Sequential Au(I)/chiral tertiary amine catalysis: a tandem C-H functionalization of anisoles or thiophene/asymmetric Michael addition sequence to quaternary oxindoles

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Supporting Information

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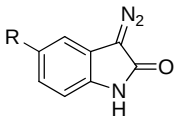
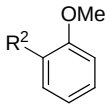
General information: Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were obtained using a Bruker DPX-300, 400 or 500 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ or $(CD_3)_2CO$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Anhydrous CH_2Cl_2 was prepared by first distillation over P_2O_5 and then from CaH_2. Anhydrous Et_2O was prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous ethanol was prepared over Na_2SO_4 and magnesium prior to use. AgOTf was purchased from TCI Company. Ph_3PAuCl was synthesized according to the literature method.[1] Phosphinamide **B, C** and phosphoramides **A, D-G** catalysts were prepared using literature procedures.[2] The chiral thiourea catalyst **C2** was prepared using literature procedures.[3] 3-Diazooxindoles[4] and nitroenynes[5] were synthesized according to the literature procedures. Aanisole and its derivatives were purchased from Energy Chemical (Shanghai) Co. Ltd and used without any purification.



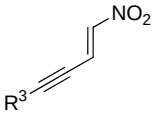
1

1a: R = Cl
1b: R = F
1c: R = Me
1d: R =H
1e: R = Br



2

2a: R^2 = H
2b: R^2 = OMe
2c: R^2 = Br
2d: R^2 = I
2e: R^2 = Me



4

4a: R^3 = Ph
4b: R^3 = *p*-$MeOC_6H_4$
4c: R^3 = *p*-FC_6H_4
4d: R^3 = *n*-pentyl
4e: R^3 = TMS

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[1] T. N. Hooper, C. P. Butts, M. Green, M. F. Haddow, J. E. McGrady and C. A. Russell, *Chem. Eur. J.,* 2009, **15**, 12196.

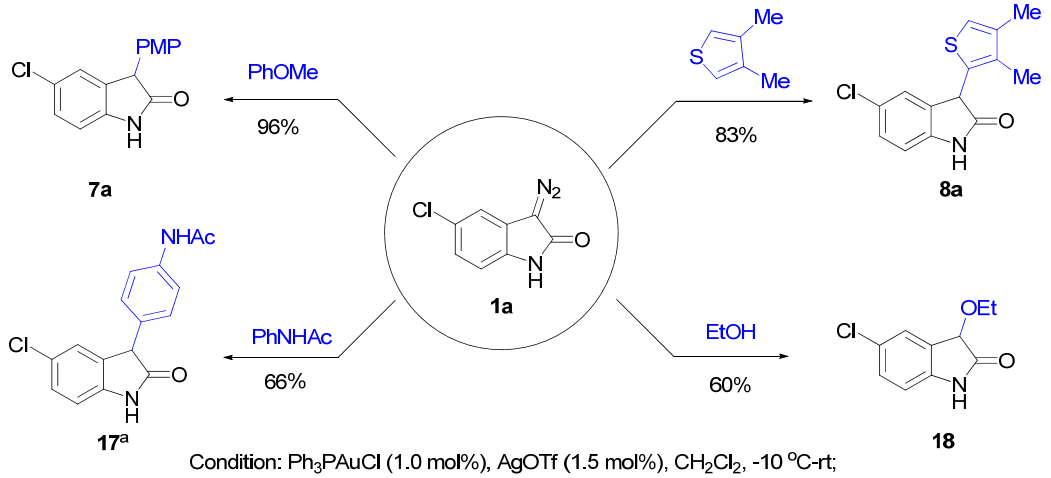
[2] M. Ding, F. Zhou, Y.-L. Liu, C.-H. Wang, X.-L. Zhao, and J. Zhou, *Chem. Sci.,* 2011, **2**, 2035.

[3] a) A. Berkessel, S. Mukherjee, T. N. Müller, F. Cleemann, K. Roland, M. Brandenburg, J.-M. Neudörfl and J. Lex, *Org. Biomol. Chem.,* 2006, **4**, 4319; b) G. Tárkányi, P. Király, S. Varga, B. Vakulya and T. Soós, *Chem. Eur. J*., 2008, **14**, 6078; c) B. Vakulya, S. Varga and T. Soós, *J. Org. Chem.,* 2008, **73**, 3475; d) A. Peschiulli, C. Quigley, S. Tallon, Y. K. Gun'ko and S. J. Connon, *J. Org. Chem*., 2008, **73**, 6409; e) B. Vakulya, S. Varga, A. Csámpai and T. Soós, *Org. Lett.,* 2005, **7**, 1967.

[4] R. Augusti and C. Kascheres, *J. Org. Chem.,* 1993, **58**, 7079.

[5] a) F. Romanov-Michailidis, C. Besnard and A. Alexakis, *Org. Lett.,* 2012, **14**, 4906; b) S. Belot, A. Massaro, A. Tenti, A. Mordini and A. Alexakis, *Org. Lett.,* 2008, **10**, 4557.

1) The Au(I)-catalyzed X-H insertion reactions of diazooxindole: comparing Au(I) with some other metal catalysts



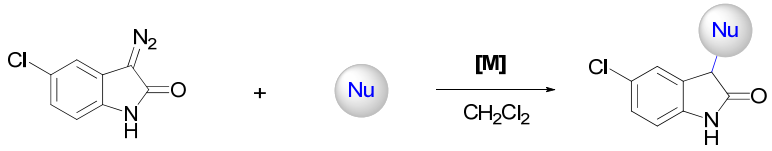
Condition: Ph_3PAuCl (1.0 mol%), AgOTf (1.5 mol%), CH_2Cl_2, -10 °C-rt;
a) $(2,4\text{-}^tBu_2C_6H_3O)_3PAuSbF_6$ (2.0 mol%) was used

We successfully utilized cationic Au(I) catalyst to realize the direct X-H insertion with diazooxindole **1a**, to construct useful 3-substituted oxindole building blocks **7**, **8**, **17** and **18** for next stereoselective addition reaction. Importantly, the above reactions not only provided a facile access to different oxindole synthons for the asymmetric construction of chiral oxindole scaffolds, but showed the great potential of Au(I) catalysis in the functionalization of diazo compounds, as it proved to be much more efficient than other five metal catalysts widely used in diazo reagents associated chemistry. To highlight these finding, we summarized in Table S1 the comparison of these metal catalysts in various insertion reactions. All the reactions were performed with only 1.0 mol% catalyst, and the cationic Au(I) species was prepared by stirring 1.0 mol% of Ph_3PAuCl with 1.5 mol% of AgOTf.

(1) In the C-H insertion reaction using PhOMe, it took only 2 h for $Ph_3PAuOTf$ to catalyze the reaction for full conversion at -10 °C, affording the desired product **7a** in 96% isolated yield. Under the same condition, all the other five metal catalysts failed to catalyze this reaction. Nevertheless, when using AgOTf as the catalyst, the reaction could work at room temperature, and gave **7a** in 54% yield with a reaction time of 14 h.

(2) When 3,4-dimethyl thiophene was used, $Ph_3PAuOTf$ catalyzed the reaction to finish within 0.5 h at room temperature, to give product **8a** in 83% yield. Noticeably, while both AgOTf and $(CuOTf)_2$•toluene could catalyze this transformation as well, but the reaction time was much longer (24 h in both cases).

Table S1. Comparing different metal catalysis



1a (0.25 mmol) **7**, **8**, **17**, **18**

[M] (X mol%)	Nucleophilic reaction partner (condition)			
	PhOMe (10.0 equivs) (-10 °C, 2 h)	3,4-Me_2TP (5.0 equivs) (rt, 0.5 h)	PhNHAc (2.0 equivs) (0 °C, 2 h)[c]	EtOH (10.0 equivs) (0 °C, 4 h)
$Ph_3PAuOTf$ (1.0 mol%)	**7a**: 96%	**8a**: 83%	**17**: 66%[d]	**18**: 60%
$Rh_2(OAc)_4$ (0.5 mol%)	-	-	-	**18**: 38%[e]
AgOTf (1.0 mol%)	**7a**: 54%[a]	**8a**: 54%[b]	-	-
[Ru] (0.5 mol%)	-	-	-	-
[Pd] (0.5 mol%)	-	-	-	-
[Cu] (0.5 mol%)	-	**8a**: 65%[b]	-	-

a) At rt for 14 h; b) At rt for 24 h; c) 1.0 mol% catalyst was used; d) 2.0 mol% of $(2,4\text{-}^tBu_2C_6H_3O)_3PAuSbF_6$ was used; e) At rt for 48 h. [Ru] = $[\{RuCl_2(p\text{-cymene})\}_2]$; [Pd] = $[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$; [Cu] = $(CuOTf)_2$•toluene.

(3) In the case of acetanilide as nucleophile, while $Ph_3PAuOTf$ failed to catalyze the reaction to afford the desired product **17**, the use of 2.0 mol% of $(2,4\text{-}^tBu_2C_6H_3O)_3PAuSbF_6$ as catalyst, reported by Liu and Zhang,[6] enabled this insertion reaction to finish within 2 h to afford **17** in 66% yield. This result suggested it was possible to tune the catalytic properties of Au(I) by varying ligands to realize more functionalization of diazo reagents. Again, no desired product was observed when the rest five metal catalysts were used.

(4) While in 2005, Nolan, Díaz-Requejo, Pérez and coworkers pioneered the Au(I)-catalyzed decomposition of ethyl diazoacetate for the O-H bond insertion reaction,[7] the potential of Au(I) catalysis in the O-H bond insertion reaction of donor-acceptor diazo reagents had not been examined. It was found that the reaction of EtOH and diazooxindole **1a** catalyzed by $Ph_3PAuOTf$ could finish within

[6] Z.-Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu and J. Zhang, *J. Am. Chem. Soc.,* 2014, **136**, 6904.
[7] M. R. Fructos, T. R. Belderrain, P. Frémont, N. M. Scott, S. P. Nolan, M. M. Díaz-Requejo and P. J. Pérez, *Angew. Chem., Int. Ed.,* 2005, **44**, 5284.

4 h at 0 °C, giving product **18** in 60% yield. In contrast, of other catalysts we screened, only $Rh_2(OAc)_4$ could catalyze the reaction, which was run at rt for 48 h to give product **18** in only 38% yield.

The product **7a** was obtained as white solid (m.p. 147-149 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.20-7.08 (m, 4H), 6.90-6.81 (m, 3H), 4.57 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.96, 159.29, 140.17, 131.58, 129.47, 128.32, 128.02, 127.62, 125.50, 114.53, 111.02, 55.28, 52.06; IR (ATR): 3186, 1704, 1614, 1511, 1476, 1251, 1181, 1109, 1029; GC-MS: 273, 275 (M^+, 100, 34), 238 (93), 244 (47), 230 (33), 201 (19), 166 (19), 105 (6), 127 (5); HRMS (EI): Exact mass calcd for $C_{15}H_{12}NO_2{}^{35}Cl$ $[M]^+$: 273.0557, Found: 273.0558.

The product **8a** was obtained as red powder (m.p. 162-164 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.35 (s, 1H), 7.26-7.13 (m, 2H), 6.84-6.81 (m, 2H), 4.90 (s, 1H), 2.16 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.56, 139.84, 138.39, 136.19, 130.91, 130.10, 128.57, 128.06, 125.38, 119.35, 111.09, 46.87, 15.28, 12.79; IR (ATR): 3169, 1699, 1617, 1477, 1374, 1325, 1227; GC-MS: 277, 279 (M^+, 52, 19), 111 (100), 234 (44), 244 (36), 262 (18), 107 (12), 199 (11), 152 (5); HRMS (EI): Exact mass calcd for $C_{14}H_{12}NOS^{35}Cl$ $[M]^+$: 277.0328, Found: 277.0327.

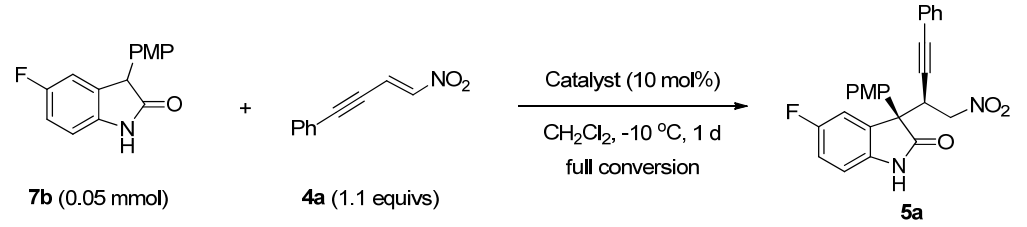
The product **17** was obtained as white solid (m.p. 198-120 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.63 (s, 1H), 9.96 (s, 1H), 7.54-7.52 (m, 2H), 7.27-7.25 (m, 1H), 7.07-7.04 (m, 3H), 6.92-6.90 (m, 1H), 4.73 (s, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 176.99, 168.33, 141.53, 138.37, 132.31, 131.41, 128.54, 127.87, 125.59, 124.64, 119.41, 110.84, 51.31; IR (ATR): 3299, 3253, 1699, 1672, 1303, 1207, 1182, 1166; EI: 300 (M^+, 9), 44 (100), 93 (99), 135 (34), 258 (17), 105 (17), 282 (15), 229 (11); HRMS (EI): Exact mass calcd for $C_{16}H_{13}N_2O_2{}^{35}Cl$ $[M]^+$: 300.0666, Found: 300.0663.

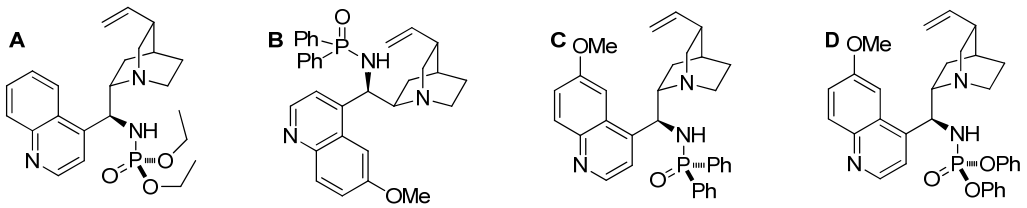
The product **18** was obtained as red solid (m.p. 113-115 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (s, 1H), 7.403-7.396 (m, 1H), 7.30-7.27 (m, 1H), 6.86-6.83 (m, 1H), 4.94 (s, 1H), 3.97-3.87 (m, 1H), 3.80-3.70 (m, 1H), 1.33 (t, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.94, 139.78, 129.80, 128.36, 127.45, 125.95, 111.32, 75.98, 64.87, 15.35; IR (ATR): 3184, 1708, 1620, 1451, 1177, 1099, 1065; GC-MS: 211, 213 (M^+, 26, 8), 167 (100), 154 (72), 127 (70), 75 (27), 138 (20), 182 (19), 102 (16); HRMS (EI): Exact mass calcd for $C_{10}H_{10}NO_2{}^{35}Cl$ $[M]^+$: 211.0400, Found: 211.0401.

2) Condition optimization for the asymmetric Michael addition of 3-aryloxindole and nitroenyne

Based on our previous finding that a simple cinchonidine derived bifunctional phosphoramide catalyst **A** was a powerful catalyst for the Michael addition of 3-substituted oxindoles to nitrolefins,[8] we first examined catalyst **A** in the conjugate reaction of unprotected 3-methoxyphenyloxindole **7b** to nitroenyne **4a** in CH_2Cl_2 at -10 ^oC. It was found that although product **5a** could be obtained in 96% ee, the dr value was moderate (Table S2). Therefore, to improve the diastereoselectivity, we prepared a variety of analogues of catalyst **A**, namely cinchona alkaloid derived phosphinamide **B-C** and phosphoramides **D-G**, in one step from the corresponding cinchonidine-derived primary amine and phosphinic chloride or chlorophosphates. The evaluation of these newly developed catalysts revealed that catalyst **C1**, with a bulkier isopropyl ester group, could slightly improve the dr value to 2.4:1.0, as indicated in Table S2. Accordingly, catalyst **C1** was used for further condition optimization.

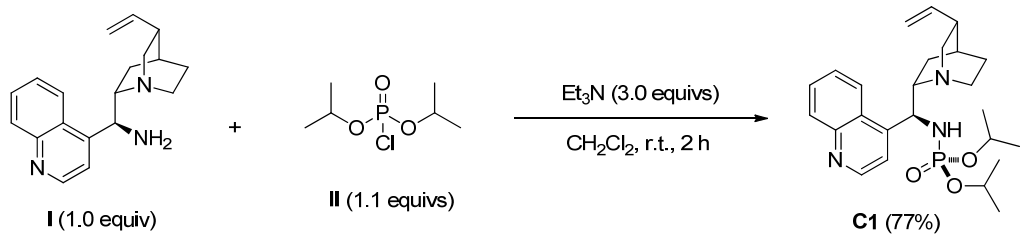
Table S2. The evaluation of different catalyst for Michael addition reaction





[8] a) M. Ding, F. Zhou, Y.-L. Liu, C.-H. Wang, X.-L. Zhao and J. Zhou, *Chem. Sci.*, 2011, **2**, 2035; b) W.-M. Gao, J.-S. Yu, Y.-L. Zhao, Y.-L. Liu, F. Zhou, H.-H. Wu and J. Zhou, *Chem. Commun.*, 2014, **50**, 15179.

The synthesis and characterization of the optimized catalyst **C1** was as follows:

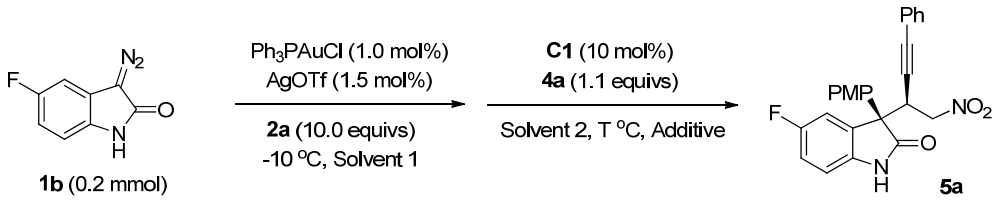


Under an atmosphere of N_2, to a flame-dried three-necked flask were added cinchonidine-derived primary amine **I** (1.47 g, 5.0 mmol) and 25 mL of anhydrous CH_2Cl_2, followed by the addition of Et_3N (2.1 mL, 15.0 mmol). Then diisopropyl phosphorochloridate **II** (1.0 mL, 5.5 mmol) was added dropwise at room temperature over 10 minutes. The resulting mixture was stirred at room temperature for another two hours, and 30 mL of H_2O was added. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (40 mL × 4). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel using EtOAc:MeOH:$NH_3 \cdot H_2O$ (200:2:1, v/v) as eluent to give product **C1** (1.76 g, 77% yield) as yellowish oil. (Due to the distinct presence of rotameric isomers, the ^{1}H NMR and ^{13}C NMR contained extra peaks, so we did not designate the data, and attached the spectra behind), ^{1}H NMR (400 MHz, $CDCl_3$): see Page 47; ^{13}C NMR (100 MHz, $CDCl_3$): see Page 48; ^{31}P NMR (162 MHz, $CDCl_3$): see Page 49; IR (ATR): 3238, 2975, 2934, 2867, 1384, 1239, 1107, 1012; HRMS (ESI): Exact mass calcd for $C_{25}H_{37}N_3O_3P$ $[M+H]^+$: 458.2567, Found: 458.2585.

3) Optimization to develop a one-pot tandem C-H functionalization/Michael addition sequence

Some typical results of optimization in combining the C-H bond functionalization and asymmetric Michael addition to form a tandem reaction were shown in Table S3. As the best solvent for the initial C-H bond functionalization was CH_2Cl_2, so we tried using CH_2Cl_2 or the analogy 1,2-dichlorethane as the solvent for both steps, but the desired product **5a** was obtained in only 2:1 dr value, although with excellent yield and ee value (entries 1-2). Then we attempted to remove solvent CH_2Cl_2 under reduced pressure after the completion of the initial C-H functionalization, and to recharge other solvent for the asymmetric Michael addition to improve diastereoselectivity. It was found that when using Et_2O as the solvent for the asymmetric Michael addition, the dr value could be improved to 4:1 (entry 3). When lowering the temperature from -10 ^oC to -40 ^oC, the dr value could be improved to 5:1 (entry 4). The evaluation of additive effects revealed that when using MS 5Å as the additive, the dr value could be further improved to 7:1 (entry 7). Therefore, all the tandem reactions involving the asymmetric Michael addition of 3-substituted oxindoles to nitroenynes were using Et_2O as the solvent for the enantioselective C-C bond forming step, with the addition of activated powdered MS 5Å as the additive.

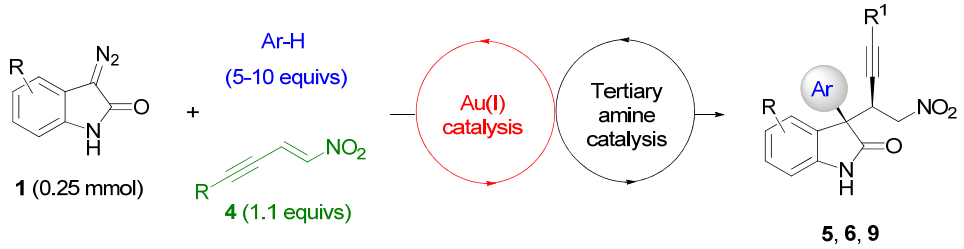
Table S3. Condition optimization for C-H insertion/Michael addition tandem reaction



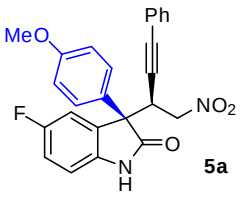
Entry	Solvent 1	Solvent 2	T (^oC)	Additive	Time (d)	Yield (%)[a]	Ee (%)[b]	Dr[c]
1	CH_2Cl_2	CH_2Cl_2	-10	-	1	95	97	2 : 1
2	$(CH_2Cl)_2$	$(CH_2Cl)_2$	-10	-	1	86	97	2 : 1
3	CH_2Cl_2	Et_2O	-10	-	1	90	98	4 : 1
4	CH_2Cl_2	Et_2O	-40	-	3	89	97	5 : 1
5	CH_2Cl_2	Et_2O	-40	MS 3 Å	3	92	98	6 : 1
6	CH_2Cl_2	Et_2O	-40	MS 4 Å	3	94	98	6 : 1
7	CH_2Cl_2	Et_2O	-40	MS 5 Å	3	93	99	7 : 1

a) Isolated yield; b) Determined by HPLC analysis; c) Determined by ^1H NMR analysis of the crude reaction mixture.

4) General procedure for the one-pot tandem C-H functionalization/Michael addition sequence



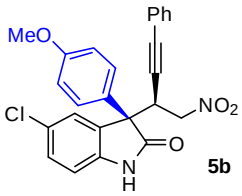
Under an atmosphere of nitrogen, to a Schlenk tube were added Ph_3PAuCl (1.2 mg, 0.0025 mmol) and AgOTf (1.0 mg, 0.0038 mmol), followed by anhydrous CH_2Cl_2 (2.5 mL). The resulting mixture was stirred at room temperature for 15-20 minutes, and then cooled down to -10 ^oC, followed by the addition of electron-rich aromatic compound (4.0 mmol) and diazooxindole **1** (0.25 mmol). The reaction was kept stirring at -10 ^oC for about 1-8 h till full conversion of diazooxindole **1** by TLC analysis. After anhydrous CH_2Cl_2 was removed under reduced pressure, Et_2O (3.0 mL), powdered MS 5 Å (125.0 mg) and chiral catalyst **C1** (11.4 mg, 0.025 mmol) were added successively. The reaction mixture was cooled down to -40 ^oC, followed by the addition of nitroenynes **4** (0.275 mmol). The resulting mixture was stirring at -40 ^oC till full conversion of 3-aryl oxindole by TLC analysis (1.5-10.0 days). The solvent was carefully removed under reduced pressure. To determine the diastereoselectivity of product, the residue was first dissolved in $CDCl_3$, and some samples were taken for NMR analysis. Then the sample for analysis and the rest mixture were recombined for column chromatographic purification using petroleum ether/CH_2Cl_2/acetone (from 100:100:0 to 0:100:1) as the eluent to give the products.



5a

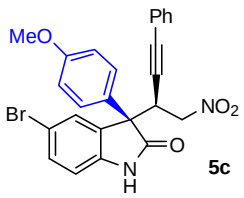
The total reaction time was 2.5 days. Product **5a** was obtained in 99% yield as white solid. (dr = 7:1, 99% ee for the major diastereomer); $[\alpha]^{25}_D$ = +70.1 (c = 0.47, $CHCl_3$), m.p. 90-91 ^oC; HPLC analysis: Chiralpak AD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 13.86 min, t_r (minor) = 16.20 min; minor diastereomer: t_r (minor) = 10.00 min, t_r (major) = 10.48 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 7.47-7.44 (m, 2H), 7.25-7.23 (m, 1H), 7.20-7.17 (m, 2H), 7.12-7.07 (m, 4H), 6.99-6.96 (m, 1H), 6.93-6.90 (m, 2H), 4.67-4.57 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.55, 159.85, 158.84 (d, J_{F-C} = 240.0 Hz), 137.67, 131.71, 130.23 (d, J_{F-C} = 8.0 Hz), 128.69, 128.58, 128.19, 125.71,

121.63, 115.96 (d, J_{F-C} = 23.0 Hz), 114.73, 114.01 (d, J_{F-C} = 25.0 Hz), 111.35 (d, J_{F-C} = 8.0 Hz), 86.01, 82.87, 75.75, 58.24, 55.36, 38.73; ^{19}F NMR (376 MHz, $CDCl_3$): δ -119.21; IR (ATR): 2930, 2839, 2349, 1712, 1607, 1556, 1486, 1459, 1254, 1138; HRMS (ESI): Exact mass calcd for $C_{25}H_{20}N_2O_4F$ $[M+H]^+$: 431.1402, Found: 431.1405.



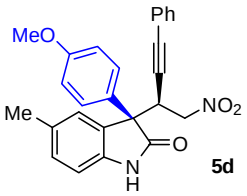
5b

The total reaction time was 2 days. Product **5b** was obtained in 96% yield as white solid. (dr = 7:1, 99% ee for the major diastereomer); $[\alpha]^{25}_D$ = +27.1 (c = 1.00, $CHCl_3$), m.p. 95-96 °C; HPLC analysis: Chiralpak IE, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 21.93 min, t_r (minor) = 31.24 min; minor diastereomer: t_r (minor) = 14.50 min, t_r (major) = 15.37 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, br, 1H), 7.46-7.44 (m, 2H), 7.38-7.35 (m, 1H), 7.30-7.30 (m, 1H), 7.28-7.18 (m, 3H), 7.11-7.09 (m, 2H), 6.97-6.91 (m, 3H), 4.66-4.58 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.59, 159.86, 140.31, 131.72, 130.49, 129.49, 128.74, 128.60, 128.21, 128.08, 126.30, 125.57, 121.56, 114.77, 111.82, 86.08, 82.82, 75.72, 58.09, 55.37, 38.68; IR (ATR): 2958, 2839, 1715, 1556, 1441, 1374, 1254, 1116, 1032; HRMS (ESI): Exact mass calcd for $C_{25}H_{20}N_2O_4{}^{35}Cl$ $[M+H]^+$: 447.1106, Found: 447.1104.



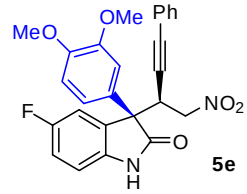
5c

The total reaction time was 2 days. Product **5c** was obtained in 97% yield as white solid. (dr = 8:1, 99% ee for the major diastereomer); $[\alpha]^{25}_D$ = +8.2 (c = 0.98, $CHCl_3$), m.p. 96-98 °C; HPLC analysis: Chiralpak IC, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; major diastereomer: t_r (minor) = 14.13 min, t_r (major) = 15.44 min; minor diastereomer: t_r (minor) = 12.61 min, t_r (major) = 18.88 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.53-7.50 (m, 1H), 7.46-7.44 (m, 3H), 7.28-7.18 (m, 3H), 7.11-7.09 (m, 2H), 6.93-6.90 (m, 3H), 4.67-4.57 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.57, 159.86, 140.79, 132.38, 131.73, 130.95, 129.00, 128.76, 128.60, 128.22, 125.58, 121.55, 115.34, 114.78, 112.33, 86.13, 82.85, 75.72, 58.05, 55.38, 38.66; IR (ATR): 2925, 1714, 1613, 1555, 1440, 1374, 1252, 1117; HRMS (ESI): Exact mass calcd for $C_{25}H_{20}N_2O_4{}^{79}Br$ $[M+H]^+$: 491.0601, Found: 447.0597.



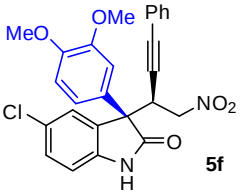
5d

The total reaction time was 4 days. Product **5d** was obtained in 44% yield as white solid. (dr = 17:1, 99% ee for the major diastereomer); $[\alpha]^{25}_{D}$ = +72.0 (c = 1.14, $CHCl_3$), m.p. 86-88 ^{o}C; HPLC analysis: Chiralpak AD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 10.84 min, t_r (minor) = 16.63 min; minor diastereomer: t_r (major) = 9.01 min, t_r (minor) = 11.98 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.26-7.13 (m, 5H), 7.09-7.05 (m, 3H), 6.98-6.91 (m, 2H), 6.81-6.79 (m, 1H), 4.72-4.59 (m, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.30, 149.43, 149.23, 139.28, 132.11, 131.73, 129.82, 128.51, 128.12, 126.99, 126.63, 121.91, 120.28, 111.16, 110.46, 85.62, 83.39, 76.12, 58.02, 56.01, 55.87, 39.08, 21.44; IR (ATR): 3296, 2920, 2851, 1711, 1624, 1556, 1463, 1442, 1375, 1259, 1149; HRMS (ESI): Exact mass calcd for $C_{27}H_{25}N_2O_5$ $[M+H]^+$: 457.1758, Found: 457.1754.



5e

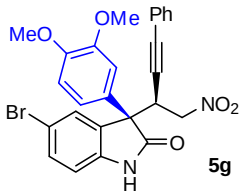
The total reaction time was 4 days. Product **5e** was obtained in 96% yield as white solid. (dr = 14:1, 99% ee for the major diastereomer); $[\alpha]^{25}_{D}$ = +85.5 (c = 0.54, $CHCl_3$), m.p. 95-97 ^{o}C; HPLC analysis: Chiralpak AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 15.16 min, t_r (minor) = 27.81 min; minor diastereomer: t_r (major) = 12.19 min, t_r (minor) = 17.77 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.24-7.24 (m, 2H), 7.22-7.18 (m, 2H), 7.14-7.08 (m, 4H), 6.98-6.93 (m, 2H), 6.83-6.81 (m, 1H), 4.66-4.61 (m, 3H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.47, 158.79 (d, J_{F-C} = 240.0 Hz), 149.51 (d, J_{F-C} = 13.0 Hz), 137.69, 131.68, 130.06 (d, J_{F-C} = 8.0 Hz), 128.74, 128.22, 126.10, 121.56, 120.09, 116.02 (d, J_{F-C} = 23.0 Hz), 113.95 (d, J_{F-C} = 25.0 Hz), 111.39 (d, J_{F-C} = 8.0 Hz), 111.23, 110.17, 86.01, 82.86, 75.86, 58.41, 56.04, 55.90, 38.91; ^{19}F NMR (376 MHz, $CDCl_3$): δ -119.19; IR (ATR): 3674, 2987, 1717, 1631, 1556, 1516, 1486, 1259, 1067; HRMS (ESI): Exact mass calcd for $C_{26}H_{22}N_2O_5F$ $[M+H]^+$: 461.1507, Found: 461.1507.



5f

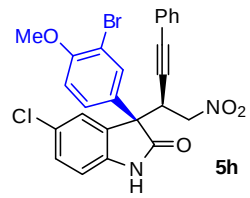
The total reaction time was 3 days. Product **5f** was obtained in 93% yield as white solid. (dr = 15:1, 99% ee for the major diastereomer); $[\alpha]^{25}_{D}$ = +48.8 (c = 0.50, $CHCl_3$), m.p. 96-98 ^{o}C; HPLC analysis: Chiralpak AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 13.08 min, t_r (minor) = 25.73

min; minor diastereomer: t_r (major) = 10.73 min, t_r (minor) = 15.95 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.39-7.36 (m, 1H), 7.32-7.31 (m, 1H), 7.25-7.24 (m, 2H), 7.22-7.18 (m, 2H), 7.11-7.09 (m, 2H), 6.97-6.95 (m, 1H), 6.93-6.91 (m, 1H), 6.83-6.81 (m, 1H), 4.66-4.58 (m, 3H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.42, 149.58, 149.47, 140.34, 131.69, 130.35, 129.51, 128.78, 128.23, 128.03, 126.29, 126.01, 121.51, 120.16, 111.81, 111.27, 110.17, 86.09, 82.88, 75.84, 58.25, 56.05, 55.90, 38.87; IR (ATR): 3292, 2932, 1718, 1619, 1556, 1477, 1374, 1258, 1146; HRMS (ESI): Exact mass calcd for $C_{26}H_{25}N_3O_5{}^{35}Cl$ $[M+NH_4]^+$: 494.1477, Found: 494.1479.



5g

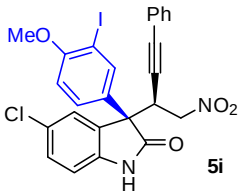
The total reaction time was 8 days. Product **5g** was obtained in 94% yield as white solid. (dr > 20:1, 99% ee for the major diastereomer); $[\alpha]^{25}_D$ = +30.1 (c = 0.53, $CHCl_3$), m.p. 106-108 °C; HPLC analysis: Chiralpak AD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 10.20 min, t_r (minor) = 18.72 min; minor diastereomer: t_r (major) = 8.63 min, t_r (minor) = 12.20 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.53-7.51 (m, 1H), 7.46-7.45 (m, 1H), 7.24-7.24 (m, 2H), 7.22-7.18 (m, 2H), 7.11-7.09 (m, 2H), 6.93-6.91 (m, 2H), 6.83-6.81 (m, 1H), 4.66-4.57 (m, 3H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.11, 149.59, 149.47, 140.69, 132.39, 131.71, 130.75, 129.07, 128.78, 128.24, 125.96, 121.51, 120.14, 115.26, 112.19, 111.24, 110.11, 86.11, 82.86, 75.82, 58.14, 56.05, 55.91, 38.88; IR (ATR): 3277, 2924, 1715, 1616, 1555, 1515, 1258, 1173, 1120; HRMS (ESI): Exact mass calcd for $C_{26}H_{25}N_3O_5{}^{79}Br$ $[M+NH_4]^+$: 538.0972, Found: 538.0973.



5h

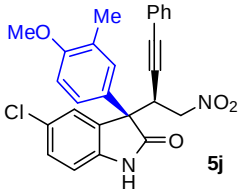
The total reaction time was 2 days. Product **5h** was obtained in 71% yield as white solid. (dr > 20:1, 99% ee for the major diastereomer); $[\alpha]^{25}_D$ = +44.3 (c = 1.05, $CHCl_3$), m.p. 124-126 °C; HPLC analysis: Chiralpak IC, ^{i}PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; major diastereomer: t_r (minor) = 23.19 min, t_r (major) = 31.12 min; minor diastereomer: t_r (minor) = 28.46 min, t_r (major) = 50.06 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.64-7.64 (m, 1H), 7.58-7.55 (m, 1H), 7.40-7.37 (m, 1H), 7.33-7.32 (m, 1H), 7.29-7.25 (m, 1H), 7.23-7.20 (m, 2H), 7.13-7.11 (m, 2H), 6.98-6.93 (m, 2H), 4.67-4.60 (m, 2H), 4.57-4.51 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.83, 156.28, 140.07, 132.22, 131.73, 129.87, 129.80, 128.85, 128.36, 128.25, 127.68, 127.13, 126.23, 121.42, 112.57, 112.35, 111.92, 86.37, 82.49, 75.53,

57.48, 56.37, 38.77; IR (ATR): 3081, 2923, 2852, 1731, 1698, 1596, 1496, 1370, 1264, 1191; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}N_3O_4{}^{35}Cl^{79}Br$ $[M+NH_4]^+$: 542.0477, Found: 542.0478.



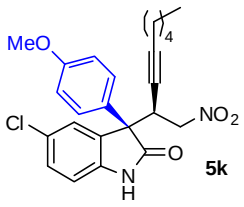
5i

The total reaction time was 1 days. Product **5i** was obtained in 56% yield as white solid. (dr > 20:1, 99% ee for the major diastereomer); $[\alpha]^{25}_D$ = +53.6 (c = 0.46, $CHCl_3$), m.p. 111-113 °C; HPLC analysis: Chiralpak IC, ^{i}PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; major diastereomer: t_r (minor) = 20.24 min, t_r (major) = 30.11 min; minor diastereomer: t_r (minor) = 25.54 min, t_r (major) = 48.92 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 1H), 7.87 (d, *J* = 2.4 Hz, 1H), 7.57-7.54 (m, 1H), 7.36-7.33 (m, 1H), 7.30-7.29 (m, 1H), 7.24-7.22 (m, 1H), 7.20-7.16 (m, 2H), 7.10-7.08 (m, 2H), 7.01-6.98 (m, 1H), 6.83-6.81 (m, 1H), 4.67-4.59 (m, 2H), 4.51-4.48 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.99, 158.54, 140.10, 138.24, 131.74, 129.98, 129.78, 128.85, 128.72, 128.34, 128.26, 127.73, 126.18, 121.44, 111.99, 111.22, 86.95, 86.40, 82.57, 75.56, 57.33, 56.51, 38.75; IR (ATR): 3184, 2838, 1716, 1618, 1594, 1489, 1373, 1259, 1199; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}N_3O_4{}^{35}ClI$ $[M+NH_4]^+$: 590.0338, Found: 590.0336.

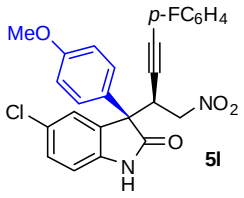


5j

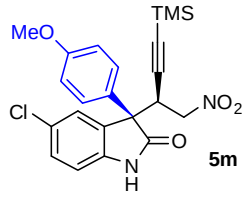
The total reaction time was 3 days. Product **5j** was obtained in 99% yield as white solid. (dr = 10:1, 99% ee for the major diastereomer); $[\alpha]^{25}_D$ = +67.4 (c = 0.54, $CHCl_3$), m.p. 97-99 °C; HPLC analysis: Chiralpak IC, ^{i}PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; major diastereomer: t_r (minor) = 14.75 min, t_r (major) = 21.46 min; minor diastereomer: t_r (minor) = 16.97 min, t_r (major) = 32.54 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51-8.44 (m, 1H), 7.36-7.34 (m, 1H), 7.31-7.28 (m, 3H), 7.25-7.23 (m, 1H), 7.21-7.17 (m, 2H), 7.10-7.08 (m, 2H), 6.97-6.95 (m, 1H), 6.82-6.80 (m, 1H), 4.70-4.57 (m, 3H), 3.81 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.45, 158.22, 140.34, 131.84, 130.82, 129.48, 129.40, 128.79, 128.30, 128.13, 128.00, 126.47, 126.07, 125.20, 121.78, 111.70, 110.49, 86.08, 83.14, 75.89, 58.16, 55.50, 38.68, 16.69; IR (ATR): 3215, 2921, 2838, 1715, 1619, 1557, 1441, 1303, 1254, 1174; HRMS (ESI): Exact mass calcd for $C_{26}H_{22}N_2O_4{}^{35}Cl$ $[M+H]^+$: 461.1263, Found: 461.1266.



The total reaction time was 3 days. Product **5k** was obtained in 98% yield as white solid. (dr = 8:1, 99% ee for the major diastereomer); $[\alpha]^{25}_{D}$ = +125.8 (c = 1.01, $CHCl_3$), m.p. 60-62 ^{o}C; HPLC analysis: Chiralpak IC, ^{i}PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; major diastereomer: t_r (minor) = 15.88 min, t_r (major) = 27.80 min; minor diastereomer: t_r (minor) = 18.00 min, t_r (major) = 38.21 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 1H), 7.39-7.32 (m, 3H), 7.21-7.20 (m, 1H), 6.98-6.96 (m, 1H), 6.89-6.86 (m, 2H), 4.54-4.51 (m, 2H), 4.39-4.36 (m, 1H), 3.77 (s, 3H), 1.95 (td, *J* = 6.8, 2.0 Hz, 2H), 1.26-1.18 (m, 4H), 1.12-1.06 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) :δ 178.76, 159.76, 140.42, 130.61, 129.25, 128.52, 127.90, 126.22, 125.82, 114.66, 111.73, 87.01, 76.26, 73.52, 58.21, 55.33, 38.23, 30.65, 27.97, 22.14, 18.39, 13.94; IR (ATR): 3208, 2930, 2857, 1714, 1618, 1556, 1478, 1375, 1253, 1184; HRMS (ESI): Exact mass calcd for $C_{24}H_{26}N_2O_4{}^{35}Cl$ $[M+H]^+$: 441.1576, Found: 441.1573.

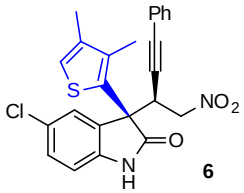


The total reaction time was 3.5 days. Product **5l** was obtained in 96% yield as yellowish solid. (dr = 8:1, 99% ee for the major diastereomer); $[\alpha]^{25}_{D}$ = +32.6 (c = 0.53, $CHCl_3$), m.p. 90-92 ^{o}C; HPLC analysis: Chiralpak IE, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 16.65 min, t_r (minor) = 22.19 min; minor diastereomer: t_r (minor) = 12.23 min, t_r (major) = 13.58 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.45-7.43 (m, 2H), 7.39-7.36 (m, 1H), 7.29-7.28 (m, 1H), 7.09-7.05 (m, 2H), 6.97-6.87 (m, 5H), 4.64-4.57 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.30, 162.65 (d, $J_{F\text{-}C}$ = 249.0 Hz), 159.91, 140.21, 133.66 (d, $J_{F\text{-}C}$ = 9.0 Hz), 130.39, 129.51, 128.55, 128.14, 126.36, 125.41, 117.60 (d, $J_{F\text{-}C}$ = 3.0 Hz), 115.53 (d, $J_{F\text{-}C}$ = 22.0 Hz), 114.80, 111.66, 84.99, 82.56, 75.64, 58.04, 55.37, 38.67; ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.85; IR (ATR): 3187, 2934, 1602, 1556, 1478, 1374, 1297, 1253, 1230, 1184; HRMS (ESI): Exact mass calcd for $C_{25}H_{19}N_2O_4F^{35}Cl$ $[M+H]^+$: 465.1012, Found: 465.1014.



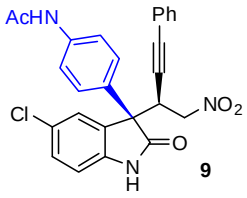
The total reaction time was 3.5 days. Product **5m** was obtained in 99% yield as yellowish solid. (dr = 8:1, 99% ee for the major diastereomer); $[\alpha]^{25}_{D}$ = +91.0 (c = 4.00, $CHCl_3$), m.p. 77-79 ^{o}C; HPLC analysis: Chiralpak IC, ^{i}PrOH/hexane = 3/97, 1.0 mL/min, 230 nm; major diastereomer: t_r (minor) = 22.06 min, t_r (major) = 44.77 min; minor diastereomer: t_r (minor) = 26.63 min, t_r (major) = 60.74 min; ^{1}H NMR (400 MHz,

$CDCl_3$): δ 8.05 (s, 1H), 7.43-7.40 (m, 2H), 7.36-7.33 (m, 1H), 7.28-7.28 (m, 1H), 6.94-6.88 (m, 3H), 4.61 (ABd, *J* = 12.4, 3.6 Hz, 1H), 4.56-4.50 (m, 1H), 4.34 (ABd, *J* = 10.8, 3.2 Hz, 1H), 3.80 (s, 3H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.76, 159.87, 140.40, 130.74, 129.32, 128.69, 128.02, 126.39, 125.65, 114.74, 111.78, 99.50, 91.84, 75.68, 57.90, 55.41, 38.78, -0.39; IR (ATR): 3223, 2838, 1718, 1620, 1511, 1479, 1374, 1251, 1185, 1117; HRMS (ESI): Exact mass calcd for $C_{22}H_{24}N_2O_4Si^{35}Cl$ $[M+H]^+$: 443.1188, Found: 443.1190.



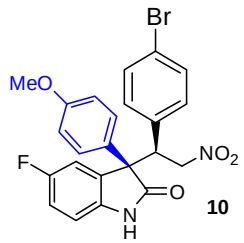
6

The total reaction time was 1.5 days. Product **6** was obtained in 82% yield as yellowish solid. (dr = 1.5:1, 99% ee for the major diastereomer); HPLC analysis: Chiralpak AD-H, ^{i}PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 20.97 min, t_r (minor) = 26.60 min; minor diastereomer: t_r (major) = 16.88 min, t_r (minor) = 23.99 min. The major diastereomer: $[\alpha]^{25}_D$ = +41.5 (c = 0.56, $CHCl_3$), m.p. 98-100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.35-7.33 (m, 1H), 7.29-7.16 (m, 6H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.86 (s, 1H), 5.03 (ABd, *J* = 12.8, 2.8 Hz, 1H), 4.88-4.83 (m, 1H), 4.68 (ABd, *J* = 10.4, 2.8 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.35, 140.22, 139.39, 136.80, 131.74, 131.48, 129.76, 129.45, 128.84, 128.25, 128.16, 126.36, 121.58, 120.04, 111.39, 86.76, 82.76, 75.81, 56.75, 37.95, 15.70, 13.75; IR (ATR): 3198, 2920, 1716, 1618, 1556, 1477, 1373, 1204, 1175; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}N_3O_3{}^{35}ClS$ $[M+NH_4]^+$: 468.1143, Found: 468.1144. The minor diastereomer: $[\alpha]^{25}_D$ = +25.2 (c = 0.16, CH_2Cl_2), m.p. 89-91 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ8.29 (s, br, 1H), 7.42-7.42 (m, 1H), 7.31-7.21 (m, 4H), 7.16-714 (m, 2H), 6.91-6.89 (m, 2H), 4.87-4.80 (m, 1H), 4.72-4.64 (m, 2H), 2.10 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.89, 139.81, 138.76, 135.77, 132.00, 131.74, 131.46, 129.46, 128.93, 128.83, 128.29, 125.71, 121.63, 119.33, 111.11, 86.59, 82.68, 75.87, 56.21, 38.69, 15.63, 13.16; IR (ATR): 3225, 2922, 1713, 1617, 1556, 1441, 1375, 1208, 1177, 1069; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}N_3O_3{}^{35}ClS$ $[M+NH_4]^+$: 468.1143, Found: 468.1149.



9

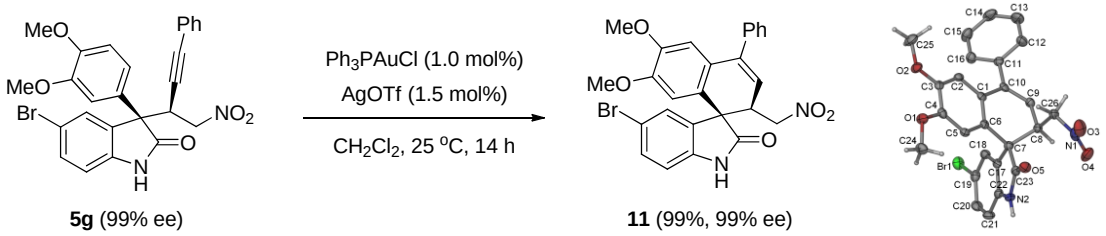
2.0 mol% of (2,4-^{t}Bu$_2$C$_6$H$_3$O)$_3$PAuSbF$_6$ and 2.0 equivalents of acetanilide were used. The total reaction time was 5 days. Product **9** was obtained in 55% yield as colorless oil. (dr = 5.0:1, 93% ee for the major diastereomer); HPLC analysis: Chiralpak OD-H, ^{i}PrOH/hexane = 25/75, 1.0 mL/min, 230 nm; major diastereomer: t_r (minor) = 6.22 min, t_r (major) = 9.35 min. The major diastereomer: $[\alpha]^{25}_{D}$ = +37.4 (c = 0.95, acetone), m.p. 121-123 ^{o}C; ^{1}H NMR (400 MHz, acetone-d_6): δ 9.90 (s, 1H), 9.31 (s, 1H), 7.71-7.67 (m, 3H), 7.53-7.49 (m, 2H), 7.45-7.42 (m, 1H), 7.34-7.26 (m, 3H), 7.15-7.12 (m, 3H), 4.94-4.79 (m, 2H), 4.64-4.60 (m, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ 177.44, 169.08, 142.76, 140.69, 132.38, 131.42, 130.18, 129.92, 129.61, 129.29, 128.70, 127.80, 127.49, 122.84, 120.27, 120.18, 112.37, 85.79, 84.99, 76.86, 58.98, 39.82, 24.26; IR (ATR): 3260, 2925, 1713, 1599, 1556, 1512, 1477, 1373, 1321; HRMS (ESI): Exact mass calcd for $C_{26}H_{24}N_4O_4{}^{35}Cl$ $[M+NH_4]^+$: 491.1481, Found: 491.1479.



10

The total reaction time was 4 days. Product **10** was obtained in 83% yield as white solid. (dr = 6:1, 97% ee for the major diastereomer); HPLC analysis: Chiralpak AD, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; major diastereomer: t_r (minor) = 24.64 min, t_r (major) = 45.61 min; The major diastereomer: $[\alpha]^{25}_{D}$ = +121.0 (c = 1.86, $CHCl_3$), m.p. 131-133 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.49-7.47 (m, 2H), 7.26-7.22 (m, 2H), 7.10-7.04 (m, 2H), 6.93-6.91 (m, 2H), 6.78-6.76 (m, 2H), 6.72-6.68 (m, 1H), 4.93-4.86 (m, 1H), 4.75-4.70 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.38, 159.80, 158.66 (d, $J_{F\text{-}C}$ = 241.0 Hz), 137.54 (d, $J_{F\text{-}C}$ = 3.0 Hz), 132.55, 131.35, 130.56, 129.14 (d, $J_{F\text{-}C}$ = 7.0 Hz), 128.55, 126.52, 122.65, 116.18 (d, $J_{F\text{-}C}$ = 23.0 Hz), 114.75, 114.08 (d, $J_{F\text{-}C}$ = 25.0 Hz), 111.54 (d, $J_{F\text{-}C}$ = 8.0 Hz), 75.73, 59.74 (d, $J_{F\text{-}C}$ = 2.0 Hz), 55.33, 49.78; ^{19}F NMR (282 MHz, $CDCl_3$): δ -118.94; IR (ATR): 3411, 2929, 1713, 15556, 1488, 1415, 1256, 1184, 1032, 1010; MS (EI): 484, 486 (M^+, 1, 1), 256 (100), 102 (32), 228 (31), 185 (26), 214 (20), 118 (15), 75 (14); HRMS (EI): Exact mass calcd for $C_{23}H_{18}N_2O_4F^{79}Br$ $[M]^+$: 484.0434, Found: 484.0427.

