Electronic Supplementary Material (ESI) for Chemical Science.

Rhodium Catalyzed Cycloisomerization and Tandem Diels-Alder Reaction for Facile Access to Diverse Bicyclic and Tricyclic Heterocycles

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General information

Reactions were monitored by TLC analysis which was performed on aluminum plates pre-coated with silica gel (MERCK, 60 F-254), and visualized by UV fluorescence (λmax = 254 nm) and/or by staining with 1% w/v $KMnO_4$ in 0.5 M aqueous K_2CO_3. Products were purified by flash column chromatography which was performed using MACHEREY-NAGEL silica gel 60® (230-400 mesh).

NMR (Nuclear Magnetic Resonance) spectra were acquired on a VARIAN Mercury (300 MHz) or on a BRUKER Avance 400 spectrometer or on a Bruker 500 DRX NMR spectrometer. Chemical shifts for ^{1}H NMR spectra are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Chemical shifts for ^{13}C NMR spectra are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, 77.16 ppm) and with complete proton decoupling.

HRMS (High Resolution Mass Spectra) was measured on a THERMO SCIENTIFIC Advantage and a THERMO SCIENTIFIC Exactive instrument equipped with an APCI or ESI source in the positive-ion mode.

The structure of **2a** and **4c** was assigned by X-ray crystallographic analysis.

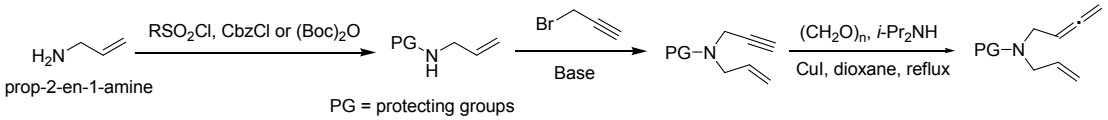
Melting points for solids were measured on a BÜCHI Dr. Tottoli melting point apparatus and are given uncorrected.

Solvents: Cyclohexane and EtOAc for column chromatography were purified prior to use by evaporation on a rotary evaporator. Unless performing reactions sensitive to air and/or moisture, the solvents were bought in p.a. quality and used without further purification. Flasks for absolute solvents were flame-dried three times under oil pump vacuum and backfilled with argon. 1,2-Dichloroethane (DCE) was freshly distilled over CaH_2 and collected and cooled under Argon. THF was freshly distilled over Na and collected and cooled under Argon.

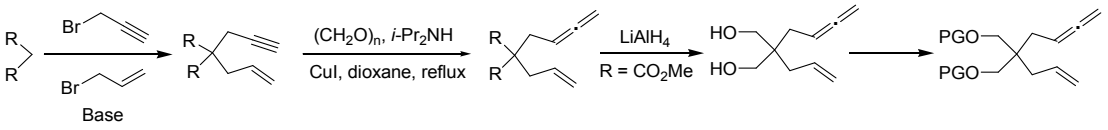
Ligands and metal catalysts were purchased from Sigma-Aldrich, ABCR, Alfa Aesar and were used as received.

Preparation and characterization of the starting materials

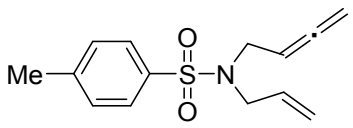
Starting materials **1a** to **1h** were synthesized according to the following route, with slightly modified literature known method.[1] Starting from commercially available allylamine, various protecting group were used to protect the free amine. Then by treatment with propargyl bromide in the presence of suitable base, 1,6-enynes were generated. Finally, terminal alkynes could be facilely transformed into allenes through classical Crabbé reaction.



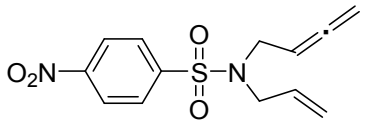
Starting materials **1i** to **1l** were synthesized according to the following route, with slightly modified literature known method.[2] Starting from activated methylene compounds, 1,6-enynes were obtained by the sequential alkylation with propargyl bromide and allyl bromide. Then, terminal allenes were prepared through Crabbé reaction from the corresponding terminal alkynes. Starting materials **1m** to **1p** were prepared by protection of the free diol, which were generated from **1i** by reduction of $LiAlH_4$.



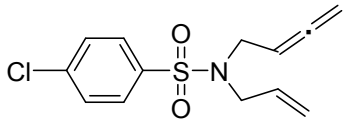
Characterization data of the starting materials



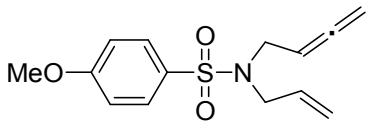
N-allyl-*N*-tosylbuta-2,3-dien-1-amine (**1a**). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.66 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 1H), 5.19 – 5.17 (m, 1H), 5.15 (t, *J* = 1.2 Hz, 1H), 4.90 (p, *J* = 6.8 Hz, 1H), 4.69 (dt, *J* = 6.6, 2.4 Hz, 2H), 3.86 – 3.84 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 143.3, 137.7, 132.7, 129.8, 127.3, 119.1, 85.8, 76.2, 49.4, 45.7, 21.6; HRMS (pos. APCI): m/z for $C_{14}H_{18}O_2NS$ $[M+H]^+$ calcd: 264.1053, found: 264.1052.



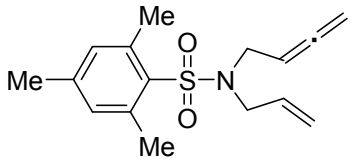
N-allyl-*N*-(4-nitrobenzenesulfonyl)-2,3-dien-1-amine (**1b**). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 5.64 (ddt, *J* = 17.6, 9.6, 6.4 Hz, 1H), 5.22 (s, 1H), 5.20 – 5.15 (m, 1H), 4.93 (p, *J* = 6.8 Hz, 1H), 4.71 (dt, *J* = 6.6, 2.4 Hz, 2H), 3.91 (dt, *J* = 6.8, 2.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 150.1, 146.7, 131.8, 128.4, 124.4, 119.9, 85.4, 76.8, 49.5, 45.8; HRMS (pos. APCI): m/z for $C_{13}H_{18}O_4N_3S$ $[M+NH_4]^+$ calcd: 312.1013, found: 312.1013.



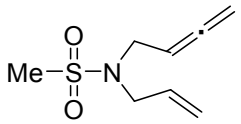
N-allyl-*N*-(4-chlorobenzenesulfonyl)-2,3-dien-1-amine (**1c**). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 5.64 (ddt, *J* = 16.2, 9.8, 6.4 Hz, 1H), 5.21 – 5.14 (m, 2H), 4.91 (p, *J* = 6.8 Hz, 1H), 4.69 (dt, *J* = 6.6, 2.4 Hz, 2H), 3.88 – 3.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 139.3, 139.0, 132.3, 129.4, 128.7, 119.4, 85.6, 76.4, 49.4, 45.7; HRMS (pos. ESI): m/z for $C_{13}H_{14}O_2ClNaS$ $[M+Na]^+$ calcd: 306,0326, found: 306,0328.



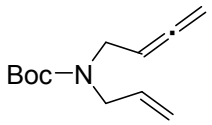
N-allyl-*N*-(4-methoxybenzenesulfonyl)-2,3-dien-1-amine (**1d**). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.2 Hz, 2H), 6.96 (d, *J* = 9.2 Hz, 2H), 5.65 (ddt, *J* = 23.2, 10.2, 6.4 Hz, 1H), 5.18 (dq, *J* = 7.6, 1.2 Hz, 1H), 5.15 (t, *J* = 1.2 Hz, 1H), 4.90 (p, *J* = 7.2 Hz, 1H), 4.69 (dt, *J* = 6.8, 2.4 Hz, 2H), 3.86 (s, 3H), 3.85 – 3.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 162.9, 132.7, 132.2, 129.4, 119.1, 114.3, 85.8, 76.2, 55.7, 49.3, 45.7; HRMS (pos. ESI): m/z for $C_{14}H_{17}O_3NNaS$ $[M+Na]^+$ calcd: 302.0821, found: 302.0823.



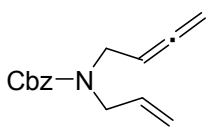
N-allyl-*N*-(2,4,6-trimethylbenzenesulfonyl)-2,3-dien-1-amine (**1e**). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 2H), 5.67 (ddt, *J* = 16.4, 9.8, 6.6 Hz, 1H), 5.21 – 5.14 (m, 2H), 5.01 (p, *J* = 6.8 Hz, 1H), 4.71 (dt, *J* = 6.6, 2.4 Hz, 2H), 3.84 – 3.77 (m, 4H), 2.61 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 142.5, 140.3, 133.3, 132.6, 132.0, 119.4, 85.8, 76.0, 48.2, 44.4, 22.9, 21.0; HRMS (pos. ESI): m/z for $C_{16}H_{22}O_2NS$ $[M+H]^+$ calcd: 292.1366, found: 292.1368.



N-allyl-*N*-methylsulfonyl-2,3-dien-1-amine (**1f**). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 16.6, 10.0, 6.4 Hz, 1H), 5.29 – 5.21 (m, 2H), 5.12 (p, *J* = 6.8 Hz, 1H), 4.81 (dt, *J* = 6.6, 2.5 Hz, 2H), 3.86 (dt, *J* = 6.8, 2.4 Hz, 4H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 132.5, 119.3, 85.9, 76.6, 49.1, 45.3, 40.2; HRMS (pos. ESI): m/z for $C_8H_{13}O_2NNaS$ $[M+Na]^+$ calcd: 210.0559, found: 210.0559.

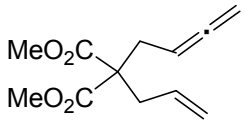


tert-butyl allylbuta-2,3-dienylcarbamate (**1g**). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 17.6, 9.9, 5.8 Hz, 1H), 5.16 – 5.05 (m, 3H), 4.75 (dt, *J* = 6.4, 2.8 Hz, 2H), 3.82 (br s, 4H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 155.4, 134.1, 116.5, 87.3, 79.8, 76.1, 49.0, 45.2, 28.5; HRMS (pos. APCI): m/z for $C_{12}H_{20}O_2N$ $[M+H]^+$ calcd: 210.1489, found: 210.1490.

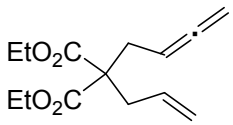


benzyl allylbuta-2,3-dienylcarbamate (**1h**). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 5.86 – 5.71 (m, 1H), 5.15 – 5.14 (m, 5H), 4.74 (br s,

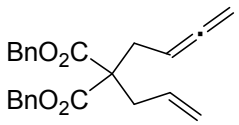
2H), 3.92 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 156.0, 136.9, 133.6, 130.1, 128.5, 128.0, 127.9, 117.4, 86.9, 67.3, 49.5, 45.5; HRMS (pos. APCI): m/z for $C_{15}H_{18}O_2N$ $[M+H]^+$ calcd: 244.1332, found: 244.1330.



dimethyl 2-allyl-2-(buta-2,3-dienyl)malonate (**1i**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 – 5.57 (m, 1H), 5.13 – 5.10 (m, 1H), 5.08 (s, 1H), 4.93 (p, *J* = 8.0 Hz, 1H), 4.65 (dt, *J* = 6.6, 2.4 Hz, 2H), 3.71 (s, 6H), 2.67 (d, *J* = 7.4 Hz, 2H), 2.59 (dt, *J* = 8.0, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 171.1, 132.3, 119.4, 84.2, 74.7, 58.0, 52.4, 37.0, 32.0; HRMS (pos. ESI): m/z for $C_{12}H_{16}O_4Na$ $[M+Na]^+$ calcd: 247.0941, found: 247.0943.

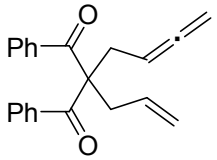


diethyl 2-allyl-2-(buta-2,3-dienyl)malonate (**1j**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (ddt, *J* = 17.6, 10.0, 7.4 Hz, 1H), 5.14 – 5.07 (m, 2H), 4.95 (p, *J* = 8.0 Hz, 1H), 4.65 (dt, *J* = 6.6, 2.4 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 4H), 2.68 (d, *J* = 7.4 Hz, 2H), 2.61 (dt, *J* = 8.0, 2.4 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 170.7, 132.5, 119.3, 84.4, 74.6, 61.4, 57.7, 36.8, 31.9, 14.2; HRMS (pos. ESI): m/z for $C_{14}H_{20}O_4Na$ $[M+Na]^+$ calcd: 275.1254, found: 275.1258.

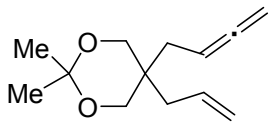


dibenzyl 2-allyl-2-(buta-2,3-dienyl)malonate (**1k**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 6H), 7.28 – 7.26 (m, 4H), 5.68 – 5.55 (m, 1H), 5.11 (s, 4H), 5.07 (s, 1H), 5.03 (dd, *J* = 3.6, 2.2 Hz, 1H), 4.95 – 4.87 (m, 1H), 4.61 (dt, *J* = 6.6, 2.4 Hz, 2H), 2.73 (d, *J* = 7.6 Hz, 2H), 2.66 (dt, *J* = 8.0, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 170.4, 135.5, 132.1, 128.6, 128.4, 128.3, 119.5, 84.2, 74.76, 67.14,

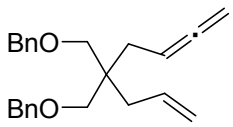
58.0, 36.9, 31.9; HRMS (pos. ESI): m/z for $C_{24}H_{24}O_4Na$ $[M+Na]^+$ calcd: 399.1567, found: 399.1567.



2-allyl-2-(buta-2,3-dienyl)-1,3-diphenylpropane-1,3-dione (**1l**). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 4H), 7.45 – 7.41 (m, 2H), 7.33 – 7.30 (m, 4H), 5.53 – 5.43 (m, 1H), 5.05 – 5.01 (m, 1H), 4.93 – 4.87 (m, 1H), 4.78 – 4.69 (m, 1H), 4.49 (dt, *J* = 6.6, 2.4 Hz, 2H), 3.01 (d, *J* = 7.6 Hz, 2H), 2.94 (dt, *J* = 8.2, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 198.5, 136.5, 133.1, 131.7, 129.0, 128.7, 119.8, 83.6, 74.5, 67.0, 37.7, 32.9; HRMS (pos. ESI): m/z for $C_{22}H_{20}O_2Na$ $[M+Na]^+$ calcd: 339.1356, found: 339.1357.

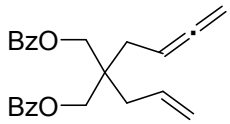


5-allyl-5-(buta-2,3-dienyl)-2,2-dimethyl-1,3-dioxane (**1m**). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 20.4, 9.4, 7.6 Hz, 1H), 5.12 (d, *J* = 1.0 Hz, 1H), 5.10 – 5.07 (m, 1H), 5.03 (ddd, *J* = 13.4, 7.4, 4.0 Hz, 1H), 4.66 (dt, *J* = 6.6, 2.4 Hz, 2H), 3.60 (s, 4H), 2.19 – 2.14 (m, 2H), 2.10 (dt, *J* = 8.0, 2.4 Hz, 2H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 133.2, 118.5, 98.2, 84.6, 74.2, 67.2, 36.8, 36.3, 31.7, 24.1, 23.8; HRMS (pos. APCI): m/z for $C_{13}H_{21}O_2$ $[M+H]^+$ calcd: 209.1536, found: 209.1535.

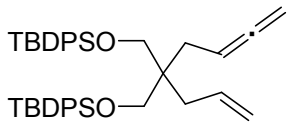


1-((2-allyl-2-((benzyloxy)methyl)hexa-4,5-dienyloxy)methyl)benzene (**1n**). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 10H), 5.79 (ddt, *J* = 17.8, 10.4, 7.6 Hz, 1H), 5.08 – 5.00 (m, 3H), 4.60 (dt, *J* = 6.6, 2.4 Hz, 2H), 4.48 (s, 4H), 3.34 (s, 4H), 2.15 (d, *J* = 7.6 Hz, 2H), 2.09 (dt, *J* = 8.2, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 139.0, 134.4, 128.3, 127.5, 127.4, 117.8, 85.5, 73.6, 73.4, 72.6, 42.6, 36.6,

31.7; HRMS (pos. APCI): m/z for $C_{24}H_{32}O_2N$ $[M+NH_4]^+$ calcd: 366.2428, found: 366.2432.



2-allyl-2-(buta-2,3-dien-1-yl)propane-1,3-diyl dibenzoate (**1o**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 4H), 7.51 – 7.45 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 4H), 5.86 – 5.74 (m, 1H), 5.11 – 5.01 (m, 3H), 4.56 (dt, *J* = 6.6, 2.4 Hz, 2H), 4.27 (s, 4H), 2.28 (d, *J* = 7.6 Hz, 2H), 2.21 (dt, *J* = 8.2, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.3, 166.3, 133.1, 132.4, 130.1, 129.7, 128.5, 119.5, 84.1, 74.5, 66.6, 41.5, 36.8, 31.9; HRMS (pos. ESI): m/z for $C_{24}H_{24}O_4Na$ $[M+Na]^+$ calcd: 399.1567, found: 399.1566.

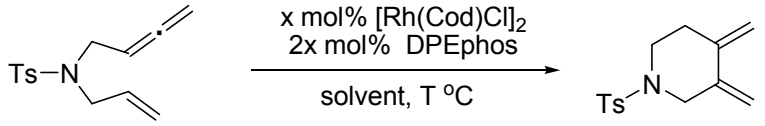


6-allyl-6-(buta-2,3-dien-1-yl)-2,2,10,10-tetramethyl-3,3,9,9-tetraphenyl-4,8-dioxa-3,9-disilaundecane (**1p**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.0, 1.2 Hz, 8H), 7.44 – 7.39 (m, 4H), 7.33 (dd, *J* = 11.2, 4.2 Hz, 8H), 5.65 (ddt, *J* = 17.4, 10.0, 7.4 Hz, 1H), 5.02 – 4.89 (m, 3H), 4.51 (dt, *J* = 6.4, 2.6 Hz, 2H), 3.56 (s, 4H), 2.19 (d, *J* = 7.4 Hz, 2H), 2.13 (dt, *J* = 8.0, 2.6 Hz, 2H), 1.06 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 135.9, 134.5, 133.7, 129.6, 127.7, 117.5, 85.7, 73.7, 65.8, 44.4, 36.3, 31.2, 27.1, 19.5; HRMS (pos. APCI): m/z for $C_{42}H_{53}O_2Si_2$ $[M+H]^+$ calcd: 645.3579, found: 645.3576.

Optimization of parameters for the cyclization

Simple 1,6-allenene **1a** was selected as model substrate to optimize the reaction conditions for cyclization. The results are summarized in Table S1. Firstly, several solvent were tested and DCE turned out to be optimal one (Table S1, entries 1-3). Then the reaction temperature was accessed and 60 centigrade degree gave better results than others (Table S1, entries 4-7). The reaction concentration investigation showed that 0.1 M was favorable for the cyclization and generated the highest yield of 80% (Table S1, entries 8-11). Finally, either increase or decrease the catalyst loading could not improve the outcomes (Table S1, entries 12-14).

Table S1. Comprehensive optimization for the cyclization.[a]

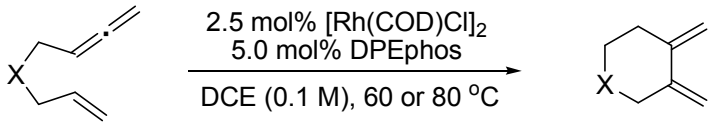


1a **2a**

entry	x mol%	solvent	C	T °C	Yield %
1	2.5	DCE	0.2 M	80	65
2	2.5	THF	0.2 M	80	58
3	2.5	Toluene	0.2 M	80	55
4	2.5	DCE	0.2 M	95	51
5	2.5	DCE	0.2 M	60	75
6	2.5	DCE	0.2 M	50	48
7	2.5	DCE	0.2 M	35	20
8	2.5	DCE	0.4 M	60	40
9	*2.5*	*DCE*	***0.1** M*	*60*	***80***
10	2.5	DCE	0.05 M	60	78
11	2.5	DCE	0.025 M	60	48
12	4	DCE	0.1 M	60	76
13	1	DCE	0.1 M	60	50
14	0.5	DCE	0.1 M	60	trace

[a] The reactions were carried out on a 0.2 mmol scale of **1a** for 20 h. Isolated yield.

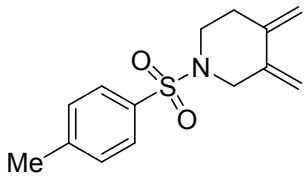
General procedure and characterization for the cyclization products



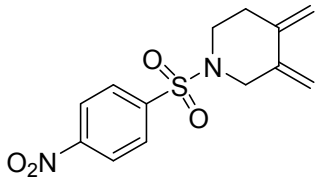
1 **2**

A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol, 2.5 mol%), DPEphos (5.4 mg, 0.01 mmol, 5.0 mol%), 1,6-allenene **1** (0.2 mmol, 1.0 equiv). The Schlenk tube was put on vacuum and backfilled with argon three times. 2.0 ml of 1,2-dichloroethane (DCE) were added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 60 or 80 °C for 20 hours. The mixture was cooled down to room temperature and the solvent was removed with rotary evaporator. The residue was purified with column chromatography on silica gel, eluting with cyclohexane and ethyl acetate to afford the corresponding six-membered ring exocyclic 1,3-diene product **2** after drying in vacuo.

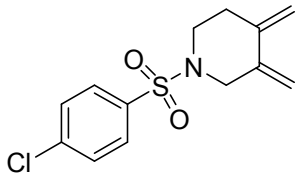
Characterization data of the cyclization products



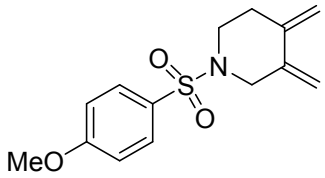
3,4-dimethylene-1-tosylpiperidine (**2a**). White solid, m.p. 125−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.15 (d, J = 0.4 Hz, 1H), 5.05 (d, J = 1.2 Hz, 1H), 4.88 (d, J = 1.2 Hz, 1H), 4.74 (d, J = 1.6 Hz, 1H), 3.65 (s, 2H), 3.16 (t, J = 6.0 Hz, 2H), 2.42 (s, 3H), 2.38 (t, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.4, 141.4, 133.6, 129.7, 127.9, 111.5, 110.9, 51.9, 46.5, 33.1, 21.6; HRMS (pos. APCI): m/z for $C_{14}H_{18}O_2NS$ $[M+H]^+$ calcd: 264.1053, found: 264.1052.



3,4-dimethylene-1-(4-nitrobenzenesulfonyl)piperidine (**2b**). Yellow solid, m.p. 114−115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 5.18 (d, *J* = 0.4 Hz, 1H), 5.08 (d, *J* = 0.8 Hz, 1H), 4.91 (d, *J* = 1.2 Hz, 1H), 4.78 (d, *J* = 1.6 Hz, 1H), 3.78 (s, 2H), 3.29 (t, *J* = 6.0 Hz, 2H), 2.37 (t, *J* = 6.0 Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 143.5, 142.5, 140.7, 128.9, 124.4, 112.0, 111.7, 51.7, 46.4, 32.9; HRMS (pos. APCI): m/z for $C_{13}H_{18}O_4N_3S$ $[M+NH_4]^+$ calcd: 312.1013, found: 312.1013.

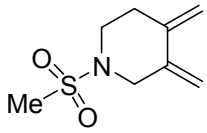


3,4-dimethylene-1-(4-chlorobenzenesulfonyl)piperidine (**2c**). Light yellow solid, m.p. 91−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 5.16 (d, *J* = 0.5 Hz, 1H), 5.06 (d, *J* = 1.0 Hz, 1H), 4.89 (d, *J* = 1.0 Hz, 1H), 4.76 (d, *J* = 1.5 Hz, 1H), 3.68 (s, 2H), 3.19 (t, *J* = 6.0 Hz, 2H), 2.38 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 141.0, 139.4, 135.3, 129.5, 129.2, 111.8, 111.3, 51.8, 46.4, 33.0; HRMS (pos. ESI): m/z for $C_{13}H_{14}O_2ClNaS$ $[M+Na]^+$ calcd: 306,0326, found: 306,0328.

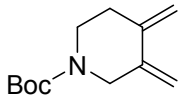


3,4-dimethylene-1-(4-methoxybenzenesulfonyl)piperidine (**2d**). White solid, m.p. 115−116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.15 (d, *J* = 0.8 Hz, 1H), 5.04 (d, *J* = 1.2 Hz, 1H), 4.88 (d, *J* = 1.2 Hz, 1H), 4.74 (d, *J* = 1.6 Hz, 1H), 3.86 (s, 3H), 3.64 (s, 2H), 3.15 (t, *J* = 6.0 Hz, 2H), 2.38 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.4, 141.5, 129.9, 128.2,

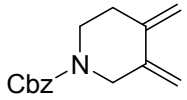
114.3, 111.5, 110.9, 55.7, 51.9, 46.5, 33.1; HRMS (pos. ESI): m/z for $C_{14}H_{17}O_3NNaS$ $[M+Na]^+$ calcd: 302.0821, found: 302.0823.



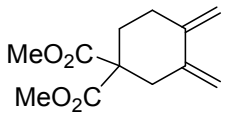
3,4-dimethylene-1-methylsulfonylpiperidine (**2e**). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 1H), 5.17 (d, *J* = 0.8 Hz, 1H), 4.92 (d, *J* = 0.8 Hz, 1H), 4.86 (d, *J* = 1.6 Hz, 1H), 3.89 (s, 2H), 3.41 (t, *J* = 6.0 Hz, 2H), 2.82 (s, 3H), 2.46 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 141.6, 111.5, 111.5, 51.4, 46.1, 36.9, 33.2; HRMS (pos. ESI): m/z for $C_8H_{13}O_2NNaS$ $[M+Na]^+$ calcd: 210.0559, found: 210.0559.



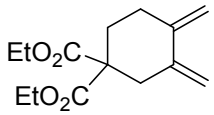
tert-butyl 3,4-dimethylenepiperidine-1-carboxylate (**2f**). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20 – 5.15 (m, 2H), 4.84 (s, 1H), 4.80 (d, *J* = 1.5 Hz, 1H), 4.01 (s, 2H), 3.49 (t, *J* = 6.0 Hz, 2H), 2.38 (t, *J* = 6.0 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 144.7, 143.3, 109.8, 109.7, 79.8, 49.7, 44.2, 33.5, 28.6; HRMS (pos. APCI): m/z for $C_{12}H_{20}O_2N$ $[M+H]^+$ calcd: 210.1489, found: 210.1490.



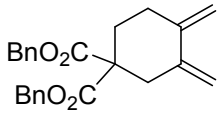
benzyl 3,4-dimethylenepiperidine-1-carboxylate (**2g**). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 5.22 – 5.18 (m, 2H), 5.16 (s, 2H), 4.87 (s, 1H), 4.82 (d, *J* = 1.5 Hz, 1H), 4.11 (s, 2H), 3.58 (t, *J* = 6.0 Hz, 2H), 2.40 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 144.3, 142.8, 137.2, 128.6, 128.1, 128.0, 110.2, 110.1, 67.3, 49.7, 44.3, 33.4; HRMS (pos. APCI): m/z for $C_{15}H_{18}O_2N$ $[M+H]^+$ calcd: 244.1332, found: 244.1330.



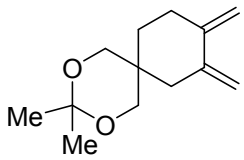
dimethyl 3,4-dimethylenecyclohexane-1,1-dicarboxylate (**2h**). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.05 (s, 1H), 4.98 (s, 1H), 4.79 (s, 1H), 4.69 (s, 1H), 3.72 (d, *J* = 2.0 Hz, 6H), 2.78 (s, 2H), 2.35 (t, *J* = 6.0 Hz, 2H), 2.15 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 146.5, 144.2, 111.5, 109.1, 55.7, 52.7, 39.5, 31.2, 30.9; HRMS (pos. ESI): m/z for $C_{12}H_{16}O_4Na$ $[M+Na]^+$ calcd: 247.0941, found: 247.0943.



diethyl 3,4-dimethylenecyclohexane-1,1-dicarboxylate (**2i**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 – 5.03 (m, 1H), 4.99 – 4.96 (m, 1H), 4.78 (d, *J* = 1.6 Hz, 1H), 4.69 (d, *J* = 1.6 Hz, 1H), 4.18 (qd, *J* = 7.2, 3.6 Hz, 4H), 2.77 (s, 2H), 2.37 (t, *J* = 6.6 Hz, 2H), 2.14 (t, *J* = 6.6 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 146.8, 144.4, 111.3, 109.0, 61.4, 55.6, 39.5, 31.2, 30.9, 14.1; HRMS (pos. ESI): m/z for $C_{14}H_{20}O_4Na$ $[M+Na]^+$ calcd: 275.1254, found: 275.1256.

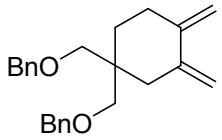


dibenzyl 3,4-dimethylenecyclohexane-1,1-dicarboxylate (**2j**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.0, 1.8 Hz, 6H), 7.26 (dd, *J* = 6.8, 2.8 Hz, 4H), 5.12 (d, *J* = 4.0 Hz, 1H), 5.05 (d, *J* = 1.6 Hz, 1H), 4.99 (d, *J* = 1.6 Hz, 1H), 4.75 (d, *J* = 1.6 Hz, 1H), 4.70 (d, *J* = 1.6 Hz, 1H), 2.83 (s, 2H), 2.37 (t, *J* = 6.4 Hz, 2H), 2.20 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 146.6, 144.05, 135.6, 128.6, 128.3, 128.1, 111.6, 109.2, 67.2, 55.8, 39.4, 31.2, 30.8; HRMS (pos. ESI): m/z for $C_{24}H_{24}O_4Na$ $[M+Na]^+$ calcd: 399.1567, found: 399.1566.

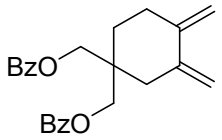


3,3-dimethyl-8,9-dimethylene-2,4-dioxaspiro[5.5]undecane (**2k**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 – 5.02 (m, 1H), 4.98 – 4.95 (m, 1H), 4.74 (d, *J* = 1.8

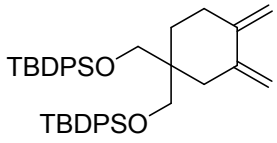
Hz, 1H), 4.68 (d, *J* = 1.8 Hz, 1H), 3.60 (s, 4H), 2.26 (t, *J* = 6.6 Hz, 2H), 2.22 (s, 2H), 1.59 (t, *J* = 6.6 Hz, 2H), 1.42 (d, *J* = 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 145.5, 110.9, 108.5, 98.3, 68.1, 40.3, 33.8, 31.1, 29.7, 24.1, 23.6; HRMS (pos. APCI): m/z for $C_{13}H_{21}O_2$ $[M+H]^+$ calcd: 209.1536, found: 209.1534.



1-(((1-((benzyloxy)methyl)-3,4-dimethylenecyclohexyl)methoxy)methyl)benzene (**2l**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 10H), 5.04 – 5.02 (m, 1H), 5.01 – 4.99 (m, 1H), 4.69 (s, 2H), 4.52 (s, 4H), 3.43 (dd, *J* = 19.6, 9.0 Hz, 4H), 2.33 – 2.25 (m, 4H), 1.64 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 146.5, 139.1, 128.3, 127.5, 127.4, 110.1, 108.0, 73.4, 73.3, 40.2, 39.5, 29.9, 29.6; HRMS (pos. APCI): m/z for $C_{24}H_{32}O_2N$ $[M+NH_4]^+$ calcd: 366.2428, found: 366.2433.



(3,4-dimethylenecyclohexane-1,1-diyl)bis(methylene) dibenzoate (**2m**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 4H), 7.58 – 7.53 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 4H), 5.12 (d, *J* = 1.6 Hz, 1H), 5.05 (d, *J* = 1.2 Hz, 1H), 4.76 (dd, *J* = 6.4, 1.6 Hz, 2H), 4.37 (dd, *J* = 25.4, 11.2 Hz, 4H), 2.44 – 2.38 (m, 4H), 1.81 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 147.2, 144.5, 133.1, 130.2, 129.7, 128.5, 111.7, 109.2, 67.2, 39.3, 39.0, 29.7, 29.5; HRMS (pos. ESI): m/z for $C_{24}H_{24}O_4Na$ $[M+Na]^+$ calcd: 399.1567, found: 399.1566.



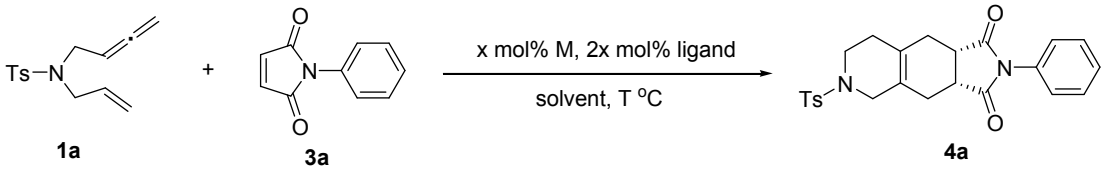
(((3,4-dimethylenecyclohexane-1,1-diyl)bis(methylene))bis(oxy))bis(tert-butyldiphen ylsilane) (**2n**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 8H), 7.41 – 7.39 (m, 4H), 7.35 – 7.31 (m, 8H), 4.97 (d, *J* = 2.0 Hz, 1H), 4.94 (d, *J* = 2.0 Hz, 1H), 4.62 (dd, *J* = 6.0, 2.0 Hz, 2H), 3.63 (s, 4H), 2.24 (s, 2H), 2.13 (t, *J* = 6.6 Hz, 2H), 1.58

(t, J = 6.6 Hz, 2H), 1.06 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 146.5, 135.8, 135.8, 133.9, 133.8, 129.6, 129.6, 127.7, 127.6, 110.1, 107.7, 66.4, 42.0, 38.4, 29.9, 28.9, 27.1, 19.5; HRMS (pos. APCI): m/z for $C_{42}H_{53}O_2Si_2$ $[M+H]^+$ calcd: 645.3579, found: 645.3577.

Optimization of parameters for the tandem Diels-Alder reaction

1,6-allenene **1a** and N-phenyl maleimide **3a** were ultilized to test the reactivity and optimization for the tandem reaction. The results are decipated in Table S2. A series of solvent was firstly evaluated for the tandem reaction and DCE and THF gave comparable high yields. Toluene and acetonitrile also provided good yields, while ethanol was not suitable for the reaction (Table S2, entries 1-5). For practical usage consideration, the catalyst loading investigation showed that 0.5 mol% is sufficient to complete the transformation. Control experiment indicated that both the rhodium catalyst and the DPEphos ligand were pivotal for the success, because no conversion was noticed in absence either of them (Table S2, entries 6-11). Examination of reaction temperature indicated that temperature did not have great influence on the process (Table S2, entries 12-14). Then a group of transition metal catalysts were assessed (Table S2, entries 15-20). Platinum, Iridium and Palladium could not promote the reaction.The alkene ligand on Rhodium catalyst did not affect the reaction, and comparable good yields of 78% and 76% were obtained for $[Rh(C_2H_4)_2Cl]_2$ and $[Rh(NBD)Cl]_2$, respectively. However, the counter anion was responsible for the high efficiency, because when chloride anion was replaced by BF_4, the Rhodium catalyst lost the catalytic ability completely. Subsequently, a large number of other bidentate and monodentate phosphine ligands were also tried, unfortunately, none of them could deliver better outcome than DPEphos (Table S2, entries 21-29). Finally, the reaction concentration was probed, but no better result was generated no matter in concentrated or dilute system (Table S2, entries 30-31).

Table S2. Comprehensive optimization for the tandem Diels-Alder reaction.[a]

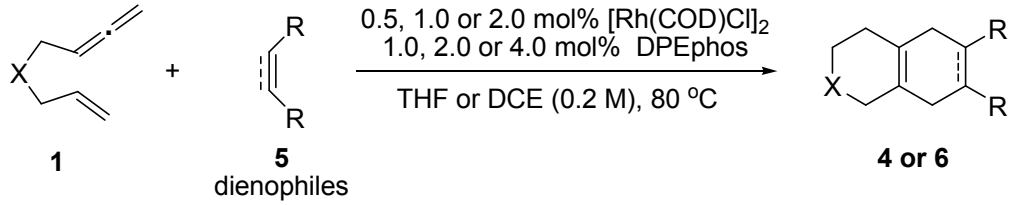


entry	M	ligand	x mol%	solvent	C	T °C	Yield %
1	$[Rh(Cod)Cl]_2$	DPEphos	2.5	DCE	0.2 M	80	80
2	$[Rh(Cod)Cl]_2$	DPEphos	2.5	THF	0.2 M	80	82
3	$[Rh(Cod)Cl]_2$	DPEphos	2.5	Toluene	0.2 M	80	69
4	$[Rh(Cod)Cl]_2$	DPEphos	2.5	MeCN	0.2 M	80	76
5	$[Rh(Cod)Cl]_2$	DPEphos	2.5	EtOH	0.2 M	80	complex
6	$[Rh(Cod)Cl]_2$	DPEphos	1.0	THF	0.2 M	80	83
7	*$[Rh(Cod)Cl]_2$*	*DPEphos*	***0.5***	*THF*	*0.2 M*	*80*	***83***
8	$[Rh(Cod)Cl]_2$	DPEphos	0.25	THF	0.2 M	80	44

9	$[Rh(Cod)Cl]_2$	DPEphos	0.1	THF	0.2 M	80	19
10	$[Rh(Cod)Cl]_2$	-	2.5	THF	0.2 M	80	NR
11	-	DPEphos	2.5	THF	0.2 M	80	NR
12	$[Rh(Cod)Cl]_2$	DPEphos	0.5	THF	0.2 M	60	69
13	$[Rh(Cod)Cl]_2$	DPEphos	0.5	THF	0.2 M	95	83
14	$[Rh(Cod)Cl]_2$	DPEphos	0.5	THF	0.2 M	110	79
15	$Pt(Cod)Cl_2$	DPEphos	2.5	THF	0.2 M	80	NR
16	$[Ir(Cod)Cl]_2$	DPEphos	2.5	THF	0.2 M	80	NR
17	$PdCl_2$*DPPF	-	2.5	THF	0.2 M	80	NR
18	$[Rh(C_2H_4)_2Cl]_2$	DPEphos	2.5	THF	0.2 M	80	78
19	$[Rh(NBD)Cl]_2$	DPEphos	2.5	THF	0.2 M	80	76
20	$[Rh(Cod)BF_4]_2$	DPEphos	2.5	THF	0.2 M	80	complex
21	$[Rh(Cod)Cl]_2$	Rac-BINAP	2.5	THF	0.2 M	80	62
22	$[Rh(Cod)Cl]_2$	DPPF	2.5	THF	0.2 M	80	33
23	$[Rh(Cod)Cl]_2$	Xantphos	2.5	THF	0.2 M	80	NR
24	$[Rh(Cod)Cl]_2$	diCy-DPEphos	2.5	THF	0.2 M	80	complex
25	$[Rh(Cod)Cl]_2$	DPPE	2.5	THF	0.2 M	80	complex
26	$[Rh(Cod)Cl]_2$	DPPP	2.5	THF	0.2 M	80	complex
27	$[Rh(Cod)Cl]_2$	DPPB	2.5	THF	0.2 M	80	trace
28	$[Rh(Cod)Cl]_2$	DPPPE	2.5	THF	0.2 M	80	complex
29	$[Rh(Cod)Cl]_2$	6-DPPon	2.5	THF	0.2 M	80	NR
30	$[Rh(Cod)Cl]_2$	DPEphos	0.5	THF	0.4 M	80	55
31	$[Rh(Cod)Cl]_2$	DPEphos	0.5	THF	0.1 M	80	78

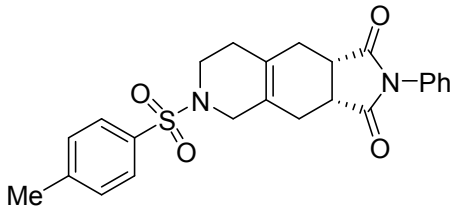
[a] The reactions were carried out on a 0.2 mmol scale of **1a** and **3a** (1 eq.) for 20 h. Isolated yield.

General procedure and characterization for the tandem Diels-Alder products

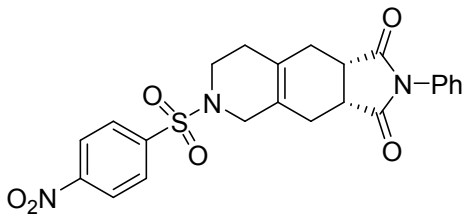


A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $[Rh(COD)Cl]_2$ (0.5, 1.0 or 2.0 mol%), DPEphos (1.0, 2.0 or 4.0 mol%), 1,6-allenene **1** (0.2 mmol, 1.0 equiv). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards dienophile **5** (0.2 mmol, 1.0 equiv) and 2.0 ml of 1,2-dichloroethane (DCE) or tetrahydrofuran (THF) were added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 80 °C for 20 hours. The mixture was cooled down to room temperature and the solvent was removed with rotary evaporator. The residue was purified with column chromatography on silica gel, eluting with cyclohexane and ethyl acetate to afford the corresponding product **4** or **6** after drying in vacuo.

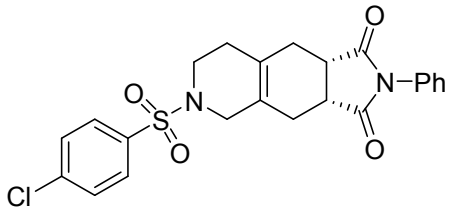
Characterization data of the tandem Diels-Alder products



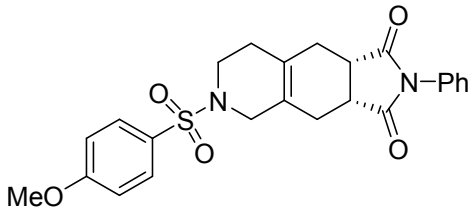
3a,4,5,6,7,8,9,9a-octahydro-2-phenyl-6-tosyl-2*H*-pyrrolo[3,4-g]isoquinoline-1,3-dion e (**4a**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.33 – 7.29 (m, 2H), 7.13 – 7.08 (m, 2H), 3.68 – 3.60 (m, 1H), 3.39 – 3.22 (m, 4H), 2.87 (ddd, J = 12.0, 6.4, 2.8 Hz, 1H), 2.48 (dd, J = 24.6, 14.6 Hz, 2H), 2.43 (s, 3H), 2.35 – 2.30 (m, 3H), 2.15 – 2.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 178.6, 143.8, 133.2, 131.9, 129.8, 129.3, 128.8, 128.6, 127.7, 126.4, 125.7, 47.8, 43.2, 39.6, 39.3, 30.1, 28.9, 26.8, 21.7; HRMS (pos. APCI): m/z for $C_{24}H_{25}O_4N_2S$ $[M+H]^+$ calcd: 437.1530, found: 437.1528.



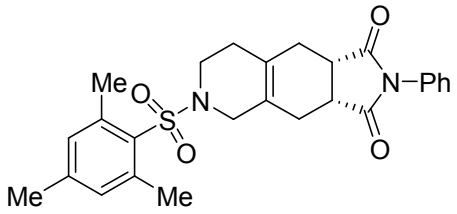
3a,4,5,6,7,8,9,9a-octahydro-2-phenyl-6-(4-nitrobenzenesulfonyl)-2*H*-pyrrolo[3,4-g]isoquinoline-1,3-dione (**4b**). Brown solid, m.p. 201−202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.31 (m, 3H), 7.15 – 7.08 (m, 2H), 3.67 (d, *J* = 15.4 Hz, 1H), 3.42 – 3.35 (m, 2H), 3.30 – 3.18 (m, 2H), 3.02 (ddd, *J* = 12.0, 7.2, 4.8 Hz, 1H), 2.47 (dd, *J* = 25.2, 15.2 Hz, 2H), 2.35 – 2.28 (m, 3H), 2.11 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 178.4, 150.2, 142.7, 131.8, 129.1, 128.7, 128.7, 128.6, 126.1, 125.4, 124.4, 47.5, 43.0, 39.4, 39.2, 29.8, 28.8, 26.5; HRMS (pos. ESI): m/z for $C_{23}H_{21}O_6N_3NaS$ $[M+Na]^+$ calcd: 490.1043, found: 490.1042.



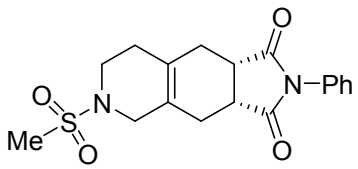
3a,4,5,6,7,8,9,9a-octahydro-2-phenyl-6-(4-chlorobenzenesulfonyl)-2*H*-pyrrolo[3,4-g]isoquinoline-1,3-dione (**4c**). Yellow solid, m.p. 159−160 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.37 – 7.34 (m, 1H), 7.12 – 7.07 (m, 2H), 3.62 (d, *J* = 16.0 Hz, 1H), 3.38 – 3.28 (m, 2H), 3.28 – 3.19 (m, 2H), 2.91 (ddd, *J* = 12.0, 7.5, 4.5 Hz, 1H), 2.47 (dd, *J* = 32.5, 15.5 Hz, 2H), 2.37 – 2.22 (m, 3H), 2.09 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 178.5, 139.4, 134.8, 131.8, 129.5, 129.2, 129.0, 128.7, 128.6, 126.2, 125.4, 47.6, 43.0, 39.5, 39.3, 29.9, 28.8, 26.6; HRMS (pos. ESI): m/z for $C_{23}H_{21}O_4N_2ClNaS$ $[M+Na]^+$ calcd: 479.0803, found: 479.0802.



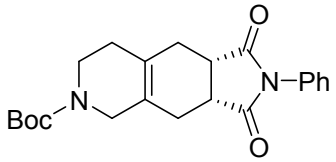
3a,4,5,6,7,8,9,9a-octahydro-2-phenyl-6-(4-methoxybenzenesulfonyl)-2*H*-pyrrolo[3,4-g]isoquinoline-1,3-dione (**4d**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.09 (dd, *J* = 7.2, 1.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.62 (d, *J* = 16.6 Hz, 1H), 3.37 – 3.19 (m, 4H), 2.86 (ddd, *J* = 11.8, 7.6, 4.8 Hz, 1H), 2.46 (dd, *J* = 24.2, 14.8 Hz, 2H), 2.37 – 2.25 (m, 3H), 2.14 – 2.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 178.5, 163.1, 131.9, 129.7, 129.2, 128.6, 128.5, 127.9, 126.3, 125.7, 114.3, 55.6, 47.8, 43.1, 39.6, 39.3, 30.0, 28.8, 26.7; HRMS (pos. ESI): m/z for $C_{24}H_{24}O_5N_2NaS$ $[M+Na]^+$ calcd: 475.1298, found: 475.1297.



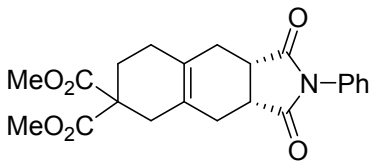
3a,4,5,6,7,8,9,9a-octahydro-2-phenyl-6-(2,4,6-trimethylbenzenesulfonyl)-2*H*-pyrrolo[3,4-g]isoquinoline-1,3-dione (**4e**). Yellow solid, m.p. 204−205 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.40 – 7.35 (m, 1H), 7.21 – 7.15 (m, 2H), 6.91 (s, 2H), 3.64 (d, *J* = 16.8 Hz, 1H), 3.51 (d, *J* = 17.2 Hz, 1H), 3.33 – 3.24 (m, 3H), 3.22 – 3.14 (m, 1H), 2.55 (s, 6H), 2.53 – 2.43 (m, 2H), 2.40 – 2.31 (m, 2H), 2.28 (s, 3H), 2.24 – 2.14 (m, 1H), 2.13 – 2.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 178.5, 142.6, 140.4, 132.0, 132.0, 131.9, 129.1, 128.7, 128.6, 126.4, 126.2, 46.1, 41.5, 39.6, 39.5, 29.7, 28.9, 26.7, 22.8, 21.0; HRMS (pos. ESI): m/z for $C_{26}H_{28}O_4N_2NaS$ $[M+Na]^+$ calcd: 487.1662, found: 487.1665.



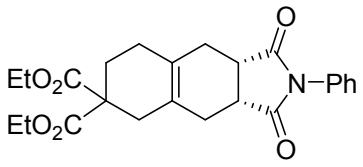
3a,4,5,6,7,8,9,9a-octahydro-2-phenyl-6methylsulfonyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**4f**). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.41 – 7.35 (m, 1H), 7.21 – 7.17 (m, 2H), 3.78 (d, *J* = 16.4 Hz, 1H), 3.55 (d, *J* = 16.6 Hz, 1H), 3.47 (dt, *J* = 12.0, 5.2 Hz, 1H), 3.33 – 3.26 (m, 2H), 3.13 (ddd, *J* = 12.2, 7.4, 4.8 Hz, 1H), 2.75 (s, 3H), 2.54 (dd, *J* = 30.0, 15.2 Hz, 2H), 2.44 – 2.30 (m, 3H), 2.15 (d, *J* = 16.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.7, 178.6, 131.9, 129.3, 128.8, 128.7, 126.3, 126.0, 47.6, 42.8, 39.6, 39.4, 35.6, 30.0, 29.0, 26.6; HRMS (pos. ESI): m/z for $C_{18}H_{20}O_4N_2NaS$ $[M+Na]^+$ calcd: 383.1036, found: 383.1035.



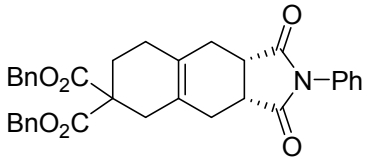
tert-butyl 2,3,3a,4,7,8,9,9a-octahydro-1,3-dioxo-2-phenyl-1H-pyrrolo[3,4-g] isoquinoline-6(5H)-carboxylate (**4g**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.40 – 7.33 (m, 1H), 7.21 – 7.14 (m, 2H), 3.90 (d, *J* = 11.6 Hz, 1H), 3.68 (d, *J* = 18.8 Hz, 1H), 3.65 – 3.56 (m, 1H), 3.33 – 3.20 (m, 3H), 2.53 (dd, *J* = 20.8, 15.2 Hz, 2H), 2.35 (t, *J* = 17.8 Hz, 2H), 2.19 (d, *J* = 16.8 Hz, 1H), 2.04 – 2.00 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 178.8, 154.8, 132.1, 129.2, 128.7, 126.4, 79.8, 39.8, 39.6, 29.9, 29.2, 28.5, 26.7; HRMS (pos. ESI): m/z for $C_{22}H_{26}O_4N_2Na$ $[M+Na]^+$ calcd: 405.1785, found: 405.1788.



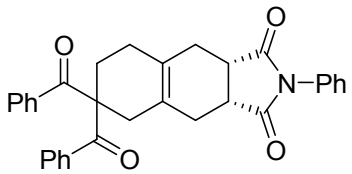
dimethyl 2,3,3a,4,7,8,9,9a-octahydro-1,3-dioxo-2-phenyl-1H-benzo[f]isoindole-6,6 (5H)-dicarboxylate (**4h**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.36 – 7.31 (m, 1H), 7.31 – 7.26 (m, 2H), 3.69 (s, 3H), 3.57 (s, 3H), 3.25 – 3.21 (m, 2H), 2.62 – 2.44 (m, 4H), 2.40 – 2.24 (m, 2H), 2.10 – 2.02 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 178.9, 171.8, 171.3, 132.2, 129.0, 128.6, 128.5, 126.9, 126.6, 53.5, 52.7, 52.6, 39.8, 39.7, 35.5, 29.2, 29.0, 27.9, 27.4; HRMS (pos. ESI): m/z for $C_{22}H_{23}O_6NNa$ $[M+Na]^+$ calcd: 420.1418, found: 420.1417.



diethyl 2,3,3a,4,7,8,9,9a-octahydro-1,3-dioxo-2-phenyl-1H-benzo[f]isoindole-6,6(5H)-dicarboxylate (**4i**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.37 – 7.32 (m, 1H), 7.31 – 7.26 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.04 (qq, *J* = 10.8, 7.2 Hz, 2H), 3.26 – 3.18 (m, 2H), 2.59 – 2.43 (m, 4H), 2.40 – 2.25 (m, 2H), 2.14 – 2.00 (m, 4H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 178.9, 171.3, 170.8, 132.2, 129.0, 128.5, 128.4, 127.0, 126.6, 61.4, 61.3, 53.4, 39.8, 39.7, 35.4, 29.2, 29.0, 27.7, 27.4, 14.1, 14,0; HRMS (pos. ESI): m/z for $C_{24}H_{27}O_6NNa$ $[M+Na]^+$ calcd: 448.1731, found: 448.1731.

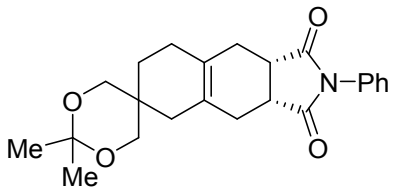


dibenzyl 2,3,3a,4,7,8,9,9a-octahydro-1,3-dioxo-2-phenyl-1H-benzo[f]isoindole-6,6(5H)-dicarboxylate (**4j**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.39 – 7.33 (m, 1H), 7.33 – 7.30 (m, 5H), 7.27 (dd, *J* = 6.2, 2.8 Hz, 3H), 7.22 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.18 – 7.13 (m, 2H), 5.09 (q, *J* = 12.4 Hz, 2H), 4.96 (q, *J* = 12.4 Hz, 2H), 3.28 – 3.14 (m, 2H), 2.65 – 2.40 (m, 4H), 2.38 – 2.20 (m, 2H), 2.15 – 2.10 (m, 2H), 2.06 – 2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 178.9, 171.0, 170.5, 135.6, 135.5, 132.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 126.9, 126.6, 67.1, 53.7, 39.8, 39.7, 35.4, 29.2, 29.0, 27.9, 27.3; HRMS (pos. ESI): m/z for $C_{34}H_{31}O_6NNa$ $[M+Na]^+$ calcd: 572.2044, found: 572.2045.

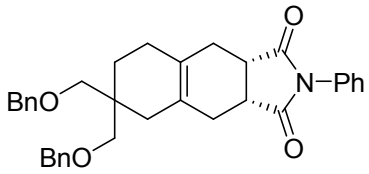


6,6-dibenzoyl-2-phenyl-3a,4,5,6,7,8,9,9a-octahydro-1H-benzo[f]isoindole-1,3(2H)-dione (**4k**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.80 – 7.75 (m, 2H), 7.56 – 7.49 (m, 2H), 7.48 – 7.39 (m, 5H), 7.37 – 7.29 (m, 4H), 3.32 – 3.20

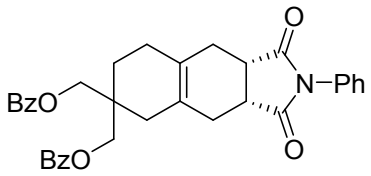
(m, 2H), 2.62 (dt, *J* = 17.2, 9.6 Hz, 3H), 2.52 – 2.31 (m, 5H), 1.89 (dd, *J* = 48.8, 18.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 197.9, 179.3, 179.1, 136.0, 135.9, 133.2, 133.1, 132.5, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 127.8, 127.3, 126.9, 63.3, 40.0, 39.9, 38.0, 29.9, 29.3, 29.1, 26.7; HRMS (pos. ESI): m/z for $C_{32}H_{27}O_4NNa$ $[M+Na]^+$ calcd: 512.1832, found: 512.1829.



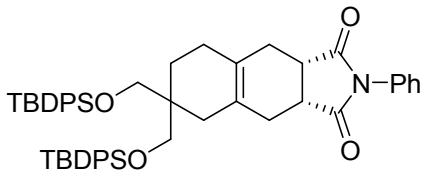
2',2'-dimethyl-2-phenyl-3a,5,7,8,9,9a-hexahydrospiro[benzo[f]isoindole-6,5'-[1,3]dioxane]-1,3(2H,4H)-dione (**4l**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.39 – 7.33 (m, 1H), 7.22 – 7.17 (m, 2H), 3.54 (s, 2H), 3.47 (q, *J* = 11.6 Hz, 2H), 3.28 – 3.19 (m, 2H), 2.49 (d, *J* = 15.0 Hz, 2H), 2.40 – 2.26 (m, 2H), 2.13 – 1.93 (m, 3H), 1.88 (d, *J* = 16.8 Hz, 1H), 1.54 (t, *J* = 6.4 Hz, 2H), 1.40 (d, *J* = 2.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 132.2, 129.2, 128.9, 128.6, 127.4, 126.4, 98.3, 68.2, 68.1, 40.1, 40.0, 36.5, 32.1, 29.7, 29.3, 27.6, 26.6, 24.0, 23.7; HRMS (pos. ESI): m/z for $C_{23}H_{27}O_4NNa$ $[M+Na]^+$ calcd: 404.1832, found: 404.1833.



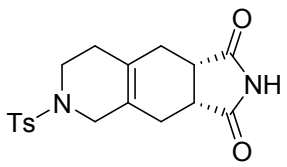
6,6-bis((benzyloxy)methyl)-3a,4,5,6,7,8,9,9a-octahydro-2-phenyl-2H-benzo[f]isoindole-1,3-dione (**4m**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 10H), 7.26 – 7.21 (m, 5H), 4.47 (s, 2H), 4.35 (s, 2H), 3.34 (dd, *J* = 26.0, 8.8 Hz, 1H), 3.29 (s, 2H), 3.24 – 3.21 (m, 2H), 2.48 (dd, *J* = 15.2, 7.2 Hz, 2H), 2.34 – 2.24 (m, 2H), 2.09 – 1.85 (m, 4H), 1.56 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 179.2, 139.0, 138.9, 132.2, 129.2, 128.8, 128.5, 128.4, 128.3, 127.8, 127.5, 127.4, 127.3, 126.3, 73.6, 73.3, 73.2, 73.1, 40.1, 38.4, 35.7, 29.8, 29.4, 26.9, 26.5; HRMS (pos. APCI): m/z for $C_{34}H_{39}O_4N_2$ $[M+NH_4]^+$ calcd: 539,2904, found: 539,2907.



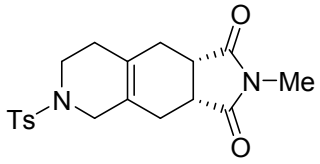
(1,3-dioxo-2-phenyl-2,3,3a,4,5,6,7,8,9,9a-decahydro-1H-benzo[f]isoindole-6,6-diyl)bis(methylene) dibenzoate (**4n**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 4H), 7.60 – 7.52 (m, 2H), 7.48 – 7.35 (m, 7H), 7.28 – 7.23 (m, 2H), 4.31 (ddd, *J* = 24.8, 12.4, 6.2 Hz, 4H), 3.34 – 3.21 (m, 2H), 2.56 (dd, *J* = 14.8, 3.2 Hz, 2H), 2.38 (d, *J* = 13.2 Hz, 2H), 2.26 – 2.06 (m, 4H), 1.85 – 1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 178.9, 166.5, 166.2, 133.1, 133.0, 132.1, 130.0, 129.9, 129.6, 129.5, 129.2, 129.1, 128.6, 128.5, 128.4, 126.8, 126.4, 67.2, 67.0, 39.9, 37.2, 35.2, 29.5, 29.3, 26.6; HRMS (pos. ESI): m/z for $C_{34}H_{31}O_6NNa$ $[M+Na]^+$ calcd: 572.2044, found: 572.2048.



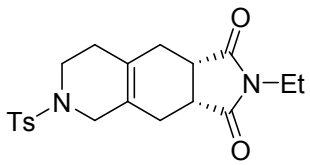
6,6-bis(((tert-butyldiphenylsilyl)oxy)methyl)-2-phenyl-3a,4,5,6,7,8,9,9a-octahydro-1H-benzo[f]isoindole-1,3(2H)-dione (**4o**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 8H), 7.43 – 7.30 (m, 15H), 7.15 – 7.09 (m, 2H), 3.62 – 3.49 (m, 4H), 3.18 – 3.10 (m, 2H), 2.36 (t, *J* = 14.2 Hz, 2H), 2.19 (t, *J* = 17.4 Hz, 2H), 1.97 (d, *J* = 17.4 Hz, 1H), 1.78 (d, *J* = 18.4 Hz, 3H), 1.65 – 1.56 (m, 1H), 1.52 – 1.44 (m, 1H), 1.04 (d, *J* = 6.4 Hz, 18H); ^{13}C NMR (100 MHz, CDCl3) δ 179.2, 179.1, 135.9, 135.8, 135.7, 135.6, 133.9, 133.8, 133.7, 133.6, 132.2, 131.4, 129.7, 129.6, 129.1, 128.5, 128.4, 127.8, 127.7, 127.68, 127.66, 127.64, 127.5, 126.4, 67.1, 65.3, 40.2, 40.1, 39.8, 34.4, 29.6, 29.2, 27.1, 26.9, 25.9, 19.5; HRMS (pos. APCI): m/z for $C_{52}H_{60}O_4NSi_2$ $[M+H]^+$ calcd: 818.4055, found: 818.4055.



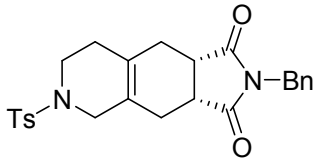
3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**6a**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (br s, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.55 (d, *J* = 15.6 Hz, 1H), 3.34 – 3.24 (m, 2H), 3.16 – 3.08 (m, 2H), 2.96 (ddd, *J* = 11.8, 7.2, 4.8 Hz, 1H), 2.42 (s, 3H), 2.35 (dd, *J* = 23.6, 15.2 Hz, 2H), 2.24 – 2.20 (m, 3H), 2.07 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 179.7, 143.7, 133.4, 129.8, 128.3, 127.7, 125.4, 47.7, 43.0, 40.5, 40.3, 29.9, 28.2, 26.2, 21.6; HRMS (pos. APCI): m/z for $C_{20}H_{25}O_4N_2S$ $[M+H]^+$ calcd: 389.1530, found: 389.1530.



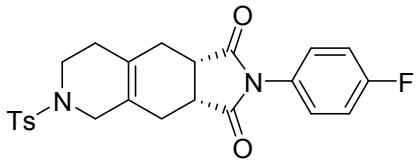
3a,4,5,6,7,8,9,9a-octahydro-2-methyl-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dion e (**6b**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.58 – 3.49 (m, 1H), 3.33 – 3.23 (m, 2H), 3.11 – 3.02 (m, 2H), 2.98 – 2.91 (m, 1H), 2.92 (s, 3H), 2.42 (s, 3H), 2.36 (dd, *J* = 24.6, 15.2 Hz, 2H), 2.29 – 2.19 (m, 3H), 2.08 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 179.6, 143.7, 133.5, 129.8, 128.2, 127.7, 125.4, 47.6, 43.0, 39.3, 39.0, 30.0, 28.4, 26.3, 25.2, 21.6; HRMS (pos. ESI): m/z for $C_{19}H_{22}O_4N_2NaS$ $[M+Na]^+$ calcd: 397.1192, found: 397.1191.



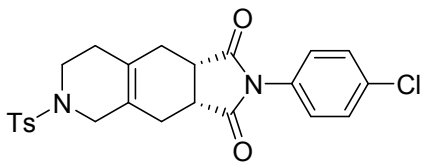
2-ethyl-3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**6c**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.56 (d, *J* = 15.6 Hz, 1H), 3.44 (q, *J* = 7.2 Hz, 2H), 3.32 – 3.20 (m, 2H), 3.08 – 2.99 (m, 2H), 2.85 (ddd, *J* = 11.8, 7.6, 4.8 Hz, 1H), 2.41 (s, 3H), 2.40 – 2.30 (m, 2H), 2.29 – 2.17 (m, 3H), 2.03 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 179.3, 143.7, 133.3, 129.7, 128.4, 127.7, 125.5, 47.7, 43.0, 39.4, 39.1, 33.9, 30.0, 28.6, 26.6, 21.6, 13.1; HRMS (pos. APCI): m/z for $C_{20}H_{28}O_4N_3S$ $[M+NH_4]^+$ calcd: 406.1795, found: 406.1796.



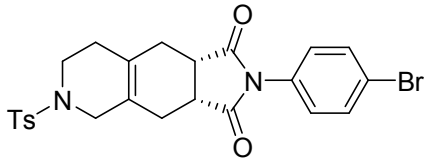
2-benzyl-3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**6d**). Yellow solid, m.p. 195−197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.08 – 6.97 (m, 3H), 4.59 – 4.49 (m, 2H), 3.57 (d, J = 16.0 Hz, 1H), 3.27 – 3.21 (m, 1H), 3.13 – 3.07 (m, 2H), 3.03 – 2.97 (m, 1H), 2.47 (s, 3H), 2.36 (t, J = 15.2 Hz, 2H), 2.29 – 2.12 (m, 4H), 1.80 – 1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 143.6, 136.0, 133.6, 129.8, 128.5, 128.4, 128.3, 127.8, 127.7, 125.6, 47.5, 42.6, 42.5, 39.6, 39.2, 30.0, 28.7, 26.7, 21.6; HRMS (pos. ESI): m/z for $C_{25}H_{26}O_4N_2NaS$ $[M+Na]^+$ calcd: 473.1505, found: 473.1505.



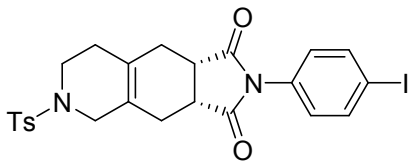
2-(4-fluorophenyl)-3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline -1,3-dione (**6e**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.14 – 7.05 (m, 4H), 3.64 – 3.53 (m, 1H), 3.39 – 3.19 (m, 4H), 2.94 (ddd, J = 11.8, 7.2, 4.8 Hz, 1H), 2.51 – 2.45 (m, 2H), 2.42 (s, 3H), 2.37 – 2.22 (m, 3H), 2.10 (d, J = 16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 178.5, 162.2 (d, $J_{C\text{-}F}$ = 247.2 Hz), 143.7, 133.3, 129.8, 128.6, 128.2 (d, $J_{C\text{-}F}$ = 8,7 Hz), 127.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 127.7, 125.7, 116.2 (d, $J_{C\text{-}F}$ = 22.8 Hz), 47.7, 43.1, 39.5, 39.3, 30.1, 28.8, 26.7, 21.6; HRMS (pos. ESI): m/z for $C_{24}H_{23}O_4N_2FNaS$ $[M+Na]^+$ calcd: 477.1255, found: 477.1256.



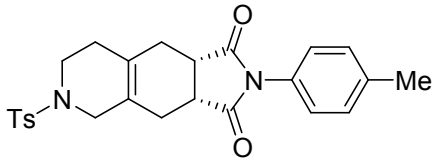
2-(4-chlorophenyl)-3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline -1,3-dione (**6f**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 3.62 – 3.54 (m, 1H), 3.37 – 3.21 (m, 4H), 2.92 (ddd, *J* = 11.8, 7.2, 4.8 Hz, 1H), 2.51 – 2.39 (m, 2H), 2.42 (s, 3H), 2.35 – 2.23 (m, 3H), 2.09 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 178.3, 143.7, 134.4, 133.2, 130.4, 129.8, 129.3, 128.6, 127.6, 127.5, 125.6, 47.7, 43.1, 39.5, 39.3, 30.0, 28.7, 26.7, 21.5; HRMS (pos. ESI): m/z for $C_{24}H_{23}O_4N_2ClNaS$ $[M+Na]^+$ calcd: 493.0959, found: 493.0958.



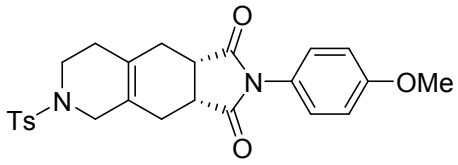
2-(4-bromophenyl)-3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline -1,3-dione (**6g**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.64 – 3.54 (m, 1H), 3.36 – 3.19 (m, 4H), 2.91 (ddd, *J* = 11.8, 7.2, 4.8 Hz, 1H), 2.52 – 2.39 (m, 2H), 2.42 (s, 3H), 2.37 – 2.21 (m, 3H), 2.09 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 178.2, 143.7, 133.3, 132.3, 130.9, 129.8, 128.6, 127.8, 127.7, 125.6, 122.5, 47.7, 43.18, 39.6, 39.3, 30.0, 28.8, 26.7, 21.6; HRMS (pos. ESI): m/z for $C_{24}H_{23}O_4N_2BrNaS$ $[M+Na]^+$ calcd: 537.0454, found: 537.0456.



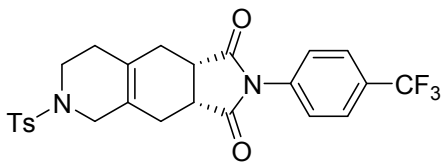
3a,4,5,6,7,8,9,9a-octahydro-2-(4-iodophenyl)-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1, 3-dione (**6h**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.62 – 3.53 (m, 1H), 3.36 – 3.19 (m, 4H), 2.90 (ddd, *J* = 11.8, 7.2, 4.8 Hz, 1H), 2.50 – 2.38 (m, 2H), 2.42 (s, 3H), 2.35 – 2.21 (m, 3H), 2.07 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 178.1, 143.7, 138.3, 133.2, 131.6, 129.7, 128.6, 128.0, 127.6, 125.6, 93.9, 47.7, 43.0, 39.5, 39.3, 30.0, 28.7, 26.7, 21.6; HRMS (pos. ESI): m/z for $C_{24}H_{23}O_4N_2INaS$ $[M+Na]^+$ calcd: 585.0315, found: 585.0314.



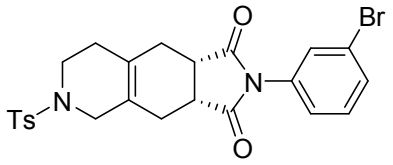
3a,4,5,6,7,8,9,9a-octahydro-2-p-tolyl-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**6i**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.63 (d, *J* = 15.6 Hz, 1H), 3.34 (dt, *J* = 24.2, 11.8 Hz, 2H), 3.26 – 3.19 (m, 2H), 2.92 – 2.82 (m, 1H), 2.53 – 2.40 (m, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.35 – 2.24 (m, 3H), 2.15 – 2.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 178.7, 143.7, 138.8, 133.3, 129.8, 129.7, 129.3, 128.6, 127.7, 126.1, 125.7, 47.7, 43.1, 39.6, 39.3, 30.1, 28.8, 26.7, 21.6, 21.2; HRMS (pos. ESI): m/z for $C_{25}H_{26}O_4N_2NaS$ $[M+Na]^+$ calcd: 473.1505, found: 473.1510.



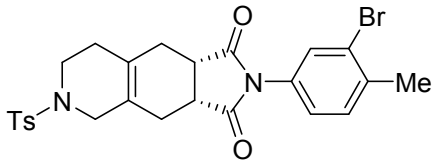
3a,4,5,6,7,8,9,9a-octahydro-2-(4-methoxyphenyl)-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**6j**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 3.60 (d, *J* = 15.2 Hz, 1H), 3.36 – 3.26 (m, 2H), 3.23 – 3.19 (m, 2H), 2.89 (ddd, *J* = 11.8, 7.4, 4.8 Hz, 1H), 2.52 – 2.40 (m, 2H), 2.42 (s, 3H), 2.35 – 2.28 (m, 3H), 2.13 – 2.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 178.8, 159.6, 143.7, 133.3, 129.8, 128.6, 127.7, 127.5, 125.6, 124.5, 114.5, 55.5, 47.7, 43.1, 39.5, 39.2, 30.1, 28.8, 26.7, 21.5; HRMS (pos. APCI): m/z for $C_{25}H_{27}O_5N_2S$ $[M+H]^+$ calcd: 467.1635, found: 467.1631.



2-(4-(trifluoromethyl)phenyl)-3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**6k**). Yellow solid, m.p. 112−113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 12.8, 8.4 Hz, 4H), 7.31 (dd, *J* = 8.4, 2.0 Hz, 4H), 3.60 (d, *J* = 14.8 Hz, 1H), 3.39 – 3.25 (m, 4H), 2.94 (ddd, *J* = 11.8, 7.2, 4.8 Hz, 1H), 2.48 (dd, *J* = 24.8, 15.2 Hz, 2H), 2.42 (s, 3H), 2.39 – 2.25 (m, 3H), 2.11 (d, *J* = 16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 178.1, 143.8, 135.0 (q, J_{C-F} = 1.4 Hz), 133.3, 130.6 (q, J_{C-F} = 32.7 Hz), 129.8, 128.7, 127.7, 126.6, 126.3 (q, J_{C-F} = 3.7 Hz), 123.7 (q, J_{C-F} = 270.7 Hz), 47.8, 43.1, 39.7, 39.4, 30.1, 28.8, 26.8, 21.5; HRMS (pos. APCI): m/z for $C_{25}H_{24}O_4N_2F_3S$ $[M+H]^+$ calcd: 505.1403, found: 505.1399.

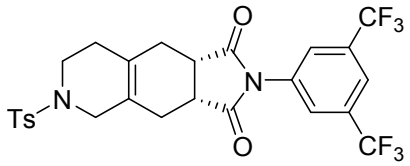


2-(3-bromophenyl)-3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**6l**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.49 (ddd, *J* = 8.2, 1.8, 1.0 Hz, 1H), 7.34 – 7.25 (m, 4H), 7.10 (ddd, *J* = 8.0, 1.8, 1.0 Hz, 1H), 3.61 (d, *J* = 15.8 Hz, 1H), 3.37 – 3.20 (m, 4H), 2.89 (ddd, *J* = 12.0, 7.6, 4.8 Hz, 1H), 2.51 – 2.39 (m, 2H), 2.41 (s, 3H), 2.31 (dd, *J* = 15.6, 5.4 Hz, 3H), 2.09 (d, *J* = 17.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 178.1, 143.7, 133.3, 133.1, 131.7, 130.4, 129.8, 129.4, 128.5, 127.7, 125.6, 125.0, 122.4, 47.7, 43.1, 39.5, 39.3, 30.0, 28.7, 26.6, 21.6; HRMS (pos. ESI): m/z for $C_{24}H_{23}O_4N_2BrNaS$ $[M+Na]^+$ calcd: 537.0454, found: 537.0455.

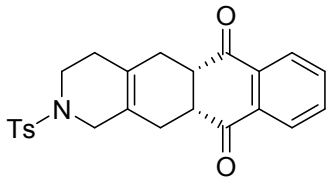


2-(3-bromo-4-methylphenyl)-3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**6m**). Yellow solid, m.p. 192−193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.24 (m, 4H), 6.98 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.61 (d, *J* = 15.6 Hz, 1H), 3.39 – 3.18 (m, 4H), 2.87 (ddd, *J* = 12.0, 7.6, 4.8 Hz, 1H), 2.50 – 2.40 (m, 2H), 2.41 (s, 3H), 2.39 (s, 3H), 2.30 (dd, *J* = 14.6, 3.6 Hz, 3H), 2.08 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 178.3, 143.7, 138.7, 133.3, 131.0, 130.5, 130.0, 129.8, 128.5, 127.6, 125.6, 125.1, 124.7, 47.7, 43.1, 39.5, 39.2,

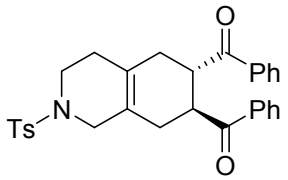
30.0, 28.7, 26.6, 22.7, 21.6; HRMS (pos. ESI): m/z for $C_{25}H_{25}O_4N_2BrNaS$ $[M+Na]^+$ calcd: 551.0611, found: 551.0613.



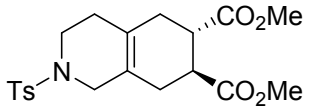
2-(3,5-bis(trifluoromethyl)phenyl)-3a,4,5,6,7,8,9,9a-octahydro-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**6n**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.75 (s, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 3.61 (d, J = 15.6 Hz, 1H), 3.40 – 3.24 (m, 4H), 2.87 (ddd, J = 12.0, 7.6, 4.8 Hz, 1H), 2.47 (dd, J = 23.2, 15.0 Hz, 2H), 2.40 (s, 3H), 2.39 – 2.27 (m, 3H), 2.11 (d, J = 16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 177.7, 143.9, 133.4, 133.1, 132.6 (q, $J_{C\text{-}F}$ = 33.8 Hz), 129.8, 128.5, 127.6, 126.3 (q, $J_{C\text{-}F}$ = 4.4 Hz), 125.6, 122.8 (q, $J_{C\text{-}F}$ = 271.3 Hz), 122.1 (dt, J = 7.5, 3.7 Hz), 47.7, 43.1, 39.5, 39.3, 30.0, 28.5, 26.5, 21.5; HRMS (pos. ESI): m/z for $C_{26}H_{22}O_4N_2F_6NaS$ $[M+Na]^+$ calcd: 595.1097, found: 595.1096.



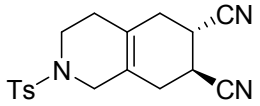
1,2,3,4,5,5a,11a,12-octahydro-2-tosylnaphtho[2,3-g]isoquinoline-6,11-dione (**6o**). Brown solid, m.p. 220−221 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.76 – 7.72 (m, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 3.55 (d, J = 15.6 Hz, 1H), 3.48 – 3.25 (m, 4H), 2.96 – 2.86 (m, 1H), 2.51 – 2.38 (m, 1H), 2.44 (s, 3H), 2.28 (dd, J = 17.8, 7.2 Hz, 1H), 2.21 – 2.05 (m, 3H), 1.97 (d, J = 16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 197.4, 143.7, 134.6, 134.5, 134.2, 133.9, 133.3, 129.8, 127.8, 127.2, 126.9, 125.0, 122.7, 47.8, 46.9, 46.3, 43.0, 29.5, 29.0, 26.2, 21.6; HRMS (pos. ESI): m/z for $C_{24}H_{23}O_4NNaS$ $[M+Na]^+$ calcd: 444.1240, found: 444.1240.



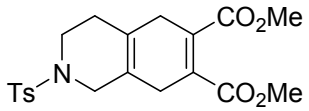
(2-tosyl-1,2,3,4,5,6,7,8-octahydroisoquinoline-6,7-diyl)bis(phenylmethanone) (**6p**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 4H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.48 – 7.41 (m, 4H), 7.33 – 7.29 (m, 2H), 4.16 – 3.97 (m, 2H), 3.62 (d, *J* = 15.5 Hz, 1H), 3.54 (dt, *J* = 11.0, 4.8 Hz, 1H), 3.17 (d, *J* = 15.8 Hz, 1H), 2.83 (ddd, *J* = 11.8, 9.0, 4.6 Hz, 1H), 2.42 (s, 3H), 2.38 – 2.16 (m, 3H), 2.13 – 1.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 202.7, 143.7, 136.1, 133.3, 133.1, 129.7, 128.8, 128.7, 128.6, 128.5, 127.8, 126.2, 123.5, 47.8, 43.8, 43.7, 43.1, 33.7, 31.6, 29.4, 21.6; HRMS (pos. ESI): m/z for $C_{30}H_{29}O_4NNaS$ $[M+Na]^+$ calcd: 522.1710, found: 522.1708.



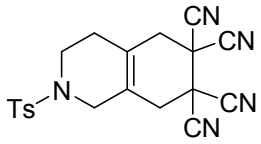
dimethyl 1,2,3,4,5,6,7,8-octahydro-2-tosylisoquinoline-6,7-dicarboxylate (**6q**). Yellow solid, m.p. 138−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 3.68 (s, 6H), 3.55 (d, *J* = 15.2 Hz, 1H), 3.46 – 3.39 (m, 1H), 3.21 (d, *J* = 15.6 Hz, 1H), 2.93 – 2.79 (m, 3H), 2.43 (s, 3H), 2.27 – 1.99 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 174.6, 143.7, 133.4, 129.7, 127.8, 125.5, 122.8, 52.1, 52.0, 47.6, 43.0, 41.3, 41.2, 31.8, 29.7, 29.3, 21.6; HRMS (pos. APCI): m/z for $C_{20}H_{26}O_6NS$ $[M+H]^+$ calcd: 408.1475, found: 408.1474.



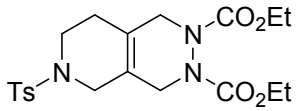
1,2,3,4,5,6,7,8-octahydro-2-tosylisoquinoline-6,7-dicarbonitrile (**6r**). Yellow solid, m.p. 177−178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.44 (dd, *J* = 37.2, 15.8 Hz, 2H), 3.26 (dt, *J* = 11.6, 5.6 Hz, 1H), 3.19 – 3.11 (m, 3H), 2.53 (dd, *J* = 16.2, 3.6 Hz, 2H), 2.44 (s, 3H), 2.27 (dd, *J* = 15.6, 12.4 Hz, 2H), 2.13 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 133.2, 129.9, 127.8, 124.6, 122.0, 118.3, 118.2, 47.3, 42.7, 30.2, 29.2, 28.2, 27.6, 27.6, 21.6; HRMS (pos. APCI): m/z for $C_{18}H_{20}O_2N_3S$ $[M+H]^+$ calcd: 342.1271, found: 342.1270.



dimethyl 1,2,3,4,5,8-hexahydro-2-tosylisoquinoline-6,7-dicarboxylate (**6s**). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 3.76 (s, 6H), 3.42 (s, 2H), 3.21 (t, *J* = 5.8 Hz, 2H), 2.85 (t, *J* = 5.3 Hz, 4H), 2.42 (s, 3H), 2.11 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 167.8, 143.8, 133.2, 132.7, 131.4, 129.8, 127.8, 123.3, 120.8, 52.4, 47.2, 43.0, 32.3, 30.1, 28.8, 21.6; HRMS (pos. ESI): m/z for $C_{20}H_{23}O_6NNaS$ $[M+Na]^+$ calcd: 428.1138, found: 428.1138.

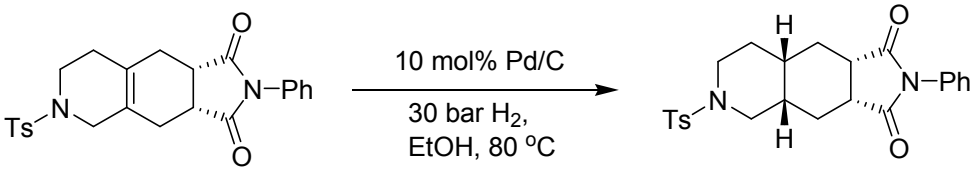


1,2,3,4-tetrahydro-2-tosylisoquinoline-6,6,7,7(5H,8H)-tetracarbonitrile (**6t**). Brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.46 (s, 2H), 3.18 (t, *J* = 5.6 Hz, 2H), 2.90 (s, 4H), 2.38 (s, 3H), 2.13 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 132.9, 130.2, 127.7, 123.4, 120.8, 110.3, 110.2, 46.7, 42.2, 37.7, 37.7, 35.7, 33.8, 28.6, 21.6; HRMS (pos. APCI): m/z for $C_{20}H_{18}O_2N_5S$ $[M+H]^+$ calcd: 392.1176, found: 392.1175.



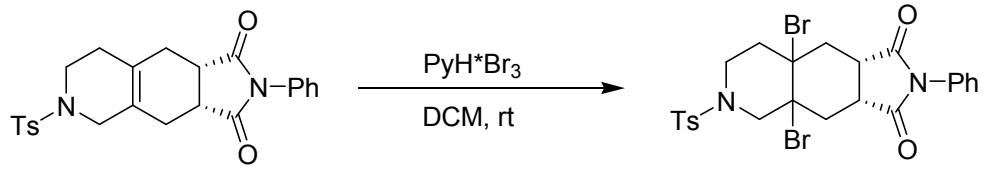
diethyl 5,6,7,8-tetrahydro-6-tosylpyrido[3,4-d]pyridazine-2,3(1H,4H)-dicarboxylate (**6u**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.26 – 4.08 (m, 6H), 3.69 – 3.66 (m, 4H), 3.19 (br s, 1H), 2.71 (br s, 1H), 2.43 (s, 3H), 2.27 (s, 1H), 1.95 (d, *J* = 16.0 Hz, 1H), 1.31 – 1.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 129.8, 127.8, (some carbon signals were missing) 62.7, 45.4, 42.7, 26.6, 21.6, 14.6, 14.5, 14.4; HRMS (pos. APCI): m/z for $C_{20}H_{28}O_6N_3S$ $[M+H]^+$ calcd: 438.1693, found: 438.1694.

Derivatizations of 4a and 4h



4a **7**, 94%, single isomer

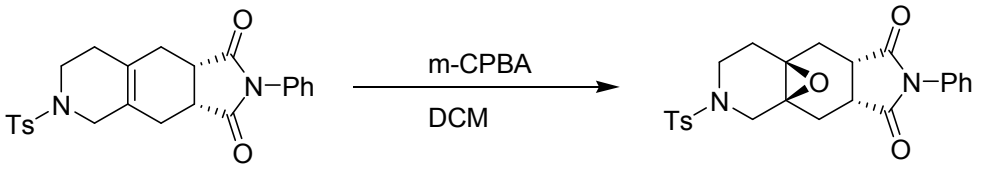
Following a modified literature procedure,[3] to a dried glass liner charged with magnetic stirring bar, **4a** (87.2 mg, 0.2 mmol), Pd/C (8 mg, 10% w/w) and 5 mL absolute EtOH were added subsequently under argon atmosphere. The glass liner was transferred into the stainless steel autoclave (100 ml). The autoclave was purged three times with 5 bar of H_2 and was pressurized to 30 bar of H_2. Then it was conducted at 80 °C for 20 h. Afterwards, the autoclave was cooled down to r.t. and depressurized, the reaction mixture was filtered through a pad of celite and washed with EtOH, and the filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford the corresponding product **7** as single isomer in 94% yield. decahydro-2-phenyl-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**7**). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 3.44 – 3.35 (m, 1H), 3.24 (dd, *J* = 11.8, 4.0 Hz, 1H), 3.07 – 2.95 (m, 2H), 2.73 (dd, *J* = 11.8, 3.2 Hz, 1H), 2.52 (ddd, *J* = 11.8, 9.0, 4.4 Hz, 1H), 2.41 (s, 3H), 2.08 (dt, *J* = 14.6, 4.8 Hz, 1H), 2.04 – 1.99 (m, 1H), 1.98 – 1.82 (m, 3H), 1.74 (dt, *J* = 9.4, 4.8 Hz, 1H), 1.66 – 1.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 178.1, 143.6, 133.1, 131.9, 129.7, 129.2, 128.5, 127.7, 126.3, 49.8, 45.3, 39.4, 38.2, 32.5, 31.4, 26.8, 25.7, 24.9, 21.6; HRMS (pos. APCI): m/z for $C_{24}H_{27}O_4N_2S$ $[M+H]^+$ calcd: 439.1686, found: 439.1686.



4a **8**, 88%, 1:1 dr

Following a modified literature procedure,[4] pyridiniumbromide perbromide (70.4 mg, 0.22 mmol) was added to a solution of the **4a** (87.2 mg, 0.2 mmol) in 5 mL dry DCM at 0 °C. And then the reaction mixture was stirred at room temperature under argon atmosphere. After consumption of the starting material (monitored by TLC), the reaction mixture was diluted with DCM (5 mL) and poured into ice-cold water (10

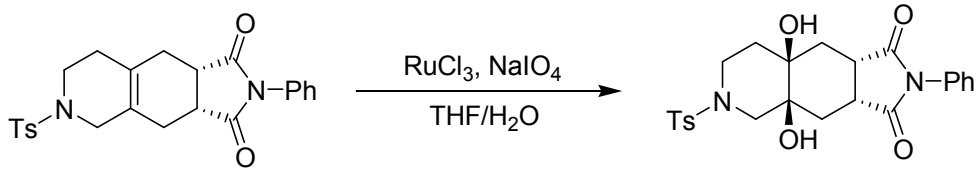
mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 5 mL). The combined organic extracts were washed successively with saturated aqueous $Na_2S_2O_5$ solution (3 x 10 mL), water (2 x 10 mL), brine (2 x 10 mL), and dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford the corresponding product **8** as 1:1 diastereo isomers in 88% yield. 4a,8a-dibromo-decahydro-2-phenyl-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dione (**8-isomer 1**). White solid, m.p. 146−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.42 – 7.37 (m, 1H), 7.36 – 7.33 (m, 2H), 7.28 – 7.26 (m, 1H), 7.26 – 7.25 (m, 1H), 3.96 – 3.85 (m, 2H), 3.59 (dt, *J* = 10.2, 9.2 Hz, 1H), 3.25 – 3.16 (m, 1H), 3.11 – 2.98 (m, 3H), 2.74 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.56 (dtd, *J* = 25.4, 15.0, 9.6 Hz, 3H), 2.44 (s, 3H), 2.06 (dt, *J* = 14.8, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 177.1, 144.1, 134.0, 131.9, 130.0, 129.3, 128.9, 127.5, 126.4, 71.9, 67.4, 54.2, 42.5, 37.0, 36.6, 36.5, 36.3, 36.1, 21.7. (**8-isomer 2**). White solid, m.p. 148−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.43 – 7.38 (m, 1H), 7.36 – 7.33 (m, 2H), 7.32 – 7.30 (m, 1H), 7.30 – 7.28 (m, 1H), 3.93 (dd, *J* = 17.8, 5.2 Hz, 2H), 3.53 (dt, *J* = 10.4, 9.0 Hz, 1H), 3.23 – 2.98 (m, 4H), 2.70 – 2.47 (m, 4H), 2.45 (s, 3H), 1.99 (dt, *J* = 14.7, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 176.8, 144.1, 134.3, 131.9, 130.0, 129.4, 128.9, 127.7, 126.5, 71.3, 67.9, 54.1, 42.6, 38.9, 37.0, 36.9, 36.2, 33.3, 21.7; HRMS (pos. APCI): m/z for $C_{24}H_{25}O_4N_2Br^{81}BrS$ $[M+H]^+$ calcd: 596.9876, found: 596.9882.



4a **9**, 84%, 6:1 dr

Following a modified literature procedure,[5] to a dried Schlenk tube were added **4a** (87.2 mg, 0.2 mmol) in 5 mL dry DCM at 0 °C. Then m-CPBA (85% purity, 61 mg, 0.3 mmol)/DCM (5 mL) was added, and then the resulting solution was warmed up to room temperature. The mixture was stirred at room temperature until completion of the reaction (monitored by TLC). DCM was removed, and Et_2O (20 mL) was added, and the organic layer was washed sequentially with saturated aqueous $Na_2S_2O_3$ solution, saturated aqueous $NaHCO_3$ solution and brine sequentially. And then dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl

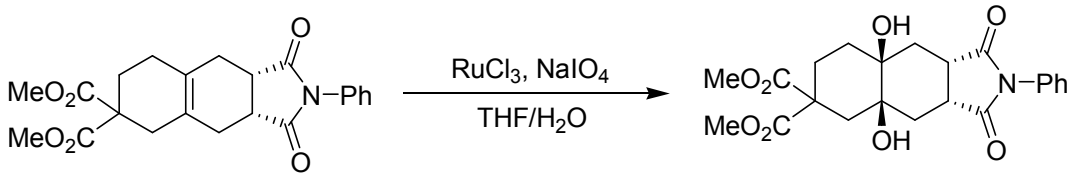
acetate to afford the corresponding product **9** as 6:1 diastereo isomers in 84% yield. 2-phenyl-6-tosyloctahydro-1H-4a,8a-epoxypyrrolo[3,4-g]isoquinoline-1,3(2H)-dione (**9-major isomer**). White solid, m.p. 229−230 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 2H), 3.66 (dd, *J* = 13.6, 1.2 Hz, 1H), 3.49 (ddd, *J* = 12.0, 3.2, 1.8 Hz, 1H), 3.03 – 2.88 (m, 3H), 2.61 (dd, *J* = 15.2, 11.6 Hz, 2H), 2.43 (s, 3H), 2.42 (dt, *J* = 9.6, 2.8 Hz, 1H), 2.34 (dd, *J* = 15.2, 6.8 Hz, 1H), 2.22 (dd, *J* = 15.2, 7.2 Hz, 1H), 2.05 (ddd, *J* = 14.8, 11.2, 5.6 Hz, 1H), 1.97 (dt, *J* = 14.6, 2.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 179.2, 144.1, 132.9, 132.5, 130.0, 129.2, 128.6, 127.7, 126.7, 59.6, 59.1, 46.9, 40.1, 36.3, 36.1, 29.1, 27.4, 27.1, 21.6; HRMS (pos. ESI): m/z for $C_{24}H_{24}O_5N_2NaS$ $[M+Na]^+$ calcd: 475.1298, found: 475.1304. (**9-minor isomer**). White solid, m.p. 232−233 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 3.63 (d, *J* = 13.6 Hz, 1H), 3.52 – 3.44 (m, 1H), 3.17 – 3.05 (m, 3H), 2.66 – 2.57 (m, 1H), 2.57 – 2.47 (m, 2H), 2.44 (s, 3H), 2.15 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.08 – 2.01 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 178.0, 144.1, 133.3, 131.6, 129.9, 129.3, 128.8, 127.7, 126.4, 57.9, 57.4, 47.0, 40.2, 36.4, 36.2, 29.0, 28.0, 27.8, 21.6.



4a **10a**, 70%, single isomer

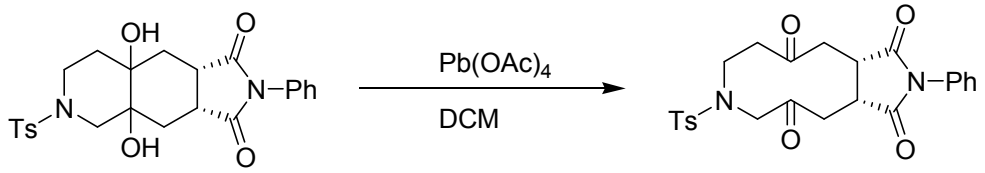
Following a modified literature procedure,[6] $RuCl_3$ (41.4 mg, 0.2 mmol) and $NaIO_4$ (428 mg, 2 mmol) were added to a solution of **4a** (87.2 mg, 0.2 mmol) in the mixture of THF and H_2O (10 mL, 1:1). The resulting biphasic dark suspension was vigorously stirred for 5 hours, and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford the corresponding product **10a** as single isomer in 70% yield. decahydro-4a,8a-dihydroxy-2-phenyl-6-tosyl-2H-pyrrolo[3,4-g]isoquinoline-1,3-dion e (**10a**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.44 – 7.37 (m, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.23 (dd, *J* = 5.4, 3.4 Hz, 2H), 3.31 – 3.19 (m, 2H), 3.08 (dd, *J* = 11.2, 5.8 Hz, 1H), 3.05 – 2.95 (m, 3H), 2.74 (br s, 1H), 2.42 (s, 3H), 2.30 – 2.18 (m, 3H), 2.14 – 1.99 (m, 2H), 1.82 – 1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 177.7, 144.1, 132.8, 131.8, 130.0, 129.2, 128.7,

127.7, 126.3, 70.5, 69.8, 52.4, 42.6, 38.8, 37.8, 34.5, 31.5, 21.6; HRMS (pos. ESI): m/z for $C_{24}H_{26}O_6N_2NaS$ $[M+Na]^+$ calcd: 493.1404, found: 493.1403.



4h **10h**, 62%, single isomer

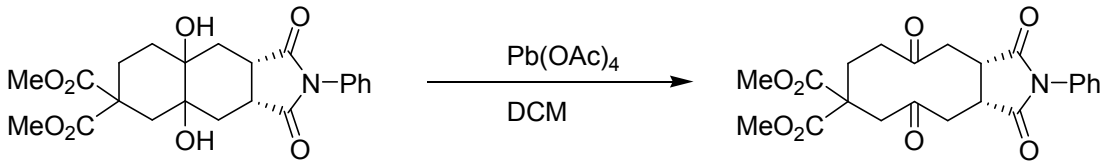
Following a similar procedure for **10a** to provide **10h** as single isomer in 62% yield. dimethyl decahydro-4a,8a-dihydroxy-1,3-dioxo-2-phenyl-1H-benzo[f]isoindole-6,6(7H)-dicarboxylate (**10h**). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dt, *J* = 10.0, 2.0 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.30 (dd, *J* = 5.2, 3.4 Hz, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.33 (dt, *J* = 10.4, 7.8 Hz, 1H), 3.23 (td, *J* = 7.8, 4.8 Hz, 1H), 3.08 (s, 1H), 2.58 – 2.50 (m, 2H), 2.34 – 2.24 (m, 1H), 2.23 – 2.08 (m, 3H), 2.07 – 1.98 (m, 2H), 1.96 – 1.85 (m, 2H), 1.56 (ddd, *J* = 13.6, 5.2, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 177.8, 173.1, 171.9, 132.0, 129.3, 128.7, 126.5, 71.0, 70.9, 53.1, 39.0, 37.4, 33.5, 33.1, 32.8, 27.6; HRMS (pos. ESI): m/z for $C_{22}H_{25}O_8N_2Na$ $[M+Na]^+$ calcd: 454.1472, found: 454.1473.



