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SUPPORTING INFORMATION

Dienyl dehydroabietic decarbonylative amide for rhodium-catalysed asymmetric arylation to nitroolefins

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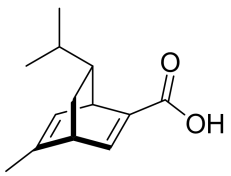
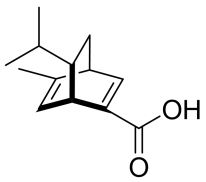
1. General information

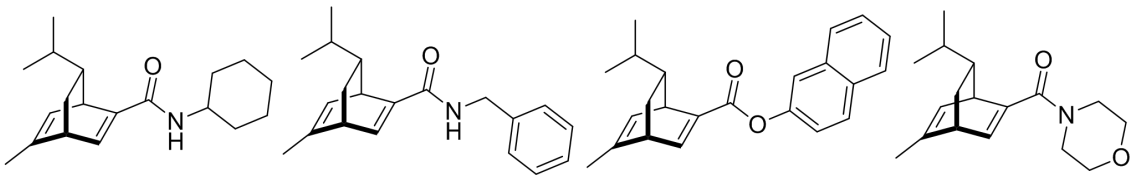
Reactions were performed in the presence of nitrogen applying Schlenk line technique unless otherwise statement. Commercially available reagents were used throughout without further purification other than those detailed below. THF (AR) and toluene were distilled over sodium benzophenone ketyl under nitrogen. EtOH was distilled over magnesium sulfate. Methylene chloride was distilled over calcium hydride. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Advance 400 operating at 400 MHz for ^{1}H NMR and ^{13}C NMR at 100 MHz, or using Bruker 300 spectrometer at 300 MHz for ^{1}H NMR and ^{13}C NMR at 75 MHz, or using Bruker Advance 500 spectrometer at 500 MHz for ^{1}H NMR and ^{13}C NMR at 125 MHz. $CDCl_3$ was used as the solvent for all samples. ^{1}H NMR chemical shifts are reported using residual proton on non-deuterated solvent ($CDCl_3$: 7.26 ppm), whereas ^{13}C NMR spectra are reported using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm). Product spots were visualized by UV light at 254 nm, and subsequently developed using potassium permanganate solution as appropriate. All chromatography was carried out using silica gel (300-400 mesh) obtained from Qingdao Puke company. The removal of solvent was performed on a rotary evaporator in vacuum. IR spectra were recorded in the range of 4000-400 cm^{-1}, on Perkin-Elmer Spectrum FT/IR spectrometer using a KBr pellet. Melting points were determined using an Electrothermal melting point apparatus. High resolution mass spectrometry was carried out on a New ultraflextreme equipped with TOF/TOF/Ultimate 3000 Nano HPLC. Optical purity of the final compounds were determined using a Agilent 1260 series HPLC system using a Daicel Chiralpak OD-H 4.6 mm × 250 mm, or Daicel Chiralpak AS-H 4.6 mm × 250 mm. Optical rotations were measured on a Rudolph Autopoll digital polarimeter. Single crystal X-ray crystallography was carried out on Bruker Apex-II CCD. Authentic racemic samples of products for chiral HPLC assay determinations were obtained using $[Rh(cod)Cl]_2$ (1.5 mol %) as an achiral precatalyst, using room temperature stirring condition. (*R*)-**3i** and (*S*)-**3i** were prepared according to the literature procedures, by employing Et_2AlCl catalysed Diels-Alder reaction of corresponding phelllandrene with ethyl propiolate, then hydrolysis in basic condition and HCl (aq.) acidification.[1,2] (*R*)-**3b**, (*R*)-**3c** and (*R*)-**3e** were prepared by phellandrene derived dienyl acid amidation with corrresponding amines by HBTU or HOBt, according to Lam's protocols.[2,3,4] (*R*)-**3d** was prepared by phellandrene derived dienyl acid *Steglich* esterification with 2-naphthol and the data are consistent with Hayashi's previous report.[5]



(*R*)-**3i**



(*S*)-**3i**

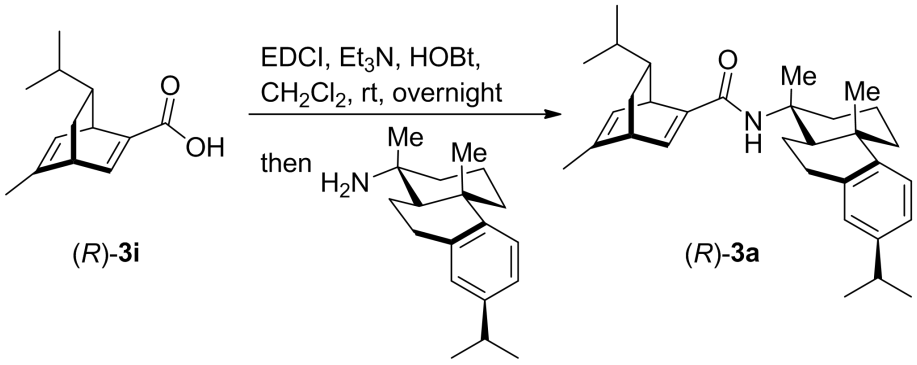


(*R*)-**3b** 45%　　(*R*)-**3c** 58%　　(*R*)-**3d** 75%　　(*R*)-**3e** 31%

2. Experimental procedures, characterisation data and HPLC traces of addition adducts

(1*R*,4*R*,7*R*)-7-Isopropyl-*N*-((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide

Procedure A:

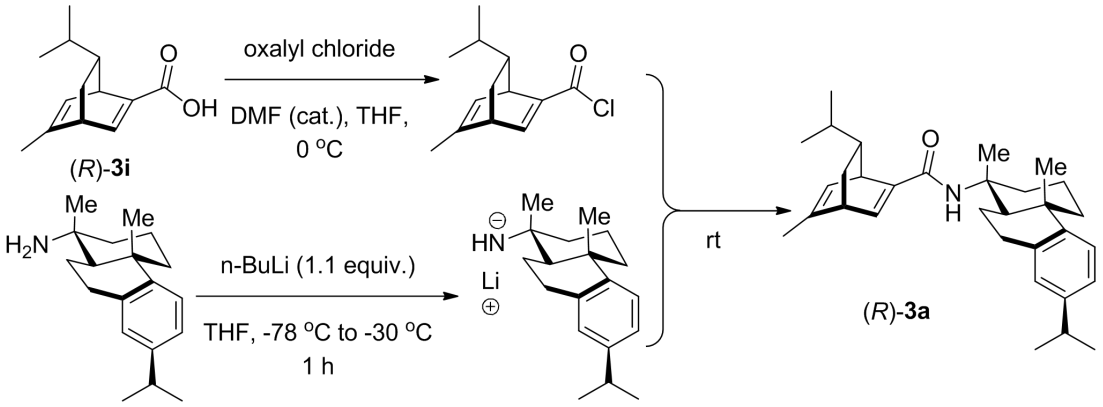


(*R*)-**3i**　　(*R*)-**3a**

To a solution of (*R*)-**3i** (1.4 g, 6.8 mmol), EDCI (1.43 g, 7.48 mmol), and Et_3N (1.88 mL, 13.6 mmol) in anhydrous CH_2Cl_2 (40 mL) at room temperature was added 1-hydroxybenzotriazole (HOBt) (1.28 g, 9.52 mmol) in one portion, and the reaction was stirred at room temperature for 5 h under nitrogen protection. Then dehydroabietic decarbonyl amine (1.84 g, 6.8 mmol) in CH_2Cl_2 (5 mL) solution was added. The reaction was stirred at room temperature overnight, then diluted with brine and the mixture was extracted with EtOAc. The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by flash chromatograph on silica gel (3.5 cm × 14 cm, eluted with petroleum ether/ethyl acetate = 100:1 then 50:1, R_f (EtOAc/petroleum ether (1:10) = 0.57)) gave the product. Further purification by recrystalization in *n*-hexane/CH_2Cl_2 gave the pure product as amorphous white solid (0.56 g, 18%); m.p. 81.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (d, J = 6 Hz, 3 H), 0.92-0.97 (m, 1 H), 1.00 (d, J = 6 Hz, 3 H), 1.06-1.13 (m, 1 H), 1.211 (s, 3 H), 1.214 (s, 3 H), 1.23 (s, 3 H), 1.38 (s, 3 H), 1.47-1.53 (m, 1 H), 1.59 (ddd, J_1 = 12 Hz, J_2 = 9 Hz, J_3 = 3 Hz, 1 H), 1.68-1.79 (m, 3 H), 1.83 (d, J = 2 Hz, 3 H), 1.84-1.86 (m, 1 H), 2.00-2.08 (m, 1 H), 2.13-2.16 (m, 1 H), 2.23-2.26 (m, 2 H), 2.81 (q, J = 7 Hz, 1 H), 2.86-2.92 (m, 2 H), 3.32 (m, 1 H), 3.98 (dt, J_1 = 6 Hz, J_2 = 2 Hz, 1 H), 5.41 (s, 1 H), 5.80 (d, J = 6 Hz, 1 H), 6.69 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1 H), 6.87 (s, 1 H), 6.98 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 1 H), 7.16 (d, J = 8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 19.7,

20.8, 21.5, 22.0, 24.1, 24.2, 25.1, 30.3, 32.1, 33.6, 34.0, 37.3, 37.8, 38.2, 40.2, 43.7, 47.4, 48.0, 57.5, 124.0, 124.36, 124.38, 126.9, 134.6, 136.7, 144.0, 145.8, 146.7, 146.8, 165.6; FT-IR (KBr) $\bar{\upsilon}$ *2*958, 1638, 1609, 1519, 1463, 1380, 1035, 814 cm^{-1}; HRMS (ESI^+) m/z calcd for $C_{32}H_{46}NO$ $[M+H]^+$ 460.3574 found 460.3568, $[\alpha]^{25}_D$ = +33.45 (c 3, CH_2Cl_2).

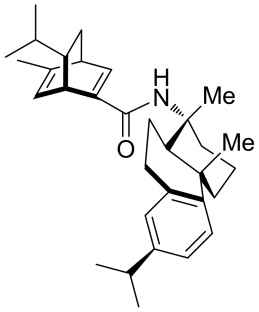
Procedure B:



To a solution of (*R*)-**3i** (1.4 g, 6.8 mmol), and DMF (1-2 drops) in anhydrous THF (40 mL) at 0 ℃ was added oxalyl chloride (0.86 mL, 10.2 mmol) dropwise over 2 min. The mixture was stirred at 0 ℃ for 3 h to give a solution of the corresponding acyl chloride.

To another flamed-dried 50 mL Schlenk-flask was charged dehydroabietic decarbonyl amine (1.84 g, 6.8 mmol) in anhydrous THF (20 mL) solution at -78 ℃, followed by *n*-BuLi (7.5 mmol) dropwise addition under nitrogen atmosphere. It was warmed up to -30 ℃ and stirred for 1 hours to form lithium dehydroabietyl amide, followed cannula transfer into dienyl acyl chloride solution at 0 ℃. It was stirred at room temperature overnight and quenched by saturated aqueous NH_4Cl solution. Remove THF in rotovap and the mixture was extracted with EtOAc three times. The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by flash chromatograph on silica gel gave amorphous white solid as the corresponding amidation product (0.78 g, 25%).

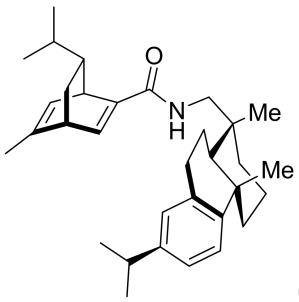
(1*S*,4*S*,7*S*)-7-Isopropyl-*N*-((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide



(*S*)-**3g**

Prepared according to procedure A from (*S*)-**3i** (0.26 g, 1 mmol) and deydroabietic decarbonyl amine (0.27 g, 1 mmol); silica gel purification (2 cm × 14 cm, petroleum ether/ethyl acetate = 100:1 then 50:1, R_f = 0.48 (EtOAc/PE = 1:10)) gave the product as viscous beige oil (0.114 g, 25%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (d, J = 6 Hz, 3 H), 0.86-0.88 (m, 1 H), 0.95-0.96 (m, 1 H), 1.00 (d, J = 6 Hz, 3 H), 1.05-1.12 (m, 1 H), 1.21 (s, 6 H), 1.23 (s, 3 H), 1.37 (s, 3 H), 1.47-1.52 (m, 1 H), 1.59 (ddd, J_1 = 12 Hz, J_2 = 9 Hz, J_3 = 3 Hz, 1 H), 1.72-1.74 (m, 2 H), 1.82 (d, J = 1 Hz, 3 H), 1.84-1.85 (m, 1 H), 2.04-2.11 (m, 3 H), 2.25 (dd, J_1 = 12 Hz, J_2 = 3 Hz, 2 H), 2.81 (q, J = 7 Hz, 1 H), 2.88-2.92 (m, 1 H), 3.30-3.32 (m, 1 H), 3.96 (dt, J_1 = 6 Hz, J_2 = 2 Hz, 1 H), 5.41 (s, 1 H), 5.80 (d, J = 6 Hz, 1 H), 6.68 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1 H), 6.87 (s, 1 H), 6.98 (d, J_1 = 8 Hz, J_2 = 1 Hz, 1 H), 7.16 (d, J = 8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.16, 19.19, 19.7, 20.9, 21.5, 22.0, 24.1, 24.2, 25.1, 30.2, 32.1, 33.6, 34.0, 37.3, 37.8, 38.2, 40.3, 43.7, 47.3, 48.0, 57.5, 124.0, 124.3, 124.4, 126.9, 134.6, 136.5, 144.1, 145.8, 146.7, 146.8, 165.6; FT-IR (KBr) $\bar{\upsilon}$ 2964, 1638, 1506, 1381, 1138, 1094, 882, 814 cm^{-1}; HRMS (ESI$^+$) m/z calcd for $C_{32}H_{46}NO$ $[M+H]^+$ 460.3574 found 460.3569. $[\alpha]^{25}_D$ = + 19.53 (c 1, CH_2Cl_2).

(1*R*,4*R*,7*R*)-7-Isopropyl-*N*-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide

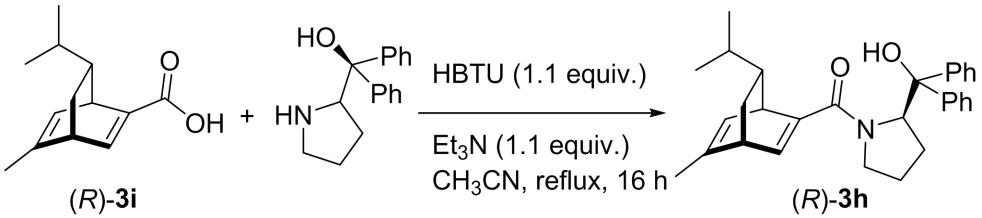


(*R*)-**3f**

Prepared according to procedure A from (*R*)-**3i** (0.082 g, 0.4 mmol) and dehydroabietyl amine (0.114 g, 0.4 mmol); silica gel purification (2 cm × 14 cm, petroleum ether/ethyl acetate = 100:1 then 50:1, R_f = 0.50 (EtOAc/PE = 1:10)) gave the product as colorless oil (0.066 g, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (d, J = 6 Hz, 3 H), 0.88-0.93 (m, 1 H), 0.95 (s, 3 H), 0.96 (s, 3 H), 0.98 (s, 3 H), 1.04-1.13 (m, 1 H), 1.15-1.19 (m, 1 H), 1.22 (s, 6 H), 1.24 (s, 3 H), 1.33-1.37 (m, 1 H), 1.42-1.45 (m, 2 H), 1.55 (ddd, J_1 = 12

Hz, J_2 = 9 Hz, J_3 = 3 Hz, 1 H), 1.64-1.77 (m, 4 H), 1.81 (d, J = 1 Hz, 3 H), 1.87-1.93 (m, 1 H), 2.27-2.30 (m, 1 H), 2.77-2.87 (m, 2 H), 2.93 (dd, J_1 = 17 Hz, J_2 = 6 Hz, 1 H), 3.16 (dd, J_1 = 14 Hz, J_2 = 6 Hz, 1 H), 3.25-3.32 (m, 2 H), 4.01 (dt, J_1 = 4 Hz, J_2 = 2 Hz, 1 H), 5.67 (t, J = 6 Hz, 1 H), 5.79 (d, J = 6 Hz, 1 H), 6.74 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1 H), 6.90 (s, 1 H), 7.00 (d, J = 8 Hz, 1 H), 7.18 (d, J = 8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.76, 18.83, 19.1, 21.5, 21.9, 24.09, 24.11, 25.5, 30.5, 31.9, 33.6, 33.9, 36.4, 37.67, 37.71, 38.5, 40.3, 43.7, 45.9, 48.0, 49.9, 124.0, 124.2, 124.4, 127.0, 134.9, 137.5, 144.0, 145.3, 145.7, 147.3, 166.3; FT-IR (KBr) $\bar{\upsilon}$ 2958, 2920, 1637, 1608, 1534, 1455, 1378, 1092, 1049, 882 cm^{-1}; HRMS (ESI$^+$) m/z calcd for $C_{33}H_{48}NO$ $[M+H]^+$ 474.3730 found 474.3727, $[\alpha]^{25}_D$ = + 3.07 (c 2, CH_2Cl_2).

((*R*)-2-(Hydroxydiphenylmethyl)pyrrolidin-1-yl)((1*R*,4*R*,7*R*)-7-isopropyl-5-methyl bicyclo[2.2.2]octa-2,5-dien-2-yl)methanone ((*R*)-3h)

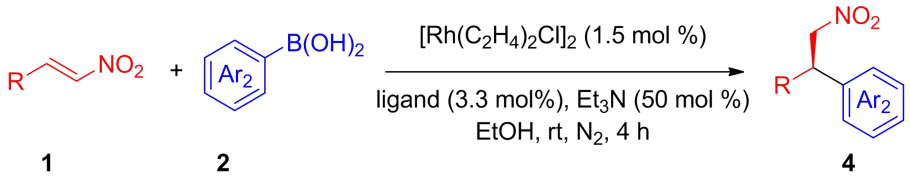


(*R*)-**3i** (*R*)-**3h**

Procedure C:

To a solution of the carboxylic acid (*R*)-**3i** (83 mg, 0.40 mmol) and HBTU (167 mg, 0.44 mmol) in MeCN (8 mL) at room temperature was added Et_3N (70 µL, 0.44 mmol) followed by (*R*)-(+)-2-(diphenylhydroxymethyl)pyrrolidine (84 mg, 0.33 mmol). The mixture was heated at reflux for 16 h, cooled to room temperature, quenched with brine (8 mL), and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with HCl (2.0 M in H_2O, 30 mL), saturated aqueous $NaHCO_3$ solution (30 mL), and brine (30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:40) gave the amide (*R*)-**3h** (56 mg, 31%) as a colourless oil. R_f = 0.81 (EtOAc/petroleum ether = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (d, J = 6 Hz, 3 H), 0.81-0.87 (m, 2 H), 0.91 (d, J = 6 Hz, 3 H), 0.94-1.03 (m, 1 H), 1.21-1.31 (m, 2 H), 1.39-1.50 (m, 2 H), 1.72 (d, J = 1 Hz, 3 H), 1.77-1.86 (m, 1 H), 1.98-2.07 (m, 1 H), 2.56 (dq, J_1 = 10 Hz, J_2 = 3 Hz, 1 H), 3.20 (dt, J_1 = 6 Hz, J_2 = 2 Hz, 1 H), 3.28 (td, J_1 = 10 Hz, J_2 = 3 Hz, 1 H), 3.67 (dt, J_1 = 6 Hz, J_2 = 2 Hz, 1 H), 5.18 (t, J = 8 Hz, 1 H), 5.65 (d, J = 6 Hz, 1 H), 6.15 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1 H), 7.18-7.19 (m, 1H), 7.21-7.27 (m, 5 H), 7.34-7.37 (m, 2 H), 7.42 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 19.3, 21.4, 22.0, 24.4, 29.7, 32.1, 34.1, 42.0, 43.7, 48.3, 51.2, 67.1, 82.6, 124.0, 127.2, 127.36, 127.38, 128.0, 128.3, 138.5, 143.2, 144.5, 144.6, 145.7, 172.2; FT-IR (KBr) $\bar{\upsilon}$ 3238, 2959, 2935, 2909, 2889, 2869, 1578, 1428, 1445, 1253, 1121, 1036, 874, 764 cm^{-1}; HRMS (ESI$^+$) m/z calcd for $C_{30}H_{36}NO_2$ $[M+H]^+$ 442.2741 found 442.2751; $[\alpha]^{25}_D$ = +57.4 (c 1.5, CH_2Cl_2).

Rhodium catalyzed asymmetric 1,4-arylation to nitroolefins



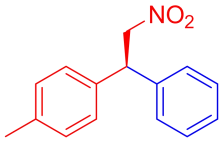
1 2 4

Procedure D:

To an oven-dried 10 mL Schlenk tube was charged $[Rh(C_2H_4)_2Cl]_2$ (2.1 mg, 1.5 mol %), (*R*)-**3a** (5.5 mg, 3.3 mol %) in EtOH (2 mL) solution. The mixture was stirred at rt under nitrogen protection for 15 min to form Rh((*R*)-**3a**)OEt complex, then transferred to another solution of nitroalkene (0.36 mmol) and aryl boronic acid (0.9 mmol) in EtOH (2 mL) *via* syringe. This was followed by Et_3N (0.18 mmol) injection. The mixture was stirred at rt for 4 h. Upon completion monitored by TLC, removed EtOH in *vacuo* and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as an eluent to give the titled compound.

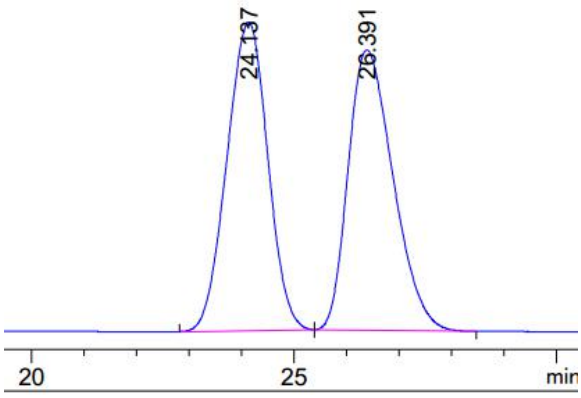
Procedure E:

To an oven-dried 10 mL Schlenk tube was charged $[Rh(C_2H_4)_2Cl]_2$ (2.1 mg, 1.5 mol %), (*R*)-**3a** (5.5 mg, 3.3 mol %) in EtOH (2 mL) solution. The mixture was stirred at rt under nitrogen protection for 15 min to form Rh((*R*)-**3a**)OEt complex, then transferred to another solution of nitroalkene (0.36 mmol) and aryl boronic acid (0.9 mmol) in EtOH (2 mL) *via* syringe. This was followed by Et_3N (0.18 mmol) injection. The mixture was warmed up to 50 ℃ and stirred overnight. After completion monitored by TLC, removed EtOH in *vacuo* and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as an eluent to give the titled compound.



(*S*)-1-Methyl-4-(2-nitro-1-phenylethyl)benzene ((*S*)-4a)[6a]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and phenylboronic acid (110 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:60, R_f = 0.32 (EtOAc/PE = 1:50)); yield: 90% (78 mg, slightly yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3 H), 4.85-4.89 (m, 1 H), 4.96 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 2 H), 7.13 (s, 4 H), 7.23-7.27 (m, 3 H), 7.30-7.34 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 48.7, 79.4, 127.6, 127.7, 129.1, 129.8, 136.3, 137.4, 139.5 (one carbon peak is missing because of overlapping); FT-IR (KBr) $\bar{\upsilon}$ 2924, 1556, 1458, 1376, 1261, 1090, 1048, 806, 700 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 254 nm, 1.0 mL/min. t_1 = 25.1 min (major), t_2 = 25.6 min (minor)]; ee = 91%, $[\alpha]^{25}_D$ = -0.71 (c 1.8, CH_2Cl_2).



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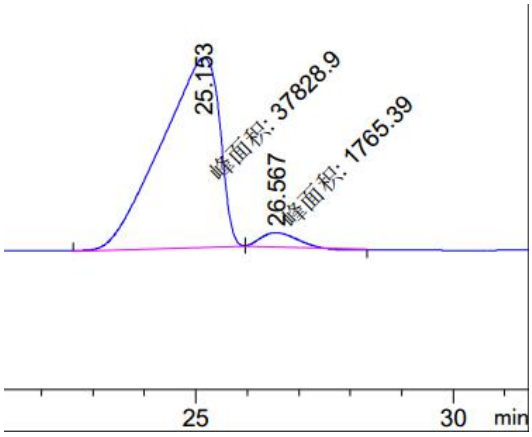

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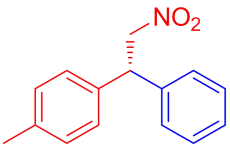
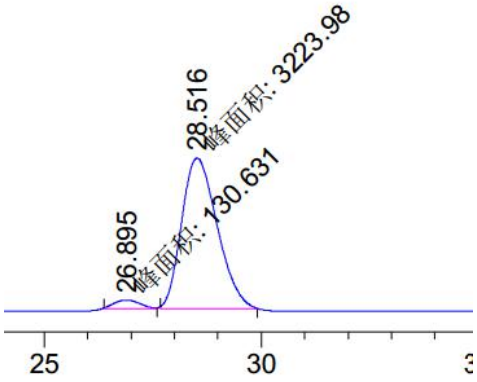


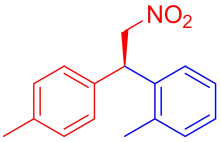
(*R*)-1-Methyl-4-(2-nitro-1-phenylethyl)benzene ((*R*)-4a)

When employing (*S*)-**3a**, yield: 86% (74 mg); HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 80/20, 254 nm, 1.0 mL/min. t_1 = 26.9 min (minor), t_2 = 28.5 min (major)]; ee = -92%, $[\alpha]^{25}_D$ = + 1.87 (c 4, CH_2Cl_2).



信号 1: DAD1 A, Sig=254,4 Ref=360,100

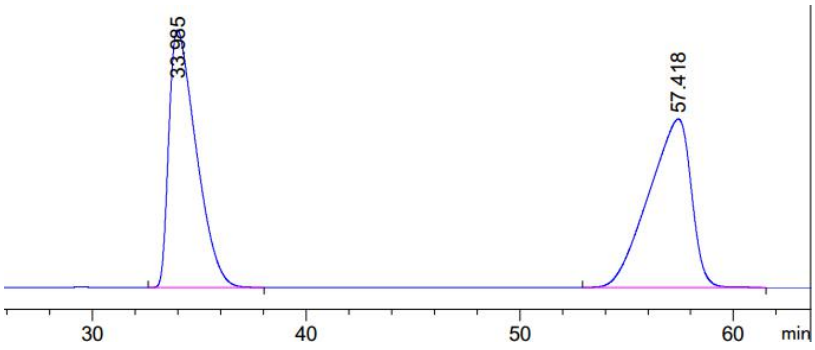
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	26.895	MM	0.6818	130.63100	3.19316	3.8941
2	28.516	MM	0.9507	3223.98291	56.51992	96.1059
总量 :				3354.61391	59.71308	



(*R*)-1-Methyl-2-(2-nitro-1-(*p*-tolyl)ethyl)benzene (4b)[6a]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and *o*-tolylboronic acid (123 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:50, R_f = 0.30 (EtOAc/PE = 1:50)); yield:

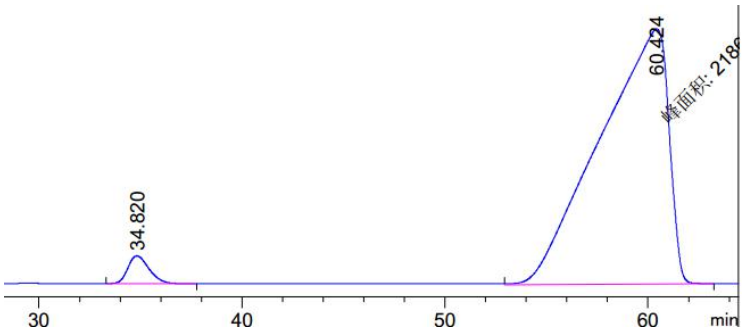
95% (87 mg, yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3 H), 2.33 (s, 3 H), 4.92 (dd, J_1 = 13 Hz, J_2 = 8 Hz, 1 H), 4.98 (dd, J_1 = 13 Hz, J_2 = 8 Hz, 1 H), 5.09 (t, J = 8 Hz, 1 H), 7.11 (dd, J_1 = 12 Hz, J_2 = 8 Hz, 4 H), 7.19 (t, J = 3 Hz, 2 H), 7.21-7.24 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 21.1, 44.8, 79.4, 125.8, 126.5, 127.5, 128.0, 129.8, 131.4, 135.8, 136.6, 137.3, 137.4; FT-IR (KBr) $\bar{\upsilon}$ 1555, 1452, 1385, 1094, 1031, 729, 685 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 90/10, 230 nm, 1 mL/min. t_1 = 34.8 min (minor), t_2 = 60.4 min (major)]; ee = 94%, $[\alpha]^{25}_D$ = -57.2 (c 3.4, CH_2Cl_2).



信号 4: DAD1 D, Sig=230,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	33.985	BB	1.3024	5.51437e4	621.93286	49.4787
2	57.418	BB	1.9258	5.63057e4	406.54495	50.5213

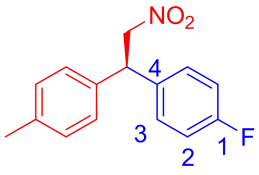
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
总量 :				1.11449e5	1028.47781	



信号 4: DAD1 D, Sig=230,4 Ref=360,100

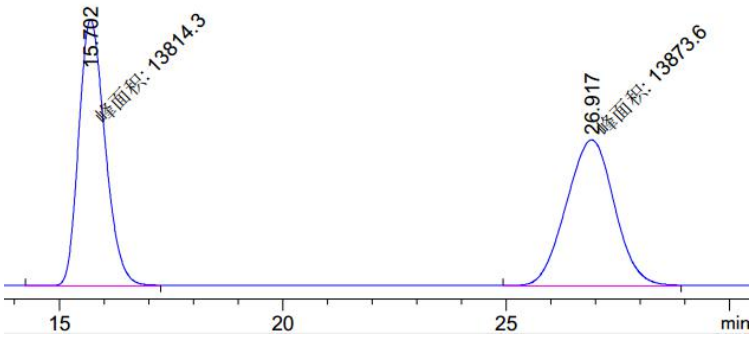
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.820	BB	1.0902	7278.39111	100.58480	3.2221
2	60.424	MM	3.9321	2.18609e5	926.61078	96.7779

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
总量 :				2.25888e5	1027.19558	



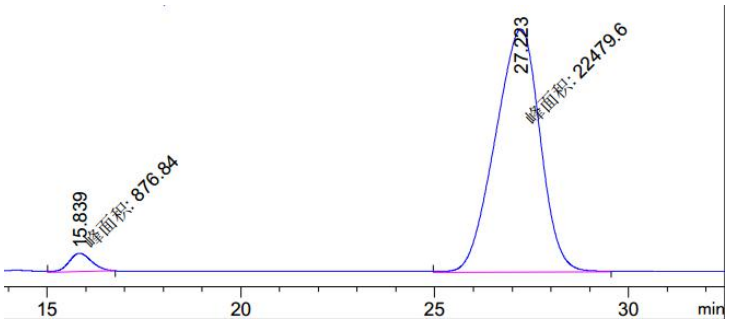
(*R*)-1-Fluoro-4-(2-nitro-1-*p*-tolylethyl)benzene (4c)[6a]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and (4-fluorophenyl)boronic acid (126 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:50, R_f = 0.33 (EtOAc/PE = 1:50)); yield: 78% (73 mg, yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 4.85-4.89 (m, 1 H), 4.95 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2 H), 6.99-7.05 (m, 2 H), 7.10-7.17 (m, 4 H), 7.19-7.24 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 48.0, 79.5, 116.0 (d, J_{CF} = 21 Hz, C^2), 127.5, 129.3 (d, J_{CF} = 8 Hz, C^3), 129.9, 135.3 (d, J_{CF} = 3 Hz, C^4), 136.1, 137.6, 162.1 (d, J_{CF} = 245 Hz, C^1); FT-IR (KBr) $\bar{\upsilon}$ 1606, 1554, 1510, 1437, 1379, 1229, 1157, 1121, 1021, 818 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 254 nm, 1.0 mL/min. t_1 = 15.8 min (minor), t_2 = 27.2 min (major)]; ee = 93%, $[\alpha]^{25}_D$ = +5.43 (c 2.1, CH_2Cl_2).



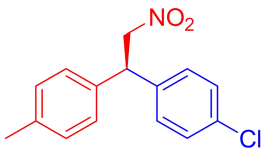
信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.702	MM	0.6847	1.38143e4	336.26801	49.8930
2	26.917	MM	1.2534	1.38736e4	184.48013	50.1070
总量：				2.76878e4	520.74814	



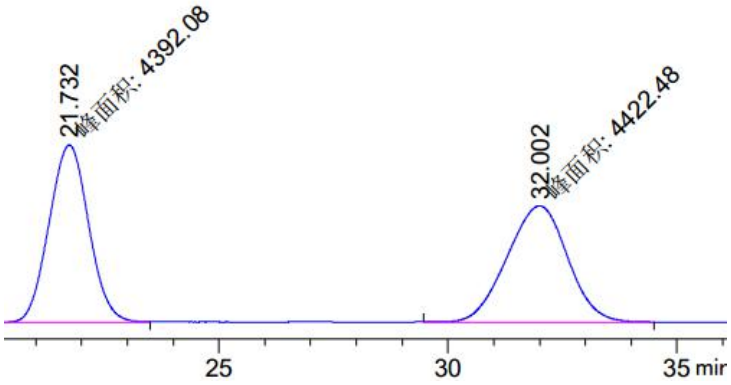
信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.839	MM	0.6859	876.83966	21.30784	3.7542
2	27.223	MM	1.3385	2.24796e4	279.91901	96.2458
总量：				2.33565e4	301.22685	



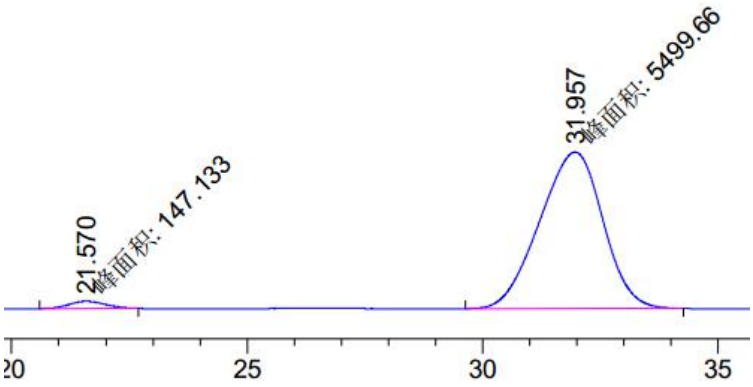
(*R*)-1-Chloro-4-(2-nitro-1-*p*-tolylethyl)benzene (4d)[6a]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and (4-chlorophenyl)boronic acid (141 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:50, R_f = 0.31 (EtOAc/PE = 1:50)); yield: 58% (42 mg, colorless oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3 H), 4.83-4.87 (m, 1 H), 4.94 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 2 H), 7.08-7.11 (m, 2 H), 7.14-7.19 (m, 4 H), 7.29-7.32 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 48.1, 79.2, 127.5, 129.1, 129.3, 129.9, 133.6, 135.8, 137.7, 138.0; FT-IR (KBr) $\bar{\upsilon}$ 1554, 1491, 1435, 1378, 1123, 816, 730, 553 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 280 nm, 1.0 mL/min. t_1 = 21.6 min (minor), t_2 = 31.9 min (major)]; ee = 95%, $[\alpha]^{25}_D$ = -1.6 (c 1, CH_2Cl_2).



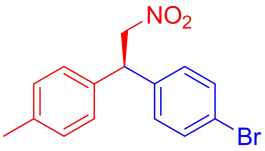
信号 2: DAD1 B, Sig=280,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.732	MM	1.0031	4392.08203	72.97330	49.8275
2	32.002	MM	1.5395	4422.48486	47.87780	50.1725
总量 :				8814.56689	120.85111	



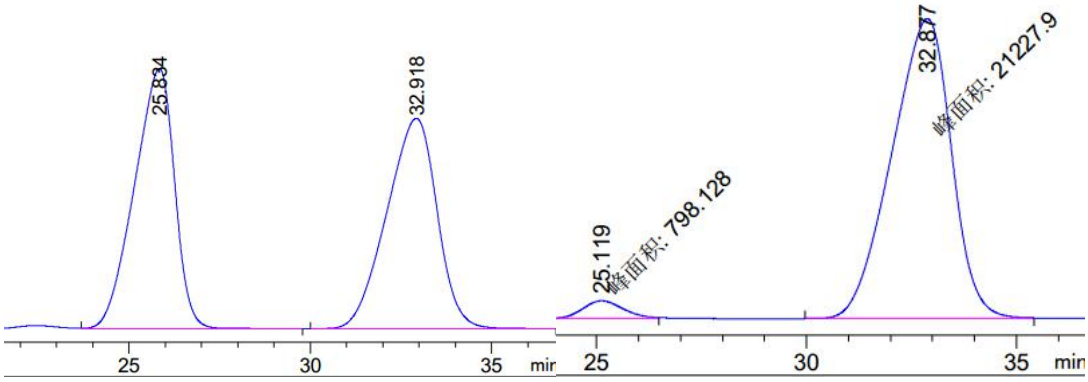
信号 2: DAD1 B, Sig=280,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.570	MM	0.8998	147.13269	2.72525	2.6056
2	31.957	MM	1.5598	5499.65820	58.76612	97.3944
总量 :				5646.79089	61.49137	



(*R*)-1-Bromo-4-(2-nitro-1-(*p*-tolyl)ethyl)benzene (4e)[6b]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and (4-bromophenyl)boronic acid (181 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:60, R_f = 0.30 (EtOAc/PE = 1:50)); yield: 83% (95 mg, colourless transparent crystal); m.p. 70.4 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 4.83-4.86 (m, 1 H), 4.95 (d, J = 8 Hz, 2 H), 7.10-7.12 (m, 3 H), 7.14-7.17 (m, 3 H), 7.45-7.47 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 48.1, 79.1, 121.6, 127.5, 129.4, 129.9, 132.2, 135.7, 137.7, 138.6; FT-IR (KBr) $\bar{\upsilon}$ 1514, 1552, 1487, 1433, 1375, 1262, 1074, 1012, 809 cm^{-1}; EI-MS m/z (%) 319.0 (M^+, 1.10), 272.0 (100.00), 256.9 (14.00), 193.0 (31.58), 178.0 (57.9), 165.0 (23.1); HRMS (EI^+) m/z calcd for $C_{15}H_{13}Br$ $[M\text{-}HNO_2]^+$ 272.0201 found 272.0197; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 254 nm, 1.0 mL/min. t_1 = 25.1 min (minor), t_2 = 32.9 min (major)]; ee = 93%, $[\alpha]^{25}_D$ = -2.37 (c 1.8, CH_2Cl_2).

