	-1.32618800
C	-3.69985200	-3.64138900	1.01818900
H	-1.95466000	-2.56886700	1.66105900
C	-4.54713600	-3.08321600	-1.16856700
H	-3.42596700	-1.60587600	-2.26006000
C	-4.64106600	-3.82703000	0.00572000
H	-3.76260000	-4.22358200	1.93224600
H	-5.26278700	-3.23681200	-1.97023400
H	-5.43677300	-4.55499300	0.12822100
C	0.04815400	-0.76490500	1.56476900
O	-0.76531600	-0.18838800	2.24723400
O	1.19100600	-1.26998600	2.03240900
C	0.79934800	-2.07595000	-0.45787900
O	1.72855100	-1.93299500	-1.21845700
O	0.39104400	-3.25576200	0.00896600
C	1.43343200	-1.06347400	3.43118400
H	0.64982600	-1.53953800	4.02345000
H	2.39888700	-1.52274200	3.63425200
H	1.46297700	0.00470800	3.65414600
C	1.15038400	-4.38844100	-0.43109200
H	2.18766300	-4.29831100	-0.10168000
H	0.67964600	-5.25663100	0.02640900
H	1.11932800	-4.46672500	-1.51939400
C	-3.84869400	1.70276000	-0.06389900
H	-4.92867900	1.84107300	0.05453300
H	-3.54547200	0.88508600	0.59965800
C	-3.10380300	2.96263500	0.29939700
C	-3.58999700	4.21640900	-0.08560300
C	-1.87070900	2.89268000	0.95442300
C	-2.86327000	5.37399300	0.18036400
H	-4.54880000	4.28346700	-0.59523700
C	-1.13817600	4.04908400	1.21664600
H	-1.49205100	1.92200200	1.26872800
C	-1.63221900	5.29271600	0.83015500
H	-3.25720800	6.34043500	-0.11963700
H	-0.18108200	3.97612800	1.72485000
H	-1.06379100	6.19449200	1.03577600

RC

C	-0.06227400	-0.43664400	0.69754900
C	1.37973000	-0.19848300	0.21538700
C	0.98869000	0.37089300	-0.96762100
C	-0.43274500	0.23229000	-0.64867200
N	-1.48503100	0.48353200	-1.29490300
N	1.49882400	0.90005700	-2.11369900
H	0.77395900	1.06664300	-2.80524200
C	-2.75319800	0.00653900	-0.76518100
H	-3.45162700	0.84898600	-0.70256800
H	-2.66046200	-0.42110400	0.24375400
C	2.80743800	0.59320500	-2.68696000
H	3.01995200	1.38607000	-3.40914300
H	3.56212300	0.65631400	-1.89959500
C	-3.31272300	-1.05832400	-1.72147900
H	-2.51899600	-1.78663200	-1.91468200
H	-3.57241600	-0.58129300	-2.67177300
C	-4.50492300	-1.75383200	-1.11680800
C	-5.77907600	-1.18199700	-1.16559000
C	-4.33682700	-2.96594300	-0.44051300
C	-6.86237600	-1.80881400	-0.55378900
H	-5.92184500	-0.24072300	-1.69135100
C	-5.41763000	-3.59593200	0.17195700
H	-3.34599600	-3.41401200	-0.40448100
C	-6.68430500	-3.01722700	0.11741700
H	-7.84754400	-1.35497200	-0.60363600
H	-5.27210100	-4.54047800	0.68803600
H	-7.52904400	-3.50681600	0.59192500
C	2.63400200	-0.53711000	0.87505700
C	3.78258700	0.24701900	0.68320000
C	2.70226600	-1.63696200	1.74291100
C	4.98315900	-0.10492000	1.29187200
H	3.71159300	1.16017800	0.09749900
C	3.90183300	-1.97919100	2.35521300
H	1.81154100	-2.22864900	1.93554700
C	5.05034300	-1.22391000	2.11966600
H	5.86407500	0.50938800	1.13324000
H	3.94150500	-2.83997000	3.01567600
H	5.98732600	-1.49431000	2.59645700
C	-0.55143700	-1.88408900	0.75330100
O	-0.73106800	-2.57014400	-0.22357100
O	-0.76787800	-2.28535300	2.00642000
C	-0.46855000	0.31171200	1.95000400
O	-1.53850400	0.90518700	2.08070600
O	0.42418200	0.25074400	2.89995400
C	-1.24389700	-3.63197200	2.15620500
H	-0.53880300	-4.33203700	1.70436500
H	-1.31720300	-3.80007600	3.22870500
H	-2.22379000	-3.73496300	1.68564600
C	0.12911400	0.97417300	4.10989400
H	-0.77327100	0.57206100	4.57219900
H	0.99375800	0.82436900	4.75222900
H	-0.00390100	2.03243900	3.88091400
C	2.89395300	-0.77116600	-3.38483300
H	2.02096200	-0.89161500	-4.03571600
H	3.77885300	-0.75145000	-4.03069300
C	3.00492700	-1.93333100	-2.42772200
C	1.89022700	-2.68790500	-2.05838400
C	4.24699800	-2.25242200	-1.86643600
C	2.01451200	-3.74872300	-1.16179000
H	0.91282900	-2.43885800	-2.46418200
C	4.37690200	-3.31220400	-0.97414600
H	5.12111600	-1.66485300	-2.13934500
C	3.25898200	-4.06904900	-0.62509500
H	1.13321400	-4.31879400	-0.88555600
H	5.34877200	-3.54628700	-0.54991200
H	3.35721600	-4.89666900	0.07125300
O	2.64014900	3.20678200	-0.66234400
H	2.17878200	3.09543000	0.17906000
H	2.12155000	2.65583900	-1.26830200

H	-1.94781600	1.98800800	1.15764600
C	-0.58939000	4.22675400	-0.98648100
F	0.35612300	5.14666800	-1.06134400
F	-0.24497100	3.17208000	-1.70861200
F	-1.73114500	4.72062100	-1.43659200
S	-0.78713600	3.74479800	0.77656500
O	0.34298400	2.89003300	1.12051300
O	-1.02336300	4.96769700	1.50600700
O	-2.08582600	2.88480500	0.66073300

TS1

C	0.77181300	0.13155800	1.54275900
C	-1.10973600	1.60246200	0.47132300
C	-0.96744000	0.46279600	-0.24443700
C	0.17044200	-0.37743600	0.27791800
N	0.53259100	-1.33975700	-0.46243900
N	-1.69153200	-0.00942200	-1.25288900
H	-1.50494500	-0.98569600	-1.46170100
C	1.68913400	-2.13571800	-0.09968600
H	1.37417200	-3.18483600	-0.06182000
H	2.10263200	-1.86417300	0.87899300
C	-2.43725000	0.77119800	-2.22123400
H	-3.44719200	0.35802500	-2.31001600
H	-2.51499300	1.79276100	-1.84729600
C	2.76357400	-1.96412200	-1.18532500
H	2.91157400	-0.88980400	-1.32949100
H	2.39792500	-2.39448000	-2.12344100
C	4.05953700	-2.60912700	-0.76615000
C	4.36718900	-3.92514100	-1.11819900
C	4.95653500	-1.89925900	0.03908900
C	5.54961100	-4.51939700	-0.68084600
H	3.67563100	-4.48570500	-1.74278100
C	6.13845000	-2.48939500	0.47741600
H	4.71182300	-0.87496700	0.31415100
C	6.43813400	-3.80290100	0.11774100
H	5.77764400	-5.54217700	-0.96559900
H	6.82776300	-1.92472500	1.09820000
H	7.36022600	-4.26461000	0.45708900
C	-0.62784200	2.90448100	0.62836200
C	-1.08400000	3.71636500	1.69453400
C	0.37442900	3.38077000	-0.25289400
C	-0.55017300	4.97886700	1.86594300
H	-1.85964600	3.32911800	2.34668600
C	0.91910700	4.63902700	-0.05355800
H	0.71567600	2.73504900	-1.05726300
C	0.45201400	5.43163400	0.99737400
H	-0.89522300	5.61607600	2.67257800
H	1.69580000	5.00702500	-0.71564000
H	0.87365900	6.42143500	1.14502000
C	2.06544200	0.78948700	1.38956800
O	2.65066000	0.85713600	0.31761100
O	2.56427000	1.33867500	2.50555500
C	0.01831600	0.05587300	2.70444100
O	-1.11806600	-0.57974500	2.81737200
O	0.42063400	0.64359600	3.81253800
C	3.80420300	2.02479700	2.33561400
H	3.70476400	2.82569900	1.59931800
H	4.04806500	2.43823800	3.31345000
H	4.58913600	1.33725000	2.01162400
C	-0.38844300	0.49315200	4.98837400
H	-0.48973600	-0.55959500	5.25623400
H	0.14736300	1.03194800	5.76766800
H	-1.37592300	0.93153900	4.83459600
C	-1.72940900	0.77449200	-3.58378200
H	-1.57842600	-0.26159600	-3.90723000
H	-2.39582400	1.25018500	-4.31047600
C	-0.41150500	1.50908600	-3.53060400
C	0.76406200	0.85535000	-3.14379400
C	-0.35199300	2.87579100	-3.82341800
C	1.97227100	1.54723300	-3.06893400

H	0.73011000	-0.20240400	-2.89206300
C	0.85422100	3.56995000	-3.75341200
H	-1.25949800	3.39689700	-4.11968200
C	2.02180300	2.90543600	-3.38002700
H	2.87396000	1.02473200	-2.76513000
H	0.88267700	4.62857400	-3.99403500
H	2.96397400	3.44262500	-3.32896400
O	-3.44808200	2.01024500	0.37737400
H	-4.03555300	2.28673100	-0.33819500
H	-3.67587600	1.07317900	0.53186500
H	-1.45629200	-1.09392300	2.01637300
C	-3.93168500	-2.92518700	-0.69662000
F	-5.22854600	-3.01412000	-0.97701100
F	-3.32275800	-2.33333800	-1.73039500
F	-3.43731100	-4.15181400	-0.56839100
S	-3.68739000	-1.96528500	0.84554700
O	-4.24477800	-0.64547000	0.51198400
O	-4.39999800	-2.72247400	1.86570800
O	-2.20363400	-1.98307200	0.96967100

IM1

C	0.95798900	0.16793700	1.12888900
C	-1.56559900	0.81250300	-0.44550300
C	-0.66276300	-0.11723600	-0.85087100
C	0.61070700	-0.49055700	-0.17026400
N	1.27934000	-1.42230100	-0.73936400
N	-1.13035400	-0.95337200	-1.90327100
H	-0.65540000	-1.85105200	-1.84933500
C	2.46262200	-1.97785100	-0.11556700
H	2.27348300	-3.04748600	0.04498900
H	2.69458200	-1.52829100	0.85616300
C	-1.02310500	-0.41180500	-3.27319900
H	-1.37917800	-1.20642000	-3.93410200
H	-1.72882000	0.42163300	-3.37066800
C	3.66985900	-1.83293200	-1.05248000
H	3.77360500	-0.77299700	-1.29837800
H	3.47883600	-2.38776900	-1.97702000
C	4.92928500	-2.32161200	-0.38351300
C	5.42828300	-3.60643900	-0.60779100
C	5.59408800	-1.49063800	0.52535400
C	6.57108300	-4.05152600	0.05517100
H	4.91902900	-4.26093500	-1.31124700
C	6.73490100	-1.93147900	1.18919600
H	5.20113900	-0.49114900	0.70161600
C	7.22730800	-3.21520300	0.95505200
H	6.94961500	-5.05181400	-0.13308800
H	7.24253600	-1.27351700	1.88834600
H	8.11852200	-3.56014300	1.47022400
C	-1.39217500	1.99573400	0.41115500
C	-2.30470800	2.31120200	1.42336000
C	-0.28878500	2.82757000	0.19017500
C	-2.09903200	3.43660400	2.21735500
H	-3.16286600	1.67372200	1.61369300
C	-0.08794300	3.94927400	0.98518100
H	0.40863700	2.57717300	-0.60451800
C	-0.99169800	4.25505400	2.00185400
H	-2.80504700	3.67112400	3.00767200
H	0.77318200	4.58601600	0.80585100
H	-0.83586800	5.13095900	2.62363000
C	2.16961000	0.99102200	1.11614000
O	2.99777700	0.95158900	0.21901100
O	2.29986700	1.82767600	2.15559400
C	0.10751900	0.06134800	2.20046100
O	-1.00441500	-0.66615000	2.21771300
O	0.34408400	0.65903900	3.35203500
C	3.44025100	2.68124000	2.10188100
H	3.43182000	3.28281600	1.18966100
H	3.36911700	3.32374000	2.97886800
H	4.36569100	2.10094500	2.13511300
C	-0.62121400	0.52724000	4.40296300

H	-0.71740000	-0.51389300	4.71624900
H	-0.22833000	1.13012300	5.21988900
H	-1.59289900	0.91097200	4.08601400
C	0.37222100	0.03949000	-3.72324400
H	1.10964700	-0.69993100	-3.39402900
H	0.37516800	0.02960100	-4.82046900
C	0.79197500	1.42046800	-3.26488700
C	1.99890700	1.61379400	-2.59155700
C	0.00708400	2.54437400	-3.55744300
C	2.42746300	2.89305800	-2.23533600
H	2.60367100	0.75258500	-2.32622200
C	0.42808800	3.82235200	-3.20179300
H	-0.93666500	2.42004400	-4.08365200
C	1.64704600	4.00313600	-2.54594300
H	3.36702700	3.00875000	-1.70416800
H	-0.19308700	4.68023700	-3.44137100
H	1.97735100	5.00094800	-2.27309200
O	-2.83584500	0.67690700	-0.99732100
H	-2.73773700	-0.17491100	-1.50833700
H	-3.87172400	0.29743800	0.00041100
H	-1.24226700	-1.05316200	1.35713500
C	-5.10420100	-2.33110800	-0.62976400
F	-6.40249500	-2.12415700	-0.51224400
F	-4.64898900	-1.70118300	-1.71022700
F	-4.86001700	-3.62454600	-0.73519500
S	-4.21953500	-1.66347900	0.83416700
O	-4.53307300	-0.14126000	0.67366200
O	-4.86289700	-2.16633600	2.01964400
O	-2.81582600	-1.92660000	0.55650500

IM2

C	-0.00615300	1.20502200	-0.93160200
C	2.70063600	-0.17892500	-1.05170600
C	1.54992100	-0.74037900	-1.51081500
C	0.17077300	-0.24258700	-1.27095700
N	-0.78227100	-1.07311800	-1.48848600
N	1.69677700	-1.79515100	-2.44703100
H	0.80465400	-1.95279000	-2.90742200
C	-2.16614100	-0.66101000	-1.39566800
H	-2.66904400	-0.95249600	-2.32670100
H	-2.30073800	0.42339300	-1.28517600
C	2.22613800	-3.07169300	-1.94856700
H	2.34203600	-3.72202500	-2.82107400
H	3.23021300	-2.89757400	-1.54768300
C	-2.84557700	-1.38801100	-0.22358500
H	-2.23279400	-1.22793500	0.66803600
H	-2.86438900	-2.46226400	-0.43884200
C	-4.23787500	-0.86354500	0.01179000
C	-5.32534000	-1.32267400	-0.73631300
C	-4.45044500	0.14354400	0.95822100
C	-6.59767400	-0.78896900	-0.54202700
H	-5.17259300	-2.10875800	-1.47240100
C	-5.72074900	0.67932400	1.15572200
H	-3.60159400	0.49804700	1.53901800
C	-6.79877200	0.21443900	0.40412600
H	-7.43390700	-1.15916600	-1.12768800
H	-5.87028100	1.45774700	1.89848800
H	-7.79058900	0.62855100	0.55721900
C	2.87152300	0.71541200	0.10285700
C	3.88770700	1.67968000	0.10297700
C	2.06421100	0.56888900	1.23773200
C	4.06922300	2.50673800	1.20779000
H	4.52963200	1.77393800	-0.76716500
C	2.24309000	1.40346600	2.33665500
H	1.29563400	-0.19916500	1.25401900
C	3.24566700	2.37406100	2.32592400
H	4.85588400	3.25513200	1.19721300
H	1.60594800	1.28159000	3.20772600
H	3.39219100	3.01665500	3.18873000
C	-0.80421900	1.56248800	0.24249800

O	-1.03262500	0.82713300	1.18528900
O	-1.32728400	2.80242700	0.15773200
C	0.54503600	2.12976900	-1.77167400
O	0.91670000	1.75991300	-2.99813700
O	0.78340300	3.42019100	-1.56900400
C	-1.99539400	3.26886900	1.32990400
H	-1.34948100	3.17376100	2.20639900
H	-2.22917100	4.31657700	1.14250800
H	-2.91739600	2.70778300	1.49748600
C	1.14496100	3.91546700	-0.27059000
H	0.34891700	4.56106800	0.09798000
H	1.32120200	3.09344700	0.42548000
H	2.06246900	4.48977500	-0.40885600
C	1.36627000	-3.79959400	-0.90642000
H	0.33030200	-3.82849000	-1.26082300
H	1.71807800	-4.83892900	-0.86637500
C	1.40139600	-3.23420500	0.49723800
C	0.21547600	-2.94063100	1.17408300
C	2.61382200	-3.05477100	1.17556500
C	0.23249900	-2.48494900	2.49255800
H	-0.73139400	-3.07422200	0.65921800
C	2.63643500	-2.60054500	2.49115000
H	3.55127500	-3.28119600	0.67252300
C	1.44394000	-2.31671500	3.15743000
H	-0.70333000	-2.26054900	2.99635200
H	3.58748300	-2.46734700	2.99831500
H	1.46223800	-1.96186300	4.18343900
O	3.88403600	-0.53070900	-1.63057700
H	3.64651200	-0.94693300	-2.47925600
H	1.50432900	2.44269600	-3.36026400

TS2

C	-0.01786700	1.17886200	-0.92937700
C	2.64265400	-0.30120900	-1.12613100
C	1.45788200	-0.81941600	-1.54904100
C	0.10540100	-0.27255600	-1.27940600
N	-0.88273900	-1.06464800	-1.48400100
N	1.54425200	-1.89455300	-2.47133300
H	0.63882400	-2.01829500	-2.91582700
C	-2.25048300	-0.60477900	-1.37862900
H	-2.76246500	-0.85958100	-2.31566800
H	-2.34596400	0.48039100	-1.24446300
C	2.01557800	-3.18523800	-1.95068000
H	2.06137000	-3.86550600	-2.80656700
H	3.04254400	-3.06017600	-1.59136900
C	-2.95928900	-1.33033000	-0.22362600
H	-2.35111900	-1.19768000	0.67527100
H	-3.00678400	-2.40054100	-0.45360400
C	-4.33868500	-0.76838200	0.00371500
C	-5.45136200	-1.26594000	-0.67903900
C	-4.51201900	0.31283900	0.87418600
C	-6.71130100	-0.69996200	-0.49320100
H	-5.32806600	-2.10676600	-1.35779300
C	-5.76918600	0.88043400	1.06308200
H	-3.64250600	0.69865300	1.40258800
C	-6.87359500	0.37467900	0.37864700
H	-7.56769100	-1.10079100	-1.02726400
H	-5.88888700	1.71573800	1.74702800
H	-7.85546100	0.81384900	0.52605600
C	2.88555600	0.59775500	0.01220600
C	3.95238900	1.50477600	-0.02338000
C	2.10315000	0.50471300	1.17073400
C	4.21080300	2.32729800	1.07025800
H	4.57416200	1.55634300	-0.91145100
C	2.35612100	1.33706900	2.25650100
H	1.30315600	-0.22956400	1.21931800
C	3.41135900	2.25015900	2.21057600
H	5.03903200	3.02848700	1.03314800
H	1.74008700	1.25417000	3.14725400
H	3.61794500	2.88813400	3.06444400

C	-0.74823900	1.56281600	0.27580100
O	-1.08416700	0.78872900	1.15331700
O	-1.04296400	2.87710000	0.33291300
C	0.58860500	2.06071200	-1.76984600
O	1.16110500	1.98723700	-2.89601300
O	0.74033500	3.48811500	-1.51569400
C	-1.63631500	3.31589600	1.55534700
H	-0.99959700	3.06102100	2.40612000
H	-1.73612600	4.39717700	1.46597200
H	-2.61998000	2.86100300	1.69185200
C	1.42978000	3.96598900	-0.31893600
H	0.80939700	4.74328500	0.12113000
H	1.55909200	3.13142900	0.36882400
H	2.39366200	4.36132000	-0.63760400
C	1.15253300	-3.83058200	-0.85726100
H	0.10278500	-3.78873000	-1.16686900
H	1.42951600	-4.89206100	-0.81106100
C	1.28778800	-3.24905500	0.53448800
C	0.15274500	-2.89355100	1.26721200
C	2.53990000	-3.11872800	1.14913900
C	0.25689400	-2.42749100	2.57795100
H	-0.82478800	-2.98844200	0.80281800
C	2.64962700	-2.65249500	2.45615700
H	3.44001400	-3.39292900	0.60373400
C	1.50690400	-2.30838100	3.17886800
H	-0.64147500	-2.15519300	3.12434200
H	3.63041300	-2.55813300	2.91282800
H	1.59364300	-1.94579700	4.19865800
O	3.79213700	-0.71022500	-1.73021900
H	3.51315000	-1.12551800	-2.56723400
H	1.29598700	3.28605300	-2.50959900

IM3

C	-1.57277300	-1.11204400	-0.45234700
C	1.37781600	-1.46208900	-0.01628800
C	0.71409700	-0.32358400	0.34809900
C	-0.76377200	-0.23679300	0.46728000
N	-1.25539500	0.69370700	1.19480700
N	1.41897600	0.86565200	0.64446600
H	0.73551000	1.61108800	0.75356600
C	-2.66223800	1.04927000	1.12953100
H	-2.91807200	1.59322000	2.04404700
H	-3.32731500	0.18354200	1.07720600
C	2.24912600	0.82469800	1.85241900
H	1.64518600	0.60122400	2.74514600
H	2.99030800	0.02634700	1.74162700
C	-2.92242200	1.96474300	-0.08194900
H	-2.53513200	1.47110300	-0.98020500
H	-2.36820100	2.89957900	0.04756700
C	-4.39670400	2.23170300	-0.24461100
C	-4.98818700	3.39026100	0.26261400
C	-5.21015300	1.27918600	-0.86804400
C	-6.36137600	3.59810800	0.14337200
H	-4.36568400	4.13625500	0.75058300
C	-6.58131200	1.48238300	-0.98929000
H	-4.75521100	0.37305400	-1.26517500
C	-7.16103000	2.64524300	-0.48293500
H	-6.80605200	4.50631900	0.53881400
H	-7.19777500	0.73593200	-1.48111800
H	-8.23008800	2.80771700	-0.57836700
C	2.79597200	-1.51035700	-0.44007700
C	3.53656700	-2.67225400	-0.18861600
C	3.40146900	-0.45743400	-1.14234000
C	4.85998800	-2.77283600	-0.60809300
H	3.06287400	-3.49313900	0.33837100
C	4.71793000	-0.56809900	-1.57207100
H	2.83648600	0.44580000	-1.34180200
C	5.45492200	-1.72157400	-1.30069300
H	5.42470900	-3.67563400	-0.39639300
H	5.17036800	0.25252500	-2.11965700

H	6.48601600	-1.79985900	-1.63166800
C	-2.76783000	-1.87535400	-0.09119500
O	-3.14786600	-2.07463800	1.05031100
O	-3.40215500	-2.35397600	-1.16585100
C	-1.10647500	-1.29991300	-1.69190400
O	-0.71066800	-1.45826400	-2.76124600
O	-0.74750700	-2.83506100	2.15736100
C	-4.54576400	-3.17945000	-0.89749000
H	-5.30723600	-2.60450400	-0.36772800
H	-4.91351300	-3.49293400	-1.87245000
H	-4.25742600	-4.04668400	-0.30067000
C	-1.09259200	-4.21571700	2.22619400
H	-1.70512800	-4.42374700	3.10883100
H	-1.63315600	-4.54403400	1.33049400
H	-0.16153500	-4.78050100	2.30166400
C	2.97545500	2.15787300	2.03931600
H	2.23455400	2.96653500	2.06062700
H	3.46638100	2.14593500	3.01784800
C	3.99686700	2.41850000	0.95956400
C	3.64748300	3.08020200	-0.22164700
C	5.31131600	1.96505600	1.10591700
C	4.58861800	3.29071700	-1.22737800
H	2.62755400	3.43349500	-0.35032600
C	6.25833600	2.17943000	0.10727700
H	5.59461700	1.44364100	2.01744700
C	5.89968300	2.84593200	-1.06291200
H	4.30019500	3.80982800	-2.13666900
H	7.27615000	1.82588200	0.24299000
H	6.63619100	3.01690500	-1.84227800
O	0.80318800	-2.68712200	0.02658600
H	0.14996100	-2.70615100	0.77312500
H	-1.57865900	-2.33661600	2.07215000

TS3

C	1.59956800	1.29785200	-0.47034600
C	-1.30349900	1.49660500	-0.10534800
C	-0.62814100	0.31807400	0.30434600
C	0.83272600	0.26570300	0.34631300
N	1.42629200	-0.69946600	0.95954400
N	-1.32150600	-0.91723600	0.50553500
H	-0.64000400	-1.67082300	0.44160500
C	2.86314800	-0.85848400	0.86159000
H	3.22854700	-1.26174200	1.81294300
H	3.38933400	0.08888900	0.67946500
C	-2.01434600	-1.03168300	1.78493000
H	-1.32325300	-0.92755800	2.64257000
H	-2.74893700	-0.21856300	1.84902500
C	3.22372500	-1.85061500	-0.25747800
H	2.82761800	-1.46950300	-1.20620700
H	2.72239900	-2.80291100	-0.05515400
C	4.71468900	-2.04121200	-0.36197200
C	5.37010800	-3.00453000	0.41012100
C	5.47785400	-1.21218600	-1.18968100
C	6.75515700	-3.14068100	0.35337800
H	4.78590900	-3.65523300	1.05672200
C	6.86275500	-1.34500800	-1.24984400
H	4.97630200	-0.46037600	-1.79576100
C	7.50541700	-2.31073700	-0.47748800
H	7.24876600	-3.89761800	0.95544800
H	7.44017500	-0.69690600	-1.90222300
H	8.58458800	-2.41818400	-0.52520200
C	-2.72714000	1.45310800	-0.58252600
C	-3.53018600	2.56747200	-0.31779000
C	-3.25498500	0.39378800	-1.33131700
C	-4.84550300	2.61768400	-0.76857900
H	-3.10004700	3.39141800	0.24231900
C	-4.56365800	0.45525100	-1.80047000
H	-2.63911000	-0.47293900	-1.53930600
C	-5.36472000	1.55988100	-1.51245900
H	-5.46273600	3.48296400	-0.54625500

H	-4.96008200	-0.36528300	-2.38985500
H	-6.38900400	1.59701400	-1.87136700
C	2.06098600	2.57459400	0.06445700
O	1.90434200	2.93925400	1.21556600
O	2.69883000	3.30750400	-0.85509000
C	1.80935400	1.05678300	-1.75746600
O	1.98615200	0.82216300	-2.87757700
O	-0.39640300	2.07643900	2.45193200
C	3.15169000	4.59403800	-0.41659700
H	3.87348100	4.48726500	0.39530300
H	3.62264200	5.05086900	-1.28518000
H	2.30732600	5.19803100	-0.07952500
C	0.60690900	1.77897400	3.46410600
H	0.09589800	1.19912300	4.23066600
H	1.42916800	1.22350700	3.01807700
H	0.94732400	2.73125200	3.86303100
C	-2.74420500	-2.37207400	1.88689600
H	-2.00985600	-3.18090900	1.78900100
H	-3.18283500	-2.45408800	2.88681900
C	-3.81920600	-2.52567900	0.83892700
C	-3.54457900	-3.13327600	-0.38974300
C	-5.10835800	-2.03693600	1.06792200
C	-4.53630600	-3.26388700	-1.35929000
H	-2.54375100	-3.51125200	-0.58296900
C	-6.10469600	-2.16539100	0.10240200
H	-5.33421400	-1.55697000	2.01755800
C	-5.82256600	-2.78576900	-1.11277500
H	-4.30643800	-3.74488500	-2.30552000
H	-7.10203100	-1.78444500	0.30122000
H	-6.59844100	-2.89267800	-1.86498300
O	-0.77883000	2.64512300	0.03929700
H	-0.08144900	2.63734500	1.66759900
H	-0.63548300	1.23827500	1.90624900

IM4

C	-1.08887600	1.98950100	0.22270600
C	1.61887300	1.07083300	0.53253800
C	0.98359300	1.01334400	-0.87057500
C	-0.53420800	0.96779300	-0.72380100
N	-1.17957100	0.08443300	-1.36368000
N	1.48979700	-0.11131500	-1.61636500
H	0.84235000	-0.34311500	-2.36530700
C	-2.61906900	-0.05008700	-1.27527000
H	-2.99852300	-0.21371300	-2.28933800
H	-3.11882500	0.84494000	-0.87710900
C	2.84447700	0.09994500	-2.10787100
H	2.89371300	0.83834700	-2.92424300
H	3.44325500	0.51402100	-1.28705300
C	-2.97315800	-1.27811500	-0.42014500
H	-2.60183300	-1.13076600	0.60109800
H	-2.44790900	-2.14559300	-0.83258200
C	-4.46198200	-1.51973500	-0.40779000
C	-5.05899800	-2.31399600	-1.39092400
C	-5.27692700	-0.91187300	0.55093700
C	-6.43875000	-2.50161500	-1.41305000
H	-4.43337600	-2.79207500	-2.14104600
C	-6.65727700	-1.09703800	0.53238200
H	-4.82397600	-0.29237100	1.32150000
C	-7.24185900	-1.89321800	-0.45030400
H	-6.88665700	-3.12605600	-2.18009500
H	-7.27576800	-0.62172600	1.28761900
H	-8.31716100	-2.04116500	-0.46431300
C	1.64505900	-0.14538000	1.40040700
C	2.33568600	-0.05309900	2.61505800
C	0.96167100	-1.32693200	1.07920800
C	2.34249600	-1.12174700	3.50246000
H	2.85721500	0.86899700	2.84937500
C	0.95206700	-2.38497300	1.98317200
H	0.45381000	-1.41917300	0.12689100
C	1.64292000	-2.28704100	3.18959000

H	2.88434000	-1.04557600	4.43979000
H	0.41689000	-3.29621500	1.73521200
H	1.64059600	-3.12161400	3.88446400
C	-0.61212400	3.38638600	0.27002200
O	0.12632300	3.89331600	-0.54341300
O	-1.12116700	4.03270900	1.32512400
C	-1.95752700	1.62969500	1.16716200
O	-2.70314100	1.30962100	1.98723600
O	3.04180200	3.55767600	-1.35699500
C	-0.72390600	5.40474700	1.45843300
H	-1.02842700	5.97515600	0.57923600
H	-1.23414200	5.77179400	2.34683900
H	0.35822600	5.47158400	1.58424700
C	2.42581500	4.19052500	-2.45502800
H	3.17246100	4.26333900	-3.25114900
H	1.56738000	3.62511100	-2.84384000
H	2.07877900	5.20445000	-2.21710000
C	3.45209700	-1.22974800	-2.55283100
H	2.86872200	-1.63334100	-3.38861500
H	4.46435700	-1.04241300	-2.92906500
C	3.49242900	-2.23979100	-1.42946200
C	2.71689400	-3.39969400	-1.47127400
C	4.29931400	-2.01763600	-0.30799900
C	2.75943700	-4.32801200	-0.43186700
H	2.07683600	-3.57923100	-2.33175000
C	4.33864100	-2.93581000	0.73709900
H	4.90505700	-1.11543200	-0.25567800
C	3.57401700	-4.10038700	0.67403100
H	2.15343400	-5.22776800	-0.48631300
H	4.96820700	-2.74395500	1.60105100
H	3.60565400	-4.81858800	1.48798100
O	2.06464400	2.13088300	0.93822700
H	2.39867500	3.48499300	-0.63544300
H	1.23242000	1.98062900	-1.32843900

IM5

C	-0.89295100	-1.48916700	0.26743800
C	1.07317600	1.35407600	-1.32109500
C	0.71694200	-0.14296200	-1.23672700
C	-0.66628300	-0.29140000	-0.59827400
N	-1.50978500	0.61563000	-0.86407400
N	1.70492200	-0.92649900	-0.49467600
H	1.62154400	-1.89308100	-0.80737400
C	-2.83045100	0.67306300	-0.27297600
H	-2.90414100	1.64285300	0.23489700
H	-3.01460500	-0.10642200	0.47554600
C	3.10172800	-0.52629200	-0.68624000
H	3.39408000	-0.51997600	-1.74820400
H	3.23361900	0.49349400	-0.30811500
C	-3.90171700	0.61056200	-1.36977900
H	-3.74252800	-0.30409600	-1.94647200
H	-3.77044100	1.46598500	-2.03987200
C	-5.28396100	0.61038900	-0.76753900
C	-6.00056100	1.79719500	-0.59576000
C	-5.84930400	-0.58754200	-0.31715200
C	-7.25751400	1.78921300	0.00639800
H	-5.56981600	2.73385800	-0.94175500
C	-7.10475600	-0.59941500	0.28442400
H	-5.28941500	-1.51132800	-0.44711500
C	-7.81304400	0.59047600	0.44792700
H	-7.80390500	2.71973600	0.12817500
H	-7.53300800	-1.53786000	0.62414600
H	-8.79324700	0.58256900	0.91458700
C	1.10879900	2.19867100	-0.08295500
C	1.15912600	3.58643300	-0.24535600
C	1.11247400	1.65334600	1.20510600
C	1.19953000	4.42047100	0.86549400
H	1.16083800	3.99371400	-1.25093800
C	1.16412800	2.48957700	2.31613400
H	1.10418400	0.57603100	1.33998400

C	1.20181900	3.87242600	2.14784500
H	1.22980600	5.49726200	0.73346400
H	1.17389500	2.06125300	3.31318300
H	1.23441900	4.52318100	3.01620100
C	-0.00670800	-1.87633800	1.19447400
O	0.65163000	-2.26478800	2.05905700
C	-2.05423700	-2.37796800	0.09038300
O	-2.86790500	-2.27917400	-0.80064000
O	-2.08940200	-3.33807300	1.02791800
C	-3.16866300	-4.27257900	0.91023000
H	-3.14334800	-4.76681400	-0.06258900
H	-3.01843000	-4.99662300	1.70902200
H	-4.12627800	-3.76301200	1.03662300
C	4.01608800	-1.46402500	0.10161000
H	3.69714500	-1.45623000	1.14953100
H	3.89397200	-2.48737600	-0.27255200
C	5.45979800	-1.04147100	-0.01160800
C	6.29553400	-1.59164000	-0.98654400
C	5.97145700	-0.04686600	0.82755200
C	7.61468700	-1.16291300	-1.11839700
H	5.90815400	-2.36525200	-1.64528600
C	7.28890200	0.38458600	0.69924800
H	5.32813600	0.38915200	1.58859700
C	8.11491200	-0.17358000	-0.27499600
H	8.25229100	-1.60348700	-1.87886300
H	7.67200900	1.15505300	1.36147900
H	9.14308500	0.16007000	-0.37475900
O	1.31080900	1.83631900	-2.40848600
H	0.64127600	-0.45879300	-2.28626800

TS4

C	-0.81792600	-1.51326400	0.11202400
C	1.05545600	1.39173000	-1.41614600
C	0.69929000	-0.10843900	-1.40496900
C	-0.66589600	-0.30067500	-0.73788400
N	-1.52477700	0.60579300	-0.95573600
N	1.69589900	-0.94546700	-0.73441300
H	1.67505000	-1.86160300	-1.18038900
C	-2.81652400	0.65653900	-0.30307400
H	-2.86915400	1.62754500	0.20572000
H	-2.96082700	-0.12118900	0.45544500
C	3.08631100	-0.47836700	-0.76459500
H	3.45351200	-0.33781900	-1.79260500
H	3.14813600	0.49160800	-0.26114800
C	-3.94179500	0.58878100	-1.34370000
H	-3.81623800	-0.33239500	-1.91817300
H	-3.83984200	1.43701100	-2.02804200
C	-5.29287500	0.60377400	-0.67457400
C	-6.00058100	1.79494800	-0.49597000
C	-5.83575800	-0.58281700	-0.16952100
C	-7.22726600	1.80235200	0.16561900
H	-5.58682500	2.72291000	-0.88365200
C	-7.06109800	-0.57930300	0.49119200
H	-5.28177000	-1.50955900	-0.30334500
C	-7.76111200	0.61471600	0.66057300
H	-7.76710400	2.73610700	0.29198700
H	-7.47242000	-1.50909700	0.87304400
H	-8.71780600	0.61859500	1.17375400
C	1.06237500	2.18383200	-0.14360800
C	1.10595800	3.57728100	-0.24437000
C	1.05015600	1.58298200	1.11919200
C	1.12473300	4.36170000	0.90287600
H	1.12005900	4.02864200	-1.23082700
C	1.08086800	2.36856100	2.26682000
H	1.04266800	0.50072100	1.20993700
C	1.11232000	3.75787900	2.15961000
H	1.15013700	5.44339100	0.81884800
H	1.07842800	1.89648400	3.24383200
H	1.12853900	4.36985600	3.05608500
C	0.18605900	-1.96933500	0.88381500

O	0.87898800	-2.46776400	1.66308800
C	-2.00467900	-2.38352200	0.05314900
O	-2.90141700	-2.27383600	-0.75399400
O	-1.96224300	-3.34827500	0.98581400
C	-3.05005500	-4.27876000	0.95567800
H	-3.10638800	-4.77185300	-0.01657700
H	-2.83737000	-5.00459600	1.73858600
H	-3.99295400	-3.76711100	1.16011800
C	3.97616300	-1.47579000	-0.02276500
H	3.58644100	-1.59803400	0.99344300
H	3.91755300	-2.45219400	-0.51798700
C	5.40717800	-1.00031300	0.01928000
C	6.33274500	-1.41693900	-0.94047000
C	5.81693400	-0.08711800	0.99579100
C	7.64103400	-0.93782300	-0.92306800
H	6.02450800	-2.12608700	-1.70498400
C	7.12300500	0.39438200	1.01662500
H	5.10297700	0.24502200	1.74629900
C	8.03951600	-0.03093600	0.05632900
H	8.34953100	-1.27501600	-1.67357600
H	7.42669000	1.09973500	1.78416300
H	9.05907500	0.34133100	0.07288500
O	1.31480200	1.91922900	-2.47722000
H	0.59928500	-0.36587200	-2.46646800

IM6

C	-0.62660200	-1.44246500	-0.42391200
C	0.99873700	1.66693500	-1.52065100
C	0.53726400	0.21221100	-1.74160100
C	-0.76836600	-0.12967400	-1.02600600
N	-1.63571600	0.80497600	-1.04015000
N	1.51486300	-0.85348400	-1.34502700
H	1.79272300	-1.35523000	-2.19516900
C	-2.86787400	0.72741100	-0.27867900
H	-2.99487500	1.69918900	0.21577400
H	-2.84726600	-0.04167300	0.50060200
C	2.79053400	-0.45195000	-0.65046200
H	3.09307900	0.52322600	-1.03923600
H	2.57205900	-0.35331900	0.41494500
C	-4.07459700	0.49288600	-1.19698900
H	-3.92964200	-0.46674400	-1.70033900
H	-4.09766000	1.28185400	-1.95608400
C	-5.36295300	0.48087700	-0.41267500
C	-6.20710500	1.59371700	-0.38616700
C	-5.70927000	-0.64259000	0.34762400
C	-7.37571700	1.58584200	0.37391000
H	-5.94646000	2.47276400	-0.97089800
C	-6.87566900	-0.65350700	1.10721000
H	-5.04855400	-1.50654800	0.33290800
C	-7.71372600	0.46128800	1.12261300
H	-8.02247800	2.45830500	0.37928300
H	-7.13369900	-1.53423700	1.68817500
H	-8.62430400	0.45224300	1.71388400
C	1.08112000	2.28501200	-0.16037800
C	1.53342400	3.60853600	-0.09784100
C	0.75572000	1.61423000	1.02467200
C	1.65899900	4.25215000	1.12645900
H	1.78209000	4.11852800	-1.02215200
C	0.88714000	2.25969300	2.24995200
H	0.39810900	0.58994100	1.01042000
C	1.33609400	3.57751100	2.30303000
H	2.00910200	5.27849300	1.16472500
H	0.63232700	1.73223700	3.16316600
H	1.43370300	4.07871500	3.26093500
C	0.68875400	-1.92507200	-0.49646100
O	1.31378900	-2.89021200	-0.13672800
C	-1.71131700	-2.31974900	0.00872200
O	-2.87485500	-2.22253100	-0.34161300
O	-1.29302900	-3.30553400	0.81910200
C	-2.29583500	-4.25120800	1.18916300

H	-2.72840200	-4.72579900	0.30543700
H	-1.79004300	-4.99294600	1.80611700
H	-3.09253200	-3.76692300	1.75896000
C	3.90553400	-1.46526000	-0.90234700
H	3.59443000	-2.44824300	-0.54538700
H	4.08529200	-1.53141700	-1.98214500
C	5.15983300	-1.01286700	-0.19343200
C	6.06258800	-0.14914000	-0.81877600
C	5.40630900	-1.41258600	1.12259400
C	7.19500900	0.30142900	-0.14470900
H	5.87860500	0.16629000	-1.84315800
C	6.53723500	-0.96312600	1.79932600
H	4.70671200	-2.08393100	1.61481400
C	7.43449300	-0.10506800	1.16632600
H	7.89152000	0.96784600	-0.64409600
H	6.71930300	-1.28513000	2.81998400
H	8.31801000	0.24349100	1.69185900
O	1.29477300	2.30176100	-2.51210300
H	0.39086400	0.12788500	-2.81944000

TS5

C	0.52361500	1.86230000	-0.75615900
C	0.20492000	-1.56650300	-1.51554600
C	-0.34473800	0.02042500	-2.03686500
C	0.70713500	0.52471300	-1.14352700
N	1.33987200	-0.57879700	-0.87388900
N	-1.47071800	0.97361200	-1.80506600
H	-1.91426400	1.23941300	-2.68996600
C	2.54903400	-0.85929500	-0.13060900
H	2.57160000	-1.94033500	0.04055700
H	2.50881200	-0.34950000	0.83725900
C	-2.54114300	0.48006900	-0.86912400
H	-2.74378100	-0.55625800	-1.14838400
H	-2.11046300	0.48263100	0.13493700
C	3.79777300	-0.41116400	-0.89942900
H	3.68427900	0.65452700	-1.12318600
H	3.84884100	-0.95982300	-1.84509100
C	5.04223800	-0.63564100	-0.07865400
C	5.85233500	-1.75495100	-0.28081400
C	5.37352600	0.26349000	0.94117700
C	6.97728300	-1.97046400	0.51345300
H	5.60044600	-2.45938000	-1.06979000
C	6.49590900	0.04997600	1.73631400
H	4.73962200	1.13322000	1.10063500
C	7.30172200	-1.06828600	1.52373500
H	7.60069400	-2.84272200	0.34130900
H	6.74464700	0.75754800	2.52162500
H	8.17868000	-1.23416500	2.14185600
C	-0.64762000	-2.08800900	-0.35954100
C	-1.53422200	-3.11998400	-0.67755000
C	-0.64497900	-1.57155500	0.93864500
C	-2.44048200	-3.59252000	0.26707300
H	-1.50231600	-3.53140300	-1.68145500
C	-1.54601000	-2.05163900	1.88841600
H	0.04814300	-0.78251700	1.21712900
C	-2.45485700	-3.05199200	1.55243000
H	-3.13530600	-4.38388300	0.00224100
H	-1.53793700	-1.63940000	2.89289100
H	-3.16449200	-3.41415500	2.28974000
C	-0.77016500	2.27669500	-1.19990000
O	-1.42365600	3.27986800	-1.15984700
C	1.41760700	2.62472800	0.10265900
O	2.45824300	2.18259400	0.55787200
O	0.98556700	3.86802300	0.34285300
C	1.83175100	4.65077000	1.18843500
H	2.82154300	4.76621700	0.74163800
H	1.34294300	5.61943600	1.28021900
H	1.93393500	4.18306700	2.17009900
C	-3.82131700	1.30755900	-0.92625300
H	-3.61976700	2.34195500	-0.64094700

H	-4.20984200	1.30584500	-1.95125700
C	-4.82321900	0.68087500	0.01591900
C	-5.61093100	-0.39619900	-0.39937200
C	-4.91995300	1.11805600	1.33906700
C	-6.48375300	-1.02021700	0.48808100
H	-5.53881400	-0.74612100	-1.42658100
C	-5.79227600	0.49605900	2.22932100
H	-4.30726300	1.95283900	1.67066100
C	-6.57583300	-0.57509900	1.80550500
H	-7.09257700	-1.85342500	0.15080000
H	-5.86028600	0.84895800	3.25376500
H	-7.25680500	-1.05976700	2.49810200
O	0.55639300	-2.34075000	-2.41673700
H	-0.06681500	0.05243500	-3.09056400

IM7

C	-0.54796700	-1.15472600	0.11159300
C	-0.88577500	2.39651500	0.44968500
C	0.18739300	0.33746600	-1.50832400
C	-0.65399900	0.17148700	-0.47340500
N	-1.46008000	1.22729800	-0.00029500
N	1.04711200	-0.83095900	-1.60161100
H	1.04641500	-1.25873200	-2.53457800
C	-2.92983700	1.16381600	-0.04433500
H	-3.28219600	2.14313200	-0.37721300
H	-3.30007800	0.98684300	0.96918600
C	2.45925200	-0.46309700	-1.21823000
H	2.73572300	0.38963900	-1.84442800
H	2.40255900	-0.12405400	-0.17904200
C	-3.45759000	0.07824000	-0.97998400
H	-3.05056600	-0.89395200	-0.68693600
H	-3.13336700	0.28179700	-2.00606600
C	-4.96382800	0.02828300	-0.90100600
C	-5.76561100	0.63964200	-1.86649700
C	-5.57871900	-0.60458000	0.18455100
C	-7.15490900	0.61463800	-1.75581700
H	-5.29652200	1.13636900	-2.71234500
C	-6.96534100	-0.63015100	0.29912700
H	-4.95529200	-1.07754400	0.94071000
C	-7.75787600	-0.02039000	-0.67290300
H	-7.76577800	1.09104500	-2.51669700
H	-7.42884700	-1.12750500	1.14577500
H	-8.83978600	-0.04146200	-0.58605400
C	0.56319100	2.32239400	0.84848200
C	1.47154500	3.25748500	0.35405500
C	0.97724200	1.36373500	1.77711100
C	2.80653400	3.20006600	0.74587700
H	1.13146000	4.01528800	-0.34564700
C	2.30692000	1.32846400	2.18964200
H	0.25246200	0.65716700	2.17385900
C	3.22590000	2.23448200	1.66061100
H	3.51968100	3.91180900	0.34218400
H	2.62706500	0.58991600	2.91823300
H	4.26661400	2.19324600	1.96663800
C	0.42895800	-1.89048400	-0.57505500
O	0.89582700	-3.00302900	-0.59247600
C	-1.29754900	-1.61875400	1.25556500
O	-2.11293500	-0.95111600	1.87627700
O	-1.00334900	-2.88807900	1.59848900
C	-1.71052700	-3.38279000	2.73338600
H	-2.78834600	-3.37830300	2.55318800
H	-1.35921800	-4.40357700	2.88012200
H	-1.49753000	-2.77966500	3.61922300
C	3.46816700	-1.59450100	-1.38829900
H	3.18680800	-2.44413900	-0.76418500
H	3.47374000	-1.92856700	-2.43163500
C	4.83112800	-1.07423200	-0.99459500
C	5.71843100	-0.58065500	-1.95330900
C	5.19806300	-1.02466800	0.35387700
C	6.95213100	-0.05487500	-1.57514600

H	5.44160100	-0.61396400	-3.00429400
C	6.42909200	-0.49810300	0.73537700
H	4.51216000	-1.40683500	1.10666000
C	7.30977500	-0.01172800	-0.22962700
H	7.63440300	0.31964300	-2.33210200
H	6.70281900	-0.47105700	1.78573900
H	8.27117700	0.39621000	0.06625900
O	-1.53000700	3.42362900	0.59195000
H	0.40216900	1.21376200	-2.10158800

TS6

C	-0.40444600	-0.32824400	1.12287000
C	-1.58885600	2.56476700	-0.72891200
C	0.53086200	0.38520100	-0.86037400
C	-0.58549900	0.46103400	-0.03067400
N	-1.70850500	1.22938900	-0.38283000
N	1.49109300	-0.50497300	-0.14696700
C	-3.02715700	0.59977000	-0.60005200
H	-3.47603100	1.11825800	-1.44910100
H	-3.64801600	0.76926100	0.28211600
C	2.94519000	-0.48725900	-0.34600600
H	3.16619600	0.19868300	-1.16729600
H	3.38460900	-0.08451100	0.57173600
C	-2.95062700	-0.89560600	-0.90119700
H	-2.46411700	-1.42283400	-0.07608300
H	-2.35337500	-1.06074500	-1.80461900
C	-4.34478400	-1.44478900	-1.08238600
C	-4.89065000	-1.64291500	-2.35198700
C	-5.13061400	-1.72290000	0.04085500
C	-6.19285800	-2.11758600	-2.49907800
H	-4.28882300	-1.42577000	-3.23114000
C	-6.43179900	-2.19541900	-0.10220700
H	-4.70979300	-1.56430200	1.03162700
C	-6.96616700	-2.39544900	-1.37452700
H	-6.60249800	-2.27094100	-3.49290900
H	-7.02885600	-2.41023500	0.77889600
H	-7.98002900	-2.76656900	-1.48785200
C	-0.35285800	3.29699600	-0.28964300
C	0.21651900	4.21298100	-1.17559000
C	0.17161300	3.15079500	0.99736100
C	1.33586400	4.94625700	-0.79358400
H	-0.22249400	4.34051200	-2.16024700
C	1.27868900	3.90041000	1.38286700
H	-0.29660000	2.46562300	1.69795200
C	1.86889200	4.78852800	0.48470700
H	1.78739500	5.64586700	-1.48973900
H	1.67889700	3.79268500	2.38586900
H	2.73840700	5.36496400	0.78474000
C	0.91643600	-0.90729400	1.11614600
O	1.55813400	-1.59382600	1.89525800
C	-1.37857900	-0.45672500	2.20351400
O	-2.48475000	0.05468900	2.20666100
O	-0.92716700	-1.20118800	3.22173400
C	-1.83887200	-1.34972200	4.31023100
H	-2.75662000	-1.84317700	3.98135000
H	-1.32298200	-1.96506700	5.04599500
H	-2.09178000	-0.37765200	4.73948100
C	3.48827400	-1.88752200	-0.63370400
H	3.16304200	-2.55004200	0.17288000
H	3.05606100	-2.25175100	-1.57207000
C	4.99400400	-1.85997500	-0.72237700
C	5.64187100	-1.74431300	-1.95435800
C	5.76467400	-1.89788900	0.44389700
C	7.03185100	-1.67379500	-2.02243600
H	5.05135100	-1.71557600	-2.86700000
C	7.15335000	-1.82615500	0.37980800
H	5.26635100	-1.98942900	1.40635100
C	7.79063200	-1.71407200	-0.85502100
H	7.52190800	-1.58954300	-2.98761600
H	7.73895700	-1.86151100	1.29334900

H	8.87365600	-1.66156100	-0.90662400
O	-2.47655900	3.15380700	-1.32401900
H	0.90393400	1.06362300	-1.61361300
H	0.80613700	-0.88169500	-1.10378000

PC

C	-0.47368900	-0.08048900	1.49044500
C	-1.56278200	2.47047900	-0.93945000
C	0.84048700	0.72420500	-0.27170200
C	-0.51687400	0.71298900	0.39812200
N	-1.63403100	1.28483900	-0.20865400
N	1.64158600	-0.07170600	0.62263300
C	-2.81935600	0.43789700	-0.41897600
H	-3.62903000	1.09331400	-0.74017500
H	-3.10551600	-0.00298300	0.53599000
C	3.04530000	-0.34651700	0.41576800
H	3.53093800	0.56082000	0.03996900
H	3.47741700	-0.58592100	1.39128100
C	-2.56698400	-0.65008600	-1.46738800
H	-1.65609300	-1.19862400	-1.19826000
H	-2.40250500	-0.17692800	-2.44023400
C	-3.73248200	-1.60531800	-1.52414200
C	-4.71814800	-1.48952000	-2.50629800
C	-3.86892500	-2.59574200	-0.54533400
C	-5.81372700	-2.35106200	-2.51760100
H	-4.62298600	-0.71973100	-3.26810900
C	-4.96175800	-3.45729200	-0.55300500
H	-3.10612100	-2.68902300	0.22590100
C	-5.93796000	-3.33677500	-1.54150400
H	-6.57016000	-2.25164900	-3.29019800
H	-5.05142800	-4.22432000	0.21027200
H	-6.79020500	-4.00910800	-1.55065700
C	-0.58299300	3.49641100	-0.46639500
C	0.01250900	4.32962100	-1.41530700
C	-0.31039400	3.66892300	0.89426800
C	0.91120600	5.30958600	-1.00800400
H	-0.23052900	4.19515100	-2.46460000
C	0.57702600	4.66187700	1.29754700
H	-0.80404400	3.04052100	1.63041900
C	1.19511400	5.47355400	0.34762400
H	1.38735600	5.94803400	-1.74505800
H	0.78378300	4.80354100	2.35328200
H	1.89377300	6.24122100	0.66507500
C	0.91771000	-0.60584400	1.65336300
O	1.35946800	-1.33130100	2.52729100
C	-1.56955600	-0.30464900	2.45652900
O	-2.42131700	0.52030600	2.71373900
O	-1.52038800	-1.51557700	3.00956300
C	-2.54353600	-1.78514300	3.97443300
H	-3.52955500	-1.73419400	3.50693600
H	-2.34710300	-2.79168300	4.33939300
H	-2.49468500	-1.06580300	4.79427200
C	3.27849100	-1.51367600	-0.55537300
H	2.78612000	-2.40237100	-0.14657200
H	2.80666500	-1.28275200	-1.51680100
C	4.75167000	-1.77057400	-0.74798900
C	5.45459100	-1.16172400	-1.79122700
C	5.45348500	-2.57775000	0.15264800
C	6.82571300	-1.35986600	-1.93777500
H	4.91896400	-0.53187200	-2.49777100
C	6.82400900	-2.77827100	0.00987600
H	4.91588100	-3.05529700	0.96855300
C	7.51411500	-2.16964200	-1.03702000
H	7.35574100	-0.88397100	-2.75728100
H	7.35314300	-3.41250800	0.71466100
H	8.58198400	-2.32786300	-1.15139100
O	-2.32223200	2.68900400	-1.86572300
H	1.25722300	1.72912700	-0.39428300
H	0.74027200	0.26987300	-1.26822300

12. The Photophysical properties of 6a

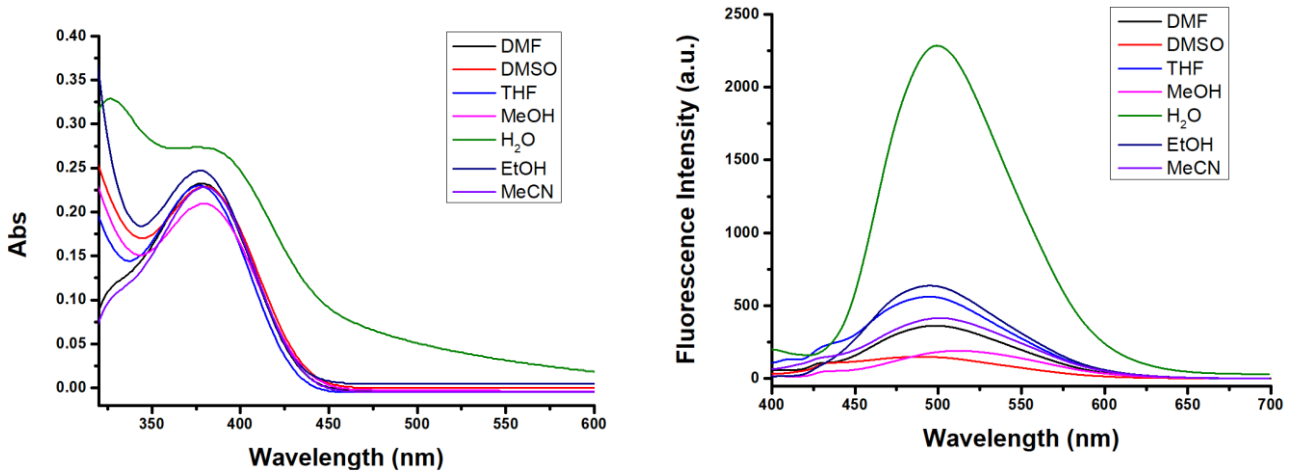


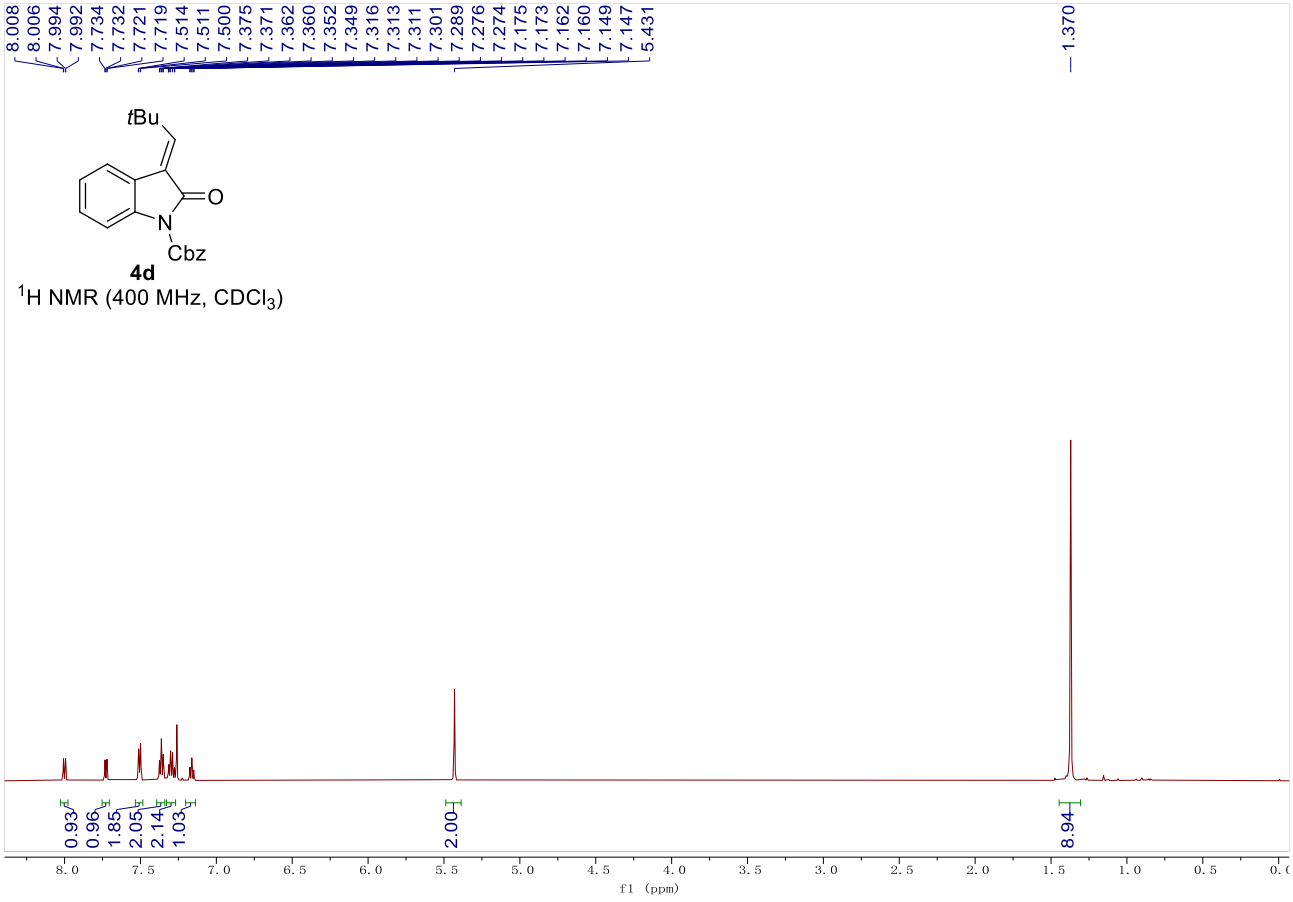
Figure 2. Absorption (left) and emission (right) spectra of **6a** in H_2O (5×10^{-5}M) and other organic solvents (1×10^{-4}M)

Table 4. Photophysical properties of **6a** in H_2O (5×10^{-5}M) and other organic solvents (1×10^{-4}M)

Entry	Solvent	λ_{abs}[a]/ nm	λ_{em}[b]/ nm	Δs/nm (cm^{-1})	Φ_F[c]/ %
1	DMSO	380	422	2676	1
2	THF	377	465	5020	1.9
3	MeOH	379	512	6854	0.7
4	EtOH	377	511	6956	1.3
5	H_2O	377	497	6404	2.0
6	MeCN	377	498	6445	1.7
7	DMF	377	499	6485	0.7

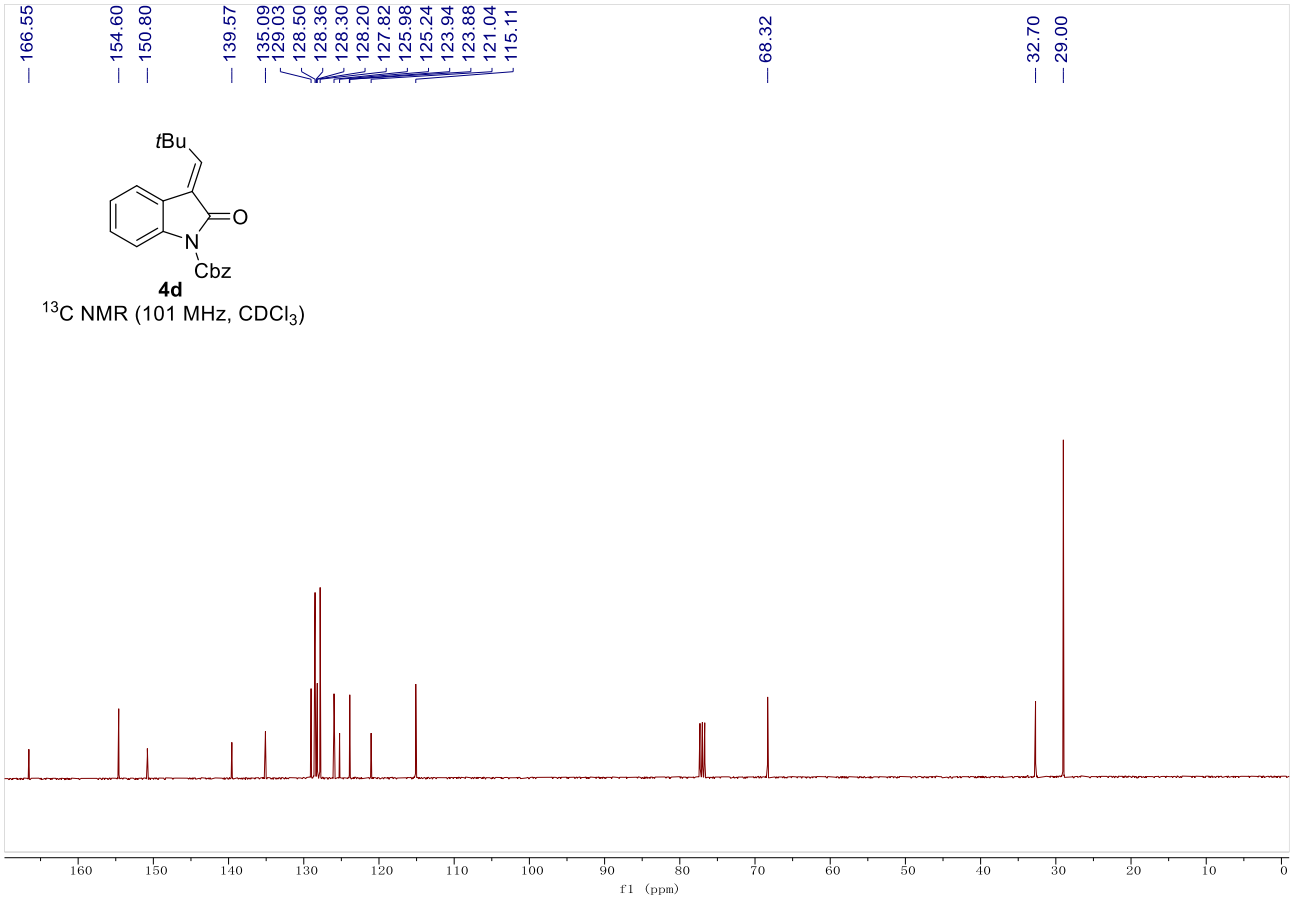
[a] Absorption maxima. [b] Fluorescent emission maxima. [c] Relative quantum yields with quinine sulfate as standard (Φ_F =0.546) (excited at 366 nm).