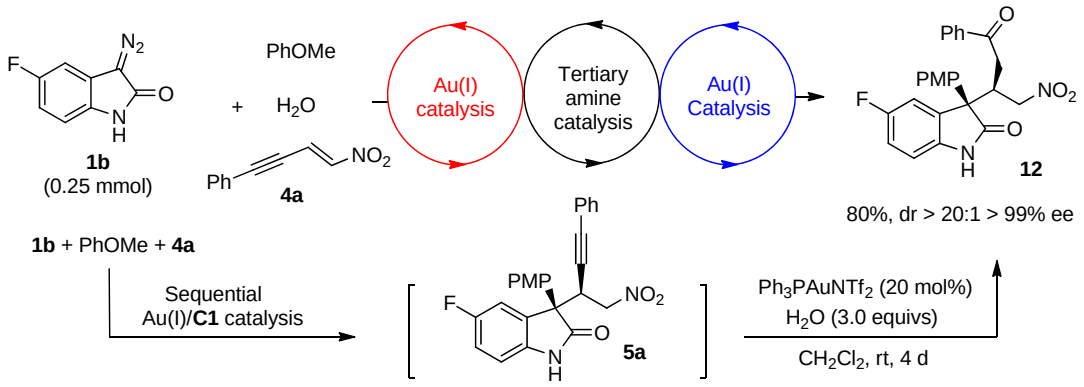
5) The synthesis of spirocyclic oxindole 11 from 5g



5g (99% ee) **11** (99%, 99% ee)

Under an atmosphere of nitrogen, to a Schlenk tube were added Ph_3PAuCl (1.2 mg, 0.0025 mmol) and AgOTf (1.0 mg, 0.0038 mmol), followed by anhydrous CH_2Cl_2 (2 mL). The resulting mixture was stirred at 25 ^oC for 15-20 minutes, and then 3,3-disubstituted oxindole **5g** (138.4 mg, 0.26 mmol) was added. The reaction was kept stirring at 25 ^oC for about 14 h till full conversion of oxindole **5g** by TLC analysis. The solvent was directly subjected to column chromatography to afford the desired product **11** (137.4 mg, 0.26 mmol), using CH_2Cl_2/acetone (100/1) as eluent. Product **11** was obtained in 99% yield as white solid. $[\alpha]^{25}_D$ = -81.1 (c = 0.38, CH_2Cl_2), m.p. 136-138 ^oC; HPLC analysis (Chiralpak IE, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; t_r (major) = 17.09 min, t_r (minor) = 25.08 min) gave the isomeric composition of the product: 99% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.49-7.44 (m, 6H), 7.38 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.71 (s, 1H), 6.43 (s, 1H), 5.84 (d, *J* = 6.0 Hz, 1H), 4.99 (ABd, *J* = 13.2, 5.6 Hz, 1H), 4.45 (ABd, *J* = 13.2, 8.8 Hz, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.62 (dt, *J* = 9.2, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.21, 149.43, 148.79, 142.72, 139.08, 138.70, 133.90, 132.08, 128.81, 128.65, 128.47, 127.78, 126.42, 125.88, 120.25, 115.75, 112.44, 111.45, 110.39, 74.48, 56.23, 56.09, 54.32, 39.86; IR (ATR): 3258, 2930, 1711, 1613, 1550, 1469, 1356, 1310, 1212, 1165; HRMS (ESI): Exact mass calcd for $C_{26}H_{22}N_2O_5{}^{79}Br$ $[M+H]^+$: 521.0707, Found: 521.0706.

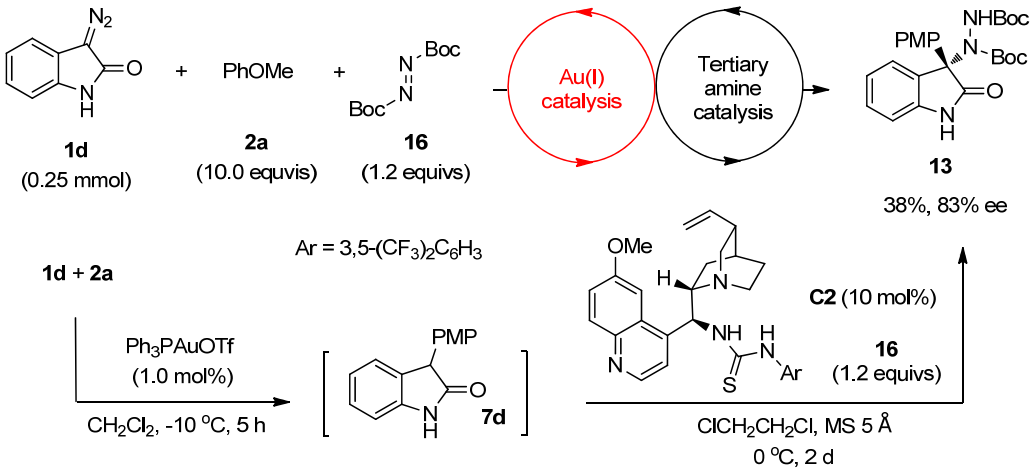
6) One-pot triple asymmetric tandem C-H insertion/Michael/hydration sequence to 12



Till the completion of the tandem C-H functionalization/Michael sequence which was conducted according to the general procedure described above, the crude reaction mixture was filtered through a short silica gel column and then solvent was carefully removed under reduced pressure. To this mixture was added Ph_3PAuCl (24.7 mg, 0.05 mmol) and $AgNTf_2$ (21.3 mg, 0.055 mmol), CH_2Cl_2 (2.5 mL), H_2O (13.5 mg, 0.75 mmol) successively and then stirred at rt for 4 days. To determine the diastereoselectivity of product, the residue was first dissolved in $CDCl_3$, and some samples were taken for NMR analysis. Then the sample for analysis and the rest mixture were recombined for column chromatographic purification using petroleum ether/ethyl acetate (from 2:1 to 1:3) as the eluent to give the product **12** in 80% yield as yellow oil. (dr > 20:1, 99% ee for the major diastereomer); $[\alpha]^{25}_D$ = -36.8 (c = 1.00, CH_2Cl_2); HPLC analysis: Chiralcel IE, ^{i}PrOH/hexane = 25/75, 1.0 mL/min, 230 nm; major diastereomer: t_r (minor) = 23.86 min, t_r (major) = 63.03 min; minor diastereomer: t_r (minor) = 22.00 min, t_r (major) = 27.77 min; ^{1}H NMR (400 MHz, acetone-d_6): δ 9.83 (s, 1H), 7.85-7.82 (m, 2H), 7.62-7.57 (m, 1H), 7.53-7.42 (m, 5H), 7.14-7.03 (m, 2H), 6.94-6.91 (m, 2H), 4.68-4.63 (m, 1H), 4.51-4.47 (m, 1H), 4.36-4.30 (m, 1H), 3.75 (s, 3H), 3.33-3.27 (m, 1H), 3.19-3.14 (m, 1H); ^{13}C NMR (125 MHz, acetone-d_6): δ 196.91, 177.69, 159.42, 158.86 (d, $J_{C\text{-}F}$ = 237.5 Hz), 138.01, 136.60, 133.14, 131.74 (d, $J_{C\text{-}F}$ = 7.5 Hz), 129.41, 128.55, 128.47, 127.85, 115.25 (d, $J_{C\text{-}F}$ = 23.8 Hz), 114.20, 113.44 (d, $J_{C\text{-}F}$ = 25.0 Hz), 111.08 (d, $J_{C\text{-}F}$ = 8.8 Hz), 76.97, 58.86, 54.64, 39.36, 38.15; ^{19}F NMR (376 MHz, acetone-d_6): δ -126.41; IR (ATR): 2927, 1711, 1607, 1554, 1511, 1486, 1294, 1253, 1182, 1031; MS (EI): 448 (M^+, 5), 105 (100), 257 (96), 77 (84), 256 (76), 228 (45), 185 (38), 51 (36); HRMS (EI): Exact mass calcd for $C_{25}H_{21}FN_2O_5$ $[M]^+$: 448.1434, Found: 448.1437.

7) Sequential catalysis for 3-heteroatom oxindoles 13-15

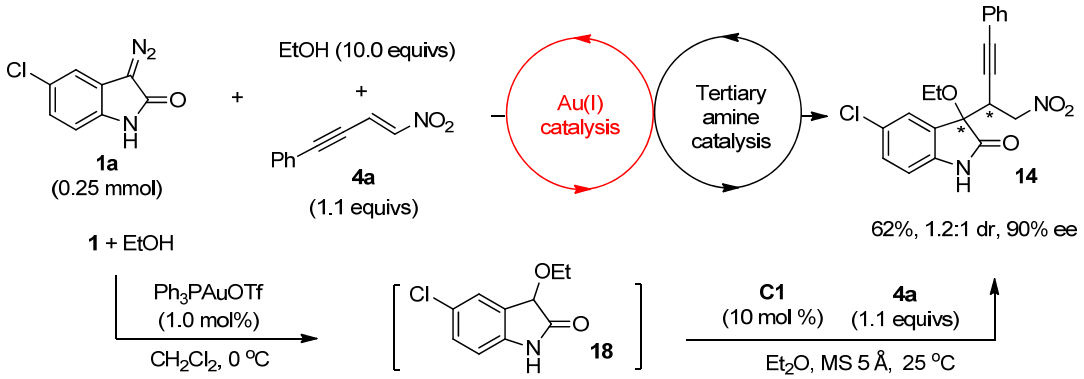
7.1) Tandem C-H insertion/asymmetric amination sequence to 13



Under an atmosphere of N_2, to a Schlenk tube were added Ph_3PAuCl (1.2 mg, 0.0025 mmol) and AgOTf (1.0 mg, 0.0038 mmol), followed by anhydrous CH_2Cl_2 (4.0 mL). The resulting mixture was stirred at 25 °C for 15 minutes. The mixture was cooled down to the -10 °C for half an hour. Anisole **2a** (2.5 mmol) and diazooxindole **1d** (0.25 mmol) were added successively. The reaction was kept stirring for 5 h till full conversion of diazooxindole **1d** by TLC analysis. After the solvent was removed under reduced pressure, $ClCH_2CH_2Cl$ (2.5 mL), 5Å MS (250 mg), catalyst **C2** (14.9 mg, 0.025 mmol) were added successively and the reaction mixture was cooled down to 0 °C for about 30 min before DBAD **16** (69.0 mg, 0.30 mmol) was added. After the full conversion of reaction by TLC analysis, the mixture was directly subjected to column chromatography using CH_2Cl_2/EtOAc (from 15:1 to 10:1) as the eluent, affording 40.9 mg of desired product **13**[9] as red solid. HPLC analysis: (Chiralcel OD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm, t_r (minor) = 4.96 min, t_r (major) = 7.62 min) gave the isomeric composition of the product: 83% ee; $[\alpha]^{25}_D$ = +46.3 (c = 1.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, br, 1H), 8.10-8.08 (m, 1H), 7.54-7.52 (m, 2H), 7.27-7.22 (m, 1H), 7.16-7.12 (m, 1H), 6.82-6.80 (m, 3H), 6.40 (s, br, 1H), 3.76 (s, 3H), 1.33 (s, 9H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.30, 159.68, 154.89, 153.43, 139.98, 130.94, 128.52, 126.76, 125.39, 122.58, 113.48, 109.91, 82.68, 80.82, 72.13, 55.28, 28.09, 27.81.

[9] F. Zhou, M. Ding, Y.-L. Liu, C.-H. Wang, C.-B. Ji, Y.-Y. Zhang and J. Zhou, *Adv. Synth. Cat.,* 2011, **353**, 2945.

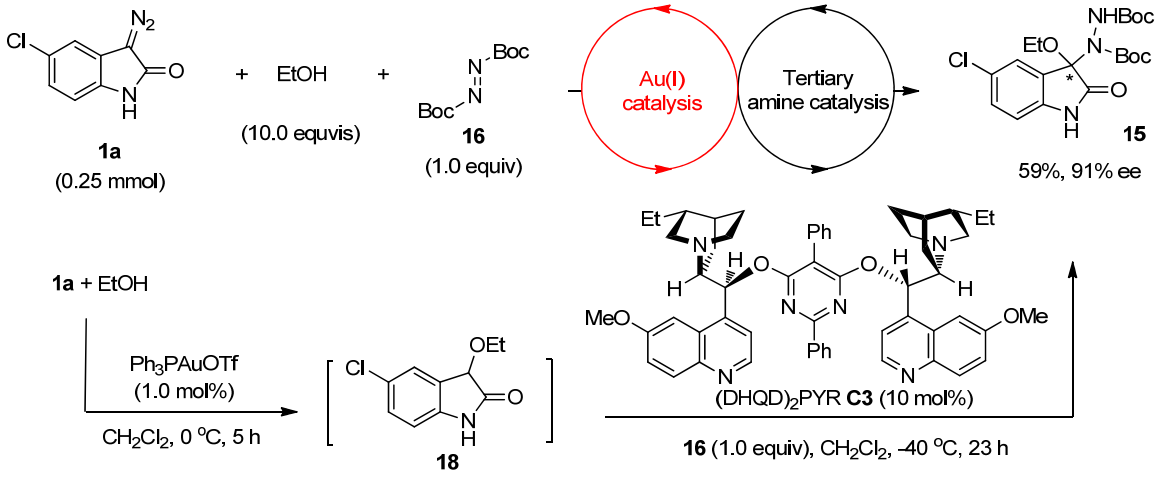
7.2) Tandem O-H insertion/ Michael addition sequence to 14



Under an atmosphere of nitrogen, to a Schlenk tube were added Ph_3PAuCl (1.2 mg, 0.0025 mmol) and AgOTf (1.0 mg, 0.0038 mmol), followed by anhydrous CH_2Cl_2 (4.0 mL). The resulting mixture was stirred at 25 ^oC for 15-20 minutes. The mixture was cooled down to the indicated temperature. EtOH (2.5 mmol) and diazooxindole **1a** (0.25 mmol) were added successively. The reaction was kept stirring for about 1-10 h till full conversion of diazooxindole **1a** by TLC analysis. After anhydrous CH_2Cl_2 and excess EtOH were removed under reduced pressure, Et_2O (4.0 mL), powdered MS 5Å (125.0 mg) and chiral catalyst **C1** (11.4 mg, 0.025 mmol) were added successively. The reaction mixture was cooled down to specified temperature, followed by the addition of nitroenynes **4a** (0.28 mmol). The resulting mixture was stirring till full conversion of 3-ethoxyoxindoles **18** by TLC analysis. The solvent was carefully removed under reduced pressure. To determine the diastereoselectivity of product, the residue was first dissolved in $CDCl_3$, and some samples were taken for the determination of diastereoselectivity by NMR analysis. Then the sample for analysis and the rest of the product were recombined for column chromatographic purification using CH_2Cl_2/petroleum ether (4:1) as the eluent. The total reaction time was 2 days. Product **14** was obtained in 62% yield as yellowish solid. (dr = 1.2:1, 90% ee for the major diastereomer); HPLC analysis: Chiralpak AD-H, ^{i}PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 14.62 min, t_r (minor) = 21.84 min; minor diastereomer: t_r (major) = 13.37 min, t_r (minor) = 19.86 min. The minor diastereomer: $[\alpha]^{25}_D$ = -96.2 (c = 1.34, CH_2Cl_2), m.p. 120-121 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.63-8.67 (m, 1H), 7.41-7.41 (m, 1H), 7.35-7.31 (m, 1H), 7.25-7.21 (m, 1H), 7.19-7.15 (m, 2H), 7.08-7.03 (m, 2H), 6.90-6.87 (m, 1H), 5.24 (ABd, *J* = 13.6, 4.4 Hz, 1H), 4.92-4.86 (m, 1H), 4.17 (ABd, *J* = 9.2, 4.4 Hz, 1H), 3.34-3.17 (m, 2H), 1.16 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100

MHz, $CDCl_3$): δ 175.88, 140.11, 131.75, 130.90, 129.29, 128.82, 128.38, 128.29, 124.85, 121.64, 111.49, 85.28, 82.46, 81.46, 73.85, 62.56, 39.10, 15.20; IR (ATR): 3397, 3046, 2925, 1727, 1552, 1473, 1376, 1275, 1121; HRMS (ESI): Exact mass calcd for $C_{20}H_{21}N_3O_4{}^{35}Cl$ $[M+NH_4]^+$: 402.1215, Found: 402.1221. The major diastereomer: $[\alpha]^{25}_D$ = -63.7 (c = 1.21, CH_2Cl_2), m.p. 152-154 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.80-8.72 (m, 1H), 7.47-7.47 (m, 1H), 7.37-7.34 (m, 1H), 7.28-7.18 (m, 5H), 6.94-6.92 (m, 1H), 5.31 (ABd, *J* = 13.2, 4.8 Hz, 1H), 4.78-4.72 (m, 1H), 4.01 (ABd, *J* = 9.6, 4.4 Hz, 1H), 3.33-3.26 (m, 1H), 3.23-3.15 (m, 1H), 1.17 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.60, 139.95, 131.83, 130.91, 128.91, 128.82, 128.39, 126.92, 126.23, 121.79, 111.96, 86.26, 82.31, 81.96, 74.13, 62.63, 38.76, 15.22; IR (ATR): 3209, 2924, 2242, 1724, 1683, 1556, 1470, 1381, 1278, 1182; HRMS (ESI): Exact mass calcd for $C_{20}H_{21}N_4O_3{}^{35}Cl$ $[M+NH_4]^+$: 402.1215, Found: 402.1221.

7.3) Tandem O-H insertion/ amination sequence to 15



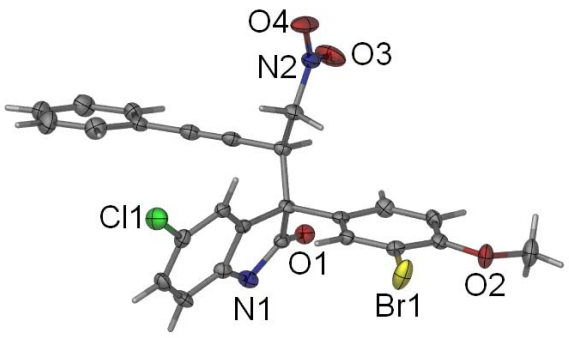
Under an atmosphere of N_2, to a Schlenk tube were added Ph_3PAuCl (1.2 mg, 0.0025 mmol) and AgOTf (1.0 mg, 0.0038 mmol), followed by anhydrous CH_2Cl_2 (4.0 mL). The resulting mixture was stirred at 25 °C for 15 minutes. The mixture was cooled down to the 0 °C for half an hour. EtOH (2.5 mmol) and diazooxindole **1a** (0.25 mmol) were added successively. The reaction was kept stirring for 5 h till full conversion of diazooxindole **1a** by TLC analysis. After anhydrous CH_2Cl_2 and excess EtOH were removed under reduced pressure, CH_2Cl_2 (2.5 mL), catalyst $(DHQD)_2PYR$ **C3** (22.0 mg, 0.025 mmol) were added successively and the reaction mixture was cooled down to -40 °C for about 30 min

before DBAD **16** (57.5 mg, 0.25 mmol) was added. After the full conversion of 3-ethoxyindole **18** by TLC analysis, the mixture was directly subjected to column chromatography using CH_2Cl_2/EtOAc (from 15:1 to 10:1) as the eluent, affording 65.3 mg desired product **15**[10] as yellow oil. (HPLC analysis: Chiralcel OZ-H, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm, t_r (minor) = 5.53 min, t_r (major) = 6.27 min) gave the isomeric composition of the product: 91% ee; $[\alpha]^{25}_{D}$ = -9.1 (c = 1.42, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, br, 1H), 7.734-7.728 (m, 1H), 7.24-7.21 (m, 1H), 6.86-6.76 (m, 2H), 3.70-3.63 (m, 1H), 3.57-3.50 (m, 1H), 1.55-1.35 (m, 9H), 1.35-1.27 (m, 9H), 1.19-1.14 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.29, 155.38, 152.99, 139.72, 130.13, 128.17, 128.10, 126.59, 111.43, 88.63, 83.06, 81.29, 62.16, 28.24, 27.88, 15.13; MS (EI): 441 (M^+, 1), 57 (100), 182 (57), 210 (56), 56 (42), 211 (23), 183 (23), 212 (21); IR (ATR): 2980, 1734, 1622, 1474, 1367, 1249, 1153, 1067; HRMS (EI): Exact mass calcd for $C_{20}H_{28}N_3O_6{}^{35}Cl$ $[M]^+$: 441.1667, Found: 441.1664.

[10] F. Zhou, X.-P. Zeng, C. Wang, X.-L. Zhao, and J. Zhou, *Chem. Commun.,* 2013, **49**, 2022.

8) Single-Crystal X-ray Crystallography data of 5h and 11

8.1) Single-Crystal X-ray Crystallography of 5h[11]



Data intensity of **5h** was collected using a Bruker SMART APEX II (Mo radiation). The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **5h**: $C_{25}H_{18}BrClN_2O_4$•$CHCl_3$, M = 644.13, T = 173(2) K, λ = 0.71073 Å, Monoclinic, space group P2(1), a = 13.0622(4) Å, b = 8.2259(2) Å, c = 13.1485(4) Å, V = 1355.79(7) $Å^3$, z = 8, d_{calc} = 1.578 Mg/m^3, 15743 reflections measured, 4332 [R(int) = 0.0346], R_1 = 0.0305, wR_2 = 0.0649 ($I > 2\sigma(I)$, final R_1 = 0.0272, wR_2 = 0.0639, GOF = 1.053, and 334 parameters.

Table S4. Crystal data and structure refinement for z.

Identification code	z	
Empirical formula	$C_{25}H_{18}BrClN_2O_4$•$CHCl_3$	
Formula weight	644.13	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P2(1)	
Unit cell dimensions	a = 13.0622(4) Å	alpha = 90 deg.
	b = 8.2259(2) Å	beta = 106.3300(10) deg.
	c = 13.1485(4) Å	gamma = 90 deg.
Volume	1355.79(7) $Å^3$	

[11] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. (CCDC 1024590).

Z, Calculated density	8, 1.578 Mg/m^3
Absorption coefficient	1.946 mm^{-1}
F(000)	646
Crystal size	0.31 x 0.29 x 0.27 mm
Theta range for data collection	1.61 to 25.01 deg.
Limiting indices	-15<=h<=15, -9<=k<=9, -15<=l<=15
Reflections collected / unique	15743 / 4332 [R(int) = 0.0346]
Completeness to theta = 25.01	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6216 and 0.5837
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4332 / 1 / 334
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R_1 = 0.0272, wR_2 = 0.0639
R indices (all data)	R_1 = 0.0305, wR_2 = 0.0649
Absolute structure parameter	0.015(6)
Largest diff. peak and hole	0.357 and -0.235 e. $Å^{-3}$

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for z U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
C(01)	3570(3)	3290(4)	6775(2)	37(1)
Cl(01)	2787(1)	3984(2)	7557(1)	74(1)
Cl(02)	4741(1)	2352(2)	7545(1)	59(1)
Cl(03)	2847(1)	1914(1)	5819(1)	58(1)
Br(1)	7348(1)	210(1)	9407(1)	41(1)
Cl(1)	12541(1)	607(1)	10949(1)	35(1)
O(1)	9274(2)	4035(2)	14329(2)	25(1)
O(2)	5669(1)	2103(3)	10007(2)	30(1)
O(3)	9480(2)	8500(3)	11925(2)	49(1)
O(4)	10179(2)	8340(3)	10629(2)	40(1)
N(1)	10295(2)	1835(3)	14162(2)	24(1)

N(2)	9892(2)	7746(3)	11355(2)	27(1)
C(1)	8546(2)	2092(3)	11139(2)	19(1)
C(2)	7531(2)	1778(3)	10495(2)	21(1)
C(3)	6639(2)	2575(3)	10636(2)	22(1)
C(4)	6798(2)	3776(4)	11397(2)	25(1)
C(5)	7818(2)	4109(4)	12041(2)	25(1)
C(6)	8700(2)	3251(3)	11935(2)	20(1)
C(7)	9810(2)	3602(3)	12687(2)	18(1)
C(8)	10657(2)	2414(3)	12589(2)	17(1)
C(9)	11173(2)	2189(3)	11810(2)	20(1)
C(10)	11895(2)	922(3)	11938(2)	23(1)
C(11)	12116(2)	-115(3)	12790(2)	26(1)
C(12)	11592(2)	95(4)	13571(2)	26(1)
C(13)	10882(2)	1364(3)	13450(2)	21(1)
C(14)	9743(2)	3235(3)	13831(2)	20(1)
C(15)	10061(2)	5955(3)	11516(2)	24(1)
C(16)	10109(2)	5439(4)	12647(2)	20(1)
C(17)	11156(2)	5767(3)	13397(2)	22(1)
C(18)	12010(2)	5992(3)	14001(2)	26(1)
C(19)	13053(2)	6254(4)	14726(2)	24(1)
C(20)	13187(2)	7220(4)	15629(2)	28(1)
C(21)	14185(2)	7420(4)	16319(2)	35(1)
C(22)	15061(2)	6663(4)	16139(3)	37(1)
C(23)	14937(2)	5739(4)	15249(3)	40(1)
C(24)	13950(2)	5526(4)	14542(2)	34(1)
C(25)	4747(2)	2822(5)	10205(3)	39(1)

Table S6. Bond lengths [Å] and angles [deg] for z

C(01)-Cl(01)	1.739(3)
C(01)-Cl(03)	1.756(3)
C(01)-Cl(02)	1.758(3)
C(01)-H(01A)	1.0000
Br(1)-C(2)	1.892(3)

Cl(1)-C(10)	1.757(3)
O(1)-C(14)	1.210(3)
O(2)-C(3)	1.361(3)
O(2)-C(25)	1.430(4)
O(3)-N(2)	1.209(4)
O(4)-N(2)	1.222(3)
N(1)-C(14)	1.363(4)
N(1)-C(13)	1.420(3)
N(2)-C(15)	1.496(4)
C(1)-C(2)	1.382(3)
C(1)-C(6)	1.388(4)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.393(4)
C(3)-C(4)	1.379(4)
C(4)-C(5)	1.390(4)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.391(4)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.536(4)
C(7)-C(8)	1.508(4)
C(7)-C(14)	1.561(4)
C(7)-C(16)	1.566(4)
C(8)-C(9)	1.388(4)
C(8)-C(13)	1.388(4)
C(9)-C(10)	1.384(4)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.373(4)
C(11)-C(12)	1.395(4)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.376(4)
C(12)-H(12A)	0.9500
C(15)-C(16)	1.531(4)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.469(4)
C(16)-H(16A)	1.0000

C(17)-C(18)	1.188(4)
C(18)-C(19)	1.441(4)
C(19)-C(24)	1.396(4)
C(19)-C(20)	1.398(4)
C(20)-C(21)	1.372(4)
C(20)-H(20A)	0.9500
C(21)-C(22)	1.380(5)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.366(5)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.372(4)
C(23)-H(23A)	0.9500
C(24)-H(24A)	0.9500
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
Cl(01)-C(01)-Cl(03)	110.33(19)
Cl(01)-C(01)-Cl(02)	111.37(18)
Cl(03)-C(01)-Cl(02)	109.6(2)
Cl(01)-C(01)-H(01A)	108.5
Cl(03)-C(01)-H(01A)	108.5
Cl(02)-C(01)-H(01A)	108.5
C(3)-O(2)-C(25)	117.3(2)
C(14)-N(1)-C(13)	110.9(2)
O(3)-N(2)-O(4)	124.6(3)
O(3)-N(2)-C(15)	119.5(3)
O(4)-N(2)-C(15)	116.0(3)
C(2)-C(1)-C(6)	120.1(2)
C(2)-C(1)-H(1A)	120.0
C(6)-C(1)-H(1A)	120.0
C(1)-C(2)-C(3)	121.6(3)
C(1)-C(2)-Br(1)	119.07(19)
C(3)-C(2)-Br(1)	119.3(2)
O(2)-C(3)-C(4)	124.7(2)
O(2)-C(3)-C(2)	117.1(2)
C(4)-C(3)-C(2)	118.2(2)

C(3)-C(4)-C(5)	120.4(2)
C(3)-C(4)-H(4A)	119.8
C(5)-C(4)-H(4A)	119.8
C(4)-C(5)-C(6)	121.2(3)
C(4)-C(5)-H(5A)	119.4
C(6)-C(5)-H(5A)	119.4
C(1)-C(6)-C(5)	118.4(2)
C(1)-C(6)-C(7)	121.6(2)
C(5)-C(6)-C(7)	120.0(2)
C(8)-C(7)-C(6)	114.0(2)
C(8)-C(7)-C(14)	101.5(2)
C(6)-C(7)-C(14)	106.6(2)
C(8)-C(7)-C(16)	115.2(2)
C(6)-C(7)-C(16)	111.0(2)
C(14)-C(7)-C(16)	107.6(2)
C(9)-C(8)-C(13)	119.0(2)
C(9)-C(8)-C(7)	132.0(2)
C(13)-C(8)-C(7)	109.0(2)
C(10)-C(9)-C(8)	117.8(3)
C(10)-C(9)-H(9A)	121.1
C(8)-C(9)-H(9A)	121.1
C(11)-C(10)-C(9)	123.1(2)
C(11)-C(10)-Cl(1)	118.6(2)
C(9)-C(10)-Cl(1)	118.3(2)
C(10)-C(11)-C(12)	119.3(3)
C(10)-C(11)-H(11A)	120.3
C(12)-C(11)-H(11A)	120.3
C(13)-C(12)-C(11)	117.6(3)
C(13)-C(12)-H(12A)	121.2
C(11)-C(12)-H(12A)	121.2
C(12)-C(13)-C(8)	123.2(2)
C(12)-C(13)-N(1)	127.1(3)
C(8)-C(13)-N(1)	109.7(2)
O(1)-C(14)-N(1)	126.2(3)
O(1)-C(14)-C(7)	126.2(2)
N(1)-C(14)-C(7)	107.6(2)

N(2)-C(15)-C(16)	112.0(2)
N(2)-C(15)-H(15A)	109.2
C(16)-C(15)-H(15A)	109.2
N(2)-C(15)-H(15B)	109.2
C(16)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
C(17)-C(16)-C(15)	112.2(2)
C(17)-C(16)-C(7)	110.4(2)
C(15)-C(16)-C(7)	111.0(2)
C(17)-C(16)-H(16A)	107.7
C(15)-C(16)-H(16A)	107.7
C(7)-C(16)-H(16A)	107.7
C(18)-C(17)-C(16)	178.3(3)
C(17)-C(18)-C(19)	179.3(3)
C(24)-C(19)-C(20)	118.6(3)
C(24)-C(19)-C(18)	120.3(3)
C(20)-C(19)-C(18)	121.1(2)
C(21)-C(20)-C(19)	119.9(3)
C(21)-C(20)-H(20A)	120.0
C(19)-C(20)-H(20A)	120.0
C(20)-C(21)-C(22)	120.8(3)
C(20)-C(21)-H(21A)	119.6
C(22)-C(21)-H(21A)	119.6
C(23)-C(22)-C(21)	119.6(3)
C(23)-C(22)-H(22A)	120.2
C(21)-C(22)-H(22A)	120.2
C(22)-C(23)-C(24)	120.9(3)
C(22)-C(23)-H(23A)	119.6
C(24)-C(23)-H(23A)	119.6
C(23)-C(24)-C(19)	120.2(3)
C(23)-C(24)-H(24A)	119.9
C(19)-C(24)-H(24A)	119.9
O(2)-C(25)-H(25A)	109.5
O(2)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
O(2)-C(25)-H(25C)	109.5

H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters ($Å^2$ x 10^3) for z

The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(01)	44(2)	36(2)	31(2)	1(2)	11(1)	-2(2)
Cl(01)	89(1)	86(1)	60(1)	-1(1)	41(1)	28(1)
Cl(02)	49(1)	82(1)	41(1)	12(1)	4(1)	6(1)
Cl(03)	52(1)	60(1)	59(1)	-18(1)	8(1)	-16(1)
Br(1)	25(1)	48(1)	50(1)	-32(1)	12(1)	-8(1)
Cl(1)	36(1)	34(1)	41(1)	-2(1)	23(1)	6(1)
O(1)	30(1)	28(1)	22(1)	-4(1)	13(1)	1(1)
O(2)	18(1)	39(1)	32(1)	-7(1)	4(1)	1(1)
O(3)	73(2)	27(1)	56(2)	6(1)	31(1)	17(1)
O(4)	58(1)	33(1)	26(1)	8(1)	8(1)	-14(1)
N(1)	33(1)	20(1)	20(1)	0(1)	9(1)	4(1)
N(2)	29(1)	23(1)	26(2)	6(1)	2(1)	-3(1)
C(1)	19(1)	18(2)	24(1)	2(1)	10(1)	1(1)
C(2)	25(1)	19(1)	21(1)	-1(1)	9(1)	-2(1)
C(3)	23(1)	22(2)	21(2)	5(1)	5(1)	1(1)
C(4)	22(1)	26(2)	27(2)	1(1)	9(1)	8(1)
C(5)	29(1)	24(2)	22(2)	-5(1)	9(1)	2(1)
C(6)	23(1)	16(1)	20(1)	4(1)	7(1)	-1(1)
C(7)	23(1)	18(1)	14(1)	4(1)	6(1)	2(1)
C(8)	19(1)	13(1)	19(1)	-3(1)	4(1)	-4(1)
C(9)	20(1)	19(1)	21(1)	1(1)	4(1)	-2(1)
C(10)	19(1)	24(2)	27(2)	-6(1)	8(1)	-2(1)
C(11)	24(1)	20(2)	32(2)	-1(1)	4(1)	5(1)
C(12)	34(1)	19(1)	23(1)	3(1)	4(1)	6(1)
C(13)	25(1)	18(1)	20(1)	-2(1)	6(1)	-2(1)

C(14)	21(1)	20(2)	18(1)	0(1)	4(1)	-4(1)
C(15)	31(2)	20(1)	21(2)	2(1)	7(1)	0(1)
C(16)	24(1)	17(1)	19(1)	0(1)	6(1)	1(1)
C(17)	31(2)	14(1)	22(1)	0(1)	7(1)	0(1)
C(18)	34(2)	17(2)	26(2)	2(1)	9(1)	1(1)
C(19)	26(1)	20(1)	26(2)	7(1)	6(1)	0(1)
C(20)	26(1)	26(2)	31(2)	1(1)	7(1)	4(1)
C(21)	39(2)	32(2)	29(2)	-4(2)	1(1)	-2(1)
C(22)	26(2)	34(2)	47(2)	7(2)	1(1)	-3(1)
C(23)	28(2)	47(2)	47(2)	2(2)	13(1)	1(1)
C(24)	37(2)	36(2)	31(2)	-3(2)	13(1)	0(1)
C(25)	19(2)	54(2)	41(2)	-8(2)	6(1)	2(2)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for z

	x	y	z	U(eq)
H(01A)	3775	4241	6401	45
H(1A)	9139	1515	11037	23
H(4A)	6207	4379	11481	30
H(5A)	7914	4937	12563	30
H(9A)	11035	2883	11209	24
H(11A)	12620	-967	12848	31
H(12A)	11722	-613	14165	31
H(15A)	10736	5646	11364	29
H(15B)	9472	5368	11010	29
H(16A)	9567	6092	12875	24
H(20A)	12589	7736	15765	33
H(21A)	14274	8087	16927	42
H(22A)	15745	6785	16630	45
H(23A)	15542	5236	15119	48
H(24A)	13877	4881	13926	41
H(25A)	4103	2383	9704	58
H(25B)	4769	4003	10115	58

H(25C)	4737	2573	10931	58

Table S9. Torsion angles [deg] for z

C(6)-C(1)-C(2)-C(3)	-1.4(4)
C(6)-C(1)-C(2)-Br(1)	179.3(2)
C(25)-O(2)-C(3)-C(4)	-4.9(4)
C(25)-O(2)-C(3)-C(2)	175.1(3)
C(1)-C(2)-C(3)-O(2)	-175.8(2)
Br(1)-C(2)-C(3)-O(2)	3.5(3)
C(1)-C(2)-C(3)-C(4)	4.2(4)
Br(1)-C(2)-C(3)-C(4)	-176.5(2)
O(2)-C(3)-C(4)-C(5)	176.4(3)
C(2)-C(3)-C(4)-C(5)	-3.5(4)
C(3)-C(4)-C(5)-C(6)	0.2(4)
C(2)-C(1)-C(6)-C(5)	-1.9(4)
C(2)-C(1)-C(6)-C(7)	178.2(2)
C(4)-C(5)-C(6)-C(1)	2.6(4)
C(4)-C(5)-C(6)-C(7)	-177.6(3)
C(1)-C(6)-C(7)-C(8)	-9.0(4)
C(5)-C(6)-C(7)-C(8)	171.1(2)
C(1)-C(6)-C(7)-C(14)	-120.1(3)
C(5)-C(6)-C(7)-C(14)	60.1(3)
C(1)-C(6)-C(7)-C(16)	123.1(3)
C(5)-C(6)-C(7)-C(16)	-56.7(3)
C(6)-C(7)-C(8)-C(9)	72.4(4)
C(14)-C(7)-C(8)-C(9)	-173.5(3)
C(16)-C(7)-C(8)-C(9)	-57.6(4)
C(6)-C(7)-C(8)-C(13)	-104.8(3)
C(14)-C(7)-C(8)-C(13)	9.3(3)
C(16)-C(7)-C(8)-C(13)	125.1(2)
C(13)-C(8)-C(9)-C(10)	-0.3(4)
C(7)-C(8)-C(9)-C(10)	-177.3(3)
C(8)-C(9)-C(10)-C(11)	0.3(4)

C(8)-C(9)-C(10)-Cl(1)	179.2(2)
C(9)-C(10)-C(11)-C(12)	0.3(4)
Cl(1)-C(10)-C(11)-C(12)	-178.6(2)
C(10)-C(11)-C(12)-C(13)	-0.9(4)
C(11)-C(12)-C(13)-C(8)	0.9(4)
C(11)-C(12)-C(13)-N(1)	-177.6(3)
C(9)-C(8)-C(13)-C(12)	-0.4(4)
C(7)-C(8)-C(13)-C(12)	177.3(3)
C(9)-C(8)-C(13)-N(1)	178.4(2)
C(7)-C(8)-C(13)-N(1)	-4.0(3)
C(14)-N(1)-C(13)-C(12)	174.5(3)
C(14)-N(1)-C(13)-C(8)	-4.2(3)
C(13)-N(1)-C(14)-O(1)	-170.7(3)
C(13)-N(1)-C(14)-C(7)	10.2(3)
C(8)-C(7)-C(14)-O(1)	169.2(3)
C(6)-C(7)-C(14)-O(1)	-71.3(3)
C(16)-C(7)-C(14)-O(1)	47.9(3)
C(8)-C(7)-C(14)-N(1)	-11.7(3)
C(6)-C(7)-C(14)-N(1)	107.8(2)
C(16)-C(7)-C(14)-N(1)	-133.0(2)
O(3)-N(2)-C(15)-C(16)	-23.6(4)
O(4)-N(2)-C(15)-C(16)	157.3(2)
N(2)-C(15)-C(16)-C(17)	-79.6(3)
N(2)-C(15)-C(16)-C(7)	156.3(2)
C(8)-C(7)-C(16)-C(17)	-50.5(3)
C(6)-C(7)-C(16)-C(17)	178.0(2)
C(14)-C(7)-C(16)-C(17)	61.8(3)
C(8)-C(7)-C(16)-C(15)	74.5(3)
C(6)-C(7)-C(16)-C(15)	-57.0(3)
C(14)-C(7)-C(16)-C(15)	-173.2(2)
C(15)-C(16)-C(17)-C(18)	-97(10)
C(7)-C(16)-C(17)-C(18)	27(10)
C(16)-C(17)-C(18)-C(19)	48(33)
C(17)-C(18)-C(19)-C(24)	-10(28)
C(17)-C(18)-C(19)-C(20)	171(100)
C(24)-C(19)-C(20)-C(21)	-0.7(4)

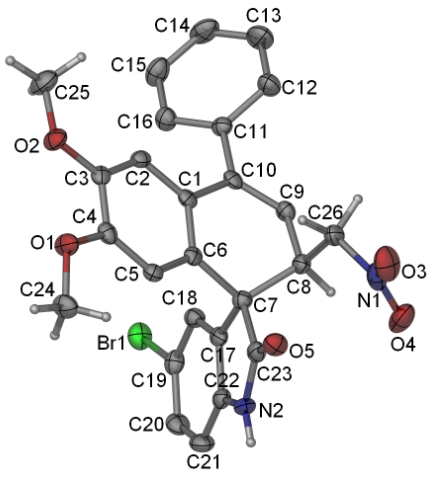
C(18)-C(19)-C(20)-C(21)	178.5(3)
C(19)-C(20)-C(21)-C(22)	-0.7(5)
C(20)-C(21)-C(22)-C(23)	1.7(5)
C(21)-C(22)-C(23)-C(24)	-1.3(5)
C(22)-C(23)-C(24)-C(19)	-0.2(5)
C(20)-C(19)-C(24)-C(23)	1.1(5)
C(18)-C(19)-C(24)-C(23)	-178.0(3)

Symmetry transformations used to generate equivalent atoms:

Table S10. Hydrogen bonds for z [Å and deg.]

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

8.2) Single-Crystal X-ray Crystallography of 11[12]



Data intensity of **11** was collected using a Bruker SMART APEX II (Mo radiation). The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **11**: $C_{26}H_{21}BrN_2O_5 \bullet CH_2Cl_2$, M = 604.27, T = 173(2) K, λ = 0.71073 Å, Orthorhombic, space group

[12] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. (CCDC 1024591).

P2(1)2(1)2(1), a = 12.3150(2) Å, b = 13.9146(3) Å, c = 15.2049(3) Å, V = 2605.49(9) Å^3, z = 4, d_{calc} = 1.540 Mg/m^3, 30314 reflections measured, 4202/4597 [R(int) = 0.0203], R_1 = 0.0282, wR_2 = 0.0609 ($I > 2\sigma(I)$, final R_1 = 0.0250, wR_2 = 0.0594, GOF = 1.036, and 334 parameters.

Table S11. Crystal data and structure refinement for Z

Identification code	z
Empirical formula	$C_{26}H_{21}BrN_2O_5 \bullet CH_2Cl_2$
Formula weight	604.27
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 12.3150(2) Å alpha = 90 deg. b = 13.9146(3) Å beta = 90 deg. c = 15.2049(3) Å gamma = 90 deg.
Volume	2605.49(9) Å^3
Z, Calculated density	4, 1.540 Mg/m^3
Absorption coefficient	1.824 mm^{-1}
F(000)	1224
Crystal size	0.29 x 0.24 x 0.11 mm
Theta range for data collection	1.98 to 25.01 deg.
Limiting indices	-14<=h<=14, -16<=k<=16, -15<=l<=18
Reflections collected / unique	30314 / 4597 [R(int) = 0.0379]
Completeness to theta = 25.01	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8246 and 0.6198
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4597 / 0 / 334
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R_1 = 0.0250, wR_2 = 0.0594
R indices (all data)	R_1 = 0.0282, wR_2 = 0.0609
Absolute structure parameter	0.004(6)
Largest diff. peak and hole	0.314 and -0.197 e. Å^{-3}

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for Z. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Br(1)	1523(1)	123(1)	18164(1)	31(1)
O(1)	3774(1)	4829(1)	20997(1)	28(1)
O(2)	3462(2)	3622(1)	22248(1)	28(1)
O(3)	-1644(2)	5980(1)	20182(2)	45(1)
O(4)	-2024(2)	5046(2)	19083(1)	42(1)
O(5)	398(2)	5444(1)	19142(1)	28(1)
N(1)	-1627(2)	5203(2)	19806(2)	31(1)
N(2)	826(2)	4402(1)	18025(1)	24(1)
C(1)	1073(2)	3029(2)	20862(2)	19(1)
C(2)	1819(2)	2988(2)	21558(2)	20(1)
C(3)	2715(2)	3592(2)	21588(2)	20(1)
C(4)	2881(2)	4258(2)	20903(2)	22(1)
C(5)	2157(2)	4292(2)	20210(2)	20(1)
C(6)	1256(2)	3690(2)	20184(2)	18(1)
C(7)	472(2)	3701(2)	19406(2)	20(1)
C(8)	-704(2)	3554(2)	19740(2)	22(1)
C(9)	-747(2)	2680(2)	20319(2)	21(1)
C(10)	68(2)	2439(2)	20858(2)	20(1)
C(11)	-52(2)	1591(2)	21443(2)	21(1)
C(12)	-1026(2)	1425(2)	21885(2)	31(1)
C(13)	-1166(2)	601(2)	22383(2)	41(1)
C(14)	-343(2)	-66(2)	22444(2)	40(1)
C(15)	625(2)	84(2)	22011(2)	36(1)
C(16)	774(2)	906(2)	21515(2)	27(1)
C(17)	789(2)	2949(2)	18724(2)	20(1)
C(18)	946(2)	1974(2)	18797(2)	23(1)
C(19)	1285(2)	1473(2)	18055(2)	25(1)
C(20)	1466(2)	1918(2)	17259(2)	29(1)
C(21)	1313(2)	2907(2)	17188(2)	29(1)

C(22)	982(2)	3407(2)	17926(2)	22(1)
C(23)	556(2)	4640(2)	18862(2)	22(1)
C(24)	4072(2)	5417(2)	20255(2)	32(1)
C(25)	3370(3)	2909(2)	22924(2)	38(1)
C(26)	-1152(2)	4381(2)	20303(2)	26(1)
Cl(2)	-1654(1)	2578(1)	14689(1)	64(1)
Cl(1)	349(1)	2739(1)	13714(1)	66(1)
C(01)	-455(3)	1981(2)	14359(2)	60(1)

Table S13. Bond lengths [Å] and angles [deg] for Z

Br(1)-C(19)	1.910(2)
O(1)-C(4)	1.365(3)
O(1)-C(24)	1.440(3)
O(2)-C(3)	1.362(3)
O(2)-C(25)	1.433(3)
O(3)-N(1)	1.224(3)
O(4)-N(1)	1.223(3)
O(5)-C(23)	1.213(3)
N(1)-C(26)	1.490(3)
N(2)-C(23)	1.357(3)
N(2)-C(22)	1.405(3)
N(2)-H(2A)	0.8800
C(1)-C(6)	1.401(3)
C(1)-C(2)	1.402(3)
C(1)-C(10)	1.486(3)
C(2)-C(3)	1.388(3)
C(2)-H(2B)	0.9500
C(3)-C(4)	1.409(3)
C(4)-C(5)	1.381(3)
C(5)-C(6)	1.391(3)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.526(3)
C(7)-C(17)	1.525(3)
C(7)-C(8)	1.548(3)

C(7)-C(23)	1.550(3)
C(8)-C(9)	1.503(3)
C(8)-C(26)	1.536(3)
C(8)-H(8A)	1.0000
C(9)-C(10)	1.338(3)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.484(3)
C(11)-C(12)	1.395(4)
C(11)-C(16)	1.398(3)
C(12)-C(13)	1.386(4)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.378(4)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.377(4)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.383(3)
C(15)-H(15A)	0.9500
C(16)-H(16A)	0.9500
C(17)-C(18)	1.376(3)
C(17)-C(22)	1.390(3)
C(18)-C(19)	1.390(3)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.377(4)
C(20)-C(21)	1.393(4)
C(20)-H(20A)	0.9500
C(21)-C(22)	1.382(3)
C(21)-H(21A)	0.9500
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
Cl(2)-C(01)	1.768(3)

Cl(1)-C(01)	1.748(3)
C(4)-O(1)-C(24)	117.03(18)
C(3)-O(2)-C(25)	117.0(2)
O(4)-N(1)-O(3)	124.8(2)
O(4)-N(1)-C(26)	118.4(2)
O(3)-N(1)-C(26)	116.6(2)
C(23)-N(2)-C(22)	111.96(19)
C(23)-N(2)-H(2A)	124.0
C(22)-N(2)-H(2A)	124.0
C(6)-C(1)-C(2)	118.5(2)
C(6)-C(1)-C(10)	119.6(2)
C(2)-C(1)-C(10)	121.8(2)
C(3)-C(2)-C(1)	121.4(2)
C(3)-C(2)-H(2B)	119.3
C(1)-C(2)-H(2B)	119.3
O(2)-C(3)-C(2)	125.4(2)
O(2)-C(3)-C(4)	115.3(2)
C(2)-C(3)-C(4)	119.3(2)
O(1)-C(4)-C(5)	125.4(2)
O(1)-C(4)-C(3)	115.0(2)
C(5)-C(4)-C(3)	119.6(2)
C(4)-C(5)-C(6)	121.1(2)
C(4)-C(5)-H(5A)	119.5
C(6)-C(5)-H(5A)	119.5
C(5)-C(6)-C(1)	120.2(2)
C(5)-C(6)-C(7)	121.4(2)
C(1)-C(6)-C(7)	118.4(2)
C(17)-C(7)-C(6)	111.03(18)
C(17)-C(7)-C(8)	111.90(19)
C(6)-C(7)-C(8)	109.68(18)
C(17)-C(7)-C(23)	101.40(19)
C(6)-C(7)-C(23)	112.29(19)
C(8)-C(7)-C(23)	110.35(19)
C(9)-C(8)-C(26)	105.50(19)
C(9)-C(8)-C(7)	109.36(19)
C(26)-C(8)-C(7)	114.87(19)

C(9)-C(8)-H(8A)	109.0
C(26)-C(8)-H(8A)	109.0
C(7)-C(8)-H(8A)	109.0
C(10)-C(9)-C(8)	122.4(2)
C(10)-C(9)-H(9A)	118.8
C(8)-C(9)-H(9A)	118.8
C(9)-C(10)-C(11)	119.5(2)
C(9)-C(10)-C(1)	119.3(2)
C(11)-C(10)-C(1)	121.3(2)
C(12)-C(11)-C(16)	118.4(2)
C(12)-C(11)-C(10)	120.3(2)
C(16)-C(11)-C(10)	121.2(2)
C(13)-C(12)-C(11)	120.5(3)
C(13)-C(12)-H(12A)	119.8
C(11)-C(12)-H(12A)	119.8
C(14)-C(13)-C(12)	120.2(3)
C(14)-C(13)-H(13A)	119.9
C(12)-C(13)-H(13A)	119.9
C(15)-C(14)-C(13)	120.2(3)
C(15)-C(14)-H(14A)	119.9
C(13)-C(14)-H(14A)	119.9
C(14)-C(15)-C(16)	120.1(3)
C(14)-C(15)-H(15A)	120.0
C(16)-C(15)-H(15A)	120.0
C(15)-C(16)-C(11)	120.7(2)
C(15)-C(16)-H(16A)	119.7
C(11)-C(16)-H(16A)	119.7
C(18)-C(17)-C(22)	120.0(2)
C(18)-C(17)-C(7)	131.1(2)
C(22)-C(17)-C(7)	108.8(2)
C(17)-C(18)-C(19)	118.0(2)
C(17)-C(18)-H(18A)	121.0
C(19)-C(18)-H(18A)	121.0
C(20)-C(19)-C(18)	122.5(2)
C(20)-C(19)-Br(1)	119.60(18)
C(18)-C(19)-Br(1)	117.91(19)

