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Electronic Supplementary Information

Alkylation-Peroxidation of α-Carbonyl Imines or Ketones Catalyzed by a Copper Salt via Radical-Mediated C_{sp^3}-H Functionalization

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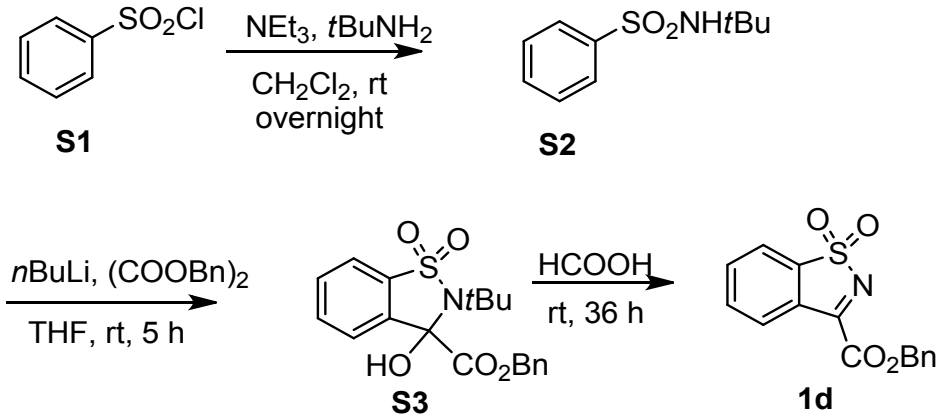
Contents

1. General Information

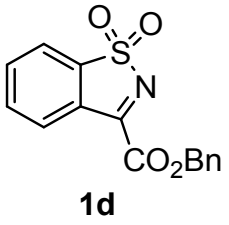
Synthesis of the substrates were carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. Catalytic reactions were performed at 25 °C in air. Solvents were distilled under argon from calcium hydride (CH_3CN, CH_2Cl_2) or sodium/benzophenone (THF, toluene). Imines **1a-c, 1g–l**[1], **1e**[2], **1f**[3], **1u**[4], **1v**[5], **1w**[6] and isatin-type ketones **4a–h**[7] were synthesized according to the published procedures. All others reagents were purchased from commercial suppliers (TCI, Aldrich, Alfa and J&K) and used without further purification. Flash column chromatography was performed with silica gel (300-400 mesh, pH = 6.7–7.0). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM (500 MHz) or Bruker AM (600 MHz) spectrometer at ambient temperature. NMR standards were used as follows: $CDCl_3$ = 7.26 ppm (^1H NMR), 77.0 ppm (^{13}C NMR). IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 T FT-MS instrument using ESI technique. Melting point was performed on Melting point M-560.

2. Synthesis of the Substrates

N-Sulfonylimines **1a-c, 1g–l**[1], **1e**[2] and **1f**[3] were prepared by published procedures. **1d** were prepared by a three-step synthesis according to a modified method.[1]



Scheme S2. Synthetic route to the *N*-sulfonylimine **1d**.



To a solution of benzenesulfonyl chloride (1.77 g, 10.0 mmol) in CH_2Cl_2 at 0 °C was added *tert*-butylamine (1.10 g, 15.0 mmol) and trimethylamine (2.02 g, 20.0 mmol) dropwise. The mixture was stirred at room temperature overnight. The mixture was washed with saturated sodium carbonate and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The crude product benzene sulfonamide (**S2**, 2.09 g, 9.80 mmol) was used in the subsequent step without further purification.

To a solution of the benzene sulfonamide (**S2**, 2.13 g, 10.0 mmol) in THF (75 mL) at 0 °C, *n*-BuLi (20.5 mmol, 2.4 M in hexanes) was added dropwise. The reaction mixture was allowed to stir for 40 min at 0 °C, then cooled to -78 °C. Dibenzyl oxalate (8.11 g, 30.0 mmol) was added. The reaction mixture was stirred for 10 min at -78 °C, then allowed to warm to room temperature and stirred at for 5 h. The reaction was quenched with H_2O (50 mL) and extracted with EtOAc (3 x 80 mL). The combined organic layer was dried over anhydrous

Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluted with PE:EtOAc = 4:1, PE = petroleum ether) to afford the pure α-hydroxyl-α-ester-sulfonylamine (**S3**, 2.97 g, 7.90 mmol).

To the α-hydroxyl-α-ester-sulfonylamine (**S3**, 2.97 g, 7.90 mmol**)** obtained above, formic acid (24 mL) was added. The suspension was stirred at room temperature for 36 h, then concentrated to dryness. The resultant solid was redissolved in CH_2Cl_2 and concentrated in vacuo. The procedure was repeated for three times to remove formic acid. The residue was subjected to silica gel chromatography (eluted with PE:EtOAc = 3:1) to afford the crude α-ester-sulfonylimine product. The crude product was further purified by recrystallization to afford the pure **1d** (1.24 g, 4.10 mmol, yield in total: 41%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.4 Hz, 1H), 7.93 (d, *J* = 7.1 Hz, 1H), 7.81–7.70 (m, 2H), 7.48 (d, *J* = 7.5, 1.8 Hz, 2H), 7.44–7.33 (m, 3H), 5.50 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 156.0, 140.2, 134.3, 134.1, 133.8, 129.1, 128.83, 128.81, 128.2, 127.5, 123.0, 69.2.

IR (film): ν (cm^{-1}) 3409, 3084, 1731, 1650, 1579, 1552, 1454, 1340, 1173, 1027, 767, 604.

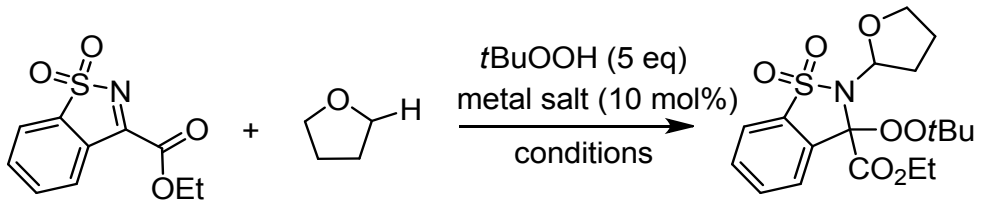
HRMS (ESI, m/z) calcd for $C_{15}H_{11}NO_4S$ $(M+H)^+$: 302.0482, found: 302.0484.

3. Copper-Catalyzed Alkylation-Peroxidation Reactions

3.1 Optimization of the Reaction Conditions

General procedure. To a solution of *N*-sulfonylimine **1a** (0.10 mmol) and tetrahydrofuran **2a** (1.0 mmol) in the indicated solvent (1.0 mL), *tert*-butyl hydroperoxide (70% in water, 0.50 mmol) and metal catalyst (0.010 mmol) were added in turn. The mixture was stirred at the indicated temperature in air for the indicated reaction time, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5).

Table S1. Optimization of reaction conditions.



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

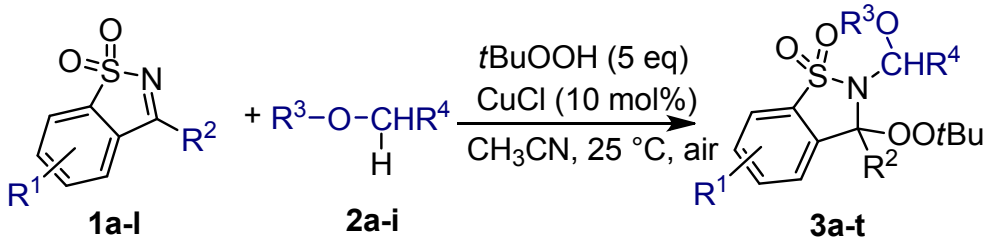
entry	metal salt	solvent	conc. (M)	additives	temp. (°C)	time (h)	yield (%)[b]
1	CuCl	THF	0.10	none	25	21	65
2	CuCl	DCE	0.10	none	25	21	15
3	CuCl	CH_3CN	0.10	none	25	21	77
4	CuCl	CH_3OH	0.10	none	25	21	12
5	CuCl	DMF	0.10	none	25	21	trace
6	$Cu(MeCN)_4PF_6$	CH_3CN	0.10	none	25	21	74
7	$CuCl_2$	CH_3CN	0.10	none	25	21	0
8	$FeCl_3$	CH_3CN	0.10	none	25	21	0
9	$Ni(Oac)_2$	CH_3CN	0.10	none	25	21	0
10	$Zn(Oac)_2$	CH_3CN	0.10	none	25	21	0
11	CuCl	CH_3CN	0.20	none	25	21	66
12	CuCl	CH_3CN	0.05	none	25	21	81
13	CuCl	CH_3CN	0.05	none	0	21	trace
14	CuCl	CH_3CN	0.05	none	50	14	75
15[a]	CuCl	CH_3CN	0.05	none	25	21	65
16	CuCl	CH_3CN	0.05	TEMPO	25	21	0
17	CuCl	CH_3CN	0.05	BHT	25	21	0

[a]performed under argon. [b]isolated yield.

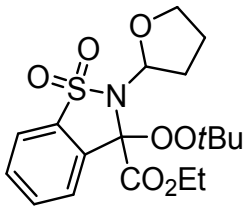
3.2 Substrate Scope

General procedure for investigation of the substrate scope.

To a solution of cyclic *N*-sulfonylimine **1a–l** (0.20 mmol) and ether **2a–i** (2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C for the indicated reaction time, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5).



Scheme S2. Copper-catalyzed alkylation-peroxidation reaction to prepare sultam-based α-amino peroxides **3a–t**.



3a

To a solution of cyclic *N*-sulfonylimine **1a** (47.9 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 21 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3a** as a white solid (64.7 mg, 0.162 mmol, 81% yield).

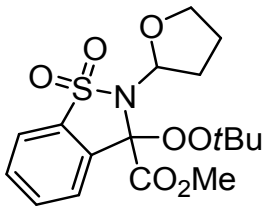
d.r. = 1.2:1, mp 97−99 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H), 7.65 – 7.59 (m, 2H), 7.54 – 7.49 (m, 1H), 5.78 – 5.61 (m, 1H), 4.27 – 3.79 (m, 4H), 3.03 – 2.62 (m, 1H), 2.36 – 2.10 (m, 2H), 2.03 – 1.90 (m, 1H), 1.25 – 1.18 (m, 3H), 1.13 (d, *J* = 5.4 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.46, 165.33, 136.38, 135.92, 134.10, 133.29, 132.79, 132.70, 131.21, 131.01, 124.02, 123.89, 120.77, 120.71, 92.77, 91.92, 86.23, 86.17, 81.29, 81.08, 69.43, 68.56, 62.77, 62.64, 32.34, 29.98, 26.36, 26.30, 24.33, 23.74, 13.85, 13.77.

IR (film): ν (cm^{-1}) 3488, 3056, 2965, 2499, 1752, 1615, 1425, 1365, 1174, 799, 599.

HRMS (ESI, m/z) calcd for $C_{18}H_{25}NnaO_7S$ $(M+Na)^+$: 422.1249, found: 422.1253.



3b

To a solution of cyclic *N*-sulfonylimine **1b** (45.4 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 20 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3b** as a white solid (58.6 mg, 0.152 mmol, 76% yield).

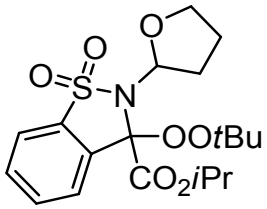
d.r. = 1.1 : 1, mp 93−97 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 1H), 7.64 – 7.58 (m, 2H), 7.51 – 7.47 (m, 1H), 5.75 – 5.57 (m, 1H), 4.14 – 3.78 (m, 2H), 3.73 (d, J = 25.6 Hz, 3H), 3.02 – 2.59 (m, 1H), 2.34 – 2.09 (m, 2H), 2.01 – 1.89 (m, 1H), 1.11 (d, J = 4.6 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.00, 165.87, 136.29, 135.77, 133.90, 133.04, 132.84, 132.75, 131.26, 131.04, 124.01, 123.92, 120.71, 120.61, 92.66, 91.62, 86.08, 85.90, 81.29, 81.08, 69.41, 68.48, 53.35, 53.21, 32.11, 29.80, 26.29, 26.23, 24.27, 23.71.

IR (film): ν (cm^{-1}) 2980, 1757, 1454, 1365, 1311, 1179, 1050, 923, 765, 588.

HRMS (ESI, m/z) calcd for $C_{17}H_{23}NnaO_7S$ $(M+Na)^+$: 408..1093, found: 408.1085.



3c

To a solution of cyclic *N*-sulfonylimine **1a** (50.7 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 18 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3c** as a white solid (67.8 mg, 0.164 mmol, 82% yield).

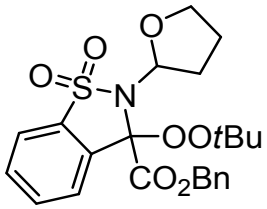
d.r. = 1.2:1, mp 104−105 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 1H), 7.64 – 7.56 (m, 2H), 7.53 – 7.46 (m, 1H), 5.68 (dd, *J* = 62.2, 5.4 Hz, 1H), 5.08 – 4.96 (m, 1H), 4.19 – 3.78 (m, 2H), 3.01 – 2.61 (m, 1H), 2.34 – 2.07 (m, 2H), 2.00 – 1.88 (m, 1H), 1.25 (dd, *J* = 13.1, 6.3 Hz, 3H), 1.17 – 1.07 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.77, 164.65, 136.35, 135.98, 134.14, 133.42, 132.64, 132.56, 131.07, 130.90, 123.88, 123.77, 120.64, 120.59, 92.79, 92.13, 86.40, 86.12, 81.15, 80.96, 70.79, 70.67, 69.27, 68.44, 32.37, 29.93, 26.31, 26.26, 24.27, 23.67, 21.37, 21.25.

IR (film): ν (cm^{-1}) 3473, 2980, 1936, 1744, 1454, 1365, 1181, 969, 768, 569.

HRMS (ESI, m/z) calcd for $C_{19}H_{27}NnaO_7S$ $(M+Na)^+$: 436.1406, found: 436.1398.



3d

To a solution of cyclic *N*-sulfonylimine **1d** (60.3 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was

stirred at 25 °C in air for 19 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3d** as a yellow oil (76.5 mg, 0.166 mmol, 83% yield).

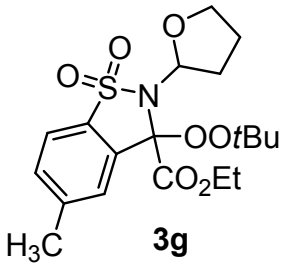
d.r. = 1.1:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 1H), 7.62 – 7.53 (m, 2H), 7.43 – 7.36 (m, 1H), 7.32 – 7.25 (m, 4H), 7.22 (dd, *J* = 6.8, 2.9 Hz, 1H), 5.69 (ddd, *J* = 72.7, 6.1, 2.3 Hz, 1H), 5.26 – 5.16 (m, 2H), 4.12 – 3.75 (m, 2H), 3.01 – 2.58 (m, 1H), 2.29 – 2.08 (m, 2H), 1.94 – 1.88 (m, 1H), 1.12 (d, *J* = 6.3 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.27, 165.19, 136.36, 135.93, 134.79, 134.71, 133.74, 133.02, 132.70, 132.61, 131.19, 131.01, 128.44, 128.37, 128.34, 128.22, 128.10, 127.85, 124.05, 123.90, 120.72, 120.64, 92.77, 91.90, 86.16, 86.14, 81.30, 81.13, 69.35, 68.45, 67.96, 67.89, 32.20, 29.92, 26.31, 26.26, 24.26, 23.70.

IR (film): ν (cm^{-1}) 3064, 2980, 2929, 1755, 1455, 1311, 1179, 1051, 763, 585.

HRMS (ESI, m/z) calcd for $C_{23}H_{27}NnaO_7S$ $(M+Na)^+$: 484.1406, found: 484.1397.



3g

To a solution of cyclic *N*-sulfonylimine **1g** (50.7 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 19 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3g** as a white solid (62.0 mg, 0.150 mmol, 75% yield).

d.r. = 1.1:1, mp 87−89 °C.

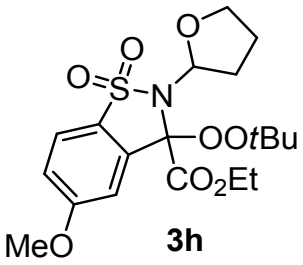
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 1H), 7.41 – 7.37 (m, 1H), 7.28 (d, *J* = 9.3 Hz, 1H), 5.67 (ddd, *J* = 67.3, 6.1, 2.2 Hz, 1H), 4.25 – 3.78 (m, 4H), 3.01 – 2.61 (m, 1H), 2.44 (d,

J = 2.5 Hz, 3H), 2.32 – 2.10 (m, 2H), 1.99 – 1.90 (m, 1H), 1.25 – 1.19 (m, 3H), 1.13 (d, *J* = 5.0 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.59, 165.45, 143.77, 143.68, 134.27, 133.76, 133.48, 133.31, 132.03, 131.83, 124.18, 124.03, 120.47, 120.40, 92.66, 91.83, 86.21, 86.12, 81.18, 80.95, 69.34, 68.46, 62.67, 62.54, 32.33, 29.89, 26.34, 26.29, 24.32, 23.71, 21.73, 21.70, 13.81, 13.74.

IR (film): ν (cm^{-1}) 3485, 2980, 2933, 1754, 1602, 1457, 1364, 1045, 715, 590.

HRMS (ESI, m/z) calcd for $C_{19}H_{27}NnaO_7S$ $(M+Na)^+$: 436.1406, found: 436.1401.



3h

To a solution of cyclic *N*-sulfonylimine **1h** (53.9 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 24 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3h** as a white solid (70.4 mg, 0.164 mmol, 82% yield).

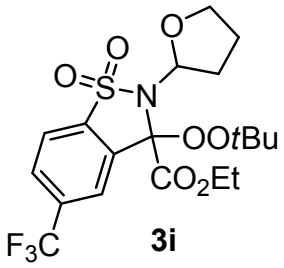
d.r. = 1.2:1, mp 112−115 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 1H), 7.11 – 7.06 (m, 1H), 6.92 (dd, *J* = 6.7, 2.2 Hz, 1H), 5.66 (ddd, *J* = 67.8, 6.1, 2.2 Hz, 1H), 4.25 – 3.80 (m, 7H), 3.02 – 2.60 (m, 1H), 2.32 – 2.09 (m, 2H), 1.99 – 1.89 (m, 1H), 1.25 – 1.19 (m, 3H), 1.15 (d, *J* = 5.1 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.50, 165.32, 163.26, 163.21, 136.47, 135.59, 128.44, 127.99, 122.18, 122.13, 117.95, 117.85, 107.91, 107.84, 92.39, 91.59, 86.16, 86.09, 81.20, 80.97, 69.34, 68.46, 62.71, 62.59, 55.88, 55.85, 32.32, 29.80, 26.39, 26.32, 24.32, 23.69, 13.82, 13.75.

IR (film): ν (cm^{-1}) 3357, 2963, 2920, 1752, 1595, 1487, 1364, 1260, 1020, 799, 585.

HRMS (ESI, m/z) calcd for $C_{19}H_{27}NnaO_8S$ $(M+Na)^+$: 452.1355 found: 452.1344.



3i

To a solution of cyclic *N*-sulfonylimine **1i** (61.5 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 20 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3i** as a white solid (74.8 mg, 0.160 mmol, 80% yield).

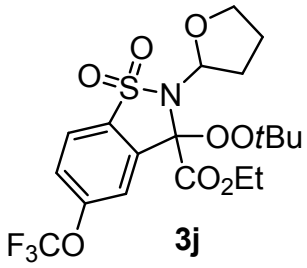
d.r. = 1.1:1, mp 90−91 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.78 (d, *J* = 6.3 Hz, 1H), 5.70 (ddd, *J* = 67.2, 6.0, 2.2 Hz, 1H), 4.28 – 3.81 (m, 4H), 2.99 – 2.61 (m, 1H), 2.33 – 2.14 (m, 2H), 2.03 – 1.94 (m, 1H), 1.26 – 1.21 (m, 3H), 1.13 (d, *J* = 2.8 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.74, 164.62, 139.48, 139.02, 135.35, 135.13, 135.07, 134.91, 134.85, 134.51, 128.39(q *J* = 11.0 Hz,), 128.17(q, *J* = 11.0 Hz), 121.75, 121.68, 121.60(q, *J* = 10.9 Hz), 121.46(q, *J* = 10.9 Hz), 92.44, 91.57, 86.35, 86.32, 81.78, 81.56, 69.58, 68.68, 63.22, 63.07, 32.43, 30.02, 26.26, 26.22, 24.27, 23.68, 13.79, 13.72.

IR (film): ν (cm^{-1}) 3359, 2982, 2921, 2850, 1756, 1659, 1469, 1366, 1331, 1176, 1043, 718, 599.

HRMS (ESI, m/z) calcd for $C_{19}H_{24}F_3NnaO_7S$ $(M+Na)^+$: 490.1123, found: 490.1115.



3j

To a solution of cyclic *N*-sulfonylimine **1j** (64.7 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 19 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3j** as a yellow oil (79.3 mg, 0.164 mmol, 82% yield).

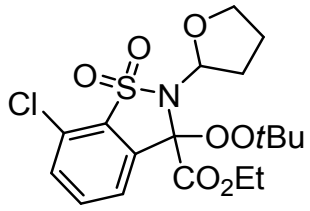
d.r. = 1.1:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (q, *J* = 15.6, 7.7 Hz, 1H), 7.45 – 7.38 (m, 2H), 5.67 (ddd, *J* = 68.0, 6.1, 2.2 Hz, 1H), 4.26 – 3.79 (m, 4H), 3.02 – 2.60 (m, 1H), 2.33 – 2.10 (m, 2H), 2.00 – 1.90 (m, 1H), 1.25 – 1.19 (m, 3H), 1.13 (d, *J* = 4.3 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.94, 164.78, 142.98(q, *J* = 4.5 Hz), 142.94(q, *J* = 4.5 Hz), 137.17, 136.39, 134.45, 134.32, 127.94, 127.61, 121.52, 121.48, 121.23, 120.99(d, *J* = 1.9 Hz), 120.63(d, *J* = 1.9 Hz), 119.14, 92.04, 91.23, 86.41, 86.20, 81.52, 81.29, 69.47, 68.57, 62.96, 62.83, 32.41, 29.84, 26.31, 26.25, 24.20, 23.65, 13.79, 13.72.

IR (film): ν (cm^{-1}) 3360, 2982, 2935, 1754, 1610, 1473, 1324, 1173, 1045, 868, 594.

HRMS (ESI, m/z) calcd for $C_{19}H_{24}F_3NnaO_8S$ $(M+Na)^+$: 506.1072, found: 506.1063.



3k

To a solution of cyclic *N*-sulfonylimine **1k** (54.7 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was

stirred at 25 °C in air for 18 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3k** as a white solid (67.7 mg, 0.156 mmol, 78% yield).

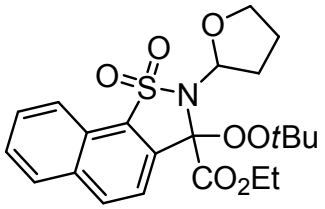
d.r. = 1.1:1, mp 94−98 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.40 (td, *J* = 6.8, 1.7 Hz, 1H), 5.68 (ddd, *J* = 69.8, 6.1, 2.2 Hz, 1H), 4.24 – 3.79 (m, 4H), 3.03 – 2.61 (m, 1H), 2.33 – 2.12 (m, 2H), 2.00 – 1.91 (m, 1H), 1.24 – 1.18 (m, 3H), 1.14 (d, *J* = 2.3 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.08, 164.91, 136.78, 135.97, 133.91, 133.89, 133.72, 133.61, 131.99, 131.76, 128.22, 128.19, 122.18, 122.09, 91.68, 90.88, 86.35, 86.17, 81.47, 81.23, 69.48, 68.56, 62.90, 62.77, 32.47, 29.86, 26.36, 26.30, 24.23, 23.66, 13.79, 13.74.

IR (film): ν (cm^{-1}) 3487, 3082, 2981, 1751, 1592, 1456, 1365, 1175, 1047, 797, 597.

HRMS (ESI, m/z) calcd for $C_{18}H_{24}ClNNaO_7S$ $(M+Na)^+$: 456.0860, found: 456.0852.



3l

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 24 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3l** as a yellow oil (83.6 mg, 0.186 mmol, 93% yield).

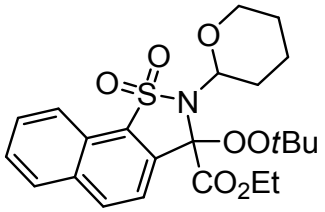
d.r. = 1.1:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 – 8.39 (m, 1H), 8.06 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.72 (M, 1H), 7.68 – 7.63 (m, 1H), 7.51 (dd, *J* = 8.5, 7.2 Hz, 1H), 5.77 (ddd, *J* = 70.0, 6.1, 2.3 Hz, 1H), 4.25 – 3.85 (m, 4H), 3.13 – 2.69 (m, 1H), 2.39 – 2.16 (m, 2H), 2.03 – 1.94 (m, 1H), 1.23 – 1.17 (m, 3H), 1.13 (d, *J* = 6.8 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.39, 165.21, 134.32, 134.17, 133.67, 133.53, 133.03, 132.07, 131.68, 131.34, 129.07, 128.66, 128.60, 128.22, 124.68, 124.61, 123.54, 123.41, 119.58, 119.43, 92.55, 91.85, 86.23, 86.14, 81.26, 81.04, 69.39, 68.47, 62.76, 62.64, 32.41, 29.83, 29.29, 26.38, 26.35, 26.32, 24.35, 23.73, 13.81, 13.75.

IR (film): ν (cm^{-1}) 3062, 2980, 1753, 1512, 1464, 1365, 1247, 1171, 1047, 826, 596.

HRMS (ESI, m/z) calcd for $C_{22}H_{27}NnaO_7S$ $(M+Na)^+$: 472.1406, found: 472.1398.



3m

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and tetrahydropyran **2b** (196 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 23 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3m** as a yellow oil (72.3 mg, 0.156 mmol, 78% yield).

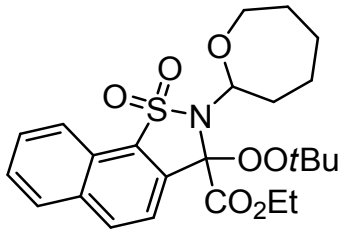
d.r. = 1.9:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 8.2 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.51 (dd, J = 44.1, 8.5 Hz, 1H), 5.04 (ddd, J = 109.4, 10.5, 2.1 Hz, 1H), 4.24 – 3.98 (m, 3H), 3.64 – 3.42 (m, 1H), 2.55 – 2.01 (m, 3H), 1.73 – 1.59 (m, 2H), 1.54 – 1.48 (m, 1H), 1.24 – 1.17 (m, 3H), 1.16 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.25, 165.14, 134.16, 134.14, 133.53(2C), 132.54, 132.43, 131.51, 130.81, 129.05, 128.97, 128.63, 128.58, 128.26, 128.12, 124.59(2C), 123.59, 123.48, 120.07, 119.94, 92.19, 91.40, 83.34, 83.18, 81.32, 81.20, 68.33, 67.61, 62.79(2C), 30.16, 28.30, 26.42, 26.32, 24.95, 24.81, 23.71, 23.56, 13.81, 13.71.

IR (film): ν (cm^{-1}) 3061, 2979, 2855, 1753, 1466, 1365, 1249, 1105, 1037, 830, 575.

HRMS (ESI, m/z) calcd for $C_{23}H_{29}NnaO_7S$ $(M+Na)^+$: 486.1562, found: 486.1559.



3n

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and hexamethylene oxide **2c** (222 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 24 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3n** as a yellow solid (87.9 mg, 0.184 mmol, 92% yield).

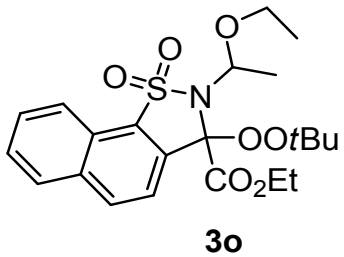
d.r. = 1.6:1, mp 118−124 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.2 Hz, 1H), 8.05 (t, *J* = 7.8 Hz, 1H), 7.98 – 7.93 (m, 1H), 7.75 – 7.70 (m, 1H), 7.68 – 7.64 (m, 1H), 7.49 (dd, *J* = 36.1, 8.5 Hz, 1H), 5.45 – 5.31 (m, 1H), 4.28 – 4.11 (m, 2H), 4.07 – 4.00 (m, 1H), 3.83 – 3.46 (m, 1H), 2.68 – 2.62 (m, 1H), 1.88 (d, 2H), 1.77 – 1.64 (m, 2H), 1.58 – 1.46 (m, 2H), 1.23 – 1.15 (m, 3H), 1.14 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.65, 165.40, 134.22, 133.63, 133.49, 132.99, 132.66, 132.40, 131.64, 131.28, 129.86, 129.04, 128.67, 128.58, 128.20, 128.14, 124.65, 123.57, 123.40, 119.62, 119.29, 99.94, 92.45, 91.65, 86.84, 85.30, 81.12, 81.03, 66.22, 64.77, 62.66, 62.61, 33.64, 30.77, 30.45, 30.28, 28.47, 28.13, 26.45, 26.33, 24.34, 24.22, 13.83, 13.76.

IR (film): ν (cm^{-1}) 3479, 2929, 2857, 1753, 1513, 1364, 1248, 1170, 961, 824, 573.

HRMS (ESI, m/z) calcd for $C_{24}H_{31}NnaO_7S$ $(M+Na)^+$: 500.1719, found: 500.1727.



3o

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and diethyl ether **2d** (208 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0

mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 24 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3o** as a yellow solid (81.3 mg, 0.180 mmol, 90% yield).

d.r. = 1.1: 1.

Note: The two diastereomers could be separated with each other by the regular silica gel chromatography in 42% and 48% yield, respectively.

Analytic data of the less polar diastereomer:

mp 116−118 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.70 – 7.65 (m, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 5.35 (q, *J* = 6.3 Hz, 1H), 4.38 – 4.30 (m, 1H), 4.24 – 4.16 (m, 1H), 3.83 – 3.76 (m, 1H), 3.61 – 3.54 (m, 1H), 1.84 (d, *J* = 6.3 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H), 1.08 (s, 9H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.41, 134.08, 133.65, 133.28, 130.68, 129.07, 128.62, 128.24, 124.54, 123.43, 120.39, 91.07, 81.26, 80.78, 64.50, 62.79, 26.36, 21.72, 14.58, 13.81.

IR (film): ν (cm^{-1}) 3359, 2980, 2850, 1753, 1632, 1365, 1245, 1190, 1052, 954, 608.

HRMS (ESI, m/z) calcd for $C_{22}H_{29}NnaO_7S$ $(M+Na)^+$: 474.1562, found: 474.1558.

Analytic data of the more polar diastereomer:

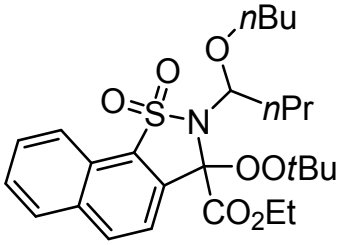
mp 110−112 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 5.31 – 5.26 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.02 – 3.95 (m, 1H), 3.65 – 3.58 (m, 1H), 1.91 (d, *J* = 6.1 Hz, 3H), 1.25 – 1.22 (m, 6H), 1.18 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.39, 134.33, 133.31, 131.99, 131.39, 129.05, 128.59, 128.35, 124.49, 123.53, 120.35, 92.38, 84.09, 81.73, 63.32, 62.77, 26.36, 20.18, 14.88, 13.88.

IR (film): ν (cm^{-1}) 3358, 2980, 2852, 1752, 1632, 1365, 1248, 1185, 1052, 957, 570.

HRMS (ESI, m/z) calcd for $C_{22}H_{29}NnaO_7S$ $(M+Na)^+$: 474.1562, found: 474.1560.



3p

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and di-*n*-butyl ether **2e** (340 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 26 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3p** as a yellow oil (85.3 mg, 0.168 mmol, 84% yield).

d.r. = 1.1: 1.

Note: The two diastereomers could be separated with each other by the regular silica gel chromatography in 44% and 40% yield, respectively.

Analytic data of the less polar diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 – 8.39 (m, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.69 – 7.65 (m, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 5.10 (dd, *J* = 8.9, 4.5 Hz, 1H), 4.38 – 4.30 (m, 1H), 4.21 – 4.12 (m, 1H), 3.74 – 3.66 (m, 1H), 3.48 (dt, *J* = 10.0, 7.0 Hz, 1H), 2.34 – 2.25 (m, 1H), 2.13 – 2.05 (m, 1H), 1.63 – 1.42 (m, 4H), 1.39 – 1.29 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.09 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.48, 134.05, 133.95, 133.09, 130.62, 129.01, 128.60, 128.19, 124.59, 123.45, 120.72, 90.79, 84.75, 81.23, 69.44, 62.66, 37.46, 31.23, 26.35, 19.48, 19.21, 13.91, 13.78, 13.70.

IR (film): ν (cm^{-1}) 3060, 2961, 2873, 1753, 1567, 1466, 1309, 1244, 1112, 824, 610.

HRMS (ESI, m/z) calcd for $C_{26}H_{37}NnaO_7S$ $(M+Na)^+$: 530.2188, found: 530.2185.

Analytic data of the more polar diastereomer:

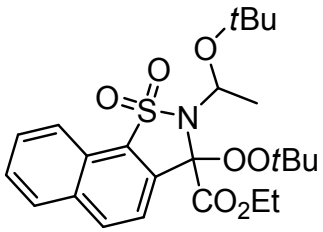
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.69 – 7.62 (m, 2H), 5.11 (dd, *J* = 9.8, 2.7 Hz, 1H), 4.26 (q,

J = 7.1 Hz, 2H), 4.08 – 4.02 (m, 1H), 3.56 – 3.49 (m, 1H), 2.53 – 2.43 (m, 1H), 2.20 – 2.11 (m, 1H), 1.64 – 1.58 (m, 4H), 1.45 – 1.39 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.20 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.45, 134.39, 133.19, 132.16, 131.02, 129.02, 128.54, 128.38, 124.47, 123.60, 120.71, 92.68, 88.83, 81.93, 68.47, 62.78, 36.65, 31.60, 26.37, 19.66, 19.38, 13.98, 13.93, 13.77.

IR (film): ν (cm^{-1}) 3060, 2959, 2872, 1753, 1576, 1465, 1313, 1247, 1108, 826, 595.

HRMS (ESI, m/z) calcd for $C_{26}H_{37}NnaO_7S$ $(M+Na)^+$: 530.2188, found: 530.2183.



3q

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and tert-butyl ethyl ether **2f** (275 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (2.0 mg, 0.020 mmol) were added in turn. The mixture was stirred at 25 °C in air for 29 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3q** as a yellow solid (64.2 mg, 0.134 mmol, 67% yield).

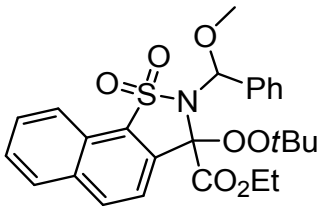
d.r. >20: 1, mp 110−112 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.68 – 7.64 (m, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 5.62 (q, *J* = 6.3 Hz, 1H), 4.41 – 4.35 (m, 1H), 4.24 – 4.17 (m, 1H), 1.76 (d, *J* = 6.3 Hz, 3H), 1.26 (s, 9H), 1.25 – 1.22 (m, 3H), 1.05 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.65, 134.41, 133.98, 132.96, 130.71, 128.96, 128.58, 128.10, 124.58, 123.41, 120.42, 91.07, 81.12, 76.51, 75.09, 62.29, 27.60, 26.35, 24.92, 13.83.

IR (film): ν (cm^{-1}) 3630, 2979, 2934, 1753, 1599, 1466, 1365, 1245, 1175, 1094, 824, 607.

HRMS (ESI, m/z) calcd for $C_{24}H_{33}NnaO_7S$ $(M+Na)^+$: 502.1875, found: 502.1878.



3r

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and Benzyl methyl ether **2g** (247 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C in air for 34 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3r** as a yellow solid (75.9 mg, 0.152 mmol, 76% yield).

d.r. = 1.3: 1.

Note: The two diastereomers could be separated with each other by the regular silica gel chromatography in 43% and 33% yield, respectively.

Analytic data of the less polar diastereomer:

mp 140−142 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.3 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.70 – 7.67 (m, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.07 (s, 1H), 4.29 – 4.23 (m, 1H), 4.14 – 4.08 (m, 1H), 3.58 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.75 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.36, 137.25, 134.06, 133.72, 133.27, 130.52, 129.11, 128.65, 128.25, 128.11, 127.58, 127.54, 124.62, 123.44, 120.50, 90.74, 85.55, 80.87, 62.64, 57.71, 25.91, 13.71.

IR (film): ν (cm^{-1}) 3062, 2979, 2852, 1958, 1752, 1512, 1454, 1365, 1245, 1057, 824, 569.

HRMS (ESI, m/z) calcd for $C_{26}H_{29}NnaO_7S$ $(M+Na)^+$: 522.1562, found: 522.1578.

Analytic data of the more polar diastereomer:

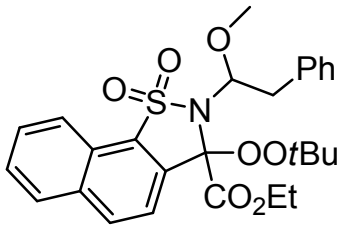
mp 138−141 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.70 (m, 3H), 7.68 – 7.64 (m, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.35 (m, 3H), 5.98 (s, 1H), 3.82 – 3.77 (m, 1H), 3.71 – 3.65 (m, 1H), 3.59 (s, 3H), 1.20 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.82, 134.98, 134.14, 133.43, 133.02, 130.92, 129.05, 129.04, 128.63, 128.56, 128.23, 127.87, 124.71, 123.49, 119.71, 91.78, 86.48, 81.40, 62.39, 57.07, 26.44, 13.55.

