

Synthesis of axially chiral *N*-aryl benzimidazoles via chiral phosphoric acid catalyzed enantioselective oxidative aromatization

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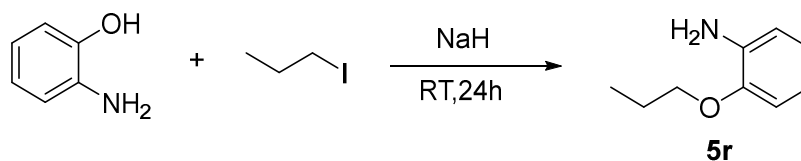
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1. General experimental information.

All reactions that required airless conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents from Tansoole and Adamas-beta were used as received. The solvents were dried by distillation over the appropriate drying reagents. All chemical reagents were obtained from commercial suppliers and used without further purification. All unknown compounds are characterized by ^1H NMR, ^{13}C NMR, HRMS.

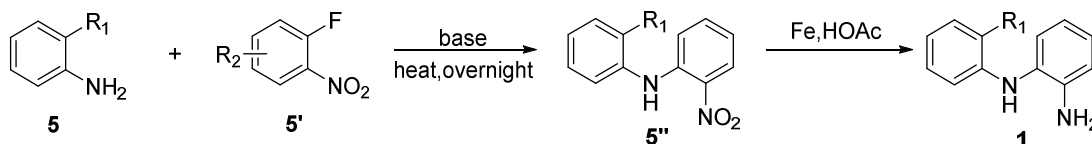
Thin-layer chromatography (TLC) was performed using glass-backed silica gel (250 μm) plates, and flash chromatography utilized 230-400 mesh silica gel from Scientific Adsorbents. Products were visualized by UV light. Melting points were measured on a Meltemp melting point apparatus and were not corrected. ^1H NMR spectra were recorded on commercial instruments (400 MHz or 600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 , $\delta = 7.28$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and, assignment. ^{13}C NMR spectra were collected on commercial instruments (101 MHz or 151 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl_3 , $\delta = 77.0$). Mass spectra were recorded on a ThermoQuest Finnigan LCQDECA system equipped with an ESI source. Enantioselectivities were analyzed on HPLC with chiral columns. Optical rotations were measured on an Autopol IV Automatic Polarimeter at the sodium D-line (589 nm), unless otherwise indicated, using a Type 40T TempTrolTM cell of 1 dm path length and reported as follows: $[\alpha]_{\text{D}}^{25.3}$ (c in g per 100 mL, CH_2Cl_2).

2. Preparation of *o*-alkoxyl phenylamines



Aminophenol (10 mmol) and NaH (30 mmol) were suspended in dry DMF (10 mL). The corresponding 1-iodopropane (15 mmol) was added dropwise and the mixture was then stirred for 24 h at room temperature. The reaction was quenched by adding distilled water and the aqueous layer was extracted with ethyl acetate. Collected organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The pure product was obtained by flash chromatography over silica gel with ethyl acetate/petroleum ether as eluent to afford the desired **5r**.¹ Other *o*-alkoxyl phenylamines were prepared according to this method.

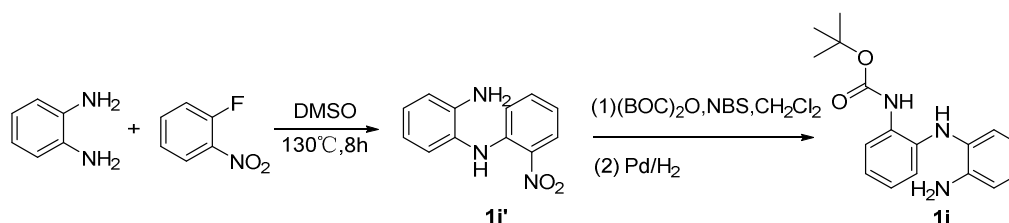
3. General procedure for the synthesis of *N*-aryl-*o*-phenylenediamines



A reaction flask was charged with the aryl fluoride **5'** (1.0 eq, 10 mmol), the aryl amines **5** (1.0 eq, 10 mmol), and triethylamine (3.0 eq, 30 mmol). After addition, the system was heated at 120 °C with stirring under a nitrogen atmosphere. The reaction was monitored by TLC. When the reaction was completed, the crude reaction mixture was allowed to reach room temperature and the mixture was diluted with H₂O. The resulting mixture was extracted with ethyl acetate. The aqueous phase was extracted three times with ethyl acetate. The combined organic layers were washed with two portions of a saturated solution of brine and then dried over anhydrous Na₂SO₄ and filtered. The solvent was removed under reduced pressure to afford the crude **5''**, which could be utilized without purification.

A mixture of **5''** (1.0 eq), Fe powder (6.0 eq), and acetic acid (12 mL) were stirred at room temperature. After stirring for 1 h, the solvent was eliminated and saturated sodium bicarbonate aqueous solution and ethyl acetate were added and the layers were

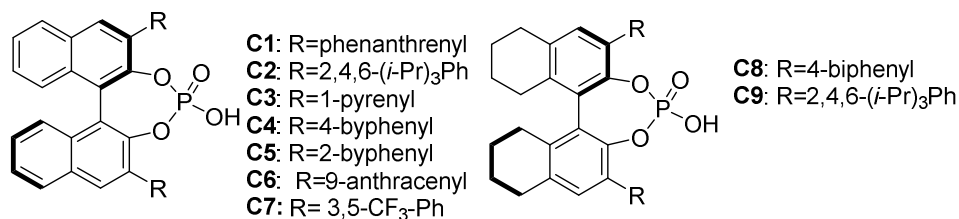
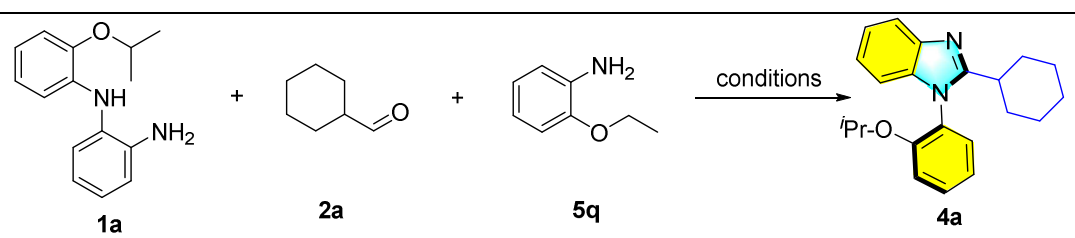
separated. The organic layers were combined, washed with saturated brine, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel with ethyl acetate/petroleum ether as eluent to afford *N*-aryl-*o*-phenylenediamines **1**.²



A reaction mixture of 1-fluoro-2-nitrobenzene (776 mg, 5.5 mmol) and 1,2-diaminobenzene (542 mg, 5 mmol) in DMSO (10 mL) was stirred at 130 °C for 8 h. After cooling to room temperature, it was quenched with H₂O (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine (3 × 10 mL), dried over anhydrous Na₂SO₄, concentrated, and purified through silica gel chromatography ethyl acetate/petroleum ether to give N¹-(2-nitrophenyl)benzene-1,2-diamine (**1i'**) as a reddish-brown solid (951 mg, 83% yield).³

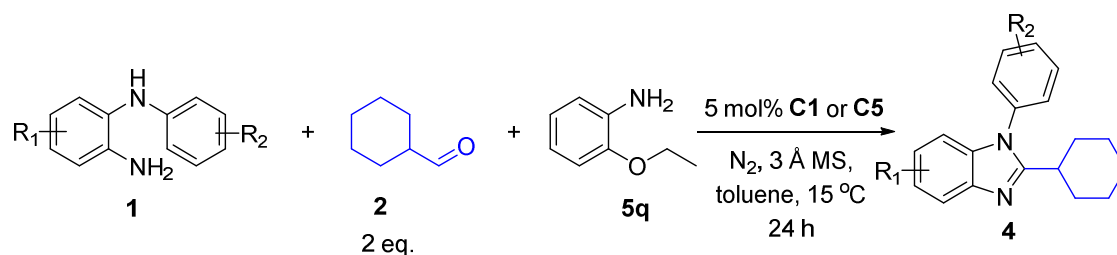
To a stirred solution of a selected amine (1 mmol, 1 equiv.) and (Boc)₂O (1 mmol, 1 equiv.) in CH₂Cl₂ (0.2 mL) was added NBS (0.1 mmol, 0.1 equiv.) or Br₃CCOCBr₃ (0.1 mmol, 0.1 equiv.) at room temperature. The mixture was stirred for the indicated time and the progress was monitored using TLC. After completion, the solvent was removed under reduced pressure and the product was purified by flash column chromatography (petroleum ether /ethyl acetate 15:1 to 10:1).⁴

4. Optimization of the reaction conditions



Entry ^a	T (°C)	Cat.	Add.	Sol.	Yield ^b (%)	Ee ^c (%)
1	15	C1	3 Å MS	toluene	75	66
2	15	C2	3 Å MS	toluene	68	50
3	15	C3	3 Å MS	toluene	66	54
4	15	C4	3 Å MS	toluene	64	54
5	15	C5	3 Å MS	toluene	60	46
6	15	C6	3 Å MS	toluene	70	22
7	15	C7	3 Å MS	toluene	65	22
8	15	C8	3 Å MS	toluene	83	79
9	15	C9	3 Å MS	toluene	46	30
10	15	C8	4 Å MS	toluene	60	52
11	15	C8	5 Å MS	toluene	59	46
12	15	C8	MgSO ₄	toluene	63	50
13	15	C8	3 Å MS	DCM	62	51
14	15	C8	3 Å MS	PhCl	66	57
15	15	C8	3 Å MS	CCl ₄	79	64
16	15	C8	3 Å MS	CHCl ₃	58	41
17	15	C8	3 Å MS	PhF	60	55
18	15	C8	3 Å MS	PhBr	69	63
19	0	C8	3 Å MS	toluene	20	40
20	30	C8	3 Å MS	toluene	85	51
21	15	C8	3 Å MS	toluene	85	79
22	15	C8	3 Å MS	toluene (10 mol% H ₂ O)	83	75
23	15	C8	-	toluene (50 mol% H ₂ O)	61	66
24	15	C8	-	toluene (10 mol% H ₂ O)	59	54

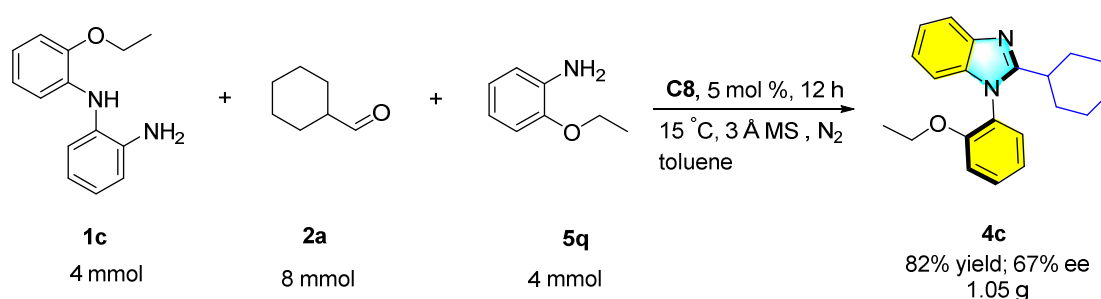
5. General procedure for the preparation of products 4



General Procedure for Syntheses of axially chiral 4: A reaction tube was charged with the **1** (0.01 mmol), aldehyde **2** (0.02 mmol), CPA (5 mmol%), phenylamine **5q** (0.01 mmol), 3 Å MS (40 mg), and toluene (0.4 mL). Then the reaction mixture was stirred for 24 h at 15 °C under a nitrogen atmosphere. After the completion of the reaction (TLC), the solvent was removed by a rotary evaporator. The crude products were purified by column chromatography eluting with petroleum ether/ethyl acetate (15:1-8:1) to give **4**.

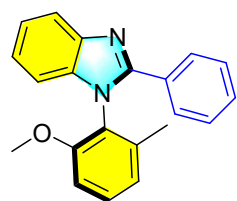
General Procedure for Syntheses of racemic 4: To a stirred solution of **1** (0.1 mmol, 1 equiv), 2-ethoxyaniline **5q** (1 equiv), and aldehyde **2** (2 equiv) in toluene (1 mL) was added diphenyl phosphonate (5 mol%) and 3 Å MS (50 mg) at rt, and then the mixture was stirred at 80 °C for overnight. After completion monitored by TLC, the resulting solution was concentrated in vacuo, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 15:1-8:1) to afford racemic **4**.

6. Gram-scale procedure for the preparation of products 4c

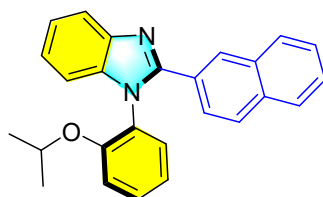


The reaction was performed with a general procedure for syntheses of axially chiral **4**. The products were purified via silica gel column chromatography.

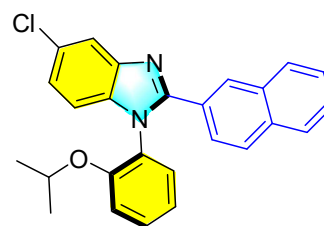
7. Aromatic aldehyde investigated under the optimal reaction condition



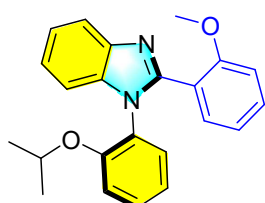
4t
52% yield, 0 ee



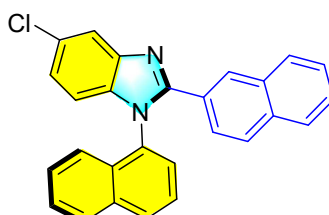
4u
63% yield, 0 ee



4v
68% yield, 0 ee



4w
52% yield, 0 ee

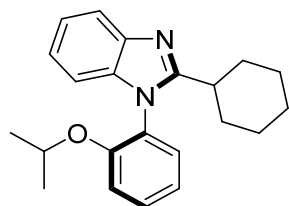


4x
55% yield, 0 ee

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8. Characterization of the selected new products



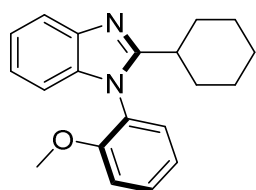
2-cyclohexyl-1-(2-isopropoxyphenyl)-1H-benzo[d]imidazole (4a)

Brown oil, yield: 85%. $[\alpha]_D^{25.3} = +0.56^\circ$ (c 0.4, CH_2Cl_2), ee = 79%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{R1} = 6.7$ min (minor), $t_{R2} = 12.2$ min (major).

^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.0$ Hz, 1H), 7.50 – 7.43 (m, 1H), 7.28 (dd, $J = 7.6, 1.4$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.11 (td, $J = 15.1, 7.7$ Hz, 3H), 6.94 (d, $J = 8.0$ Hz, 1H), 4.45 (dt, $J = 12.1, 6.0$ Hz, 1H), 2.58 (ddd, $J = 11.8, 8.2, 3.6$ Hz, 1H), 2.00 (d, $J = 13.0$ Hz, 1H), 1.97 – 1.88 (m, 1H), 1.88 – 1.71 (m, 3H), 1.66 (qd, $J = 12.8, 3.5$ Hz, 2H), 1.37 – 1.19 (m, 2H), 1.17 (d, $J = 6.1$ Hz, 3H), 1.15 – 1.10 (m, 1H), 1.02 (d, $J = 6.0$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 160.21, 153.73, 142.77, 136.42, 130.29, 129.75, 125.52, 121.95, 121.72, 120.90, 118.89, 114.99, 109.96, 77.25, 77.04, 76.83, 70.77, 36.49, 32.56, 30.92, 26.21 (d, $J = 10.8$ Hz), 25.78, 21.69.

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}$ 335.2118; Found 335.2113.



2-cyclohexyl-1-(2-methoxyphenyl)-1H-benzo[d]imidazole(4b)

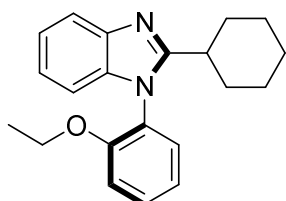
Brown solid, yield: 82%, Mp: 77-79 °C. $[\alpha]_D^{25.3} = +0.55^\circ$ (c 0.4, CH_2Cl_2), ee = 51%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 95:5; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{R1} = 16.1$ min (minor), $t_{R2} = 22.4$ min (major).

^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.0$ Hz, 1H), 7.53 (td, $J = 8.1, 1.4$ Hz, 1H), 7.37 – 7.22 (m, 2H), 7.16 (dd, $J = 14.4, 7.5$ Hz, 3H), 6.97 (d, $J = 8.0$ Hz, 1H), 3.74 (s, 3H), 2.54 (dd, $J = 9.4, 5.6$ Hz, 1H), 1.93 (s, 1H), 1.91 – 1.79 (m, 3H), 1.76 (d, $J = 10.8$

Hz, 1H), 1.70 (dd, $J = 10.9, 8.1$ Hz, 1H), 1.41 – 1.11 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 160.08, 155.40, 142.69, 136.27, 130.58, 129.55, 124.41, 122.16, 121.91, 121.12, 119.01, 112.36, 109.93, 77.39, 77.07, 76.76, 55.59, 36.55, 32.38, 31.30, 26.24 (d, $J = 3.6$ Hz), 25.77.

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}$ 307.1805; Found 307.1815.



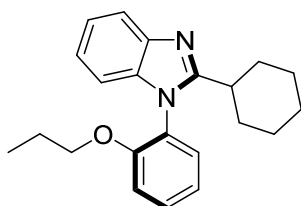
2-cyclohexyl-1-(2-ethoxyphenyl)-1H-benzo[d]imidazole(4c)

Brown oil, yield: 87%. $[\alpha]_{\text{D}}^{25.3} = -1.8^\circ$ (c 0.4, CH_2Cl_2), ee = 67%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{\text{R}1} = 6.8$ min (minor), $t_{\text{R}2} = 11.6$ min (major).

^1H NMR (600 MHz, CDCl_3) δ 7.79 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 1H), 7.29 (d, $J = 7.7$ Hz, 1H), 7.23 (t, $J = 7.5$ Hz, 1H), 7.18 – 7.07 (m, 3H), 6.95 (d, $J = 7.9$ Hz, 1H), 4.07 – 3.92 (m, 2H), 2.57 (t, $J = 11.6$ Hz, 1H), 1.93 (dt, $J = 37.7, 12.6$ Hz, 2H), 1.82 (s, 2H), 1.78 – 1.62 (m, 3H), 1.37 – 1.17 (m, 3H), 1.15 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 160.08, 154.65, 142.50, 136.31, 130.48, 129.57, 124.61, 122.12, 121.90, 120.97, 118.88, 113.39, 109.98, 77.24, 77.03, 76.82, 64.08, 36.55, 32.44, 31.05, 26.23, 25.75, 14.44.

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}$ 321.1961; Found 321.1952.



2-cyclohexyl-1-(2-propoxyphenyl)-1H-benzo[d]imidazole(4d)

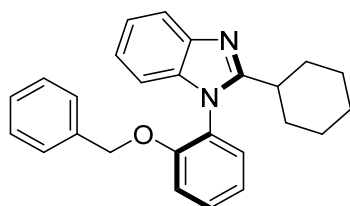
Brown oil, yield: 74%. $[\alpha]_{\text{D}}^{25.3} = +10.3^\circ$ (c 0.4, CH_2Cl_2), ee = 65%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{\text{R}1} = 7.4$ min (minor), $t_{\text{R}2} = 11.9$ min (major).

^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.0$ Hz, 1H), 7.47 (t, $J = 7.9$ Hz, 1H), 7.33 – 7.19 (m, 2H), 7.19 – 7.05 (m, 3H), 6.93 (d, $J = 8.0$ Hz, 1H), 3.91 (dd, $J = 15.4, 6.4$

Hz, 1H), 3.81 (dd, $J = 15.5, 6.6$ Hz, 1H), 2.57 (t, $J = 11.7$ Hz, 1H), 2.03 – 1.78 (m, 4H), 1.78 – 1.59 (m, 3H), 1.59 – 1.34 (m, 2H), 1.25 (ddd, $J = 50.4, 26.0, 13.1$ Hz, 3H), 1.14 (d, $J = 13.0$ Hz, 1H), 0.68 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 160.04, 154.97, 142.67, 136.50, 130.47, 129.62, 124.71, 122.01, 121.76, 120.92, 118.92, 113.41, 109.95, 77.25, 77.03, 76.82, 70.08, 36.51, 32.41, 31.01, 26.20 (d, $J = 6.3$ Hz), 25.78, 22.24, 10.15.

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}$ 335.2118; Found 335.2127.



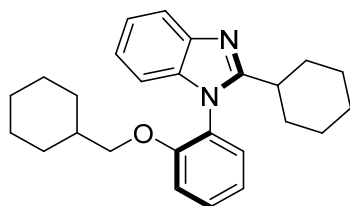
1-(2-(benzyloxy)phenyl)-2-cyclohexyl-1H-benzo[d]imidazole(4e)

Brown solid, yield: 88%, Mp: 87-90 °C. $[\alpha]_{\text{D}}^{25.3} = +0.56^\circ$ (c 0.4, CH_2Cl_2), ee = 63%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 95:5; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{\text{R}1} = 8.3$ min (minor), $t_{\text{R}2} = 10.7$ min (major).

^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.0$ Hz, 1H), 7.54 – 7.45 (m, 1H), 7.35 (dd, $J = 7.6, 1.5$ Hz, 2H), 7.26 – 7.22 (m, 3H), 7.17 (dd, $J = 14.2, 6.5$ Hz, 3H), 7.11 – 7.03 (m, 2H), 6.98 (d, $J = 7.9$ Hz, 1H), 5.04 (d, $J = 3.1$ Hz, 2H), 2.63 (s, 1H), 1.96 – 1.84 (m, 3H), 1.82 – 1.73 (m, 2H), 1.72 – 1.64 (m, 1H), 1.41 – 1.26 (m, 2H), 1.26 – 1.12 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 160.09, 154.46, 142.71, 136.46, 136.06, 130.55, 129.80, 128.50, 127.92, 126.75, 124.98, 122.18, 121.94, 121.52, 119.05, 114.20, 110.02, 77.34 (d, $J = 11.5$ Hz), 77.08, 76.76, 70.31, 36.55, 32.53, 31.02, 26.22 (d, $J = 4.6$ Hz), 25.78.

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}$ 383.2118; Found 383.2130.



2-cyclohexyl-1-(2-(cyclohexylmethoxy)phenyl)-1H-benzo[d]imidazole(4f)

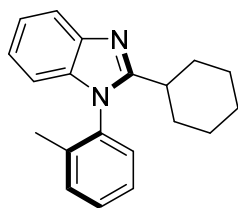
Brown oil, yield: 81%. $[\alpha]_{\text{D}}^{25.3} = -22.38^\circ$ (c 0.4, CH_2Cl_2), ee = 59%; HPLC analysis:

Daicel Chiralpak IC-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{R1} = 6.0$ min (minor), $t_{R2} = 9.3$ min (major).

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.9$ Hz, 1H), 7.49 (dd, $J = 11.3, 4.5$ Hz, 1H), 7.32 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.13 (dd, $J = 14.9, 7.8$ Hz, 3H), 6.94 (d, $J = 8.0$ Hz, 1H), 3.76 (dd, $J = 9.0, 6.0$ Hz, 1H), 3.71 (ddd, $J = 38.5, 9.0, 6.0$ Hz, 2H), 3.66 (dd, $J = 8.9, 5.9$ Hz, 1H), 2.73 – 2.20 (m, 2H), 2.74 – 2.51 (m, 1H), 2.20 – 1.72 (m, 7H), 2.00 – 1.63 (m, 9H), 1.72 – 1.51 (m, 6H), 1.55 (d, $J = 9.5$ Hz, 3H), 1.47 (d, $J = 11.0$ Hz, 2H), 1.47 (d, $J = 11.0$ Hz, 2H), 1.42 – 1.30 (m, 3H), 1.28 (s, 1H), 1.25 – 1.16 (m, 2H), 1.42 – 0.94 (m, 10H), 1.02 (td, $J = 22.0, 11.6$ Hz, 3H), 0.71 (dd, $J = 23.5, 11.8$ Hz, 2H), 0.71 (dd, $J = 23.5, 11.8$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.99, 155.18, 142.67, 130.46, 129.64, 124.78, 121.85 (d, $J = 36.3$ Hz), 120.83, 118.91, 113.47, 109.98, 77.21, 76.90 (d, $J = 31.9$ Hz), 76.76 – 76.50 (m), 74.00, 37.28, 36.49, 32.39, 30.94, 29.37 (d, $J = 17.7$ Hz), 26.17 (d, $J = 9.9$ Hz), 25.79, 25.53.

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{33}\text{N}_2\text{O}$ 389.2587; Found 389.2571.



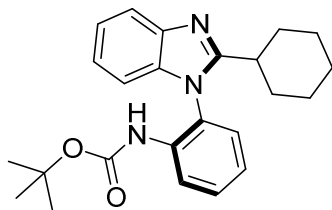
2-cyclohexyl-1-(o-tolyl)-1H-benzo[d]imidazole(4g)

Brown oil, yield: 86%. $[\alpha]_{\text{D}}^{25.3} = +33.06^\circ$ (c 0.4, CH_2Cl_2), ee = 61%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{R1} = 6.3$ min (minor), $t_{R2} = 7.4$ min (major).

^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.0$ Hz, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 7.26 (dd, $J = 12.6, 6.5$ Hz, 2H), 7.17 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 2.50 (ddd, $J = 15.1, 7.6, 3.9$ Hz, 1H), 1.97 (s, 3H), 1.96 – 1.64 (m, 7H), 1.40 – 1.11 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.31, 142.65, 136.47, 135.81, 134.73, 131.47, 129.51, 128.67, 127.32, 122.42, 122.11, 119.23, 109.98, 77.34 (d, $J = 11.5$ Hz), 77.07, 76.76, 36.41, 32.37, 31.32, 26.12, 25.67, 17.34.

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2$ 291.1856; Found 291.1839.



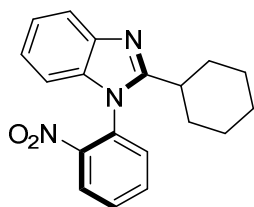
tert-butyl (2-(2-cyclohexyl-1H-benzo[d]imidazol-1-yl)phenyl)carbamate(4h)

Brown solid, yield: 88%, Mp: 129-131 °C. $[\alpha]_D^{25.3} = +160.8^\circ$ (c 0.4, CH₂Cl₂), ee = 69%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{R1} = 6.3$ min (minor), $t_{R2} = 7.4$ min (major).

¹H NMR (600 MHz, CDCl₃) δ 8.28 (d, $J = 8.2$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 7.8$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.24 – 7.16 (m, 3H), 6.95 (d, $J = 8.0$ Hz, 1H), 5.94 (s, 1H), 2.67 – 2.40 (m, 1H), 1.86 (d, $J = 10.3$ Hz, 3H), 1.82 – 1.72 (m, 3H), 1.68 (s, 1H), 1.40 (s, 9H), 1.30 (dd, $J = 21.0, 8.4$ Hz, 1H), 1.24 – 1.15 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 159.86, 152.37, 142.98, 135.65 (d, $J = 14.4$ Hz), 130.41, 128.62, 123.78, 123.05, 122.81, 119.46, 109.92, 77.22, 77.01, 76.80, 36.36, 32.18, 31.49, 28.14, 26.01 (d, $J = 7.1$ Hz), 25.60.