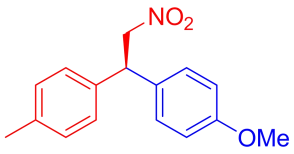


信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.834	VB	1.1898	1.90644e4	247.72464	49.6654
2	32.918	BBA	1.5059	1.93213e4	200.21440	50.3346
总量 :				3.83857e4	447.93904	

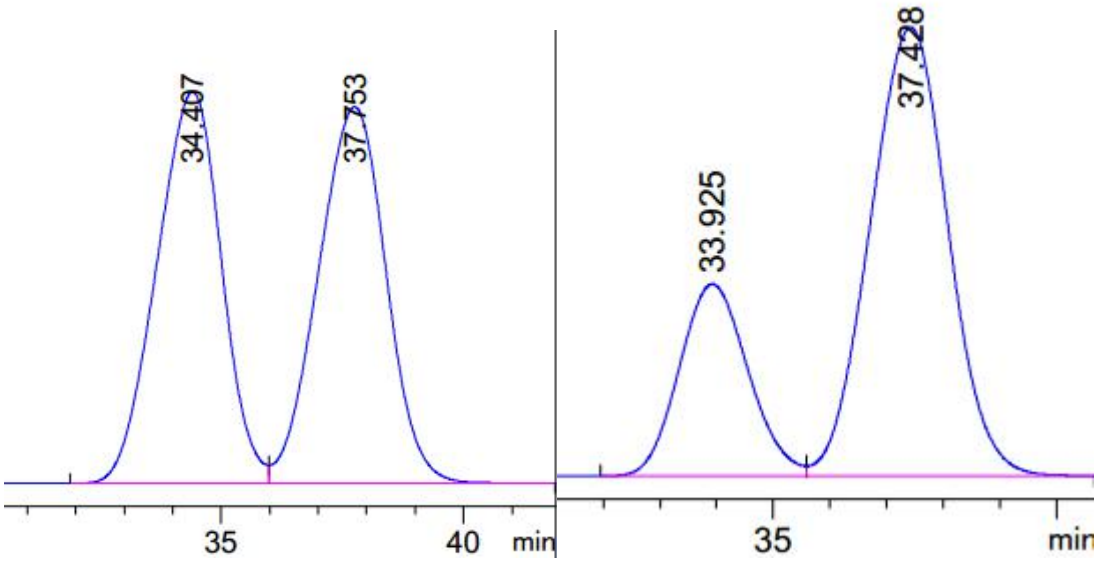
信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.119	MM	1.0771	798.12848	12.35017	3.6236
2	32.877	MM	1.6393	2.12279e4	215.82893	96.3764
总量 :				2.20260e4	228.17911	



(*R*)-1-Methoxy-4-(2-nitro-1-(*p*-tolyl)ethyl)benzene (4f)[6a]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and (4-methoxyphenyl)boronic acid (137 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:50, R_f = 0.24 (EtOAc/PE = 1:50)); yield: 99% (97 mg, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3 H), 3.78 (s, 3 H), 4.85 (t, J = 7 Hz, 1 H), 4.94 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2 H), 6.86-6.88 (m, 2 H), 7.12-7.17 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 48.0, 55.4, 79.7, 114.4, 127.5, 128.8, 129.8, 131.5, 136.6, 137.3, 158.9; FT-IR (KBr) $\tilde{\upsilon}$ 1610, 1552, 1511, 1437, 1378, 1252, 1180, 1135, 1091, 1043, 880, 812 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 254 nm, 1.0 mL/min. t_1 = 33.9 min (minor), t_2 = 37.4 min (major)]; ee = 46%, $[\alpha]^{25}_D$ = +8.0 (c 3.4, CH_2Cl_2).

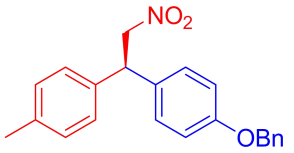


信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.407	BV	1.4511	1.02310e4	110.20859	49.8463
2	37.753	VB	1.5301	1.02941e4	105.90062	50.1537
总量 :				2.05251e4	216.10921	

信号 1: DAD1 A, Sig=254,4 Ref=360,100

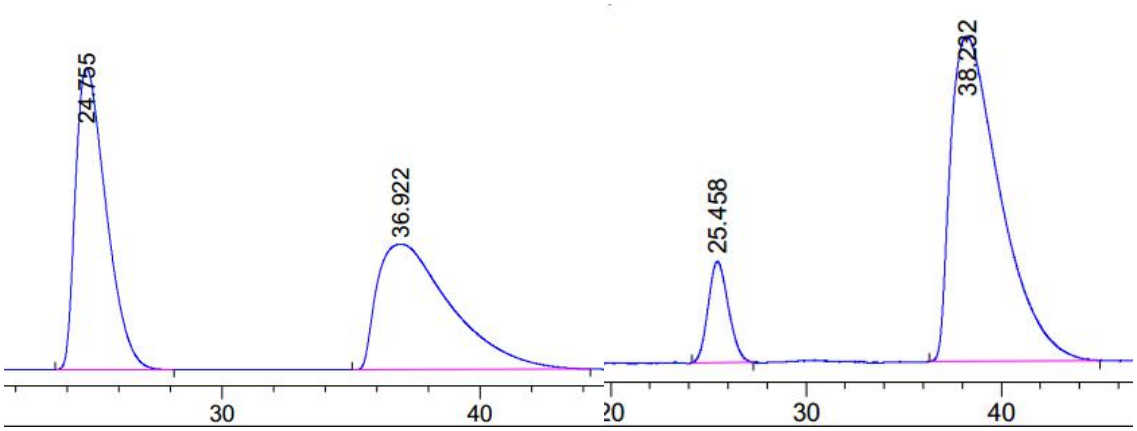
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	33.925	BV	1.3065	3067.05859	36.27033	27.4164
2	37.428	VBA	1.4811	8119.88330	84.80549	72.5836
总量 :				1.11869e4	121.07582	



(*R*)-1-(Benzyloxy)-4-(2-nitro-1-(*p*-tolyl)ethyl)benzene (4g)

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and (4-(benzyloxy)phenyl)boronic acid (205 mg, 0.9 mmol); silica gel

purification (2 cm × 15 cm, ethyl acetate/petroleum ether = 1:50, R_f = 0.31 (EtOAc/PE = 1:20)); yield: 98% (117 mg, white solid); m.p. 73.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3 H), 4.85 (t, J = 8 Hz, 1 H), 4.95 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2 H), 5.05 (s, 2 H), 6.96 (d, J = 9 Hz, 2 H), 7.13-7.19 (m, 6 H), 7.34-7.38 (m, 1 H), 7.40-7.46 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 48.0, 70.1, 79.6, 115.3, 127.49, 127.53, 128.1, 128.7, 128.8, 129.7, 131.8, 136.5, 136.9, 137.3, 158.1; FT-IR (KBr) $\bar{\upsilon}$ 2981, 2870, 1609, 1551, 1509, 1379, 1245, 1136, 1022, 810, 736 cm^{-1}; EI-MS m/z (%) 313.2 (38.50), 300.1 (1.32), 281.0 (19.23), 207.0 (30.77), 91.0 (100); HRMS (EI$^+$) m/z calcd for $C_{20}H_{20}O$ $[M\text{-}HNO_2]^+$ 300.1514 found 300.1506; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 50/50, 254 nm, 1 mL/min. t_1 = 25.5 min (minor), t_2 = 38.2 min (major)]; ee = 77%, $[\alpha]^{25}_D$ = +6.24 (c 2.5, CH_2Cl_2).

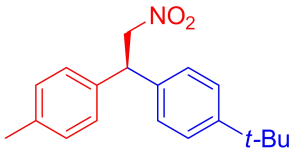


信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.755	BB	1.2569	7655.16650	92.74763	49.9591
2	36.922	BB	2.3275	7667.71436	38.63378	50.0409
总量：				1.53229e4	131.38141	

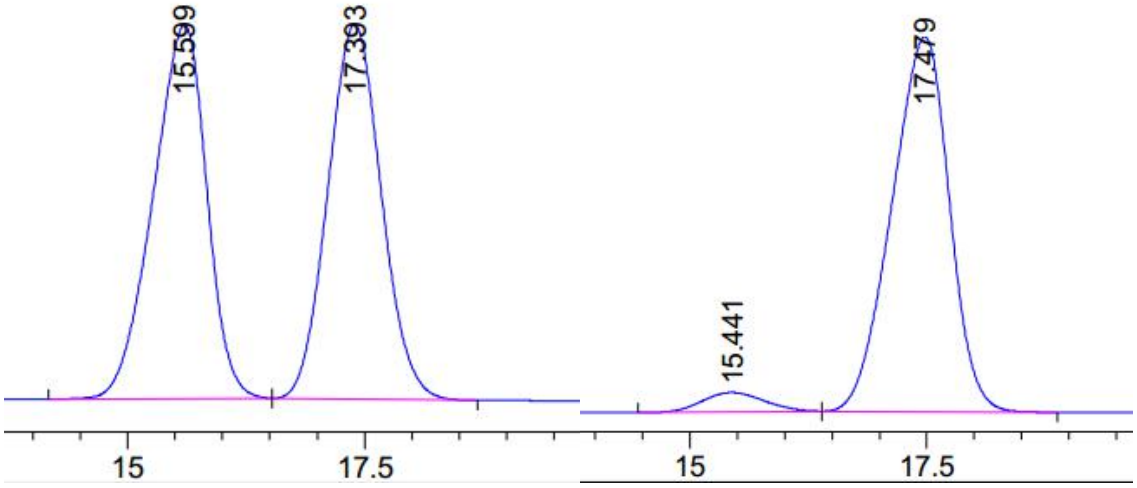
信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.458	BB	0.8724	376.16946	5.19748	11.3150
2	38.232	BB	2.0708	2948.35620	16.69134	88.6850
总量：				3324.52567	21.88882	



(*R*)-1-(*tert*-Butyl)-4-(2-nitro-1-(*p*-tolyl)ethyl)benzene (4h)[6a]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and (4-(*tert*-butyl)phenyl)boronic acid (160 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:50, R_f = 0.28 (EtOAc/PE = 1:50)); yield: 64% (68 mg, white crystal); m.p. 78.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9 H), 2.32 (s, 3 H), 4.83-4.87 (m, 1 H), 4.97 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 2 H), 7.13-7.18 (m, 6 H), 7.32-7.35 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 31.4, 34.6, 48.4, 79.5, 126.0, 127.3, 127.6, 129.8, 136.46, 136.50, 137.3, 150.5; FT-IR (KBr) $\bar{\upsilon}$ 3392, 2967, 1650, 1555, 1513, 1435, 1376, 1091, 1049, 879, 816, 715, 666 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 80/20, 254 nm, 1.0 mL/min. t_1 = 15.4 min (minor), t_2 = 17.5 min (major)]; ee = 90%, $[\alpha]^{25}_D$ = -2.48 (c 1.8, CH_2Cl_2).

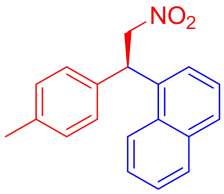


信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.599	BB	0.6082	3190.44385	80.87649	50.0613
2	17.393	BB	0.6084	3182.62427	81.00124	49.9387
总量：				6373.06812	161.87772	

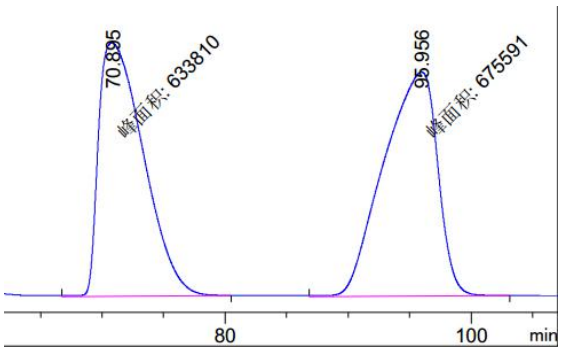
信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.441	BB	0.6720	455.57138	10.06675	5.2112
2	17.479	BB	0.6592	8286.64648	196.03038	94.7888
总量：				8742.21786	206.09713	



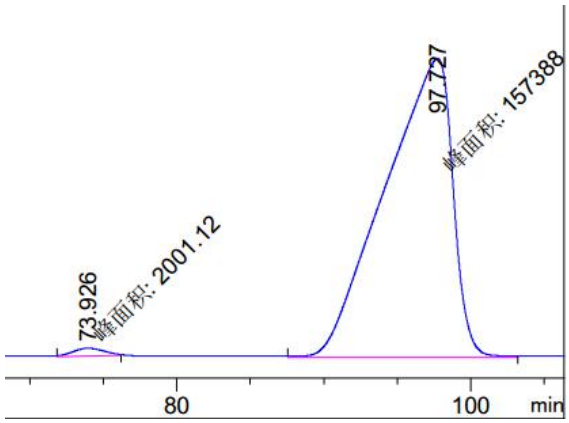
(*R*)-1-(2-Nitro-1-*p*-tolylethyl)naphthalene (4i)[6a]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and naphthalen-1-ylboronic acid (155 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:100, R_f = 0.28 (EtOAc/PE = 1:50)); yield: 93% (102 mg, yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 5.06 (dd, J_1 = 13 Hz, J_2 = 9 Hz, 1H), 5.13 (dd, J_1 = 13 Hz, J_2 = 7 Hz, 1 H), 5.76 (t, J = 8 Hz, 1 H), 7.15 (d, J = 8 Hz, 2 H), 7.24 (d, J = 8 Hz, 2 H), 7.39 (d, J = 7 Hz, 1 H), 7.47-7.58 (m, 3 H), 7.84 (d, J = 8 Hz, 1 H), 7.90 (d, J = 8 Hz, 1 H), 8.17 (d, J = 8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 44.4, 79.2, 123.1, 124.2, 125.3, 126.0, 126.9, 127.9, 128.5, 129.2, 129.8, 131.2, 134.3, 134.9, 136.0, 137.4; FT-IR (KBr) $\bar{\upsilon}$ 3050, 2971, 2923, 2859, 1553, 1513, 1436, 1377, 1113, 780 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 90/10, 254 nm, 1.0 mL/min. t_1 = 73.9 min (minor), t_2 = 97.7 min (major)]; ee = 98%, $[\alpha]^{25}_D$ = -14.42 (c 6, CH_2Cl_2).



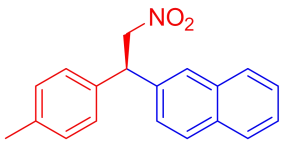
信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	70.775	MM	3.6275	9.57056e4	439.72415	49.6958
2	95.967	MM	4.5739	9.68771e4	353.00354	50.3042
总量 :				1.92583e5	792.72769	



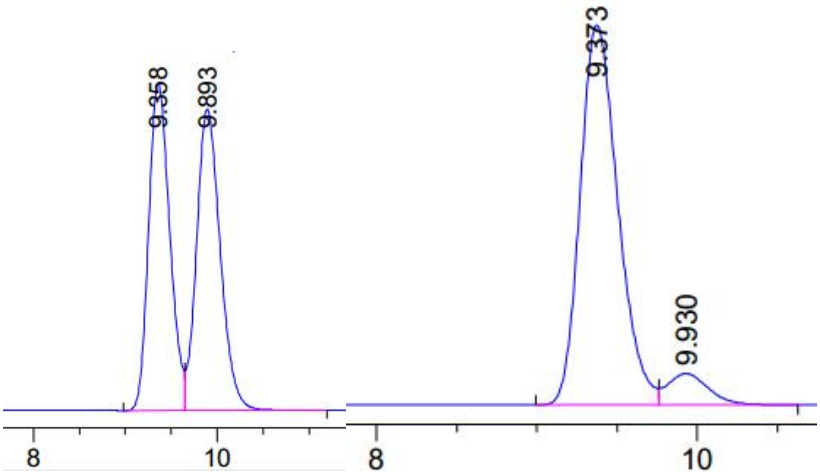
信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	73.926	MM	2.5331	2001.11572	13.16626	1.2555
2	97.727	MM	5.3398	1.57388e5	491.23892	98.7445
总量 :				1.59389e5	504.40519	



(*R*)-2-(2-Nitro-1-(*p*-tolyl)ethyl)naphthalene (4j)[6a]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and naphthalen-2-ylboronic acid (155 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:100, R_f = 0.36 (EtOAc/PE = 1:50)); yield: 91% (96 mg, yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3 H), 5.03-5.12 (m, 3 H), 7.15-7.20 (m, 4 H), 7.34 (dd, J_1 = 9 Hz, J_2 = 2 Hz, 1 H), 7.46-7.53 (m, 2 H), 7.71 (s, 1 H), 7.80-7.83 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 48.8, 79.4, 126.0, 126.1, 126.3, 126.6, 127.8, 128.0, 129.0, 129.9, 132.7, 133.5, 136.2, 137.0, 137.5 (one carbon is missing due to overlapping); FT-IR (KBr) $\bar{\upsilon}$ 2925, 2859, 1636, 1555, 1458, 1378, 1121, 816, 749 cm^{-1}; HPLC [Daicel Chiralpak AS-H, hexane/*i*-PrOH = 80/20, 254 nm, 1.0 mL/min. t_1 = 9.4 min (major), t_2 = 9.9 min (minor)]; ee = 84%, $[\alpha]^{25}_D$ = -22.48 (c 2.2, CH_2Cl_2).

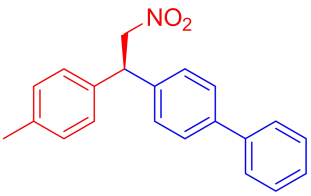


信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.358	BV	0.2457	5425.47754	340.88852	49.0721
2	9.893	VB	0.2753	5630.66211	313.92142	50.9279
总量 :				1.10561e4	654.80994	

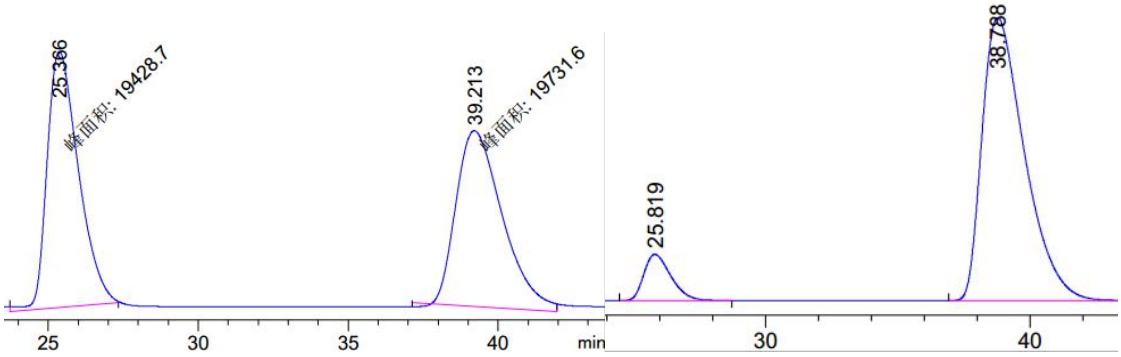
信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.373	BV	0.2528	6094.47314	372.63235	91.9000
2	9.930	VB	0.2646	537.16309	30.62756	8.1000
总量 :				6631.63623	403.25992	



(*R*)-4-(2-Nitro-1-*p*-tolylethyl)biphenyl (4k)[6a]

Prepared according to procedure D from (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and 4-biphenylboronic acid (124 mg, 0.625 mmol); silica gel purification (2 cm × 15 cm, ethyl acetate/petroleum ether = 1:100, R_f = 0.25 (EtOAc/PE = 1:50)); yield: 93% (79 mg, white solid): m.p. 80.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3 H), 4.91-4.95 (m, 1 H), 5.01 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2 H), 7.15-7.20 (m, 4 H), 7.31-7.33 (m, 2 H), 7.35-7.37 (m, 1 H), 7.44 (dt, J_1 = 7 Hz, J_2 = 2 Hz, 2 H), 7.56 (d, J = 8 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 48.5, 79.4, 127.2, 127.6, 127.7, 127.8, 128.1, 128.9, 129.9, 136.3, 137.5, 138.6, 140.57, 140.59; FT-IR (KBr) $\tilde{\nu}$ 1551, 1514, 1487, 1438, 1376, 817, 730, 693 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 230 nm, 0.8 mL/min. t_1 = 25.8 min (minor), t_2 = 38.8 min (major)]; ee = 81%, $[\alpha]^{25}_D$ = -1.36 (c 2.4, CH_2Cl_2).

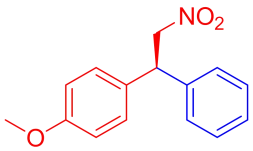


信号 4: DAD1 D, Sig=230,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.366	MM	1.2140	1.94287e4	266.73453	49.6134
2	39.213	MM	1.7955	1.97316e4	183.15643	50.3866
总量 :				3.91603e4	449.89096	

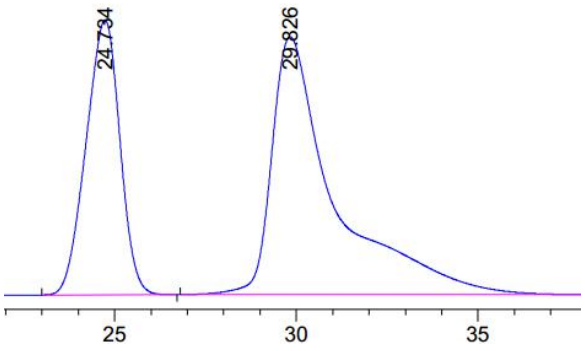
信号 4: DAD1 D, Sig=230,4 Ref=360,100

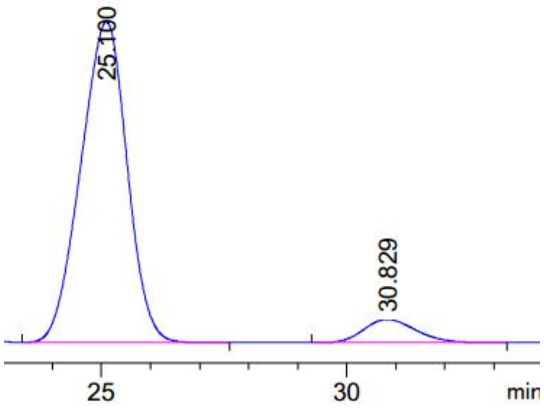
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.819	BB	1.0795	7582.95996	106.91373	9.4059
2	38.788	BB	1.6823	7.30363e4	654.30542	90.5941
总量：				8.06193e4	761.21915	



(*S*)-1-Methoxy-4-(2-nitro-1-phenylethyl)benzene (4l)[6c,6d]

Prepared according to procedure D from (*E*)-1-methoxy-4-(2-nitrovinyl)benzene (65 mg, 0.36 mmol) and phenylboronic acid (110 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:50, R_f = 0.23 (EtOAc/PE = 1:50)); yield: 97% (90 mg, colorless oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3 H), 4.82-4.86 (m, 1 H), 4.92 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2 H), 6.82-6.85 (m, 2 H), 7.12-7.15 (m, 2 H), 7.20-7.25 (m, 3 H), 7.28-7.32 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.3, 55.3, 79.5, 114.5, 127.57, 127.64, 128.8, 129.1, 131.3, 139.6, 159.0; FT-IR (KBr) $\bar{\upsilon}$ 1610, 1553, 1512, 1455, 1378, 1303, 1252, 1181, 1137, 1033, 829, 700 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 254 nm, 1.0 mL/min. t_1 = 25.1 min (major), t_2 = 30.8 min (minor)]; ee = 85%, $[\alpha]^{25}_D$ = -8.21 (c 5.5, CH_2Cl_2).



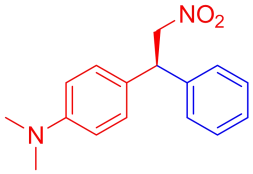


信号 2: DAD1 B, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.734	BB	1.0004	1.53580e4	236.86832	36.3772
2	29.826	BB	1.6957	2.68607e4	222.29951	63.6228
总量：				4.22187e4	459.16783	

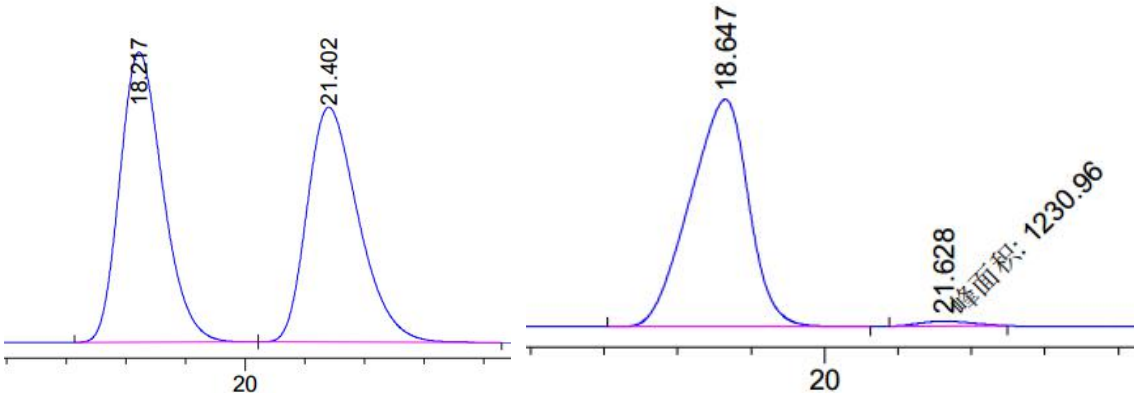
信号 2: DAD1 B, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.100	VB	1.0227	1.43831e4	218.87488	92.4525
2	30.829	BB	1.1124	1174.18201	15.92070	7.5475
总量：				1.55573e4	234.79558	



(*S*)-*N*,*N*-Dimethyl-4-(2-nitro-1-phenylethyl)aniline (4m)[6c]

Prepared according to procedure E from (*E*)-N,N-dimethyl-4-(2-nitrovinyl)aniline (69 mg, 0.36 mmol) and phenyl boronic acid (110 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:20, R_f = 0.5 (EtOAc/PE = 1:5)); yield: 52% (50 mg, yellow oil); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.91 (s, 6 H), 4.81 (t, J = 8 Hz, 1 H), 4.90-4.98 (m, 2 H), 6.66-6.67 (m, 2 H), 7.08-7.10 (m, 2 H), 7.23-7.25 (m, 3 H), 7.29-7.32 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 40.6, 48.3, 79.7, 112.8, 126.7, 127.4, 127.7, 128.5, 129.0, 129.4, 140.1, 149.9; FT-IR (KBr) $\bar{\upsilon}$ 2926, 2868, 1613, 1521, 1552, 1450, 1379, 1137, 813, 699 cm^{-1}; HRMS (ESI$^+$) m/z calcd for $C_{16}H_{19}N_2O_2$ $[M+H]^+$ 271.1441 found 271.1437; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 280 nm, 1.0 mL/min. t_1 = 18.6 min (major), t_2 = 21.6 min (minor)]; ee = 96 %, $[\alpha]^{25}_D$ = -13.0 (c 1.2, CH_2Cl_2).

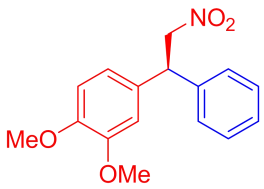


信号 2: DAD1 B, Sig=280,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.217	BB	0.7815	8326.95508	165.92062	50.8510
2	21.402	BB	0.9213	8048.24805	134.26984	49.1490
总量 :				1.63752e4	300.19046	

信号 2: DAD1 B, Sig=280,4 Ref=360,100

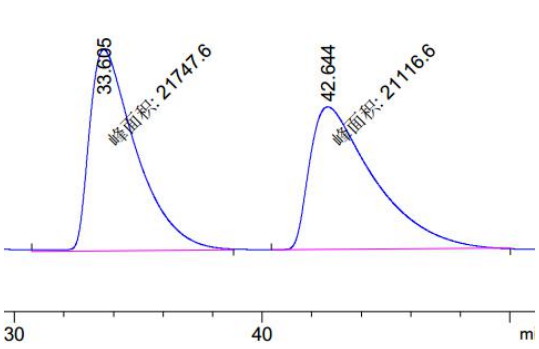
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.647	BB	0.8630	6.42521e4	1151.51550	98.1202
2	21.628	MM	0.8181	1230.95728	25.07742	1.8798
总量 :				6.54831e4	1176.59292	



(*S*)-1,2-Dimethoxy-4-(2-nitro-1-phenylethyl)benzene (4n)[6a]

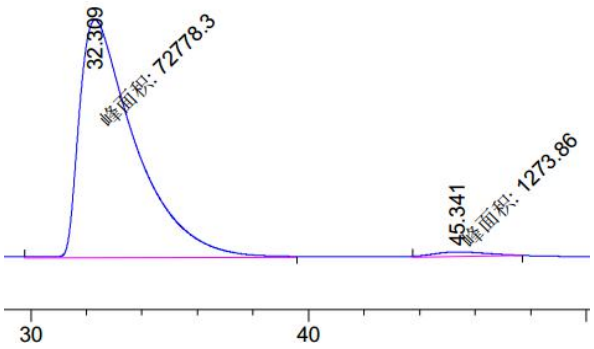
Prepared according to procedure E from (*E*)-1,2-dimethoxy-4-(2-nitrovinyl)benzene (75 mg, 0.36 mmol) and phenyl boronic acid (110 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:30, R_f = 0.29 (EtOAc/PE = 1:5)); yield: 64% (66 mg, colorless oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3 H), 3.85 (s, 3 H), 4.84-4.88 (m, 1 H), 4.96 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 2 H), 6.72 (d, J = 2 Hz, 1 H), 6.79-6.84 (m, 2 H), 7.23-7.29 (m, 3 H), 7.32-7.36 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.7, 55.99, 56.01, 79.5, 111.3, 111.5, 119.6, 127.66, 127. 69, 129.1, 131.7, 139.5, 148.6, 149.4; FT-IR (KBr) ν 2931, 2844, 1551, 1515, 1454, 1378, 1261, 1025, 804, 701

cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 280 nm, 1.0 mL/min. t_1 = 32.3 min (major), t_2 = 45.3 min (minor)]; ee = 97 %, $[\alpha]^{25}_D$ = -2.2 (c 3.7, CH_2Cl_2).



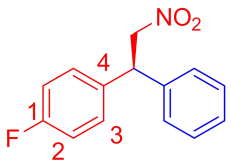
信号 2: DAD1 B, Sig=280,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	33.605	MM	2.1941	2.17476e4	165.19669	50.7360
2	42.644	MM	3.0085	2.11166e4	116.98259	49.2640
总量 :				4.28641e4	282.17928	



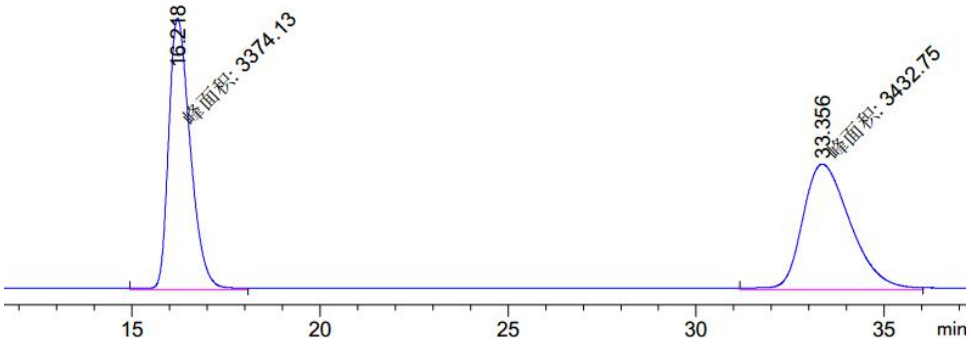
信号 2: DAD1 B, Sig=280,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	32.309	MM	2.3312	7.27782e4	520.32202	98.2798
2	45.341	MM	1.5494	1273.85706	9.62928	1.7202
总量 :				7.40521e4	529.95131	



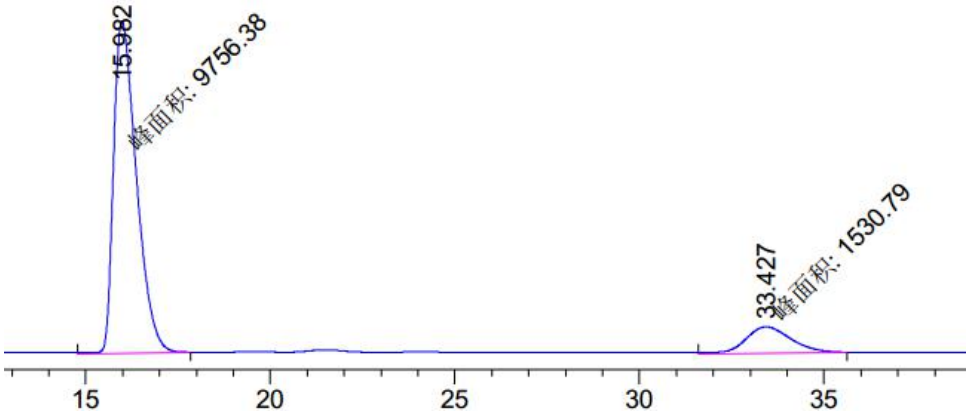
(*S*)-1-Fluoro-4-(2-nitro-1-phenylethyl)benzene (4o)[6c,6d]

Prepared according to procedure D from (*E*)-1-fluoro-4-(2-nitrovinyl)benzene (60 mg, 0.36 mmol) and phenylboronic acid (110 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:50, R_f = 0.49 (EtOAc/PE = 1:10)); yield: 83% (88 mg, white solid); m.p. 77.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88-4.91 (m, 1 H), 4.96 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2 H), 7.00-7.04 (m, 2 H), 7.19-7.22 (m, 4 H), 7.26-7.29 (m, 1 H), 7.32-7.35 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 48.4, 79.4, 116.1 (d, J = 21 Hz, C^2), 127.7, 127.9, 129.3, 129.4 (d, J = 8 Hz, C^3), 135.1 (d, J = 3 Hz, C^4), 139.1, 162.2 (d, J = 245 Hz, C^1); FT-IR (KBr) $\bar{\upsilon}$ 1603, 1552, 1505, 1373, 1228, 1159, 832, 779, 712, 536 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 254 nm, 1.0 mL/min. t_1 = 15.9 min (major), t_2 = 33.4 min (minor)]; ee = 73%, $[\alpha]^{25}_D$ = -7.31 (c 2.6, CH_2Cl_2).



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.218	MM	0.6654	3374.13013	84.50789	49.5694
2	33.356	MM	1.4675	3432.74561	38.98698	50.4306
总量：				6806.87573	123.49487	



信号 1: DAD1 A, Sig=254,4 Ref=360,100

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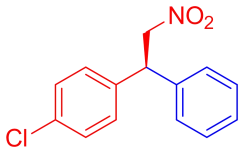
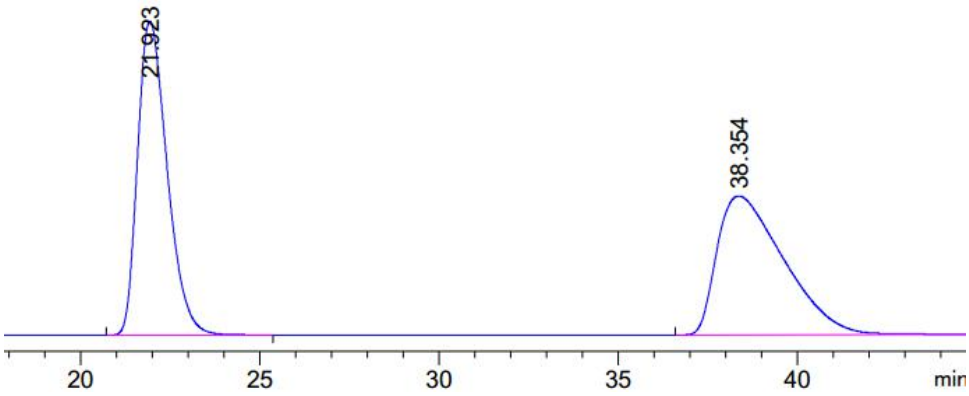
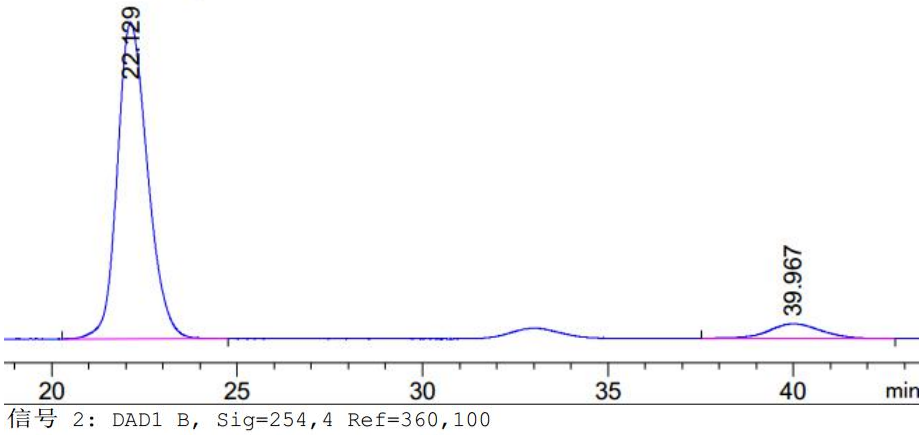
1	15.982	MM	0.7170	9756.38086	226.80142	86.4378
2	33.427	MM	1.4255	1530.79163	17.89792	13.5622
总量：				1.12872e4	244.69934	



(*S*)-1-Chloro-4-(2-nitro-1-phenylethyl)benzene (4p)[6a,6c]

Prepared according to procedure D from (*E*)-1-chloro-4-(2-nitrovinyl)benzene (66 mg, 0.36 mmol) and phenylboronic acid (110 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:100, R_f = 0.32 (EtOAc/PE = 1:50)); yield: 96% (107 mg, white solid); m.p. 57.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (dd, J_1 = 9 Hz, J_2 = 7 Hz, 1 H), 4.94 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2 H), 7.15-7.21 (m, 4 H), 7.24-7.34 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.4, 79.1, 127.7, 127.9, 129.1, 129.27, 129.31, 133.6, 137.8, 138.8; FT-IR (KBr) $\bar{\upsilon}$ 1549, 1490, 1452, 1428, 1377, 1092, 830, 752, 703, 658 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 254 nm, 1.0 mL/min. t_1 = 22.1 min (major), t_2 = 40.0 min (minor)]; ee = 86%, $[\alpha]^{25}_D$ = +0.26 (c 2.3, CH_2Cl_2).





信号 2: DAD1 B, Sig=254,4 Ref=360,100

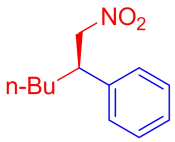
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.923	BB	0.8927	1.36924e4	238.87305	49.9096
2	38.354	BBA	1.9107	1.37421e4	105.84609	50.0904

总量 : 2.74345e4 344.71914

信号 2: DAD1 B, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.127	MM	0.9629	7312.94092	126.57405	92.8919
2	40.015	BB	1.3510	559.58936	5.83440	7.1081

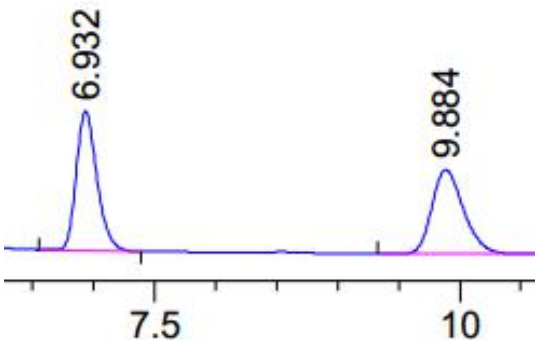
总量 : 7872.53027 132.40845

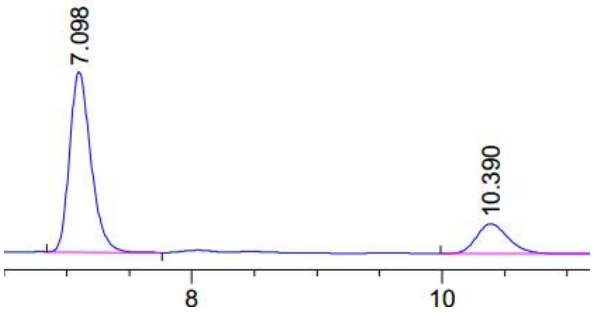


(*R*)-(1-Nitrohexan-2-yl)benzene (4q)[6e]

Prepared according to procedure D from (*E*)-1-nitrohex-1-ene (46 mg, 0.36 mmol) and phenylboronic acid (110 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:100, R_f = 0.44 (EtOAc/PE = 1:40)); yield: 64% (48 mg, colourless oil); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (t, J = 7 Hz, 3 H), 1.15-1.23 (m, 2

H), 1.29-1.33 (m, 2 H), 1.69 (q, J = 8 Hz, 2 H), 3.42-3.48 (m, 1 H), 4.52-4.60 (m, 2 H), 7.19-7.21 (m, 2 H), 7.26-7.29 (m, 1 H), 7.33-7.36 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 29.2, 32.9, 44.5, 81.2, 127.6, 127.7, 129.0, 139.7; FT-IR (KBr) $\bar{\upsilon}$ 2932, 1636, 1554, 1497, 1458, 1378, 1202, 1182, 1124, 906, 702; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 90/10, 230 nm, 1.0 mL/min. t_1 = 7.1 min (major), t_2 = 10.4 min (minor)]; ee = 61%, $[\alpha]^{25}_D$ = +9.33 (c 0.8, CH_2Cl_2).