IR (film): ν (cm^{-1}) 3563, 2978, 2850, 1958, 1753, 1633, 1574, 1388, 1306, 1173, 1085, 824, 571.

HRMS (ESI, m/z) calcd for $C_{26}H_{29}NnaO_7S$ $(M+Na)^+$: 522.1562, found: 522.1575.



3s

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and (2-Methoxyethyl)benzene **2h** (287 μL, 2.0 mmol) in acetonitrile (4.0 mL), tert-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C in air for 35 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3s** as a yellow solid (50.3 mg, 0.098 mmol, 49% yield).

d. r. = 1: 1.

Note: The two diastereomers could be separated with each other by the regular silica gel chromatography in 25% and 24% yield, respectively.

Analytic data of the less polar diastereomer:

mp 143−148 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 8.3, 0.6 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.73 – 7.68 (m, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.38 –

7.31 (m, 4H), 7.26 – 7.23 (m, 1H), 5.18 (dd, *J* = 10.6, 2.2 Hz, 1H), 4.39 – 4.32 (m, 1H), 4.24 – 4.16 (m, 1H), 3.71 (dd, *J* = 14.4, 10.6 Hz, 1H), 3.36 (dd, *J* = 14.4, 2.1 Hz, 1H), 3.32 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.33, 138.40, 134.13, 133.43, 133.40, 130.79, 129.49, 129.16, 128.66, 128.32, 128.29, 126.46, 124.59, 123.47, 120.36, 91.00, 87.24, 81.49, 62.88, 57.66, 42.06, 26.42, 13.83.

IR (film): ν (cm^{-1}) 3366, 3028, 2978, 2852, 1753, 1454, 1365, 1245, 1173, 823, 700.

HRMS (ESI, m/z) calcd for $C_{27}H_{31}NnaO_7S$ $(M+Na)^+$: 536.1719, found: 536.1725.

Analytic data of the more polar diastereomer:

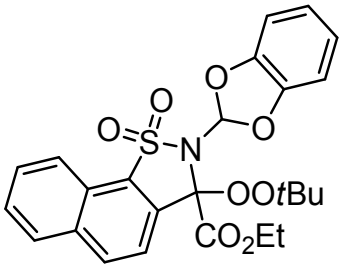
mp 142−144 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 – 8.44 (m, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.72 – 7.67 (m, 2H), 7.38 (d, *J* = 6.9 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 5.25 (dd, *J* = 10.4, 2.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.79 (dd, *J* = 14.4, 10.4 Hz, 1H), 3.57 (dd, *J* = 14.5, 2.1 Hz, 1H), 3.50 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.20, 138.42, 134.43, 133.37, 132.08, 130.99, 129.38, 129.18, 128.61, 128.51, 128.27, 126.35, 124.47, 123.59, 120.68, 92.90, 90.73, 82.27, 63.00, 57.05, 40.85, 26.47, 13.93.

IR (film): ν (cm^{-1}) 3062, 3028, 2979, 2852, 1752, 1454, 1365, 1257, 1170, 824, 698.

HRMS (ESI, m/z) calcd for $C_{27}H_{31}NnaO_7S$ $(M+Na)^+$: 536.1719, found: 536.1721.



3t

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and 1,3-Benzodioxole **2i** (229 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL,

1.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C in air for 51 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3t** as a yellow solid (40.0 mg, 0.080 mmol, 40% yield).

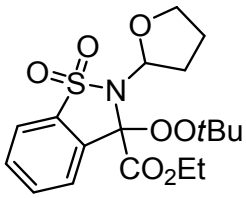
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.2 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.71 (dt, *J* = 21.6, 7.0 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.59 (s, 1H), 7.03 – 7.00 (m, 1H), 6.97 – 6.92 (m, 3H), 4.30 – 4.21 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.65, 145.96, 145.67, 134.45, 134.15, 131.26, 130.68, 129.36, 128.69, 128.66, 124.56, 123.52, 122.40, 122.28, 119.93, 109.25, 109.05, 108.64, 91.86, 82.10, 63.26, 26.26, 13.77.

IR (film): ν (cm^{-1}) 3358, 3066, 2981, 2851, 1754, 1632, 1484, 1326, 1178, 1067, 827, 737.

HRMS (ESI, m/z) calcd for $C_{25}H_{25}NnaO_8S$ $(M+Na)^+$: 522.1199, found: 522.1193.

3.3 A Scale-up Catalytic Reaction



3a

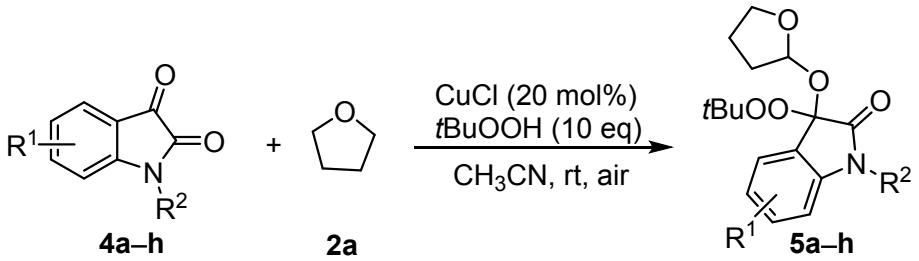
To a solution of cyclic *N*-sulfonylimine **1a** (957 mg, 4.0 mmol) and tetrahydrofuran **2a** (3.2 mL, 40.0 mmol) in acetonitrile (80 mL), *tert*-butyl hydroperoxide (70% in water, 5.6 mL, 20 mmol) and copper chloride (39.6 mg, 0. 40 mmol) were added in turn. The mixture was stirred at 25 °C in air for 48 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afforded **3a** as a white solid (1246 mg, 3.12 mmol, 78% yield).

d.r. = 1.2:1.

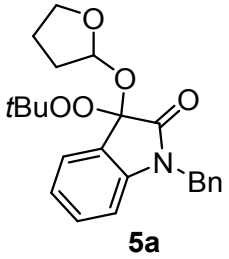
4. Application to Alkylation-Peroxidation of the Isatin-Type ketones

General procedure for investigation of the substrate scope.

To a solution of isatin-type ketones **4a–h** (0.20 mmol) and tetrahydrofuran **2a** (2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 2.0 mmol) and copper chloride (0.040 mmol) were added in turn. The mixture was stirred at 25 °C for the indicated reaction time, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5).



Scheme S3. Copper-catalyzed alkylation-peroxidation of the isatin-type ketones.



To a solution of isatin-type ketone **4a** (47.5 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 280 μL, 2.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C for the 5 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afford **5a** as an orange oil (73.1 mg, 0.184 mmol, 92% yield).

d.r. = 1: 1.

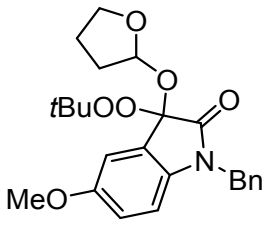
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.1 Hz, 1H), 7.36 – 7.22 (m, 6H), 7.08 – 7.01 (m, 1H), 6.67 (dd, *J* = 36.9, 7.9 Hz, 1H), 5.89 (dd, *J* = 452.6, 4.6 Hz, 1H), 5.02 – 4.95 (m, 1H),

4.86 (dd, *J* = 15.9, 10.2 Hz, 1H), 4.00 – 3.71 (m, 2H), 2.22 – 2.16 (m, 1H), 2.08 – 2.01 (m, 1H), 1.96 – 1.77 (m, 2H), 1.17 (d, *J* = 31.6 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.00, 169.32, 143.24, 141.97, 135.49, 135.37, 130.76, 130.24, 128.65, 128.61, 127.52, 127.49, 127.47, 127.08 (2C), 126.42, 125.96, 122.81, 122.42, 121.92, 109.79, 109.31, 100.38, 100.36, 99.84, 99.15, 81.61, 81.15, 67.87, 67.78, 43.63, 43.49, 32.98, 32.59, 26.31, 26.17, 23.28, 23.27.

IR (film): ν (cm^{-1}) 3461, 2977, 1731, 1614, 1468, 1363, 1184, 1025, 917, 753, 578.

HRMS (ESI, m/z) calcd for $C_{23}H_{27}NnaO_5$ $(M+Na)^+$: 420.1787, found: 420.1783.



5b

To a solution of isatin-type ketone **4b** (53.5 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 280 μL, 2.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C for the 8 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afford **5b** as a red oil (57.3 mg, 0.134 mmol, 67% yield).

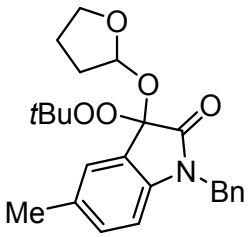
d.r. = 1.4: 1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 7.26 – 7.22 (m, 1H), 7.17 (dd, *J* = 4.5, 2.7 Hz, 1H), 6.74 (ddd, *J* = 27.9, 8.5, 2.7 Hz, 1H), 6.53 (dd, *J* = 30.6, 8.5 Hz, 1H), 6.27 – 5.52 (m, 1H), 4.97 – 4.90 (m, 1H), 4.81 (dd, *J* = 15.9, 5.8 Hz, 1H), 3.99 – 3.70 (m, 5H), 2.19 – 2.14 (m, 1H), 2.06 – 1.98 (m, 1H), 1.95 – 1.74 (m, 2H), 1.16 (d, *J* = 22.2 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.80, 169.07, 155.60, 155.24, 136.57, 135.55, 135.41, 135.26, 128.63, 128.59, 127.46, 127.44, 127.12, 127.07 (2C), 123.96, 115.47, 114.91, 114.44, 113.42, 110.23, 109.77, 100.55, 100.39, 99.82, 99.32, 81.66, 81.18, 67.91, 67.79, 55.79, 55.75, 43.70, 43.56, 32.97, 32.65, 26.33, 26.22, 23.27 (2C).

IR (film): ν (cm^{-1}) 3454, 2978, 1731, 1605, 1493, 1364, 1184, 1024, 965, 733, 514.

HRMS (ESI, m/z) calcd for $C_{24}H_{29}NnaO_6$ $(M+Na)^+$: 450.1893, found: 450.1888.



5c

To a solution of isatin-type ketone **4c** (50.3 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 280 μL, 2.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C for the 9 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afford **5c** as an orange oil (57.6 mg, 0.140 mmol, 70% yield).

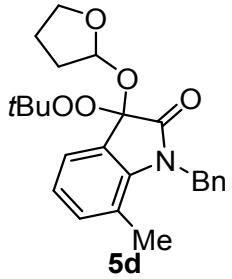
d.r. = 1.1: 1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.33 – 7.27 (m, 4H), 7.23 (dd, *J* = 6.6, 4.2 Hz, 1H), 7.00 (dd, *J* = 30.7, 7.8 Hz, 1H), 6.52 (dd, *J* = 36.3, 8.0 Hz, 1H), 5.89 (dd, *J* = 449.3, 4.5 Hz, 1H), 4.95 (dd, *J* = 15.9, 10.1 Hz, 1H), 4.81 (dd, *J* = 15.9, 2.3 Hz, 1H), 3.98 – 3.67 (m, 2H), 2.30 (d, *J* = 12.6 Hz, 3H), 2.19 – 2.13 (m, 1H), 2.07 – 1.99 (m, 1H), 1.92 – 1.75 (m, 2H), 1.15 (d, *J* = 32.2 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.94, 169.25, 140.77, 139.51, 135.57, 135.44, 131.90, 131.39, 130.97, 130.45, 128.57, 128.53, 128.15, 127.40, 127.37, 127.08 (2C), 127.04, 125.80, 122.75, 109.49, 109.02, 100.48, 100.31, 99.75, 99.24, 81.51, 81.06, 67.82, 67.71, 43.58, 43.44, 32.96, 32.57, 26.31, 26.19, 23.27 (2C), 20.99, 20.98.

IR (film): ν (cm^{-1}) 3457, 2978, 1735, 1624, 1496, 1363, 1171, 1026, 965, 733, 554.

HRMS (ESI, m/z) calcd for $C_{24}H_{29}NnaO_5$ $(M+Na)^+$: 434.1943, found: 434.1938.



5d

To a solution of isatin-type ketone **4d** (50.3 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 280 μL, 2.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C for the 6 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afford **5d** as an orange oil (62.6 mg, 0.152 mmol, 76% yield).

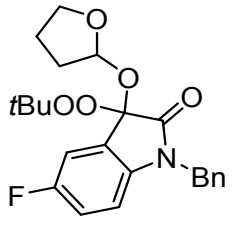
d.r. = 1.4: 1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 1H), 7.33 – 7.29 (m, 3H), 7.27 – 7.24 (m, 2H), 7.07 – 6.97 (m, 2H), 6.32 – 5.56 (m, 1H), 5.30 – 5.11 (m, 2H), 4.00 – 3.72 (m, 2H), 2.25 (d, *J* = 6.3 Hz, 3H), 2.22 – 2.17 (m, 1H), 2.09 – 2.03 (m, 1H), 1.99 – 1.75 (m, 2H), 1.20 (d, *J* = 34.7 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.05, 170.29, 141.33, 139.92, 137.61, 137.21, 134.84, 134.28, 128.70, 128.64, 127.05 (2C), 127.00, 126.72, 125.70, 125.65, 125.45, 124.30, 123.45, 122.55, 122.02, 120.26, 119.83, 100.25, 99.79, 99.52, 98.32, 81.49, 81.07, 67.82, 67.74, 44.99, 44.81, 33.02, 32.63, 26.34, 26.21, 23.28, 23.24, 18.83, 18.78.

IR (film): ν (cm^{-1}) 3448, 2979, 1732, 1605, 1497, 1363, 1164, 1027, 918, 734, 543.

HRMS (ESI, m/z) calcd for $C_{24}H_{29}NnaO_5$ $(M+Na)^+$: 434.1943, found: 434.1942.



5e

To a solution of isatin-type ketone **4e** (51.1 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 280 μL, 2.0

mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C for the 6 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afford **5e** as an orange oil (73.9 mg, 0.178 mmol, 89% yield).

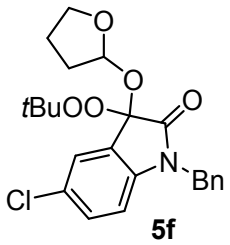
d.r. = 1.1: 1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 6H), 6.93 (dtd, *J* = 35.2, 8.8, 2.7 Hz, 1H), 6.57 (ddd, *J* = 36.8, 8.6, 4.0 Hz, 1H), 5.90 (dd, *J* = 450.2, 4.4 Hz, 1H), 4.97 (dd, *J* = 16.0, 8.8 Hz, 1H), 4.85 (d, *J* = 15.9 Hz, 1H), 4.01 – 3.71 (m, 2H), 2.21 – 2.16 (m, 1H), 2.08 – 2.02 (m, 1H), 1.98 – 1.77 (m, 2H), 1.19 (d, *J* = 24.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.73, 169.01, 159.62, 159.27, 158.02, 157.67, 139.05, 137.74, 135.04 (d, *J* = 19.6 Hz), 128.67 (d, *J* = 5.6 Hz), 127.58 (d, *J* = 4.1 Hz), 127.00 (2C), 117.00 (d, *J* = 23.5 Hz), 116.50, 116.34, 115.46, 114.52, 114.36, 110.39 (d, *J* = 7.8 Hz), 109.92 (d, *J* = 7.9 Hz), 100.39, 99.83, 81.81, 81.35, 67.90 (d, *J* = 19.2 Hz), 43.73, 43.59, 32.93, 32.62, 26.27, 26.17, 23.21, 23.17.

IR (film): ν (cm^{-1}) 3462, 2980, 1739, 1622, 1489, 1364, 1178, 1025, 917, 733, 557.

HRMS (ESI, m/z) calcd for $C_{23}H_{26}FNNaO_5$ $(M+Na)^+$: 438.1693, found: 438.1687.



5f

To a solution of isatin-type ketone **4f** (54.3 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 280 μL, 2.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C for the 6 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afford **5f** as an orange oil (75.9 mg, 0.176 mmol, 88% yield).

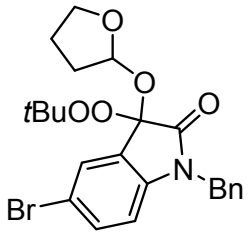
d.r. = 2.2: 1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.31 – 7.25 (m, 5H), 7.18 (ddd, *J* = 32.2, 8.4, 2.2 Hz, 1H), 6.55 (dd, *J* = 36.5, 8.4 Hz, 1H), 5.87 (dd, *J* = 458.4, 4.4 Hz, 1H), 4.96 – 4.91 (m, 1H), 4.82 (d, *J* = 16.0 Hz, 1H), 3.96 – 3.69 (m, 2H), 2.18 – 2.13 (m, 1H), 2.06 – 2.00 (m, 1H), 1.94 – 1.79 (m, 2H), 1.17 (d, *J* = 25.9 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.58, 168.88, 141.69, 140.41, 135.01, 134.89, 130.58, 130.06, 128.75, 128.71, 127.94, 127.76, 127.68, 127.65, 127.59, 127.56, 127.36, 127.03, 126.79, 124.53, 110.82, 110.37, 100.49, 99.95, 99.91, 98.73, 81.91, 81.46, 68.04, 67.91, 43.75, 43.62, 32.98, 32.64, 26.32, 26.22, 23.24, 23.22.

IR (film): ν (cm^{-1}) 3468, 2979, 1742, 1612, 1481, 1364, 1137, 1026, 965, 738, 546.

HRMS (ESI, m/z) calcd for $C_{23}H_{26}ClNNaO_5$ $(M+Na)^+$: 454.1397, found: 454.1395.



5g

To a solution of isatin-type ketone **4g** (63.2 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 280 μL, 2.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C for the 6 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afford **5g** as an orange oil (82.7 mg, 0.174 mmol, 87% yield).

d.r. = 1.4: 1.

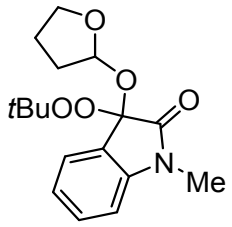
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 9.7, 2.0 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.30 – 7.25 (m, 5H), 6.51 (dd, *J* = 36.6, 8.4 Hz, 1H), 5.87 (dd, *J* = 459.6, 4.4 Hz, 1H), 4.96 – 4.91 (m, 1H), 4.81 (d, *J* = 16.0 Hz, 1H), 3.95 – 3.69 (m, 2H), 2.17 – 2.13 (m, 1H), 2.05 – 2.01 (m, 1H), 1.93 – 1.78 (m, 2H), 1.16 (d, *J* = 26.4 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.43, 168.75, 142.15, 140.89, 134.96, 134.83, 133.45, 132.94, 130.48, 129.51, 128.74, 128.70, 127.90, 127.68, 127.65, 127.01(s, 2C), 124.87,

115.21, 114.77, 111.30, 110.86, 100.49, 99.93, 99.90, 98.65, 81.90, 81.46, 68.03, 67.89, 43.70, 43.57, 32.96, 32.62, 26.30, 26.19, 23.22, 23.20.

IR (film): ν (cm^{-1}) 3464, 2979, 1739, 1610, 1479, 1364, 1138, 1025, 964, 735, 532.

HRMS (ESI, m/z) calcd for $C_{23}H_{26}BrNaO_5$ $(M+Na)^+$: 498.0892, found: 498. 0892.



5h

To a solution of isatin-type ketone **4h** (32.2 mg, 0.20 mmol) and tetrahydrofuran **2a** (160 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 280 μL, 2.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) were added in turn. The mixture was stirred at 25 °C for the 6 h, then concentrated to dryness. The residue was purified by silica gel chromatography (elution with EtOAc/PE = 1:5) to afford **5h** as an orange oil (58.5 mg, 0.182 mmol, 91% yield).

d.r. = 1.2: 1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 1H), 7.35 (dtd, *J* = 21.9, 7.8, 1.2 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.81 (dd, *J* = 26.8, 7.8 Hz, 1H), 6.20 – 5.43 (m, 1H), 3.97 – 3.66 (m, 2H), 3.18 (d, *J* = 1.9 Hz, 3H), 2.17 – 2.11 (m, 1H), 2.04 – 1.96 (m, 1H), 1.93 – 1.71 (m, 2H), 1.12 (d, *J* = 18.1 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.82, 168.94, 143.98, 142.79, 130.87, 130.35, 127.55, 126.56, 125.90, 125.28, 123.81, 122.90, 122.43, 121.95, 109.88, 108.63, 108.19, 100.24, 99.58, 99.09, 81.52, 80.98, 67.99, 67.86, 33.02, 32.56, 26.25, 26.14, 23.28, 23.27.

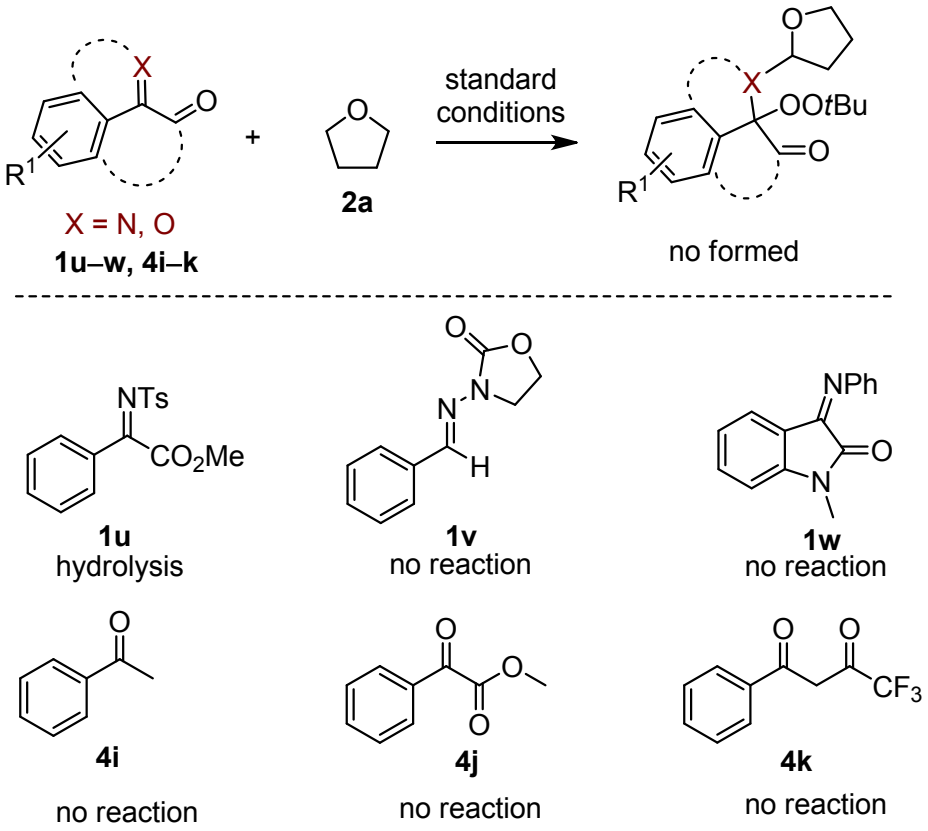
IR (film): ν (cm^{-1}) 3463, 2978, 1739, 1614, 1472, 1366, 1193, 1024, 964, 754, 536.

HRMS (ESI, m/z) calcd for $C_{17}H_{23}NnaO_5$ $(M+Na)^+$: 344.1474, found: 344.1467.

5. Scope Limitation of the Copper-Catalyzed Alkylation-Peroxidation Reactions

General procedure

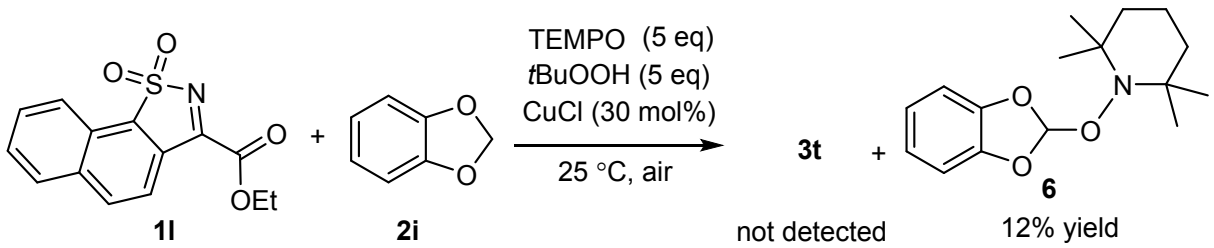
To a solution of imines **1u-w** or ketones **4i–k** (0.20 mmol) and tetrahydrofuran **2a** (2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 1.0 or 2.0 mmol) and copper chloride (0.020 or 0.040 mmol) were added in turn. After being stirred at 25 °C for 10-24 h, the reaction mixture was dectected by TLC and ^{1}H NMR analysis. The desired difunctionalized products were not formed.



Scheme S5. Scope limitation.

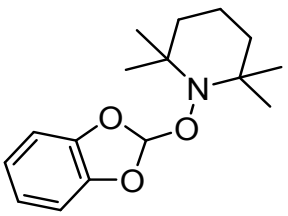
Conclusions: An α-carbonyl substituent next to the imino or carbonyl moiety was typically required, probably for stabilization of the products. Some of imines underwent hydrolysis other than the alkylation-peroxidation process.

6. Control Experiments



Scheme S6. Reaction **1l**+**2i**→**3t** in the presence of TEMPO.

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and **2i** (229 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, 156.2 mg, 1.0 mmol) were added in turn. Then the reaction was stirred at 25°C for 35 h, compound **3t** was not formed (detected by TLC and crude ^{1}H NMR analysis). The reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with EtOAc/PE = 1:20) to afford product **6** as a brown solid (33.3 mg, 0.120 mmol, yield: 12% based on TEMPO), mp 82−84 °C**.**



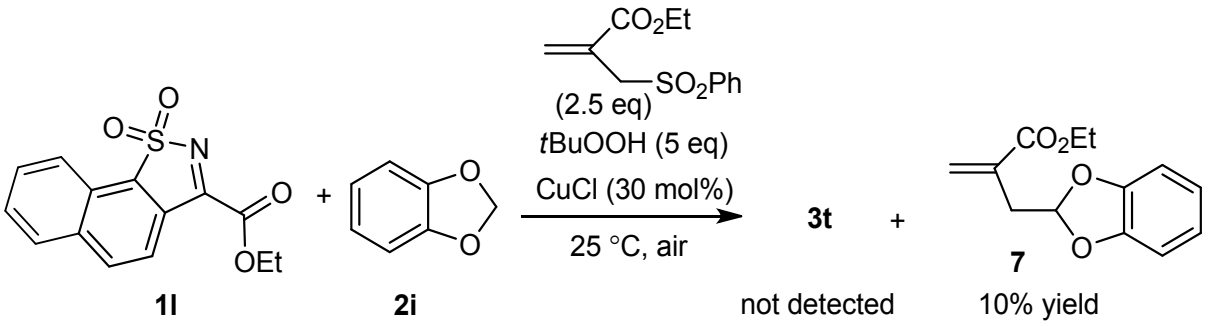
6

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.90 – 6.83 (m, 4H), 1.67 – 1.46 (m, 6H), 1.31 (s, 6H), 1.13 (s, 6H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.66, 126.77, 121.20, 108.15, 60.40, 39.97, 32.83, 20.38, 16.99.

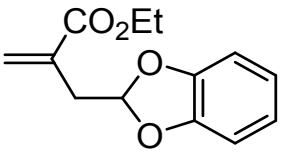
IR (film): ν (cm^{-1}) 3359, 3065, 2933, 2850, 2614, 1863, 1750, 1630, 1471, 1340, 1232, 1043, 919, 799, 640.

HRMS (ESI, m/z) calcd for $C_{16}H_{23}NNaO_3$ $(M+Na)^+$: 300.1576, found: 300.1569.



Scheme S7. Reaction **1l**+**2i**→**3t** in the presence of ethyl 2-((phenylsulfonyl)methyl)acrylate.

To a solution of cyclic *N*-sulfonylimine **1l** (57.9 mg, 0.20 mmol) and **2i** (229 μL, 2.0 mmol) in acetonitrile (4.0 mL), *tert*-butyl hydroperoxide (70% in water, 140 μL, 1.0 mmol) and copper chloride (4.0 mg, 0.040 mmol) ethyl 2-((phenylsulfonyl)methyl)acrylate (127.2 mg, 0.50 mmol) were added in turn. Then the reaction was stirred at 25°C for 35 h, compound **3t** was not formed (detected by TLC and crude ^{1}H NMR analysis). The reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with EtOAc/PE = 1:20) to afford product **7** as a white solid (11.7 mg, 0.050 mmol, yield: 10% based on ethyl 2-((phenylsulfonyl)methyl)acrylate), mp 73−74 °C**.**



7

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 – 6.75 (m, 4H), 6.37 (s, 1H), 6.31 (t, *J* = 5.1 Hz, 1H), 5.80 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.96 (d, *J* = 5.0 Hz, 2H), 1.33 – 1.30 (t, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.45, 147.32, 133.55, 129.38, 121.47, 109.45, 108.54, 61.06, 37.43, 14.18.

IR (film): ν (cm^{-1}) 3358, 2962, 2850, 1725, 1658, 1469, 1260, 1091, 799, 702, 626.

6. X-Ray Diffraction

Crystals of compound **3a** were obtained by slow diffusion from the solution in dichloromethane layered with *n*-hexane. Diffraction data were collected on a Bruker Apex CCD area detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 173 K during data collection. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on F^2 data of one twin domain using SHELXL-97. The structure is shown in Figure S1. Data collection and refinement statistics are given in Table S2. Crystallographic data (excluding structure factors) for **3a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1842572.

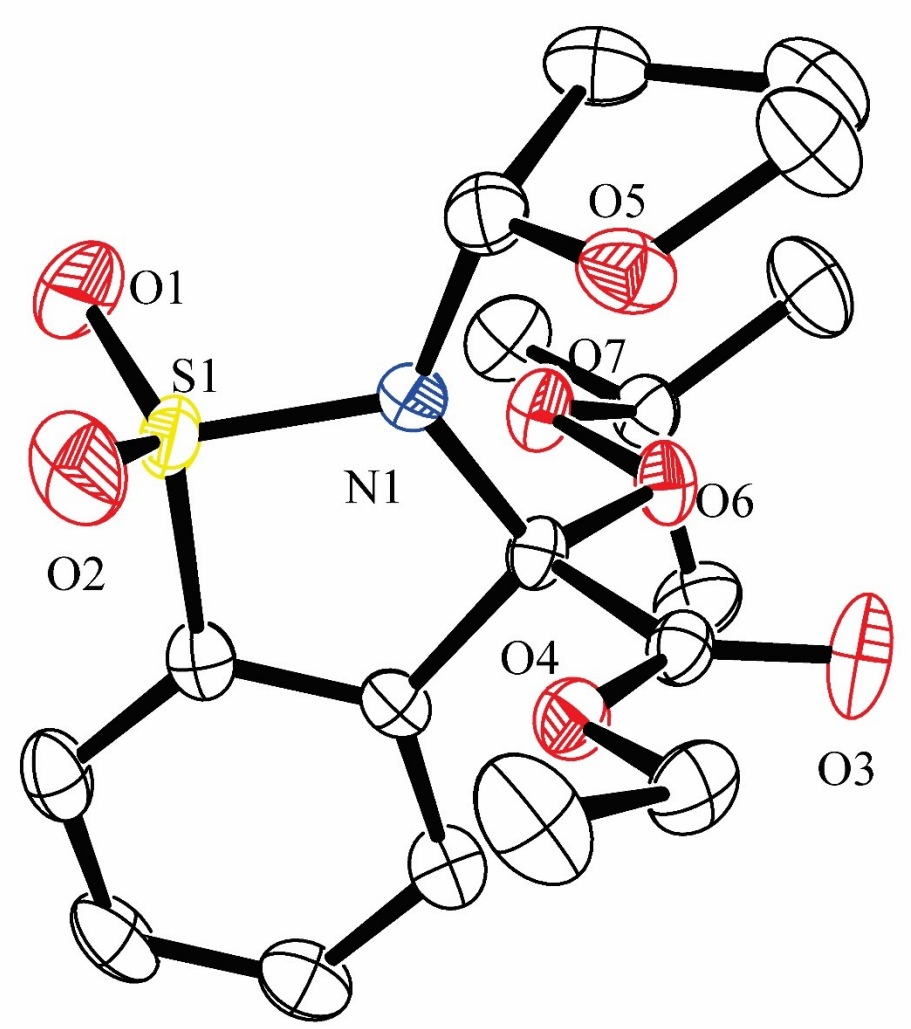


Figure S1. Ortep drawing of **3a** with 50% probability thermal ellipsoids.

