

N-Heterocyclic Carbene-Catalyzed [3+2] Annulation of Isoindigos with Enals: Enantioselective Construction of Three Contiguous Stereogenic Centers

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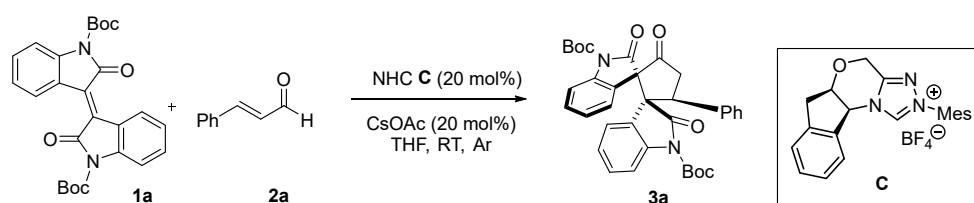
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Part 1: General Information

Unless otherwise specified, all reactions were carried out under an argon atmosphere in an oven dried sealed tube, with dry, freshly distilled solvents in anhydrous conditions. THF was distilled from Na and used directly. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petroleum was 60-90 °C. ¹H and ¹³C NMR spectra were recorded on Bruker 600 or 400 MHz instrument in CDCl₃, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. The high-resolution mass spectra (HRMS) were measured on a Thermo Q-Exactive spectrometer by ESI, and mass analyzer type is Orbitrap. Data collections for crystal structure were performed at 295.13 K using Cu K α (λ = 1.54184) radiation on a SuperNova, Dual, Cu at zero, Eos diffractometer. The determination of enantiomeric excess was performed via chiral HPLC analysis Thermo Ulti Mate 3000 HPLC, (RIGOL) L-3000 or Agilent 1260 Infinity II. Optical rotations were measured by Rudolph Research Analytical Autopol-I instrument, cell length = 1 dm, concentrations (c) are quoted in g/100 mL, sodium D line (589 nm). NHC catalysts **A-D** were purchased from Energy Chemical and used as received. Isoindigos were prepared according to the reported literature procedures.¹

Part 2: Experimental Section

1. General procedure for the synthesis of bisporooxindoles **3** (**3a** as an example).

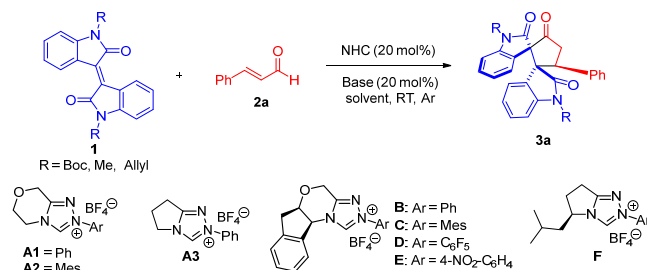


A dry 25 mL Schlenk tube with stir bar was charged with isoindigo **1a** (46 mg, 0.1 mmol, 1.0 equiv), NHC **C** (8.4 mg, 0.02 mmol, 20 mol %), CsOAc (3.8 mg, 0.02 mmol, 20 mol %). The tube was evacuated, and refilled with nitrogen. Then enals **2a** (15.6 mg, 1.2 mmol, 1.2 equiv) was added and the mixture was dissolved with newly distilled solvent THF (1.0 mL). The mixture was stirred at room temperature for 24 hours when the substrate was consumed completely (monitored by

1. Y.-Y. Gui, J. Yang, L.-W. Qi, X. Wang, F. Tian, X.-N. Li, and L.-X. Wang, *Org. Biomol. Chem.*, 2015, **13**, 6371-6379.

TLC). The reaction mixture was concentrated under vacuum and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to afford product **3a** as white solid (38 mg, 65% yield).

2. Optimization of Reaction Conditions^a



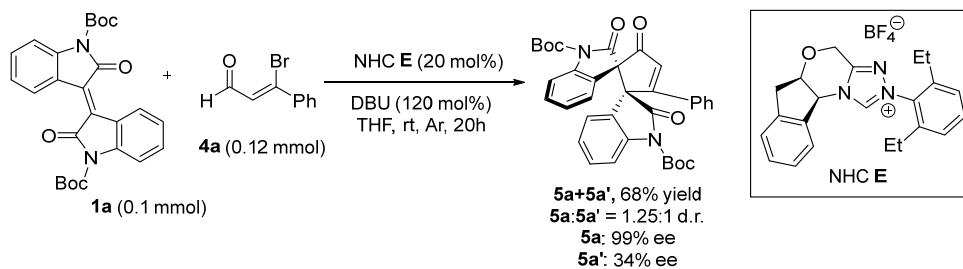
entry	NHC	R	base	solvent	yield (%) ^b	ee (%) ^c
1	A1	Boc	DBU	THF	62	-
2	A2	Boc	DBU	THF	65	-
3	A3	Boc	DBU	THF	51	-
4	B	Boc	DBU	THF	30	32
5	C	Boc	DBU	THF	61	88
6	D	Boc	DBU	THF	trace	-
7	E	Boc	DBU	THF	trace	-
8	F	Boc	DBU	THF	54	43
9	C	Me	DBU	THF	50	0
10	C	Allyl	DBU	THF	72	44
11	C	Bn	DBU	THF	53	0
12	C	Boc	K ₂ CO ₃	THF	54	84
13	C	Boc	KOAc	THF	64	86
14	C	Boc	Cs ₂ CO ₃	THF	80	84
15	C	Boc	K ₃ PO ₄	THF	64	84
16	C	Boc	KO ^t Bu	THF	52	86
17	C	Boc	CsOAc	THF	65	90
18	C	Boc	CsOAc	DCM	30	90
19	C	Boc	CsOAc	1,4-dioxane	49	90
20	C	Boc	CsOAc	DCE	15	90
21	C	Boc	CsOAc	DME	56	86
22	C	Boc	CsOAc	toluene	35	84
23	C	Boc	CsOAc	CH ₃ CN	27	86
24	C	Boc	CsOAc	ether	15	84
25	C	Boc	CsOAc	THF	trace	-
26 ^d	C	Boc	CsOAc	THF	30	90
27 ^e	C	Boc	CsOAc	THF	54	90
28 ^f	C	Boc	CsOAc	THF	15	90

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), NHC (0.02 mmol), base (0.02 mmol), solvent (1 mL), under Ar at 25 °C for 24 h. ^b Isolated yield based on **1a**. ^c Enantiomeric excess of **3a**, determined via chiral phase HPLC analysis. The dr (>20:1) value were determined by ¹H NMR spectroscopy. ^d 50 mg 4 Å MS was added. ^e 50 mg Na₂SO₄ was added. ^f 50 mg MgSO₄ was added.

3. 1 mmol Scale preparation of **3a**.

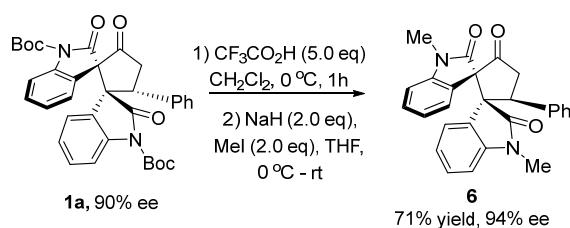
A dry 50 mL Schlenk tube with stir bar was charged with isoindigo **1a** (460 mg, 0.1 mmol, 1.0 equiv), NHC **C** (84 mg, 0.2 mmol, 20 mol %), CsOAc (38 mg, 0.2 mmol, 20 mol %). The tube was evacuated, and refilled with nitrogen. Then enals **2a** (156 mg, 1.2 mmol, 1.2 equiv) was added and the mixture was dissolved with newly distilled solvent THF (10 mL). The mixture was stirred at room temperature for 18 hours when the substrate was consumed completely (monitored by TLC). The reaction mixture was concentrated under vacuum and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to afford product **3a** as white solid (356 mg, 60% yield).

4. The procedure for the synthesis of bisporooxindoles **5a** using β -bromoenal **4a** as the starting material.



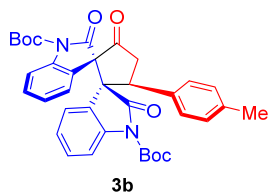
A dry 25 mL Schlenk tube with stir bar was charged with isoindigo **1a** (69 mg, 0.1 mmol, 1.0 equiv), NHC **E** (8.7 mg, 0.02 mmol, 20 mol %), DBU (18 mg, 0.12 mmol, 120 mol %). The tube was evacuated, and refilled with nitrogen. Then β -bromoenal **4a** (25 mg, 0.12 mmol, 1.2 equiv) was added and the mixture was dissolved with newly distilled solvent THF (1.0 mL). The mixture was stirred at room temperature for 20 hours when the substrate was consumed completely (monitored by TLC). The reaction mixture was concentrated under vacuum and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford products **5a** and **5a'** as white solid (40 mg, 68% yield).

5. The procedure for the synthesis of compound **6** and **7** using compound **3a** as the starting material.

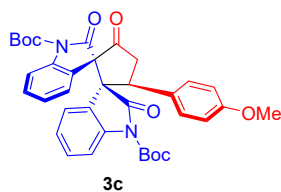


To a CH₂Cl₂ (4 mL) solution of **3a** (0.2 mmol) in round bottle flask under ice bath,

m/z: $[M+Na]^+$ Calcd for $C_{35}H_{34}N_2NaO_7^+$ 617.2258; Found 617.2263. **HPLC:** CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.6 min (minor), 15.8 min (major), 90% ee. **Optical rotation:** $[\alpha]_D^{25}$ = -375 (*c* = 1.0 in EtOAc).

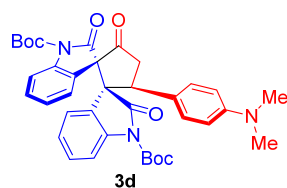


3b, Prepared according to the general procedure in 0.1 mmol scale, 89% yield, 54 mg, white solid, m.p. 121-124°C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, $CDCl_3$) δ 7.65-7.61 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.26-7.05 (m, 5H), 6.92 (s, 4H), 4.96 (t, *J* = 10.4 Hz, 1H), 3.68 (dd, *J* = 19.2, 11.2 Hz, 1H), 3.25 (dd, *J* = 19.6, 10.0 Hz, 1H), 2.22 (s, 3H), 1.65 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (100 MHz, $CDCl_3$): δ 206.7, 173.8, 170.8, 148.1, 148.0, 140.6, 140.3, 137.3, 131.3, 129.9, 129.6, 128.9, 128.3, 126.1, 125.0, 124.6, 123.8, 123.4, 122.2, 114.9, 114.7, 85.0, 84.4, 70.0, 65.3, 46.0, 40.5, 28.0, 27.9, 20.9; **HRMS (ESI) m/z:** $[M+H]^+$ Calcd for $C_{36}H_{37}N_2O_7^+$ 609.2595; Found 609.2599. **HPLC:** CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.4 min (minor), 14.5 min (major), 92% ee. **Optical rotation:** $[\alpha]_D^{25}$ = -641 (*c* = 1.0 in EtOAc).

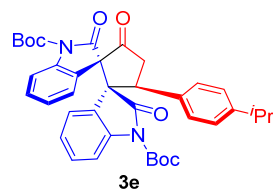


3c, Prepared according to the general procedure in 0.1 mmol scale, 75% yield, 47 mg, white solid, m.p. 127-130°C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (600 MHz, $CDCl_3$) δ 7.63 (t, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.26-7.18 (m, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 4.95 (t, *J* = 10.8 Hz, 1H), 3.70 (s, 3H), 3.65 (dd, *J* = 19.2, 11.4 Hz, 1H), 3.24 (dd, *J* = 19.8, 10.2 Hz, 1H), 1.65 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (150 MHz, $CDCl_3$): δ 206.5, 173.9, 170.8, 159.0, 148.1, 148.0, 140.7, 140.4, 129.9, 129.6, 126.4, 126.1, 125.0, 124.6, 123.9, 123.5, 122.3, 114.9, 114.7, 113.6, 85.0, 84.5, 70.1, 65.4, 55.1, 45.7, 40.7, 28.1, 27.9; **HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{36}H_{36}N_2NaO_8^+$ 647.2364; Found 647.2369. **HPLC:** CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 10.5 min (minor), 17.3 min

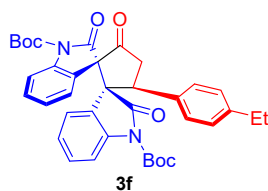
(major), 92% ee. **Optical rotation:** $[\alpha]^{25}_D = +90$ ($c = 1.0$ in EtOAc);



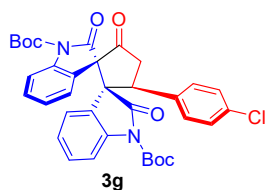
3d, Prepared according to the general procedure in 0.1 mmol scale, 52% yield, 33 mg, yellow solid, m.p. 106-108 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.64-7.61 (m, 2H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.26-7.05 (m, 4H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.47 (d, $J = 8.8$ Hz, 2H), 4.91 (t, $J = 10.8$ Hz, 1H), 3.65 (dd, $J = 19.2, 11.2$ Hz, 1H), 3.22 (dd, $J = 19.2, 10.0$ Hz, 1H), 2.85 (s, 6H), 1.65 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 207.1, 174.1, 170.9, 149.8, 148.2, 148.1, 140.6, 140.3, 129.8, 129.4, 129.2, 126.1, 125.0, 124.5, 124.1, 123.4, 122.3, 121.6, 115.0, 114.7, 112.1, 85.0, 84.3, 70.2, 65.5, 45.7, 40.8, 40.3, 29.6, 28.1, 27.9; **HRMS (ESI) m/z:** $[M+H]^+$ Calcd for C₃₇H₄₀N₃O₇⁺ 660.2861; Found 638.2850. **HPLC:** CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, $t_R = 10.4$ min (minor), 13.8 min (major), 86% ee. **Optical rotation:** $[\alpha]^{25}_D = -125$ ($c = 1.0$ in EtOAc);



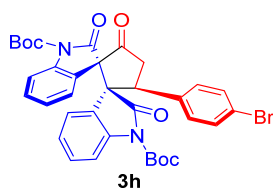
3e, Prepared according to the general procedure in 0.1 mmol scale, 65% yield, 41 mg, white solid, m.p. 92-95 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.65-7.61 (m, 2H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.32 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.29-7.06 (m, 4H), 6.96 (dd, $J = 12.0, 8.8$ Hz, 4H), 4.97 (t, $J = 10.4$ Hz, 1H), 3.68 (dd, $J = 19.2, 11.2$ Hz, 1H), 3.26 (dd, $J = 19.6, 10.0$ Hz, 1H), 2.81-2.74 (m, 1H), 1.65 (s, 9H), 1.50 (s, 9H), 1.16 (d, $J = 2.8$ Hz, 3H), 1.14 (d, $J = 2.8$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.8, 173.9, 170.8, 148.2, 148.1, 140.0, 140.6, 140.3, 131.7, 129.9, 129.6, 128.4, 126.2, 126.17, 125.0, 124.6, 123.8, 123.4, 122.2, 114.9, 114.7, 85.1, 84.4, 70.1, 65.3, 46.0, 40.6, 33.5, 28.1, 28.0, 23.9, 23.7; **HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for C₃₈H₄₀N₂NaO₇⁺ 659.2728; Found 659.2739. **HPLC:** CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, $t_R = 6.7$ min (minor), 7.7 min (major), 90% ee. **Optical rotation:** $[\alpha]^{25}_D = +406$ ($c = 1.0$ in EtOAc);



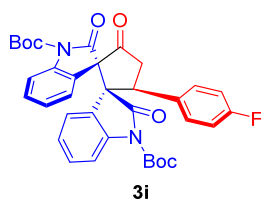
3f, Prepared according to the general procedure in 0.1 mmol scale, 51% yield, 32 mg, white solid, m.p. 103-106 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.64 (t, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.32 (dd, J = 8.0 Hz, 1H), 7.26-7.06 (m, 5H), 6.96 (s, 4H), 4.97 (t, J = 10.4 Hz, 1H), 3.69 (dd, J = 19.6, 11.2 Hz, 1H), 3.26 (dd, J = 19.2, 9.6 Hz, 1H), 2.52 (q, J = 7.6 Hz, 2H), 1.66 (s, 9H), 1.50 (s, 9H), 1.16 (d, J = 2.8 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.7, 173.9, 170.8, 148.1, 148.0, 143.6, 140.6, 140.3, 131.6, 129.9, 129.6, 128.4, 127.7, 126.2, 125.0, 124.6, 123.8, 123.4, 122.2, 114.9, 114.7, 85.0, 84.4, 70.1, 65.4, 46.0, 40.6, 28.3, 28.1, 27.9, 15.2; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₇H₃₈N₂NaO₇⁺ 645.2571; Found 645.2579. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.1 min (minor), 9.3 min (major), 94% ee. **Optical rotation**: [α]_D²⁵ = -560 (c = 1.0 in EtOAc);



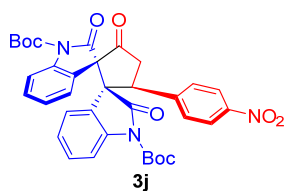
3g, Prepared according to the general procedure in 0.1 mmol scale, 64% yield, 40 mg, white solid, m.p. 102-105 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (600 MHz, CDCl₃) δ 7.63 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.26-7.20 (m, 2H), 7.14 (t, J = 7.8 Hz, 1H), 7.10-7.06 (m, 3H), 6.97 (d, J = 8.4 Hz, 2H), 4.97 (t, J = 10.8 Hz, 1H), 3.64 (dd, J = 19.2, 10.8 Hz, 1H), 3.26 (dd, J = 19.2, 9.6 Hz, 1H), 1.65 (s, 9H), 1.52 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 205.9, 173.7, 170.7, 148.1, 147.8, 140.7, 140.3, 133.7, 133.2, 130.0, 129.9, 128.4, 126.1, 125.0, 124.7, 123.4, 122.0, 115.1, 114.8, 85.1, 84.8, 70.0, 65.2, 45.7, 40.3, 28.1, 27.9; **HRMS (ESI) m/z**: [M+H]⁺ Calcd for C₃₅H₃₄ClN₂O₇⁺ 629.2049; Found 629.2056. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.6 min (minor), 12.9 min (major), 88% ee. **Optical rotation**: [α]_D²⁵ = -413 (c = 1.0 in EtOAc);