13. Copy of NMR spectra



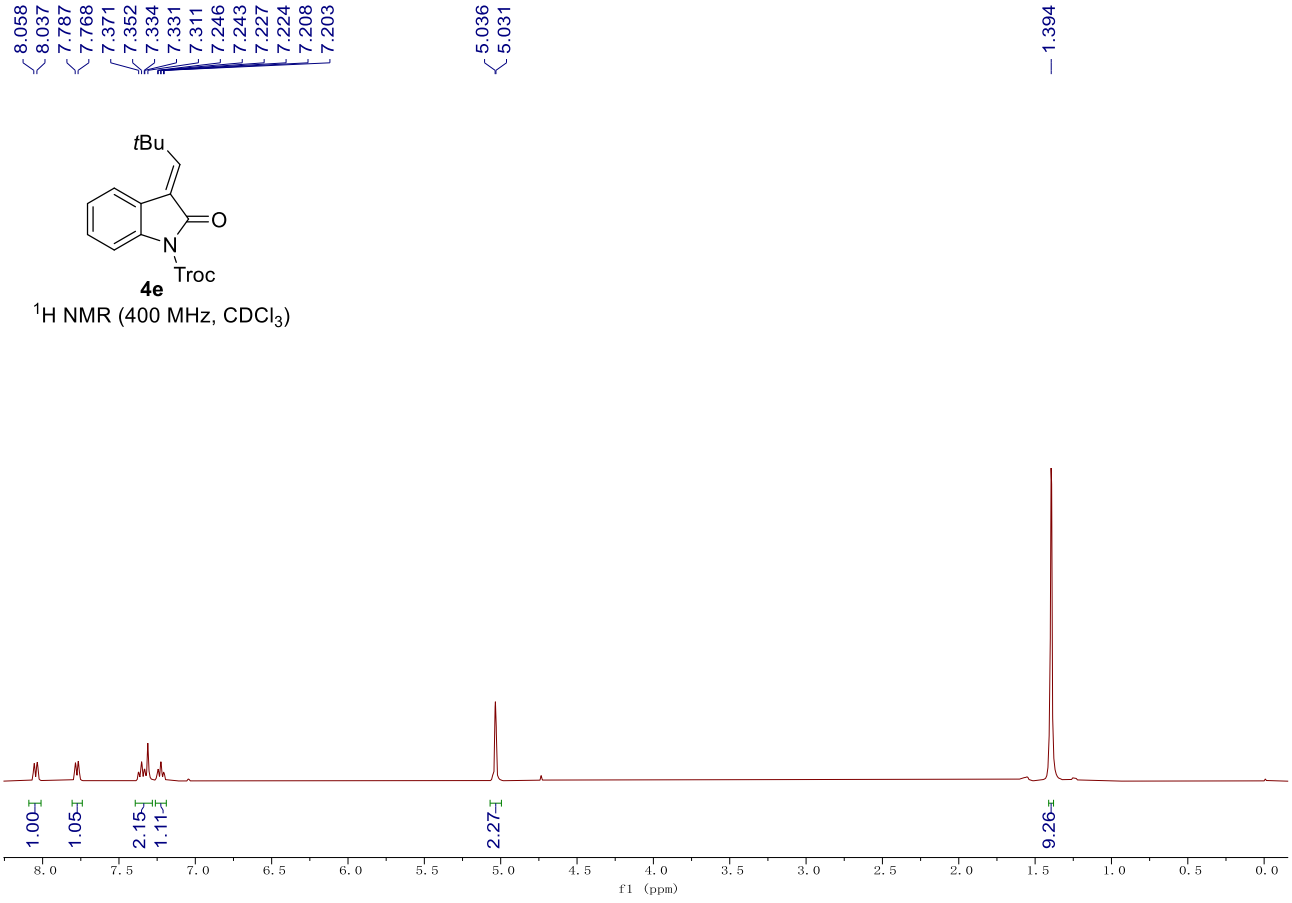
4d

^{1}H NMR (400 MHz, $CDCl_3$)



4d

^{13}C NMR (101 MHz, $CDCl_3$)



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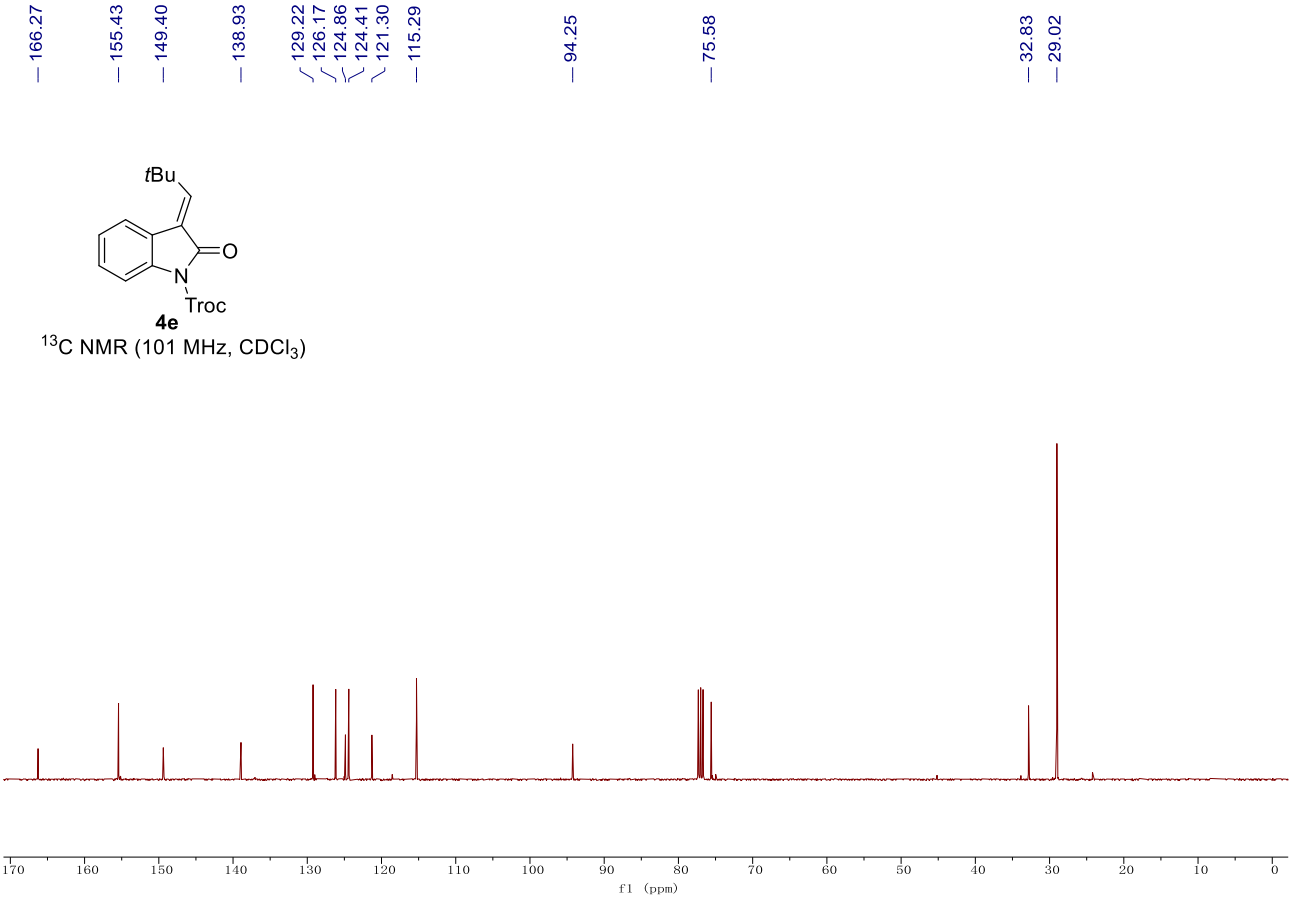

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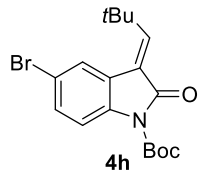

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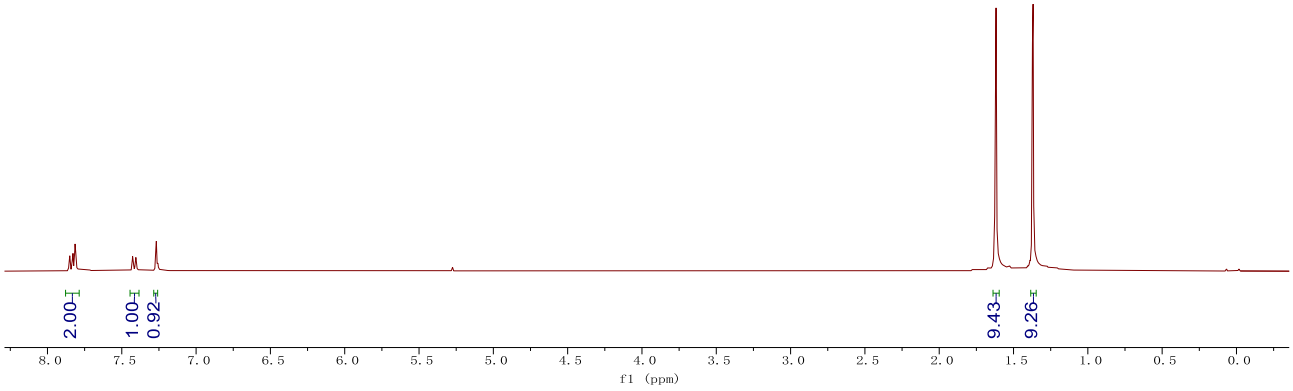

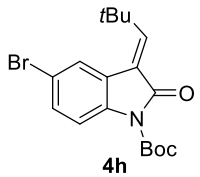

4h

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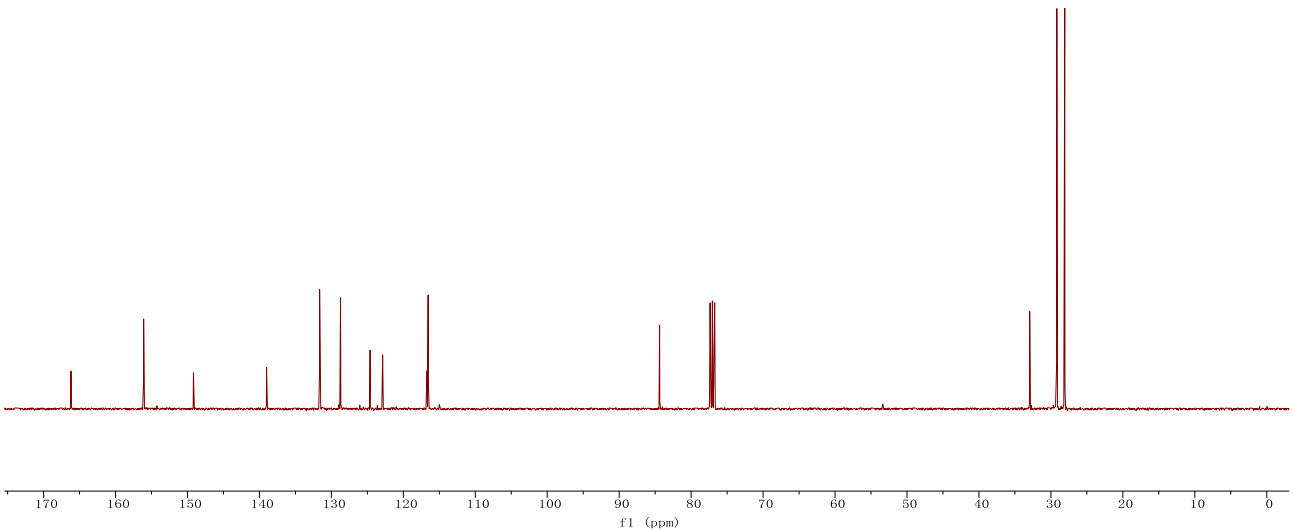
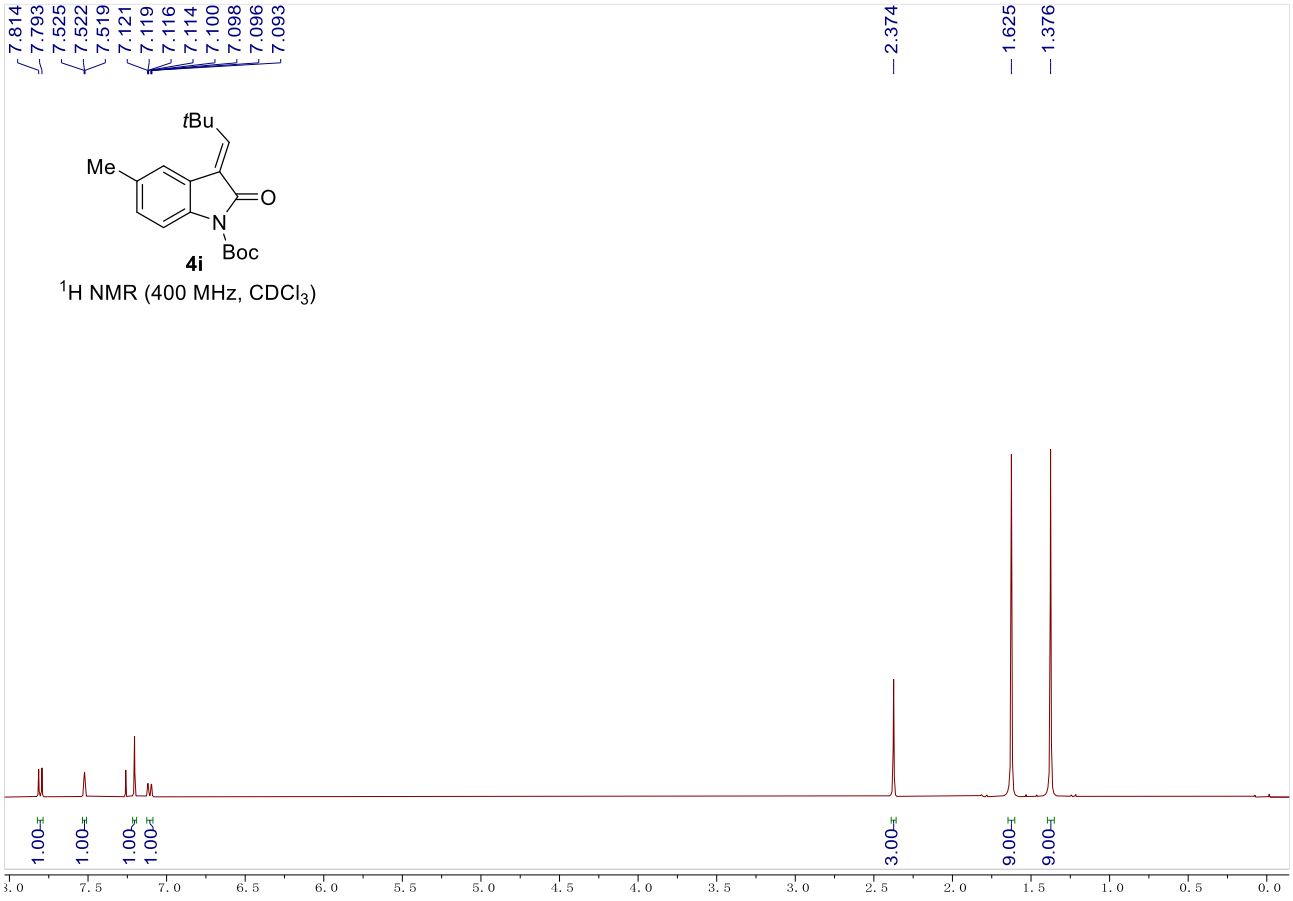
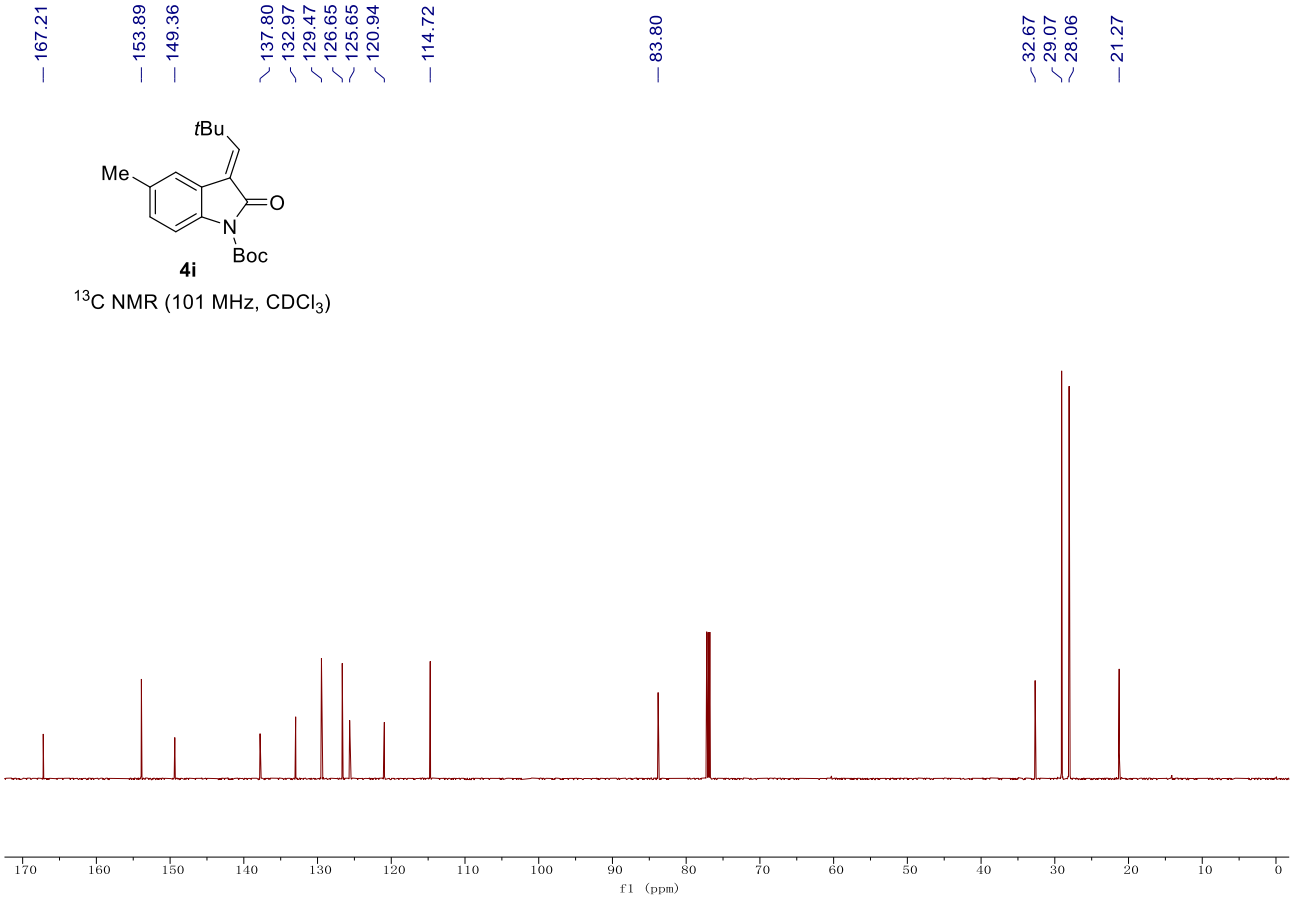




4i

^{1}H NMR (400 MHz, $CDCl_3$)



4i

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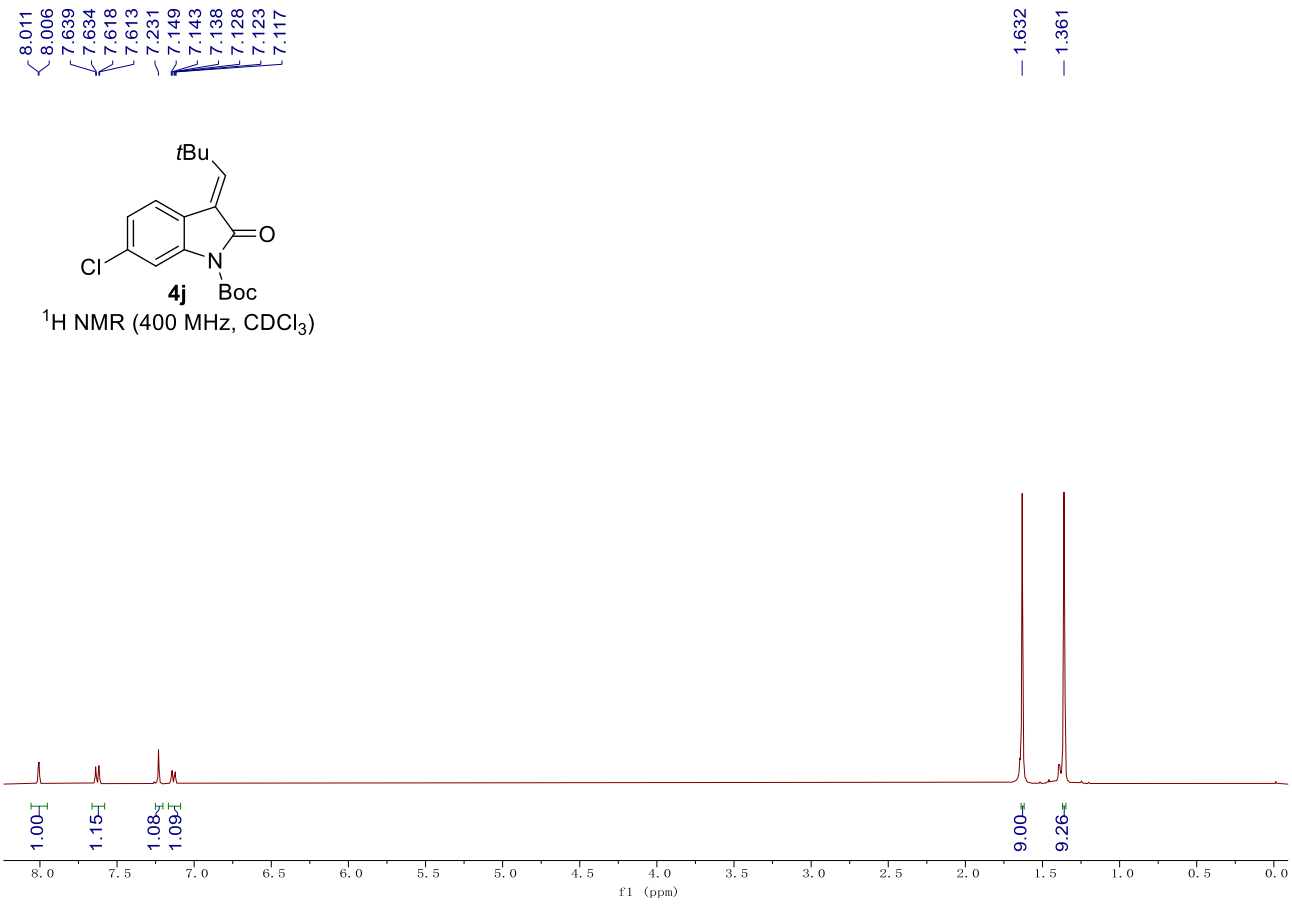

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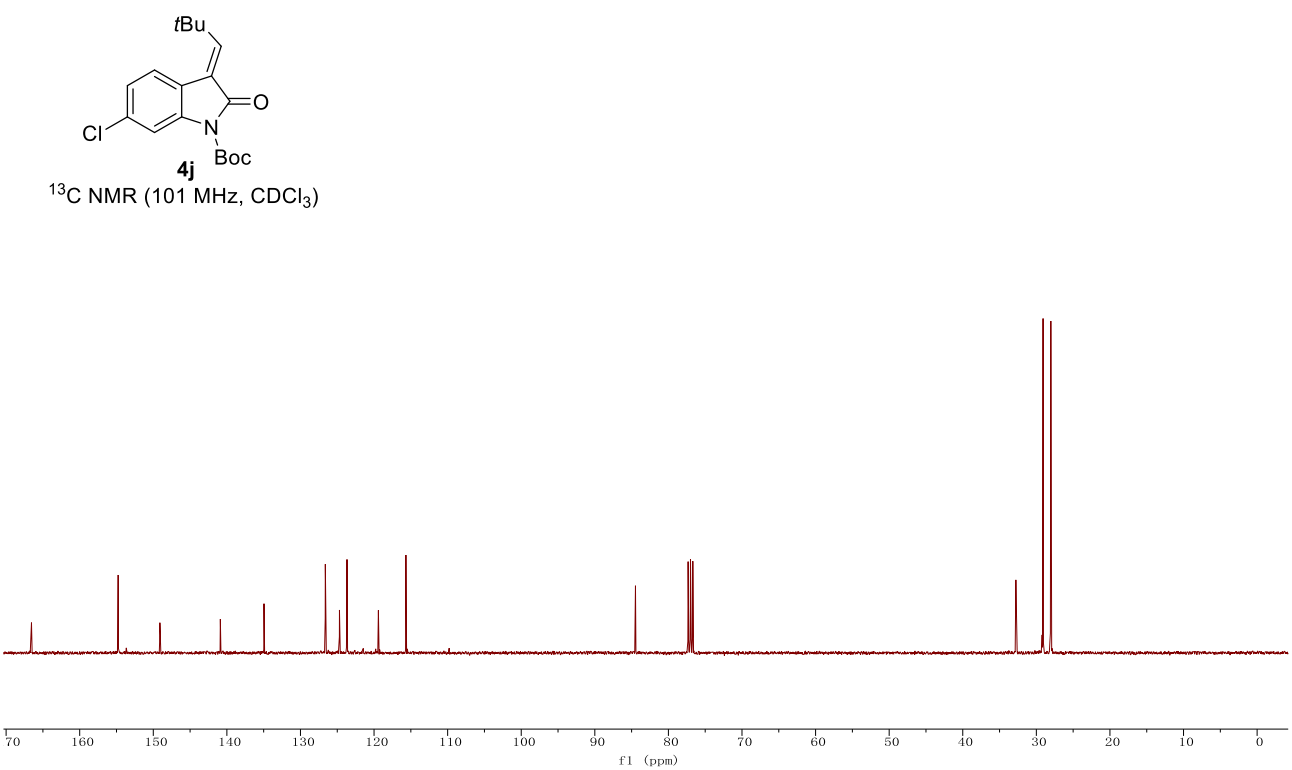
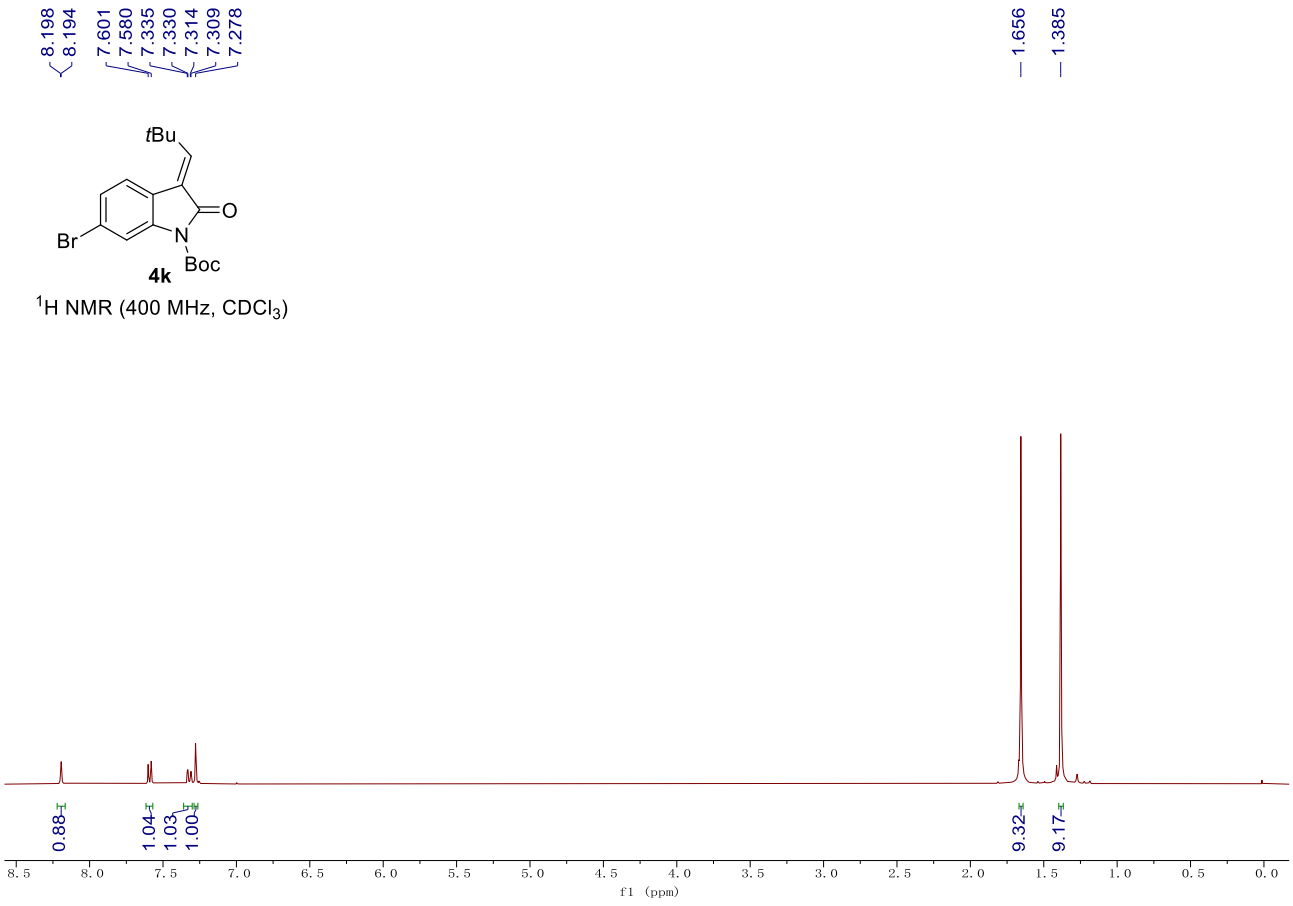


^{13}C NMR (101 MHz, $CDCl_3$)



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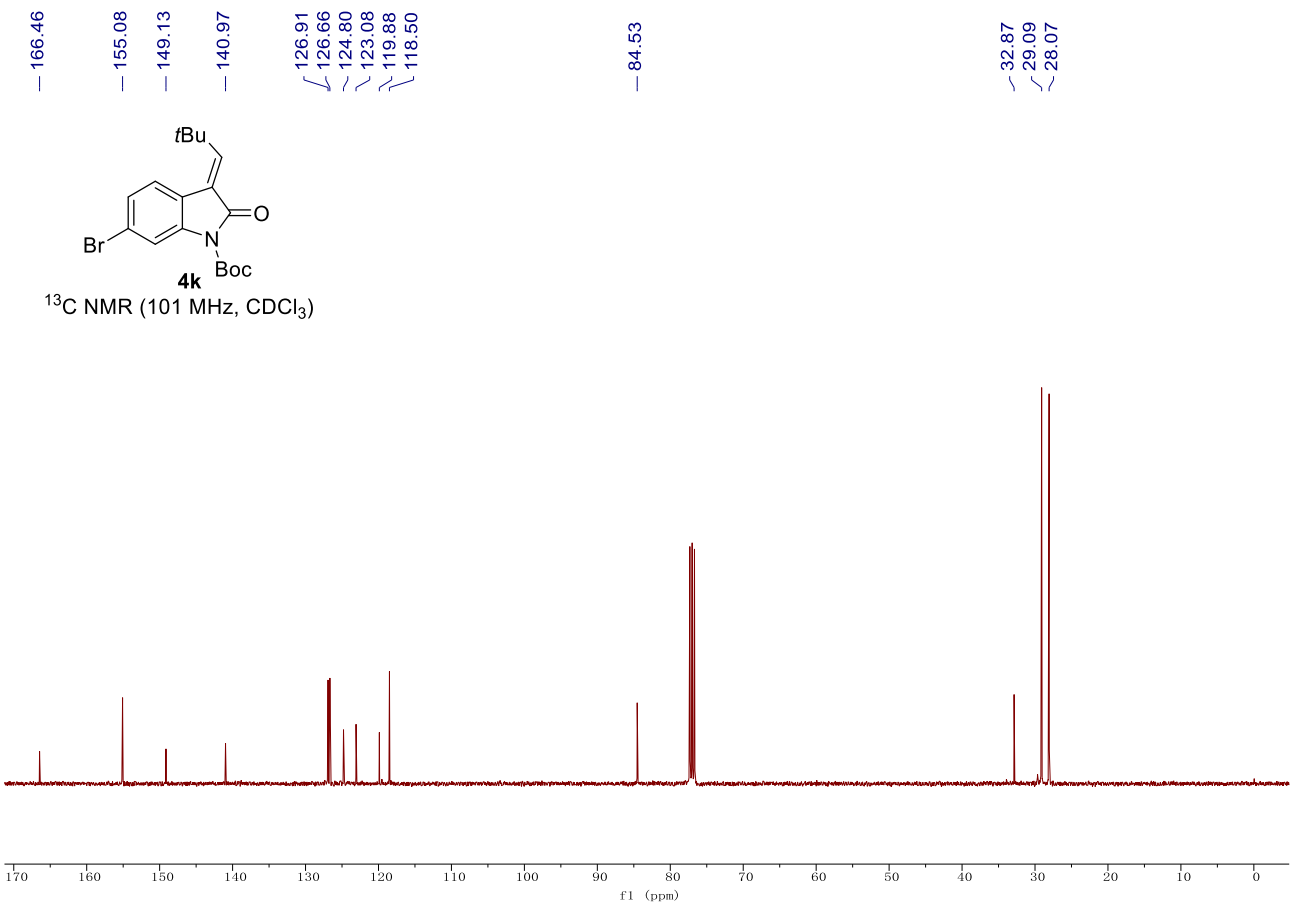
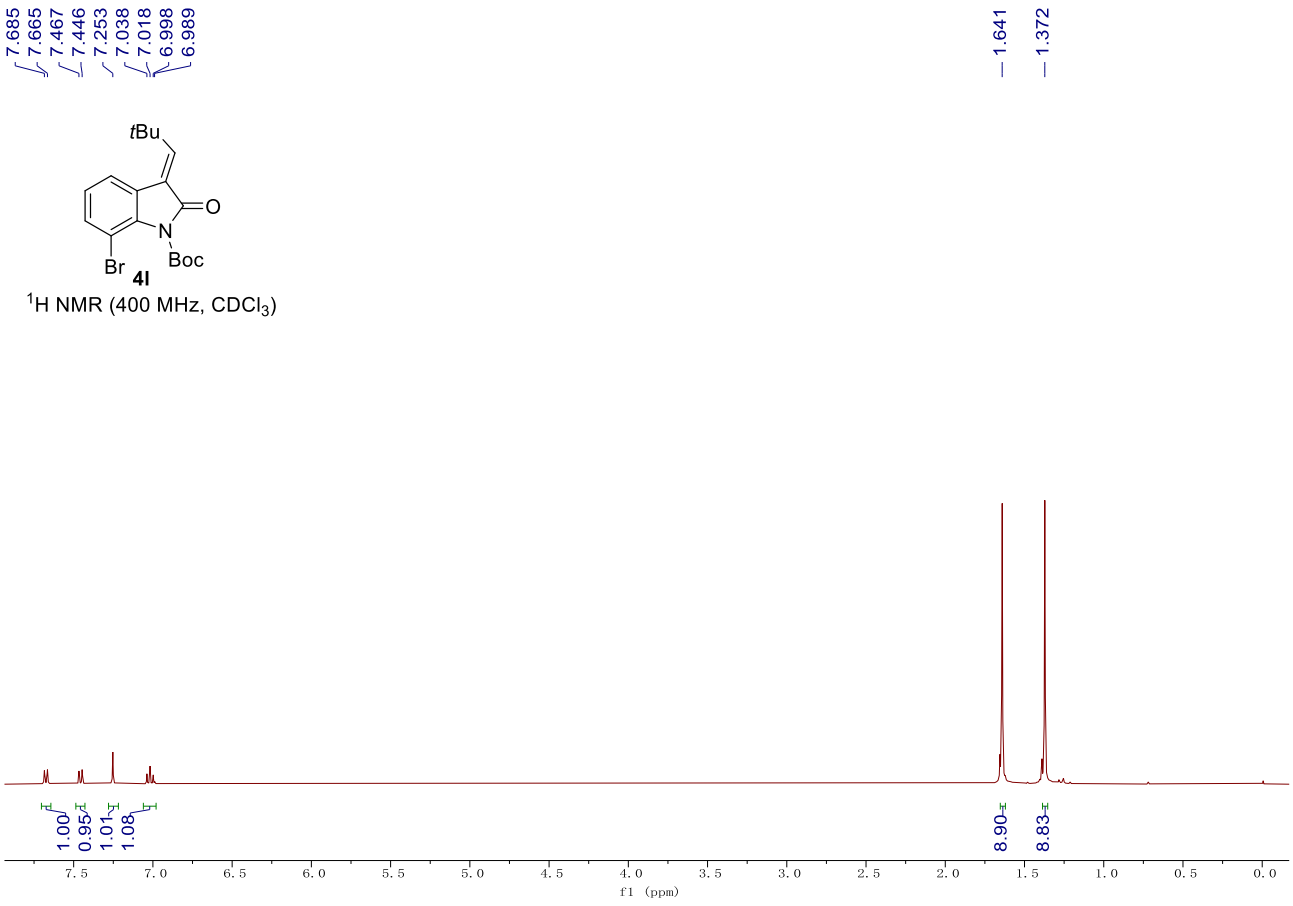


^{13}C NMR (101 MHz, $CDCl_3$)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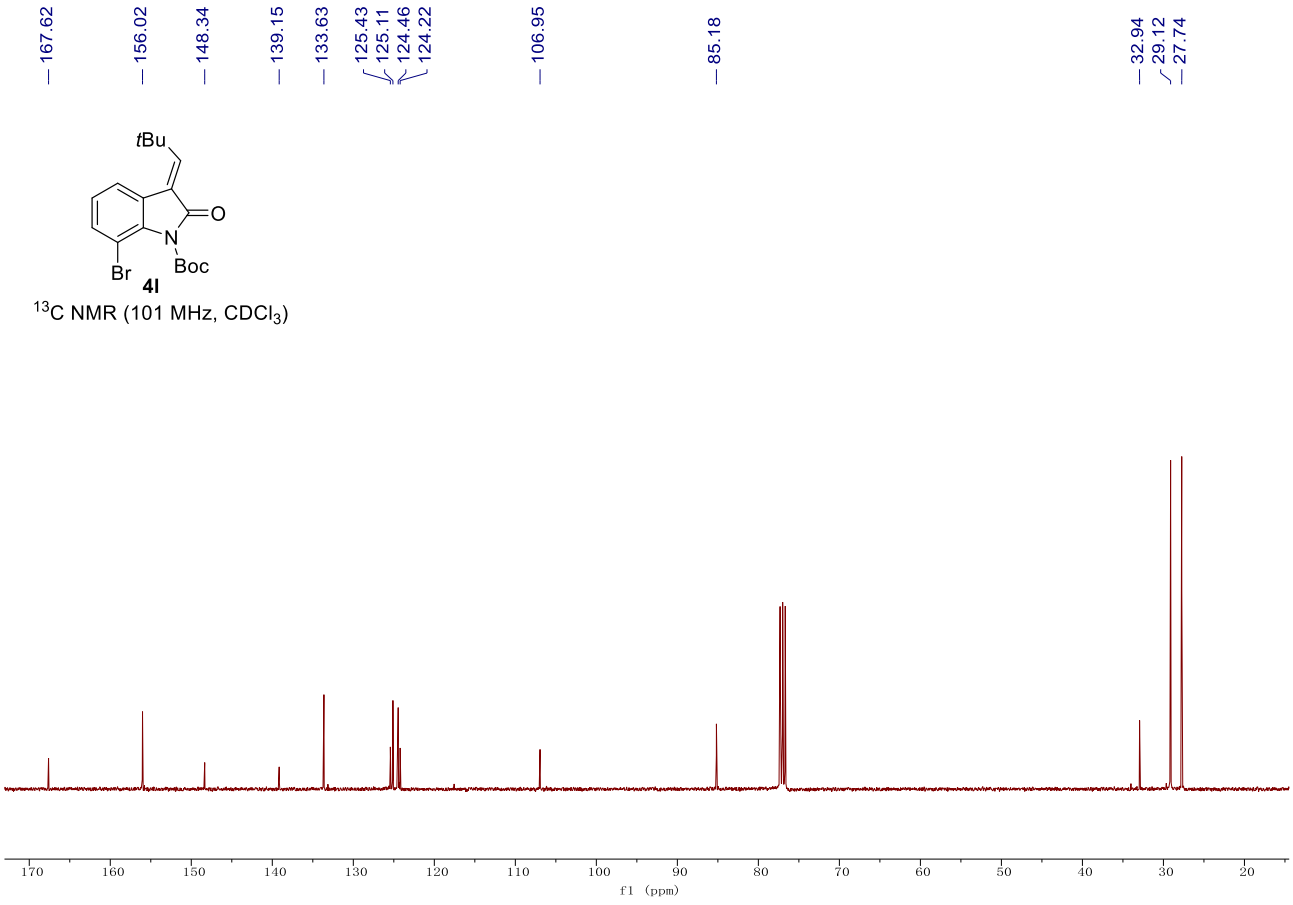
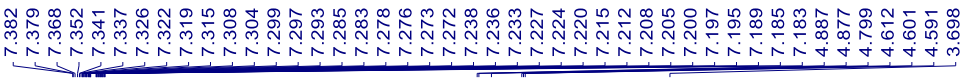
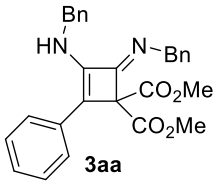
7.665
7.467
7.446
7.253
7.038
7.018
6.998
6.989
1.641
1.372
tBu
O
N
Boc
Br
4l
1H NMR (400 MHz, CDCl3)
1.00
0.95
1.01
1.08
8.90
8.83
f1 (ppm)

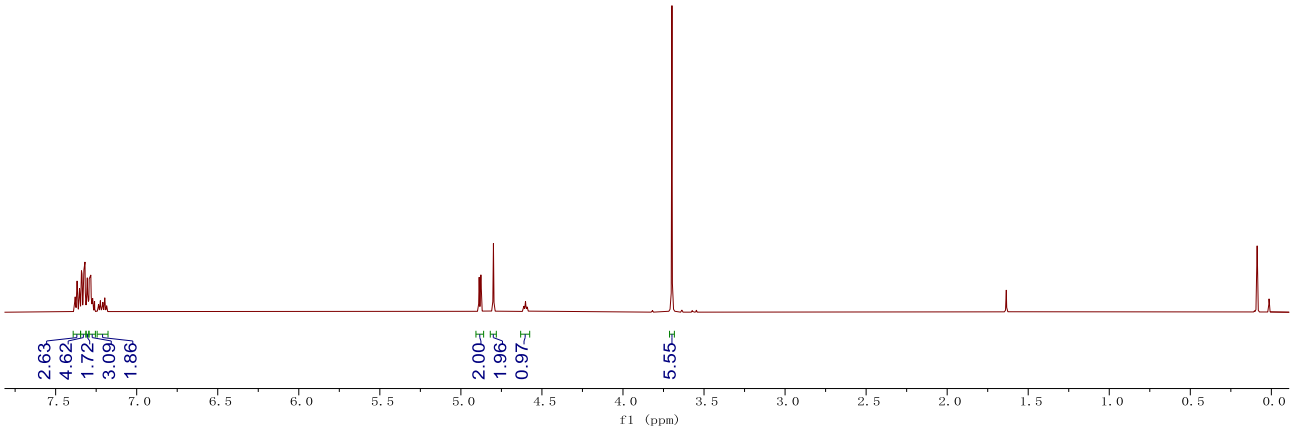

167.62
156.02
148.34
139.15
133.63
125.43
125.11
124.46
124.22
106.95
85.18
32.94
29.12
27.74
tBu
O
N
Boc
Br
4l
13C NMR (101 MHz, CDCl3)
f1 (ppm)

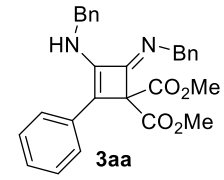




3aa

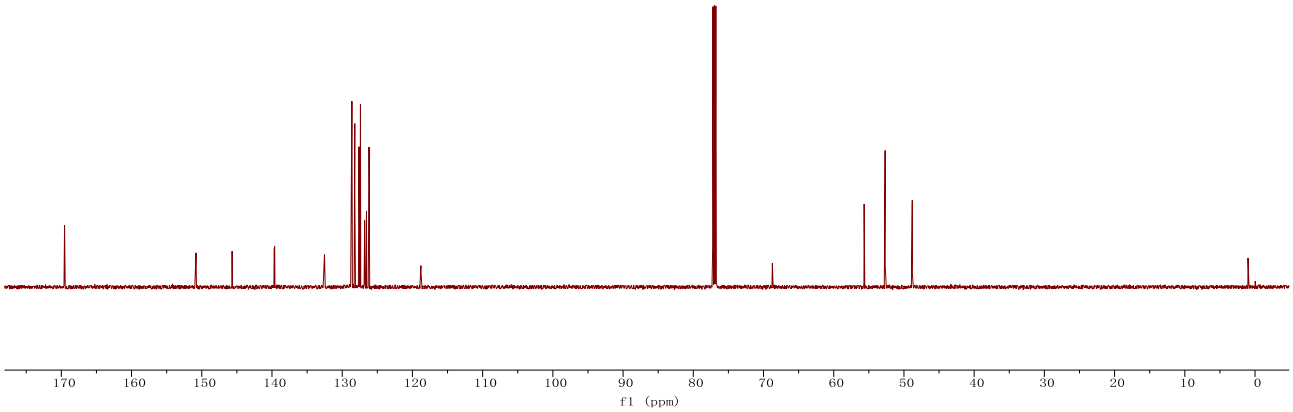
^{1}H NMR (600 MHz, $CDCl_3$)

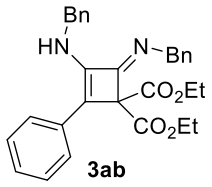




3aa

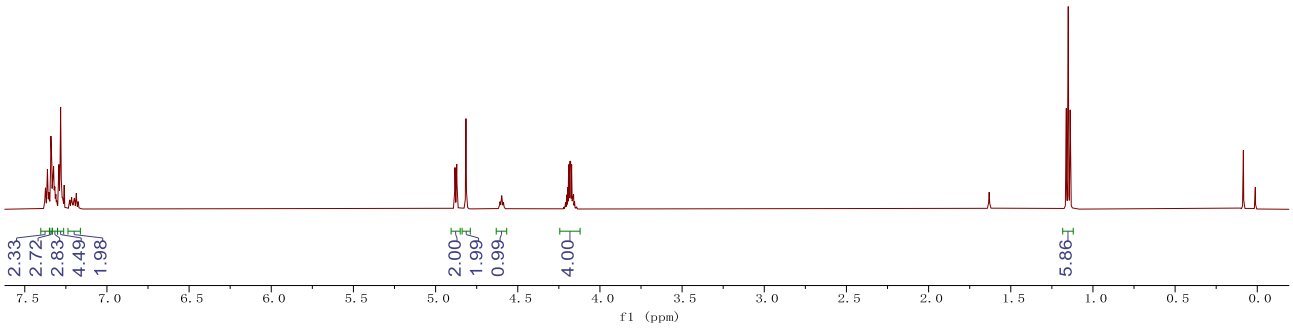
^{13}C NMR (151 MHz, $CDCl_3$)

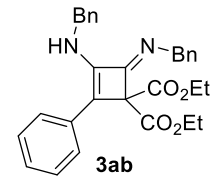




3ab

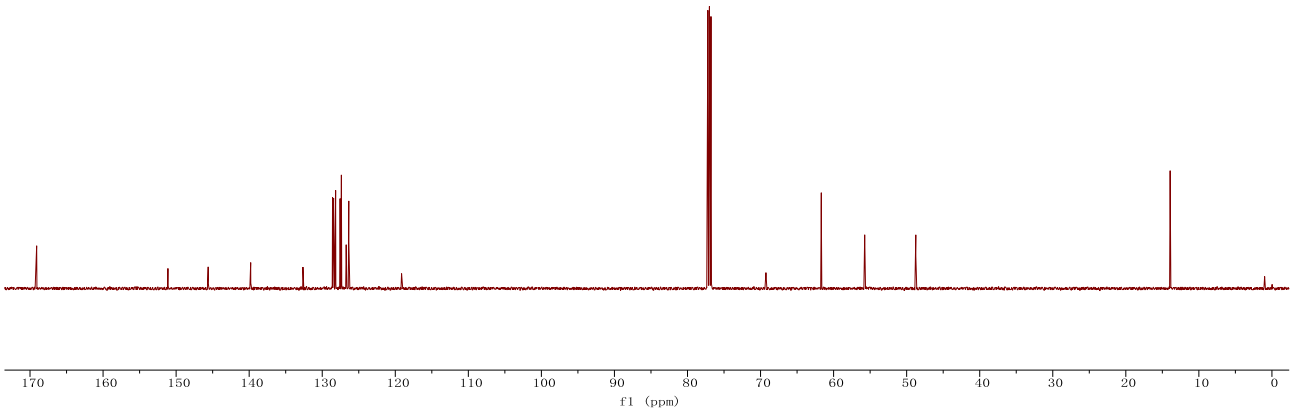
^{1}H NMR (600 MHz, $CDCl_3$)

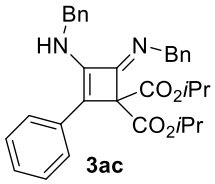




3ab

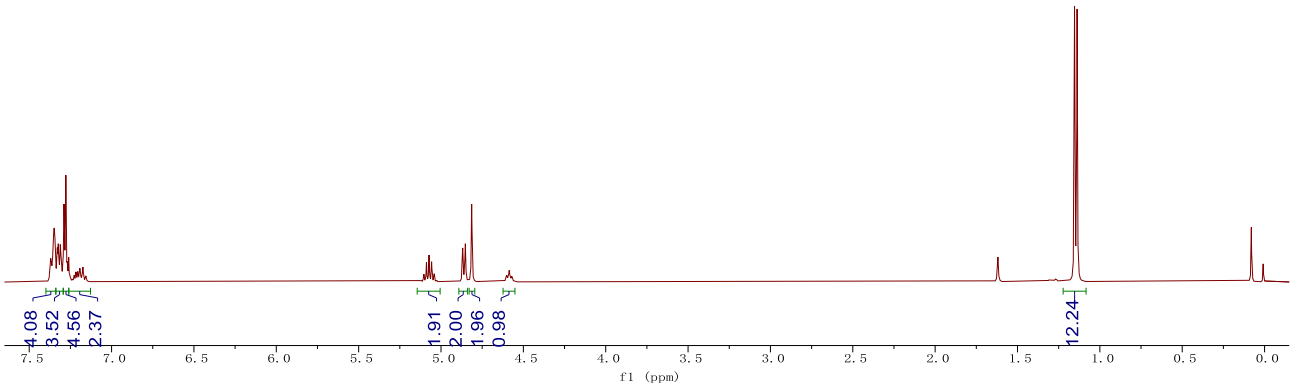
^{13}C NMR (151 MHz, $CDCl_3$)

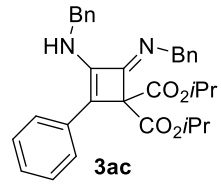




3ac

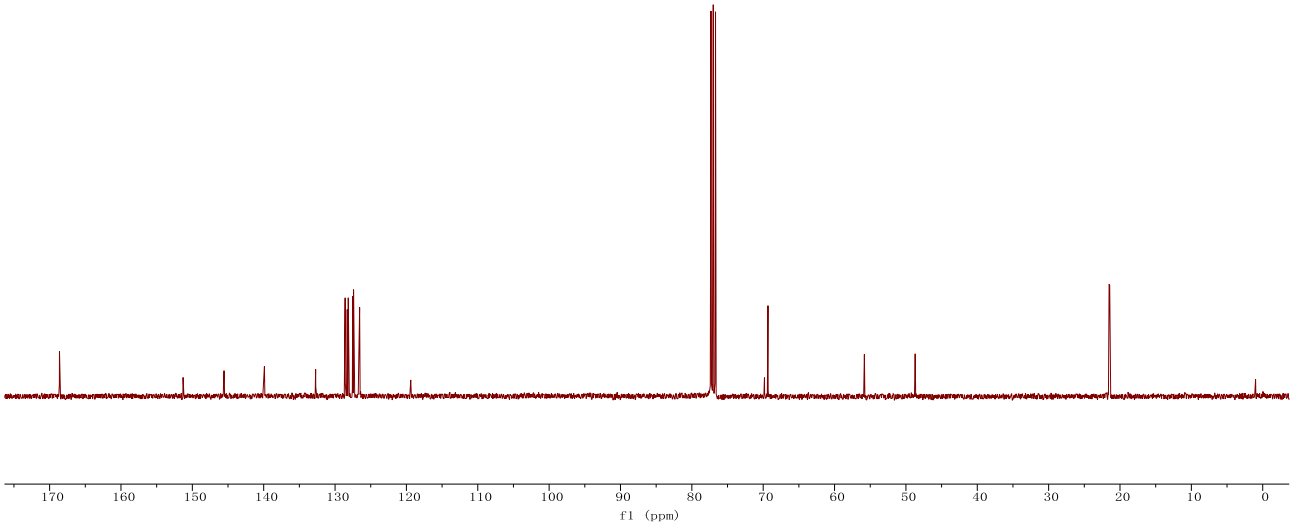
^{1}H NMR (400 MHz, $CDCl_3$)

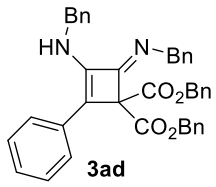




3ac

^{13}C NMR (101 MHz, $CDCl_3$)





3ad

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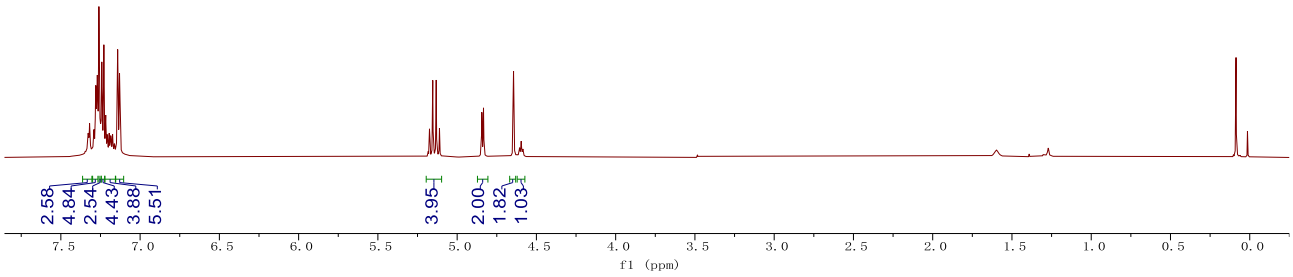

