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NBS-Mediated dinitrogen extrusion of diazoacetamides under catalyst-free conditions: a practical access to the 3-bromooxindole derivatives

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Supporting Information

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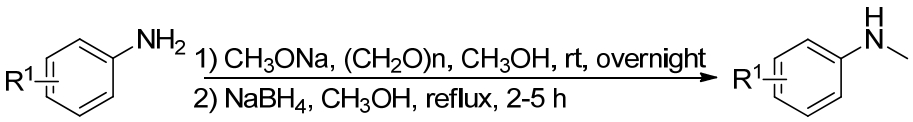
General Information

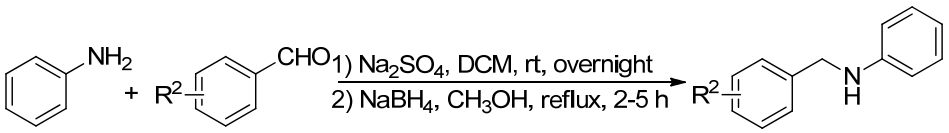
All reactions were performed in oven-dried (140 °C) glassware under argon atmosphere. DCM (dichloromethane) and toluene were distilled prior to use kept over activated 3 Å molecular sieves. TBME (*tert*-butyl methyl ether), DMB (2,2-dimethylbutane) acetonitrile and $DCCl_3$ were purchased from Sigma Aldrich and used without further treatment. Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). Liquid chromatography was performed using flash chromatography of the indicated system on silica gel (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova-400 NMR spectrometer; chemical shifts were reported in ppm with the solvent signals as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI Source).

General Procedure for the Preparation of Diazoacetamides 1.[1,2]



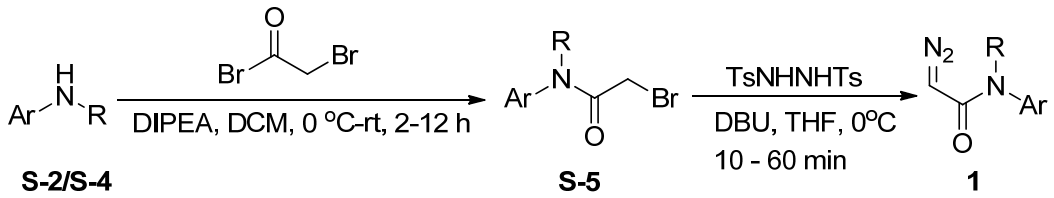
S-1 **S-2**

Synthesis of S-2: To a 50-mL oven-dried flask with a magnetic stirring bar, arylamine **S-1** (10.0 mmol) and paraformaldehyde (0.5 g, 15.0 mmol) was dissolved in CH_3OH (20.0 mL), and CH_3ONa (2.7 g, 50 mmol) was added slowly over 5 min. After stirring at room temperature overnight, $NaBH_4$ (415 mg, 11.0 mmol) was added slowly. The mixture was refluxed for 2-5 h, and then the residue was quenched with saturated ammonium chloride solution (50 mL). The aqueous phase was extracted with ethyl acetate (25.0 mL X 2). The combined organic phase was dried with anhydrous Na_2SO_4, the crude product was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 20:1) to obtain **S-2** in 50-75% yields.



S-3 **S-4**

Synthesis of S-4: To a 50-mL oven-dried flask with a magnetic stirring bar, aniline (0.93 g, 10.0 mmol) and aromatic aldehyde **S-3** (10.0 mmol) was dissolved in DCM (20.0 mL), anhydrous Na_2SO_4 (2.5 g) was added. The solution was stirred at room temperature overnight. After filter the salt, DCM was evaporated under reduced pressure, then the residue was dissolved in CH_3OH (20.0 mL), and $NaBH_4$ (415 mg, 11.0 mmol) was added. The mixture was refluxed for 2-5 h, and then the reaction mixture was quenched with saturated ammonium chloride solution (50.0 mL). The aqueous phase was extracted with ethyl acetate (25.0 mL X 2). The combined organic phase was dried with anhydrous Na_2SO_4, the crude product was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 20:1) to give **S-4**.



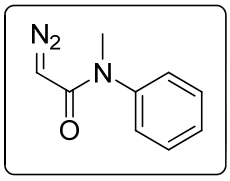
S-2/S-4 **S-5** **1**

Synthesis of 1: To a 50-mL oven-dried flask with a magnetic stirring bar, amine **S-2/S-4** (3.8 mmol) and DIPEA (*N*,*N*-Diisopropylethylamine, 0.66 mL, 3.8 mmol) were dissolved in dry DCM (20.0 mL), bromoacetyl bromide (0.34 mL, 3.8 mmol) was added slowly at 0 °C, then the mixture was stirred at room temperature for 2-12 h. After the reaction was completed, DCM was removed under reduced pressure. The obtained crude **S-5** was directly used for the next step without further purification. **S-5** and *N*,*N*'-ditosylhydrazine (3.2 g, 9.5 mmol) were dissolved in THF (20.0 mL), DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene, 2.7 mL, 18.0 mmol) was added slowly over 5 min at 0 °C, and the reaction mixture was stirred for 10-60 minutes until no more gas was generated from the reaction mixture. The reaction was quenched by saturated

$NaHCO_3$ solution (30 mL), and the aqueous phase was extracted with ethyl acetate (20 mL X 3), The combined organic phase was dried with anhydrous Na_2SO_4, the crude product was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 10:1 to 2:1) to give the diazoacetamides **1**.

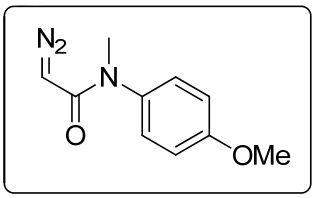
Diazoacetamides **1r**[3], **1s**[4] and **1t**[5] were prepared according to the reported references, and the characteristic data are consistent with the reported reference.

2-Diazo-*N*-methyl-*N*-phenylacetamide (1a)[6] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$)



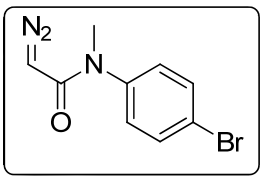
δ (ppm): 7.42-7.37 (m, 2H), 7.34-7.29 (m, 1H), 7.21-7.17 (m, 2H), 4.50 (s, 1H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 143.2, 129.9, 128.0, 127.1, 47.4, 37.2.

2-Diazo-*N*-(4-methoxyphenyl)-*N*-methylacetamide (1b) Yellow solid. ^{1}H NMR



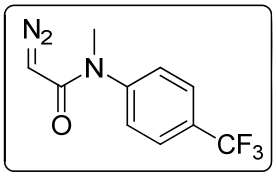
(400 MHz, $CDCl_3$) δ (ppm): 7.10 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.47 (s, 1H), 3.82 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.2, 159.2, 135.9, 128.6, 115.0, 55.6, 47.2, 37.4.

***N*-(4-Bromophenyl)-2-diazo-*N*-methylacetamide (1c)** Yellow solid. ^{1}H NMR (400



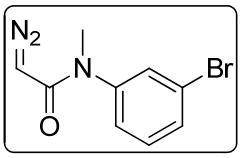
MHz, $CDCl_3$) δ (ppm): 7.53 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 4.52 (s, 1H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7, 142.3, 133.1, 129.1, 121.7, 47.6, 37.2.

2-Diazo-*N*-methyl-*N*-[4-(trifluoromethyl)phenyl]acetamide (1d) Yellow solid. ^{1}H

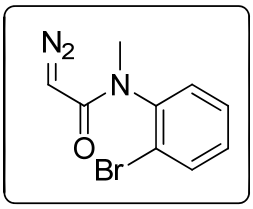


NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 4.57 (s, 1H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 146.5, 129.8 (d, *J* = 32.9 Hz), 127.5, 127.01 (q, *J* = 3.7 Hz), 123.8 (d, *J* = 272.2 Hz), 47.8, 37.1.

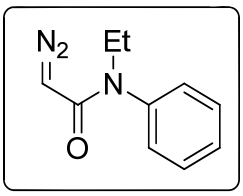
***N*-(3-Bromophenyl)-2-diazo-*N*-methylacetamide (1e)** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46-7.43 (m, 1H), 7.37 (t, *J* = 1.9 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.16-7.12 (m, 1H), 4.54 (s, 1H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 144.5, 131.11, 131.12, 130.6, 126.1, 123.0, 47.6, 37.2.



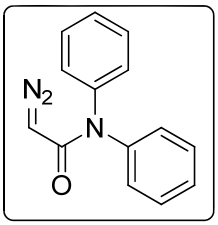
***N*-(2-Bromophenyl)-2-diazo-*N*-methylacetamide (1f)** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):7.66 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.37-7.21 (comp, 3H), 4.27 (s, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7, 141.6, 134.1, 130.3, 130.2, 129.1, 123.7, 47.3, 35.8.



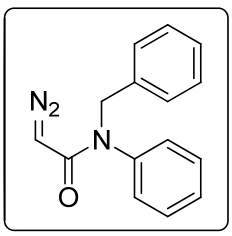
2-Diazo-*N*-ethyl-*N*-phenylacetamide (1g) Red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43-7.37 (m, 2H), 7.34 (m, 1H), 7.18-7.13 (m, 2H), 4.36 (s, 1H), 3.78 (q, *J* = 7.1 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 141.4, 129.8, 128.6, 128.2, 47.4, 44.1, 13.5.



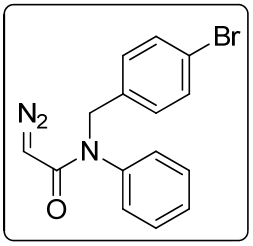
2-Diazo-*N*,*N*-diphenylacetamide (1h) Red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41-7.37 (comp, 4H), 7.32-7.27 (comp, 6H), 4.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 142.4, 129.4, 127.5, 127.0, 49.1.



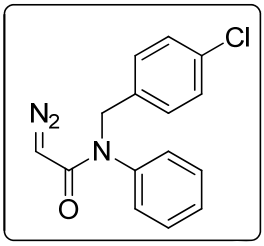
***N*-Benzyl-2-diazo-*N*-phenylacetamide (1i)**[6] Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33-7.26 (comp, 4H), 7.26-7.21 (comp, 4H), 7.03-7.00 (comp, 2H), 4.93 (s, 2H), 4.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.0, 141.6, 137.7, 129.7, 128.8, 128.6, 128.5, 128.3, 127.5, 53.0, 47.5.



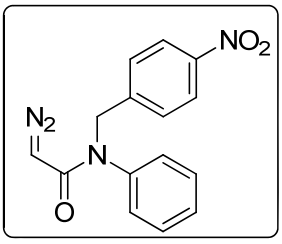
***N*-(4-Bromobenzyl)-2-diazo-*N*-phenylacetamide (1j)** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38 (d, *J* = 8.3 Hz, 2H), 7.36-7.29 (comp, 3H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.3, 2H), 4.86 (s, 2H), 4.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1, 141.3, 136.7, 131.7, 130.6, 129.9, 128.52, 128.45, 121.5, 52.4, 47.6.



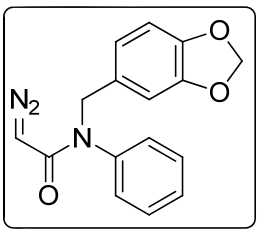
***N*-(4-Chlorobenzyl)-2-diazo-*N*-phenylacetamide (1k)** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37-7.30 (comp, 3H), 7.24-7.21 (comp, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.00 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.88 (s, 2H), 4.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1, 141.3, 136.2, 133.4, 130.2, 129.9, 128.7, 128.6, 128.5, 52.4, 47.6.



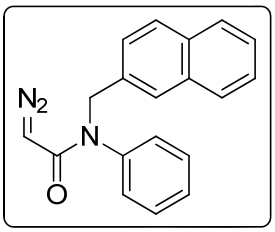
2-Diazo-*N*-(4-nitrobenzyl)-*N*-phenylacetamide (1l) Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.13 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.39-7.32 (comp, 3H), 7.06-7.01 (comp, 2H), 5.00 (s, 2H), 4.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.2, 147.3, 145.2, 141.1, 130.0, 129.4, 128.6, 128.2, 123.8, 52.5, 47.6.



***N*-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-2-diazo-*N*-phenylacetamide (1m)** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41-7.35 (comp, 3H), 7.09-7.05 (comp, 2H), 6.84 (d, *J* = 1.4 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.66 (dd, *J* = 7.9, 1.2 Hz, 1H), 5.98 (s, 2H), 4.87 (s, 2H), 4.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.0, 147.8, 147.0, 141.4, 131.6, 129.8, 128.7, 128.3, 122.3, 109.4, 108.1, 101.1, 52.8, 47.6.

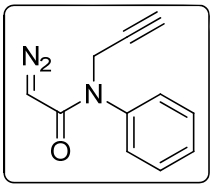


2-Diazo-*N*-(naphthalen-2-ylmethyl)-*N*-phenylacetamide (1n) Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82-7.73 (comp, 3H), 7.61 (s, 1H), 7.47-7.42



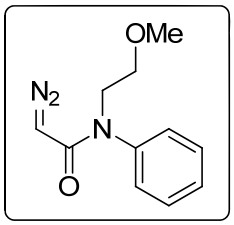
(comp, 3H), 7.30-7.00 (comp, 5H), 5.10 (s, 2H), 4.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.1, 141.5, 135.2, 133.3, 132.9, 129.7, 128.6, 128.34, 128.30, 127.9, 127.7, 127.5, 126.8, 126.1, 125.9, 53.1, 47.6.

2-Diazo-*N*-phenyl-*N*-(prop-2-yn-1-yl)acetamide (1o) Red oil. ^{1}H NMR (400 MHz,



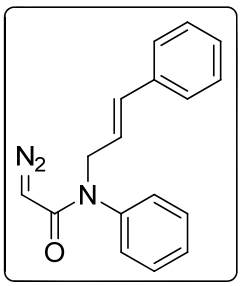
$CDCl_3$) δ (ppm): 7.42-7.35 (comp, 3H), 7.29-7.25 (comp, 2H), 4.47 (d, J = 2.5 Hz, 2H), 4.45 (s, 1H), 2.20 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 140.8, 129.8, 128.7, 128.3, 79.2, 72.2, 47.6, 38.3.

2-Diazo-*N*-(2-methoxyethyl)-*N*-phenylacetamide (1p) Red oil. ^{1}H NMR (400 MHz,



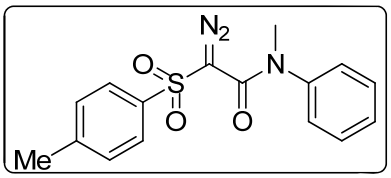
$CDCl_3$) δ (ppm): 7.40-7.34 (m, 2H), 7.33-7.28 (m, 1H), 7.24-7.18 (m, 2H), 4.40 (s, 1H), 3.89 (t, J = 5.8 Hz, 2H), 3.49 (t, J = 5.8 Hz, 2H), 3.28(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 141.8, 129.7, 128.5, 128.2, 69.8, 58.6, 48.6.

***N*-Cinnamyl-2-diazo-*N*-phenylacetamide (1q)** Yellow solid. ^{1}H NMR (400 MHz,



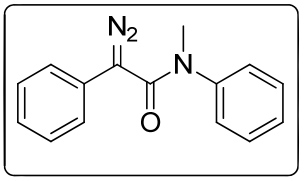
$CDCl_3$) δ (ppm): 7.42-7.37 (comp, 2H), 7.36-7.27 (comp, 5H), 7.23-7.18 (comp, 3H), 6.40 (d, J = 15.9 Hz, 1H), 6.28 (m, 1H), 4.49 (dd, J = 6.4, 0.5 Hz, 2H), 4.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7, 141.6, 136.7, 133.3, 129.8, 128.6, 128.5, 128.3, 127.7, 126.5, 124.7, 51.7, 47.5.

2-Diazo-*N*-methyl-*N*-phenyl-2-tosylacetamide (1s)[4] Yellow solid. ^{1}H NMR (400



MHz, $CDCl_3$) δ (ppm): 7.92 (d, J = 8.4 Hz, 2H), 7.47-7.37 (comp, 3H), 7.34 (d, J = 8.4 Hz, 2H), 7.24-7.20 (comp, 2H), 3.26 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 144.9, 142.1, 139.5, 130.5, 129.6, 128.8, 128.4, 126.9, 38.3, 21.8.

2-Diazo-*N*-methyl-*N*,2-diphenylacetamide (1t)[3] Red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36-7.26 (comp, 5H), 7.25-7.09 (comp, 5H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 144.0, 129.8, 128.7, 127.2, 126.7, 125.6, 125.5, 124.7, 38.6.

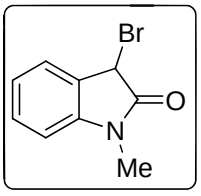


General Procedures for the Preparation of 3.

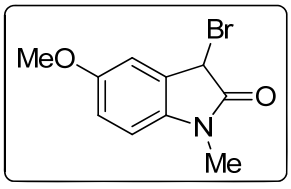
To a 10-mL oven-dried vial with a magnetic stirring bar, NBS (35.6 mg, 0.2 mol) was dissolved in CH_3CN (1.0 mL), diazo compound **1** (0.2 mmol) in CH_3CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 1-5 h, The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1 to 3:1) to give the desired products **3** with high yields.

Characteristic data of products **3r** and **3t** are consistent with the reported references.[7]

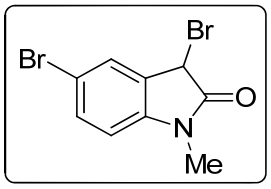
3-Bromo-1-methylindolin-2-one (3a) White solid, 43.8 mg, 97% yield, mp: 107~109 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):7.40 (d, *J* = 7.5 Hz, 1H), 7. 34 (t, *J* = 7.8 Hz, 1H), 7.13-7.08 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.26 (s, 1H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.6, 143.9, 130.5, 126.2, 126.1, 123.5, 108.9, 38.8, 26.9; HRMS (ESI) calculated for C_9H_9BrNO $[M+H]^+$: 227.9847, found 227.9866.



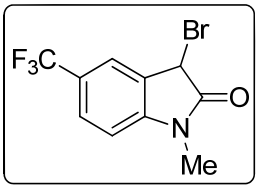
3-Bromo-5-methoxy-1-methylindolin-2-one (3b) White solid, 49.7 mg, 97% yield, mp: 122~124 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.01 (d, *J* = 2.3 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 1H), 5.22 (s, 1H), 3.80 (s, 3H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 156.6, 137.3, 127.3, 115.3, 112.9, 109.4, 56.0, 39.1, 27.0; HRMS (ESI) calculated for $C_{10}H_{10}BrNNaO_2$ $[M+Na]^+$: 277.9793, found 277.9796.



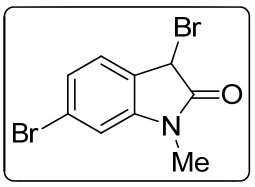
3,5-Dibromo-1-methylindolin-2-one (3c) White solid, 51.8 mg, 85% yield, mp: 150~151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29-7.26 (comp, 2H), 7.00 (s, 1H), 5.21 (s, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 142.9, 133.4, 129.3, 128.1, 116.0, 110.3, 37.7, 27.0; HRMS (ESI) calculated for $C_9H_7Br_2NNaO$ $[M+Na]^+$: 327.8772, found 327.8767.



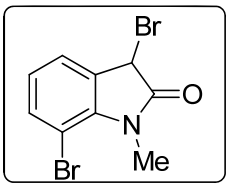
3-Bromo-1-methyl-5-(trifluoromethyl)indolin-2-one (3d) White solid, 38.2 mg, 65% yield, mp: 150~152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67-7.61 (comp, 2H), 6.92 (d, J = 8.1 Hz, 1H), 5.28 (s, 1H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 146.5, 130.0, 129.6, 127.5, 127.0 (q, J = 3.7 Hz), 125.1, 122.4, 47.8, 37.1; HRMS (ESI) calculated for $C_{10}H_7BrF_3NNaO$ $[M+Na]^+$: 315.9561, found 315.9556.



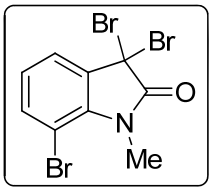
3,6-Dibromo-1-methylindolin-2-one (3e) Yellow solid, 51.8 mg, 85% yield, mp: 186~188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.25-7.20 (comp, 2H), 6.98 (s, 1H), 5.19 (s, 1H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 145.1, 127.3, 126.3, 125.0, 124.3, 112.5, 37.8, 27.0; HRMS (ESI) calculated for $C_9H_7Br_2NNaO$ $[M+Na]^+$: 327.8772, found 327.8763.



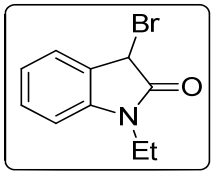
3,7-Dibromo-1-methylindolin-2-one (3f) White solid, 30.5 mg, 50% yield, mp: 157~160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 7.4 Hz, 1H), 6.95 (t, J = 8.1 Hz, 1H), 5.24 (s, 1H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.9, 141.2, 136.1, 129.1, 125.5, 124.6, 103.0, 37.9, 30.6; HRMS (ESI) calculated for $C_9H_7Br_2NNaO$ $[M+Na]^+$: 327.8772, found 327.8769.



3,3,7-Tribromo-1-methylindolin-2-one (3f') White solid, 17.6 mg, 23% yield, mp:

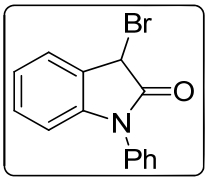


104~107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.44 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.02 (dd, *J* = 8.1, 7.6 Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.4, 137.4, 137.1, 133.8, 125.6, 125.3, 103.1, 44.0, 31.1; HRMS (ESI) calculated for $C_9H_7Br_3NO$ $[M+H]^+$: 383.8057, found 383.8069.



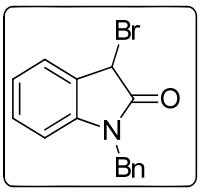
3-Bromo-1-ethylindolin-2-one (3g) White solid, 44.2 mg, 92% yield, mp: 112~114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.09 (td, *J* = 7.6, 0.7 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 5.24 (s, 1H), 3.80-3.74 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.1, 143.0, 130.4, 126.4, 126.3, 123.3, 109.0, 39.0, 35.4, 12.5; HRMS (ESI) calculated for $C_{10}H_{10}BrNNaO$ $[M+Na]^+$: 261.9843, found 261.9855.

3-Bromo-1-phenylindolin-2-one (3h) White solid, 50.1 mg, 87% yield, mp: 123~125



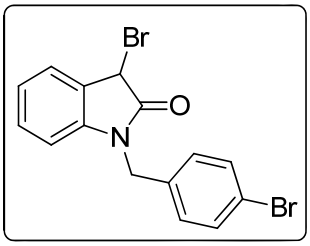
°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57-7.51 (m, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.46-7.41 (comp, 3H), 7.26 (t, *J* = 3.8 Hz, 1H), 7.14 (td, *J* = 7.6, 0.7 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 5.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.8, 144.0, 133.9, 130.4, 129.9, 128.7, 126.54, 126.47, 126.1, 123.9, 110.2, 39.1; HRMS (ESI) calculated for $C_{14}H_{10}BrNNaO$ $[M+Na]^+$: 309.9843, found 309.9828.

1-Benzyl-3-bromoindolin-2-one (3i) White solid, 54.2 mg, 90% yield, mp: 142~144

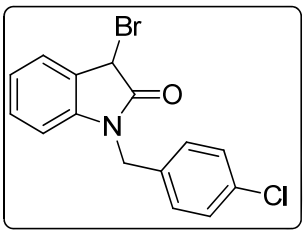


°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41 (d, *J* = 7.5 Hz, 1H), 7.37-7.26 (comp, 5H), 7.25-7.18 (m, 1H), 7.09-7.04(m, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 5.35 (s, 1H), 4.92 (q, *J* = 15.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.7, 143.0, 135.2, 130.4, 129.0, 128.0, 127.4, 126.24, 126.22, 123.5, 109.9, 44.3, 38.8; HRMS (ESI) calculated for $C_{15}H_{12}BrNNaO$ $[M+Na]^+$: 324.0000, found 324.0010.

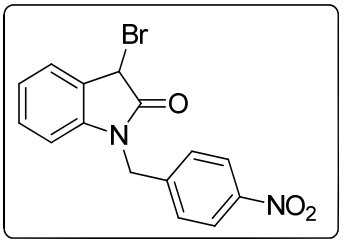
3-Bromo-1-(4-bromobenzyl)indolin-2-one (3j) White solid, 73.0 mg, 96% yield, mp: 140~142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47-7.44 (m, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.26-7.15 (comp, 3H), 7.01-7.05 (m, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 5.35 (s, 1H), 4.86 (q, *J* = 15.8 Hz,, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.7, 142.7, 134.2, 132.2, 130.5, 129.1, 126.3, 126.2, 123.7, 122.0, 109.7, 43.7, 38.6; HRMS (ESI) calculated for $C_{15}H_{11}Br_2NNaO$ $[M+Na]^+$: 403.9085, found 403.9103.



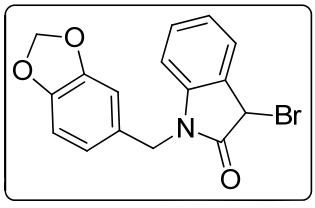
3-Bromo-1-(4-chlorobenzyl)indolin-2-one (3k) White solid, 63.9 mg, 95% yield, mp: 126~128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 (d, *J* = 7.5 Hz, 1H), 7.32-7.29 (m, 2H), 7.26-7.20 (comp, 3H), 7.10-7.06 (m, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 5.35 (s, 1H), 4.88 (q, *J* = 15.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.8, 142.7, 133.9, 133.7, 130.5, 129.3, 128.8, 126.4, 126.2, 123.7, 109.7, 43.6, 38.6; HRMS (ESI) calculated for $C_{15}H_{12}BrClNO$ $[M+H]^+$: 335.9791, found 335.9796.



3-Bromo-1-(4-nitrobenzyl)indolin-2-one (3l) White solid, 65.0 mg, 94% yield, mp: 160~162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.19 (d, *J* = 8.6 Hz, 2H), 7.49-7.42 (comp, 3H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 5.38 (s, 1H), 5.01 (q, *J* = 16.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.8, 147.8, 142.6, 142.3, 130.6, 128.1, 126.6, 126.2, 124.4, 124.1, 109.4, 43.6, 38.3; HRMS (ESI) calculated for $C_{15}H_{11}BrN_2NaO_3$ $[M+Na]^+$: 368.9851, found 368.9865.

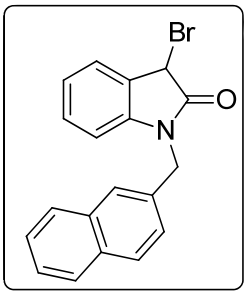


1-(Benzo[d][1,3]dioxol-5-ylmethyl)-3-bromoindolin-2-one (3m) White solid, 64.1 mg, 93% yield, mp: 139~141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.8

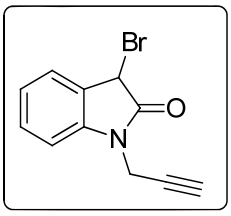


Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.83-6.71 (comp, 4H), 5.93 (s, 2H), 5.33 (s, 1H), 4.82 (q, *J* = 15.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.7, 148.3, 147.4, 142.9, 130.4, 129.0, 126.23, 126.23, 123.5, 121.0, 109.9, 108.6, 108.0, 101.3, 44.1, 38.8; HRMS (ESI) calculated for $C_{16}H_{13}BrNO_3$ $[M+H]^+$: 346.0079, found 346.0062.

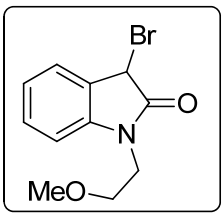
3-Bromo-1-(naphthalen-2-ylmethyl)indolin-2-one (3n) White solid, 65.2 mg, 93% yield, mp: 140~142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89-7.74 (comp, 4H), 7.72 (s, 1H), 7.53 (d, *J* = 1.3 Hz, 1H), 7.50-7.46 (m, 2H), 7.38 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.29 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 5.36 (s, 1H), 5.06 (q, *J* = 15.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 142.0, 133.4, 133.3, 133.1, 132.1, 129.4, 129.2, 128.2, 127.91, 127.88, 126.7, 126.5, 126.3, 125.0, 116.1, 111.5, 44.7, 37.7; HRMS (ESI) calculated for $C_{19}H_{14}BrNNaO$ $[M+Na]^+$: 374.0156, found 374.0147.



3-Bromo-1-(prop-2-yn-1-yl)indolin-2-one (3o) White solid, 44.8 mg, 90% yield, mp: 126~129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.14 (td, *J* = 7.7, 0.7 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 5.30 (s, 1H), 4.60 (dd, *J* = 17.7, 2.5 Hz, 1H), 4.44 (dd, *J* = 17.7, 2.5 Hz, 1H), 2.27 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.6, 142.0, 130.5, 126.3, 126.1, 123.9, 110.0, 76.3, 73.1, 38.5, 30.0; HRMS (ESI) calculated for $C_{11}H_8BrNNaO$ $[M+Na]^+$: 271.9687, found 271.9691.

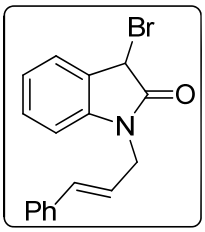


3-Bromo-1-(2-methoxyethyl)indolin-2-one (3p) White solid, 46.8 mg, 87% yield, mp: 104~106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):7.38 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.08 (td, *J* = 7.6, 0.8 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 5.26 (s, 1H), 3.96-3.82 (m, 2H), 3.63 (t, *J* = 5.6 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.8, 143.7, 130.4, 126.10, 126.07, 123.3, 109.8, 69.9, 59.1, 40.8, 38.8; HRMS

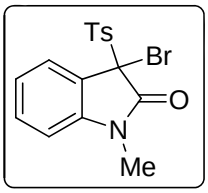


(ESI) calculated for $C_{11}H_{12}BrNNaO_2$ $[M+Na]^+$: 291.9949, found 291.9939.

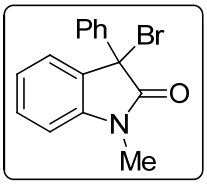
3-Bromo-1-cinnamylindolin-2-one (3q) White solid, 52.3 mg, 80% yield, mp: 146~146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 (d, *J* = 7.5 Hz, 1H), 7.36-7.29 (comp, 4H), 7.28-7.22 (m, 2H), 7.09 (td, *J* = 7.6, 0.8 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.18 (dt, *J* = 15.9, 6.0 Hz, 1H), 5.31 (s, 1H), 4.51 (dd, *J* = 6.0, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 143.1, 136.1, 133.6, 130.5, 128.7, 128.2, 126.6, 126.3, 123.5, 122.2, 109.8, 42.6, 38.8; HRMS (ESI) calculated for $C_{17}H_{14}BrNNaO$ $[M+Na]^+$: 350.0156, found 350.0153.



3-Bromo-1-methyl-3-tosylindolin-2-one (3s) Yellow solid, 60.8 mg, 80% yield, mp: 184~186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.40 (td, *J* = 7.8, 1.2 Hz, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 7.18 (td, *J* = 7.7, 0.9 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 3.07 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.5, 146.4, 143.9, 132.4, 131.7, 130.3, 129.2, 128.2, 124.0, 122.2, 109.0, 66.9, 27.2, 21.9; HRMS (ESI) calculated for $C_{16}H_{15}BrNO_3S$ $[M+H]^+$: 379.9956, found 379.9955.

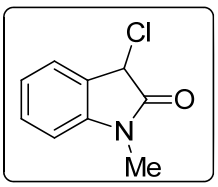


3-Bromo-1-methyl-3-phenylindolin-2-one (3t)[7] Yellow solid, 42.7 mg, 71% yield, mp:124 ~126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.50 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.41-7.32 (comp, 4H), 7.18 (td, *J* = 7.6, 0.9 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 3.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.7, 142.3, 136.5, 130.5, 130.4, 129.0, 128.62, 128.61, 126.7, 123.6, 109.2, 57.0, 27.1; HRMS (ESI) calculated for $C_{15}H_{13}BrNO$ $[M+H]^+$: 302.0181, found 302.0167.

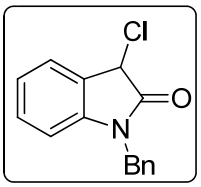


General Procedures for the Preparation of 5a and 5b.

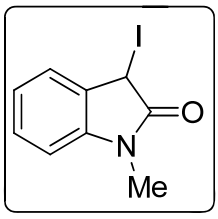
To a 10-mL oven-dried vial with a magnetic stirring bar, NCS (26.7 mg, 0.2 mol) was dissolved in CH_3CN (1.0 mL), diazo compound **1** (0.2 mmol) in CH_3CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 5 h, The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1 to 3:1) to give the desired products.

3-Chloro-1-methylindolin-2-one (5a) White solid, 19.0 mg, 53% yield, mp: 97~100 

^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.13 (s, 1H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 144.0, 130.6, 125.83, 125.75, 123.5, 108.8, 51.6, 26.8; HRMS (ESI) calculated for C_9H_9ClNO $[M+H]^+$: 182.0373, found 182.0385.

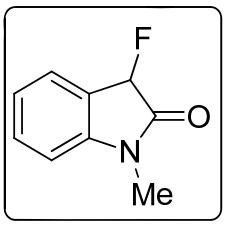
1-Benzyl-3-chloroindolin-2-one (5b) White solid, 30.0 mg, 59% yield, mp: 146~148 

^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):7.43 (d, *J* = 7.4 Hz, 1H), 7.34-7.27 (comp, 5H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.23 (s, 1H), 4.92 (q, *J* = 15.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.4, 143.1, 135.1, 130.5, 129.0, 128.0, 127.4, 125.81, 125.79, 123.5, 109.9, 51.6, 44.3; HRMS (ESI) calculated for $C_{15}H_{13}ClNO$ $[M+H]^+$: 258.0686, found 258.0595.

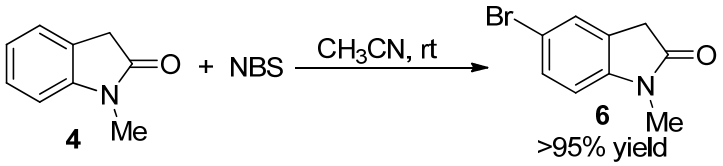
3-Iodo-1-methylindolin-2-one (5c) Yellow solid, 36.6 mg, 67% yield, mp: 97~99 ^{o}C; 

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35 (d, *J* = 7.5 Hz, 1H), 7.32-7.26 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.66 (s, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm):174.3, 143.2, 129.9, 127.9, 126.2, 123.4, 109.0, 27.1, 12.8; HRMS (ESI) calculated for C_9H_9INO $[M+H]^+$: 273.9729, found: 273.9740.

3-Fluoro-1-methylindolin-2-one (5d) White solid, mp: 64~66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 (d, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 5.66 (d, *J* = 51.0 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.2 (d, *J* = 18.2 Hz), 144.8 (d, *J* = 5.3 Hz), 131.6 (d, *J* = 3.3 Hz), 126.1 (d, *J* = 1.2 Hz), 123.4 (d, *J* = 2.9 Hz), 122.9 (d, *J* = 16.2 Hz), 108.9 (d, *J* = 1.3 Hz), 85.6, 26.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -193.33; HRMS (ESI) calculated for C_9H_9FNO $[M+H]^+$: 166.0668, found 166.0667.

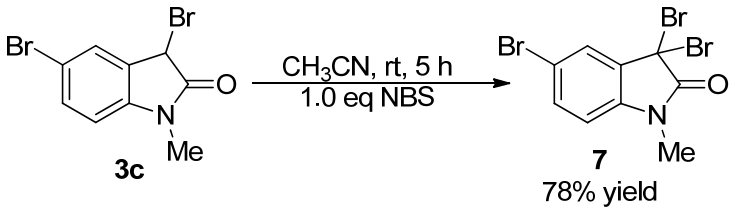


General Procedures for the Preparation of 6.



To a 10-mL oven-dried vial with a magnetic stirring bar, NBS (35.6 mg, 0.2 mol) was dissolved in CH_3CN (1.0 mL), 1-methylindolin-2-one **4** (30.0 mg, 0.2 mmol) in CH_3CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 5 h, the crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1 to 3:1) to give the desired products **6** with high yield (>95%). And the characteristic data are consistent with the reported reference.[8]

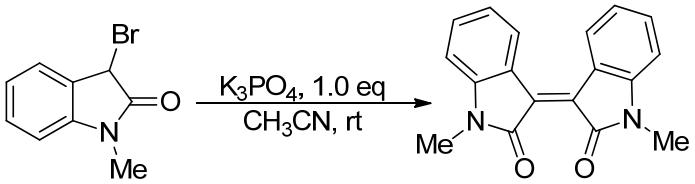
General Procedures for the Preparation of 7.