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₄H₃₀N₃O₂ 392.2333; Found 392.2343.



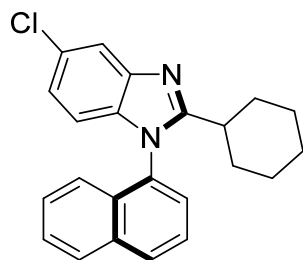
2-cyclohexyl-1-(2-nitrophenyl)-1H-benzo[d]imidazole(4i)

Brown oil, yield: 40%. $[\alpha]_D^{25.3} = +8.45^\circ$ (c 0.4, CH₂Cl₂), ee = 43%; HPLC analysis: Daicel Chiralpak OD-H; Hexane/iPrOH = 80:20; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{R1} = 6.3$ min (minor), $t_{R2} = 7.8$ min (major).

¹H NMR (600 MHz, CDCl₃) δ 8.20 (d, $J = 8.1$ Hz, 1H), 7.86 (t, $J = 7.7$ Hz, 1H), 7.83 – 7.74 (m, 2H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.25 – 7.24 (m, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 7.9$ Hz, 1H), 2.48 (t, $J = 11.4$ Hz, 1H), 1.83 (ddd, $J = 34.7, 25.9, 14.2$ Hz, 7H), 1.32 (d, $J = 13.2$ Hz, 2H), 1.17 (dd, $J = 13.0, 9.4$ Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 159.15, 146.94, 142.80, 135.90, 134.30, 131.32, 130.54, 129.74, 125.97, 123.02, 122.76, 119.57, 109.02, 36.80, 32.58, 31.01, 29.69, 26.11 (d, $J = 14.8$ Hz), 25.61.

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₁₉H₂₀N₃O₂ 322.1550; Found 322.1554.



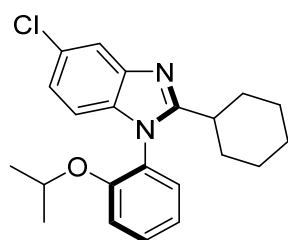
6-chloro-2-cyclohexyl-1-(naphthalen-1-yl)-1H-benzo[d]imidazole(4j)

Brown oil, yield: 78%. ee = 50%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 70:30; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 5.2 min (minor), t_{R2} = 6.4 min (major).

¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.86 (s, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.09 (dd, J = 7.7, 5.7 Hz, 2H), 6.69 (d, J = 8.5 Hz, 1H), 2.49 (dd, J = 15.5, 7.6 Hz, 1H), 1.97 (d, J = 12.1 Hz, 1H), 1.87 – 1.59 (m, 6H), 1.37 – 1.22 (m, 2H), 1.02 (ddt, J = 21.6, 12.2, 10.7 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.82 (s), 144.97 (s), 142.86 (s), 135.82 (s), 130.52 (s), 129.17 (s), 122.48 (s), 122.20 (s), 120.34 (s), 118.80 (s), 116.82 (s), 111.86 (s), 109.93 (s), 48.32 (s), 10.55 (s), 9.61 (s), 9.20 (s), 7.79 (s), 3.47 (d, J = 8.5 Hz).

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₃H₂₂ClN₂ 361.1472; Found 361.1463.



5-chloro-2-cyclohexyl-1-(2-isopropoxyphenyl)-1H-benzo[d]imidazole(4k)

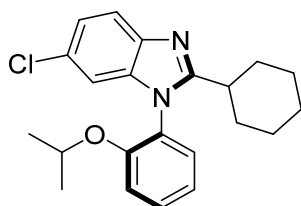
Brown oil, yield: 89%. $[\alpha]_D^{25.3}$ = -12.05° (c 0.4, CH₂Cl₂), ee = 73%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 95:5; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 8.3 min (minor), t_{R2} = 10.7 min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.5 Hz, 1H), 7.58 – 7.45 (m, 1H), 7.27 (s, 1H), 7.20 (dd, J = 8.5, 1.9 Hz, 1H), 7.11 (dd, J = 12.8, 4.9 Hz, 2H), 6.95 (d, J = 1.7 Hz, 1H), 6.86 – 6.70 (m, 1H), 4.52 (dt, J = 12.1, 6.0 Hz, 1H), 2.57 (ddd, J = 11.7, 7.6, 3.4

Hz, 1H), 2.04 – 1.89 (m, 2H), 1.89 – 1.74 (m, 3H), 1.72 – 1.60 (m, 2H), 1.51 – 1.38 (m, 1H), 1.32 (dd, $J = 9.3, 6.4$ Hz, 1H), 1.20 (d, $J = 6.0$ Hz, 3H), 1.14 (dd, $J = 7.9, 4.7$ Hz, 1H), 1.07 (d, $J = 6.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.14, 153.59, 141.40, 137.01, 130.65, 129.57, 127.69, 124.79, 122.32, 120.92, 119.72, 114.74, 110.12, 77.35, 77.03, 76.71, 70.71, 36.47, 32.44, 30.87, 26.14 (d, $J = 7.2$ Hz), 25.73, 21.70 (d, $J = 2.2$ Hz).

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{ClN}_2\text{O}$ 369.1728; Found 369.1722.



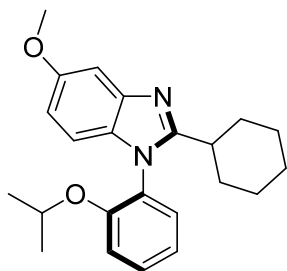
6-chloro-2-cyclohexyl-1-(2-isopropoxyphenyl)-1H-benzo[d]imidazole(4l)

Brown oil, yield: 70%. $[\alpha]_{\text{D}}^{25.3} = -36.45^\circ$ (c 0.4, CH_2Cl_2), ee = 81%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 98:2; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{\text{R}1} = 8.9$ min (minor), $t_{\text{R}2} = 10.3$ min (major).

^1H NMR (600 MHz, CDCl_3) δ 7.66 (d, $J = 8.5$ Hz, 1H), 7.47 (t, $J = 7.9$ Hz, 1H), 7.26 (d, $J = 5.9$ Hz, 1H), 7.17 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.09 (dd, $J = 12.1, 8.0$ Hz, 2H), 6.92 (d, $J = 1.6$ Hz, 1H), 4.48 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.55 (dd, $J = 13.4, 10.1$ Hz, 1H), 1.96 (d, $J = 13.0$ Hz, 1H), 1.92 – 1.71 (m, 5H), 1.70 – 1.62 (m, 2H), 1.37 – 1.20 (m, 2H), 1.17 (d, $J = 6.0$ Hz, 3H), 1.05 (d, $J = 6.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.14, 153.58, 141.37, 137.00, 130.66, 129.55, 127.70, 124.76, 122.33, 120.92, 119.69, 114.74, 110.12, 77.36, 77.05, 76.73, 70.71, 36.47, 32.43, 30.87, 26.13 (d, $J = 7.2$ Hz), 25.72, 21.69 (d, $J = 2.1$ Hz).

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{ClN}_2\text{O}$ 369.1728; Found 369.1720.



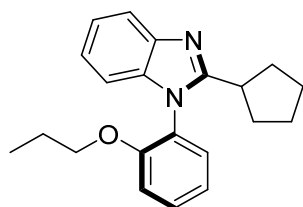
2-cyclohexyl-1-(2-isopropoxyphenyl)-5-methoxy-1H-benzo[d]imidazole(4m)

Brown oil, yield: 63%. $[\alpha]_D^{25.3} = -10.36^\circ$ (c 0.4, CH₂Cl₂), ee = 43%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 95:5; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{R1} = 7.8$ min (minor), $t_{R2} = 10.4$ min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.43 (m, 1H), 7.33 (d, $J = 2.1$ Hz, 1H), 7.31 – 7.27 (m, 2H), 7.16 – 7.06 (m, 2H), 6.81 (dt, $J = 8.7, 5.5$ Hz, 2H), 4.46 (dd, $J = 12.1, 6.0$ Hz, 1H), 3.87 (s, 3H), 2.55 (dd, $J = 9.3, 5.7$ Hz, 1H), 2.06 – 1.89 (m, 2H), 1.88 – 1.71 (m, 3H), 1.67 (dd, $J = 12.3, 2.8$ Hz, 2H), 1.41 – 1.22 (m, 2H), 1.19 (d, $J = 6.1$ Hz, 3H), 1.17 – 1.10 (m, 1H), 1.05 (d, $J = 6.0$ Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.49, 155.90, 153.66, 143.31, 130.98, 130.24, 129.68, 125.52, 120.89, 114.98, 111.63, 110.30, 101.46, 77.31 (d, $J = 11.6$ Hz), 77.05, 76.73, 70.75, 55.80, 36.53, 32.59, 30.95, 26.21 (d, $J = 6.6$ Hz), 25.79, 21.72.

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₃H₂₉N₂O₂ 365.2224; Found 365.2234.



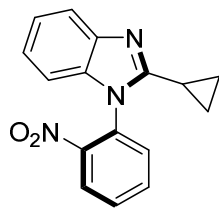
2-cyclopentyl-1-(2-propoxyphenyl)-1H-benzo[d]imidazole(4n)

White oil, yield: 42%. $[\alpha]_D^{25.3} = -19.71^\circ$ (c 0.4, CH₂Cl₂), ee = 39%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; $\lambda = 254$ nm; 25 °C; Retention times: $t_{R1} = 6.5$ min (minor), $t_{R2} = 9.4$ min (major).

¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, $J = 8.0$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 1H), 7.30 (d, $J = 7.4$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.19 – 7.06 (m, 3H), 6.93 (d, $J = 8.0$ Hz, 1H), 3.86 (dq, $J = 15.5, 6.6$ Hz, 2H), 3.09 – 2.95 (m, 1H), 2.11 (d, $J = 8.0$ Hz, 1H), 1.90 (dd, $J = 15.9, 6.7$ Hz, 3H), 1.85 (s, 2H), 1.63 – 1.48 (m, 4H), 0.68 (t, $J = 7.4$ Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 160.01, 155.14, 136.86, 130.48, 129.77, 124.91, 121.98, 121.75, 120.85, 118.86, 113.34, 109.85, 70.09, 37.47, 32.91, 31.73, 29.69, 25.85 (d, $J = 19.0$ Hz), 22.24, 10.18.

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₁H₂₅N₂O 321.1961; Found 321.1952.



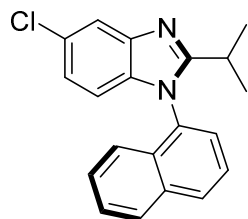
2-cyclopropyl-1-(2-nitrophenyl)-1H-benzo[d]imidazole(4o)

Brown oil, yield: 41%. ee = 41%; HPLC analysis: Daicel Chiralpak OD-H; Hexane/iPrOH = 80:20; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 8.4 min (minor), t_{R2} = 10.5 min (major).

^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, J = 8.1 Hz, 1H), 7.89 (t, J = 7.7 Hz, 1H), 7.76 (dd, J = 10.3, 8.7 Hz, 2H), 7.64 (d, J = 7.8 Hz, 1H), 7.39 – 7.25 (m, 1H), 7.19 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 1.62 (ddd, J = 13.0, 8.3, 4.8 Hz, 1H), 1.48 – 1.36 (m, 1H), 1.34 – 1.21 (m, 2H), 1.02 (dd, J = 8.2, 2.9 Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.65 (s), 146.84 (s), 142.66 (s), 136.29 (s), 134.36 (s), 131.17 (s), 130.34 (s), 129.68 (s), 126.00 (s), 122.81 (d, J = 8.4 Hz), 119.21 (s), 108.81 (s), 77.37 (s), 77.05 (s), 76.74 (s), 9.82 (s), 8.85 (s), 7.98 (s).

HRMS (ESI-TOF) m/z [$M + H$] $^+$ Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}_2$ 280.1086; Found 280.1079.



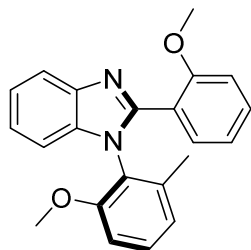
5-chloro-2-isopropyl-1-(naphthalen-1-yl)-1H-benzo[d]imidazole (4p)

White solid, yield: 80%, Mp: 123-124 °C. ee = 63%; HPLC analysis: Daicel Chiralpak AD-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 7.5 min (minor), t_{R2} = 9.4 min (major).

^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 1.6 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.08–7.05 (m, 2H), 6.69 (d, J = 8.4 Hz, 1H), 2.84–2.77 (m, 1H), 1.32 (d, J = 6.8 Hz, 3H), 1.22 (d, J = 6.8 Hz, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 162.5, 143.5, 135.8, 134.6, 132.0, 130.6, 130.3, 128.7, 128.0, 127.3, 126.5, 125.7, 123.1, 122.3, 119.2, 111.1, 27.1, 22.2, 21.5;

HRMS (MALDI-TOF) m/z calcd. for C₂₀H₁₈ClN₂ [M+H]⁺ 321.1153, found 321.1152;



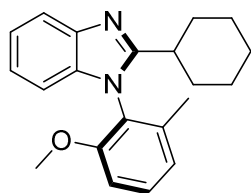
1-(2-methoxy-6-methylphenyl)-2-(2-methoxyphenyl)-1H-benzo[d]imidazole (4q)

Brown oil, yield: 50%; ee = 13%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 85:15; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 20.2 min (minor), t_{R2} = 25.1 min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.0 Hz, 1H), 7.52 (dd, J = 7.6, 1.6 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.27 – 7.21 (m, 2H), 7.01 (d, J = 7.9 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.78 (d, J = 8.3 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 3.55 (s, 3H), 3.49 (s, 3H), 2.08 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.37 (s), 155.28 (s), 152.50 (s), 143.37 (s), 137.84 (s), 135.80 (s), 132.27 (s), 130.84 (s), 129.28 (s), 124.34 (s), 122.72 (s), 122.46 (s), 122.03 (s), 120.33 (s), 119.96 (d, J = 16.1 Hz), 110.47 (d, J = 5.6 Hz), 109.04 (s), 77.39 (s), 77.07 (s), 76.75 (s), 55.29 (s), 54.91 (s), 17.82 (s).

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₂H₂₁N₂O₂ 344.1598; Found 344.1598.



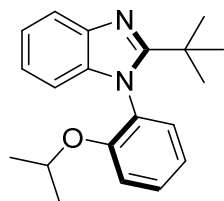
2-cyclohexyl-1-(2-methoxy-6-methylphenyl)-1H-benzo[d]imidazole (4r)

Brown oil, yield: 65%; ee = 43%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 95:5; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 14.5 min (minor), t_{R2} = 20.5 min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.35 – 7.21 (m, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 3.69 (s, 3H), 2.48 – 2.34 (m, 1H), 1.99 (d, J = 10.9 Hz, 3H), 1.87 – 1.75 (m, 5H), 1.68 (d, J = 12.6 Hz, 1H), 1.43 – 1.26 (m, 3H), 1.20 (dt, J = 26.1, 8.1 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 160.01 (s), 155.97 (s), 142.77 (s), 138.26 (s), 135.07 (s), 130.02 (s), 123.25 (s), 122.81 (s), 122.23 (s), 121.94 (s), 119.10 (s), 109.72 (s), 109.45 (s), 55.62 (s), 36.67 (s), 31.87 (s), 31.50 (s), 26.24 (d, *J* = 2.6 Hz), 25.74 (s), 17.44 (s).

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₁H₂₅N₂O 321.1961; Found 321.1977.



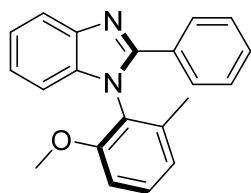
2-(tert-butyl)-1-(2-isopropoxyphenyl)-1H-benzo[d]imidazole (4s)

Brown oil, yield: 43%; ee = 29%; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH =90:10; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 7.1 min (minor), t_{R2} =12.5 min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.50 (dt, *J* = 9.4, 6.4 Hz, 1H), 7.34 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.09 (dt, *J* = 17.2, 7.2 Hz, 3H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.51 (dd, *J* = 12.1, 6.0 Hz, 1H), 1.38 (s, 9H), 1.16 (d, *J* = 6.1 Hz, 3H), 0.99 (d, *J* = 6.0 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 161.87 (s), 154.44 (s), 138.55 (s), 130.93 (d, *J* = 95.6 Hz), 129.38 (s), 127.22 (s), 121.84 (d, *J* = 64.4 Hz), 120.11 (s), 118.84 (s), 113.73 (s), 109.80 (s), 77.23 (s), 77.02 (s), 76.80 (s), 70.20 (s), 34.90 (s), 21.51 (s).

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₀H₂₅N₂O 309.1961; Found 309.1974.



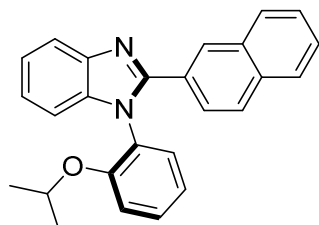
1-(2-methoxy-6-methylphenyl)-2-phenyl-1H-benzo[d]imidazole (4t)

Brown oil, yield: 52%; ee = 0; HPLC analysis: Daicel Chiralpak AD-H; Hexane/iPrOH =80:20; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 5.5 min (minor), t_{R2} = 9.4 min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.46 – 7.20 (m, 6H), 6.97 (dd, *J* = 7.8, 4.1 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 3.58 (s, 3H), 1.95 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.76 (s), 153.11 (s), 143.24 (s), 137.82 (s), 136.53 (s), 130.63 (s), 130.04 (s), 129.38 (s), 128.20 (d, *J* = 5.8 Hz), 124.75 (s), 122.95 (d, *J* = 14.8 Hz), 122.55 (s), 119.73 (s), 110.41 (s), 109.66 (s), 77.37 (s), 77.05 (s), 76.74 (s), 55.69 (s), 17.58 (s).

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₁H₁₉N₂O 315.1492; Found 315.1501.



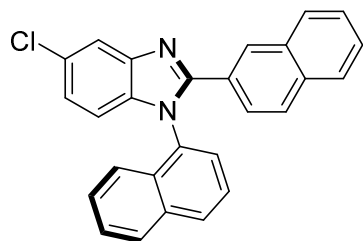
1-(2-isopropoxyphenyl)-2-(naphthalen-2-yl)-1H-benzo[d]imidazole (4u)

Brown oil, yield: 63%; ee = 0; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 13.7 min (minor), t_{R2} = 17.5 min (major).

¹H NMR (400 MHz, CDCl₃) δ 8.14 (s, 1H), 7.95 (s, 1H), 7.80 (d, *J* = 2.3 Hz, 3H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.46 (dd, *J* = 8.2, 4.5 Hz, 4H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.28 (s, 1H), 7.20 (s, 1H), 7.09 (s, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 4.36 – 4.27 (m, 1H), 1.02 (d, *J* = 6.0 Hz, 3H), 0.69 (d, *J* = 6.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.23 (d, *J* = 17.4 Hz), 143.21 (s), 137.55 (s), 133.44 (s), 132.89 (s), 130.19 (s), 129.39 (s), 128.66 – 128.25 (m), 127.70 (d, *J* = 15.9 Hz), 126.80 (s), 126.36 (d, *J* = 17.6 Hz), 125.77 (s), 122.96 (s), 122.60 (s), 120.70 (s), 119.57 (s), 114.43 (s), 110.73 (s), 77.42 (s), 77.10 (s), 76.78 (s), 70.09 (s), 21.72 (s), 20.84 (s).

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₆H₂₃N₂O 379.1805; Found 379.1820.

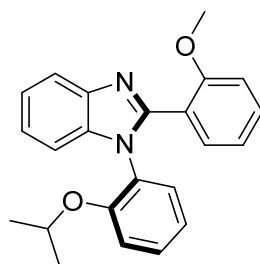


5-chloro-1-(naphthalen-1-yl)-2-(naphthalen-2-yl)-1H-benzo[d]imidazole (4v)

Brown oil, yield: 55%; ee = 0; HPLC analysis: Daicel Chiralpak AD-H; Hexane/iPrOH = 80:20; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 23.5 min (minor), t_{R2} = 37.3 min (major).

¹H NMR (400 MHz, CDCl₃) δ 8.14 – 7.98 (m, 4H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.52 (m, 5H), 7.49 – 7.38 (m, 5H), 7.19 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.83 (dd, *J* = 11.9, 5.5 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 154.49 (s), 143.84 (s), 136.97 (s), 134.51 (s), 133.57 (s), 133.16 (s), 132.73 (s), 130.07 (d, *J* = 6.9 Hz), 129.18 (s), 128.66 (s), 128.02 (d, *J* = 4.4 Hz), 127.58 (s), 127.22 (s), 126.73 (d, *J* = 12.3 Hz), 126.47 (s), 125.73 (s), 125.38 (s), 123.88 (s), 122.56 (s), 120.98 (s), 119.60 (s), 118.46 (s), 115.07 (s), 111.78 (s), 111.47 (s).



1-(2-isopropoxyphenyl)-2-(2-methoxyphenyl)-1H-benzo[d]imidazole (4w)

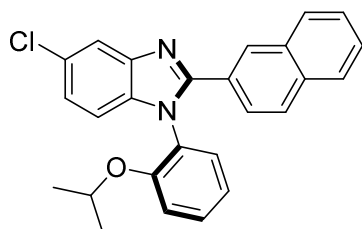
Brown oil, yield: 52%; ee = 0; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 85:15; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: *t*_{R1} = 18.0 min (minor), *t*_{R2} = 23.8 min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.61 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.40 – 7.21 (m, 5H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.05 – 6.89 (m, 3H), 6.77 (d, *J* = 8.3 Hz, 1H), 4.52 – 4.30 (m, 1H), 3.49 (s, 3H), 1.09 (d, *J* = 6.0 Hz, 3H), 0.96 (d, *J* = 6.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.13 (s), 152.76 (s), 152.23 (s), 143.19 (s), 136.68 (s), 132.41 (s), 130.92 (s), 129.27 (d, *J* = 4.8 Hz), 126.39 (s), 122.47 (s), 121.96 (s), 120.52 (s), 120.29 (s), 119.82 (s), 119.59 (s), 113.87 (s), 110.84 (s), 110.59 (s), 77.38 (s), 77.06 (s), 76.74 (s), 70.00 (s), 54.83 (s), 21.80 (s), 21.15 (s).

HRMS (ESI-TOF) *m/z* [M + H]⁺ Calcd for C₂₃H₂₃N₂O₂ 359.1754; Found 359.1762.

HRMS (ESI-TOF) *m/z* [M + H]⁺ Calcd for C₂₇H₁₈ClN₂ 405.1153; Found 405.1164.



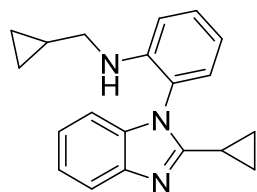
5-chloro-1-(2-isopropoxyphenyl)-2-(naphthalen-2-yl)-1H-benzo[d]imidazole (4x)

Brown oil, yield: 68%. ee = 0; HPLC analysis: Daicel Chiralpak AD-H; Hexane/iPrOH = 80:20; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 8.8 min (minor), t_{R2} = 12.7 min (major).

¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 7.78 (ddd, J = 26.0, 21.0, 8.3 Hz, 5H), 7.55 – 7.40 (m, 4H), 7.31 (dd, J = 13.1, 4.6 Hz, 1H), 7.16 (d, J = 1.6 Hz, 1H), 7.10 (s, 1H), 6.99 (d, J = 8.3 Hz, 1H), 4.42 – 4.31 (m, 1H), 1.05 (d, J = 6.0 Hz, 3H), 0.71 (d, J = 6.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.13 (s), 153.03 (s), 141.80 (s), 138.10 (s), 133.52 (s), 132.83 (s), 130.52 (s), 129.25 (s), 128.83 – 128.44 (m), 127.88 (s), 127.63 (s), 126.97 (s), 126.37 (s), 125.85 (s), 125.58 (s), 123.26 (s), 120.77 (s), 120.39 (s), 114.33 (s), 110.83 (s), 77.37 (s), 77.05 (s), 76.74 (s), 70.15 (s), 21.73 (s), 20.84 (s).

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₆H₂₂ClN₂O 413.1415; Found 413.1422.



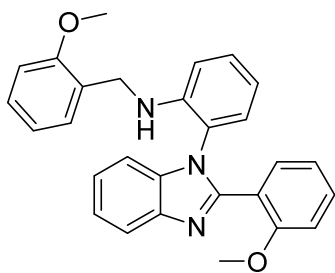
2-(2-cyclopropyl-1H-benzo[d]imidazol-1-yl)-N-(cyclopropylmethyl)aniline (7a)

Brown oil, yield: 78%; ee = 0; HPLC analysis: Daicel Chiralpak IC-H; Hexane/iPrOH = 95:5; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 8.4 min (minor), t_{R2} = 10.5 min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.9 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 7.8 Hz, 1H), 7.18 (t, J = 7.8 Hz, 2H), 7.04 (d, J = 7.8 Hz, 1H), 6.95 – 6.78 (m, 2H), 3.62 (s, 1H), 2.99 (d, J = 4.9 Hz, 2H), 1.79 (d, J = 4.0 Hz, 1H), 1.31 (d, J = 24.6 Hz, 3H), 1.15 – 0.83 (m, 3H), 0.58 – 0.35 (m, 2H), 0.10 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.82 (s), 144.97 (s), 142.86 (s), 135.82 (s), 130.52 (s), 129.17 (s), 122.48 (s), 122.20 (s), 120.34 (s), 118.80 (s), 116.82 (s), 111.86 (s), 109.93 (s), 48.32 (s), 10.55 (s), 9.61 (s), 9.20 (s), 7.79 (s), 3.47 (d, J = 8.5 Hz).

HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for C₂₀H₂₂N₃ 304.1814; Found 304.1806.