C(19)-C(20)-C(21)	119.3(2)
C(19)-C(20)-H(20A)	120.3
C(21)-C(20)-H(20A)	120.3
C(22)-C(21)-C(20)	118.4(2)
C(22)-C(21)-H(21A)	120.8
C(20)-C(21)-H(21A)	120.8
C(21)-C(22)-C(17)	121.8(2)
C(21)-C(22)-N(2)	128.6(2)
C(17)-C(22)-N(2)	109.6(2)
O(5)-C(23)-N(2)	126.4(2)
O(5)-C(23)-C(7)	125.5(2)
N(2)-C(23)-C(7)	108.2(2)
O(1)-C(24)-H(24A)	109.5
O(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
O(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
O(2)-C(25)-H(25A)	109.5
O(2)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
O(2)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
N(1)-C(26)-C(8)	115.7(2)
N(1)-C(26)-H(26A)	108.4
C(8)-C(26)-H(26A)	108.4
N(1)-C(26)-H(26B)	108.4
C(8)-C(26)-H(26B)	108.4
H(26A)-C(26)-H(26B)	107.4
Cl(1)-C(01)-Cl(2)	110.42(18)

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters ($Å^2$ x 10^3) for Z
The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

	U11	U22	U33	U23	U13	U12
Br(1)	31(1)	26(1)	36(1)	-8(1)	-1(1)	1(1)
O(1)	26(1)	32(1)	28(1)	2(1)	-4(1)	-12(1)
O(2)	28(1)	33(1)	24(1)	2(1)	-8(1)	-6(1)
O(3)	38(1)	29(1)	68(1)	-1(1)	2(1)	6(1)
O(4)	36(1)	42(1)	48(1)	17(1)	-15(1)	-5(1)
O(5)	32(1)	22(1)	30(1)	3(1)	2(1)	-1(1)
N(1)	20(1)	27(1)	47(1)	6(1)	2(1)	0(1)
N(2)	26(1)	27(1)	18(1)	6(1)	0(1)	0(1)
C(1)	19(1)	18(1)	19(1)	-4(1)	5(1)	1(1)
C(2)	24(1)	21(1)	16(1)	0(1)	2(1)	2(1)
C(3)	21(1)	24(1)	17(1)	-6(1)	0(1)	2(1)
C(4)	19(1)	23(1)	24(1)	-6(1)	3(1)	-1(1)
C(5)	21(1)	20(1)	18(1)	-1(1)	3(1)	0(1)
C(6)	19(1)	18(1)	18(1)	-4(1)	2(1)	3(1)
C(7)	21(1)	21(1)	19(1)	0(1)	0(1)	-1(1)
C(8)	18(1)	26(1)	21(1)	1(1)	-3(1)	-2(1)
C(9)	19(1)	21(1)	23(1)	-1(1)	1(1)	-4(1)
C(10)	19(1)	22(1)	19(1)	-5(1)	5(1)	0(1)
C(11)	21(1)	23(1)	19(1)	0(1)	-2(1)	-4(1)
C(12)	27(1)	34(1)	33(2)	7(1)	4(1)	-1(1)
C(13)	32(2)	50(2)	41(2)	16(1)	4(1)	-12(1)
C(14)	44(2)	36(2)	40(2)	18(1)	-10(1)	-13(1)
C(15)	32(1)	28(1)	47(2)	9(1)	-10(1)	-2(1)
C(16)	23(1)	26(1)	32(1)	2(1)	-1(1)	-4(1)
C(17)	16(1)	27(1)	18(1)	-3(1)	-4(1)	-4(1)
C(18)	22(1)	26(1)	21(1)	0(1)	0(1)	-3(1)
C(19)	22(1)	23(1)	30(1)	-6(1)	-6(1)	-1(1)
C(20)	29(1)	38(1)	21(1)	-8(1)	2(1)	-1(1)
C(21)	32(2)	37(1)	18(1)	1(1)	2(1)	-2(1)
C(22)	18(1)	26(1)	22(1)	2(1)	-4(1)	-2(1)
C(23)	18(1)	25(1)	25(1)	3(1)	-1(1)	-4(1)
C(24)	28(1)	35(1)	32(2)	2(1)	1(1)	-12(1)

C(25)	39(2)	42(2)	32(2)	9(1)	-13(1)	-8(1)
C(26)	24(1)	30(1)	26(1)	4(1)	3(1)	6(1)
Cl(2)	50(1)	90(1)	52(1)	7(1)	2(1)	31(1)
Cl(1)	85(1)	62(1)	53(1)	6(1)	21(1)	-12(1)
C(01)	60(2)	51(2)	68(2)	22(2)	32(2)	22(2)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for Z

	x	y	z	U(eq)
H(2A)	896	4821	17595	28
H(2B)	1708	2537	22019	24
H(5A)	2277	4734	19744	24
H(8A)	-1194	3454	19224	26
H(9A)	-1375	2284	20302	25
H(12A)	-1598	1881	21844	37
H(13A)	-1832	495	22683	49
H(14A)	-442	-630	22787	48
H(15A)	1190	-379	22052	43
H(16A)	1445	1006	21220	32
H(18A)	826	1651	19339	27
H(20A)	1693	1554	16763	35
H(21A)	1433	3229	16646	35
H(24A)	4720	5793	20402	48
H(24B)	3472	5853	20113	48
H(24C)	4226	5005	19748	48
H(25A)	3949	3001	23357	57
H(25B)	3435	2268	22662	57
H(25C)	2662	2969	23214	57
H(26A)	-1718	4118	20698	32
H(26B)	-557	4628	20678	32

Table S16. Torsion angles [deg] for Z

C(6)-C(1)-C(2)-C(3)	0.7(3)
C(10)-C(1)-C(2)-C(3)	-175.2(2)
C(25)-O(2)-C(3)-C(2)	6.2(3)
C(25)-O(2)-C(3)-C(4)	-175.4(2)
C(1)-C(2)-C(3)-O(2)	178.0(2)
C(1)-C(2)-C(3)-C(4)	-0.3(3)
C(24)-O(1)-C(4)-C(5)	-9.4(3)
C(24)-O(1)-C(4)-C(3)	170.9(2)
O(2)-C(3)-C(4)-O(1)	0.7(3)
C(2)-C(3)-C(4)-O(1)	179.2(2)
O(2)-C(3)-C(4)-C(5)	-179.1(2)
C(2)-C(3)-C(4)-C(5)	-0.6(3)
O(1)-C(4)-C(5)-C(6)	-178.7(2)
C(3)-C(4)-C(5)-C(6)	1.1(3)
C(4)-C(5)-C(6)-C(1)	-0.6(3)
C(4)-C(5)-C(6)-C(7)	-178.0(2)
C(2)-C(1)-C(6)-C(5)	-0.3(3)
C(10)-C(1)-C(6)-C(5)	175.7(2)
C(2)-C(1)-C(6)-C(7)	177.2(2)
C(10)-C(1)-C(6)-C(7)	-6.8(3)
C(5)-C(6)-C(7)-C(17)	92.9(2)
C(1)-C(6)-C(7)-C(17)	-84.5(2)
C(5)-C(6)-C(7)-C(8)	-142.9(2)
C(1)-C(6)-C(7)-C(8)	39.7(3)
C(5)-C(6)-C(7)-C(23)	-19.8(3)
C(1)-C(6)-C(7)-C(23)	162.7(2)
C(17)-C(7)-C(8)-C(9)	72.0(2)
C(6)-C(7)-C(8)-C(9)	-51.7(2)
C(23)-C(7)-C(8)-C(9)	-175.93(19)
C(17)-C(7)-C(8)-C(26)	-169.7(2)
C(6)-C(7)-C(8)-C(26)	66.7(2)
C(23)-C(7)-C(8)-C(26)	-57.6(3)
C(26)-C(8)-C(9)-C(10)	-88.1(3)
C(7)-C(8)-C(9)-C(10)	36.0(3)
C(8)-C(9)-C(10)-C(11)	177.1(2)
C(8)-C(9)-C(10)-C(1)	-2.6(3)

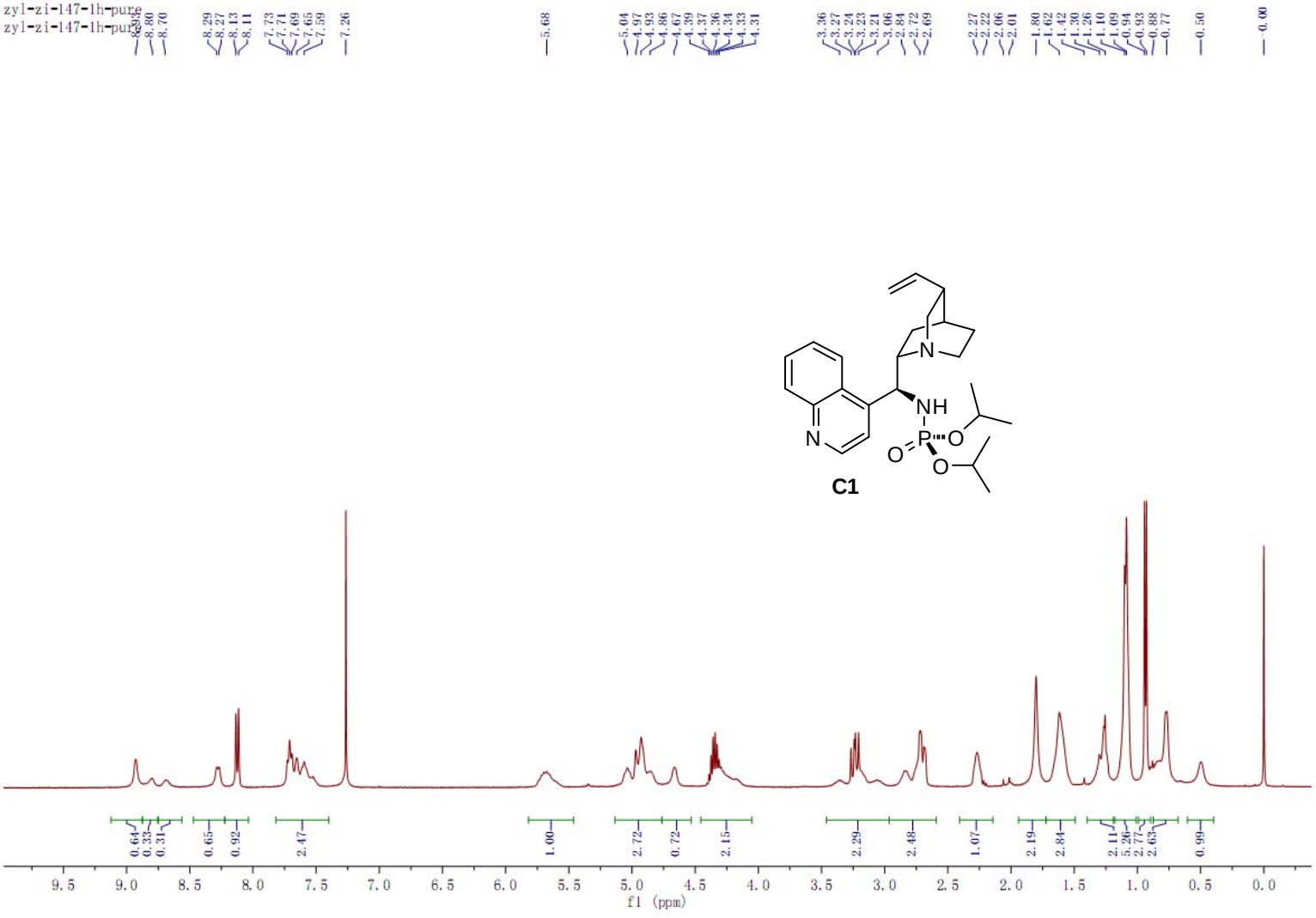
C(6)-C(1)-C(10)-C(9)	-13.8(3)
C(2)-C(1)-C(10)-C(9)	162.1(2)
C(6)-C(1)-C(10)-C(11)	166.5(2)
C(2)-C(1)-C(10)-C(11)	-17.6(3)
C(9)-C(10)-C(11)-C(12)	-42.2(3)
C(1)-C(10)-C(11)-C(12)	137.6(2)
C(9)-C(10)-C(11)-C(16)	133.2(3)
C(1)-C(10)-C(11)-C(16)	-47.1(3)
C(16)-C(11)-C(12)-C(13)	0.1(4)
C(10)-C(11)-C(12)-C(13)	175.6(2)
C(11)-C(12)-C(13)-C(14)	-0.2(4)
C(12)-C(13)-C(14)-C(15)	0.0(5)
C(13)-C(14)-C(15)-C(16)	0.3(4)
C(14)-C(15)-C(16)-C(11)	-0.4(4)
C(12)-C(11)-C(16)-C(15)	0.2(4)
C(10)-C(11)-C(16)-C(15)	-175.3(2)
C(6)-C(7)-C(17)-C(18)	55.7(3)
C(8)-C(7)-C(17)-C(18)	-67.3(3)
C(23)-C(7)-C(17)-C(18)	175.1(2)
C(6)-C(7)-C(17)-C(22)	-121.1(2)
C(8)-C(7)-C(17)-C(22)	116.0(2)
C(23)-C(7)-C(17)-C(22)	-1.6(2)
C(22)-C(17)-C(18)-C(19)	-0.8(3)
C(7)-C(17)-C(18)-C(19)	-177.2(2)
C(17)-C(18)-C(19)-C(20)	0.0(4)
C(17)-C(18)-C(19)-Br(1)	179.02(18)
C(18)-C(19)-C(20)-C(21)	0.4(4)
Br(1)-C(19)-C(20)-C(21)	-178.6(2)
C(19)-C(20)-C(21)-C(22)	0.0(4)
C(20)-C(21)-C(22)-C(17)	-0.7(4)
C(20)-C(21)-C(22)-N(2)	176.7(2)
C(18)-C(17)-C(22)-C(21)	1.2(4)
C(7)-C(17)-C(22)-C(21)	178.3(2)
C(18)-C(17)-C(22)-N(2)	-176.7(2)
C(7)-C(17)-C(22)-N(2)	0.4(3)
C(23)-N(2)-C(22)-C(21)	-176.5(3)

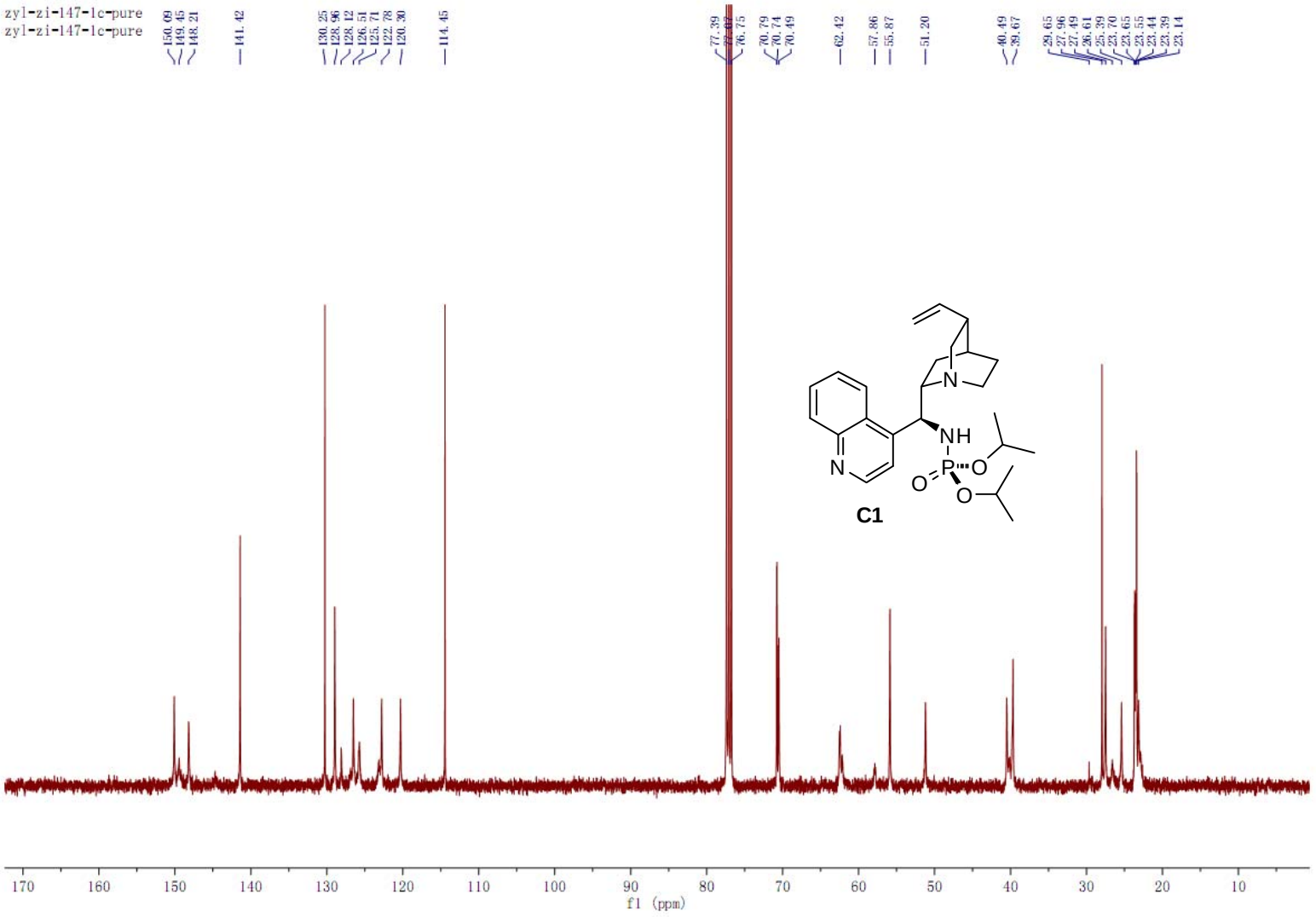
C(23)-N(2)-C(22)-C(17)	1.2(3)
C(22)-N(2)-C(23)-O(5)	178.2(2)
C(22)-N(2)-C(23)-C(7)	-2.2(3)
C(17)-C(7)-C(23)-O(5)	-178.1(2)
C(6)-C(7)-C(23)-O(5)	-59.6(3)
C(8)-C(7)-C(23)-O(5)	63.1(3)
C(17)-C(7)-C(23)-N(2)	2.3(2)
C(6)-C(7)-C(23)-N(2)	120.8(2)
C(8)-C(7)-C(23)-N(2)	-116.5(2)
O(4)-N(1)-C(26)-C(8)	28.5(3)
O(3)-N(1)-C(26)-C(8)	-155.7(2)
C(9)-C(8)-C(26)-N(1)	-155.3(2)
C(7)-C(8)-C(26)-N(1)	84.2(3)

Symmetry transformations used to generate equivalent atoms:

Table S17. Hydrogen bonds for Z [Å and deg.]

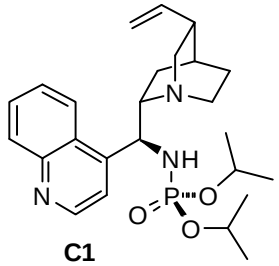
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)


zyl-zi-147-1h-pure
zyl-zi-147-1h-pure
8.80
8.70
8.29
8.27
8.13
8.11
7.73
7.71
7.69
7.65
7.59
7.26
5.68
5.04
4.97
4.93
4.86
4.67
4.39
4.37
4.36
4.34
4.33
4.31
3.36
3.27
3.24
3.23
3.21
3.06
2.84
2.72
2.69
2.27
2.22
2.06
2.01
1.80
1.62
1.42
1.36
1.26
1.10
1.09
0.94
0.93
0.88
0.77
0.50
0.00
N
NH
P
O
O
O
N
C1
0.64
0.33
0.31
0.65
0.92
2.47
1.00
2.72
0.72
2.15
2.29
2.48
1.07
2.19
2.84
2.11
5.26
2.77
2.63
0.99
9.5
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)

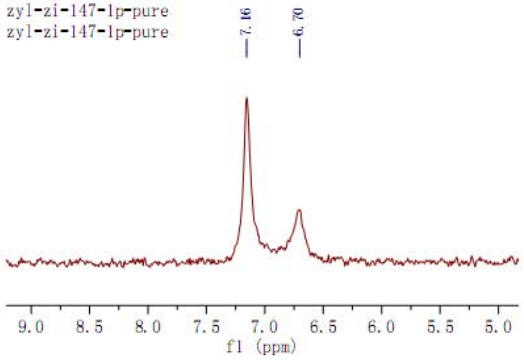

zyl-zi-147-1c-pure
zyl-zi-147-1c-pure
150.09
149.45
148.21
141.42
130.25
128.96
128.12
126.51
125.71
122.78
120.30
114.45
77.39
76.75
70.79
70.74
70.49
62.42
57.86
55.87
51.20
40.49
39.67
29.65
27.96
27.49
26.61
25.39
23.70
23.65
23.55
23.44
23.39
23.14
N
NH
N
P
O
O
O
C1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

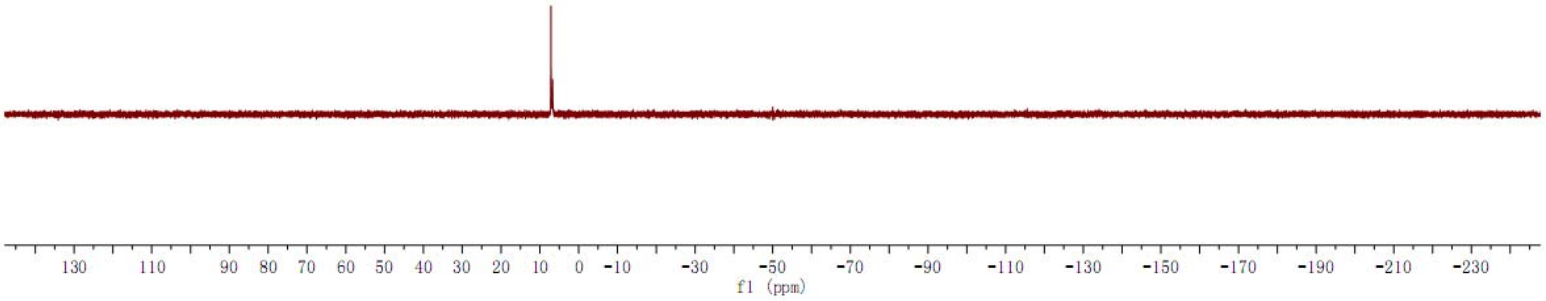
zyl-zi-147-1p-pure
zyl-zi-147-1p-pure

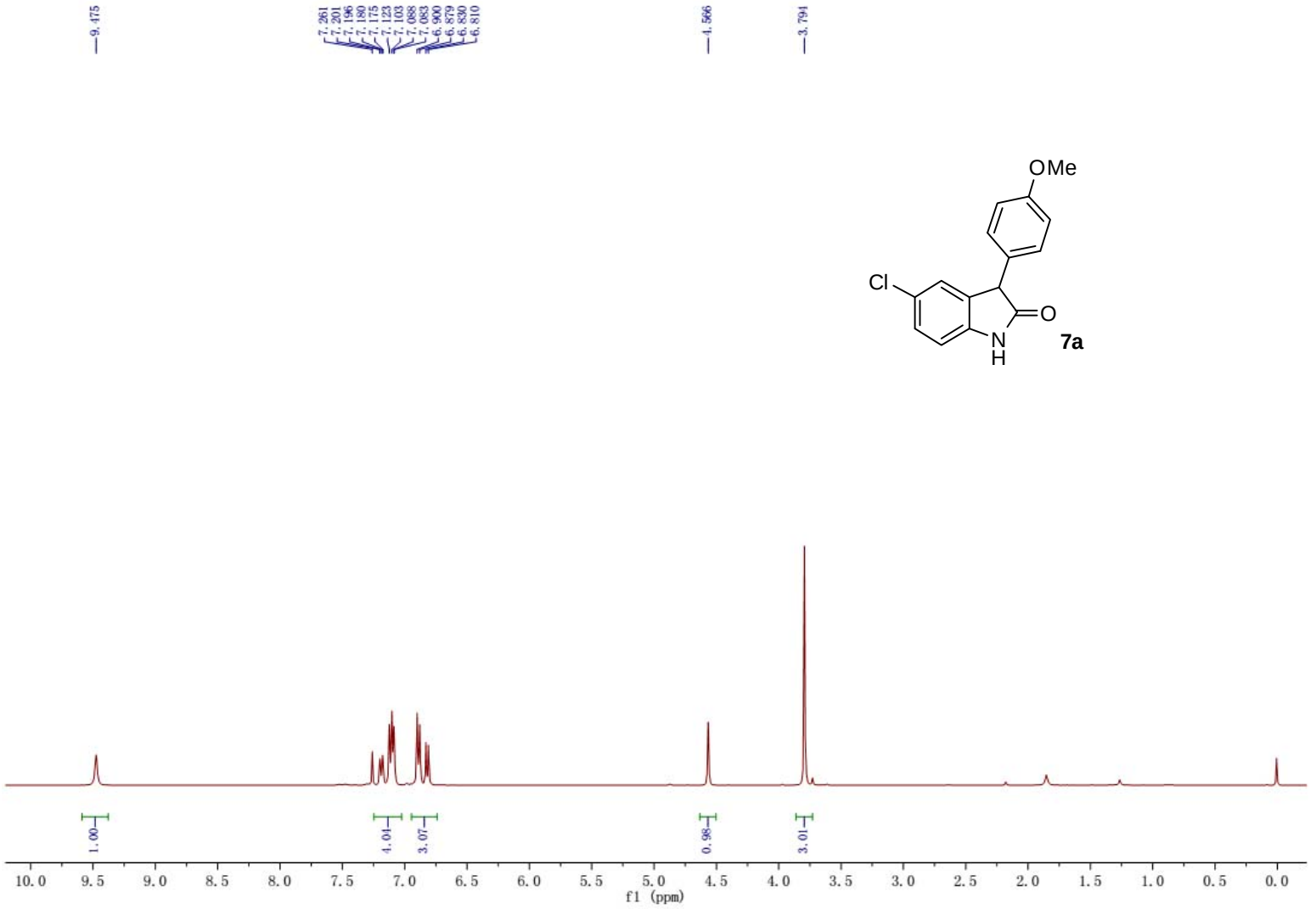
7.16
6.70

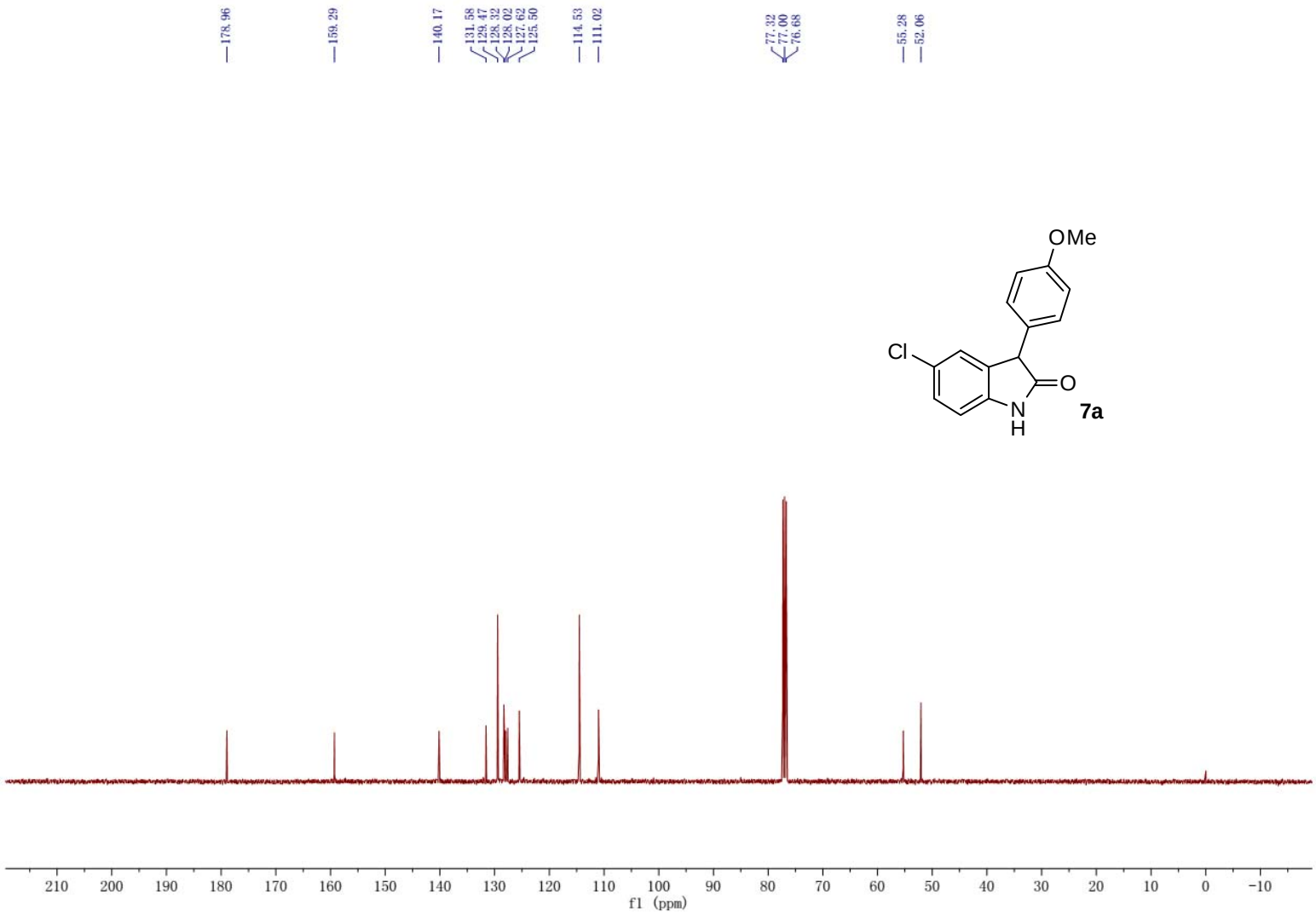


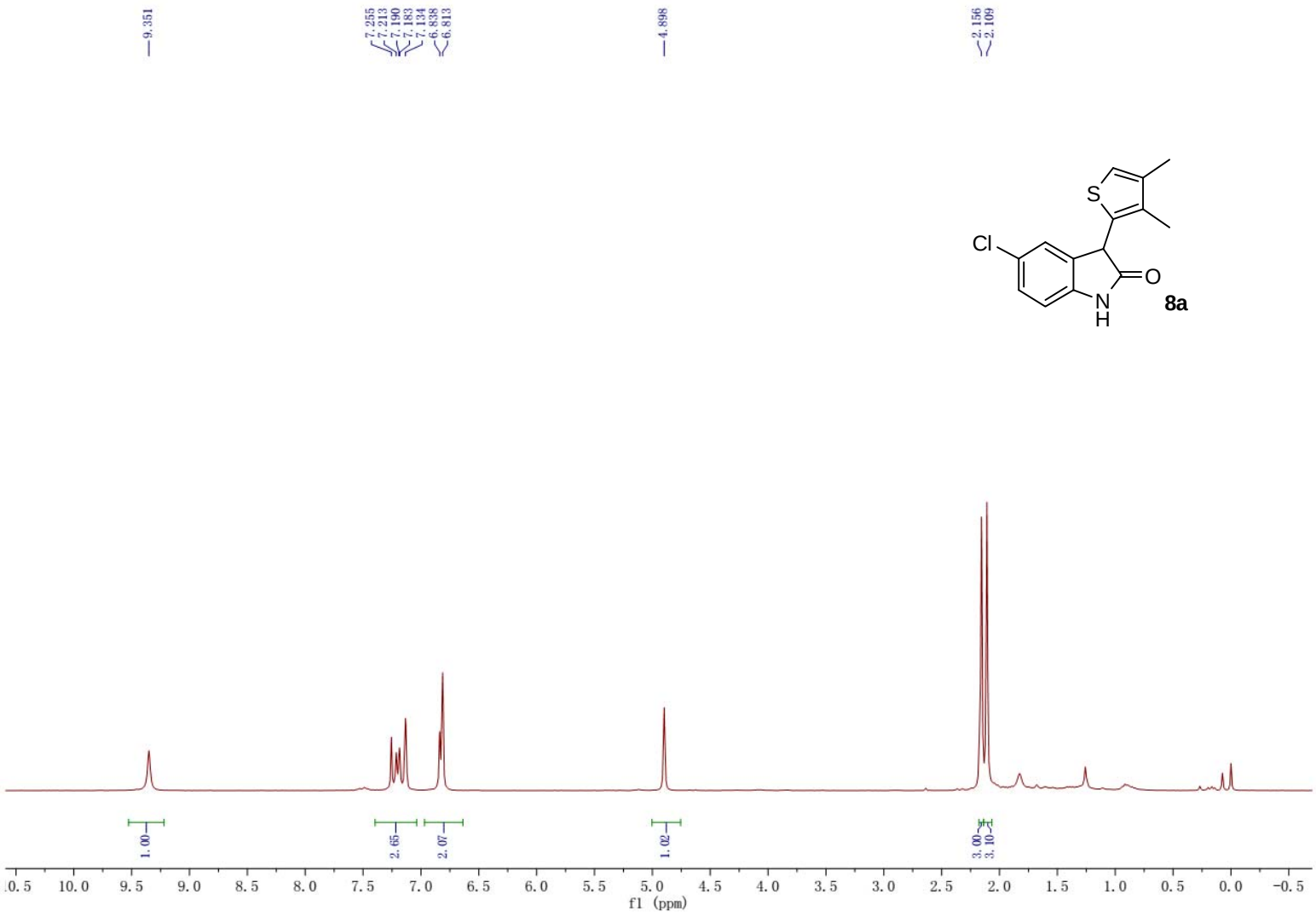
C1

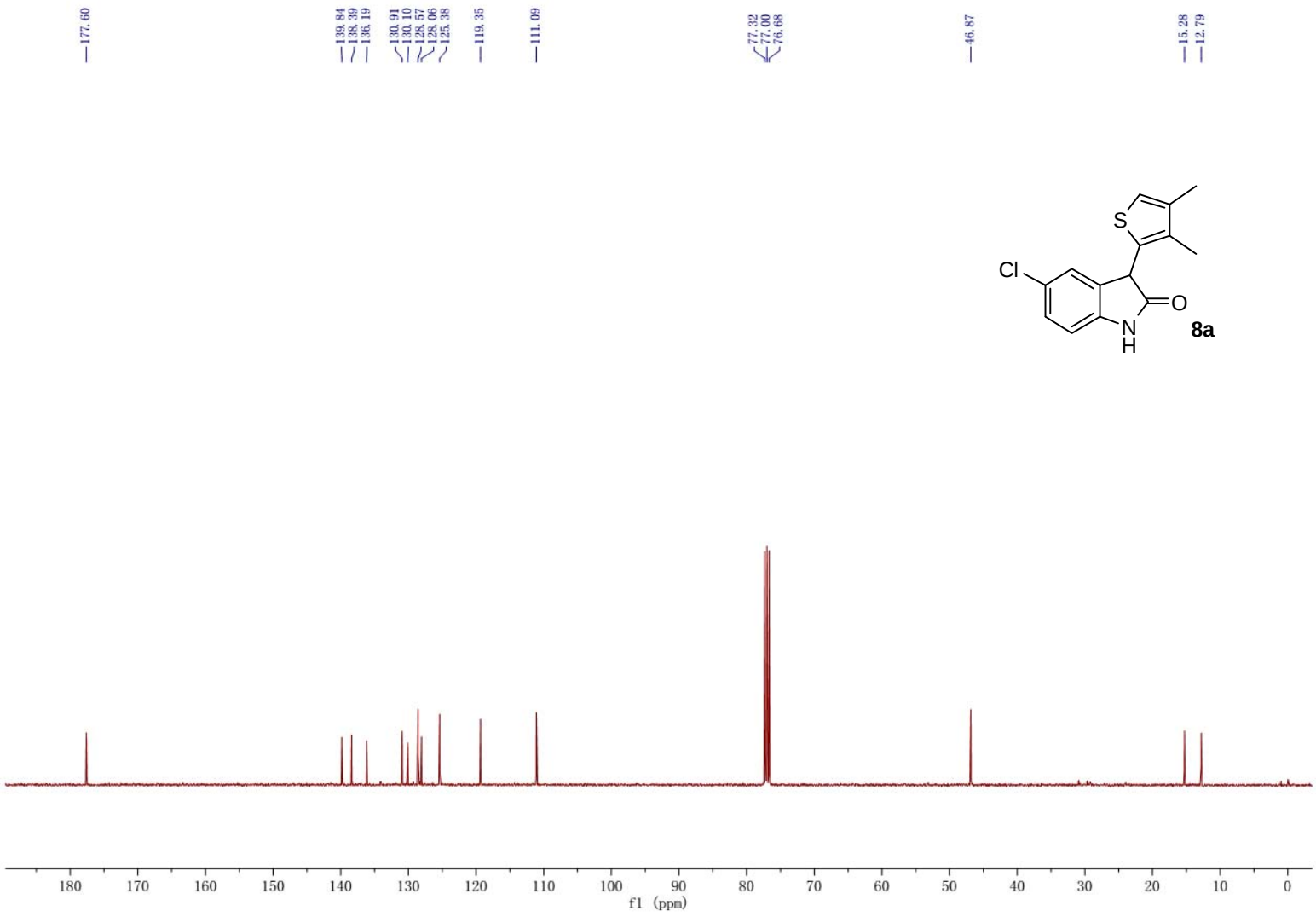


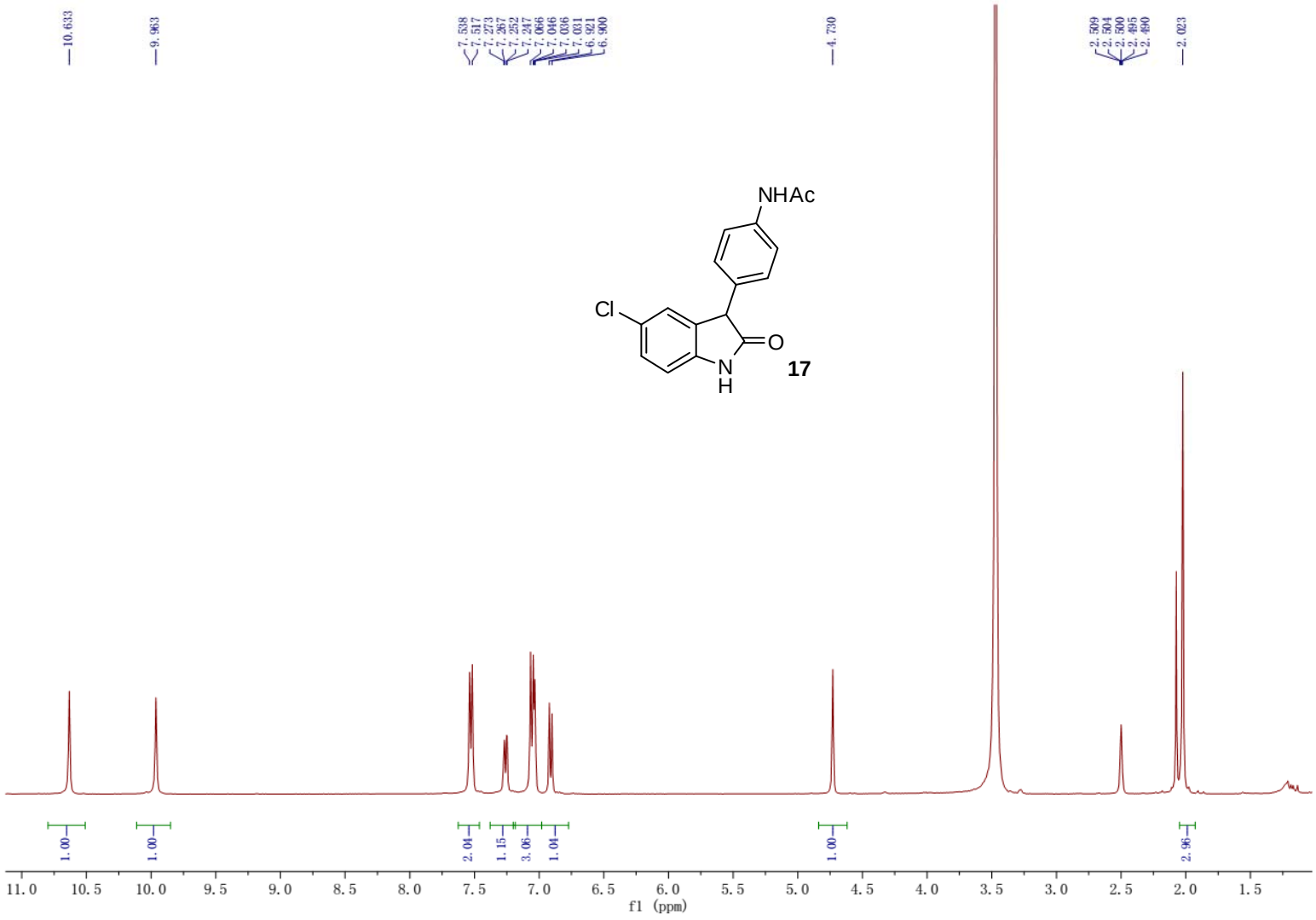


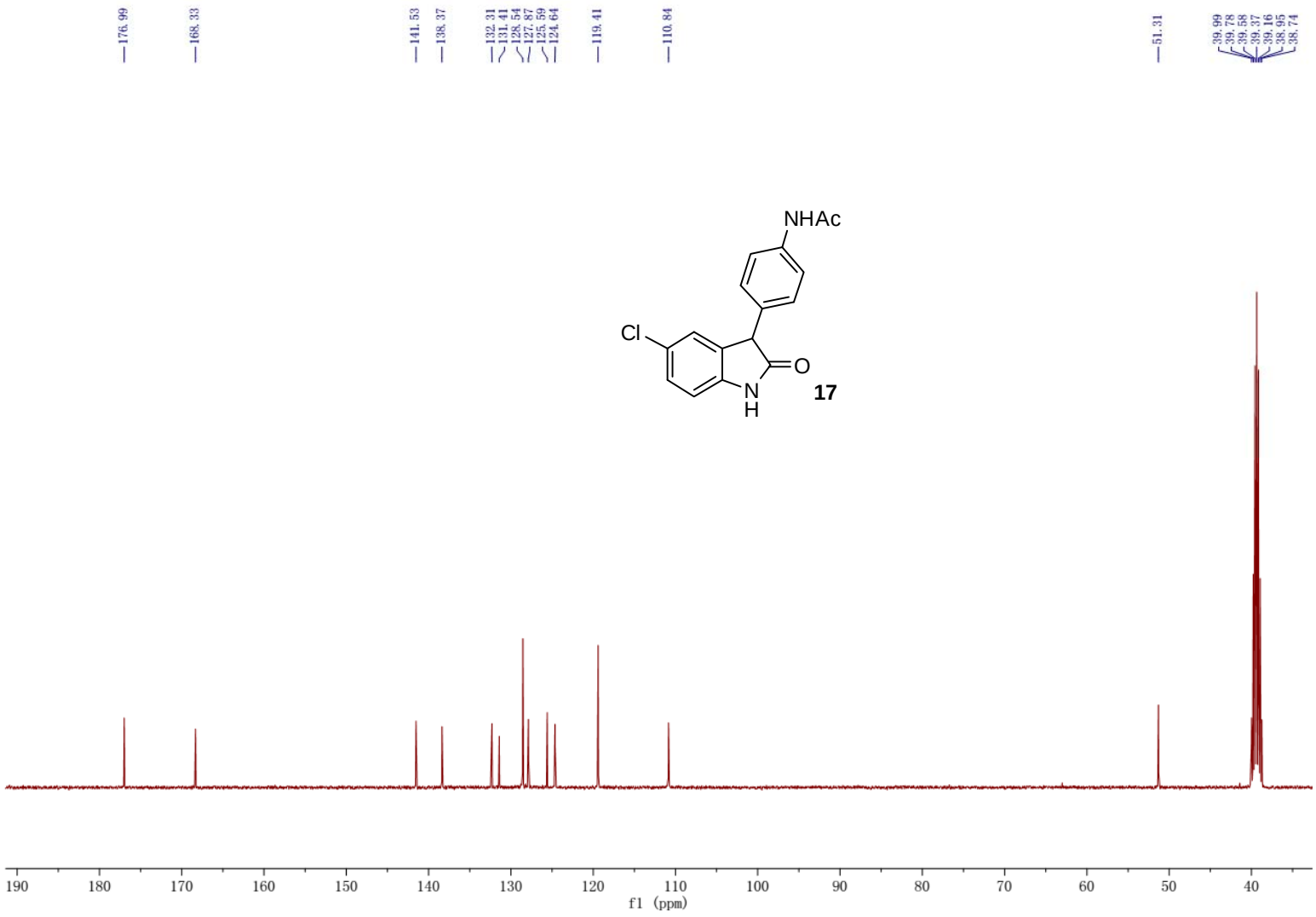

9.475
7.261
7.201
7.196
7.180
7.175
7.123
7.103
7.088
7.083
6.900
6.879
6.830
6.810
4.566
3.794
OMe
Cl
O
N
H
7a
1.00
4.04
3.07
0.98
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

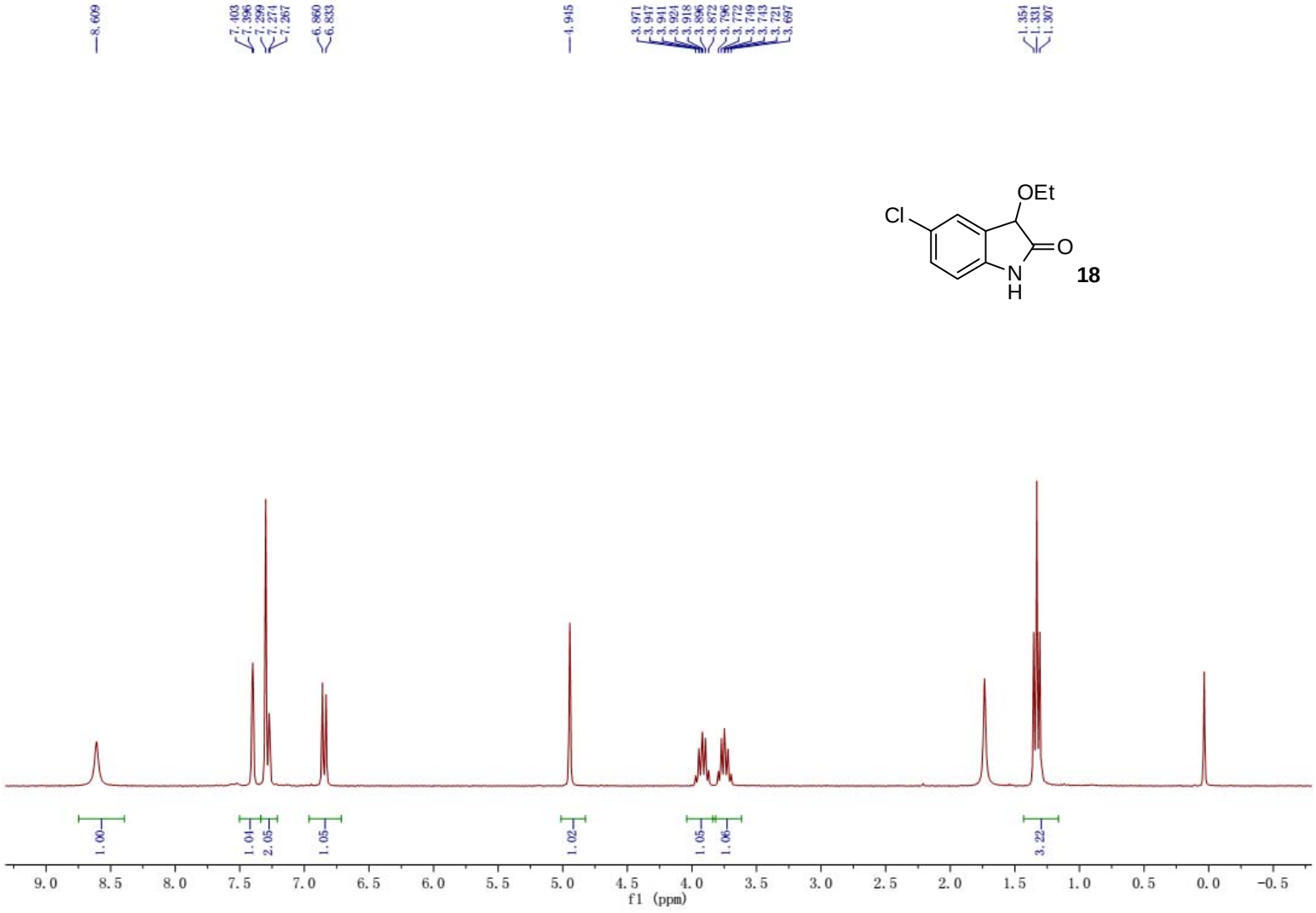

178.96
159.29
140.17
131.58
129.47
128.32
128.02
127.62
125.50
114.53
111.02
77.32
77.00
76.68
55.28
52.06
OMe
Cl
O
N
H
7a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