To a 10-mL oven-dried vial with a magnetic stirring bar, NBS (35.6 mg, 0.2 mol) was dissolved in CH_3CN (1.0 mL), 3,5-Dibromo-1-methylindolin-2-one **3c** (61.0 mg, 0.2 mmol) in CH_3CN (1.0 mL) was added under argon over 60 min. After stirring at room

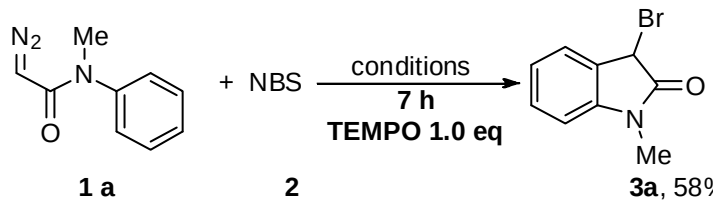
temperature for 5 h, The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 8:1) to give the compound **7** as white solid (59.2 mg, 78%). White solid, 60.5 mg, 78% yield, mp: 111~113 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 (d, *J* = 1.9 Hz, 1H), 7.47 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 138.9, 134.5, 132.7, 129.1, 116.6, 110.7, 43.7, 27.5; HRMS (ESI) calculated for $C_9H_7Br_3NO$ $[M+H]^+$: 383.8057, found 383.8066.

General Procedures for the Preparation of 8.



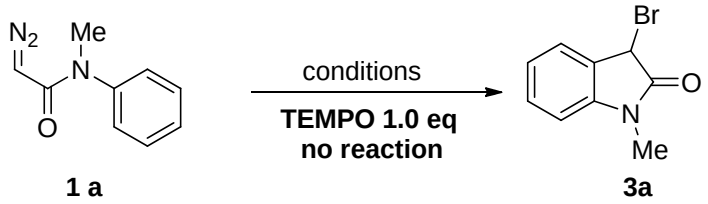
To a 10-mL oven-dried vial with a magnetic stirring bar, K_3PO_4 (42.4 mg, 0.2 mol) was dissolved in CH_3CN (1.0 mL), 3-Bromo-1-methylindolin-2-one **3a** (44.5 mg, 0.2 mmol) in CH_3CN (1.0 mL) was added under argon over 30 min. After stirring at room temperature overnight, the crude prodcut was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1) to give the compound **8** as dark violet solid (49.0 mg, 85%). And the characteristic data are consistent with the reported reference.[9]

Control Reactions with TEMPO



To a 10-mL oven-dried vial with a magnetic stirring bar, NBS (35.6 mg, 0.2 mmol) and TEMPO (28.3 mg, 0.2 mmol) were dissolved in CH_3CN (1.0 mL), diazo compound **1a** (35.4mg, 0.2 mmol) in CH_3CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 7 h, the crude reaction mixture was

purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1 to 5:1) to give the desired products 26.2mg (yield: 58%).



1 a **3a**

To a 10-mL oven-dried vial with a magnetic stirring bar, TEMPO (28.3 mg, 0.2 mmol) were dissolved in CH_3CN (1.0 mL), diazo compound **1a** (35.4mg, 0.2 mmol) in CH_3CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 5 h, the TLC analysis showed that no reaction was occurred at all. And all the diazo compound **1a** was recovered.

References

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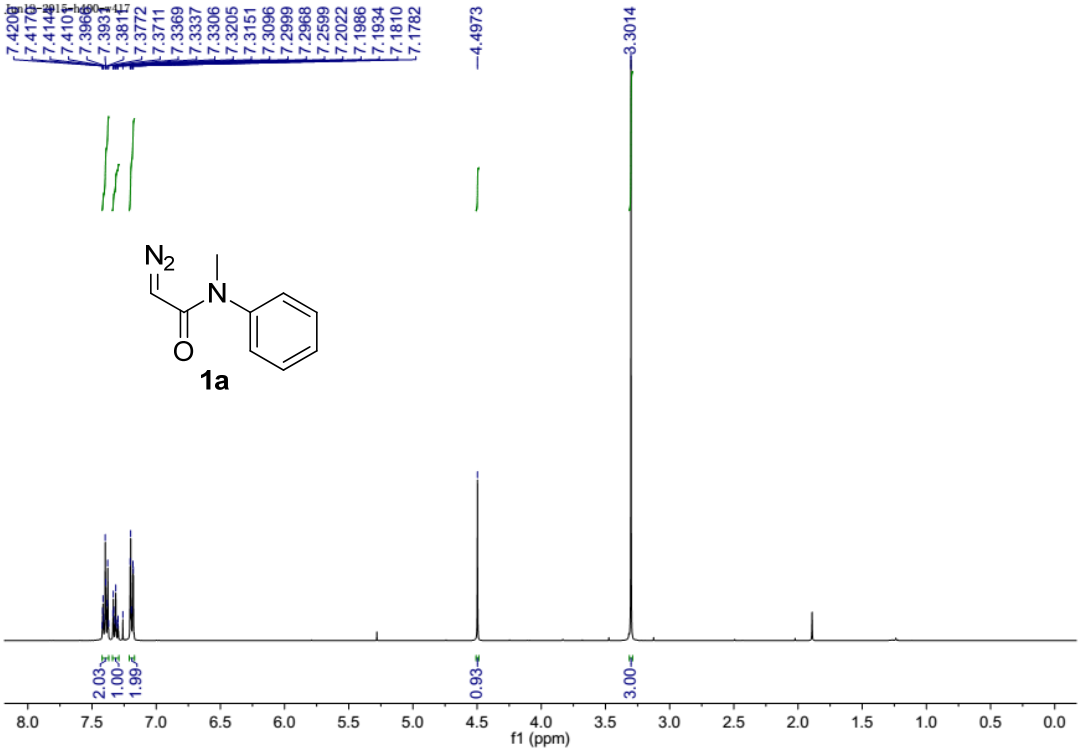
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7.3772
7.3711
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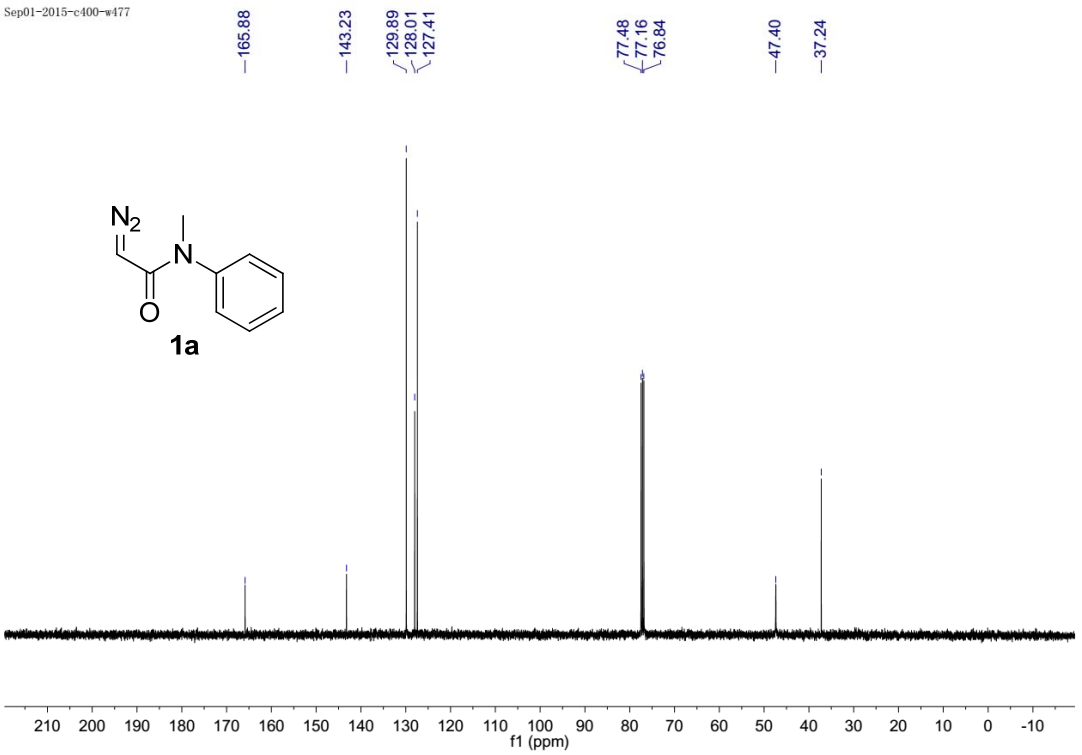
7.3337
7.3306
7.3205
7.3151
7.3096
7.2999
7.2968
7.2599
7.2022
7.1986
7.1934
7.1810
7.1782
4.4973
3.3014
N2
N
O
1a
2.03
1.00
1.99
0.93
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.01
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47.40
37.24
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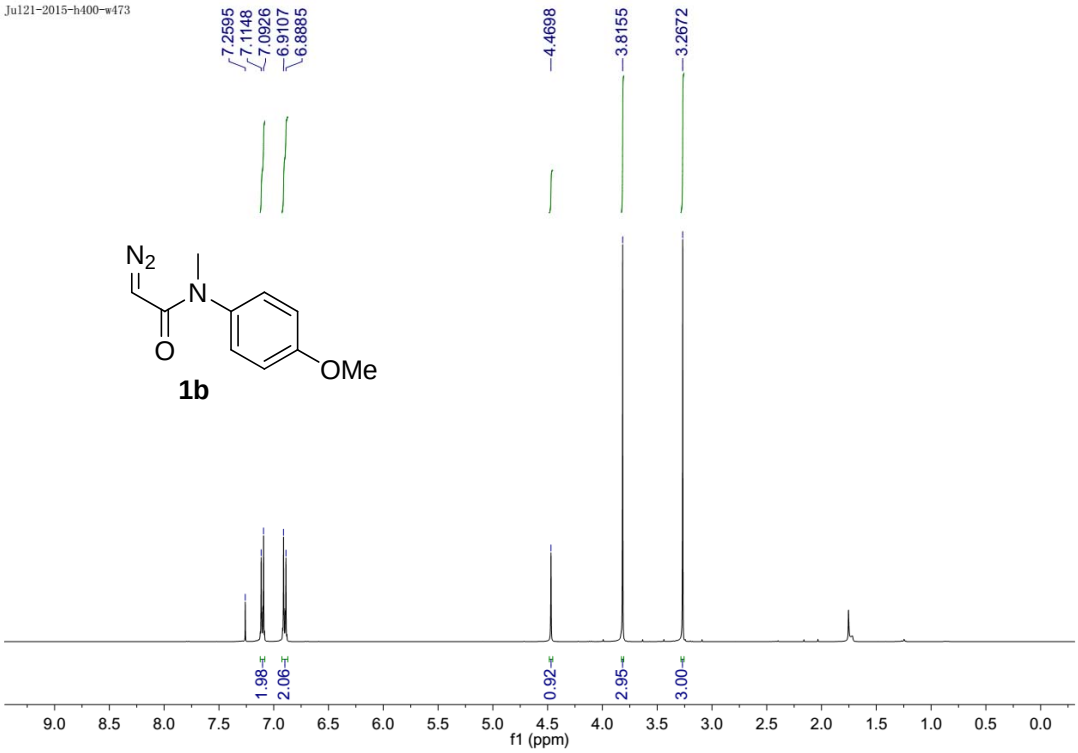
N
O
1a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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O
OMe
1b
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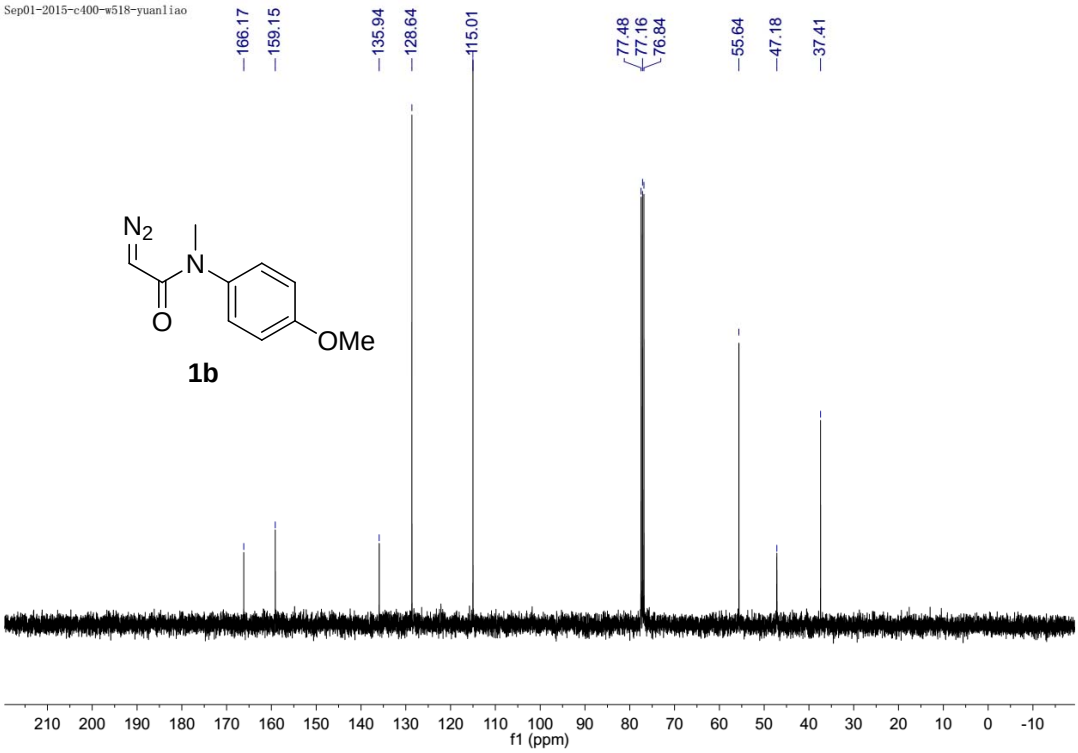
2.95
3.00
f1 (ppm)


Sep01-2015-c400-w518-yuanliao
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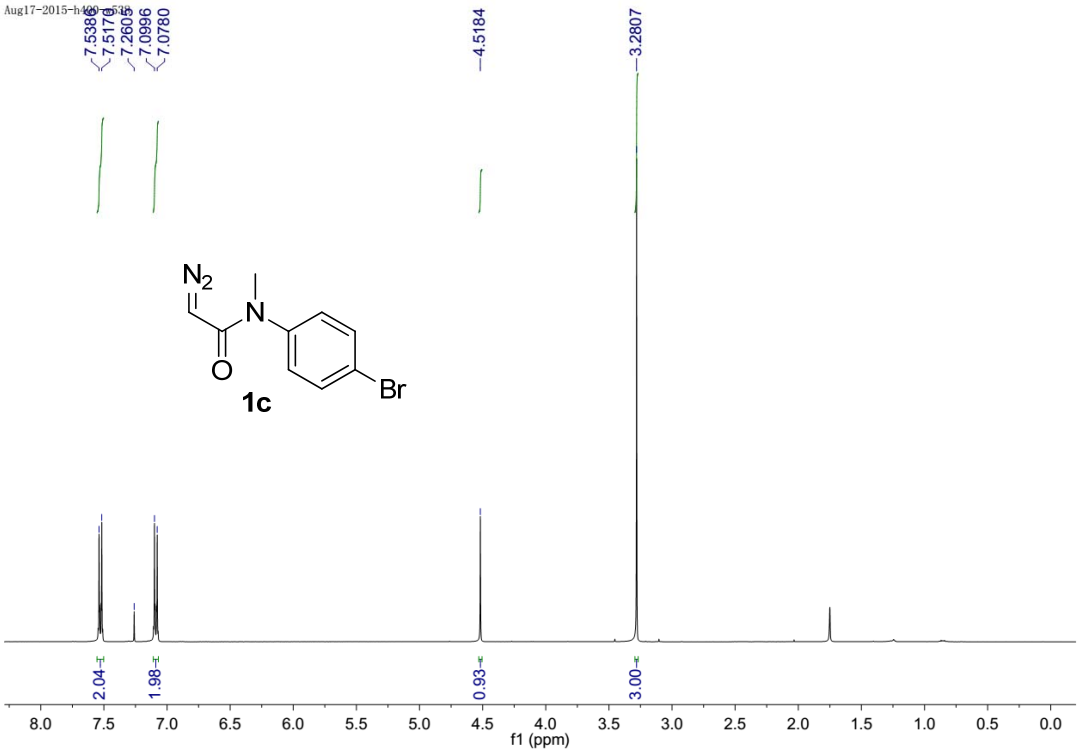
N2
N
O
OMe
1b
f1 (ppm)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7.2605
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7.0780
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3.2807
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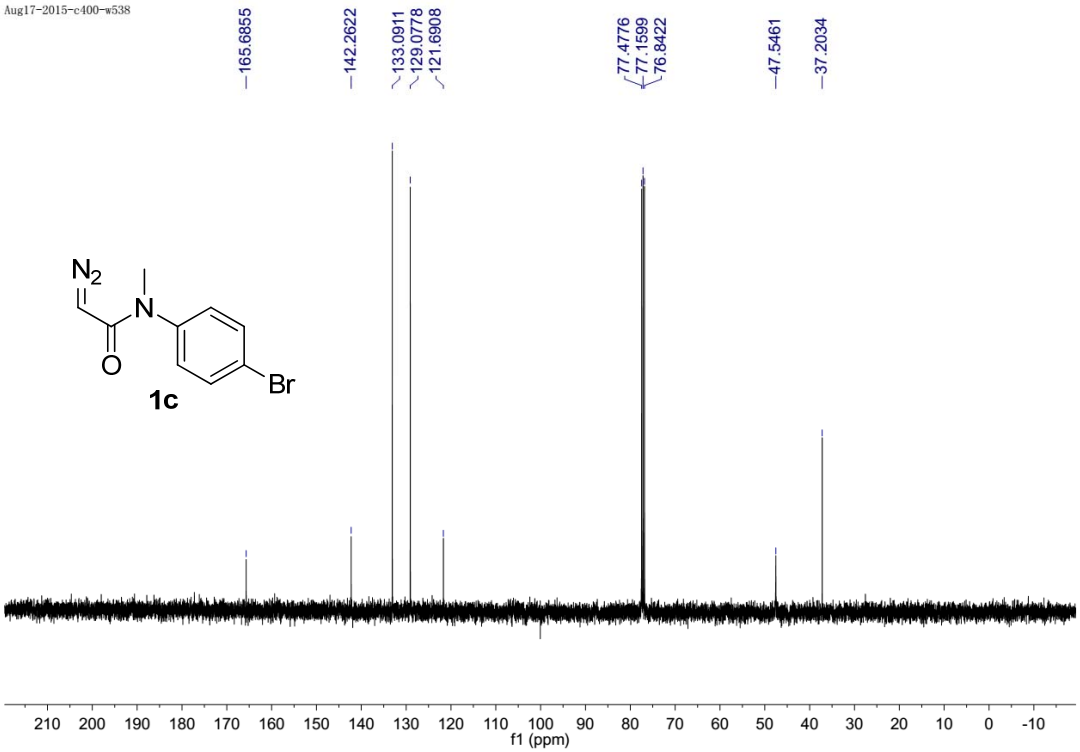
1.98
0.93
3.00
f1 (ppm)

1c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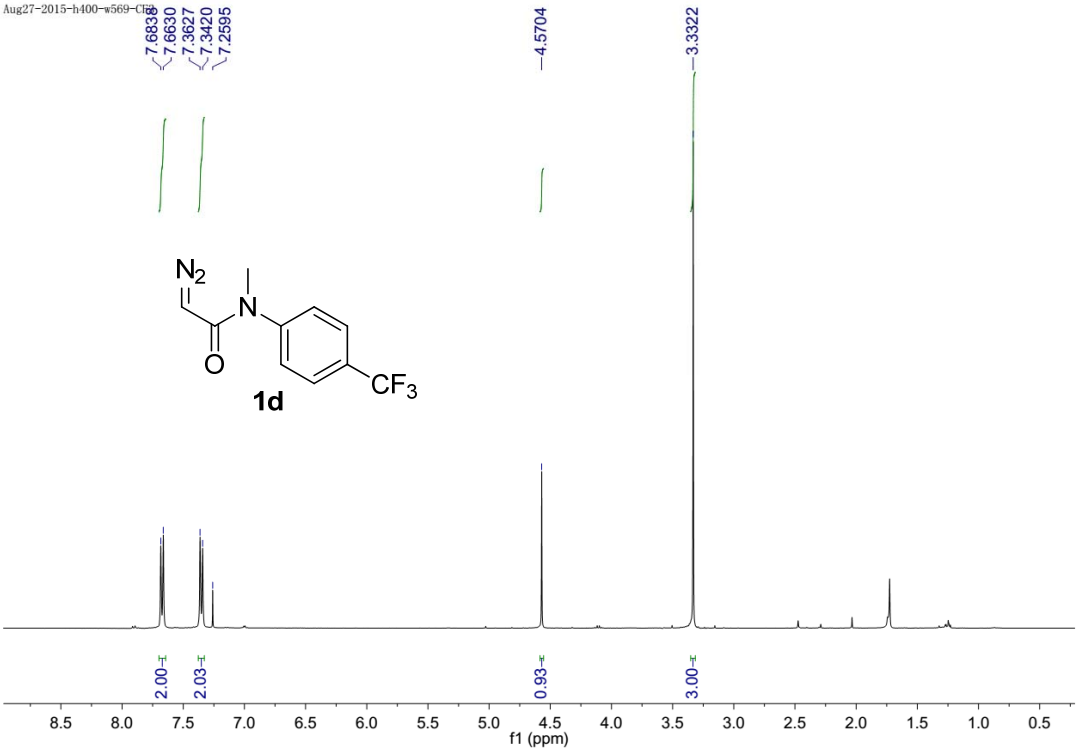
f1 (ppm)