N-(2-methoxybenzyl)-2-(2-(2-methoxyphenyl)-1H-benzo[d]imidazol-1-yl)aniline(7b)

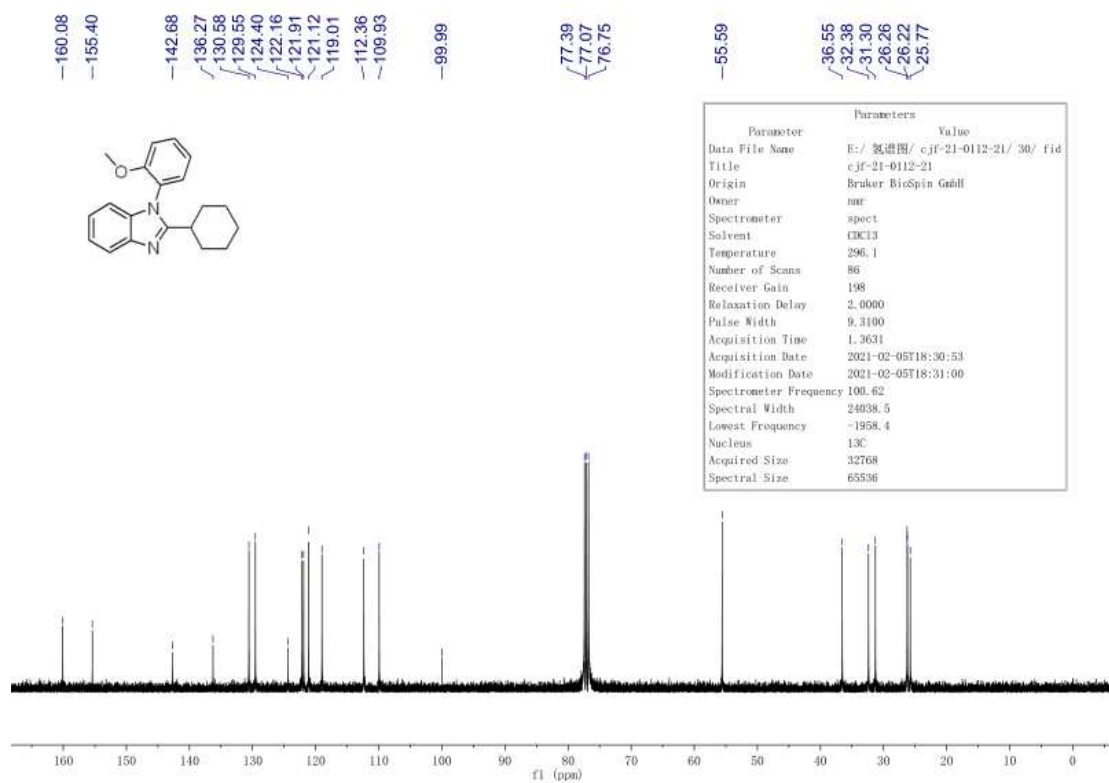
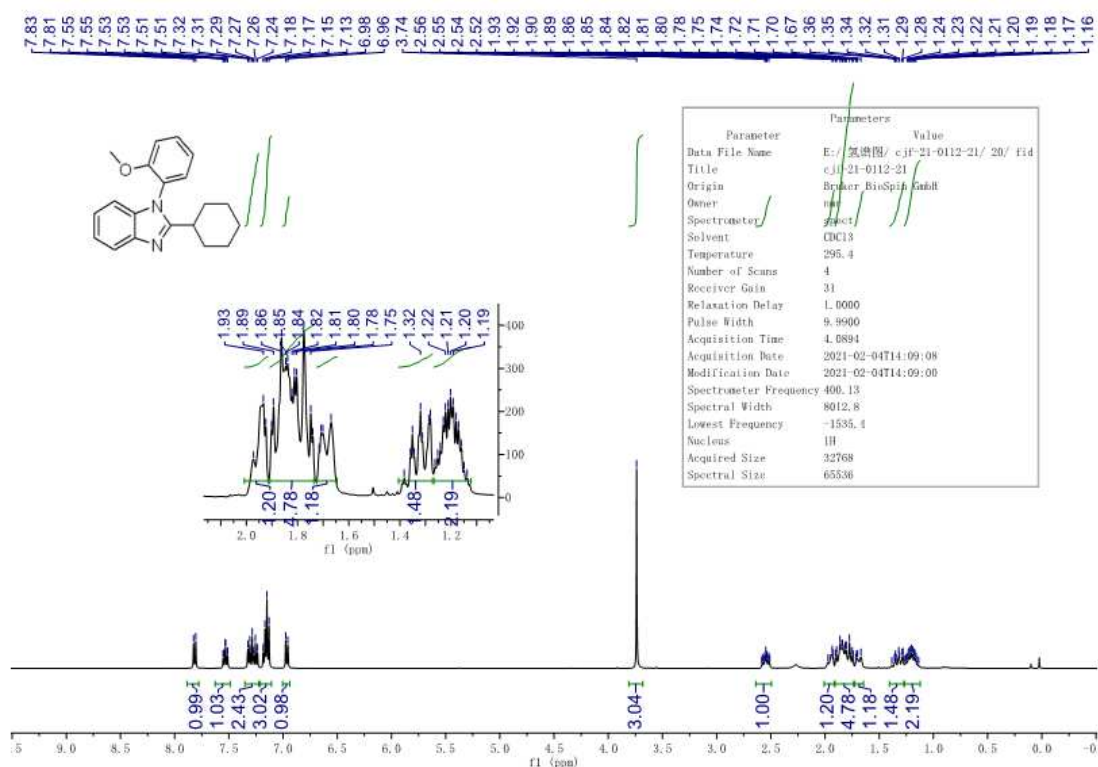
Brown oil, yield: 65%; ee = 0; HPLC analysis: Daicel Chiralpak OD-H; Hexane/iPrOH = 90:10; flow: 1.0 mL/min; λ = 254 nm; 25 °C; Retention times: t_{R1} = 7.5 min (minor), t_{R2} = 9.6 min (major).

^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 7.9 Hz, 1H), 7.58 (d, J = 7.4 Hz, 1H), 7.37 (dd, J = 13.6, 7.0 Hz, 2H), 7.31 – 7.14 (m, 4H), 7.08 (d, J = 7.3 Hz, 1H), 6.99 (t, J = 7.3 Hz, 1H), 6.93 – 6.76 (m, 5H), 6.58 (t, J = 7.4 Hz, 1H), 4.32 (d, J = 12.3 Hz, 3H), 3.66 (s, 3H), 3.50 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 157.42 (s), 157.17 (s), 152.11 (s), 144.19 (s), 143.38 (s), 135.64 (s), 132.07 (s), 131.26 (s), 129.72 (s), 128.63 – 128.24 (m), 126.60 (s), 123.01 (s), 122.54 (s), 122.10 (s), 120.44 (d, J = 7.2 Hz), 119.90 (s), 119.66 (s), 116.34 (s), 111.65 (s), 111.25 (s), 110.78 (s), 110.14 (s), 77.50 (s), 77.18 (s), 76.86 (s), 54.98 (s), 43.03 (s).

HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{26}\text{N}_3\text{O}_2$ 436.2025; Found 436.2017.

9. NMR spectrum of the obtained new products

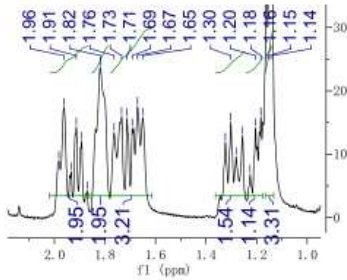
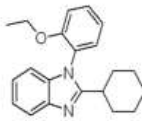


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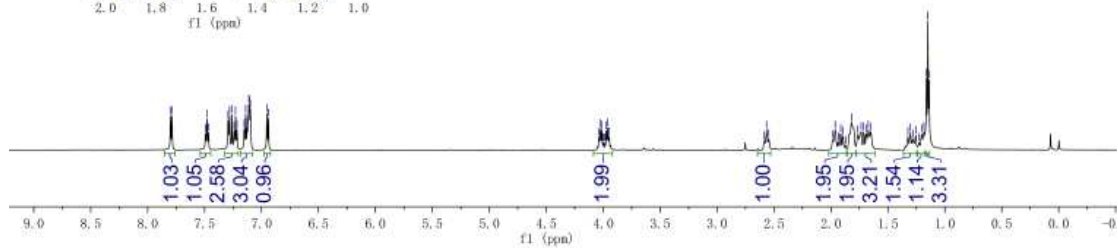
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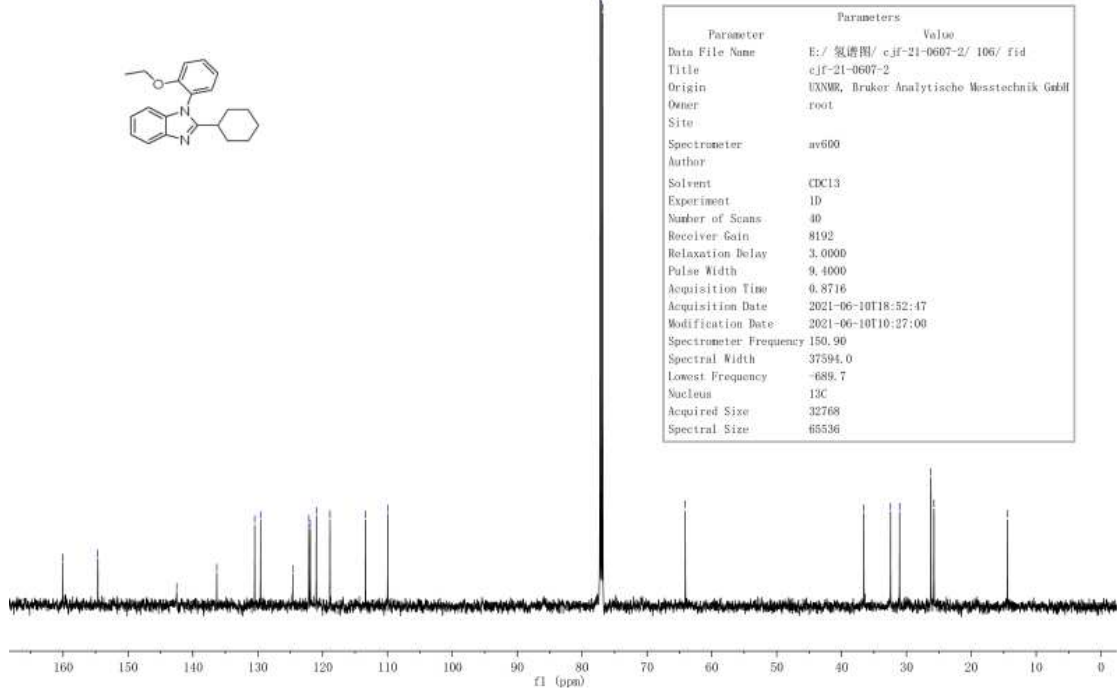
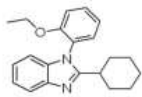
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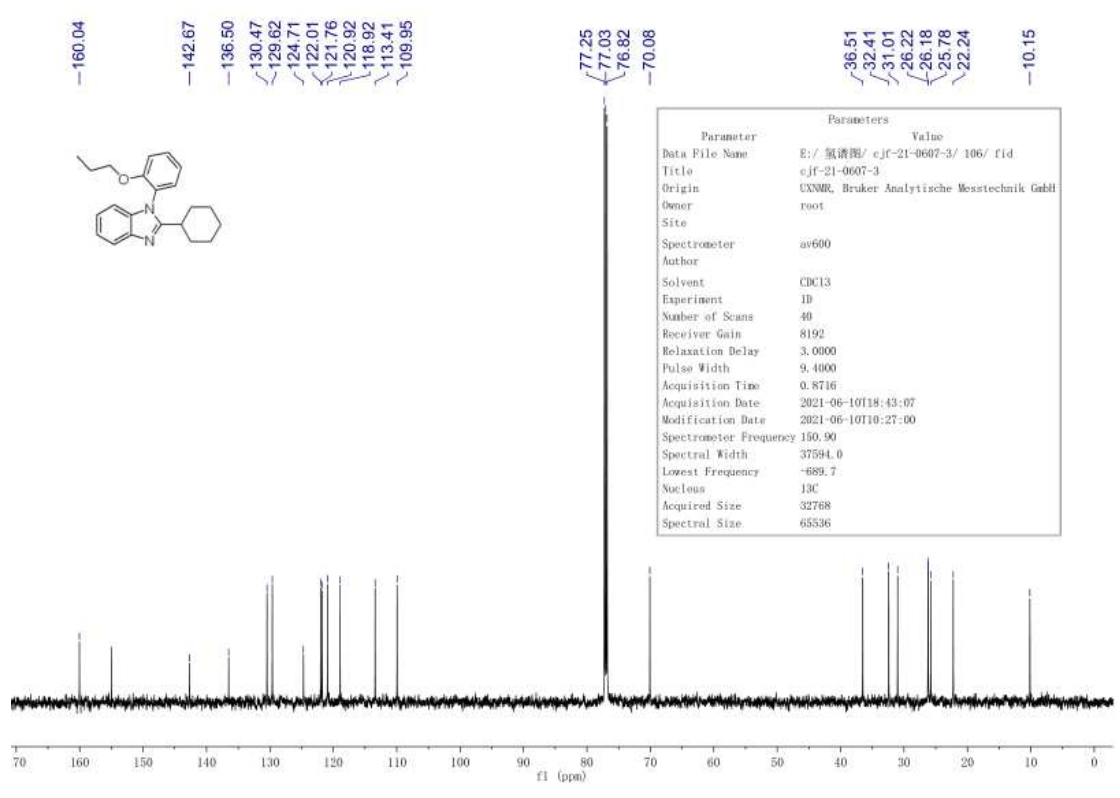
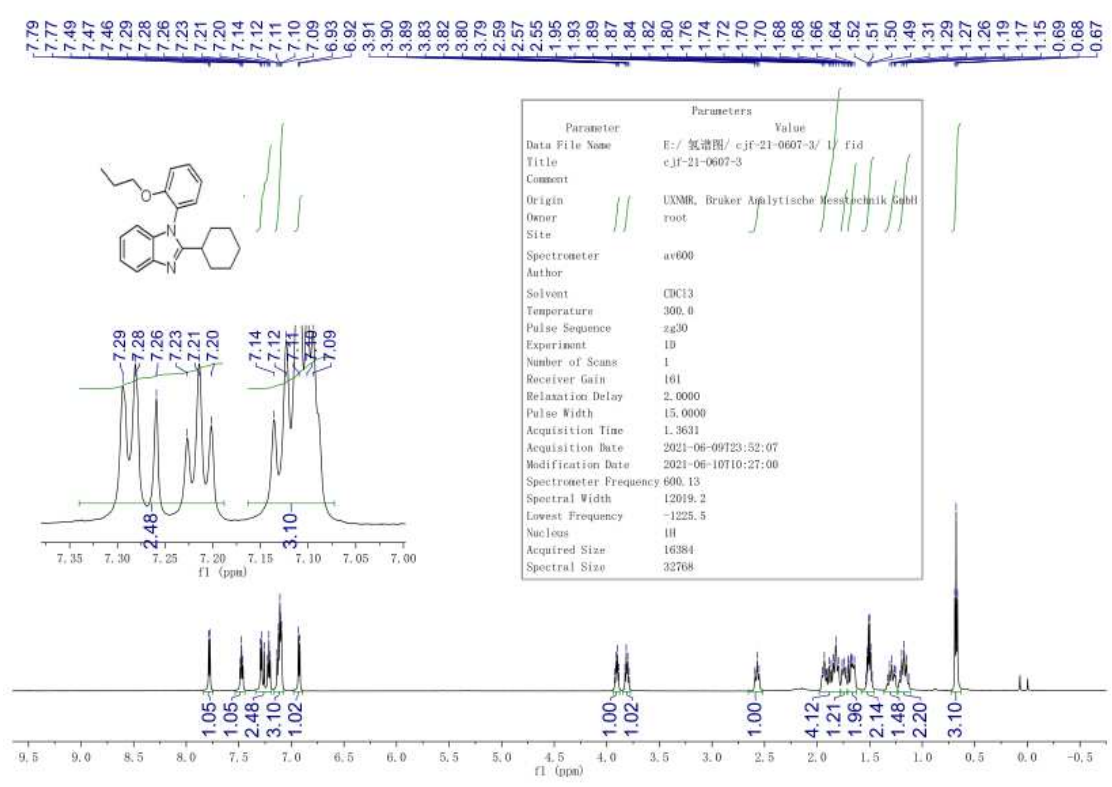
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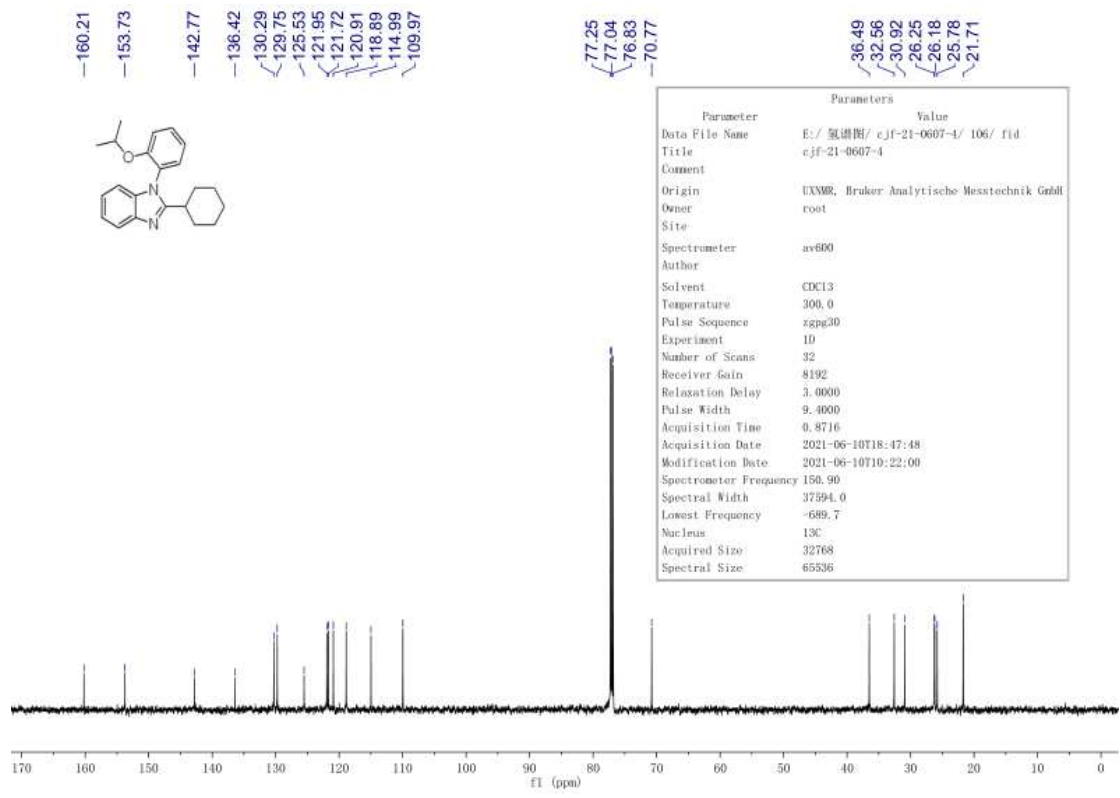
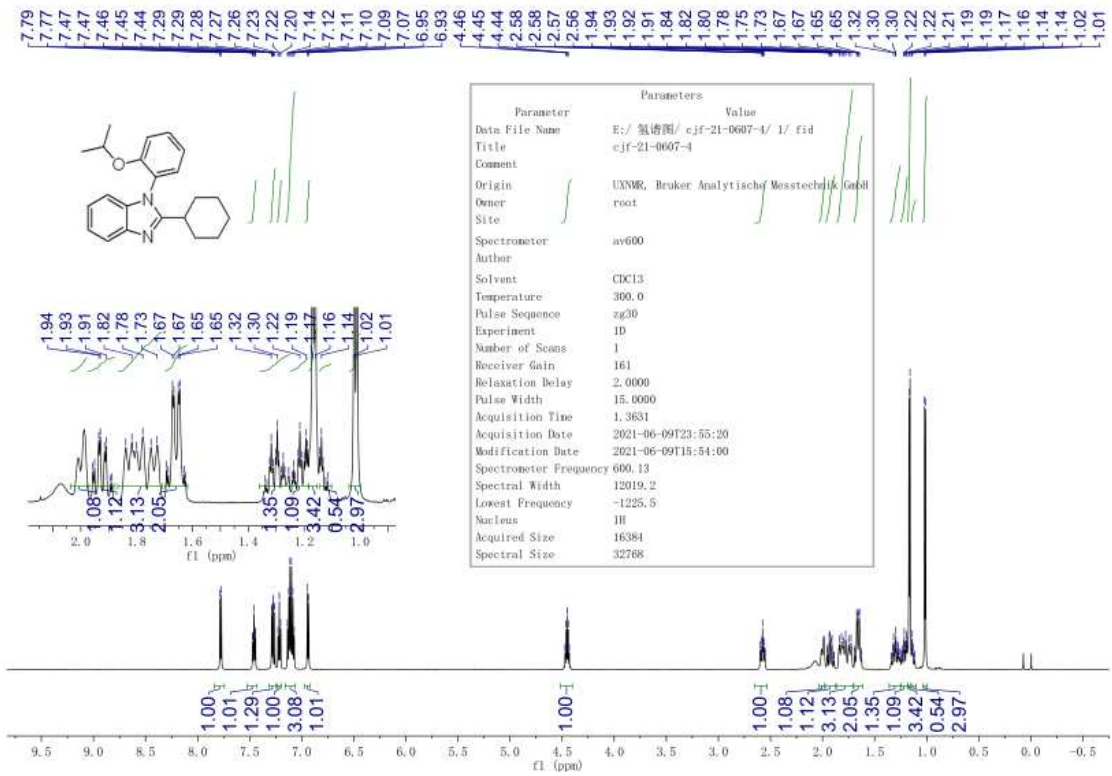
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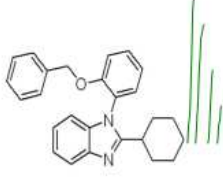


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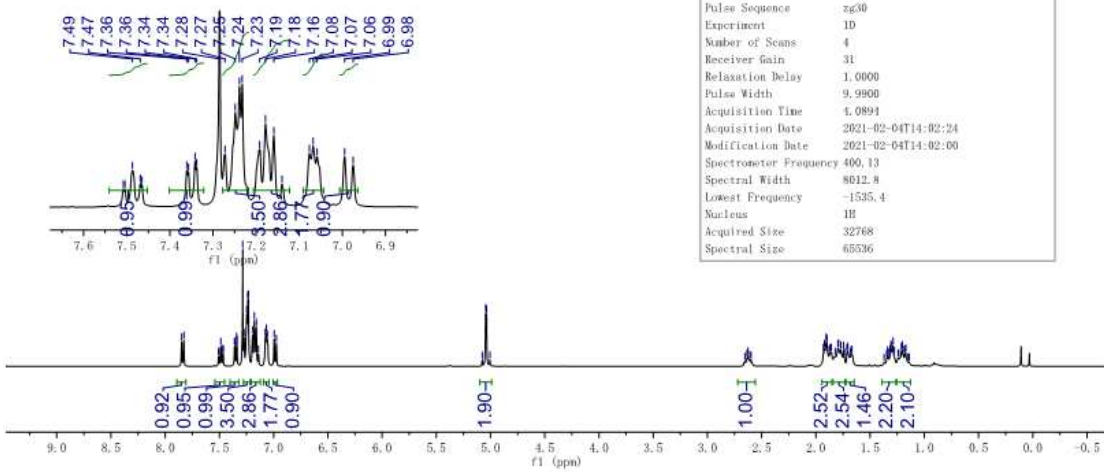




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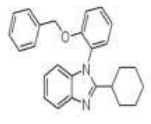


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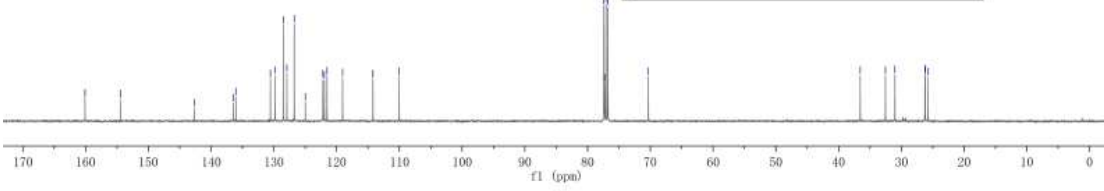