10a **11a**, 91%

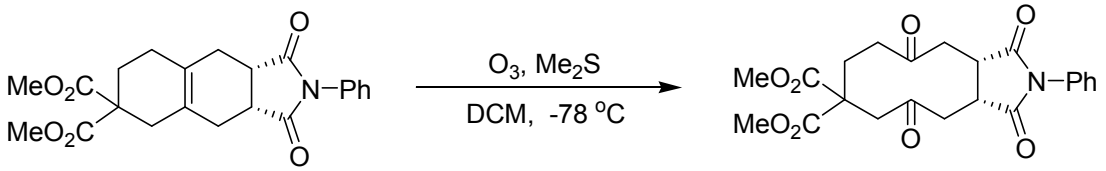
Following a modified literature procedure,[7] the cooled reaction mixture of **10a** (94 mg, 0.2 mmol) in 5 mL dry DCM was added portionwise with lead tetraacetate (89 mg, 0.2 mmol), stirred for 30 min at room temperature, and concentrated in vacuo. The residue was taken up in ether (10 mL) and the solids were removed by filtration through a short pad of silica gel. The pad was rinsed with ether (10 mL) and the filtrate was washed with dilute $NaHCO_3$ solution and water, and dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford the corresponding product **11a** in 91% yield. octahydro-2-phenyl-7-tosyl-2H-pyrrolo[3,4-e]azecine-1,3,5,10-tetraone (**11a**). White solid, m.p. 224−225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.52

– 7.46 (m, 2H), 7.44 – 7.31 (m, 5H), 4.17 (d, *J* = 15.6 Hz, 1H), 3.90 – 3.75 (m, 2H), 3.65 (d, *J* = 14.2 Hz, 1H), 3.49 – 3.21 (m, 4H), 3.11 (qd, *J* = 18.2, 6.8 Hz, 2H), 2.93 (d, *J* = 18.2 Hz, 1H), 2.53 (d, *J* = 13.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 205.2, 177.6, 177.5, 144.8, 134.6, 132.0, 130.3, 129.3, 128.8, 127.3, 126.5, 61.6, 49.2, 44.8, 39.7, 38.5, 35.0, 21.7; HRMS (pos. APCI): m/z for $C_{24}H_{25}O_6N_2S$ $[M+H]^+$ calcd: 469.1428, found: 469.1430.



10h **11h**, 93%

Following a similar procedure for **11a** to provide **11h** in 93% yield. dimethyl decahydro-1,3,5,10-tetraoxo-2-phenyl-1H-cyclodeca[c]pyrrole-7,7(8H)-dicarboxylate (**11h**). Yellow solid, m.p. 175−176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 7.33 (dd, *J* = 5.4, 3.2 Hz, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 3.58 – 3.44 (m, 2H), 3.26 (d, *J* = 1.4 Hz, 2H), 3.09 – 2.88 (m, 4H), 2.69 – 2.58 (m, 2H), 2.57 – 2.49 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.5, 207.2, 176.9, 176.6, 170.5, 131.9, 129.2, 128.7, 126.5, 54.8, 53.2, 53.1, 46.0, 41.3, 41.1, 40.3, 39.5, 28.9; HRMS (pos. ESI): m/z for $C_{22}H_{23}O_8NNa$ $[M+Na]^+$ calcd: 452.1316, found: 452.1311.

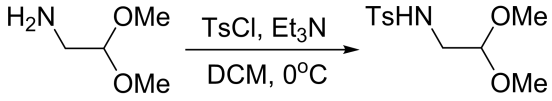


4h **11h**, 48%

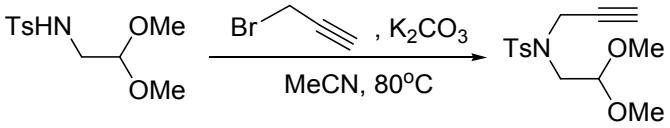
Following a modified literature procedure,[8] to a solution of adduct **4h** (79.4 mg, 0.2 mmol) in 10 mL dry DCM was bubbled ozone for 0.5 h at -78 °C. Methyl sufide (0.3 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The mixture was diluted with ethyl ether (10 mL), washed with aqueous $Na_2S_2O_3$ (10 mL) and aqueous K_2CO_3 (10 mL) and dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford the corresponding product **11h** in 48% yield.

Deuterium labelling experiments

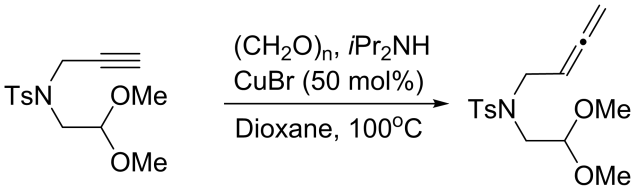
Preparation of deuterated starting material



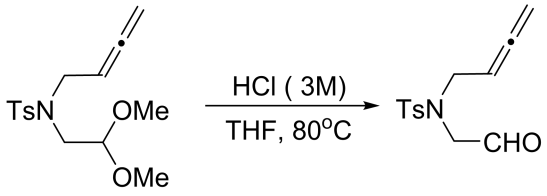
2,2-Dimethoxyethylamine (3.15 g, 30.0 mmol) and Et_3N (12.7 mL, 90.0 mmol) were dissolved in 10 mL DCM and the mixture was cooled to 0 °C. p-Toluenesulfonyl chloride (5.70 g, 30.0 mmol) was added dropwise to the solution, and the mixture was stirred at room temperature for 24 hours. The resulting solution was extracted with DCM. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford *N*-(2,2-dimethoxyethyl)-4-methylbenzenesulfonamide (7.18 g, 27.7 mmol, 92% yield) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.90 (br s, 1H), 4.31 (t, *J* = 5.6 Hz, 1H), 3.29 (s, 6H), 3.01 (t, *J* = 6.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 136.9, 130.0, 129.7, 127.1, 102.6, 54.5, 44.5, 21.5.



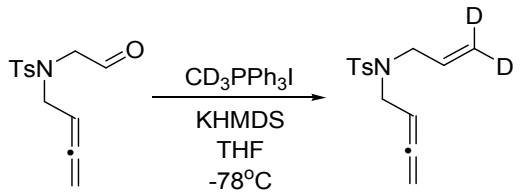
N-(2,2-dimethoxyethyl)-4-methylbenzenesulfonamide (1 equiv, 20 mmol), K_2CO_3 (1.4 equiv, 28.0 mmol) and acetonitrile (0.4 M) were added to a oven dried flask. The corresponding propargyl bromide (1.5 equiv, 30 mmol) was added and the reaction mixture was heated under reflux overnight. Then, the mixture was cooled to rt and the salts were filtered. Solvent was removed under vacuum, and the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford *N*-(2,2-dimethoxyethyl)-*N*-tosylprop-2-yn-1-amine in 89% Yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.55 (t, *J* = 5.5 Hz, 1H), 4.25 (d, *J* = 2.0 Hz, 2H), 3.39 (s, 6H), 3.26 (d, *J* = 5.5 Hz, 2H), 2.41 (s, 3H), 2.00 (t, *J* = 2,5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 136.0, 129.5, 127.8, 127.7, 104.3, 77.1, 73.7, 54.7, 47.5, 38.2, 21.6.



CuBr (0.5 eq) and paraformaldehyde (2.2 eq) were added into a oven-dried vial under argon atmosphere. Then *N*-(2,2-dimethoxyethyl)-*N*-tosylprop-2-yn-1-amine (1.0 eq) was added dissolved in dry 1,4-dioxane, followed by the addition of *i*-Pr_2NH (2.1 eq) dropwise. The reaction mixture was heated at 100 °C overnight. The crude of the reaction was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford *N*-(2,2-dimethoxyethyl)-N-tosylbuta-2,3-dien-1-amine in 76% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.85 (p, *J* = 6.8 Hz, 1H), 4.64 (dt, *J* = 6.4, 2.4 Hz, 2H), 4.52 (t, *J* = 5.6 Hz, 1H), 3.97 (dt, *J* = 6.8, 2.4 Hz, 2H), 3.38 (s, 6H), 3.25 (d, *J* = 5.2 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 143.4, 137.5, 129.7, 127.3, 104.5, 85.8, 76.2, 54.8, 48.2, 47.9, 21.5.

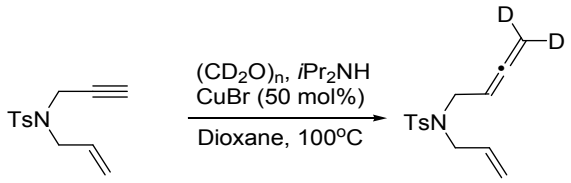


A mixture of *N*-(2,2-dimethoxyethyl)-N-tosylbuta-2,3-dien-1-amine (10 mmol) and M HCl (25 mL) in THF (35 mL) was refluxed for 4 h. After removal of the organic solvent in vacuo, the mixture was extracted with Et_2O. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford 2-(*N*-(buta-2,3-dienyl)-*N*-tosylamino)acetaldehyde in 80% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.62 (t, *J* = 1.5 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.00 (p, *J* = 7.0 Hz, 1H), 4.73 (dt, *J* = 6.5, 2.5 Hz, 2H), 3.83 (dt, *J* = 7.0, 2.5 Hz, 2H), 3.81 (d, *J* = 1.5 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.3, 198.5, 144.2, 135.6, 130.0, 127.4, 85.4, 76.9, 56.2, 48.9, 21.6.



1a-1

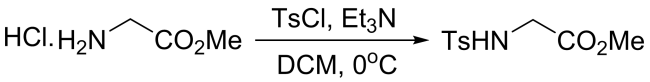
D_3-Methyltriphenylphosphonium iodide (651 mg, 1.6 mmol) was suspended in THF (7 mL) at room temperature and KHMDS (3 ml, 0.5 M, 1.5 mmol) was added. The resultant yellow suspension was stirred at room temperature for 1 hour and then cooled to -78 ºC and a solution of 2-(*N*-(buta-2,3-dienyl)-*N*-tosylamino)acetaldehyde (265 mg, 1 mmol) dissolved in THF (1.5 mL) was added dropwise. The cooling bath was removed and the mixture was stirred for another 2 hours. The reaction was quenched with MeOH (100 mL) and the resulting mixture was poured into saturated ammonium chloride solution (5 mL). Extraction with Et_2O (3 x 10 mL) and then dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford product **1a-1** (183 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.65 – 5.61 (m, 1H), 5.18 – 5.12 (m, 0.4H), 4.89 (p, *J* = 6.8 Hz, 1H), 4.68 (dt, *J* = 6.6, 2.4 Hz, 2H), 3.86 – 3.84 (m, 4H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 143.3, 137.6, 132.4, 129.7, 127.2, 85.7, 76.1, 49.2, 45.6, 21.5; HRMS (pos. ESI): m/z for $C_{14}H_{16}{}^2H_2O_2NS$ $[M+H]^+$ calcd: 266.1178, found: 266.1180.



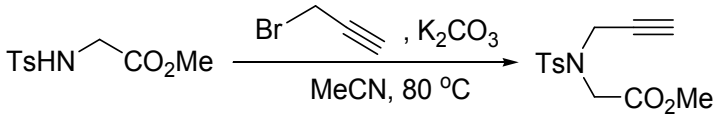
1a-2

CuBr (0.5 eq) and paraformaldehyde-d_2 (2.0 eq) were added into an oven-dried schlenk flask under argon atmosphere. Then N-(prop-2-ynyl)-N-tosylprop-2-en-1-amine (1.0 eq) was added dissolved in dry 1,4-dioxane, followed by the addition of *i*-Pr_2NH (2.1 eq) dropwise under argon atmosphere. The reaction mixture was heated at 100ºC overnight. The crude of the reaction was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford product **1a-2** in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.66 (ddt, *J* = 20.8, 12.8, 8.0 Hz, 1H), 5.19 – 5.14 (m, 2H), 4.90 (t, *J* = 7.5 Hz, 1H), 4.68 – 4.66 (m, 0.11H), 3.86 – 3.84 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.7, 143.3, 137.6, 132.6,

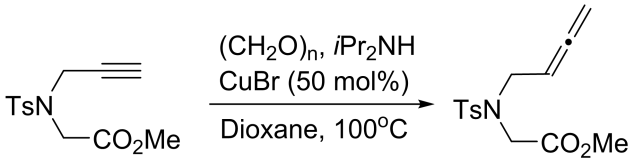
129.8, 127.2, 119.1, 85.9, 49.3, 45.6, 21.6; HRMS (pos. ESI): m/z for $C_{14}H_{16}{}^2H_2O_2NS$ $[M+H]^+$ calcd: 266.1178, found: 266.1178.



To a mixture of methyl glycinate hydrogen chloride (6.28 g, 50 mmol) and Et_3N (17 mL) in dry DCM (50 mL) was added TsCl (10.45 g) in several portions at 0 °C within 20 min. The reaction mixture was stirred at room temperature overnight before being washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and filtered through a thin silica gel pad. After being concentrated, the crude product was recrystallized in a mixture of hexanes and ethyl acetate (87% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 5.18 (br s, 1H), 3.80 (d, *J* = 5.4 Hz, 2H), 3.65 (s, 3H), 2.44 (s, 3H).

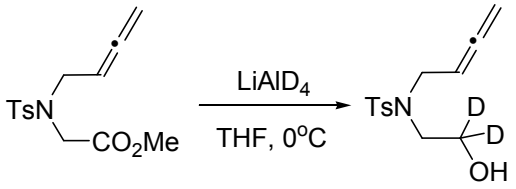


N-tosylate glycinate (4 mmol) was dissolved in acetonitrile (10.0 mL), and propargyl bromide (1.5 eq, 6 mmol) and K_2CO_3 (1.4 eq, 5.6 mmol) were added to the mixture. After being stirred for 20 h at 80 °C, the reaction mixture was filtered through Celite. The filtrate was concentrated under reduced pressure to afford the crude product which is directly used for next step. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.28 (dd, *J* = 2.4, 0.9 Hz, 1H), 3.71 (s, 3H), 2.44 (s, 3H), 2.17 (t, *J* = 2.4 Hz, 1H).

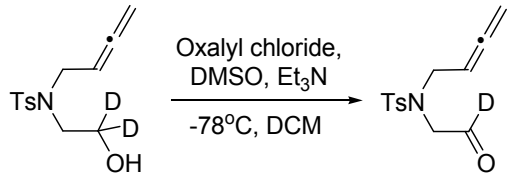


CuBr (0.5 eq) and paraformaldehyde (2.2 eq) were added into a oven-dried vial under argon atmosphere. Then the corresponding alkyne derivative (1.0 eq, 0.4) was added dissolved in dry 1,4-dioxane, followed by the addition of *i*-Pr_2NH (2.1 eq) dropwise. The reaction mixture was heated at 100 °C overnight. The crude of the reaction was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford methyl 2-(*N*-(buta-2,3-dienyl)-*N*-tosylamino)acetate in 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.98 (p, *J* = 6.8 Hz, 1H), 4.71 (dt, *J* = 6.4, 2.4 Hz, 2H), 4.05 (s, 2H), 3.90 (dt, *J* = 7.2, 2.4 Hz,

2H), 3.64 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 169.3, 143.5, 137.0, 129.6, 127.4, 85.5, 76.4, 52.1, 47.3, 47.0, 21.5; HRMS (pos. ESI): m/z for $C_{14}H_{18}O_4NS$ $[M+H]^+$ calcd: 296.0951, found: 296.0951.

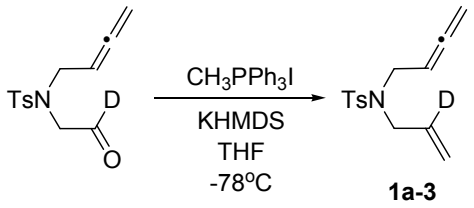


In a round-bottomed flask charged with $LiAlD_4$ (2.8 mmol, 0.8 equiv.) and THF (20 mL), was added methyl 2-(*N*-(buta-2,3-dienyl)-*N*-tosylamino)acetate (1.03 g, 3.5 mmol) in THF (5 mL) at 0 ºC. The mixture was stirred at rt. After the complete consumption of the starting material (TLC monitoring), the reaction mixture was quenched with NaOH (1M) (10 mL), extracted with EtOAc (3 x 30 mL), dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford 2-(*N*-(buta-2,3-dienyl)-*N*-tosylamino)ethanol-d_2 as colorless oil (0.77 g, 2.85mmol, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.97 (p, *J* = 6.8 Hz, 1H), 4.72 (dt, *J* = 6.4, 2.8 Hz, 2H), 3.89 (dt, *J* = 7.2, 2.4 Hz, 2H), 3.29 (s, 2H), 2.42 (s, 3H), 2.13 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 143.7, 136.6, 129.8, 127.4, 86.2, 76.6, 49.6, 48.2, 21.6; HRMS (pos. ESI): m/z for $C_{13}H_{16}{}^2H_2O_3NS$ $[M+H]^+$ calcd: 270.1127, found: 270.1127.



In a round-bottomed flask containing oxalyl chloride (0.297 mL, 3.5 mmol, 1.3 equiv.) in DCM (15 mL) at -78 ºC was added DMSO (0.254 mL, 6.2 mmol, 2.3 equiv.) dropwise. The mixture was stirred 5 min at -78 ºC and 2-(*N*-(buta-2,3-dienyl)-*N*-tosylamino)ethanol-d_2 (0.40 g, 2.7 mmol) was slowly added keeping stirring another 5 min. Et_3N (1.88 mL, 13.5 mmol, 5.0 equiv.) was added and the reaction mixture was stirred 30 min at -78 ºC and allowed to warm at room temperature. After complete consumption of the starting material (monitored by TLC), the reaction was quenched with saturated ammonium chloride solution (10 mL), extracted with DCM (3 x 20 mL), dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the residue was purified by silica gel column

chromatography, eluting with cyclohexane and ethyl acetate to afford 2-(*N*-(buta-2,3-dienyl)-*N*-tosylamino)acetaldehyde-d as light yellow oil (0.53 g, 2.0 mmol 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.01 (p, *J* = 6.8 Hz, 1H), 4.73 (dt, *J* = 6.8, 2.4 Hz, 2H), 3.84 (dt, *J* = 7.2, 2.4 Hz, 2H), 3.81 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.3, 198.1 (t, *J* = 28.0 Hz), 144.1, 135.7, 130.0, 127.5, 85.5, 76.9, 56.2 (t, *J* = 3.9 Hz), 48.9, 21.6; HRMS (pos. APCI): m/z for $C_{13}H_{18}{}^{2}HO_3N_2S$ $[M+NH_4]^+$ calcd: 284.1174, found: 284.1174.



1a-3

Methyltriphenylphosphonium iodide (651 mg, 1.6 mmol) was suspended in THF (7 mL) at room temperature and KHMDS (300 mg, 1.5 mmol) was added. The resultant yellow suspension was stirred at room temperature for 1 hour and then cooled to -78 ºC and a solution of 2-(*N*-(buta-2,3-dienyl)-*N*-tosylamino)acetaldehyde-d (266 mg, 1 mmol) dissolved in THF (1.5 mL) was added dropwise. The cooling bath was removed and the mixture was stirred for another 2 hours. The reaction was quenched with MeOH (100 mL) and the resulting mixture was poured into saturated ammonium chloride solution (5 mL). Extraction with Et_2O (3 x 10 mL), dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the residue was purified by silica gel column chromatography, eluting with cyclohexane and ethyl acetate to afford **1a-3** in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.16 (s, 2H), 4.89 (p, *J* = 7.0 Hz, 1H), 4.68 (dt, *J* = 6.5, 2.5 Hz, 2H), 3.86 – 3.84 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 143.3, 137.6, 132.3 (t, *J* = 19.2 Hz), 129.7, 127.2, 119.0, 85.7, 76.2, 49.2, 45.7, 21.6; HRMS (pos. APCI): m/z for $C_{14}H_{17}{}^{2}HO_2NS$ $[M+H]^+$ calcd: 265.1116, found: 265.1116.

Cyclization of 1a-1, 1a-2 and 1a-3

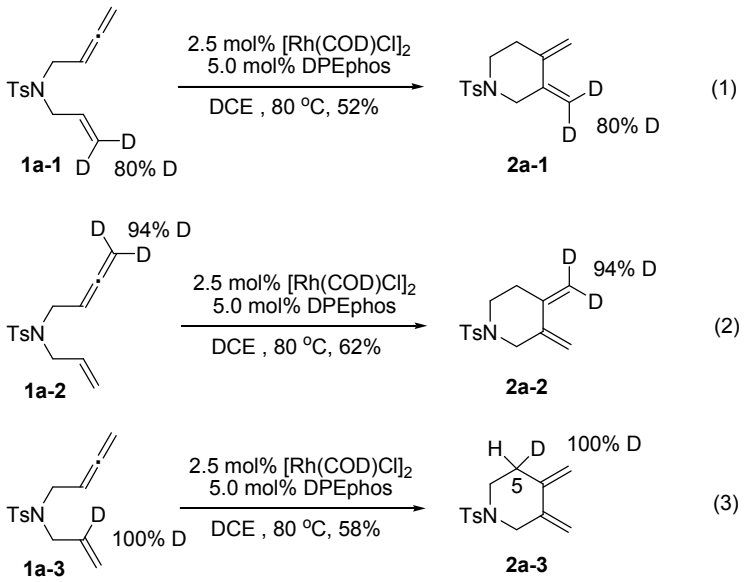
With the deuterated starting materials 1a-1, 1a-2 and 1a-3 in hand, the cyclization under standard conditions were performed to gain more insights for the mechanism. The results are summarized in Scheme S1. In case of **1a-1** and **1a-2**, deuterium atoms at terminal positions of alkene and allene completely remained in their original place, thus these carbon-hydrogen bonds should not change during the process. (equation 1 and 2). However the deuterium atom at the internal position of alkene completely incorporated into the 5 position of piperidine ring (**2a-3**), which showed that there

might involve a isomerization step in the catalytic cycle to form the exocyclic carbon-carbon double bonds (equation 3).

2a-1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 5.14 (s, 0.2H), 5.04 (s, 1H), 4.87 (s, 0.2H), 4.74 (d, J = 1.5 Hz, 1H), 3.64 (s, 2H), 3.15 (t, J = 6.0 Hz, 2H), 2.42 (s, 3H), 2.38 (t, J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 143.3, 141.2, 133.4, 129.7, 127.8, 110.9, 51.8, 46.4, 33.1, 21.6; HRMS (pos. ESI): m/z for $C_{14}H_{16}{}^{2}H_2O_2NS$ $[M+H]^+$ calcd: 266.1178, found: 266.1179.

2a-2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.15 (d, J = 0.5 Hz, 1H), 5.03 (s, 0.06H), 4.88 (d, J = 1.0 Hz, 1H), 4.72 (s, 0.06H), 3.64 (s, 2H), 3.15 (t, J = 6.0 Hz, 2H), 2.42 (s, 3H), 2.38 (t, J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 143.2, 141.3, 133.4, 129.7, 127.8, 111.5, 51.9, 46.5, 33.0, 21.6; HRMS (pos. ESI): m/z for $C_{14}H_{16}{}^{2}H_2O_2NS$ $[M+H]^+$ calcd: 266.1178, found: 266.1177.

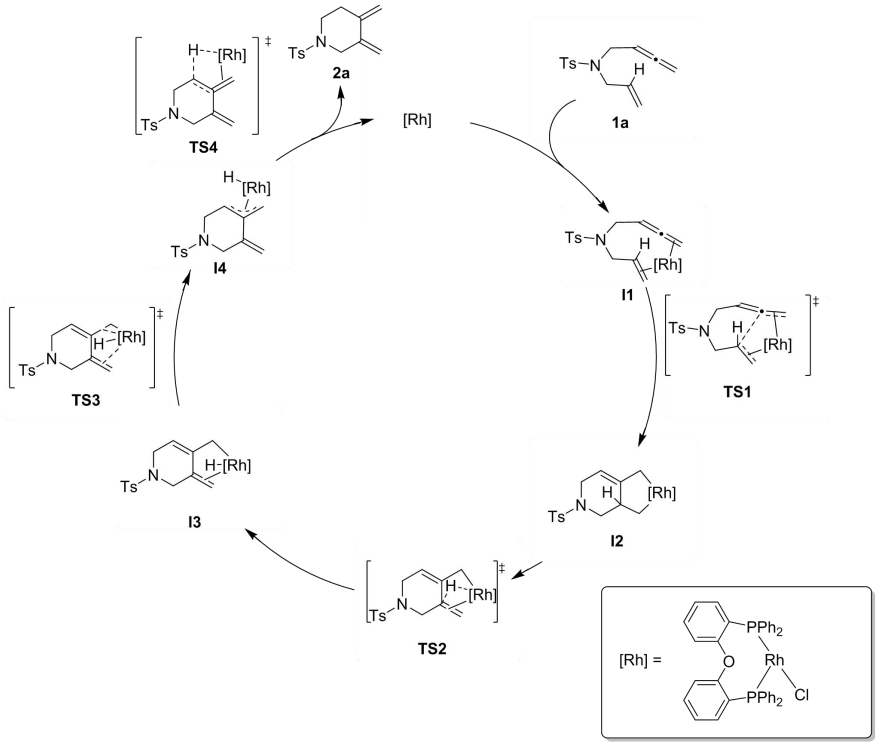
2a-3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.15 (d, J = 0.8 Hz, 1H), 5.05 (s, 1H), 4.88 (d, J = 1.2 Hz, 1H), 4.74 (t, J = 1.6 Hz, 1H), 3.65 (s, 2H), 3.16 – 3.14 (m, 2H), 2.42 (s, 3H), 2.36 (t, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.3, 141.4, 133.6, 129.7, 127.8, 111.5, 110.9, 51.9, 46.4, 32.8 (t, J = 19.8 Hz), 21.6; HRMS (pos. APCI): m/z for $C_{14}H_{17}{}^{2}HO_2NS$ $[M+H]^+$ calcd: 265.1116, found: 265.1116.



Scheme S1. Deuterium labelling experiments.

DFT calculations for six-membered ring diene

In order to understand the mechanism of the found catalytic system we performed DFT computations. All structures were optimized by the BP86-functional[1] in combination with the def2SVP[2] basic set. For more precise energy values, single-point energies were performed using the M06[3] functional with the def2SVP basis set. The solvent 1,2-dichloroethane was considered by the IEFPCM model. The chosen methodology showed an excellent accuracy in benchmark calculations which our group performed for similar investigations on Rh catalysis with the DPEphos ligand.[4] All calculations were done using Gaussian 09.[5] Based on a proposed mechanism shown in scheme S2 we performed the DFT calculations starting from a monomeric [ClRh(DPEphos)] complex ([Rh]). The substrate **1a** could coordinate the Rh with its vinyl moiety and terminal double bond of the allene group to form intermediate **I1.** From here, first ring closure takes place (**TS1**), followed by a β-hydride elimination (**TS2**) and a change of the coordination mode (**TS3**). Finally after a reductive elimination (**TS4**) the product **2a** is released. All the computed energies are shown in Figure S1. The highest energetic barriers are the 6-ring formation (**TS1**) with a magnitude of approximately ΔG = 14.6 kcal/mol (M06/def2SVP) and the reductive elimination (**TS4**) with a magnitude of approximately ΔG = 14.5 kcal/mol (M06/def2SVP).



Scheme S2. Proposed mechanism for the Rh catalyzed cyclization of 1,6-allenenes to six-membered exocyclic 1,3-dienes.

[1] (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824.
[2] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305
[3] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215−241.
[4] Gellrich, U.; Meißner, A.; Steffani, A.; Kähny, M.; Drexler, H.-J.; Heller, D.; Plattner, D. A.; Breit, B. *J. Am. Chem. Soc.* **2014**, *136*, 1097.
[5] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, rev. B.01; Gaussian, Inc.: Wallingford, CT, 2010.

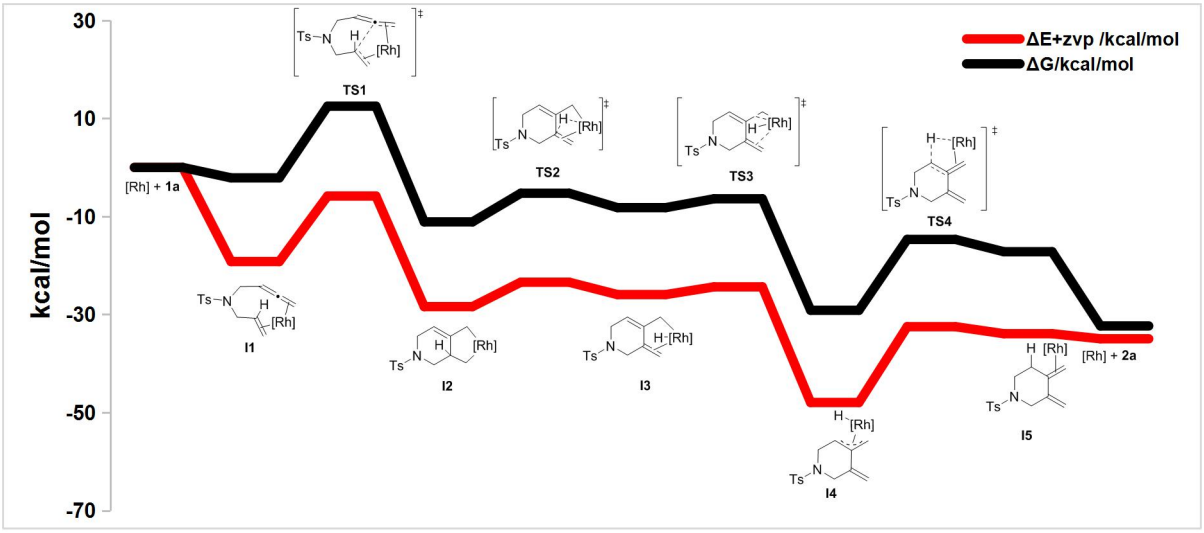
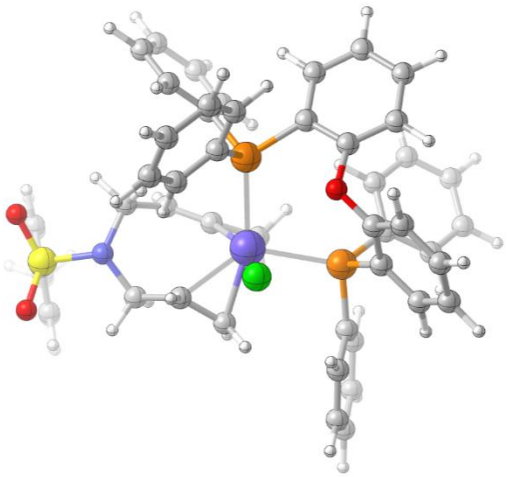


Figure S1. Computed catalytic cycle of the Rh catalyzed cyclization of 1,6-allenenes to six-membered exocyclic 1,3-dienes. All energies(PCM-M06/def2SVP//BP86/def2SVP) given with respect to energies of the [ClRh(DPEphos)] complex and the substrate.

Table S3

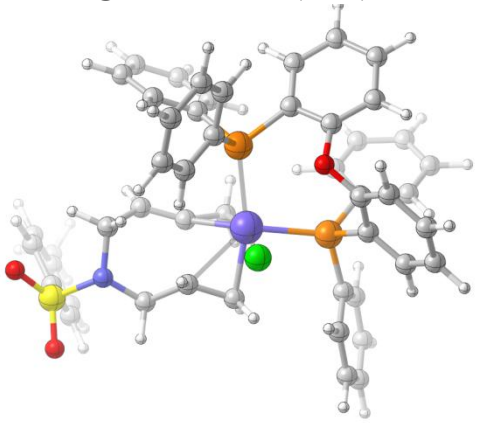
	PCM-M06/def2SVP//BP86/def2SVP		
	ΔE/kcal/mol	**ΔE+zvp /kcal/mol**	**ΔG/kcal/mol**
[Rh] + 1a	0.00	0.00	0.00
Substrate Complex (I1)	-21.90	-19.20	-2.12
TS-Ring Formation (TS1)	-8.13	-5.83	12.50
Intermediate 2 (I2)	-32.41	-28.39	-11.10
TS β-Hydride Elimination (TS2)	-24.15	-23.41	-5.26
Intermediate 3 (I3)	-27.62	-25.94	-8.20
TS coordination exchange (TS3)	-25.64	-24.37	-6.39
Intermediate 4 (I4)	-50.11	-47.96	-29.14
TS Reductive Elimination (TS4)	-33.11	-32.49	-14.69
Product Complex (I5)	-36.01	-33.92	-17.19
[Rh] + 2a	-37.80	-34.96	-32.34

Substrate Complex (I1)



Rh	0.1814663	0.4183999	-0.7546589
Cl	1.2839123	0.0320839	-2.8836929
C	-0.6732127	2.0805369	-1.7758529
C	-1.5193847	0.9751599	-2.1037859
H	0.0763503	2.4212749	-2.5058239
H	-1.0694057	2.8733139	-1.1128779
C	-1.3470357	0.3651589	0.6320761
C	-2.5420677	-0.2323601	0.7022491
C	-0.4008097	1.2555109	1.1464661
H	0.2568893	0.9593619	1.9823681
H	-0.5709127	2.3466859	1.0715351
H	-1.2799747	0.4086869	-3.0205659
C	-2.9977787	1.0428829	-1.7723729
H	-3.1882347	-0.0260301	1.5753211
C	-3.0821377	-1.0800471	-0.4237849
H	-3.8681097	-1.7837481	-0.0911599
H	-2.2623447	-1.6963601	-0.8471969
N	-3.6368457	-0.2563131	-1.5248019
H	-3.5019817	1.4688829	-2.6663669
H	-3.1616307	1.7481739	-0.9236959
S	-5.3056807	-0.3678551	-1.8408789
O	-5.5305187	0.3402499	-3.1212759
O	-5.6690427	-1.7895731	-1.6463499
C	-6.1675607	0.5782369	-0.5561239
C	-6.3582277	1.9611899	-0.7186309
C	-6.6292737	-0.0798201	0.5993381
C	-6.9935567	2.6902409	0.3002431
H	-6.0337877	2.4516279	-1.6485819
C	-7.2630117	0.6641239	1.6047111
H	-6.5104467	-1.1704111	0.6854841
C	-7.4517597	2.0606869	1.4782071
H	-7.1475997	3.7743399	0.1716651
H	-7.6317727	0.1468949	2.5062641
C	-8.1397527	2.8449679	2.5723981
H	-7.5920407	2.7591419	3.5353601
H	-8.2155647	3.9211559	2.3204701
H	-9.1681117	2.4655949	2.7543041
P	0.6829273	-2.0060951	-0.1314089
C	2.2782523	-2.4440721	0.7448081
C	0.7115293	-3.1409941	-1.6006559
C	-0.5171527	-2.8851681	0.9967111
C	3.4813983	-1.9130031	0.2141971
C	2.3649343	-3.2070891	1.9296311
C	1.5750983	-4.2550621	-1.6711069
C	-0.1952347	-2.9047861	-2.6567279
C	-0.7561467	-2.3540731	2.2867571
C	-1.2054967	-4.0562751	0.6130251
C	4.7147233	-2.0793381	0.8707591
O	3.3414893	-1.2680811	-0.9883949
C	3.5944723	-3.3974321	2.5859361
H	1.4540393	-3.6554981	2.3516941
C	1.5256203	-5.1225581	-2.7764019
H	2.2887483	-4.4512621	-0.8557849
C	-0.2540417	-3.7828251	-3.7518469
H	-0.8503857	-2.0215891	-2.6248899
C	-1.6368337	-2.9898991	3.1762661
H	-0.2402877	-1.4354911	2.6077151
C	-2.1036717	-4.6823081	1.4977751
H	-1.0410547	-4.4875871	-0.3856259
C	4.7635323	-2.8204771	2.0623461
H	5.6253123	-1.6320651	0.4464251
C	4.2513603	-0.3138781	-1.4058979
H	3.6337673	-3.9969651	3.5086511
C	0.6089593	-4.8906571	-3.8167689
H	2.2076173	-5.9869451	-2.8214369
H	-0.9697207	-3.5879821	-4.5660059
C	-2.3187737	-4.1557121	2.7819051
H	-1.7999607	-2.5648631	4.1796231
H	-2.6338107	-5.5930581	1.1765551
H	5.7281713	-2.9525621	2.5776911
C	3.9818133	1.0485729	-1.1386579
C	5.3793163	-0.7136441	-2.1418719
H	0.5701673	-5.5719581	-4.6818289
H	-3.0174477	-4.6507291	3.4751431
P	2.4245293	1.5089659	-0.2060969
C	4.9237013	1.9995229	-1.5908629
C	6.2936743	0.2520149	-2.5906199
H	5.5170883	-1.7832001	-2.3604889
C	3.1376443	1.6359319	1.5204271
C	2.1947413	3.2829549	-0.6891059
C	6.0705183	1.6091979	-2.3030019
H	4.7507433	3.0692189	-1.3997029
H	7.1791223	-0.0576201	-3.1678159
C	4.0644273	2.6428159	1.8798251
C	2.8013133	0.6548059	2.4772001
C	2.2563183	3.6485589	-2.0562269
C	1.7926733	4.2559919	0.2554231
H	6.7855823	2.3739959	-2.6443709
C	4.6208243	2.6750329	3.1688421
H	4.3552963	3.4120799	1.1479081
C	3.3613933	0.6847819	3.7674371
H	2.1128223	-0.1583121	2.2015971
C	1.9619733	4.9627689	-2.4568829
H	2.5220393	2.8917709	-2.8112829
C	1.4923903	5.5678059	-0.1523569
H	1.7201053	3.9938889	1.3223781
C	4.2678303	1.6981509	4.1181651
H	5.3389673	3.4681639	3.4322591
H	3.0880743	-0.0936631	4.4969311
C	1.5837063	5.9287769	-1.5077349
H	2.0221373	5.2293519	-3.5241949
H	1.1886463	6.3135929	0.5997951
H	4.7054093	1.7255599	5.1288871
H	1.3540313	6.9584579	-1.8246149

TS 6-Ring Formation (TS1)



Rh	0.2860947	0.3904110	-0.7545048
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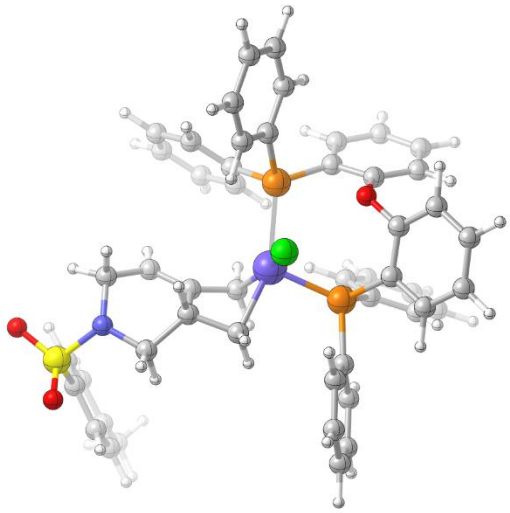
C	-0.6935883	2.1208380	-1.5369348
C	-1.6658243	1.1063220	-1.8710578
H	-0.0441893	2.4594840	-2.3575518
H	-0.9818363	2.9077460	-0.8149218
C	-1.6788223	0.0126960	-0.0176128
C	-2.7586253	-0.7931990	-0.0920668
C	-0.8893013	0.6923350	0.9648252
H	-0.6839643	0.1297770	1.8933852
H	-1.0883683	1.7645090	1.1591762
H	-1.3870603	0.5086990	-2.7604268
C	-3.1682433	1.3407500	-1.8147418
H	-3.3483283	-0.9797700	0.8244762
C	-3.3504273	-1.1423270	-1.4279688
H	-4.1573103	-1.8966110	-1.3802968
H	-2.5742553	-1.5398870	-2.1165538
N	-3.9122333	0.0922950	-2.0473148
H	-3.4129823	2.0283750	-2.6528648
H	-3.4553813	1.8482420	-0.8624208
S	-5.6009033	0.2269790	-2.2051418
O	-5.8270892	1.3904300	-3.0906138
O	-6.0938512	-1.1308670	-2.5259308
C	-6.2658872	0.6680220	-0.5784048
C	-6.3691713	2.0211690	-0.2131148
C	-6.6681732	-0.3492790	0.3076262
C	-6.8546352	2.3512020	1.0634612
H	-6.0977762	2.8030880	-0.9380728
C	-7.1529652	-0.0003390	1.5756232
H	-6.6225973	-1.4003220	-0.0151358
C	-7.2492752	1.3526080	1.9799322
H	-6.9398012	3.4123790	1.3499192
H	-7.4763673	-0.7966390	2.2666132
C	-7.7767822	1.7079670	3.3512942
H	-7.1548362	1.2537790	4.1521862
H	-7.7921072	2.8036750	3.5139932
H	-8.8111352	1.3286590	3.4953812
P	0.9137367	-1.9273700	-0.1770678
C	2.5345947	-2.2615050	0.6808062
C	0.9759368	-3.1339270	-1.5907208
C	-0.2820203	-2.7818290	0.9728422
C	3.6778948	-1.6811290	0.0803502
C	2.7165878	-2.9942190	1.8726112
C	1.7413408	-4.3184190	-1.5060988
C	0.2024047	-2.8953860	-2.7459558
C	-0.3844073	-2.3706880	2.3234022
C	-1.1540173	-3.7943820	0.5140972
C	4.9469788	-1.7543880	0.6814862
O	3.4475478	-1.1023550	-1.1449838
C	3.9840857	-3.0957290	2.4737702
H	1.8558007	-3.4912360	2.3430332
C	1.7239227	-5.2517280	-2.5562128
H	2.3545587	-4.5157110	-0.6128508
C	0.1802697	-3.8360450	-3.7912338
H	-0.3524233	-1.9509550	-2.8404108
C	-1.3272753	-2.9536670	3.1872002
H	0.2946657	-1.5976090	2.7156132
C	-2.0999082	-4.3745600	1.3774002
H	-1.0933543	-4.1370450	-0.5296038
C	5.0913788	-2.4605580	1.8867182
H	5.8098918	-1.2708850	0.2005402
C	4.2270358	-0.0529430	-1.5944638
H	4.1020358	-3.6699890	3.4057632
C	0.9403968	-5.0140990	-3.6999938
H	2.3270417	-6.1707180	-2.4788128
H	-0.4245333	-3.6342960	-4.6894788
C	-2.1927383	-3.9562860	2.7156002
H	-1.3830833	-2.6221010	4.2365662
H	-2.7678663	-5.1639970	0.9970552
H	6.0835888	-2.5239120	2.3610812
C	3.8476528	1.2704760	-1.2705928
C	5.3346188	-0.3290210	-2.4117738
H	0.9283307	-5.7458370	-4.5237528
H	-2.9326743	-4.4137520	3.3915292
P	2.3011758	1.5598420	-0.2508468
C	4.6681718	2.3146190	-1.7534418
C	6.1243717	0.7277730	-2.8915438
H	5.5539328	-1.3765500	-2.6671538
C	3.0040737	1.4987540	1.4768532
C	2.0522618	3.3862490	-0.4905018
C	5.7972328	2.0497040	-2.5487918
H	4.4142838	3.3585910	-1.5183418
H	6.9937008	0.5159590	-3.5337558
C	4.2923638	2.0055280	1.7663282
C	2.2290648	0.9702410	2.5283532
C	1.9368657	3.9014670	-1.8049828
C	1.8683737	4.2585610	0.6042152
H	6.4143418	2.8867190	-2.9111668
C	4.7855147	1.9866770	3.0809732
H	4.9182918	2.4161450	0.9592002
C	2.7223738	0.9545040	3.8456182
H	1.2297277	0.5750330	2.2985732
C	1.6672838	5.2641460	-2.0122828
H	2.0604417	3.2257930	-2.6674018
C	1.5873667	5.6205680	0.3902442
H	1.9505427	3.8763500	1.6333612
C	4.0018228	1.4619280	4.1250152
H	5.7915458	2.3840810	3.2908512
H	2.1028858	0.5390810	4.6564652
C	1.4912557	6.1285160	-0.9162048
H	1.5883927	5.6511970	-3.0408188
H	1.4500077	6.2889720	1.2554212
H	4.3915418	1.4466680	5.1554242
H	1.2776317	7.1965000	-1.0816878

Intermediate 2 (I2)



Rh	0.4689834	0.0319276	-1.0413711
Cl	1.5181684	0.0147976	-3.2544591
C	-1.0665166	1.1919436	-1.8926721
C	-2.0391946	0.0238446	-1.8740791
H	-0.7819856	1.5320766	-2.9047231
H	-1.3985926	2.0426766	-1.2649541
C	-1.9568536	-0.6396874	-0.4897931
C	-2.7446396	-1.7381634	-0.3088861
C	-1.0136786	-0.0077224	0.4618749
H	-0.8682976	-0.6103254	1.3784769
H	-1.3000056	1.0285516	0.7387999
H	-1.6968136	-0.7161374	-2.6402781
C	-3.5224256	0.3124126	-2.2225981
H	-2.7693576	-2.2956204	0.6421399
C	-3.6550586	-2.1200114	-1.4498971
H	-4.4578106	-2.8207874	-1.1526721
H	-3.0792686	-2.6445274	-2.2518481
N	-4.3009496	-0.9328234	-2.0693941
H	-3.6145026	0.6917646	-3.2615011
H	-3.8956206	1.1060576	-1.5324111
S	-5.9851236	-0.7769724	-1.9755181
O	-6.3592586	0.1973316	-3.0240781
O	-6.5341696	-2.1519774	-1.9298451
C	-6.3664406	0.0035556	-0.3848881
C	-6.4963216	1.4007406	-0.3107411
C	-6.5239736	-0.7949724	0.7638849
C	-6.7604016	2.0002116	0.9327429
H	-6.4193696	2.0011466	-1.2294971
C	-6.7901896	-0.1796334	1.9942509
H	-6.4629366	-1.8903374	0.6791729
C	-6.9067296	1.2268606	2.1040569
H	-6.8667126	3.0960506	0.9910809
H	-6.9223756	-0.8057554	2.8924409
C	-7.1911506	1.8711426	3.4418229
H	-6.3730656	1.6704796	4.1668669
H	-7.3014906	2.9699516	3.3527939
H	-8.1239966	1.4706046	3.8929409
P	1.6793934	-2.0017224	-0.1412831
C	3.1055324	-1.7099354	1.0134349
C	2.4172374	-3.2088654	-1.3522451
C	0.5708394	-3.1289024	0.8465159
C	4.0422544	-0.7475494	0.5614389
C	3.3226054	-2.3063124	2.2719539
C	3.4090824	-4.1309274	-0.9464181
C	1.9433014	-3.2446794	-2.6808591
C	0.1426174	-2.7705004	2.1480599
C	0.0495464	-4.3116264	0.2735589
C	5.1175454	-0.3289064	1.3631159
O	3.8176114	-0.3140764	-0.7231981
C	4.4093034	-1.9158764	3.0760849
H	2.6316204	-3.0827384	2.6331869
C	3.9112044	-5.0785324	-1.8532011
H	3.7928704	-4.1097354	0.0857469
C	2.4459604	-4.2001744	-3.5836301
H	1.2164954	-2.4917344	-3.0223101
C	-0.7622796	-3.5779404	2.8586529
H	0.5305624	-1.8571054	2.6246619
C	-0.8635366	-5.1127784	0.9811189
H	0.3645024	-4.6148434	-0.7364401
C	5.2909104	-0.9176684	2.6273479
H	5.8119364	0.4411196	0.9962829
C	4.2601894	0.9064796	-1.1915141
H	4.5626814	-2.3919714	4.0569619
C	3.4275704	-5.1175084	-3.1740861
H	4.6853454	-5.7909454	-1.5252641
H	2.0733384	-4.2130184	-4.6203001
C	-1.2717936	-4.7520014	2.2764369
H	-1.0718646	-3.2840204	3.8744839
H	-1.2539546	-6.0309974	0.5138599
H	6.1335984	-0.5976124	3.2605089
C	3.3645714	2.0015016	-1.1894751
C	5.5487944	1.0048256	-1.7404131
H	3.8230384	-5.8603964	-3.8854551
H	-1.9822486	-5.3842884	2.8322859
P	1.6515374	1.8161876	-0.4408111
C	3.8333704	3.2238406	-1.7204921
C	5.9878374	2.2286866	-2.2699961
H	6.1859034	0.1078926	-1.7580181
C	2.0556044	2.0712566	1.3616749
C	0.8606884	3.4201686	-0.9302291
C	5.1307744	3.3402366	-2.2504341
H	3.1720344	4.1020126	-1.7325031
H	6.9970514	2.3085226	-2.7035721
C	2.9342344	3.1100926	1.7507229
C	1.4938304	1.2429796	2.3519149
C	0.7369044	3.7121546	-2.3105611
C	0.2967524	4.3010966	0.0166129
H	5.4634874	4.3062296	-2.6611151
C	3.2287484	3.3188546	3.1074179
H	3.3947904	3.7600626	0.9905749
C	1.7930714	1.4517926	3.7104589
H	0.8216914	0.4312996	2.0417739
C	0.0892864	4.8854676	-2.7268501
H	1.1406554	3.0039116	-3.0537501
C	-0.3627726	5.4694666	-0.4092271
H	0.3723554	4.0802136	1.0922899
C	2.6585994	2.4899286	4.0912639
H	3.9125984	4.1326146	3.3972899
H	1.3478274	0.7949856	4.4744499
C	-0.4613436	5.7679676	-1.7781931
H	0.0047674	5.1067606	-3.8027251
H	-0.7988296	6.1505766	0.3389599
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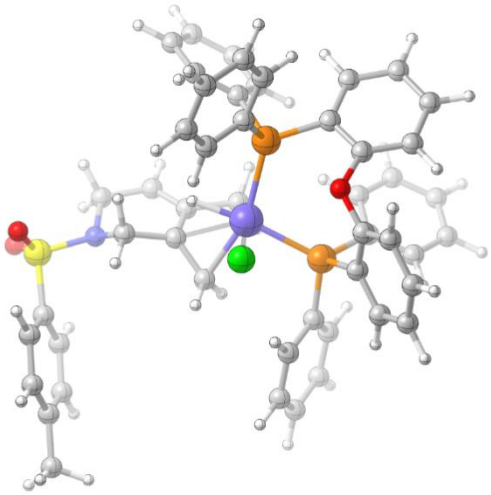
H	-0.9740136	6.6852716	-2.1088501

TS β-H-Elimination (TS2)



Rh	-0.1111180	-0.1285058	0.0496101
Cl	0.1149330	0.5884722	2.4309671
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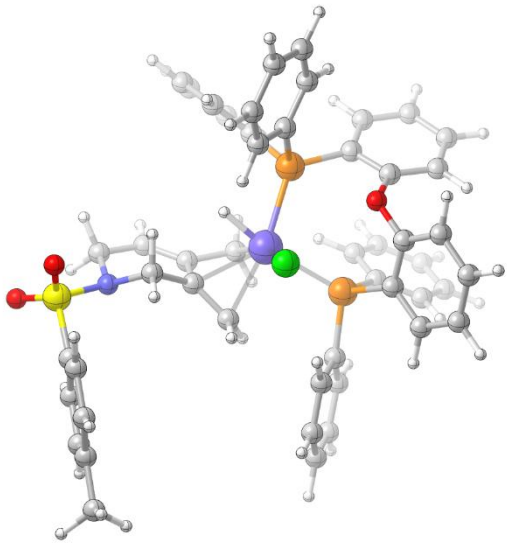
C	2.0231130	-0.5260558	-0.4779999
H	2.1770220	1.3380562	0.6646841
H	1.6948250	1.5426292	-1.1280859
C	1.6015520	-1.0415228	-1.8222959
C	2.3468280	-1.9582518	-2.4804149
C	0.2119650	-0.5219278	-2.0385529
H	-0.4459810	-1.2449968	-2.5568909
H	0.1880370	0.4493202	-2.5790939
H	0.9526820	-1.3078548	0.3882451
C	3.1453020	-1.3311308	0.1945591
H	1.9863750	-2.4210478	-3.4142729
C	3.6955760	-2.4060448	-1.9741529
H	4.4597730	-2.3415178	-2.7765809
H	3.6520800	-3.4862058	-1.6751719
N	4.1485570	-1.5537298	-0.8563629
H	2.7731870	-2.2976268	0.6107351
H	3.5945140	-0.7571168	1.0287611
S	5.7332110	-1.9061738	-0.2792469
O	5.6740420	-2.7671078	0.9290991
O	6.5059820	-2.3223198	-1.4721259
C	6.2969390	-0.2736448	0.2446731
C	6.5967910	-0.0573128	1.5972581
C	6.4947840	0.7336492	-0.7178539
C	7.0901110	1.1981902	1.9927751
H	6.4444290	-0.8724528	2.3206371
C	6.9856360	1.9777042	-0.3039419
H	6.2644260	0.5378442	-1.7756779
C	7.2913860	2.2334272	1.0557201
H	7.3244200	1.3751842	3.0551601
H	7.1398310	2.7724462	-1.0524779
C	7.8222210	3.5837912	1.4787631
H	7.1110130	4.3957102	1.2155211
H	8.0024500	3.6304582	2.5707301
H	8.7794110	3.8177302	0.9652961
P	-1.6905440	-1.9070178	0.3653251
C	-3.5149380	-1.5966228	0.1634441
C	-1.6405990	-2.7794648	2.0086951
C	-1.3774810	-3.3275618	-0.8020219
C	-4.0186450	-0.4714478	0.8625321
C	-4.4156950	-2.3398578	-0.6275559
C	-2.7021830	-3.6290008	2.3966261
C	-0.5191170	-2.6465118	2.8533011
C	-1.7687330	-3.2633108	-2.1613309
C	-0.6423250	-4.4551558	-0.3703819
C	-5.3489130	-0.0427168	0.7111381
O	-3.1203260	0.1122392	1.7224401
C	-5.7568540	-1.9387478	-0.7665309
H	-4.0664520	-3.2442998	-1.1471789
C	-2.6359550	-4.3420228	3.6045411
H	-3.5877290	-3.7365708	1.7506451
C	-0.4559830	-3.3666688	4.0607491
H	0.2813090	-1.9389528	2.5884111
C	-1.4499350	-4.3016988	-3.0539399
H	-2.3437480	-2.4005928	-2.5309239
C	-0.3157230	-5.4878098	-1.2663679
H	-0.3247290	-4.5321328	0.6806571
C	-6.2132750	-0.7808798	-0.1139549
H	-5.7004230	0.8526752	1.2445461
C	-3.1938040	1.4482782	2.0697351
H	-6.4429330	-2.5320838	-1.3906669
C	-1.5097010	-4.2148908	4.4384841
H	-3.4699210	-5.0008338	3.8956171
H	0.4221940	-3.2482858	4.7152641
C	-0.7202120	-5.4178238	-2.6102249
H	-1.7739740	-4.2338188	-4.1049039
H	0.2560400	-6.3575448	-0.9051379
H	-7.2578090	-0.4521368	-0.2338439
C	-2.4579910	2.3890382	1.3125691
C	-3.9198190	1.8224672	3.2114541
H	-1.4588190	-4.7732598	5.3871501
H	-0.4687540	-6.2306178	-3.3099329
P	-1.4842090	1.8106692	-0.1747799
C	-2.5092360	3.7390132	1.7231131
C	-3.9532220	3.1711312	3.6010261
H	-4.4375210	1.0422172	3.7893101
C	-2.7958830	1.9073642	-1.4966369
C	-0.4320460	3.2989232	-0.5296879
C	-3.2536260	4.1298122	2.8502991
H	-1.9426330	4.4984532	1.1639801
H	-4.5206810	3.4690992	4.4967011
C	-3.6789480	3.0098062	-1.5762959
C	-2.9197790	0.8653682	-2.4375229
C	0.4786360	3.7227372	0.4693301
C	-0.4379520	3.9526852	-1.7800139
H	-3.2725580	5.1898962	3.1478821
C	-4.6540870	3.0691652	-2.5846409
H	-3.6078710	3.8275732	-0.8422669
C	-3.8973600	0.9256342	-3.4473739
H	-2.2418860	0.0031762	-2.3679779
C	1.3399270	4.8033712	0.2243971
H	0.5125870	3.1825212	1.4314891
C	0.4401130	5.0265332	-2.0232879
H	-1.1317120	3.6286902	-2.5708289
C	-4.7650170	2.0271852	-3.5240439
H	-5.3350800	3.9339212	-2.6346689
H	-3.9820510	0.1034022	-4.1755189
C	1.3233690	5.4597582	-1.0213819
H	2.0372550	5.1304232	1.0123681
H	0.4260540	5.5278742	-3.0043689
H	-5.5324170	2.0740192	-4.3132119
H	2.0038780	6.3052022	-1.2112029

Intermediate 3 (I3)



Rh	-0.0754714	-0.3166610	0.0247812
Cl	0.2413576	0.4166860	2.3884252
C	1.8160526	0.8438550	-0.3819938
C	2.0890266	-0.5216340	-0.5689818
H	2.1995366	1.3498400	0.5155782
H	1.5658096	1.4827000	-1.2413808
C	1.6392946	-1.1961060	-1.8180558
C	2.3500276	-2.2275650	-2.3365668
C	0.2400626	-0.7354080	-2.0620448
H	-0.3940144	-1.4891460	-2.5637918
H	0.1799166	0.2319850	-2.6061648
H	0.4990116	-1.7214460	0.4323832
C	3.0931956	-1.3185370	0.2547762
H	1.9576856	-2.8217410	-3.1785658
C	3.6748406	-2.6608830	-1.7609928
H	4.4619376	-2.6982560	-2.5435978
H	3.5849576	-3.7073500	-1.3669418
N	4.1301256	-1.7281900	-0.7101088
H	2.6203866	-2.1996170	0.7467782
H	3.5474376	-0.6931320	1.0479752
S	5.6562576	-2.1137340	-0.0190348
O	5.4873366	-2.8284030	1.2714822
O	6.4526326	-2.7077330	-1.1178578
C	6.3119636	-0.4731480	0.3538572
C	6.5349896	-0.1134490	1.6906092
C	6.6530306	0.3924450	-0.7018008
C	7.0963916	1.1440840	1.9730032
H	6.2711576	-0.8215560	2.4905742
C	7.2104686	1.6408570	-0.4004098
H	6.4814276	0.0838930	-1.7438278
C	7.4420576	2.0396920	0.9392512
H	7.2704946	1.4335910	3.0222372
H	7.4773566	2.3249350	-1.2229828
C	8.0527956	3.3891410	1.2403792
H	7.4617946	4.2106790	0.7825092
H	8.1133946	3.5784020	2.3302032
H	9.0811036	3.4649900	0.8256022
P	-1.8097634	-1.8832290	0.3069792
C	-3.5921924	-1.3787690	0.1236922
C	-1.8488404	-2.7725010	1.9411522
C	-1.6567094	-3.3083760	-0.8840678
C	-3.9830294	-0.2431420	0.8739032
C	-4.5665564	-2.0086160	-0.6787298
C	-2.9809744	-3.5461630	2.2875302
C	-0.7447304	-2.7314630	2.8171272
C	-2.0527464	-3.1849180	-2.2374488
C	-1.0456854	-4.5132820	-0.4703068
C	-5.2727024	0.3059780	0.7637842
O	-3.0260024	0.2255480	1.7404902
C	-5.8683864	-1.4856840	-0.7780768
H	-4.3088744	-2.9205380	-1.2364988
C	-3.0009594	-4.2772510	3.4859492
H	-3.8537784	-3.5813410	1.6167602
C	-0.7703584	-3.4679060	4.0162142
H	0.1132686	-2.0820150	2.5840322
C	-1.8654154	-4.2451110	-3.1418798
H	-2.5242874	-2.2563670	-2.5934528
C	-0.8491144	-5.5677900	-1.3786648
H	-0.7218894	-4.6328850	0.5747682
C	-6.2108584	-0.3193620	-0.0731668
H	-5.5359624	1.2054640	1.3393152
C	-2.9913044	1.5536430	2.1236912
H	-6.6129104	-1.9910230	-1.4124518
C	-1.8928484	-4.2418230	4.3526152
H	-3.8882524	-4.8774860	3.7439142
H	0.0952486	-3.4214580	4.6959522
C	-1.2621314	-5.4406430	-2.7157198
H	-2.1901404	-4.1306640	-4.1884878
H	-0.3717334	-6.4984500	-1.0328298
H	-7.2238924	0.1042690	-0.1610858
C	-2.2407504	2.4652840	1.3467422
C	-3.6415134	1.9417720	3.3055462
H	-1.9096224	-4.8138990	5.2942962
H	-1.1128544	-6.2702010	-3.4249208
P	-1.3372554	1.8470410	-0.1703958
C	-2.2087984	3.8101530	1.7781592
C	-3.5860134	3.2826310	3.7176982
H	-4.1740624	1.1781630	3.8919832
C	-2.6592944	2.0350390	-1.4732018
C	-0.2307344	3.2960730	-0.5247998
C	-2.8785384	4.2182120	2.9452092
H	-1.6355574	4.5519190	1.2028852
H	-4.0933384	3.5932890	4.6445772
C	-3.5320534	3.1479810	-1.4941778
C	-2.7852074	1.0510230	-2.4755938
C	0.6995696	3.6873190	0.4697752
C	-0.2150804	3.9494990	-1.7755418
H	-2.8329724	5.2736790	3.2560552
C	-4.5001324	3.2748160	-2.5032518
H	-3.4576024	3.9209680	-0.7133928
C	-3.7539674	1.1805850	-3.4876668
H	-2.1156014	0.1789690	-2.4552938
C	1.6022976	4.7326970	0.2205692
H	0.7149126	3.1526990	1.4349522
C	0.7024776	4.9884660	-2.0232488
H	-0.9247704	3.6528040	-2.5630068
C	-4.6124544	2.2919340	-3.5041138
H	-5.1736704	4.1468610	-2.5066088
H	-3.8387834	0.4048700	-4.2652598
C	1.6068386	5.3875180	-1.0258218
H	2.3144816	5.0332070	1.0057642
H	0.7028436	5.4900560	-3.0042798
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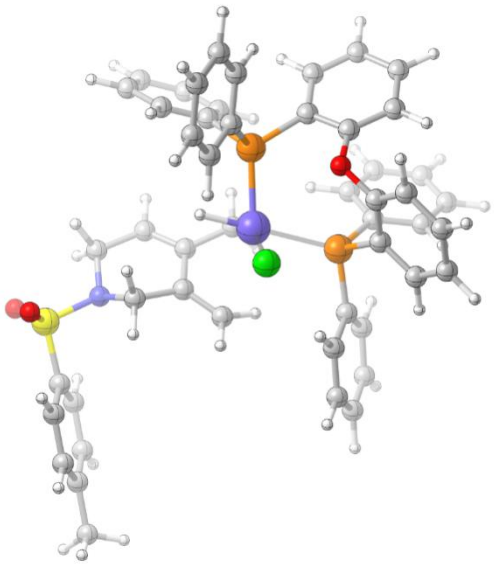
H	2.3191696	6.2053860	-1.2193098

TS Coordination Exchange (TS3)



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C	2.3698965	-0.0630780	-0.2257614
H	2.3935015	1.7105190	0.9910256
H	1.2853665	1.7820320	-0.5159794
C	1.7457085	-0.8318610	-1.3332234
C	2.3828775	-1.9309120	-1.8251814
C	0.3448735	-0.4254530	-1.6373684
H	-0.1536415	-1.1443270	-2.3124424
H	0.2810415	0.5911420	-2.0846224
H	0.4776825	-1.4544260	0.8247876
C	3.4605485	-0.7997420	0.5281106
H	1.8857605	-2.5639480	-2.5792254
C	3.7288785	-2.4020930	-1.3502854
H	4.4144355	-2.5899880	-2.2036214
H	3.6076705	-3.3909320	-0.8330684
N	4.3602505	-1.4030740	-0.4704744
H	3.0117985	-1.5687990	1.2036876
H	4.0410415	-0.0995620	1.1611976
S	5.9009045	-1.8661900	0.1365566
O	5.7870825	-2.4378290	1.5026126
O	6.5426895	-2.6337300	-0.9558154
C	6.7221485	-0.2649770	0.2875586
C	7.1354895	0.1726580	1.5539276
C	6.9979485	0.4855660	-0.8702624
C	7.8259475	1.3925610	1.6611886
H	6.9151375	-0.4471460	2.4361976
C	7.6848515	1.6988770	-0.7428294
H	6.6735875	0.1175160	-1.8550194
C	8.1108095	2.1745620	0.5219986
H	8.1515625	1.7426770	2.6544036
H	7.9009855	2.2935650	-1.6458294
C	8.8532085	3.4862770	0.6349046
H	8.2468705	4.3272880	0.2355356
H	9.1118315	3.7225900	1.6858236
H	9.7968045	3.4654270	0.0486116
P	-1.7460215	-1.9510350	0.2769286
C	-3.5269385	-1.6520920	-0.1803114
C	-1.9377595	-2.9017080	1.8664726
C	-1.2028945	-3.2941250	-0.8964434
C	-4.1892445	-0.6207990	0.5326226
C	-4.2627525	-2.3535740	-1.1593584
C	-2.9475835	-3.8881670	1.9566766
C	-1.0776485	-2.6863160	2.9614016
C	-1.4094595	-3.2006470	-2.2935854
C	-0.4631055	-4.3906460	-0.3988114
C	-5.5040415	-0.2352270	0.2155306
O	-3.4814165	-0.0831210	1.5793936
C	-5.5872915	-1.9951660	-1.4666894
H	-3.7981405	-3.1950260	-1.6929024
C	-3.0839685	-4.6569660	3.1233226
H	-3.6321385	-4.0607210	1.1111166
C	-1.2210855	-3.4598600	4.1285536
H	-0.3279445	-1.8800500	2.9154636
C	-0.9188385	-4.1923560	-3.1616734
H	-1.9666795	-2.3513080	-2.7165664
C	0.0353555	-5.3754900	-1.2687014
H	-0.2760125	-4.4790250	0.6822336
C	-6.1961865	-0.9225710	-0.7939124
H	-5.9788095	0.5876720	0.7699636
C	-3.6745305	1.2273190	1.9828436
H	-6.1396255	-2.5549010	-2.2372184
C	-2.2179795	-4.4454790	4.2123736
H	-3.8726615	-5.4241800	3.1820006
H	-0.5486325	-3.2775630	4.9818676
C	-0.1954875	-5.2842250	-2.6521484
H	-1.1011255	-4.1052090	-4.2447654
H	0.6064575	-6.2230190	-0.8574744
H	-7.2272345	-0.6249160	-1.0423304
C	-2.9417445	2.2567260	1.3475066
C	-4.5280025	1.4851670	3.0669596
H	-2.3271475	-5.0470910	5.1291536
H	0.1900915	-6.0602100	-3.3323034
P	-1.7625935	1.8149860	-0.0324514
C	-3.1293845	3.5745100	1.8188626
C	-4.6940405	2.8039890	3.5196076
H	-5.0410605	0.6397210	3.5493366
C	-2.8873555	1.9369190	-1.5162474
C	-0.7622585	3.3765350	-0.1665934
C	-4.0004905	3.8493330	2.8878946
H	-2.5675665	4.4001370	1.3567326
H	-5.3615055	3.0114690	4.3707656
C	-3.8651695	2.9525720	-1.6306754
C	-2.7556695	0.9979540	-2.5604664
C	0.0035445	3.7752000	0.9577406
C	-0.6589615	4.1142800	-1.3661194
H	-4.1238335	4.8869120	3.2356956
C	-4.6821625	3.0303710	-2.7701164
H	-3.9929105	3.6872870	-0.8203934
C	-3.5727785	1.0783500	-3.7028994
H	-2.0065285	0.1984420	-2.4694074
C	0.8275605	4.9090910	0.8833306
H	-0.0415475	3.1722340	1.8815946
C	0.1815115	5.2416360	-1.4367144
H	-1.2399475	3.8142750	-2.2516734
C	-4.5365515	2.0942940	-3.8106924
H	-5.4400125	3.8267830	-2.8448464
H	-3.4564525	0.3386980	-4.5109674
C	0.9195075	5.6464940	-0.3125834
H	1.4104865	5.2144880	1.7671656
H	0.2526055	5.8076770	-2.3793964
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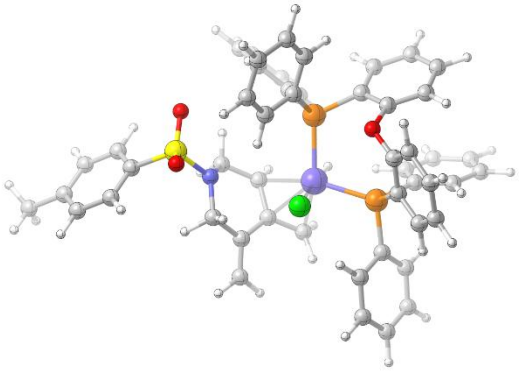
H	1.5709935	6.5332660	-0.3680604

Intermediate 4 (I4)



Cl	-0.1262087	1.4447456	1.8550000
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H	2.6195083	4.6582426	0.2916770
H	1.2031483	4.6173316	-0.9449720
C	1.0481433	1.9217356	-1.1778800
C	1.4578323	0.6001356	-1.5330610
C	-0.2302667	2.3788146	-1.6319160
H	-0.6136567	3.3279116	-1.2290070
H	-0.5605387	2.1393646	-2.6556100
H	-0.9976797	-0.0168574	-1.8451640
C	2.9231573	1.9945586	0.6237780
H	1.1577353	0.1987416	-2.5147180
C	2.8012503	0.0975276	-1.0604560
H	3.5743643	0.4301936	-1.8064830
H	2.8240953	-1.0092064	-1.0487220
N	3.1060643	0.5717106	0.2878270
H	2.5317733	2.0438116	1.6609930
H	3.8942893	2.5452776	0.5836580
S	4.3137713	-0.2487774	1.1546920
O	4.2362843	-1.6710134	0.7493520
O	4.1874763	0.1879696	2.5635960
C	5.8915263	0.3933796	0.5445770
C	6.5040913	1.4745946	1.2013820
C	6.4805893	-0.1842894	-0.5967470
C	7.7071683	1.9921426	0.6921730
H	6.0504833	1.8804456	2.1179970
C	7.6812103	0.3459436	-1.0887270
H	6.0083053	-1.0579034	-1.0705880
C	8.3131303	1.4450576	-0.4595400
H	8.1924463	2.8359316	1.2097480
H	8.1476033	-0.1110064	-1.9773780
C	9.6035533	2.0069986	-1.0108880
H	10.0233623	2.7930846	-0.3527640
H	10.3717913	1.2139306	-1.1300340
H	9.4478193	2.4558776	-2.0157940
Rh	-0.5547957	0.5425886	-0.4576460
P	-2.7872327	1.1159056	0.0389020
C	-3.5132507	0.8485226	1.7438070
C	-4.1240897	0.4105326	-1.0583340
C	-3.0728227	2.9491836	-0.1647490
C	-3.2994847	-0.3673214	2.4353860
C	-4.2807497	1.8386396	2.3978970
C	-5.4764407	0.3765586	-0.6462190
C	-3.7995477	-0.0385654	-2.3554770
C	-3.9524817	3.4736286	-1.1352670
C	-2.3378617	3.8405616	0.6554970
C	-3.7903057	-0.5763794	3.7347060
O	-2.5119857	-1.3483024	1.8663610
C	-4.7962377	1.6316276	3.6893120
H	-4.4665407	2.7985226	1.8943430
C	-6.4758227	-0.0929604	-1.5148900
H	-5.7531817	0.7207156	0.3622330
C	-4.8007197	-0.5034034	-3.2261760
H	-2.7447047	-0.0241674	-2.6753060
C	-4.1014097	4.8664376	-1.2814830
H	-4.5288427	2.7982226	-1.7850240
C	-2.5012347	5.2274896	0.5107940
H	-1.6218377	3.4291366	1.3894560
C	-4.5433727	0.4265846	4.3646600
H	-3.5567237	-1.5271554	4.2367640
C	-3.0128467	-2.2258254	0.9302090
H	-5.3866637	2.4261806	4.1717570
C	-6.1418587	-0.5327964	-2.8081660
H	-7.5242667	-0.1150234	-1.1766090
H	-4.5278657	-0.8500064	-4.2357660
C	-3.3824527	5.7466246	-0.4571030
H	-4.7902007	5.2605756	-2.0460200
H	-1.9273187	5.9094826	1.1587570
H	-4.9270097	0.2661666	5.3845540
C	-2.0751487	-2.6500844	-0.0406200
C	-4.3265087	-2.7219464	0.9557440
H	-6.9266247	-0.9018784	-3.4877680
H	-3.5050077	6.8359256	-0.5692180
P	-0.4374897	-1.7762634	0.0172590
C	-2.4758747	-3.6296674	-0.9700500
C	-4.7086937	-3.6816724	0.0028460
H	-5.0334977	-2.3627084	1.7184350
C	0.2936843	-2.4434204	1.5835310
C	0.5304653	-2.6791234	-1.2969250
C	-3.7857887	-4.1437384	-0.9508920
H	-1.7585607	-3.9927274	-1.7214720
H	-5.7368917	-4.0766784	0.0152180
C	-0.0292577	-3.7430774	2.0391360
C	1.2145633	-1.6610614	2.3070640
C	1.6554223	-3.4714504	-0.9780440
C	0.1658293	-2.5364914	-2.6575250
H	-4.0843007	-4.9062814	-1.6869620
C	0.5705713	-4.2503244	3.2029040
H	-0.7509277	-4.3621714	1.4826830
C	1.8214733	-2.1792184	3.4653870
H	1.4393763	-0.6365714	1.9773990
C	2.3881453	-4.1126714	-1.9949820
H	1.9777163	-3.5745974	0.0682600
C	0.8890923	-3.1903264	-3.6683700
H	-0.6925467	-1.9001234	-2.9270020
C	1.5000813	-3.4693774	3.9161140
H	0.3130243	-5.2634294	3.5522730
H	2.5562953	-1.5589554	4.0007290
C	2.0053133	-3.9821354	-3.3395820
H	3.2687253	-4.7168154	-1.7246010
H	0.5828503	-3.0746944	-4.7206720
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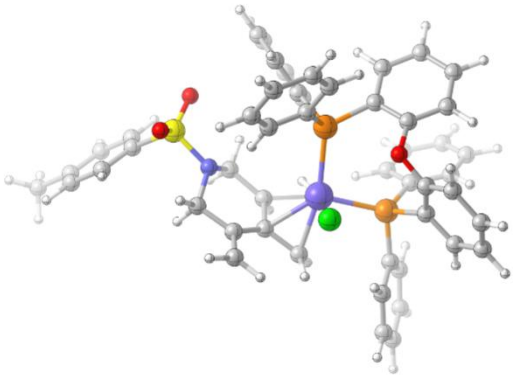
TS Reductive Elimination (TS4)



Cl	1.2353856	0.5608503	-2.8737301
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C	-1.9686794	1.9153183	-2.0171531
H	-2.4231314	2.1487763	-4.0944641
H	-0.7184814	2.7363403	-3.5607011
C	-1.0446544	2.0761823	-0.8816621
C	-1.3567034	1.5213483	0.4372199
C	0.2184446	2.7842363	-0.8840131
H	0.6008146	3.1678483	-1.8407171
H	0.4726006	3.4041353	-0.0052511
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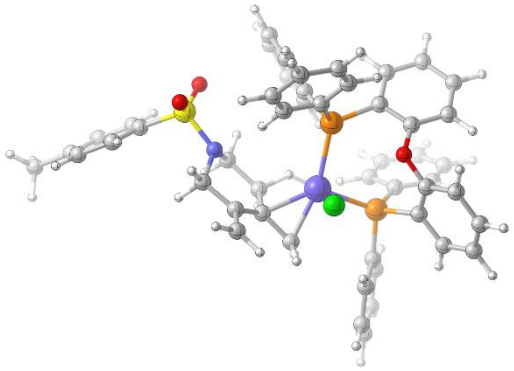
Product Complex (I5)



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H	0.7412211	-5.4088955	-3.7084281
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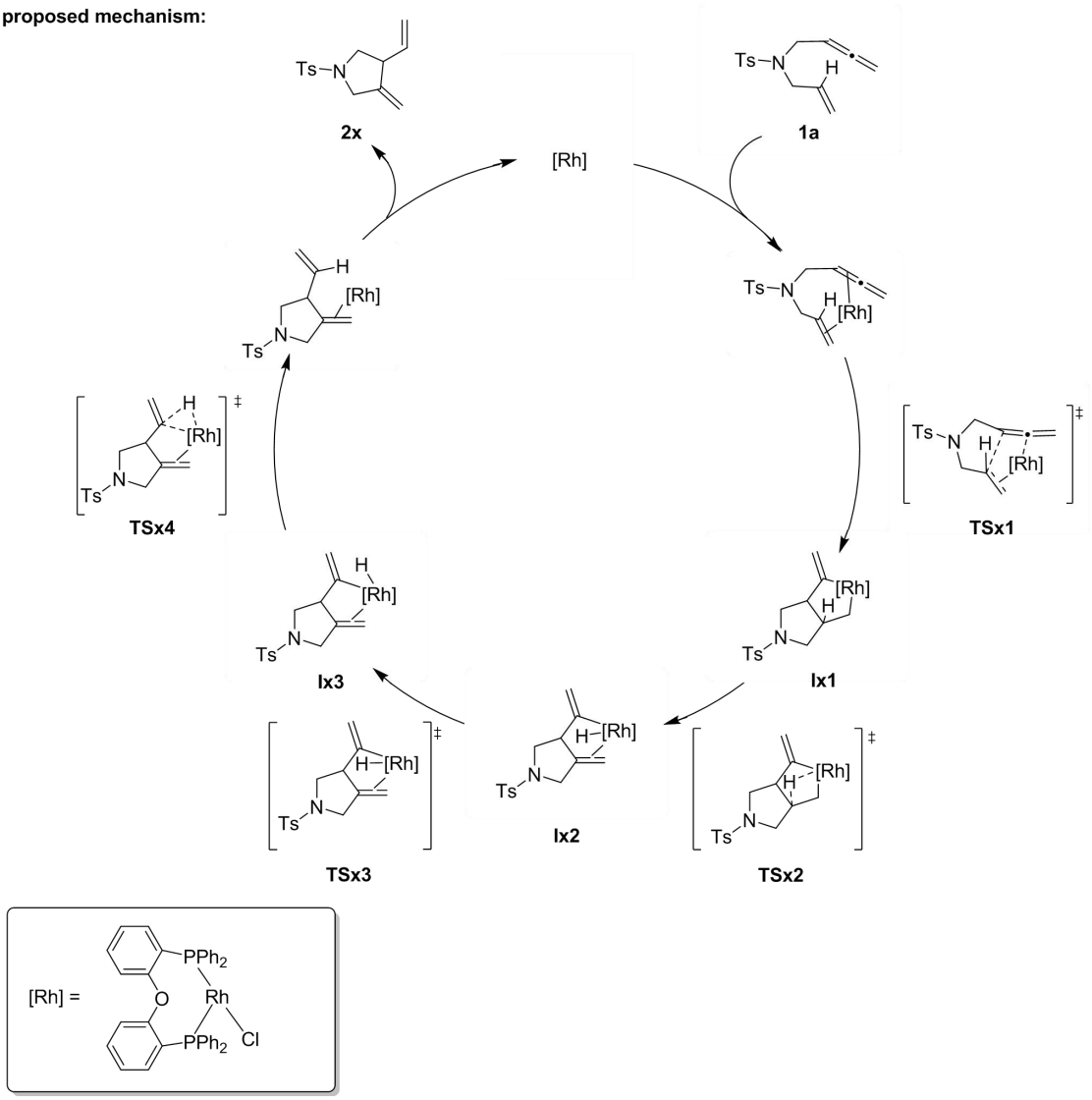
DFT calculations for five-membered ring diene

proposed mechanism:



Scheme S3 Proposed mechanism for Rh catalyzed cyclization of 1,6-allenenes to the (not observed) five-membered product.

To rationalize why just the 6-ring product was obtained, we performed DFT calculations for the formation of a five-ring product, which was not observed experimentally. For this we proposed the mechanism shown in scheme 1. Starting again from the monomeric rhodium complex the substrate 1a could coordinate by its vinyl moiety and its internal double bound of the allene. After the formation of the ring (TSx1) the intermediate Ix1 is formed. Ix1 was found as very low on the potential energetic surface. This seems to be induced by a stabilization over an additional coordination of the oxygen of the DPEphos backbone to the rhodium center, which has been shown to be possible for this ligand.[1] After this the β-hydride elimination would take place (TSx2) followed by a change of the conformation (TSx3). After the final reductive elimination (TSx4) the product 2x would be released. As the highest energetic barrier the β-hydride elimination (TSx2) was detected with a magnitude of approximately ΔG = 40 kcal/mol. Intermediate Ix1 would be the expected resting state of these catalytic cycle, but for the formation of this complex TSx1 must be passed with a barrier of ΔG = 27 kcal/mol. These barrier is 13 kcal/mol higher than the highest calculated energetic barrier in the catalytic cycle for the formation of the product 2a. An alternative transition state for the formation of the five ring product (TSy1) starting from the vinyl group of the substrate and the external double bond of the allene was investigated too. This TSy1 has a significantly higher energetic barrier of ΔG = 40 kcal/mol. After TSy1 would follow a conformation change which would lead again to intermediate Ix1. Considering all calculated data it seems reasonable that we never could observe the formation of the five ring product 2x in our experimental work.

[1] Chem. Eur. J. 2008, 14, 8383–8397

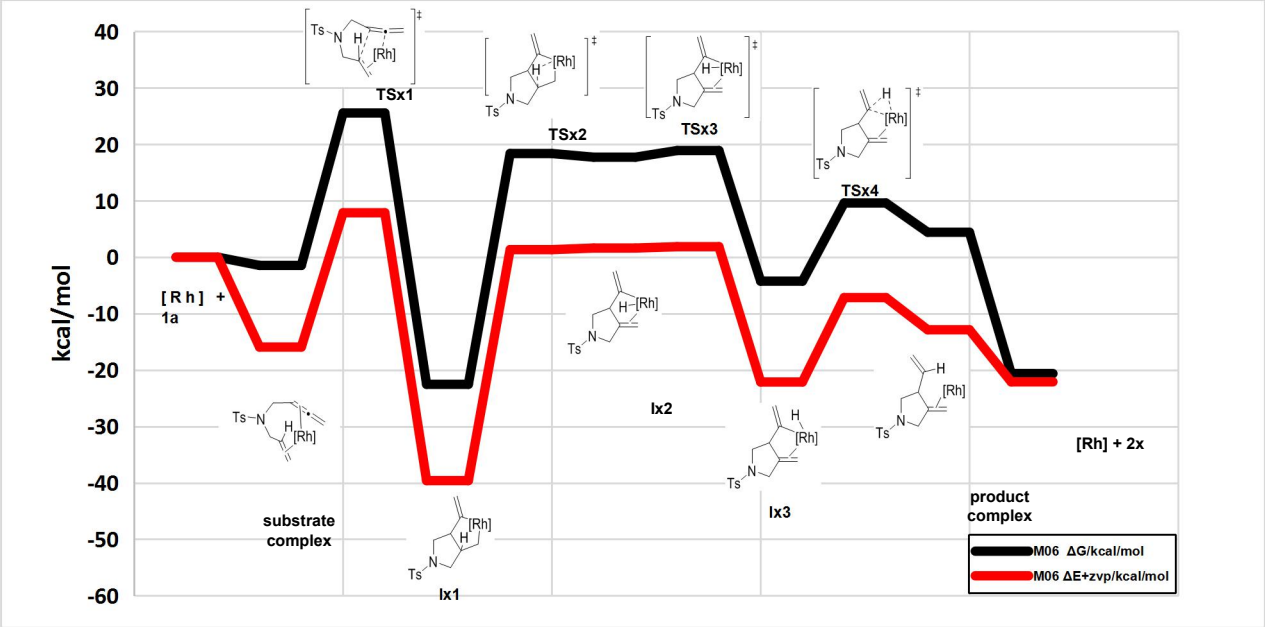
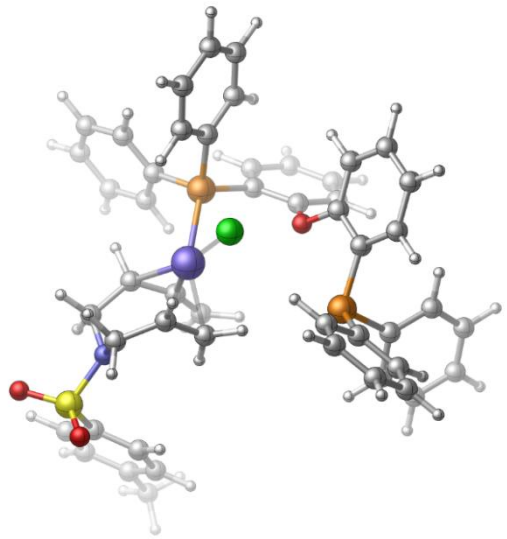


Figure S2 Computed catalytic cycle of the Rh catalyzed cyclization of 1,6-allenenes to the (unobserved) five-membered product. All energies(PCM-M06/def2SVP//BP86/def2SVP) given with respect to energies of the [ClRh(DPEphos)] complex and the substrate.