1c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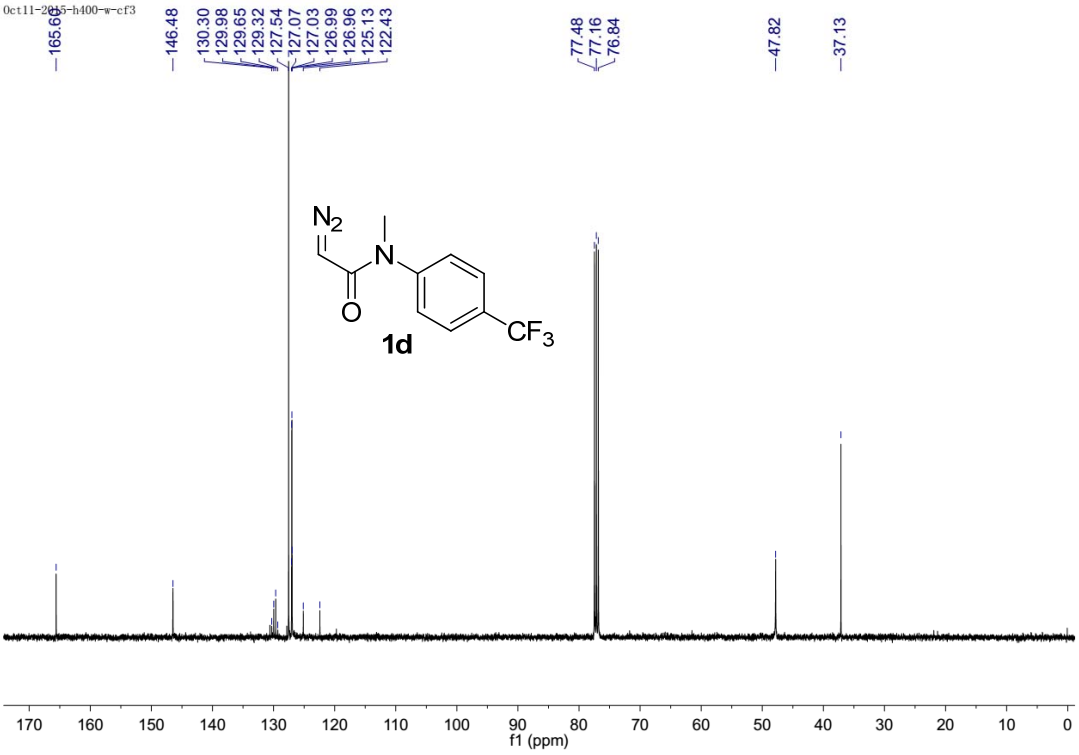
3.00
f1 (ppm)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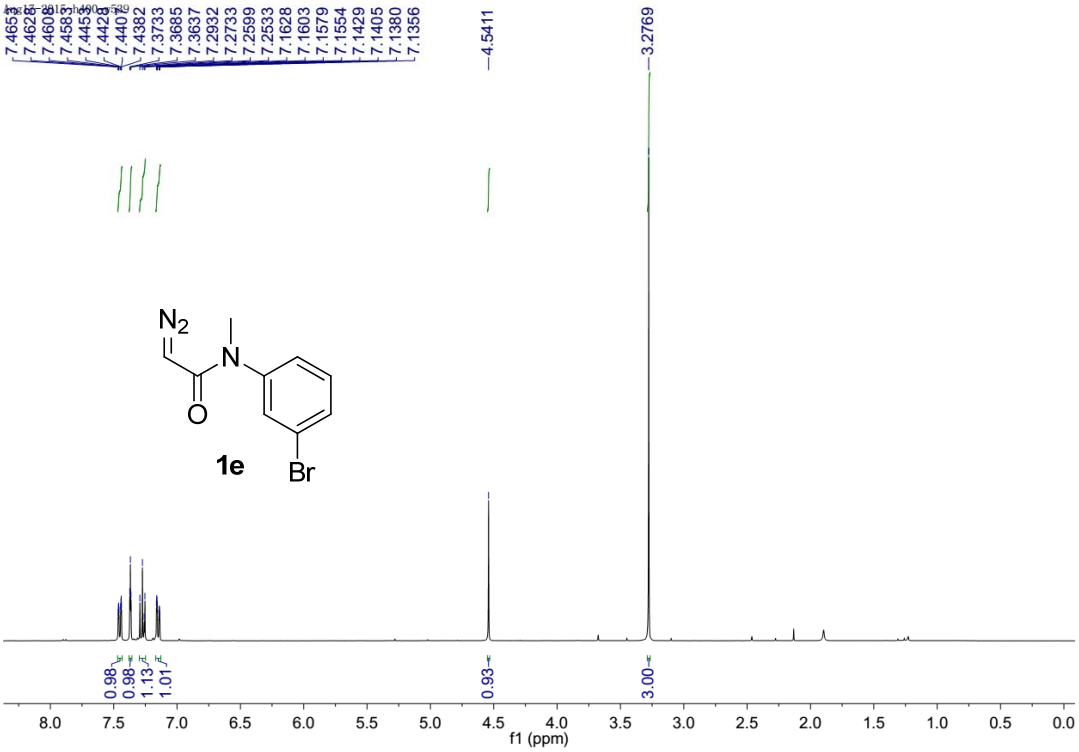
N
O
CF3
1d
f1 (ppm)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7.2533
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7.1429
7.1405
7.1380
7.1356
4.5411
3.2769
N2
N
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1e
Br
0.98
0.98
1.13
1.01
0.93
3.00
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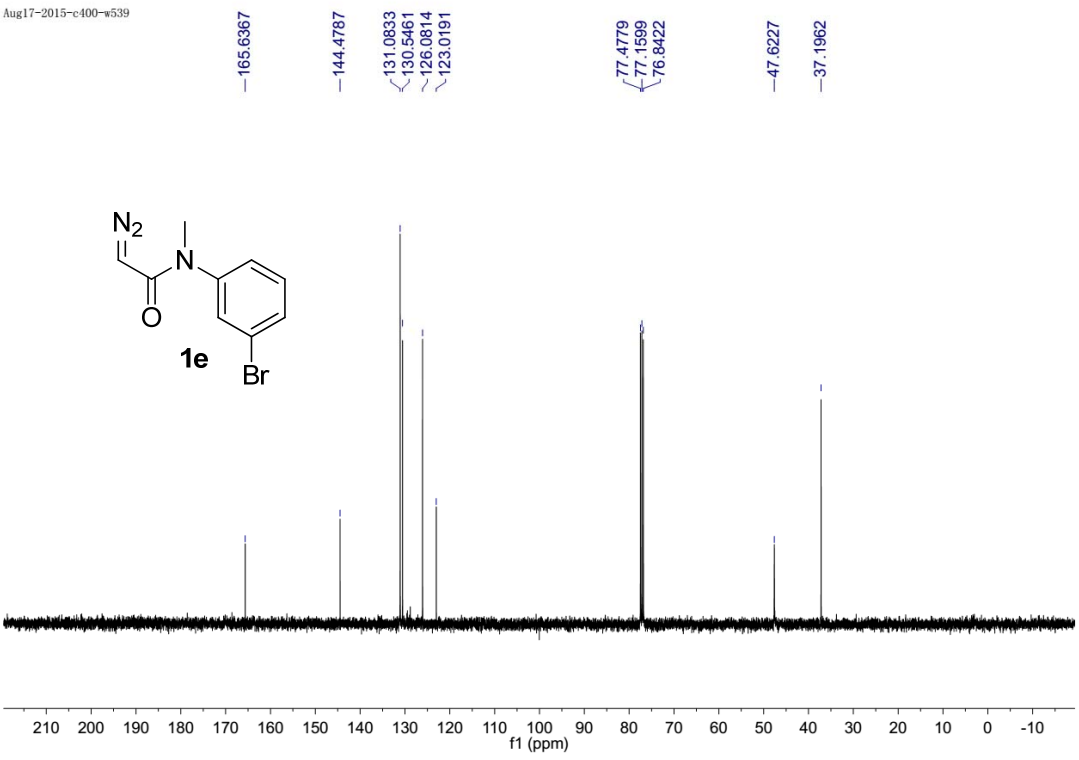
f1 (ppm)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N2
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O
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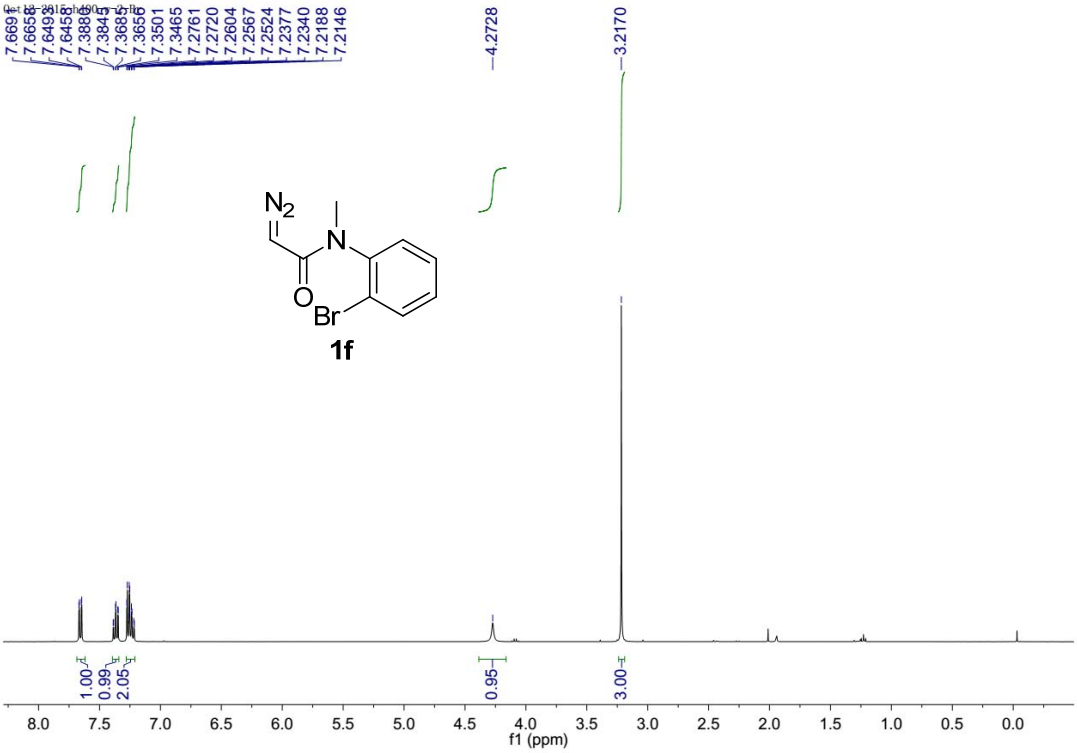
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.2761
7.2720
7.2604
7.2567
7.2524
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7.2340
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7.2146
4.2728
3.2170
N2
N
O
Br
1f
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2.05
0.95
3.00
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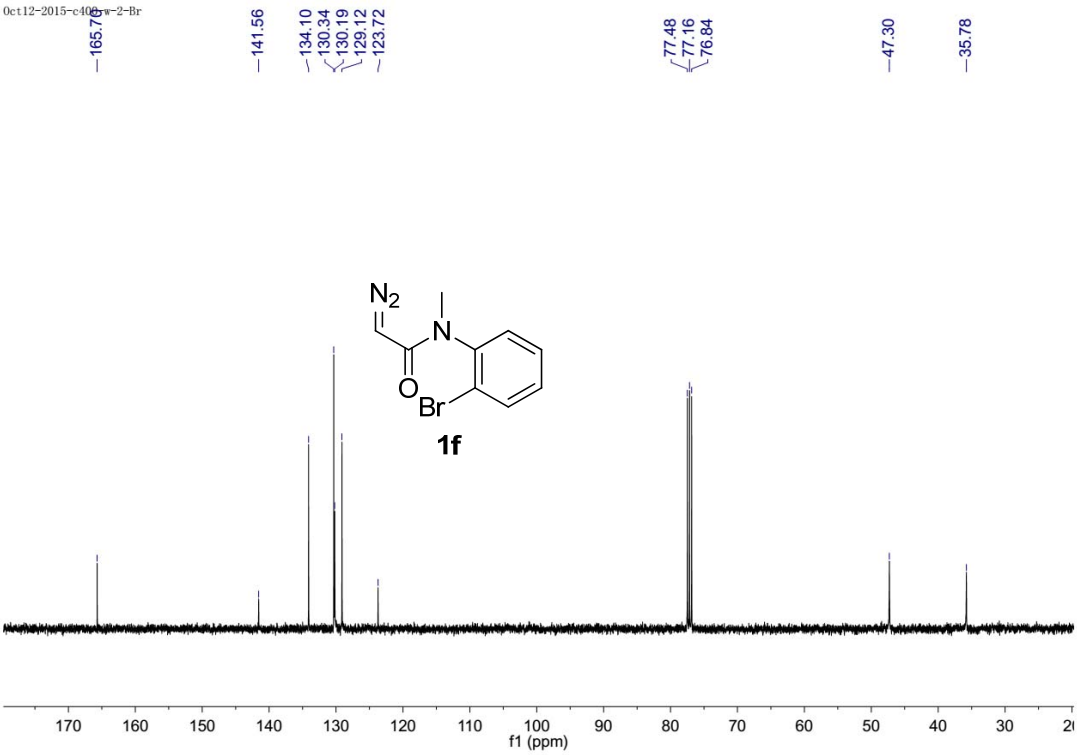
f1 (ppm)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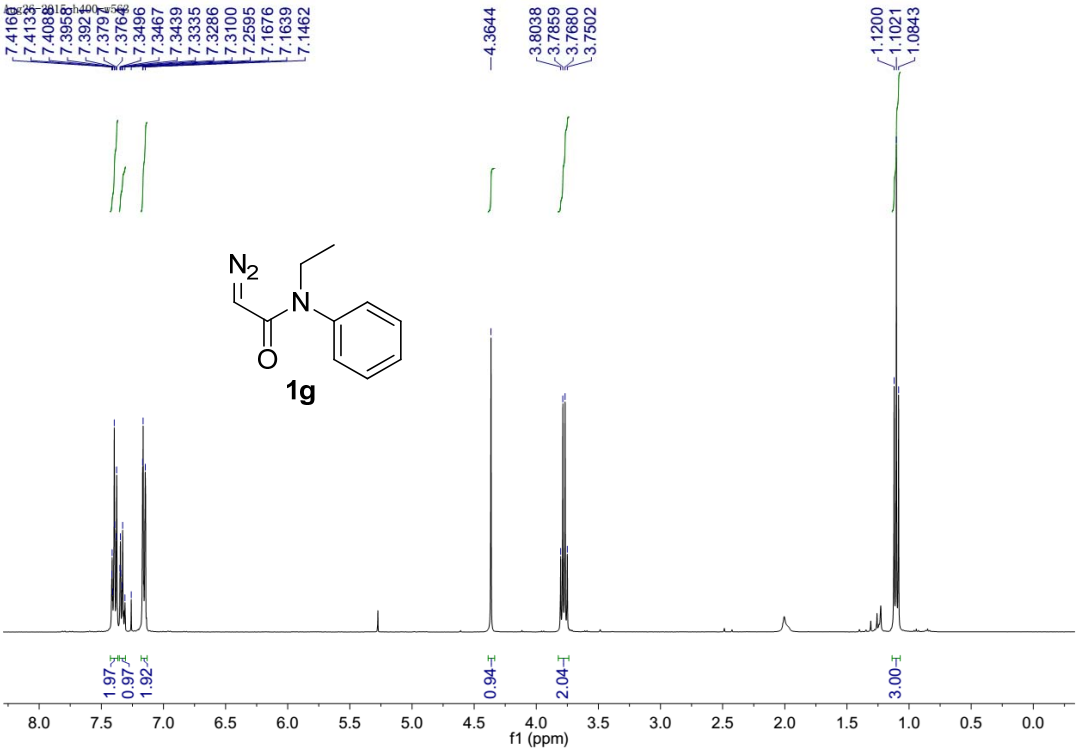
f1 (ppm)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3.7859
3.7680
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O
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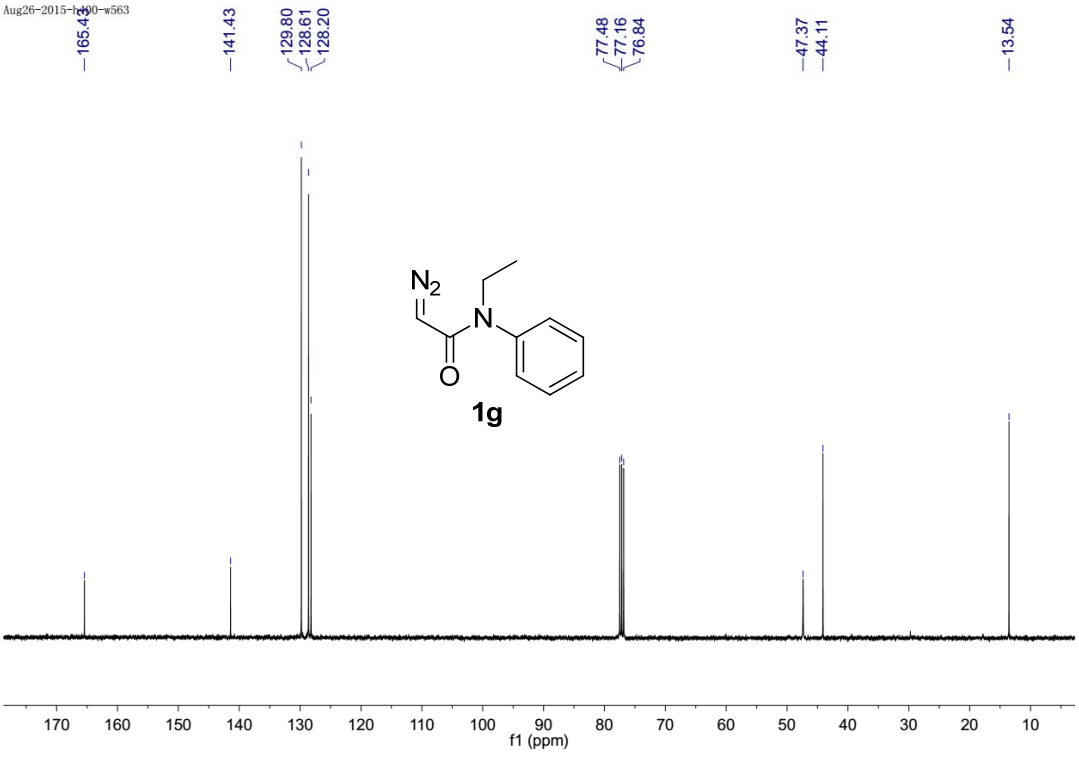
3.00
f1 (ppm)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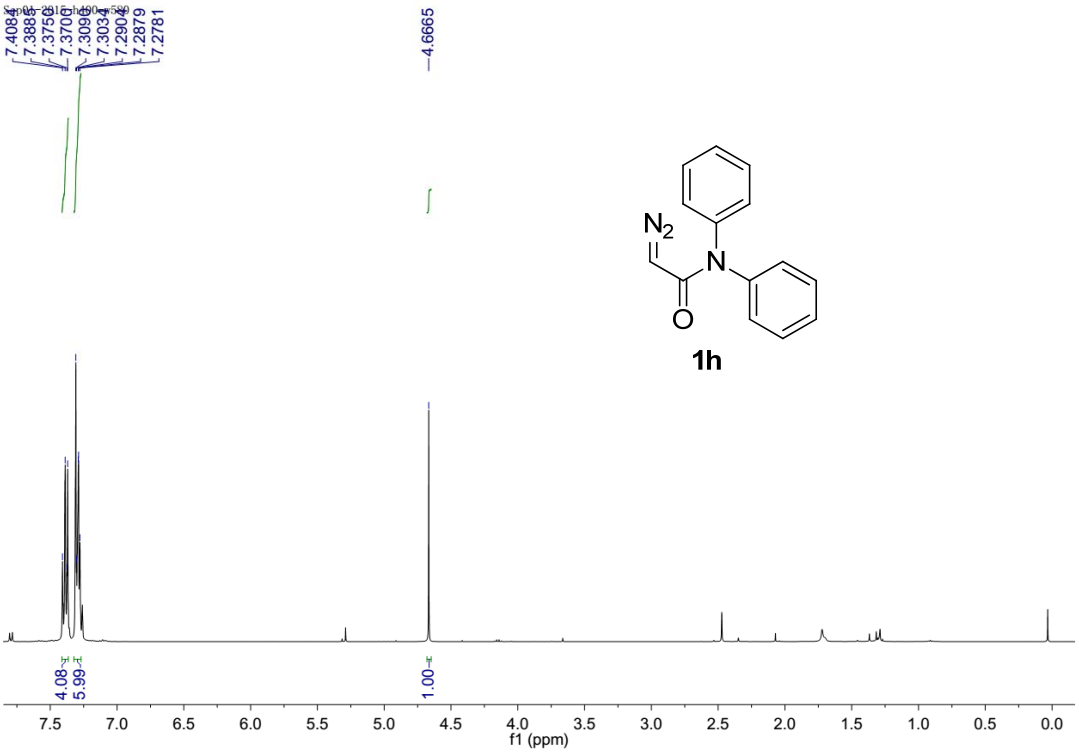
1g
f1 (ppm)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4.08
5.99
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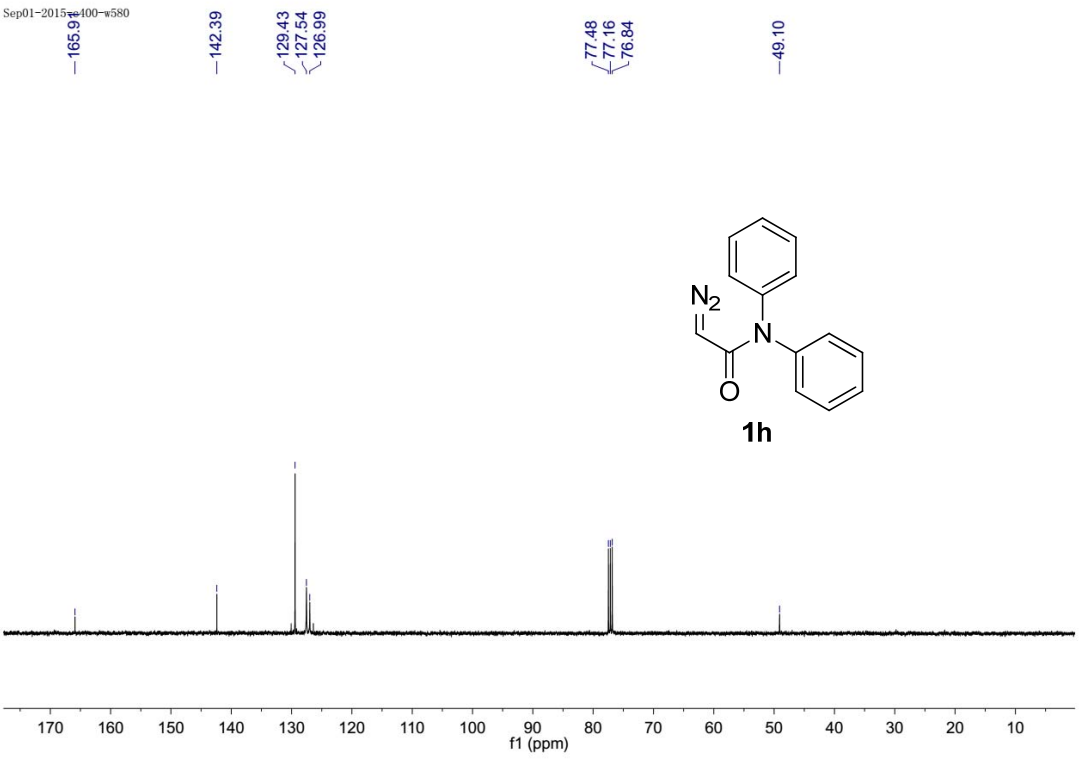
f1 (ppm)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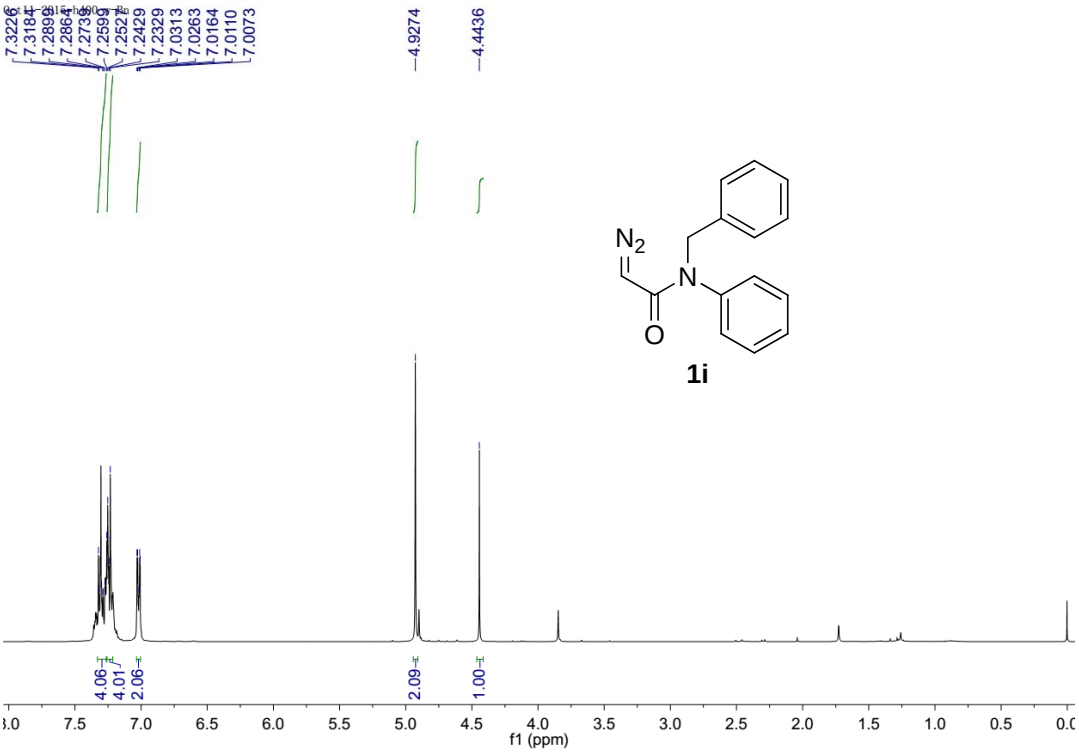
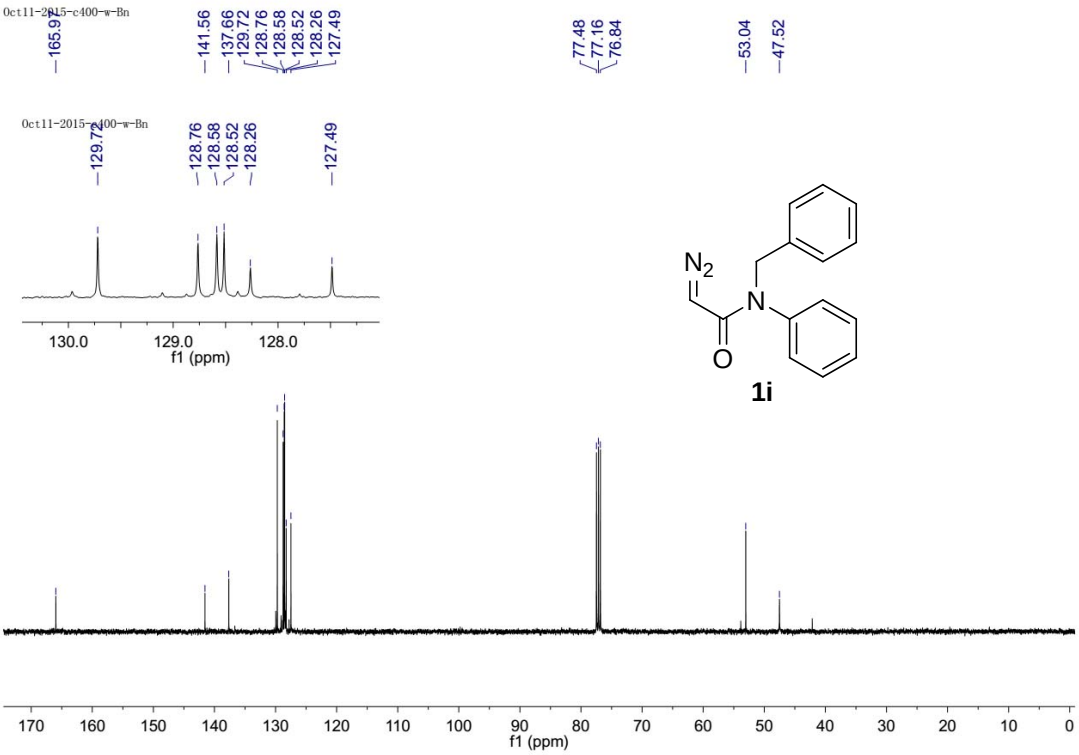
76.84
49.10
N2
N
O
1h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.3226
7.3184
7.2896
7.2867
7.2730
7.2597
7.2527
7.2429
7.2329
7.0313
7.0263
7.0164
7.0110
7.0073
4.9274
4.4436
4.06
4.01
2.06
2.09
1.00
f1 (ppm)

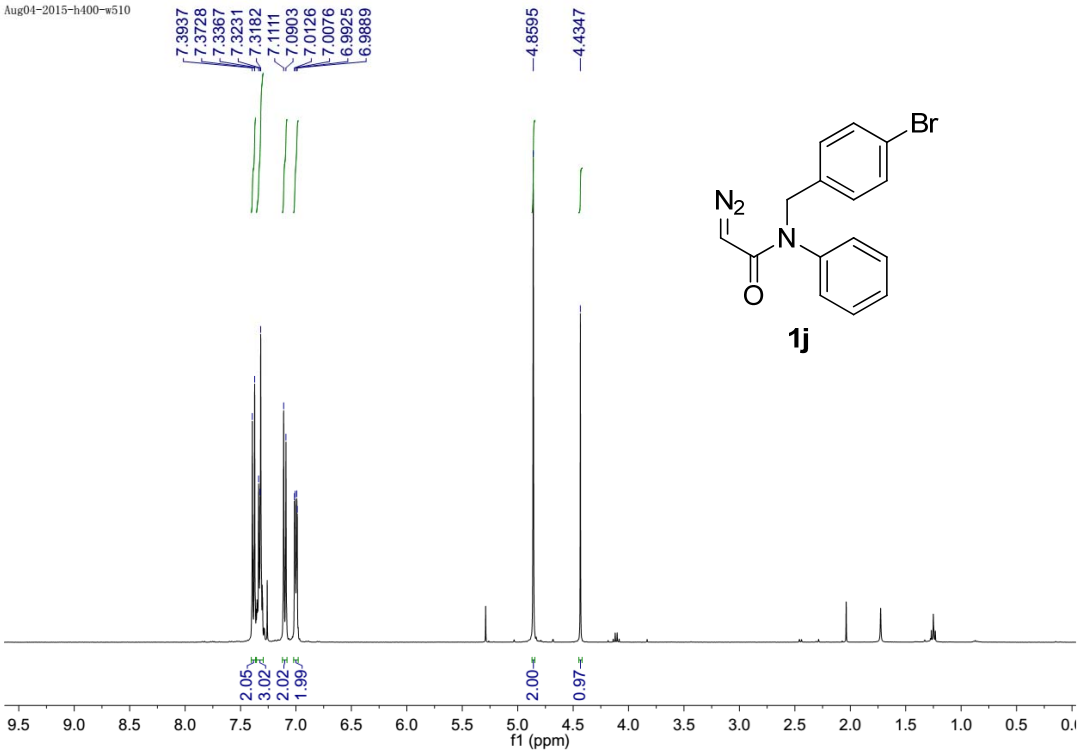
N2
N
O

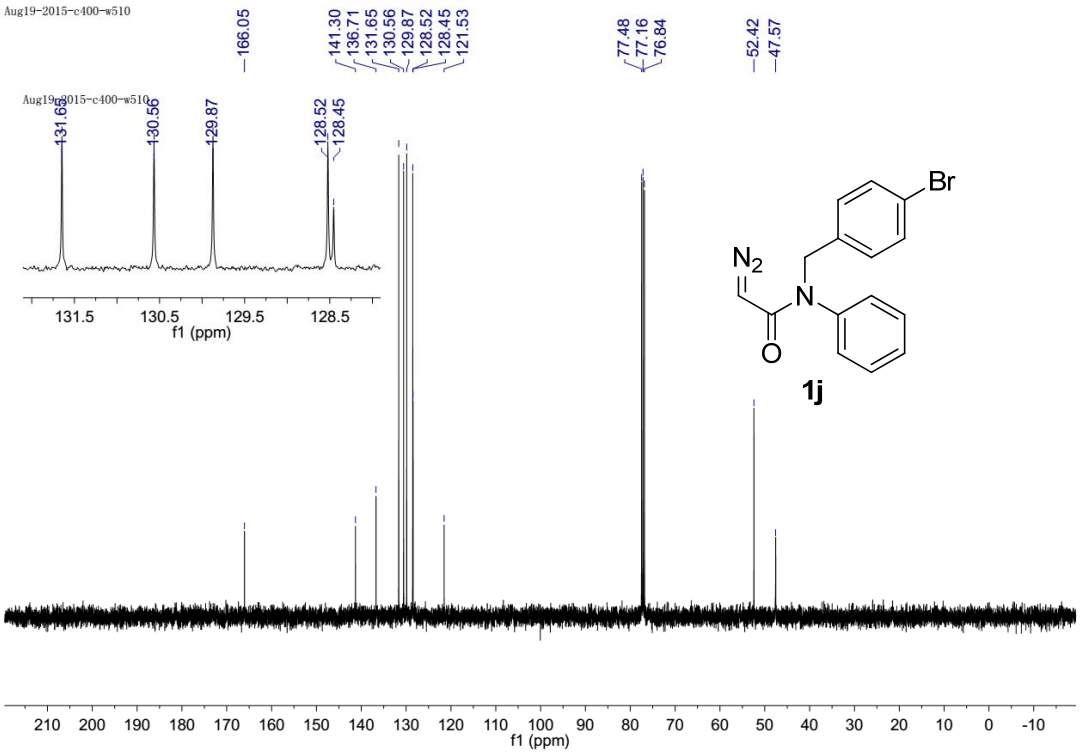
1i

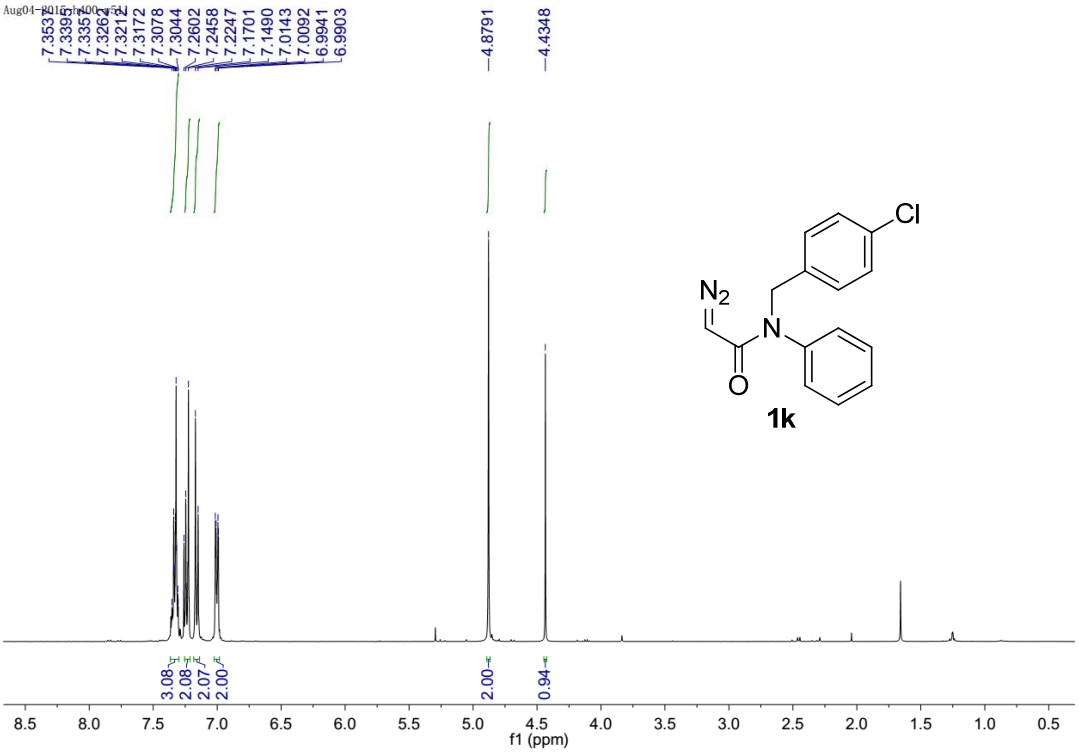

165.9
141.56
137.66
129.72
128.76
128.58
128.52
128.26
127.49
77.48
77.16
76.84
53.04
47.52
129.72
128.76
128.58
128.52
128.26
127.49
130.0
129.0
128.0
f1 (ppm)
f1 (ppm)

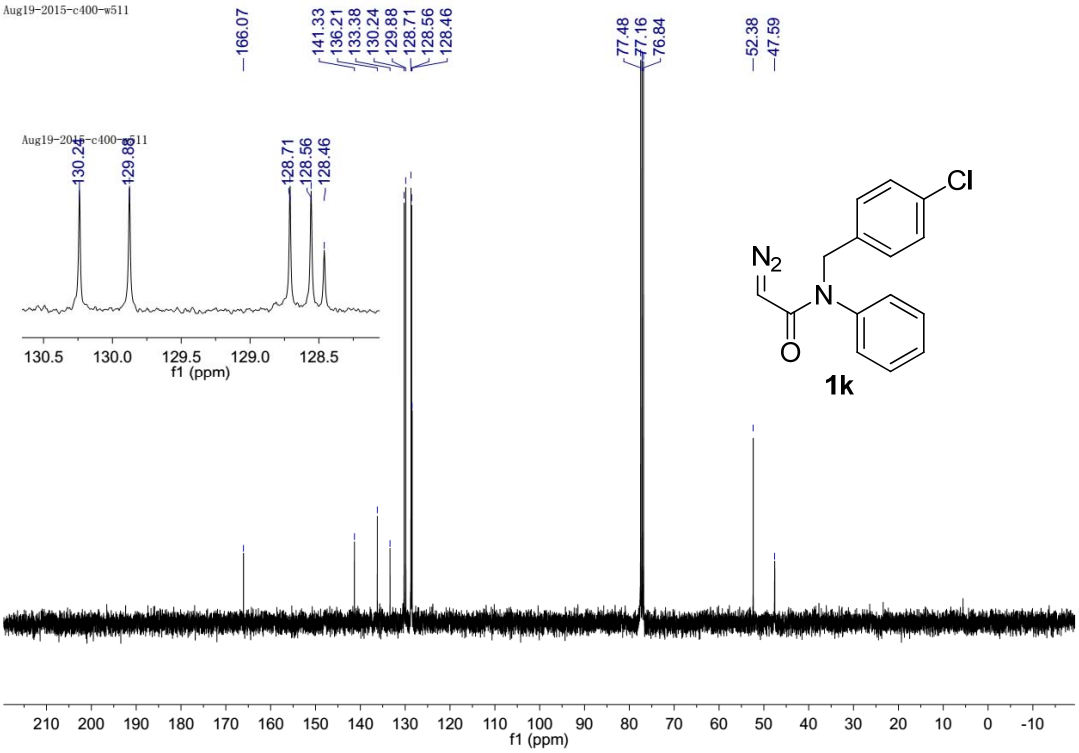
N2
N
O

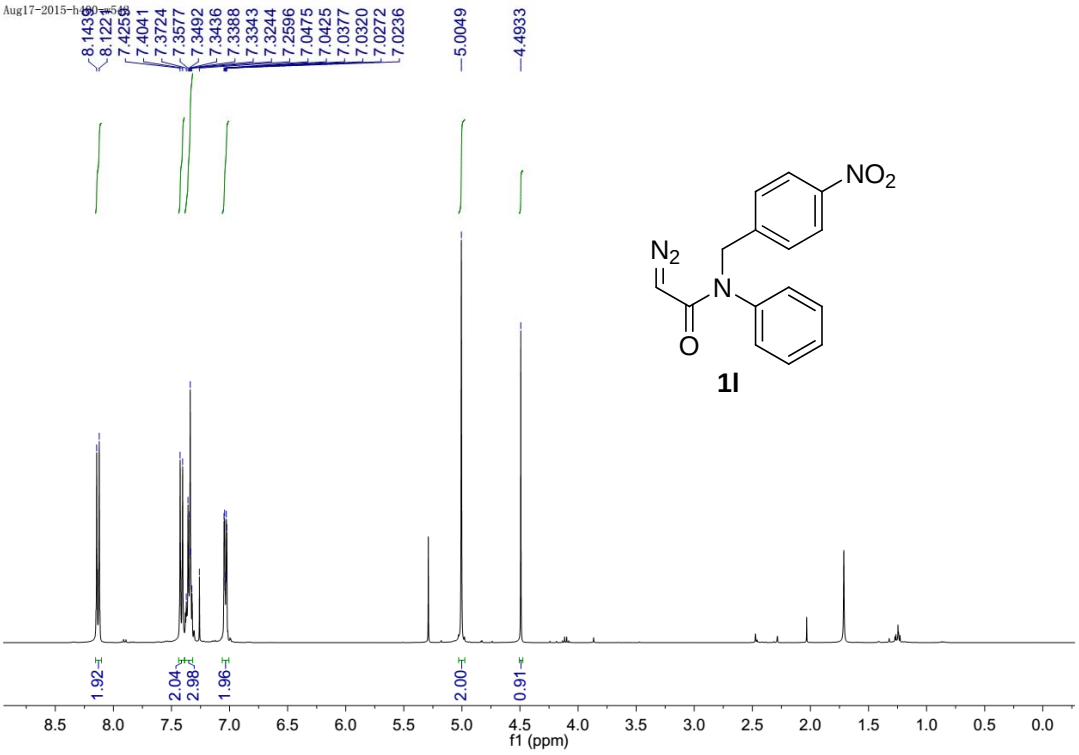
1i


Aug04-2015-h400-w510
7.3937
7.3728
7.3367
7.3231
7.3182
7.1111
7.0903
7.0126
7.0076
6.9925
6.9889
4.8595
4.4347
2.05
3.02
2.02
1.99
2.00
0.97
f1 (ppm)
Br
N2
N
O
1j


Aug19-2015-c400-w510
166.05
141.30
136.71
131.65
130.56
129.87
128.52
128.45
121.53
77.48
77.16
76.84
52.42
47.57
131.5
130.5
129.5
128.5
f1 (ppm)
Br
N2
N
O
1j

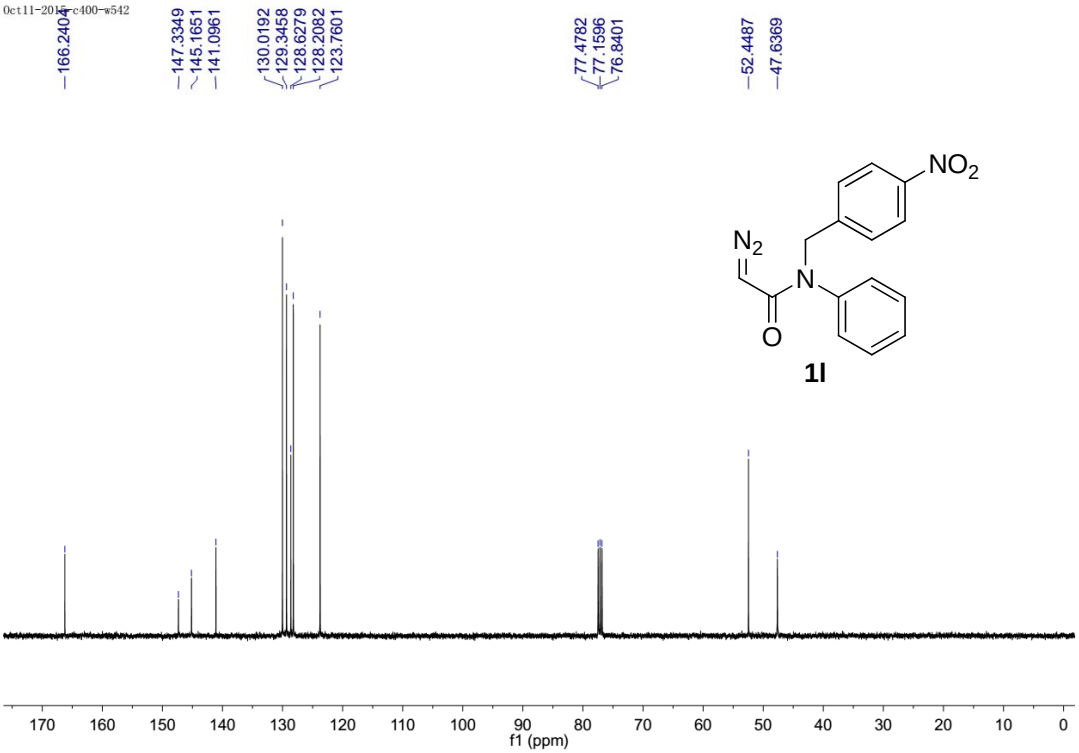

7.3531
7.3395
7.3357
7.3262
7.3212
7.3172
7.3078
7.3044
7.2602
7.2458
7.2247
7.1701
7.1490
7.0143
7.0092
6.9941
6.9903
4.8791
4.4348
3.08
2.08
2.07
2.00
2.00
0.94
f1 (ppm)
Cl
N2
N
O
1k


Aug19-2015-c400-w511
166.07
141.33
136.21
133.38
130.24
129.88
128.71
128.56
128.46
77.48
77.16
76.84
52.38
47.59
130.24
129.88
128.71
128.56
128.46
f1 (ppm)
f1 (ppm)
Cl
N2
N
O
1k


8.1439
8.1221
7.4259
7.4041
7.3724
7.3577
7.3492
7.3436
7.3388
7.3343
7.3244
7.2596
7.0475
7.0425
7.0377
7.0320
7.0272
7.0236
5.0049
4.4933
1.92
2.04
2.98
1.96
2.00
0.91
f1 (ppm)

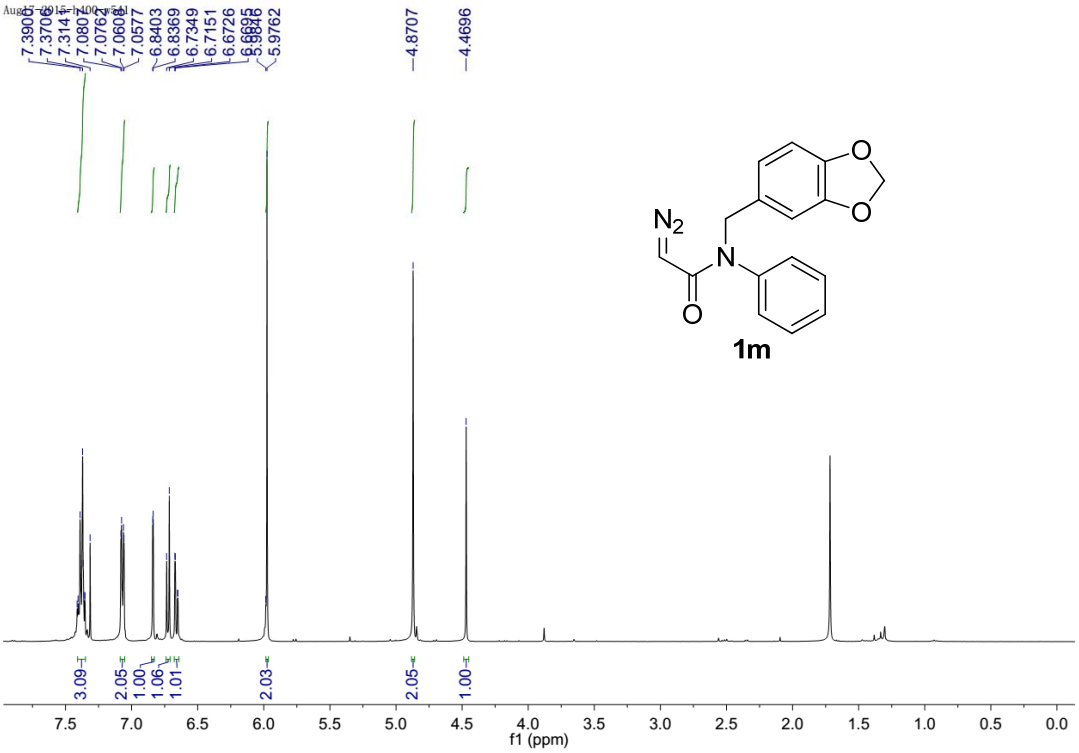
NO2
N2
N
O

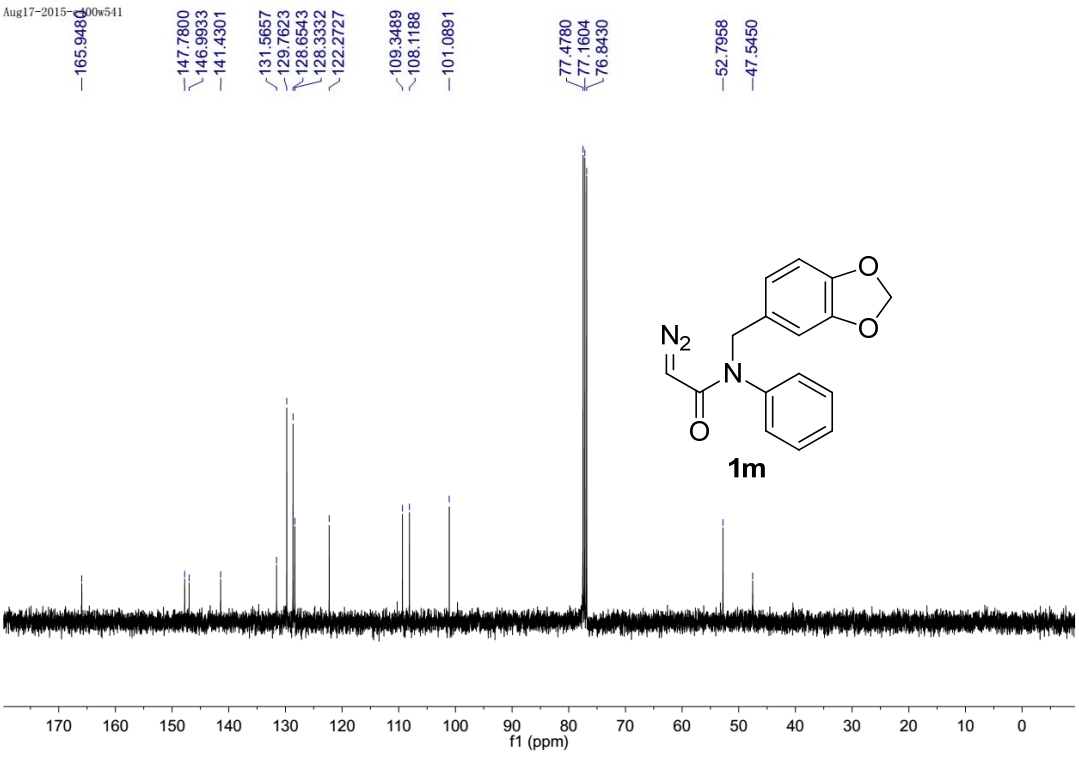
1l

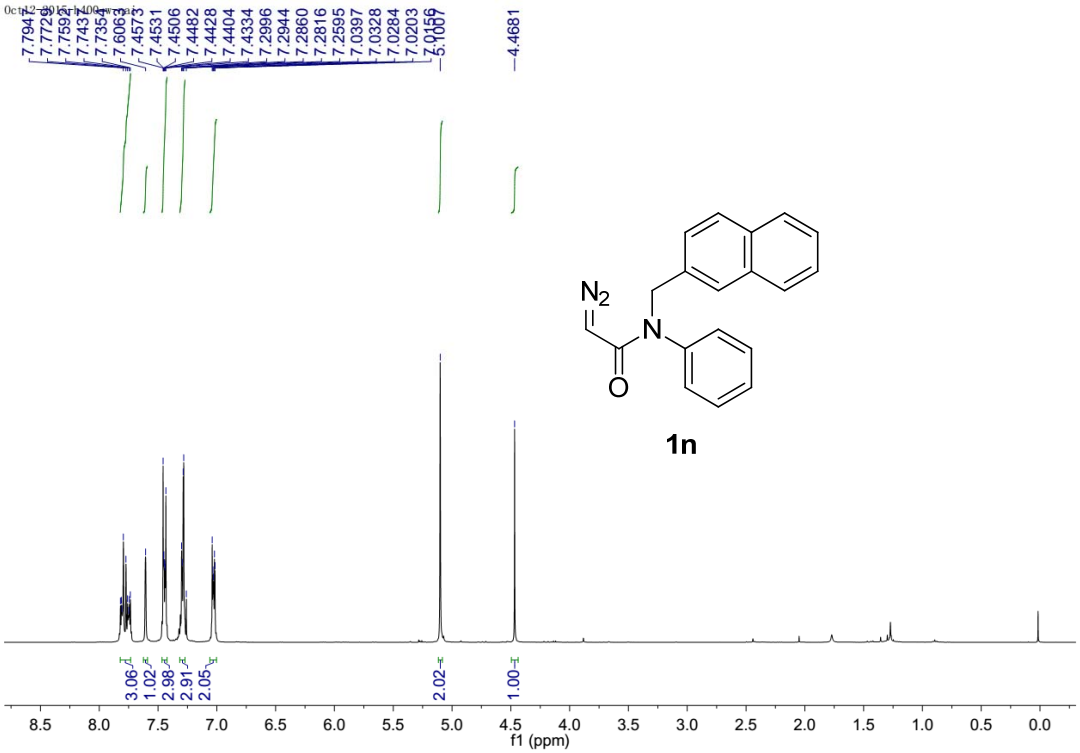

166.2404
147.3349
145.1651
141.0961
130.0192
129.3458
128.6279
128.2082
123.7601
77.4782
77.1596
76.8401
52.4487
47.6369
f1 (ppm)