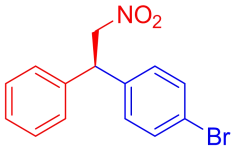


信号 4: DAD1 D, Sig=230,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.932	BB	0.1811	2733.96118	232.58972	52.1275
2	9.884	BB	0.2776	2510.79663	139.78159	47.8725
总量 :				5244.75781	372.37131	

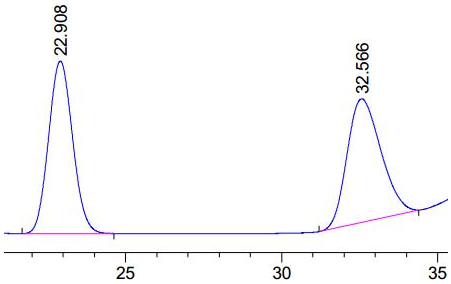
信号 4: DAD1 D, Sig=230,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.098	BB	0.1800	2629.94287	222.41635	80.3226
2	10.390	BB	0.2711	644.28241	36.64083	19.6774
总量 :				3274.22528	259.05719	



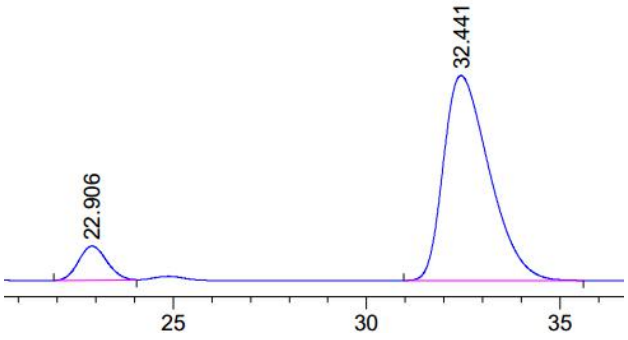
(*R*)-1-Bromo-4-(2-nitro-1-phenylethyl)benzene (4r)[6d]

Prepared according to procedure D from (*E*)-(2-nitrovinyl)benzene (53.6 mg, 0.36 mmol) and 4-bromophenylboronic acid (180.7 mg, 0.9 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:100, R_f = 0.36 (EtOAc/PE = 1:40)); yield: 91% (100 mg, white solid); m.p. 78.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (dd, J_1 = 9 Hz, J_2 = 7 Hz, 1 H), 4.95 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 2 H), 7.12 (dt, J_1 = 8 Hz, J_2 = 3 Hz, 2 H), 7.19-7.21 (m, 2 H), 7.25-7.29 (m, 1 H), 7.31-7.35 (m, 2 H), 7.45 (dt, J_1 = 8 Hz, J_2 = 3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.5, 79.0, 121.8, 127.7, 128.0, 129.3, 129.5, 132.3, 138.3, 138.7; FT-IR (KBr) $\bar{\upsilon}$ 1550, 1488, 1377, 1441, 1196, 1076, 1012, 703 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 60/40, 280 nm, 1.0 mL/min. t_1 = 22.9 min (minor), t_2 = 32.4 min (major)]; ee = 82%; $[\alpha]^{25}_D$ = +3.07 (c 1, CH_2Cl_2).



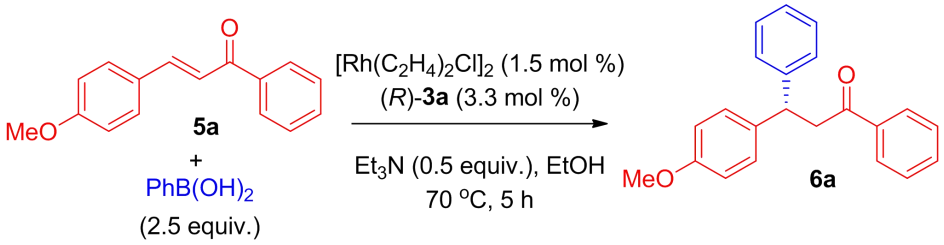
信号 5: DAD1 E, Sig=280,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.908	BB	0.8116	986.52667	18.39730	49.9449
2	32.566	BB	1.0643	988.70313	13.16300	50.0551
总量：				1975.22980	31.56031	



信号 5: DAD1 E, Sig=280,4 Ref=360,100

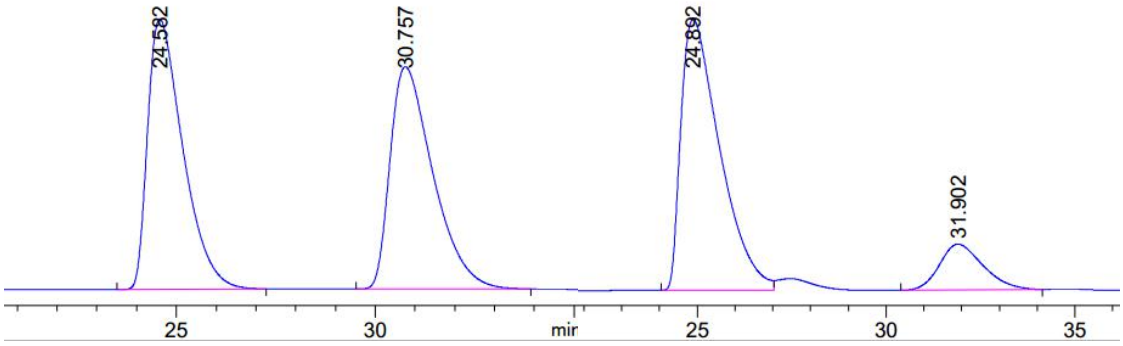
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.906	BB	0.6336	198.08969	3.91962	9.2409
2	32.441	BB	1.1772	1945.53967	23.61488	90.7591
总量：				2143.62936	27.53450	



(*S*)-3-(4-Methoxyphenyl)-1,3-diphenylpropan-1-one (6a)[6f]

Procedure F: To an oven-dried 10 mL Schlenk tube was charged $[Rh(C_2H_4)_2Cl]_2$ (1.1 mg, 1.5 mol %), (*R*)-**3a** (2.8 mg, 3.3 mol %) in EtOH (1 mL) solution. The mixture was stirred at rt under nitrogen protection for 15 min to form Rh((*R*)-**3a**)OEt complex, then transferred to another solution of *trans*-4-methoxy-chalcone (43 mg, 0.18 mmol) and phenyl boronic acid (55 mg, 0.45 mmol) in EtOH (2 mL) *via* syringe. This was followed by Et_3N (13 μL, 0.09 mmol) injection. The mixture was warmed up to 70 ℃ and stirred for 5 h under nitrogen protection. Removed EtOH in *vacuo* and the residue was purified by flash chromatography on silica gel (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:60, R_f = 0.44 (EtOAc/PE = 1:10)); yield: 90% (51 mg, white solid); m.p. 93.3-94.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (d, J = 7 Hz, 2 H), 3.76 (s, 3 H), 4.79 (t, J = 7 Hz, 1 H), 6.80-6.84 (m, 2 H), 7.16-7.21 (m, 3 H), 7.26-7.28 (m, 4 H), 7.45 (t, J = 8 Hz, 2 H), 7.55 (t, J = 7 Hz, 1 H), 7.93-7.95 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.0, 45.3, 55.3, 114.1, 126.4, 127.9, 128.2, 128.67, 128.71, 128.9, 133.2, 136.4, 137.2, 144.7, 158.2, 198.3; FT-IR (KBr) $\bar{\upsilon}$ 3010, 2930, 2833, 1672, 1600, 1509, 1451, 1375, 1265,

1210, 1034, 837, 740, 691 cm^{-1}; HRMS (ESI^+) m/z calcd for $C_{22}H_{21}O_2$ $[M+H]^+$ 317.1536 found 317.1532; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 99.2/0.8, 230 nm, 1.0 mL/min. t_1 = 24.9 min (major), t_2 = 31.9 min (minor)]; ee = 68%, $[\alpha]^{25}_D$ = +1.45 (c 2.6, CH_2Cl_2).



信号 4: DAD1 D, Sig=230,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.582	BB	0.9387	4.99668e4	811.06812	50.0242
2	30.757	BB	1.1278	4.99184e4	666.49451	49.9758

DAD 2016/3/29 20:29:59 系统

文件: C:\CHEM32\1\DATA\DEMO\ZYJ 2016-03-29 19-51-29\SIG1
名称: 33

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
总量 :				9.98852e4	1477.56262	

信号 4: DAD1 D, Sig=230,4 Ref=360,100

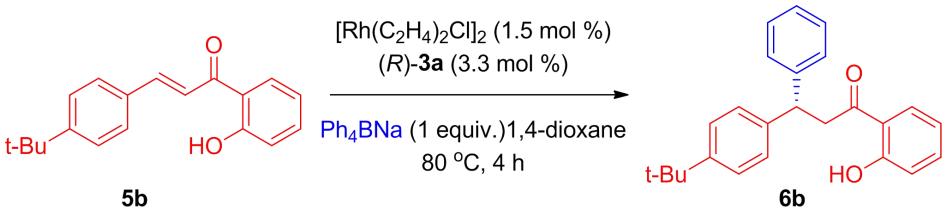
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.892	BV	1.0675	1.11434e5	1559.75891	84.1206
2	31.902	BB	1.2117	2.10353e4	262.83350	15.8794

DAD 2016/3/30 10:38:48 系统

文件: C:\CHEM32\1\DATA\DEMO\ZYJ 2016-03-30 09-57-45\SIG10
名称: 33

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
总量 :				1.32469e5	1822.59241	

(*S*)-3-(4-(*tert*-Butyl)phenyl)-1-(2-hydroxyphenyl)-3-phenylpropan-1-one (6b)

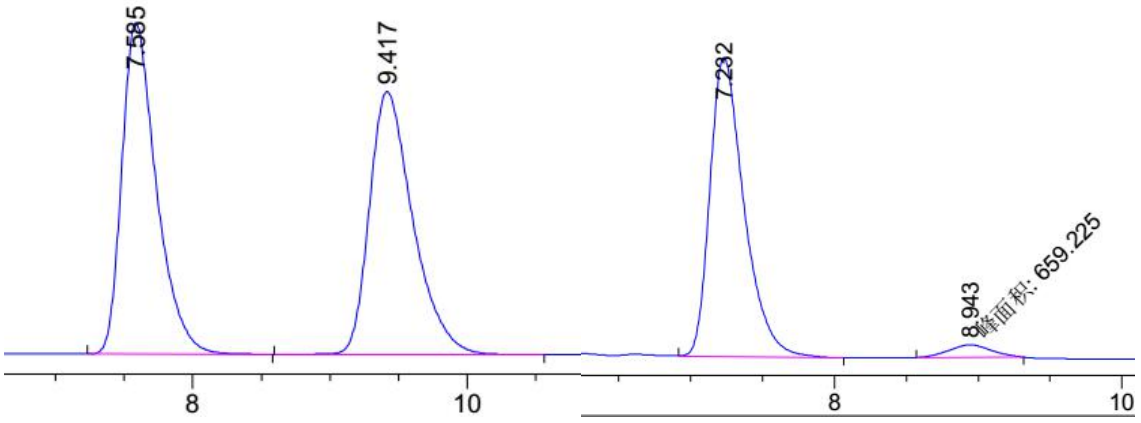


5b **6b**

Compound **5b** was prepared from 2'-hydroxyacetophenone (1.2 mmol, 0.15 mL) and 4-*tert*-butylbenzaldehyde (1.2 mmol, 0.2 mL) according to Aldol condensation protocol.[7] R_f = 0.60 (EtOAc/PE = 1:20); yield: 51% (171 mg, yellow solid); m.p. 77.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 9 H), 6.95-6.98 (m, 1 H), 7.04 (d, J = 8 Hz, 1 H), 7.47-7.52 (m, 3 H), 7.62-7.67 (m, 3 H), 7.92-7.95 (m, 2 H), 12.91 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 35.1, 118.7, 118.9, 119.3, 120.2, 126.2, 128.7, 129.8, 132.0, 136.4, 145.6, 154.8, 163.7, 193.9; FT-IR (KBr) $\bar{\upsilon}$ 2951, 1583, 1487, 1358, 1201, 829, 756 cm^{-1}; HRMS (ESI^+) m/z calcd for $C_{19}H_{21}O_2$ $[M+H]^+$ 281.1542 found 281.1536.

Procedure G: To an oven-dried 10 mL Schlenk tube was charged $[Rh(C_2H_4)_2Cl]_2$ (1.1 mg, 1.5 mol%), (*R*)-**3a** (2.7 mg, 3.3 mol%) in 1,4-dioxane (1 mL) solution. The mixture was stirred at room temperature under nitrogen protection for 15 min, then transferred to another solution of **5b** (50.4 mg, 0.18 mmol) and sodium tetraphenylboron (61.8 mg,

0.18 mmol) in 1,4-dioxane (1 mL) *via* syringe. The mixture was stirred at 80 ℃ for 4 h. Upon completion monitored by TLC, removed 1,4-dioxane in *vacuo* and the residue was purified by flash chromatography on silica gel (2 cm × 14 cm) with petroleum ether/ethyl acetate = 1:100 as an eluent to give **6b**; R_f = 0.52 (EtOAc/PE = 1:20); yield: 78% (50 mg, white solid); m.p. 84.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (s, 9 H), 3.78 (d, J = 7 Hz, 2 H), 4.80 (t, J = 7 Hz, 1 H), 6.90 (dt, J_1 = 1 Hz, J_2 = 7 Hz, 1 H), 6.98 (d, J = 8 Hz, 1 H), 7.20-7.22 (m, 3 H), 7.30-7.33 (m, 6 H), 7.47 (dt, J_1 = 1 Hz, J_2 = 7 Hz, 1 H), 7.84 (dd, J_1 = 1 Hz, J_2 = 7 Hz, 1 H), 12.21 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.5, 34.5, 44.4, 45.5, 118.7, 119.0, 119.6, 125.7, 126.6, 127.4, 127.9, 128.7, 129.9, 136.5, 140.8, 144.0, 149.4, 162.6, 204.3; FT-IR (KBr) $\tilde{\upsilon}$ 3671, 2968, 1727, 1644, 1396, 1273, 1064, 758 cm^{-1}; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 99/1, 254 nm, 1.0 mL/min. t_1 = 7.2 min (major), t_2 = 8.9 min (minor); ee = 90%; HRMS (ESI$^+$) m/z calcd for $C_{25}H_{27}O_2$ $[M+H]^+$ 359.2011 found 359.2006, $[\alpha]^{25}_D$ = +57.4 (c 1.5, CH_2Cl_2).



信号 2: DAD1 B, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.585	VB	0.2644	1.19231e4	680.45123	50.0470
2	9.417	BB	0.3353	1.19007e4	539.63751	49.9530
总量 :				2.38239e4	1220.08875	

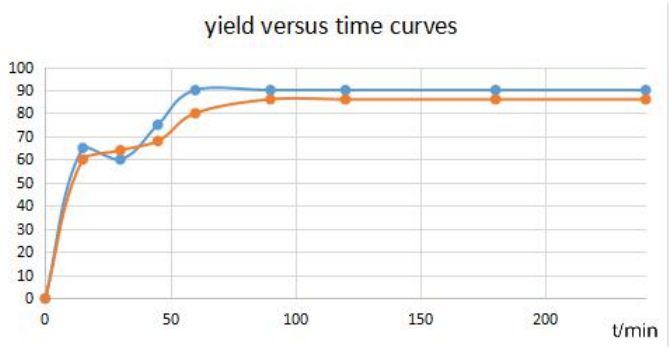
信号 2: DAD1 B, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.232	VB	0.2510	1.28095e4	774.21973	95.1055
2	8.943	MM	0.3393	659.22516	32.38042	4.8945
总量 :				1.34687e4	806.60015	

3. Kinetic control experiment

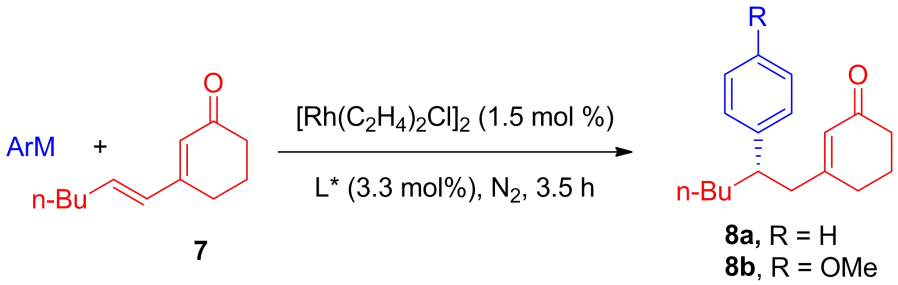
To an oven-dried 10 mL Schlenk tube was charged $[Rh(C_2H_4)_2Cl]_2$ (2.1 mg, 1.5 mol %), (*R*)-**3a** (5.5 mg, 3.3 mol %) in EtOH (2 mL) solution. The mixture was stirred at rt under nitrogen atmosphere for 15 min to form Rh((*R*)-**3a**)OEt complex, then transferred to another solution of (*E*)-1-methyl-4-(2-nitrovinyl) benzene (58.7 mg, 0.36 mmol) and phenylboronic acid (110 mg, 0.9 mmol) in EtOH (2 mL) *via* syringe. This was followed by Et_3N (0.18 mmol) injection. The mixture was stirred at rt and 0.4 mL samples were taken, the first after 15 min and the others after 15 min intervals, and concentrated *in vacuo* to remove EtOH. $CDCl_3$ dissolved the residue into the NMR tube with final addition of 4'-Methylacetophenone (24 μL, 0.18 mmol) as an external standard and submitted to ^{1}HNMR for calibration. The results expressed as a percentage of **4a** are

reported herein. (*S*)-**3g** kinetic experiment was using the same procedure as described above.



(*R*)-**3a** —— —— (*S*)-**3g**

4. Optimization table for asymmetric 1,6-addition to dienone



entry	PhM (equiv.)	L*	T (℃)	solvent	yield (brsm) (%)[a]	ee (%)
1	*p*-OMe-$C_6H_4B(OH)_2$/ Et_3N (2/0.5)	(*R*)-**3a**	80	EtOH	N.R.	-
2	*p*-OMe-$C_6H_4B(OH)_2$/ KHF_2 (2/4)	(*R*)-**3a**	80	EtOH	-[b]	-
3	*p*-OMe-ZnBr/TMSCl (1.4/1.5)	(*R*)-**3a**	r.t.	THF	N.R.	-
4	$NaBPh_4$ (2)	(*R*)-**3a**	80	1,4-dioxane	94	35
5	$NaBPh_4$/TMSCl (2/1)	(*R*)-**3a**	80	1,4-dioxane	-[c]	-
6	$NaBPh_4$ (2)	(*R*)-**3d**	80	1,4-dioxane	26 (38)	15
7	$NaBPh_4$ (2)	(*R*)-**3f**	80	1,4-dioxane	28 (69)	9
8	$NaBPh_4$ (2)	(*R*)-**3a**	50[d]	1,4-dioxane	93	91
9	$NaBPh_4$ (2)	(*R*)-**3b**	50[d]	1,4-dioxane	69	81
10	$NaBPh_4$ (2)	(*R*)-**3c**	50[d]	1,4-dioxane	28	41
11	$NaBPh_4$ (2)	(*R*)-**3d**	50[d]	1,4-dioxane	4	56

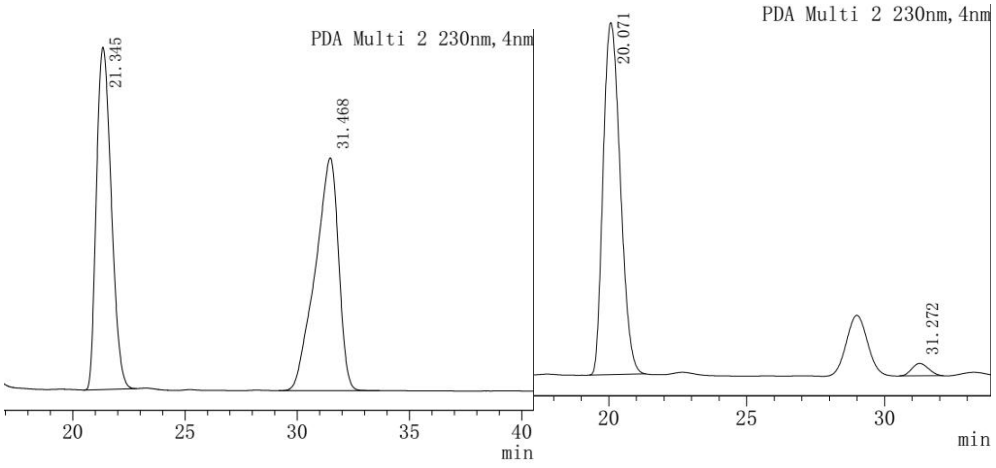
12	$NaBPh_4$ (2)	(*R*)-**3e**	50[d]	1,4-dioxane	69	83
13	$NaBPh_4$ (2)	(*R*)-**3h**	50[d]	1,4-dioxane	87	93

[a] isolated yield after 3 h at 80 °C unless specified; brsm = based on staring matierial's yield; [b] 1,4-, and 1,6-adducts mixed complex; [c] slow conversion after 7 h stirring; [d] 16 h.

(*S*)-3-(2-Phenylhexyl)cyclohex-2-en-1-one (8a)[6g]

Prepared according to procedure G at 50 ℃ for 16 hours from 3-((*E*)-hexenyl)-2-cyclohexenone[6g,8] (32.1 mg, 0.18 mmol) and sodium tetraphenylboron (123 mg, 0.36 mmol); silica gel purification (2 cm × 14 cm, ethyl acetate/petroleum ether = 1:30, R_f = 0.51 (EtOAc/PE = 1:10)); yield: 93% (43 mg, yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7 Hz, 3 H), 1.08-1.18 (m, 2 H), 1.20-1.30 (m, 2 H), 1.58-1.66 (m, 2 H), 1.82-1.88 (m, 2 H), 2.07 (dt, J_1 = 18 Hz, J_2 = 6 Hz, 1 H), 2.17 (dt, J_1 = 18 Hz, J_2 = 6 Hz, 1H), 2.23-2.27 (m, 2 H), 2.44 (dd, J_1 = 14 Hz, J_2 = 9 Hz, 1 H), 2.55 (dd, J_1 = 14 Hz, J_2 = 6 Hz, 1 H), 2.78 (tt, J_1 = 9 Hz, J_2 = 6 Hz, 1 H), 5.76 (s, 1 H), 7.11 (d, J = 7 Hz, 2 H), 7.18 (t, J = 7 Hz, 1 H), 7.27 (t, J = 8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.72, 22.74, 29.7, 30.0, 36.4, 37.3, 44.5, 45.8, 126.5, 127.49, 127.53, 128.5, 144.3, 165.0, 199.9; FT-IR (KBr) $\bar{\upsilon}$ 2956, 2929, 1728, 1670, 1623, 1454, 1374, 1254, 968, 886, 701 cm^{-1}; HPLC [Daicel Chiralpak OJ-H, hexane/*i*-PrOH = 95/5, 230 nm, 0.5 mL/min. t_1 = 19.5 min (major, (*S*)-enantiomer), t_2 = 30.5 min (minor, (*R*)-enantiomer)]; ee = 91%; HRMS (ESI$^+$) m/z calcd for $C_{18}H_{25}O_1$ $[M+H]^+$ 257.1900 found 257.1899.

When employing (*R*)-**3h** at 50 ℃ for 16 hours, yield: 87% (40 mg); HPLC [Daicel Chiralpak OJ-H, hexane/*i*-PrOH = 95/5, 230 nm, 0.5 mL/min. t_1 = 20.1 min (major, (*S*)-enantiomer), t_2 = 31.3 min (minor, (*R*)-enantiomer)]; ee = 93%, $[\alpha]^{25}_D$ = +33.2 (c 2.8, CH_2Cl_2).



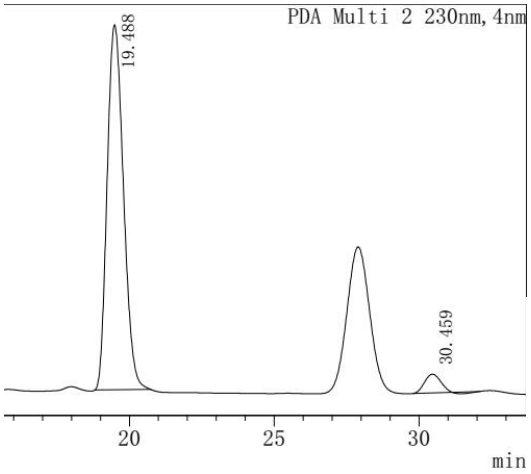
PDA Ch2 230nm

峰号	保留时间	面积%
1	21.345	48.425
2	31.468	51.575
总计		100.000

PDA Ch2 230nm

峰号	保留时间	面积%
1	20.071	96.686
2	31.272	3.314
总计		100.000

When employing (*R*)-**3a** at 50 ℃ for 16 hours, yield: 93% (43 mg); HPLC [Daicel Chiralpak OJ-H, hexane/*i*-PrOH = 95/5, 230 nm, 0.5 mL/min. t_1 = 19.5 min (major, (*S*)-enantiomer), t_2 = 30.5 min (minor, (*R*)-enantiomer)]; ee = 91%.



PDA Ch2 230nm

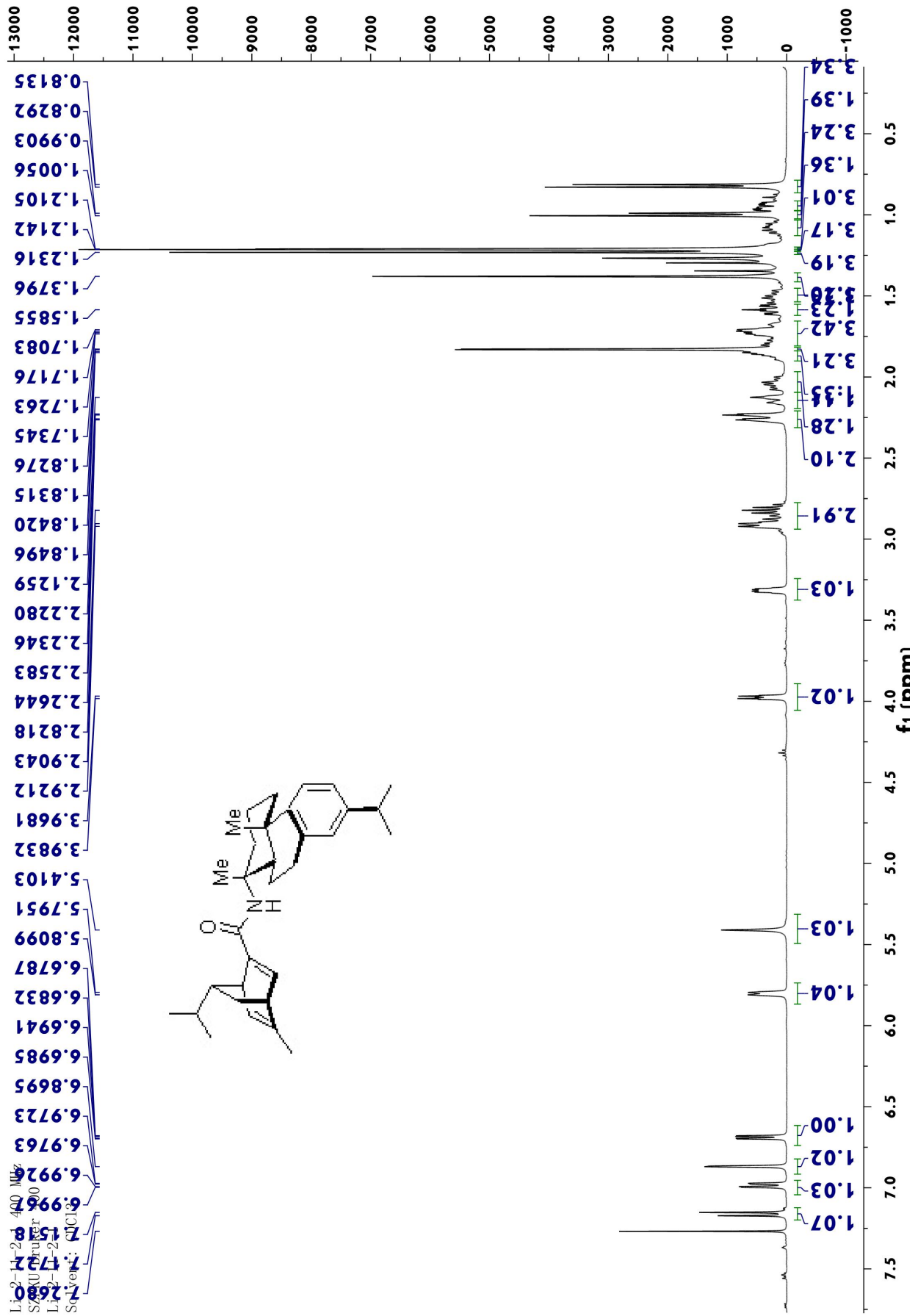
峰号	保留时间	面积%
1	19.488	95.520
2	30.459	4.480
总计		100.000

5. References

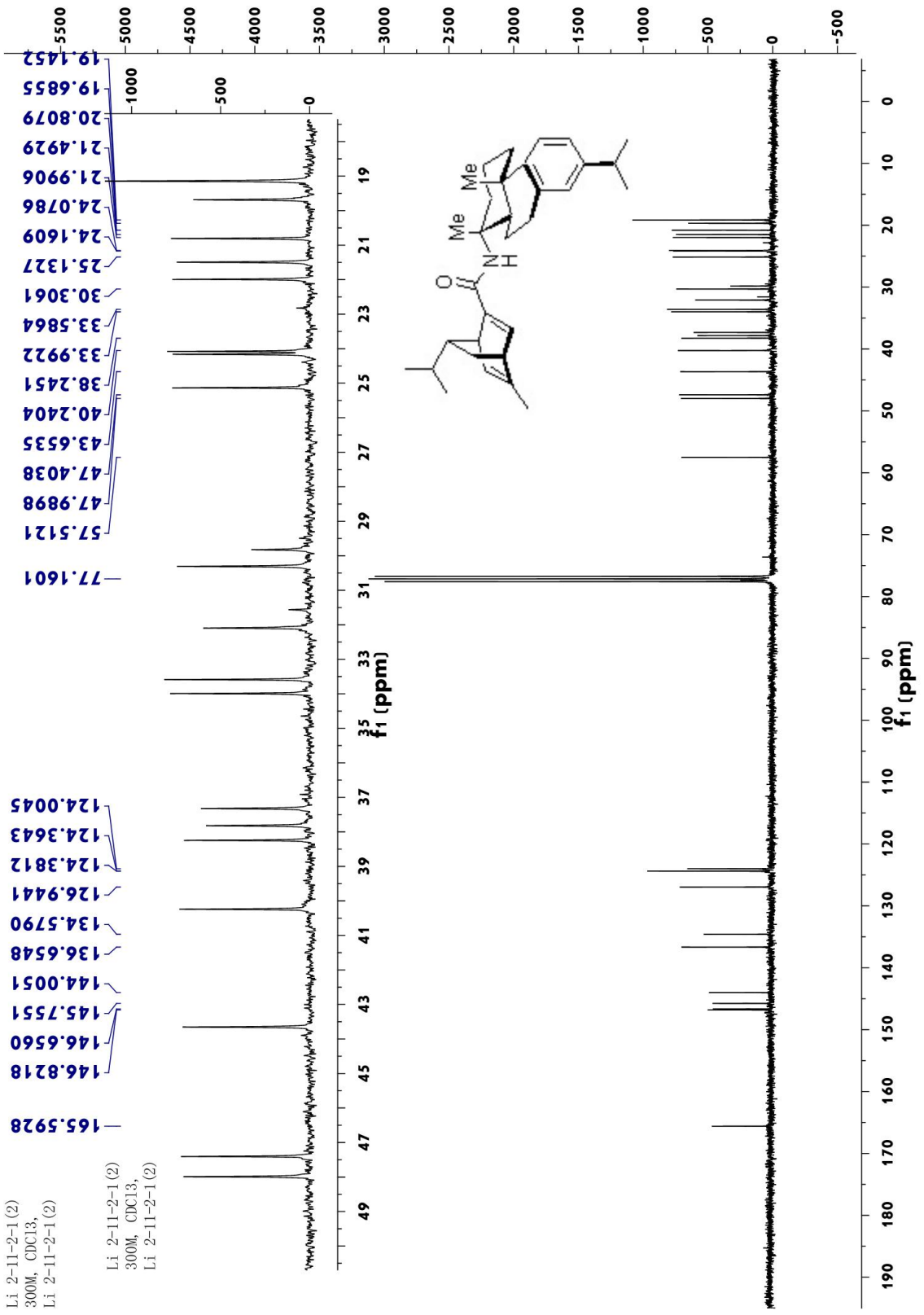
(1) K. Okamoto, T. Hayashi and V. H. Rawal, *Org. Lett.*, 2008, **10**, 4387.
(2) G. Pattison, G. Piraux and H. -W. Lam, *J. Am. Chem. Soc.*, 2010, **132**, 14373.
(3) A. Saxena and H.- W. Lam, *Chem. Sci.*, 2011, **2**, 2326.
(4) I. D. Roy, A. R. Burns, G. Pattison, B. Michel, A. J. Parker and H. -W. Lam, *Chem. Commun.*, 2014, **50**, 2865.
(5) K. Okamoto, T. Hayashi and Viresh H. Rawal, *Chem. Commun.*, 2009, **32**, 4815.
(6) These compounds have been previously reported, for their literature data, please see: (a) K. -C. Huang, B. Gopula, T. -S. Kuo, C. -W. Chiang, P. -Y. Wu, J. P. Henschke and H. -L. Wu, *Org. Lett.*, 2013, **15**, 5730; (b) T. Ohe and S. Uemura, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1423; (c) F. Lang, G. Chen, L. Li, J. Xing, F. Han, L. Cun and Jian Liao, *Chem. Eur. J.,* 2011, **17**, 5242; (d) Z.-Q. Wang, C.-G. Feng, S.-S. Zhang, M.-H. Xu and G.-Q. Lin, *Angew. Chem. Int. Ed.,* 2010, **49**, 5780; (e) F. Xue, D. Wang, X. Li and B. Wan, *J. Org. Chem.,* 2012, **77**, 3071; (f) C. Wu, G. Yue, C. D.-T. Nielsen, K. Xu, H. Hirao and J. Zhou, *J. Am. Soc. Chem.,* 2016, **138**, 742; (g) T. Hayashi, S. Yamamoto and N. Tokunaga, *Angew. Chem. Int. Ed.,* 2005, **44**, 4224.
(7) X. Li, J. Han, A. X. Jones and X. Lei, *J. Org. Chem.,* 2016, **81**, 458.
(8) X. Fu, S. Zhang, J. Yin and D. P. Schumacher, *Tetrahedron Lett.*, 2002, **43**, 6673.

6. ^{1}H and ^{13}C-NMR spectra for adducts

(*R*)-**3a**


Li-2-1-2 400 MHz
SZKU Bruker 400
Li-2-1-2
Solvent CDCl3
Me
Me
N
H
O
f1 (ppm)

(*R*)-**3a**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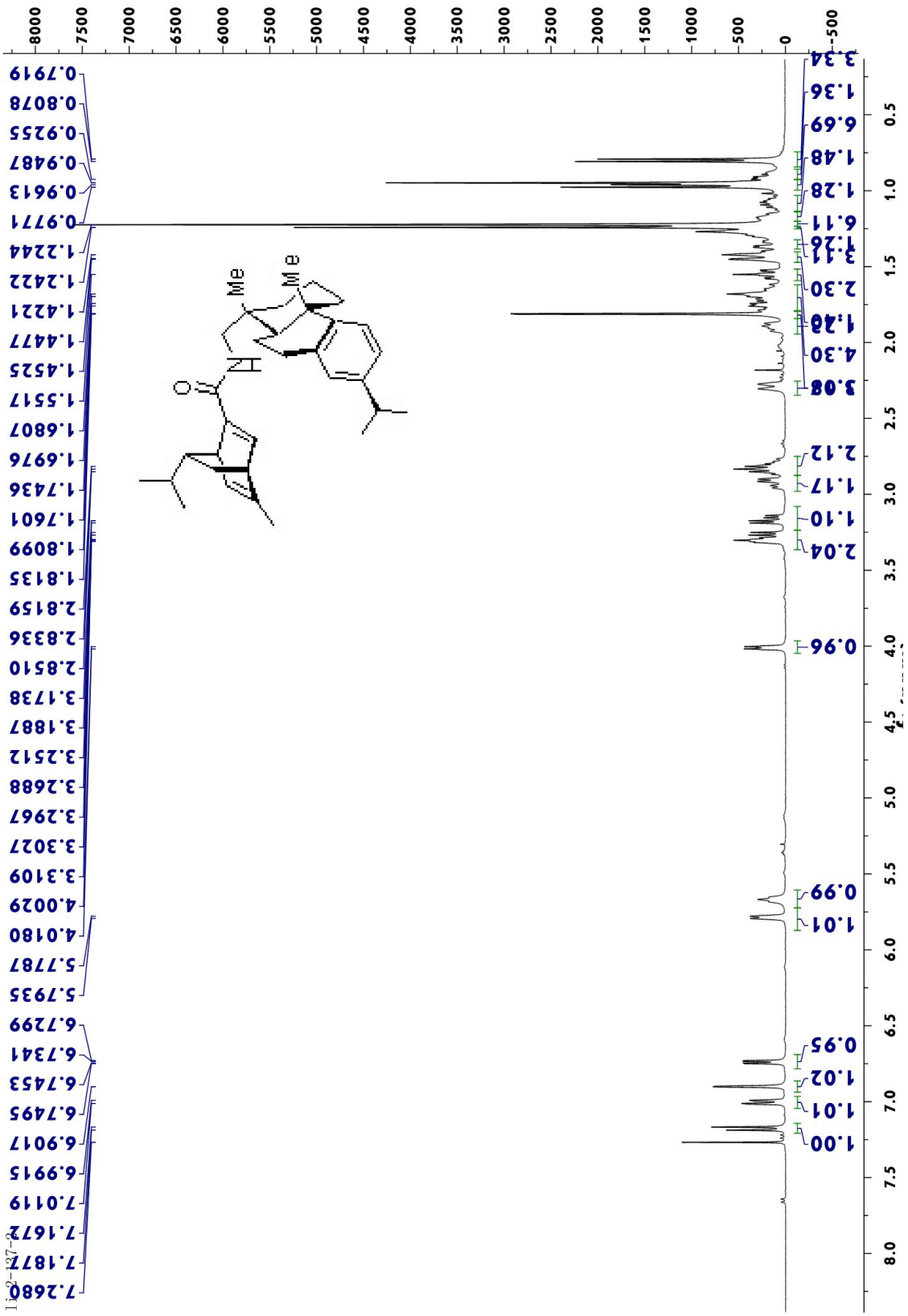
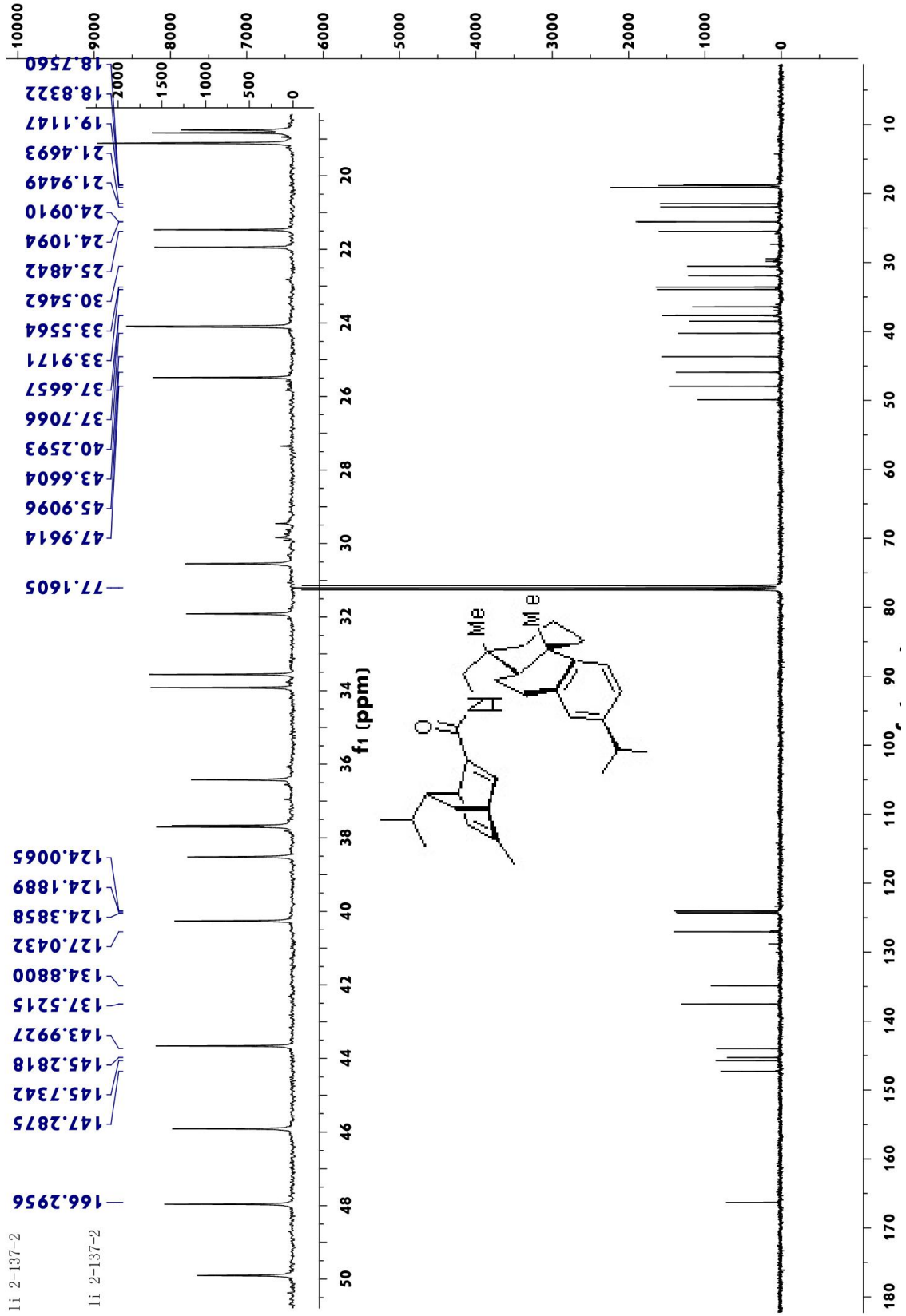
19.6855
20.8079
21.4929
21.9906
24.0786
24.1609
25.1327
30.3061
33.5864
33.9922
38.2451
40.2404
43.6535
47.4038
47.9898
57.5121
77.1601
124.0045
124.3643
124.3812
126.9441
134.5790
136.6548
144.0051
145.7551
146.6560
146.8218
165.5928
Me
Me
N
H
O
f1 (ppm)
Li 2-11-2-1(2)
300M, CDCl3,
Li 2-11-2-1(2)