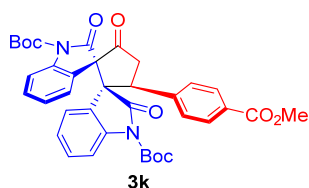
3h, Prepared according to the general procedure in 0.1 mmol scale, 52% yield, 35 mg, white solid, m.p. 138-141 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.63 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.31-7.20 (m, 5H), 7.15 (t, J = 7.6 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 4.96 (t, J = 10.8 Hz, 1H), 3.64 (dd, J = 19.2, 10.8 Hz, 1H), 3.27 (dd, J = 19.2, 10.0 Hz, 1H), 1.65 (s, 9H), 1.52 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.0, 173.8, 170.7, 148.0, 147.7, 140.6, 140.2, 133.6, 131.3, 130.2, 130.0, 129.9, 126.0, 125.1, 124.8, 123.4, 123.3, 121.9, 121.8, 115.1, 114.8, 85.1, 84.8, 69.9, 65.1, 45.7, 40.2, 28.0, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₅H₃₃BrN₂NaO₇⁺ 695.1363; Found 695.1373. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.0 min (minor), 12.1 min (major), 86% ee. **Optical rotation**: [α]_D²⁵ = +483 (c = 1.0 in EtOAc);



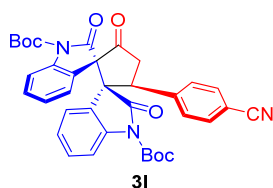
3i, Prepared according to the general procedure in 0.1 mmol scale, 82% yield, 50 mg, white solid, m.p. 123-125 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (600 MHz, CDCl₃) δ 7.63 (t, J = 7.2 Hz, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H), 7.03-7.00 (m, 2H), 6.81 (t, J = 8.4 Hz, 2H), 4.98 (t, J = 10.8 Hz, 1H), 3.64 (dd, J = 19.2, 11.4 Hz, 1H), 3.27 (dd, J = 19.8, 10.2 Hz, 1H), 1.65 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 206.1, 173.8, 170.8, 163.1 (C-F, d, $^1J_{C-F}$ = 246.0 Hz), 148.1, 147.8, 140.7, 140.3, 130.2 (C-F, d, $^3J_{C-F}$ = 2.4 Hz), 130.1, 130.06, 130.0, 129.8, 126.1, 125.1, 124.7, 123.5, 123.4, 122.0, 115.2 (C-F, d, $^2J_{C-F}$ = 60.0 Hz), 115.0, 85.2, 84.7, 70.0, 65.3, 45.7, 40.5, 28.1, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₅H₃₃FN₂NaO₇⁺ 635.2164; Found 635.2155. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.2 min (minor), 11.0 min (major), 88% ee. **Optical rotation**: [α]_D²⁵ = -312 (c = 1.0 in EtOAc).



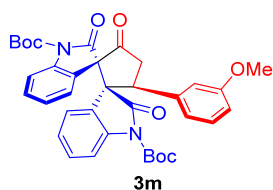
3j, Prepared according to the general procedure in 0.1 mmol scale, 55% yield, 35 mg, white solid, m.p. 101-104 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (600 MHz, CDCl₃) δ 7.99 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.29-7.23 (m, 5H), 7.18 (t, J = 7.2 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H), 5.13 (t, J = 10.2 Hz, 1H), 3.71 (dd, J = 19.2, 9.6 Hz, 1H), 3.27 (dd, J = 19.2, 10.2 Hz, 1H), 1.65 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 205.1, 173.5, 170.6, 148.0, 147.6, 147.5, 142.4, 140.7, 140.2, 130.25, 130.2, 129.5, 125.9, 125.1, 125.0, 123.4, 123.3, 122.8, 121.5, 115.2, 114.9, 85.3, 85.1, 70.0, 64.9, 45.8, 40.2, 28.1, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₅H₃₃N₃NaO₉⁺ 662.2109; Found 662.2122. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 11.9 min (minor), 18.7 min (major), 86% ee. **Optical rotation**: $[\alpha]_D^{25}$ = +413 (c = 1.0 in EtOAc).



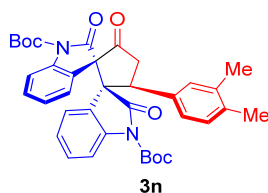
3k, Prepared according to the general procedure in 0.1 mmol scale, 43% yield, 28 mg, white solid, m.p. 89-91 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (600 MHz, CDCl₃) δ 7.79 (d, J = 8.4 Hz, 2H), 7.65 (dd, J = 15.0, 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.26-7.19 (m, 2H), 7.16-7.06 (m, 4H), 5.07 (t, J = 10.8 Hz, 1H), 3.85 (s, 3H), 3.72 (dd, J = 19.2, 10.8 Hz, 1H), 3.29 (dd, J = 19.8, 10.2 Hz, 1H), 1.65 (s, 9H), 1.50 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 205.8, 173.6, 170.7, 166.6, 148.1, 147.7, 140.7, 140.2, 140.0, 130.0, 129.9, 129.6, 129.4, 128.6, 126.1, 125.0, 124.8, 123.4, 123.3, 121.9, 115.1, 114.8, 85.2, 84.8, 70.0, 65.1, 52.0, 46.1, 40.2, 28.1, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₇H₃₆N₂NaO₉⁺ 675.2313; Found 675.2315. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 13.6 min (minor), 20.2 min (major), 86% ee. **Optical rotation**: $[\alpha]_D^{25}$ = +252 (c = 1.0 in EtOAc).



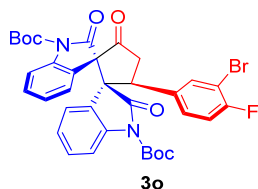
3l, Prepared according to the general procedure in 0.1 mmol scale, 45% yield, 28 mg, white solid, m.p. 89-92 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.64 (t, J = 7.6 Hz, 2H), 7.45-7.42 (m, 3H), 7.29-7.22 (m, 3H), 7.19-7.15 (m, 3H), 7.08 (td, J = 7.6, 0.4 Hz, 1H), 5.07 (t, J = 10.8 Hz, 1H), 3.68 (dd, J = 19.2, 11.2 Hz, 1H), 3.30 (dd, J = 19.2, 10.0 Hz, 1H), 1.65 (s, 9H), 1.52 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 205.3, 173.6, 170.6, 147.9, 147.6, 140.7, 140.3, 140.2, 131.9, 130.2, 129.3, 126.0, 125.1, 125.0, 123.4, 122.9, 121.6, 118.4, 115.2, 114.9, 111.7, 85.3, 85.1, 70.0, 64.9, 46.1, 40.0, 28.0, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₆H₃₃N₃NaO₇⁺ 642.2211; Found 642.2216. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 15.0 min (minor), 26.0 min (major), 86% ee. **Optical rotation**: [α]_D²⁵ = -193 (c = 1.0 in EtOAc);



3m, Prepared according to the general procedure in 0.1 mmol scale, 60% yield, 37 mg, white solid, m.p. 79-81 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.64 (t, J = 7.6 Hz, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.27-7.02 (m, 5H), 6.71-6.65 (m, 2H), 6.51 (s, 1H), 4.98 (t, J = 10.8 Hz, 1H), 3.68 (dd, J = 19.2, 11.2 Hz, 1H), 3.57 (s, 3H), 3.27 (dd, J = 19.2, 10.0 Hz, 1H), 1.65 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.4, 173.8, 170.8, 159.2, 148.1, 147.9, 140.7, 140.4, 136.0, 129.9, 129.7, 129.1, 126.2, 125.0, 124.6, 123.8, 123.4, 122.1, 120.6, 115.0, 114.7, 114.0, 113.4, 85.1, 84.5, 69.9, 65.3, 54.9, 46.4, 40.4, 28.1, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₆H₃₆N₂NaO₈⁺ 647.2364; Found 647.2356. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.3 min (minor), 20.3 min (major), 90% ee. **Optical rotation**: [α]_D²⁵ = -131 (c = 1.0 in EtOAc).

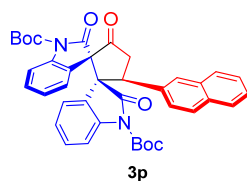


3n, Prepared according to the general procedure in 0.1 mmol scale, 66% yield, 41 mg, white solid, m.p. 113-115 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (600 MHz, CDCl₃) δ 7.63 (t, J = 6.6 Hz, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 7.8 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.80 (s, 1H), 6.75 (d, J = 7.2 Hz, 1H), 4.93 (t, J = 10.8 Hz, 1H), 3.67 (dd, J = 19.2, 11.4 Hz, 1H), 3.23 (dd, J = 19.8, 10.2 Hz, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 1.65 (s, 9H), 1.50 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 206.7, 173.8, 170.8, 148.2, 148.1, 140.7, 140.4, 136.2, 135.9, 131.8, 129.9, 129.7, 129.5, 129.4, 126.2, 125.9, 125.0, 124.5, 124.0, 123.5, 122.3, 114.9, 114.7, 85.0, 84.3, 70.1, 65.4, 46.0, 40.6, 28.1, 27.9, 19.6, 19.2; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₇H₃₈N₂NaO₇⁺ 645.2571; Found 645.2579. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 6.7 min (minor), 10.4 min (major), 92% ee. **Optical rotation**: $[\alpha]_D^{25}$ = -55 (c = 1.0 in EtOAc);

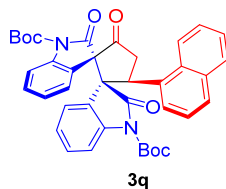


3o, Prepared according to the general procedure in 0.1 mmol scale, 40% yield, 28 mg, white solid, m.p. 138-141 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (600 MHz, CDCl₃) δ 7.63 (t, J = 7.8 Hz, 2H), 7.48 (d, J = 8.4 Hz, 1H), 7.29-7.22 (m, 4H), 7.16 (t, J = 7.8 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H), 6.93-6.91 (m, 1H), 6.86 (t, J = 8.4 Hz, 1H), 4.95 (t, J = 10.8 Hz, 1H), 3.59 (dd, J = 19.2, 10.8 Hz, 1H), 3.27 (dd, J = 19.2, 10.2 Hz, 1H), 1.65 (s, 9H), 1.54 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 205.5, 173.36, 170.7, 158.6 (C-F, d, $^1J_{C-F}$ = 255.0 Hz), 148.0, 147.8, 140.7, 140.3, 133.4, 132.2 (C-F, d, $^4J_{C-F}$ = 4.3 Hz), 130.1 (C-F, d, $^3J_{C-F}$ = 4.8 Hz), 129.2 (C-F, d, $^3J_{C-F}$ = 7.0 Hz), 126.0, 125.1, 124.9, 123.3, 123.2, 121.9, 116.2, 116.0, 115.1, 114.8, 108.8 (C-F, d, $^2J_{C-F}$ = 21.0 Hz), 85.2, 85.0, 69.9, 65.1, 45.4, 40.3, 28.1, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₅H₃₂BrFN₂NaO₇⁺ 713.1269; Found 713.1259. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 6.4 min (minor), 11.0 min

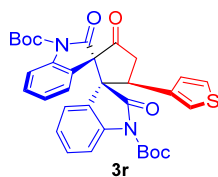
(major), 68% ee. **Optical rotation:** $[\alpha]^{25}_D = -74$ ($c = 1.0$ in EtOAc).



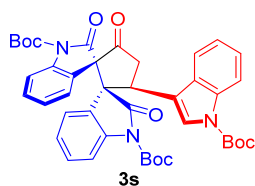
3p, Prepared according to the general procedure in 0.1 mmol scale, 76% yield, 49 mg, white solid, m.p. 104-106 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (600 MHz, CDCl₃) δ 7.73-7.67 (m, 3H), 7.64-7.61 (m, 2H), 7.56 (d, $J = 8.4$ Hz, 1H), 7.41-7.38 (m, 2H), 7.37-7.33 (m, 2H), 7.25-7.23 (m, 1H), 7.19-7.15 (m, 2H), 7.09-7.04 (m, 2H), 5.18 (t, $J = 10.2$ Hz, 1H), 3.85 (dd, $J = 19.2, 10.8$ Hz, 1H), 3.35 (dd, $J = 19.2, 9.6$ Hz, 1H), 1.67 (s, 9H), 1.37 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 206.3, 173.8, 170.9, 148.2, 147.8, 140.7, 140.4, 133.1, 132.8, 132.1, 129.9, 129.7, 128.0, 127.7, 127.5, 127.3, 126.5, 126.2, 126.0, 125.97, 125.0, 124.6, 123.8, 123.5, 122.2, 115.0, 114.7, 85.1, 84.5, 70.2, 65.4, 46.4, 40.5, 28.1, 27.8; **HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for C₃₉H₃₆N₂NaO₇⁺ 667.2415; Found 667.2422. **HPLC:** CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 8.1 min (minor), 13.7 min (major), 90% ee. **Optical rotation:** $[\alpha]^{25}_D = -134$ ($c = 1.0$ in EtOAc).



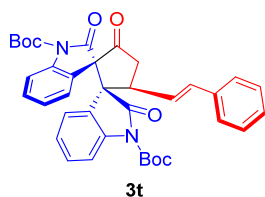
3q, Prepared according to the general procedure in 0.1 mmol scale, 50% yield, 32 mg, white solid, m.p. 157-160 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (400 MHz, CDCl₃) δ 8.07-8.05 (m, 1H), 7.77-7.66 (m, 4H), 7.60 (d, $J = 8.8$ Hz, 1H), 7.42-7.38 (m, 2H), 7.33-7.28 (m, 2H), 7.24-7.19 (m, 1H), 7.10 (t, $J = 6.8$ Hz, 1H), 6.98-6.93 (m, 2H), 6.22 (t, $J = 10.8$ Hz, 1H), 3.73 (dd, $J = 19.2, 11.2$ Hz, 1H), 3.42 (dd, $J = 19.6, 10.0$ Hz, 1H), 1.68 (s, 9H), 1.53 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.2, 174.3, 171.3, 148.0, 147.9, 140.6, 139.8, 133.6, 132.4, 131.3, 129.9, 129.5, 128.5, 128.3, 126.5, 125.6, 125.4, 125.1, 125.0, 124.3, 124.0, 123.3, 123.1, 122.2, 114.7, 114.6, 85.4, 84.6, 70.4, 65.7, 42.5, 39.4, 28.1, 28.0; **HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for C₃₉H₃₆N₂NaO₇⁺ 667.2415; Found 667.2423. **HPLC:** CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 6.8 min (minor), 17.0 min (major), 90% ee. **Optical rotation:** $[\alpha]^{25}_D = -154$ ($c = 1.0$ in EtOAc);



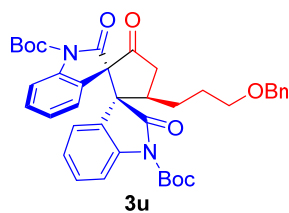
3r, Prepared according to the general procedure in 0.1 mmol scale, 80% yield, 48 mg, white solid, m.p. 101-104 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.64-7.61 (m, 2H), 7.50 (d, J = 8.8 Hz, 1H), 7.31-7.22 (m, 3H), 7.17-7.13 (m, 1H), 7.10-7.06 (m, 2H), 6.91-6.90 (m, 1H), 6.55 (dd, J = 4.8, 1.2 Hz, 1H), 5.06 (t, J = 10.4 Hz, 1H), 3.61 (dd, J = 19.6, 11.2 Hz, 1H), 3.32 (dd, J = 19.6, 9.6 Hz, 1H), 1.65 (s, 9H), 1.53 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.3, 174.1, 170.7, 148.1, 148.0, 140.7, 140.4, 136.0, 130.0, 129.8, 127.2, 126.0, 125.5, 125.1, 124.7, 124.0, 123.3, 122.8, 122.0, 115.1, 114.8, 85.1, 84.6, 69.9, 64.6, 42.0, 41.4, 28.1, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₃H₃₂N₂NaO₇S⁺ 623.1822; Found 623.1830. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.2 min (minor), 11.9 min (major), 88% ee. **Optical rotation**: $[\alpha]_D^{25}$ = -308 (c = 1.0 in EtOAc);



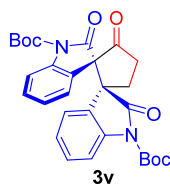
3s, Prepared according to the general procedure in 0.1 mmol scale, 70% yield, 51 mg, white solid, m.p. 113-115 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 8.01 (d, J = 6.8 Hz, 1H), 7.72-7.69 (m, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.53 (s, 1H), 7.38-7.32 (m, 2H), 7.28-7.23 (m, 1H), 7.18-7.07 (m, 5H), 6.96 (t, J = 7.6 Hz, 1H), 5.28 (t, J = 10.4 Hz, 1H), 3.56 (dd, J = 19.6, 10.8 Hz, 1H), 3.44 (dd, J = 19.6, 10.0 Hz, 1H), 1.67 (s, 9H), 1.64 (s, 9H), 1.53 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.2, 174.5, 170.8, 148.1, 148.0, 140.7, 140.3, 130.0, 129.9, 129.8, 126.0, 125.1, 124.6, 124.3, 124.27, 123.9, 123.4, 122.2, 122.0, 118.8, 115.8, 115.0, 114.82, 114.8, 85.2, 84.6, 83.8, 70.3, 64.6, 42.5, 37.3, 28.1, 28.08, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₄₂H₄₃N₃NaO₉⁺ 756.2892; Found 756.2913. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 5.6 min (minor), 8.6 min (major), 96% ee. **Optical rotation**: $[\alpha]_D^{25}$ = +594 (c = 1.0 in EtOAc).