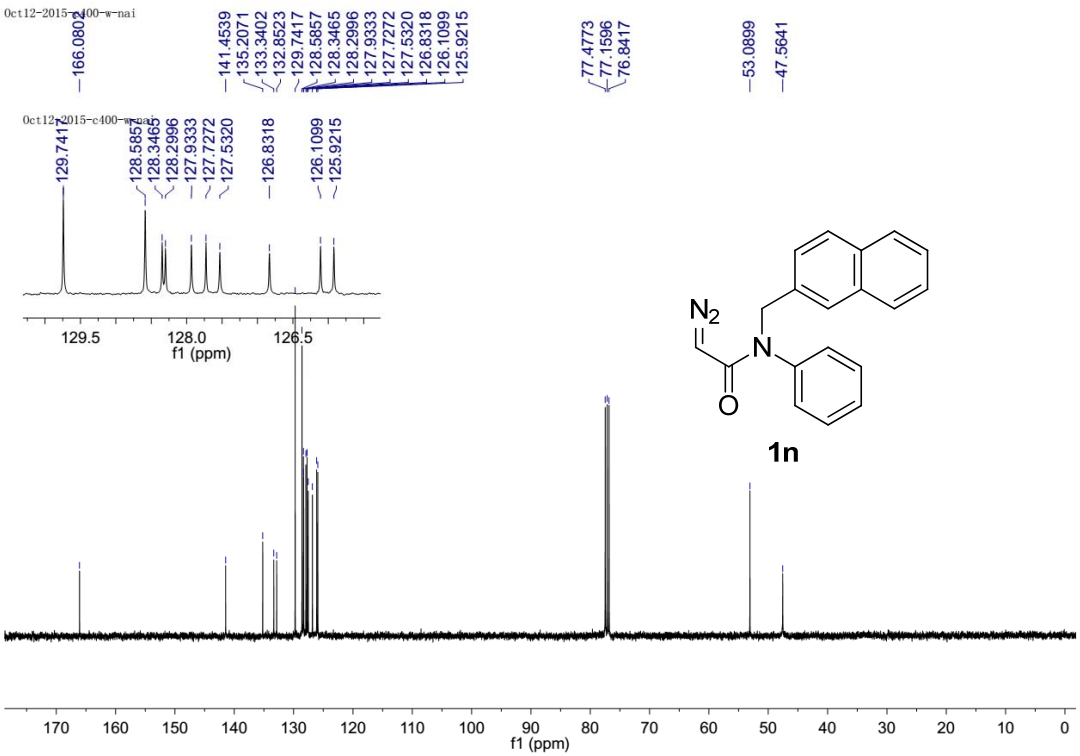
NO2
N2
N
O

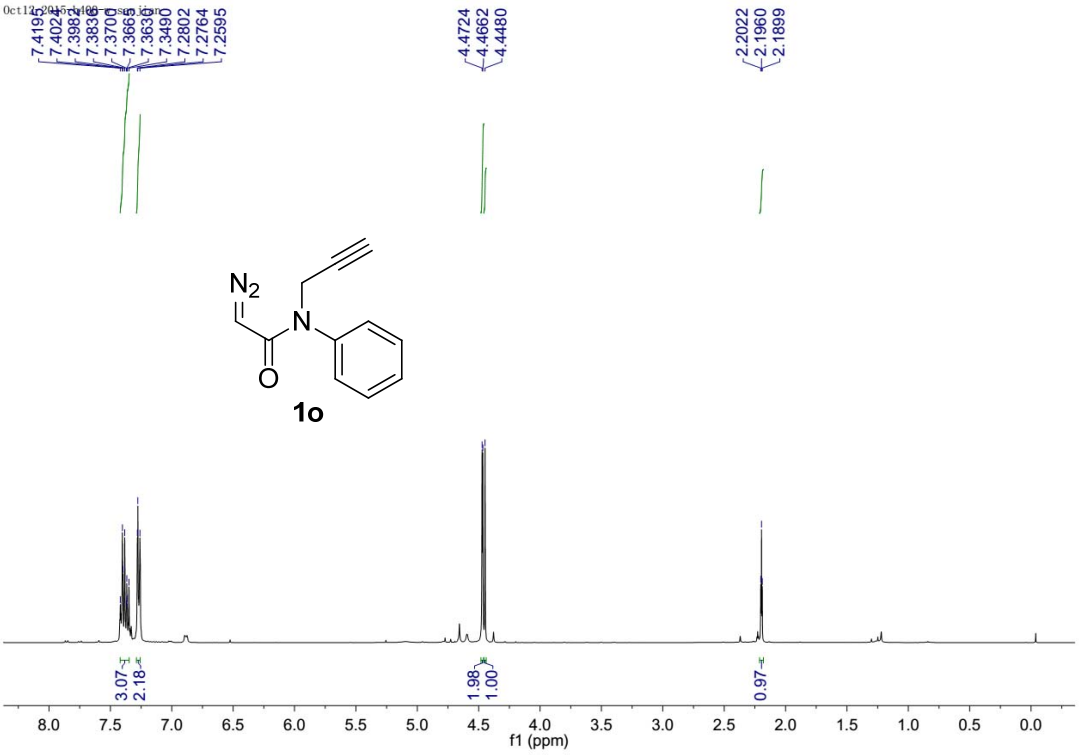
1l

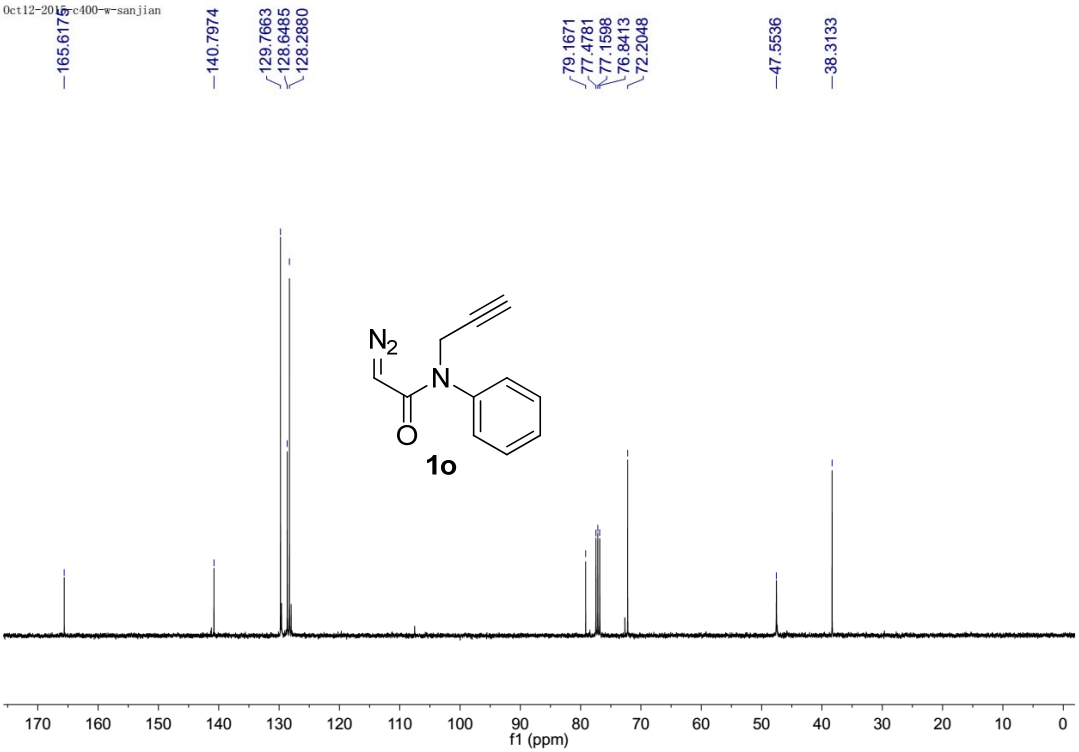

7.3906
7.3706
7.3141
7.0807
7.0762
7.0608
7.0577
6.8403
6.8369
6.7349
6.7151
6.6726
5.9762
4.8707
4.4696
3.09
2.05
1.00
1.06
1.01
2.03
2.05
1.00
f1 (ppm)
N2
O
N
O
O
1m

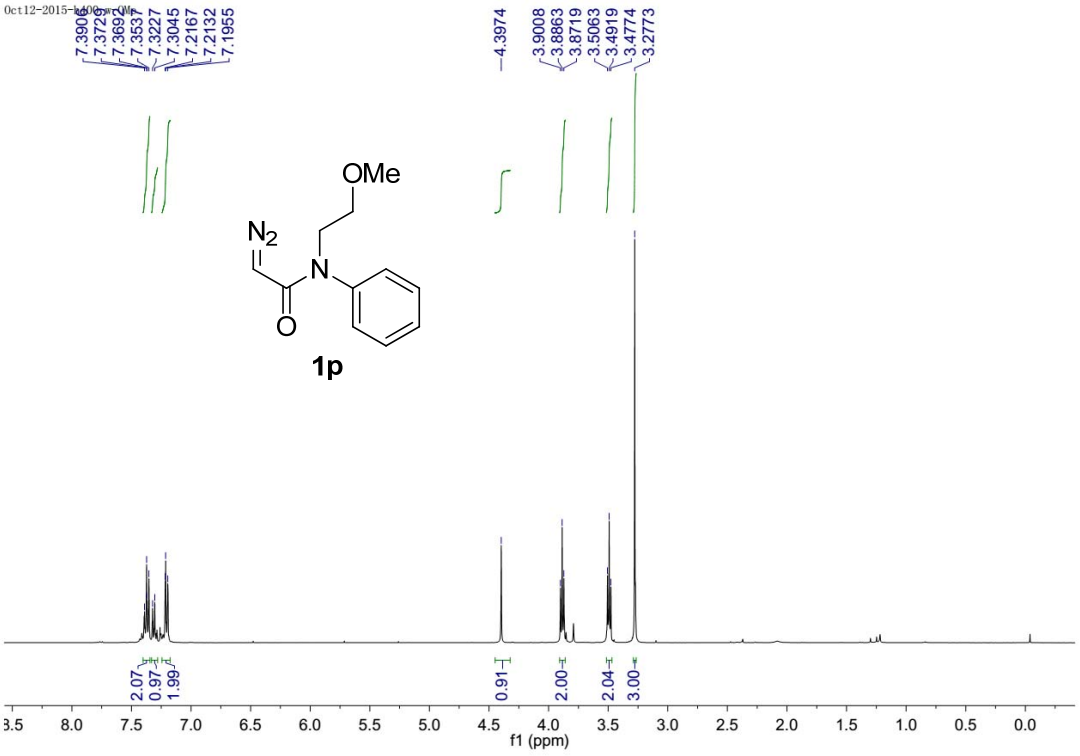

Aug17-2015-c400w541
165.9484
147.7800
146.9933
141.4301
131.5657
129.7623
128.6543
128.3332
122.2727
109.3489
108.1188
101.0891
77.4780
77.1604
76.8430
52.7958
47.5450
f1 (ppm)
N2
O
N
O
O
1m

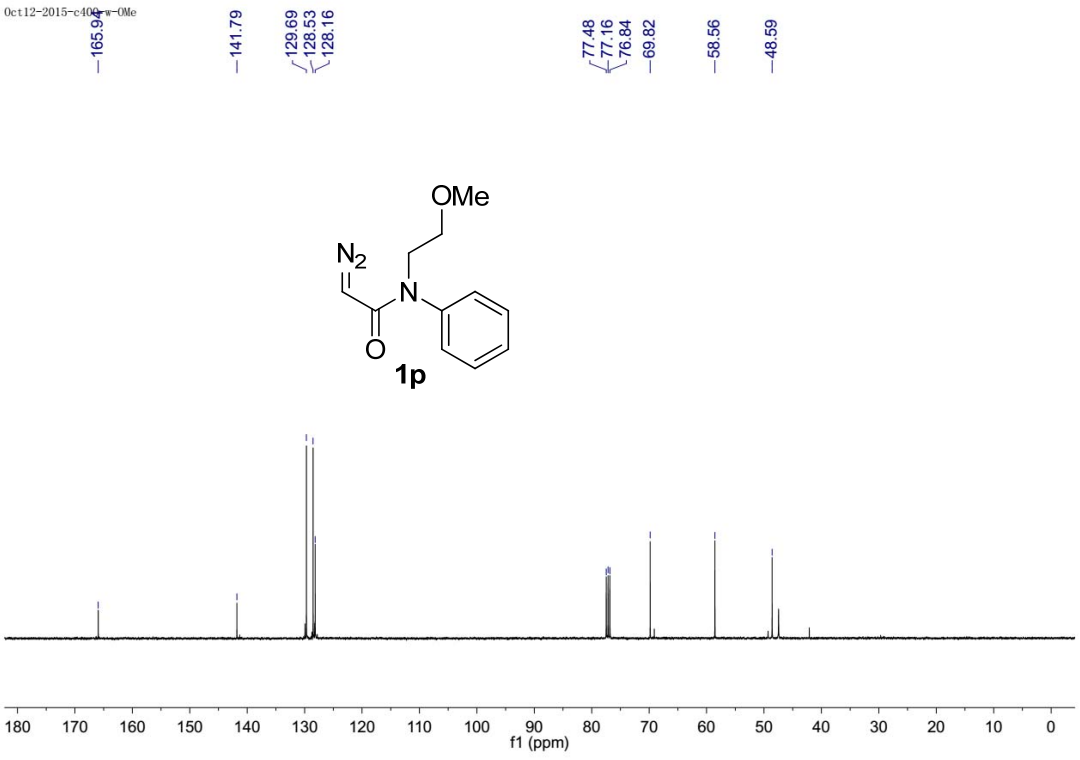

7.7944
7.7728
7.7594
7.7431
7.7352
7.6063
7.4573
7.4531
7.4506
7.4482
7.4428
7.4404
7.4334
7.2996
7.2944
7.2860
7.2816
7.2595
7.0397
7.0328
7.0284
7.0203
7.0156
5.1007
4.4681
3.06
1.02
2.98
2.91
2.05
2.02
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
N2
N
O
1n

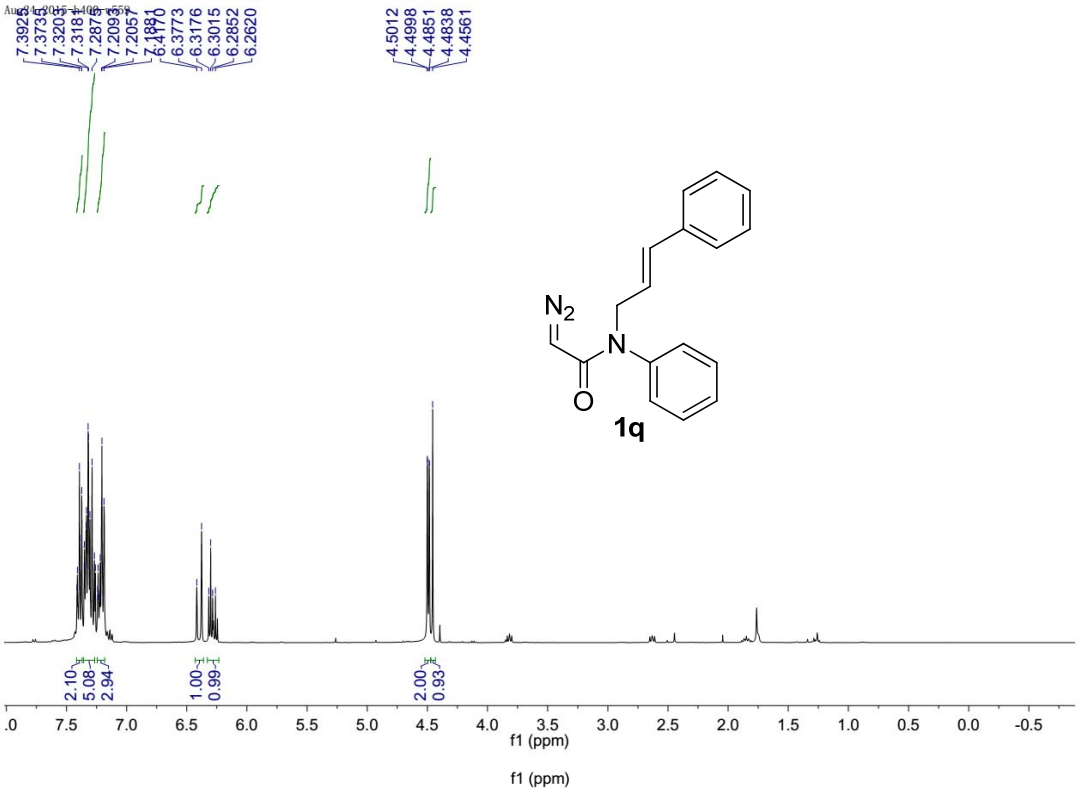

166.0800
141.4539
135.2071
133.3402
132.8523
129.7417
128.5857
128.3465
128.2996
127.9333
127.7272
127.5320
126.8318
126.1099
125.9215
77.4773
77.1596
76.8417
53.0899
47.5641
129.5 128.0 126.5
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
N2
N
O
1n

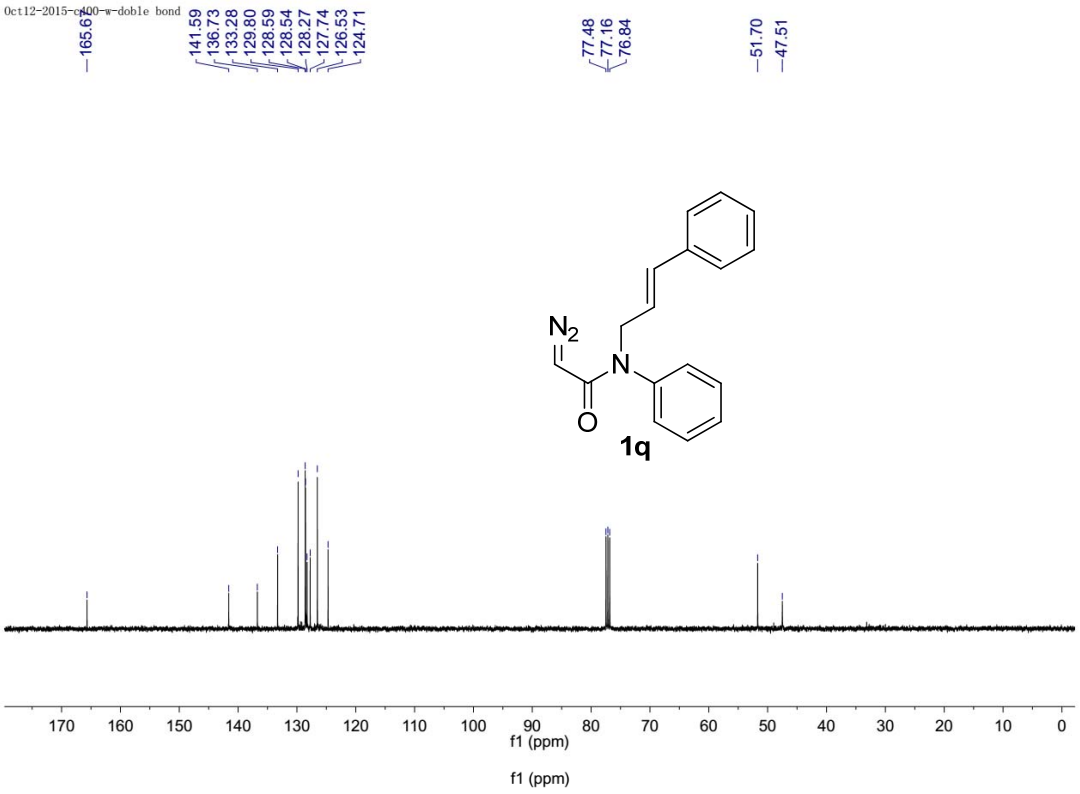

7.4195
7.4023
7.3982
7.3836
7.3706
7.3665
7.3630
7.3490
7.2802
7.2764
7.2595
4.4724
4.4662
4.4480
2.2022
2.1960
2.1899
N2
N
O
1o
3.07
2.18
1.98
1.00
0.97
f1 (ppm)

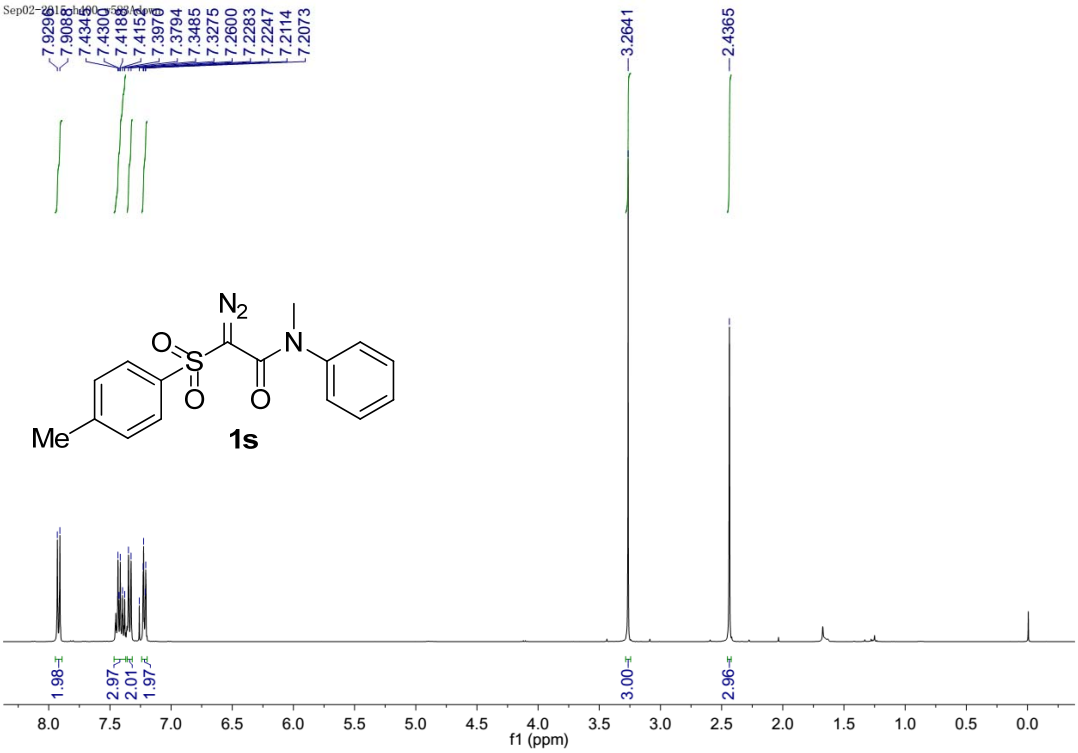

165.6174
140.7974
129.7663
128.6485
128.2880
79.1671
77.4781
77.1598
76.8413
72.2048
47.5536
38.3133
N2
N
O
1o
f1 (ppm)

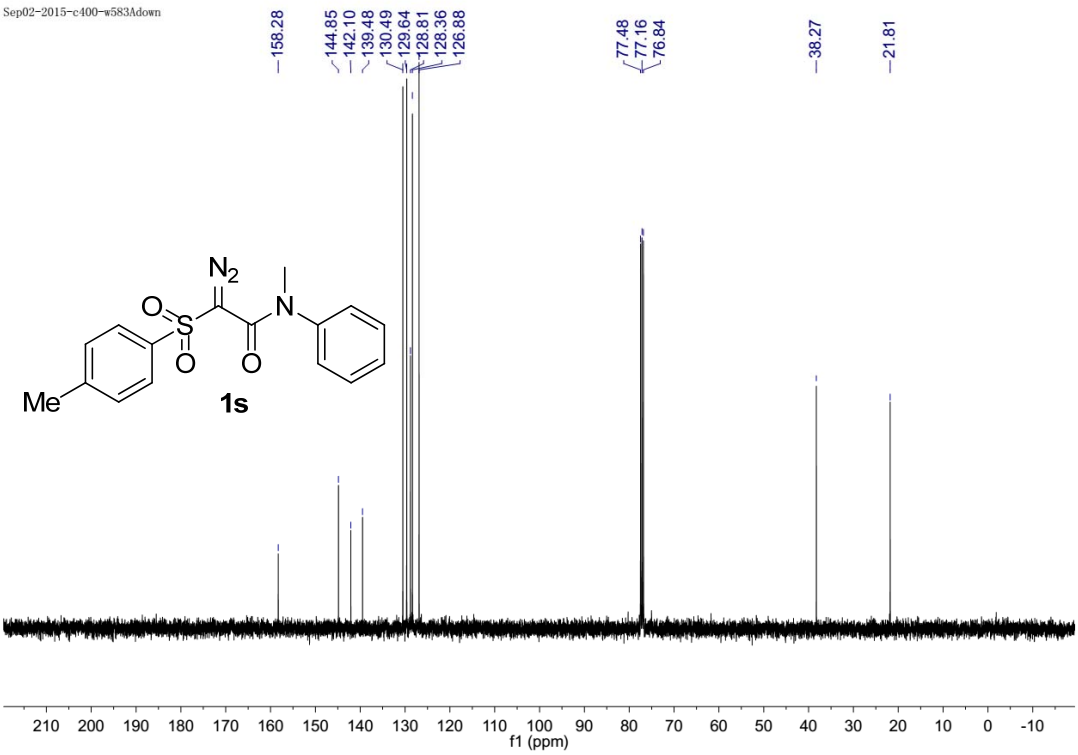

7.3906
7.3729
7.3692
7.3537
7.3227
7.3045
7.2167
7.2132
7.1955
4.3974
3.9008
3.8863
3.8719
3.5063
3.4919
3.4774
3.2773
OMe
N2
N
O
1p
2.07
0.97
1.99
0.91
2.00
2.04
3.00
f1 (ppm)

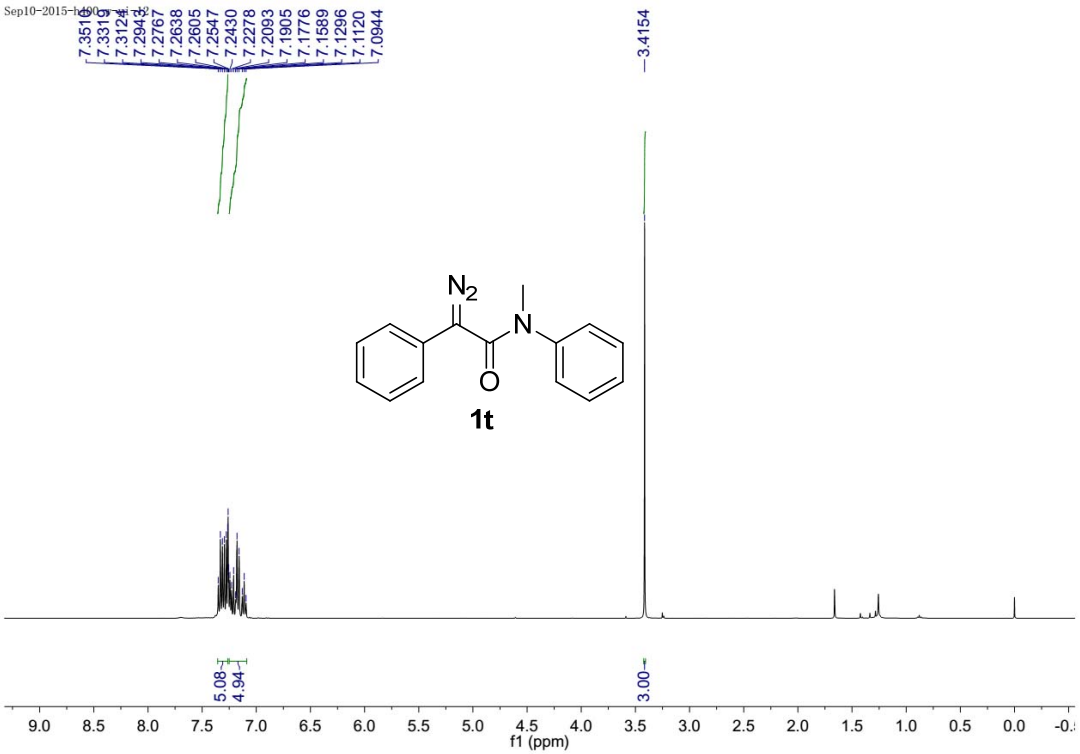

165.94
141.79
129.69
128.53
128.16
77.48
77.16
76.84
69.82
58.56
48.59
OMe
N2
N
O
1p
f1 (ppm)

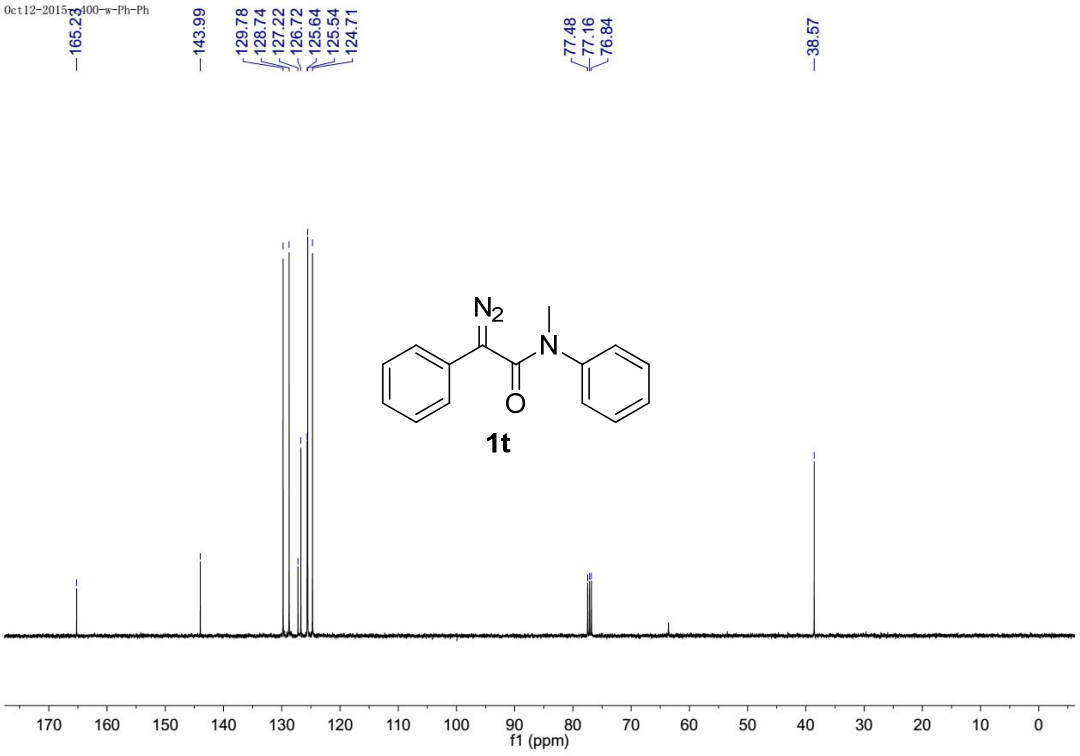

7.3925
7.3731
7.3205
7.3181
7.2875
7.2093
7.2057
7.1881
6.4170
6.3773
6.3176
6.3015
6.2852
6.2620
4.5012
4.4998
4.4851
4.4838
4.4561
N2
N
O
1q
2.10
5.08
2.94
1.00
0.99
2.00
0.93
f1 (ppm)

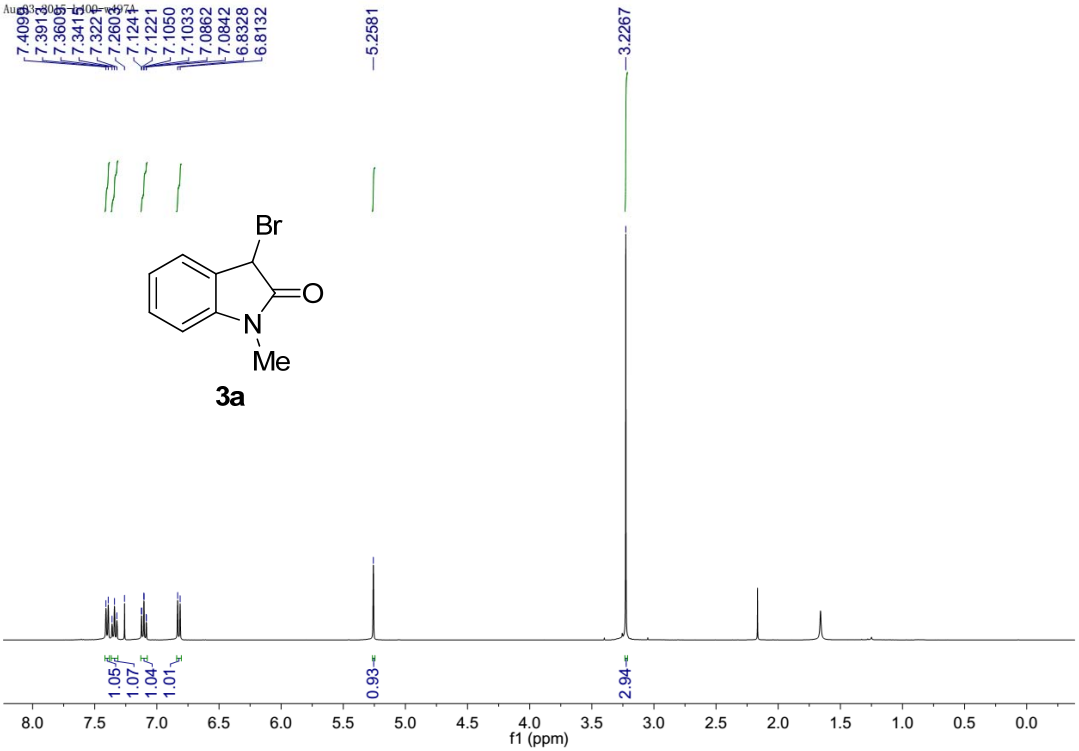

165.61
141.59
136.73
133.28
129.80
128.59
128.54
128.27
127.74
126.53
124.71
77.48
77.16
76.84
51.70
47.51
N2
N
O
1q
f1 (ppm)

