Supporting information for

Facile Access to 2,2-Disubstituted Indolin-3-ones via Cascade Fischer Indolization/[3,3]-Claisen Rearrangement Reaction†

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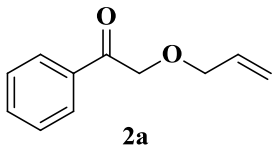
1. Experimental part

General Information. Unless otherwise specified, all reagents purchased from commercial suppliers were used as received. Non-aqueous reactions were conducted under an inert atmosphere of argon in flame-dried glassware. Anhydrous solvents were treated as followed: tetrahydrofuran, toluene and diethyl ether were distilled from benzophenone ketyl under nitrogen atmosphere, dimethylformamide was distilled over calcium hydride under reduced pressure, dichloromethane was distilled from calcium hydride under nitrogen atmosphere. Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60 μm, 230-400 mesh, Silicycle P60). NMR data including ^{1}H NMR or ^{13}C NMR spectra were recorded on Mercury 300 and MR 400. ^{1}H NMR Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$:7.27 ppm). ^{13}C NMR chemical shifts were reported in ppm relative to the solvent ($CDCl_3$:77 ppm). Infrared spectra were performed on a Nicolet 380FT-IR and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were measured on a Shimadzu LCMS-2010EV mass spectrometer (ESI). High resolution mass spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI) and Bruker APEXIII 7.0 TESLA FTMS (ESI).

Synthesis of substrates 2a-2u



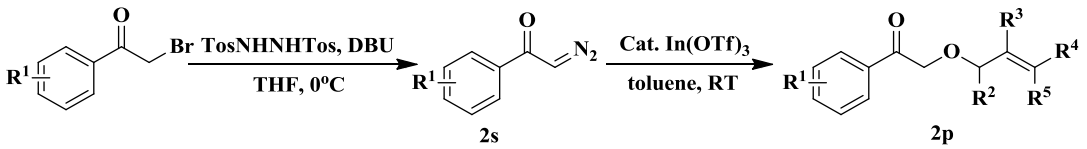
2a

2a is synthesized according to related literature[1].

To a solution of 2-hydroxyacetophenone (6.8 g, 50 mmol) in 100 mL of allyl bromide was added 30 g of $CaSO_4$. This suspension was cooled to 0 ^{o}C and Ag_2O (19.8 g, 80 mmol) was added in several portions over 1h. The reaction mixture was warmed to room temperature and allowed to stir an additional 24 h. EA was added and the reaction mixture was filtered through Celite. Solvent removal followed by flash chromatography (PE:EA = 30:1, V/V) afforded **2a** as a slightly yellowish oil (8.4 g, 84%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 1701,1449, 1226, 1137, 755, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.55 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.93 (ddt, *J* = 22.2, 10.5, 5.8 Hz, 1H), 5.26 (ddd, *J* = 13.8, 11.6, 1.4 Hz, 2H), 4.73 (s, 2H), 4.14 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.23, 134.93, 133.95, 133.51, 128.69, 127.86, 118.18, 72.51; HRMS-EI calcd. for $C_{11}H_{12}O_2$ M^+ 176.0837, found: 176.0837.

General procedure for the synthesis of 2pa-2pc, 2pe-2pi, 2pl-2pr and 2pu:

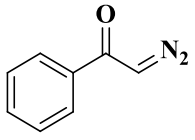


TosNHNHTos and diazoacetates are synthesized according to related literature[2].

To a mixture of p-toluenesulfonyl hydrazide (25.8 g, 134 mmol, 1.0 equiv) and p-toluenesulfonyl chloride (33.2 g, 174 mmol, 1.3 equiv) under N_2, 140 mL DCM is added. This suspension is cooled to 0 ^oC and pyridine (14.1 mL, 13.8 g, 174 mmol, 1.3 equiv) is added dropwise. During the addition, the reaction mixture becomes homogenous and turns yellow. White precipitate is observed and the reaction mixture is stirred for 30 min. N-Hexane (200 mL) and H_2O (300 mL) are added and stirred in an ice bath for 15 min. The white precipitates is collected by filtration and washed with ice-cooled Et_2O (200 mL), and then dried under vacuum (25 ℃, 32 mmHg, 3 h). The solid thus obtained is dissolved in boiling acetone (320 mL), and H_2O (150 mL) is slowly added. The mixture is then cooled in an ice bath for 1 h and the white precipitates are collected by by filtration. The precipitate is washed with ice-cooled Et_2O (100 mL) and dried under vacuum over P_2O_5 (25 ℃, 10 mmHg, 3 h) to afford *N*,*N'*-ditosylhydrazine (42g, 92%).

General procedure for the synthesis of diazoacetates:

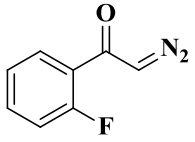
To a mixture of 2-bromoacetophenones (5 mmol, 1.0 equiv) and *N*,*N'*-ditosylhydrazine (5.5 mmol, 1.1 equiv) under N_2, 25 mL THF is added. This suspension is cooled to 0^oC and DBU (7.5 mmol, 1.5 equiv) is added dropwise and the reaction mixture is stirred for 30 min. The reaction mixture is poured into saturated aqueous sodium hydrogen carbonate solution and is extracted with EA. The organic solutions are combined, washed with brine, dried and concentrated, and then purified by flash chromatography to afford diazoacetates.



2sH

Following the general procedure, **2sH** was obtained as orange oil (600 mg, 82%).

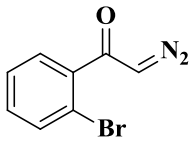
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3079, 2104, 1613, 1574, 1363, 1226, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 5.92 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.36, 136.63, 132.70, 128.64, 126.67, 54.18. HRMS-EI calcd. for $C_8H_6N_2O$ M^+ 146. 0480. found: 146.0481.



2sa

Following the general procedure, **2sa** was obtained as orange oil (680 mg, 83%).

R*f* = 0.5 (PE/EA = 12:1, V/V); IR (film): 2107, 1610, 1454, 1360, 1211, 878, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, *J* = 7.0 Hz, 1H), 7.52 – 7.39 (m, 1H), 7.29 – 7.17 (m, 1H), 7.07 (dd, *J* = 11.1, 8.7 Hz, 1H), 6.07 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.24 (s), 162.45 (s), 134.02 (d, *J* = 9.1 Hz), 130.29 (d, *J* = 2.4 Hz), 124.49 (dd, *J* = 20.2, 7.5 Hz), 116.41 (s), 116.22 (s), 58.15 (d, *J* = 16.2 Hz). ^{19}F NMR (376 MHz, $cdcl_3$) δ -111.92 (s). HRMS-EI calcd. for $C_8H_5FN_2O$ M^+ 164.0386, found: 164.0390.

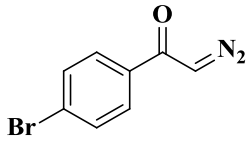


2sb

The starting material 2-bromo-1-(2-bromophenyl)ethanone for **2sc** was not commercially available and it was synthesized according to related literature[3].

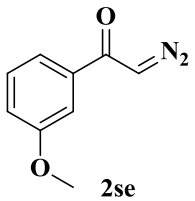
To a stirring mixture of 2-bromo-1-(2-bromophenyl)ethanone (10 mmol, 1.0 equiv) in 30ml dry Et_2O under N_2 at 0^oC, a solution bromine (10 mmol, 1.0 equiv) in 5ml dry Et_2O was added dropwise in 5 min. After addition of bromine, when the purple color faded to orange in about 5 min, the reaction mixture was poured into water and stirred until the orange color disappeared. And then the mixture was extracted with EA. The combined organic layers were washed with brine, dried and concentrated. The obtained crude product was used for the next step without further purification (NMR showed that the ration of starting material, target product and di-substituted by-product was 3:17:1).

Following the general procedure, **2sb** was obtained as yellow solid (1.3 g, 58% for two steps).
R*f* = 0.5 (PE/EA = 12:1, V/V); IR (film): 3109, 2114, 1611, 1587, 1402 , 754, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (m, 1H), 7.45 (d, *J* = 6.9 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.30 (m, 1H), 5.72 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.82, 139.54, 133.71, 131.81, 129.00, 127.51, 119.23, 57.48. HRMS-EI calcd. for $C_8H_5BrN_2O$ M^+ 223. 9585. found: 223.9581.



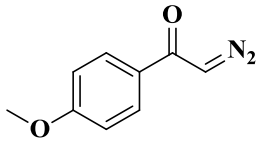
2sc

Following the general procedure, **2sc** was obtained as yellow solid (850 mg, 76%).
R*f* = 0.5 (PE/EA = 12:1, V/V); IR (film): 3115, 2113, 1607, 1590, 1400, 833, 733, 670 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (td, *J* = 8.7, 6.6 Hz, 4H), 5.87 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.10, 135.37, 131.92, 128.21, 127.61, 54.43. HRMS-EI calcd. for $C_8H_5BrN_2O$ M^+ 223. 9585. found: 223.9580.



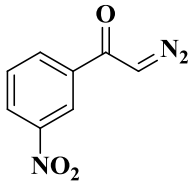
2se

Following the general procedure, **2se** was obtained as orange oil (770 mg, 87%). R*f* = 0.5 (PE/EA=8:1, V/V); IR (film): 2105, 1596, 1577,1357, 1262, 798, 732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 11.2, 4.5 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.06 (dd, *J* = 8.1, 1.7 Hz, 1H), 5.89 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.12, 159.89, 138.04, 129.61, 118.94, 118.89, 111.46, 55.45, 54.32. HRMS-EI calcd. for $C_9H_8N_2O_2$ M^+ 176. 0586. found: 176.0582.



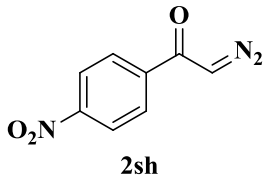
2sf

Following the general procedure, **2sf** was obtained as yellow solid (790 mg, 89%). R*f* = 0.5 (PE/EA=8:1, V/V); IR (film): 3099, 2107, 1611, 1567, 1364, 1020, 753, 732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.85 (s, 1H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.2, 163.26, 129.42, 128.71, 113.77, 55.42, 53.48. HRMS-EI calcd. for $C_9H_8N_2O_2$ M^+ 176. 0586. found: 176.0589.



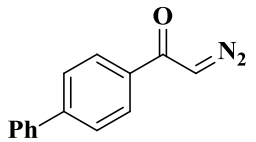
2sg

Following the general procedure, **2sg** was obtained as yellow solid (650mg, 68%). R*f* = 0.5 (PE/EA=6:1, V/V); IR (film): 3078, 2114, 1604, 1529, 1441, 1379, 1348, 913, 707 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (t, *J* = 1.9 Hz, 1H), 8.40 (ddd, *J* = 8.2, 2.2, 1.1 Hz, 1H), 8.16 – 8.10 (m, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 6.01 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.93, 145.77, 135.28, 129.89, 127.38, 124.41, 119.05, 52.71. HRMS-EI calcd. for $C_8H_5N_3O_3$ M^+ 191. 0331. found: 191.0330.



2sh

Following the general procedure, **2sh** was obtained as yellow solid (580 mg, 60%). R*f* = 0.5 (PE/EA=6:1, V/V); IR (film): 3088, 2108, 1613, 1588, 1523, 1380, 1343, 846, 705 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (m, 2H), 7.91 (m, 2H), 5.98 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.47, 147.54, 138.82, 125.22, 121.33, 53.15. HRMS-EI calcd. for $C_8H_5N_3O_3$ M^+ 191.0331. found: 191.0328.



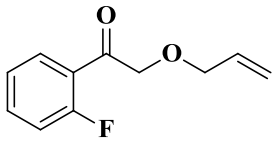
2si

Following the general procedure, **2si** was obtained as yellow solid (930 mg, 84%).
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3079, 2115, 1598, 1579, 1404, 1368, 737, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (m, 2H), 7.67 (m, 2H), 7.62 (m, 2H), 7.47 (m, 2H), 7.39 (m, 1H), 5.94 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.81, 145.47, 139.82, 135.39, 128.96, 128.19, 127.28, 127.26, 127.22, 54.18. HRMS-EI calcd. for $C_{14}H_{10}N_2O$ M^+ 222.0793, found: 222.0796.

General procedure for the synthesis of 2-(allyloxy)-1-phenylethanones and 2pu:

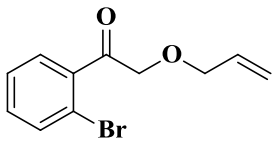
Substrates including**2pa-2pc, 2pe-2pi, 2pl-2pr and 2pu** are synthesized according to related literature[4].

To a stirring mixture of diazoacetate (1 mmol, 1.0 equiv) and alcohol (1.5 mmol, 1.5 equiv) in dry toluene (10 mL) at room temperature under argon, indium (III) trifluoromethanesulfonate (56.2 mg, 0.1 mmol, 10 mol%) was added and a rapid evolution of nitrogen gas was observed. The reaction was monitored by TLC, and when complete consumption of the starting material was observed, saturated $NaHCO_3$ was added and the reaction mixture was extracted with EA. The organic solutions were combined, washed with brine, dried and concentrated, and then purified by flash chromatography to afford the target products.



2pa

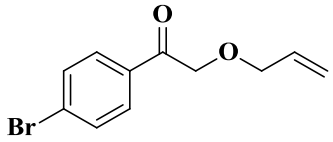
Following the general procedure, **2pa** was obtained as slightly yellow oil (140 mg, 72%).
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 1700, 1610, 1480, 1453, 1272, 1214, 1142, 1100, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (td, *J* = 7.6, 1.7 Hz, 1H), 7.52 (tdd, *J* = 7.2, 5.2, 1.8 Hz, 1H), 7.24 (m, 1H), 7.10 (m, 1H), 5.93 (ddt, *J* = 16.2, 10.4, 5.8 Hz, 1H), 5.25 (ddd, *J* = 13.8, 11.4, 1.3 Hz, 2H), 4.66 (d, *J* = 3.4 Hz, 2H), 4.13 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.72 (d, *J* = 5.4 Hz), 163.09 (s), 161.07 (s), 135.05 (d, *J* = 9.0 Hz), 134.01 (s), 130.62 (d, *J* = 3.4 Hz), 124.71 (d, *J* = 3.1 Hz), 123.23 (d, *J* = 15.2 Hz), 118.03 (s), 116.56 (s), 116.37 (s), 77.29 (s), 77.04 (s), 76.78 (s), 75.74 (d, *J* = 11.7 Hz), 72.48 (s). ^{19}F NMR (376 MHz, $cdcl_3$) δ -107.91 (tdt, *J* = 7.2, 5.2, 3.5 Hz). HRMS-EI calcd. for $C_{11}H_{11}FNO_2$ M^+ 194.0743, found: 194.0742.



2pb

Following the general procedure, **2pb** was obtained as slightly yellow oil (120 mg, 47%).

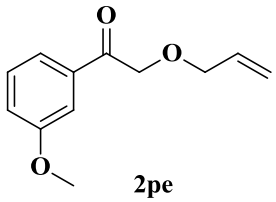
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 1705, 1584, 1389, 1224, 1132, 1072, 987, 930, 750, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.35 (m, 3H), 5.92 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.30 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.23 (ddd, *J* = 10.4, 2.7, 1.2 Hz, 1H), 4.59 (s, 2H), 4.14 (dt, *J* = 5.8, 1.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.07, 139.19, 133.74, 133.58, 132.00, 128.84, 127.37, 119.05, 118.25, 74.31, 72.43. HRMS-EI calcd. for $C_{11}H_{11}BrO_2$ M^+ 253.9942, found: 253.9944.



2pc

Following the general procedure, **2pc** was obtained as slightly yellow oil (140 mg, 55%).

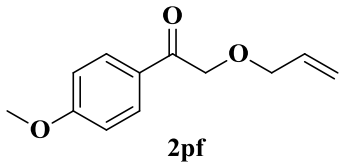
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 1701, 1585, 1397, 1223, 1134, 1071, 983, 932, 818 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 5.92 (ddd, *J* = 16.2, 11.0, 5.8 Hz, 1H), 5.33 – 5.20 (m, 2H), 4.66 (s, 2H), 4.12 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.47, 133.75, 132.02, 129.53, 128.71, 118.36, 72.65, 72.49. HRMS-EI calcd. for $C_{11}H_{11}BrO_2$ M^+ 253.9942, found: 253.9940.



2pe

Following the general procedure, **2pe** was obtained as slightly yellow oil (170 mg, 82%).

R*f* = 0.5 (PE/EA=8:1, V/V); IR (film): 1691, 1601, 1261, 1235, 1173, 1133, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 5.5 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.12 – 7.04 (m, 1H), 5.92 (ddt, *J* = 16.2, 10.6, 5.8 Hz, 1H), 5.25 (ddd, *J* = 13.8, 11.5, 1.3 Hz, 2H), 4.70 (s, 2H), 4.12 (d, *J* = 5.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.00, 159.86, 136.19, 133.94, 129.68, 120.29, 119.95, 118.16, 112.17, 72.58, 72.42, 55.44. HRMS-EI calcd. for $C_{12}H_{14}O_2$ M^+ 206.0943, found: 206.0941.

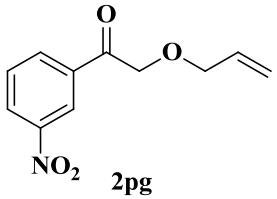


2pf

Following the general procedure, **2pf** was obtained as slightly yellow oil (180 mg, 87%).

R*f* = 0.5 (PE/EA=8:1, V/V); IR (film): 1701, 1597, 1583, 1430, 1262, 755 cm^{-1}; ^1H

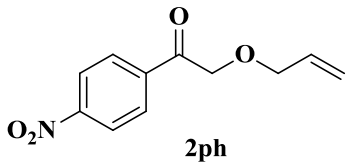
NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.95 (m, 1H), 5.28 (m, 2H), 4.70 (s, 2H), 4.14 (d, *J* = 5.8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.81, 163.76, 134.04, 130.24, 128.02, 118.08, 113.85, 72.49, 72.40, 55.48. HRMS-EI calcd. for $C_{12}H_{14}O_3$ M^+ 206.0943, found: 206.0930.



2pg

Following the general procedure, **2pg** was obtained as slightly yellow oil (110 mg, 50%).

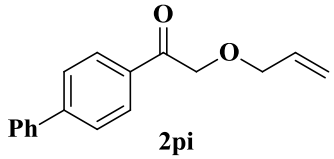
R*f* = 0.5 (PE/EA = 6:1, V/V); IR (film): 1709,1531, 1351, 1224, 1083, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.78 (t, *J* = 1.9 Hz, 1H), 8.44 (ddd, *J* = 8.2, 2.2, 1.1 Hz, 1H), 8.30 (m, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 5.94 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.34 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (ddd, *J* = 10.4, 2.6, 1.2 Hz, 1H), 4.74 (s, 2H), 4.16 (dt, *J* = 5.8, 1.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.57, 148.39, 136.10, 133.79, 133.44, 129.97, 127.74, 123.16, 118.70, 73.07, 72.62. HRMS-EI calcd. for $C_{11}H_{11}NO_4$ M^+ 221.0688, found: 221.0684.



2ph

Following the general procedure, **2ph** was obtained as slightly yellow oil (100 mg, 45%).

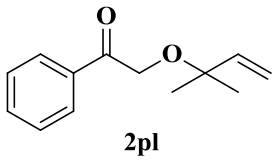
R*f* = 0.5 (PE/EA = 6:1, V/V); IR (film): 1708,1602, 1525, 1347, 1219, 854 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (m, 2H), 8.10 (m, 2H), 5.92 (m, 1H), 5.30 (m, 2H), 4.73 (s, 2H), 4.15 (dt, *J* = 5.8, 1.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.27, 139.38, 133.46, 129.26, 123.88, 118.67, 73.07, 72.62. HRMS-EI calcd. for $C_{11}H_{11}NO_4$ M^+ 221.0688, found: 221.0684.



2pi

Following the general procedure, **2pi** was obtained as slightly yellow oil (190 mg, 76%).

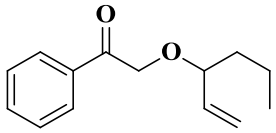
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 1704, 1685, 1145, 1117, 979, 766 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.63 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.48 (m, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 5.98 (ddd, *J* = 16.2, 11.0, 5.8 Hz, 1H), 5.35 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 4.78 (s, 2H), 4.18 (dd, *J* = 5.8, 1.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.29, 143.63, 137.18, 131.37, 131.02, 126.38, 125.83, 125.73, 124.71, 124.67, 115.66, 70.09, 69.90. HRMS-EI calcd. for $C_{17}H_{16}O_2$ M^+ 252. 1150. found: 252.1149.



2pl

Following the general procedure, **2pl** was obtained as slightly yellow oil (65 mg, 32%).

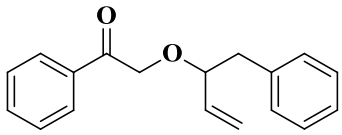
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 2977, 1704, 1685, 1145, 1117, 979, 755, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.85 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.18 (dd, *J* = 14.2, 7.8 Hz, 2H), 4.59 (s, 2H), 1.35 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.84, 142.86, 133.20, 128.55, 127.98, 115.00, 66.91, 25.73. HRMS-EI calcd. for $C_{13}H_{16}O_2$ M^+ 204.1150, found: 204.1148.



2pm

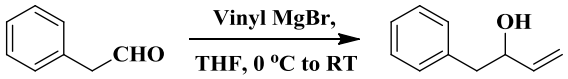
Following the general procedure, **2pm** was obtained as slightly yellow oil (185 mg, 85%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 2959, 2932, 2872, 1703, 1449, 1224, 1123, 754, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.68 (ddd, *J* = 17.2, 10.4, 8.1 Hz, 1H), 5.18 (m, 2H), 4.74 (d, *J* = 16.6 Hz, 1H), 4.61 (d, *J* = 16.6 Hz, 1H), 3.78 (dd, *J* = 14.3, 6.8 Hz, 1H), 1.52 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.74, 138.29, 135.20, 133.33, 128.59, 127.94, 118.09, 82.15, 70.97, 37.42, 18.52, 13.96. HRMS-EI calcd. for $C_{14}H_{18}O_2$ M^+ 218.1307, found: 218.1303.



2pn

The starting material for **2pn** was not commercially available and it was synthesized from phenylacetadehyde.

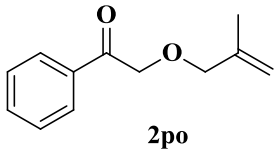


2sn

To a solution of phenylacetadehyde (100 mmol, 1.0 equiv) in THF under N_2 cooled to 0°C, a solution of vinyl MgBr (120 mmol, 1.2 equiv) is added dropwise and and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was poured into dilute aqueous HCl and extracted with EA. The combined organic layers were washed with saturated $NaHCO_3$ and brine successively, dried and concentrated, and then purified by flash chromatography to afford the target product (12.7 g, 86%).

Following the general procedure, **2pn** was obtained as slightly yellow oil (140mg, 52%).

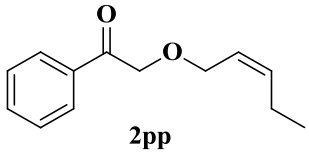
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 1702,1682, 1448, 1225, 1126, 753, 690, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.21 (m, 6H), 5.72 (ddd, *J* = 17.3, 10.3, 8.0 Hz, 1H), 5.16 (m, 2H), 4.73 (d, *J* = 16.4 Hz, 1H), 4.58 (d, *J* = 16.4 Hz, 1H), 4.04 (dd, *J* = 14.4, 6.7 Hz, 1H), 3.09 (dd, *J* = 13.7, 6.6 Hz, 1H), 2.86 (dd, *J* = 13.7, 6.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.49, 137.78, 137.25, 135.04, 133.32, 129.68, 128.56, 128.14, 128.07, 126.25, 118.67, 83.13, 71.42, 42.09. HRMS-EI calcd. for $C_{18}H_{18}O$ M^+ 266. 1307. found: 266.1310;



2po

Following the general procedure, **2po** was obtained as slightly yellow oil (150 mg, 79%).

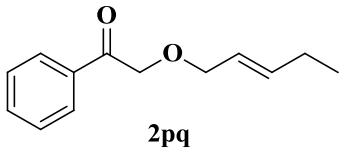
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 2919, 1701,1597, 1449, 1226, 1137, 755, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 4.98 (d, *J* = 22.9 Hz, 2H), 4.72 (m, 2H), 4.06 (s, 2H), 1.77 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 196.35, 141.39, 134.94, 133.49, 128.66, 127.88, 113.31, 75.36, 72.38, 19.42. HRMS-EI calcd. for $C_{12}H_{14}O_2$ M^+ 190.0994, found: 190.0993.



2pp

Following the general procedure, **2pp** was obtained as slightly yellow oil (180 mg, 88%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 2964, 2932, 2873, 1701, 1449, 1225, 1140, 755, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.58 (m, 2H), 4.71 (s, 2H), 4.18 (d, *J* = 6.6 Hz, 2H), 2.06 (p, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.55, 136.62, 134.99, 133.47, 128.67, 127.90, 124.40, 72.51, 66.70, 20.89, 14.15. HRMS-EI calcd. for $C_{13}H_{16}O_2$ M^+ 204.1150, found: 204.1159.

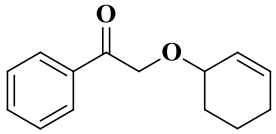


2pq

Following the general procedure, **2pq** was obtained as slightly yellow oil (185 mg, 90%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 2963, 1701, 1685, 1449, 1225, 1134, 969, 754, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.84 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.77 (m, 1H), 5.57 (m, 1H), 4.70 (s, 2H), 4.08 (dd, *J* = 6.4, 0.9 Hz, 2H), 2.05 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$)

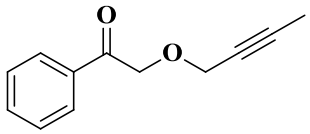
δ 196.37, 137.68, 133.44, 128.66, 127.89, 124.44, 77.26, 77.00, 76.75, 72.33, 72.27, 25.27, 13.23. HRMS-EI calcd. for $C_{13}H_{16}O_2$ M^+ 204.1150, found: 204.1148.



2pr

Following the general procedure, **2pr** was obtained as slightly yellow oil (180 mg, 83%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 2931, 2863, 1701,1685, 1225, 1127, 754, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.84 (m, 2H), 4.76 (d, *J* = 2.0 Hz, 2H), 4.00 (s, 1H), 2.11 – 1.68 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.04, 135.15, 133.37, 131.73, 128.61, 128.09, 127.00, 73.69, 71.19, 28.18, 25.17, 19.12. HRMS-EI calcd. for $C_{14}H_{16}O_2$ M^+ 216.1150, found: 216.1155.

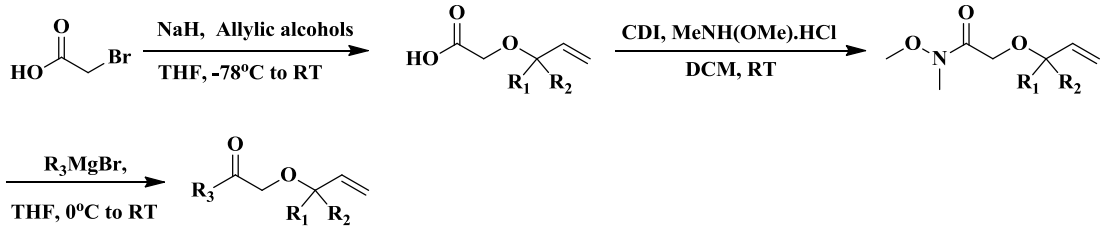


2pu

Following the general procedure, **2pu** was obtained as slightly yellow oil (160 mg, 85%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 2919, 2854, 1700, 1597, 1448, 1140, 1117, 755, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.58 (m, 1H), 7.47 (m, 2H), 4.84 (s, 2H), 4.31 (q, *J* = 2.3 Hz, 2H), 1.84 (t, *J* = 2.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.84, 134.87, 133.53, 128.69, 127.86, 83.76, 74.28, 71.59, 59.01. HRMS-EI calcd. for $C_{12}H_{12}O_2$ M^+ 188.0837, found: 188.0840.

General procedure for the synthesis of 2pd, 2pj, 2pk and 2ps:



2-(allyloxy)acetic acids are synthesized according to related literature[5].

A mixture of NaH (210 mmol, 2.1 equiv) in THF (50 ml) was cooled to –78 ℃ and a solution of bromoacetic acid (100 mmol, 1.0 equiv) in THF (50 ml) was carefully added over 30 min. The resulting gray suspension was stirred until the H_2 formation had ceased, and allylic alcohol (150 mmol, 1.5 equiv) was added and the reaction mixture was allowed to warm to room temperature overnight. The excess NaH was carefully quenched by the addition of 1N aqueous KOH solution until the white precipitate was dissolved. After addition of EA, The phases were separated, the organic layer was washed with aqueous 1N KOH and dilute aqueous HCl was

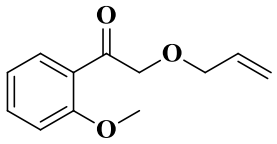
carefully added to the combined aqueous phases until pH 4. And then the aqueous layer was extracted with DCM/MeOH (V/V=10:1). The combined organic layers were washed with brine, dried and concentrated. The obtained crude products were used for the next step without further purification.

General procedure for the synthesis of Weinreb's amides:

To a stirring mixture of CDI (1.2 equiv according to acetic acid used in last step) under N_2, a solution of 2-(allyloxy)acetic acid (1.0 equiv) in DCM was carefully added over 10 min. And then N,O-Dimethylhydroxylamine hydrochloride (1.5 equiv) was added in one portion. The mixture was stirred at r.t. overnight. The reaction mixture was poured into dilute aqueous HCl and extracted with DCM/MeOH(V/V=10:1). The combined organic layers were washed with saturated Na_2CO_3 and brine successively, dried and concentrated. The obtained crude products were used for the next step without further purification.

General procedure for the synthesis of 2pd, 2pj, 2pk and 2ps:

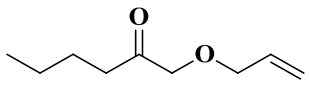
To a solution of Weinreb's amide (1.0 equiv) in THF under N_2 cooled to 0^oC, a solution of R_3MgBr (1.5 equiv according to acetic acid used in the first step) is added dropwise and and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was poured into dilute aqueous HCl and extracted with EA. The combined organic layers were washed with saturated $NaHCO_3$ and brine successively, dried and concentrated, and then purified by flash chromatography to afford the target products.



2pd

Following the general procedure, **2pu** was obtained as slightly yellow oil (80% for three steps).

R*f* = 0.5 (PE/EA=8:1, V/V); IR (film): 1691, 1601, 1261, 1235, 1173, 1133, 754, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.00 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.95 (ddt, *J* = 22.0, 10.4, 5.8 Hz, 1H), 5.29 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.19 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.67 (s, 2H), 4.11 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.72, 159.10, 134.45, 134.23, 130.67, 120.90, 117.55, 111.45, 76.45, 72.32, 55.49. HRMS-EI calcd. for $C_{12}H_{14}O_3$ M^+ 206.0943, found: 206.0941.

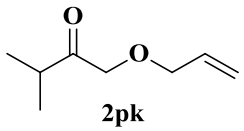


2pj

Following the general procedure, **2pu** was obtained as slightly yellow oil (85% for three steps).

R*f* = 0.5 (PE/EA = 15:1, V/V); IR (film): 2957, 2931, 2872, 1719 cm^{-1}; ^1H NMR (500

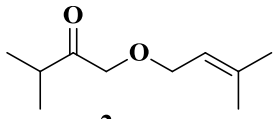
MHz, $CDCl_3$) δ 5.91 (ddt, *J* = 17.1, 10.4, 5.7 Hz, 1H), 5.29 (ddd, *J* = 17.3, 3.1, 1.6 Hz, 1H), 5.22 (ddd, *J* = 10.4, 2.7, 1.2 Hz, 1H), 4.04 (m, 4H), 2.45 (t, *J* = 7.5 Hz, 2H), 1.57 (ddd, *J* = 13.4, 10.3, 7.5 Hz, 2H), 1.31 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.99, 133.86, 117.94, 74.96, 72.32, 38.66, 25.44, 22.34, 13.81. HRMS-EI calcd. for $C_9H_{16}O_2$ M^+ 156.1150, found: 156.1154.



2pk

Following the general procedure, **2pu** was obtained as slightly yellow oil (80% for three steps).

R*f* = 0.5 (PE/EA = 15:1, V/V); IR (film): 2971, 2934, 2874, 1728, 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 16.2, 10.9, 5.3 Hz, 1H), 5.24 (m, 2H), 4.09 (d, *J* = 10.8 Hz, 2H), 4.02 (d, *J* = 5.7 Hz, 2H), 2.74 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.07 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.95, 133.90, 117.92, 73.37, 72.29, 37.02, 17.96. HRMS-EI calcd. for $C_8H_{14}O_2$ M^+ 142.0994, found: 142.1000.



2ps

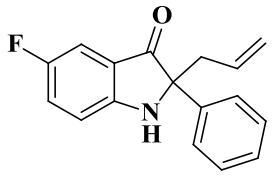
Following the general procedure, **2ps** was obtained as slightly yellow oil (85% for three steps).

R*f* = 0.5 (PE/EA = 15:1, V/V); IR (film): 2971, 2927, 2874, 1728, 1716 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.35 (dddd, *J* = 7.0, 5.7, 2.8, 1.4 Hz, 1H), 4.10 (s, 2H), 4.03 (d, *J* = 7.1 Hz, 2H), 2.77 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.71 (d, *J* = 36.8 Hz, 6H), 1.09 (dd, *J* = 7.0, 1.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.37, 138.12, 120.28, 73.18, 67.60, 36.94, 25.77, 18.01, 17.99. HRMS-EI calcd. for $C_{10}H_{18}O_2$ M^+ 170.1307, found: 170.1311.

General procedure for the synthesis of 2,2-Disubstituted Indoline-3-ones:

2,2-Disubstituted Indoline-3-ones are synthesized according to related literature[6] after optimization.

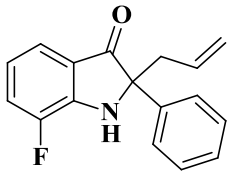
A mixture of substrate **2** (0.1 mmol, 1.0 equiv), phenylhydrazine hydrochloride (0.105 mmol, 1.05 equiv), 180 mg L-(+)-tartaric acid and 420 mg DMU mixture was stirred at 70 ^oC for 4h. The reaction was monitored by TLC, and when complete consumption of the starting material was observed (Note: If the staring material was not consumed after 4h, 0.25 equiv of phenylhydrazine hydrochloride was added to consume the staring material completely). After completion of the reaction, the reaction mixture was quenched by adding water while still hot. The reaction mixture was cooled to room temperature and extracted with DCM. The combined organic layers were dried and concentrated, and then purified by prepared-TLC to afford the target products.



3a

Following the general procedure, **3a** was obtained as golden yellow viscous oil (24 mg, 91%).

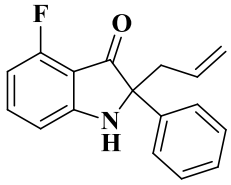
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3345, 1690, 1629, 1502, 1340, 1028, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.36 (m, 2H), 7.26 (m, 3H), 6.94 (m, 1H), 5.58 (dddd, *J* = 16.9, 10.1, 8.4, 6.0 Hz, 1H), 5.18 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.09 (m, 1H), 4.98 (s, 1H), 3.04 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.66 (dd, *J* = 14.0, 8.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.14 (d, *J* = 3.5 Hz), 157.56 (s), 157.06 (s), 155.66 (s), 138.33 (s), 132.28 (s), 128.71 (d, *J* = 7.8 Hz), 127.82 (d, *J* = 12.0 Hz), 125.85 (s), 125.50 (d, *J* = 25.6 Hz) , 119.91 (d, *J* = 10.2 Hz), 113.51 (d, *J* = 7.6 Hz), ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.14 (d, *J* = 3.5 Hz), 157.56 (s), 157.06 (s), 155.66 (s), 138.33 (s), 132.28 (s), 128.71 (d, *J* = 7.8 Hz), 127.82 (d, *J* = 12.0 Hz), 125.85 (s), 125.50 (d, *J* = 25.6 Hz), 125.85, 125.60, 125.40, 119.91 (d, *J* = 10.2 Hz), 113.51 (d, *J* = 7.6 Hz), 110.07 (s), 109.97 (d, *J* = 22.5 Hz), 71.95 (s), 42.95 (s). ^{19}F NMR (376 MHz, $cdcl_3$) δ -124.54 (ddd, *J* = 7.9, 6.5, 3.8 Hz). HRMS-EI calcd. for $C_{17}H_{14}FNO$ M^+ 267.1059, found: 267.1056.



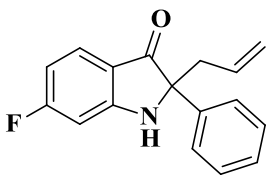
3b

Following the general procedure, **3b** was obtained as golden yellow viscous oil (22 mg, 82%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3337, 1692, 1633, 1508, 1232, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.38 (m, 3H), 7.30 (ddd, *J* = 7.3, 3.7, 1.0 Hz, 1H), 7.25 (m, 1H), 6.79 (td, *J* = 7.8, 4.1 Hz, 1H), 5.59 (dddd, *J* = 16.9, 10.1, 8.4, 6.0 Hz, 1H), 5.16 (ddd, *J* = 19.9, 13.9, 5.6 Hz, 3H), 3.07 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.67 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.22 (d, *J* = 3.5 Hz), 150.71 (s), 148.76 (s), 148.27 (d, *J* = 14.4 Hz), 137.97 (s), 132.04 (s), 128.70 (s), 127.84 (s), 125.78 (s), 122.72 (d, *J* = 4.3 Hz), 121.96 (d, *J* = 16.1 Hz), 120.79 (d, *J* = 4.0 Hz), 120.17 (s), 119.24 (d, *J* = 4.8 Hz), 71.36 (s), 42.99 (s). ^{19}F NMR (376 MHz, $cdcl_3$) δ -136.43 (dd, *J* = 10.5, 4.1 Hz). HRMS-EI calcd. for $C_{17}H_{14}FNO$ M^+ 267.1059, found: 267.1061.



3c-1

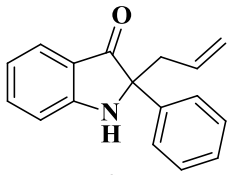


3c-2

Following the general procedure, **3c** was obtained as separable **3c-1** and **3c-2** (1:1) in 85% of total yield (23 mg).

3c-1: IR (film): 3349, 1689, 1627, 1465, 1316, 1151, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.22 (m, 7H), 6.54 (m, 2H), 5.50 (m, 1H), 5.17 (m, 3H), 3.02 (dd, *J* = 14.0, 5.9 Hz, 1H), 2.63 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.04 (s), 170.55 (s), 161.49 (s), 138.16 (s), 132.27 (s), 128.69 (s), 127.72 (d, *J* = 14.0 Hz), 125.71 (s), 119.96 (s), 115.98 (s), 108.05 (s), 107.85 (s), 98.63 (s), 98.42 (s), 71.47 (s), 42.71 (s). ^{19}F NMR (376 MHz, $cdcl_3$) δ -99.34 (td, *J* = 9.4, 5.8 Hz). HRMS-EI calcd. for $C_{17}H_{14}FNO$ M^+ 267.1059, found: 267.1064.

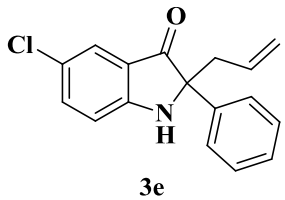
3c-2: IR (film): 3350, 1687, 1626, 1467, 1310, 1152, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 7H), 6.69 (d, *J* = 8.2 Hz, 1H), 6.39 (t, *J* = 8.6 Hz, 1H), 5.56 (ddd, *J* = 16.1, 9.2, 5.9 Hz, 1H), 5.14 (m, 3H), 3.03 (dd, *J* = 14.0, 5.8 Hz, 1H), 2.64 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.06 (s), 161.20 (s), 160.94 (d, *J* = 6.1 Hz), 158.59 (s), 138.99 (d, *J* = 10.1 Hz), 137.97 (s), 132.22 (s), 128.66 (s), 127.82 (s), 125.74 (s), 120.02 (s), 107.71 (d, *J* = 4.0 Hz), 105.13 (d, *J* = 19.0 Hz), 71.14 (s), 42.78 (s). ^{19}F NMR (376 MHz, $cdcl_3$) δ -111.72 (dd, *J* = 9.1, 5.5 Hz). HRMS-EI calcd. for $C_{17}H_{14}FNO$ M^+ 267.1059, found: 267.1062.



3d

Following the general procedure, **3d** was obtained as golden yellow viscous oil (22 mg, 89%). And its characterization data is same as reported[7].

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3356, 1685, 1618, 1488, 1468, 1323, 751, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (m, 2H), 7.57 (dd, *J* = 4.4, 3.9 Hz, 1H), 7.48 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.34 (m, 2H), 7.28 (dt, *J* = 4.1, 1.6 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.83 (m, 1H), 5.58 (dddd, *J* = 16.9, 10.1, 8.4, 5.9 Hz, 1H), 5.16 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.07 (m, 2H), 3.05 (m, 1H), 2.64 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.06, 163.99, 160.18, 138.49, 137.36, 132.57, 128.60, 127.60, 125.84, 125.42, 119.73, 119.27, 112.24, 70.66, 42.77. HRMS-EI calcd. for $C_{17}H_{15}NO$ M^+ 249.1154, found: 249.1157.

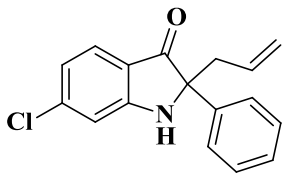


3e

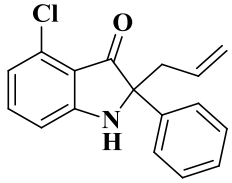
Following the general procedure, **3e** was obtained as golden yellow viscous oil (24 mg, 86%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3355, 1692, 1614, 1474, 1259, 1169, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.40 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 8.7

Hz, 1H), 5.54 (m, 1H), 5.10 (dd, *J* = 32.0, 13.5 Hz, 3H), 3.01 (dd, *J* = 14.0, 5.9 Hz, 1H), 2.63 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.94, 158.43, 138.02, 137.28, 132.20, 128.71, 127.83, 125.74, 124.65, 124.50, 120.03, 113.42, 71.58, 42.81. HRMS-EI calcd. for $C_{17}H_{14}ClNO$ M^+ 283.0764, found: 283.0759.



3f-1

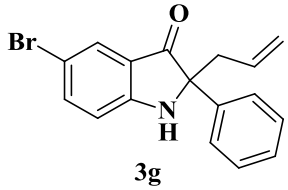


3f-2

Following the general procedure, **3f** was obtained as separable **3f-1** and **3f-2** (1:1) in 88% of total yield(25 mg).

3f-1 IR (film): 3354, 1689, 1610, 1459, 1319, 1063, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.26 (m, 2H), 6.95 (d, *J* = 1.2 Hz, 1H), 6.77 (dd, *J* = 8.2, 1.6 Hz, 1H), 5.53 (m, 1H), 5.11 (m, 3H), 3.02 (dd, *J* = 14.0, 5.8 Hz, 1H), 2.63 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.61, 160.34, 143.87, 138.02, 132.21, 128.73, 127.83, 126.43, 125.71, 120.07, 117.97, 112.08, 71.27, 42.73. HRMS-EI calcd. for $C_{17}H_{14}ClNO$ M^+ 283.0764, found: 283.0760.

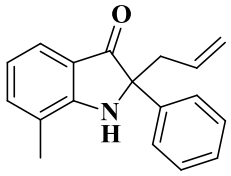
3f-2 IR (film): 3349, 1690, 1608, 1485, 1316, 1152, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 3H), 7.27 (d, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 5.54 (ddd, *J* = 16.0, 9.2, 6.0 Hz, 1H), 5.11 (dd, *J* = 31.4, 13.7 Hz, 3H), 3.04 (dd, *J* = 13.9, 5.8 Hz, 1H), 2.62 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.10, 161.26, 138.03, 137.51, 133.09, 132.32, 128.68, 127.82, 125.79, 120.23, 120.05, 115.05, 110.41, 77.28, 77.03, 76.78 , 43.03. HRMS-EI calcd. for $C_{17}H_{14}ClNO$ M^+ 283.0764, found: 283.0768.



3g

Following the general procedure, **3g** was obtained as golden yellow viscous oil (27 mg, 83%).

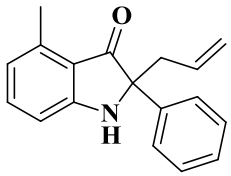
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3337, 1690, 1612, 1472, 1259, 1166, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.8 Hz, 1H), 7.53 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 5.54 (ddd, *J* = 16.1, 9.2, 6.0 Hz, 1H), 5.10 (dd, *J* = 31.7, 13.5 Hz, 3H), 3.01 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.63 (dd, *J* = 13.9, 8.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.68, 158.69, 139.85, 137.96, 132.17, 128.72, 127.84, 127.80, 125.72, 121.18, 120.05, 113.80, 111.32, 71.44, 42.77. HRMS-EI calcd. for $C_{17}H_{14}BrNO$ M^+ 327.0259, found: 327.0263.



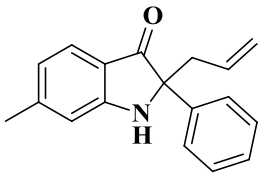
3h

Following the general procedure, **3h** was obtained as golden yellow viscous oil (23.5 mg, 83%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3355, 1686, 1609, 1500, 1327, 1240, 749, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dt, *J* = 3.1, 1.8 Hz, 2H), 7.44 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.34 (m, 3H), 7.28 (m, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 5.59 (dddd, *J* = 16.9, 10.1, 8.4, 6.0 Hz, 1H), 5.16 (dd, *J* = 17.0, 1.1 Hz, 1H), 5.07 (m, 1H), 4.86 (brs, 1H), 3.06 (m, 1H), 2.64 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.46, 163.98, 159.41, 138.61, 137.21, 132.72, 128.57, 127.59, 125.87, 122.72, 121.32, 119.65, 119.41, 119.04, 70.67, 42.89, 15.74. HRMS-EI calcd. for $C_{18}H_{17}NO$ M^+ 263.1310, found: 263.1308.



3i-1

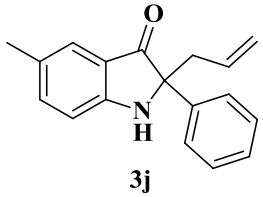


3i-2

Following the general procedure, **3f** was obtained as separable **3i-1** and **3i-2** (1:2) in 88% of total yield(23 mg).

3i-1: IR (film): 3347, 1672, 1607, 1591, 1504, 703 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.33 (m, 3H), 7.28 (dt, *J* = 4.0, 1.6 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.57 (m, 1H), 5.58 (dddd, *J* = 17.0, 10.1, 8.5, 5.9 Hz, 1H), 5.16 (ddd, *J* = 17.0, 2.8, 1.7 Hz, 1H), 5.07 (m, 1H), 5.02 (brs, 1H), 3.06 (m, 1H), 2.61 (dd, *J* = 14.0, 8.5 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.56, 160.73, 140.78, 138.83, 136.78, 132.80, 128.57, 127.52, 125.88, 120.78, 119.60, 117.46, 109.44, 70.41, 42.94, 18.19. HRMS-EI calcd. for $C_{18}H_{17}NO$ M^+ 263.1310, found: 263.1315.

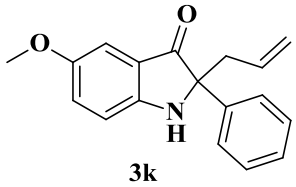
3i-2: IR (film): 3348, 1682, 1619, 1466, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dt, *J* = 3.2, 1.9 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.34 (m, 2H), 7.27 (dd, *J* = 3.9, 2.7 Hz, 1H), 6.77 (s, 1H), 6.66 (dd, *J* = 7.9, 0.5 Hz, 1H), 5.58 (dddd, *J* = 16.9, 10.1, 8.3, 6.0 Hz, 1H), 5.15 (m, 3H), 3.03 (m, 1H), 2.64 (dd, *J* = 14.0, 8.3 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, d_2o) δ 197.78, 158.13, 146.46, 136.18, 130.12, 125.99, 124.95, 123.25, 122.56, 118.50, 117.02, 114.73, 109.72, 68.29, 40.18, 19.91. HRMS-EI calcd. for $C_{18}H_{17}NO$ M^+ 263.1310, found: 263.1313.



3j

Following the general procedure, **3j** was obtained as golden yellow viscous oil (24 mg, 92%).

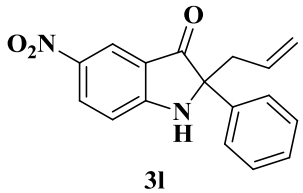
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3342, 1682, 1626, 1498, 1282, 1127, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.33 (ddd, *J* = 9.7, 7.3, 4.0 Hz, 4H), 7.27 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 5.56 (m, 1H), 5.15 (d, *J* = 17.0 Hz, 1H), 5.06 (dd, *J* = 10.1, 0.8 Hz, 1H), 4.95 (s, 1H), 3.03 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.65 (dd, *J* = 14.0, 8.3 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.28, 158.75, 138.80, 132.68, 128.86, 128.57, 127.54, 125.89, 124.70, 119.78, 119.63, 112.28, 71.03, 42.83, 20.51. HRMS-EI calcd. for $C_{18}H_{17}NO$ M^+ 263.1310, found: 263.1313.



3k

Following the general procedure, **3k** was obtained as golden yellow viscous oil (25 mg, 89%).

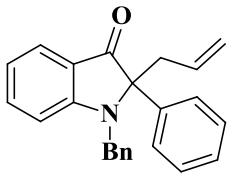
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3354, 1685, 1494, 1272, 1029, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (m, 2H), 7.35 (m, 2H), 7.28 (dt, *J* = 2.9, 1.1 Hz, 1H), 7.18 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 5.59 (dddd, *J* = 17.0, 10.1, 8.3, 6.0 Hz, 1H), 5.17 (m, 1H), 5.08 (m, 1H), 4.80 (brs, 1H), 3.77 (s, 3H), 3.04 (m, 1H), 2.67 (dd, *J* = 14.0, 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.52, 156.05, 153.68, 138.80, 132.66, 128.56, 127.95, 127.55, 125.90, 119.94, 119.66, 113.97, 105.10, 71.57, 55.77, 42.95. HRMS-EI calcd. for $C_{18}H_{17}NO_2$ M^+ 279.1259, found: 279.1263.



3l

Following the general procedure, **3l** was obtained as golden yellow viscous oil (12 mg, 42%).

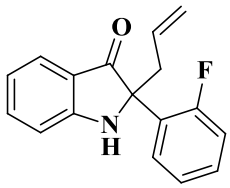
R*f* = 0.5 (PE/EA=2:1, V/V); IR (film): 3357, 1706, 1617, 1518, 1321, 1079, 745, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.3 Hz, 1H), 8.38 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.53 (m, 2H), 7.38 (m, 2H), 7.32 (ddd, *J* = 7.3, 3.7, 1.2 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 5.85 (s, 1H), 5.56 (dddd, *J* = 16.9, 10.1, 8.4, 6.0 Hz, 1H), 5.20 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.12 (dd, *J* = 10.1, 0.7 Hz, 1H), 3.07 (dd, *J* = 14.1, 6.0 Hz, 1H), 2.72 (dd, *J* = 14.1, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.66, 162.03, 140.23, 136.74, 132.73, 131.38, 128.99, 128.32, 125.44, 122.79, 120.70, 118.70, 111.10, 72.62, 42.48. HRMS-EI calcd. for $C_{17}H_{14}N_2O_3$ M^+ 294.1004, found: 294.1006.



3m

Following the general procedure, **3m** was obtained as golden yellow viscous oil (29.5 mg, 87%).

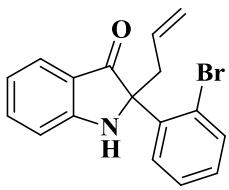
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 1702, 1611, 1484, 1468, 1320, 751, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 1H), 7.25 (m, 12H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.50 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1H), 4.99 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.90 (d, *J* = 10.2 Hz, 1H), 4.54 (d, *J* = 16.6 Hz, 1H), 4.28 (d, *J* = 16.6 Hz, 1H), 3.15 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.95 (dd, *J* = 14.2, 6.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.30, 161.74, 137.61, 137.45, 131.60, 128.96, 128.50, 128.12, 127.29, 127.26, 126.67, 125.29, 120.01, 119.56, 117.84, 109.23, 76.47, 48.31, 37.95. HRMS-EI calcd. for $C_{24}H_{21}NO$ M^+ 339.1623, found: 339.1624.



3da

Following the general procedure, **3da** was obtained as golden yellow viscous oil (22.5 mg, 85%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3355, 1691, 1618, 1468, 1323, 1219, 752 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (td, *J* = 8.0, 1.2 Hz, 2H), 7.45 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.27 (m, 1H), 7.10 (m, 2H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.80 (m, 1H), 5.64 (m, 1H), 5.43 (brs, 1H), 5.13 (ddd, *J* = 17.0, 3.1, 1.4 Hz, 1H), 5.03 (m, 1H), 3.02 (ddd, *J* = 13.9, 6.9, 1.0 Hz, 1H), 2.77 (ddd, *J* = 13.9, 7.4, 0.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.65 (s), 137.56 (s), 131.75 (s), 129.47 (d, *J* = 8.9 Hz), 127.82 (d, *J* = 3.9 Hz), 124.88 (s), 124.21 (d, *J* = 3.3 Hz), 119.55 (s), 118.87 (s), 116.53 (s), 116.34 (s), 112.01 (s), 69.44 (s), 42.47 (s). ^{19}F NMR (376 MHz, $cdcl_3$) δ -113.02 (dd, *J* = 12.1, 6.1 Hz). HRMS-EI calcd. for $C_{17}H_{14}FNO$ M^+ 267.1059, found: 267.1057.

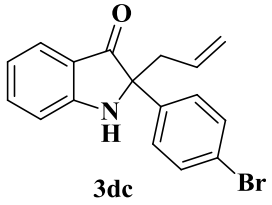


3db

Following the general procedure, **3db** was obtained as golden yellow viscous oil (27 mg, 83%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3351, 1689, 1617, 1486, 1468, 1324, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (m, 3H), 7.43 (m, 1H), 7.26 (m, 1H), 7.12 (m, 1H), 6.81 (ddd, *J* = 14.9, 8.0, 3.9 Hz, 2H), 5.59 (ddt, *J* = 17.1, 9.7, 7.1 Hz, 1H),

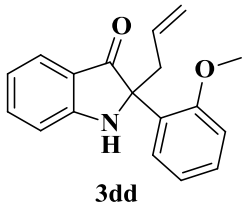
5.06 (ddd, *J* = 13.6, 11.0, 1.0 Hz, 3H), 3.25 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.86 (dd, *J* = 14.0, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.14, 159.88, 137.54, 137.32, 135.23, 131.50, 129.32, 129.29, 127.51, 124.61, 122.84, 121.03, 119.56, 118.90, 112.21, 71.66, 41.52. HRMS-EI calcd. for $C_{17}H_{14}BrNO$ M^+ 327. 0259. found: 327.0250.



3dc

Following the general procedure, **3dc** was obtained as golden yellow viscous oil (28 mg, 85%).

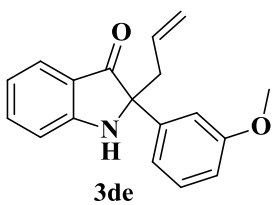
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3349, 1684, 1618, 1486, 1467, 1324, 1009, 751, 668 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.49 (m, 5H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.85 (m, 1H), 5.54 (dddd, *J* = 16.9, 10.1, 8.5, 5.9 Hz, 1H), 5.16 (dd, *J* = 17.0, 1.1 Hz, 1H), 5.10 (m, 1H), 5.01 (brs, 1H), 3.00 (m, 1H), 2.58 (dd, *J* = 14.1, 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.55, 163.99, 160.08, 137.66, 137.53, 132.14, 131.62, 127.79, 125.47, 121.83, 120.17, 119.62, 119.45, 112.46, 70.18, 42.88. HRMS-EI calcd. for $C_{17}H_{14}BrNO$ M^+ 327. 0259. found: 327.0250.



3dd

Following the general procedure, **3dd** was obtained as golden yellow viscous oil (24.5 mg, 88%).

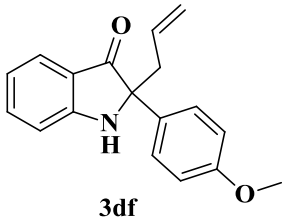
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3357, 1687, 1618, 1509, 1488, 1323, 1250, 752 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.40 (m, 1H), 7.26 (m, 1H), 6.94 (dd, *J* = 10.9, 4.3 Hz, 2H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 5.64 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.10 (dd, *J* = 17.0, 0.8 Hz, 1H), 4.97 (m, 1H), 3.88 (s, 3H), 3.04 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.80 (dd, *J* = 13.8, 7.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.03, 160.01, 157.62, 137.11, 132.52, 128.92, 127.19, 127.08, 124.51, 121.02, 120.90, 118.54, 118.15, 111.89, 111.70, 70.72, 55.47, 41.74. HRMS-EI calcd. for $C_{18}H_{17}NO_2$ M^+ 279.1259, found: 279.1261.



3de

Following the general procedure, **3de** was obtained as golden yellow viscous oil (25 mg, 90%).

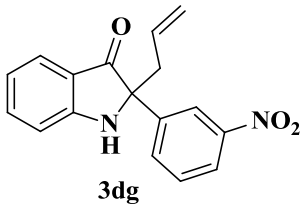
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3356, 1687, 1618, 1487, 1323, 1256, 752, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 1H), 7.47 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.25 (m, 1H), 7.19 (m, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.82 (m, 2H), 5.59 (dddd, *J* = 16.9, 10.1, 8.4, 5.9 Hz, 1H), 5.16 (dd, *J* = 17.0, 1.1 Hz, 1H), 5.06 (m, 2H), 3.80 (s, 3H), 3.04 (m, 1H), 2.61 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.89, 160.16, 159.78, 140.19, 137.36, 132.59, 129.60, 125.41, 119.73, 119.56, 119.28, 118.23, 112.68, 112.27, 112.06, 70.60, 55.26, 42.85. HRMS-EI calcd. for $C_{18}H_{17}NO_2$ M^+ 279.1259, found: 279.1255.



3df

Following the general procedure, **3df** was obtained as golden yellow viscous oil (25.5 mg, 92%).

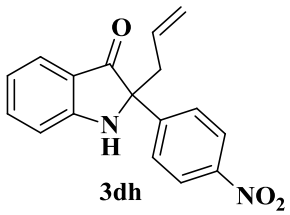
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3354, 1689, 1616, 1485, 1325, 1258, 752 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 1H), 7.51 (m, 2H), 7.47 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.87 (m, 2H), 6.82 (m, 1H), 5.59 (dddd, *J* = 17.0, 10.1, 8.4, 5.9 Hz, 1H), 5.16 (m, 1H), 5.04 (m, 2H), 3.78 (s, 3H), 3.01 (m, 1H), 2.61 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.42, 160.15, 159.10, 137.30, 132.67, 130.48, 127.02, 125.42, 119.63, 119.20, 113.99, 112.21, 70.27, 55.26, 42.62. HRMS-EI calcd. for $C_{18}H_{17}NO_2$ M^+ 279.1259, found: 279.1258.



3dg

Following the general procedure, **3dg** was obtained as golden yellow viscous oil (25.5 mg, 87%).

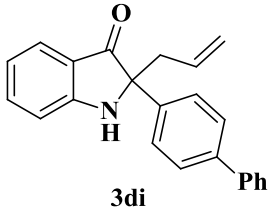
R*f* = 0.5 (PE/EA=2:1, V/V); IR (film): 3374, 1693, 1617, 1527, 1348, 1325, 753 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (t, *J* = 2.0 Hz, 1H), 8.14 (ddd, *J* = 8.1, 2.2, 0.9 Hz, 1H), 8.09 (ddd, *J* = 7.9, 1.7, 1.0 Hz, 1H), 7.55 (m, 3H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.90 (m, 1H), 5.50 (m, 1H), 5.16 (m, 3H), 3.05 (m, 1H), 2.65 (dd, *J* = 14.1, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.94, 160.15, 148.40, 141.13, 137.89, 132.57, 131.47, 129.59, 125.48, 122.65, 121.27, 120.85, 120.13, 119.32, 112.94, 70.01, 43.34. HRMS-EI calcd. for $C_{17}H_{14}N_2O_3$ M^+ 294.1004, found: 294.1000.



3dh

Following the general procedure, **3dh** was obtained as golden yellow viscous oil (25 mg, 86%).

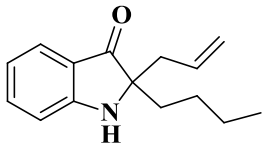
R*f* = 0.5 (PE/EA=2:1, V/V); IR (film): 3374, 1692, 1618, 1518, 1488, 1347, 1324, 854, 752 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (m, 2H), 7.86 (m, 2H), 7.59 (ddd, *J* = 7.8, 1.1, 0.7 Hz, 1H), 7.53 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.90 (m, 1H), 5.50 (dddd, *J* = 16.9, 10.1, 8.5, 5.9 Hz, 1H), 5.11 (m, 3H), 3.05 (m, 1H), 2.63 (dd, *J* = 14.1, 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.60, 160.11, 146.04, 137.88, 131.48, 127.17, 125.56, 123.64, 120.83, 120.16, 119.30, 112.81, 70.46, 43.37. HRMS-EI calcd. for $C_{17}H_{14}N_2O_3$ M^+ 294.1004, found: 294.1001.



3di

Following the general procedure, **3di** was obtained as golden yellow viscous oil (29.5 mg, 91%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3354, 1686, 1618, 1486, 1467, 1323, 754, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.57 (m, 5H), 7.50 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.43 (dd, *J* = 10.5, 4.8 Hz, 2H), 7.34 (m, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.85 (m, 1H), 5.64 (m, 1H), 5.15 (m, 3H), 3.10 (dd, *J* = 14.0, 5.9 Hz, 1H), 2.68 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.11, 160.28, 140.63, 140.54, 137.56, 137.45, 132.55, 128.76, 127.36, 127.33, 127.07, 126.34, 125.48, 119.85, 119.55, 119.34, 112.32, 70.64, 42.75. HRMS-EI calcd. for $C_{23}H_{19}NO$ M^+ 325.1467, found: 325.1470.

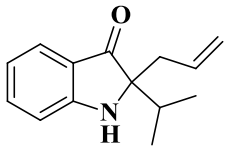


3dj

Following the general procedure, **3dj** was obtained as golden yellow viscous oil (21.5 mg, 94%).

R*f* = 0.5 (PE/EA = 12:1, V/V); IR (film): 3341, 2956, 2933, 1678, 1620, 1490, 1468, 1324, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 6.97 – 6.67 (m, 2H), 5.65 (td, *J* = 17.2, 8.1 Hz, 1H), 5.05 (dd, *J* = 23.2, 13.5 Hz, 2H), 4.57 (brs, 1H), 2.37 (p, *J* = 13.5 Hz, 2H), 1.69 (dt, *J* = 25.4, 11.8 Hz, 2H), 1.12 (m, 4H), 0.79 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.54,

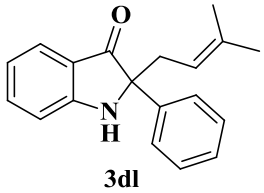
160.59, 137.14, 132.26, 124.50, 121.36, 119.19, 118.61, 112.22, 69.52, 41.79, 36.42, 25.32, 22.97, 13.91. HRMS-EI calcd. for $C_{15}H_{19}NO$ M^+ 229.1467, found: 229.1467.



3dk

Following the general procedure, **3dk** was obtained as golden yellow viscous oil (19.5 mg, 91%).

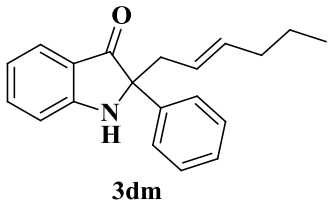
R*f* = 0.5 (PE/EA = 12:1, V/V); IR (film): 3345, 2960, 2928, 2837, 1678, 1620, 1491, 1467, 1325, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.8, 0.4 Hz, 1H), 7.42 (m, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 5.58 (ddt, *J* = 17.2, 10.1, 7.3 Hz, 1H), 5.08 (dd, *J* = 16.9, 1.7 Hz, 1H), 4.96 (m, 1H), 4.52 (brs, 1H), 2.50 (d, *J* = 7.3 Hz, 2H), 2.08 (dt, *J* = 13.6, 6.8 Hz, 1H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.89, 161.10, 136.99, 132.02, 124.16, 122.26, 118.69, 118.51, 111.99, 109.99, 72.16, 40.10, 34.13, 16.99, 16.67. HRMS-EI calcd. for $C_{14}H_{17}NO$ M^+ 215.1310, found: 215.1309.



3dl

Following the general procedure, **3dl** was obtained as golden yellow viscous oil (22.5 mg, 81%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3350, 2912, 1685, 1618, 1490, 1468, 1324, 751, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, 3H), 7.46 (m, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 5.11 (m, 2H), 2.90 (dd, *J* = 14.7, 5.6 Hz, 1H), 2.68 (dd, *J* = 14.7, 8.5 Hz, 1H), 1.61 (d, *J* = 7.6 Hz, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.49, 160.28, 138.74, 137.23, 136.58, 128.50, 127.46, 126.00, 125.42, 119.62, 119.13, 117.86, 112.10, 71.49, 36.72, 25.85, 18.20. HRMS-EI calcd. for $C_{19}H_{19}NO$ M^+ 277.1467, found: 277.1471.

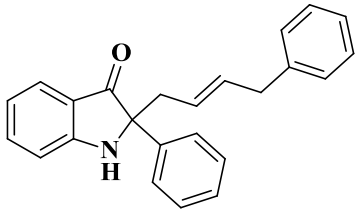


3dm

Following the general procedure, **3dm** was obtained as golden yellow viscous oil (23.5 mg, 81%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3355, 2956, 2927, 1685, 1618, 1490, 1467, 1323, 750, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (m, 2H), 7.55 (m, 1H), 7.47 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.33 (m, 2H), 7.28 (m, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.82 (m, 1H), 5.55 (dt, *J* = 14.9, 6.8 Hz, 1H), 5.18 (dddd, *J* = 9.8, 7.2, 4.6, 1.3 Hz, 1H), 5.01 (brs, 1H), 2.97 (ddd, *J* = 14.0, 5.9, 1.2 Hz, 1H), 2.58 (dd, *J* = 14.0, 8.4 Hz, 1H),

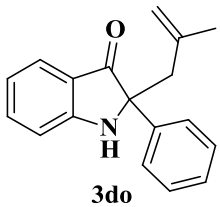
1.87 (dt, *J* = 10.5, 7.1 Hz, 2H), 1.26 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.78 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.41, 160.27, 138.78, 137.22, 136.07, 128.51, 127.47, 125.95, 125.36, 123.72, 119.20, 112.30, 70.97, 41.78, 34.50, 22.38, 13.49. HRMS-EI calcd. for $C_{20}H_{21}NO$ M^+ 291.1623, found: 291.1617.



3dn

Following the general procedure, **3dn** was obtained as golden yellow viscous oil (30 mg, 88%). And ***(S)*-3dn** was obtained as golden yellow viscous oil (30.5 mg, 89%), and the enantiomeric excess of ***(S)*-3dn** was determined to be 84% (HPLC trace in S94).

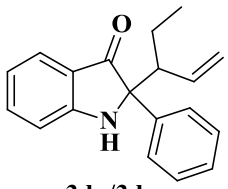
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3352, 1686,1619, 1491, 1323, 751, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.47 (m, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.22 (ddt, *J* = 29.7, 22.4, 7.3 Hz, 4H), 6.87 (m, 4H), 5.71 (dt, *J* = 14.0, 6.9 Hz, 1H), 5.30 (m, 1H), 5.09 (brs, 1H), 3.21 (d, *J* = 6.8 Hz, 2H), 2.94 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.71 (dd, *J* = 13.9, 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.43, 160.33, 140.07, 138.88, 137.34, 134.53, 128.61, 128.41, 128.39, 127.59, 126.03, 125.91, 125.33, 125.11, 119.80, 119.20, 112.30, 71.15, 41.80, 38.96. HRMS-EI calcd. for $C_{24}H_{21}NO$ M^+ 339.1623. found: 339.1624; Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AS-H column, hexane/*i*-PrOH 80:20 0.7 mL/min, t_{major} = 10.56 min, t_{minor} = 8.60 min, HPLC trace in S94).



3do

Following the general procedure, **3do** was obtained as golden yellow viscous oil (22 mg, 85%).

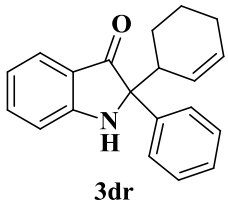
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3357, 1686, 1620, 1492, 1467, 1323, 755 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.49 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.35 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.28 (dd, *J* = 5.1, 4.2 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 5.22 (s, 1H), 4.86 (m, 1H), 4.72 (d, *J* = 0.8 Hz, 1H), 3.01 (d, *J* = 14.2 Hz, 1H), 2.70 (d, *J* = 14.2 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.36, 160.27, 141.73, 139.11, 137.32, 128.48, 127.52, 125.83, 125.54, 119.45, 119.28, 115.56, 112.34, 70.17, 45.96, 23.85. HRMS-EI calcd. for $C_{18}H_{17}NO$ M^+ 263.1310, found: 263.1308.



3dp/3dq

Following the general procedure, **3dp** was obtained as golden yellow viscous oil (25.5 mg, 93%, dr = 1:10). And **3dq** was obtained as inseparable golden yellow viscous oil (25 mg, 92%, dr = 1.5:1).