Table S4

	PCM-M06/def2SVP//BP86/def2SVP		
	ΔE/kcal/mol	**ΔE+zvp /kcal/mol**	**ΔG/kcal/mol**
[Rh] + 1a	0.00	0.00	0.00
Substrate complex	-17.82	-15.93	-1.46
TS-5-Ring formation (TSx1)	5.82	7.87	25.56
Intermediate 1 (Ix1)	-43.60	-39.61	-22.54
TS β-Hydride elimination (TSx2)	0.58	1.34	18.38
Intermediate 2 (Ix2)	0.34	1.62	17.73
TS conformation change (TSx3)	0.80	1.86	18.91
Intermediate 3 (Ix3)	-23.71	-22.12	-4.25
TS Reductive elimination (TSx4)	-7.56	-7.16	9.61
Product complex	-14.92	-12.87	4.42
[Rh] + 2x	-24.11	-22.10	-20.63
[Rh] + 1a	**0,00**	**0,00**	**0,00**
TS-5-Ring formation (TSy1)	20,88	21,82	39,23
Intermediate Y (Iy1)	-3,32	-0,21	17,08
Ts conformation change (TSy2)	-16,44	-13,68	4,38
Intermediate 1 (Ix1)	-43,60	-39,61	-22,54

Substrate Complex



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H	-5.5026982	-3.4357739	3.6673604
H	-1.7041862	-5.5207519	3.3463874
C	-3.7022342	-5.0203569	-3.8353646
H	-2.8799162	-3.4227069	-5.0700956
H	-4.4494722	-6.4280249	-2.3514196
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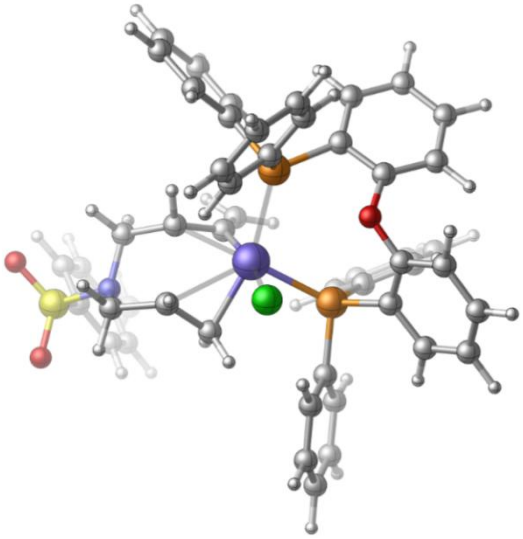
H	-3.9460282	-5.6689019	-4.6921026

TS-5-Ring Formation (TSx1)



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H	-1.9947618	1.2915278	-1.5791475
C	-1.0605698	-0.6715622	0.3764265
C	-1.4900938	-1.6587272	-0.6001435
C	-1.5397668	-0.3838912	1.6022965
H	-1.1053438	0.3923648	2.2490965
H	-2.3780408	-0.9690102	2.0285275
H	-0.6470518	-0.8951262	-3.3454645
C	-2.8010458	-1.0439252	-2.9437305
H	-0.9022188	-2.5927942	-0.6245645
C	-2.9776928	-1.9622952	-0.7810085
H	-3.4722028	-1.8688062	0.2116215
H	-3.1054848	-3.0138402	-1.1296985
N	-3.6013648	-1.0278252	-1.7209245
H	-2.7462718	-2.0662502	-3.3929125
H	-3.2702468	-0.3700872	-3.6914825
S	-5.3044638	-1.2242032	-1.9465915
O	-5.6397898	-0.4269532	-3.1486835
O	-5.6898608	-2.6548532	-1.8433285
C	-5.9496638	-0.3774252	-0.4905095
C	-6.5784598	-1.1260342	0.5145235
C	-5.8666928	1.0250178	-0.4147595
C	-7.1204308	-0.4546372	1.6243425
H	-6.6449128	-2.2196172	0.4113365
C	-6.4114978	1.6751348	0.6991985
H	-5.3869298	1.5915538	-1.2267155
C	-7.0459908	0.9498258	1.7377175
H	-7.6167828	-1.0368502	2.4179085
H	-6.3501578	2.7740358	0.7653705
C	-7.6337178	1.6739708	2.9270875
H	-8.4399398	2.3713678	2.6133705
H	-8.0641488	0.9693598	3.6655845
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Rh	0.3089922	-0.1906622	-0.9937085
P	1.8028622	-1.9686862	-0.0227525
C	2.9737332	-1.5038562	1.3421295
C	2.9207412	-2.8474272	-1.2202595
C	0.9131552	-3.4272382	0.7388455
C	3.8385422	-0.4269782	1.0355905
C	3.0637482	-2.0839462	2.6234295
C	4.1698022	-3.3706722	-0.8213315
C	2.4766582	-3.0578302	-2.5434025
C	0.1648262	-3.2590342	1.9303705
C	0.9249772	-4.7038222	0.1288975
C	4.7275192	0.1015298	1.9887405
O	3.7605272	-0.0028302	-0.2694665
C	3.9557612	-1.5737172	3.5843135
H	2.4291832	-2.9453922	2.8774165
C	4.9605262	-4.0936652	-1.7307955
H	4.5278962	-3.2177592	0.2087655
C	3.2645802	-3.7929002	-3.4466085
H	1.5229092	-2.6218132	-2.8733045
C	-0.5345208	-4.3379852	2.4978835
H	0.1161722	-2.2720652	2.4117305
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H	1.4984022	-4.8653072	-0.7958445
C	4.7747302	-0.4767252	3.2688545
H	5.3840782	0.9433178	1.7239845
C	4.0962552	1.2928188	-0.6075025
H	4.0082652	-2.0378892	4.5812645
C	4.5085512	-4.3085982	-3.0450045
H	5.9350882	-4.4937912	-1.4075955
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H	-1.0660998	-6.4451652	2.3260525
P	1.2643902	1.8851488	-0.3622795
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C	5.8015282	2.8904288	-1.2716565
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C	1.0250652	2.4662418	1.3897385
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H	2.7439612	4.4026078	-0.9855965
H	6.8463042	3.1179568	-1.5358895
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C	-0.2920238	2.6247338	1.8822305
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C	-0.1427038	4.4016508	-0.7763715
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C	1.8790582	3.1917758	3.5662785
H	3.1401472	2.6468108	1.8875585
C	-0.5176558	3.0799568	3.1924565
H	-1.1492438	2.3873168	1.2336795
C	0.3371512	4.3922928	-3.5415865
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C	-0.6150338	5.4567908	-1.5810305
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H	0.5341552	4.3797088	-4.6256405
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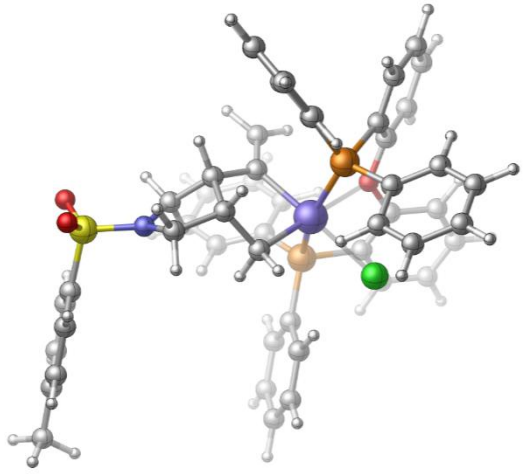
Intermediate 1 (Ix1)



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H	1.3489010	-0.2477151	1.1384861
C	-0.3785030	-0.6797921	-1.4543169
C	0.6657330	-1.7684401	-1.2030079
C	-0.7638450	-0.3570001	-2.7113499
H	-0.3435660	-0.8740311	-3.5972539
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C	2.0987600	-2.8029971	0.4974791
H	0.4627930	-2.6618421	-1.8361049
C	2.1272700	-1.3247541	-1.4684359
H	2.2589260	-0.2486311	-1.2178819
H	2.4418160	-1.4703551	-2.5193219
N	2.9136560	-2.1826241	-0.5661759
H	2.0795750	-3.9069691	0.3752831
H	2.5074310	-2.5809041	1.5095711
S	4.3968780	-2.8355741	-1.0062379
O	4.4532550	-4.2209901	-0.4810569
O	4.6126370	-2.5224081	-2.4394409
C	5.6130920	-1.8770781	-0.0682989
C	6.0210900	-2.3230101	1.1993351
C	6.1340730	-0.6915891	-0.6177039
C	6.9413000	-1.5547091	1.9315641
H	5.6323470	-3.2752271	1.5905341
C	7.0528770	0.0611739	0.1269741
H	5.8312220	-0.3855341	-1.6304999
C	7.4680130	-0.3505041	1.4155291
H	7.2665290	-1.9052441	2.9250691
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C	8.4453360	0.4838899	2.2121421
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Rh	-1.0932920	0.1490359	0.2737991
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C	-3.7167840	-1.6957501	1.9065481
C	-2.6951650	-3.1923681	-0.3495729
C	-3.9114530	0.6854769	-1.2075539
C	-5.0677050	-1.4316741	-1.4488799
C	-5.1155670	-1.5647931	2.0219301
C	-2.9581170	-2.0393751	3.0486131
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C	-2.8647140	-4.3177091	0.4888931
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H	-5.1688540	-2.4975671	-1.1921039
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C	-3.5952120	-2.2828041	4.2754061
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H	-2.2435610	-2.5302141	-2.3787549
C	-2.7257080	-5.6185461	-0.0274969
H	-3.1150430	-4.1827921	1.5517911
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H	-4.6027090	2.3042479	-2.4868209
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H	-6.7424500	-1.4634071	-2.8352329
C	-4.9920200	-2.1580651	4.3832581
H	-6.8416700	-1.6814301	3.3370601
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H	-2.0249720	-4.8427031	-3.2941529
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H	-6.4344290	0.9446739	-3.5093309
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H	-4.9296320	5.3770229	0.4202231
C	-0.1236640	3.1864309	-2.7535059
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H	1.9009410	4.5041499	-0.2501379
C	1.7915490	3.1143269	-4.2594159
H	-0.1848860	3.8290729	-4.8282419
H	3.6415420	2.3529849	-3.3958239
C	2.8440510	4.1765559	3.0316801
H	2.0382660	2.7127829	4.4288951
H	3.4428040	5.5196109	1.4224661
H	2.2326290	3.2919349	-5.2530379
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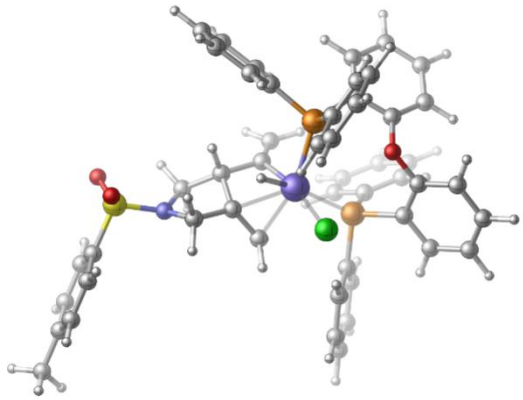
TS-β-H-Elimination (TSx2)



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H	-1.2922525	1.8287849	0.4586727
C	-0.4240385	-0.3907541	1.5317737
C	-1.8226495	-0.7705921	1.1042887
C	0.0809665	-0.2964931	2.7753777
H	-0.5619265	-0.4486091	3.6644267
H	1.1444315	-0.0859201	2.9691337
C	-3.1652455	-0.6947641	-0.8882493
H	-1.7925695	-1.8772741	0.9636477
C	-3.2439745	-0.4583201	1.6177237
H	-3.3392975	0.5899159	1.9793837
H	-3.6234985	-1.1478201	2.3950487
N	-4.0204915	-0.6499471	0.3478977
H	-3.0794855	-1.7341291	-1.2689263
H	-3.5818515	-0.0481941	-1.6872823
S	-5.4510465	-1.5648281	0.3528397
O	-5.3733725	-2.5499071	-0.7529883
O	-5.7053095	-1.9727801	1.7552157
C	-6.7256895	-0.3670231	-0.1005863
C	-7.1324405	-0.2636191	-1.4398293
C	-7.2990015	0.4431019	0.8964887
C	-8.1114875	0.6837199	-1.7841083
H	-6.6943025	-0.9341731	-2.1942113
C	-8.2746465	1.3809129	0.5335037
H	-6.9892675	0.3199019	1.9452317
C	-8.6953345	1.5228319	-0.8107903
H	-8.4353445	0.7665009	-2.8346263
H	-8.7290775	2.0147069	1.3131377
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H	-9.9906065	2.5080079	-2.2616153
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P	1.6588135	-2.1115211	-0.1940913
C	3.2433525	-1.9366191	0.7529137
C	2.2433045	-2.9575541	-1.7456603
C	0.7689405	-3.5266951	0.6409617
C	4.1283845	-0.9607971	0.2295247
C	3.6385795	-2.6457421	1.9040307
C	3.3817195	-3.7947811	-1.7123353
C	1.5088645	-2.8387651	-2.9441523
C	0.4962985	-3.5196531	2.0304527
C	0.2822415	-4.6076381	-0.1316973
C	5.3522435	-0.6650251	0.8528057
O	3.7007595	-0.3970671	-0.9476593
C	4.8636365	-2.3626681	2.5365497
H	2.9863985	-3.4326861	2.3102857
C	3.7784655	-4.5005751	-2.8600533
H	3.9619175	-3.9018801	-0.7823973
C	1.9080345	-3.5528851	-4.0890643
H	0.6511425	-2.1515571	-2.9953803
C	-0.2298545	-4.5664021	2.6250037
H	0.8270155	-2.6764711	2.6512567
C	-0.4542215	-5.6454701	0.4650447
H	0.4774525	-4.6433971	-1.2134803
C	5.7099825	-1.3696091	2.0155777
H	6.0204925	0.0951539	0.4218257
C	4.1235695	0.8405509	-1.3897423
H	5.1554955	-2.9239981	3.4374937
C	3.0406345	-4.3827831	-4.0519663
H	4.6685495	-5.1490361	-2.8204163
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C	5.2702165	0.9203699	-2.1990513
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H	-1.2859915	-6.4474561	2.3129437
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C	5.6753665	2.1637259	-2.7072713
H	5.8189245	-0.0046981	-2.4311303
C	2.4413055	2.2739639	1.6384527
C	0.9502505	3.4529829	-0.5357643
C	4.9263175	3.3145859	-2.4085463
H	3.1814545	4.1243309	-1.4107413
H	6.5717375	2.2302729	-3.3438043
C	3.8191475	2.4104719	1.9150417
C	1.5169015	2.4901769	2.6889957
C	0.3700675	3.5444399	-1.8240383
C	0.9111015	4.5833149	0.3104297
H	5.2343685	4.2954669	-2.8028443
C	4.2625605	2.7458069	3.2069777
H	4.5571175	2.2681629	1.1125527
C	1.9612375	2.8399979	3.9749307
H	0.4382015	2.3850089	2.5018347
C	-0.2392815	4.7379229	-2.2438343
H	0.4058805	2.6659519	-2.4933533
C	0.2902135	5.7734629	-0.1144543
H	1.3729005	4.5506409	1.3075247
C	3.3365535	2.9635419	4.2403707
H	5.3425095	2.8449389	3.4010777
H	1.2245005	3.0103869	4.7761577
C	-0.2875845	5.8558529	-1.3911783
H	-0.6824405	4.7908009	-3.2514383
H	0.2675935	6.6425499	0.5626477
H	3.6845815	3.2322809	5.2504887
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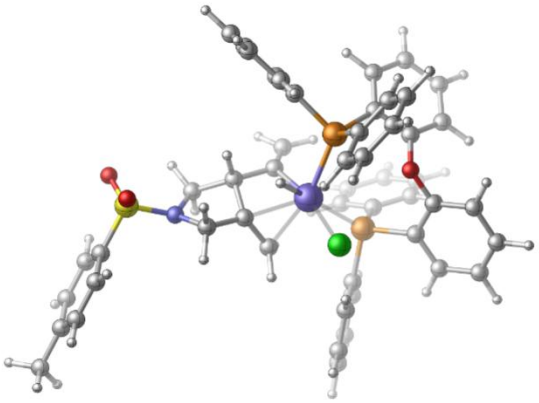
Intermediate 2 (Ix2)



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H	-1.2168528	1.8073007	0.5224183
C	-0.4285728	-0.4610263	1.5360303
C	-1.8387008	-0.8038563	1.1218003
C	0.0973342	-0.3529403	2.7699213
H	-0.5332658	-0.4775593	3.6720173
H	1.1669502	-0.1531473	2.9416463
C	-3.1935508	-0.6526703	-0.8530527
H	-1.8231068	-1.9033653	0.9308653
C	-3.2546798	-0.5095963	1.6621573
H	-3.3486038	0.5264257	2.0575973
H	-3.6283668	-1.2246673	2.4189223
N	-4.0423928	-0.6601633	0.3914543
H	-3.1019738	-1.6766603	-1.2717817
H	-3.6222328	0.0197177	-1.6239017
S	-5.4556598	-1.6016333	0.3755023
O	-5.3603408	-2.5699753	-0.7438647
O	-5.7080888	-2.0348173	1.7708343
C	-6.7482058	-0.4181423	-0.0655127
C	-7.1611658	-0.3111523	-1.4024497
C	-7.3294548	0.3767067	0.9392603
C	-8.1551248	0.6243497	-1.7366287
H	-6.7155158	-0.9697633	-2.1629267
C	-8.3199208	1.3026867	0.5864613
H	-7.0137298	0.2511017	1.9859423
C	-8.7475708	1.4478907	-0.7553677
H	-8.4837228	0.7100197	-2.7854527
H	-8.7805498	1.9244887	1.3721093
C	-9.8159508	2.4551697	-1.1148697
H	-9.4918958	3.4895637	-0.8700377
H	-10.0620608	2.4245687	-2.1945967
H	-10.7524708	2.2701787	-0.5466197
Rh	0.2738392	-0.2185573	-0.4165447
P	1.6874542	-2.1227633	-0.1997517
C	3.2408102	-1.8874953	0.7839343
C	2.3359592	-2.9173363	-1.7515277
C	0.8472972	-3.5881083	0.6013953
C	4.1103842	-0.8917363	0.2725653
C	3.6223962	-2.5703853	1.9550533
C	3.5190062	-3.6898613	-1.7109127
C	1.6086202	-2.8302833	-2.9570497
C	0.5061322	-3.5900273	1.9755803
C	0.4808322	-4.7082543	-0.1816057
C	5.3088562	-0.5548593	0.9232253
O	3.6943612	-0.3524783	-0.9194417
C	4.8218252	-2.2450603	2.6157853
H	2.9801832	-3.3692063	2.3540813
C	3.9678582	-4.3621753	-2.8595227
H	4.0931202	-3.7732743	-0.7748227
C	2.0607822	-3.5107733	-4.1027027
H	0.7129512	-2.1937343	-3.0129527
C	-0.1694118	-4.6829053	2.5460223
H	0.7419402	-2.7185223	2.6008843
C	-0.2053688	-5.7931753	0.3910313
H	0.7295412	-4.7385553	-1.2522447
C	5.6544202	-1.2357953	2.1037023
H	5.9664552	0.2192937	0.5009623
C	4.1051512	0.8823407	-1.3801347
H	5.1045002	-2.7859183	3.5320083
C	3.2381412	-4.2754973	-4.0590807
H	4.8922952	-4.9602353	-2.8144237
H	1.4880602	-3.4277723	-5.0400847
C	-0.5302558	-5.7882873	1.7573433
H	-0.4225208	-4.6614663	3.6182103
H	-0.4850458	-6.6499793	-0.2424237
H	6.5927152	-0.9781703	2.6201103
C	3.2956052	2.0106377	-1.1168207
C	5.2593552	0.9648187	-2.1781727
H	3.5908542	-4.8026183	-4.9602067
H	-1.0664058	-6.6400813	2.2050343
P	1.7462812	1.8601507	-0.0803397
C	3.7093392	3.2469487	-1.6631757
C	5.6466102	2.2044757	-2.7090357
H	5.8274422	0.0453327	-2.3842787
C	2.3906392	2.3232667	1.6080533
C	0.8859182	3.4505257	-0.5810837
C	4.8726222	3.3472617	-2.4441327
H	3.1036322	4.1465687	-1.4796587
H	6.5485962	2.2742687	-3.3372227
C	3.7603882	2.5390777	1.8753383
C	1.4630292	2.4868887	2.6651723
C	0.3241612	3.5255027	-1.8788627
C	0.8042532	4.5798777	0.2630893
H	5.1668712	4.3247097	-2.8570907
C	4.1927292	2.8996587	3.1642053
H	4.4997802	2.4399317	1.0675053
C	1.8954232	2.8613497	3.9482993
H	0.3906712	2.3198317	2.4867223
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H	0.3849202	2.6449857	-2.5435627
C	0.1627692	5.7544457	-0.1744097
H	1.2483522	4.5581057	1.2686313
C	3.2631162	3.0634997	4.2043563
H	5.2665082	3.0611837	3.3508003
H	1.1556222	2.9890637	4.7546263
C	-0.3943988	5.8215667	-1.4612127
H	-0.7348358	4.7442617	-3.3252787
H	0.1073942	6.6235397	0.5007933
H	3.6022612	3.3514197	5.2122053
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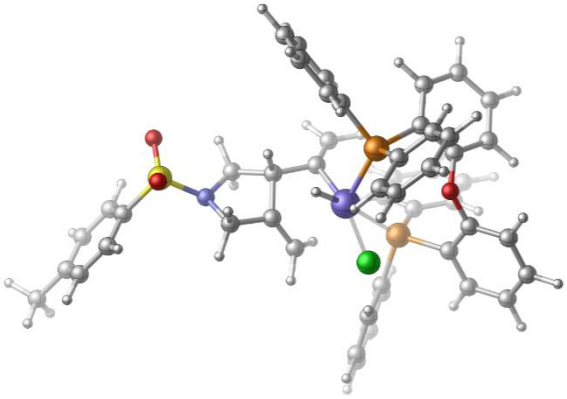
H	-0.4950288	-1.4683253	-0.9773077

TS Conformation Change (TSx3)



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H	-1.6372360	1.9341720	-1.6543215
H	-0.8863220	1.9042500	0.0630935
C	-0.4953920	-0.3502840	1.2981775
C	-1.9055970	-0.5884040	0.8210905
C	-0.0784610	-0.2312610	2.5744775
H	-0.7969440	-0.2605160	3.4172405
H	0.9844670	-0.1166780	2.8411775
C	-3.3485290	-0.3048810	-1.0779075
H	-1.9400620	-1.6744510	0.5661445
C	-3.2979690	-0.2960000	1.4264205
H	-3.3645740	0.7269450	1.8593785
H	-3.6424220	-1.0343770	2.1744865
N	-4.1461050	-0.3959200	0.1919585
H	-3.2854810	-1.2963360	-1.5753135
H	-3.7952930	0.4266280	-1.7821905
S	-5.5063970	-1.4219840	0.1892795
O	-5.4080650	-2.3286960	-0.9806115
O	-5.6695150	-1.9352140	1.5706045
C	-6.8796440	-0.2940960	-0.1346505
C	-7.3628490	-0.1512750	-1.4443265
C	-7.4534220	0.4199080	0.9330945
C	-8.4225870	0.7392190	-1.6866905
H	-6.9186930	-0.7473790	-2.2555395
C	-8.5098560	1.3020210	0.6713235
H	-7.0795220	0.2668090	1.9566615
C	-9.0110680	1.4817900	-0.6405565
H	-8.8064270	0.8531570	-2.7138075
H	-8.9643240	1.8609540	1.5062105
C	-10.1542940	2.4361060	-0.9001445
H	-10.4165260	2.4796280	-1.9755915
H	-11.0654640	2.1337280	-0.3406055
H	-9.9024240	3.4662040	-0.5688785
Rh	0.4117810	-0.2289050	-0.5590405
P	1.6168550	-2.1396440	-0.1688875
C	3.0786070	-1.9498710	0.9547205
C	2.3603340	-2.9907150	-1.6459745
C	0.6373570	-3.5542130	0.5707125
C	4.0637360	-1.0367140	0.5004225
C	3.2823430	-2.5920610	2.1917635
C	3.5173190	-3.7875930	-1.4938755
C	1.7251090	-2.9272290	-2.9037535
C	0.1362010	-3.5039640	1.8939845
C	0.3405300	-4.6938170	-0.2138195
C	5.2021690	-0.7412600	1.2688375
O	3.8324260	-0.5390640	-0.7573375
C	4.4193570	-2.3059910	2.9701435
H	2.5483310	-3.3283680	2.5503815
C	4.0335630	-4.5055300	-2.5854075
H	4.0178890	-3.8547730	-0.5152305
C	2.2434380	-3.6534360	-3.9914485
H	0.8477840	-2.2785800	-3.0423395
C	-0.6274080	-4.5632770	2.4142545
H	0.3166610	-2.6159290	2.5144135
C	-0.4335120	-5.7452430	0.3071845
H	0.7120960	-4.7664340	-1.2457905
C	5.3687540	-1.3776350	2.5110755
H	5.9530230	-0.0333670	0.8876765
C	4.3456450	0.6641710	-1.2013475
H	4.5614080	-2.8137330	3.9365215
C	3.3966350	-4.4408550	-3.8378025
H	4.9377330	-5.1214820	-2.4537105
H	1.7427830	-3.5889340	-4.9705885
C	-0.9182050	-5.6877710	1.6238085
H	-1.0054040	-4.4998250	3.4472945
H	-0.6560400	-6.6172140	-0.3282605
H	6.2589390	-1.1505030	3.1188705
C	3.5888710	1.8449240	-1.0218365
C	5.5601270	0.6609740	-1.9089235
H	3.8022440	-5.0032070	-4.6942625
H	-1.5240160	-6.5128510	2.0308455
P	1.9572830	1.8089140	-0.1094785
C	4.1174210	3.0411240	-1.5580225
C	6.0610680	1.8625460	-2.4324185
H	6.0852180	-0.2952680	-2.0521415
C	2.4957800	2.2894050	1.6121315
C	1.2264970	3.4317690	-0.7079625
C	5.3398920	3.0548120	-2.2499865
H	3.5543100	3.9786800	-1.4392995
H	7.0107620	1.8639870	-2.9902495
C	3.8492450	2.4618750	1.9767915
C	1.5001220	2.5119980	2.5940325
C	0.7533470	3.4965300	-2.0413115
C	1.1465350	4.5878710	0.1001355
H	5.7225480	4.0031340	-2.6584605
C	4.1989040	2.8365880	3.2865395
H	4.6418370	2.3174690	1.2283505
C	1.8505790	2.8991470	3.8983235
H	0.4378840	2.3815800	2.3394645
C	0.2144850	4.6917620	-2.5447895
H	0.8126520	2.5942780	-2.6767825
C	0.5963700	5.7795570	-0.4092155
H	1.5205630	4.5719240	1.1340465
C	3.2023330	3.0571930	4.2515345
H	5.2613790	2.9642630	3.5490265
H	1.0587280	3.0724730	4.6445235
C	0.1291270	5.8369410	-1.7319535
H	-0.1441370	4.7244980	-3.5863735
H	0.5412930	6.6696400	0.2381515
H	3.4771380	3.3552970	5.2759095
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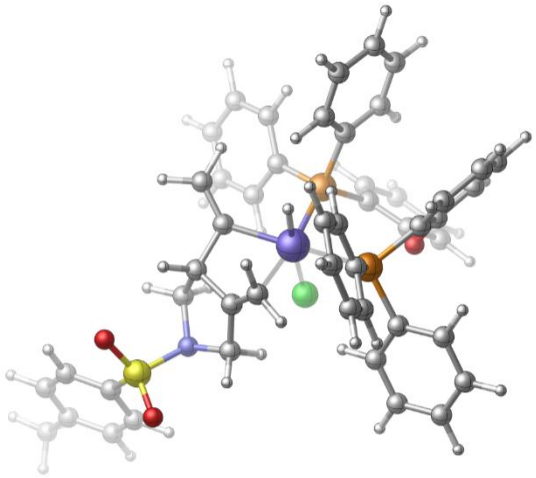
H	-0.4335840	-1.4085110	-1.1581685

Intermediate 3 (Ix3)



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H	0.4696223	-3.0878597	-0.9617627
H	0.3641693	-2.0209617	-2.4912747
C	1.0785853	0.7134143	-1.8534337
C	2.3108943	-0.1431277	-1.6985677
C	0.9549713	1.6431273	-2.8222417
H	1.8019303	1.8493623	-3.5057537
H	0.0526693	2.2551843	-2.9737367
C	2.7544093	-1.7634697	0.1324753
H	2.8099903	-0.3930457	-2.6644997
C	3.4038913	0.3533983	-0.7072767
H	2.9478873	0.9733293	0.0904333
H	4.2145653	0.9204953	-1.2021697
N	3.9260873	-0.8741347	-0.0637827
H	3.0659403	-2.8269117	0.1280623
H	2.3013073	-1.5064347	1.1166433
S	5.2679313	-1.6065457	-0.8775827
O	5.2995503	-3.0180247	-0.4237707
O	5.2935673	-1.2791247	-2.3295217
C	6.6465083	-0.7268907	-0.1115257
C	6.8513563	-0.8281957	1.2767963
C	7.5348973	-0.0121267	-0.9268867
C	7.9580673	-0.1877597	1.8468603
H	6.1438333	-1.3979677	1.8973403
C	8.6418033	0.6224473	-0.3362407
H	7.3501703	0.0376073	-2.0105297
C	8.8724583	0.5482673	1.0534373
H	8.1206903	-0.2593907	2.9350913
H	9.3424963	1.1876533	-0.9724997
C	10.0607943	1.2310033	1.6910463
H	10.7145943	0.4979263	2.2103743
H	10.6780793	1.7652163	0.9421333
H	9.7379783	1.9695913	2.4557903
Rh	-0.2787847	-0.1992457	-0.5806987
P	-2.0294157	-1.9058157	0.1034953
C	-3.7799127	-1.3359507	0.3413823
C	-1.7993367	-2.9736077	1.6086263
C	-2.2612207	-3.1558417	-1.2612917
C	-3.9399377	-0.3341657	1.3247863
C	-4.9210837	-1.7690717	-0.3627707
C	-2.8251777	-3.8266357	2.0786213
C	-0.5735317	-2.9174377	2.3036533
C	-2.6061697	-2.6875057	-2.5520207
C	-2.0446447	-4.5397447	-1.0828227
C	-5.1885027	0.2522523	1.5890353
O	-2.7849487	-0.0333107	2.0156083
C	-6.1810397	-1.1990637	-0.1030487
H	-4.8237957	-2.5540497	-1.1278407
C	-2.6145807	-4.6303147	3.2109073
H	-3.7954567	-3.8612447	1.5575343
C	-0.3677207	-3.7246237	3.4378963
H	0.1965903	-2.1967067	1.9848643
C	-2.7487327	-3.5801397	-3.6268107
H	-2.7626317	-1.6096097	-2.7174087
C	-2.1747837	-5.4311907	-2.1643077
H	-1.7677387	-4.9302227	-0.0919347
C	-6.3097297	-0.1877617	0.8644273
H	-5.2784617	1.0366673	2.3550063
C	-2.5597637	1.2456383	2.4855043
H	-7.0634657	-1.5461507	-0.6626997
C	-1.3821917	-4.5846387	3.8898093
H	-3.4190697	-5.2934857	3.5678893
H	0.5908313	-3.6668917	3.9778493
C	-2.5304117	-4.9570887	-3.4373787
H	-3.0238757	-3.1952957	-4.6219127
H	-1.9948177	-6.5064097	-2.0046687
H	-7.2944247	0.2632003	1.0657303
C	-1.9407527	2.1993443	1.6432743
C	-2.8918487	1.5350043	3.8191553
H	-1.2192087	-5.2140307	4.7795383
H	-2.6325707	-5.6564397	-4.2823207
P	-1.4011467	1.7884503	-0.1123477
C	-1.7197147	3.4856433	2.1883583
C	-2.6492287	2.8161743	4.3375573
H	-3.3305367	0.7353923	4.4347593
C	-2.9481907	2.0981863	-1.1032707
C	-0.3953827	3.3148303	-0.4747747
C	-2.0744227	3.7956073	3.5126913
H	-1.2456077	4.2606913	1.5704513
H	-2.9075267	3.0448703	5.3835043
C	-4.0115637	2.8802423	-0.5998987
C	-3.0263007	1.6117603	-2.4267037
C	0.8767973	3.4332793	0.1304143
C	-0.8642287	4.3486283	-1.3106527
H	-1.8822637	4.8079633	3.9008663
C	-5.1289637	3.1650793	-1.4042077
H	-3.9670867	3.2733663	0.4272143
C	-4.1393267	1.9063483	-3.2321757
H	-2.2008397	0.9981943	-2.8233867
C	1.6584743	4.5763633	-0.0939957
H	1.2349093	2.6203123	0.7850133
C	-0.0680787	5.4867793	-1.5428537
H	-1.8513817	4.2725943	-1.7906047
C	-5.1955407	2.6815253	-2.7220227
H	-5.9530267	3.7709843	-0.9948237
H	-4.1816187	1.5235873	-4.2643667
C	1.1920853	5.6043773	-0.9352397
H	2.6461863	4.6610853	0.3868993
H	-0.4417887	6.2847853	-2.2043267
H	-6.0716687	2.9065253	-3.3509337
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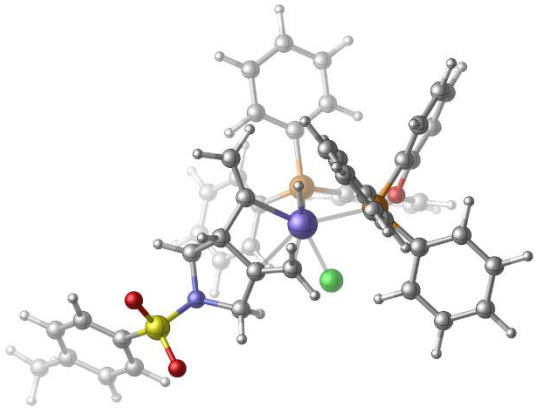
TS-Reductive Elimination (TSx4)



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H	0.0894499	-3.2371095	-1.0761286
H	0.2998679	-3.2332655	0.7785494
C	-0.6243871	-0.7053305	1.8266474
C	-1.8141411	-1.5147015	1.3739114
C	-0.3951641	-0.3493355	3.1102694
H	-1.1482351	-0.5874335	3.8854444
H	0.5109429	0.1781405	3.4452944
C	-2.4797801	-1.9074235	-0.9929926
H	-2.1092991	-2.3311305	2.0774674
C	-3.0832011	-0.7043185	0.9889074
H	-2.8128741	0.3339375	0.7061574
H	-3.8357861	-0.6722655	1.7982194
N	-3.6281891	-1.3865695	-0.2060556
H	-2.7466141	-2.8843035	-1.4462706
H	-2.2207961	-1.2136965	-1.8213386
S	-4.8979731	-2.5179495	0.1141514
O	-4.8353601	-3.5406365	-0.9578416
O	-4.9124791	-2.9086845	1.5491334
C	-6.3690401	-1.5096935	-0.1719606
C	-6.6952111	-1.1203555	-1.4841906
C	-7.1934761	-1.1726115	0.9103834
C	-7.8554831	-0.3669725	-1.7000596
H	-6.0462291	-1.4146805	-2.3226736
C	-8.3545541	-0.4156855	0.6738274
H	-6.9236321	-1.5132165	1.9212484
C	-8.7048551	0.0009755	-0.6274786
H	-8.1155821	-0.0599695	-2.7267496
H	-9.0056551	-0.1477645	1.5221034
C	-9.9567811	0.8080965	-0.8848136
H	-10.6648181	0.2531755	-1.5373516
H	-10.4870721	1.0544345	0.0561534
H	-9.7230191	1.7614645	-1.4049296
Rh	0.4297809	-0.6112245	0.0174694
P	2.8847699	-1.5604365	-0.1708176
C	4.2636869	-0.3953875	0.2452224
C	3.5305029	-2.3112545	-1.7478576
C	3.1340679	-2.9266005	1.0600234
C	4.2389589	0.8265265	-0.4728456
C	5.2882009	-0.5957335	1.1916574
C	4.9126269	-2.5530365	-1.9290446
C	2.6291079	-2.6630555	-2.7750466
C	2.9222449	-2.6501335	2.4333184
C	3.4222349	-4.2558205	0.6764274
C	5.2077359	1.8226025	-0.2607396
O	3.2117479	0.9110965	-1.3835536
C	6.2609109	0.3957815	1.4185554
H	5.3230179	-1.5381595	1.7599334
C	5.3801129	-3.1530365	-3.1097576
H	5.6291599	-2.2712835	-1.1413326
C	3.1030669	-3.2643275	-3.9558286
H	1.5605879	-2.4197795	-2.6698416
C	3.0236309	-3.6677345	3.3955144
H	2.6756779	-1.6256665	2.7580744
C	3.5086909	-5.2760775	1.6413144
H	3.5814769	-4.4980375	-0.3851976
C	6.2181059	1.5979105	0.6921664
H	5.1741889	2.7598525	-0.8358916
C	2.7284759	2.1066595	-1.8774436
H	7.0557099	0.2238855	2.1608714
C	4.4749589	-3.5134585	-4.1252716
H	6.4588749	-3.3386045	-3.2374866
H	2.3897769	-3.5271035	-4.7533096
C	3.3158159	-4.9867445	3.0023814
H	2.8625069	-3.4290805	4.4589074
H	3.7312109	-6.3067355	1.3214304
H	6.9813199	2.3741845	0.8611764
C	1.5129789	2.6248695	-1.3662026
C	3.4075169	2.7266365	-2.9421626
H	4.8429739	-3.9817155	-5.0524336
H	3.3857149	-5.7872045	3.7559034
P	0.5522259	1.7777005	0.0145504
C	1.0261139	3.8156055	-1.9525506
C	2.9013249	3.9091415	-3.5011256
H	4.3223519	2.2539855	-3.3303186
C	1.2044549	2.6633465	1.5198064
C	-1.1200031	2.5896705	-0.2182286
C	1.7102769	4.4572815	-2.9978996
H	0.0812979	4.2465205	-1.5909126
H	3.4320359	4.3929265	-4.3362336
C	2.4743929	3.2804335	1.5272964
C	0.4322439	2.6997635	2.7066894
C	-2.0157361	2.0138385	-1.1483896
C	-1.5047531	3.7728345	0.4538364
H	1.2976779	5.3827405	-3.4289116
C	2.9679559	3.9007145	2.6883074
H	3.0878789	3.2904315	0.6159684
C	0.9228699	3.3299755	3.8627904
H	-0.5660631	2.2398545	2.7253384
C	-3.2710921	2.5982905	-1.3850706
H	-1.7029341	1.1150935	-1.7048686
C	-2.7674491	4.3484385	0.2201894
H	-0.8186661	4.2594455	1.1623054
C	2.1954459	3.9276585	3.8609764
H	3.9634689	4.3718785	2.6683084
H	0.3014349	3.3526555	4.7724404
C	-3.6563401	3.7617725	-0.6957686
H	-3.9554491	2.1315665	-2.1108896
H	-3.0520761	5.2663925	0.7593584
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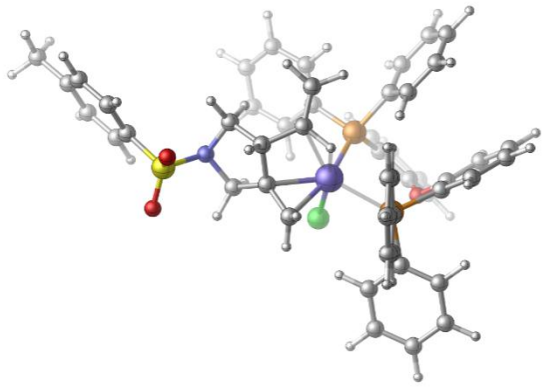
Product Complex



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H	-0.2912136	-2.9712660	-1.7003505
H	-0.1859336	-3.3081840	0.1236095
C	-0.7994036	-0.6822660	1.6602555
C	-1.9612986	-1.3559350	0.9721155
C	-0.8728186	0.1000660	2.7633435
H	-1.8470746	0.3038000	3.2395755
H	0.0143184	0.5528980	3.2295265
C	-2.5949486	-1.2139830	-1.4209835
H	-2.2622446	-2.3023980	1.4843745
C	-3.2298916	-0.4895630	0.7552355
H	-2.9603556	0.5849110	0.6692125
H	-3.9897106	-0.6020100	1.5515905
N	-3.7680826	-0.9323300	-0.5483095
H	-2.8532326	-1.9988670	-2.1586565
H	-2.3411666	-0.2919590	-1.9825585
S	-4.9344796	-2.2091840	-0.4390885
O	-4.9355386	-2.8870860	-1.7565135
O	-4.7778156	-2.9868680	0.8207855
C	-6.4690986	-1.2683040	-0.2896045
C	-6.9035516	-0.4758080	-1.3680875
C	-7.2402826	-1.3958230	0.8740025
C	-8.1210576	0.2068850	-1.2608175
H	-6.2892656	-0.4012690	-2.2778455
C	-8.4607586	-0.7032300	0.9628875
H	-6.8803906	-2.0392490	1.6909355
C	-8.9212986	0.1072680	-0.0957585
H	-8.4656096	0.8304010	-2.1025365
H	-9.0705376	-0.7997270	1.8762045
C	-10.2360236	0.8476580	-0.0051475
H	-10.9434236	0.5067280	-0.7914555
H	-10.7249786	0.6974970	0.9775325
H	-10.0955016	1.9396800	-0.1533375
Rh	0.4454524	-0.6695410	-0.3216845
P	2.7731044	-1.6121320	-0.1599995
C	4.1549264	-0.5080350	0.4065625
C	3.5426684	-2.3930670	-1.6645645
C	2.8346684	-3.0023600	1.0751145
C	4.2696204	0.7182830	-0.2988895
C	5.0116704	-0.7246420	1.5052645
C	4.9370834	-2.6182620	-1.7379285
C	2.7261234	-2.7886400	-2.7450605
C	2.4675324	-2.7421120	2.4185945
C	3.1226344	-4.3359640	0.7066705
C	5.1754964	1.7153210	0.0981135
O	3.4483304	0.8174130	-1.4002245
C	5.9346184	0.2600440	1.9048545
H	4.9488194	-1.6734980	2.0606805
C	5.4997434	-3.2400240	-2.8648665
H	5.5887234	-2.3058070	-0.9066545
C	3.2933364	-3.4130450	-3.8709625
H	1.6491234	-2.5696890	-2.7200575
C	2.4140404	-3.7756830	3.3675175
H	2.2227674	-1.7143320	2.7336075
C	3.0535184	-5.3732470	1.6547495
H	3.4032214	-4.5678780	-0.3317965
C	6.0062904	1.4785100	1.2076025
H	5.2265074	2.6645880	-0.4554635
C	3.0258194	2.0286780	-1.9176785
H	6.5978244	0.0727570	2.7638795
C	4.6779144	-3.6419460	-3.9338845
H	6.5877094	-3.4103920	-2.9079345
H	2.6441764	-3.7103220	-4.7100365
C	2.7047094	-5.0988170	2.9874655
H	2.1341334	-3.5467660	4.4082935
H	3.2778724	-6.4063970	1.3441615
H	6.7197674	2.2562700	1.5229345
C	1.7775384	2.5575720	-1.5066805
C	3.7965364	2.6495720	-2.9146935
H	5.1199604	-4.1273500	-4.8189425
H	2.6534434	-5.9126540	3.7279985
P	0.8002364	1.6860510	-0.1680095
C	1.3450064	3.7549090	-2.1174275
C	3.3439494	3.8400320	-3.5057495
H	4.7396354	2.1751020	-3.2252345
C	1.6199334	2.4575130	1.3239475
C	-0.8392976	2.5550770	-0.2468095
C	2.1185104	4.3945650	-3.1019305
H	0.3763964	4.1899710	-1.8283825
H	3.9466994	4.3272070	-4.2883305
C	1.7200134	3.8608410	1.4704805
C	2.2072494	1.6313840	2.3027095
C	-1.5871426	2.4649310	-1.4478505
C	-1.4259076	3.1795310	0.8766305
H	1.7521494	5.3260290	-3.5612545
C	2.3695874	4.4175450	2.5842375
H	1.2898734	4.5268220	0.7059925
C	2.8630884	2.1868840	3.4162385
H	2.1675784	0.5394680	2.1725985
C	-2.8774266	3.0121800	-1.5237875
H	-1.1516346	1.9433100	-2.3162035
C	-2.7250246	3.7157610	0.7968235
H	-0.8707696	3.2473310	1.8240985
C	2.9397364	3.5816300	3.5622965
H	2.4356174	5.5127150	2.6860665
H	3.3228194	1.5242040	4.1660635
C	-3.4522486	3.6405830	-0.4024795
H	-3.4426396	2.9387830	-2.4666165
H	-3.1679046	4.1982970	1.6830805
H	3.4522204	4.0200070	4.4335255
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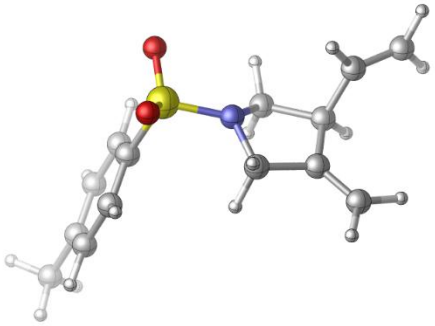
H	0.2751894	-1.1197410	1.4538105

5-Ring-Product (2x)



C	1.3180463	-0.0570828	1.4185662
C	2.4642763	-0.8927378	0.8604702
C	2.7795973	-0.4107128	-0.5660998
C	1.5085783	0.3999522	-0.9370178
H	0.4172943	-0.7019518	1.5856812
H	1.5591463	0.4410052	2.3794132
H	2.9110863	-1.2746758	-1.2508048
H	1.7009223	1.2223812	-1.6519158
H	0.7343353	-0.2806938	-1.3727728
N	1.1025623	0.9449392	0.3642022
C	3.0938623	-1.8887538	1.5076732
H	3.9145333	-2.4482208	1.0304522
H	2.8203283	-2.1753678	2.5363262
C	4.0290073	0.4431522	-0.5994578
C	5.1439923	0.1435502	-1.2901198
H	3.9832893	1.3712012	-0.0000128
H	6.0247583	0.8054152	-1.2745238
H	5.2191543	-0.7750568	-1.8979848
S	-0.1764677	2.0487552	0.4839612
O	-0.1911157	2.4908072	1.8944042
O	-0.0122927	2.9791962	-0.6524878
C	-1.6856977	1.0944152	0.1963572
C	-2.3590747	0.5162992	1.2865222
C	-2.1595557	0.9229762	-1.1184688
C	-3.5075237	-0.2569968	1.0487902
H	-1.9957747	0.6995692	2.3089782
C	-3.3074427	0.1476432	-1.3348208
H	-1.6415807	1.4199392	-1.9526418
C	-3.9993217	-0.4588288	-0.2595258
H	-4.0412867	-0.7062858	1.9023312
H	-3.6838997	0.0180872	-2.3631378
C	-5.2410207	-1.2824098	-0.5135988
H	-6.0504287	-0.6613438	-0.9541818
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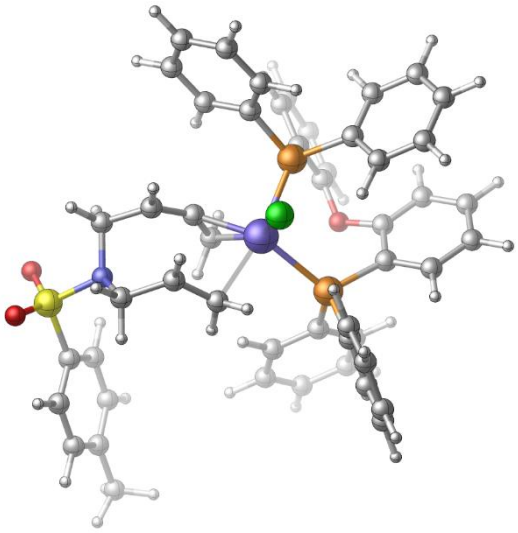
H	-5.6322127	-1.7342748	0.4190932

Alternative TS-5-Ring Formation (TSy1)



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H	-1.0477327	0.5632313	-2.5378694
H	-2.2847947	0.6355243	-1.1450484
C	-0.8245957	-2.0782877	-0.2440174
C	-1.5475167	-3.0216948	-0.9276404
C	-0.9284997	-1.1474307	0.8325556
H	-1.8568877	-0.5521627	0.9346936
H	-0.4691987	-1.3926227	1.8099966
H	-1.5979487	-1.6829077	-3.0595484
C	-3.5951937	-1.6877398	-2.0349404
H	-1.1045867	-3.4951547	-1.8190694
C	-2.9168257	-3.4665677	-0.4720464
H	-2.9572407	-3.7075688	0.6087316
H	-3.2561977	-4.3612678	-1.0452324
N	-3.8096617	-2.2915518	-0.7044964
H	-3.8668587	-2.4002717	-2.8494214
H	-4.2672617	-0.8060637	-2.1215964
S	-5.4712487	-2.5853038	-0.3171354
C	-6.0376887	-0.9371157	0.1545216
C	-6.9157607	-0.2440357	-0.6919904
C	-5.6473317	-0.4039127	1.3964416
C	-7.3924387	1.0166943	-0.2938734
H	-7.2277157	-0.7051907	-1.6413244
C	-6.1356937	0.8530383	1.7765976
H	-4.9829467	-0.9807947	2.0570766
C	-7.0107097	1.5879133	0.9390536
H	-8.0844087	1.5647283	-0.9540144
H	-5.8427857	1.2714133	2.7538676
C	-7.5104497	2.9511813	1.3583416
H	-6.7058357	3.7137923	1.2705686
H	-8.3578167	3.2888563	0.7296066
H	-7.8429257	2.9542423	2.4171626
O	-5.4445487	-3.4406278	0.8912966
O	-6.2315727	-2.9912697	-1.5267974
Rh	0.3211073	-0.5502057	-0.7700734
P	0.8271583	1.8305053	-0.4403204
C	2.5672083	2.2006313	0.0782446
C	-0.1314777	2.7119113	0.9019136
C	0.5965123	2.9960223	-1.8773844
C	3.0431473	1.5280233	1.2296136
C	3.4667943	3.0177403	-0.6354054
C	0.4668883	3.6842333	1.7350306
C	-1.5024137	2.4278403	1.0792536
C	0.8664163	2.4984163	-3.1743874
C	0.1649893	4.3343972	-1.7297304
C	4.3790113	1.6369543	1.6473356
O	2.0865263	0.8165623	1.9333146
C	4.8058683	3.1418463	-0.2243914
H	3.1137113	3.5517853	-1.5309834
C	-0.2867827	4.3518652	2.7164286
H	1.5347493	3.9251143	1.6162706
C	-2.2580587	3.0995953	2.0553106
H	-1.9844277	1.6672593	0.4502776
C	0.7230213	3.3349763	-4.2963264
H	1.1671603	1.4421883	-3.3069494
C	0.0180873	5.1622723	-2.8562354
H	-0.0608347	4.7342622	-0.7292364
C	5.2601543	2.4452273	0.9085656
H	4.7217643	1.0922273	2.5397436
C	2.4041153	-0.3292727	2.6378086
H	5.4970373	3.7800713	-0.7964134
C	-1.6526457	4.0631162	2.8800976
H	0.1999413	5.1053602	3.3566726
H	-3.3269097	2.8596652	2.1722506
C	0.2999913	4.6664892	-4.1418644
H	0.9352983	2.9335673	-5.3003714
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H	6.3106303	2.5312192	1.2280726
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C	2.5445653	-0.2340197	4.0332756
H	-2.2423157	4.5866823	3.6496176
H	0.1823723	5.3172773	-5.0233774
P	2.2331663	-1.6193588	0.1084776
C	2.7777773	-2.7156307	2.7492696
C	2.8121693	-1.3859327	4.7895796
H	2.4355983	0.7543933	4.5045436
C	3.9535393	-1.1760887	-0.4699384
C	2.1615493	-3.4300367	-0.2787864
C	2.9392973	-2.6264547	4.1431356
H	2.8748483	-3.6967257	2.2612736
H	2.9237713	-1.3113197	5.8827626
C	5.0734703	-1.7038238	0.2153886
C	4.1585753	-0.3724597	-1.6093574
C	1.2763423	-4.2901578	0.4151376
C	2.8943683	-3.9448147	-1.3718034
H	3.1612343	-3.5355547	4.7236316
C	6.3748573	-1.4356377	-0.2369694
H	4.9328813	-2.3317838	1.1085976
C	5.4660243	-0.1051167	-2.0559684
H	3.2877163	-0.0011457	-2.1701014
C	1.1651853	-5.6436498	0.0522876
H	0.6739233	-3.9097387	1.2538096
C	2.7680573	-5.2949968	-1.7398904
H	3.5617413	-3.2845547	-1.9442464
C	6.5746843	-0.6332657	-1.3752684
H	7.2373103	-1.8576657	0.3036946
H	5.6124223	0.5198463	-2.9511994
C	1.9120283	-6.1506438	-1.0251094
H	0.4832013	-6.3025318	0.6132036
H	3.3468793	-5.6792087	-2.5948244
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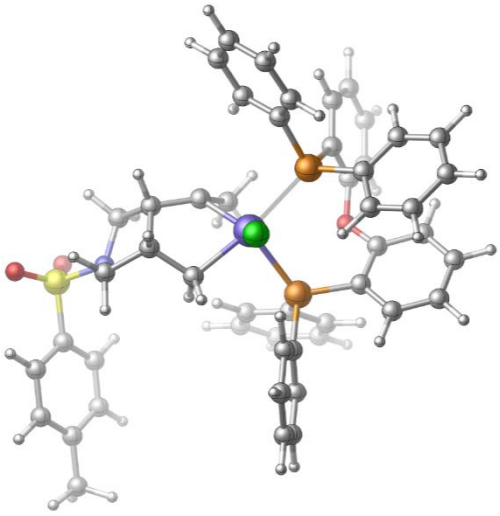
H	1.8220203	-7.2108438	-1.3108434

Intermediate Y



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H	1.5191998	0.1234301	-2.1450498
H	2.1988578	0.2386851	-0.4798178
C	0.3396918	2.3482821	0.2729162
C	1.5356878	3.0518331	-0.2737938
C	0.0064258	1.7104261	1.4784882
H	0.8176168	1.3176141	2.1268082
H	-0.9411242	1.8758871	2.0186342
H	1.5828108	2.5369191	-2.4283478
C	3.5424878	2.3337381	-1.4418808
H	1.1794198	4.0416871	-0.6392218
C	2.7810528	3.2612021	0.6416122
H	2.6149328	2.9497241	1.6909362
H	3.0793398	4.3348111	0.6500172
N	3.8176198	2.4029601	0.0108632
H	3.8679538	3.2648931	-1.9650718
H	4.0770108	1.4716371	-1.8935758
S	5.4276898	2.7930311	0.4658622
C	6.2851198	1.2397331	0.1374092
C	7.1358508	1.1422231	-0.9730838
C	6.1237688	0.1642611	1.0293682
C	7.8201478	-0.0639779	-1.2021768
H	7.2607408	2.0117061	-1.6358978
C	6.8129898	-1.0298449	0.7842902
H	5.4732198	0.2794341	1.9091412
C	7.6692528	-1.1675239	-0.3355988
H	8.4903468	-0.1472339	-2.0733698
H	6.6901488	-1.8769139	1.4792822
C	8.3993568	-2.4672989	-0.5844378
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H	9.0638858	-2.4023869	-1.4683538
H	9.0211008	-2.7541489	0.2902472
O	5.3802088	3.0168071	1.9295432
O	6.0010028	3.8213091	-0.4411088
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C	-2.9264872	-1.8912639	1.0899002
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C	-0.0106792	-3.0681389	2.3200802
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H	2.0561858	-0.5687959	1.2027502
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H	-0.2765432	-1.4814079	-3.0174898
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H	-4.8939702	-1.9475979	2.0077182
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C	1.8552998	-2.7350299	3.8535992
H	0.2828688	-4.2152269	4.1411752
H	3.2682128	-1.1771079	3.2880862
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H	0.7637958	-2.9514819	-4.7581278
H	2.4022558	-5.4981979	-1.6405108
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C	-4.2383742	1.0845771	4.3959042
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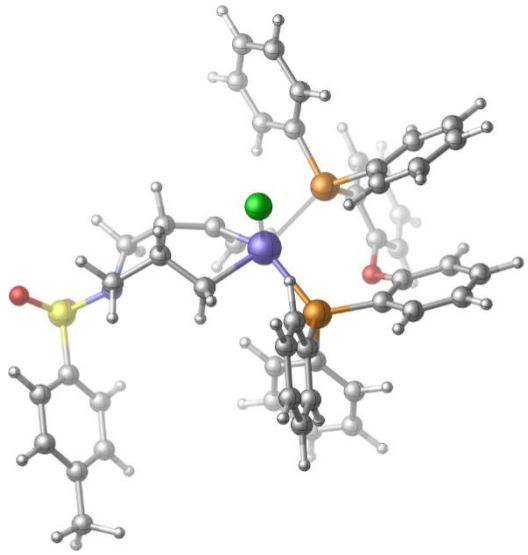
TS Conformation Change (TSy2)



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[1] a) K. T. Sylvester, P, J. Chirik, *J. Am. Chem. Soc.* **2009**, *131*, 8772–8774; b) H. Luo, S. Ma, *Eur. J. Org. Chem.* **2013**, 3041–3048; c) K.Yamashita, S. Hase, Y. Kayaki, T. Ikariya, *Org. Lett.* **2015**, *17*, 2334–2337; d) W. Song, J. C. Lynch, X. Shu, W. Tang, *Adv. Synth. Catal.* **2016**, *358*, 2007–2011; e) D. Zhu, J. Ma, K. Luo, H. Fu, L. Zhang, S. Zhu, *Angew. Chem. Int. Ed.* **2016**, *55*, 8452–8456;

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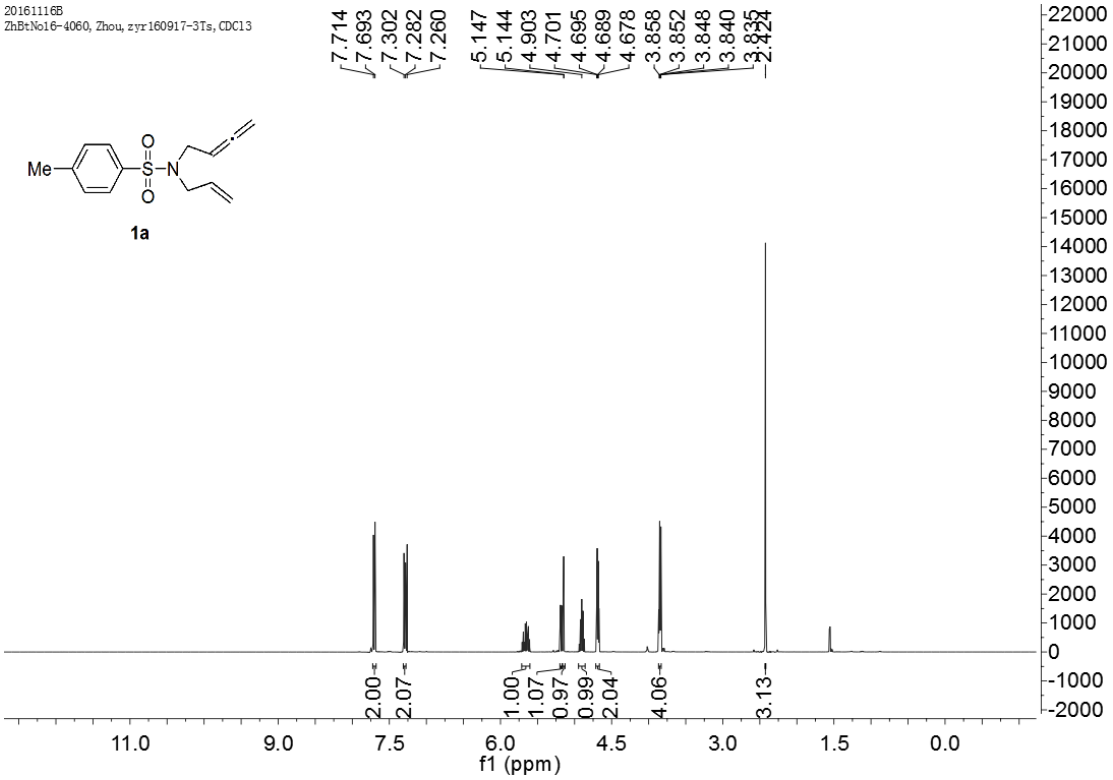
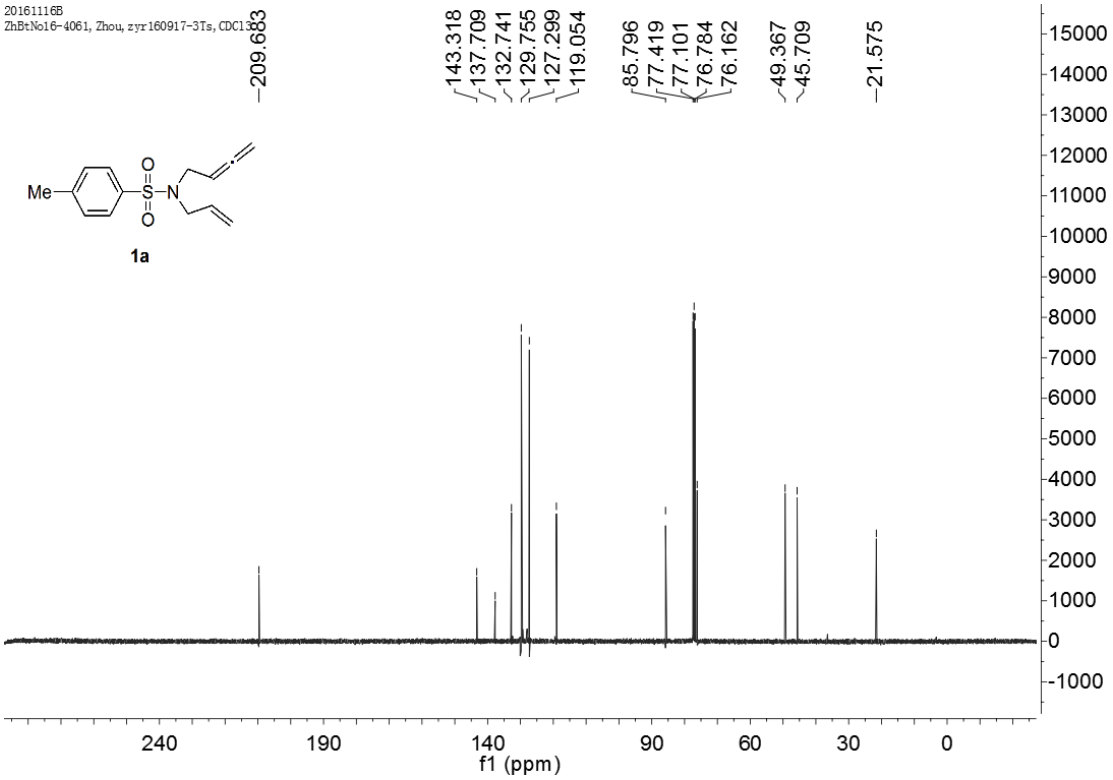
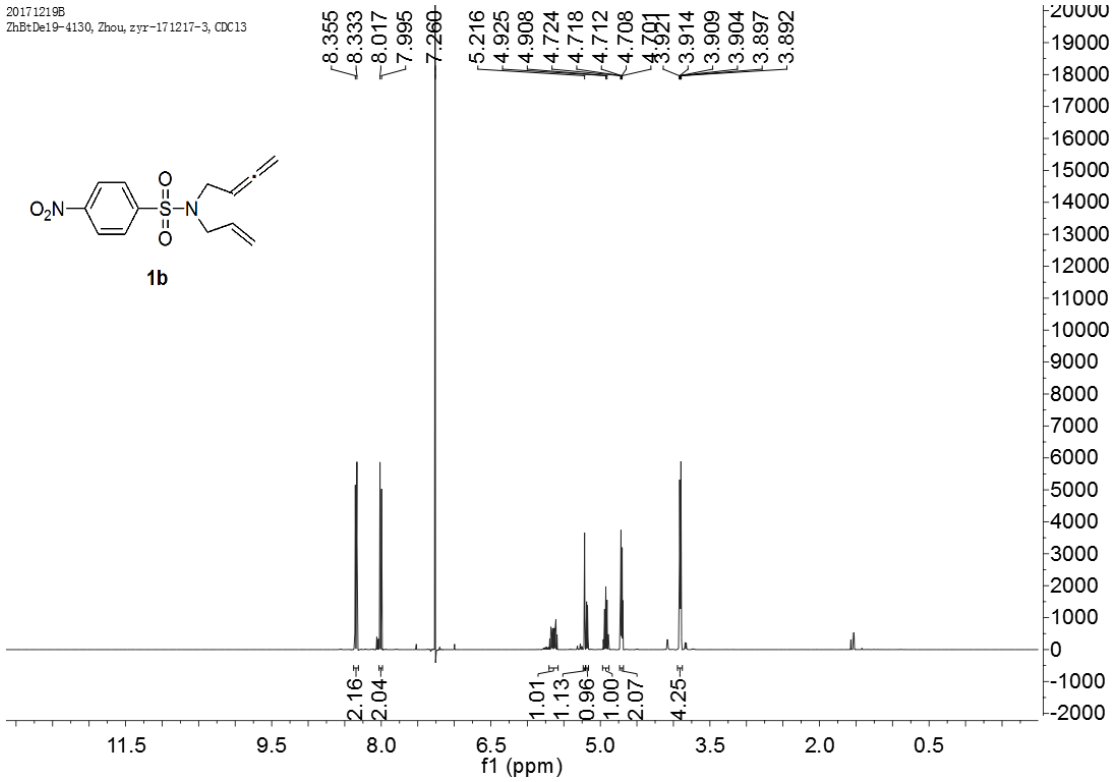
Copies of NMR spectra of the starting materials



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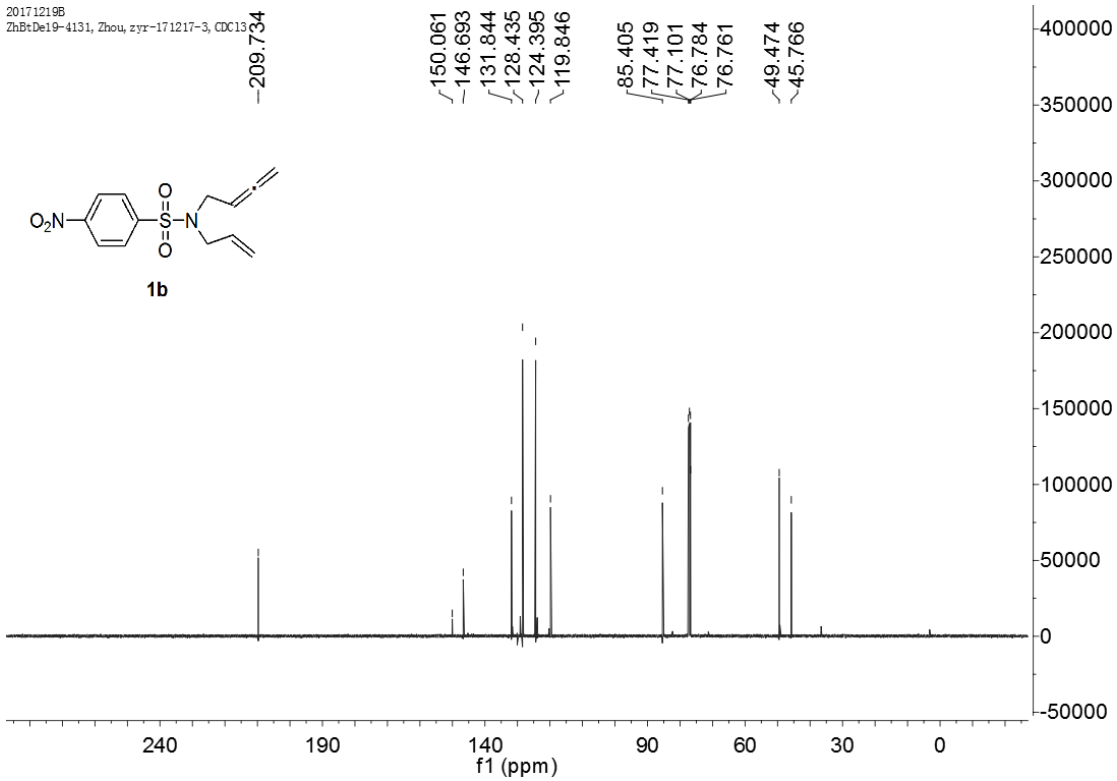
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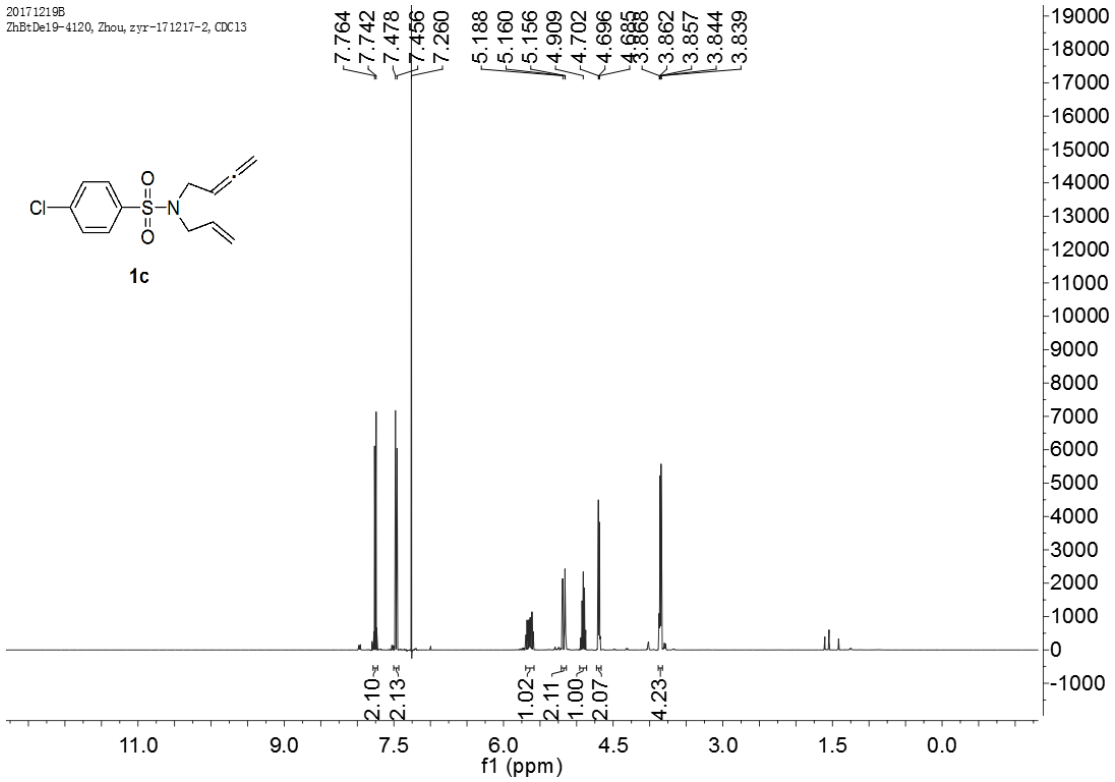
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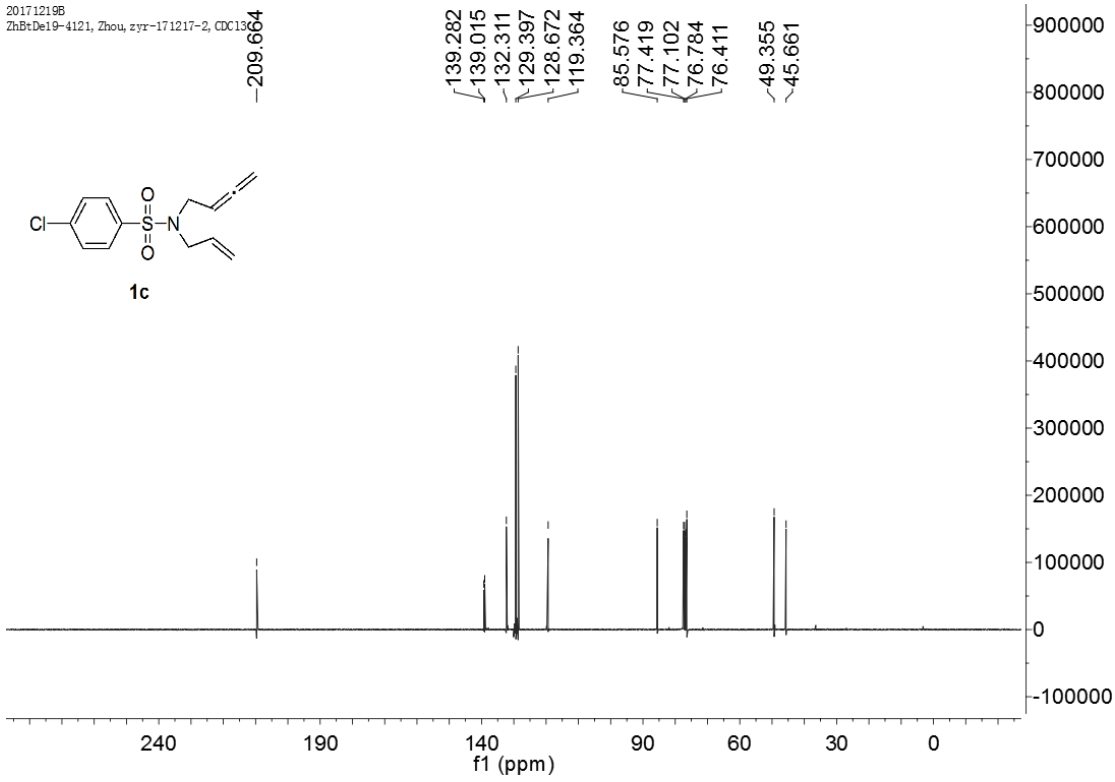
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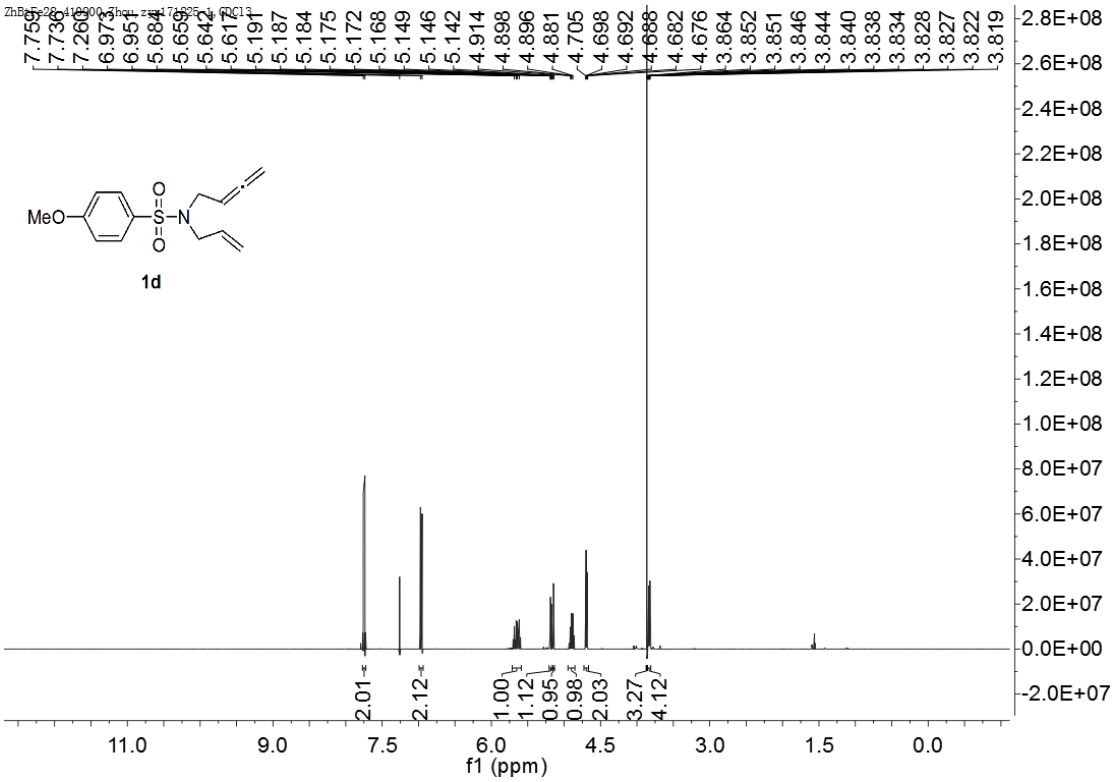
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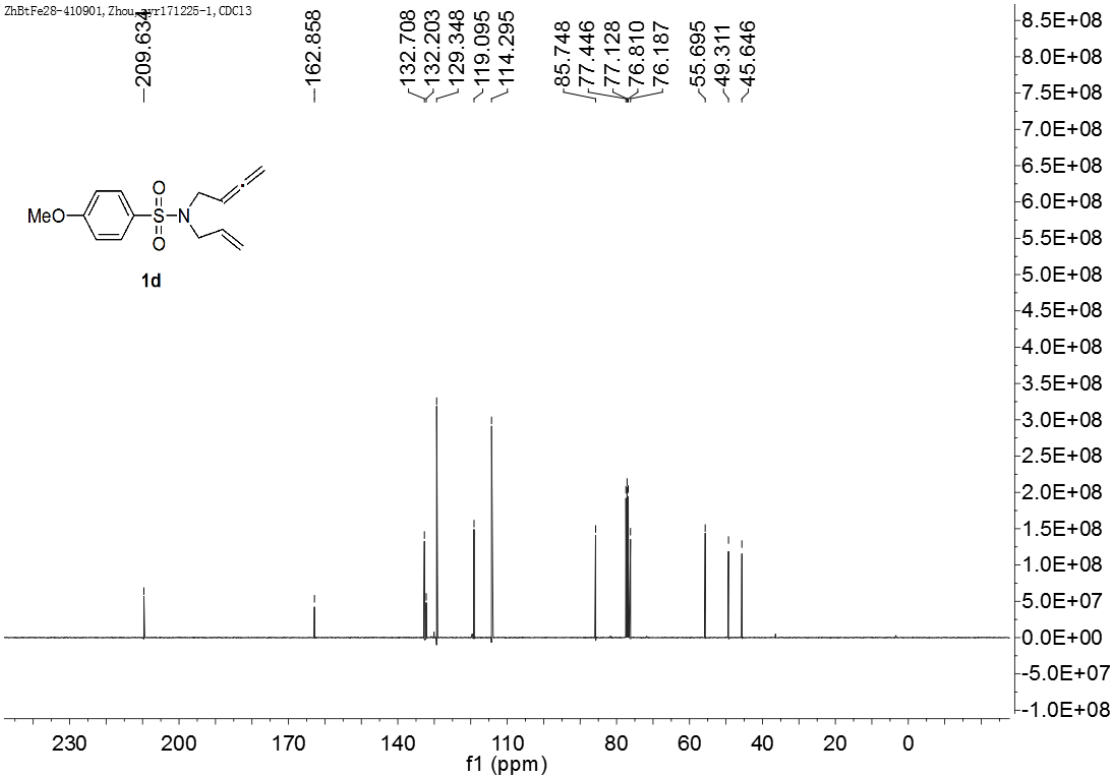
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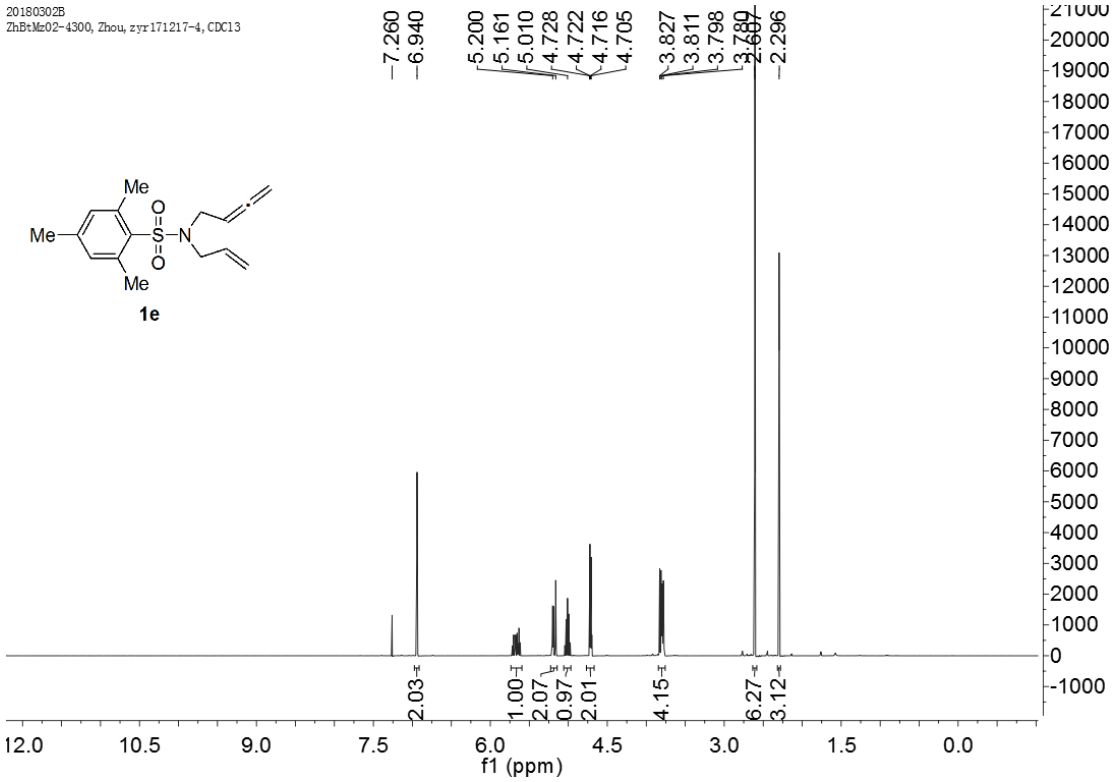
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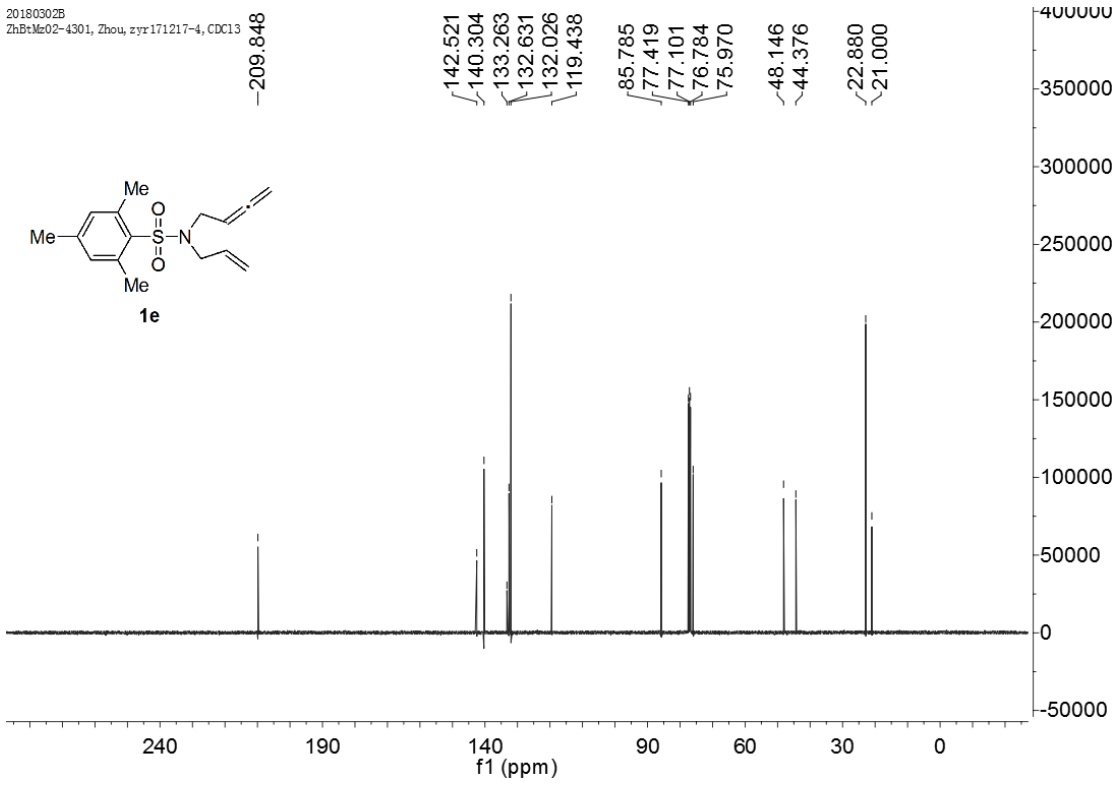
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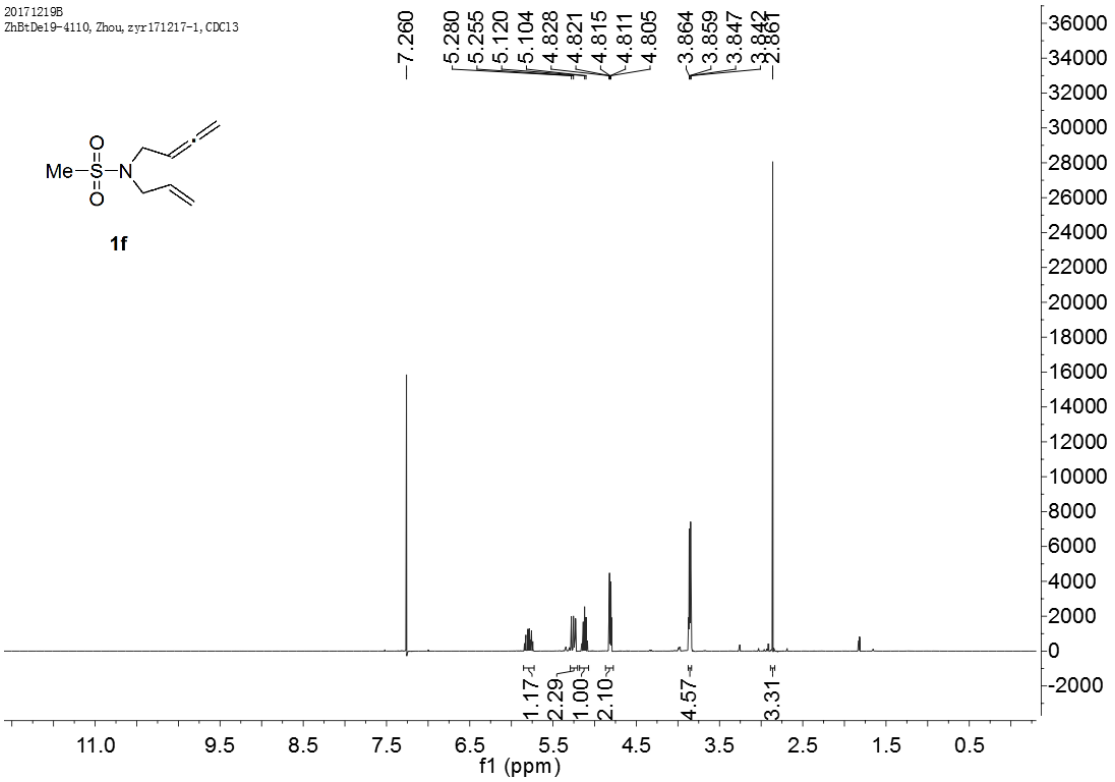
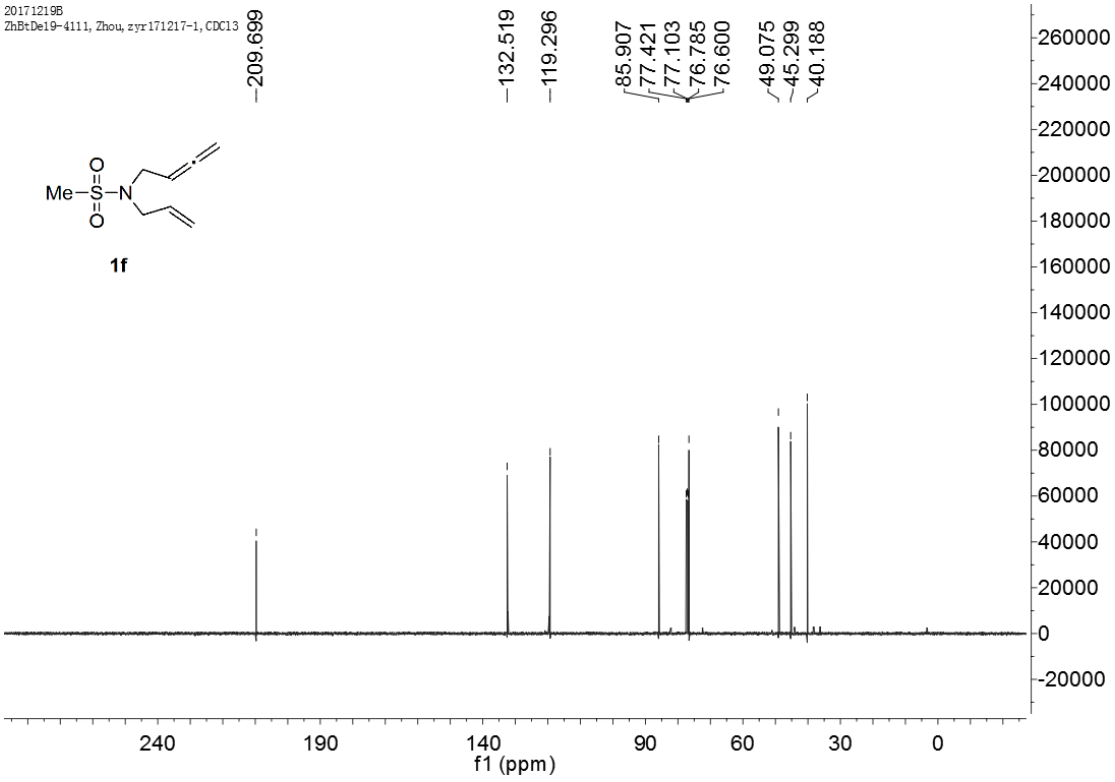
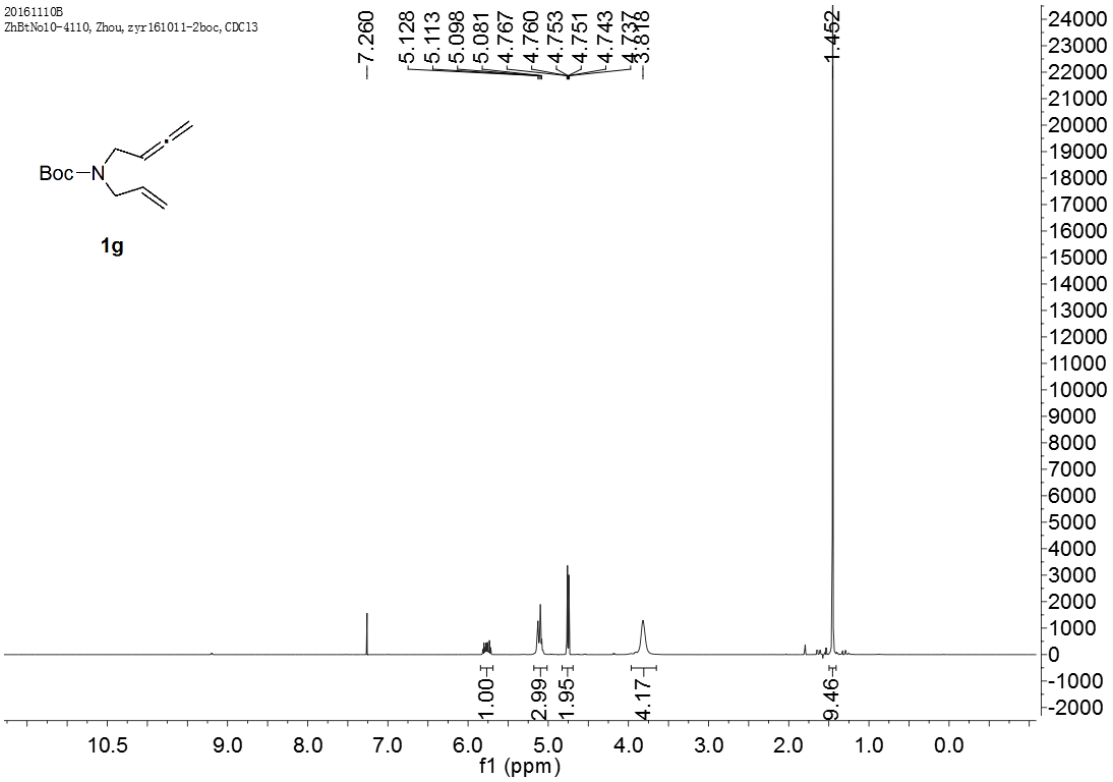
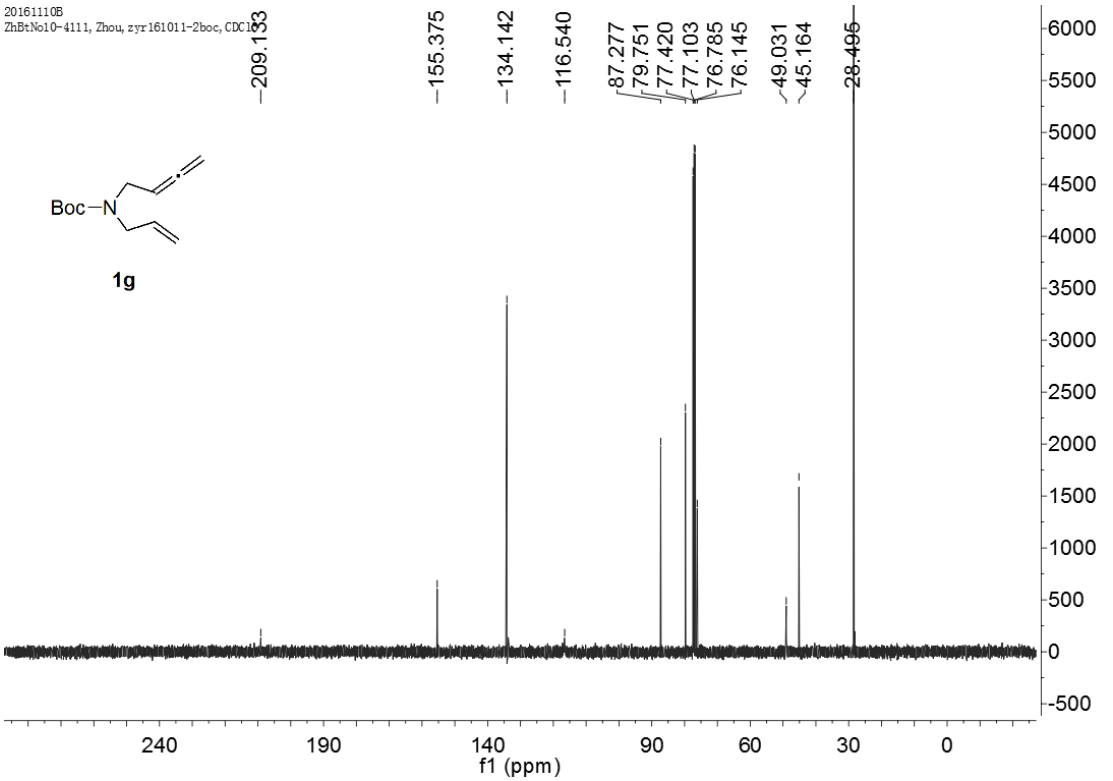
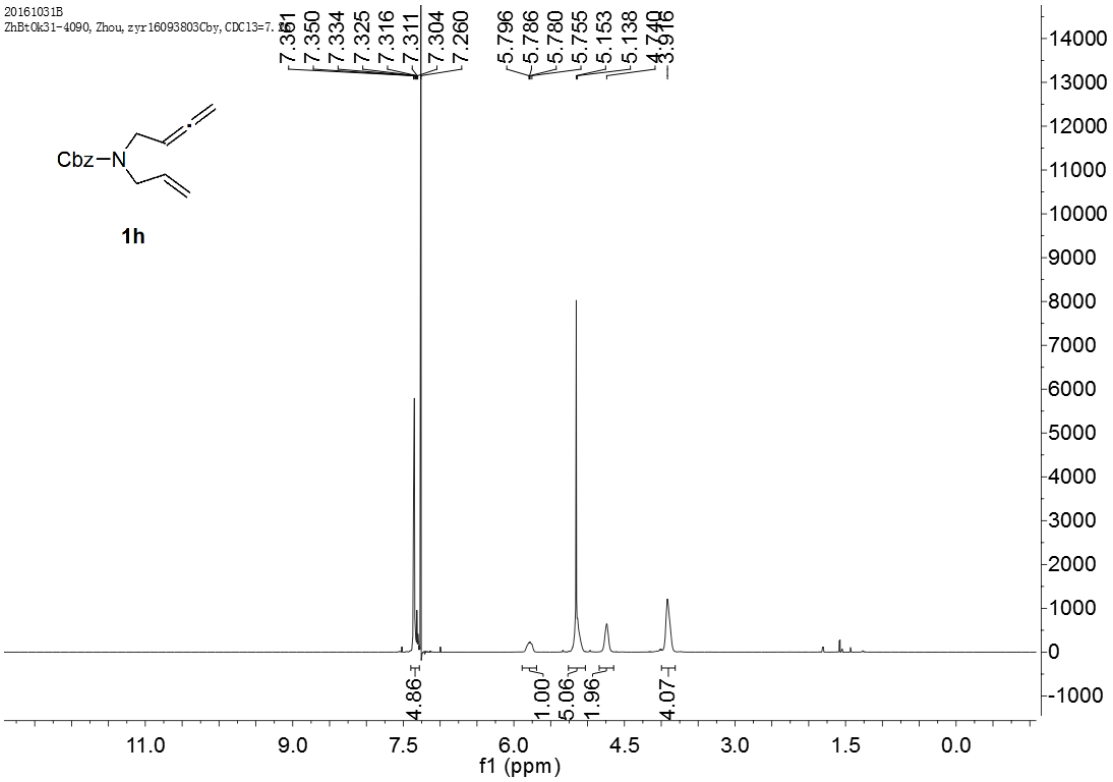
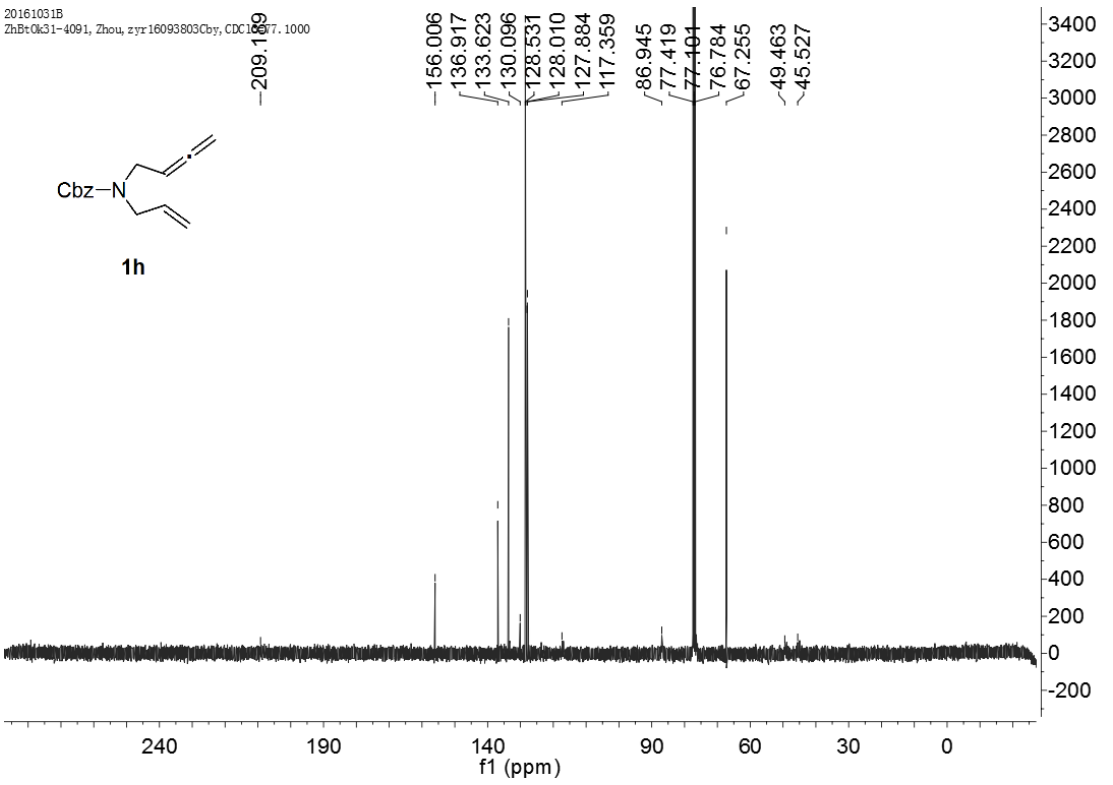

20171219B
ZhBtDe19-4110, Zhou, zyr171217-1, CDCl3
7.260
5.280
5.255
5.120
5.104
4.828
4.821
4.815
4.811
4.805
3.864
3.859
3.847
3.842
2.861
Me
S
N
O
1f
1.17
2.29
1.00
2.10
4.57
3.31
f1 (ppm)

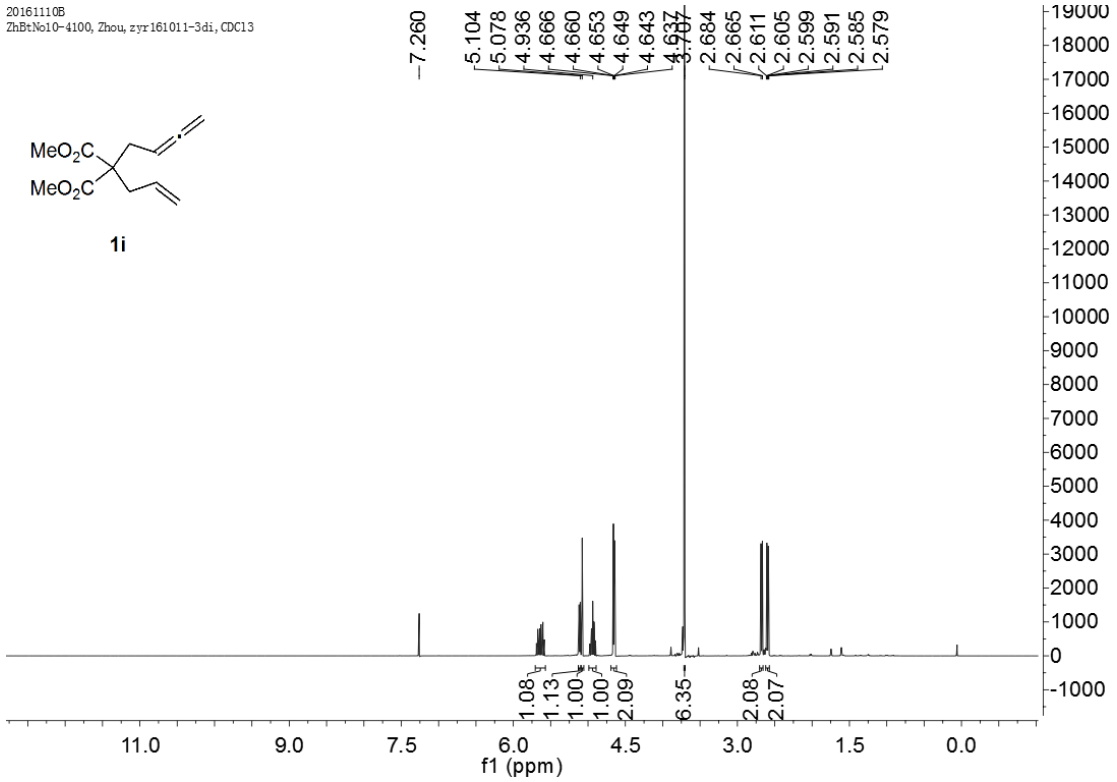

20171219B
ZhBtDe19-4111, Zhou, zyr171217-1, CDCl3
209.699
132.519
119.296
85.907
77.421
77.103
76.785
76.600
49.075
45.299
40.188
Me
S
N
O
1f
f1 (ppm)

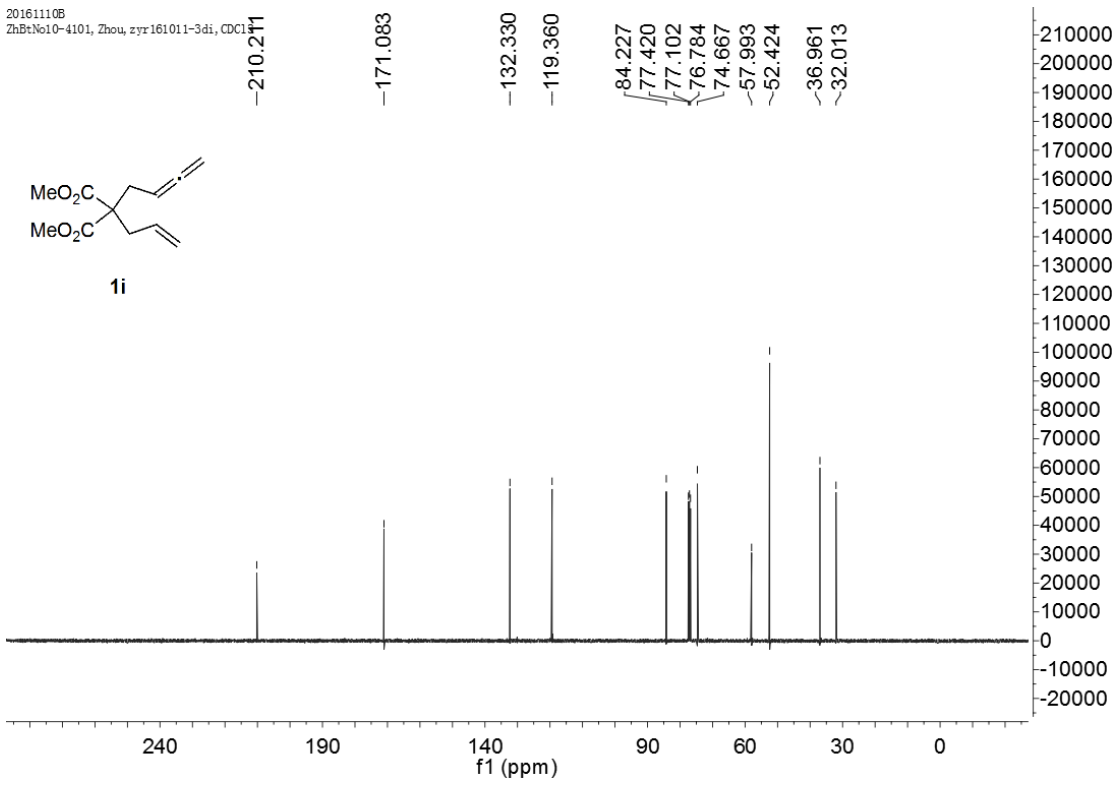

20161110B
ZhBtNo10-4110, Zhou, zyr161011-2boc, CDCl3
7.260
5.128
5.113
5.098
5.081
4.767
4.760
4.753
4.751
4.743
4.737
3.818
1.452
Boc—N
1g
1.00
2.99
1.95
4.17
9.46
f1 (ppm)