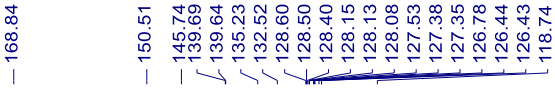

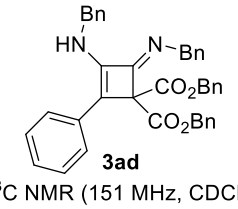

3ad

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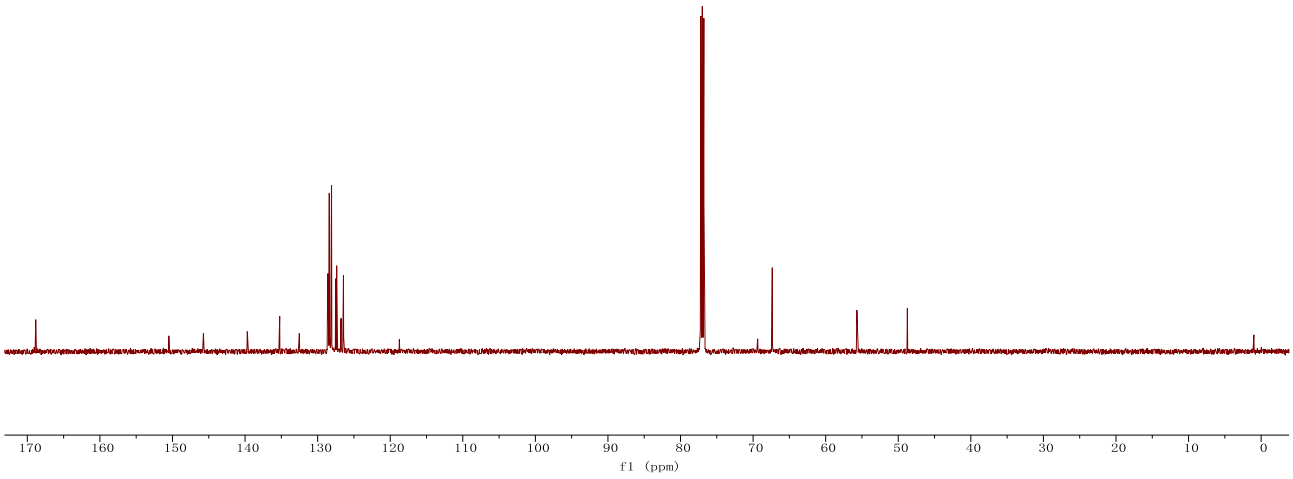
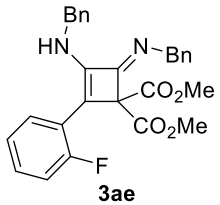
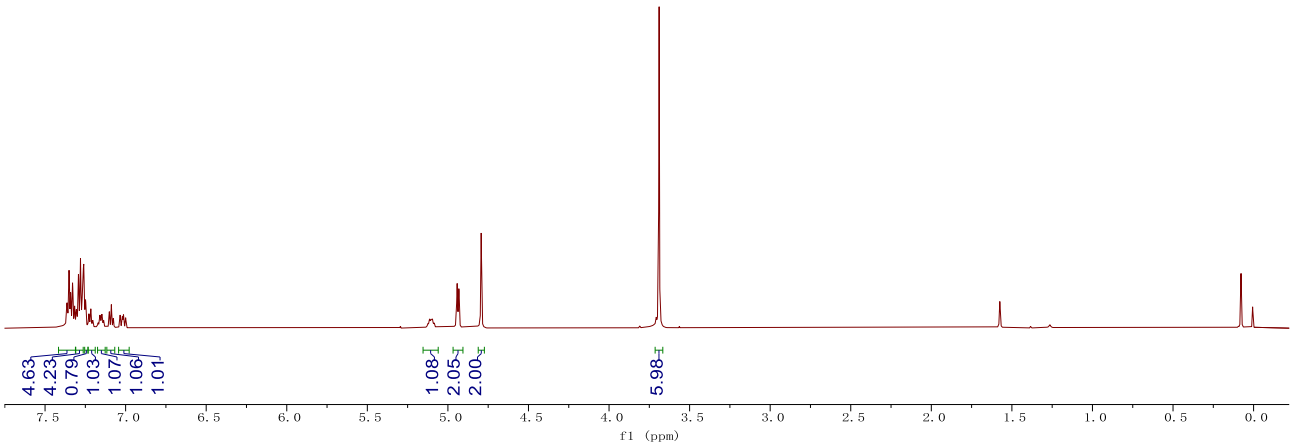
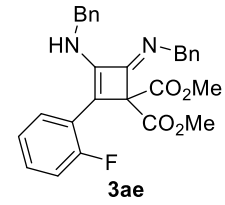




3ae

^{1}H NMR (600 MHz, $CDCl_3$)





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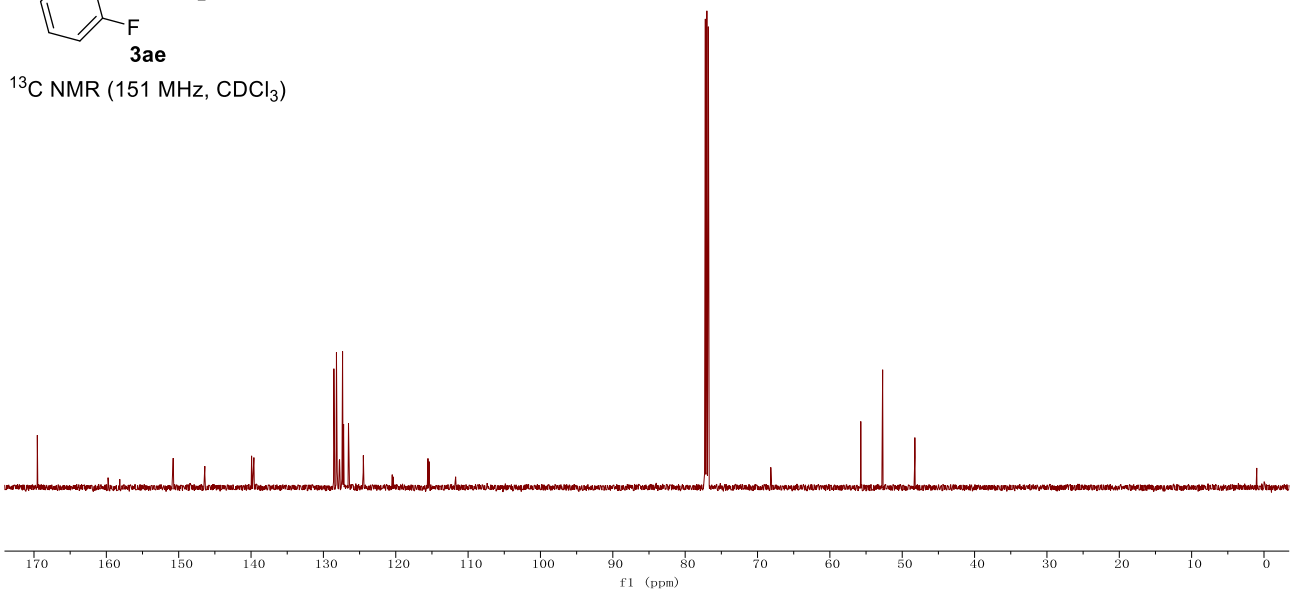
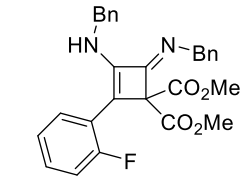
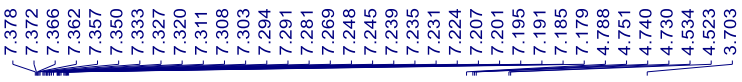
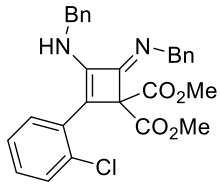




3ae

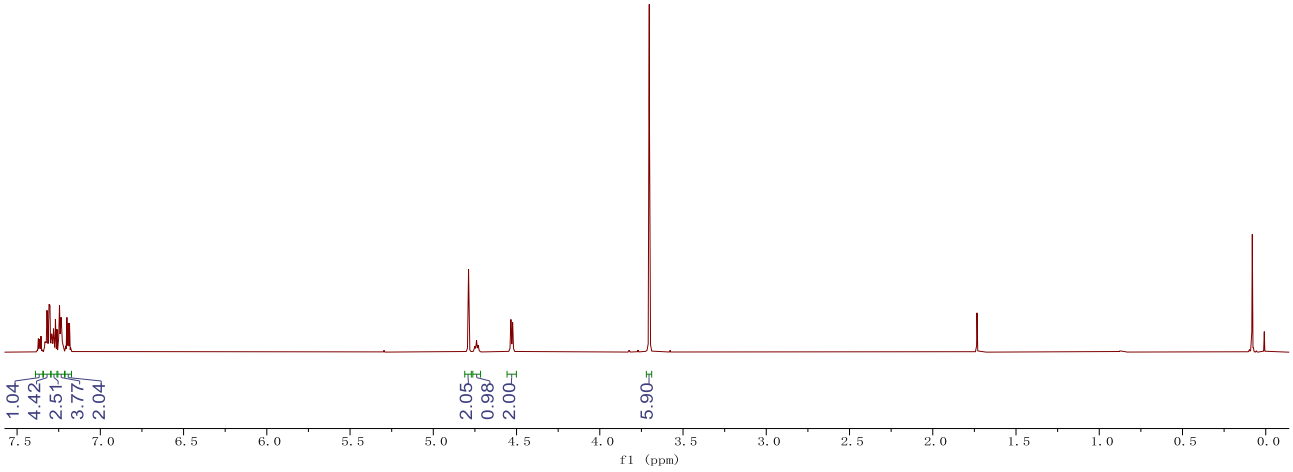
^{19}F NMR (376 MHz, $CDCl_3$)

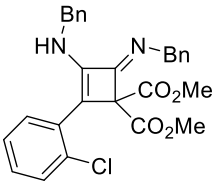




3af

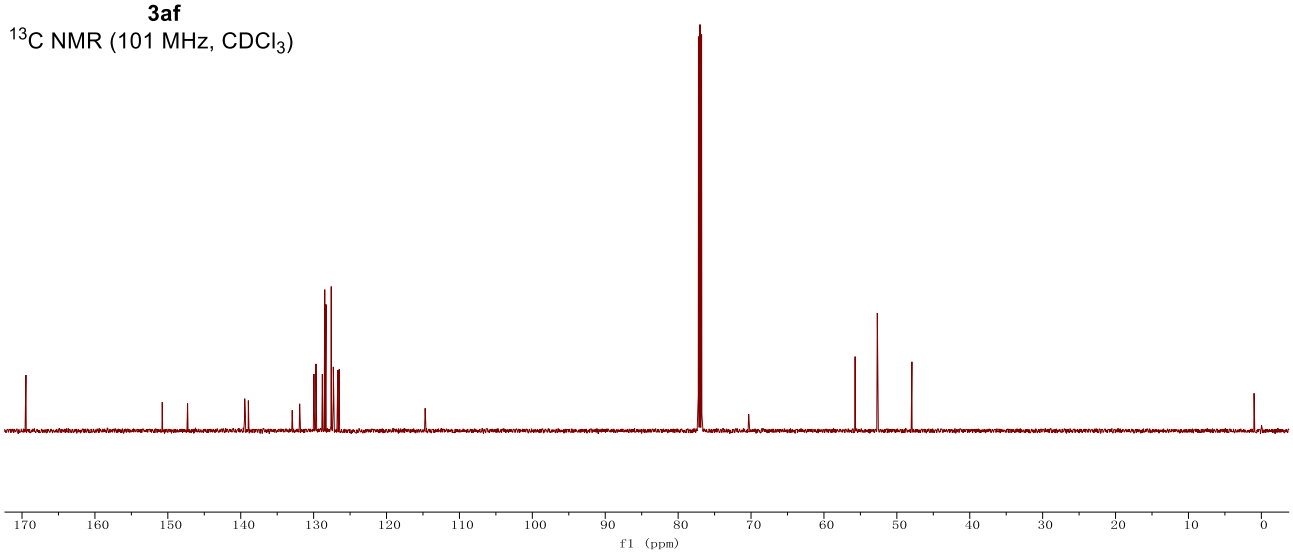
^{1}H NMR (400 MHz, $CDCl_3$)

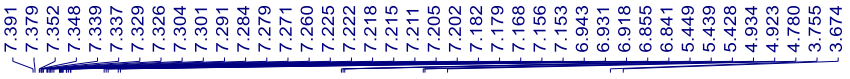


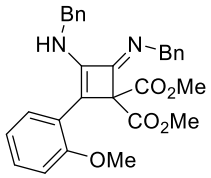


3af

^{13}C NMR (101 MHz, $CDCl_3$)

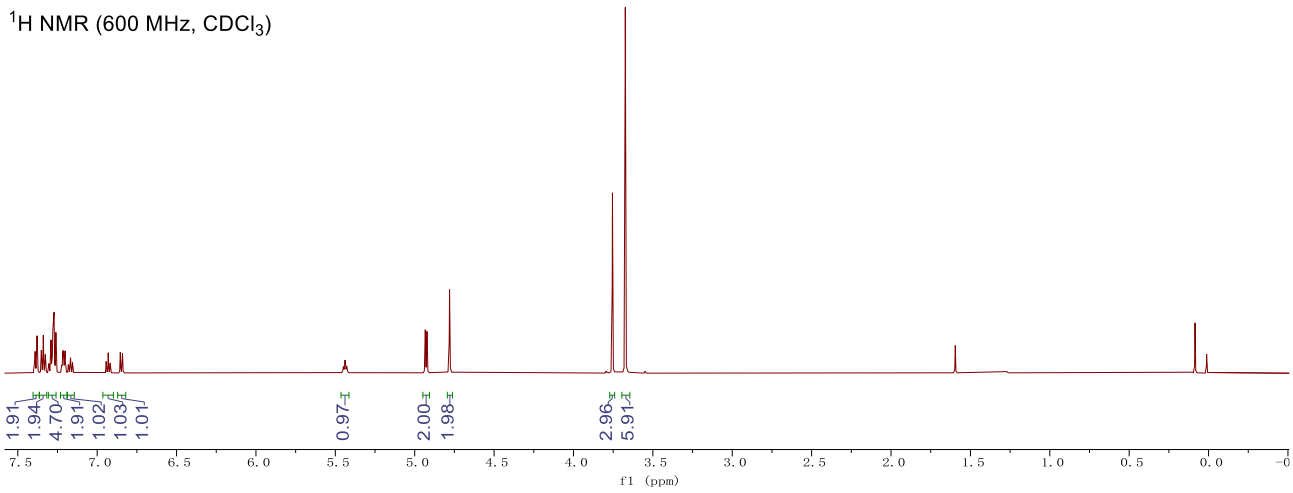


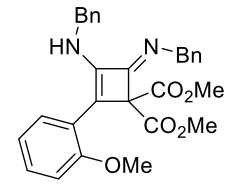




3ag

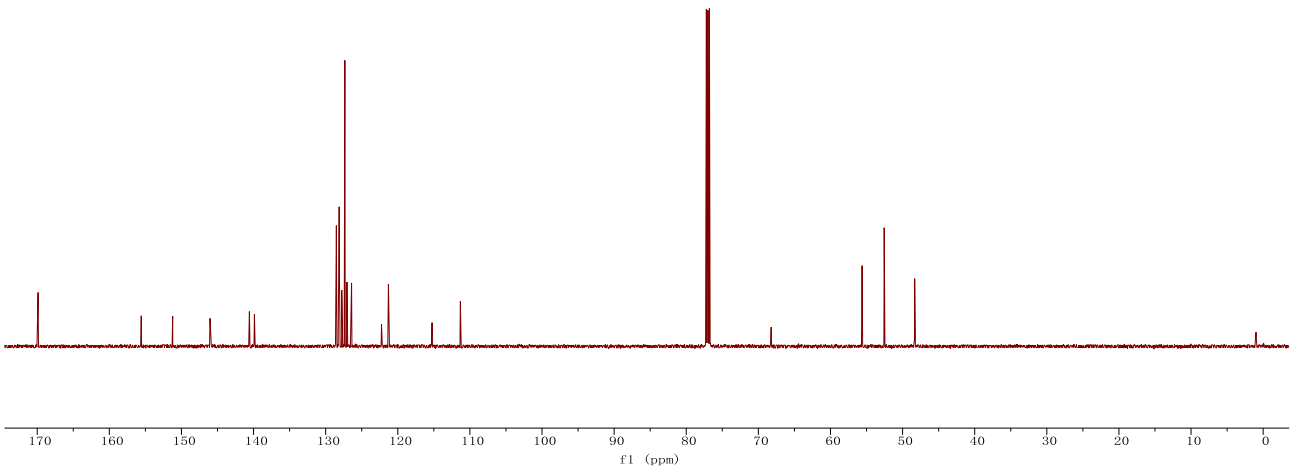
^{1}H NMR (600 MHz, $CDCl_3$)

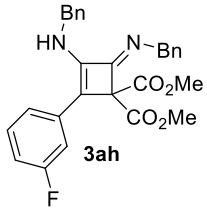




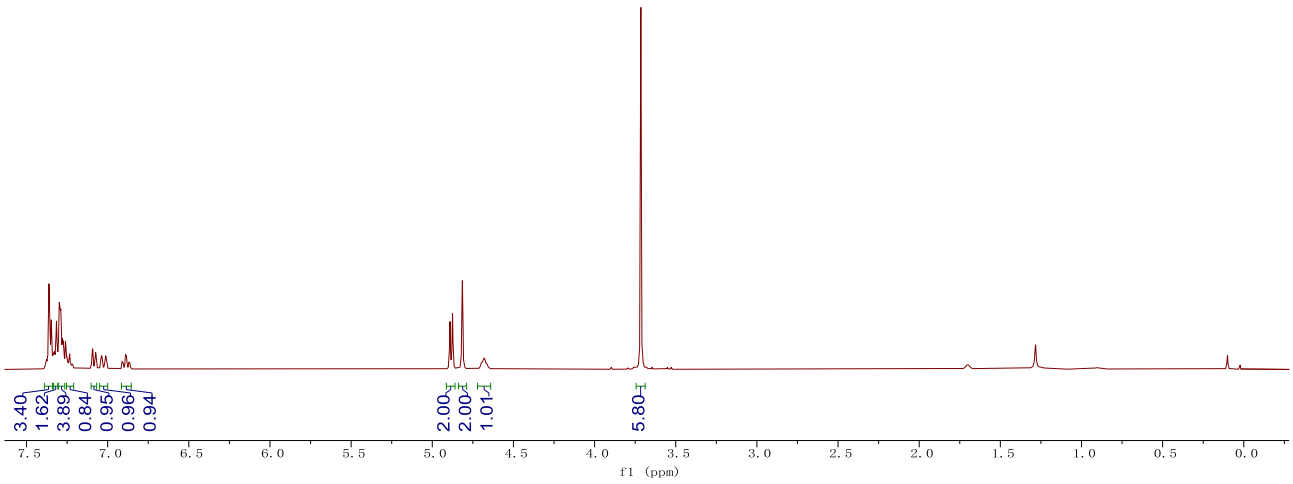
3ag

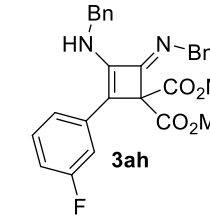
^{13}C NMR (151 MHz, $CDCl_3$)



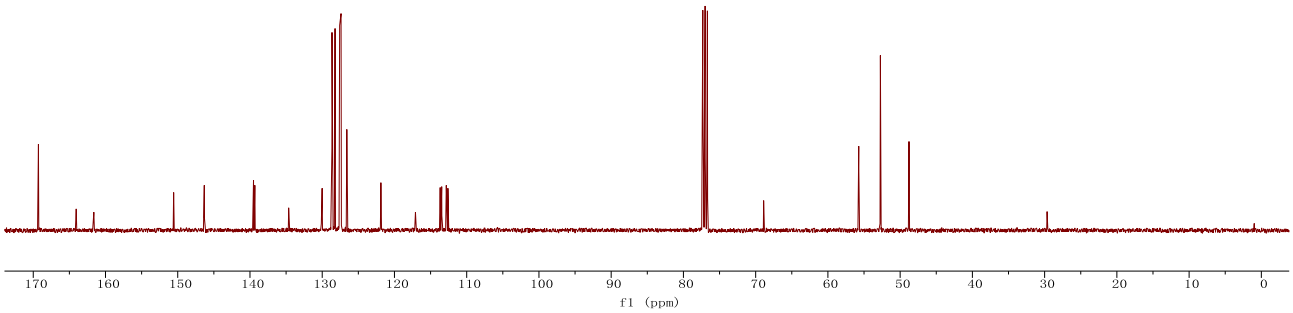


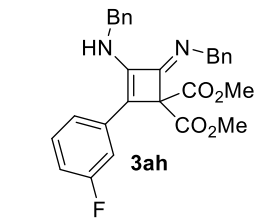
^{1}H NMR (400 MHz, $CDCl_3$)



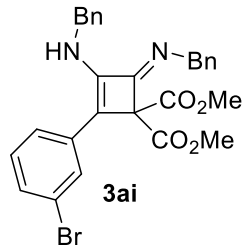


^{13}C NMR (101 MHz, $CDCl_3$)



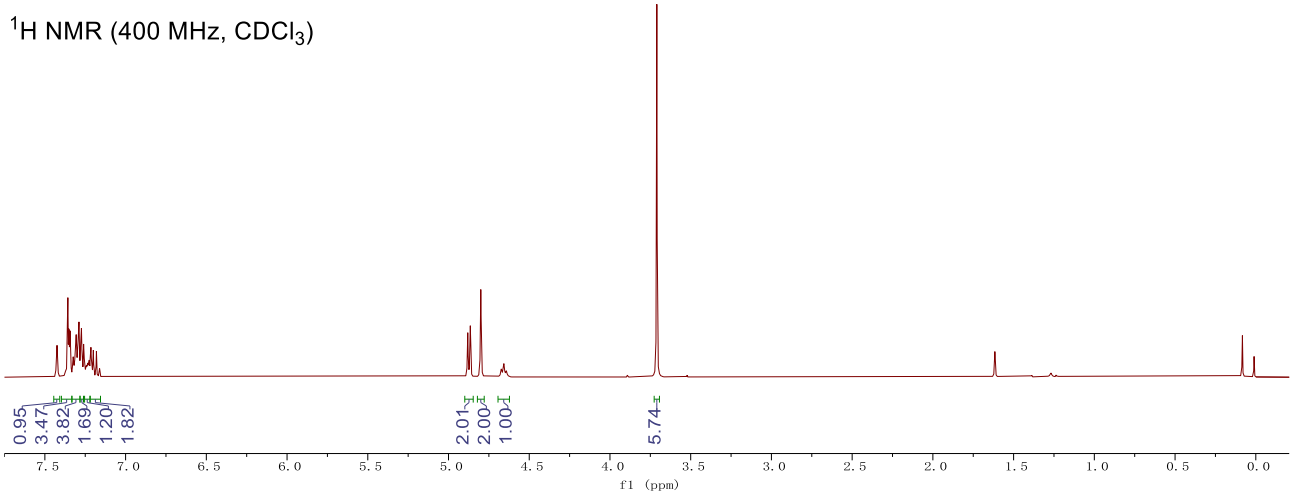


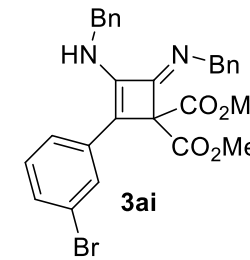
^{19}F NMR (376 MHz, $CDCl_3$)



3ai

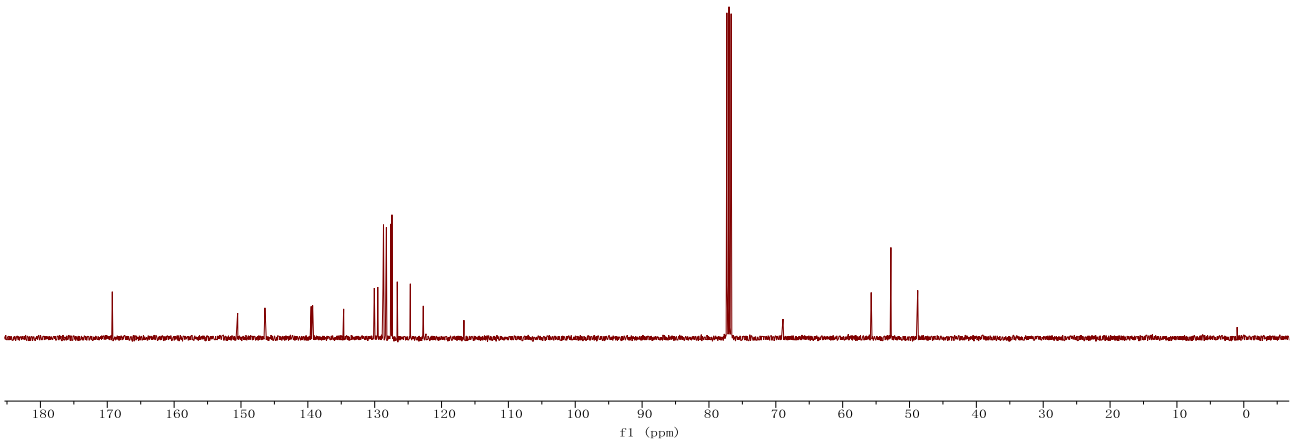
^{1}H NMR (400 MHz, $CDCl_3$)

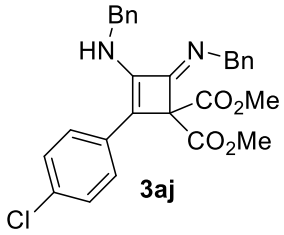




3ai

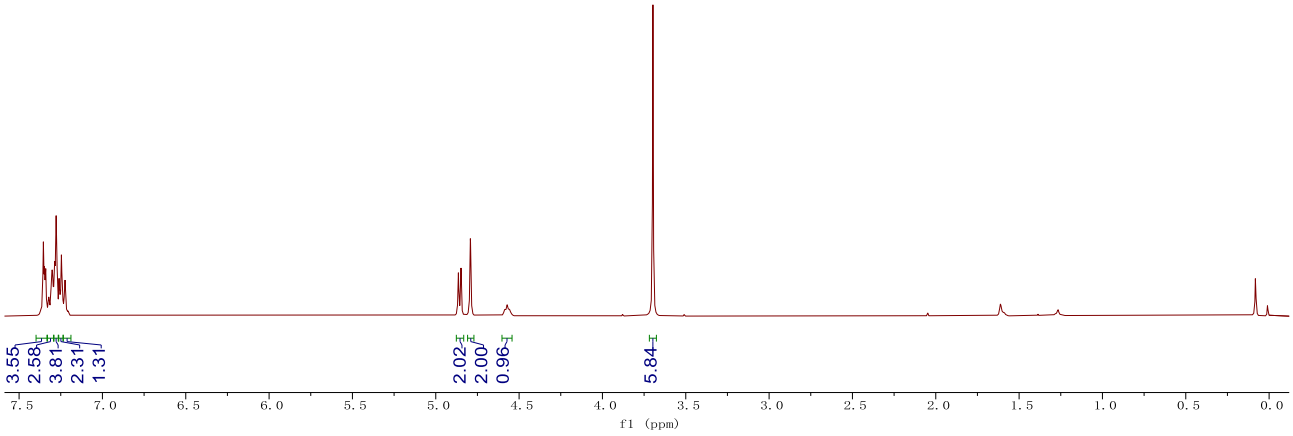
^{13}C NMR (101 MHz, $CDCl_3$)

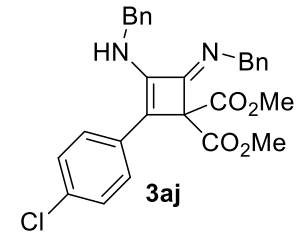




3aj

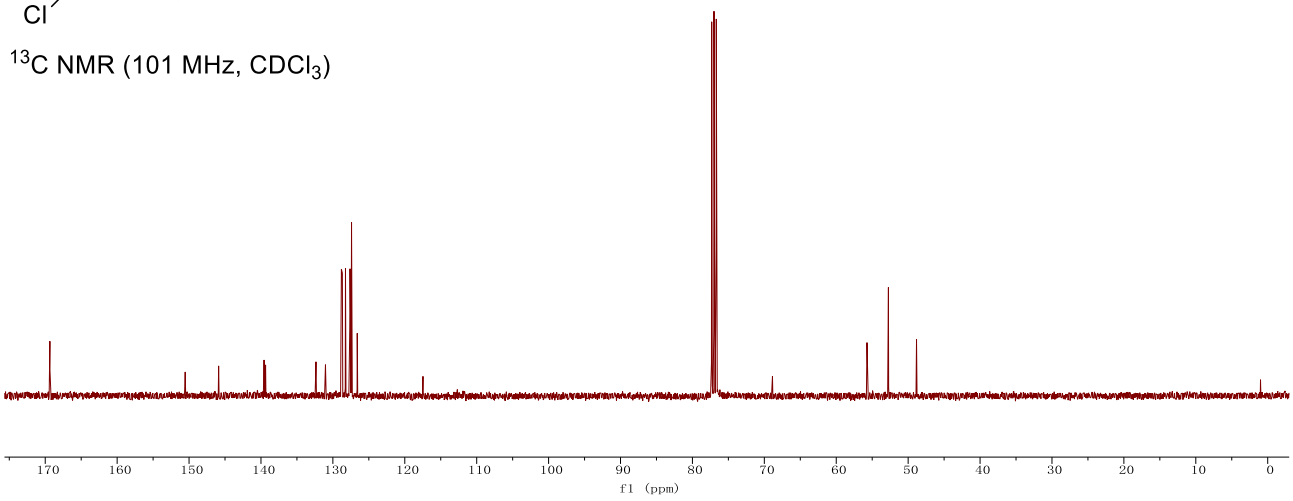
^{1}H NMR (400 MHz, $CDCl_3$)

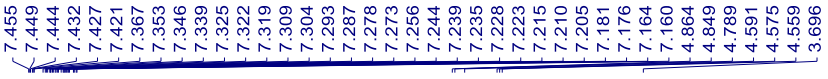


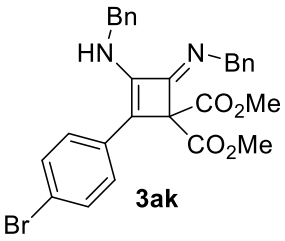


3aj

^{13}C NMR (101 MHz, $CDCl_3$)

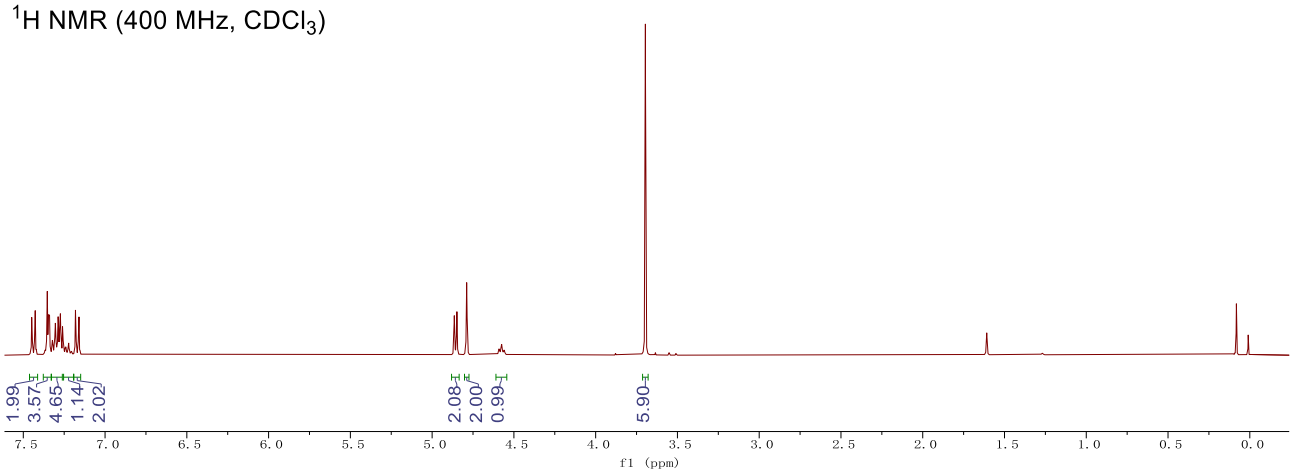


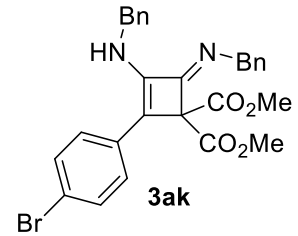




3ak

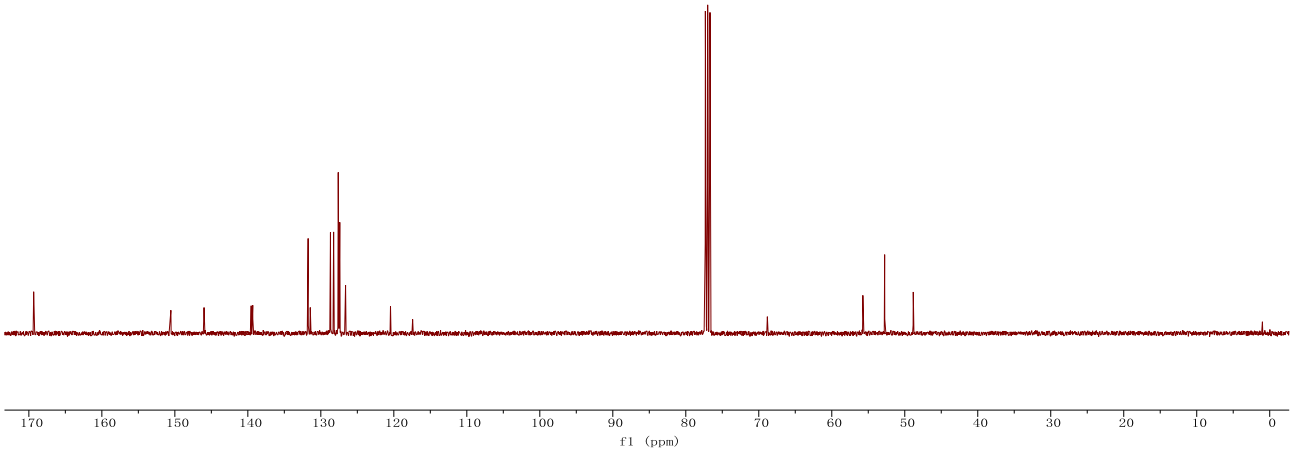
^{1}H NMR (400 MHz, $CDCl_3$)

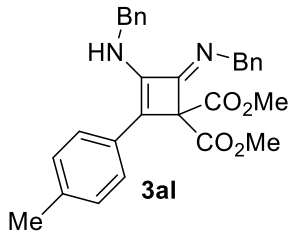




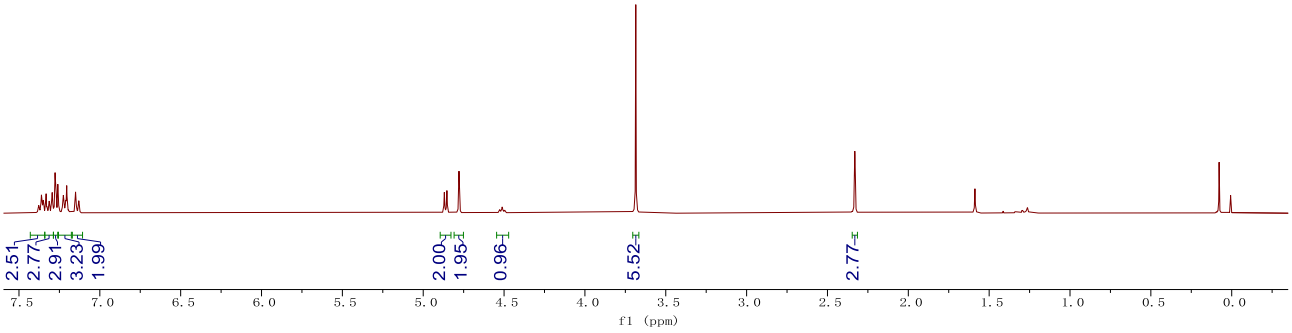
3ak

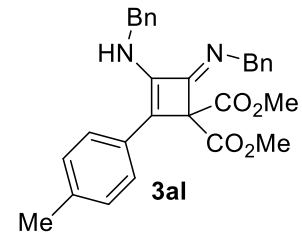
^{13}C NMR (101 MHz, $CDCl_3$)



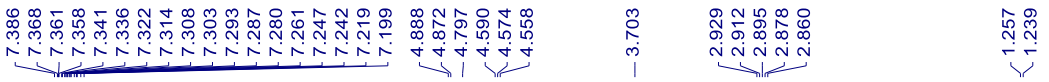


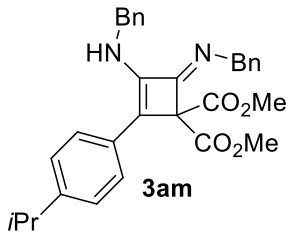
^{1}H NMR (400 MHz, $CDCl_3$)



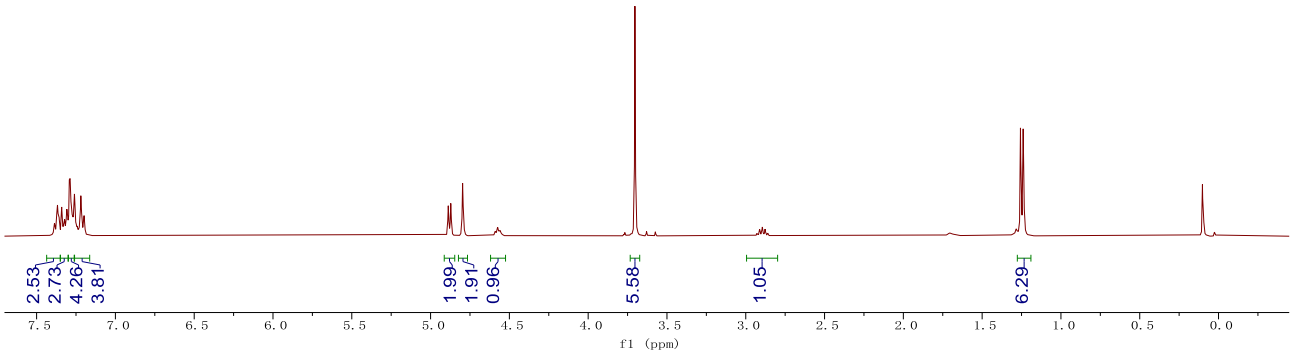


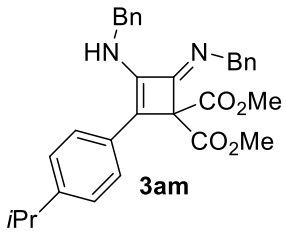
^{13}C NMR (101 MHz, $CDCl_3$)



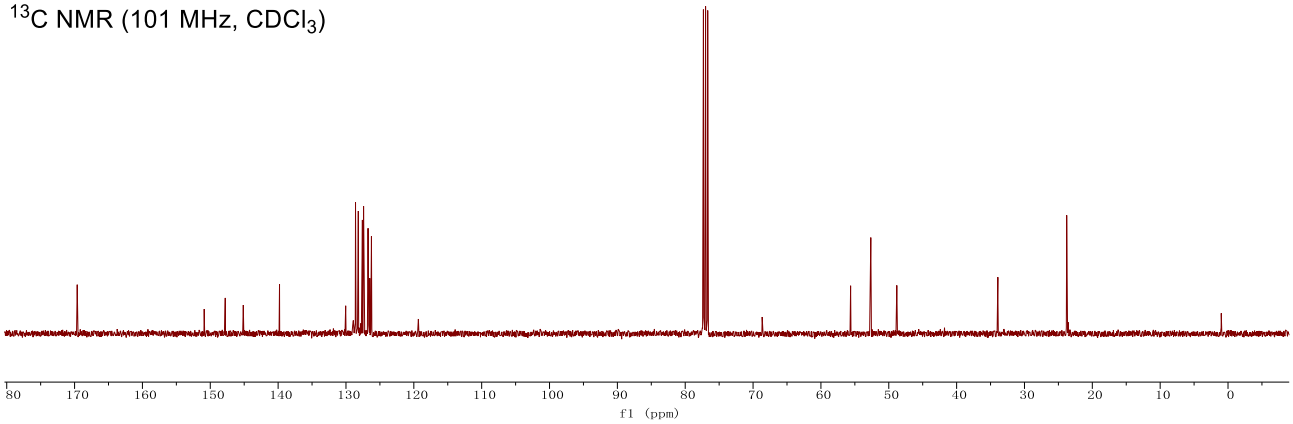


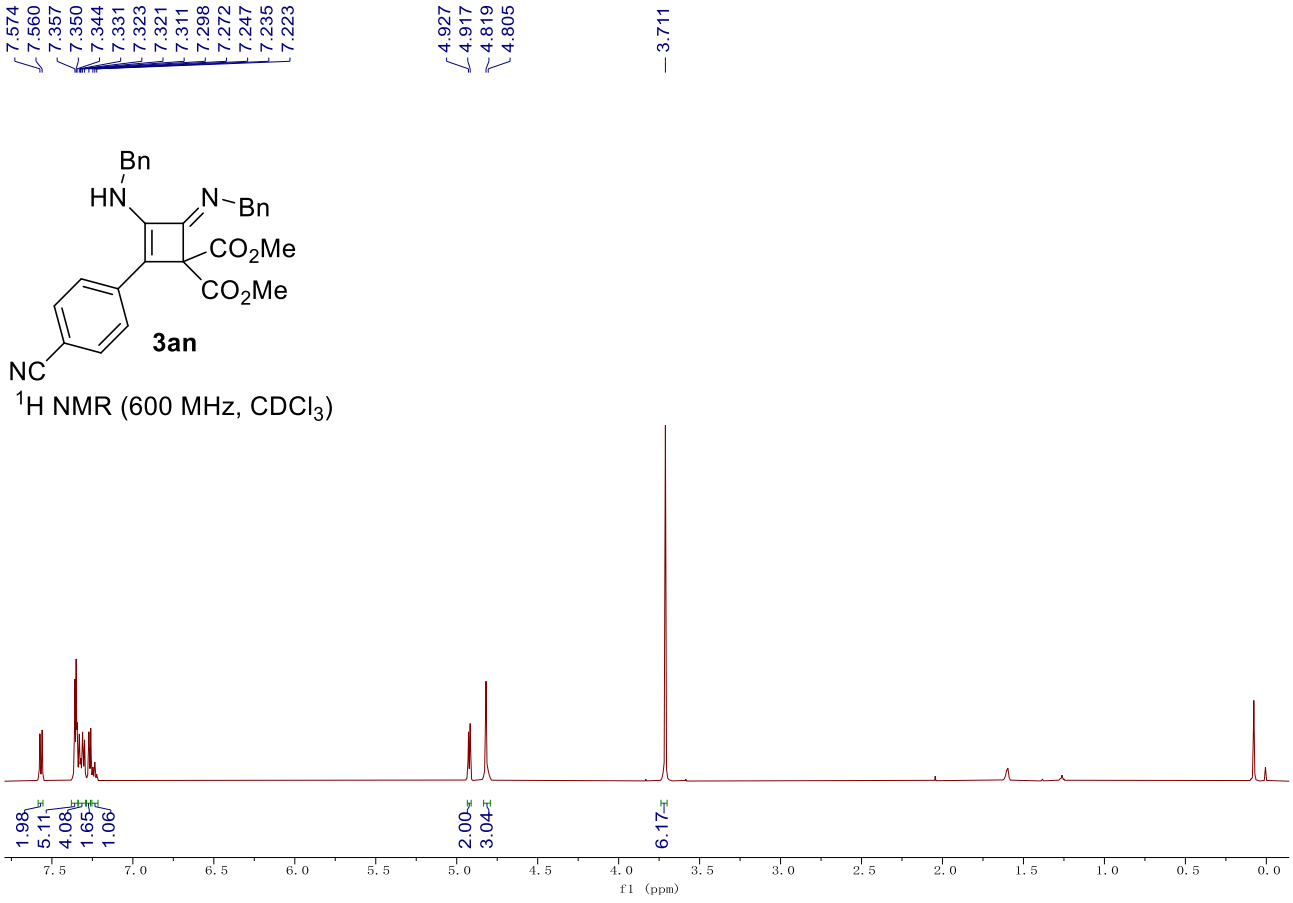
^{1}H NMR (400 MHz, $CDCl_3$)

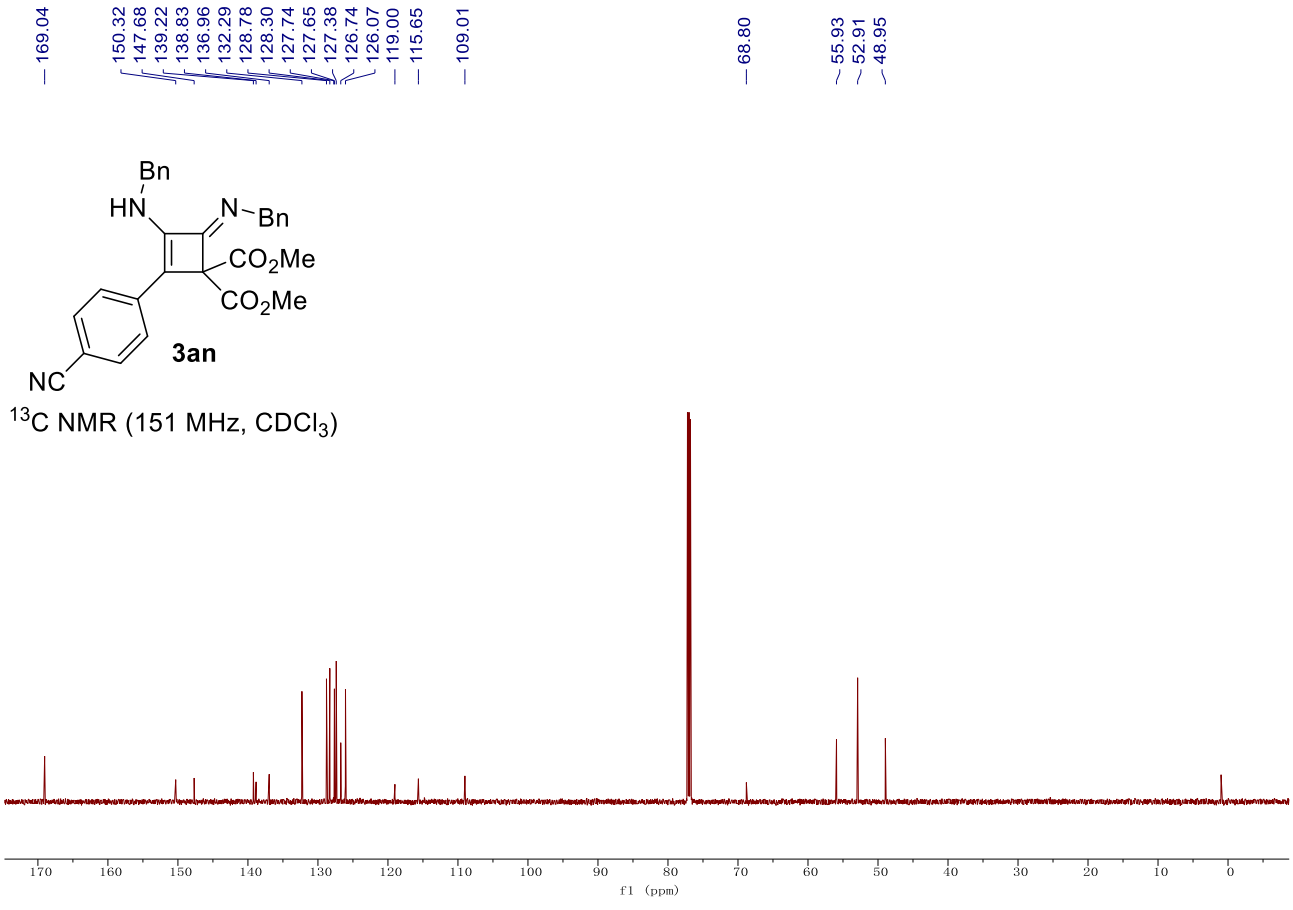


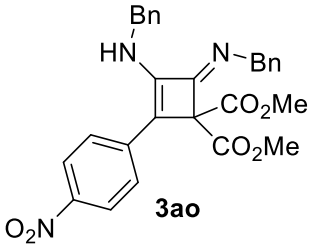


^{13}C NMR (101 MHz, $CDCl_3$)



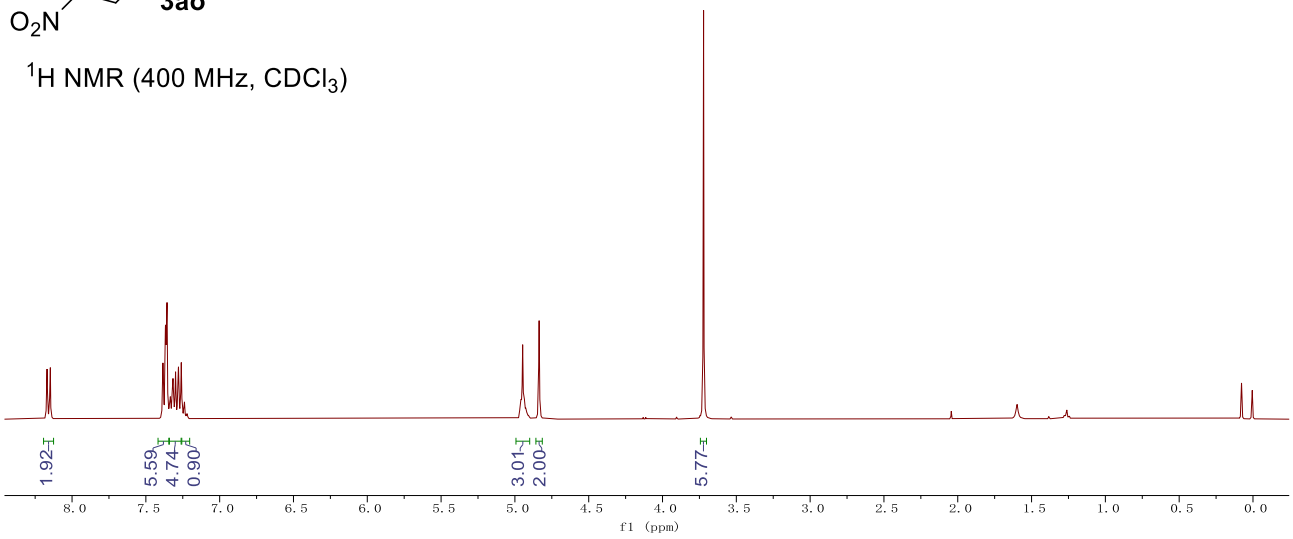

7.574
7.560
7.357
7.350
7.344
7.331
7.323
7.321
7.311
7.298
7.272
7.247
7.235
7.223
4.927
4.917
4.819
4.805
3.711
Bn
HN
N
Bn
CO2Me
CO2Me
NC
3an
1H NMR (600 MHz, CDCl3)
1.98
5.11
4.08
1.65
1.06
2.00
3.04
6.17
f1 (ppm)

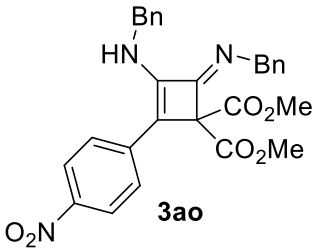

169.04
150.32
147.68
139.22
138.83
136.96
132.29
128.78
128.30
127.74
127.65
127.38
126.74
126.07
119.00
115.65
109.01
68.80
55.93
52.91
48.95
Bn
HN
N
Bn
CO2Me
CO2Me
NC
3an
13C NMR (151 MHz, CDCl3)
f1 (ppm)



3ao

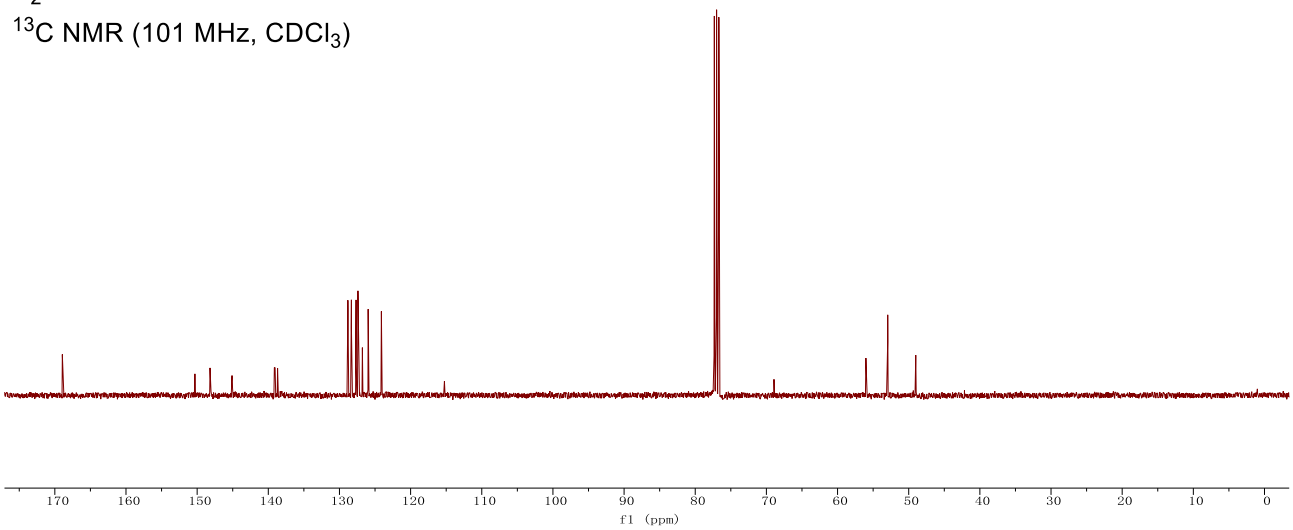
^{1}H NMR (400 MHz, $CDCl_3$)

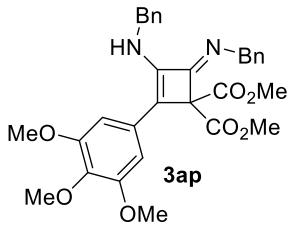




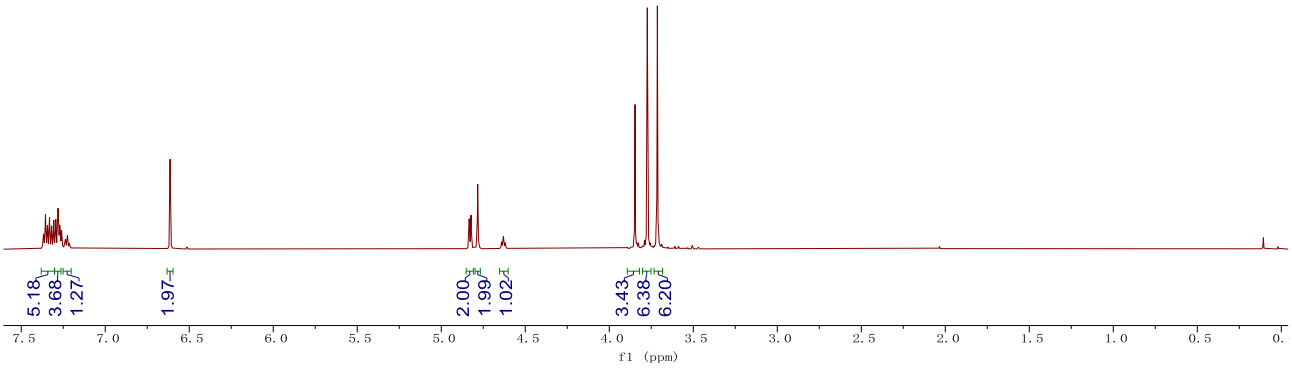
3ao

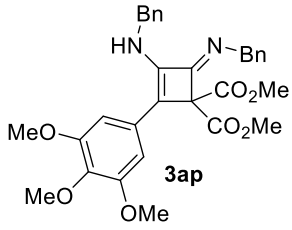
^{13}C NMR (101 MHz, $CDCl_3$)



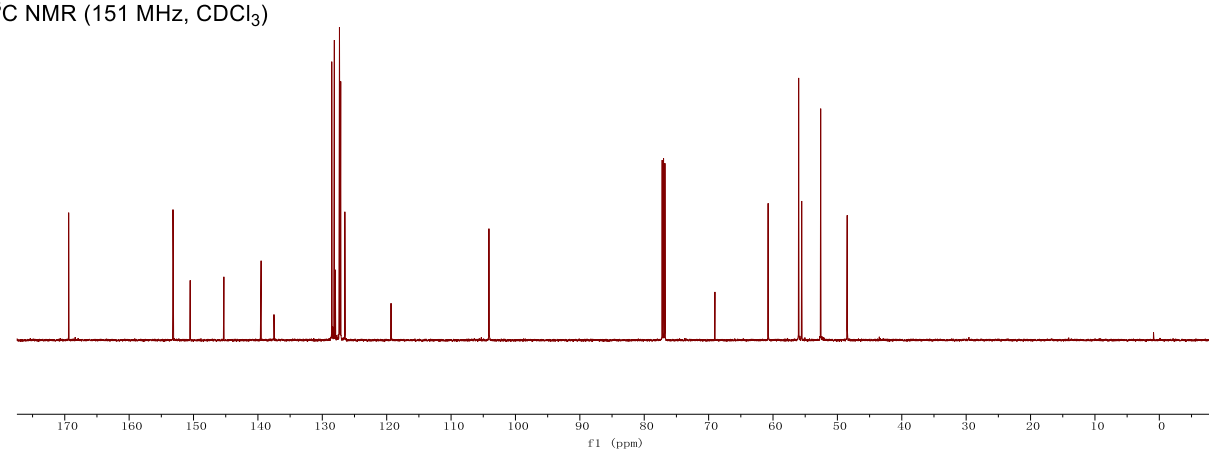


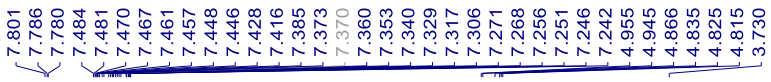
^{1}H NMR (600 MHz, $CDCl_3$)

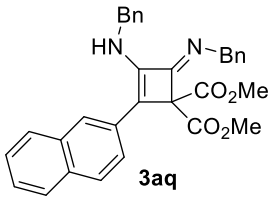




^{13}C NMR (151 MHz, $CDCl_3$)

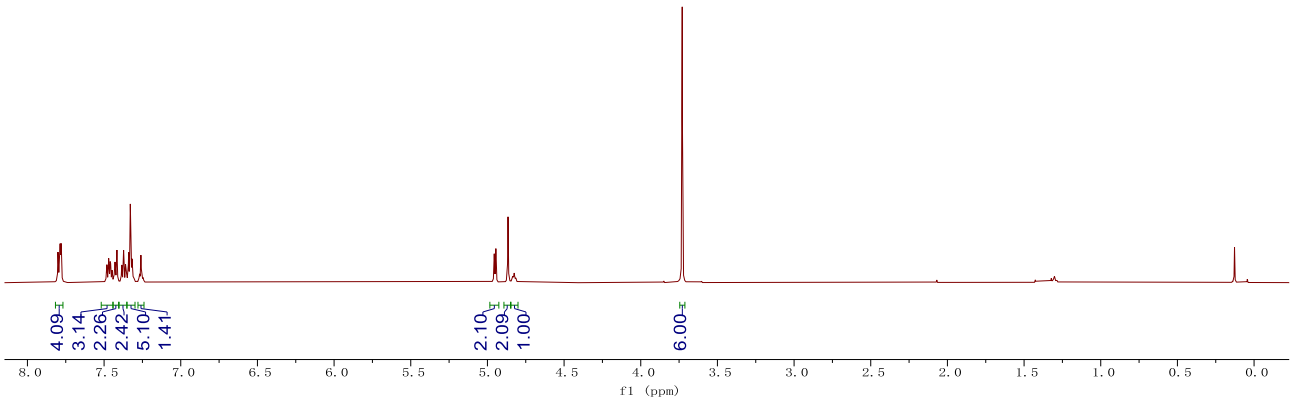


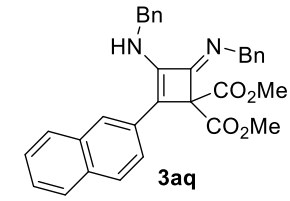




3aq

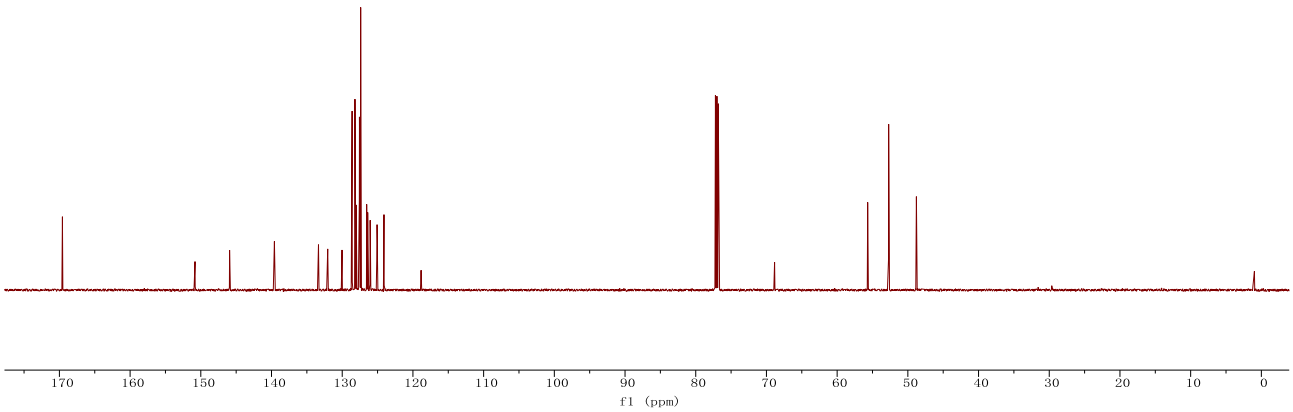
^{1}H NMR (600 MHz, $CDCl_3$)