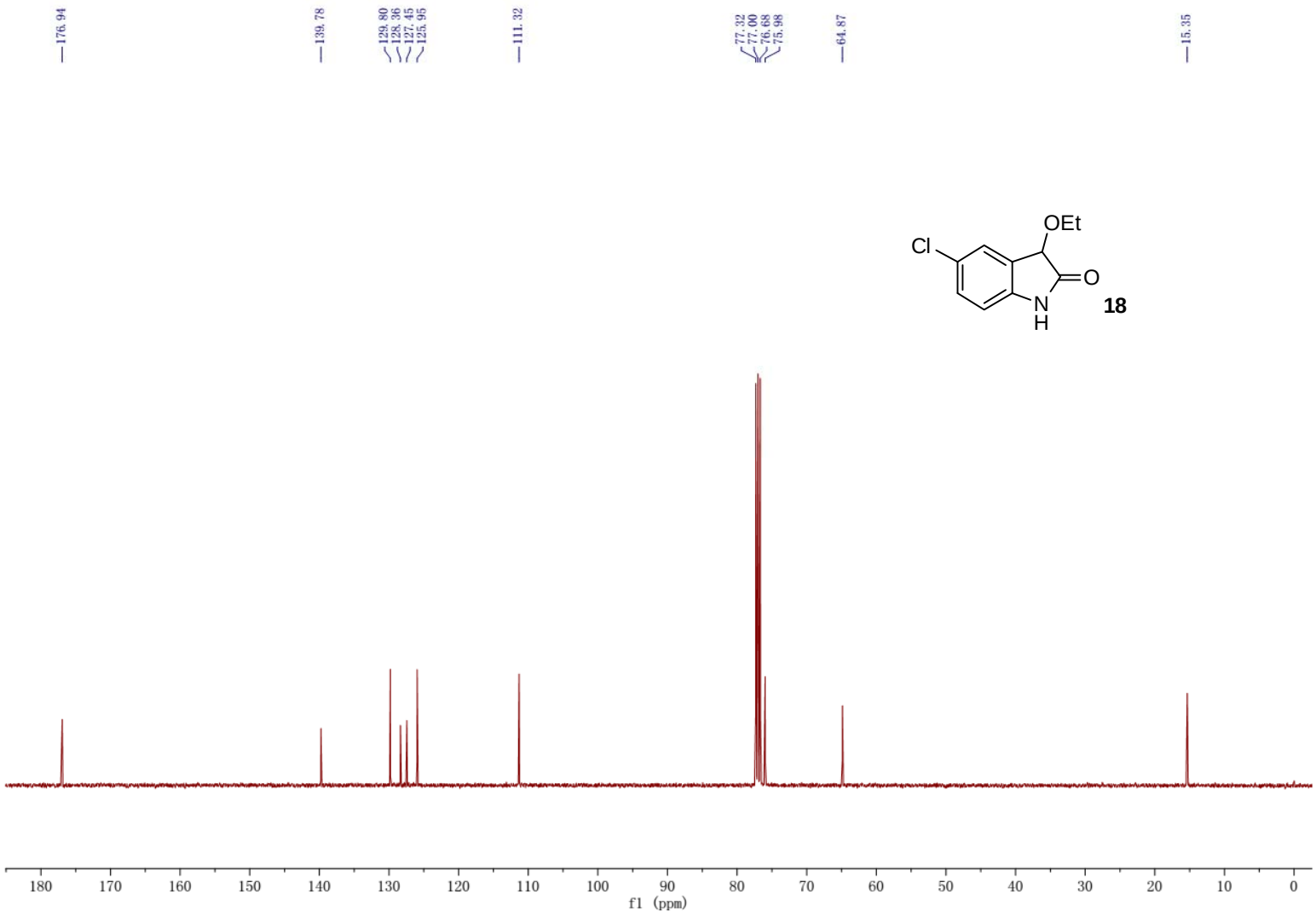

9.351
7.255
7.213
7.190
7.183
7.134
6.838
6.813
4.898
2.156
2.109
S
Cl
O
N
H
8a
1.00
2.65
2.07
1.02
3.00
3.10
f1 (ppm)


177.60
139.84
138.39
136.19
130.91
130.10
128.57
128.06
125.38
119.35
111.09
77.32
77.00
76.68
46.87
15.28
12.79
S
Cl
O
N
H
8a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

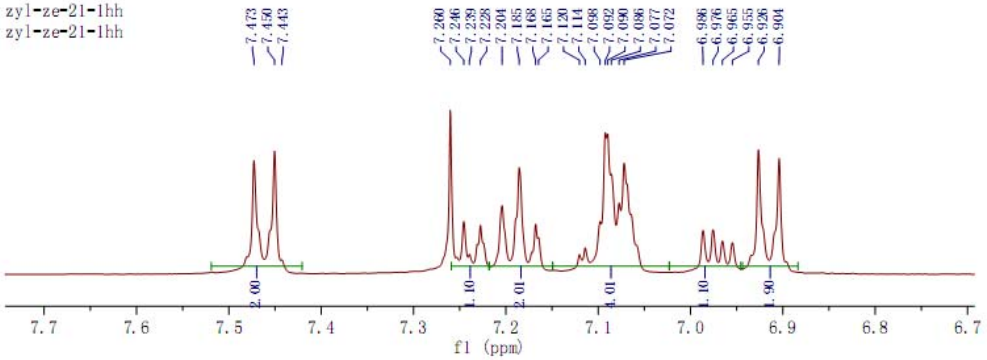

10.633
9.963
7.538
7.517
7.273
7.267
7.252
7.247
7.066
7.046
7.036
7.031
6.921
6.900
4.730
2.509
2.504
2.500
2.495
2.490
2.023
NHAc
Cl
O
N
H
17
1.00
1.00
2.04
1.15
3.06
1.04
1.00
2.96
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

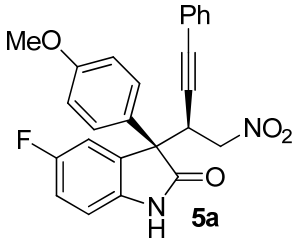

176.99
168.33
141.53
138.37
132.31
131.41
128.54
127.87
125.59
124.64
119.41
110.84
51.31
39.99
39.78
39.58
39.37
39.16
38.95
38.74
NHAc
Cl
O
N
H
17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

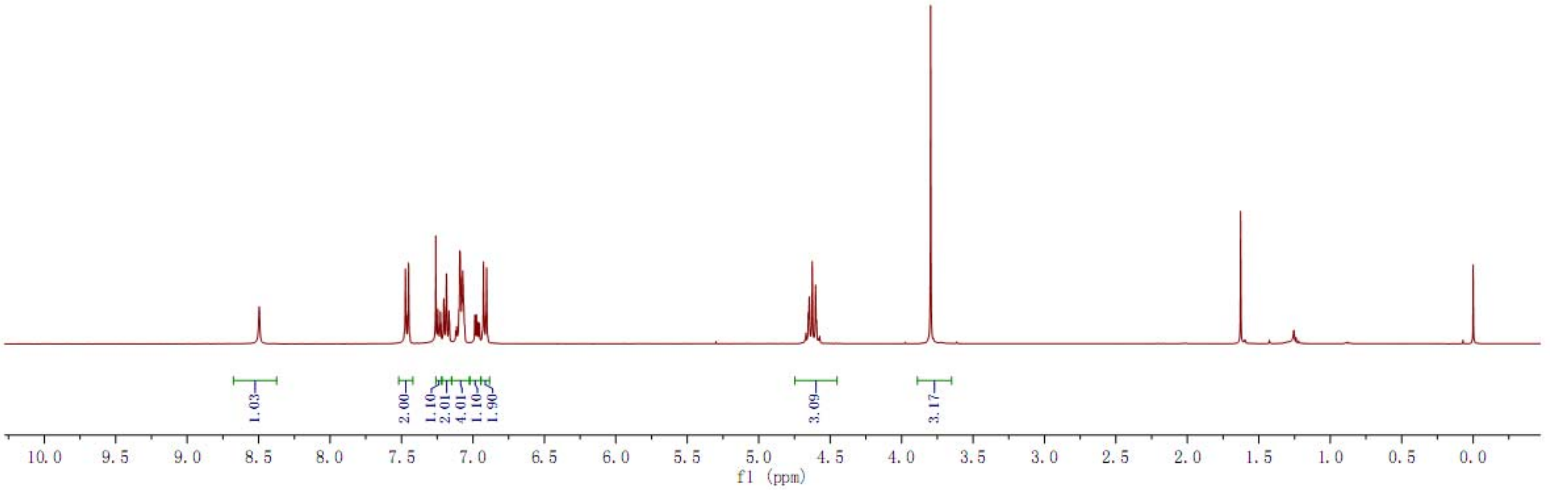

8.609
7.403
7.396
7.299
7.274
7.267
6.860
6.833
4.945
3.971
3.947
3.941
3.924
3.918
3.896
3.872
3.796
3.772
3.749
3.743
3.721
3.697
1.354
1.331
1.307
Cl
OEt
O
N
H
18
1.00
1.04
2.05
1.05
1.02
1.05
1.06
3.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


176.94
139.78
129.80
128.36
127.45
125.95
111.32
77.32
77.00
76.68
75.98
64.87
15.35
OEt
Cl
O
N
H
18
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

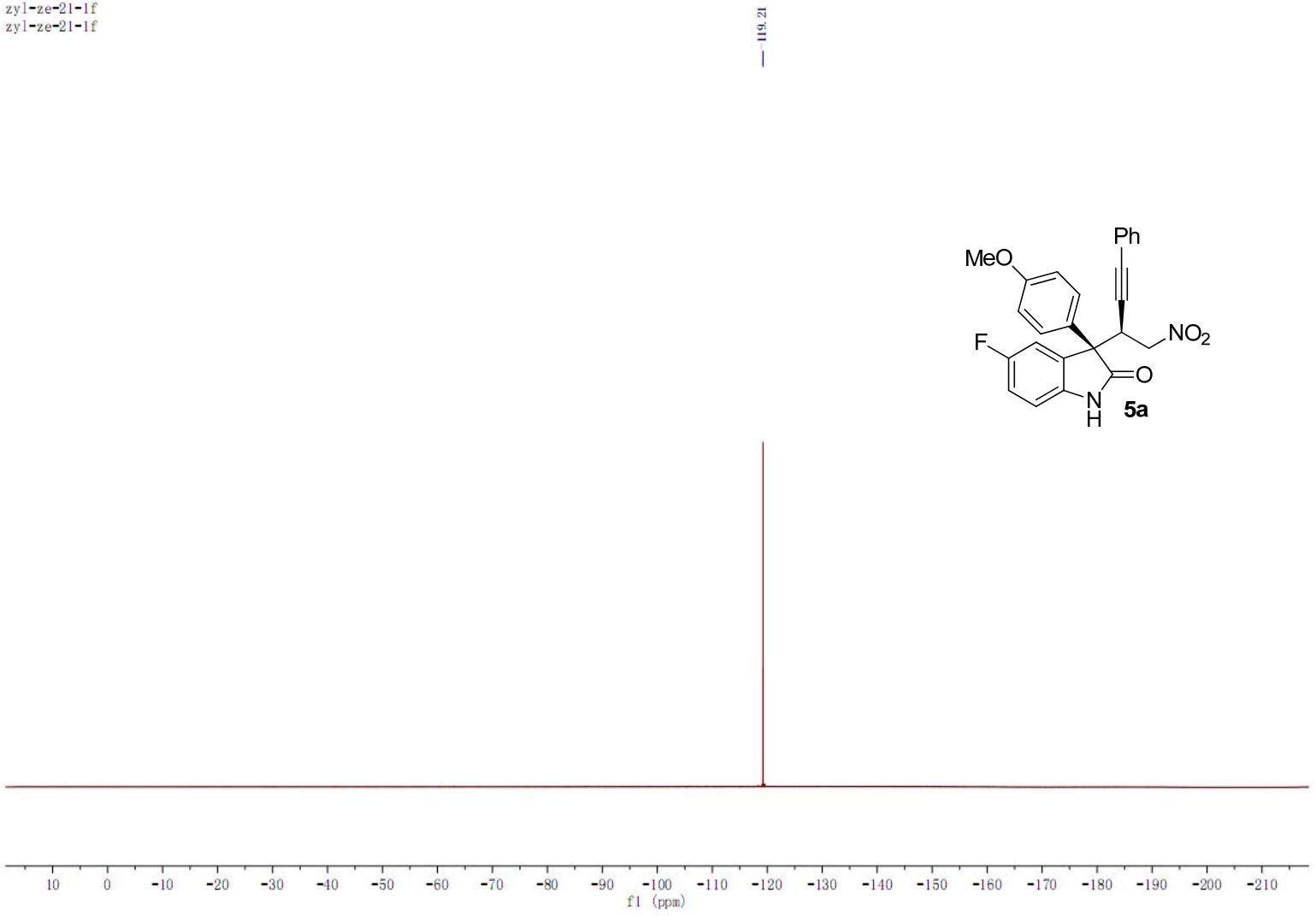

zyl-ze-21-1hh
zyl-ze-21-1hh
8.496
7.473
7.450
7.443
7.260
7.246
7.239
7.228
7.204
7.185
7.168
7.165
7.120
7.114
7.098
7.092
7.090
7.086
7.077
7.072
6.986
6.976
6.965
6.955
6.926
6.904
4.670
4.653
4.646
4.626
4.602
4.595
4.574
3.797
1.628
0.000

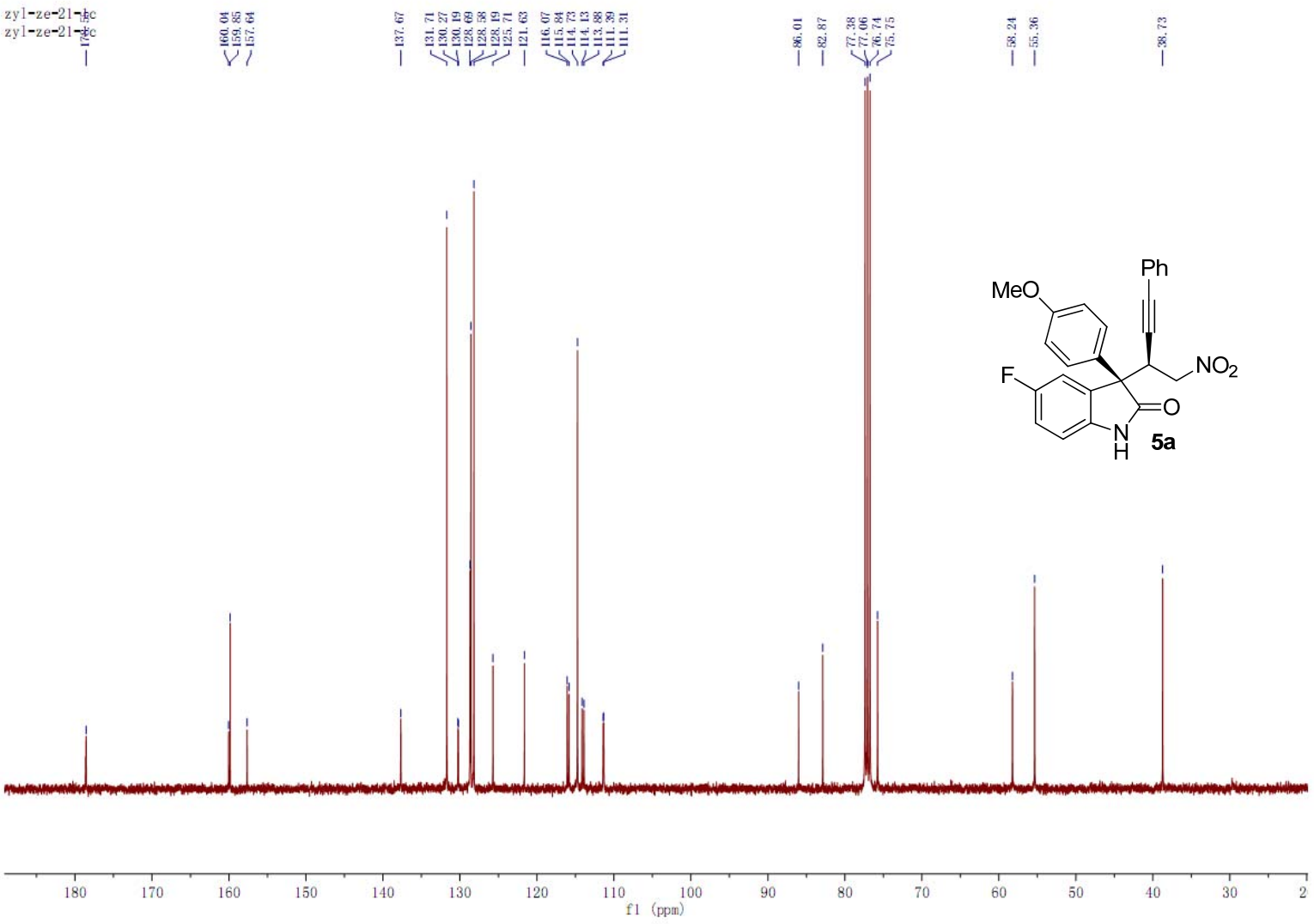

zyl-ze-21-1hh
zyl-ze-21-1hh
7.473
7.450
7.443
7.260
7.246
7.239
7.228
7.204
7.185
7.168
7.165
7.120
7.114
7.098
7.092
7.090
7.086
7.077
7.072
6.986
6.976
6.965
6.955
6.926
6.904
2.00
1.10
2.01
4.01
1.10
1.90
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)


Ph
MeO
NO2
F
O
N
H
5a

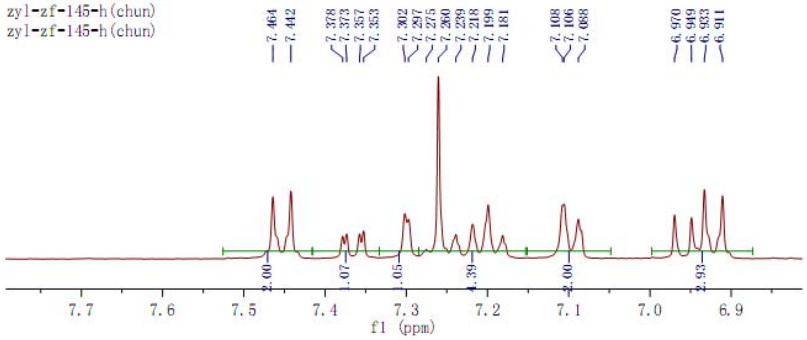

1.03
2.00
1.10
2.01
4.01
1.10
1.90
3.09
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

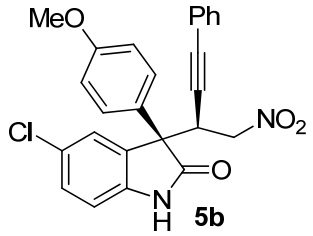
zyl-ze-21-1f
zyl-ze-21-1f



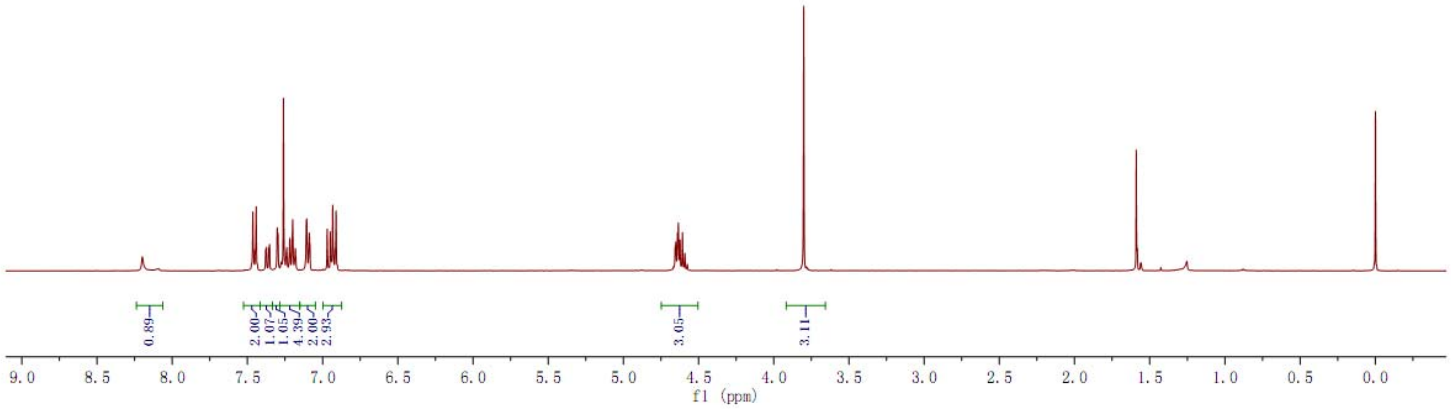

zyl-ze-21-hc
zyl-ze-21-hc
160.04
159.85
157.64
137.67
131.71
130.27
130.19
128.69
128.58
128.19
125.71
121.63
116.07
115.84
114.73
114.13
113.88
111.39
111.31
86.01
82.87
77.38
77.06
76.74
75.75
58.24
55.36
38.73
MeO
Ph
NO2
F
O
N
H
5a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
2
f1 (ppm)

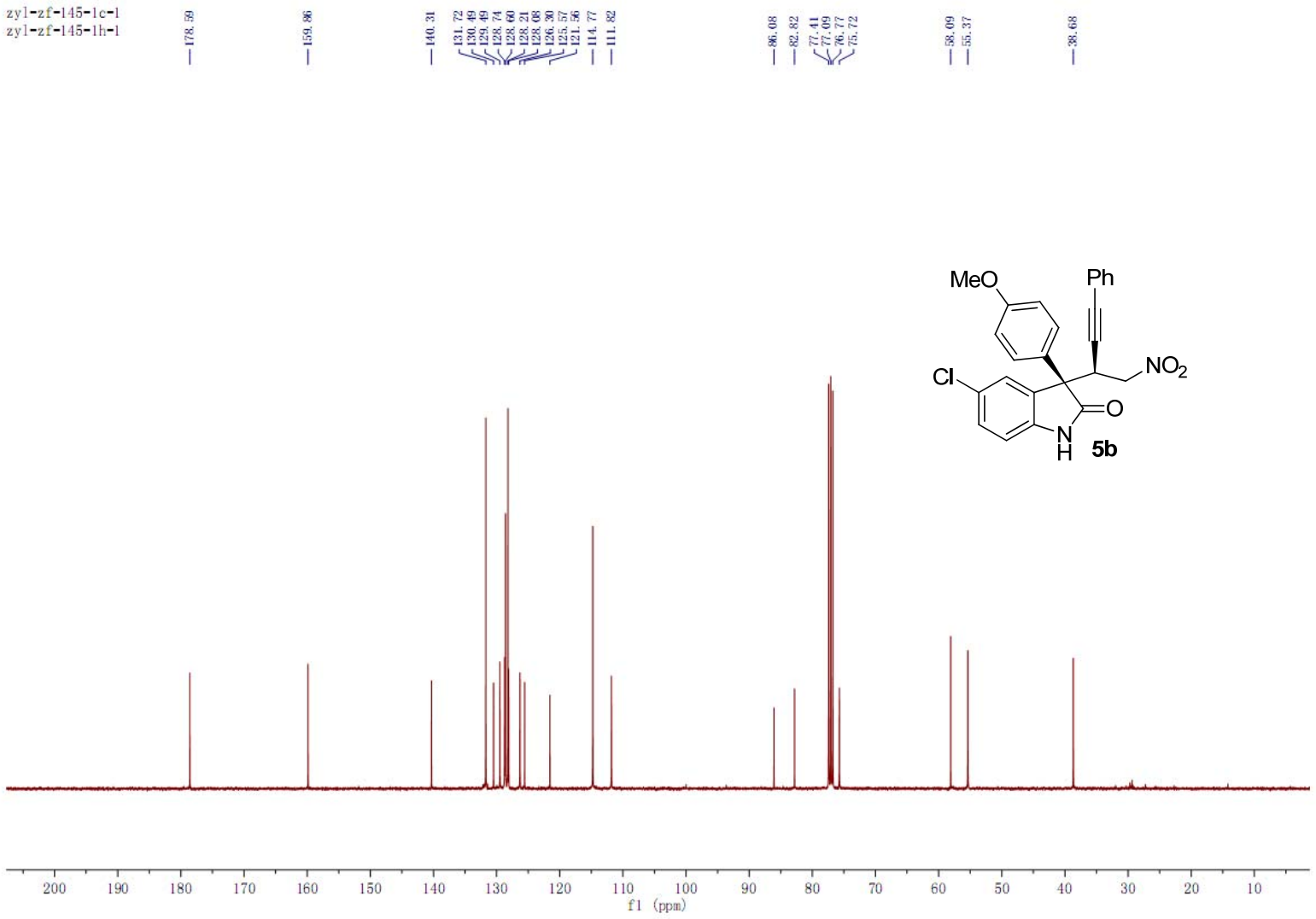

zyl-zf-145-h(chun)
zyl-zf-145-h(chun)

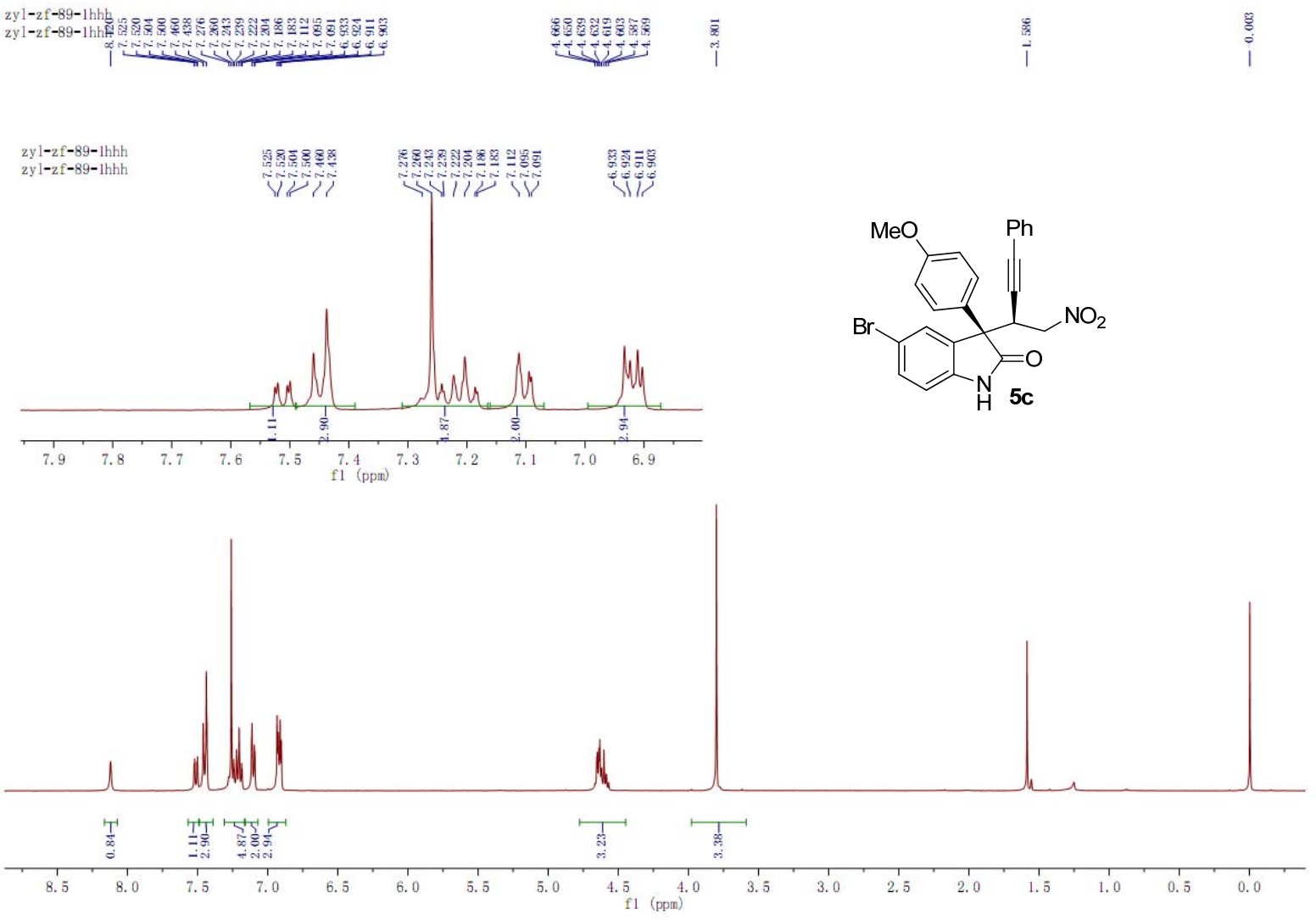

zyl-zf-145-h(chun)
zyl-zf-145-h(chun)
f1 (ppm)

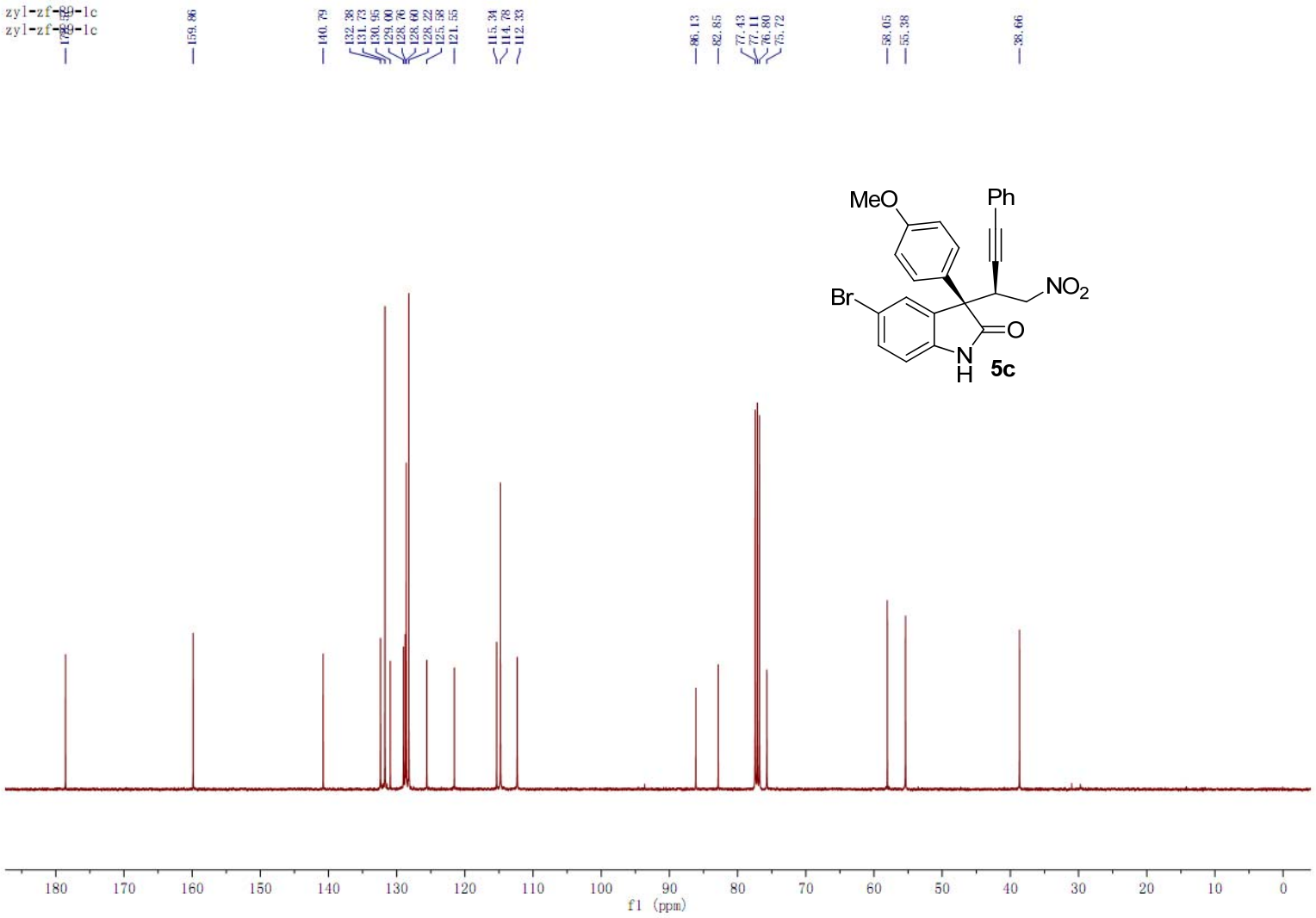

MeO
Ph
NO2
Cl
O
N
H

5b

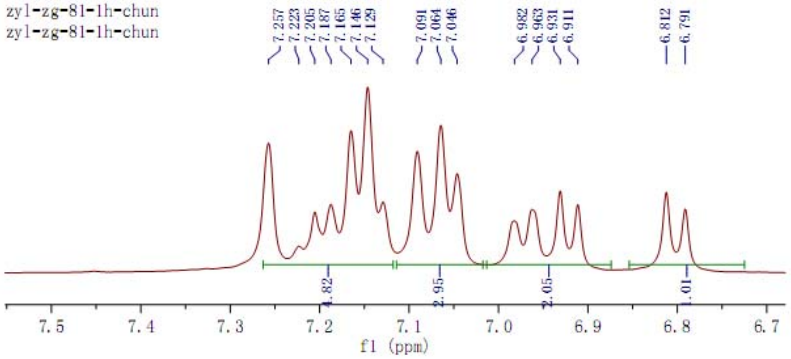

f1 (ppm)

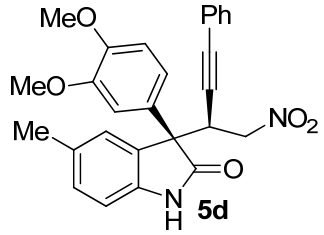

zyl-zf-145-1c-1
zyl-zf-145-1h-1
178.59
159.86
140.31
131.72
130.49
129.49
128.74
128.60
128.21
128.08
126.30
125.57
121.56
114.77
111.82
86.08
82.82
77.41
77.09
76.77
75.72
58.09
55.37
38.68
MeO
Ph
NO2
Cl
O
N
H
5b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


zyl-zf-89-1hhh
zyl-zf-89-1hhh
MeO
Ph
NO2
Br
O
N
H
5c
f1 (ppm)

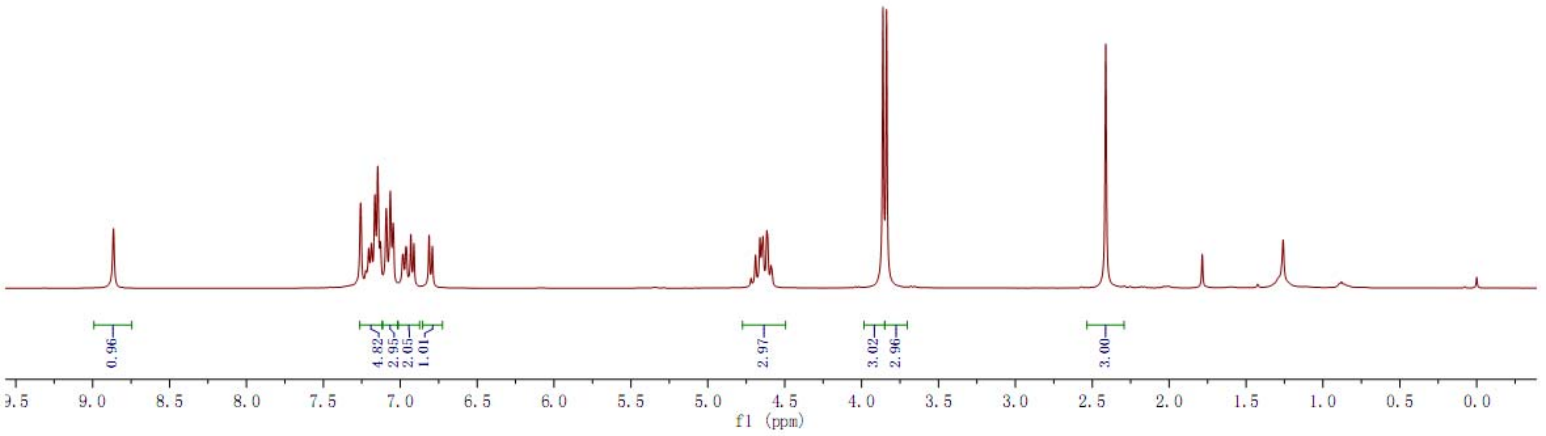

zyl-zf-89-1c
zyl-zf-89-1c
159.86
140.79
132.38
131.73
130.95
129.00
128.76
128.60
128.22
125.38
121.55
115.34
114.78
112.33
86.13
82.85
77.43
77.11
76.80
75.72
58.05
55.38
38.66
MeO
Ph
NO2
Br
O
N
H
5c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

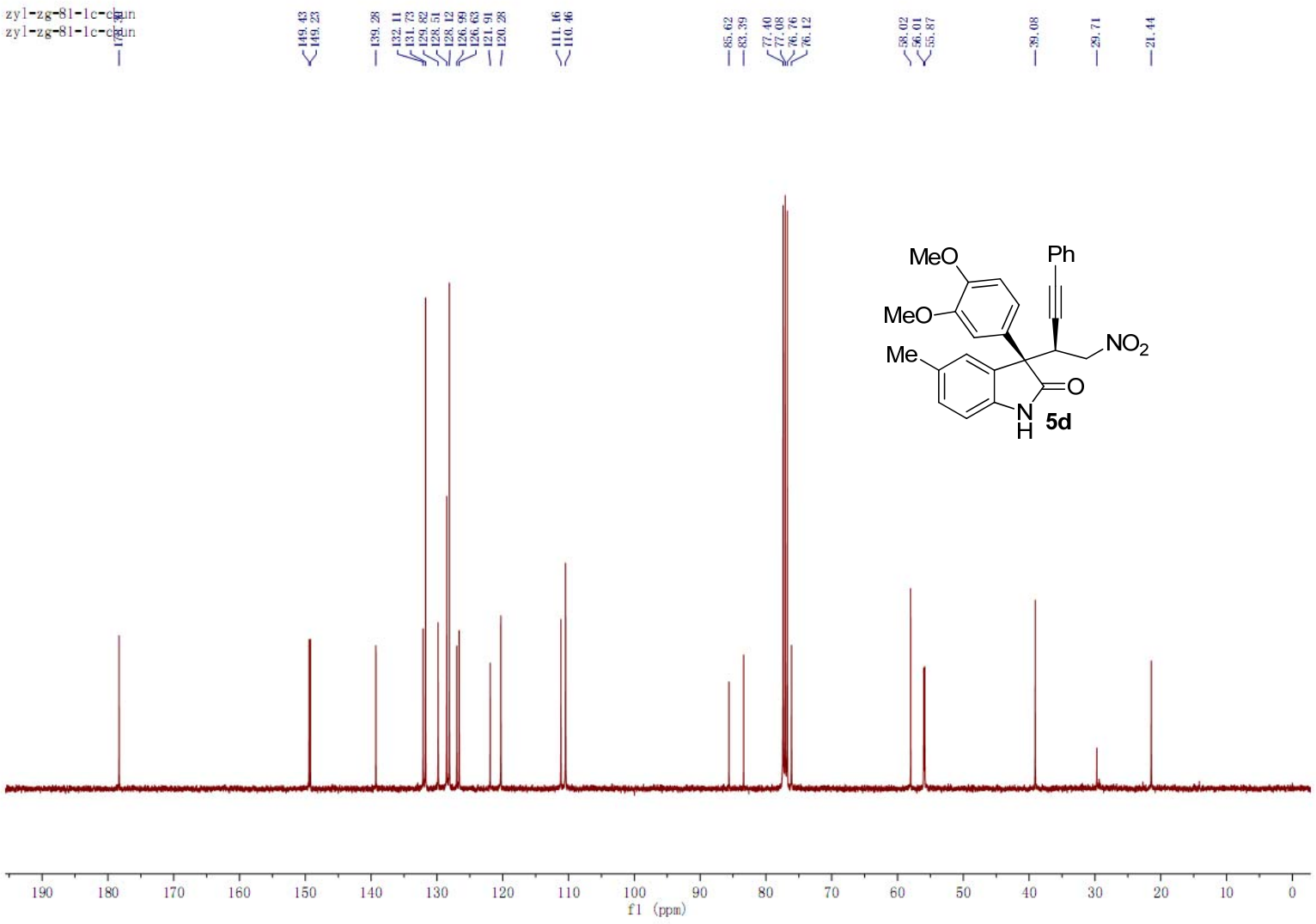

zyl-zg-81-1h-chun
zyl-zg-81-1h-chun
7.257
7.223
7.205
7.187
7.165
7.146
7.129
7.091
7.064
7.046
6.982
6.963
6.931
6.911
6.812
6.791
4.719
4.690
4.661
4.641
4.616
4.589
3.861
3.838
2.412
1.785
1.259
0.000

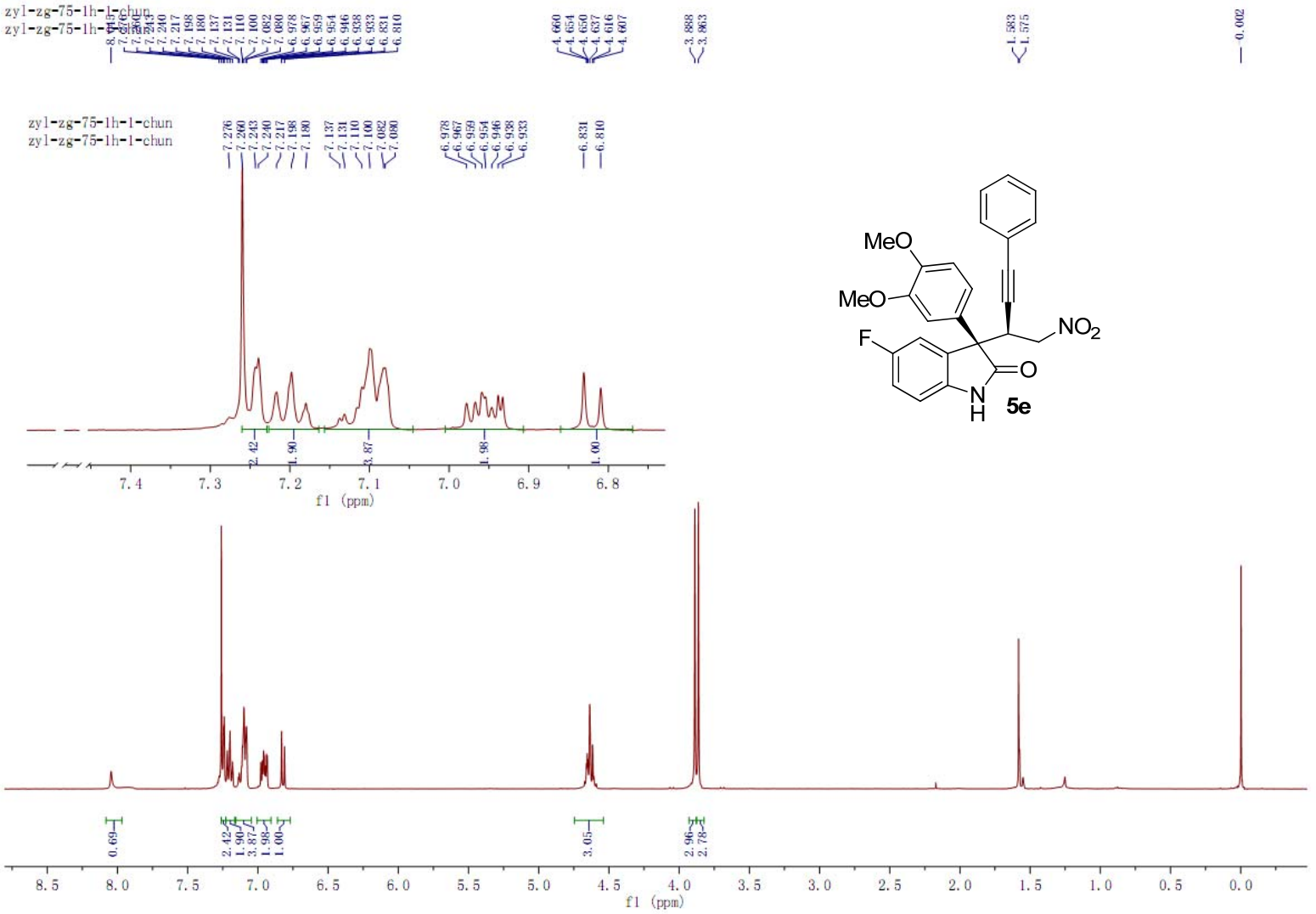

zyl-zg-81-1h-chun
zyl-zg-81-1h-chun
7.257
7.223
7.205
7.187
7.165
7.146
7.129
7.091
7.064
7.046
6.982
6.963
6.931
6.911
6.812
6.791
4.82
2.95
2.05
1.01
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)


MeO
MeO
Me
Ph
NO2
O
N
H

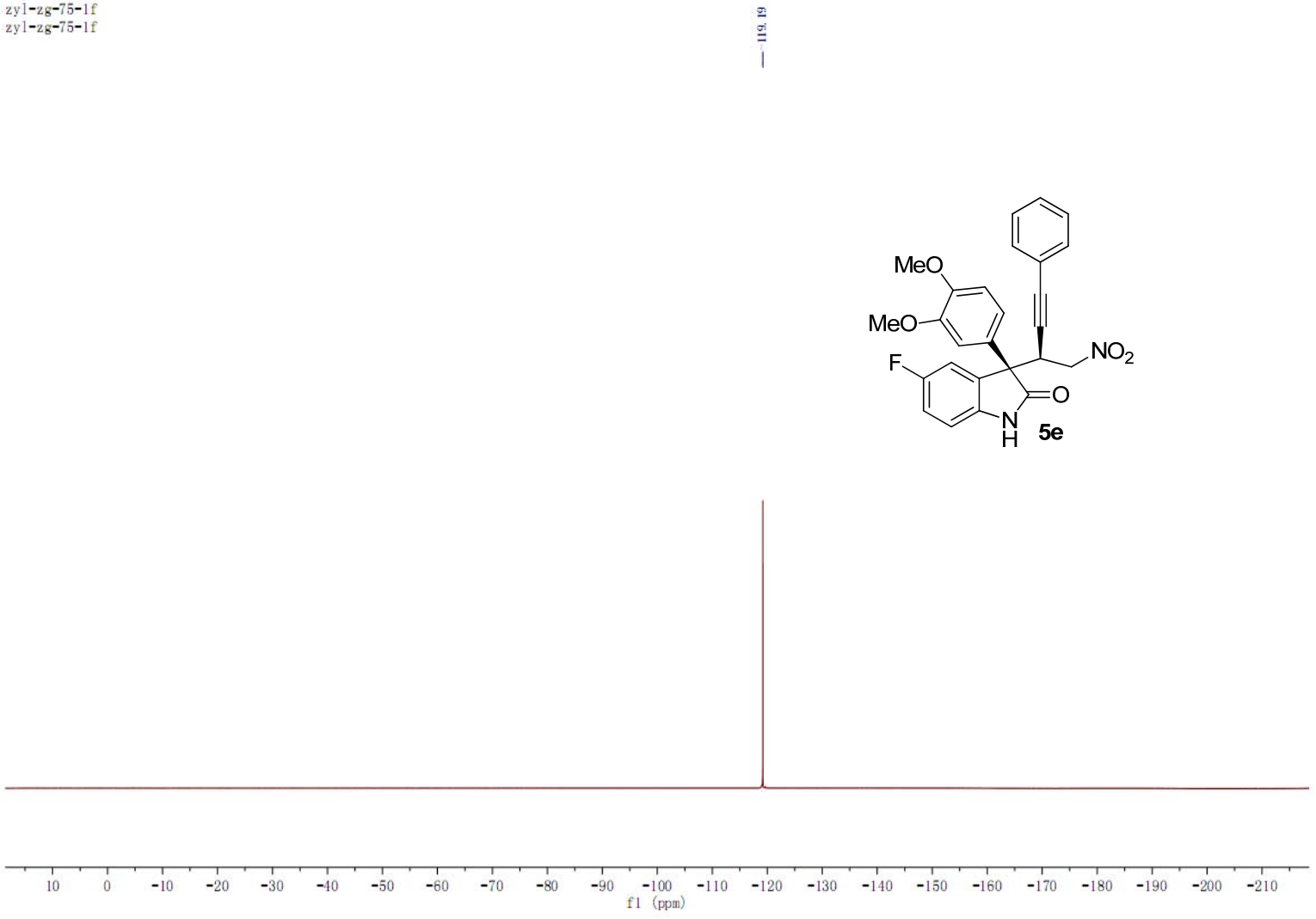
5d

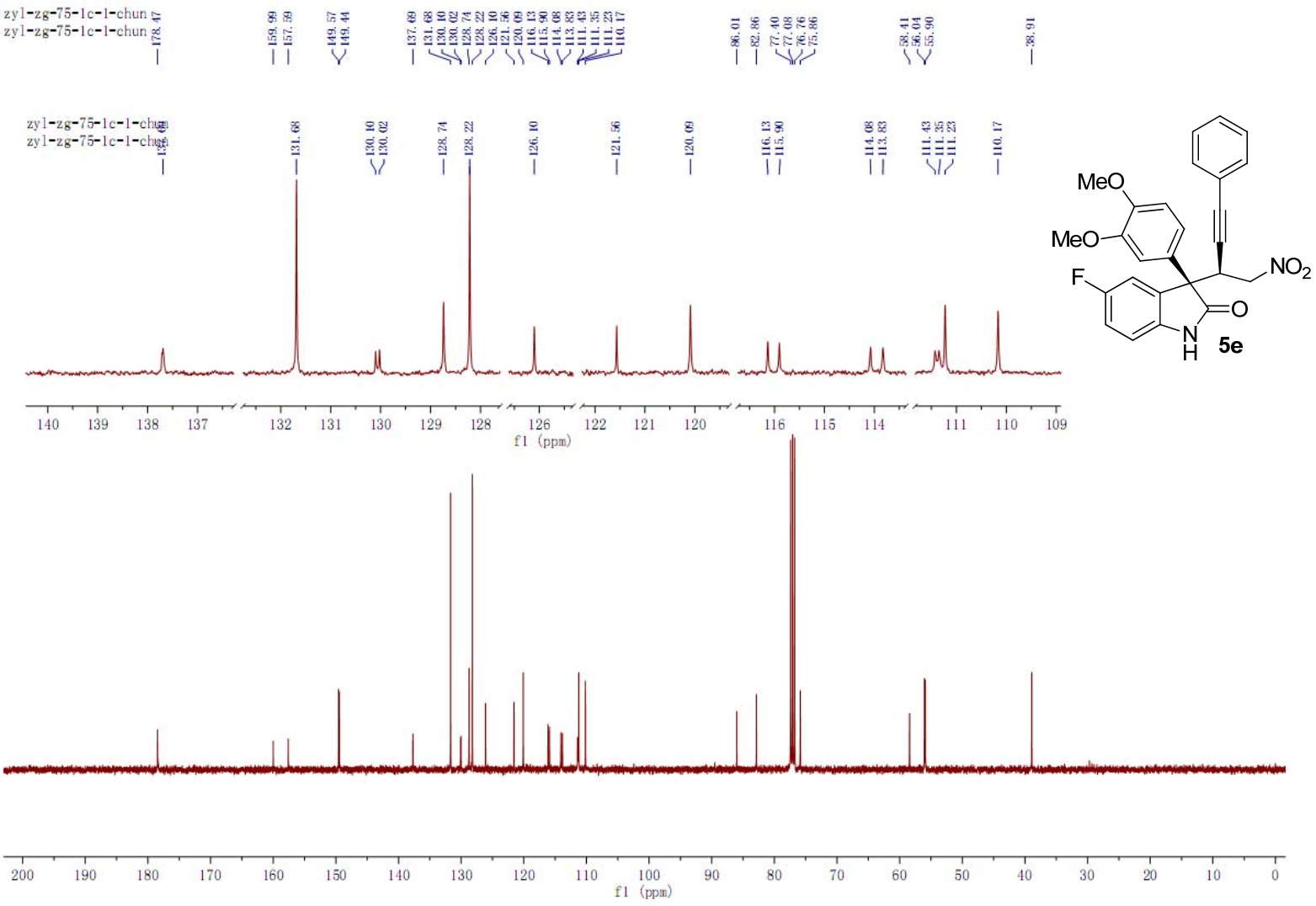

0.96
4.82
2.95
2.05
1.01
2.97
3.02
2.96
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