Table S2. Data collection and refinement statistics for the compounds **3a.**

	3a
Empirical formula	$C_{45}H_{44}ClIrN_4OS_2$
Formula weight	948.61
Temperature (K)	173(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Cell dimensions	
a, b, c (Å)	18.999, 13.938, 18.330
α, β, γ (°)	90, 100.52, 90
Volume ($Å^3$)	4772.4(17)
Z	4
Density (calculated, mg/m^3)	1.320
Absorption coefficient (mm^{-1})	2.975
F(000)	1904
Crystal size (mm^3)	0.20 x 0.17 x 0.14
Theta range for data collection	2.18 to 26.00°
Index ranges	-23<=h<=23, -17<=k<=17, -22<=l<=22
Reflections collected	28219
Independent reflections	8827 [R(int) = 0.0727]
Completeness	94.0 %
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8827 / 0 / 487
Goodness-of-fit on F^2	0.999
Final R indices [I>2sigma(I)]	R1 = 0.0597, wR2 = 0.1642
R indices (all data)	R1 = 0.0751, wR2 = 0.1909
Largest diff. peak and hole ($e.Å^{-3}$)	1.322 and -2.400

7. References

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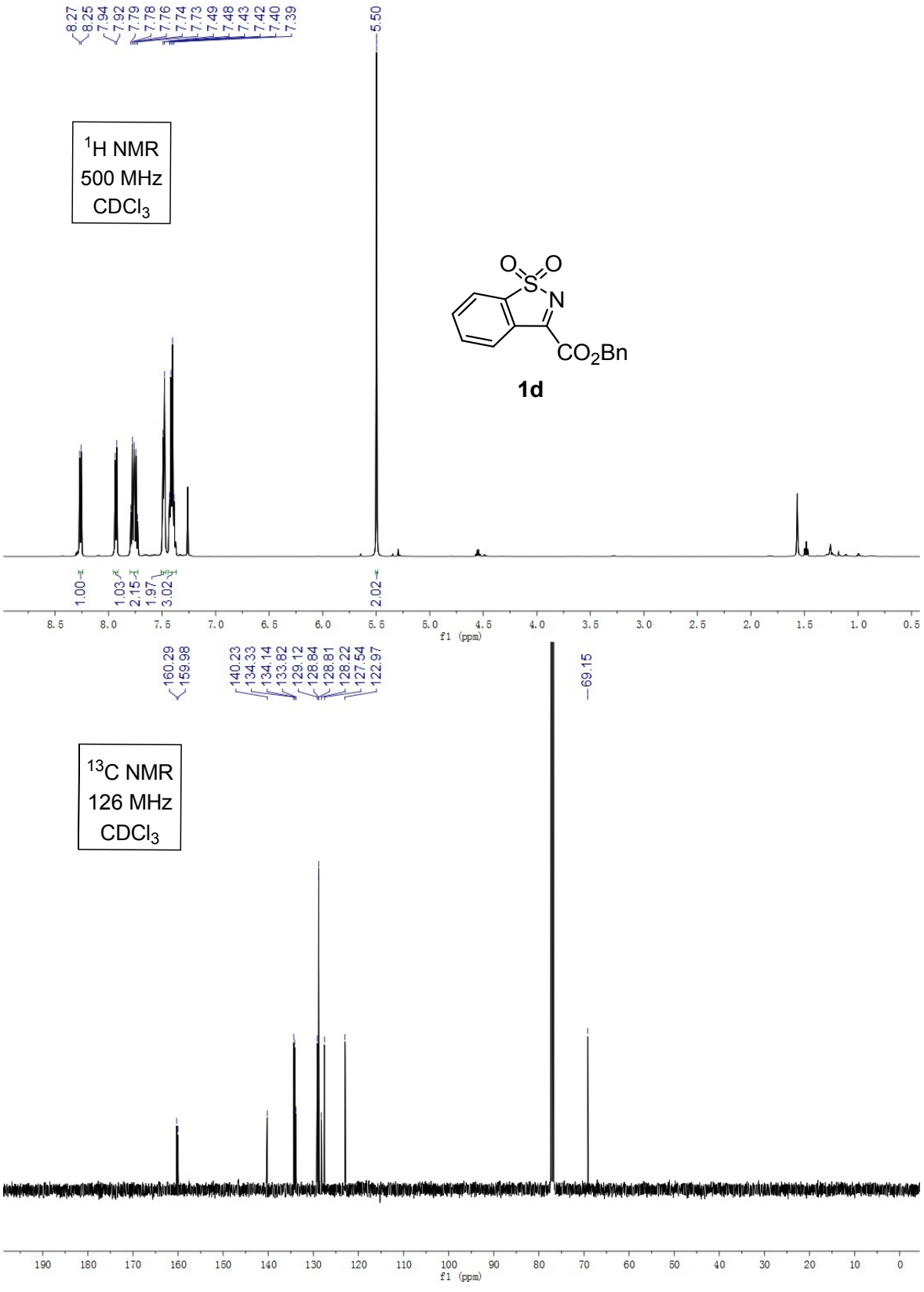
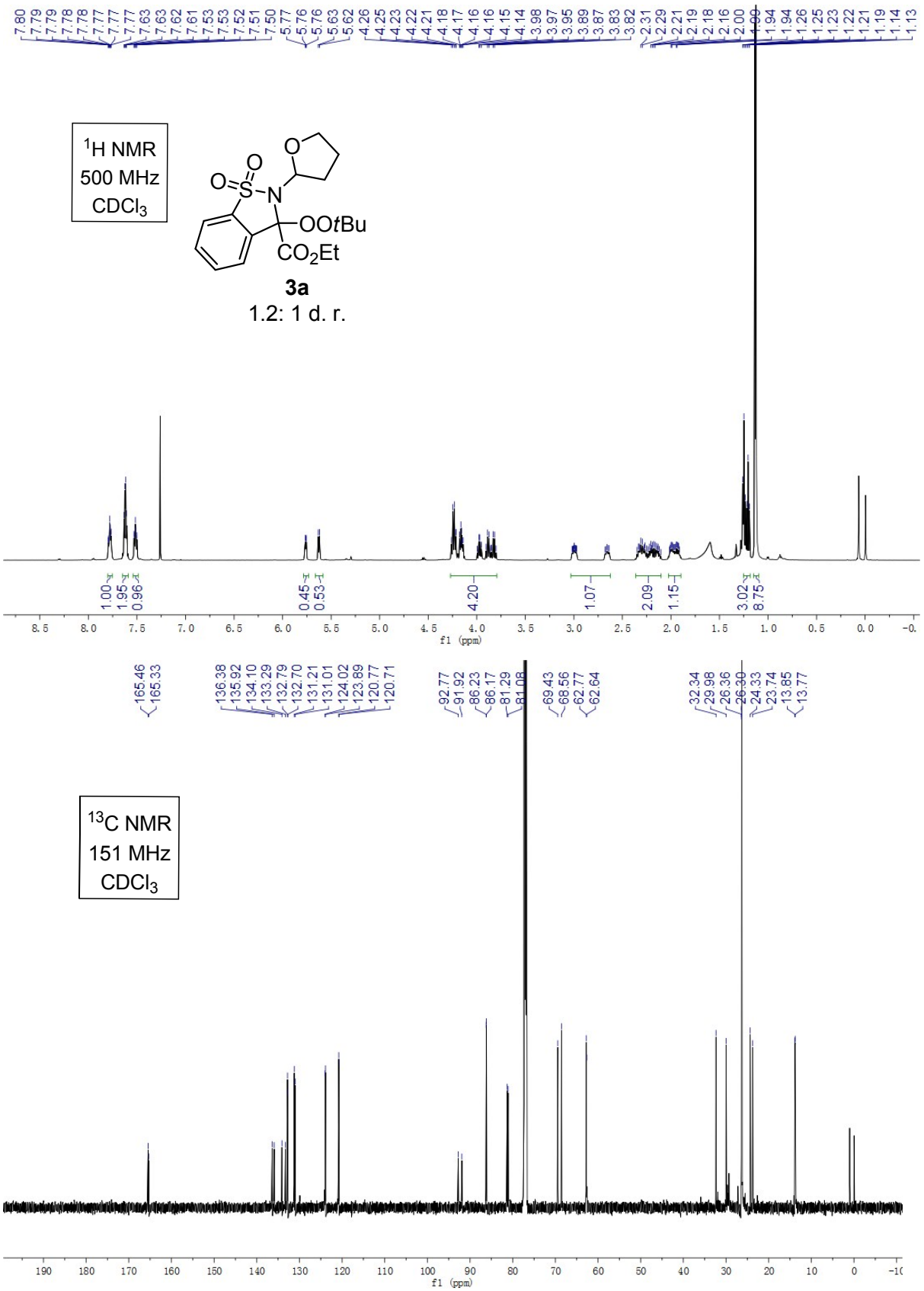
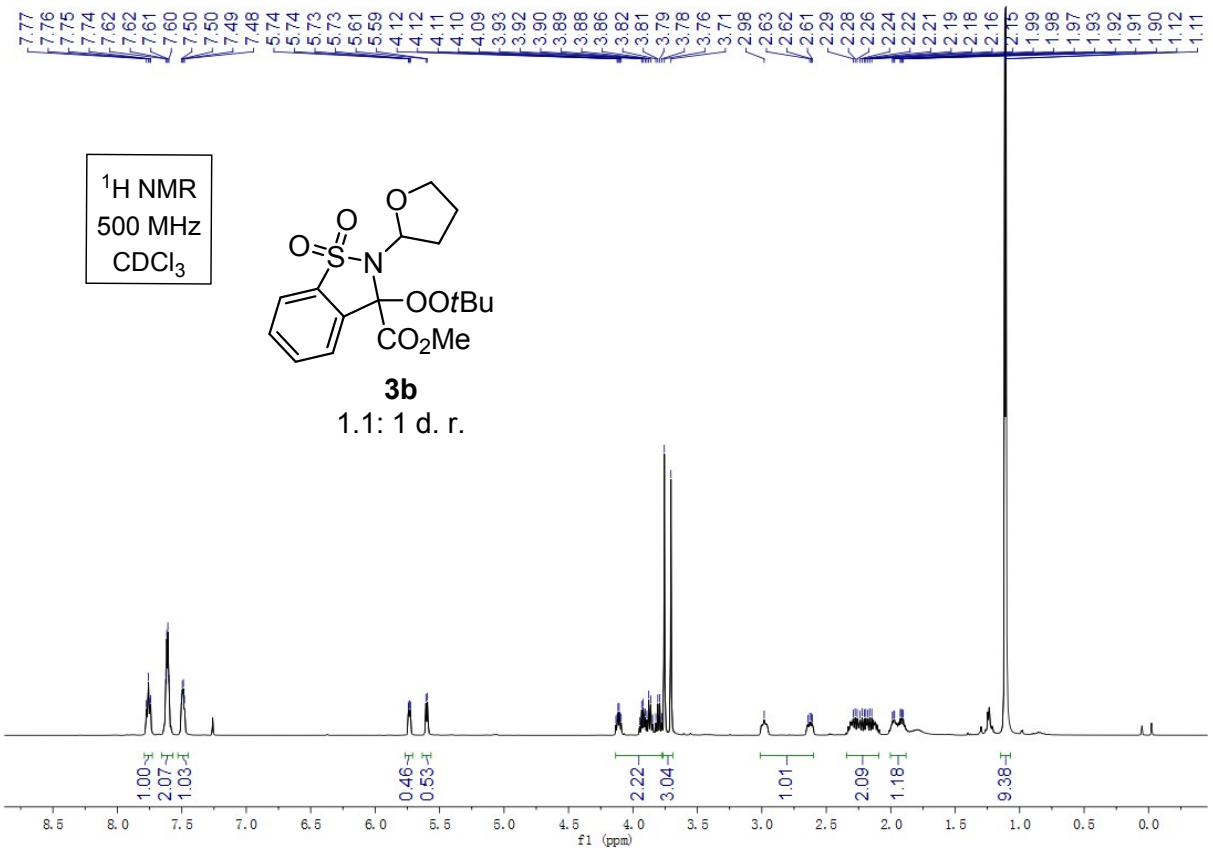
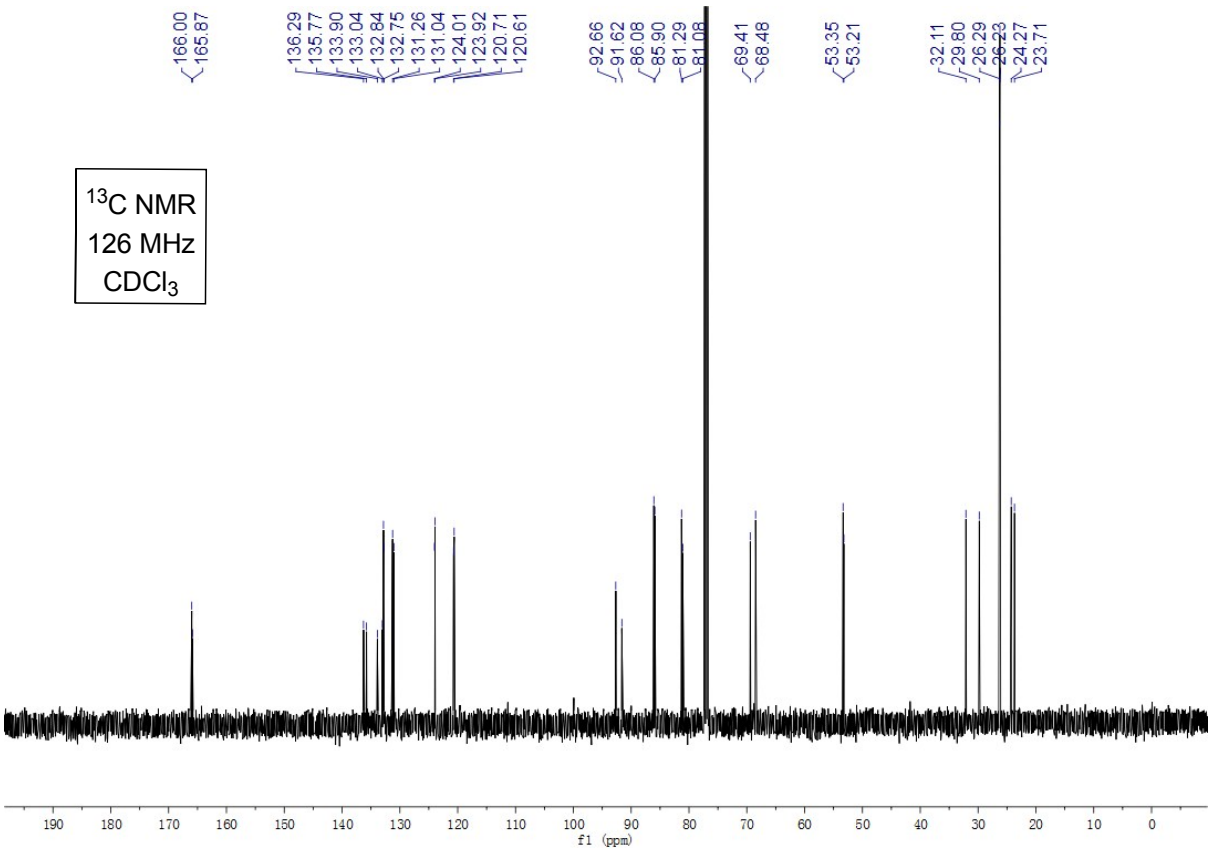
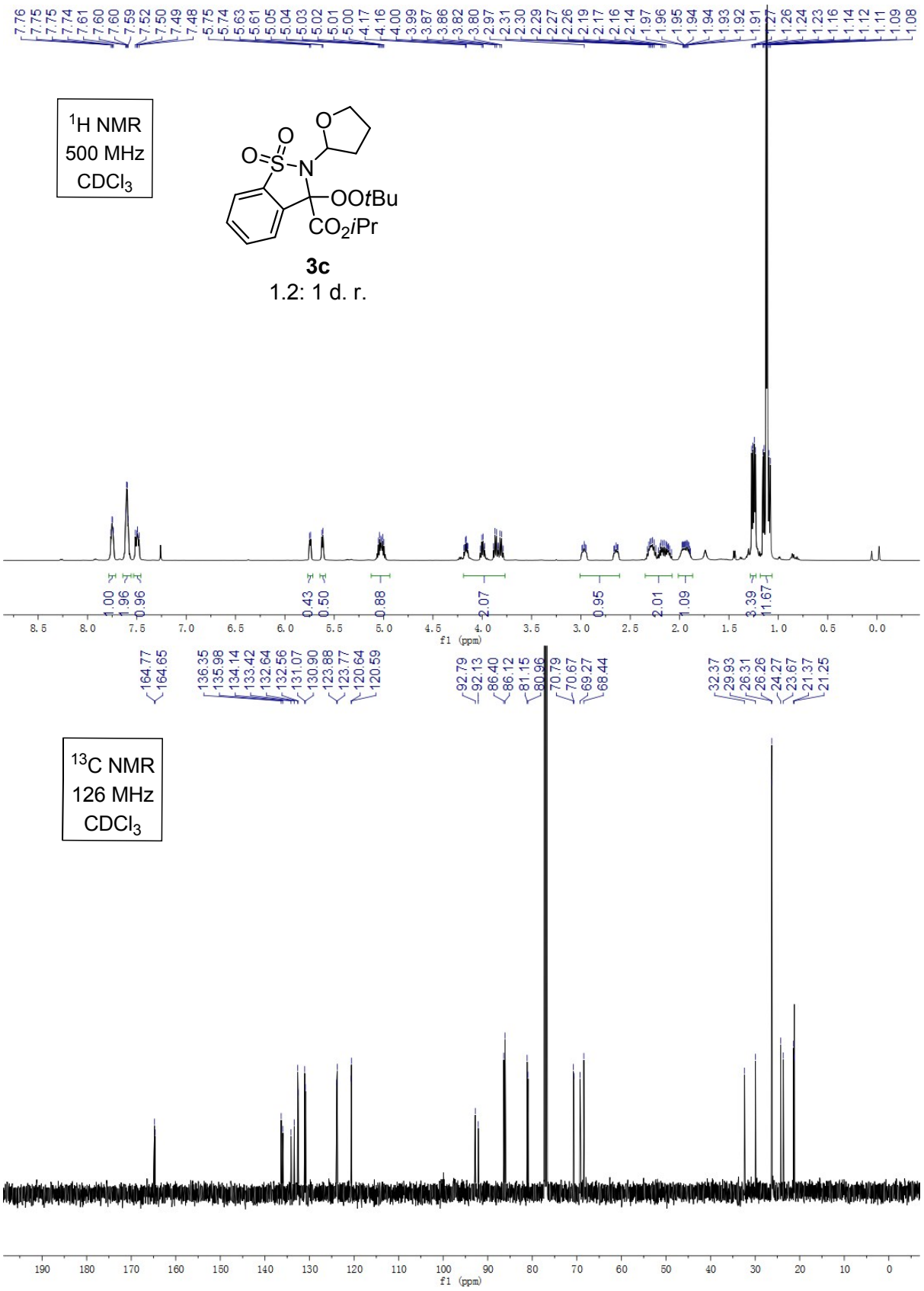
8. ^{1}H and ^{13}C NMR Spectrum

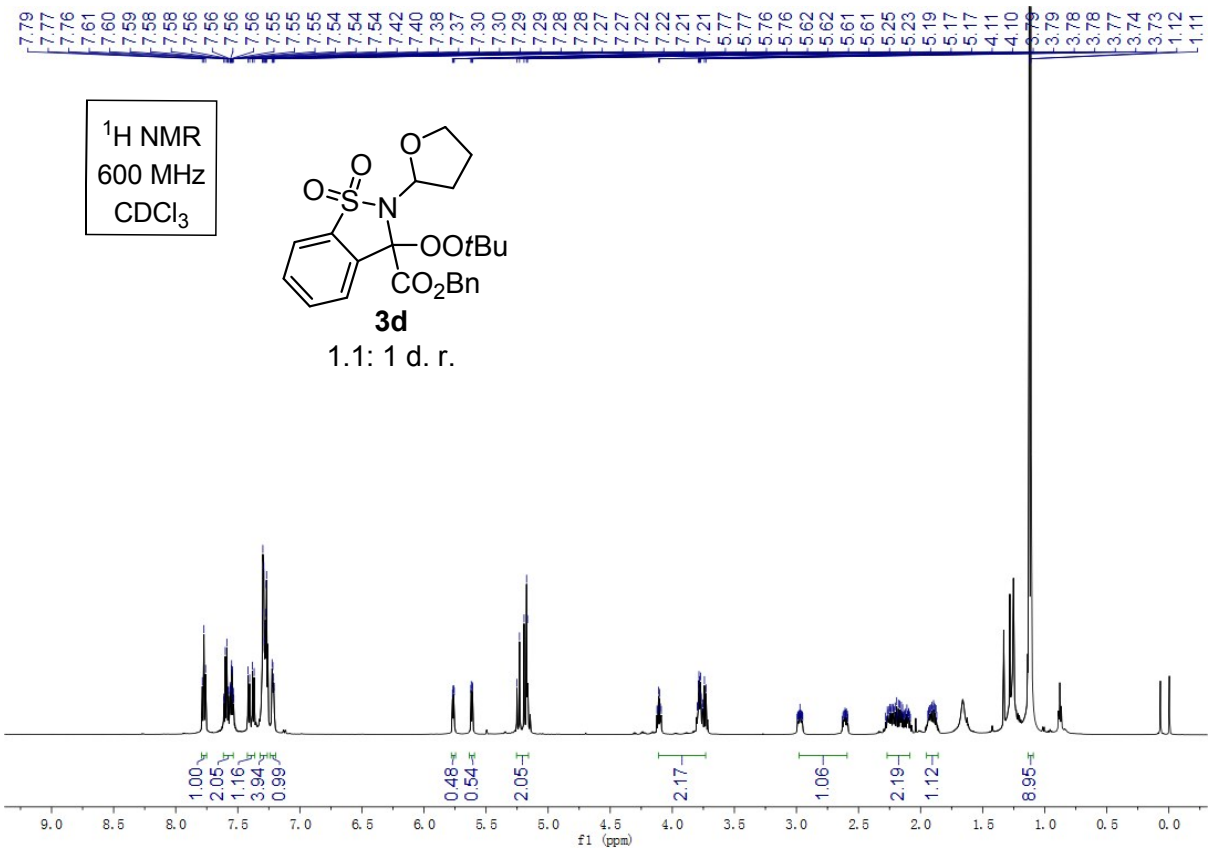



7.80 7.79 7.79 7.78 7.78 7.77 7.77 7.77 7.63 7.62 7.61 7.53 7.53 7.52 7.51 7.50 5.77 5.76 5.76 5.63 5.62 4.26 4.25 4.23 4.22 4.21 4.18 4.17 4.16 4.16 4.15 4.14 3.98 3.97 3.95 3.89 3.87 3.83 3.82 2.31 2.29 2.21 2.19 2.18 2.16 2.00 1.94 1.94 1.26 1.25 1.23 1.22 1.21 1.19 1.14 1.13
1H NMR
500 MHz
CDCl3
O
O
O=S-N
OOtBu
CO2Et
3a
1.2: 1 d. r.
1.00 1.95 0.96 0.45 0.53 4.20 1.07 2.09 1.15 3.02 8.75
f1 (ppm)
165.46 165.33 136.38 135.92 134.10 133.29 132.79 132.70 131.21 131.01 124.02 123.89 120.77 120.71 92.77 91.92 86.23 86.17 81.29 81.08 69.43 68.56 62.77 62.64 32.34 29.98 26.36 26.30 24.33 23.74 13.85 13.77
13C NMR
151 MHz
CDCl3
f1 (ppm)


7.77 7.76 7.75 7.74 7.62 7.62 7.61 7.60 7.50 7.50 7.49 7.48 5.74 5.74 5.73 5.73 5.61 5.59 4.12 4.12 4.11 4.10 4.09 3.93 3.92 3.90 3.89 3.88 3.86 3.82 3.81 3.79 3.78 3.76 3.71 2.98 2.63 2.62 2.61 2.29 2.28 2.26 2.24 2.22 2.21 2.19 2.18 2.16 2.15 1.99 1.98 1.97 1.93 1.92 1.91 1.90 1.12 1.11
1H NMR
500 MHz
CDCl3
O
O
O=S-N
OOtBu
CO2Me
3b
1.1: 1 d. r.
1.00 2.07 1.03 0.46 0.53 2.22 3.04 1.01 2.09 1.18 9.38
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

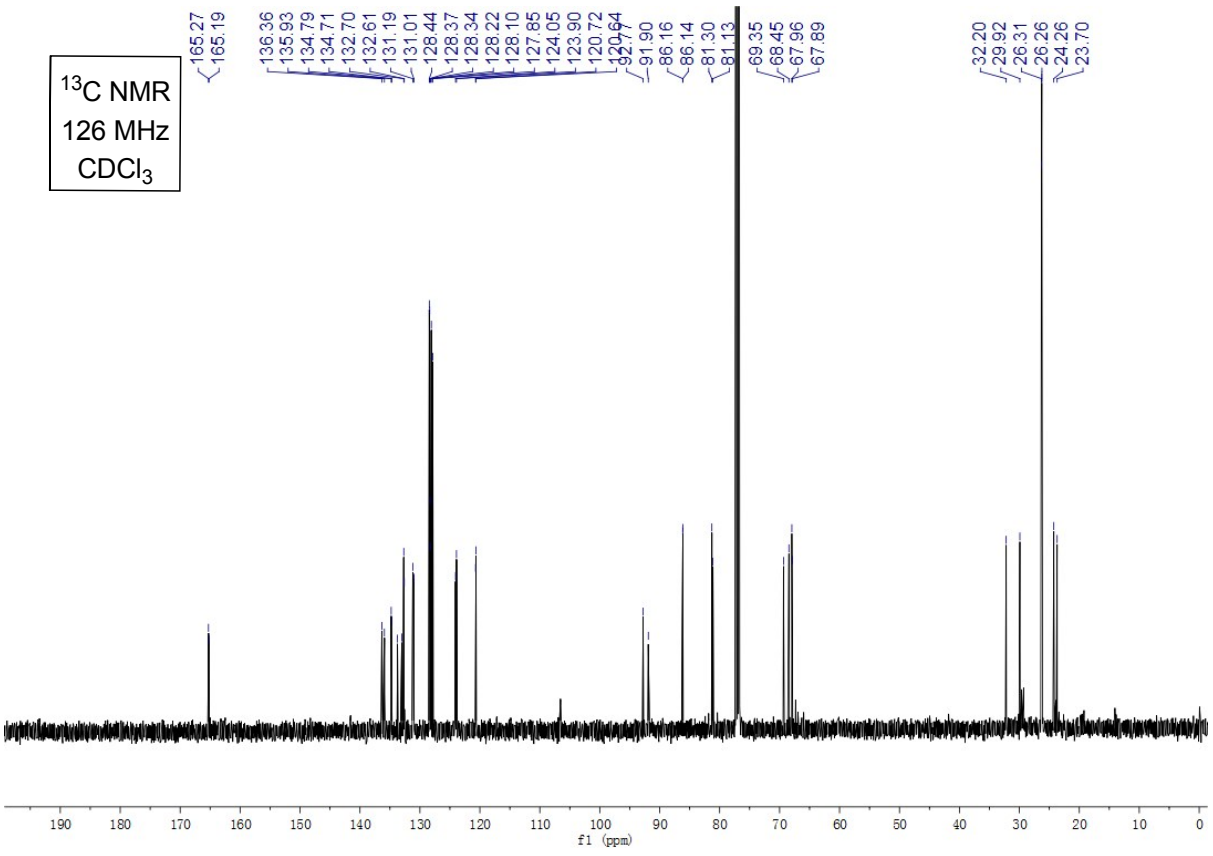

166.00 165.87 136.29 135.77 133.90 133.04 132.84 132.75 131.26 131.04 124.01 123.92 120.71 120.61 92.66 91.62 86.08 85.90 81.29 81.08 69.41 68.48 53.35 53.21 32.11 29.80 26.29 26.23 24.27 23.71
13C NMR
126 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

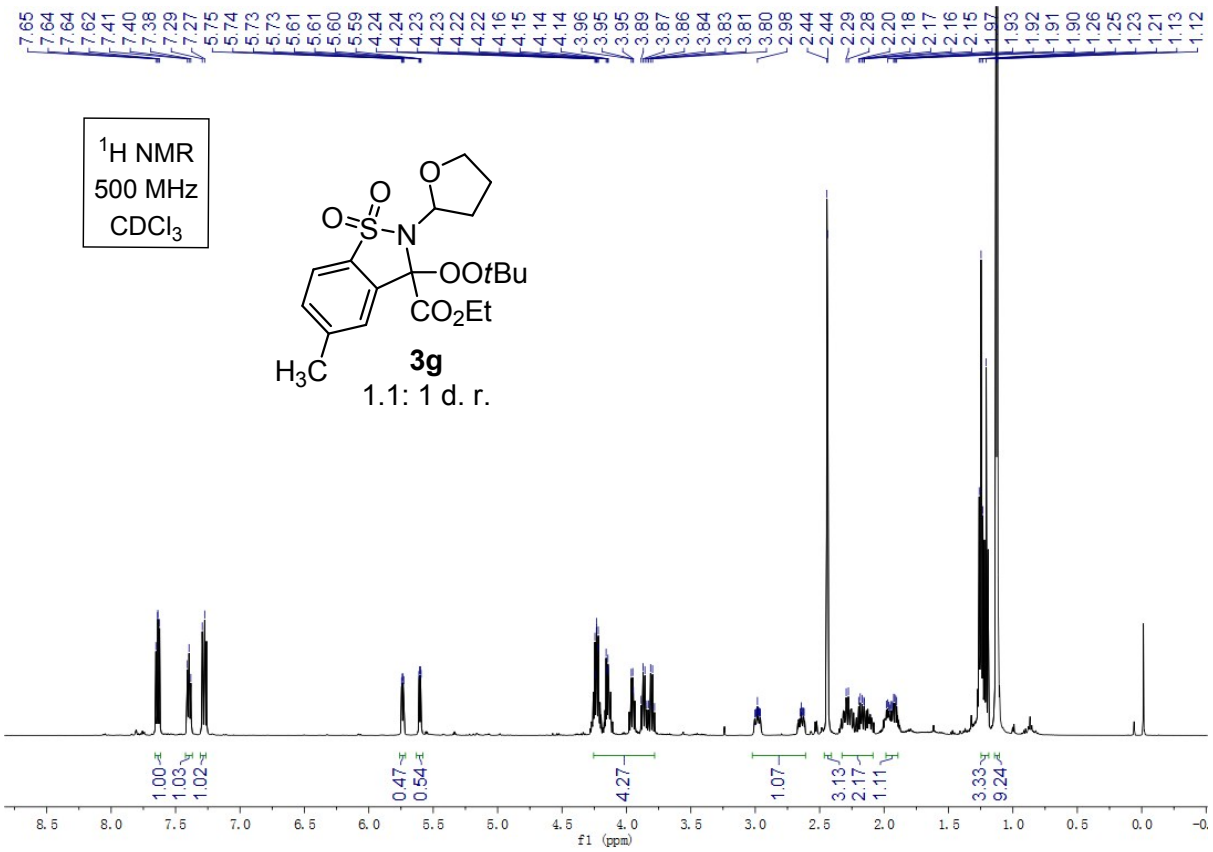

^{1}H NMR
500 MHz
$CDCl_3$
OOtBu
CO_2iPr
3c
1.2: 1 d. r.
^{13}C NMR
126 MHz
$CDCl_3$
f1 (ppm)

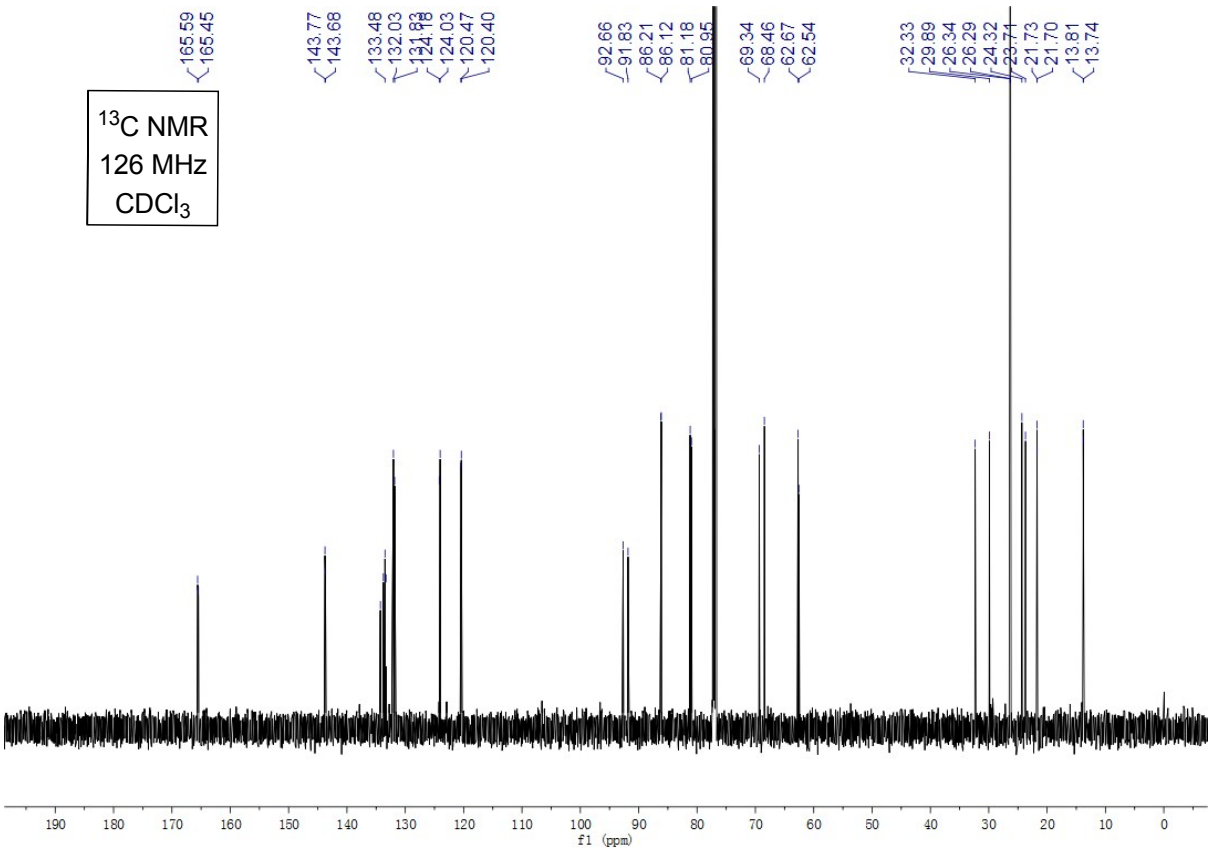


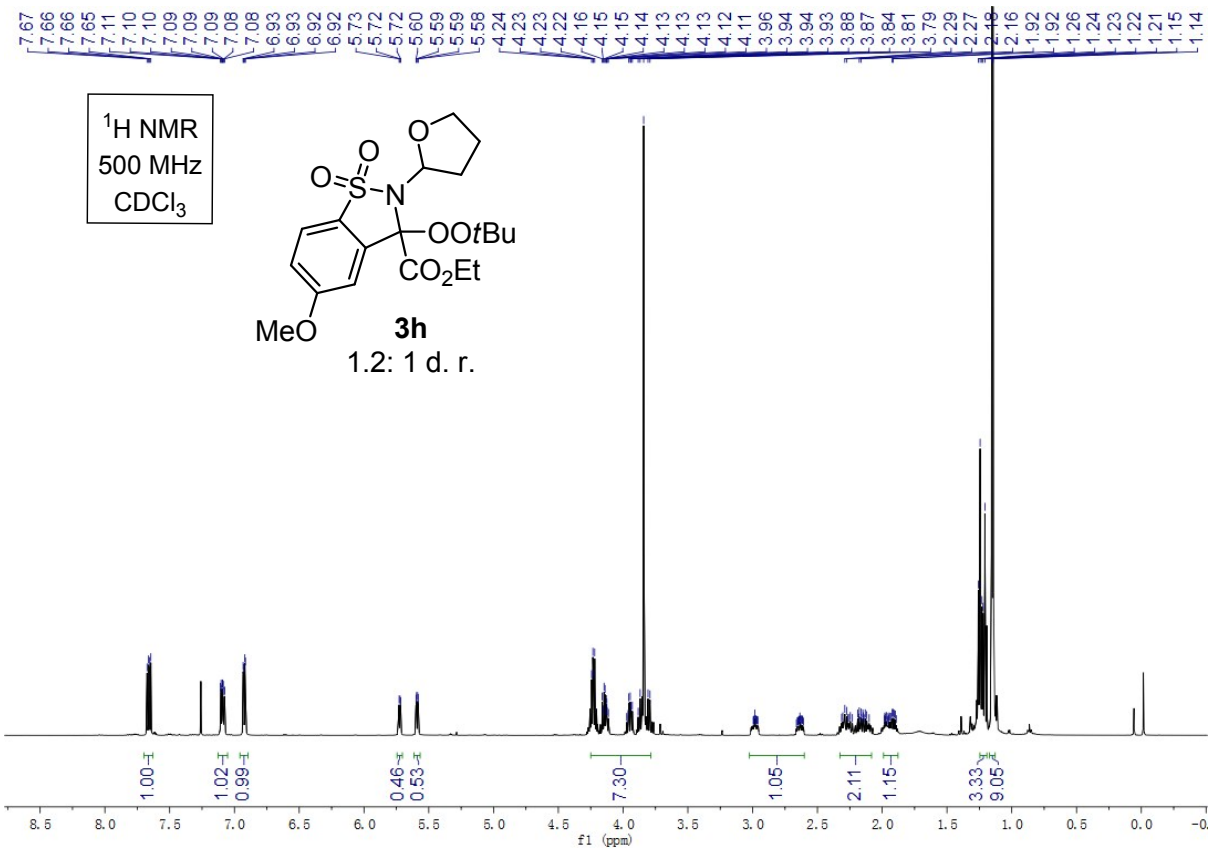
3d

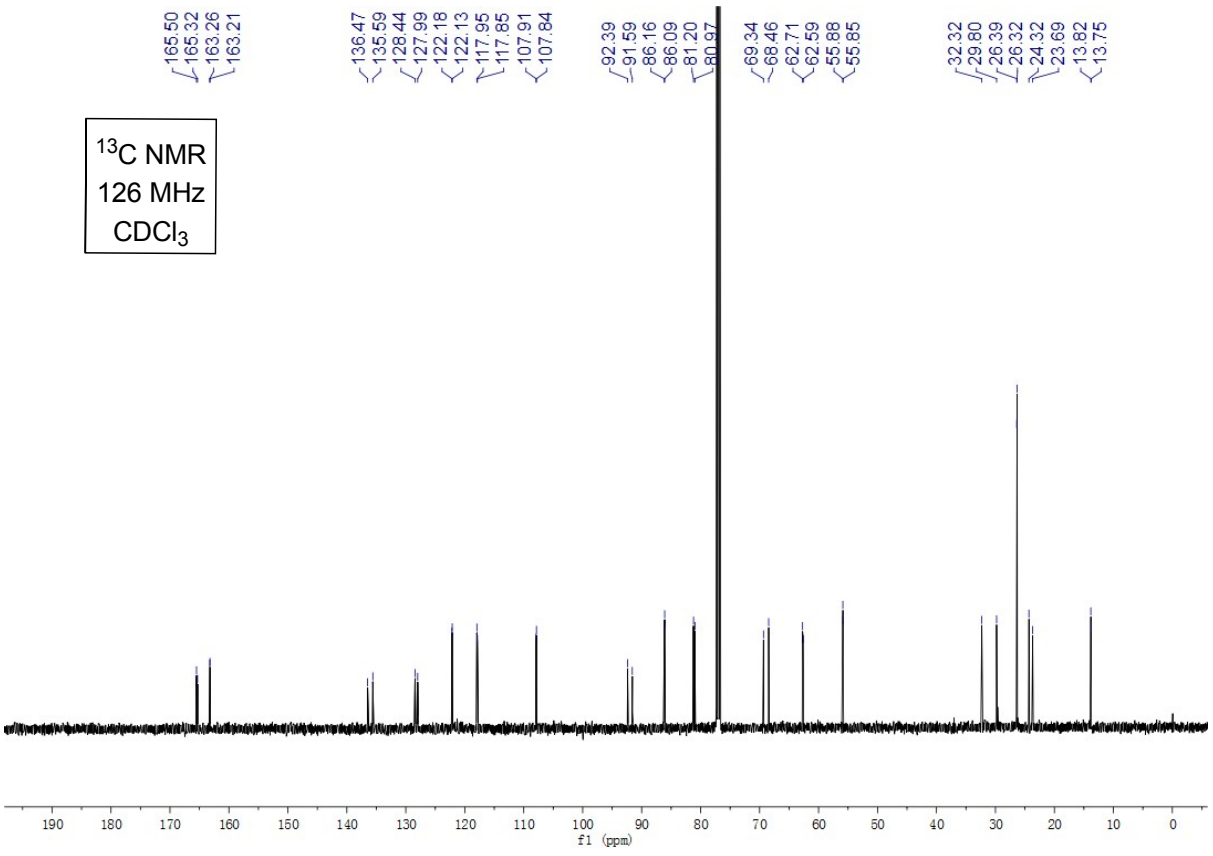
1.1: 1 d. r.