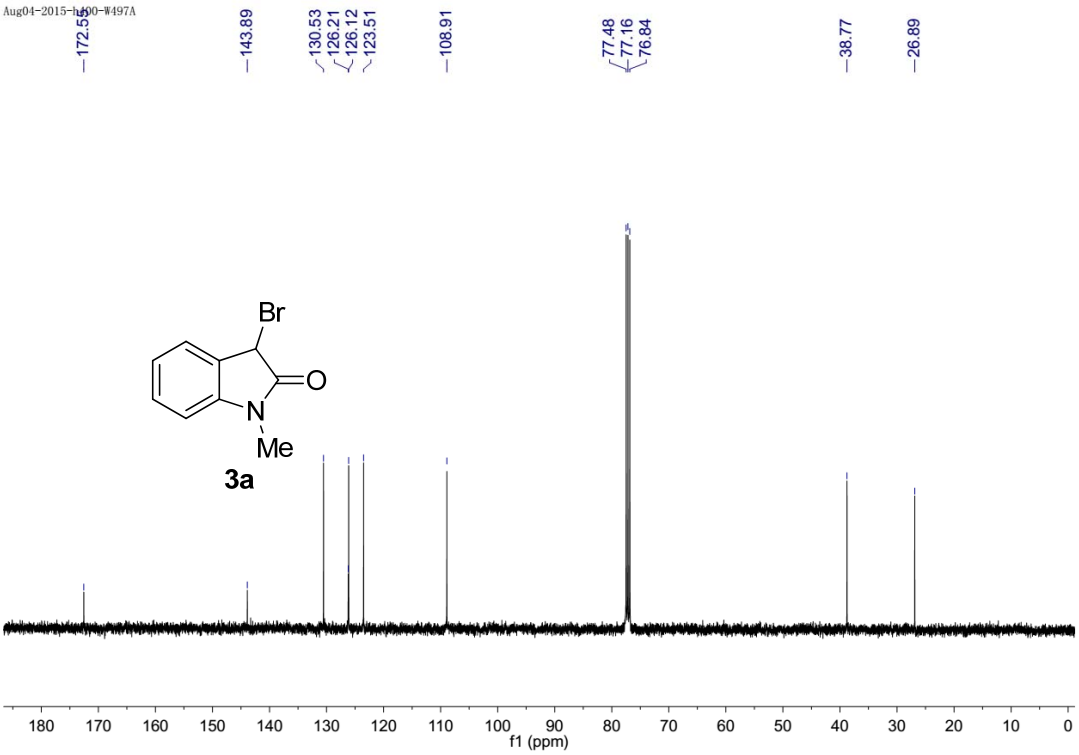

7.9298
7.9085
7.4340
7.4300
7.4188
7.4152
7.3976
7.3794
7.3485
7.3275
7.2600
7.2283
7.2247
7.2114
7.2073
3.2641
2.4365
N2
O
S
O
O
N
Me
1s
1.98
2.97
2.01
1.97
3.00
2.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

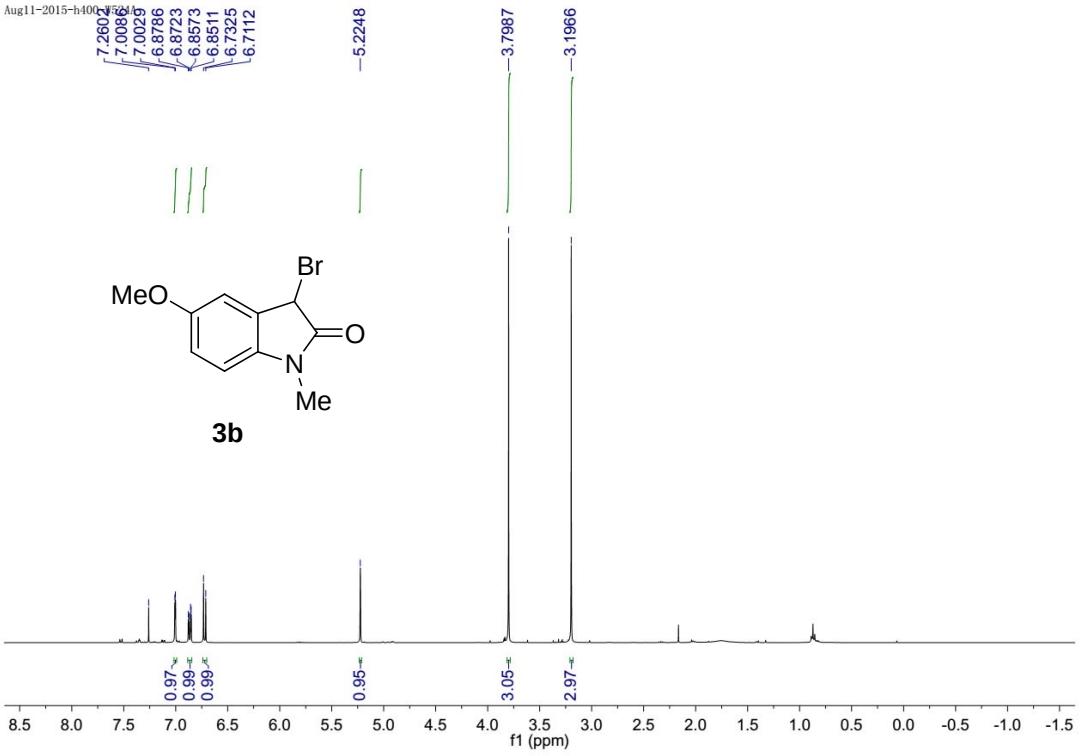

Sep02-2015-c400-w583Adown
158.28
144.85
142.10
139.48
130.49
129.64
128.81
128.36
126.88
77.48
77.16
76.84
38.27
21.81
N2
O
S
O
O
N
Me
1s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.3516
7.3319
7.3124
7.2943
7.2767
7.2638
7.2605
7.2547
7.2430
7.2278
7.2093
7.1905
7.1776
7.1589
7.1296
7.1120
7.0944
3.4154
N2
N
O
1t
5.08
4.94
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

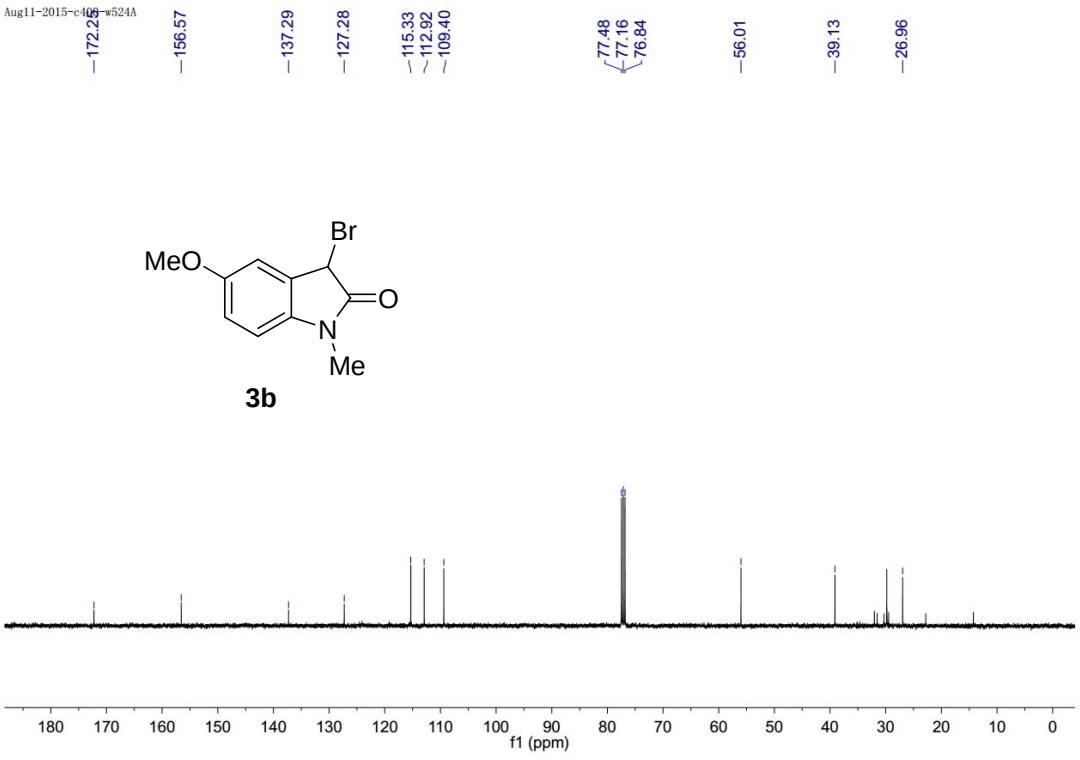

165.23
143.99
129.78
128.74
127.22
126.72
125.64
125.54
124.71
77.48
77.16
76.84
38.57
N2
N
O
1t
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.4099
7.3913
7.3609
7.3413
7.3221
7.2603
7.1241
7.1221
7.1050
7.1033
7.0862
7.0842
6.8328
6.8132
5.2581
3.2267
Br
O
N
Me
3a
1.05
1.07
1.04
1.01
0.93
2.94
f1 (ppm)

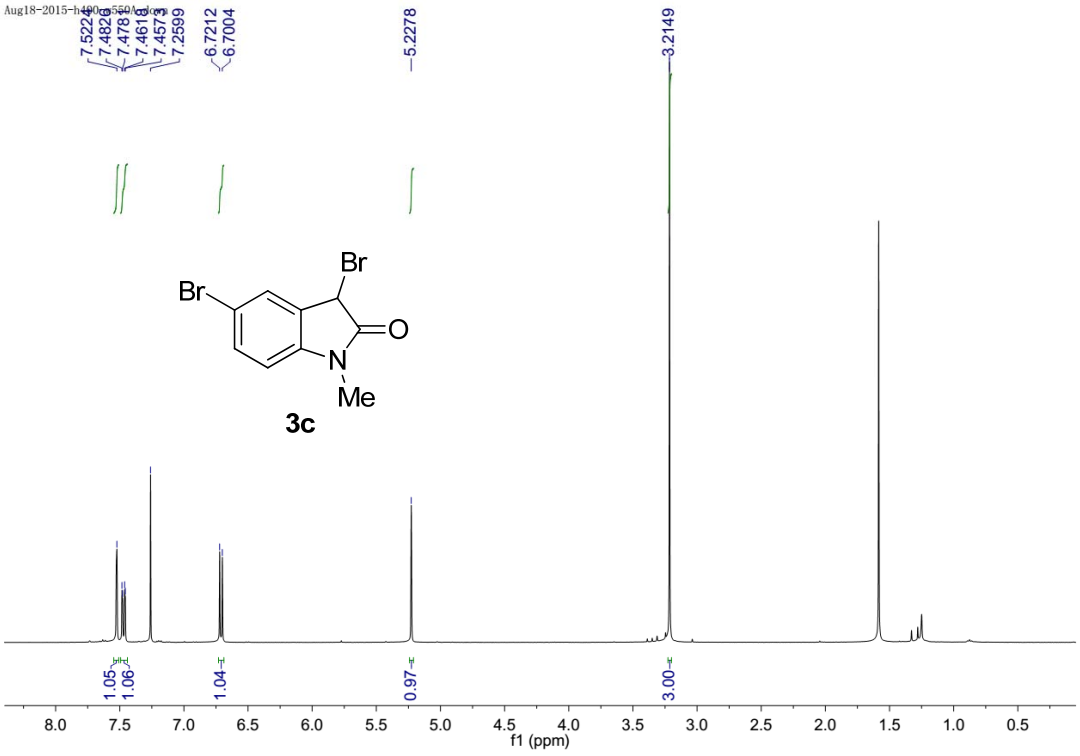

172.55
143.89
130.53
126.21
126.12
123.51
108.91
77.48
77.16
76.84
38.77
26.89
Br
O
N
Me
3a
f1 (ppm)

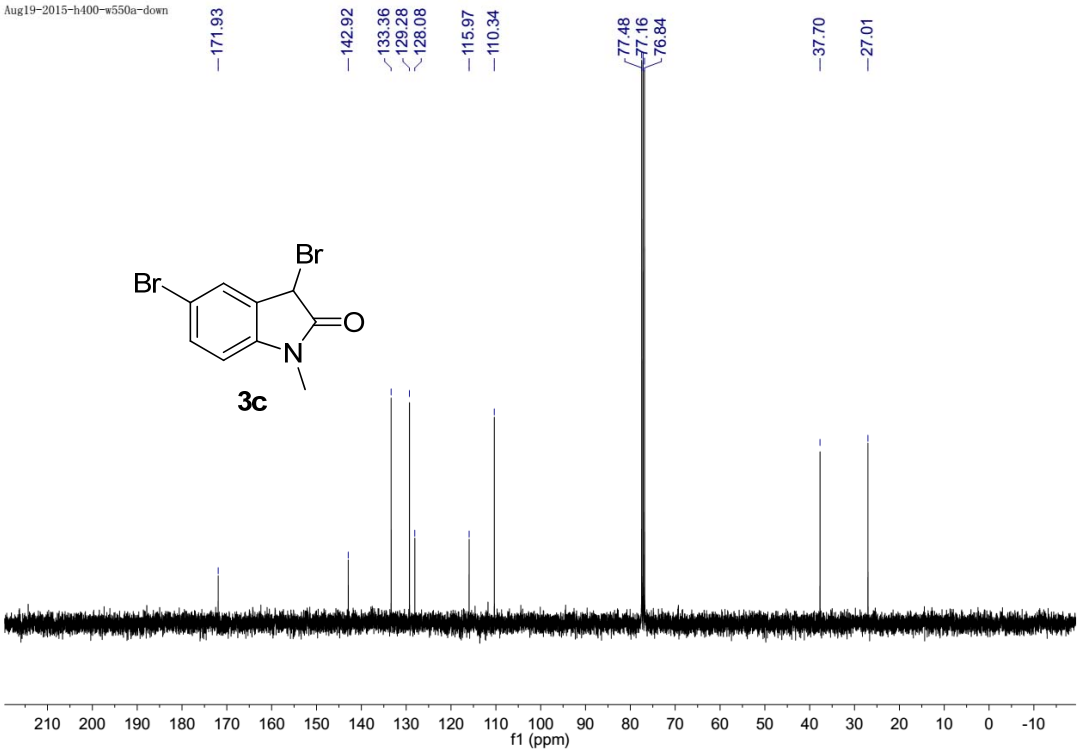

7.2602
7.0086
7.0029
6.8786
6.8723
6.8573
6.8511
6.7325
6.7112
5.2248
3.7987
3.1966
Br
MeO
O
N
Me
0.97
0.99
0.99
0.95
3.05
2.97
f1 (ppm)

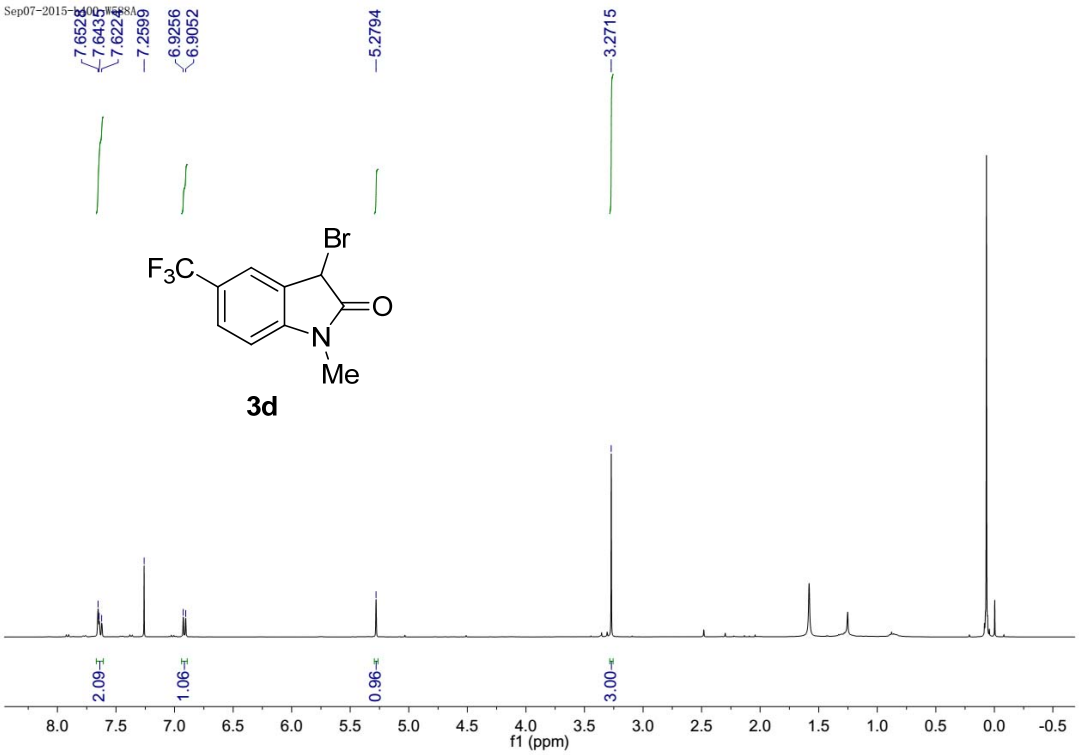
3b


172.26
156.57
137.29
127.28
115.33
112.92
109.40
77.48
77.16
76.84
56.01
39.13
26.96
Br
MeO
O
N
Me
f1 (ppm)

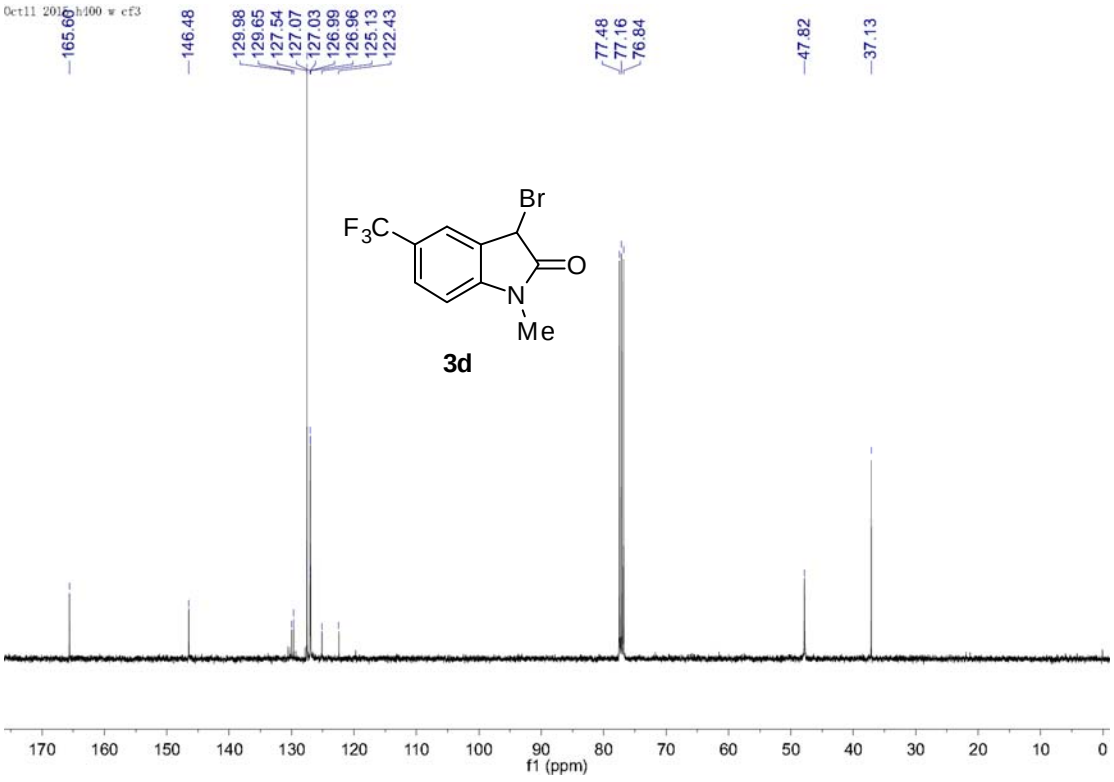
3b


7.5222
7.4826
7.4781
7.4616
7.4573
7.2599
6.7212
6.7004
5.2278
3.2149
Br
Br
O
N
Me
3c
1.05
1.06
1.04
0.97
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

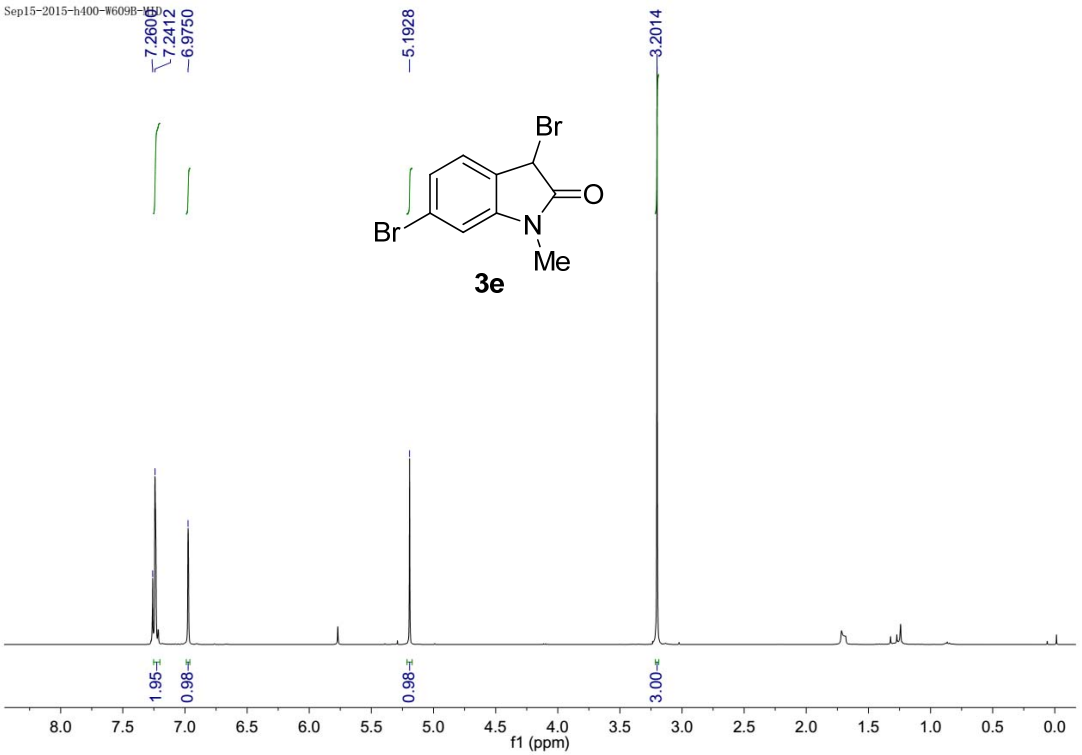

Aug19-2015-h400-w550a-down
171.93
142.92
133.36
129.28
128.08
115.97
110.34
77.48
77.16
76.84
37.70
27.01
Br
Br
O
N
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.6528
7.6435
7.6224
7.2599
6.9256
6.9052
5.2794
3.2715
Br
F3C
O
N
Me
2.09
1.06
0.96
3.00
f1 (ppm)

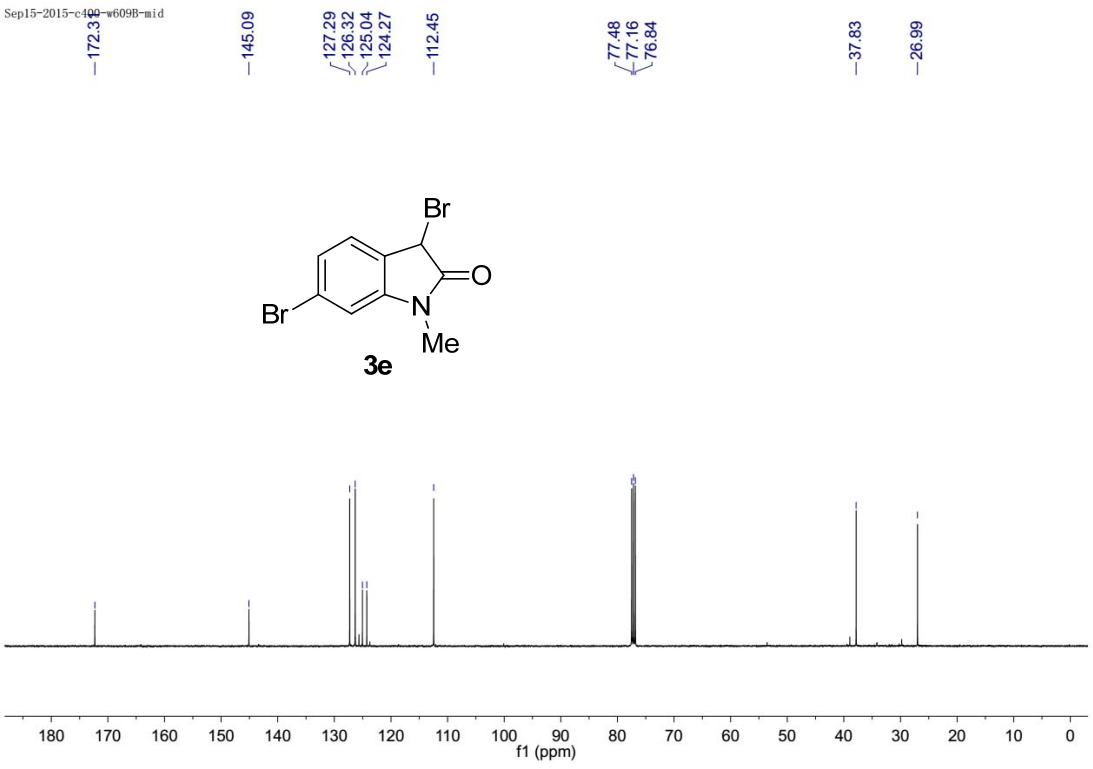
3d


165.60
146.48
129.98
129.65
127.54
127.07
127.03
126.99
126.96
125.13
122.43
77.48
77.16
76.84
47.82
37.13
Br
F3C
O
N
Me
f1 (ppm)

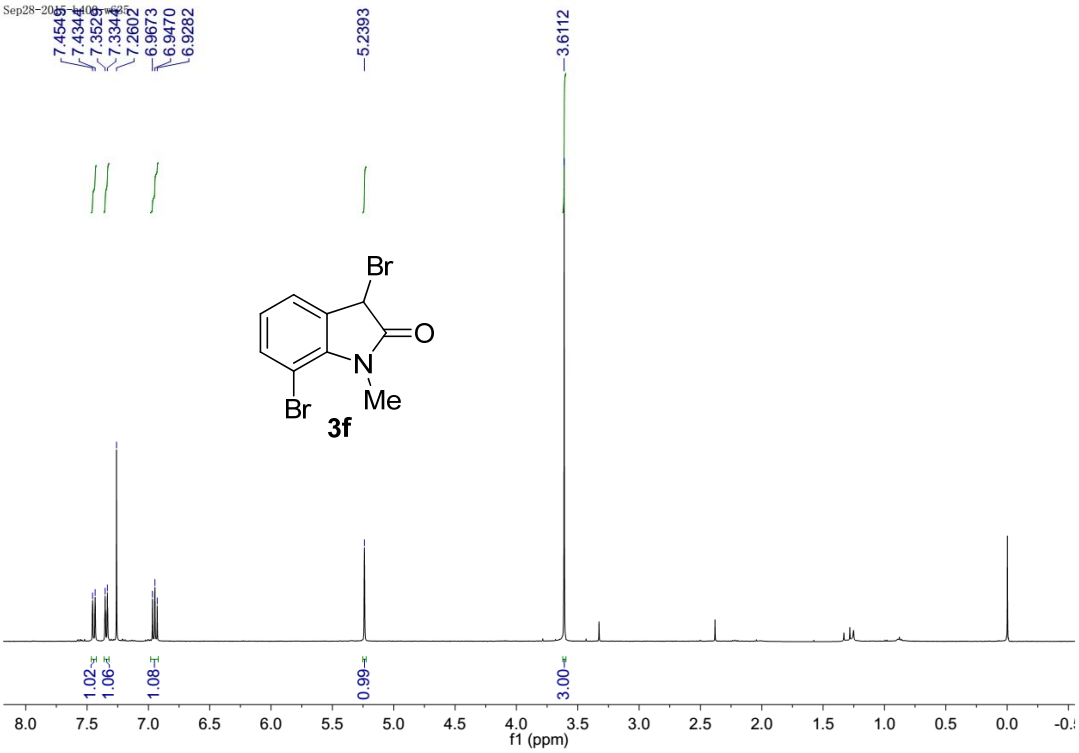
3d

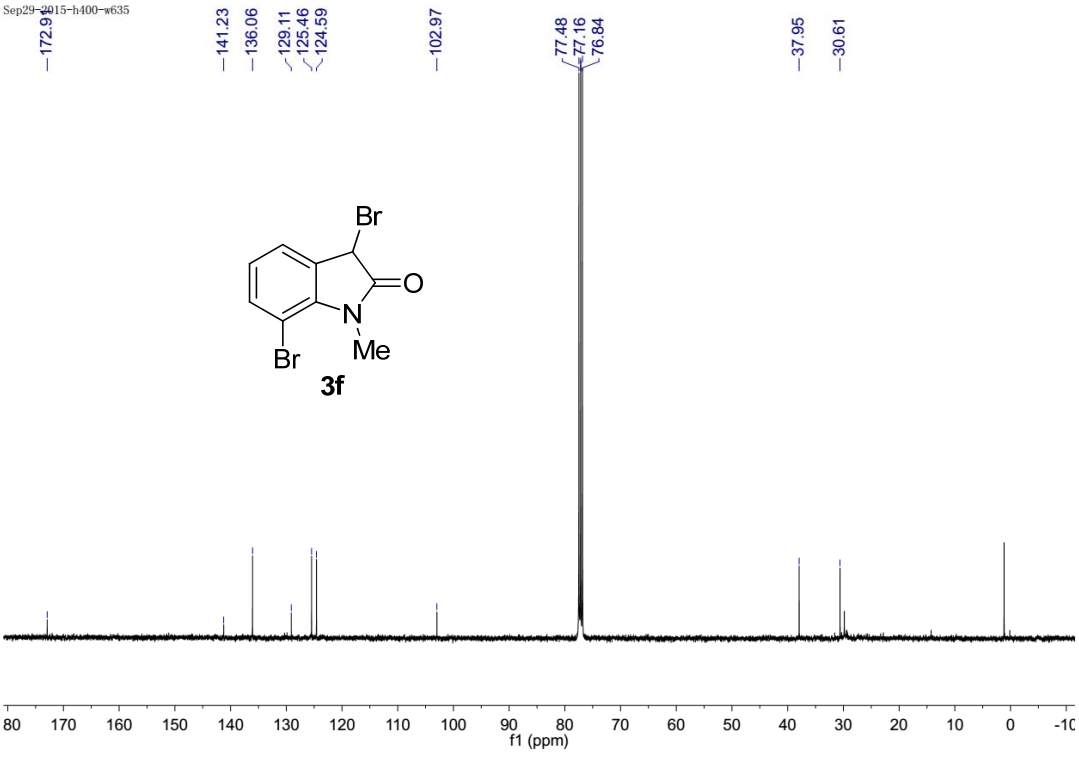

7.2606
7.2412
6.9750
5.1928
3.2014
Br
Br
O
N
Me
1.95
0.98
0.98
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

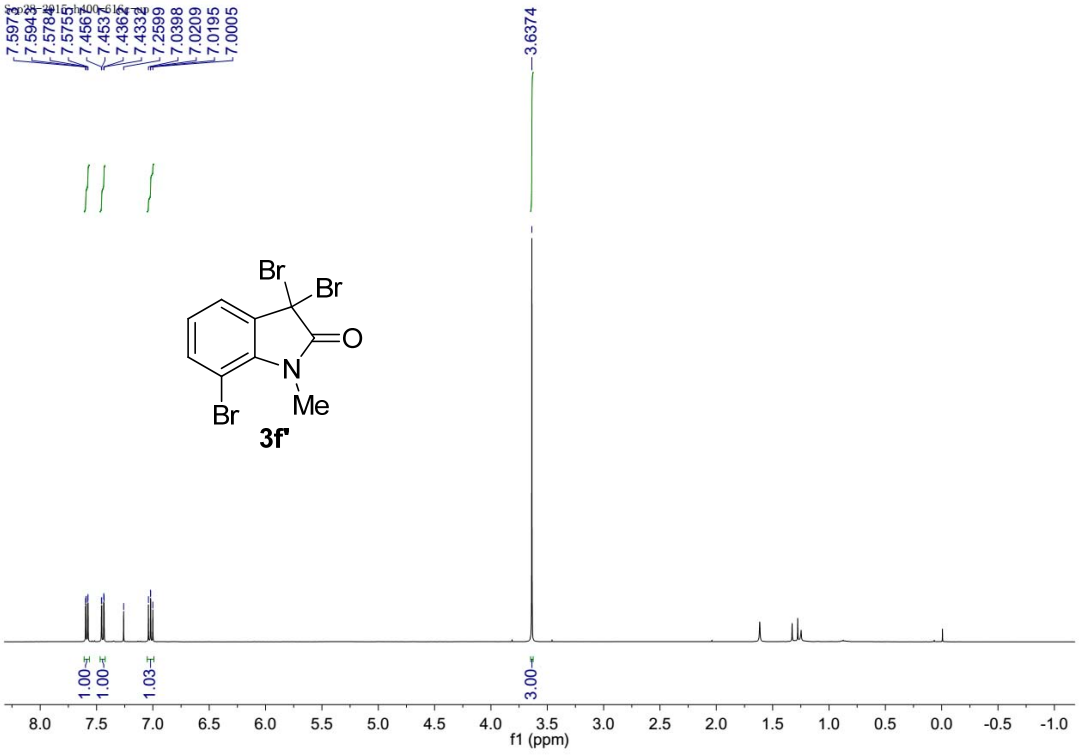
3e

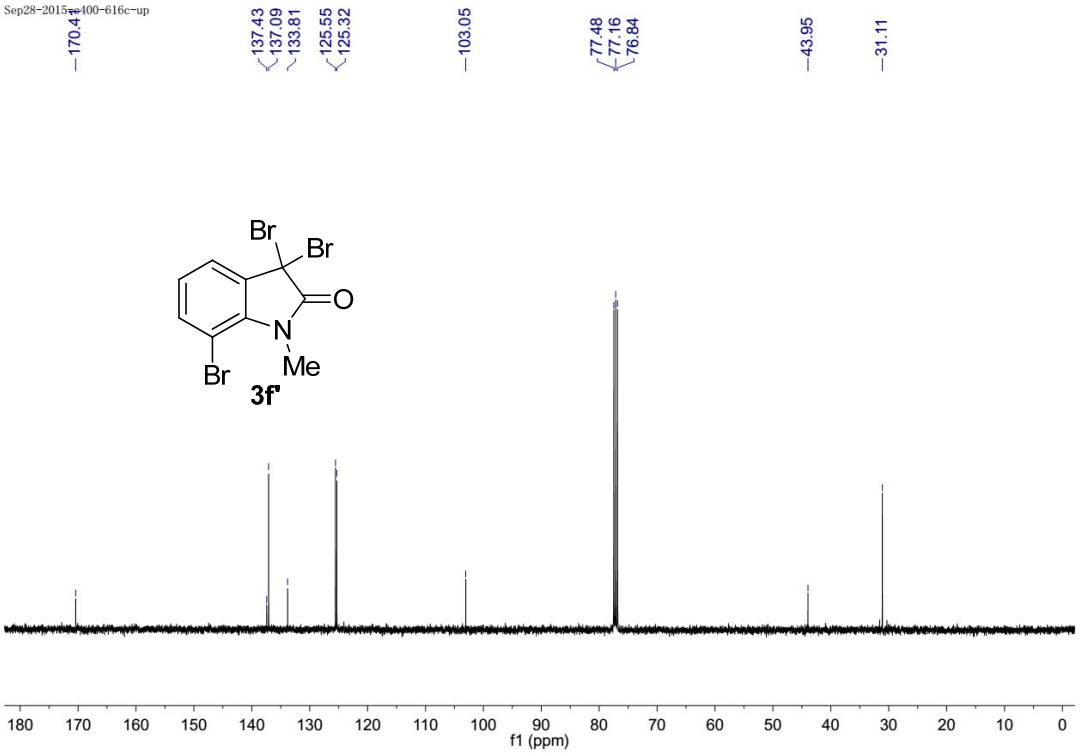

172.31
145.09
127.29
126.32
125.04
124.27
112.45
77.48
77.16
76.84
37.83
26.99
Br
Br
O
N
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