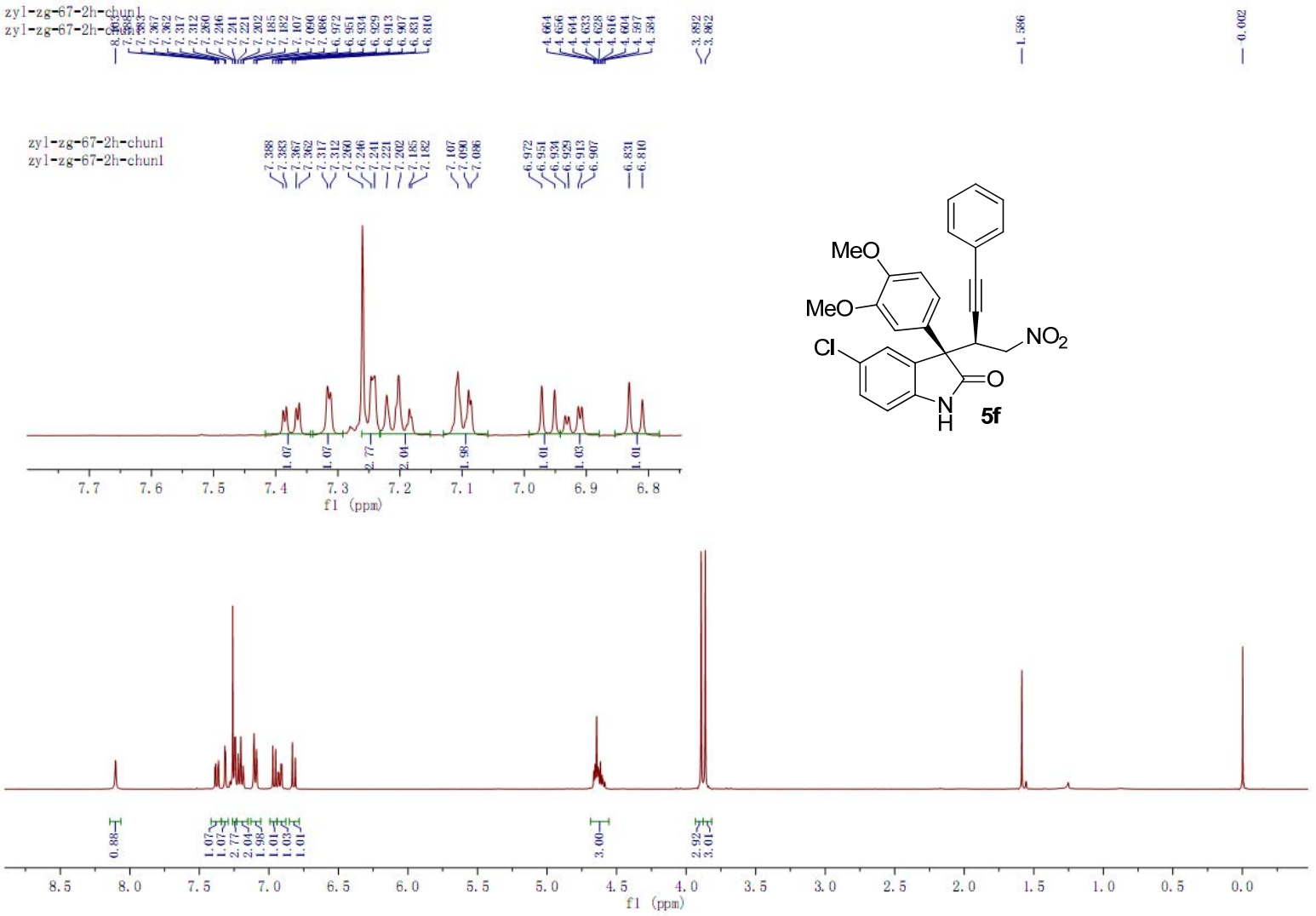

zyl-zg-81-1c-cdun
zyl-zg-81-1c-cdun
149.43
149.23
139.28
132.11
131.73
129.82
128.51
128.12
126.99
126.63
121.91
120.28
111.16
110.46
85.62
83.39
77.40
77.08
76.76
76.12
58.02
56.01
55.87
39.08
29.71
21.44
MeO
MeO
Ph
NO2
Me
O
N
H
5d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

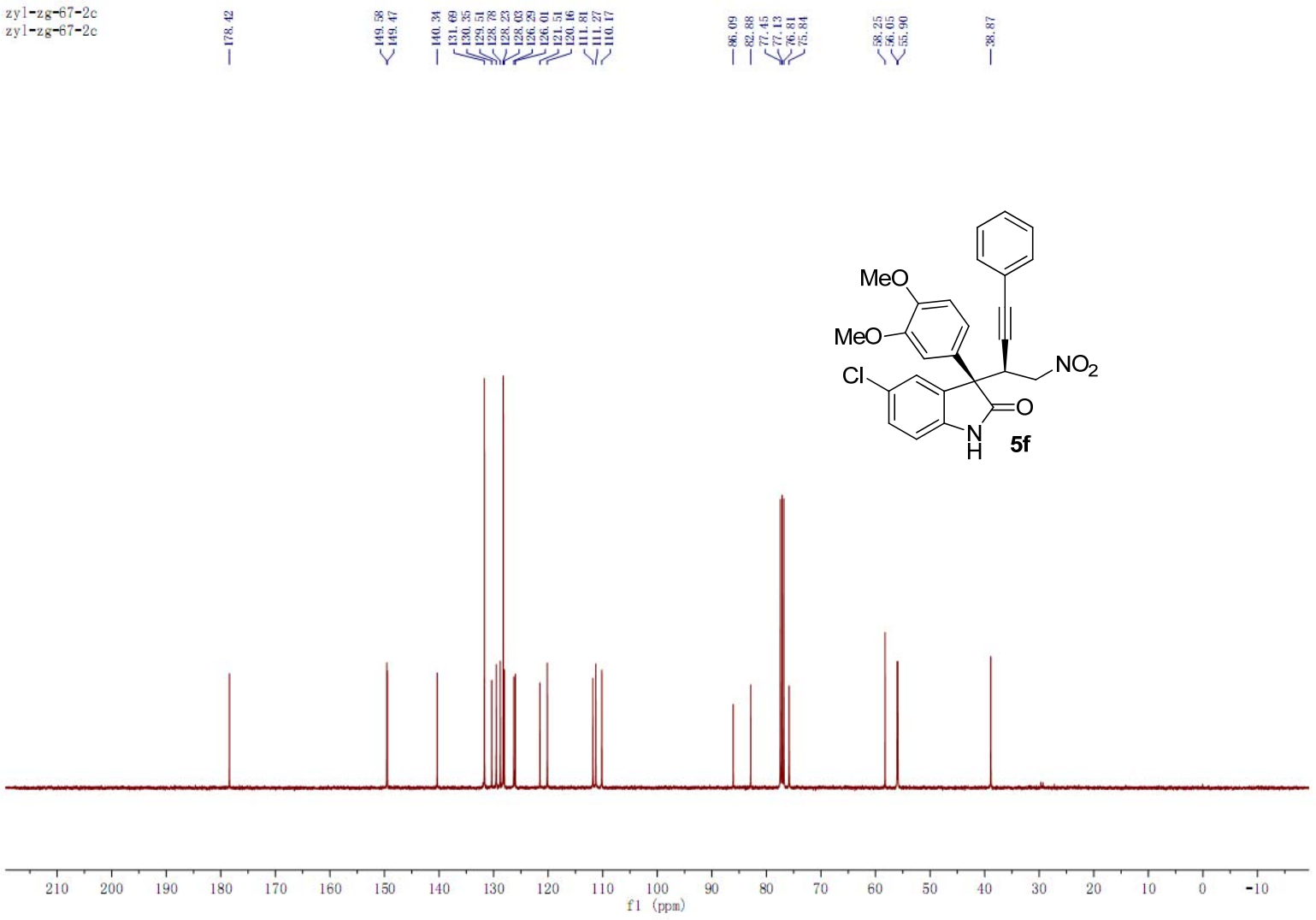

zyl-zg-75-1h-1-chun
zyl-zg-75-1h-1-chun
MeO
MeO
F
NO2
O
N
H
5e
f1 (ppm)

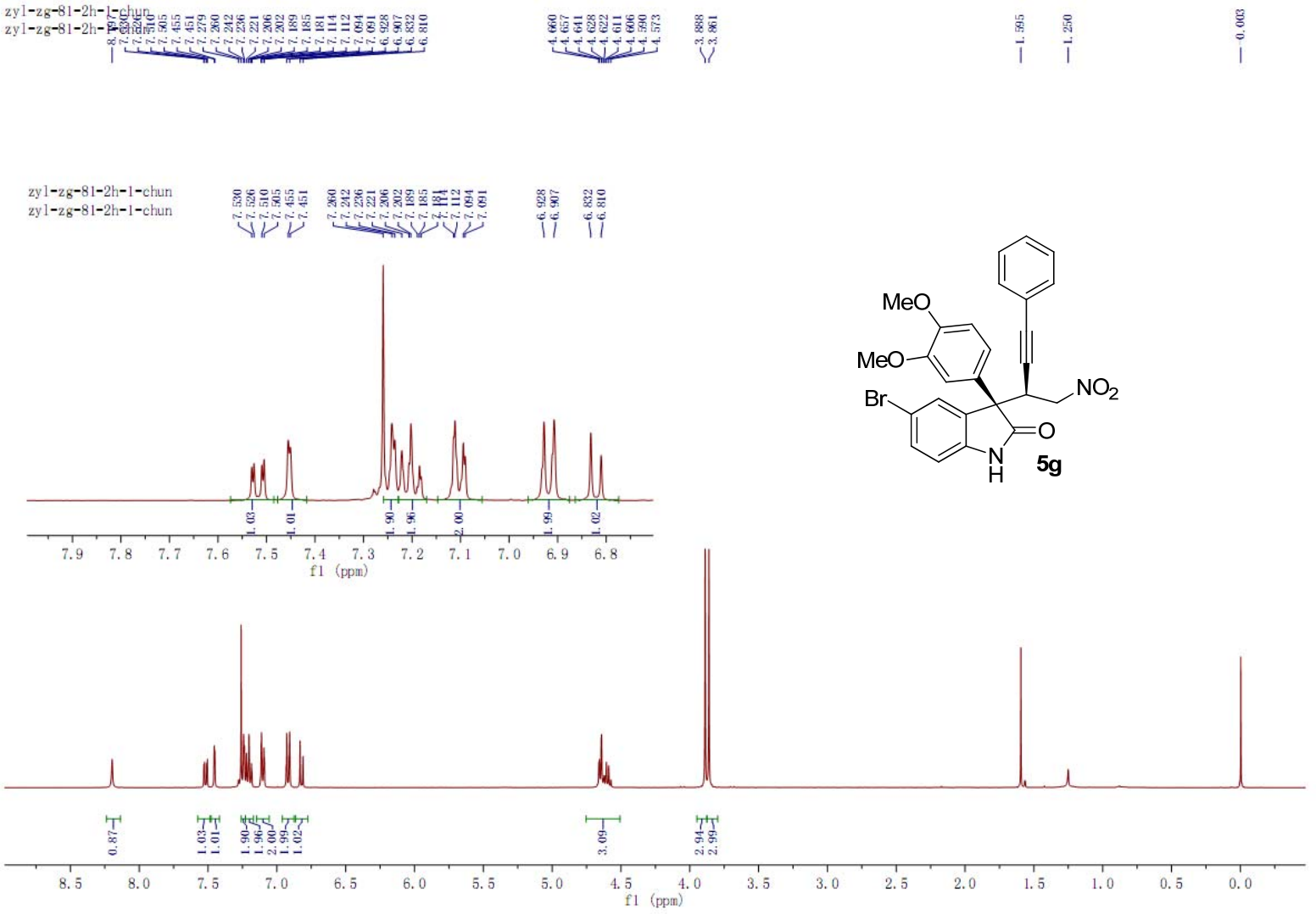
zyl-zg-75-1f
zyl-zg-75-1f

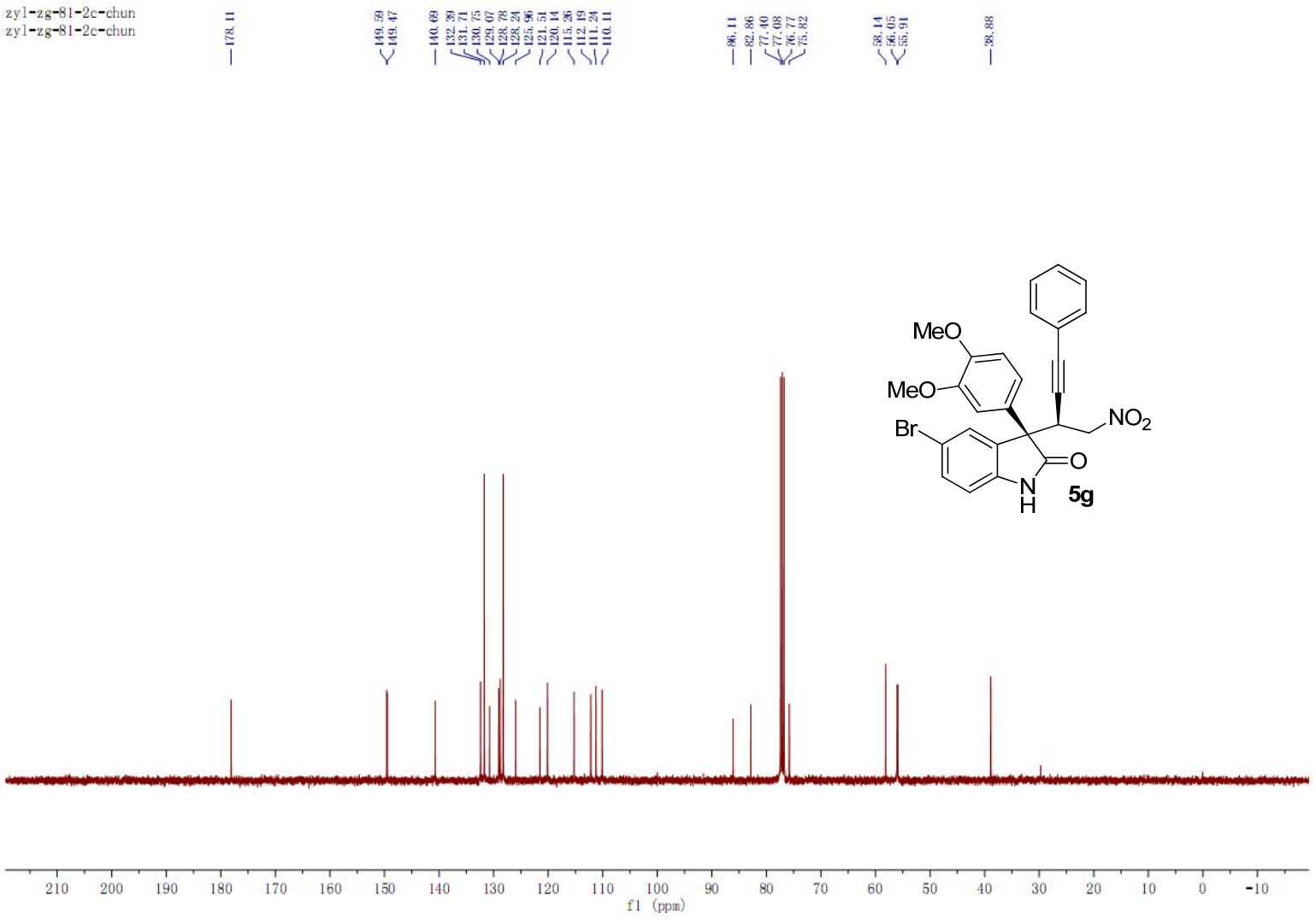


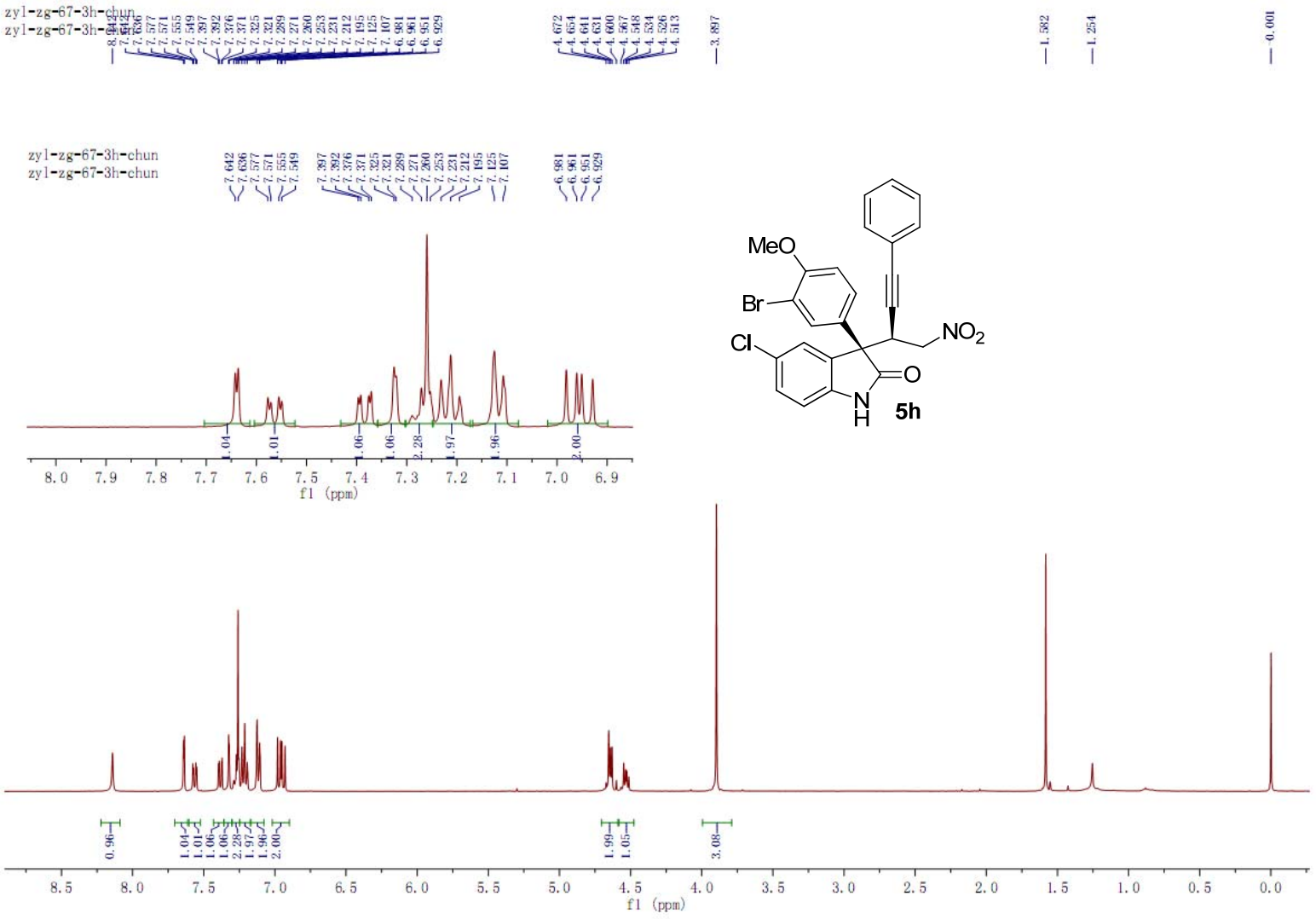

zyl-zg-75-1c-1-chun
zyl-zg-75-1c-1-chun
178.47
159.99
157.59
149.57
149.44
137.69
131.68
130.10
130.02
128.74
128.22
126.10
121.56
120.09
116.13
115.90
114.08
113.83
111.43
111.35
111.23
110.17
86.01
82.86
77.40
77.08
76.76
75.86
58.41
56.04
55.90
38.91
MeO
MeO
F
O
N
H
NO2
5e
f1 (ppm)
f1 (ppm)

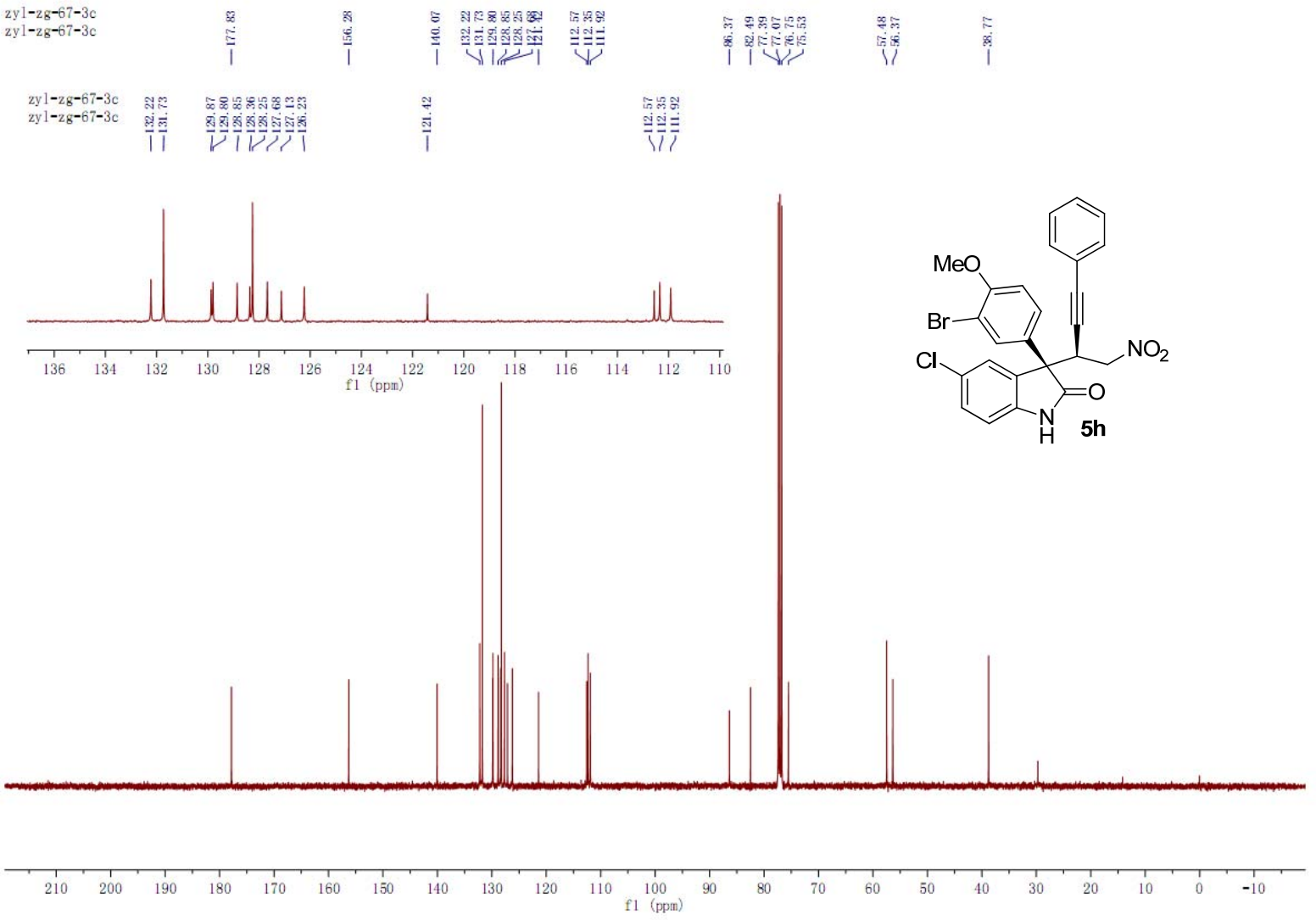

zyl-zg-67-2h-chunl
zyl-zg-67-2h-chunl
MeO
MeO
Cl
NO2
O
N
H
5f
f1 (ppm)


zyl-zg-67-2c
zyl-zg-67-2c
178.42
149.58
149.47
140.34
131.69
130.35
129.51
128.78
128.23
128.03
126.29
126.01
121.51
120.16
111.81
111.27
110.17
86.09
82.88
77.45
77.13
76.81
75.84
58.25
56.05
55.90
38.87
MeO
MeO
Cl
NO2
O
N
H
5f
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)

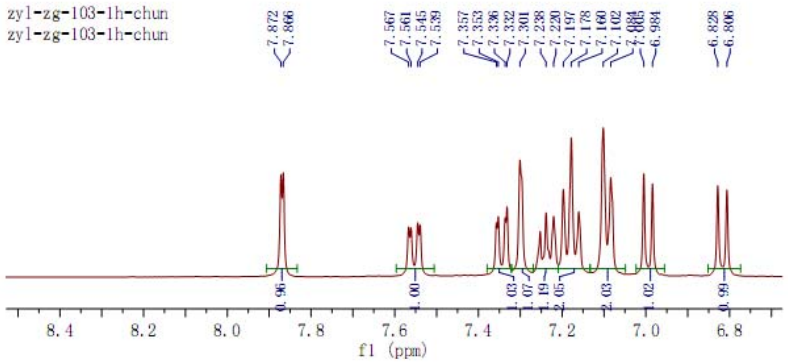

zyl-zg-81-2h-1-chun
zyl-zg-81-2h-1-chun
MeO
MeO
Br
NO2
O
N
H
5g
f1 (ppm)

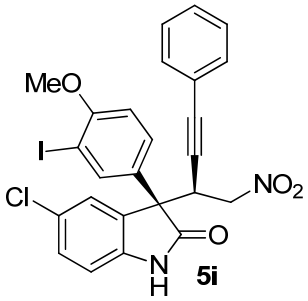

zyl-zg-81-2c-chun
zyl-zg-81-2c-chun
178.11
149.59
149.47
140.69
132.39
131.71
130.75
129.67
128.78
128.24
125.96
121.51
120.14
115.26
112.19
111.24
110.11
86.11
82.86
77.40
77.08
76.77
75.82
58.14
56.05
55.91
38.88
MeO
MeO
Br
NO2
O
N
H
5g
f1 (ppm)


zyl-zg-67-3h-chun
zyl-zg-67-3h-chun
MeO
Br
Cl
NO2
O
N
H
5h
f1 (ppm)

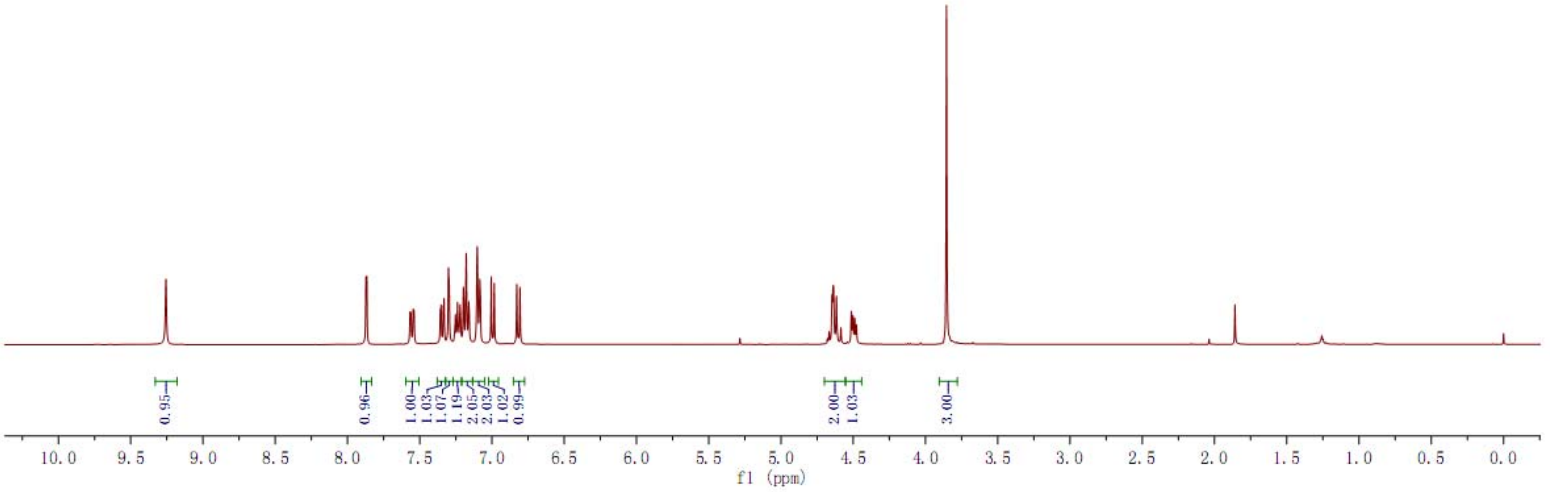

zyl-zg-67-3c
zyl-zg-67-3c
177.83
156.28
140.07
132.22
131.73
129.80
128.85
128.25
127.68
121.42
112.57
112.35
111.92
86.37
82.49
77.39
77.07
76.75
75.53
57.48
56.37
38.77
zyl-zg-67-3c
zyl-zg-67-3c
132.22
131.73
129.87
129.80
128.85
128.36
128.25
127.68
127.13
126.23
121.42
112.57
112.35
111.92
f1 (ppm)
f1 (ppm)
MeO
Br
Cl
NO2
O
N
H
5h

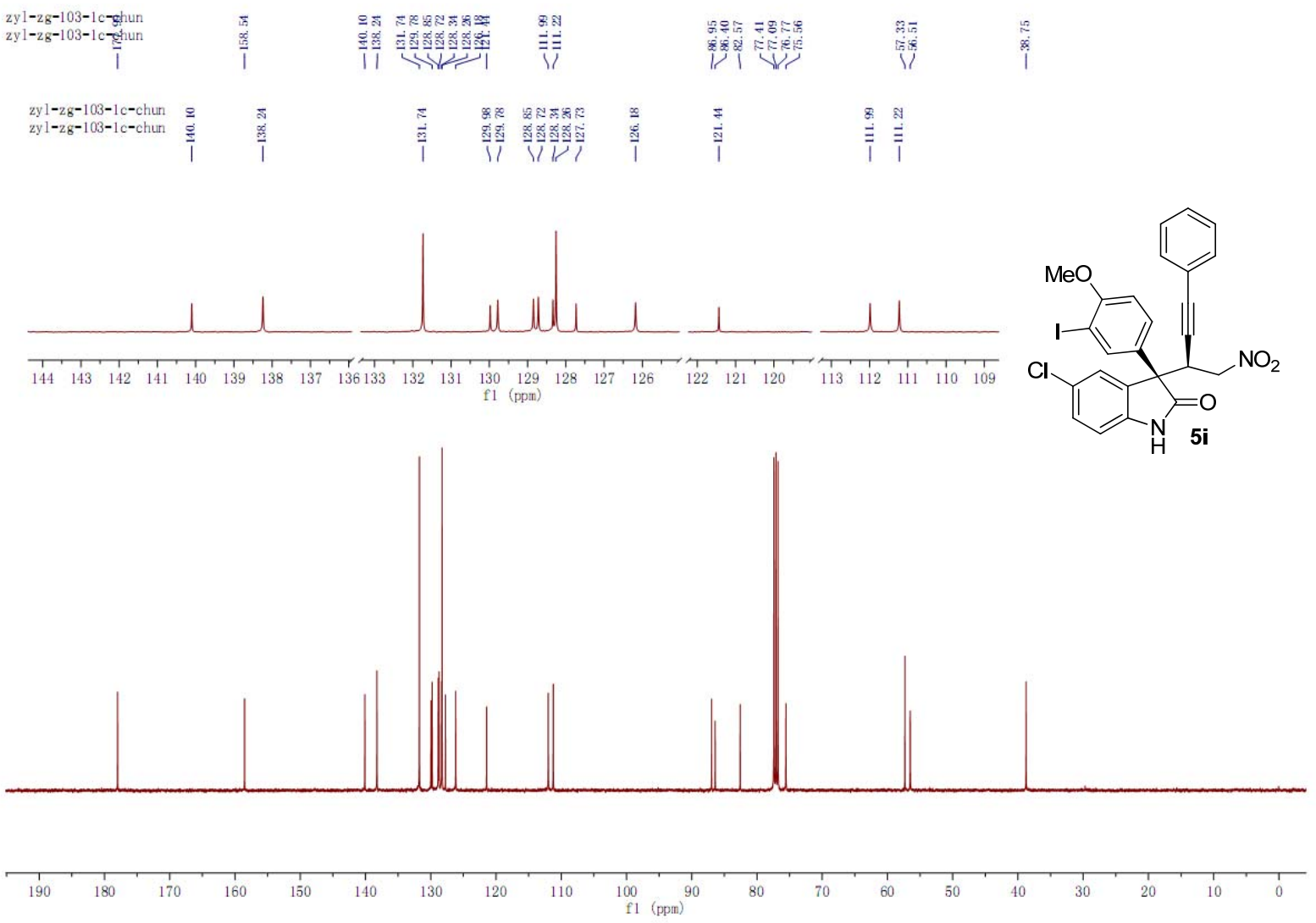

zyl-zg-103-1h-chun
zyl-zg-103-1h-chun

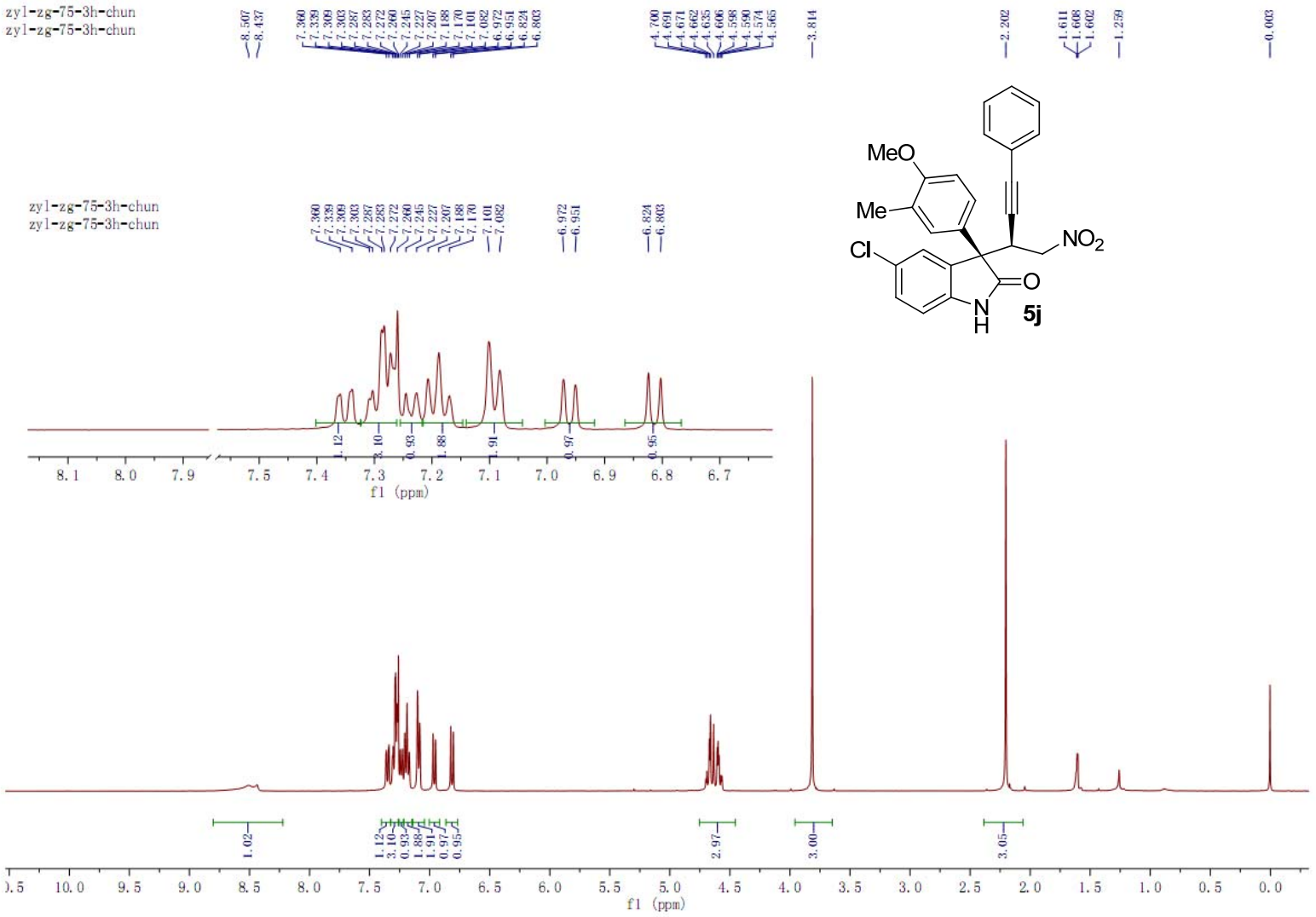

zyl-zg-103-1h-chun
zyl-zg-103-1h-chun
f1 (ppm)

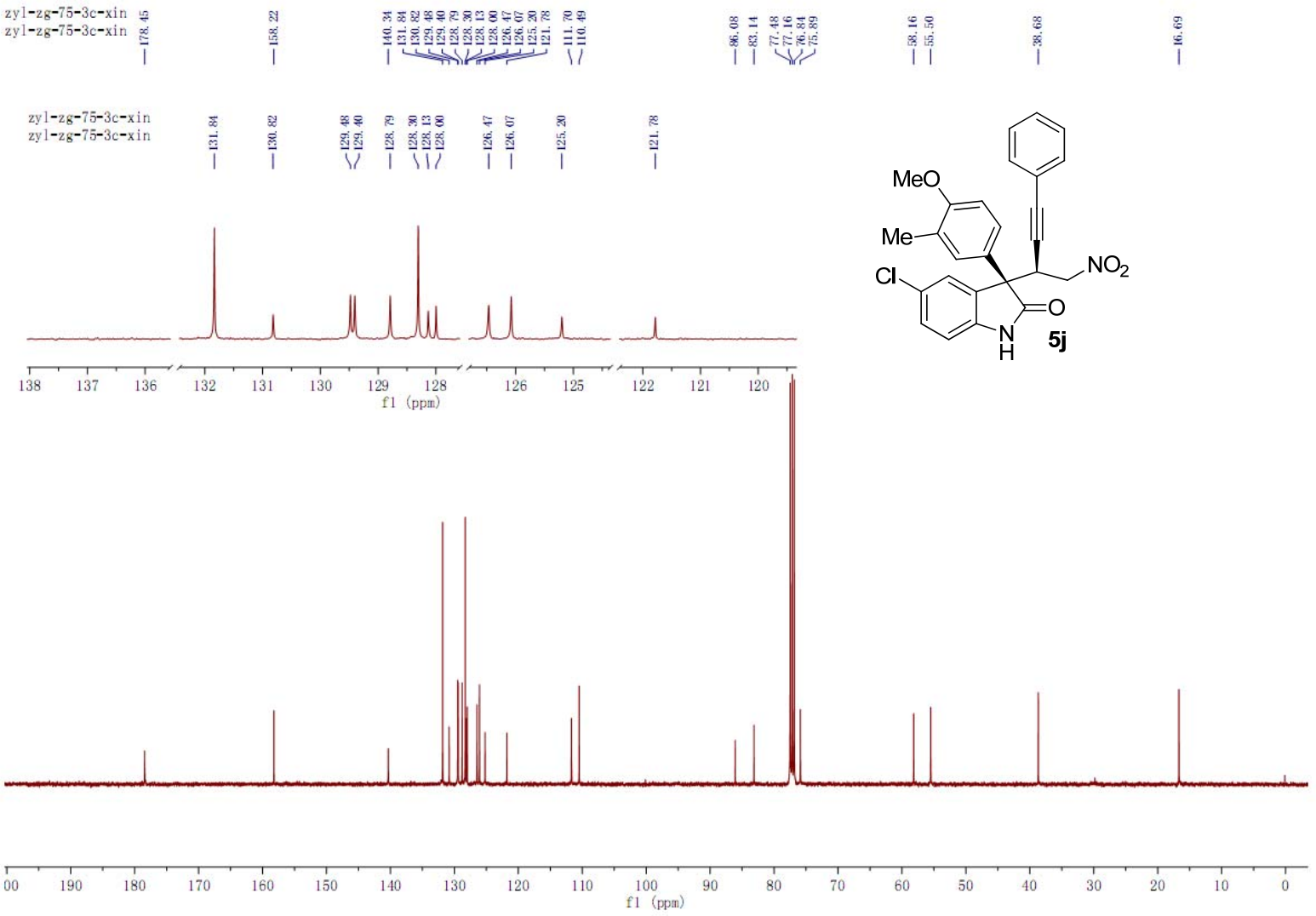

MeO
I
Cl
NO2
O
N
H

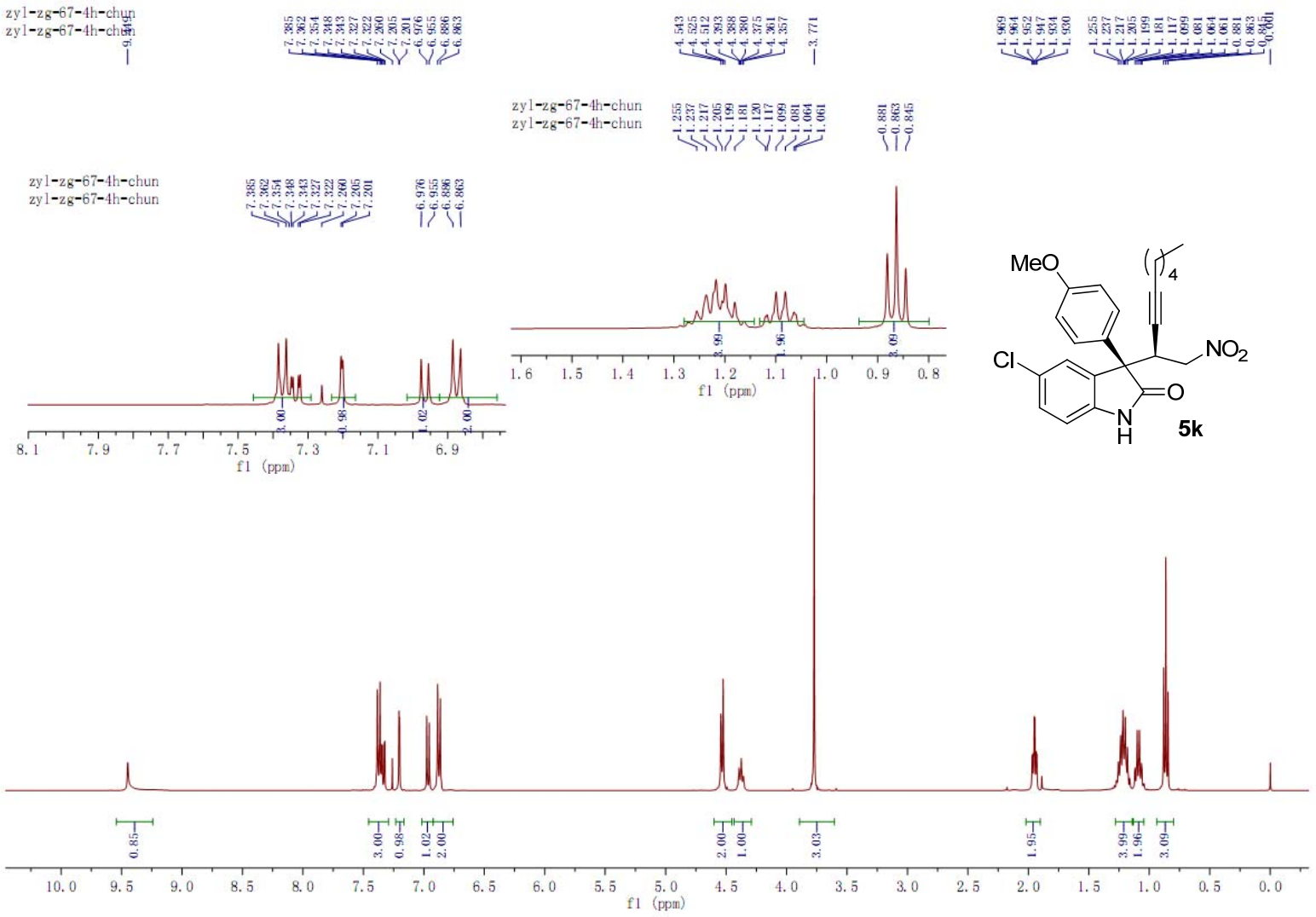
5i

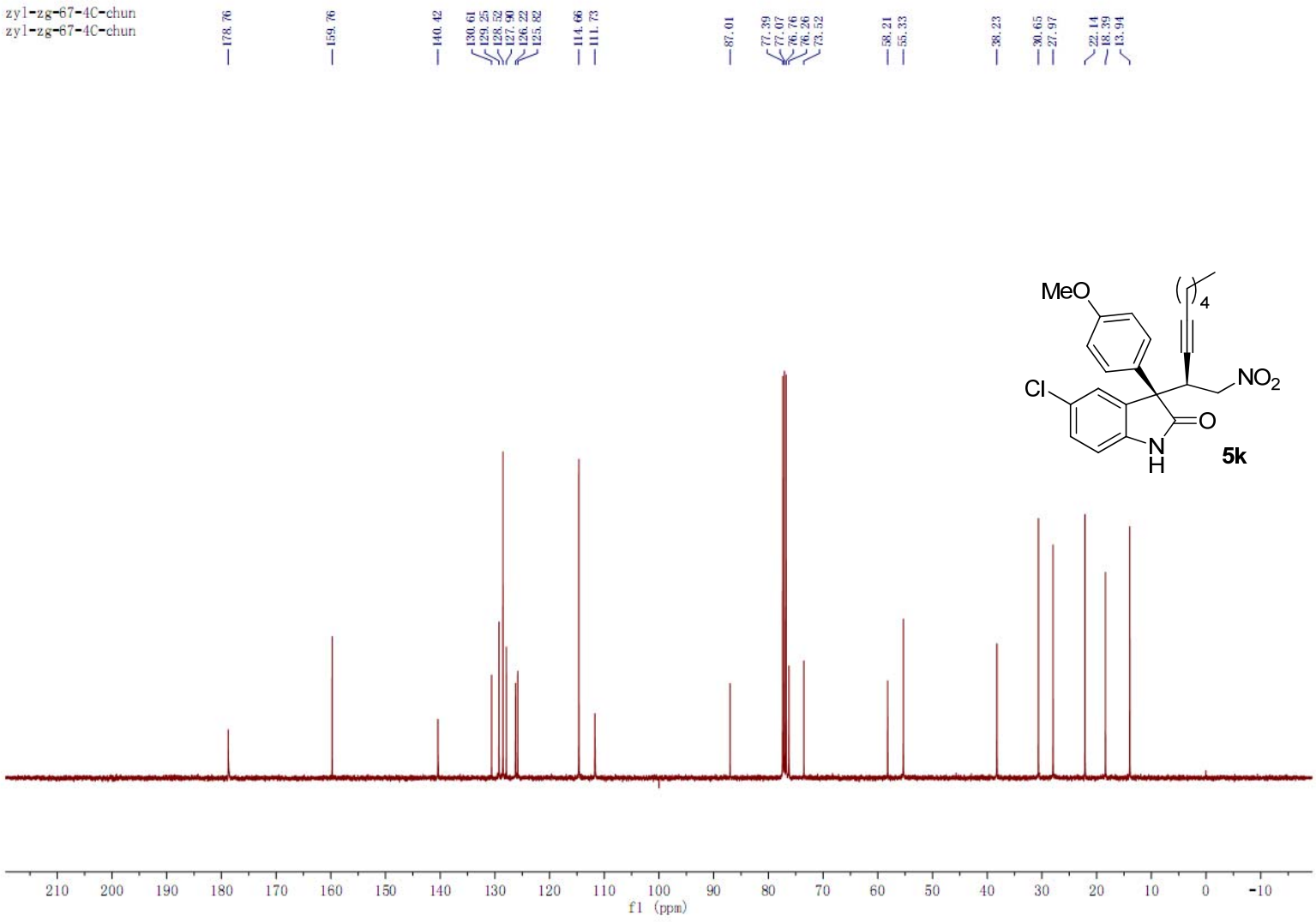

f1 (ppm)


zyl-zg-103-1c-chun
zyl-zg-103-1c-chun
158.54
140.10
138.24
131.74
129.78
128.85
128.72
128.34
128.26
127.73
126.18
121.44
111.99
111.22
86.95
86.40
82.57
77.41
77.09
76.77
75.56
57.33
56.51
38.75
zyl-zg-103-1c-chun
zyl-zg-103-1c-chun
140.10
138.24
131.74
129.98
129.78
128.85
128.72
128.34
128.26
127.73
126.18
121.44
111.99
111.22
f1 (ppm)
f1 (ppm)
MeO
I
Cl
NO2
O
N
H
5i

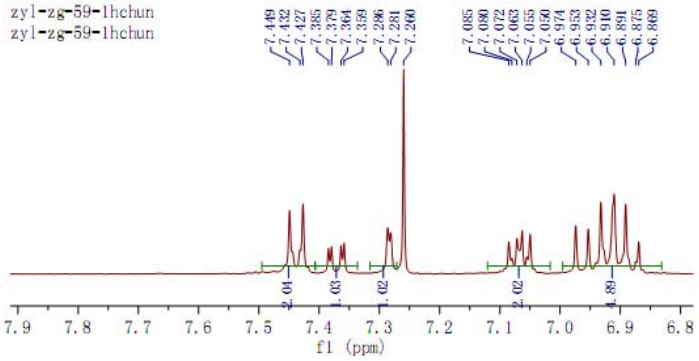

zyl-zg-75-3h-chun
zyl-zg-75-3h-chun
MeO
Me
Cl
NO2
O
N
H
5j
f1 (ppm)

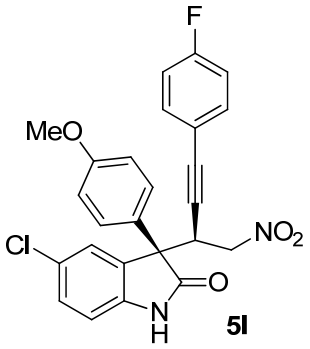

zyl-zg-75-3c-xin
zyl-zg-75-3c-xin
178.45
158.22
140.34
131.84
130.82
129.48
129.40
128.79
128.30
128.13
128.00
126.47
126.07
125.20
121.78
111.70
110.49
86.08
83.14
77.48
77.16
76.84
75.89
58.16
55.50
38.68
16.69
MeO
Me
Cl
NO2
O
N
H
5j
f1 (ppm)


zyl-zg-67-4h-chun
zyl-zg-67-4h-chun
MeO
Cl
NO2
O
N
H
5k
f1 (ppm)