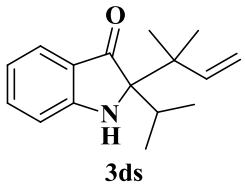
3dp: R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3361, 1680, 1619, 1491, 1468, 1325, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.51 (m, 1H), 7.45 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.35 (m, 2H), 7.27 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 5.45 (dddd, *J* = 17.1, 10.0, 9.1, 0.9 Hz, 1H), 5.20 (m, 2H), 5.04 (dd, *J* = 10.2, 1.9 Hz, 1H), 2.93 (ddd, *J* = 11.4, 9.2, 2.4 Hz, 1H), 1.46 (m, 1H), 1.18 (m, 1H), 0.83 (t, *J* = 7.4 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.12, 160.38, 138.21, 137.10, 135.61, 128.61, 127.50, 125.81, 125.21, 120.25, 119.34, 118.92, 111.55, 74.77, 52.95, 21.84, 12.07. HRMS-EI calcd. for $C_{19}H_{19}NO$ M^+ 277.1467, found: 277.1465.



3dr

Following the general procedure, **3dr** was obtained as golden yellow viscous oil (25.5 mg, 89%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3366, 1676, 1620, 1492, 1467, 1325, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.44 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.21 (s, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.79 (t, *J* = 7.1 Hz, 1H), 5.69 (d, *J* = 7.7 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 4.98 (s, 1H), 3.33 (d, *J* = 8.3 Hz, 1H), 1.96 (m, 2H), 1.72 (d, *J* = 12.5 Hz, 1H), 1.49 (m, 2H), 1.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.35, 160.94, 138.30, 137.18, 130.81, 128.49, 127.41, 125.92, 125.79, 124.91, 120.86, 119.09, 112.27, 76.67, 74.10, 44.59, 25.06, 24.92, 22.25. HRMS-EI calcd. for $C_{20}H_{19}NO$ M^+ 289.1467, found: 289.1466.

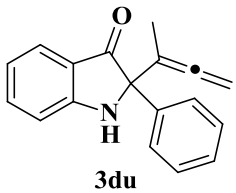


3ds

Following the general procedure, **3ds** was obtained as golden yellow viscous oil (10 mg, 41%).

R*f* = 0.5 (PE/EA = 12:1, V/V); IR (film): 3344, 2966, 1677, 1618, 1490, 1468, 1322, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.6 Hz,

1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.17 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.05 (m, 2H), 4.72 (brs, 1H), 2.41 (dt, *J* = 13.1, 6.6 Hz, 1H), 1.26 (s, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 3H), 0.61 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.52, 161.53, 145.91, 136.74, 124.01, 122.80, 118.05, 112.91, 111.07, 74.93, 43.27, 32.74, 23.89, 21.81, 19.80, 18.75. HRMS-EI calcd. for $C_{16}H_{21}NO$ M^+ 243.1623, found: 243.1625.



3du

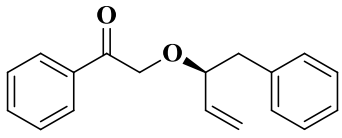
Following the general procedure, **3du** was obtained as golden yellow viscous oil (25 mg, 87%).

R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3349, 1960, 1687, 1616, 1488, 1468, 1323, 749, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (ddd, *J* = 7.8, 1.3, 0.7 Hz, 1H), 7.54 (m, 2H), 7.46 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.34 (m, 2H), 7.29 (ddd, *J* = 7.2, 3.8, 1.3 Hz, 1H), 6.91 (dt, *J* = 8.3, 0.7 Hz, 1H), 6.84 (td, *J* = 7.5, 0.7 Hz, 1H), 5.15 (brs, 1H), 4.81 (qd, *J* = 3.0, 2.1 Hz, 2H), 1.74 (dd, *J* = 3.8, 2.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.36, 198.97, 159.91, 138.14, 137.30, 128.47, 127.85, 126.92, 125.35, 120.08, 119.37, 112.29, 100.30, 78.08, 72.59, 14.88. HRMS-EI calcd. for $C_{18}H_{15}NO$ M^+ 261.1154, found: 261.1157.

Gram scale synthesis of 3dd

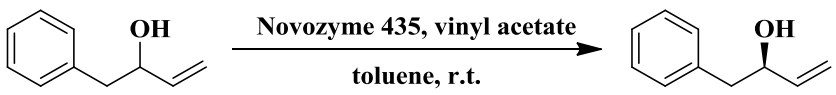
A mixture of substrate **2pd** (8 mmol, 1.0 equiv), phenylhydrazine hydrochloride (8.4 mmol, 1.05 equiv), 720 mg L-(+)-tartaric acid and 1.6 g DMU mixture was stirred at 70 ^{o}C for 4h. TLC (PE:DCM = 5:4, V/V) showed no starting material remained. The reaction mixture was quenched by adding water while still hot. The reaction mixture was cooled to room temperature and extracted with DCM. The combined organic layers were dried and concentrated, and then purified by flash chromatography (PE:DCM = 10:1) to afford **3dd** (1.78 g, 80%).

Chirality Transfer Using Enantiopure Substrate



***(R)*-2pn**

The starting material for **R-2pn** was not commercially available and it was synthesized according to related literature[9].

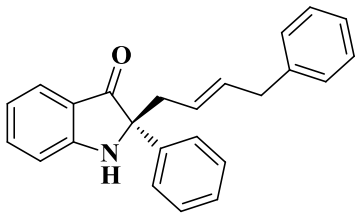


2sn ***(R)*-2sn**

To a solution of **2sn** (5.92 g, 40 mmol) in toluene (40 mL) were added vinyl acetate

(3.44 g, 40 mmol) and Novozyme 435 (800 mg). The reaction mixture was stirred at room temperature for about 60h until HPLC showed the high ee value, and then the reaction mixture was filtered through silic gel. The filtrate was concentrated, and then purified by flash chromatography (PE:EA = 20:1) to afford the target product (2.66 g, 45%). $[\alpha]^{D}_{23.6}$ = 0.16 (*c* 2.00, $CHCl_3$); Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AD-H column, hexane/*i*-PrOH 95:5 0.7 mL/min, t_{major} = 10.42 min, t_{minor} = 11.74 min, HPLC trace in S99).

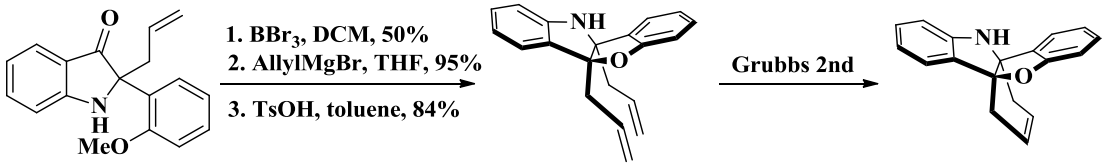
Following the general procedure ***(R)*-2pn** was obtained as slightly yellow oil (130 mg, 49%).
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 1702,1682, 1448, 1225, 1126, 753, 690, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.21 (m, 6H), 5.72 (ddd, *J* = 17.3, 10.3, 8.0 Hz, 1H), 5.16 (m, 2H), 4.73 (d, *J* = 16.4 Hz, 1H), 4.58 (d, *J* = 16.4 Hz, 1H), 4.04 (dd, *J* = 14.4, 6.7 Hz, 1H), 3.09 (dd, *J* = 13.7, 6.6 Hz, 1H), 2.86 (dd, *J* = 13.7, 6.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.49, 137.78, 137.25, 135.04, 133.32, 129.68, 128.56, 128.14, 128.07, 126.25, 118.67, 83.13, 71.42, 42.09. HRMS-EI calcd. for $C_{18}H_{18}O$ M^+ 266. 1307. found: 266.1310; $[\alpha]^{D}_{23.6}$ = 65.9 (*c* 1.80, $CHCl_3$); Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AS-H column, hexane/*i*-PrOH 80:20 0.7 mL/min, t_{major} = 6.92 min, t_{minor} = 7.58 min, HPLC trace in S101).



***(S)*-3dn**

Following the general procedure ***(S)*-3dn** was obtained as golden yellow viscous oil (30.5 mg, 89%).
R*f* = 0.5 (PE/EA = 10:1, V/V); IR (film): 3352, 1686,1619, 1491, 1323, 751, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.47 (m, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.22 (ddt, *J* = 29.7, 22.4, 7.3 Hz, 4H), 6.87 (m, 4H), 5.71 (dt, *J* = 14.0, 6.9 Hz, 1H), 5.30 (m, 1H), 5.09 (s, 1H), 3.21 (d, *J* = 6.8 Hz, 2H), 2.94 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.71 (dd, *J* = 13.9, 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.43, 160.33, 140.07, 138.88, 137.34, 134.53, 128.61, 128.41, 128.39, 127.59, 126.03, 125.91, 125.33, 125.11, 119.80, 119.20, 112.30, 71.15, 41.80, 38.96. HRMS-EI calcd. for $C_{24}H_{21}NO$ M^+ 339.1623. found: 339.1624; $[\alpha]^{D}_{23.8}$ = 232.4 (*c* 0.20, $CHCl_3$); Enantiomeric excess was found to be 84% by chiral HPLC (ChiralPak AS-H column, hexane/*i*-PrOH 80:20 0.7 mL/min, t_{major} = 10.56 min, t_{minor} = 8.60 min, HPLC trace in S103).

Synthesis of Core Structure of Phalarine

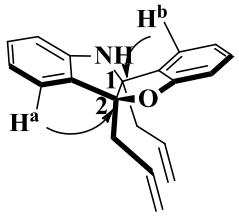


3dd **4** **5**

To a solution of **3dd** (2 mmol, 1.0 equiv) in 30ml dry DCM under N_2 at 0°C, a solution BBr_3 (10 mmol, 5.0 equiv) in 5ml DCM was added dropwise in 10 min. The reaction was warmed to room temperature in 2h, and the reaction mixture was poured into ice-water and extracted with DCM. The combined organic layers were washed with saturated $NaHCO_3$ and brine successively, dried and concentrated, and then purified by fast chromatography to afford the target product(Note: The target product is unstable in d-chloroform and d-acetone, and even in -40°C for 48h. Thus, it is advisable that using the product for the next step as soon as possible).

To a solution of the product from last step (1 mmol, 1.0 equiv) in 10ml dry THF under N_2 at 0°C, a solution of allyl MgBr (3 mmol, 3.0 equiv) is added dropwise and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was poured into aqueous NH_4Cl and extracted with EA. The combined organic layers were washed with brine, dried and concentrated. The obtained crude product was used for the next step without further purification. (Note: The target product is unstable in d-chloroform and d-acetone. Thus, it is advisable that using the product for the next step as soon as possible).

To a solution of the product from last step (0.4 mmol, 1.0 equiv) in 5ml dry toluene under N_2, TsOH (0.1 mmol, 25%) was added in one portion and the reaction mixture was stirred at room temperature for 48h, at which time TLC (PE:EA=8:1) showed no starting material remained. The reaction mixture was purified by prepared-TLC to afford **4** (41% from **3dd**). (Note: The target product is unstable in d-chloroform). The HMBC experiment exhibited a three bond correlation of the quaternary carbon C1 to the proton H^b and a three bond correlation of C2 to the proton H^a, indicating that the five-membered ring had been closed.



R*f* = 0.5 (PE/EA = 8:1, V/V); IR (film): 3368, 3075, 2978, 2925, 1618,1484, 1475, 1467, 1235, 1019, 917, 747 cm^{-1}; ^1H NMR (400 MHz, d-Acetone) δ 7.35 (m, 1H), 7.29 (m, 1H), 7.10 (ddd, *J* = 8.0, 7.5, 1.4 Hz, 1H), 7.03 (ddd, *J* = 8.7, 7.7, 1.3 Hz, 1H), 6.83 (td, *J* = 7.5, 0.9 Hz, 1H), 6.73 (m, 1H), 6.64 (td, *J* = 7.4, 0.9 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 5.93 (m, 2H), 5.83 (s, 1H), 5.14 (m, 4H), 3.00 (ddt, *J* = 14.7, 5.9, 1.7 Hz, 1H), 2.87 (m, 3H), 2.76 (m, 1H). ^{13}C NMR (101 MHz, d-Acetone) δ 158.51, 150.33,

133.64, 133.25, 132.98,129.67, 129.57, 128.98, 125.07, 124.39, 120.35, 118.00, 117.91, 117.74, 109.67, 97.39, 74.77, 39.91, 38.61. HRMS-EI calcd. for $C_{20}H_{19}NO$ M^+ 289.1467, found: 289.1469.

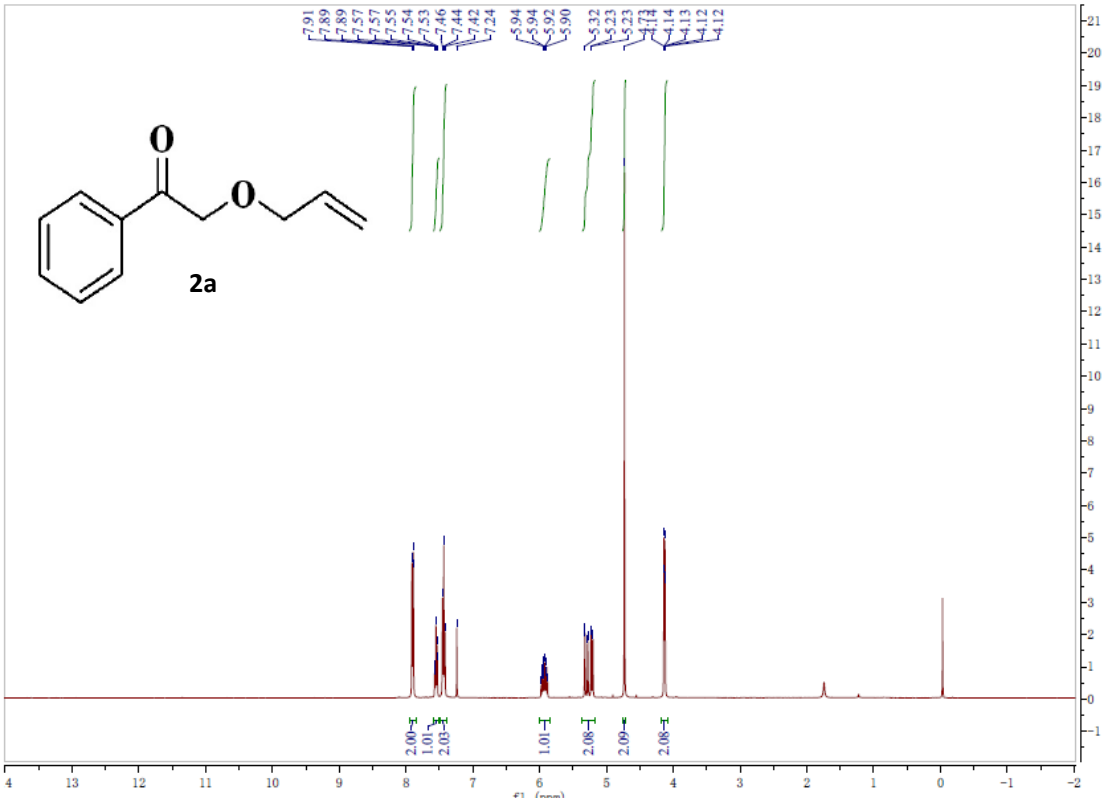
A solution of **4** (0.2 mmol, 1.0 equiv) in 10 ml toluene was added to Grubb's 2nd (10%) under N_2, and the reaction mixture was stirred at 110^{o}C overnight. TLC (PE:EA=8:1) showed no starting material remained. The reaction mixture was purified by prepared-TLC to afford **5** as a white solid (45 mg, 87%).

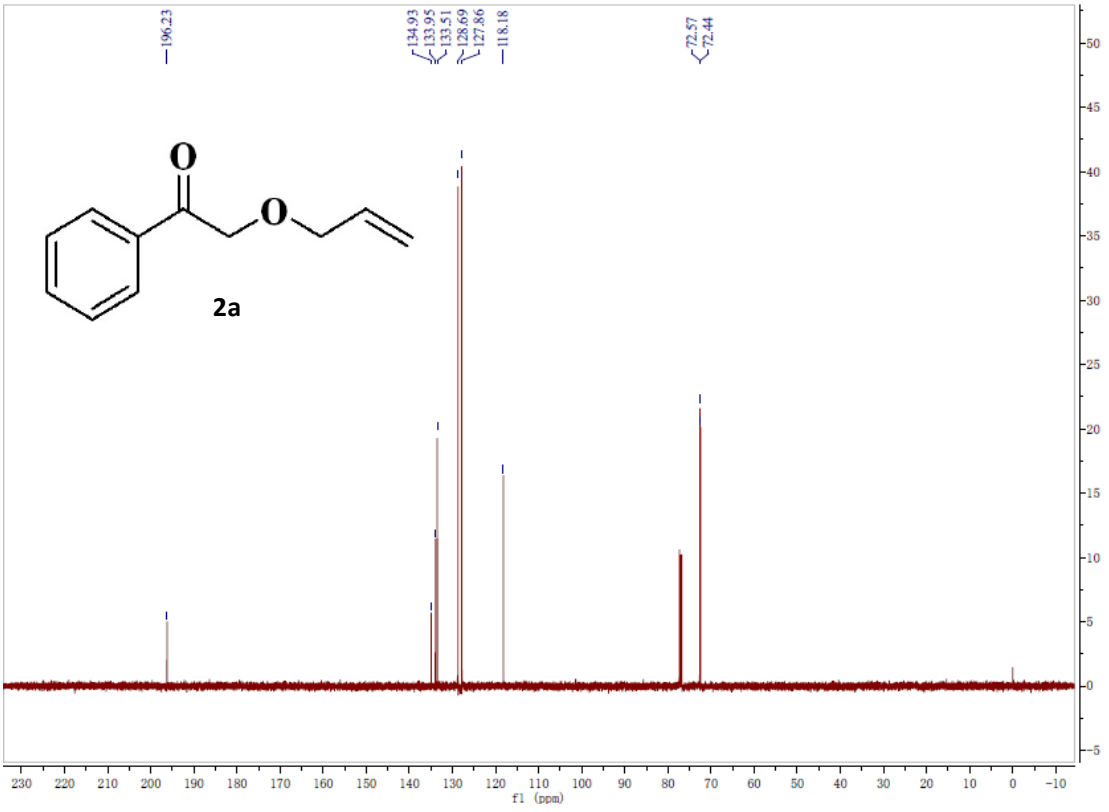
R*f* = 0.5 (PE/EA = 7:1, V/V); IR (film): 3365, 2954, 2924, 2852, 1610, 1484, 1465, 745 cm^{-1}; ^{1}H NMR (500 MHz, d-Acetone) δ 7.38 – 7.33 (m, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.05 (dddd, *J* = 9.1, 8.5, 7.7, 1.3 Hz, 2H), 6.84 (td, *J* = 7.4, 0.9 Hz, 1H), 6.66 (ddd, *J* = 7.1, 6.0, 0.6 Hz, 2H), 6.51 (d, *J* = 7.9 Hz, 1H), 5.91 – 5.82 (m, 2H), 5.77 (s, 1H), 2.95 (dd, *J* = 15.1, 4.9 Hz, 1H), 2.78 – 2.68 (m, 3H). ^{13}C NMR (126 MHz, d-Acetone) δ 160.91, 152.42, 134.39, 131.01, 130.63, 129.63, 128.39, 127.44, 125.08, 124.56, 121.31, 118.79, 110.49, 110.30, 99.61, 75.12, 35.81, 33.87. HRMS-EI calcd. for $C_{18}H_{15}NO$ M^+ 261.1154, found: 261.1151.

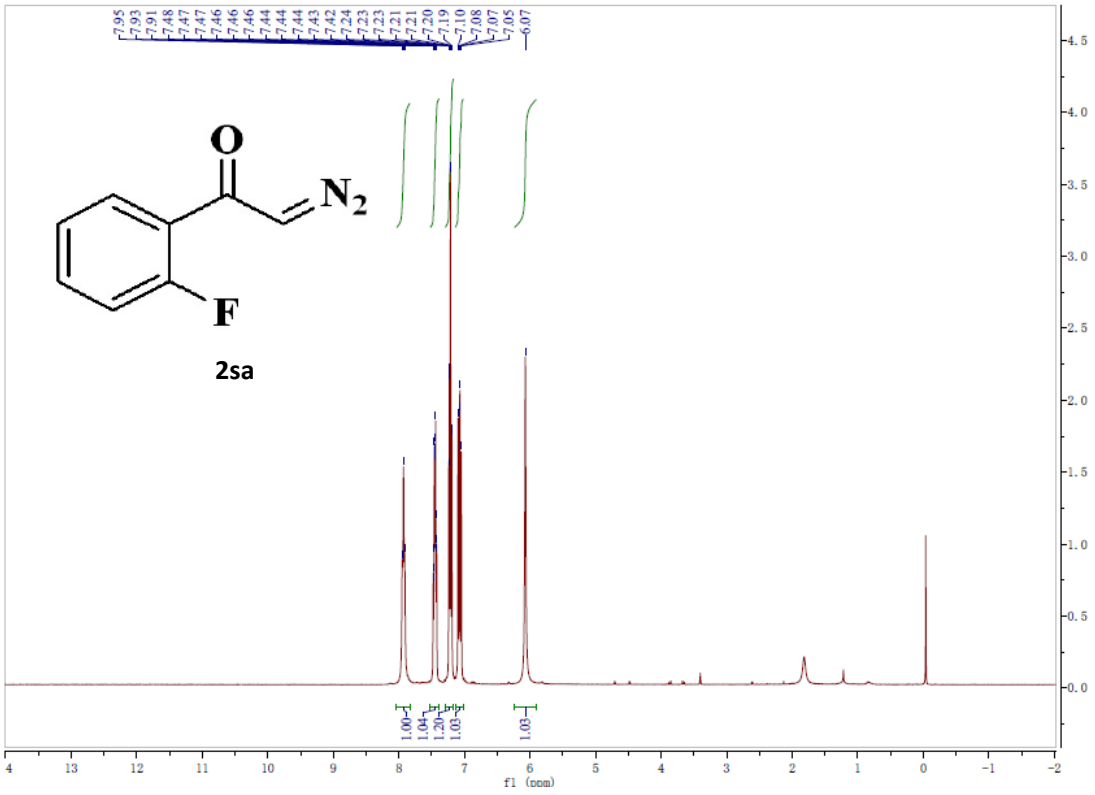
2. References

[1] Gary A. Molander, Jeffrey A. McKie, *J. Org. Chem.* **1995**, *60*, 872-882.
[2] Eiji Ideue, Tatsuya Toma, Jun Shimokawa, Tohru Fukuyama, *Org. Synth.* **2012**, *89*, 501-509.
[3] Yveline Rival, Gerard Grassy, Georges Michel, *Chem. Pharm. Bull.* **1992**, *40(5)*, 1170-1176.
[4] Juan R. Sosa, Armen A. Tudjarian, Thomas G. Minehan, *Org. Lett*. **2008**, *10*, 5091-5094.
[5] Julia Rehbein, Sabine Leick, Martin Hiersemann, *J. Org. Chem.* **2009**, *74*, 1531-1540.
[6] Sangram Gore, Sundarababu Baskaran, Burkhard Konig, *Org. Lett*. **2012**, *10*, 4568-4571.
[7] Yahua Liu, William W. McWhorter, Jr, *J. Org. Chem.* **2003**, *68*, 2618-2622.
[8] Anthony E. Rosamilia, Fabio Arico, Pietro Tundo, *J. Org. Chem.* **2008**, *73*, 1559-1562.
[9] Om V. Singh, Hyunsoo Han, *Org. Lett*. **2007**, *9*, 4801-4804.

3. Copies of NMR spectra of synthesized compounds



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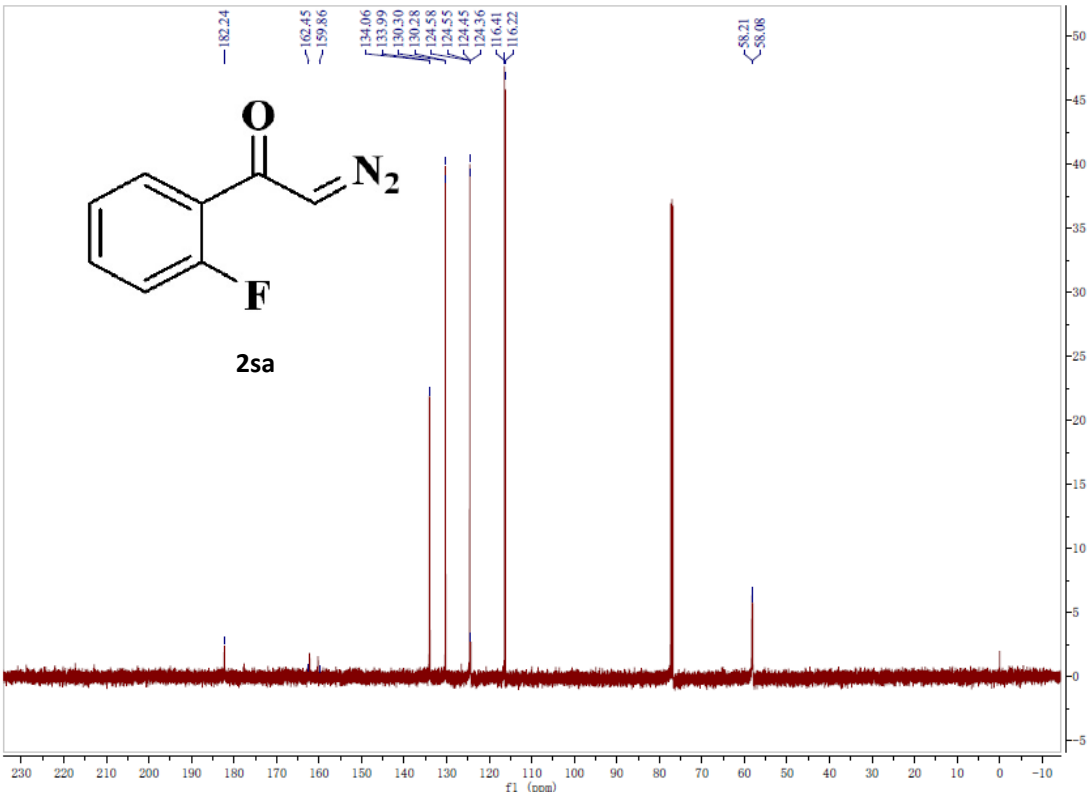
N2
F
2sa
f1 (ppm)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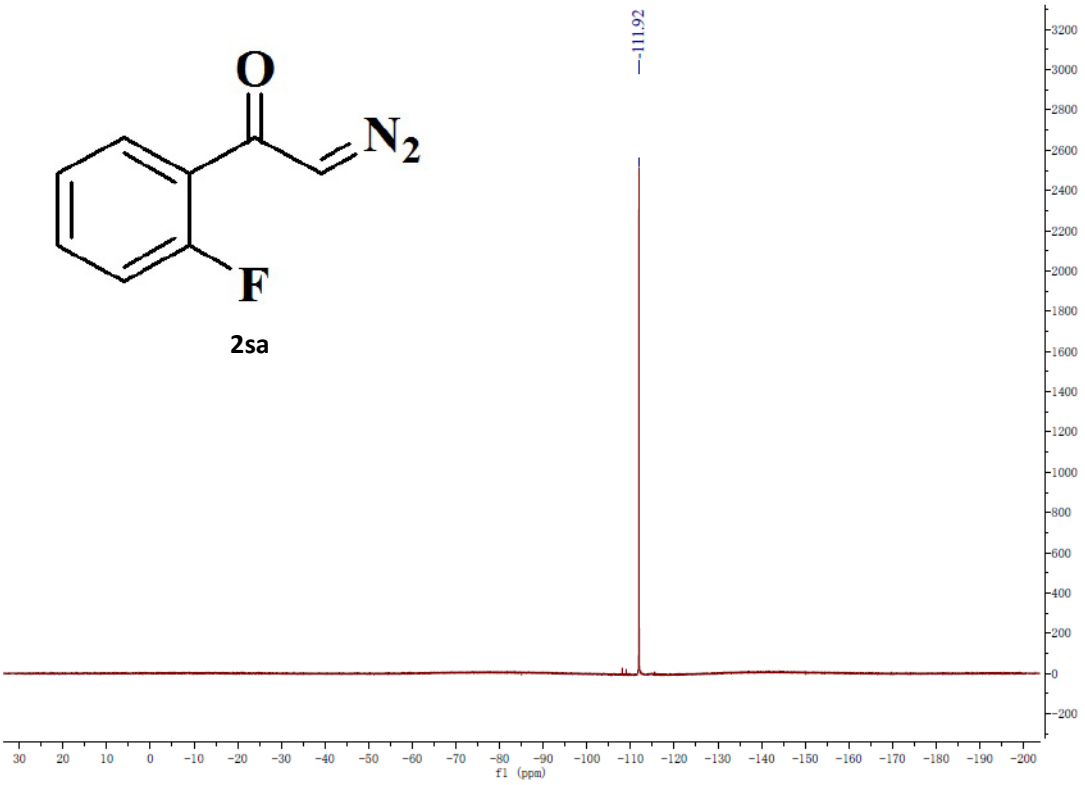
O
N2
F
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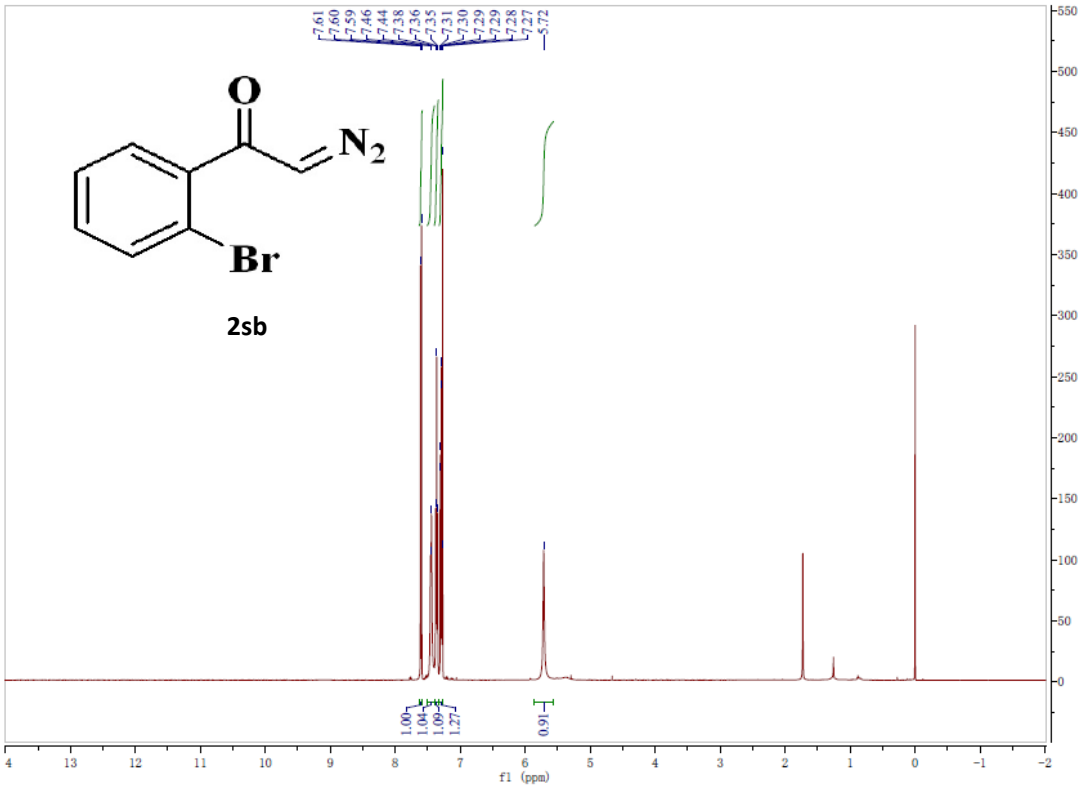
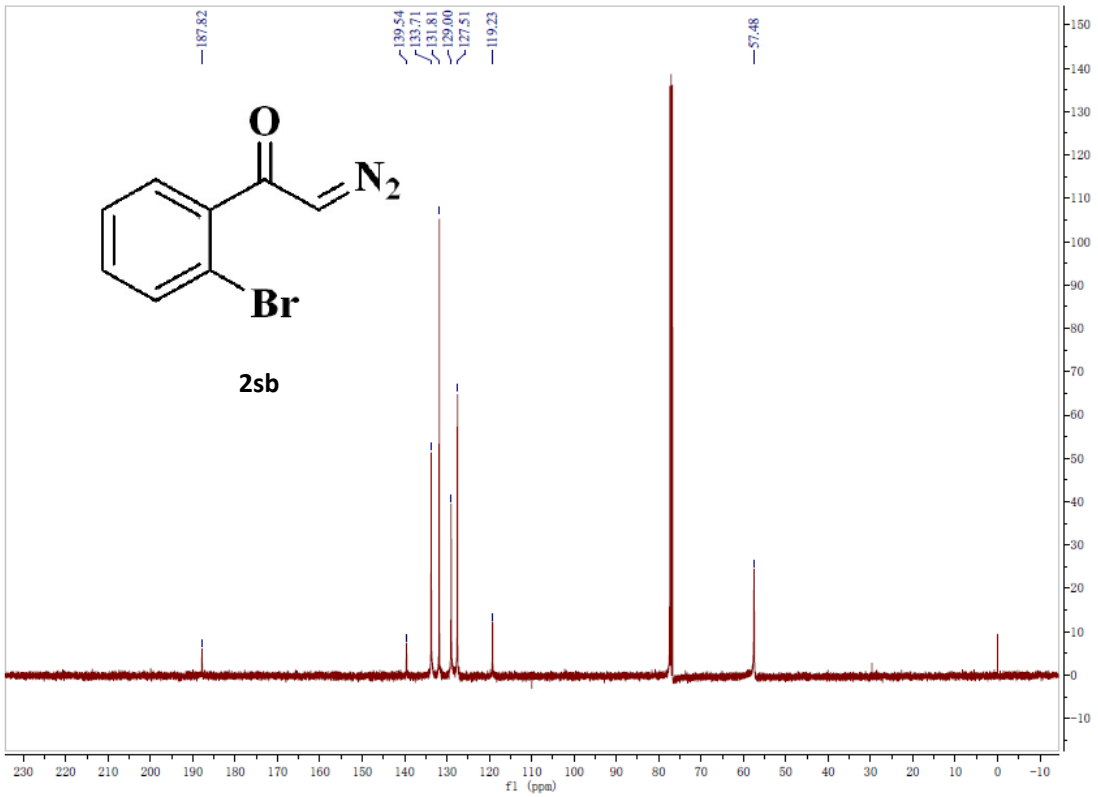
f1 (ppm)

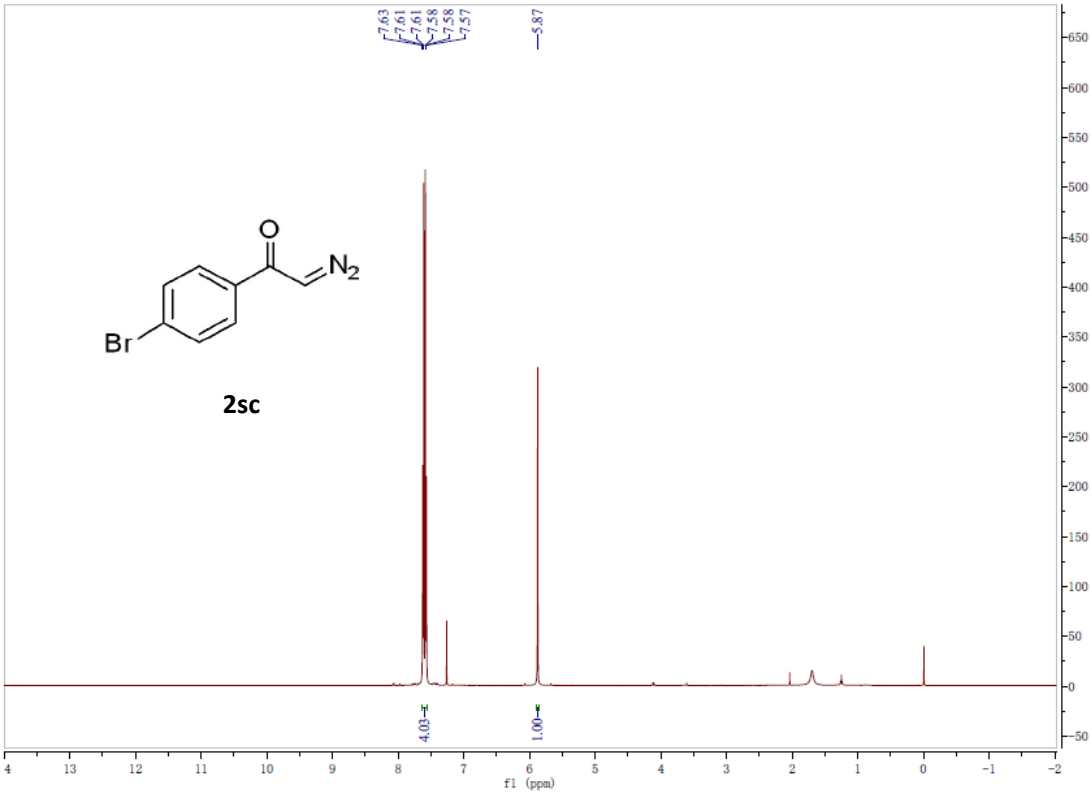
2sa


7.61
7.60
7.59
7.46
7.44
7.38
7.36
7.35
7.31
7.30
7.29
7.29
7.28
7.27
5.72
O
N2
Br
1.00
1.04
1.09
1.27
0.91
f1 (ppm)

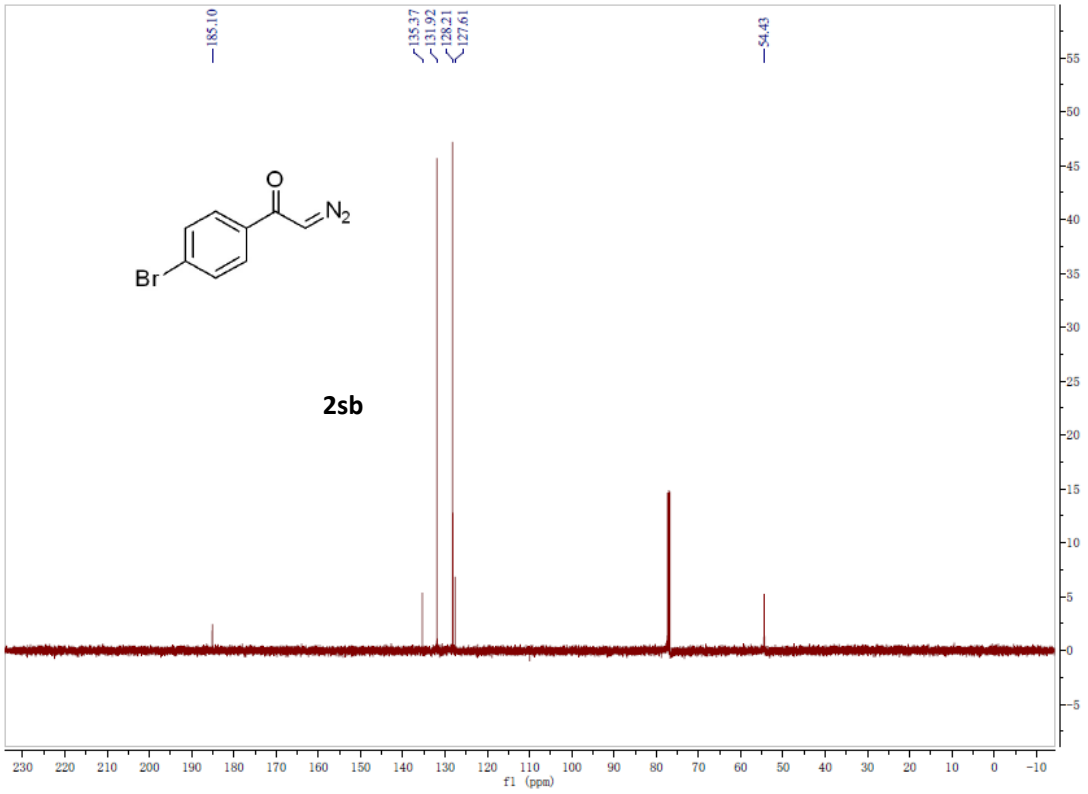
2sb

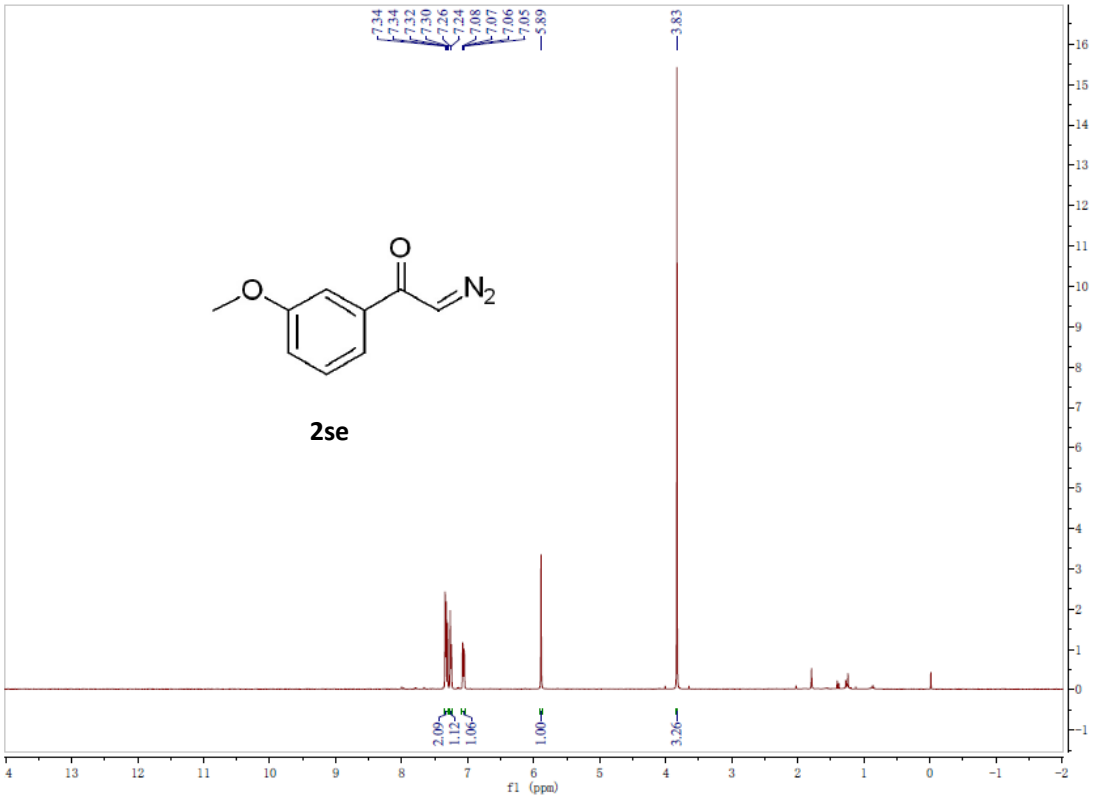

187.82
139.54
133.71
131.81
129.00
127.51
119.23
57.48
O
N2
Br
f1 (ppm)

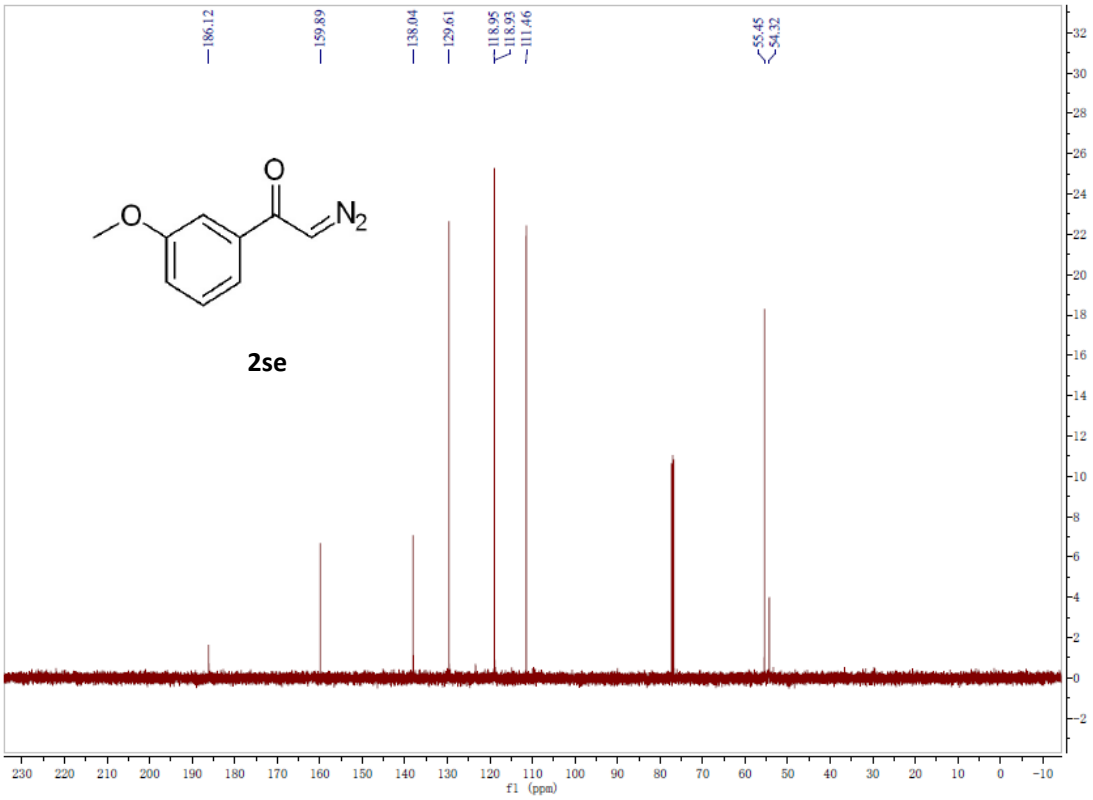
2sb


7.63
7.61
7.61
7.58
7.58
7.57
5.87
4.03
1.00
O
N2
Br
f1 (ppm)

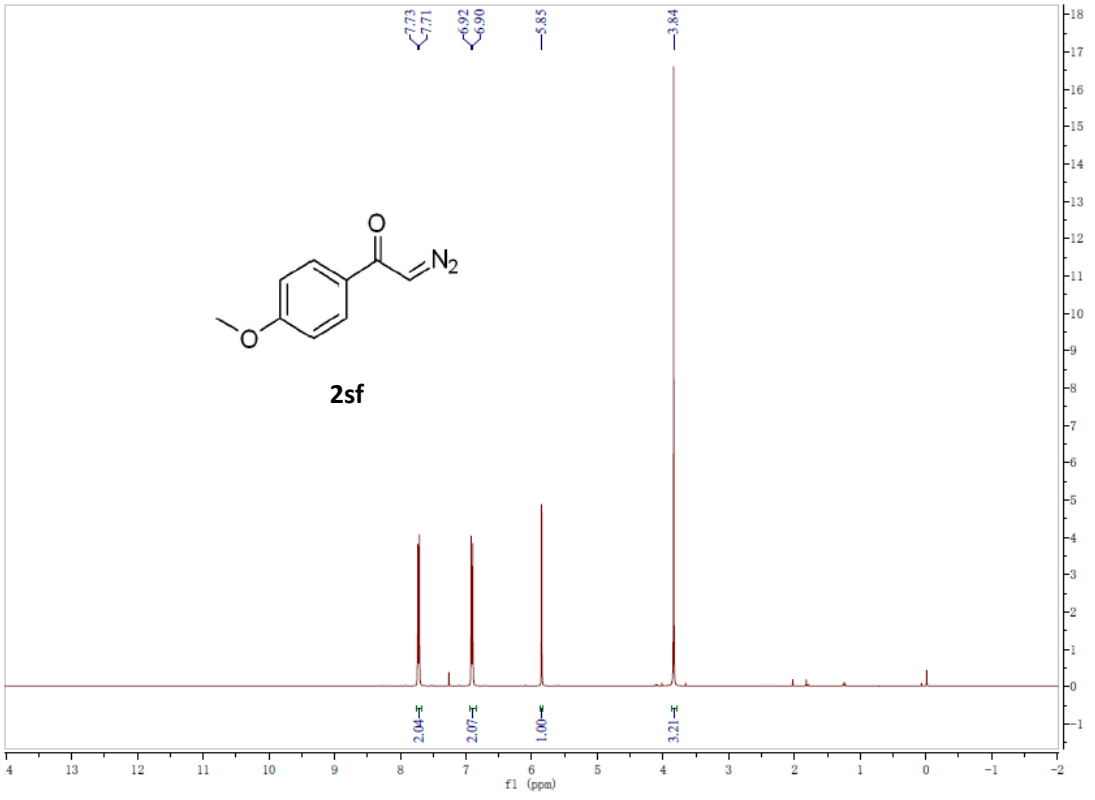
2sc


185.10
135.37
131.92
128.21
127.61
54.43
O
N2
Br
2sb
f1 (ppm)

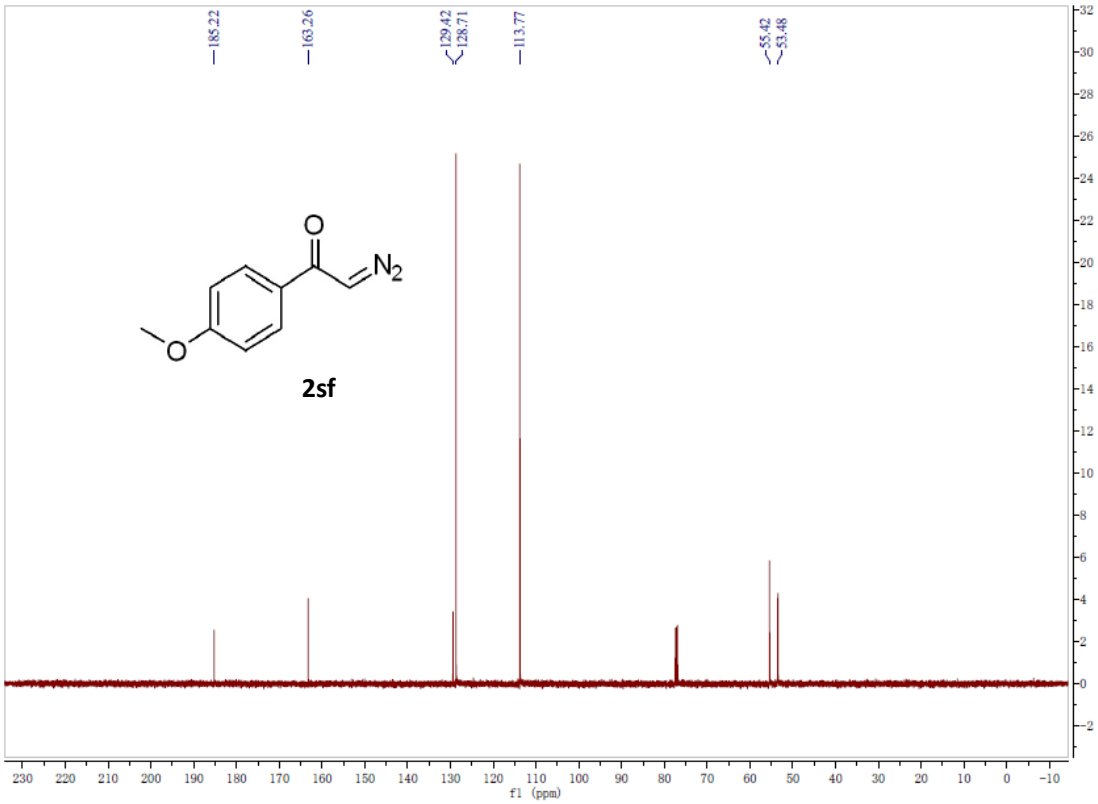

7.34
7.34
7.32
7.30
7.26
7.24
7.08
7.07
7.06
7.05
5.89
3.83
O
N2
2se
2.09
1.12
1.06
1.00
3.26
f1 (ppm)

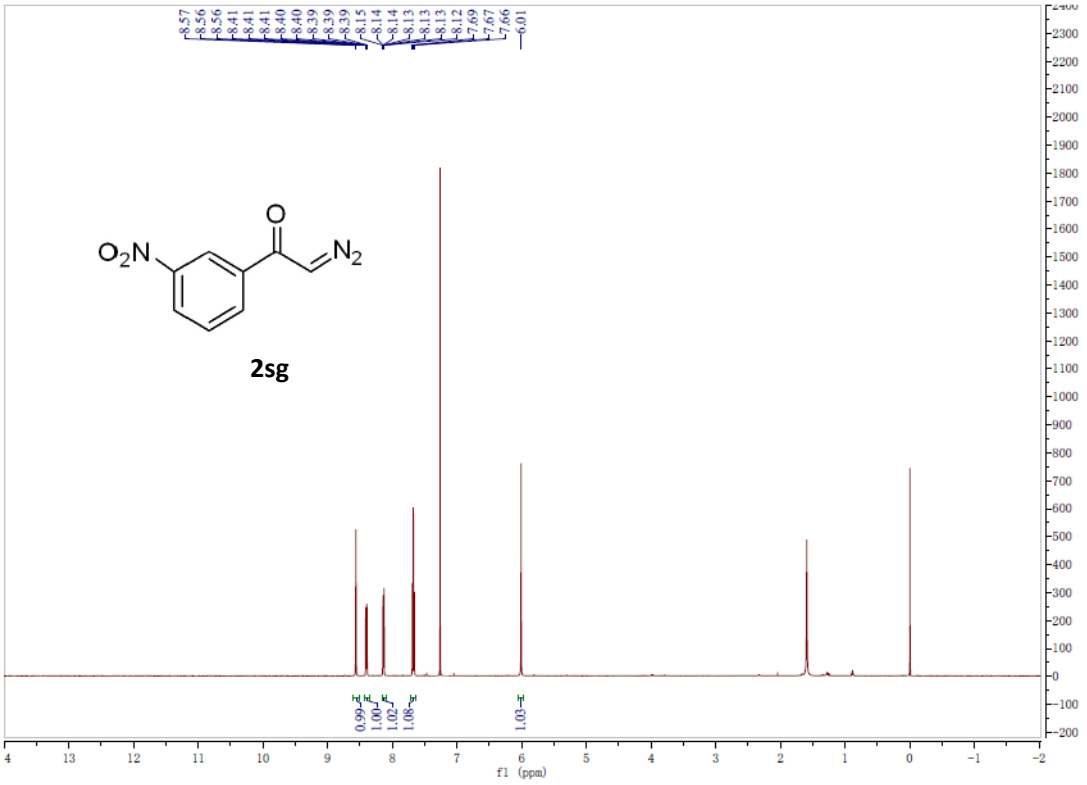

186.12
159.89
138.04
129.61
118.95
118.93
111.46
55.45
54.32
O
O
N2
f1 (ppm)

2se


7.73
7.71
6.92
6.90
5.85
3.84
2.04
2.07
1.00
3.21
O
O
N2
f1 (ppm)

2sf


185.22
163.26
129.42
128.71
113.77
55.42
53.48
O
N2
O
2sf
f1 (ppm)


8.57
8.56
8.56
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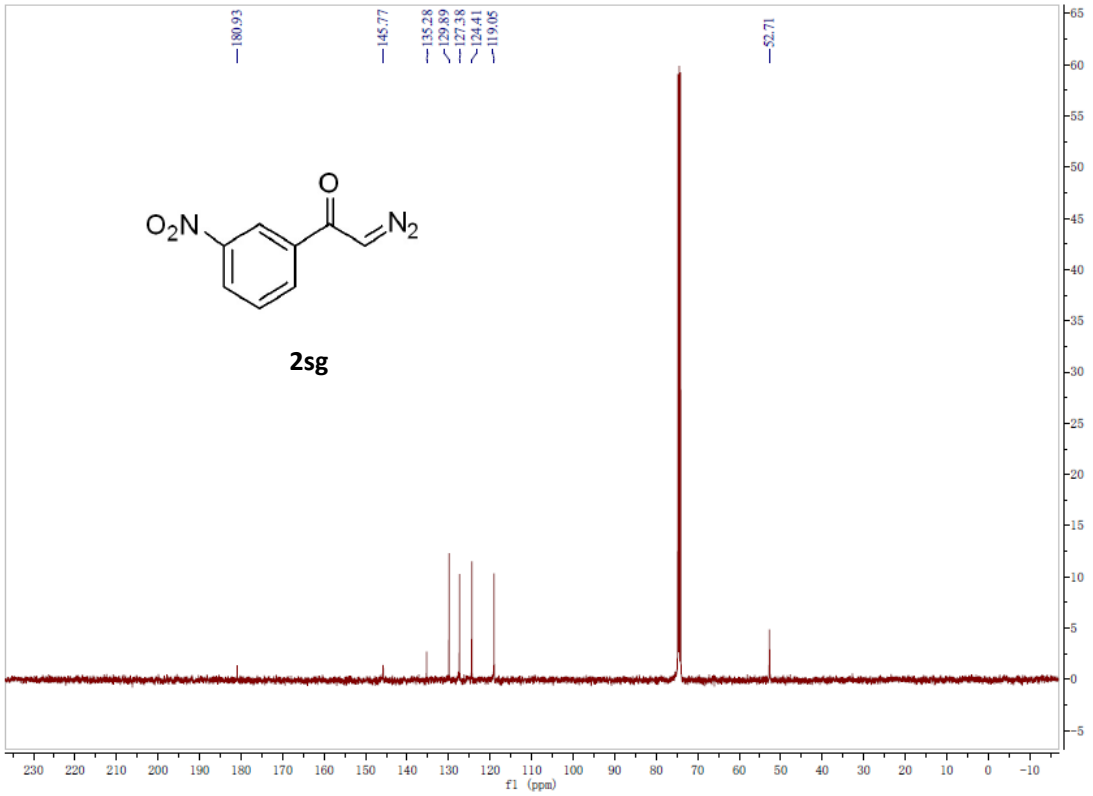
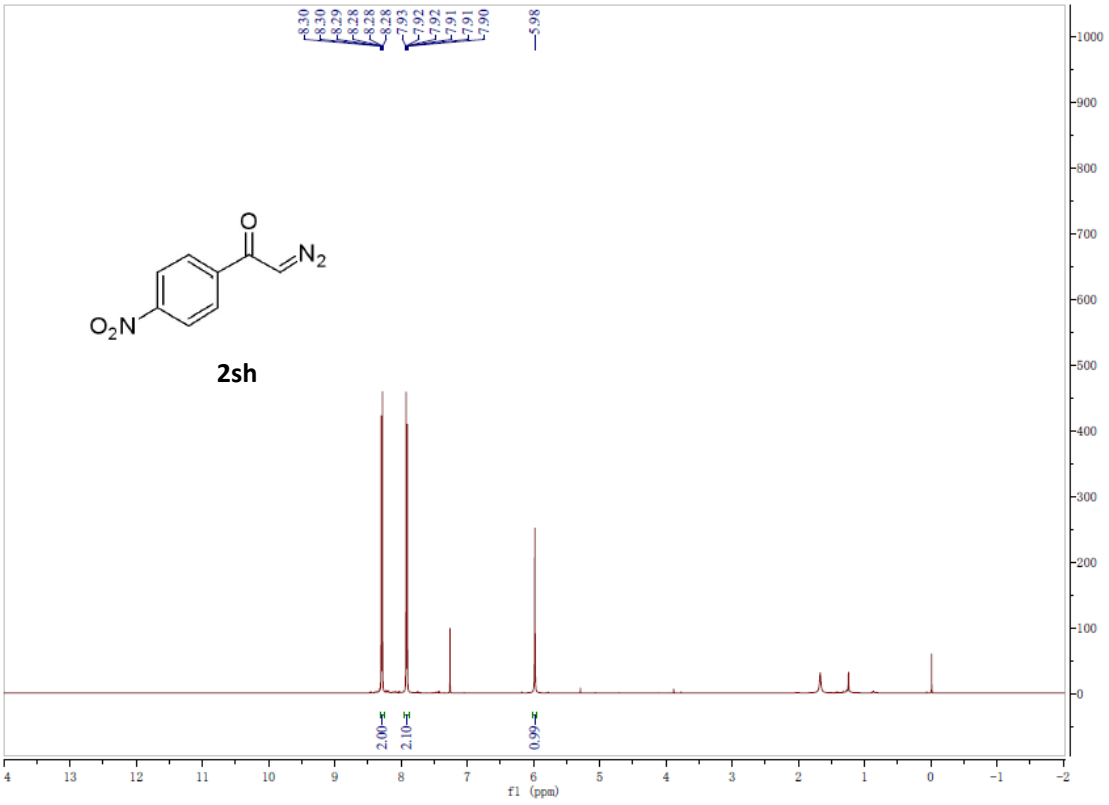
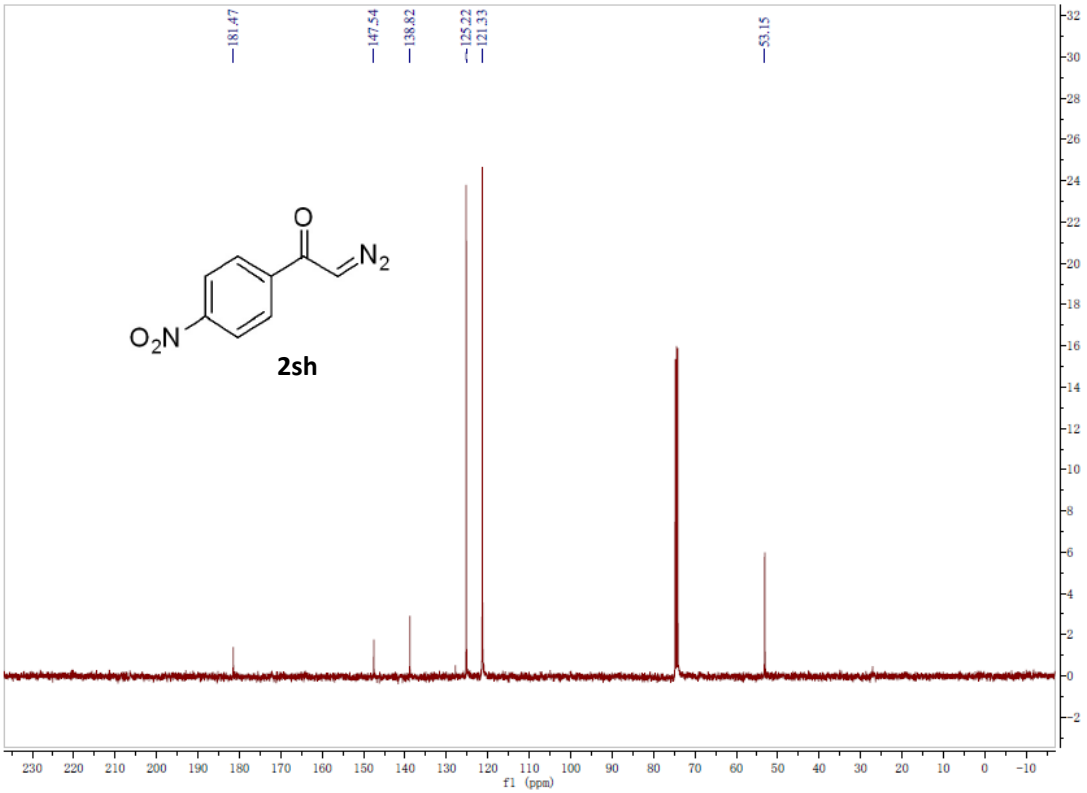
8.41
8.40
8.40
8.39
8.39
8.39
8.15
8.14
8.14
8.13
8.13
8.13
8.12
7.69
7.67
7.66
6.01
O
O2N
N2
2sg
0.99
1.00
1.02
1.08
1.03
f1 (ppm)

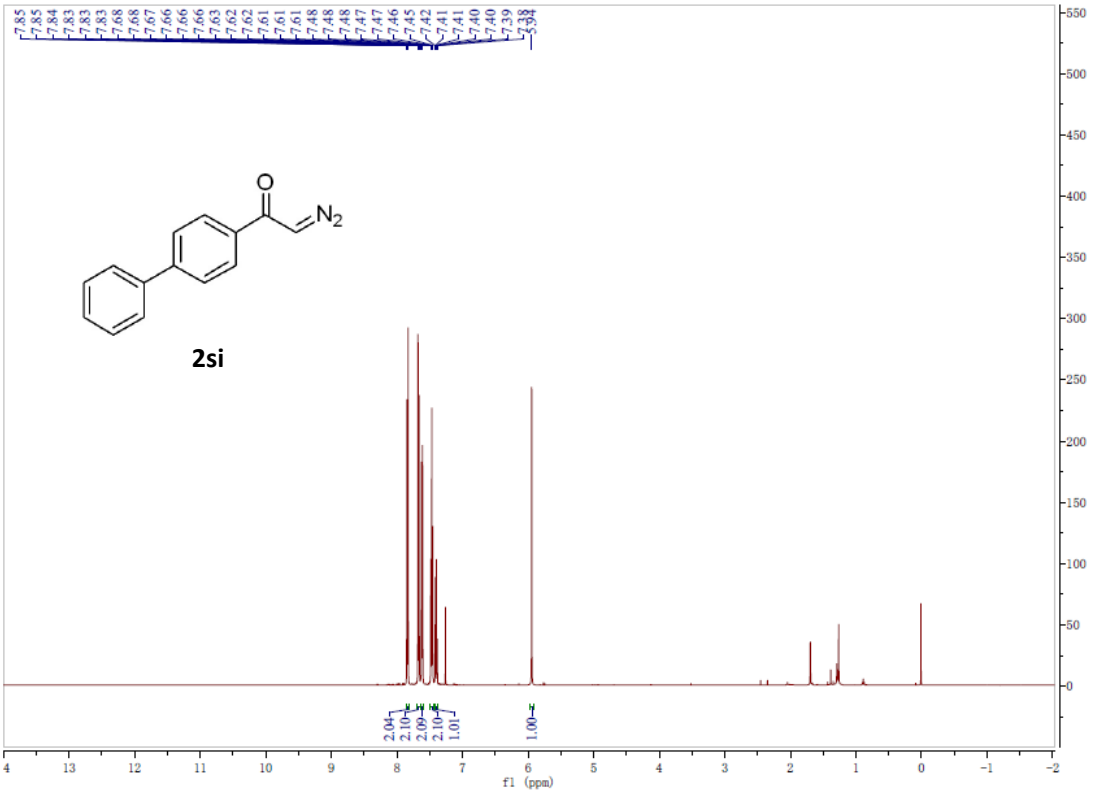

180.93
145.77
135.28
129.89
127.38
124.41
119.05
52.71
O
O2N
N2
f1 (ppm)

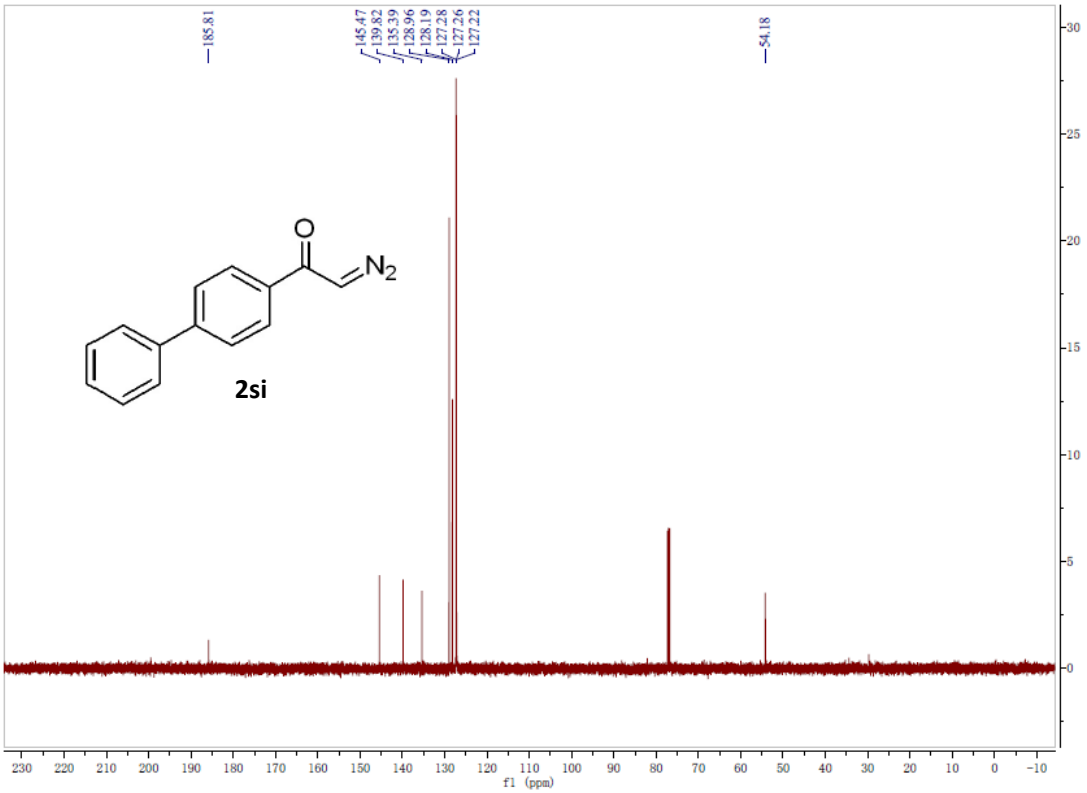
2sg

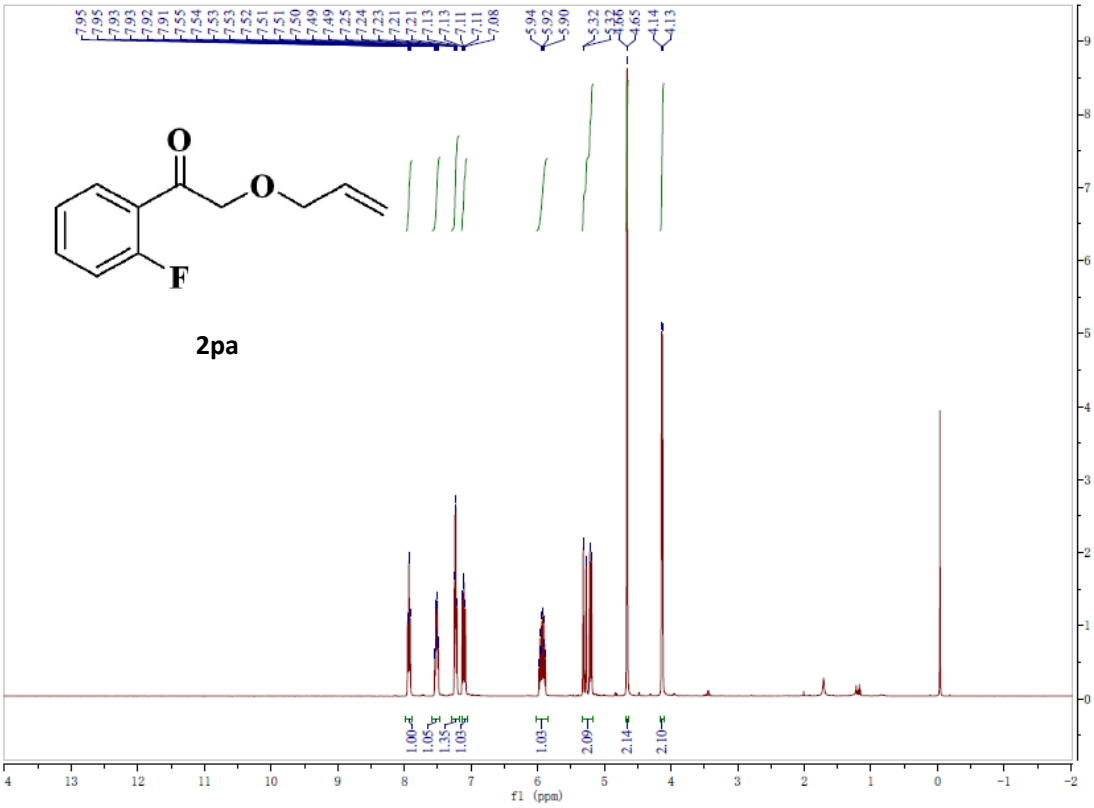

8.30
8.30
8.29
8.28
8.28
8.28
7.93
7.92
7.92
7.91
7.91
7.90
5.98
O
O2N
N2
2.00
2.10
0.99
f1 (ppm)