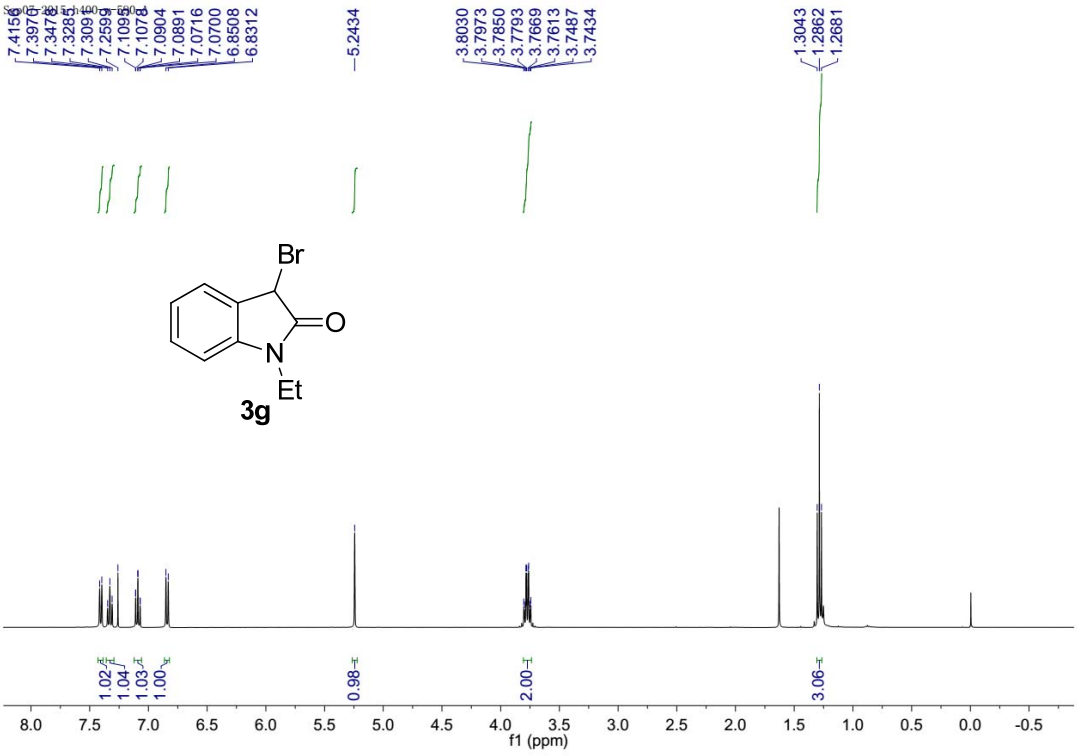
3e

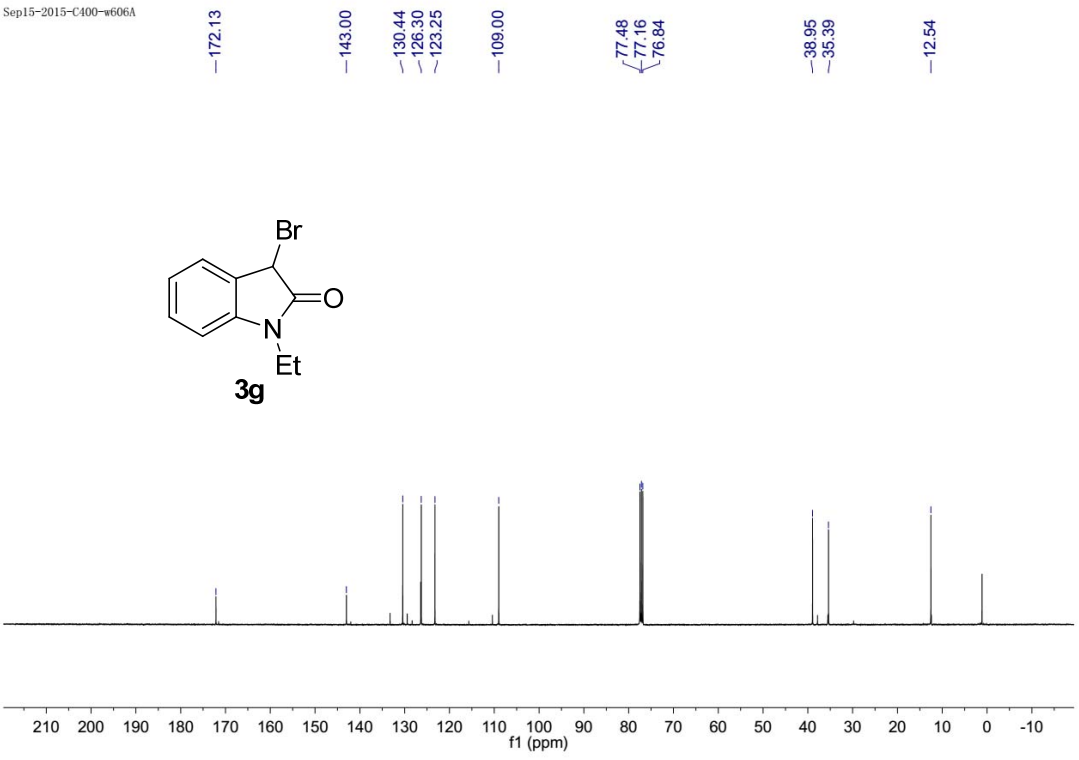

7.4548
7.4344
7.3525
7.3344
7.2602
6.9673
6.9470
6.9282
5.2393
3.6112
Br
O
N
Me
Br
3f
1.02
1.06
1.08
0.99
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

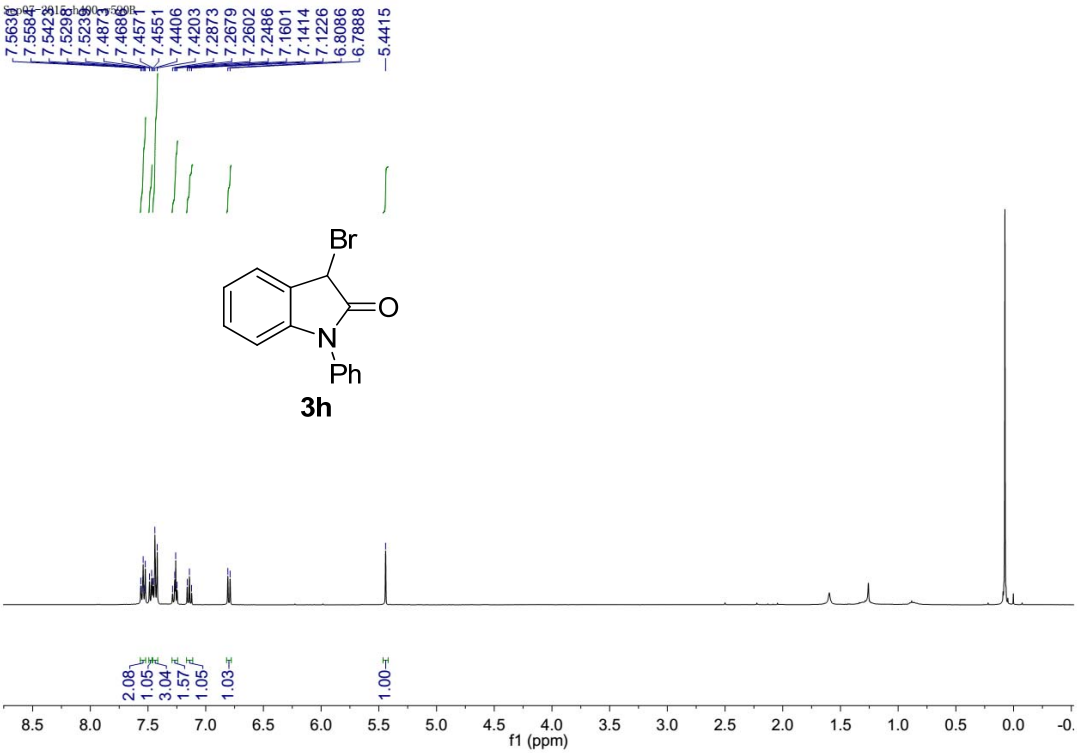

172.91
141.23
136.06
129.11
125.46
124.59
102.97
77.48
77.16
76.84
37.95
30.61
Br
O
N
Me
Br
3f
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

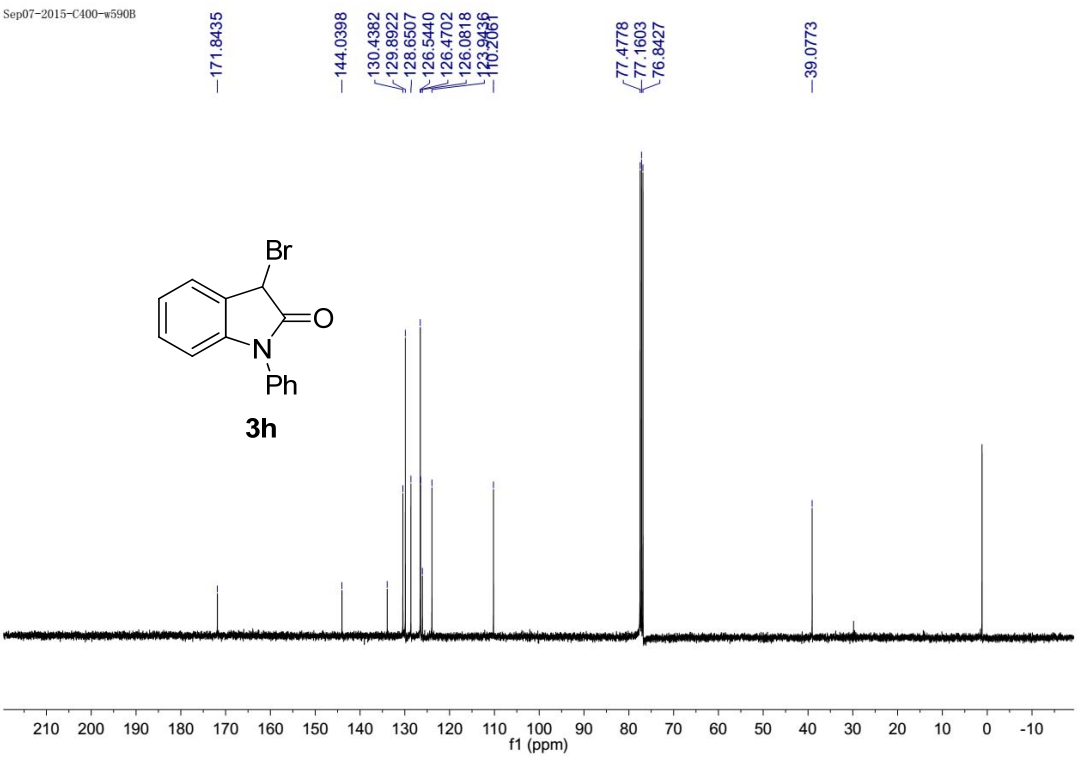

7.5974
7.5944
7.5784
7.5755
7.4567
7.4537
7.4364
7.4332
7.2599
7.0398
7.0209
7.0195
7.0005
3.6374
Br
Br
O
N
Me
Br
3f'
1.00
1.00
1.03
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

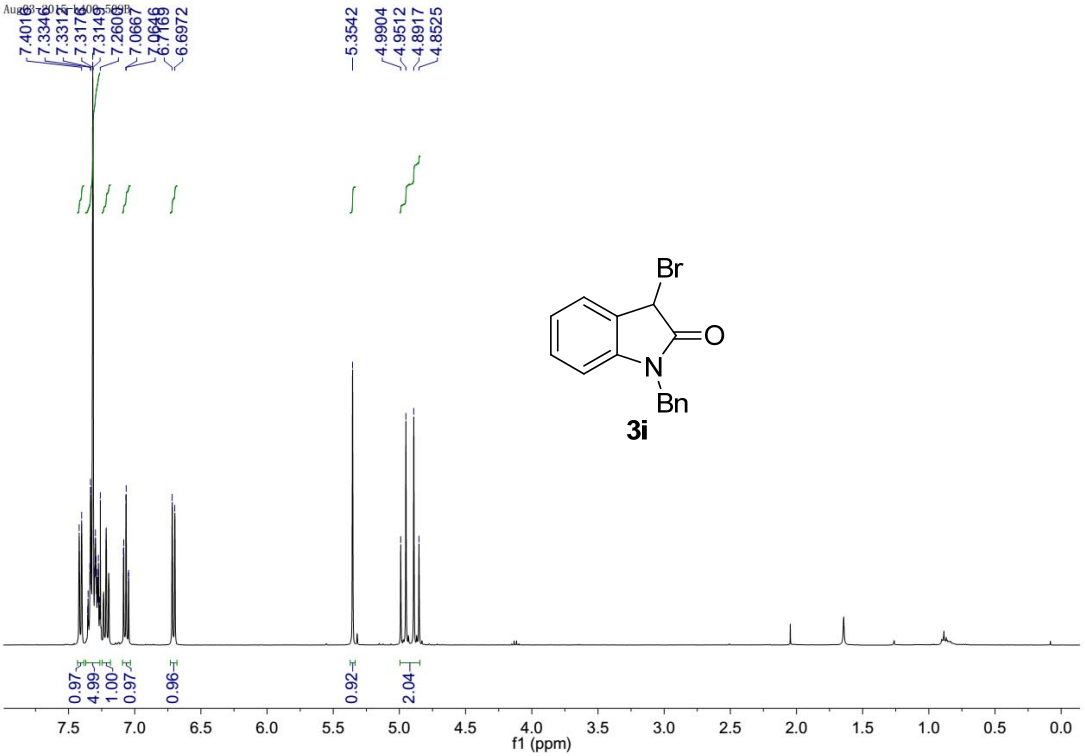

Sep28-2015-c400-616c-up
170.41
137.43
137.09
133.81
125.55
125.32
103.05
77.48
77.16
76.84
43.95
31.11
Br
Br
O
N
Me
Br
3f'
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

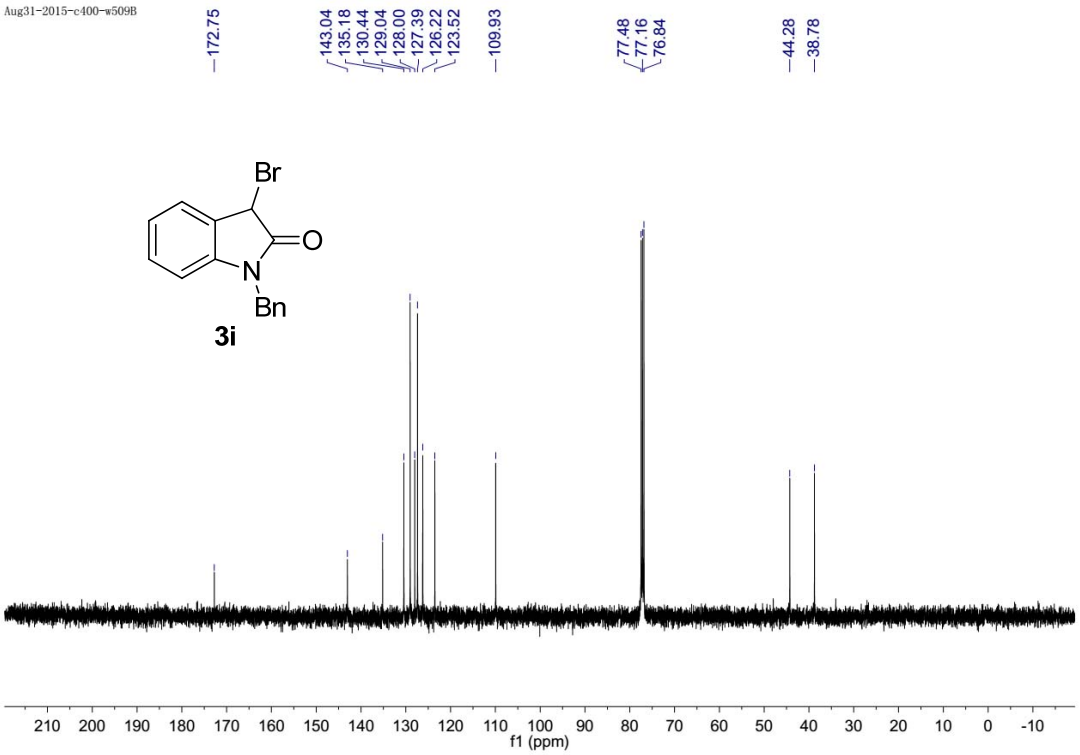

7.4156
7.3970
7.3478
7.3285
7.3091
7.2599
7.1095
7.1078
7.0904
7.0891
7.0716
7.0700
6.8508
6.8312
5.2434
3.8030
3.7973
3.7850
3.7793
3.7669
3.7613
3.7487
3.7434
1.3043
1.2862
1.2681
Br
O
N
Et
3g
1.02
1.04
1.03
1.00
0.98
2.00
3.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

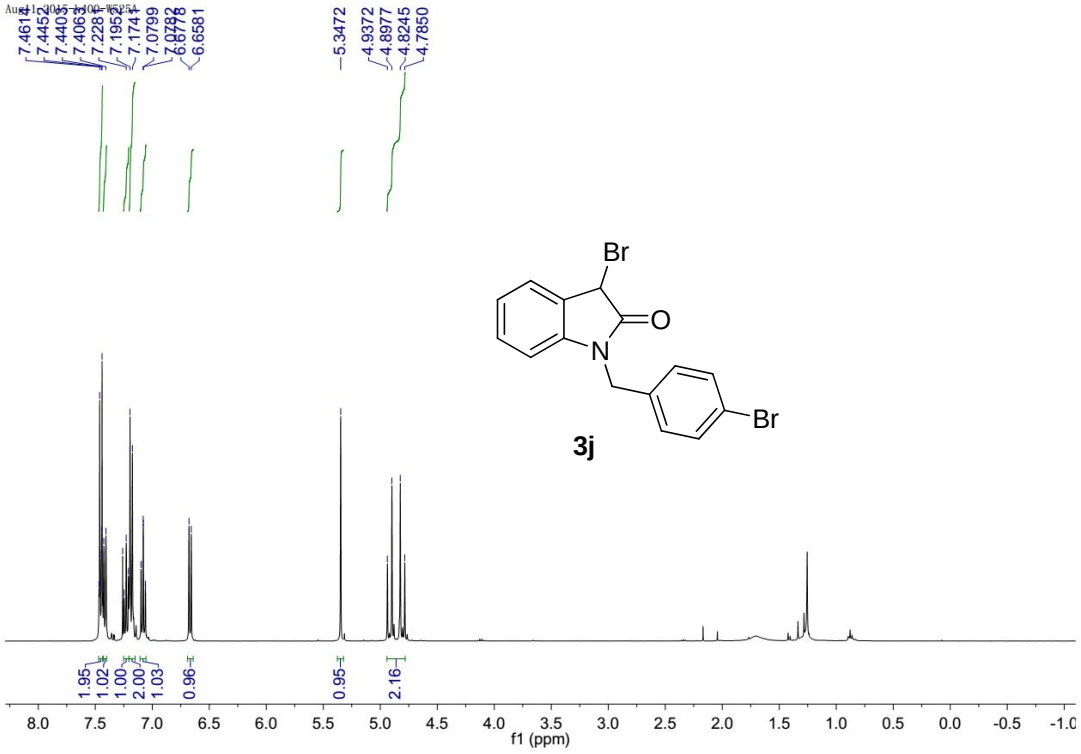

Sep15-2015-C400-w606A
172.13
143.00
130.44
126.30
123.25
109.00
77.48
77.16
76.84
38.95
35.39
12.54
Br
O
N
Et
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

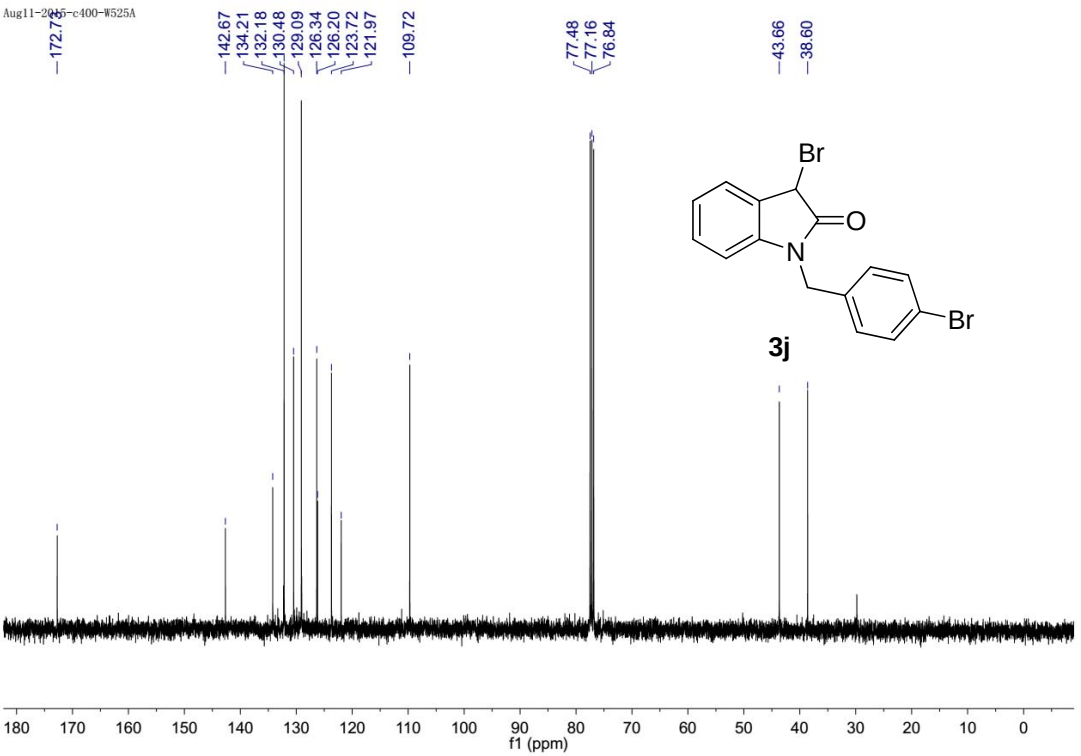

7.5630
7.5584
7.5423
7.5296
7.5239
7.4873
7.4688
7.4571
7.4551
7.4406
7.4203
7.2873
7.2679
7.2602
7.2486
7.1601
7.1414
7.1226
6.8086
6.7888
5.4415
Br
O
N
Ph
3h
2.08
1.05
3.04
1.57
1.05
1.03
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

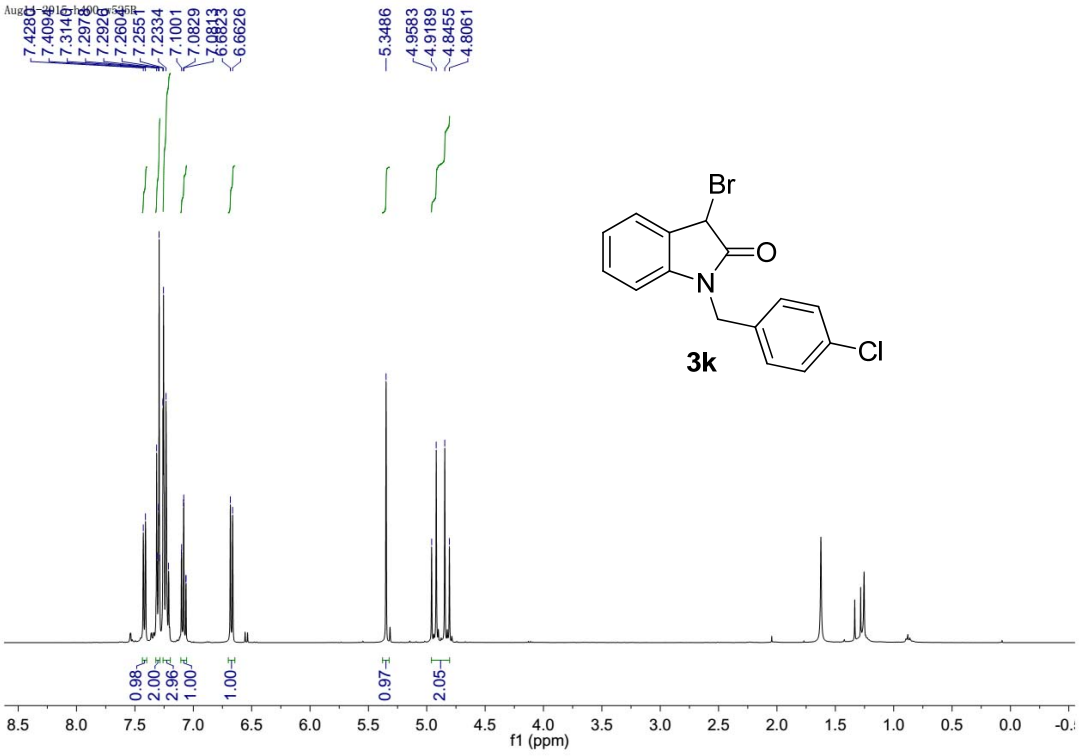

Sep07-2015-C400-w590B
171.8435
144.0398
130.4382
129.8922
128.6507
126.5440
126.4702
126.0818
123.9436
110.2061
77.4778
77.1603
76.8427
39.0773
Br
O
N
Ph
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

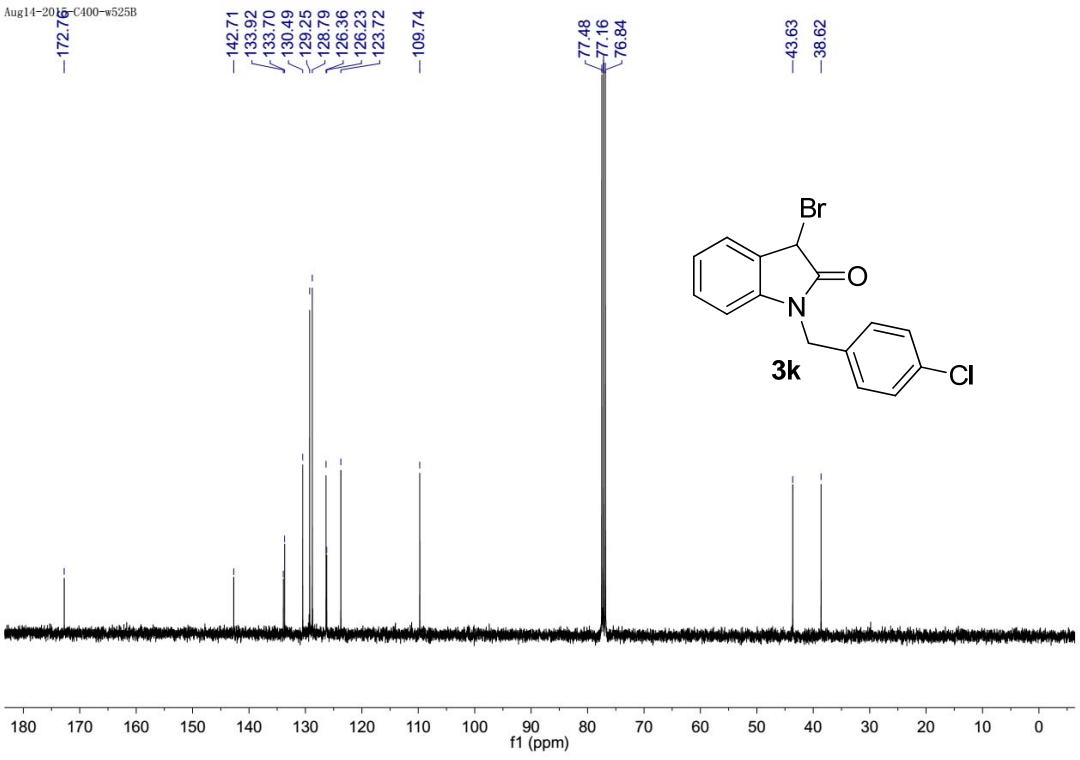

7.4016
7.3346
7.3312
7.3176
7.3149
7.2607
7.0667
7.0648
7.0468
6.6972
5.3542
4.9904
4.9512
4.8917
4.8525
Br
O
N
Bn
3i
0.97
4.99
1.00
0.97
0.96
0.92
2.04
f1 (ppm)

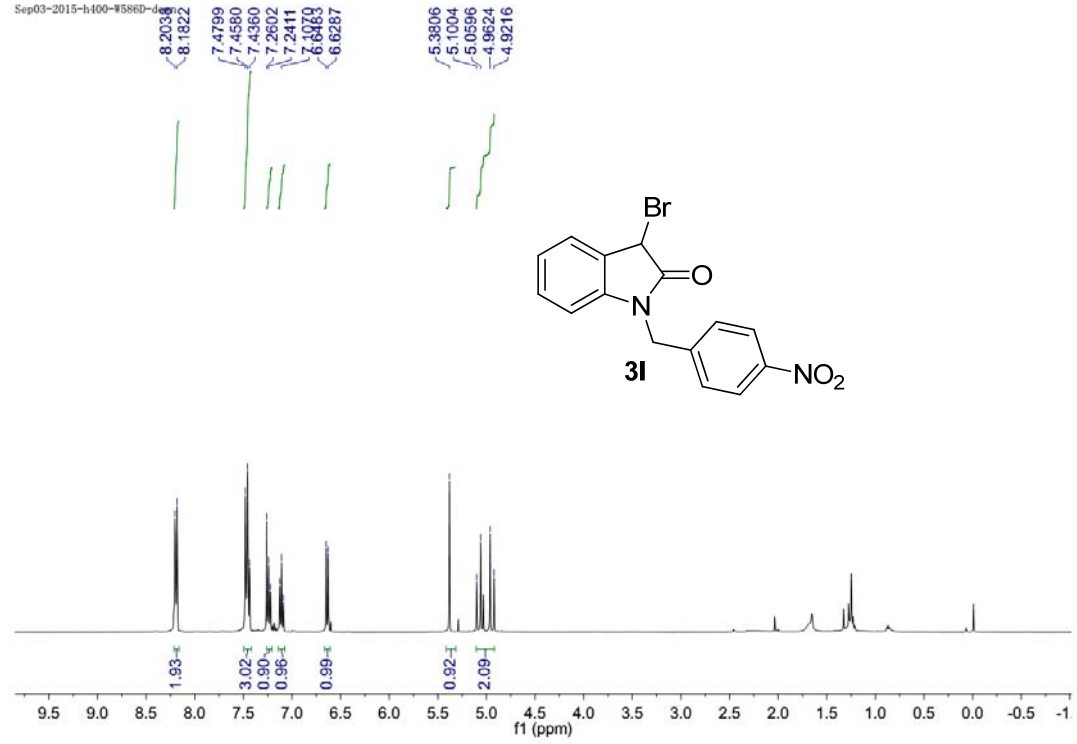

Aug31-2015-c400-w509B
172.75
143.04
135.18
130.44
129.04
128.00
127.39
126.22
123.52
109.93
77.48
77.16
76.84
44.28
38.78
Br
O
N
Bn
3i
f1 (ppm)

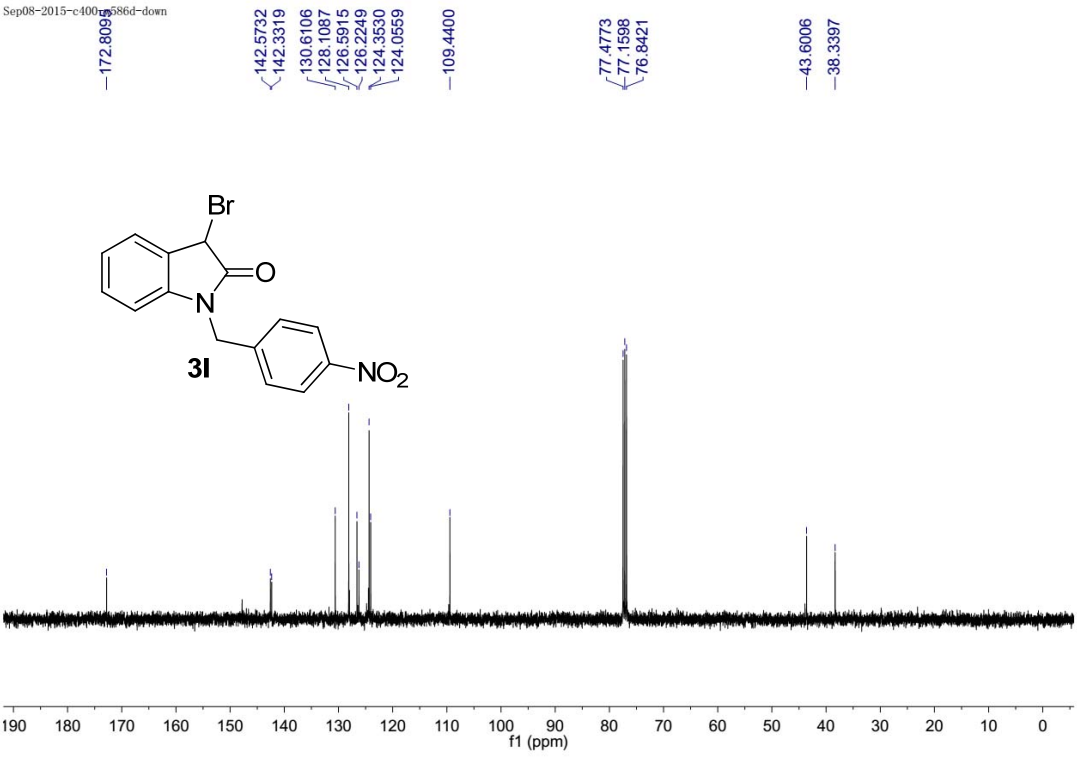

7.4615
7.4452
7.4403
7.4063
7.2281
7.1951
7.1741
7.0799
6.8778
6.6581
5.3472
4.9372
4.8977
4.8245
4.7850
Br
O
N
Br
3j
1.95
1.02
1.00
2.00
1.03
0.96
0.95
2.16
f1 (ppm)