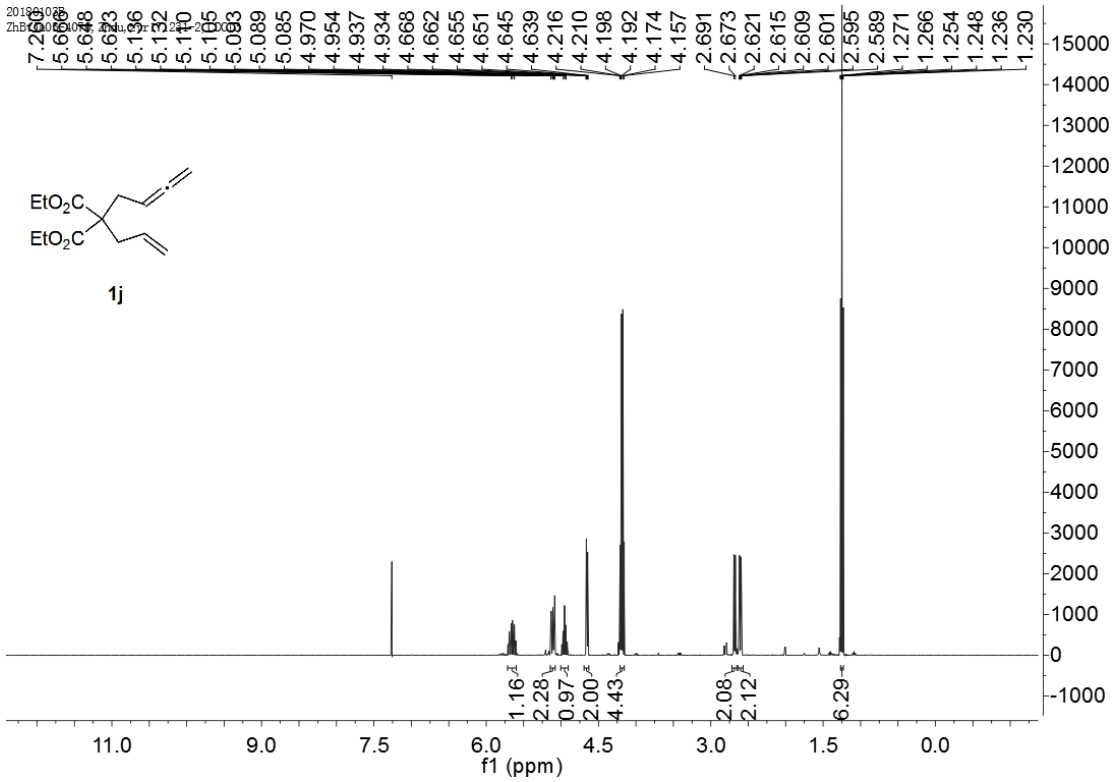

20161110B
ZhBtNo10-4111, Zhou, zyr161011-2boc, CDCl3
209.133
155.375
134.142
116.540
87.277
79.751
77.420
77.103
76.785
76.145
49.031
45.164
28.496
Boc—N
1g
f1 (ppm)

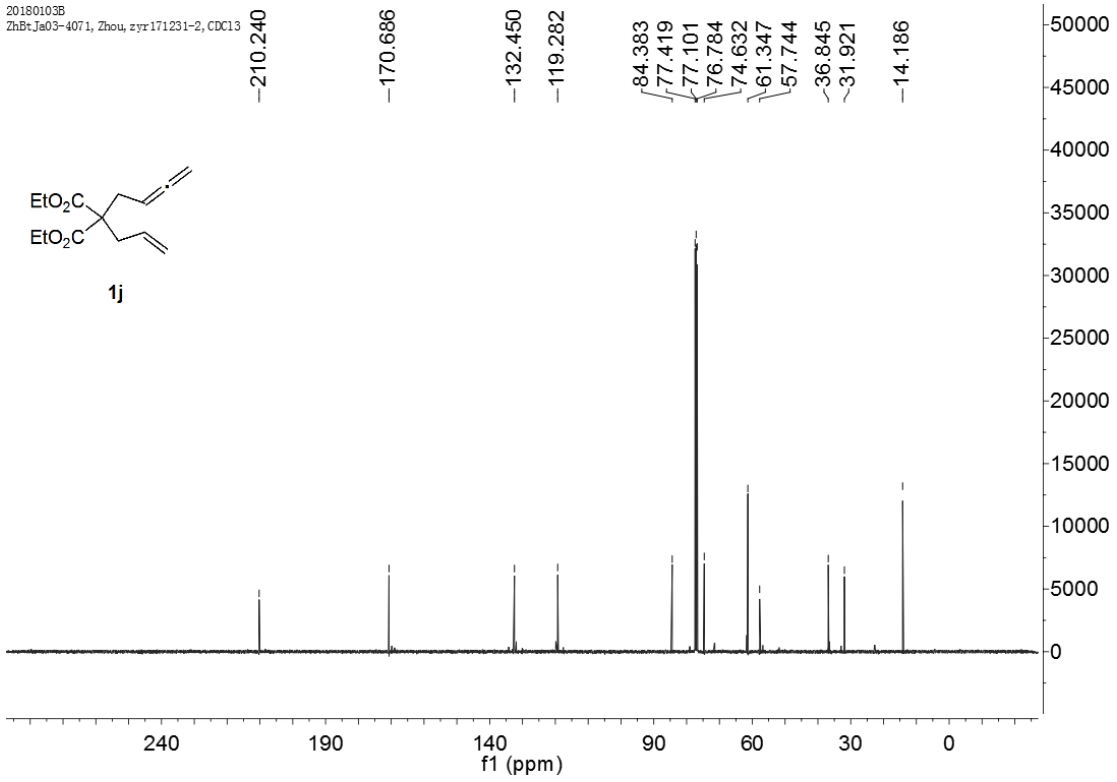

20161031B
ZhBt0k31-4090, Zhou, zyr16093803Cby, CDCl3=7.
7.361
7.350
7.334
7.325
7.316
7.311
7.304
7.260
5.796
5.786
5.780
5.755
5.153
5.138
4.740
3.916
Cbz—N
1h
4.86
1.00
5.06
1.96
4.07
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

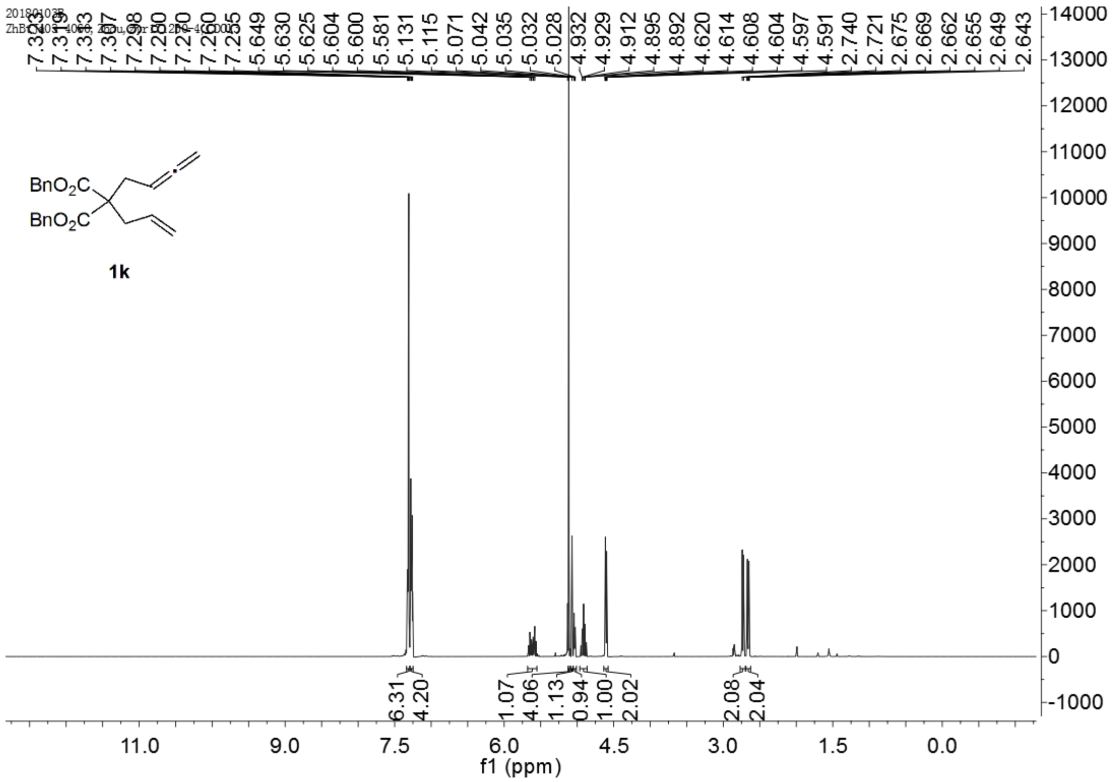

20161031B
ZhBt0k31-4091, Zhou, zyr16093803Cby, CDCl3=7.1000
209.169
156.006
136.917
133.623
130.096
128.531
128.010
127.884
117.359
86.945
77.419
77.104
76.784
67.255
49.463
45.527
Cbz—N
1h
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
240
190
140
90
60
30
0
f1 (ppm)


20161110B
ZhBtNo10-4100, Zhou, zyr161011-3di, CDCl3
MeO2C
MeO2C
1i
7.260
5.104
5.078
4.936
4.666
4.660
4.653
4.649
4.643
4.637
3.707
2.684
2.665
2.611
2.605
2.599
2.591
2.585
2.579
1.08
1.13
1.00
1.00
2.09
6.35
2.08
2.07
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

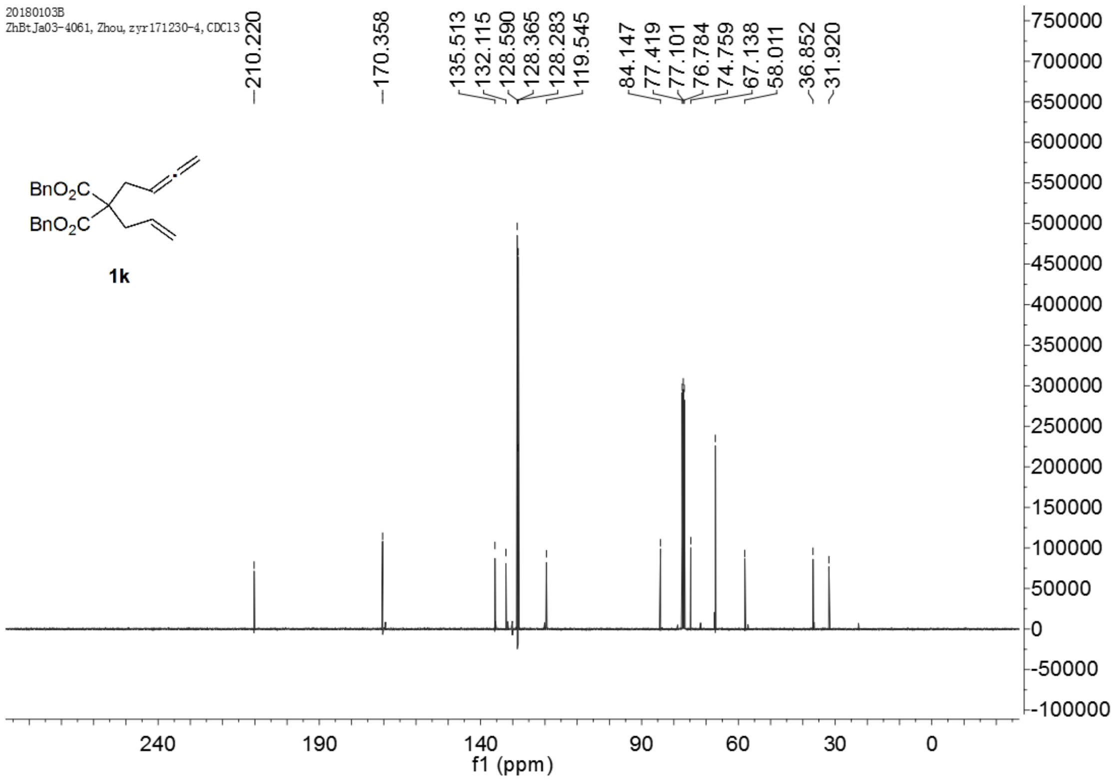

20161110B
ZhBtNo10-4101, Zhou, zyr161011-3di, CDCl3
MeO2C
MeO2C
1i
210.211
171.083
132.330
119.360
84.227
77.420
77.102
76.784
74.667
57.993
52.424
36.961
32.013
240
190
140
90
60
30
0
f1 (ppm)


1j
f1 (ppm)

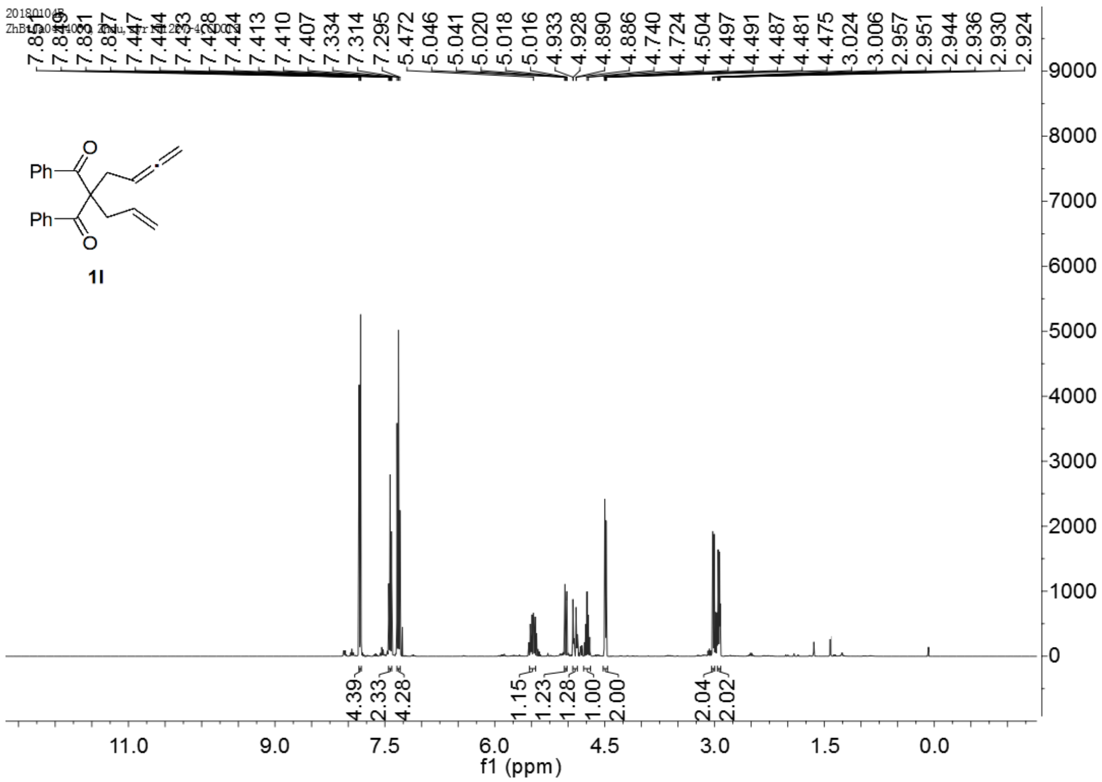

1j
f1 (ppm)

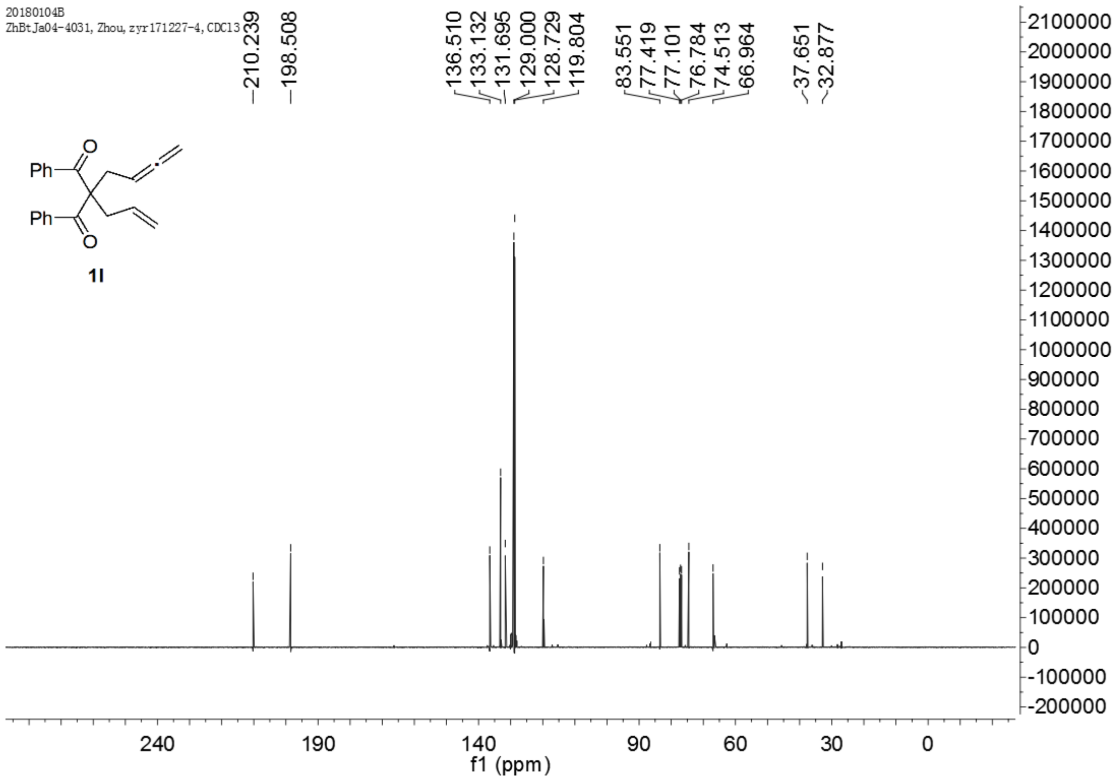


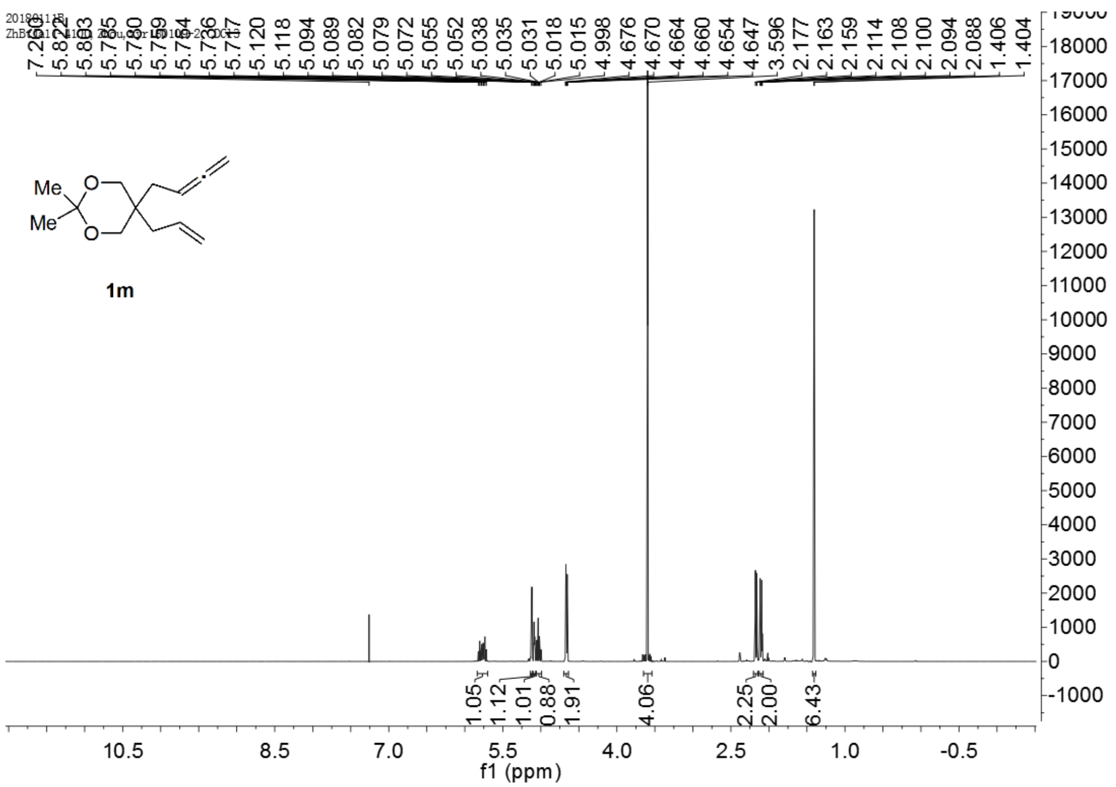
7.333
7.313
7.303
7.297
7.298
7.280
7.270
7.260
7.255
5.649
5.630
5.625
5.604
5.600
5.581
5.131
5.115
5.071
5.042
5.035
5.032
5.028
4.932
4.929
4.912
4.895
4.892
4.620
4.614
4.608
4.604
4.597
4.591
2.740
2.721
2.675
2.669
2.662
2.655
2.649
2.643
BnO_2C
BnO_2C
1k
6.31
4.20
1.07
4.06
1.13
0.94
1.00
2.02
2.08
2.04
f1 (ppm)

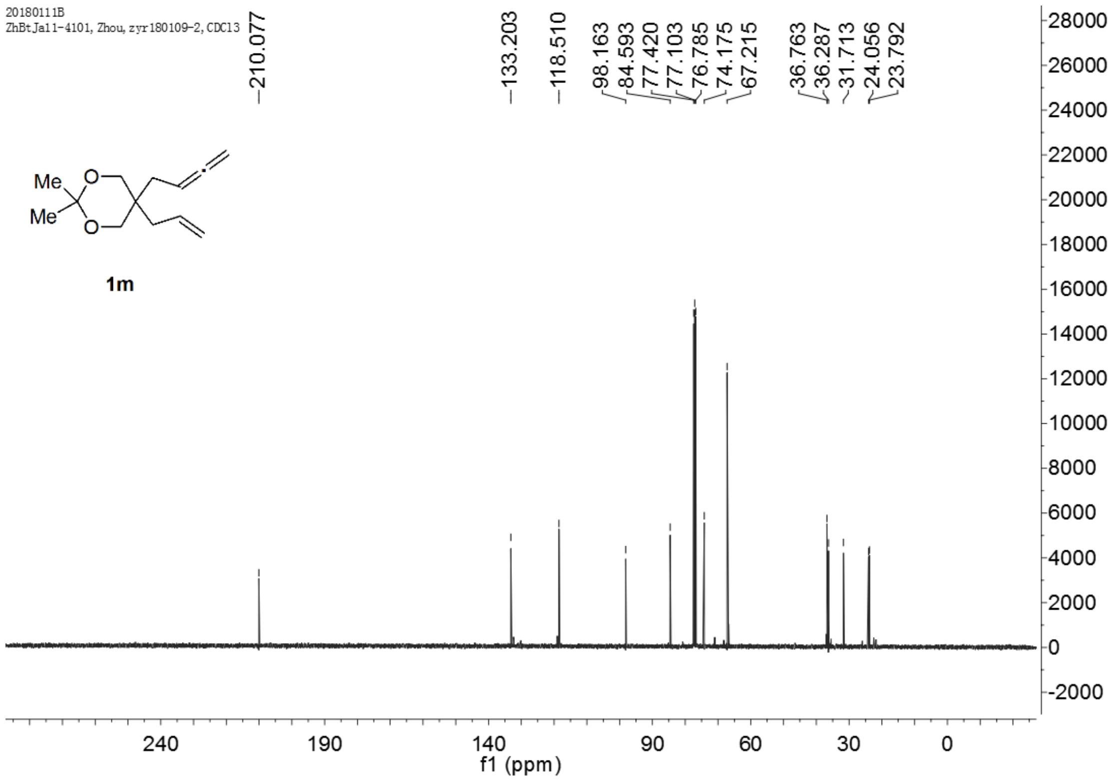


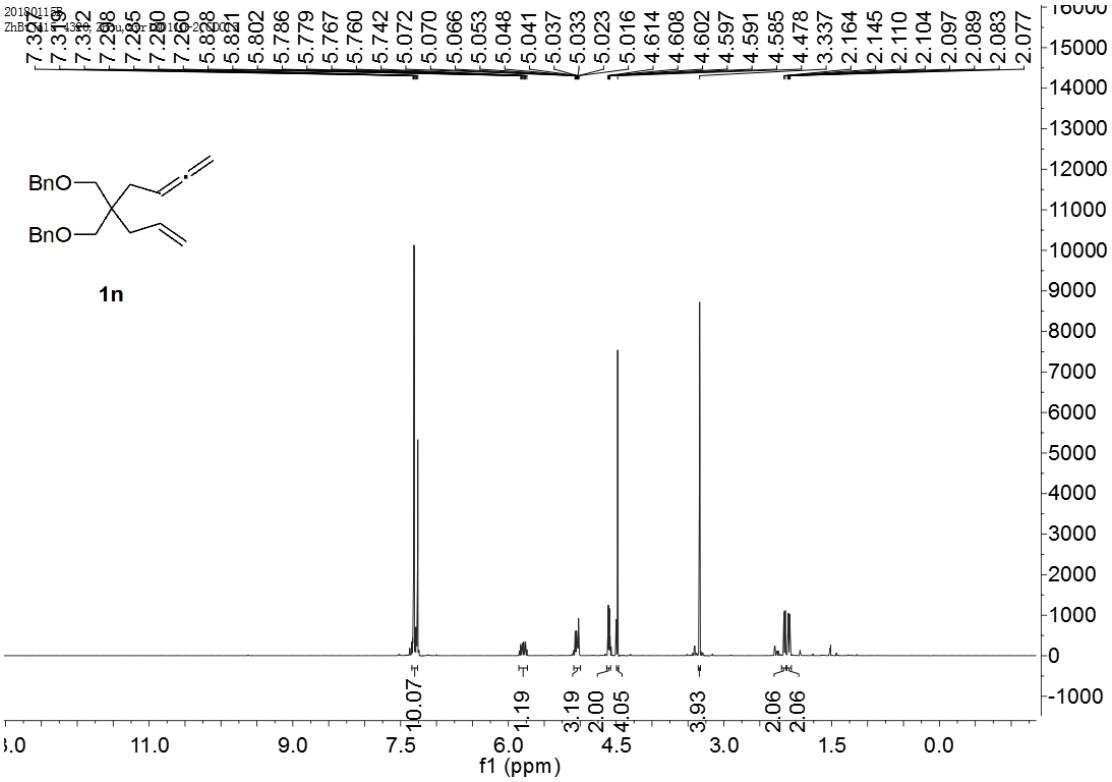
20180103B
ZhBtJa03-4061, Zhou, zyr171230-4, CDCl3
210.220
170.358
135.513
132.115
128.590
128.365
128.283
119.545
84.147
77.419
77.101
76.784
74.759
67.138
58.011
36.852
31.920
BnO_2C
BnO_2C
1k
f1 (ppm)

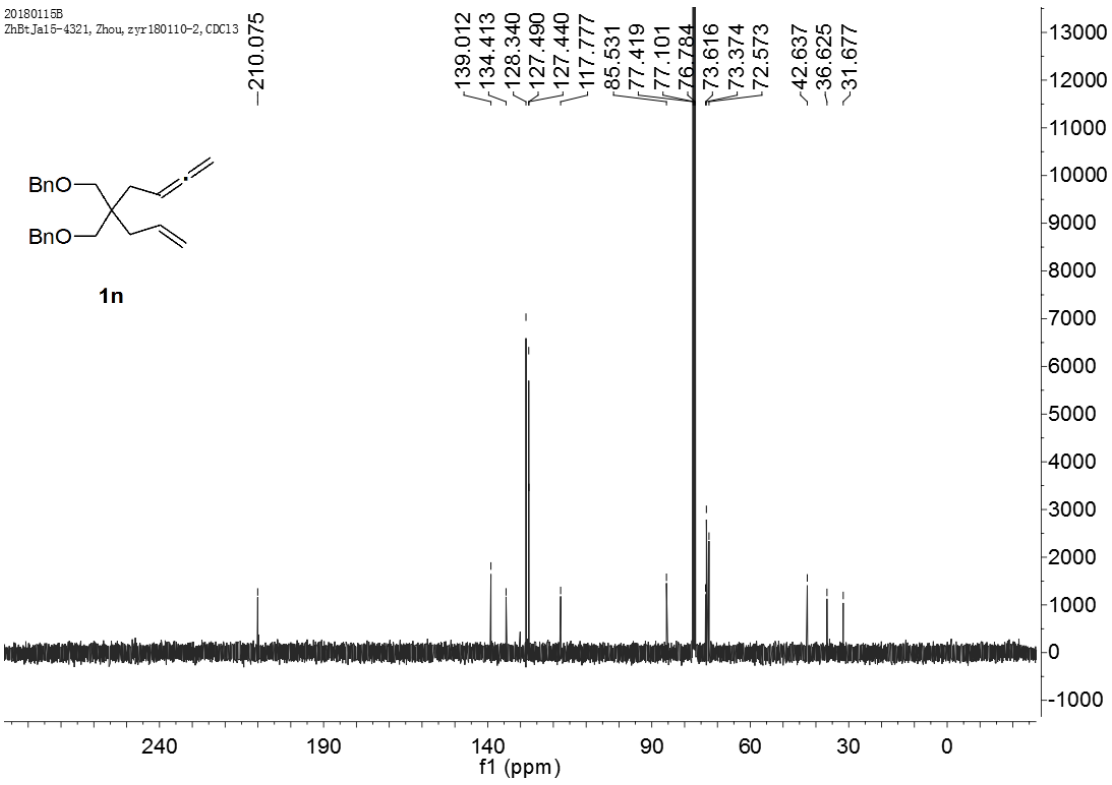

20180104B
7.851
7.849
7.831
7.827
7.447
7.444
7.433
7.428
7.424
7.413
7.410
7.407
7.334
7.314
7.295
5.472
5.046
5.041
5.020
5.018
5.016
4.933
4.928
4.890
4.886
4.740
4.724
4.504
4.497
4.491
4.487
4.481
4.475
3.024
3.006
2.957
2.951
2.944
2.936
2.930
2.924
Ph
Ph
O
O
1l
4.39
2.33
4.28
1.15
1.23
1.28
1.00
2.00
2.04
2.02
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

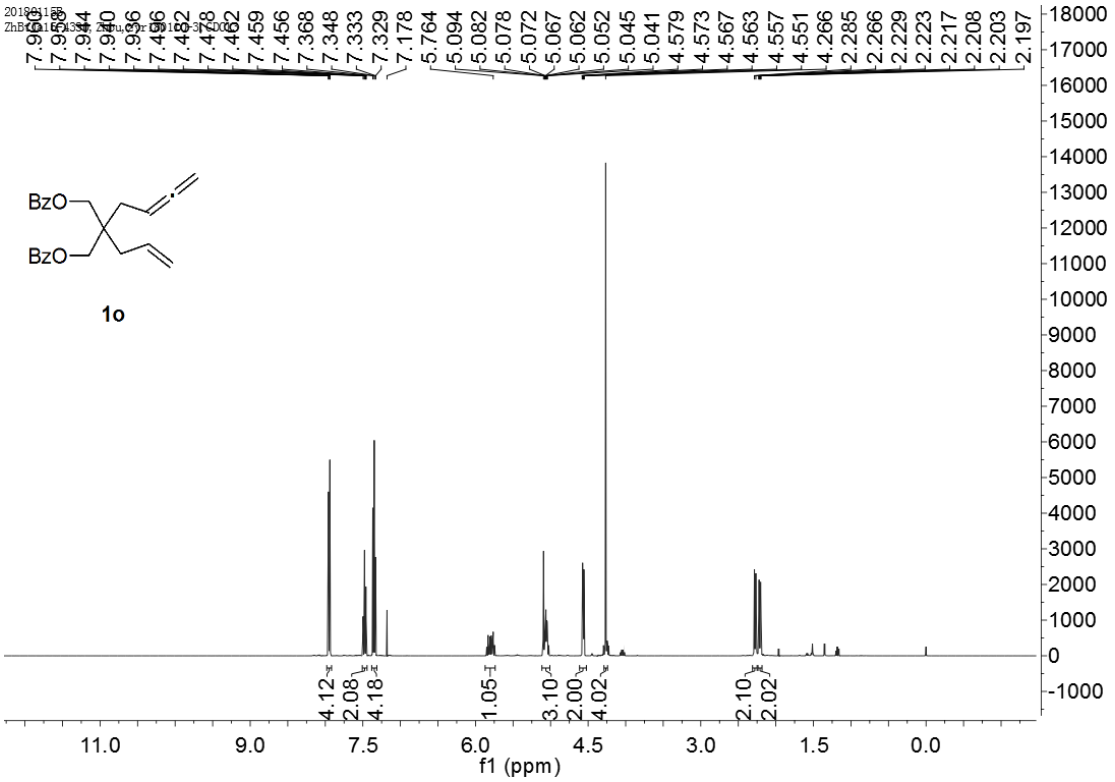

20180104B
ZhBtJa04-4031, Zhou, zyr171227-4, CDCl3
210.239
198.508
136.510
133.132
131.695
129.000
128.729
119.804
83.551
77.419
77.101
76.784
74.513
66.964
37.651
32.877
Ph
Ph
O
O
1l
240
190
140
90
60
30
0
f1 (ppm)
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000

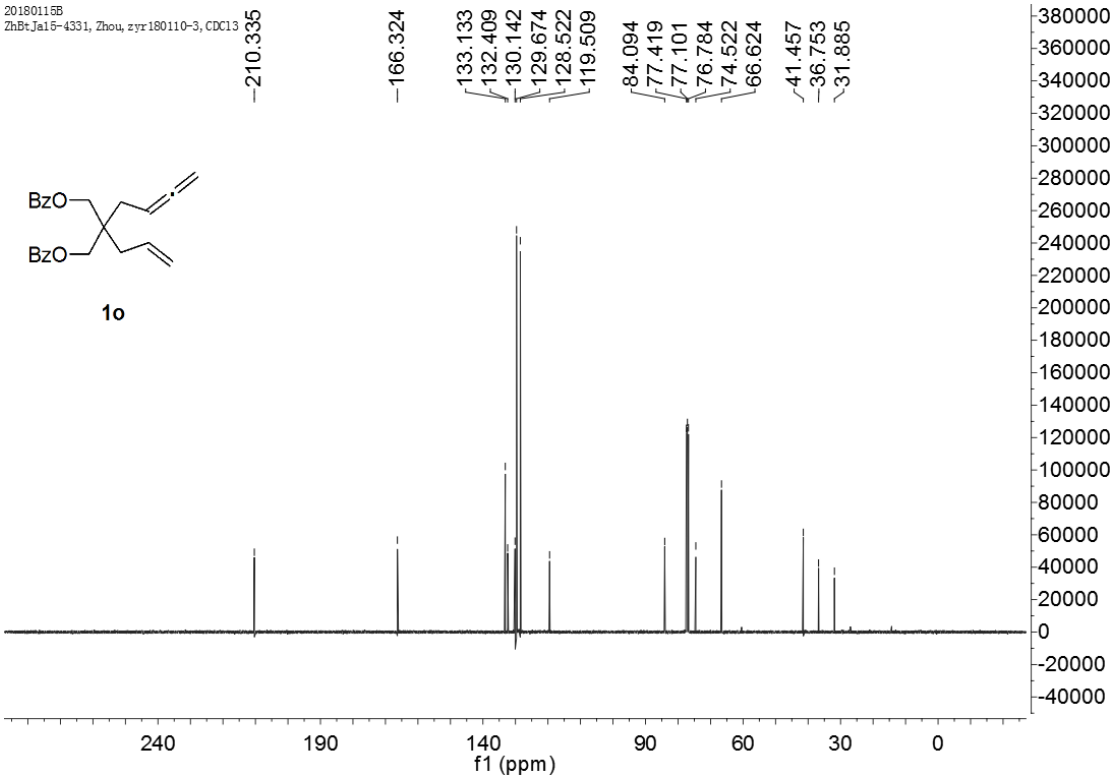

20180111B
7.260
5.822
5.803
5.785
5.780
5.769
5.764
5.746
5.747
5.120
5.118
5.094
5.089
5.082
5.079
5.072
5.055
5.052
5.038
5.035
5.031
5.018
5.015
4.998
4.676
4.670
4.664
4.660
4.654
4.647
3.596
2.177
2.163
2.159
2.114
2.108
2.100
2.094
2.088
1.406
1.404
Me
Me
O
O
1m
1.05
1.12
1.01
0.88
1.91
4.06
2.25
2.00
6.43
f1 (ppm)

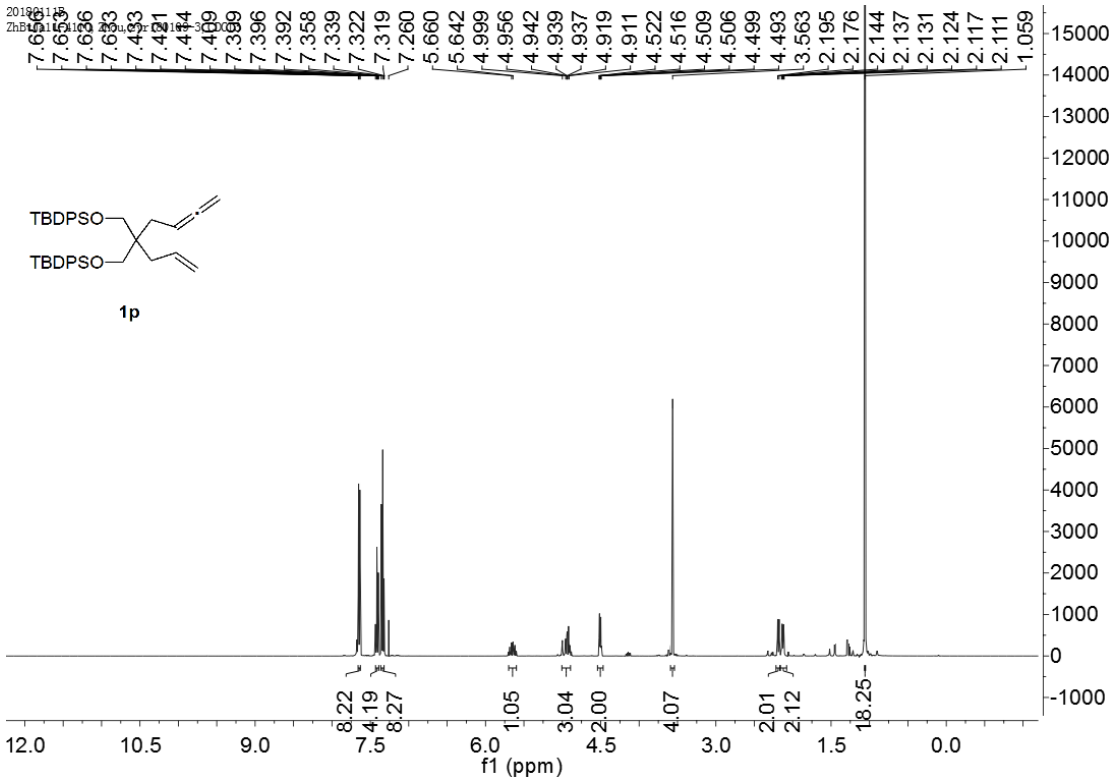

20180111B
ZhBtJa11-4101, Zhou, zyr180109-2, CDCl3
210.077
133.203
118.510
98.163
84.593
77.420
77.103
76.785
74.175
67.215
36.763
36.287
31.713
24.056
23.792
Me
Me
O
O
1m
f1 (ppm)

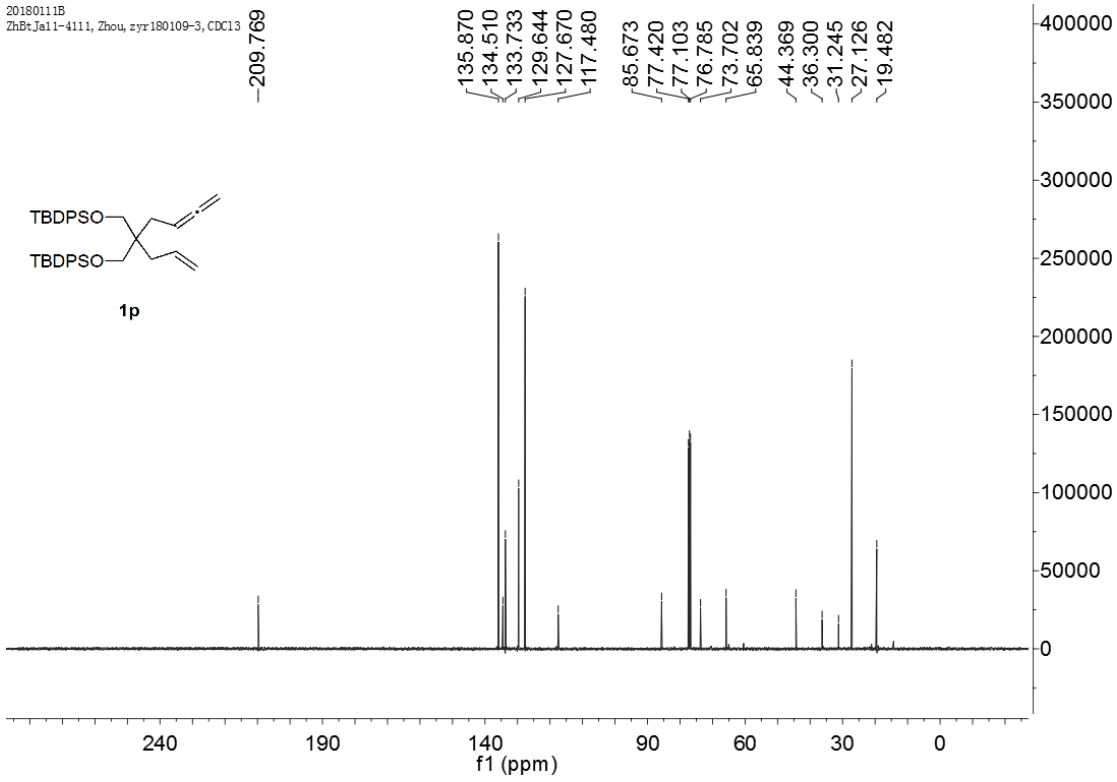

BnO
BnO
1n
10.07
1.19
3.19
2.00
4.05
3.93
2.06
2.06
f1 (ppm)


20180115B
ZhBtJa15-4321, Zhou, zyr180110-2, CDCl3
210.075
139.012
134.413
128.340
127.490
127.440
117.777
85.531
77.419
77.101
76.784
73.616
73.374
72.573
42.637
36.625
31.677
BnO
BnO
1n
f1 (ppm)

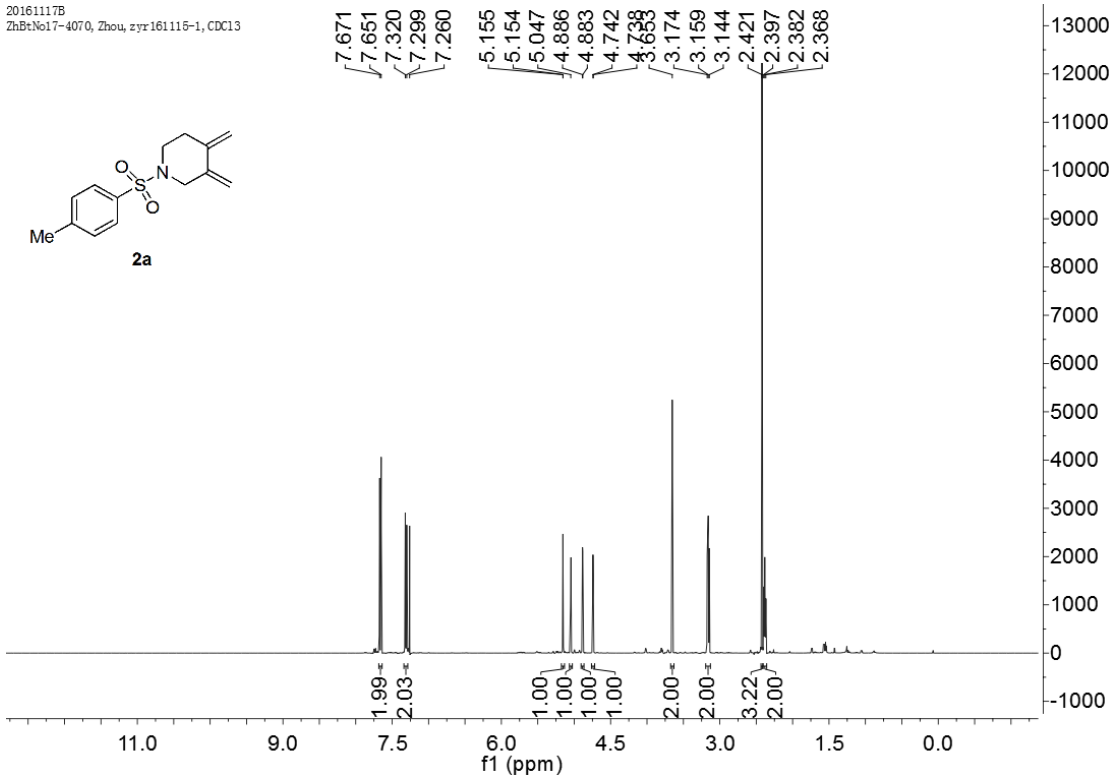

BzO
BzO
1o
f1 (ppm)

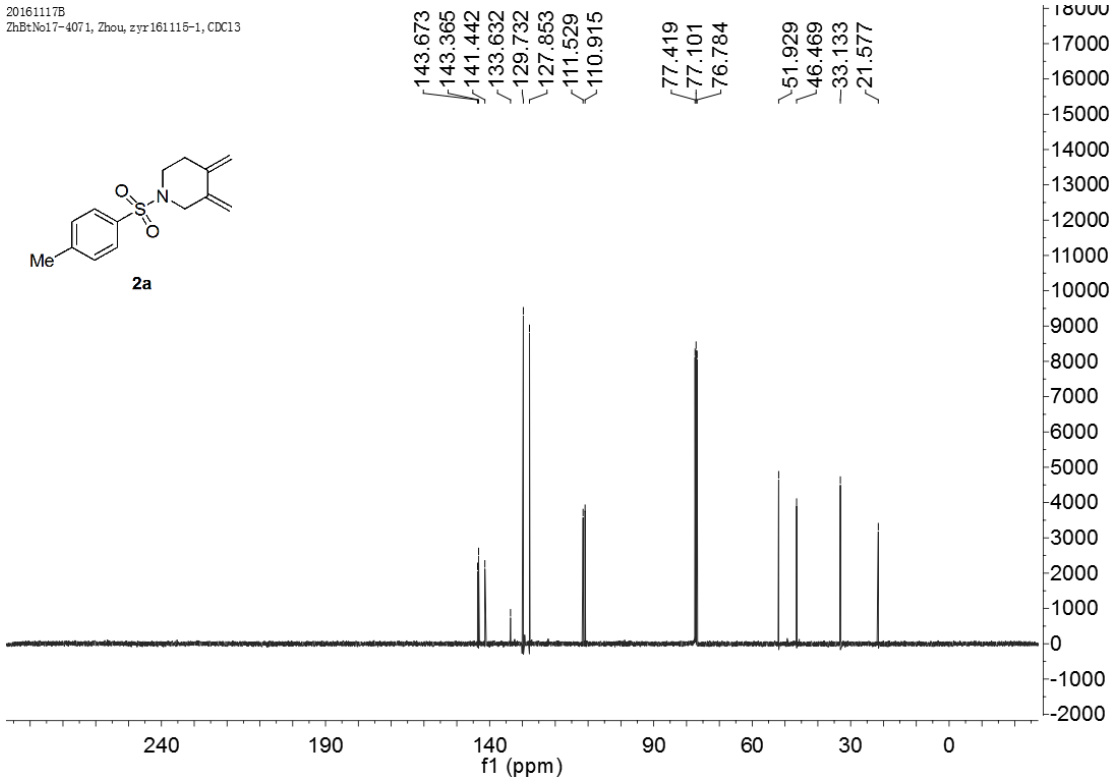

20180115B
ZhBtJa16-4331, Zhou, zyr180110-3, CDCl3
BzO
BzO
1o
f1 (ppm)

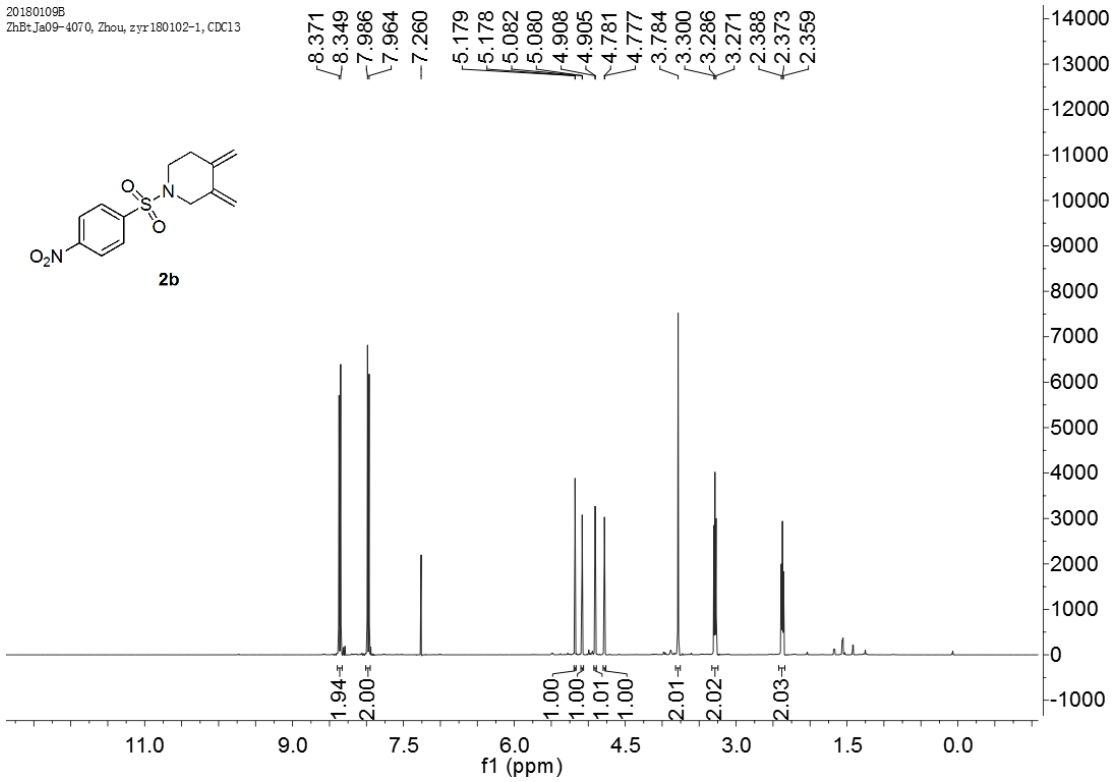

TBDPSO
TBDPSO
1p
f1 (ppm)

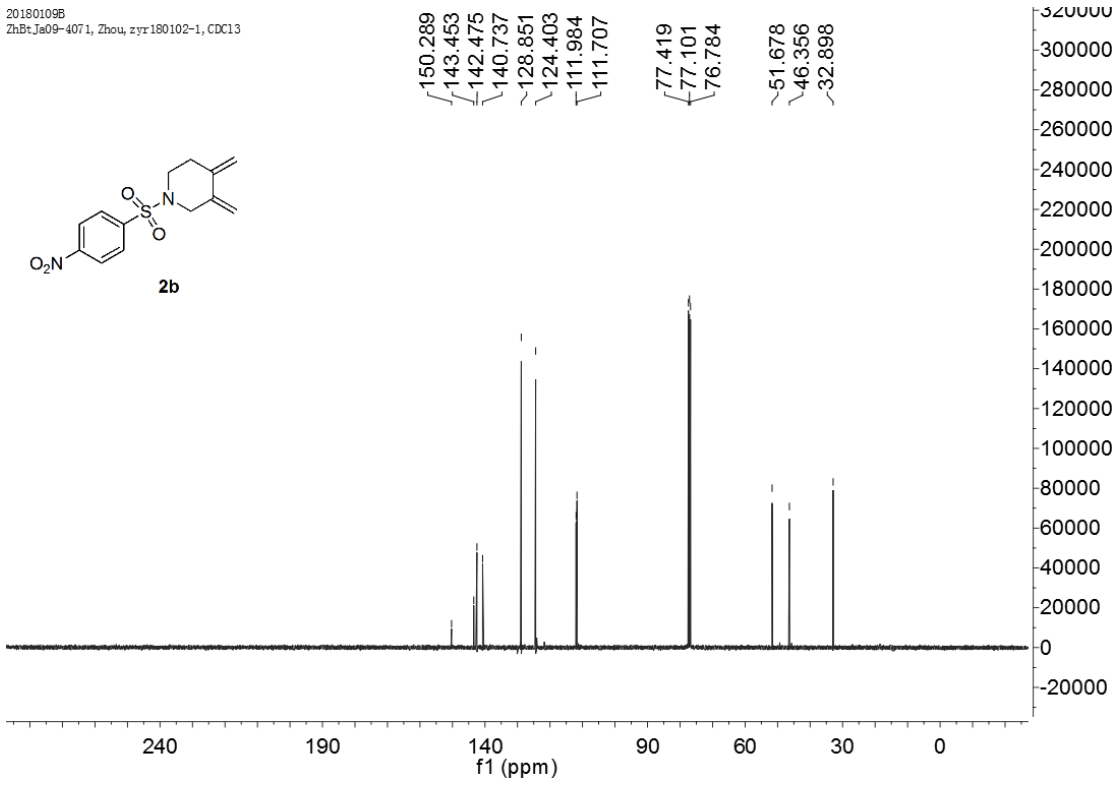

20180111B
ZhBtJa11-4111, Zhou, zyr180109-3, CDCl3
TBDPSO
TBDPSO
1p
f1 (ppm)

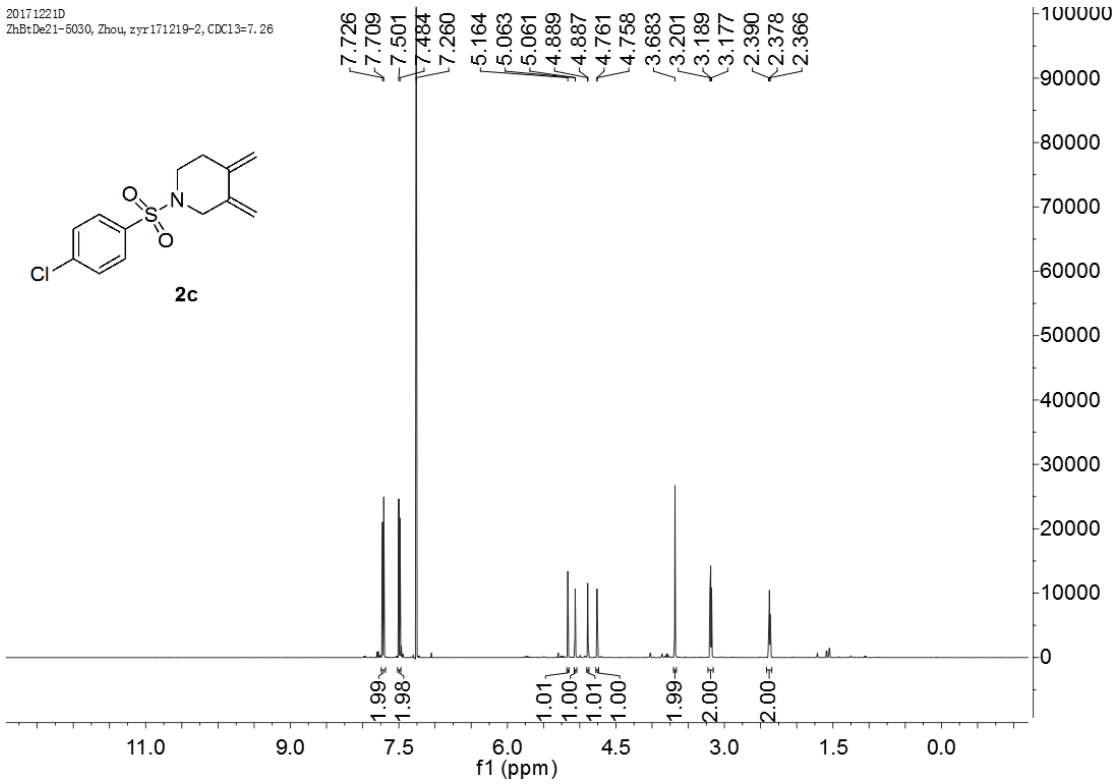
Copies of NMR spectra of the products






20180109B
ZhBtJa09-4070, Zhou, zyr180102-1, CDCl3
8.371
8.349
7.986
7.964
7.260
5.179
5.178
5.082
5.080
4.908
4.905
4.781
4.777
3.784
3.300
3.286
3.271
2.388
2.373
2.359
2b
1.94
2.00
1.00
1.00
1.01
1.00
2.01
2.02
2.03
f1 (ppm)


20180109B
ZhBtJa09-4071, Zhou, zyr180102-1, CDCl3
150.289
143.453
142.475
140.737
128.851
124.403
111.984
111.707
77.419
77.101
76.784
51.678
46.356
32.898
2b
f1 (ppm)


20171221D
ZhBtDe21-5030, Zhou, zyr171219-2, CDCl3=7.26
7.726
7.709
7.501
7.484
7.260
5.164
5.063
5.061
4.889
4.887
4.761
4.758
3.683
3.201
3.189
3.177
2.390
2.378
2.366
2c
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1.98
1.01
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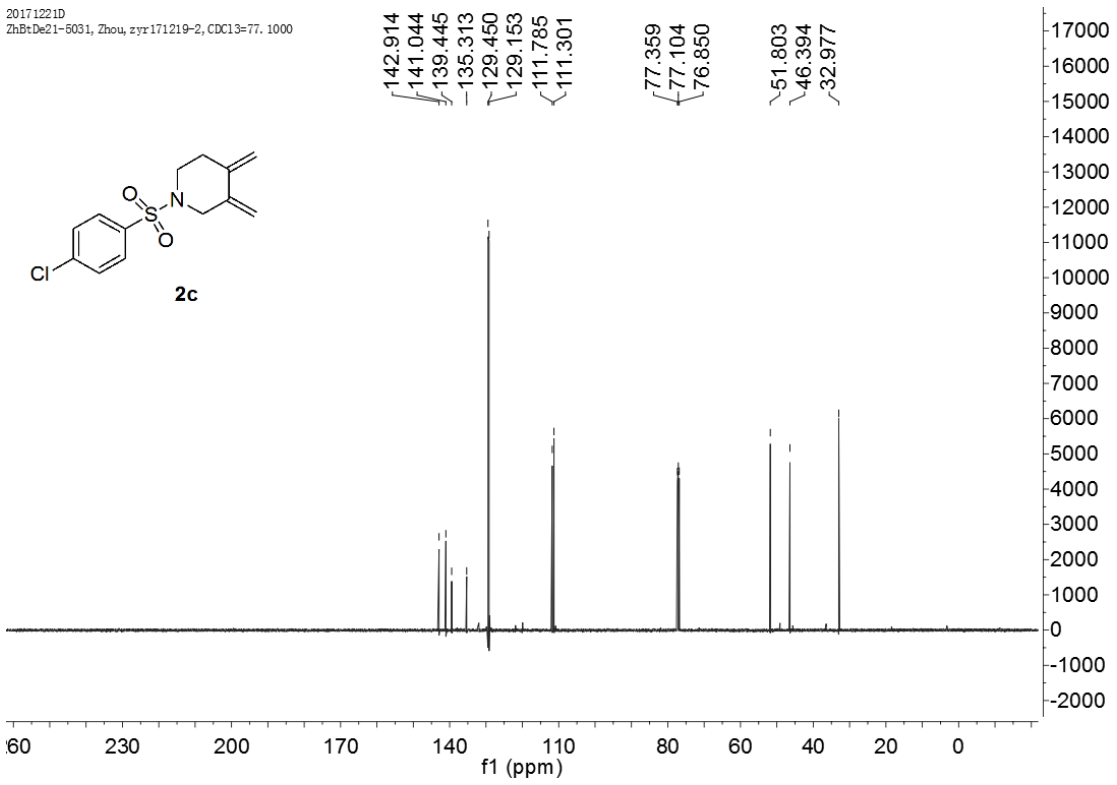
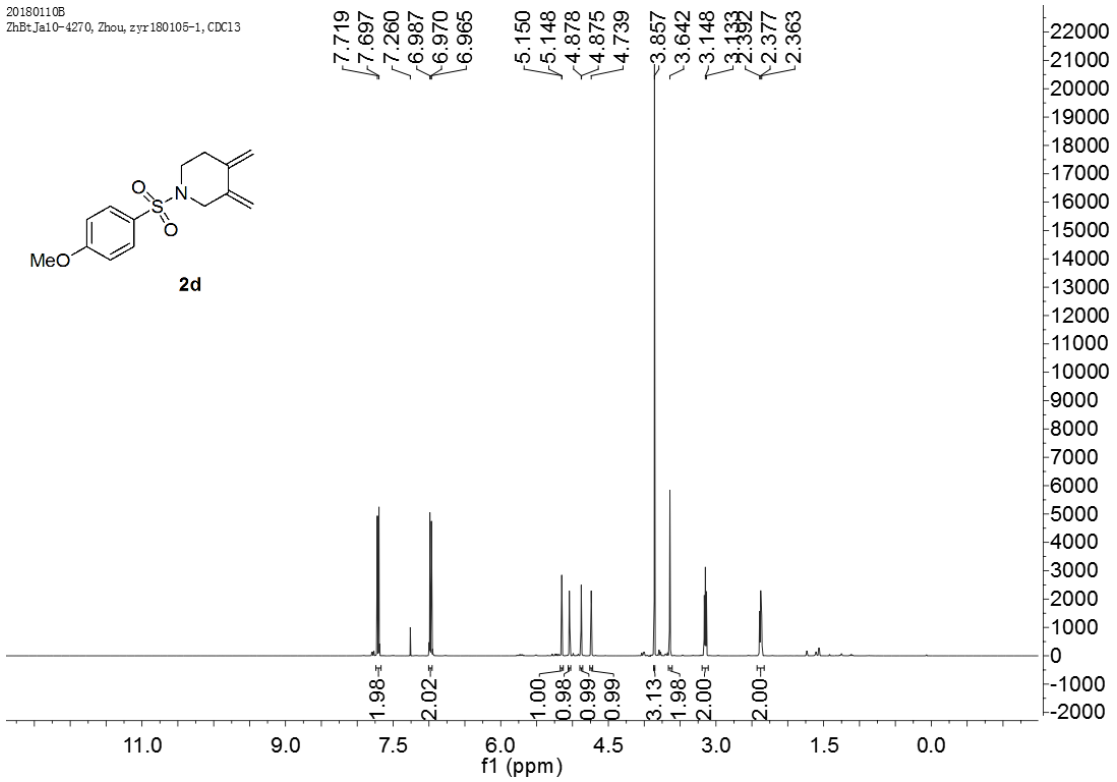
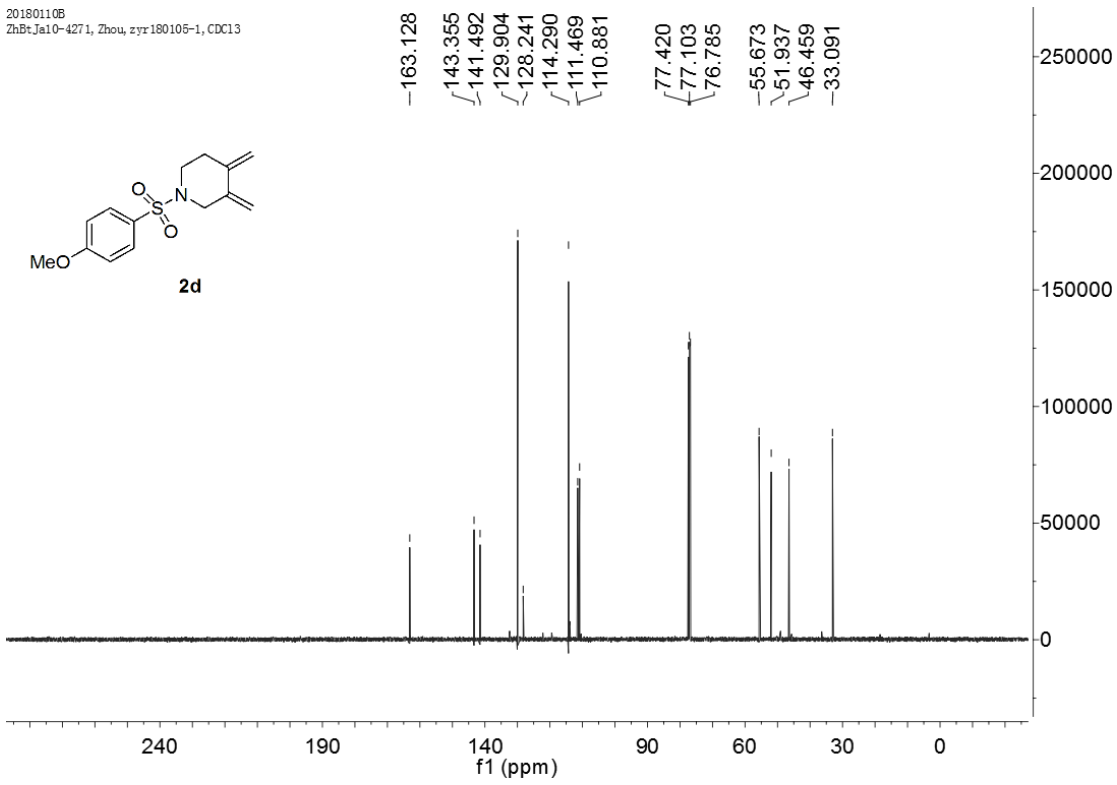
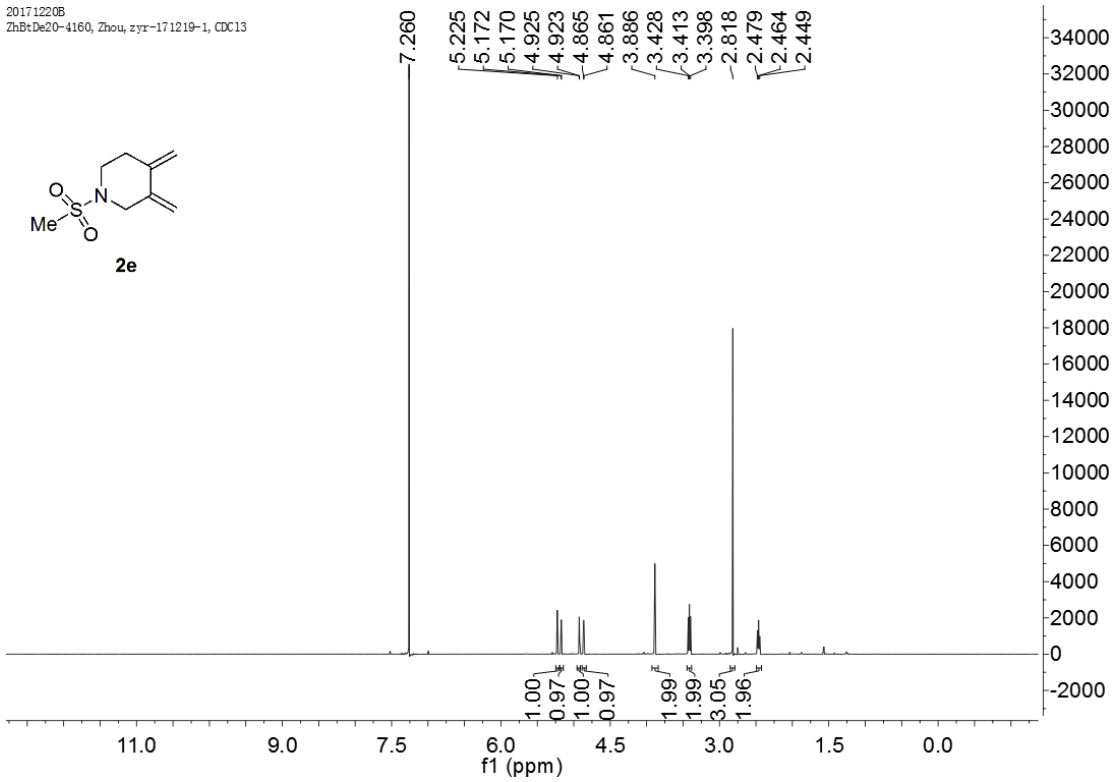
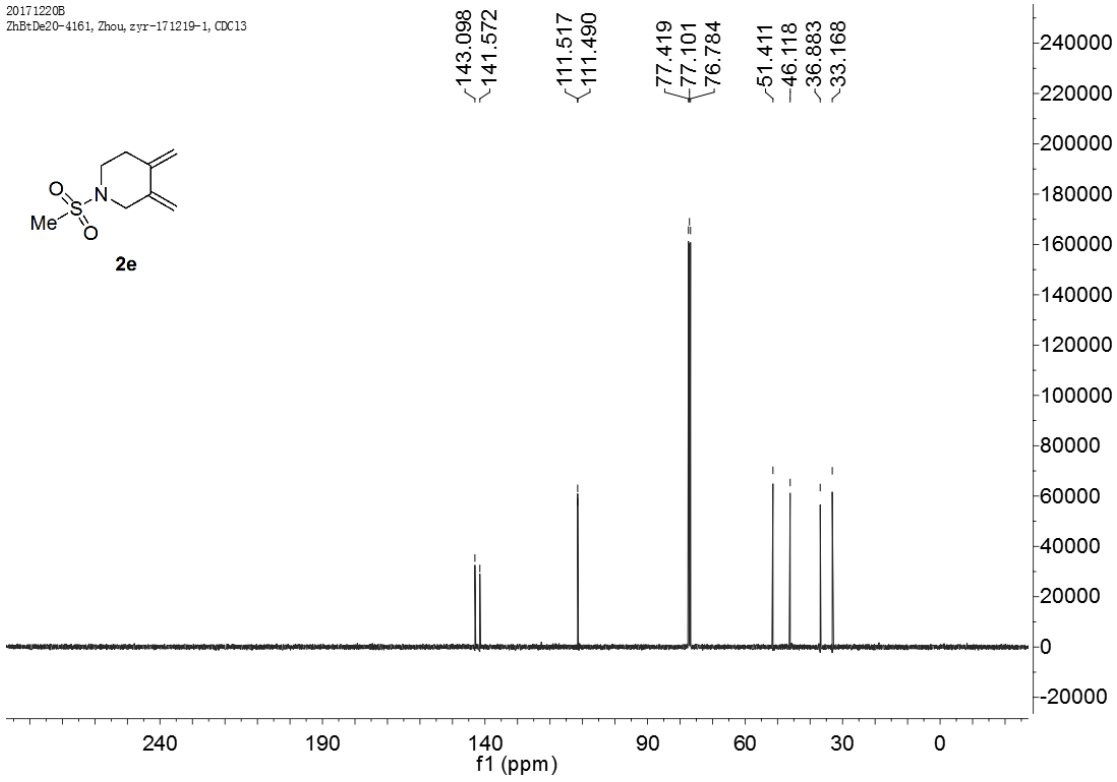
1.01
1.00
1.99
2.00
2.00
f1 (ppm)

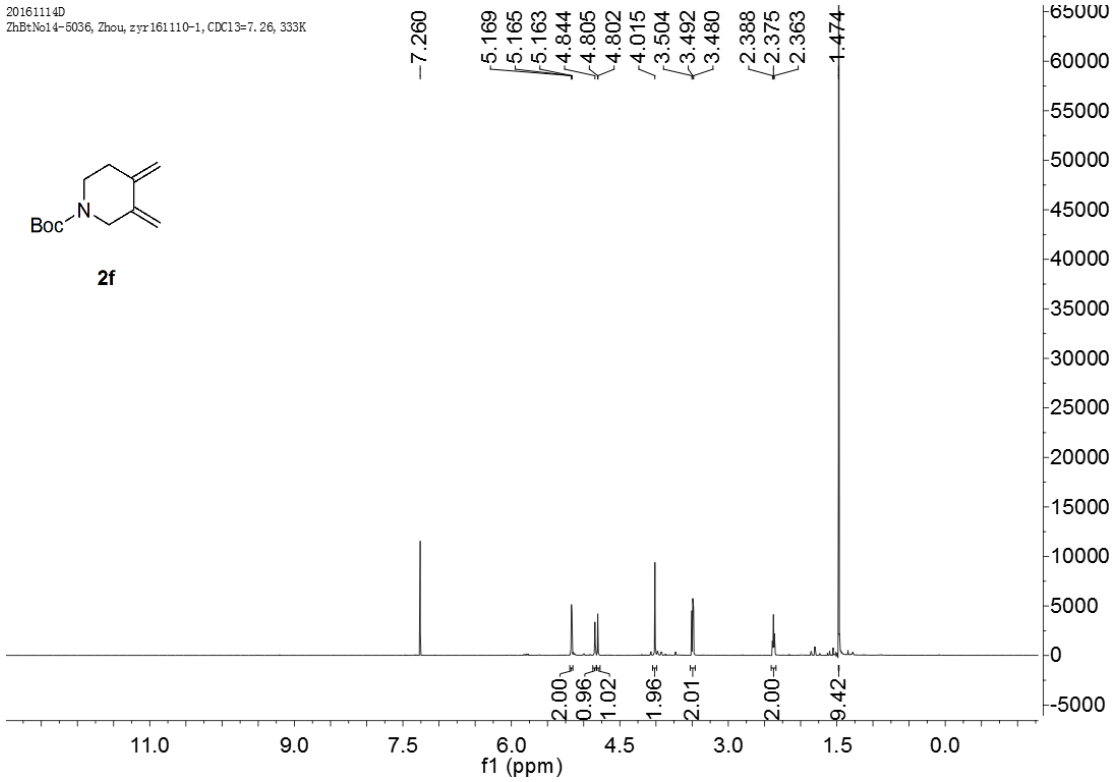

20171221D
ZhBtDe21-5031, Zhou, zyr171219-2, CDCl3=77.1000
142.914
141.044
139.445
135.313
129.450
129.153
111.785
111.301
77.359
77.104
76.850
51.803
46.394
32.977
2c
f1 (ppm)

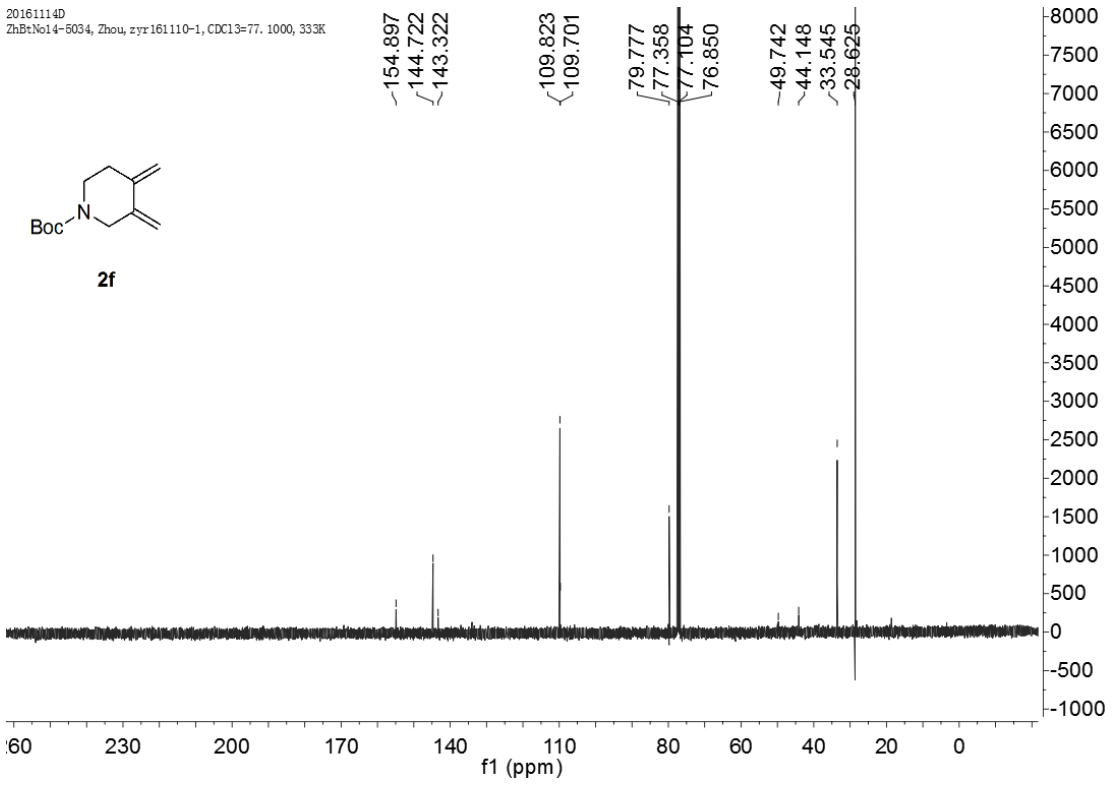

20180110B
ZhBtJa10-4270, Zhou, zyr180105-1, CDCl3
7.719
7.697
7.260
6.987
6.970
6.965
5.150
5.148
4.878
4.875
4.739
3.857
3.642
3.148
2.377
2.363
MeO
2d
1.98
2.02
1.00
0.98
0.99
0.99
3.13
1.98
2.00
2.00
f1 (ppm)

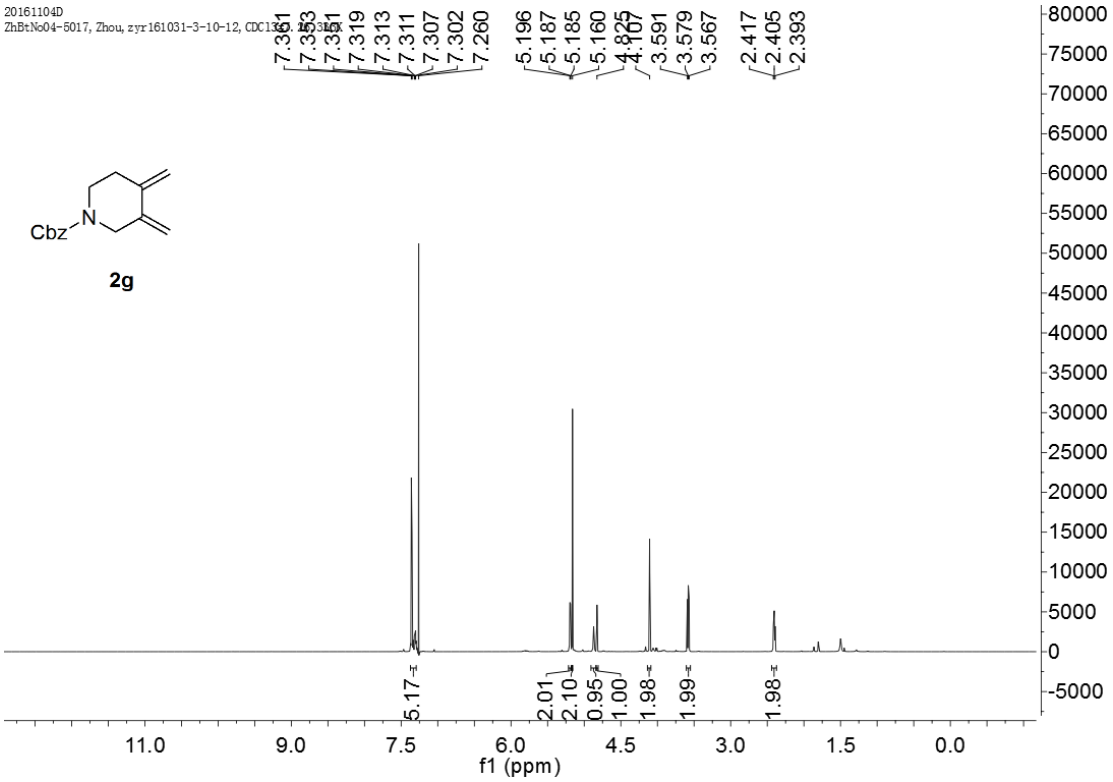

20180110B
ZhBtJa10-4271, Zhou, zyr180105-1, CDCl3
163.128
143.355
141.492
129.904
128.241
114.290
111.469
110.881
77.420
77.103
76.785
55.673
51.937
46.459
33.091
MeO
2d
f1 (ppm)

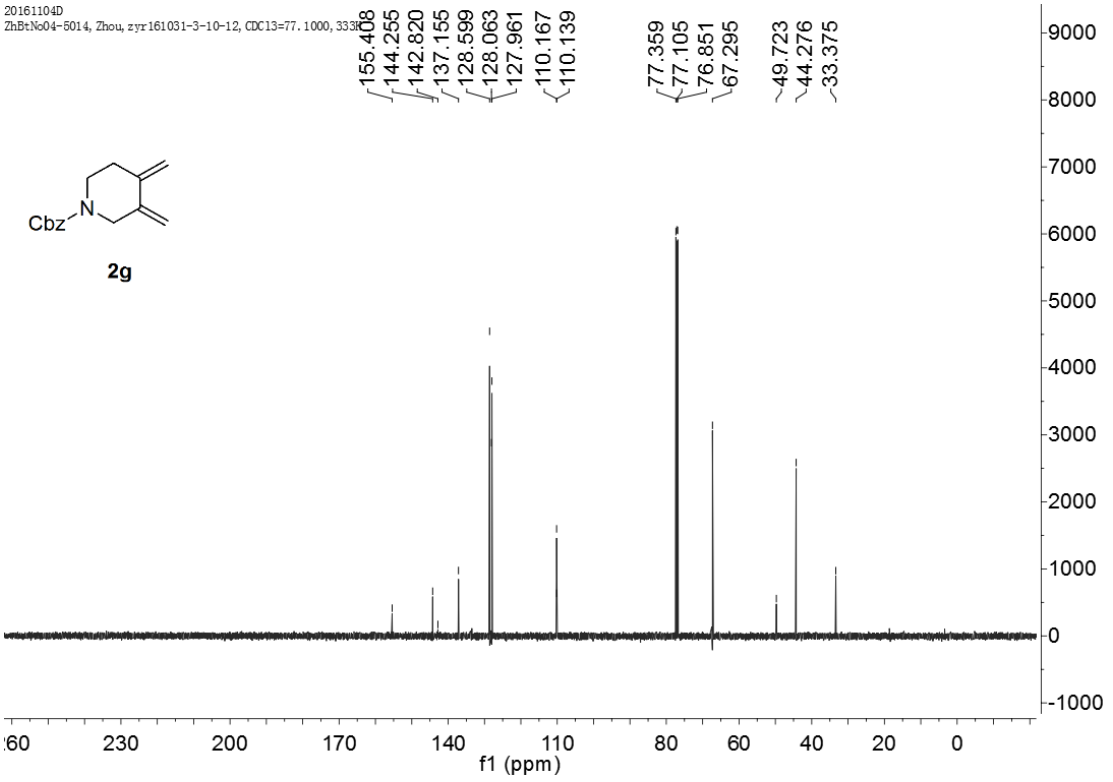

20171220B
ZhBtDe20-4160, Zhou, zyr-171219-1, CDCl3
7.260
5.225
5.172
5.170
4.925
4.923
4.865
4.861
3.886
3.428
3.413
3.398
2.818
2.479
2.464
2.449
Me
2e
1.00
0.97
1.00
0.97
1.99
1.99
3.05
1.96
f1 (ppm)

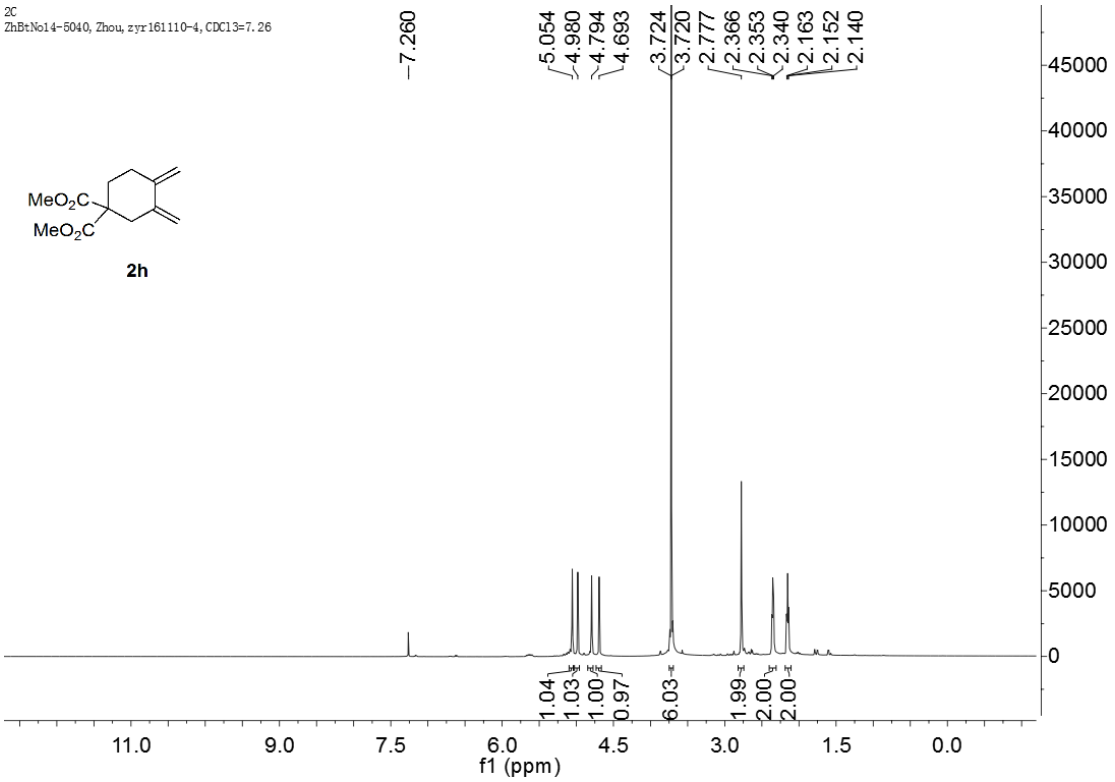

20171220B
ZhBtDe20-4161, Zhou, zyr-171219-1, CDCl3
143.098
141.572
111.517
111.490
77.419
77.101
76.784
51.411
46.118
36.883
33.168
Me
2e
f1 (ppm)

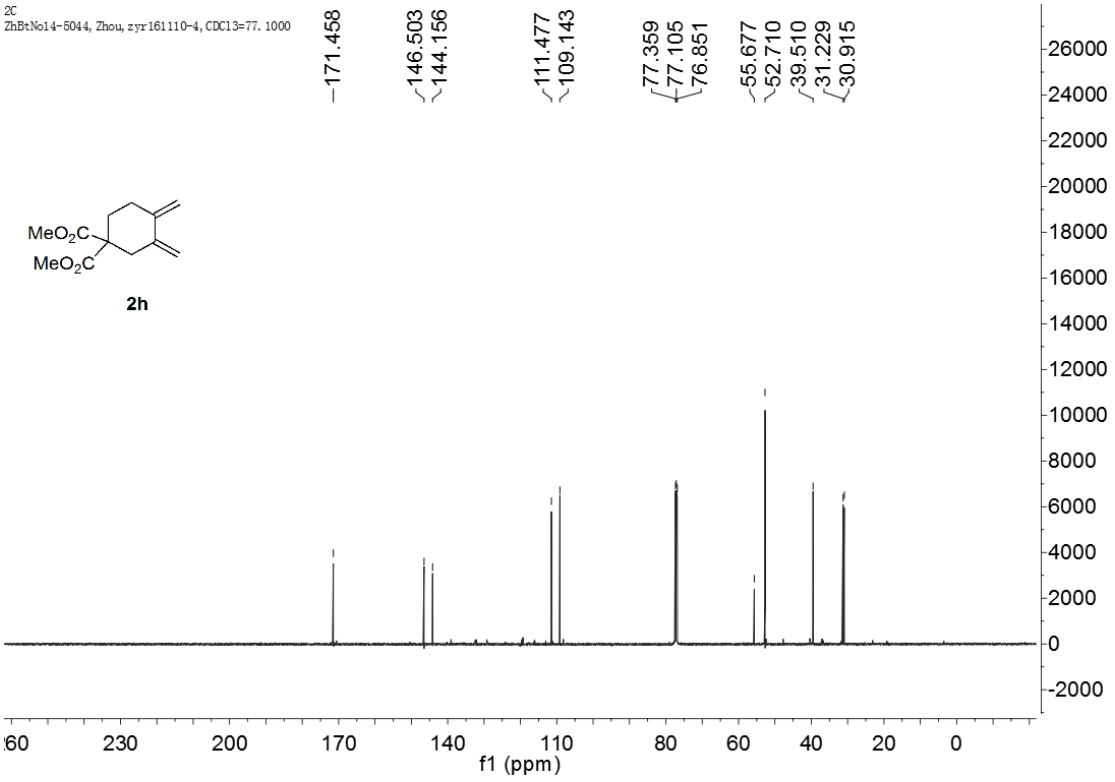

20161114D
ZhBtNo14-5036, Zhou, zyr161110-1, CDCl3=7.26, 333K
7.260
5.169
5.165
5.163
4.844
4.805
4.802
4.015
3.504
3.492
3.480
2.388
2.375
2.363
1.474
Boc
N
2f
2.00
0.96
1.02
1.96
2.01
2.00
9.42
f1 (ppm)

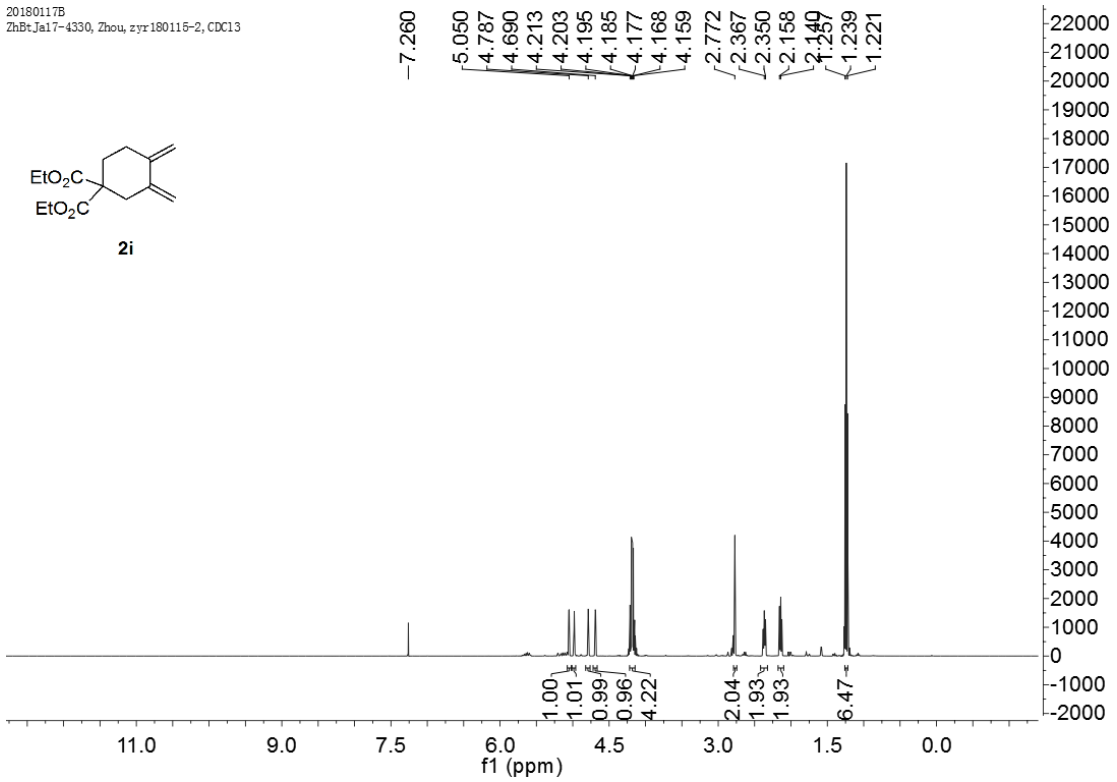

20161114D
ZhBtNo14-5034, Zhou, zyr161110-1, CDCl3=77.1000, 333K
154.897
144.722
143.322
109.823
109.701
79.777
77.358
77.104
76.850
49.742
44.148
33.545
28.625
Boc
N
2f
f1 (ppm)

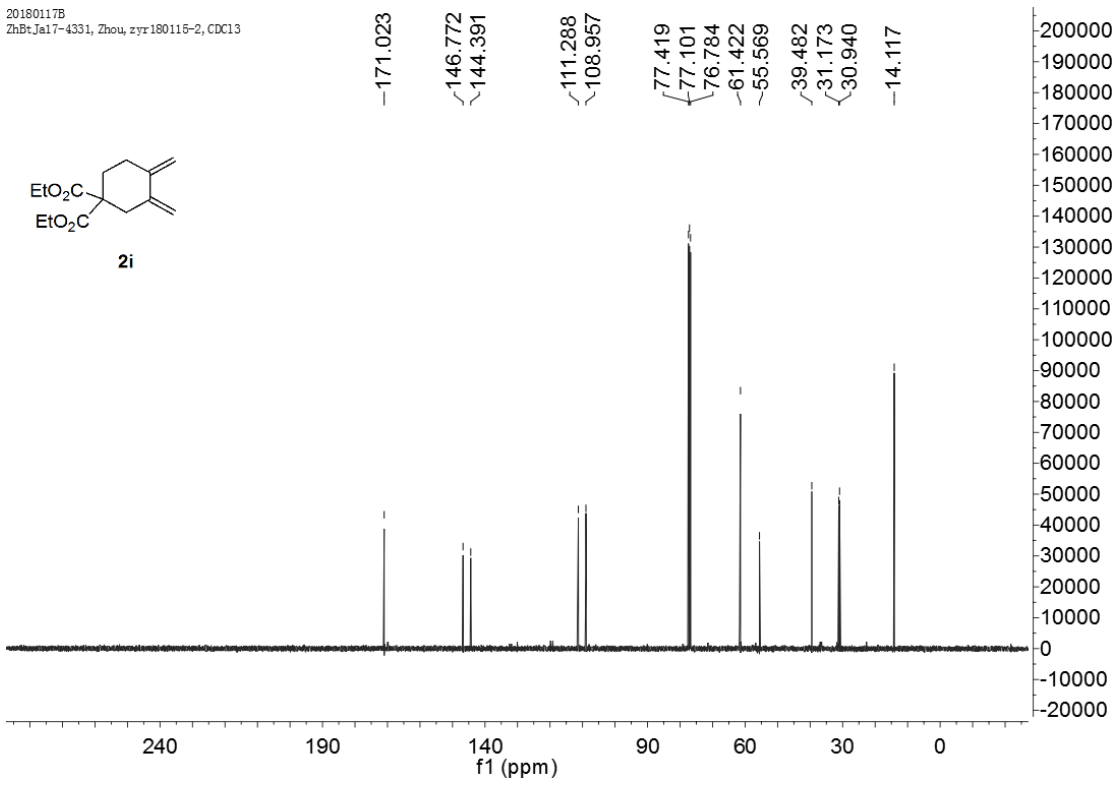

20161104D
7.361
7.353
7.351
7.319
7.313
7.311
7.307
7.302
7.260
5.196
5.187
5.185
5.160
4.825
4.107
3.591
3.579
3.567
2.417
2.405
2.393
Cbz
N
2g
5.17
2.01
2.10
0.95
1.00
1.98
1.99
1.98
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