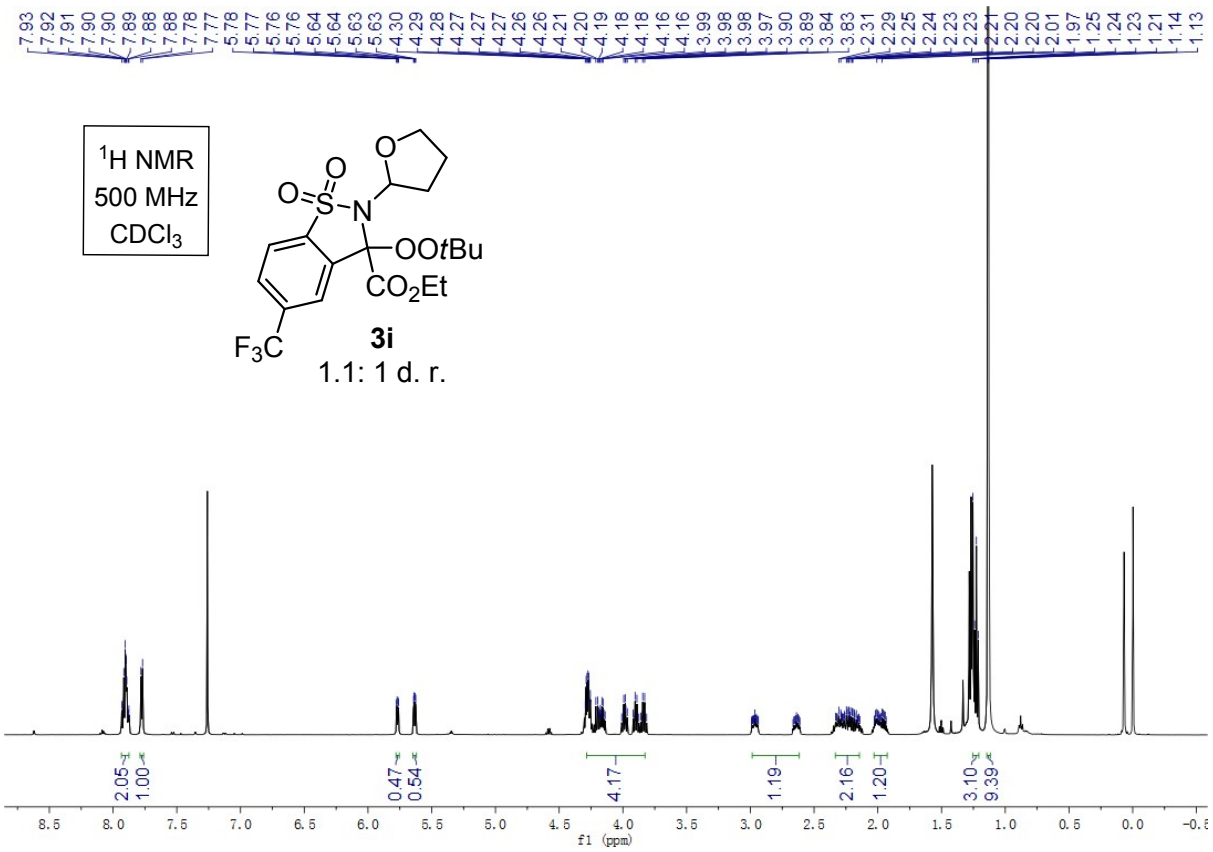


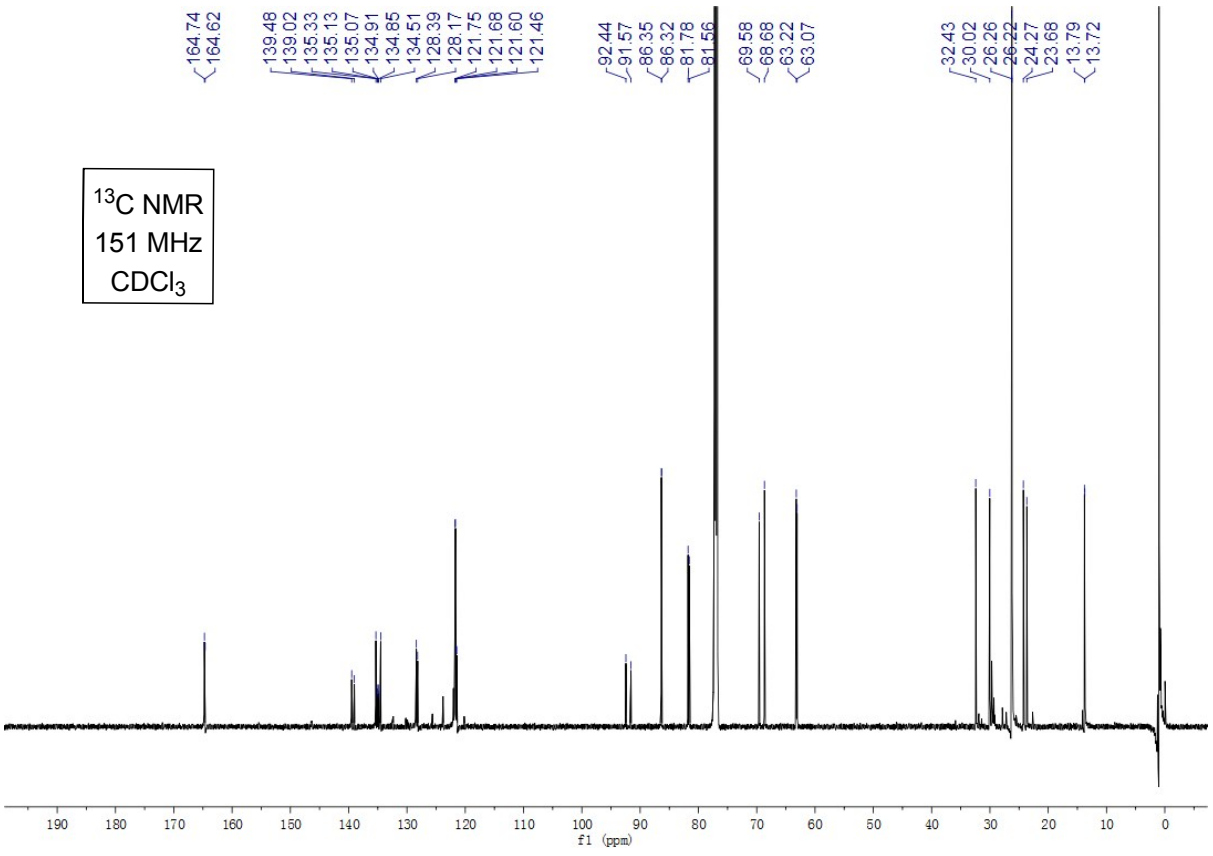

^{1}H NMR
500 MHz
$CDCl_3$
O
O
O=S-N
OO*t*Bu
CO_2Et
H_3C
3g
1.1: 1 d. r.
f1 (ppm)

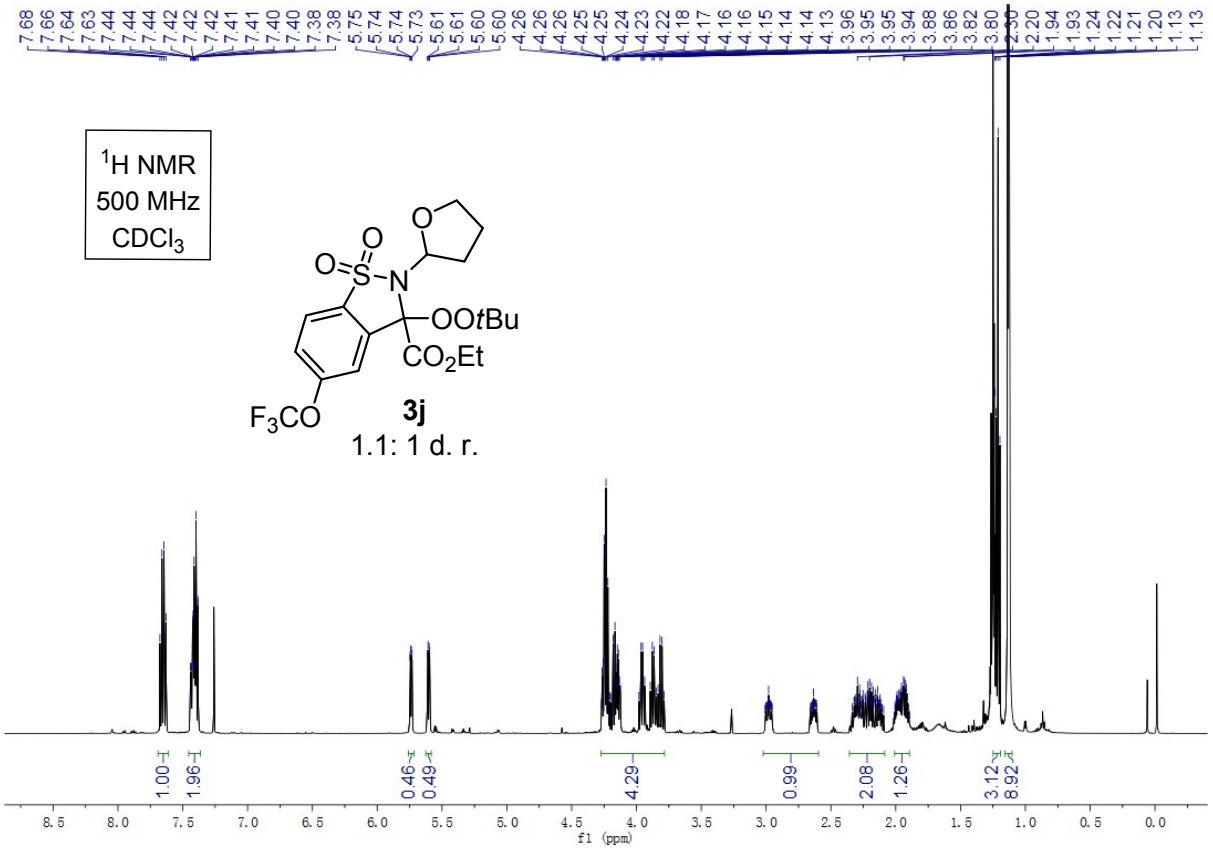

^{13}C NMR
126 MHz
$CDCl_3$
f1 (ppm)

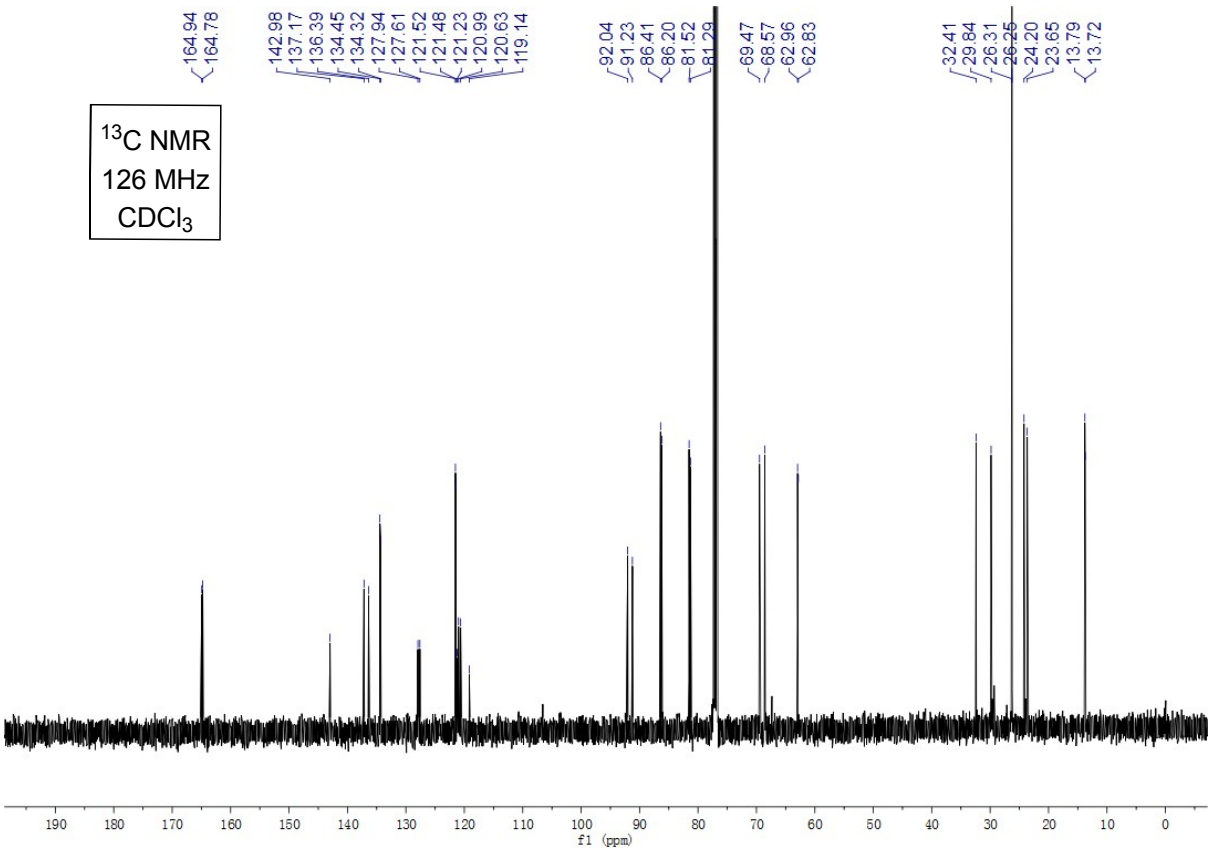

^{1}H NMR
500 MHz
$CDCl_3$
OOtBu
CO_2Et
MeO
3h
1.2: 1 d. r.
f1 (ppm)

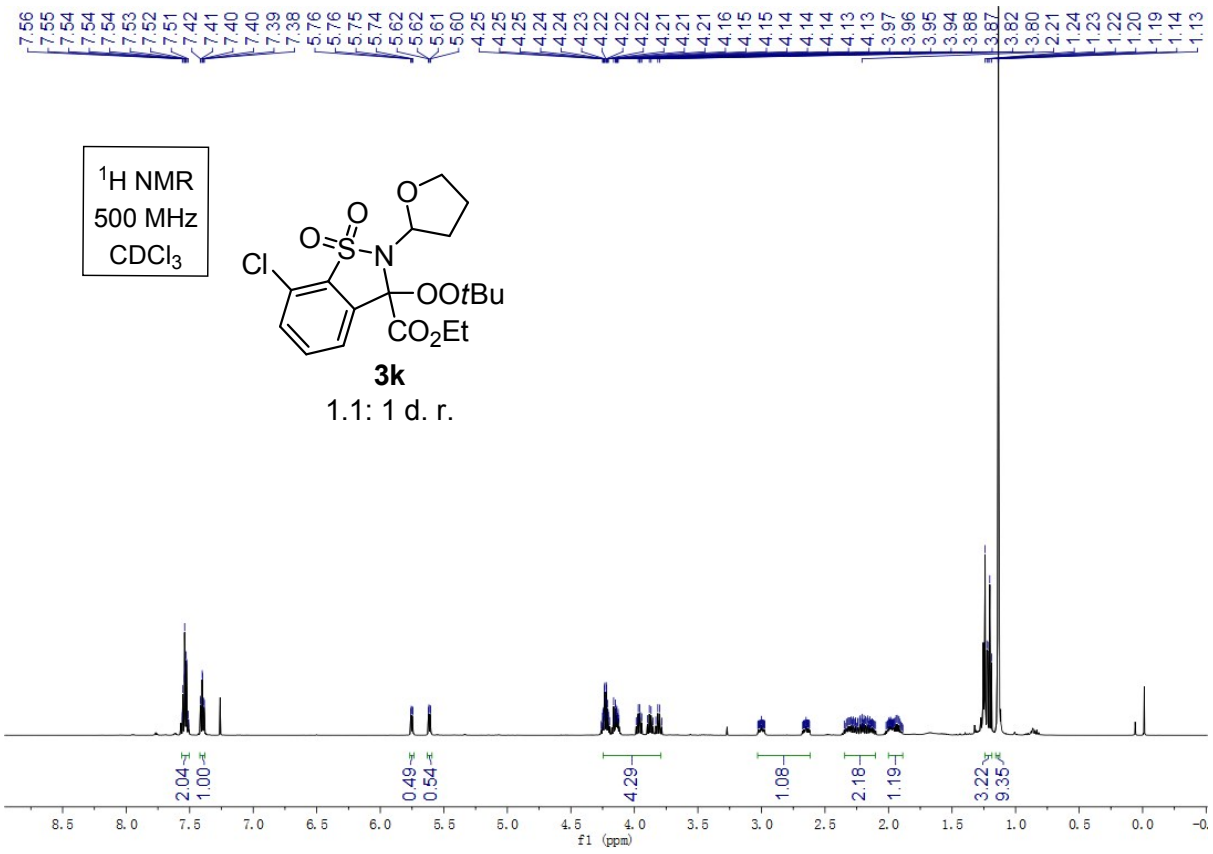

^{13}C NMR
126 MHz
$CDCl_3$
f1 (ppm)

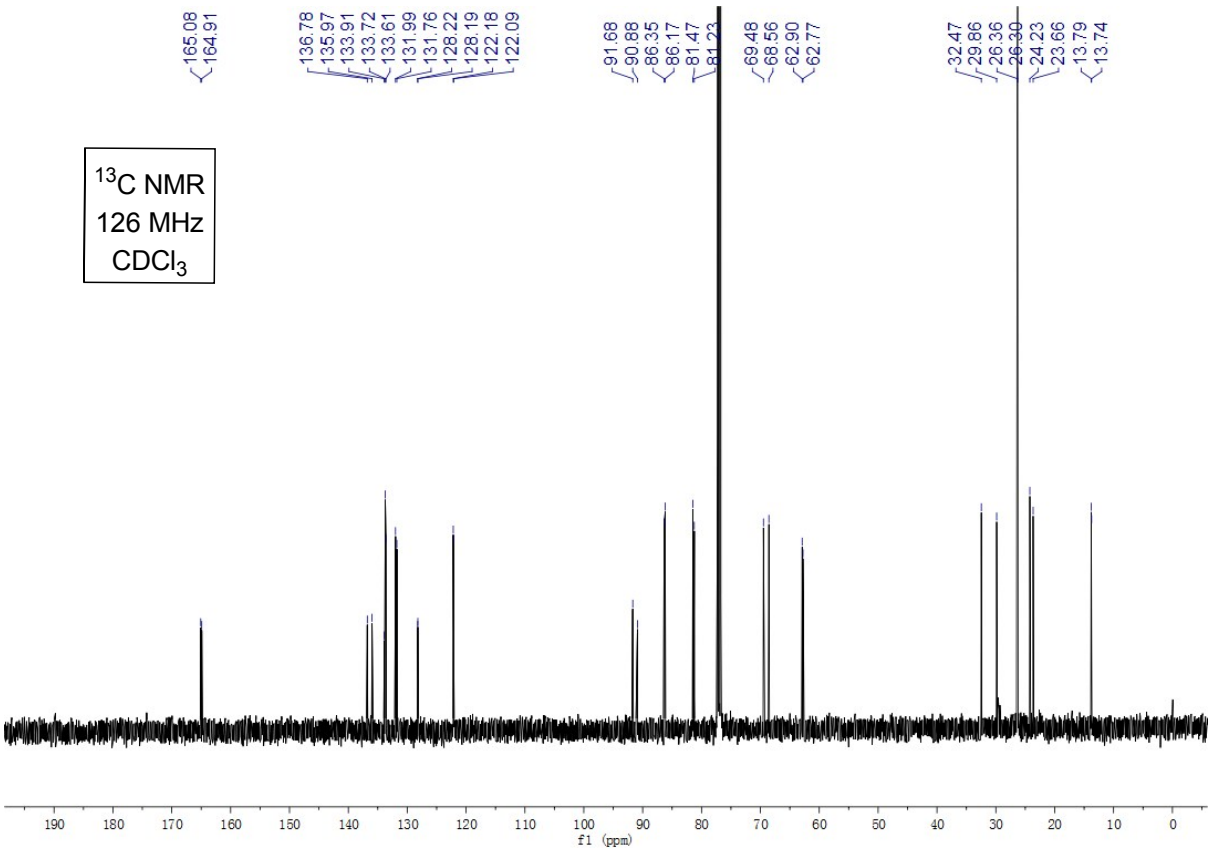

7.93 7.92 7.91 7.90 7.90 7.89 7.88 7.88 7.78 7.77 5.78 5.77 5.76 5.76 5.64 5.64 5.63 5.63 4.30 4.29 4.28 4.27 4.27 4.27 4.26 4.26 4.21 4.20 4.19 4.18 4.18 4.16 4.16 3.99 3.98 3.98 3.97 3.90 3.89 3.84 3.83 2.31 2.29 2.25 2.24 2.23 2.23 2.21 2.20 2.20 2.01 1.97 1.25 1.24 1.23 1.21 1.14 1.13
1H NMR
500 MHz
CDCl3
O
O
O=S-N
OOtBu
CO2Et
F3C
3i
1.1: 1 d. r.
2.05
1.00
0.47
0.54
4.17
1.19
2.16
1.20
3.10
9.39
f1 (ppm)

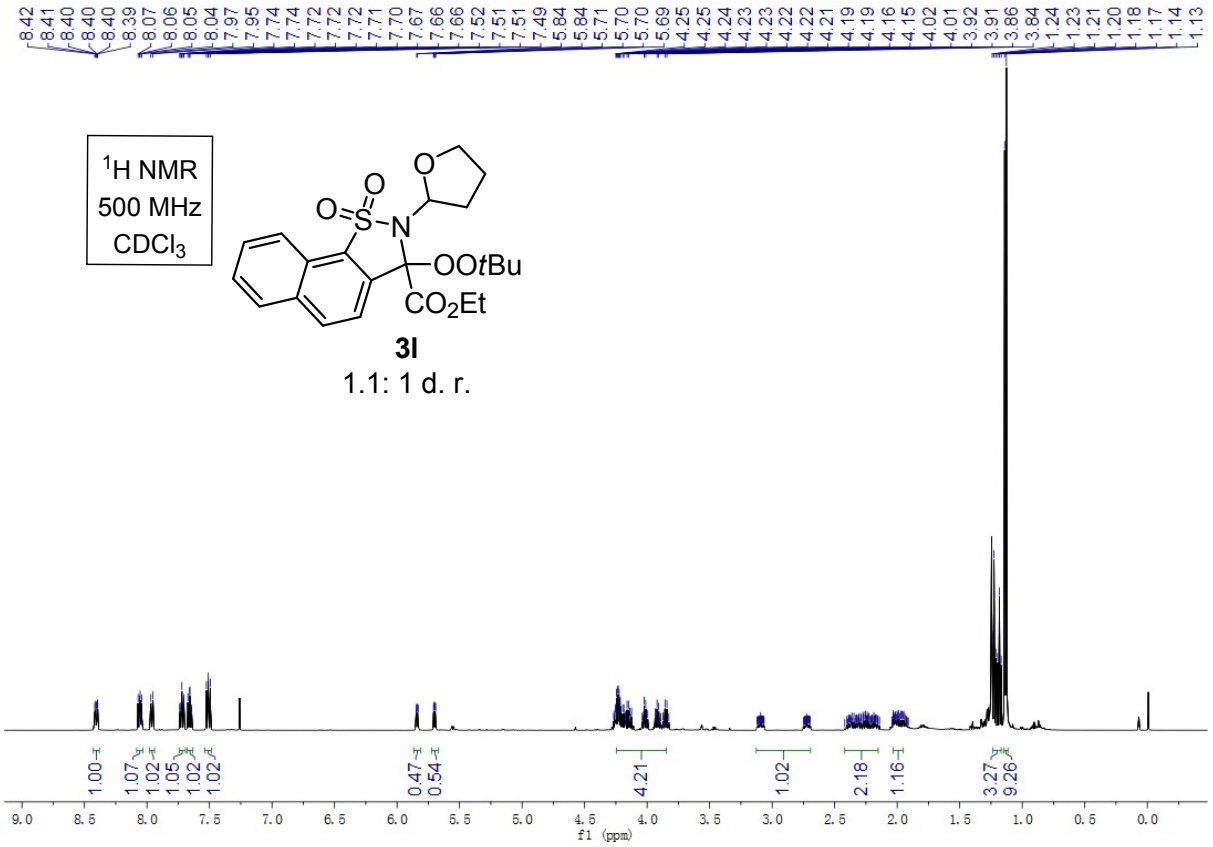

164.74 164.62 139.48 139.02 135.33 135.13 135.07 134.91 134.85 134.51 128.39 128.17 121.75 121.68 121.60 121.46 92.44 91.57 86.35 86.32 81.78 81.56 69.58 68.68 63.22 63.07 32.43 30.02 26.26 26.22 24.27 23.68 13.79 13.72
13C NMR
151 MHz
CDCl3
f1 (ppm)


7.68 7.66 7.64 7.63 7.44 7.44 7.44 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.38 7.38
5.75 5.74 5.74 5.73 5.61 5.61 5.60 5.60
4.26 4.26 4.25 4.25 4.24 4.23 4.22 4.18 4.17 4.16 4.16 4.15 4.14 4.14 4.13
3.96 3.95 3.95 3.94 3.88 3.86 3.82 3.80 2.30 2.20 1.94 1.93 1.24 1.22 1.21 1.20 1.13 1.13
1H NMR
500 MHz
CDCl3
O
O
O=S-N
OOtBu
CO2Et
F3CO
3j
1.1: 1 d. r.
1.00 1.96 0.46 0.49 4.29 0.99 2.08 1.26 3.12 8.92
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.94 164.78
142.98 137.17 136.39 134.45 134.32 127.94 127.61 121.52 121.48 121.23 120.99 120.63 119.14
92.04 91.23 86.41 86.20 81.52 81.29
69.47 68.57 62.96 62.83
32.41 29.84 26.31 26.25 24.20 23.65 13.79 13.72
13C NMR
126 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.56 7.55 7.54 7.54 7.54 7.53 7.52 7.51 7.42 7.41 7.40 7.40 7.39 7.38 5.76 5.76 5.75 5.74 5.62 5.62 5.61 5.60 4.25 4.25 4.24 4.24 4.23 4.22 4.22 4.21 4.21 4.21 4.16 4.15 4.15 4.14 4.14 4.14 4.13 4.13 3.97 3.96 3.95 3.94 3.88 3.87 3.82 3.80 2.21 1.24 1.23 1.22 1.20 1.19 1.14 1.13
1H NMR
500 MHz
CDCl3
Cl
O
O
S
N
O
OOtBu
CO2Et
3k
1.1: 1 d. r.
2.04
1.00
0.49
0.54
4.29
1.08
2.18
1.19
3.22
9.35
f1 (ppm)

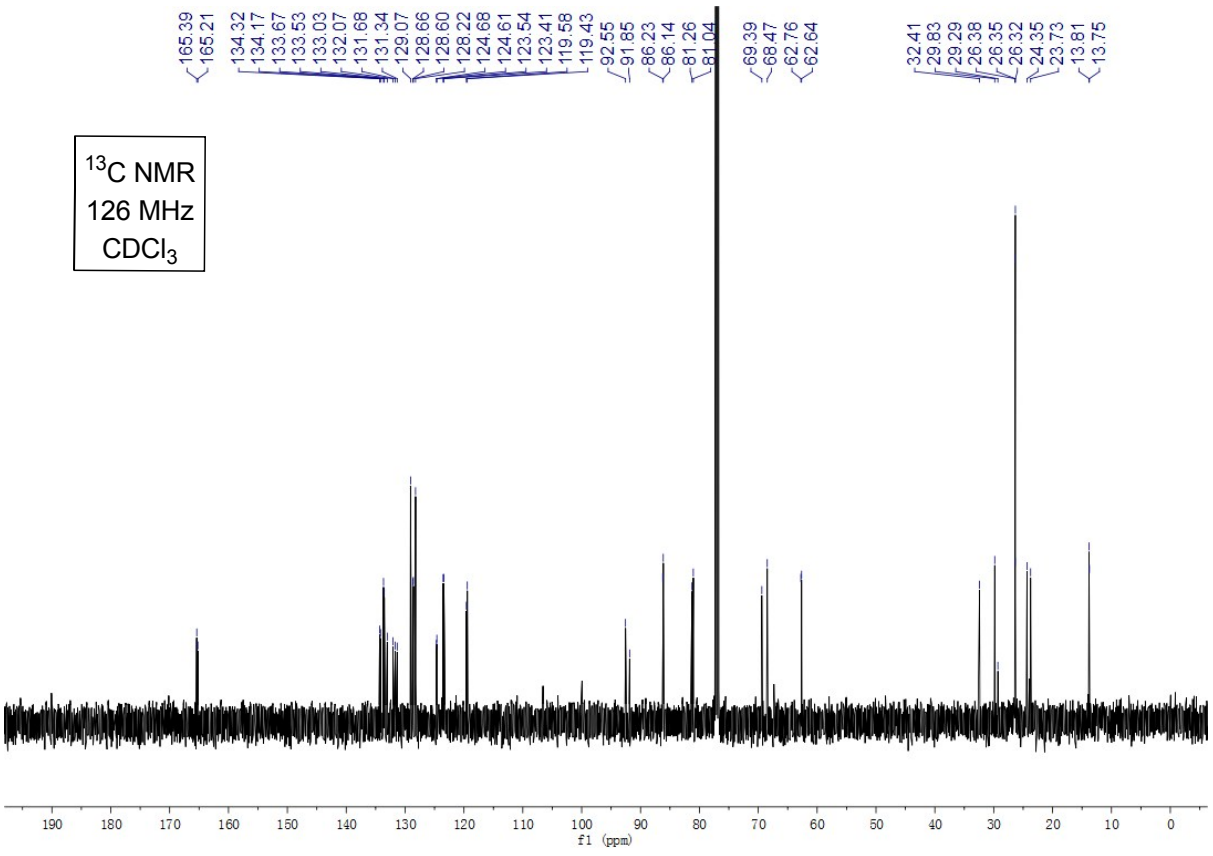

165.08 164.91 136.78 135.97 133.91 133.72 133.61 131.99 131.76 128.22 128.19 122.18 122.09 91.68 90.88 86.35 86.17 81.47 81.23 69.48 68.56 62.90 62.77 32.47 29.86 26.36 26.30 24.23 23.66 13.79 13.74
13C NMR
126 MHz
CDCl3
f1 (ppm)



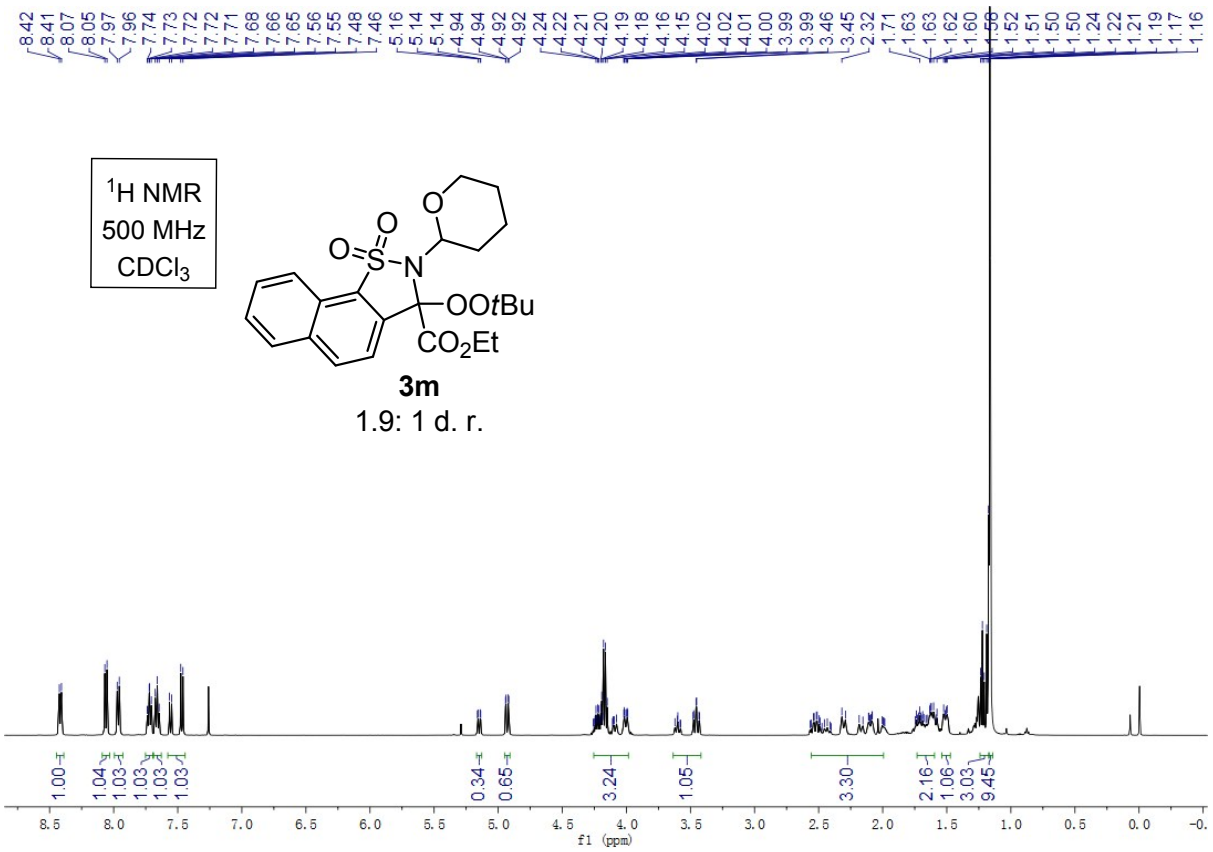
^{1}H NMR
500 MHz
$CDCl_3$

3l

1.1: 1 d. r.

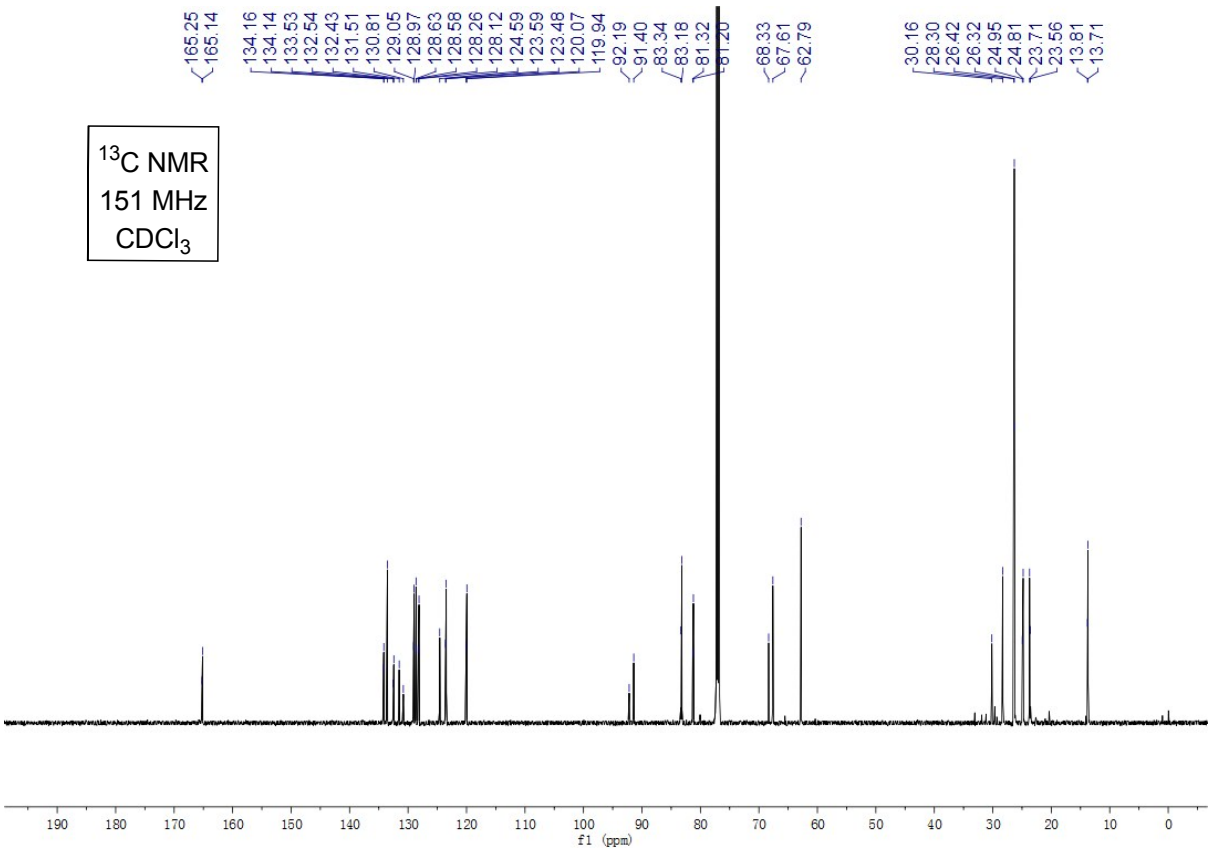


^{13}C NMR
126 MHz
$CDCl_3$

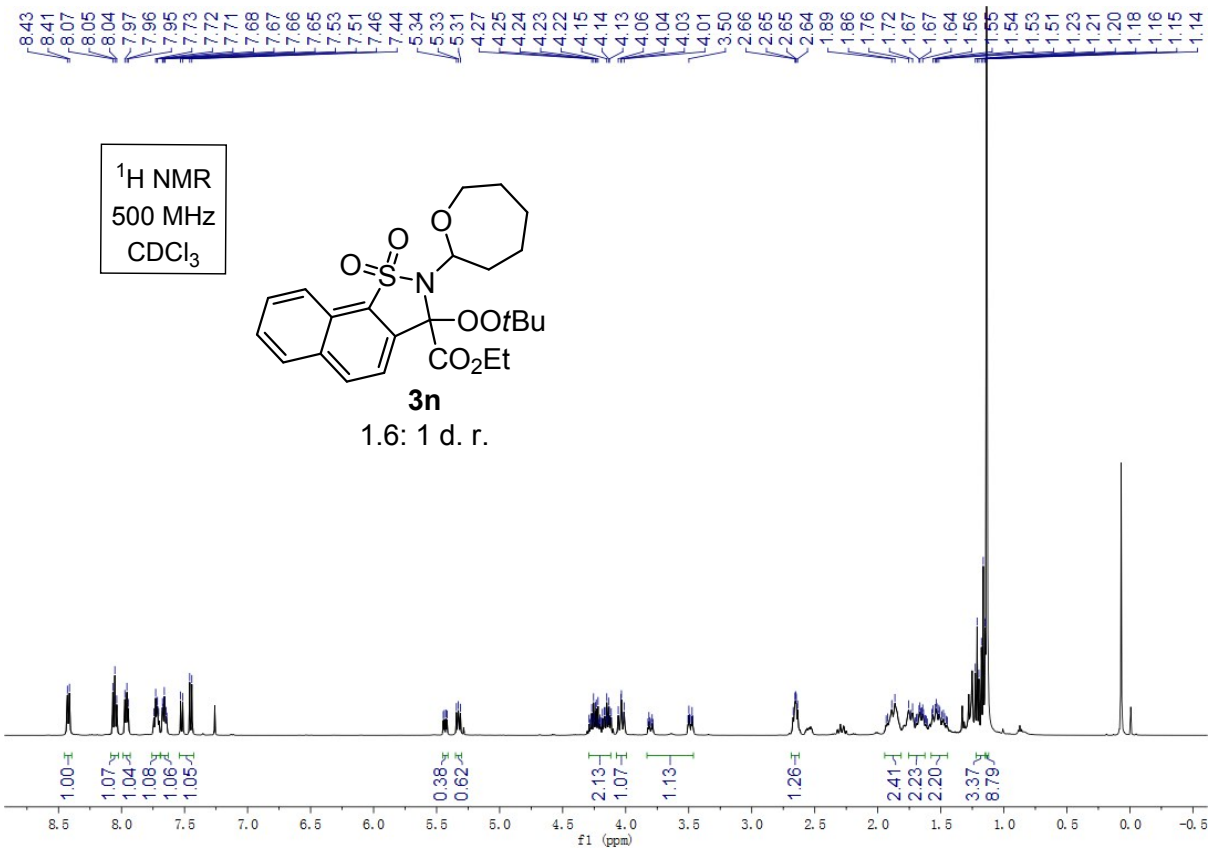


^{1}H NMR
500 MHz
$CDCl_3$

3m
1.9: 1 d. r.