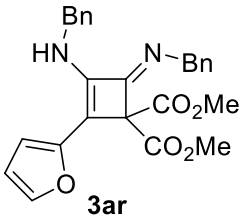




3aq

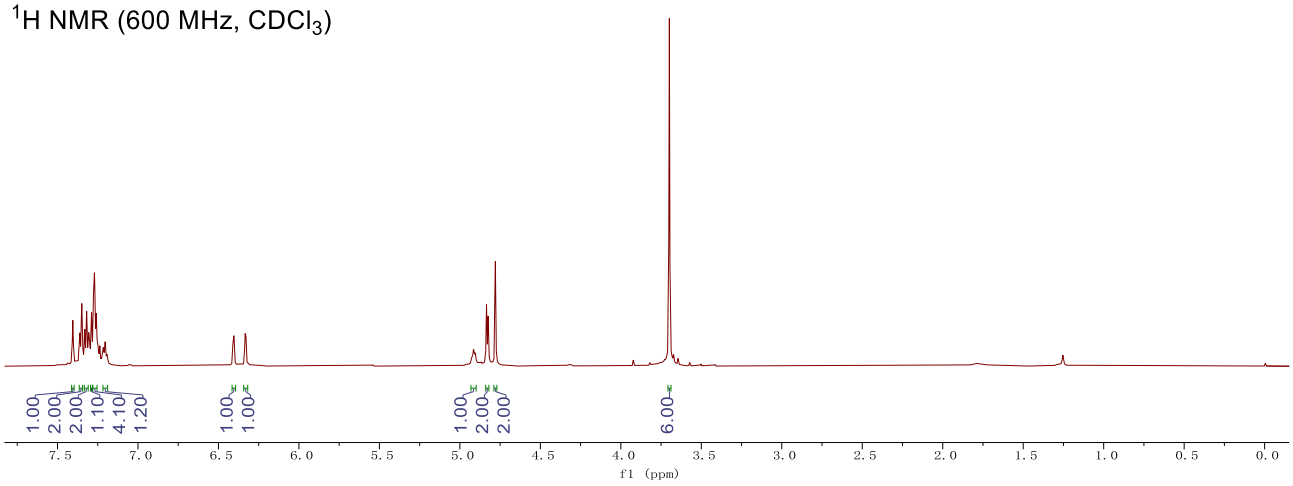
^{13}C NMR (151 MHz, $CDCl_3$)

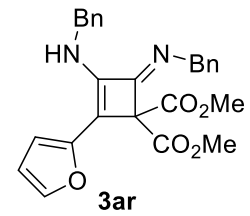




3ar

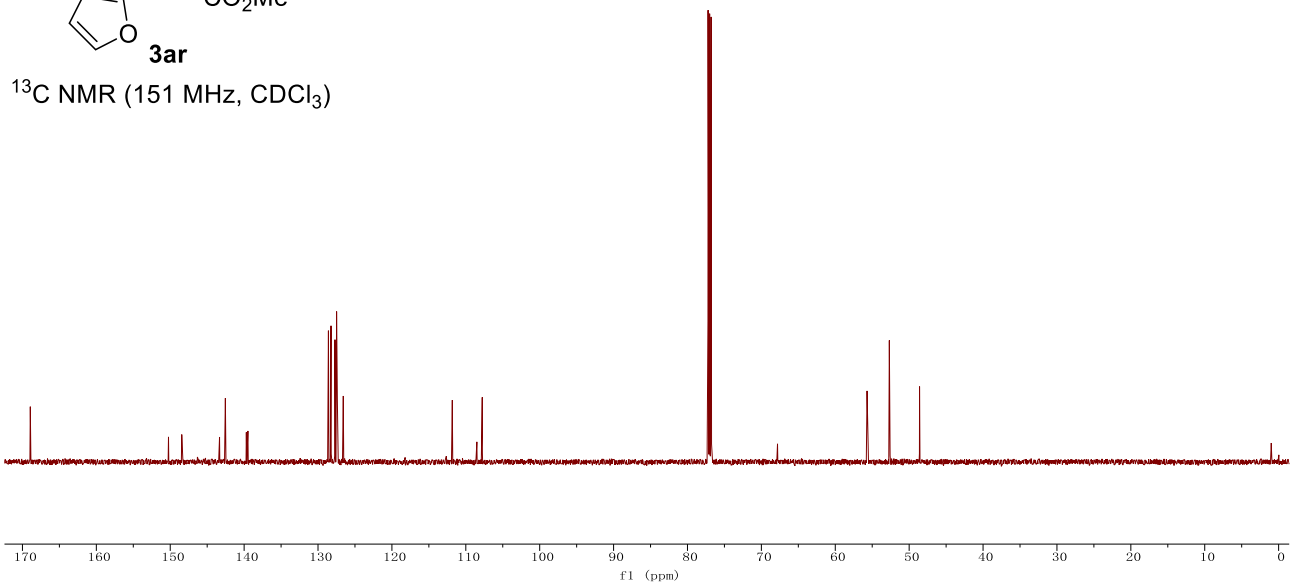
^{1}H NMR (600 MHz, $CDCl_3$)

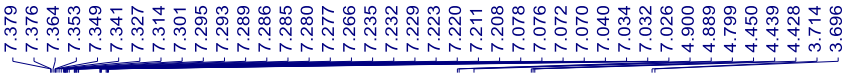


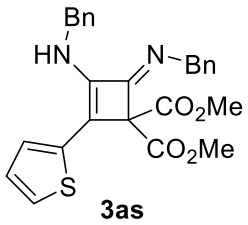


3ar

^{13}C NMR (151 MHz, $CDCl_3$)

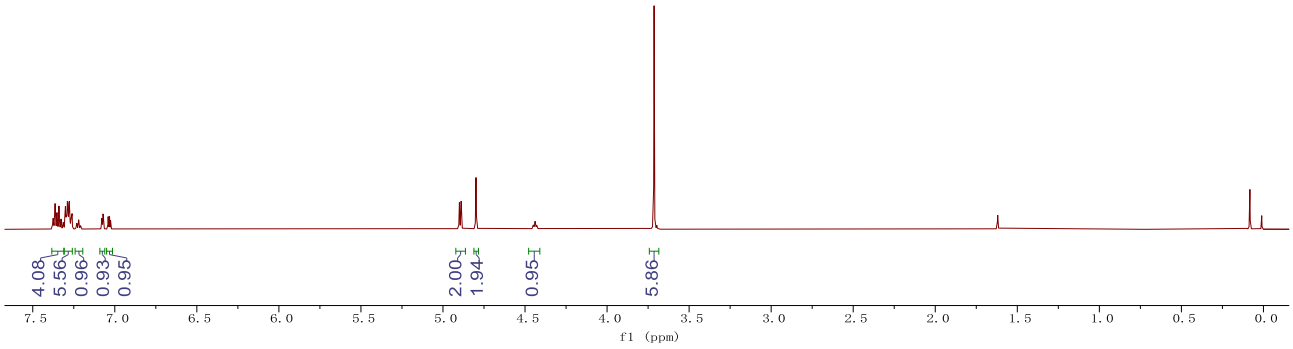


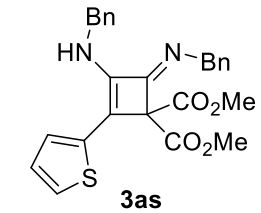




3as

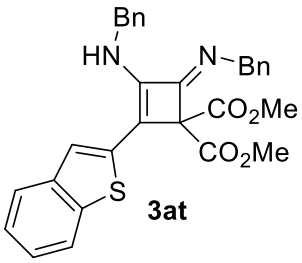
^{1}H NMR (600 MHz, $CDCl_3$)





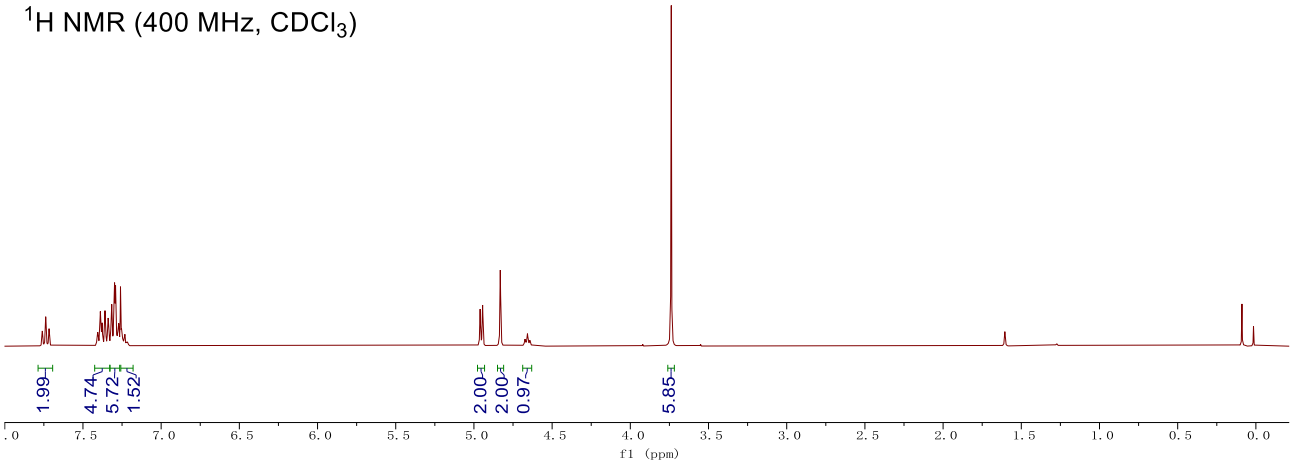
3as

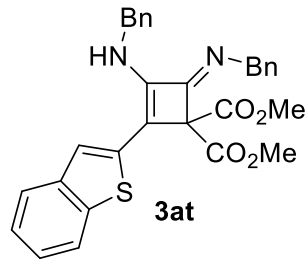
^{13}C NMR (151 MHz, $CDCl_3$)



3at

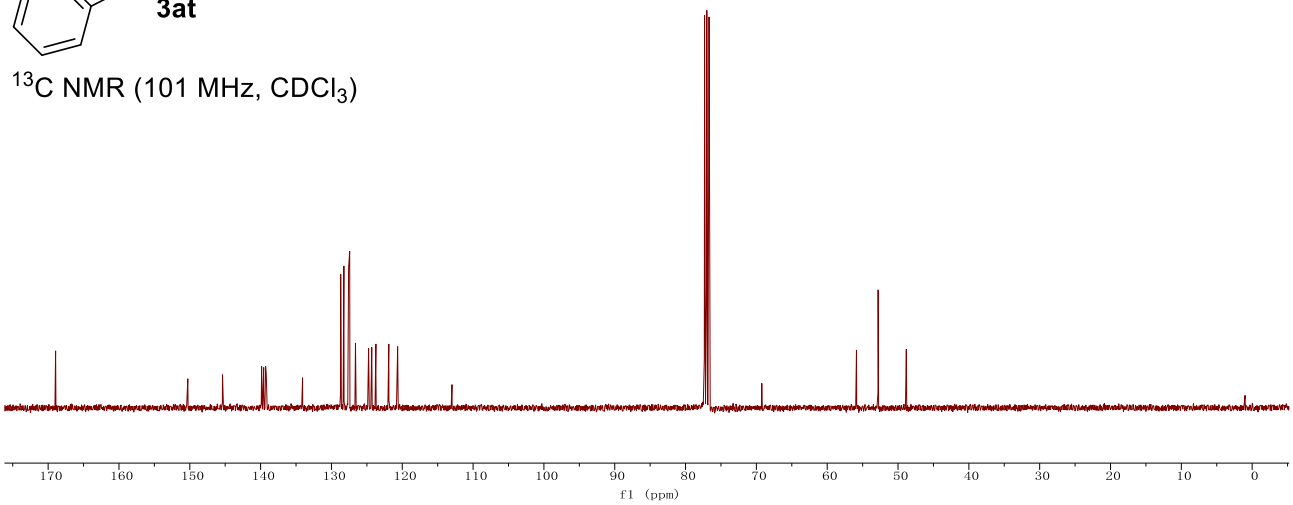
^{1}H NMR (400 MHz, $CDCl_3$)

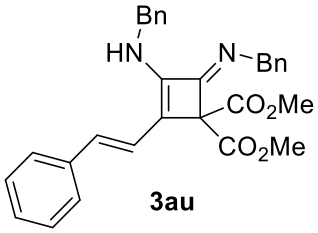




3at

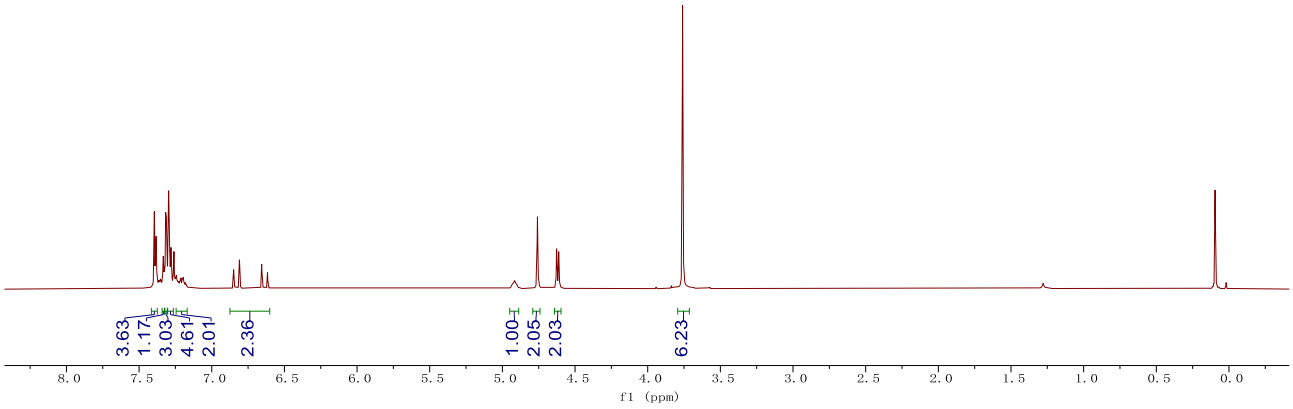
^{13}C NMR (101 MHz, $CDCl_3$)

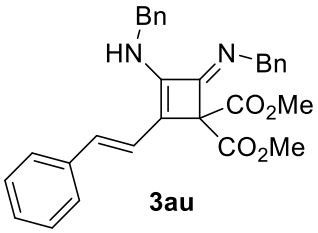




3au

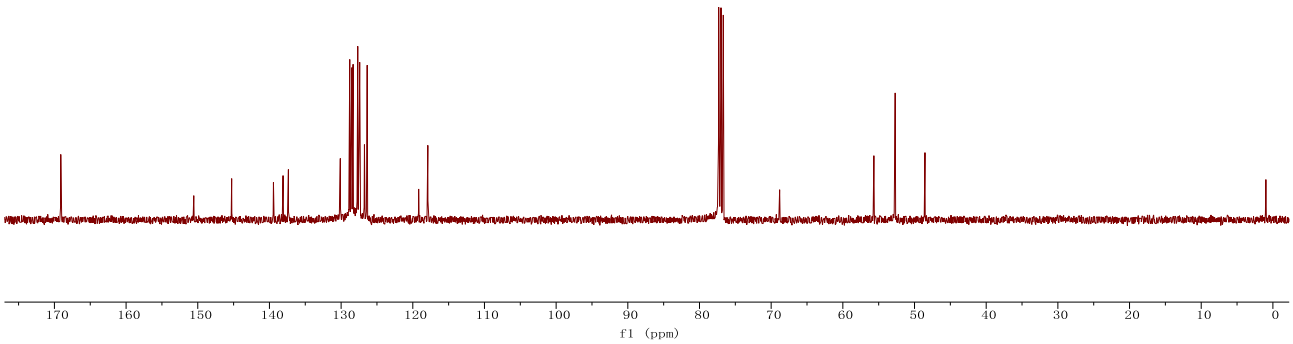
^{1}H NMR (400 MHz, $CDCl_3$)

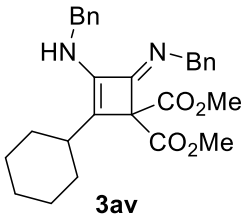




3au

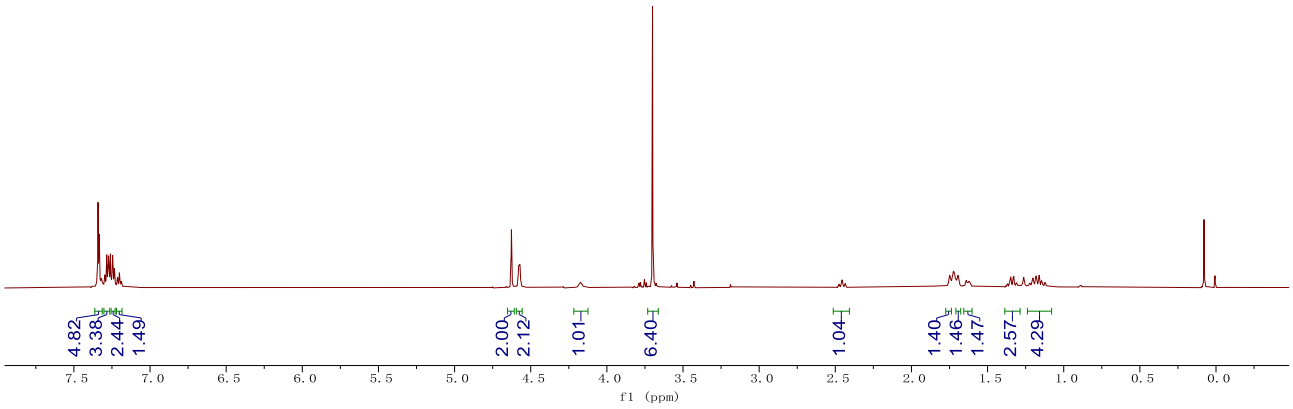
^{13}C NMR (101 MHz, $CDCl_3$)

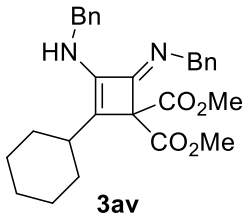




3av

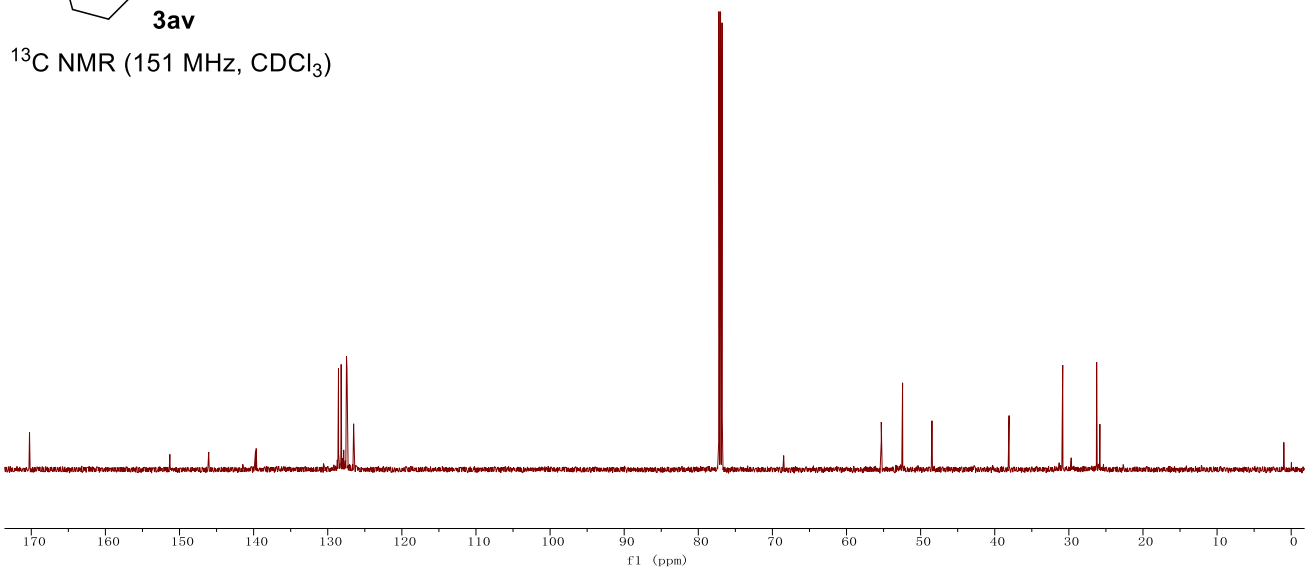
^{13}H NMR (600 MHz, $CDCl_3$)

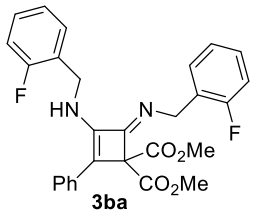




3av

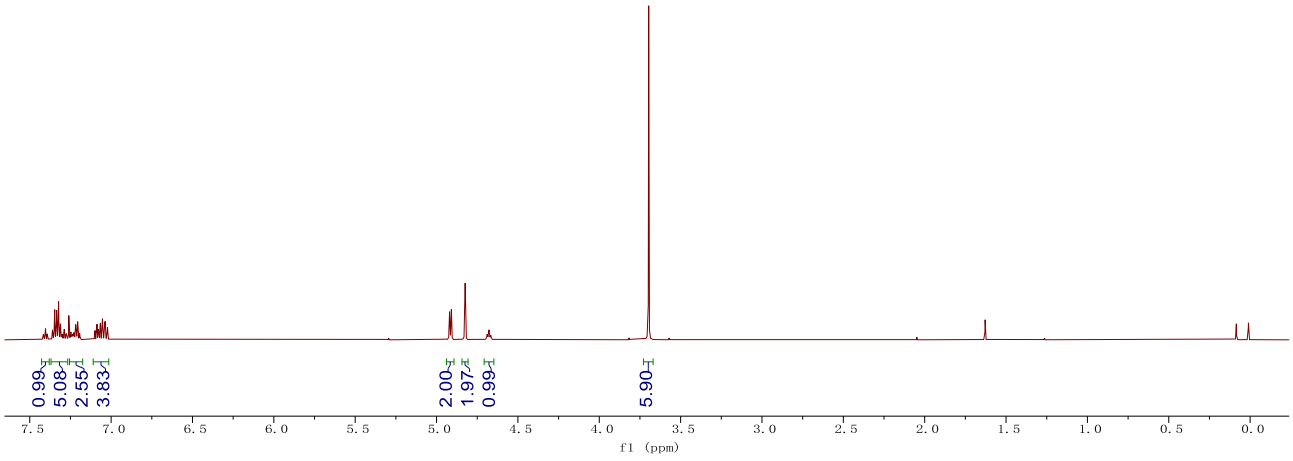
^{13}C NMR (151 MHz, $CDCl_3$)

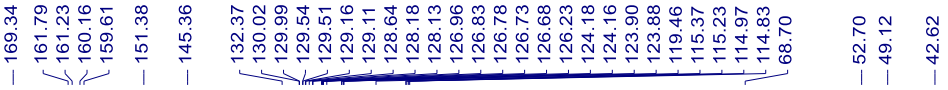


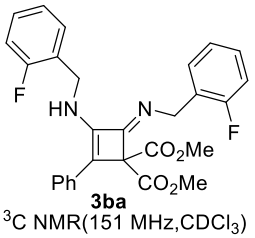


3ba

^{1}H NMR(600 MHz,$CDCl_3$)

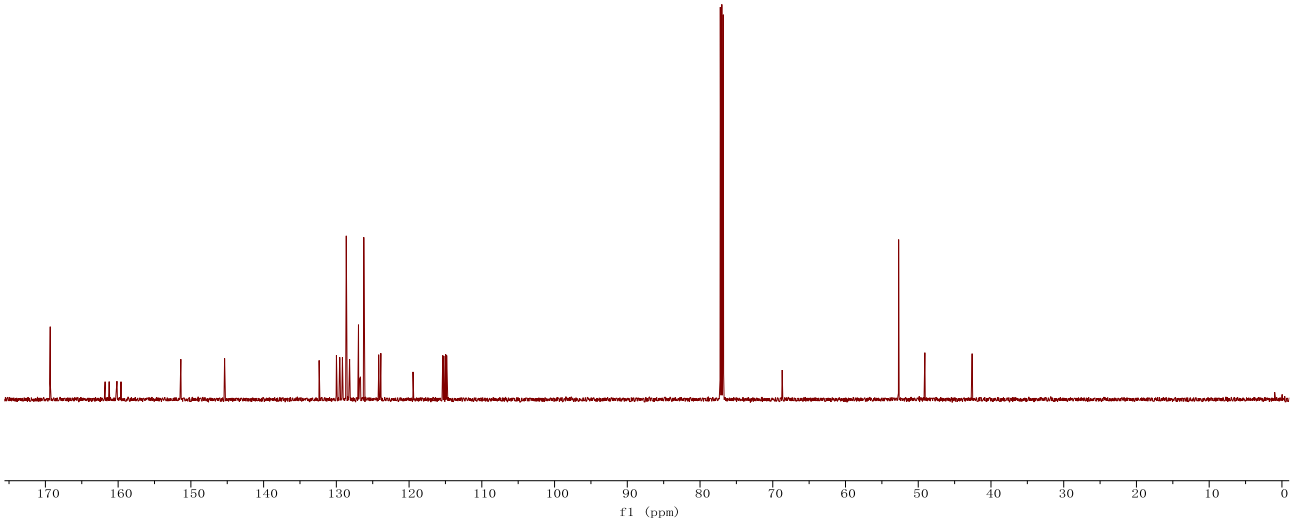


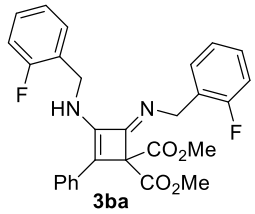




3ba

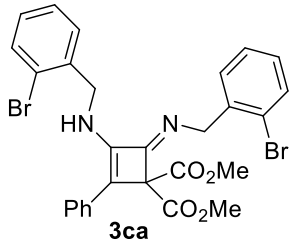
^{13}C NMR(151 MHz,$CDCl_3$)





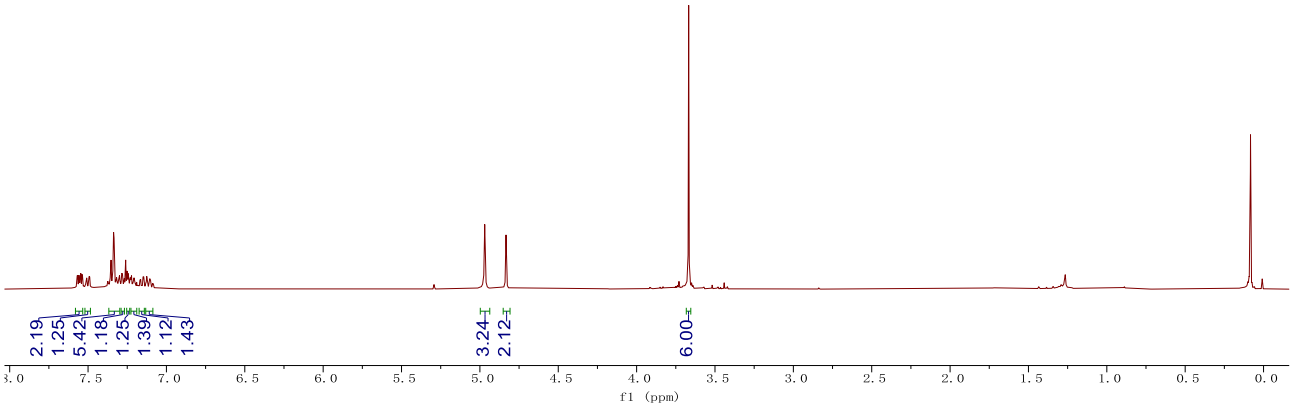
3ba

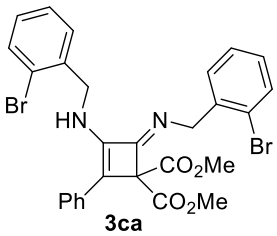
^{19}F NMR(376 MHz,$CDCl_3$)



3ca

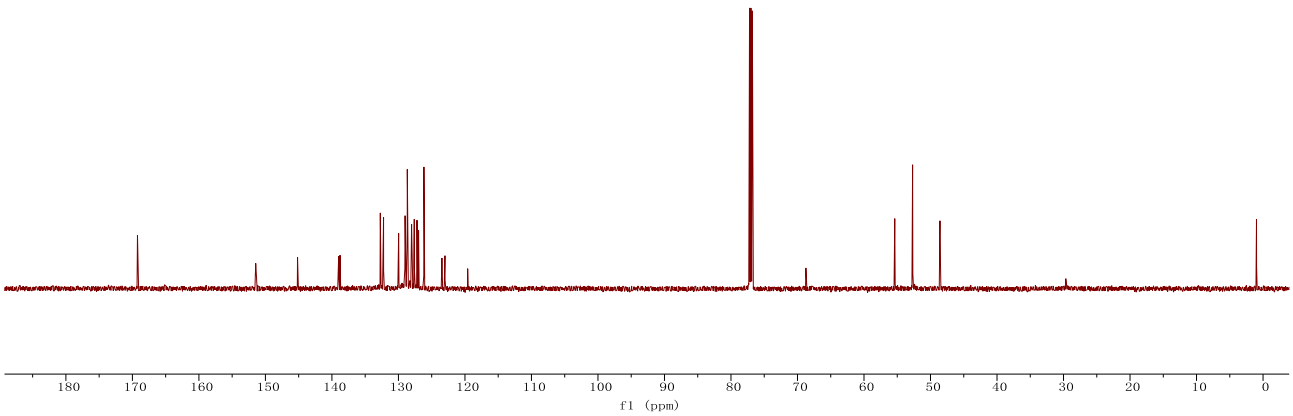
^{1}H NMR (400 MHz, $CDCl_3$)

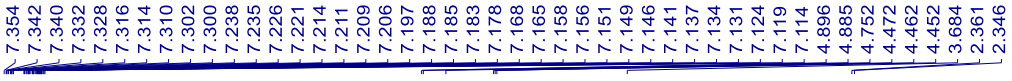


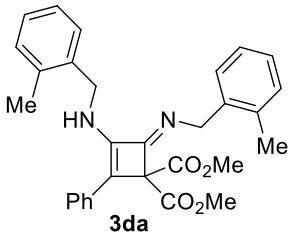


3ca

^{13}C NMR (101 MHz, $CDCl_3$)

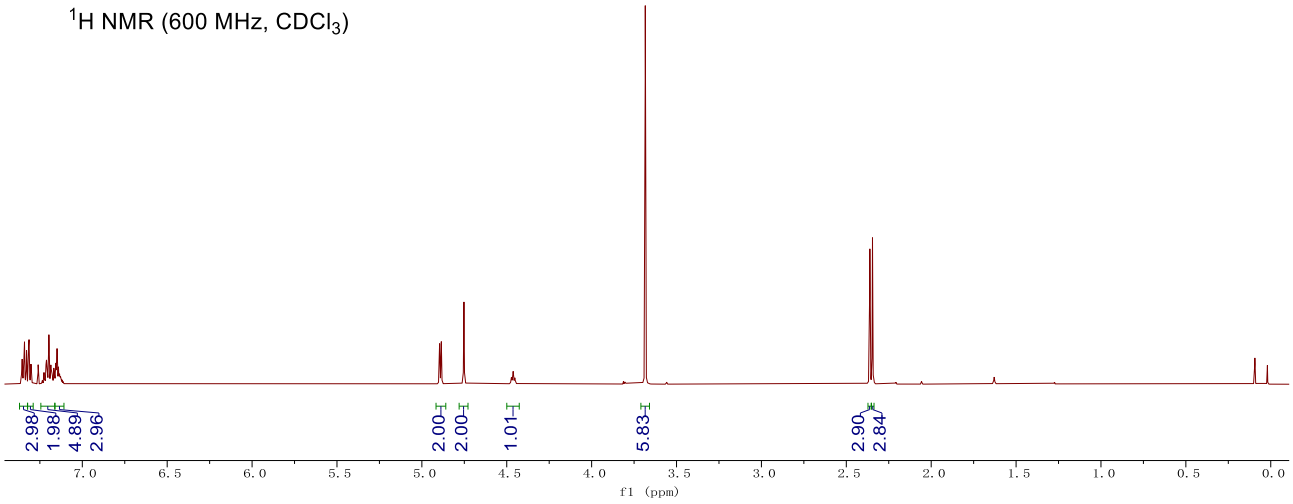


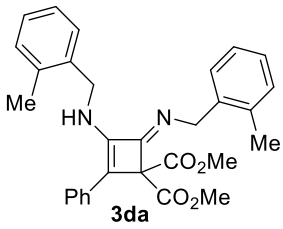




3da

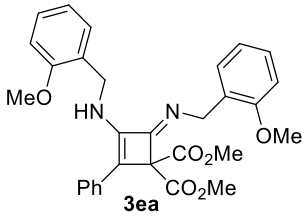
^{1}H NMR (600 MHz, $CDCl_3$)





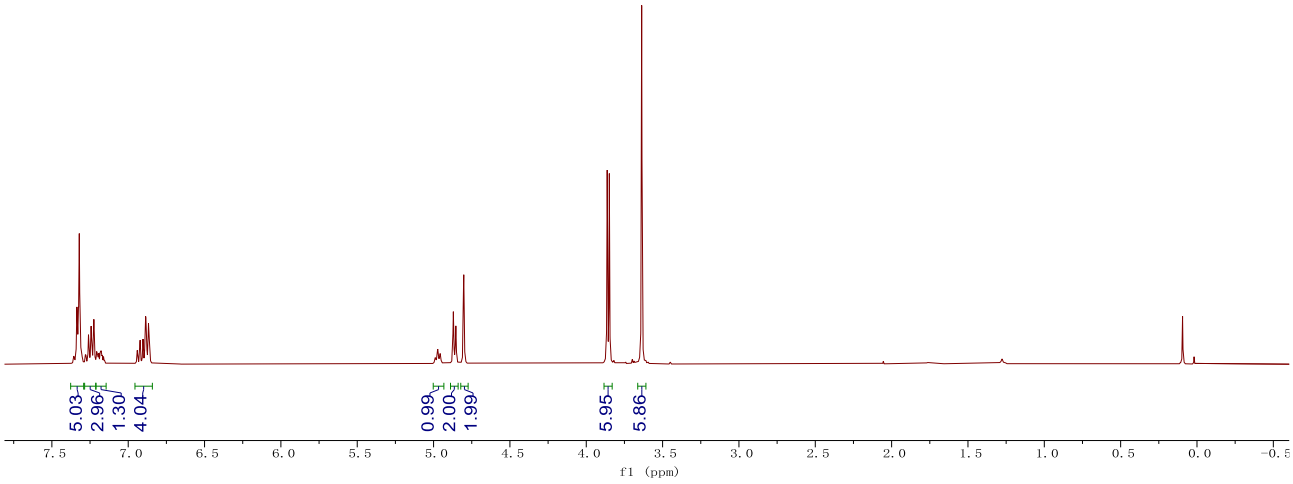
3da

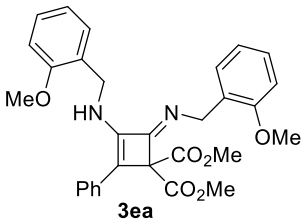
^{13}C NMR (151 MHz, $CDCl_3$)



3ea

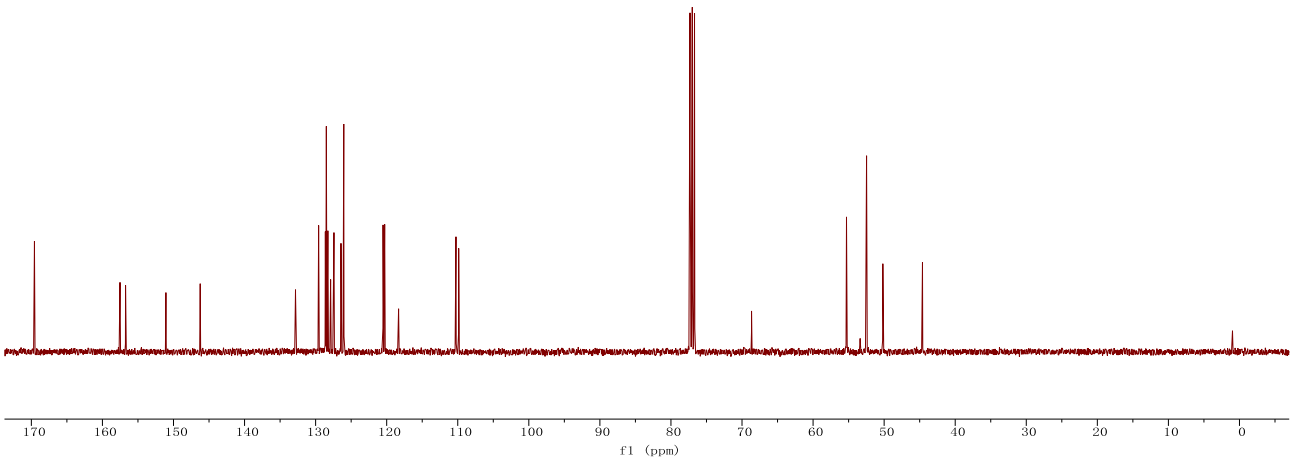
^{1}H NMR (400 MHz, $CDCl_3$)

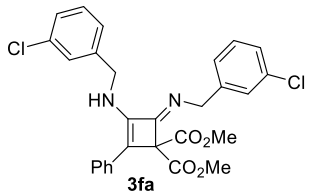




3ea

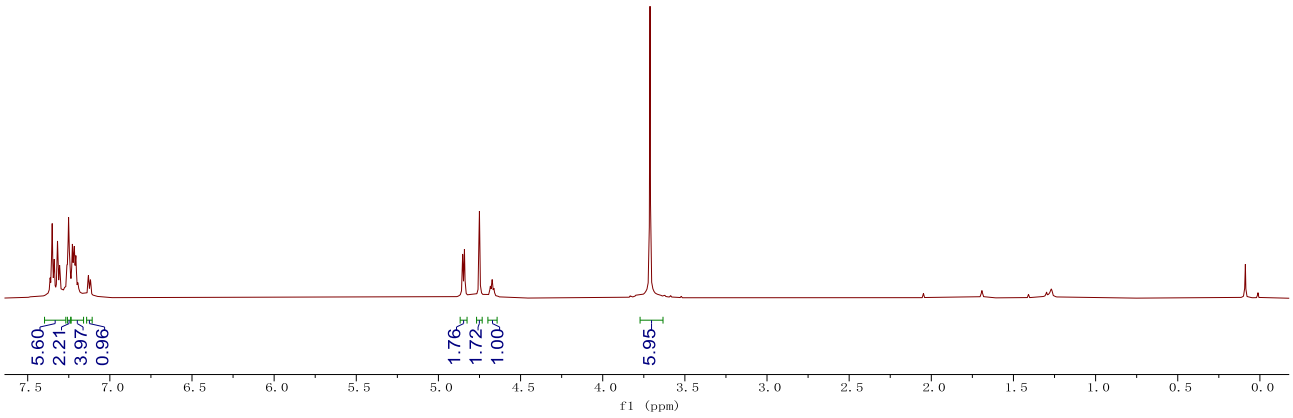
^{13}C NMR(101 MHz,$CDCl_3$)

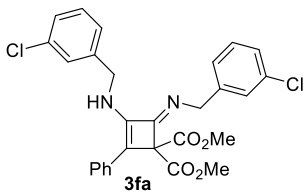




3fa

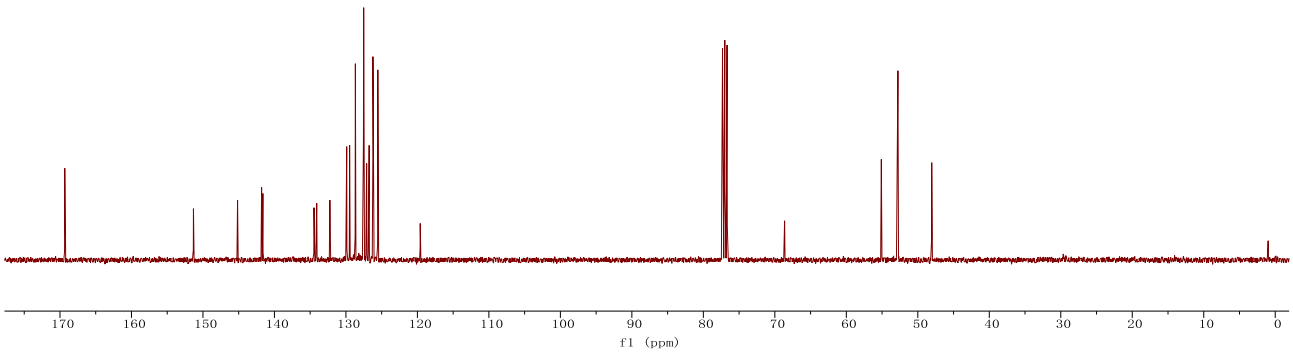
^{1}H NMR (600 MHz,$CDCl_3$)

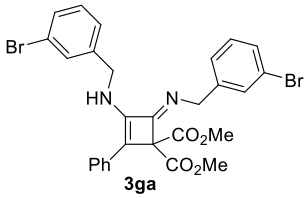




3fa

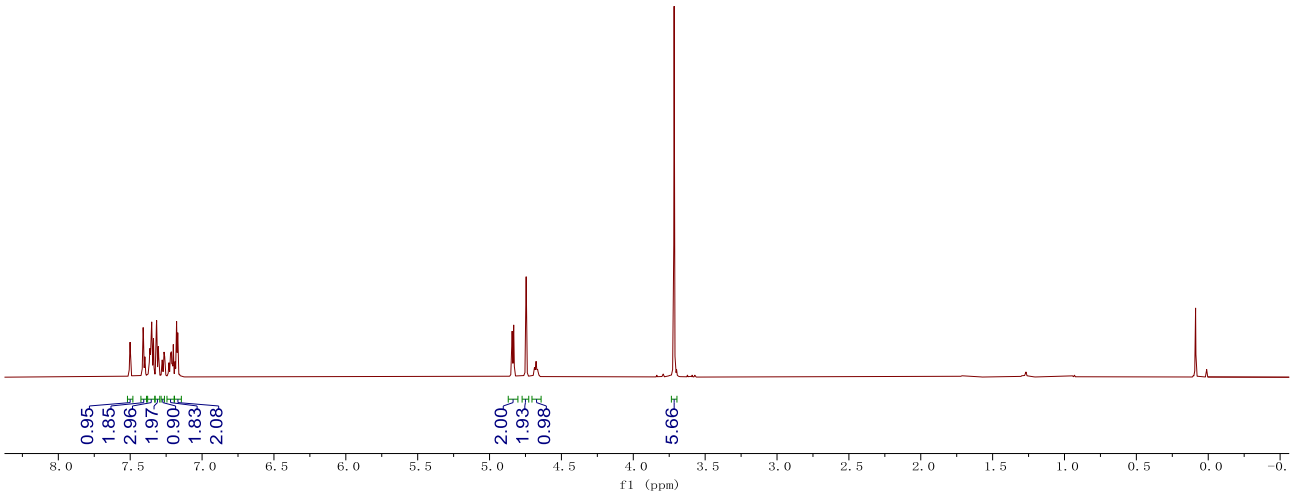
^{13}C NMR (151 MHz,$CDCl_3$)

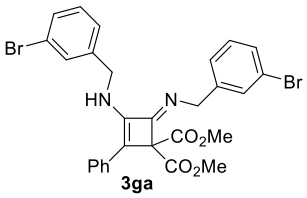




3ga

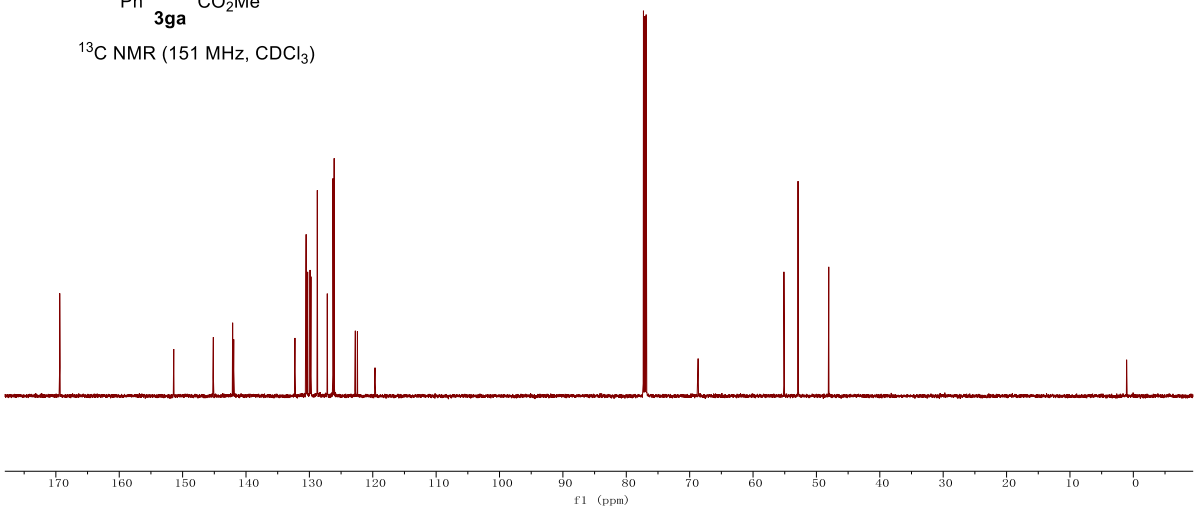
^{1}H NMR (600 MHz, $CDCl_3$)

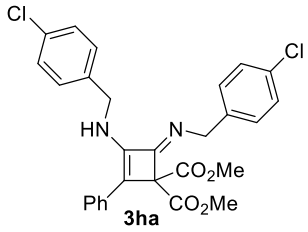




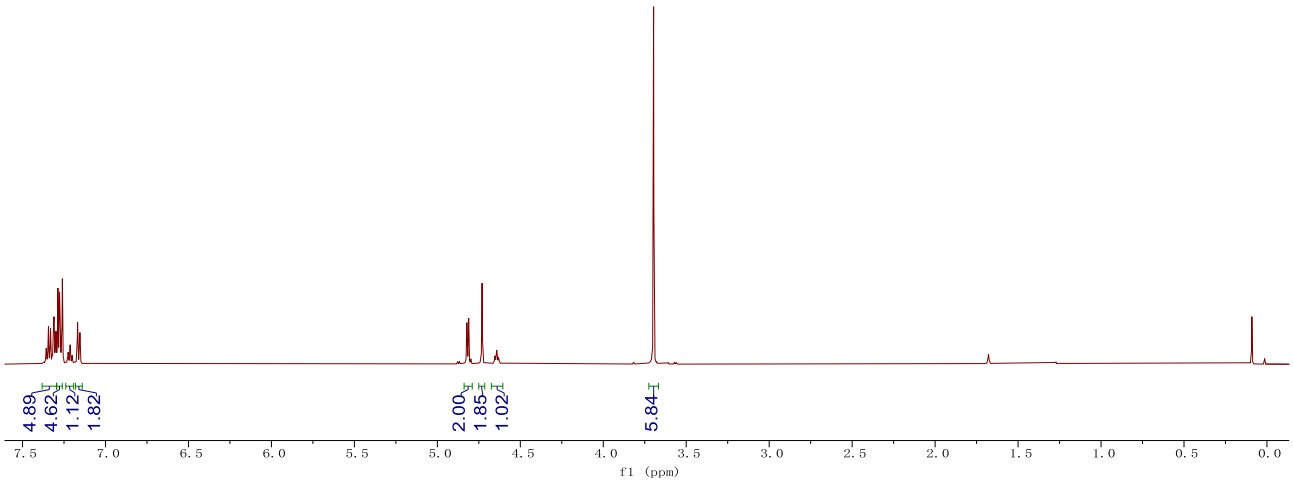
3ga

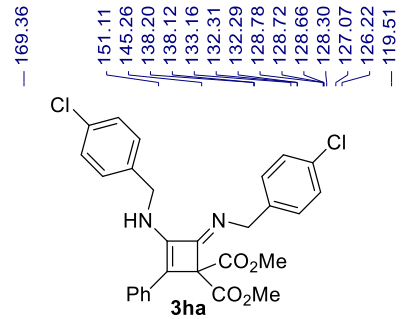
^{13}C NMR (151 MHz, $CDCl_3$)



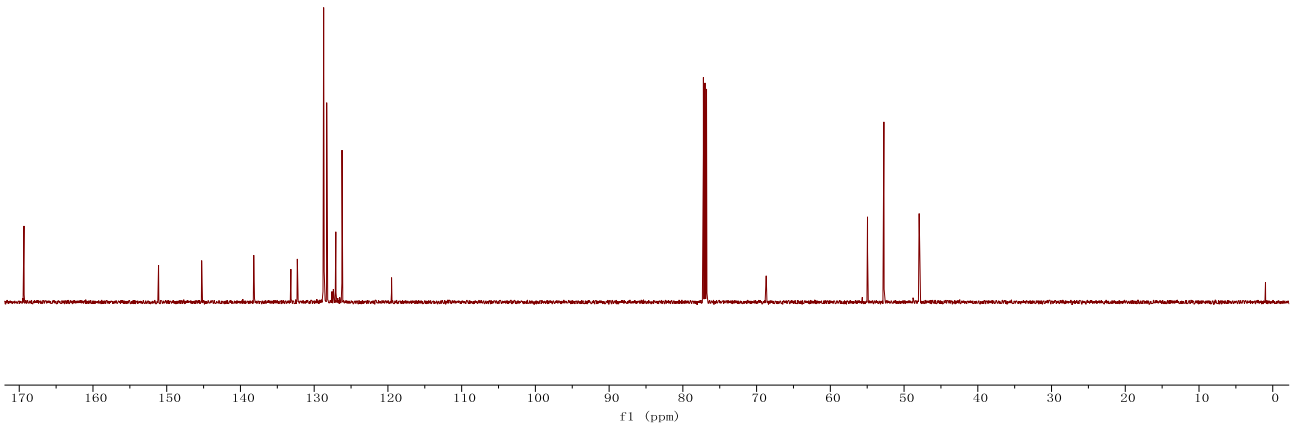


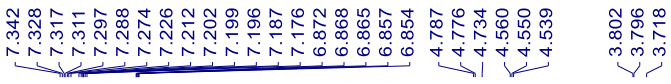
^{1}H NMR (600 MHz, $CDCl_3$)

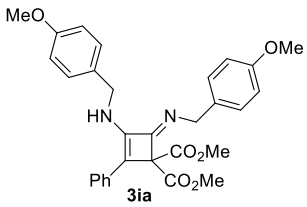




^{13}C NMR (151 MHz, $CDCl_3$)

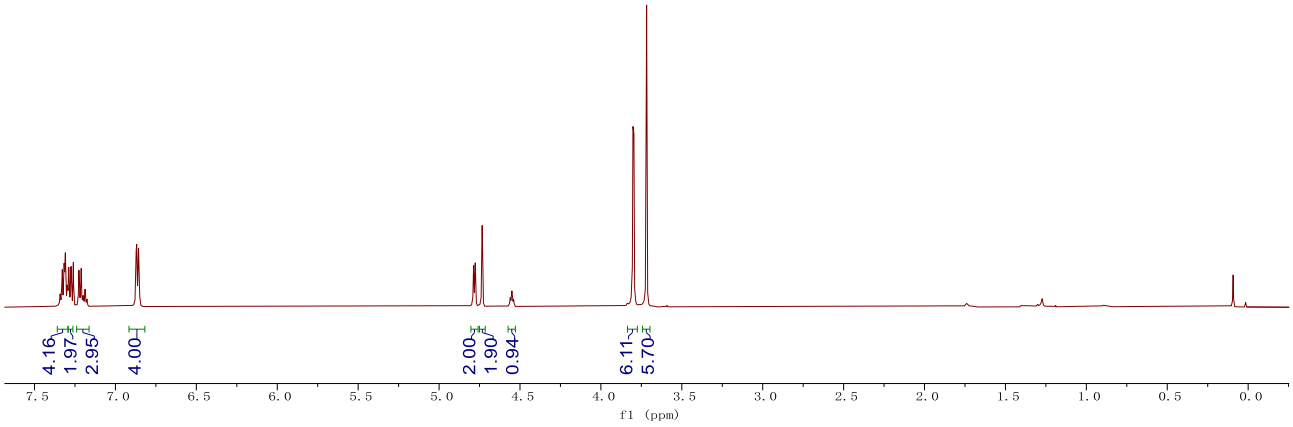


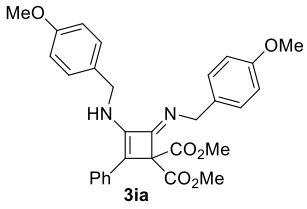




3ia

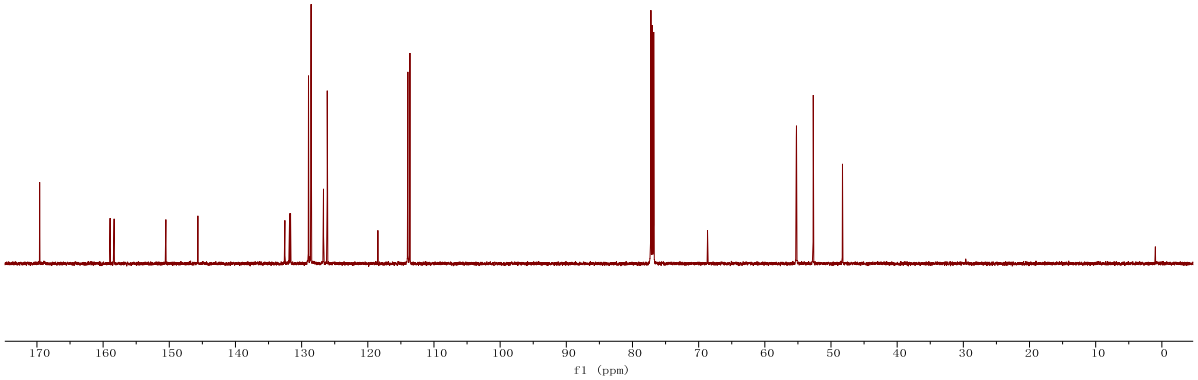
^{1}H NMR(600 MHz,$CDCl_3$)

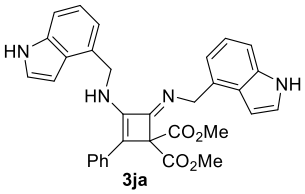




3ia

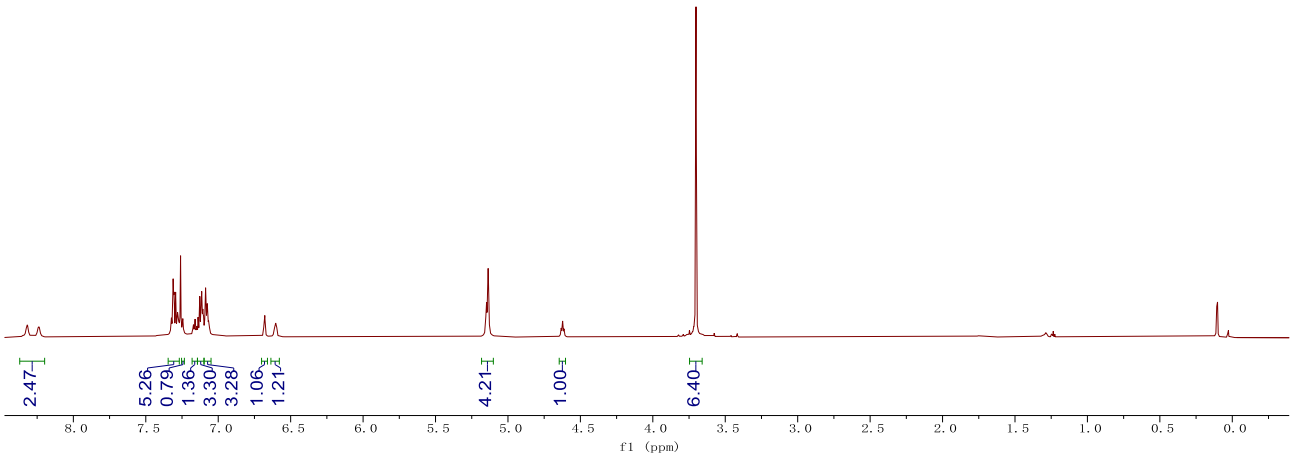
^{13}C NMR (151 MHz, $CDCl_3$)

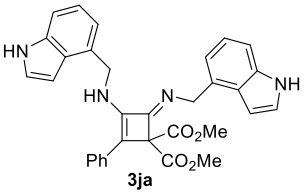




3ja

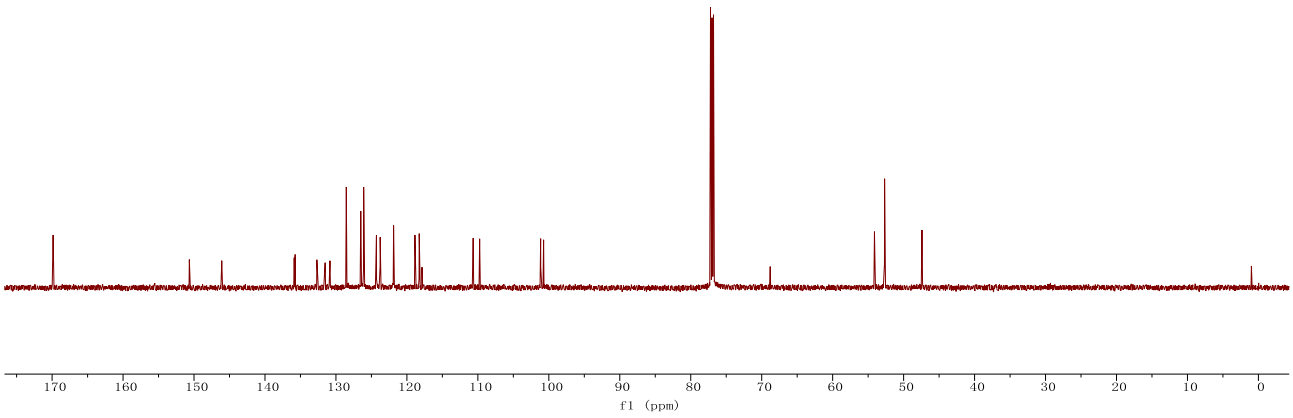
^{1}H NMR (600 MHz, $CDCl_3$)

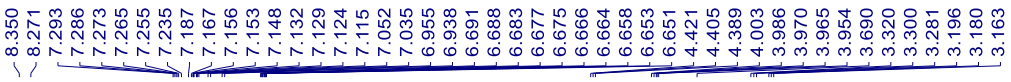


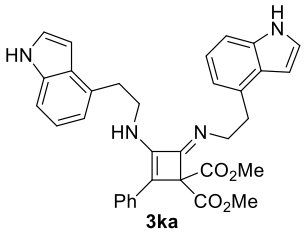


3ja

^{13}C NMR (151 MHz, $CDCl_3$)

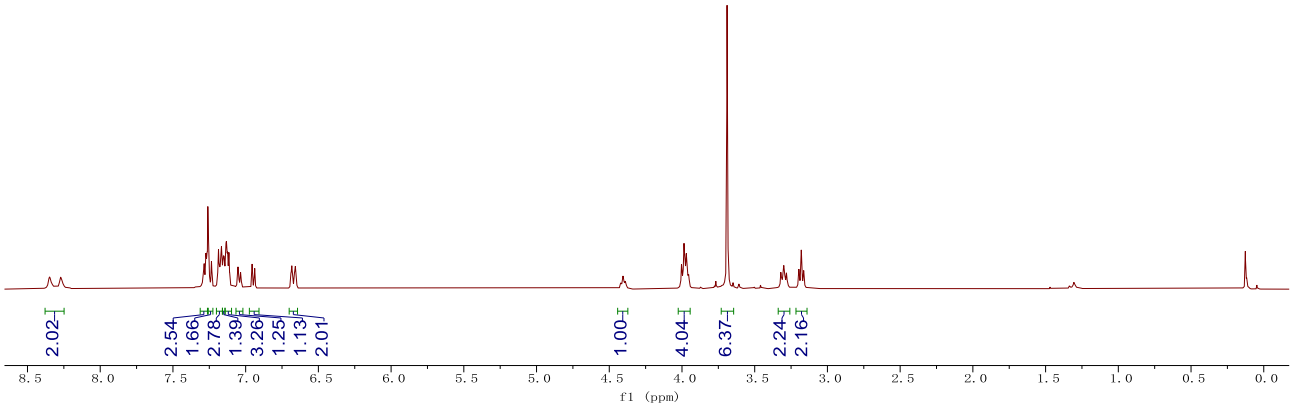


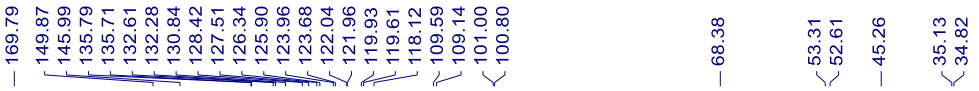


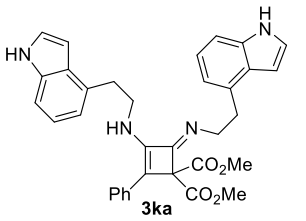


3ka

^{1}H NMR (400 MHz, $CDCl_3$)