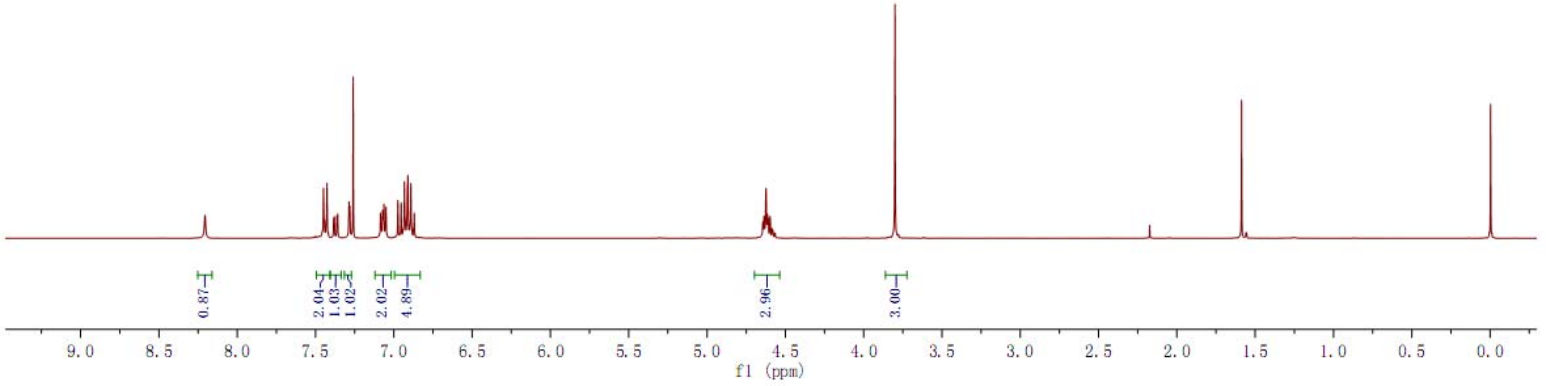

zyl-zg-67-4C-chun
zyl-zg-67-4C-chun
178.76
159.76
140.42
130.61
129.25
128.52
127.90
126.22
125.82
114.66
111.73
87.01
77.39
77.07
76.76
76.26
73.52
58.21
55.33
38.23
30.65
27.97
22.14
18.39
13.94
MeO
Cl
NO2
O
N
H
4
5k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


zyl-zg-59-1hchun
zyl-zg-59-1hchun
8.206
7.449
7.432
7.427
7.385
7.379
7.364
7.359
7.286
7.281
7.260
7.085
7.080
7.072
7.063
7.055
7.050
6.974
6.953
6.932
6.910
6.891
6.875
6.869
4.644
4.637
4.623
4.614
4.610
4.598
4.585
4.580
4.566
3.800
2.174
1.587
0.003


zyl-zg-59-1hchun
zyl-zg-59-1hchun
7.449
7.432
7.427
7.385
7.379
7.364
7.339
7.286
7.281
7.260
7.085
7.080
7.072
7.063
7.055
7.050
6.974
6.953
6.932
6.910
6.891
6.875
6.869
2.04
1.03
1.02
2.02
4.89
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)

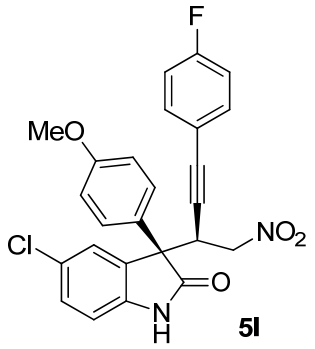

F
MeO
NO2
Cl
O
N
H

5l

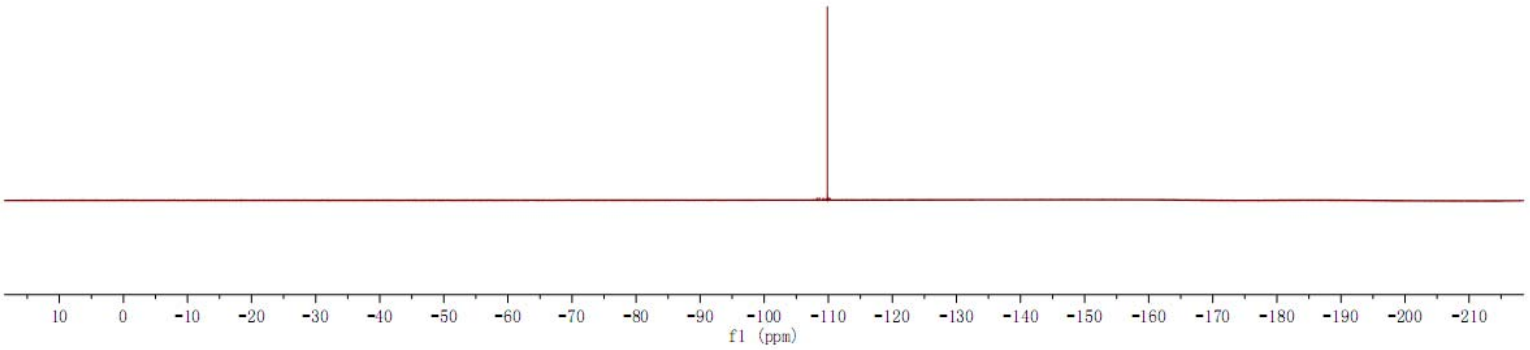

0.87
2.04
1.03
1.02
2.02
4.89
2.96
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

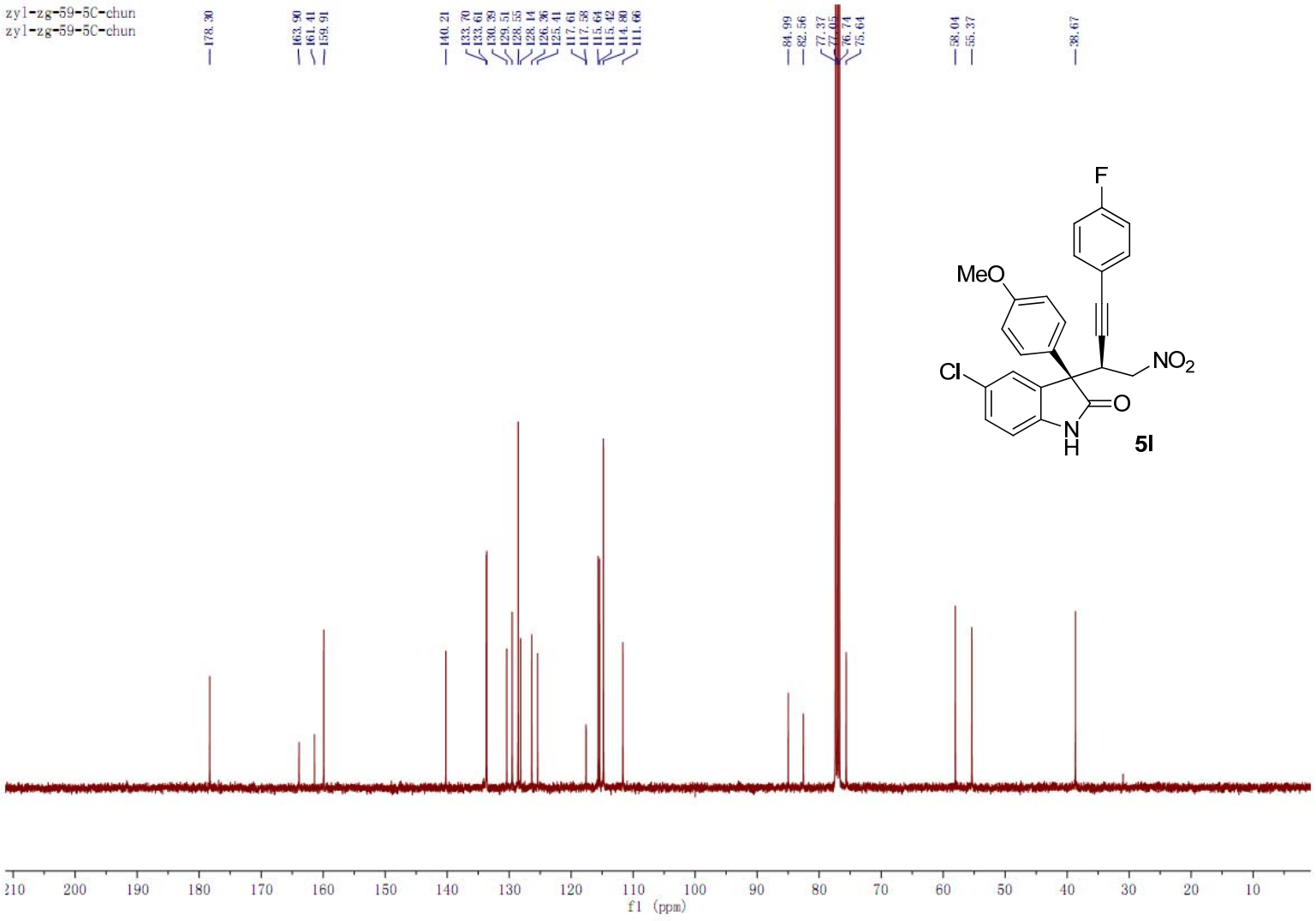
zyl-zg-59-5f
zyl-zg-59-5f

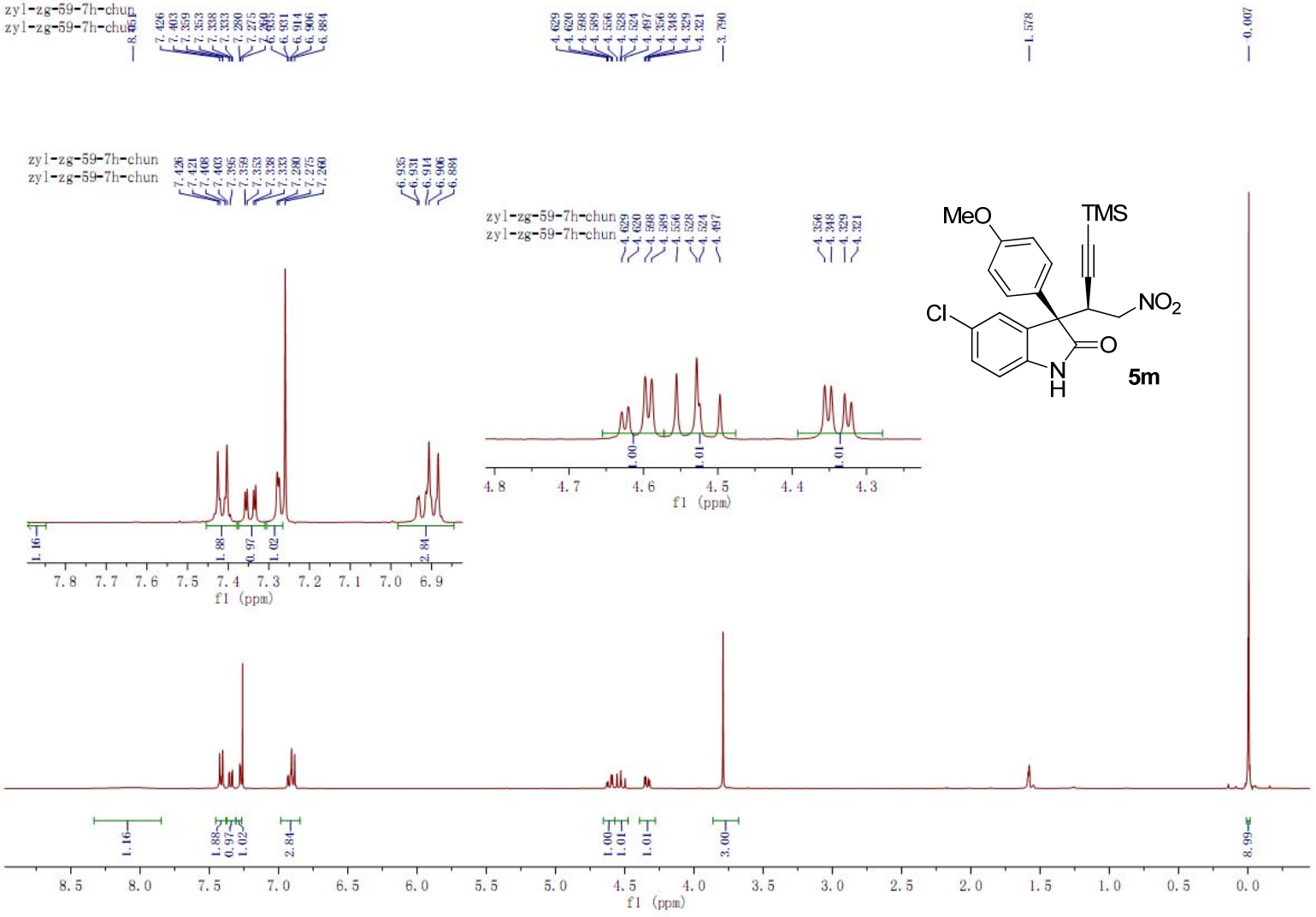
-109.85

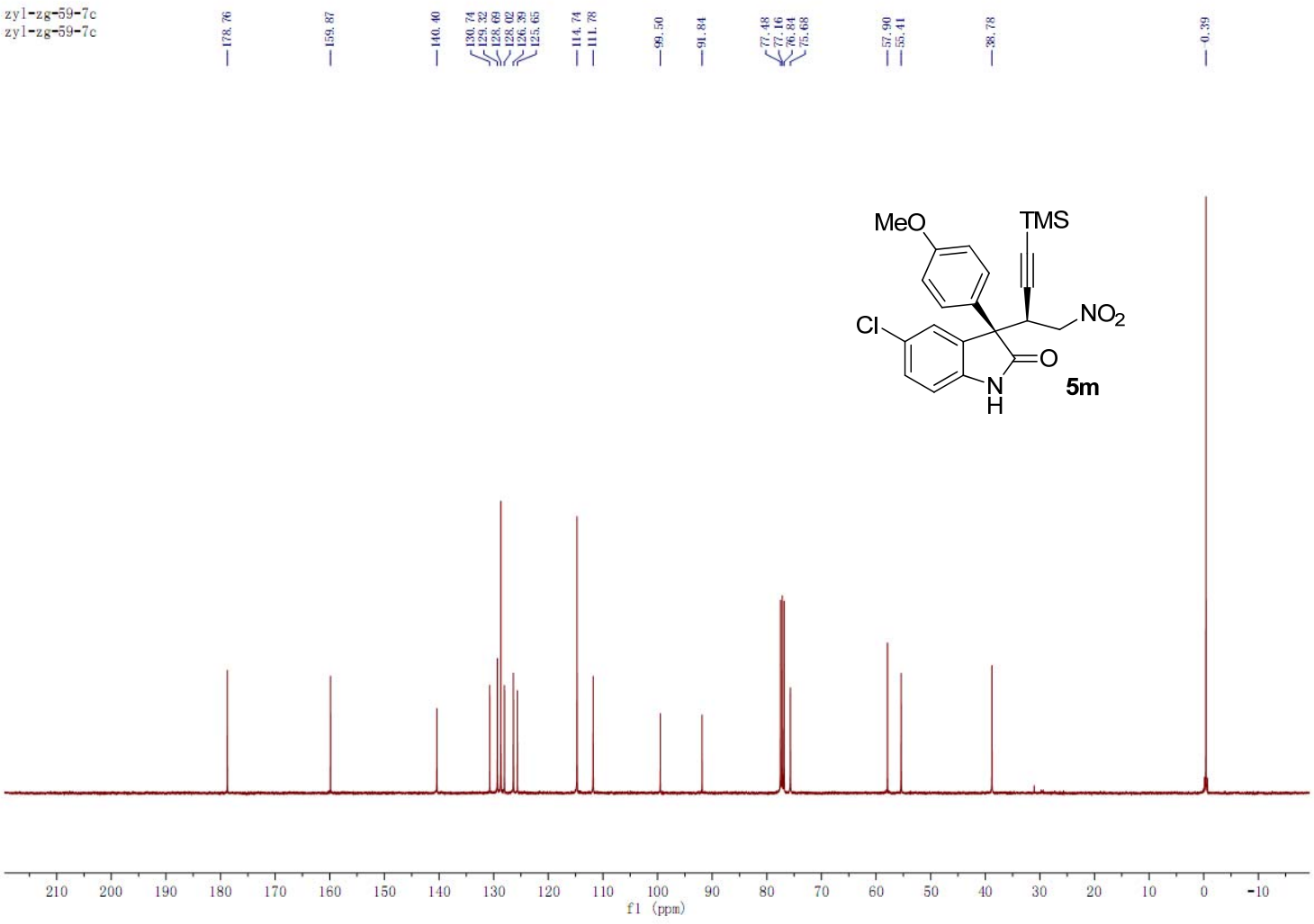


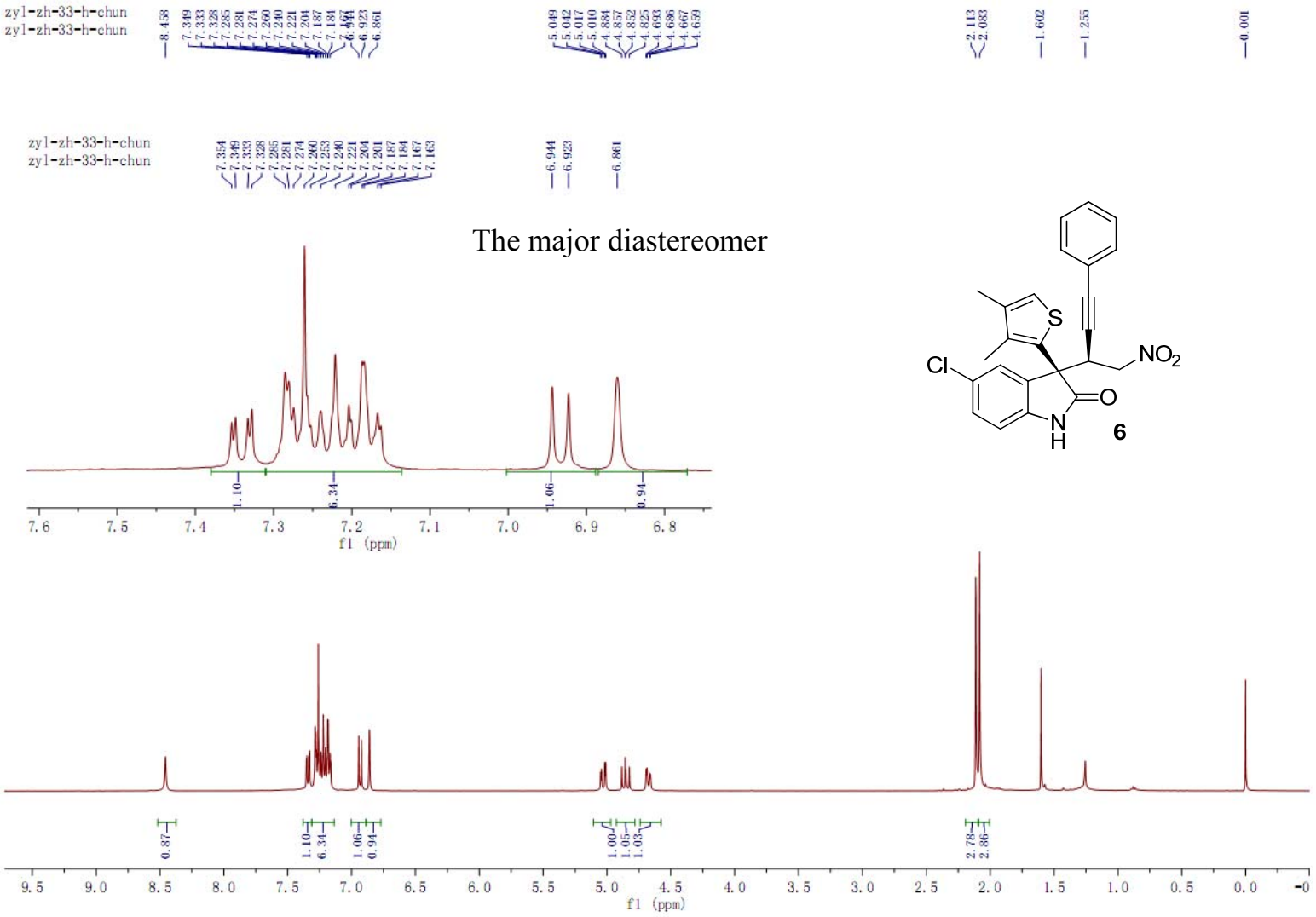
5l

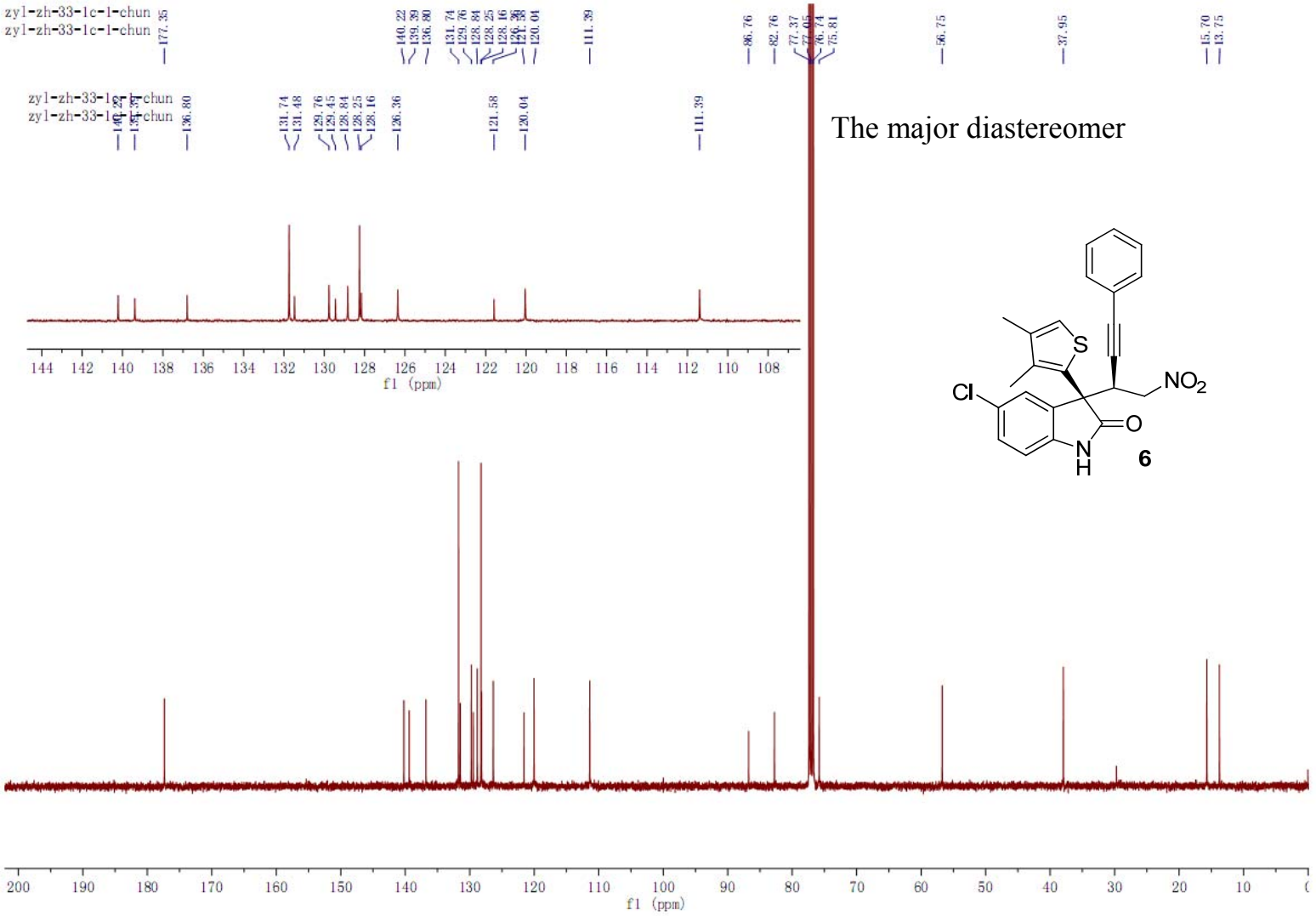



zyl-zg-59-5C-chun
zyl-zg-59-5C-chun
178.30
163.90
161.41
159.91
140.21
133.70
133.61
130.39
129.51
128.55
128.14
126.36
125.41
117.61
117.38
115.64
115.42
114.80
111.66
84.99
82.56
77.37
77.05
76.74
75.64
58.04
55.37
38.67
F
MeO
NO2
Cl
O
N
H
5l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

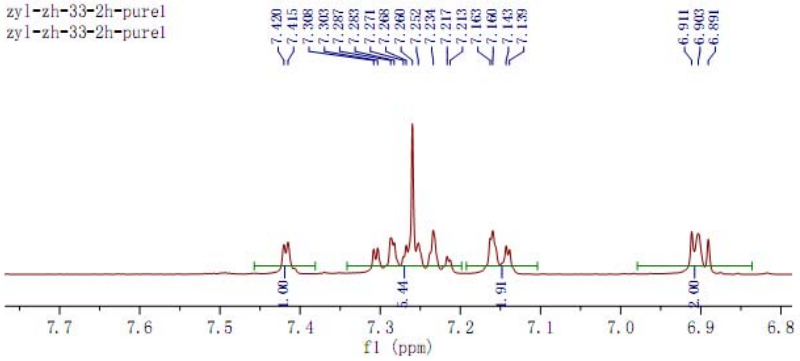

zyl-zg-59-7h-chun
zyl-zg-59-7h-chun
MeO
TMS
NO2
Cl
O
N
H
5m
f1 (ppm)

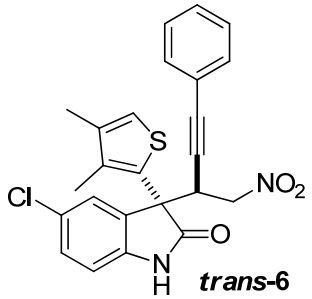

zyl-zg-59-7c
zyl-zg-59-7c
178.76
159.87
140.40
130.74
129.32
128.69
128.02
126.39
125.65
114.74
111.78
99.50
91.84
77.48
77.16
76.84
75.68
57.90
55.41
38.78
0.39
MeO
TMS
NO2
Cl
O
N
H
5m
f1 (ppm)

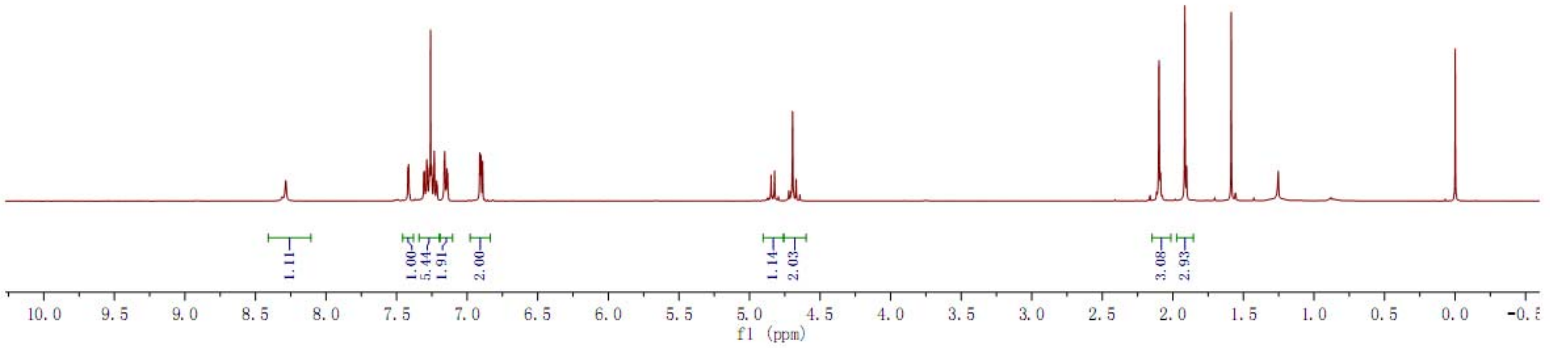

zyl-zh-33-h-chun
zyl-zh-33-h-chun
zyl-zh-33-h-chun
zyl-zh-33-h-chun
The major diastereomer
Cl
S
NO2
O
N
H
6
f1 (ppm)
f1 (ppm)

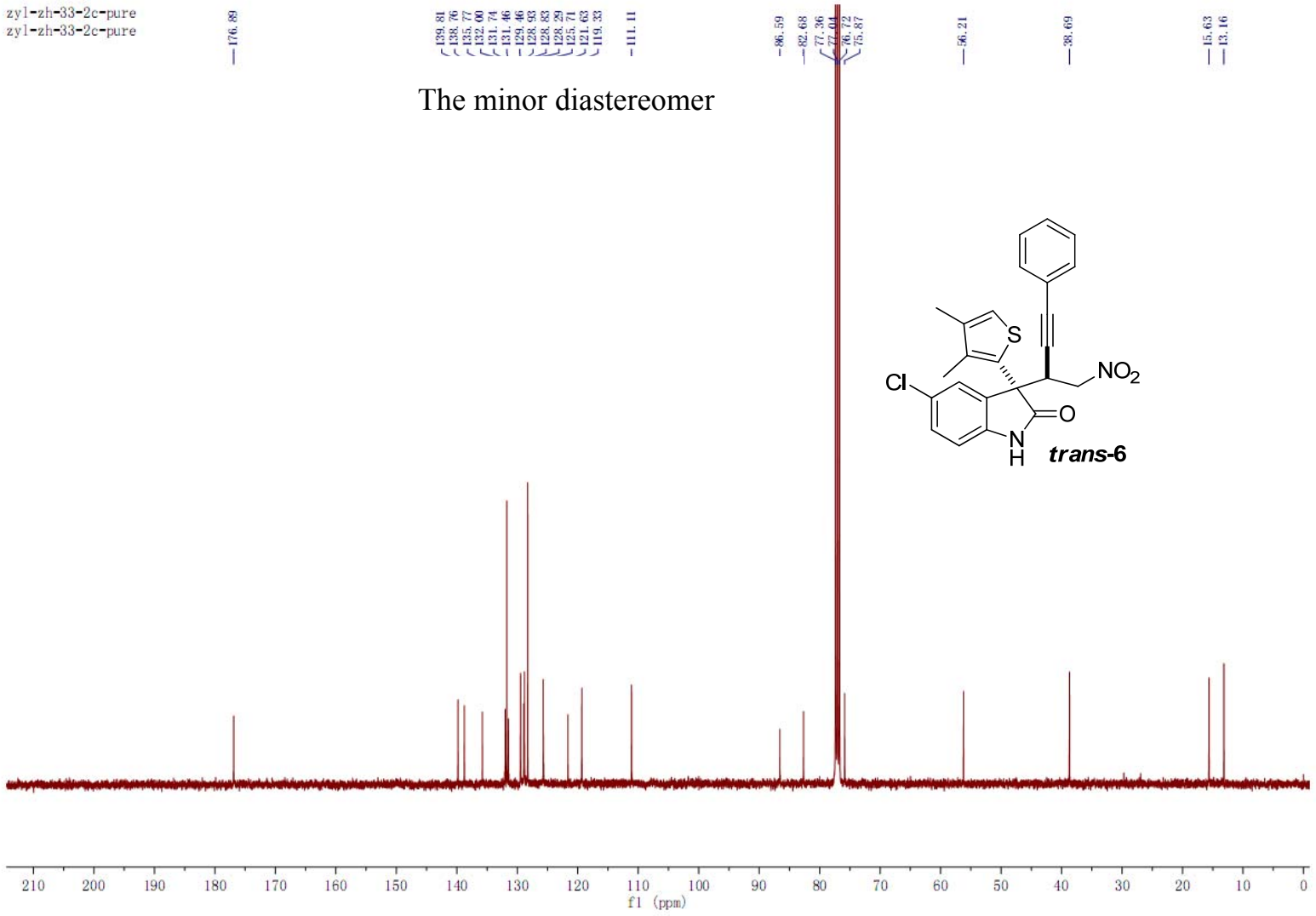

zyl-zh-33-1c-1-chun
zyl-zh-33-1c-1-chun
177.35
140.22
139.39
136.80
131.74
129.76
128.84
128.25
128.16
120.04
111.39
86.76
82.76
77.37
77.05
76.74
75.81
56.75
37.95
15.70
13.75
zyl-zh-33-1c-1-chun
zyl-zh-33-1c-1-chun
136.80
131.74
131.48
129.76
129.45
128.84
128.25
128.16
126.36
121.58
120.04
111.39
144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
The major diastereomer
S
Cl
NO2
O
N
H
6

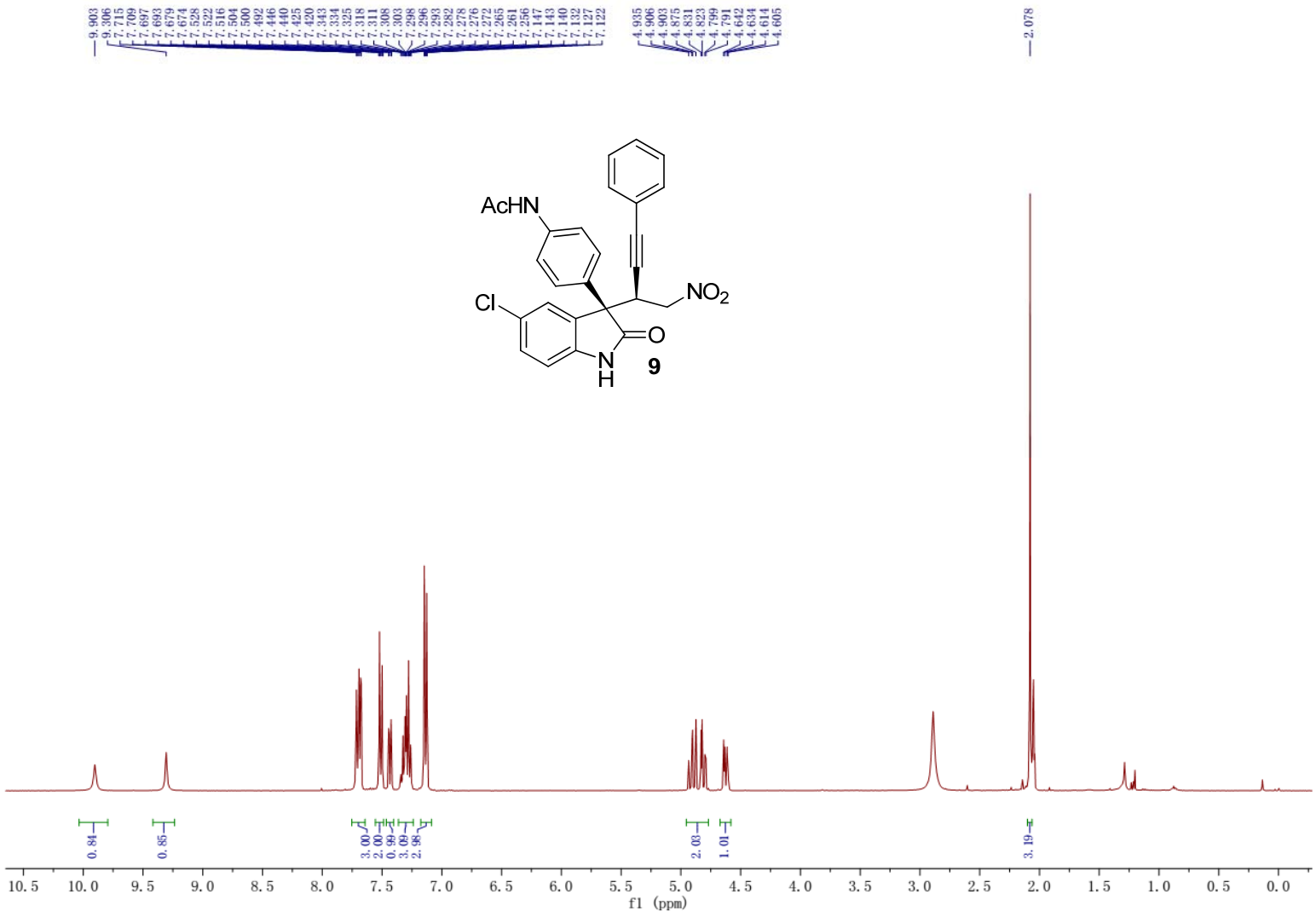
The minor diastereomer

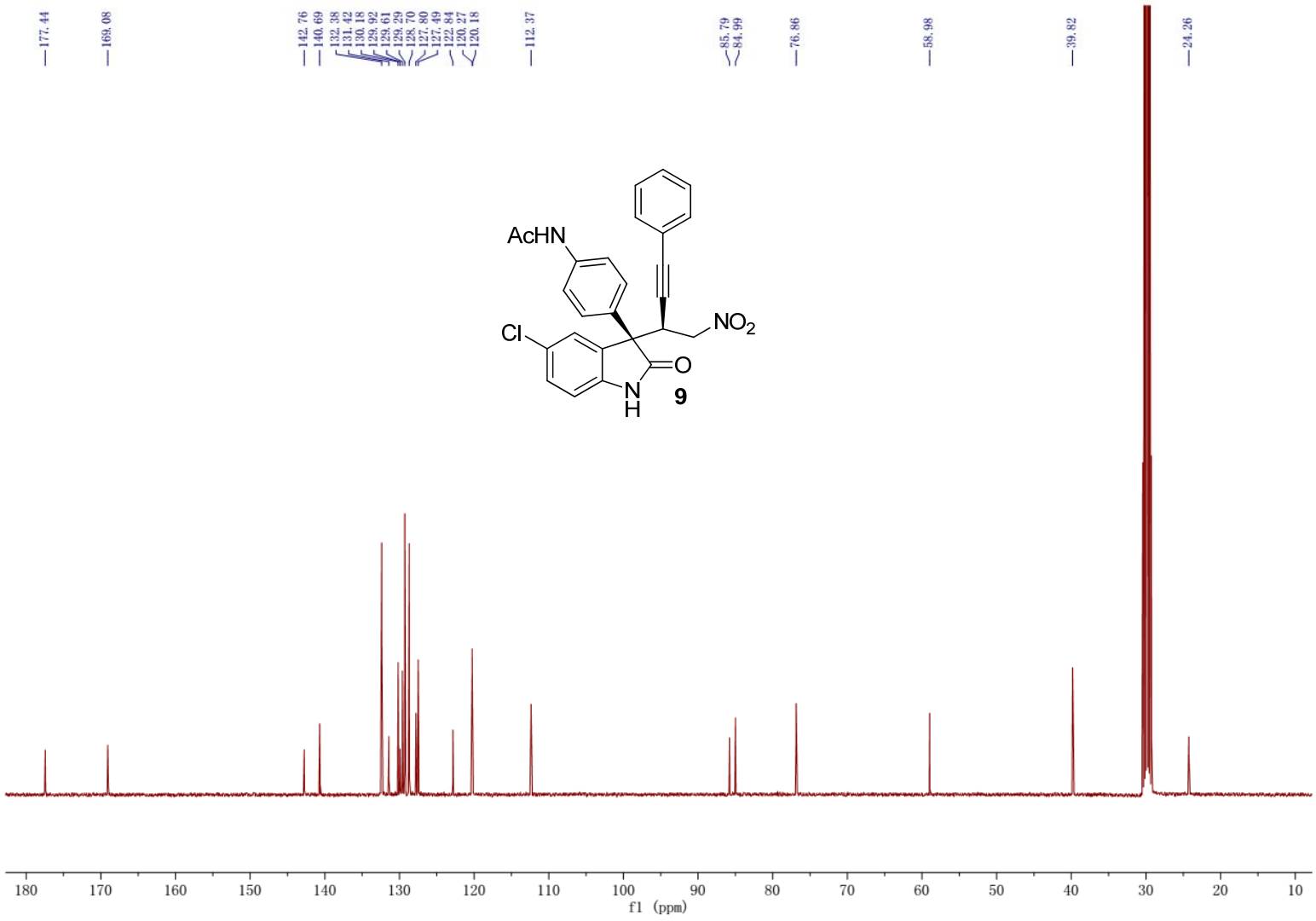


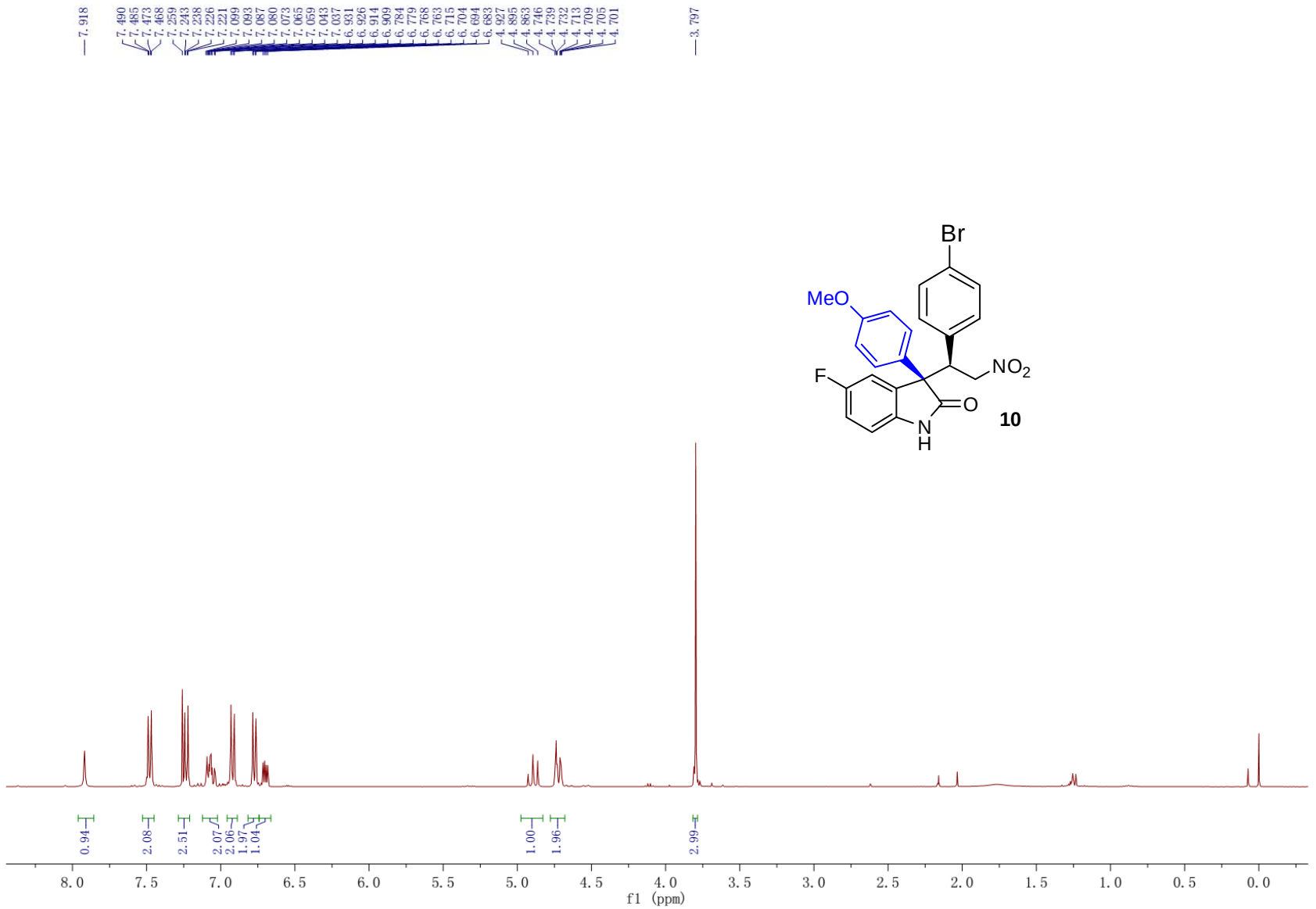


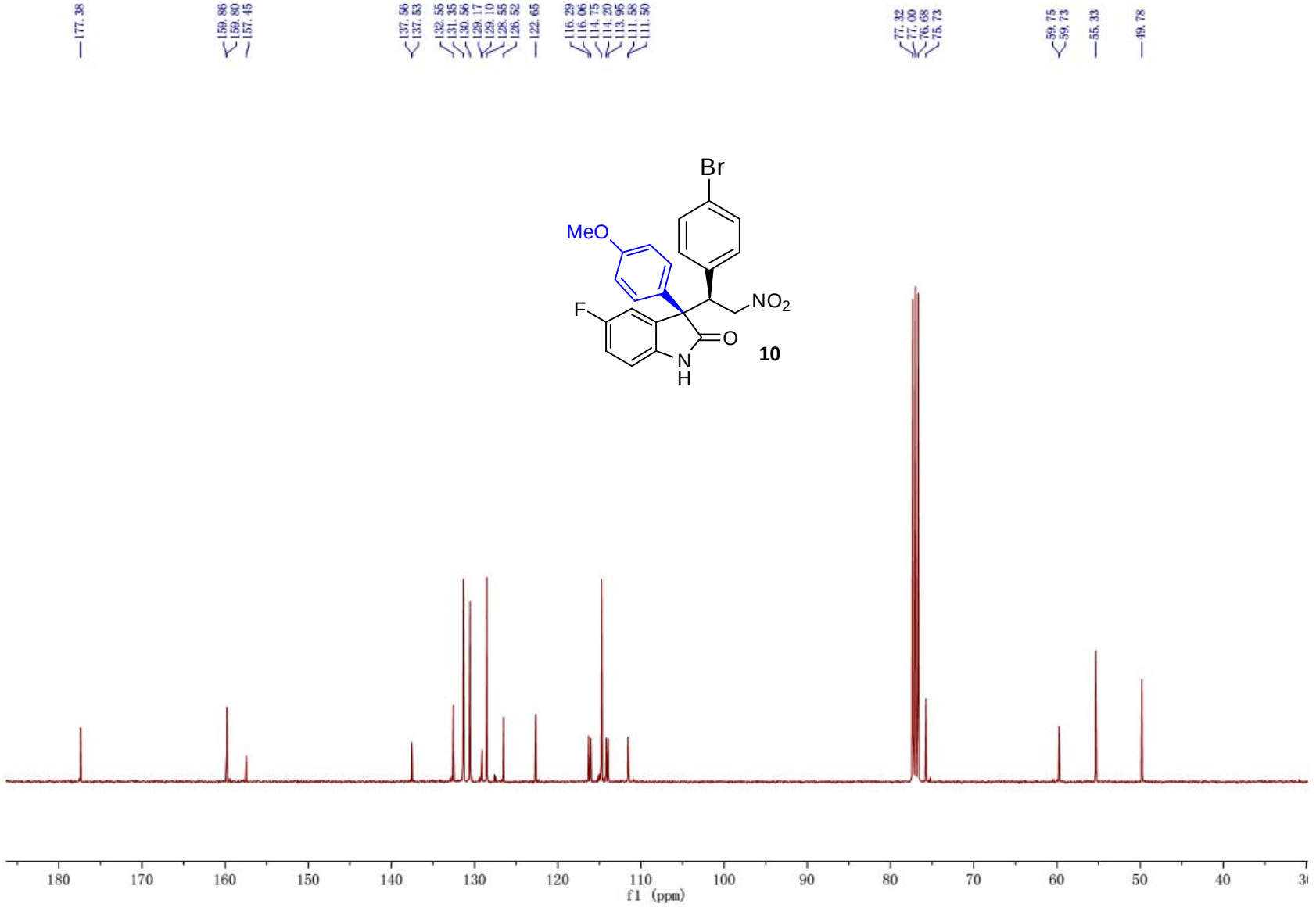


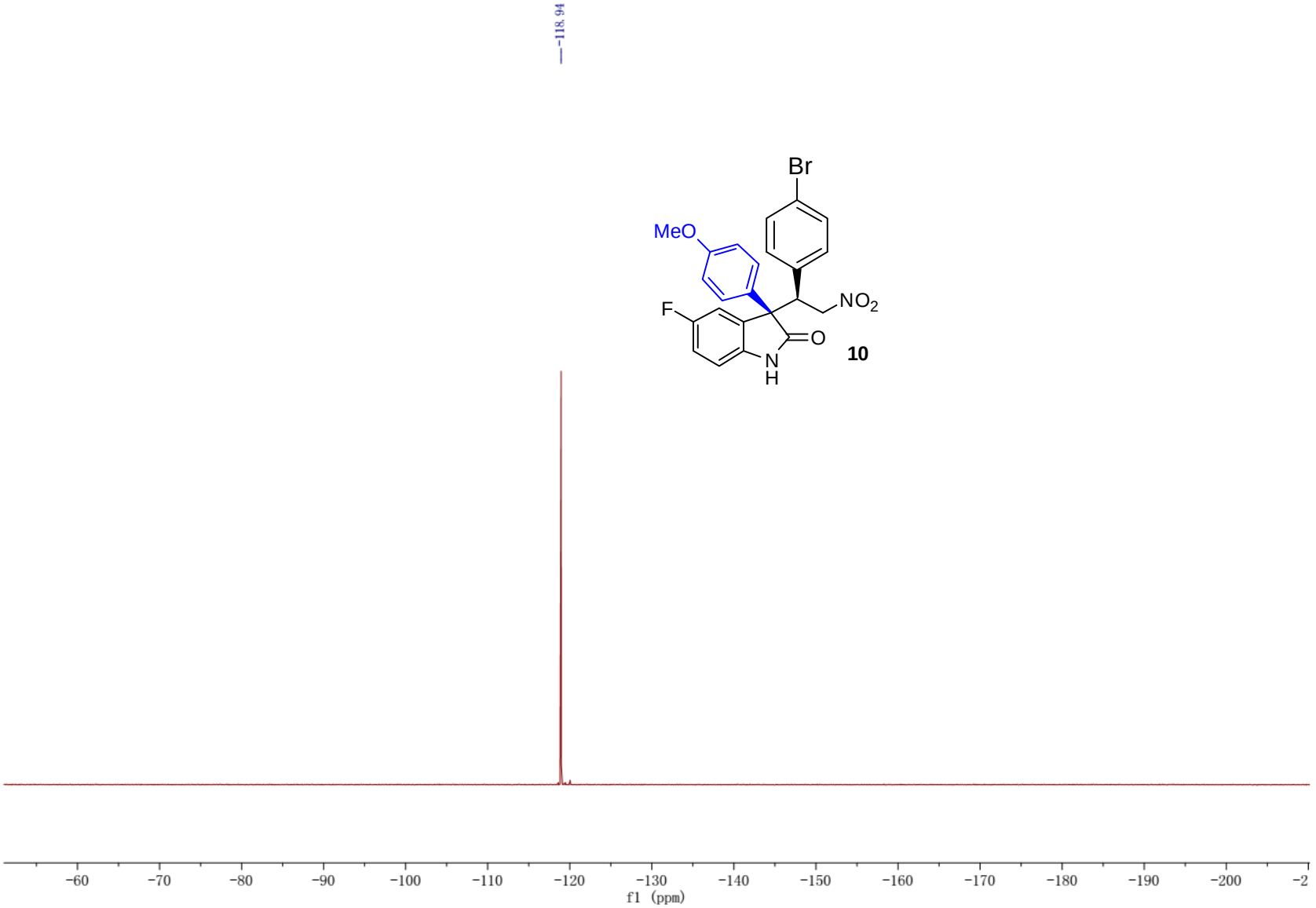

zyl-zh-33-2c-pure
zyl-zh-33-2c-pure
176.89
139.81
138.76
135.77
132.60
131.74
131.46
129.46
128.93
128.83
128.29
125.71
121.63
119.33
111.11
86.59
82.68
77.36
77.04
76.72
75.87
56.21
38.69
15.63
13.16
The minor diastereomer
S
Cl
NO2
O
N
H
trans-6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