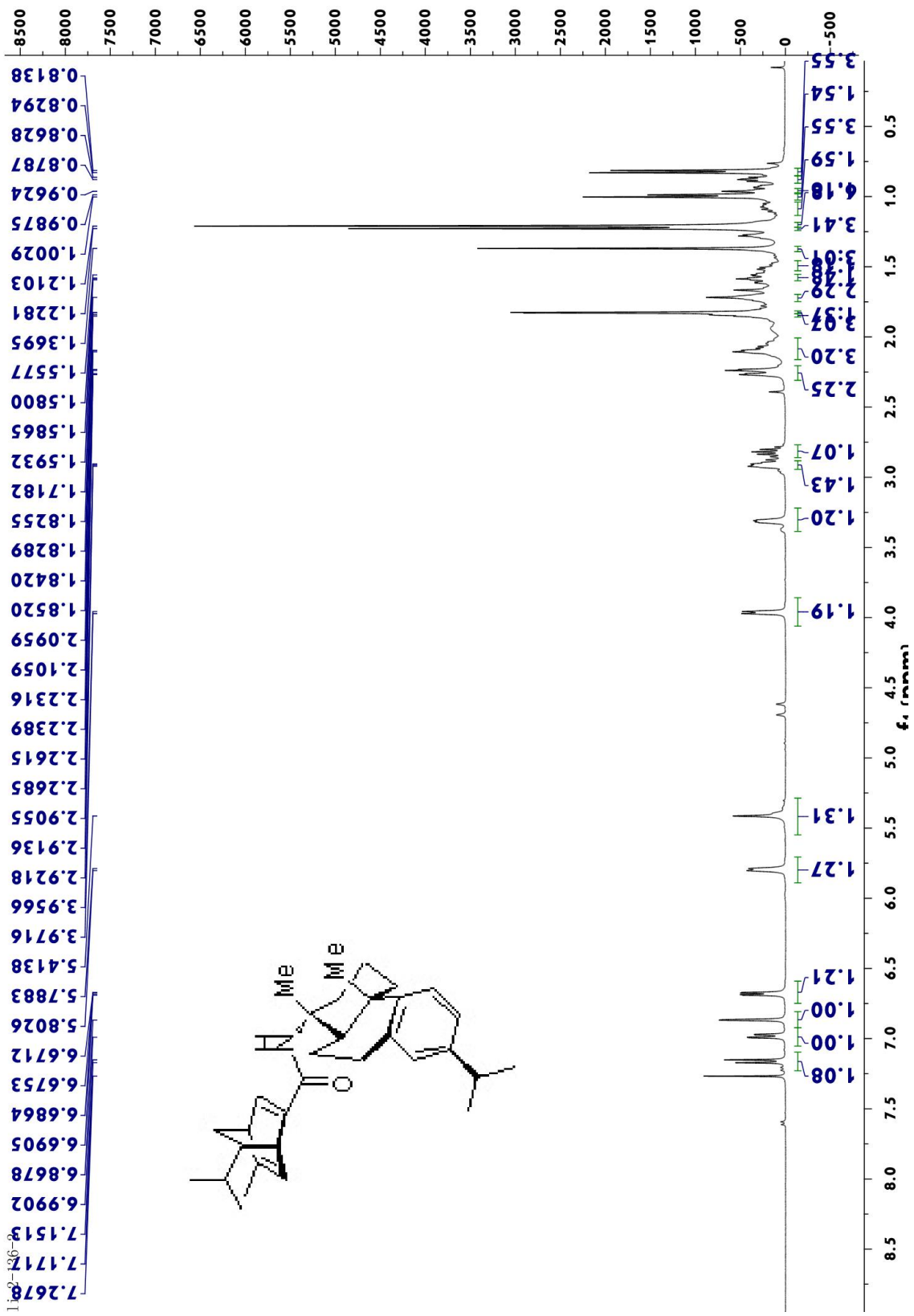
(*R*)-**3f**



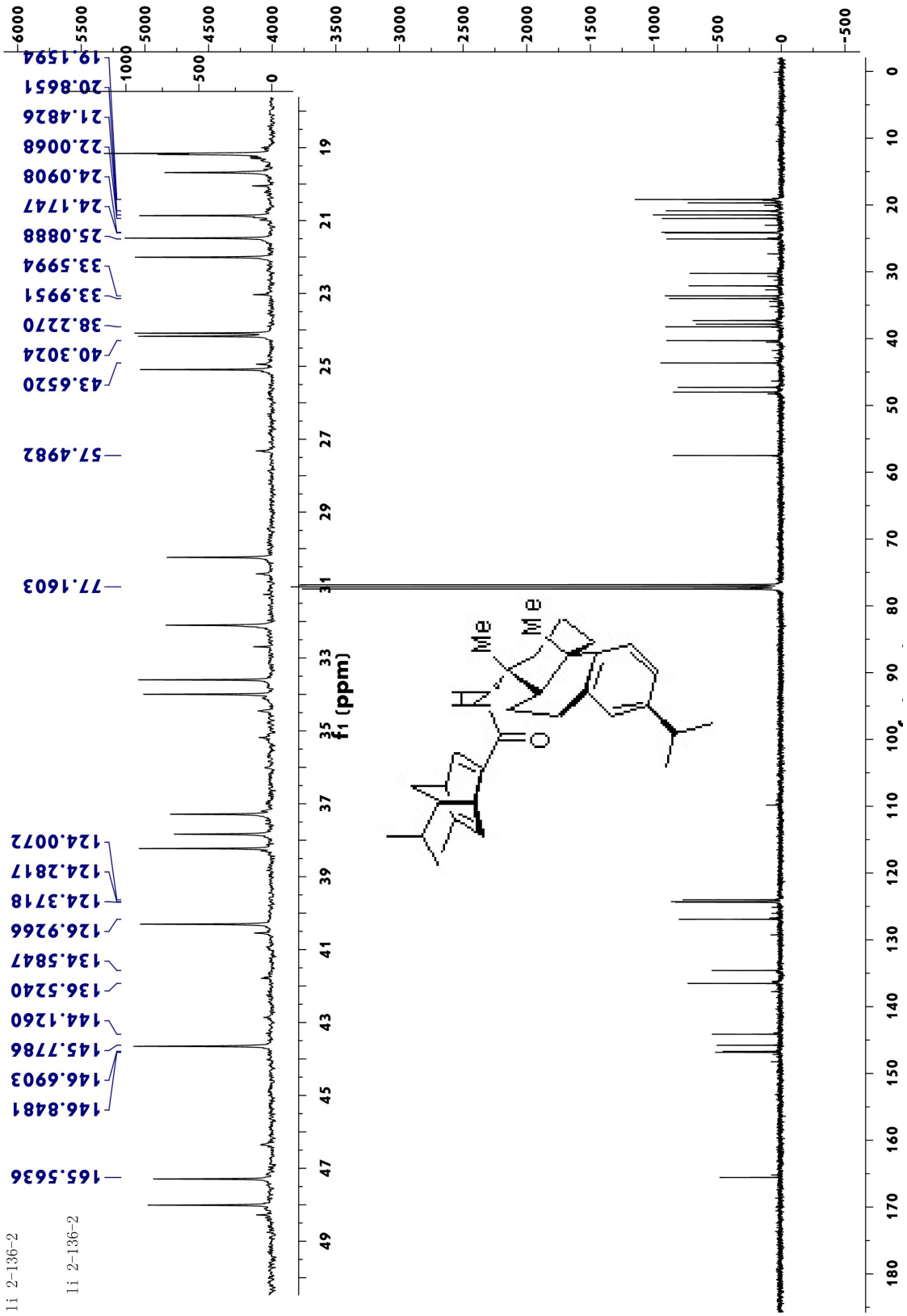
(*R*)-**3f**


18.7560
18.8322
19.1147
21.4693
21.9449
24.0910
24.1094
25.4842
30.5462
33.5564
33.9171
37.6657
37.7066
40.2593
43.6604
45.9096
47.9614
77.1605
124.0065
124.1889
124.3858
127.0432
134.8800
137.5215
143.9927
145.2818
145.7342
147.2875
166.2956
Me
Me
N
H
O
f1 (ppm)
li 2-137-2
li 2-137-2

(*S*)-**3g**



(*S*)-**3g**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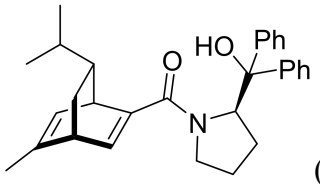
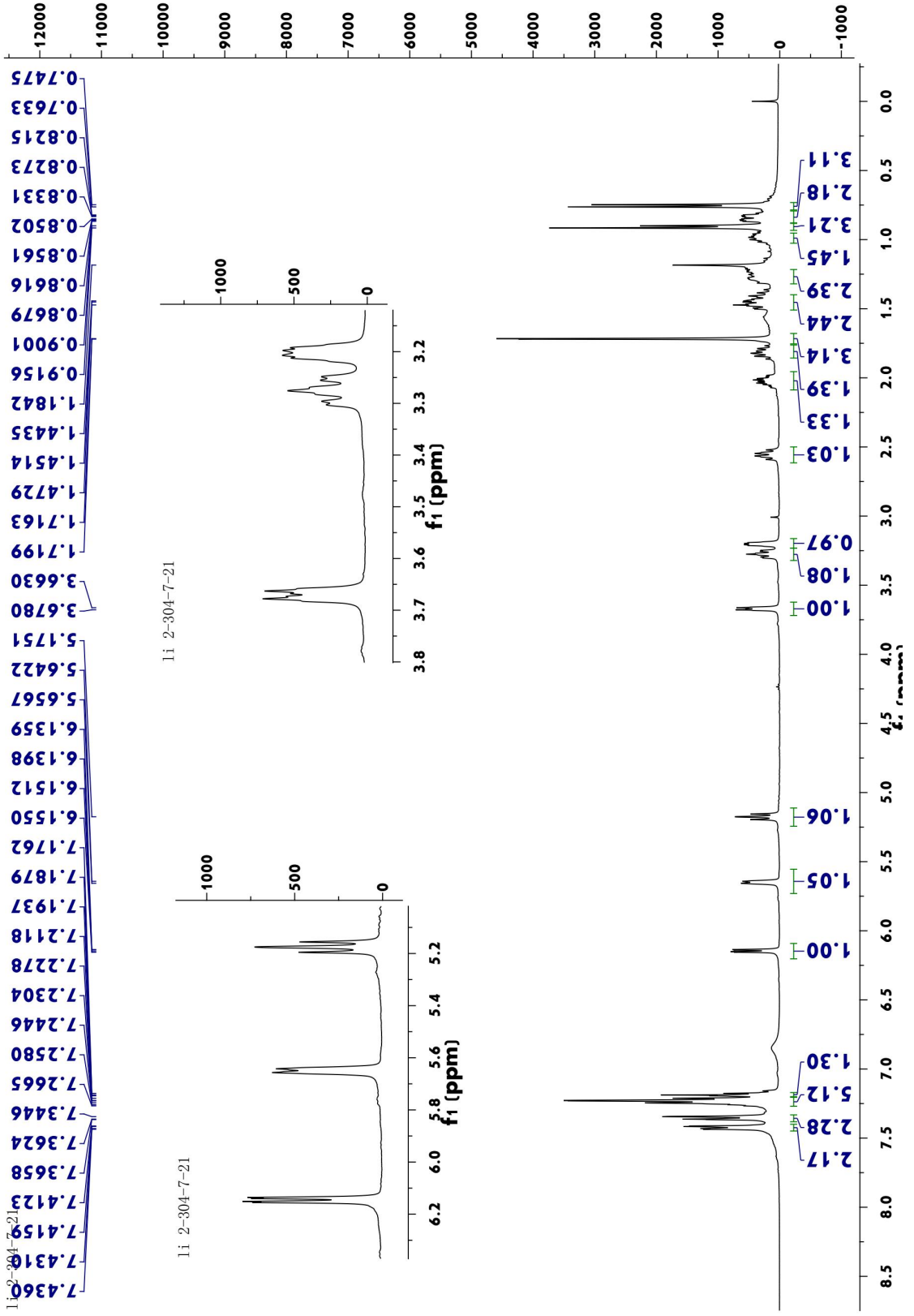
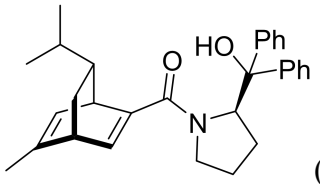
20.8651
21.4826
22.0068
24.0908
24.1747
25.0888
33.5994
33.9951
38.2270
40.3024
43.6520
57.4982
77.1603
124.0072
124.2817
124.3718
126.9266
134.5847
136.5240
144.1260
145.7786
146.6903
146.8481
165.5636
Me
Me
H
N
O
f1 (ppm)
li 2-136-2
li 2-136-2

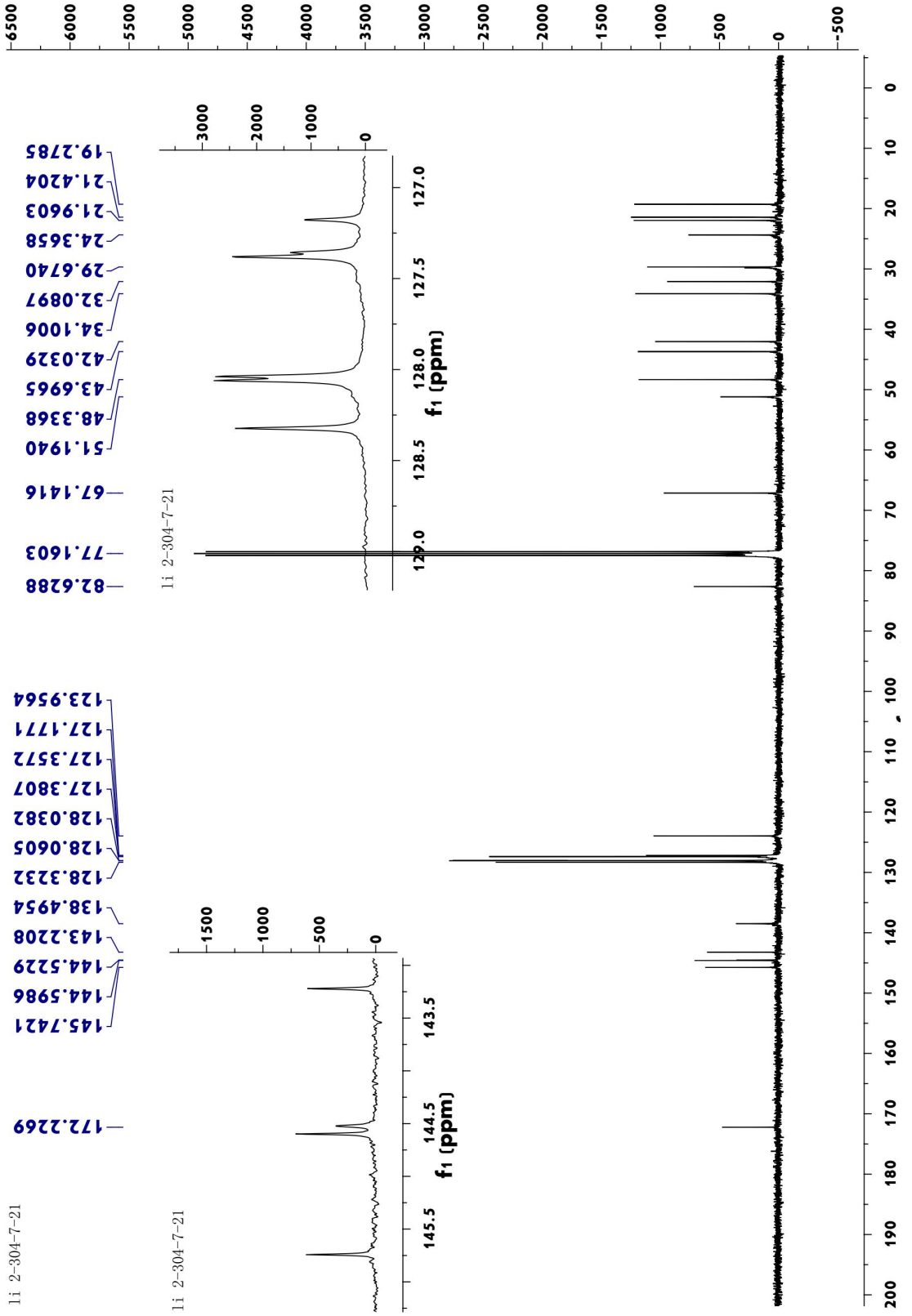


(*R*)-**3h**




HO
Ph
Ph
O
N

(*R*)-**3h**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145.7421
144.5986
144.5229
143.2208
138.4954
128.3232
128.0605
128.0382
127.3807
127.3572
127.1771
123.9564
82.6288
77.1603
67.1416
51.1940
48.3368
43.6965
42.0329
34.1006
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29.6740
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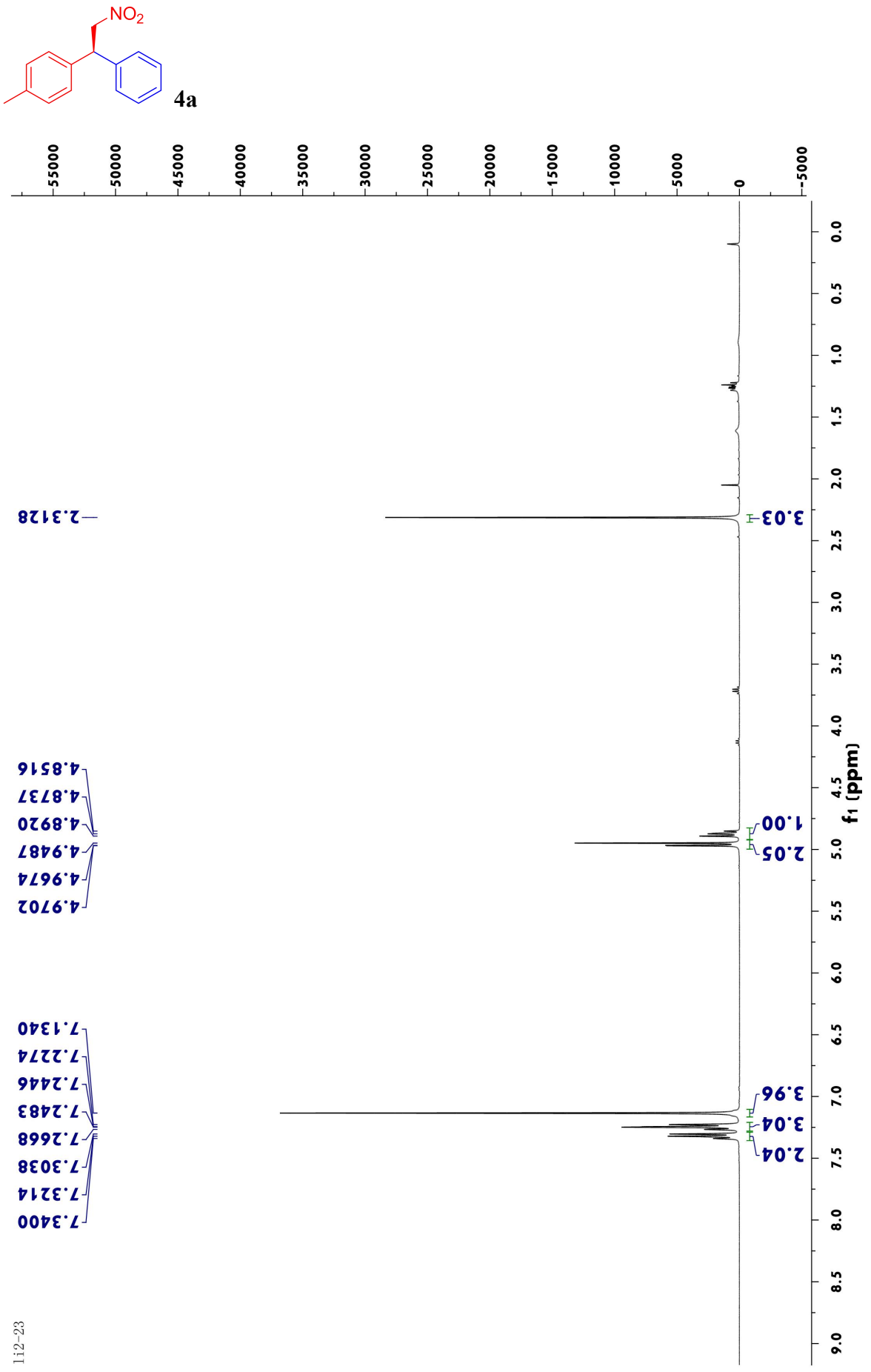
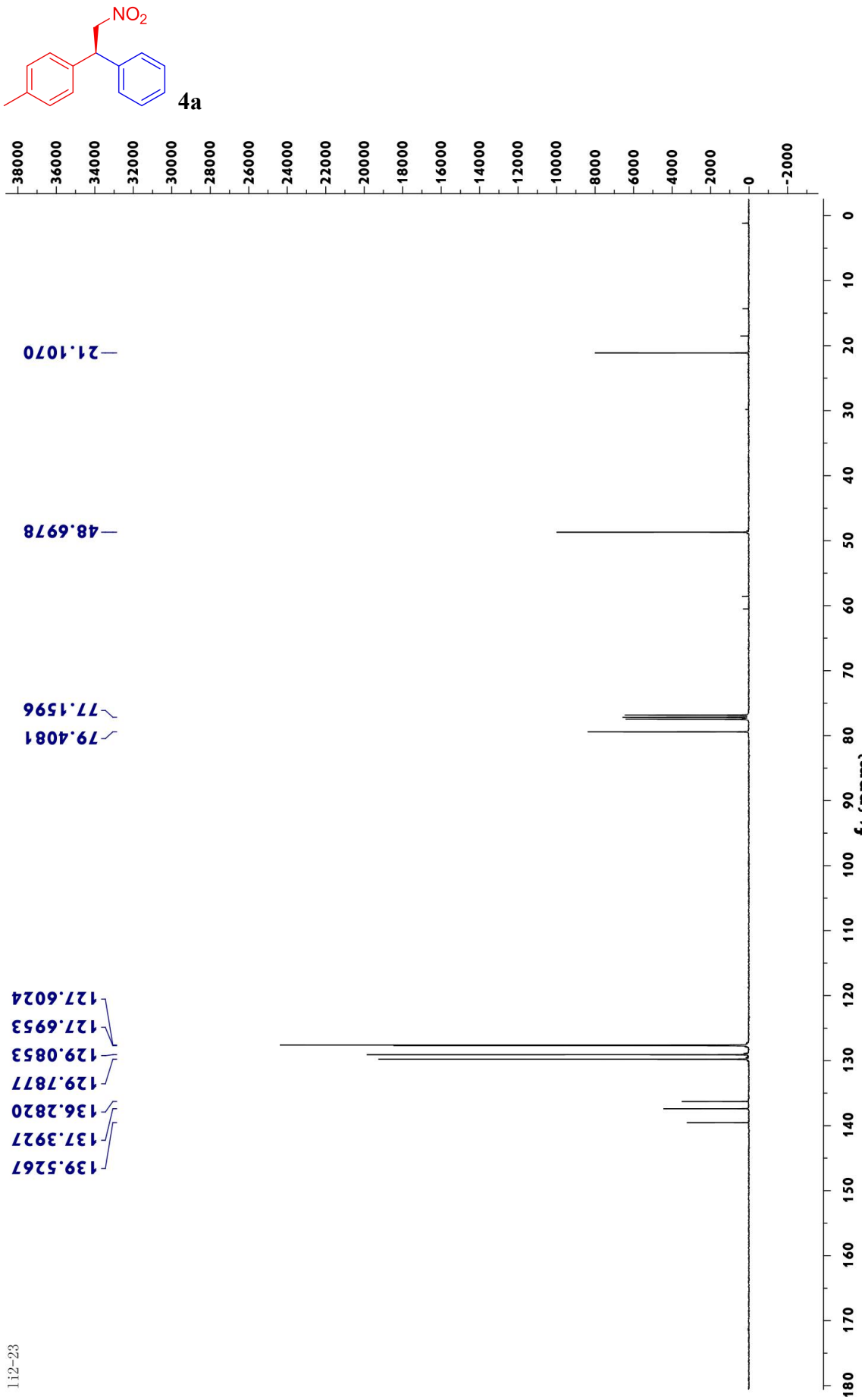
21.4204
19.2785
li 2-304-7-21
f1 (ppm)


NO2
4a
7.3400
7.3214
7.3038
7.2668
7.2483
7.2446
7.2274
7.1340
4.9702
4.9674
4.9487
4.8920
4.8737
4.8516
2.3128
3.96
3.04
2.04
1.00
2.05
3.03
f1 (ppm)
112-23


NO2
4a
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48.6978
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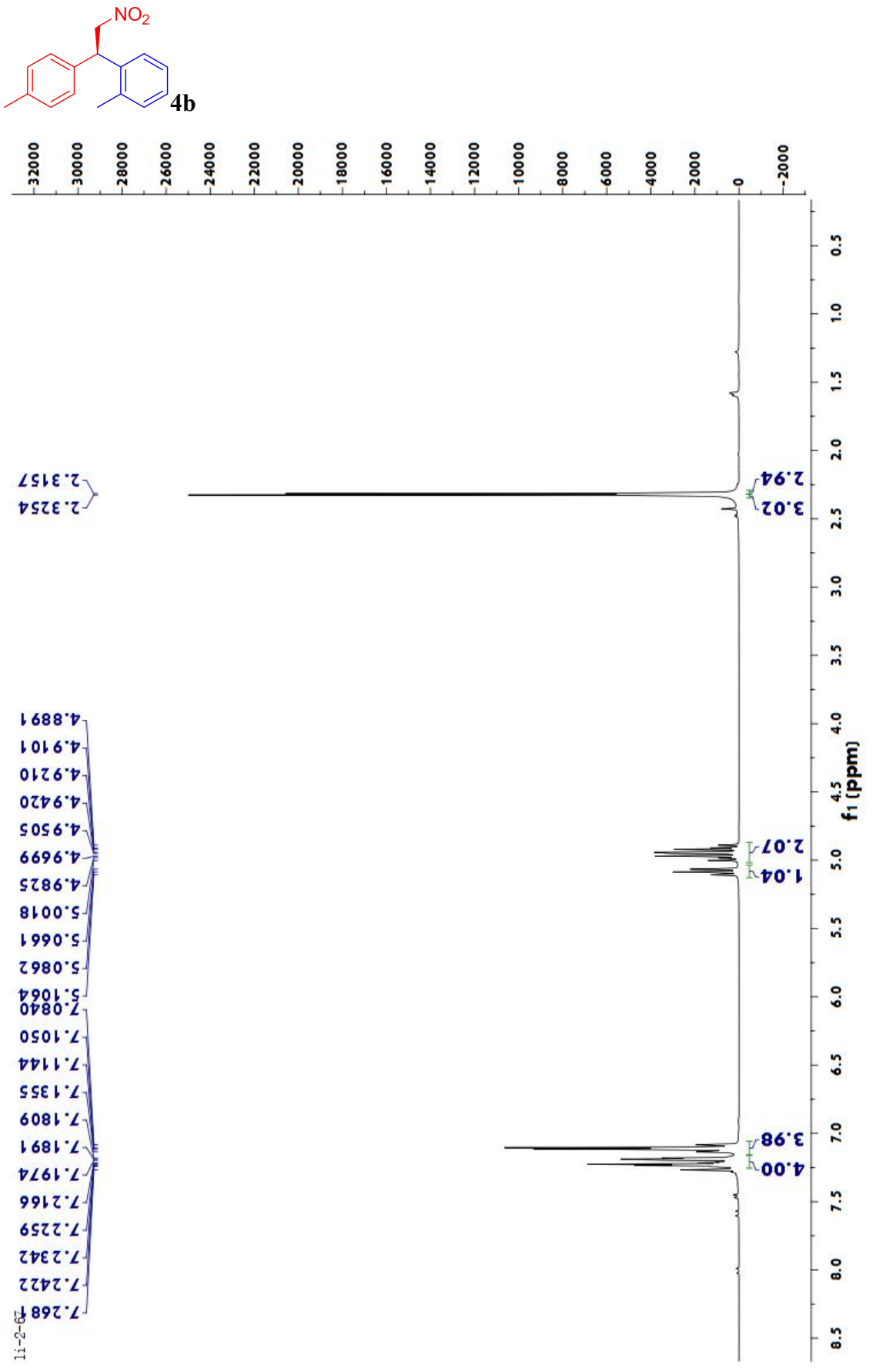
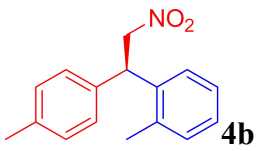
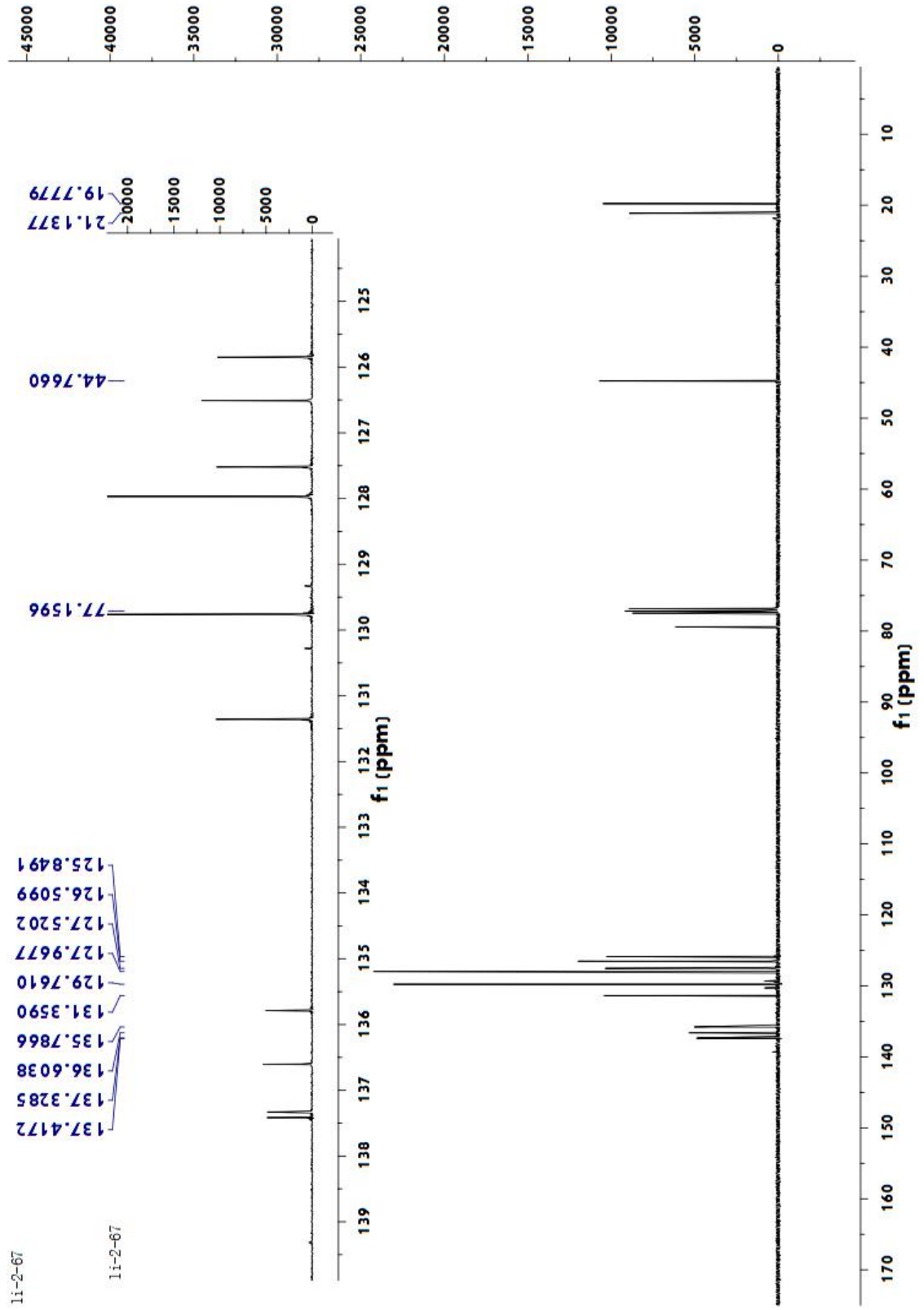
136.2820
137.3927
139.5267
1i2-23


NO2
4b
f1 (ppm)
li-2-67


NO2

4b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44.7660
77.1596
125.8491
126.5099
127.5202
127.9677
129.7610
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136.6038
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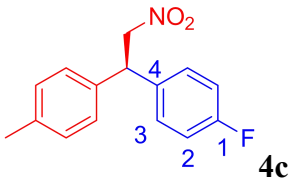
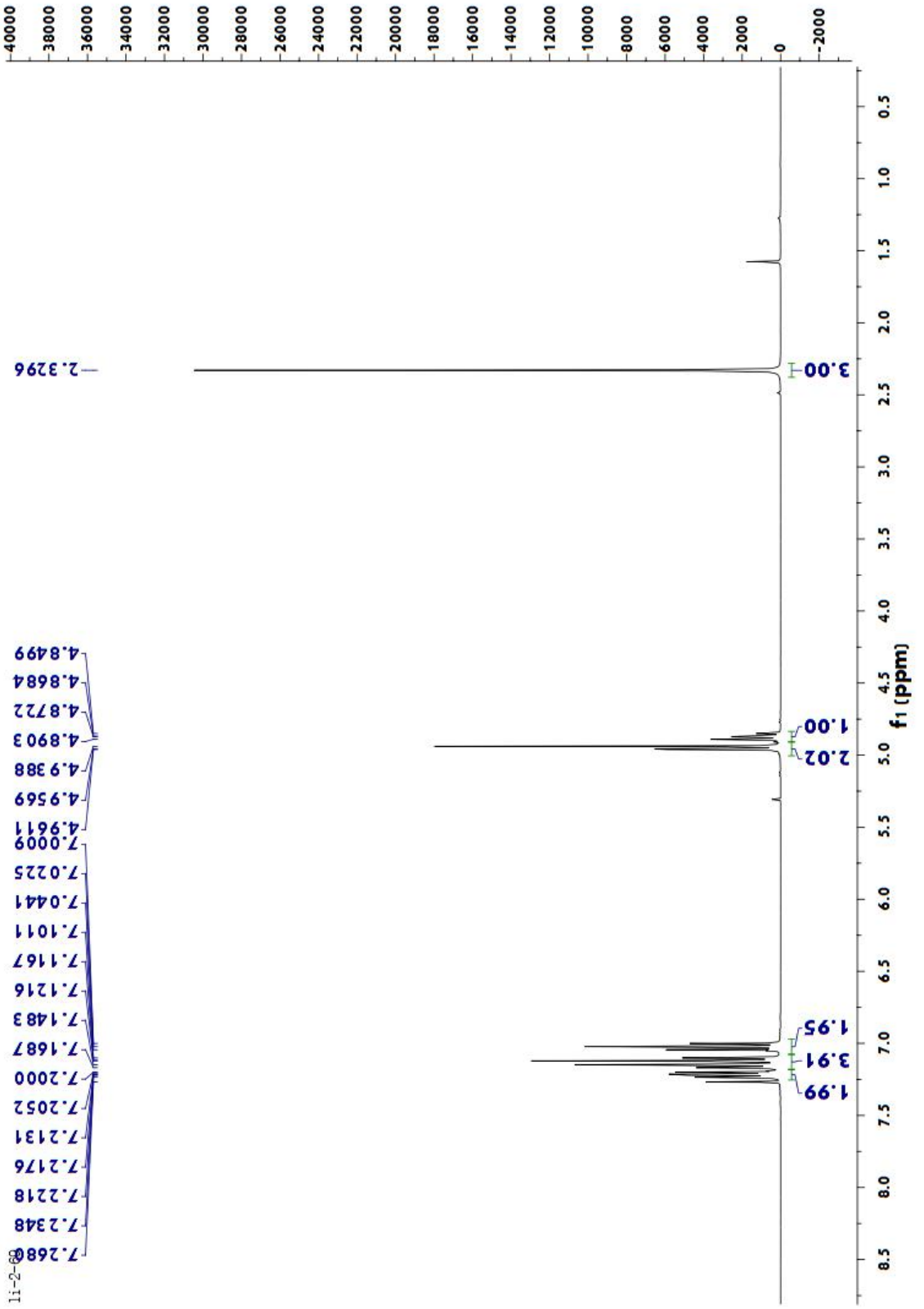
li-2-67
li-2-67
f1 (ppm)
f1 (ppm)