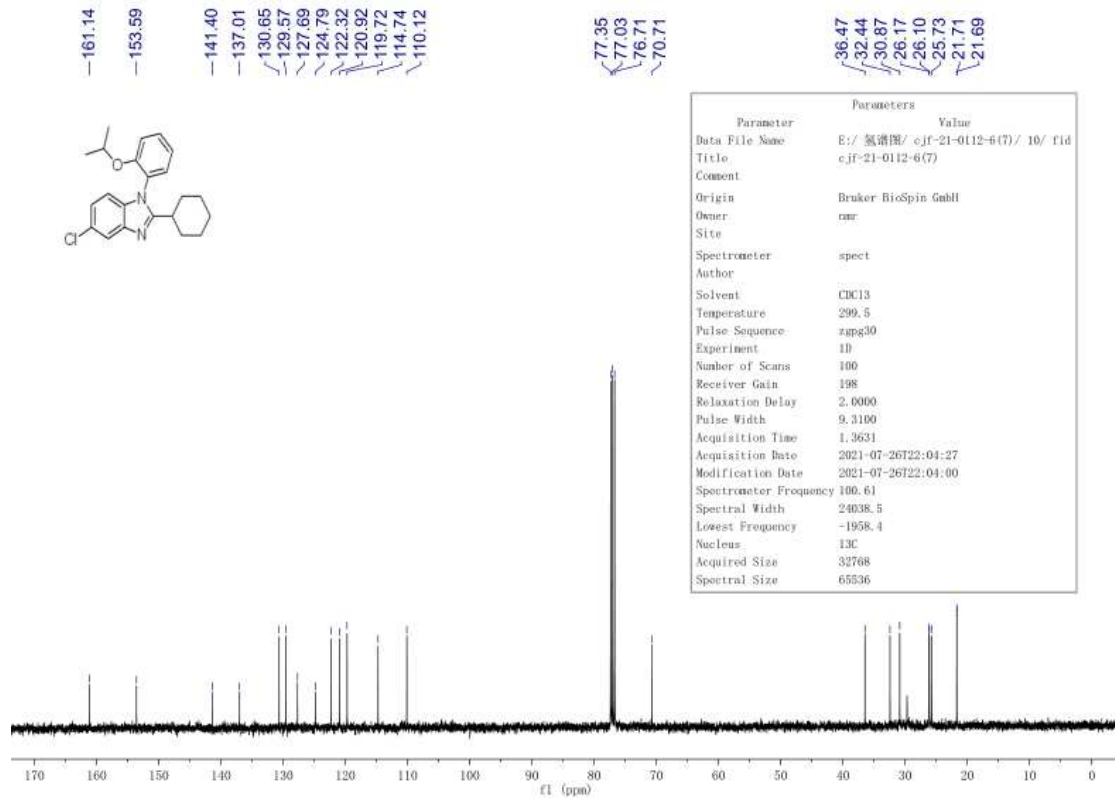
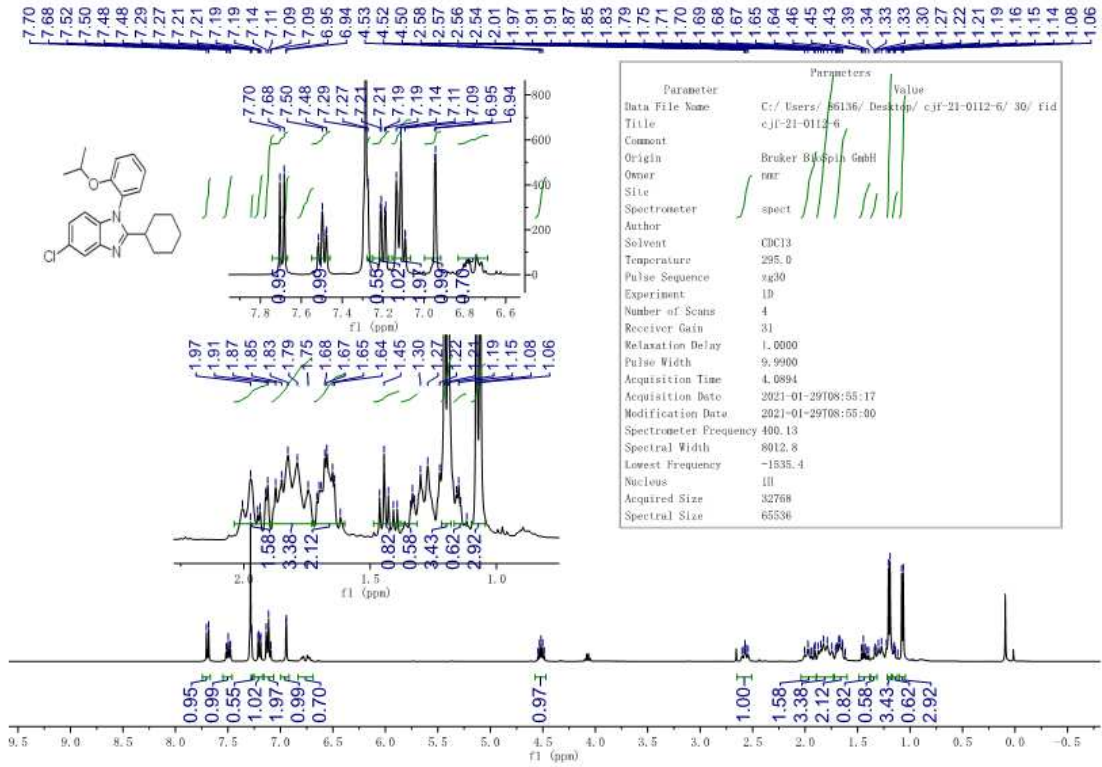
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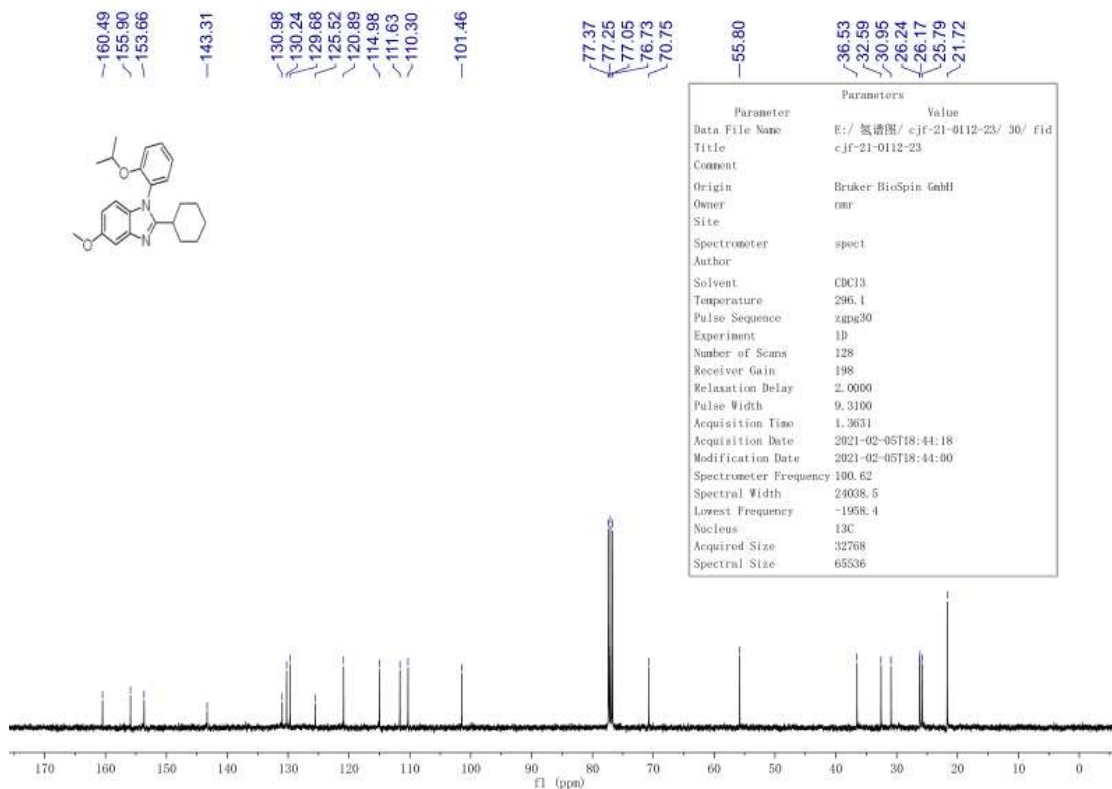
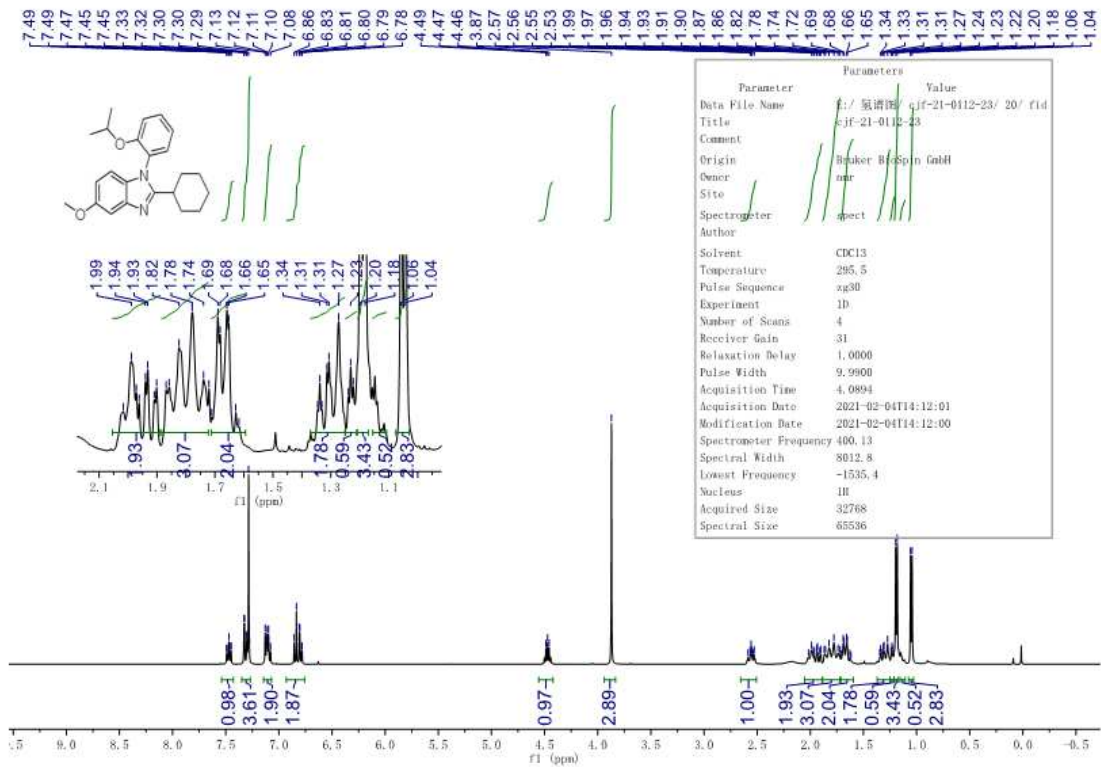
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32.53
31.02
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26.20
25.78

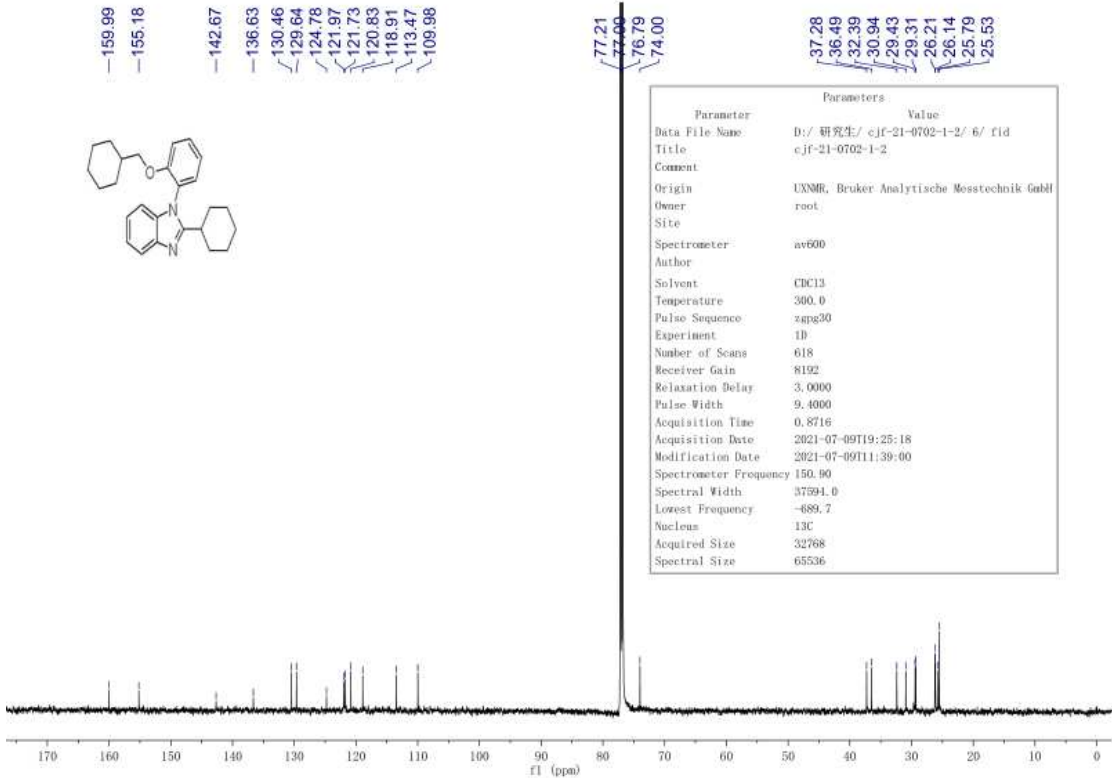
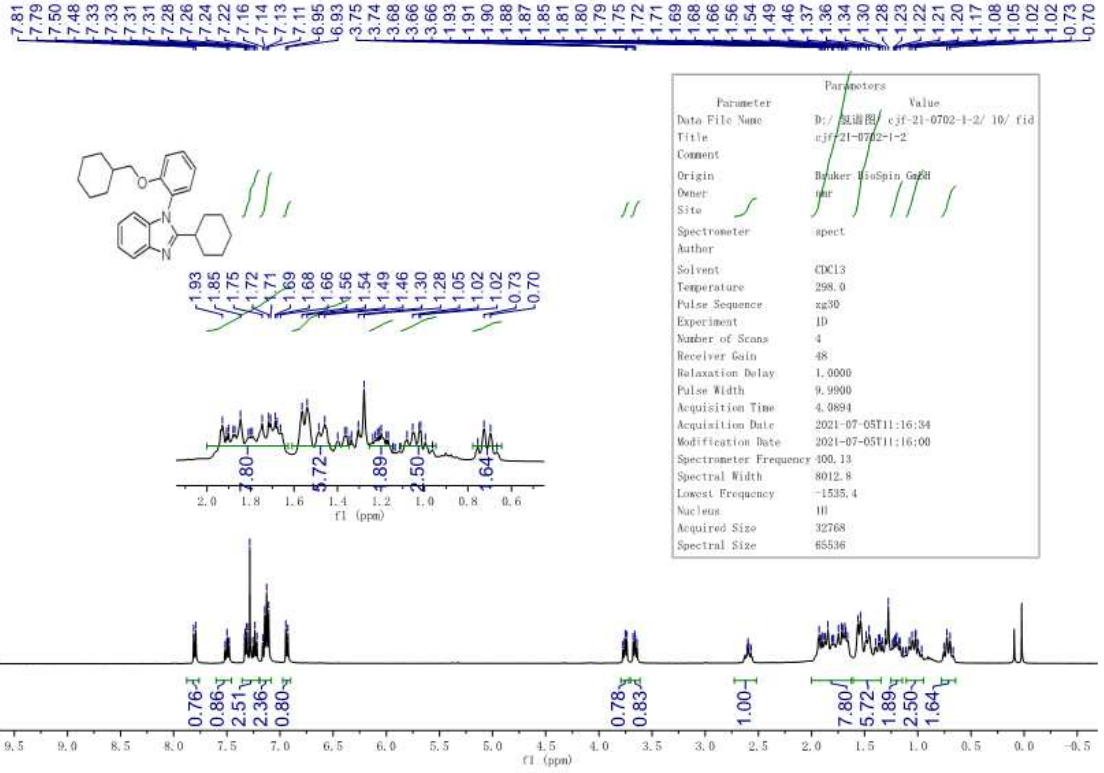


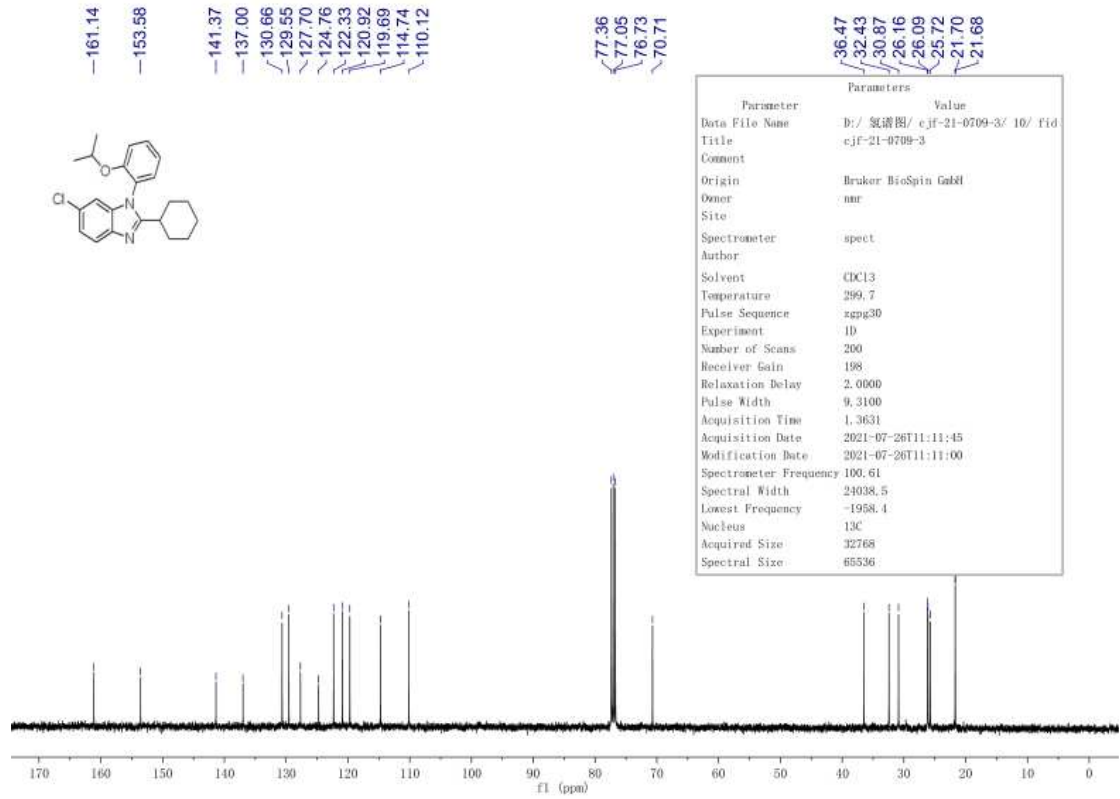
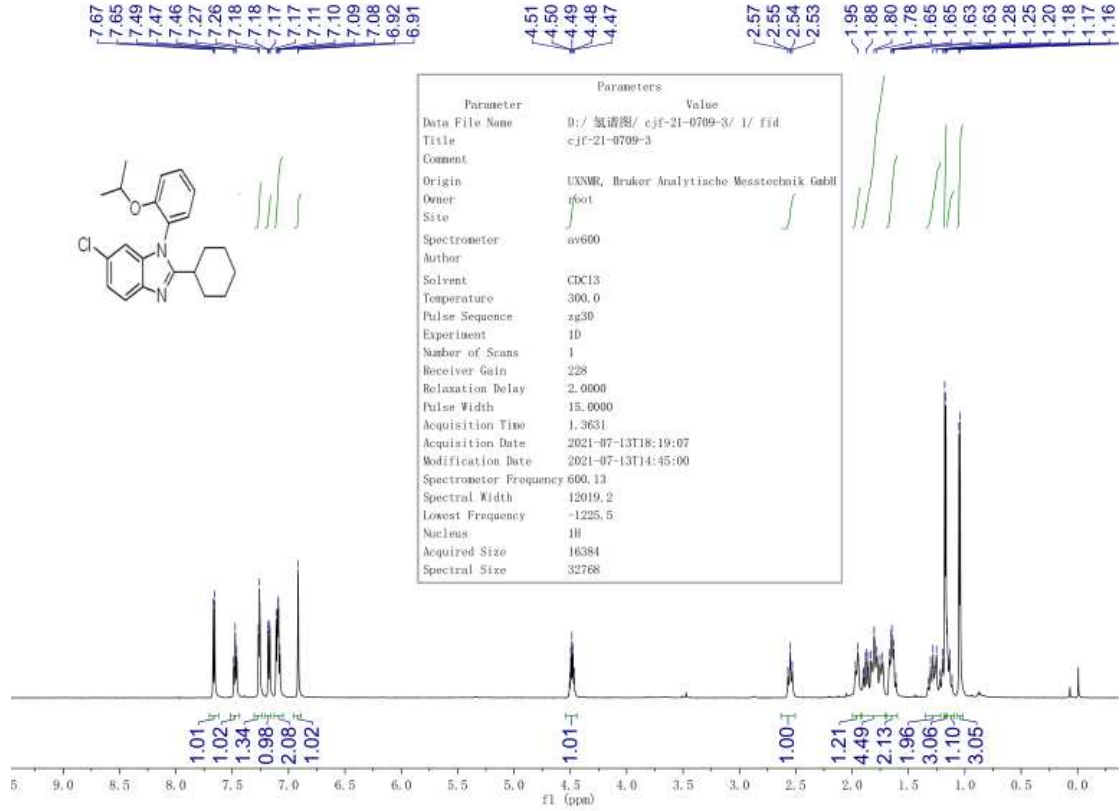
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Origin	Bruker BioSpin GmbH
Owner	nur
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	296.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	198
Relaxation Delay	2.0000
Pulse Width	9.3100
Acquisition Time	1.3631
Acquisition Date	2021-02-07T20:45:17
Modification Date	2021-02-07T20:45:00
Spectrometer Frequency	100.61
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

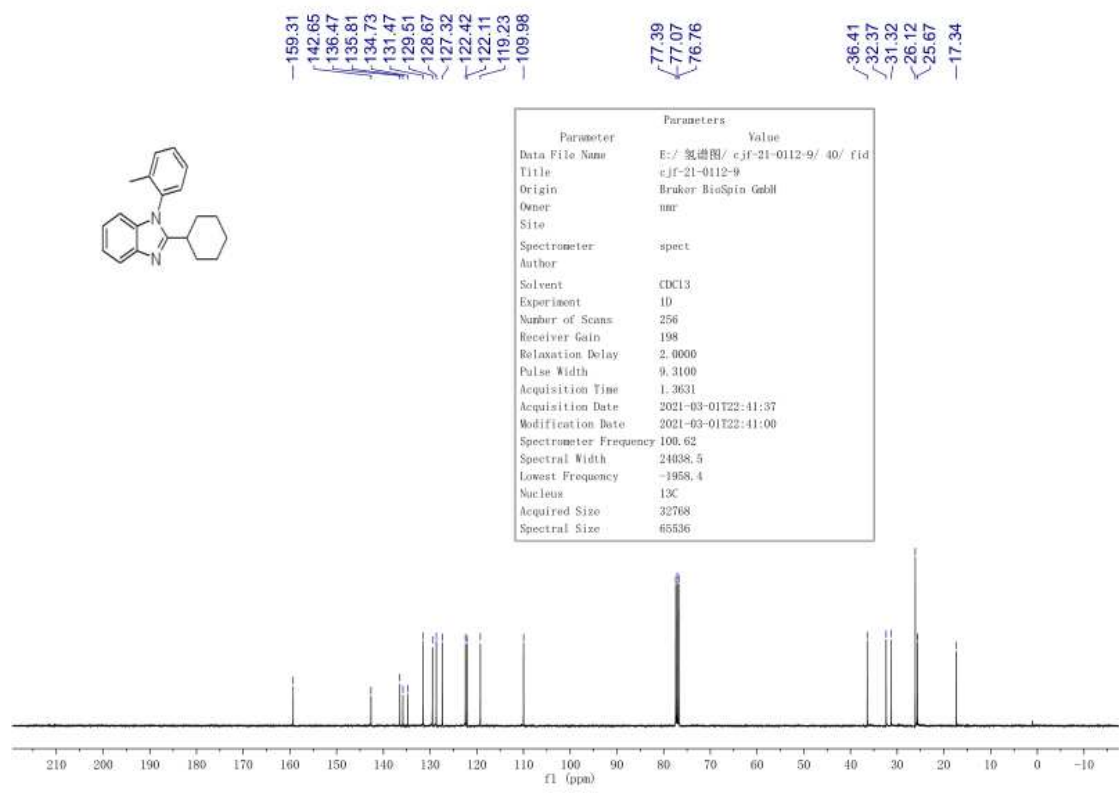
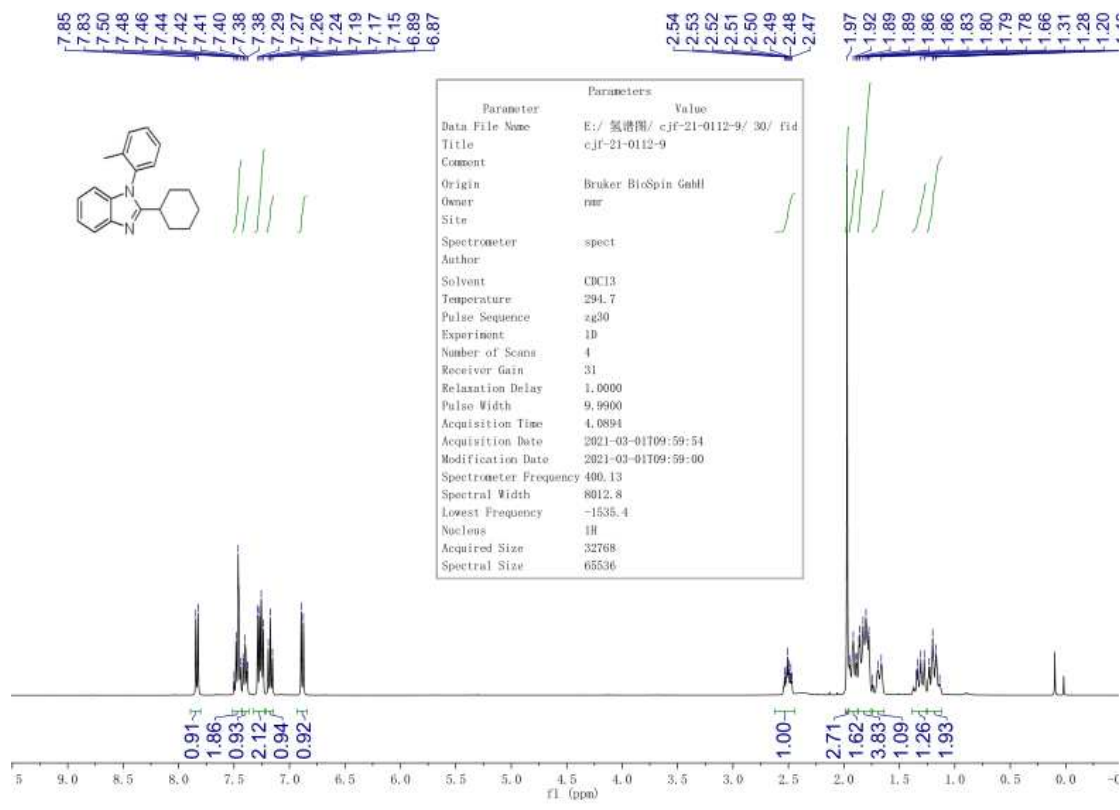


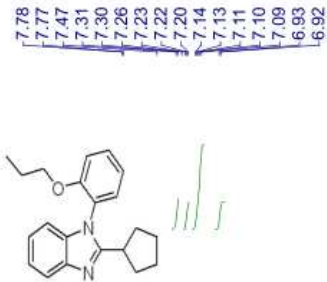






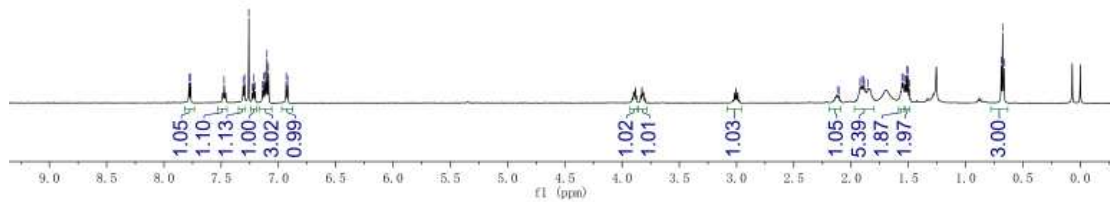




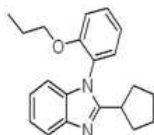


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2.11
1.92
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1.88
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1.56
1.54
1.53
1.52
1.50
1.49
0.68
0.66

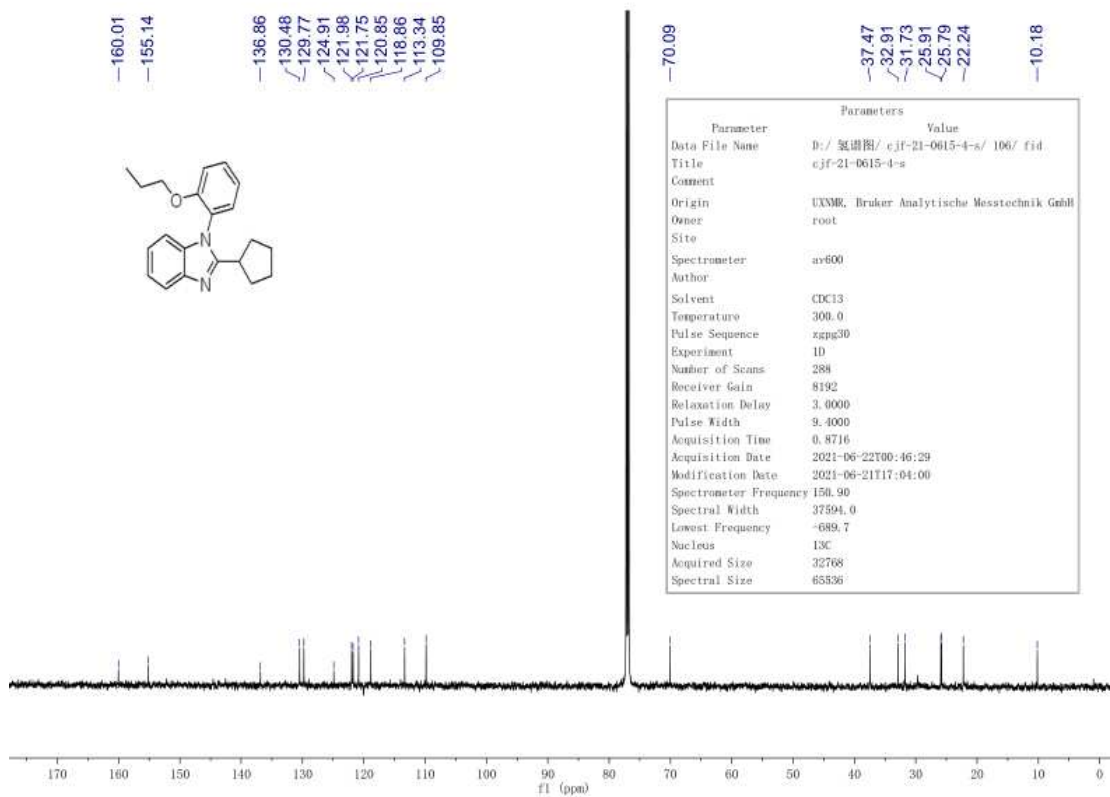
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Comment	
Origin	UXMR, Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	av600
Author	
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	1
Receiver Gain	575
Relaxation Delay	2.0000
Pulse Width	15.0000
Acquisition Time	1.3631
Acquisition Date	2021-06-17T19:05:54
Modification Date	2021-06-17T10:37:00
Spectrometer Frequency	600.13
Spectral Width	12019.2
Lowest Frequency	-1225.5
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