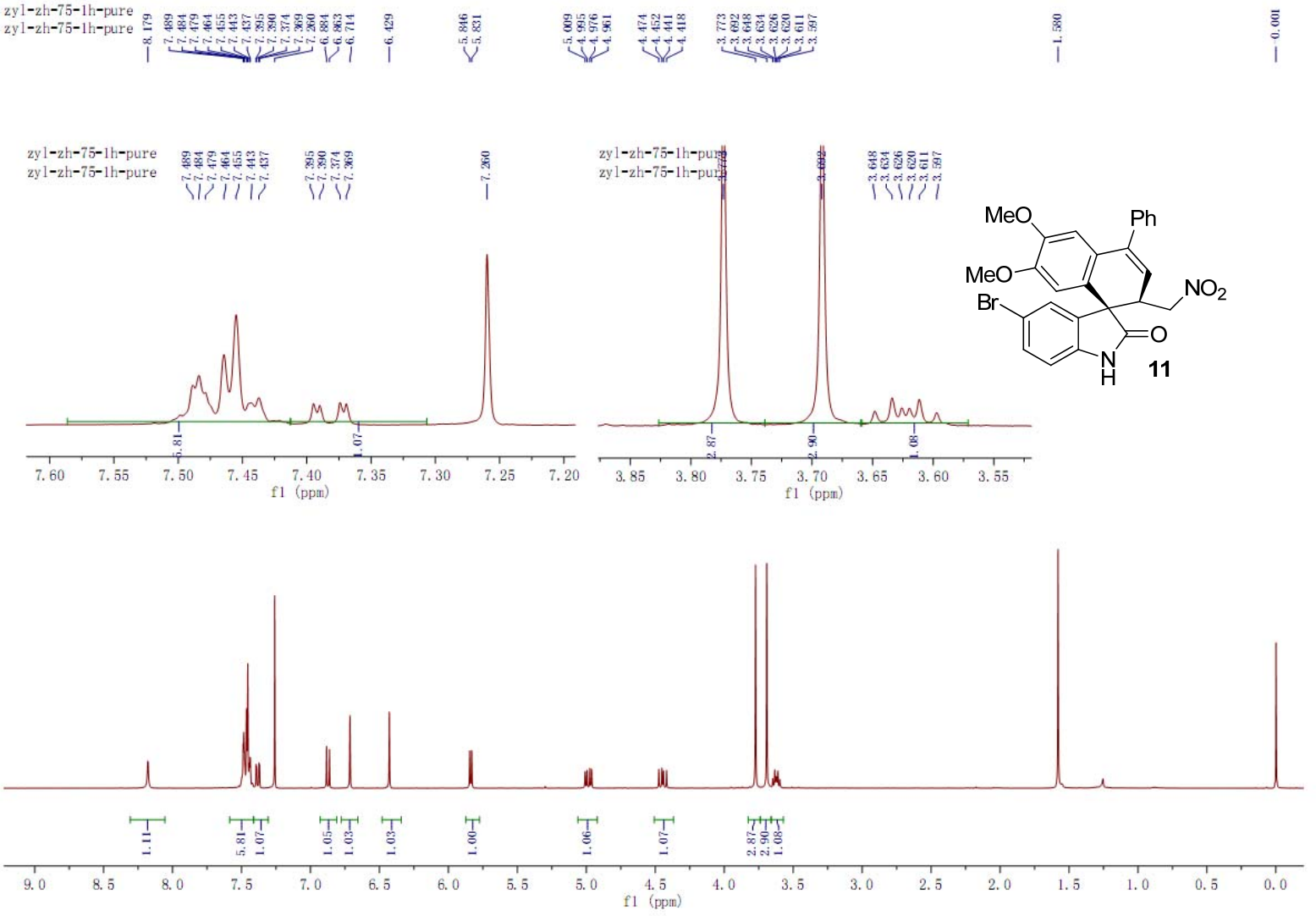

9.903
9.306
7.715
7.709
7.697
7.693
7.679
7.674
7.528
7.522
7.516
7.504
7.500
7.492
7.446
7.440
7.425
7.420
7.343
7.334
7.325
7.318
7.311
7.308
7.303
7.298
7.296
7.293
7.282
7.278
7.276
7.272
7.265
7.261
7.256
7.147
7.143
7.140
7.132
7.127
7.122
4.935
4.906
4.903
4.875
4.831
4.823
4.799
4.791
4.642
4.634
4.614
4.605
2.078
AcHN
Cl
NO2
O
N
H
9
0.84
0.85
3.00
2.00
0.99
3.09
2.98
2.03
1.01
3.19
10.5
10.0
9.5
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)

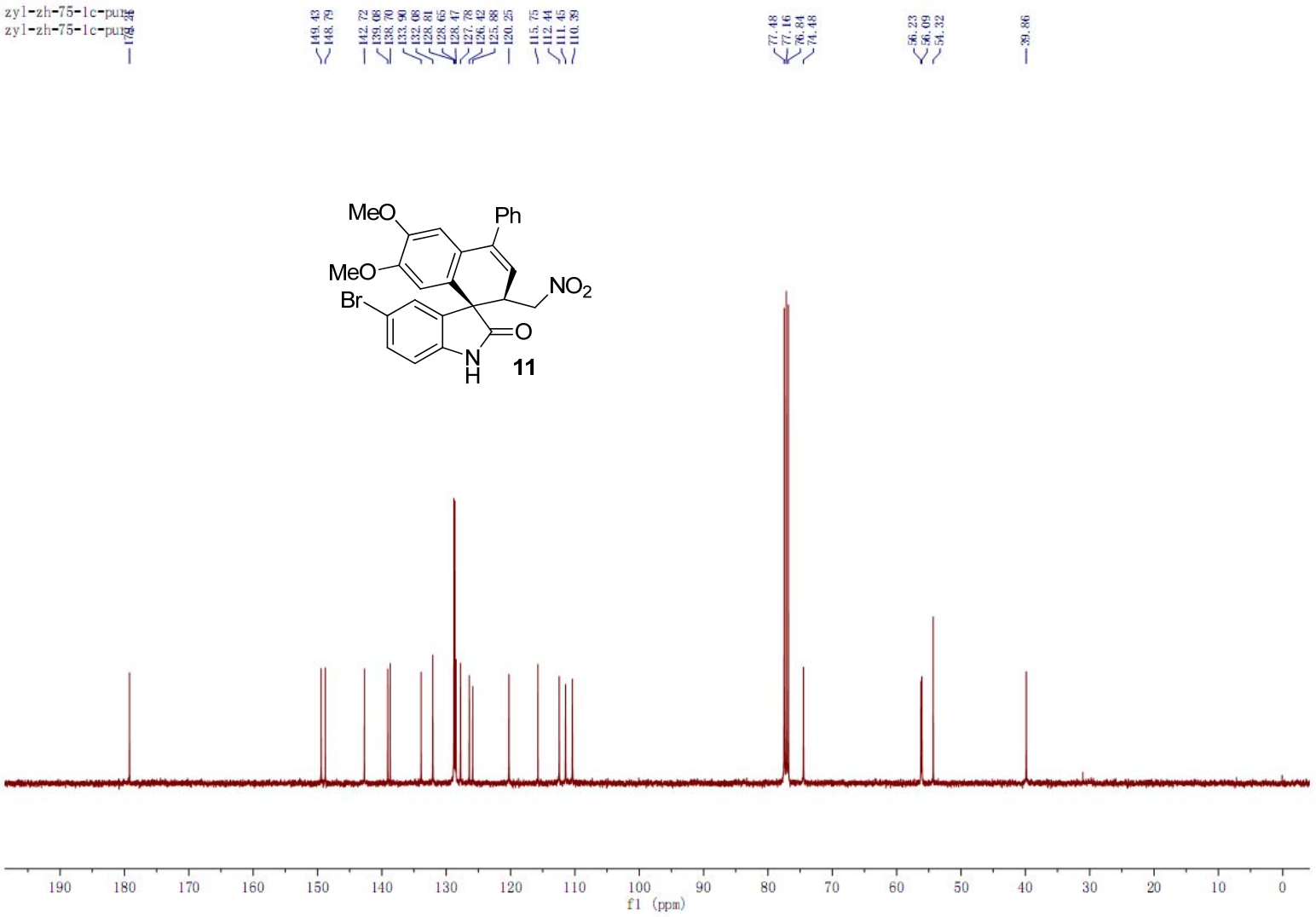

177.44
169.08
142.76
140.69
132.38
131.42
130.18
129.92
129.61
129.29
128.70
127.80
127.49
122.84
120.27
120.18
112.37
85.79
84.99
76.86
58.98
39.82
24.26
AcHN
Cl
NO2
O
N
H
9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

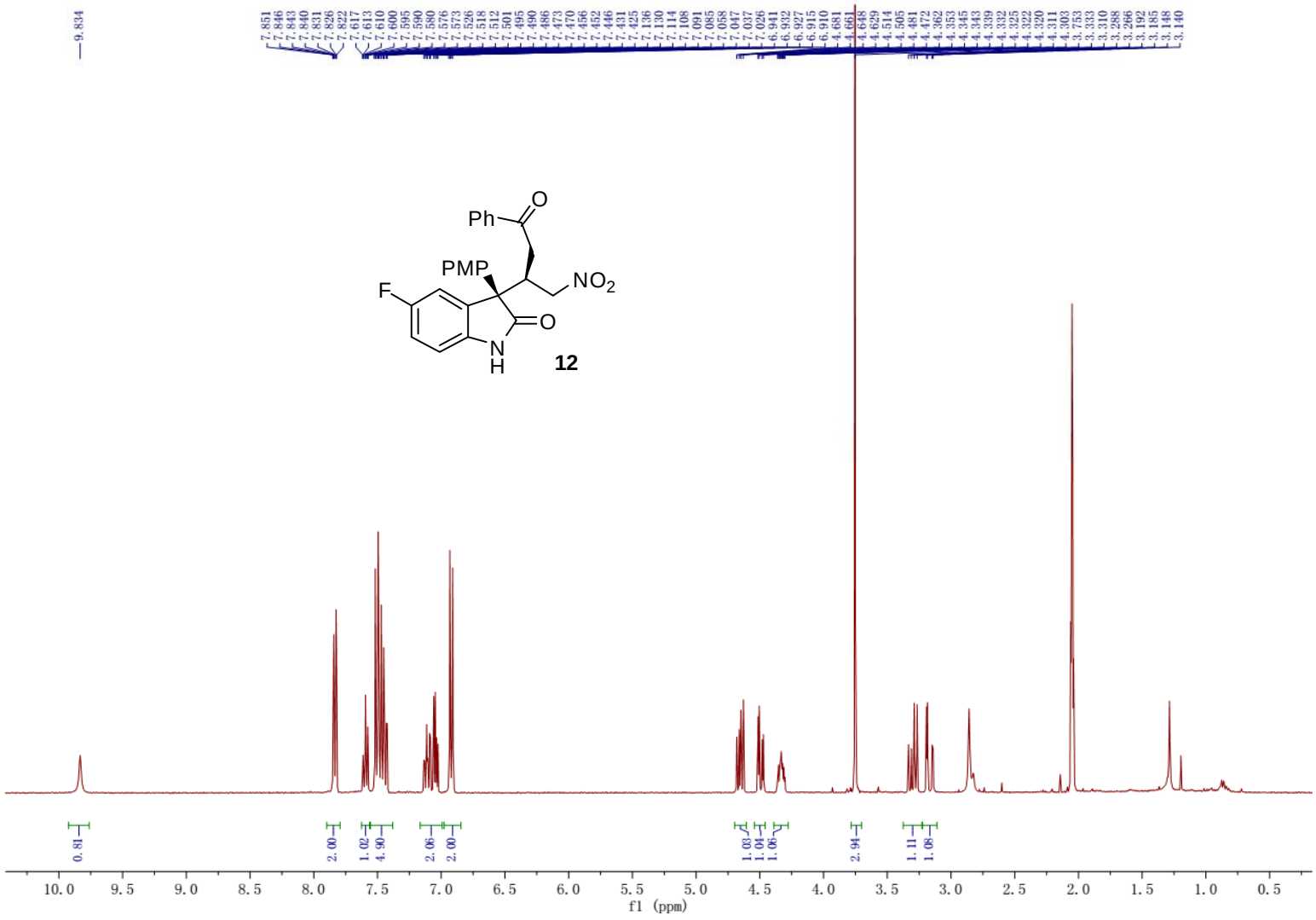

7.918
7.490
7.485
7.473
7.468
7.259
7.243
7.238
7.226
7.221
7.099
7.093
7.087
7.080
7.073
7.065
7.059
7.043
7.037
6.931
6.926
6.914
6.909
6.784
6.779
6.768
6.763
6.715
6.704
6.694
6.683
4.927
4.895
4.863
4.746
4.739
4.732
4.713
4.709
4.705
4.701
3.797
Br
MeO
NO2
F
O
N
H
10
0.94
2.08
2.51
2.07
2.06
1.97
1.04
1.00
1.96
2.99
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)

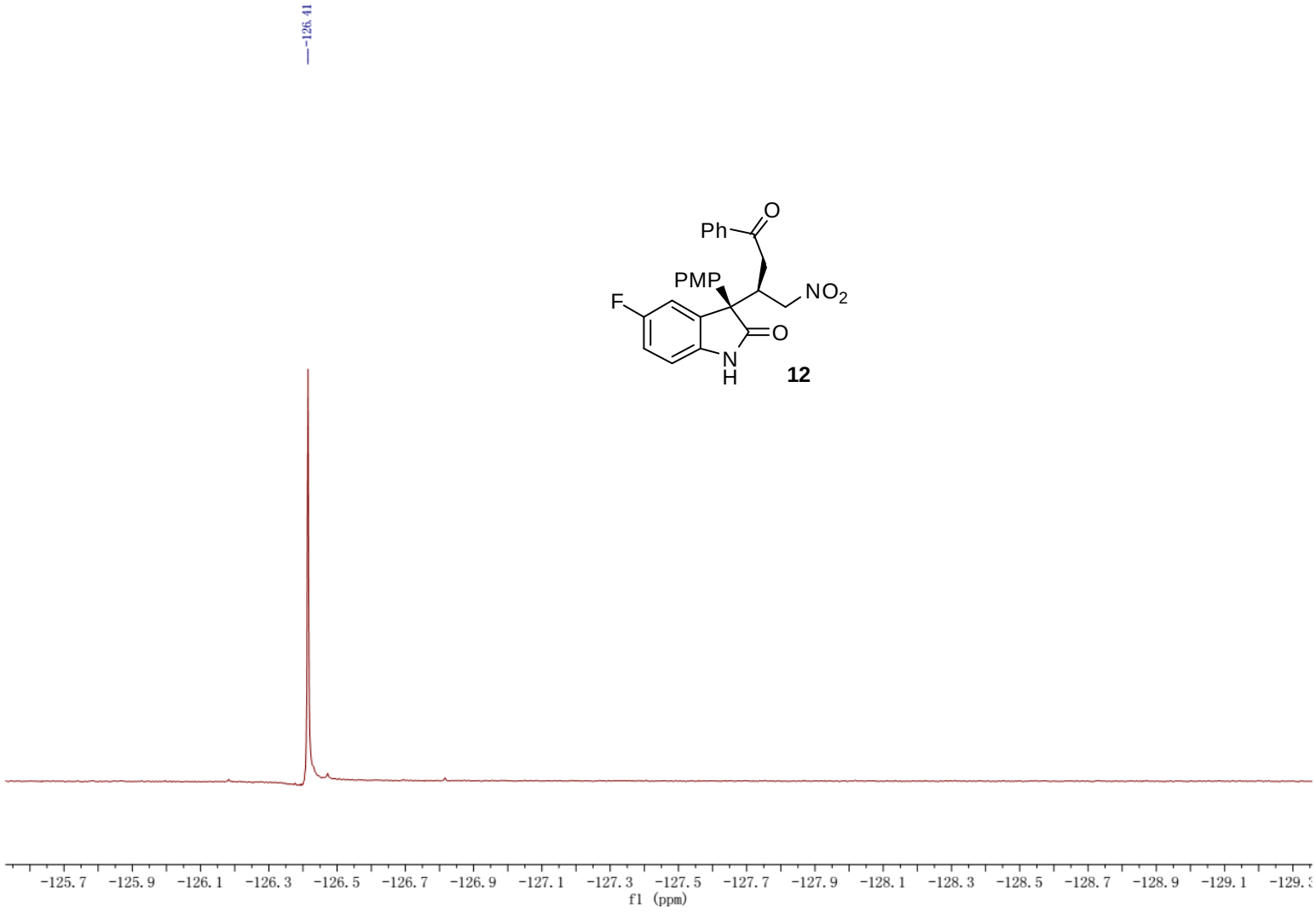

177.38
159.86
159.80
157.45
137.56
137.53
132.55
131.35
130.56
129.17
129.10
128.55
126.52
122.65
116.29
116.06
114.75
114.20
113.95
111.58
111.50
77.32
77.00
76.68
75.73
59.75
59.73
55.33
49.78
Br
MeO
NO2
F
O
N
H
10
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

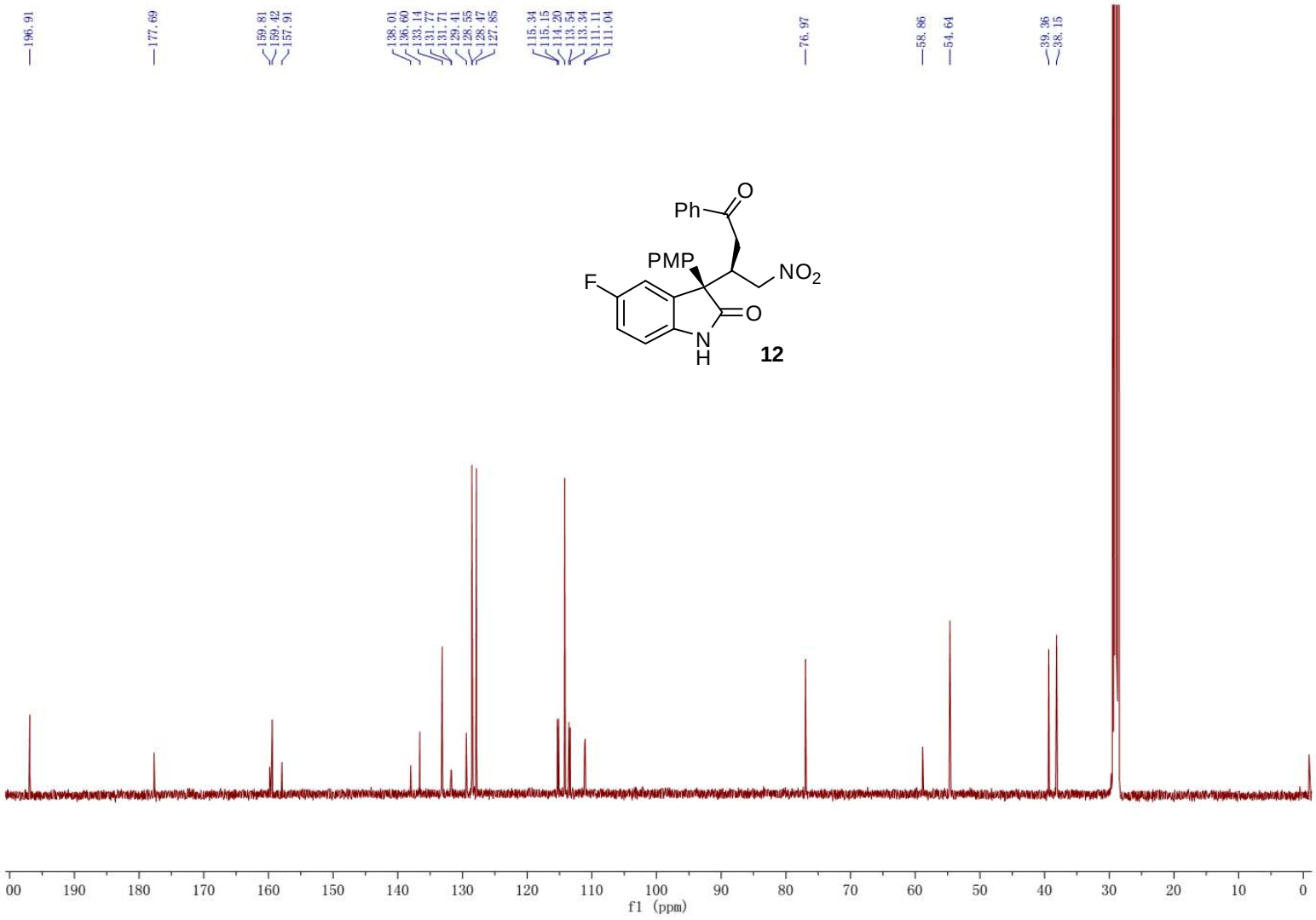

−118.94
Br
MeO
NO2
F
O
N
H
10
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−2
f1 (ppm)

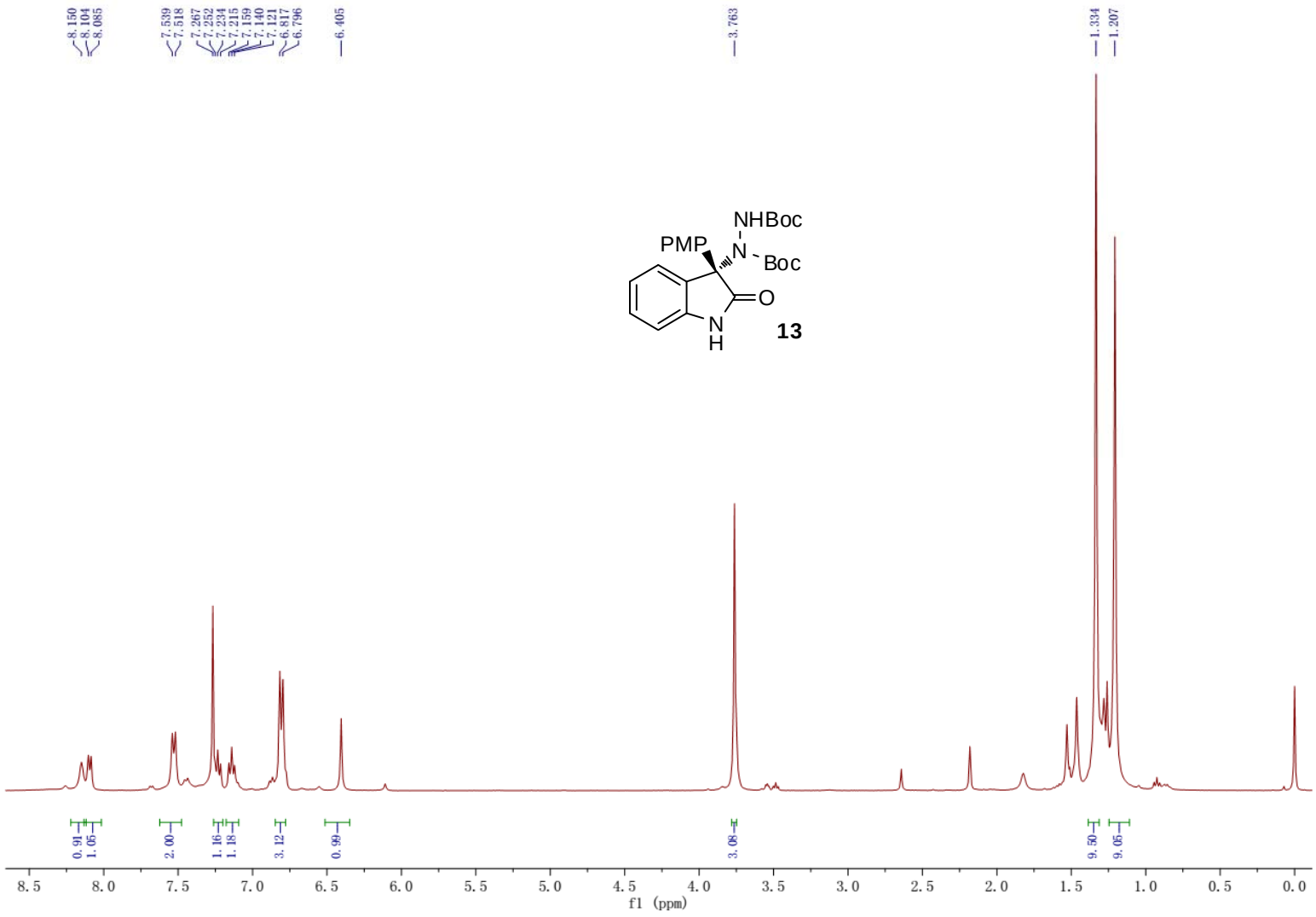

zyl-zh-75-1h-pure
zyl-zh-75-1h-pure
MeO
MeO
Br
Ph
NO2
O
N
H
11
f1 (ppm)
f1 (ppm)
f1 (ppm)

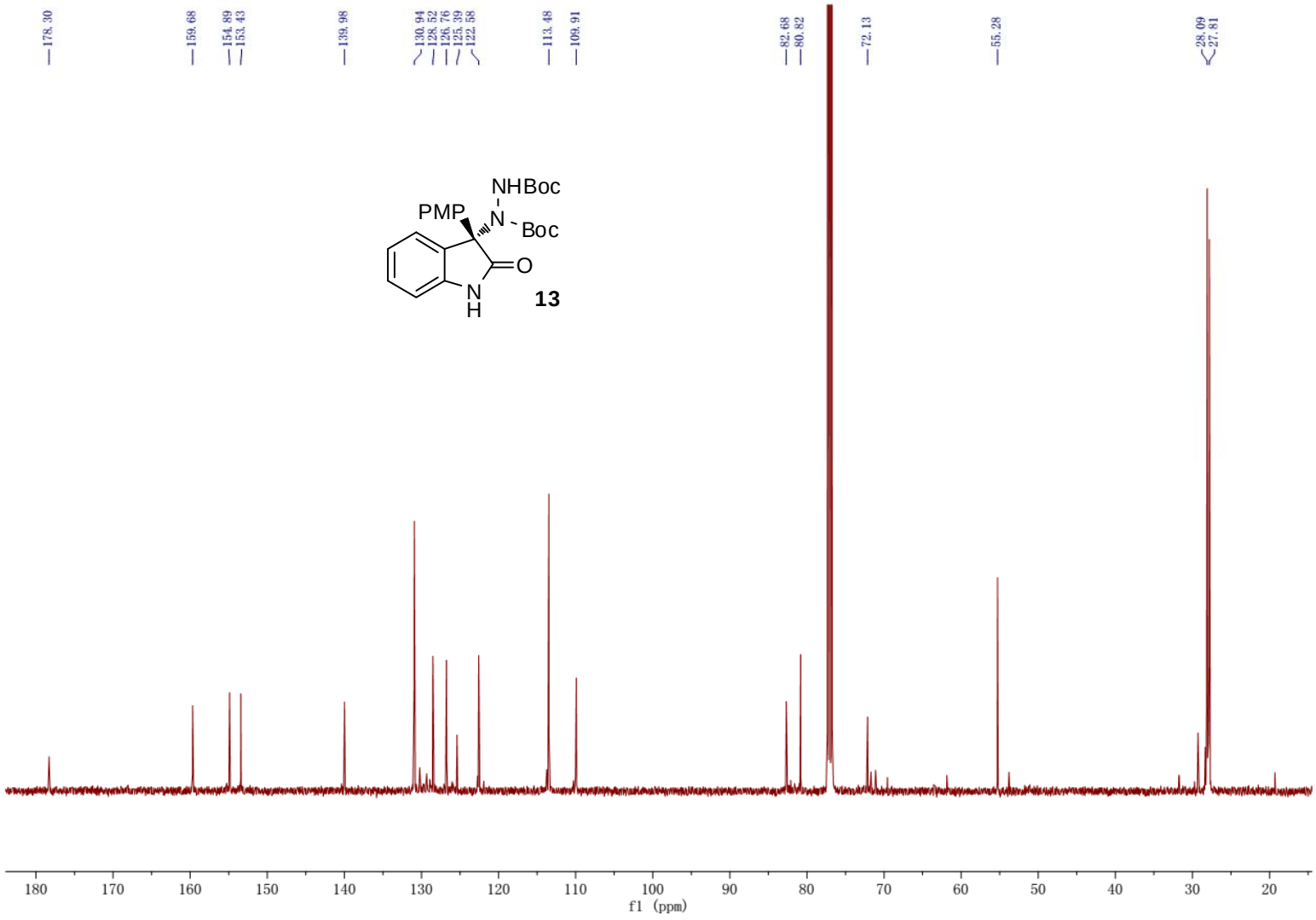

zyl-zh-75-1c-pure
zyl-zh-75-1c-pure
149.43
148.79
142.72
139.08
138.70
133.90
132.08
128.81
128.65
128.47
127.78
126.42
125.88
120.25
115.75
112.44
111.45
110.39
77.48
77.16
76.84
74.48
56.23
56.09
54.32
39.86
MeO
Ph
MeO
NO2
Br
O
N
H
11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
O
PMP
NO2
F
O
N
H
12
f1 (ppm)

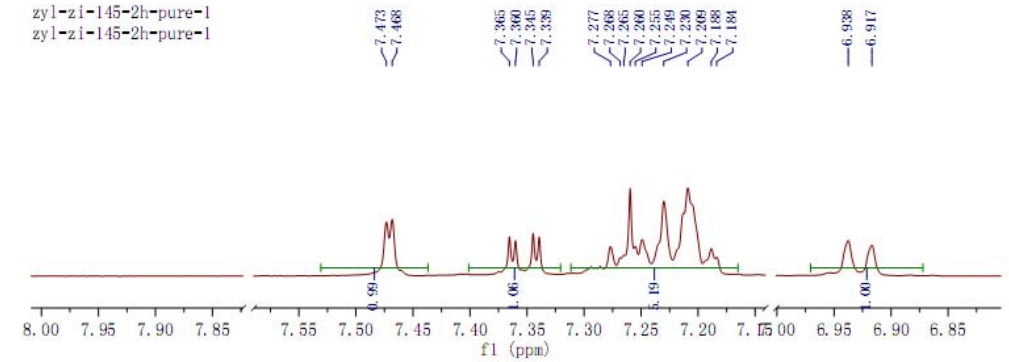

-126.41
Ph
O
PMP
NO2
F
O
N
H
12
-125.7
-125.9
-126.1
-126.3
-126.5
-126.7
-126.9
-127.1
-127.3
-127.5
-127.7
-127.9
-128.1
-128.3
-128.5
-128.7
-128.9
-129.1
f1 (ppm)

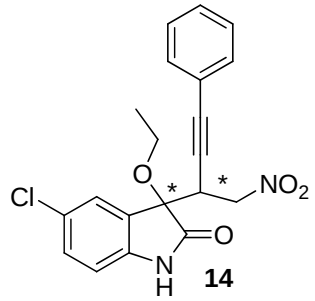

196.91
177.69
159.81
159.42
157.91
138.01
136.60
133.14
131.77
131.71
129.41
128.55
128.47
127.85
115.34
115.15
114.20
113.54
113.34
111.11
111.04
76.97
58.86
54.64
39.36
38.15
Ph
O
PMP
NO2
F
O
N
H
12
f1 (ppm)

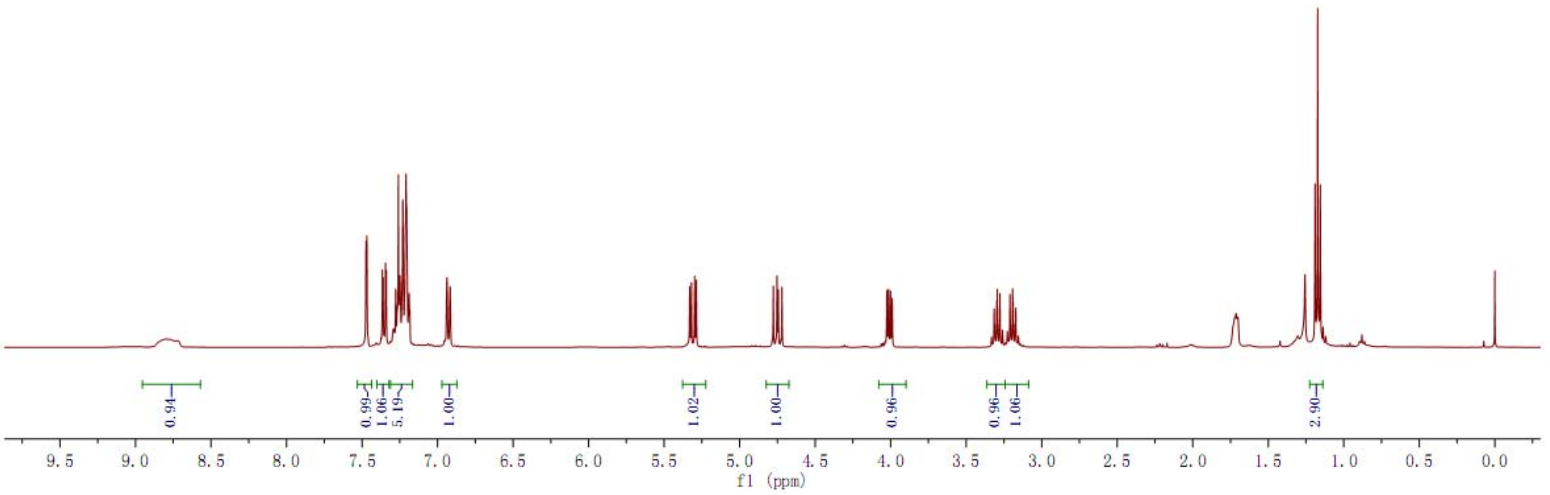

8.150
8.104
8.085
7.539
7.518
7.267
7.252
7.234
7.215
7.159
7.140
7.121
6.817
6.796
6.405
3.763
1.334
1.207
NHBoc
PMP
N
Boc
O
N
H
13
0.91
1.05
2.00
1.16
1.18
3.12
0.99
3.08
9.50
9.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

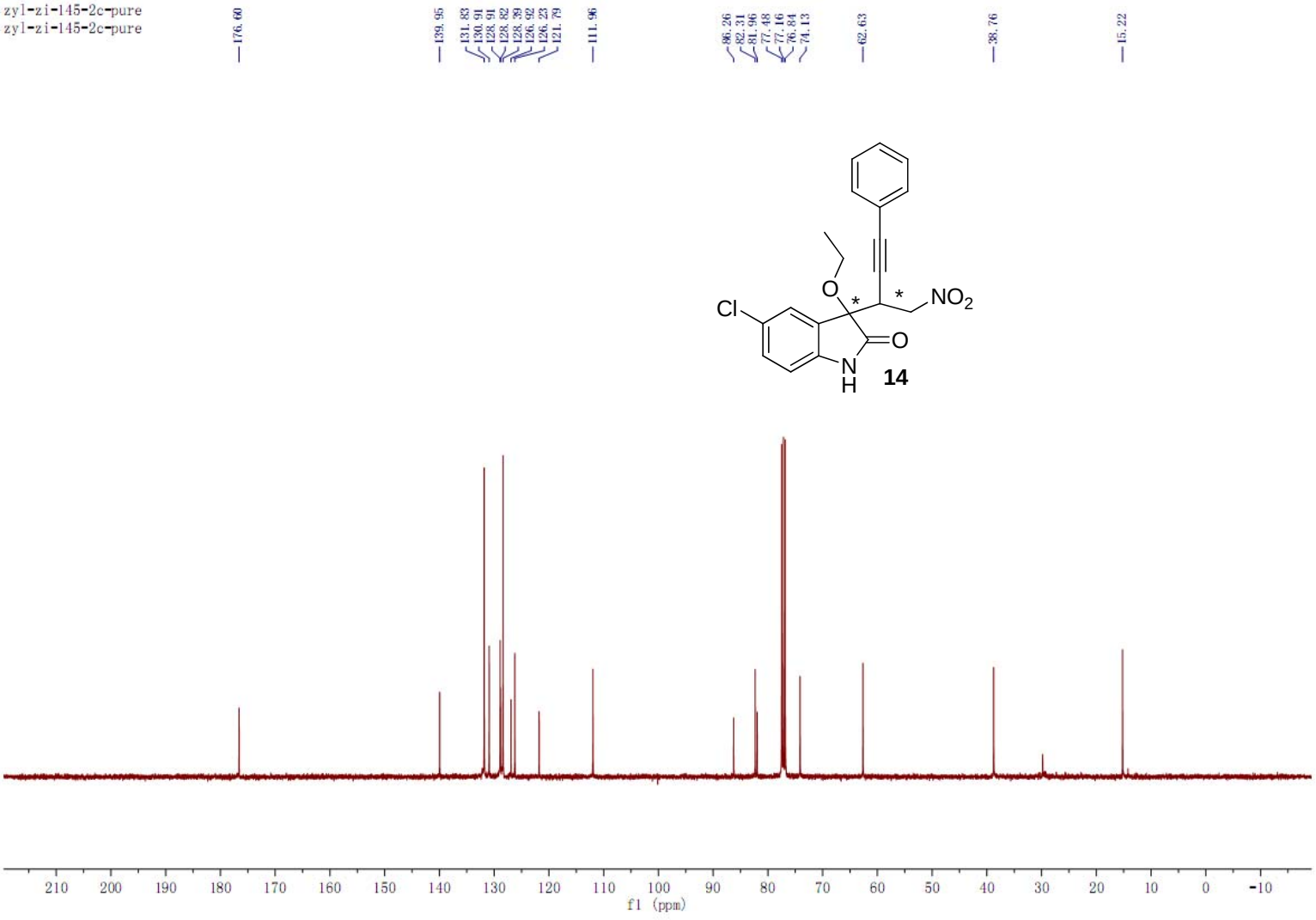

178.30
159.68
154.89
153.43
139.98
130.94
128.52
126.76
125.39
122.58
113.48
109.91
82.68
80.82
72.13
55.28
28.09
27.81
NHBoc
PMP
N
Boc
O
N
H
13
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

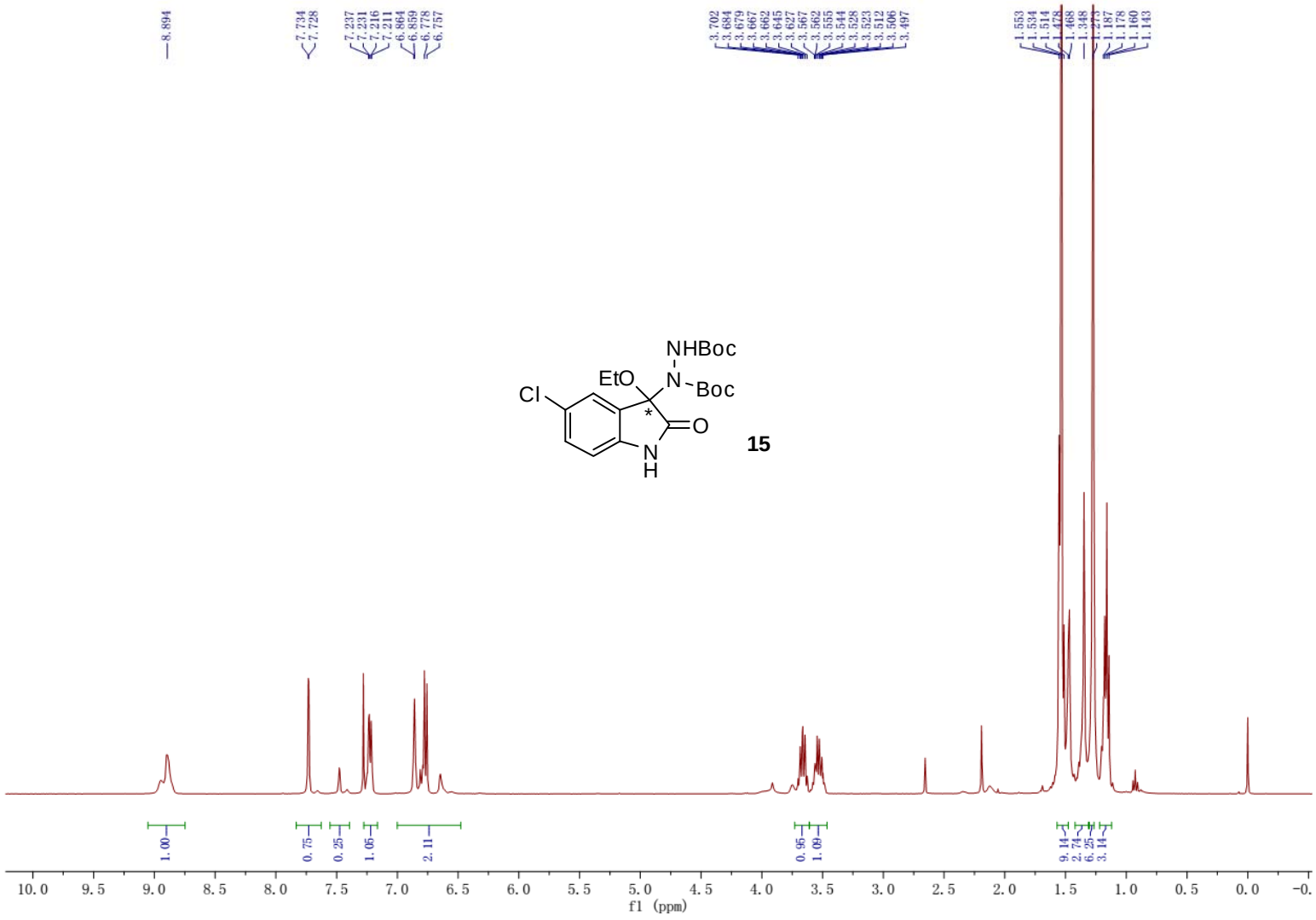

zyl-zi-145-2h-pure-1
zyl-zi-145-2h-pure-1

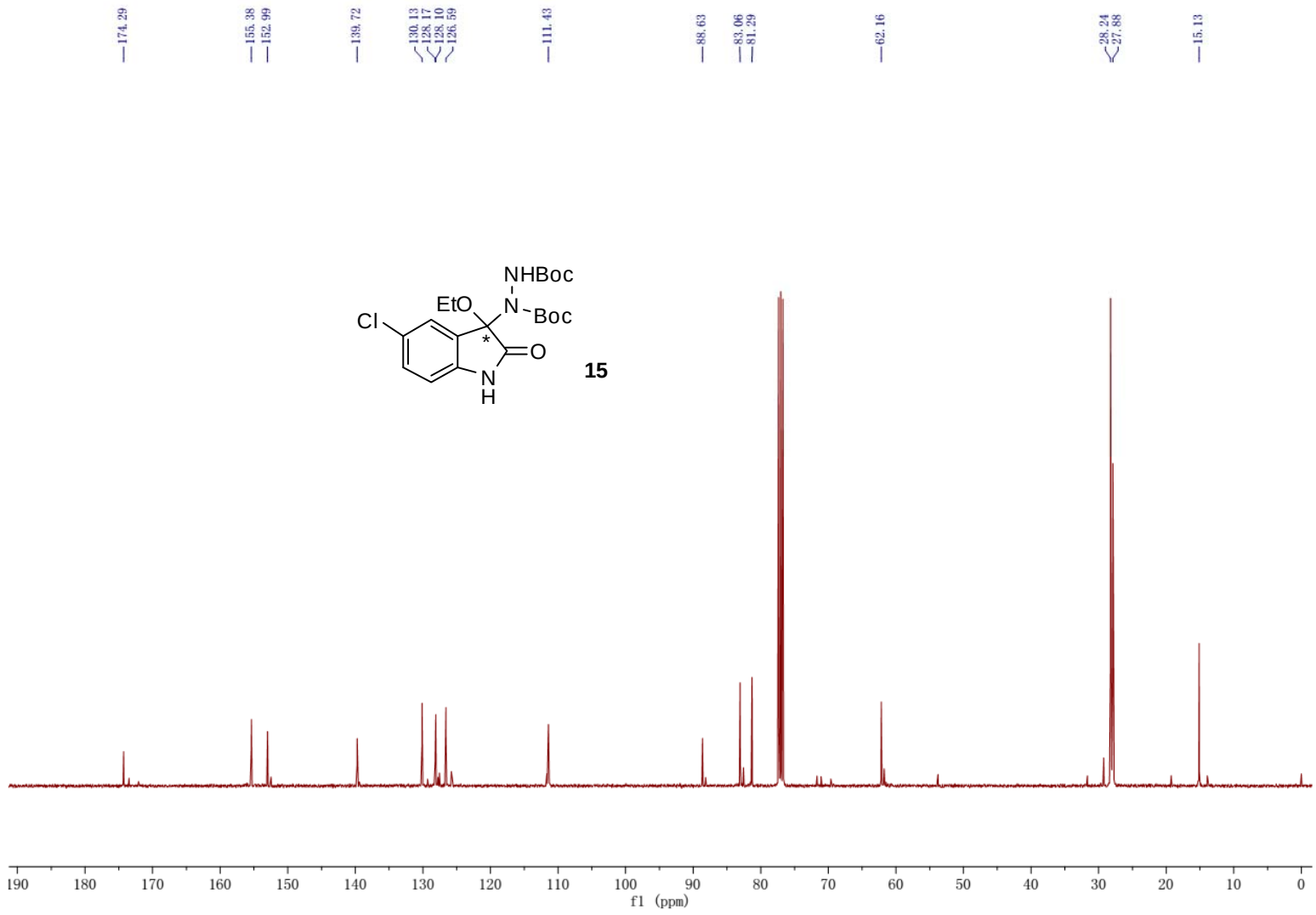

zyl-zi-145-2h-pure-1
zyl-zi-145-2h-pure-1
f1 (ppm)


Cl
O
*
*
NO2
O
N
H
14


f1 (ppm)


zyl-zi-145-2c-pure
zyl-zi-145-2c-pure
176.60
139.95
131.83
130.91
128.91
128.82
128.39
126.92
126.23
121.79
111.96
86.26
82.31
81.96
77.48
77.16
76.84
74.13
62.63
38.76
15.22
Cl
O
*
*
NO2
O
N
H
14
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)


8.894
7.734
7.728
7.237
7.231
7.216
7.211
6.864
6.859
6.778
6.757
3.702
3.684
3.679
3.667
3.662
3.645
3.627
3.567
3.562
3.555
3.544
3.528
3.523
3.512
3.506
3.497
1.553
1.534
1.514
1.478
1.468
1.348
1.187
1.178
1.160
1.143
NHBoc
EtO
N
Boc
Cl
*
O
N
H
15
1.00
0.75
0.25
1.05
2.11
0.95
1.09
9.14
2.74
6.25
3.14
10.0 9.5 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 -0.
f1 (ppm)

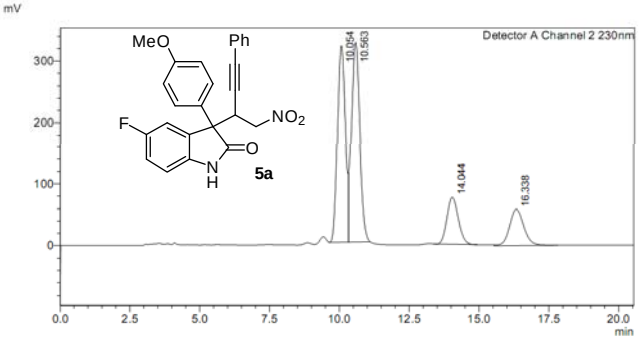

174.29
155.38
152.99
139.72
130.13
128.17
128.10
126.59
111.43
88.63
83.06
81.29
62.16
28.24
27.88
15.13
NHBoc
EtO
N
Boc
Cl
*
O
N
H
15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-1-RAC-ADH-80-20-205-230-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-77-1-RAC-ADH-80-20-205-230-1.1.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-30 9:22:13	Acquired by	: System Administrator
Date Processed	: 2013-12-30 10:48:35	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

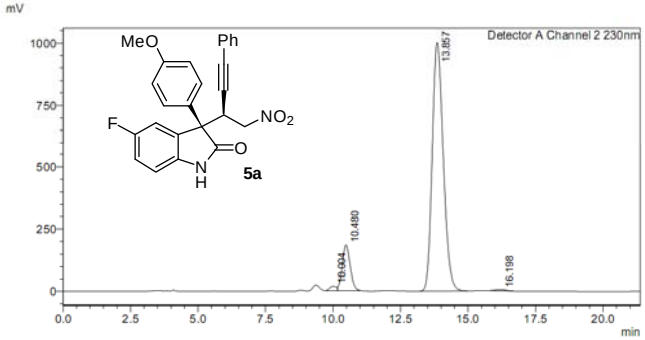
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.054	6314443	319340	36.398		M	
2	10.563	6781505	324373	39.090		V M	
3	14.044	2168185	76141	12.498		M	
4	16.338	2084110	58990	12.013		M	
Total		17348243	778844				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-1-ASY-ADH-80-20-205-230-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-77-1-ASY-ADH-80-20-205-230-1.0.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-30 9:45:23	Acquired by	: System Administrator
Date Processed	: 2013-12-30 10:50:08	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.004	298306	17544	0.912		M	
2	10.480	3728068	182370	11.400		V M	
3	13.857	28536673	1002438	87.263		M	
4	16.198	139029	4975	0.425		M	
Total		32702076	1207327				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-59-2-RAC-IE-90-10-205-230-1		
Sample ID	:		
Data Filename	: ZYL-ZG-59-2-RAC-IE-90-10-205-230-1.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-20 22:05:11	Acquired by	: System Administrator
Date Processed	: 2014-10-10 21:59:50	Processed by	: System Administrator

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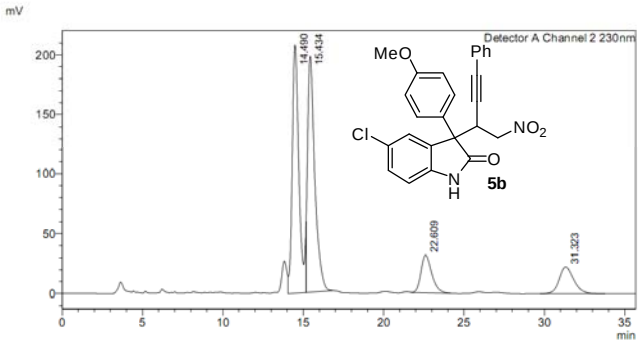

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.490	6048131	208043	40.039		M	
2	15.434	6161607	197821	40.791		V M	
3	22.609	1468426	31432	9.721		M	
4	31.323	1427279	22535	9.449		M	
Total		15105443	459831				

E:\data\zyl\ZYL-ZG-59-2-RAC-IE-90-10-205-230-1.lcd

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-59-2-RAC-IE-90-10-205-230-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-59-2-asy-IE-90-10-205-230-1.4.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
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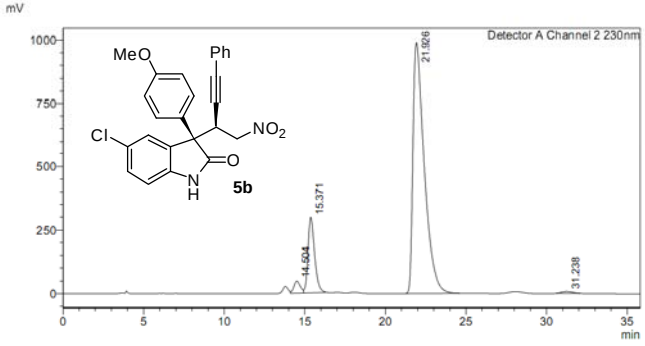

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.504	1337597	48036	2.286		M	
2	15.371	8491130	295144	14.511		V M	
3	21.926	48353180	989944	82.635		M	
4	31.238	332423	6952	0.568		M	
Total		58514331	1340076				