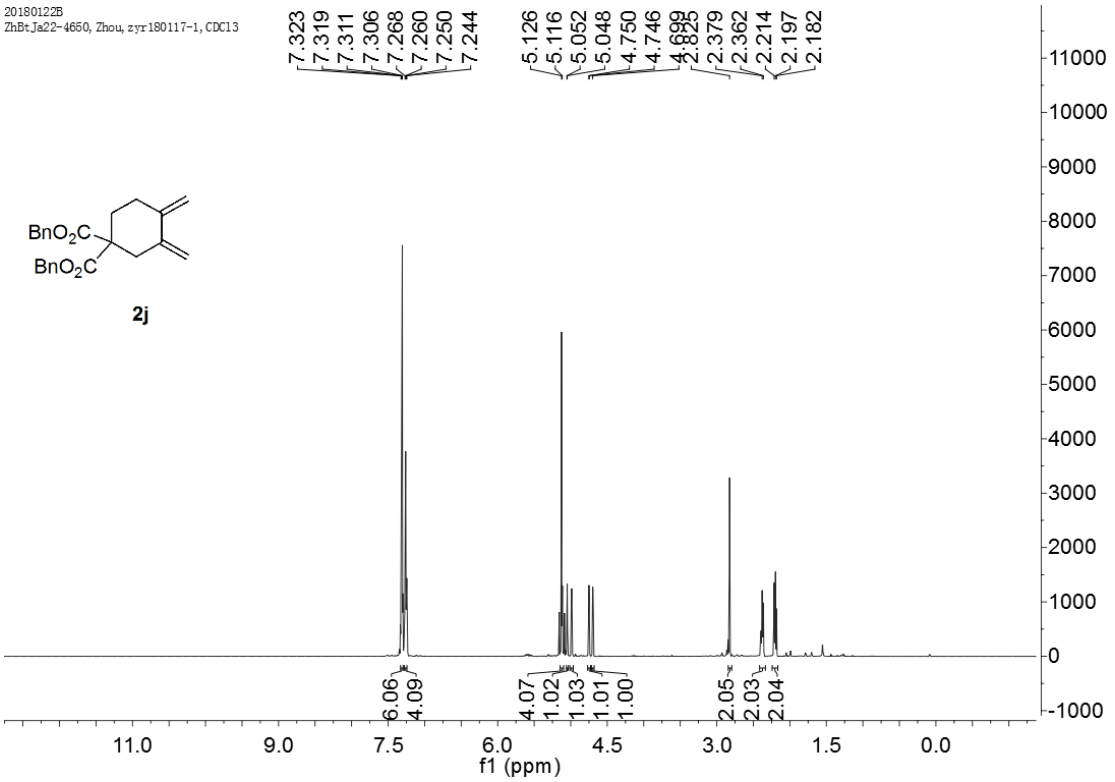

20161104D
155.408
144.255
142.820
137.155
128.599
128.063
127.961
110.167
110.139
77.359
77.105
76.851
67.295
49.723
44.276
33.375
Cbz
N
2g
230
200
170
140
110
80
60
40
20
0
f1 (ppm)

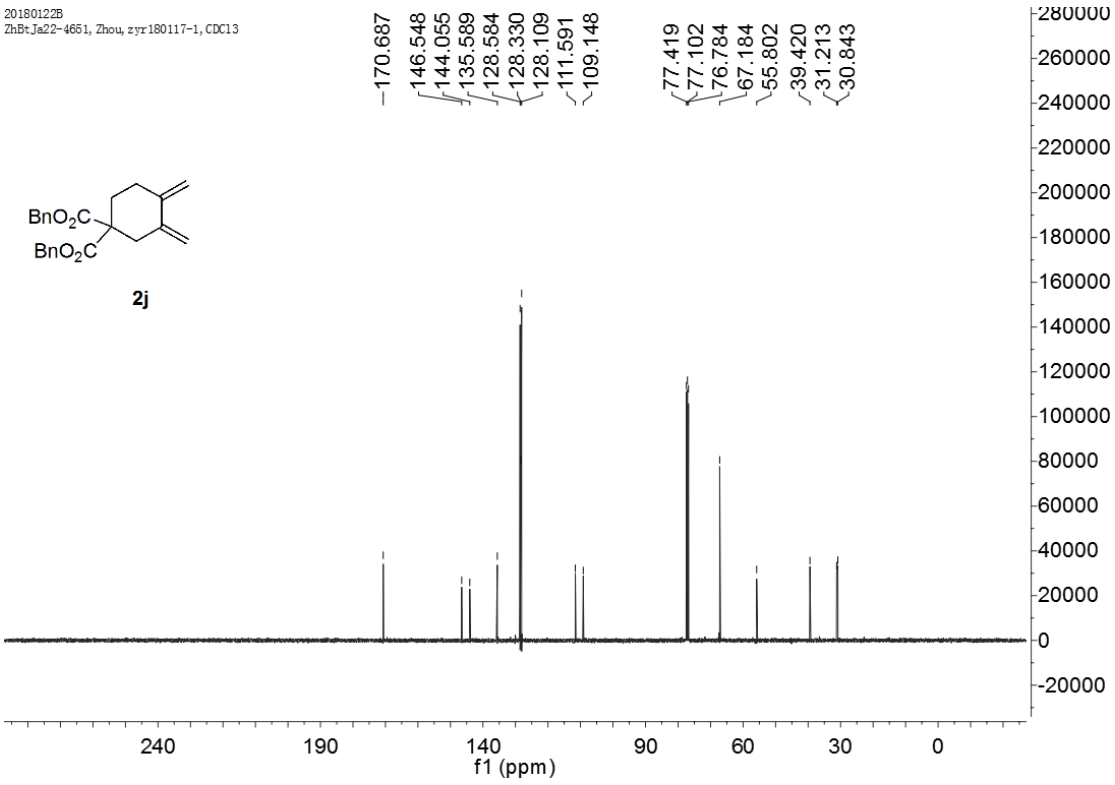

2C
ZhBtNo14-5040, Zhou, zyr161110-4, CDCl3=7.26
7.260
5.054
4.980
4.794
4.693
3.724
3.720
2.777
2.366
2.353
2.340
2.163
2.152
2.140
MeO2C
MeO2C
2h
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
1.04
1.03
1.00
0.97
6.03
1.99
2.00
2.00
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

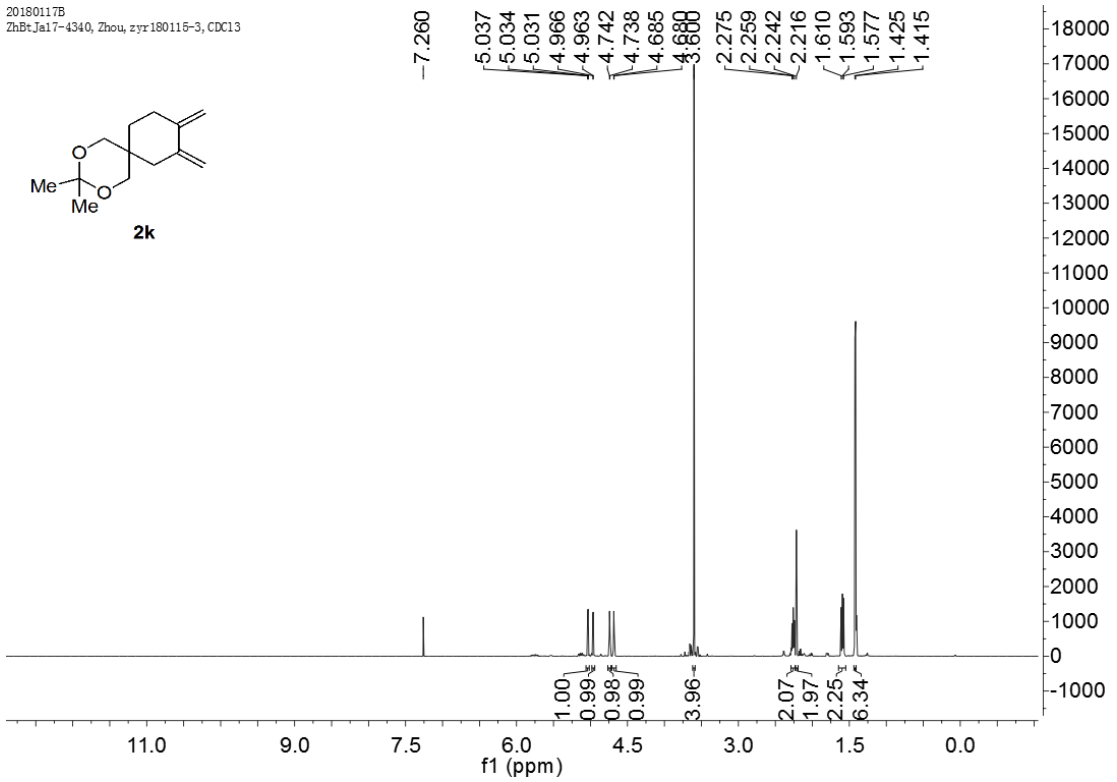

2C
ZhBtNo14-5044, Zhou, zyr161110-4, CDCl3=77.1000
171.458
146.503
144.156
111.477
109.143
77.359
77.105
76.851
55.677
52.710
39.510
31.229
30.915
MeO2C
MeO2C
2h
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
230
200
170
140
110
80
60
40
20
0
f1 (ppm)

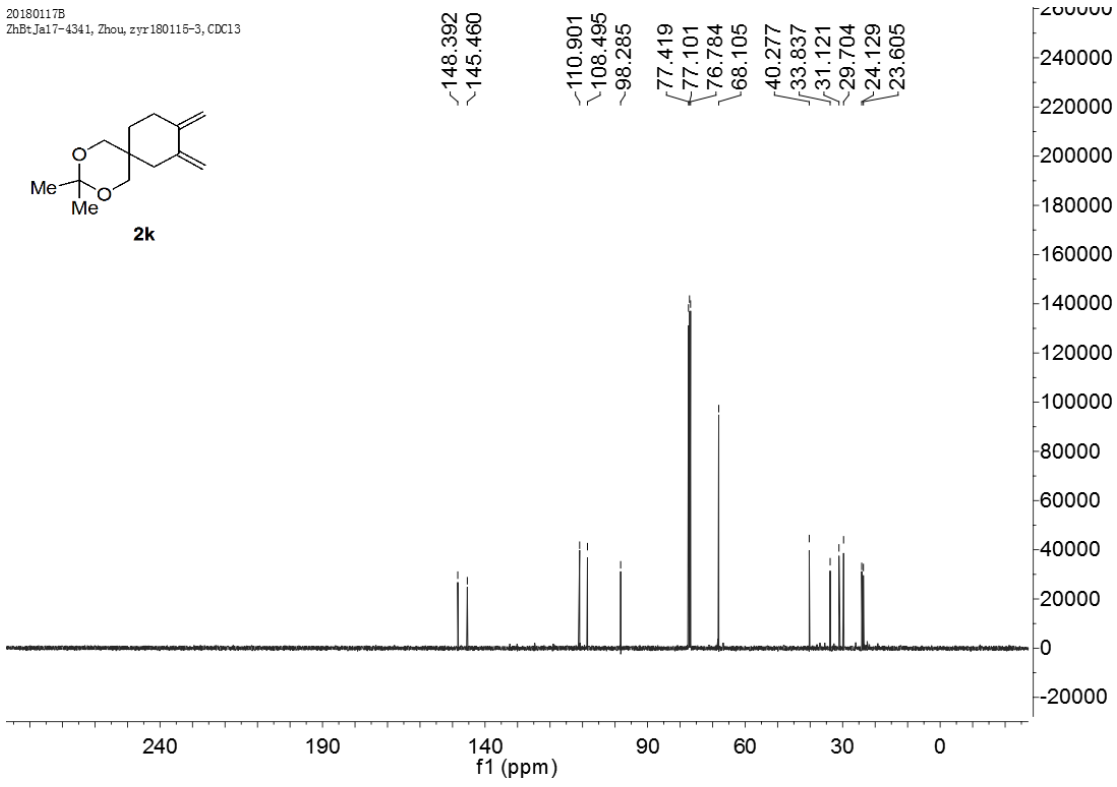

20180117B
ZhBtJa17-4330, Zhou, zyr180115-2, CDCl3
7.260
5.050
4.787
4.690
4.213
4.203
4.195
4.185
4.177
4.168
4.159
2.772
2.367
2.350
2.158
2.140
2.137
1.239
1.221
EtO2C
EtO2C
2i
1.00
1.01
0.99
0.96
4.22
2.04
1.93
1.93
6.47
f1 (ppm)

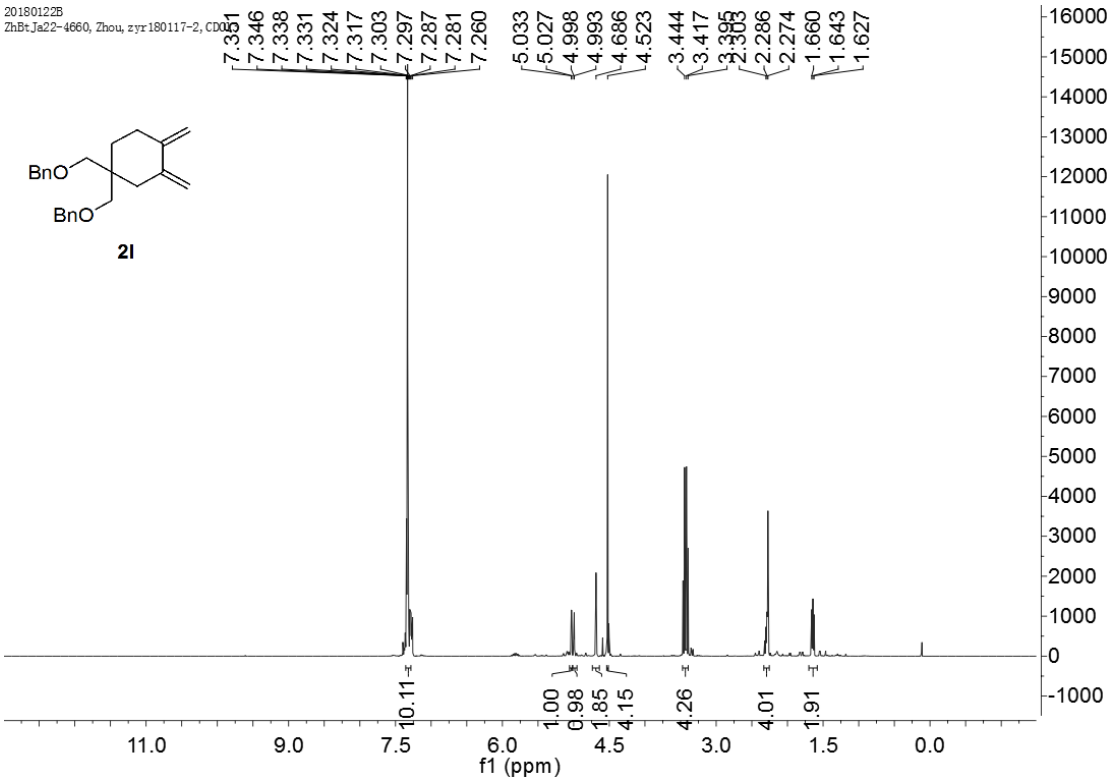

20180117B
ZhBtJa17-4331, Zhou, zyr180115-2, CDCl3
171.023
146.772
144.391
111.288
108.957
77.419
77.101
76.784
61.422
55.569
39.482
31.173
30.940
14.117
EtO2C
EtO2C
2i
f1 (ppm)

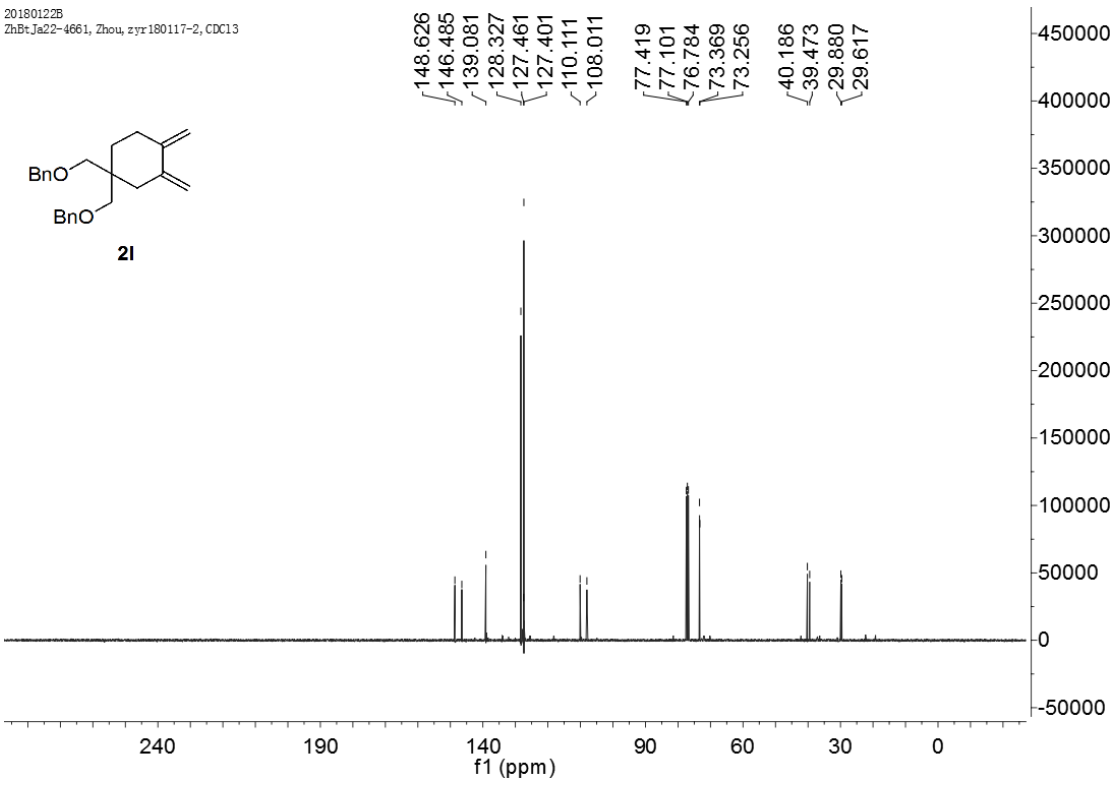

20180122B
ZhBtJa22-4650, Zhou, zyr180117-1, CDCl3
7.323
7.319
7.311
7.306
7.268
7.260
7.250
7.244
5.126
5.116
5.052
5.048
4.750
4.746
4.689
4.685
2.379
2.362
2.214
2.197
2.182
BnO2C
BnO2C
2j
6.06
4.09
4.07
1.02
1.03
1.01
1.00
2.05
2.03
2.04
f1 (ppm)

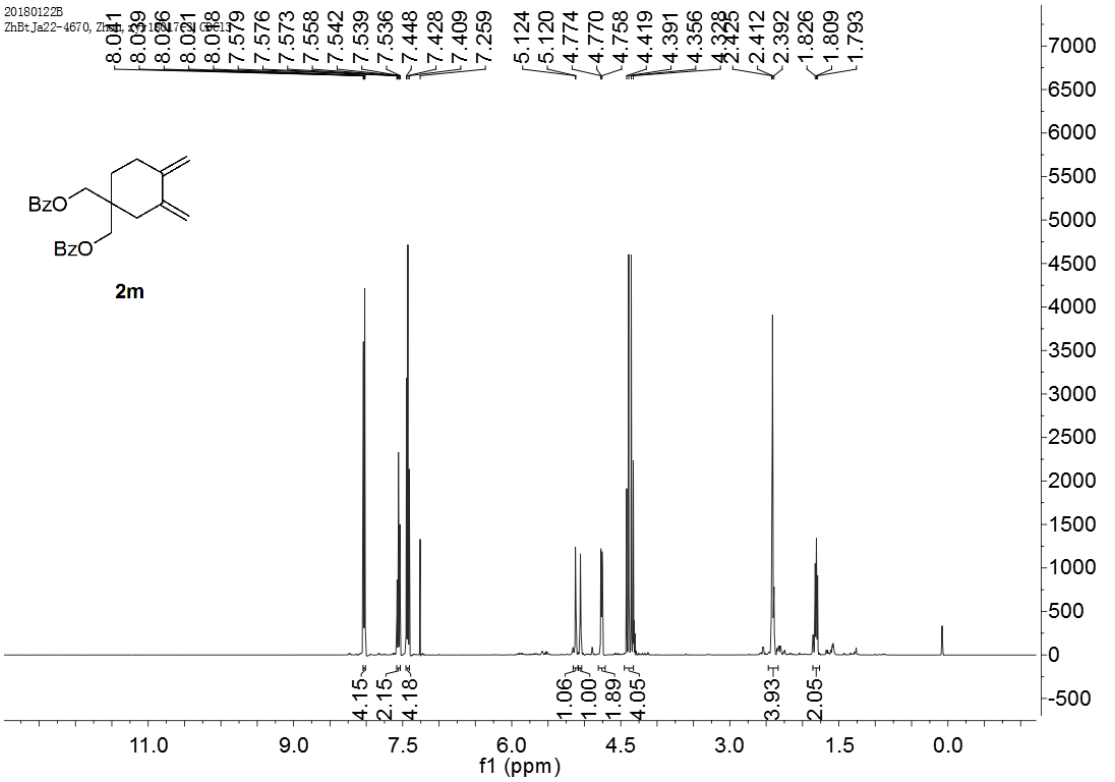

20180122B
ZhBtJa22-4651, Zhou, zyr180117-1, CDCl3
170.687
146.548
144.055
135.589
128.584
128.330
128.109
111.591
109.148
77.419
77.102
76.784
67.184
55.802
39.420
31.213
30.843
BnO2C
BnO2C
2j
f1 (ppm)

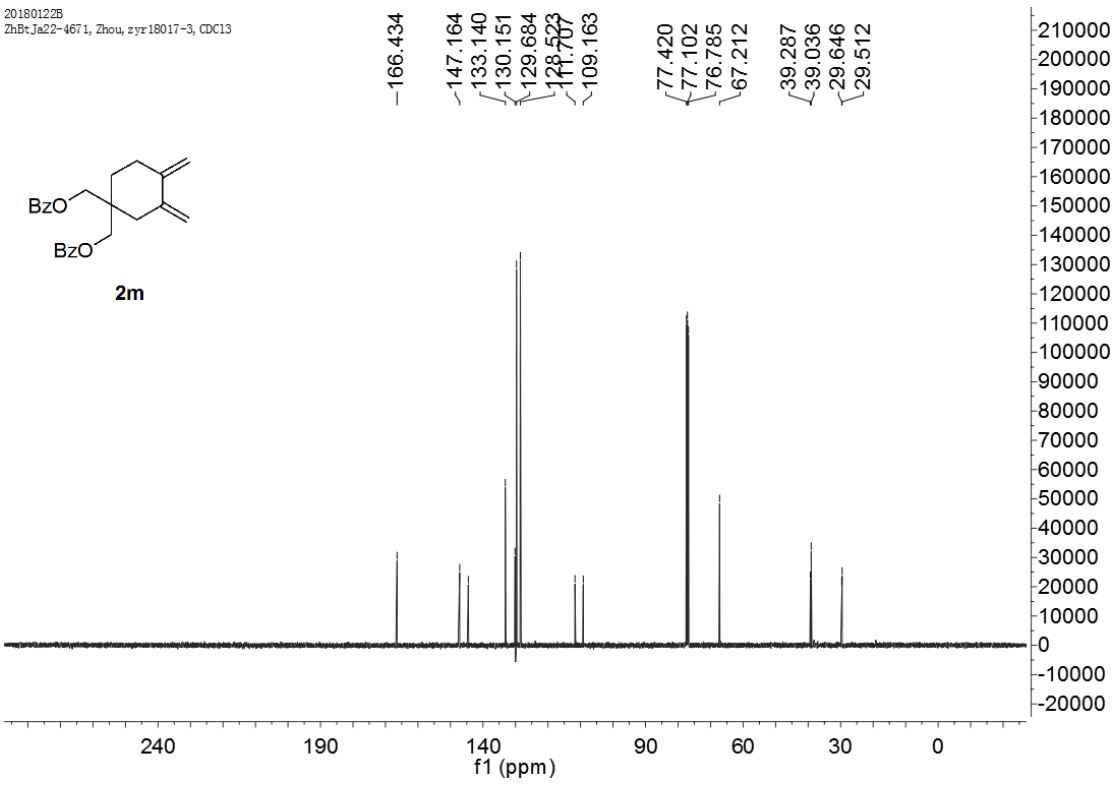

20180117B
ZhBtJa17-4340, Zhou, zyr180115-3, CDCl3
Me
Me
2k
7.260
5.037
5.034
5.031
4.966
4.963
4.742
4.738
4.685
4.680
3.800
2.275
2.259
2.242
2.216
1.610
1.593
1.577
1.425
1.415
1.00
0.99
0.98
0.99
3.96
2.07
1.97
2.25
6.34
f1 (ppm)

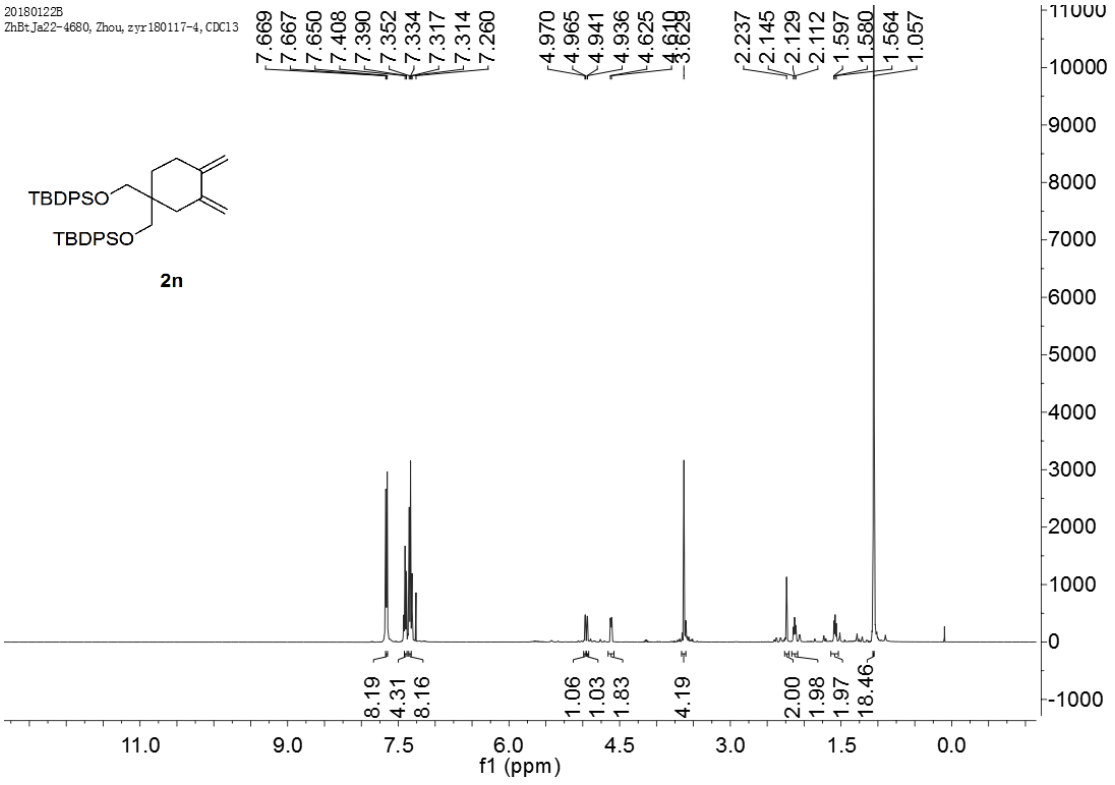

20180117B
ZhBtJa17-4341, Zhou, zyr180115-3, CDCl3
Me
Me
2k
148.392
145.460
110.901
108.495
98.285
77.419
77.101
76.784
68.105
40.277
33.837
31.121
29.704
24.129
23.605
f1 (ppm)

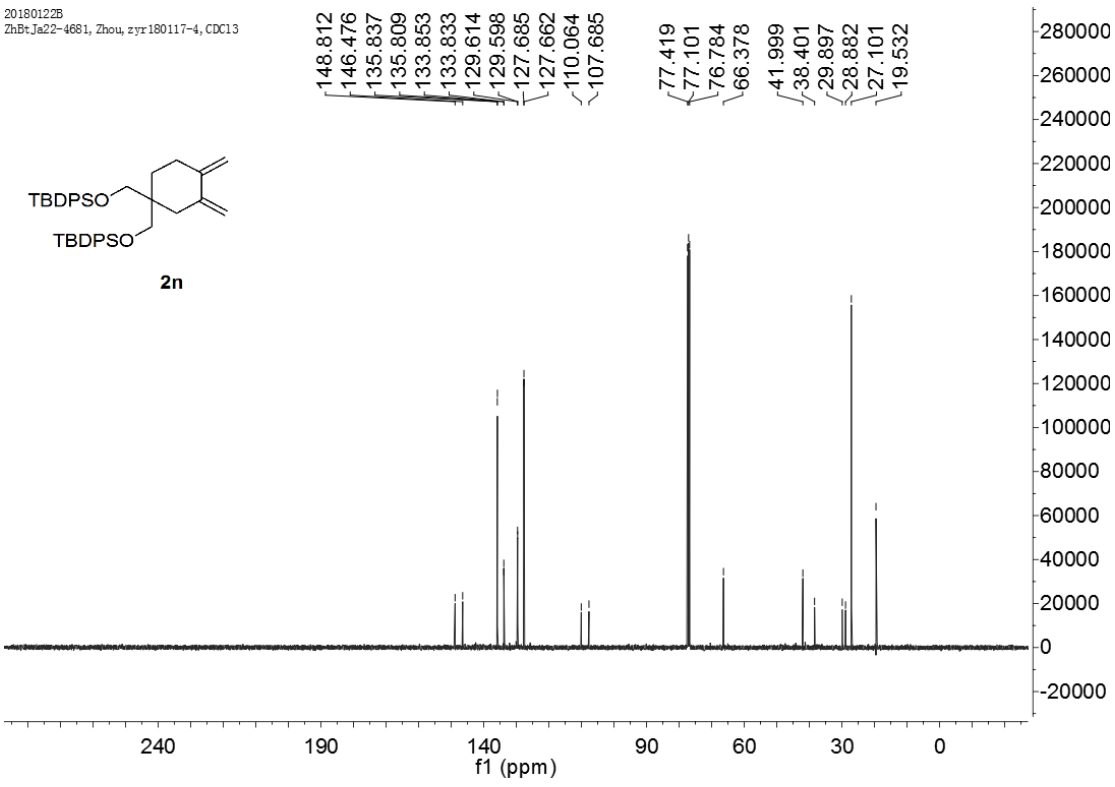

20180122B
ZhBtJa22-4660, Zhou, zyr180117-2, CDCl3
7.351
7.346
7.338
7.331
7.324
7.317
7.303
7.297
7.287
7.281
7.260
5.033
5.027
4.998
4.993
4.686
4.523
3.444
3.417
3.395
3.303
2.286
2.274
1.660
1.643
1.627
BnO
BnO
2l
10.11
1.00
0.98
1.85
4.15
4.26
4.01
1.91
f1 (ppm)

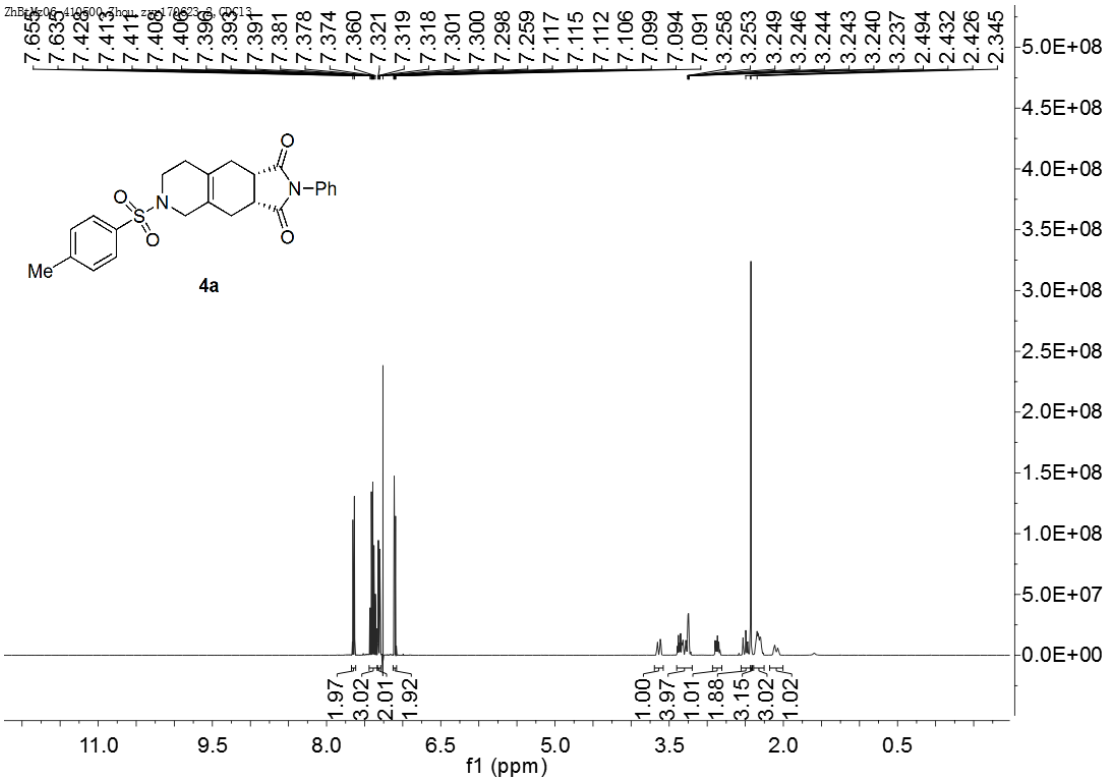

20180122B
ZhBtJa22-4661, Zhou, zyr180117-2, CDCl3
148.626
146.485
139.081
128.327
127.461
127.401
110.111
108.011
77.419
77.101
76.784
73.369
73.256
40.186
39.473
29.880
29.617
BnO
BnO
2l
f1 (ppm)

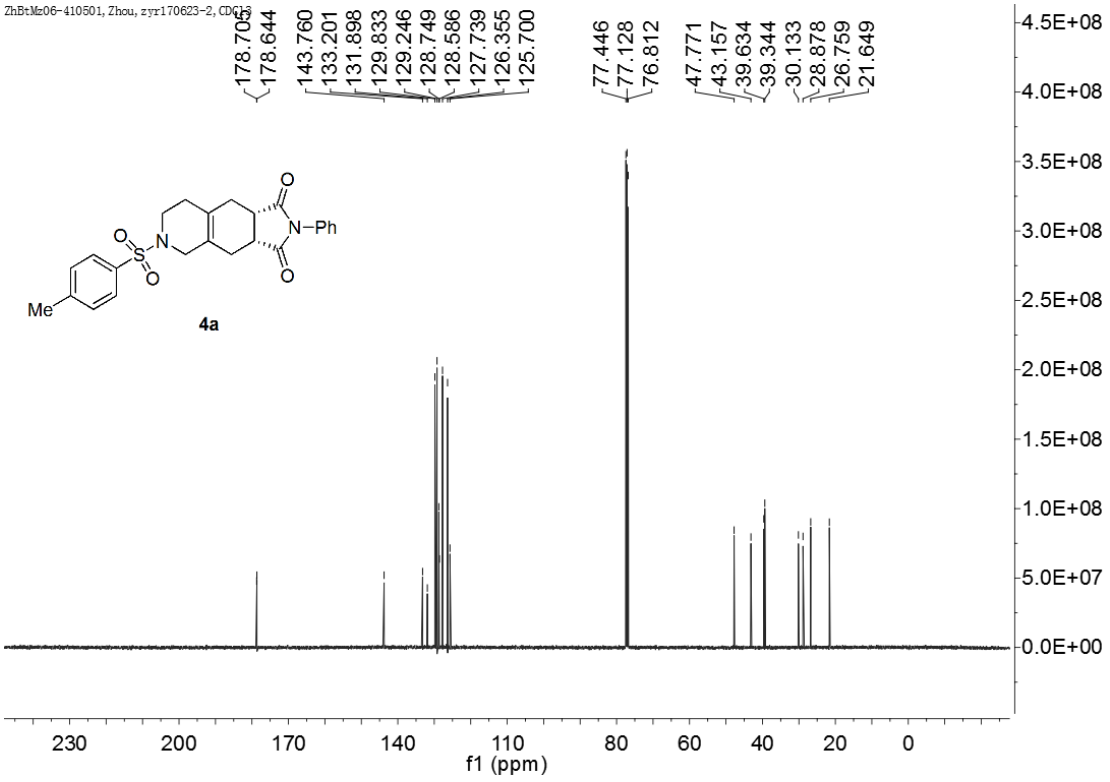

20180122B
8.041
8.039
8.026
8.021
8.018
7.579
7.576
7.573
7.558
7.542
7.539
7.536
7.448
7.428
7.409
7.259
5.124
5.120
4.774
4.770
4.758
4.419
4.391
4.356
2.425
2.412
2.392
1.826
1.809
1.793
BzO
BzO
2m
4.15
2.15
4.18
1.06
1.00
1.89
4.05
3.93
2.05
f1 (ppm)

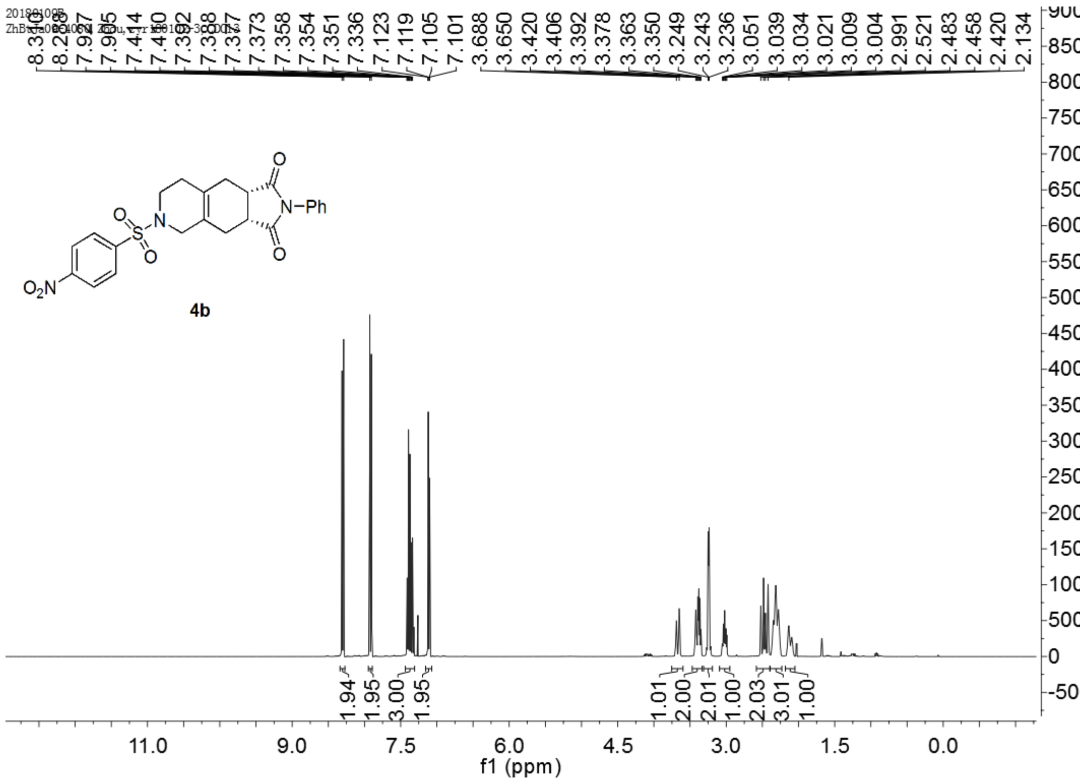

20180122B
ZhBtJa22-4671, Zhou, zyr18017-3, CDCl3
166.434
147.164
133.140
130.151
129.684
128.523
111.707
109.163
77.420
77.102
76.785
67.212
39.287
39.036
29.646
29.512
BzO
BzO
2m
f1 (ppm)

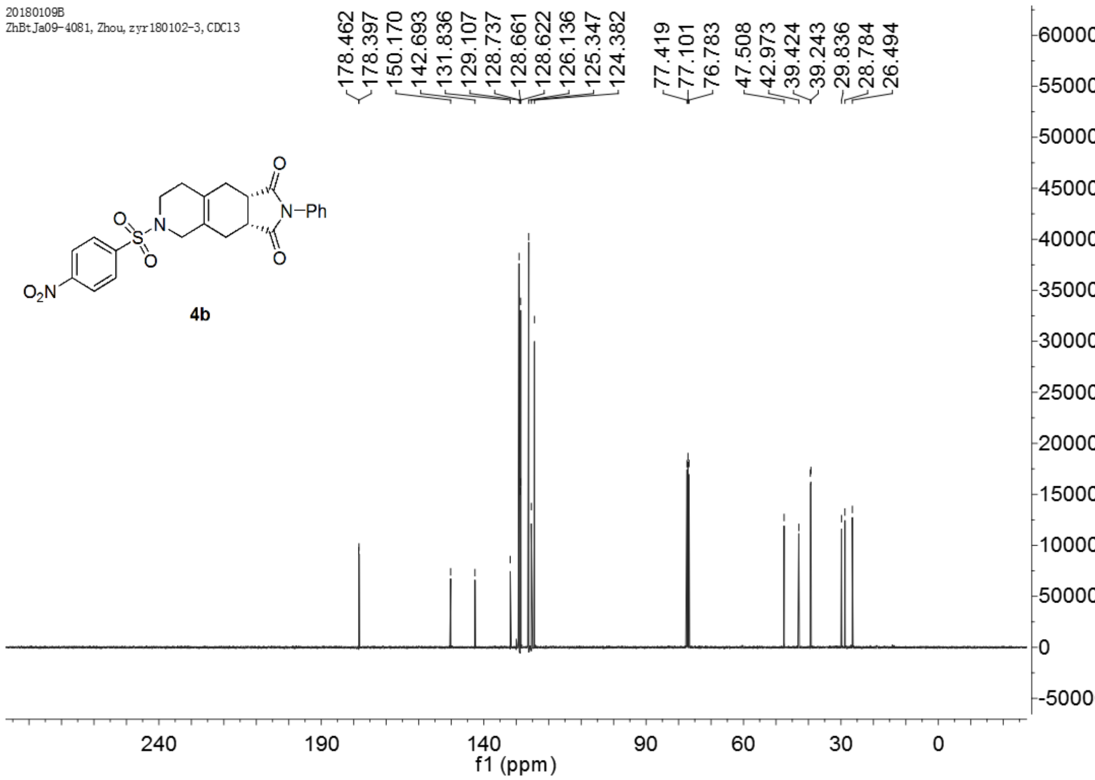

20180122B
ZhBtJa22-4680, Zhou, zyr180117-4, CDCl3
7.669
7.667
7.650
7.408
7.390
7.352
7.334
7.317
7.314
7.260
4.970
4.965
4.941
4.936
4.625
4.610
3.629
2.237
2.145
2.129
2.112
1.597
1.580
1.564
1.057
TBDPSO
TBDPSO
2n
8.19
4.31
8.16
1.06
1.03
1.83
4.19
2.00
1.98
1.97
18.46
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

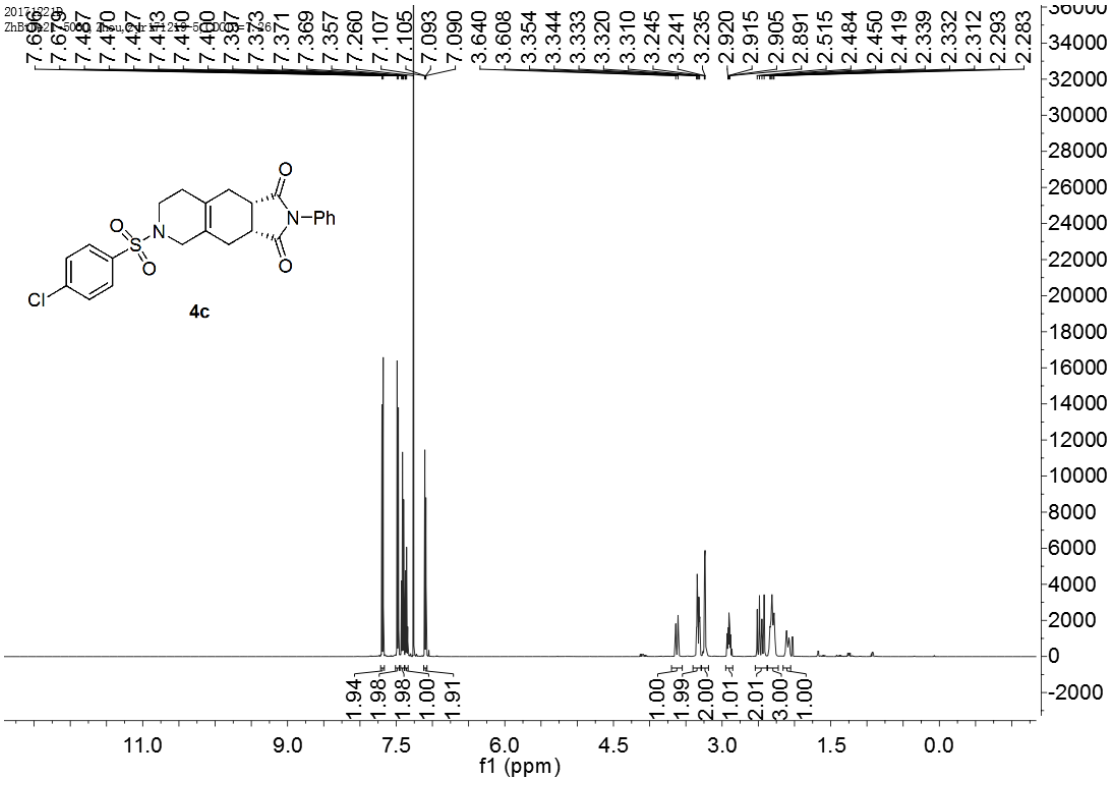

20180122B
ZhBtJa22-4681, Zhou, zyr180117-4, CDCl3
148.812
146.476
135.837
135.809
133.853
133.833
129.614
129.598
127.685
127.662
110.064
107.685
77.419
77.101
76.784
66.378
41.999
38.401
29.897
28.882
27.101
19.532
TBDPSO
TBDPSO
2n
240
190
140
90
60
30
0
f1 (ppm)

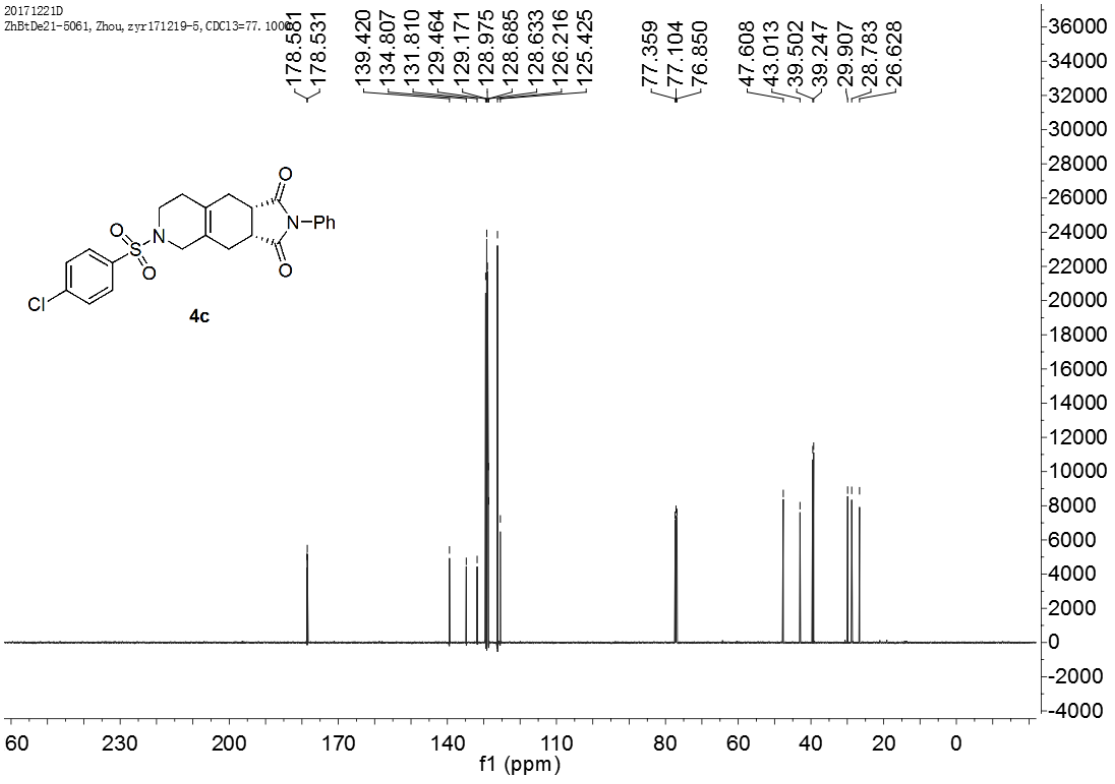

7.655
7.635
7.429
7.413
7.411
7.408
7.406
7.396
7.393
7.391
7.381
7.378
7.374
7.360
7.321
7.319
7.318
7.301
7.300
7.298
7.259
7.117
7.115
7.112
7.106
7.099
7.094
7.091
3.258
3.253
3.249
3.246
3.244
3.243
3.240
3.237
2.494
2.432
2.426
2.345
N–Ph
Me
4a
1.97
3.02
2.01
1.92
1.00
3.97
1.01
1.88
3.15
3.02
1.02
11.0
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00

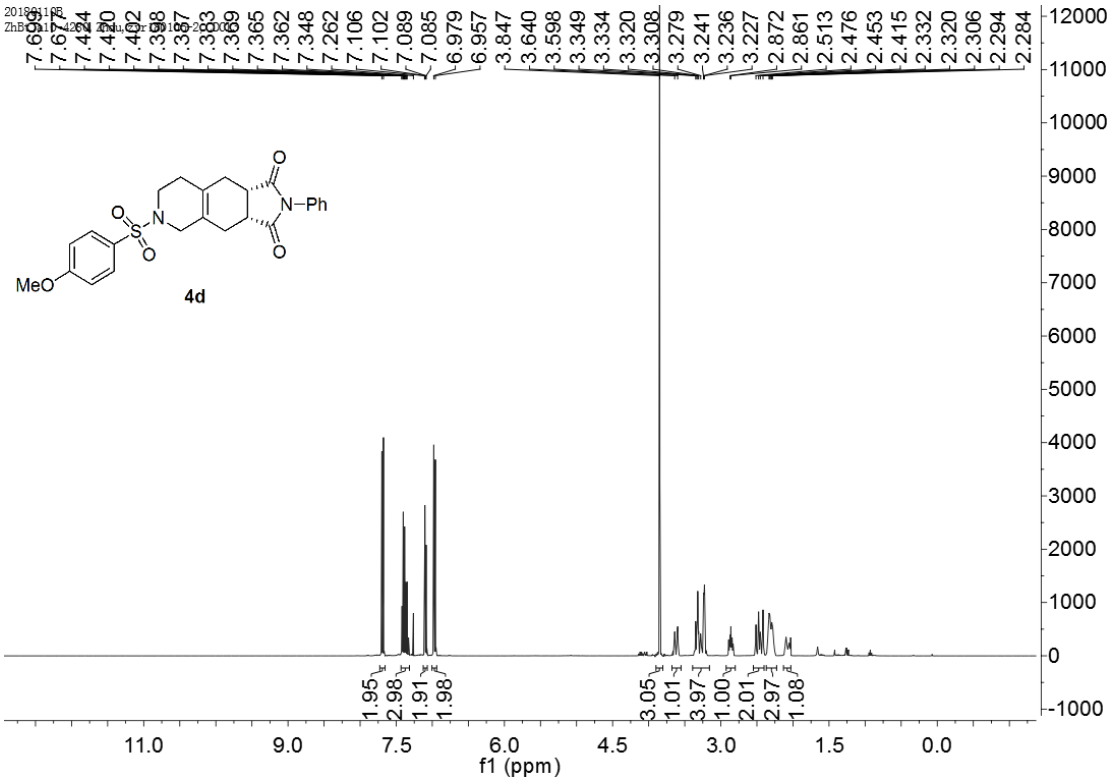

178.705
178.644
143.760
133.201
131.898
129.833
129.246
128.749
128.586
127.739
126.355
125.700
77.446
77.128
76.812
47.771
43.157
39.634
39.344
30.133
28.878
26.759
21.649
N–Ph
Me
4a
230
200
170
140
110
80
60
40
20
0
f1 (ppm)
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00

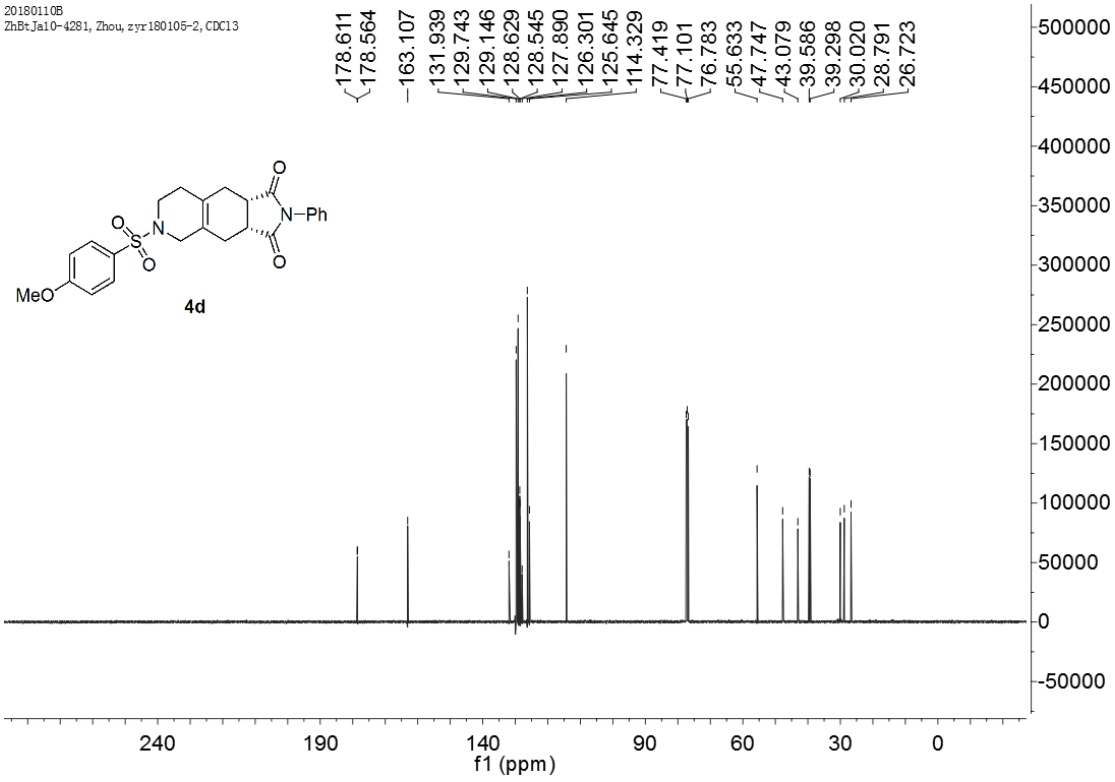

20180109B
8.340
8.2..
7.987
7.965
7.414
7.400
7.392
7.388
7.377
7.373
7.358
7.354
7.351
7.336
7.123
7.119
7.105
7.101
3.688
3.650
3.420
3.406
3.392
3.378
3.363
3.350
3.249
3.243
3.236
3.051
3.039
3.034
3.021
3.009
3.004
2.991
2.521
2.483
2.458
2.420
2.134
N–Ph
4b
1.94
1.95
3.00
1.95
1.01
2.00
2.01
1.00
2.03
3.01
1.00
f1 (ppm)

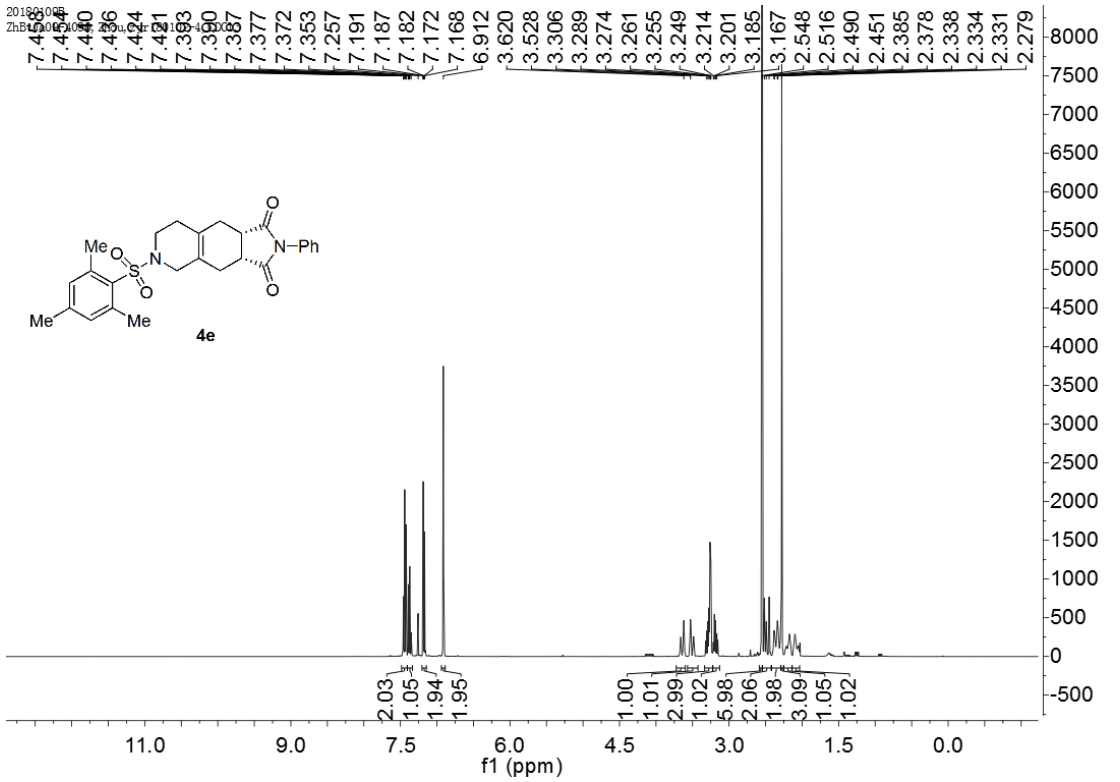

20180109B
ZhBtJa09-4081, Zhou, zyr180102-3, CDCl3
178.462
178.397
150.170
142.693
131.836
129.107
128.737
128.661
128.622
126.136
125.347
124.382
77.419
77.101
76.783
47.508
42.973
39.424
39.243
29.836
28.784
26.494
N–Ph
4b
f1 (ppm)

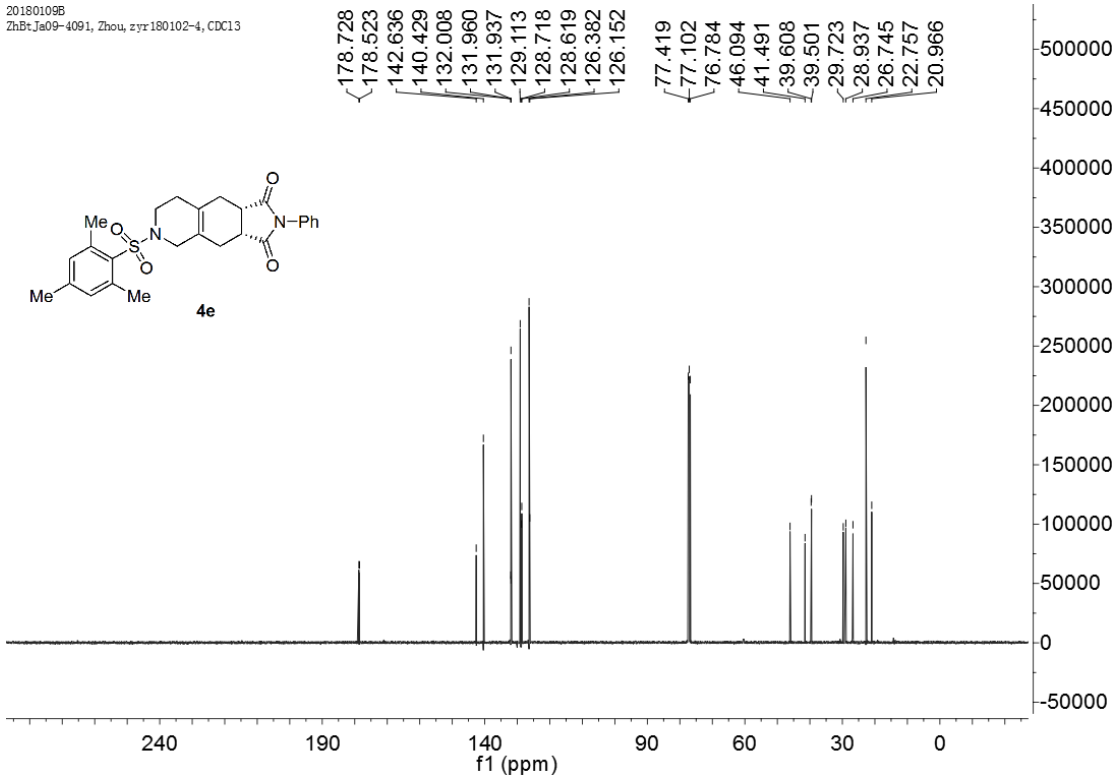

7.696
7.693
7.487
7.480
7.427
7.413
7.410
7.400
7.397
7.373
7.371
7.369
7.357
7.260
7.107
7.105
7.093
7.090
3.640
3.608
3.354
3.344
3.333
3.320
3.310
3.245
3.241
3.235
2.920
2.915
2.905
2.891
2.515
2.484
2.450
2.419
2.339
2.332
2.312
2.293
2.283
1.94
1.98
1.98
1.00
1.91
1.00
1.99
2.00
1.01
2.01
3.00
1.00
f1 (ppm)
4c

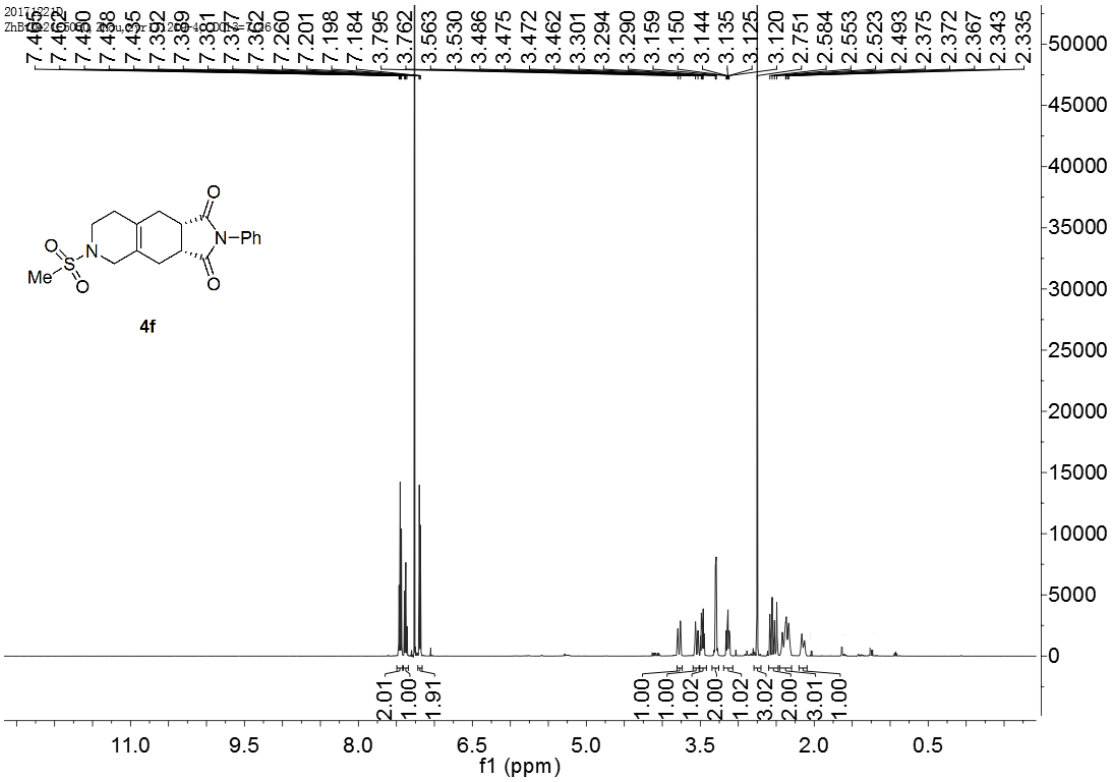

20171221D
178.581
178.531
139.420
134.807
131.810
129.464
129.171
128.975
128.685
128.633
126.216
125.425
77.359
77.104
76.850
47.608
43.013
39.502
39.247
29.907
28.783
26.628
f1 (ppm)
4c

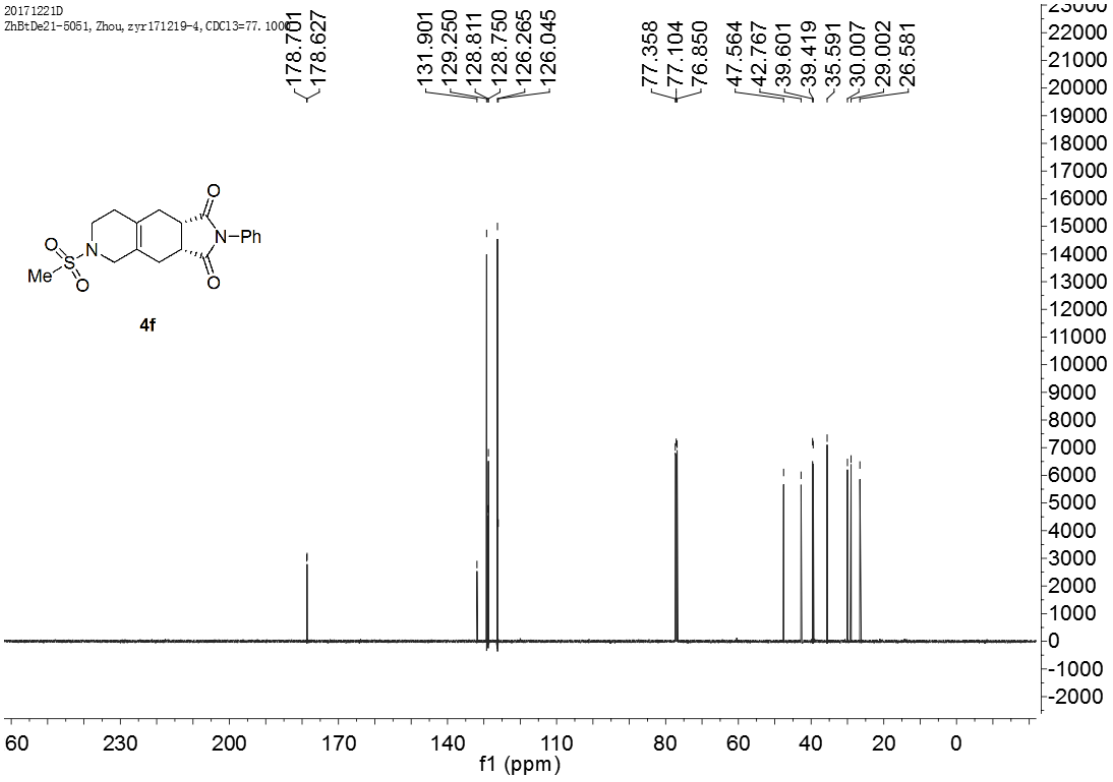

7.693
7.672
7.444
7.440
7.402
7.398
7.387
7.383
7.369
7.365
7.362
7.348
7.262
7.106
7.102
7.089
7.085
6.979
6.957
3.847
3.640
3.598
3.349
3.334
3.320
3.308
3.279
3.241
3.236
3.227
2.872
2.861
2.513
2.476
2.453
2.415
2.332
2.320
2.306
2.294
2.284
1.95
2.98
1.91
1.98
3.05
1.01
3.97
1.00
2.01
2.97
1.08
f1 (ppm)
4d

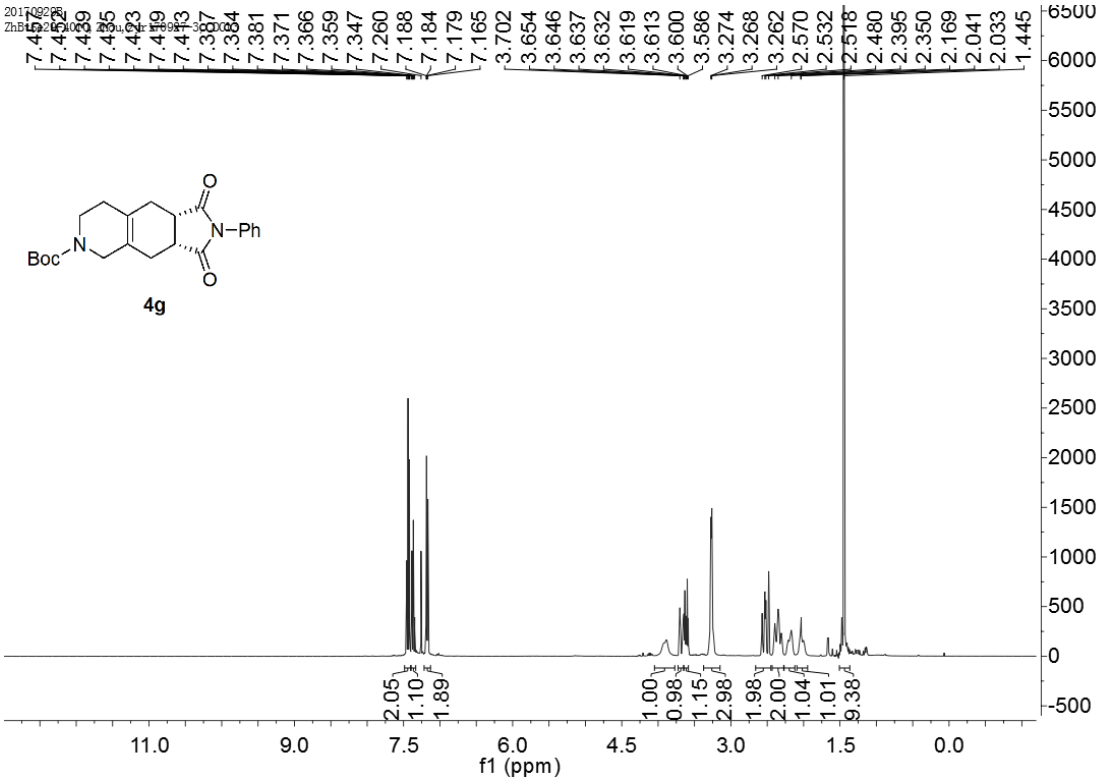

20180110B
ZhBtJa10-4281, Zhou, zyr180105-2, CDCl3
178.611
178.564
163.107
131.939
129.743
129.146
128.629
128.545
127.890
126.301
125.645
114.329
77.419
77.101
76.783
55.633
47.747
43.079
39.586
39.298
30.020
28.791
26.723
f1 (ppm)
4d

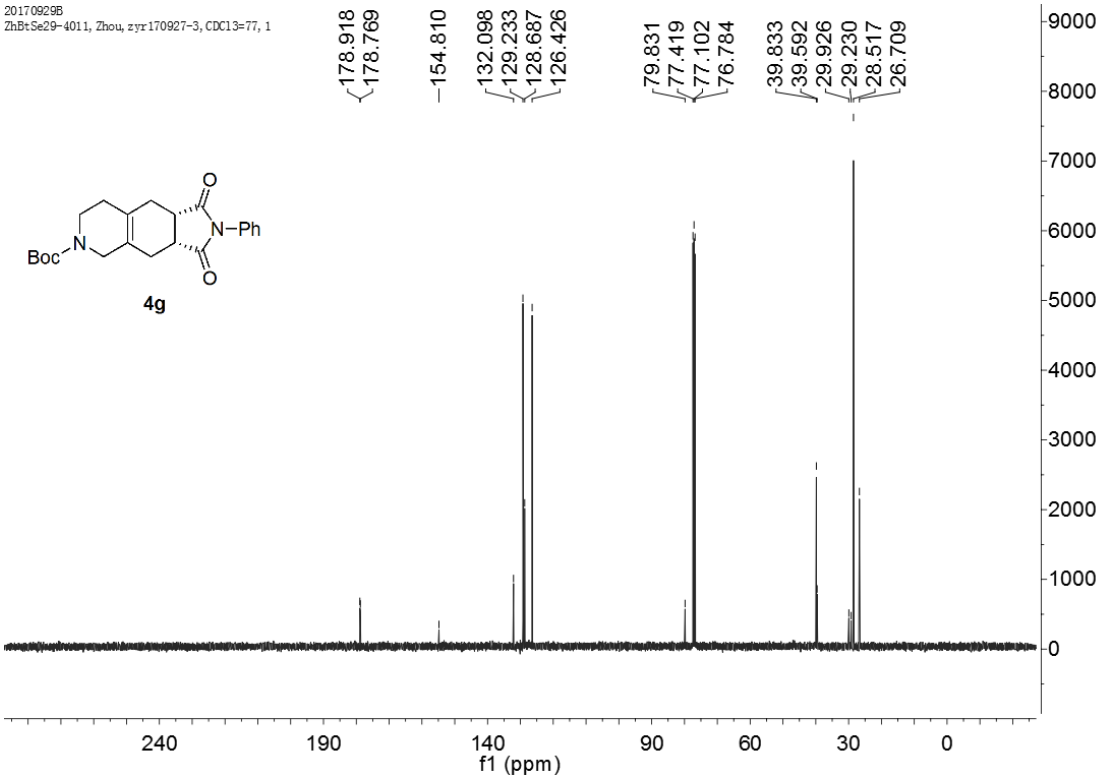

7.443
7.440
7.436
7.424
7.421
7.393
7.390
7.387
7.377
7.372
7.353
7.257
7.191
7.187
7.182
7.172
7.168
6.912
3.620
3.528
3.306
3.289
3.274
3.261
3.255
3.249
3.214
3.201
3.185
3.167
2.548
2.516
2.490
2.451
2.385
2.378
2.338
2.334
2.331
2.279
2.03
1.05
1.94
1.95
1.00
1.01
2.99
1.02
5.98
2.06
1.98
3.09
1.05
1.02
f1 (ppm)
Me
Me
Me
N–Ph
4e

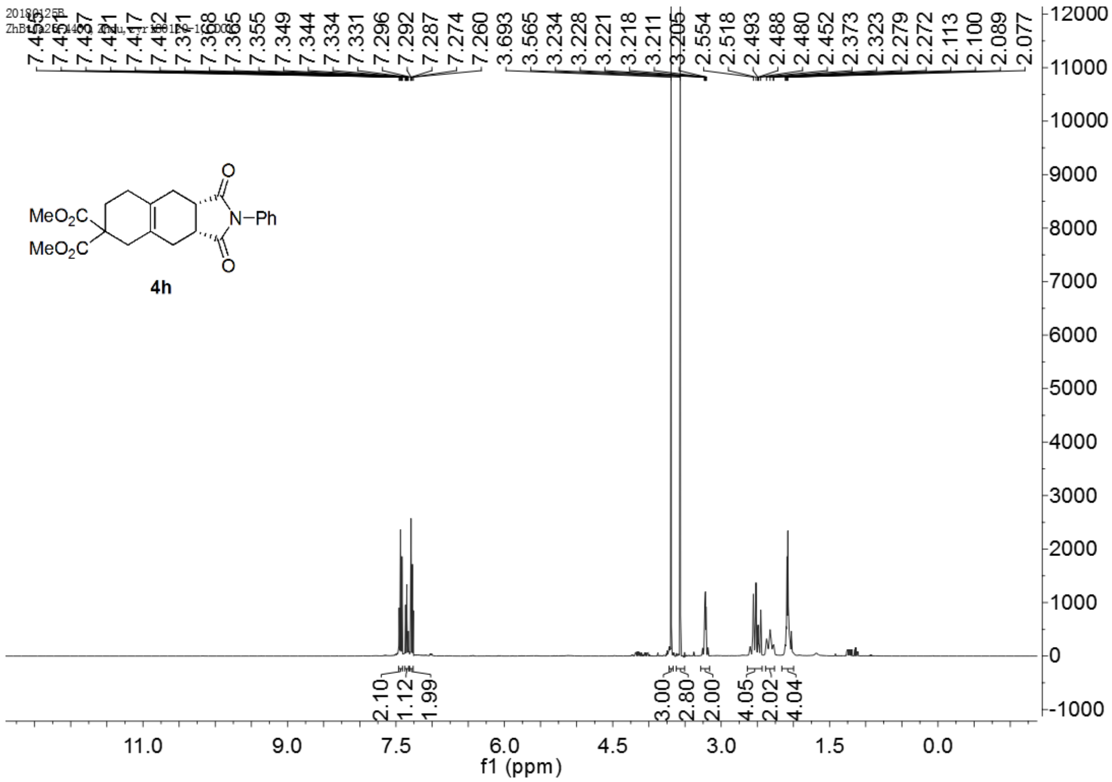

20180109B
ZhBtJa09-4091, Zhou, zyr180102-4, CDCl3
178.728
178.523
142.636
140.429
132.008
131.960
131.937
129.113
128.718
128.619
126.382
126.152
77.419
77.102
76.784
46.094
41.491
39.608
39.501
29.723
28.937
26.745
22.757
20.966
f1 (ppm)
Me
Me
Me
N–Ph
4e

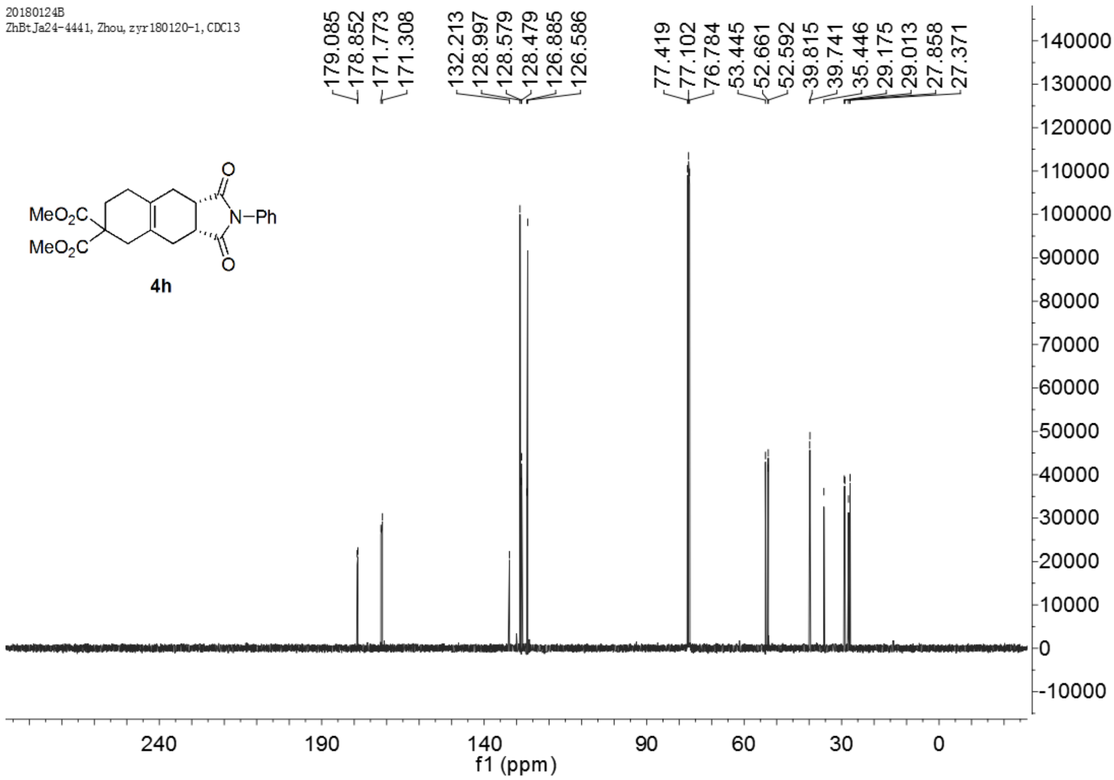

4f
f1 (ppm)

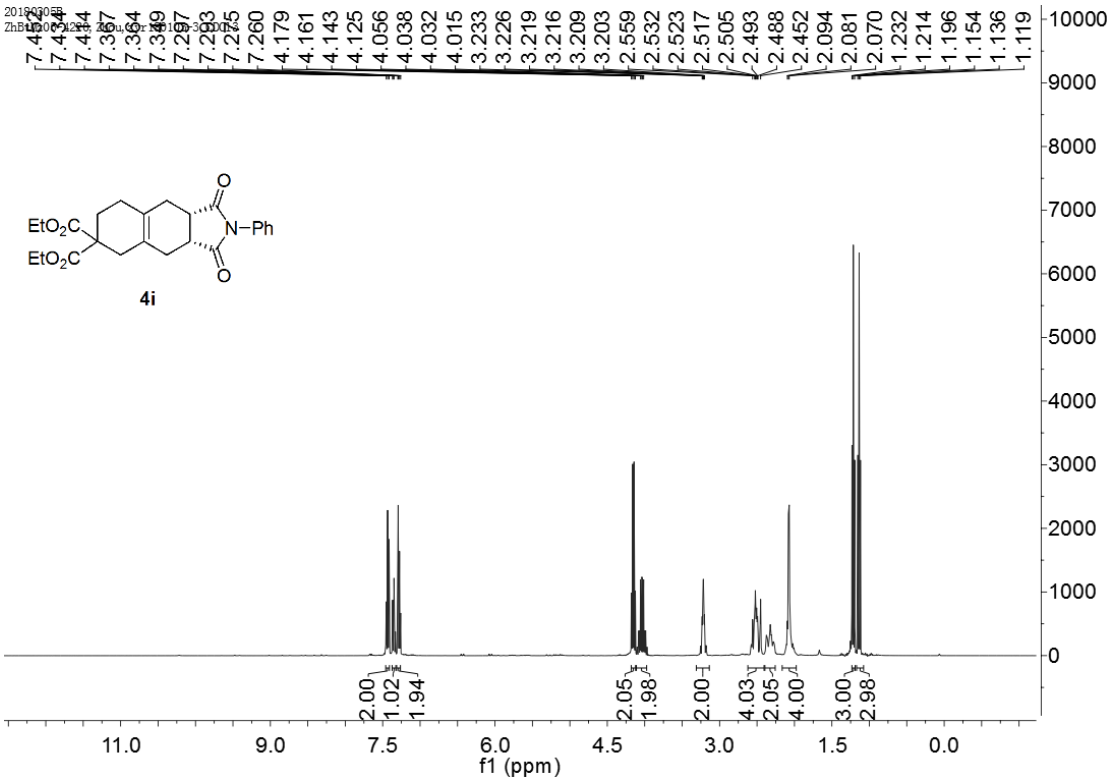

4f
f1 (ppm)

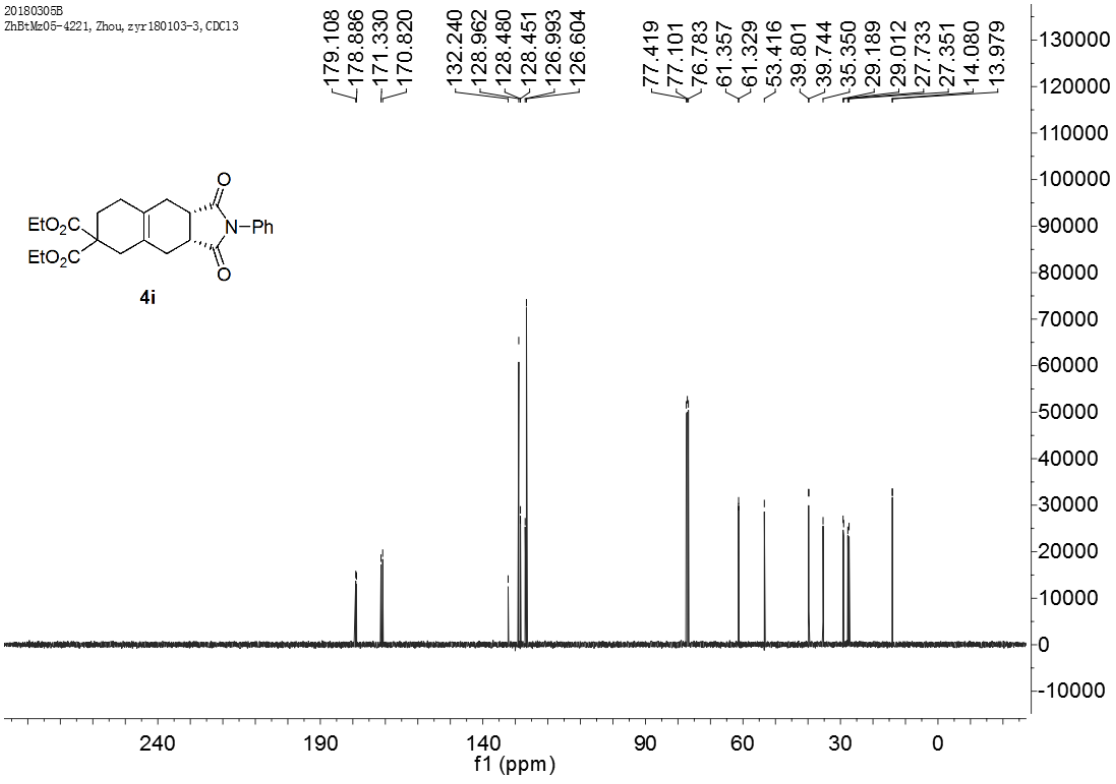

7.452
7.439
7.435
7.423
7.419
7.413
7.387
7.384
7.381
7.371
7.366
7.359
7.347
7.260
7.188
7.184
7.179
7.165
3.702
3.654
3.646
3.637
3.632
3.619
3.613
3.600
3.586
3.274
3.268
3.262
2.570
2.532
2.518
2.480
2.395
2.350
2.169
2.041
2.033
1.445
Boc
N
N–Ph
O
O
O
4g
2.05
1.10
1.89
1.00
0.98
1.15
2.98
1.98
2.00
1.04
1.01
9.38
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

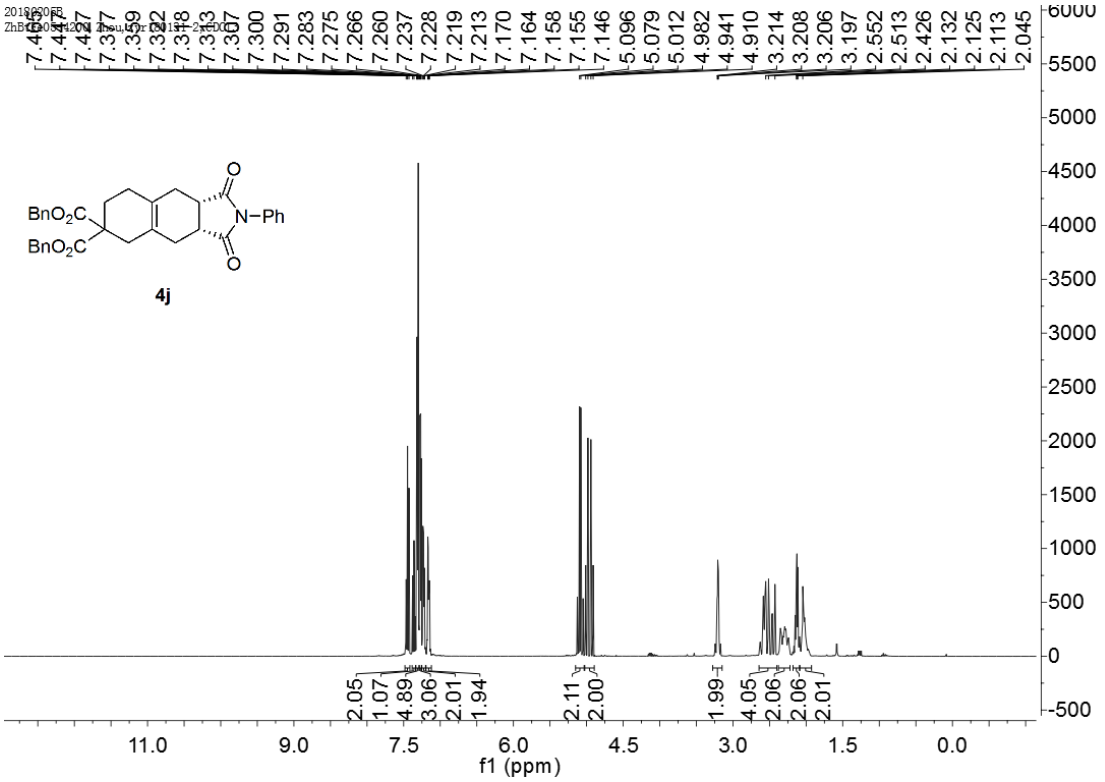

20170929B
ZhBtSe29-4011, Zhou, zyr170927-3, CDCl3=77, 1
178.918
178.769
154.810
132.098
129.233
128.687
126.426
79.831
77.419
77.102
76.784
39.833
39.592
29.926
29.230
28.517
26.709
Boc
N
N–Ph
O
O
O
4g
240
190
140
90
60
30
0
f1 (ppm)

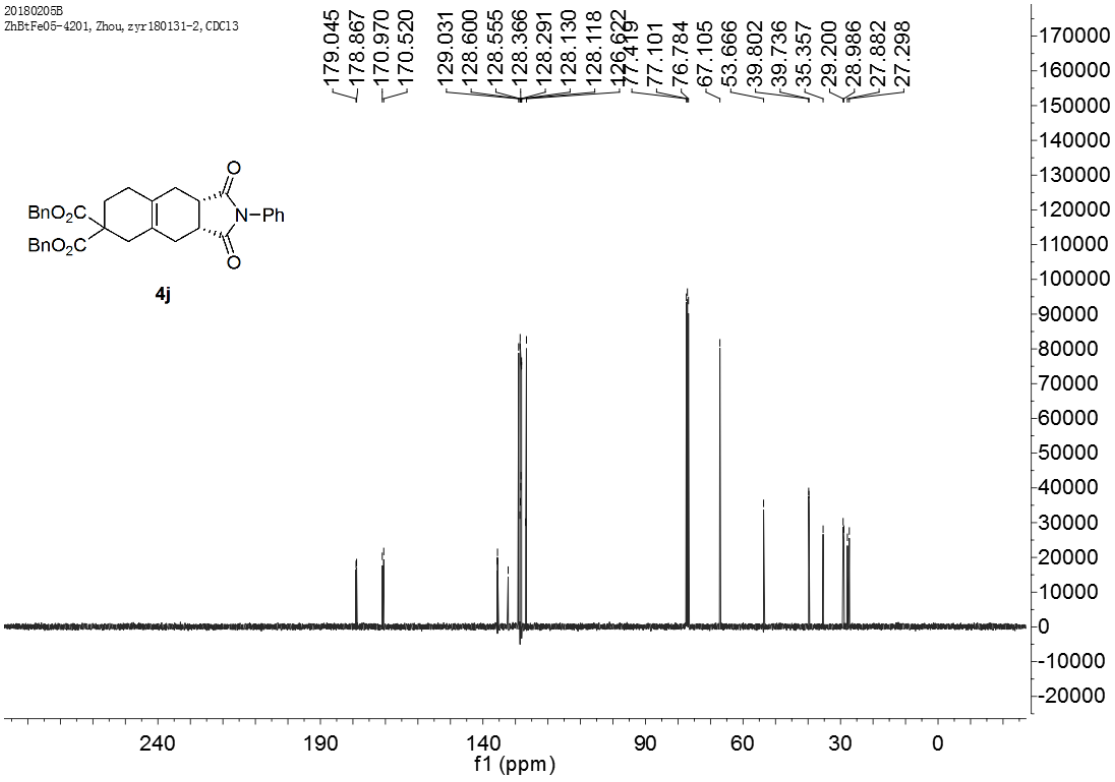

7.453
7.451
7.437
7.421
7.417
7.402
7.371
7.368
7.365
7.355
7.349
7.344
7.334
7.331
7.296
7.292
7.287
7.274
7.260
3.693
3.565
3.234
3.228
3.221
3.218
3.211
3.205
2.554
2.518
2.493
2.488
2.480
2.452
2.373
2.323
2.279
2.272
2.113
2.100
2.089
2.077
MeO2C
MeO2C
N–Ph
O
O
4h
2.10
1.12
1.99
3.00
2.80
2.00
4.05
2.02
4.04
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

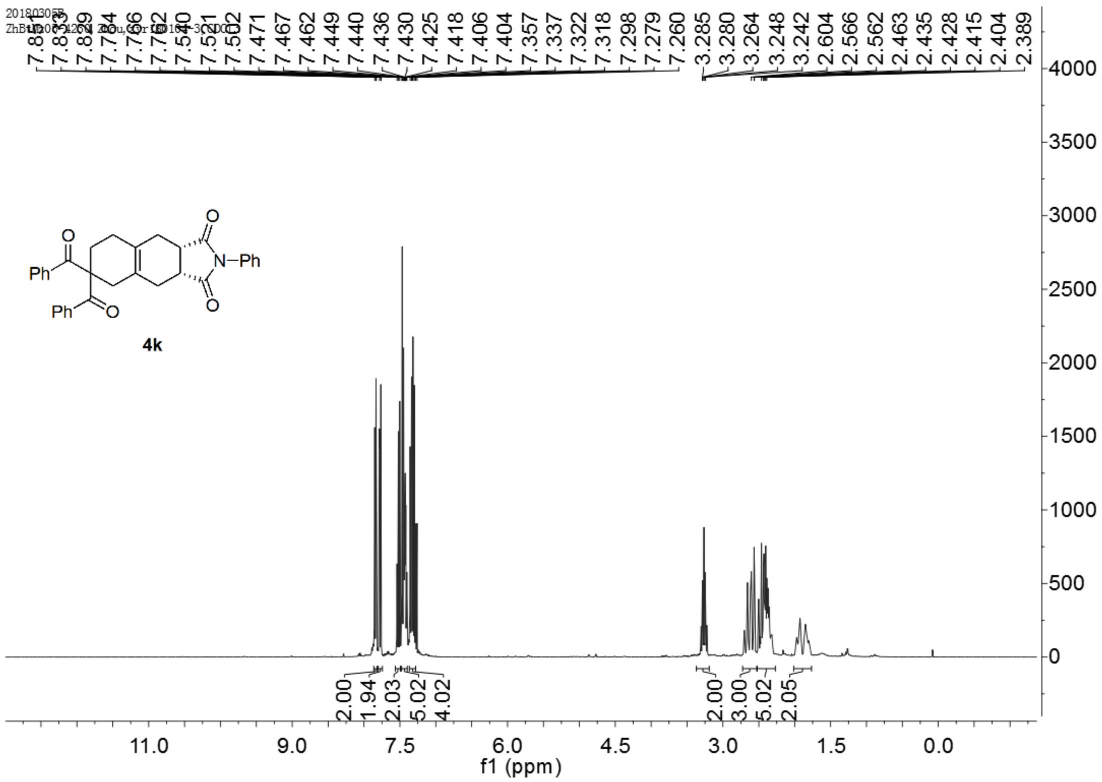

20180124B
ZhBtJa24-4441, Zhou, zyr180120-1, CDCl3
179.085
178.852
171.773
171.308
132.213
128.997
128.579
128.479
126.885
126.586
77.419
77.102
76.784
53.445
52.661
52.592
39.815
39.741
35.446
29.175
29.013
27.858
27.371
MeO2C
MeO2C
N–Ph
O
O
4h
240
190
140
90
60
30
0
f1 (ppm)