NO2
4
3
2
1
F

4c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1.00
2.02
1.95
3.91
1.99
4.8499
4.8684
4.8722
4.8903
4.9388
4.9569
4.9611
7.0009
7.0225
7.0441
7.1011
7.1167
7.1216
7.1483
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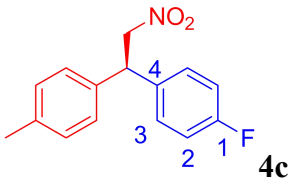
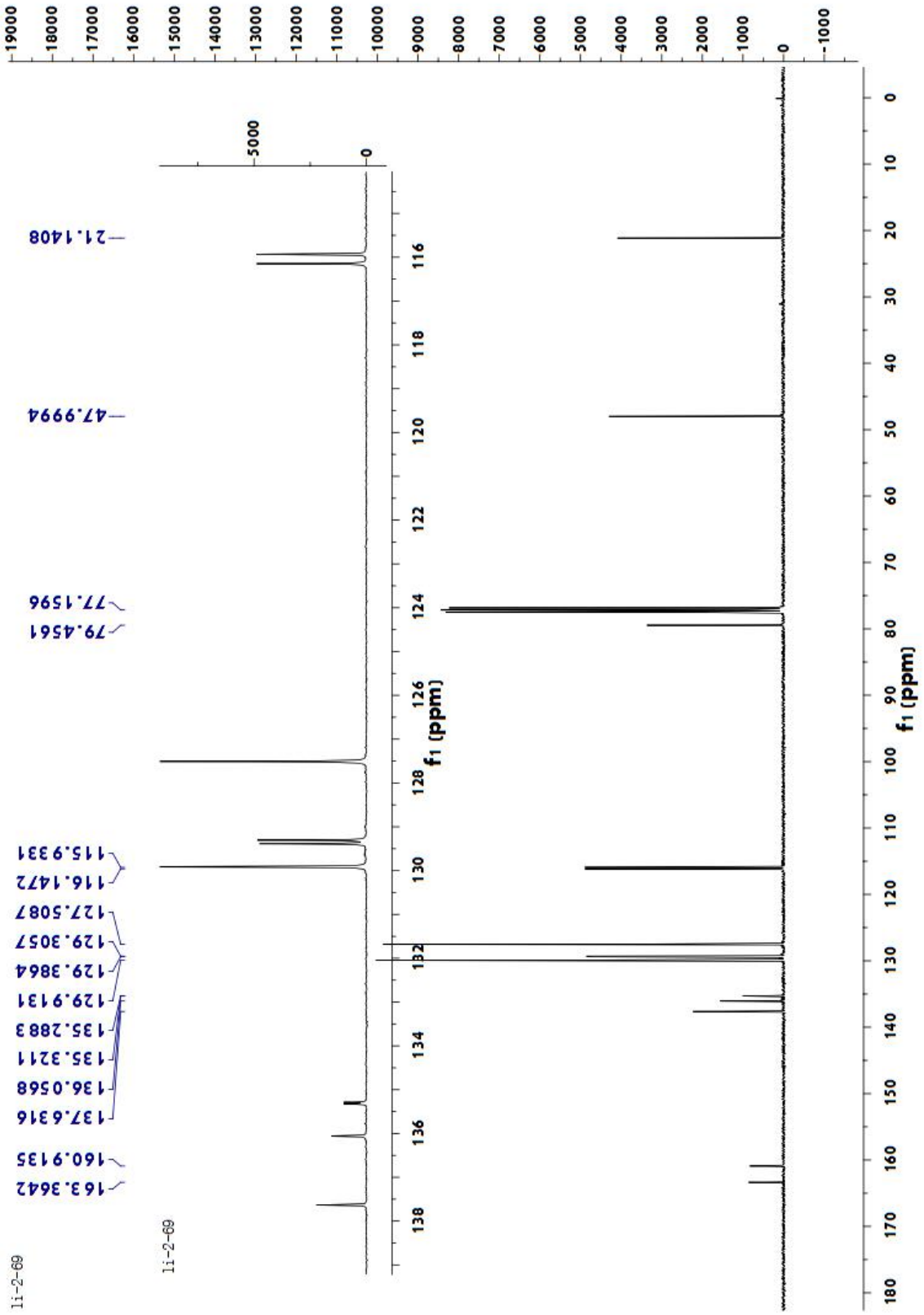
7.2000
7.2052
7.2131
7.2176
7.2218
7.2348
7.2680
f1 (ppm)


NO2
4
3
2
1
F

4c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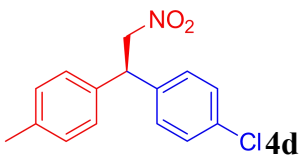
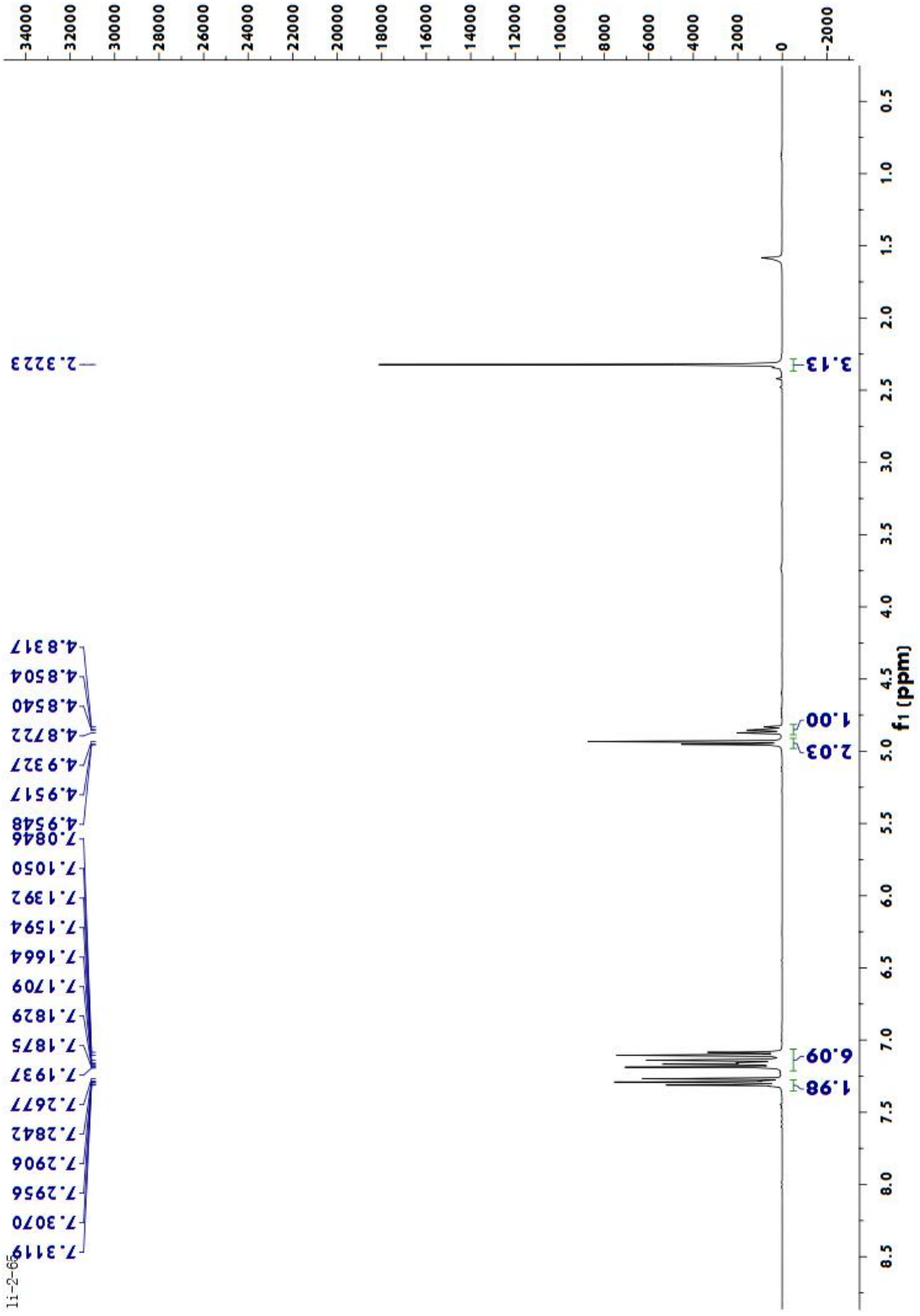
79.4561
115.9331
116.1472
127.5087
129.3057
129.3864
129.9131
135.2883
135.3211
136.0568
137.6316
160.9135
163.3642
li-2-69
li-2-69
f1 (ppm)
f1 (ppm)


NO2
Cl

4d


li-2-65
f1 (ppm)
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3.13
1.00
2.03
6.09
1.98
4.8317
4.8504
4.8540
4.8722
4.9327
4.9517
4.9548
7.0846
7.1050
7.1392
7.1594
7.1664
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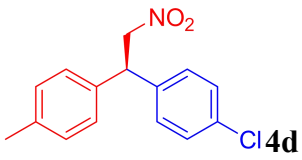
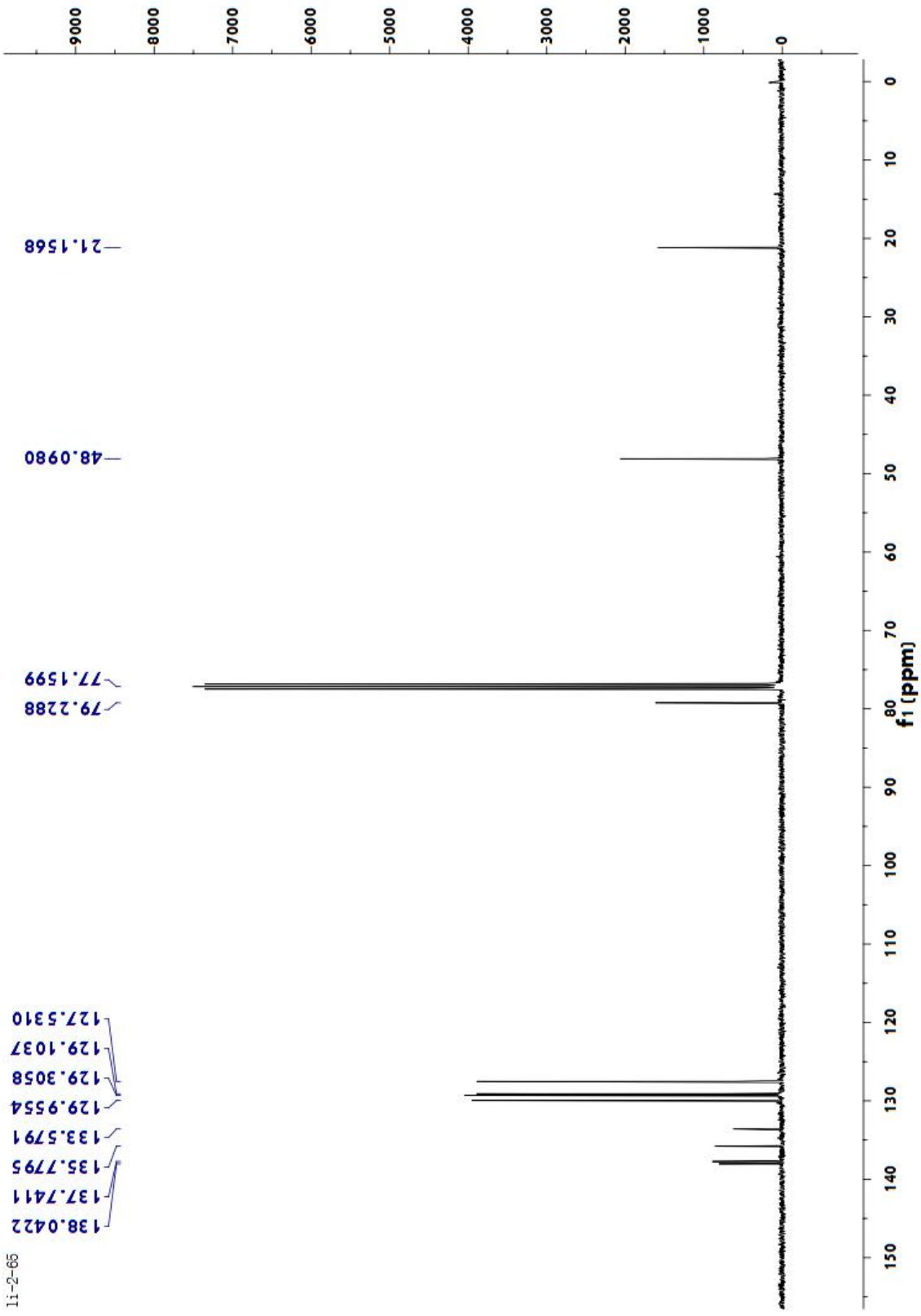
7.3119


NO2
Cl

4d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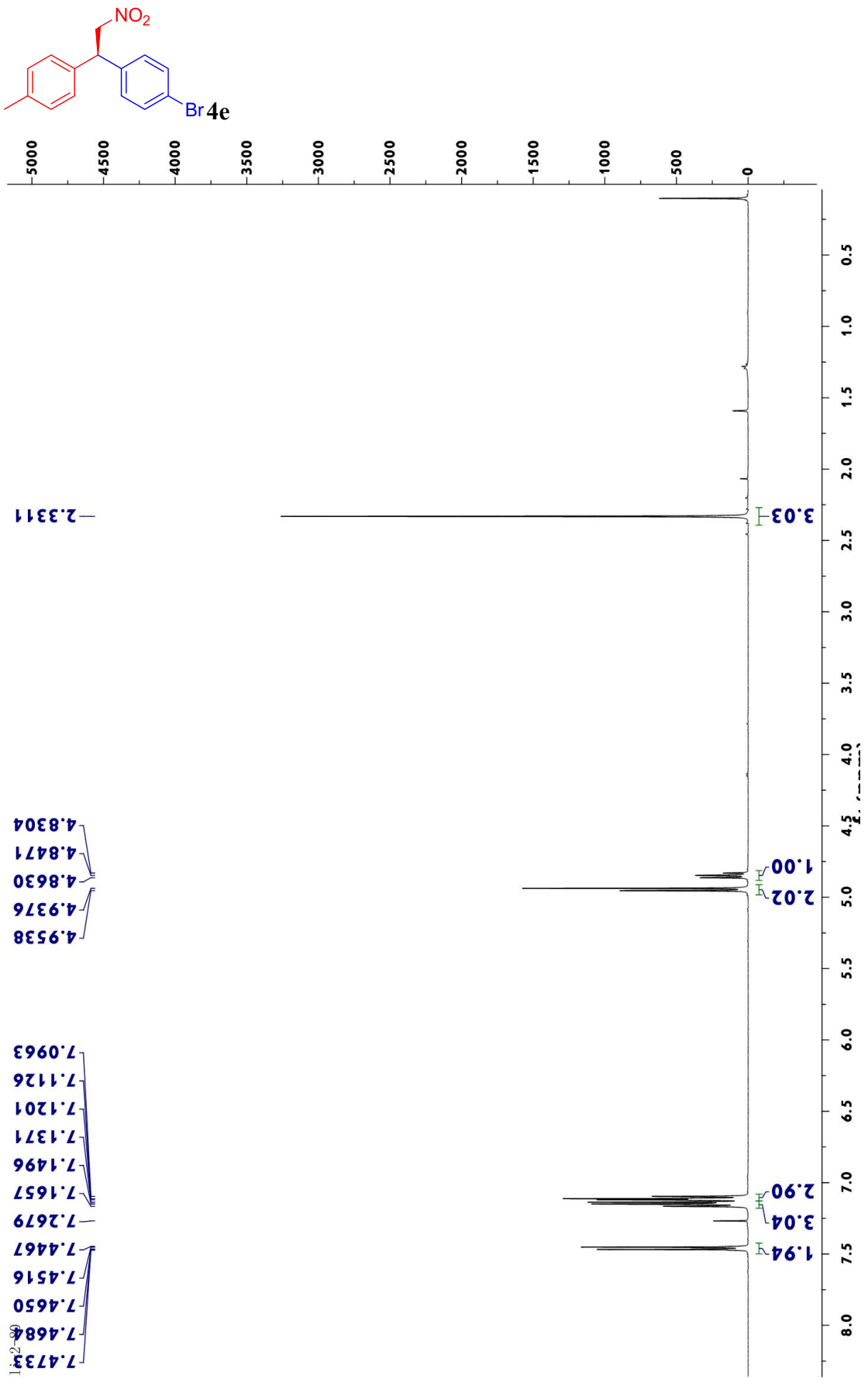
77.1599
79.2288
127.5310
129.1037
129.3058
129.9554
133.5791
135.7795
137.7411
138.0422
li-2-65
f1 (ppm)


NO2
Br
4e
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
2.3311
3.03
4.8304
4.8471
4.8630
4.9376
4.9538
1.00
2.02
7.0963
7.1126
7.1201
7.1371
7.1496
7.1657
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3.04
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7.4516
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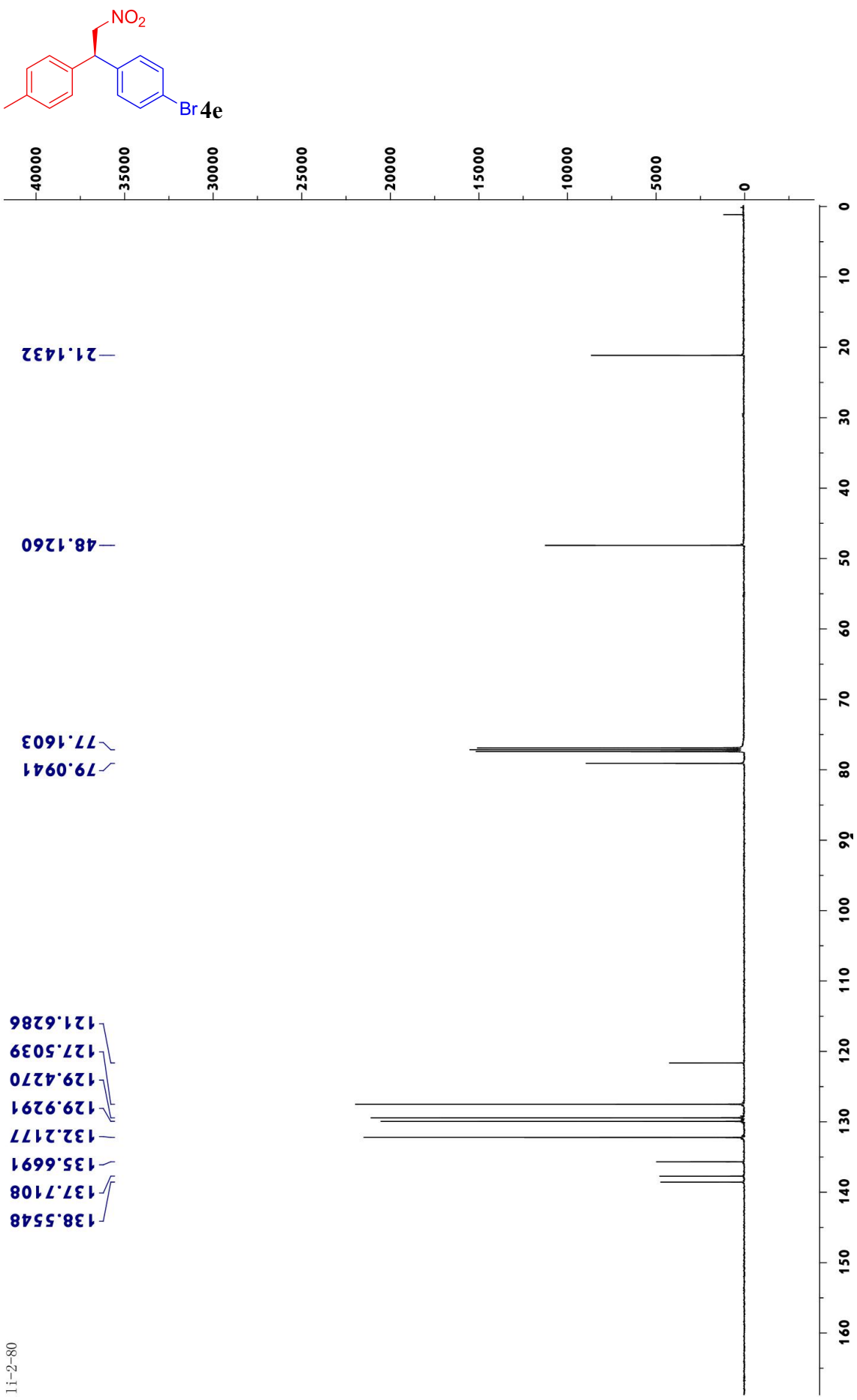
7.4684
7.4733
1.94
li-2-30


NO2
Br
4e
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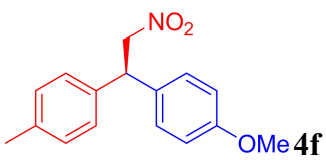
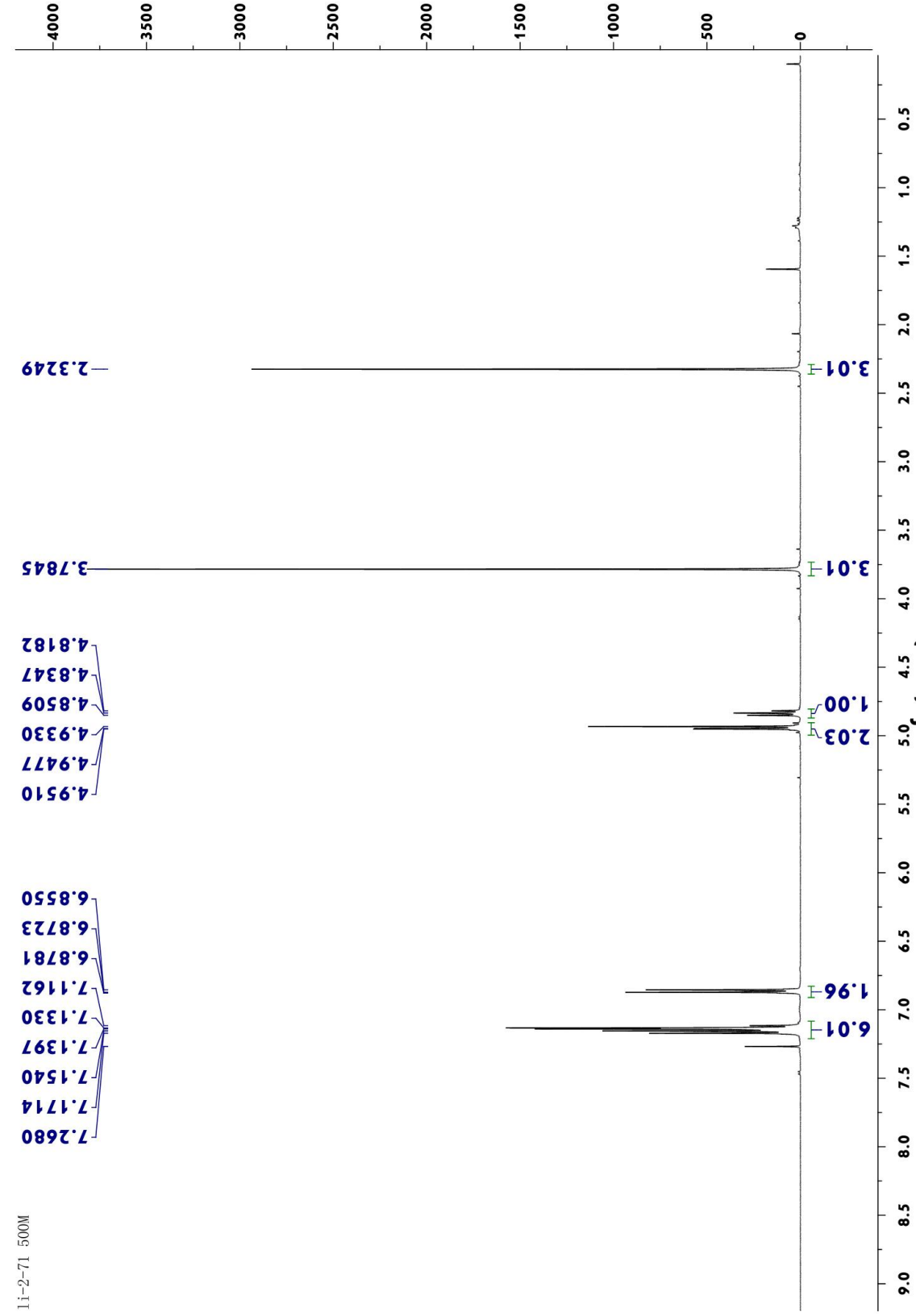
li-2-80


NO2
OMe

4f


2.3249
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4.8182
4.8347
4.8509
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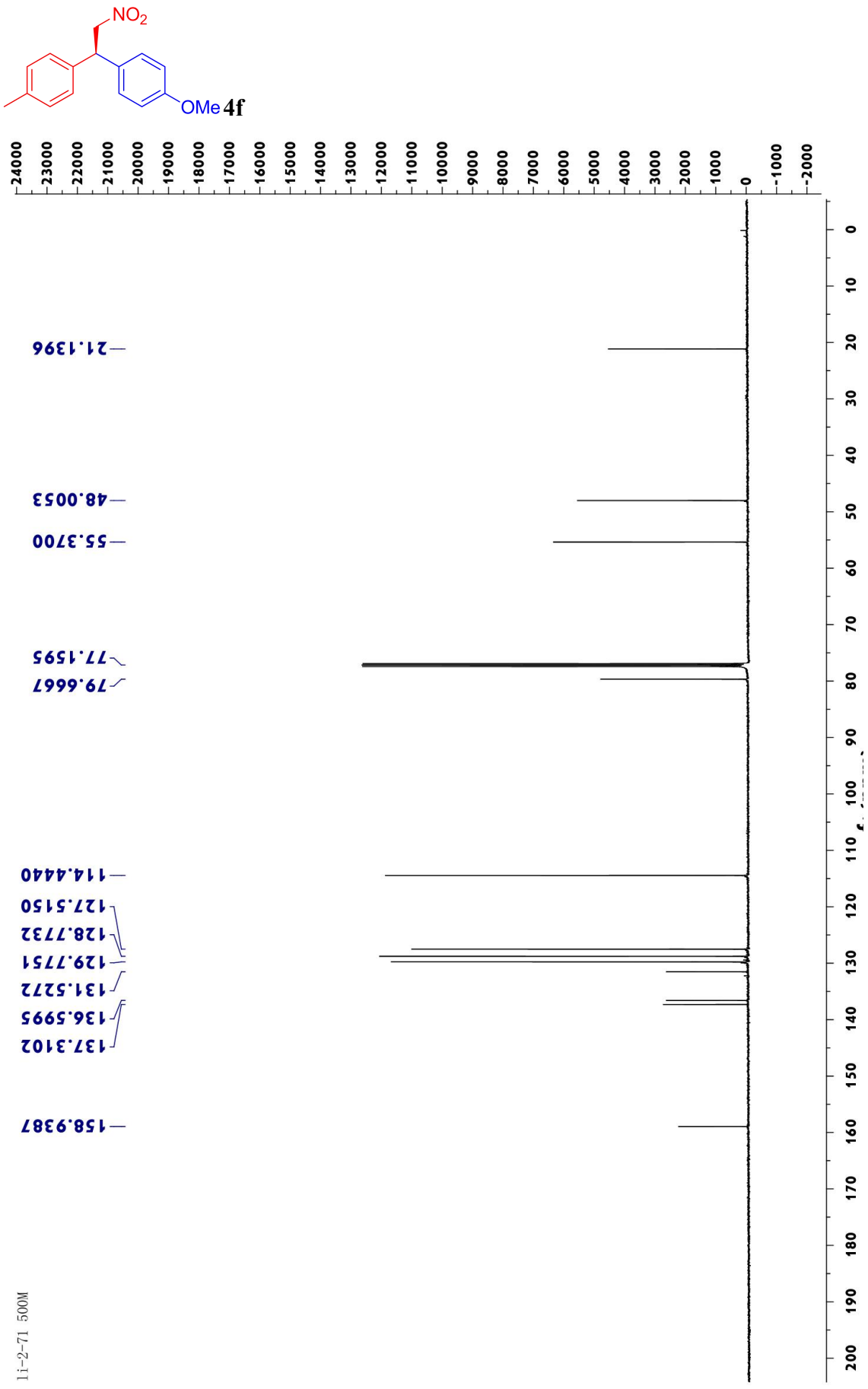
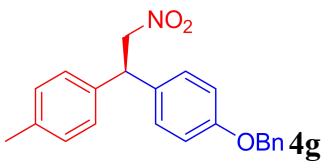
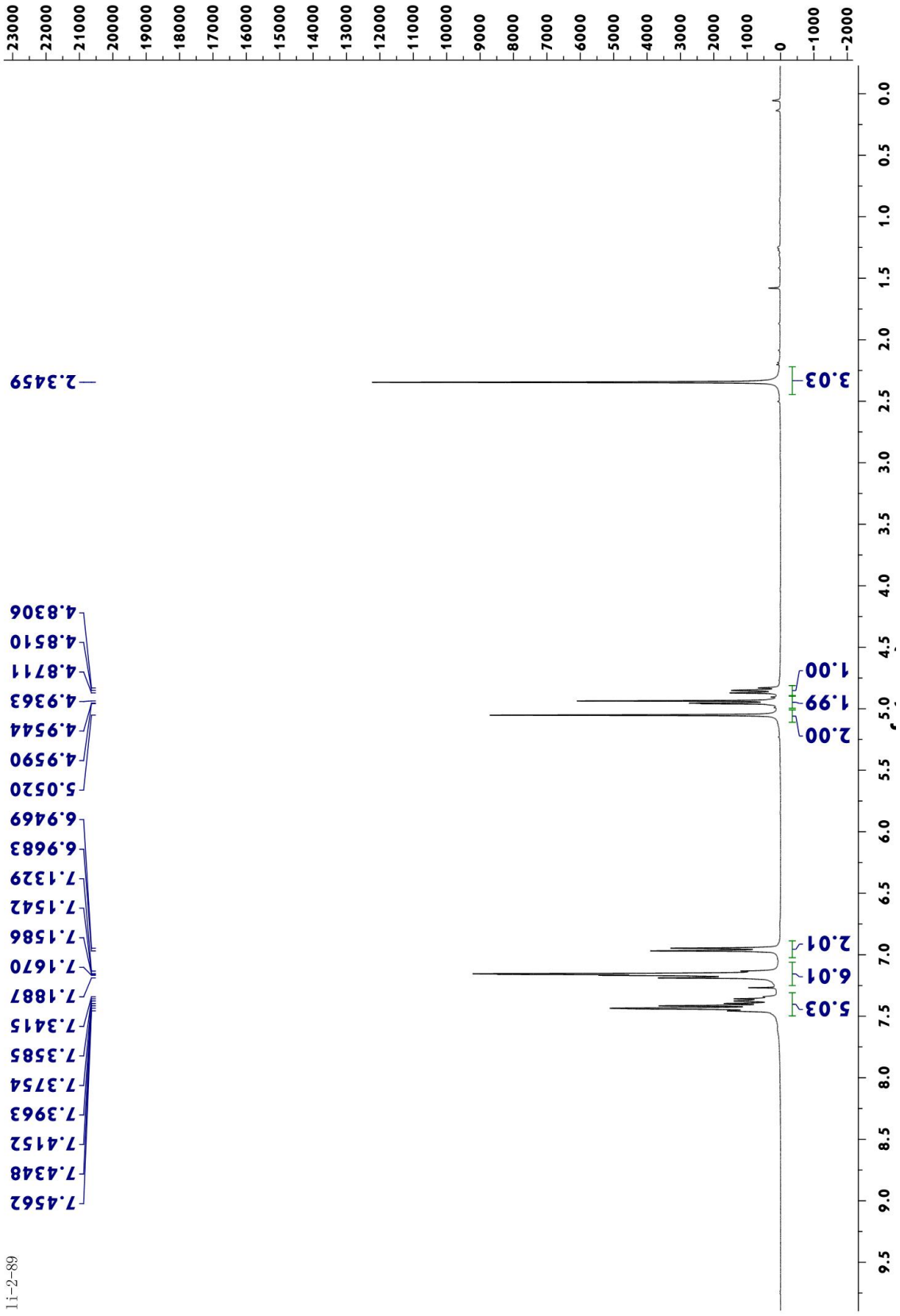
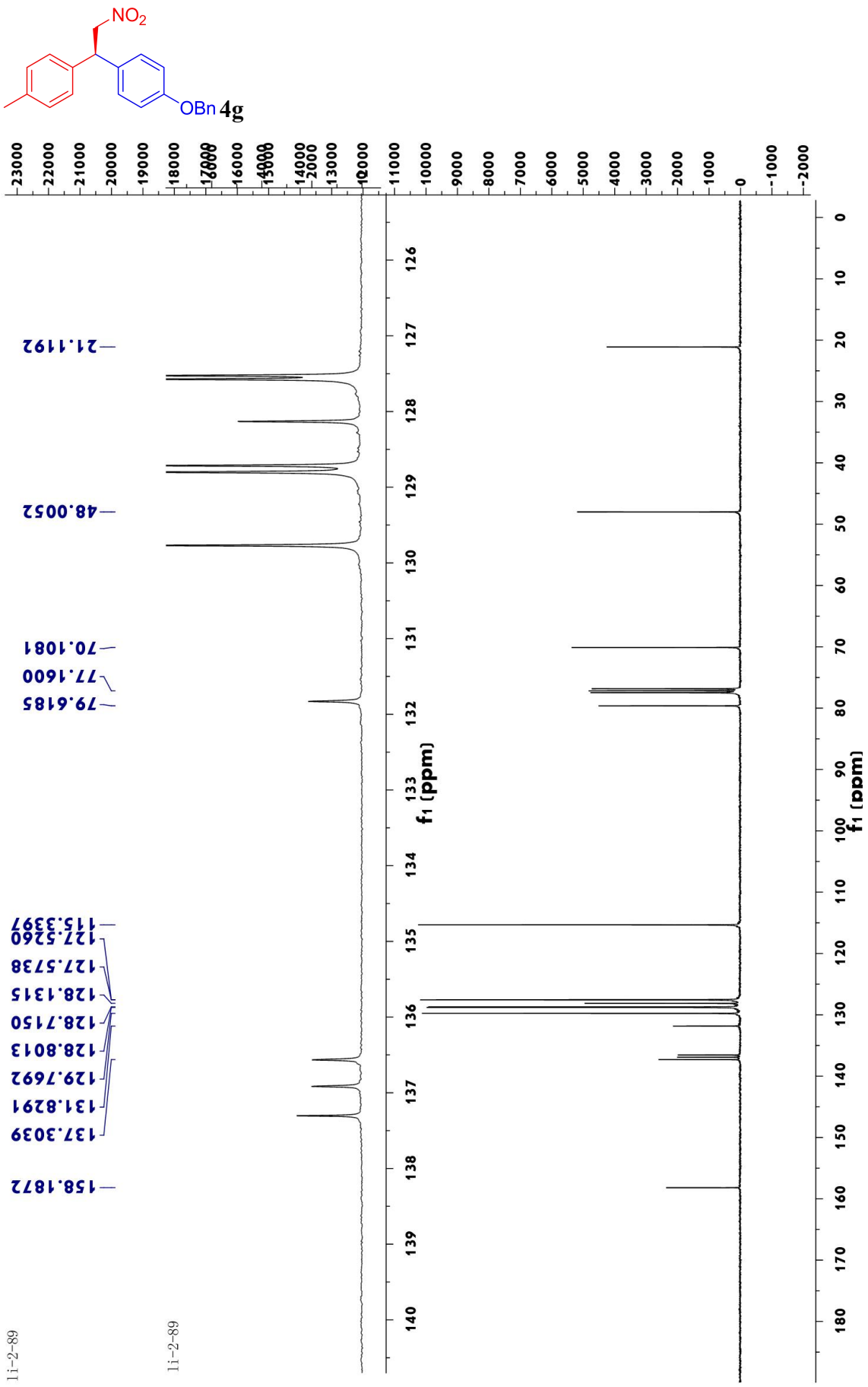
4.9477
4.9510
6.8550
6.8723
6.8781
7.1162
7.1330
7.1397
7.1540
7.1714
7.2680
3.01
3.01
1.00
2.03
1.96
6.01
li-2-71 500M

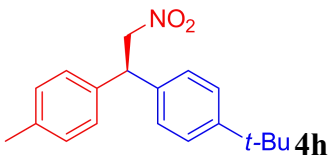

NO2
OMe
4f
21.1396
48.0053
55.3700
77.1595
79.6667
114.4440
127.5150
128.7732
129.7751
131.5272
136.5995
137.3102
158.9387
li-2-71 500M


NO2
OBn

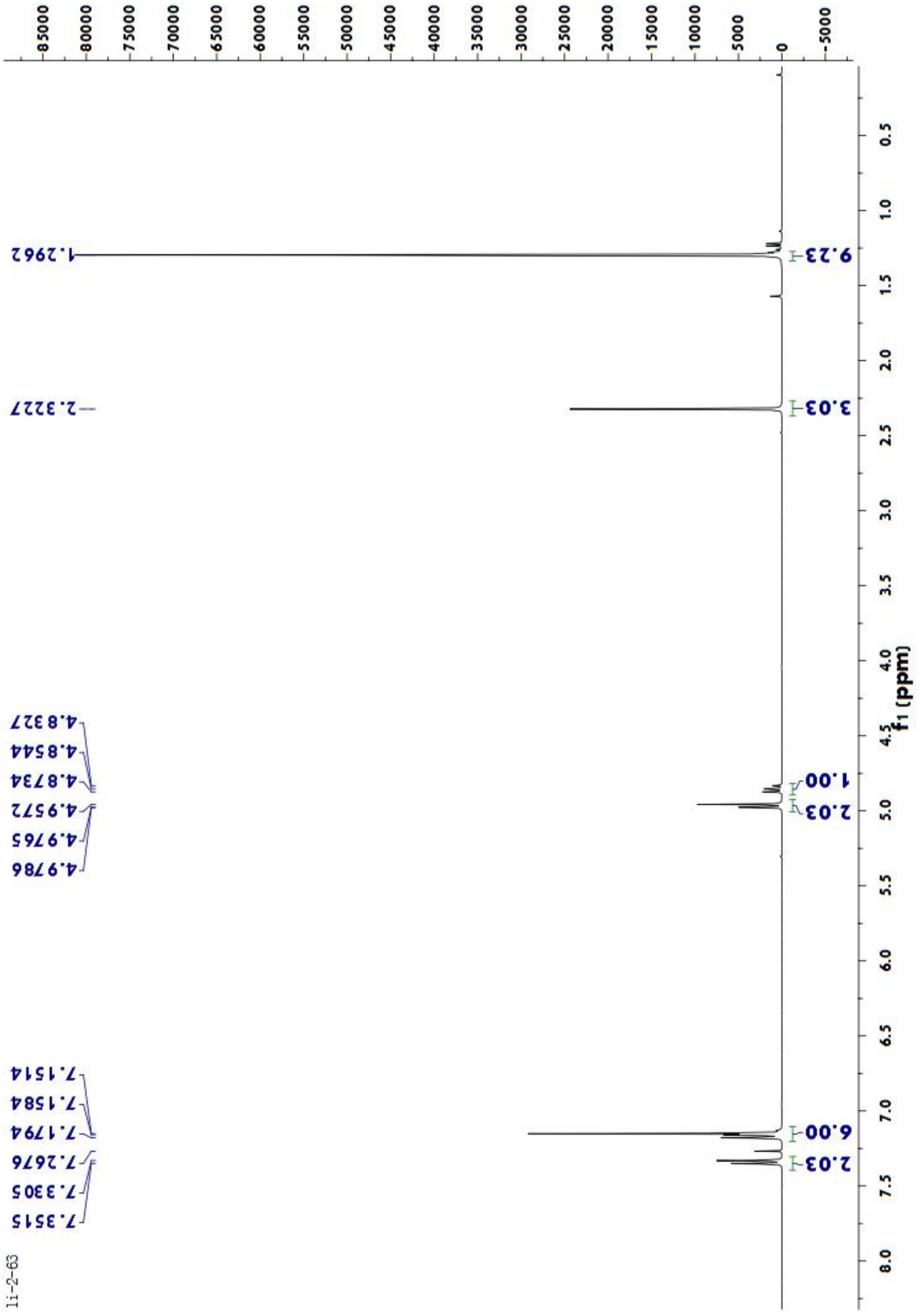
4g

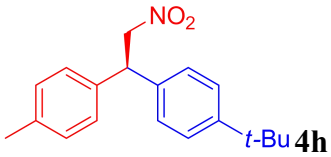

2.3459
4.8306
4.8510
4.8711
4.9363
4.9544
4.9590
5.0520
6.9469
6.9683
7.1329
7.1542
7.1586
7.1670
7.1887
7.3415
7.3585
7.3754
7.3963
7.4152
7.4348
7.4562
3.03
1.00
1.99
2.00
2.01
6.01
5.03
li-2-89


NO2
OBn
4g
21.1192
48.0052
70.1081
77.1600
79.6185
115.3397
127.5260
127.5738
128.1315
128.7150
128.8013
129.7692
131.8291
137.3039
158.1872
f1 (ppm)
li-2-89
li-2-89