2sh


181.47
147.54
138.82
125.22
121.33
53.15
O
N2
O2N
2sh
f1 (ppm)


O
N2
2si
f1 (ppm)


185.81
145.47
139.82
135.39
128.96
128.19
127.28
127.26
127.22
54.18
O
N2
2si
f1 (ppm)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7.92
7.91
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7.54
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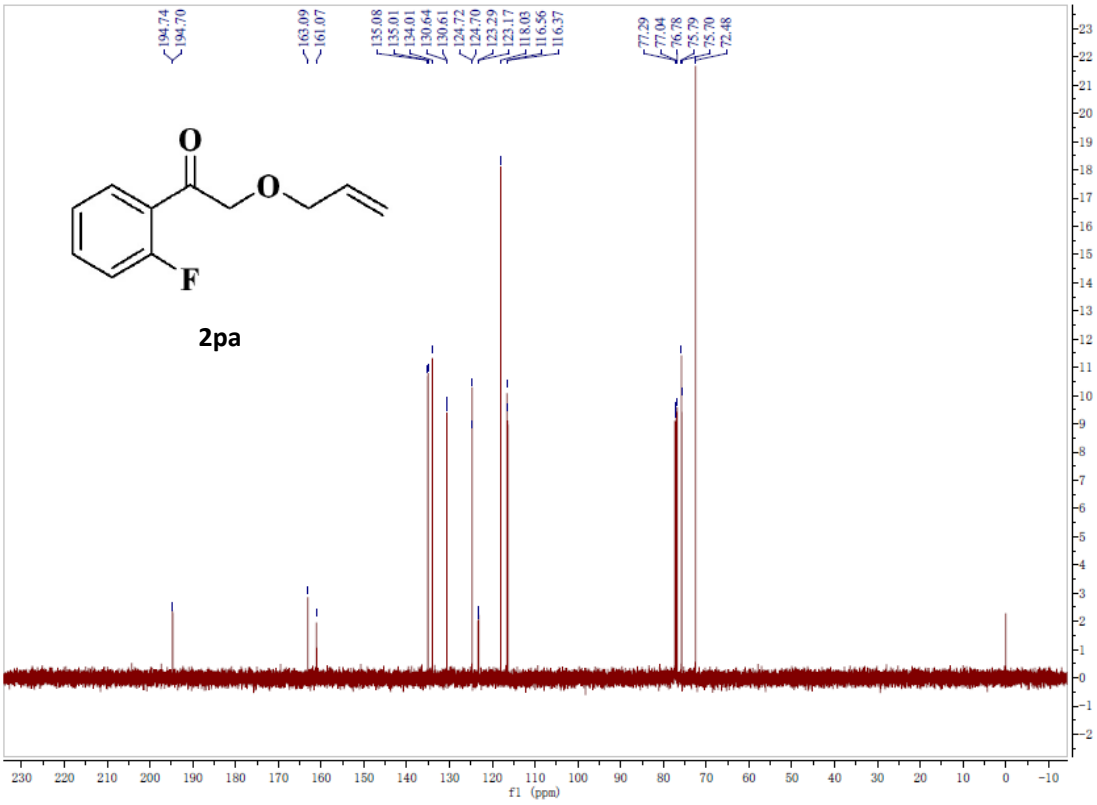
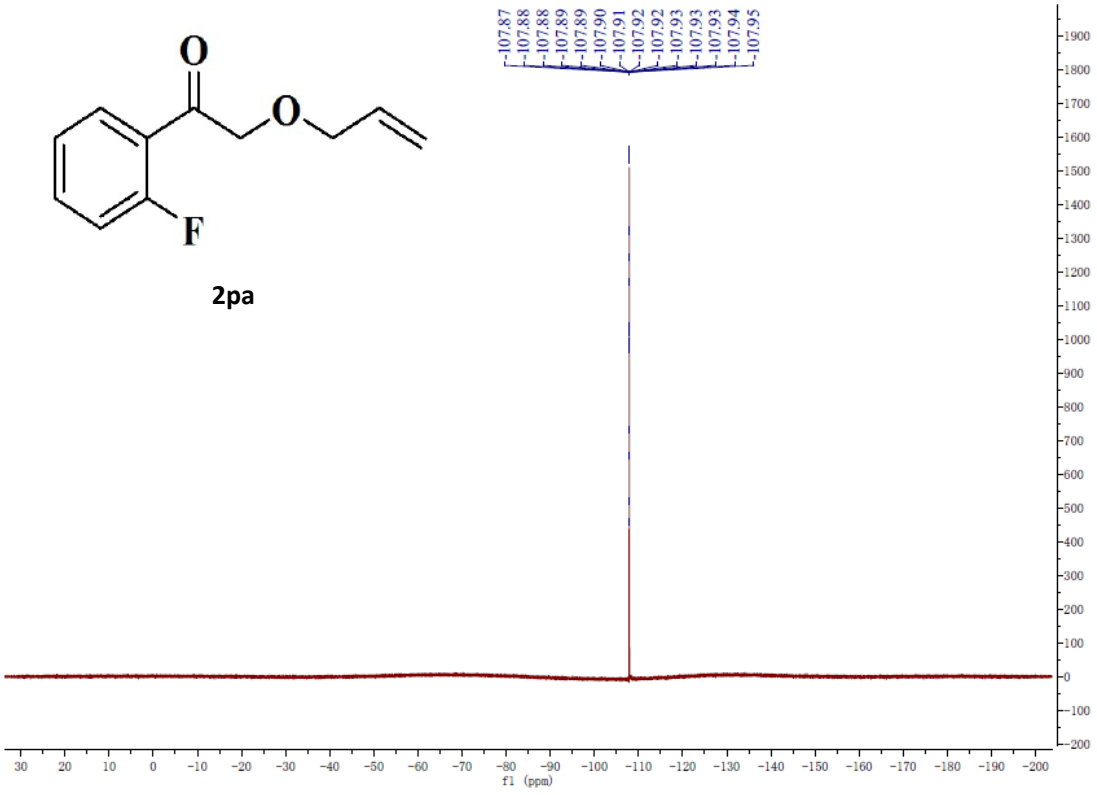
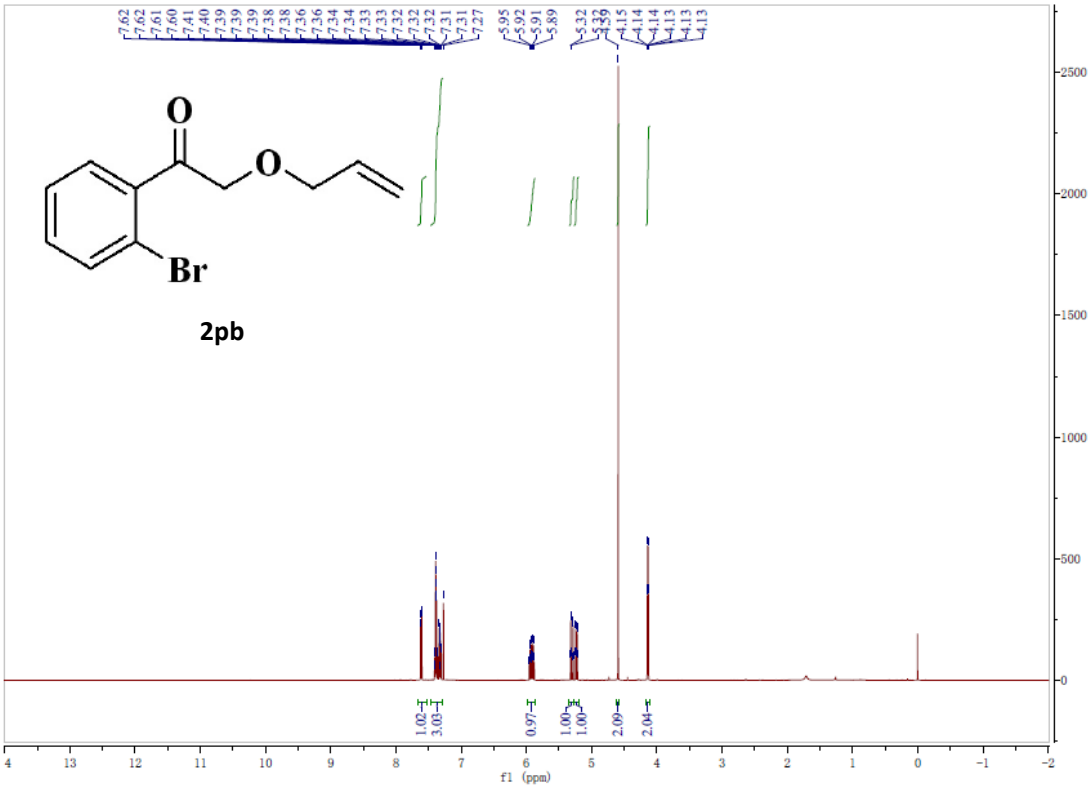
7.53
7.52
7.51
7.51
7.50
7.49
7.49
7.25
7.24
7.23
7.21
7.21
7.13
7.13
7.11
7.11
7.08
5.94
5.92
5.90
5.32
4.65
4.14
4.13
O
O
F
2pa
1.00
1.05
1.35
1.03
1.03
2.09
2.14
2.10
f1 (ppm)


194.74
194.70
163.09
161.07
135.08
135.01
134.01
130.64
130.61
124.72
124.70
123.29
123.17
118.08
116.56
116.37
77.29
77.04
76.78
75.79
75.70
72.48
O
O
F
2pa
f1 (ppm)


-107.87
-107.88
-107.88
-107.89
-107.89
-107.90
-107.91
-107.92
-107.92
-107.93
-107.93
-107.93
-107.94
-107.95
O
O
F
2pa
f1 (ppm)


7.62
7.62
7.61
7.60
7.41
7.40
7.39
7.39
7.39
7.38
7.38
7.36
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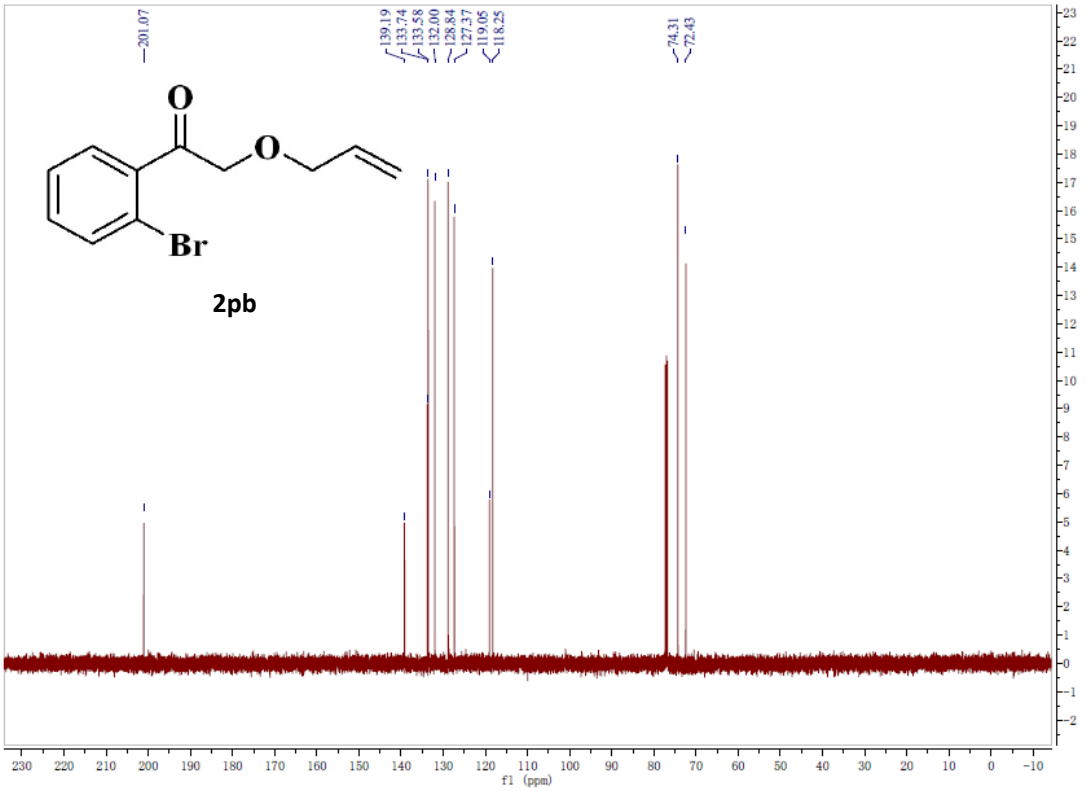
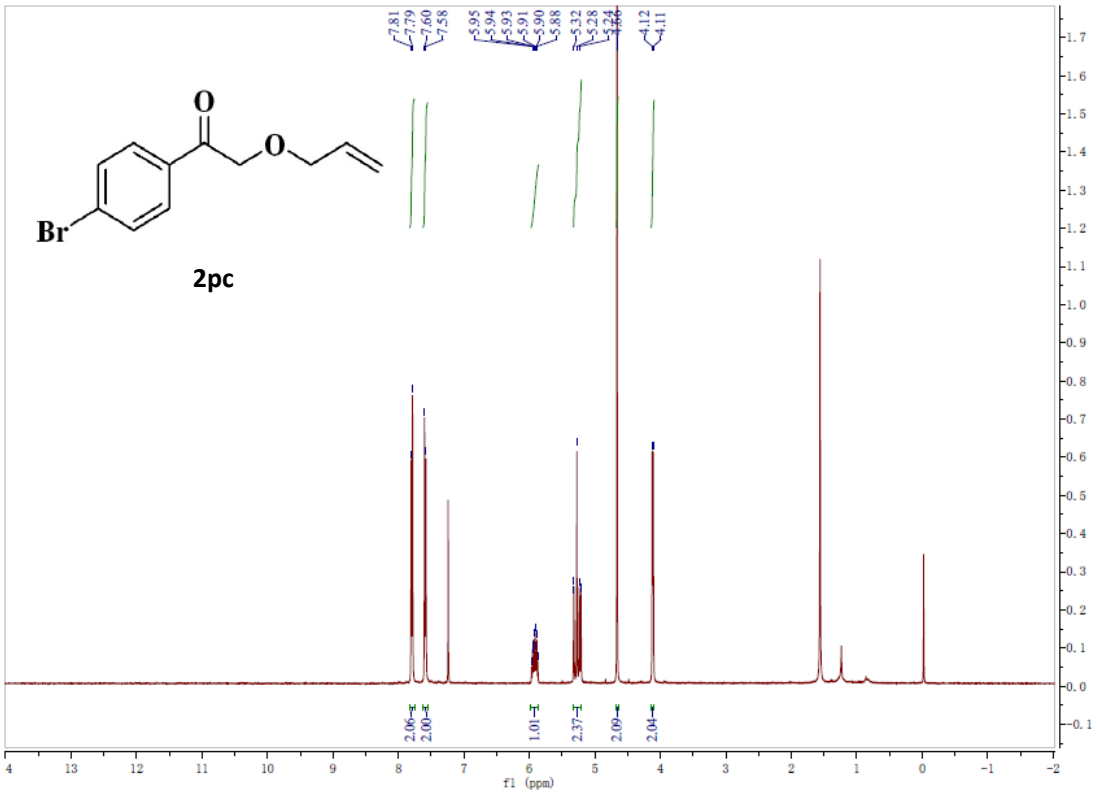
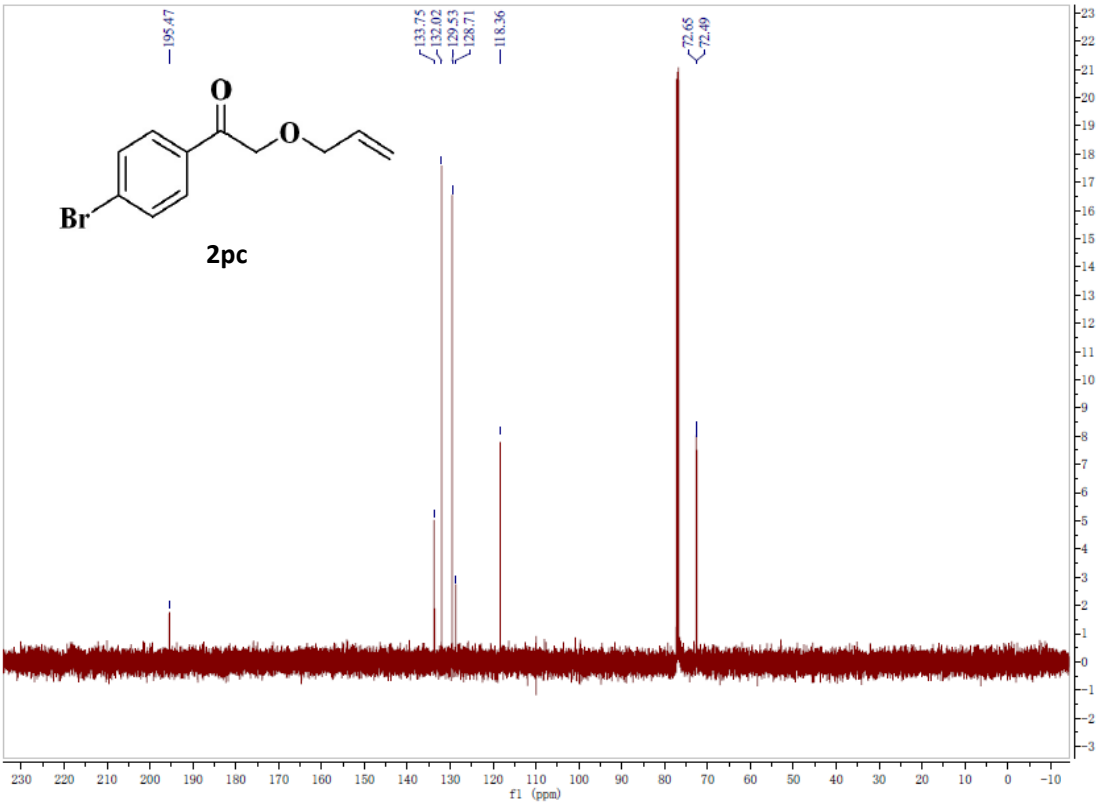
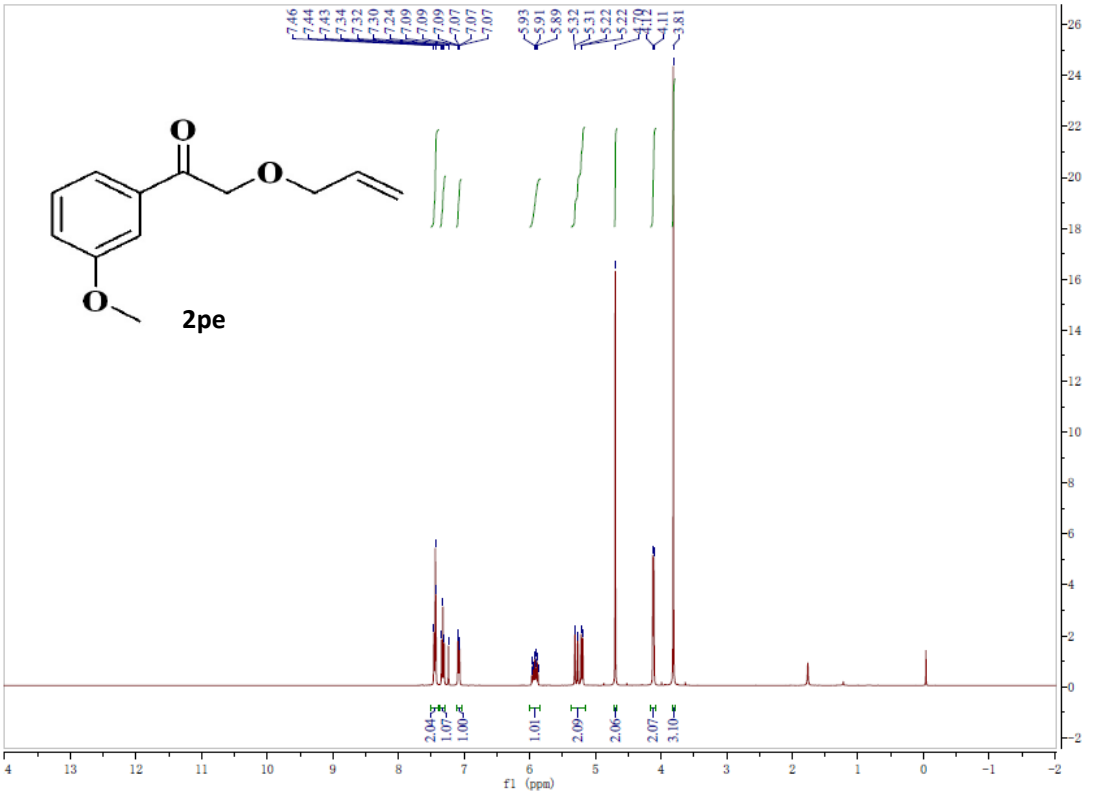
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.27
5.95
5.92
5.91
5.89
5.32
5.32
5.30
5.30
4.15
4.14
4.14
4.13
4.13
4.13
O
O
Br
2pb
1.02
3.03
0.97
1.00
1.00
2.09
2.04
f1 (ppm)


201.07
139.19
133.74
133.58
132.00
128.84
127.37
119.05
118.25
74.31
72.43
O
O
Br
2pb
f1 (ppm)


7.81
7.79
7.60
7.58
5.95
5.94
5.93
5.91
5.90
5.88
5.32
5.28
5.24
4.86
4.12
4.11
O
O
Br
2pc
2.06
2.00
1.01
2.37
2.09
2.04
f1 (ppm)


195.47
133.75
132.02
129.53
128.71
118.36
72.65
72.49
O
O
Br
2pc
f1 (ppm)


7.46
7.44
7.43
7.34
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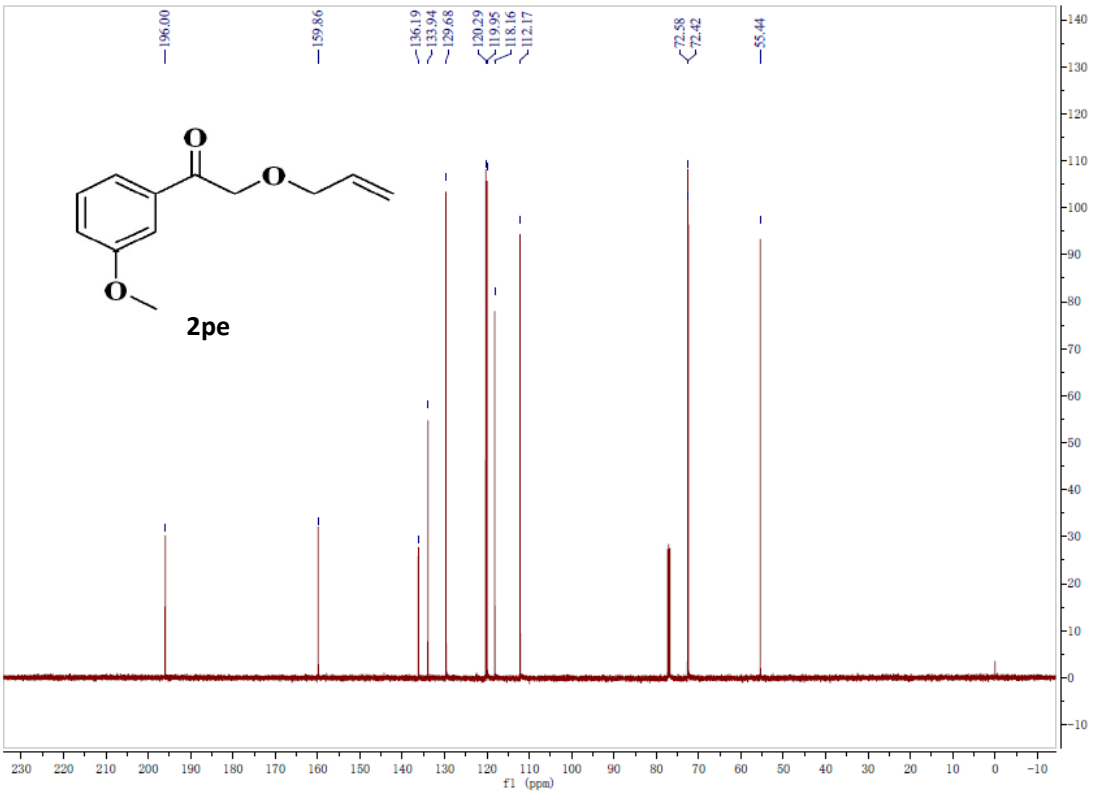
7.30
7.24
7.09
7.09
7.09
7.07
7.07
7.07
5.93
5.91
5.89
5.32
5.31
5.22
4.12
4.11
3.81
2pe
2.04
1.07
1.00
1.01
2.09
2.06
2.07
3.10
f1 (ppm)


196.00
159.86
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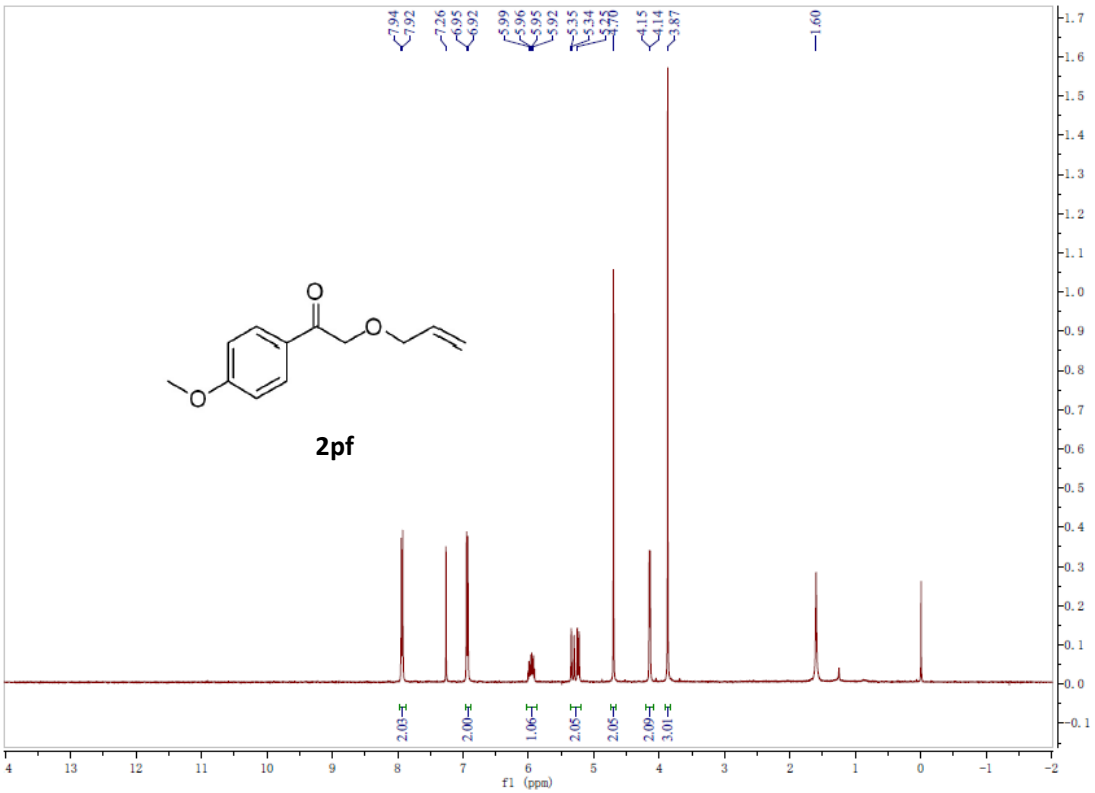
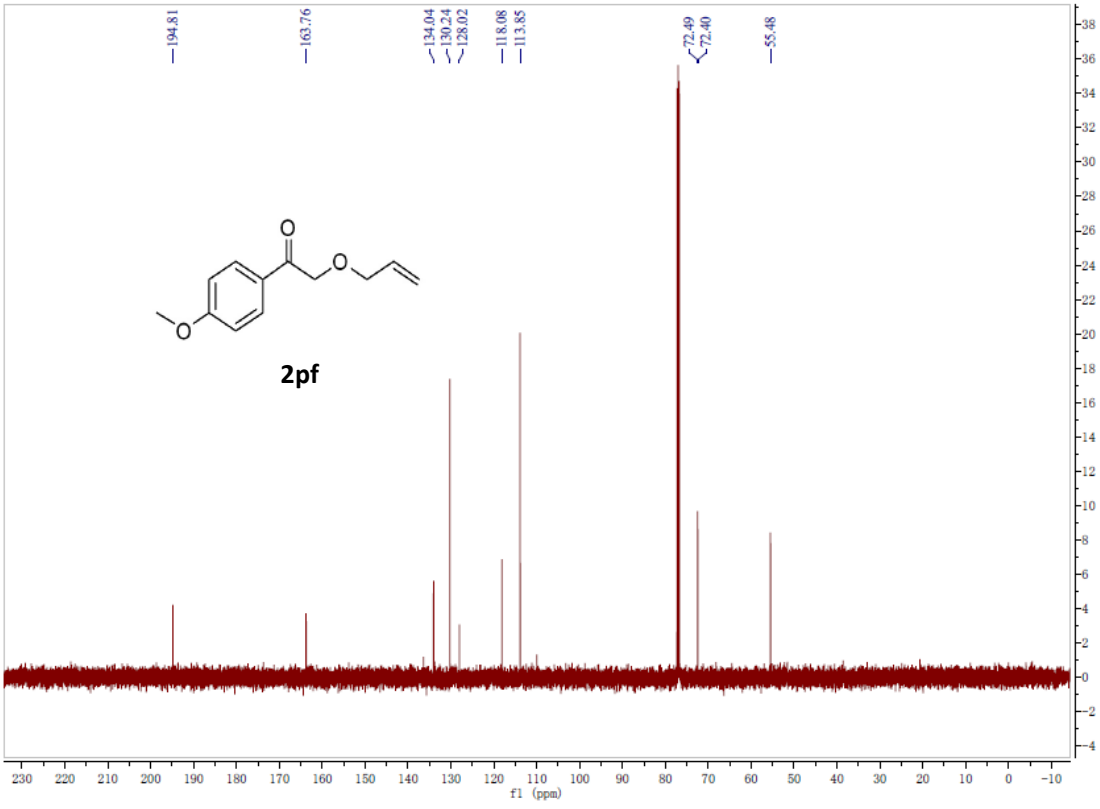
133.94
129.68
120.29
119.95
118.16
112.17
72.58
72.42
55.44
2pe
f1 (ppm)


7.94
7.92
7.26
6.95
6.92
5.99
5.96
5.95
5.92
5.35
5.34
4.70
4.15
4.14
3.87
1.60
2.03
2.00
1.06
2.05
2.05
2.09
3.01
f1 (ppm)

2pf


194.81
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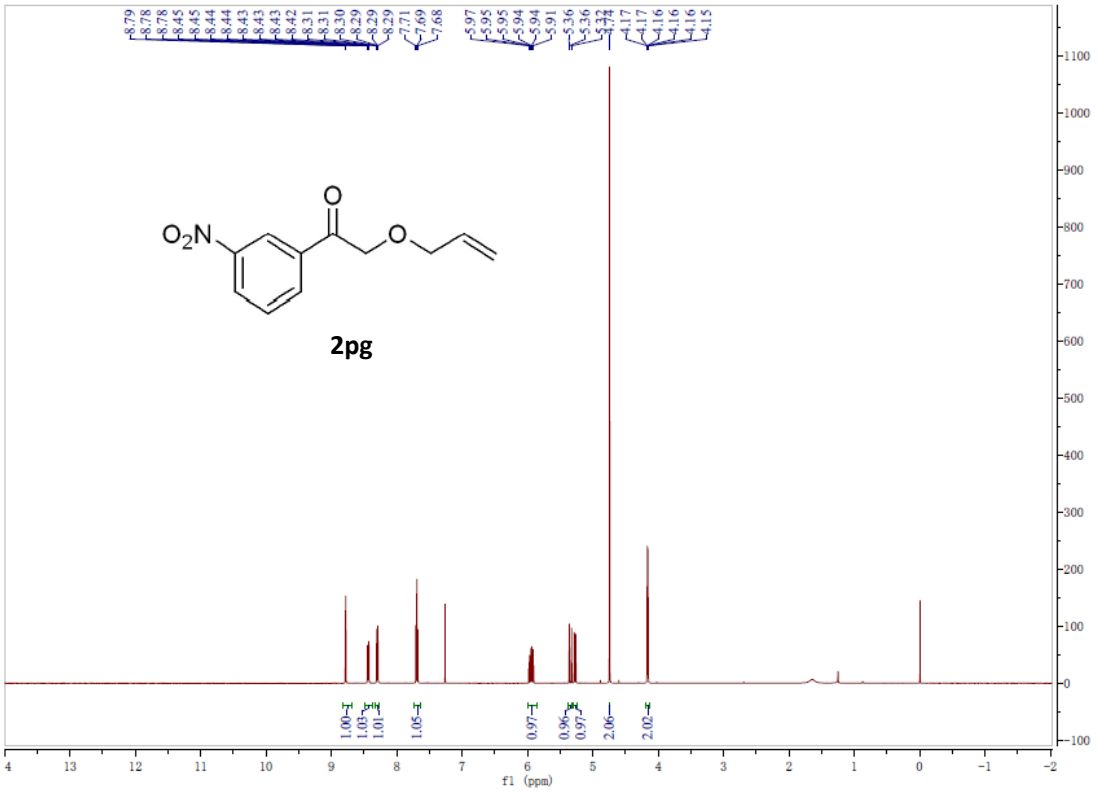
130.24
128.02
118.08
113.85
72.49
72.40
55.48
f1 (ppm)

2pf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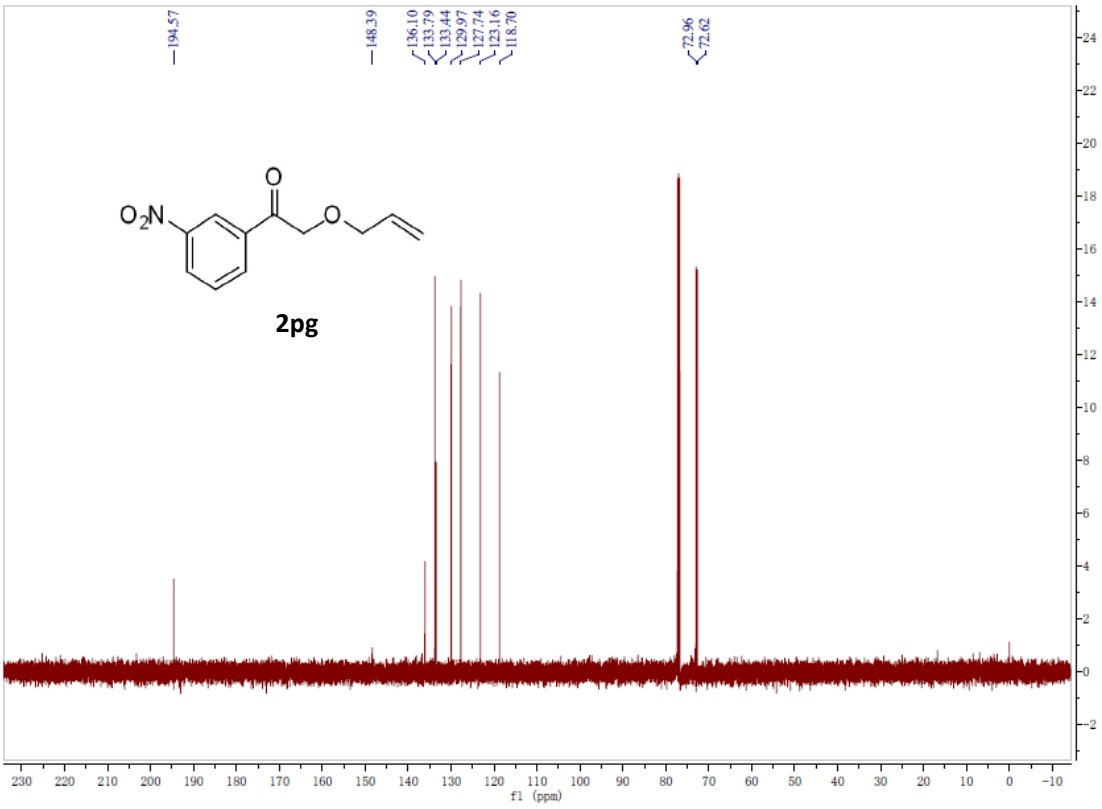
8.42
8.31
8.31
8.30
8.29
8.29
8.29
7.71
7.69
7.68
5.97
5.95
5.95
5.94
5.94
5.91
5.36
5.36
5.32
4.74
4.17
4.17
4.16
4.16
4.16
4.15
O
O2N
O
2pg
1.00
1.03
1.01
1.05
0.97
0.96
0.97
2.06
2.02
f1 (ppm)


194.57
148.39
136.10
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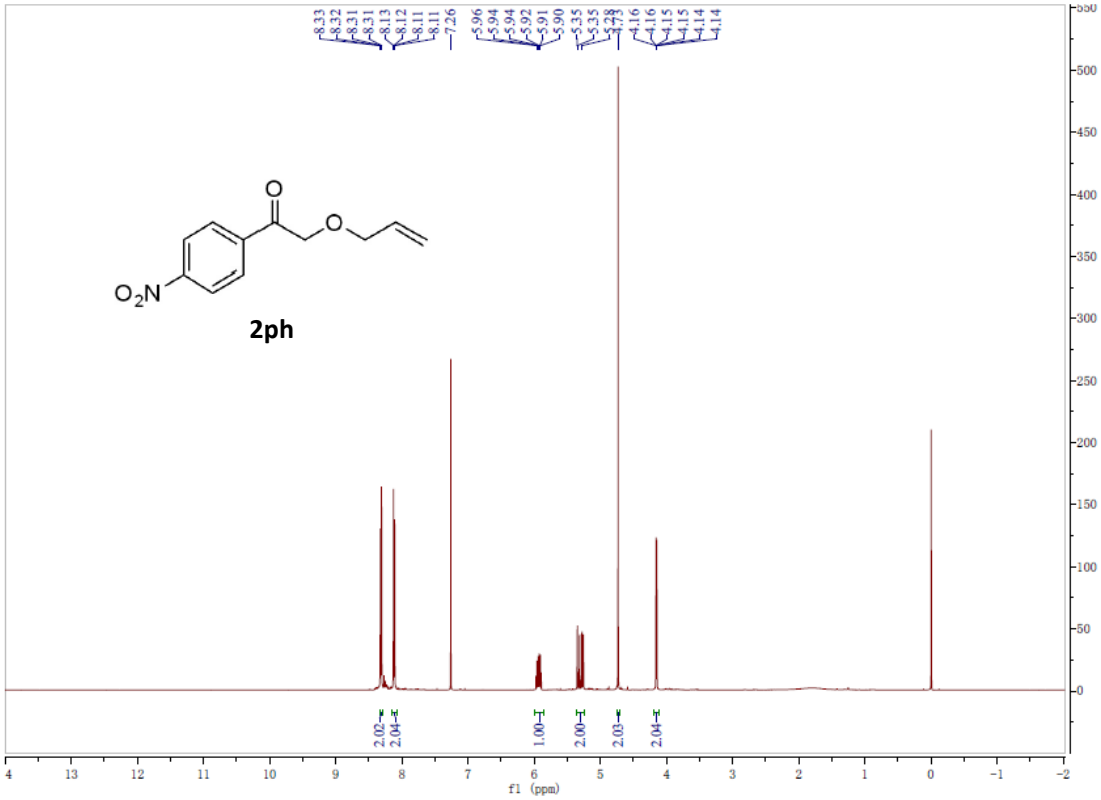
133.44
129.97
127.74
123.16
118.70
72.96
72.62
O
O2N
O
2pg
f1 (ppm)


8.33
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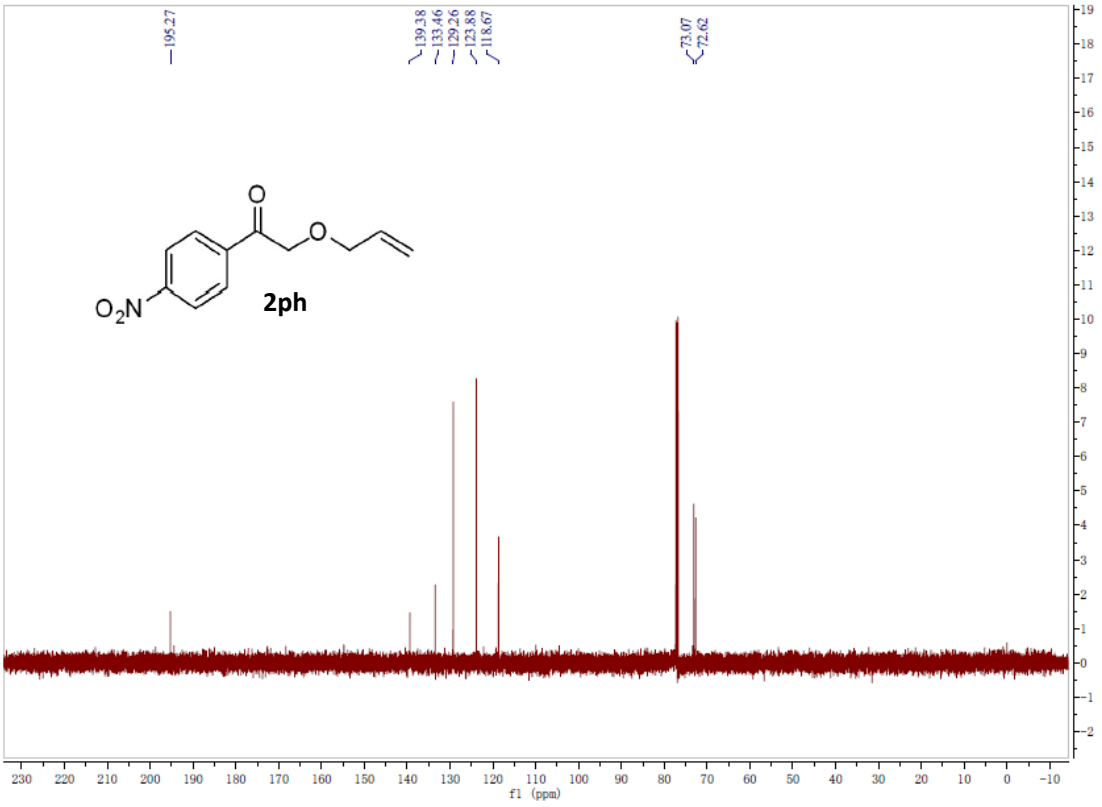
8.31
8.31
8.13
8.12
8.11
8.11
7.26
5.96
5.94
5.94
5.92
5.91
5.90
5.35
5.35
4.16
4.16
4.15
4.15
4.14
4.14
O
O
O_2N
2ph
2.02
2.04
1.00
2.00
2.03
2.04
f1 (ppm)


195.27
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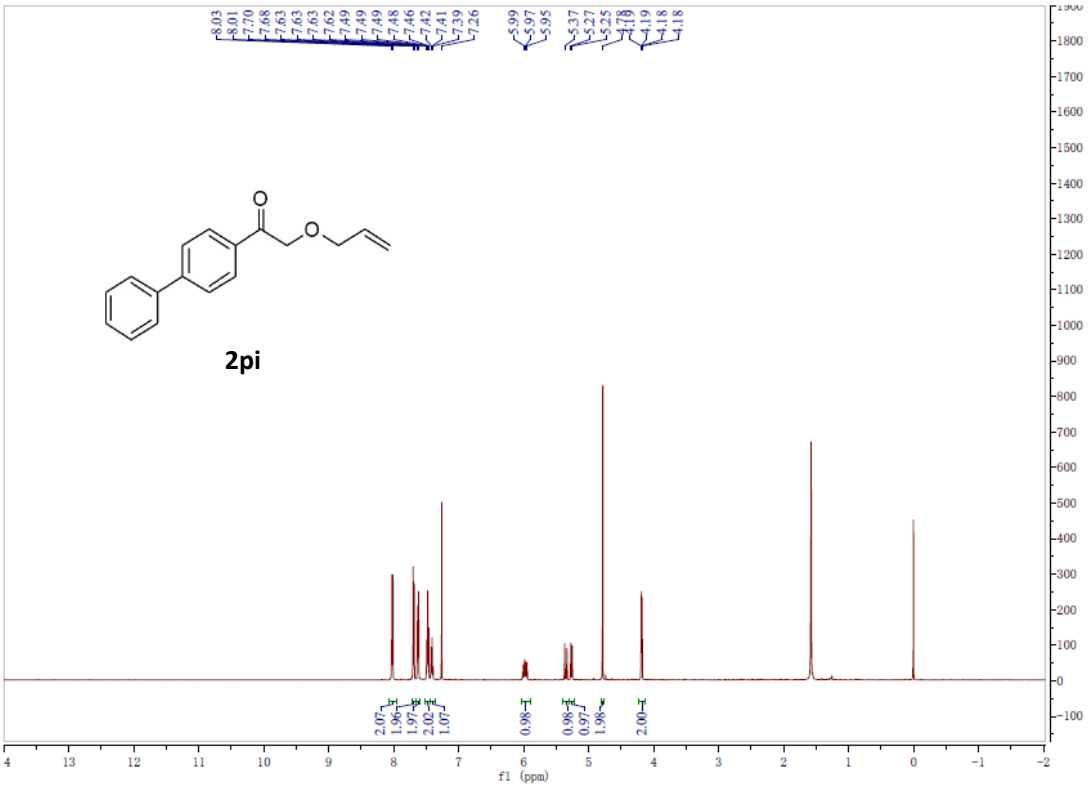
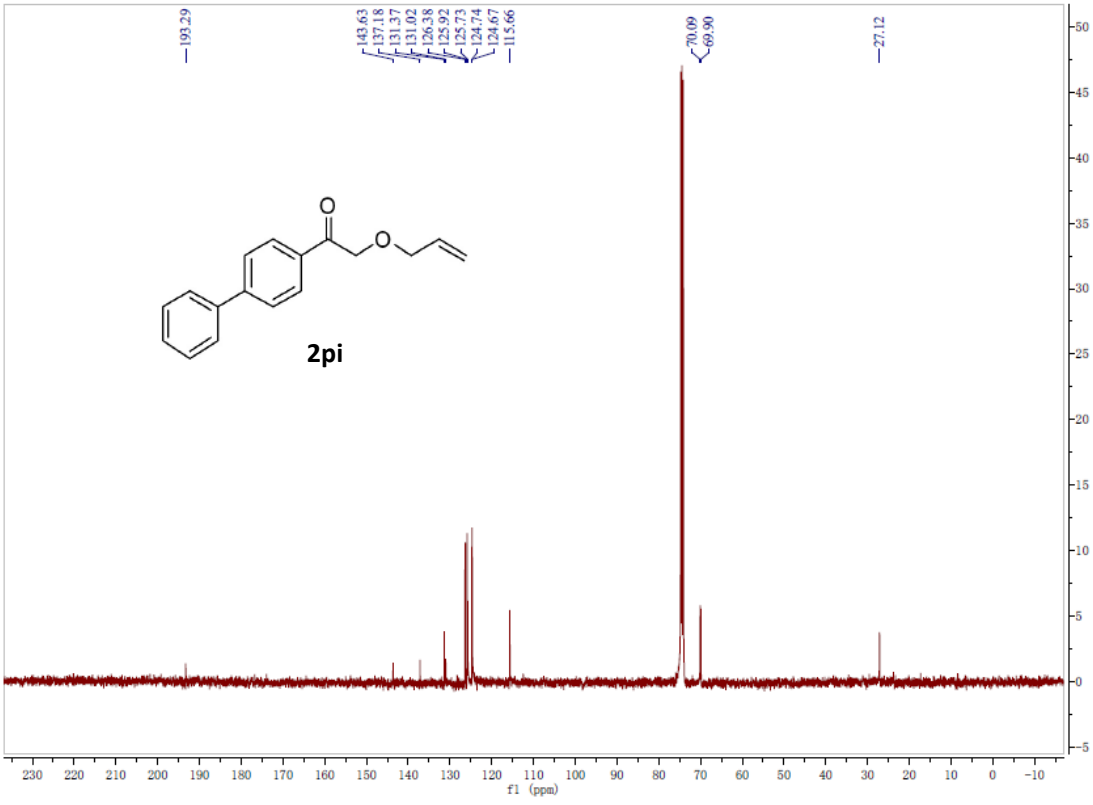
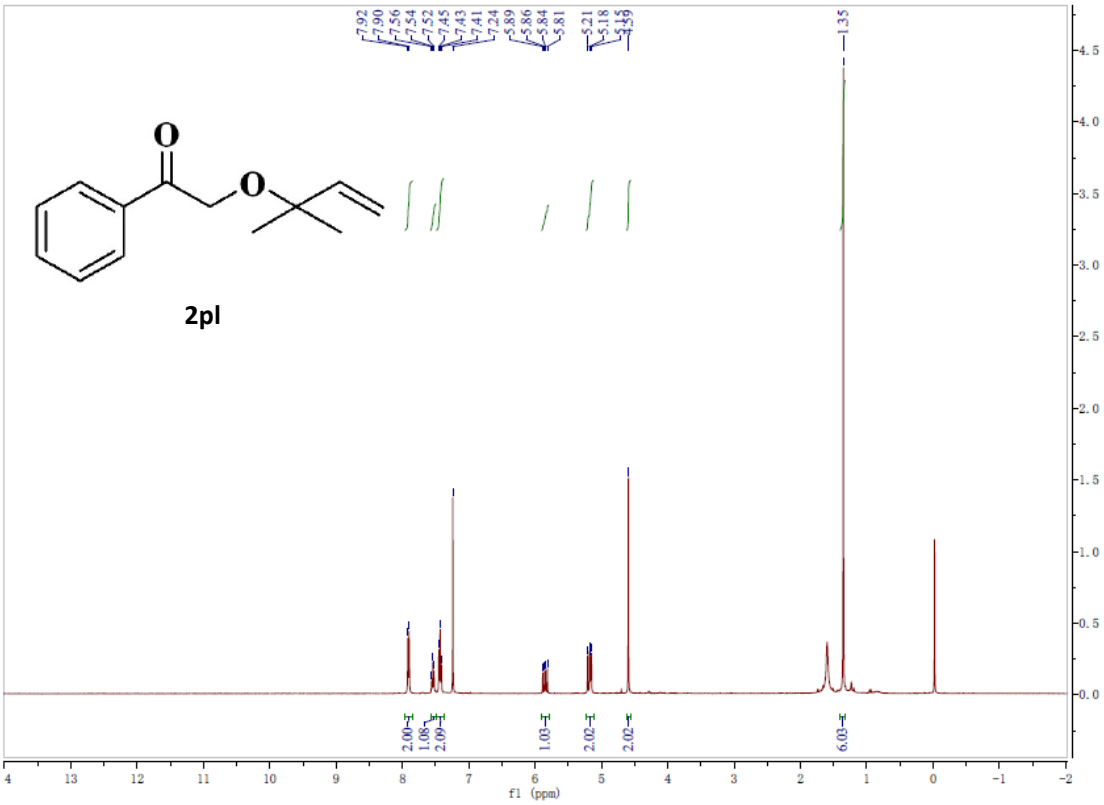
129.26
123.88
118.67
73.07
72.62
O
O
O_2N
2ph
f1 (ppm)


8.03
8.01
7.70
7.68
7.63
7.63
7.63
7.62
7.49
7.49
7.49
7.48
7.46
7.42
7.41
7.39
7.26
5.99
5.97
5.95
5.37
5.27
5.25
4.19
4.18
4.18
2pi
2.07
1.96
1.97
2.02
1.07
0.98
0.98
0.97
1.98
2.00
f1 (ppm)


193.29
143.63
137.18
131.37
131.02
126.38
125.92
125.73
124.74
124.67
115.66
70.09
69.90
27.12
2pi
f1 (ppm)


7.92
7.90
7.56
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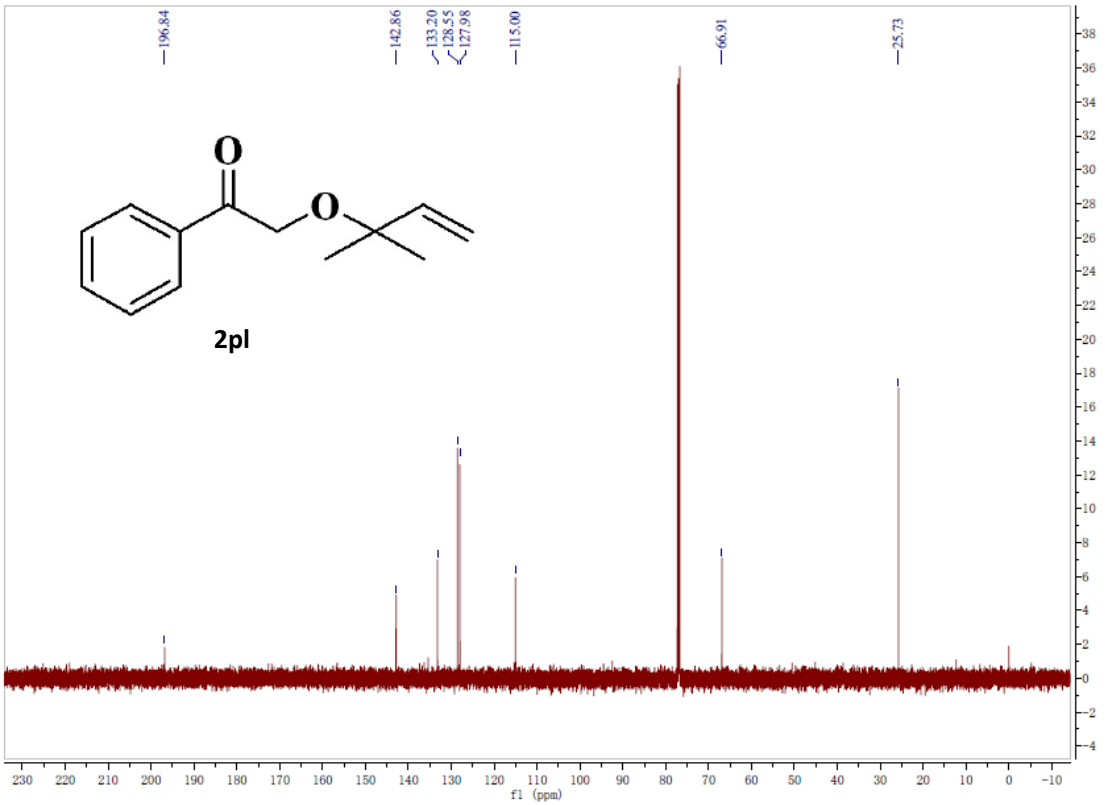
7.45
7.43
7.41
7.24
5.89
5.86
5.84
5.81
5.21
5.18
5.15
4.59
1.35
2.00
1.08
2.09
1.03
2.02
2.02
6.03
f1 (ppm)

2pl


196.84
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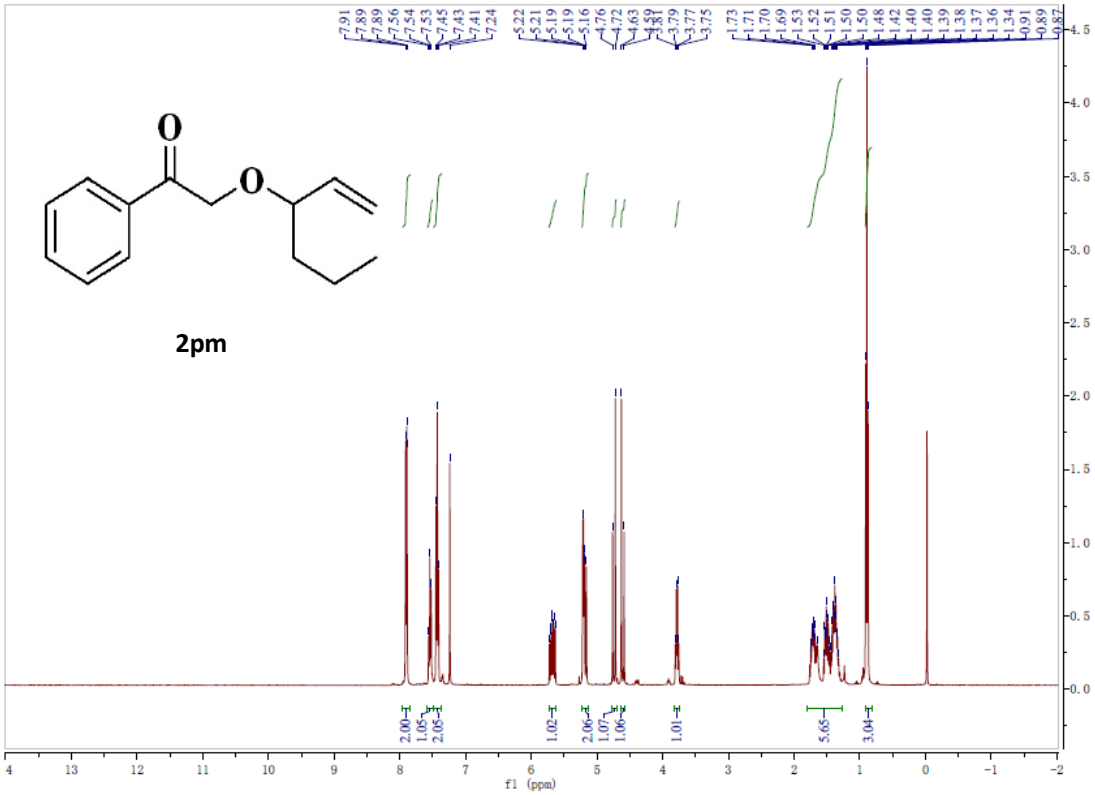
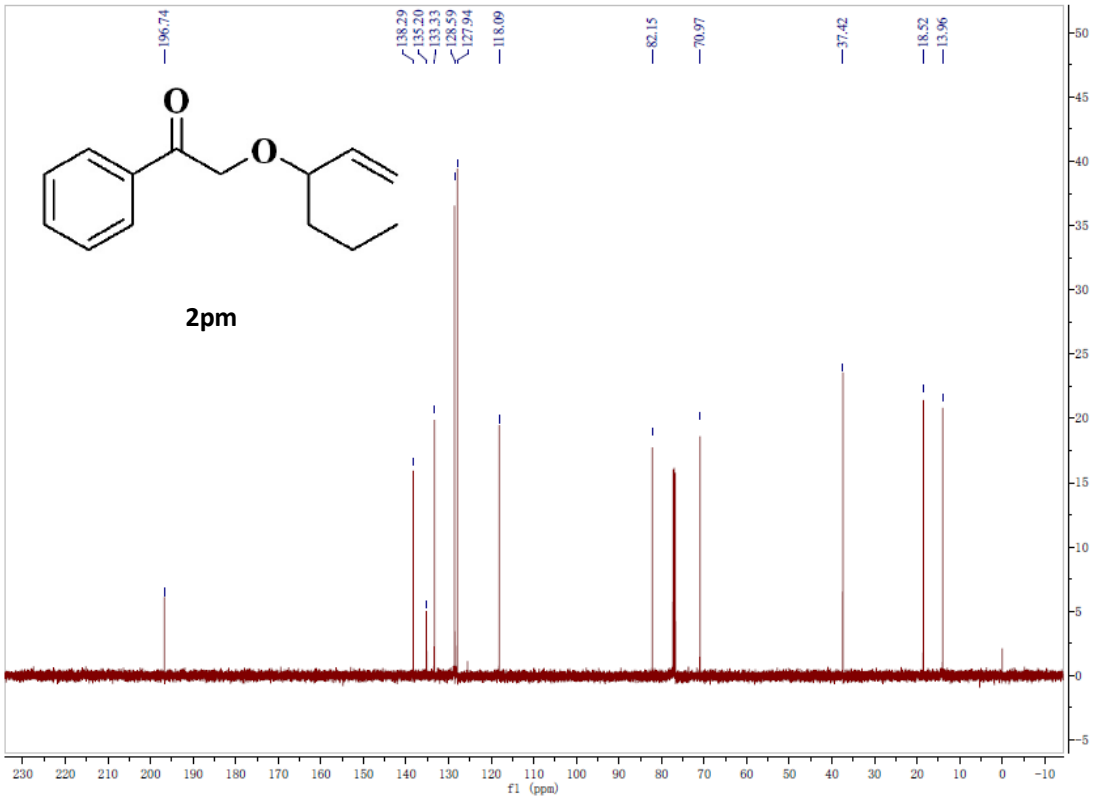
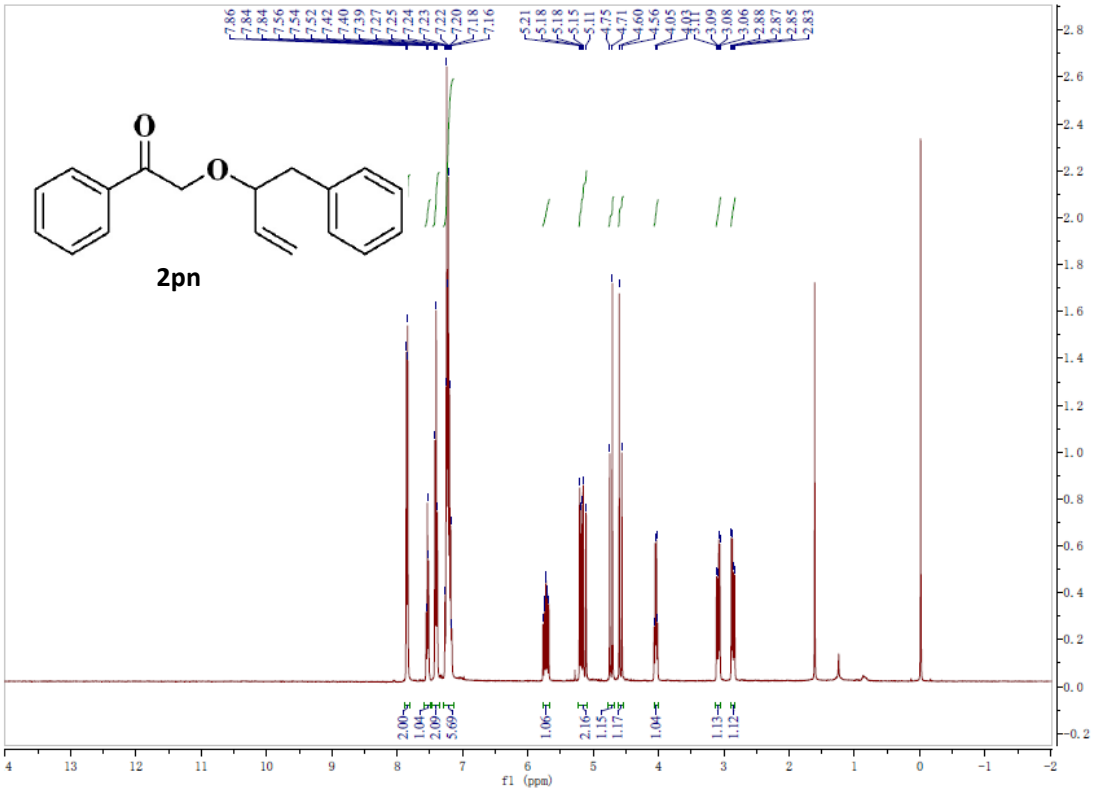
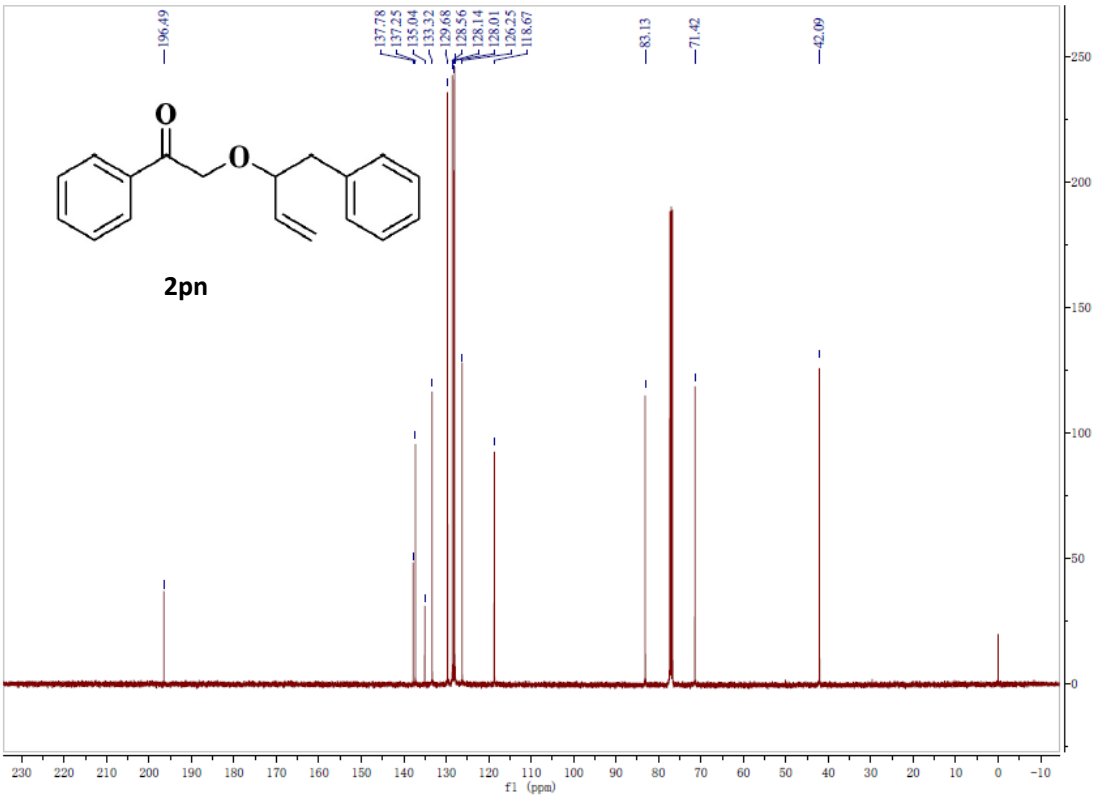
128.55
127.98
115.00
66.91
25.73
f1 (ppm)