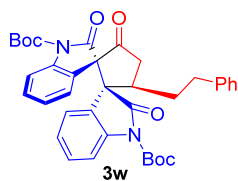
3t, Prepared according to the general procedure in 0.1 mmol scale, 46% yield, 28 mg, white solid, m.p. 83-86 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.58-7.52 (m, 2H), 7.30-7.27 (m, 1H), 7.25-7.17 (m, 7H), 7.14-7.06 (m, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 6.02 (dd, *J* = 16.0, 8.8 Hz, 1H), 4.45 (dd, *J* = 18.8, 9.6 Hz, 1H), 3.33-3.17 (m, 2H), 1.63 (s, 9H), 1.57 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.6, 174.5, 170.4, 148.1, 148.0, 140.7, 140.4, 136.3, 134.8, 130.0, 129.7, 128.4, 127.8, 126.4, 125.7, 124.9, 124.8, 124.5, 123.5, 123.4, 121.8, 115.1, 114.8, 85.0, 84.9, 69.8, 63.9, 44.7, 41.8, 28.0, 27.97; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₇H₄₀N₃O₇⁺ 643.2415; Found 643.2412. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, *t*_R = 7.7 min (minor), 12.7 min (major), 80% ee. **Optical rotation**: [α]_D²⁵ = +504 (c = 1.0 in EtOAc).



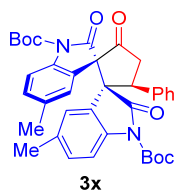
3u, Prepared according to the general procedure in 0.1 mmol scale, 39% yield, 26 mg, white solid, m.p. 123-125 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.34-7.21 (m, 8H), 7.11-7.03 (m, 2H), 4.41 (s, 2H), 3.71-3.62 (m, 1H), 3.41-3.33 (m, 2H), 3.13 (dd, *J* = 19.2, 10.0 Hz, 1H), 2.92 (dd, *J* = 19.2, 10.8 Hz, 1H), 1.67-1.59 (m, 19H), 1.53-1.49 (m, 2H), 1.28-1.21 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 207.1, 174.7, 170.3, 148.3, 148.1, 140.7, 140.5, 138.3, 129.9, 129.7, 128.4, 127.6, 125.6, 124.9, 124.8, 124.1, 123.3, 121.9, 141.9, 115.0, 114.7, 84.9, 84.8, 72.8, 70.4, 69.7, 63.5, 41.9, 40.5, 28.5, 28.0, 26.1; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₉H₄₂N₂NaO₈⁺ 689.2833; Found 689.2824. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, *t*_R = 8.4 min (minor), 12.2 min (major), 82% ee. **Optical rotation**: [α]_D²⁵ = -312 (c = 1.0 in EtOAc).



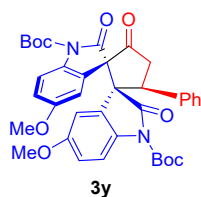
3v, Prepared according to the general procedure in 0.1 mmol scale, 12% yield, 6 mg, white solid, m.p. 155-157 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 10:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.65 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.26-7.22 (m, 3H), 7.12-7.05 (m, 2H), 3.25-3.01 (m, 3H), 2.46-2.38 (m, 1H), 1.61 (s, 9H), 1.61 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 207.8, 176.7, 170.0, 148.6, 148.1, 140.9, 139.8, 129.9, 129.7, 125.4, 124.9, 124.8, 123.7, 121.7, 115.0, 114.8, 84.89, 84.88, 69.0, 59.1, 36.1, 28.5, 28.1; **HRMS (ESI) m/z**: [M+NH₄]⁺ Calcd for C₂₉H₃₄N₃O₇⁺ 536.2391; Found 536.2406. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.6 min (minor), 10.8 min (major), 84% ee. **Optical rotation**: [α]_D²⁵ = +686 (c = 1.0 in EtOAc).



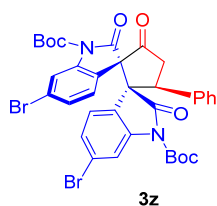
3w, Prepared according to the general procedure in 0.1 mmol scale, 42% yield, 26 mg, white solid, m.p. 125-127 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.55 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.18-7.14 (m, 5H), 7.11-7.07 (m, 1H), 7.04-6.96 (m, 4H), 3.66-3.58 (m, 1H), 3.06 (dd, J = 19.6, 10.0 Hz, 1H), 2.88 (dd, J = 19.6, 10.4 Hz, 1H), 2.61-2.54 (m, 1H), 2.47-2.40 (m, 1H), 1.76-1.66 (m, 1H), 1.53 (s, 9H), 1.52 (s, 9H), 1.39-1.30 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 207.1, 174.7, 170.2, 148.2, 148.0, 141.1, 140.7, 140.5, 129.9, 129.7, 128.4, 128.2, 126.1, 125.5, 124.8, 124.7, 123.9, 123.2, 115.0, 114.7, 84.9, 84.8, 70.2, 63.5, 41.8, 40.5, 34.8, 31.5, 28.0; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₇H₃₈N₂NaO₇⁺ 645.2571; Found 645.2567. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 6.5 min (minor), 7.8 min (major), 86% ee. **Optical rotation**: [α]_D²⁵ = -135 (c = 1.0 in EtOAc).



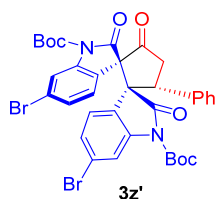
3x, Prepared according to the general procedure in 0.1 mmol scale, 60% yield, 38 mg, white solid, m.p. 125-127 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.51 (d, J = 8.4 Hz, 1H), 7.45 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.15-7.10 (m, 4H), 7.04 (d, J = 7.6 Hz, 3H), 6.98 (d, J = 8.4 Hz, 1H), 4.97 (t, J = 10.8 Hz, 1H), 3.68 (dd, J = 19.2, 11.2 Hz, 1H), 3.26 (dd, J = 19.2, 10.0 Hz, 1H), 2.35 (s, 3H), 2.26 (s, 3H), 1.66 (s, 9H), 1.50 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.9, 173.9, 171.0, 148.3, 148.1, 138.2, 137.9, 134.7, 134.3, 130.4, 130.1, 128.5, 128.2, 127.6, 126.6, 123.9, 123.7, 122.1, 114.6, 114.4, 84.8, 84.2, 70.1, 65.3, 46.2, 40.5, 28.1, 27.9, 21.2, 21.1; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₇H₃₈N₂NaO₇⁺ 645.2571; Found 645.2567. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 5.1 min (minor), 9.9 min (major), 86% ee. **Optical rotation**: [α]_D²⁵ = -171 (c = 1.0 in EtOAc).



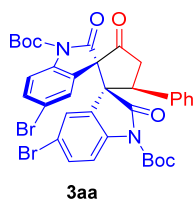
3y, Prepared according to the general procedure in 0.1 mmol scale, 74% yield, 48 mg, white solid, m.p. 91.3-92.1 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.57 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 9.6 Hz, 1H), 7.23 (s, 1H), 7.16-7.11 (m, 3H), 7.08-7.06 (m, 2H), 6.91 (d, J = 2.4 Hz, 1H), 6.77 (dd, J = 8.8, 2.8 Hz, 1H), 6.71 (dd, J = 9.6, 1.2 Hz, 1H), 4.97 (t, J = 10.8 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.70 (dd, J = 19.2, 10.8 Hz, 1H), 3.27 (dd, J = 19.6, 9.6 Hz, 1H), 1.64 (s, 9H), 1.49 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.5, 173.9, 170.8, 157.04, 157.0, 148.3, 148.0, 133.8, 133.5, 128.5, 128.2, 127.7, 124.9, 123.1, 115.9, 115.6, 114.6, 111.4, 109.4, 85.0, 84.4, 70.2, 65.5, 55.5, 55.4, 46.4, 40.4, 28.0, 27.8; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₇H₃₈N₂NaO₉⁺ 622.2470; Found 677.2466. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 6.8 min (minor), 16.9 min (major), 87% ee. **Optical rotation**: [α]_D²⁵ = -162 (c = 1.0 in EtOAc).



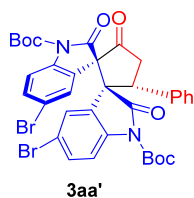
3z+3z', Prepared according to the general procedure in 0.1 mmol scale, 36% yield, 26 mg. **3z**, white solid, m.p. 99-101 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.68 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.30-7.22 (m, 2H), 7.19-7.13 (m, 4H), 7.03 (d, J = 7.2 Hz, 2H), 4.94 (t, J = 10.4 Hz, 1H), 3.66 (dd, J = 19.2, 11.2 Hz, 1H), 3.26 (dd, J = 19.6, 10.0 Hz, 1H), 1.66 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 205.4, 173.3, 170.1, 147.7, 147.5, 141.6, 141.2, 133.8, 128.4, 128.2, 128.1, 127.8, 127.4, 124.6, 124.2, 123.7, 122.5, 120.9, 118.6, 118.5, 85.9, 85.3, 69.5, 65.0, 46.5, 40.1, 28.0, 27.9; **HRMS (ESI)** m/z : M^+ Calcd for C₃₅H₃₂Br₂N₂NaO₇⁺ 750.0571; Found 750.0565. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 3.6 min (minor), 4.4 min (major), 78% ee. **Optical rotation**: $[\alpha]^{25}_D$ = +217 (c = 1.0 in EtOAc).



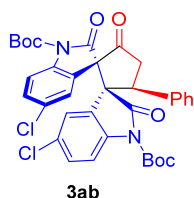
3z', white solid, m.p. 101-102 °C, **¹H NMR** (400 MHz, CDCl₃) δ 8.07 (d, J = 1.6 Hz, 1H), 7.70 (d, J = 1.2 Hz, 1H), 7.34-7.32 (m, 1H), 7.12-7.09 (m, 4H), 7.00-6.96 (m, 3H), 6.25 (d, J = 8.4 Hz, 1H), 5.36 (t, J = 11.2 Hz, 1H), 3.51 (dd, J = 20.0, 10.0 Hz, 1H), 3.27 (dd, J = 19.6, 11.2 Hz, 1H), 1.68 (s, 9H), 1.52 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 205.8, 172.0, 168.5, 148.4, 147.7, 141.9, 141.0, 134.4, 128.2, 127.9, 127.6, 127.2, 126.8, 126.78, 125.2, 124.2, 123.6, 122.8, 119.8, 119.1, 118.7, 85.4, 85.3, 69.9, 65.9, 45.7, 39.8, 28.1, 27.9; **HRMS (ESI)** m/z : M^+ Calcd for C₃₅H₃₂Br₂N₂NaO₇⁺ 750.0571; Found 750.0563. **HPLC**: CHIRALPAK IA, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 4.3 min (minor), 4.6 min (major), 78% ee. **Optical rotation**: $[\alpha]^{25}_D$ = +209 (c = 1.0 in EtOAc).



3aa+3aa', Prepared according to the general procedure in 0.1 mmol scale, 76% yield, 57 mg. **3aa**, white solid, m.p. 126-128 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.75 (d, J = 2.0 Hz, 1H), 7.66-7.64 (m, 1H), 7.43-7.39 (m, 3H), 7.36-7.33 (m, 1H), 7.19-7.14 (m, 3H), 7.06-7.04 (m, 2H), 4.92 (t, J = 10.8 Hz, 1H), 3.67 (dd, J = 19.6, 10.8 Hz, 1H), 3.26 (dd, J = 19.6, 10.0 Hz, 1H), 1.69 (s, 9H), 1.54 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 205.3, 172.7, 169.8, 140.2, 147.8, 139.8, 139.4, 133.8, 133.2, 132.9, 129.1, 128.5, 128.4, 128.1, 126.4, 125.7, 123.8, 118.2, 117.9, 116.7, 116.5, 85.9, 85.4, 69.5, 65.0, 46.5, 40.3, 28.0, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₅H₃₂Br₂N₂NaO₇⁺ 775.0448; Found 775.0456. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 3.9 min (major), 4.4 min (minor), 64% ee. **Optical rotation**: [α]_D²⁵ = +68 (c = 1.0 in EtOAc).

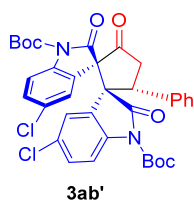


3aa', white solid, m.p. 103-105 °C: **¹H NMR** (400 MHz, CDCl₃) δ 7.73 (d, J = 8.8 Hz, 1H), 7.39-7.37 (m, 4H), 7.11 (t, J = 3.2 Hz, 3H), 7.01-6.99 (m, 2H), 6.54 (d, J = 2.0 Hz, 1H), 5.36 (t, J = 10.8 Hz, 1H), 3.52 (dd, J = 20.0, 11.2 Hz, 1H), 3.31 (dd, J = 20.0, 11.2 Hz, 1H), 1.67 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 205.8, 171.8, 168.3, 148.4, 147.8, 139.9, 138.8, 134.2, 132.9, 129.0, 128.3, 127.8, 127.6, 126.9, 125.8, 122.8, 117.2, 117.1, 116.8, 116.7, 85.3, 85.2, 69.9, 66.1, 45.8, 39.6, 28.0, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₅H₃₂Br₂N₂NaO₇⁺ 775.0448; Found 775.0459. **HPLC**: CHIRALPAK IA, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 3.9 min (major), 4.3 min (minor), 80% ee. **Optical rotation**: [α]_D²⁵ = -167 (c = 1.0 in EtOAc).

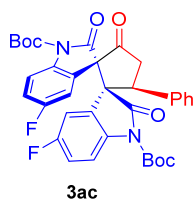


3ab+3ab', Prepared according to the general procedure in 0.1 mmol scale, 50% yield, 33 mg. **3ab**: white solid, m.p. 104-105 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.70 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 1.6 Hz, 1H), 7.47 (d, J = 9.2 Hz, 1H), 7.31-7.24 (m, 3H), 7.21-7.14 (m, 3H), 7.06 (d, J = 6.8 Hz, 2H), 4.93 (t, J = 10.8 Hz,

1H), 3.68 (dd, $J = 19.6, 11.2$ Hz, 1H), 3.27 (dd, $J = 19.2, 10.0$ Hz, 1H), 1.69 (s, 9H), 1.54 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): δ 205.4, 172.9, 169.9, 148.0, 147.8, 139.3, 138.9, 133.9, 130.6, 130.4, 130.2, 130.0, 128.5, 128.4, 128.1, 126.3, 125.3, 123.6, 123.5, 116.3, 116.1, 85.9, 85.3, 69.6, 65.0, 46.4, 40.3, 28.0, 27.8; **HRMS (ESI) m/z:** M^+ Calcd for $\text{C}_{35}\text{H}_{32}\text{Cl}_2\text{N}_2\text{NaO}_7^+$ 662.1581; Found 662.1582. **HPLC:** CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 3.8 min (minor), 4.4 min (major), 76% ee. **Optical rotation:** $[\alpha]_D^{25} = -40$ ($c = 1.0$ in EtOAc).

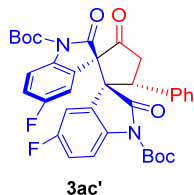


3ab', white solid, m.p. 101-103 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 9.6$ Hz, 1H), 7.24-7.19 (m, 3H), 7.11-7.09 (m, 3H), 7.01-6.99 (m, 2H), 6.38 (d, $J = 2.4$ Hz, 1H), 5.37 (t, $J = 10.8$ Hz, 1H), 3.53 (dd, $J = 20.0, 10.4$ Hz, 1H), 3.31 (dd, $J = 19.6, 10.8$ Hz, 1H), 1.67 (s, 9H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 205.8, 171.9, 168.4, 148.4, 147.9, 139.4, 138.4, 134.2, 130.0, 129.9, 129.6, 128.2, 127.8, 127.6, 126.1, 125.4, 124.1, 122.5, 116.9, 116.3, 85.3, 85.1, 69.9, 66.1, 45.8, 36.6, 28.1, 27.9; **HRMS (ESI) m/z:** $[\text{M}+\text{NH}_4]^+$ Calcd for $\text{C}_{35}\text{H}_{36}\text{Cl}_2\text{N}_3\text{O}_7^+$ 680.1925; Found 680.1933. **HPLC:** CHIRALPAK IA, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 3.8 min (minor), 4.2 min (major), 72% ee. **Optical rotation:** $[\alpha]_D^{25} = -131$ ($c = 1.0$ in EtOAc).

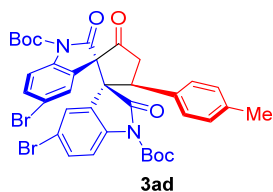


3ac+3ac', Prepared according to the general procedure in 0.1 mmol scale, 53% yield, 34 mg, white solid, m.p. **3ac:** 85-88 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **3ac:** ^1H NMR (400 MHz, CDCl_3) δ 7.71 (dd, $J = 9.0, 4.8$ Hz, 1H), 7.49 (dd, $J = 8.8, 4.4$ Hz, 1H), 7.39 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.20-7.13 (m, 3H), 7.08-7.06 (m, 3H), 7.01-6.90 (m, 2H), 4.94 (t, $J = 10.4$ Hz, 1H), 3.69 (dd, $J = 19.2, 11.6$ Hz, 1H), 3.27 (dd, $J = 19.6, 10.0$ Hz, 1H), 1.67 (s, 9H), 1.52 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): δ 205.5, 173.2, 170.2, 161.1, 158.6, 148.5, 147.9, 136.7 (d = 1.9 Hz), 136.2 (d = 1.8 Hz), 133.9, 128.4 (d = 8.9 Hz), 128.0, 125.2 (d = 8.1 Hz), 123.5 (d = 8.8

Hz), 116.9, 116.7 (d = 4.7 Hz), 116.4, 116.3, 116.1 (d = 7.9 Hz), 113.9 (d = 28.0 Hz), 111.1 (d = 25.0 Hz), 85.6, 85.1, 69.8, 65.2, 46.4, 40.3, 27.9, 27.8; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₅H₃₂F₂N₂NaO₇⁺ 653.2070; Found 653.2086. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, *t*_R = 3.7 min (major), 4.6 min (minor), 80% ee. **Optical rotation**: [α]_D²⁵ = +247 (c = 1.0 in EtOAc).