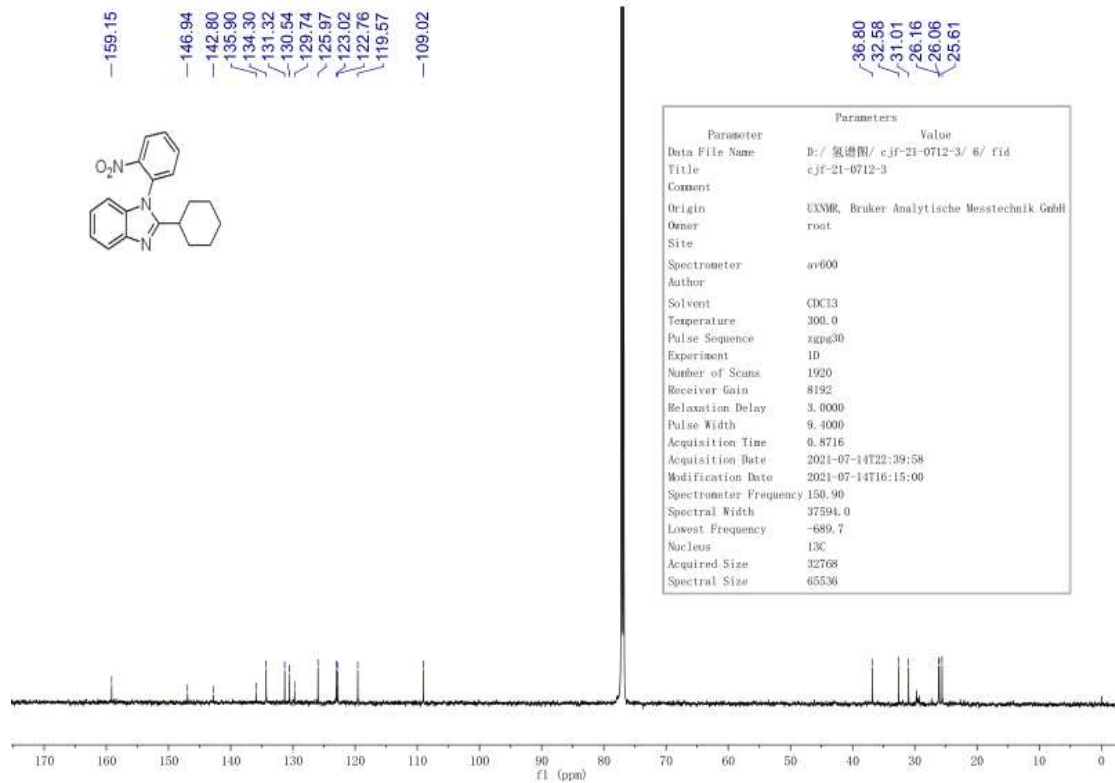
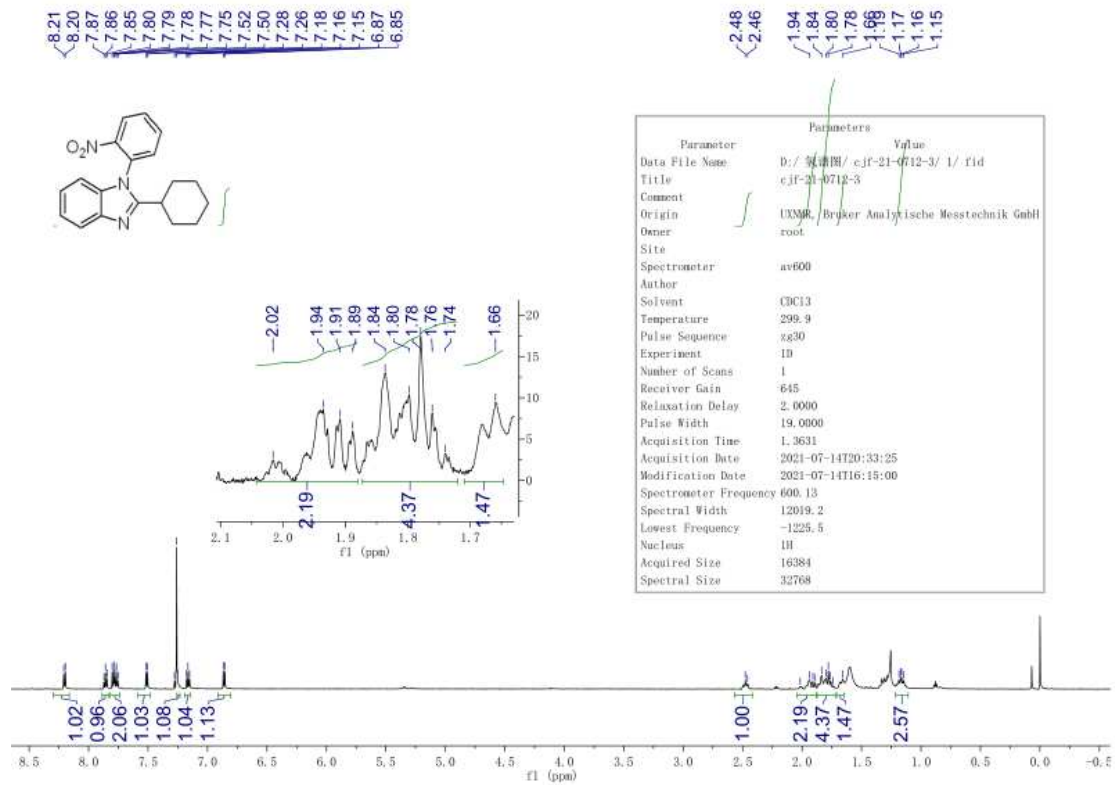


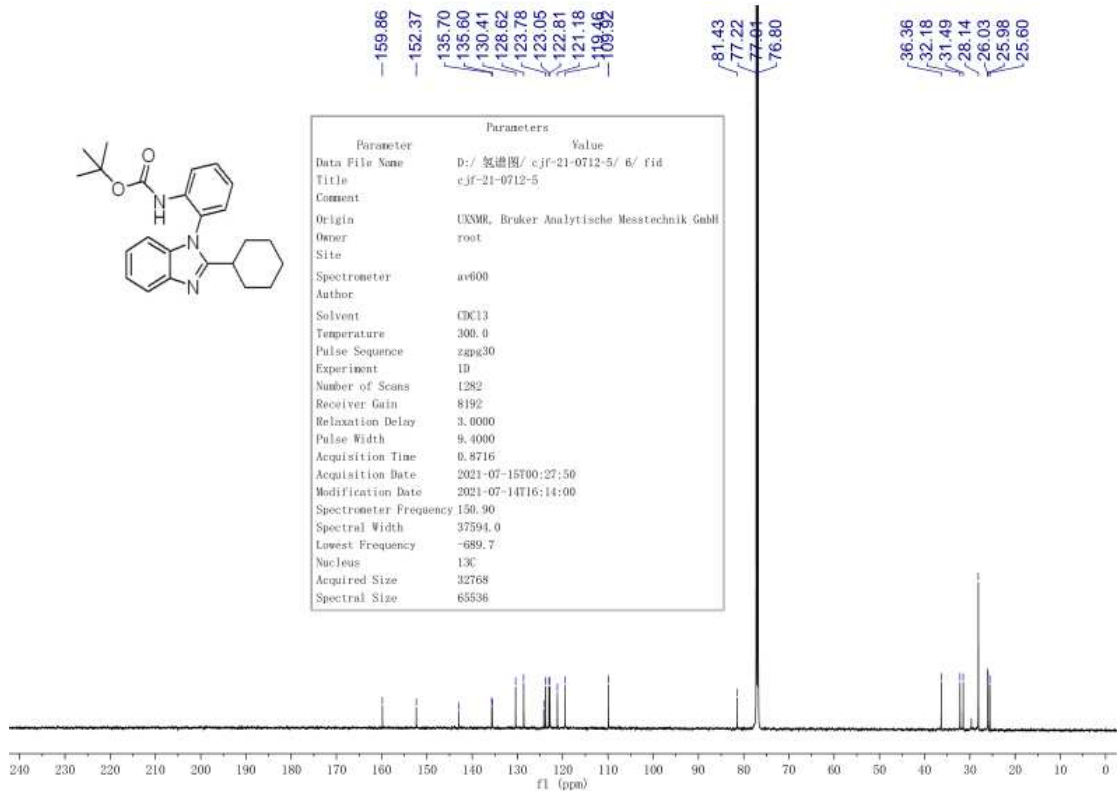
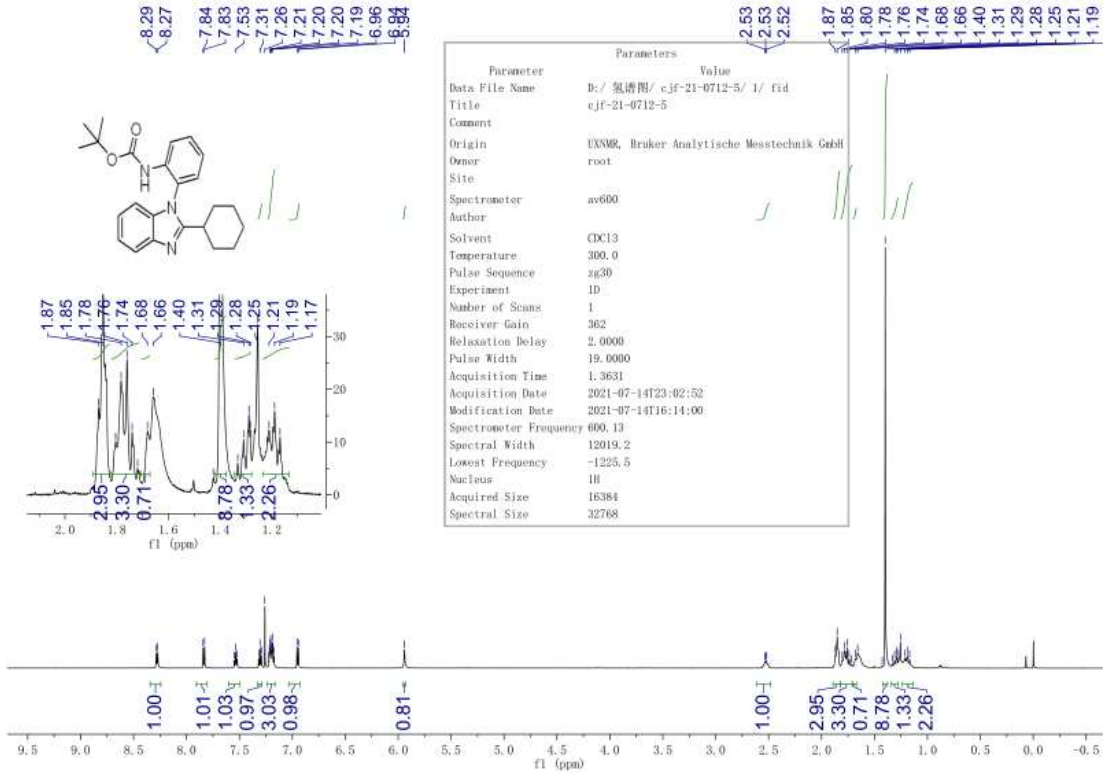
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121.75
120.85
118.86
113.34
109.85

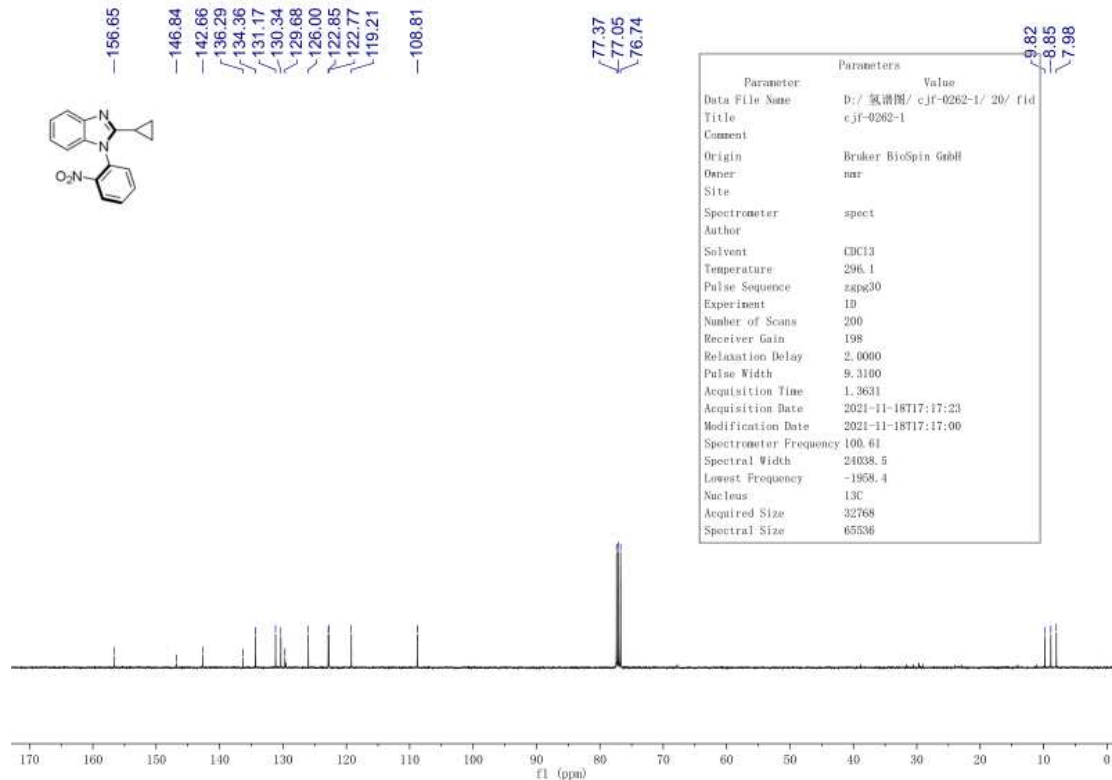
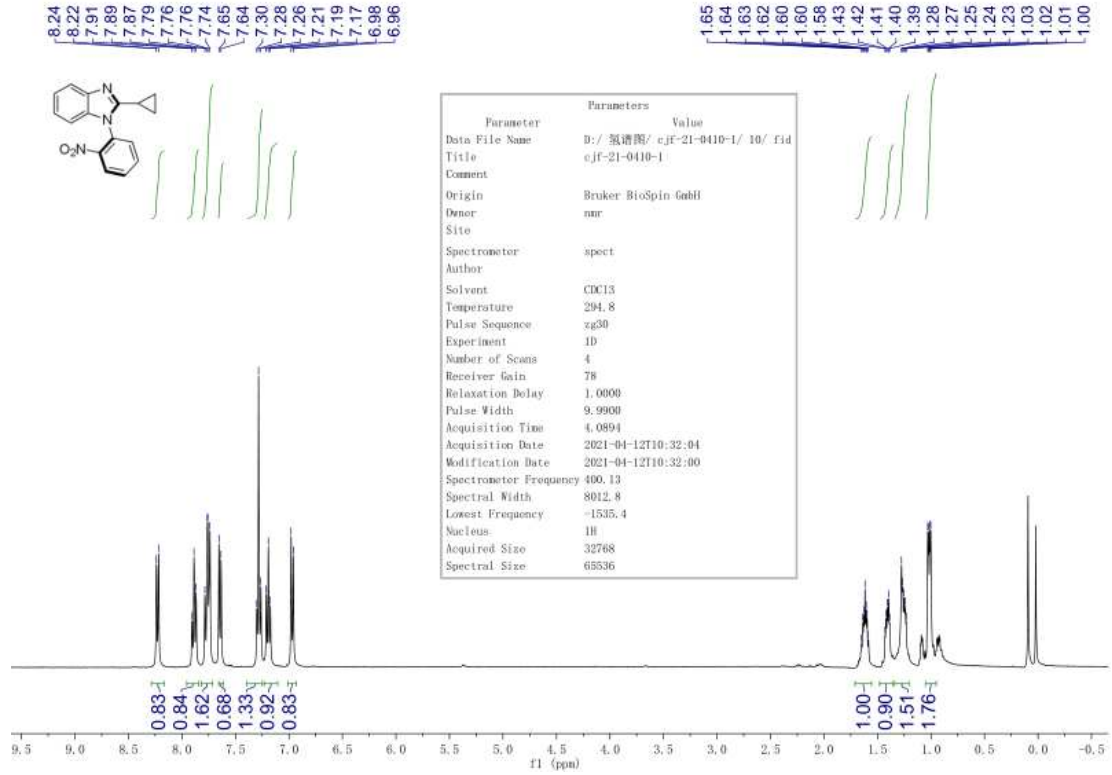


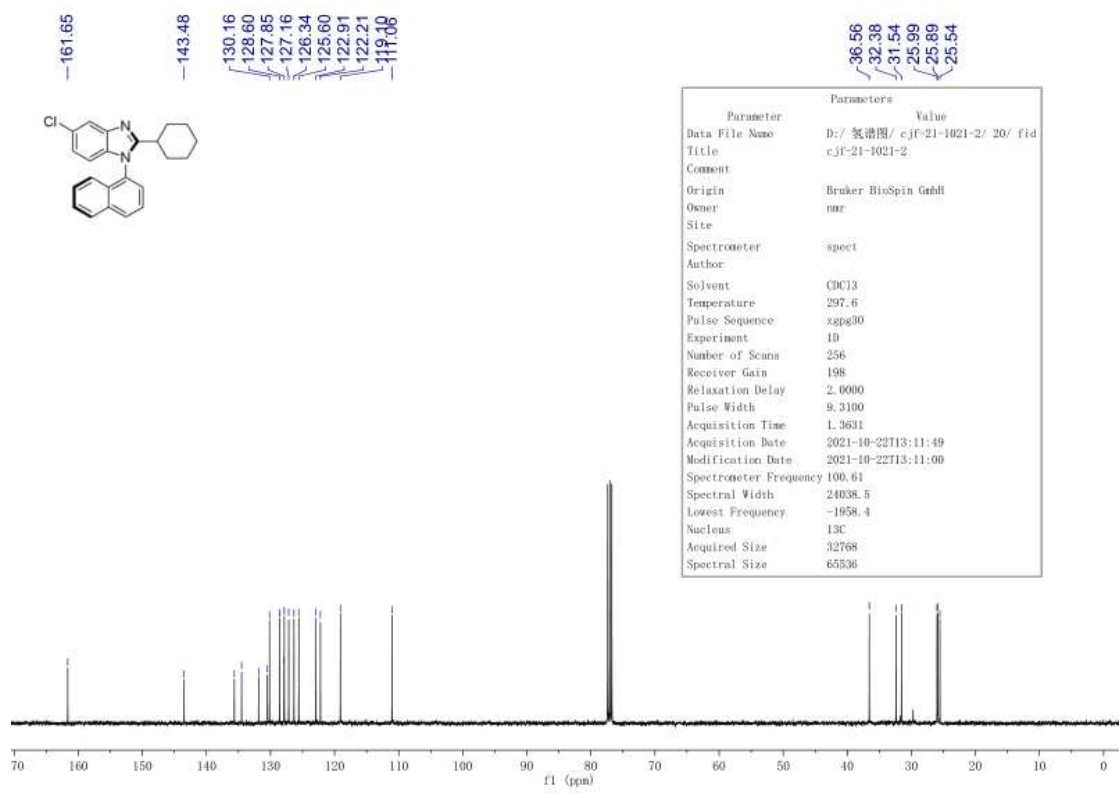
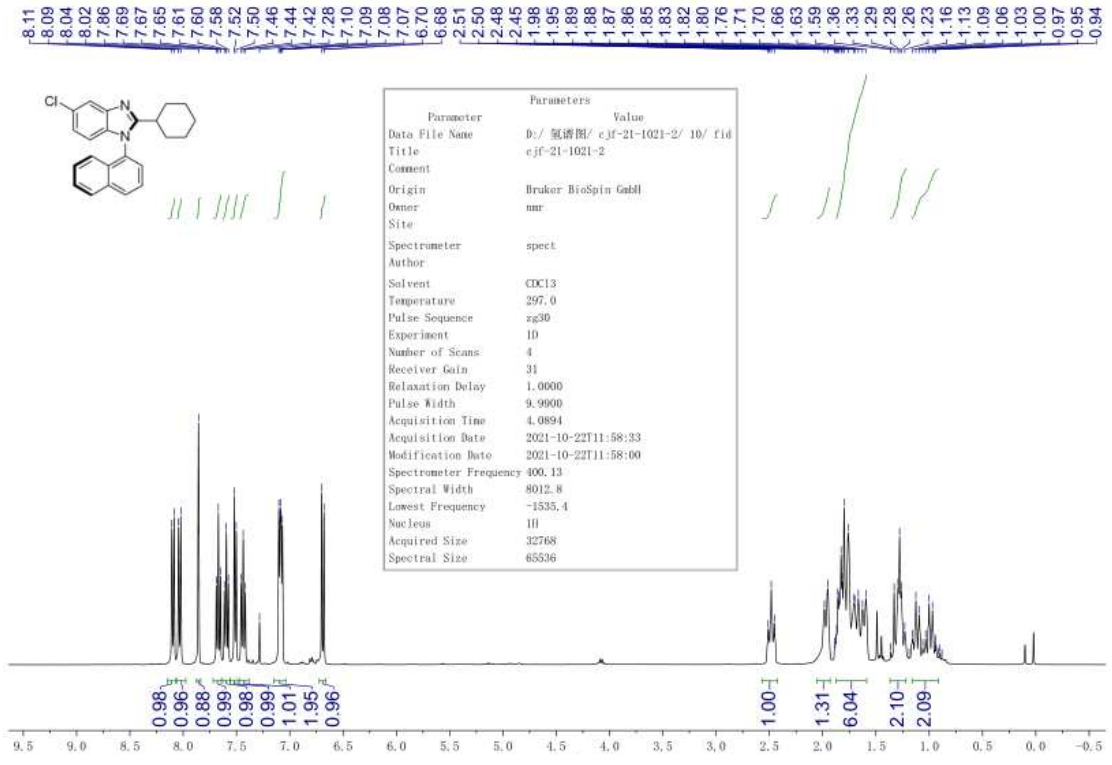
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Title	cjf-21-0615-4-s
Comment	
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Owner	root
Site	
Spectrometer	av600
Author	
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	288
Receiver Gain	8192
Relaxation Delay	3.0000
Pulse Width	9.4000
Acquisition Time	0.8716
Acquisition Date	2021-06-22T00:46:29
Modification Date	2021-06-21T17:04:00
Spectrometer Frequency	150.90
Spectral Width	37594.0
Lowest Frequency	-689.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



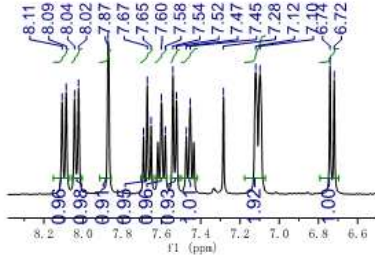
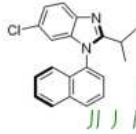








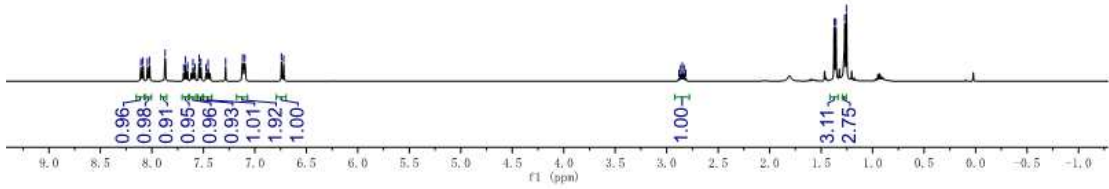
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7.52
7.47
7.45
7.28
7.12
7.10
6.74
6.72



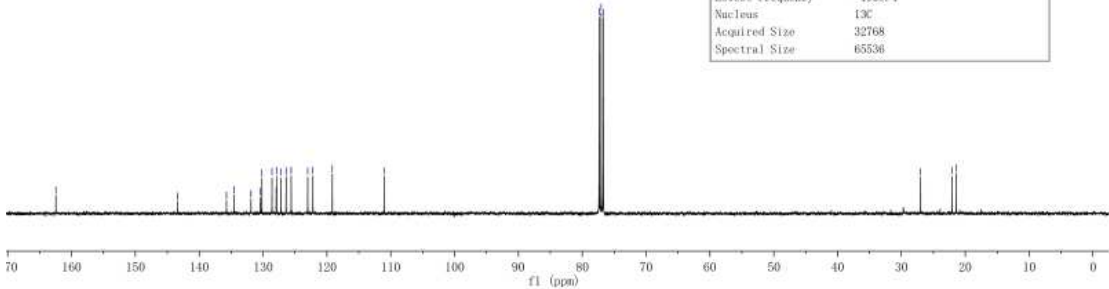
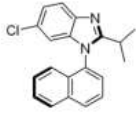
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2.85
2.83
2.81

1.37
1.36
1.27
1.25

Parameter	Value
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Comment	
Origin	Bruker BioSpin GmbH
Owner	mr
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	297.4
Pulse Sequence	zg30
Experiment	10
Number of Scans	4
Receiver Gain	63
Relaxation Delay	1.0000
Pulse Width	9.9900
Acquisition Time	4.0894
Acquisition Date	2021-10-19T11:23:38
Modification Date	2021-10-19T11:23:08
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1535.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