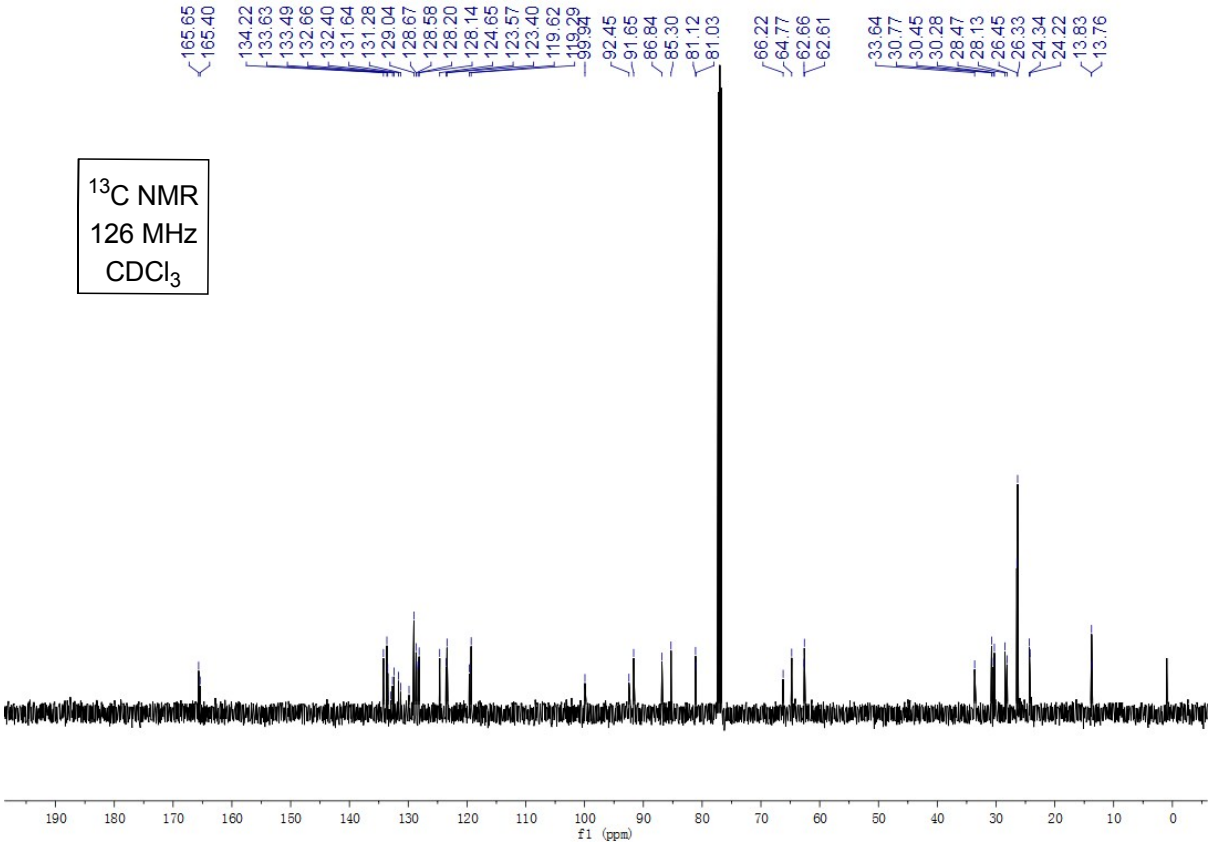


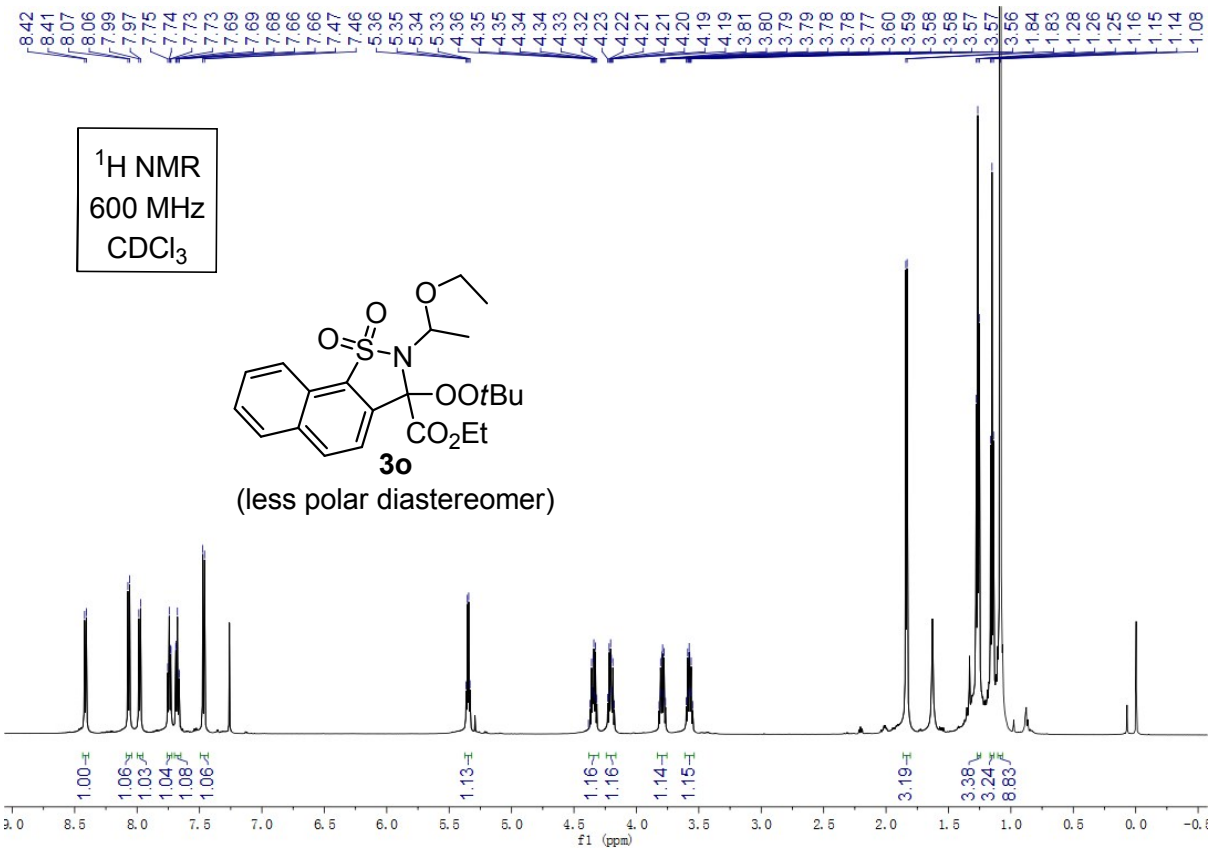
^{13}C NMR
151 MHz
$CDCl_3$

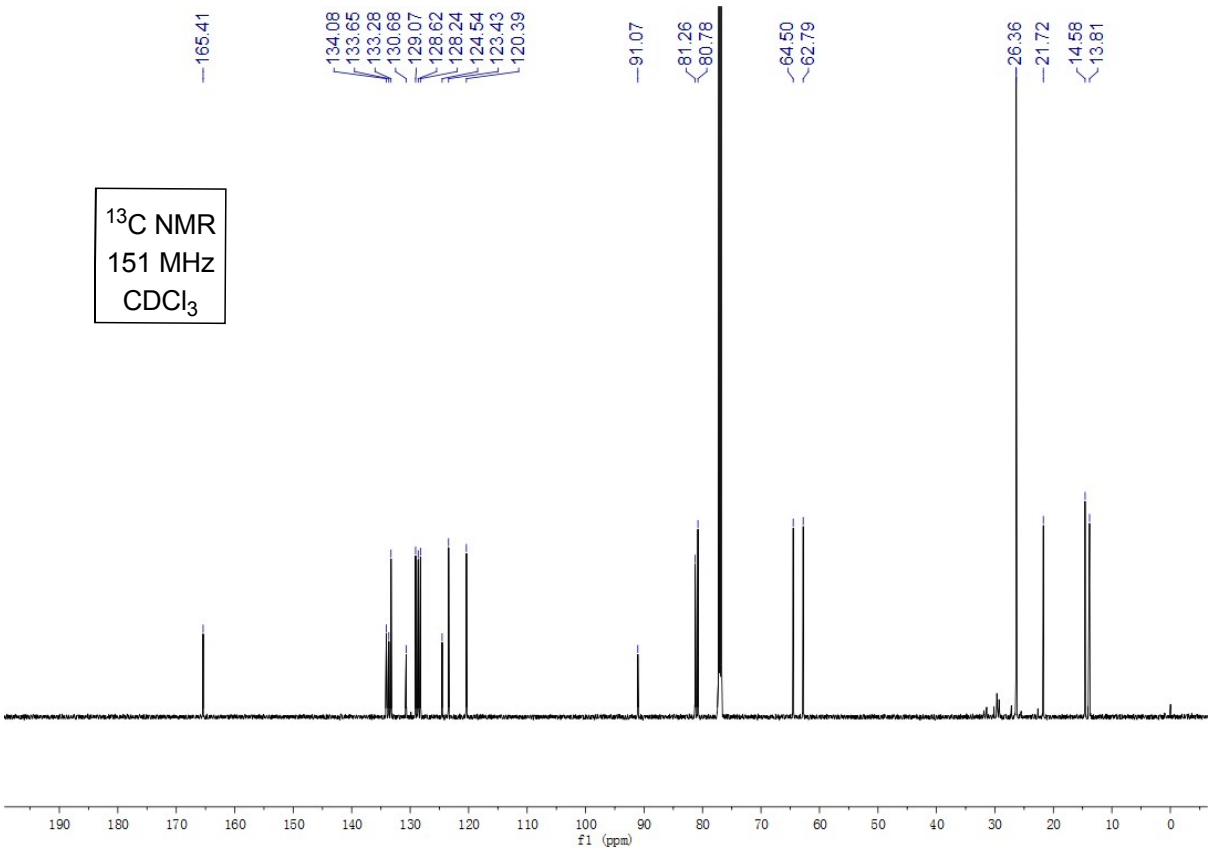

^{1}H NMR
500 MHz
$CDCl_3$
OO*t*Bu
CO_2Et
f1 (ppm)

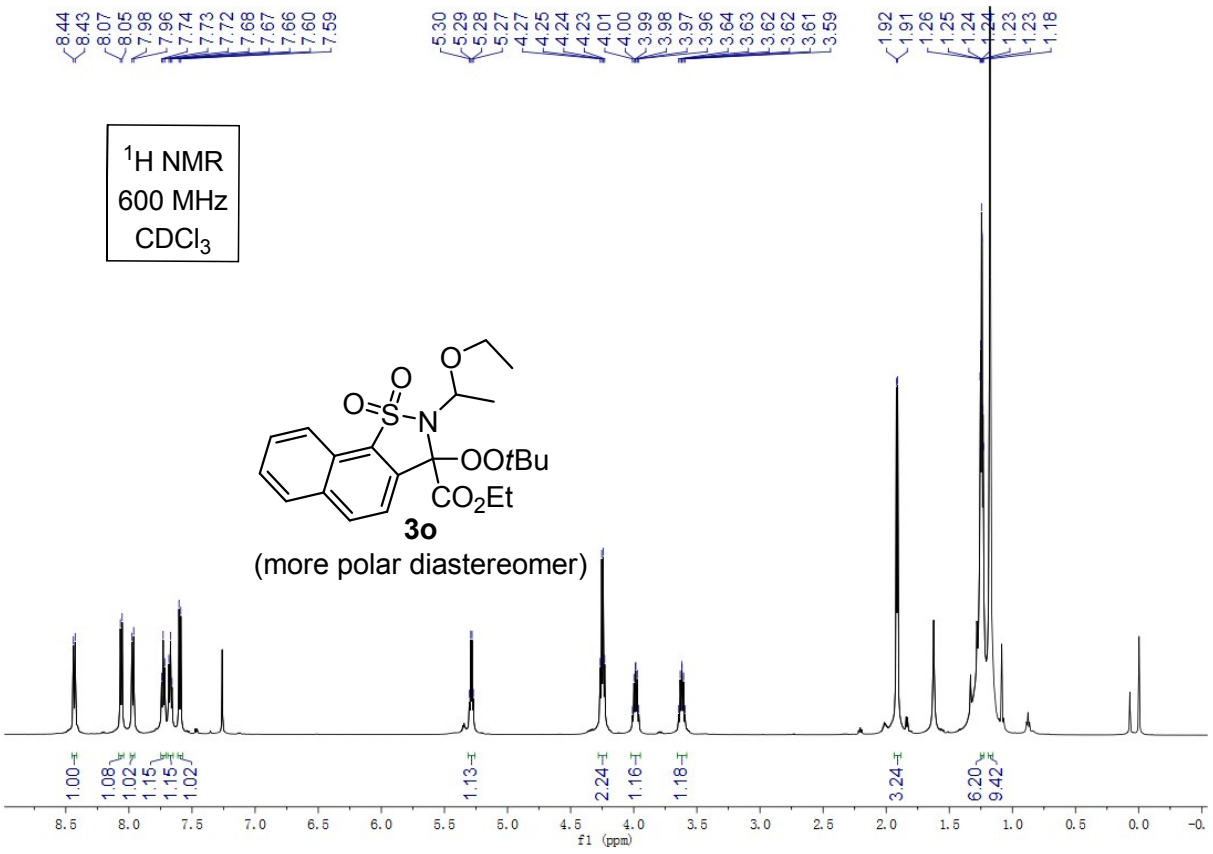
3n

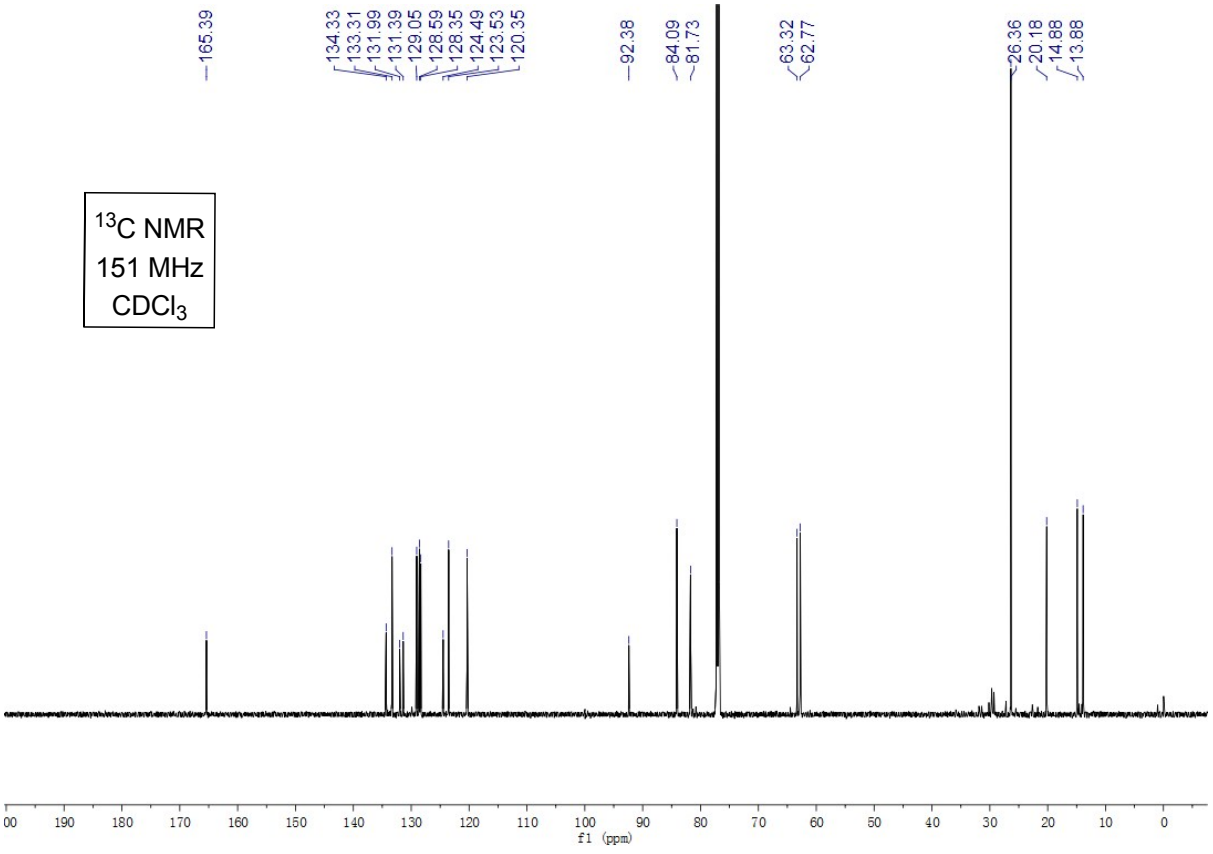
1.6: 1 d. r.

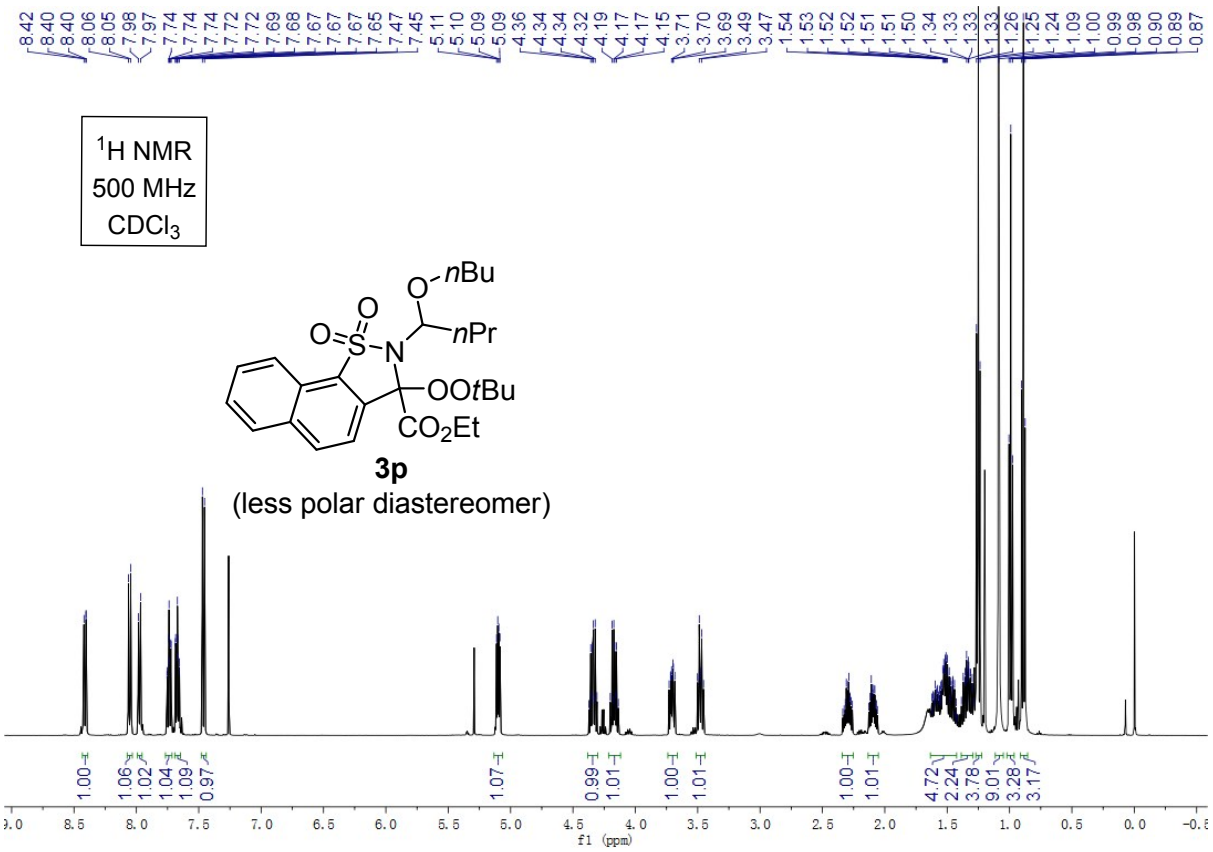

^{13}C NMR
126 MHz
$CDCl_3$
f1 (ppm)

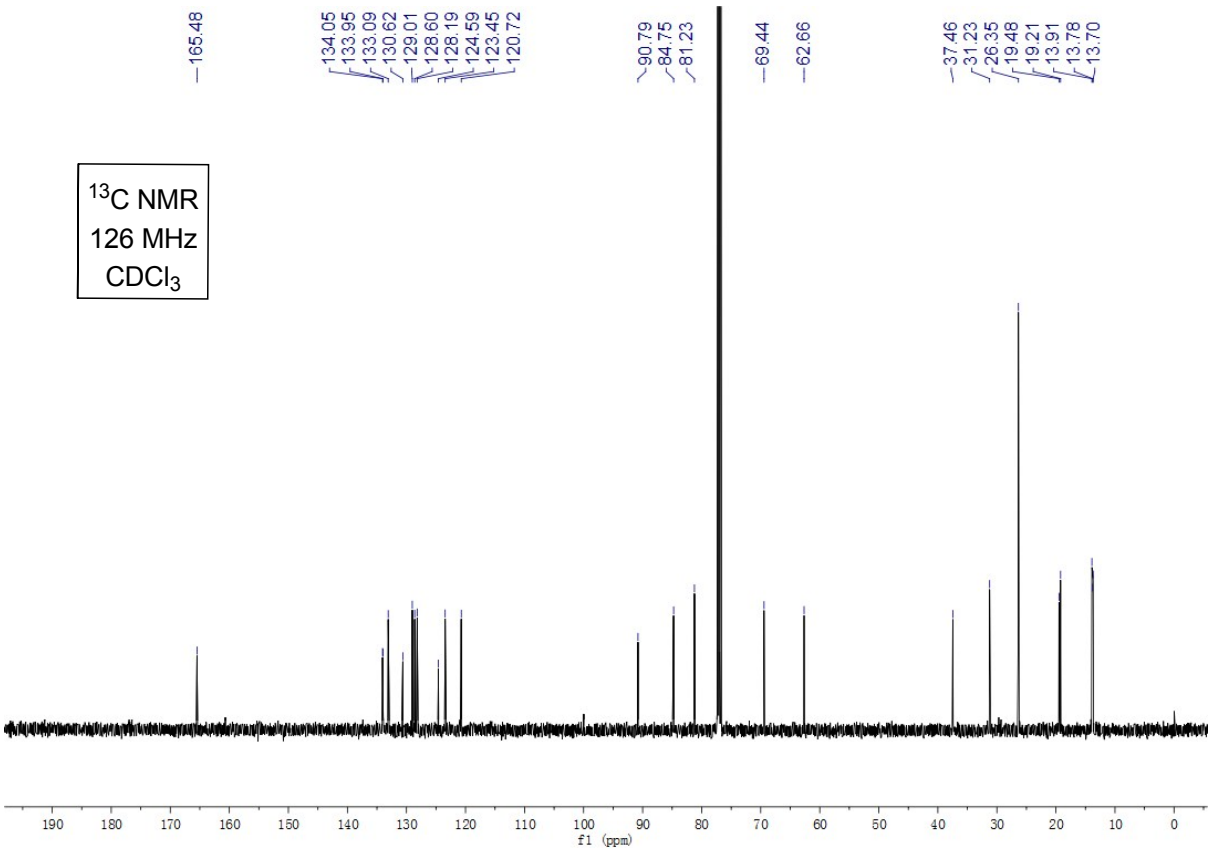

8.42 8.41 8.07 8.06 7.99 7.97 7.75 7.74 7.73 7.73 7.69 7.69 7.68 7.66 7.66 7.47 7.46 5.36 5.35 5.34 5.33 4.36 4.35 4.35 4.34 4.34 4.33 4.32 4.23 4.22 4.21 4.21 4.20 4.19 4.19 3.81 3.80 3.79 3.79 3.78 3.78 3.77 3.60 3.59 3.58 3.58 3.57 3.57 3.56 1.84 1.83 1.28 1.26 1.25 1.16 1.15 1.14 1.08
1H NMR
600 MHz
CDCl3
O
O
O=S-N
OOtBu
CO2Et
3o
(less polar diastereomer)
1.00 1.06 1.03 1.04 1.08 1.06 1.13 1.16 1.16 1.14 1.15 3.19 3.38 3.24 8.83
f1 (ppm)

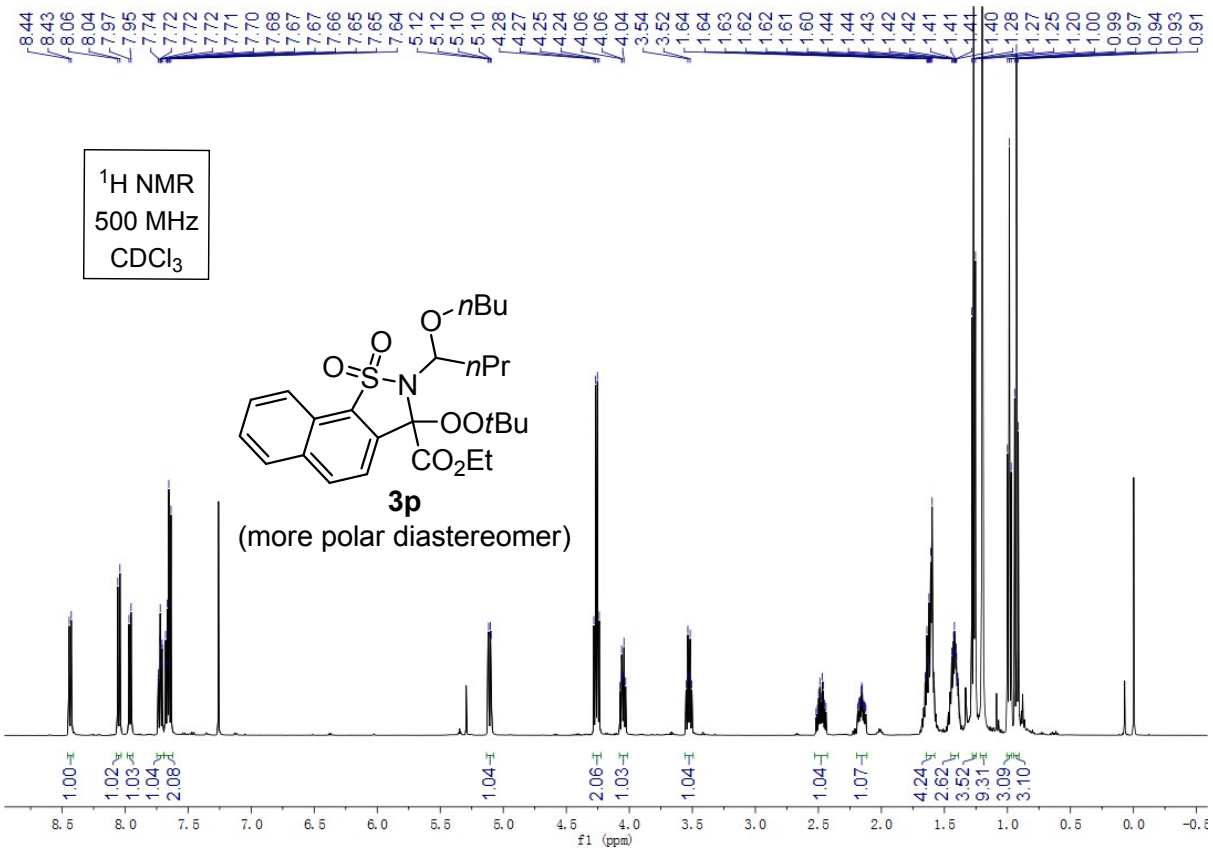

165.41
134.08 133.65 133.28 130.68 129.07 128.62 128.24 124.54 123.43 120.39
91.07
81.26 80.78
64.50 62.79
26.36 21.72 14.58 13.81
13C NMR
151 MHz
CDCl3
f1 (ppm)

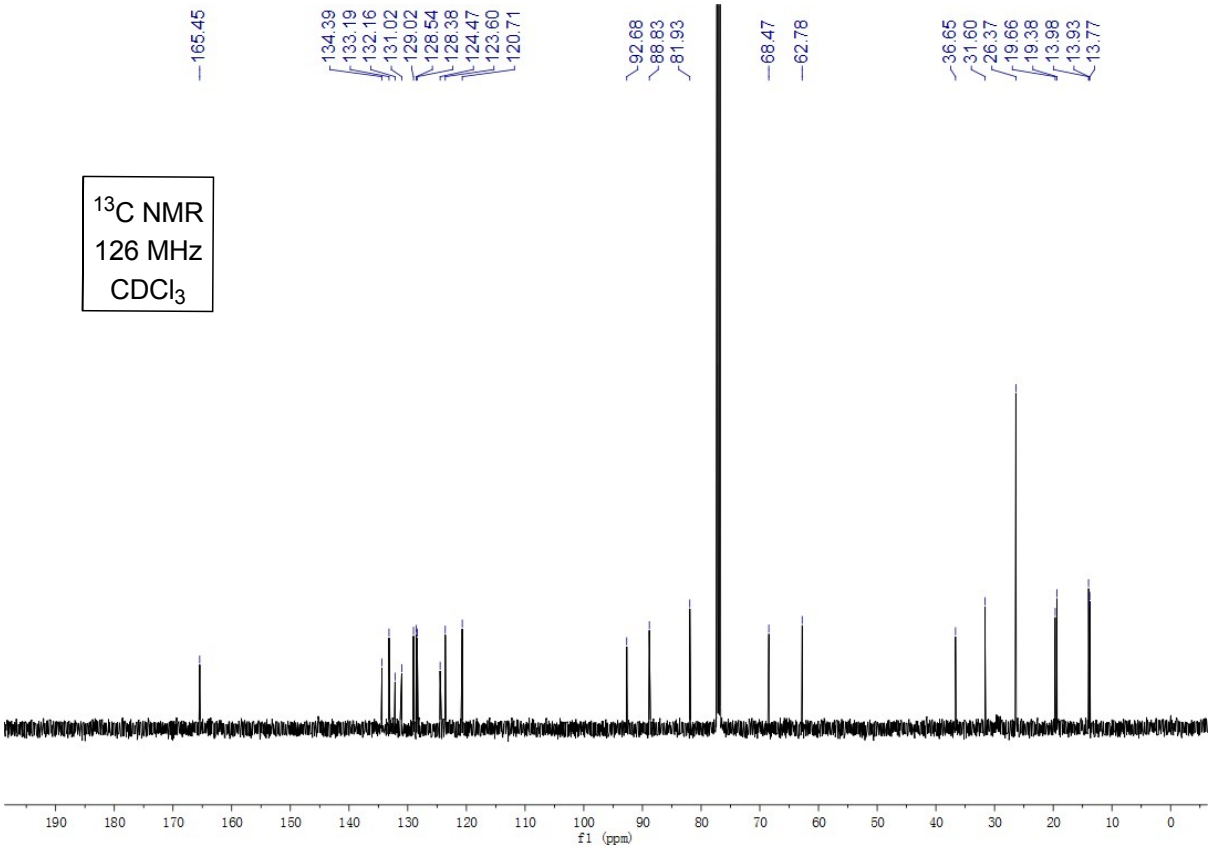

8.44
8.43
8.07
8.05
7.98
7.96
7.74
7.73
7.72
7.68
7.67
7.66
7.60
7.59
5.30
5.29
5.28
5.27
4.27
4.25
4.24
4.23
4.01
4.00
3.99
3.98
3.97
3.96
3.64
3.63
3.62
3.62
3.61
3.59
1.92
1.91
1.26
1.25
1.24
1.24
1.23
1.23
1.18
1H NMR
600 MHz
CDCl3
O
O
O=S-N
OOtBu
CO2Et
3o
(more polar diastereomer)
1.00
1.08
1.02
1.15
1.15
1.02
1.13
2.24
1.16
1.18
3.24
6.20
9.42
f1 (ppm)

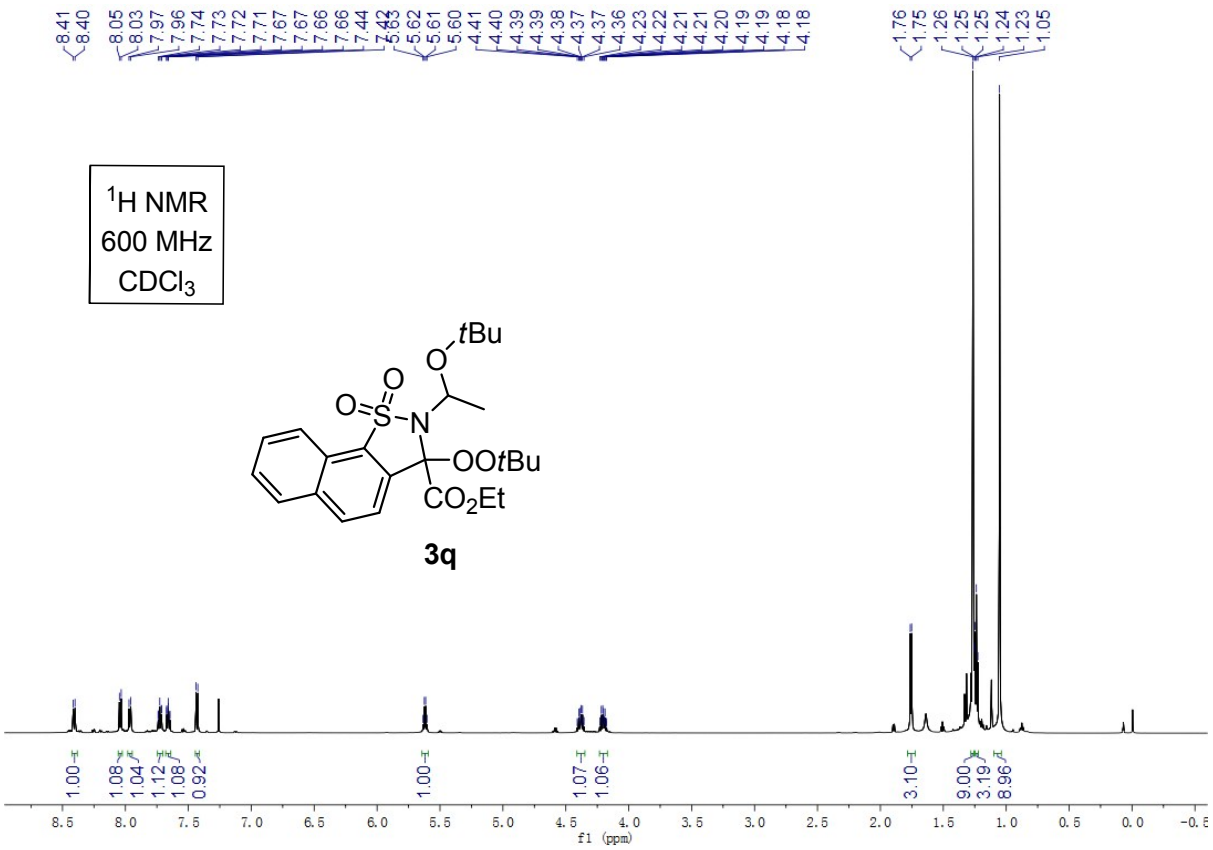

165.39
134.33
133.31
131.99
131.39
129.05
128.59
128.35
124.49
123.53
120.35
92.38
84.09
81.73
63.32
62.77
26.36
20.18
14.88
13.88
13C NMR
151 MHz
CDCl3
f1 (ppm)