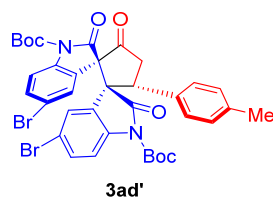


3ac': white solid, M.P. = 89-91°C, **¹H NMR** (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.48 (dd, *J* = 8.2, 4.8 Hz, 1H), 7.11-7.06 (m, 3H), 7.02-6.92 (m, 5H), 6.17 (d, *J* = 8.8 Hz, 1H), 5.41 (t, *J* = 10.0 Hz, 1H), 3.54 (dd, *J* = 19.6, 10.0 Hz, 1H), 3.29 (dd, *J* = 19.6, 10.8 Hz, 1H), 1.68 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): 205.8, 172.2, 168.6, 160.3 (d = 12.0 Hz), 157.9 (d = 10.0 Hz), 148.5, 147.9, 136.9 (d = 2.0 Hz), 136.2, 134.2, 128.2, 127.8, 127.5, 125.3 (d = 7.0 Hz), 122.5 (d = 8.0 Hz), 117.0 (d = 7.0 Hz), 116.7 (d = 9.0 Hz), 116.6 (d = 7.0 Hz), 116.4 (d = 4.0 Hz), 113.3 (d = 26.0 Hz), 111.5 (d = 26.0 Hz), 85.1, 85.0, 70.1, 66.2, 45.8, 39.5, 28.1, 27.9; **HRMS (ESI) m/z**: [M+NH₄]⁺ Calcd for C₃₅H₃₆F₂N₃O₇⁺ 648.2516; Found 648.2520. **HPLC**: CHIRALPAK IA, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, *t*_R = 3.8 min (major), 4.3 min (minor), 74% ee. **Optical rotation**: [α]_D²⁵ = +76 (c = 1.0 in EtOAc).

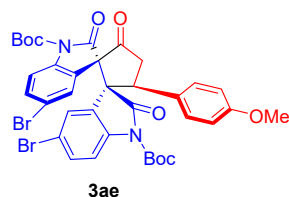


3ad+3ad', Prepared according to the general procedure in 0.1 mmol scale, 55% yield, 42 mg. **3ad**, white solid, m.p. 117-120°C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.74 (d, *J* = 1.6 Hz, 1H), 7.66-7.64 (m, 1H), 7.44-7.39 (m, 3H), 7.36-7.33 (m, 1H), 6.97-6.92 (m, 4H), 4.89 (t, *J* = 10.8 Hz, 1H), 3.64 (dd, *J* = 19.6, 11.6 Hz, 1H), 3.23 (dd, *J* = 19.6, 10.0 Hz, 1H), 2.24 (s, 3H), 1.69 (s, 9H), 1.55 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 205.5, 172.8, 169.8, 148.1, 147.9, 139.8, 139.4, 137.7, 133.2, 132.8, 130.7, 129.1, 129.0, 128.4, 126.4, 125.8, 123.9, 118.2, 117.9, 116.7, 116.5, 85.9, 85.3, 69.6, 65.0, 46.2, 40.5, 28.0, 27.9; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₆H₃₄N₂NaO₇⁺ 789.0605; Found 789.0617. **HPLC**: CHIRALPAK

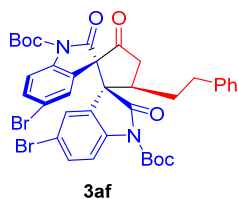
IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 4.0 min (minor), 4.5 min (major), 76% ee. **Optical rotation:** $[\alpha]^{25}_D = -42$ ($c = 1.0$ in EtOAc).



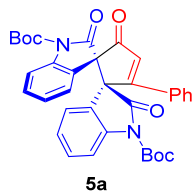
3ad', white solid, m.p. 107-119°C, **¹H NMR** (400 MHz, CDCl₃) δ 7.73 (d, $J = 8.8$ Hz, 1H), 7.41-7.36 (m, 4H), 6.90 (dd, $J = 11.6, 8.0$ Hz, 4H), 6.51 (d, $J = 2.0$ Hz, 1H), 5.31 (t, $J = 10.8$ Hz, 1H), 3.50 (dd, $J = 20.0, 10.0$ Hz, 1H), 3.29 (dd, $J = 20.0, 11.2$ Hz, 1H), 2.20 (s, 3H), 1.67 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.0, 171.8, 168.3, 148.4, 147.8, 139.8, 138.9, 137.5, 132.8, 132.78, 131.0, 129.0, 127.5, 126.9, 125.9, 122.8, 117.2, 117.0, 116.8, 116.6, 85.2, 85.1, 70.0, 66.0, 45.4, 39.9, 28.0, 27.9; $[M+Na]^+$ Calcd for C₃₆H₃₄N₂NaO₇⁺ 789.0605; Found 789.0620. **HPLC:** CHIRALPAK IA, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 3.9 min (minor), 4.2 min (major), 88% ee. **Optical rotation:** $[\alpha]^{25}_D = -121$ ($c = 1.0$ in EtOAc).



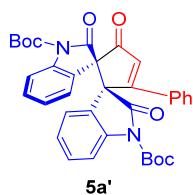
3ae, Prepared according to the general procedure in 0.1 mmol scale, 46% yield, 36 mg, white solid, m.p.: 89-91°C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.74 (s, 1H), 7.64 (d, $J = 8.4$ Hz, 1H), 7.44-7.39 (m, 3H), 7.36-7.33 (m, 1H), 6.97 (d, $J = 8.8$ Hz, 2H), 6.68 (d, $J = 8.8$ Hz, 2H), 4.87 (t, $J = 10.4$ Hz, 1H), 3.72 (s, 3H), 3.62 (dd, $J = 19.6, 11.6$ Hz, 1H), 3.23 (dd, $J = 19.6, 11.6$ Hz, 1H), 1.69 (s, 9H), 1.55 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃): δ 205.4, 172.9, 169.8, 159.2, 148.0, 147.8, 139.8, 139.4, 133.1, 132.8, 129.6, 129.1, 126.4, 125.8, 125.6, 123.9, 118.2, 117.9, 116.7, 116.5, 113.8, 85.9, 85.3, 69.6, 65.0, 55.1, 45.9, 40.6, 28.0, 27.9; **HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for C₃₆H₃₄Br₂N₂NaO₈⁺ 803.0575; Found 803.0574. **HPLC:** CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 4.9 min (major), 7.0 min (minor), 62% ee. **Optical rotation:** $[\alpha]^{25}_D = -69$ ($c = 1.0$ in EtOAc).



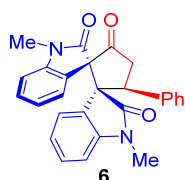
3af, Prepared according to the general procedure in 0.1 mmol scale, 63% yield, 49 mg, white solid, m.p.: 82-83°C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.65 (d, J = 8.8 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 1.6 Hz, 1H), 7.41-7.37 (m, 2H), 7.34 (d, J = 1.6 Hz, 1H), 7.28-7.25 (m, 2H), 7.20 (d, J = 7.2 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 3.66-3.57 (m, 1H), 3.12 (dd, J = 18.8, 9.6 Hz, 1H), 2.91 (dd, J = 19.2, 10.4 Hz, 1H), 2.685-2.612 (m, 1H), 2.587-2.511 (m, 1H), 1.80-1.70 (m, 1H), 1.65 (s, 9H), 1.64 (s, 9H), 1.44-1.35 (m, 1H); **¹³C NMR** (150 MHz, CDCl₃): δ 205.7, 173.5, 169.2, 148.2, 147.99, 140.8, 139.8, 139.6, 133.1, 132.9, 128.5, 128.3, 126.3, 125.9, 123.6, 118.2, 118.0, 116.8, 116.5, 85.8, 85.7, 69.7, 63.1, 41.6, 40.8, 34.8, 31.5, 28.0; **HRMS (ESI) m/z**: [M+Na]⁺ Calcd for C₃₇H₃₆Br₂N₂NaO₇⁺ 803.0761; Found 803.0779. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 4.2 min (minor), 5.3 min (major), 57% ee. **Optical rotation**: [α]_D²⁵ = -48 (c = 1.0 in EtOAc).



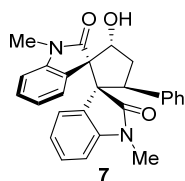
5a+5a', Prepared according to the general procedure in 0.1 mmol scale, 68% yield, 40 mg, **5a**: white solid, m.p. 107-108 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **5a**: **¹H NMR** (400 MHz, CDCl₃) δ 7.76 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.39-7.30 (m, 3H), 7.26-7.19 (m, 5H), 7.16-7.10 (m, 3H), 6.98 (t, J = 8.0 Hz, 1H), 1.58 (s, 9H), 1.51 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): 196.6, 172.0, 169.2, 168.6, 148.3, 148.1, 141.1, 139.6, 133.3, 131.5, 131.1, 130.3, 130.2, 128.8, 127.8, 126.9, 126.2, 124.8, 124.7, 123.1, 120.8, 115.1, 114.8, 85.1, 84.6, 72.1, 66.8, 28.0, 27.9; **HRMS (ESI) m/z**: [M+H]⁺ Calcd for C₃₅H₃₃N₂O₇⁺ 593.2282; Found 593.2280. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 14.3 min (major), 45.0 min (minor), >99:1 er. **Optical rotation**: [α]_D²⁵ = +23 (c = 1.0 in EtOAc).



5a': white solid, m.p. 95-97 °C, ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.31-7.17 (m, 5H), 7.11 (d, J = 8.0 Hz, 2H), 7.04 (s, 1H), 6.91-6.82 (m, 3H), 6.71 (d, J = 8.0 Hz, 1H), 1.51 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): 196.1, 170.1, 169.3, 167.5, 148.8, 148.7, 140.8, 139.8, 131.5, 131.3, 130.4, 130.38, 130.1, 129.1, 127.7, 125.0, 124.8, 124.5, 124.3, 123.7, 122.2, 115.7, 115.2, 84.8, 84.6, 28.0, 27.9; **HRMS (ESI) m/z**: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{33}\text{N}_2\text{O}_7^+$ 593.2282; Found 593.2278. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 20.7 min (major), 48.1 min (minor), 34% ee. **Optical rotation**: $[\alpha]_D^{25}$ = -8 (c = 1.0 in EtOAc).

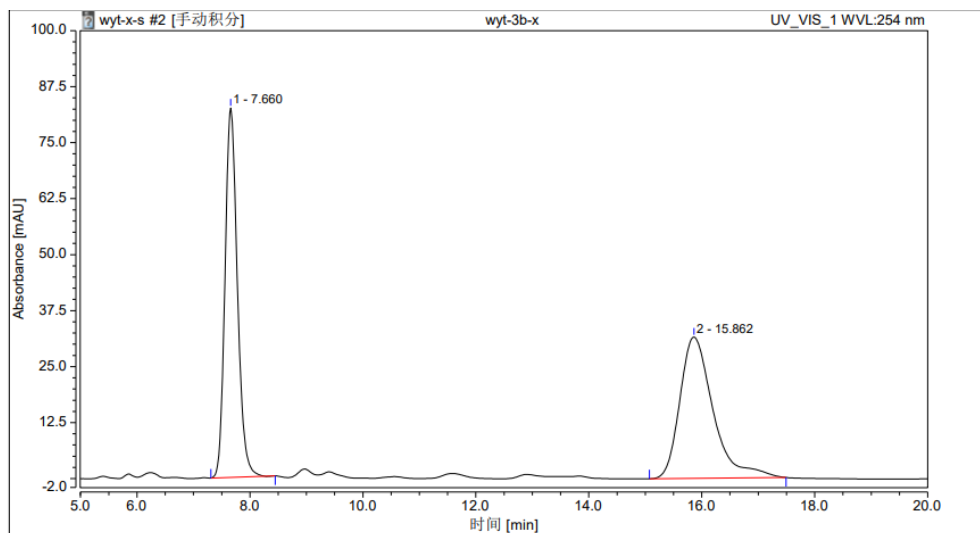
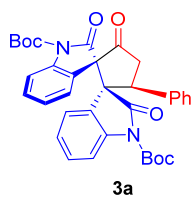


6, Prepared according to the general procedure in 0.2 mmol scale, 71% yield, 60 mg, white solid, m.p. 231-233 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 7.2 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.17-7.03 (m, 6H), 7.01-6.93 (m, 2H), 6.64 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 7.6 Hz, 1H), 5.15 (t, J = 10.8 Hz, 1H), 3.74 (dd, J_I = 19.2 Hz, J_I = 12.0 Hz, 1H), 3.19 (dd, J_I = 19.2 Hz, J_I = 10.0 Hz, 1H), 3.15 (s, 1H), 2.75 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 208.1, 175.0, 171.6, 144.4, 143.9, 135.3, 129.4, 129.0, 128.2, 127.8, 127.3, 125.9, 125.5, 124.1, 123.7, 123.2, 122.8, 108.2, 108.0, 69.3, 64.0, 45.8, 40.3, 26.3, 25.3. **HRMS (ESI) m/z**: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_3^+$ 423.1703; Found 423.1705. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 22.4 min (minor), 43.1 min (major), 92% ee. **Optical rotation**: $[\alpha]_D^{25}$ = +12 (c = 1.0 in EtOAc).

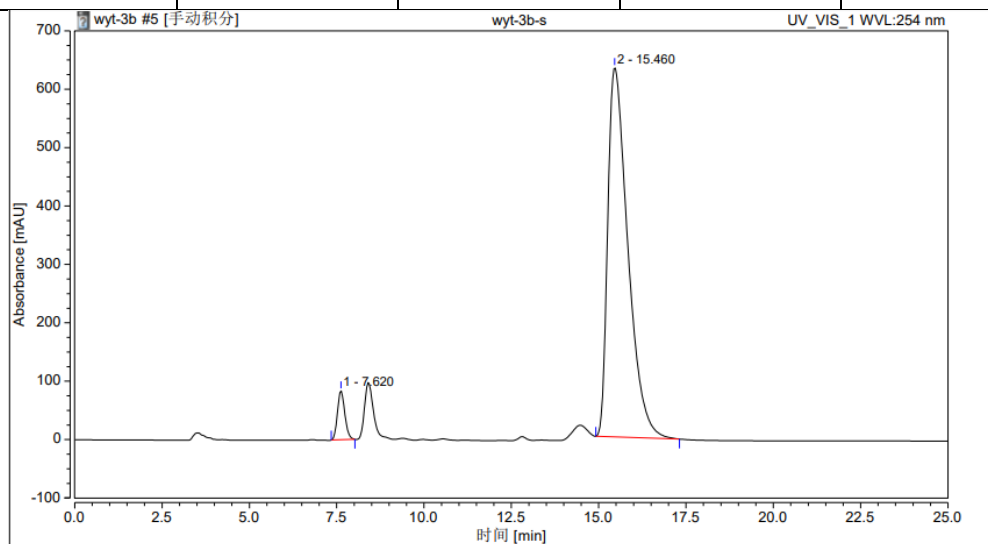


7, Prepared according to the general procedure in 0.14 mmol scale, 82% yield, 49 mg, white solid, m.p. 247-248 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.49 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.08-7.02 (m, 6H), 6.97-6.92 (m, 2H), 6.61 (d, J = 8.0 Hz, 1H), 6.32 (d, J = 8.0 Hz, 1H), 5.76-5.70 (m, 1H), 5.01 (t, J = 10.4 Hz, 1H), 3.49-3.41 (m, 1H), 3.19 (s, 1H), 2.72 (s, 1H), 2.61-2.53 (m, 1H), 2.24 (d, J = 9.2 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 175.9, 175.4, 144.1, 143.6, 137.4, 128.7, 128.6, 128.5, 127.6, 126.8, 126.1, 124.3, 123.6, 122.8, 122.4, 107.9, 107.6, 66.7, 65.6, 48.7, 37.4, 26.0, 25.4; **HRMS (ESI) m/z**: [M+H]⁺ Calcd for C₂₇H₂₅N₂O₃⁺ 425.1860; Found 425.1848; **HRMS (ESI) m/z**: [M+H]⁺ Calcd for C₂₇H₂₅N₂O₃⁺ 425.1860; Found 425.1848. **HPLC**: CHIRALPAK IC, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 38.6 min (major), 62.3 min (minor), 82% ee. **Optical rotation**: $[\alpha]_D^{25}$ = -11 (c = 1.0 in EtOAc).