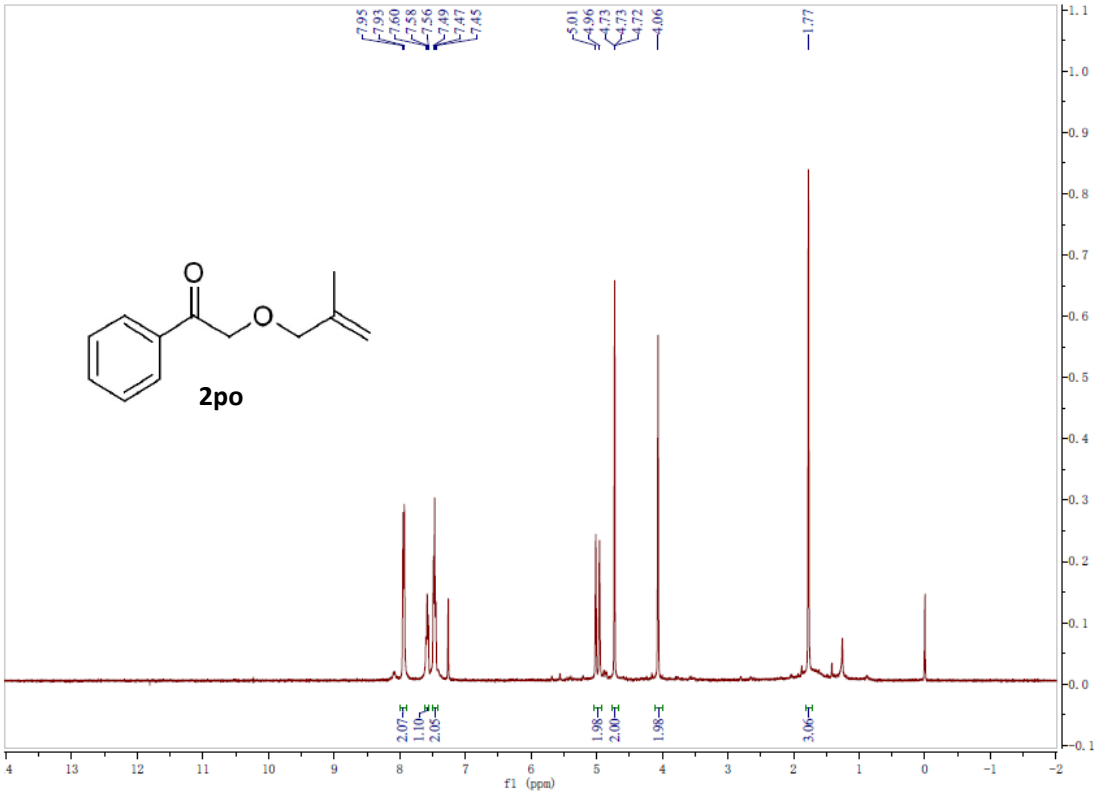
2pl


2pm
f1 (ppm)


2pm
f1 (ppm)


2pn
f1 (ppm)


2pn
f1 (ppm)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7.93
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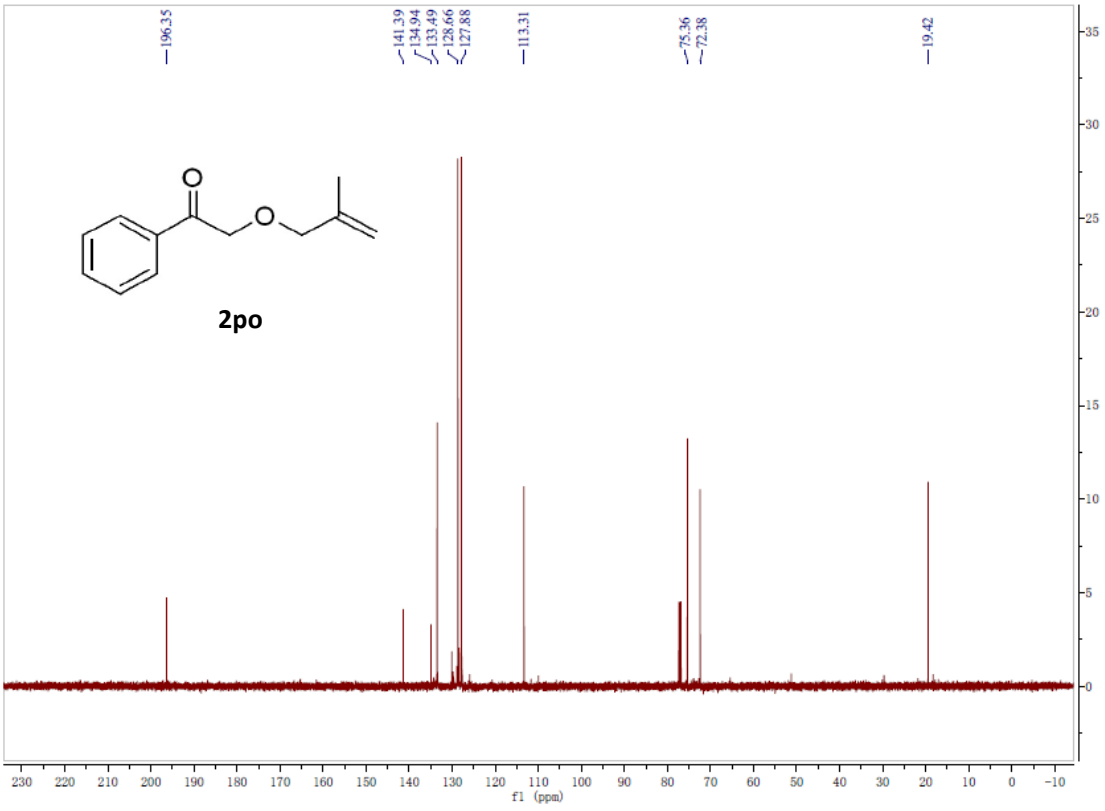
7.58
7.56
7.49
7.47
7.45
5.01
4.96
4.73
4.73
4.72
4.06
1.77
2.07
1.10
2.05
1.98
2.00
1.98
3.06
f1 (ppm)
2po


196.35
141.39
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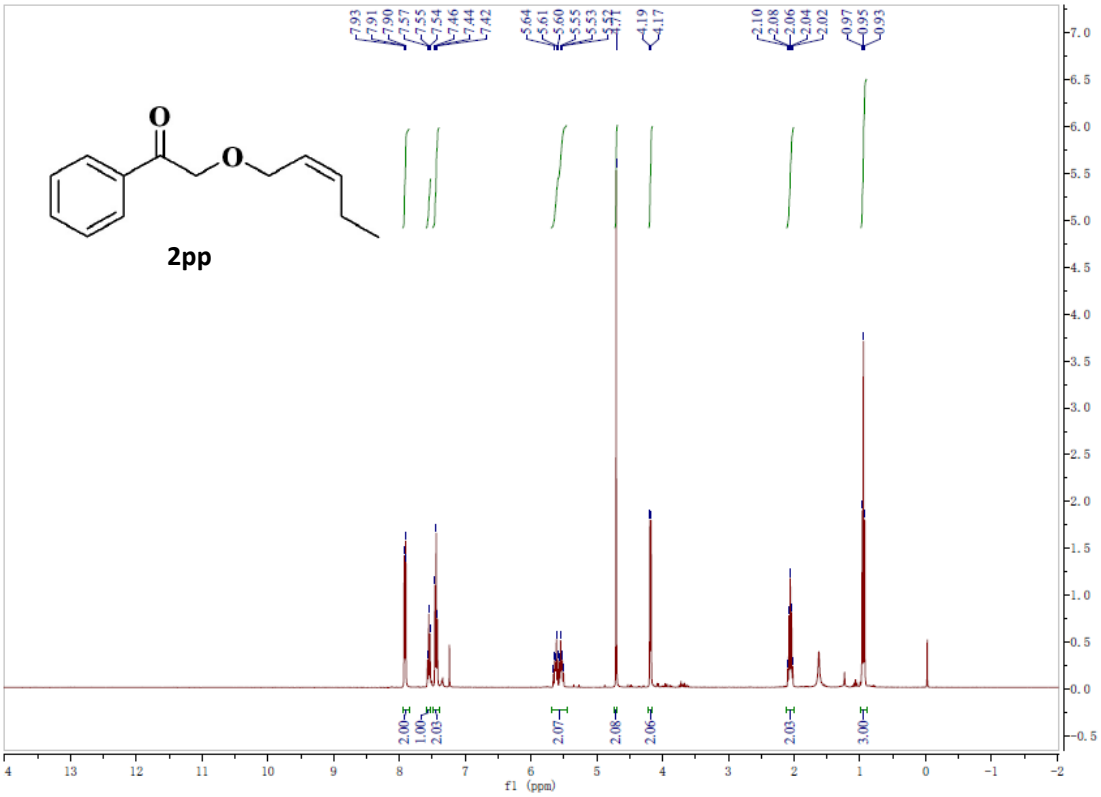
133.49
128.66
127.88
113.31
75.36
72.38
19.42
f1 (ppm)
2po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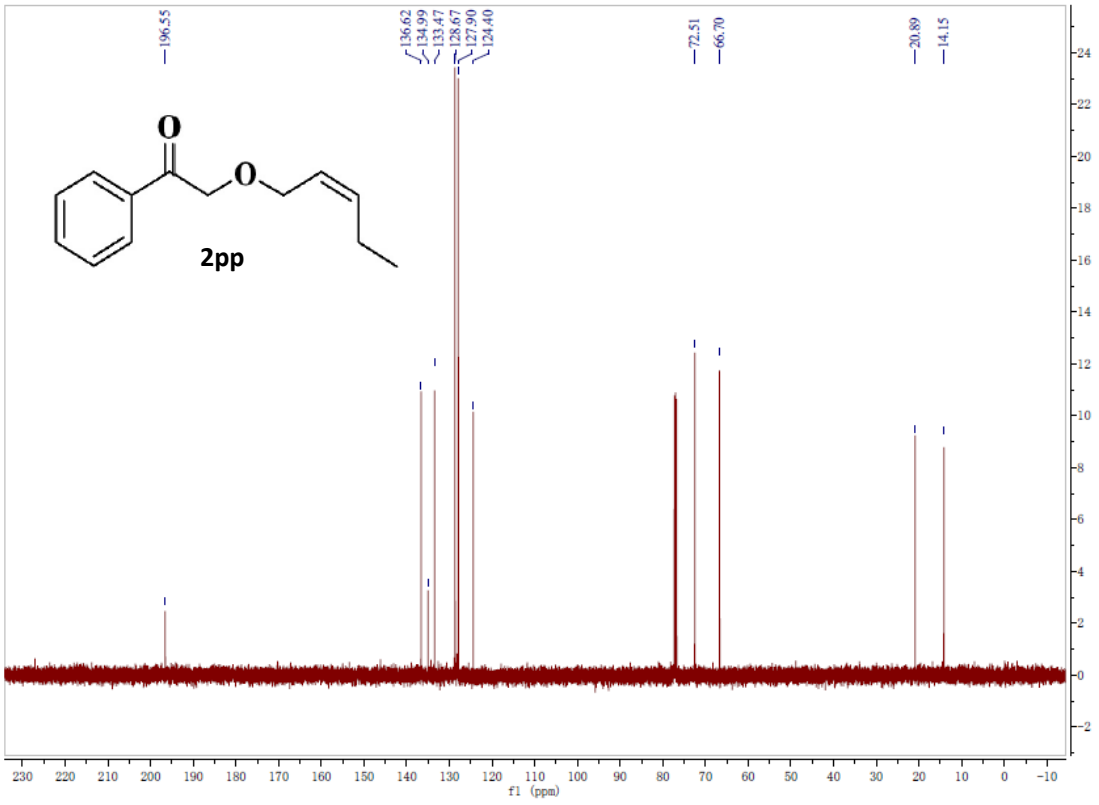
7.91
7.90
7.57
7.55
7.54
7.46
7.44
7.42
5.64
5.61
5.60
5.55
5.53
4.19
4.17
2.10
2.08
2.06
2.04
2.02
0.97
0.95
0.93
2.00
1.00
2.03
2.07
2.08
2.06
2.03
3.00
f1 (ppm)

2pp


196.55
136.62
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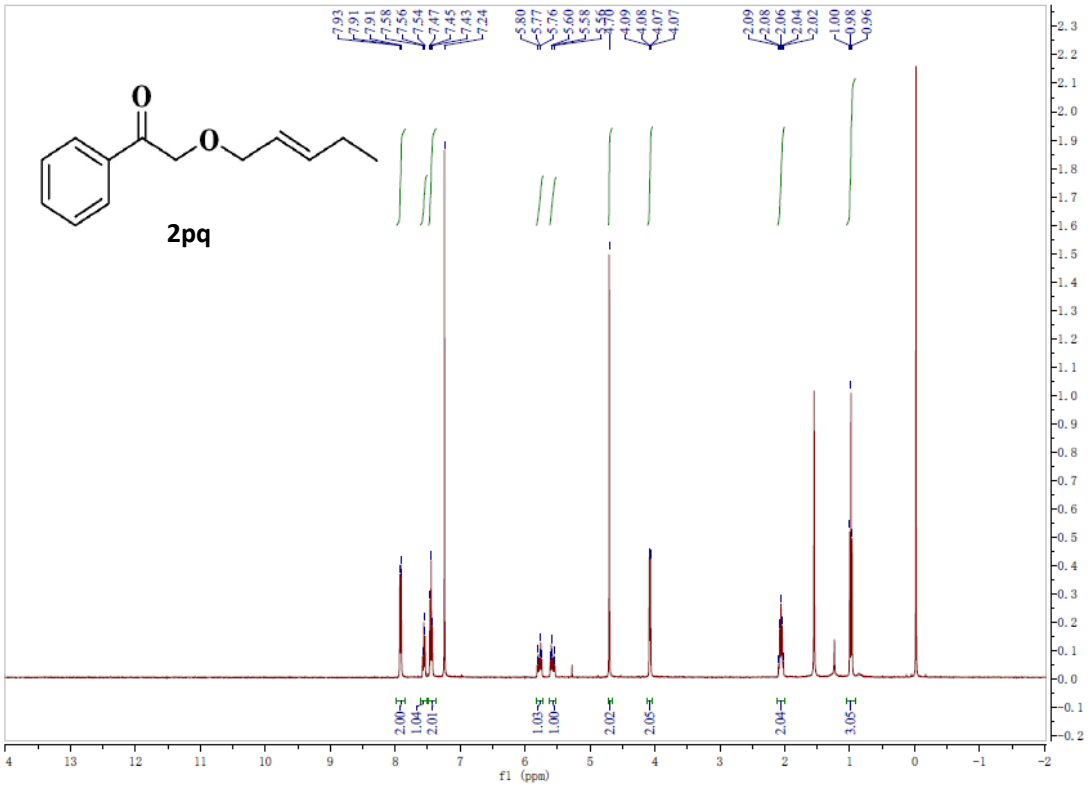
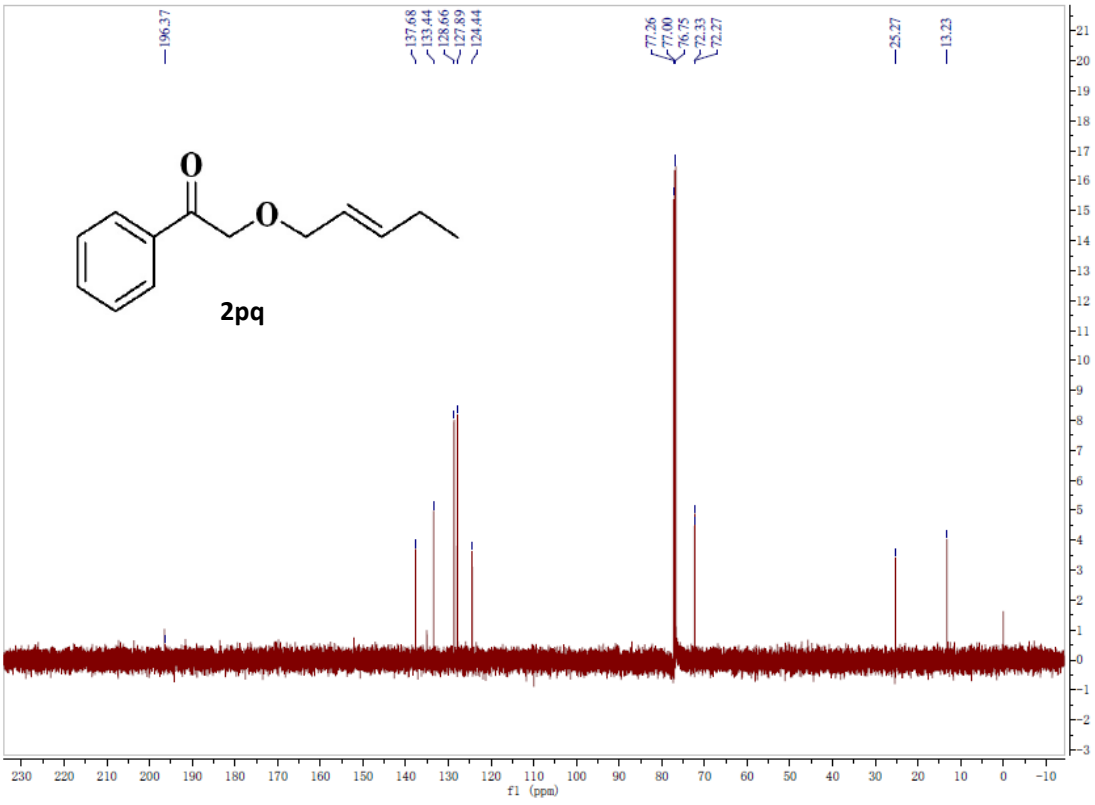
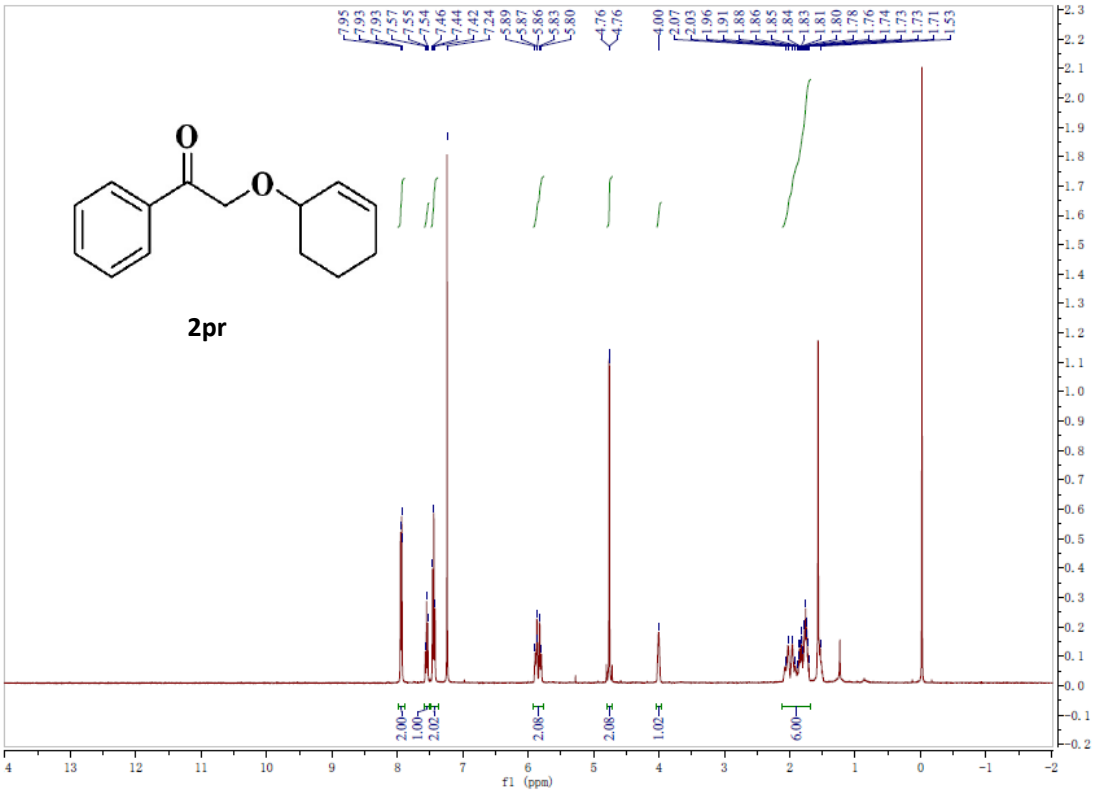
128.67
127.90
124.40
72.51
66.70
20.89
14.15
f1 (ppm)

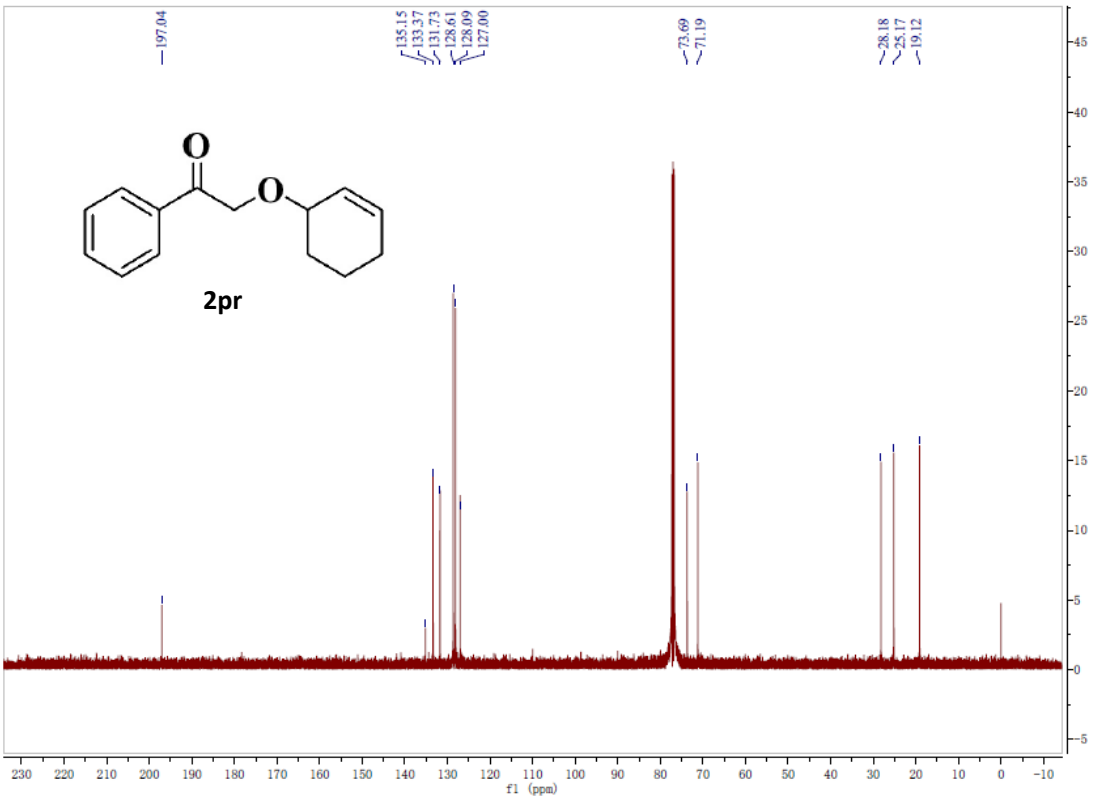
2pp


2pq
f1 (ppm)

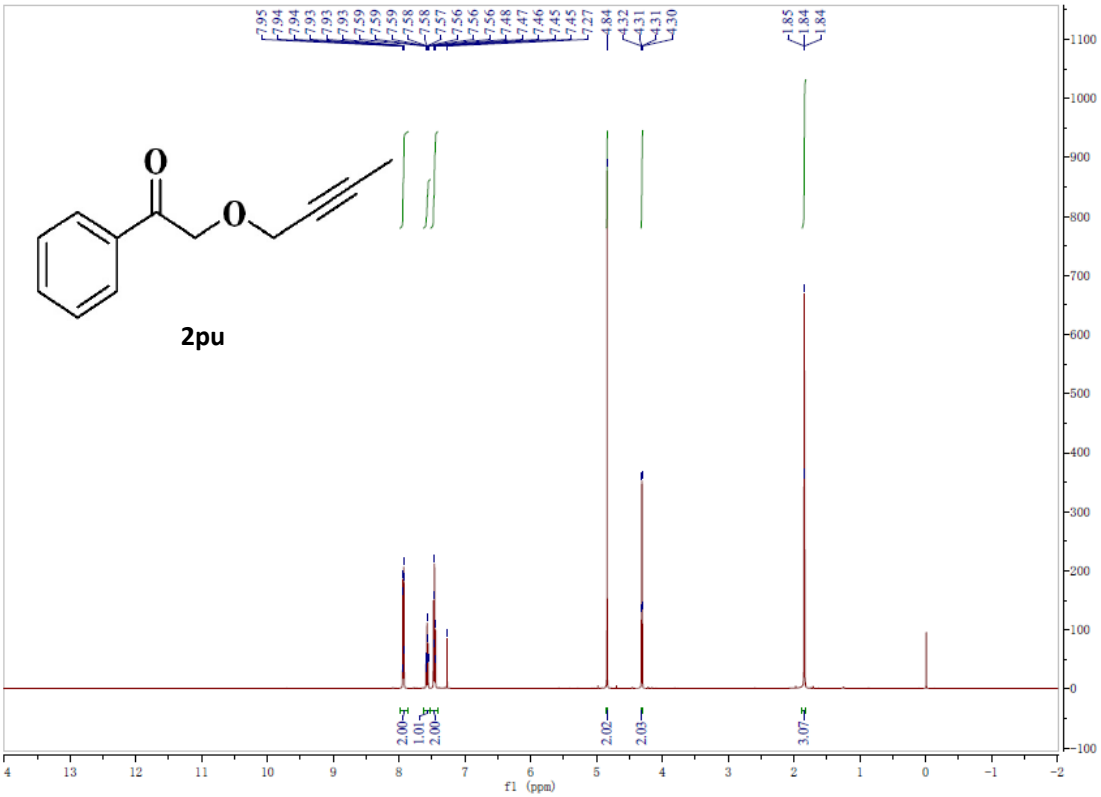

2pq
f1 (ppm)

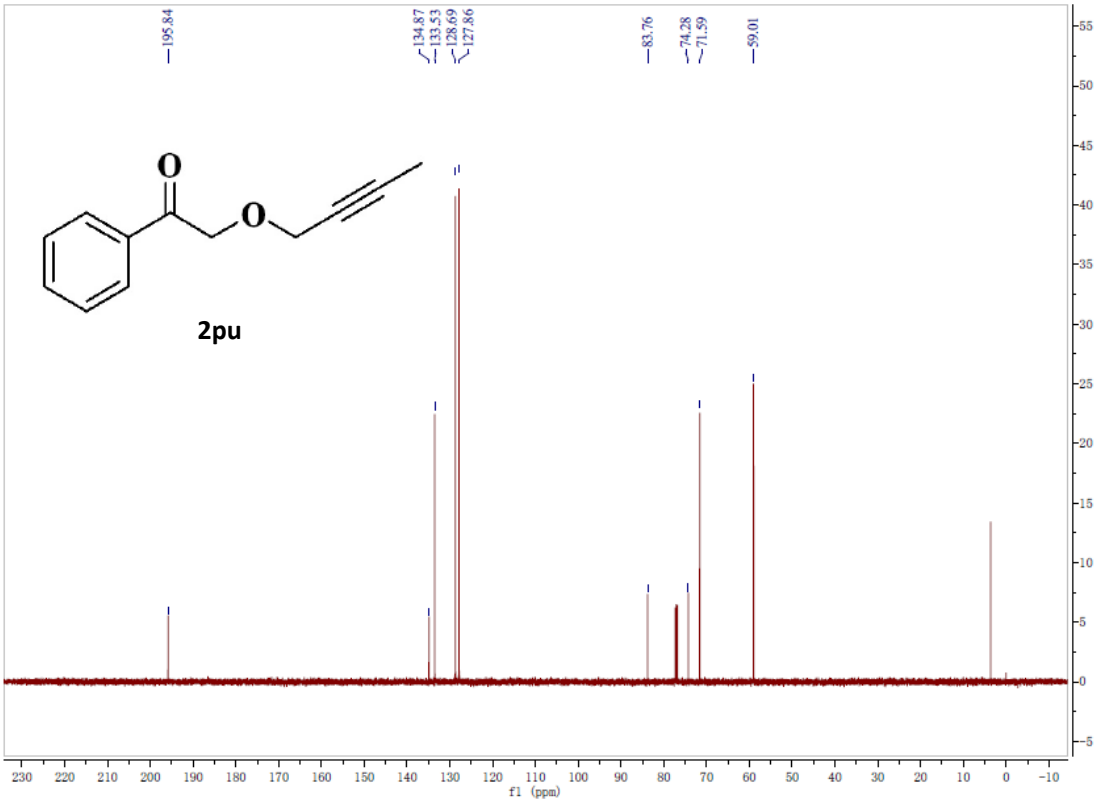

7.95
7.93
7.93
7.57
7.55
7.54
7.46
7.44
7.42
7.24
5.89
5.87
5.86
5.83
5.80
4.76
4.76
4.00
2.07
2.03
1.96
1.91
1.88
1.86
1.85
1.84
1.83
1.81
1.80
1.78
1.76
1.74
1.73
1.73
1.71
1.53
2.00
1.00
2.02
2.08
2.08
1.02
6.00
f1 (ppm)

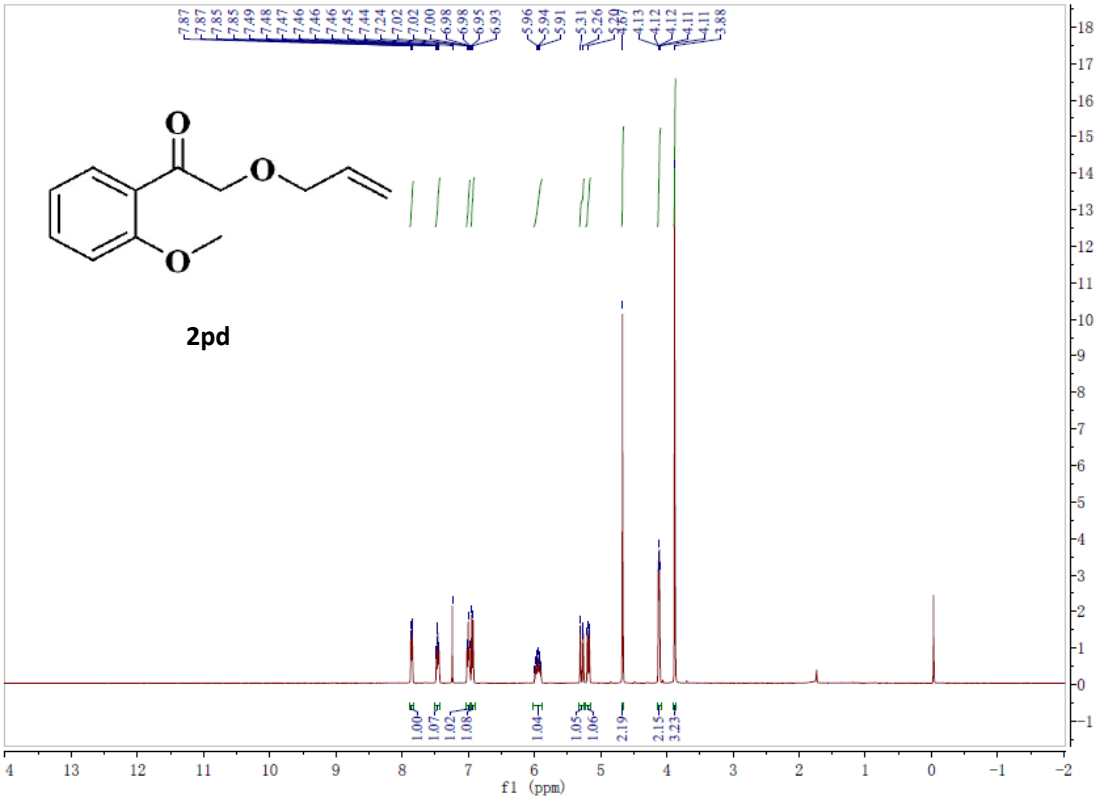
2pr

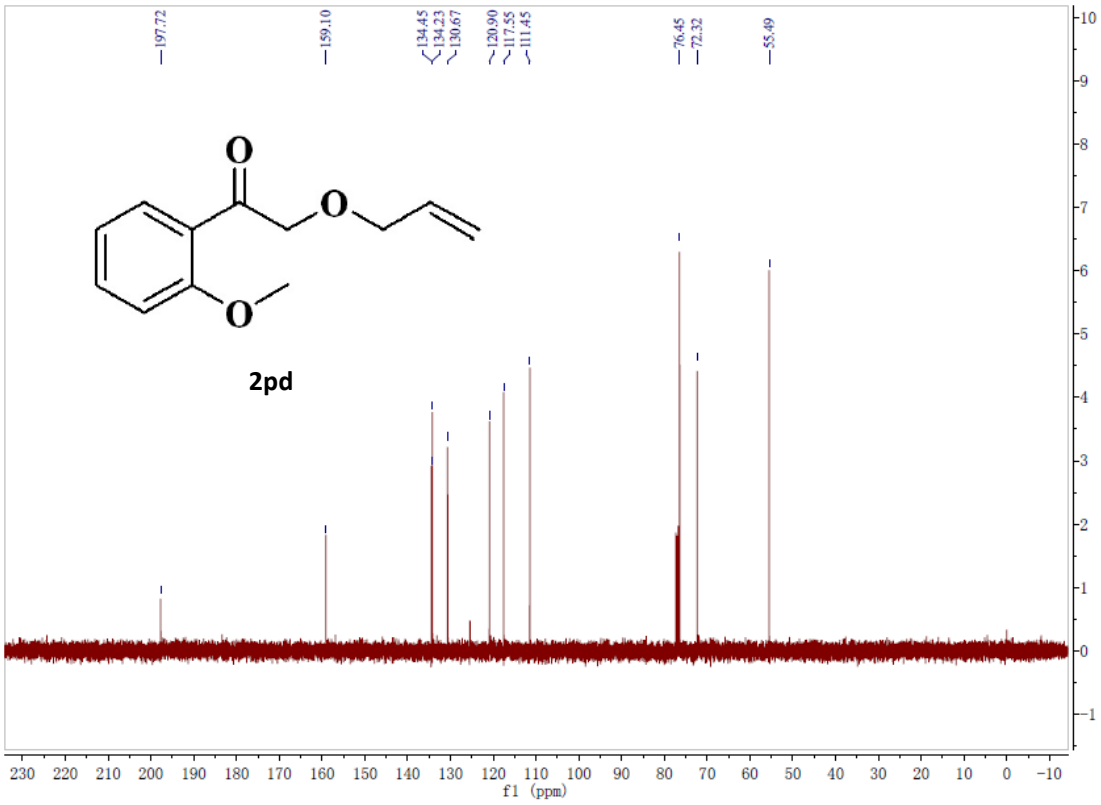

197.04
135.15
133.37
131.73
128.61
128.09
127.00
73.69
71.19
28.18
25.17
19.12
f1 (ppm)

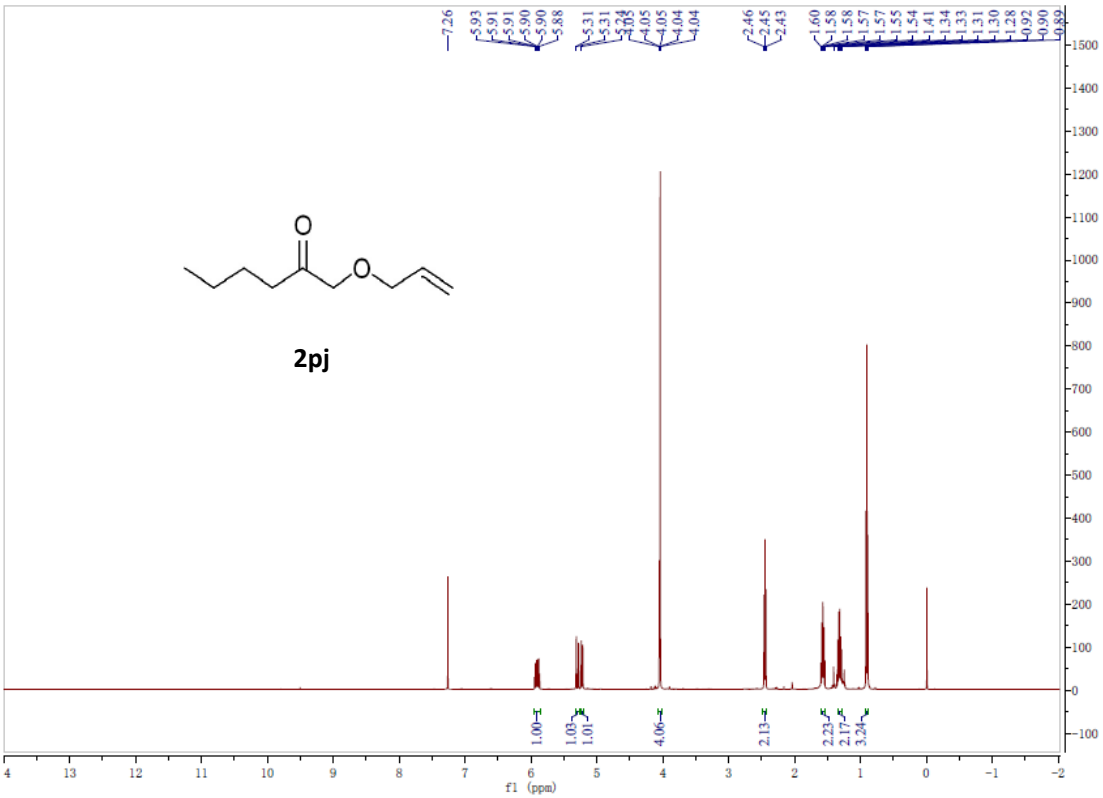
2pr

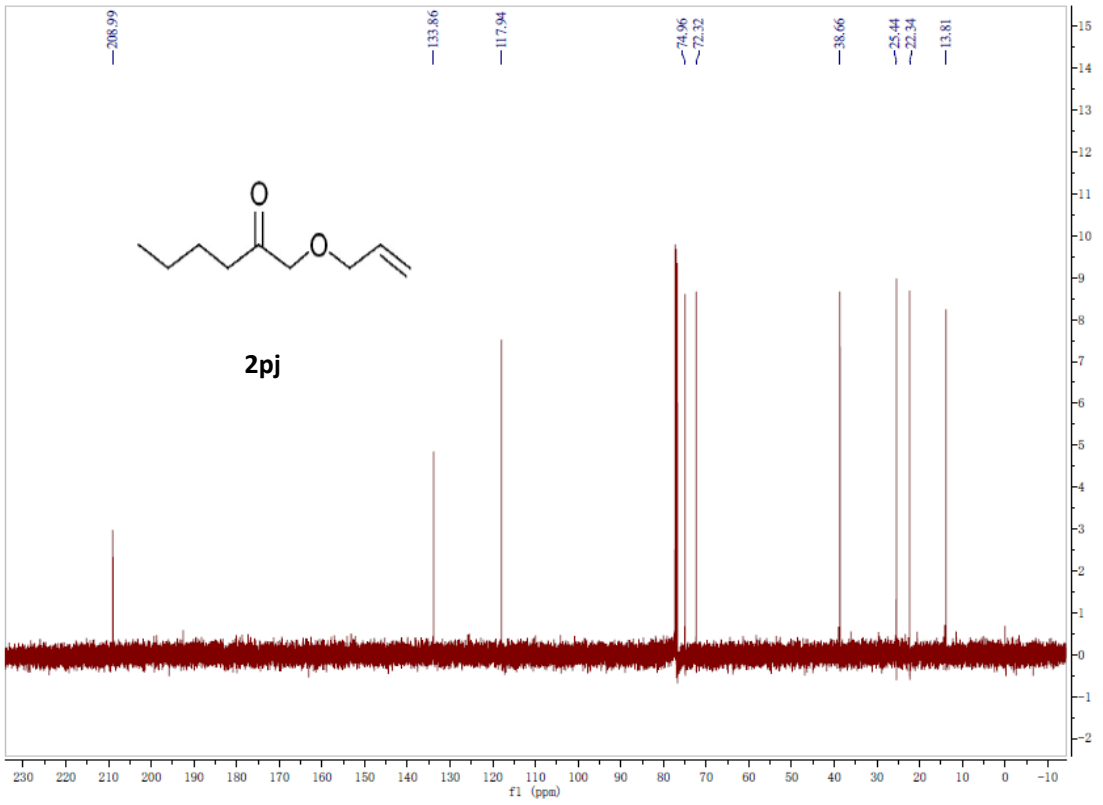

7.95
7.94
7.94
7.93
7.93
7.93
7.59
7.59
7.59
7.58
7.58
7.57
7.56
7.56
7.56
7.48
7.47
7.46
7.45
7.45
7.27
4.84
4.32
4.31
4.31
4.30
1.85
1.84
1.84
O
O
2pu
2.00
1.01
2.00
2.02
2.03
3.07
f1 (ppm)

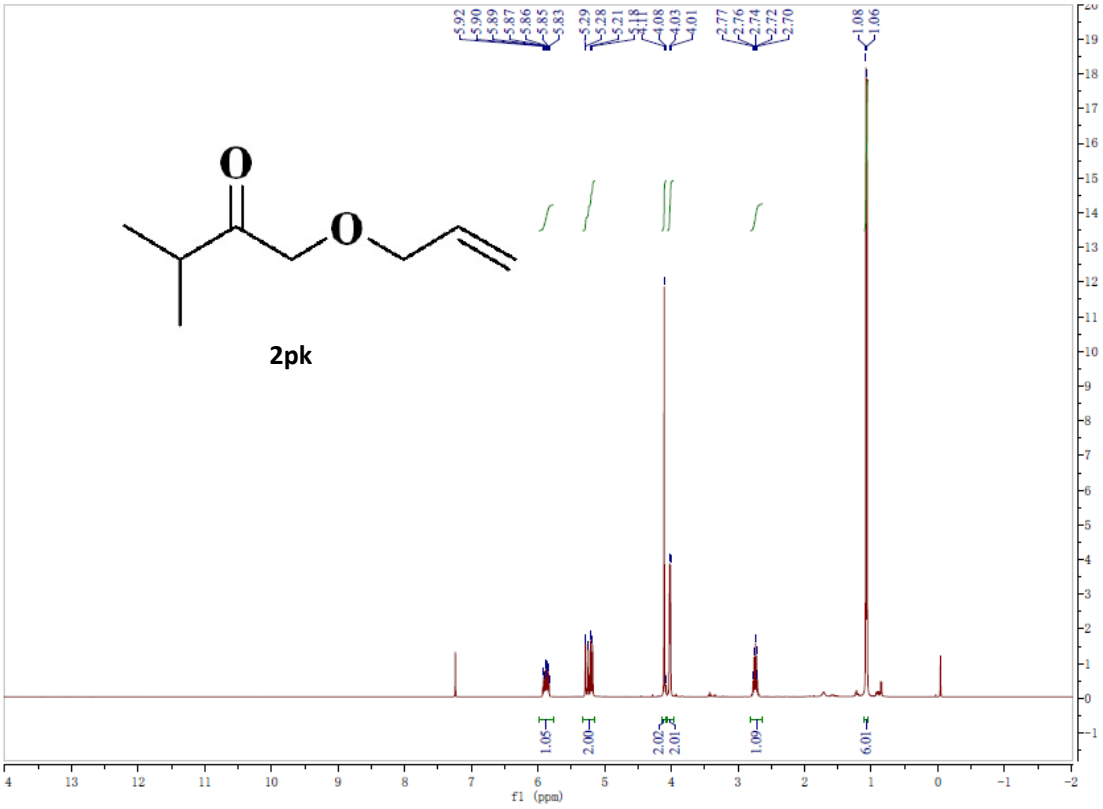

195.84
134.87
133.53
128.69
127.86
83.76
74.28
71.59
59.01
O
O
2pu
f1 (ppm)

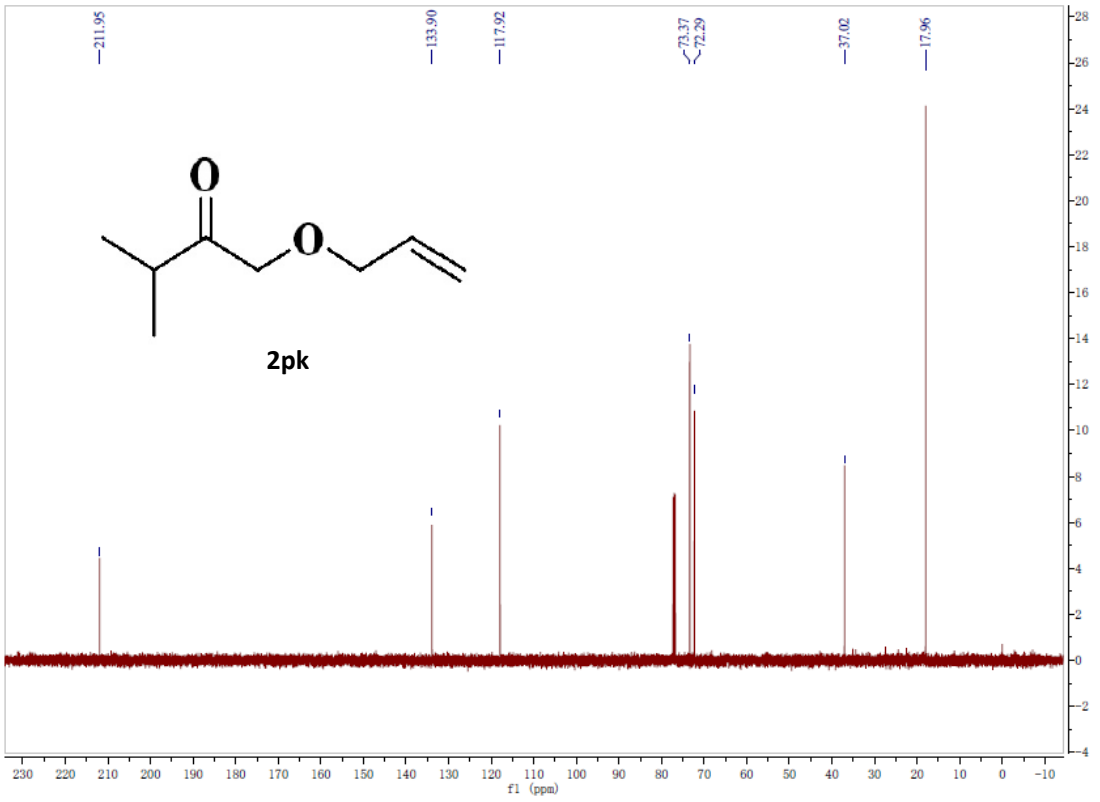

2pd
f1 (ppm)

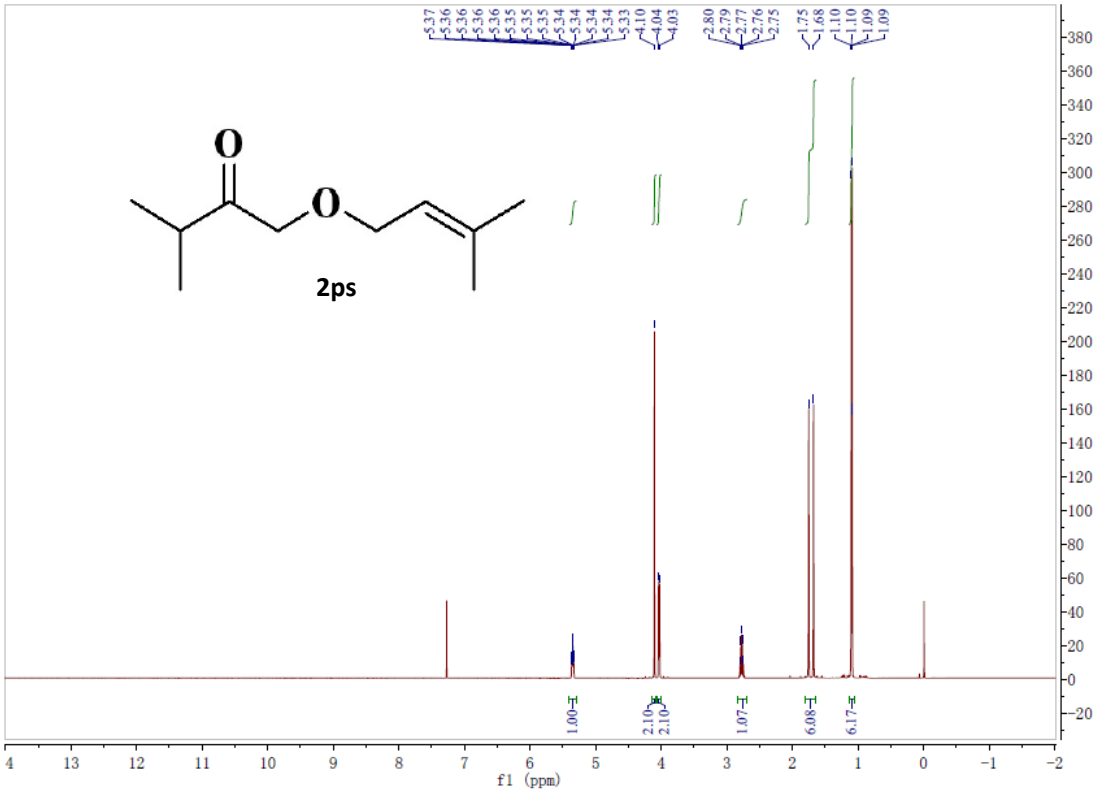

2pd
f1 (ppm)

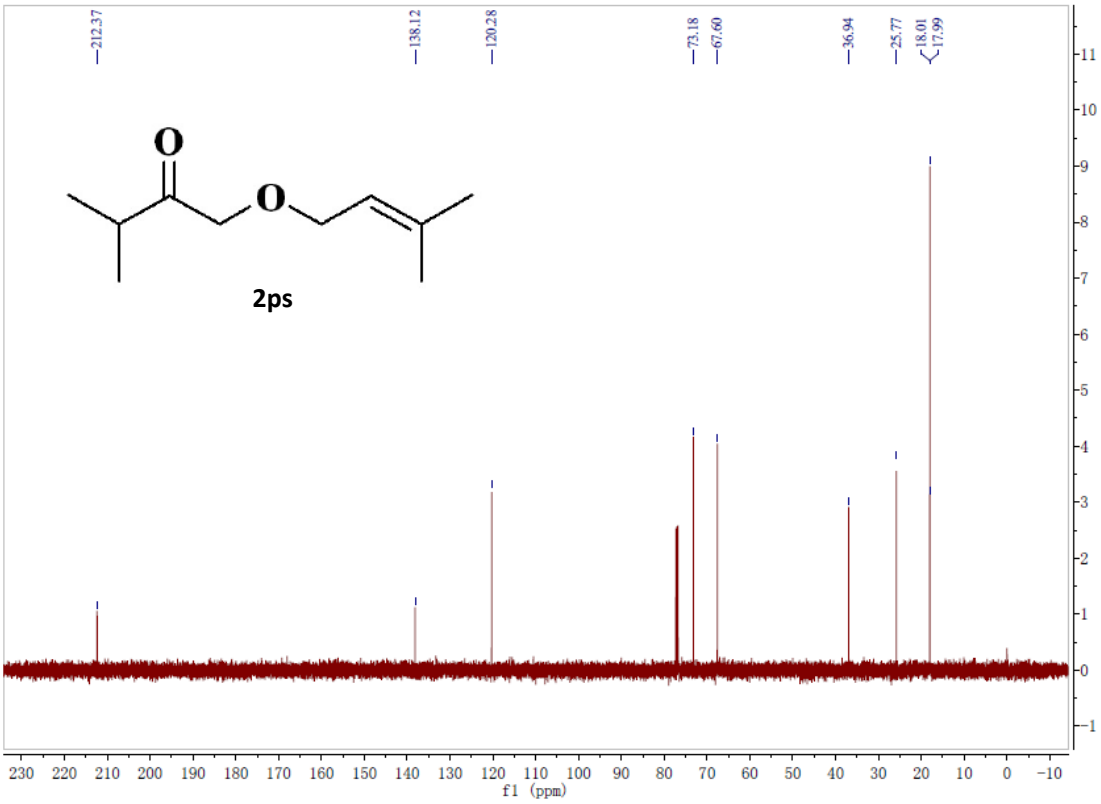

2pj
f1 (ppm)

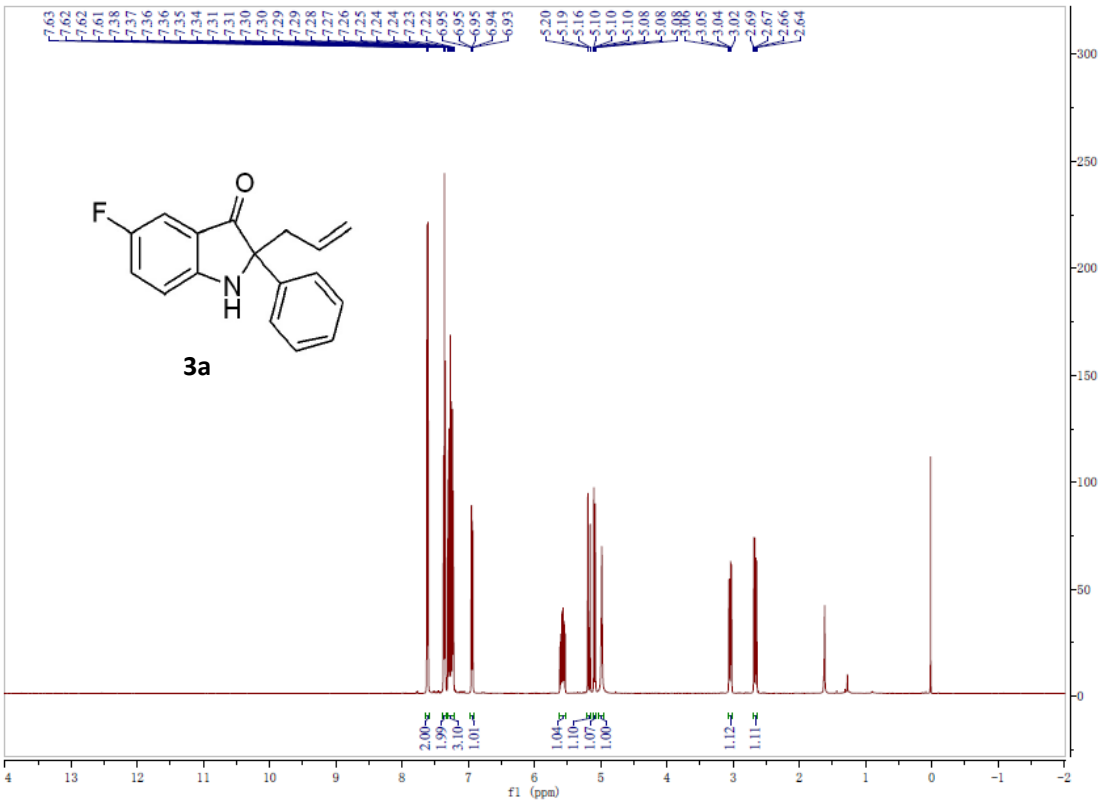

2pj
f1 (ppm)


5.92
5.90
5.89
5.87
5.86
5.85
5.83
5.29
5.28
5.21
5.18
4.08
4.03
4.01
2.77
2.76
2.74
2.72
2.70
1.08
1.06
O
O
2pk
1.05
2.00
2.02
2.01
1.09
6.01
f1 (ppm)

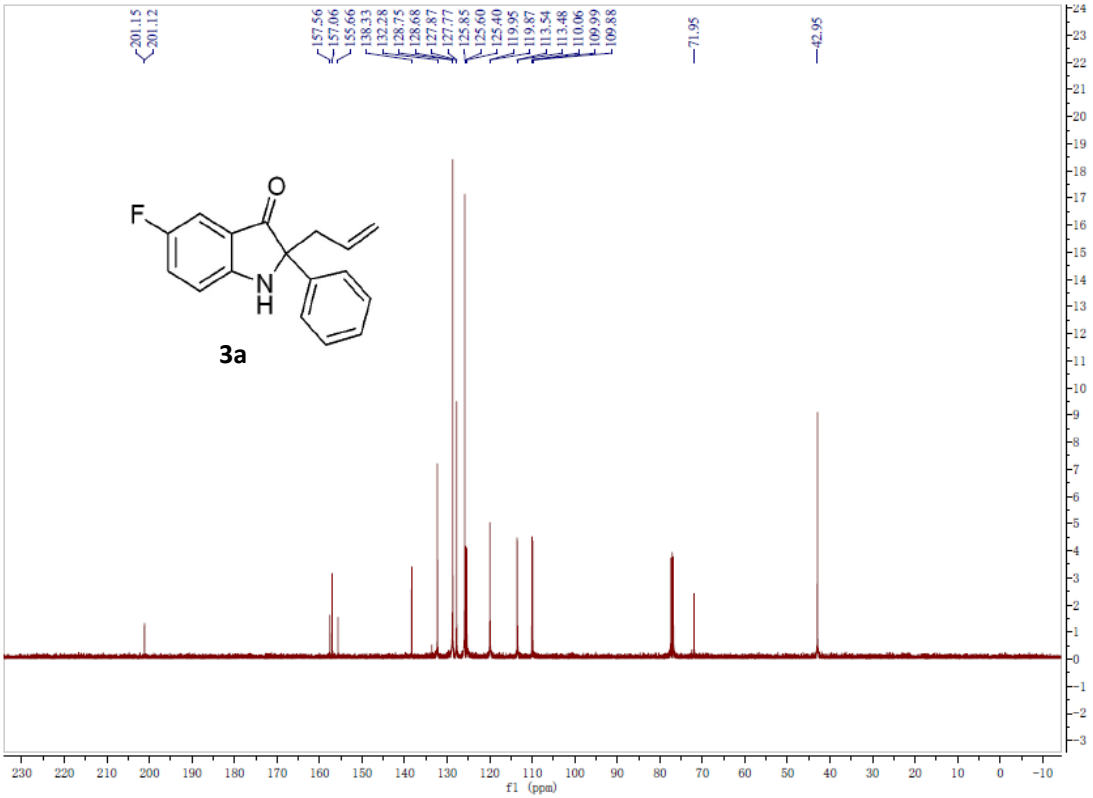

211.95
133.90
117.92
73.37
72.29
37.02
17.96
O
O
2pk
f1 (ppm)

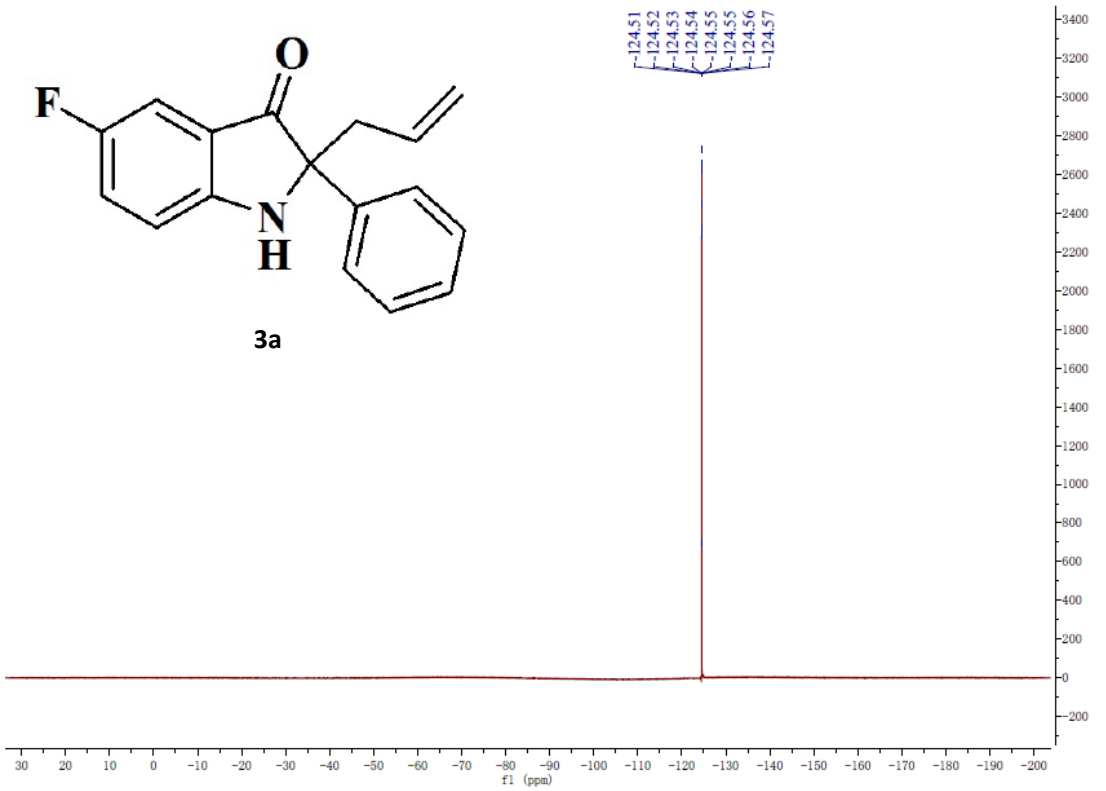

2ps
f1 (ppm)


2ps
f1 (ppm)

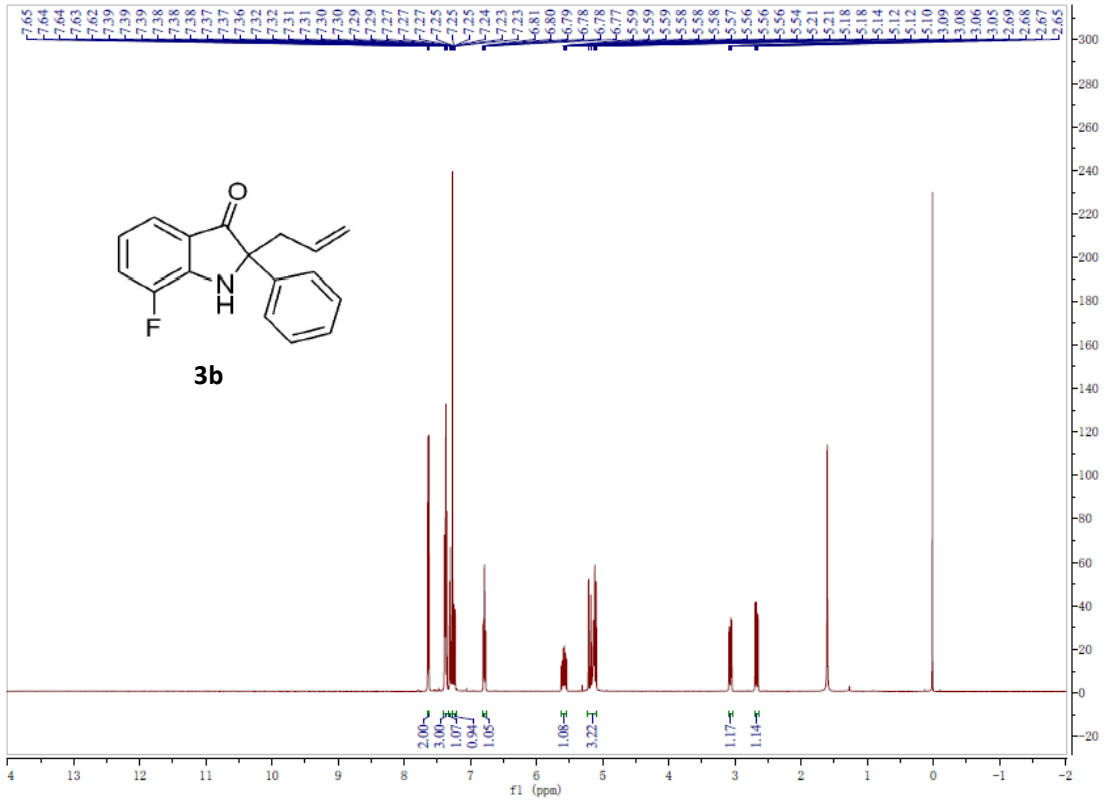


ZZ

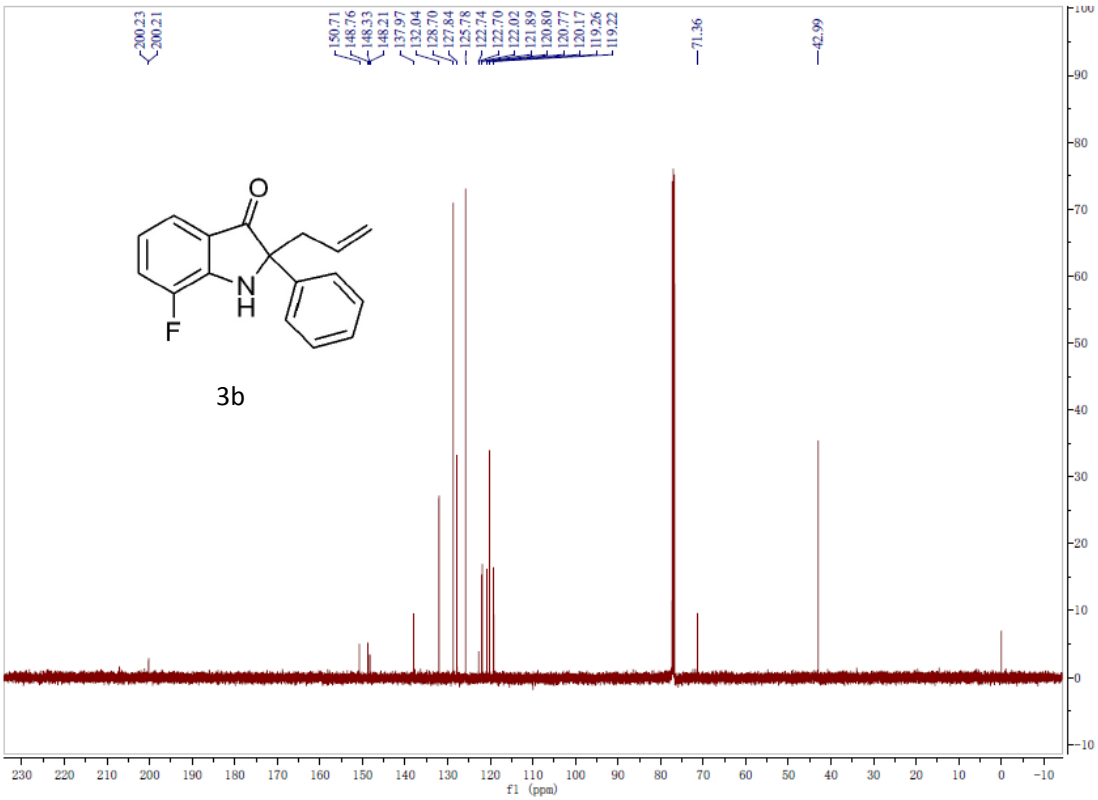



F
O
N
H
-124.51
-124.52
-124.53
-124.54
-124.55
-124.55
-124.56
-124.57
f1 (ppm)

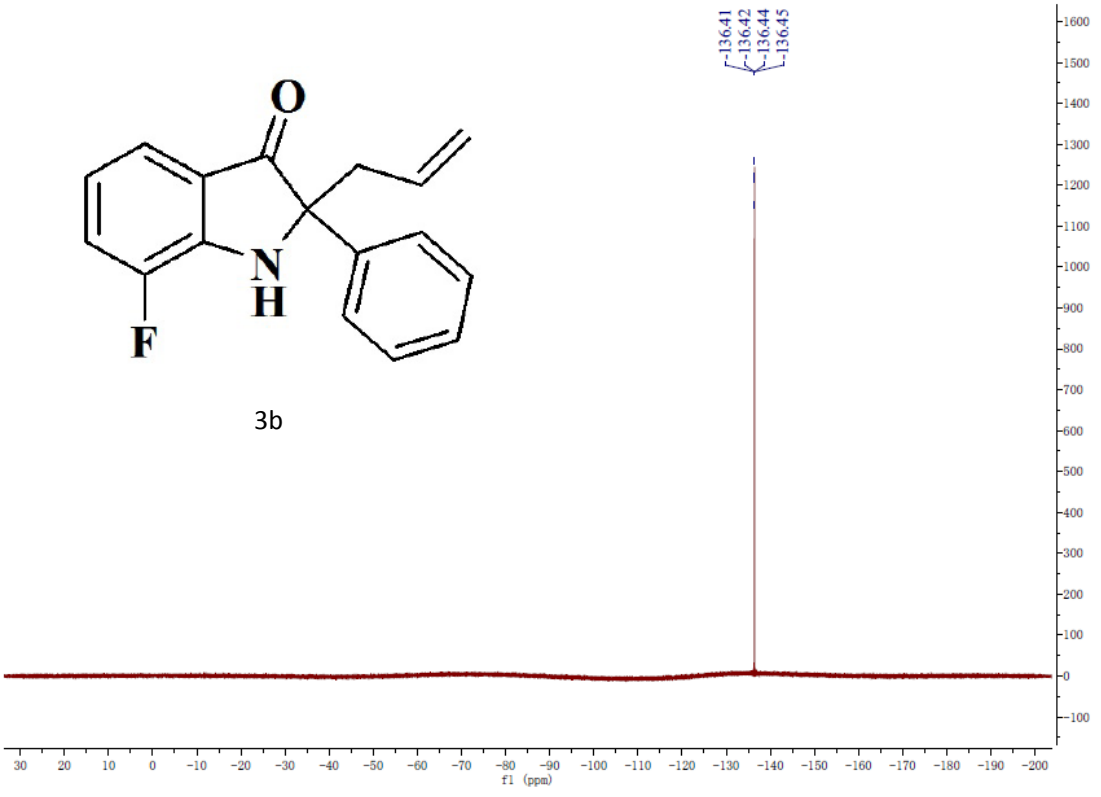
3a


O
N
H
F
f1 (ppm)