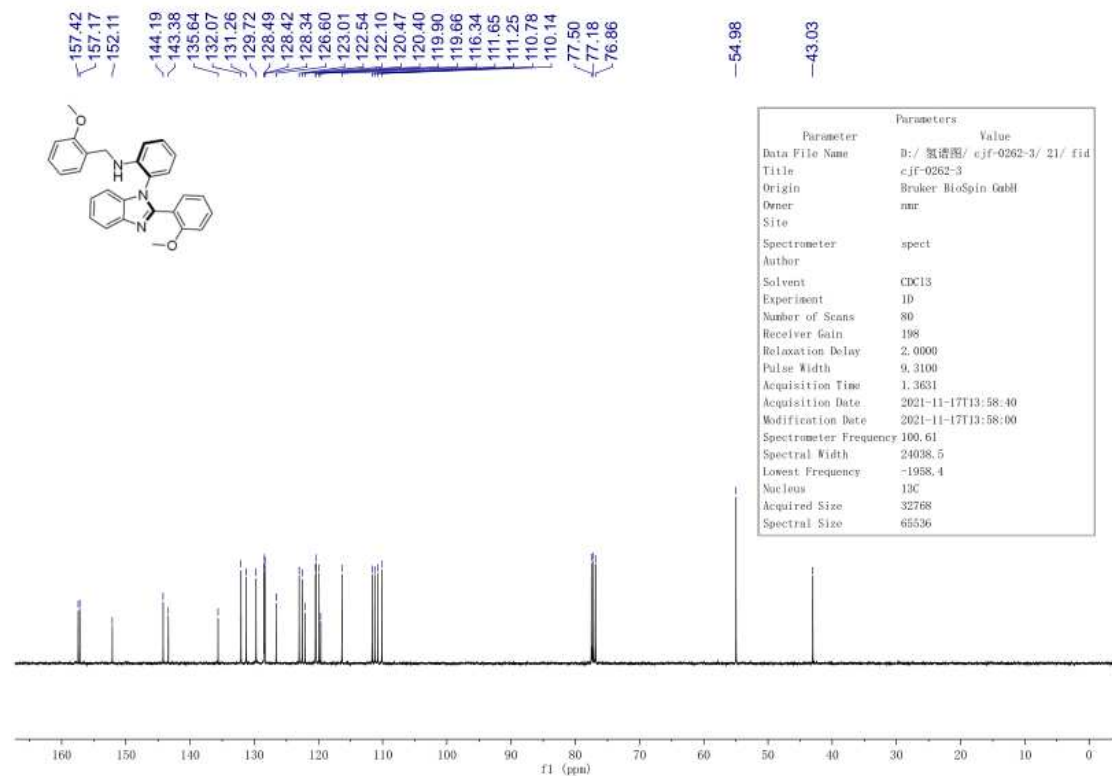
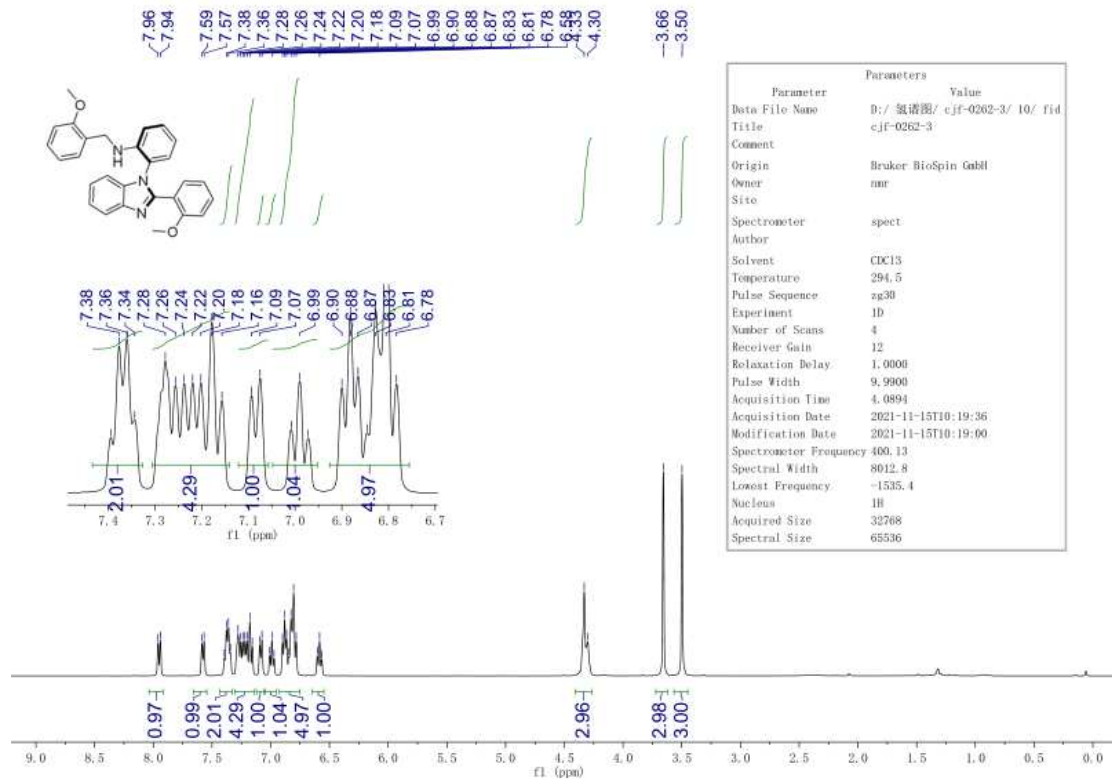
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127.88
127.18
126.40
125.59
123.01
122.19
119.06

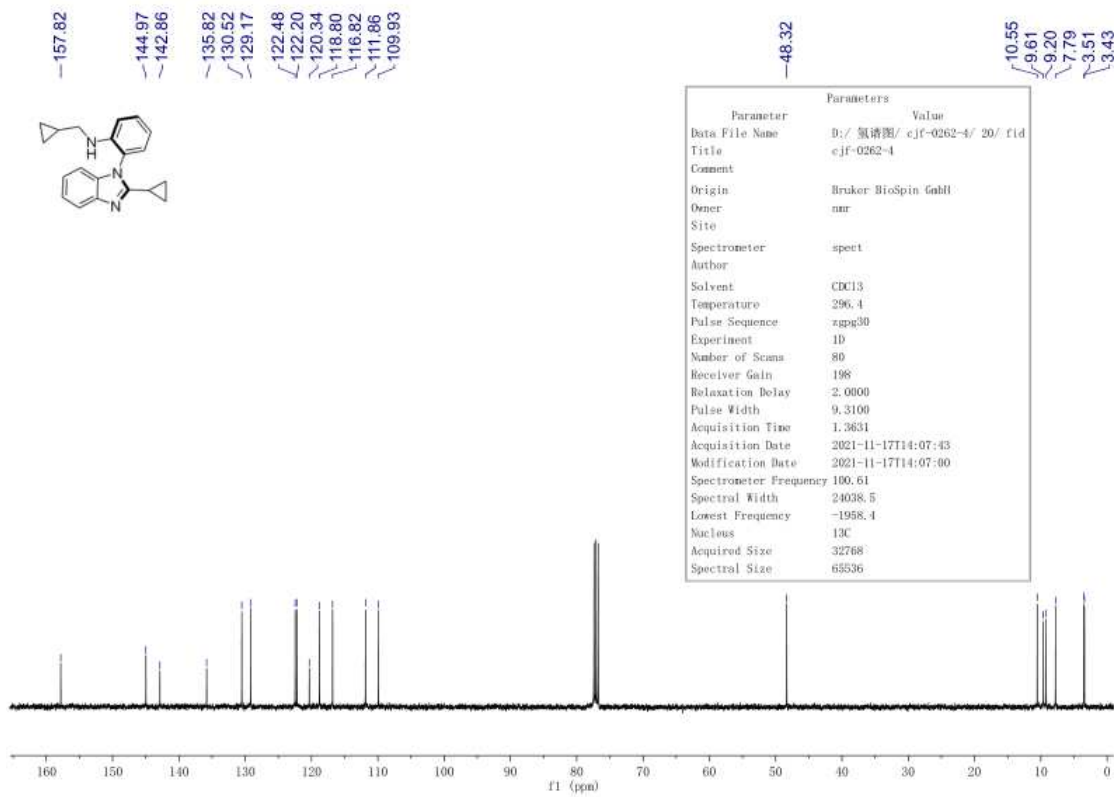
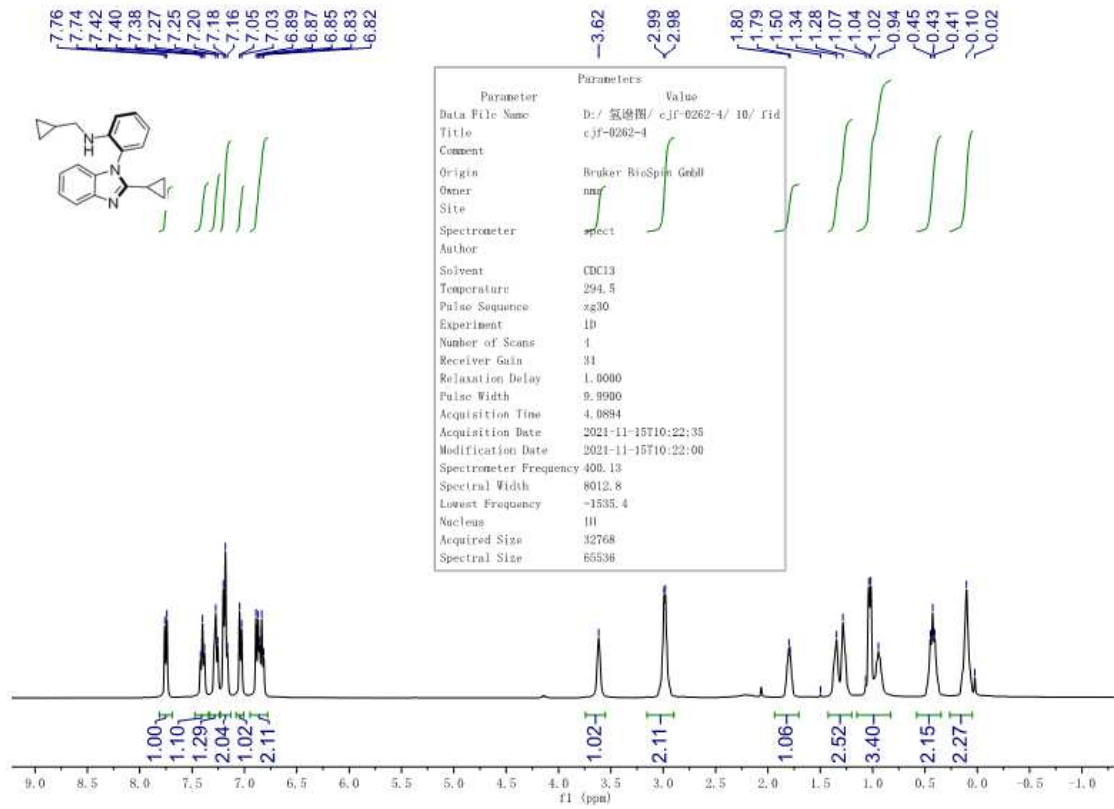


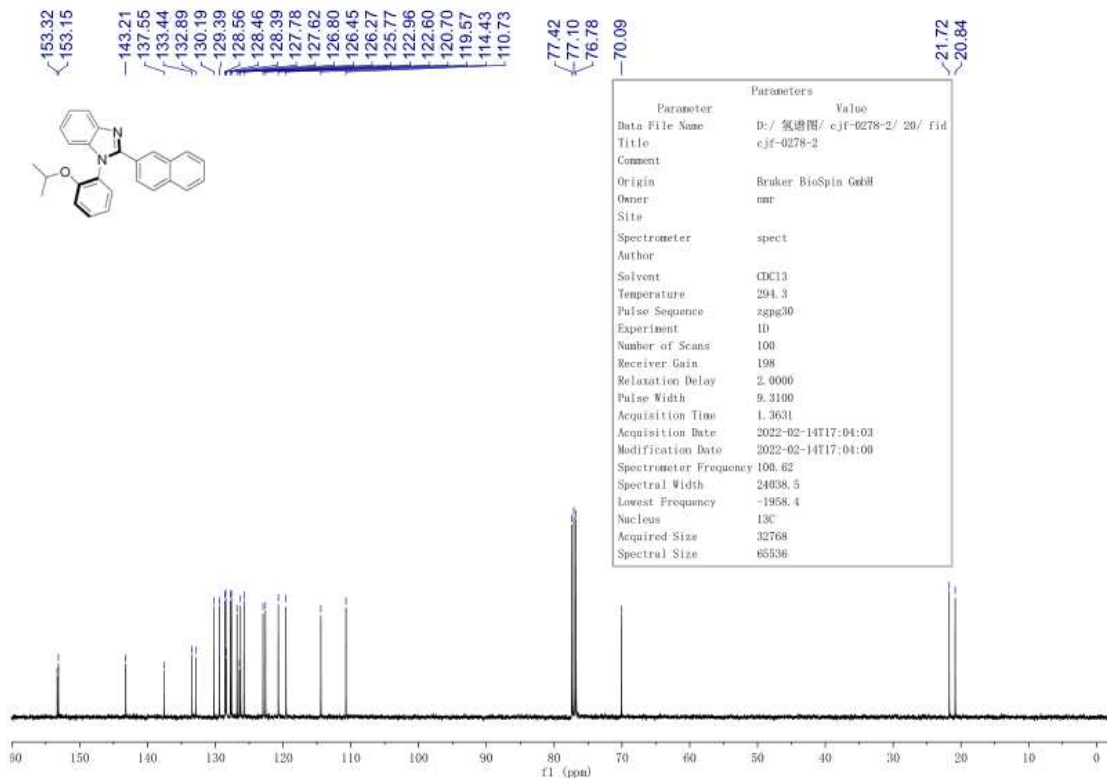
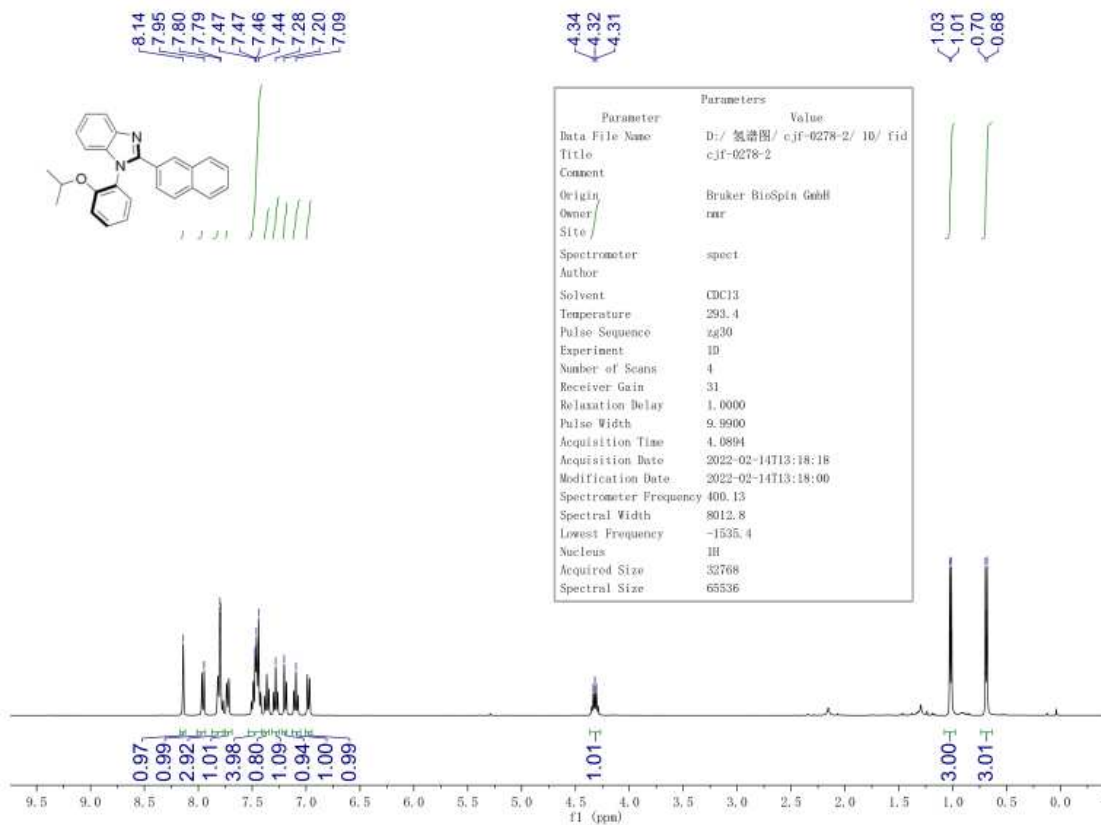
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77.04
76.72

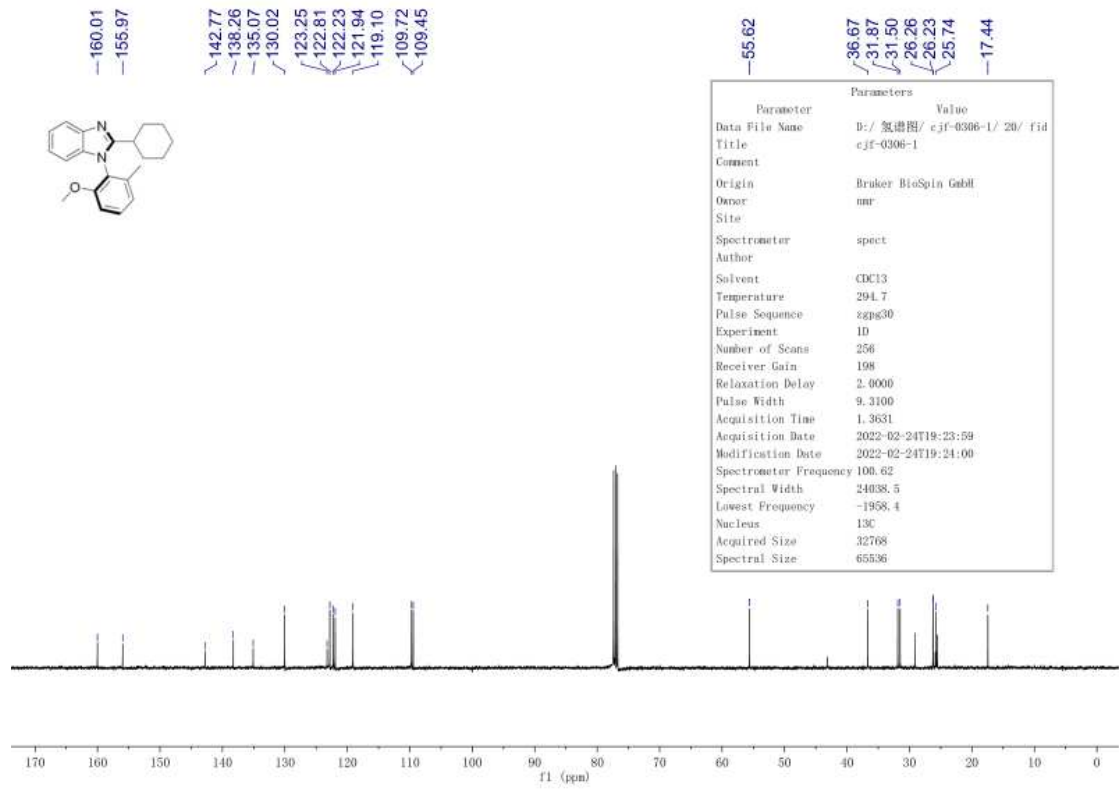
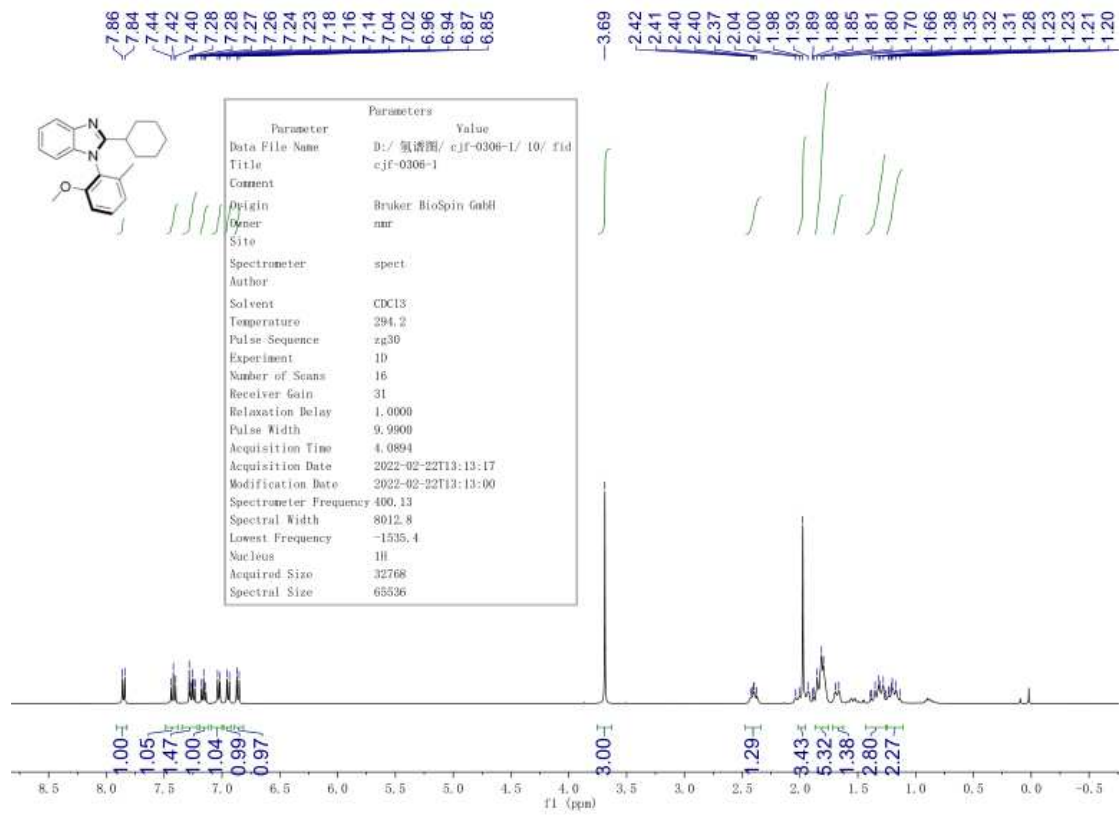
27.00
22.08
21.45

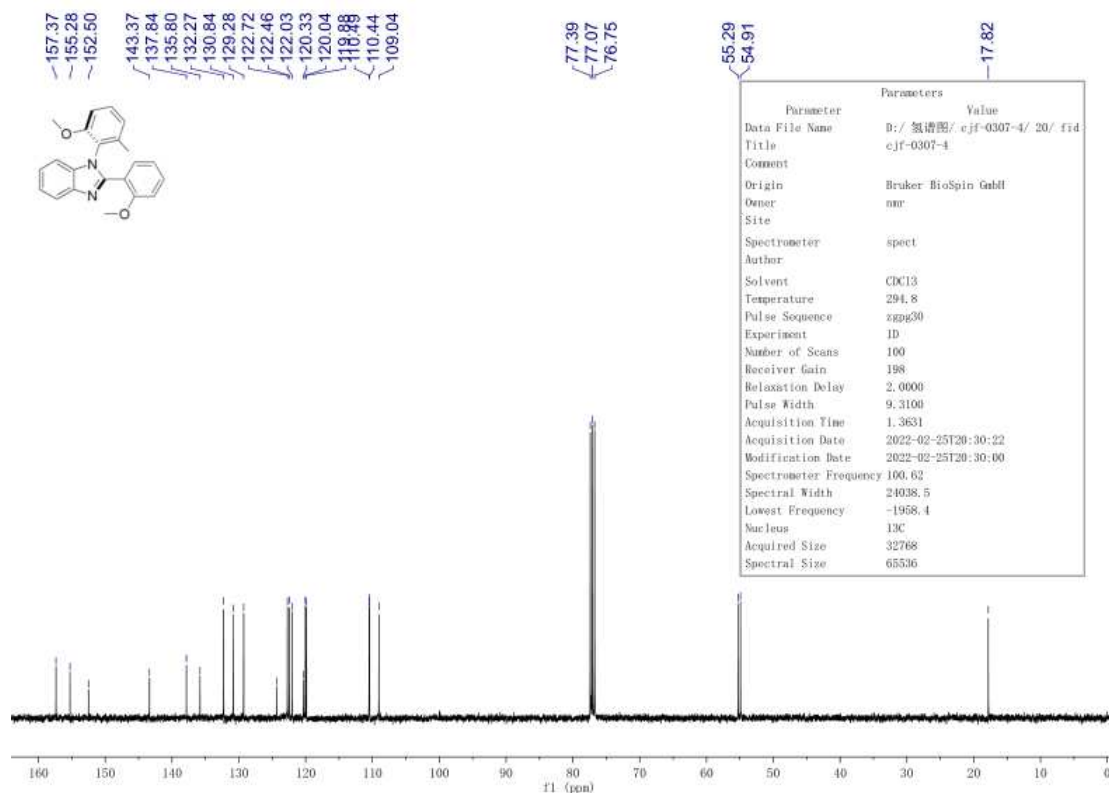
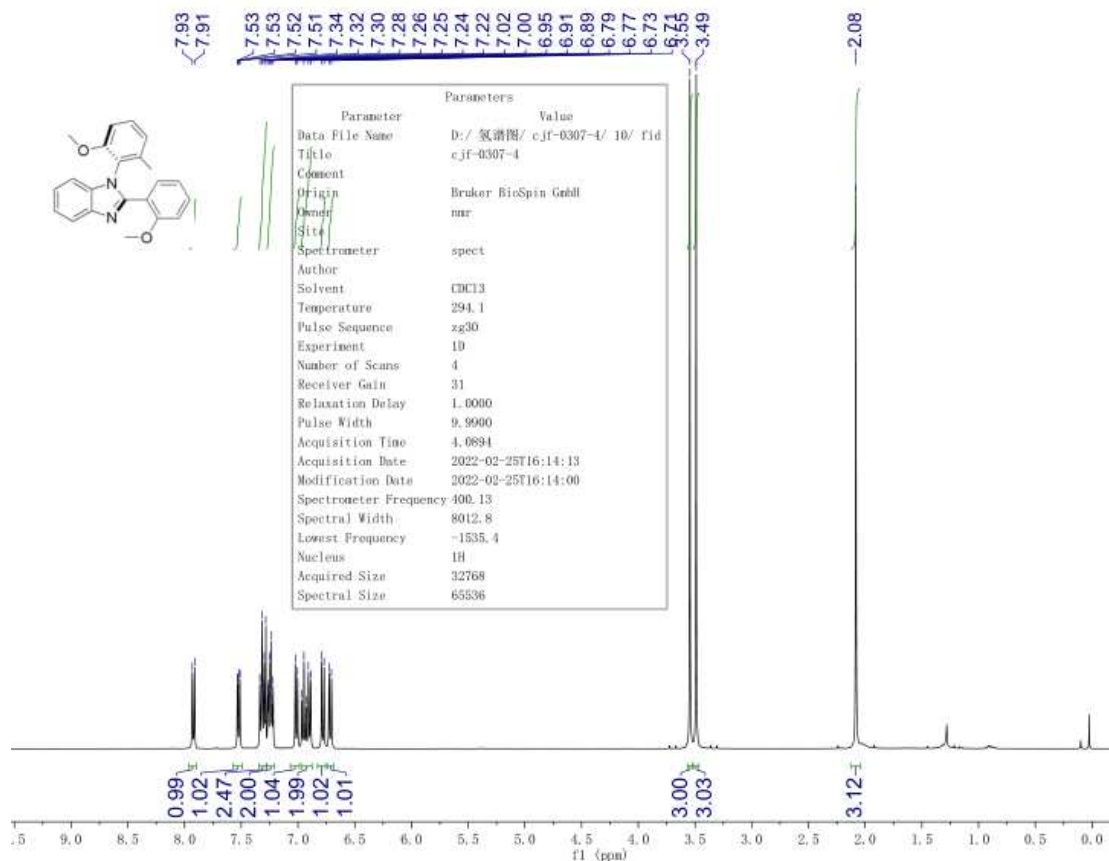
Parameter	Value
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Comment	
Origin	Bruker BioSpin GmbH
Owner	mr
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	10
Number of Scans	256
Receiver Gain	198
Relaxation Delay	2.0000
Pulse Width	9.3100
Acquisition Time	1.3631
Acquisition Date	2021-10-19T11:44:11
Modification Date	2021-10-19T11:44:00
Spectrometer Frequency	100.61
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