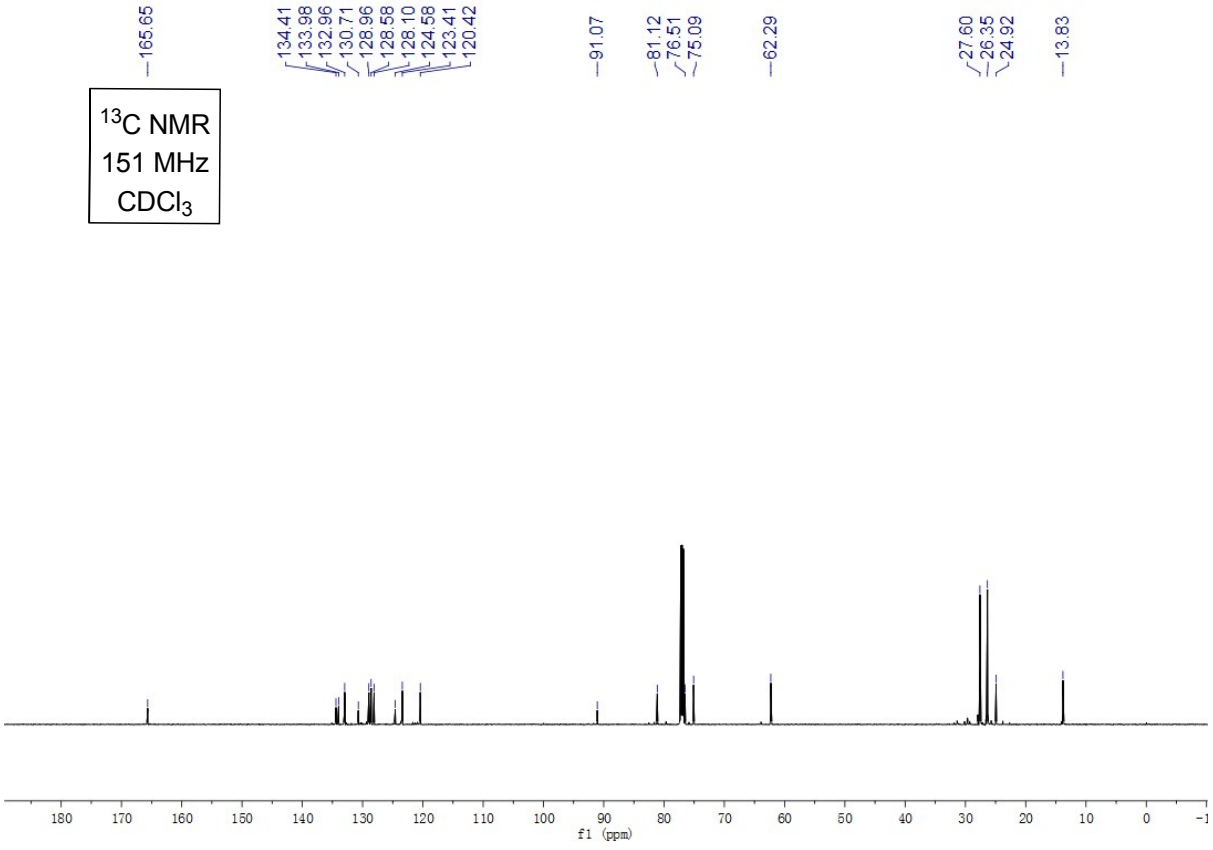

8.42 8.40 8.40 8.06 8.05 7.98 7.97 7.74 7.74 7.74 7.72 7.72 7.69 7.68 7.67 7.67 7.67 7.65 7.47 7.45 5.11 5.10 5.09 5.09 4.36 4.34 4.34 4.32 4.19 4.17 4.17 4.15 3.71 3.70 3.69 3.49 3.47 1.54 1.53 1.52 1.52 1.51 1.51 1.50 1.34 1.33 1.33 1.26 1.25 1.24 1.09 1.00 0.99 0.98 0.90 0.89 0.87
1H NMR
500 MHz
CDCl3
nBu
nPr
OOtBu
CO2Et
3p
(less polar diastereomer)
1.00 1.06 1.02 1.04 1.09 0.97 1.07 0.99 1.01 1.00 1.01 1.00 1.01 4.72 2.24 3.78 9.01 3.28 3.17
f1 (ppm)


165.48
134.05 133.95 133.09 130.62 129.01 128.60 128.19 124.59 123.45 120.72
90.79 84.75 81.23
69.44
62.66
37.46 31.23 26.35 19.48 19.21 13.91 13.78 13.70
13C NMR
126 MHz
CDCl3
f1 (ppm)


^{1}H NMR
500 MHz
$CDCl_3$
O-*n*Bu
*n*Pr
OO*t*Bu
CO_2Et
3p
(more polar diastereomer)
f1 (ppm)


^{13}C NMR
126 MHz
$CDCl_3$
f1 (ppm)


8.41
8.40
8.05
8.03
7.97
7.96
7.74
7.73
7.72
7.71
7.67
7.67
7.66
7.66
7.44
5.62
5.61
5.60
4.41
4.40
4.39
4.39
4.38
4.37
4.37
4.36
4.23
4.22
4.21
4.21
4.20
4.19
4.19
4.18
4.18
1.76
1.75
1.26
1.25
1.25
1.24
1.23
1.05
1H NMR
600 MHz
CDCl3
tBu
O
O
O=S
N
OOtBu
CO2Et
3q
1.00
1.08
1.04
1.12
1.08
0.92
1.00
1.07
1.06
3.10
9.00
3.19
8.96
f1 (ppm)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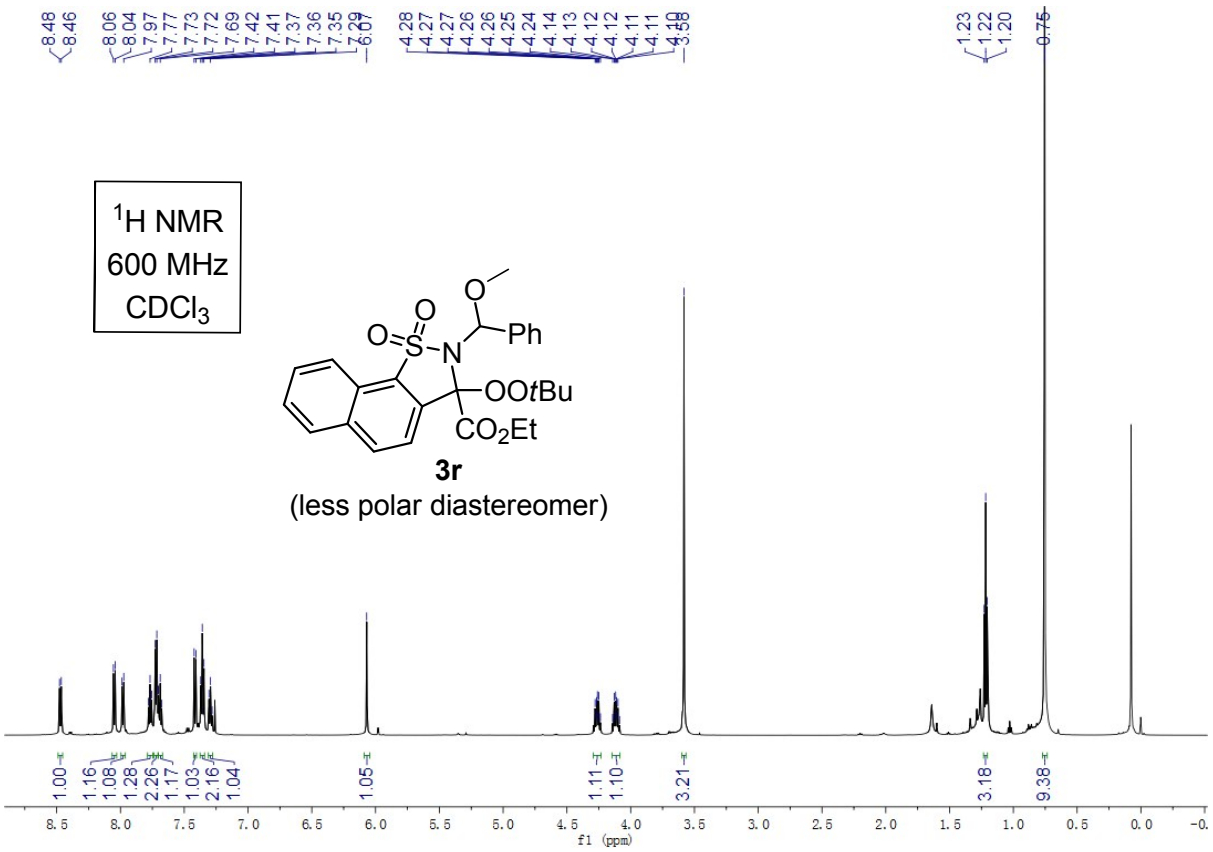
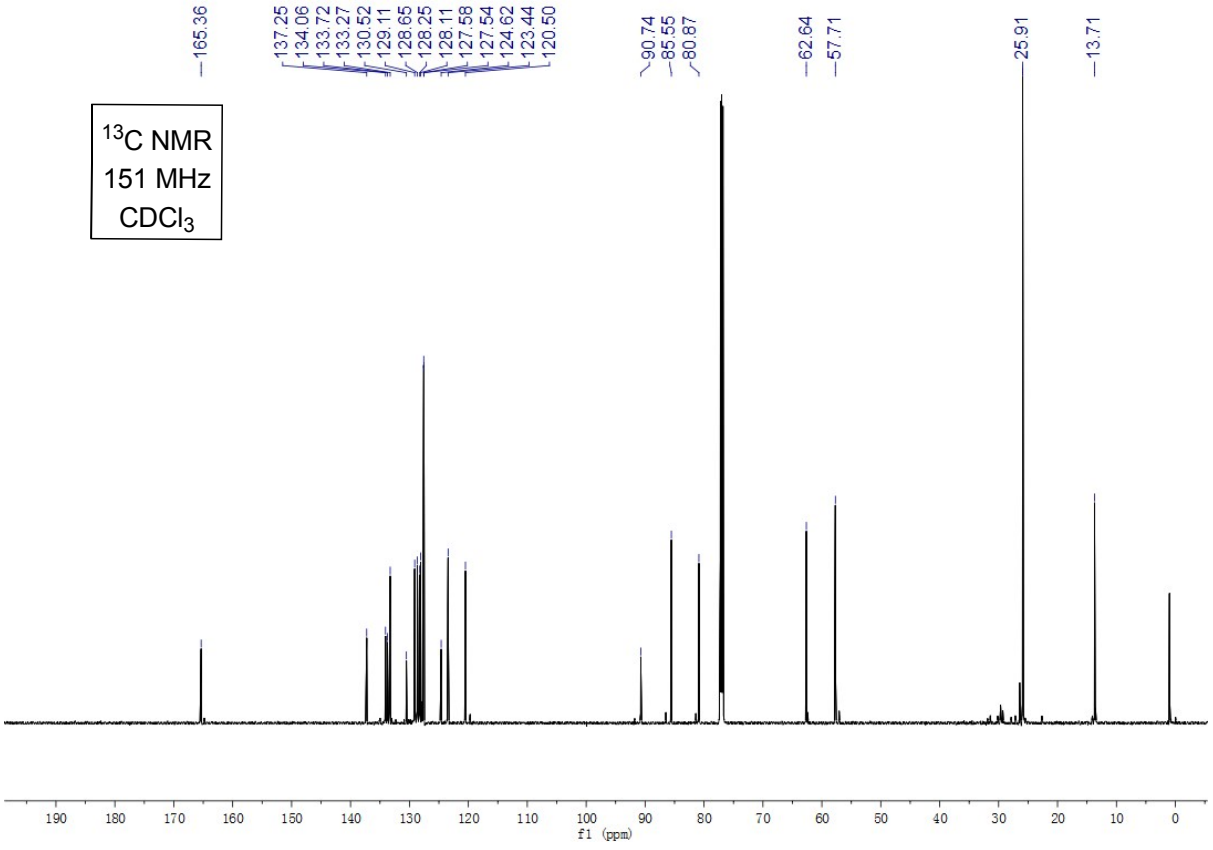
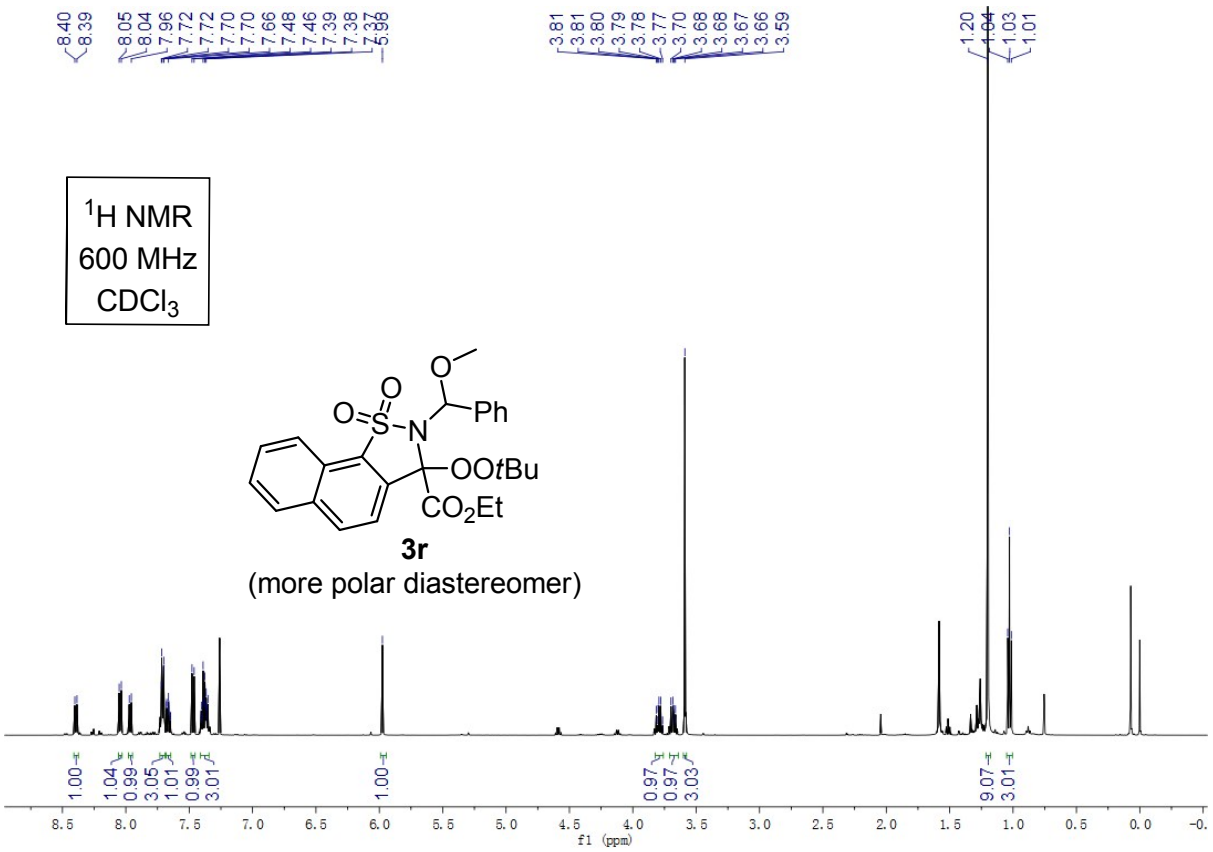
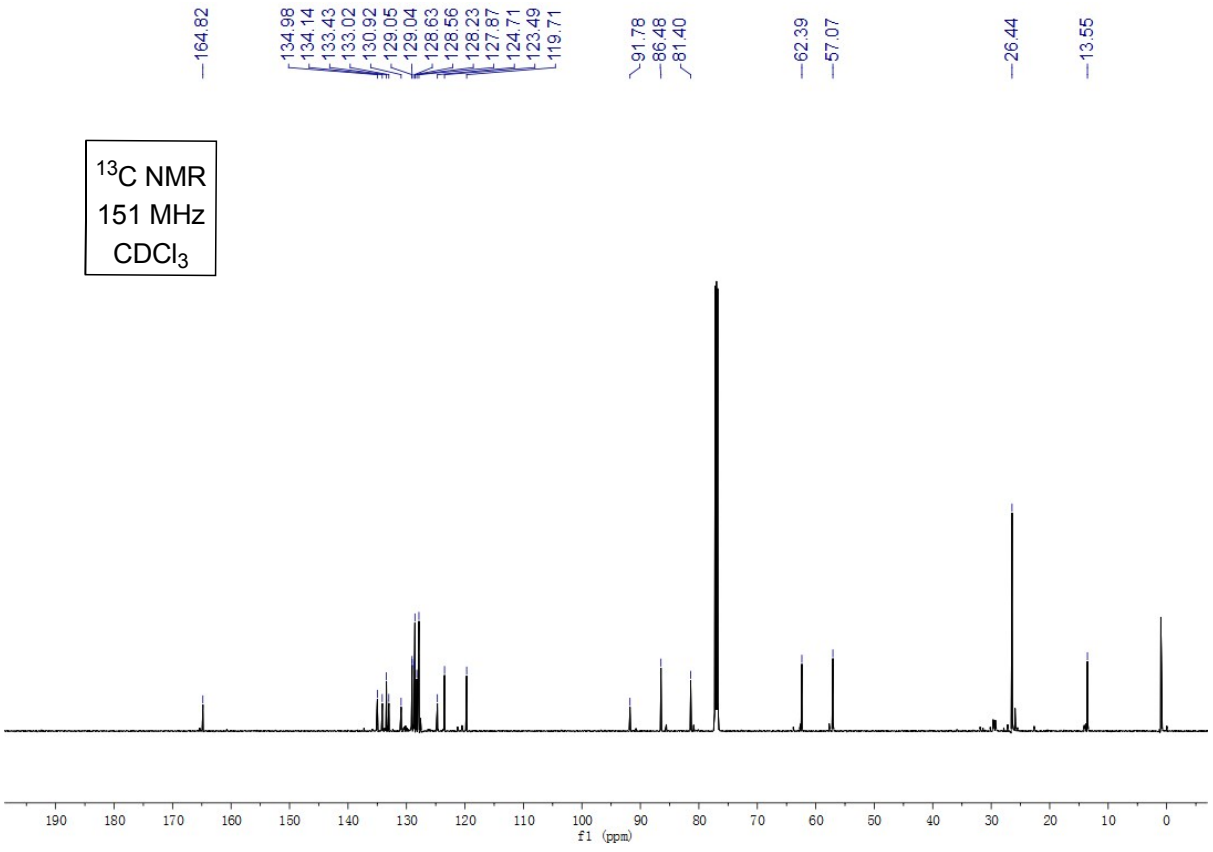
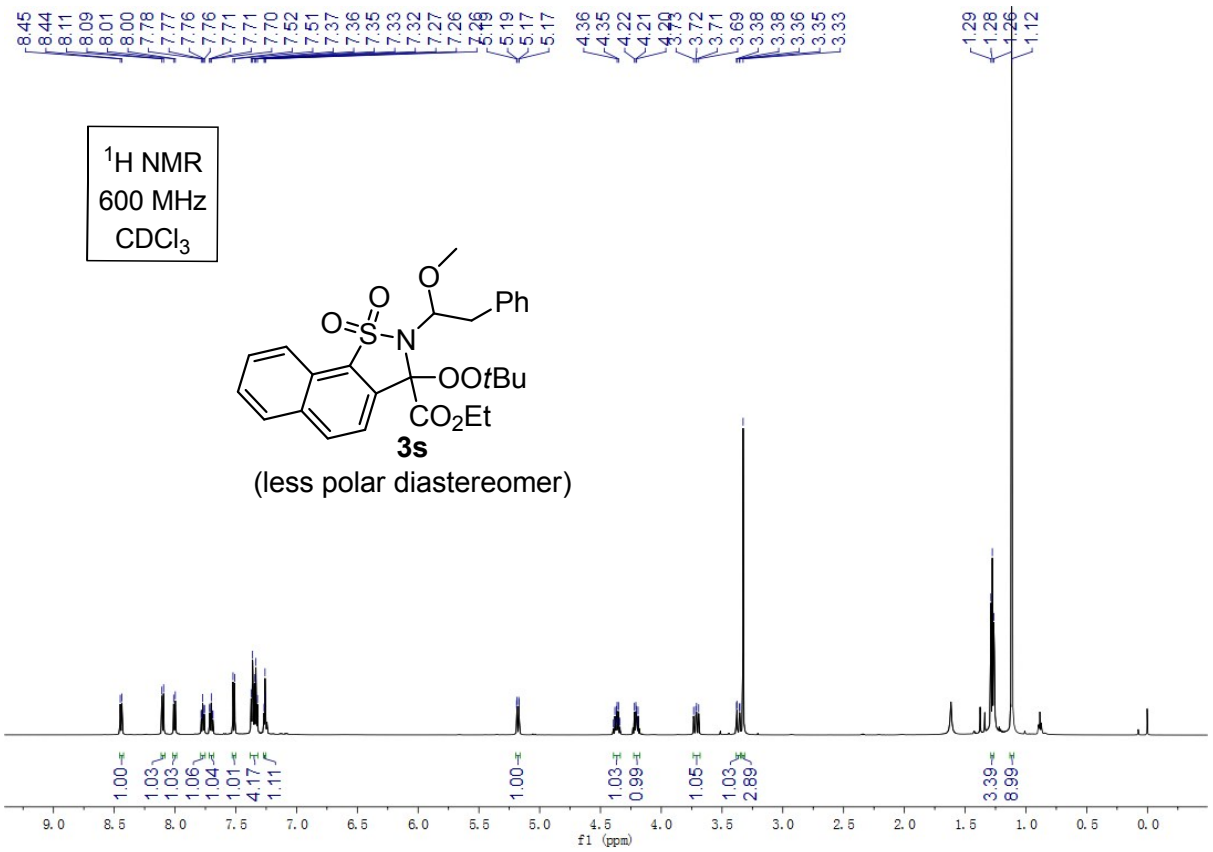
134.41
133.98
132.96
130.71
128.96
128.58
128.10
124.58
123.41
120.42
91.07
81.12
76.51
75.09
62.29
27.60
26.35
24.92
13.83
13C NMR
151 MHz
CDCl3
f1 (ppm)

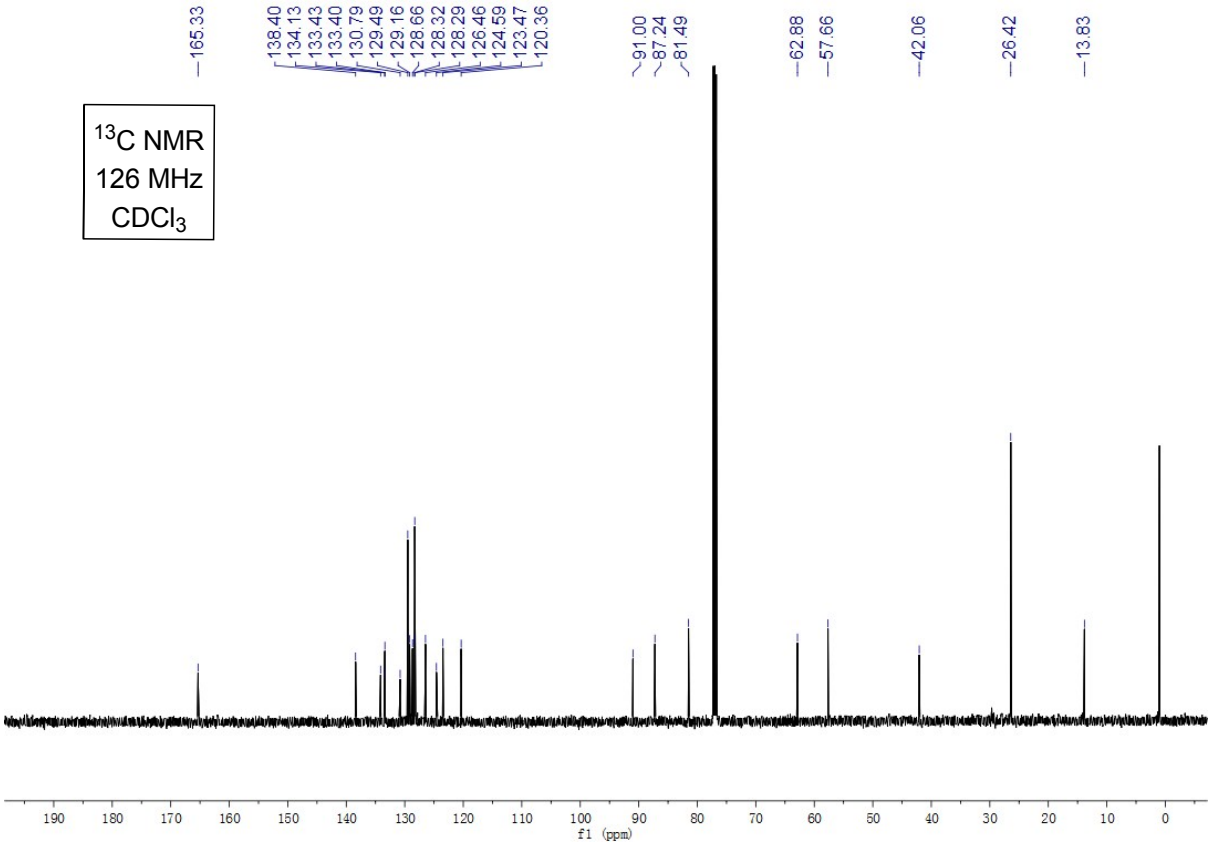

8.48
8.46
8.06
8.04
7.97
7.77
7.73
7.72
7.69
7.42
7.41
7.37
7.36
7.35
7.29
6.07
4.28
4.27
4.27
4.26
4.26
4.25
4.24
4.14
4.13
4.12
4.12
4.11
4.11
3.58
1.23
1.22
1.20
0.75
1H NMR
600 MHz
CDCl3
O
O
O=S-N
Ph
OOtBu
CO2Et
3r
(less polar diastereomer)
1.00
1.16
1.08
1.28
2.26
1.17
1.03
2.16
1.04
1.05
1.11
1.10
3.21
3.18
9.38
f1 (ppm)

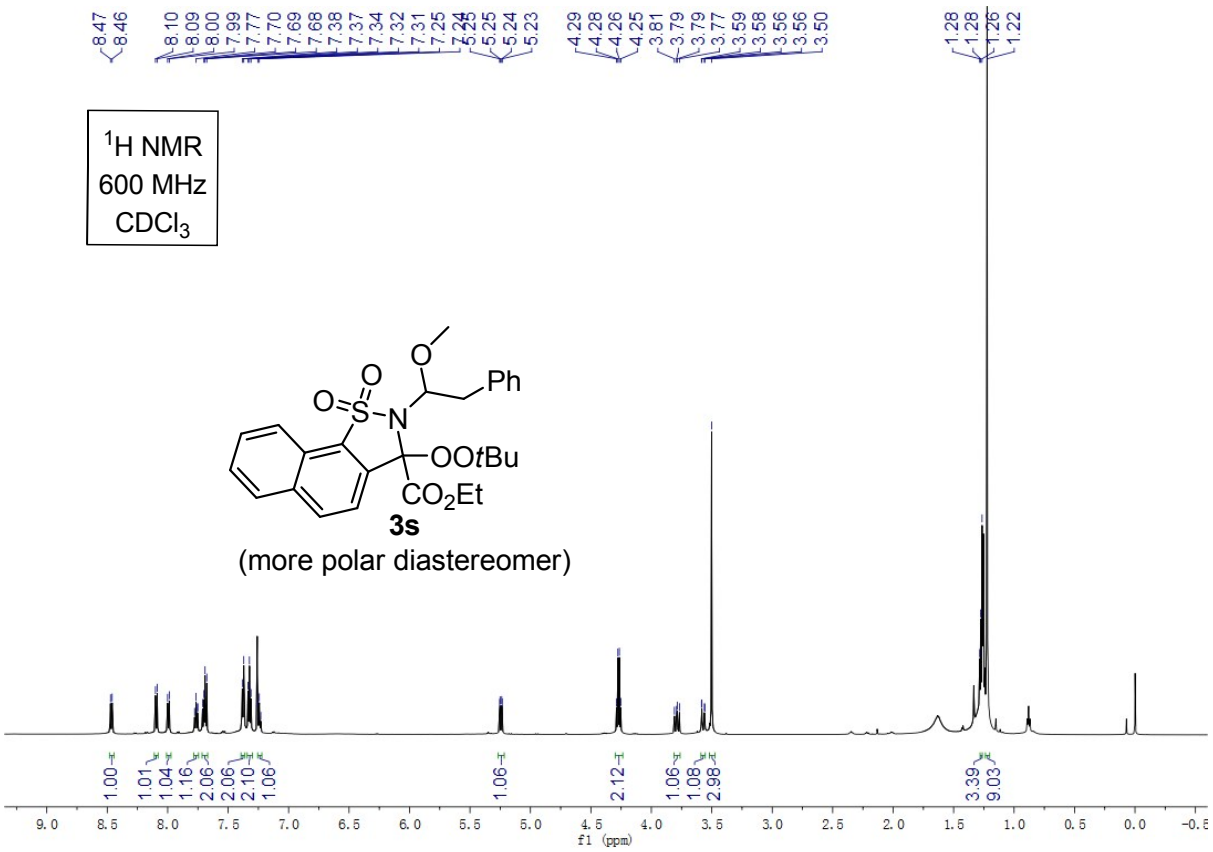

165.36
137.25
134.06
133.72
133.27
130.52
129.11
128.65
128.25
128.11
127.58
127.54
124.62
123.44
120.50
90.74
85.55
80.87
62.64
57.71
25.91
13.71
13C NMR
151 MHz
CDCl3
f1 (ppm)

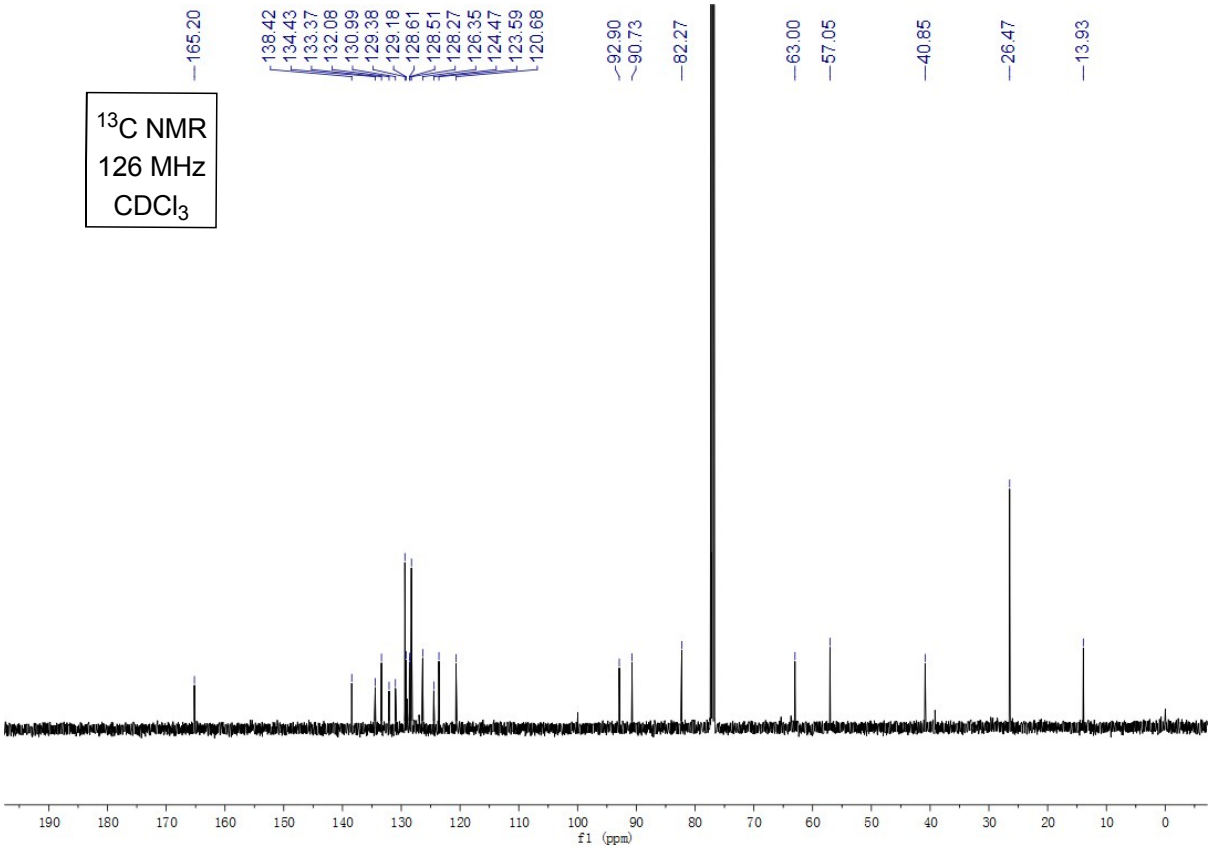

8.40
8.39
8.05
8.04
7.96
7.72
7.72
7.70
7.70
7.66
7.48
7.46
7.39
7.38
7.37
7.36
3.81
3.81
3.80
3.79
3.78
3.77
3.70
3.68
3.68
3.67
3.66
3.59
1.20
1.04
1.03
1.01
1H NMR
600 MHz
CDCl3
O
O
S
N
Ph
OOtBu
CO2Et
3r
(more polar diastereomer)
1.00
1.04
0.99
3.05
1.01
0.99
3.01
1.00
0.97
0.97
3.03
9.07
3.01
f1 (ppm)

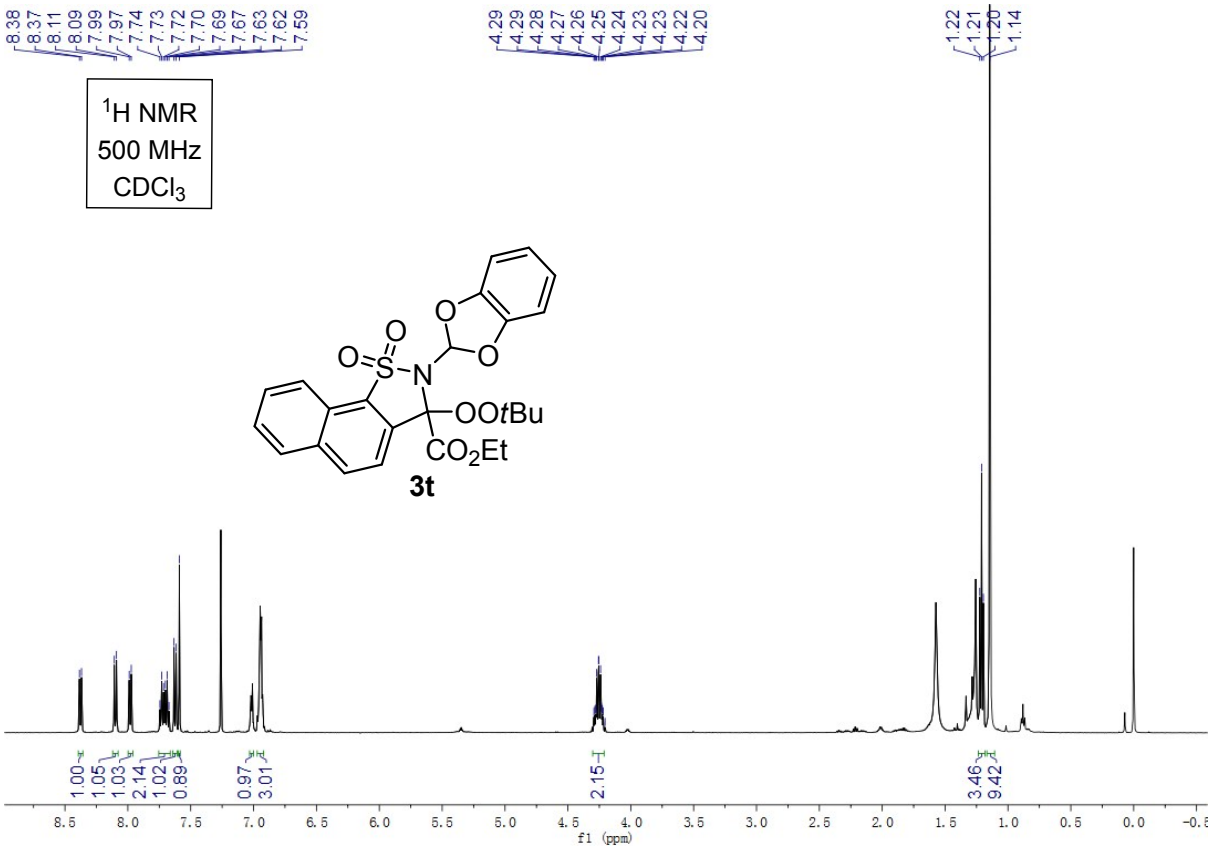

164.82
134.98
134.14
133.43
133.02
130.92
129.05
129.04
128.63
128.56
128.23
127.87
124.71
123.49
119.71
91.78
86.48
81.40
62.39
57.07
26.44
13.55
13C NMR
151 MHz
CDCl3
f1 (ppm)

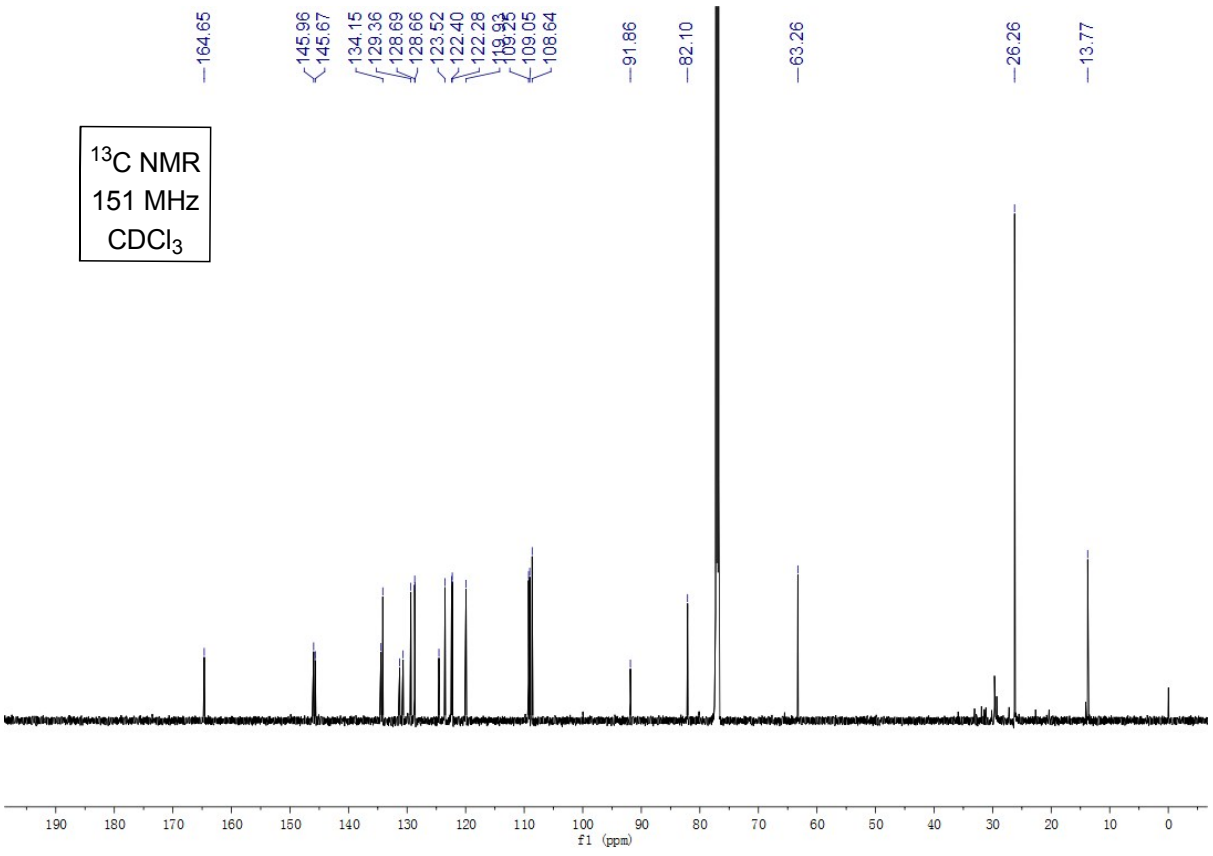

^{1}H NMR
600 MHz
$CDCl_3$
O
Ph
O
O=S
N
OO*t*Bu
CO_2Et
3s
(less polar diastereomer)
f1 (ppm)