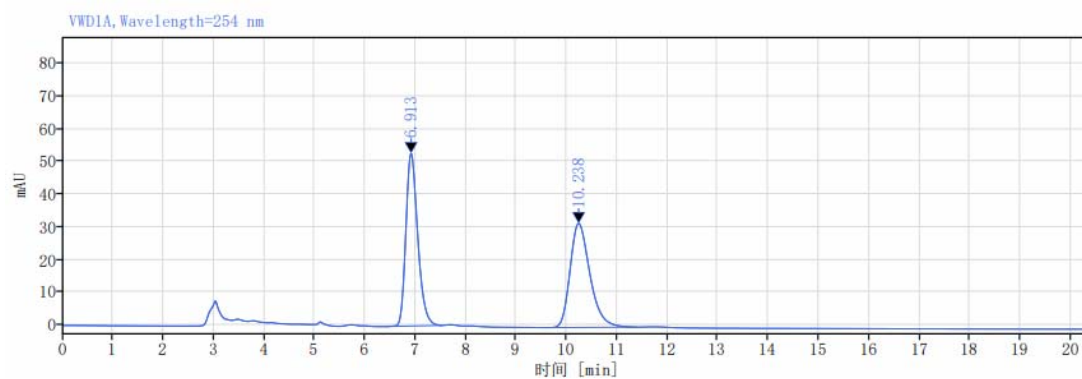
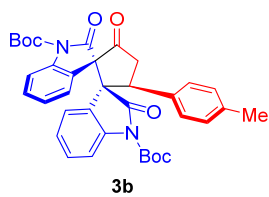
Part 5: HPLC spectra for all the products



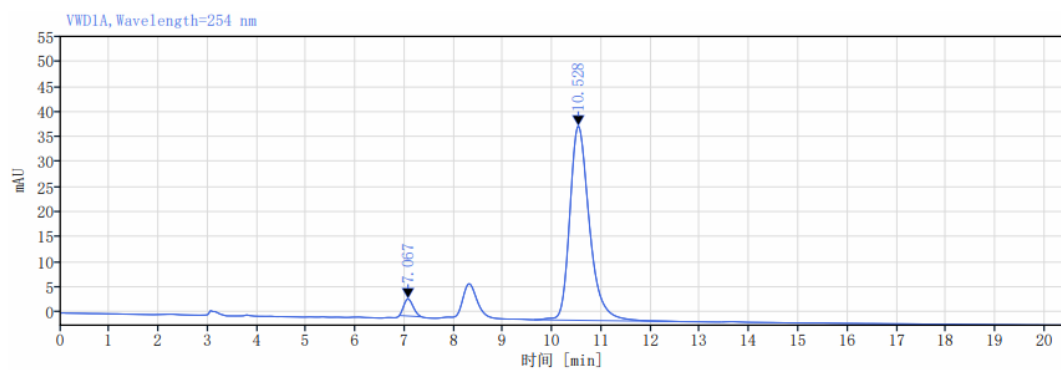
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.660	20.892	82.483	49.25
2	15.862	21.530	31.563	50.75
Total		42.422	114.046	100



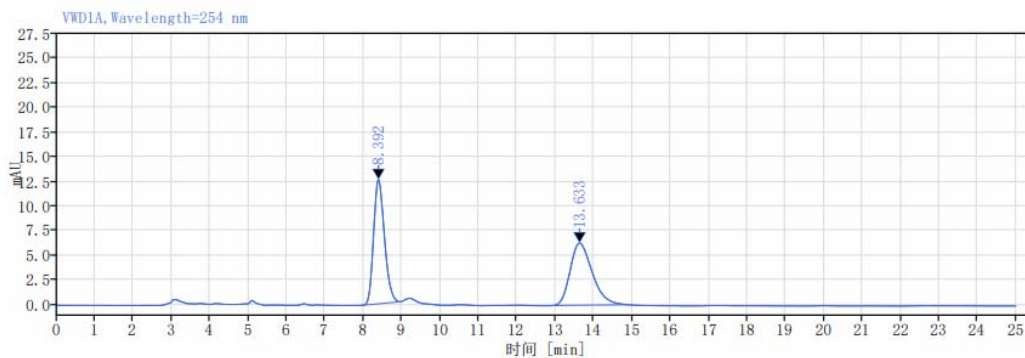
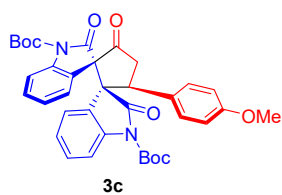
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.620	1.823	7.314	4.67
2	15.460	37.252	57.003	95.33
Total		39.074	64.317	100



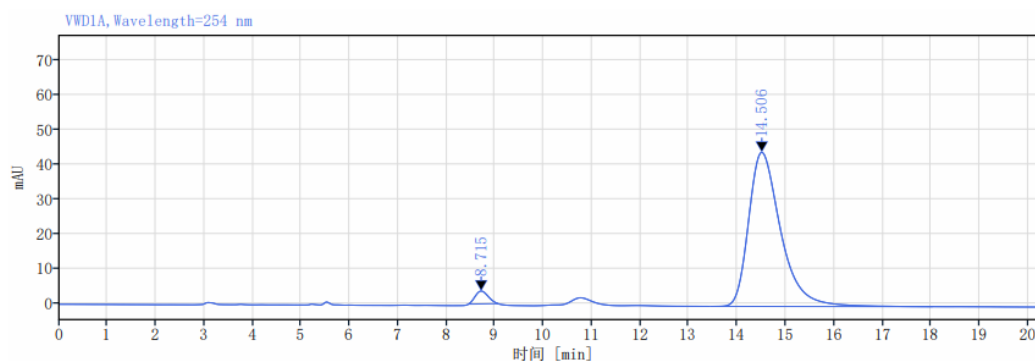
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.913	863.05	52.85	49.79
2	10.238	870.22	31.84	50.21
Total		1733.27		100



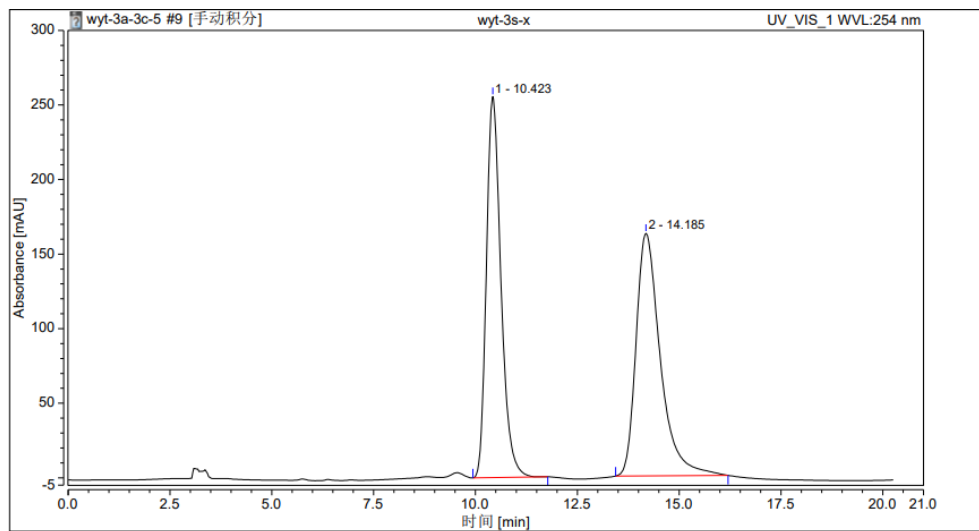
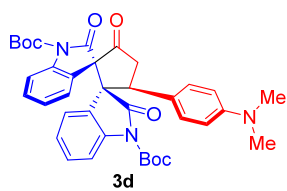
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.067	44.82	3.38	4.00
2	10.528	1075.85	38.76	96.00
Total		1120.67		100



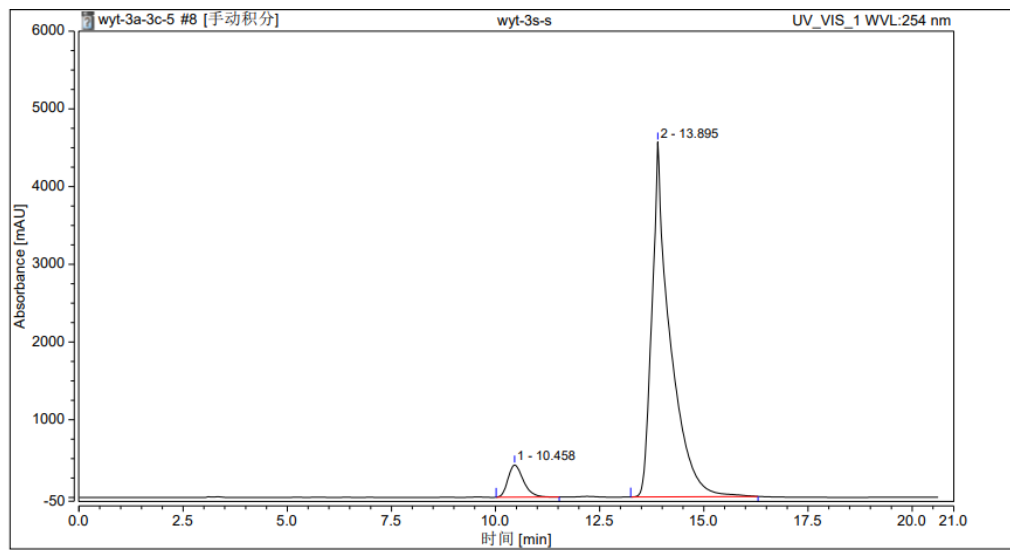
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.392	246.78	12.58	49.53
2	13.633	251.44	6.30	50.47
Total		498.22		100



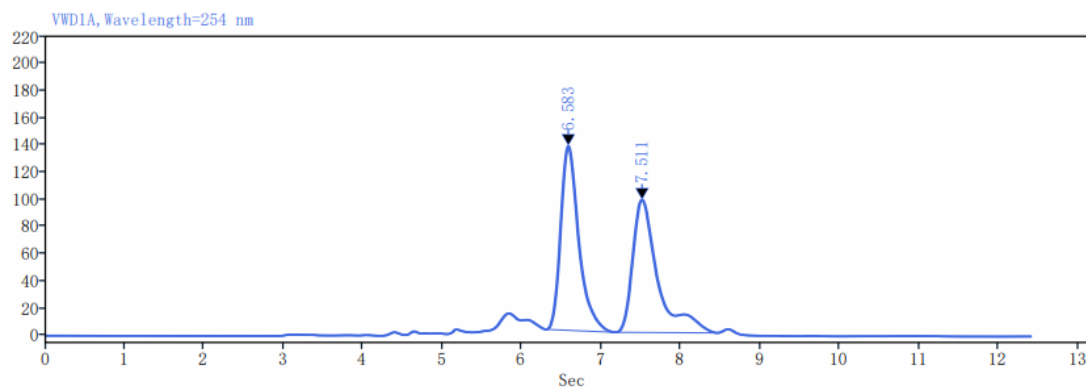
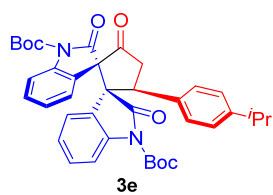
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.715	68.83	3.70	3.27
2	14.506	2036.30	44.34	96.73
Total		2106.12		100



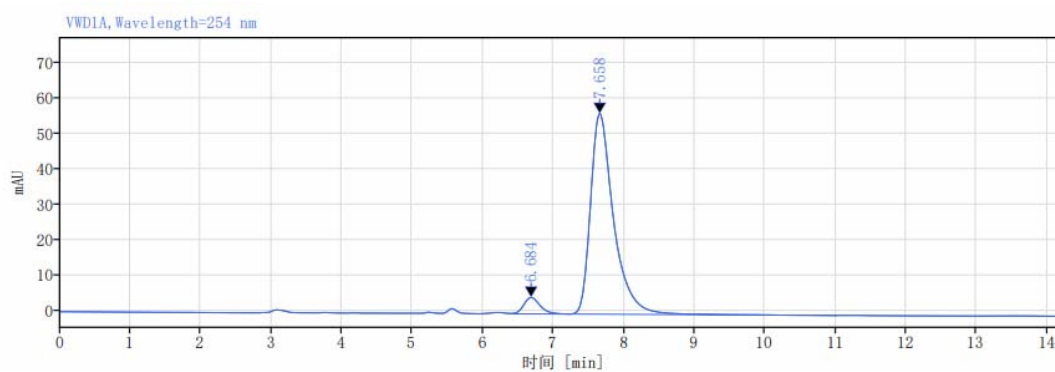
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	10.423	105.886	255.507	48.55
2	14.185	112.194	162.658	51.45
Total		218.080	418.164	100



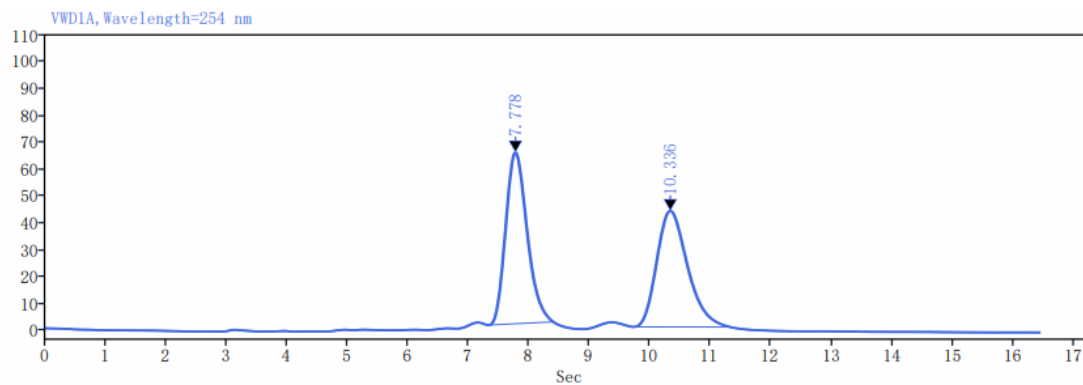
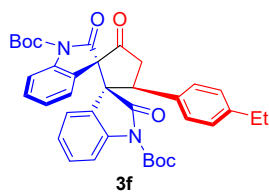
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	10.458	178.436	415.316	7.22
2	13.895	2294.1110	4566.961	92.78
Total		2472.547	4982.277	100



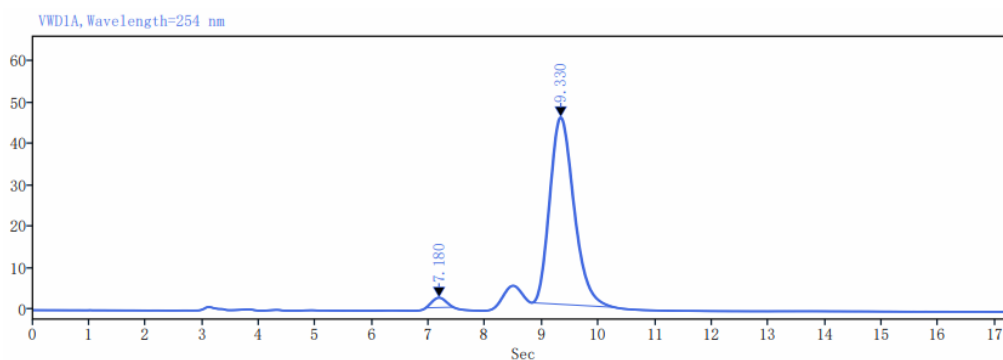
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.583	2141.54	135.65	50.06
2	7.511	2136.11	97.61	49.94
Total		4277.64	233.26	100



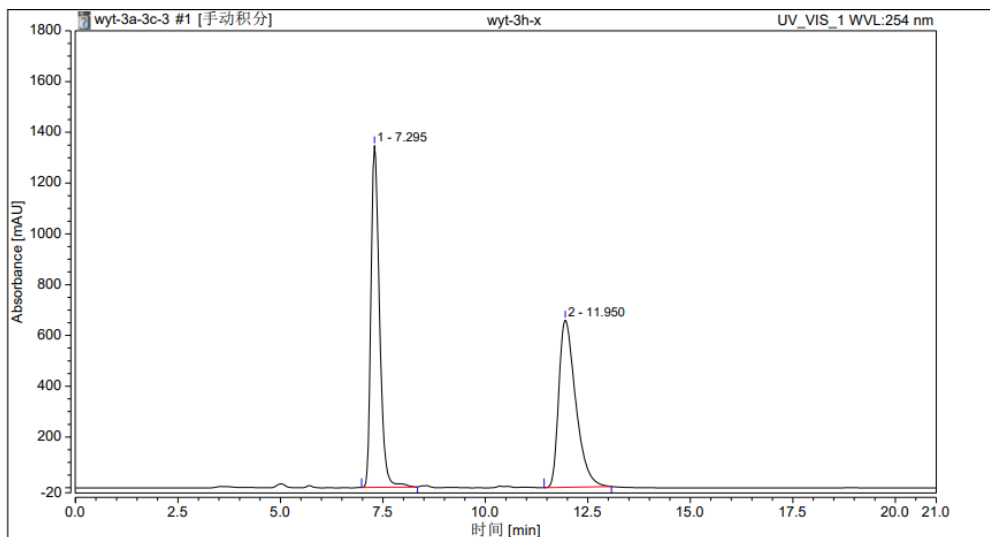
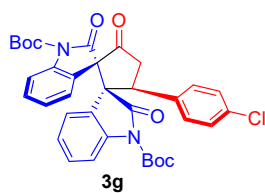
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.684	74.23	4.63	5.45
2	7.658	1288.88	56.58	94.55
Total		1363.10		100



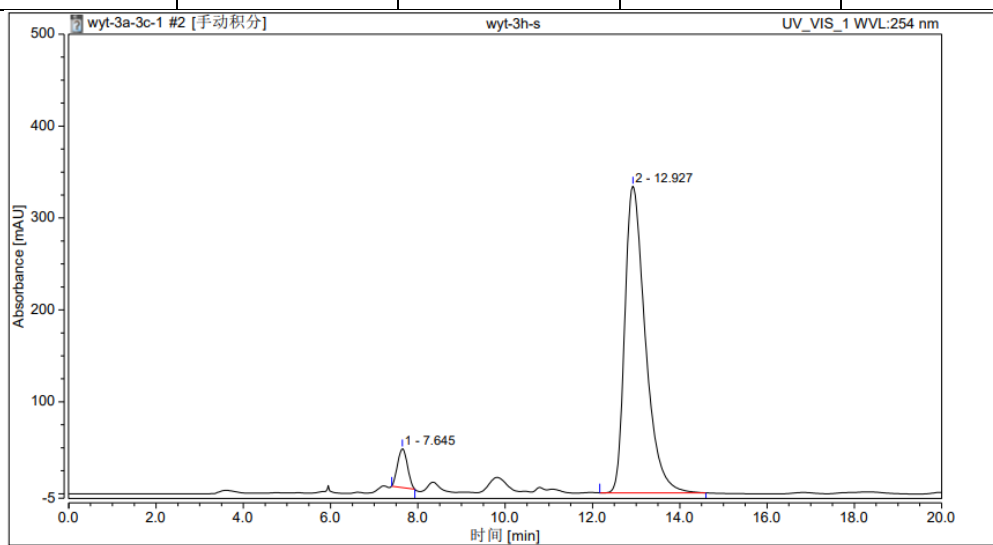
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.778	1568.52	63.69	50.78
2	10.336	1520.56	43.16	49.22
Total		3089.07	106.85	100