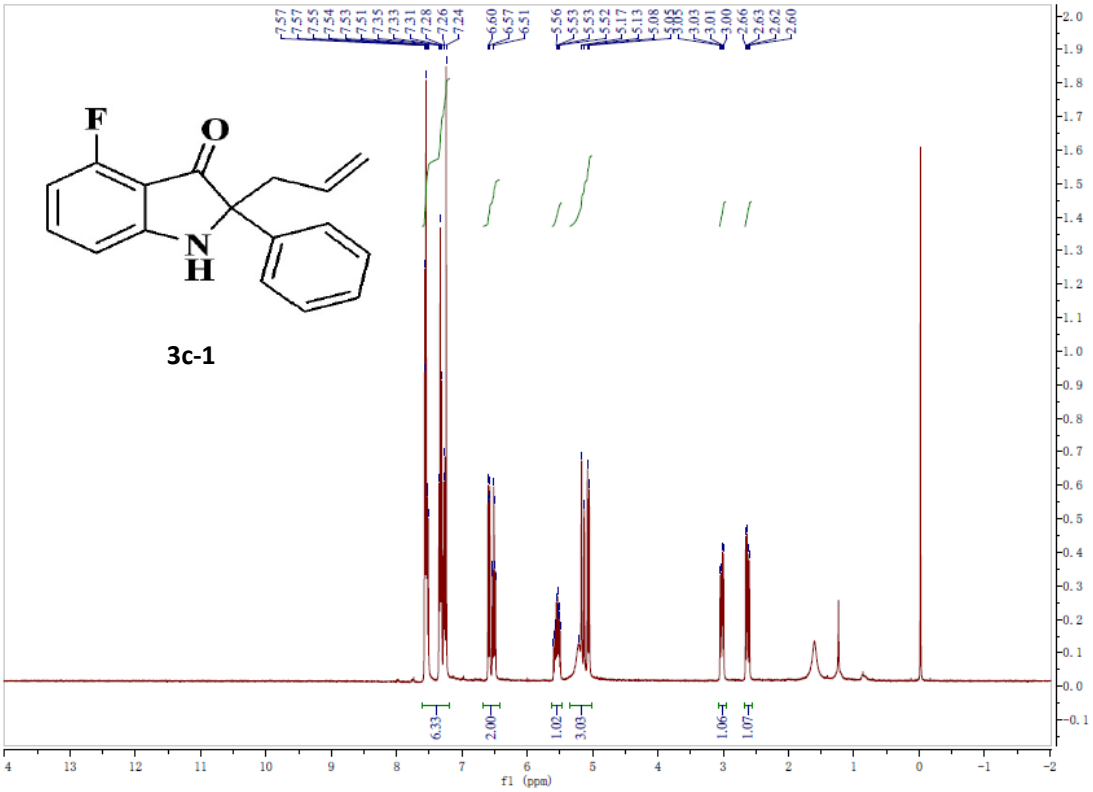
3b

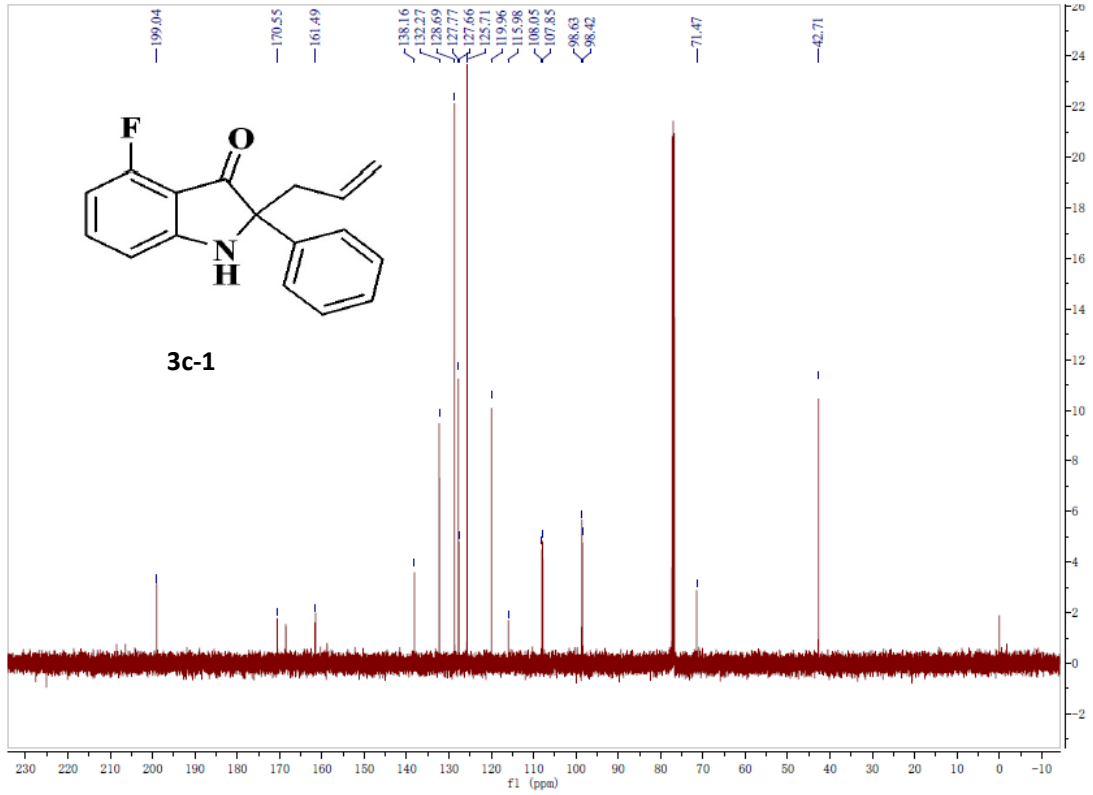

200.23
200.21
150.71
148.76
148.33
148.21
137.97
132.04
128.70
127.84
125.78
122.74
122.70
122.02
121.89
120.80
120.77
120.17
119.26
119.22
71.36
42.99
O
N
H
F
f1 (ppm)

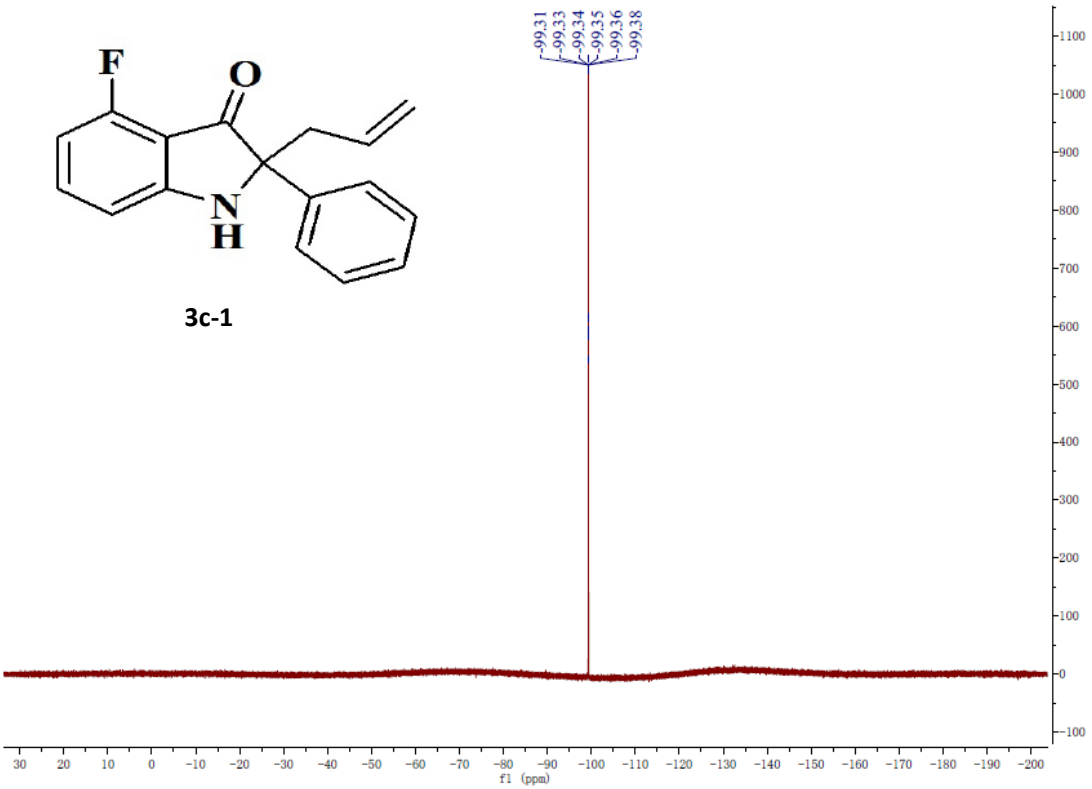
3b


136.41
136.42
136.44
136.45
O
N
H
F
f1 (ppm)

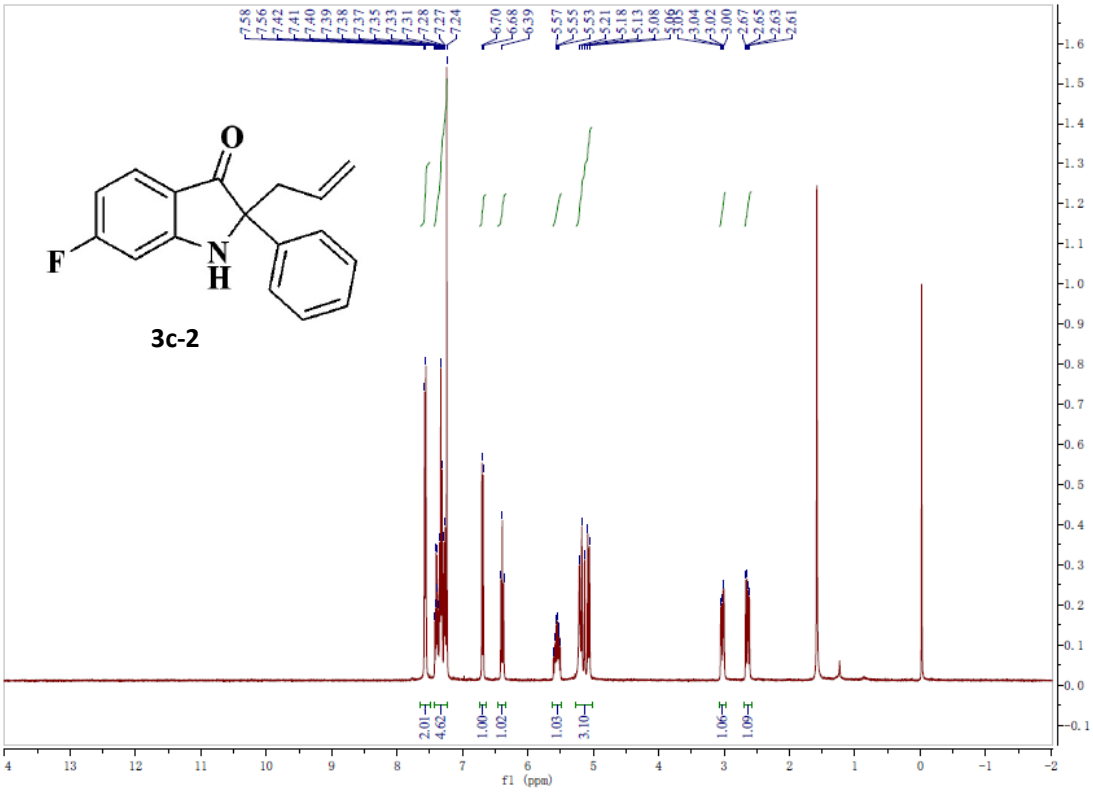
3b


F
O
N
H
3c-1
f1 (ppm)

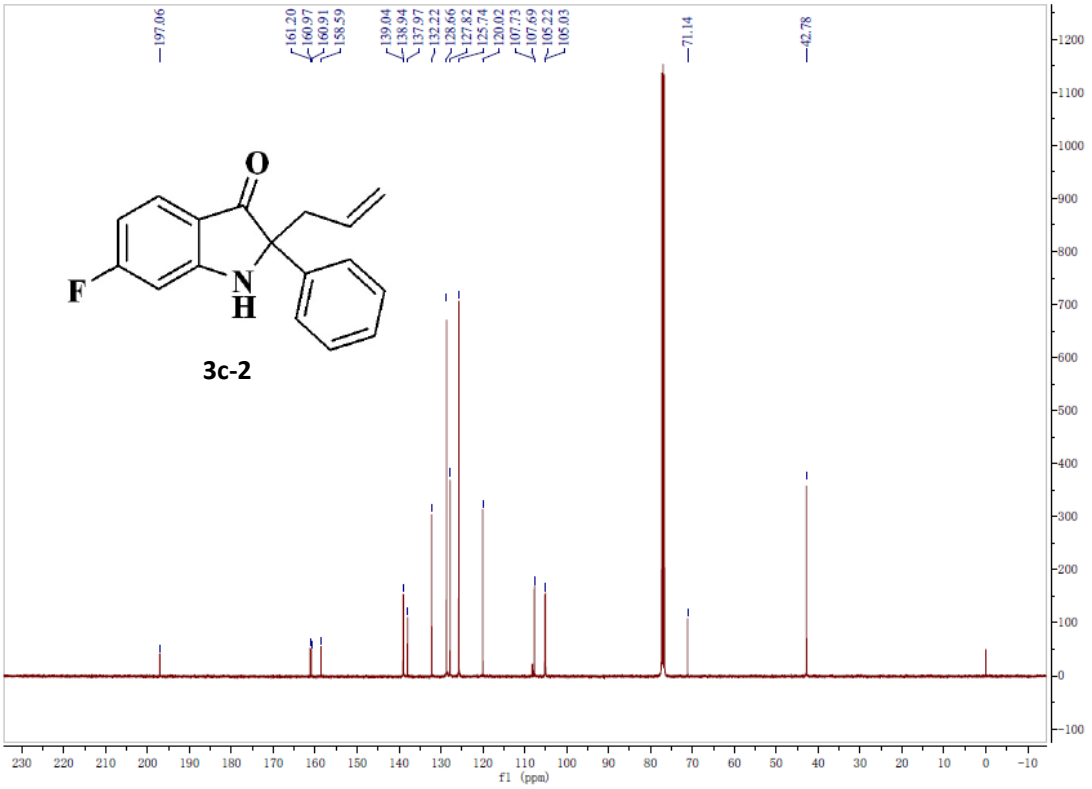

F
O
N
H
3c-1
f1 (ppm)


F
O
N
H
-99.31
-99.33
-99.34
-99.35
-99.36
-99.38
f1 (ppm)

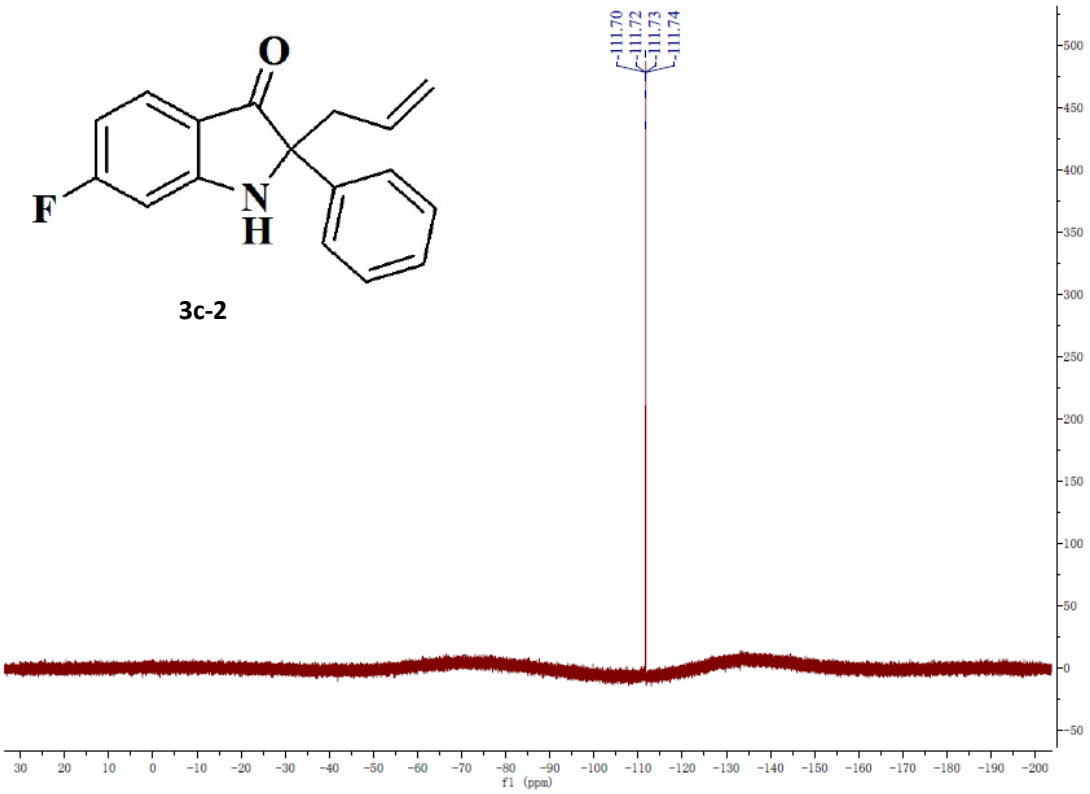
3c-1


7.58
7.56
7.42
7.41
7.40
7.39
7.38
7.37
7.35
7.33
7.31
7.28
7.27
7.24
6.70
6.68
6.39
5.57
5.55
5.53
5.21
5.18
5.13
5.08
3.04
3.02
3.00
2.67
2.65
2.63
2.61
O
N
H
F
2.01
4.62
1.00
1.02
1.03
3.10
1.06
1.09
f1 (ppm)

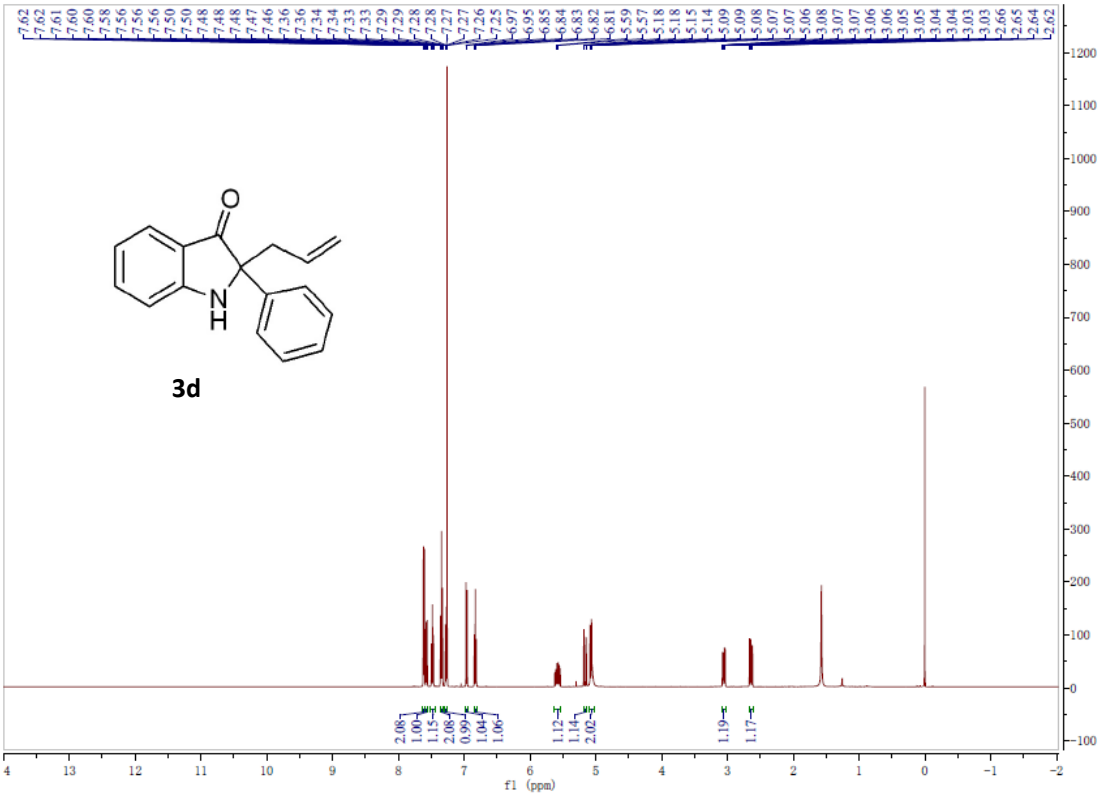
3c-2

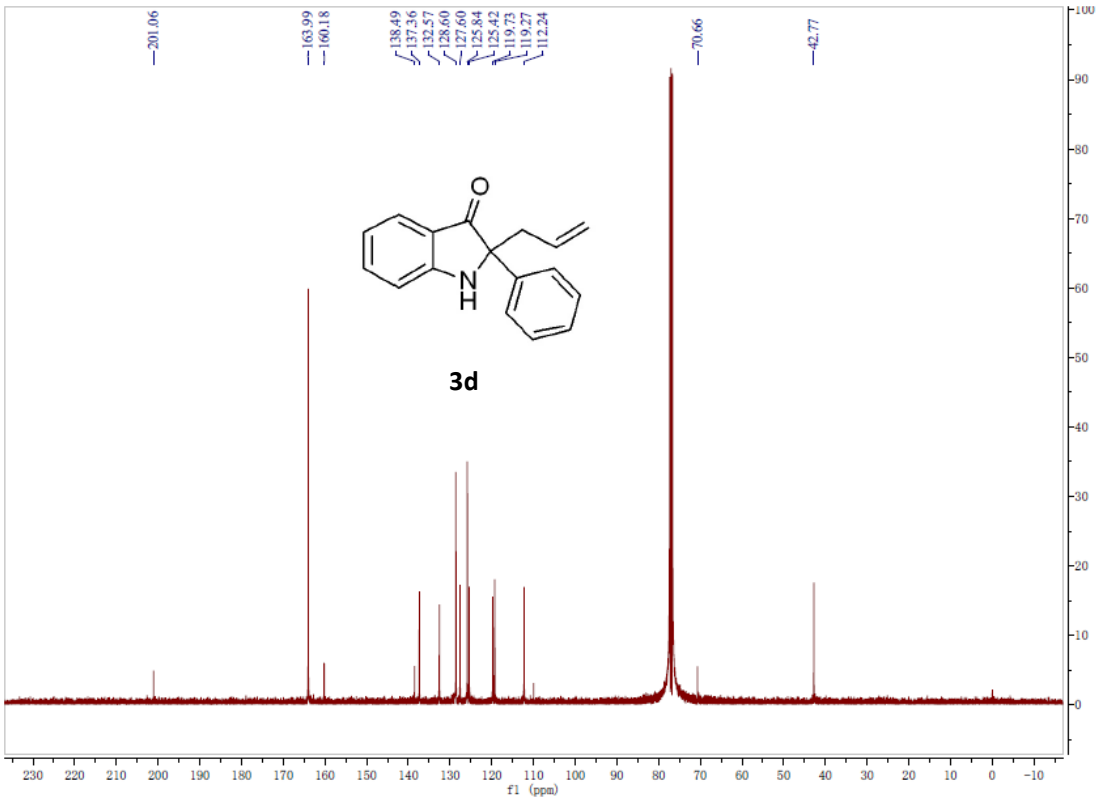

197.06
161.20
160.97
160.91
158.59
139.04
138.94
137.97
132.22
128.66
127.82
125.74
120.02
107.73
107.69
105.22
105.03
71.14
42.78
O
F
N
H
f1 (ppm)

3c-2


111.70
111.72
111.73
111.74
O
F
N
H
f1 (ppm)

3c-2


7.62
7.62
7.61
7.60
7.60
7.58
7.56
7.56
7.56
7.50
7.50
7.48
7.48
7.48
7.47
7.46
7.36
7.36
7.34
7.34
7.33
7.33
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
6.97
6.95
6.85
6.84
6.83
6.82
6.81
5.59
5.57
5.18
5.18
5.15
5.14
5.09
5.09
5.08
5.07
5.07
5.06
3.08
3.07
3.07
3.06
3.06
3.05
3.05
3.04
3.04
3.03
3.03
2.66
2.65
2.64
2.62
O
N
H
3d
2.08
1.00
1.15
2.08
0.99
1.04
1.06
1.12
1.14
2.02
1.19
1.17
f1 (ppm)


201.06
163.99
160.18
138.49
137.36
132.57
128.60
127.60
125.84
125.42
119.73
119.27
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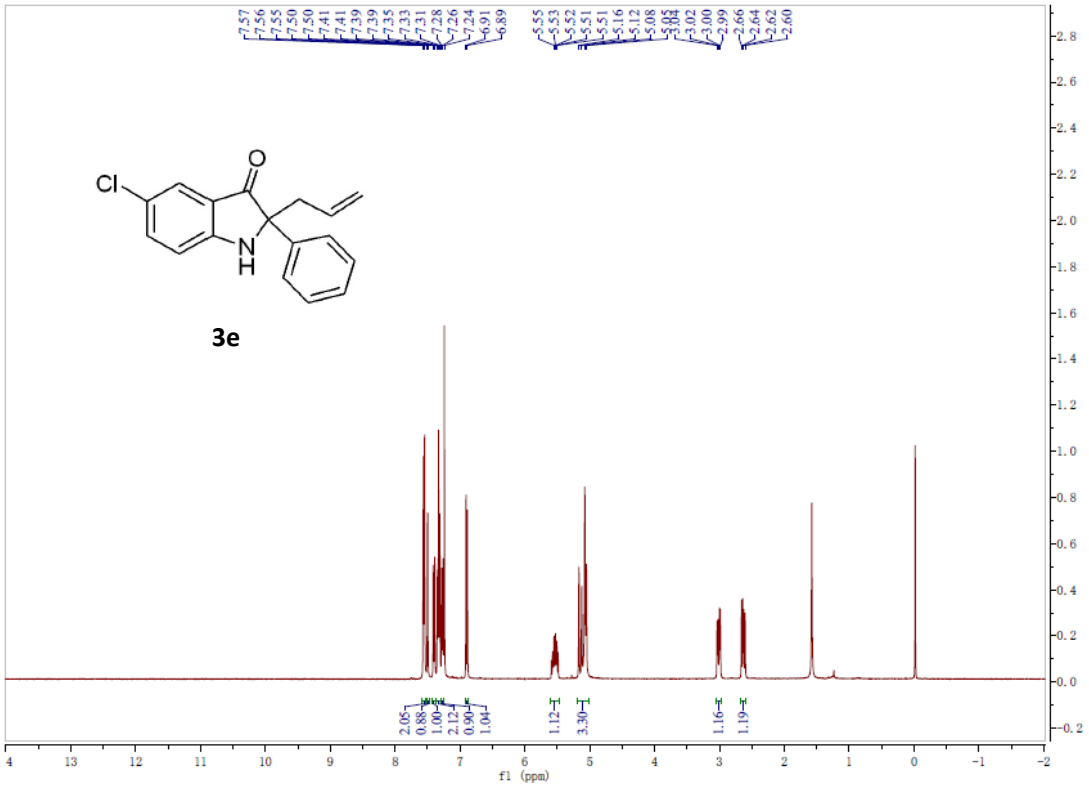
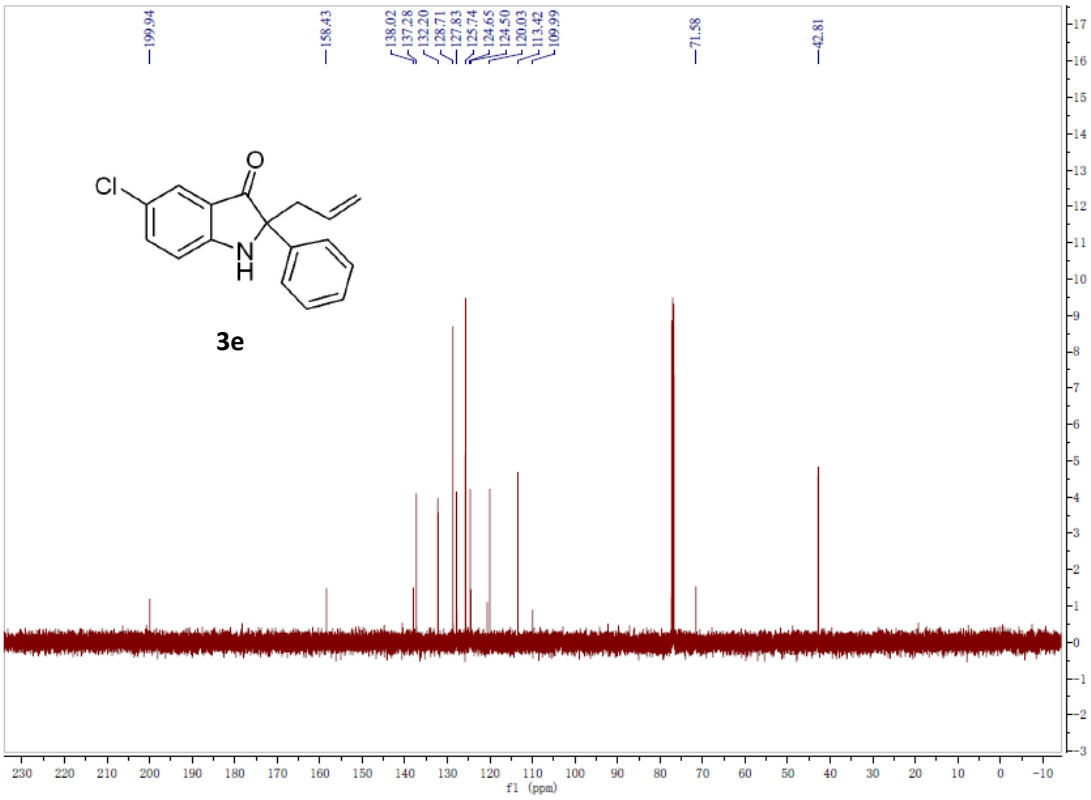
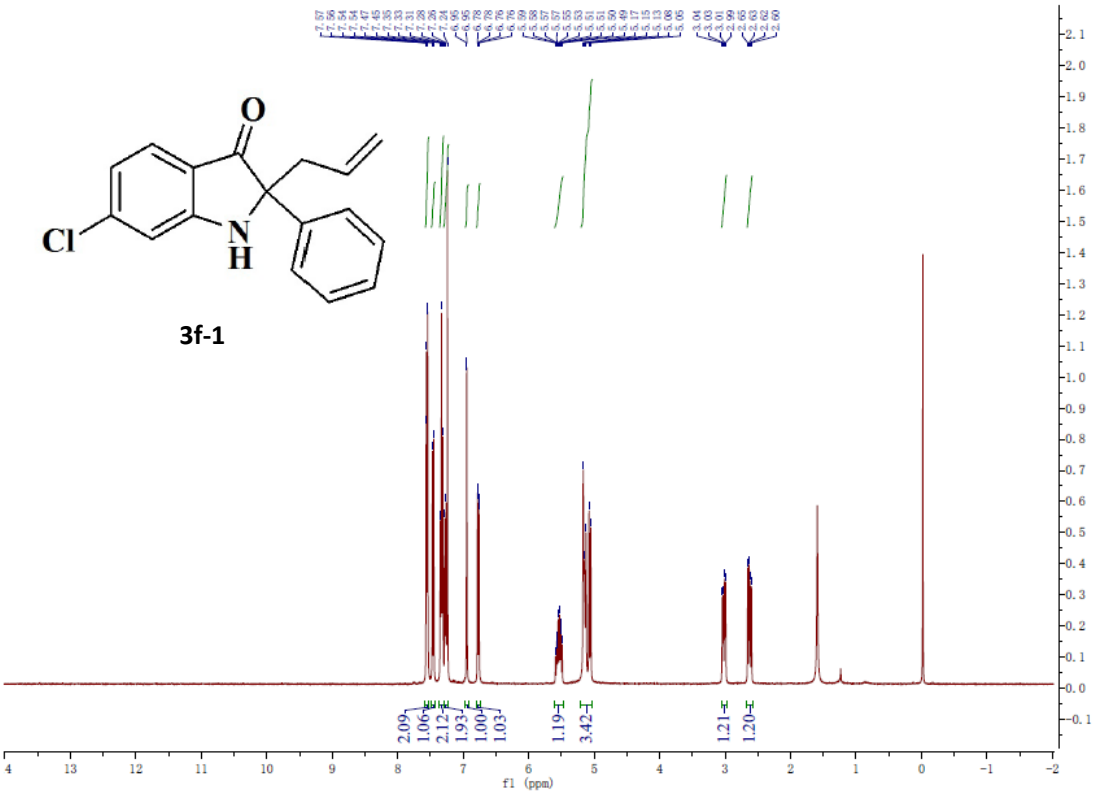
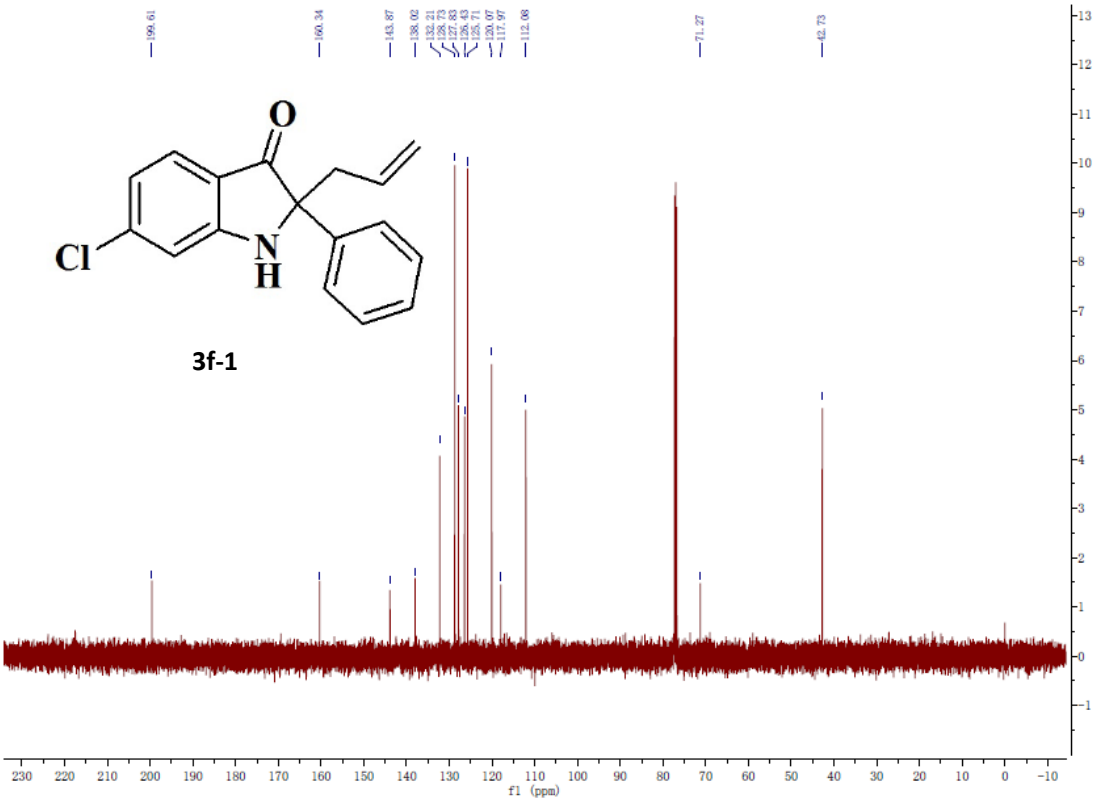
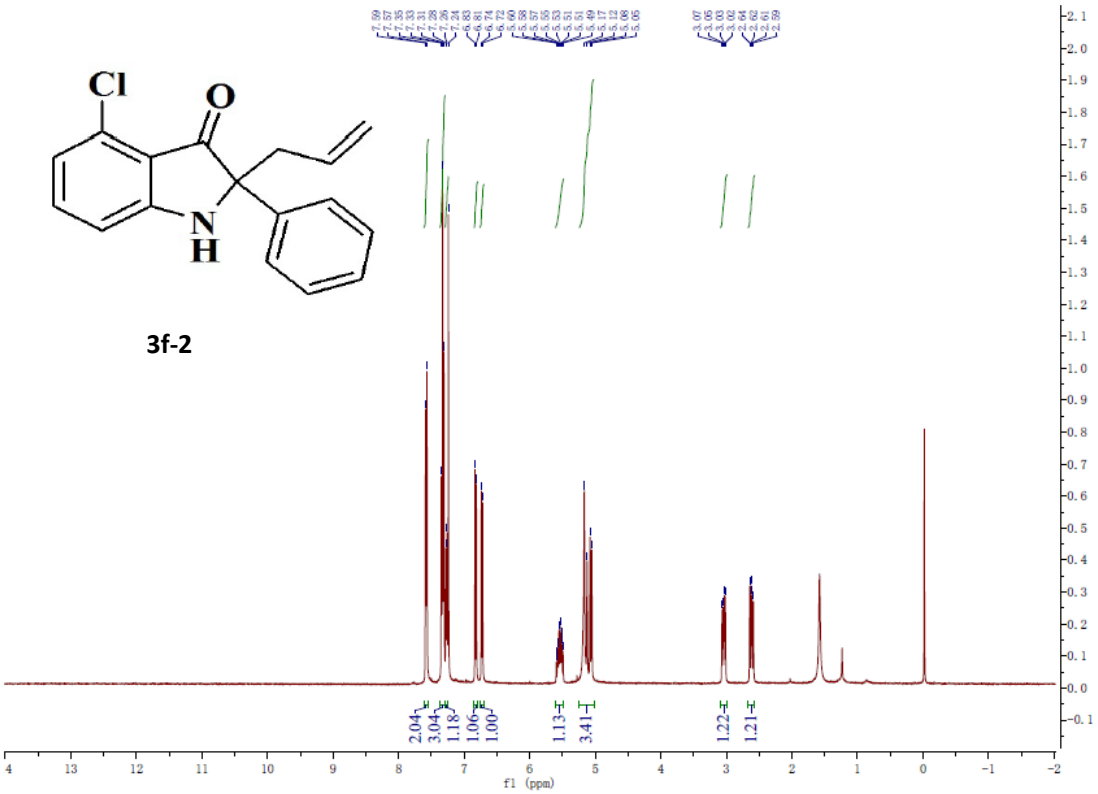
70.66
42.77
O
N
H
3d
f1 (ppm)

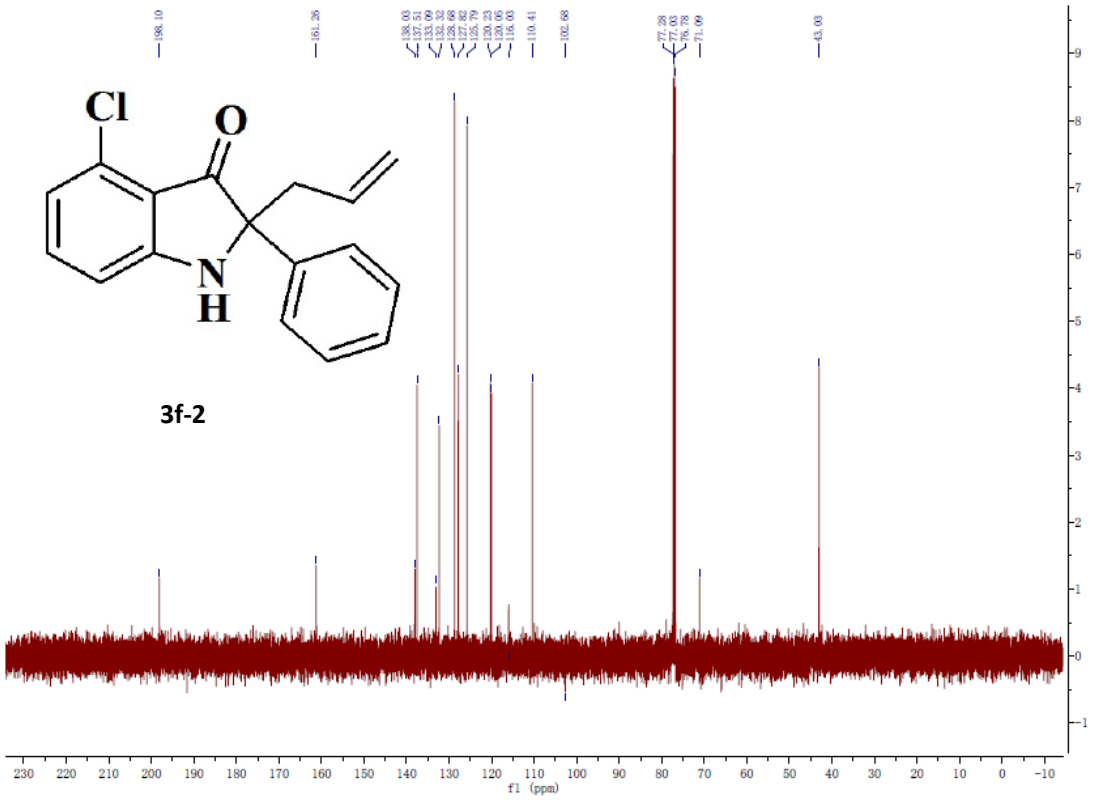

7.57
7.56
7.55
7.50
7.50
7.41
7.41
7.39
7.39
7.35
7.33
7.31
7.28
7.26
7.24
6.91
6.89
5.55
5.53
5.52
5.51
5.51
5.16
5.12
5.08
3.02
3.00
2.99
2.66
2.64
2.62
2.60
Cl
O
N
H
3e
2.05
0.88
1.00
2.12
0.90
1.04
1.12
3.30
1.16
1.19
f1 (ppm)

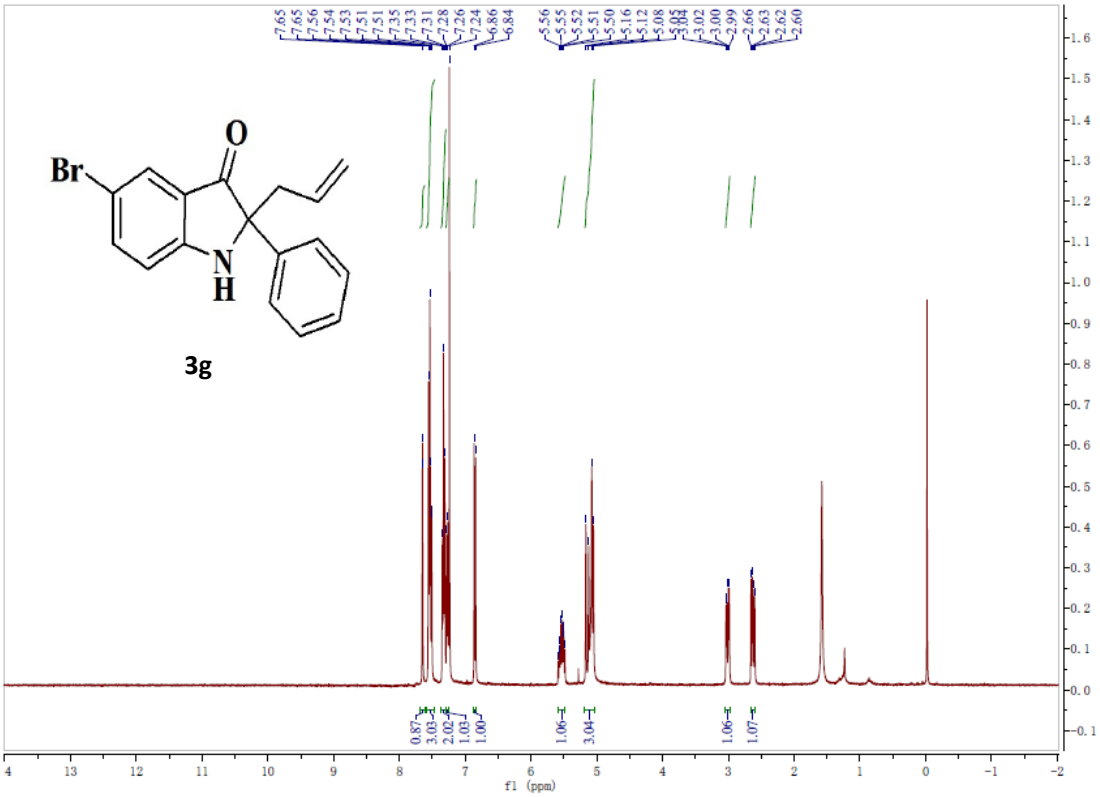

199.94
158.43
138.02
137.28
132.20
128.71
127.83
125.74
124.65
124.50
120.03
113.42
109.99
71.58
42.81
Cl
O
N
H
3e
f1 (ppm)

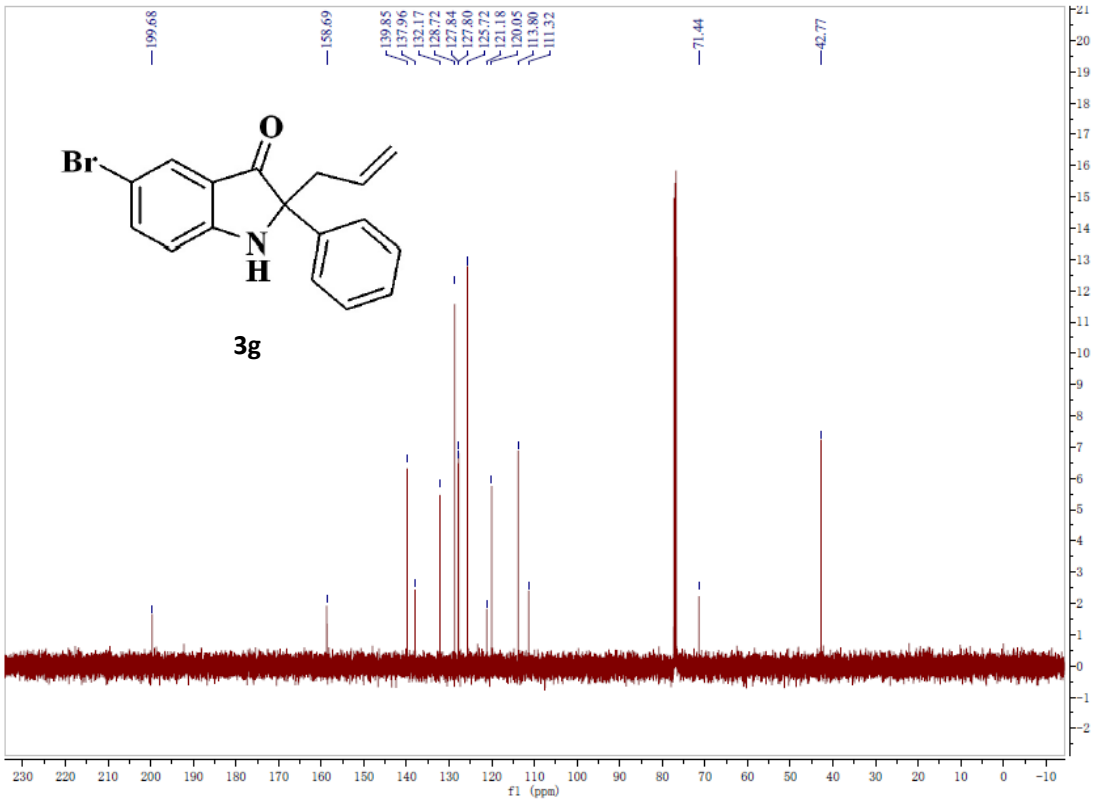

O
Cl
N
H
3f-1
f1 (ppm)


O
Cl
N
H
3f-1
f1 (ppm)


Cl
O
N
H
3f-2
2.04
3.04
1.18
1.06
1.00
1.13
3.41
1.22
1.21
f1 (ppm)


Cl
O
N
H
3f-2
f1 (ppm)


7.65
7.56
7.54
7.53
7.51
7.35
7.33
7.31
7.28
7.26
7.24
6.86
6.84
5.56
5.55
5.52
5.51
5.50
5.16
5.12
5.08
3.04
3.02
3.00
2.99
2.66
2.63
2.62
2.60
0.87
3.03
2.02
1.03
1.00
1.06
3.04
1.06
1.07
f1 (ppm)
Br
O
N
H
3g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158.69
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132.17
128.72
127.84
127.80
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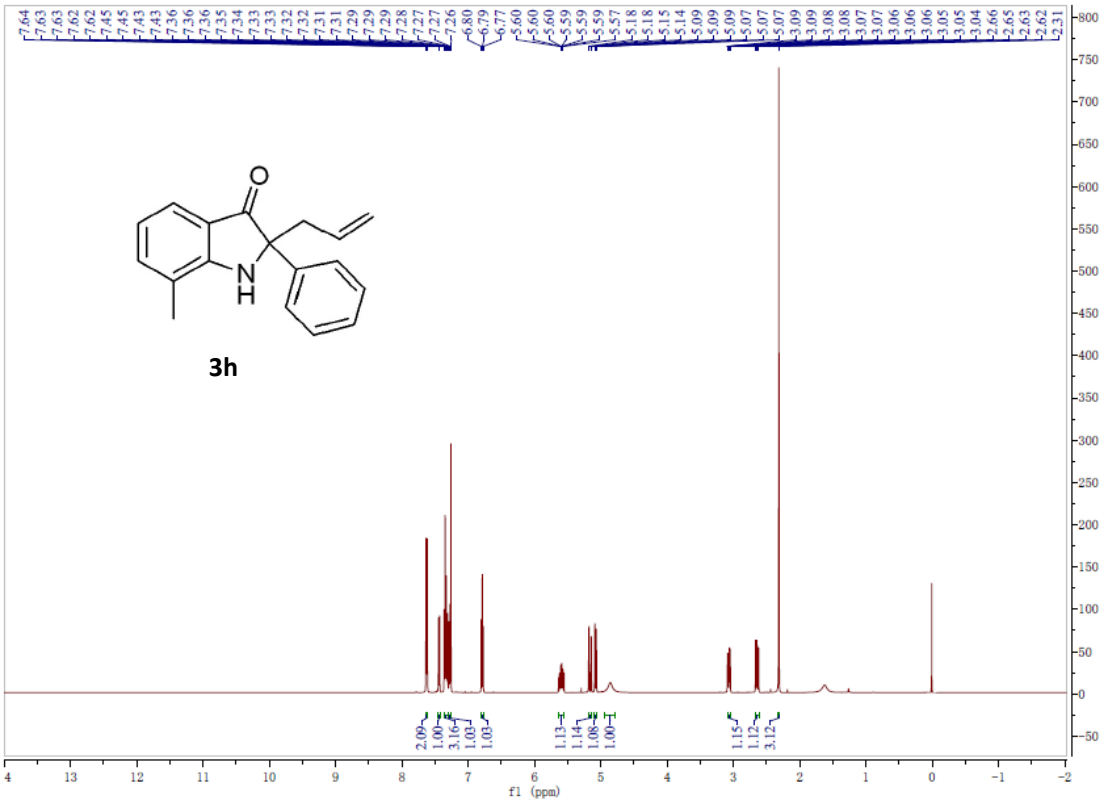
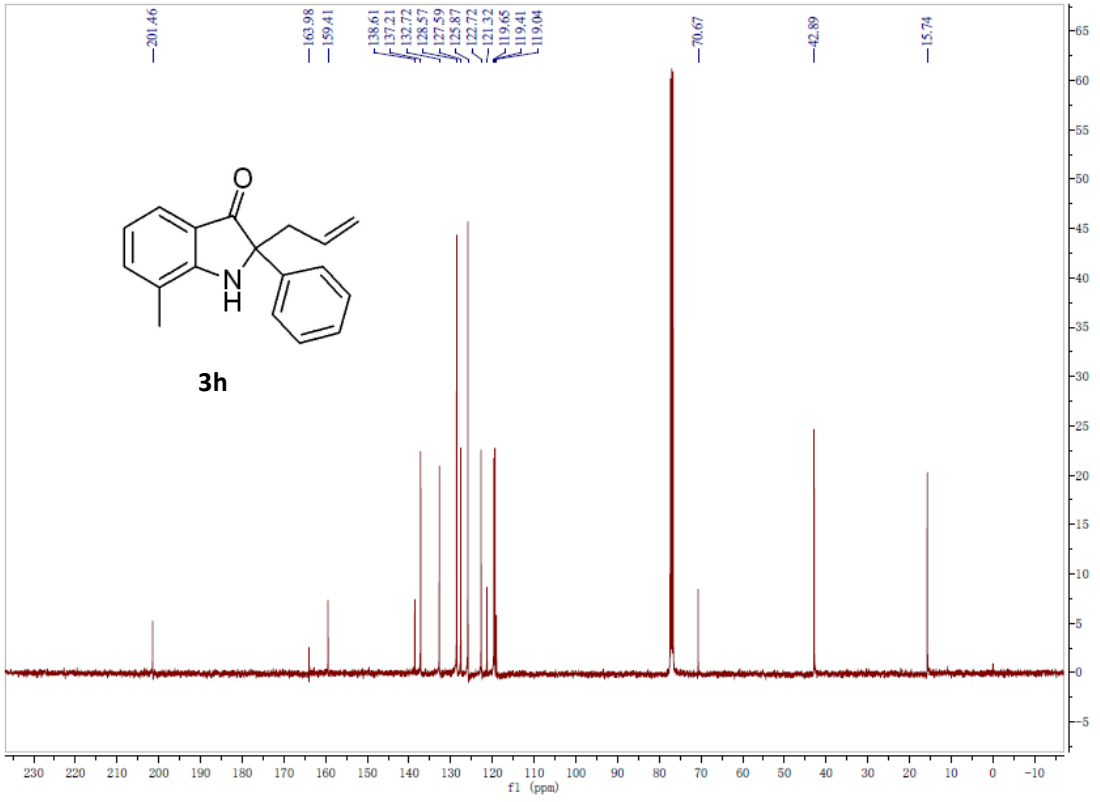
120.05
113.80
111.32
71.44
42.77
f1 (ppm)
Br
O
N
H
3g


3h
f1 (ppm)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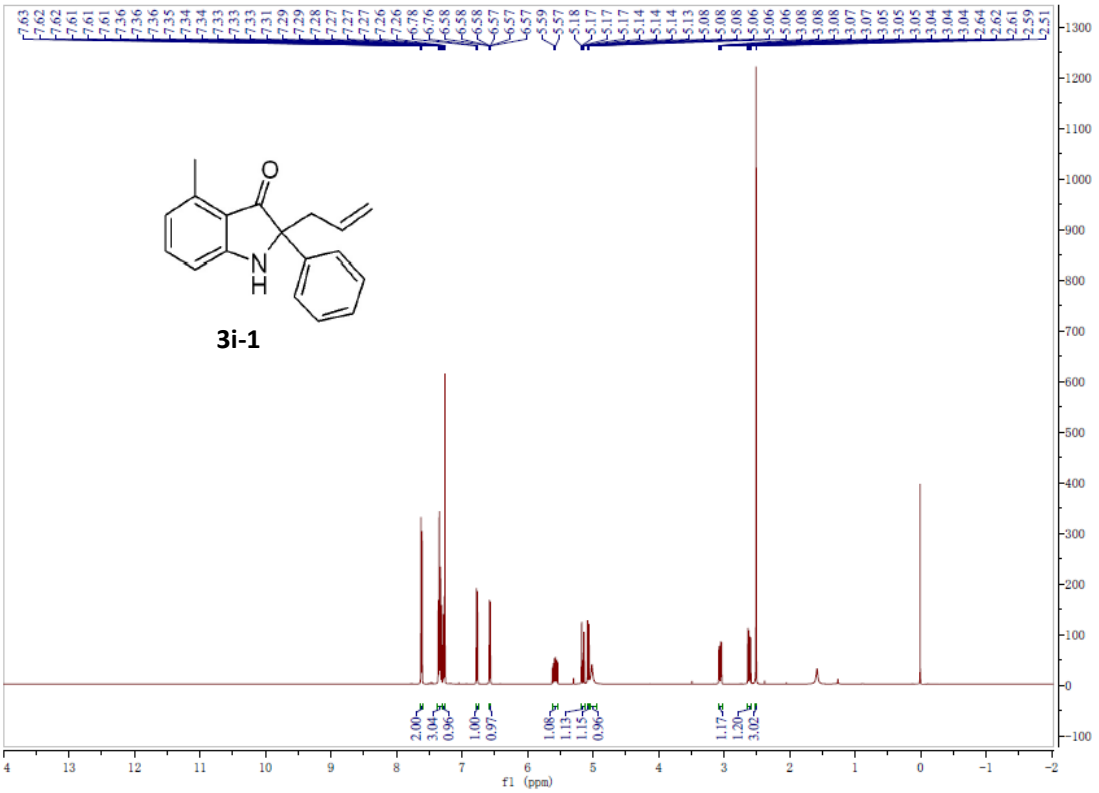
f1 (ppm)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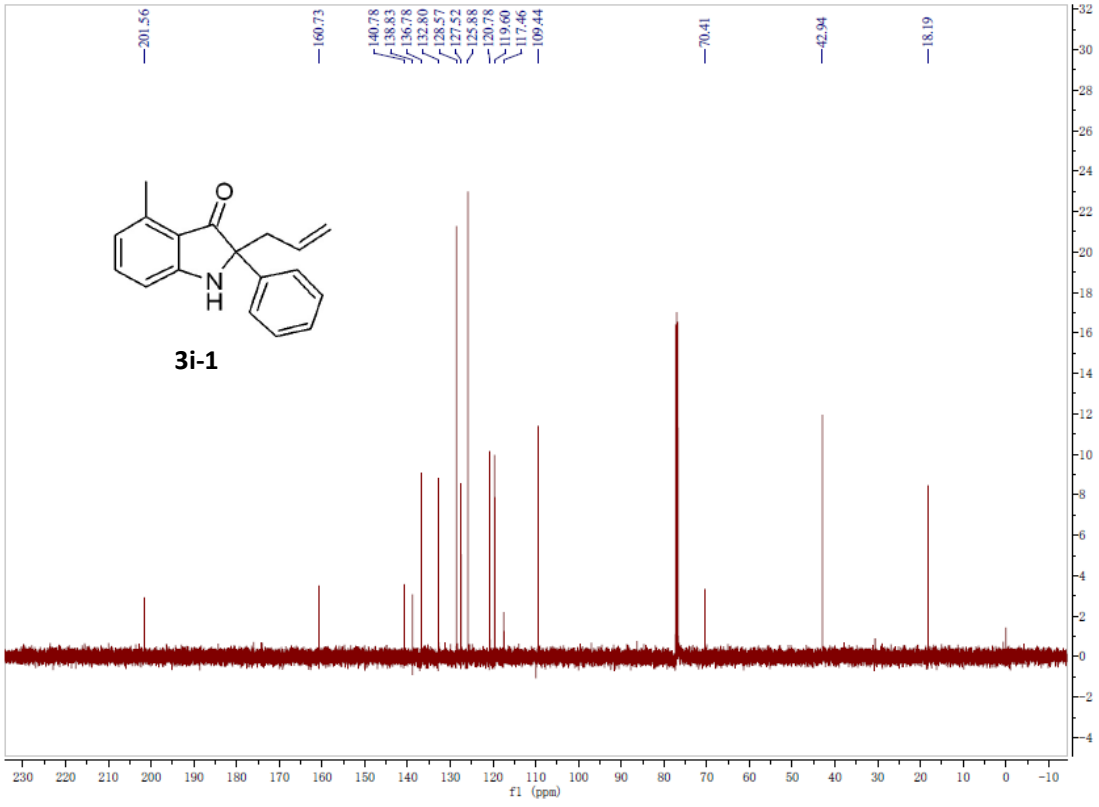
f1 (ppm)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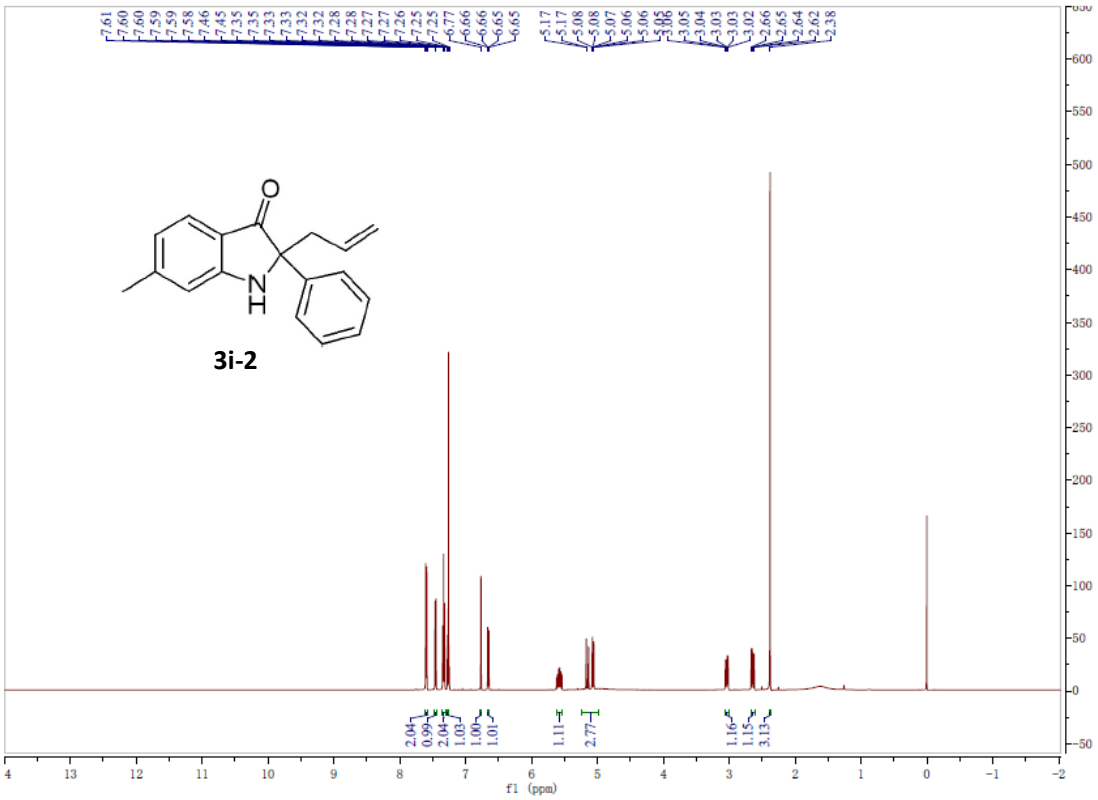
f1 (ppm)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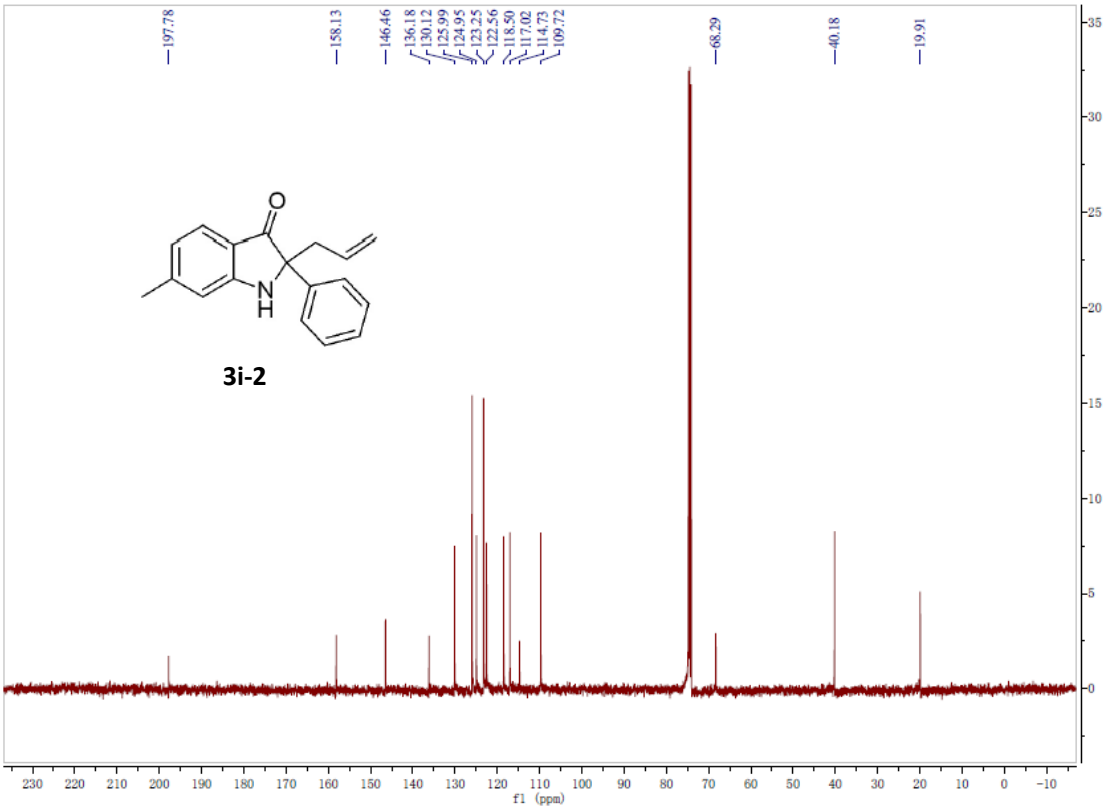
f1 (ppm)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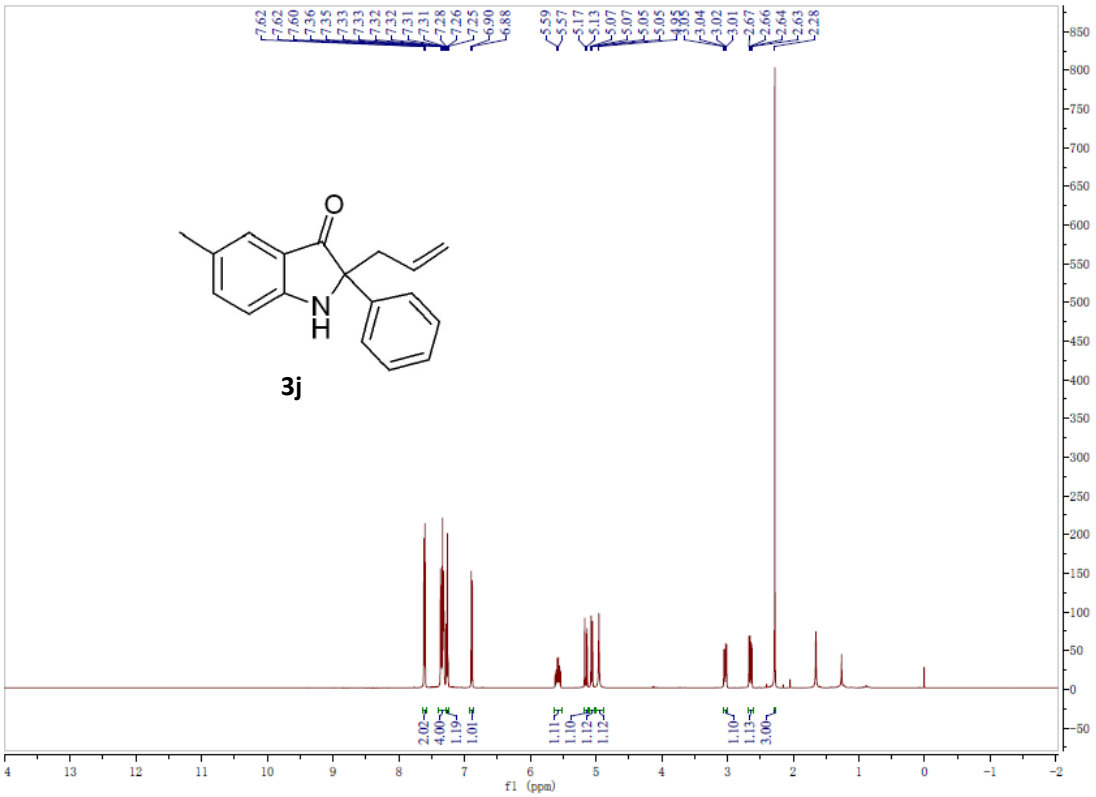
f1 (ppm)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7.62
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7.33
7.32
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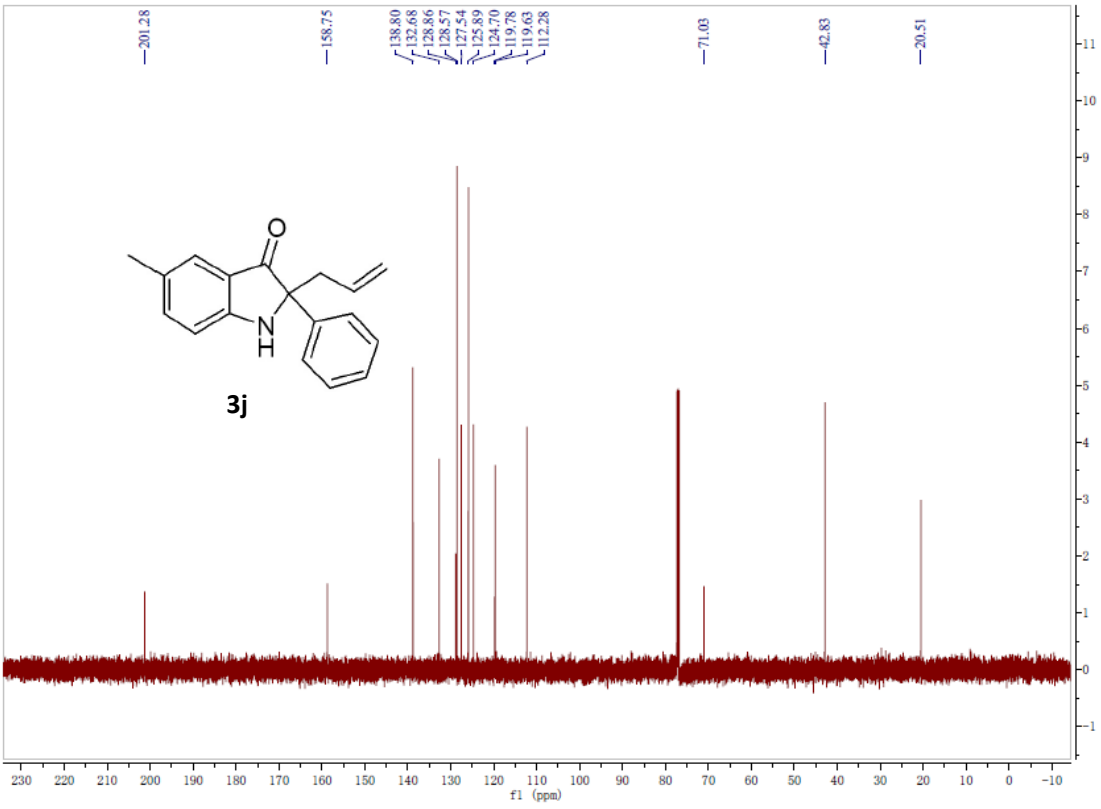
7.31
7.28
7.26
7.25
6.90
6.88
5.59
5.57
5.17
5.13
5.07
5.07
5.05
5.05
3.05
3.04
3.02
3.01
2.67
2.66
2.64
2.63
2.28
O
N
H
3j
2.02
4.00
1.19
1.01
1.11
1.10
1.12
1.12
1.10
1.13
3.00
f1 (ppm)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127.54
125.89
124.70
119.78
119.63
112.28
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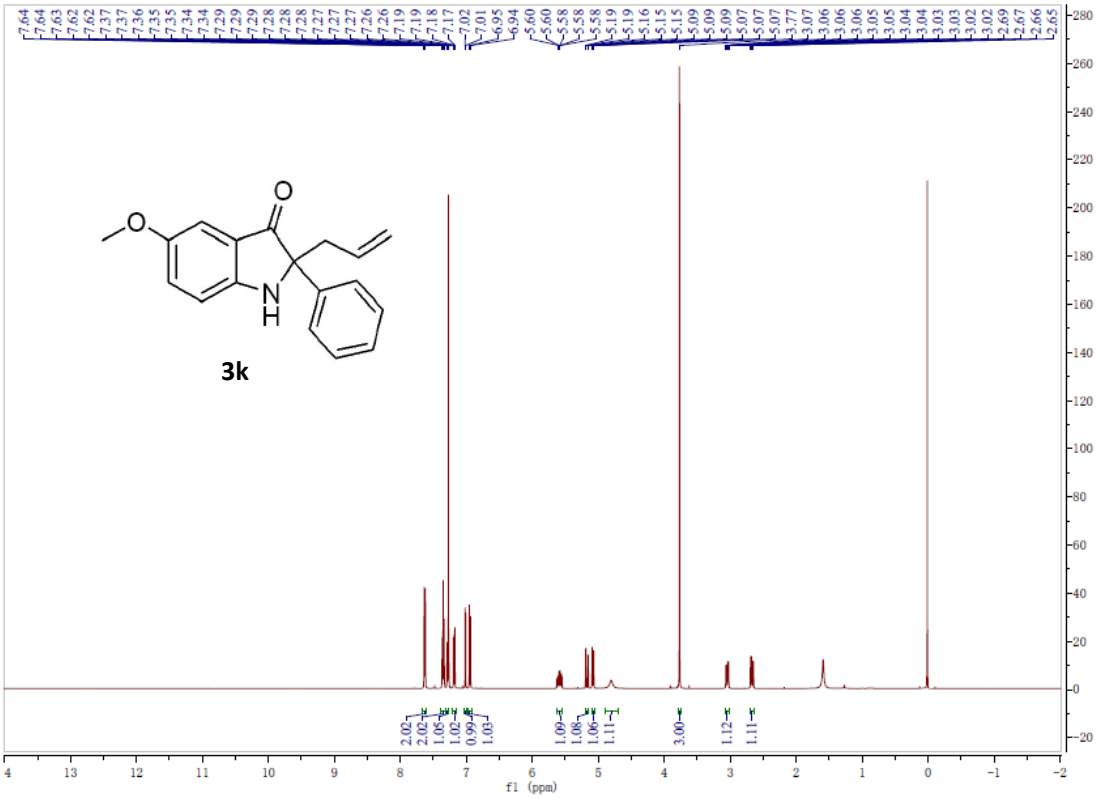
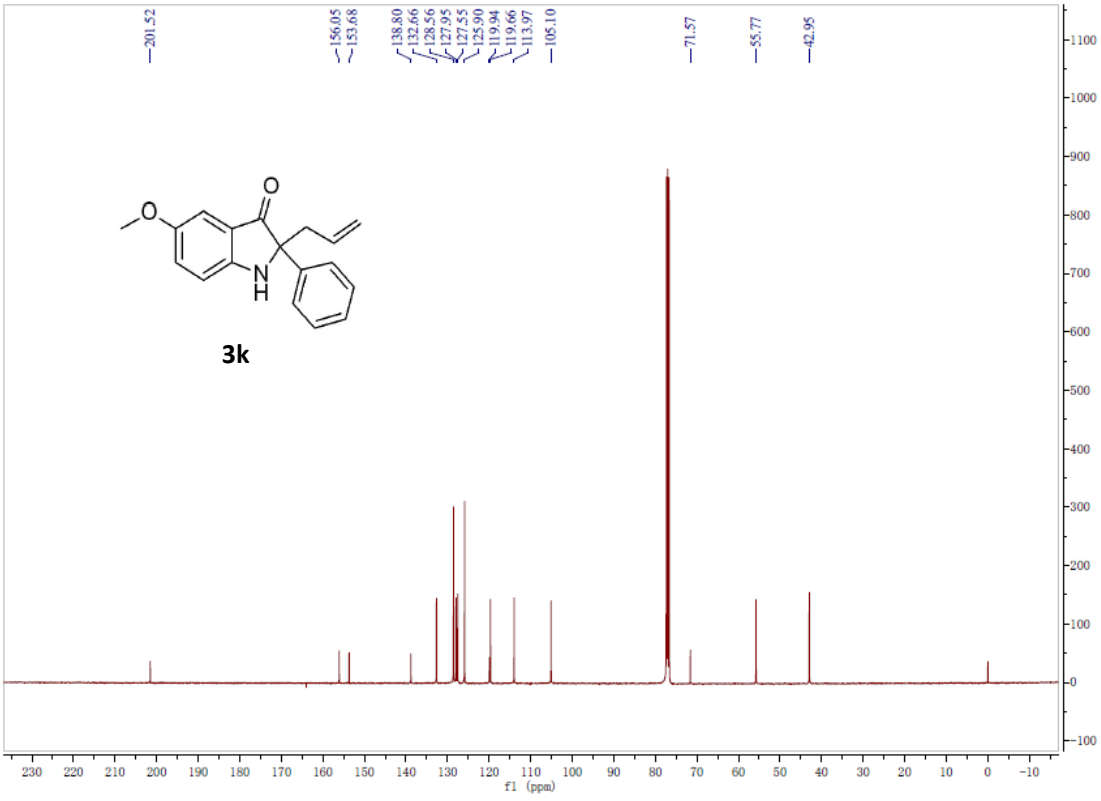
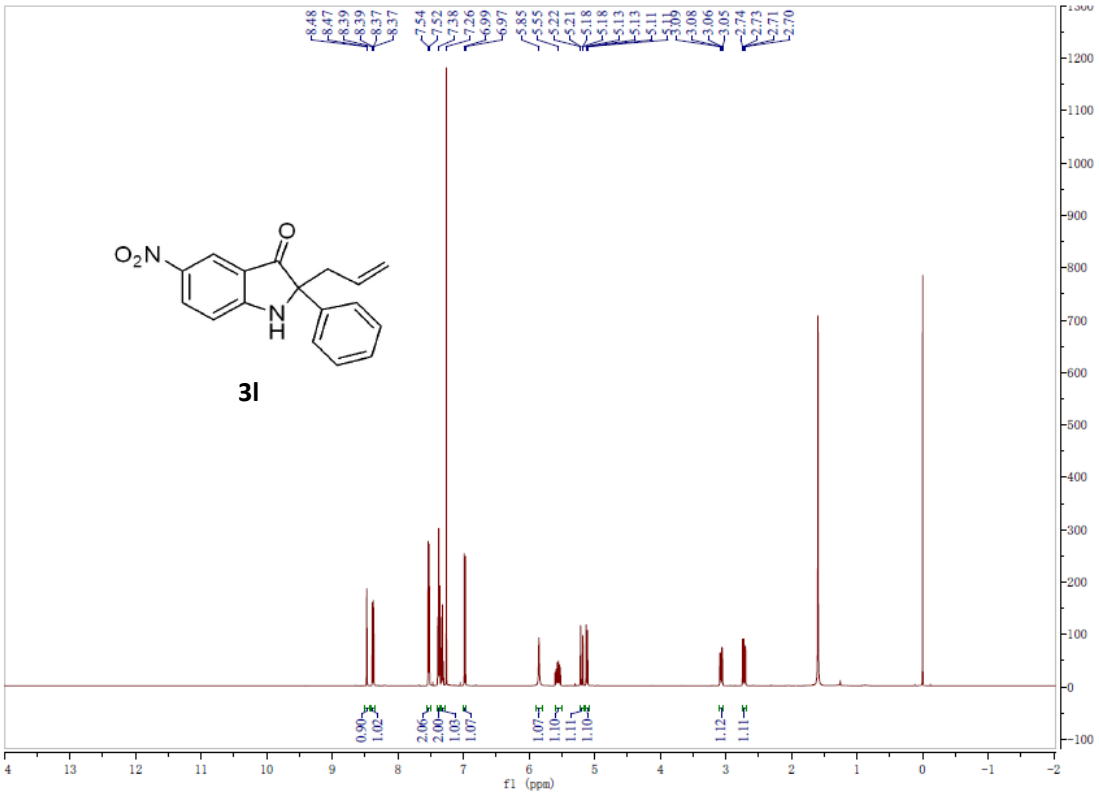
42.83
20.51
O
N
H
3j
f1 (ppm)