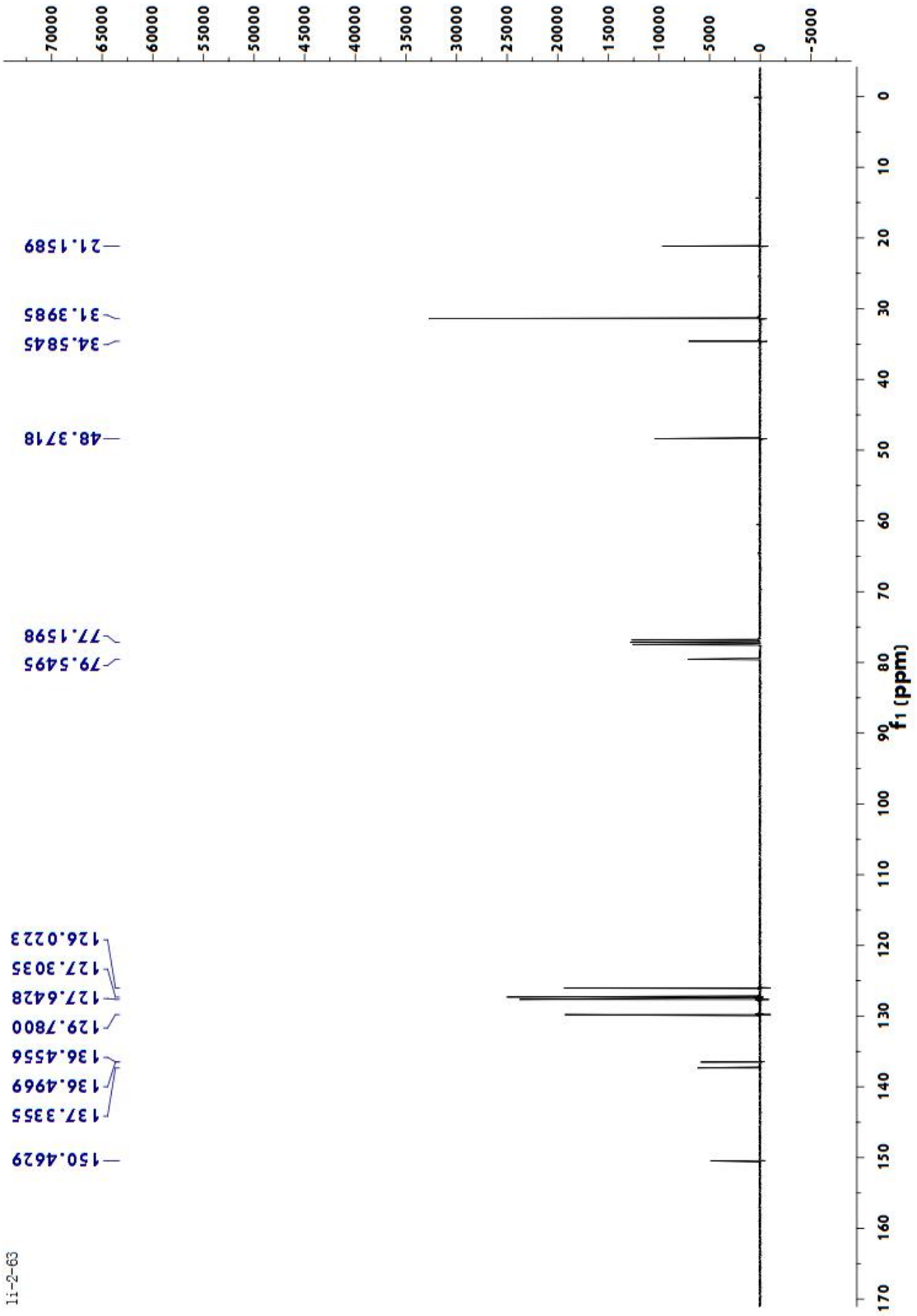

NO2
t-Bu

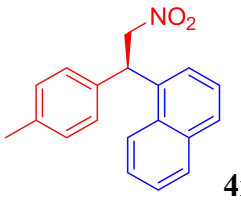
4h


1.2962
2.3227
4.8327
4.8544
4.8734
4.9572
4.9765
4.9786
7.1514
7.1584
7.1794
7.2676
7.3305
7.3515
9.23
3.03
1.00
2.03
6.00
2.03
f1 (ppm)
1i-2-63

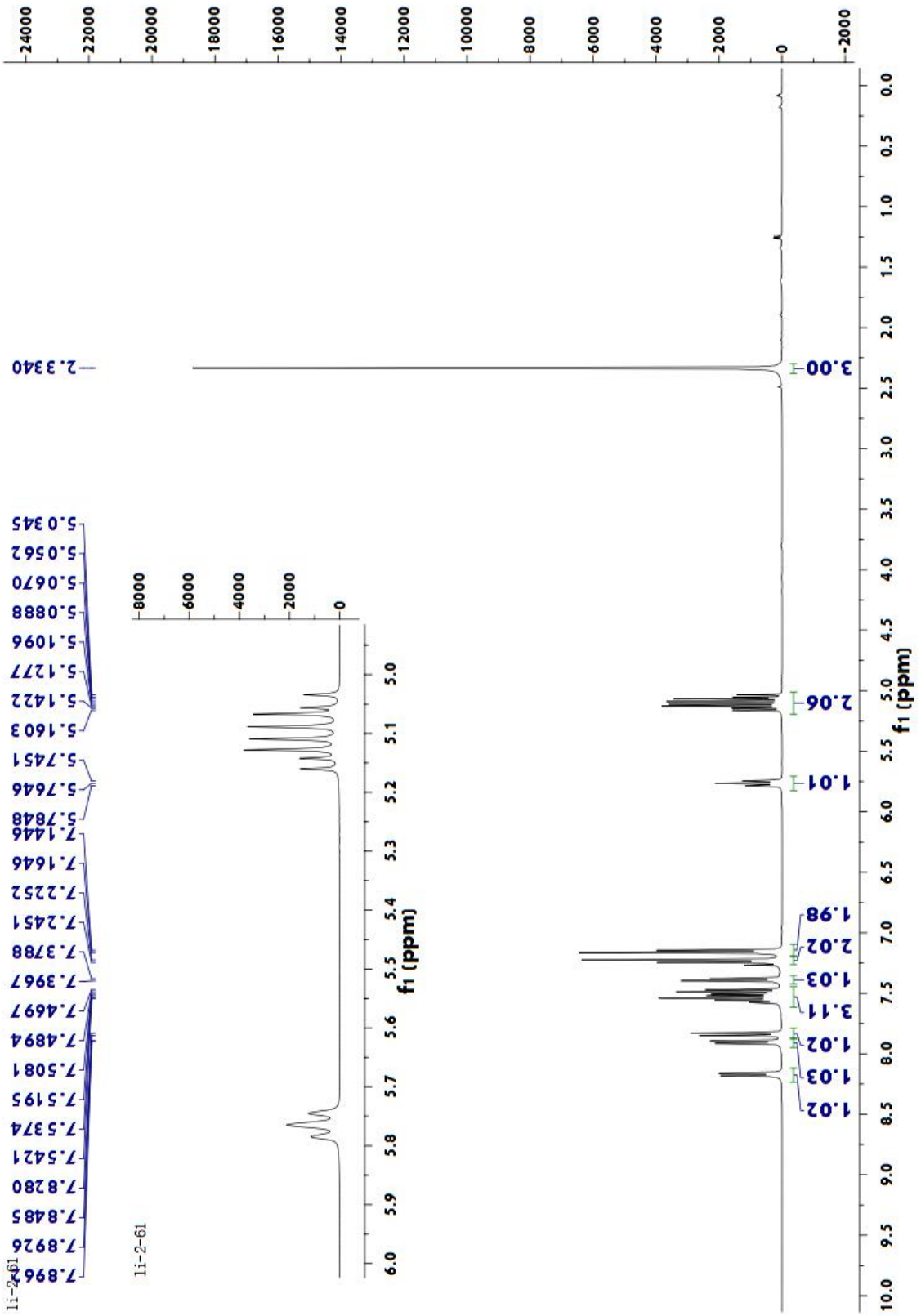

NO2
t-Bu

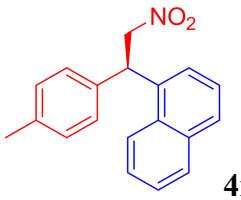
4h


21.1589
31.3985
34.5845
48.3718
77.1598
79.5495
126.0223
127.3035
127.6428
129.7800
136.4556
136.4969
137.3355
150.4629
li-2-63
f1 (ppm)

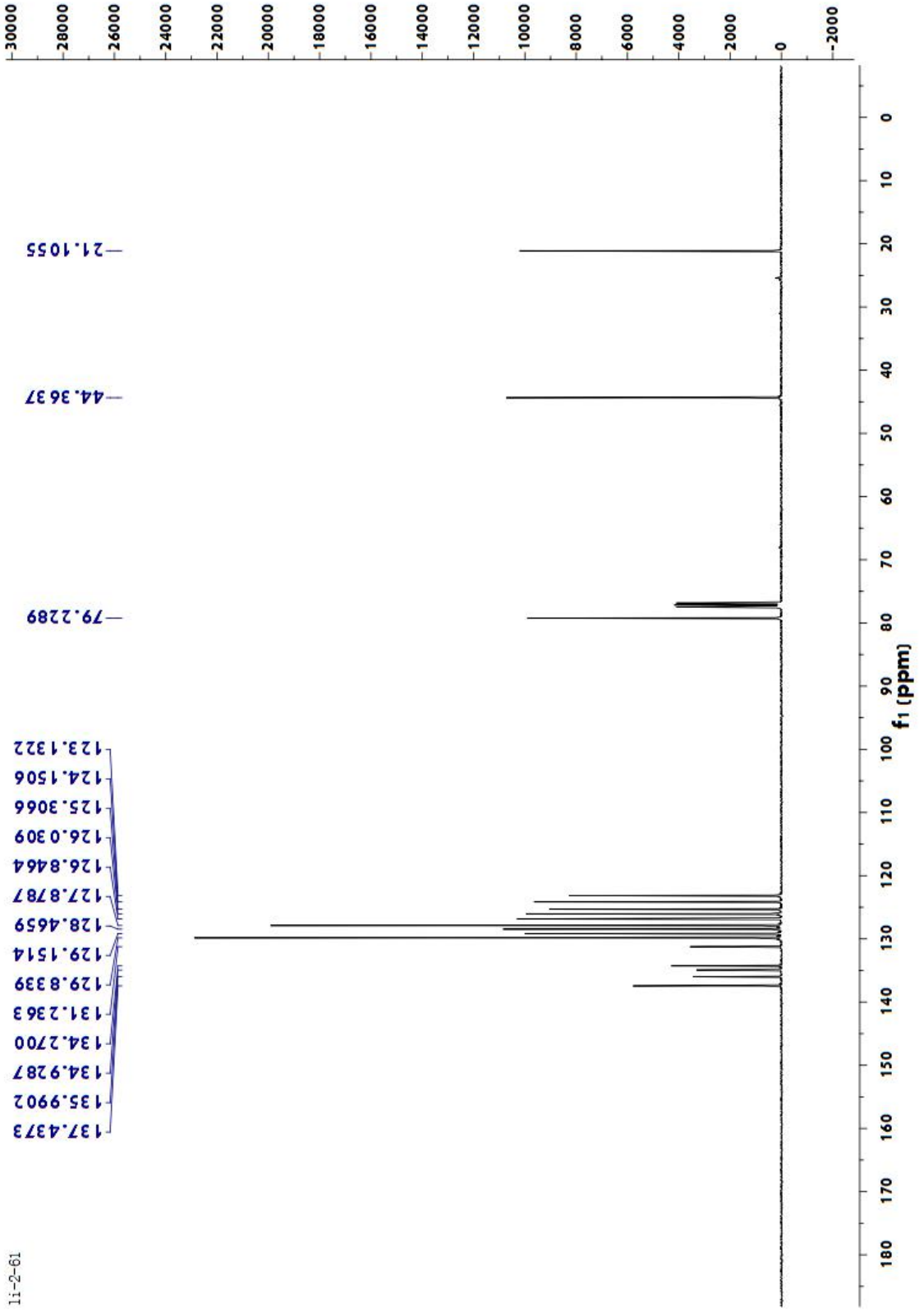


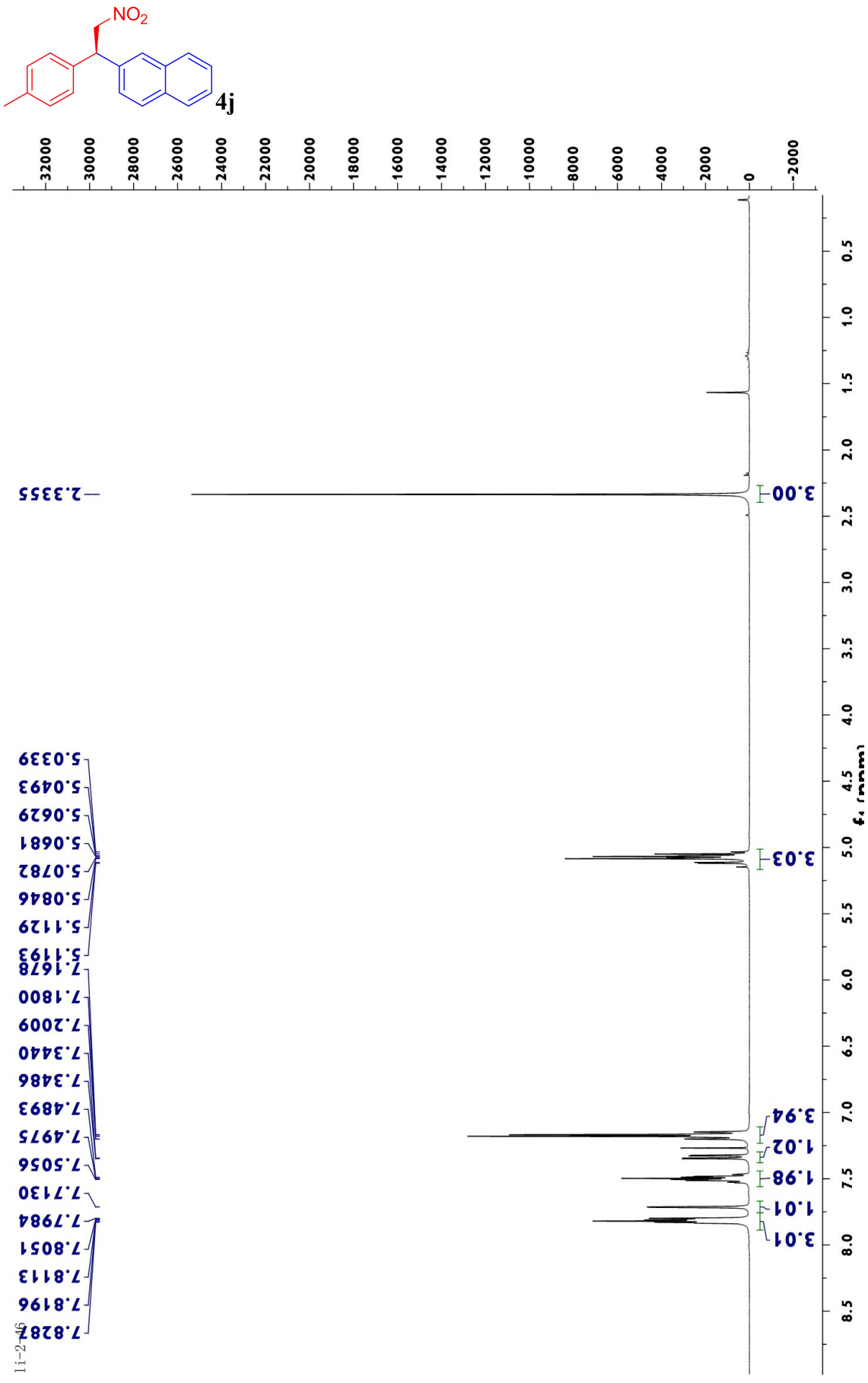
4i

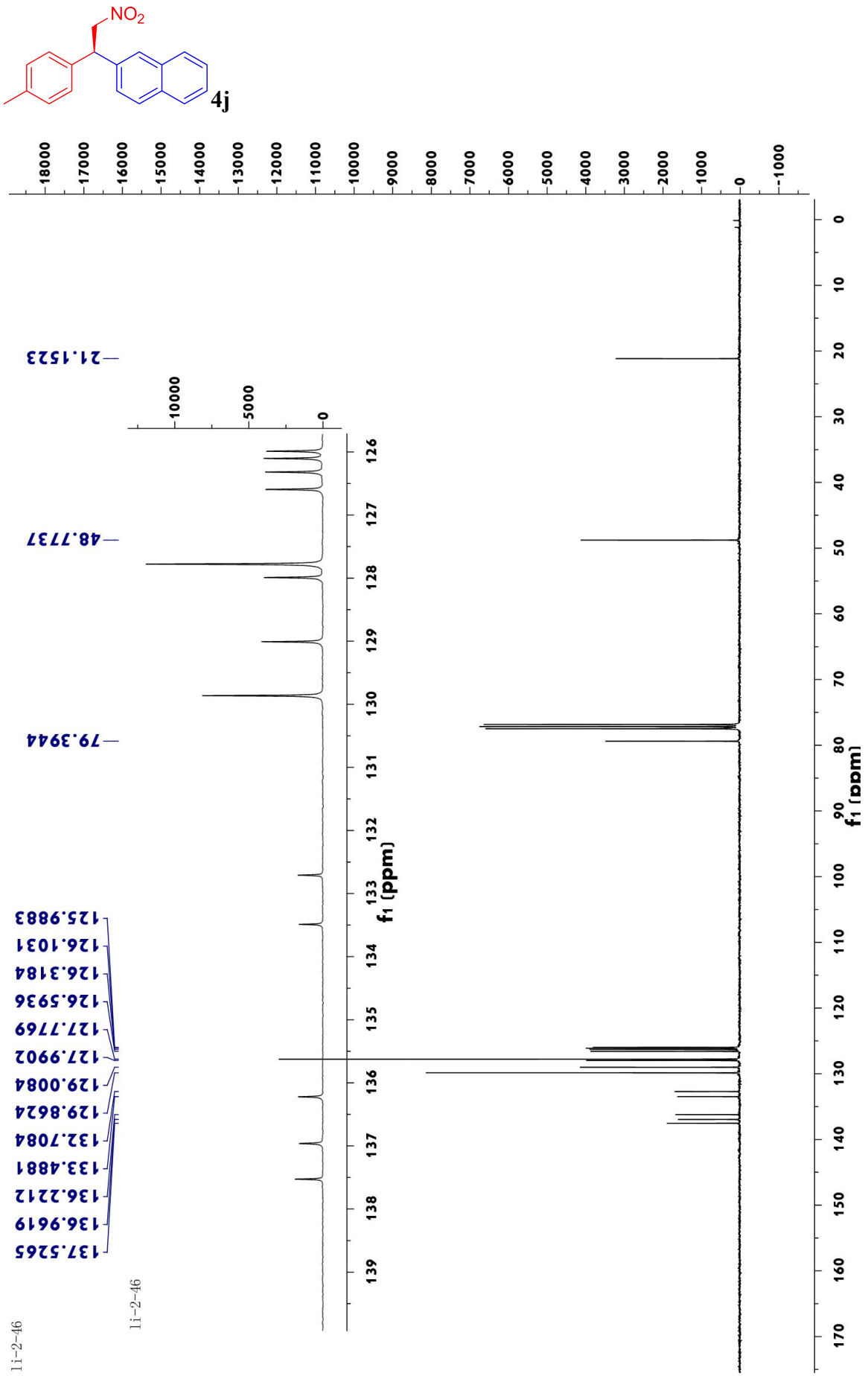


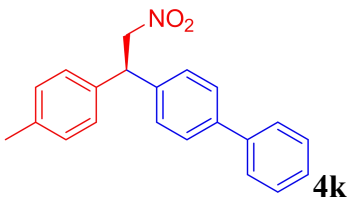

NO2

4i

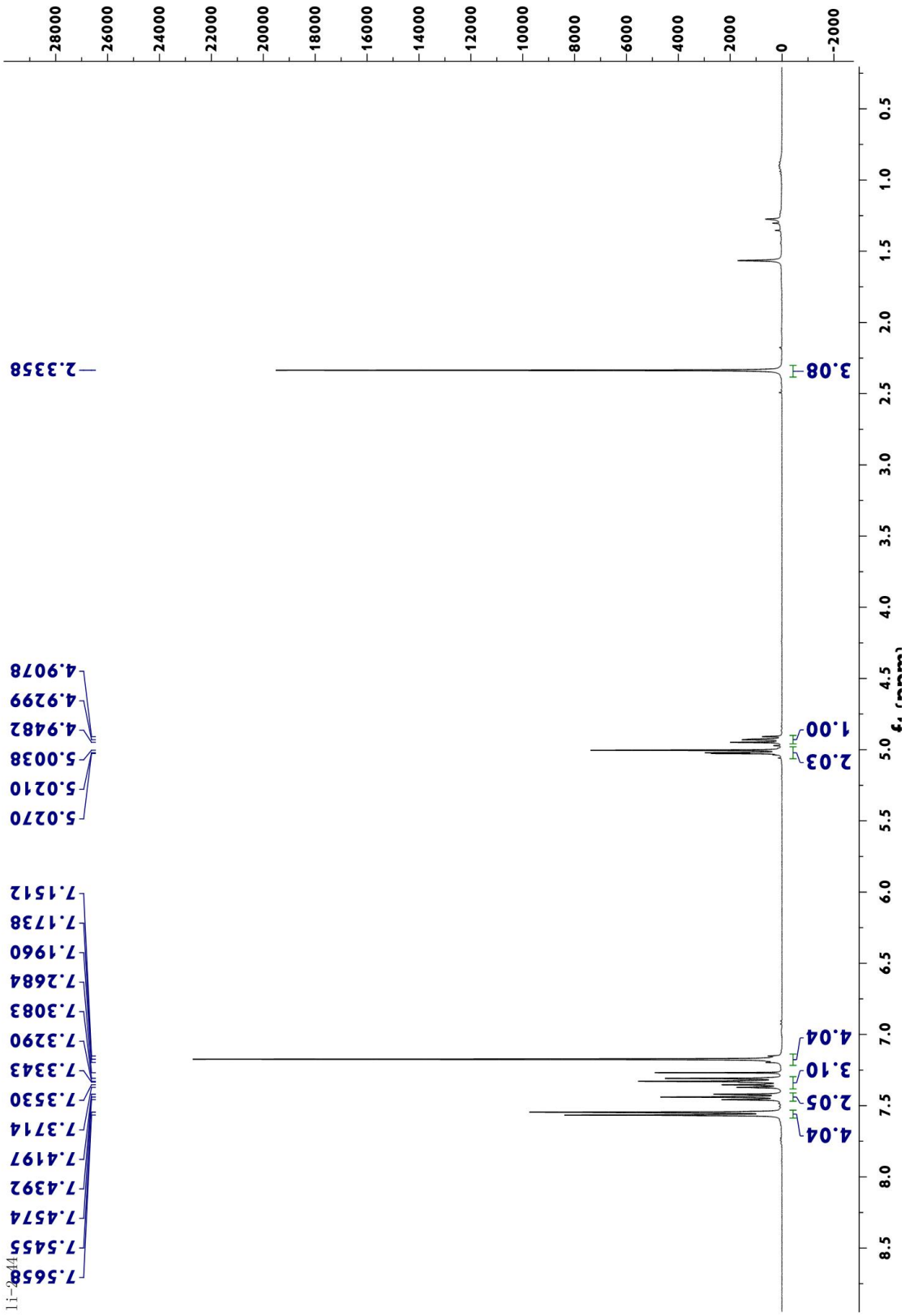

21.1055
44.3637
79.2289
123.1322
124.1506
125.3066
126.0309
126.8464
127.8787
128.4659
129.1514
129.8339
131.2363
134.2700
134.9287
135.9902
137.4373
f1 (ppm)
li-2-61

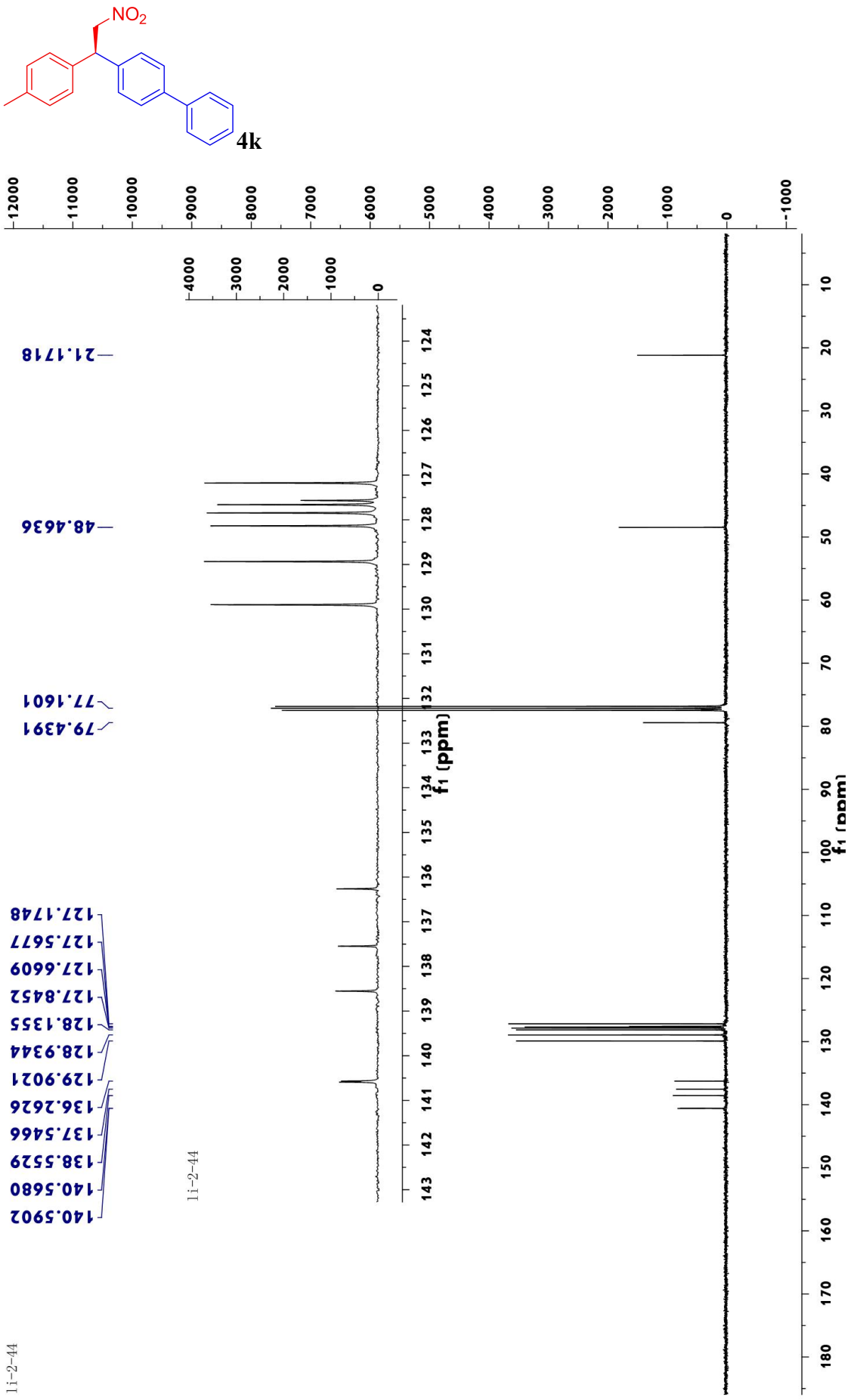

NO2
4j
li-2-46
f1 (ppm)

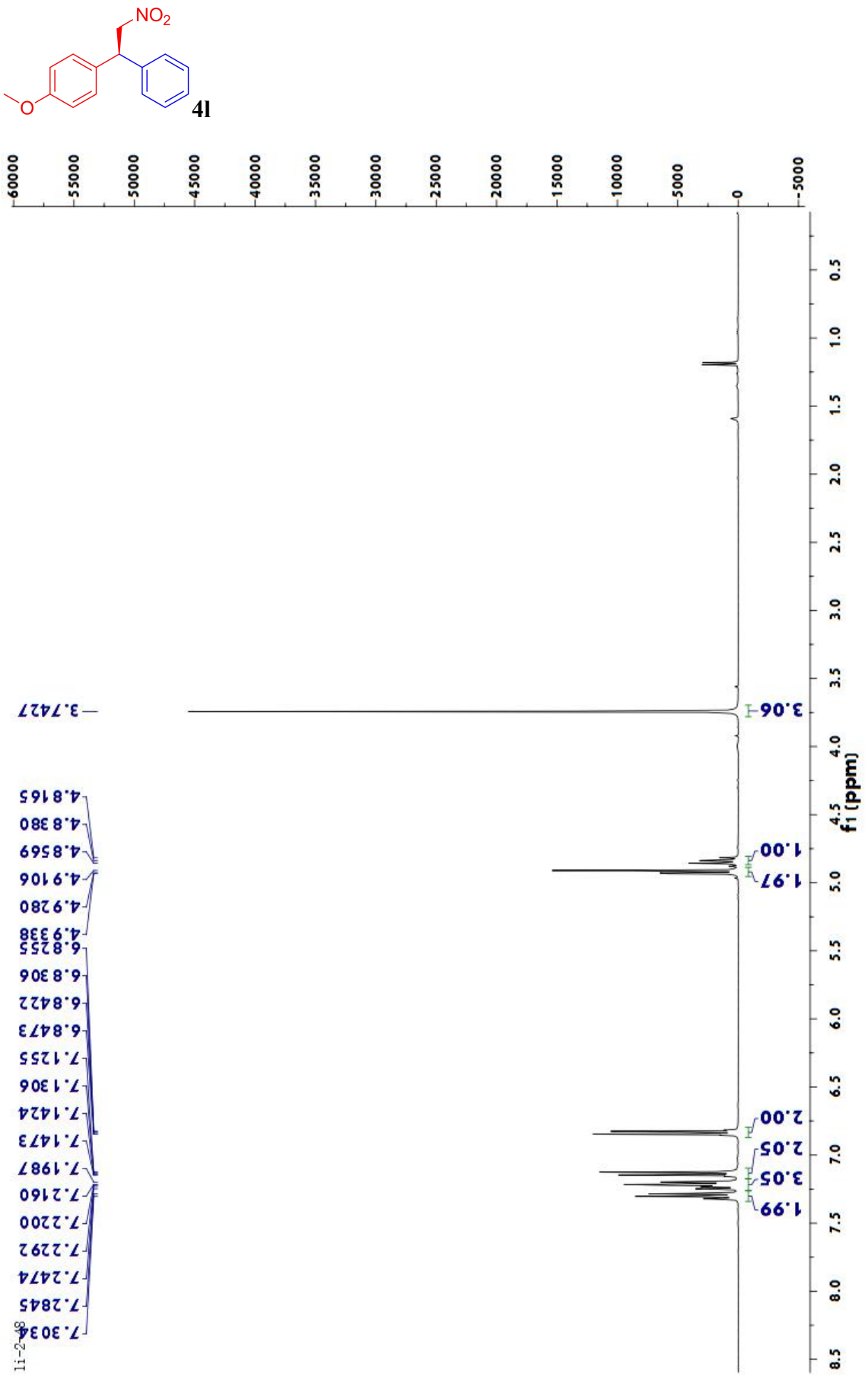

NO2
4j
21.1523
48.7737
79.3944
125.9883
126.1031
126.3184
126.5936
127.7769
127.9902
129.0084
129.8624
132.7084
133.4881
136.2212
136.9619
137.5265
f1 (ppm)
li-2-46

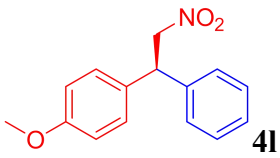

NO2

4k

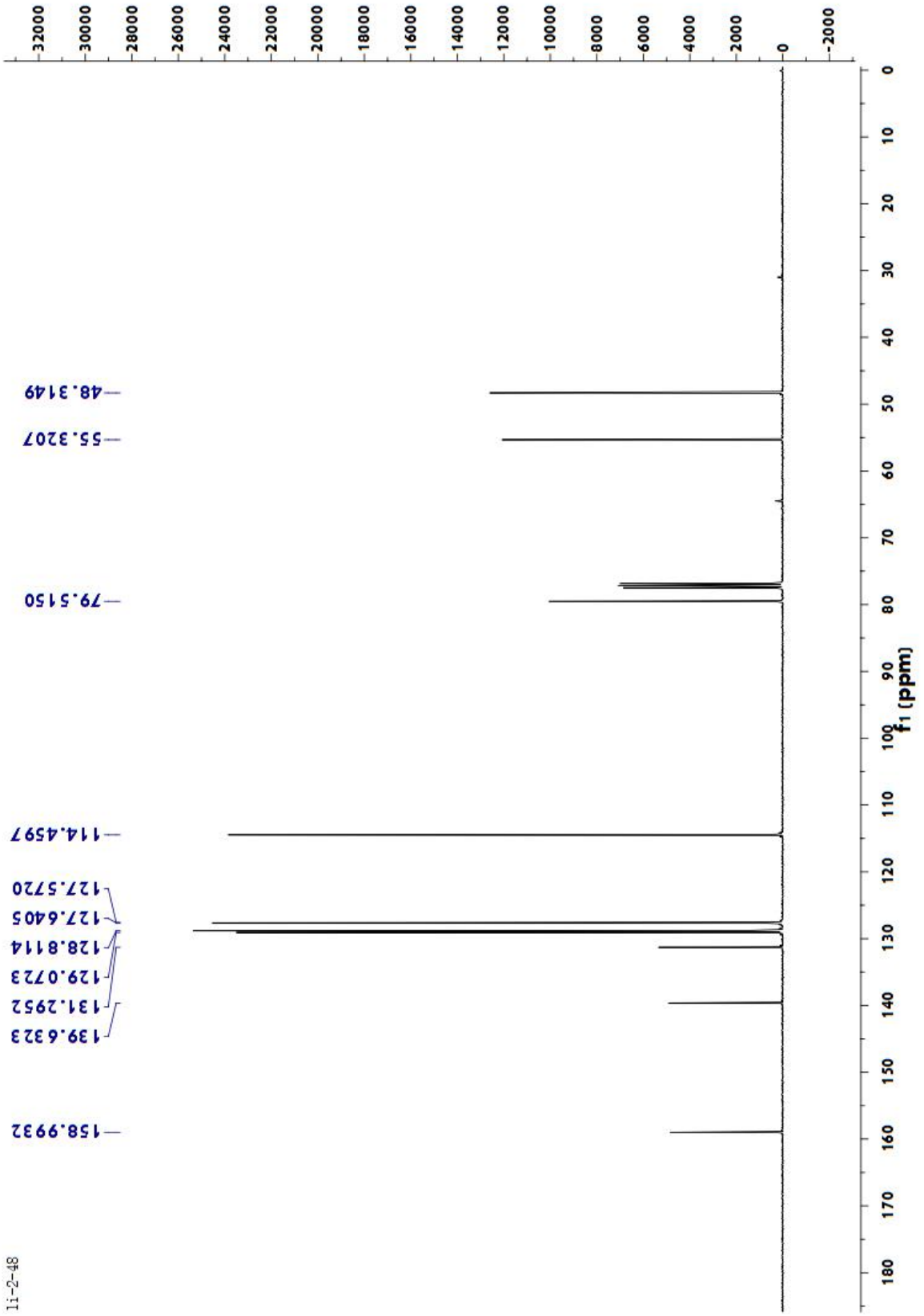

2.3358
4.9078
4.9299
4.9482
5.0038
5.0210
5.0270
7.1512
7.1738
7.1960
7.2684
7.3083
7.3290
7.3343
7.3530
7.3714
7.4197
7.4392
7.4574
7.5455
7.5658
3.08
1.00
2.03
4.04
3.10
2.05
4.04
11-244

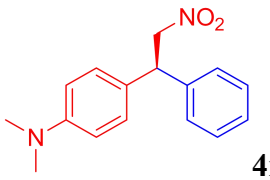

NO2
4k
21.1718
48.4636
77.1601
79.4391
127.1748
127.5677
127.6609
127.8452
128.1355
128.9344
129.9021
136.2626
137.5466
138.5529
140.5680
140.5902
li-2-44
f1 (ppm)


NO2
O
4l
f1 (ppm)
3.7427
4.8165
4.8380
4.8569
4.9106
4.9280
4.9338
6.8255
6.8306
6.8422
6.8473
7.1255
7.1306
7.1424
7.1473
7.1987
7.2160
7.2200
7.2292
7.2474
7.2845
7.3034
3.06
1.00
1.97
2.00
2.05
3.05
1.99
li-2-48

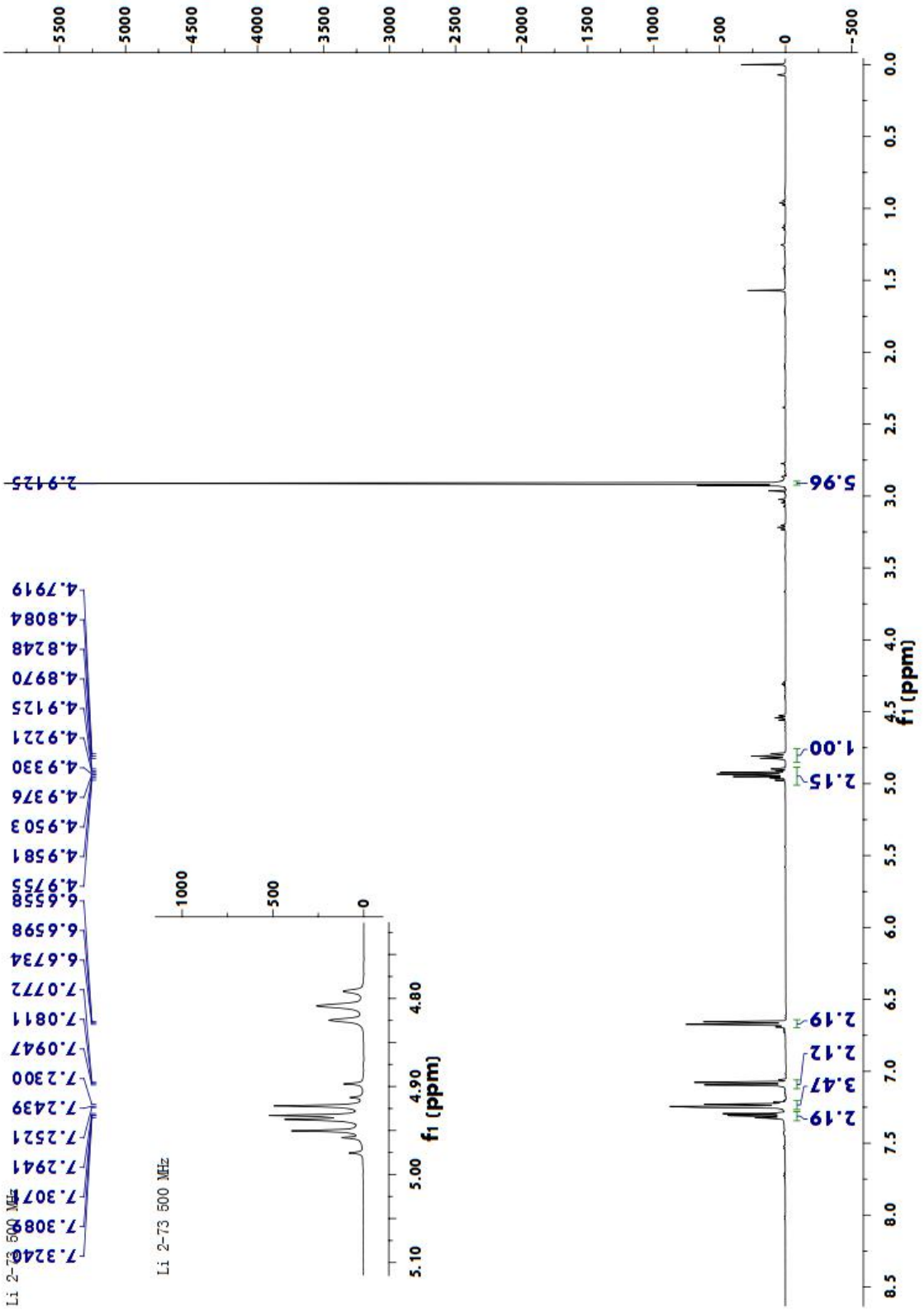

NO2
O

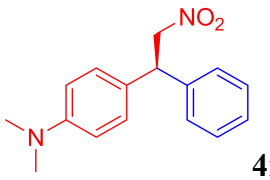
4l


48.3149
55.3207
79.5150
114.4597
127.5720
127.6405
128.8114
129.0723
131.2952
139.6323
158.9932
f1 (ppm)
1i-2-48