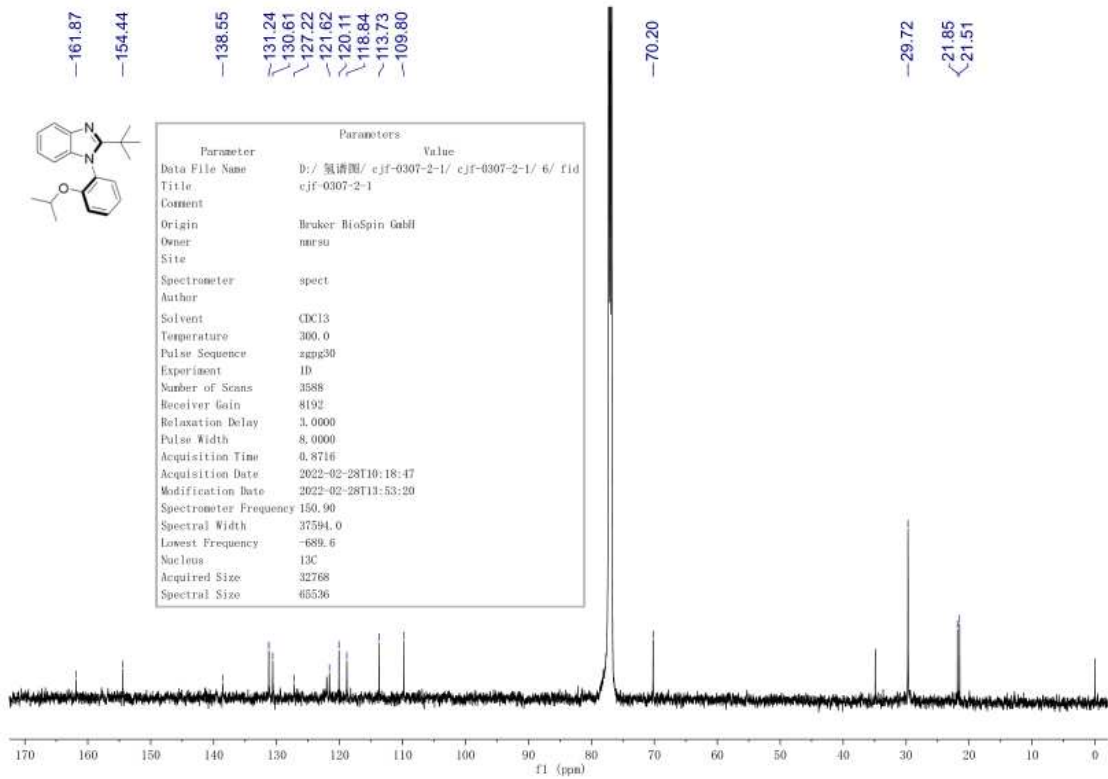
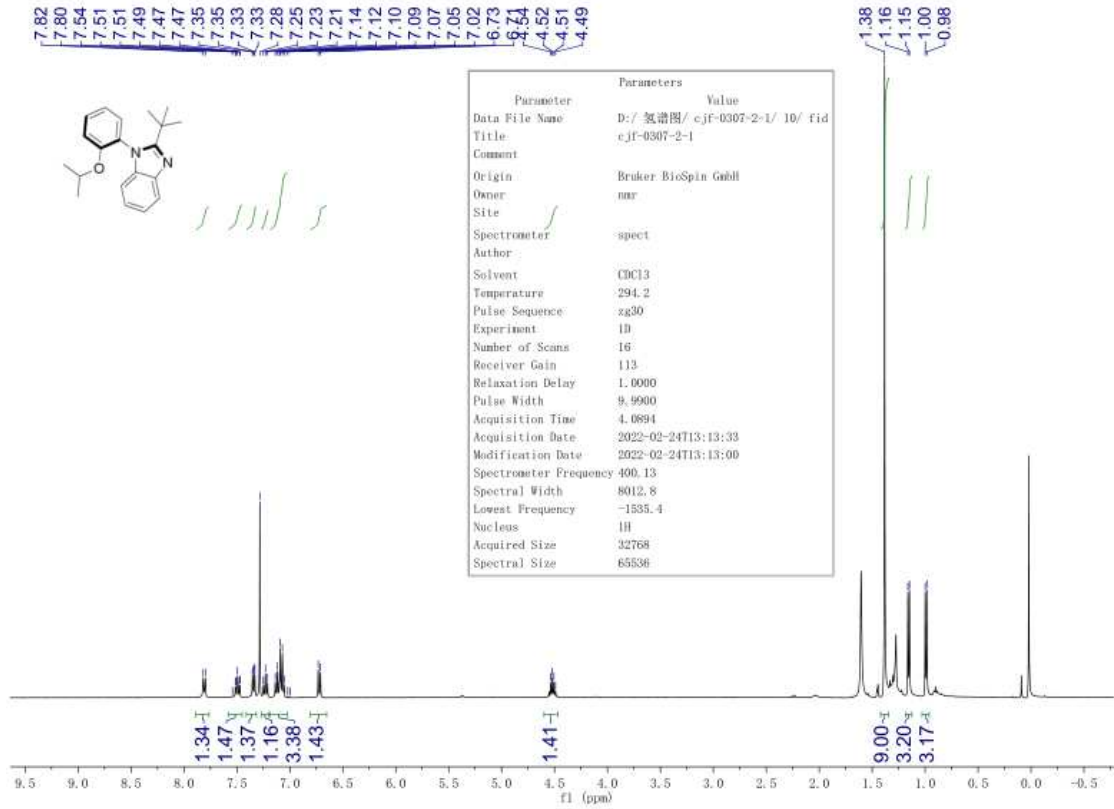




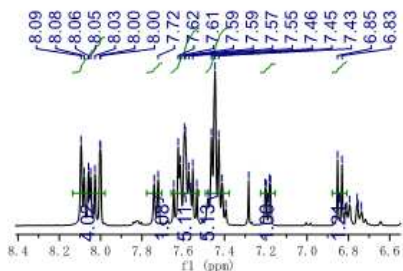
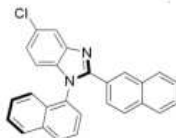




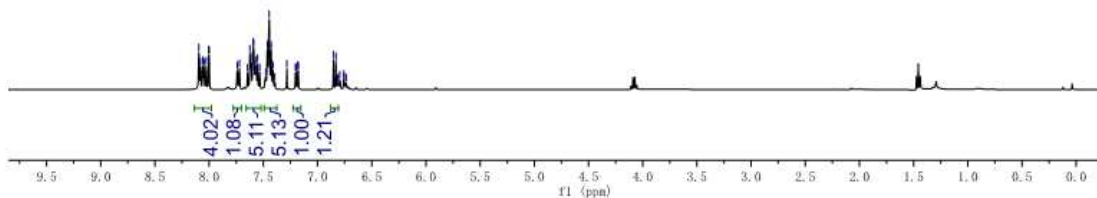




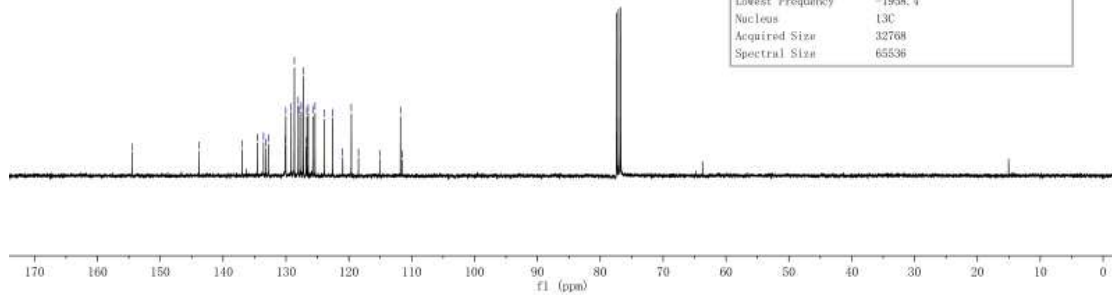
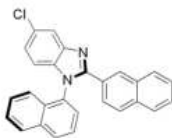
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8.05
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8.00
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7.57
7.56
7.55
7.53
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7.46
7.45
7.43
7.41
7.39
7.28
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6.83
6.81
6.81
6.79
6.76
6.75
6.74



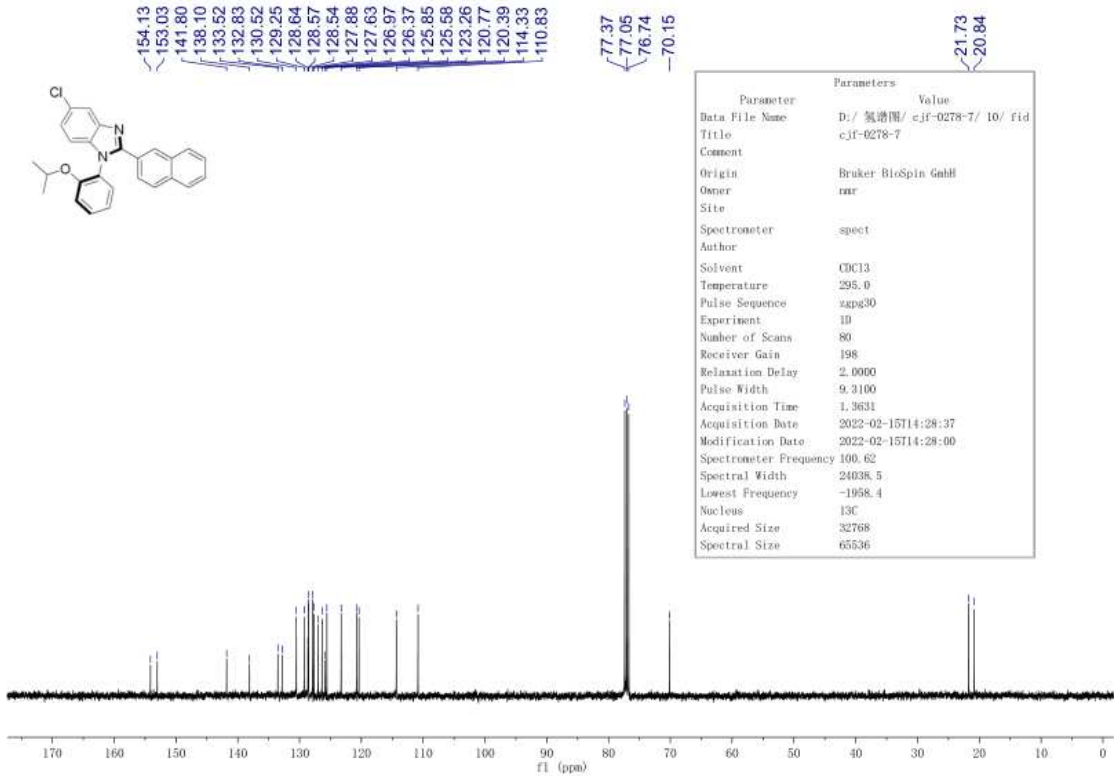
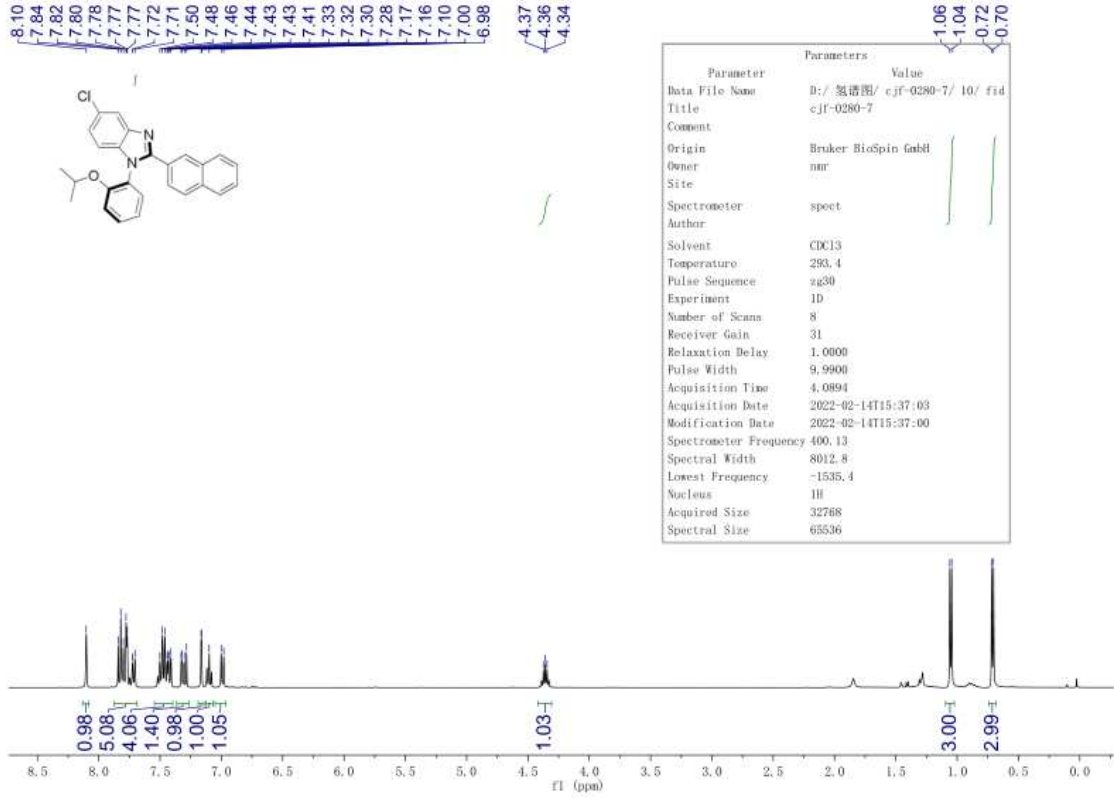
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Comment	
Origin	Bruker BioSpin GmbH
Owner	nir
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	10
Number of Scans	4
Receiver Gain	31
Relaxation Delay	1.0000
Pulse Width	9.9900
Acquisition Time	4.0894
Acquisition Date	2022-02-14T13:21:36
Modification Date	2022-02-14T13:21:00
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1535.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

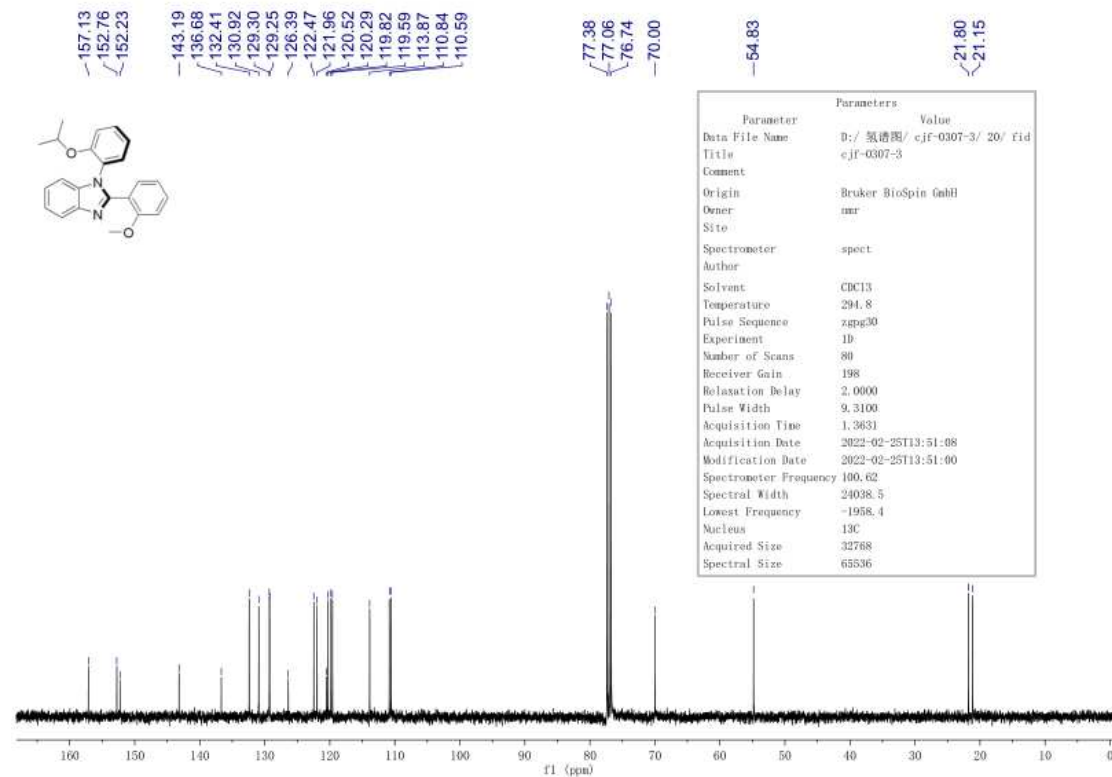
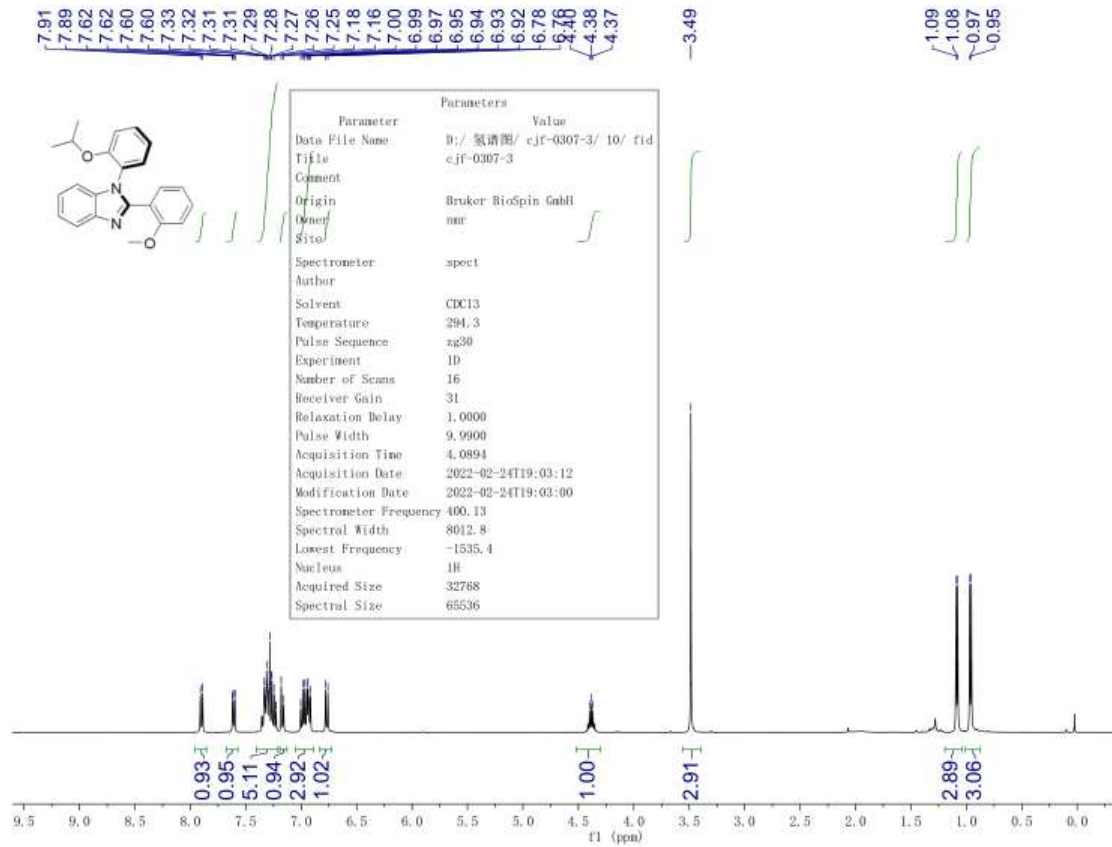


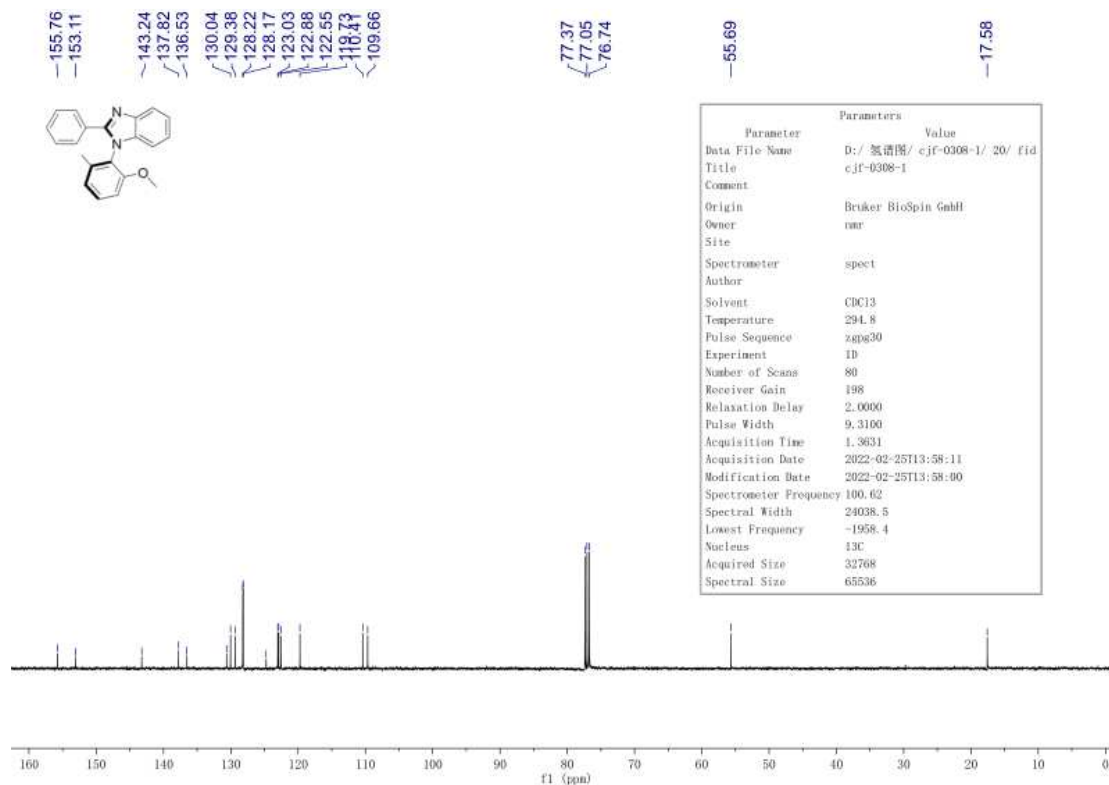
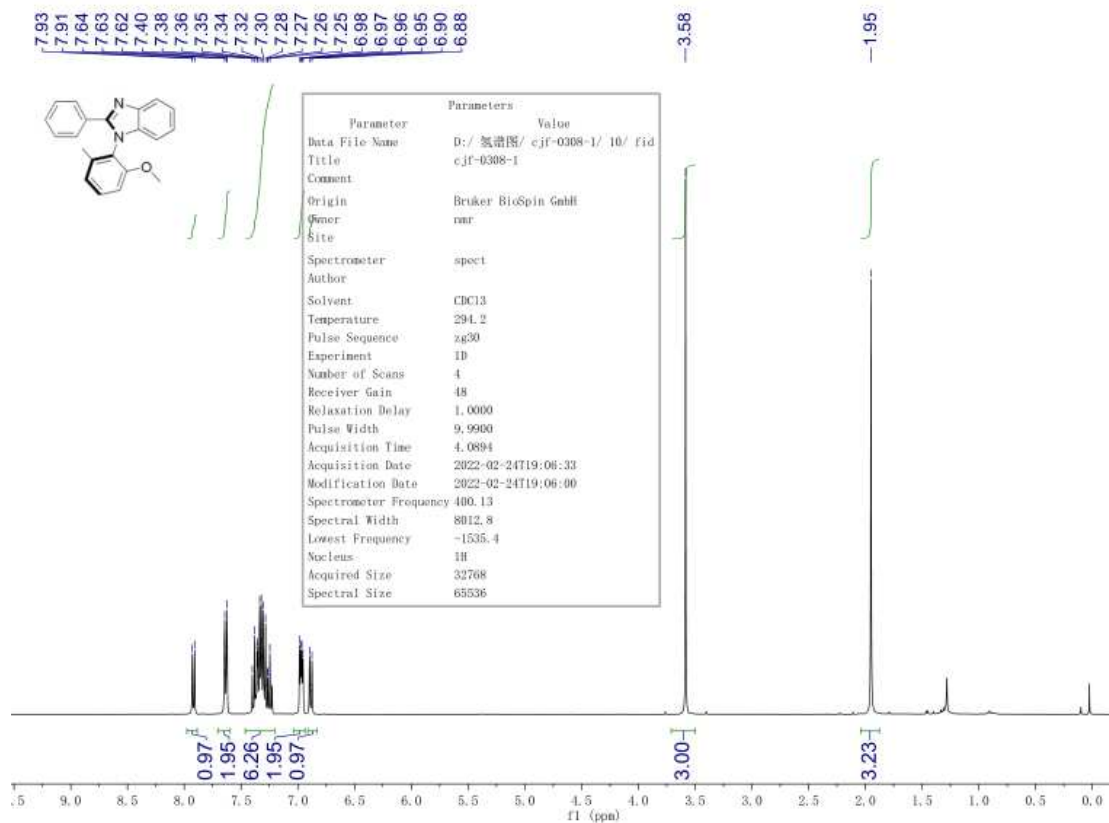
154.49
143.84
136.97
134.51
133.57
133.16
132.73
130.10
130.04
129.18
128.66
128.04
127.99
127.58
127.22
126.80
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120.98
119.60
118.46
115.07
111.78
111.47



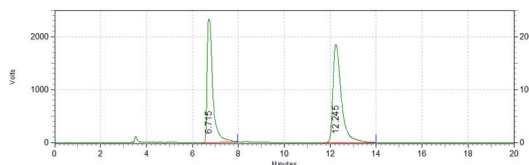
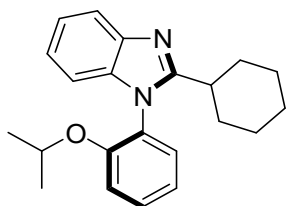
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Comment	
Origin	Bruker BioSpin GmbH
Owner	nir
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	294.2
Pulse Sequence	zgpg30
Experiment	10
Number of Scans	100
Receiver Gain	198
Relaxation Delay	2.0000
Pulse Width	9.3100
Acquisition Time	1.3631
Acquisition Date	2022-02-14T17:12:36
Modification Date	2022-02-14T17:12:00
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



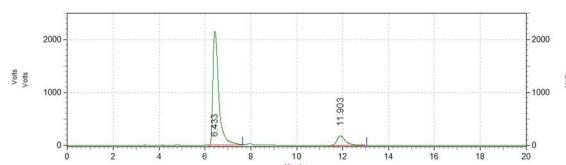




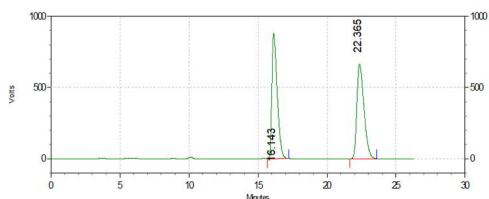
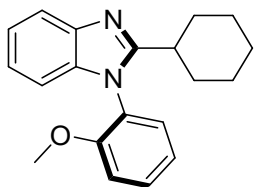
10. HPLC analysis spectrums