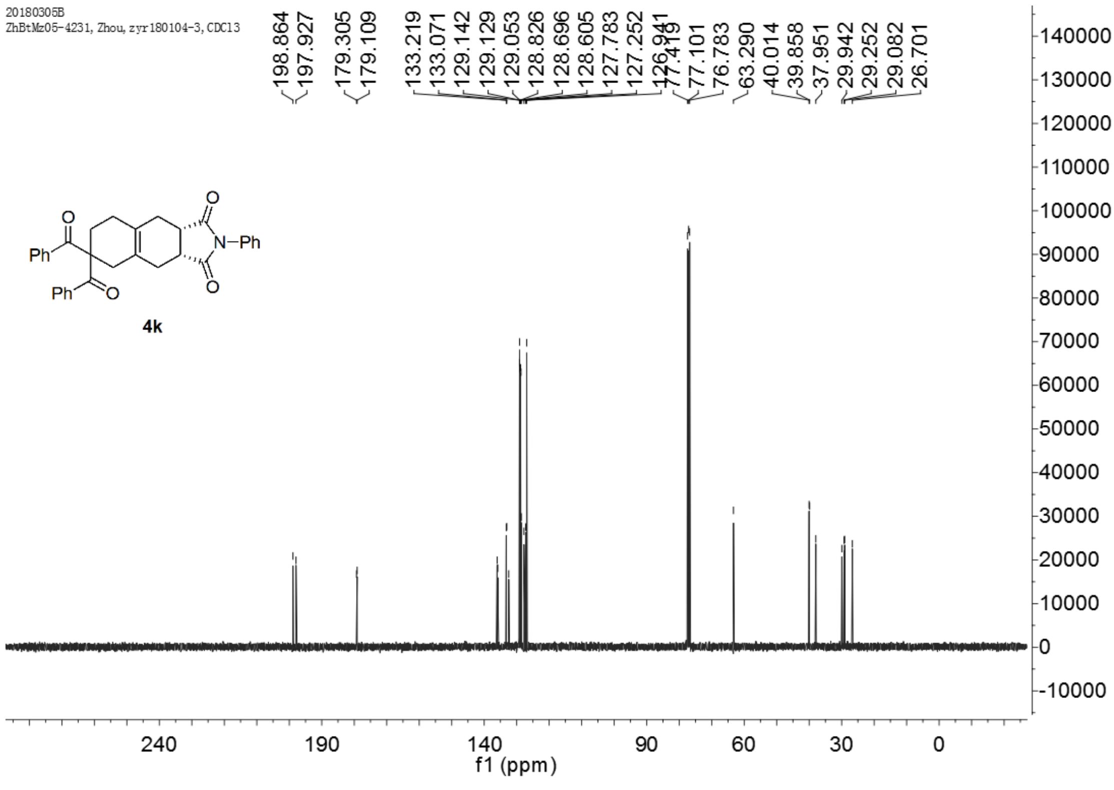

4i
f1 (ppm)

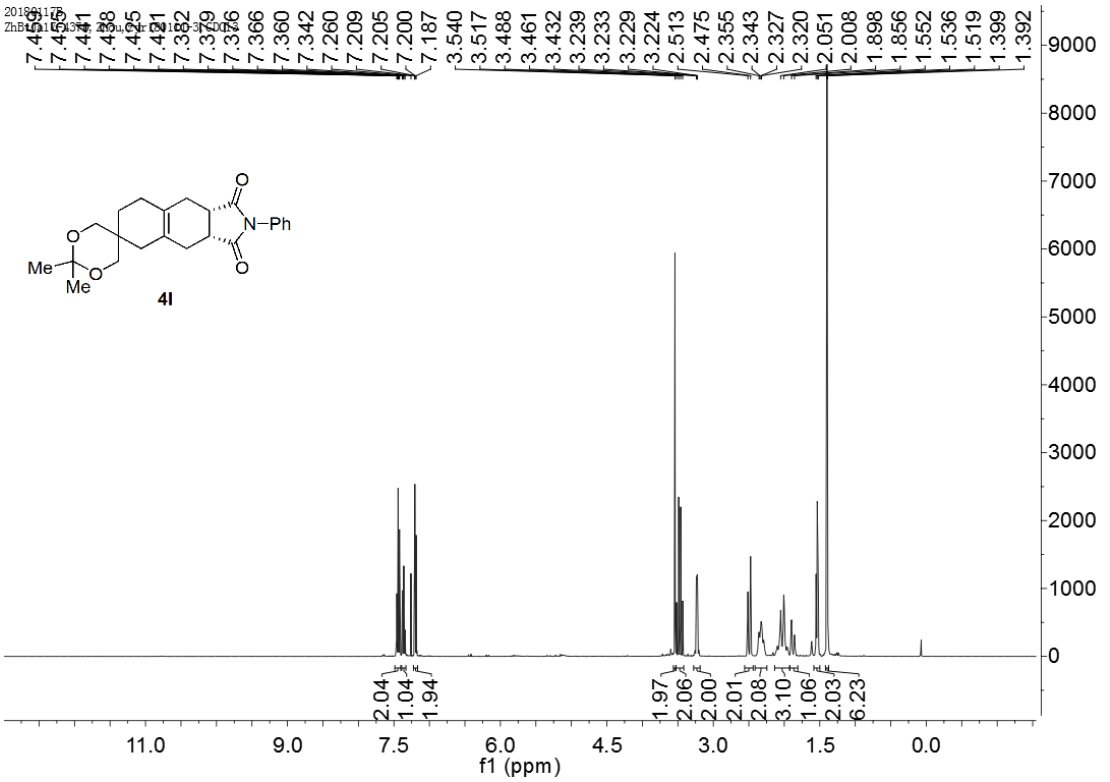

4i
f1 (ppm)

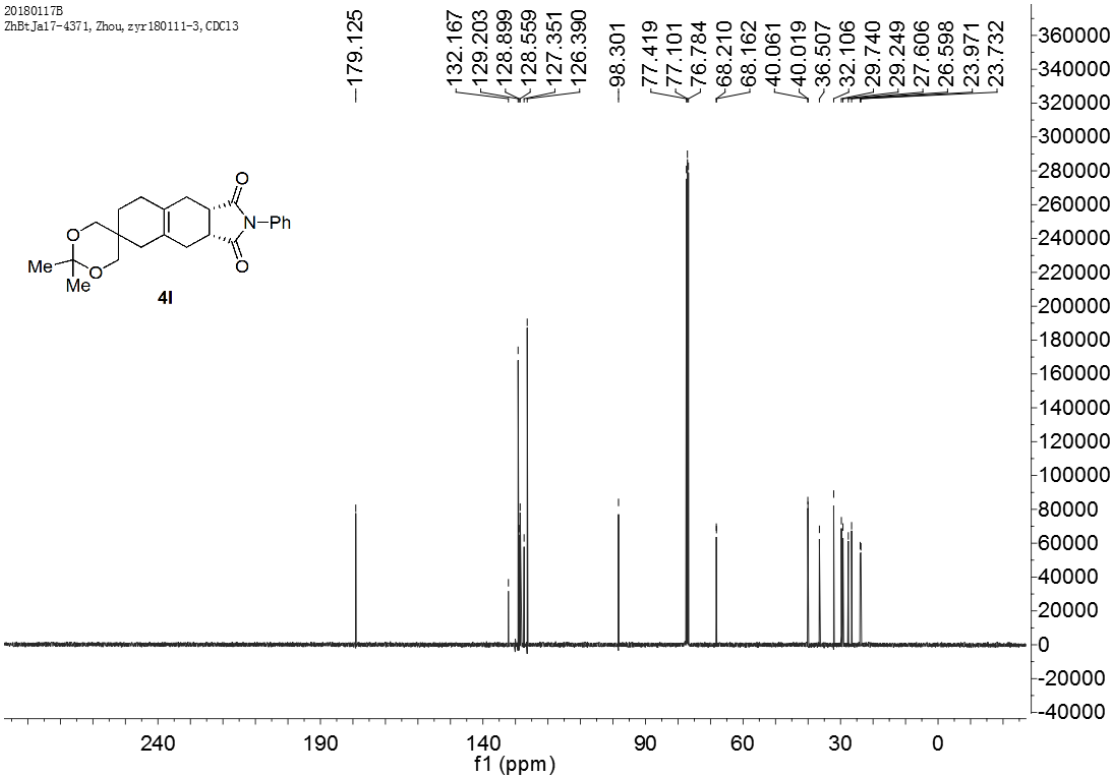

4j
f1 (ppm)

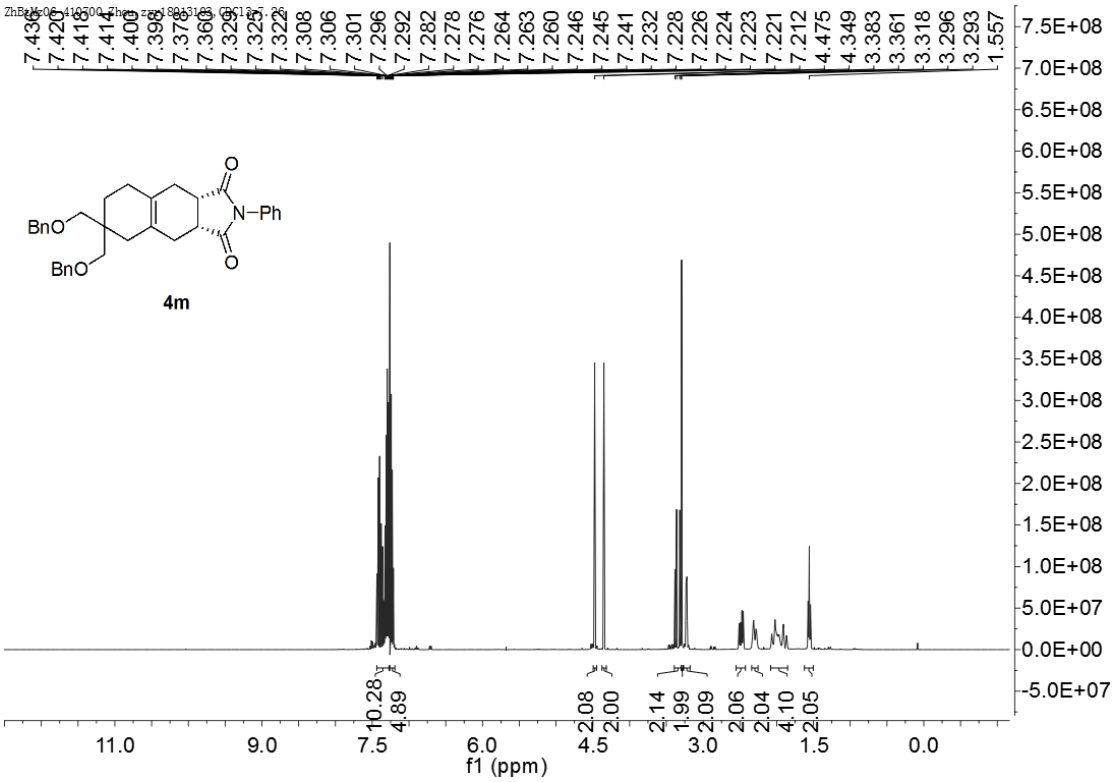

4j
f1 (ppm)

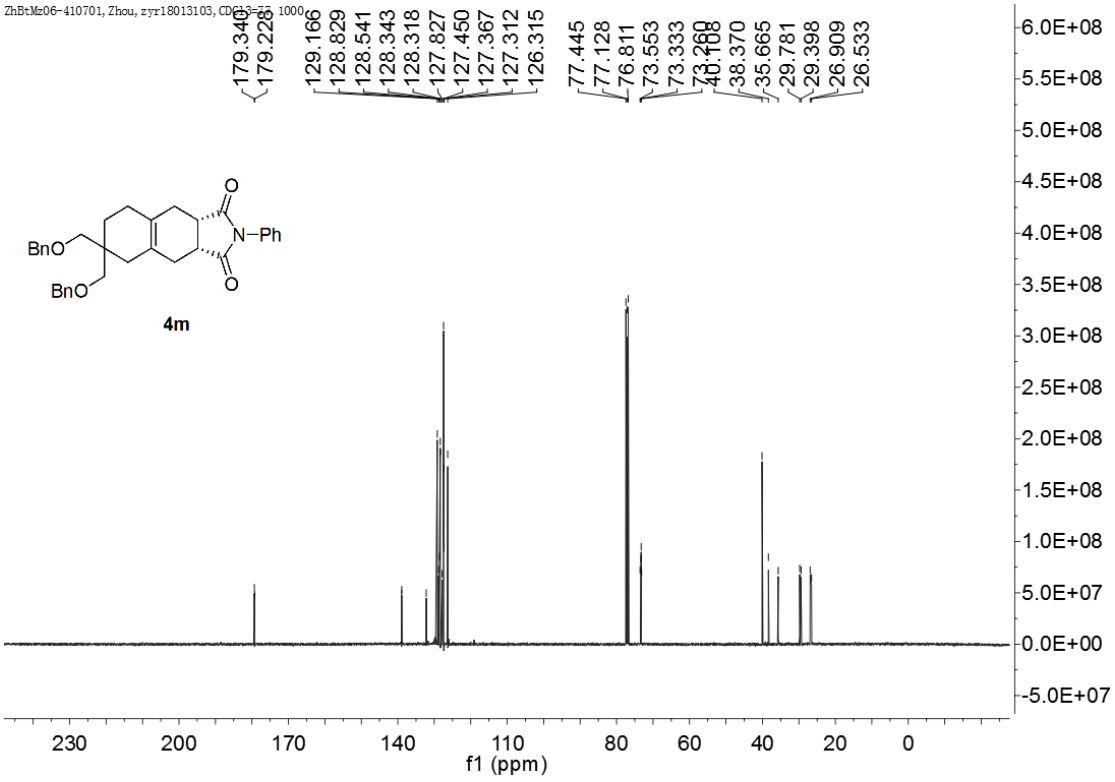

7.829
7.784
7.766
7.762
7.540
7.521
7.502
7.471
7.467
7.462
7.449
7.440
7.436
7.430
7.425
7.418
7.406
7.404
7.357
7.337
7.322
7.318
7.298
7.279
7.260
3.285
3.280
3.264
3.248
3.242
2.604
2.566
2.562
2.463
2.435
2.428
2.415
2.404
2.389
Ph
O
N–Ph
4k
2.00
1.94
2.03
5.02
4.02
2.00
3.00
5.02
2.05
f1 (ppm)

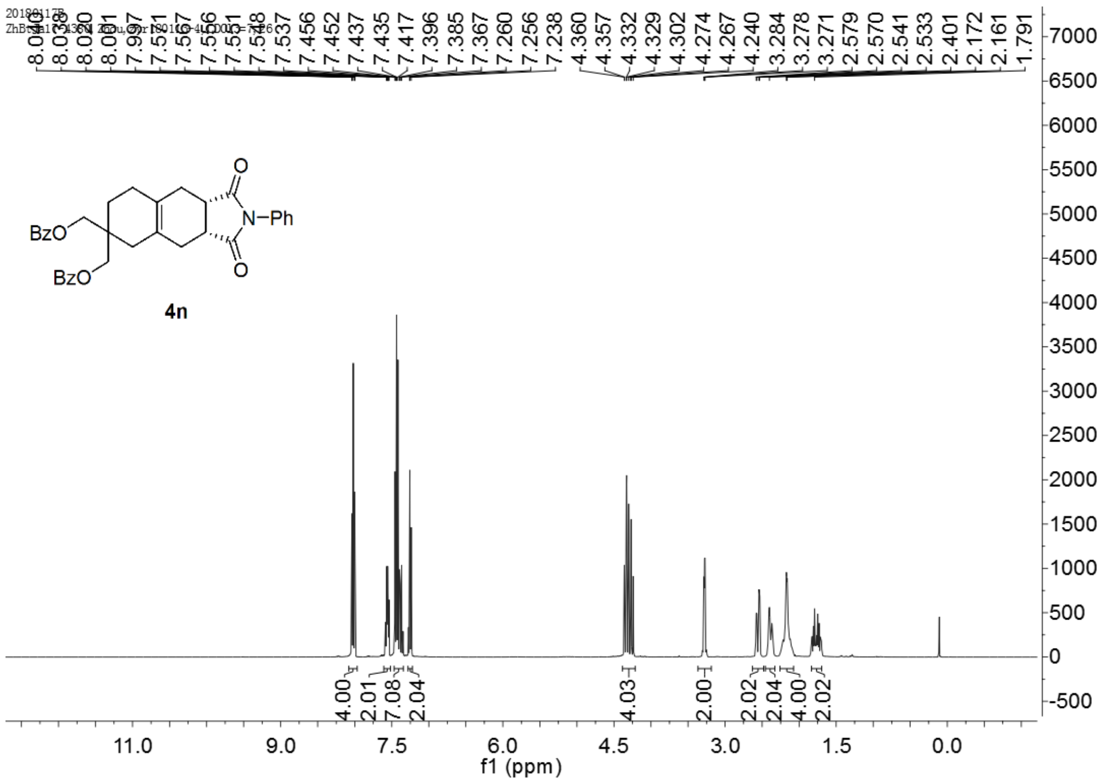

20180305B
ZhBtMz05-4231, Zhou, zyr180104-3, CDCl3
198.864
197.927
179.305
179.109
133.219
133.071
129.142
129.129
129.053
128.826
128.696
128.605
127.783
127.252
126.941
77.419
77.101
76.783
63.290
40.014
39.858
37.951
29.942
29.252
29.082
26.701
Ph
O
N–Ph
4k
f1 (ppm)


7.455
7.451
7.441
7.438
7.425
7.421
7.382
7.379
7.376
7.366
7.360
7.342
7.260
7.209
7.205
7.200
7.187
3.540
3.517
3.488
3.461
3.432
3.239
3.233
3.229
3.224
2.513
2.475
2.355
2.343
2.327
2.320
2.051
2.008
1.898
1.856
1.552
1.536
1.519
1.399
1.392
N–Ph
Me
Me
4l
2.04
1.04
1.94
1.97
2.06
2.00
2.01
2.08
3.10
1.06
2.03
6.23
f1 (ppm)

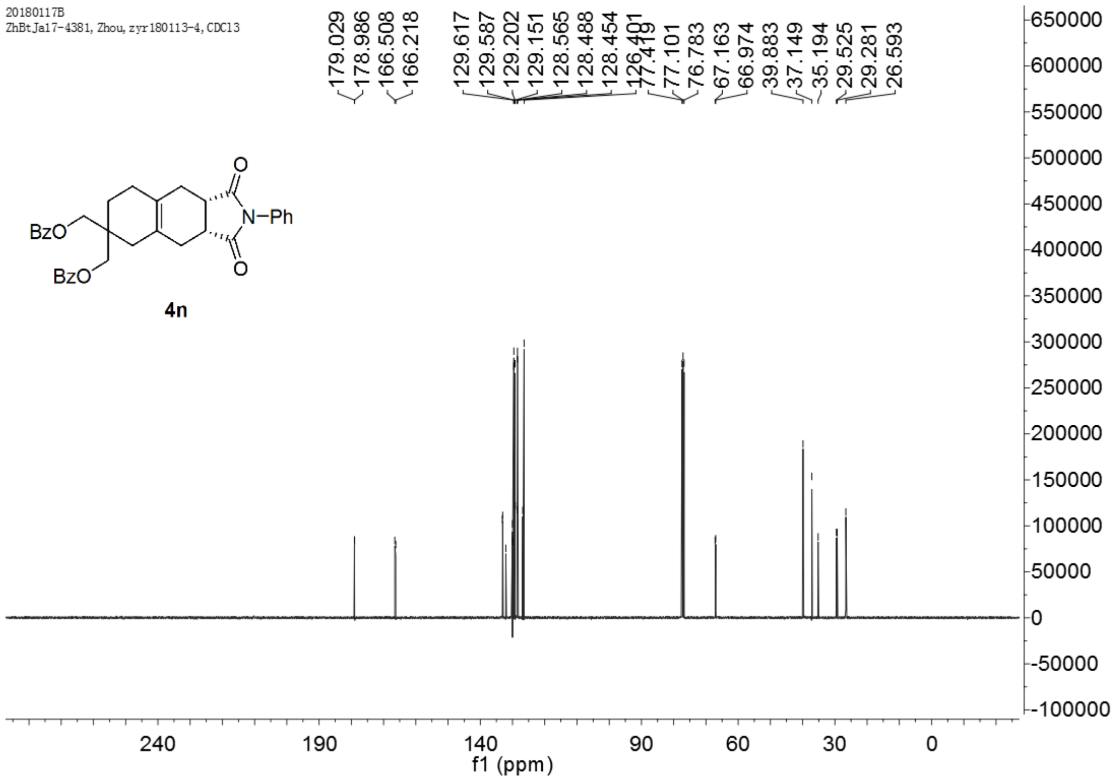

20180117B
ZhBtJa17-4371, Zhou, zyr180111-3, CDCl3
179.125
132.167
129.203
128.899
128.559
127.351
126.390
98.301
77.419
77.101
76.784
68.210
68.162
40.061
40.019
36.507
32.106
29.740
29.249
27.606
26.598
23.971
23.732
N–Ph
Me
Me
4l
f1 (ppm)


7.436
7.420
7.418
7.414
7.400
7.396
7.376
7.360
7.329
7.325
7.322
7.308
7.306
7.301
7.296
7.292
7.282
7.278
7.276
7.264
7.263
7.260
7.246
7.245
7.241
7.232
7.228
7.226
7.224
7.223
7.221
7.212
4.475
4.349
3.383
3.361
3.318
3.296
3.293
1.557
BnO
BnO
N–Ph
O
O
4m
10.28
4.89
2.08
2.00
2.14
1.99
2.09
2.06
2.04
4.10
2.05
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07

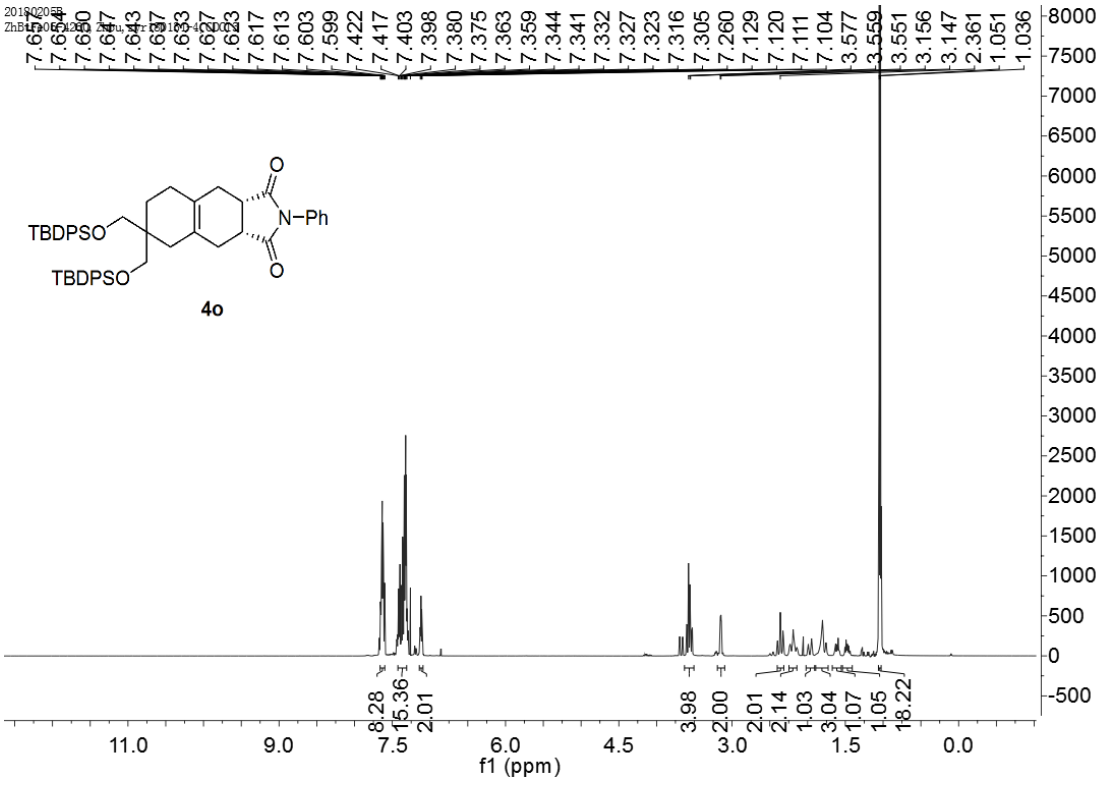

179.340
179.228
129.166
128.829
128.541
128.343
128.318
127.827
127.450
127.367
127.312
126.315
77.445
77.128
76.811
73.553
73.333
73.260
40.168
38.370
35.665
29.781
29.398
26.909
26.533
BnO
BnO
N–Ph
O
O
4m
230
200
170
140
110
80
60
40
20
0
f1 (ppm)
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07

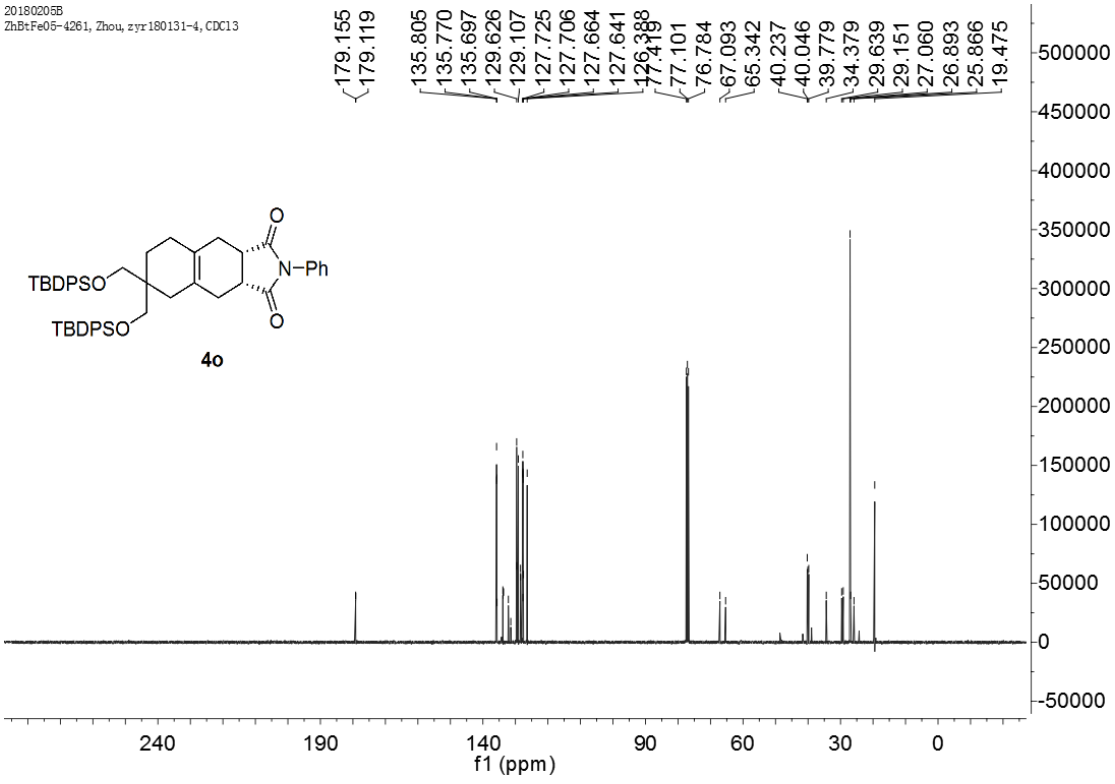


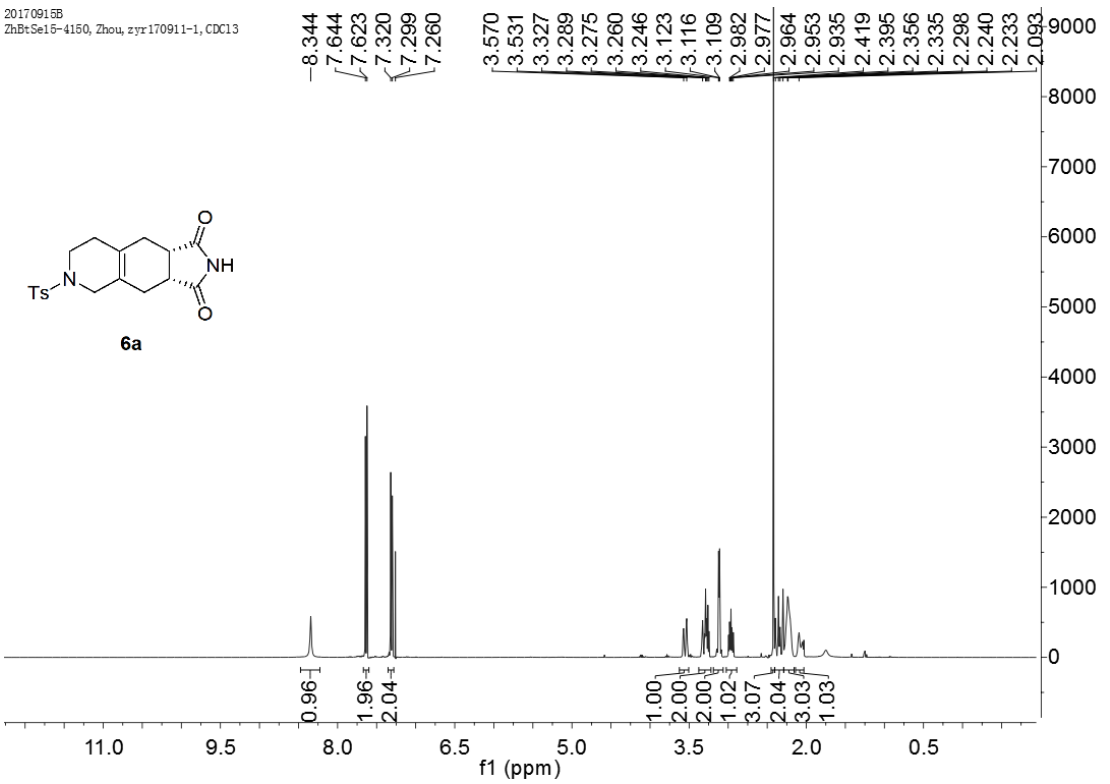
8.001
7.997
7.571
7.567
7.551
7.537
7.456
7.452
7.437
7.435
7.417
7.396
7.385
7.367
7.260
7.256
7.238
4.360
4.357
4.332
4.329
4.302
4.274
4.267
4.240
3.284
3.278
3.271
2.579
2.570
2.541
2.533
2.401
2.172
2.161
1.791
BzO
BzO
O
O
N–Ph
4n
4.00
2.01
7.08
2.04
4.03
2.00
2.02
2.04
4.00
2.02
f1 (ppm)

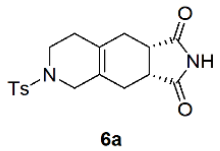


20180117B
ZhBtJa17-4381, Zhou, zyr180113-4, CDCl3
179.029
178.986
166.508
166.218
129.617
129.587
129.202
129.151
128.565
128.488
128.454
126.401
77.419
77.101
76.783
67.163
66.974
39.883
37.149
35.194
29.525
29.281
26.593
BzO
BzO
O
O
N–Ph
4n
f1 (ppm)


TBDPSO
TBDPSO
N–Ph
O
O
O
4o
f1 (ppm)


TBDPSO
TBDPSO
N–Ph
O
O
O
4o
f1 (ppm)


20170915B
ZhBtSe15-4150, Zhou, zyr170911-1, CDCl3
8.344
7.644
7.623
7.320
7.299
7.260
3.570
3.531
3.327
3.289
3.275
3.260
3.246
3.123
3.116
3.109
2.982
2.977
2.964
2.953
2.935
2.419
2.395
2.356
2.335
2.298
2.240
2.233
2.093
0.96
1.96
2.04
1.00
2.00
2.00
1.02
3.07
2.04
3.03
1.03
f1 (ppm)

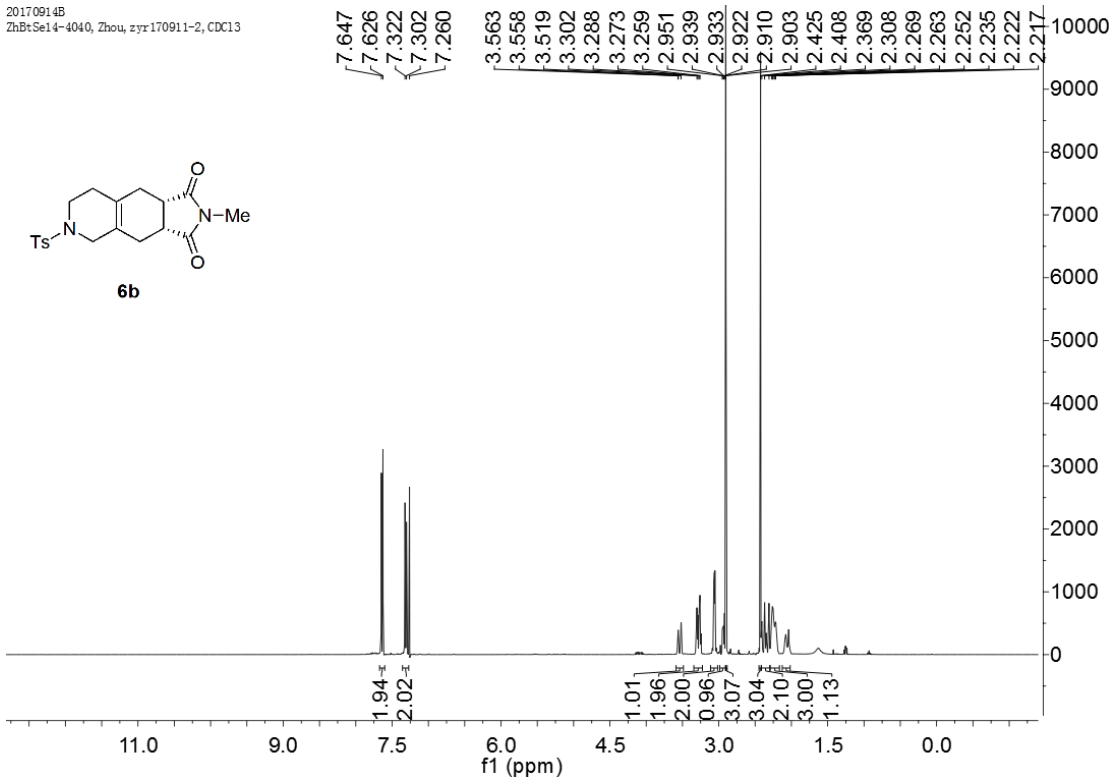

Ts
N
O
NH
O

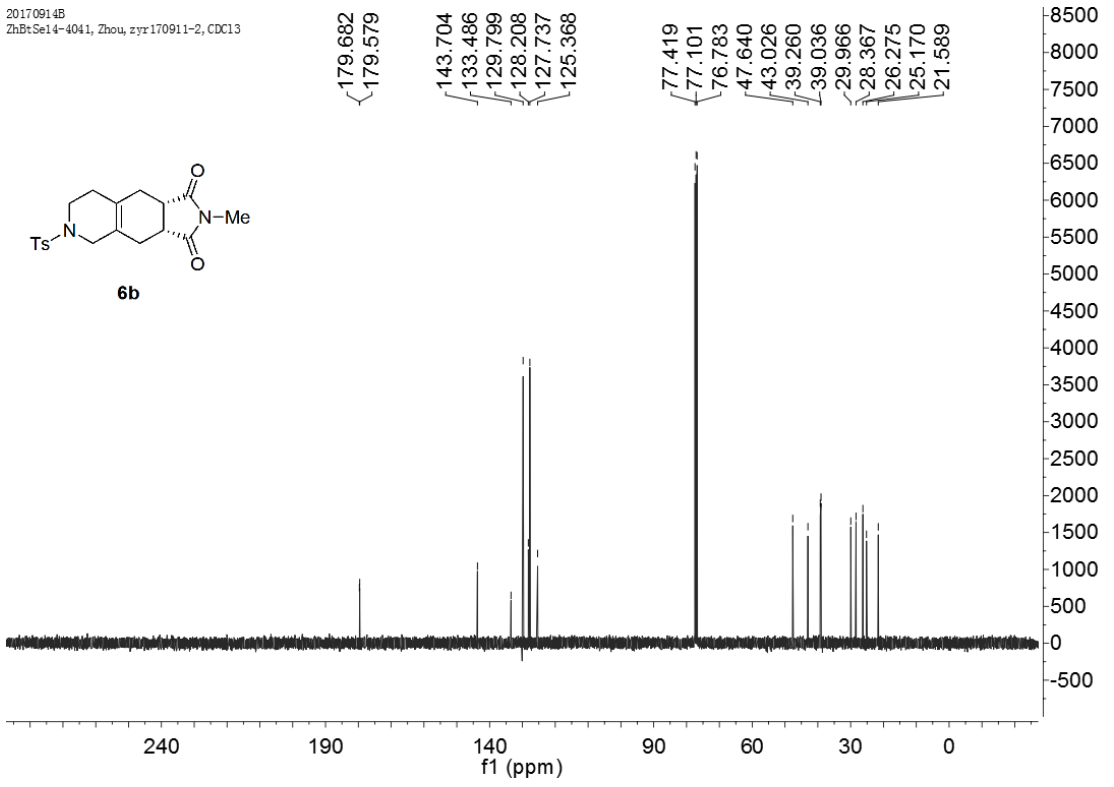
6a

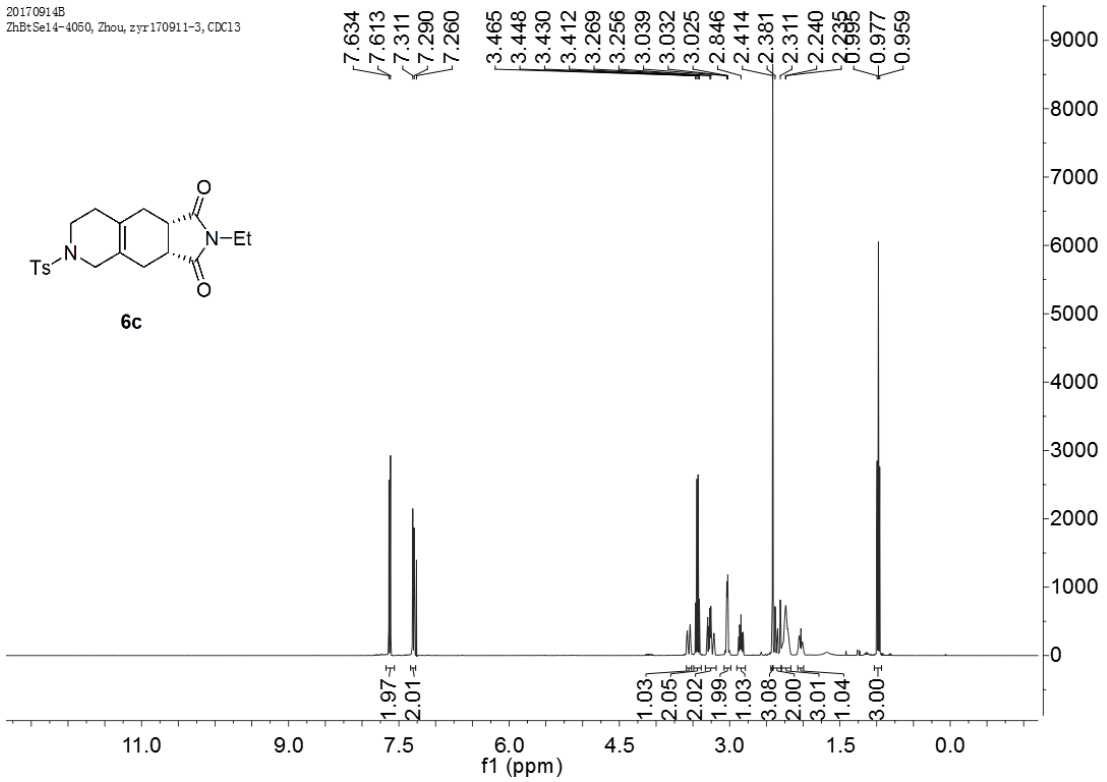
20170915B
ZhBtSe15-4151, Zhou, zyr170911-1, CDCl3
179.756
179.652
143.739
133.386
129.810
128.336
127.710
125.439
77.419
77.101
76.783
47.685
42.991
40.532
40.321
29.937
28.222
26.170
21.572
f1 (ppm)

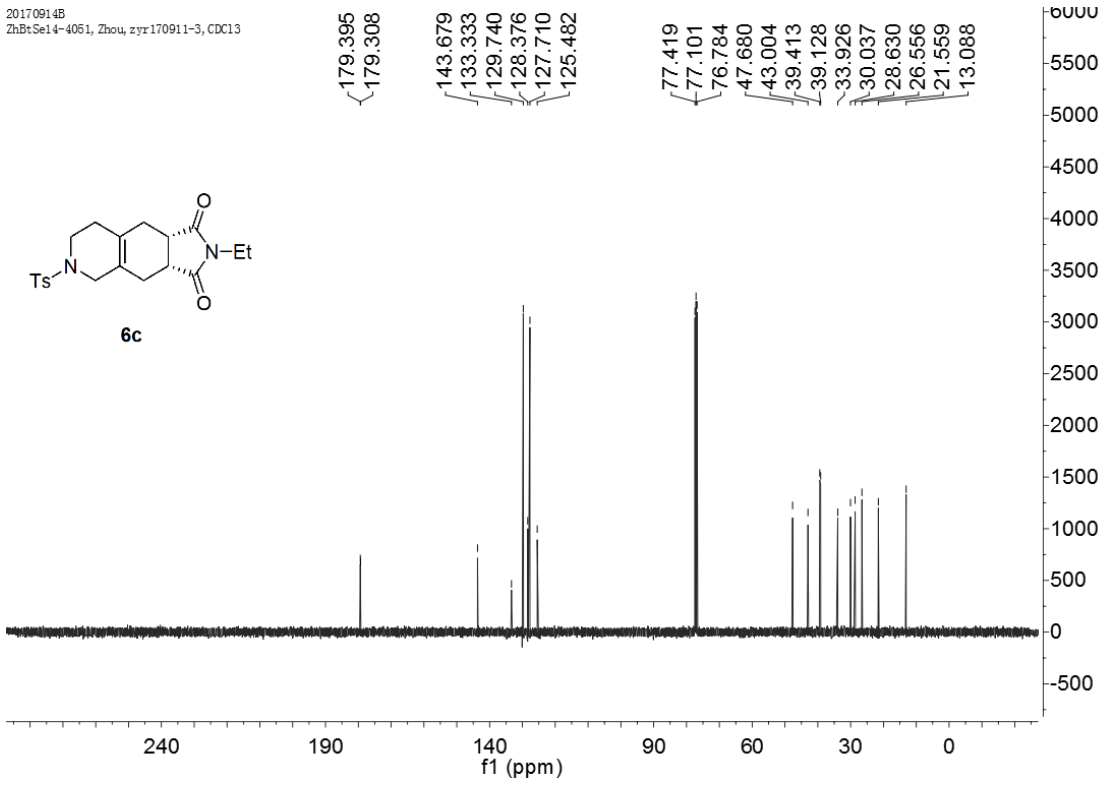
Ts
N
O
NH
O

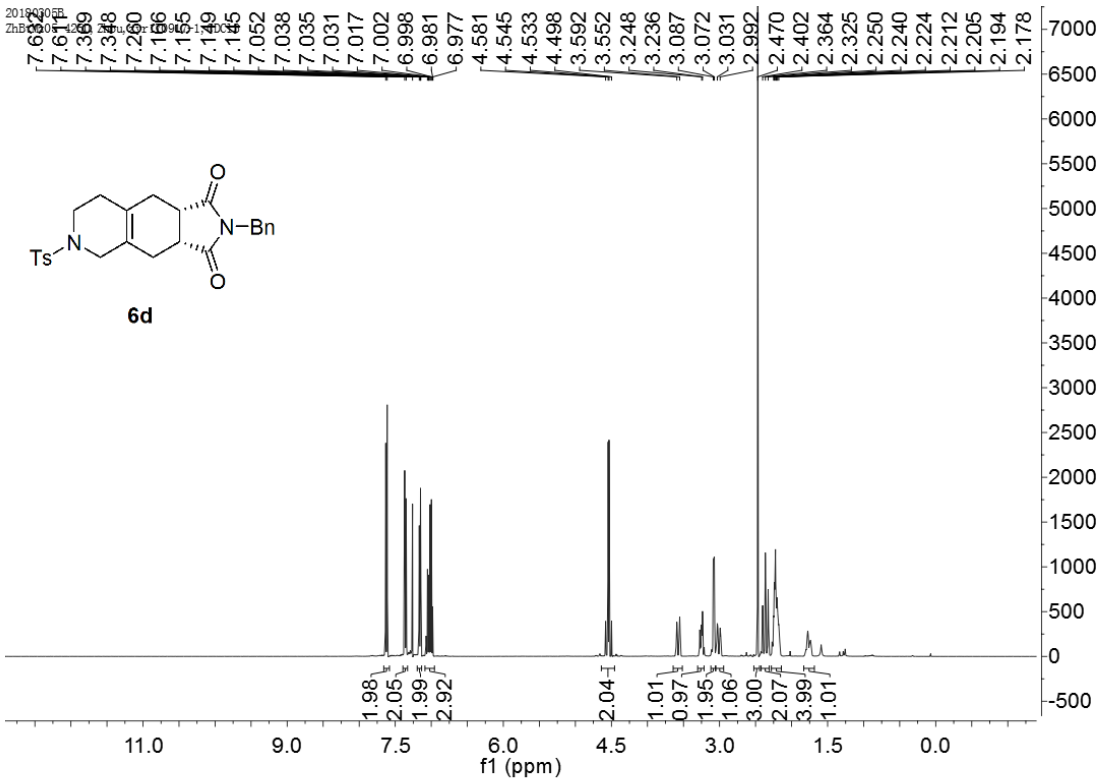
6a

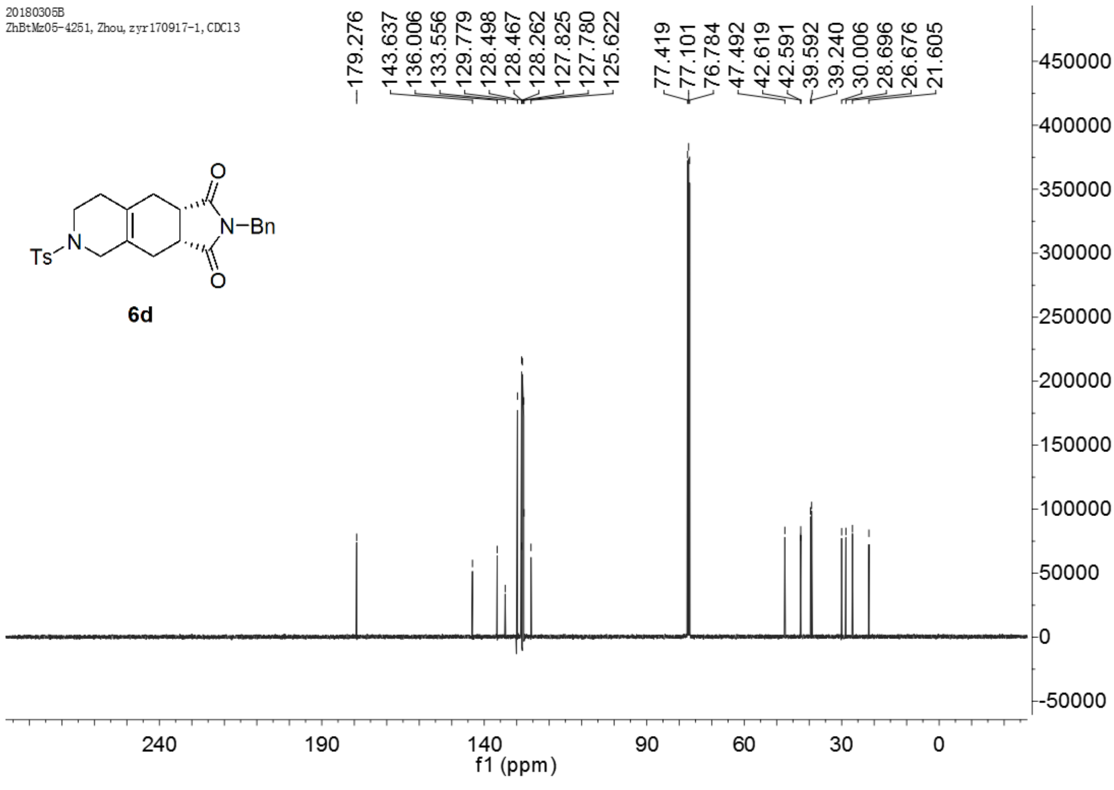

20170914B
ZhBtSe14-4040, Zhou, zyr170911-2, CDCl3
7.647
7.626
7.322
7.302
7.260
3.563
3.558
3.519
3.302
3.288
3.273
3.259
2.951
2.939
2.933
2.922
2.910
2.903
2.425
2.408
2.389
2.308
2.269
2.263
2.252
2.235
2.222
2.217
1.94
2.02
1.01
1.96
2.00
0.96
3.07
3.04
2.10
3.00
1.13
f1 (ppm)
6b

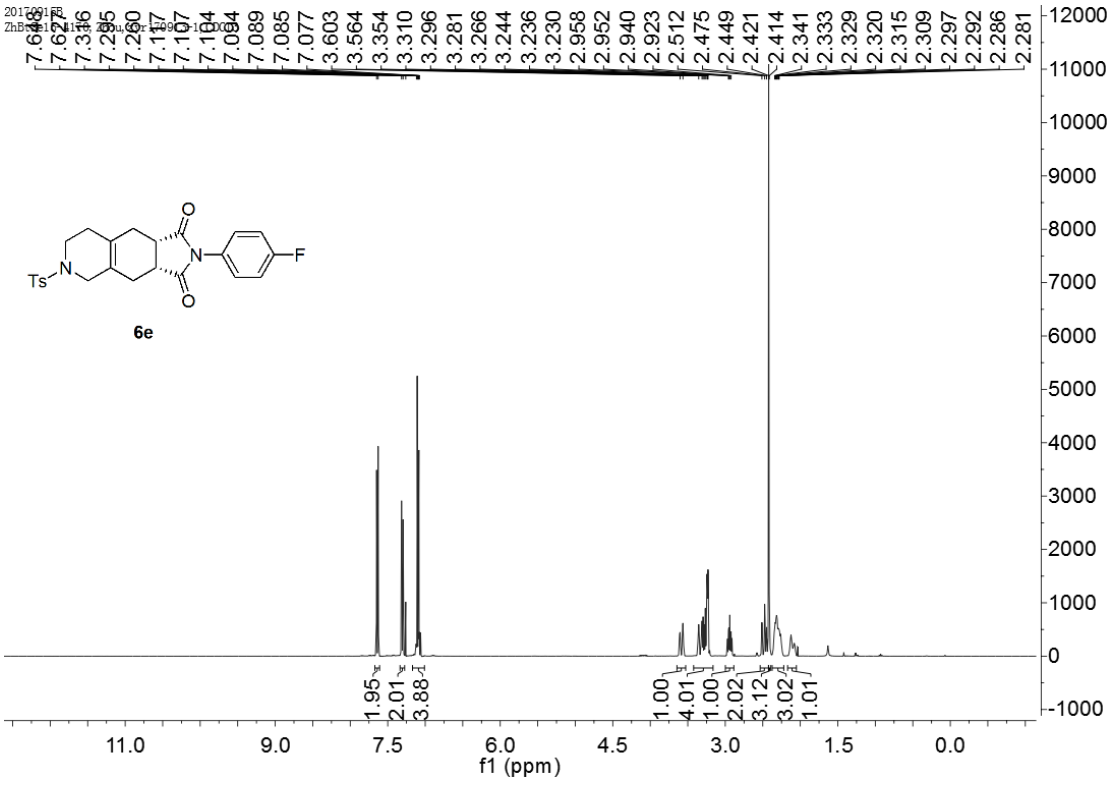

20170914B
ZhBtSe14-4041, Zhou, zyr170911-2, CDCl3
179.682
179.579
143.704
133.486
129.799
128.208
127.737
125.368
77.419
77.101
76.783
47.640
43.026
39.260
39.036
29.966
28.367
26.275
25.170
21.589
f1 (ppm)
6b

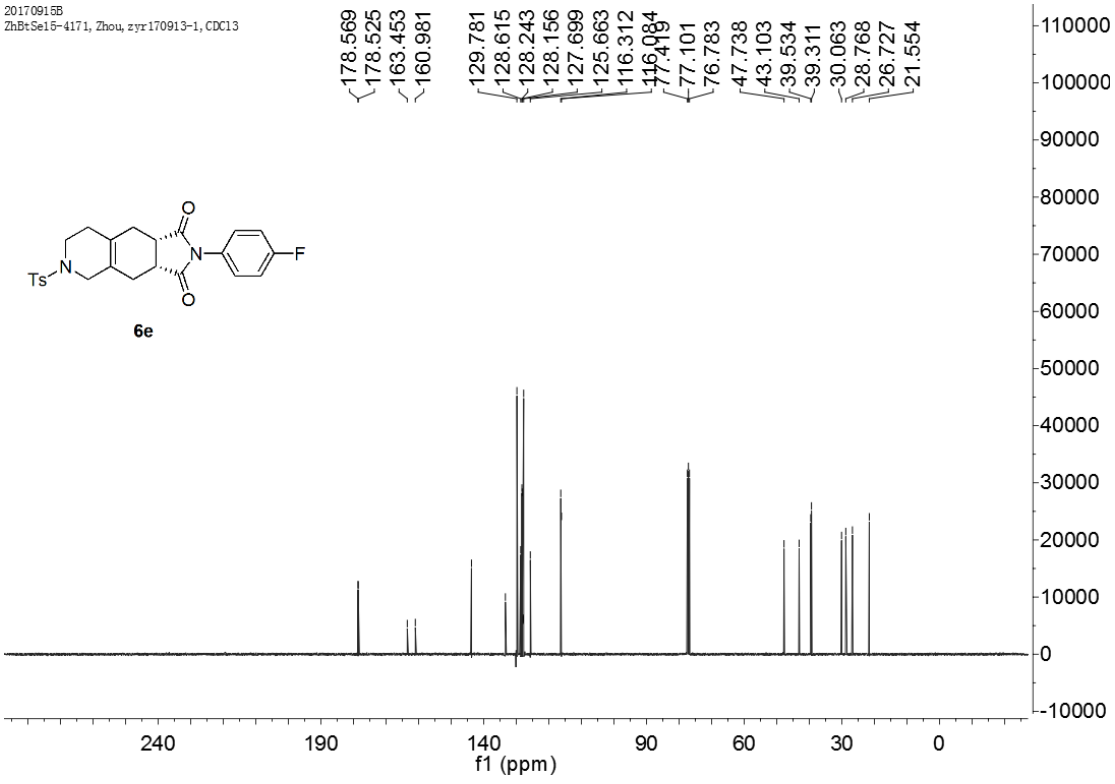

20170914B
ZhBtSe14-4060, Zhou, zyr170911-3, CDCl3
7.634
7.613
7.311
7.290
7.260
3.465
3.448
3.430
3.412
3.269
3.256
3.039
3.032
3.025
2.846
2.414
2.381
2.311
2.240
0.977
0.959
1.97
2.01
1.03
2.05
2.02
1.99
1.03
3.08
2.00
3.01
1.04
3.00
Ts
N
O
N–Et
O
6c
f1 (ppm)

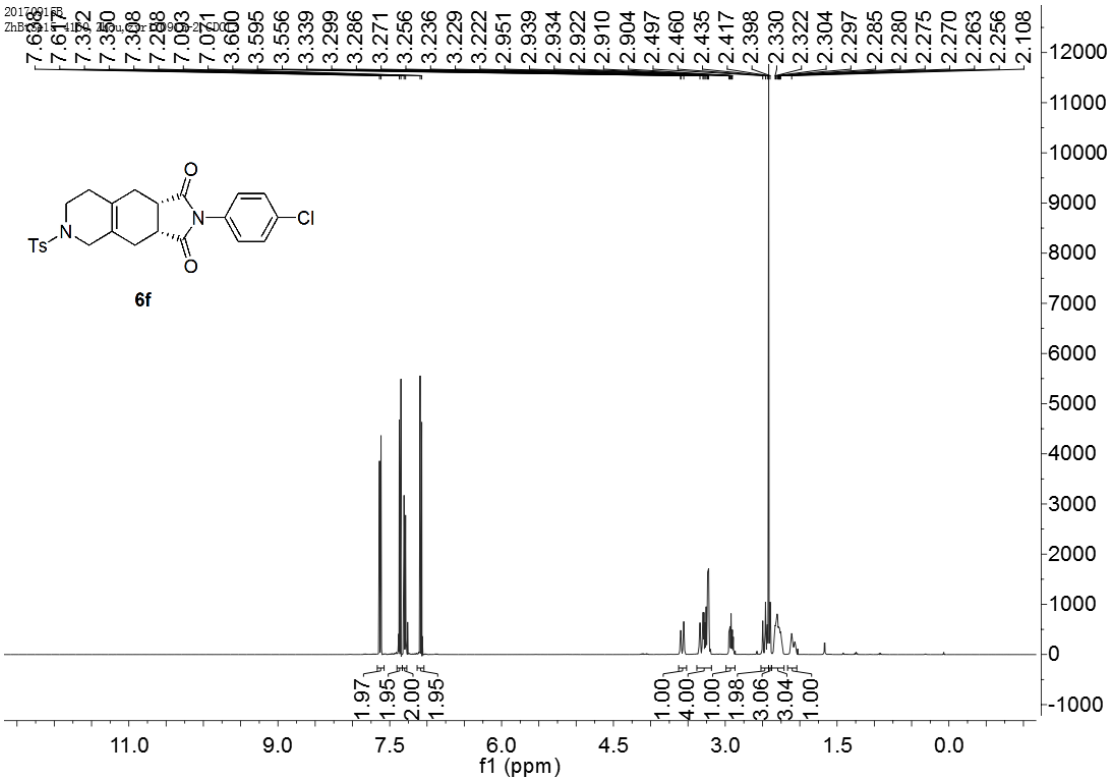

20170914B
ZhBtSe14-4061, Zhou, zyr170911-3, CDCl3
179.395
179.308
143.679
133.333
129.740
128.376
127.710
125.482
77.419
77.101
76.784
47.680
43.004
39.413
39.128
33.926
30.037
28.630
26.556
21.559
13.088
Ts
N
O
N–Et
O
6c
f1 (ppm)

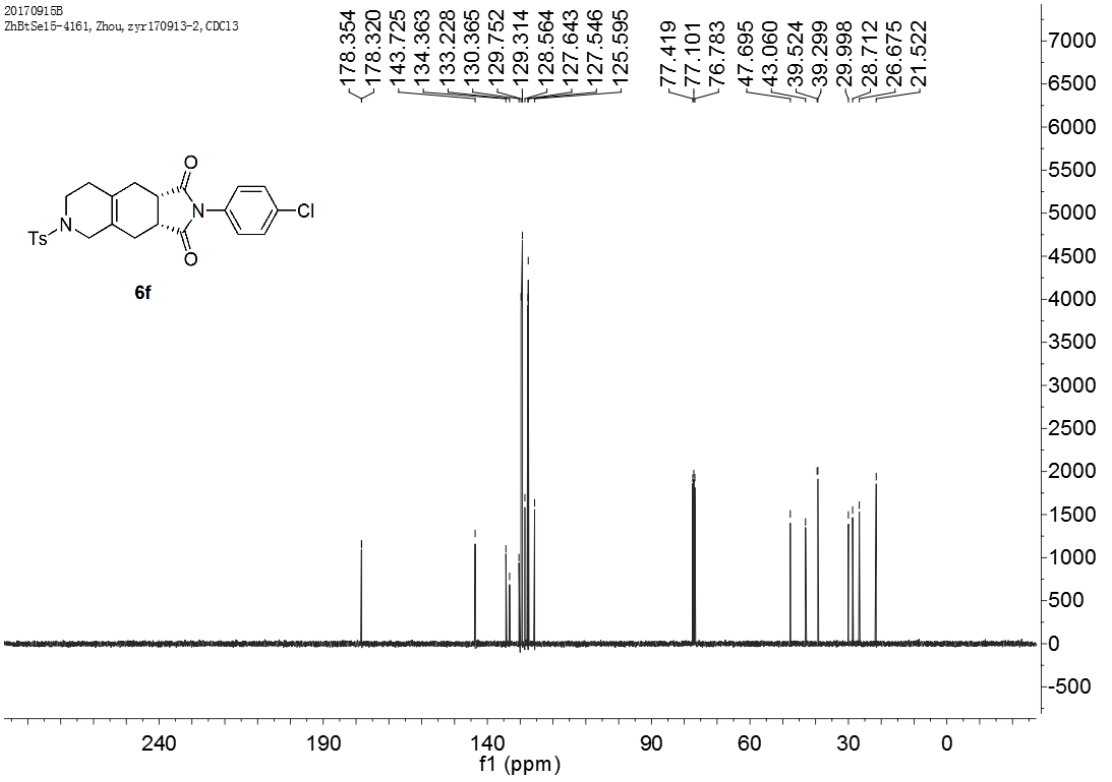

20180305B
7.369
7.348
7.200
7.186
7.165
7.149
7.145
7.052
7.038
7.035
7.031
7.017
7.002
6.998
6.981
6.977
4.581
4.545
4.533
4.498
3.592
3.552
3.248
3.236
3.087
3.072
3.031
2.992
2.470
2.402
2.364
2.325
2.250
2.240
2.224
2.212
2.205
2.194
2.178
N–Bn
Ts
N
O
O
6d
1.98
2.05
1.99
2.92
2.04
1.01
0.97
1.95
1.06
3.00
2.07
3.99
1.01
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

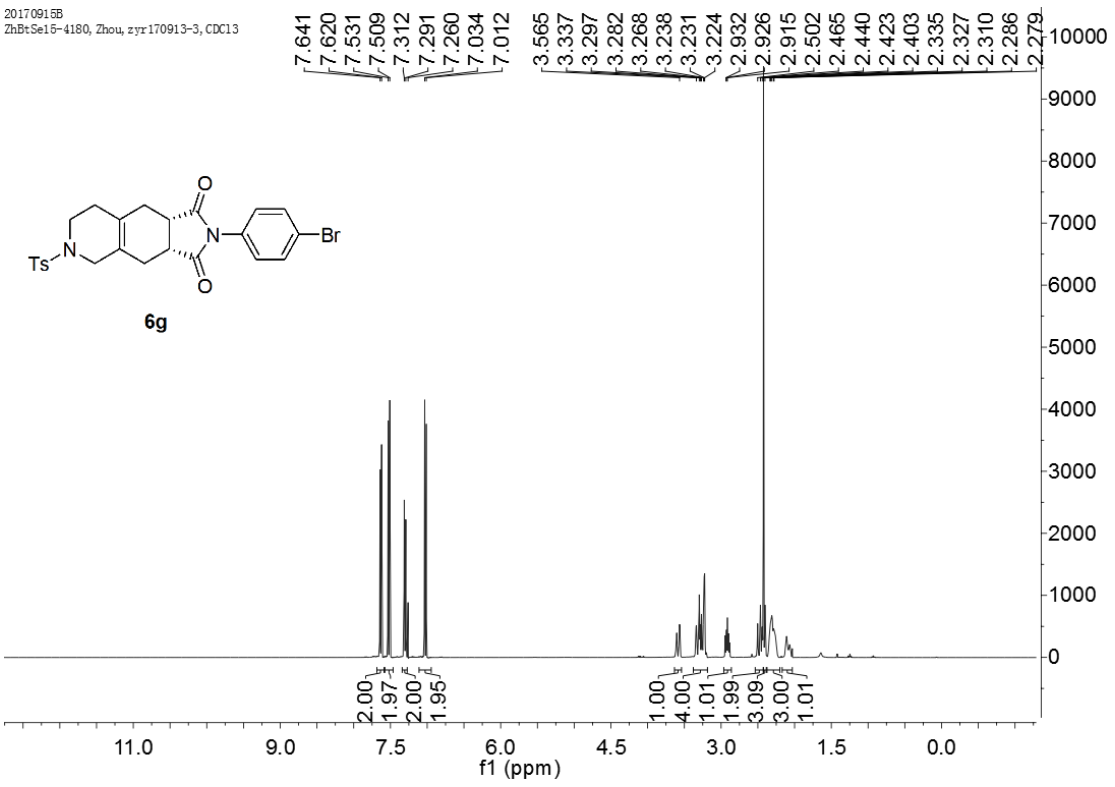

20180305B
ZhBtMz05-4251, Zhou, zyr170917-1, CDCl3
179.276
143.637
136.006
133.556
129.779
128.498
128.467
128.262
127.825
127.780
125.622
77.419
77.101
76.784
47.492
42.619
42.591
39.592
39.240
30.006
28.696
26.676
21.605
N–Bn
Ts
N
O
O
6d
240
190
140
90
60
30
0
f1 (ppm)

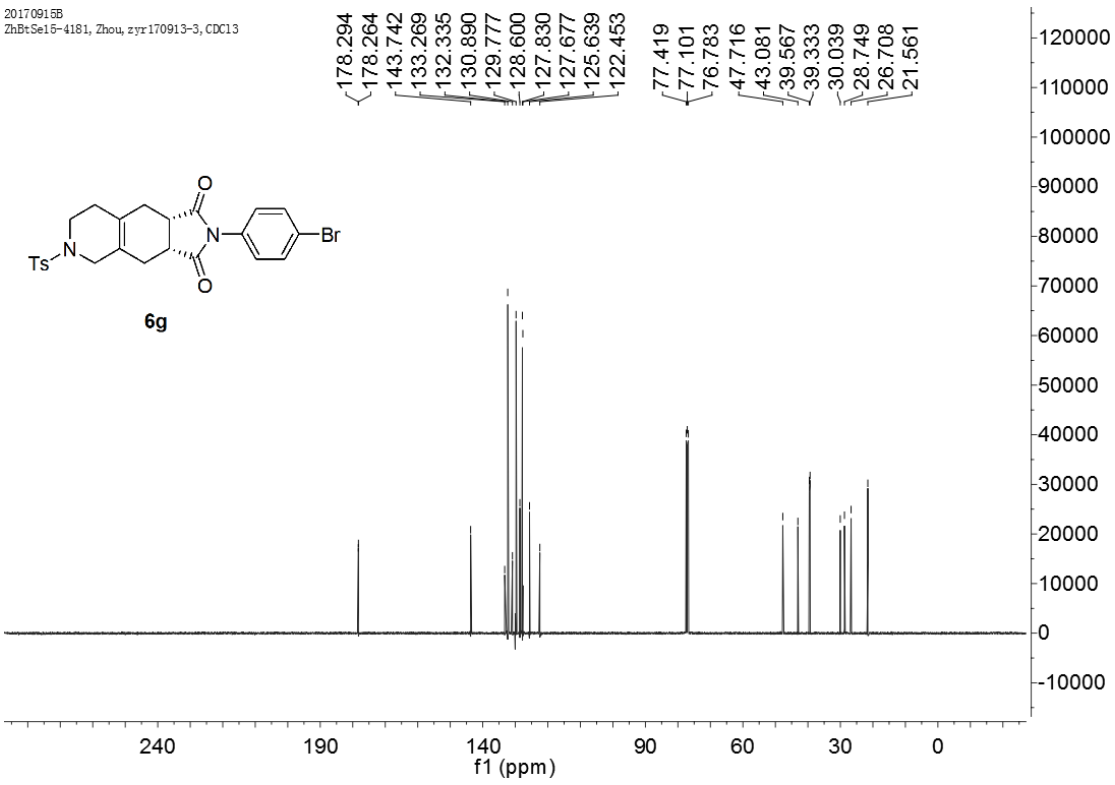

7.643
7.627
7.316
7.295
7.260
7.177
7.157
7.104
7.094
7.089
7.085
7.077
3.603
3.564
3.354
3.310
3.296
3.281
3.266
3.244
3.236
3.230
2.958
2.952
2.940
2.923
2.512
2.475
2.449
2.421
2.414
2.341
2.333
2.329
2.320
2.315
2.309
2.297
2.292
2.286
2.281
Ts
N
O
O
N
F
6e
1.95
2.01
3.88
1.00
4.01
1.00
2.02
3.12
3.02
1.01
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

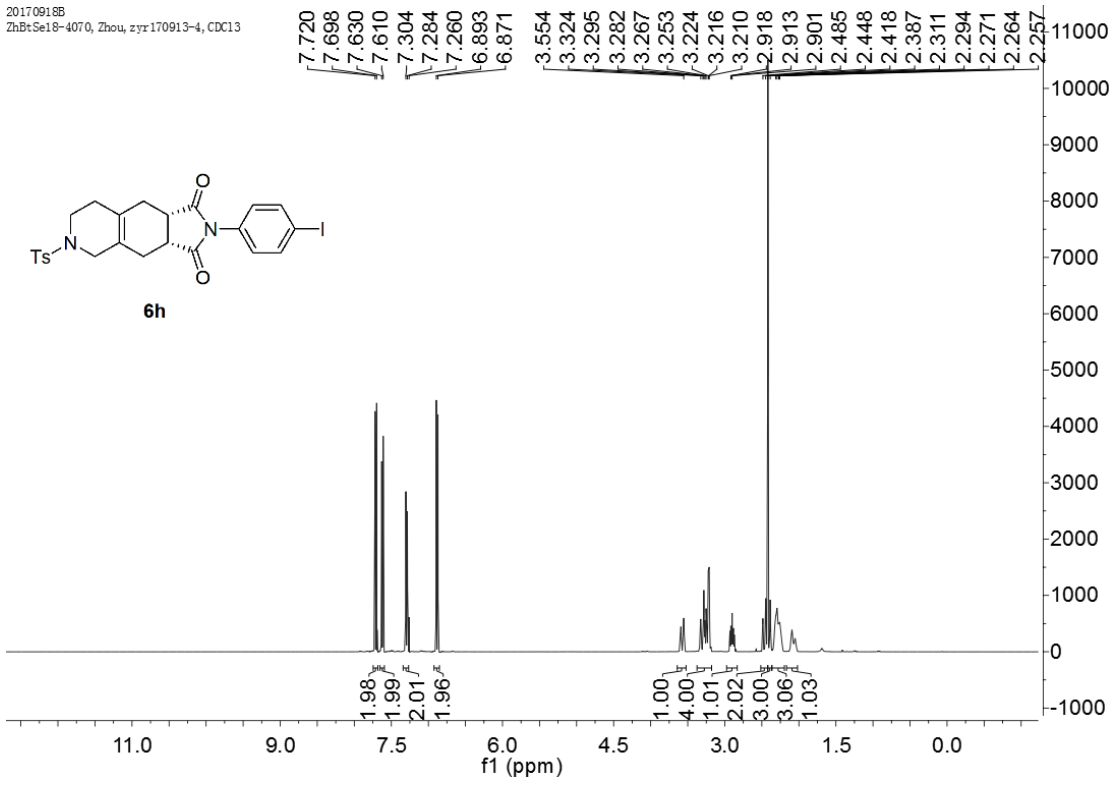

20170915B
ZhBtSe15-4171, Zhou, zyr170913-1, CDCl3
178.569
178.525
163.453
160.981
129.781
128.615
128.243
128.156
127.699
125.663
116.312
116.084
77.419
77.101
76.783
47.738
43.103
39.534
39.311
30.063
28.768
26.727
21.554
Ts
N
O
O
N
F
6e
240
190
140
90
60
30
0
f1 (ppm)

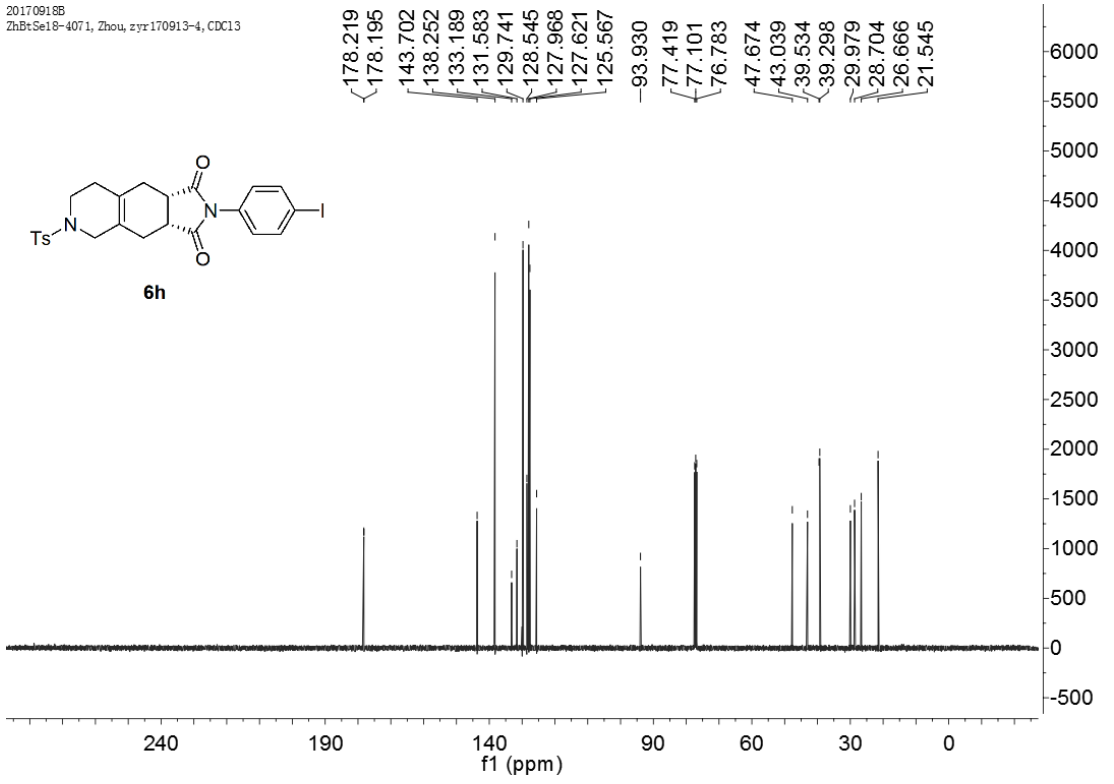

7.639
7.617
7.352
7.350
7.308
7.288
7.093
7.071
3.600
3.595
3.556
3.339
3.299
3.286
3.271
3.256
3.236
3.229
3.222
2.951
2.939
2.934
2.922
2.910
2.904
2.497
2.460
2.435
2.417
2.398
2.330
2.322
2.304
2.297
2.285
2.280
2.275
2.270
2.263
2.256
2.108
Ts
N
O
O
N
Cl
6f
1.97
1.95
2.00
1.95
1.00
4.00
1.00
1.98
3.06
3.04
1.00
f1 (ppm)

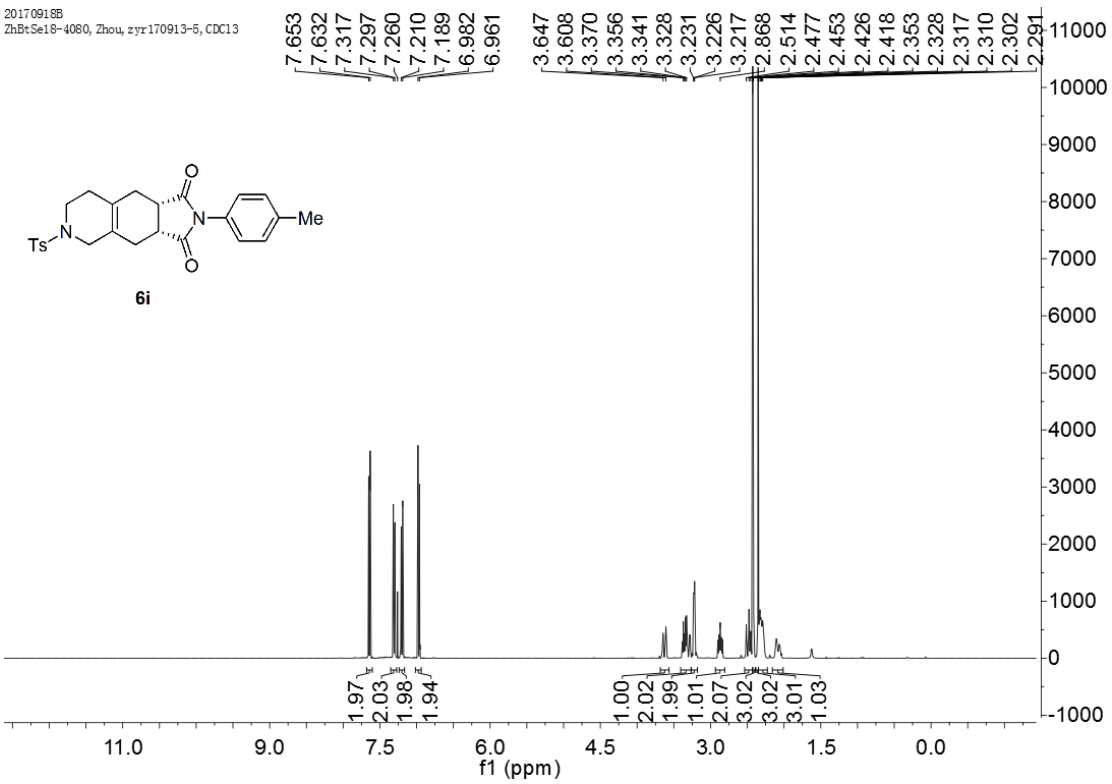

20170915B
ZhBtSe15-4161, Zhou, zyr170913-2, CDCl3
178.354
178.320
143.725
134.363
133.228
130.365
129.752
129.314
128.564
127.643
127.546
125.595
77.419
77.101
76.783
47.695
43.060
39.524
39.299
29.998
28.712
26.675
21.522
Ts
N
O
O
N
Cl
6f
f1 (ppm)

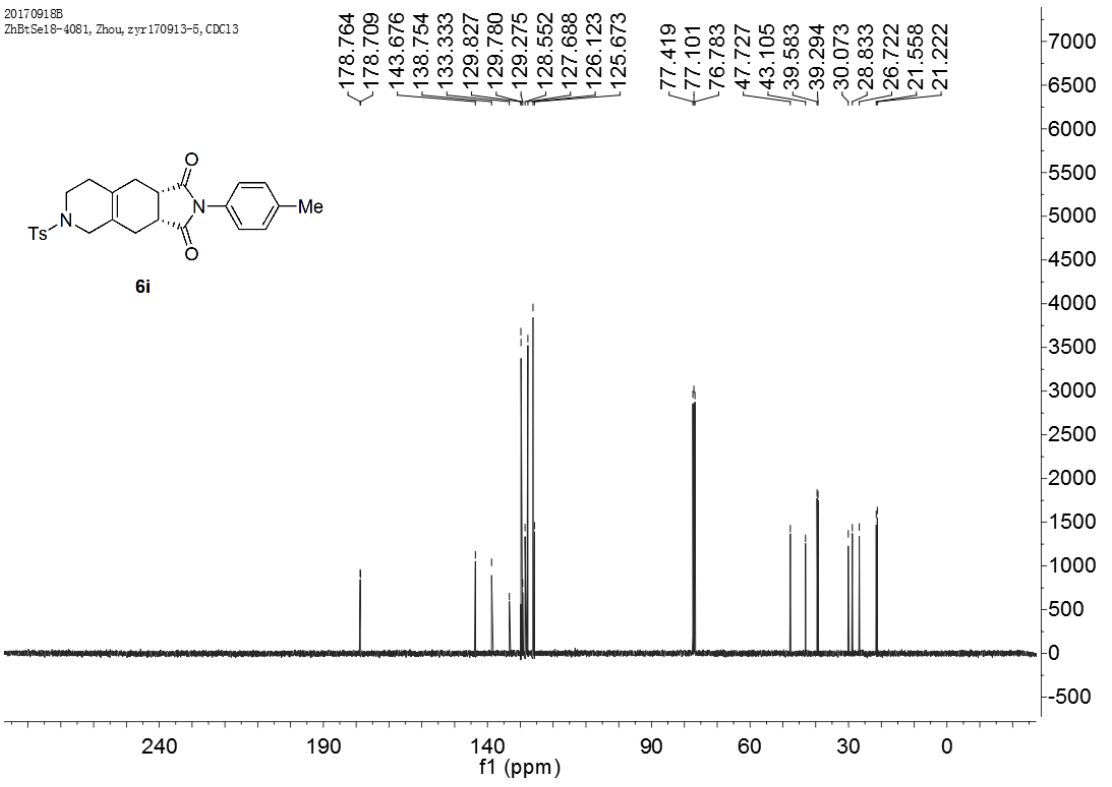

20170915B
ZhBtSe15-4180, Zhou, zyr170913-3, CDC13
7.641
7.620
7.531
7.509
7.312
7.291
7.260
7.034
7.012
3.565
3.337
3.297
3.282
3.268
3.238
3.231
3.224
2.932
2.926
2.915
2.502
2.465
2.440
2.423
2.403
2.335
2.327
2.310
2.286
2.279
Ts
N
O
O
N
Br
O
6g
2.00
1.97
2.00
1.95
1.00
4.00
1.01
1.99
3.09
3.00
1.01
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

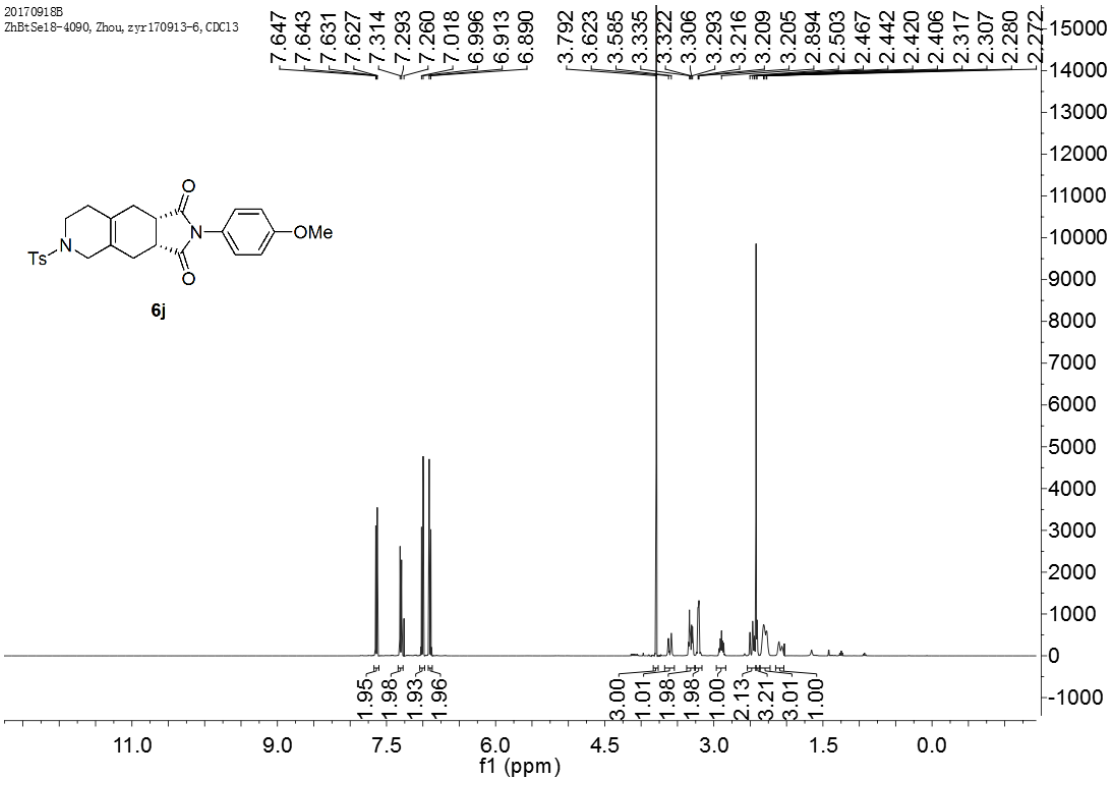

20170915B
ZhBtSe15-4181, Zhou, zyr170913-3, CDC13
178.294
178.264
143.742
133.269
132.335
130.890
129.777
128.600
127.830
127.677
125.639
122.453
77.419
77.101
76.783
47.716
43.081
39.567
39.333
30.039
28.749
26.708
21.561
Ts
N
O
O
N
Br
O
6g
240
190
140
90
60
30
0
f1 (ppm)

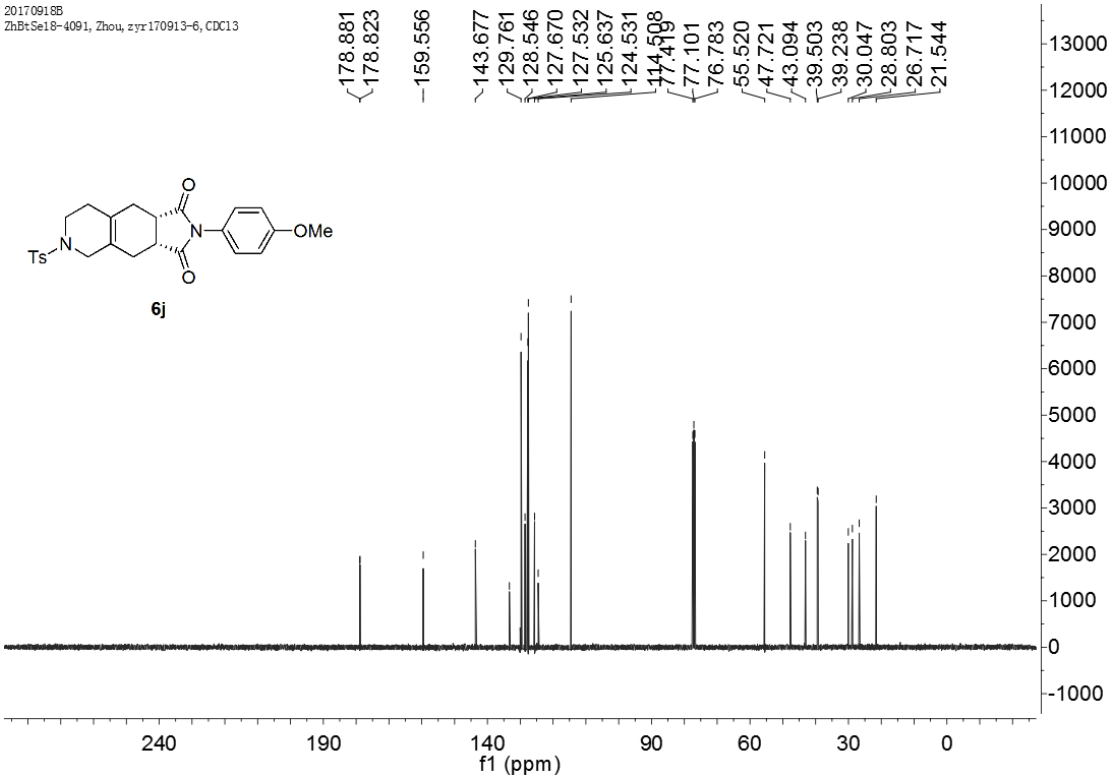

20170918B
ZhBtSe18-4070, Zhou, zyr170913-4, CDCl3
7.720
7.698
7.630
7.610
7.304
7.284
7.260
6.893
6.871
3.554
3.324
3.295
3.282
3.267
3.253
3.224
3.216
3.210
2.918
2.913
2.901
2.485
2.448
2.418
2.387
2.311
2.294
2.271
2.264
2.257
Ts
N
O
O
N
I
6h
1.98
1.99
2.01
1.96
1.00
4.00
1.01
2.02
3.00
3.06
1.03
f1 (ppm)

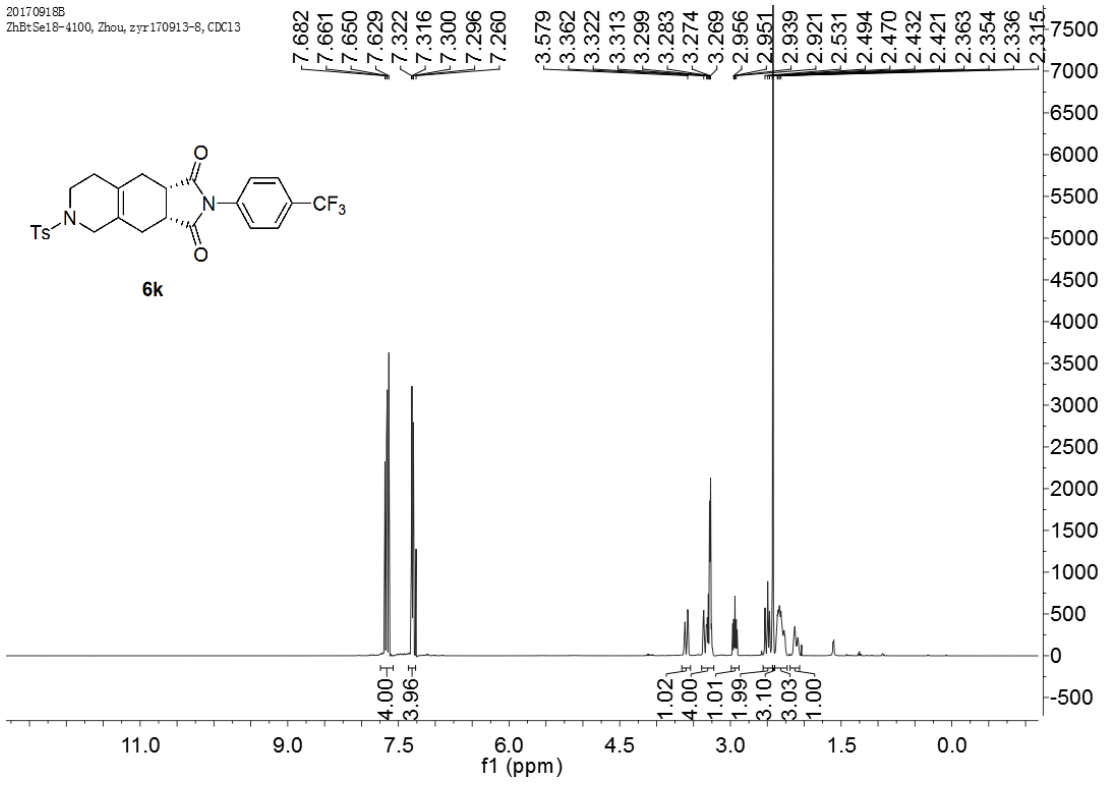

20170918B
ZhBtSe18-4071, Zhou, zyr170913-4, CDCl3
178.219
178.195
143.702
138.252
133.189
131.583
129.741
128.545
127.968
127.621
125.567
93.930
77.419
77.101
76.783
47.674
43.039
39.534
39.298
29.979
28.704
26.666
21.545
Ts
N
O
O
N
I
6h
f1 (ppm)


20170918B
ZhBtSe18-4080, Zhou, zyr170913-5, CDCl3
7.653
7.632
7.317
7.297
7.260
7.210
7.189
6.982
6.961
3.647
3.608
3.370
3.356
3.341
3.328
3.231
3.226
3.217
2.868
2.514
2.477
2.453
2.426
2.418
2.353
2.328
2.317
2.310
2.302
2.291
Ts
N
O
N
Me
O
6i
1.97
2.03
1.98
1.94
1.00
2.02
1.99
1.01
2.07
3.02
3.02
3.01
1.03
f1 (ppm)


20170918B
ZhBtSe18-4081, Zhou, zyr170913-5, CDCl3
178.764
178.709
143.676
138.754
133.333
129.827
129.780
129.275
128.552
127.688
126.123
125.673
77.419
77.101
76.783
47.727
43.105
39.583
39.294
30.073
28.833
26.722
21.558
21.222
Ts
N
O
N
Me
O
6i
f1 (ppm)


20170918B
ZhBtSe18-4090, Zhou, zyr170913-6, CDCl3
7.647
7.643
7.631
7.627
7.314
7.293
7.260
7.018
6.996
6.913
6.890
3.792
3.623
3.585
3.335
3.322
3.306
3.293
3.216
3.209
3.205
2.894
2.503
2.467
2.442
2.420
2.406
2.317
2.307
2.280
2.272
Ts
N
O
OMe
6j
1.95
1.98
1.93
1.96
3.00
1.01
1.98
1.98
1.00
2.13
3.21
3.01
1.00
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)


20170918B
ZhBtSe18-4091, Zhou, zyr170913-6, CDCl3
178.881
178.823
159.556
143.677
129.761
128.546
127.670
127.532
125.637
124.531
114.508
77.419
77.101
76.783
55.520
47.721
43.094
39.503
39.238
30.047
28.803
26.717
21.544
Ts
N
O
OMe
6j
240
190
140
90
60
30
0
f1 (ppm)


20170918B
ZhBtSe18-4100, Zhou, zyr170913-8, CDCl3
7.682
7.661
7.650
7.629
7.322
7.316
7.300
7.296
7.260
3.579
3.362
3.322
3.313
3.299
3.283
3.274
3.269
2.956
2.951
2.939
2.921
2.531
2.494
2.470
2.432
2.421
2.363
2.354
2.336
2.315
Ts
CF3
6k
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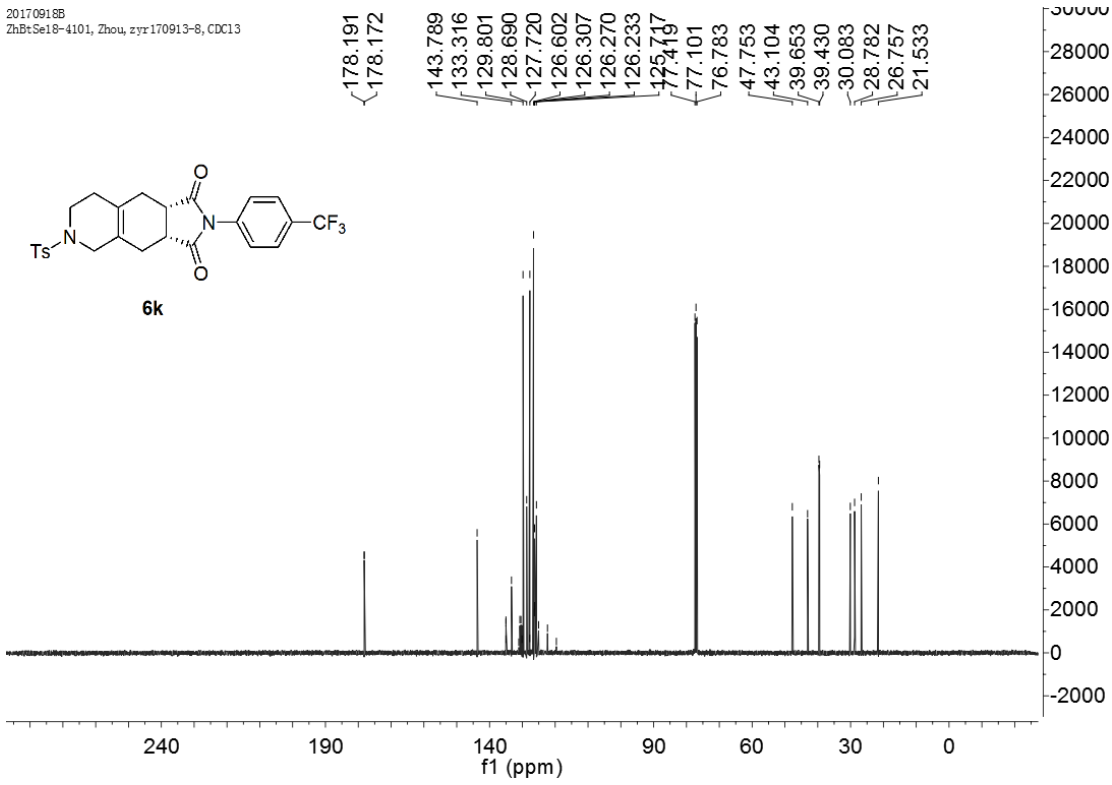
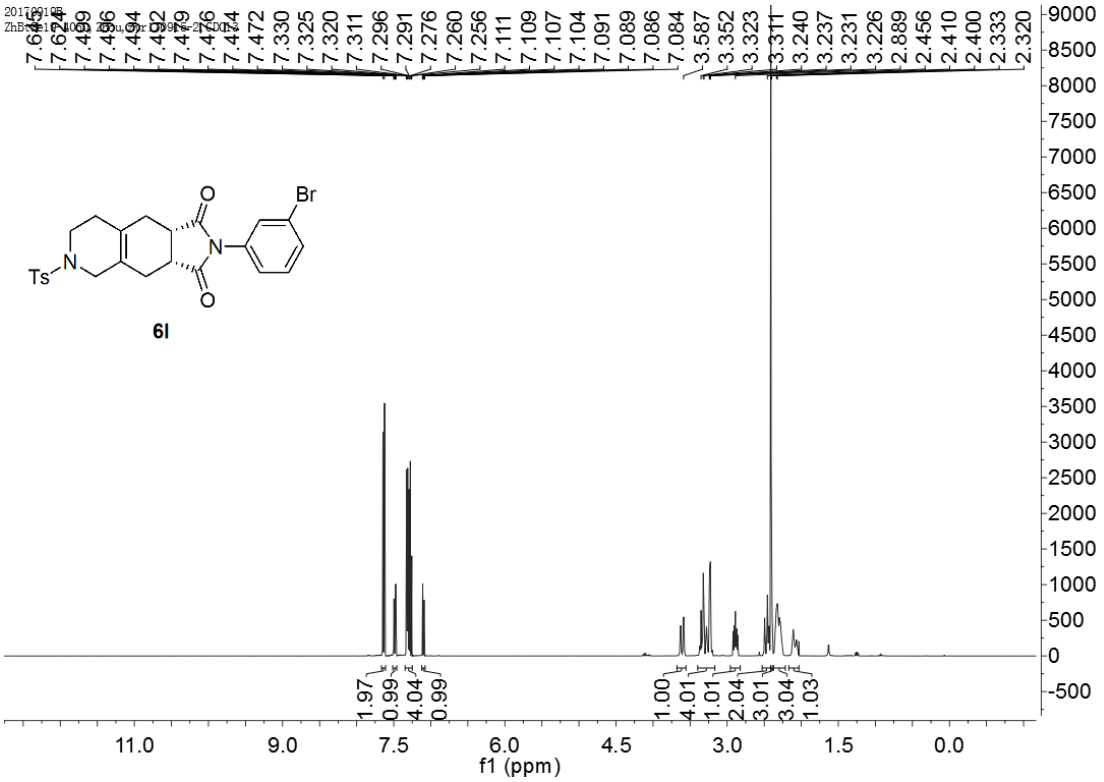
3.96
1.02
4.00
1.01
1.99
3.10
3.03
1.00
f1 (ppm)