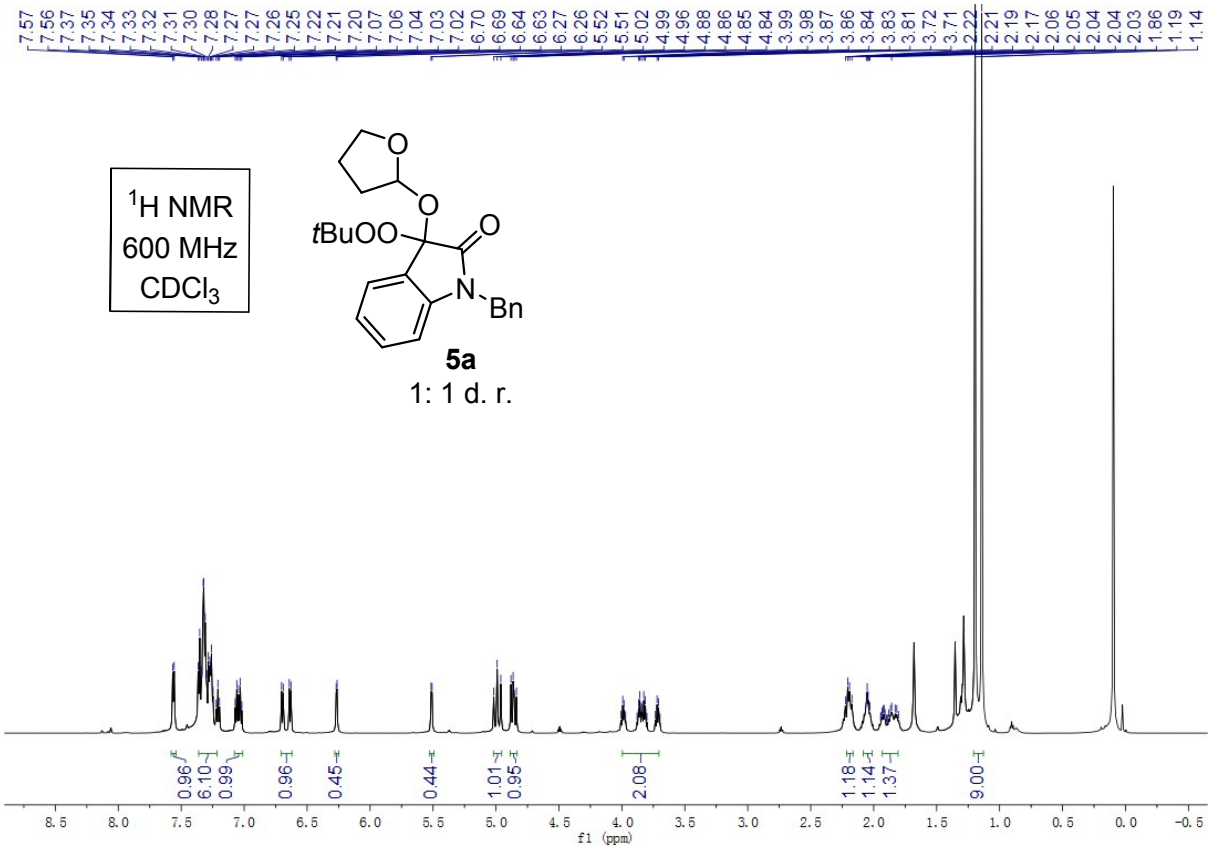

^{13}C NMR
126 MHz
$CDCl_3$
f1 (ppm)

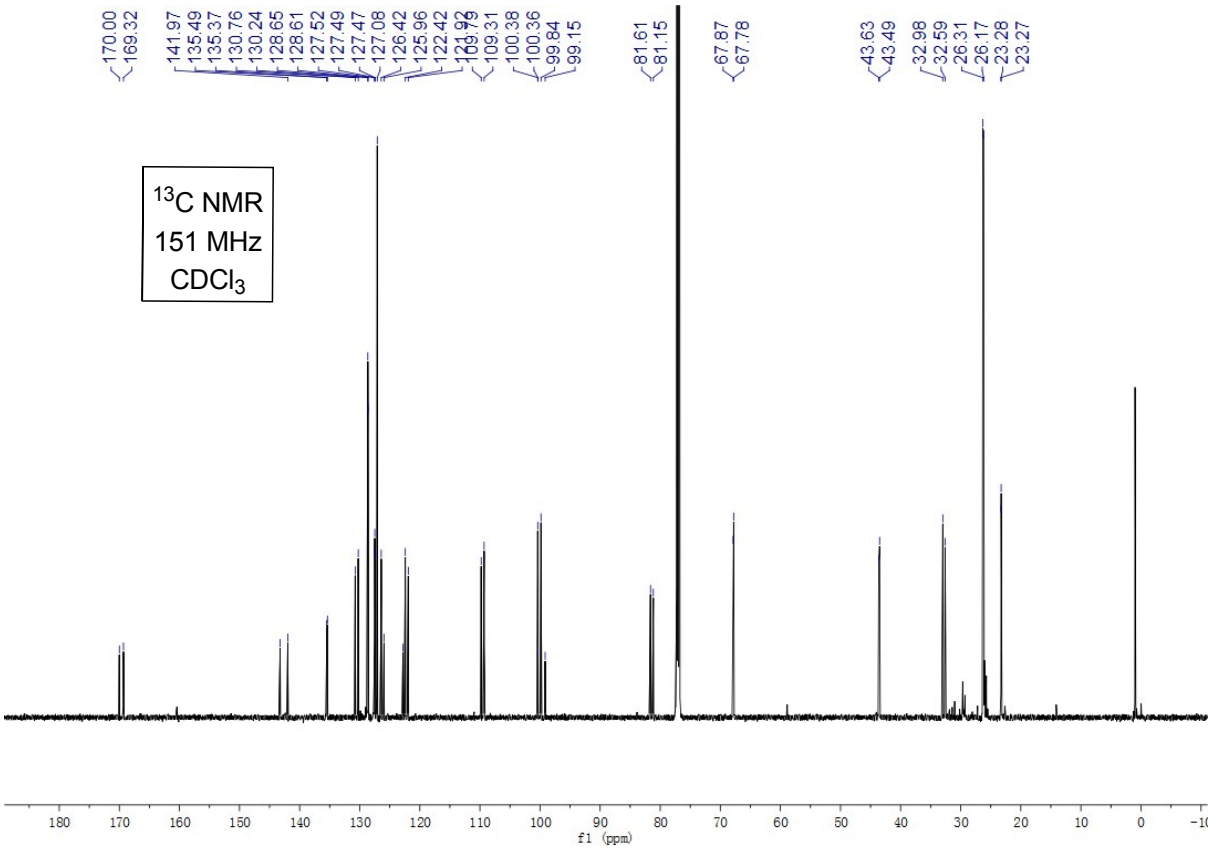

8.47
8.46
8.10
8.09
8.00
7.99
7.77
7.70
7.69
7.68
7.38
7.37
7.34
7.32
7.31
7.25
5.25
5.24
5.23
4.29
4.28
4.26
4.25
3.81
3.79
3.79
3.77
3.59
3.58
3.56
3.56
3.50
1.28
1.28
1.26
1.22
1H NMR
600 MHz
CDCl3
O
O
O=S-N
Ph
OOtBu
CO2Et
3s
(more polar diastereomer)
1.00
1.01
1.04
1.16
2.06
2.06
2.10
1.06
1.06
2.12
1.06
1.08
2.98
3.39
9.03
f1 (ppm)

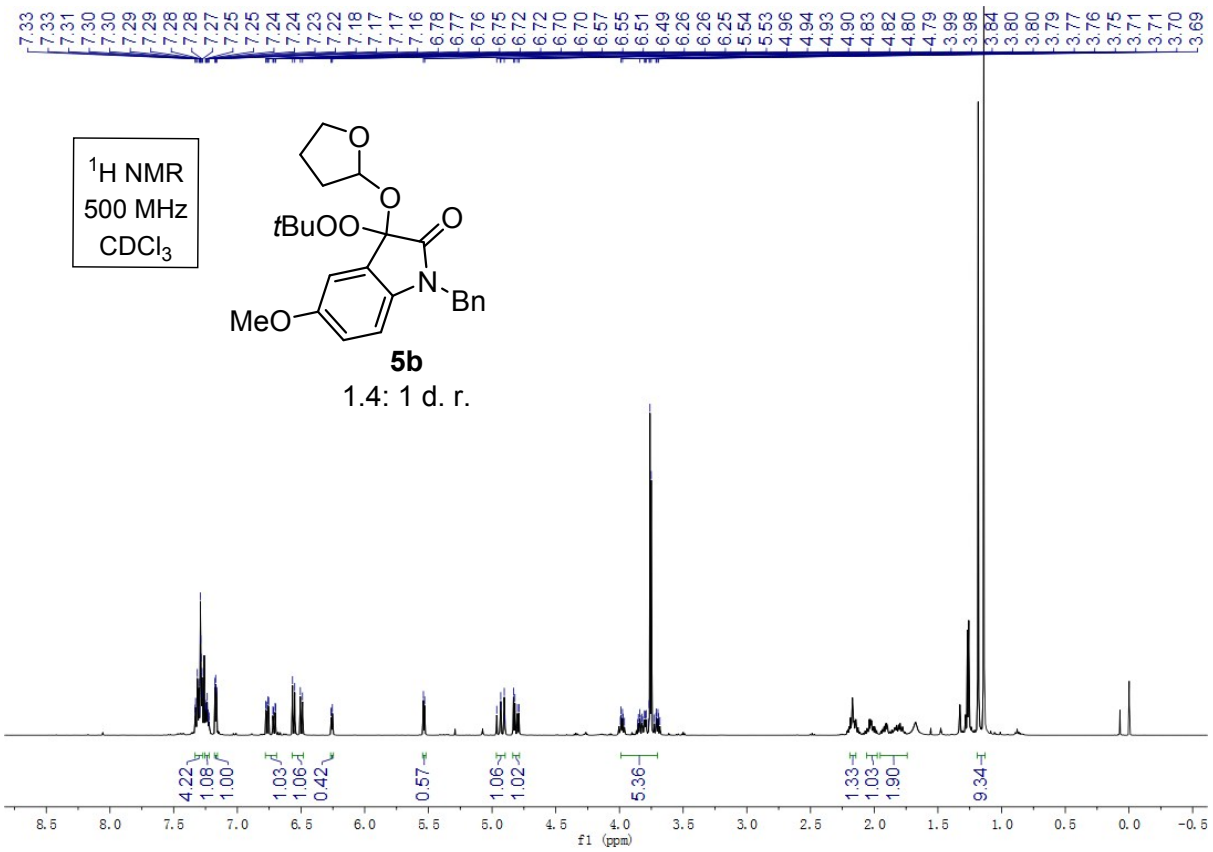

165.20
138.42
134.43
133.37
132.08
130.99
129.38
129.18
128.61
128.51
128.27
126.35
124.47
123.59
120.68
92.90
90.73
82.27
63.00
57.05
40.85
26.47
13.93
13C NMR
126 MHz
CDCl3
f1 (ppm)

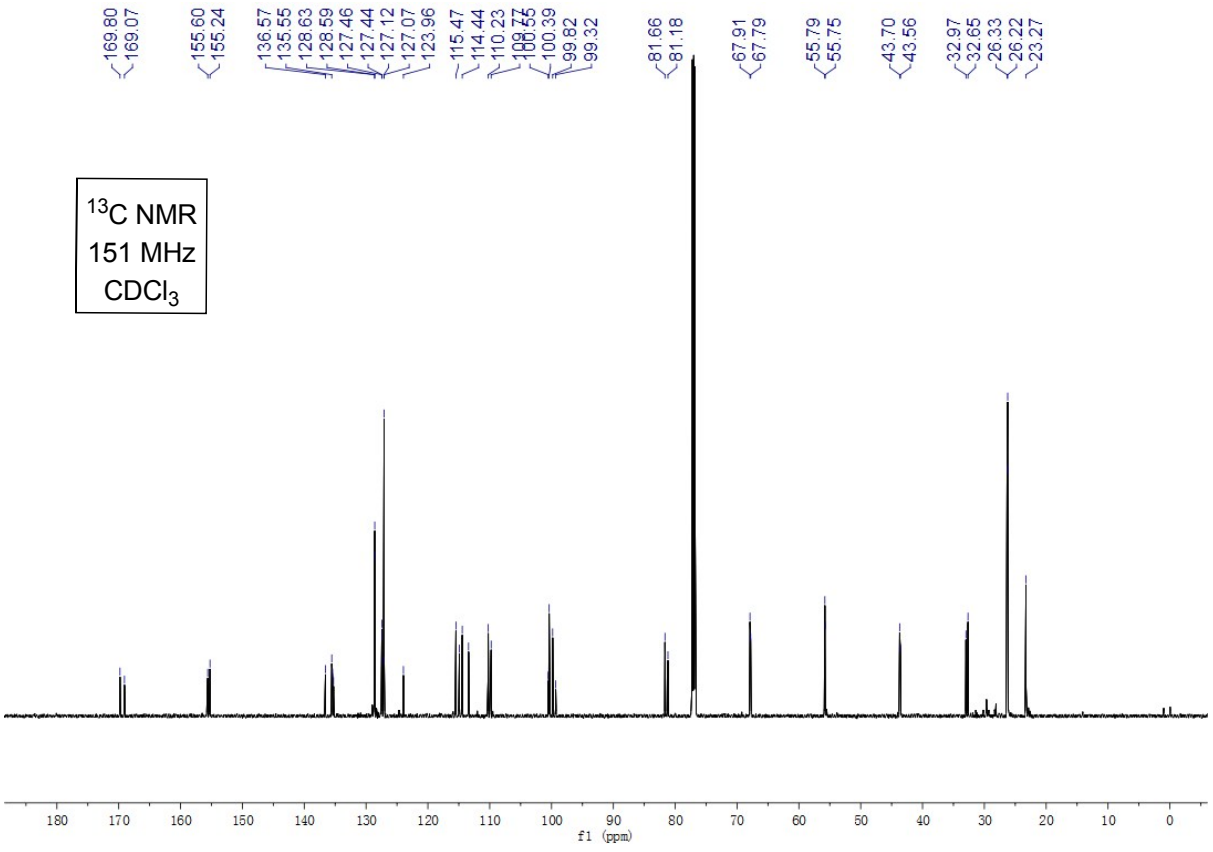

8.38
8.37
8.11
8.09
7.99
7.97
7.74
7.73
7.72
7.70
7.69
7.67
7.63
7.62
7.59
4.29
4.29
4.28
4.27
4.26
4.25
4.24
4.23
4.22
4.20
1.22
1.21
1.20
1.14
1H NMR
500 MHz
CDCl3
O
O
O=S-N
O
O
OOtBu
CO2Et
3t
1.00
1.05
1.03
2.14
1.02
0.89
0.97
3.01
2.15
3.46
9.42
f1 (ppm)

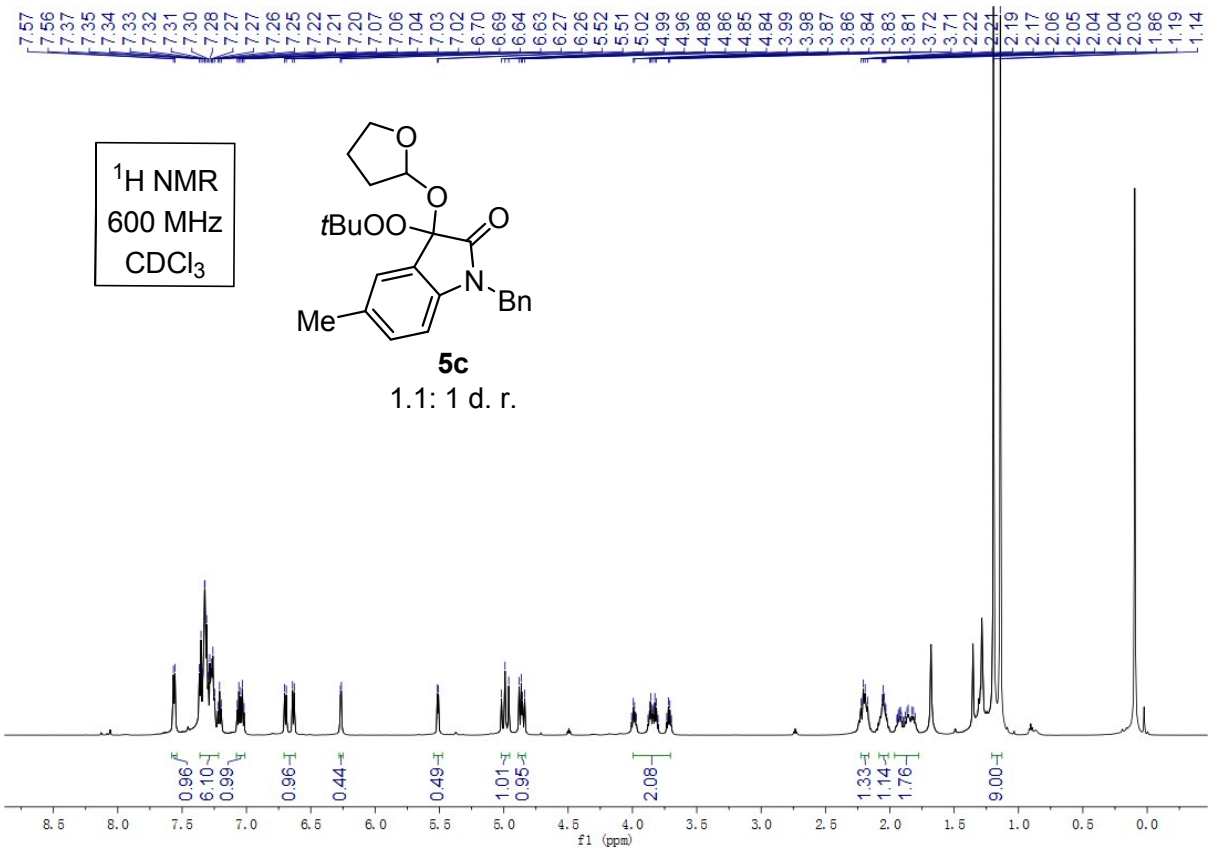

164.65
145.96
145.67
134.15
129.36
128.69
128.66
123.52
122.40
122.28
109.05
108.64
91.86
82.10
63.26
26.26
13.77
13C NMR
151 MHz
CDCl3
f1 (ppm)


7.57 7.56 7.37 7.35 7.34 7.33 7.32 7.31 7.30 7.28 7.27 7.27 7.26 7.25 7.22 7.21 7.20 7.07 7.06 7.04 7.03 7.02 6.70 6.69 6.64 6.63 6.27 6.26 5.52 5.51 5.02 4.99 4.96 4.88 4.86 4.85 4.84 3.99 3.98 3.87 3.86 3.84 3.83 3.81 3.72 3.71 2.22 2.21 2.19 2.17 2.06 2.05 2.04 2.04 2.03 1.86 1.19 1.14
^{1}H NMR
600 MHz
$CDCl_3$
tBuOO
O
O
N
Bn
5a
1: 1 d. r.
0.96 6.10 0.99 0.96 0.45 0.44 1.01 0.95 2.08 1.18 1.14 1.37 9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


170.00 169.32 141.97 135.49 135.37 130.76 130.24 128.65 128.61 127.52 127.49 127.47 127.08 126.42 125.96 122.42 121.92 109.79 109.31 100.38 100.36 99.84 99.15 81.61 81.15 67.87 67.78 43.63 43.49 32.98 32.59 26.31 26.17 23.28 23.27
^{13}C NMR
151 MHz
$CDCl_3$
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

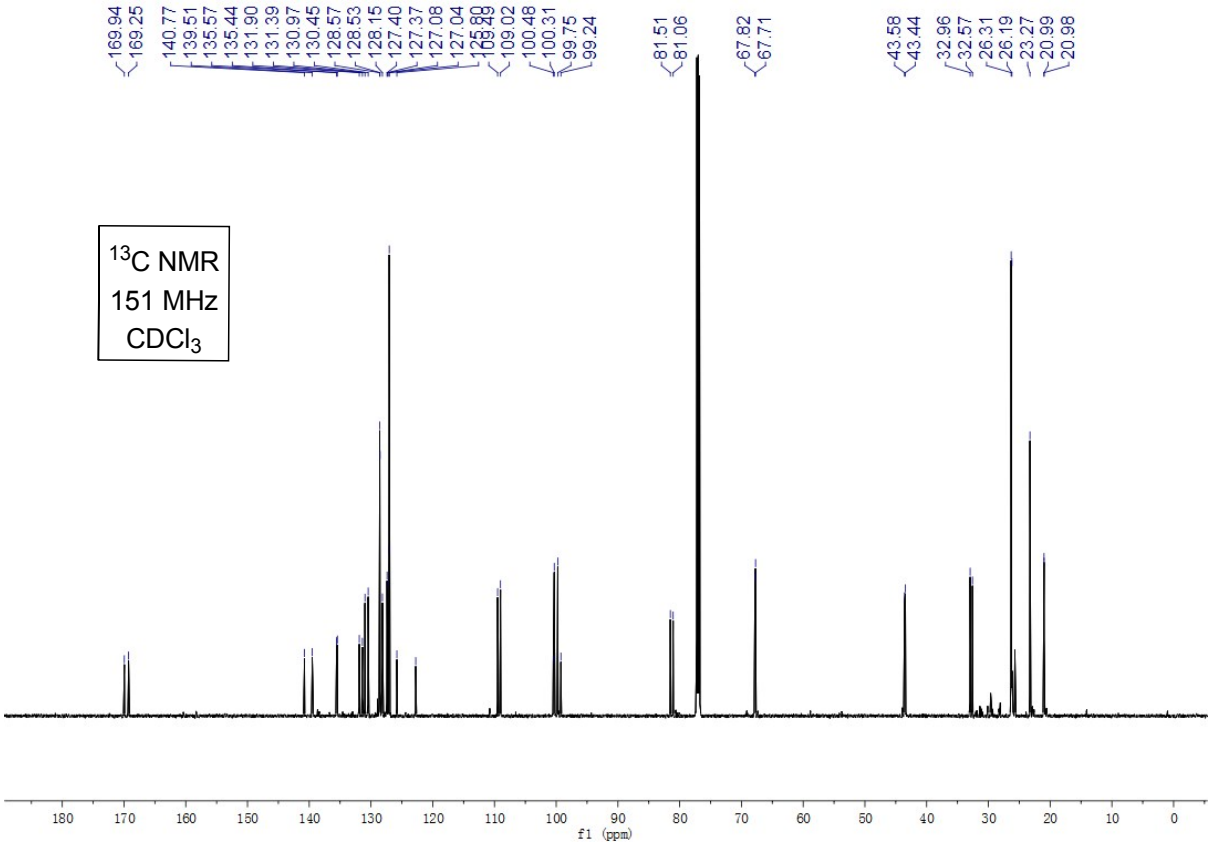

^{1}H NMR
500 MHz
$CDCl_3$
tBuOO
O
O
N
Bn
MeO
5b
1.4: 1 d. r.
f1 (ppm)

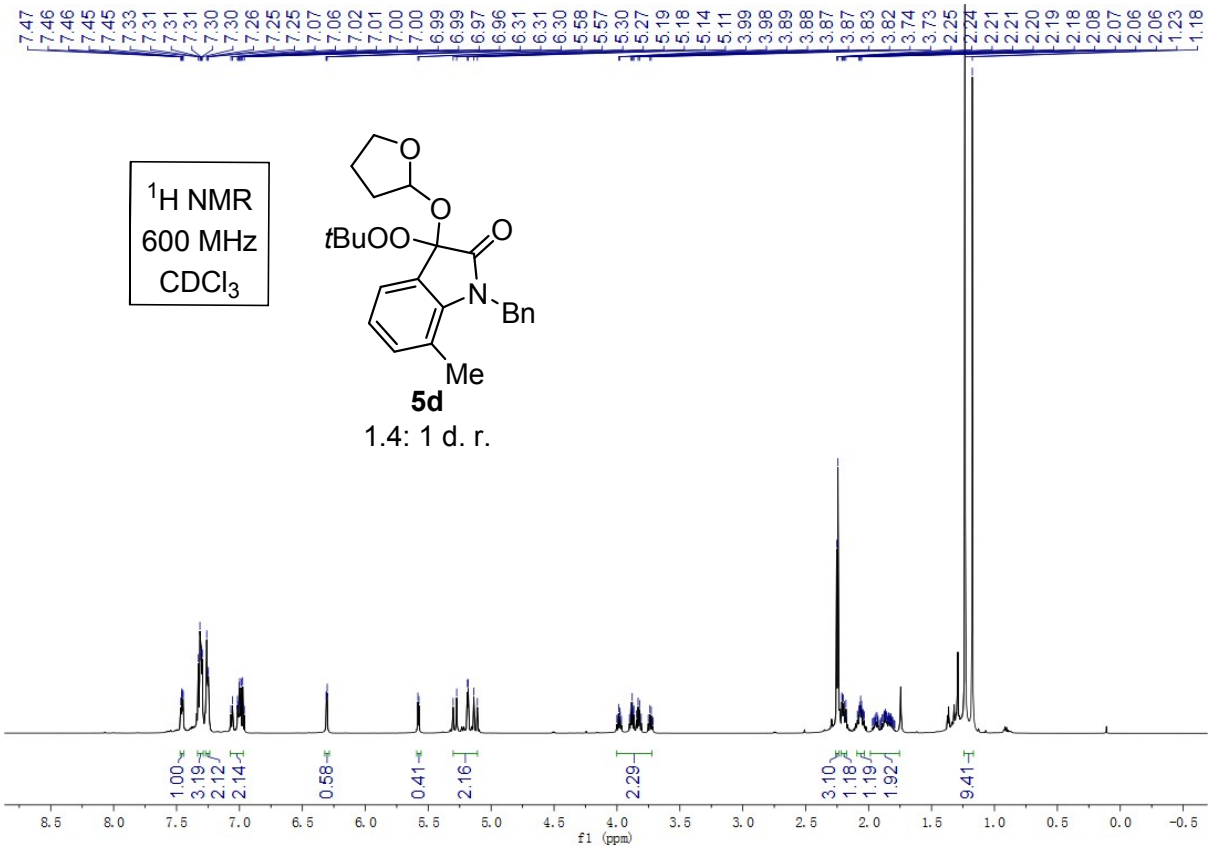

^{13}C NMR
151 MHz
$CDCl_3$
f1 (ppm)

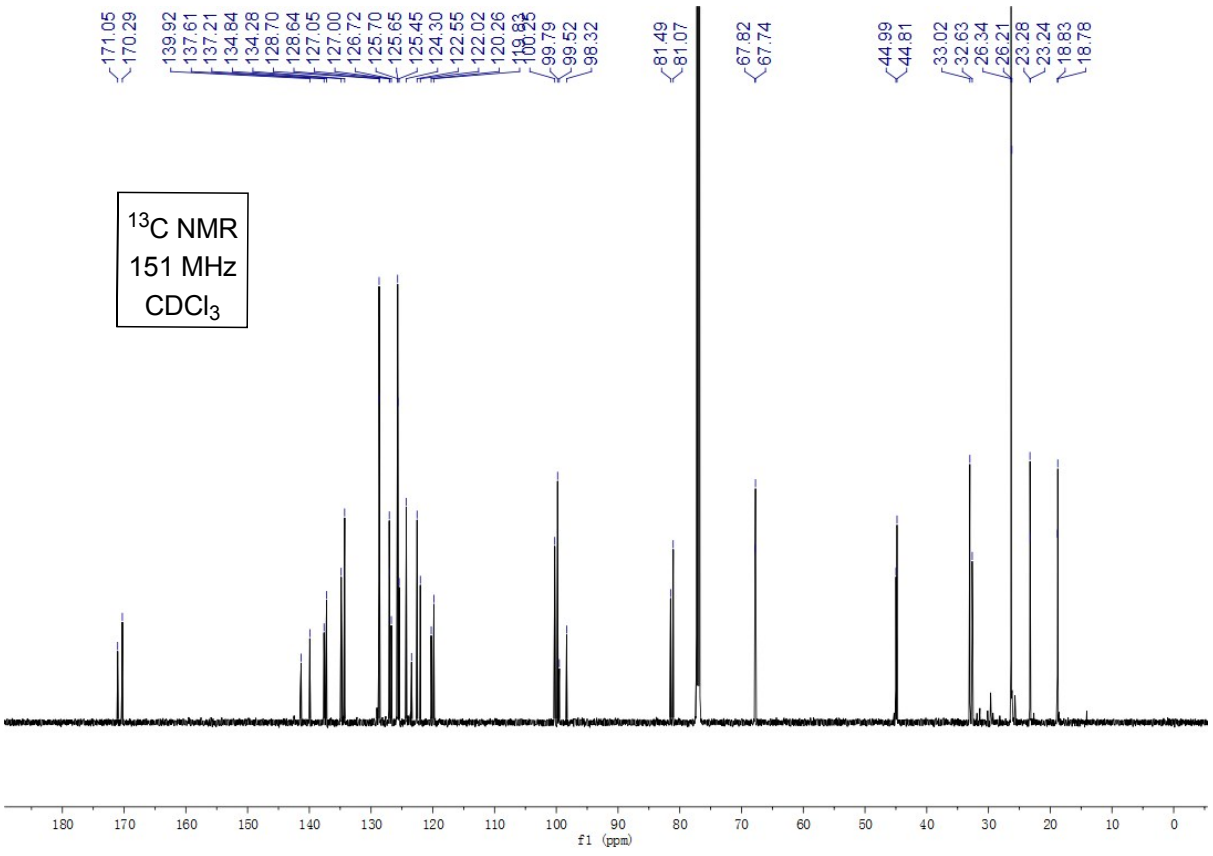

7.57 7.56 7.37 7.35 7.34 7.33 7.32 7.31 7.30 7.28 7.27 7.27 7.26 7.25 7.22 7.21 7.20 7.07 7.06 7.04 7.03 7.02 6.70 6.69 6.64 6.63 6.27 6.26 5.52 5.51 5.02 4.99 4.96 4.88 4.86 4.85 4.84 3.99 3.98 3.87 3.86 3.84 3.83 3.81 3.72 3.71 2.22 2.21 2.19 2.17 2.06 2.05 2.04 2.04 2.03 1.86 1.19 1.14
1H NMR
600 MHz
CDCl3
tBuOO
O
O
O
N
Bn
Me
0.96 6.10 0.99 0.96 0.44 0.49 1.01 0.95 2.08 1.33 1.14 1.76 9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

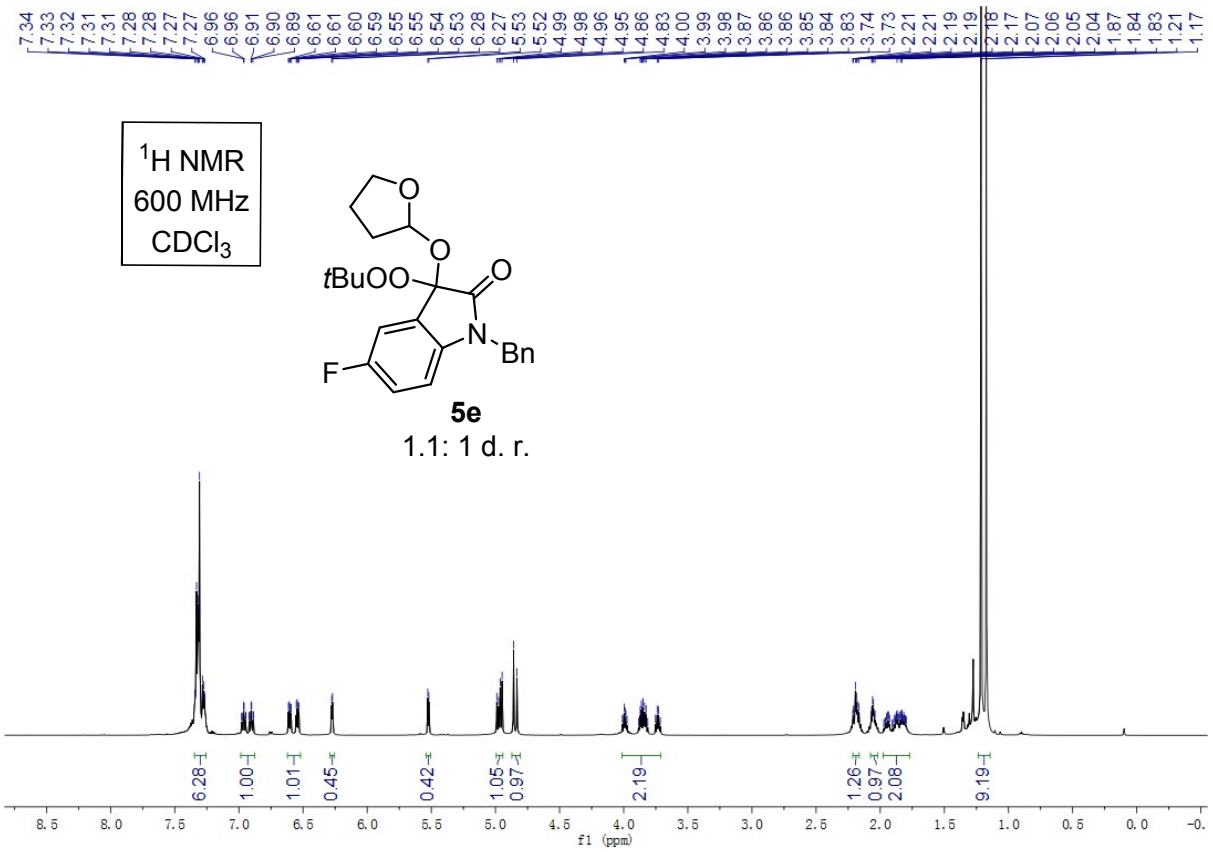
5c

1.1: 1 d. r.