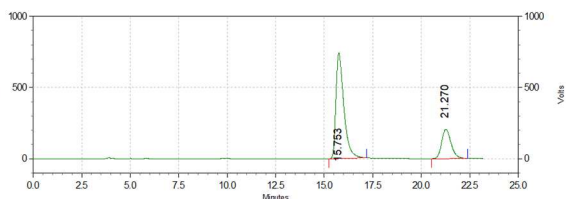
Peak#	Retention Time	Area	Area%
1	6.715	39974910	46.255
2	12.245	46448202	53.745
totals		86423112	100.000



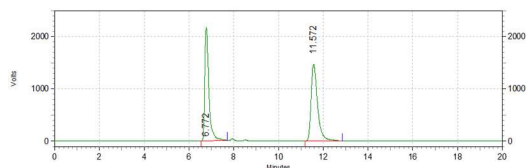
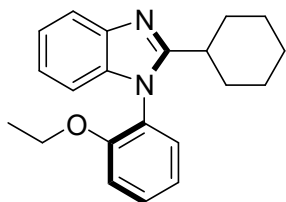
Peak#	Retention Time	Area	Area%
1	6.433	37965333	89.402
2	11.903	4500371	10.598
totals		42465704	100.000



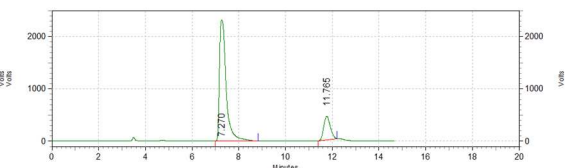
Peak#	Retention Time	Area	Area%
1	16.143	23644263	49.960
2	22.365	23682357	50.040
totals		47326620	100.000



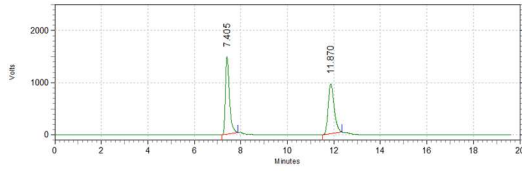
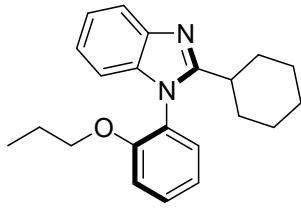
Peak#	Retention Time	Area	Area%
1	15.753	20947983	75.330
2	21.270	6860260	24.670
totals		27808243	100.000



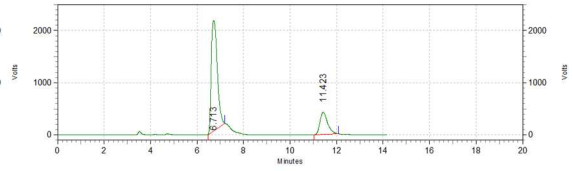
Peak#	Retention Time	Area	Area%
1	6.772	27724150	48.310
2	11.572	29663833	51.690
totals		57387983	100.000



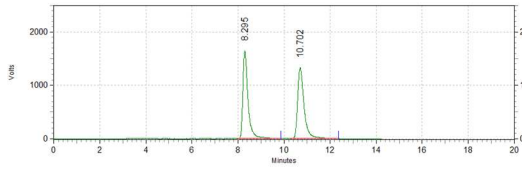
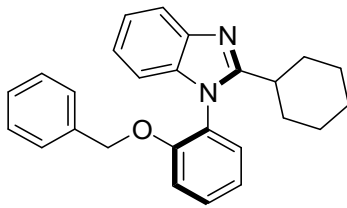
Peak#	Retention Time	Area	Area%
1	7.270	45997438	83.795
2	11.765	8895136	16.205
totals		54892574	100.000



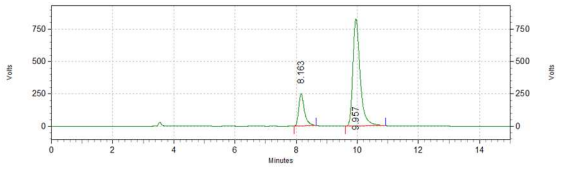
Peak#	Retention Time	Area	Area%
1	7.405	17705952	50.914
2	11.870	17070557	49.086
totals		34776509	100.000



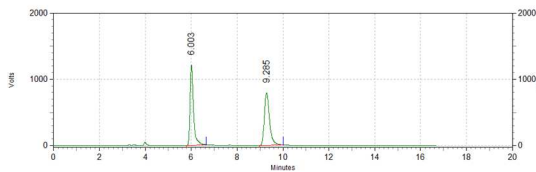
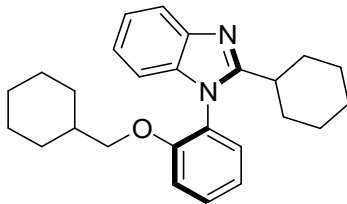
Peak#	Retention Time	Area	Area%
1	6.713	37841549	79.525
2	11.423	9742905	20.475
totals		47584454	100.000



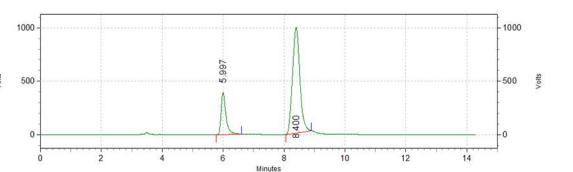
Peak#	Retention Time	Area	Area%
1	8.295	25574232	49.964
2	10.702	25610792	50.036
totals		51185024	100.000



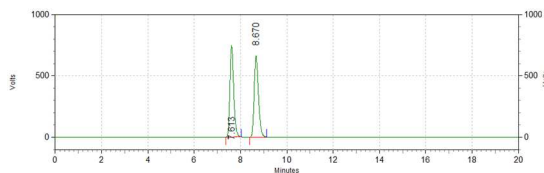
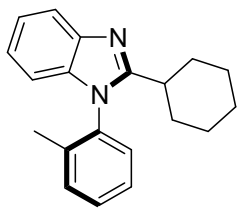
Peak#	Retention Time	Area	Area%
1	8.163	3206785	18.960
2	9.957	13707081	81.040
totals		16913866	100.000



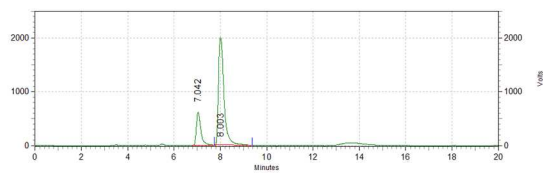
Peak#	Retention Time	Area	Area%
1	6.003	12656469	50.611
2	9.285	12350770	49.389
totals		25007239	100.000



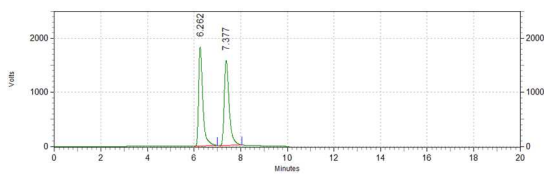
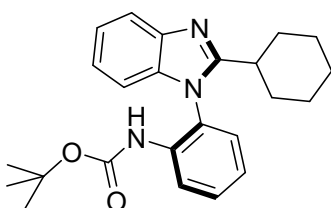
Peak#	Retention Time	Area	Area%
1	5.997	4318053	20.780
2	8.400	16462239	79.220
totals		20780292	100.000



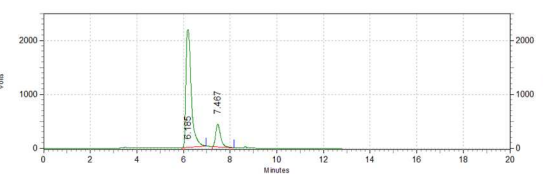
Peak#	Retention Time	Area	Area%
1	7.613	8416800	49.729
2	8.670	8508577	50.271
totals		16925377	100.000



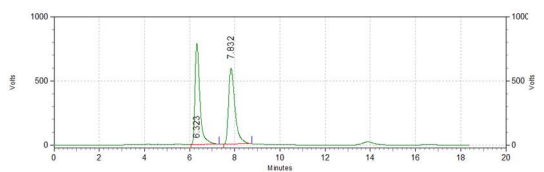
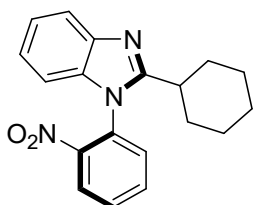
Peak#	Retention Time	Area	Area%
1	7.042	8177654	19.917
2	8.003	32881779	80.083
totals		41059433	100.000



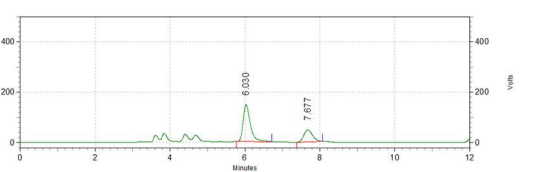
Peak#	Retention Time	Area	Area%
1	6.262	22947594	50.056
2	7.377	22896595	49.944
totals		45844189	100.000



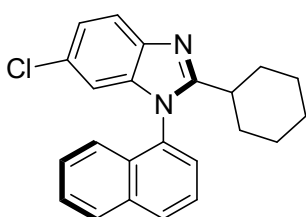
Peak#	Retention Time	Area	Area%
1	6.185	34546303	84.835
2	7.467	6175427	15.165
totals		40721730	100.000



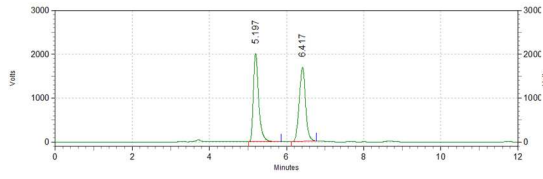
Peak#	Retention Time	Area	Area%
1	6.323	11680413	50.187
2	7.832	11593512	49.813
totals		23273925	100.000



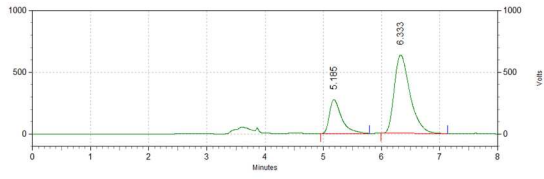
Peak#	Retention Time	Area	Area%
1	6.030	1936560	71.796
2	7.677	760744	28.204
totals		2697304	100.000



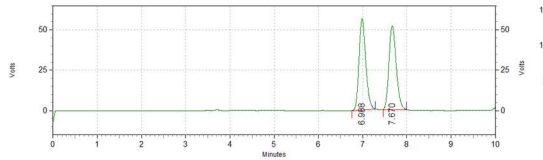
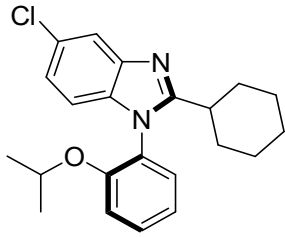
Peak#	Retention Time	Area	Area%
1	6.323	11680413	50.187
2	7.832	11593512	49.813
totals		23273925	100.000



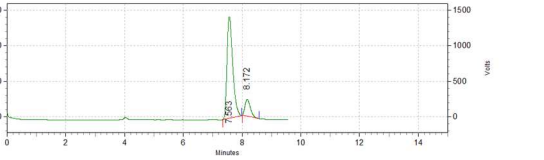
Peak#	Retention Time	Area	Area%
1	5.197	19404805	50.232
2	6.417	19225659	49.768
totals		38630464	100.000



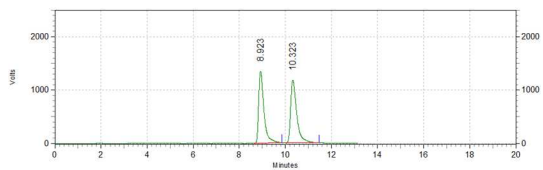
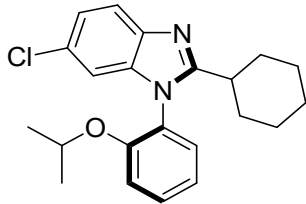
Peak#	Retention Time	Area	Area%
1	5.185	3990846	25.015
2	6.333	11963193	74.985
totals		15954039	100.000



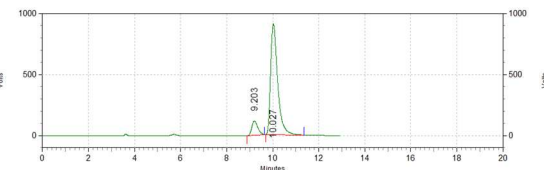
Peak#	Retention Time	Area	Area%
1	6.988	597967	50.343
2	7.670	589816	49.657
totals		1187783	100.000



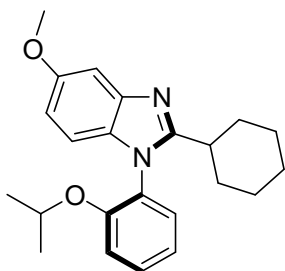
Peak#	Retention Time	Area	Area%
1	7.563	19315082	86.223
2	8.172	3086247	13.777
totals		22401329	100.000

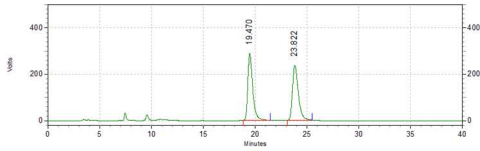


Peak#	Retention Time	Area	Area%
1	8.923	21285133	50.076
2	10.323	21220283	49.924
totals		42505416	100.000

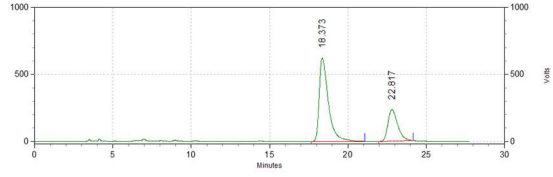


Peak#	Retention Time	Area	Area%
1	9.203	2116545	9.889
2	10.027	19286948	90.111
totals		21403493	100.000

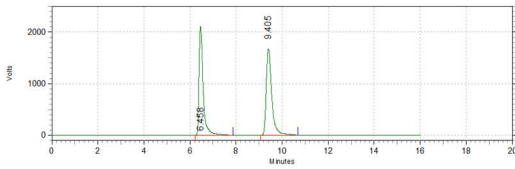
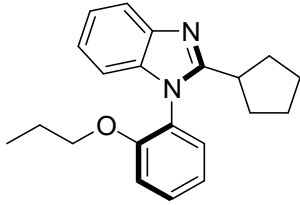




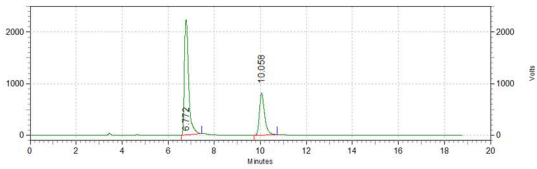
Peak#	Retention Time	Area	Area%
1	19.470	9532097	50.777
2	23.822	9240360	49.223
totals		18772457	100.000



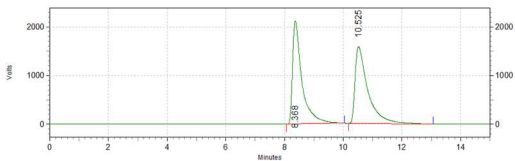
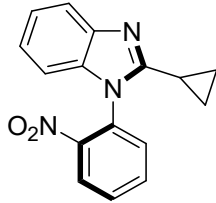
Peak#	Retention Time	Area	Area%
1	18.373	25243267	71.528
2	22.817	10048407	28.472
totals		35291674	100.000



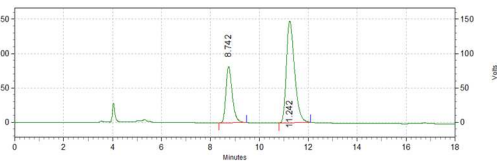
Peak#	Retention Time	Area	Area%
1	6.458	26565884	48.875
2	9.405	27788672	51.125
totals		54354556	100.000



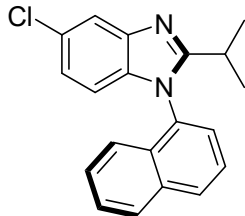
Peak#	Retention Time	Area	Area%
1	6.772	28523839	69.009
2	10.058	12809725	30.991
totals		41333564	100.000

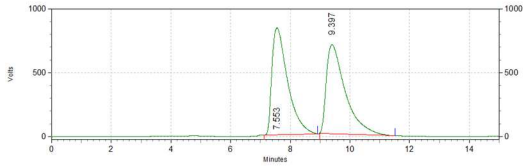


Peak#	Retention Time	Area	Area%
1	8.368	47043274	49.730
2	10.525	47553205	50.270
totals		94596479	100.000

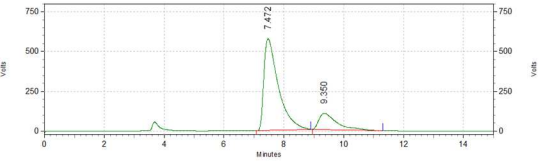


Peak#	Retention Time	Area	Area%
1	8.742	1460348	29.842
2	11.242	3433214	70.158
totals		4893562	100.000

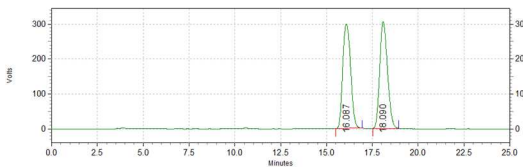
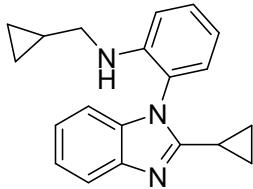




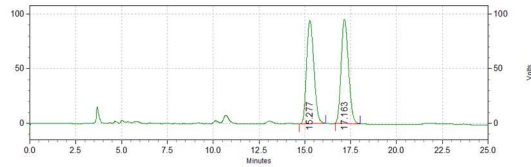
Peak#	Retention Time	Area	Area%
1	7.553	30592674	49.947
2	9.397	30657795	50.053
totals		61250469	100.000



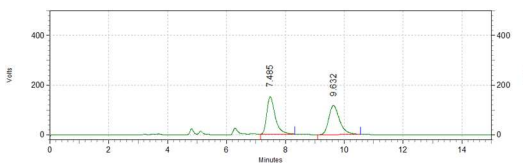
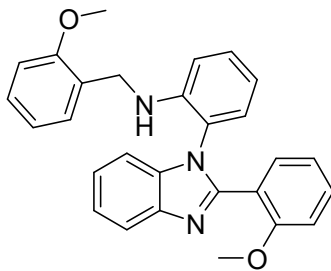
Peak#	Retention Time	Area	Area%
1	7.472	19410139	81.978
2	9.350	4266974	18.022
totals		23677113	100.000



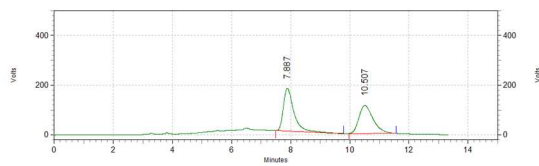
Peak#	Retention Time	Area	Area%
1	16.087	8964567	49.932
2	18.090	8989010	50.068
totals		17953577	100.000



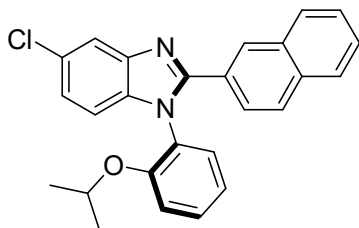
Peak#	Retention Time	Area	Area%
1	15.277	2614606	49.699
2	17.163	2646271	50.301
totals		5260877	100.000

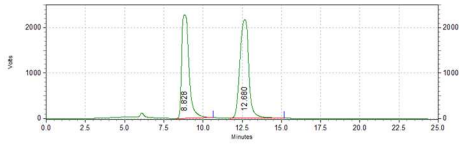


Peak#	Retention Time	Area	Area%
1	7.485	2956575	49.923
2	9.632	2965727	50.077
totals		5922302	100.000

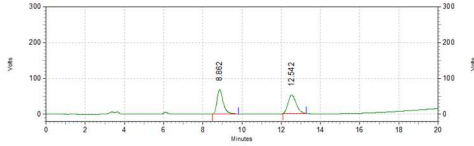


Peak#	Retention Time	Area	Area%
1	7.887	4236831	53.047
2	10.507	3750072	46.953
totals		7986903	100.000

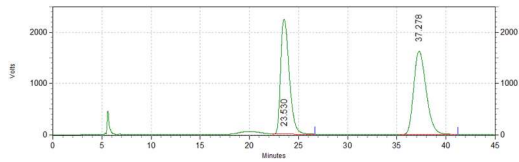
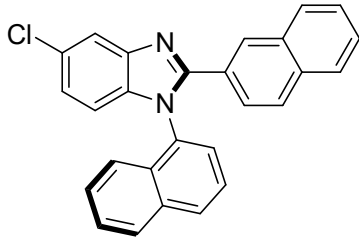




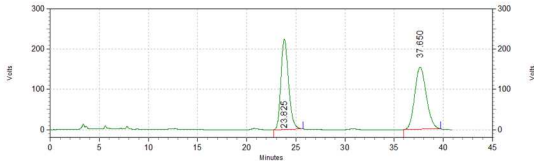
Peak#	Retention Time	Area	Area%
1	8.828	73292526	46.314
2	12.680	84957212	53.686
totals		158249738	100.000



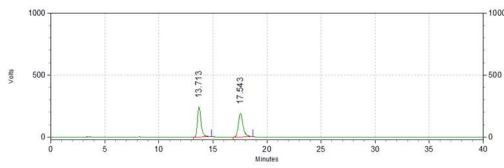
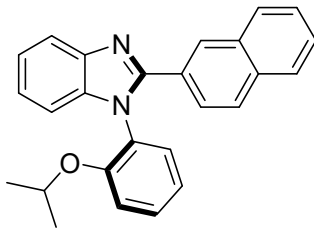
Peak#	Retention Time	Area	Area%
1	8.862	1480376	49.816
2	12.542	1491318	50.184
totals		2971694	100.000



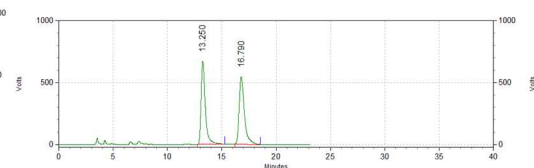
Peak#	Retention Time	Area	Area%
1	23.530	136776120	48.765
2	37.278	143703831	51.235
totals		280479951	100.000



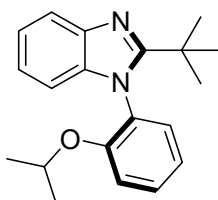
Peak#	Retention Time	Area	Area%
1	23.825	12055803	48.769
2	37.650	12664225	51.231
totals		24720028	100.000

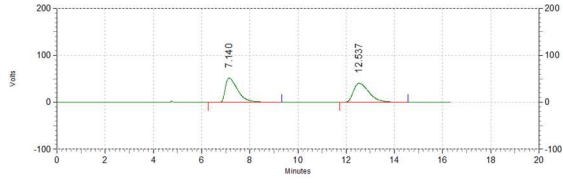


Peak#	Retention Time	Area	Area%
1	13.713	5586493	49.718
2	17.543	5649858	50.282
totals		11236351	100.000

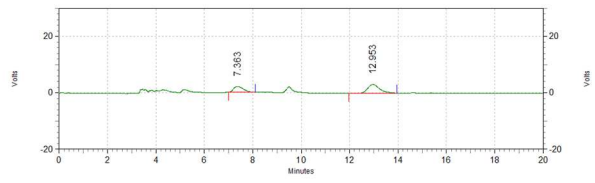


Peak#	Retention Time	Area	Area%
1	13.250	17750750	49.581
2	16.790	18050708	50.419
totals		35801458	100.000

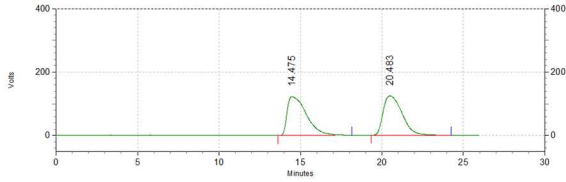
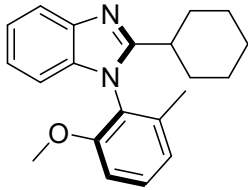




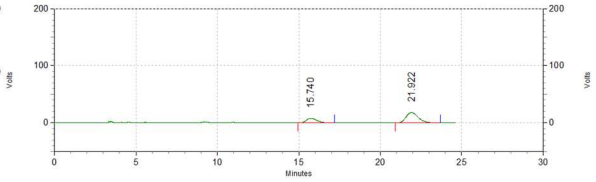
Peak#	Retention Time	Area	Area%
1	7.140	1860892	50.255
2	12.537	1842002	49.745
totals		3702894	100.000



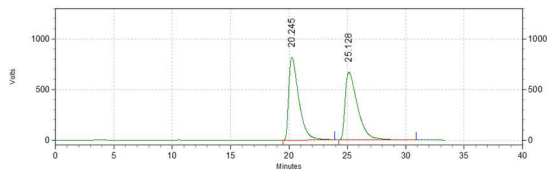
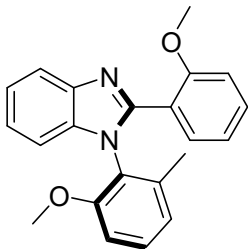
Peak#	Retention Time	Area	Area%
1	7.363	57222	35.039
2	12.953	106087	64.961
totals		163309	100.000



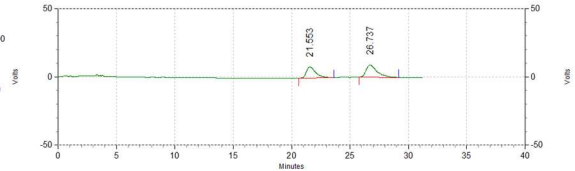
Peak#	Retention Time	Area	Area%
1	14.475	10045817	50.086
2	20.483	10011152	49.914
totals		20056969	100.000



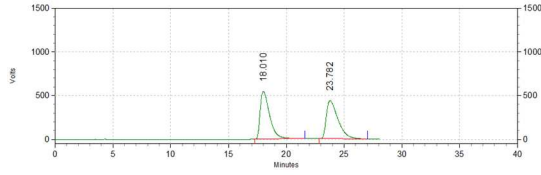
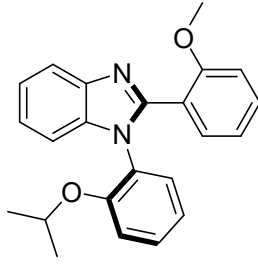
Peak#	Retention Time	Area	Area%
1	15.740	373203	28.184
2	21.922	950960	71.816
totals		1324163	100.000



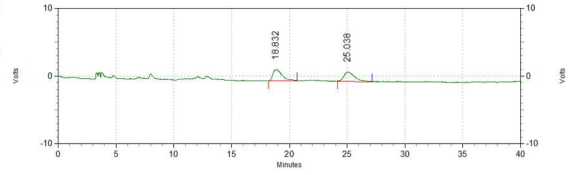
Peak#	Retention Time	Area	Area%
1	20.245	48953527	49.961
2	25.128	49029353	50.039
totals		97982880	100.000



Peak#	Retention Time	Area	Area%
1	21.553	451347	43.923
2	26.737	576237	56.077
totals		1027584	100.000



Peak#	Retention Time	Area	Area%
1	18.010	31184859	50.604
2	23.782	30440087	49.396
totals		61624946	100.000



Peak#	Retention Time	Area	Area%
1	18.832	89084	50.428
2	25.038	87572	49.572
totals		176656	100.000