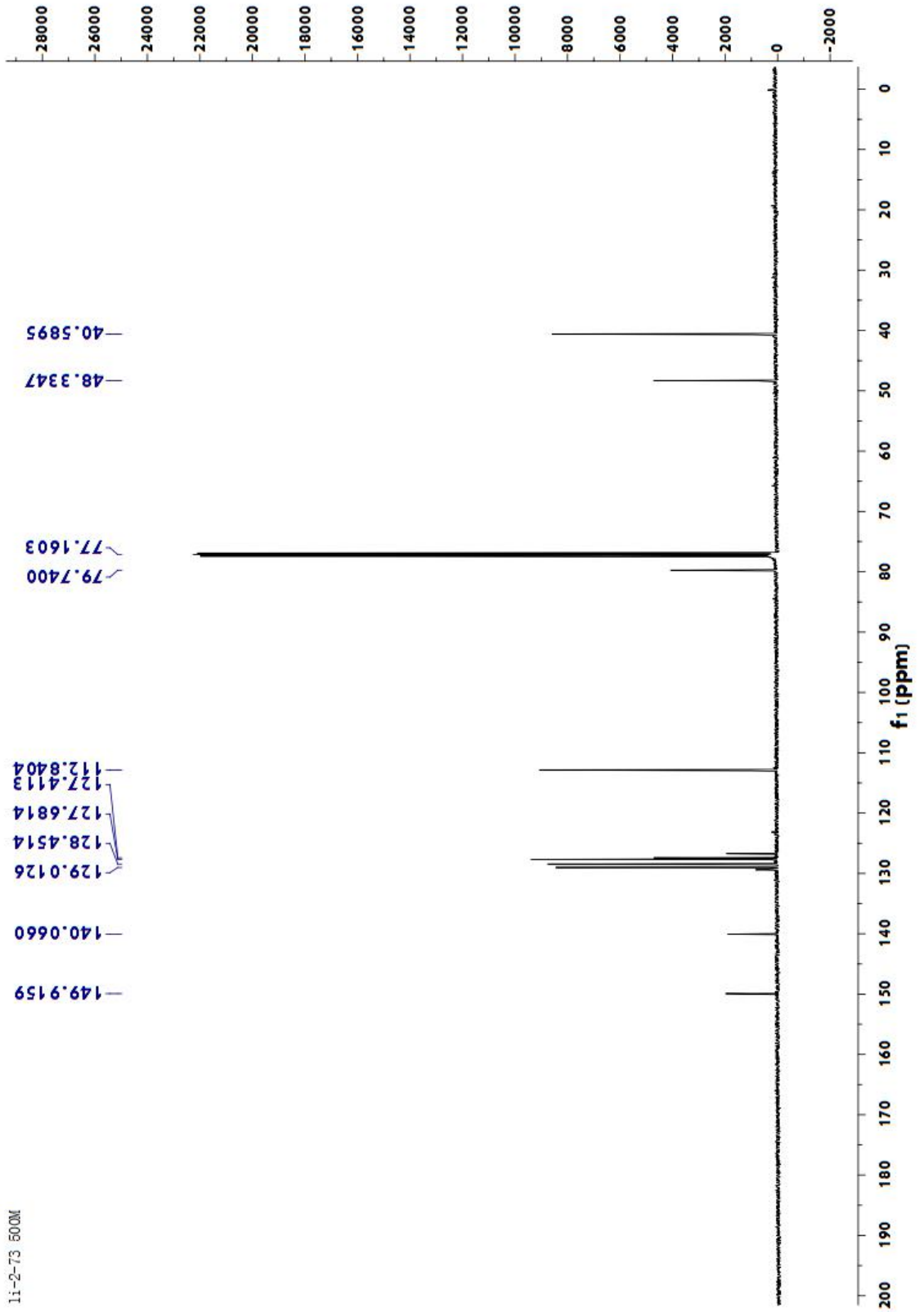


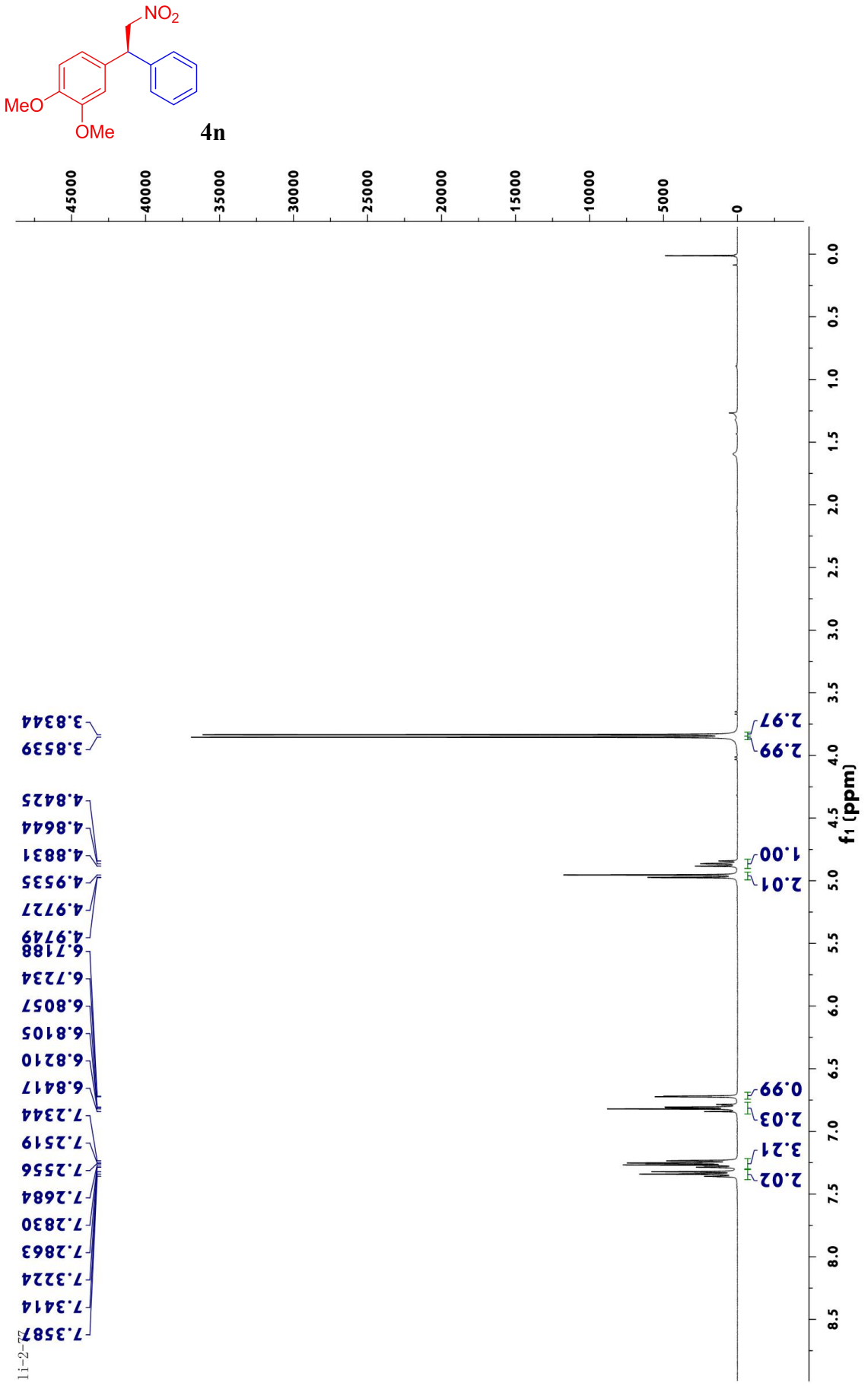
4m

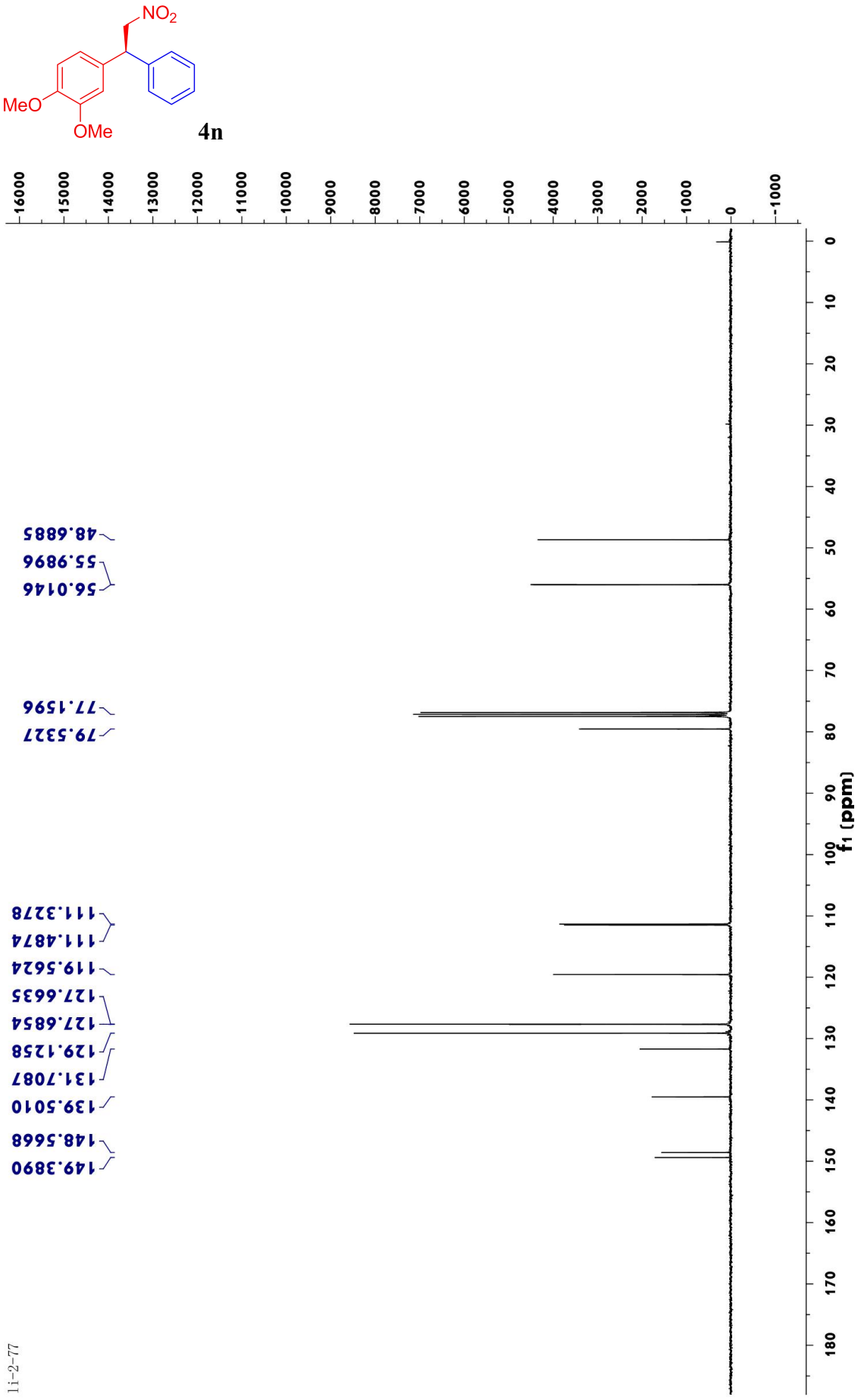


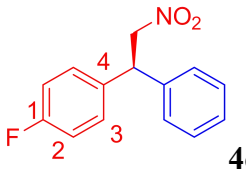

NO2
N

4m

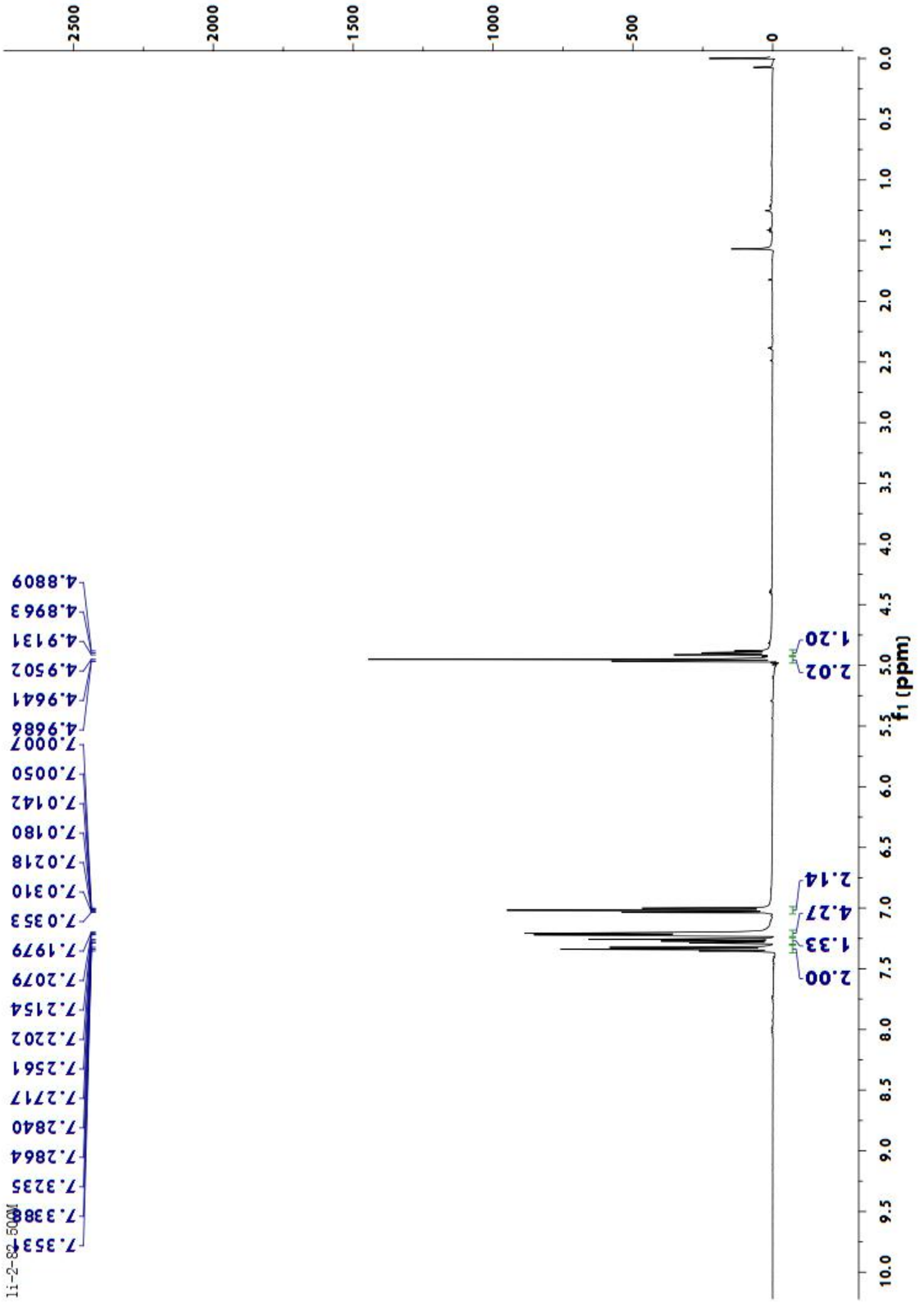

40.5895
48.3347
77.1603
79.7400
112.8404
127.4113
127.6814
128.4514
129.0126
140.0660
149.9159
f1 (ppm)
1i-2-73 500M

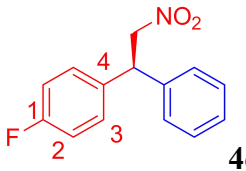

NO2
MeO
OMe
4n
f1 (ppm)
li-2-77


NO2
MeO
OMe
4n
48.6885
55.9896
56.0146
77.1596
79.5327
111.3278
111.4874
119.5624
127.6635
127.6854
129.1258
131.7087
139.5010
148.5668
149.3890
f1 (ppm)
li-2-77

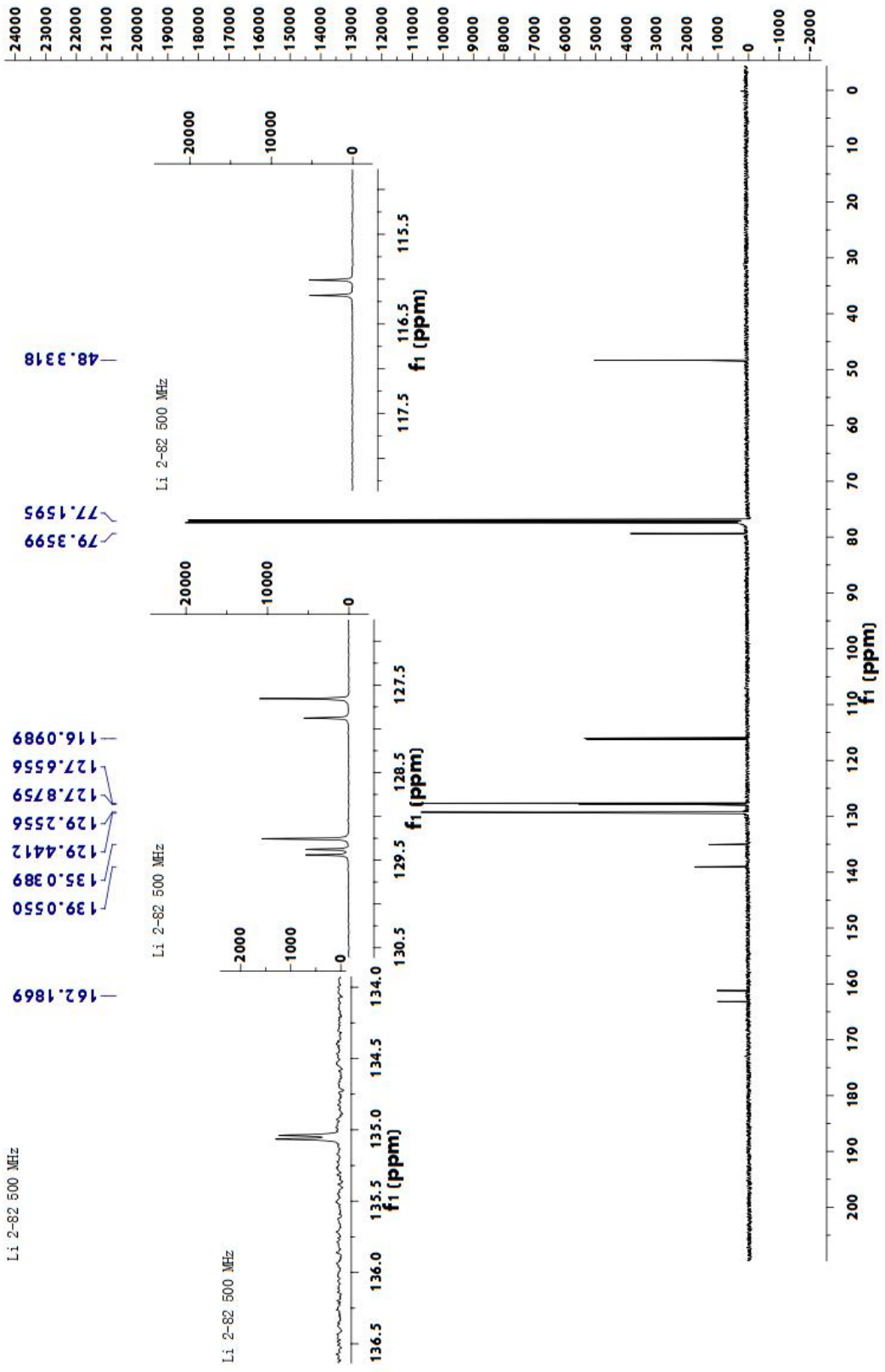

NO2
4
1
F
2
3

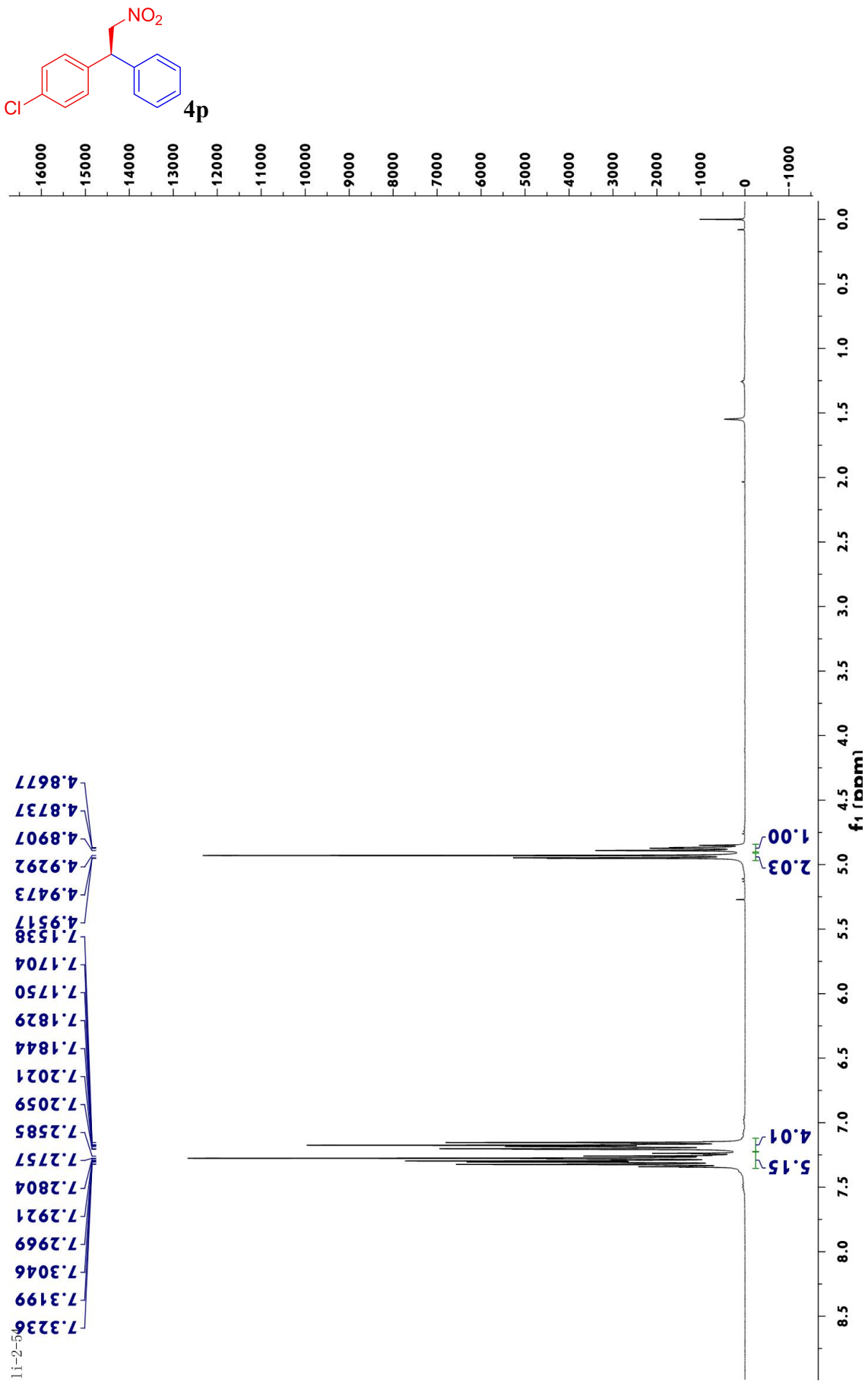
4o

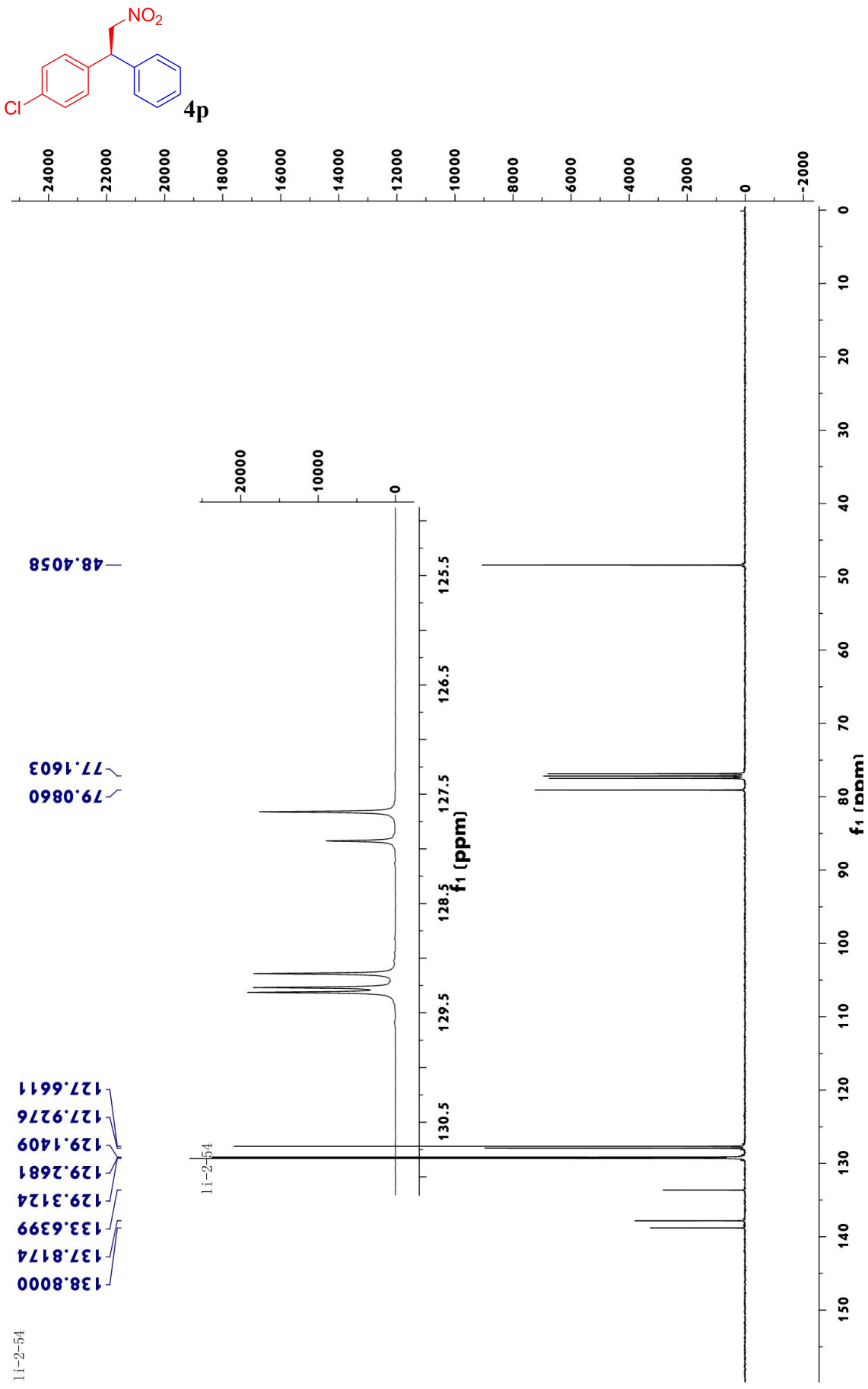

2500
2000
1500
1000
500
0
f1 (ppm)
1.20
2.02
2.14
4.27
1.33
2.00
4.8809
4.8963
4.9131
4.9502
4.9641
4.9686
7.0007
7.0050
7.0142
7.0180
7.0218
7.0310
7.0353
7.1979
7.2079
7.2154
7.2202
7.2561
7.2717
7.2840
7.2864
7.3235
7.3388
7.3531
li-2-82-500M

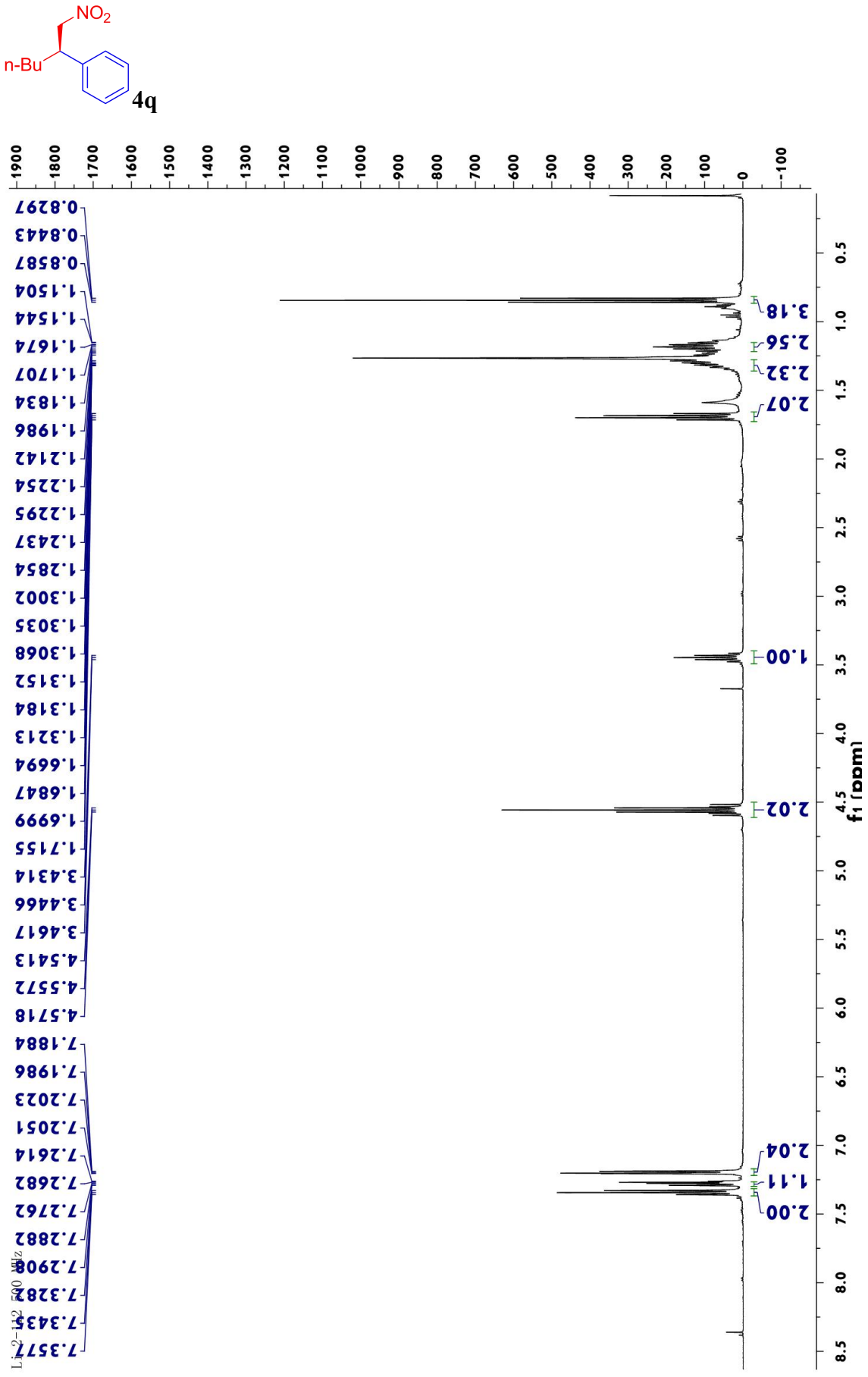

NO2
4
1
F
2
3

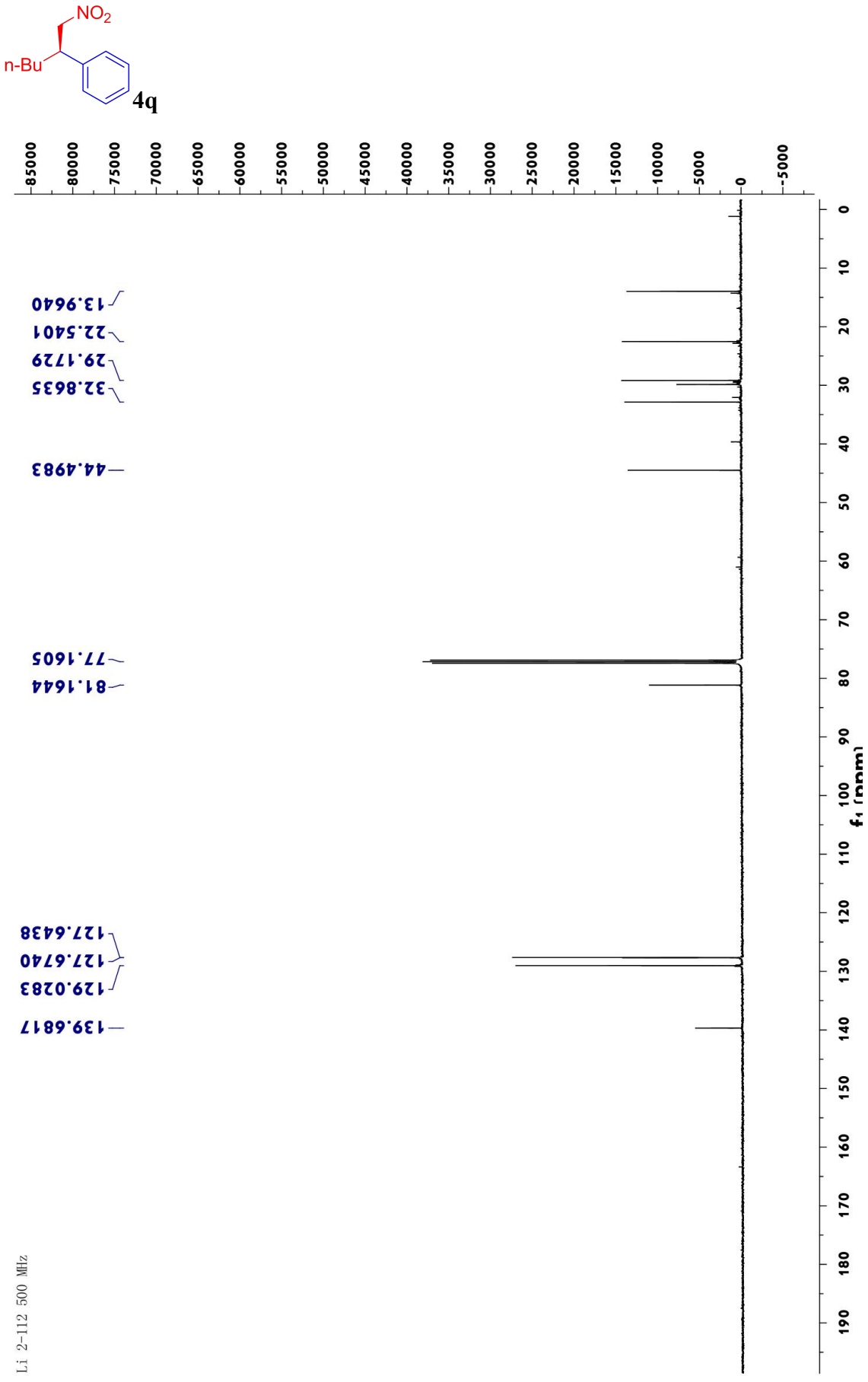
4o

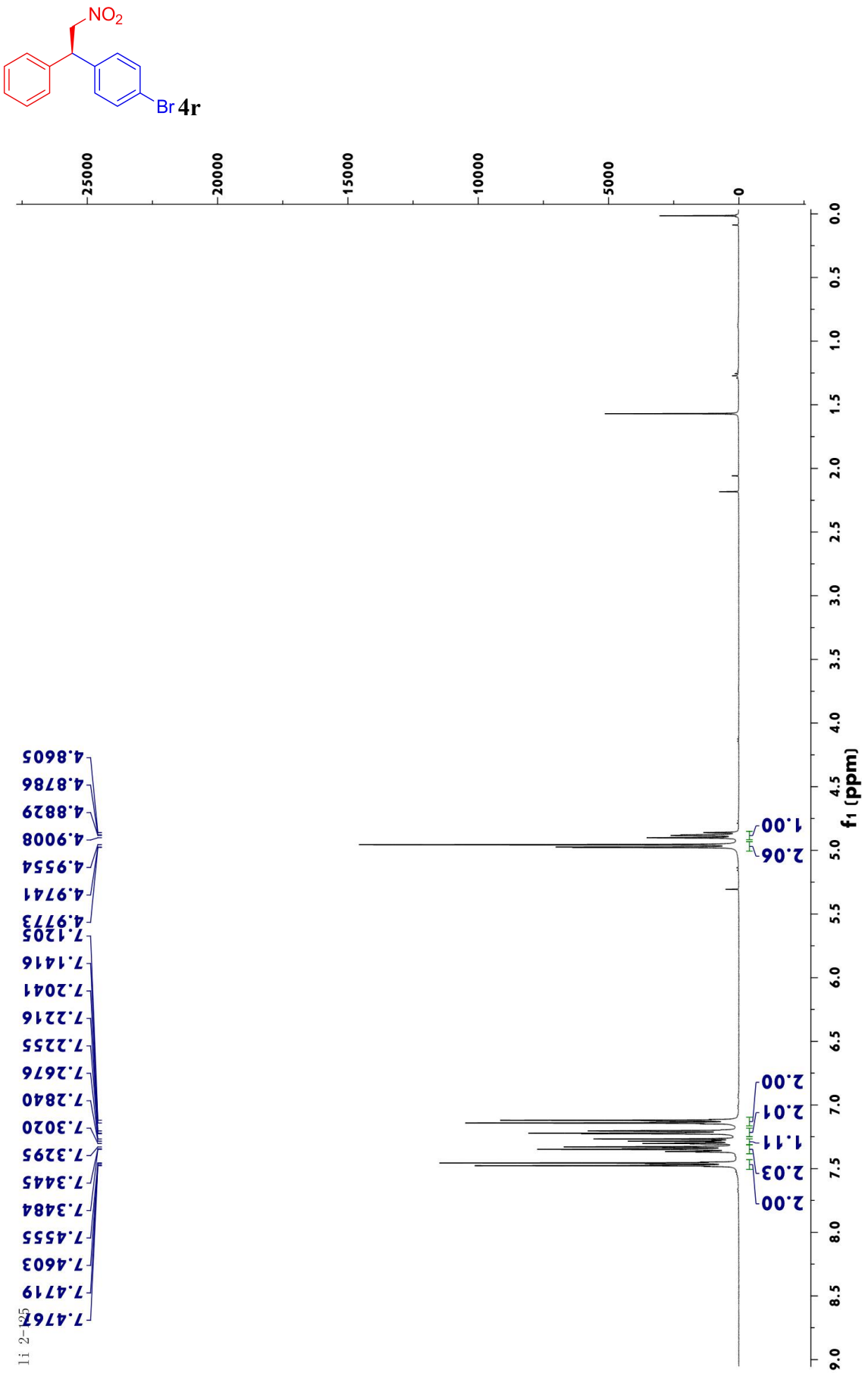

48.3318
77.1595
79.3599
116.0989
127.6556
127.8759
129.2556
129.4412
135.0389
139.0550
162.1869
Li 2-82 500 MHz
f1 (ppm)

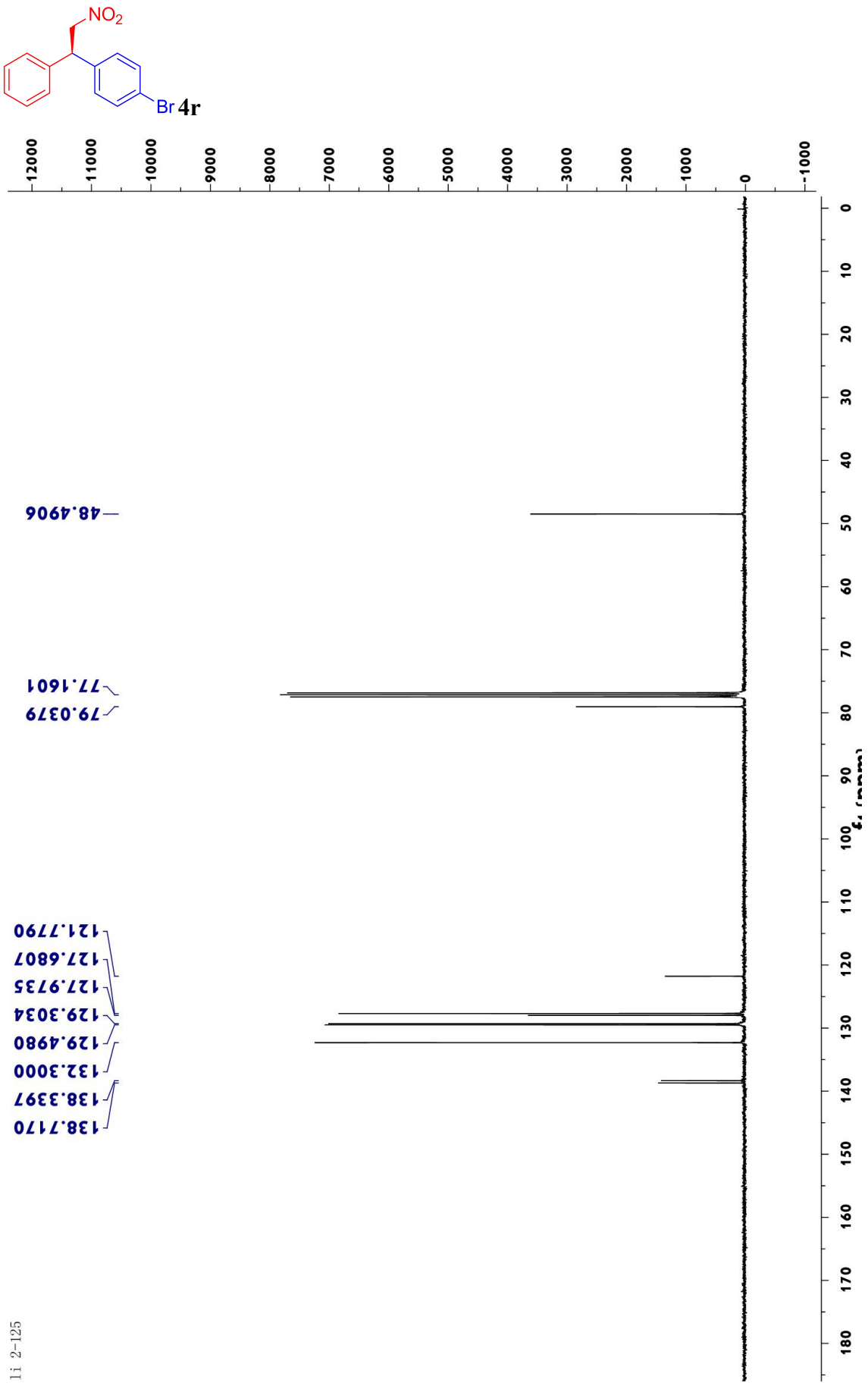

NO2
Cl
4p
f1 (ppm)
1.00
2.03
4.01
5.15
4.8677
4.8737
4.8907
4.9292
4.9473
4.9517
7.1538
7.1704
7.1750
7.1829
7.1844
7.2021
7.2059
7.2585
7.2757
7.2804
7.2921
7.2969
7.3046
7.3199
7.3236
li-2-5a