3k
f1 (ppm)


3k
f1 (ppm)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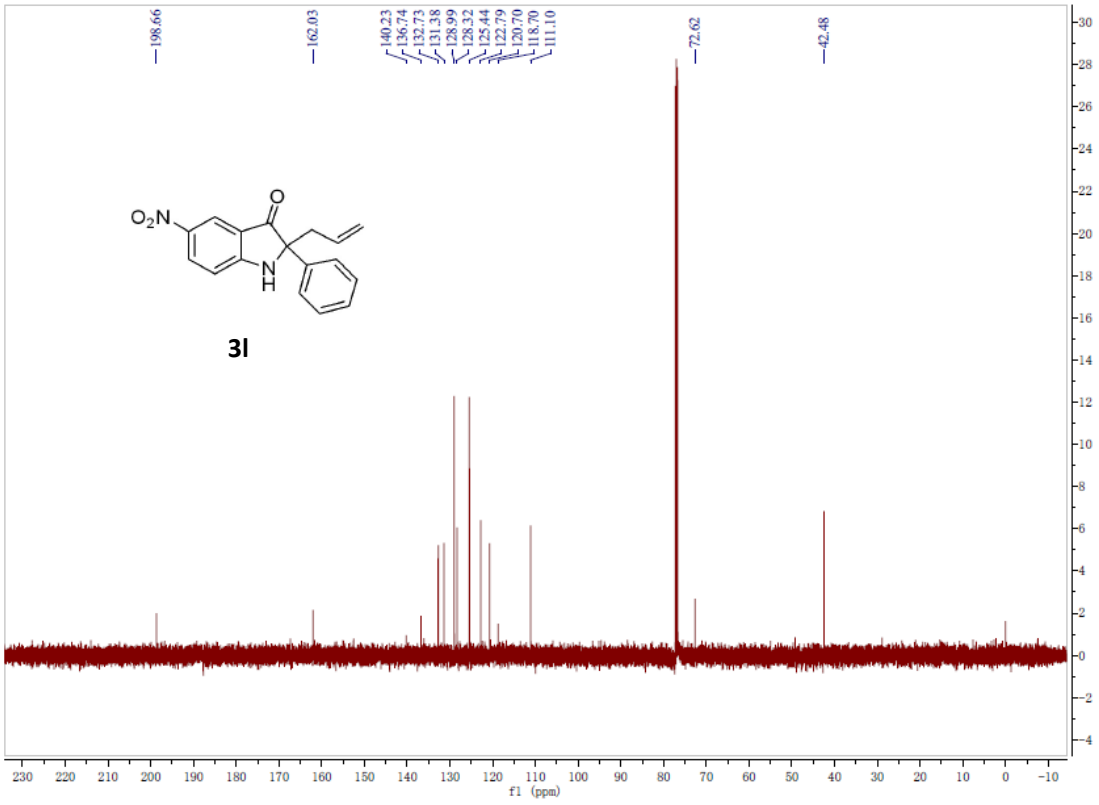
8.47
8.39
8.39
8.37
8.37
7.54
7.52
7.38
7.26
6.99
6.97
5.85
5.55
5.22
5.21
5.18
5.18
5.13
5.13
5.11
5.11
3.09
3.08
3.06
3.05
2.74
2.73
2.71
2.70
O2N
O
N
H
3l
0.90
1.02
2.06
2.00
1.03
1.07
1.07
1.10
1.11
1.10
1.12
1.11
f1 (ppm)


198.66
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140.23
136.74
132.73
131.38
128.99
128.32
125.44
122.79
120.70
118.70
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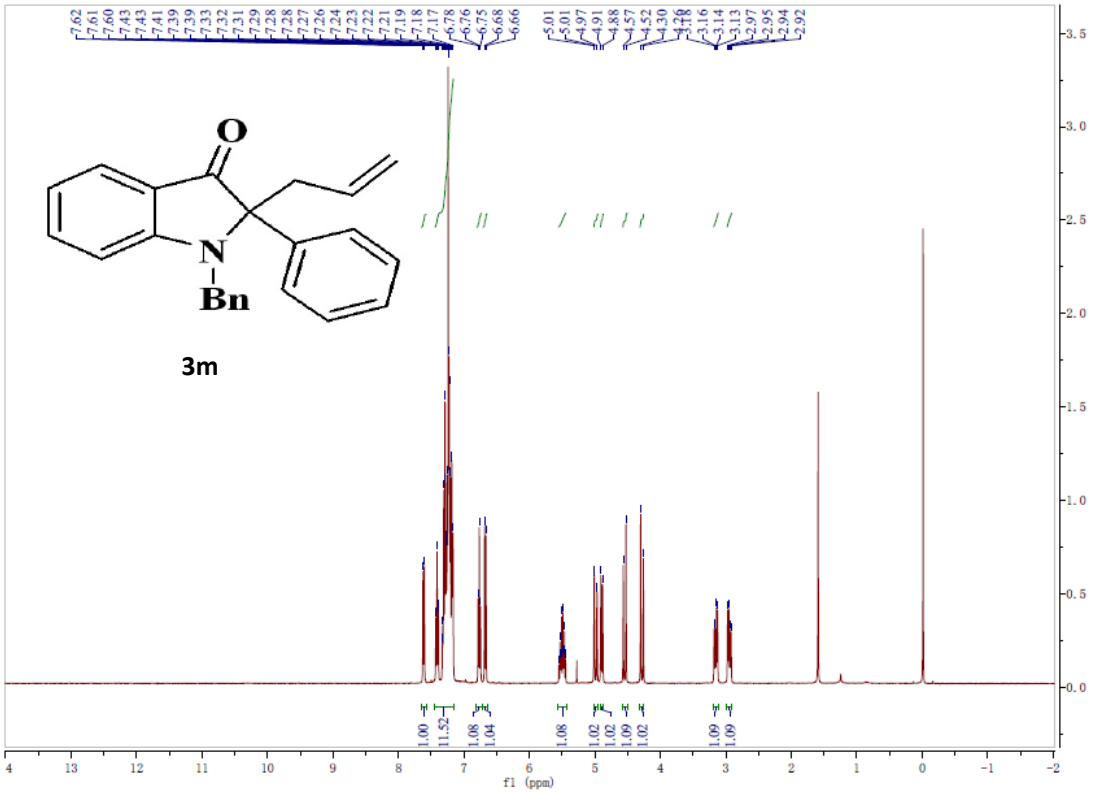
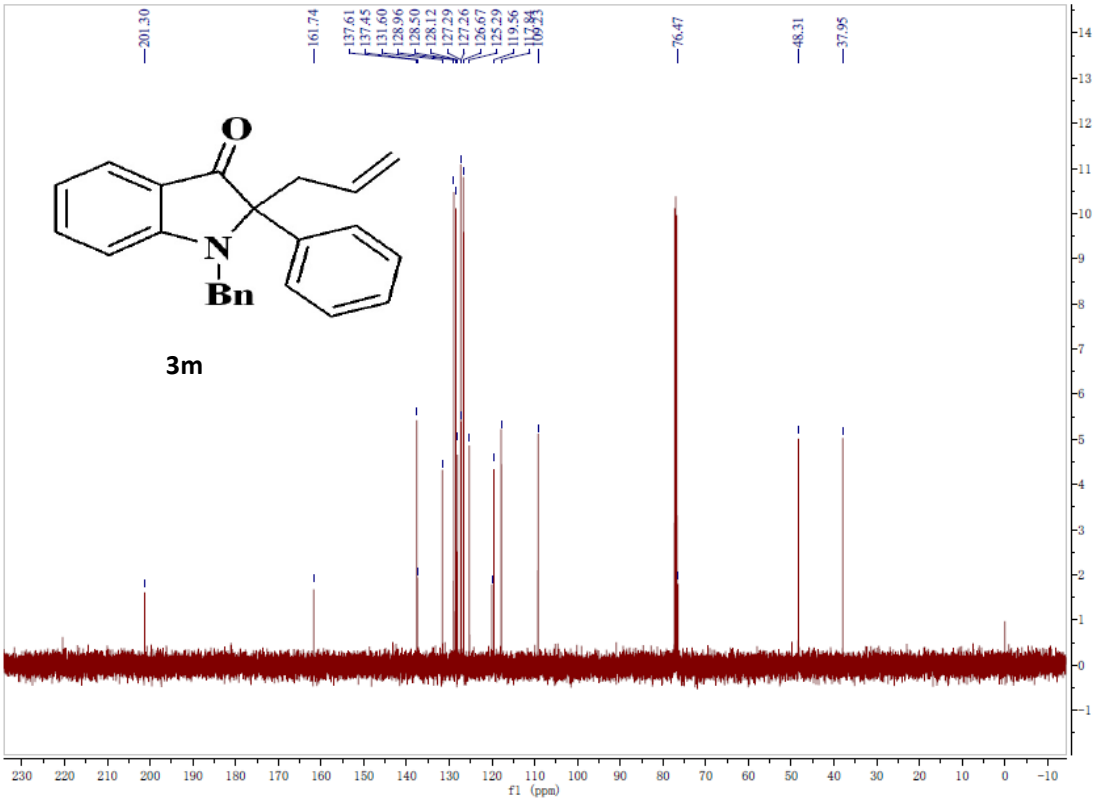
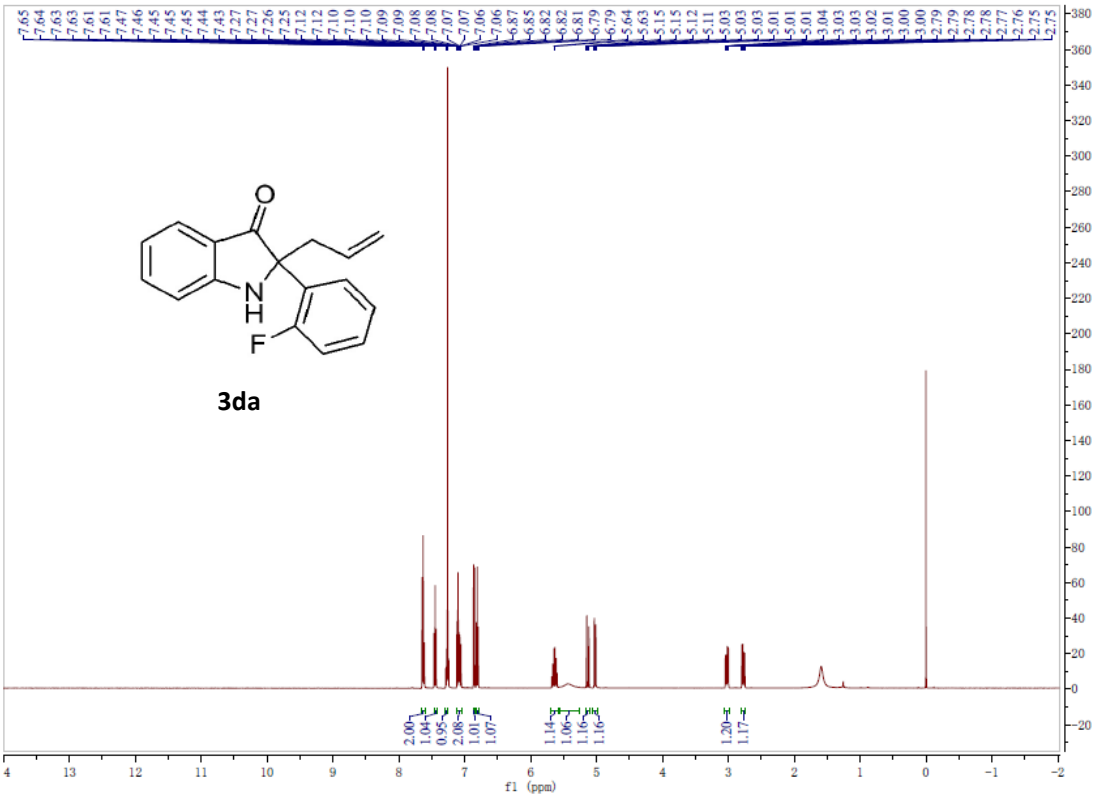
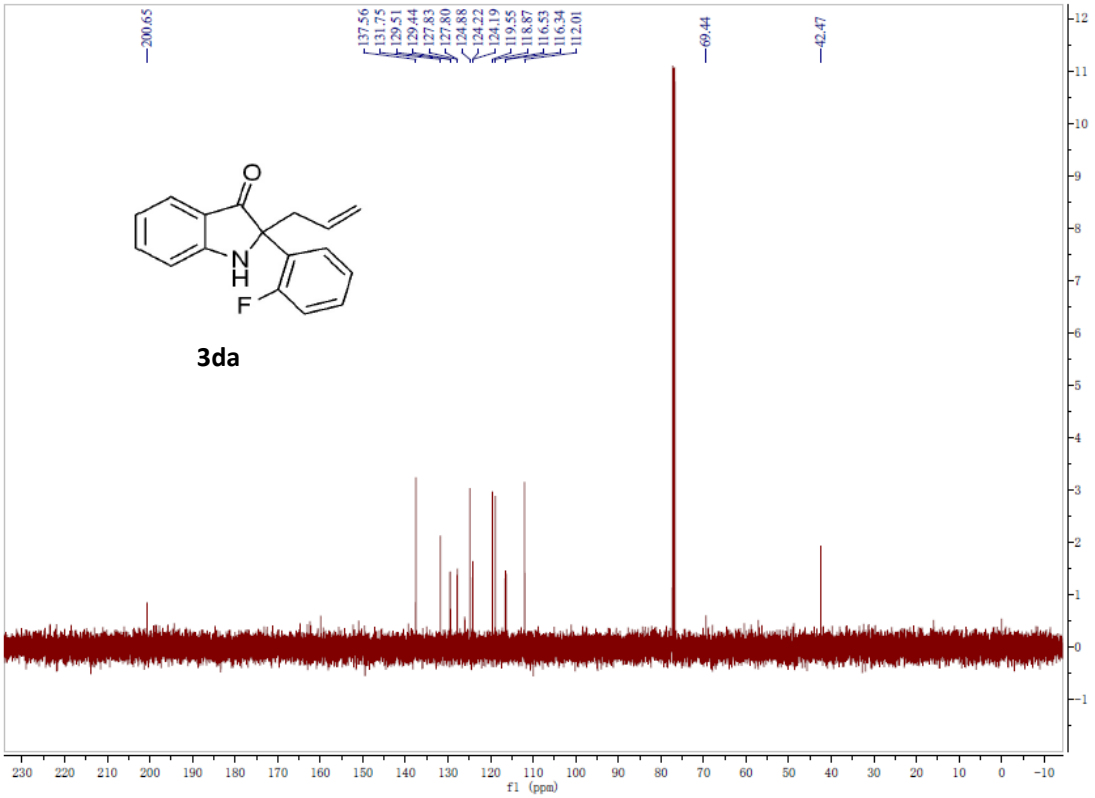
72.62
42.48
O2N
O
N
H
3l
f1 (ppm)


O
N
Bn
3m
f1 (ppm)


O
N
Bn
3m
f1 (ppm)


O
N
H
F
3da
f1 (ppm)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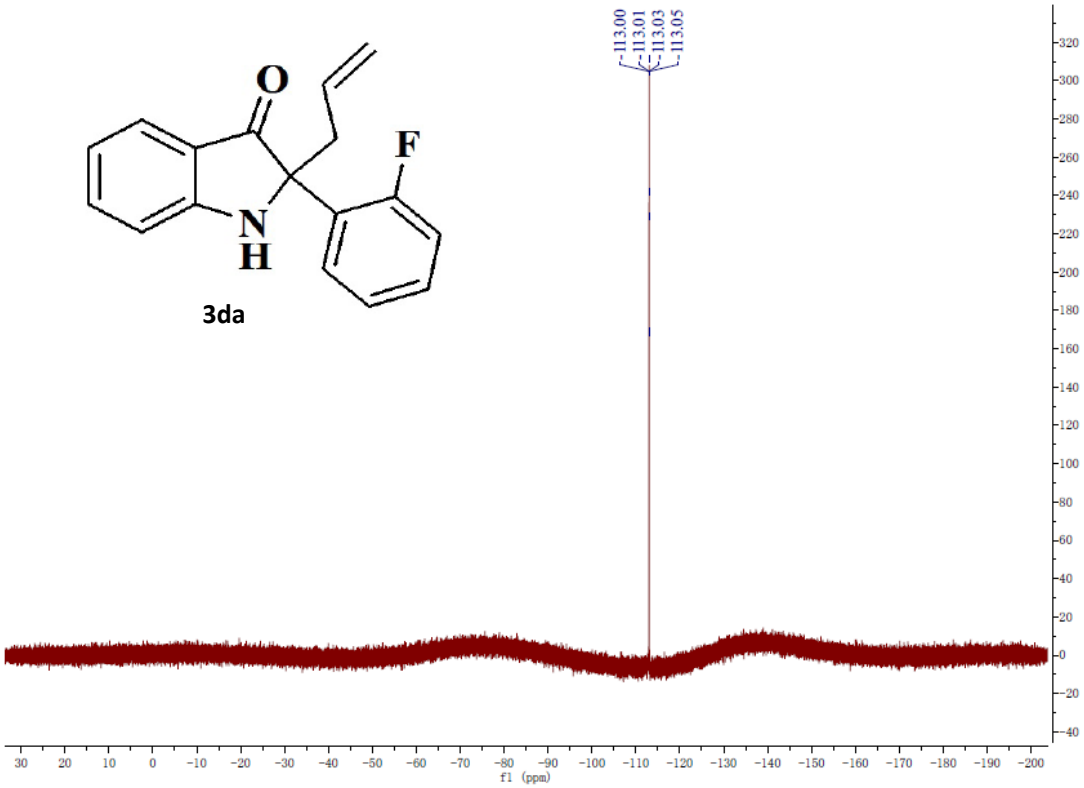
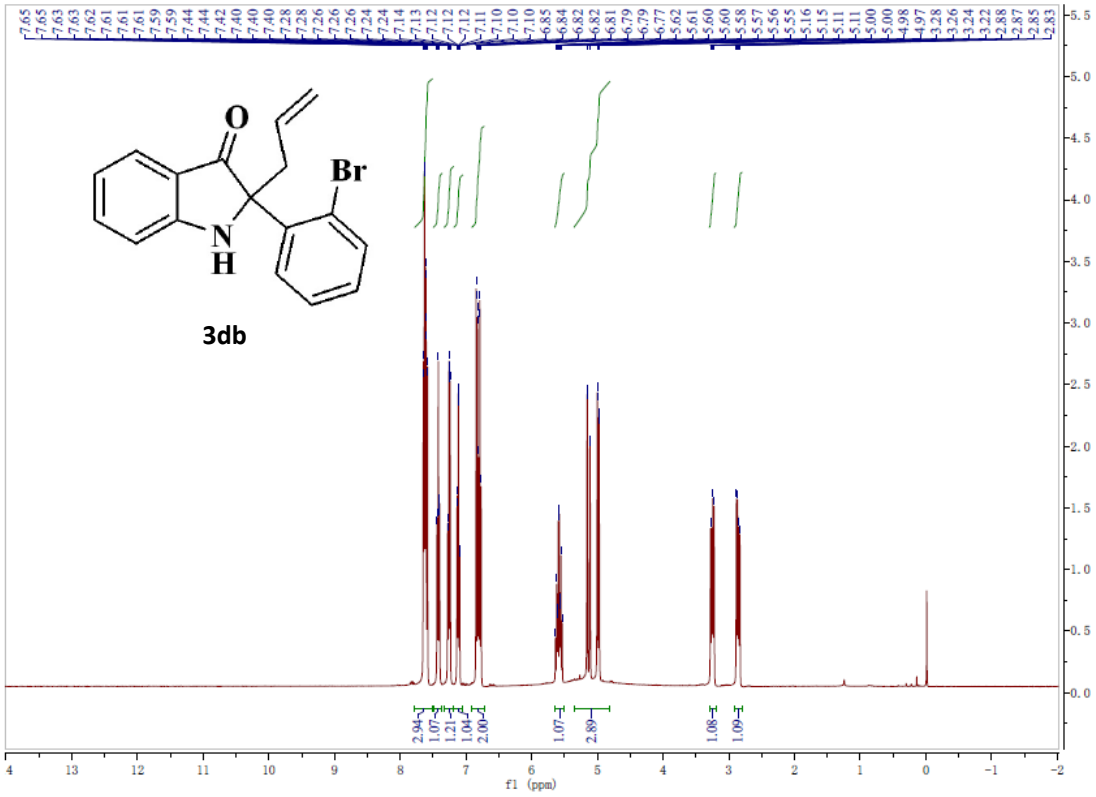
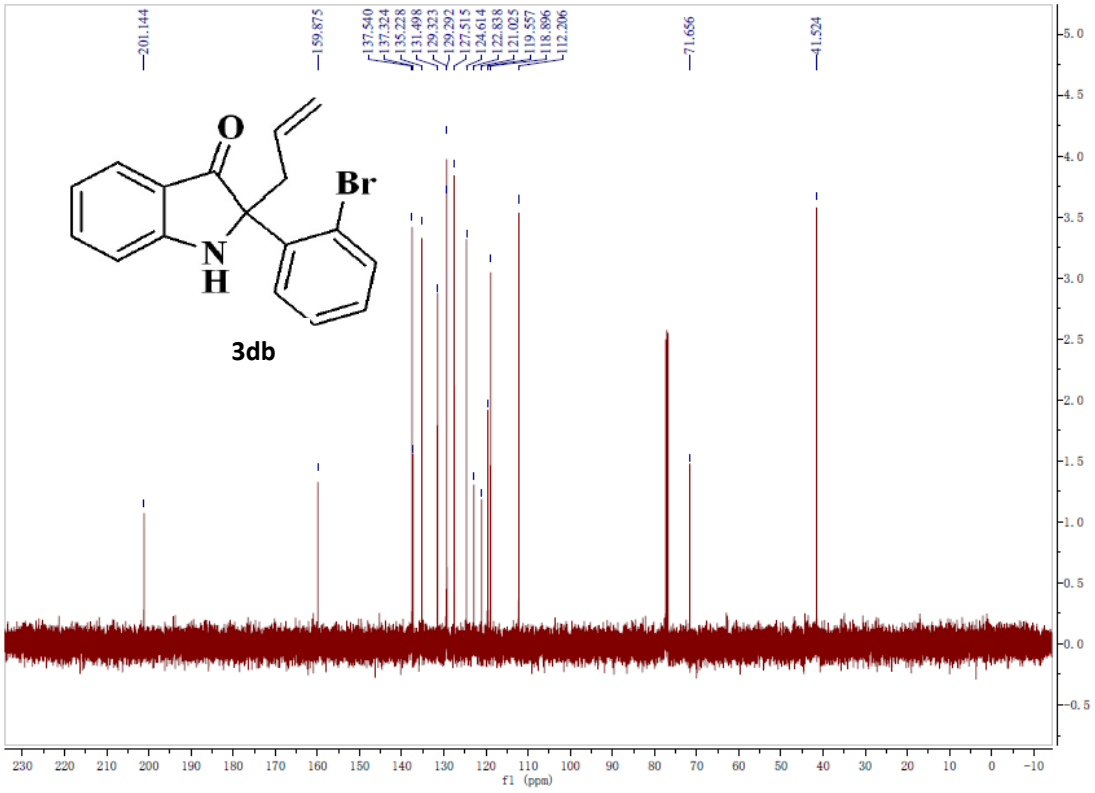
131.75
129.51
129.44
127.83
127.80
124.88
124.22
124.19
119.55
118.87
116.53
116.34
112.01
69.44
42.47
O
N
H
F
3da
f1 (ppm)


O
F
N
H
3da
-113.00
-113.01
-113.03
-113.05
f1 (ppm)


O
Br
N
H
3db
f1 (ppm)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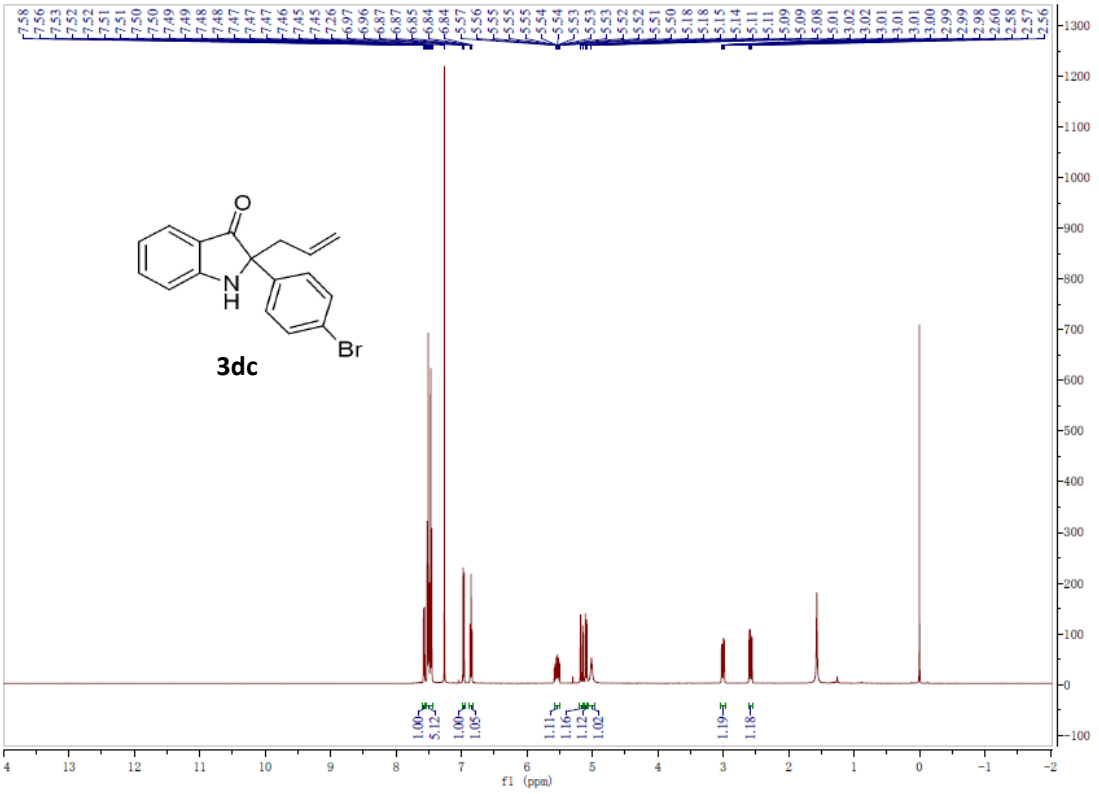
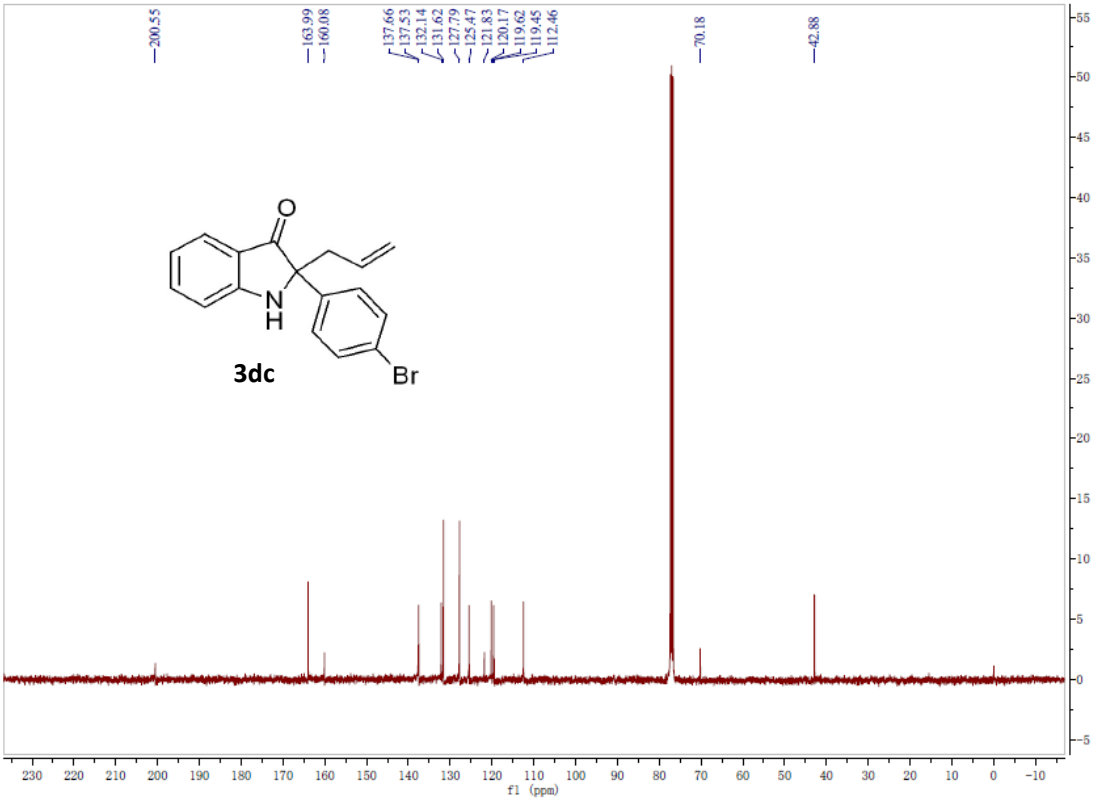
137.324
135.228
131.498
129.323
129.292
127.515
124.614
122.838
121.025
119.557
118.896
112.206
71.656
41.524
O
Br
N
H
3db
f1 (ppm)


O
N
H
Br
3dc
f1 (ppm)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160.08
137.66
137.53
132.14
131.62
127.79
125.47
121.83
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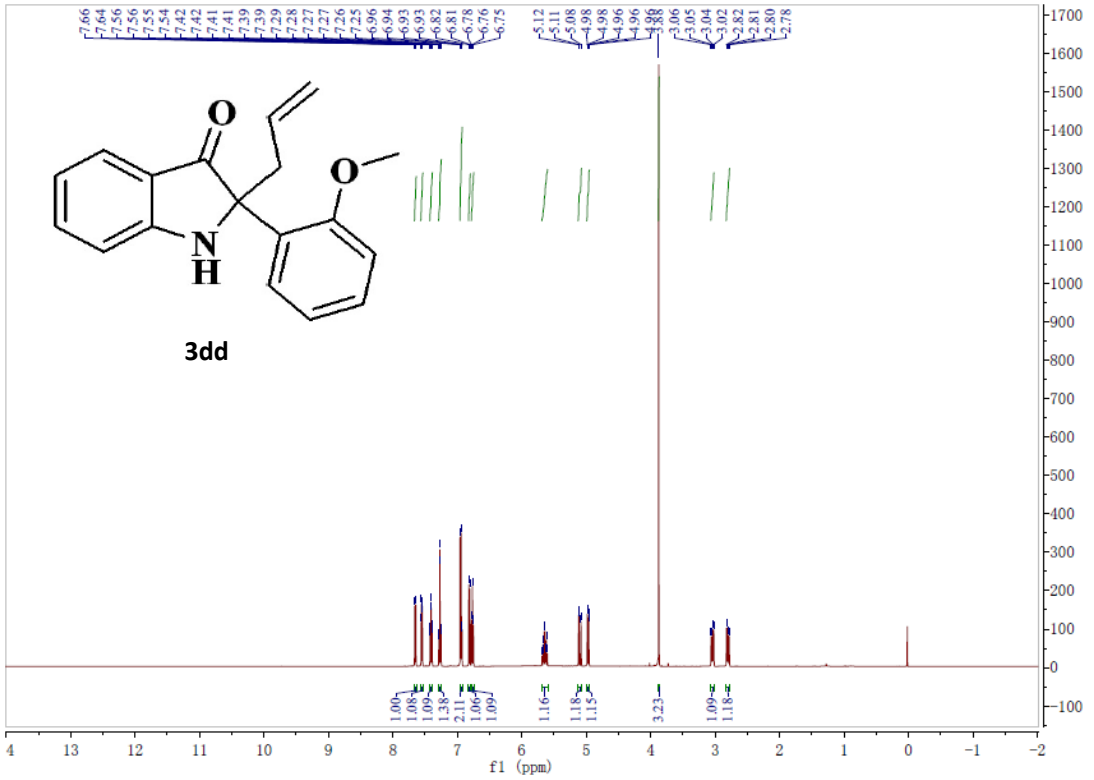
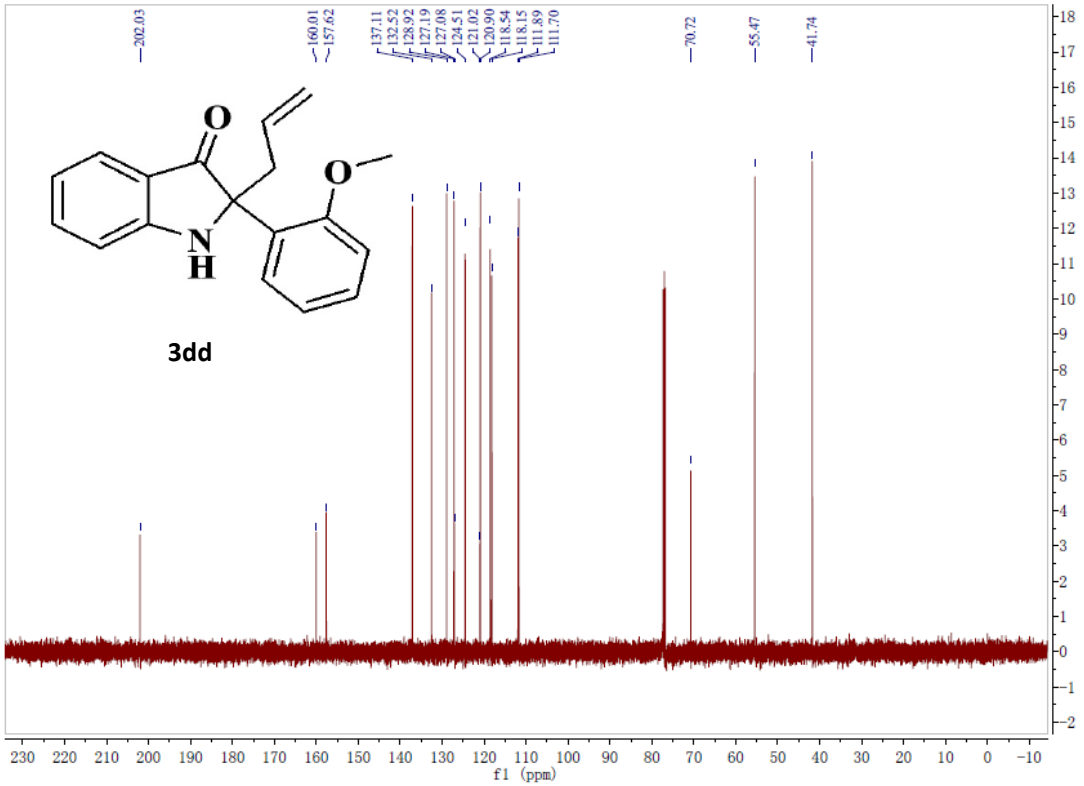
119.62
119.45
112.46
70.18
42.88
O
N
H
Br
3dc
f1 (ppm)


7.66
7.64
7.56
7.56
7.55
7.54
7.42
7.42
7.41
7.41
7.39
7.39
7.29
7.28
7.27
7.27
7.26
7.25
6.96
6.94
6.93
6.93
6.82
6.81
6.78
6.76
6.75
5.12
5.11
5.08
4.98
4.98
4.96
4.96
3.86
3.06
3.05
3.04
3.02
2.82
2.81
2.80
2.78
O
O
N
H
3dd
1.00
1.08
1.09
1.38
2.11
1.06
1.09
1.16
1.18
1.15
3.23
1.09
1.18
f1 (ppm)


202.03
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157.62
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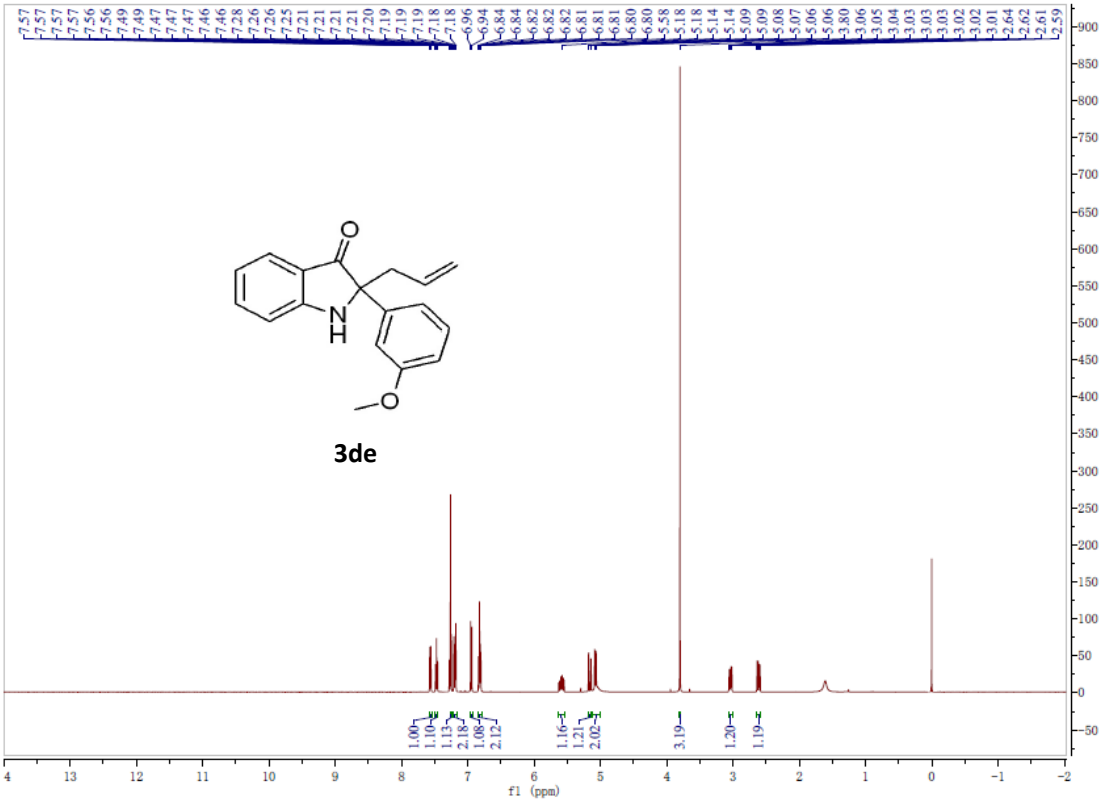
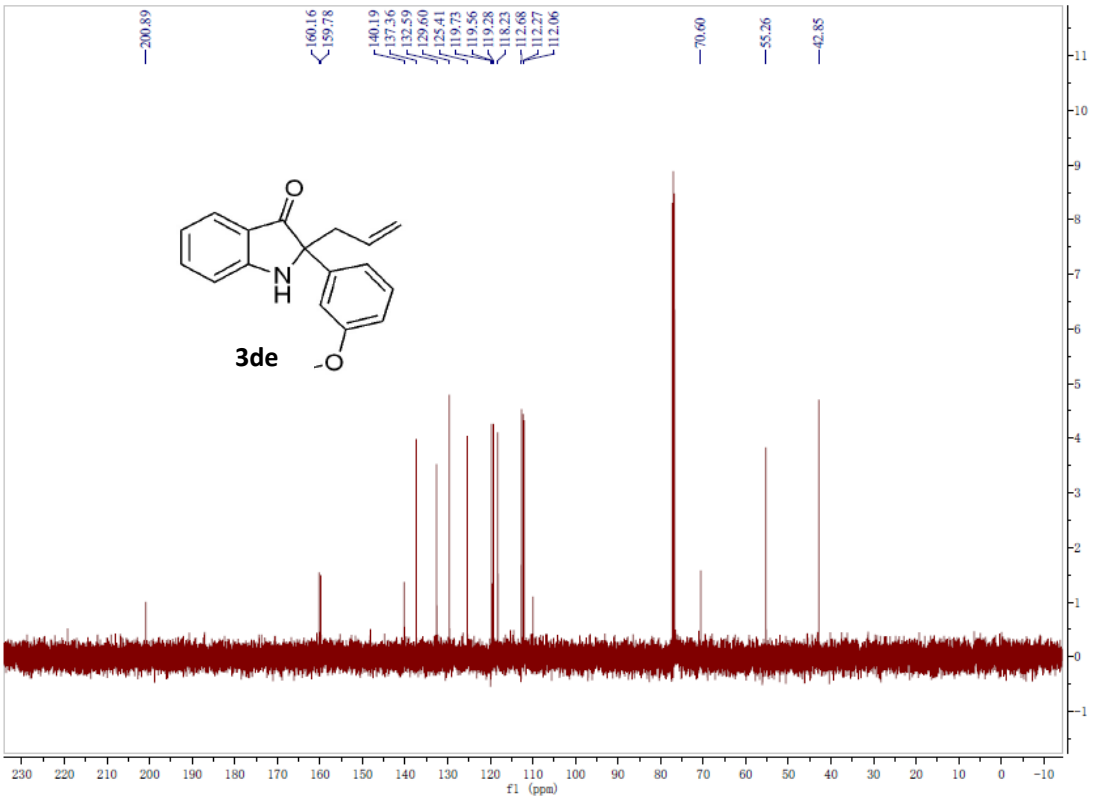
132.52
128.92
127.19
127.08
124.51
121.02
120.90
118.54
118.15
111.89
111.70
70.72
55.47
41.74
O
O
N
H
f1 (ppm)

3dd


O
N
H
O
1.00
1.10
1.13
2.18
1.08
2.12
1.16
1.21
2.02
3.19
1.20
1.19
f1 (ppm)

3de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140.19
137.36
132.59
129.60
125.41
119.73
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118.23
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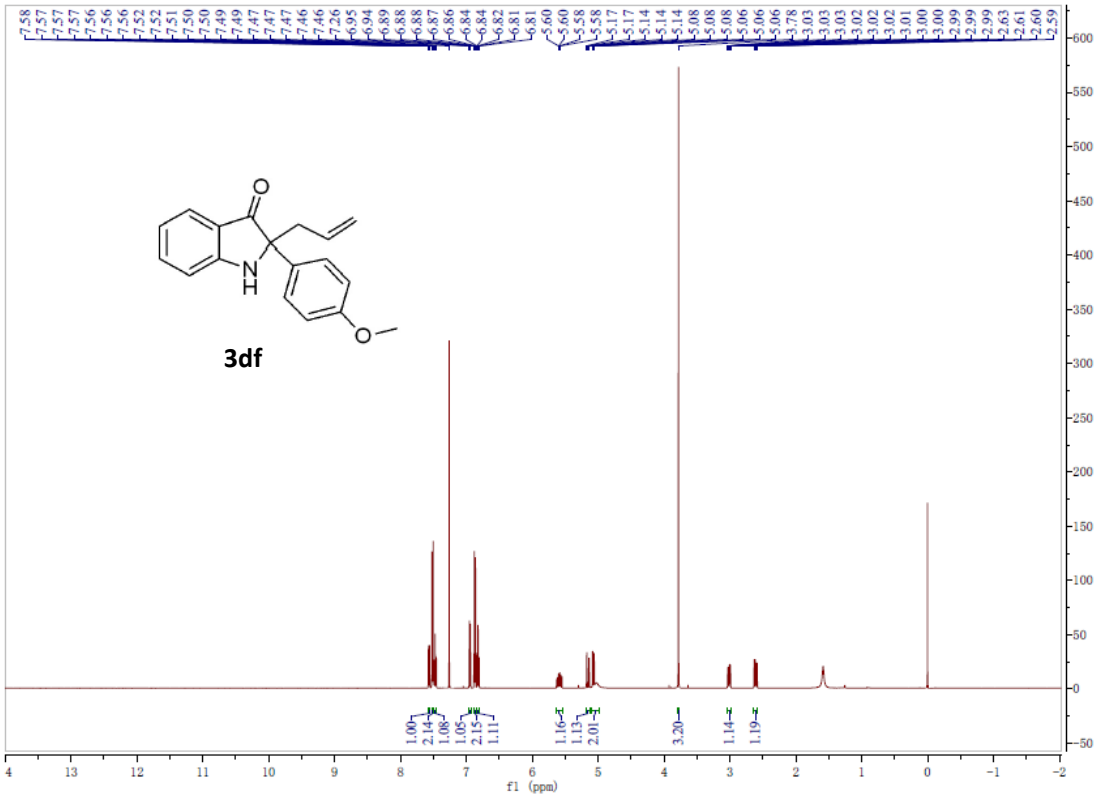
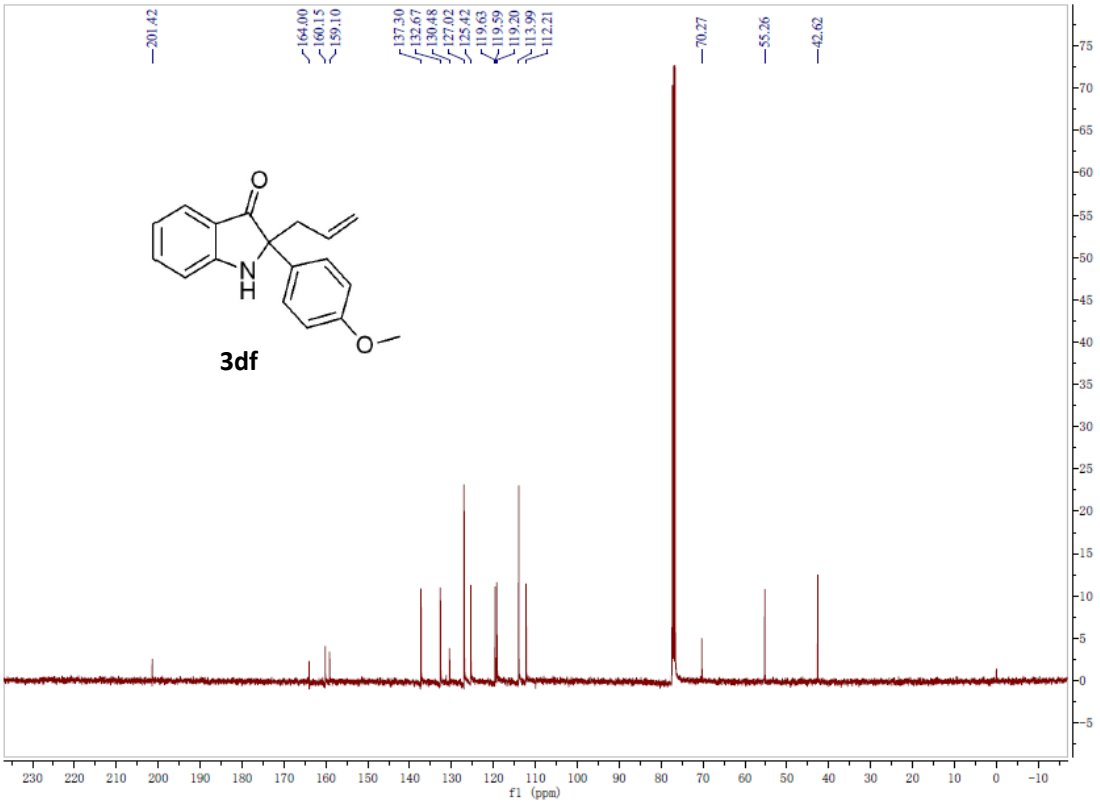
112.27
112.06
70.60
55.26
42.85
3de
f1 (ppm)


3df
1.00
2.14
1.08
1.05
2.15
1.11
1.16
1.13
2.01
3.20
1.14
1.19
f1 (ppm)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130.48
127.02
125.42
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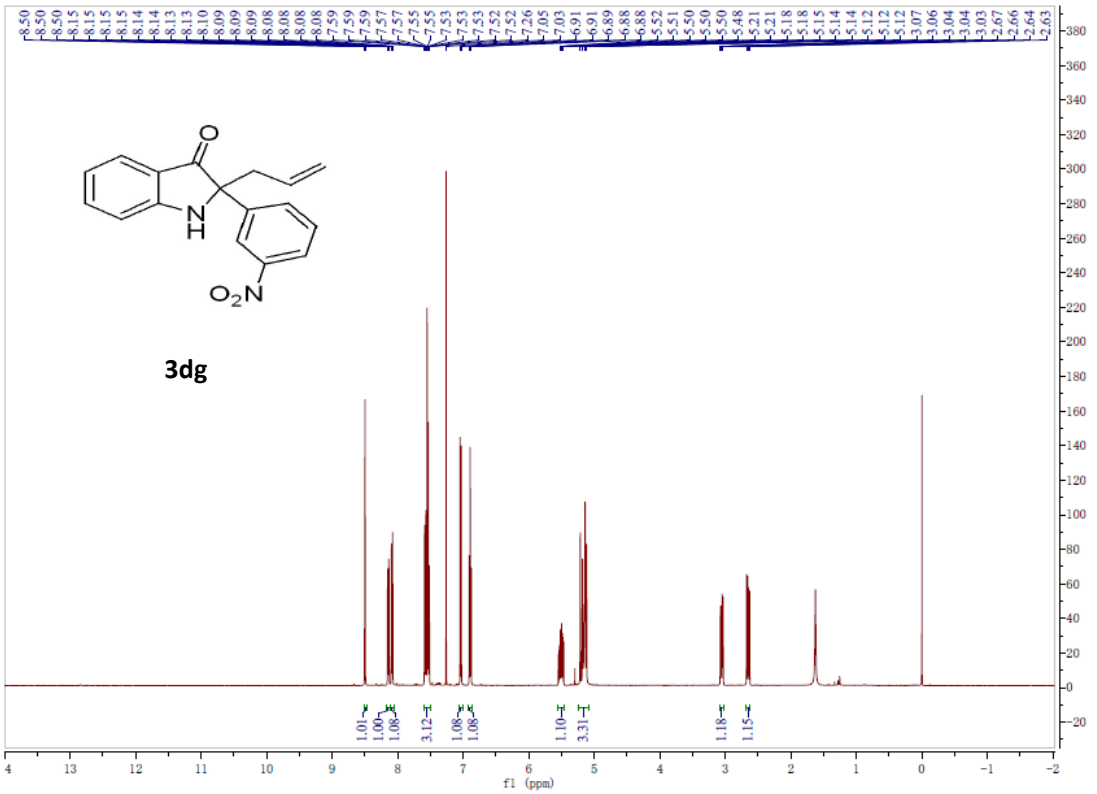
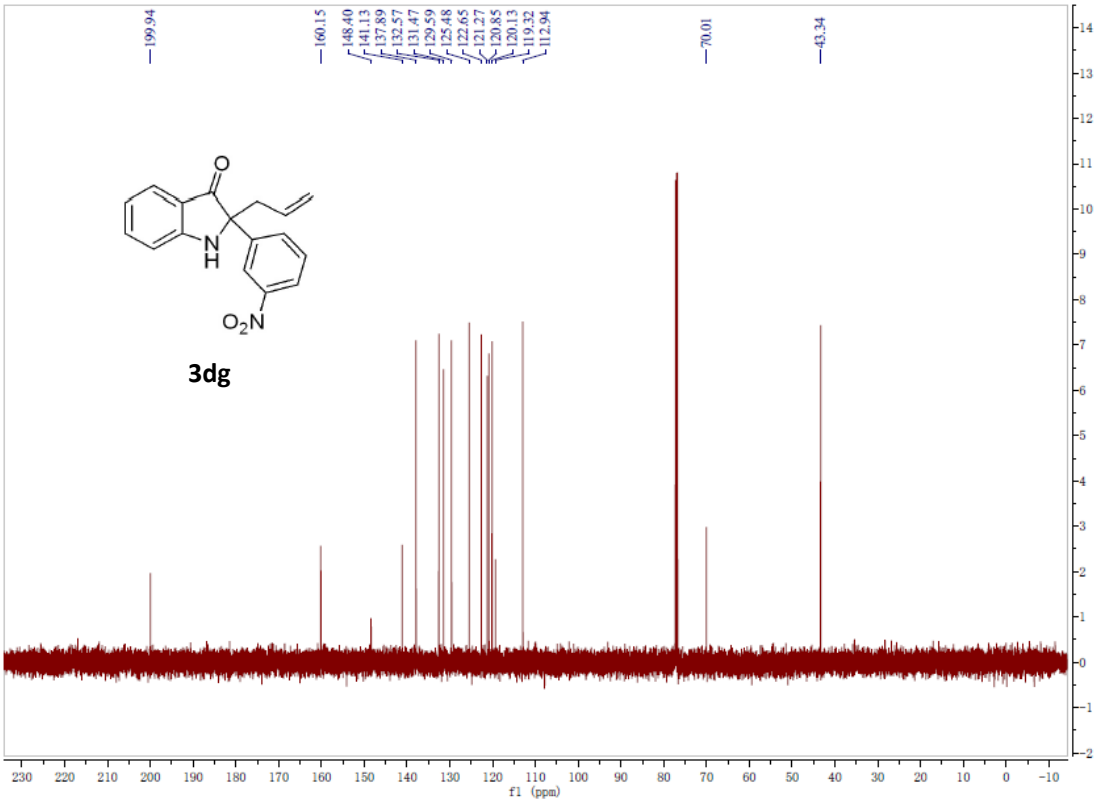
113.99
112.21
70.27
55.26
42.62
O
N
H
O
3df
f1 (ppm)


O
N
H
O2N
3dg
f1 (ppm)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132.57
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129.59
125.48
122.65
121.27
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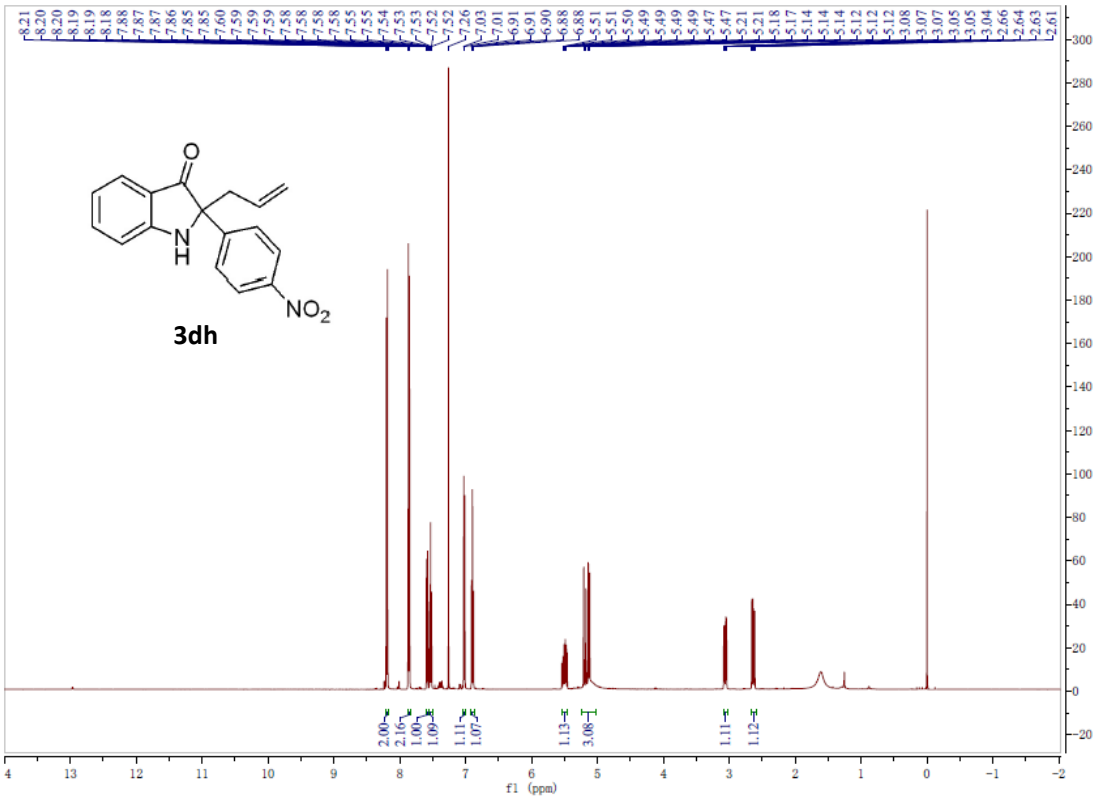
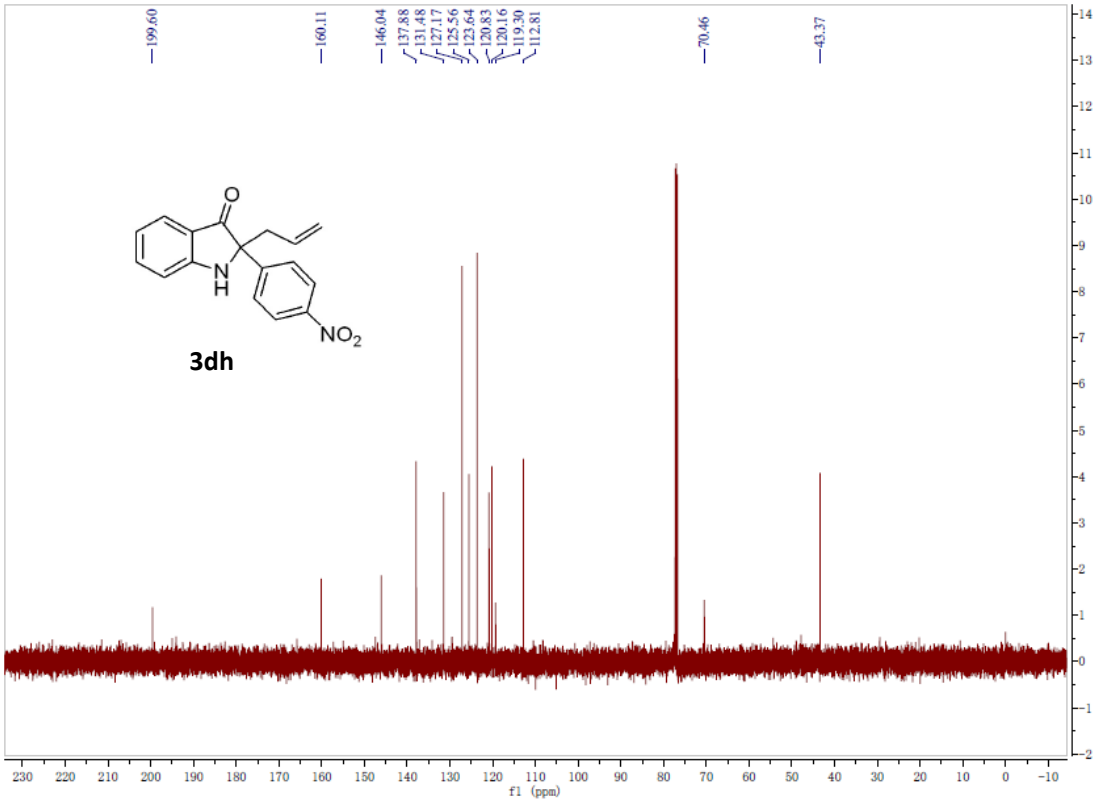
120.13
119.32
112.94
70.01
43.34
O
N
H
O2N
3dg
f1 (ppm)