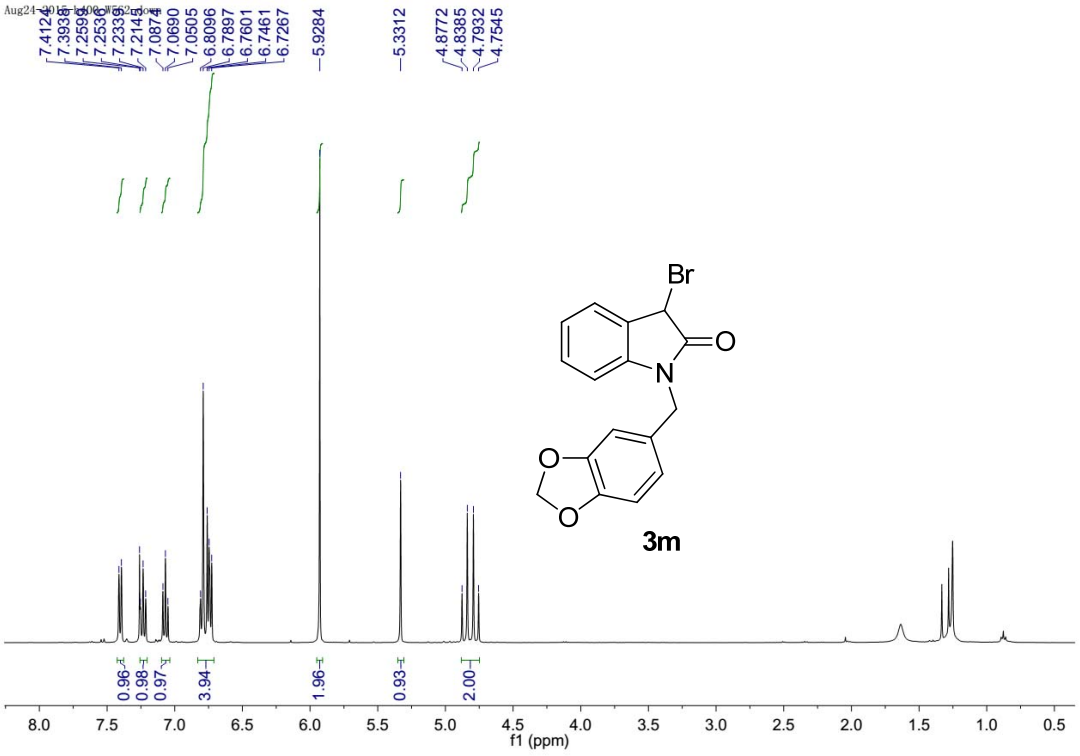

172.75
142.67
134.21
132.18
130.48
129.09
126.34
126.20
123.72
121.97
109.72
77.48
77.16
76.84
43.66
38.60
Br
O
N
Br
3j
f1 (ppm)

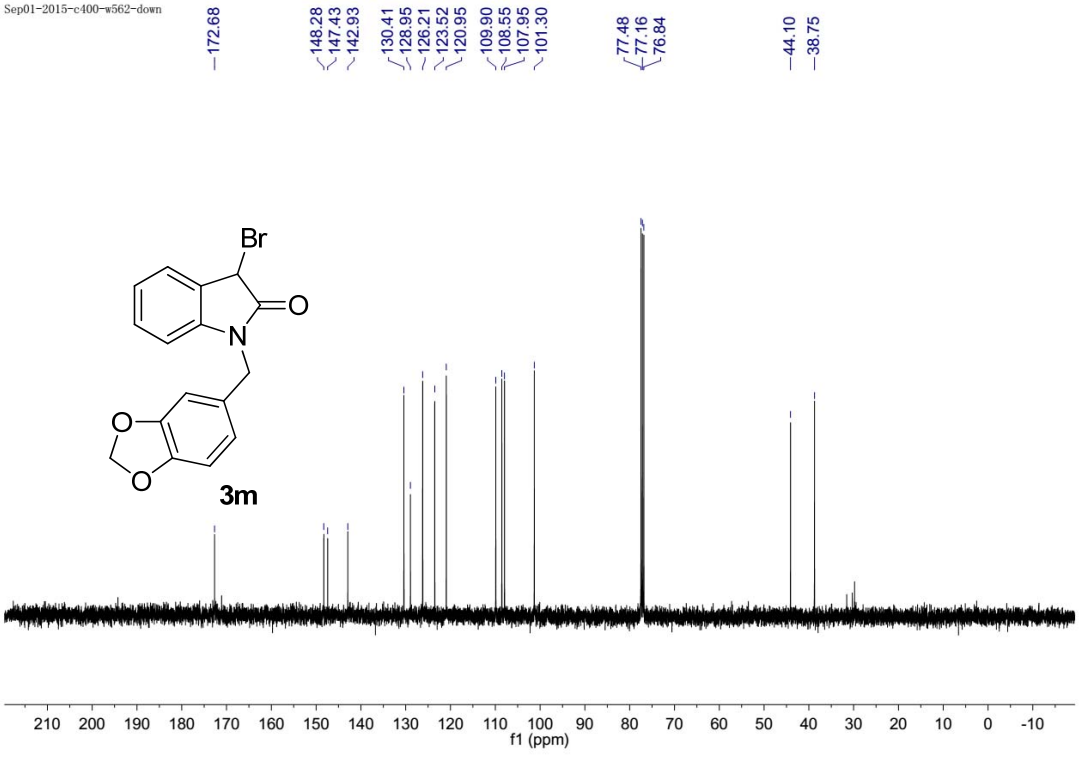

7.4280
7.4094
7.3147
7.2976
7.2926
7.2604
7.2551
7.2334
7.1001
7.0829
6.8823
6.6626
5.3486
4.9583
4.9189
4.8455
4.8061
0.98
2.00
2.96
1.00
1.00
0.97
2.05
f1 (ppm)
Br
O
N
Cl
3k

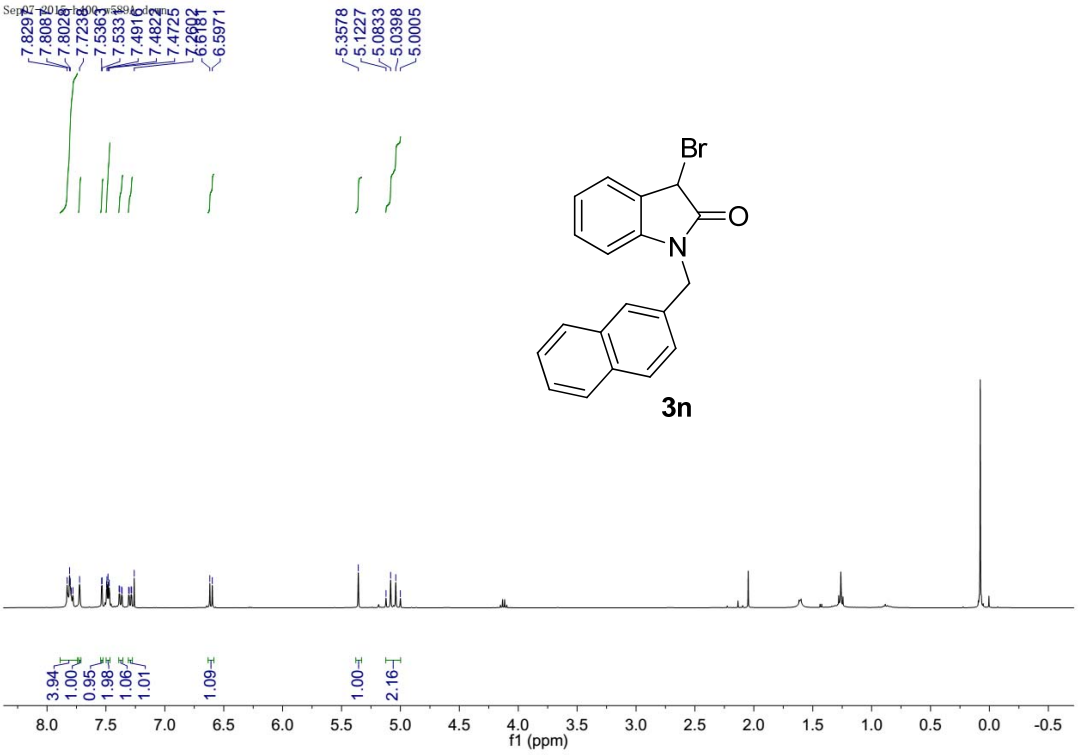

172.76
142.71
133.92
133.70
130.49
129.25
128.79
126.36
126.23
123.72
109.74
77.48
77.16
76.84
43.63
38.62
f1 (ppm)
Br
O
N
Cl
3k

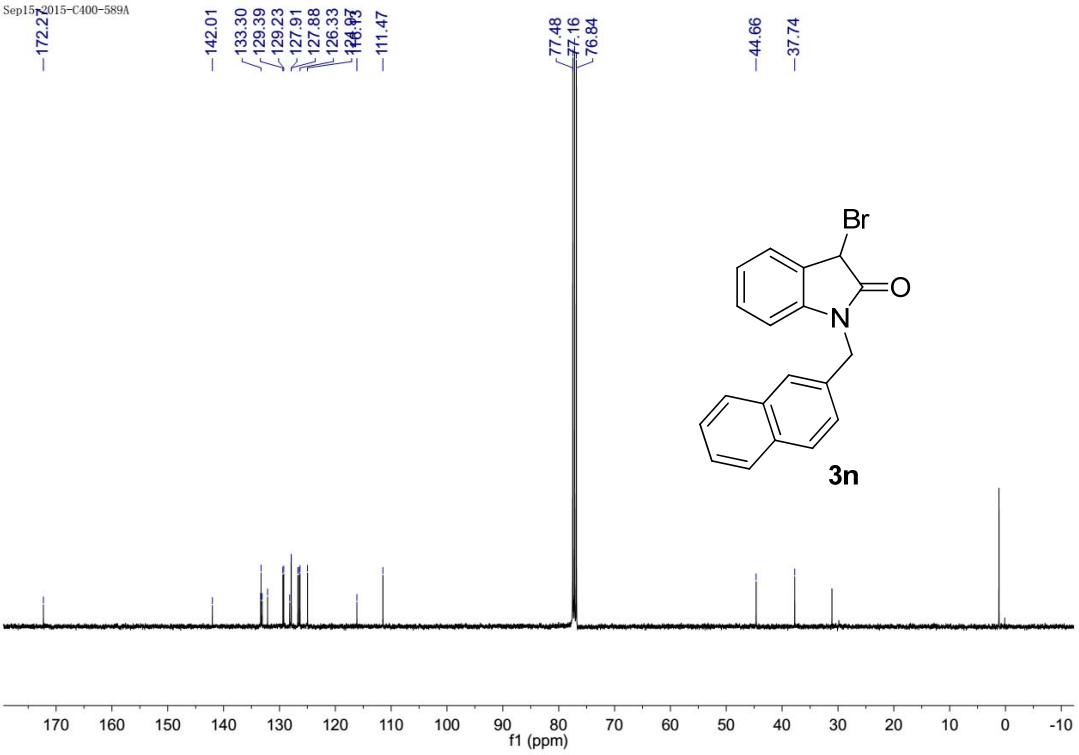

8.2036
8.1822
7.4799
7.4580
7.4360
7.2602
7.2411
6.6463
6.6267
5.3806
5.1004
5.0596
4.9624
4.9216
Br
O
N
NO2
3l
1.93
3.02
0.90
0.96
0.99
0.92
2.09
f1 (ppm)

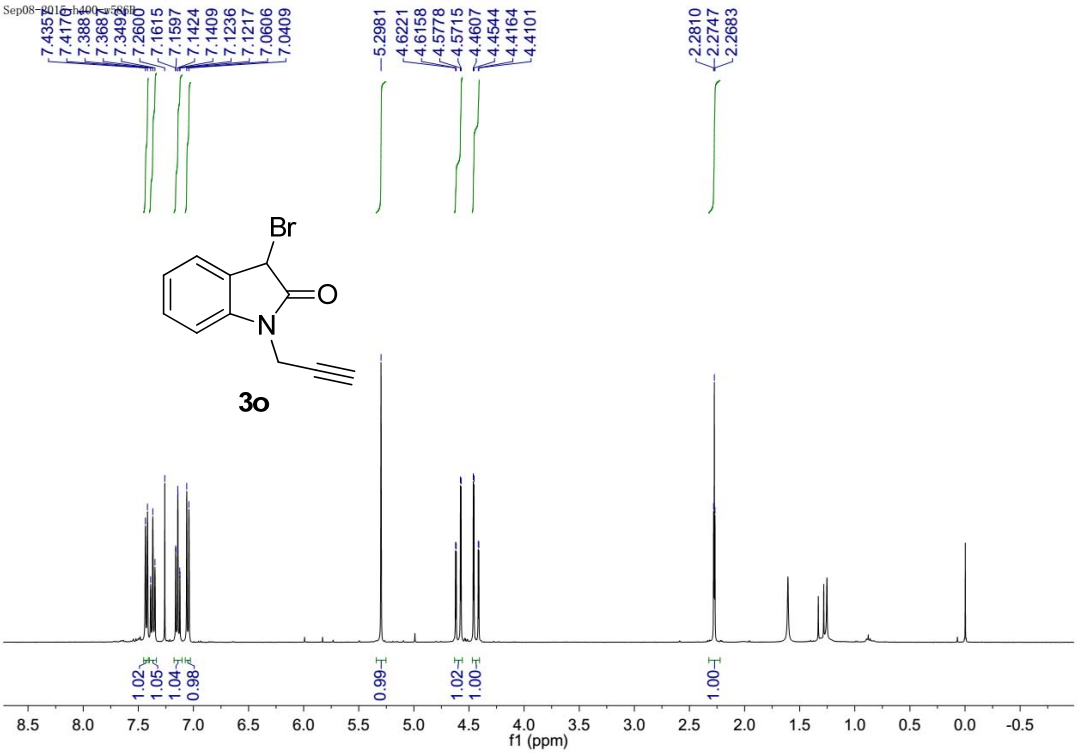

172.8095
142.5732
142.3319
130.6106
128.1087
126.5915
126.2249
124.3530
124.0559
109.4400
77.4773
77.1598
76.8421
43.6006
38.3397
Br
O
N
NO2
3l
f1 (ppm)

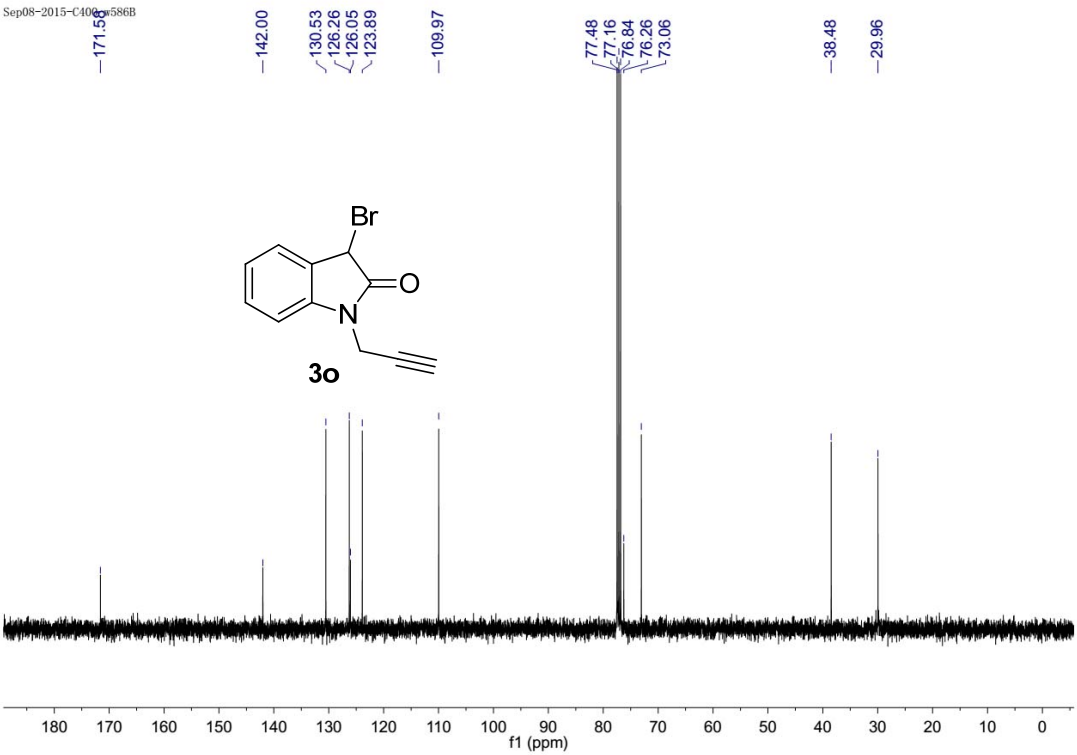

7.4124
7.3938
7.2599
7.2538
7.2339
7.2145
7.0874
7.0690
7.0505
6.8096
6.7897
6.7601
6.7461
6.7267
5.9284
5.3312
4.8772
4.8385
4.7932
4.7545
Br
O
N
O
O
3m
0.96
0.98
0.97
3.94
1.96
0.93
2.00
f1 (ppm)

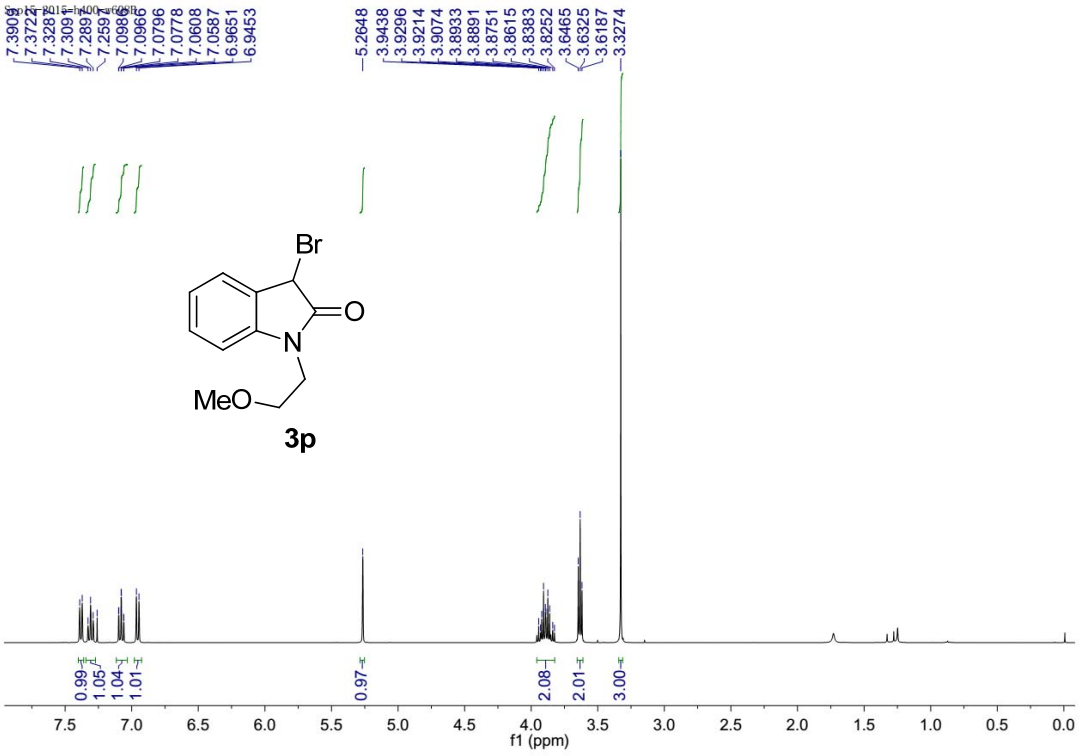

Sep01-2015-c400-w562-down
172.68
148.28
147.43
142.93
130.41
128.95
126.21
123.52
120.95
109.90
108.55
107.95
101.30
77.48
77.16
76.84
44.10
38.75
Br
O
N
O
O
3m
f1 (ppm)

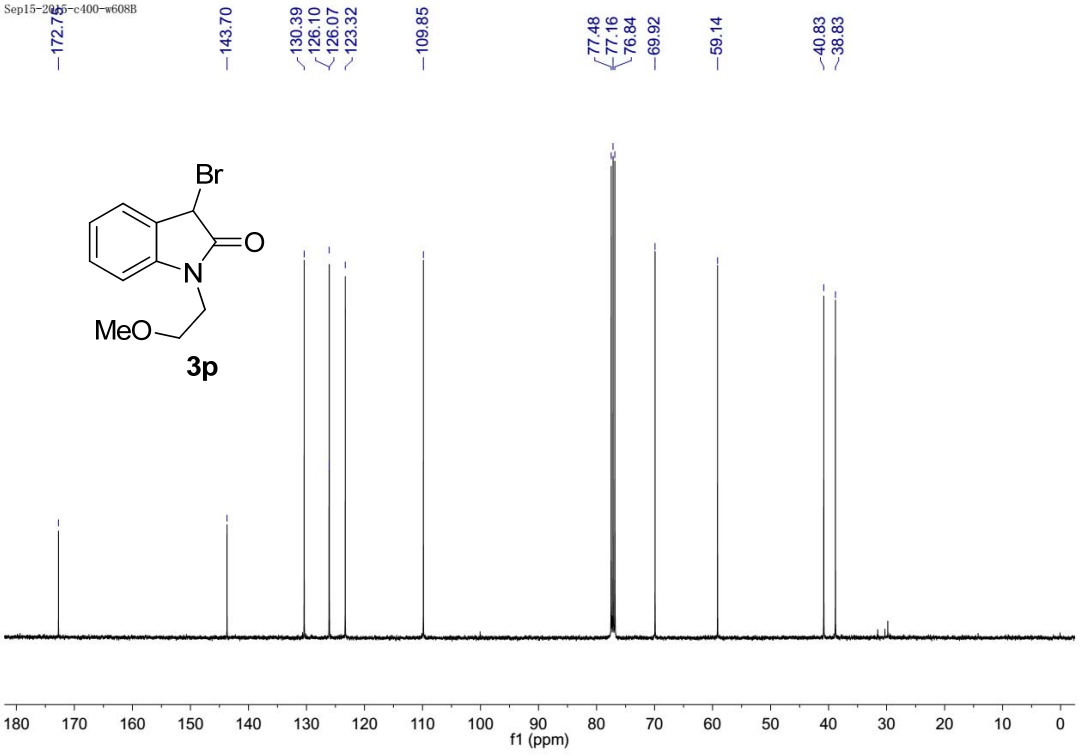

7.8297
7.8081
7.8026
7.7236
7.5361
7.5331
7.4911
7.4822
7.4725
7.2602
6.6181
6.5971
5.3578
5.1227
5.0833
5.0398
5.0005
Br
O
N
3n
3.94
1.00
0.95
1.98
1.06
1.01
1.09
1.00
2.16
f1 (ppm)

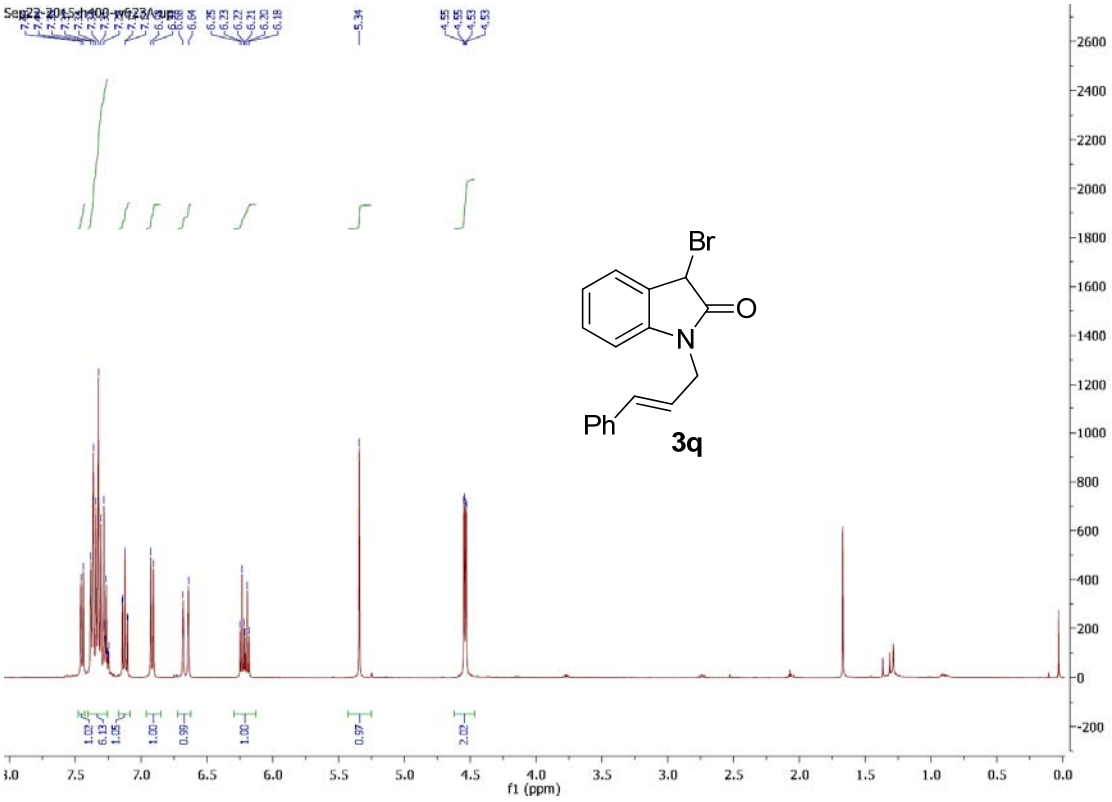

Sep15-2015-C400-589A
172.2
142.01
133.30
129.39
129.23
127.91
127.88
126.33
111.47
77.48
77.16
76.84
44.66
37.74
Br
O
N
3n
f1 (ppm)

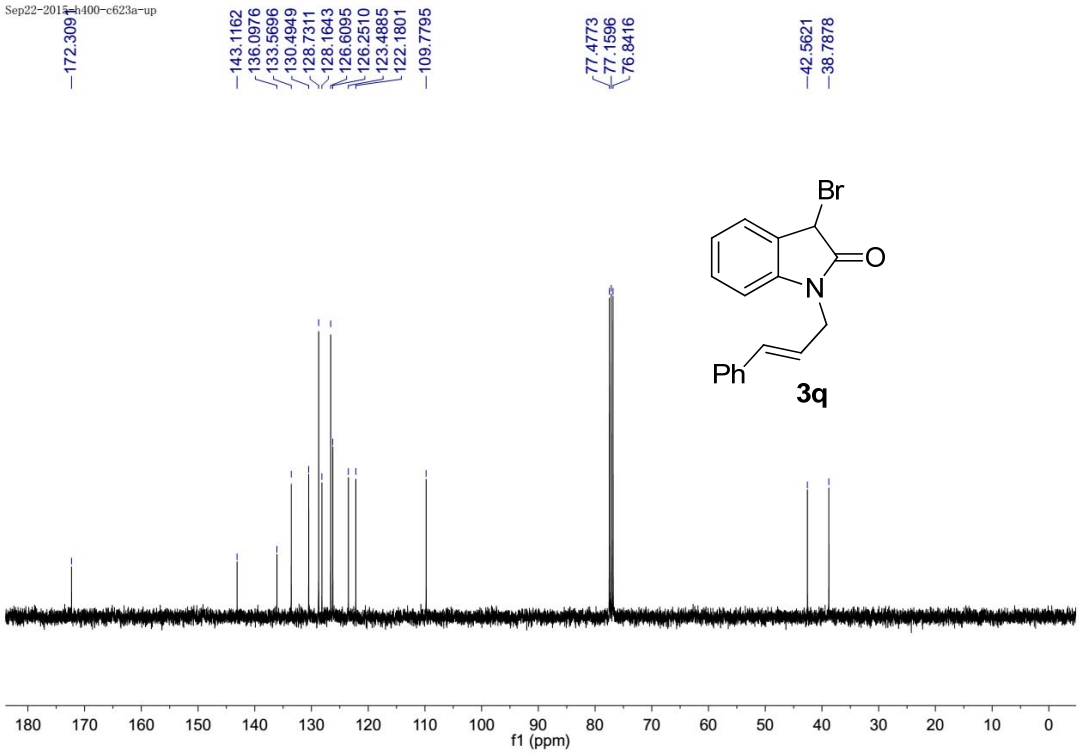

7.4357
7.4176
7.3881
7.3681
7.3491
7.2600
7.1615
7.1597
7.1424
7.1409
7.1236
7.1217
7.0606
7.0409
5.2981
4.6221
4.6158
4.5778
4.5715
4.4607
4.4544
4.4164
4.4101
2.2810
2.2747
2.2683
Br
O
N
3o
1.02
1.05
1.04
0.98
0.99
1.02
1.00
1.00
f1 (ppm)

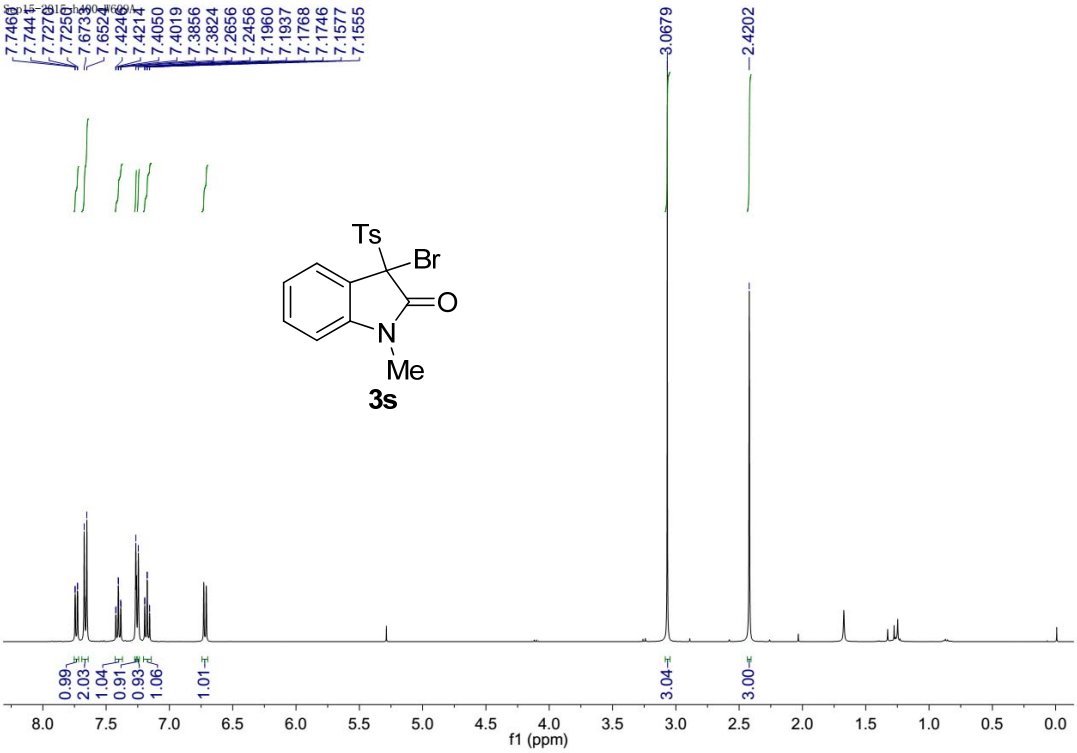

171.58
142.00
130.53
126.26
126.05
123.89
109.97
77.48
77.16
76.84
76.26
73.06
38.48
29.96
Br
O
N
3o
f1 (ppm)

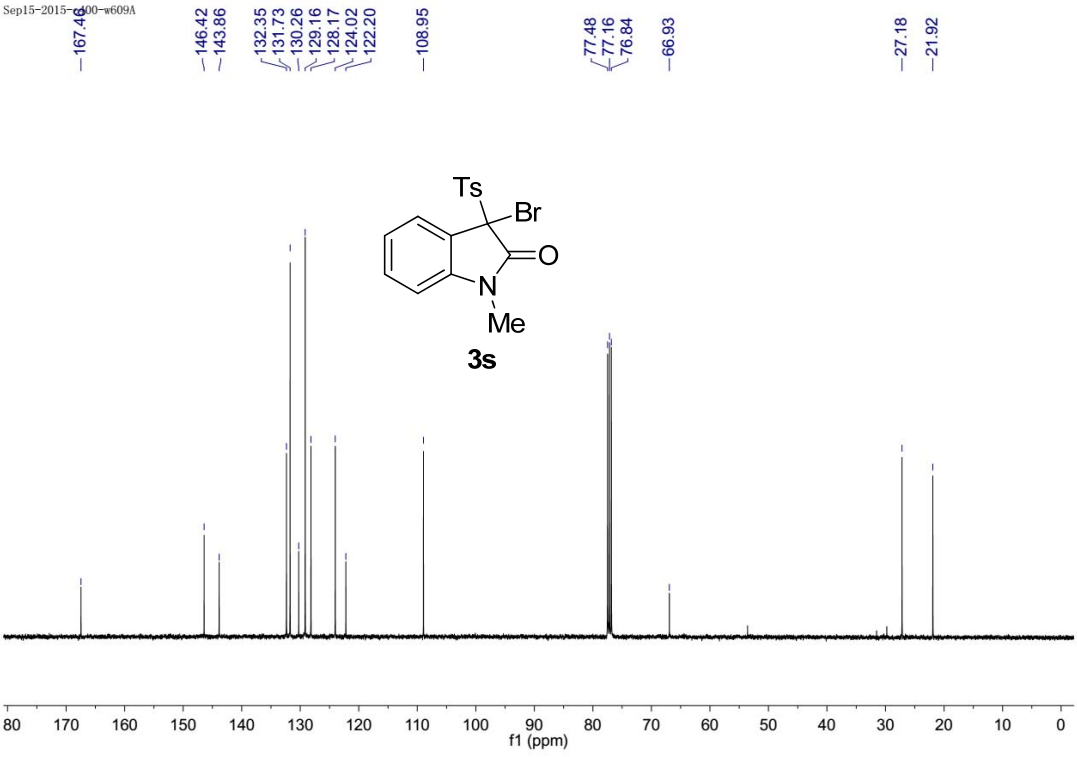

7.3909
7.3722
7.3287
7.3091
7.2891
7.2591
7.0986
7.0966
7.0796
7.0778
7.0608
7.0587
6.9651
6.9453
5.2648
3.9438
3.9296
3.9214
3.9074
3.8933
3.8891
3.8751
3.8615
3.8383
3.8252
3.6465
3.6325
3.6187
3.3274
Br
O
N
MeO
3p
0.99
1.05
1.04
1.01
0.97
2.08
2.01
3.00
f1 (ppm)

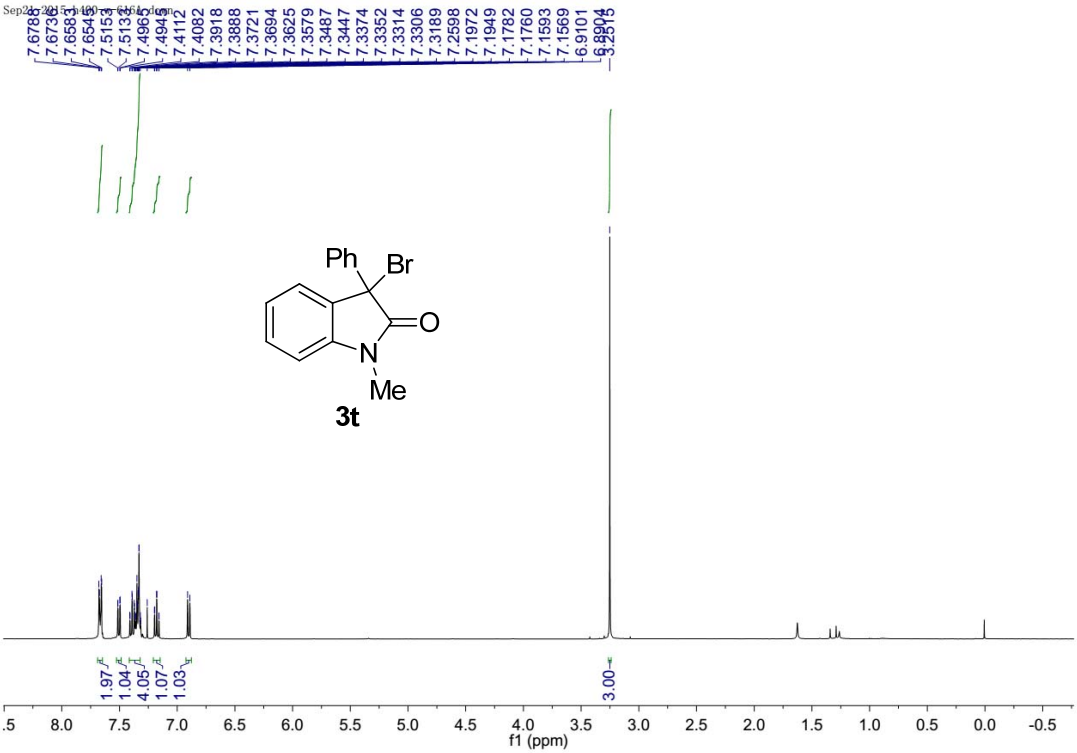

172.75
143.70
130.39
126.10
126.07
123.32
109.85
77.48
77.16
76.84
69.92
59.14
40.83
38.83
Br
O
N
MeO
3p
f1 (ppm)