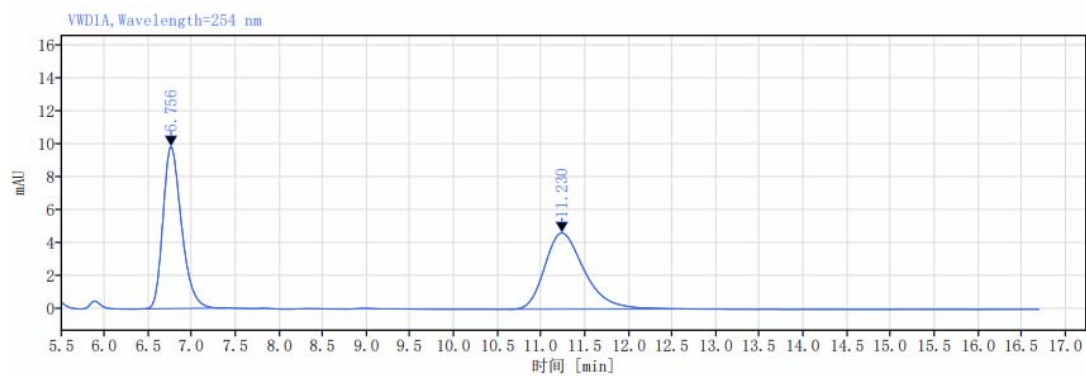
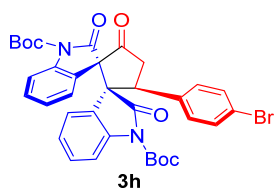
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.180	38.99	2.37	2.82
2	9.330	1343.99	45.18	97.18
Total		1382.98	47.55	100



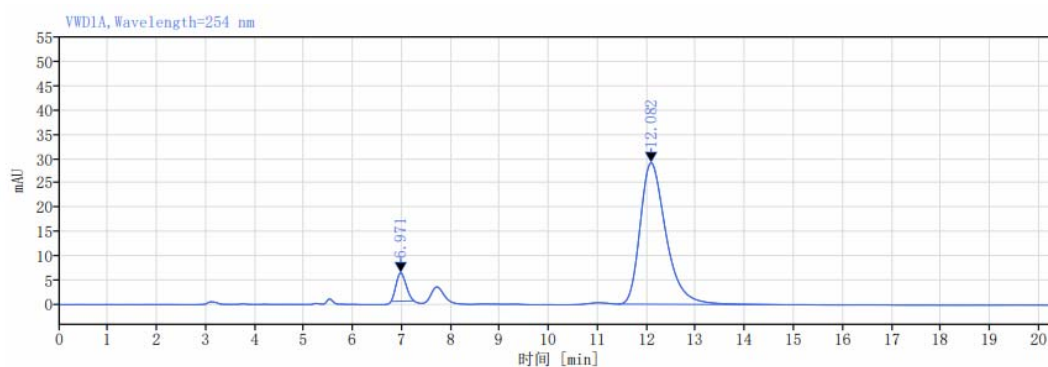
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.295	324.873	1345.543	50.72
2	11.950	315.681	658.909	49.28
Total		640.554	2004.452	100



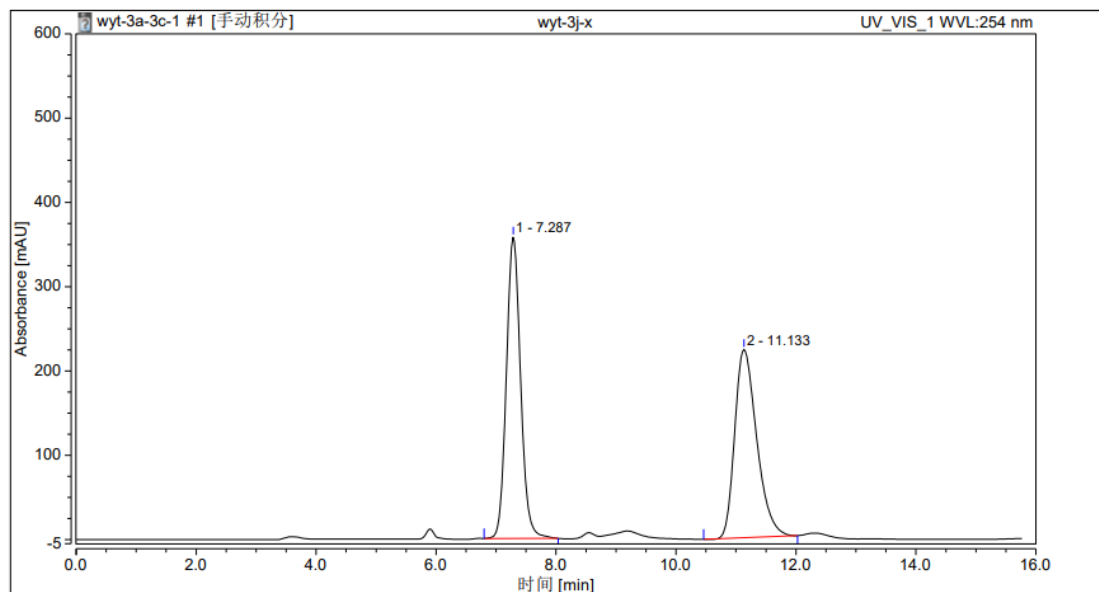
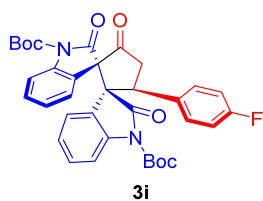
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.645	11.862	43.793	6.17
2	12.927	180.235	333.166	93.83
Total		192.097	376.958	100



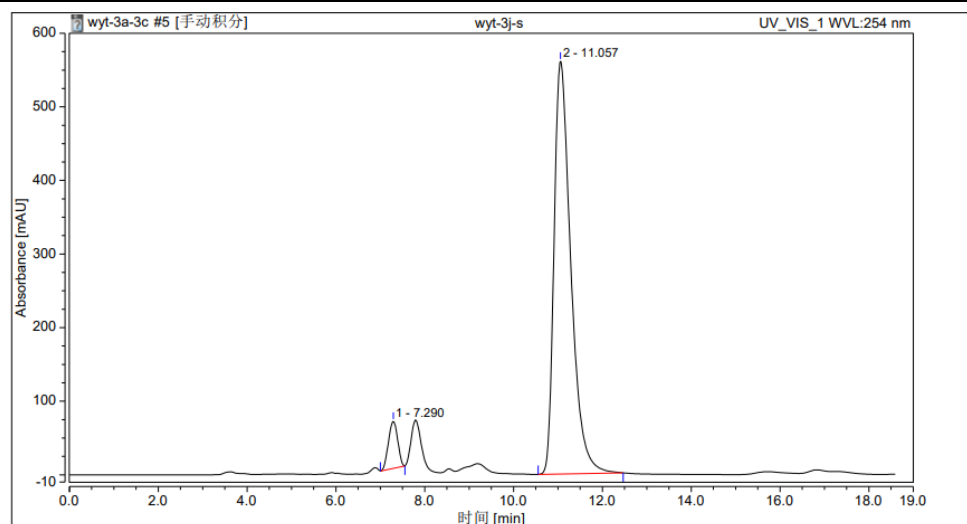
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.756	145.30	9.84	49.85
2	11.230	146.18	4.63	50.15
Total		291.48		100



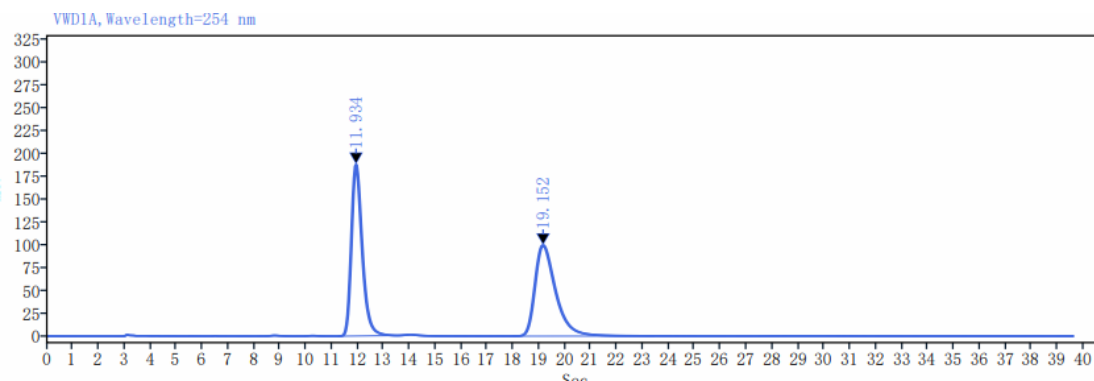
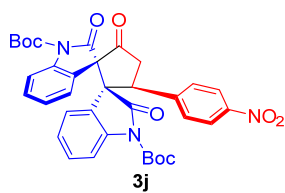
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.971	81.53	5.81	7.09
2	12.082	1067.79	29.19	92.91
Total		1149.32		100



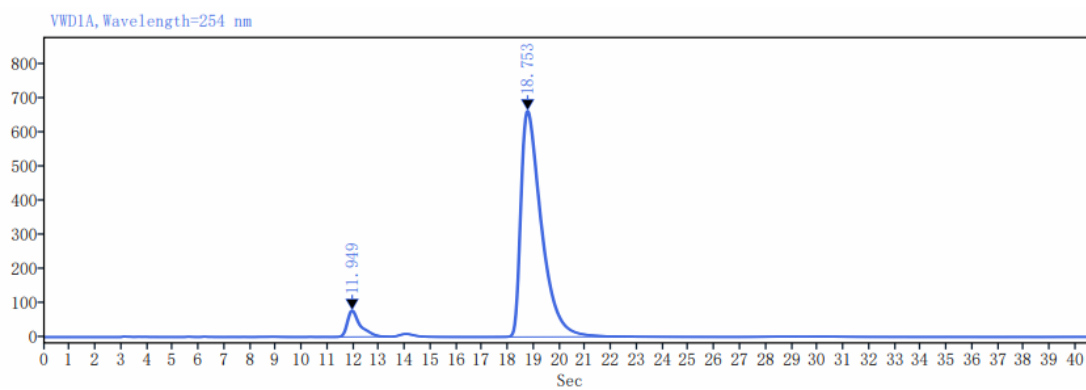
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.287	97.916	357.272	50.82
2	11.133	94.768	223.466	49.18
Total		192.684	580.738	100



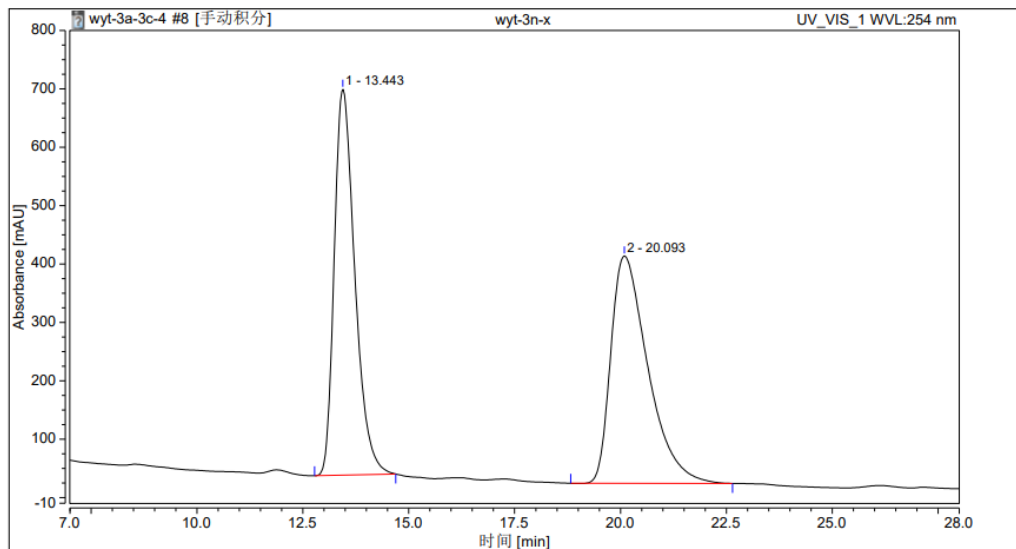
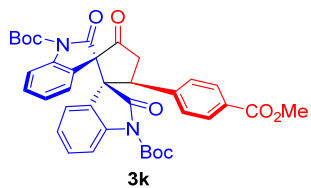
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.290	14.892	63.110	5.71
2	11.057	246.035	561.074	94.29
Total		260.926	624.184	100



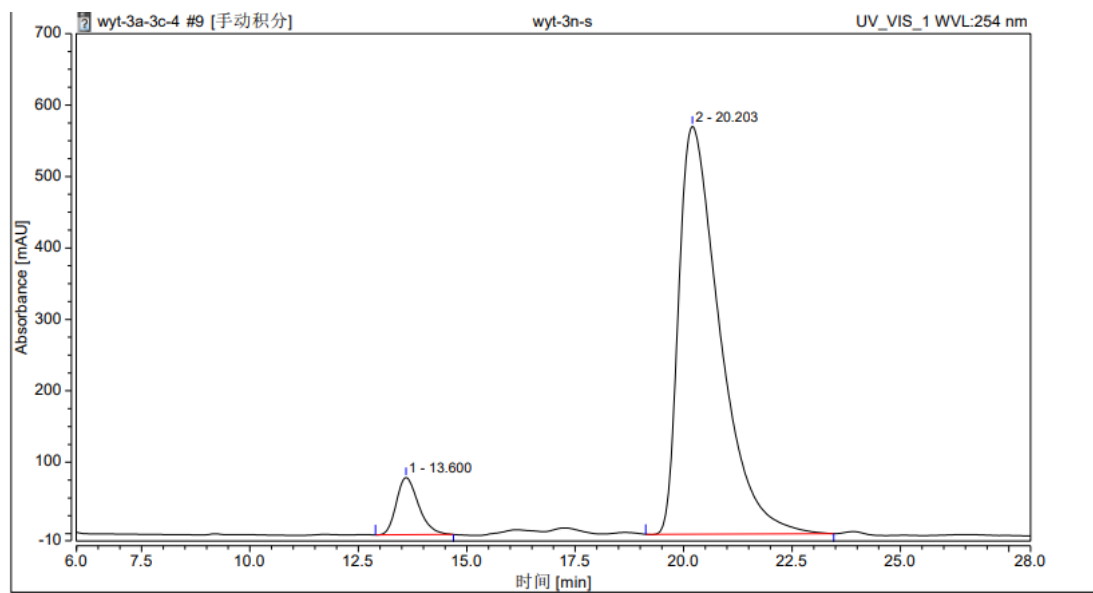
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	11.934	5489.91	188.68	49.70
2	19.152	5556.19	100.02	50.30
Total		11046	288.70	100



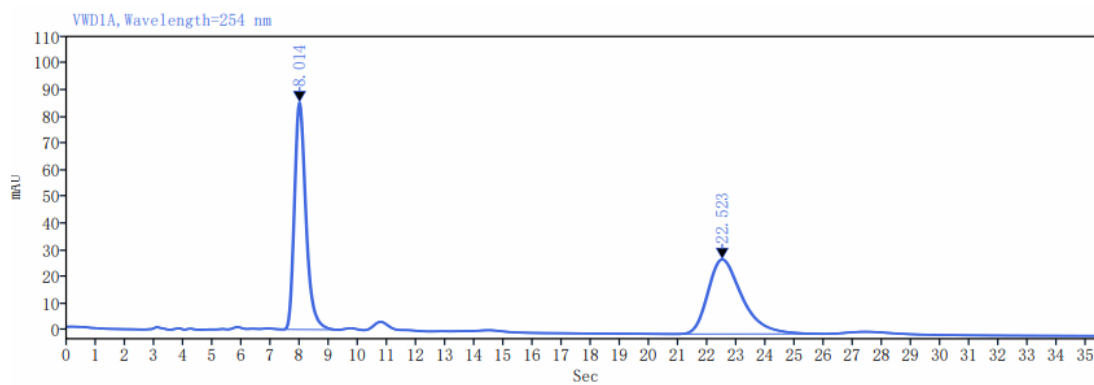
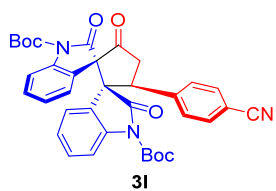
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	11.949	2696.17	77.55	6.84
2	18.753	36717.06	663.89	93.16
Total		39413.06	741.44	100



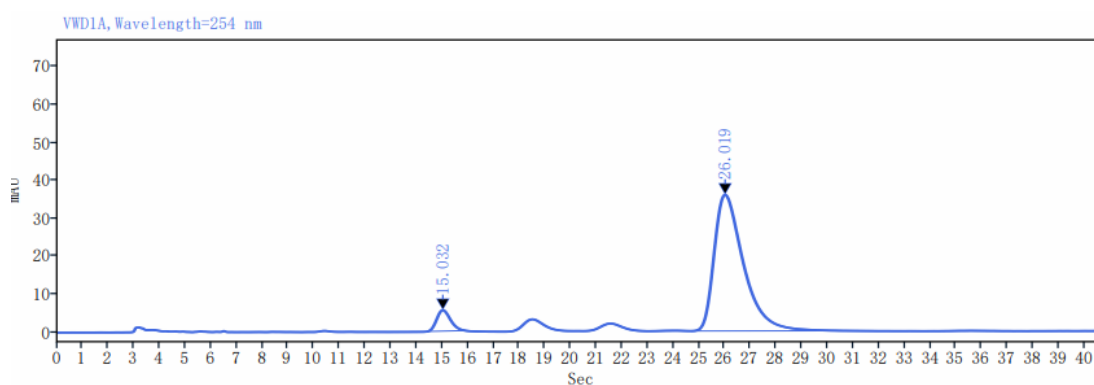
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.443	378.888	663.109	49.31
2	20.093	389.469	388.247	50.69
Total		768.358	1051.356	100