20170918B
ZhBtSe18-4101, Zhou, zyr170913-8, CDCl3
178.191
178.172
143.789
133.316
129.801
128.690
127.720
126.602
126.307
126.270
126.233
125.717
77.419
77.101
76.783
47.753
43.104
39.653
39.430
30.083
28.782
26.757
21.533
Ts
CF3
6k
f1 (ppm)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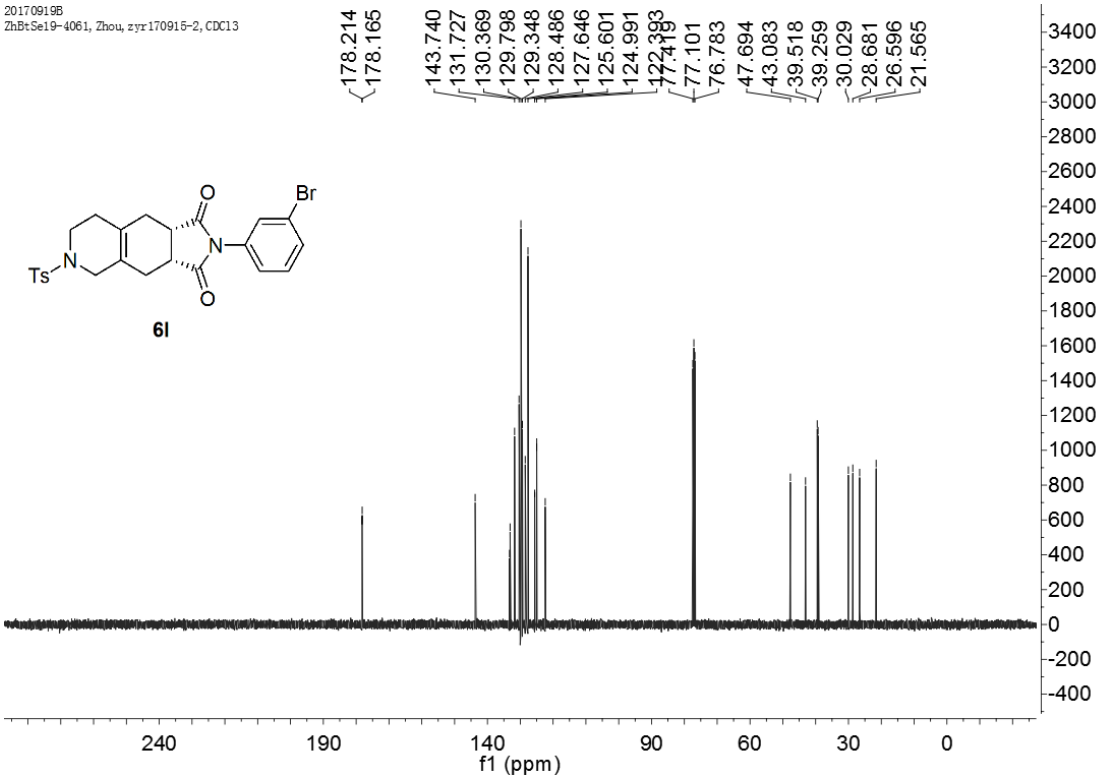
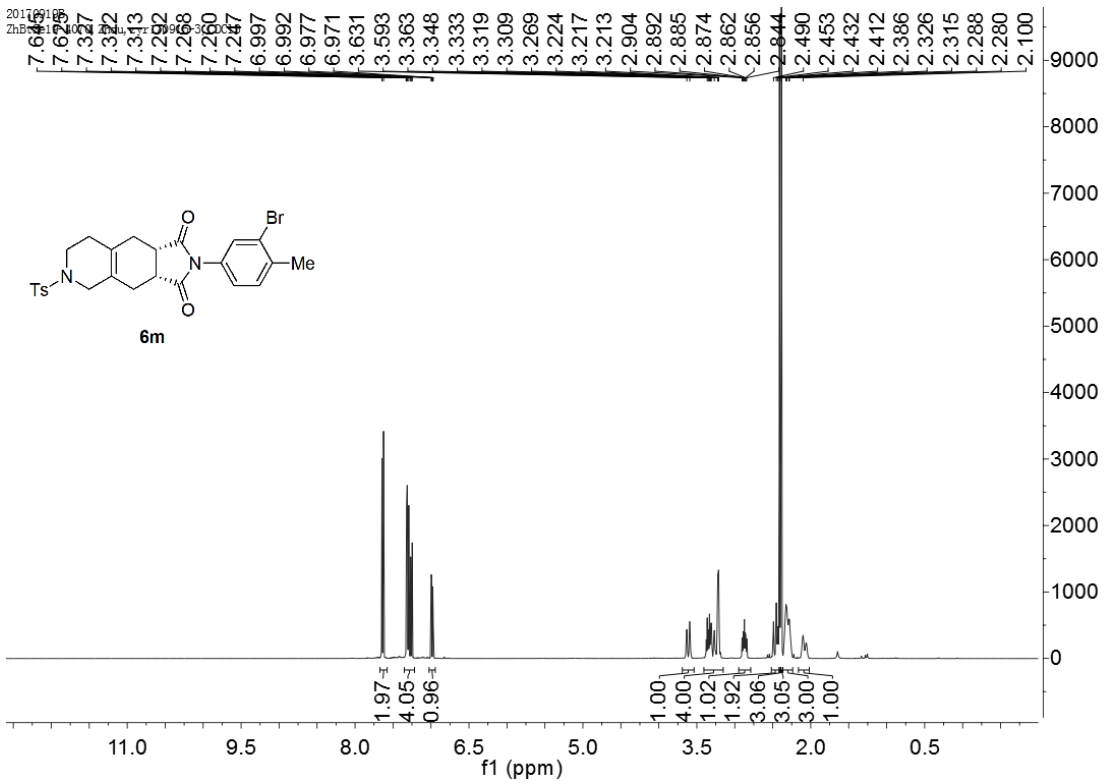
7.639
7.496
7.494
7.492
7.479
7.476
7.474
7.472
7.330
7.325
7.320
7.311
7.296
7.291
7.276
7.260
7.256
7.111
7.109
7.107
7.104
7.091
7.089
7.086
7.084
3.587
3.352
3.323
3.311
3.240
3.237
3.231
3.226
2.889
2.456
2.410
2.400
2.333
2.320
Br
O
N
Ts
6l
1.97
0.99
4.04
0.99
1.00
4.01
1.01
2.04
3.01
3.04
1.03
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)


20170919B
ZhBtSe19-4061, Zhou, zyr170915-2, CDCl3
178.214
178.165
143.740
131.727
130.369
129.798
129.348
128.486
127.646
125.601
124.991
122.393
77.419
77.101
76.783
47.694
43.083
39.518
39.259
30.029
28.681
26.596
21.565
Br
O
N
Ts
6l
240
190
140
90
60
30
0
f1 (ppm)


7.645
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7.327
7.322
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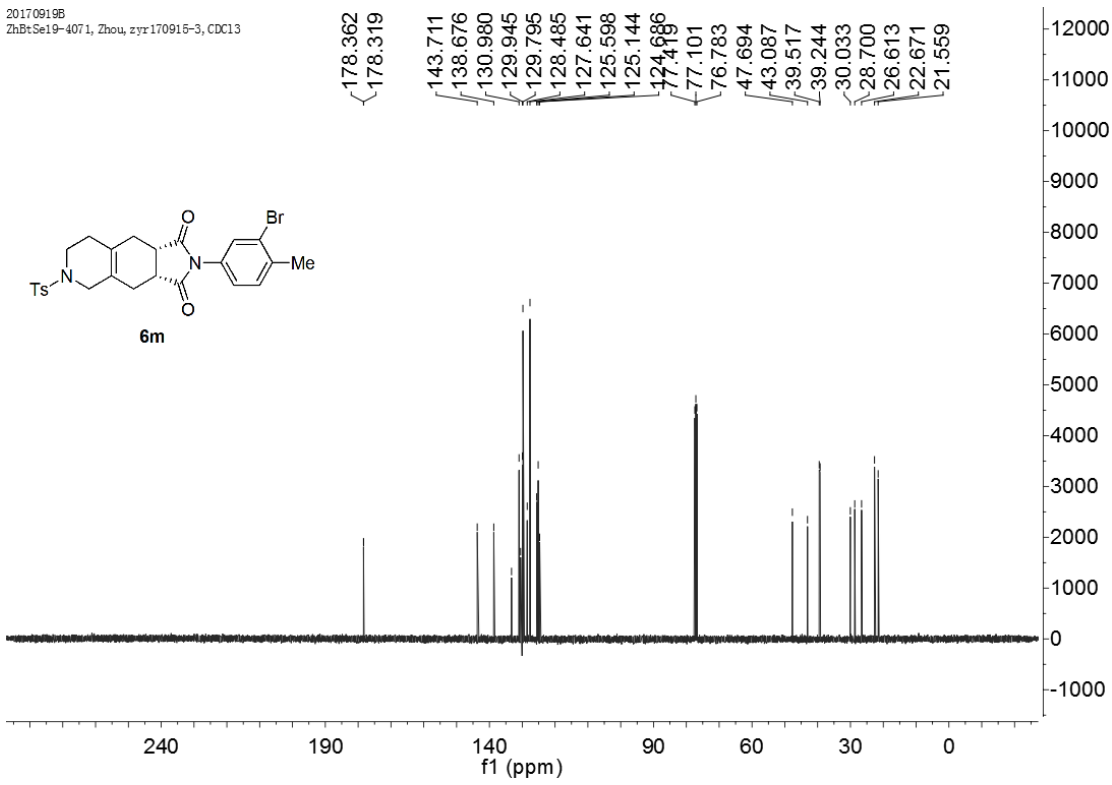
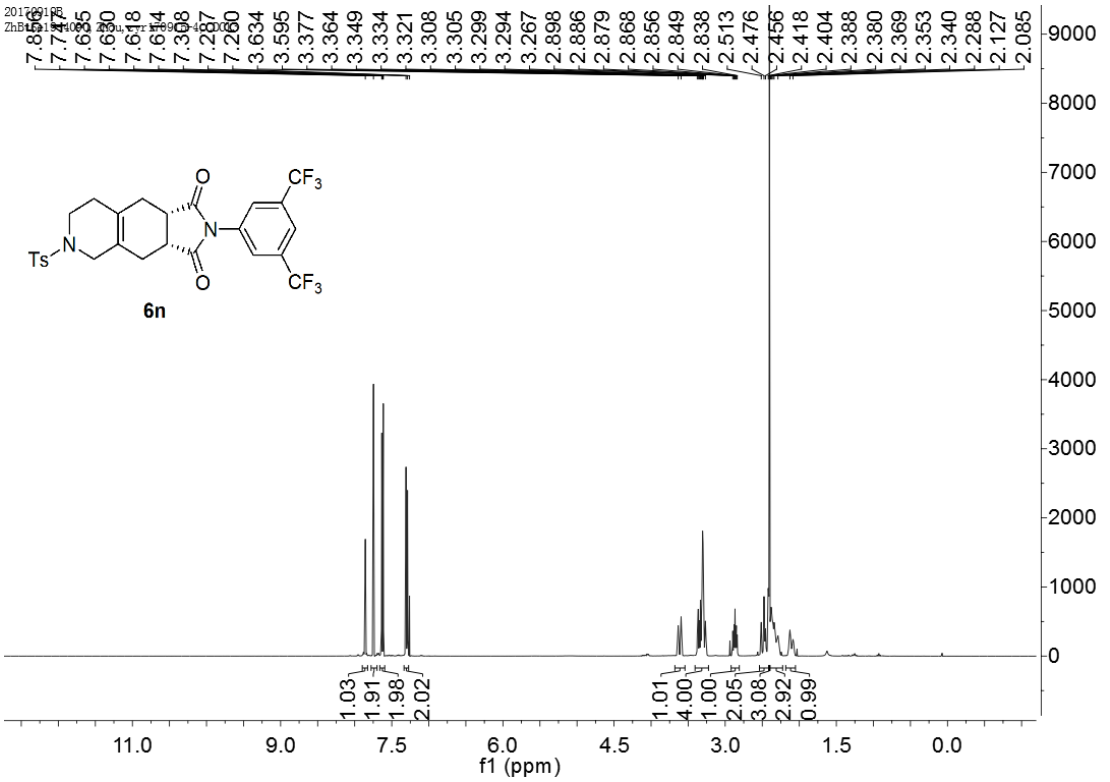
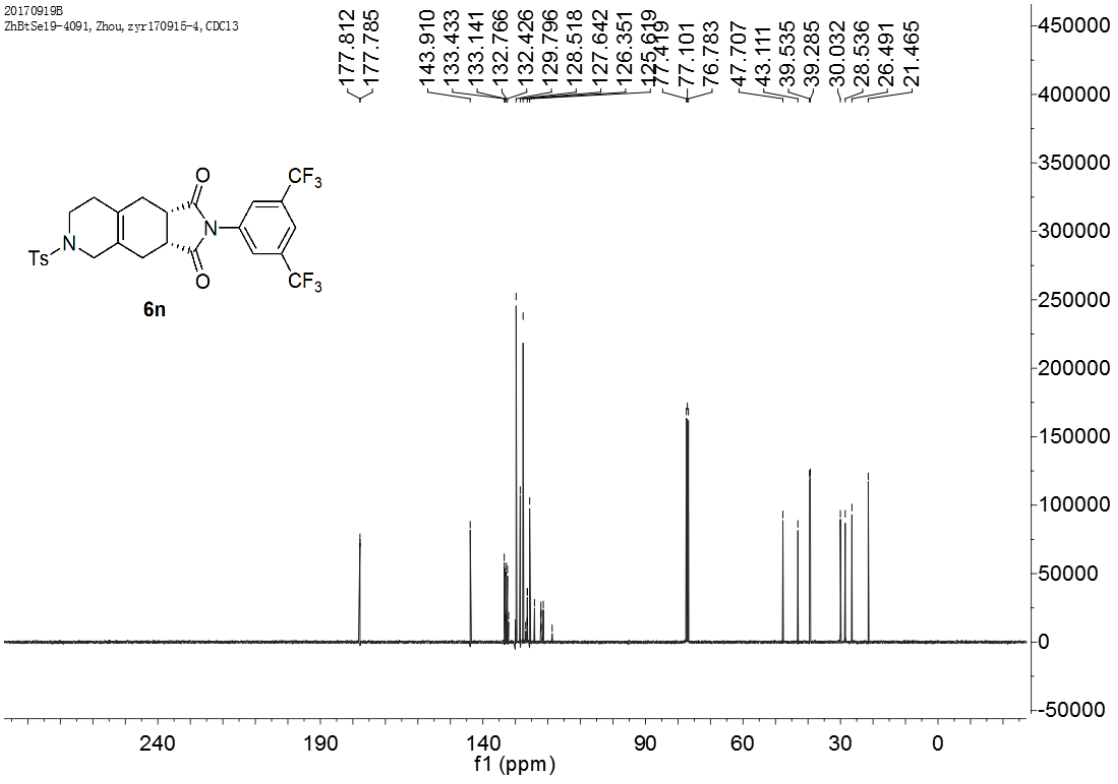
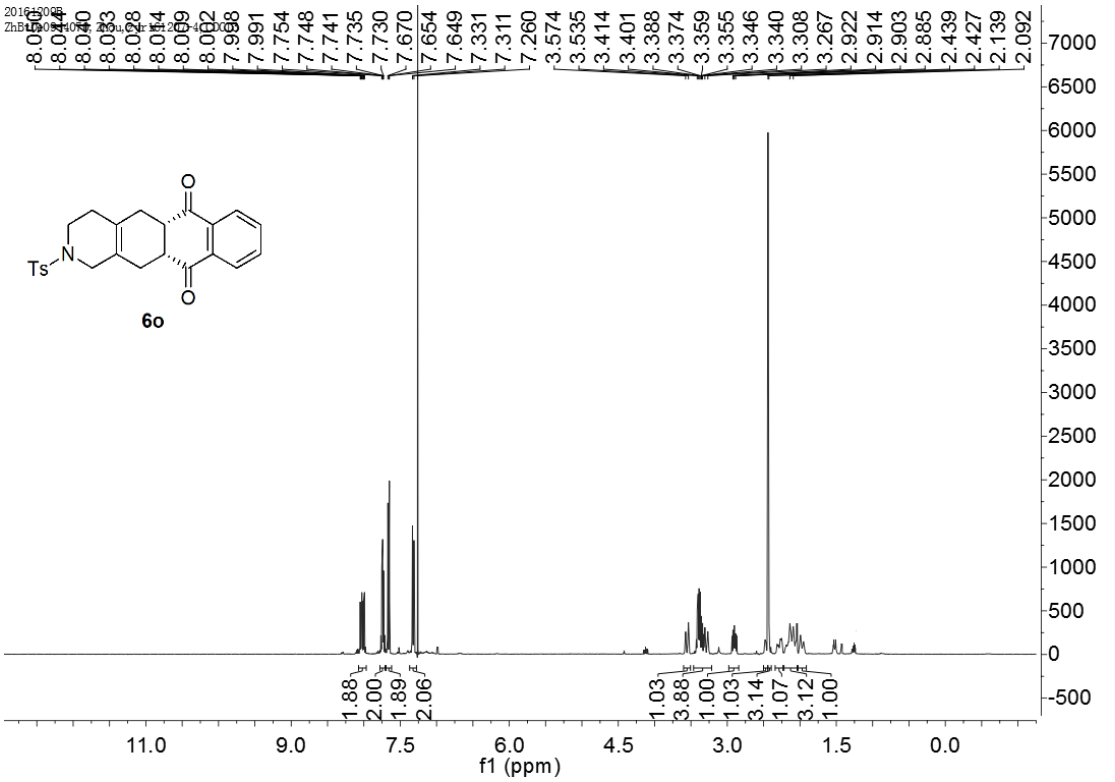
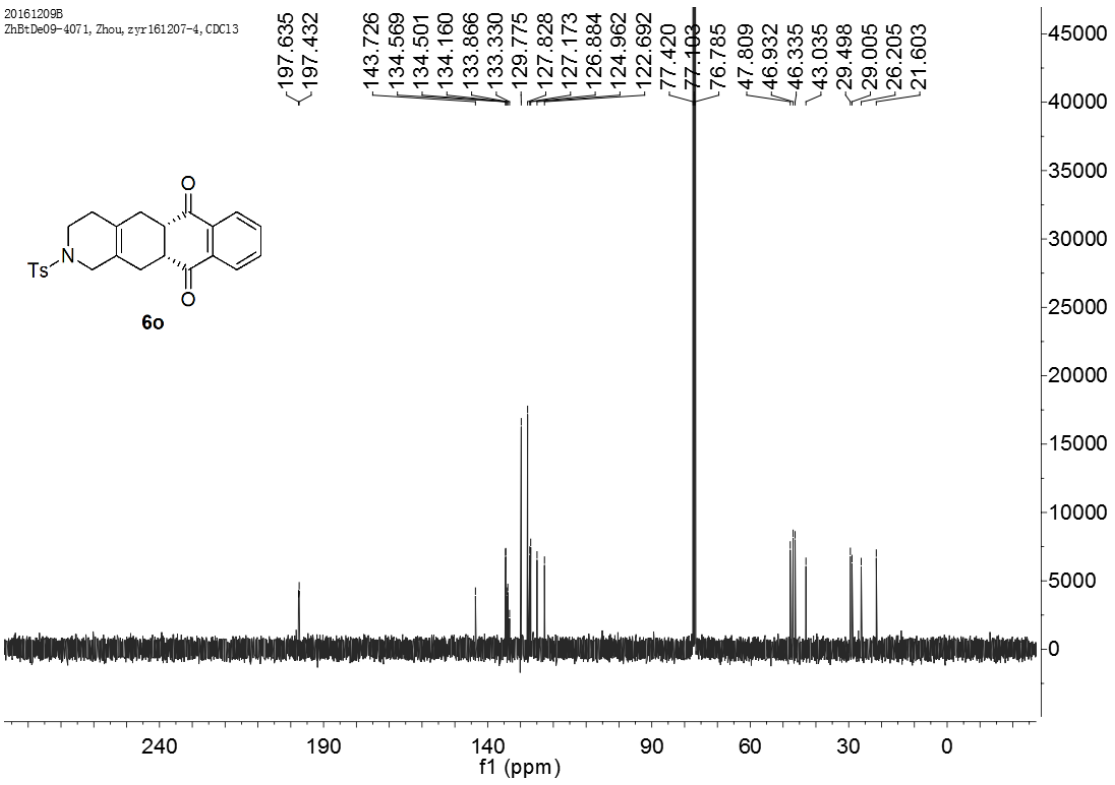
7.292
7.268
7.260
7.247
6.997
6.992
6.977
6.971
3.631
3.593
3.363
3.348
3.333
3.319
3.309
3.269
3.224
3.217
3.213
2.904
2.892
2.885
2.874
2.862
2.856
2.844
2.490
2.453
2.432
2.412
2.386
2.326
2.315
2.288
2.280
2.100
Br
Me
Ts
N
O
O
O
6m
1.97
4.05
0.96
1.00
4.00
1.02
1.92
3.06
3.05
3.00
1.00
f1 (ppm)

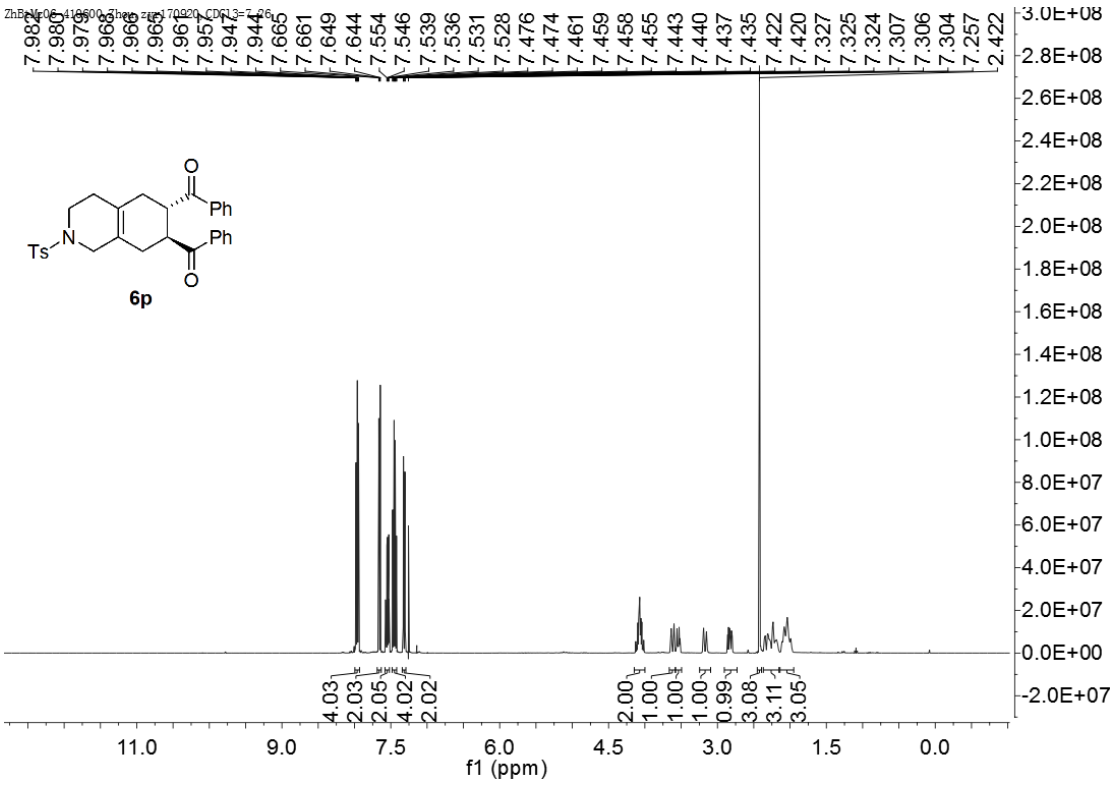

20170919B
ZhBtSe19-4071, Zhou, zyr170915-3, CDCl3
178.362
178.319
143.711
138.676
130.980
129.945
129.795
128.485
127.641
125.598
125.144
124.686
77.419
77.101
76.783
47.694
43.087
39.517
39.244
30.033
28.700
26.613
22.671
21.559
Br
Me
Ts
N
O
O
O
6m
f1 (ppm)

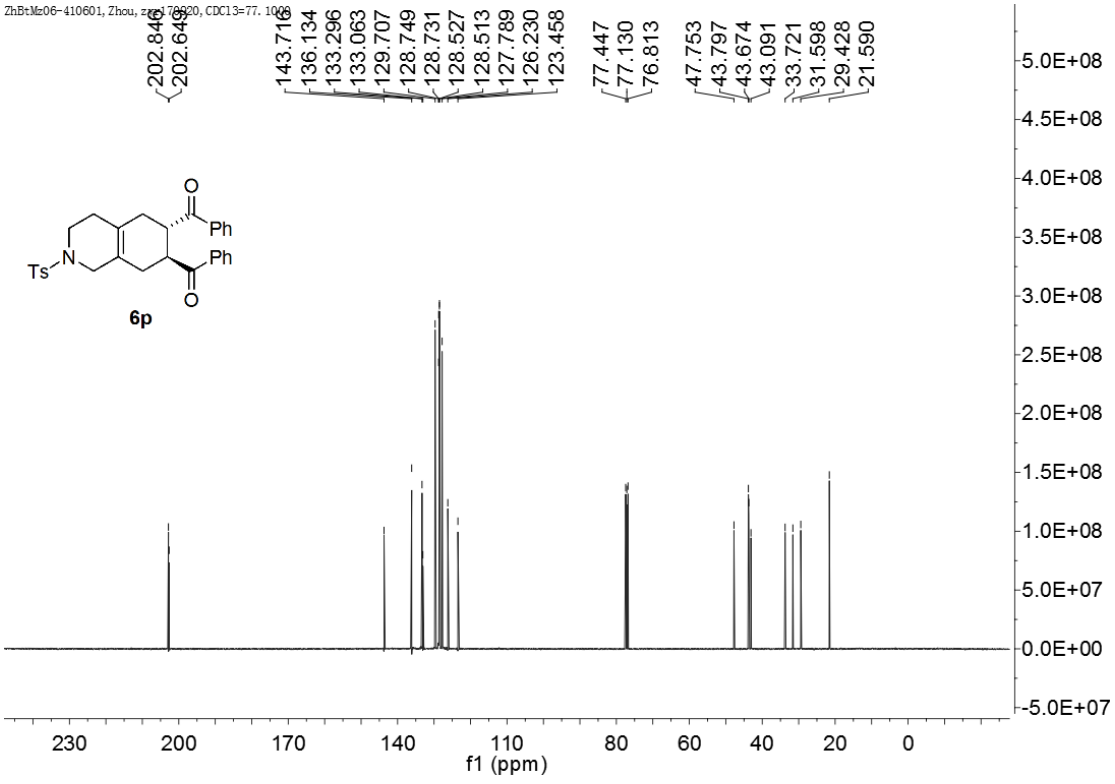

7.856
7.772
7.635
7.630
7.618
7.614
7.387
7.287
7.260
3.634
3.595
3.377
3.364
3.349
3.334
3.321
3.308
3.305
3.299
3.294
3.267
2.898
2.886
2.879
2.868
2.856
2.849
2.838
2.513
2.476
2.456
2.418
2.404
2.388
2.380
2.369
2.353
2.340
2.288
2.127
2.085
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.03
1.91
1.98
2.02
1.01
4.00
1.00
2.05
3.08
2.92
0.99
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)
O
CF3
N
Ts
N
O
CF3
6n

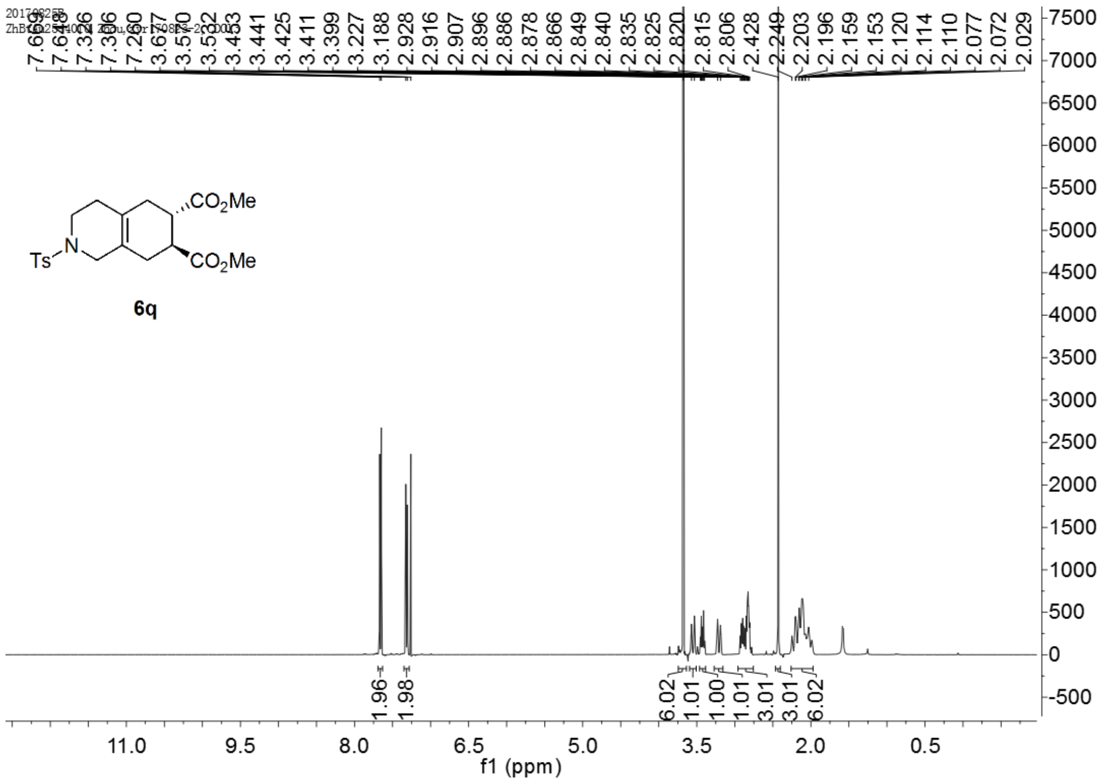

20170919B
ZhBtSe19-4091, Zhou, zyr170915-4, CDCl3
177.812
177.785
143.910
133.433
133.141
132.766
132.426
129.796
128.518
127.642
126.351
125.619
77.419
77.101
76.783
47.707
43.111
39.535
39.285
30.032
28.536
26.491
21.465
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
240
190
140
90
60
30
0
f1 (ppm)
O
CF3
N
Ts
N
O
CF3
6n

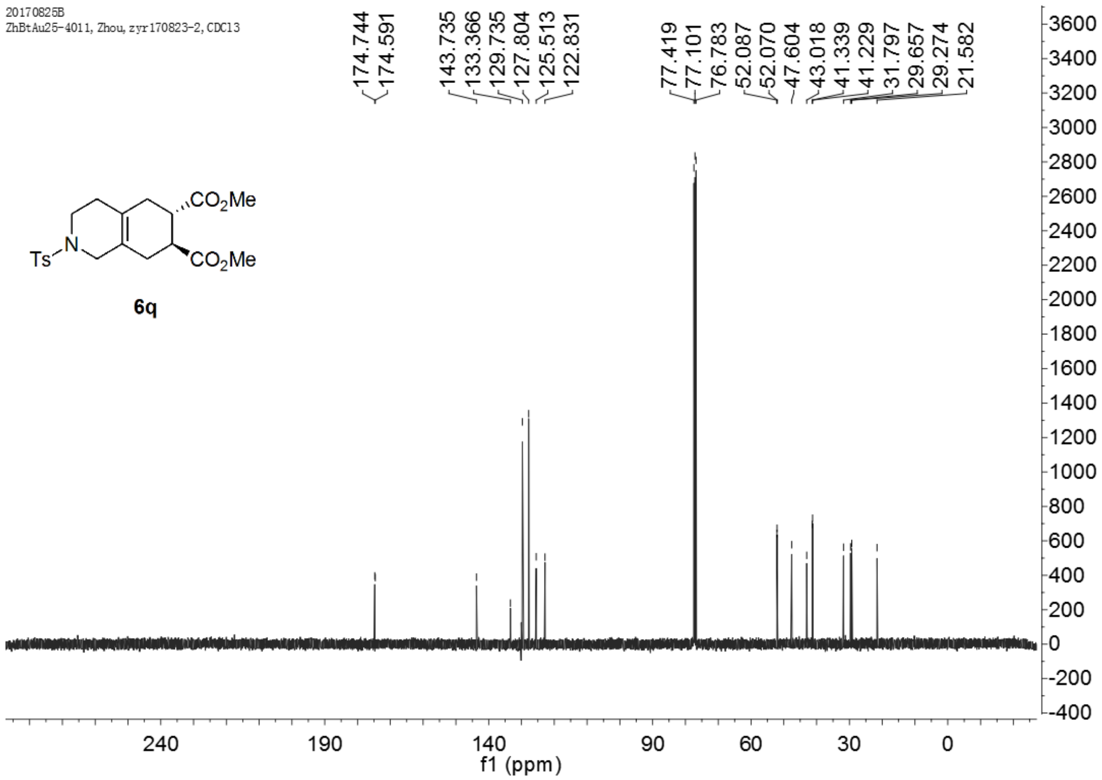

8.052
8.047
8.040
8.033
8.028
8.014
8.009
8.002
7.998
7.991
7.754
7.748
7.741
7.735
7.730
7.670
7.654
7.649
7.331
7.311
7.260
3.574
3.535
3.414
3.401
3.388
3.374
3.359
3.355
3.346
3.340
3.308
3.267
2.922
2.914
2.903
2.885
2.439
2.427
2.139
2.092
1.88
2.00
1.89
2.06
1.03
3.88
1.00
1.03
3.14
1.07
3.12
1.00
Ts
N
O
O
6o
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

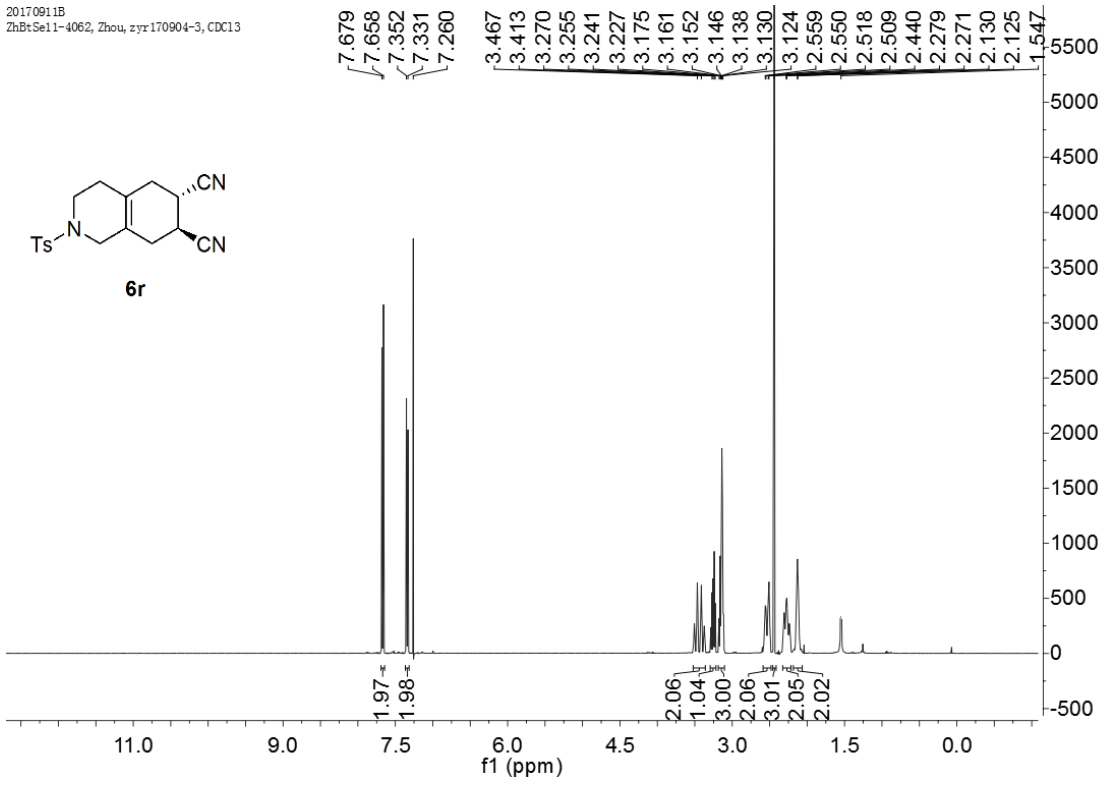

20161209B
ZhBtDe09-4071, Zhou, zyr161207-4, CDCl3
197.635
197.432
143.726
134.569
134.501
134.160
133.866
133.330
129.775
127.828
127.173
126.884
124.962
122.692
77.420
77.103
76.785
47.809
46.932
46.335
43.035
29.498
29.005
26.205
21.603
Ts
N
O
O
6o
240
190
140
90
60
30
0
f1 (ppm)

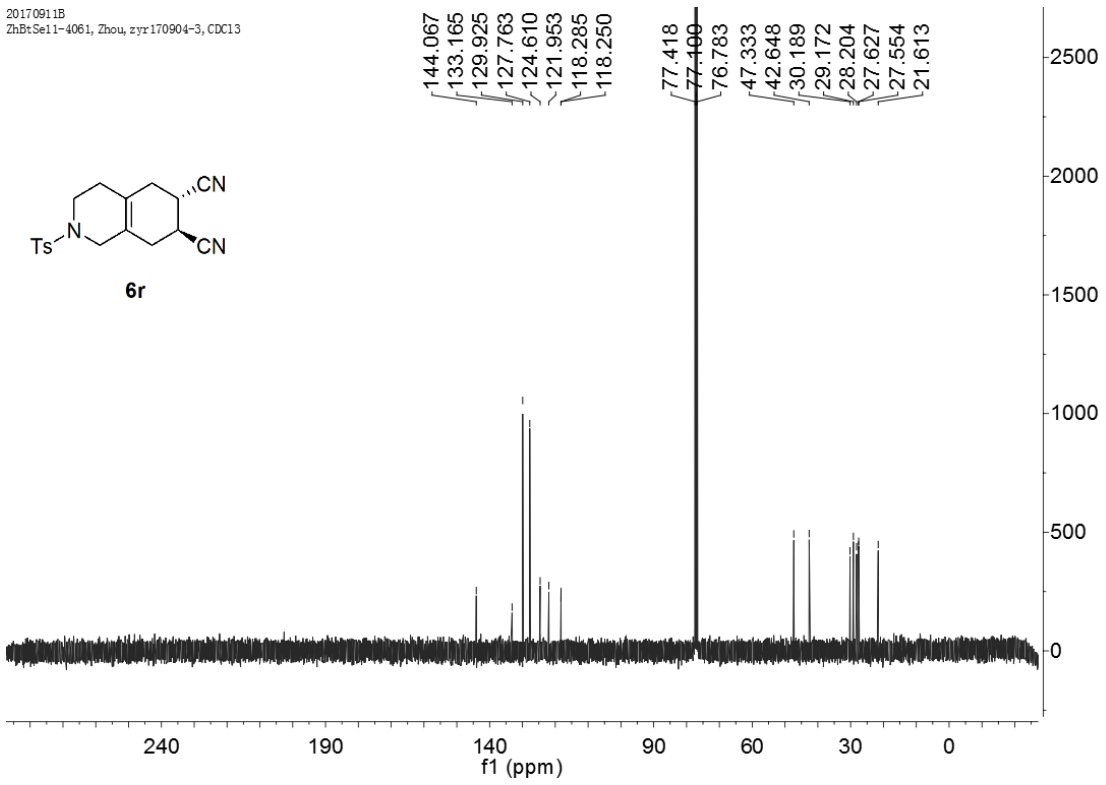

7.982 7.980 7.979 7.968 7.966 7.965 7.961 7.957 7.947 7.944 7.665 7.661 7.649 7.644 7.554 7.546 7.539 7.536 7.531 7.528 7.476 7.474 7.461 7.459 7.458 7.455 7.443 7.440 7.437 7.435 7.422 7.420 7.327 7.325 7.324 7.307 7.306 7.304 7.257 2.422
Ph
Ph
Ts
N
O
O
6p
4.03 2.03 2.05 4.02 2.02 2.00 1.00 1.00 1.00 0.99 3.08 3.11 3.05
11.0 9.0 7.5 6.0 4.5 3.0 1.5 0.0
f1 (ppm)

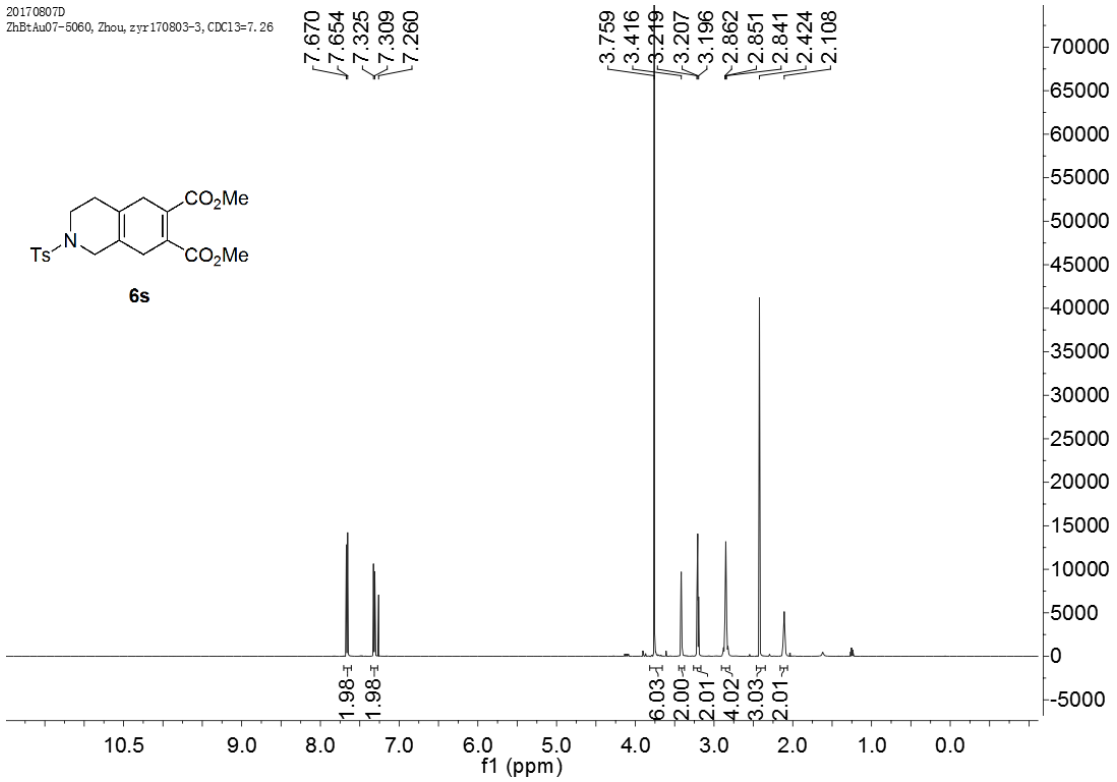

202.846 202.643 143.716 136.134 133.296 133.063 129.707 128.749 128.731 128.527 128.513 127.789 126.230 123.458 77.447 77.130 76.813 47.753 43.797 43.674 43.091 33.721 31.598 29.428 21.590
Ph
Ph
Ts
N
O
O
6p
230 200 170 140 110 80 60 40 20 0
f1 (ppm)

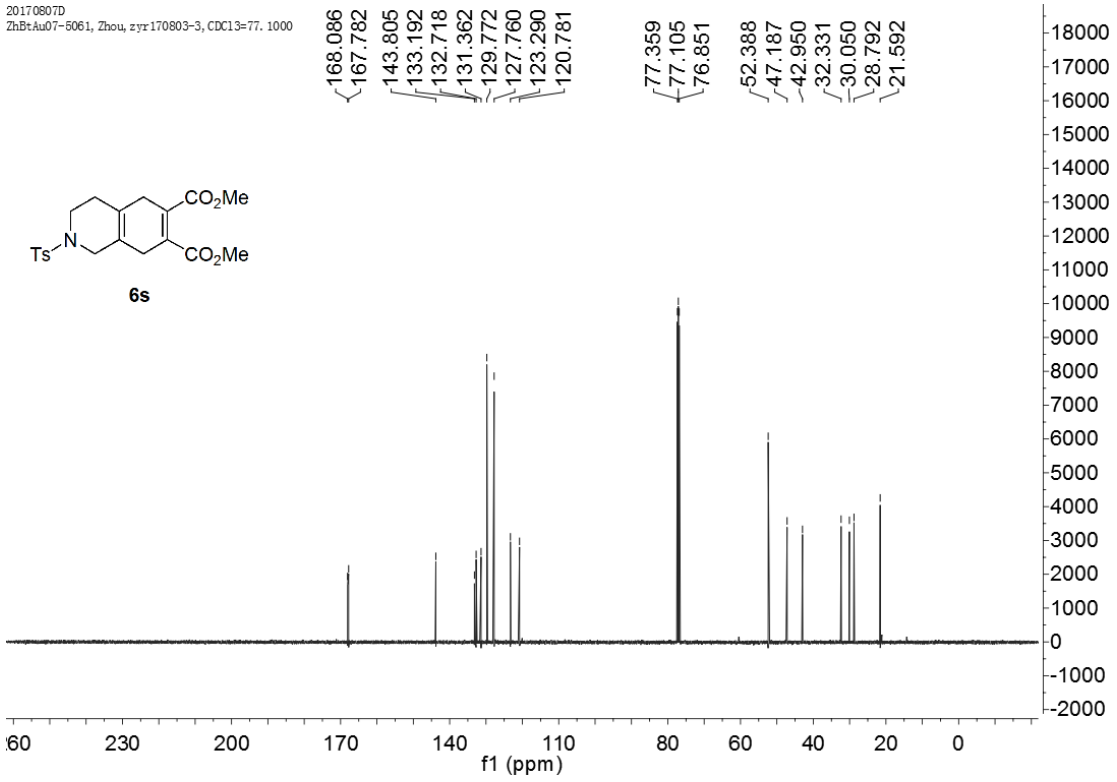

7.326
7.306
7.260
3.677
3.441
3.425
3.411
3.399
3.227
3.188
2.928
2.916
2.907
2.896
2.886
2.878
2.866
2.849
2.840
2.835
2.825
2.820
2.815
2.806
2.428
2.249
2.203
2.196
2.159
2.153
2.120
2.114
2.110
2.077
2.072
2.029
CO2Me
CO2Me
Ts
N
6q
1.96
1.98
6.02
1.01
1.00
1.01
3.01
3.01
6.02
f1 (ppm)

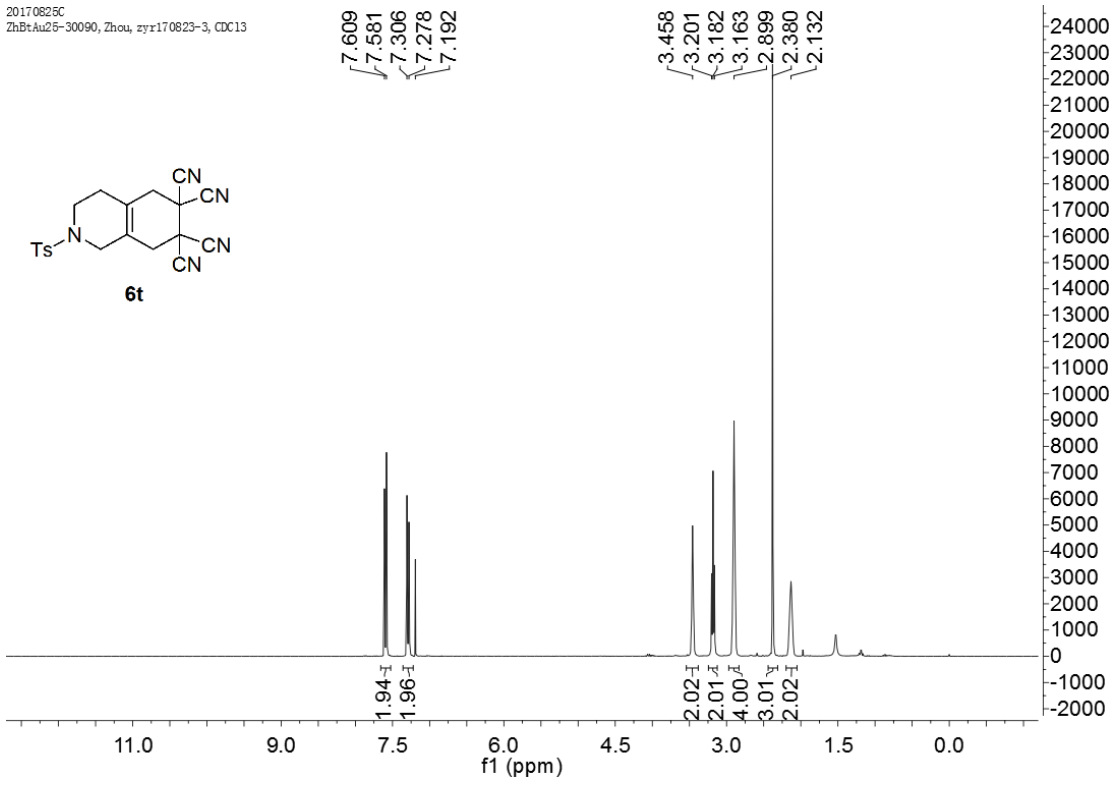

20170825B
ZhBtAu25-4011, Zhou, zyr170823-2, CDCl3
174.744
174.591
143.735
133.366
129.735
127.804
125.513
122.831
77.419
77.101
76.783
52.087
52.070
47.604
43.018
41.339
41.229
31.797
29.657
29.274
21.582
CO2Me
CO2Me
Ts
N
6q
f1 (ppm)

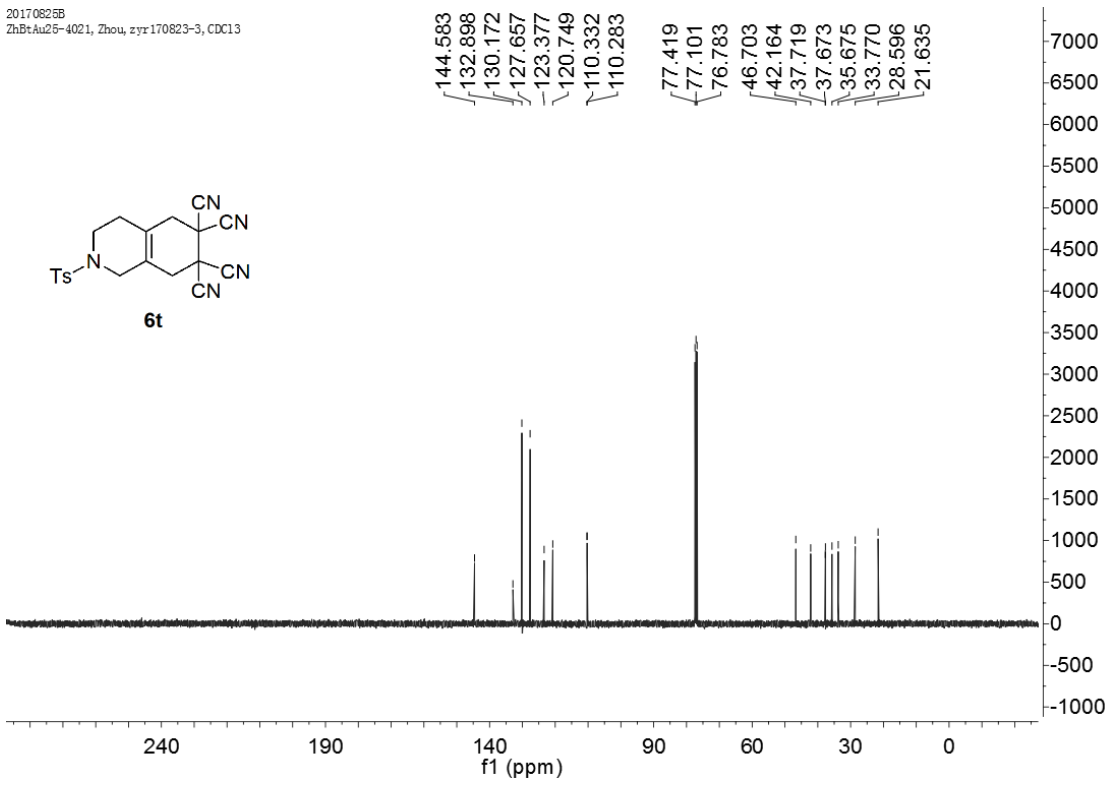

20170911B
ZhBtSe11-4062, Zhou, zyr170904-3, CDCl3
7.679
7.658
7.352
7.331
7.260
3.467
3.413
3.270
3.255
3.241
3.227
3.175
3.161
3.152
3.146
3.138
3.130
3.124
2.559
2.550
2.518
2.509
2.440
2.279
2.271
2.130
2.125
1.547
CN
CN
Ts
N
6r
1.97
1.98
2.06
1.04
3.00
2.06
3.01
2.05
2.02
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

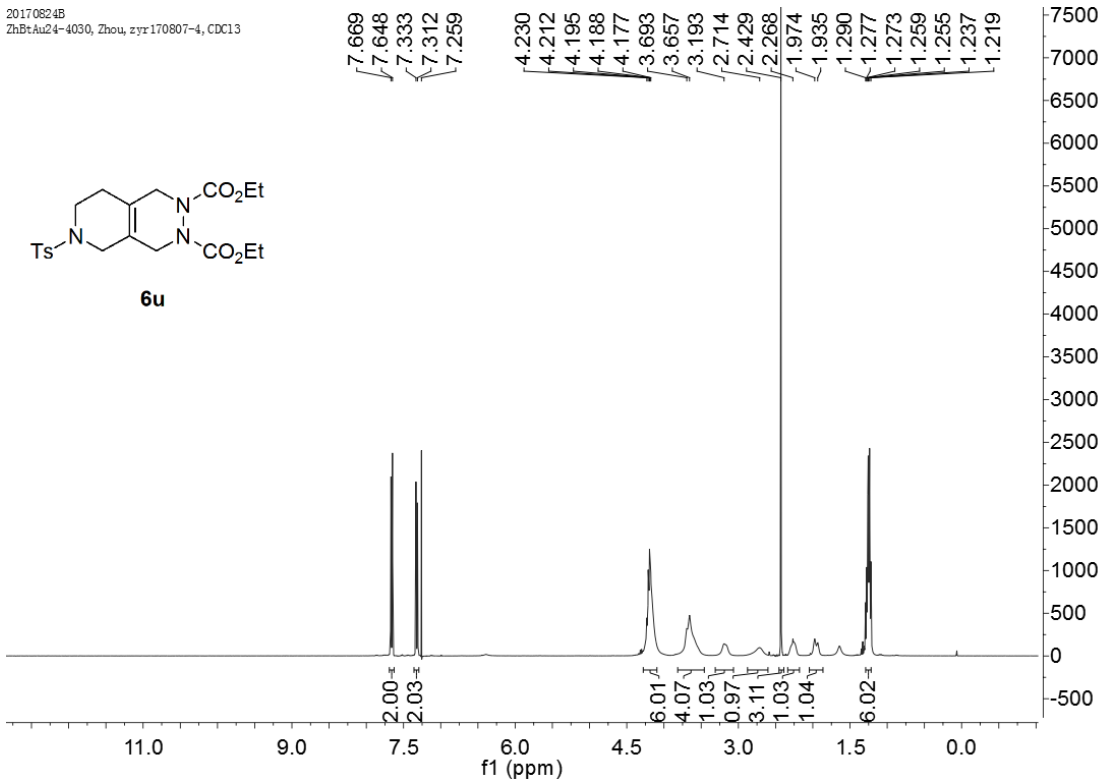

20170911B
ZhBtSe11-4061, Zhou, zyr170904-3, CDCl3
144.067
133.165
129.925
127.763
124.610
121.953
118.285
118.250
77.418
77.100
76.783
47.333
42.648
30.189
29.172
28.204
27.627
27.554
21.613
CN
CN
Ts
N
6r
240
190
140
90
60
30
0
f1 (ppm)

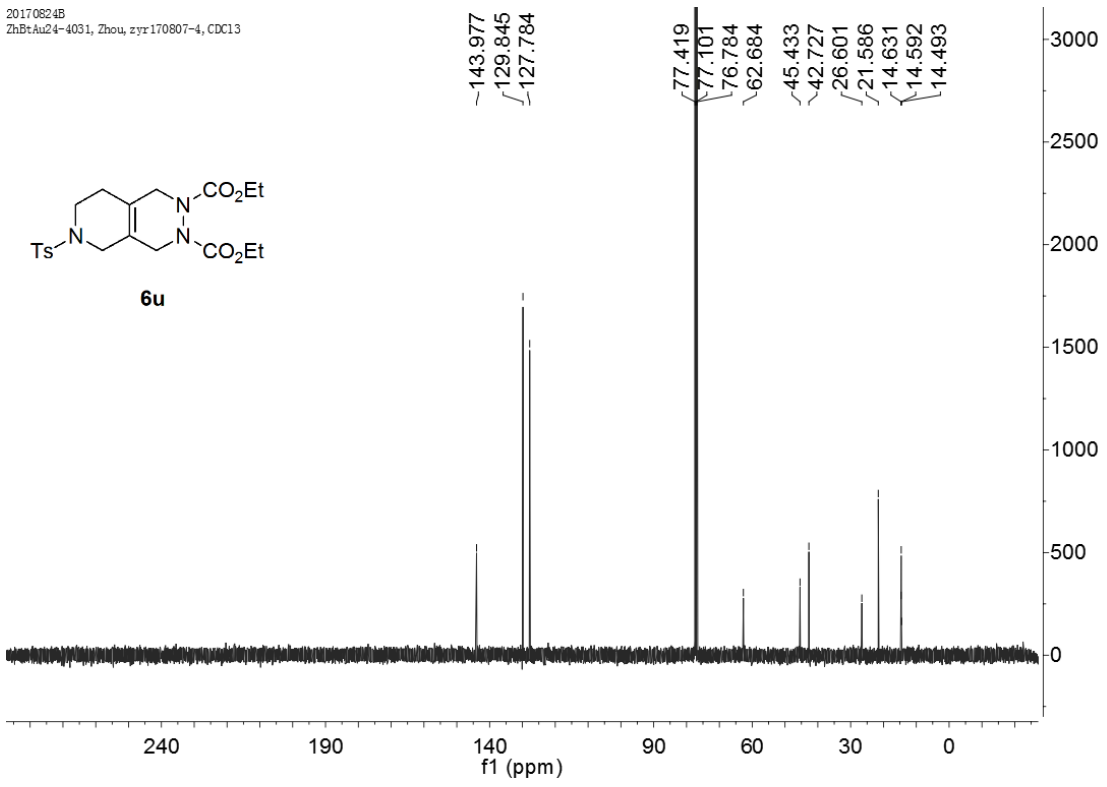

20170807D
ZhBtAu07-5060, Zhou, zyr170803-3, CDCl3=7.26
7.670
7.654
7.325
7.309
7.260
3.759
3.416
3.219
3.207
3.196
2.862
2.851
2.841
2.424
2.108
CO2Me
CO2Me
Ts
N
6s
1.98
1.98
6.03
2.00
2.01
4.02
3.03
2.01
f1 (ppm)

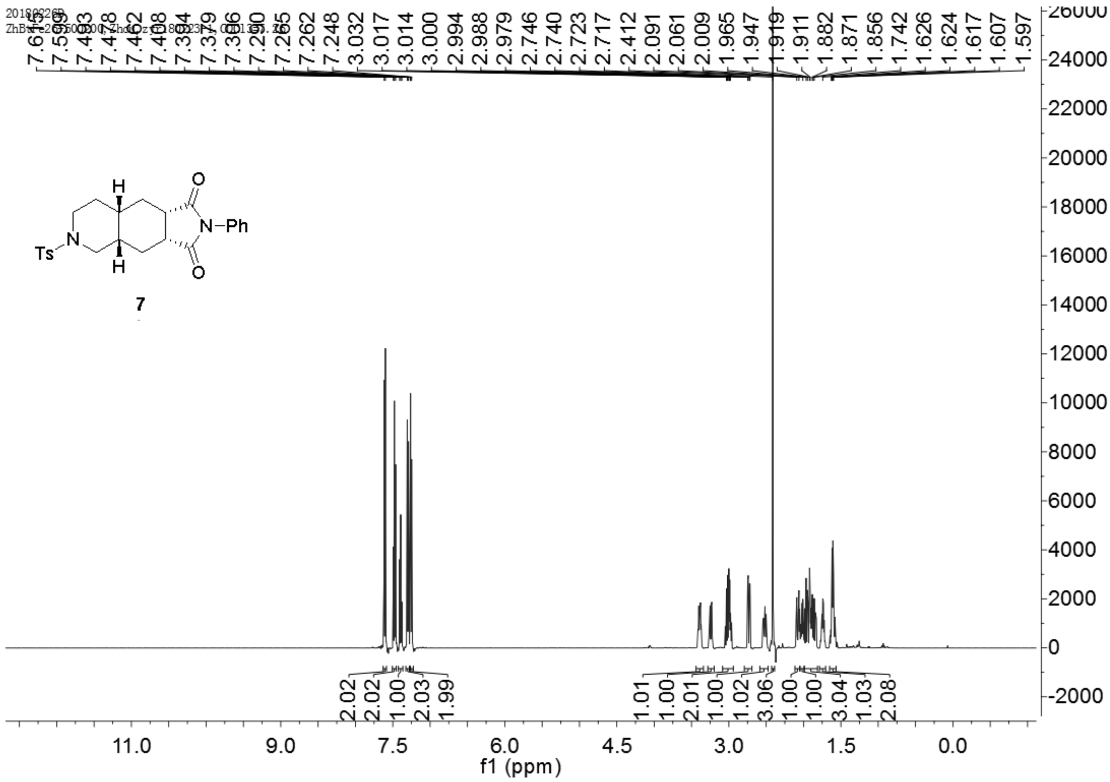

20170807D
ZhBtAu07-5061, Zhou, zyr170803-3, CDCl3=77.1000
168.086
167.782
143.805
133.192
132.718
131.362
129.772
127.760
123.290
120.781
77.359
77.105
76.851
52.388
47.187
42.950
32.331
30.050
28.792
21.592
CO2Me
CO2Me
Ts
N
6s
f1 (ppm)

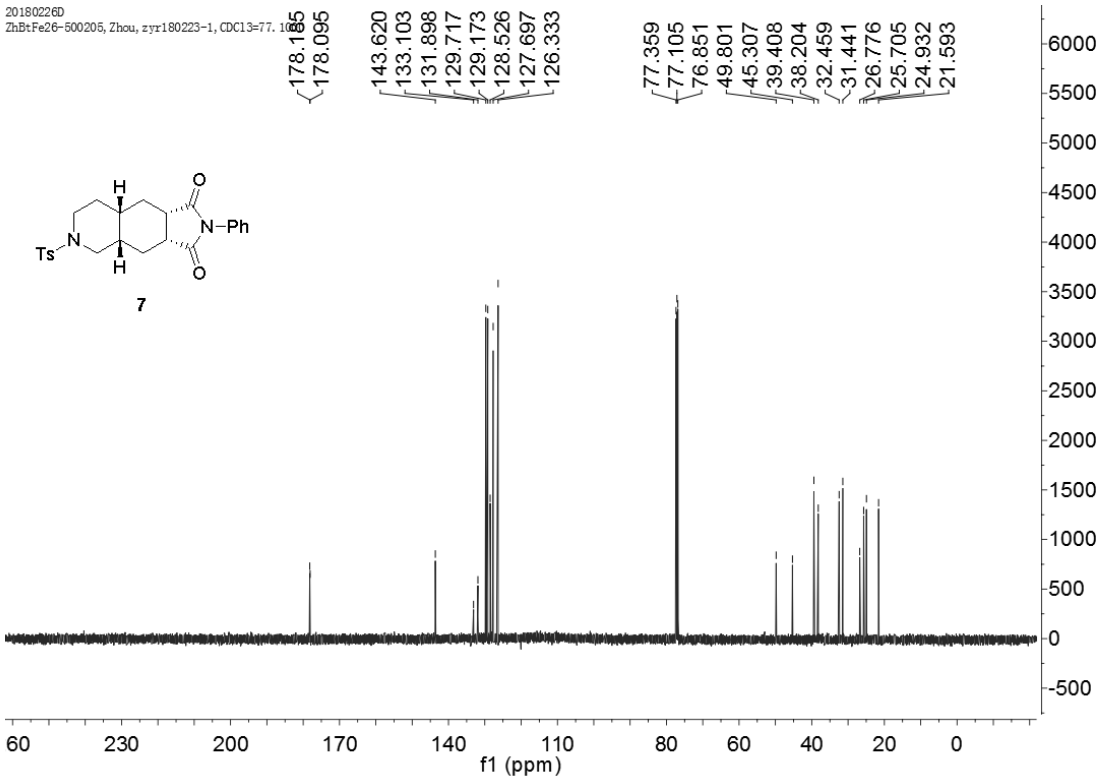

20170825C
ZhBtAu25-30090, Zhou, zyr170823-3, CDCl3
7.609
7.581
7.306
7.278
7.192
3.458
3.201
3.182
3.163
2.899
2.380
2.132
CN
CN
CN
CN
Ts
N
6t
1.94
1.96
2.02
2.01
4.00
3.01
2.02
f1 (ppm)

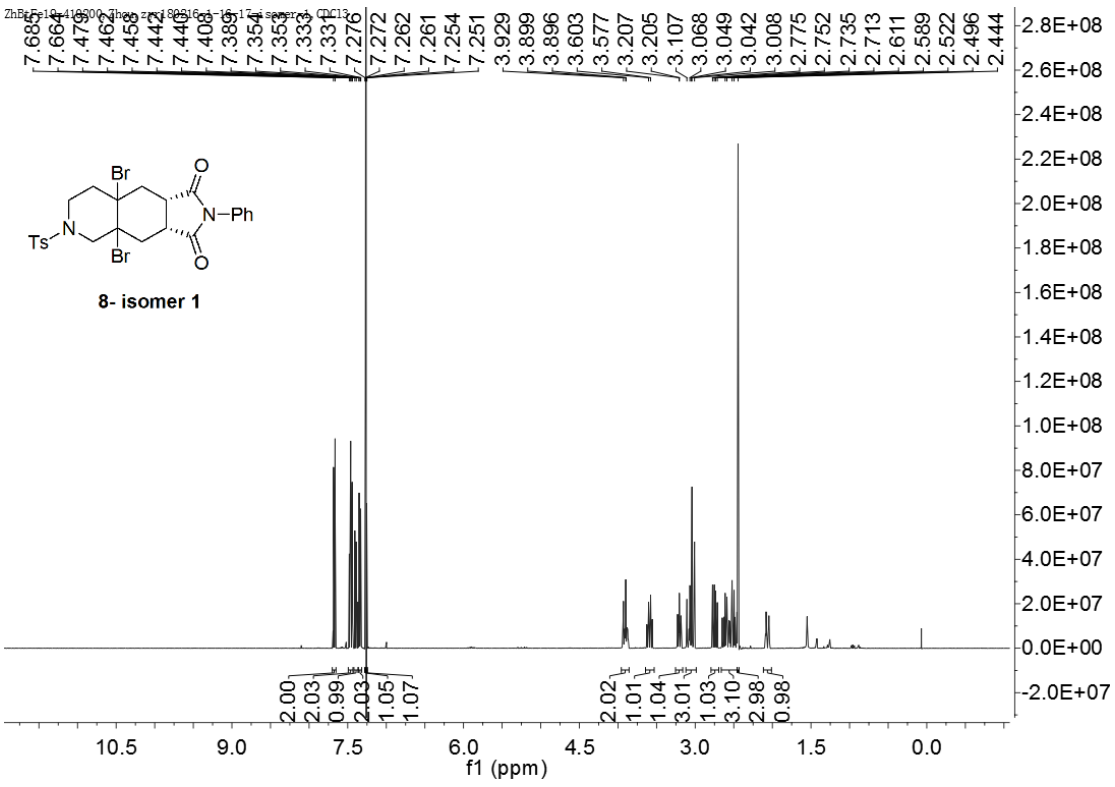

20170825B
ZhBtAu25-4021, Zhou, zyr170823-3, CDCl3
144.583
132.898
130.172
127.657
123.377
120.749
110.332
110.283
77.419
77.101
76.783
46.703
42.164
37.719
37.673
35.675
33.770
28.596
21.635
CN
CN
CN
CN
Ts
N
6t
f1 (ppm)

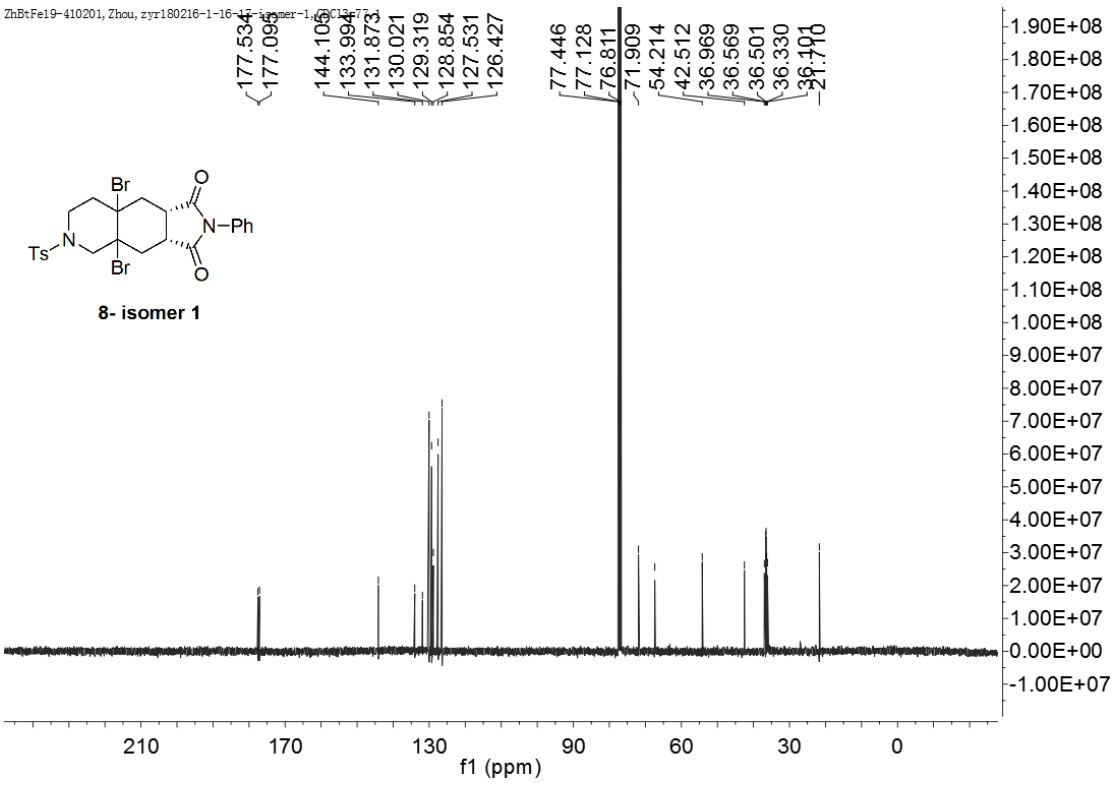

20170824B
ZhBtAu24-4030, Zhou, zyr170807-4, CDCl3
7.669
7.648
7.333
7.312
7.259
4.230
4.212
4.195
4.188
4.177
3.693
3.657
3.193
2.714
2.429
2.268
1.974
1.935
1.290
1.277
1.273
1.259
1.255
1.237
1.219
CO2Et
N
N
Ts
N
CO2Et
6u
2.00
2.03
6.01
4.07
1.03
0.97
3.11
1.03
1.04
6.02
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

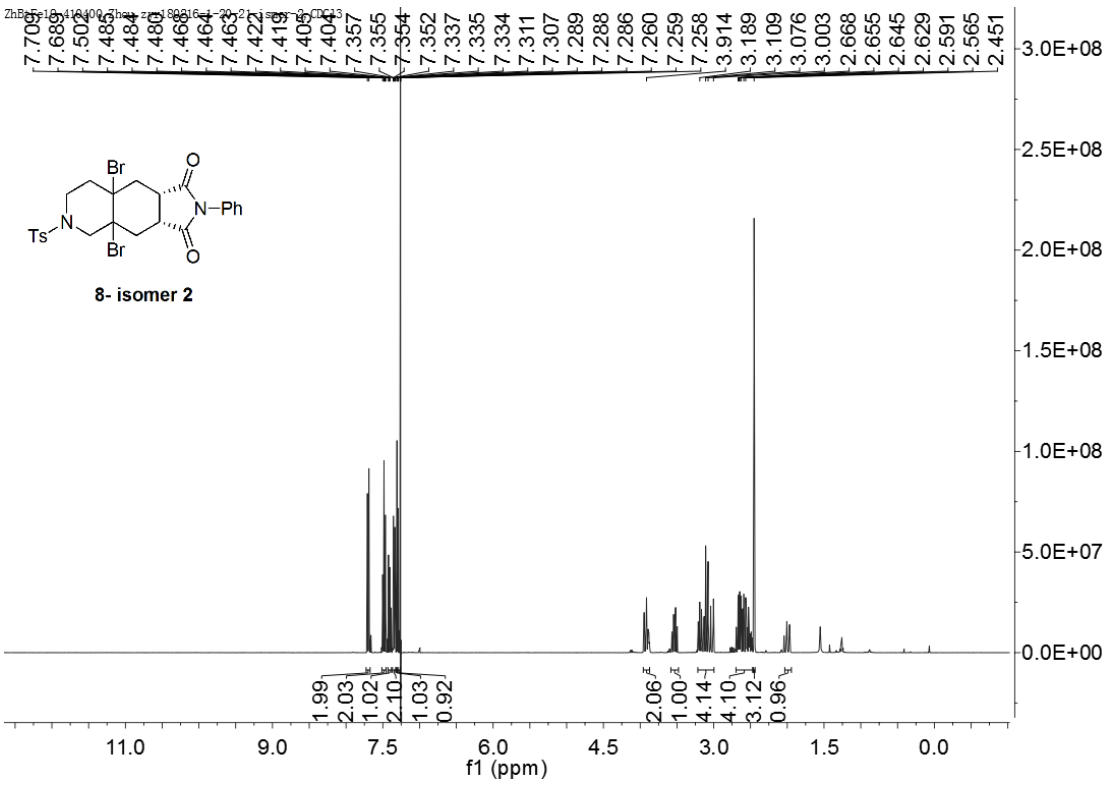

20170824B
ZhBtAu24-4031, Zhou, zyr170807-4, CDCl3
143.977
129.845
127.784
77.419
77.101
76.784
62.684
45.433
42.727
26.601
21.586
14.631
14.592
14.493
CO2Et
N
N
Ts
N
CO2Et
6u
240
190
140
90
60
30
0
f1 (ppm)

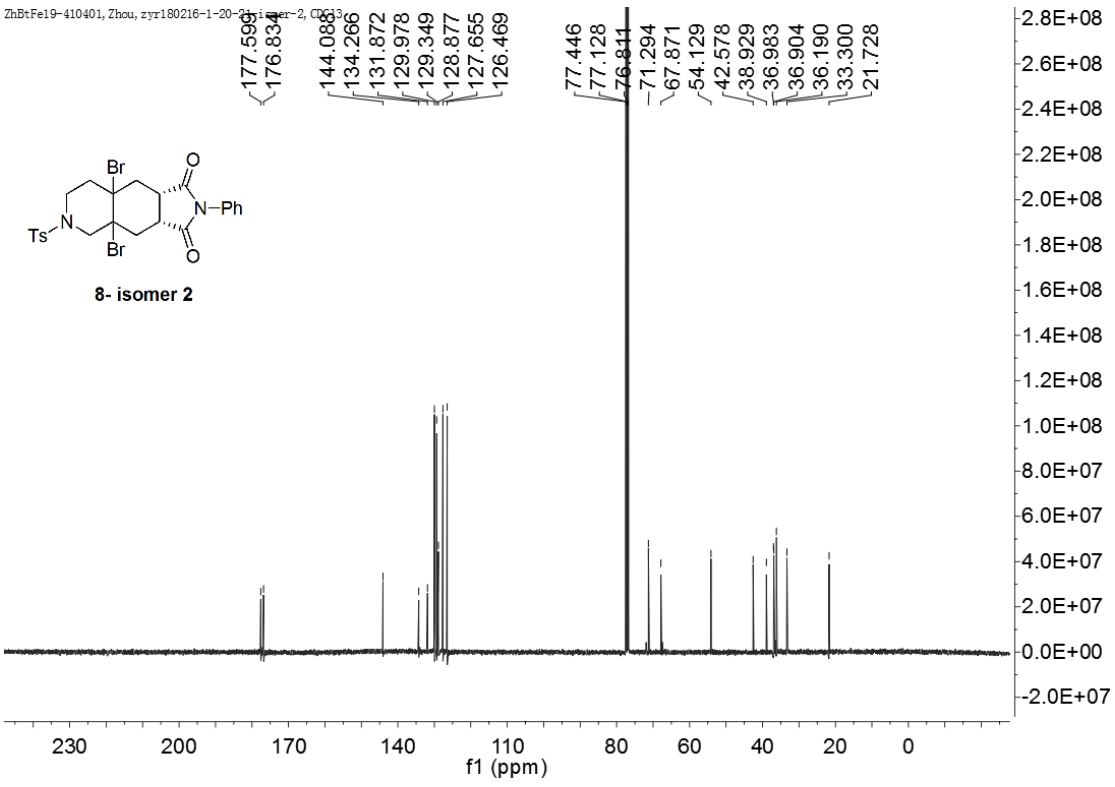


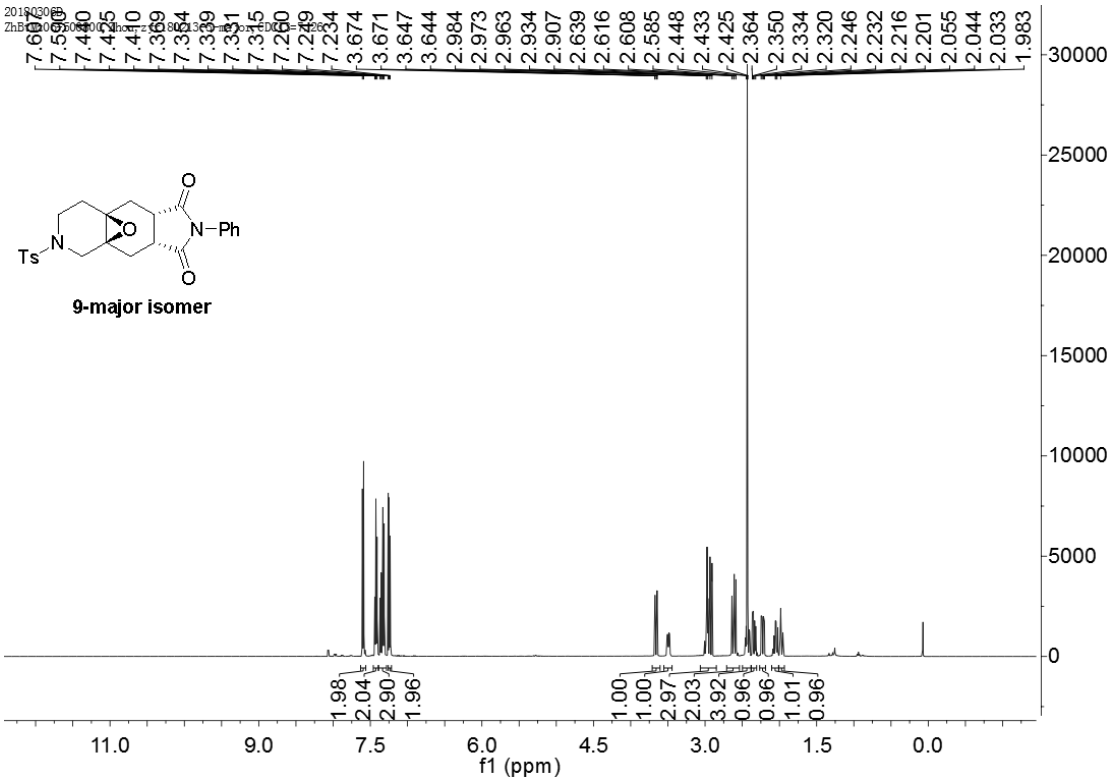


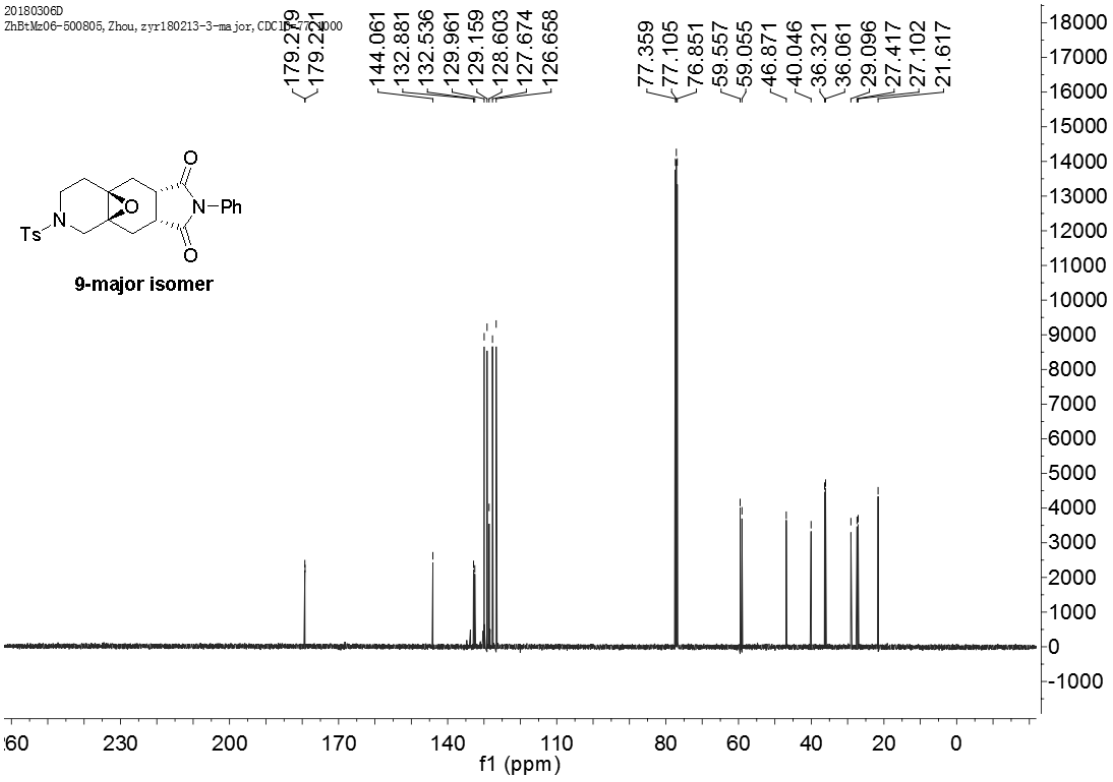

8- isomer 1
f1 (ppm)

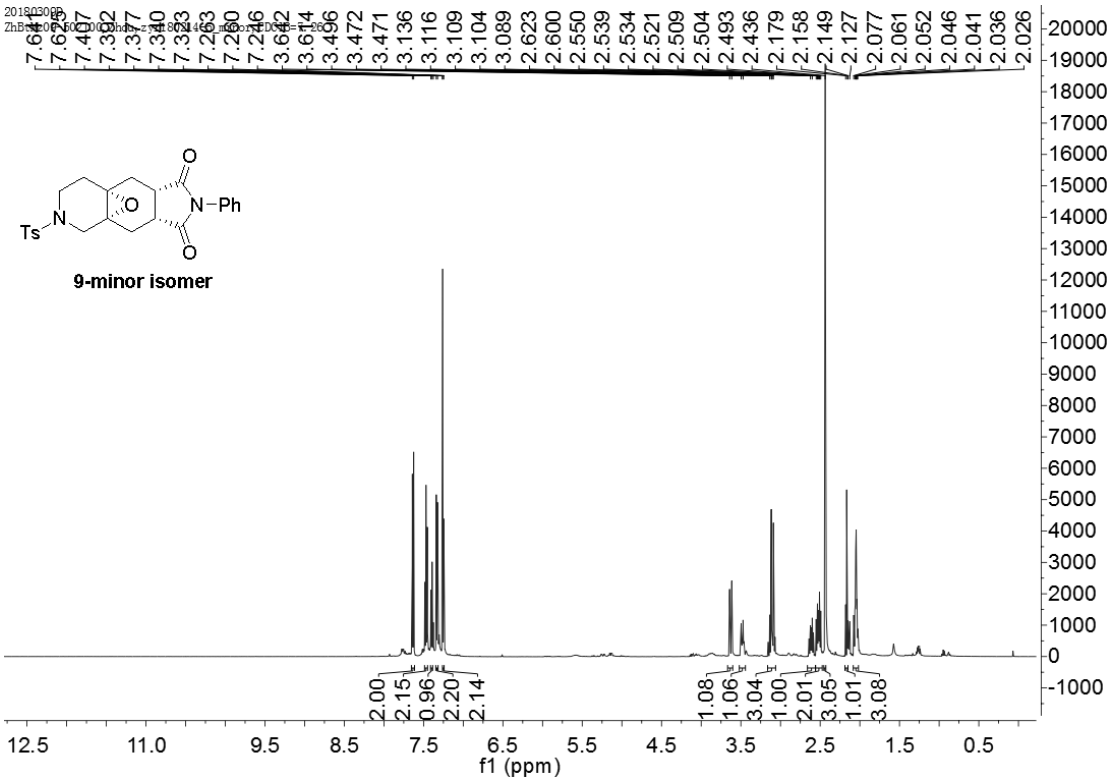

8- isomer 1
f1 (ppm)

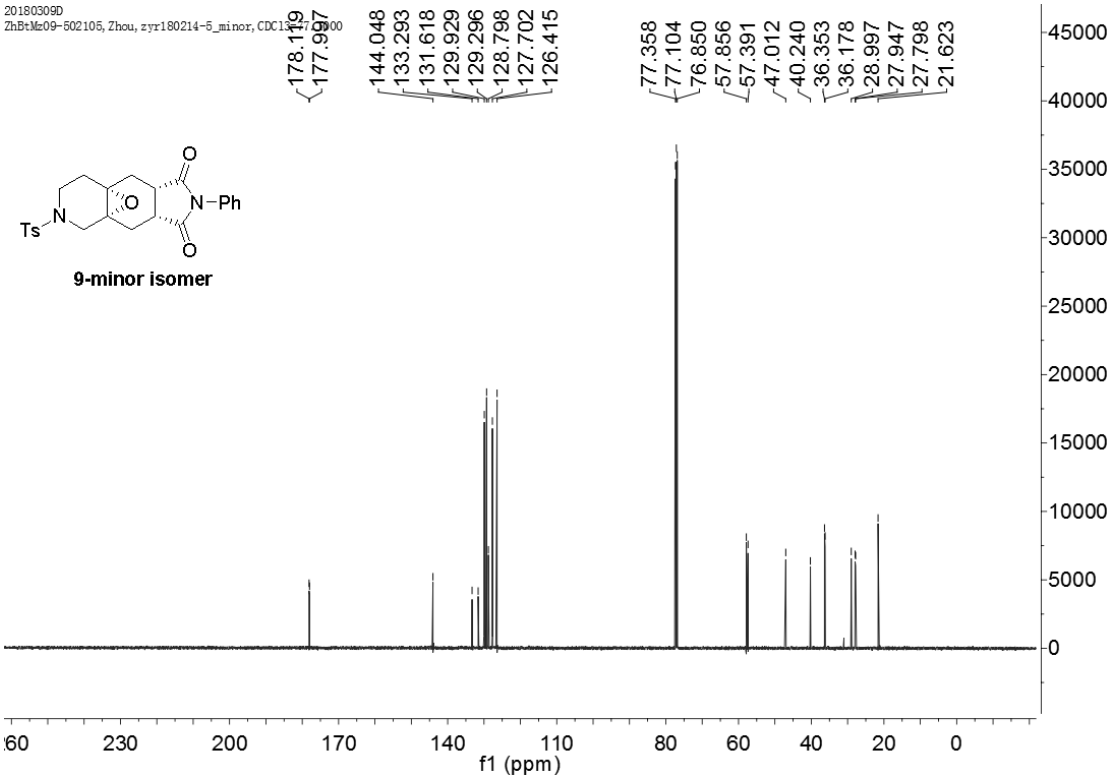

8- isomer 2
f1 (ppm)

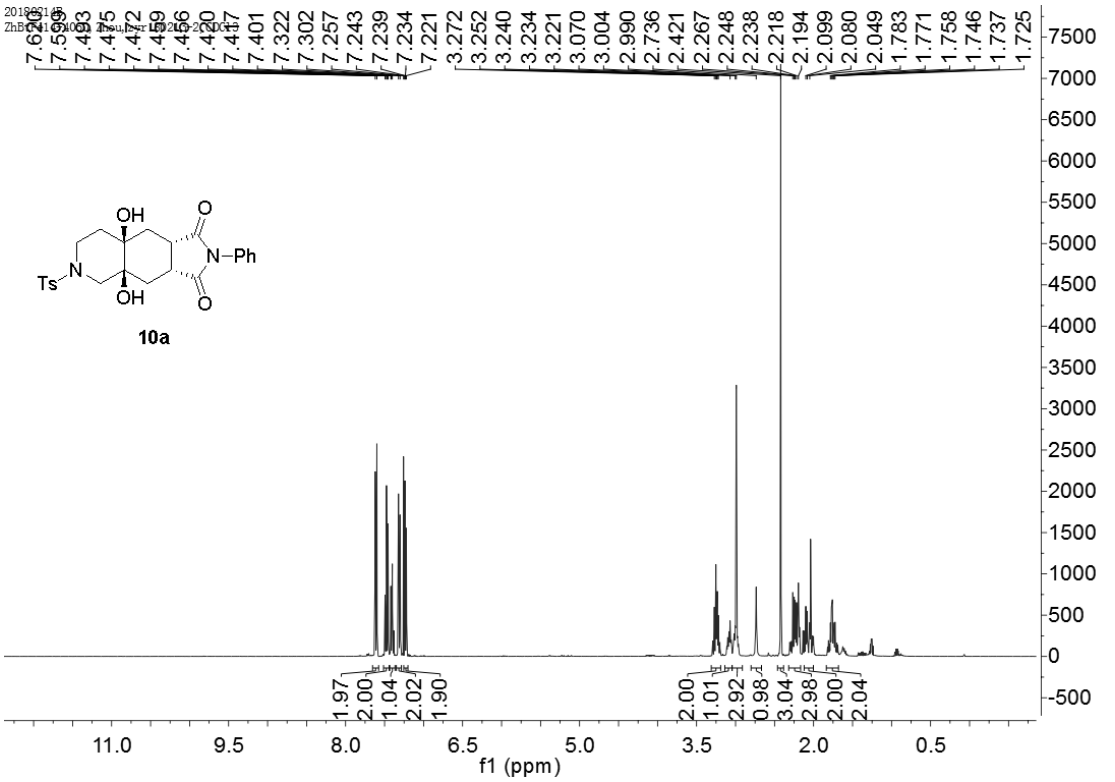

8- isomer 2
f1 (ppm)

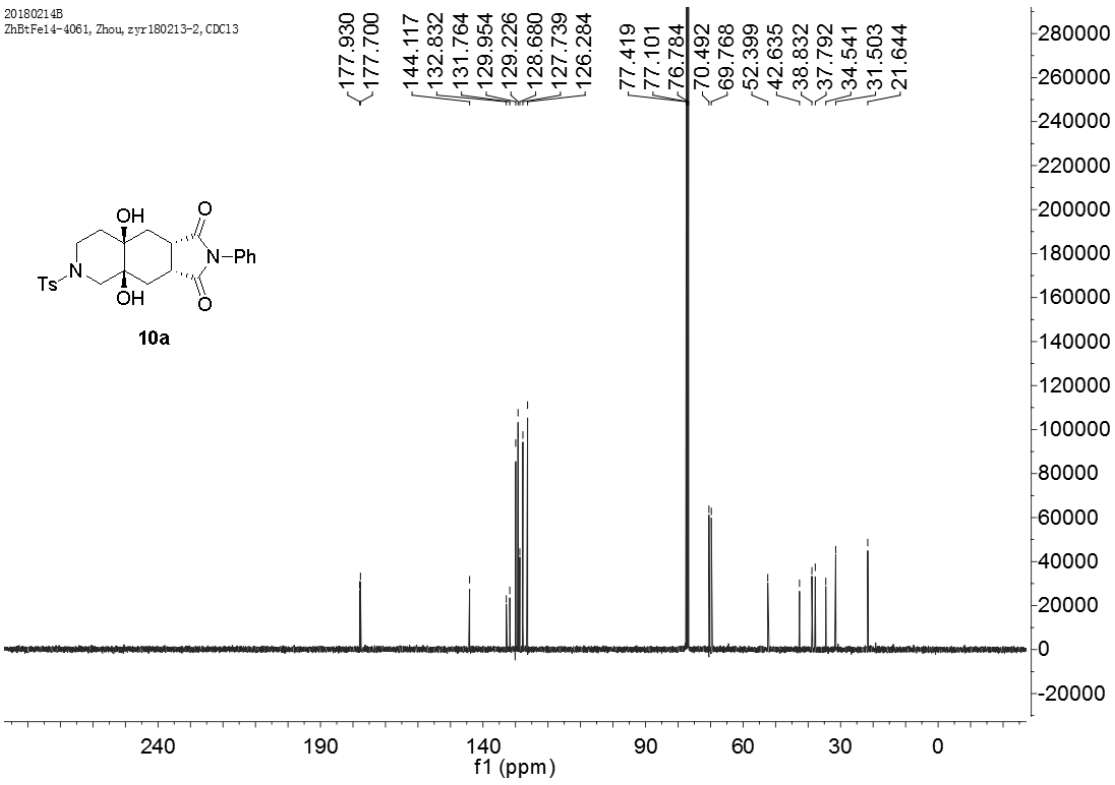

9-major isomer
f1 (ppm)