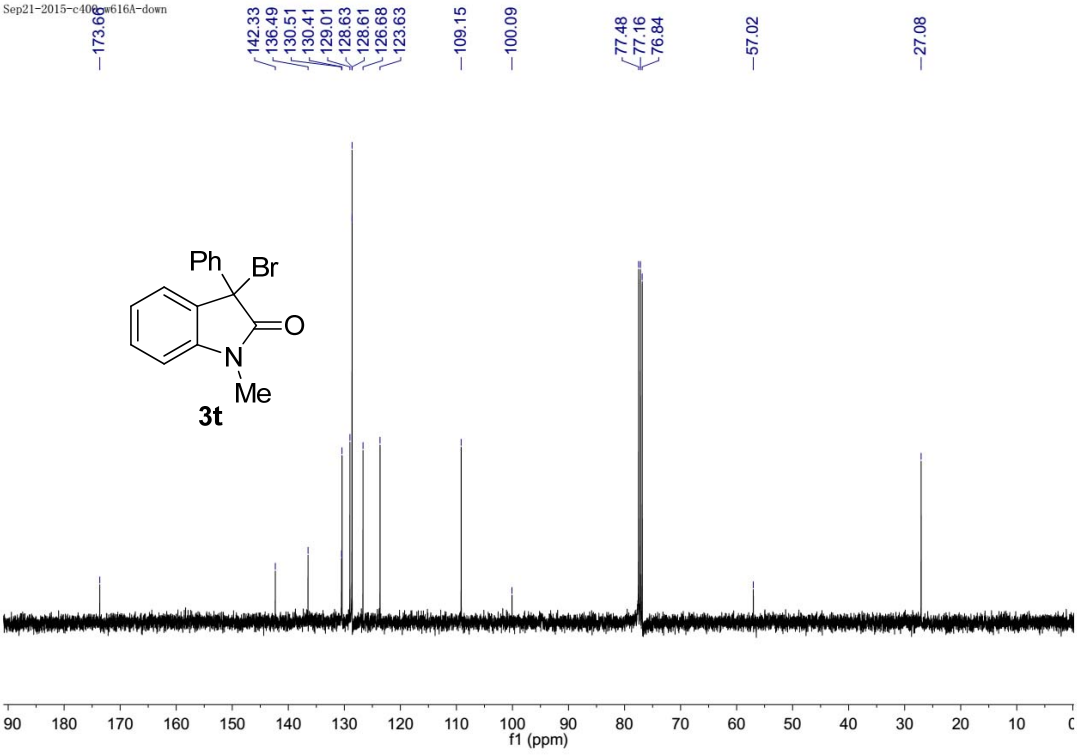

Br
O
N
Ph
3q
f1 (ppm)

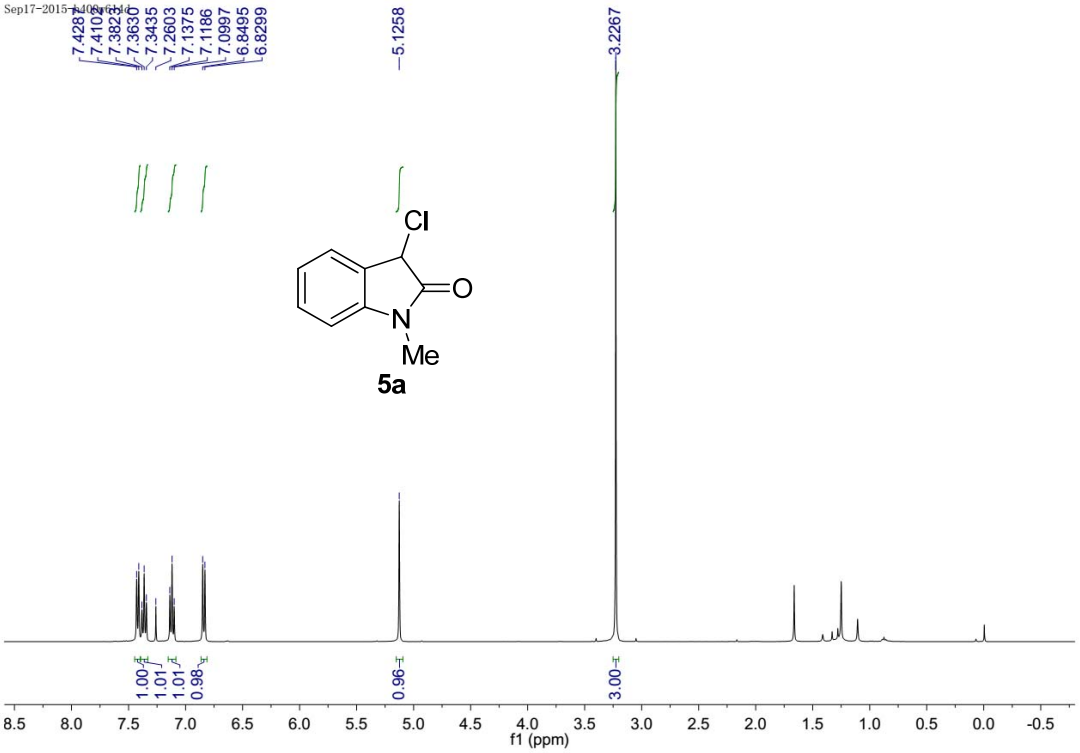

Sep22-2015-h400-c623a-up
172.3091
143.1162
136.0976
133.5696
130.4949
128.7311
128.1643
126.6095
126.2510
123.4885
122.1801
109.7795
77.4773
77.1596
76.8416
42.5621
38.7878
Br
O
N
Ph
3q
f1 (ppm)

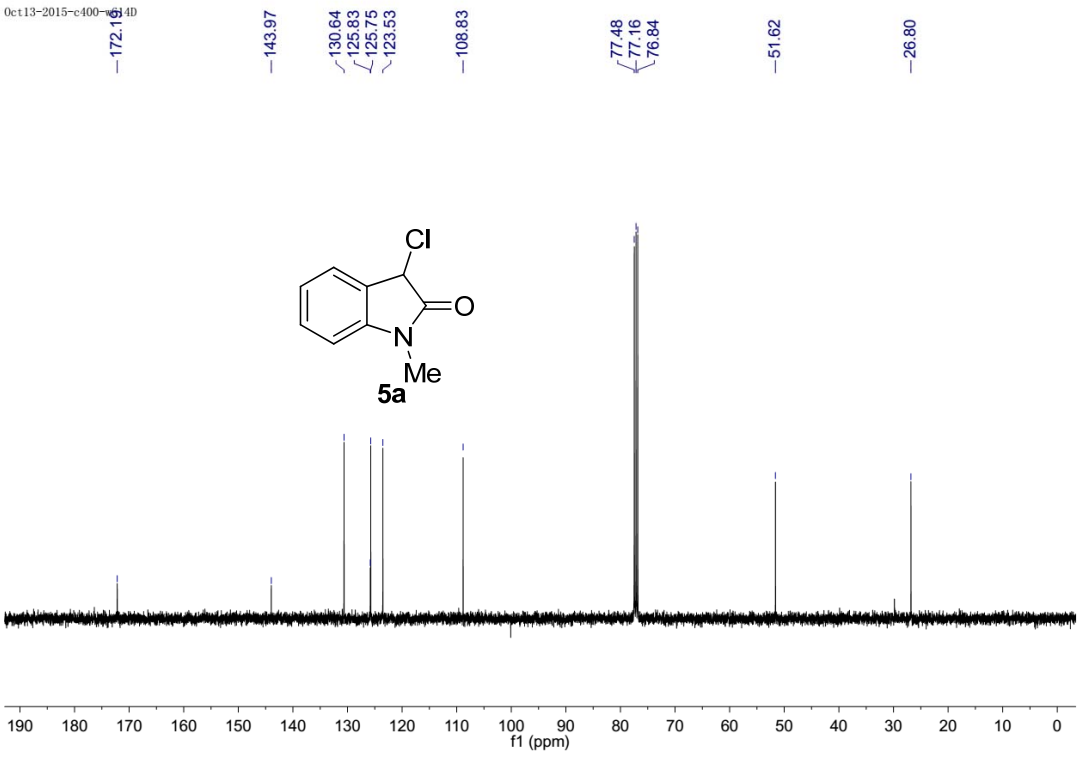

7.7466
7.7441
7.7276
7.7255
7.6739
7.6524
7.4244
7.4214
7.4050
7.4019
7.3856
7.3824
7.2656
7.2456
7.1960
7.1937
7.1768
7.1746
7.1577
7.1555
3.0679
2.4202
Ts
Br
O
N
Me
3s
0.99
2.03
1.04
0.91
0.93
1.06
1.01
3.04
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

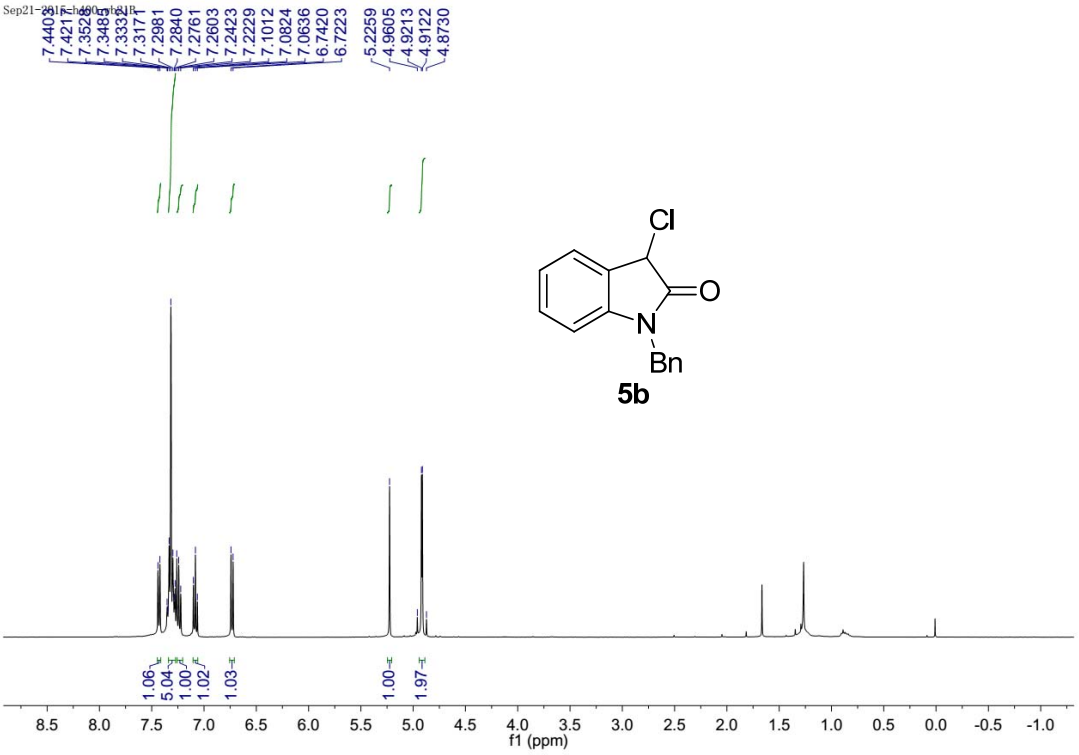

Sep15-2015-400-w609A
167.46
146.42
143.86
132.35
131.73
130.26
129.16
128.17
124.02
122.20
108.95
77.48
77.16
76.84
66.93
27.18
21.92
Ts
Br
O
N
Me
3s
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

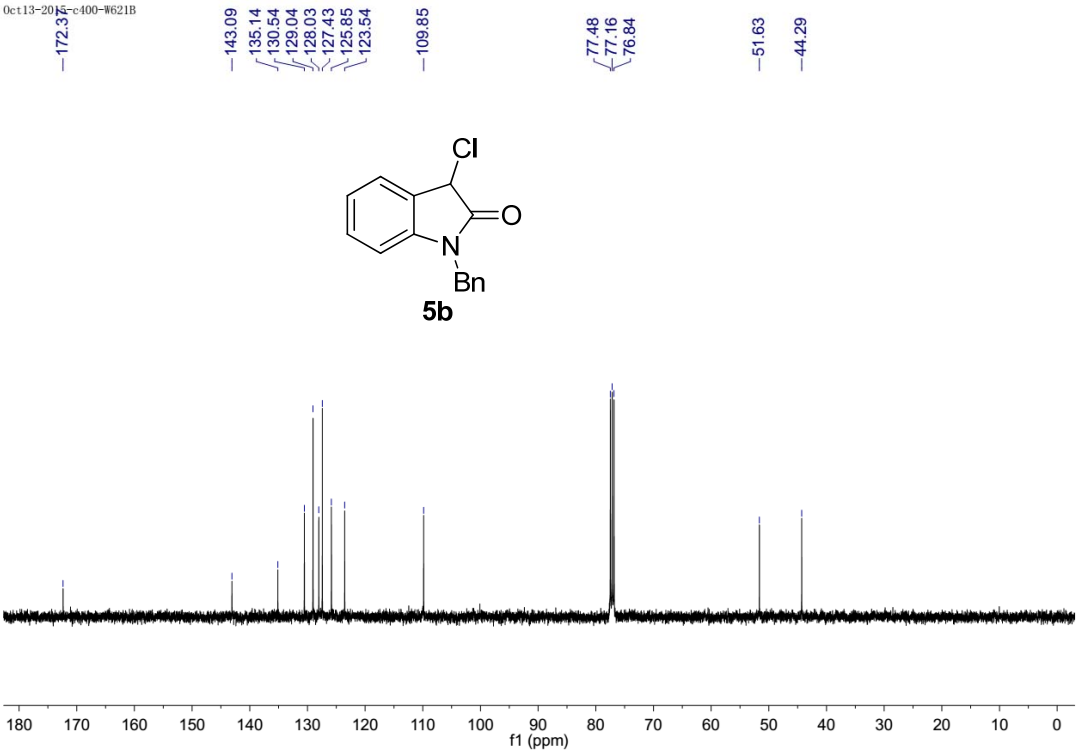

Ph
Br
O
N
Me
3t
1.97
1.04
4.05
1.07
1.03
3.00
f1 (ppm)

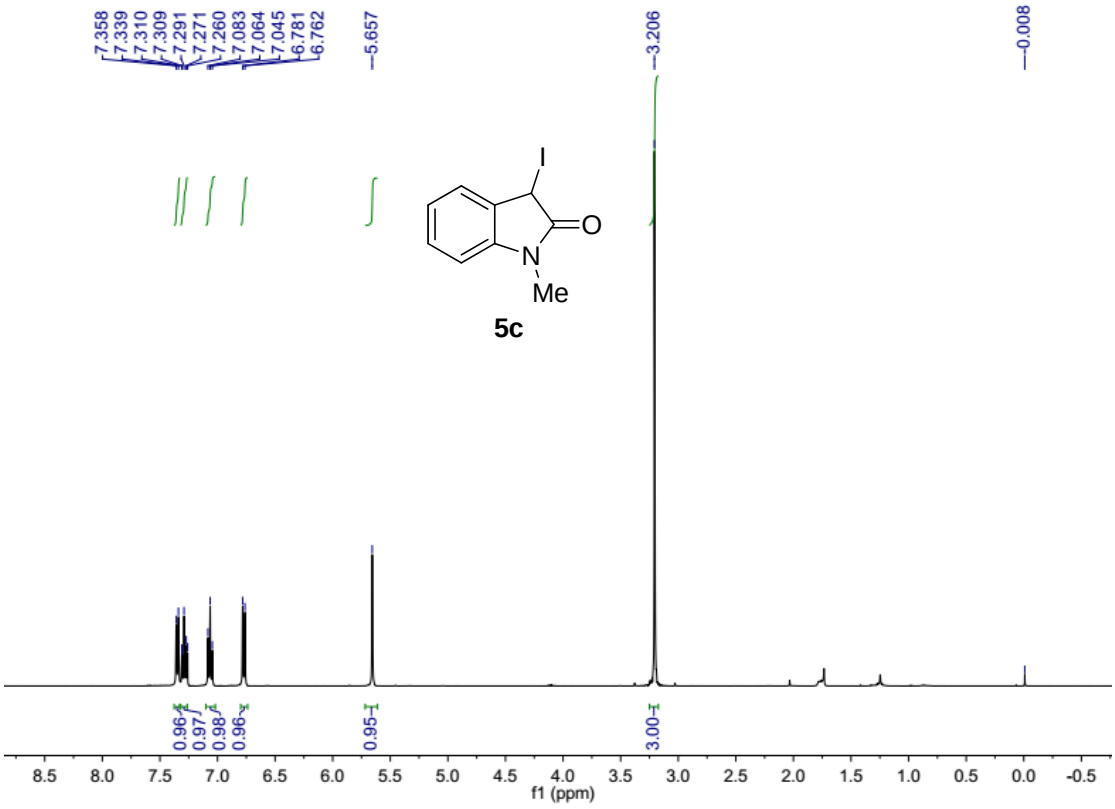

Ph
Br
O
N
Me
3t
f1 (ppm)


7.4287
7.4102
7.3825
7.3630
7.3435
7.2603
7.1375
7.1186
7.0997
6.8495
6.8299
5.1258
3.2267
Cl
O
N
Me
5a
1.00
1.01
1.01
0.98
0.96
3.00
f1 (ppm)

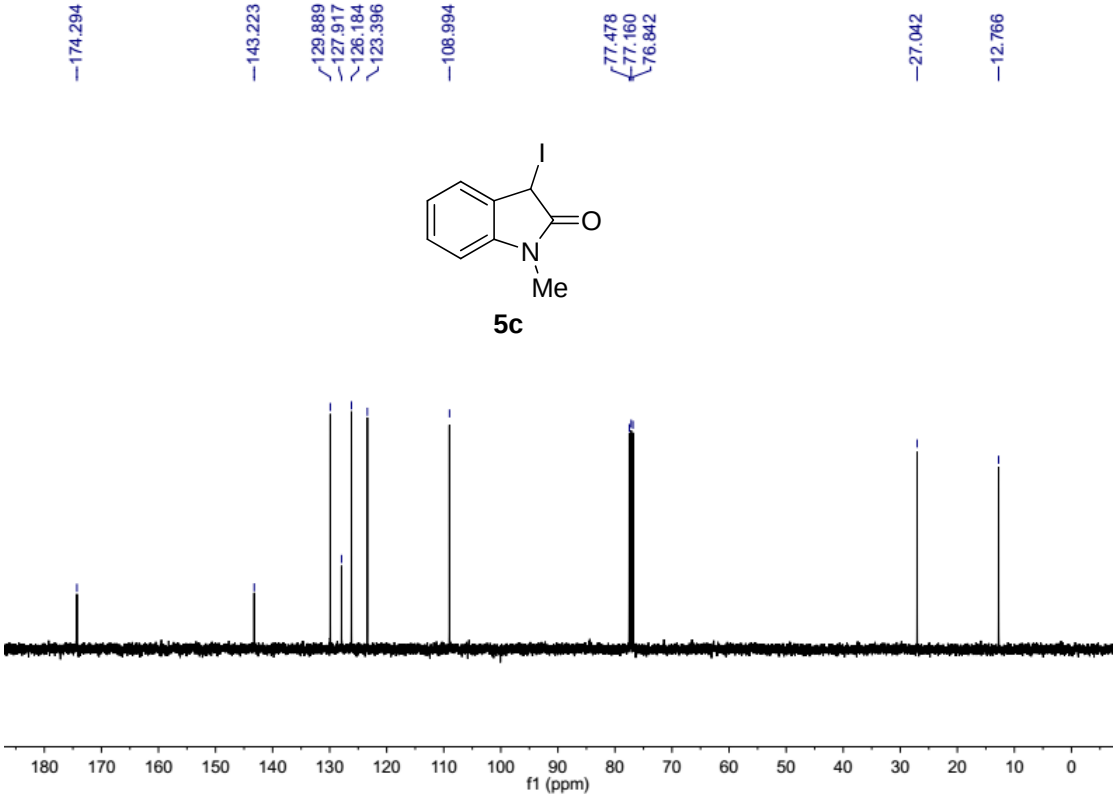

172.16
143.97
130.64
125.83
125.75
123.53
108.83
77.48
77.16
76.84
51.62
26.80
Cl
O
N
Me
5a
f1 (ppm)


7.4401
7.4217
7.3528
7.3483
7.3337
7.3171
7.2981
7.2840
7.2761
7.2603
7.2423
7.2229
7.1012
7.0824
7.0636
6.7420
6.7223
5.2259
4.9605
4.9213
4.9122
4.8730
Cl
O
N
Bn
5b
1.06
5.04
1.00
1.02
1.03
1.00
1.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

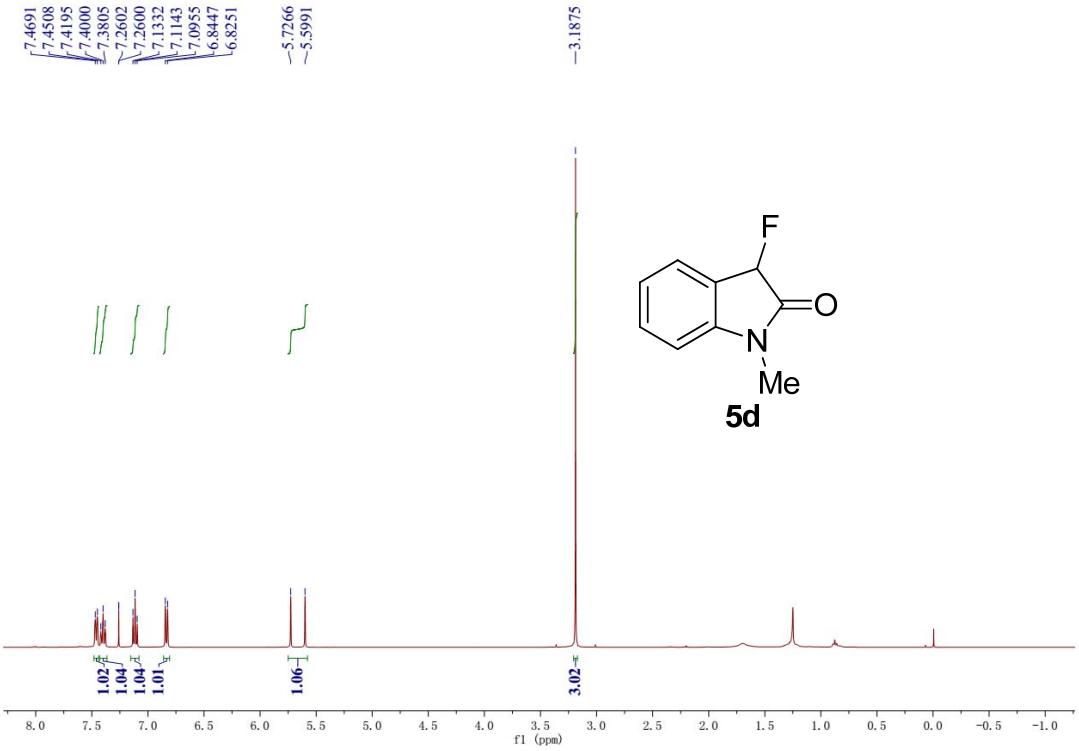

172.31
143.09
135.14
130.54
129.04
128.03
127.43
125.85
123.54
109.85
77.48
77.16
76.84
51.63
44.29
Cl
O
N
Bn
5b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

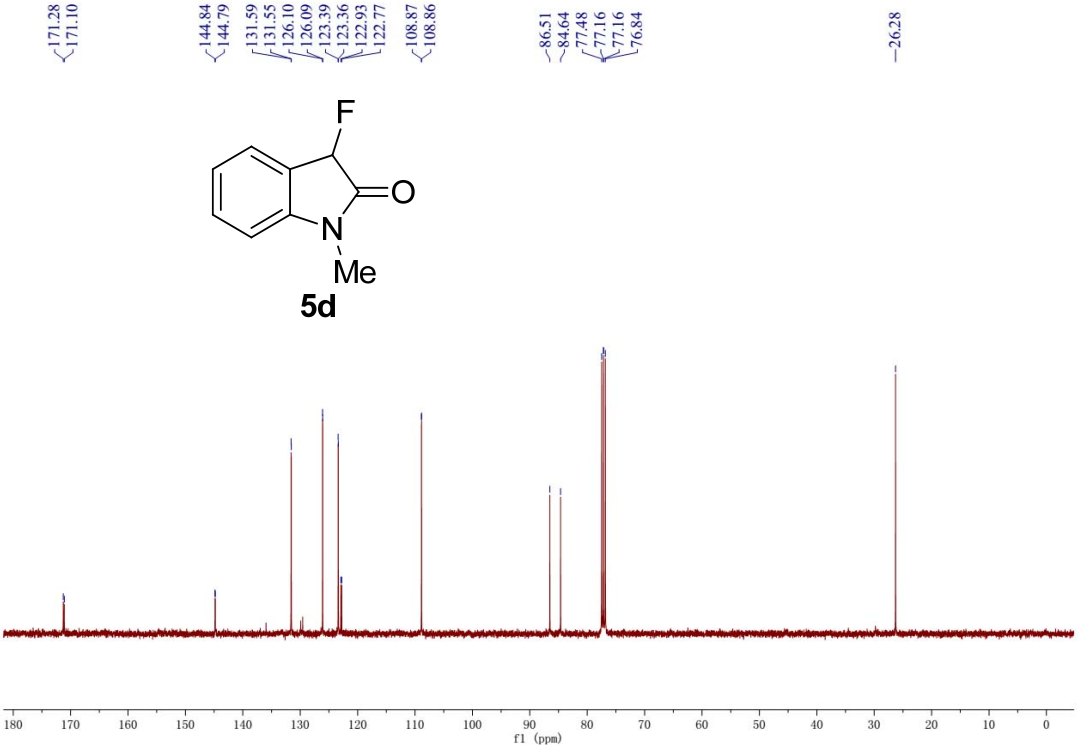

7.358
7.339
7.310
7.309
7.291
7.271
7.260
7.083
7.064
7.045
6.781
6.762
5.657
3.206
0.008
I
O
N
Me
0.96
0.97
0.98
0.96
0.95
3.00
f1 (ppm)

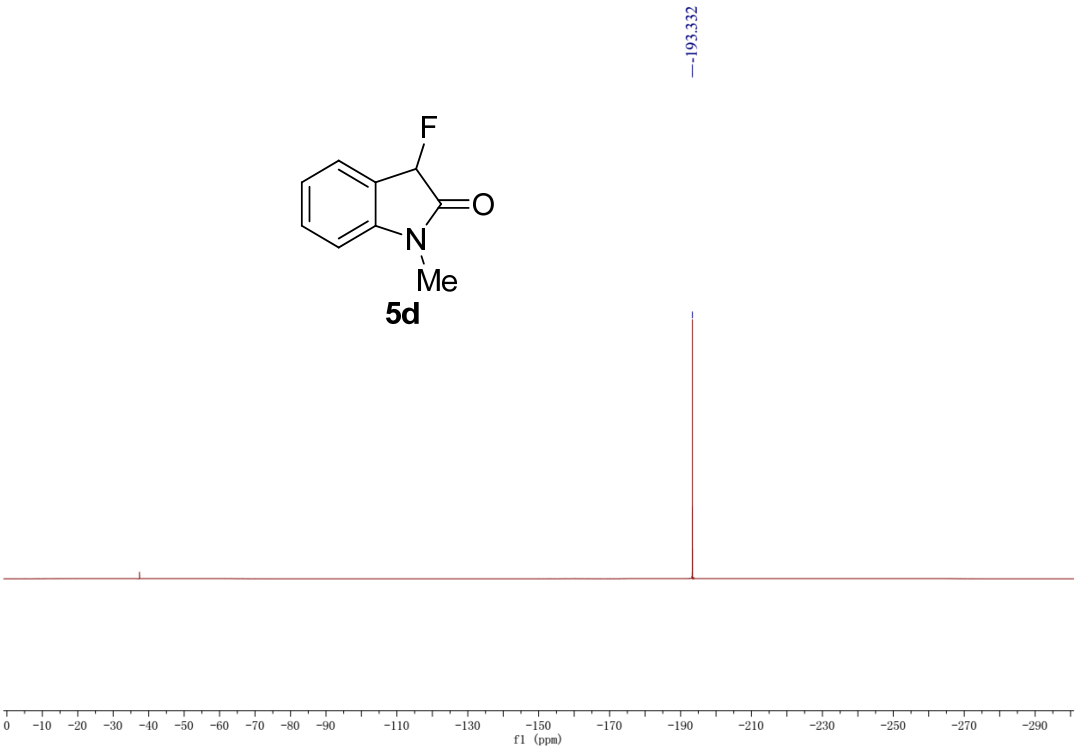
5c


174.294
143.223
129.889
127.917
126.184
123.396
108.994
77.478
77.160
76.842
27.042
12.766
I
O
N
Me
f1 (ppm)

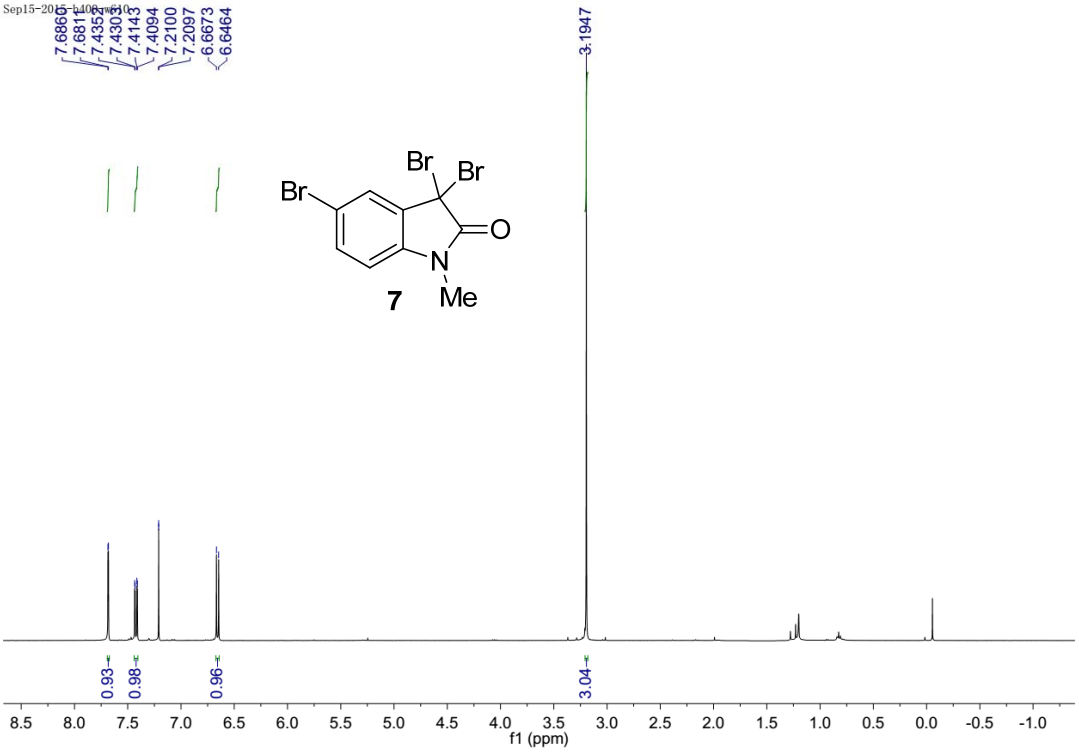
5c

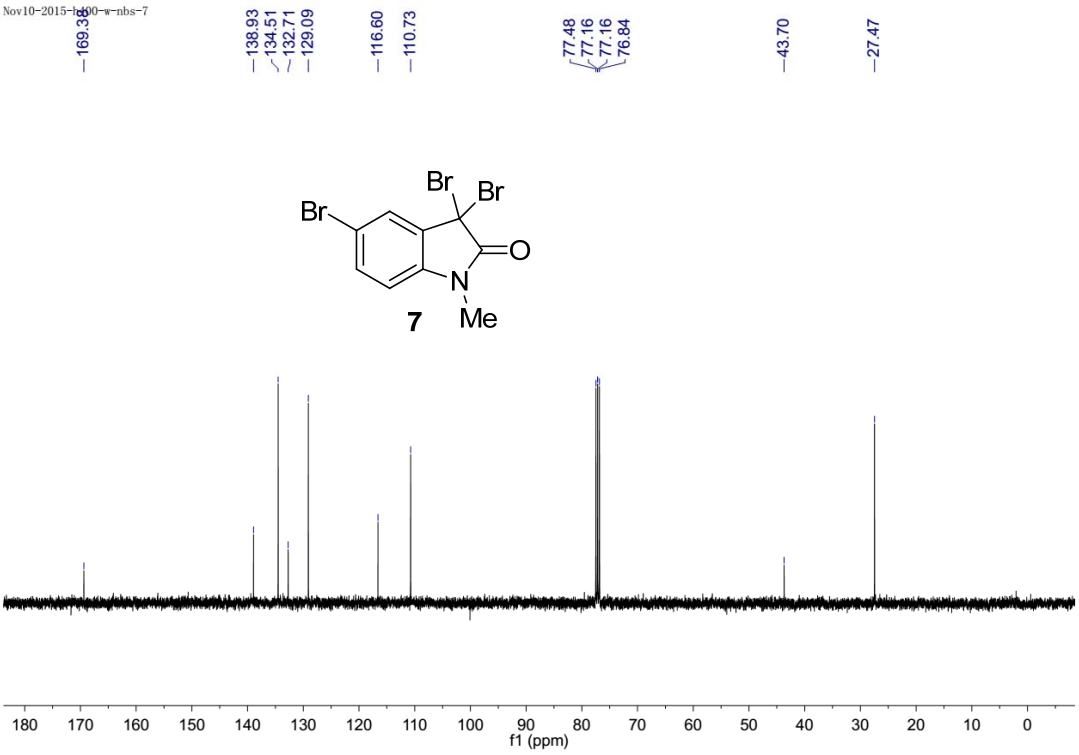

7.4691
7.4508
7.4195
7.4000
7.3805
7.2602
7.2600
7.1332
7.1143
7.0955
6.8447
6.8251
5.7266
5.5991
3.1875
F
O
N
Me
5d
1.02
1.04
1.04
1.01
1.06
3.02
f1 (ppm)


171.28
171.10
144.84
144.79
131.59
131.55
126.10
126.09
123.39
123.36
122.93
122.77
108.87
108.86
86.51
84.64
77.48
77.16
77.16
76.84
26.28
F
O
N
Me
5d
f1 (ppm)

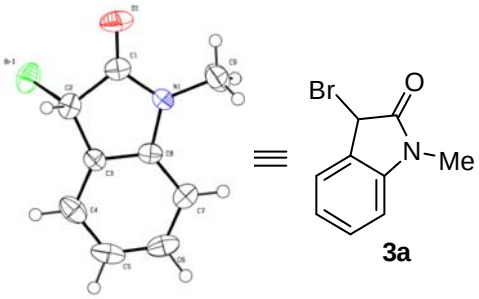

F
O
N
Me
-193.332
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

5d


7.6866
7.6811
7.4352
7.4303
7.4143
7.4094
7.2100
7.2097
6.6673
6.6464
3.1947
Br
Br
Br
O
N
Me
7
0.93
0.98
0.96
3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


169.38
138.93
134.51
132.71
129.09
116.60
110.73
77.48
77.16
77.16
76.84
43.70
27.47
Br
Br
Br
O
N
Me
7
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Single-crystal X-ray diffraction of 3a



3a

Datablock: g150806a

Bond precision: C-C = 0.0049 A Wavelength=0.71073

Cell: a=12.9498(4) b=8.2018(3) c=16.5817(5)
alpha=90 beta=97.327(3) gamma=90

Temperature: 223 K

	Calculated	Reported
Volume	1746.79(10)	1746.79(10)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C9 H8 Br N O	C9 H8 Br N O
Sum formula	C9 H8 Br N O	C9 H8 Br N O
Mr	226.06	226.07
Dx,g cm-3	1.719	1.719
Z	8	8
Mu (mm-1)	4.653	4.653
F000	896.0	896.0
F000'	894.11	
h,k,lmax	15,9,20	15,9,20
Nref	3243	3239
Tmin,Tmax	0.214,0.394	0.293,0.456
Tmin'	0.180	

Correction method= # Reported T Limits: Tmin=0.293
Tmax=0.456 AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.500

R(reflections)= 0.0369(2525) wR2(reflections)= 0.0852(3239)

S = 1.039 Npar= 219