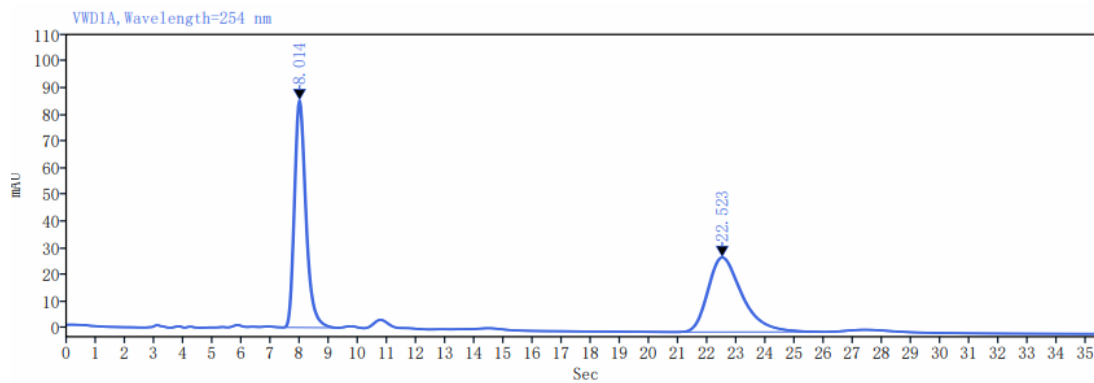
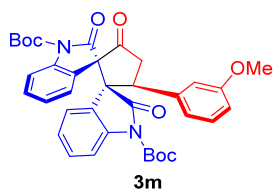
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.600	47.383	80.118	7.05
2	20.203	624.794	570.903	92.95
Total		672.177	651.021	100



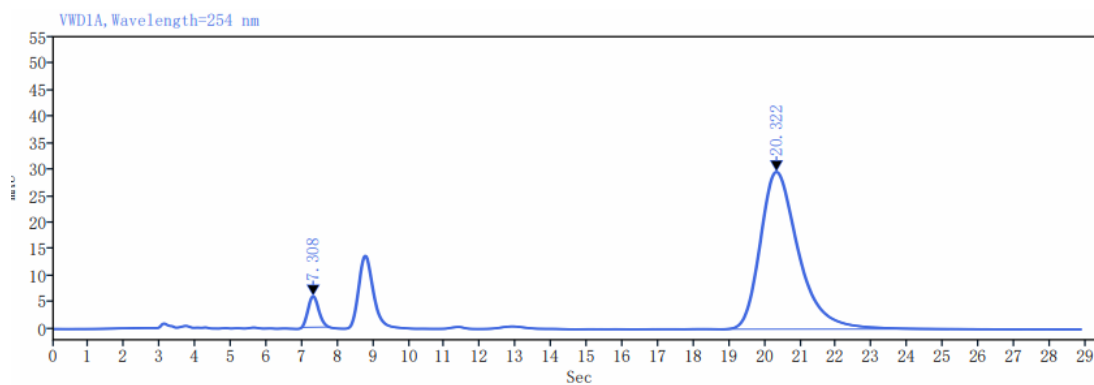
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.606	9349.65	229.44	50.07
2	26.559	9322.58	115.05	49.93
Total		18672.24	344.49	100



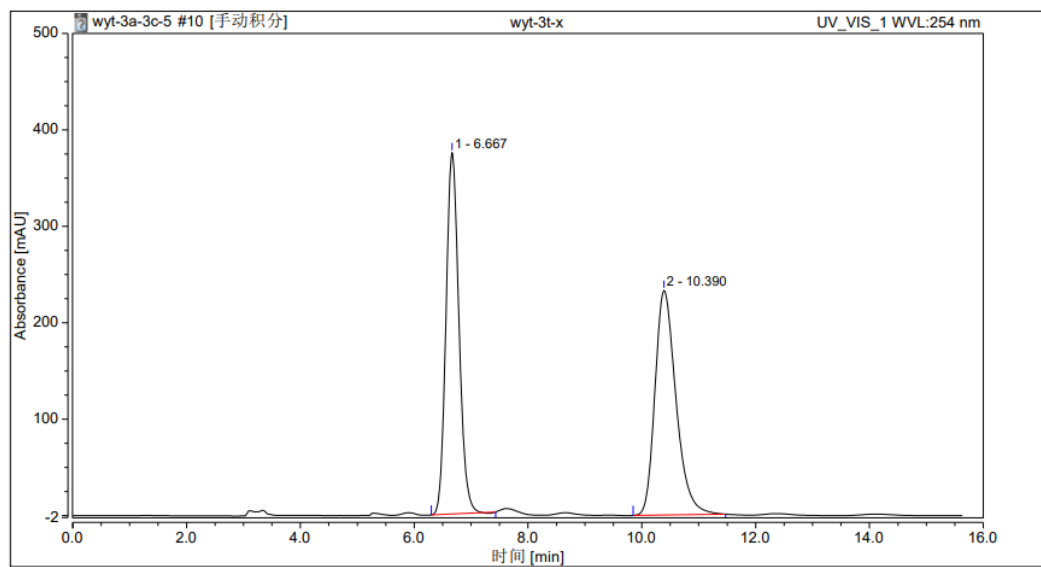
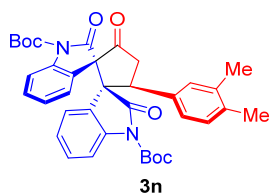
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.032	203.18	5.52	6.67
2	26.019	2843.39	35.88	93.33
Total		3046.58	41.40	100



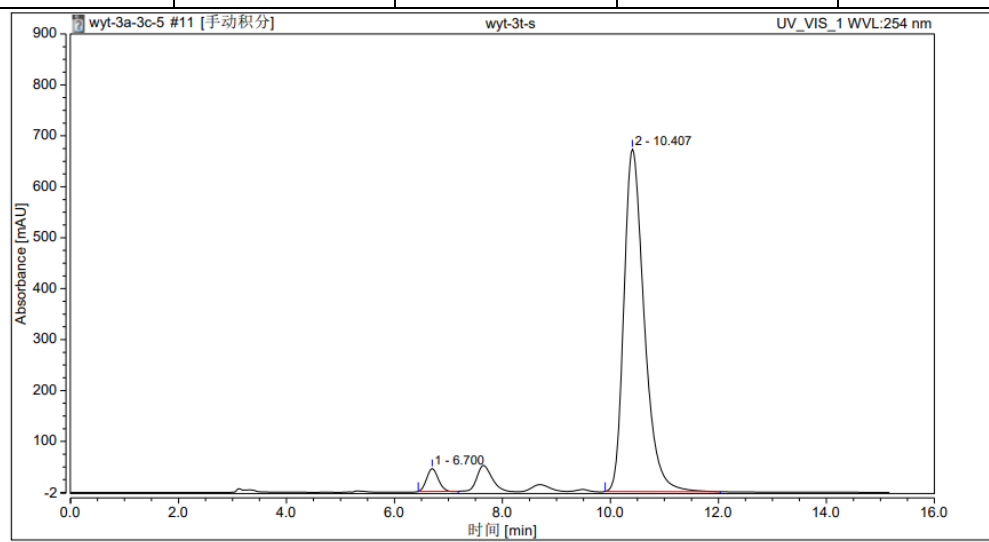
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.014	2326.75	84.95	50.61
2	22.523	2270.72	27.93	49.39
Total		4597.47	112.88	100



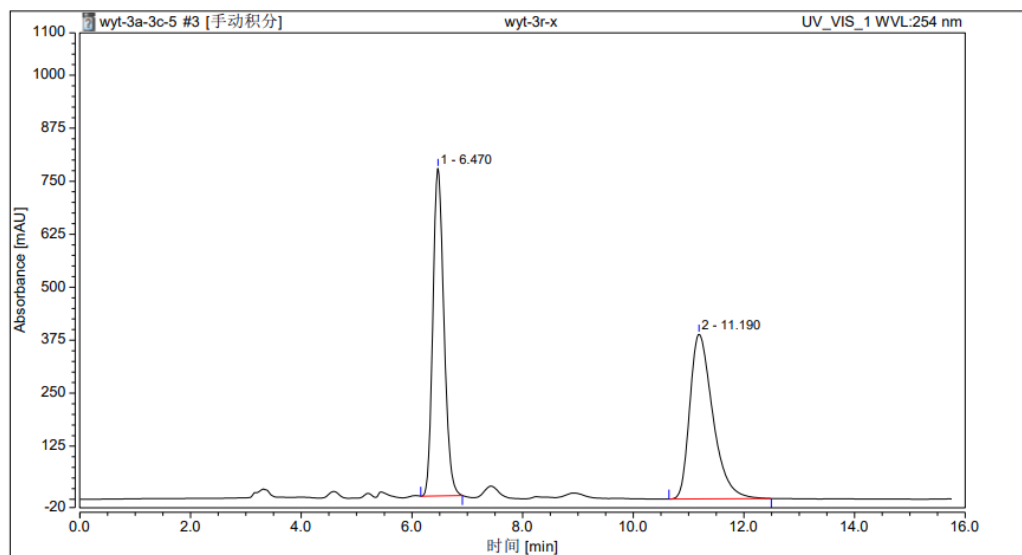
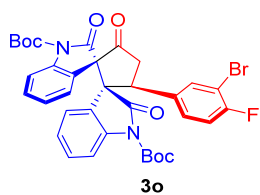
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.308	121.30	5.85	5.19
2	20.322	2214.57	29.65	94.81
Total		2335.88	35.50	100



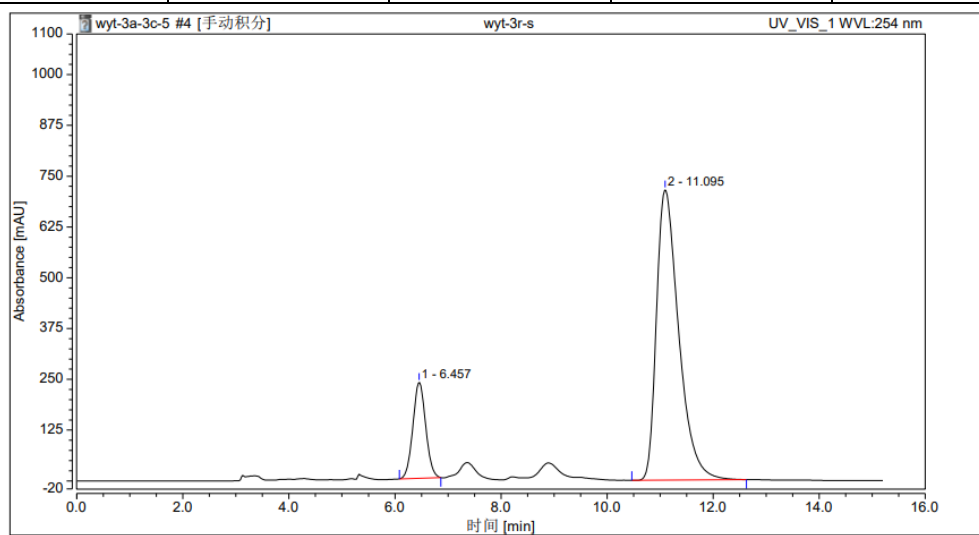
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.667	98.526	374.801	49.71
2	10.390	99.677	232.974	50.29
Total		198.203	607.776	100



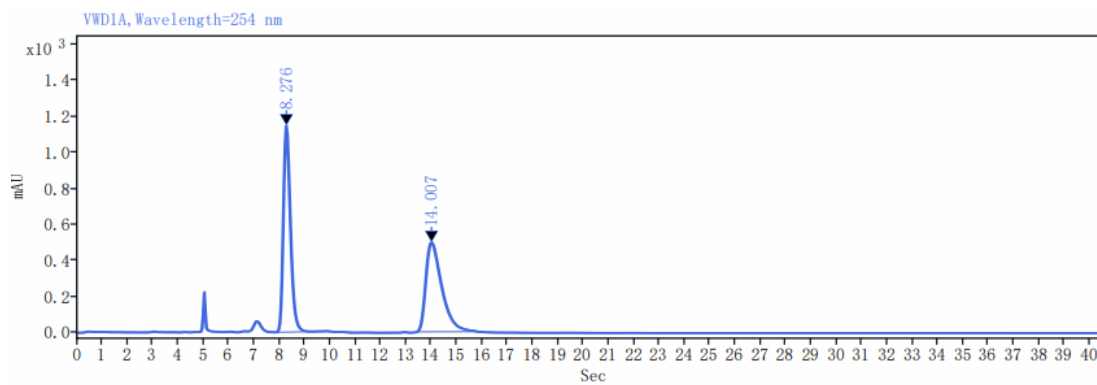
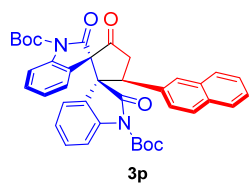
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.700	11.030	44.621	6.22
2	10.407	292.036	672.290	93.78
Total		303.066	716.911	100



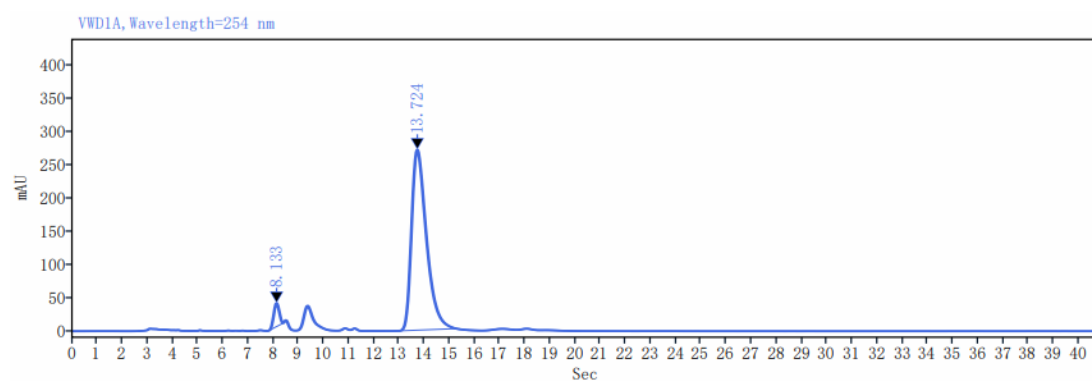
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.470	181.093	774.506	49.09
2	11.190	187.784	386.957	50.91
Total		368.876	1163.463	100



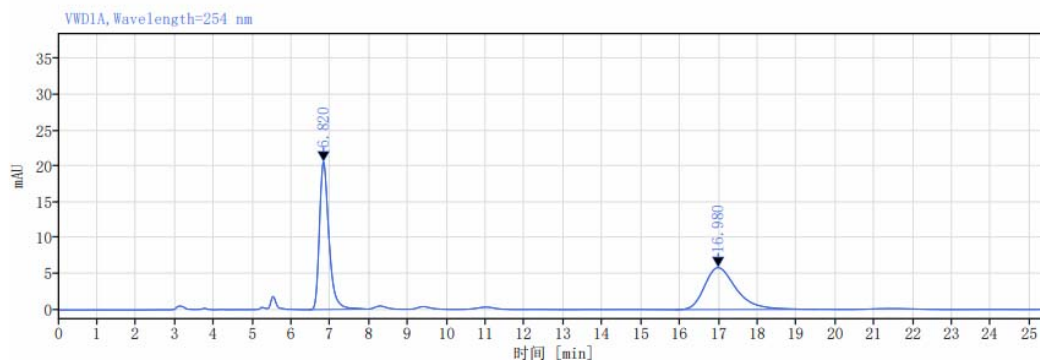
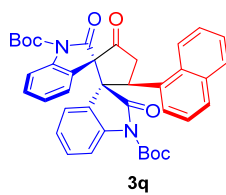
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.457	66.762	237.258	16.12
2	11.095	347.287	715.031	83.88
Total		414.049	952.289	100



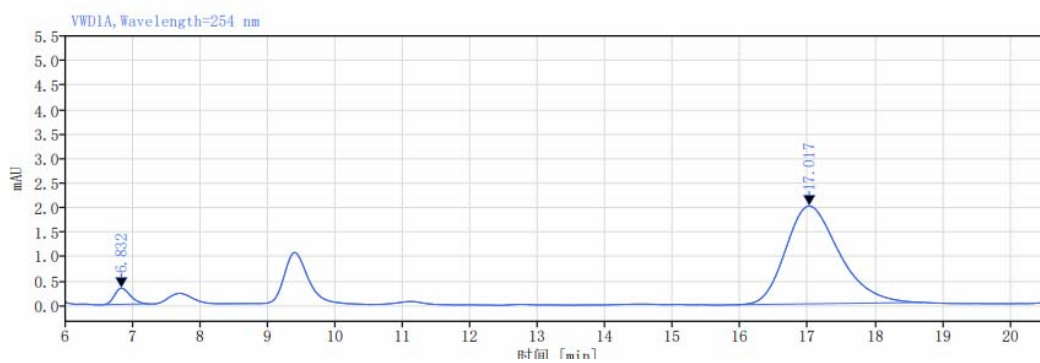
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.276	22365.94	1147.50	50.73
2	14.007	21723.49	496.88	49.27
Total		414.049	1644.38	100