O
N
H
NO2
3dh
f1 (ppm)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127.17
125.56
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120.16
119.30
112.81
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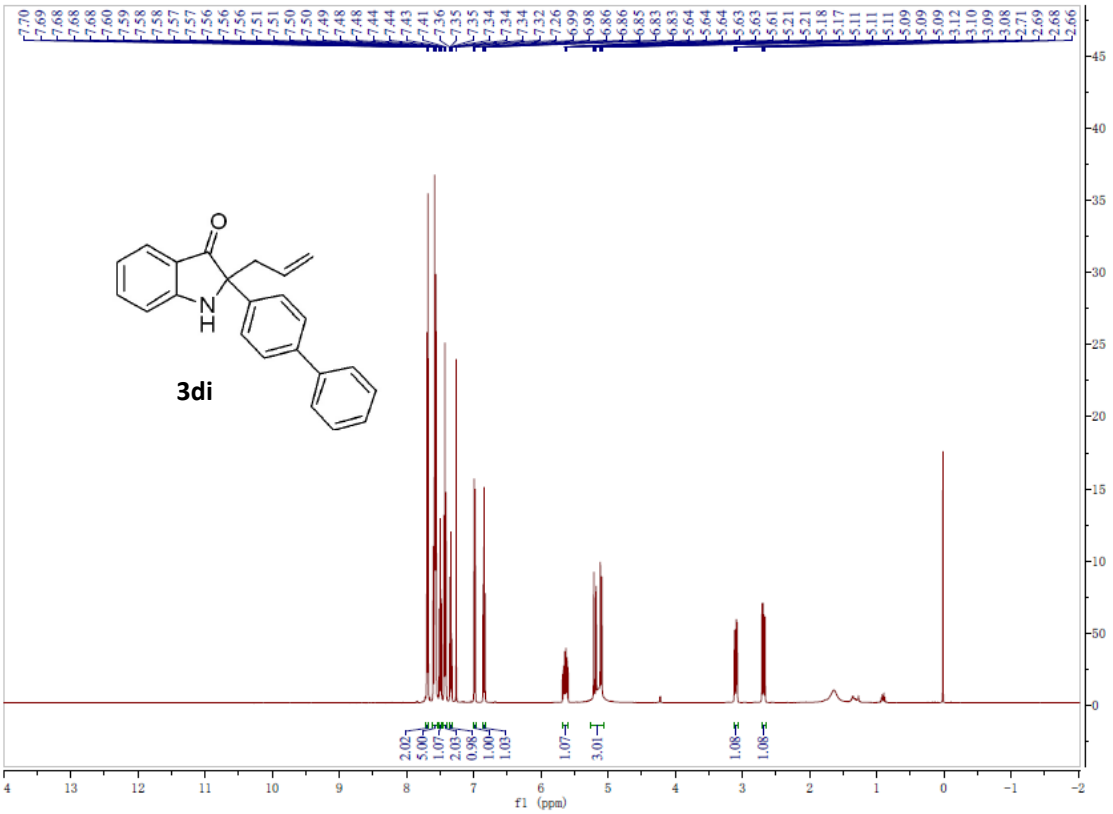
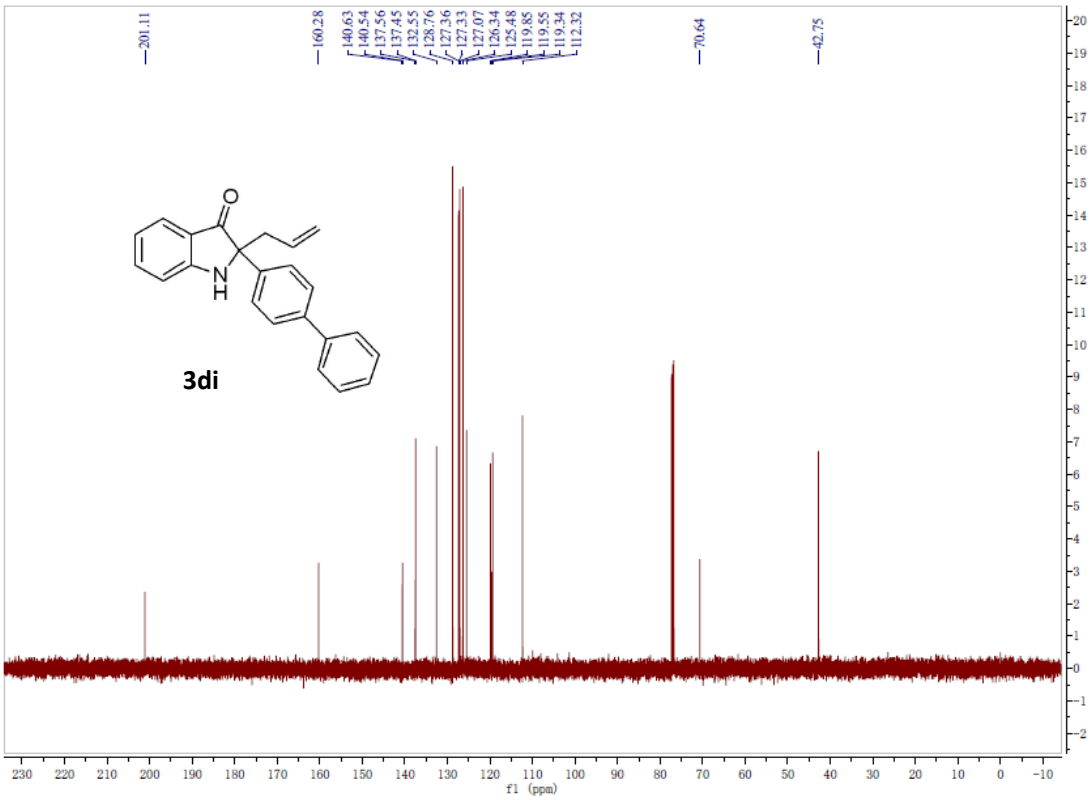
43.37
O
N
H
NO2
3dh
f1 (ppm)


O
N
H
3di
f1 (ppm)


201.11
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137.56
137.45
132.55
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127.33
127.07
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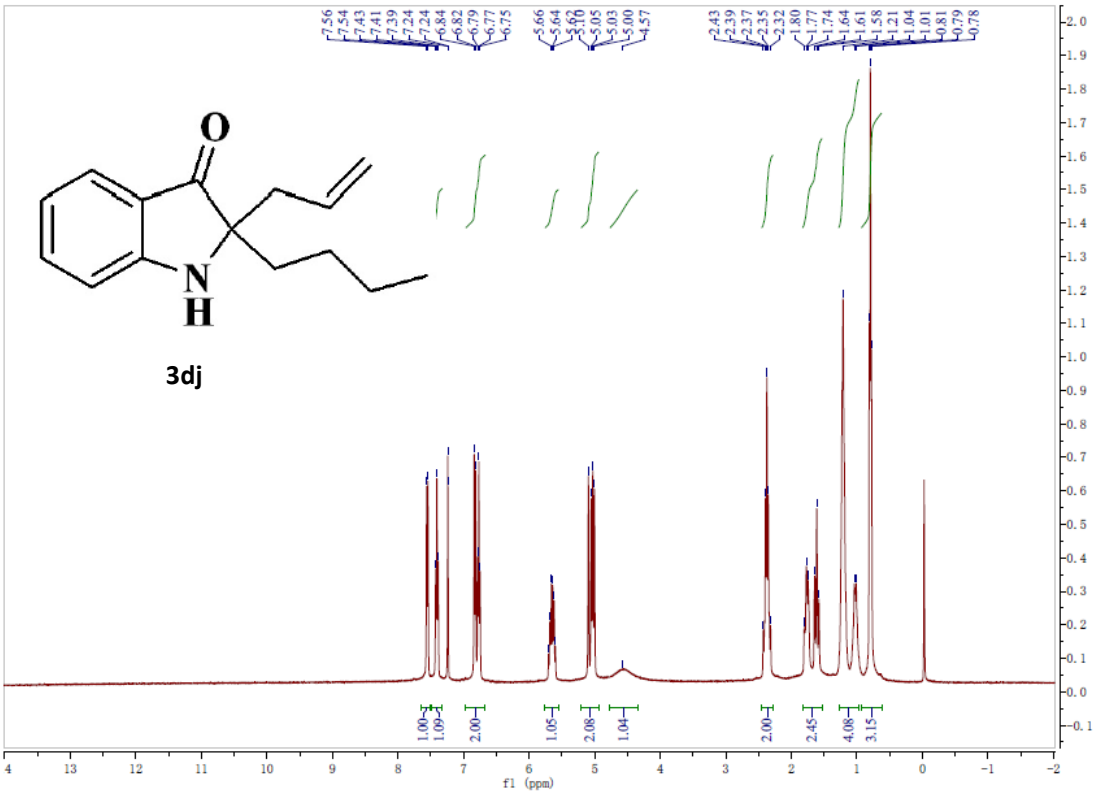
119.55
119.34
112.32
70.64
42.75
O
N
H
3di
f1 (ppm)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6.77
6.75
5.66
5.64
5.62
5.10
5.05
5.03
5.00
4.57
2.43
2.39
2.37
2.35
2.32
1.80
1.77
1.74
1.64
1.61
1.58
1.21
1.04
1.01
0.81
0.79
0.78
1.00
1.09
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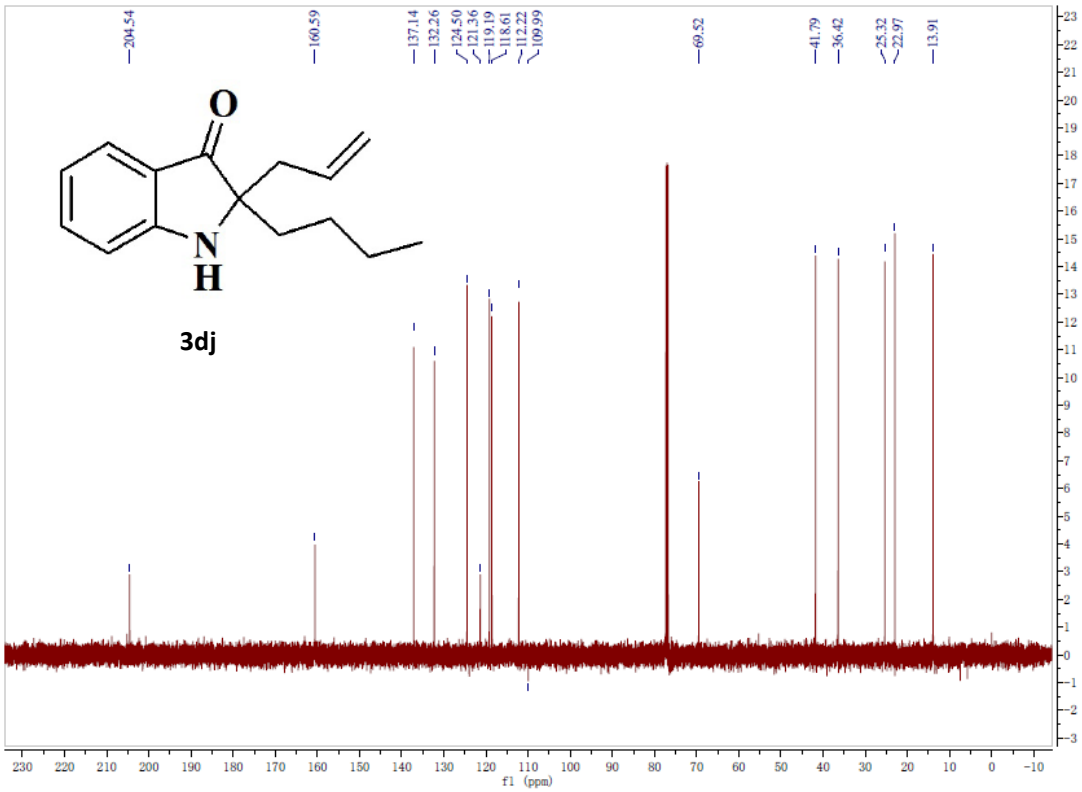
1.04
2.00
2.45
4.08
3.15
O
N
H
3dj
f1 (ppm)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124.50
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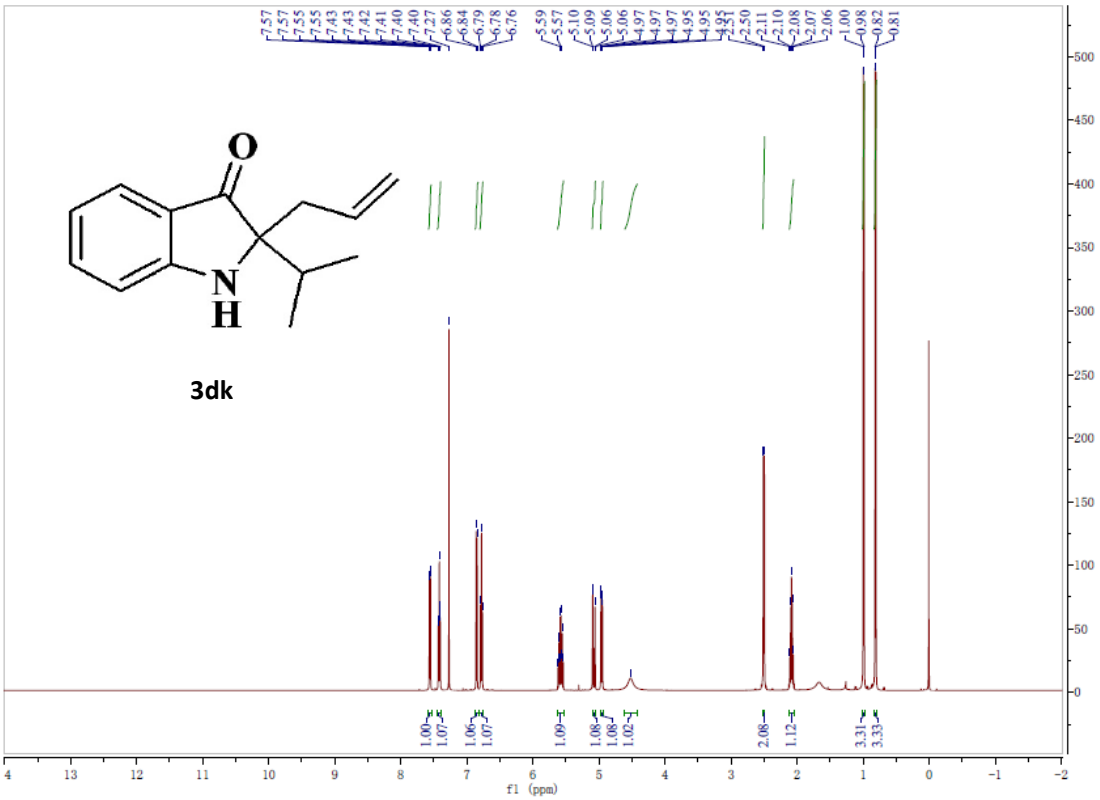
119.19
118.61
112.22
109.99
69.52
41.79
36.42
25.32
22.97
13.91
O
N
H
f1 (ppm)

3dj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7.55
7.55
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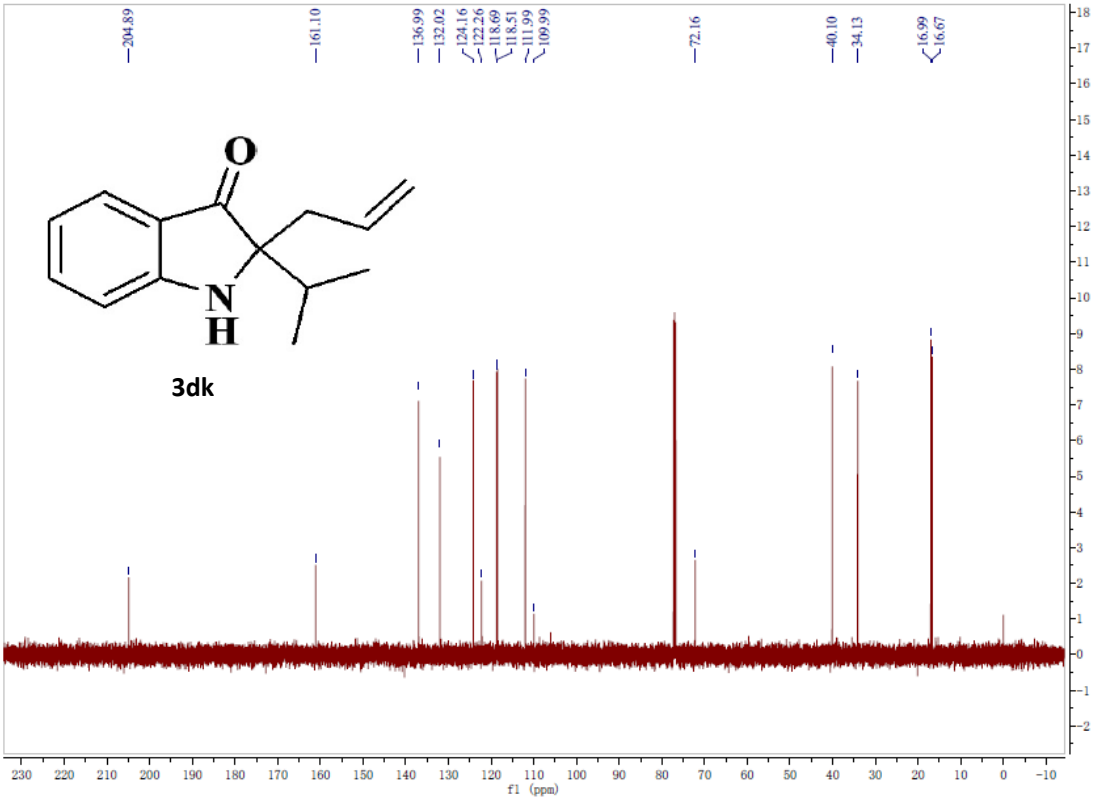
7.43
7.42
7.41
7.40
7.40
7.27
6.86
6.84
6.79
6.78
6.76
5.59
5.57
5.10
5.09
5.06
5.06
4.97
4.97
4.95
4.95
2.50
2.11
2.10
2.08
2.07
2.06
1.00
0.98
0.82
0.81
1.00
1.07
1.06
1.07
1.09
1.08
1.08
1.02
2.08
1.12
3.31
3.33
O
N
H
f1 (ppm)

3dk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136.99
132.02
124.16
122.26
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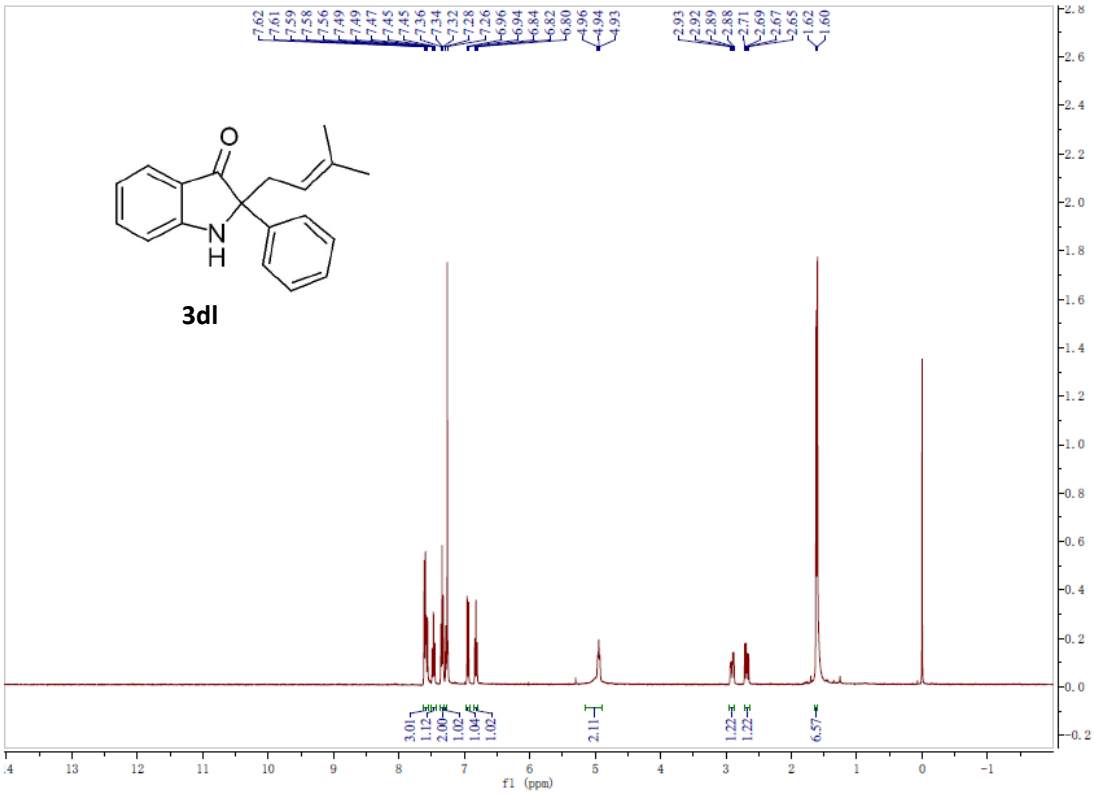
118.51
111.99
109.99
72.16
40.10
34.13
16.99
16.67
O
N
H
f1 (ppm)

3dk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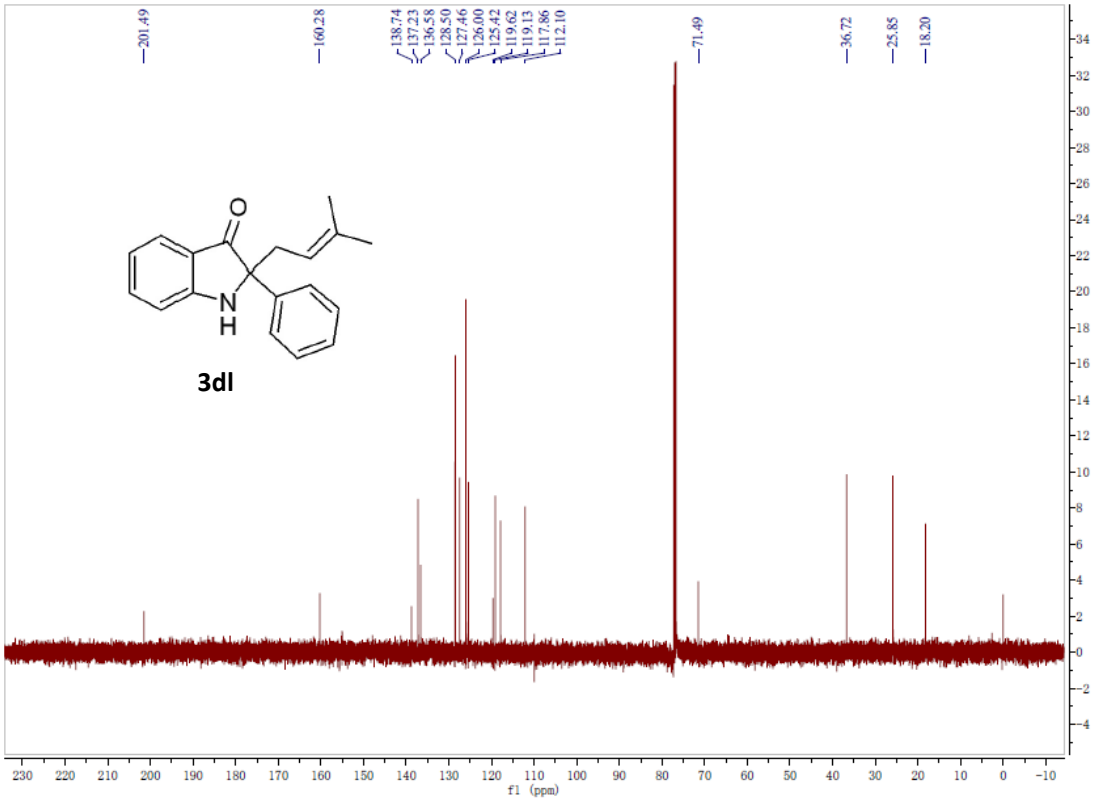
7.61
7.59
7.58
7.56
7.49
7.49
7.47
7.45
7.45
7.36
7.34
7.32
7.28
7.26
6.96
6.94
6.84
6.82
6.80
4.96
4.94
4.93
2.93
2.92
2.89
2.88
2.71
2.69
2.67
2.65
1.62
1.60
3.01
1.12
2.00
1.02
1.04
1.02
2.11
1.22
1.22
6.57
O
N
H
f1 (ppm)

3dl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138.74
137.23
136.58
128.50
127.46
126.00
125.42
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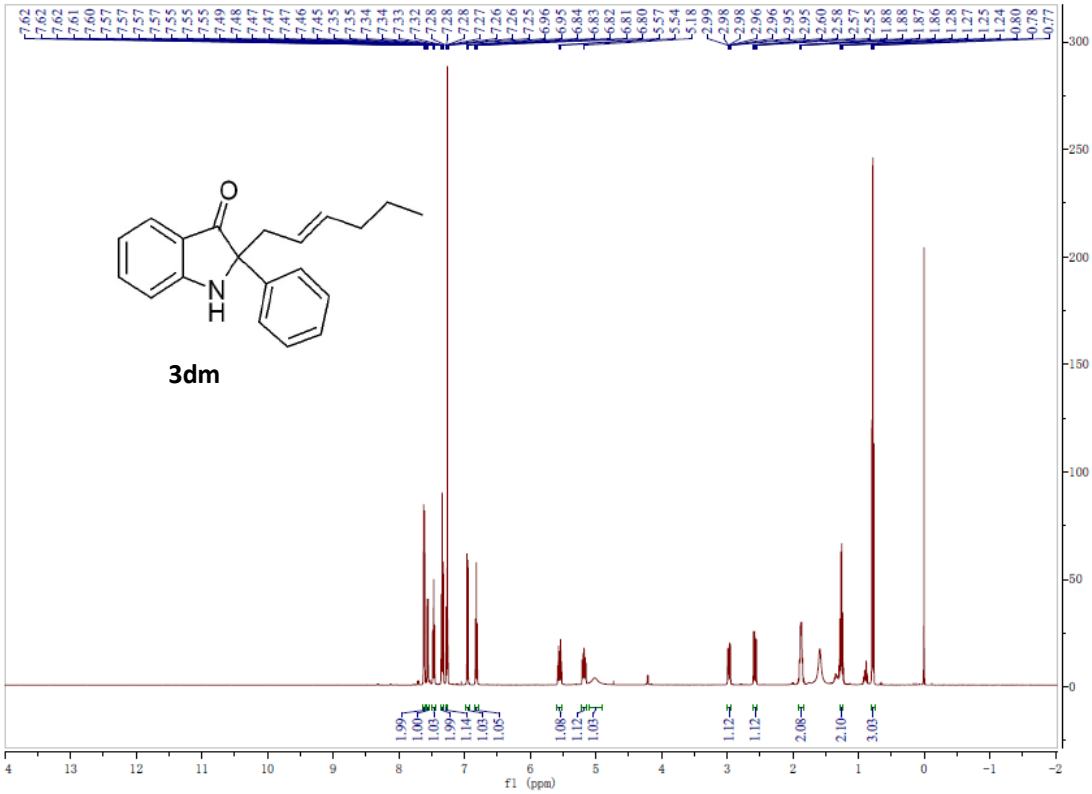
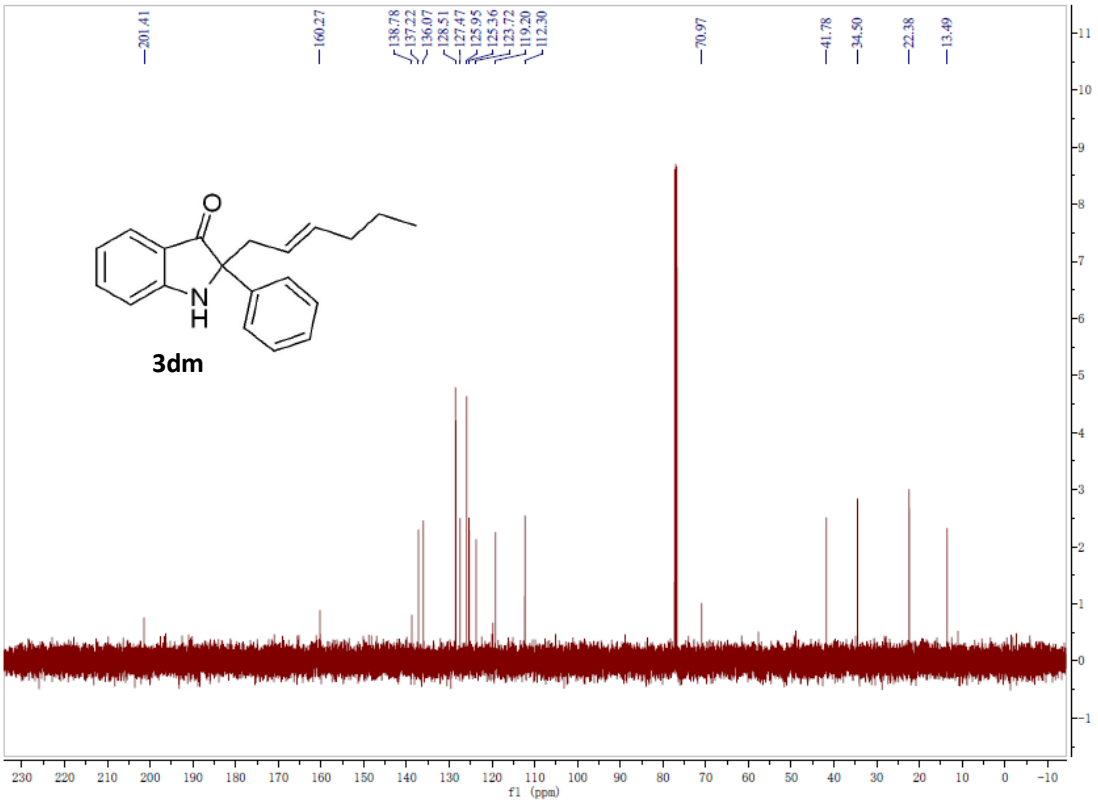
119.13
117.86
112.10
71.49
36.72
25.85
18.20
O
N
H
3dl
f1 (ppm)


O
N
H
3dm
f1 (ppm)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138.78
137.22
136.07
128.51
127.47
125.95
125.36
123.72
119.20
112.30
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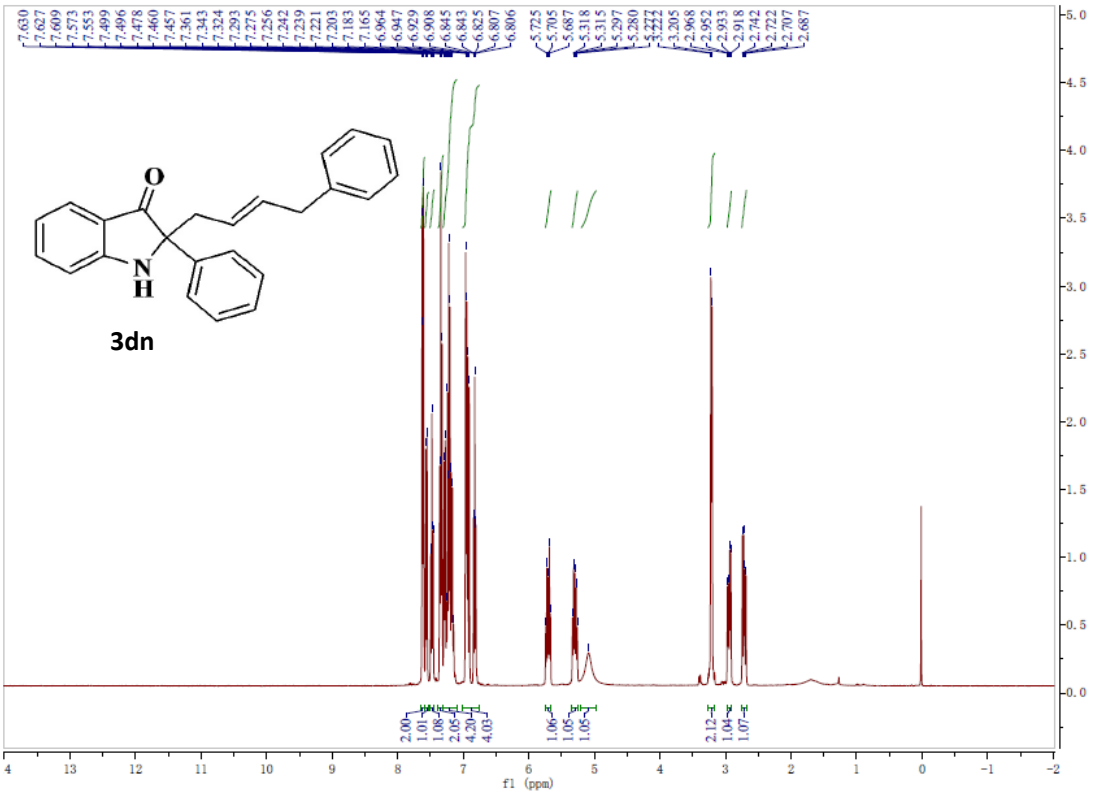
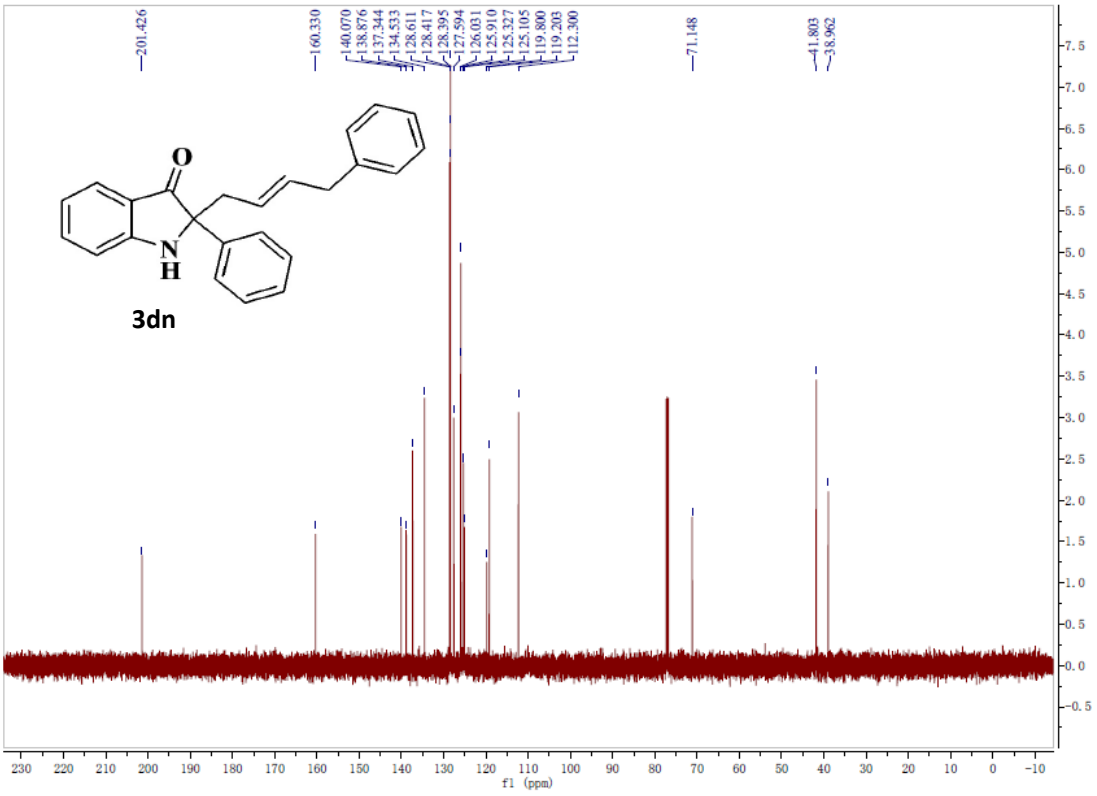
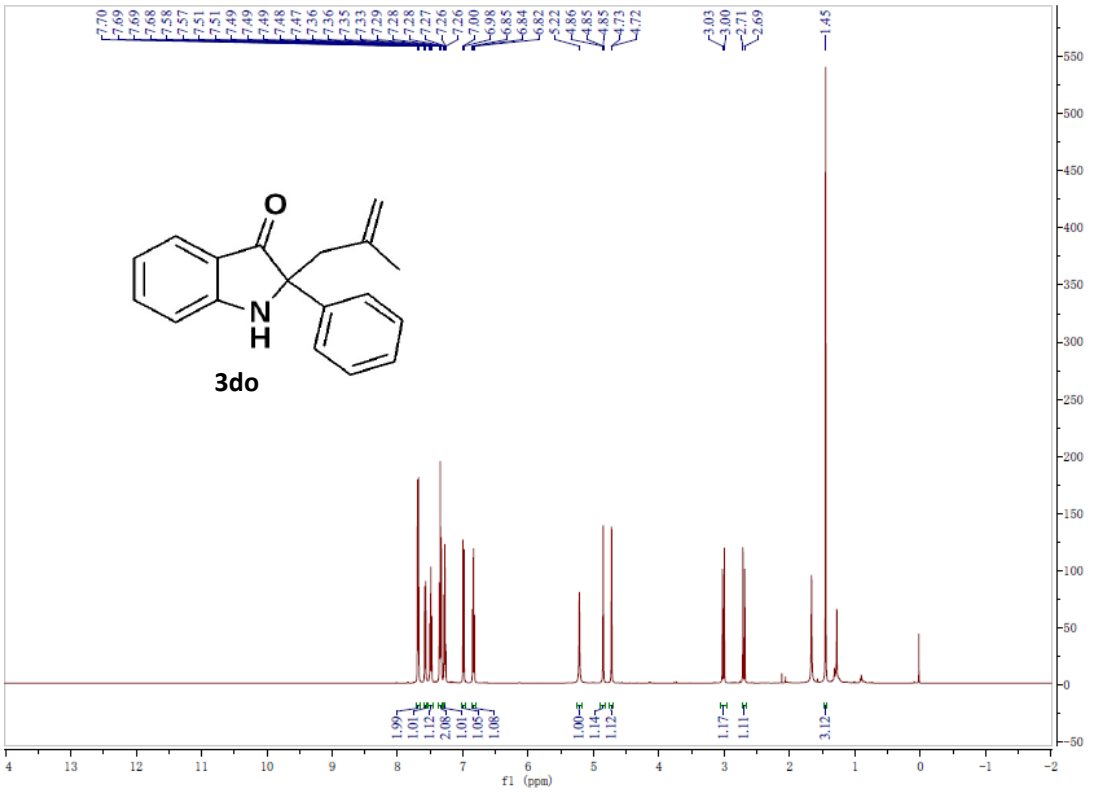
34.50
22.38
13.49
3dm
f1 (ppm)


3dn
f1 (ppm)


201.426
160.330
140.070
138.876
137.344
134.533
128.611
128.417
128.395
127.594
126.031
125.910
125.327
125.105
119.800
119.203
112.300
71.148
41.803
38.962
O
N
H
3dn
f1 (ppm)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7.69
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7.58
7.57
7.51
7.51
7.49
7.49
7.49
7.48
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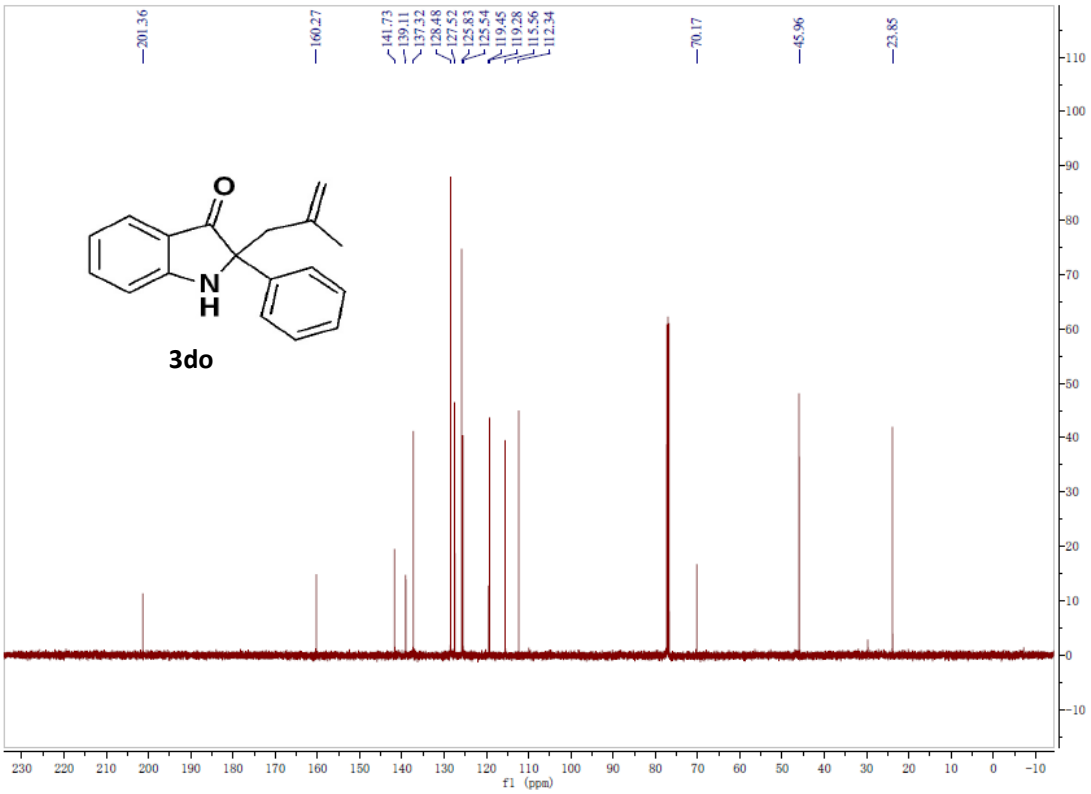
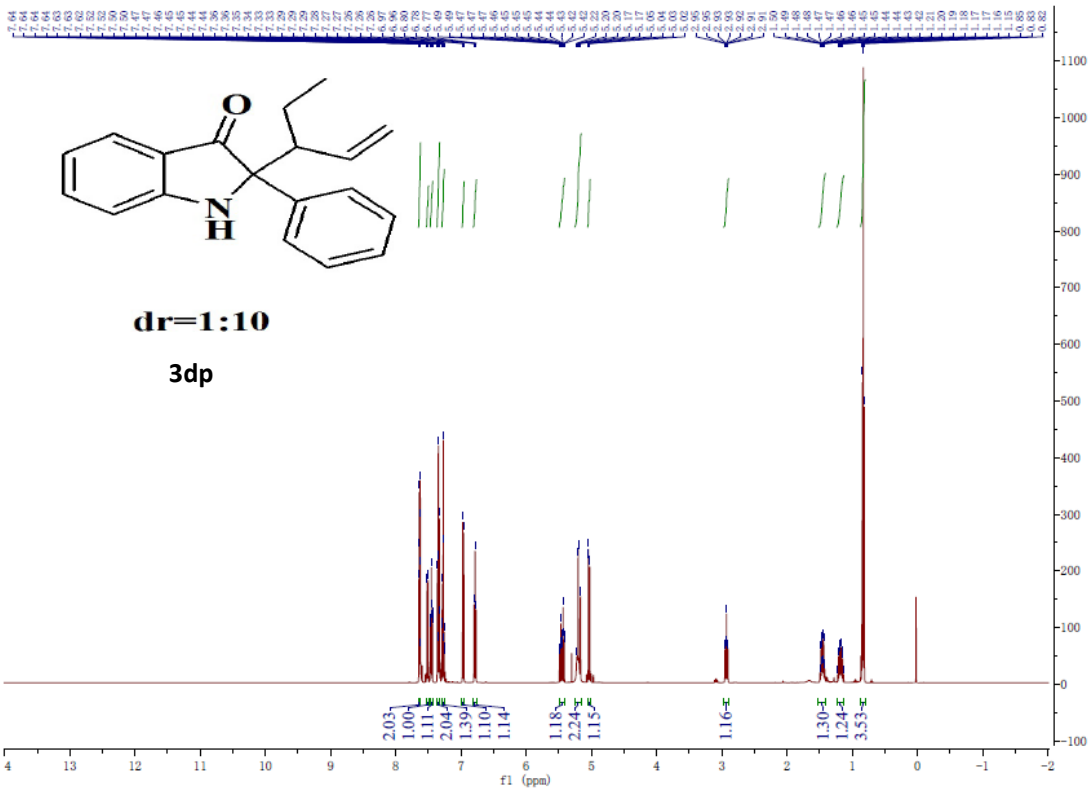
7.35
7.33
7.29
7.28
7.28
7.27
7.26
7.26
7.00
6.98
6.85
6.84
6.82
5.22
4.86
4.85
4.85
4.73
4.72
3.03
3.00
2.71
2.69
1.45
1.99
1.01
1.12
2.08
1.01
1.05
1.08
1.00
1.14
1.12
1.17
1.11
3.12
O
N
H
3do
f1 (ppm)

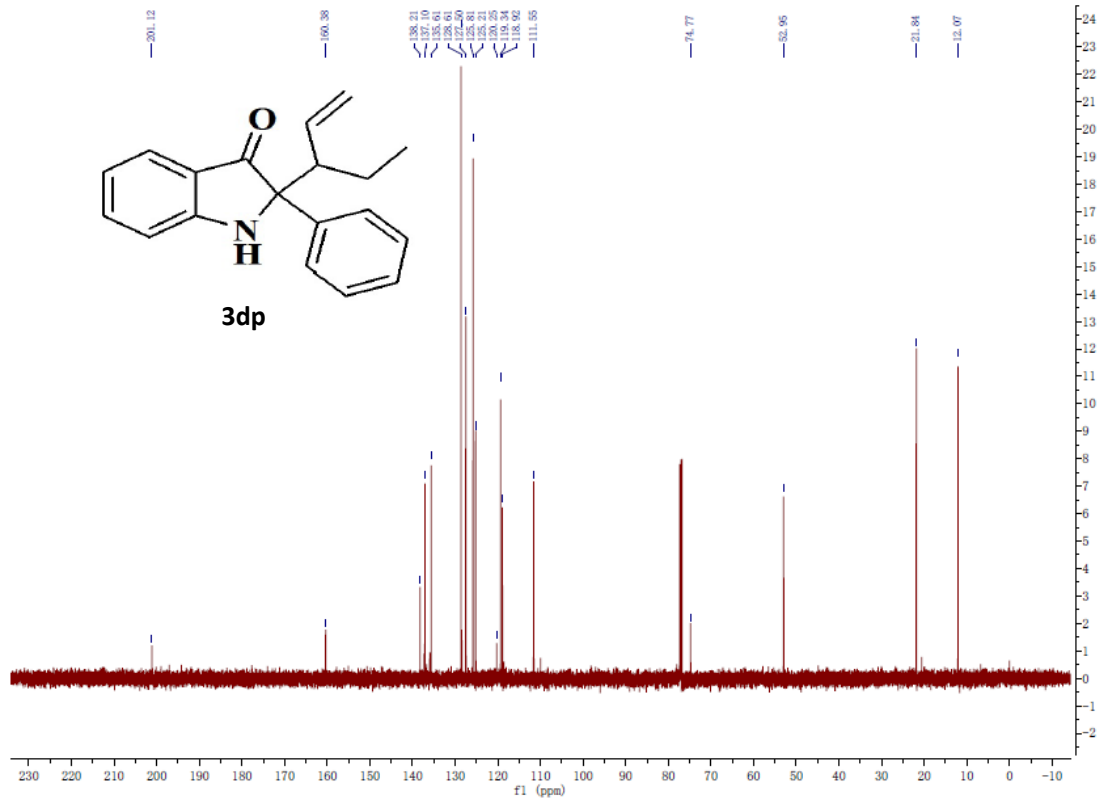


3do



dr=1:10

3dp


201.12
160.38
138.21
137.10
135.61
128.61
127.50
125.81
125.21
120.25
119.34
118.92
111.55
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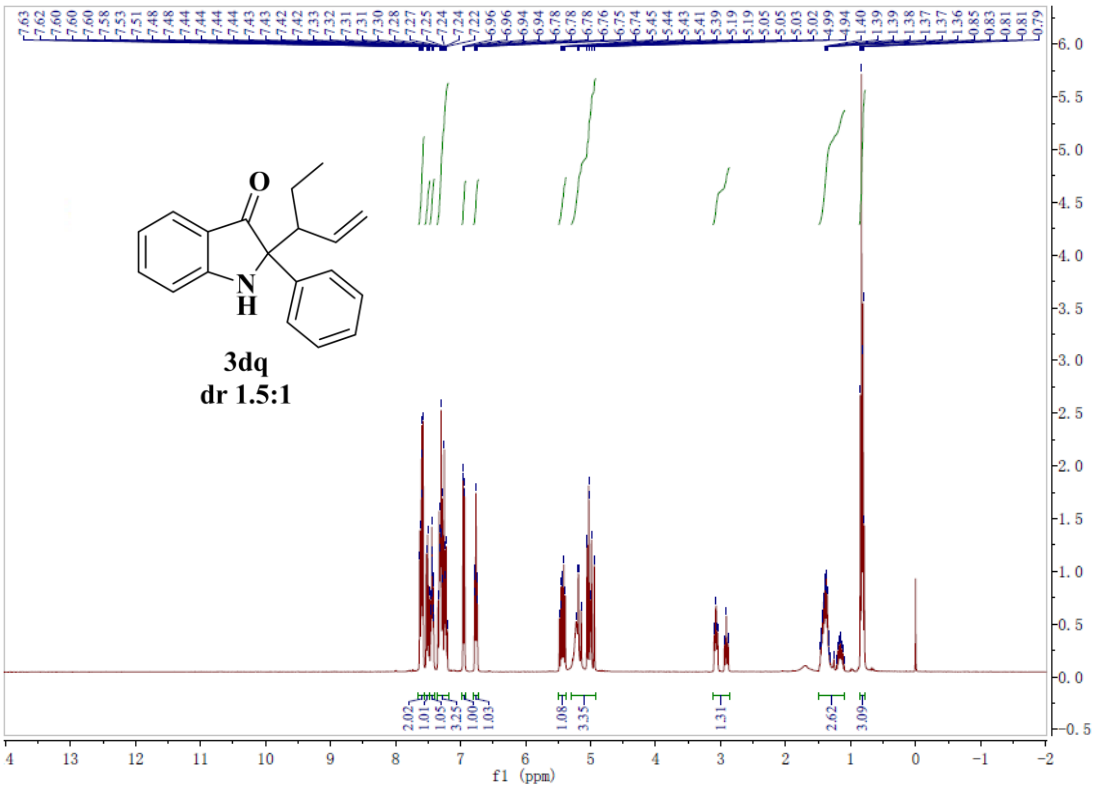
21.84
12.07
O
N
H
3dp
f1 (ppm)


O
N
H
3dq
dr 1.5:1
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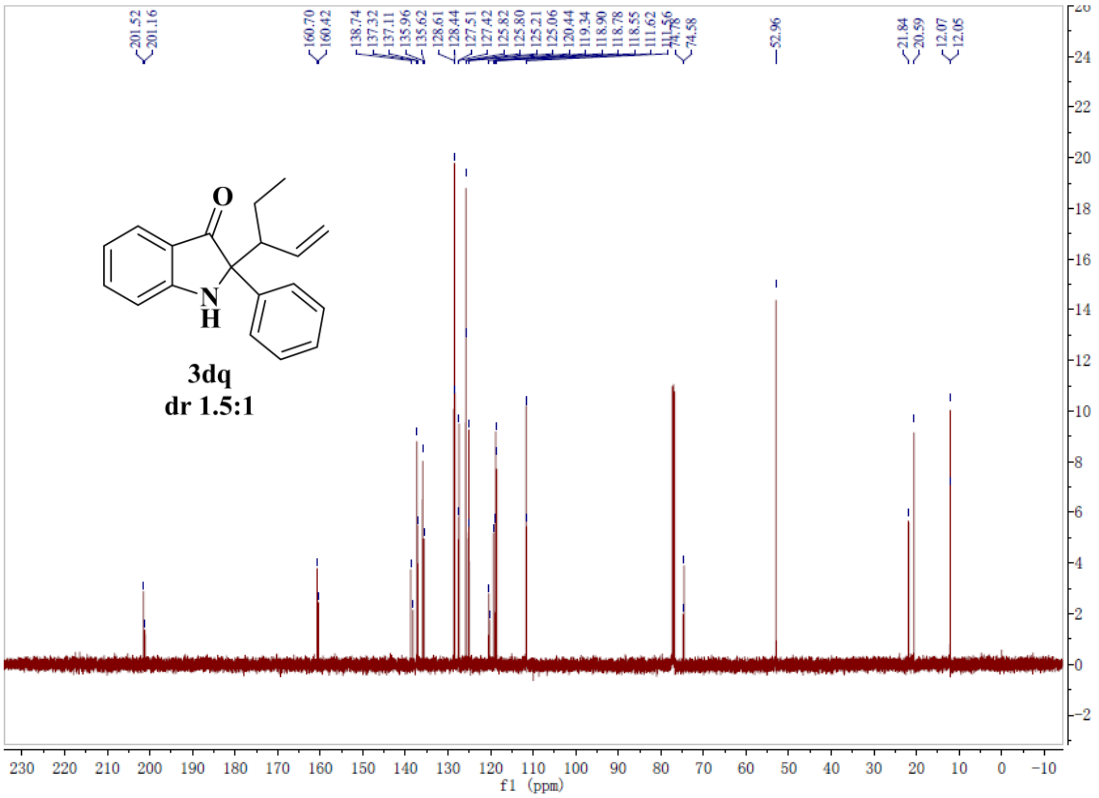
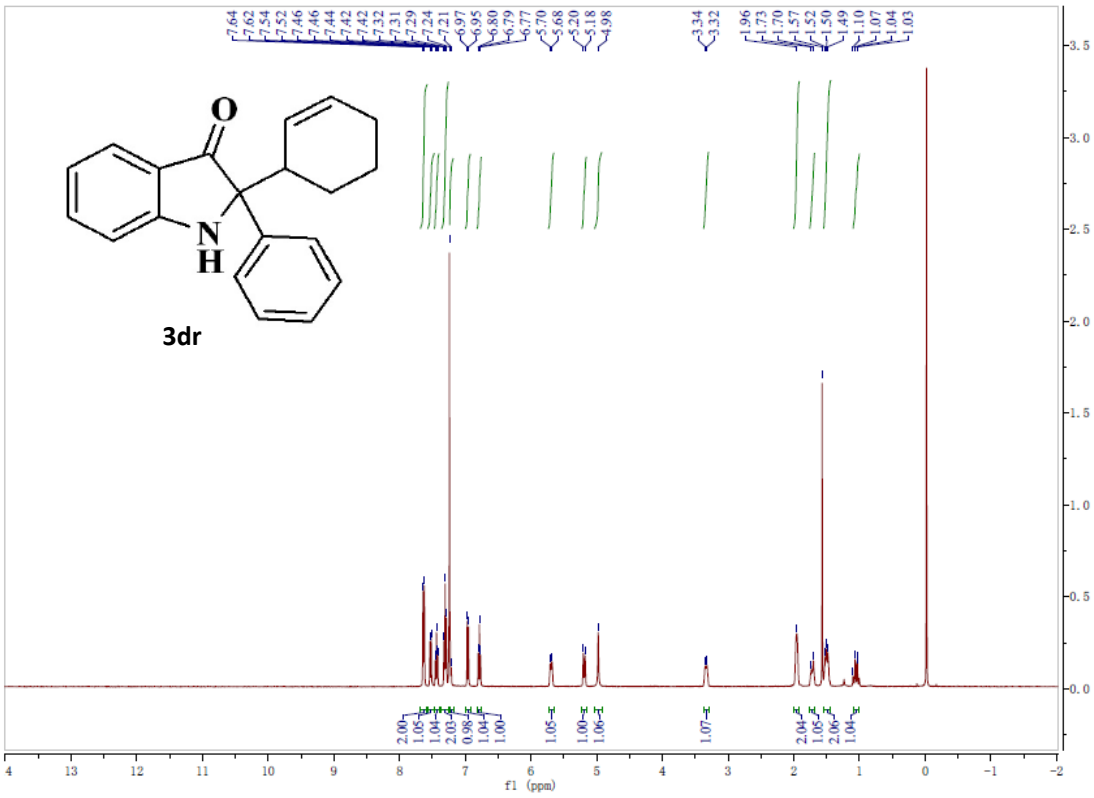
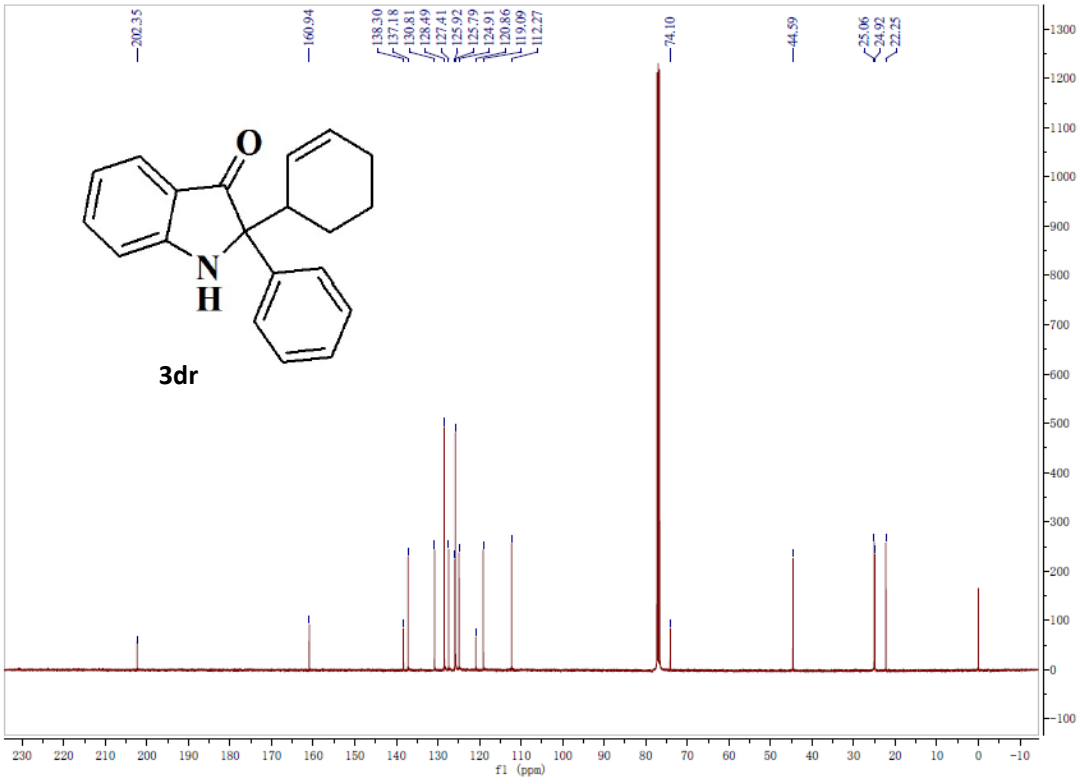
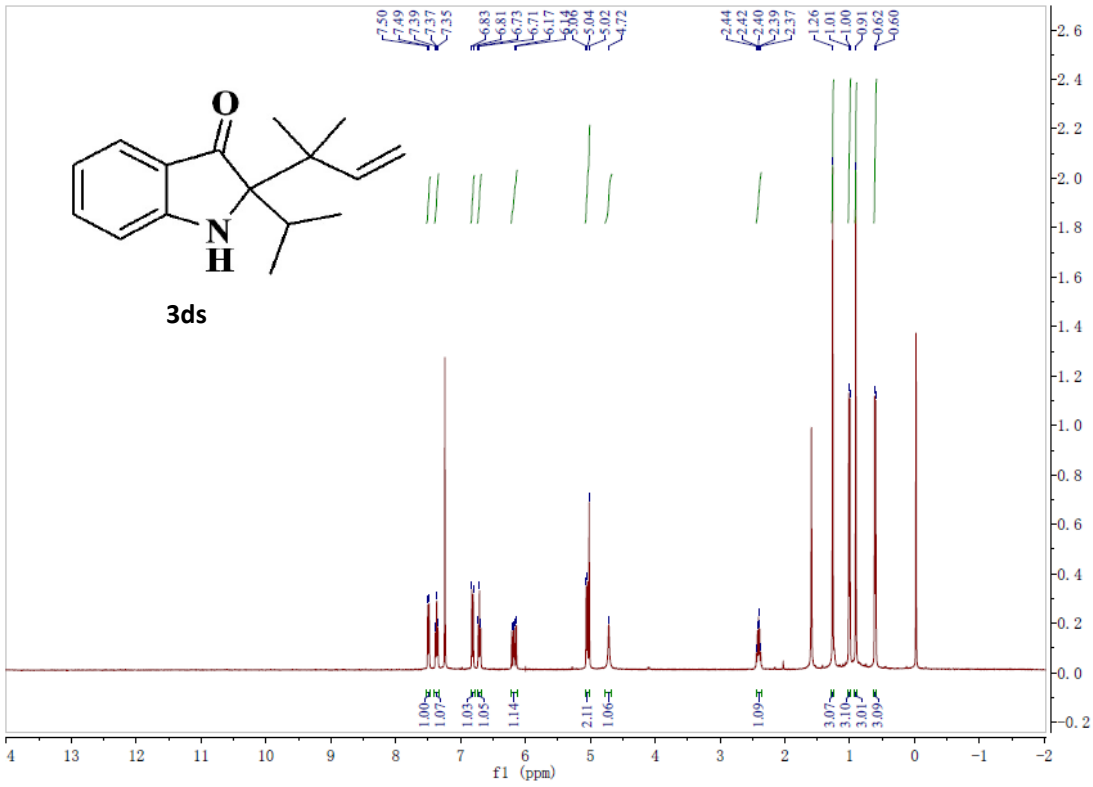
1.01
1.05
3.25
1.00
1.03
1.08
3.35
1.31
2.62
3.09
f1 (ppm)


3dq
dr 1.5:1
f1 (ppm)

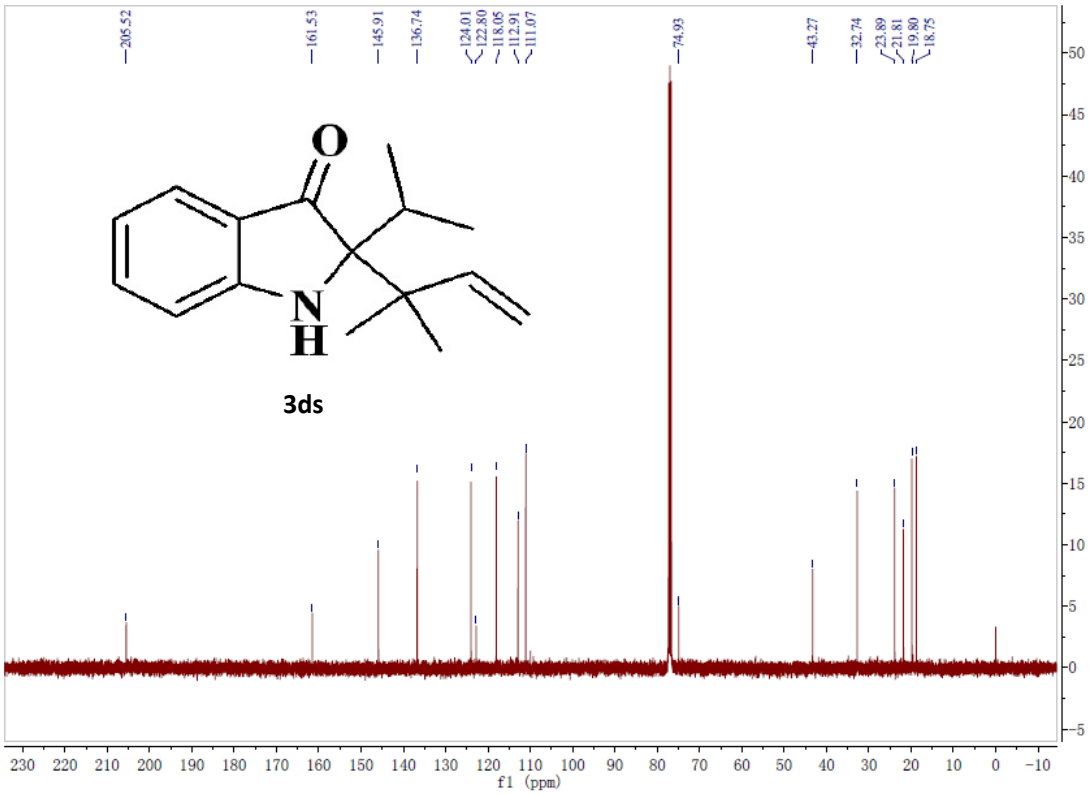

3dr
f1 (ppm)


202.35
160.94
138.30
137.18
130.81
128.49
127.41
125.92
125.79
124.91
120.86
119.09
112.27
74.10
44.59
25.06
24.92
22.25
O
N
H
f1 (ppm)

3dr


7.50
7.49
7.39
7.37
7.35
6.83
6.81
6.73
6.71
6.17
5.14
5.06
5.04
5.02
4.72
2.44
2.42
2.40
2.39
2.37
1.26
1.01
1.00
0.91
0.62
0.60
1.00
1.07
1.03
1.05
1.14
2.11
1.06
1.09
3.07
3.10
3.01
3.09
O
N
H
f1 (ppm)

3ds


205.52
161.53
145.91
136.74
124.01
122.80
118.05
112.91
111.07
74.93
43.27
32.74
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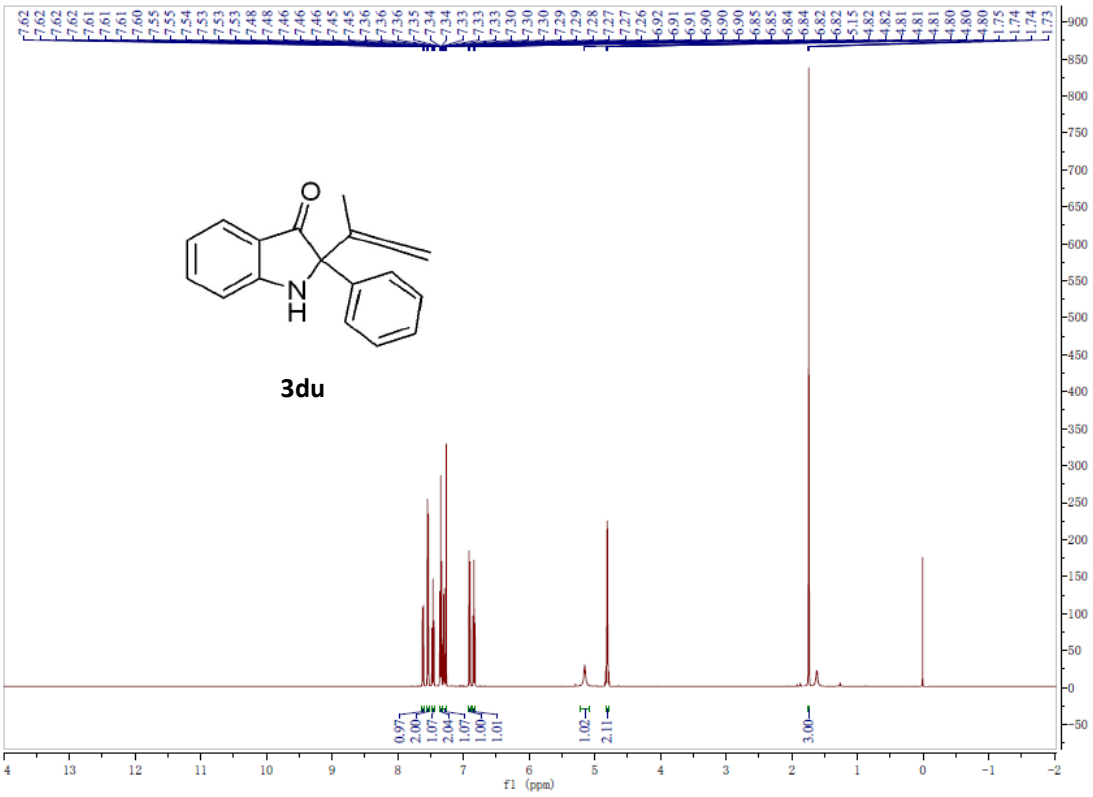
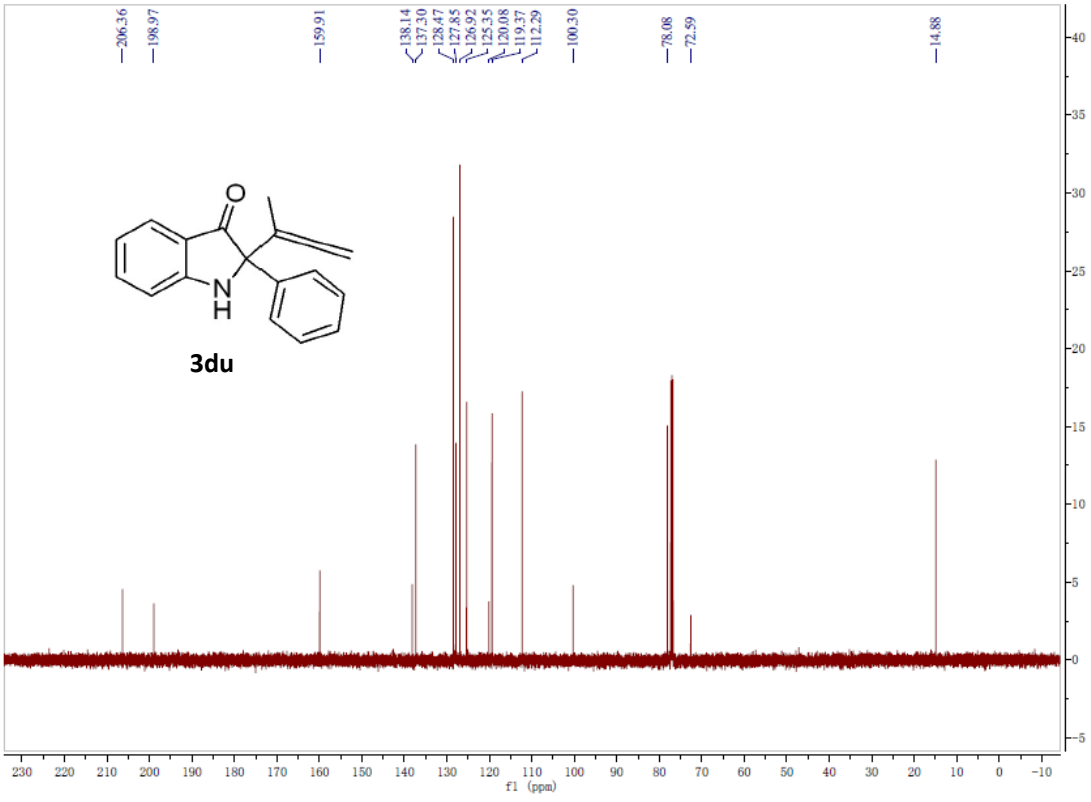
19.80
18.75
O
N
H
f1 (ppm)