E:\data\zyl\ZYL-ZG-59-2-asy-IE-90-10-205-230-1.4.lcd

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-3-RAC-IC-90-10-205-230-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-77-3-RAC-IC-90-10-205-230-1.0.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
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Date Processed	: 2013-12-30 21:16:56	Processed by	: System Administrator

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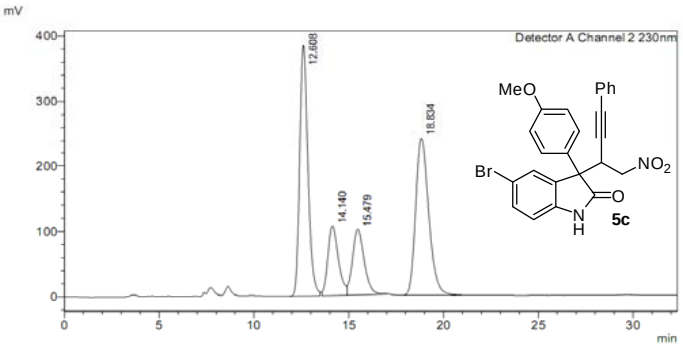


<Peak Table>

Detector A Channel 2 230nm

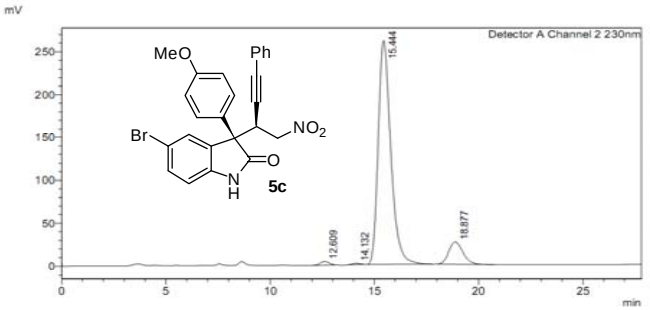
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.608	11608477	384820	36.753		M	
2	14.140	4123859	106277	13.056		M	
3	15.479	4269950	100012	13.519		V M	
4	18.834	11582711	241688	36.672		M	
Total		31584997	832796				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-3-ASY-IC-90-10-205-230-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-77-3-ASY-IC-90-10-205-230-1.0.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-30 15:43:25	Acquired by	: System Administrator
Date Processed	: 2013-12-30 21:18:58	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.609	136157	4544	1.101		M	
2	14.132	43569	1549	0.352		M	
3	15.444	10964423	260830	88.629		M	
4	18.877	1227033	25989	9.918		M	
Total		12371183	292911				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-15-1-1-RAC-ADH-80/20-230/190-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-15-1-1-RAC-ADH-80-20-230-190-1.5.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
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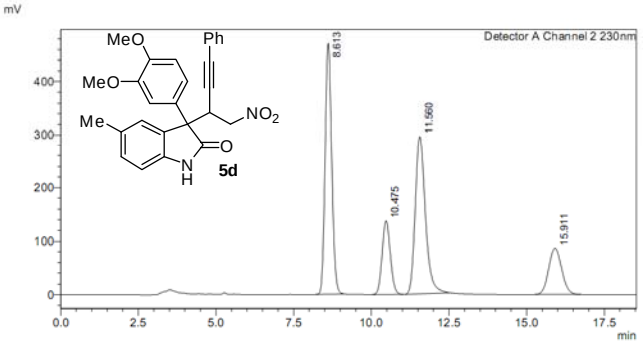

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.613	6963814	470646	37.178		M	
2	10.475	2529778	137491	13.506		M	
3	11.560	6720450	295378	35.879		M	
4	15.911	2516869	86440	13.437		M	
Total		18730911	989956				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-81-2-ASY-ADH-80-20-205-230-1.0-		
Sample ID	:		
Data Filename	: ZYL-ZG-81-2-ASY-ADH-80-20-205-230-1.0-.lcd		
Method Filename	: zyl-biao.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-16 22:18:24	Acquired by	: System Administrator
Date Processed	: 2014-1-16 22:43:54	Processed by	: System Administrator

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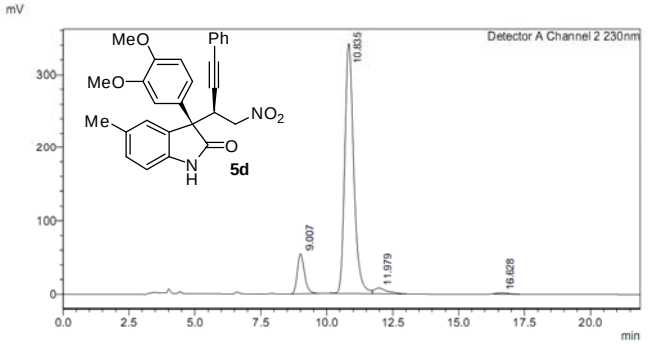

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.007	1039959	54744	11.000		M	
2	10.835	8092119	341526	85.589		M	
3	11.979	264794	7842	2.801		V M	
4	16.628	57703	1724	0.610		M	
Total		9454574	405836				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-12-RAC-ADH-85-15-205-230-1.0-		
Sample ID	:		
Data Filename	: ZYL-ZG-77-12-RAC-ADH-85-15-205-230-1.0-2.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-6 10:16:50	Acquired by	: System Administrator
Date Processed	: 2014-1-6 19:32:58	Processed by	: System Administrator

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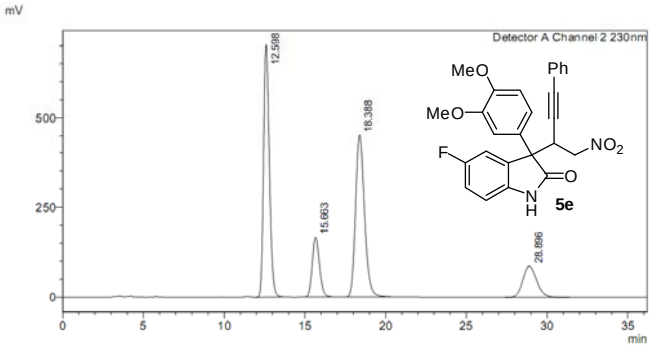

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.598	17469304	702787	38.690		M	
2	15.663	5158062	165682	11.424		M	
3	18.388	17369207	451679	38.469		M	
4	28.896	5155011	86666	11.417			
Total		45151584	1406814				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-12-ASY-ADH-85-15-205-230-1.0-x		
Sample ID	:		
Data Filename	: ZYL-ZG-77-12-ASY-ADH-85-15-205-230-1.0-x4.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-6 18:40:57	Acquired by	: System Administrator
Date Processed	: 2014-1-6 19:32:05	Processed by	: System Administrator

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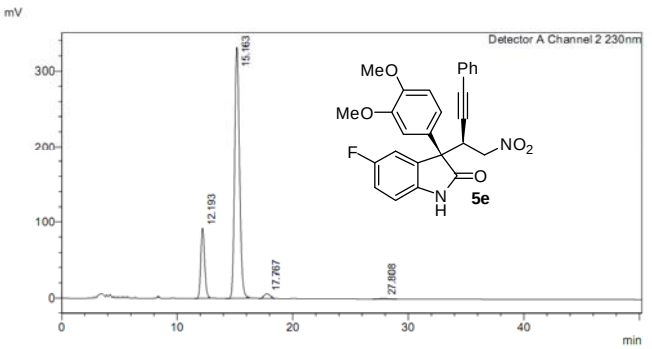

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.193	2111278	92019	17.495		M	
2	15.163	9726535	332301	80.599		M	
3	17.767	186290	5513	1.544		M	
4	27.808	43645	801	0.362		V	
Total		12067748	430633				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-13-RAC-ADH-85-15-205-230-1.0-		
Sample ID	:		
Data Filename	: ZYL-ZG-77-13-RAC-ADH-85-15-205-230-1.0-3.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-6 10:54:33	Acquired by	: System Administrator
Date Processed	: 2014-1-6 20:37:21	Processed by	: System Administrator

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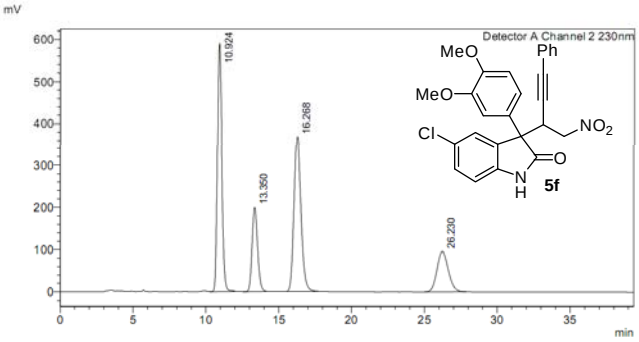

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.924	12481106	590112	35.382		M	
2	13.350	5239758	199000	14.854		M	
3	16.268	12349053	368555	35.007		M	
4	26.230	5205797	96214	14.757		M	
Total		35275714	1253881				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-13-ASY-ADH-85-15-205-230-1.0-x		
Sample ID	:		
Data Filename	: ZYL-ZG-77-13-ASY-ADH-85-15-205-230-1.0-x5.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-6 19:41:54	Acquired by	: System Administrator
Date Processed	: 2014-1-6 20:39:30	Processed by	: System Administrator

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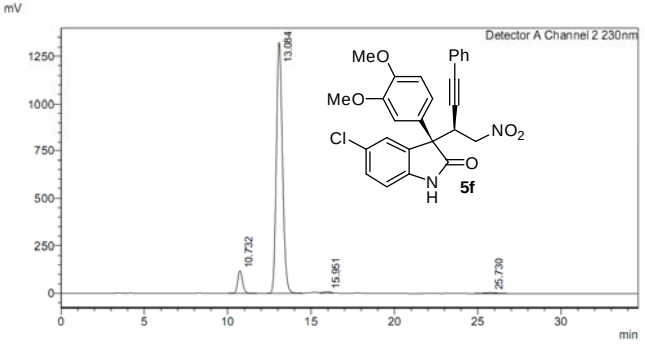

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.732	2400909	118208	6.535		M	
2	13.084	33851362	1323462	92.138		M	
3	15.951	282715	8409	0.770		M	
4	25.730	204900	3956	0.558		M	
Total		36739886	1454034				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-81-1-RAC-ADH-80-20-205-230-1.0-		
Sample ID	:		
Data Filename	: ZYL-ZG-81-1-RAC-ADH-80-20-205-230-1.0-.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-20 10:51:06	Acquired by	: System Administrator
Date Processed	: 2014-1-20 11:20:25	Processed by	: System Administrator

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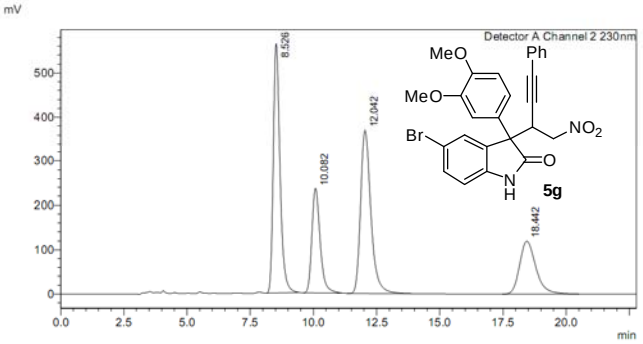

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.526	10399917	563091	32.956		M	
2	10.082	5363304	235390	16.996		M	
3	12.042	10471404	369249	33.183		M	
4	18.442	5322300	119409	16.866		M	
Total		31556924	1287140				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-81-1-ASY-ADH-80-20-205-230-1.0-		
Sample ID	:		
Data Filename	: ZYL-ZG-81-1-ASY-ADH-80-20-205-230-1.0-.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-20 10:10:14	Acquired by	: System Administrator
Date Processed	: 2014-1-20 10:53:28	Processed by	: System Administrator

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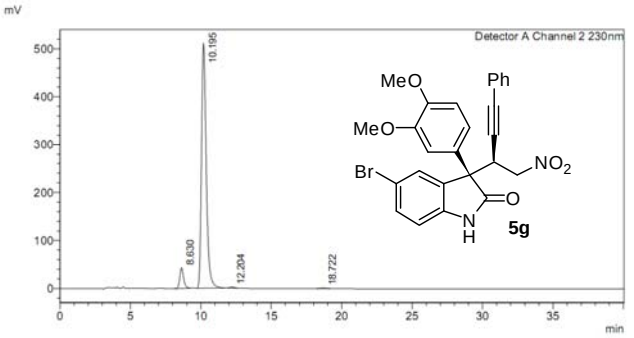

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.630	799411	42688	6.267		M	
2	10.195	11879535	510496	93.135		M	
3	12.204	46550	2045	0.365		M	
4	18.722	29672	921	0.233		M	
Total		12755168	556150				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: zyl-zg-43-3-rac-ic-95-5-230-205-1		
Sample ID	:		
Data Filename	: zyl-zg-41-3-rac-ic-95-5-230-205-8.lcd		
Method Filename	: zyl-biao.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-17 12:39:25	Acquired by	: System Administrator
Date Processed	: 2013-12-30 19:33:20	Processed by	: System Administrator

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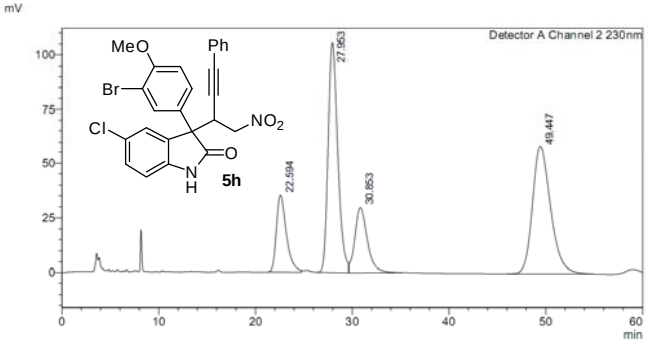

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.594	2512062	35030	12.468		M	
2	27.953	7336954	105691	36.415		M	
3	30.853	2692292	29957	13.363		M	
4	49.447	7606704	58227	37.754		M	
Total		20148013	228906				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-53-1-ASY-IC-95-5-205-230-1		
Sample ID	:		
Data Filename	: ZYL-ZG-53-1-ASY-IC-95-5-205-230-2.lcd		
Method Filename	: RUN-0.8.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-19 17:05:52	Acquired by	: System Administrator
Date Processed	: 2013-12-19 18:19:52	Processed by	: System Administrator

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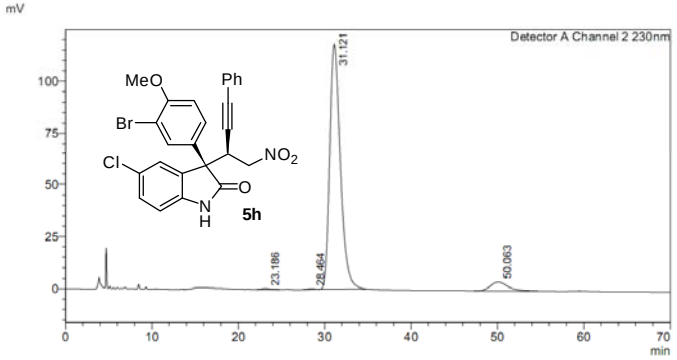

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.186	38073	560	0.351		M	
2	28.464	24646	496	0.227		M	
3	31.121	10126117	118086	93.421		M	
4	50.063	650347	4475	6.000		M	
Total		10839183	123617				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-103-1-RAC-IC-95-5-205-230-1.0-		
Sample ID	:		
Data Filename	: ZYL-ZG-103-1-RAC-IC-95-5-205-230-1.0-.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-20 11:41:38	Acquired by	: System Administrator
Date Processed	: 2014-1-20 12:41:17	Processed by	: System Administrator

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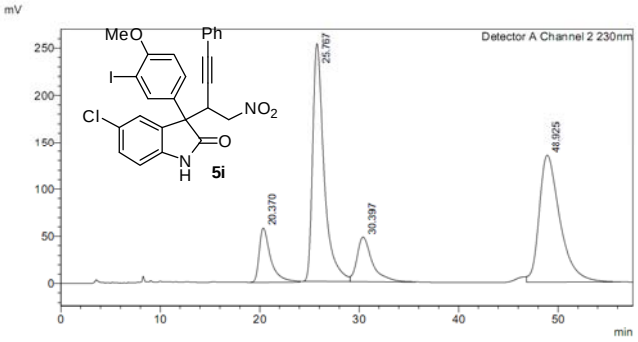

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.370	4633290	57627	9.346		M	
2	25.767	20272902	252875	40.893		M	
3	30.397	5129337	47338	10.346		V M	
4	48.925	19540305	134209	39.415		M	
Total		49575834	492049				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-103-1-ASY-IC-95-5-205-230-1.0-		
Sample ID	:		
Data Filename	: ZYL-ZG-103-1-ASY-IC-95-5-205-230-1.0-.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-20 12:43:16	Acquired by	: System Administrator
Date Processed	: 2014-1-20 14:02:39	Processed by	: System Administrator

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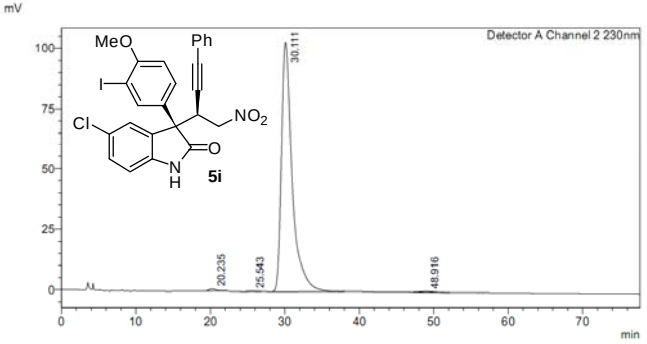


<Peak Table>

Detector A Channel 2 230nm

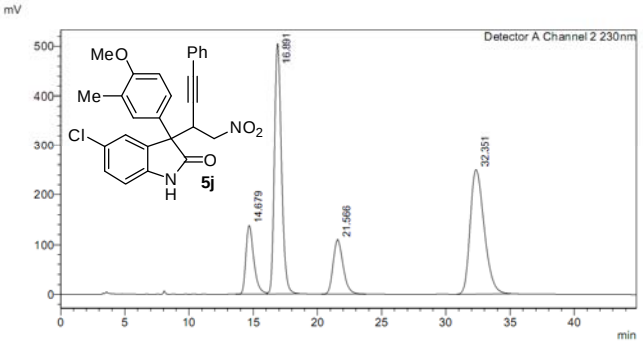
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.235	56877	854	0.544		M	
2	25.543	12385	229	0.118		M	
3	30.111	10341964	103116	98.875		M	
4	48.916	48443	375	0.463		M	
Total		10459670	104574				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-14-RAC-IC-95-5-205-230-1.0-x		
Sample ID	:		
Data Filename	: ZYL-ZG-77-14-RAC-IC-95-5-205-230-1.0-x2.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-6 15:50:10	Acquired by	: System Administrator
Date Processed	: 2014-1-6 17:34:31	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

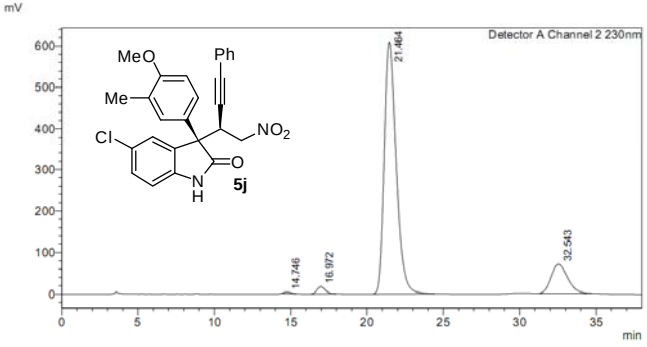
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.679	5894054	137495	11.747		M	
2	16.891	19256818	504029	38.379		V M	
3	21.566	5923481	108984	11.806		M	
4	32.351	19101090	250008	38.069		M	
Total		50175442	1000515				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-14-ASY-IC-95-5-205-230-1.0-x		
Sample ID	:		
Data Filename	: ZYL-ZG-77-14-ASY-IC-95-5-205-230-1.0-x3.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-6 16:53:42	Acquired by	: System Administrator
Date Processed	: 2014-1-6 17:33:40	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.746	118457	3625	0.303		M	
2	16.972	652194	17656	1.666		M	
3	21.464	33082904	609543	84.520		M	
4	32.543	5288603	70518	13.511		M	
Total		39142157	701341				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: zyl-zg-41-1-rac-ic-95-5-230-245-1		
Sample ID	:		
Data Filename	: zyl-zg-41-1-rac-ic-95-5-230-245-2.lcd		
Method Filename	: wyh-wb-17-rac-ADH-1.0-230-254.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-16 20:14:19	Acquired by	: System Administrator
Date Processed	: 2013-12-30 18:11:48	Processed by	: System Administrator

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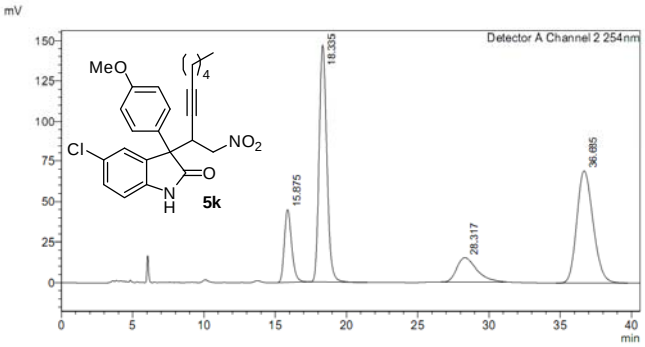

<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.875	1608740	44866	11.373		M	
2	18.335	5538328	146863	39.154		M	
3	28.317	1484498	15002	10.495		M	
4	36.685	5513443	69256	38.978		M	
Total		14145009	275987				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-67\77-4-ASY-IC-95-5-205-230-1.0-		
Sample ID	:		
Data Filename	: ZYL-ZG-67-77-4-ASY-IC-95-5-205-230-1.0-.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2014-1-20 14:23:37	Acquired by	: System Administrator
Date Processed	: 2014-3-17 19:57:15	Processed by	: System Administrator

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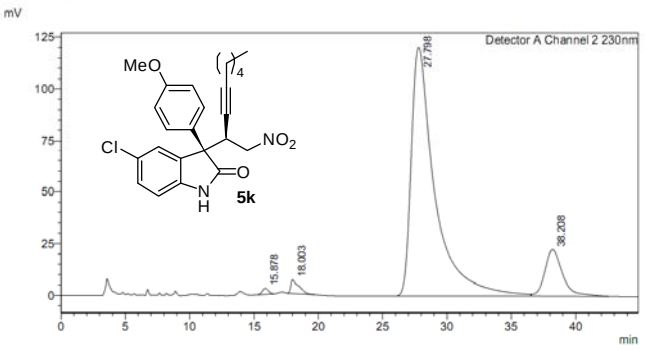

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.878	94762	2898	0.530		M	
2	18.003	285505	6591	1.597		M	
3	27.798	15363796	120493	85.934		M	
4	38.208	2134487	22368	11.939		M	
Total		17878551	152350				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-5-RAC-IE-90-10-205-230-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-77-5-RAC-IE-90-10-205-230-1.1.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-30 12:18:47	Acquired by	: System Administrator
Date Processed	: 2013-12-30 14:52:41	Processed by	: System Administrator

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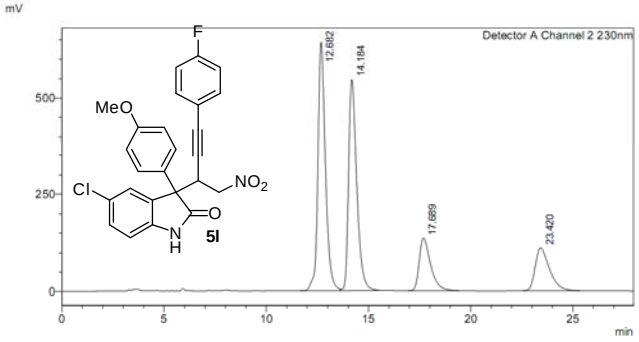

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.682	16457233	641844	38.927		M	
2	14.184	15139805	546354	35.811		V M	
3	17.689	5279732	135354	12.488		M	
4	23.420	5400238	110250	12.773		M	
Total		42277007	1433801				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-5-ASY-IE-90-10-205-230-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-77-5-ASY-IE-90-10-205-230-1.0.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-30 14:17:44	Acquired by	: System Administrator
Date Processed	: 2013-12-30 14:54:40	Processed by	: System Administrator

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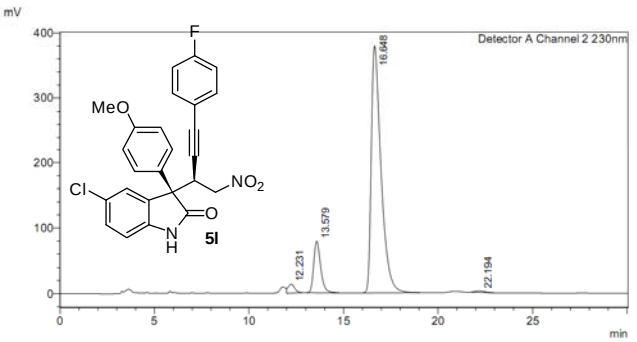

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.231	328816	13643	2.053		M	
2	13.579	2024229	78566	12.639		M	
3	16.648	13580272	378948	84.794		M	
4	22.194	82220	2293	0.513		M	
Total		16015536	473449				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-7-RAC-IC-97-3-205-230-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-77-7-RAC-IC-97-3-205-230-1.0.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-30 19:44:37	Acquired by	: System Administrator
Date Processed	: 2013-12-30 21:23:13	Processed by	: System Administrator

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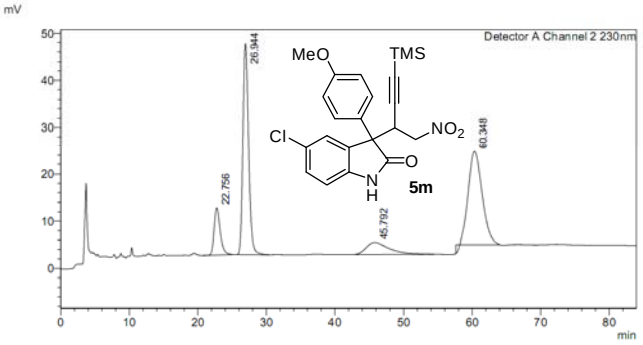

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.756	616848	10025	9.397		M	
2	26.944	2577290	44869	39.260		M	
3	45.792	598195	2566	9.112		M	
4	60.348	2772302	19759	42.231		M	
Total		6564635	77220				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-77-7-ASY-IC-97-3-205-230-1.0		
Sample ID	:		
Data Filename	: ZYL-ZG-77-7-ASY-IC-97-3-205-230-1.0.lcd		
Method Filename	: method 1.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2013-12-30 21:11:32	Acquired by	: System Administrator
Date Processed	: 2013-12-30 22:23:29	Processed by	: System Administrator

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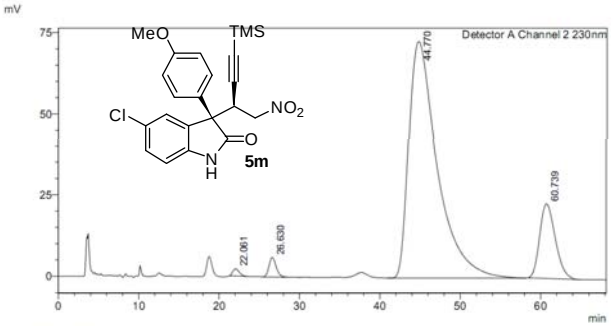

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.061	122973	2195	0.573		M	
2	26.630	367911	5947	1.714		M	
3	44.770	17879609	72798	83.279		M	
4	60.739	3099144	22898	14.435		M	
Total		21469638	103839				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-147-1-RAC-ADH-95-5-205-230-1-		
Sample ID	:		
Data Filename	: ZYL-ZG-147-1-RAC-ADH-95-5-205-230-1-5.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2014-2-28 21:09:02	Acquired by	: System Administrator
Date Processed	: 2014-3-3 10:10:32	Processed by	: System Administrator

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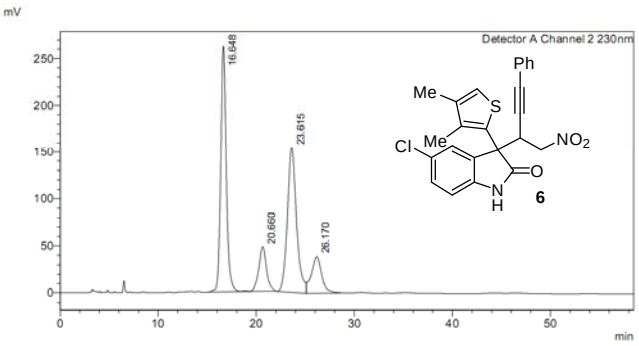

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.648	10282487	262254	39.748		M	
2	20.660	2636390	47456	10.191		M	
3	23.615	10014337	154844	38.712		M	
4	26.170	2935788	39366	11.349		M	
Total		25869001	503921				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZG-147-1-ASY-ADH-95-5-205-230-1.0-		
Sample ID	:		
Data Filename	: ZYL-ZG-147-1-ASY-ADH-95-5-205-230-1.0-1.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2014-3-3 9:37:41	Acquired by	: System Administrator
Date Processed	: 2014-3-3 10:11:34	Processed by	: System Administrator

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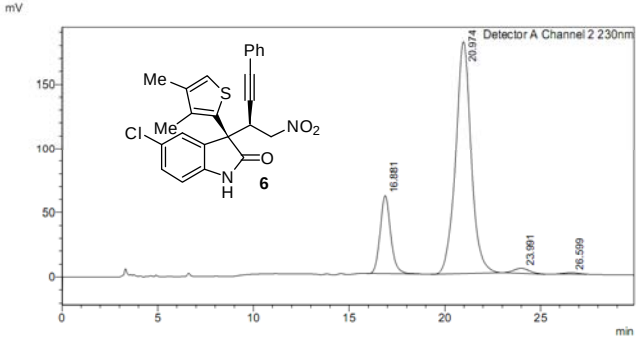


<Peak Table>

Detector A Channel 2 230nm

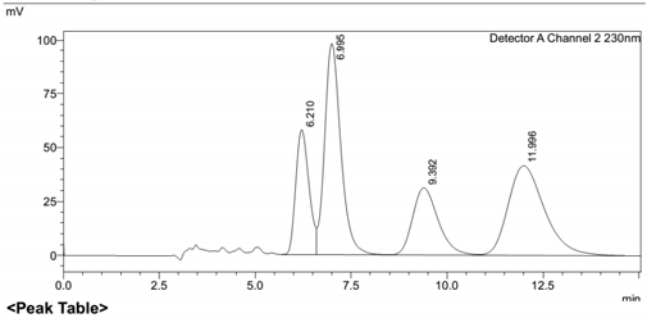
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.881	2317289	60291	18.159		M	
2	20.974	10166657	180313	79.668		M	
3	23.991	217675	3858	1.706		M	
4	26.599	59681	1205	0.468		M	
Total		12761301	245667				

Analysis Report

<Sample Information>

Sample Name	: czy-cr-36-rac		
Sample ID	:		
Data Filename	: czy-cr-36-rac-rac-od-75-25.lcd		
Method Filename	: RUN-1.0.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2015/6/1 15:45:39	Acquired by	: System Administrator
Date Processed	: 2015/6/1 16:13:38	Processed by	: System Administrator

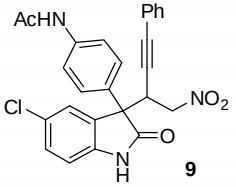
<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	6.210	1392478	57891	16.445
2	6.995	2874282	98157	33.945
3	9.392	1446737	31148	17.086
4	11.996	2753962	41604	32.524
Total		8467457	228800	



9

Analysis Report

<Sample Information>

Sample Name	: czy-cr-35-as		
Sample ID	:		
Data Filename	: czy-cr-35-as-od-75-25.lcd		
Method Filename	: RUN-1.0.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2015/6/1 16:01:22	Acquired by	: System Administrator
Date Processed	: 2015/6/1 16:16:32	Processed by	: System Administrator

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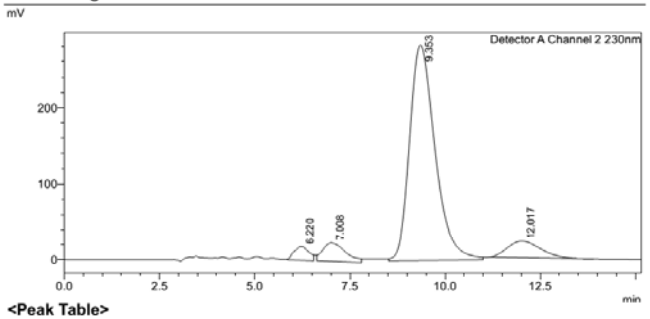
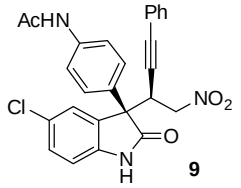


<Peak Table>

Detector A Channel 2 230nm

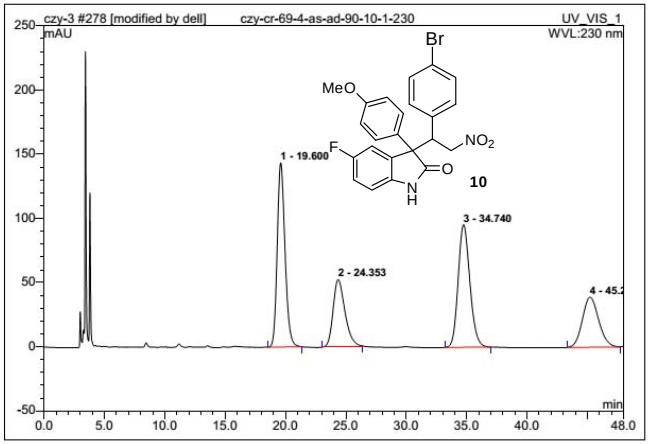
Peak#	Ret. Time	Area	Height	Conc.
1	6.220	506029	18455	3.151
2	7.008	1023721	24198	6.374
3	9.353	13217813	283217	82.304
4	12.017	1312108	21617	8.170
Total		16059671	347486	



9

278 czy-cr-69-4-as-ad-90-10-1-230

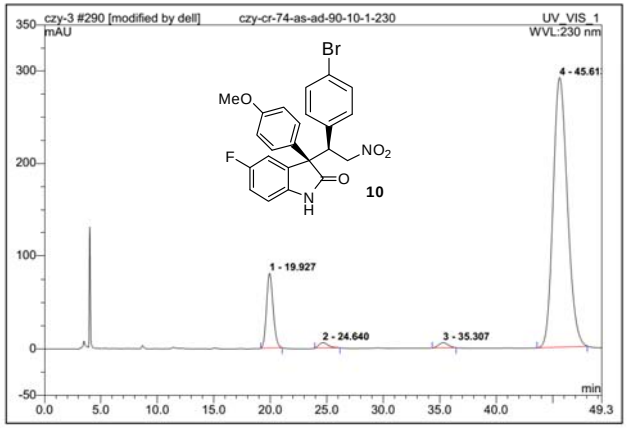
Sample Name:	**czy-cr-69-4-as-ad-90-10-1-230**	*Injection Volume:*	**20.0**
Vial Number:	**384**	*Channel:*	**UV_VIS_1**
Sample Type:	**standard**	*Wavelength:*	**230**
Control Program:	**czy**	*Bandwidth:*	**n.a.**
Quantif. Method:	**czy**	*Dilution Factor:*	**1.0000**
Recording Time:	**2015-9-9 23:04**	*Sample Weight:*	**1.0000**
Run Time (min):	**48.00**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.60	n.a.	143.521	107.195	31.86	n.a.	BMB*
2	24.35	n.a.	52.716	60.826	18.08	n.a.	BM *
3	34.74	n.a.	95.438	107.222	31.87	n.a.	BMB*
4	45.22	n.a.	39.073	61.168	18.18	n.a.	BMB*
Total:			330.747	336.412	100.00	0.000	

290 czy-cr-74-as-ad-90-10-1-230

Sample Name:	**czy-cr-74-as-ad-90-10-1-230**	*Injection Volume:*	**20.0**
Vial Number:	**396**	*Channel:*	**UV_VIS_1**
Sample Type:	**standard**	*Wavelength:*	**230**
Control Program:	**czy**	*Bandwidth:*	**n.a.**
Quantif. Method:	**czy**	*Dilution Factor:*	**1.0000**
Recording Time:	**2015-10-4 17:28**	*Sample Weight:*	**1.0000**
Run Time (min):	**49.33**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.93	n.a.	80.639	54.374	11.07	n.a.	BMB*
2	24.64	n.a.	5.754	5.399	1.10	n.a.	BMB*
3	35.31	n.a.	5.574	5.492	1.12	n.a.	BMB*
4	45.61	n.a.	290.772	426.060	86.72	n.a.	BMB*
Total:			382.740	491.324	100.00	0.000	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZJ-63-RAC-IE-90-10-205-230-1-		
Sample ID	:		
Data Filename	: ZYL-ZJ-63-RAC-IE-90-10-205-230-1-.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2014-8-19 16:01:11	Acquired by	: System Administrator
Date Processed	: 2014-8-19 17:32:39	Processed by	: System Administrator

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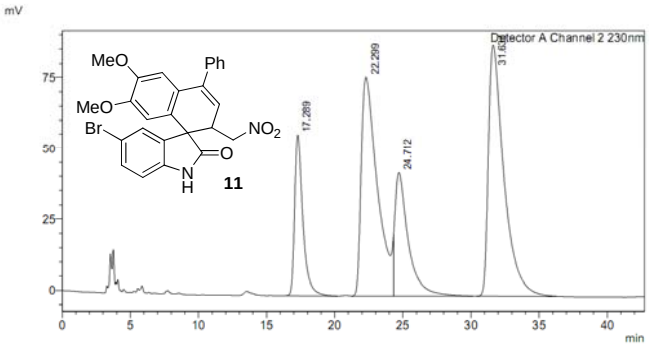

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.289	2397102	56657	12.786		V	
2	22.299	6381819	76991	34.042		M	
3	24.712	2935218	43329	15.657		V M	
4	31.631	7033029	88531	37.515			
Total		18747168	265508				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZJ-63-ASY-IE-90-10-205-230-1-		
Sample ID	:		
Data Filename	: ZYL-ZJ-63-ASY-IE-90-10-205-230-1-.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2014-8-19 16:47:01	Acquired by	: System Administrator
Date Processed	: 2014-9-8 21:50:12	Processed by	: System Administrator

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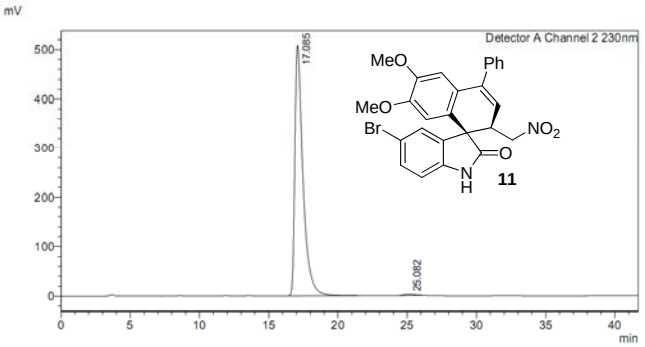

<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.085	20684263	509082	99.274			
2	25.082	151272	2597	0.726		M	
Total		20835535	511678				

Analysis Report

<Sample Information>

Sample Name	: czy-cp-134		
Sample ID	:		
Data Filename	: czy-cp-134-rac-ie-75-25.lcd		
Method Filename	: 1.0.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2015/1/24 14:26:16	Acquired by	: System Administrator
Date Processed	: 2015/1/24 17:09:44	Processed by	: System Administrator

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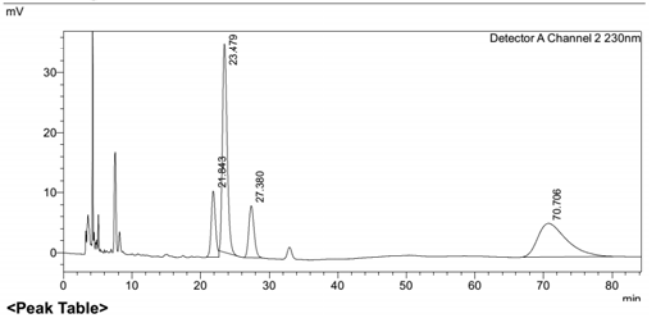
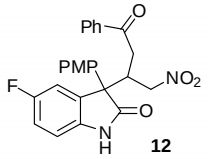


<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	21.843	470314	11001	11.052
2	23.479	1680155	34881	39.481
3	27.380	460556	8632	10.822
4	70.706	1644583	5598	38.645
Total		4255609	60111	



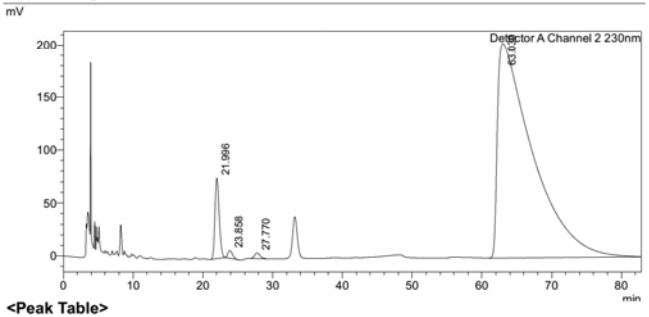
12

Analysis Report

<Sample Information>

Sample Name	: czy-cp-139		
Sample ID	:		
Data Filename	: czy-cp-134-as-ie-75-25.lcd		
Method Filename	: 1.0.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2015/1/24 13:02:45	Acquired by	: System Administrator
Date Processed	: 2015/1/24 14:28:39	Processed by	: System Administrator

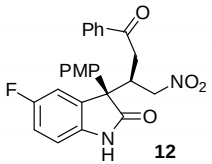
<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

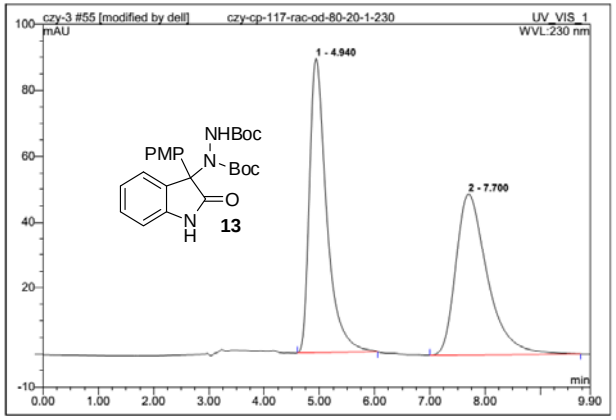
Peak#	Ret. Time	Area	Height	Conc.
1	21.996	3211730	76202	4.296
2	23.858	348371	7622	0.466
3	27.770	285432	5306	0.382
4	63.030	70920803	203263	94.857
Total		74766336	292393	



12

55 czy-cp-117-rac-od-80-20-1-230

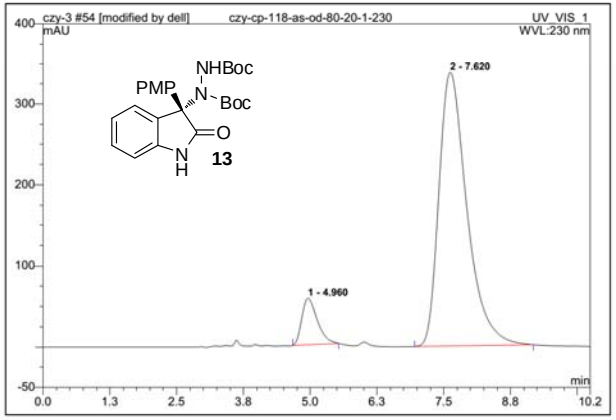
Sample Name:	**czy-cp-117-rac-od-80-20-1-230**	*Injection Volume:*	**20.0**
Vial Number:	**154**	*Channel:*	**UV_VIS_1**
Sample Type:	**standard**	*Wavelength:*	**230**
Control Program:	**czy**	*Bandwidth:*	**n.a.**
Quantif. Method:	**czy**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014-12-22 16:56**	*Sample Weight:*	**1.0000**
Run Time (min):	**9.90**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4.94	n.a.	89.195	32.088	49.94	n.a.	BMB*
2	7.70	n.a.	48.828	32.169	50.06	n.a.	BMB
Total:			138.023	64.257	100.00	0.000	

54 czy-cp-118-as-od-80-20-1-230

Sample Name:	**czy-cp-118-as-od-80-20-1-230**	*Injection Volume:*	**20.0**
Vial Number:	**153**	*Channel:*	**UV_VIS_1**
Sample Type:	**standard**	*Wavelength:*	**230**
Control Program:	**czy**	*Bandwidth:*	**n.a.**
Quantif. Method:	**czy**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014-12-22 16:45**	*Sample Weight:*	**1.0000**
Run Time (min):	**10.24**	*Sample Amount:*	**1.0000**



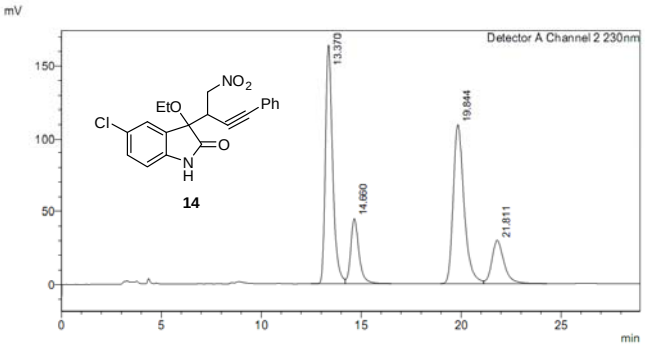
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4.96	n.a.	57.395	19.255	8.60	n.a.	BMB*
2	7.62	n.a.	338.152	204.673	91.40	n.a.	BMB*
Total:			395.547	223.928	100.00	0.000	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZI-145-RAC-ADH-95-5-205-230-1-		
Sample ID	:		
Data Filename	: ZYL-ZI-145-RAC-ADH-95-5-205-230-1-.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2014-6-14 9:16:47	Acquired by	: System Administrator
Date Processed	: 2014-6-14 9:45:45	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

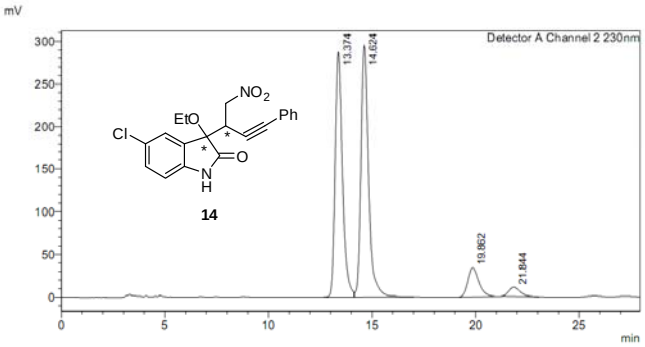
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.370	4132552	163934	38.248			
2	14.660	1279285	44601	11.840		SV	
3	19.844	4130180	109392	38.227		V	
4	21.811	1262469	29503	11.685		V	
Total		10804485	347431				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: ZYL-ZI-145-ASY-ADH-95-5-205-230-1-		
Sample ID	:		
Data Filename	: ZYL-ZI-145-ASY-ADH-95-5-205-230-1-.lcd		
Method Filename	: ZYL-A.lcm		
Batch Filename	:		
Vial #	: 0-0	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2014-6-14 9:46:21	Acquired by	: System Administrator
Date Processed	: 2014-9-8 17:28:43	Processed by	: System Administrator

<Chromatogram>



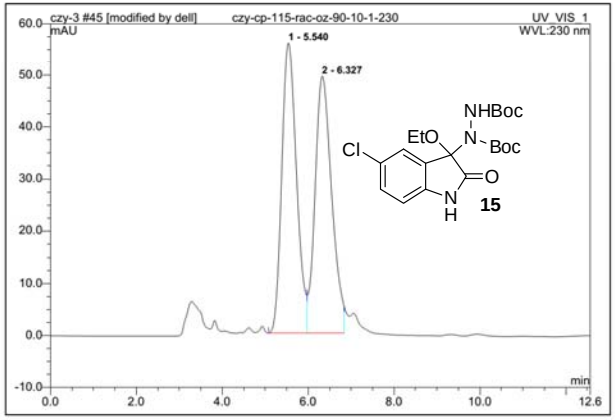
<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.374	7038085	287182	43.419		M	
2	14.624	7503408	295350	46.290		M	
3	19.862	1258584	33999	7.764		M	
4	21.844	409462	10633	2.526		M	
Total		16209538	627164				

45 czy-cp-115-rac-oz-90-10-1-230

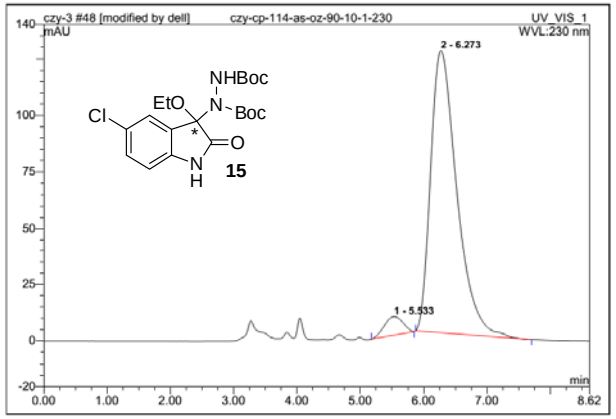
Sample Name:	**czy-cp-115-rac-oz-90-10-1-230**	*Injection Volume:*	**20.0**
Vial Number:	**144**	*Channel:*	**UV_VIS_1**
Sample Type:	**standard**	*Wavelength:*	**230**
Control Program:	**czy**	*Bandwidth:*	**n.a.**
Quantif. Method:	**czy**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014-12-17 14:39**	*Sample Weight:*	**1.0000**
Run Time (min):	**12.57**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.54	n.a.	55.898	22.179	49.90	n.a.	BM *
2	6.33	n.a.	49.340	22.270	50.10	n.a.	M *
Total:			105.238	44.449	100.00	0.000	

48 czy-cp-114-as-oz-90-10-1-230

Sample Name:	**czy-cp-114-as-oz-90-10-1-230**	*Injection Volume:*	**20.0**
Vial Number:	**147**	*Channel:*	**UV_VIS_1**
Sample Type:	**standard**	*Wavelength:*	**230**
Control Program:	**czy**	*Bandwidth:*	**n.a.**
Quantif. Method:	**czy**	*Dilution Factor:*	**1.0000**
Recording Time:	**2014-12-18 9:12**	*Sample Weight:*	**1.0000**
Run Time (min):	**8.62**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.53	n.a.	8.085	2.763	4.43	n.a.	BMB*
2	6.27	n.a.	124.736	59.601	95.57	n.a.	BMB*
Total:			132.821	62.364	100.00	0.000	