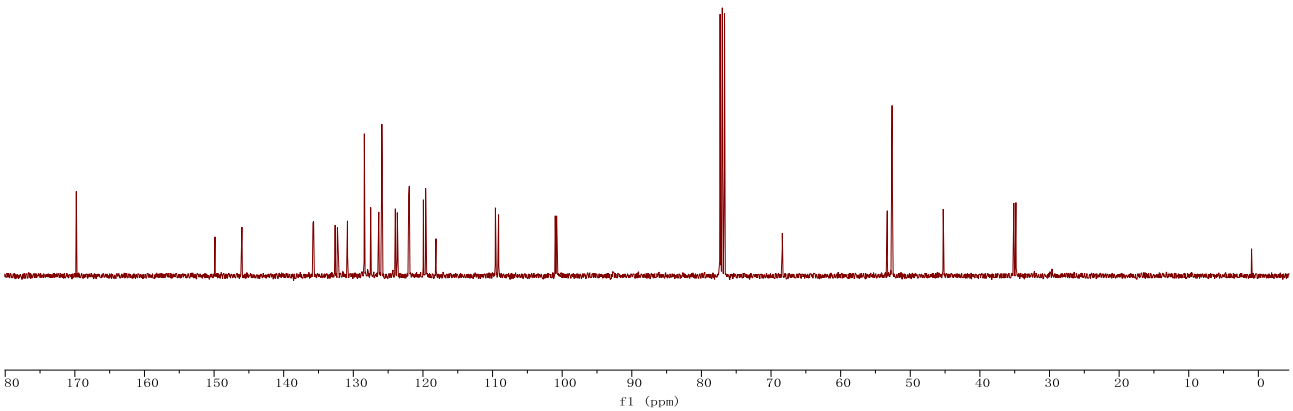


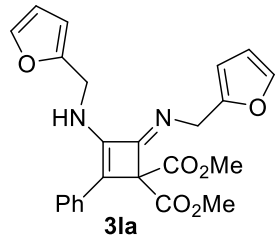




3ka

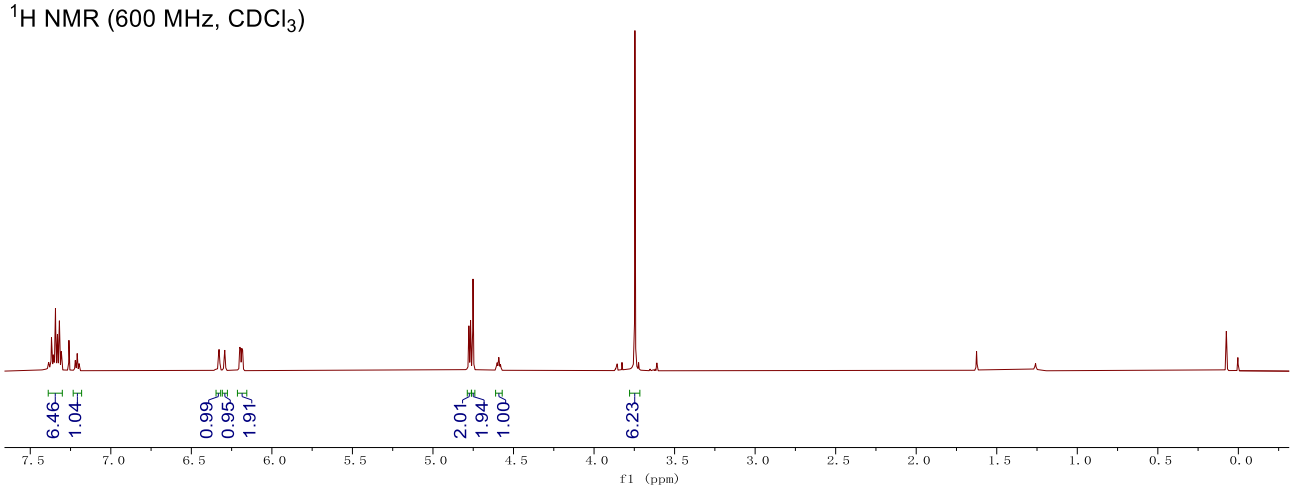
^{13}C NMR (101 MHz, $CDCl_3$)

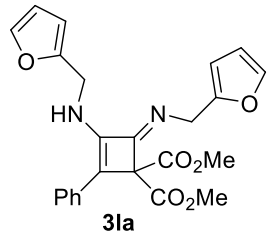




3la

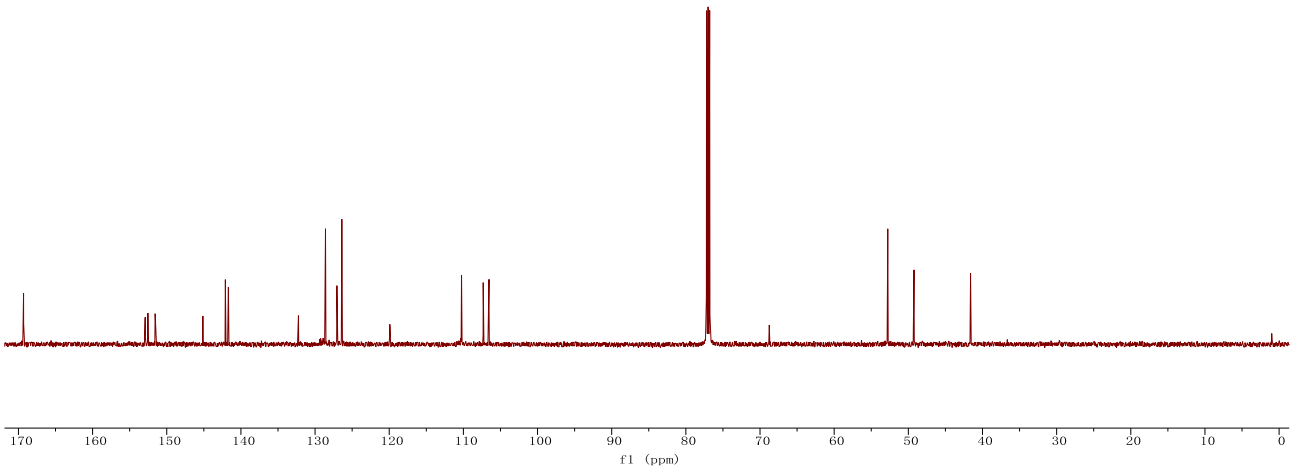
^{1}H NMR (600 MHz, $CDCl_3$)

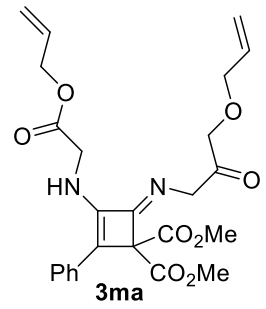




3la

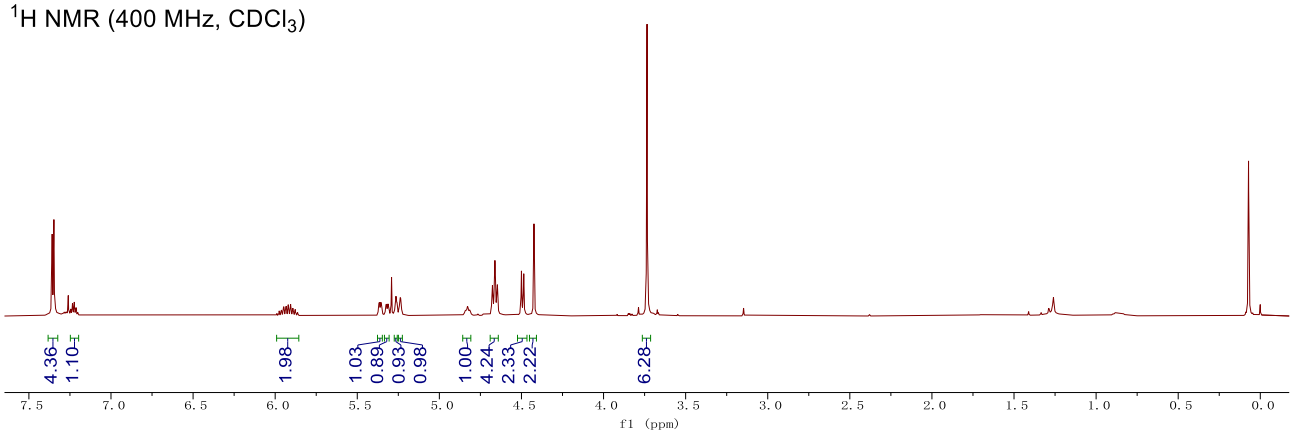
^{13}C NMR (151 MHz, $CDCl_3$)

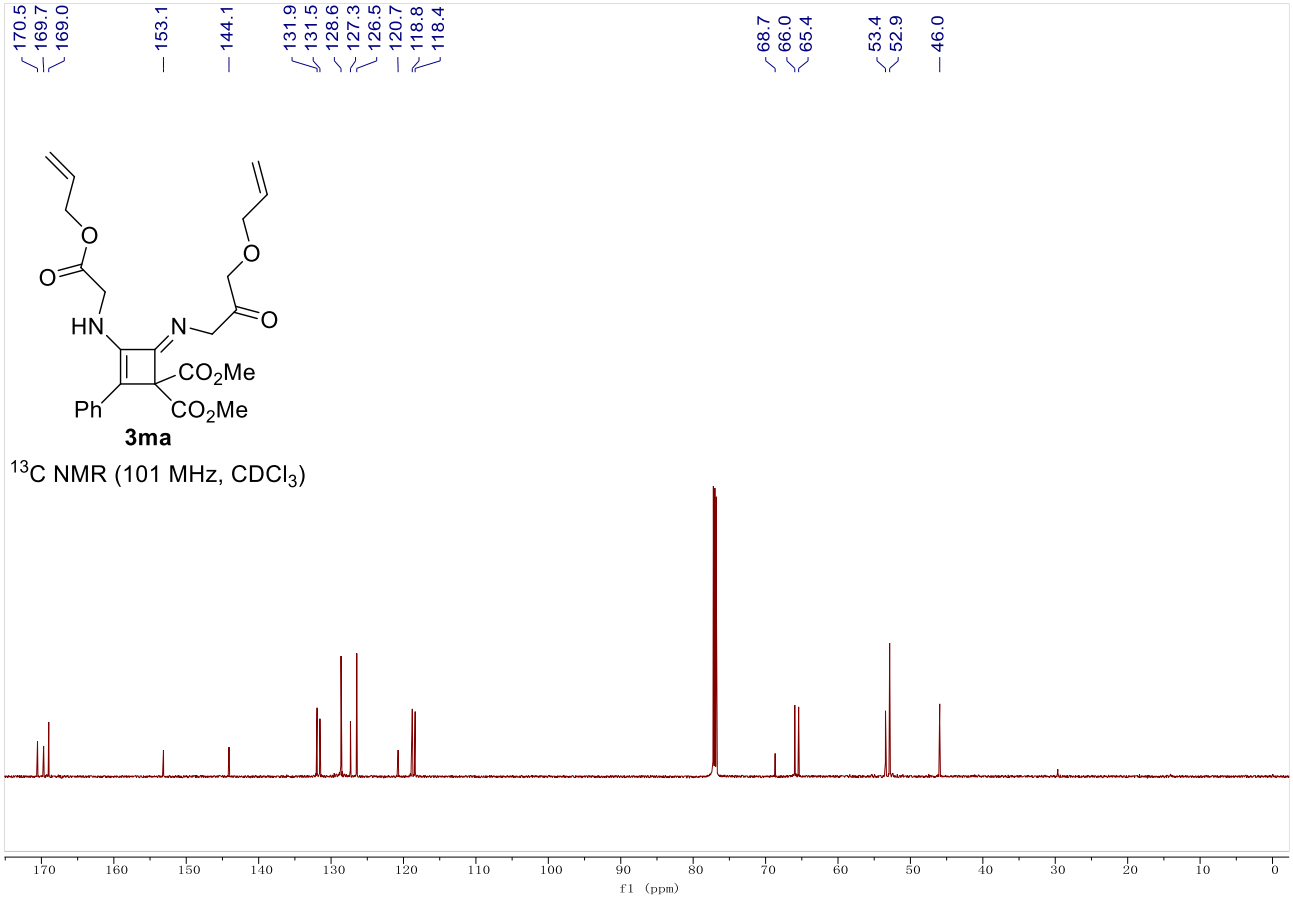




3ma

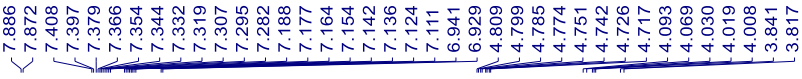
^{1}H NMR (400 MHz, $CDCl_3$)

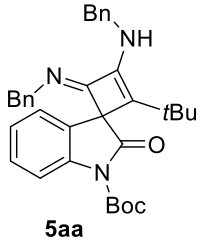




3ma

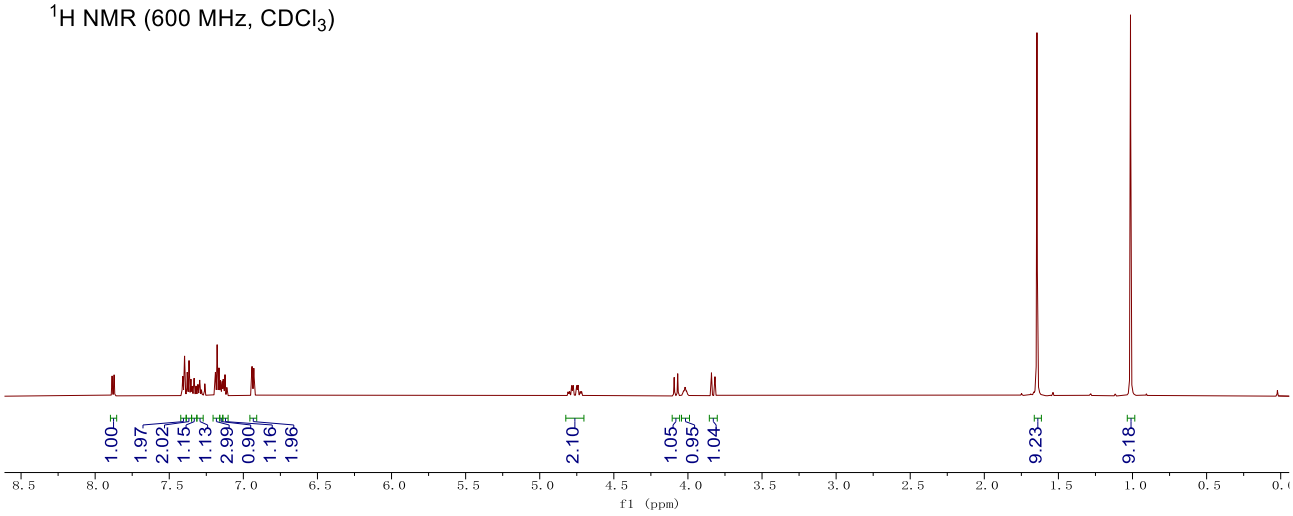
^{13}C NMR (101 MHz, $CDCl_3$)

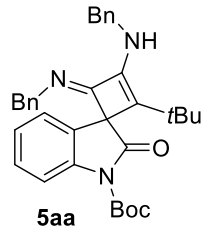




5aa

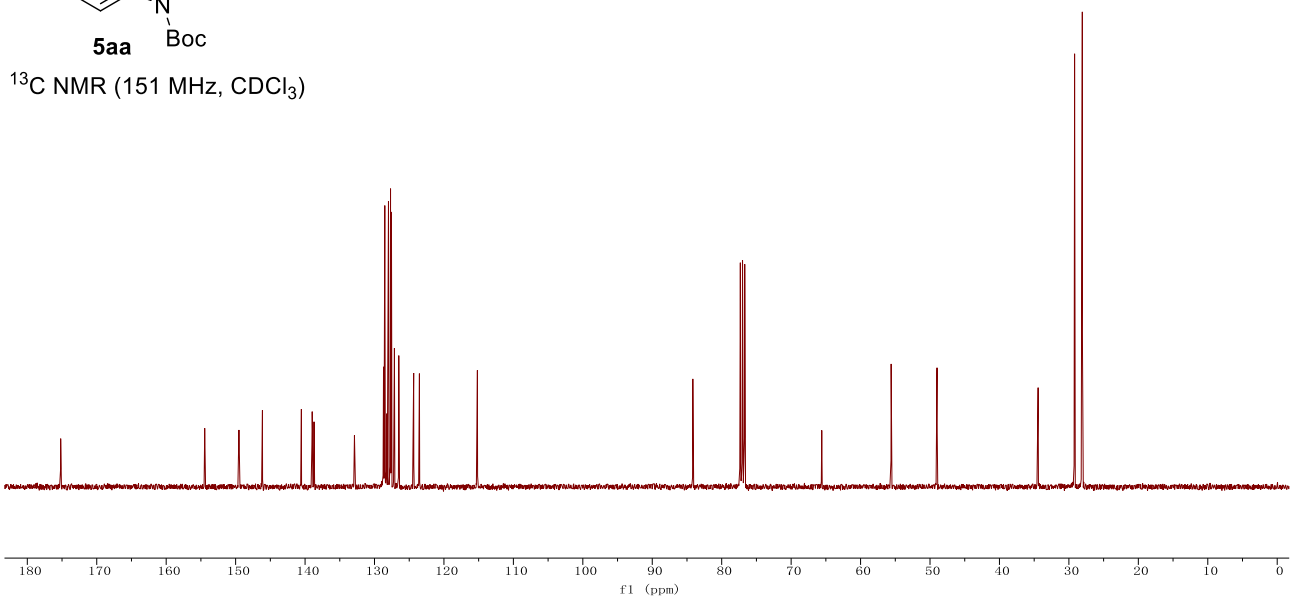
^{1}H NMR (600 MHz, $CDCl_3$)

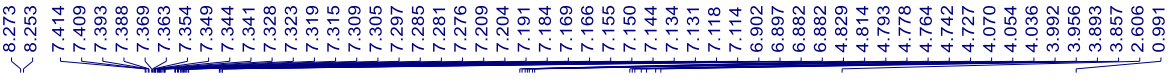


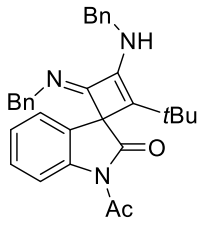


5aa

^{13}C NMR (151 MHz, $CDCl_3$)

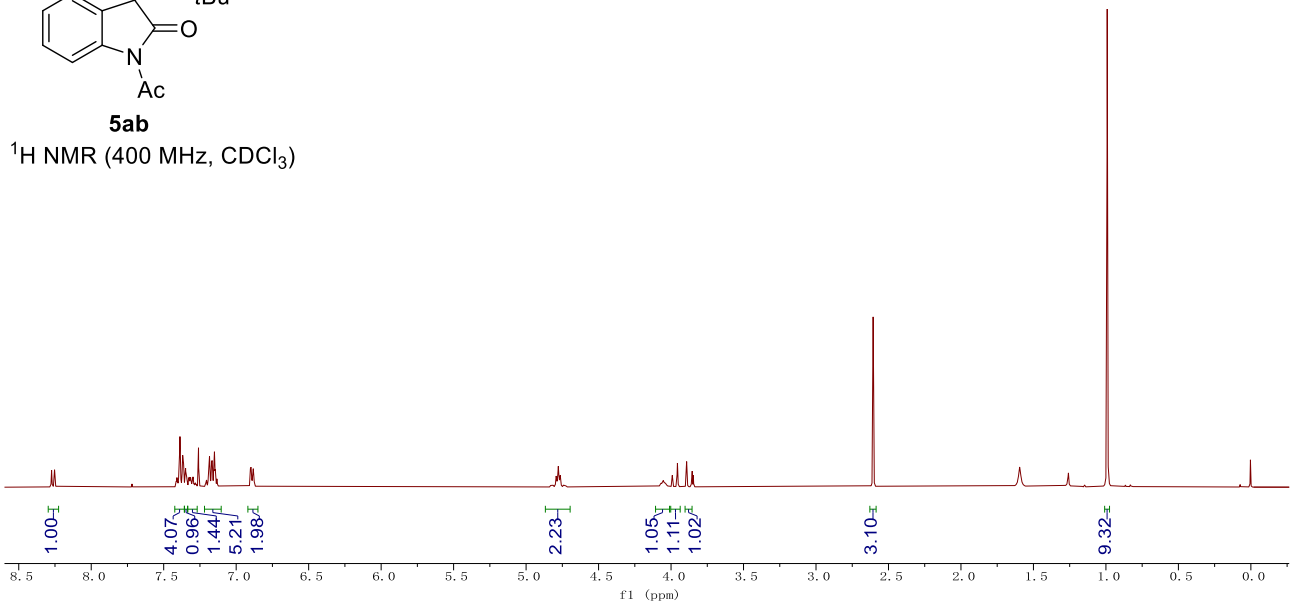


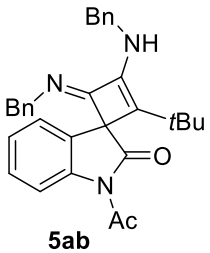




5ab

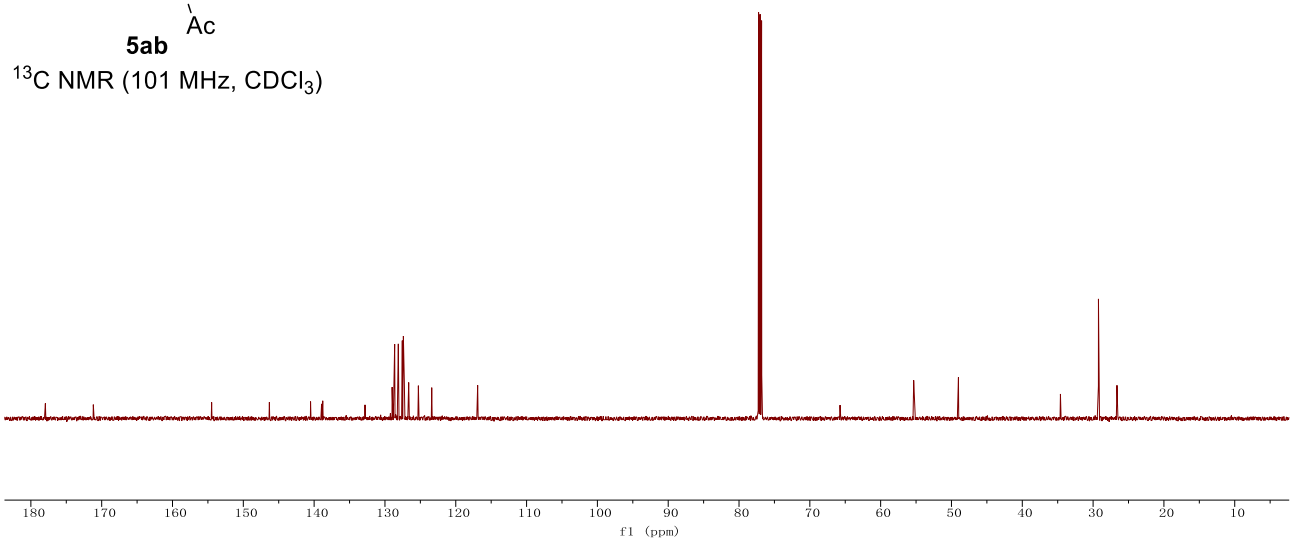
^{1}H NMR (400 MHz, $CDCl_3$)

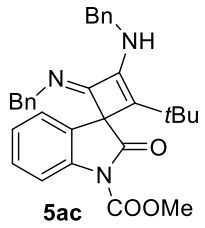




5ab

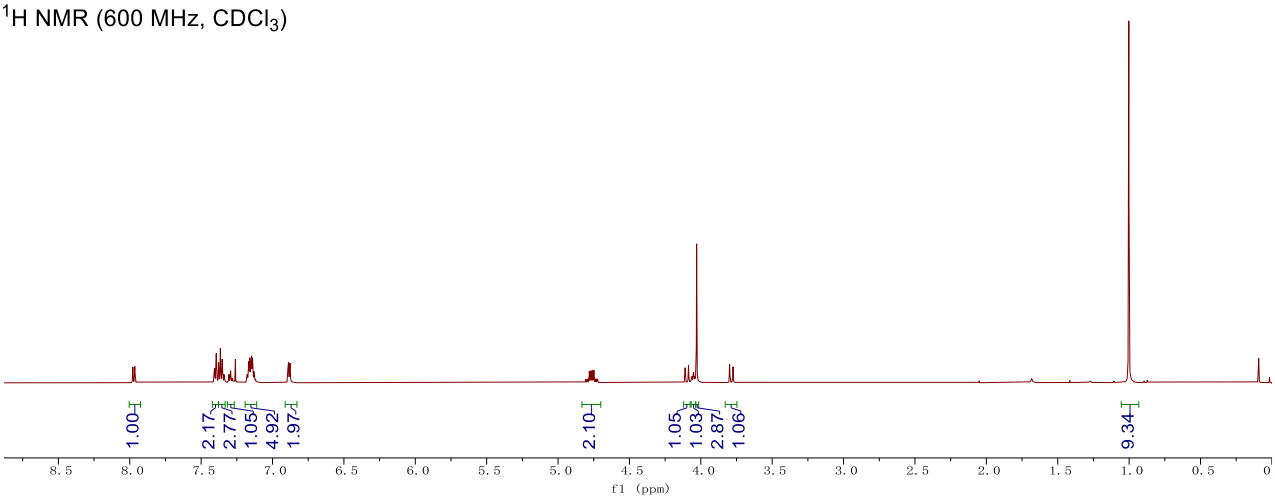
^{13}C NMR (101 MHz, $CDCl_3$)

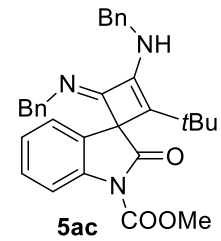




5ac

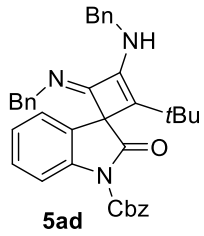
^{1}H NMR (600 MHz, $CDCl_3$)





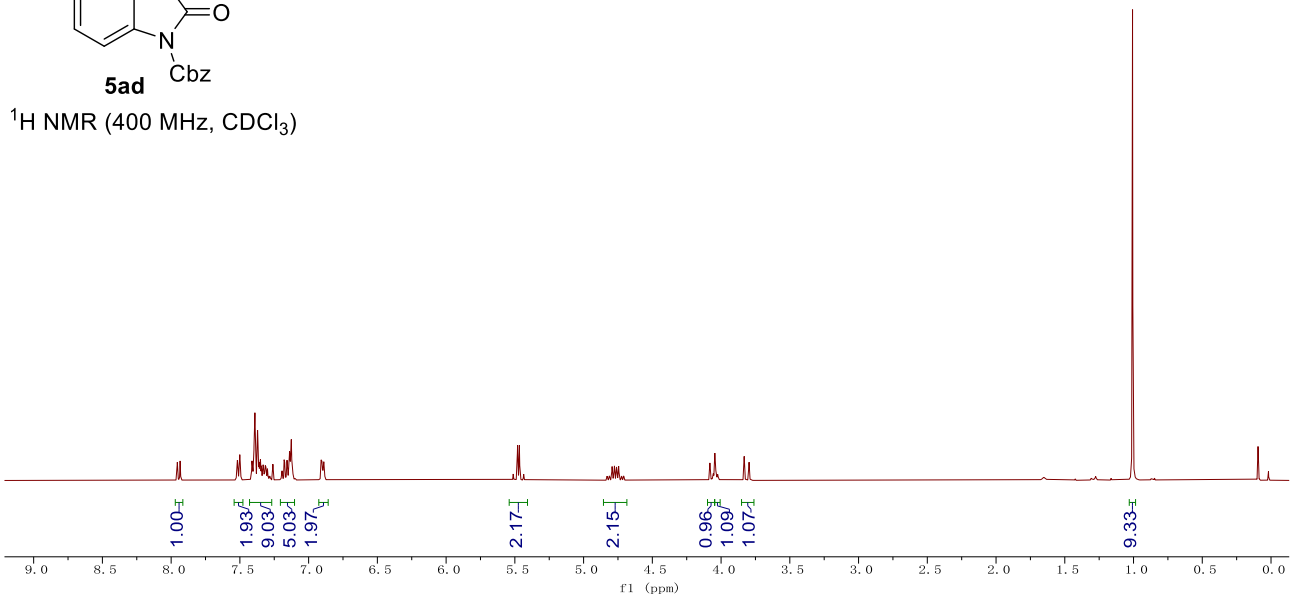
5ac

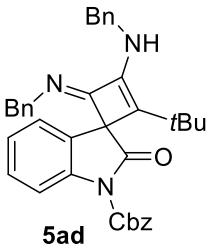
^{13}C NMR (151 MHz, $CDCl_3$)



5ad

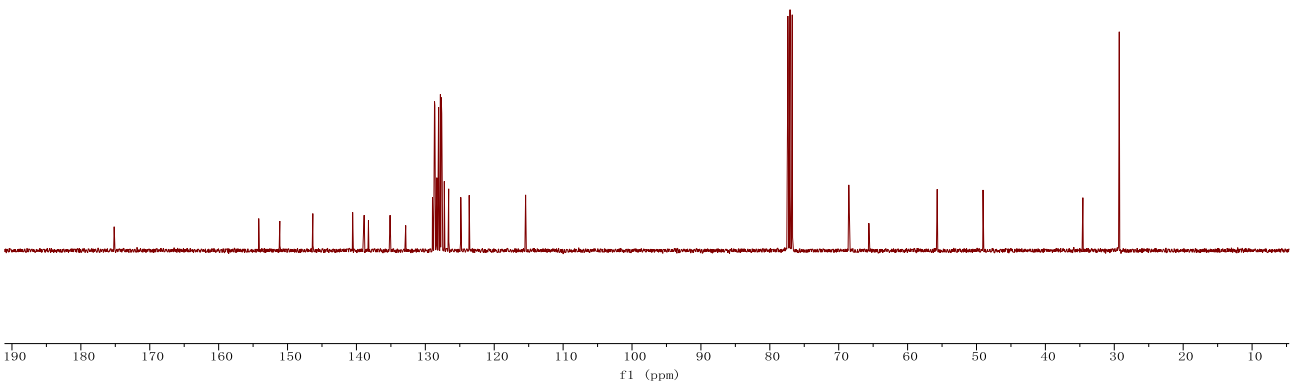
^{1}H NMR (400 MHz, $CDCl_3$)

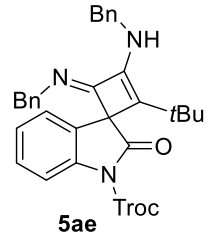




5ad

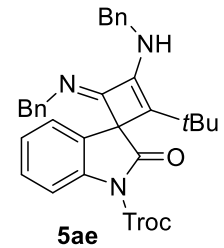
^{13}C NMR (101 MHz, $CDCl_3$)





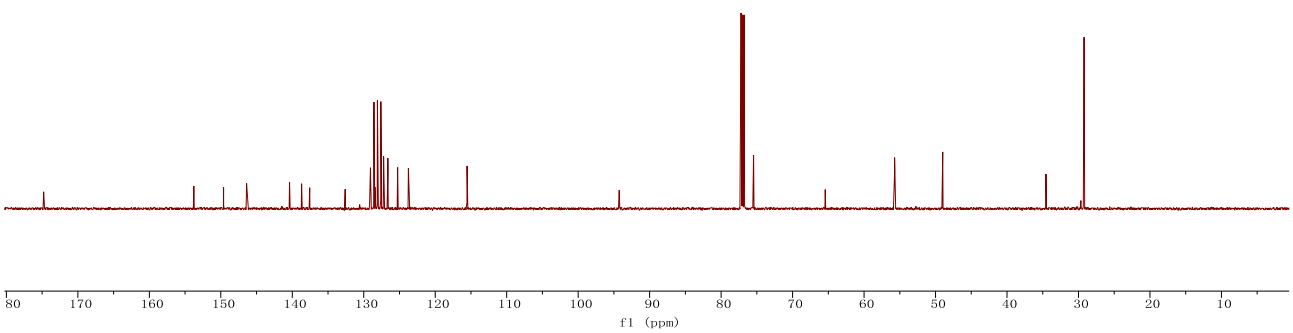
5ae

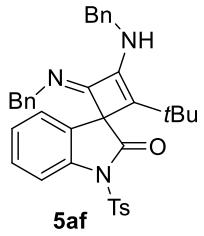
^{1}H NMR (400 MHz, $CDCl_3$)



5ae

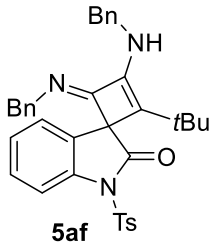
^{13}C NMR (101 MHz, $CDCl_3$)





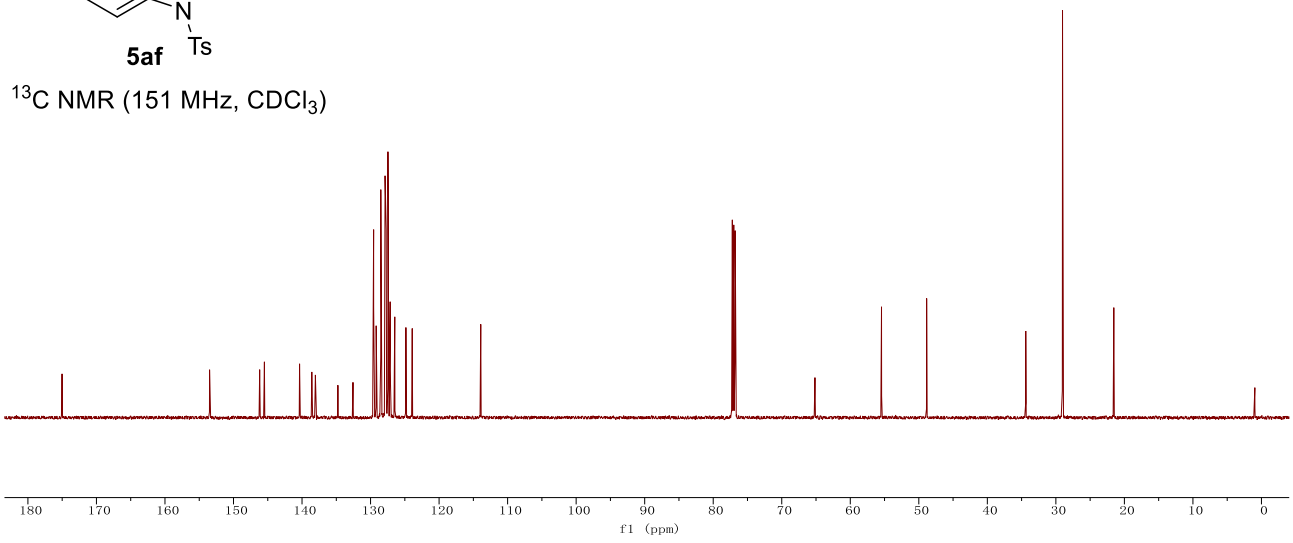
5af

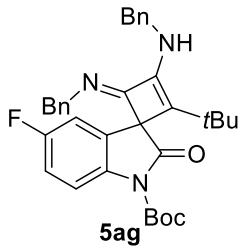
^{1}H NMR (600 MHz, $CDCl_3$)



5af

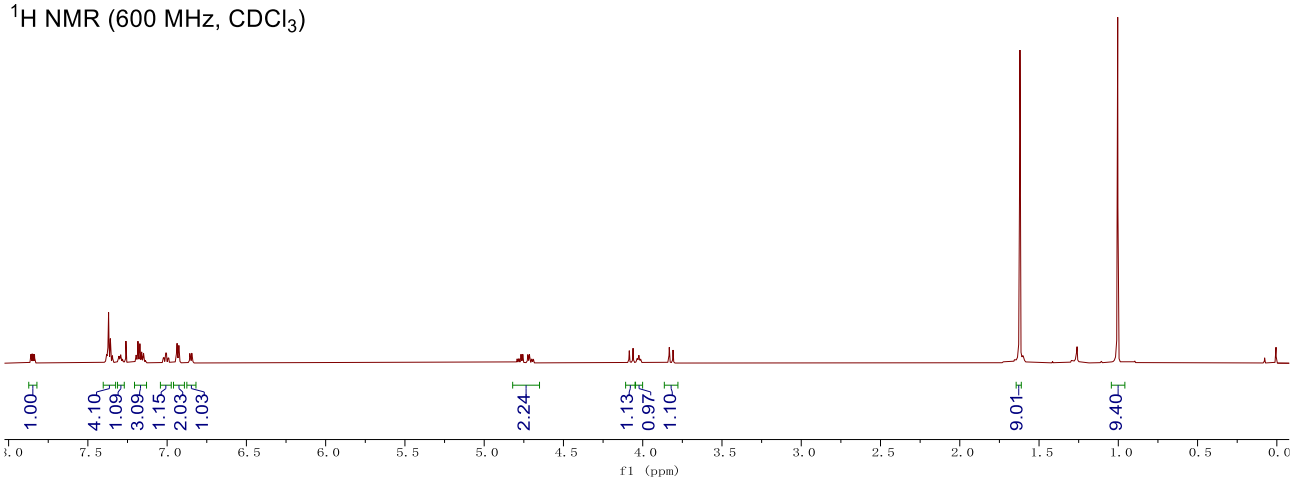
^{13}C NMR (151 MHz, $CDCl_3$)

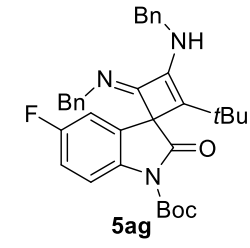




5ag

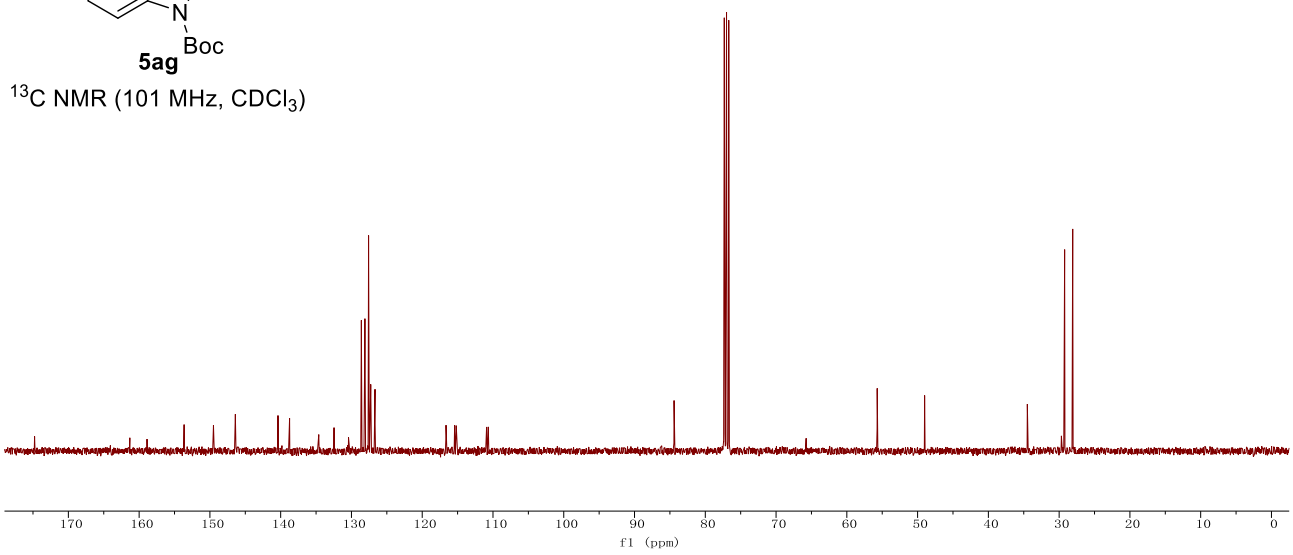
^{1}H NMR (600 MHz, $CDCl_3$)

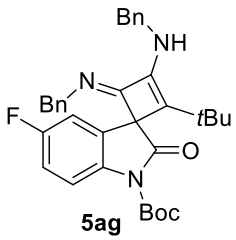




5ag

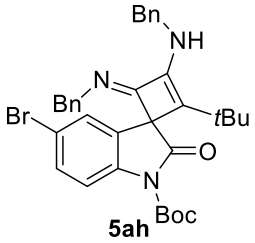
^{13}C NMR (101 MHz, $CDCl_3$)





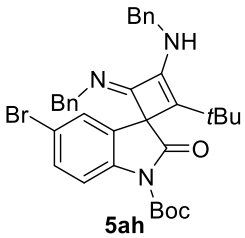
5ag

^{19}F NMR (565 MHz, $CDCl_3$)



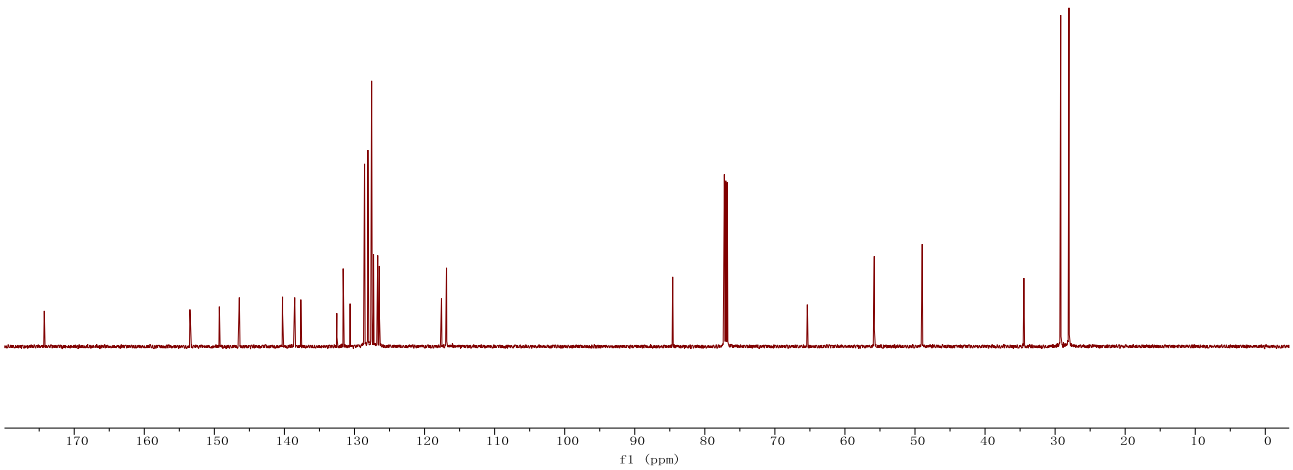
5ah

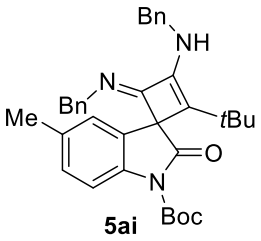
^{1}H NMR (600 MHz, $CDCl_3$)



5ah

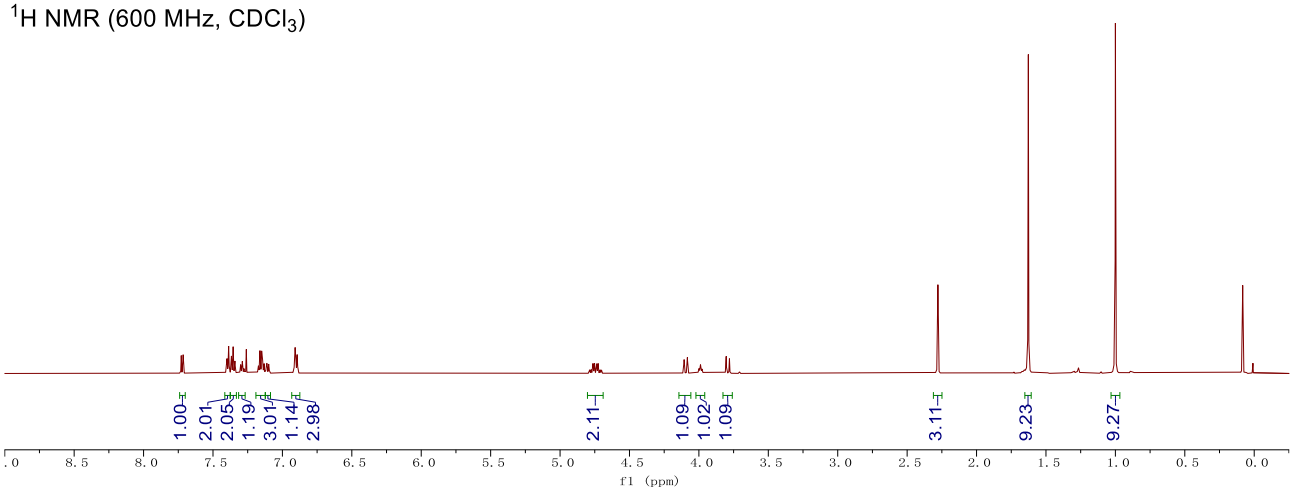
^{13}C NMR (151 MHz, $CDCl_3$)

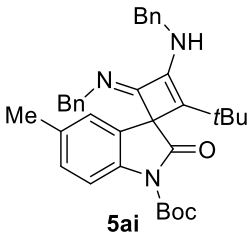




5ai

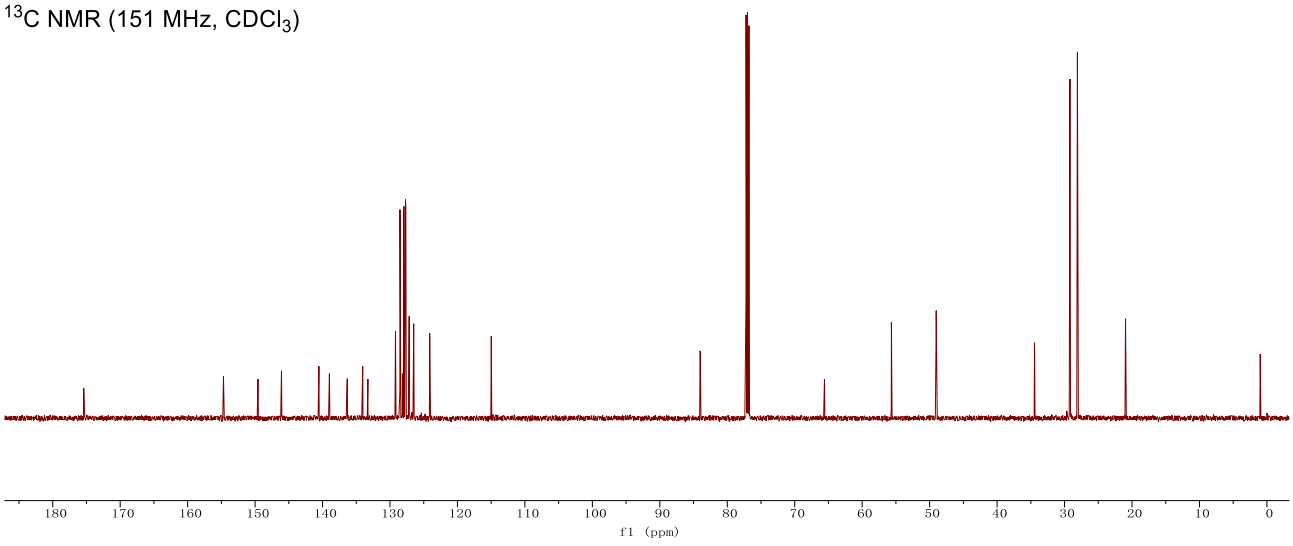
^{1}H NMR (600 MHz, $CDCl_3$)

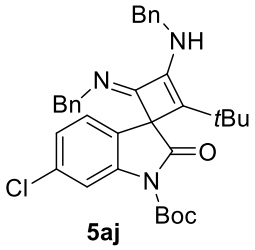




5ai

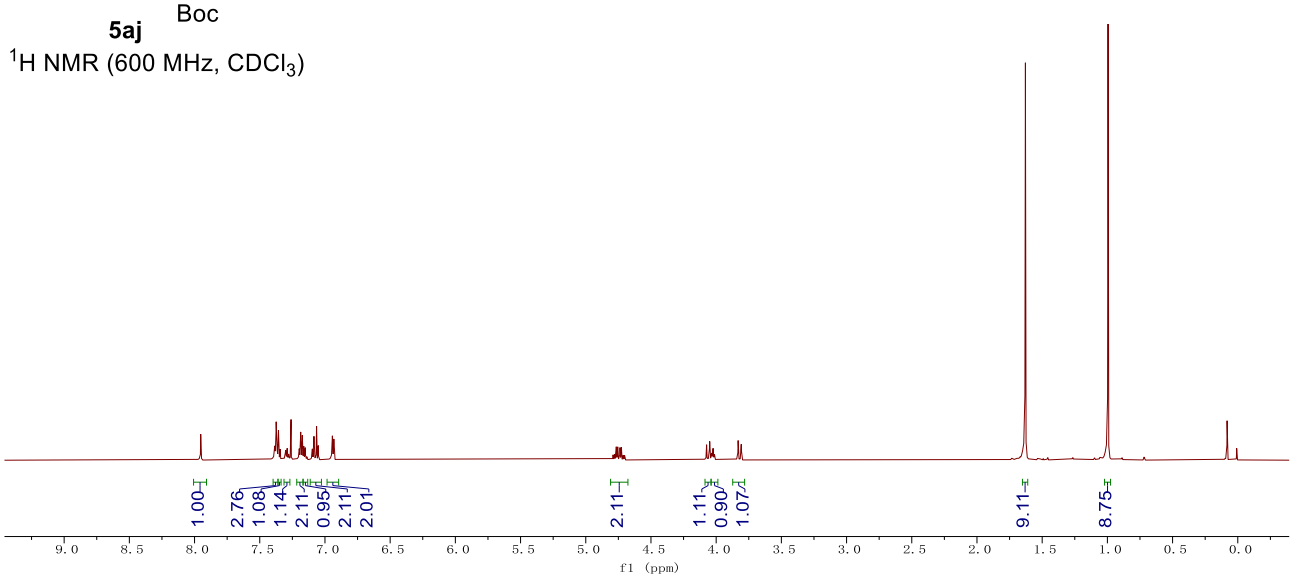
^{13}C NMR (151 MHz, $CDCl_3$)

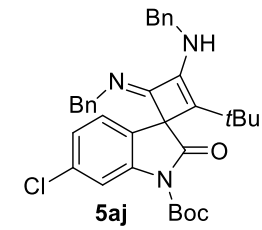




5aj

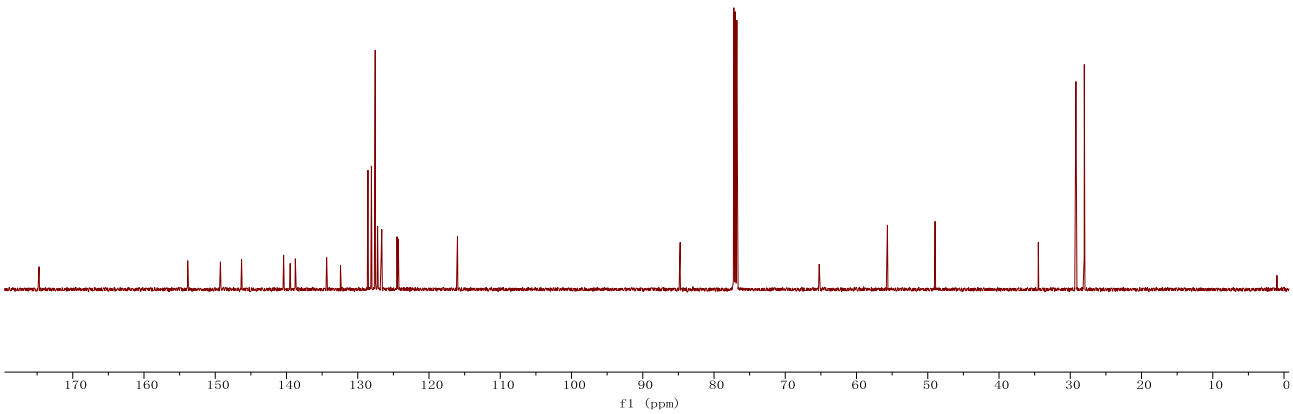
^{1}H NMR (600 MHz, $CDCl_3$)

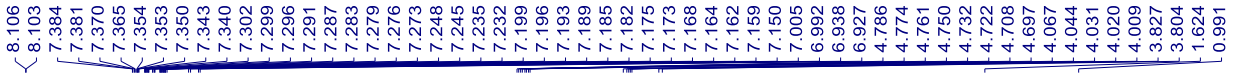


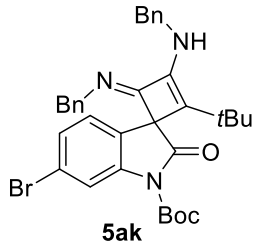


5aj

^{13}C NMR (151 MHz, $CDCl_3$)

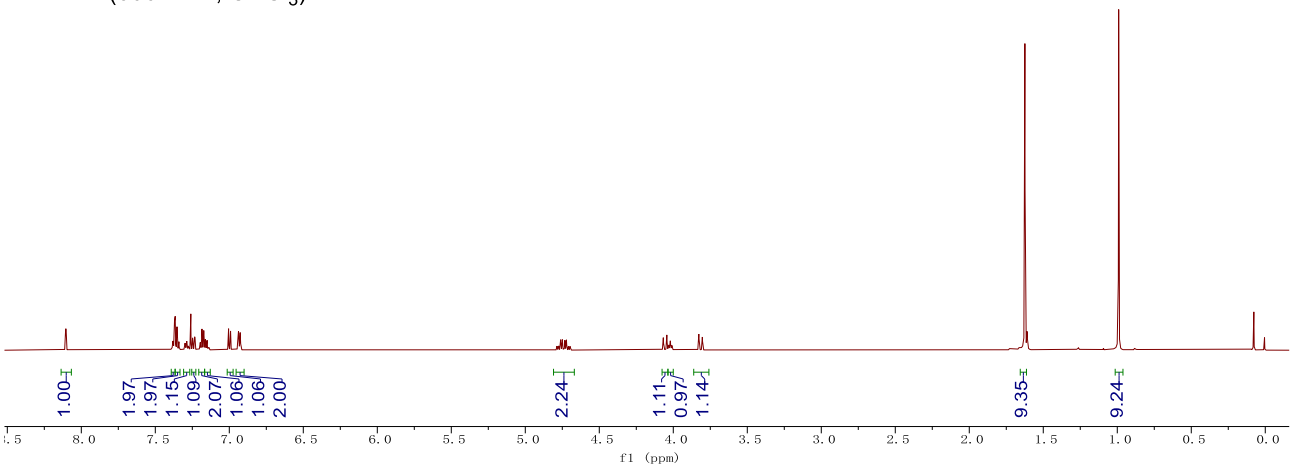


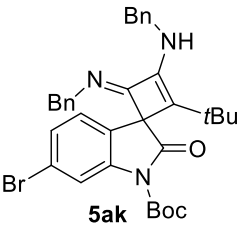




5ak

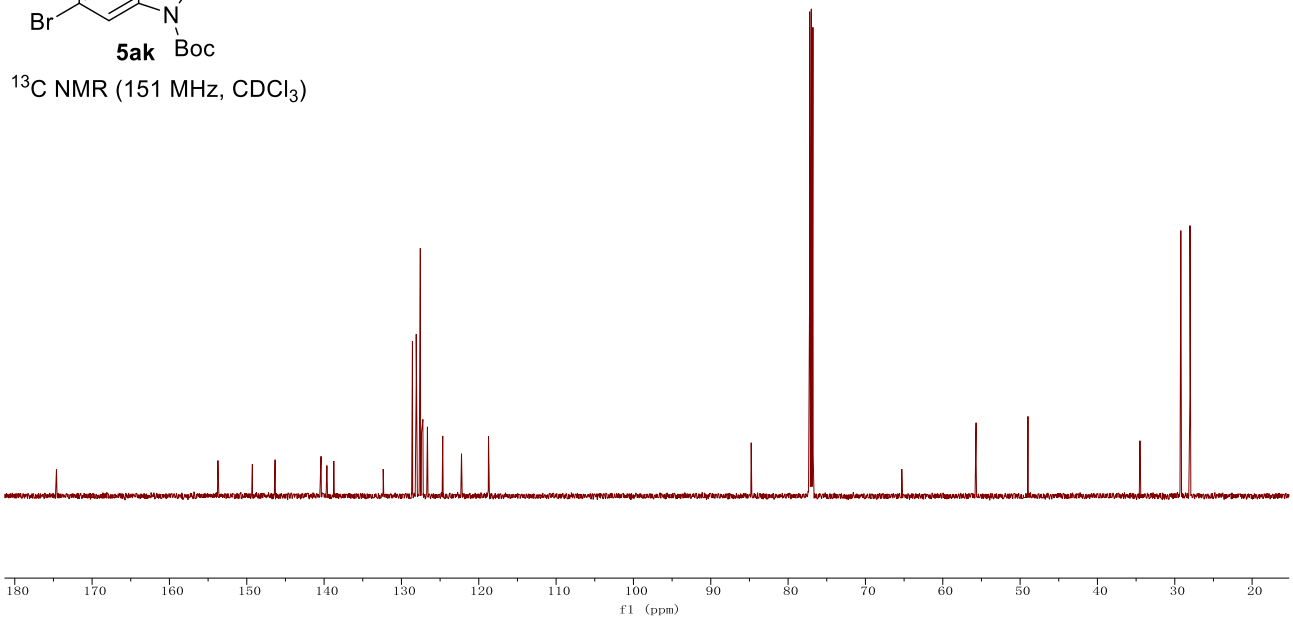
^{1}H NMR (600 MHz, $CDCl_3$)

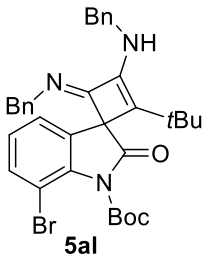




5ak

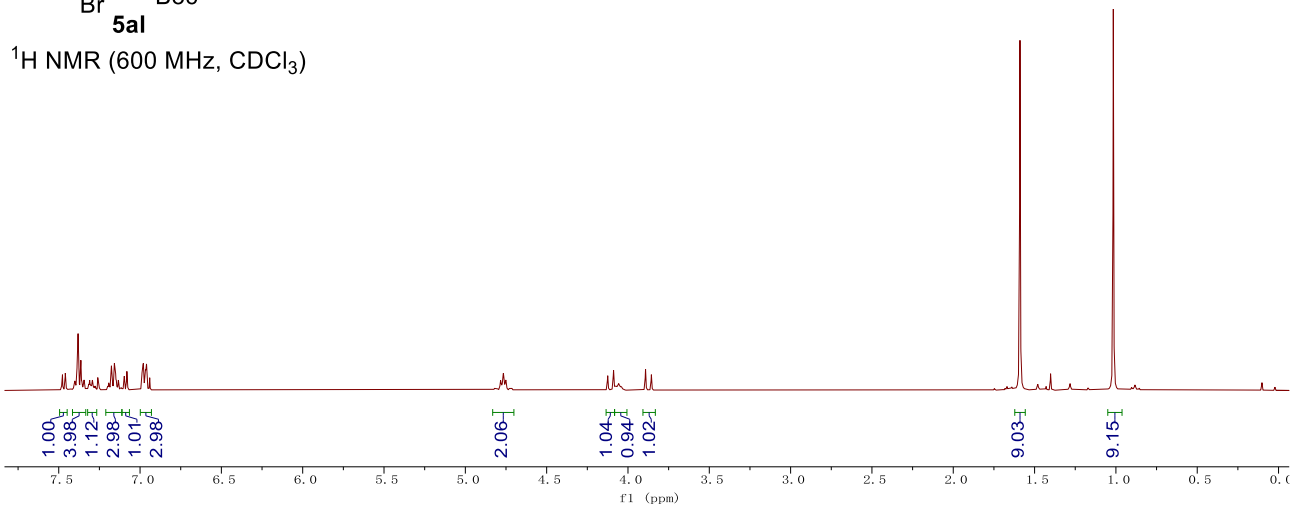
^{13}C NMR (151 MHz, $CDCl_3$)

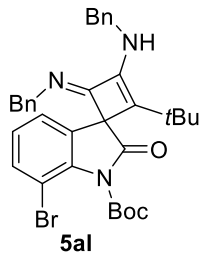




5al

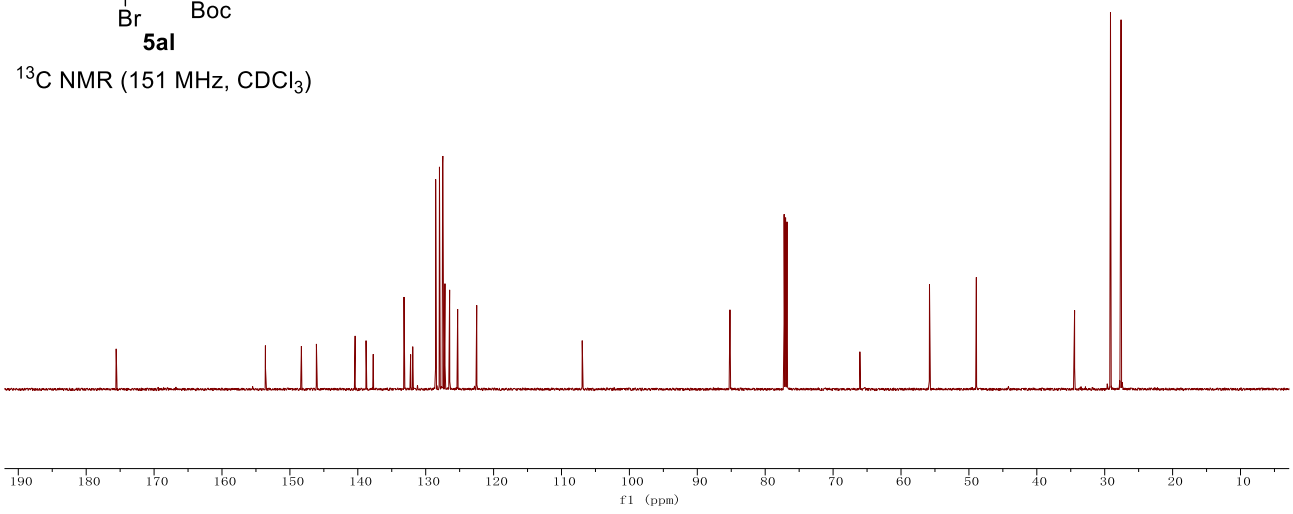
^{1}H NMR (600 MHz, $CDCl_3$)