3ds


O
N
H
0.97
2.00
1.07
2.04
1.07
1.00
1.01
1.02
2.11
3.00
f1 (ppm)

3du


206.36
198.97
159.91
138.14
137.30
128.47
127.85
126.92
125.35
120.08
119.37
112.29
100.30
78.08
72.59
14.88
O
N
H
3du
f1 (ppm)

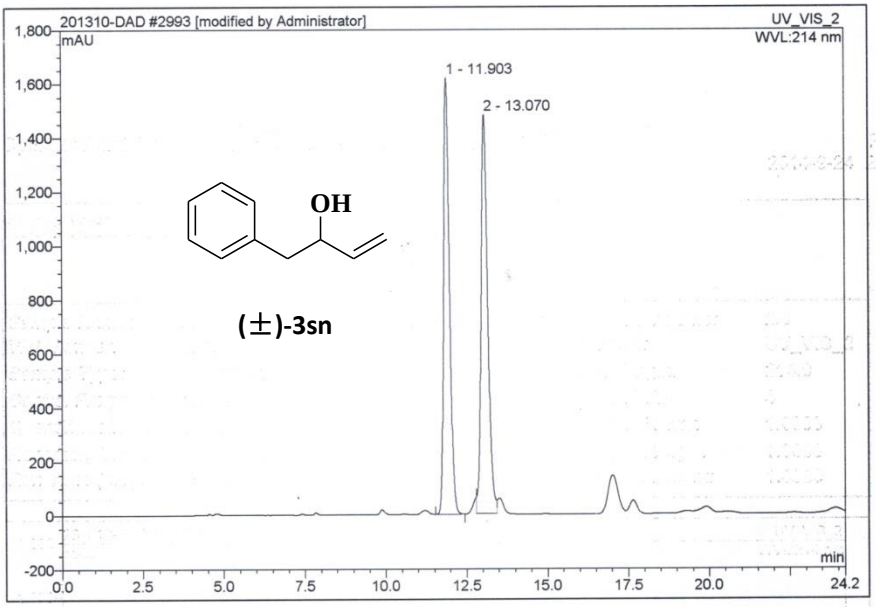
4. HPLC reports for Chirality Transfer

Operator:Administrator Timebase:HPLC Sequence:201310-DAD

Page 1-1
2014-9-24 2:39 下午

2993 XZL-2042-1+- AD-H 955 214 0.7

Sample Name:	**XZL-2042-1+- AD-H 955 214 0.7**	*Injection Volume:*	**2.0**
Vial Number:	**RC4**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**214.0**
Control Program:	**test-dad**	*Bandwidth:*	**4**
Quantif. Method:	**WXL**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014-9-24 13:19**	*Sample Weight:*	**1.0000**
Run Time (min):	**24.22**	*Sample Amount:*	**1.0000**



(±)-3sn

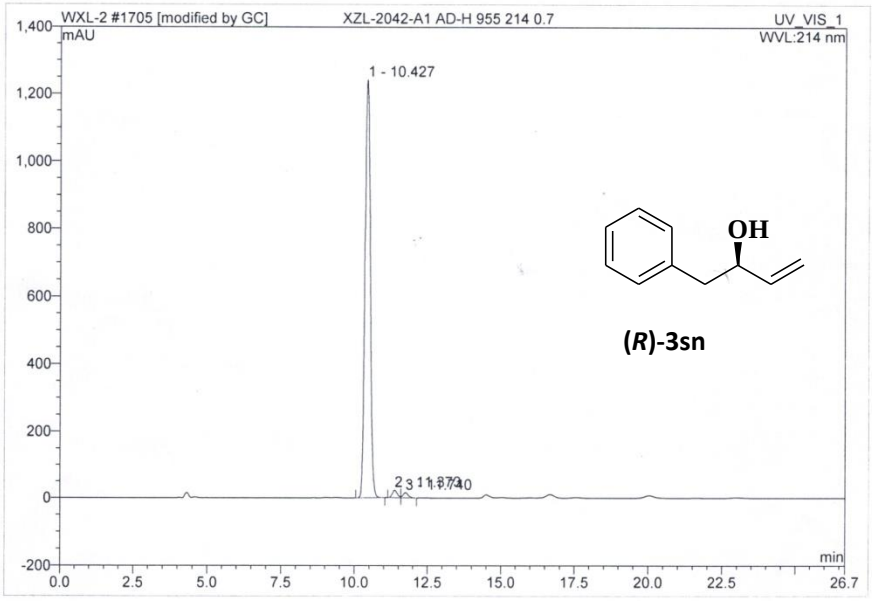
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.90	n.a.	1618.859	343.066	49.00	n.a.	BMB*
2	13.07	n.a.	1479.911	357.111	51.00	n.a.	M *
Total:			3098.770	700.178	100.00	0.000	

defltdad/Integration

Chromeleon (c) Dionex 1996-200
Version 6.80 SR14 Build 4527 (238909

1705 XZL-2042-A1 AD-H 955 214 0.7

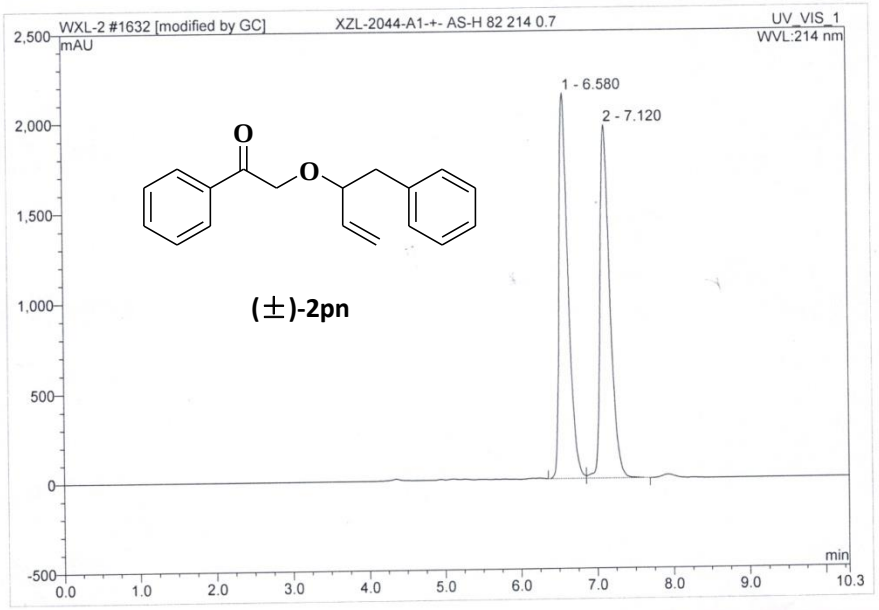
Sample Name:	**XZL-2042-A1 AD-H 955 214 0.7**	*Injection Volume:*	**10.0**
Vial Number:	**RA4**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**WXL-2014**	*Bandwidth:*	**n.a.**
Quantif. Method:	**WXL**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014/10/9 16:00**	*Sample Weight:*	**1.0000**
Run Time (min):	**26.69**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.43	n.a.	1241.150	261.720	97.19	n.a.	BMB*
2	11.37	n.a.	22.535	4.426	1.64	n.a.	BM *
3	11.74	n.a.	15.127	3.142	1.17	n.a.	MB*
Total:			1278.812	269.288	100.00	0.000	

1632 XZL-2044-A1-+- AS-H 82 214 0.7

Sample Name:	**XZL-2044-A1-+- AS-H 82 214 0.7**	*Injection Volume:*	**5.0**
Vial Number:	**RD7**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**WXL-2014**	*Bandwidth:*	**n.a.**
Quantif. Method:	**WXL**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014/9/26 12:53**	*Sample Weight:*	**1.0000**
Run Time (min):	**10.31**	*Sample Amount:*	**1.0000**

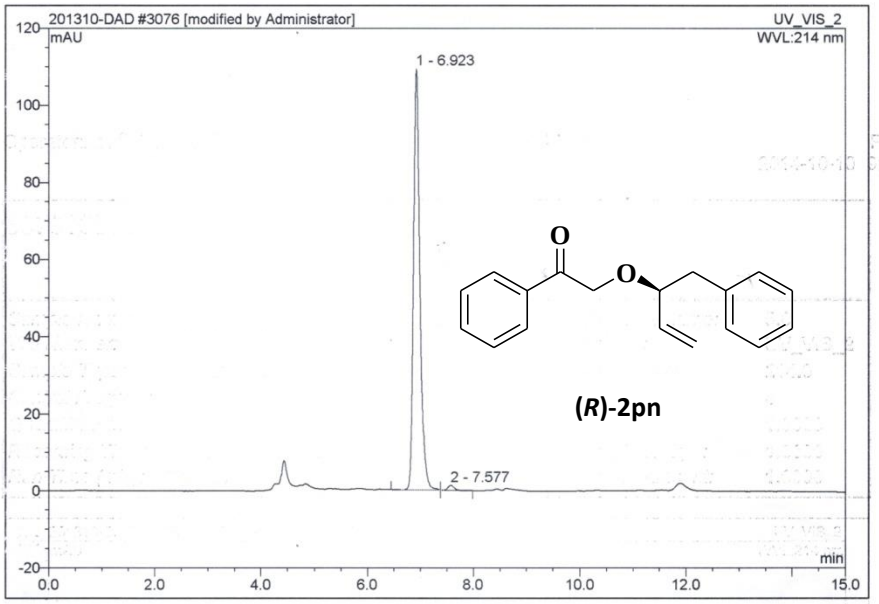


(±)-2pn

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.58	n.a.	2145.738	296.173	49.82	n.a.	BM *
2	7.12	n.a.	1965.778	298.355	50.18	n.a.	MB*
Total:			4111.516	594.529	100.00	0.000	

3076 XZL-2044-A2 AS-H 82 214 0.7

Sample Name:	**XZL-2044-A2 AS-H 82 214 0.7**	*Injection Volume:*	**5.0**
Vial Number:	**BC7**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**214.0**
Control Program:	**test-dad2**	*Bandwidth:*	**4**
Quantif. Method:	**WXL**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014-10-9 16:08**	*Sample Weight:*	**1.0000**
Run Time (min):	**15.00**	*Sample Amount:*	**1.0000**

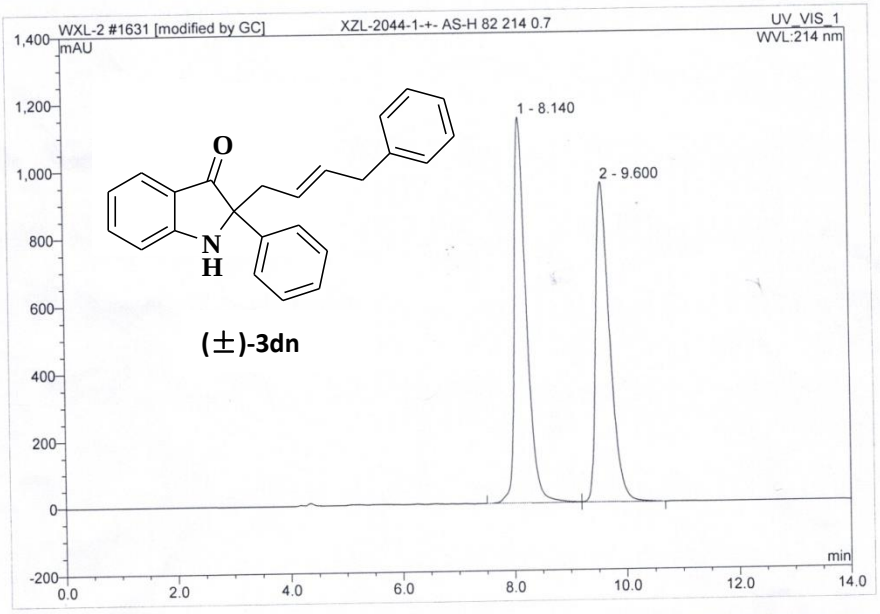


(*R*)-2pn

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.92	n.a.	109.109	15.190	98.91	n.a.	BMb*
2	7.58	n.a.	1.257	0.167	1.09	n.a.	bMB*
Total:			110.367	15.358	100.00	0.000	

1631 XZL-2044-1-+- AS-H 82 214 0.7

Sample Name:	**XZL-2044-1-+- AS-H 82 214 0.7**	*Injection Volume:*	**5.0**
Vial Number:	**RD6**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**WXL-2014**	*Bandwidth:*	**n.a.**
Quantif. Method:	**WXL**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014/9/26 12:11**	*Sample Weight:*	**1.0000**
Run Time (min):	**40.00**	*Sample Amount:*	**1.0000**

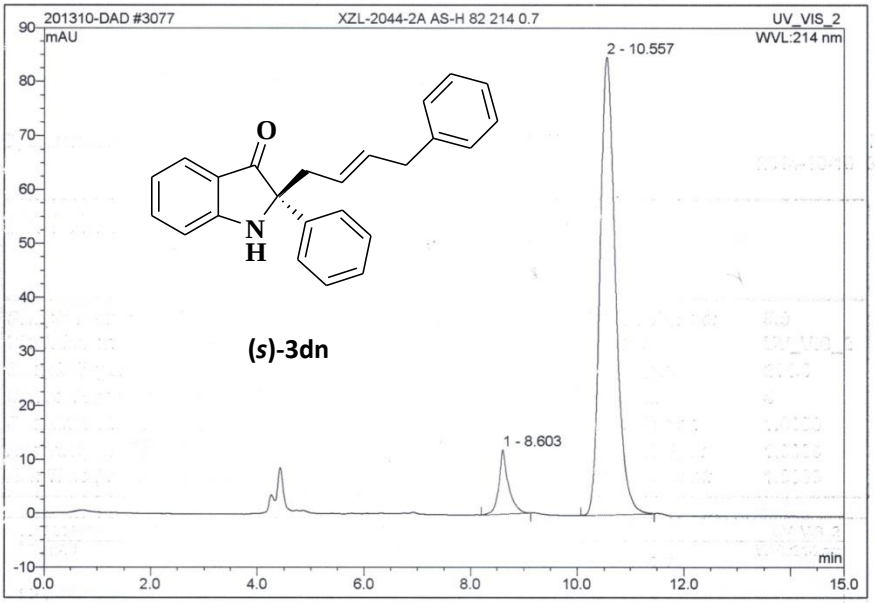


(±)-3dn

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.14	n.a.	1147.889	286.926	50.97	n.a.	BM *
2	9.60	n.a.	952.504	276.031	49.03	n.a.	MB*
Total:			2100.393	562.957	100.00	0.000	

3077 XZL-2044-2A AS-H 82 214 0.7

Sample Name:	**XZL-2044-2A AS-H 82 214 0.7**	*Injection Volume:*	**5.0**
Vial Number:	**BD7**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**214.0**
Control Program:	**test-dad2**	*Bandwidth:*	**4**
Quantif. Method:	**WXL**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014-10-9 15:49**	*Sample Weight:*	**1.0000**
Run Time (min):	**15.00**	*Sample Amount:*	**1.0000**

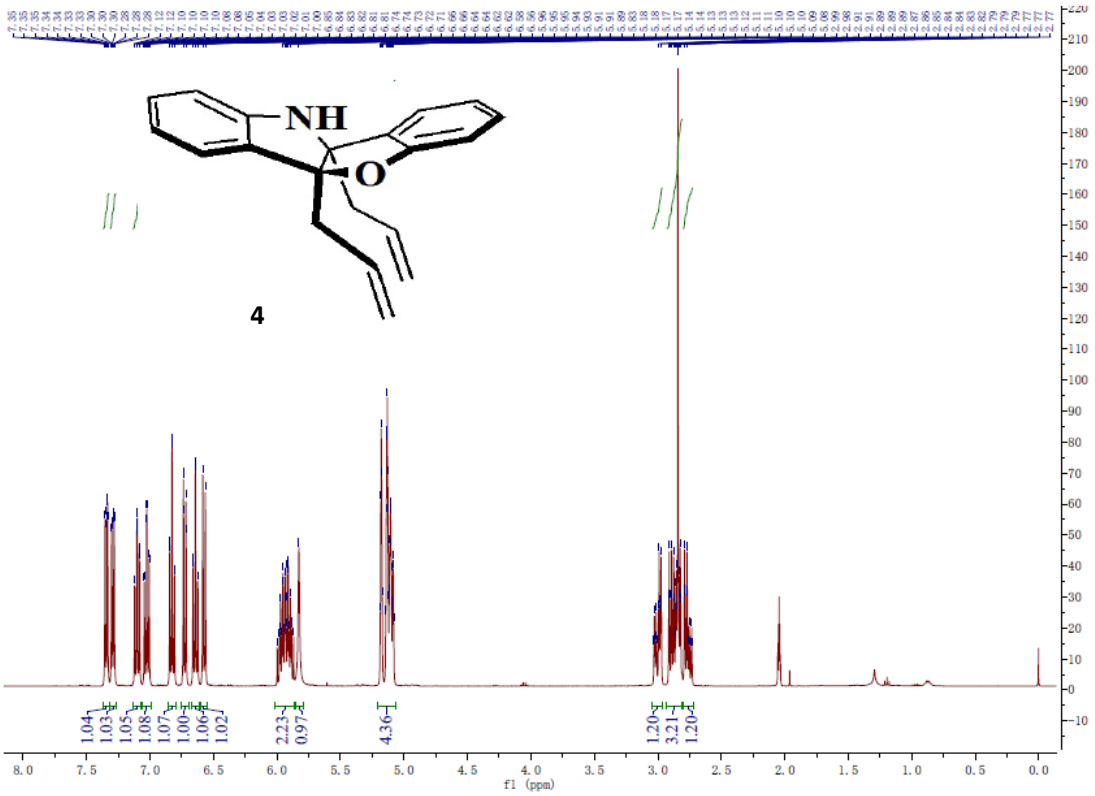


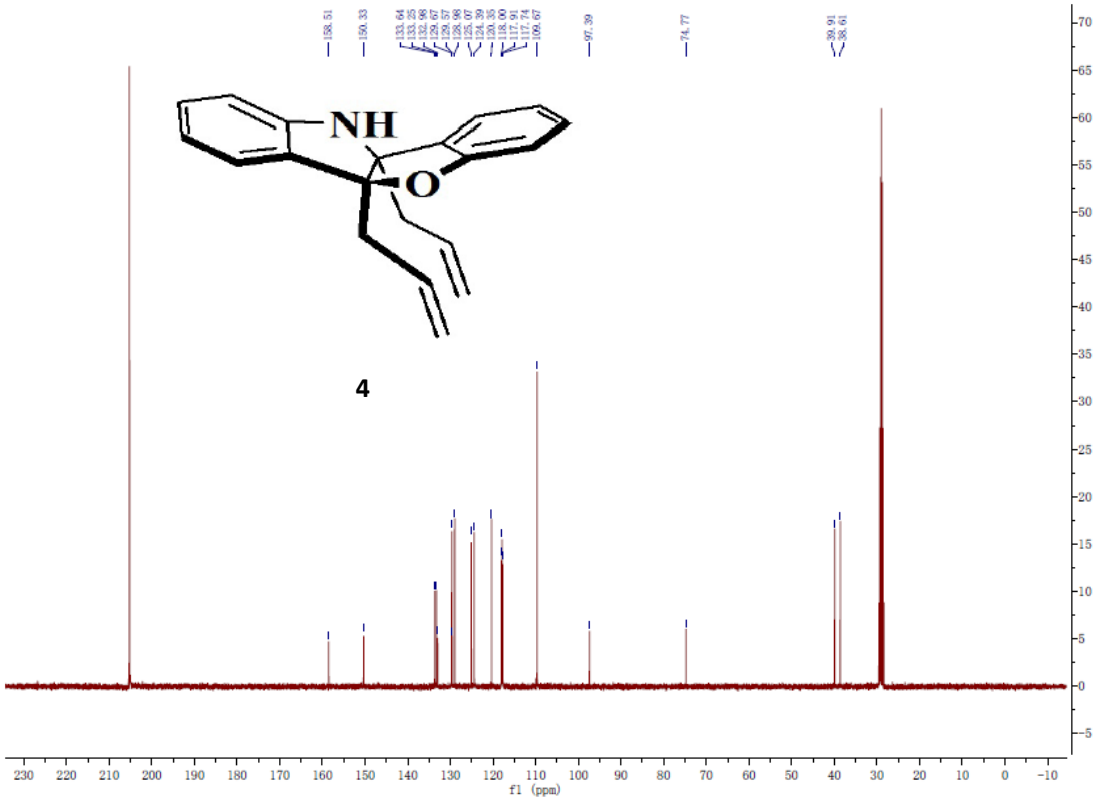
(*s*)-3dn

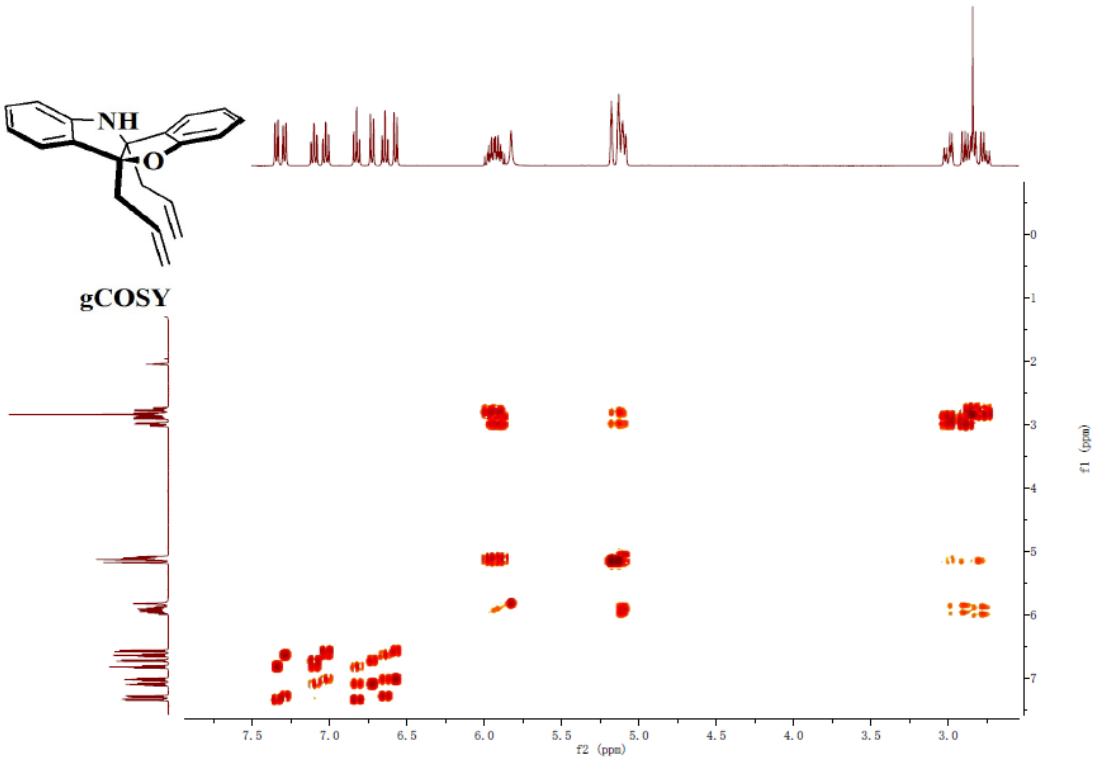
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.60	n.a.	12.003	2.509	8.07	n.a.	BMB
2	10.56	n.a.	84.829	28.568	91.93	n.a.	BMB
Total:			96.832	31.077	100.00	0.000	

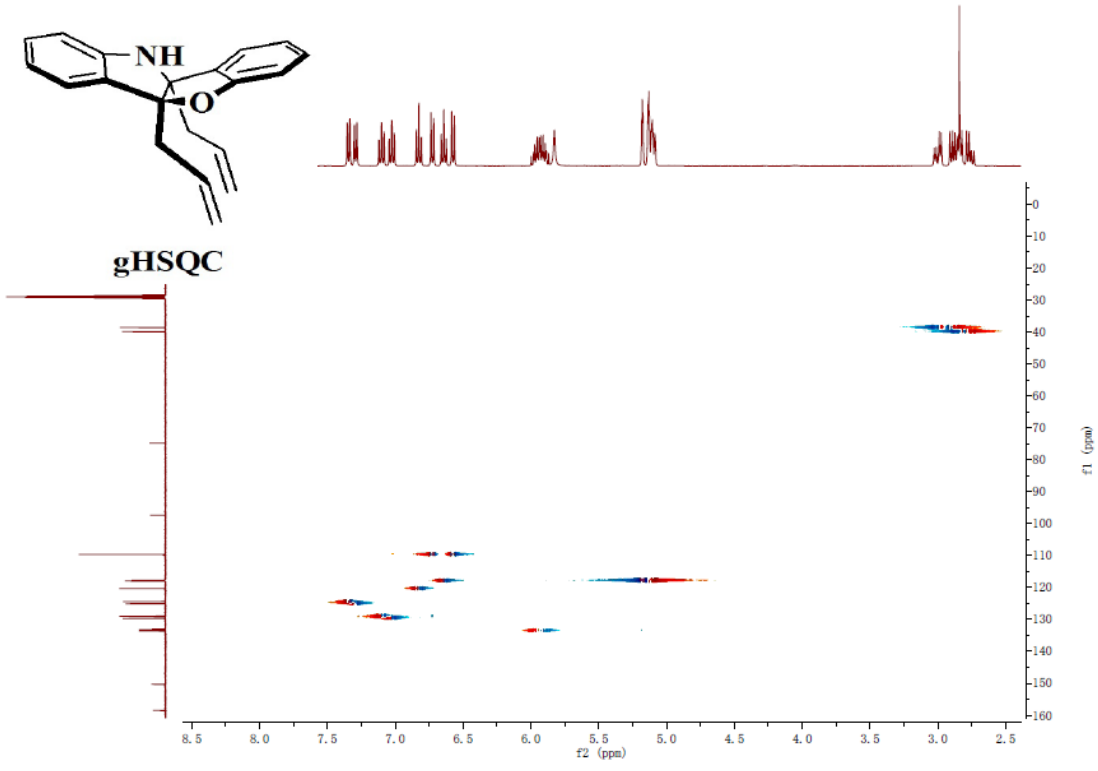
defltdad/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR14 Build 4527 (238909)


NH
O
4
1.04
1.03
1.05
1.08
1.07
1.00
1.06
1.02
2.23
0.97
4.36
1.20
3.21
1.20
f1 (ppm)


NH
O
4
f1 (ppm)


NH
O
gCOSY
f2 (ppm)
f1 (ppm)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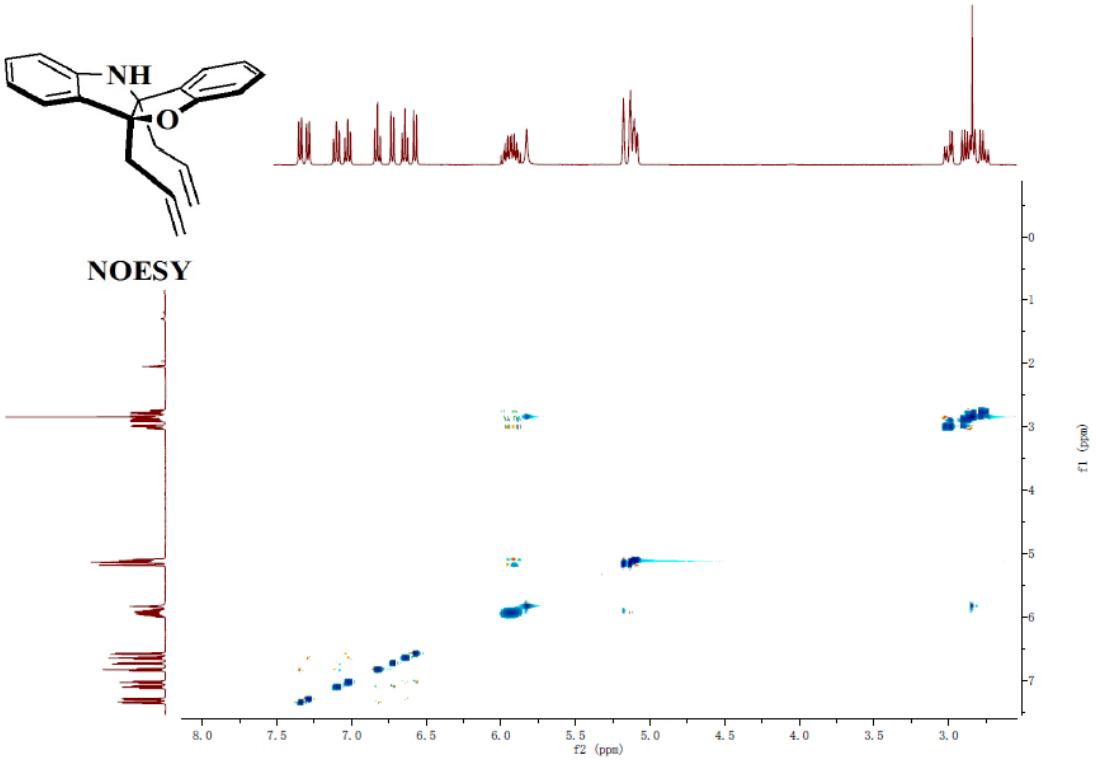
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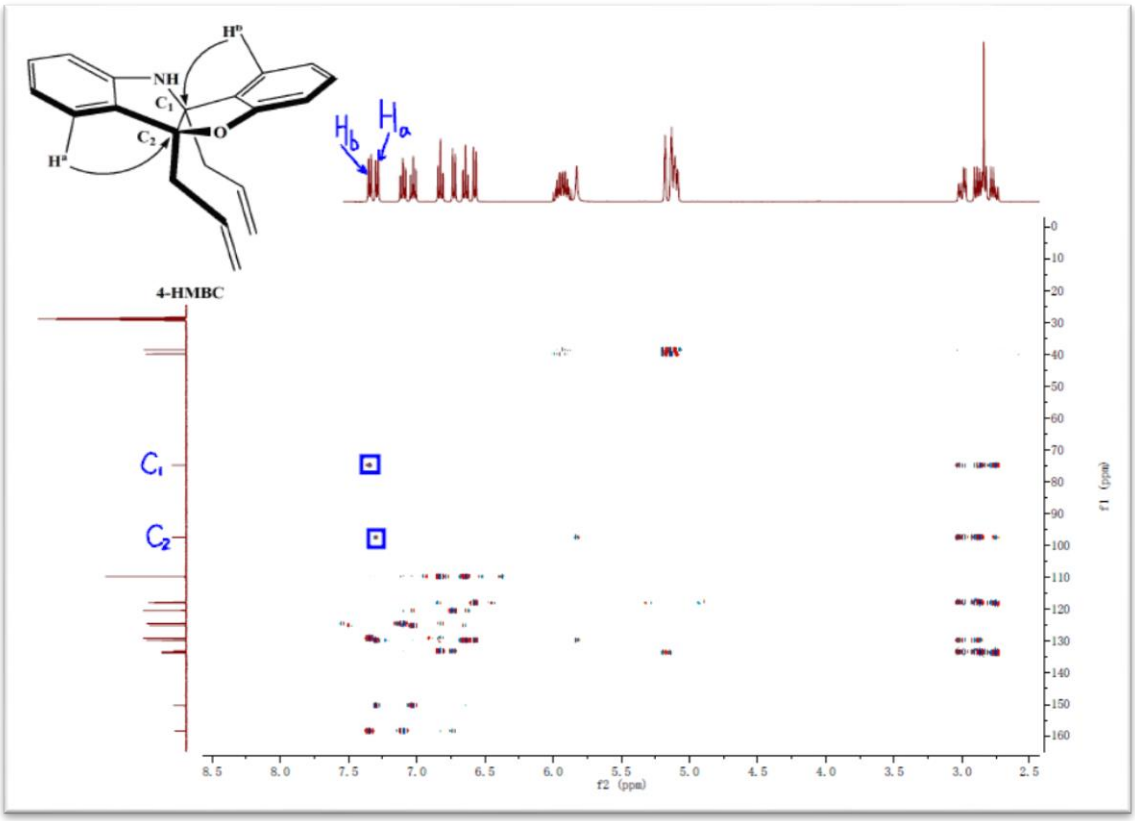
f2 (ppm)
f1 (ppm)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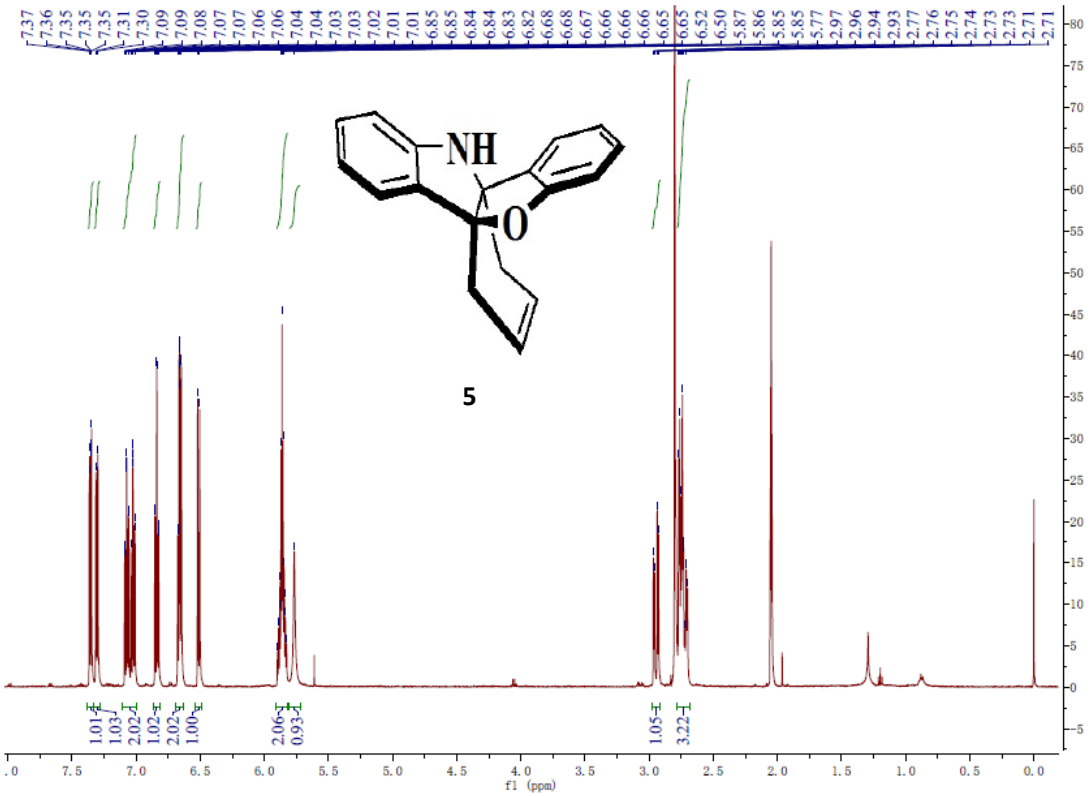
f1 (ppm)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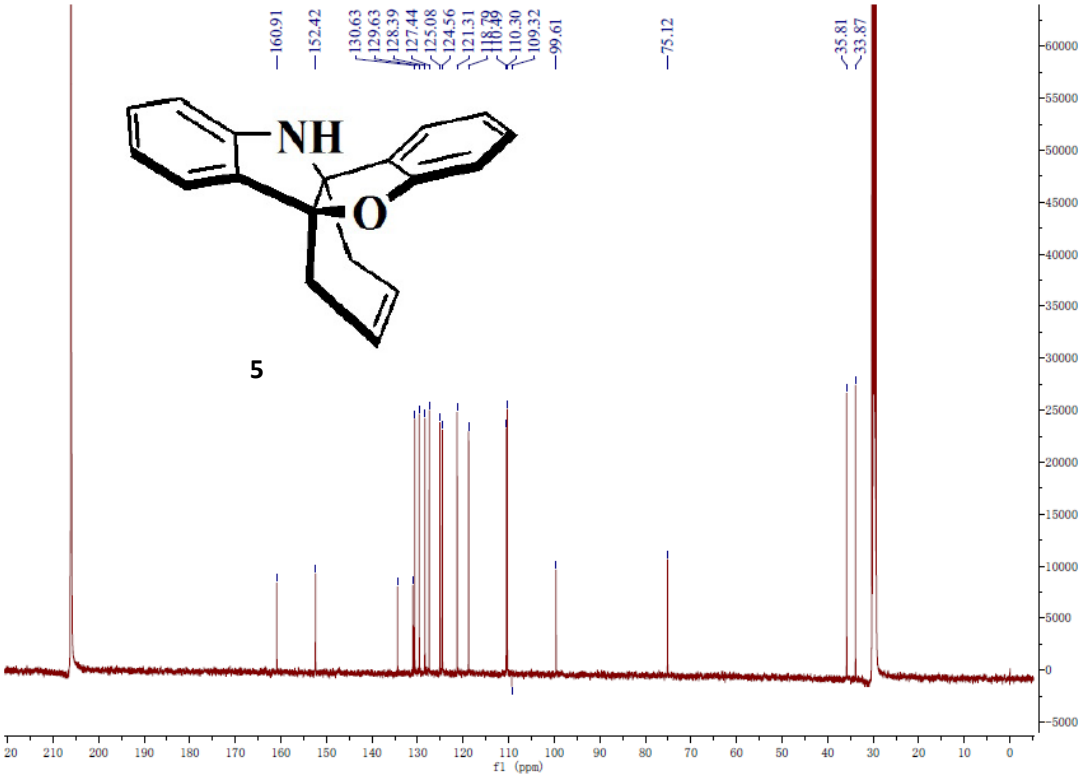
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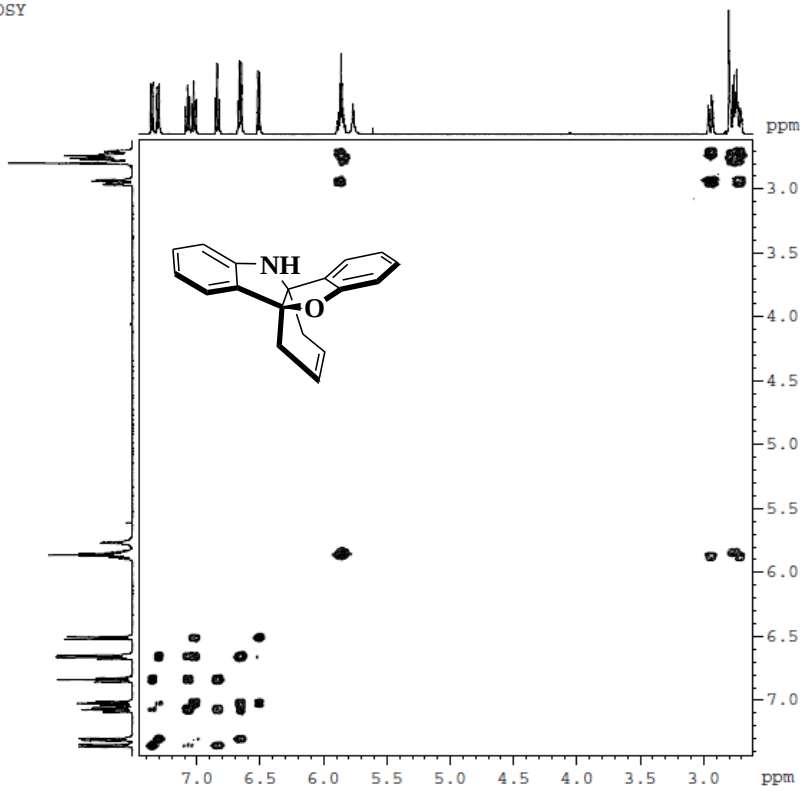


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GPNAM3               SINE.100
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GPZ3                  40.00 %
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WDW                     SINE
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.40

F1 - Processing parameters
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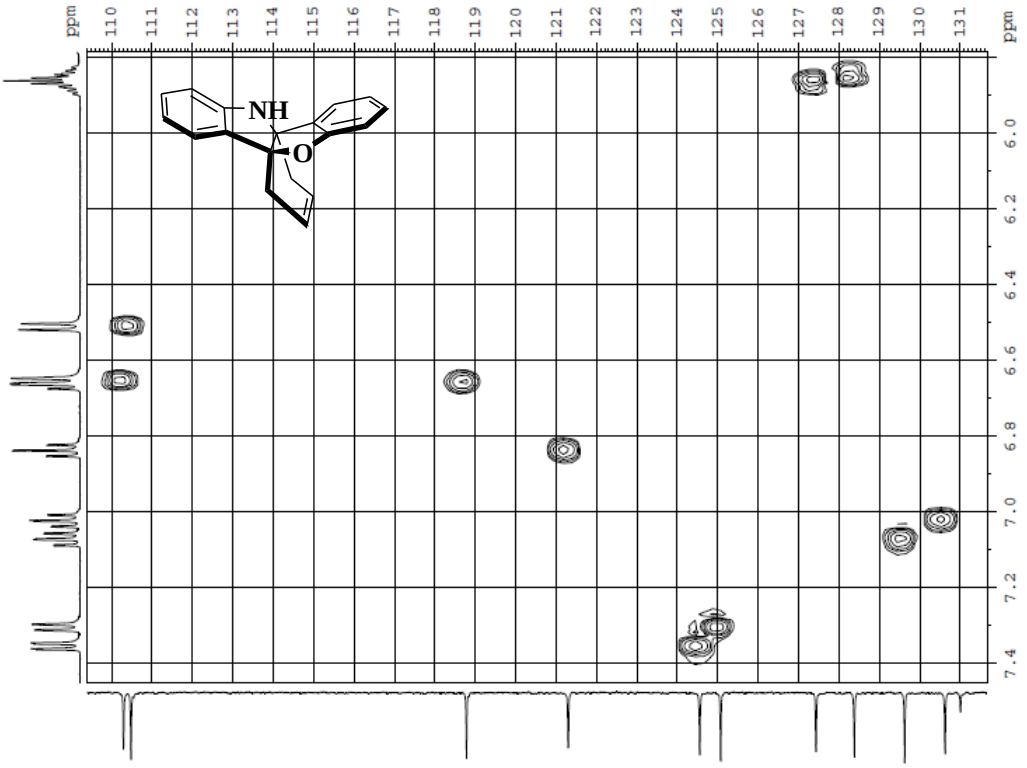

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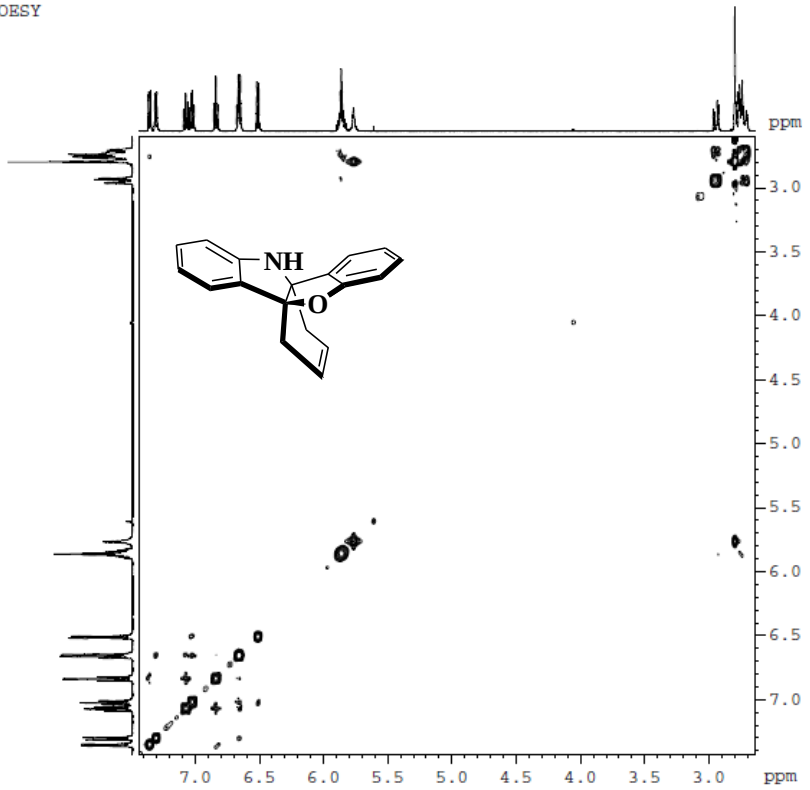

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DS 16
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FIDRES 3.989226 Hz
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RG 574.7
DW 122.400 usec
DE 6.50 usec
TE 300.0 K
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D1 2.00000000 sec
D16 0.00020000 sec
D8 1.00000000 sec
IN0 0.00024480 sec
ST1CNT 256
TAU 0.49880001 sec

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P1 10.20 usec
p2 20.40 usec
PL1 -4.00 dB
SFO1 500.1319860 MHz

====== GRADIENT CHANNEL =====
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GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 -40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
ND0 1
TD 512
SFO1 500.132 MHz
FIDRES 7.978452 Hz
SW 8.168 ppm
FnMODE States-TPPI

F2 - Processing parameters
SI 1024
SF 500.1300106 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
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SSB 2
LB 0.00 Hz
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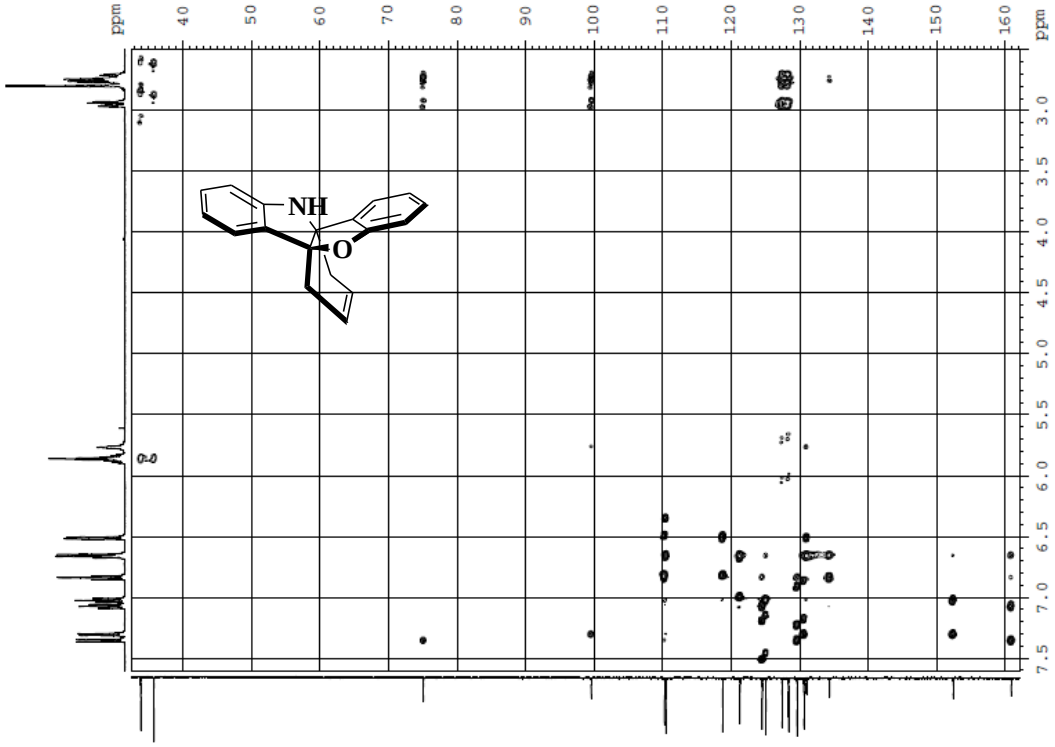


5. VCD and IR experimental of 3dn

VCD and IR measurements were performed on a BioTools ChiralIR-2X FT-VCD spectrometer, equipped with a single photoelastic modulation and a mercury cadmium tellurium detector. A solution of **3dn** (7.5 mg) in $CDCl_3$ (150μL) was placed in a BaF_2 cell with a pathlength of 75μm. Data were acquired at a resolution of 4 cm^{-1} for 8 h. To obtain VCD baseline, the racemate was measured under the same conditions.

VCD and IR calculations

Conformational analysis of **3dn** was carried out with Compute VOA (BioTools Inc., Jupiter, FL) at the molecular mechanic force field MMFF94 level within a 5 kcal/mol window. The predicted energetically distinct conformers were submitted to Gaussian 09 (Gaussian Inc., Wallingford, CT) to perform geometry optimization followed by VCD and IR calculation at the B3PW91/cc-pVTZ level of theory. Boltzmann-population-weighted composite VCD and IR spectra were then generated by Compute VOA. As shown in Fig. S1, the experimental and theoretical spectra are in agreement. The absolute configuration of **3dn** is assigned as (*S*).

Quantitative evaluation of this assignment was achieved by Compare VOA. The related results, including spectral similarities and enantiomeric similarity index (the difference between the VCD spectral similarity of the correct and the incorrect enantiomers, ESI) can be seen in Table S1.As a result, the confidence level of the (*S*) assignment is 93%.

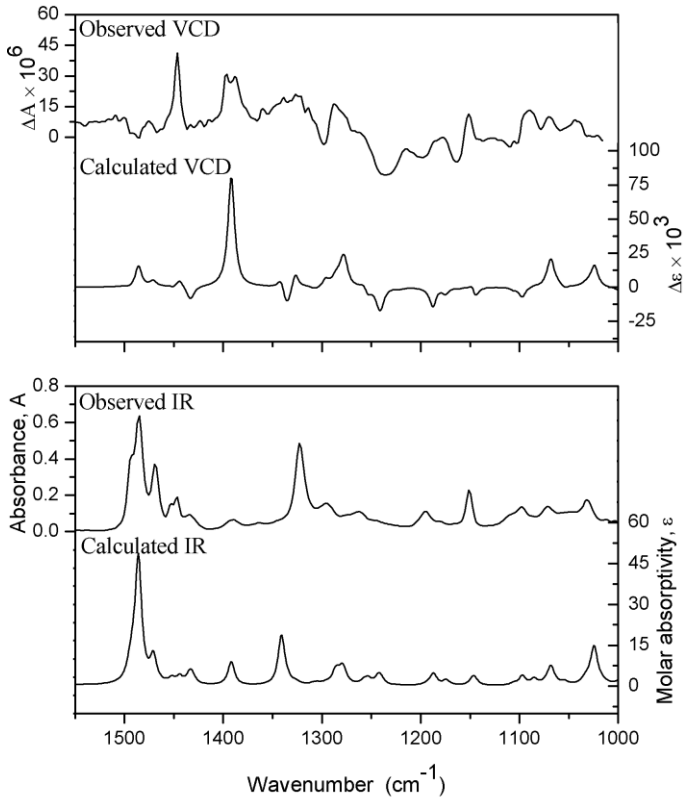


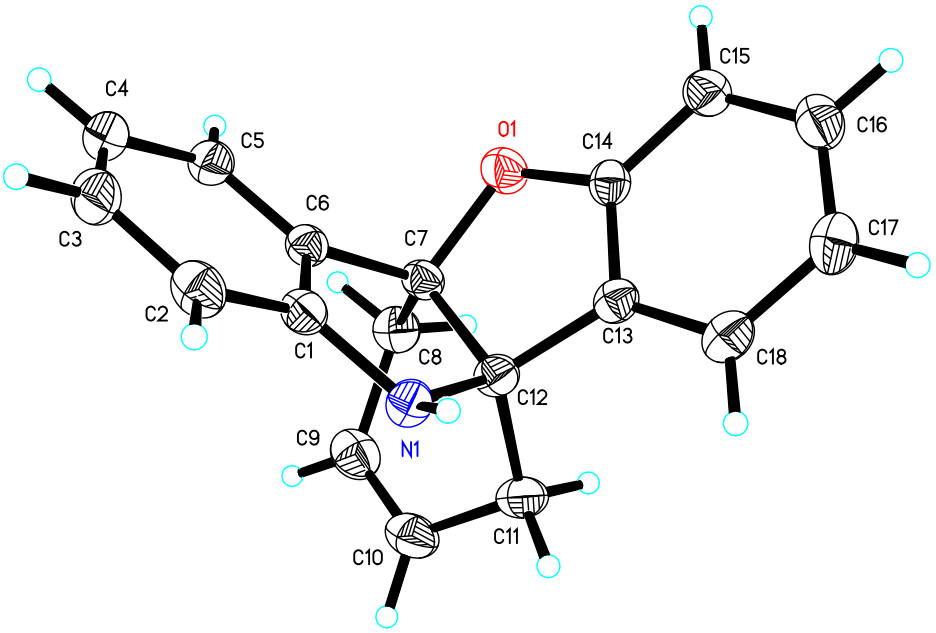
Fig. S1 VCD and IR spectra observed for **2dn** compared with the corresponding calculated spectra of (*S*)

Table S1 Compare VOA result for VCD and IR spectra of **3dn**

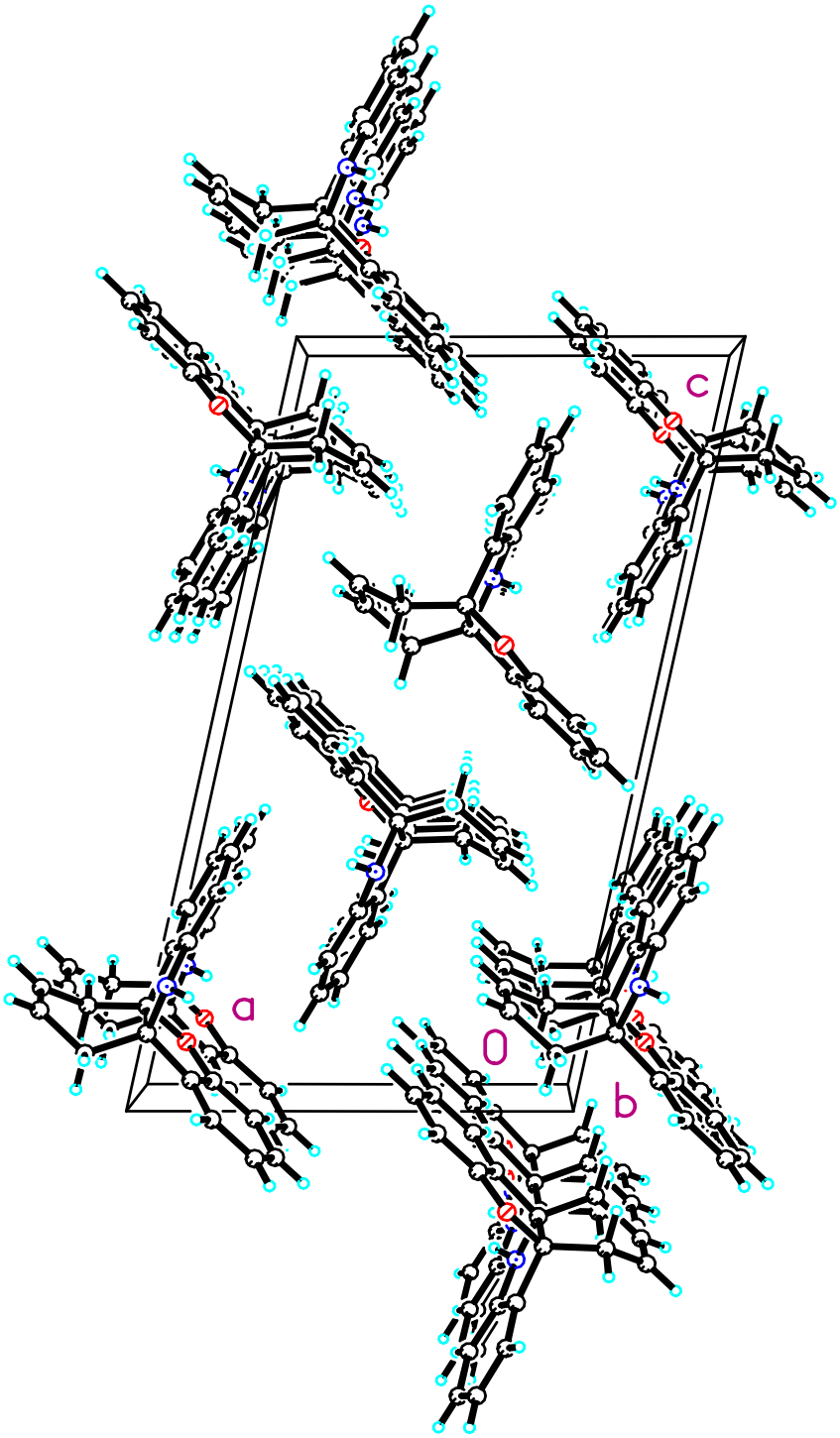
Calculation Method	[a]S_{IR}	[b]S_S	[c]S_R	[d]*ESI*
DFT//B3PW91/cc-pVTZ	80.4	63.2	5.7	57.5

[a] IR spectral similarity
[b] VCD spectral similarity for the (*S*)- configuration
[c] VCD spectral similarity for the (*R*)- configuration
[d] Enantiomeric similarity index.

6. ORTEP drawings of 5



Figrue 1. ORTEP drawing of **5**



Figrue 2. X-ray crystallography of **5**

Table S1. Crystal data and structure refinement for cd214692.

Identification code	cd214692
Empirical formula	C18 H15 N O
Formula weight	261.31
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 10.6138(16) Å = 90°. b = 6.4500(10) Å = 102.117(4) °. c = 19.342(3) Å = 90°.
Volume	1294.7(3) $Å^3$
Z	4
Density (calculated)	1.341 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	552
Crystal size	0.211 x 0.156 x 0.123 mm^3
Theta range for data collection	2.031 to 25.998 °.
Index ranges	-13<=h<=8, -7<=k<=7, -23<=l<=23
Reflections collected	7497
Independent reflections	2541 [R(int) = 0.0466]
Completeness to theta = 25.242 °	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5635
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2541 / 1 / 185
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.1203
R indices (all data)	R1 = 0.0753, wR2 = 0.1318
Extinction coefficient	n/a
Largest diff. peak and hole	0.234 and -0.170 $e.Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for cd214692. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	9416(2)	8416(3)	1840(1)	37(1)
O(1)	8881(1)	3704(2)	1015(1)	47(1)
C(1)	9222(2)	7053(3)	2361(1)	38(1)
C(2)	8802(2)	7526(4)	2970(1)	48(1)
C(3)	8757(2)	5943(4)	3442(1)	52(1)
C(4)	9112(2)	3942(4)	3317(1)	50(1)
C(5)	9510(2)	3480(3)	2697(1)	42(1)
C(6)	9547(2)	5044(3)	2218(1)	35(1)
C(7)	9865(2)	4947(3)	1499(1)	35(1)
C(8)	11193(2)	4091(3)	1486(1)	46(1)
C(9)	12210(2)	5657(4)	1753(1)	54(1)
C(10)	12045(2)	7583(4)	1528(1)	53(1)
C(11)	10850(2)	8129(3)	1010(1)	47(1)
C(12)	9667(2)	7234(3)	1232(1)	37(1)
C(13)	8501(2)	7078(3)	648(1)	36(1)
C(14)	8091(2)	5048(3)	568(1)	36(1)
C(15)	7012(2)	4484(4)	71(1)	45(1)
C(16)	6358(2)	6045(4)	-350(1)	51(1)
C(17)	6760(2)	8074(4)	-282(1)	51(1)
C(18)	7845(2)	8611(3)	220(1)	45(1)

Table S3. Bond lengths [Å] and angles [°] for cd214692.

N(1)-C(1)	1.385(3)
N(1)-C(12)	1.473(2)
N(1)-H(1)	0.771(16)
O(1)-C(14)	1.378(2)
O(1)-C(7)	1.483(2)
C(1)-C(2)	1.377(3)
C(1)-C(6)	1.384(3)
C(2)-C(3)	1.378(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.380(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.385(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.377(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.499(3)
C(7)-C(8)	1.519(3)
C(7)-C(12)	1.562(3)
C(8)-C(9)	1.489(3)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.316(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.485(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.523(3)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.493(3)
C(13)-C(14)	1.378(3)
C(13)-C(18)	1.380(3)
C(14)-C(15)	1.380(3)
C(15)-C(16)	1.386(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.374(3)
C(16)-H(16)	0.9300

C(17)-C(18)	1.385(3)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300

C(1)-N(1)-C(12)	109.39(16)
C(1)-N(1)-H(1)	115.6(19)
C(12)-N(1)-H(1)	112.7(18)
C(14)-O(1)-C(7)	108.13(15)
C(2)-C(1)-C(6)	121.2(2)
C(2)-C(1)-N(1)	127.3(2)
C(6)-C(1)-N(1)	111.53(17)
C(1)-C(2)-C(3)	117.7(2)
C(1)-C(2)-H(2)	121.1
C(3)-C(2)-H(2)	121.1
C(2)-C(3)-C(4)	121.8(2)
C(2)-C(3)-H(3)	119.1
C(4)-C(3)-H(3)	119.1
C(3)-C(4)-C(5)	119.8(2)
C(3)-C(4)-H(4)	120.1
C(5)-C(4)-H(4)	120.1
C(6)-C(5)-C(4)	118.8(2)
C(6)-C(5)-H(5)	120.6
C(4)-C(5)-H(5)	120.6
C(5)-C(6)-C(1)	120.52(19)
C(5)-C(6)-C(7)	129.62(19)
C(1)-C(6)-C(7)	109.83(17)
O(1)-C(7)-C(6)	110.00(15)
O(1)-C(7)-C(8)	109.06(15)
C(6)-C(7)-C(8)	114.85(16)
O(1)-C(7)-C(12)	105.89(14)
C(6)-C(7)-C(12)	103.08(15)
C(8)-C(7)-C(12)	113.50(17)
C(9)-C(8)-C(7)	110.83(18)
C(9)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8A)	109.5
C(9)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	108.1

C(10)-C(9)-C(8)	119.3(2)
C(10)-C(9)-H(9)	120.4
C(8)-C(9)-H(9)	120.4
C(9)-C(10)-C(11)	118.9(2)
C(9)-C(10)-H(10)	120.6
C(11)-C(10)-H(10)	120.6
C(10)-C(11)-C(12)	111.00(18)
C(10)-C(11)-H(11A)	109.4
C(12)-C(11)-H(11A)	109.4
C(10)-C(11)-H(11B)	109.4
C(12)-C(11)-H(11B)	109.4
H(11A)-C(11)-H(11B)	108.0
N(1)-C(12)-C(13)	112.28(16)
N(1)-C(12)-C(11)	109.05(16)
C(13)-C(12)-C(11)	114.42(16)
N(1)-C(12)-C(7)	105.02(15)
C(13)-C(12)-C(7)	102.67(15)
C(11)-C(12)-C(7)	112.93(17)
C(14)-C(13)-C(18)	120.34(19)
C(14)-C(13)-C(12)	109.93(17)
C(18)-C(13)-C(12)	129.73(19)
O(1)-C(14)-C(13)	113.00(17)
O(1)-C(14)-C(15)	125.31(19)
C(13)-C(14)-C(15)	121.68(19)
C(14)-C(15)-C(16)	117.2(2)
C(14)-C(15)-H(15)	121.4
C(16)-C(15)-H(15)	121.4
C(17)-C(16)-C(15)	121.9(2)
C(17)-C(16)-H(16)	119.1
C(15)-C(16)-H(16)	119.1
C(16)-C(17)-C(18)	120.0(2)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(13)-C(18)-C(17)	118.8(2)
C(13)-C(18)-H(18)	120.6
C(17)-C(18)-H(18)	120.6

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cd214692. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	50(1)	26(1)	35(1)	-3(1)	12(1)	3(1)
O(1)	53(1)	38(1)	46(1)	-3(1)	2(1)	-4(1)
C(1)	35(1)	41(1)	36(1)	-5(1)	7(1)	-3(1)
C(2)	47(1)	53(1)	46(1)	-14(1)	13(1)	1(1)
C(3)	49(1)	72(2)	38(1)	-9(1)	17(1)	-9(1)
C(4)	51(1)	59(2)	39(1)	6(1)	8(1)	-10(1)
C(5)	40(1)	44(1)	42(1)	2(1)	7(1)	-2(1)
C(6)	30(1)	38(1)	36(1)	-1(1)	5(1)	-1(1)
C(7)	37(1)	33(1)	34(1)	-6(1)	7(1)	-4(1)
C(8)	49(1)	44(1)	47(1)	-7(1)	16(1)	2(1)
C(9)	38(1)	69(2)	54(1)	-8(1)	11(1)	-1(1)
C(10)	45(1)	60(2)	56(1)	-12(1)	13(1)	-13(1)
C(11)	53(1)	41(1)	50(1)	-5(1)	18(1)	-12(1)
C(12)	44(1)	32(1)	36(1)	-4(1)	13(1)	-3(1)
C(13)	41(1)	35(1)	35(1)	-1(1)	14(1)	0(1)
C(14)	39(1)	40(1)	31(1)	-1(1)	10(1)	2(1)
C(15)	47(1)	45(1)	43(1)	-3(1)	9(1)	-5(1)
C(16)	44(1)	62(2)	45(1)	0(1)	4(1)	1(1)
C(17)	53(1)	56(2)	45(1)	8(1)	10(1)	12(1)
C(18)	54(1)	38(1)	46(1)	4(1)	17(1)	2(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

for cd214692.

	x	y	z	U(eq)
H(2)	8558	8868	3058	57
H(3)	8480	6232	3857	63
H(4)	9084	2907	3648	60
H(5)	9748	2136	2606	50
H(8A)	11348	2856	1778	55
H(8B)	11231	3705	1006	55
H(9)	12953	5278	2076	64
H(10)	12667	8585	1690	64
H(11A)	10900	7595	548	56
H(11B)	10771	9626	975	56
H(15)	6735	3114	21	54
H(16)	5626	5709	-689	61
H(17)	6303	9088	-573	62
H(18)	8125	9979	268	54
H(1)	8890(20)	9250(30)	1732(12)	54(8)

Table S6. Torsion angles [°] for cd214692.

C(12)-N(1)-C(1)-C(2)	-171.07(19)
C(12)-N(1)-C(1)-C(6)	10.9(2)
C(6)-C(1)-C(2)-C(3)	2.1(3)
N(1)-C(1)-C(2)-C(3)	-175.7(2)
C(1)-C(2)-C(3)-C(4)	-0.3(3)
C(2)-C(3)-C(4)-C(5)	-0.9(3)
C(3)-C(4)-C(5)-C(6)	0.3(3)
C(4)-C(5)-C(6)-C(1)	1.5(3)
C(4)-C(5)-C(6)-C(7)	-176.26(19)
C(2)-C(1)-C(6)-C(5)	-2.8(3)
N(1)-C(1)-C(6)-C(5)	175.35(18)
C(2)-C(1)-C(6)-C(7)	175.43(18)
N(1)-C(1)-C(6)-C(7)	-6.4(2)
C(14)-O(1)-C(7)-C(6)	104.53(17)
C(14)-O(1)-C(7)-C(8)	-128.69(17)
C(14)-O(1)-C(7)-C(12)	-6.21(18)
C(5)-C(6)-C(7)-O(1)	65.1(3)
C(1)-C(6)-C(7)-O(1)	-112.94(18)
C(5)-C(6)-C(7)-C(8)	-58.4(3)
C(1)-C(6)-C(7)-C(8)	123.60(19)
C(5)-C(6)-C(7)-C(12)	177.6(2)
C(1)-C(6)-C(7)-C(12)	-0.4(2)
O(1)-C(7)-C(8)-C(9)	160.47(17)
C(6)-C(7)-C(8)-C(9)	-75.6(2)
C(12)-C(7)-C(8)-C(9)	42.7(2)
C(7)-C(8)-C(9)-C(10)	-45.6(3)
C(8)-C(9)-C(10)-C(11)	-0.3(3)
C(9)-C(10)-C(11)-C(12)	46.3(3)
C(1)-N(1)-C(12)-C(13)	100.27(19)
C(1)-N(1)-C(12)-C(11)	-131.84(18)
C(1)-N(1)-C(12)-C(7)	-10.6(2)
C(10)-C(11)-C(12)-N(1)	72.8(2)
C(10)-C(11)-C(12)-C(13)	-160.51(18)
C(10)-C(11)-C(12)-C(7)	-43.5(2)
O(1)-C(7)-C(12)-N(1)	121.98(16)
C(6)-C(7)-C(12)-N(1)	6.43(19)

C(8)-C(7)-C(12)-N(1)	-118.42(18)
O(1)-C(7)-C(12)-C(13)	4.42(18)
C(6)-C(7)-C(12)-C(13)	-111.13(15)
C(8)-C(7)-C(12)-C(13)	124.02(17)
O(1)-C(7)-C(12)-C(11)	-119.31(17)
C(6)-C(7)-C(12)-C(11)	125.14(17)
C(8)-C(7)-C(12)-C(11)	0.3(2)
N(1)-C(12)-C(13)-C(14)	-113.51(18)
C(11)-C(12)-C(13)-C(14)	121.50(19)
C(7)-C(12)-C(13)-C(14)	-1.2(2)
N(1)-C(12)-C(13)-C(18)	66.2(3)
C(11)-C(12)-C(13)-C(18)	-58.8(3)
C(7)-C(12)-C(13)-C(18)	178.45(19)
C(7)-O(1)-C(14)-C(13)	5.8(2)
C(7)-O(1)-C(14)-C(15)	-175.76(18)
C(18)-C(13)-C(14)-O(1)	177.48(17)
C(12)-C(13)-C(14)-O(1)	-2.8(2)
C(18)-C(13)-C(14)-C(15)	-1.0(3)
C(12)-C(13)-C(14)-C(15)	178.69(17)
O(1)-C(14)-C(15)-C(16)	-177.83(19)
C(13)-C(14)-C(15)-C(16)	0.5(3)
C(14)-C(15)-C(16)-C(17)	0.1(3)
C(15)-C(16)-C(17)-C(18)	-0.2(3)
C(14)-C(13)-C(18)-C(17)	0.9(3)
C(12)-C(13)-C(18)-C(17)	-178.73(19)
C(16)-C(17)-C(18)-C(13)	-0.3(3)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for cd214692 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)