169.94 169.25 140.77 139.51 135.57 135.44 131.90 131.39 130.97 130.45 128.57 128.53 128.15 127.40 127.37 127.08 127.04 109.49 109.02 100.48 100.31 99.75 99.24 81.51 81.06 67.82 67.71 43.58 43.44 32.96 32.57 26.31 26.19 23.27 20.99 20.98
13C NMR
151 MHz
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

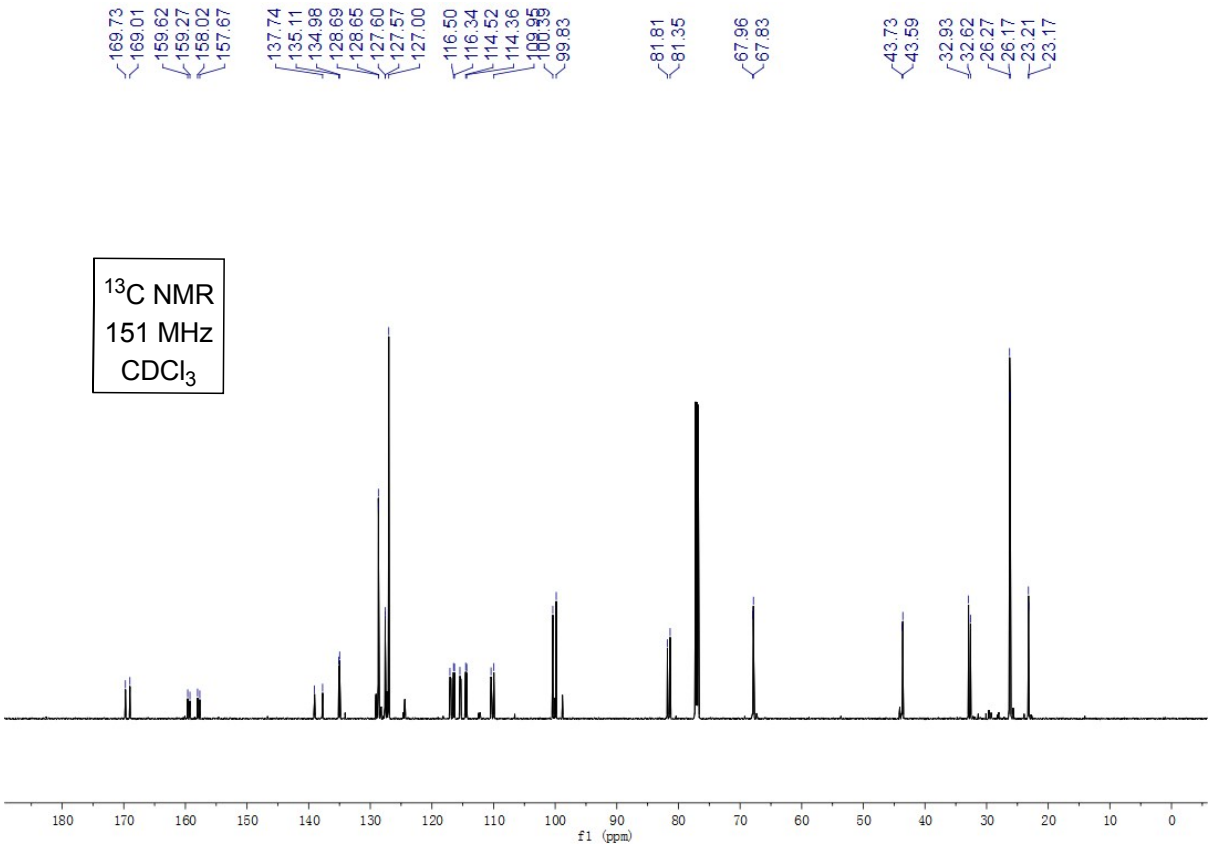

7.47 7.46 7.46 7.45 7.45 7.33 7.31 7.31 7.31 7.30 7.30 7.26 7.25 7.07 7.06 7.02 7.01 7.00 7.00 6.99 6.99 6.97 6.96 6.31 6.30 5.58 5.57 5.30 5.27 5.19 5.18 5.14 5.11 3.99 3.98 3.89 3.88 3.87 3.87 3.83 3.82 3.74 3.73 2.25 2.24 2.21 2.21 2.20 2.19 2.18 2.08 2.07 2.06 2.06 1.23 1.18
1H NMR
600 MHz
CDCl3
O
O
tBuOO
O
N
Bn
Me
5d
1.4: 1 d. r.
1.00 3.19 2.12 2.14 0.58 0.41 2.16 2.29 3.10 1.18 1.19 1.92 9.41
f1 (ppm)


171.05 170.29 139.92 137.61 137.21 134.84 134.28 128.70 128.64 127.05 127.00 126.72 125.70 125.65 125.45 124.30 122.55 122.02 120.26 99.79 99.52 98.32 81.49 81.07 67.82 67.74 44.99 44.81 33.02 32.63 26.34 26.21 23.28 23.24 18.83 18.78
13C NMR
151 MHz
CDCl3
f1 (ppm)

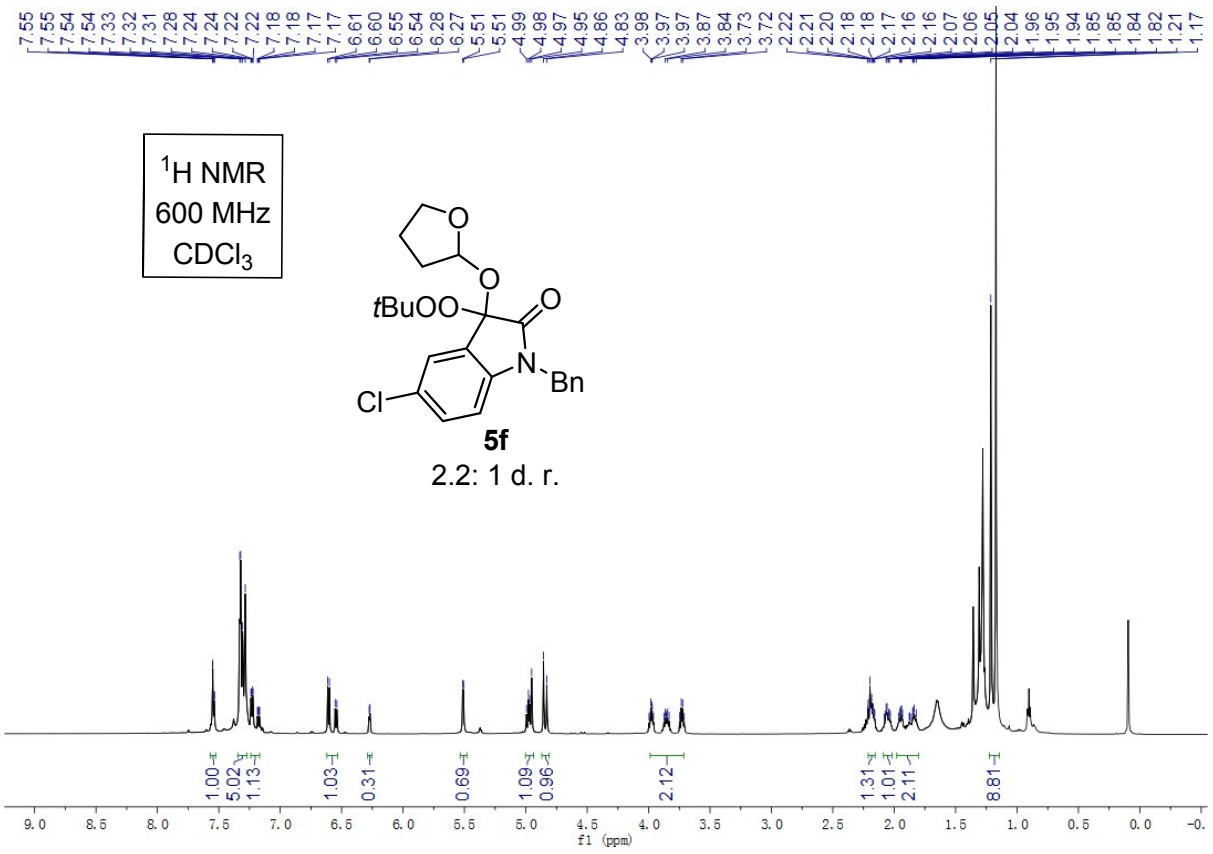


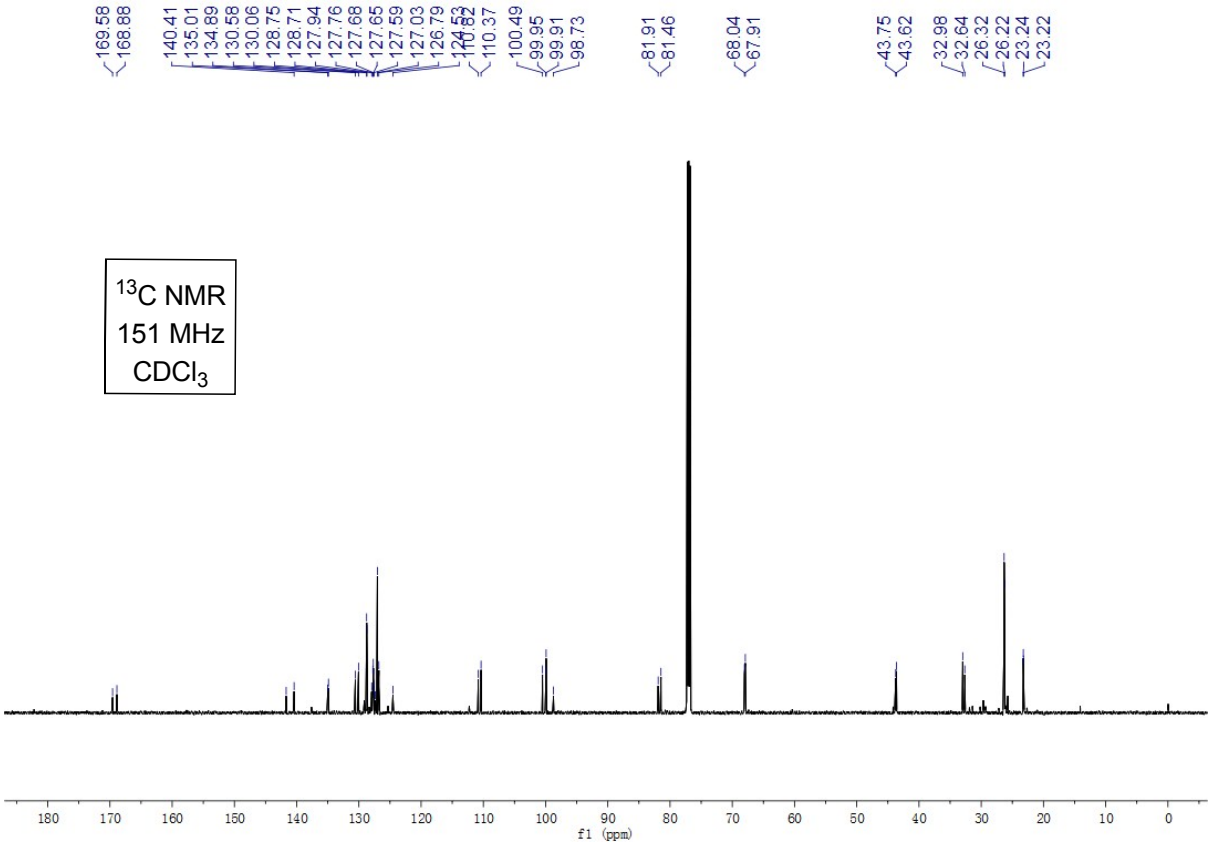
^{1}H NMR
600 MHz
$CDCl_3$

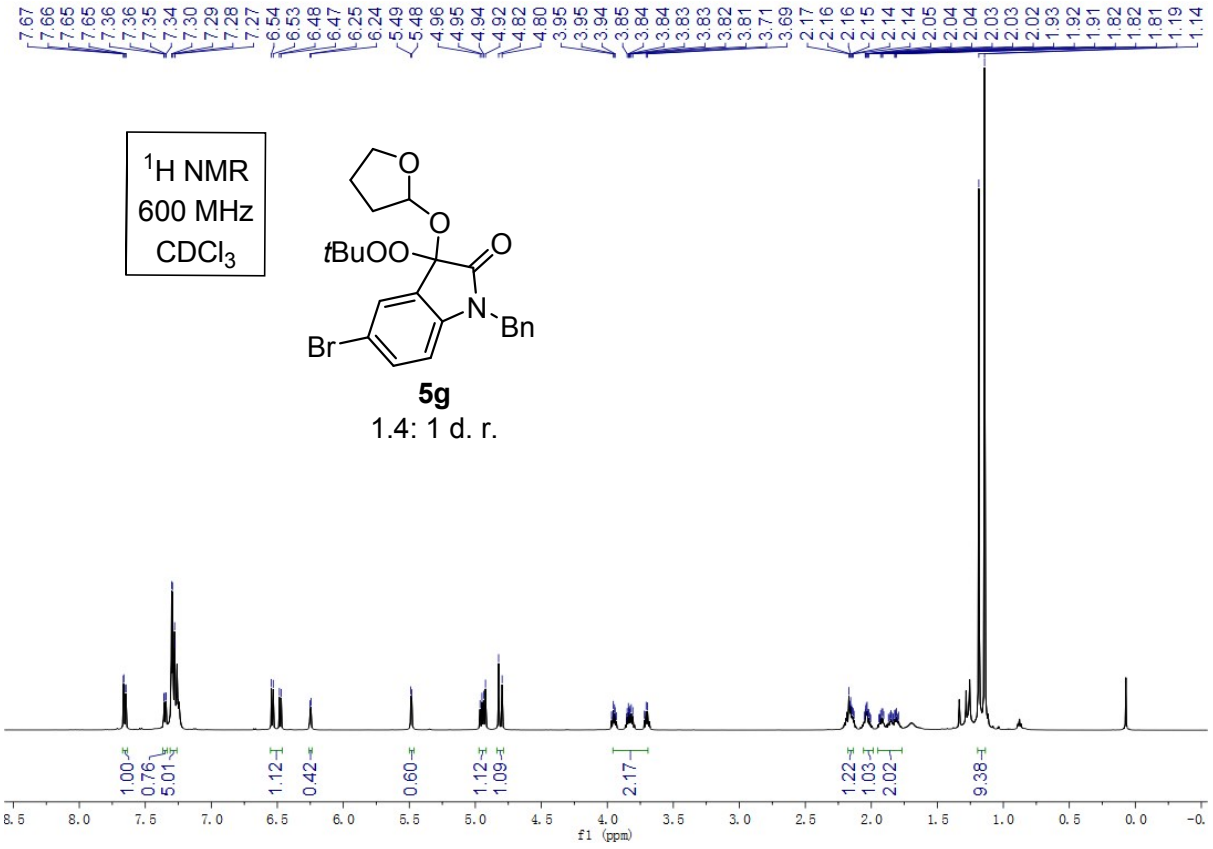
5e
1.1: 1 d. r.



^{13}C NMR
151 MHz
$CDCl_3$

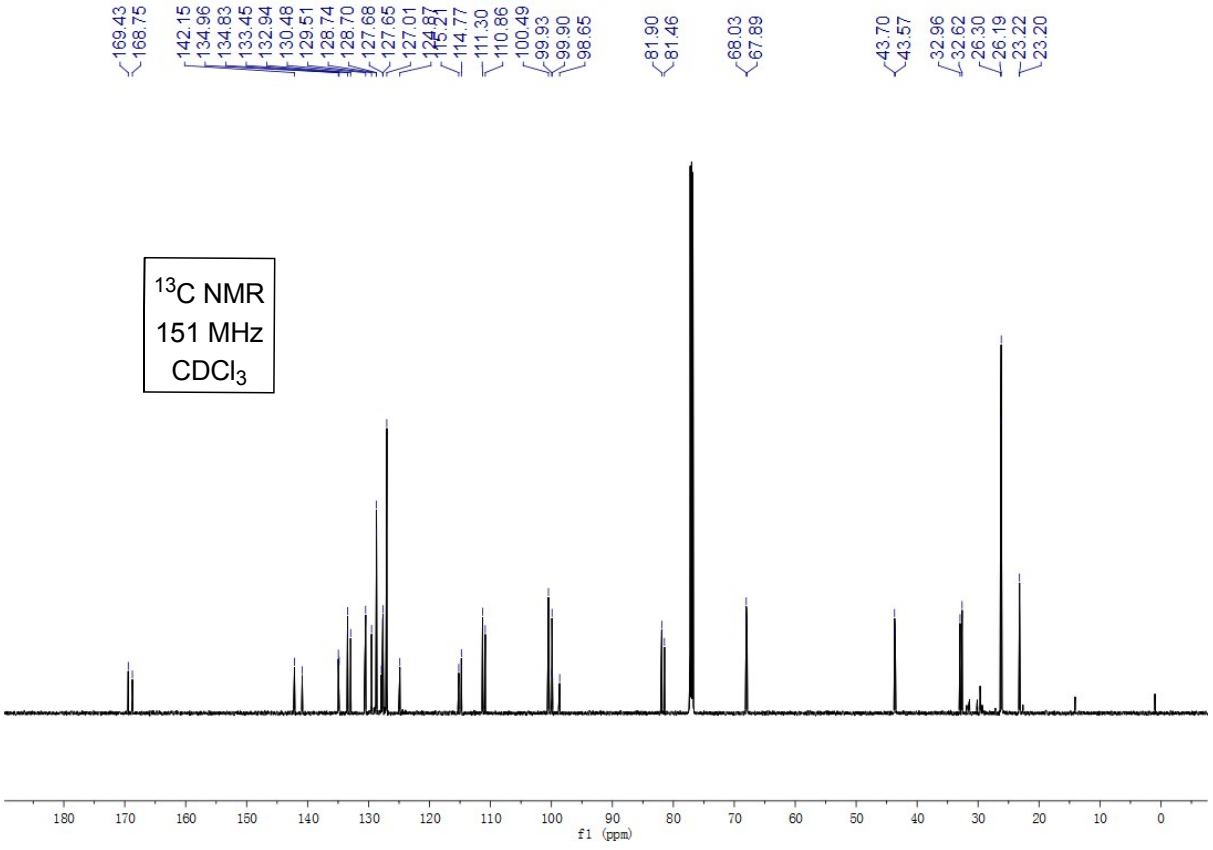

^{1}H NMR
600 MHz
$CDCl_3$
tBuOO
O
O
N
Bn
Cl
5f
2.2: 1 d. r.
f1 (ppm)

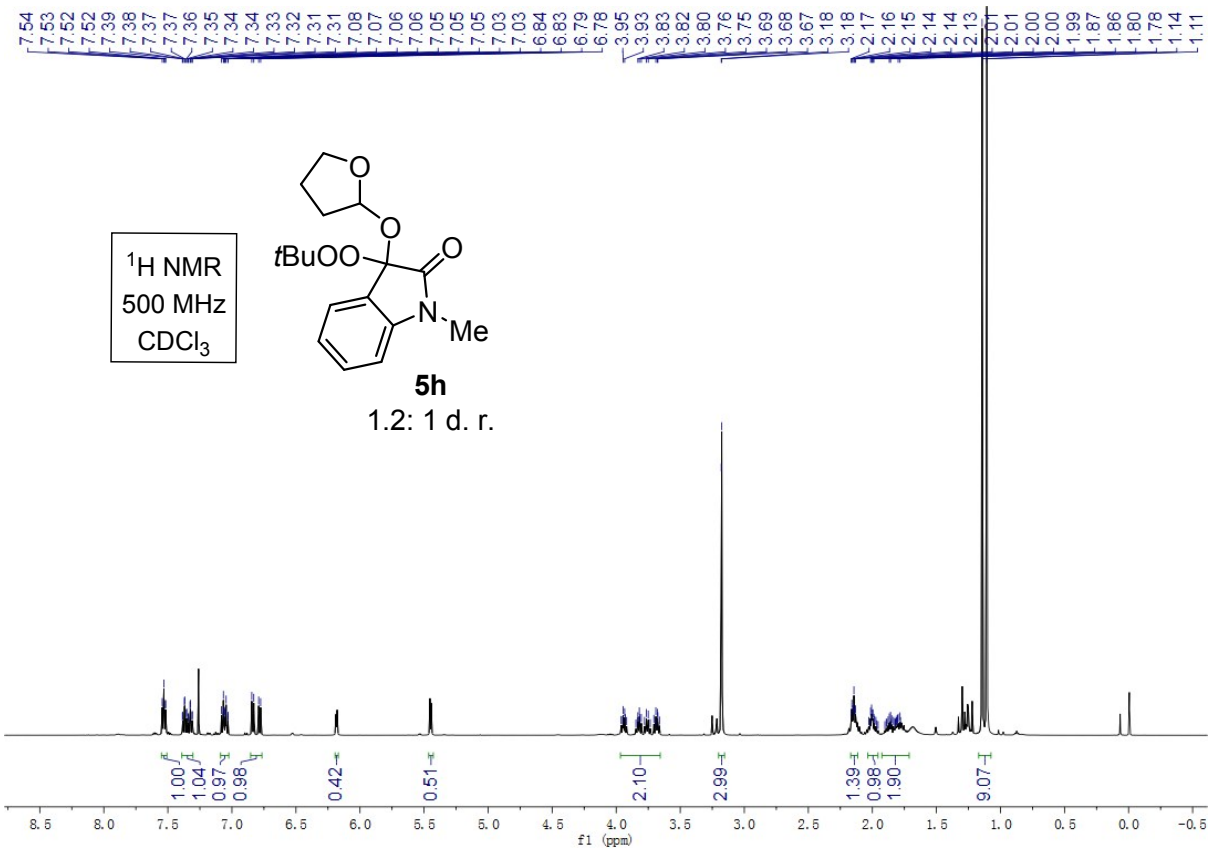

^{13}C NMR
151 MHz
$CDCl_3$
f1 (ppm)

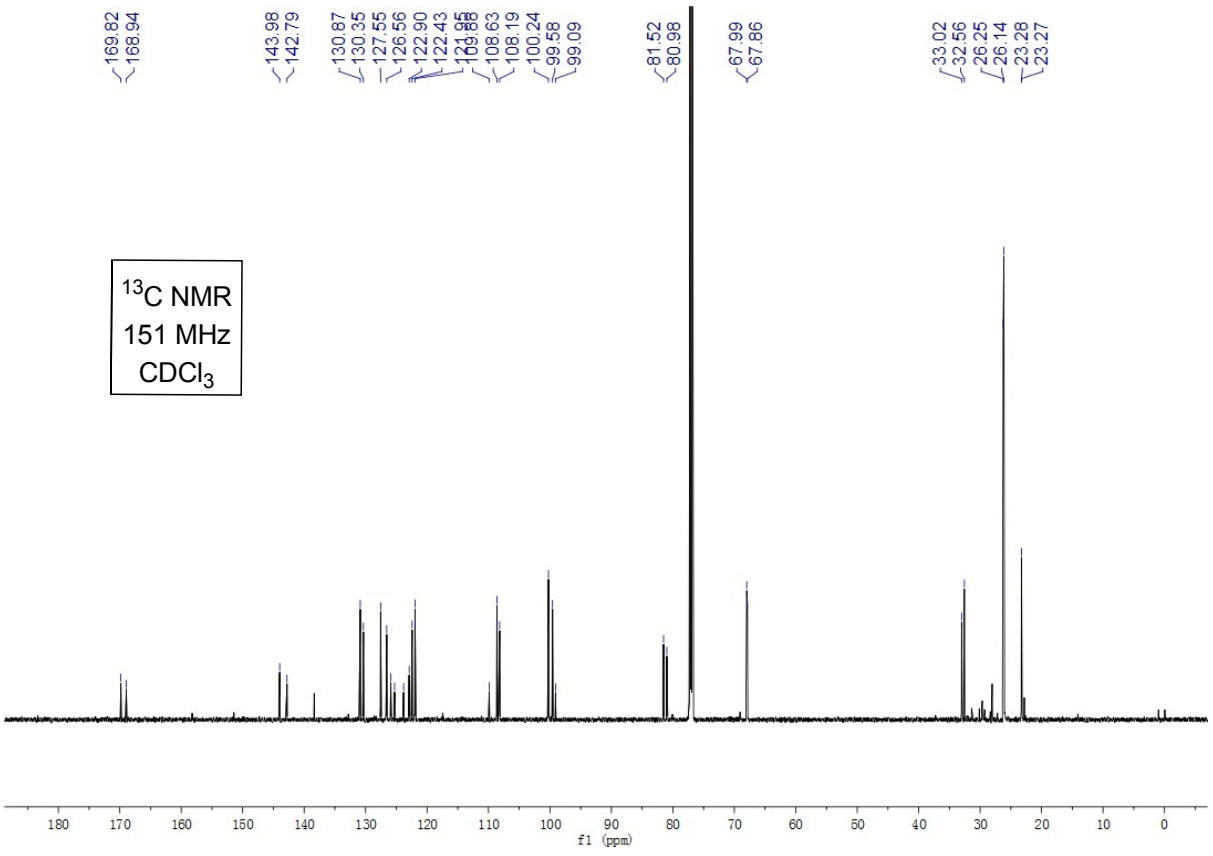

7.67 7.66 7.65 7.65 7.36 7.35 7.34 7.30 7.29 7.28 7.27 6.54 6.53 6.48 6.47 6.25 6.24 5.49 5.48 4.96 4.95 4.94 4.92 4.82 4.80 3.95 3.95 3.94 3.85 3.84 3.84 3.83 3.83 3.82 3.81 3.71 3.69 2.17 2.16 2.16 2.15 2.14 2.14 2.05 2.04 2.04 2.03 2.03 2.02 1.93 1.92 1.91 1.82 1.82 1.81 1.19 1.14
1H NMR
600 MHz
CDCl3
tBuOO
O
O
O
N
Bn
Br
1.00 0.76 5.01 1.12 0.42 0.60 1.12 1.09 2.17 1.22 1.03 2.02 9.38
f1 (ppm)

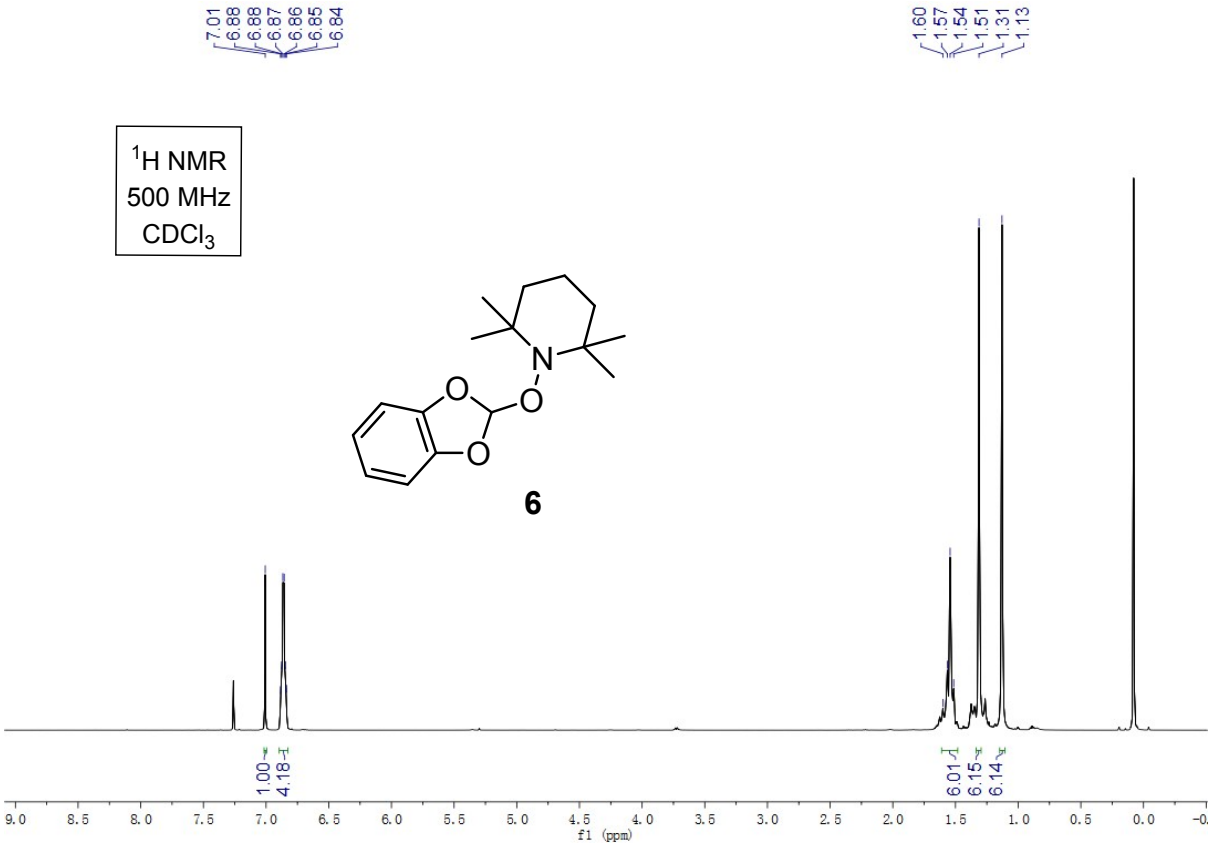
5g

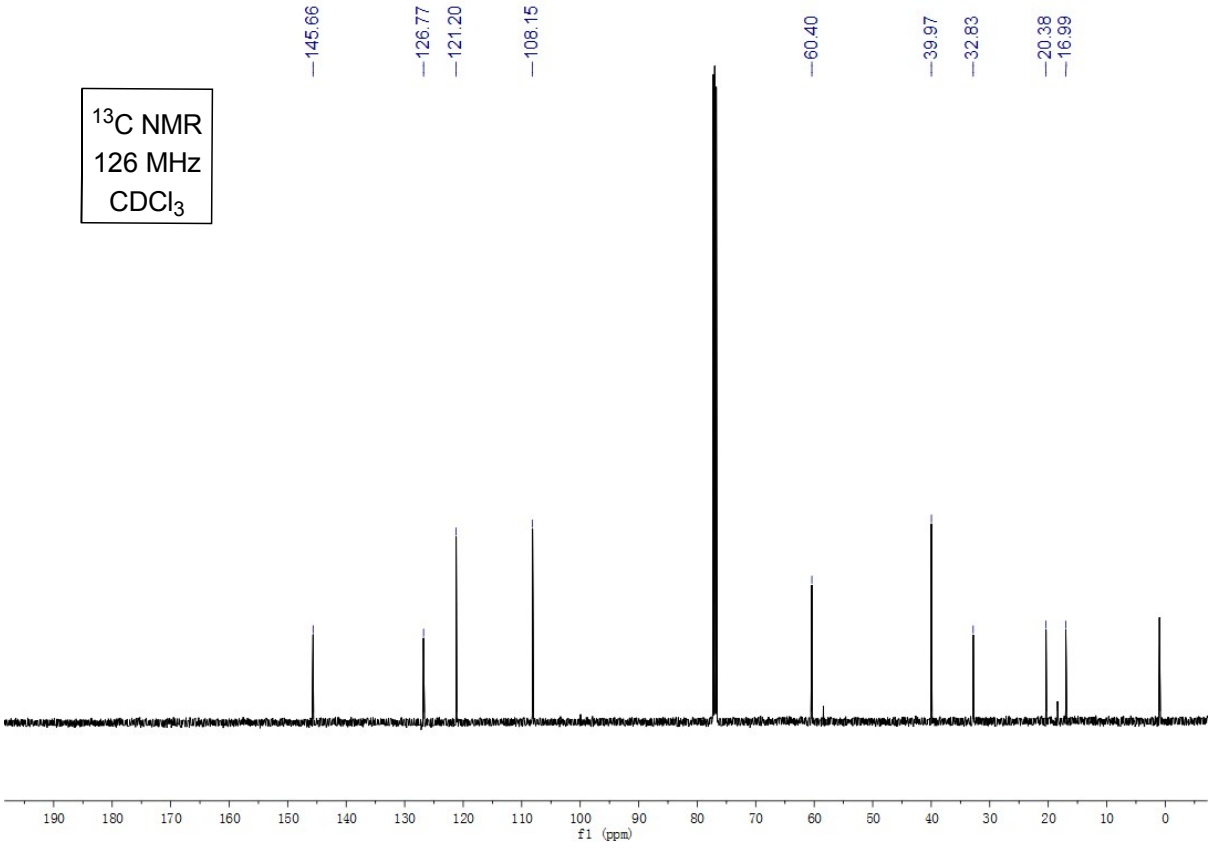
1.4: 1 d. r.

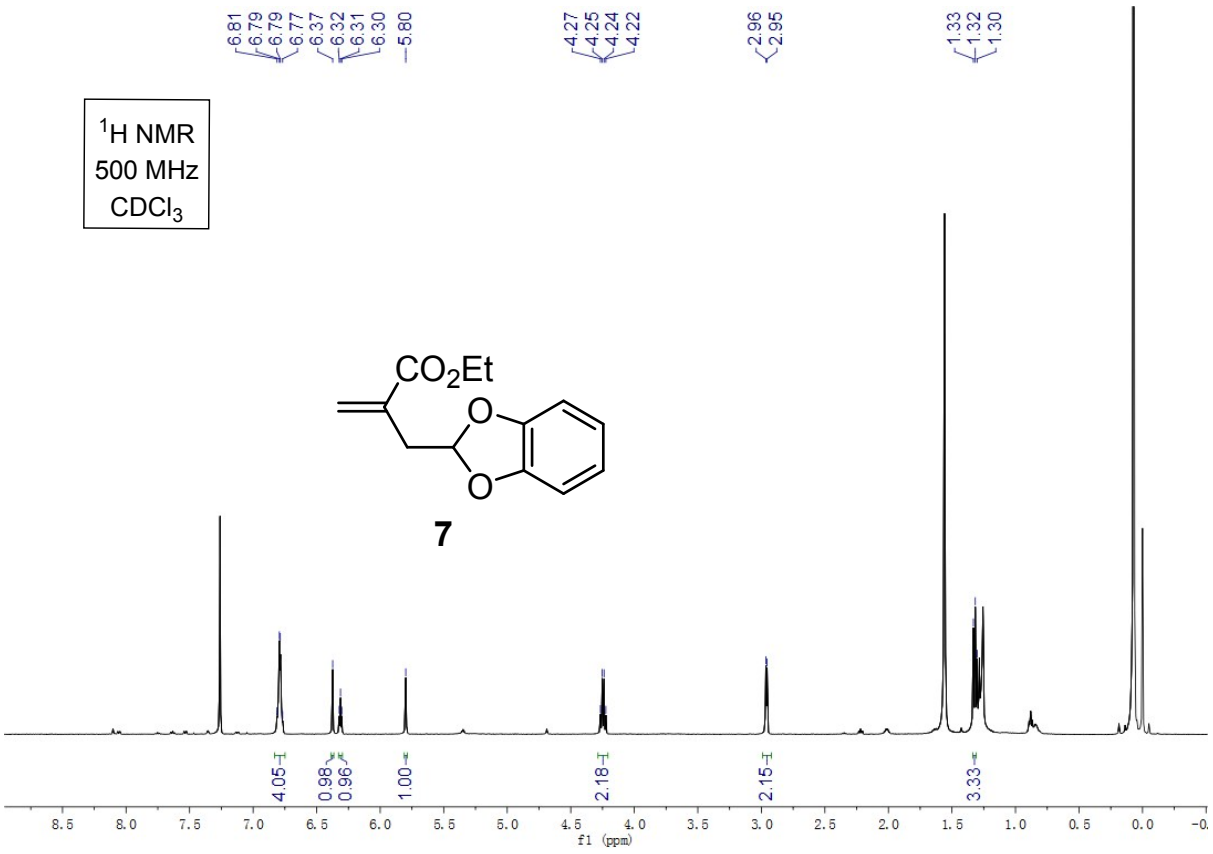

169.43 168.75 142.15 134.96 134.83 133.45 132.94 130.48 129.51 128.74 128.70 127.68 127.65 127.01 124.87 115.21 114.77 111.30 110.86 100.49 99.93 99.90 98.65 81.90 81.46 68.03 67.89 43.70 43.57 32.96 32.62 26.30 26.19 23.22 23.20
13C NMR
151 MHz
CDCl3
f1 (ppm)


^{1}H NMR
500 MHz
$CDCl_3$
tBuOO
O
O
O
N
Me
5h
1.2: 1 d. r.
f1 (ppm)

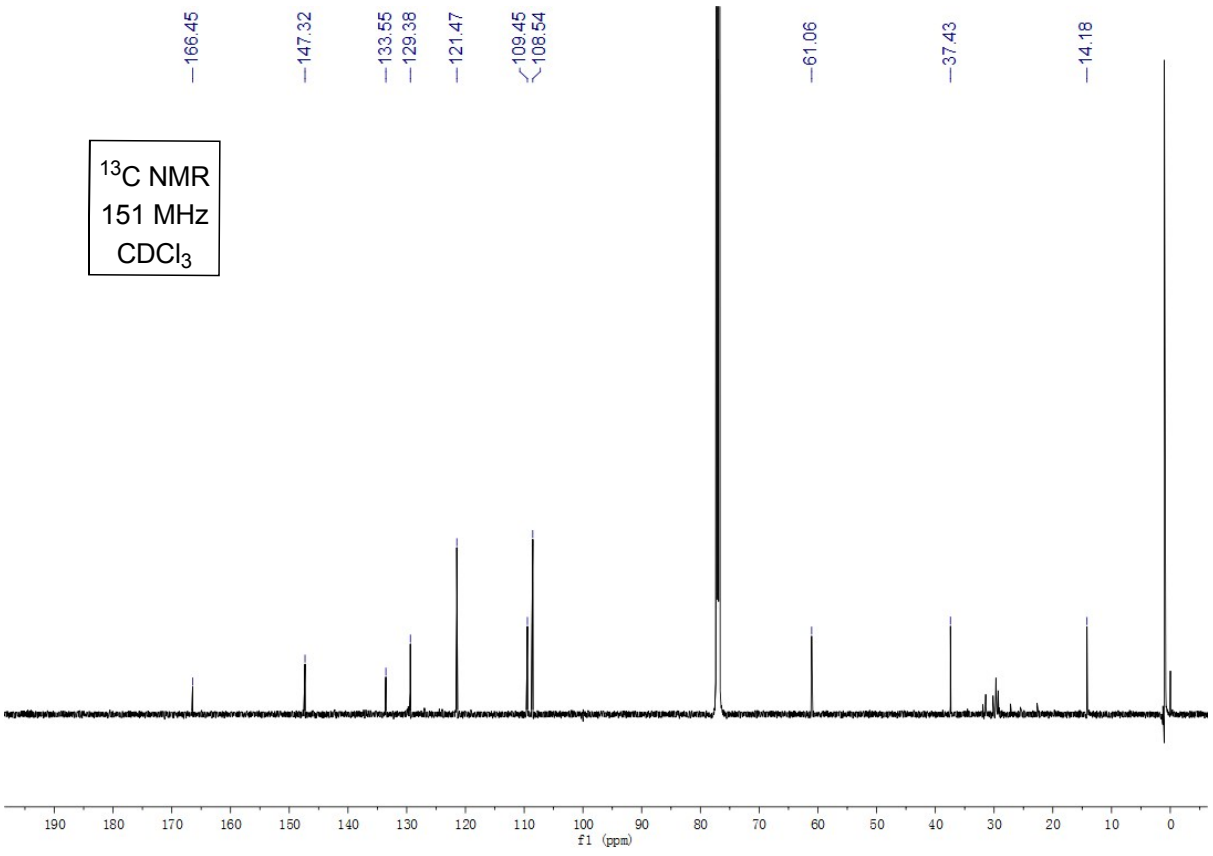

^{13}C NMR
151 MHz
$CDCl_3$
f1 (ppm)


7.01
6.88
6.88
6.87
6.86
6.85
6.84
1.60
1.57
1.54
1.51
1.31
1.13
1H NMR
500 MHz
CDCl3
N
O
O
O
6
1.00
4.18
6.01
6.15
6.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.66
126.77
121.20
108.15
60.40
39.97
32.83
20.38
16.99
13C NMR
126 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


6.81
6.79
6.79
6.77
6.37
6.32
6.31
6.30
5.80
4.27
4.25
4.24
4.22
2.96
2.95
1.33
1.32
1.30
^{1}H NMR
500 MHz
$CDCl_3$
CO_2Et
O
O
4.05
0.98
0.96
1.00
2.18
2.15
3.33
f1 (ppm)

7


166.45
147.32
133.55
129.38
121.47
109.45
108.54
61.06
37.43
14.18
^{13}C NMR
151 MHz
$CDCl_3$
f1 (ppm)