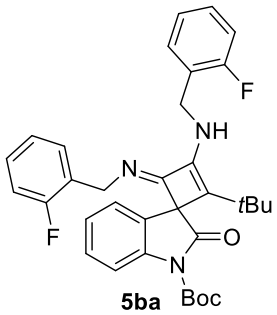




5al

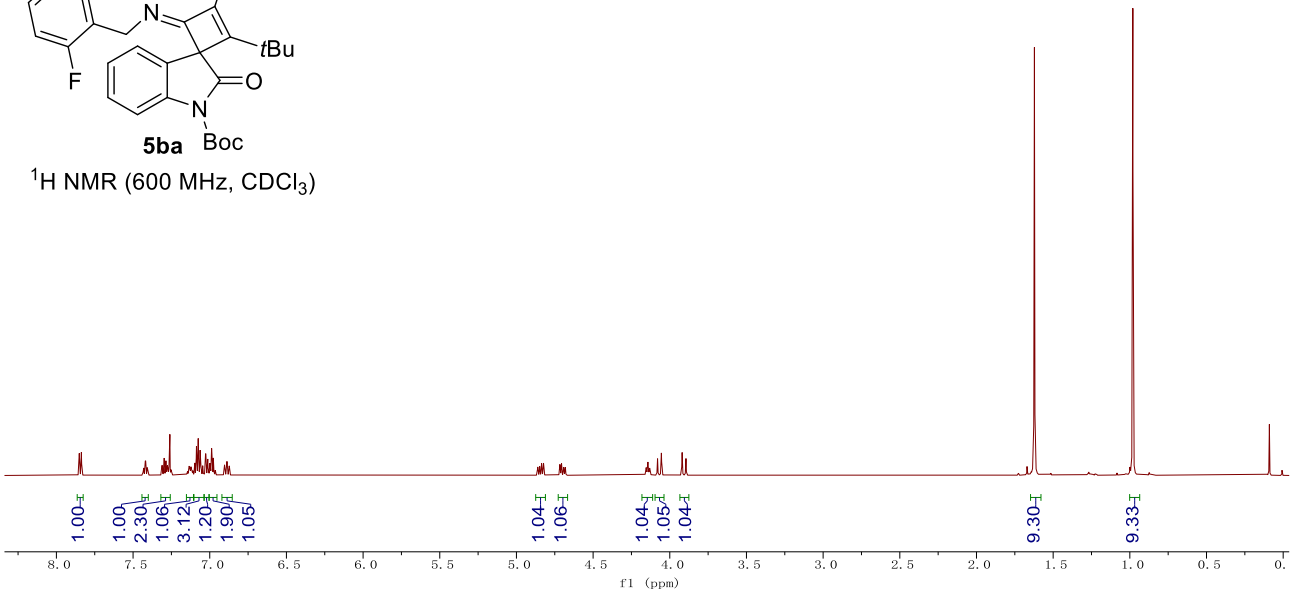
^{13}C NMR (151 MHz, $CDCl_3$)

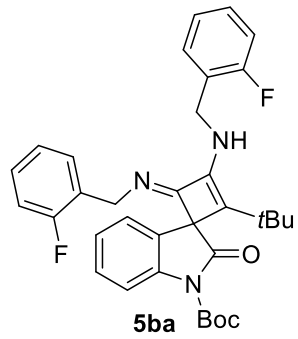




5ba

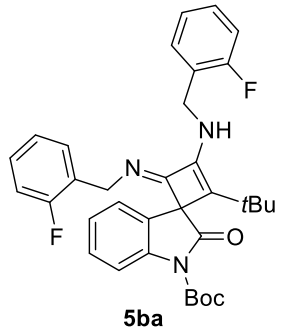
^{1}H NMR (600 MHz, $CDCl_3$)





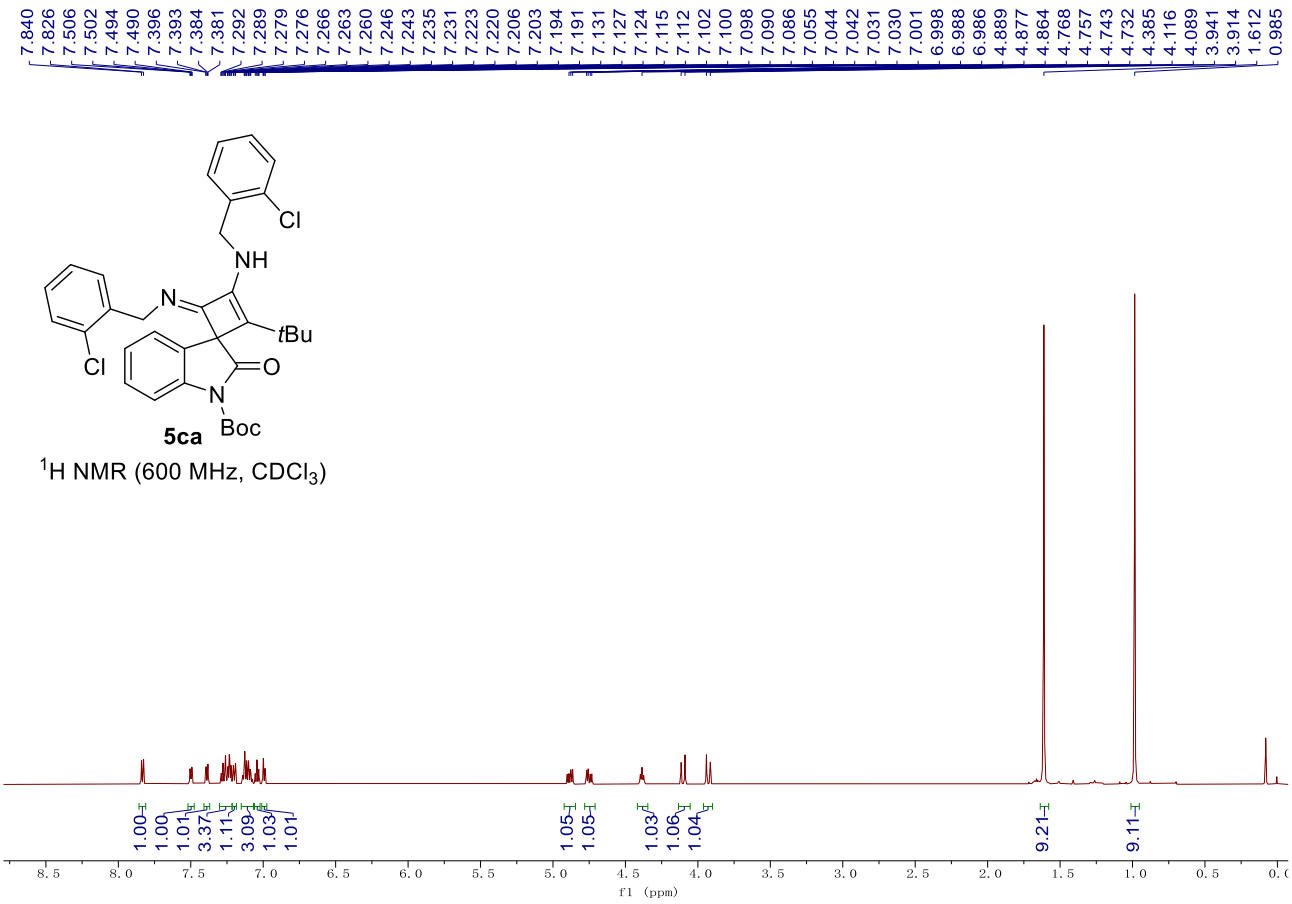
5ba

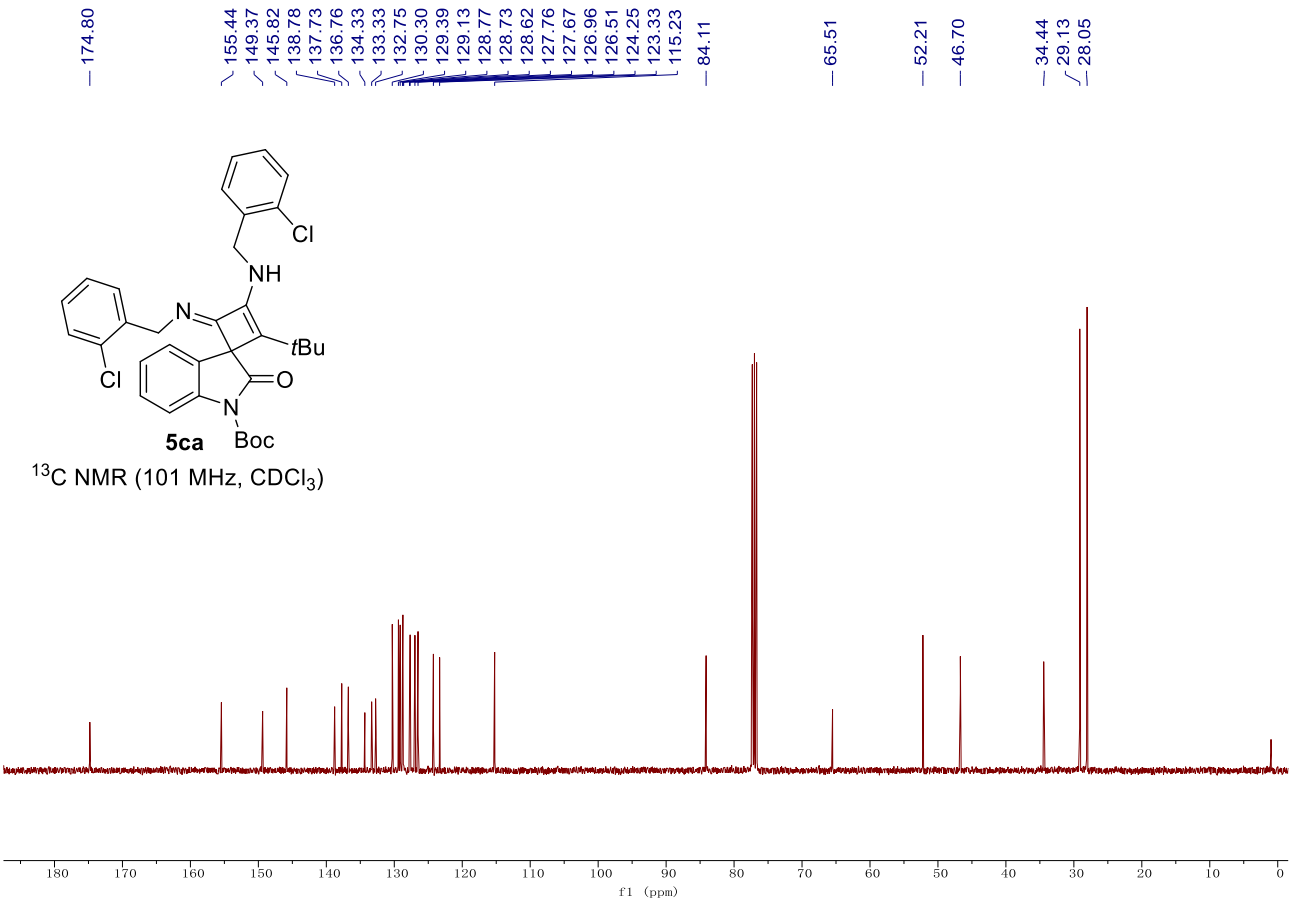
^{13}C NMR (151 MHz, $CDCl_3$)

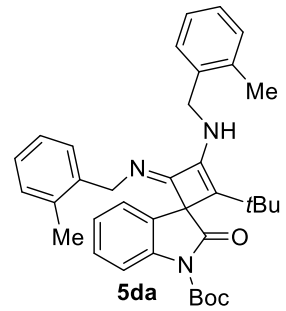


5ba

^{19}F NMR (565 MHz, $CDCl_3$)

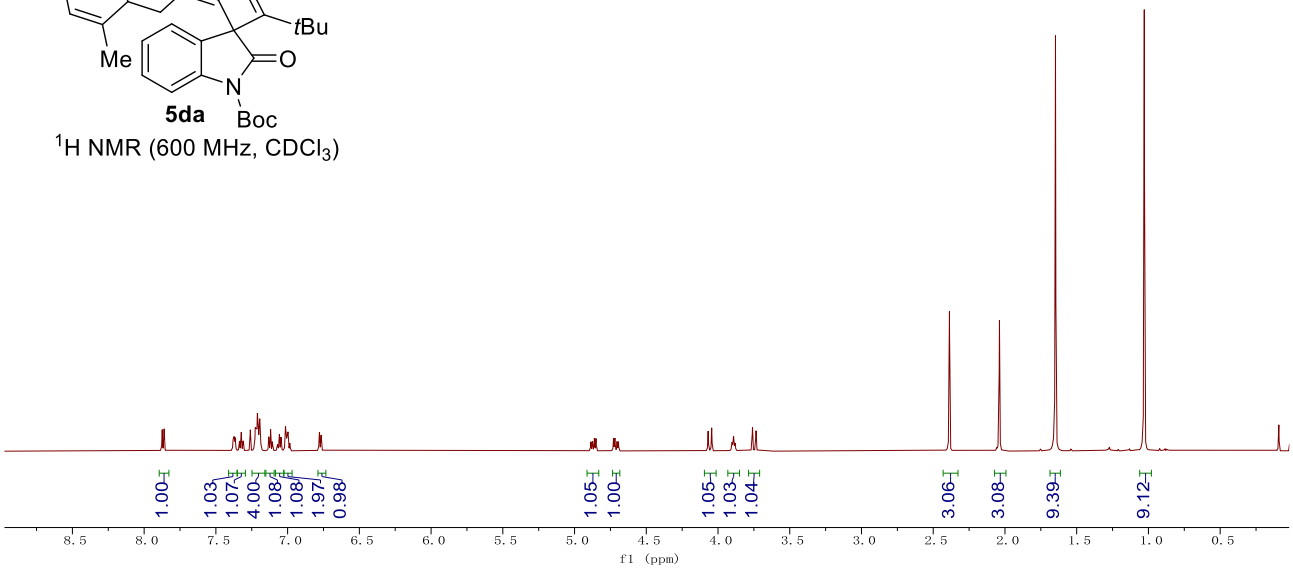

7.840
7.826
7.506
7.502
7.494
7.490
7.396
7.393
7.384
7.381
7.292
7.289
7.279
7.276
7.266
7.263
7.260
7.246
7.243
7.235
7.231
7.223
7.220
7.206
7.203
7.194
7.191
7.131
7.127
7.124
7.115
7.112
7.102
7.100
7.098
7.090
7.086
7.055
7.044
7.042
7.031
7.030
7.001
6.998
6.988
6.986
4.889
4.877
4.864
4.768
4.757
4.743
4.732
4.385
4.116
4.089
3.941
3.914
1.612
0.985
Cl
NH
N
tBu
Cl
O
N
Boc
5ca
1H NMR (600 MHz, CDCl3)
1.00
1.00
1.01
3.37
1.11
3.09
1.03
1.01
1.05
1.05
1.03
1.06
1.04
9.21
9.11
f1 (ppm)

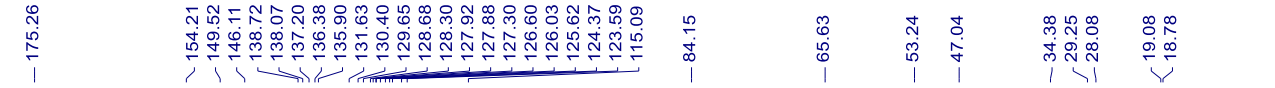

174.80
155.44
149.37
145.82
138.78
137.73
136.76
134.33
133.33
132.75
130.30
129.39
129.13
128.77
128.73
128.62
127.76
127.67
126.96
126.51
124.25
123.33
115.23
84.11
65.51
52.21
46.70
34.44
29.13
28.05
Cl
NH
N
tBu
Cl
O
N
Boc
5ca
13C NMR (101 MHz, CDCl3)
f1 (ppm)

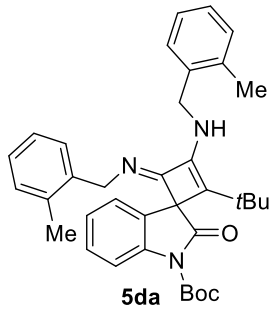


5da

^{1}H NMR (600 MHz, $CDCl_3$)

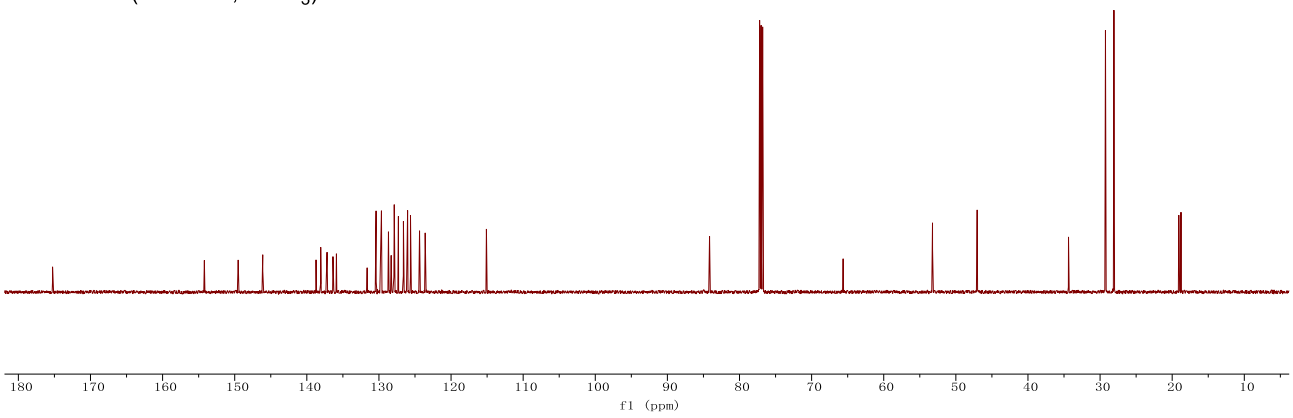


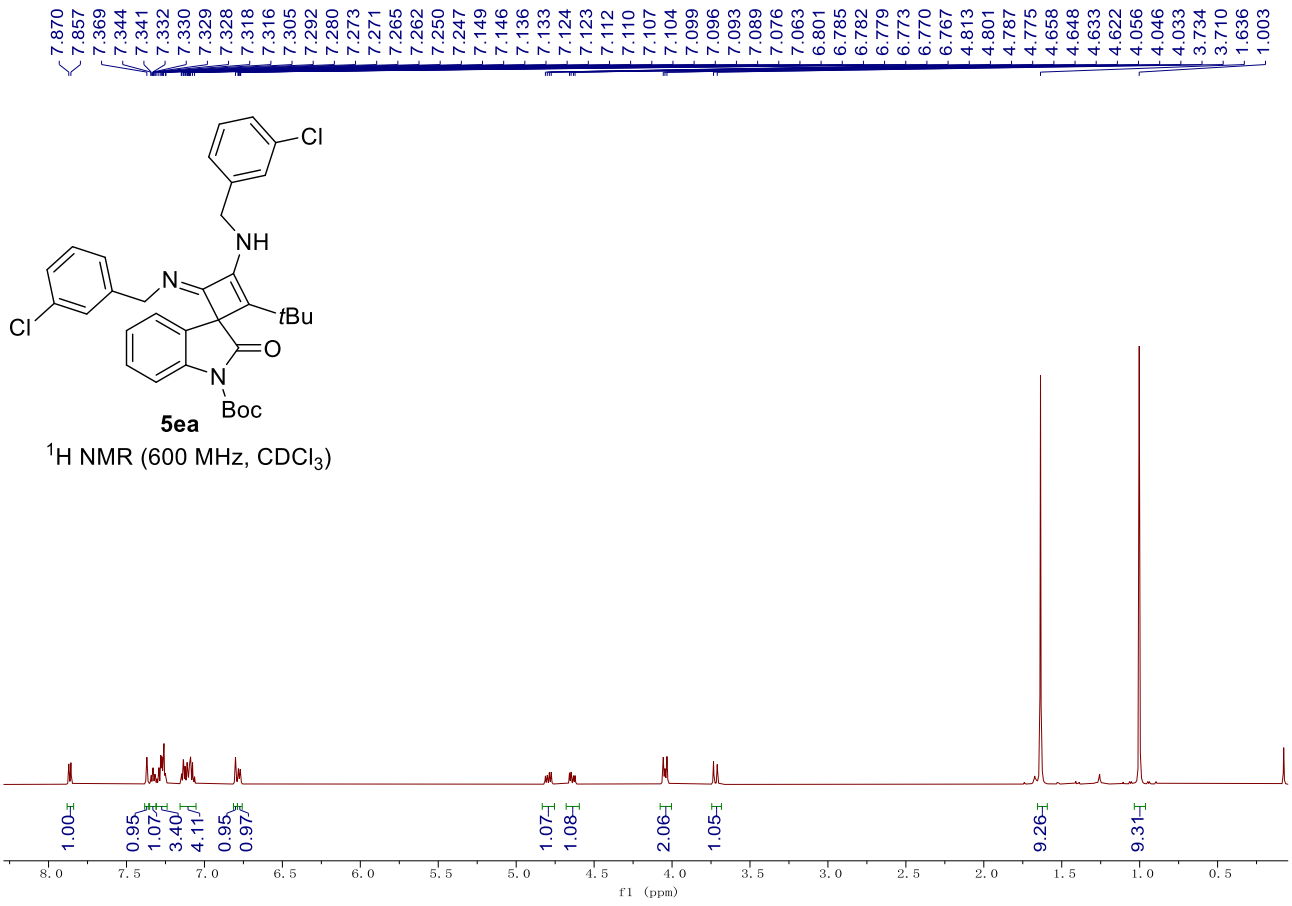




5da

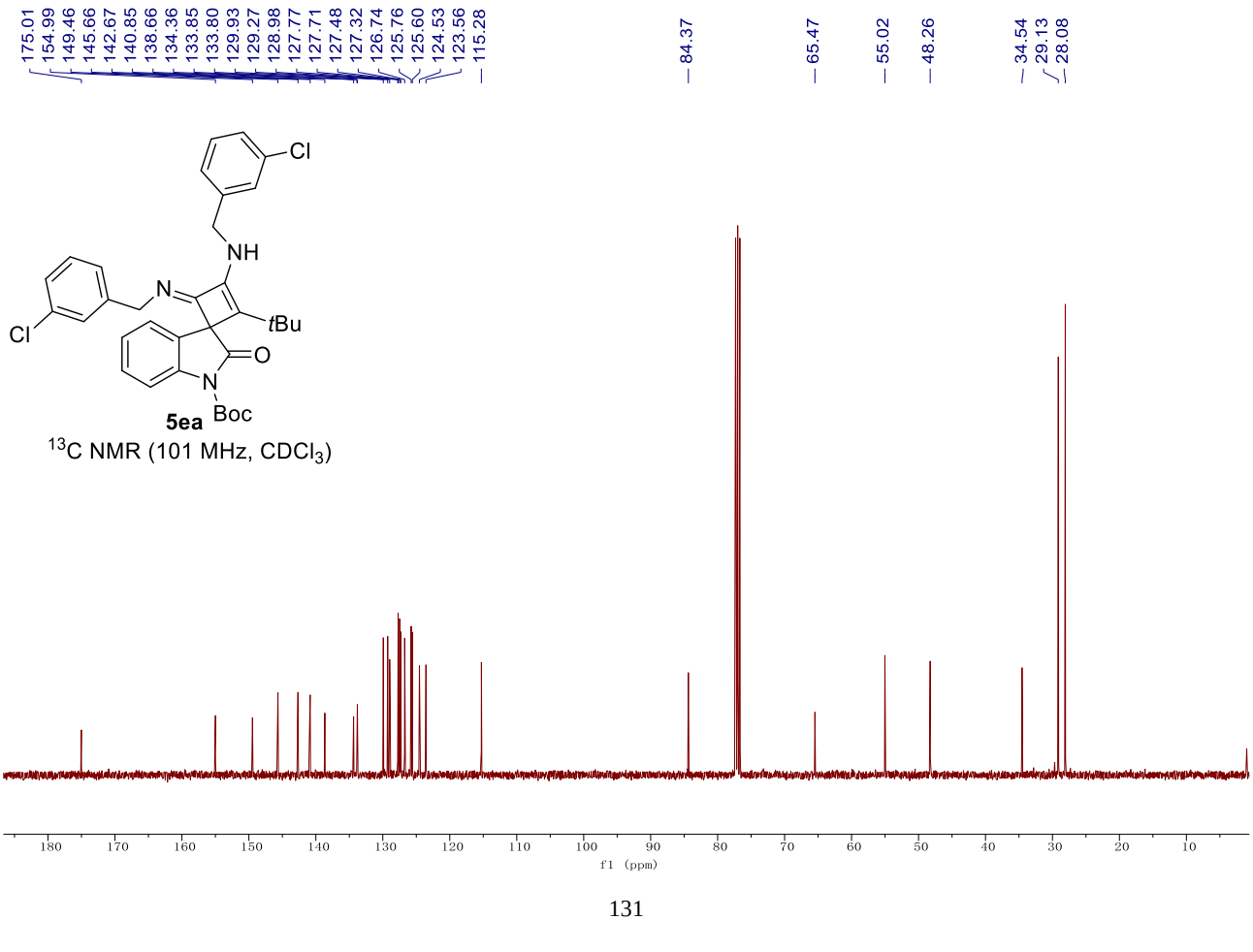
^{13}C NMR (151 MHz, $CDCl_3$)





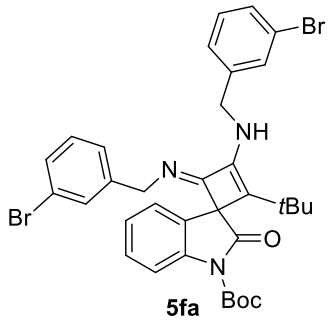
5ea

^{1}H NMR (600 MHz, $CDCl_3$)



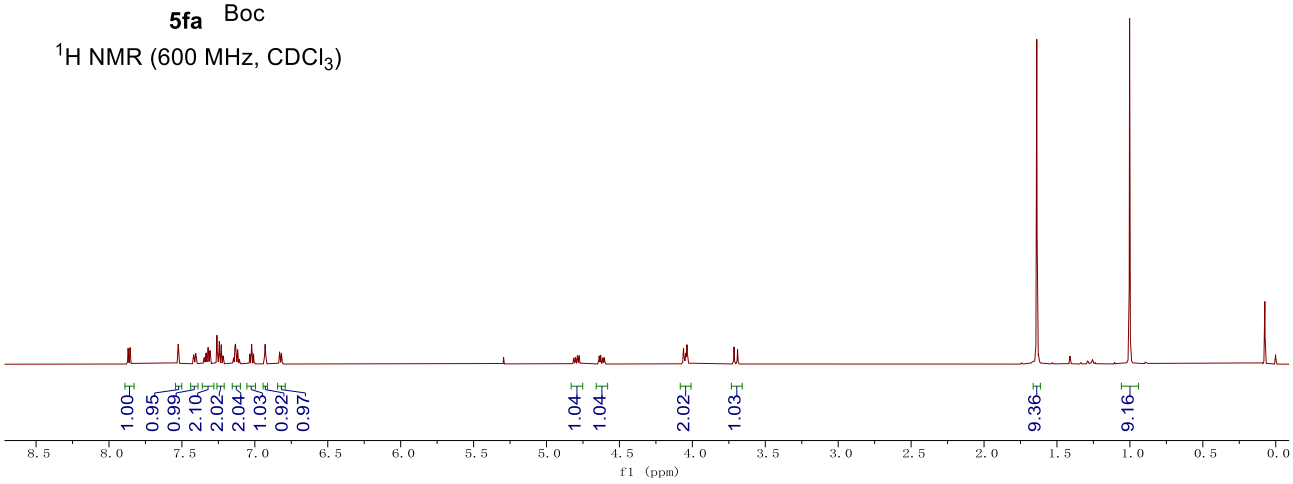
5ea

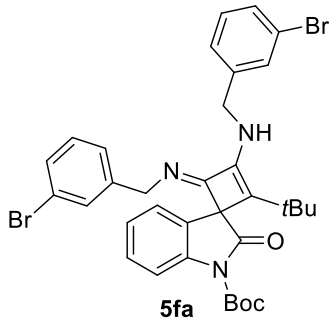
^{13}C NMR (101 MHz, $CDCl_3$)



5fa

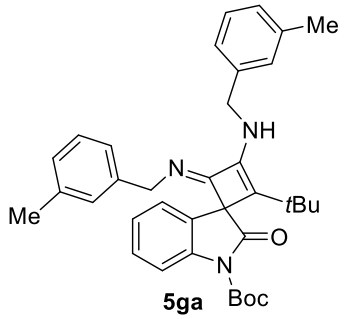
^{1}H NMR (600 MHz, $CDCl_3$)





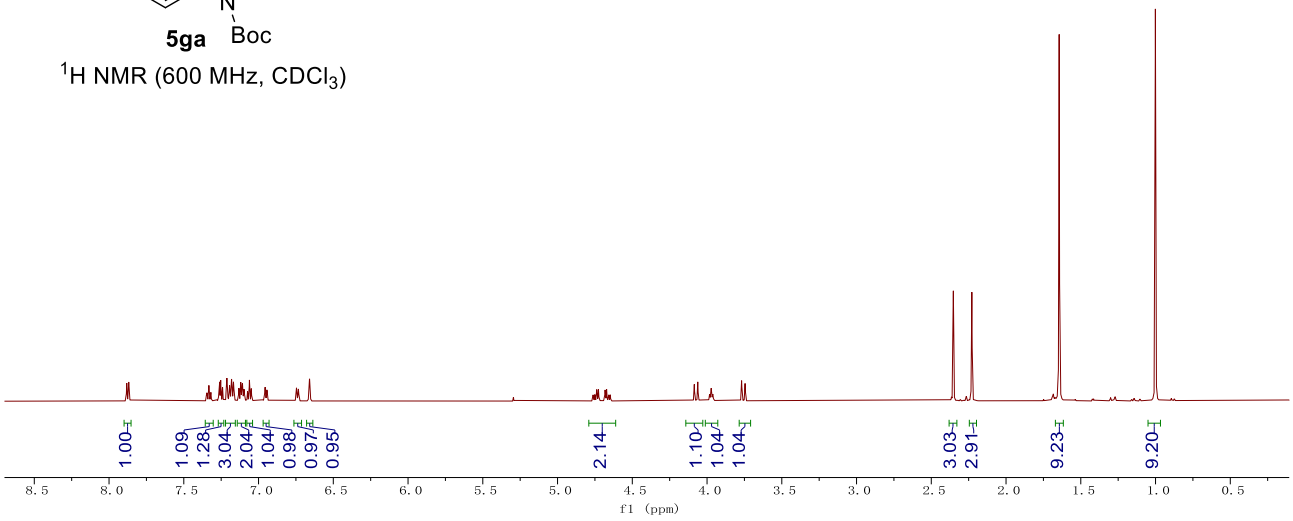
5fa

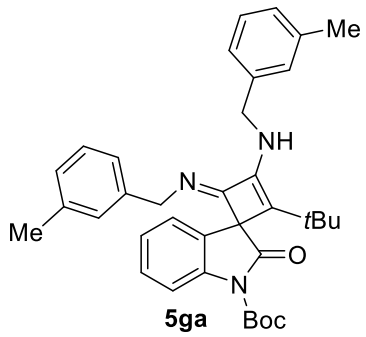
^{13}C NMR (151 MHz, $CDCl_3$)



5ga

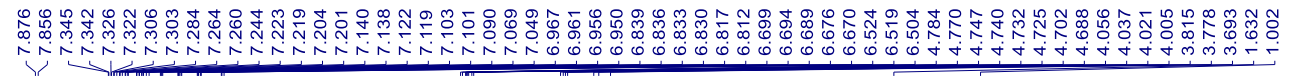
^{1}H NMR (600 MHz, $CDCl_3$)

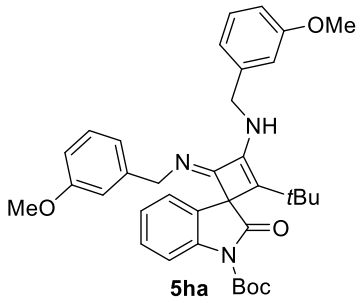




5ga

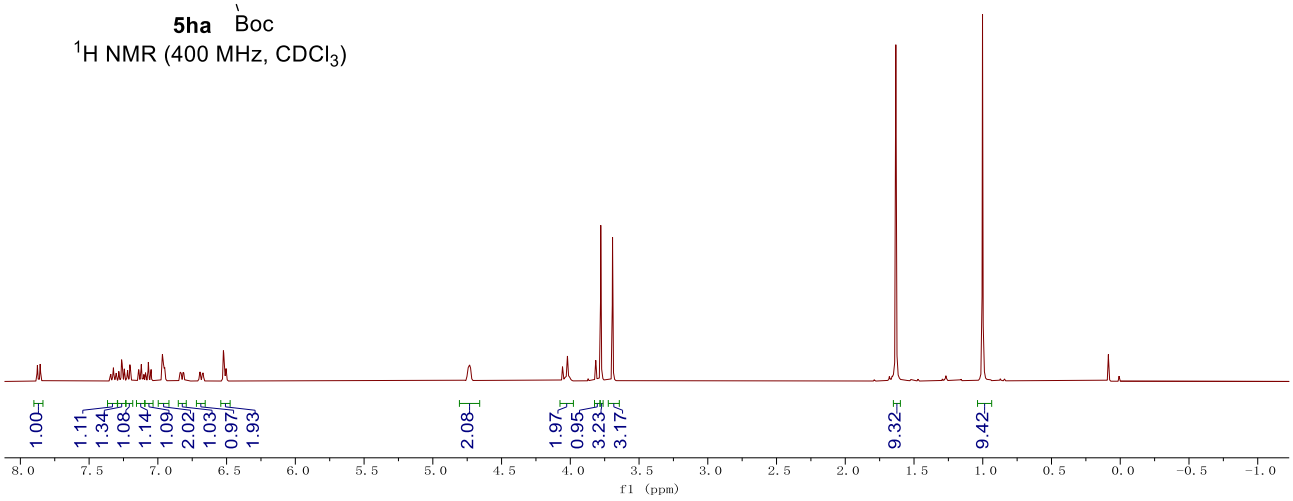
^{13}C NMR (151 MHz, $CDCl_3$)

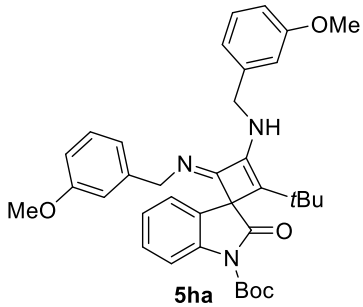




5ha

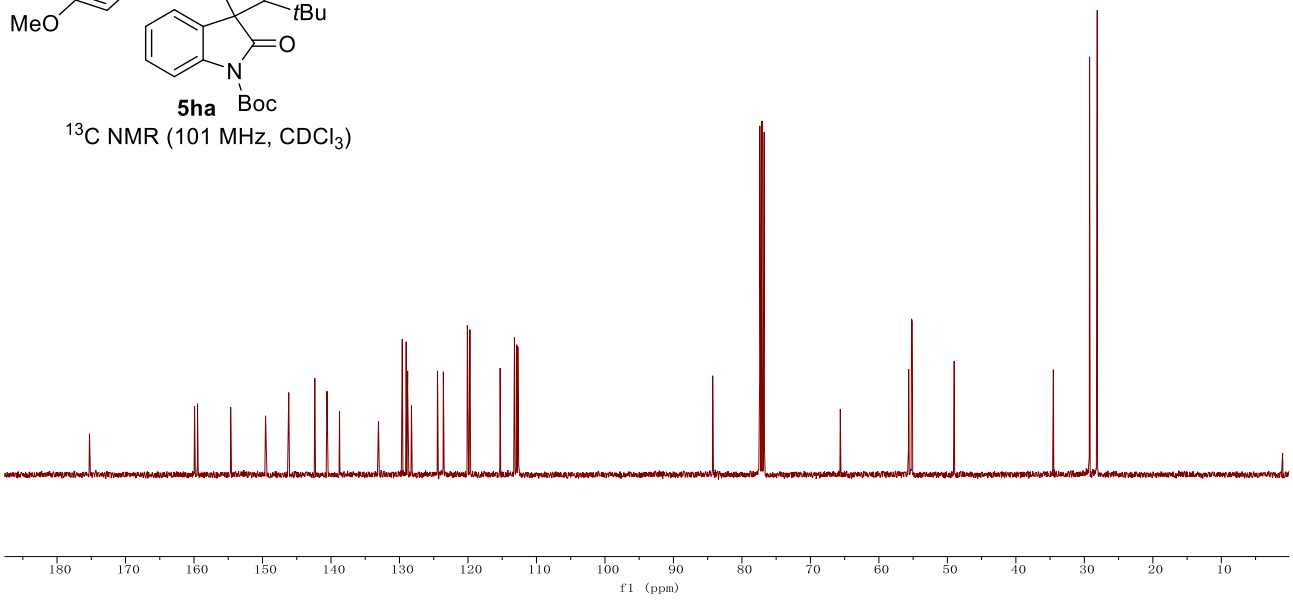
^{1}H NMR (400 MHz, $CDCl_3$)

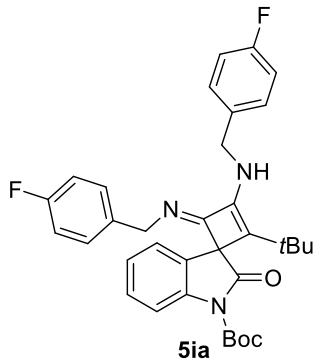




5ha

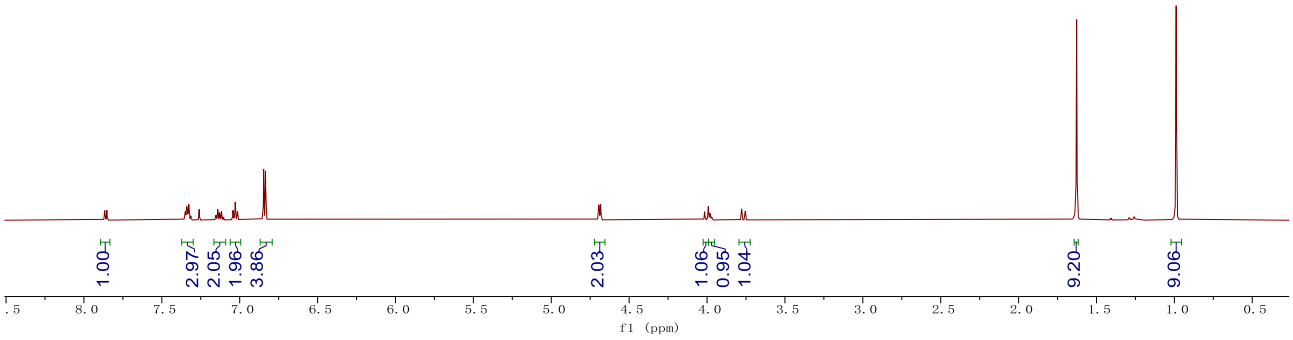
^{13}C NMR (101 MHz, $CDCl_3$)

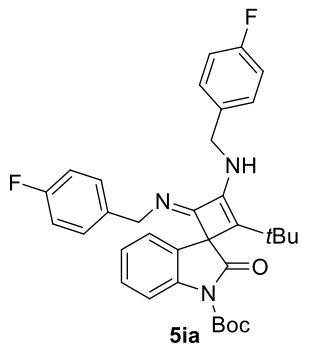




5ia

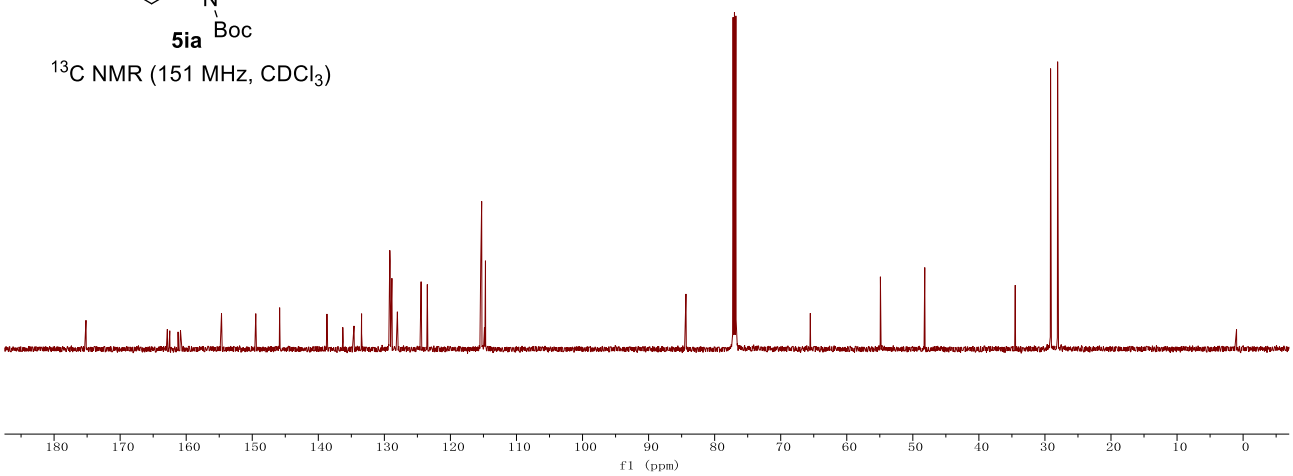
^{1}H NMR (600 MHz, $CDCl_3$)

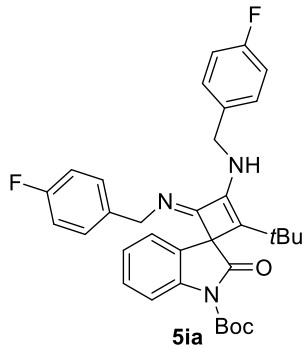




5ia

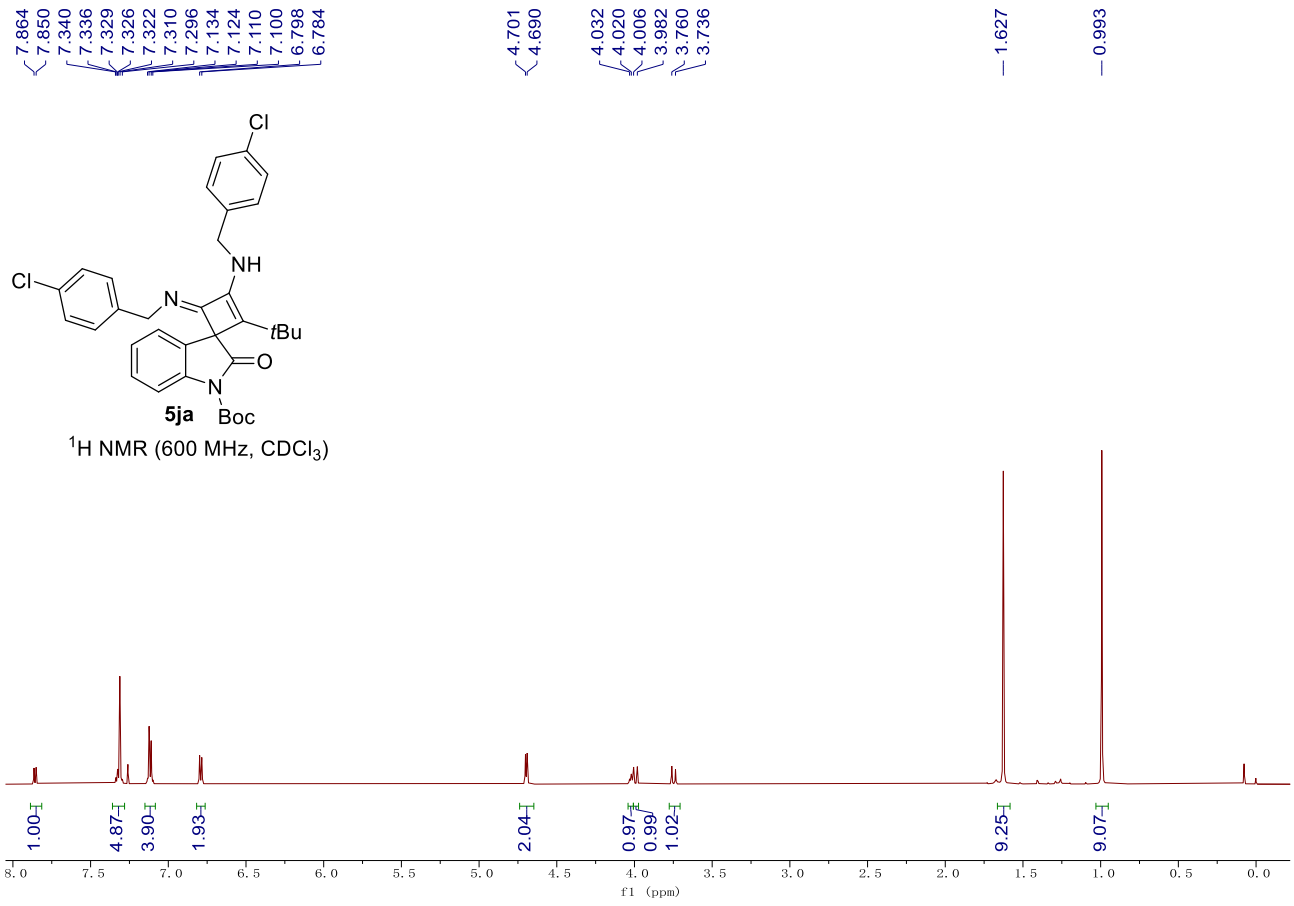
^{13}C NMR (151 MHz, $CDCl_3$)

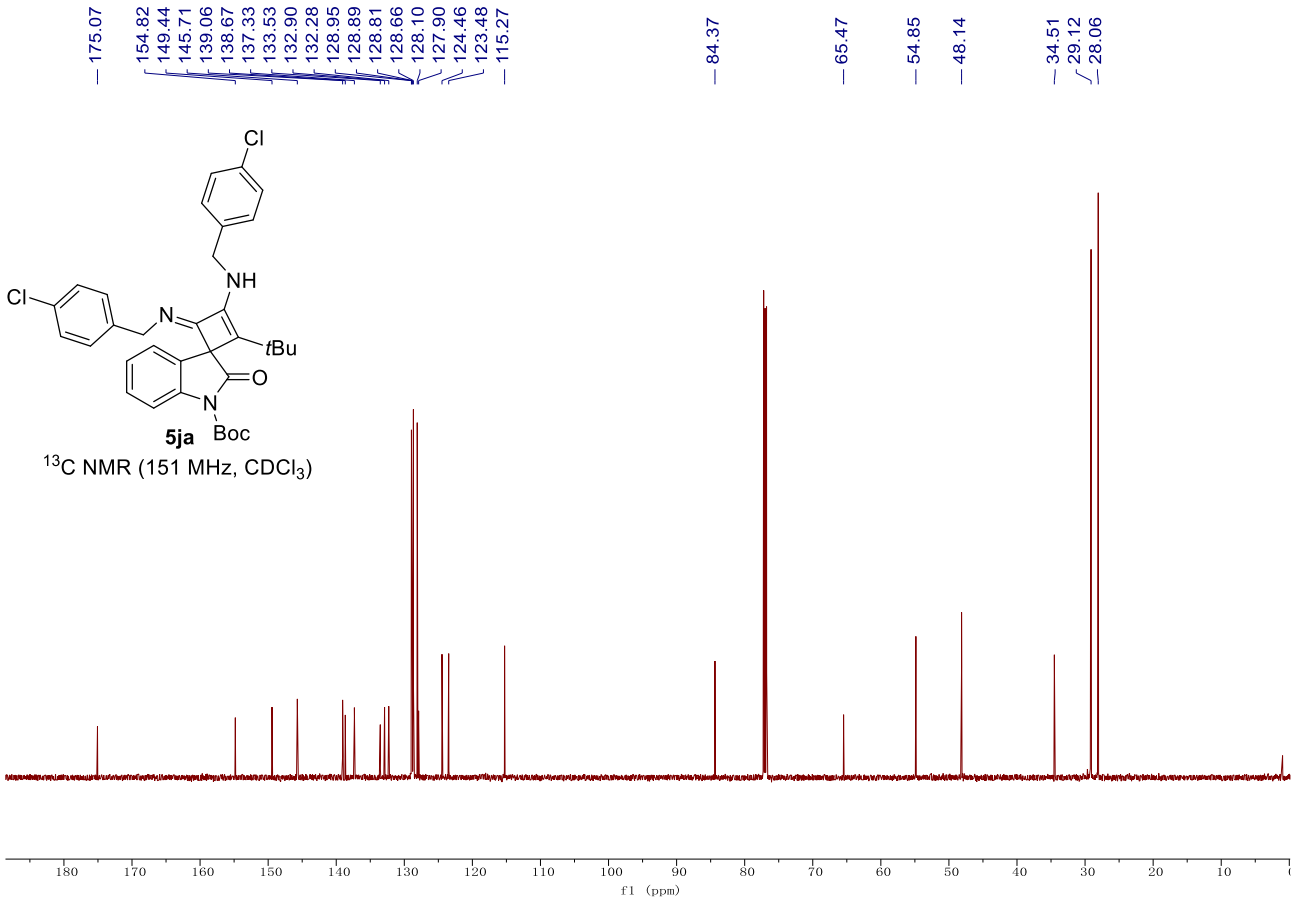


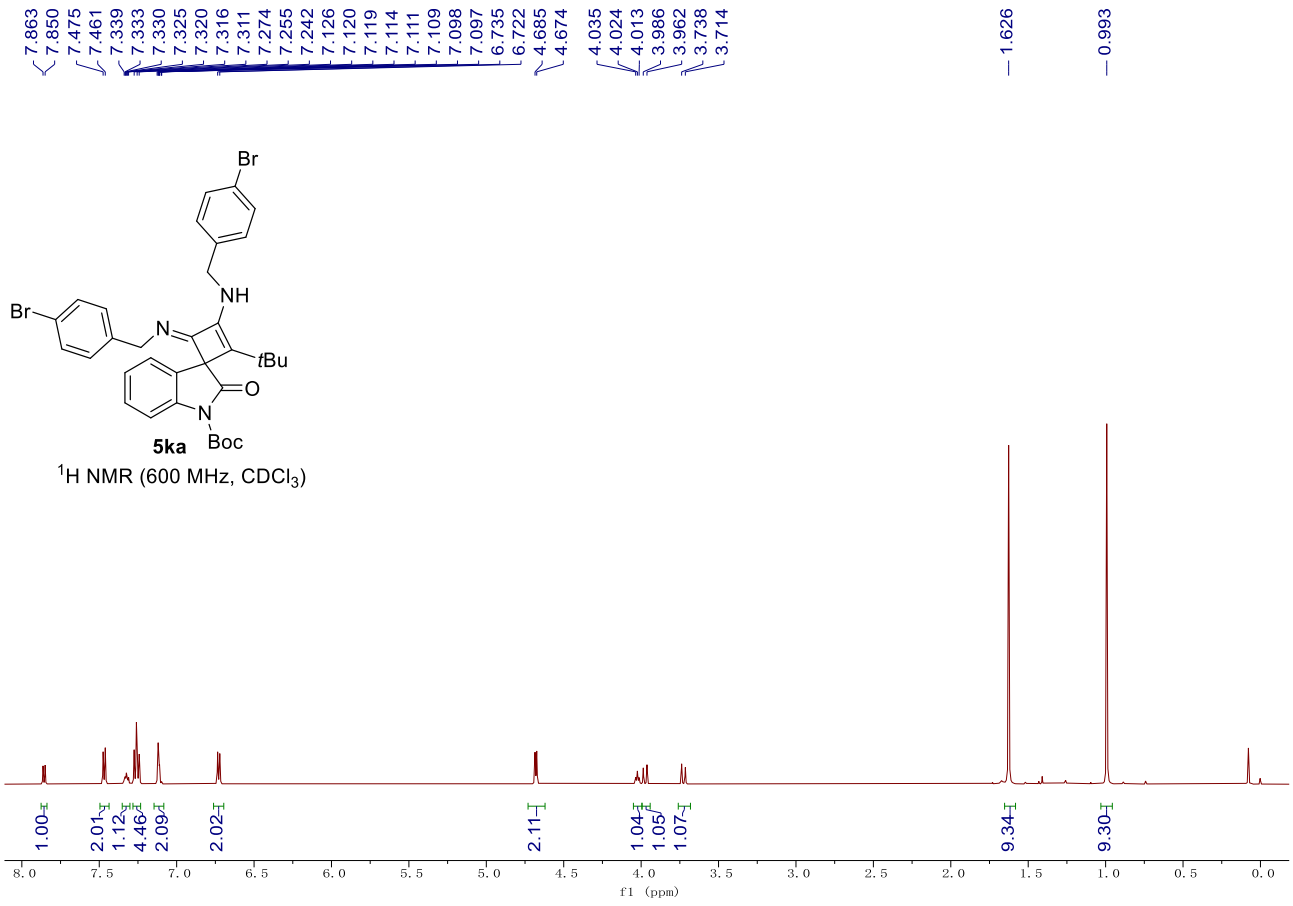


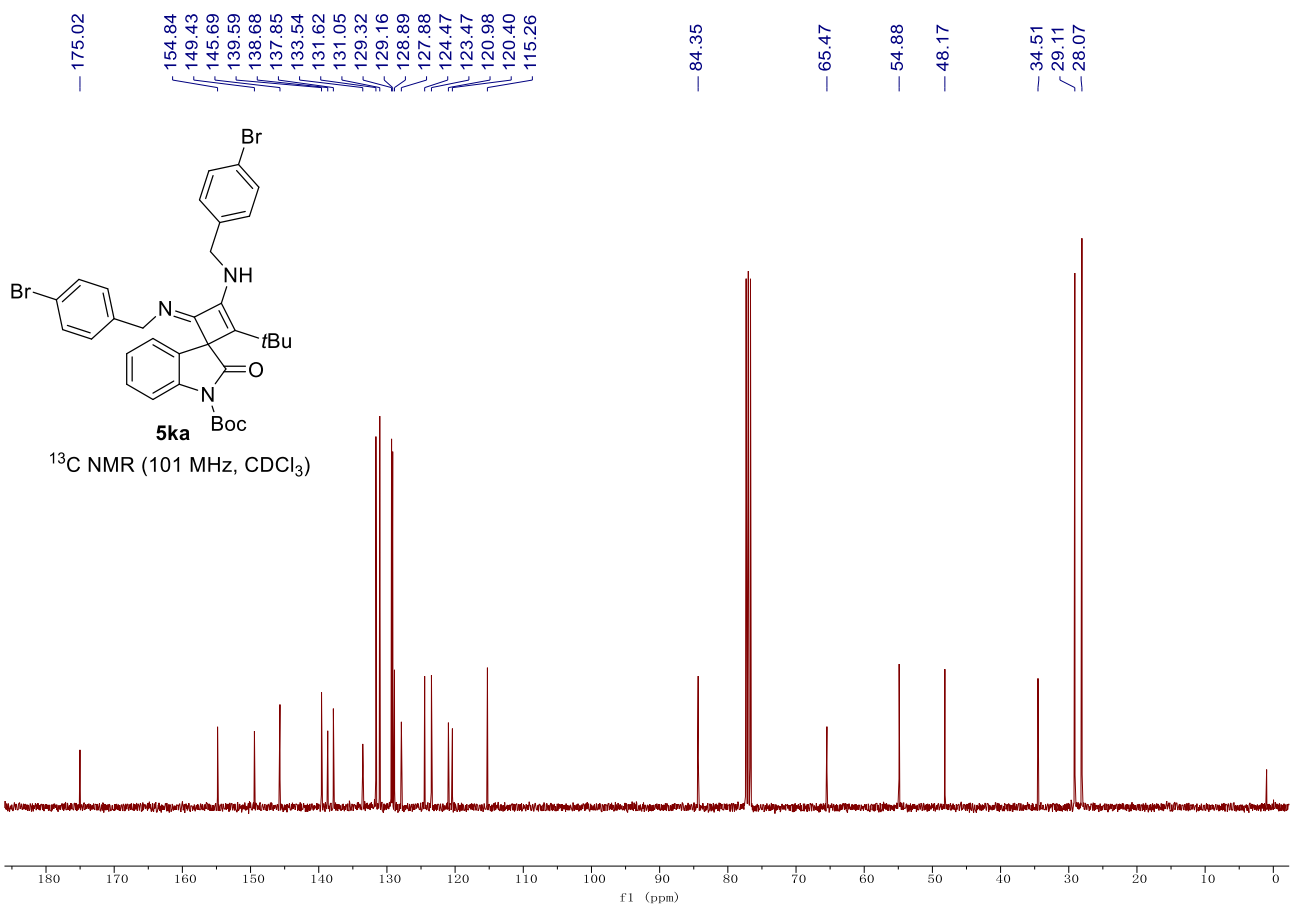
5ia

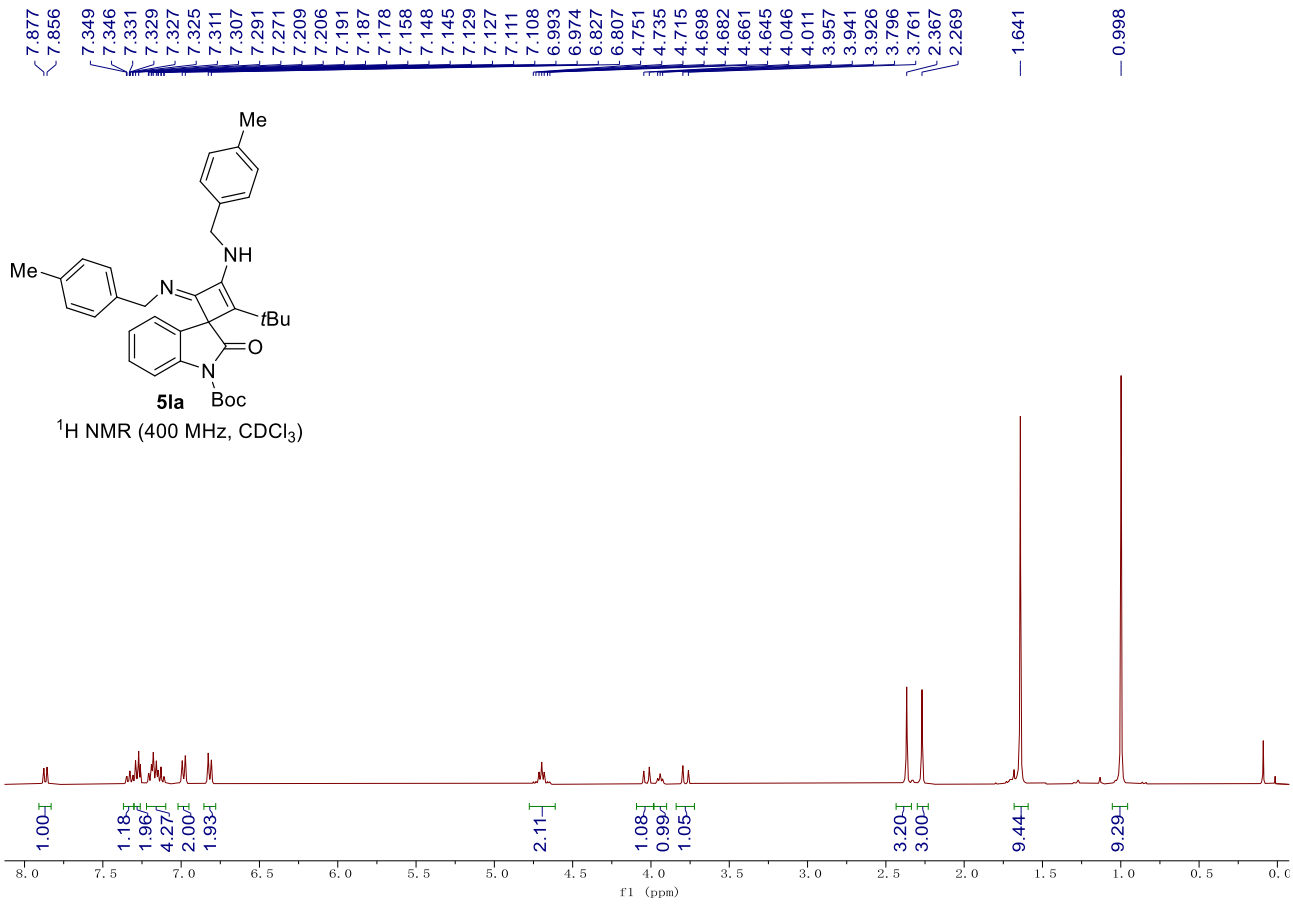
^{19}F NMR (565 MHz, $CDCl_3$)