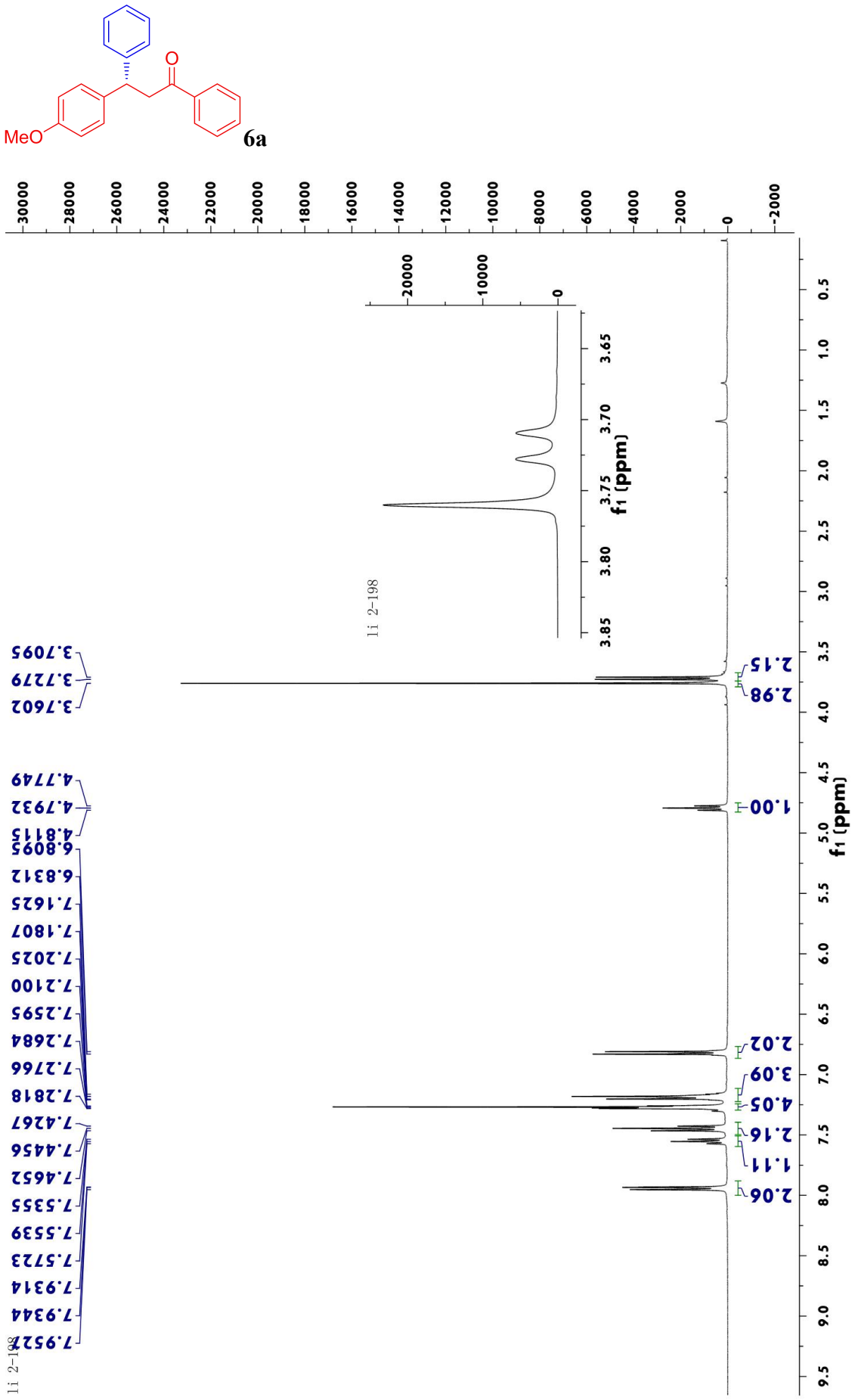

NO2
Cl
4p
138.8000
137.8174
133.6399
129.3124
129.2681
129.1409
127.9276
127.6611
79.0860
77.1603
48.4058
li-2-54
f1 (ppm)

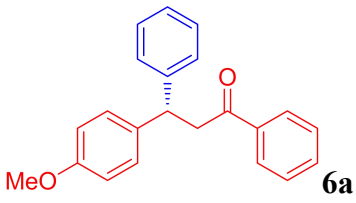

NO2
n-Bu
4q
f1 (ppm)
3.18
2.56
2.32
2.07
1.00
2.02
2.04
1.11
2.00


NO2
n-Bu
4q
13.9640
22.5401
29.1729
32.8635
44.4983
77.1605
81.1644
127.6438
127.6740
129.0283
139.6817
f1 (ppm)
Li 2-112 500 MHz

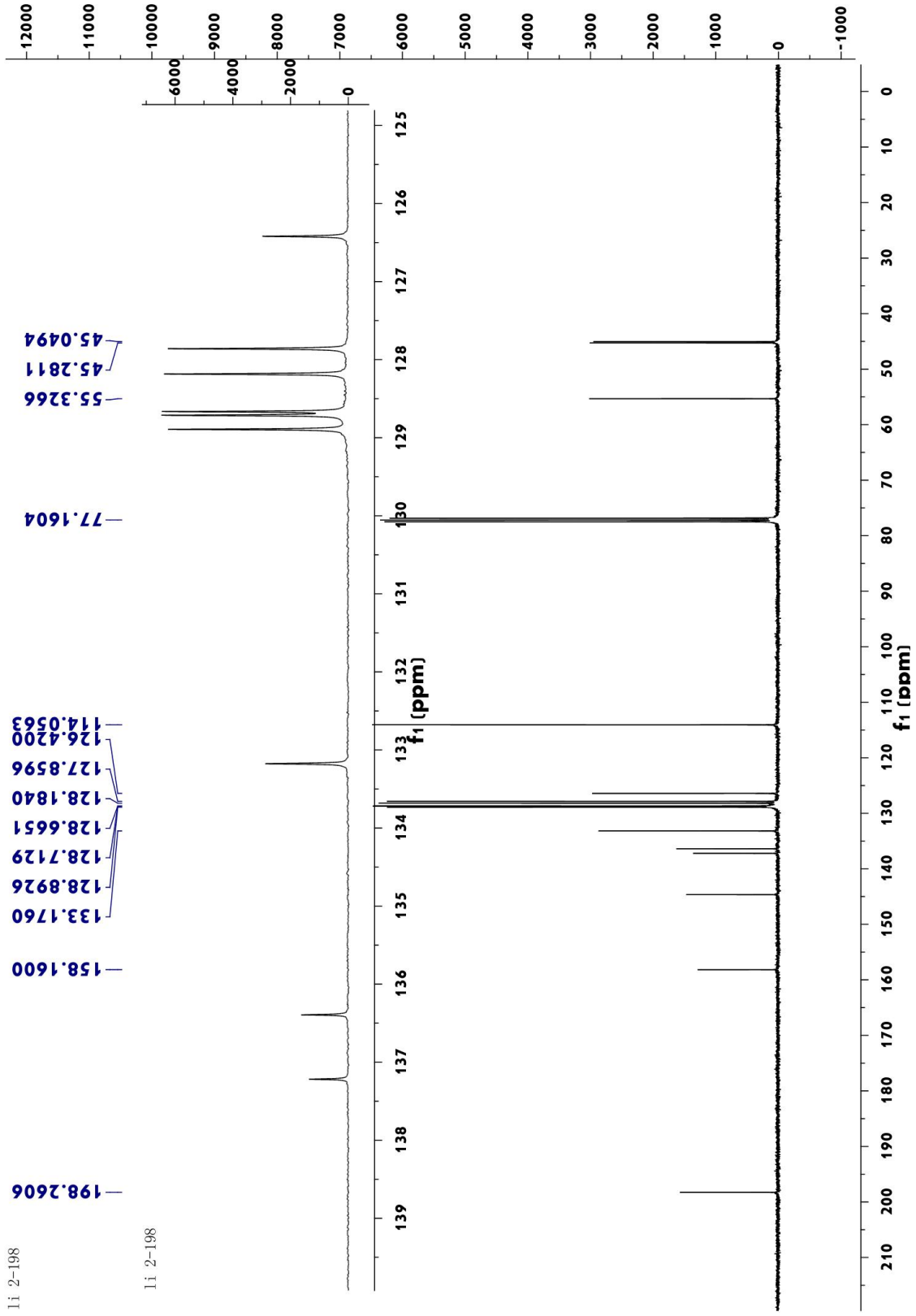

NO2
Br
4r
4.8605
4.8786
4.8829
4.9008
4.9554
4.9741
4.9773
7.1205
7.1416
7.2041
7.2216
7.2255
7.2676
7.2840
7.3020
7.3295
7.3445
7.3484
7.4555
7.4603
7.4719
7.4767
1.00
2.06
2.00
2.01
1.11
2.03
2.00
f1 (ppm)

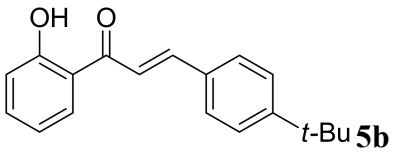

NO2
Br
4r
48.4906
77.1601
79.0379
121.7790
127.6807
127.9735
129.3034
129.4980
132.3000
138.3397
138.7170
li 2-125


MeO
O
6a
li 2-198
f1 (ppm)
3.7095
3.7279
3.7602
4.7749
4.7932
4.8115
6.8095
6.8312
7.1625
7.1807
7.2025
7.2100
7.2595
7.2684
7.2766
7.2818
7.4267
7.4456
7.4652
7.5355
7.5539
7.5723
7.9314
7.9344
7.9527
2.15
2.98
1.00
2.02
3.09
4.05
2.16
1.11
2.06

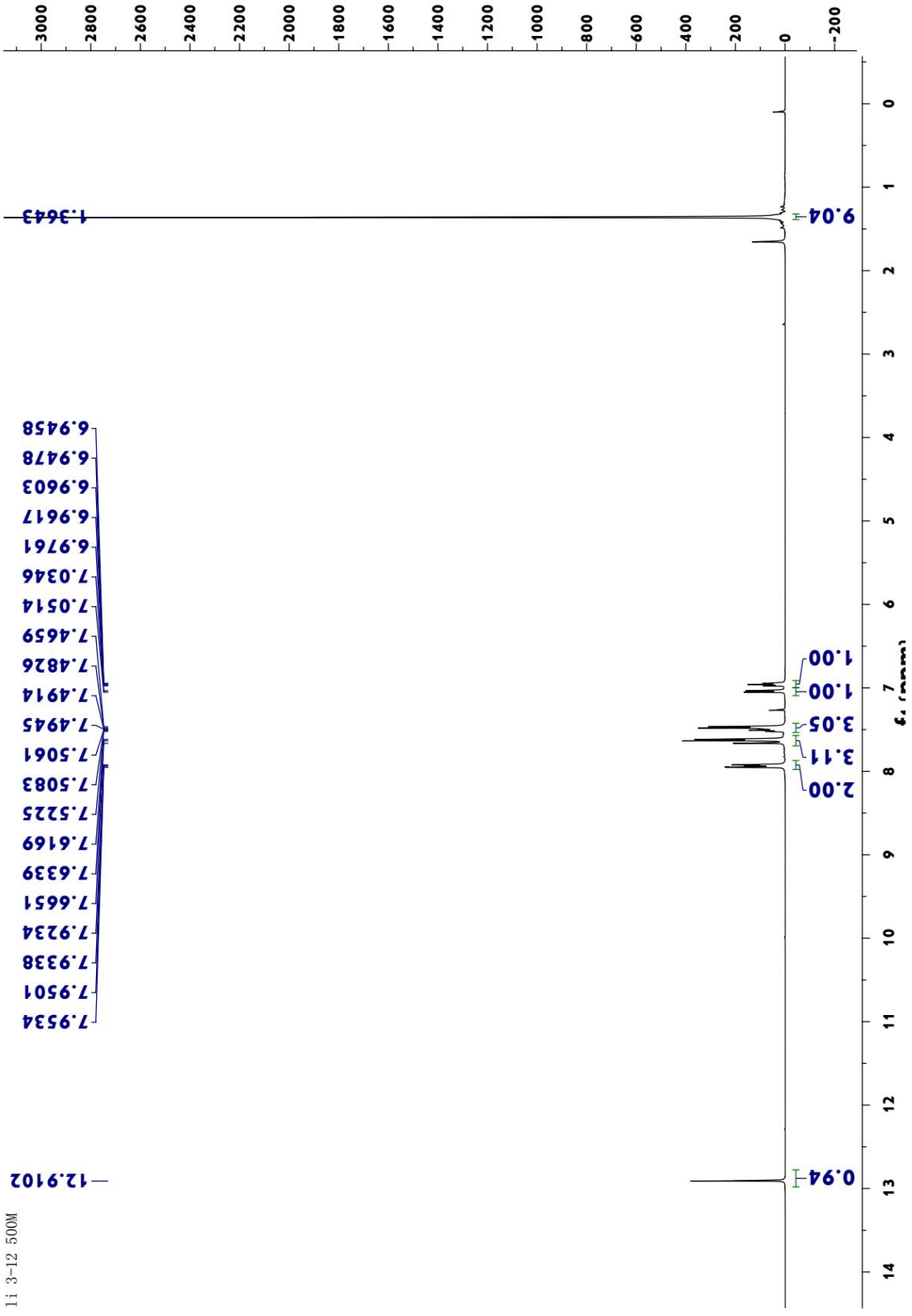

O
MeO

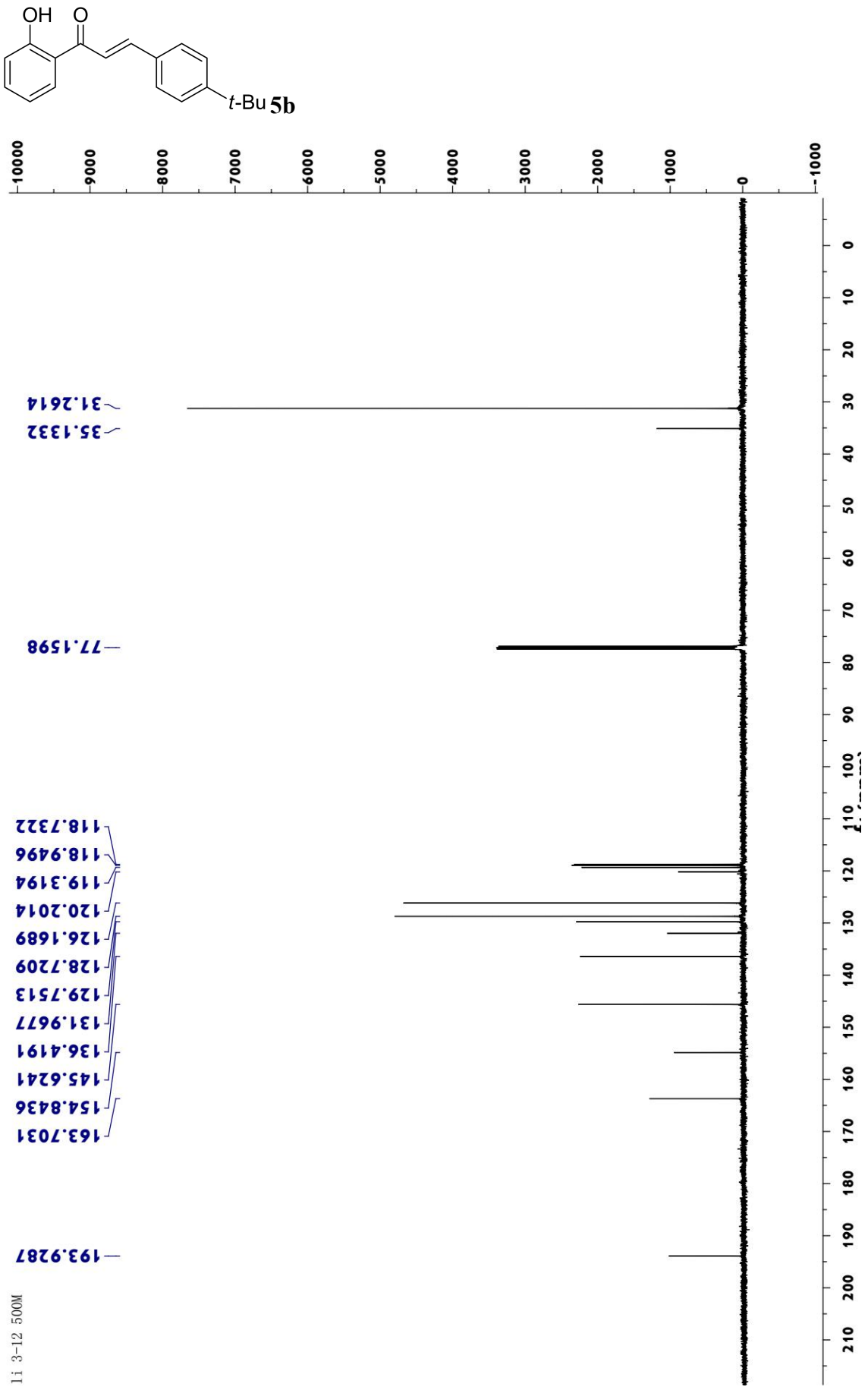
6a

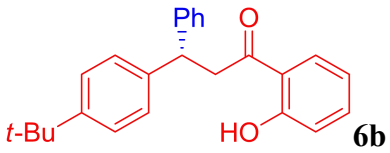

198.2606
158.1600
133.1760
128.8926
128.7129
128.6651
128.1840
127.8596
126.4200
114.0563
77.1604
55.3266
45.2811
45.0494
f1 (ppm)
li 2-198
li 2-198


OH
O
t-Bu

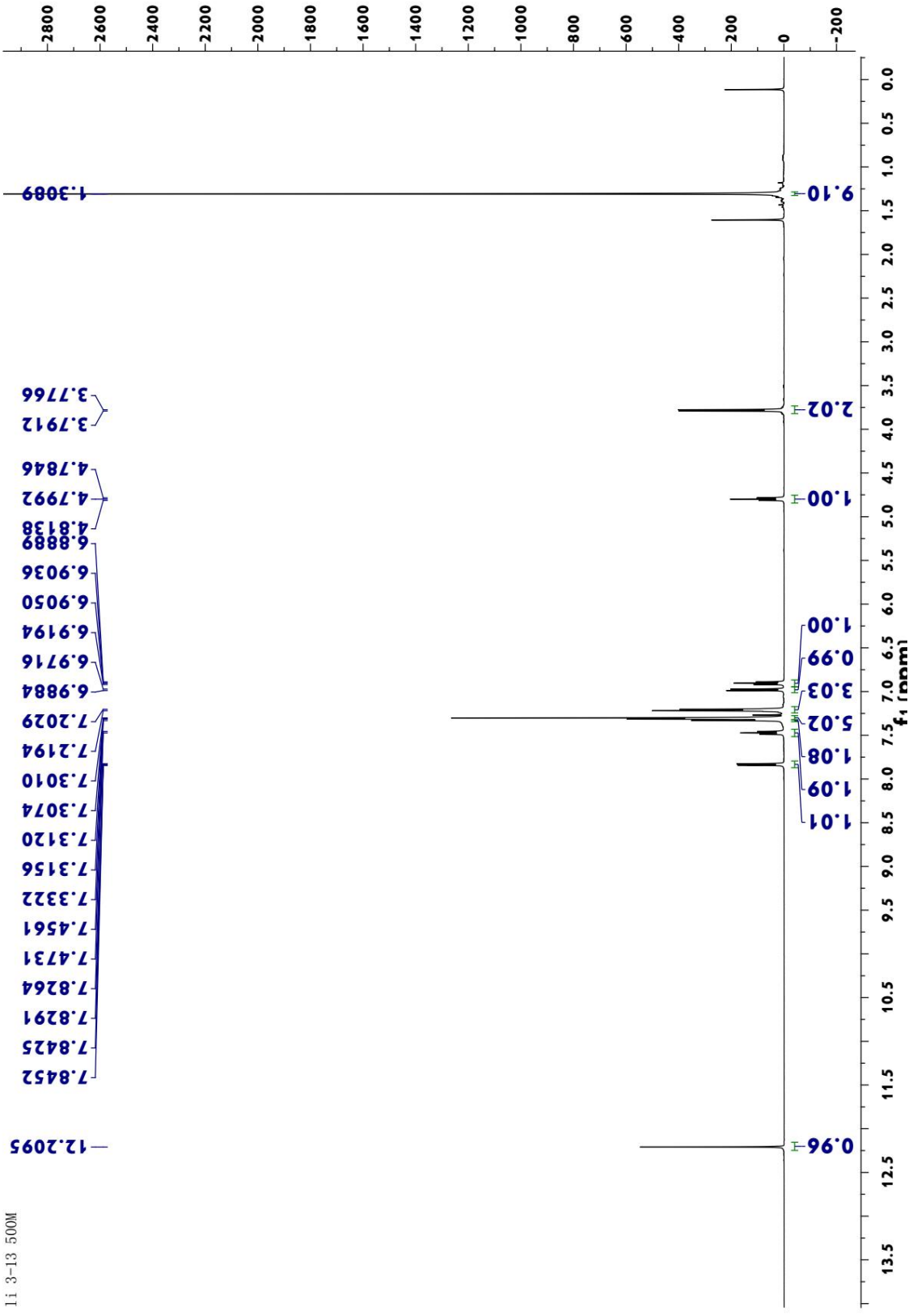
5b

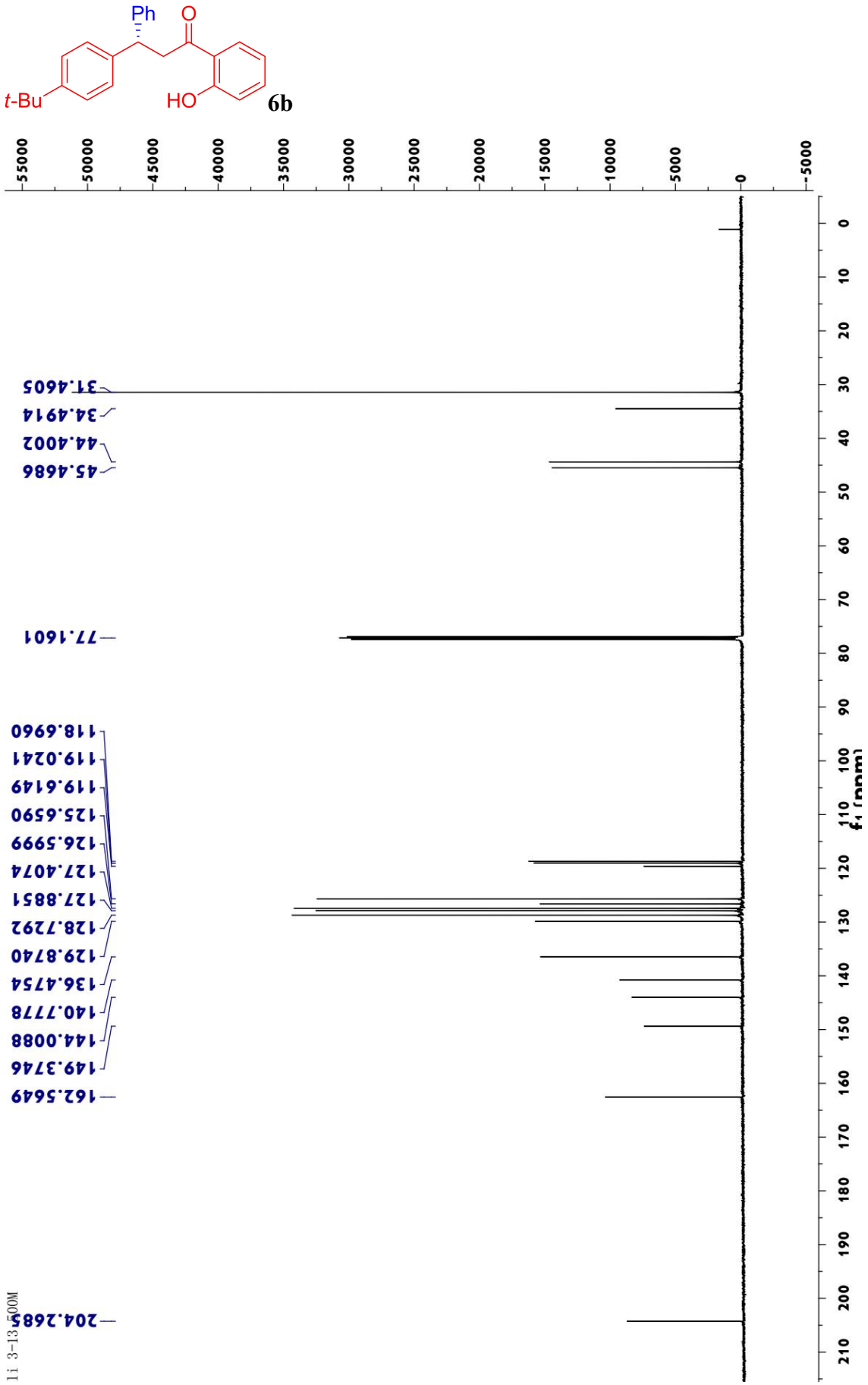

12.9102
7.9534
7.9501
7.9338
7.9234
7.6651
7.6339
7.6169
7.5225
7.5083
7.5061
7.4945
7.4914
7.4826
7.4659
7.0514
7.0346
6.9761
6.9617
6.9603
6.9478
6.9458
1.3643
0.94
2.00
3.11
3.05
1.00
1.00
9.04
1i 3-12 500M

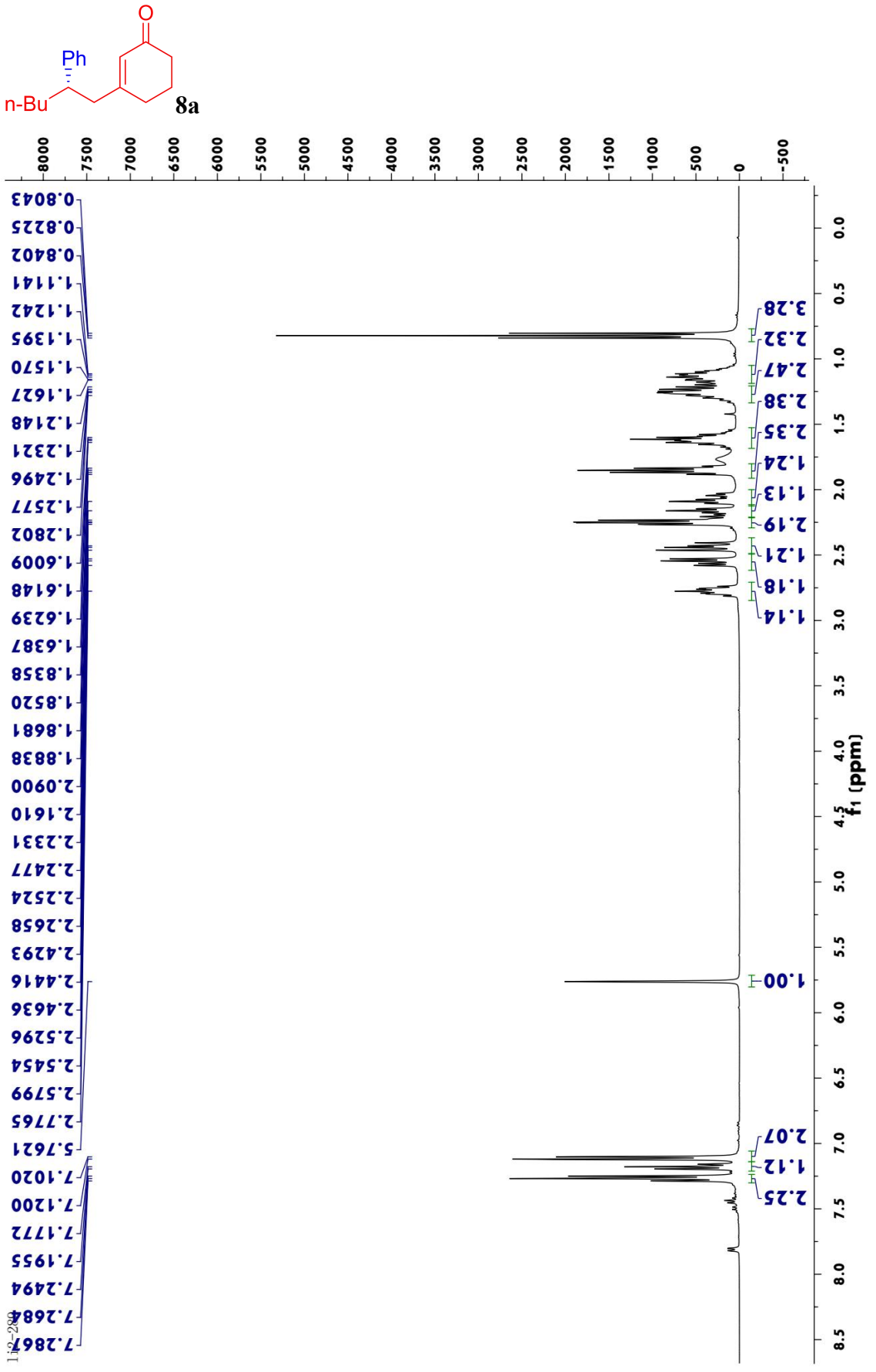

OH
O
t-Bu
5b
31.2614
35.1332
77.1598
118.7322
118.9496
119.3194
120.2014
126.1689
128.7209
129.7513
131.9677
136.4191
145.6241
154.8436
163.7031
193.9287
li 3-12 500M

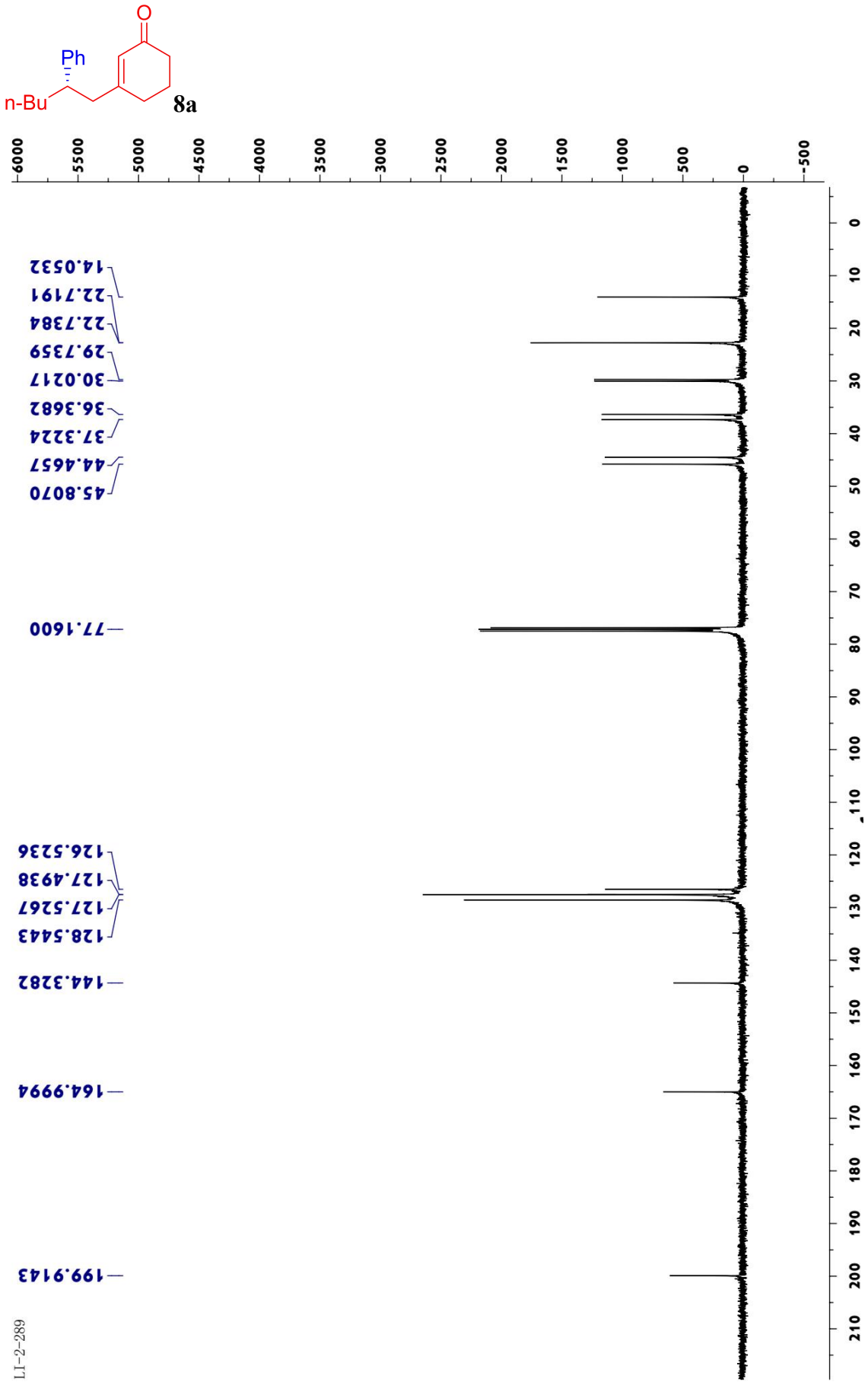

Ph
O
t-Bu
HO

6b

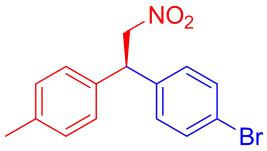

12.2095
7.8452
7.8425
7.8291
7.8264
7.4731
7.4561
7.3322
7.3156
7.3120
7.3074
7.3010
7.2194
7.2029
6.9884
6.9716
6.9194
6.9050
6.9036
6.8889
4.8138
4.7992
4.7846
3.7912
3.7766
1.3089
0.96
2.02
1.00
1.00
0.99
3.03
5.02
1.08
1.09
1.01
f1 (ppm)
1i 3-13 500M


Ph
O
t-Bu
HO
6b
31.4605
34.4914
44.4002
45.4686
77.1601
118.6960
119.0241
119.6149
125.6590
126.5999
127.4074
127.8851
128.7292
129.8740
136.4754
140.7778
144.0088
149.3746
162.5649
204.2685
f1 (ppm)


O
Ph
n-Bu
8a
f1 (ppm)

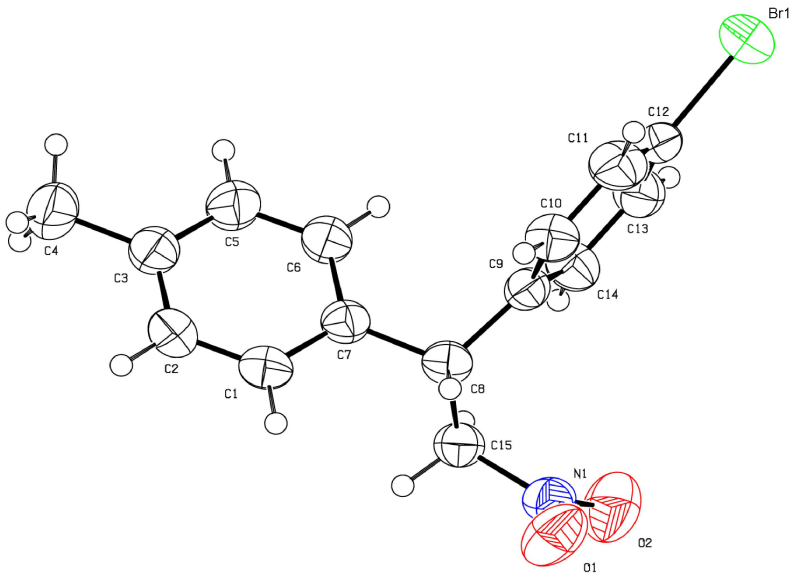

O
Ph
n-Bu
8a
14.0532
22.7191
22.7384
29.7359
30.0217
36.3682
37.3224
44.4657
45.8070
77.1600
126.5236
127.4938
127.5267
128.5443
144.3282
164.9994
199.9143
LI-2-289

7. X-ray crystal structures



(*R*)-1-Bromo-4-(2-nitro-1-(*p*-tolyl)ethyl)benzene (4e)

Colourless crystal, crystalization in *n*-hexane/chloroform. CIF files of this compound has been uploaded to the Cambridge Crystallographic Database with codes CCDC 1470002.



（displacement ellipsoids are drawn at the 45% probability level).

Compounds	**4e**
CCDC	1470002
Formula	$C_{15}H_{14}BrNO_2$
M*r*	320.18
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	5.4842 (15)
b (Å)	15.284 (4)
c (Å)	16.885 (5)
α (deg)	90
β(deg)	90
γ(deg)	90
V (Å^3)	1415.4 (7)
Z	4
D_c (g cm^{-3})	1.503
M(mm^{-1})	2.901
F(000)	648.0
GOF	1.030
$R_1{}^a$	0.0356(2300)
$wR_2{}^a$	0.0881(2905)

Selected bond lengths and angles for compund **4e**

Br1—C12	1.906 (3)	C6—C7	1.376 (5)
O1—N1	1.207 (4)	C7—C8	1.526 (5)
O2—N1	1.208 (4)	C8—C9	1.523 (4)
N1—C15	1.497 (4)	C8—C15	1.529 (5)
C1—C2	1.375 (5)	C9—C10	1.377 (4)
C1—C7	1.389 (5)	C9—C14	1.390 (5)
C2—C3	1.391 (5)	C10—C11	1.372 (5)
C3—C4	1.508 (5)	C11—C12	1.370 (5)
C3—C5	1.377 (5)	C12—C13	1.365 (5)
C5—C6	1.379 (5)	C13—C14	1.391 (5)
O1—N1—O2	123.8 (4)	C9—C8—C7	112.9 (3)
O1—N1—C15	117.6 (3)	C9—C8—C15	114.3 (3)
O2—N1—C15	118.6 (3)	C10—C9—C8	119.5 (3)
C2—C1—C7	121.7 (3)	C10—C9—C14	117.6 (3)
C1—C2—C3	121.2 (3)	C14—C9—C8	122.7 (3)

C2—C3—C4	121.7 (3)	C11—C10—C9	121.9 (3)
C5—C3—C2	116.8 (3)	C12—C11—C10	119.3 (3)
C5—C3—C4	121.5 (3)	C11—C12—Br1	120.2 (3)
C3—C5—C6	122.0 (3)	C13—C12—Br1	118.8 (3)
C7—C6—C5	121.4 (3)	C13—C12—C11	121.0 (3)
C1—C7—C8	119.4 (3)	C12—C13—C14	119.1 (3)
C6—C7—C1	116.9 (3)	C9—C14—C13	121.0 (3)
C6—C7—C8	123.7 (3)	N1—C15—C8	110.6 (3)
C7—C8—C15	108.4 (3)		