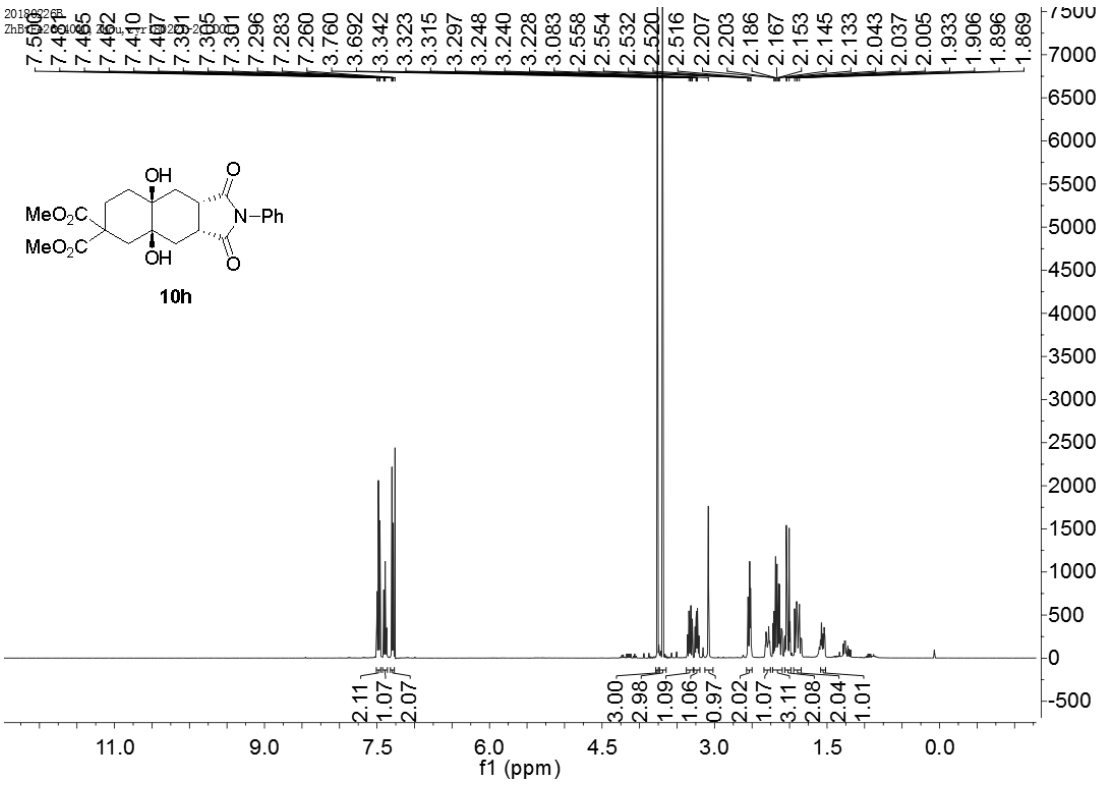

9-major isomer
f1 (ppm)

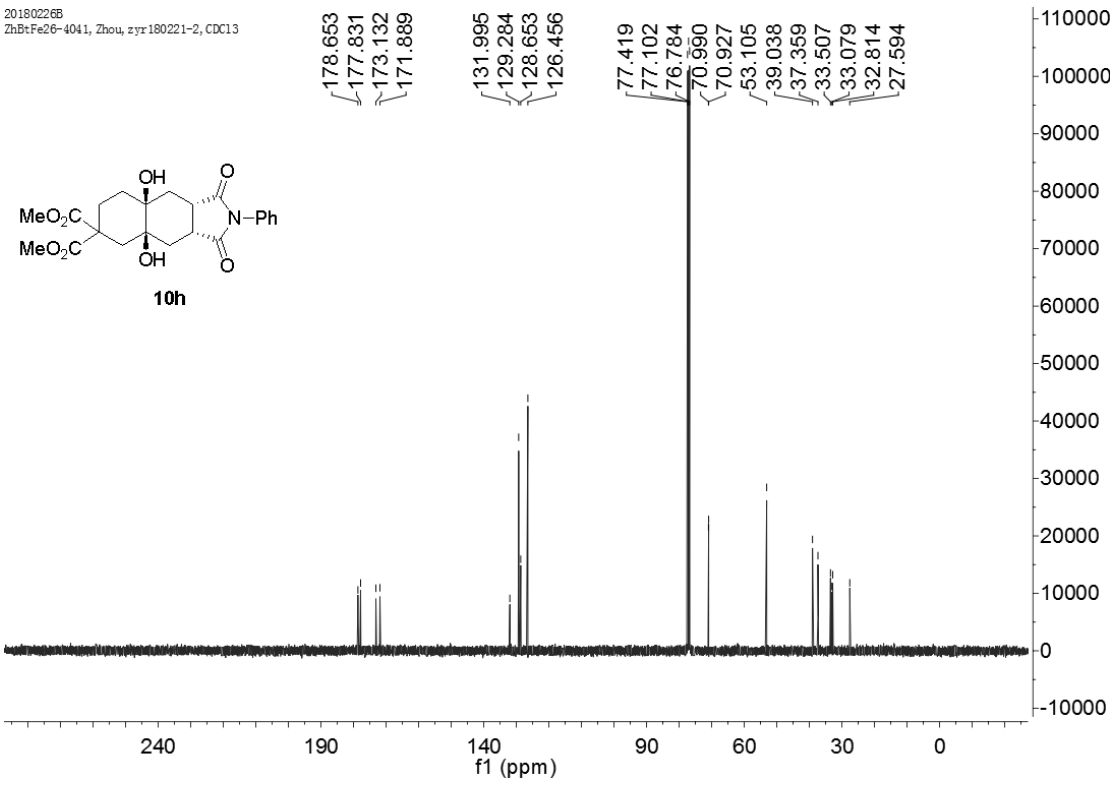

9-minor isomer
f1 (ppm)

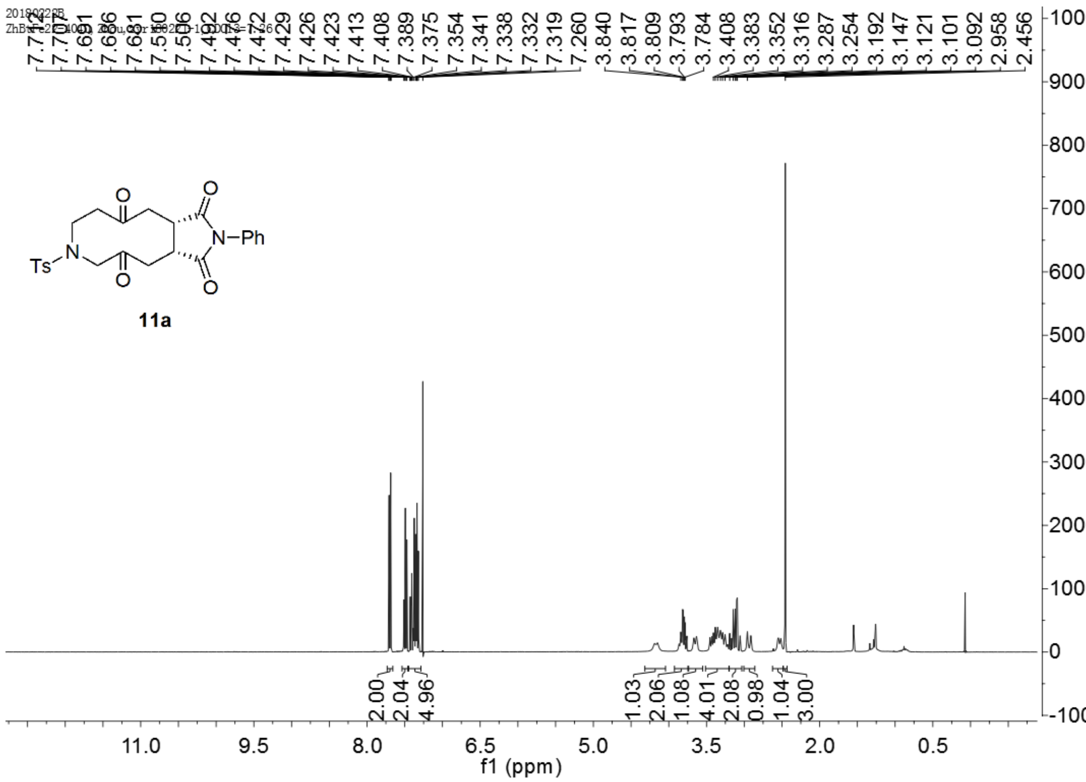

9-minor isomer
f1 (ppm)


7.625
7.593
7.493
7.475
7.472
7.459
7.456
7.420
7.417
7.401
7.322
7.302
7.257
7.243
7.239
7.234
7.221
3.272
3.252
3.240
3.234
3.221
3.070
3.004
2.990
2.736
2.421
2.267
2.248
2.238
2.218
2.194
2.099
2.080
2.049
1.783
1.771
1.758
1.746
1.737
1.725
OH
O
N–Ph
Ts
N
OH
O
10a
1.97
2.00
1.04
2.02
1.90
2.00
1.01
2.92
0.98
3.04
2.98
2.00
2.04
11.0
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)

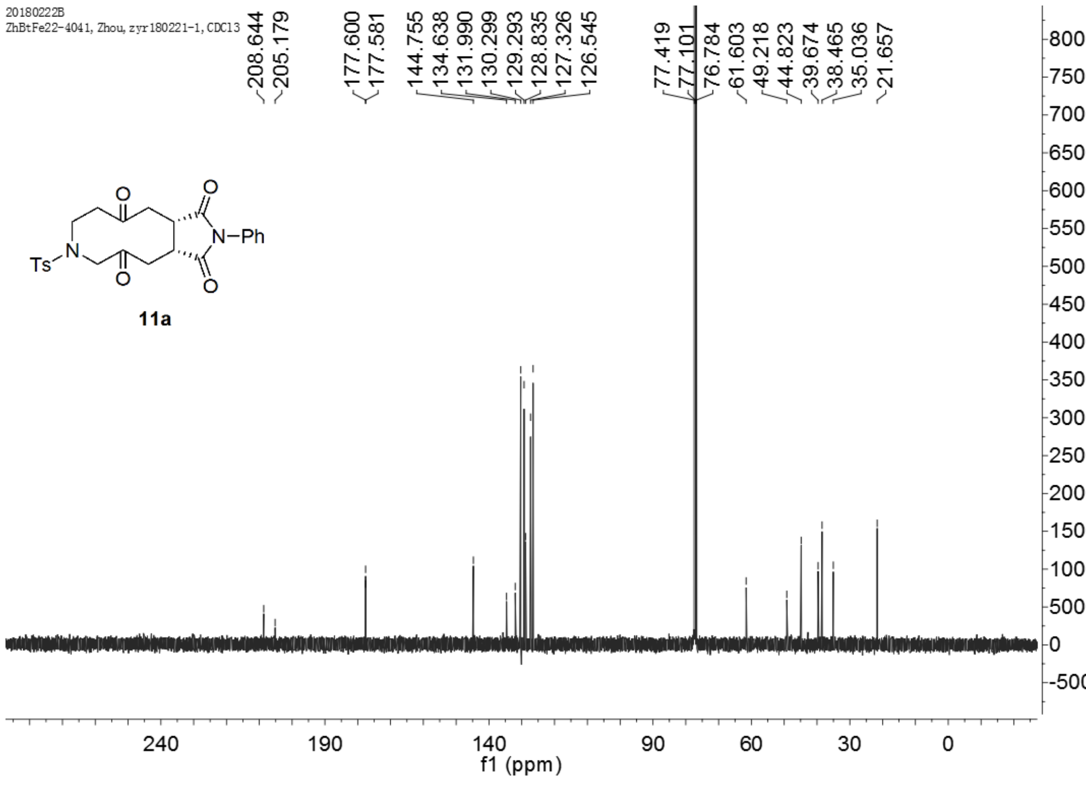

20180214B
ZhBtFe14-4061, Zhou, zyr180213-2, CDCl3
177.930
177.700
144.117
132.832
131.764
129.954
129.226
128.680
127.739
126.284
77.419
77.101
76.784
70.492
69.768
52.399
42.635
38.832
37.792
34.541
31.503
21.644
OH
O
N–Ph
Ts
N
OH
O
10a
240
190
140
90
60
30
0
f1 (ppm)


OH
MeO2C
MeO2C
OH
O
N–Ph
O
10h
f1 (ppm)

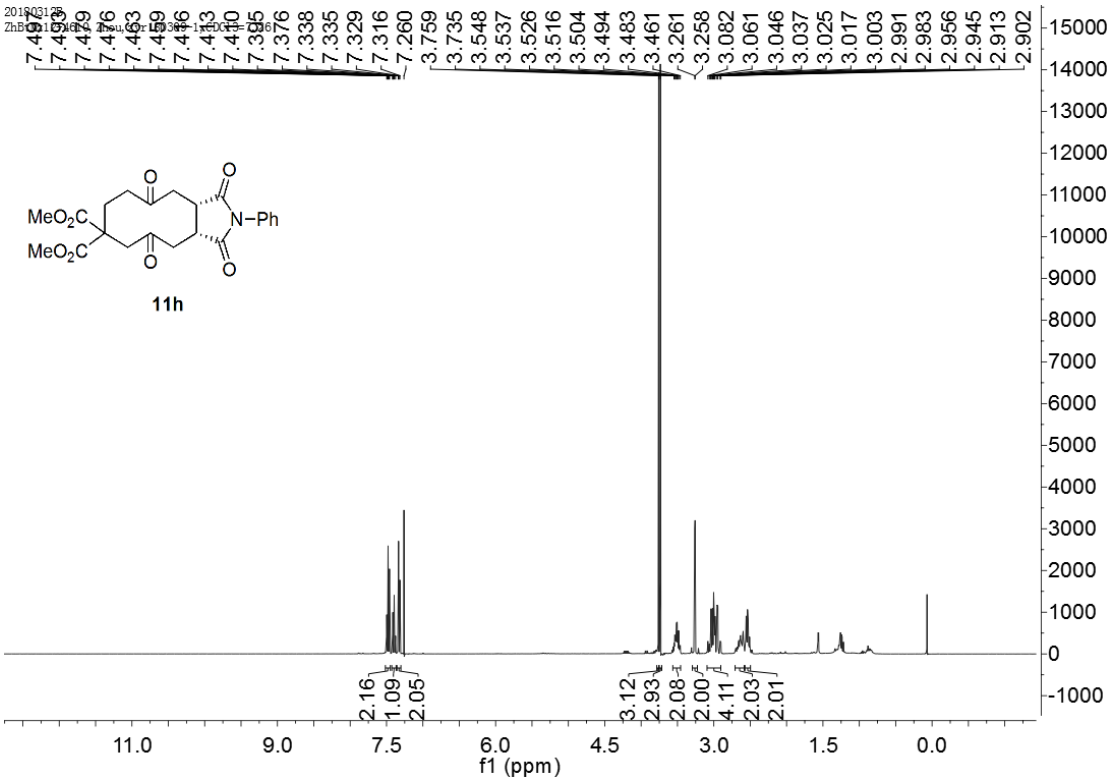

20180226B
ZhBtFe26-4041, Zhou, zyr180221-2, CDCl3
OH
MeO2C
MeO2C
OH
O
N–Ph
O
10h
f1 (ppm)

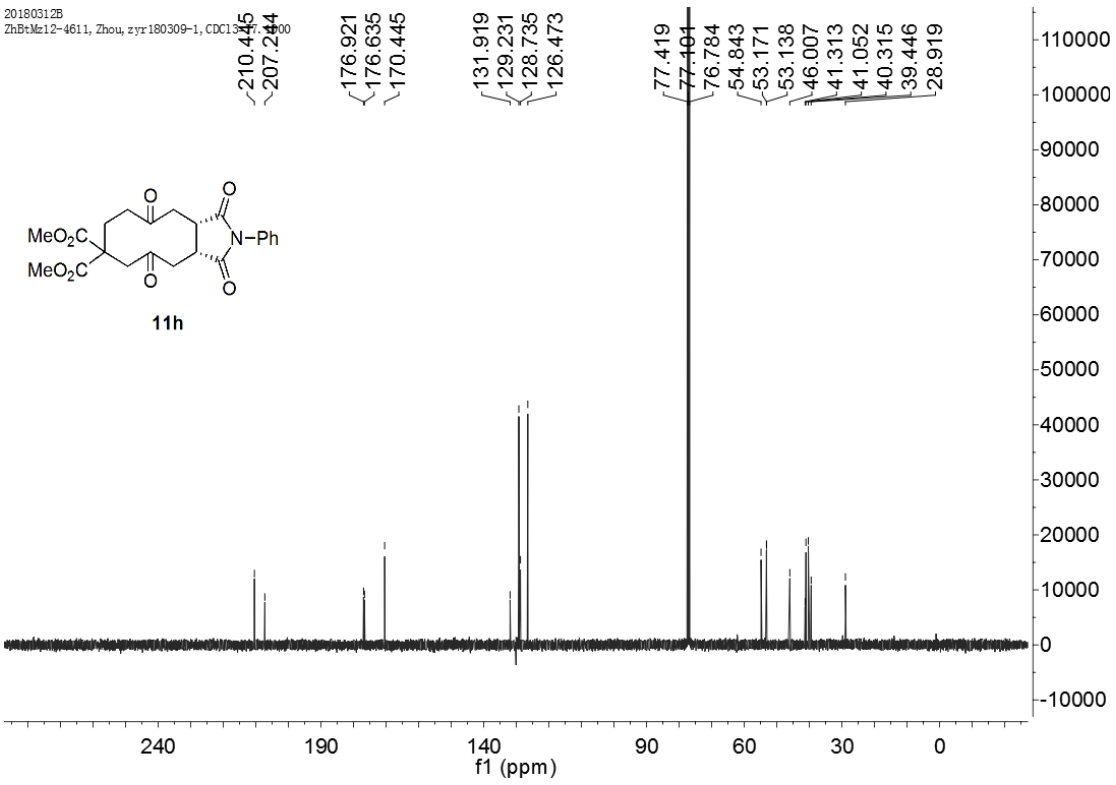


11a
f1 (ppm)

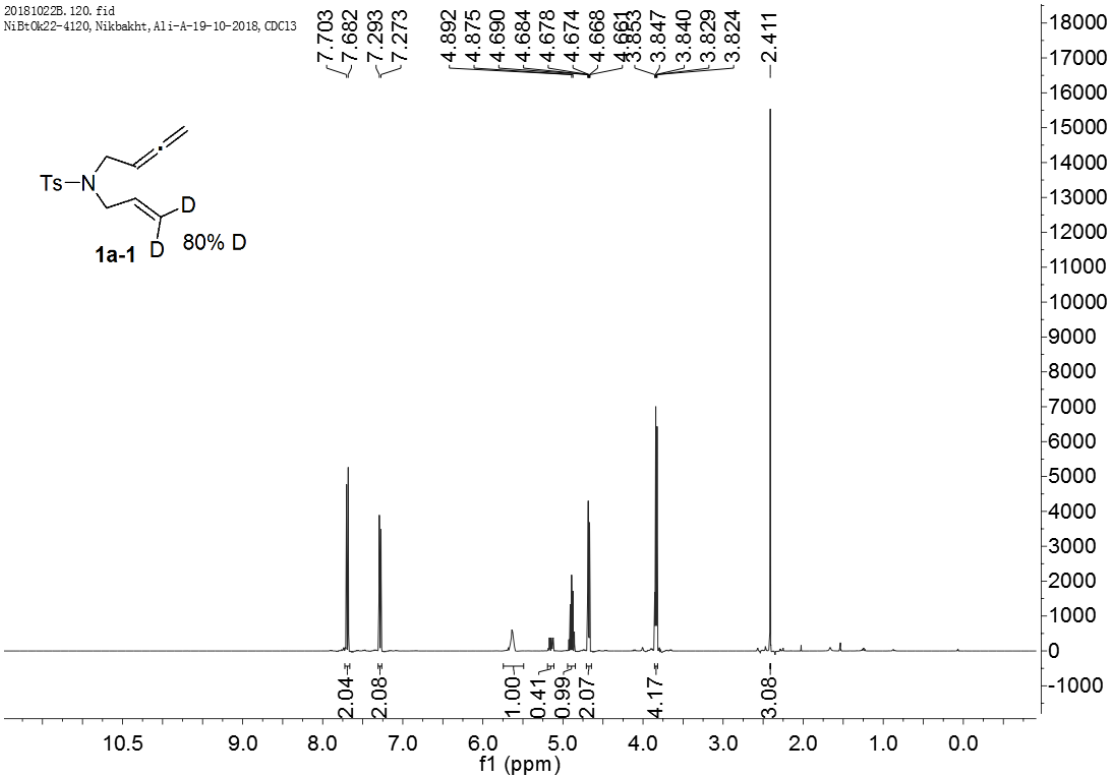


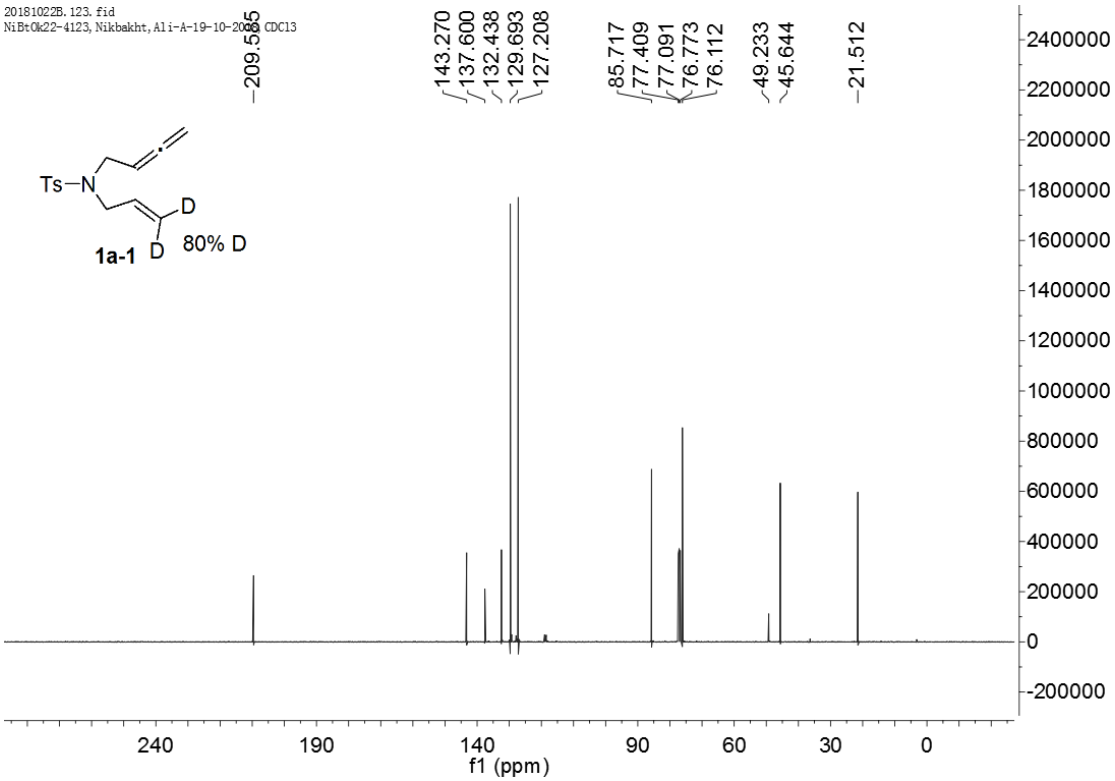
20180222B
ZhBtFe22-4041, Zhou, zyr180221-1, CDCl3
208.644
205.179
177.600
177.581
144.755
134.638
131.990
130.299
129.293
128.835
127.326
126.545
77.419
77.101
76.784
61.603
49.218
44.823
39.674
38.465
35.036
21.657
11a
f1 (ppm)

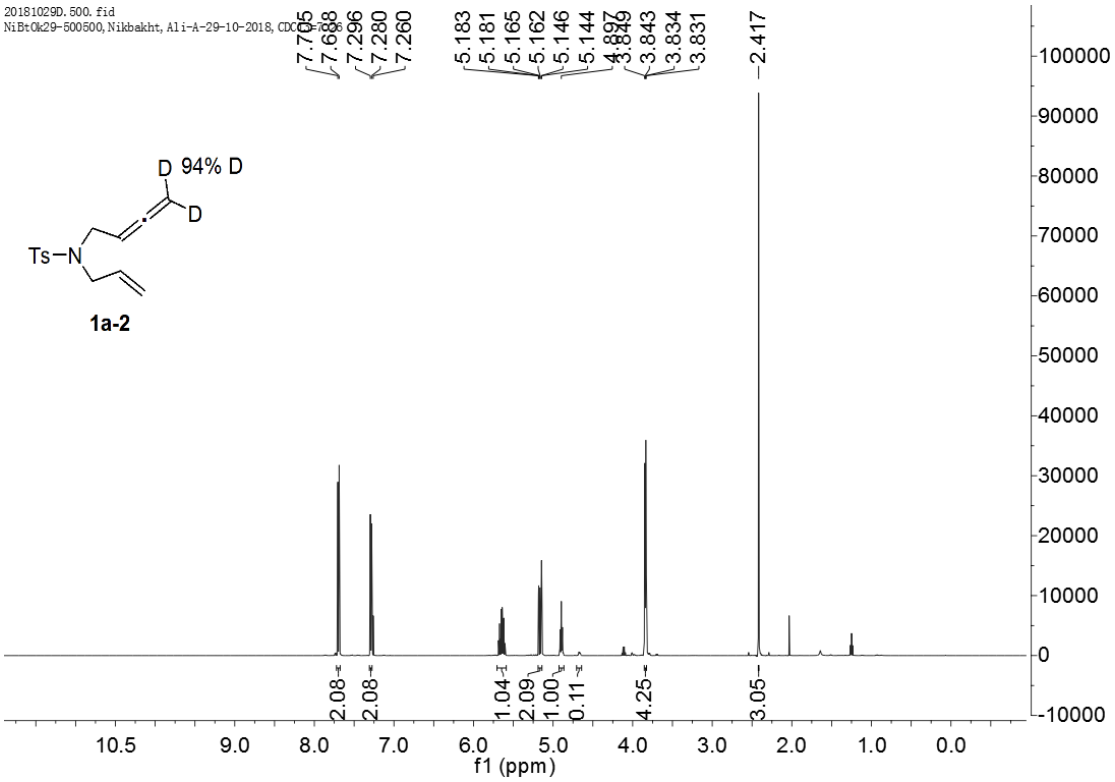

MeO2C
MeO2C
N–Ph
11h
f1 (ppm)

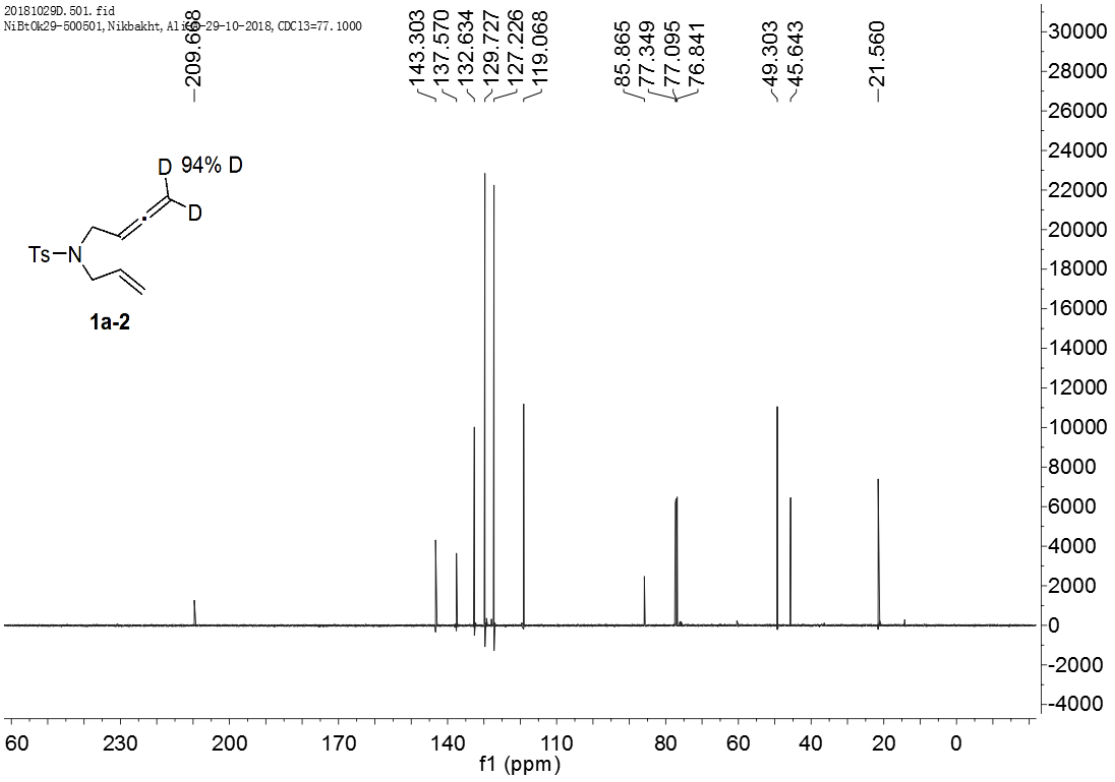

MeO2C
MeO2C
N–Ph
11h
f1 (ppm)

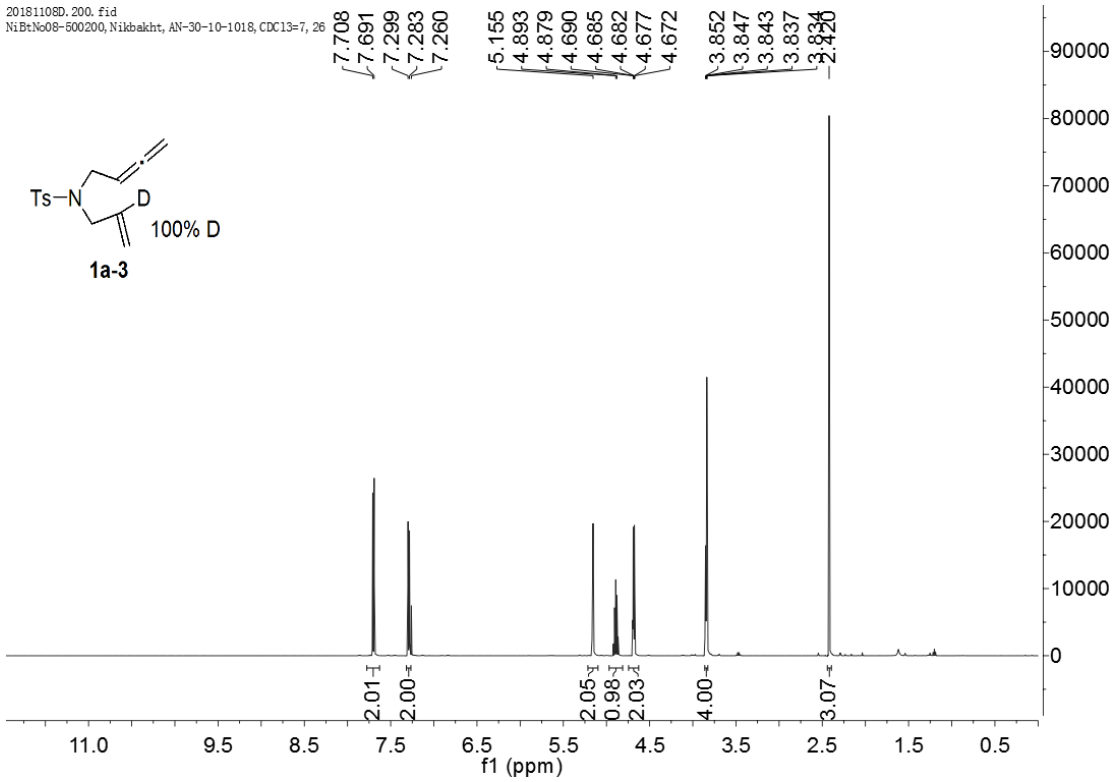
Copies of NMR spectra of deuterium labelling experiments

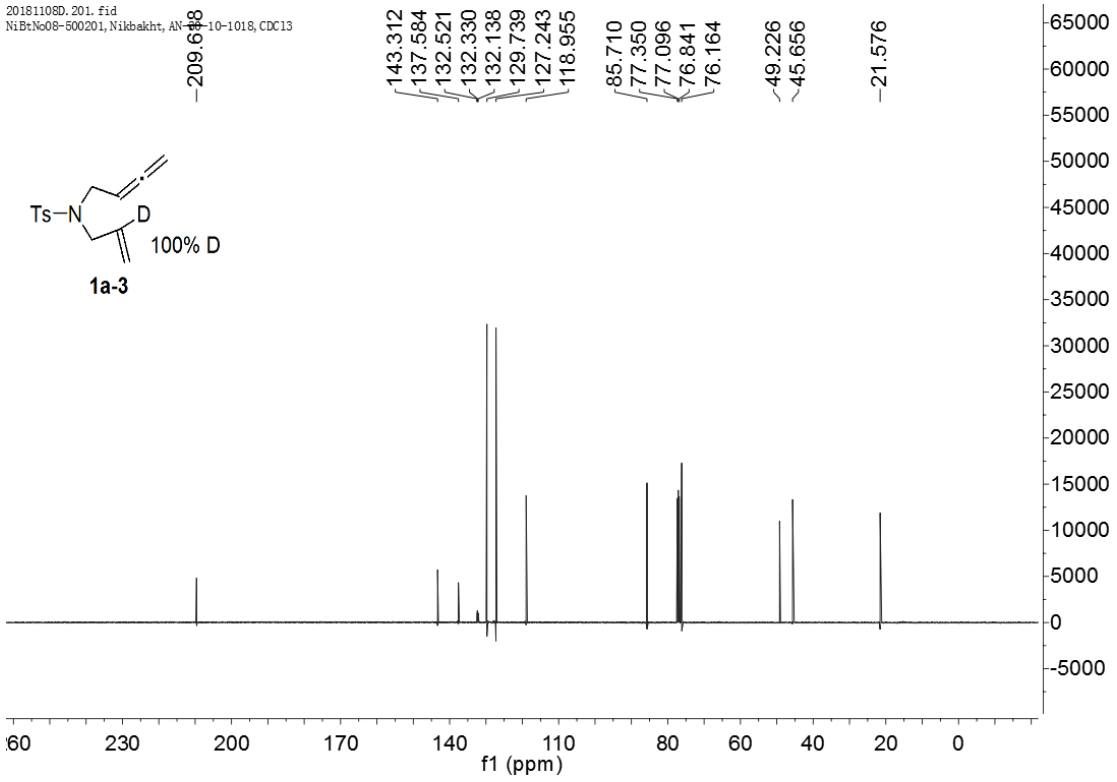


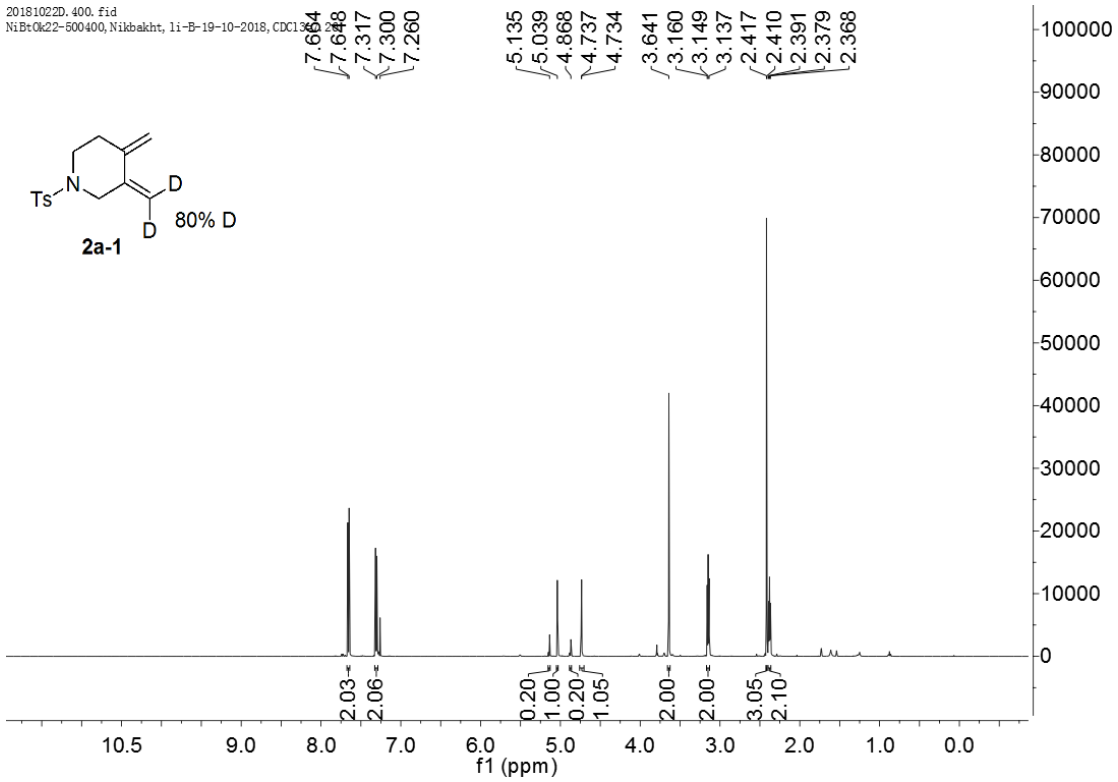


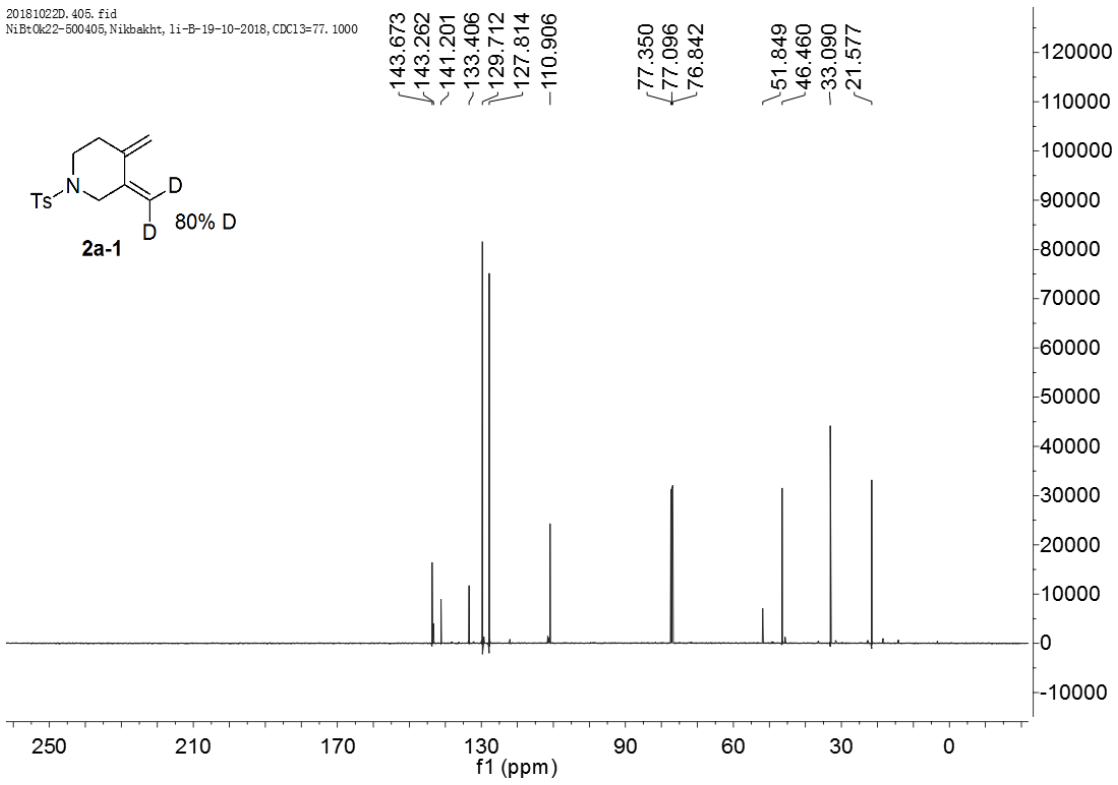

20181029D.500.fid
7.705
7.688
7.296
7.280
7.260
5.183
5.181
5.165
5.162
5.146
5.144
4.897
3.849
3.843
3.834
3.831
2.417
D 94% D
D
Ts–N
1a-2
2.08
2.08
1.04
2.09
1.00
0.11
4.25
3.05
f1 (ppm)

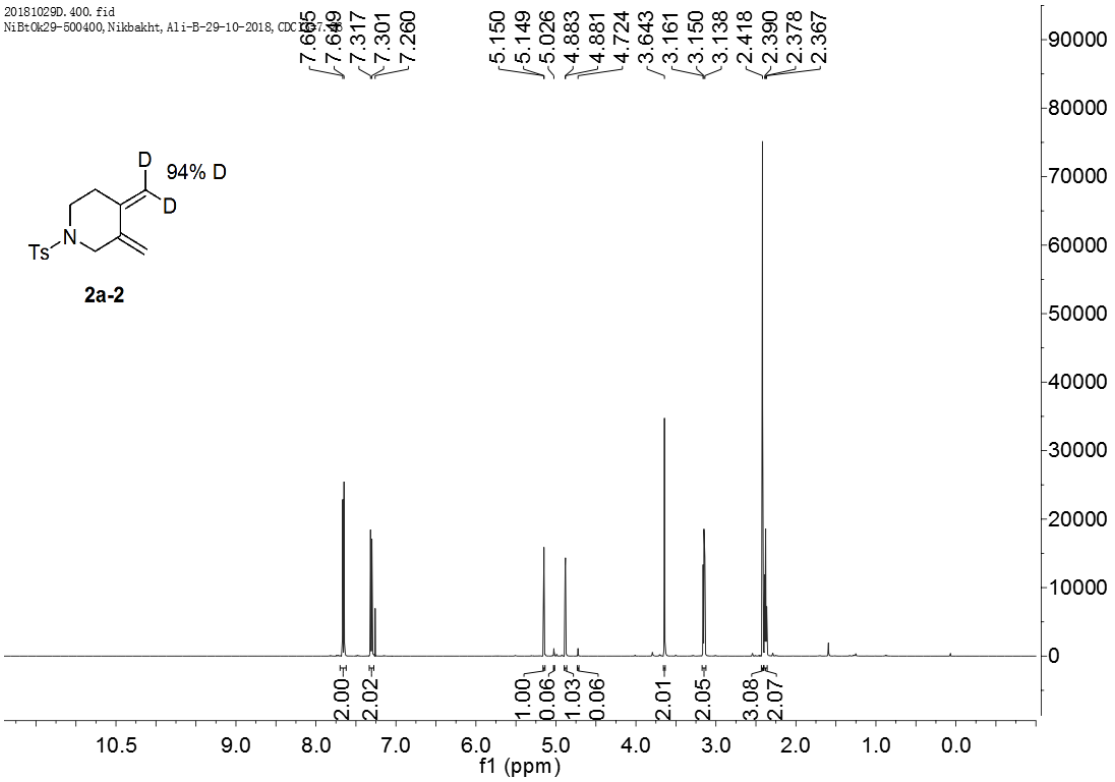

20181029D.501.fid
209.668
143.303
137.570
132.634
129.727
127.226
119.068
85.865
77.349
77.095
76.841
49.303
45.643
21.560
D 94% D
D
Ts–N
1a-2
f1 (ppm)

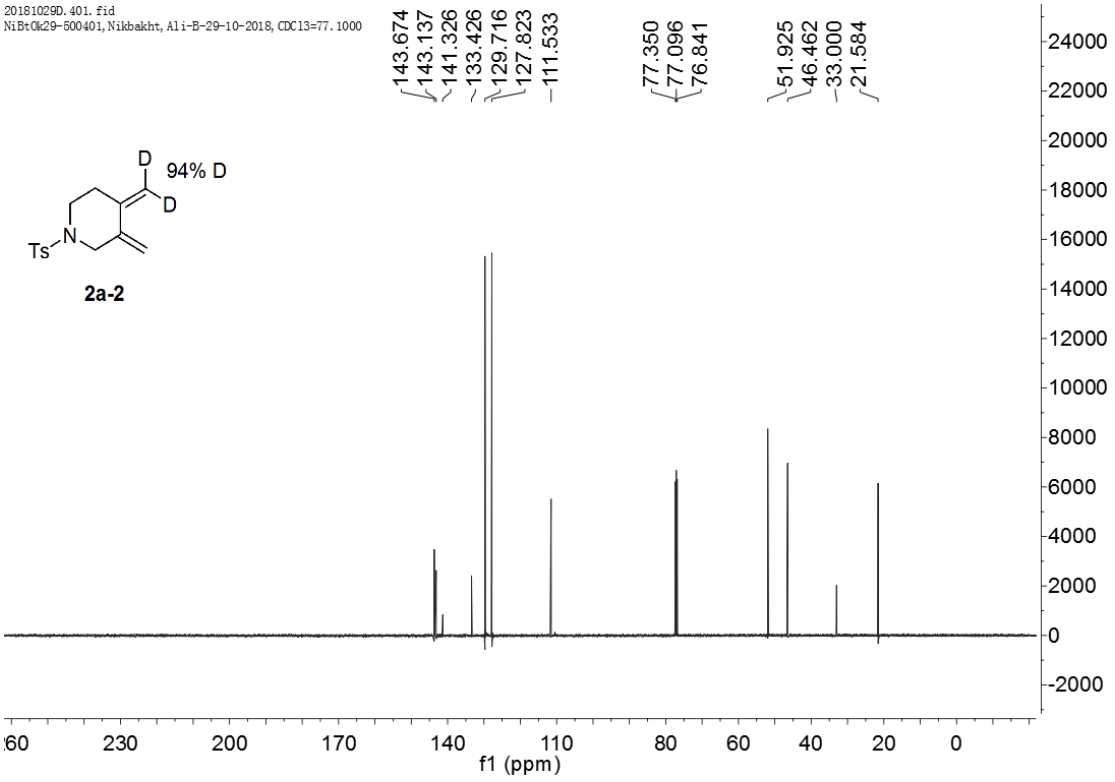

20181108D.200.fid
NiBtNo08-500200, Nikbakht, AN-30-10-1018, CDC13=7, 26
7.708
7.691
7.299
7.283
7.260
5.155
4.893
4.879
4.690
4.685
4.682
4.677
4.672
3.852
3.847
3.843
3.837
3.834
3.820
2.420
Ts—N
D
100% D
1a-3
2.01
2.00
2.05
0.98
2.03
4.00
3.07
f1 (ppm)

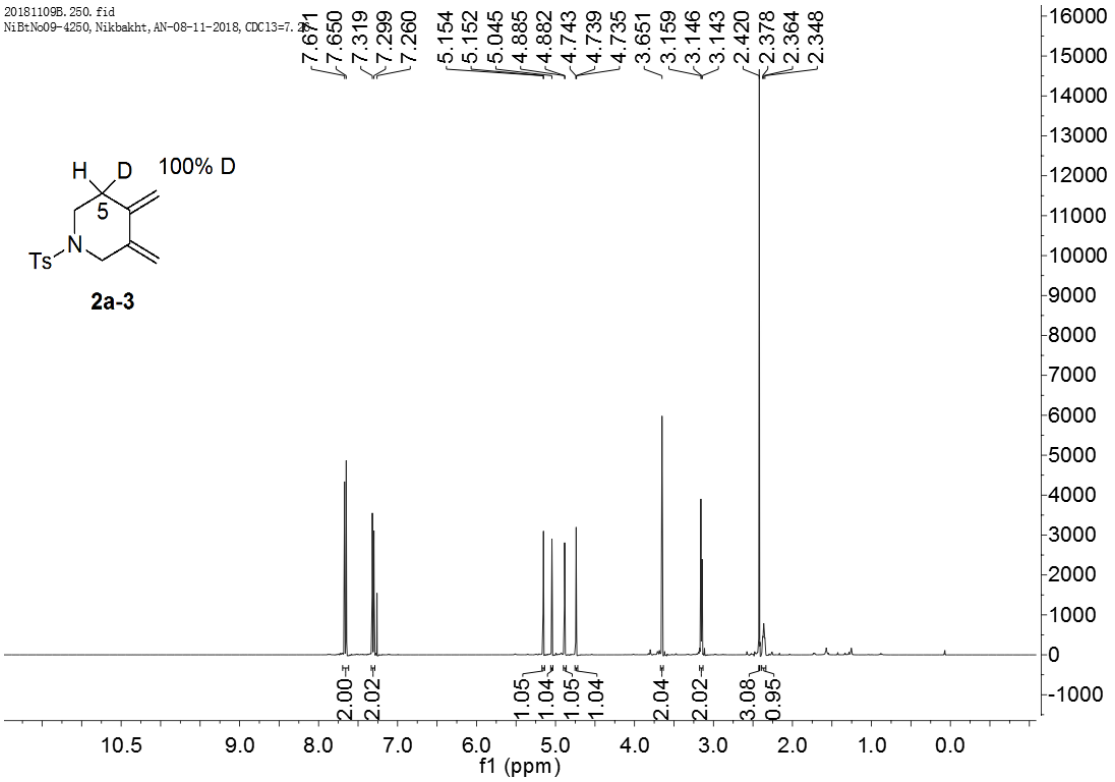

20181108D.201.fid
NiBtNo08-500201, Nikbakht, AN-30-10-1018, CDC13
209.648
143.312
137.584
132.521
132.330
132.138
129.739
127.243
118.955
85.710
77.350
77.096
76.841
76.164
49.226
45.656
21.576
Ts—N
D
100% D
1a-3
f1 (ppm)

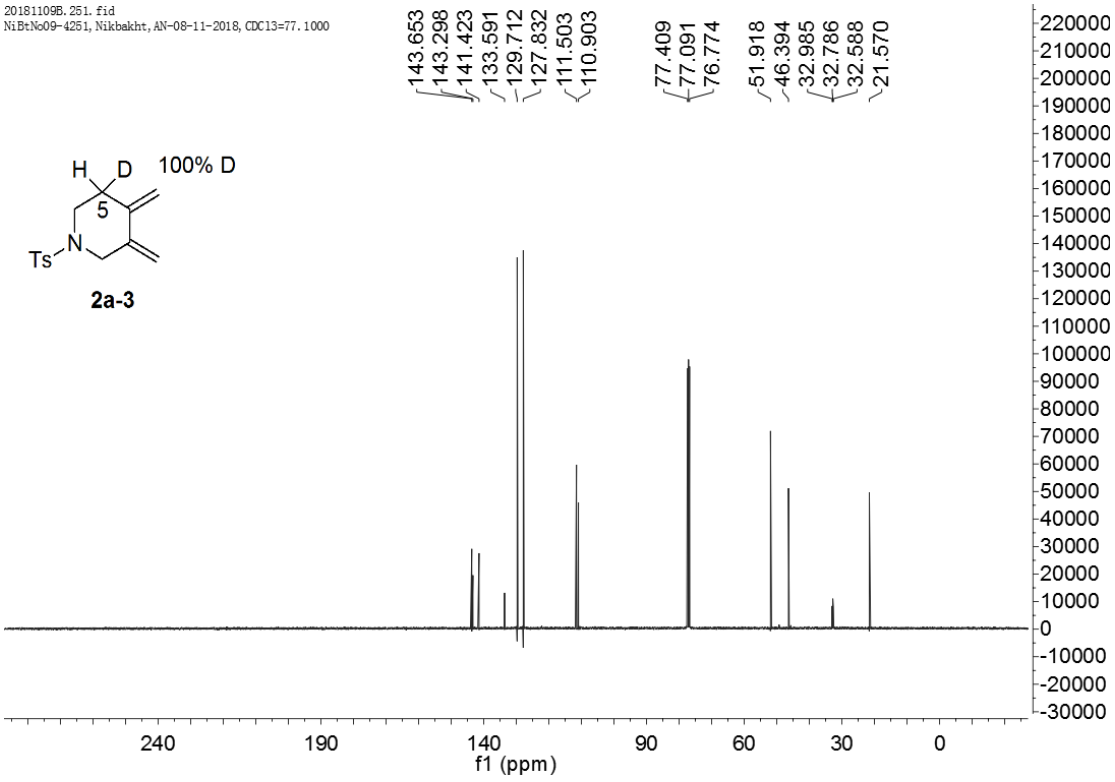

20181022D.400.fid
NiBt0k22-500400,Nikbakht,li-B-19-10-2018,CDCl3=7.260
7.684
7.648
7.317
7.300
7.260
5.135
5.039
4.868
4.737
4.734
3.641
3.160
3.149
3.137
2.417
2.410
2.391
2.379
2.368
Ts
N
D
D
80% D
2a-1
2.03
2.06
0.20
1.00
0.20
1.05
2.00
2.00
3.05
2.10
f1 (ppm)

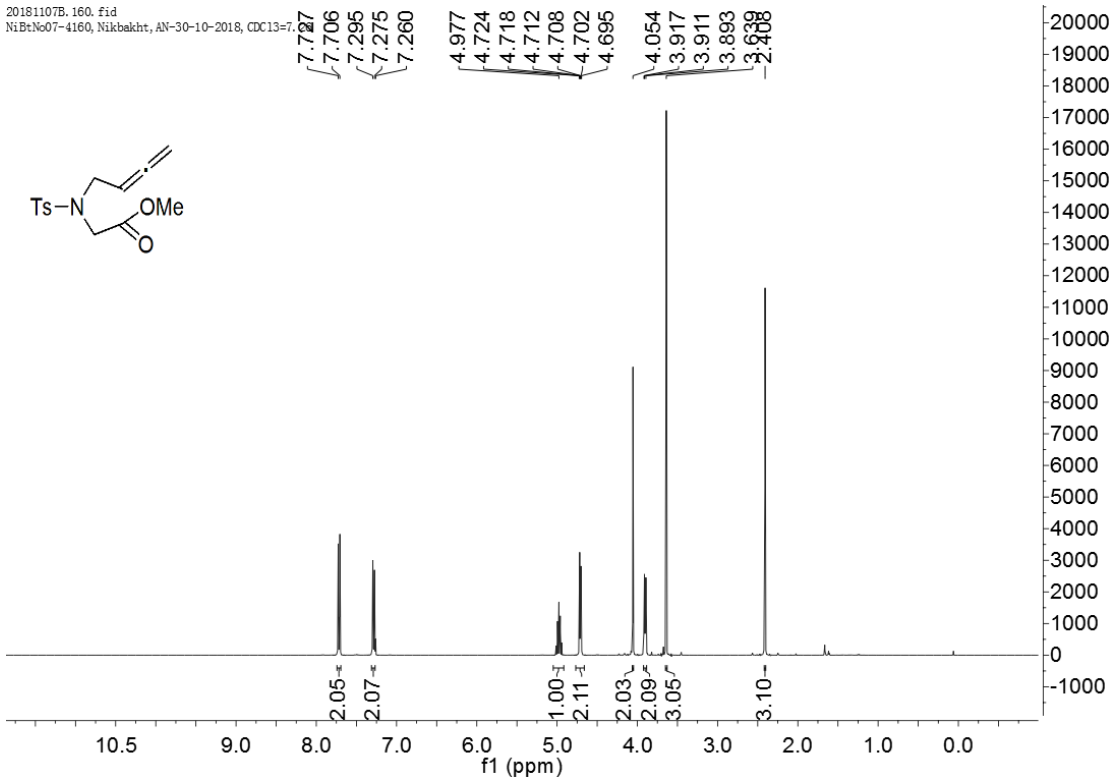

20181022D.405.fid
NiBt0k22-500405,Nikbakht,li-B-19-10-2018,CDCl3=77.1000
143.673
143.262
141.201
133.406
129.712
127.814
110.906
77.350
77.096
76.842
51.849
46.460
33.090
21.577
Ts
N
D
D
80% D
2a-1
f1 (ppm)

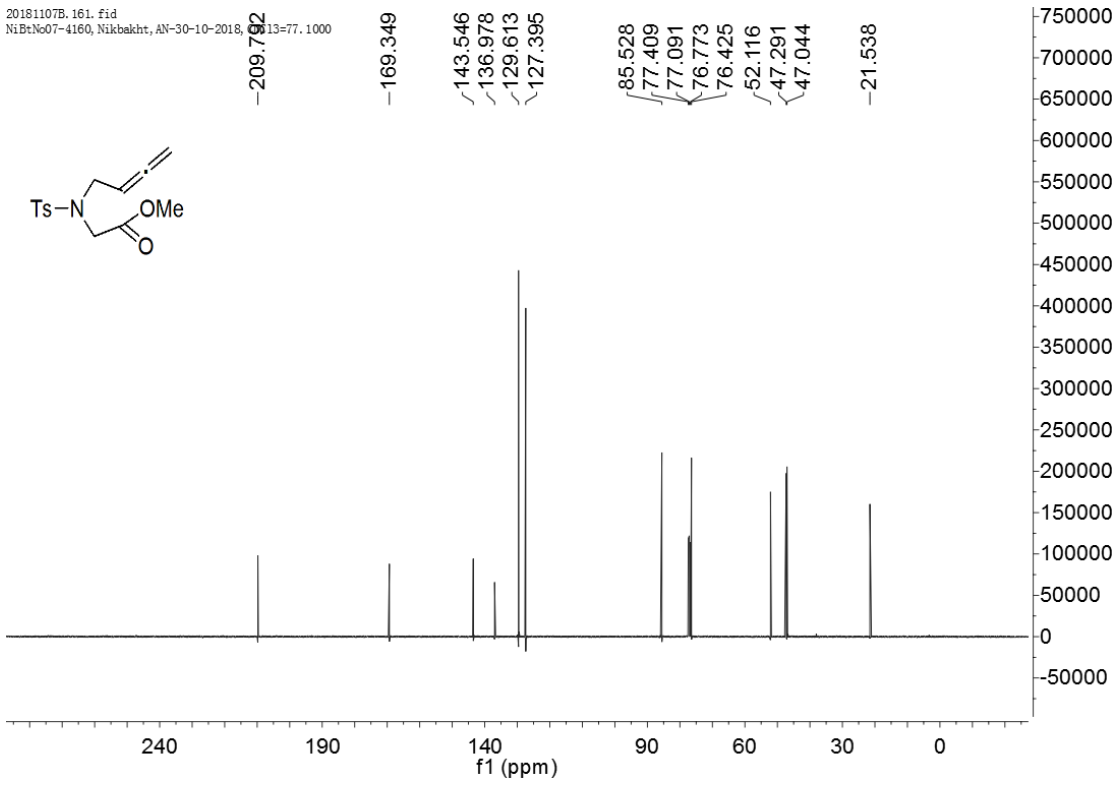

20181029D.400.fid
NiBt0k29-500400, Nikbakht, Ali-B-29-10-2018, CDCl3=77.
7.665
7.649
7.317
7.301
7.260
5.150
5.149
5.026
4.883
4.881
4.724
3.643
3.161
3.150
3.138
2.418
2.390
2.378
2.367
D
94% D
D
N
Ts
2a-2
2.00
2.02
1.00
0.06
1.03
0.06
2.01
2.05
3.08
2.07
f1 (ppm)

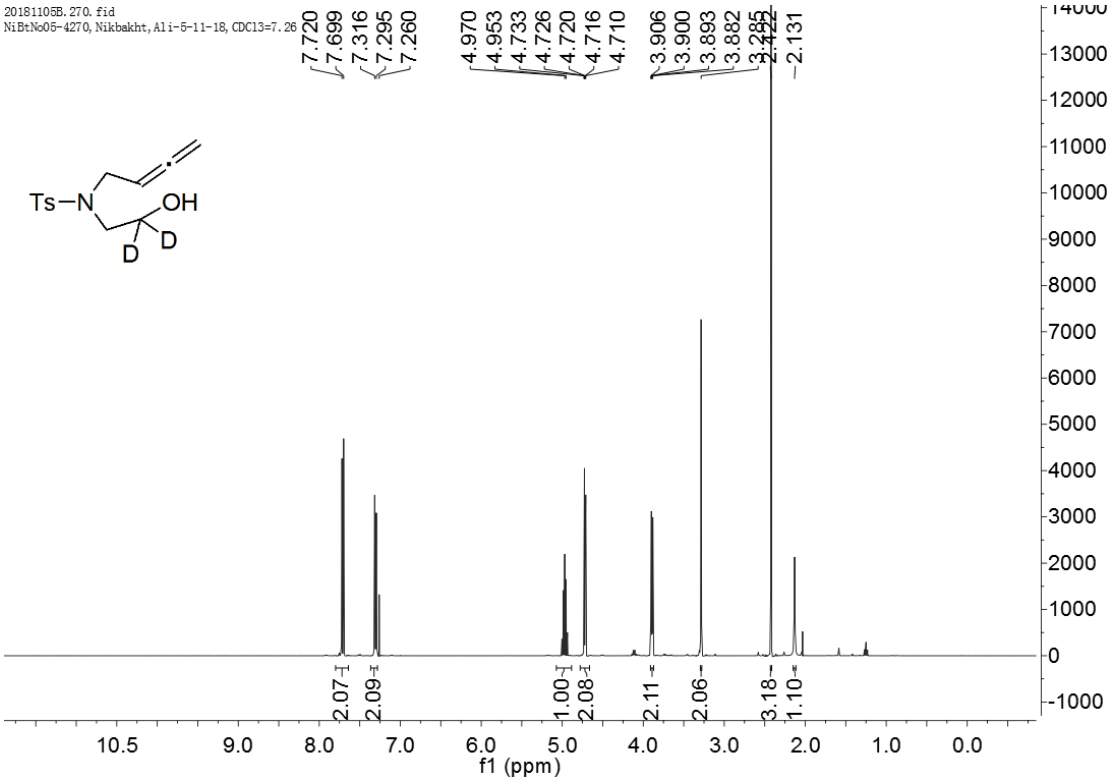

20181029D.401.fid
NiBt0k29-500401, Nikbakht, Ali-B-29-10-2018, CDCl3=77.1000
143.674
143.137
141.326
133.426
129.716
127.823
111.533
77.350
77.096
76.841
51.925
46.462
33.000
21.584
D
94% D
D
N
Ts
2a-2
f1 (ppm)

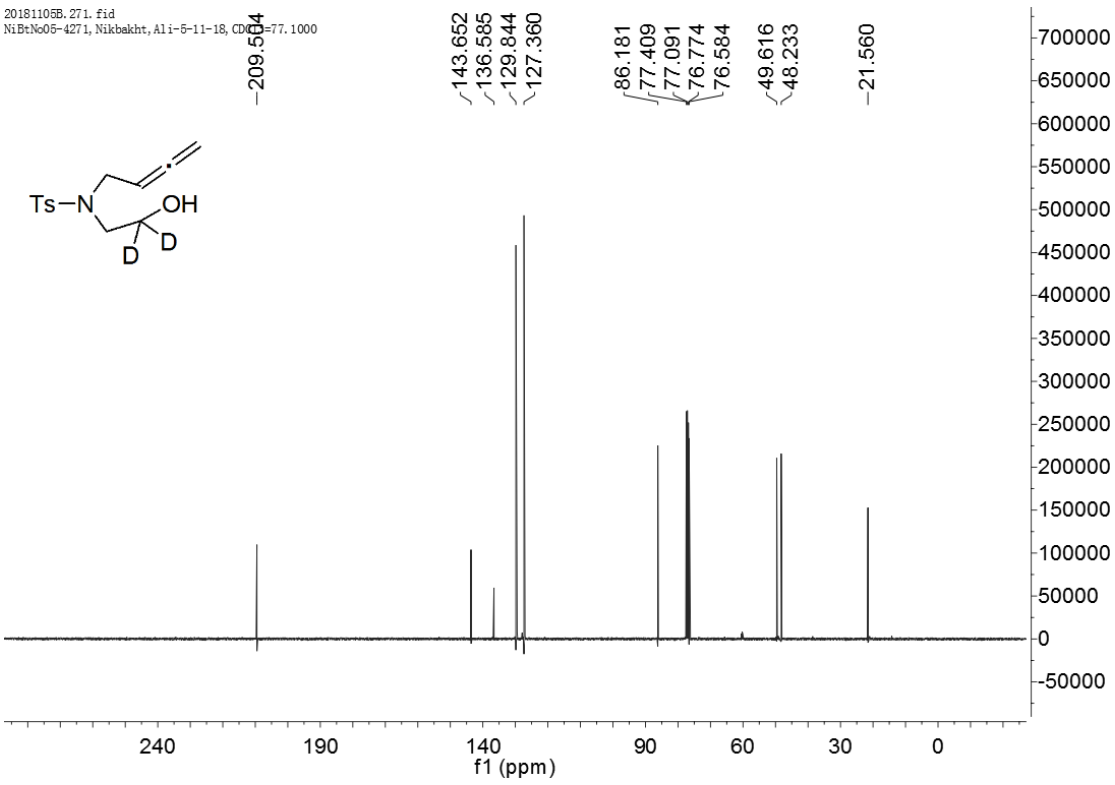

20181109B.250.fid
NiBtNo09-4250, Nikbakht, AN-08-11-2018, CDC13=7.2
7.671
7.650
7.319
7.299
7.260
5.154
5.152
5.045
4.885
4.882
4.743
4.739
4.735
3.651
3.159
3.146
3.143
2.420
2.378
2.364
2.348
H
D
100% D
5
N
Ts
2a-3
2.00
2.02
1.05
1.04
1.05
1.04
2.04
2.02
3.08
0.95
f1 (ppm)

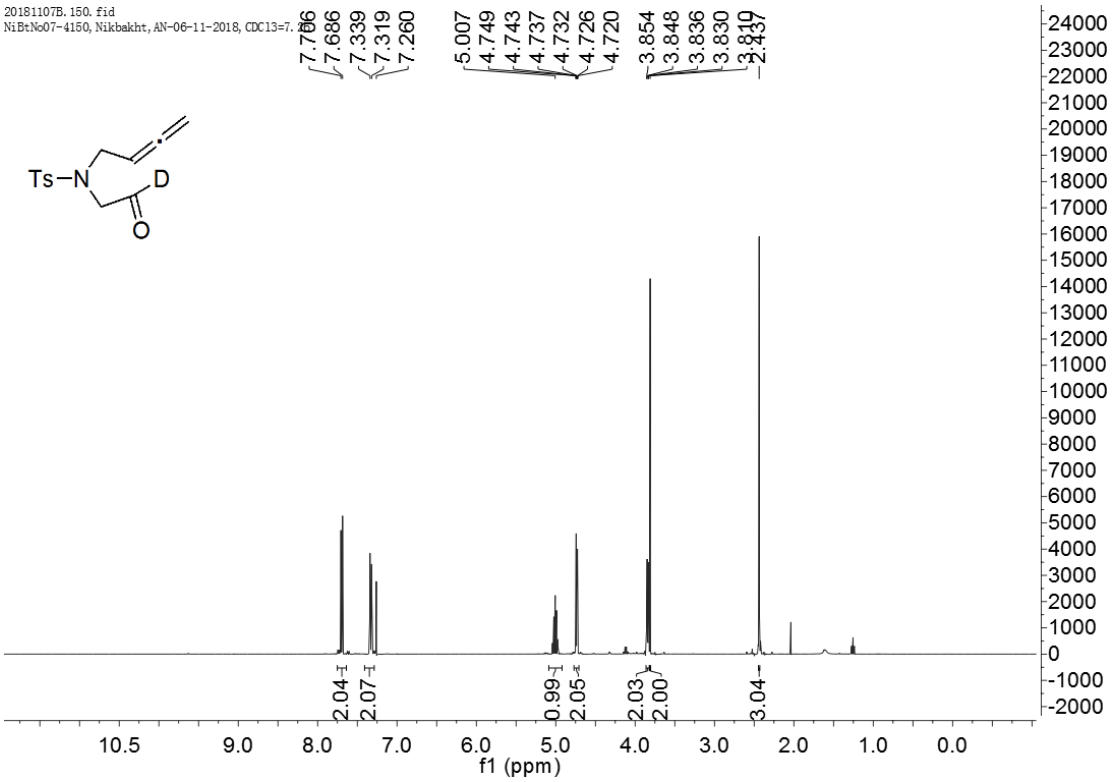

20181109B.251.fid
NiBtNo09-4251, Nikbakht, AN-08-11-2018, CDC13=77.1000
143.653
143.298
141.423
133.591
129.712
127.832
111.503
110.903
77.409
77.091
76.774
51.918
46.394
32.985
32.786
32.588
21.570
H
D
100% D
5
N
Ts
2a-3
f1 (ppm)

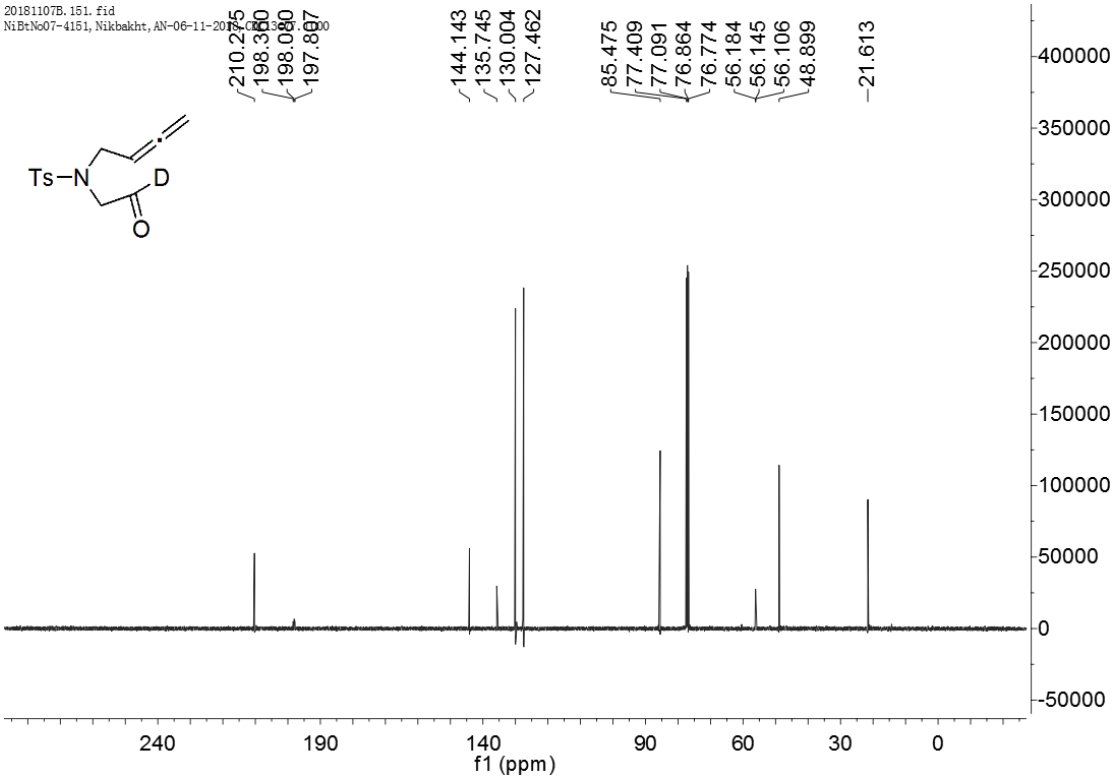

20181107B.160.fid
NiBtNo07-4160, Nikbakht, AN-30-10-2018, CDC13=7.
7.727
7.706
7.295
7.275
7.260
4.977
4.724
4.718
4.712
4.708
4.702
4.695
4.054
3.917
3.911
3.893
3.639
3.638
2.408
Ts—N
OMe
O
2.05
2.07
1.00
2.11
2.03
2.09
3.05
3.10
f1 (ppm)


20181107B.161.fid
NiBtNo07-4160, Nikbakht, AN-30-10-2018,
209.792
169.349
143.546
136.978
129.613
127.395
85.528
77.409
77.091
76.773
76.425
52.116
47.291
47.044
21.538
Ts—N
OMe
O
f1 (ppm)


20181105B.270.fid
NiBtNo05-4270, Nikbakht, Ali-5-11-18, CDCl3=7.26
7.720
7.699
7.316
7.295
7.260
4.970
4.953
4.733
4.726
4.720
4.716
4.710
3.906
3.900
3.893
3.882
3.285
3.272
2.131
Ts—N
OH
D
D
2.07
2.09
1.00
2.08
2.11
2.06
3.18
1.10
f1 (ppm)

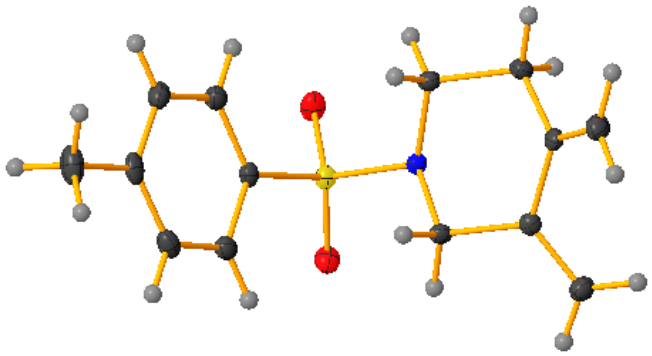

20181105B.271.fid
NiBtNo05-4271, Nikbakht, Ali-5-11-18, CDCl3=77.1000
209.504
143.652
136.585
129.844
127.360
86.181
77.409
77.091
76.774
76.584
49.616
48.233
21.560
Ts—N
OH
D
D
f1 (ppm)


20181107B.150.fid
NiBtNo07-4150, Nikbakht, AN-06-11-2018, CDC13=7.
7.766
7.686
7.339
7.319
7.260
5.007
4.749
4.743
4.737
4.732
4.726
4.720
3.854
3.848
3.836
3.830
3.819
3.813
2.437
Ts−N
D
O
2.04
2.07
0.99
2.05
2.03
2.00
3.04
f1 (ppm)


20181107B.151.fid
NiBtNo07-4151, Nikbakht, AN-06-11-2018, CDCl3=7.00
210.275
198.360
198.080
197.807
144.143
135.745
130.004
127.462
85.475
77.409
77.091
76.864
76.774
56.184
56.145
56.106
48.899
21.613
Ts−N
D
O
f1 (ppm)

Submitted by: **Daniel Kratzert**
Albert-Ludwigs-Universitaet Freiburg
Solved by: **Daniel Kratzert**
Sample ID: **Breit_Zyr_2_a**

Crystal Data and Experimental



Experimental. Single colourless needle-shaped crystals of (**Breit_Zyr_2_a**) were recrystallised from a mixture of ethyl acetate and n-pentane by waiting. A suitable crystal (0.36×0.12×0.10) mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Bruker SMART APEX CCD area detector diffractometer. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the ShelXT 2014/5 (Sheldrick, 2014) structure solution program, using the intrinsic phasing methods solution method. The model was refined with version 2017/1 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{14}H_{17}NO_2S$, M_r = 263.34, monoclinic, $P2_1/c$ (No. 14), a = 6.0835(5) Å, b = 9.3137(7) Å, c = 22.9507(17) Å, β = 95.237(4)°, α = γ = 90°, V = 1294.96(17) Å^3, T = 100(2) K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.243, 21906 reflections measured, 2987 unique (R_{int} = 0.0295) which were used in all calculations. The final wR_2 was 0.0814 (all data) and R_1 was 0.0308 (I > 2(I)).

Compound	**Breit_Zyr_2_a**
CCDC	1579171
Formula	$C_{14}H_{17}NO_2S$
$D_{calc.}$/ g cm^{-3}	1.351
μ/mm^{-1}	0.243
Formula Weight	263.34
Colour	colourless
Shape	needle
Size/mm^3	0.36×0.12×0.10
T/K	100(2)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	6.0835(5)
b/Å	9.3137(7)
c/Å	22.9507(17)
α/°	90
β/°	95.237(4)
γ/°	90
V/Å^3	1294.96(17)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.782
Θ_{max}/°	27.562
Measured Refl.	21906
Independent Refl.	2987
Reflections Used	2789
R_{int}	0.0295
Parameters	164
Restraints	0
Largest Peak	0.397
Deepest Hole	-0.407
GooF	1.081
wR_2 (all data)	0.0814
wR_2	0.0800
R_1 (all data)	0.0329
R_1	0.0308

A colourless needle-shaped crystal with dimensions 0.36×0.12×0.10 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. X-ray diffraction data were collected using a Bruker SMART APEX CCD area detector diffractometer equipped with a Oxford Cryosystems 800 low-temperature device, operating at T = 100(2) K.

Data were measured using ω and ϕ scans scans of 0.50 ° per frame for 50.00 s using MoK_α radiation (sealed tube, 50 kV, 1 mA). The total number of runs and images was based on the strategy calculation from the program Bruker APEXII.The maximum resolution achieved was Θ = 27.562°.

Cell parameters were retrieved using the **SAINT** (Bruker, V8.38A, after 2013) software and refined using **SAINT** (Bruker, V8.38A, after 2013) on 9932 reflections, 45 % of the observed reflections. Data reduction was performed using the **SAINT** (Bruker, V8.38A, after 2013) software which corrects for Lorentz polarisation. The final completeness is 100.00 % out to 27.562° in Θ.

A multi-scan absorption correction was performed using SADABS-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1510 before and 0.0435 after correction. The Ratio of minimum to maximum transmission is 0.9394. The $\lambda/2$ correction factor is Not present. The absorption coefficient μ of this material is 0.243 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.7004 and 0.7456..

The structure was solved in the space group $P2_1/c$ (# 14) by intrinsic phasing methods using the ShelXT 2014/5 (Sheldrick, 2014) structure solution program and refined by Least Squares using version 2017/1 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: SADABS-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1510 before and 0.0435 after correction. The Ratio of minimum to maximum transmission is 0.9394. The $\lambda/2$ correction factor is Not present.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

Citations

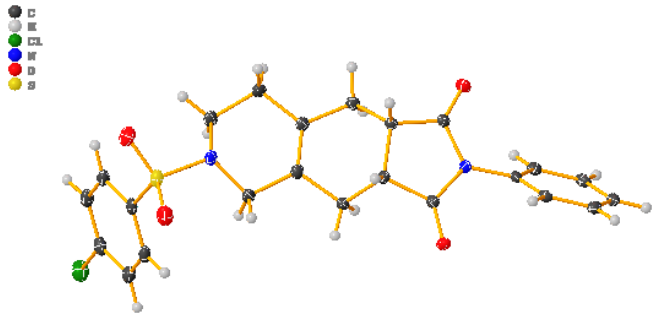
O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Bruker axs, Madison, WI (after 2013).

Submitted by: **Daniel Kratzert**
Albert-Ludwigs-Universitaet Freiburg
Solved by: **Daniel Kratzert**
Sample ID: **Breit_Zyr_3_0m_a**

Crystal Data and Experimental



Experimental. Single colourless block-shaped crystals of (**Breit_Zyr_3_0m_a**) were recrystallised from a mixture of ethyl acetate and n-pentane by cooling. A suitable crystal (0.21×0.20×0.07) mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Bruker SMART APEX2 area detector diffractometer. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{23}H_{21}ClN_2O_4S$, M_r = 456.93, monoclinic, $P2_1/c$ (No. 14), a = 30.444(9) Å, b = 6.0806(14) Å, c = 11.172(3) Å, β = 95.156(14)°, $\alpha = \gamma = 90°$, V = 2059.8(9) Å^3, T = 100(2) K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.322, 34669 reflections measured, 5104 unique (R_{int} = 0.0389) which were used in all calculations. The final wR_2 was 0.0920 (all data) and R_1 was 0.0362 (I > 2(I)).

Compound	**Breit_Zyr_3_0m_a**
CCDC	1834751
Formula	$C_{23}H_{21}ClN_2O_4S$
$D_{calc.}$/ g cm^{-3}	1.473
μ/mm^{-1}	0.322
Formula Weight	456.93
Colour	colourless
Shape	block
Size/mm^3	0.21×0.20×0.07
T/K	100(2)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	30.444(9)
b/Å	6.0806(14)
c/Å	11.172(3)
α/°	90
β/°	95.156(14)
γ/°	90
V/Å^3	2059.8(9)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.343
Θ_{max}/°	28.366
Measured Refl.	34669
Independent Refl.	5104
Reflections Used	4241
R_{int}	0.0389
Parameters	280
Restraints	0
Largest Peak	0.395
Deepest Hole	-0.375
GooF	1.044
wR_2 (all data)	0.0920
wR_2	0.0864
R_1 (all data)	0.0477
R_1	0.0362

A colourless block-shaped crystal with dimensions 0.21×0.20×0.07 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. X-ray diffraction data were collected using a Bruker SMART APEX2 area detector diffractometer equipped with a Oxford Cryosystems 800 low-temperature device, operating at T = 100(2) K.

Data were measured using ω and ϕ scans scans of 0.50 ° per frame for 50.00 s using MoK_α radiation (microfocus sealed X-ray tube, 50 kV, 1 mA). The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker).The maximum resolution achieved was Θ = 28.366°.

Cell parameters were retrieved using the **SAINT** (Bruker, V8.38A, after 2013) software and refined using **SAINT** (Bruker, V8.38A, after 2013) on 8494 reflections, 25 % of the observed reflections. Data reduction was performed using the **SAINT** (Bruker, V8.38A, after 2013) software which corrects for Lorentz polarisation. The final completeness is 100.00 % out to 28.366° in Θ.

A multi-scan absorption correction was performed using SADABS-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.0999 before and 0.0463 after correction. The Ratio of minimum to maximum transmission is 0.9366. The $\lambda/2$ correction factor is Not present. The absorption coefficient μ of this material is 0.322 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.6984 and 0.7457.

The structure was solved in the space group $P2_1/c$ (# 14) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: SADABS-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.0999 before and 0.0463 after correction. The Ratio of minimum to maximum transmission is 0.9366. The $\lambda/2$ correction factor is Not present.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **Breit_Zyr_3_0m_a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
S1	3473.8(2)	6150.0(7)	8912.8(3)	18.29(10)
N1	3016.6(4)	5340(2)	8140.5(12)	16.7(3)
C1	3907.3(5)	5109(3)	8127.6(14)	17.0(3)
O1	3481.9(4)	8503.1(19)	8848.0(11)	25.1(3)
Cl1	4911.8(2)	2085.3(8)	5928.0(4)	28.05(11)
O3	1593.1(4)	9821.3(18)	3820.2(9)	18.0(2)
C3	4352.1(5)	5332(3)	6462.3(15)	21.8(3)
O2	3491.3(4)	5083(2)	10059.4(10)	25.0(3)
N2	1168.0(4)	6746(2)	4098.0(11)	13.3(3)
C2	4039.6(5)	6252(3)	7143.9(14)	19.9(3)
C7	2944.7(5)	2933(3)	8087.8(15)	18.3(3)
C6	4080.3(5)	3036(3)	8437.4(15)	19.3(3)
C5	4394.0(5)	2123(3)	7760.5(15)	20.9(3)
O4	905.5(4)	3454.4(18)	4784(1)	18.1(2)
C4	4522.9(5)	3273(3)	6781.3(15)	21.0(3)
C9	2256.0(5)	3938(2)	6799.8(13)	15.1(3)
C8	2450.4(5)	2521(3)	7815.4(14)	17.7(3)
C10	2469.7(5)	5678(3)	6410.7(13)	16.3(3)
C11	2917.0(5)	6401(3)	6956.8(14)	18.2(3)
C12	1809.5(5)	3331(2)	6191.2(14)	16.4(3)

Atom	x	y	z	U_{eq}
C13	1518.6(5)	5363(2)	5914.2(13)	12.9(3)
C14	1767.8(5)	7418(2)	5548.8(13)	13.6(3)
C15	2257.8(5)	6984(3)	5358.9(14)	17.0(3)
C16	1160.9(5)	4981(2)	4902.6(13)	13.4(3)
C17	1513.6(5)	8220(2)	4405.3(13)	13.6(3)
C18	854.3(5)	7047(2)	3068.9(12)	12.8(3)
C19	793.4(5)	5390(2)	2213.7(13)	14.4(3)
C20	498.1(5)	5738(3)	1206.8(13)	16.6(3)
C21	267.4(5)	7703(3)	1066.4(13)	16.7(3)
C22	327.5(5)	9340(3)	1934.2(13)	15.9(3)
C23	622.8(5)	9020(2)	2944.7(13)	13.7(3)

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) **Breit_Zyr_3_0m_a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	18.3(2)	16.47(19)	19.16(19)	-3.05(15)	-3.26(14)	2.83(15)
N1	15.1(6)	13.8(6)	20.4(6)	1.5(5)	-2.7(5)	1.9(5)
C1	14.2(7)	16.5(7)	19.2(7)	-2.1(6)	-5.2(6)	0.5(6)
O1	25.4(6)	16.1(6)	32.3(7)	-6.2(5)	-5.0(5)	2.3(5)
Cl1	23.7(2)	34.1(2)	26.1(2)	-6.71(17)	0.84(16)	6.27(18)
O3	19.9(6)	16.3(6)	17.2(5)	3.6(4)	-1.5(4)	-4.6(4)
C3	19.7(8)	24.0(9)	20.7(8)	2.2(6)	-3.0(6)	-0.3(7)
O2	28.8(7)	27.2(7)	18.3(6)	-2.2(5)	-2.2(5)	4.7(5)
N2	13.4(6)	12.4(6)	13.6(6)	-0.2(5)	-1.4(5)	-2.2(5)
C2	16.4(8)	17.5(8)	24.3(8)	1.1(6)	-6.1(6)	0.6(6)
C7	17.9(8)	13.7(7)	22.8(8)	1.9(6)	-1.2(6)	3.0(6)
C6	16.7(8)	17.6(8)	22.4(8)	2.2(6)	-4.3(6)	0.2(6)
C5	18.8(8)	16.5(8)	26.2(8)	-1.2(6)	-5.5(6)	2.8(6)
O4	17.3(5)	14.6(5)	22.1(6)	0.3(4)	0.5(4)	-4.6(4)
C4	14.9(7)	25.4(9)	21.8(8)	-6.0(6)	-3.0(6)	1.5(6)
C9	14.5(7)	13.3(7)	17.5(7)	0.5(6)	1.0(5)	2.0(6)
C8	17.9(8)	12.9(7)	22.3(8)	3.4(6)	0.9(6)	2.0(6)
C10	14.7(7)	16.6(7)	17.6(7)	1.0(6)	0.6(6)	2.1(6)
C11	15.8(7)	15.6(8)	22.6(8)	5.3(6)	-1.8(6)	0.0(6)
C12	15.7(7)	12.7(7)	20.8(7)	0.7(6)	1.6(6)	-0.8(6)
C13	13.1(7)	12.2(7)	13.3(7)	-0.4(5)	1.4(5)	-1.4(5)
C14	15.9(7)	11.8(7)	13.0(7)	-0.3(5)	0.0(5)	-0.8(6)
C15	14.0(7)	18.6(8)	18.2(7)	3.9(6)	0.2(6)	-1.9(6)
C16	13.0(7)	12.9(7)	14.6(7)	-1.1(5)	3.1(5)	0.4(6)
C17	13.8(7)	13.1(7)	13.8(7)	-2.4(5)	1.0(5)	-0.6(6)
C18	11.0(7)	15.7(7)	11.7(6)	0.3(5)	1.0(5)	-2.7(6)
C19	13.7(7)	13.1(7)	16.8(7)	-1.4(5)	3.9(5)	-1.0(6)
C20	18.6(8)	18.2(8)	13.3(7)	-4.7(6)	3.0(6)	-6.5(6)
C21	16.7(7)	20.8(8)	12.1(7)	1.8(6)	-0.9(5)	-3.9(6)
C22	15.7(7)	16.3(7)	16.1(7)	1.7(6)	2.7(6)	0.2(6)
C23	14.8(7)	13.5(7)	13.0(7)	-2.5(5)	3.3(5)	-2.9(6)

Table 3: Bond Lengths in Å for **Breit_Zyr_3_0m_a**.

Atom	Atom	Length/Å
S1	N1	1.6458(14)
S1	C1	1.7663(17)
S1	O1	1.4330(13)
S1	O2	1.4326(13)
N1	C7	1.480(2)
N1	C11	1.478(2)
C1	C2	1.390(2)
C1	C6	1.398(2)
Cl1	C4	1.7422(17)
O3	C17	1.2094(18)
C3	C2	1.388(2)

Atom	Atom	Length/Å
C3	C4	1.390(2)
N2	C16	1.4012(19)
N2	C17	1.4012(19)
N2	C18	1.4389(18)
C7	C8	1.529(2)
C6	C5	1.386(2)
C5	C4	1.385(2)
O4	C16	1.2103(18)
C9	C8	1.503(2)
C9	C10	1.335(2)
C9	C12	1.510(2)

Atom	Atom	Length/Å
C10	C11	1.507(2)
C10	C15	1.514(2)
C12	C13	1.535(2)
C13	C14	1.536(2)
C13	C16	1.515(2)
C14	C15	1.548(2)
C14	C17	1.514(2)
C18	C19	1.390(2)
C18	C23	1.392(2)
C19	C20	1.392(2)
C20	C21	1.388(2)
C21	C22	1.390(2)
C22	C23	1.392(2)

Table 4: Bond Angles in ° for **Breit_Zyr_3_0m_a**.

Atom	Atom	Atom	Angle/°
N1	S1	C1	105.49(7)
O1	S1	N1	106.85(7)
O1	S1	C1	108.40(8)
O2	S1	N1	107.16(7)
O2	S1	C1	108.22(8)
O2	S1	O1	119.85(8)
C7	N1	S1	115.58(10)
C11	N1	S1	115.74(10)
C11	N1	C7	112.21(12)
C2	C1	S1	119.75(12)
C2	C1	C6	121.13(15)
C6	C1	S1	118.81(13)
C2	C3	C4	118.75(16)
C16	N2	C18	124.25(12)
C17	N2	C16	112.79(12)
C17	N2	C18	122.96(12)
C3	C2	C1	119.60(15)
N1	C7	C8	108.02(12)
C5	C6	C1	119.27(16)
C4	C5	C6	119.13(15)
C3	C4	Cl1	119.34(14)
C5	C4	Cl1	118.56(13)
C5	C4	C3	122.10(16)
C8	C9	C12	118.49(13)
C10	C9	C8	121.99(14)
C10	C9	C12	119.51(14)
C9	C8	C7	111.71(13)
C9	C10	C11	123.25(14)
C9	C10	C15	118.84(14)
C11	C10	C15	117.91(13)
N1	C11	C10	109.89(13)
C9	C12	C13	111.92(12)
C12	C13	C14	114.74(12)
C16	C13	C12	112.94(12)
C16	C13	C14	105.40(11)
C13	C14	C15	113.77(12)
C17	C14	C13	105.02(12)
C17	C14	C15	111.41(12)
C10	C15	C14	109.37(12)
N2	C16	C13	108.03(12)
O4	C16	N2	124.32(13)
O4	C16	C13	127.64(14)
O3	C17	N2	124.41(14)
O3	C17	C14	127.13(14)
N2	C17	C14	108.44(12)
C19	C18	N2	119.67(13)
C19	C18	C23	121.42(13)
C23	C18	N2	118.90(13)
C18	C19	C20	118.82(14)
C21	C20	C19	120.40(14)
C20	C21	C22	120.27(14)
C21	C22	C23	120.02(15)
C18	C23	C22	119.06(14)

Table 5: Torsion Angles in ° for **Breit_Zyr_3_0m_a**.

Atom	Atom	Atom	Atom	Angle/°
S1	N1	C7	C8	157.21(11)
S1	N1	C11	C10	-174.25(11)
S1	C1	C2	C3	-174.13(12)
S1	C1	C6	C5	174.50(12)
N1	S1	C1	C2	82.72(14)
N1	S1	C1	C6	-90.90(13)
N1	C7	C8	C9	46.83(17)
C1	S1	N1	C7	64.45(13)
C1	S1	N1	C11	-69.66(13)
C1	C6	C5	C4	-1.0(2)
O1	S1	N1	C7	179.67(11)
O1	S1	N1	C11	45.56(13)
O1	S1	C1	C2	-31.43(15)
O1	S1	C1	C6	154.94(12)
O2	S1	N1	C7	-50.70(13)
O2	S1	N1	C11	175.19(11)

Atom	Atom	Atom	Atom	Angle/°
O2	S1	C1	C2	-162.86(12)
O2	S1	C1	C6	23.52(14)
N2	C18	C19	C20	-178.11(13)
N2	C18	C23	C22	178.33(13)
C2	C1	C6	C5	1.0(2)
C2	C3	C4	Cl1	179.46(12)
C2	C3	C4	C5	-0.5(2)
C7	N1	C11	C10	50.13(17)
C6	C1	C2	C3	-0.7(2)
C6	C5	C4	Cl1	-179.14(12)
C6	C5	C4	C3	0.9(2)
C4	C3	C2	C1	0.4(2)
C9	C10	C11	N1	-15.7(2)
C9	C10	C15	C14	46.06(19)
C9	C12	C13	C14	35.98(17)
C9	C12	C13	C16	156.81(12)
C8	C9	C10	C11	-1.0(2)
C8	C9	C10	C15	178.20(14)
C8	C9	C12	C13	139.09(14)
C10	C9	C8	C7	-15.1(2)
C10	C9	C12	C13	-42.19(19)
C11	N1	C7	C8	-67.10(16)
C11	C10	C15	C14	-134.71(14)
C12	C9	C8	C7	163.59(13)
C12	C9	C10	C11	-179.65(14)
C12	C9	C10	C15	-0.5(2)
C12	C13	C14	C15	7.84(17)
C12	C13	C14	C17	129.92(13)
C12	C13	C16	N2	-131.75(13)
C12	C13	C16	O4	48.8(2)
C13	C14	C15	C10	-47.76(17)
C13	C14	C17	O3	178.96(15)
C13	C14	C17	N2	-2.71(15)
C14	C13	C16	N2	-5.74(15)
C14	C13	C16	O4	174.85(15)
C15	C10	C11	N1	165.09(13)
C15	C14	C17	O3	-57.4(2)
C15	C14	C17	N2	120.90(13)
C16	N2	C17	O3	177.43(14)
C16	N2	C17	C14	-0.96(16)
C16	N2	C18	C19	-56.0(2)
C16	N2	C18	C23	125.00(15)
C16	C13	C14	C15	-117.06(13)
C16	C13	C14	C17	5.03(15)
C17	N2	C16	O4	-176.25(14)
C17	N2	C16	C13	4.31(16)
C17	N2	C18	C19	124.61(15)
C17	N2	C18	C23	-54.41(19)
C17	C14	C15	C10	-166.23(12)
C18	N2	C16	O4	4.3(2)
C18	N2	C16	C13	-175.15(13)
C18	N2	C17	O3	-3.1(2)
C18	N2	C17	C14	178.51(12)

Atom	Atom	Atom	Atom	Angle/°
C18	C19	C20	C21	-0.4(2)
C19	C18	C23	C22	-0.7(2)
C19	C20	C21	C22	-0.3(2)
C20	C21	C22	C23	0.5(2)
C21	C22	C23	C18	0.0(2)
C23	C18	C19	C20	0.9(2)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Breit_Zyr_3_0m_a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3	4447.37	6096.41	5790.45	26
H2	3916.87	7652.82	6939.19	24
H7A	3050.77	2251.46	8865.22	22
H7B	3109.26	2278.45	7450.77	22
H6	3984.03	2261.47	9104.39	23
H5	4518.75	726.23	7965.8	25
H8A	2401.27	954.09	7603.04	21
H8B	2298.2	2830.3	8543.84	21
H11A	3144.62	5992.22	6417.27	22
H11B	2921.46	8019.16	7053.01	22
H12A	1659.16	2322.21	6717.95	20
H12B	1849.18	2543.14	5432.93	20
H13	1371.71	5730.87	6654.14	15
H14	1752.72	8564.3	6185.39	16
H15A	2278.22	6153.42	4603.78	20
H15B	2414.51	8399.7	5293.47	20
H19	950.44	4043.01	2314.65	17
H20	454.19	4624.39	611.95	20
H21	67.54	7930.68	374.42	20
H22	167.05	10678.13	1837.65	19
H23	665.64	10131.82	3541.07	16

Citations

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