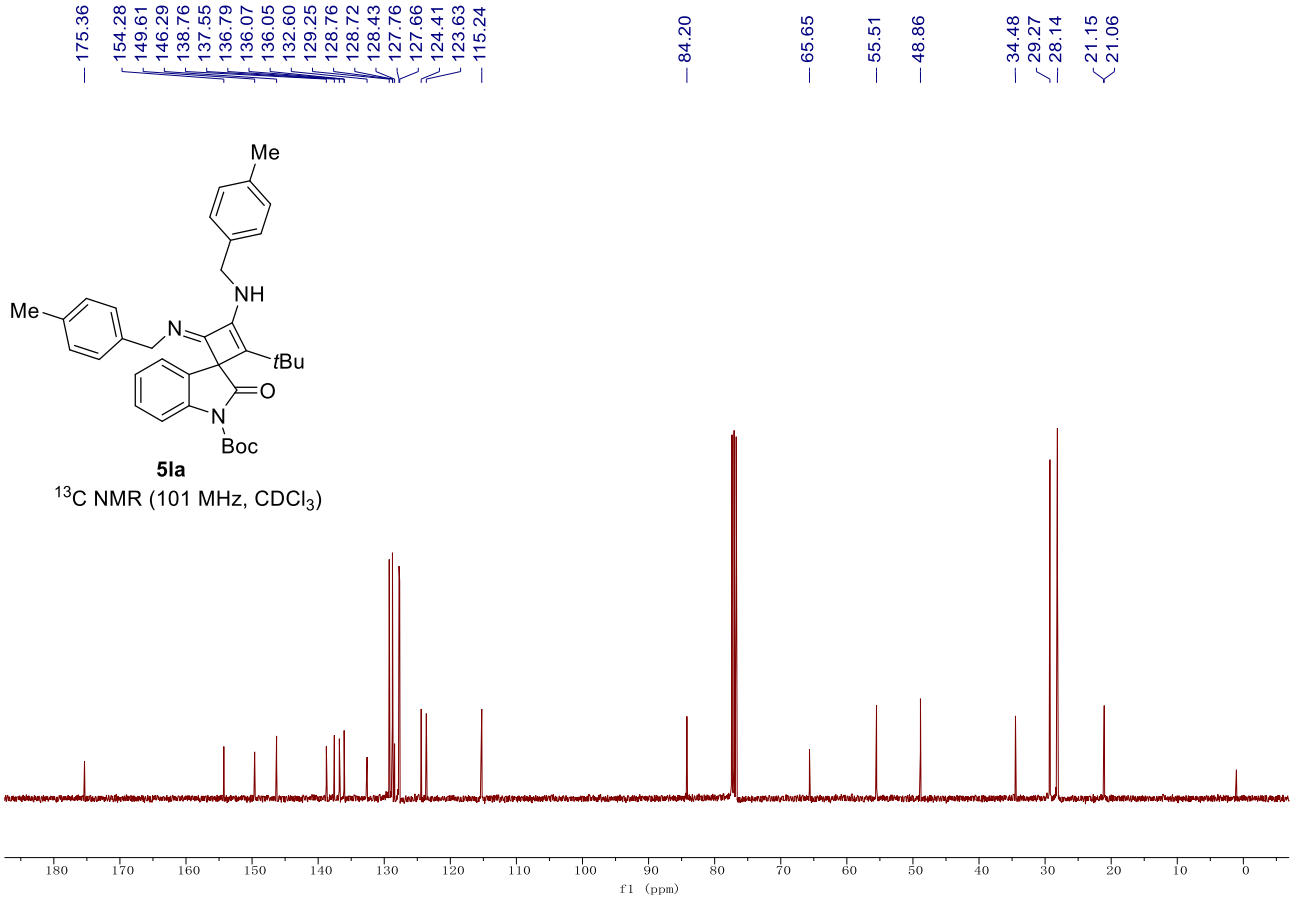

7.864
7.850
7.340
7.336
7.329
7.326
7.322
7.310
7.296
7.134
7.124
7.110
7.100
6.798
6.784
4.701
4.690
4.032
4.020
4.006
3.982
3.760
3.736
1.627
0.993
Cl
NH
Cl
N
tBu
O
N
Boc
5ja
1H NMR (600 MHz, CDCl3)
1.00
4.87
3.90
1.93
2.04
0.97
0.99
1.02
9.25
9.07
f1 (ppm)

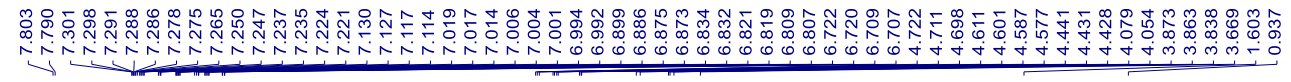

175.07
154.82
149.44
145.71
139.06
138.67
137.33
133.53
132.90
132.28
128.95
128.89
128.81
128.66
128.10
127.90
124.46
123.48
115.27
84.37
65.47
54.85
48.14
34.51
29.12
28.06
Cl
NH
Cl
N
tBu
O
N
Boc
5ja
13C NMR (151 MHz, CDCl3)
f1 (ppm)

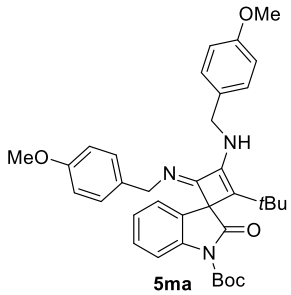

7.863
7.850
7.475
7.461
7.339
7.333
7.330
7.325
7.320
7.316
7.311
7.274
7.255
7.242
7.126
7.120
7.119
7.114
7.111
7.109
7.098
7.097
6.735
6.722
4.685
4.674
4.035
4.024
4.013
3.986
3.962
3.738
3.714
1.626
0.993
Br
NH
N
Br
tBu
O
N
Boc
5ka
1H NMR (600 MHz, CDCl3)
1.00
2.01
1.12
4.46
2.09
2.02
2.11
1.04
1.05
1.07
9.34
9.30
f1 (ppm)


175.02
154.84
149.43
145.69
139.59
138.68
137.85
133.54
131.62
131.05
129.32
129.16
128.89
127.88
124.47
123.47
120.98
120.40
115.26
84.35
65.47
54.88
48.17
34.51
29.11
28.07
Br
NH
N
Br
tBu
O
N
Boc
5ka
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.877
7.856
7.349
7.346
7.331
7.329
7.327
7.325
7.311
7.307
7.291
7.271
7.209
7.206
7.191
7.187
7.178
7.158
7.148
7.145
7.129
7.127
7.111
7.108
6.993
6.974
6.827
6.807
4.751
4.735
4.715
4.698
4.682
4.661
4.645
4.046
4.011
3.957
3.941
3.926
3.796
3.761
2.367
2.269
1.641
0.998
Me
NH
Me
N
tBu
O
N
Boc
5la
1H NMR (400 MHz, CDCl3)
1.00
1.18
1.96
4.27
2.00
1.93
2.11
1.08
0.99
1.05
3.20
3.00
9.44
9.29
f1 (ppm)

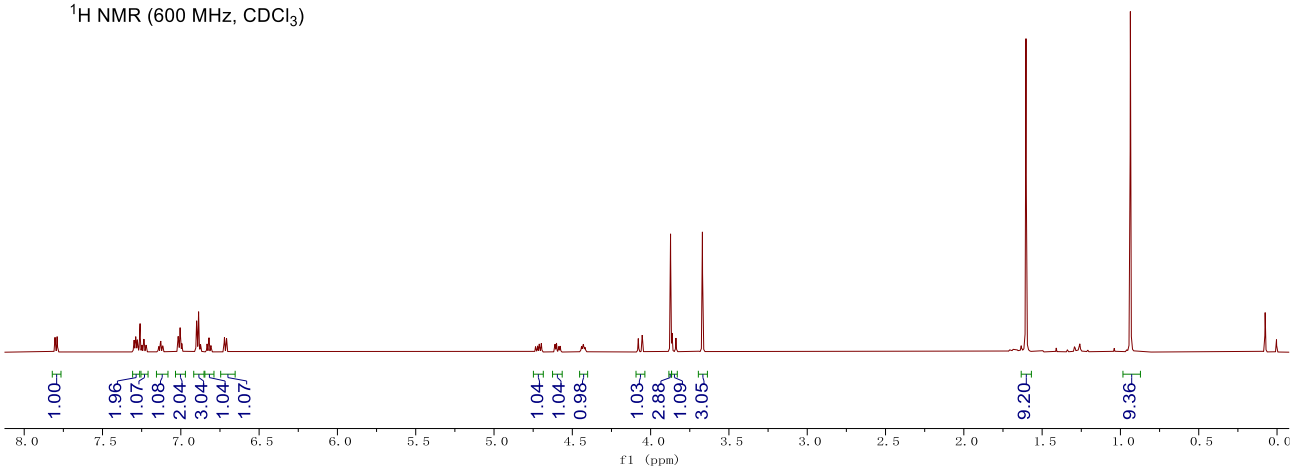

175.36
154.28
149.61
146.29
138.76
137.55
136.79
136.07
136.05
132.60
129.25
128.76
128.72
128.43
127.76
127.66
124.41
123.63
115.24
84.20
65.65
55.51
48.86
34.48
29.27
28.14
21.15
21.06
Me
NH
Me
N
tBu
O
N
Boc
5la
13C NMR (101 MHz, CDCl3)
f1 (ppm)

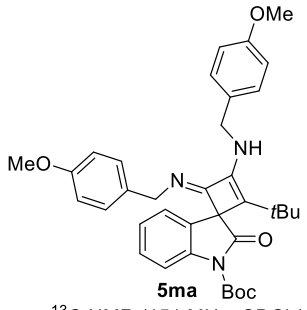




5ma

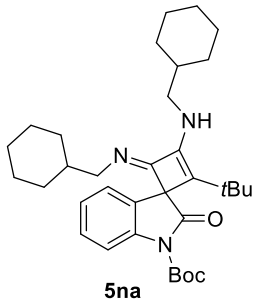
^{1}H NMR (600 MHz, $CDCl_3$)





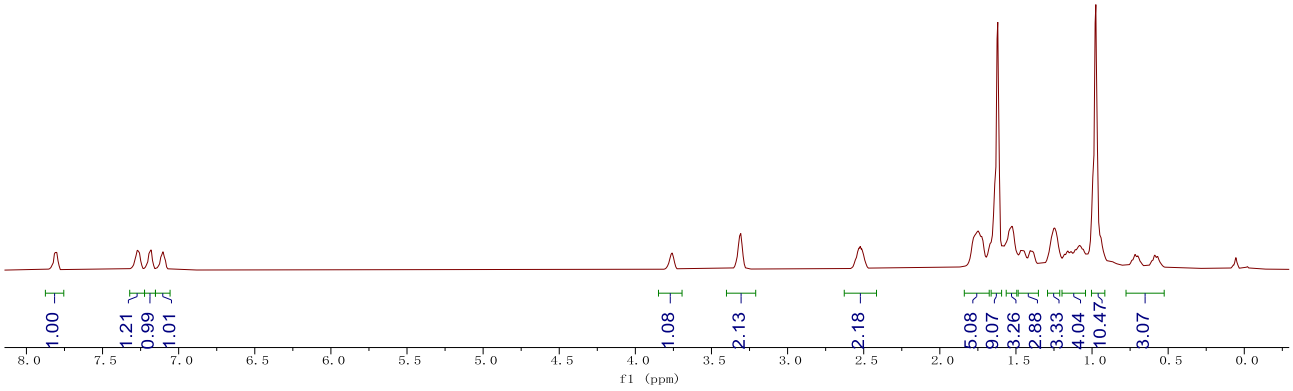
5ma

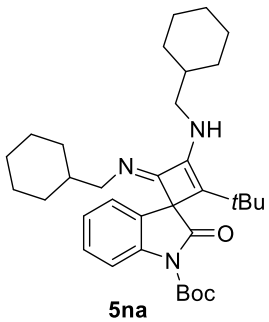
^{13}C NMR (151 MHz, $CDCl_3$)



5na

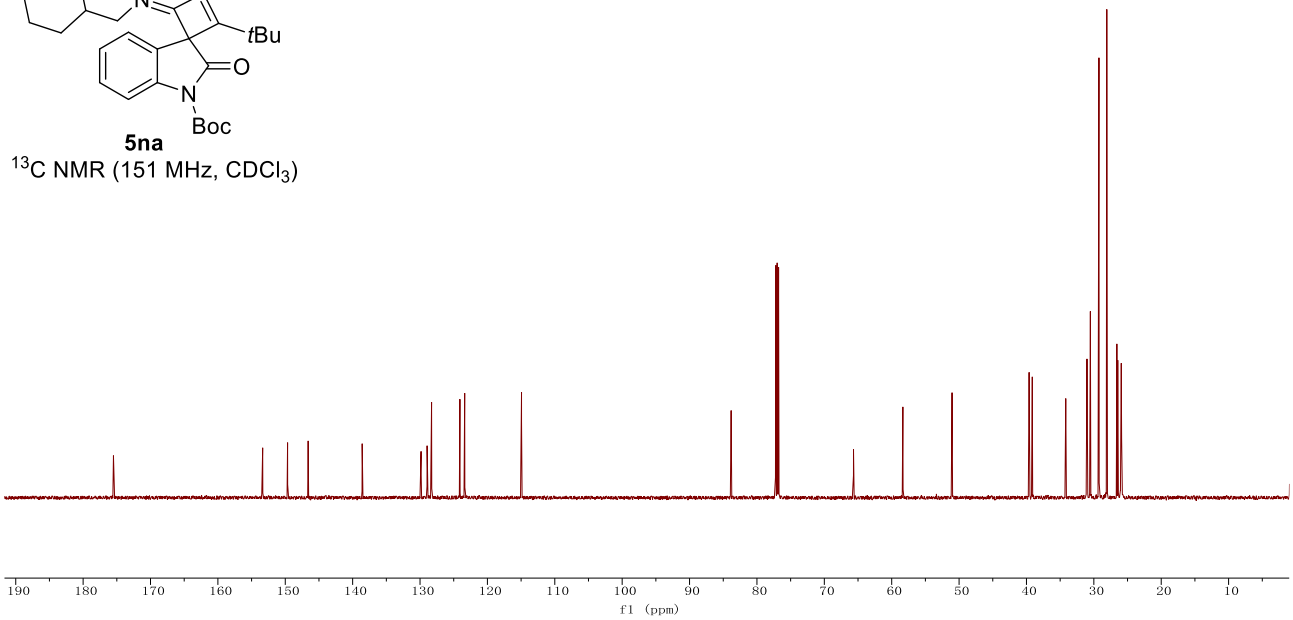
^{1}H NMR (600 MHz, $CDCl_3$)

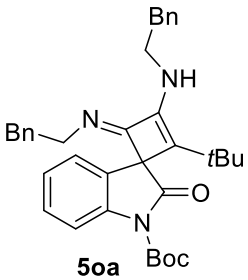




5na

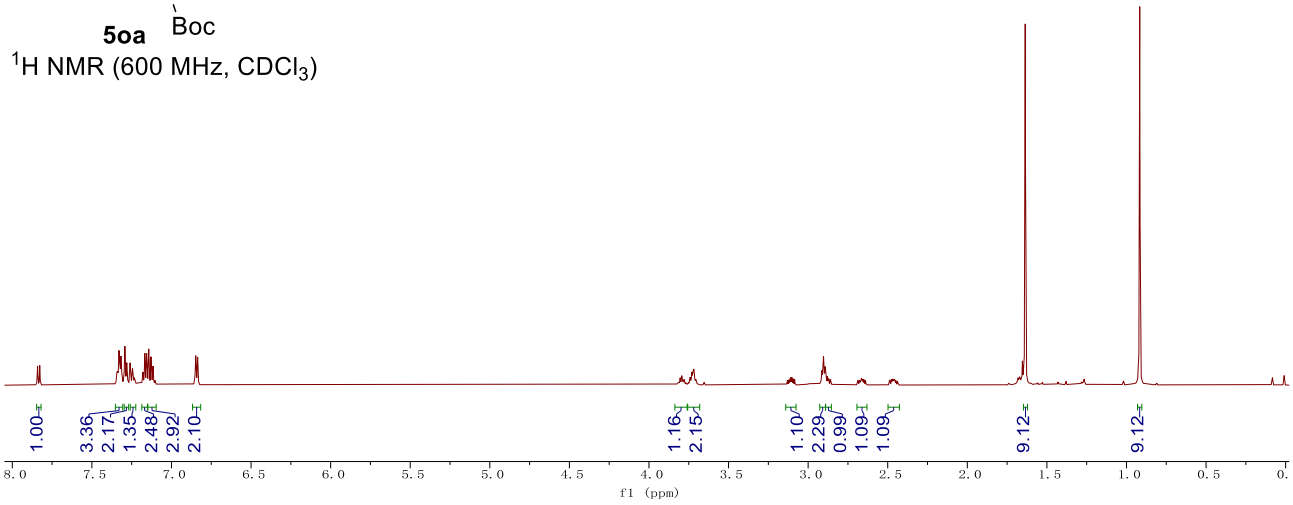
^{13}C NMR (151 MHz, $CDCl_3$)

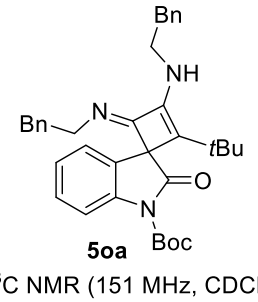




5oa

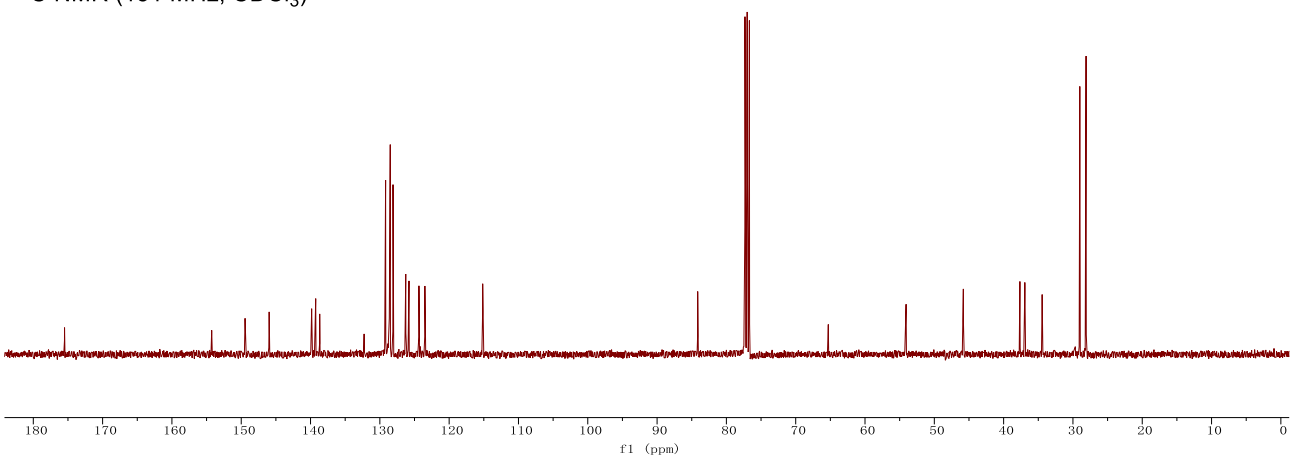
^{1}H NMR (600 MHz, $CDCl_3$)

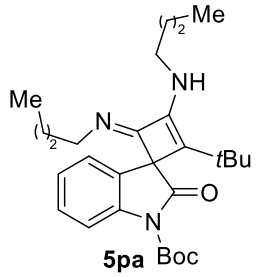




5oa

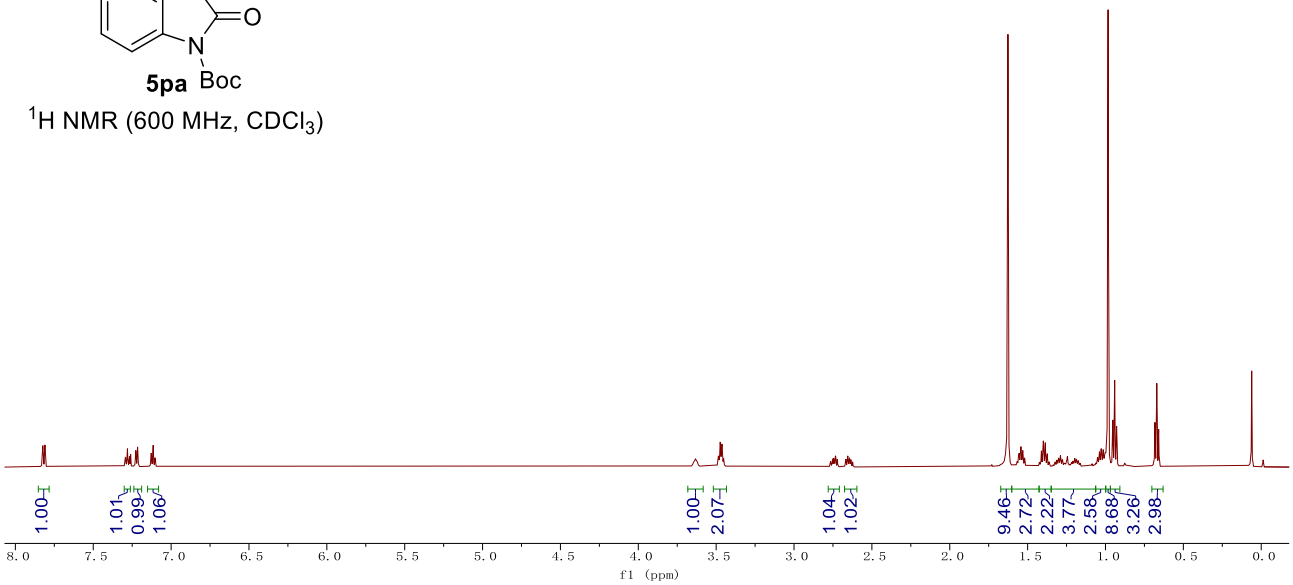
^{13}C NMR (151 MHz, $CDCl_3$)

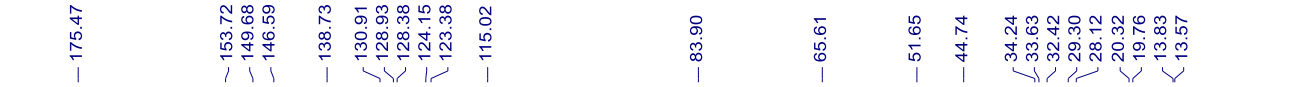


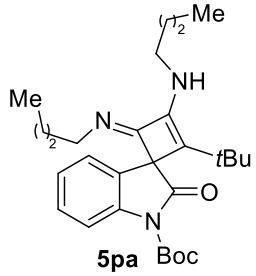


5pa

^{1}H NMR (600 MHz, $CDCl_3$)

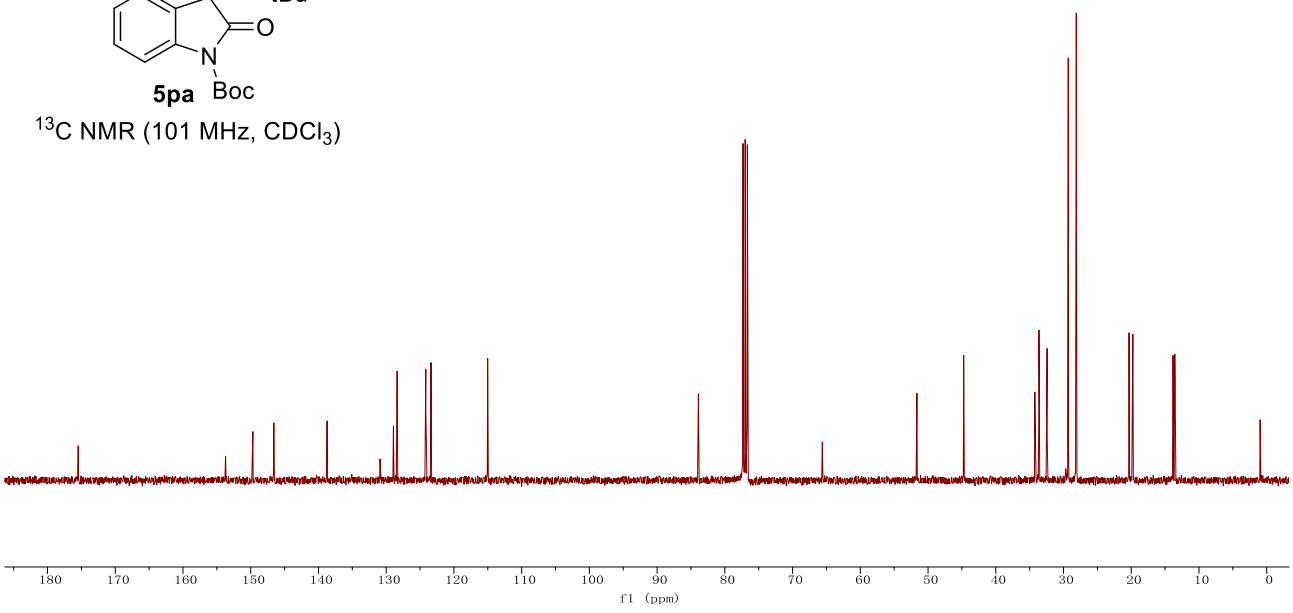


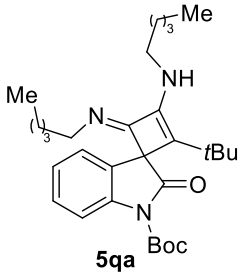




5pa

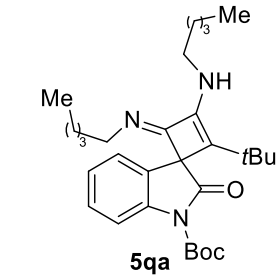
^{13}C NMR (101 MHz, $CDCl_3$)





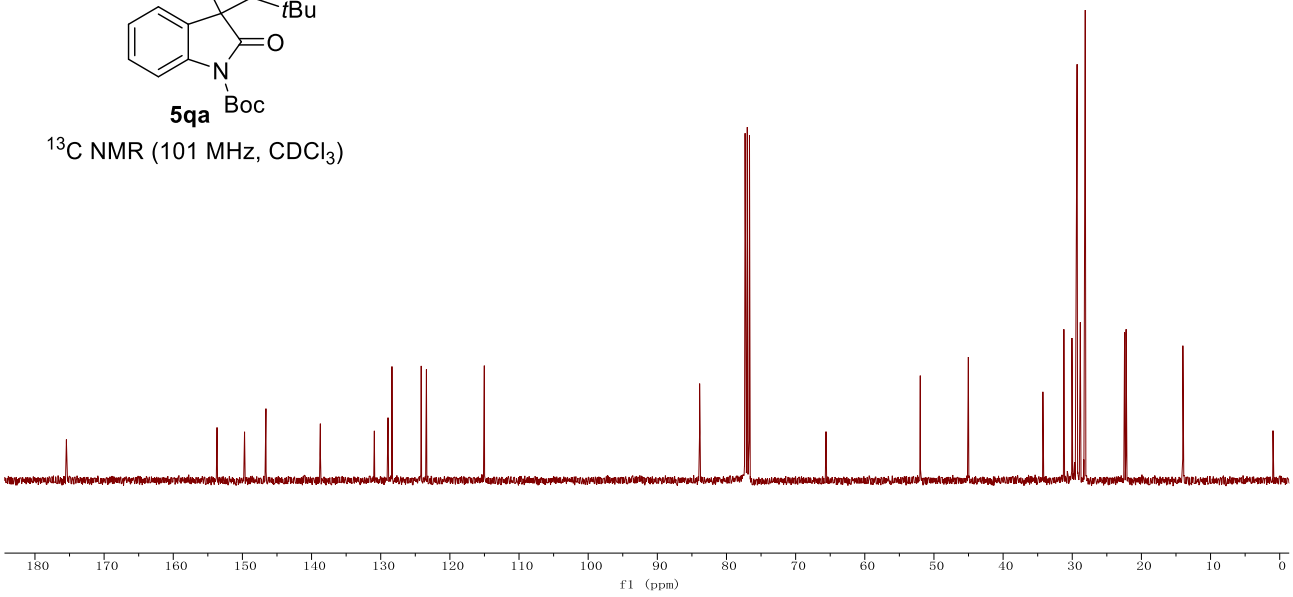
5qa

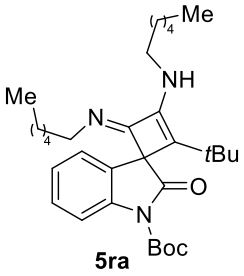
^{1}H NMR (600 MHz, $CDCl_3$)



5qa

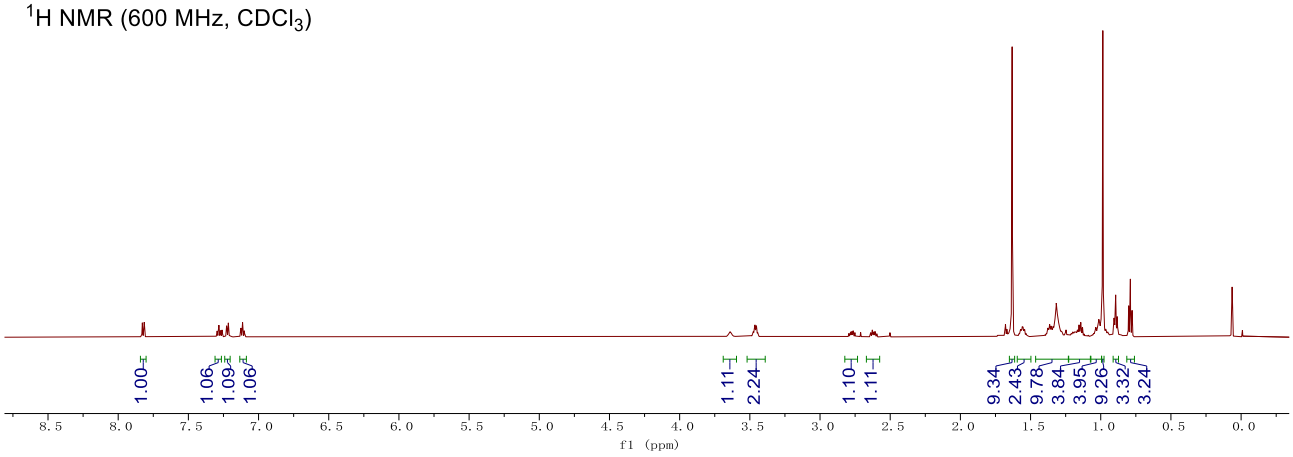
^{13}C NMR (101 MHz, $CDCl_3$)

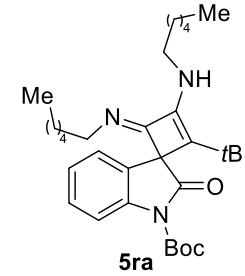




5ra

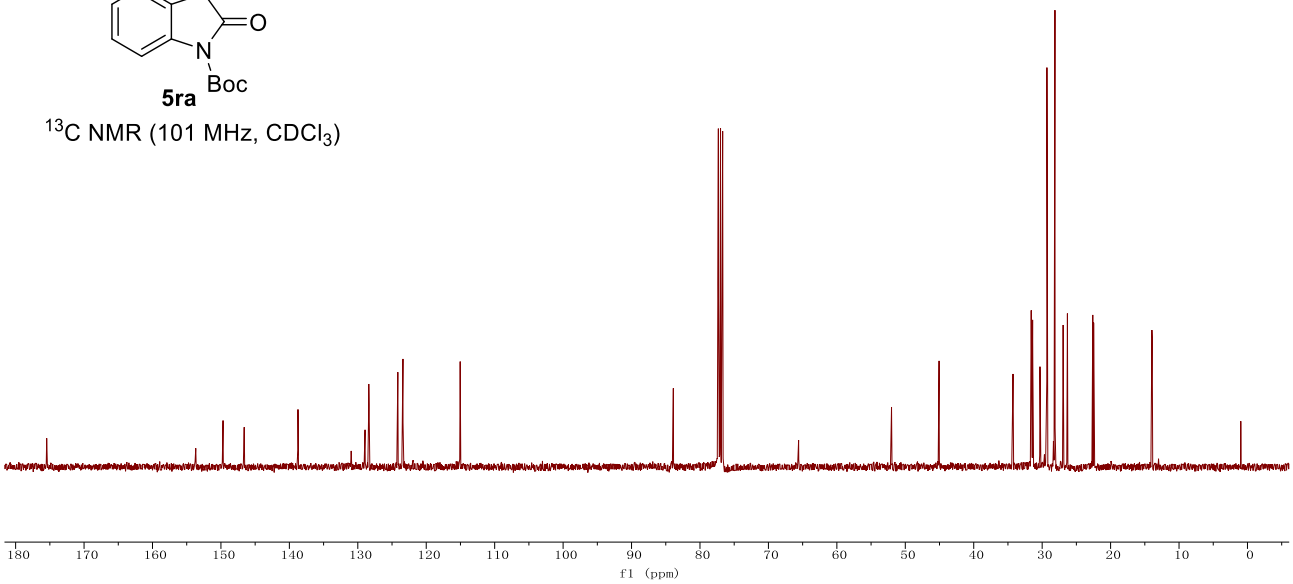
^{1}H NMR (600 MHz, $CDCl_3$)

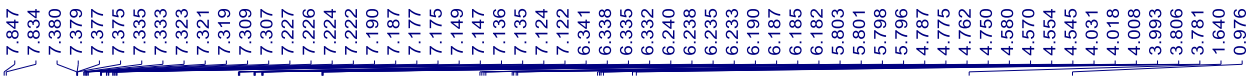


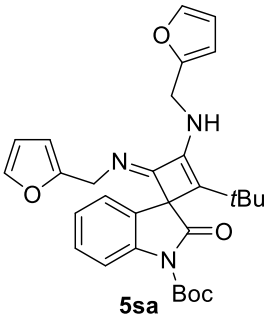


5ra

^{13}C NMR (101 MHz, $CDCl_3$)

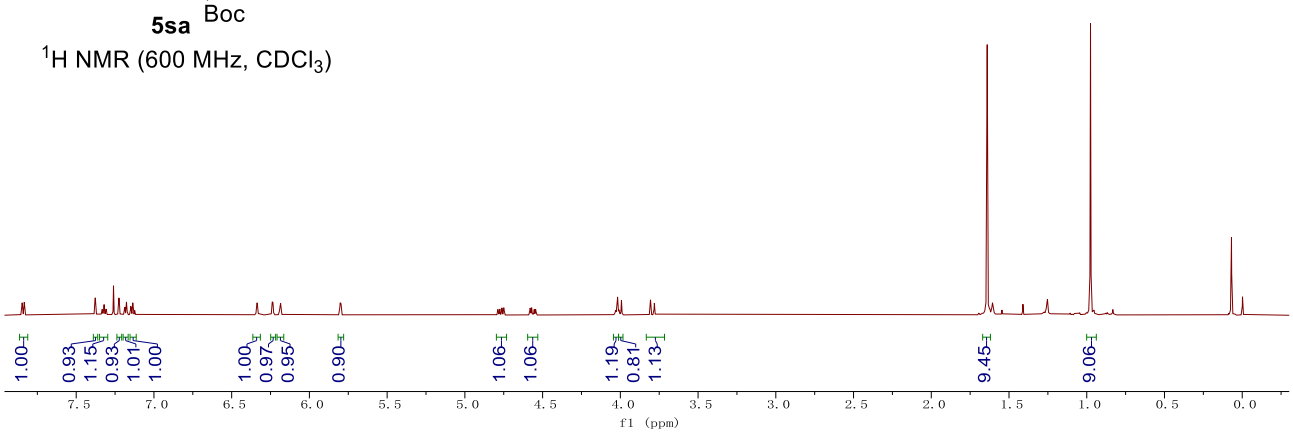


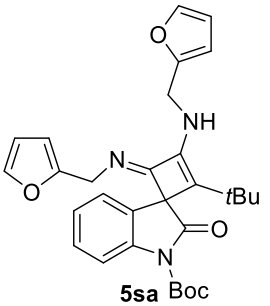




5sa

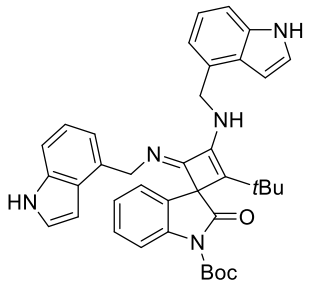
^{1}H NMR (600 MHz, $CDCl_3$)





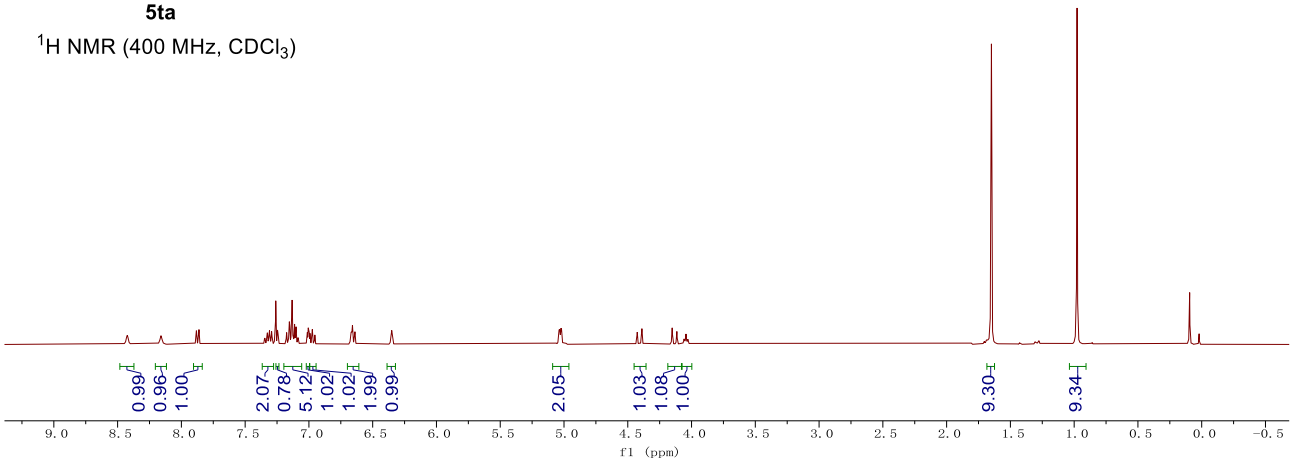
5sa

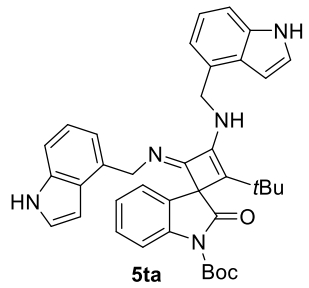
^{13}C NMR (101 MHz, $CDCl_3$)



5ta

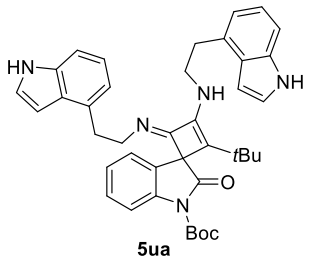
^{1}H NMR (400 MHz, $CDCl_3$)





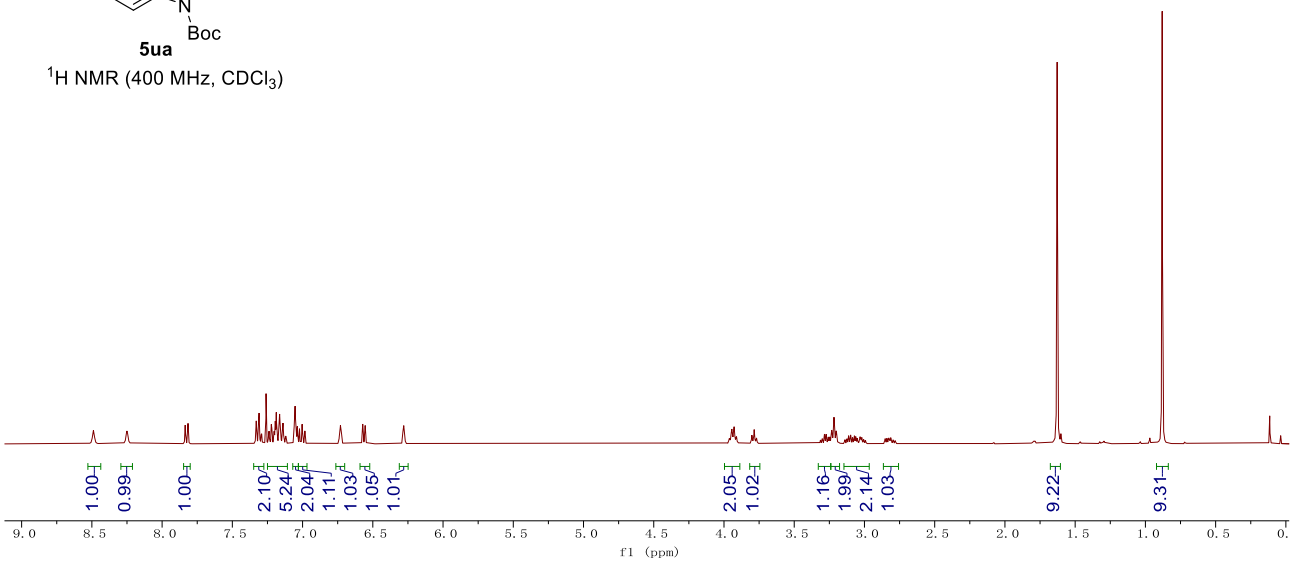
5ta

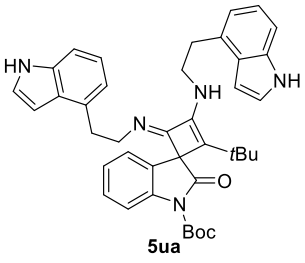
^{13}C NMR (101 MHz, $CDCl_3$)



5ua

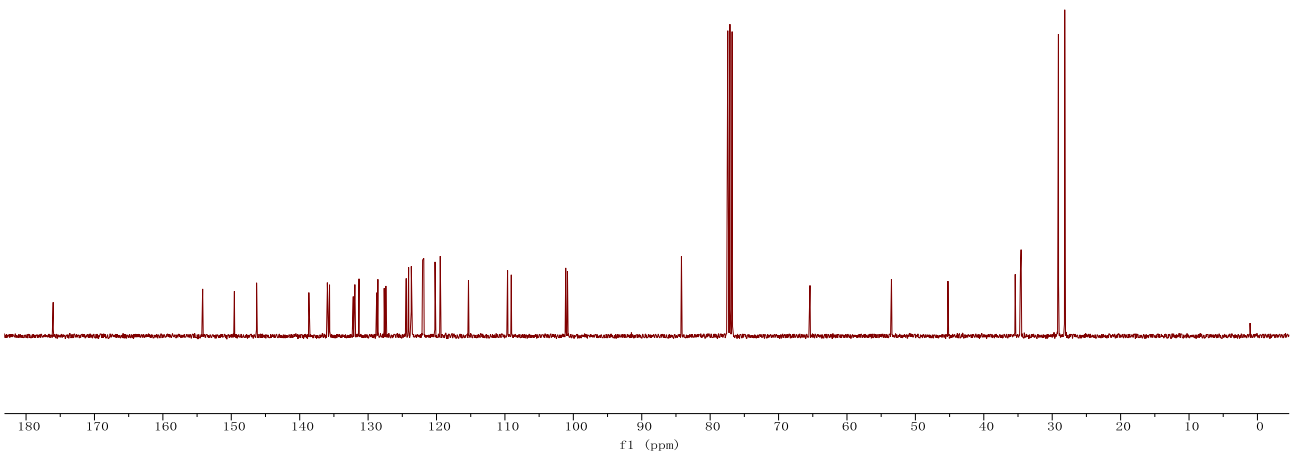
^{1}H NMR (400 MHz, $CDCl_3$)

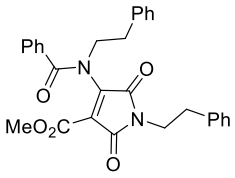




5ua

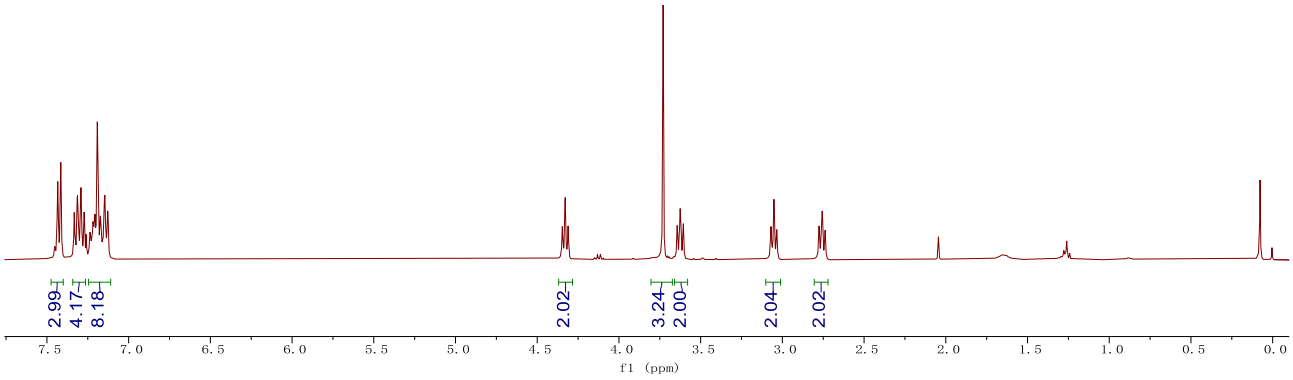
^{13}C NMR (101 MHz, $CDCl_3$)

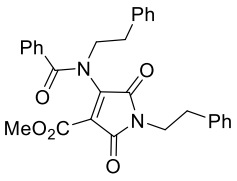




6a

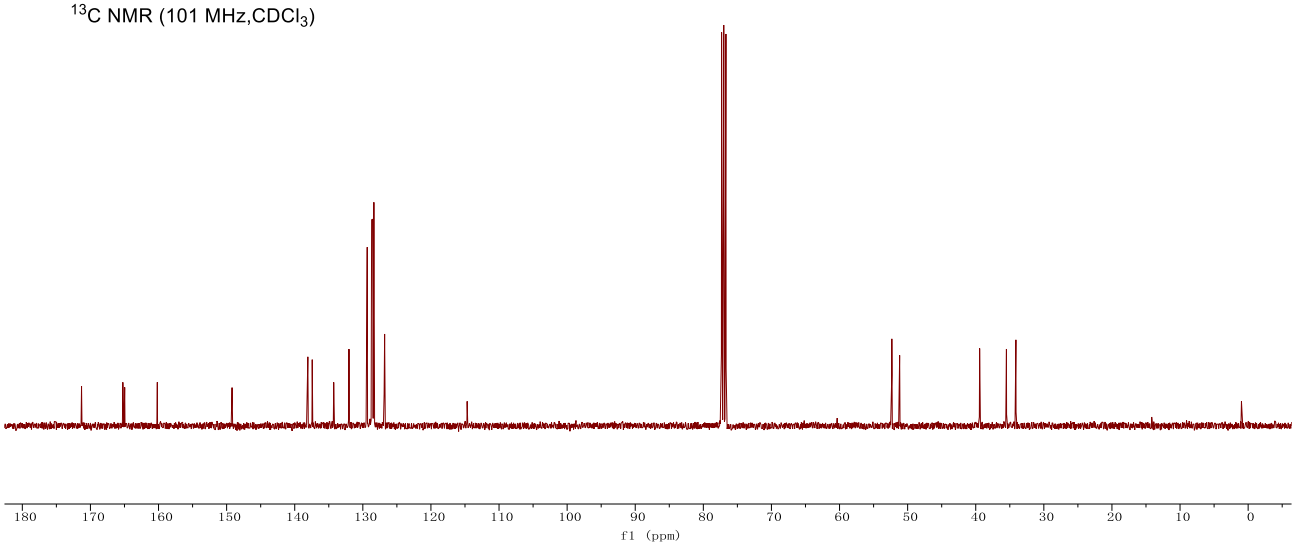
^{1}H NMR (400 MHz,$CDCl_3$)

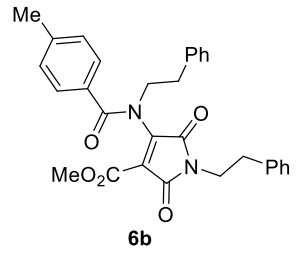




6a

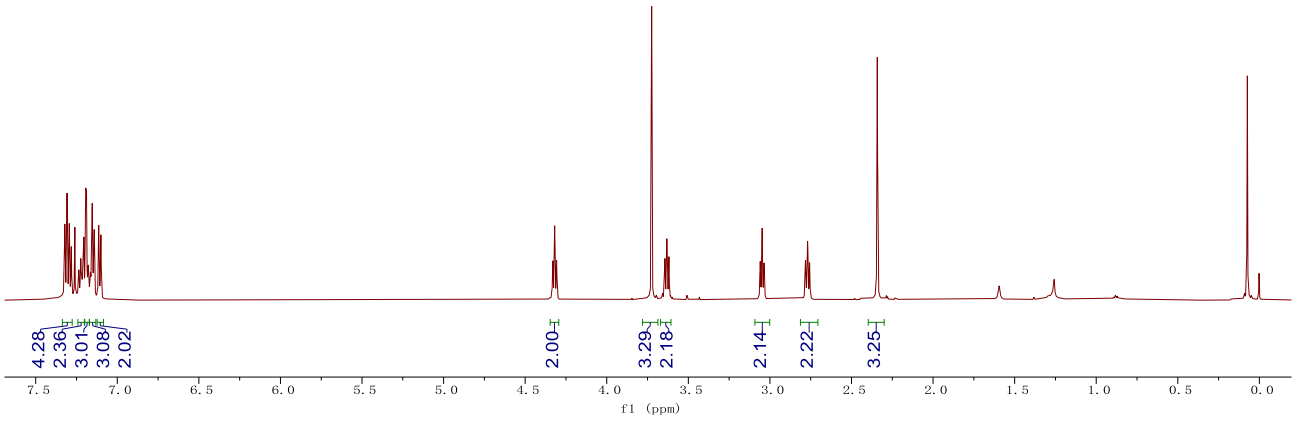
^{13}C NMR (101 MHz,$CDCl_3$)

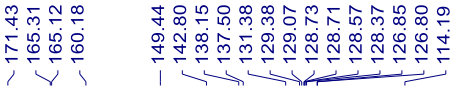


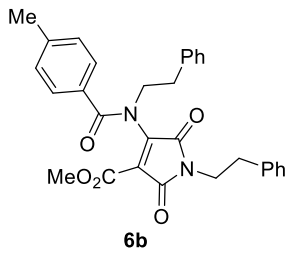


6b

^{1}H NMR (600 MHz,$CDCl_3$)

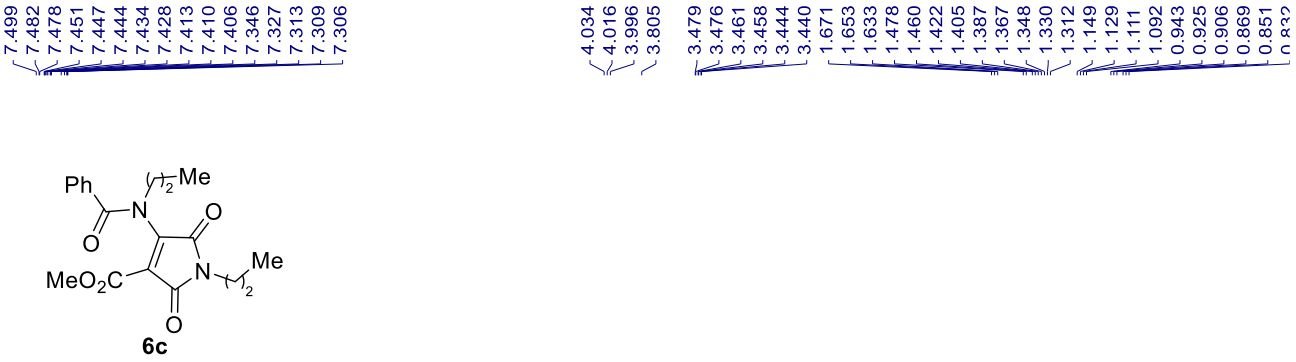






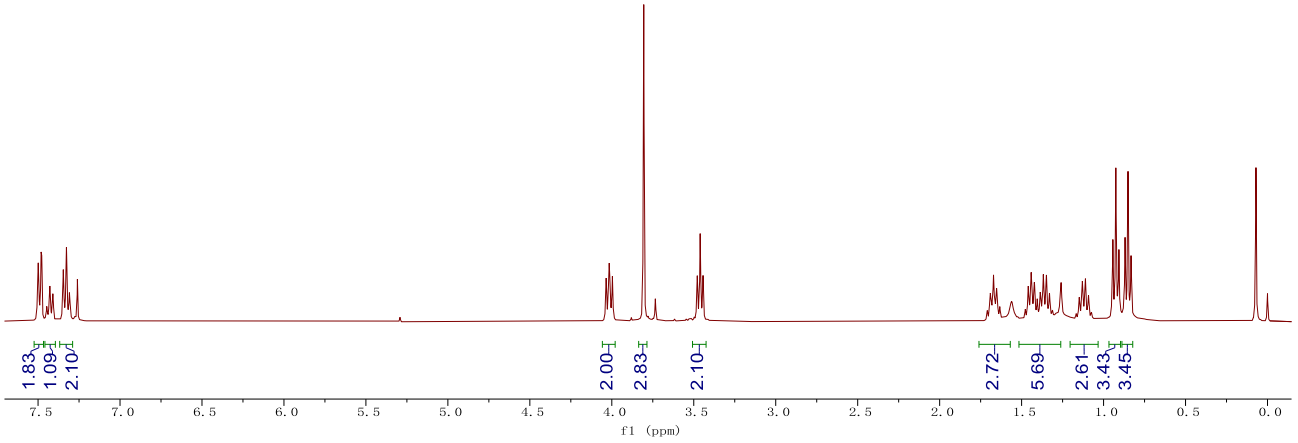
6b

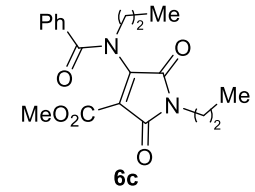
^{13}C NMR (151 MHz,$CDCl_3$)



6c

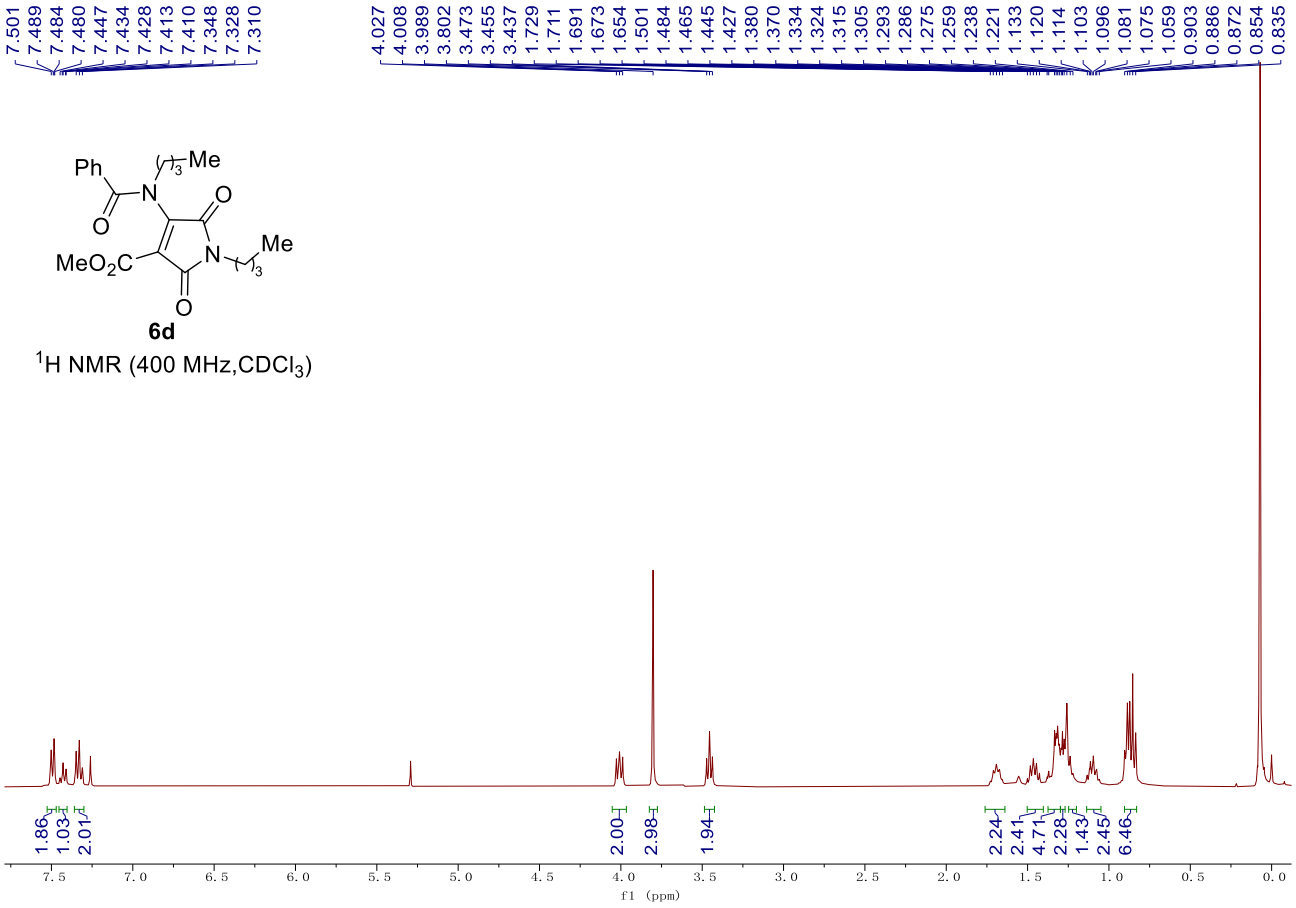
^{1}H NMR (400 MHz,$CDCl_3$)

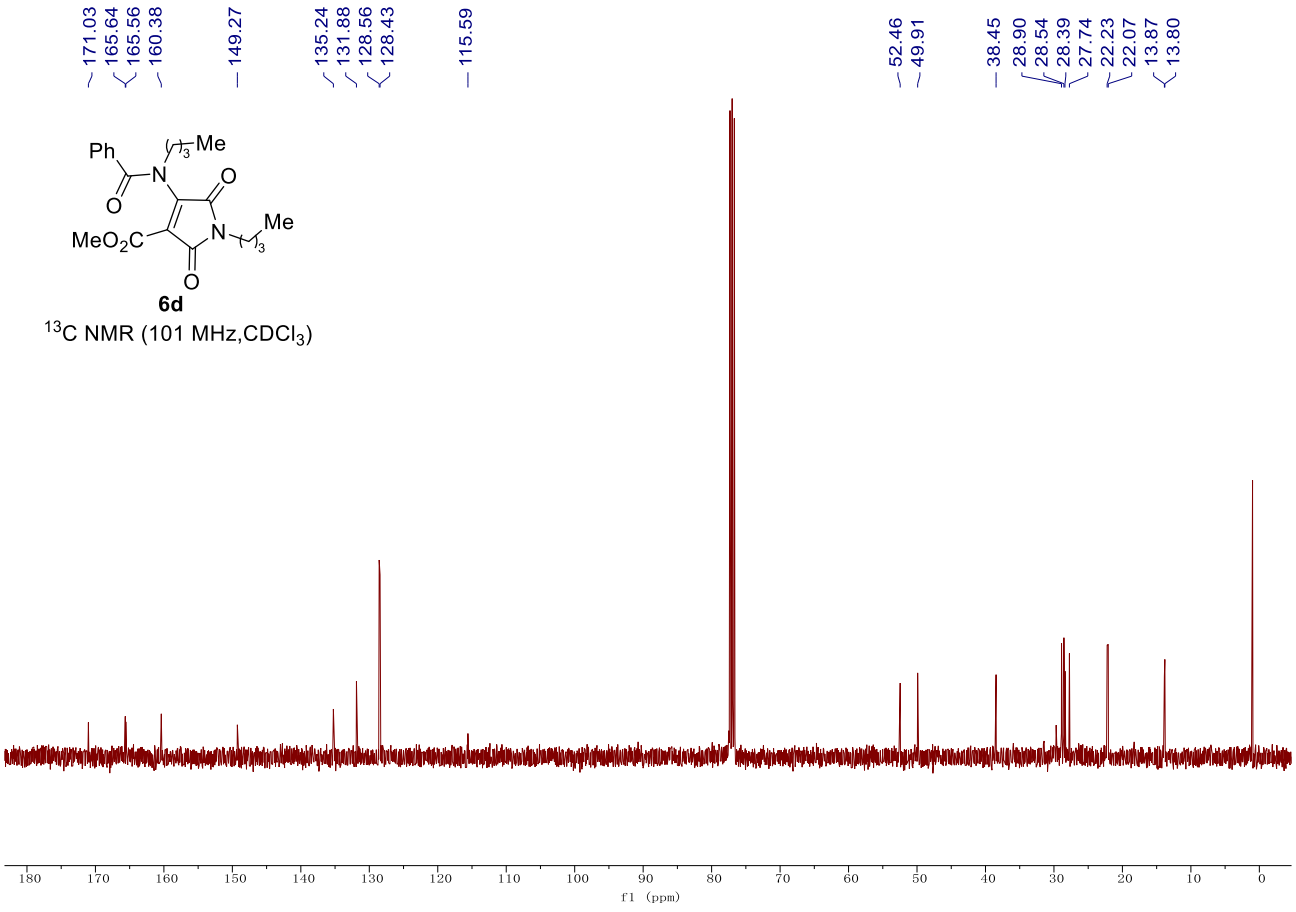


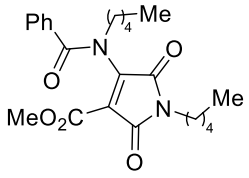


6c

^{13}C NMR (101 MHz,$CDCl_3$)

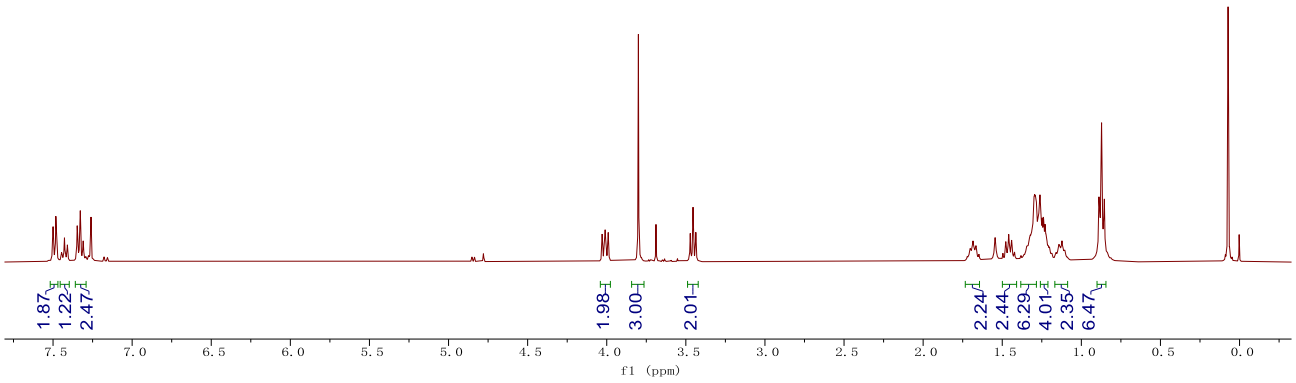

7.501
7.489
7.484
7.480
7.447
7.434
7.428
7.413
7.410
7.348
7.328
7.310
4.027
4.008
3.989
3.802
3.473
3.455
3.437
1.729
1.711
1.691
1.673
1.654
1.501
1.484
1.465
1.445
1.427
1.380
1.370
1.334
1.324
1.315
1.305
1.293
1.286
1.275
1.259
1.238
1.221
1.133
1.120
1.114
1.103
1.096
1.081
1.075
1.059
0.903
0.886
0.872
0.854
0.835
Ph
Me
MeO2C
Me
6d
1H NMR (400 MHz,CDCl3)
1.86
1.03
2.01
2.00
2.98
1.94
2.24
2.41
4.71
2.28
1.43
2.45
6.46
f1 (ppm)

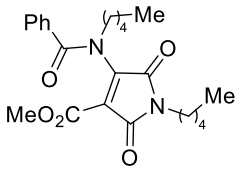

171.03
165.64
165.56
160.38
149.27
135.24
131.88
128.56
128.43
115.59
52.46
49.91
38.45
28.90
28.54
28.39
27.74
22.23
22.07
13.87
13.80
Ph
Me
MeO2C
Me
6d
13C NMR (101 MHz,CDCl3)
f1 (ppm)



6e

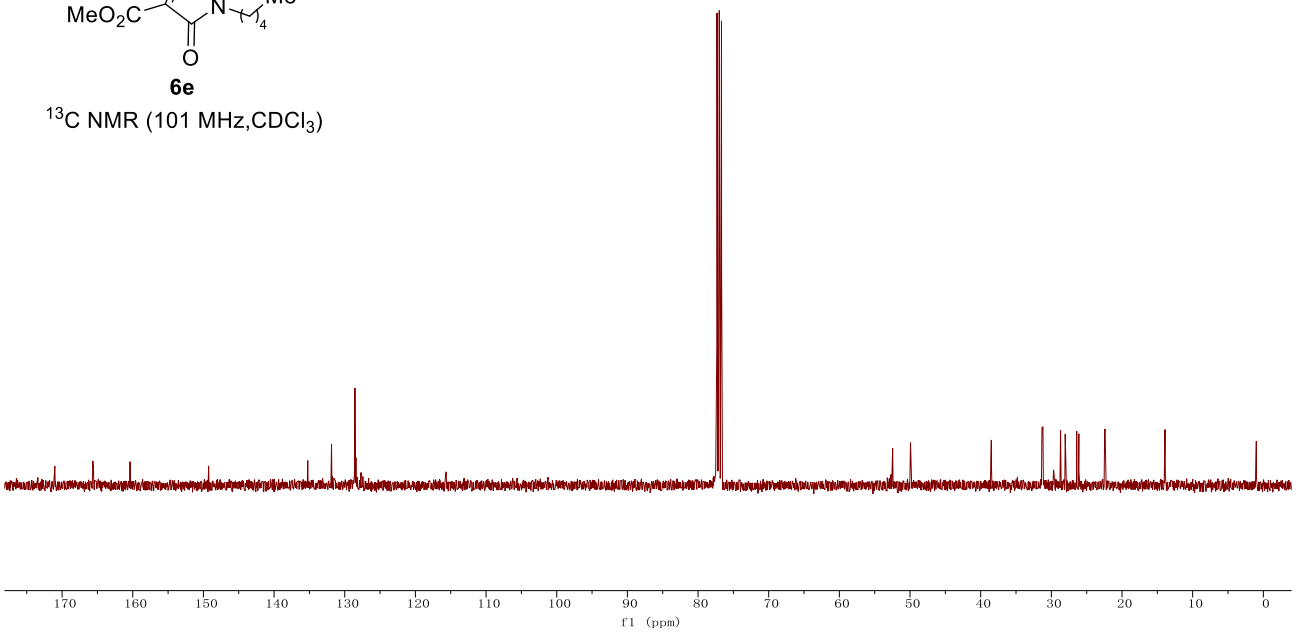
^{1}H NMR (400 MHz,$CDCl_3$)

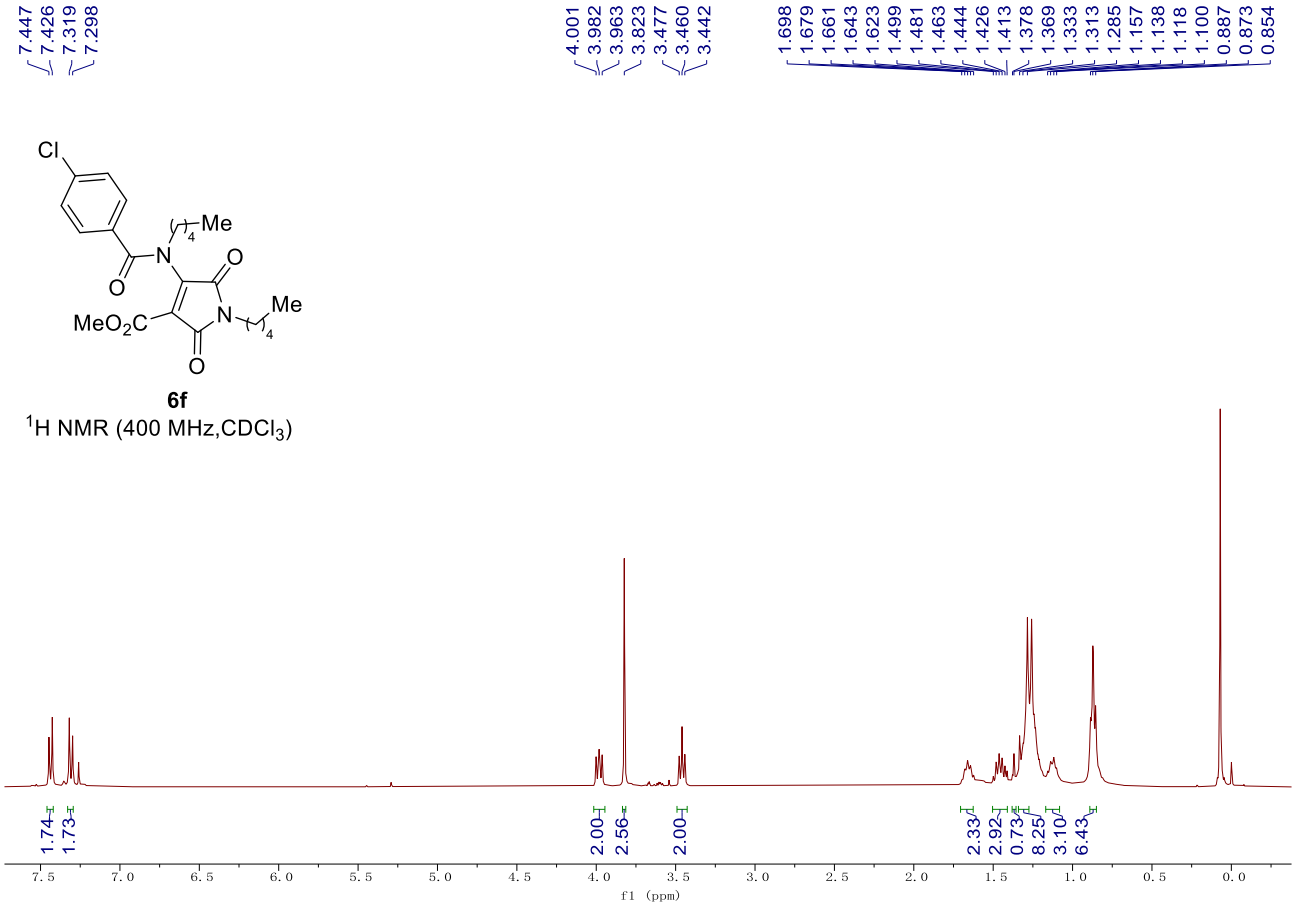




6e

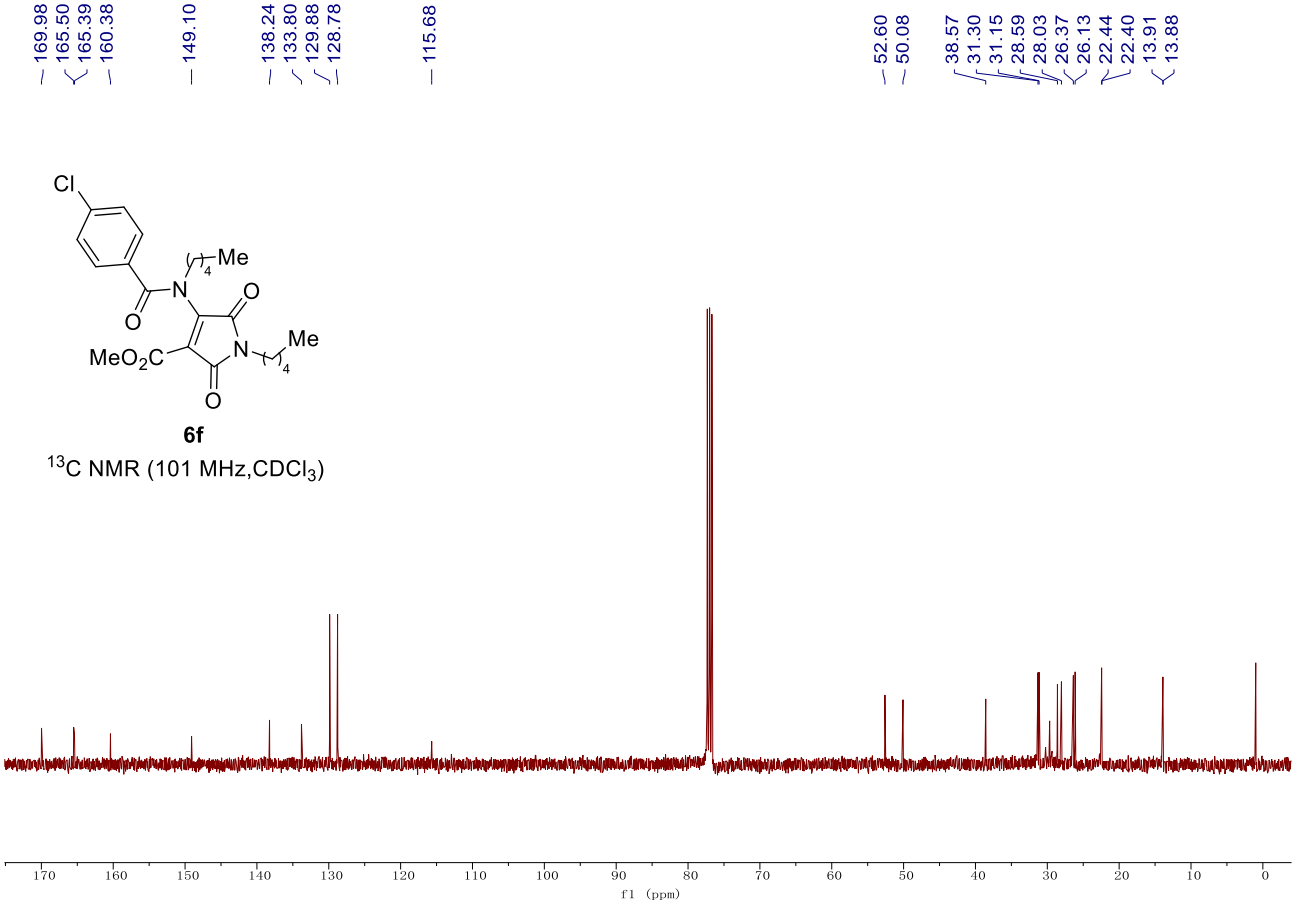
^{13}C NMR (101 MHz,$CDCl_3$)





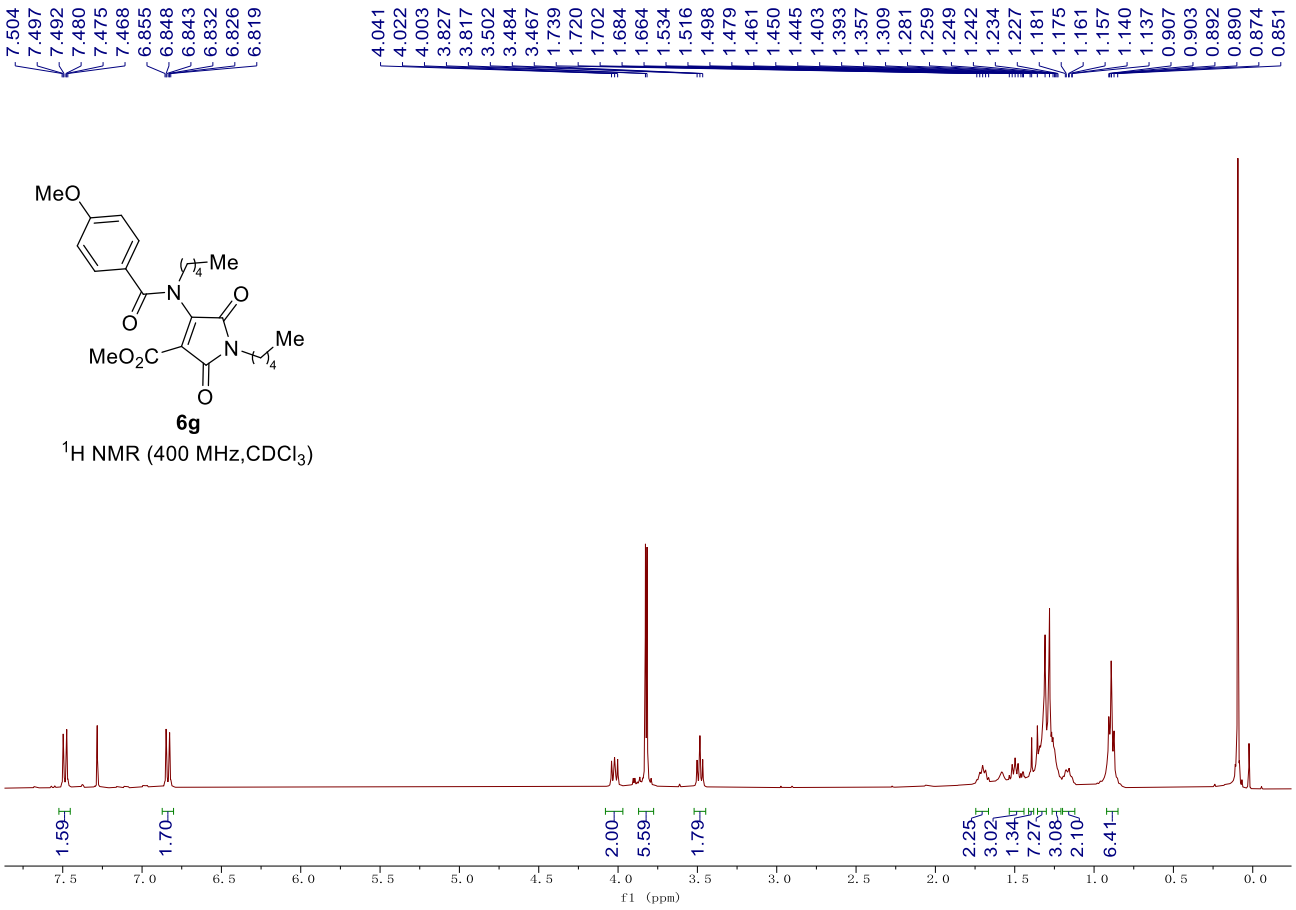
6f

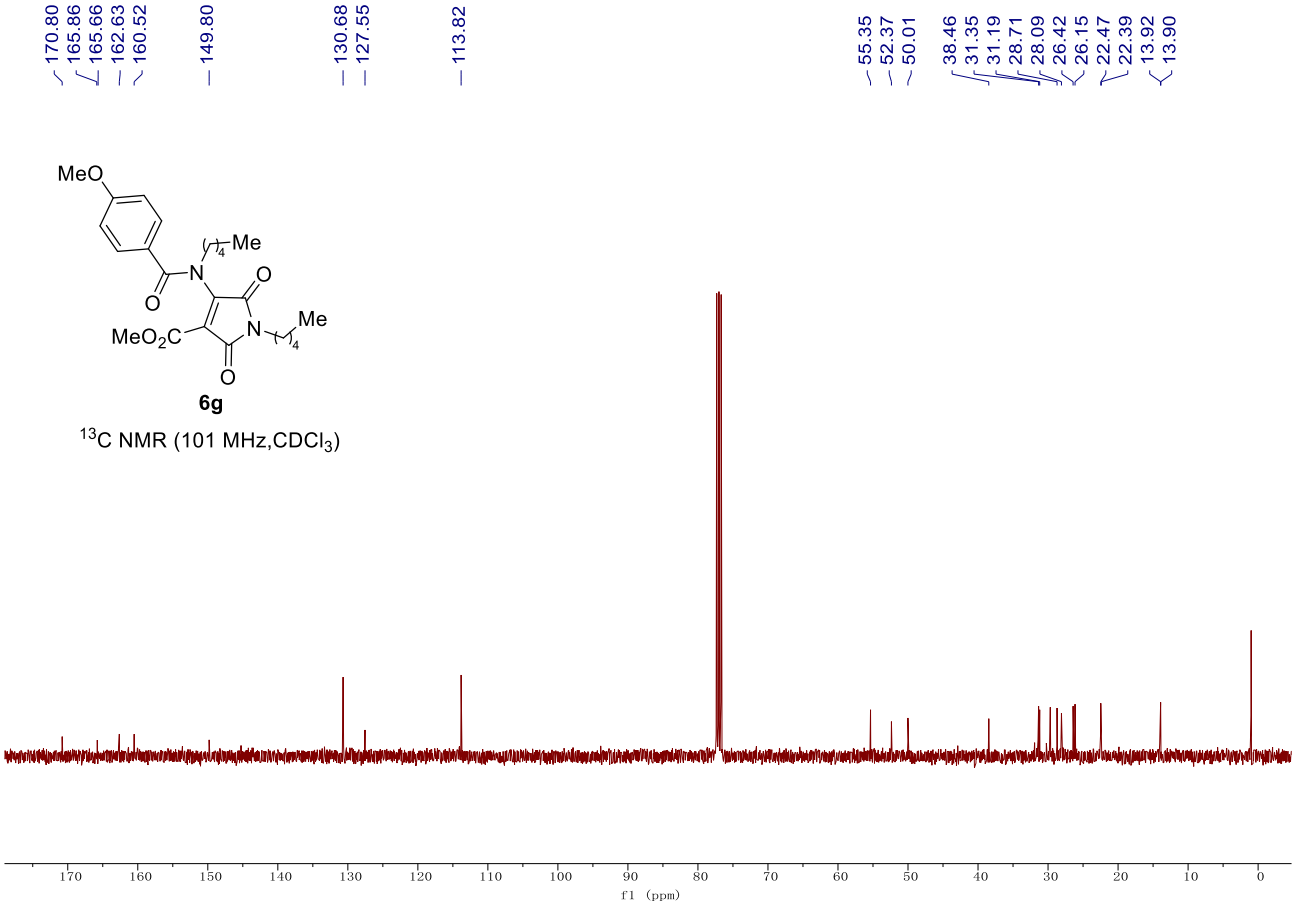
^{1}H NMR (400 MHz,$CDCl_3$)

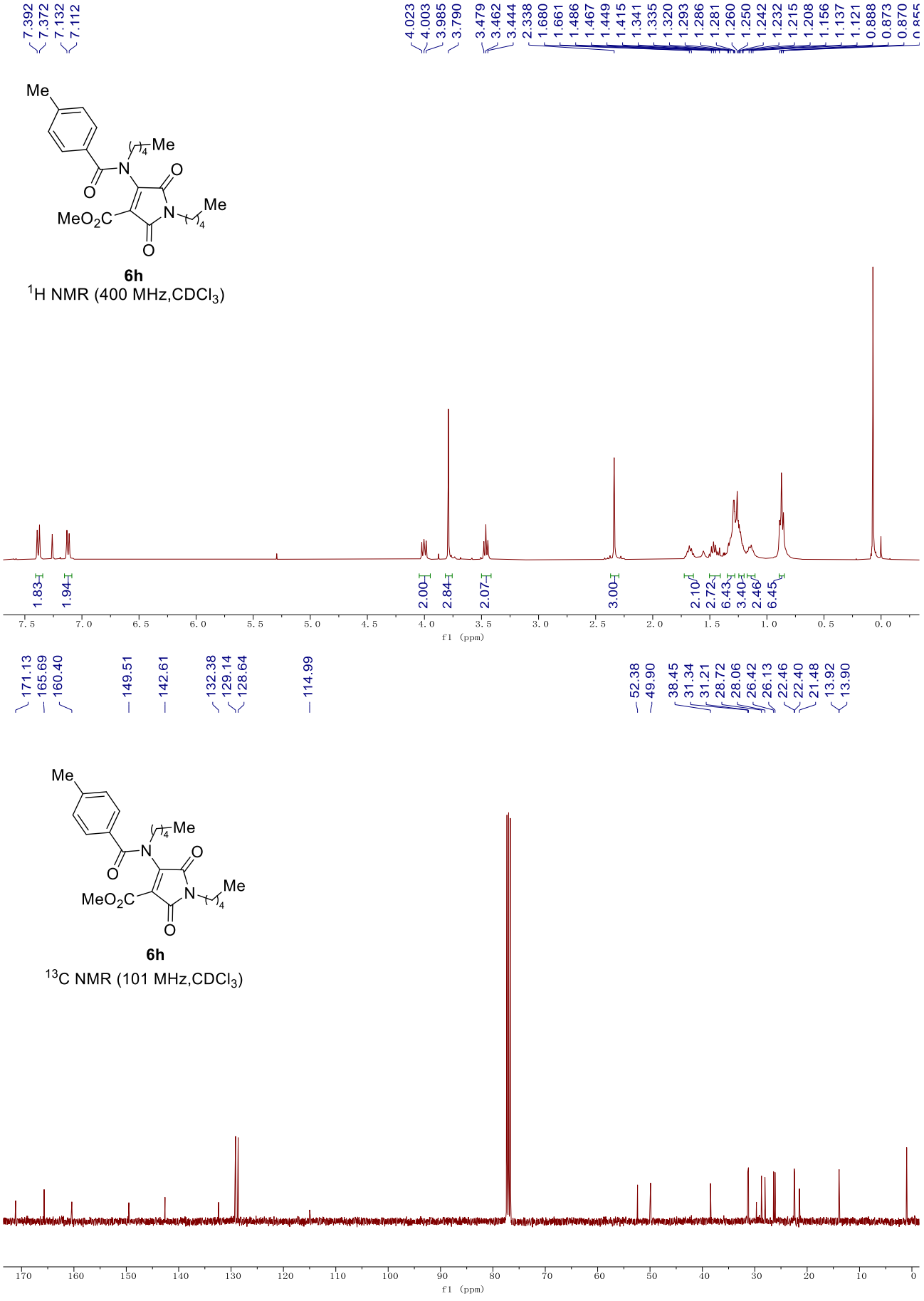


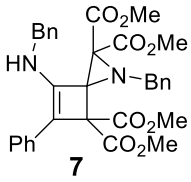
6f

^{13}C NMR (101 MHz,$CDCl_3$)


7.504
7.497
7.492
7.480
7.475
7.468
6.855
6.848
6.843
6.832
6.826
6.819
4.041
4.022
4.003
3.827
3.817
3.502
3.484
3.467
1.739
1.720
1.702
1.684
1.664
1.534
1.516
1.498
1.479
1.461
1.450
1.445
1.403
1.393
1.357
1.309
1.281
1.259
1.249
1.242
1.234
1.227
1.181
1.175
1.161
1.157
1.140
1.137
0.907
0.903
0.892
0.890
0.874
0.851
MeO
Me
N
O
O
MeO2C
N
Me
O
6g
1H NMR (400 MHz,CDCl3)
1.59
1.70
2.00
5.59
1.79
2.25
3.02
1.34
7.27
3.08
2.10
6.41
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)

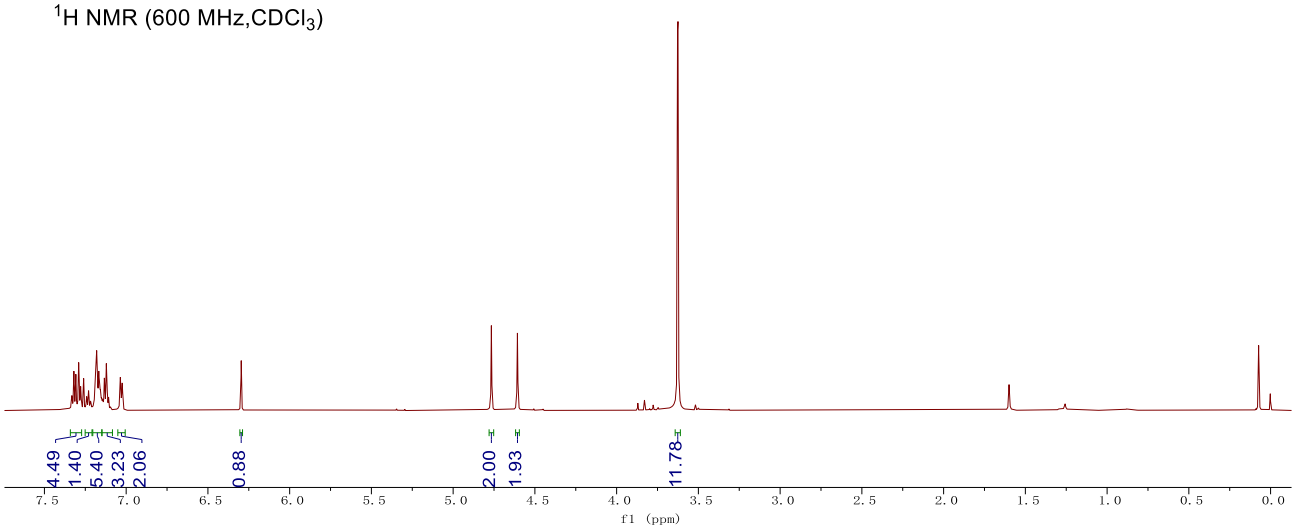

170.80
165.86
165.66
162.63
160.52
149.80
130.68
127.55
113.82
55.35
52.37
50.01
38.46
31.35
31.19
28.71
28.09
26.42
26.15
22.47
22.39
13.92
13.90
MeO
Me
N
O
O
MeO2C
N
Me
O
6g
13C NMR (101 MHz,CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

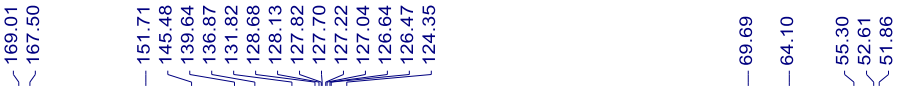

7.392
7.372
7.132
7.112
4.023
4.003
3.985
3.790
3.479
3.462
3.444
2.338
1.680
1.661
1.486
1.467
1.449
1.415
1.341
1.335
1.320
1.293
1.286
1.281
1.260
1.250
1.242
1.232
1.215
1.208
1.156
1.137
1.121
0.888
0.873
0.870
Me
Me
N
O
O
MeO2C
N
Me
O
6h
1H NMR (400 MHz,CDCl3)
1.83
1.94
2.00
2.84
2.07
3.00
2.10
2.72
6.43
3.40
2.46
6.45
f1 (ppm)
171.13
165.69
160.40
149.51
142.61
132.38
129.14
128.64
114.99
52.38
49.90
38.45
31.34
31.21
28.72
28.06
26.42
26.13
22.46
22.40
21.48
13.92
13.90
Me
Me
N
O
O
MeO2C
N
Me
O
6h
13C NMR (101 MHz,CDCl3)
f1 (ppm)

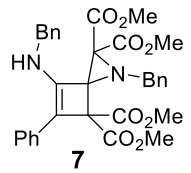


7

^{1}H NMR (600 MHz,$CDCl_3$)

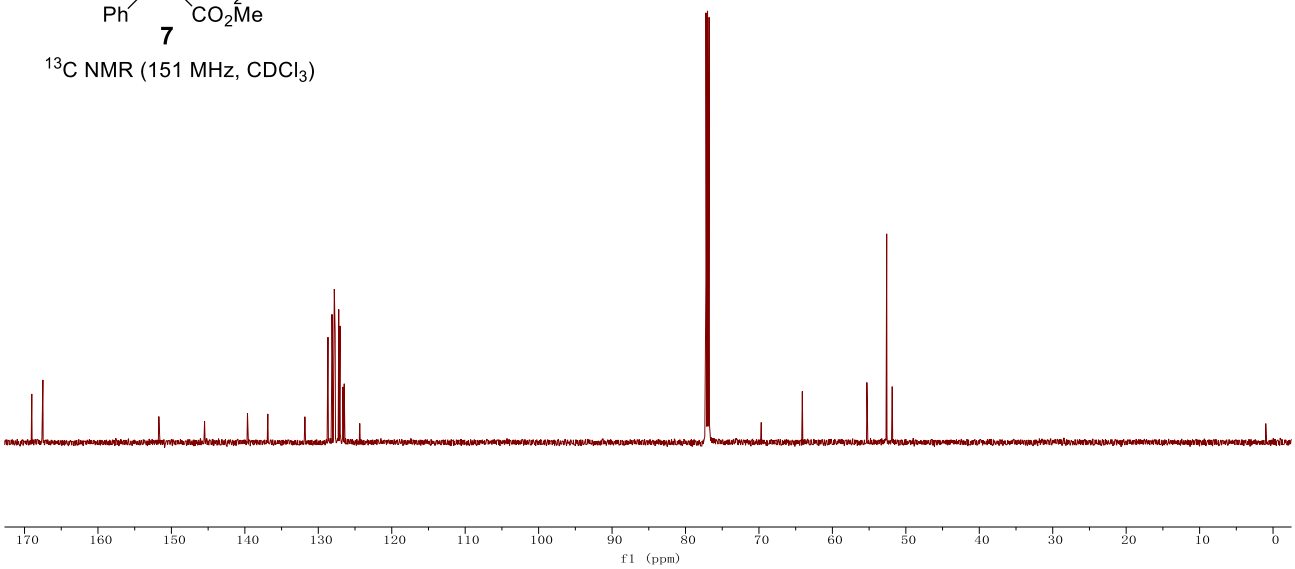


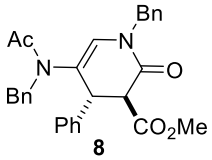




7

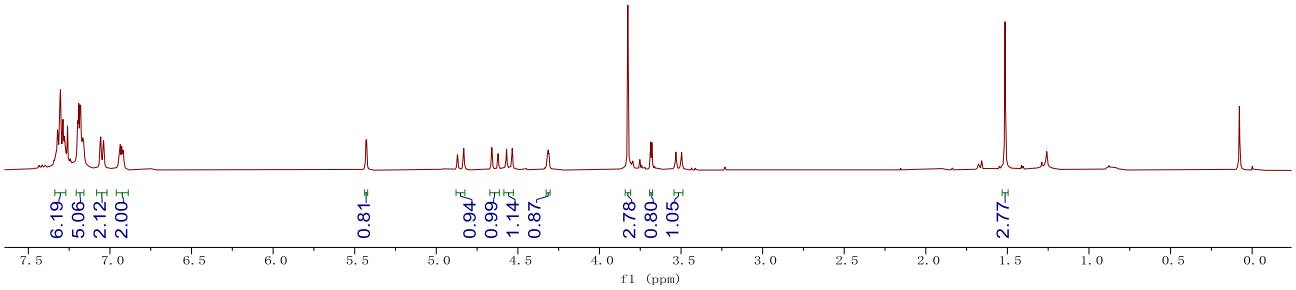
^{13}C NMR (151 MHz, $CDCl_3$)

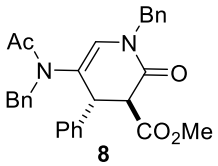




8

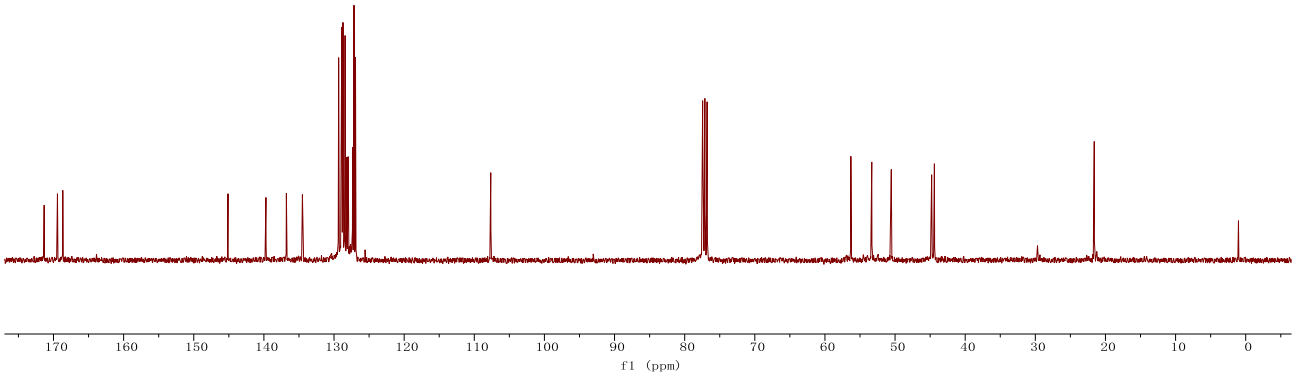
^{1}H NMR (400 MHz, $CDCl_3$)

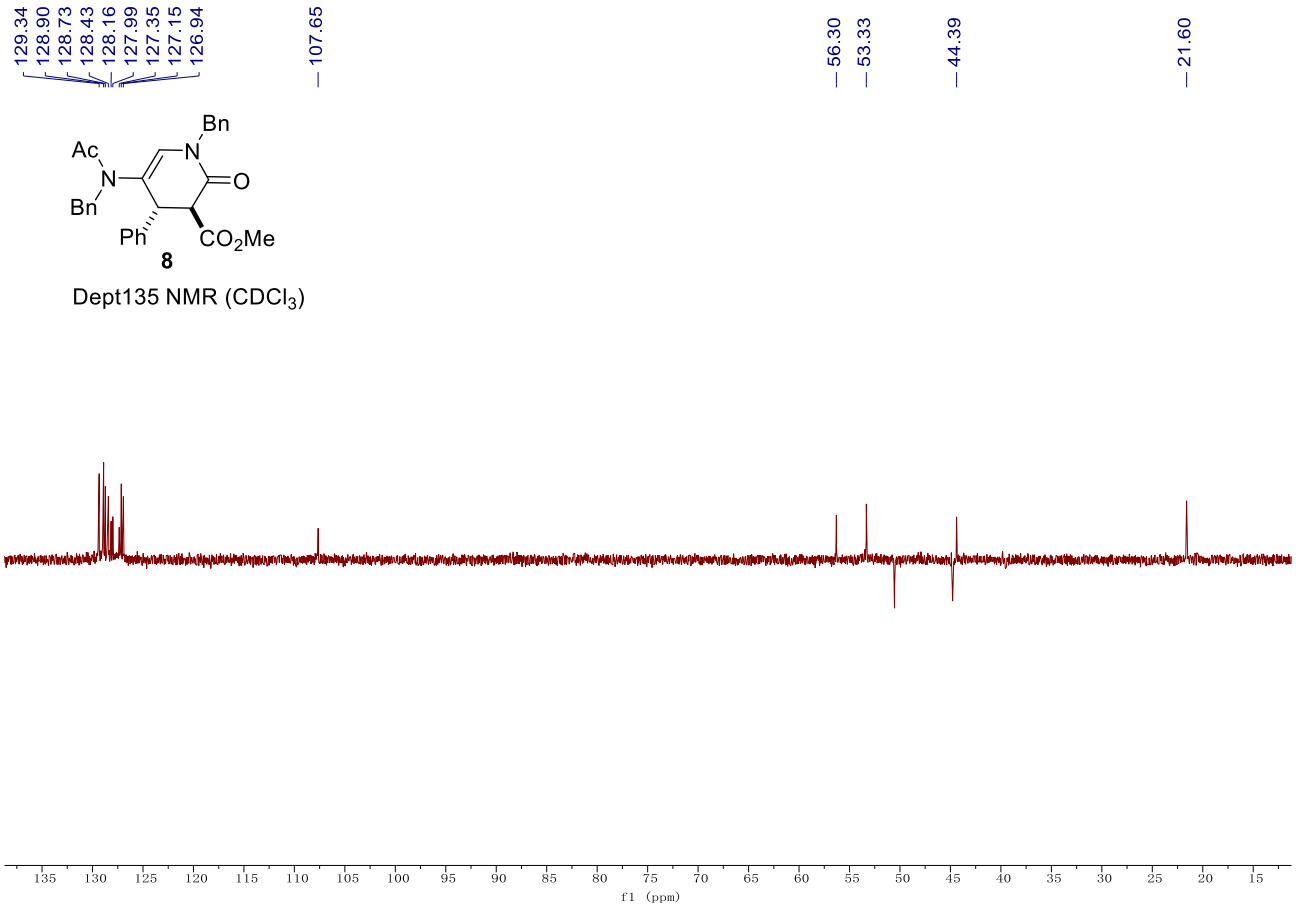




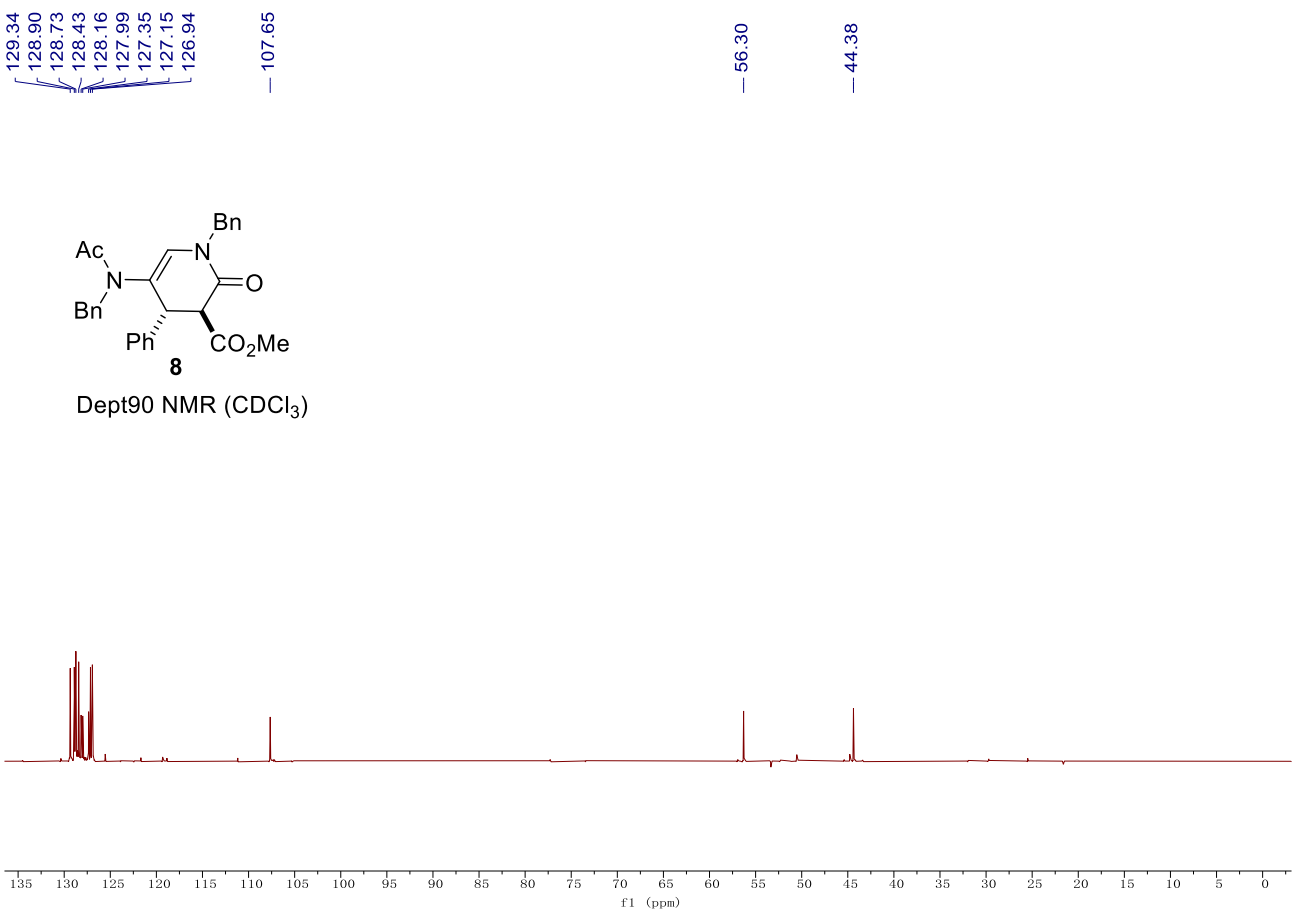
8

^{13}C NMR(101 MHz,$CDCl_3$)

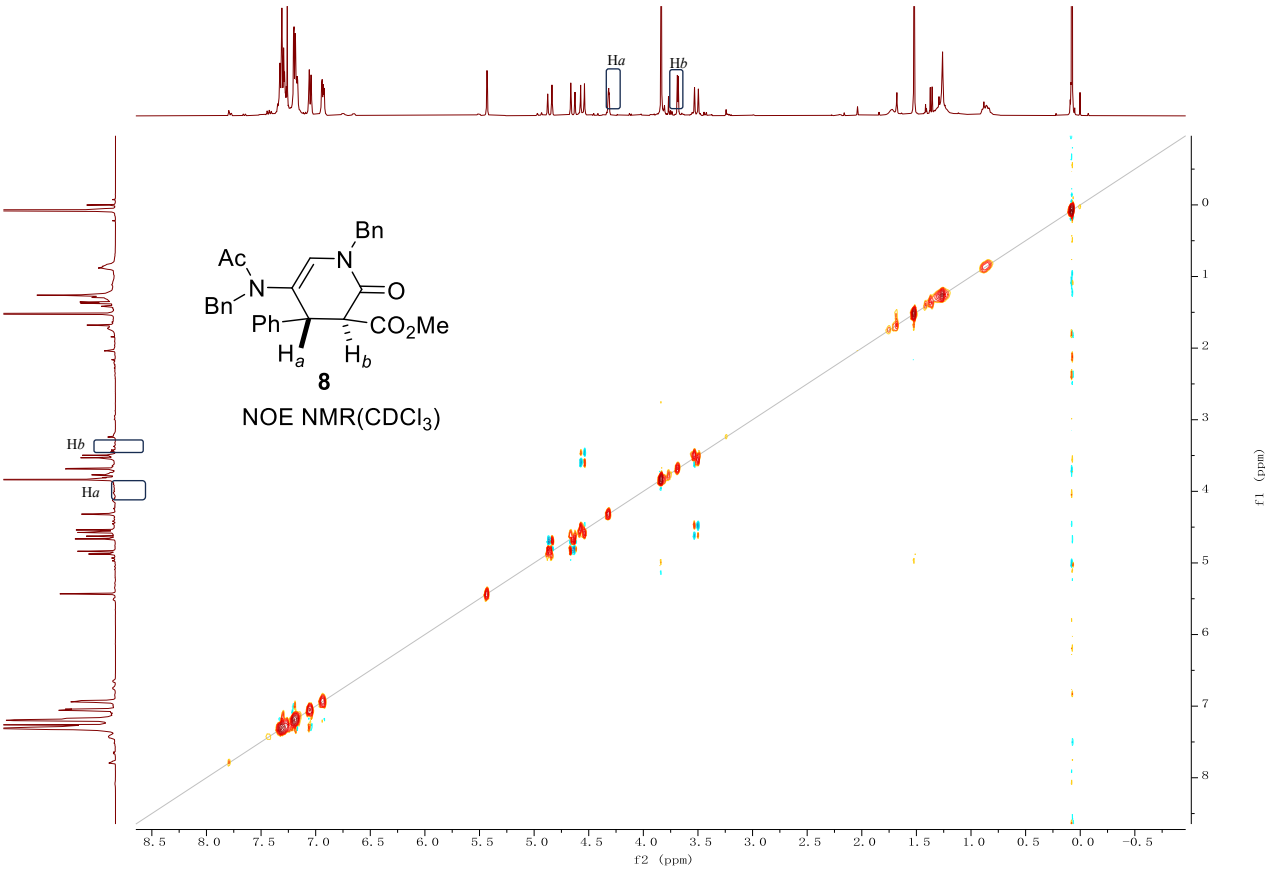


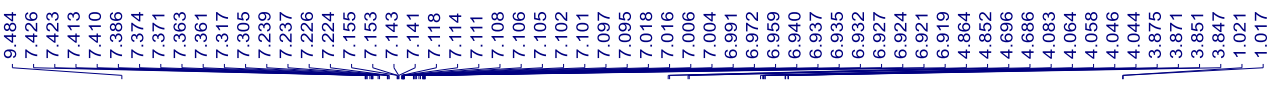


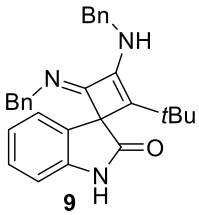
Dept135 NMR ($CDCl_3$)



Dept90 NMR ($CDCl_3$)

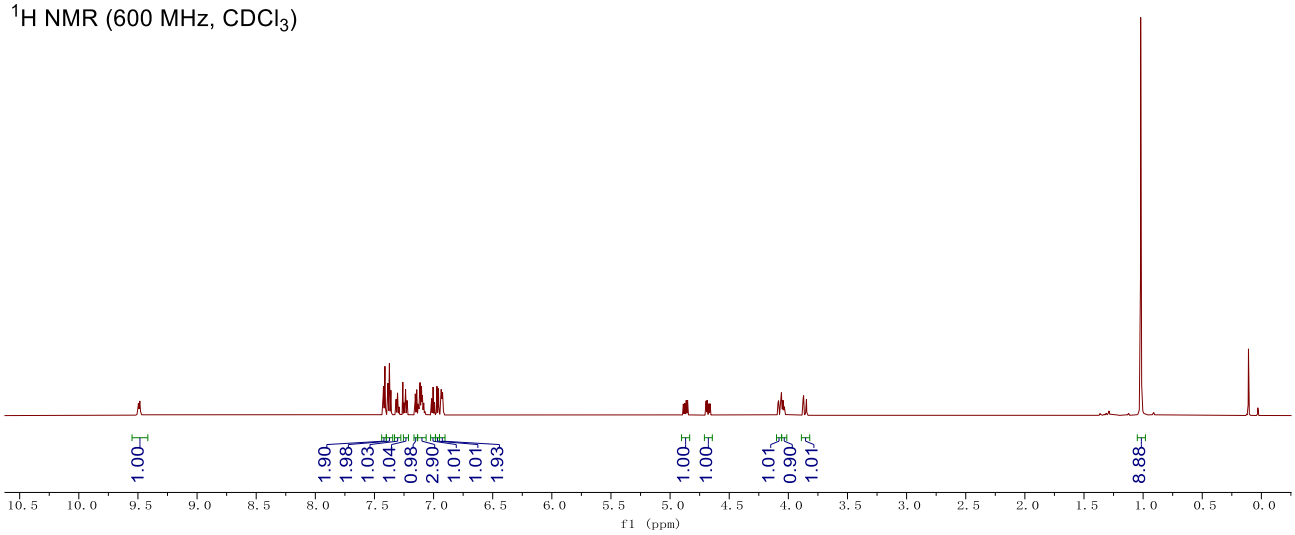

Ha
Hb
Bn
Ac
N
Bn
O
Ph
CO2Me
Ha
Hb
8
NOE NMR(CDCl3)
Hb
Ha
f2 (ppm)
f1 (ppm)

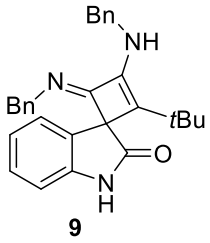




9

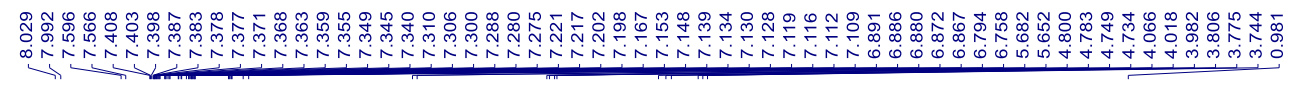
^{1}H NMR (600 MHz, $CDCl_3$)

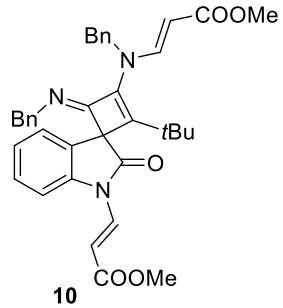




9

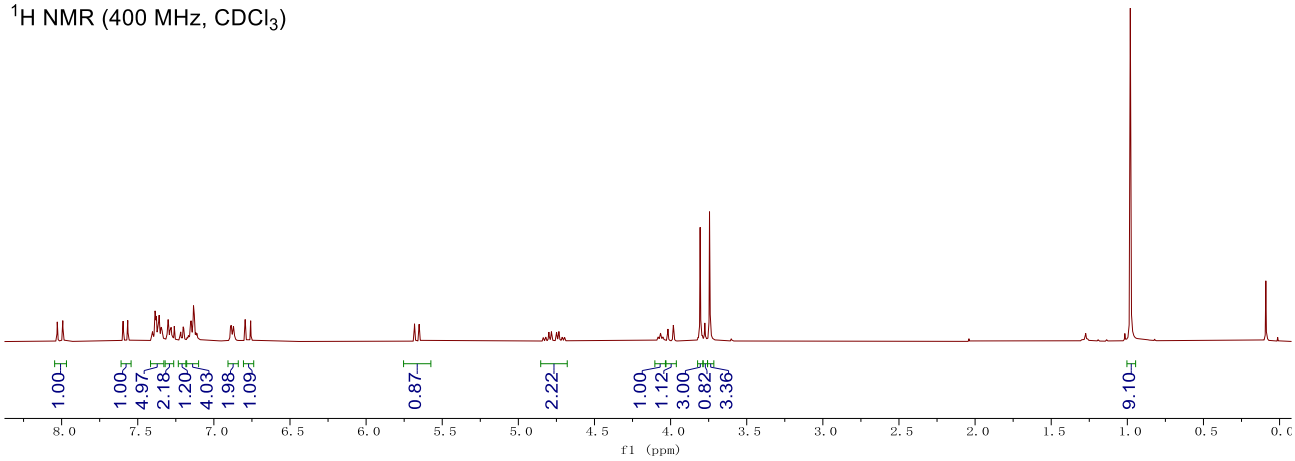
^{13}C NMR (151 MHz, $CDCl_3$)

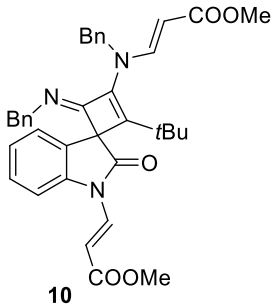




10

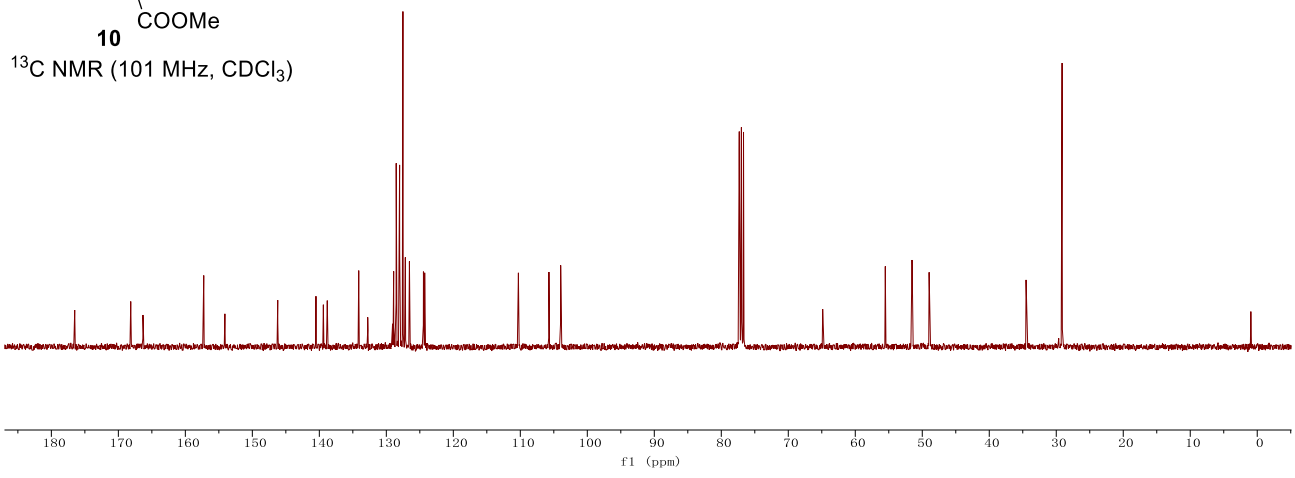
^{1}H NMR (400 MHz, $CDCl_3$)

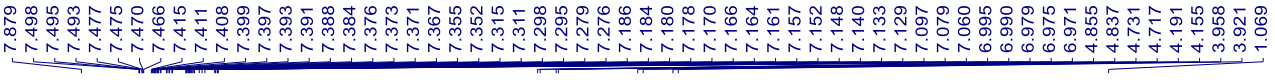


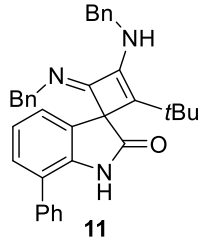


10

^{13}C NMR (101 MHz, $CDCl_3$)

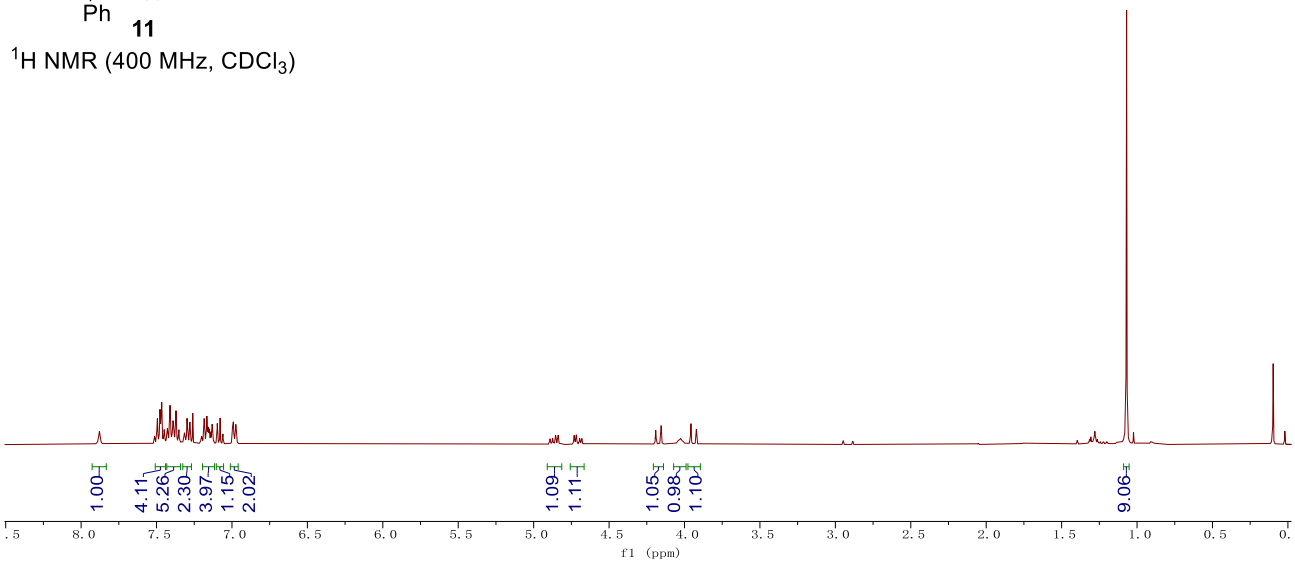


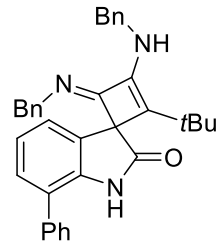




11

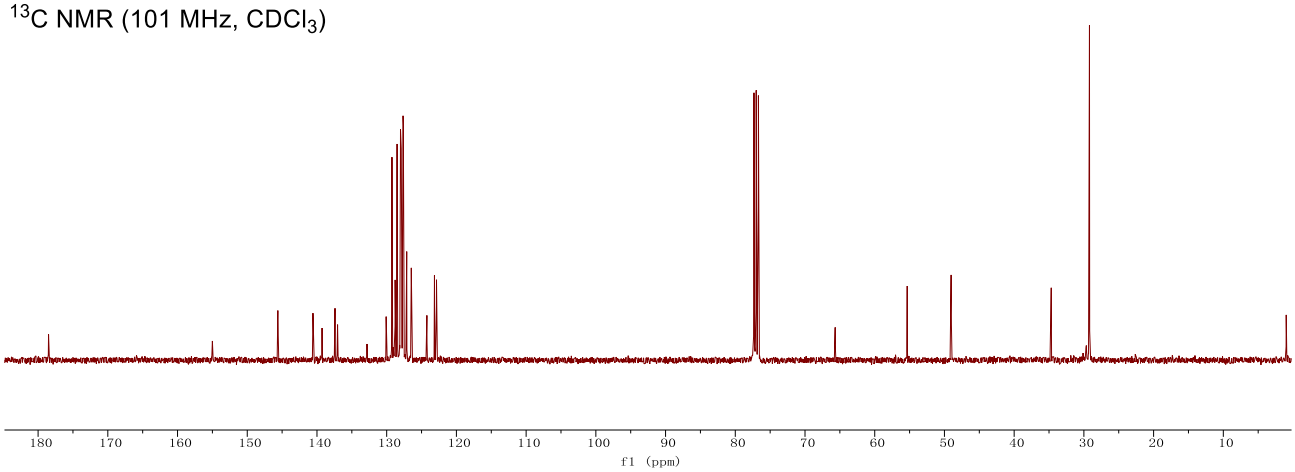
^{1}H NMR (400 MHz, $CDCl_3$)

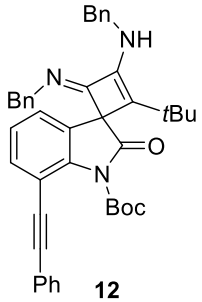




11

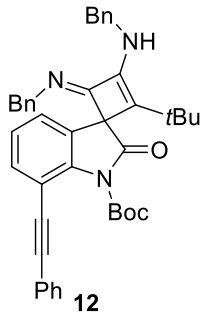
^{13}C NMR (101 MHz, $CDCl_3$)





12

^{1}H NMR (400 MHz, $CDCl_3$)



12

^{13}C NMR (101 MHz, $CDCl_3$)

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