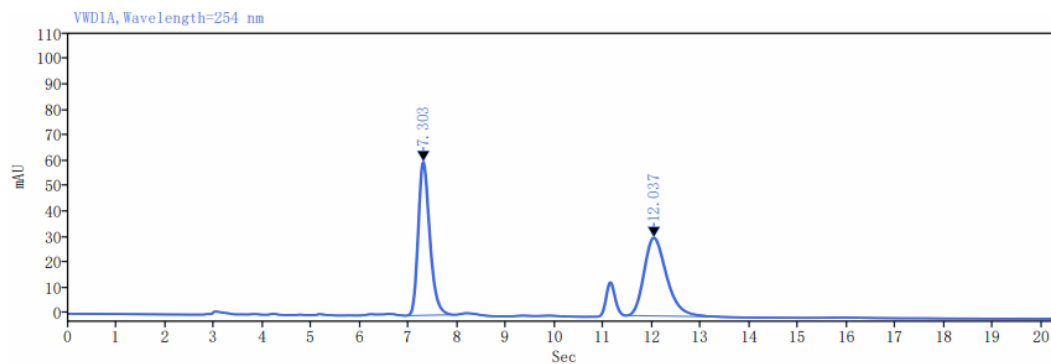
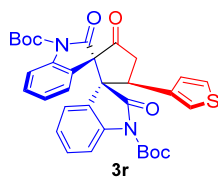
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.133	531.00	35.40	4.52
2	13.724	11224.45	272.32	95.48
Total		11755.45	307.72	100



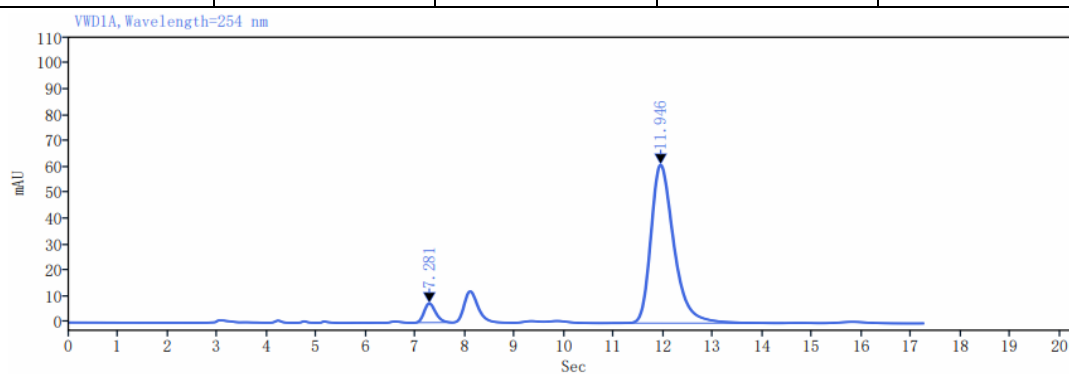
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.820	349.20	20.57	51.36
2	16.980	330.73	5.85	48.64
Total		679.93		100



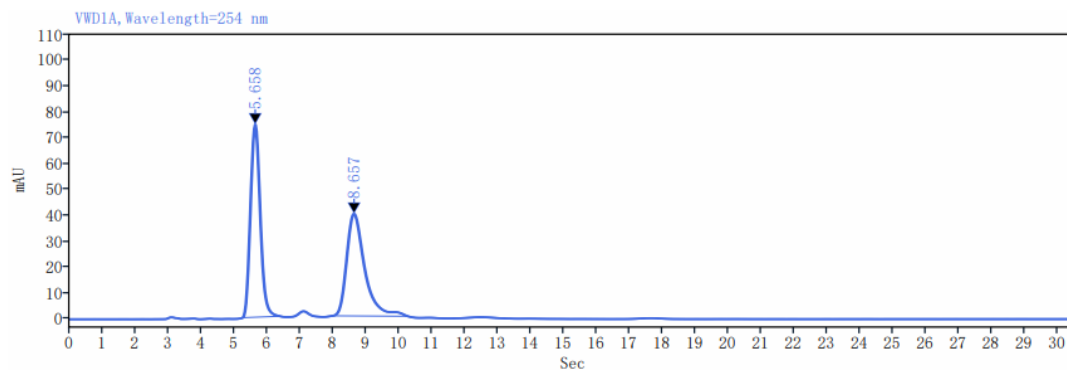
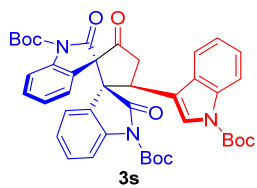
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.832	5.34	0.33	4.64
2	17.017	109.78	2.00	95.36
Total		115.12		100



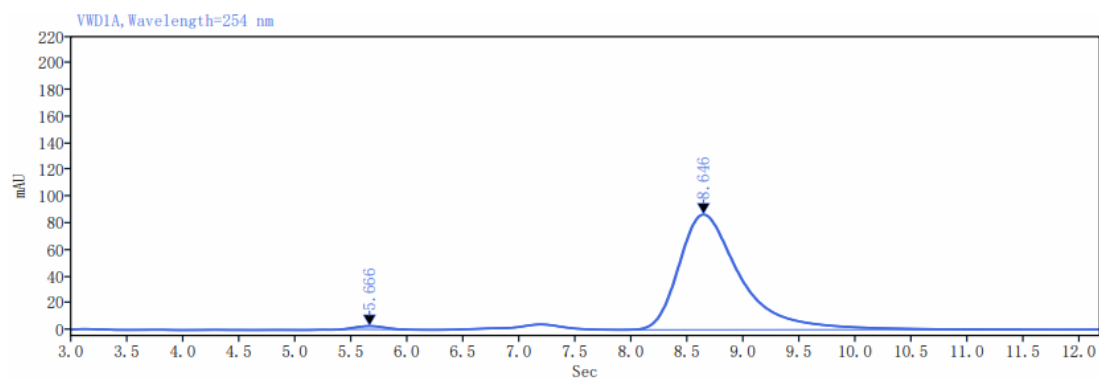
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.303	999.14	60.32	50.23
2	12.037	989.96	30.74	49.77
Total		1989.11	91.06	100



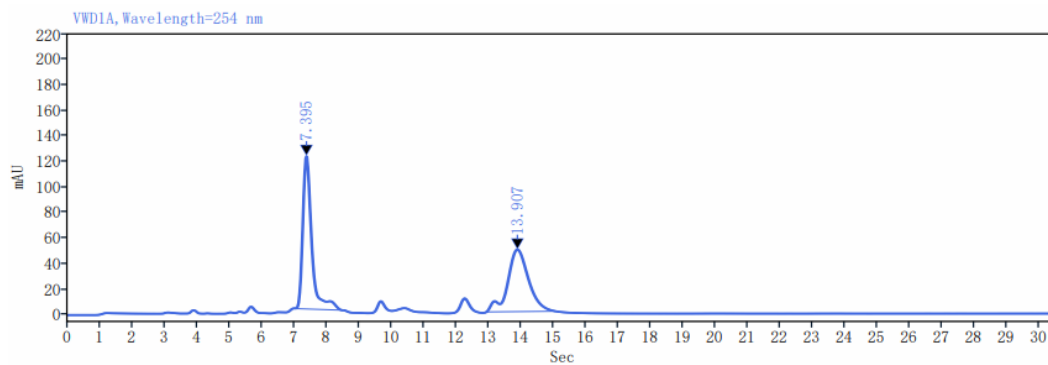
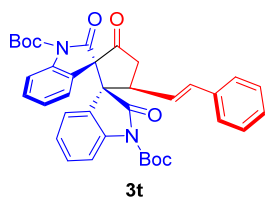
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.281	119.07	7.41	5.69
2	11.946	1971.72	61.13	94.31
Total		2090.78	68.54	100



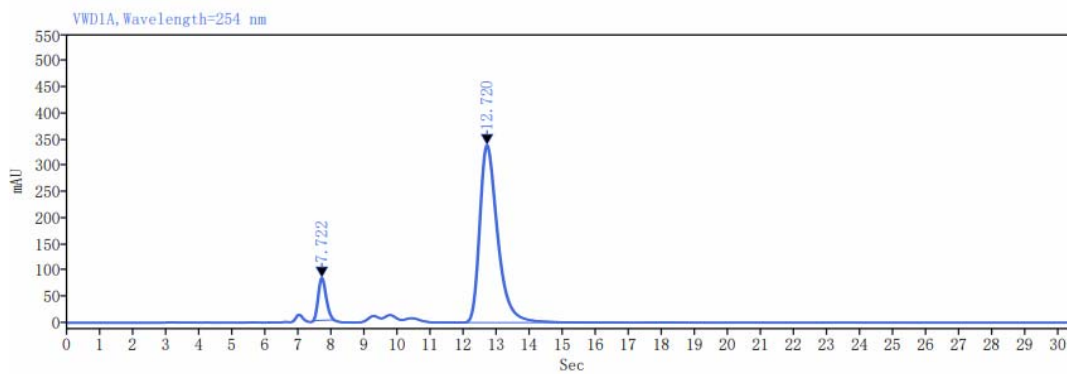
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	5.658	1539.35	74.49	50.70
2	8.657	1496.81	39.48	49.30
Total		3036.16	113.97	100



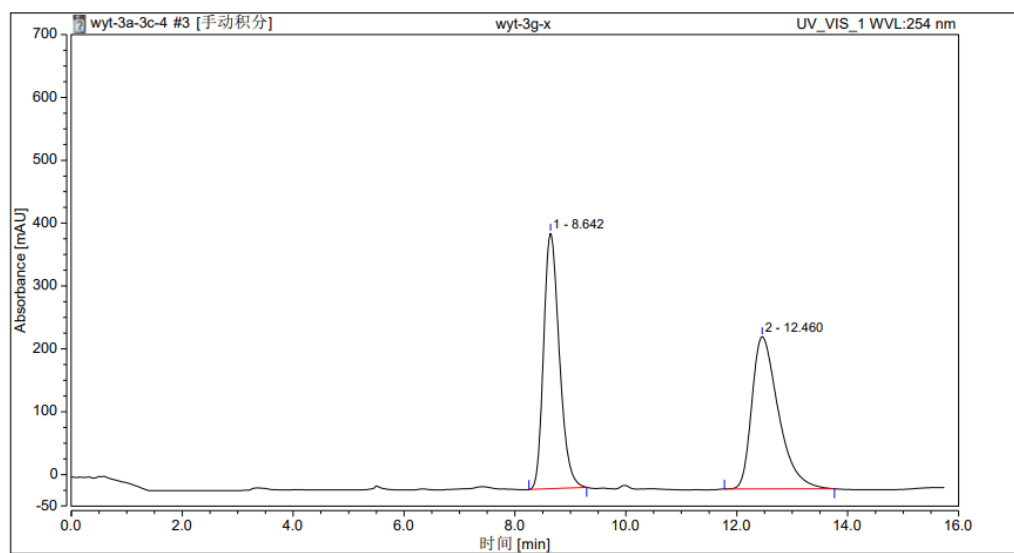
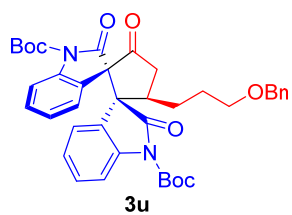
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	5.666	45.99	2.55	1.38
2	8.646	3293.73	86.41	98.62
Total		3339.73	88.96	100



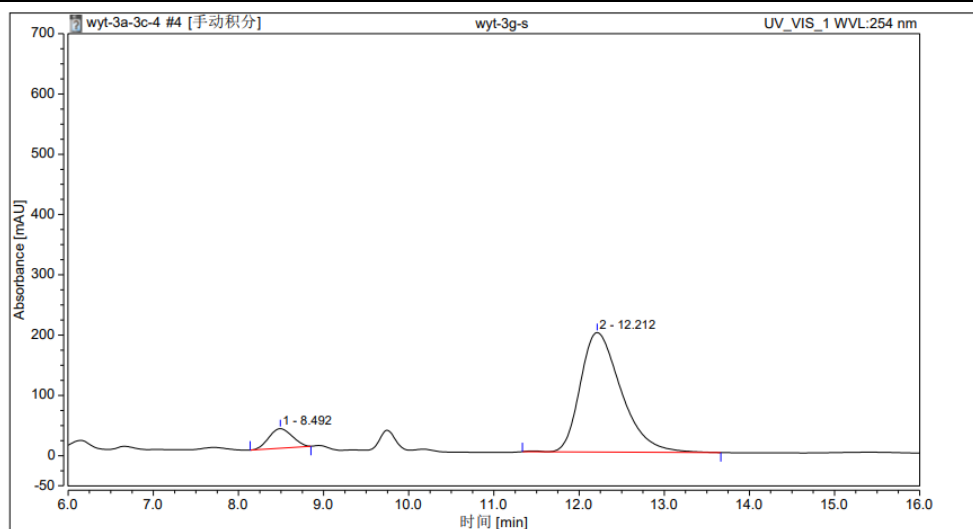
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.395	2308.56	119.90	51.51
2	13.907	2173.18	48.68	48.49
Total		4481.74		100



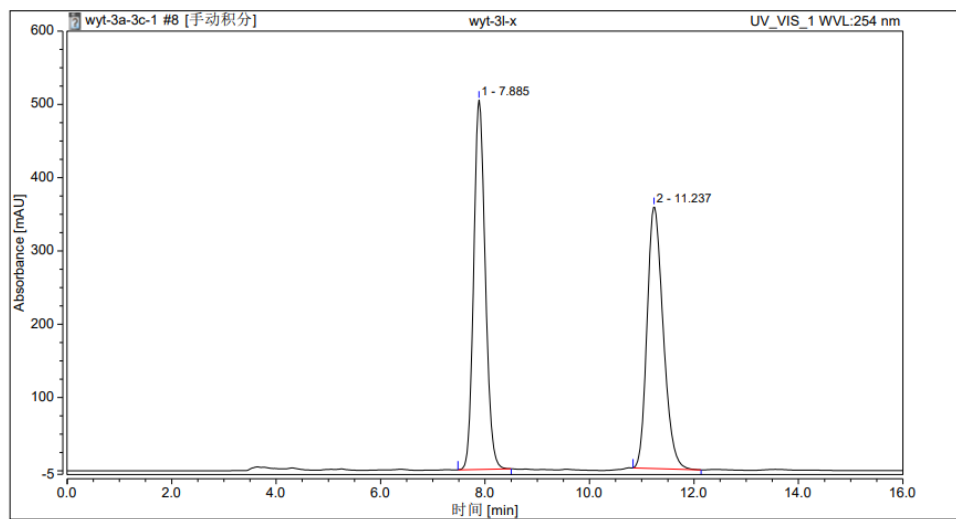
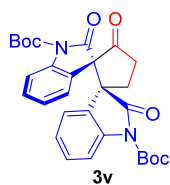
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.722	1342.21	81.09	9.51
2	12.720	12764.43	338.76	90.49
Total		14106.64		100



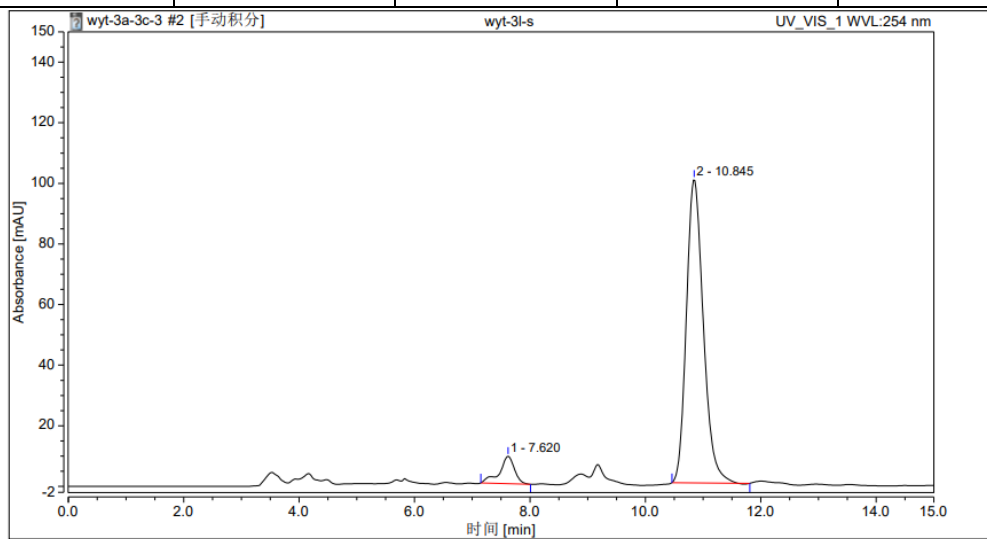
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.642	134.066	407.479	49.91
2	12.460	134.532	241.858	50.09
Total		268.598	649.337	100



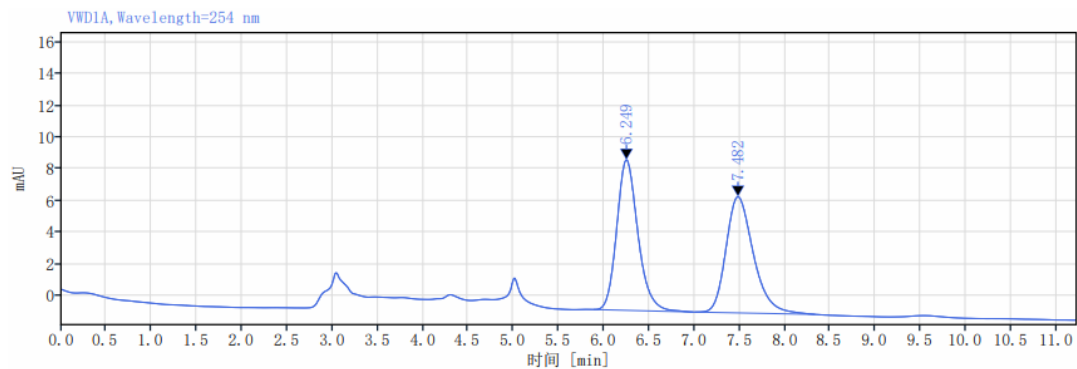
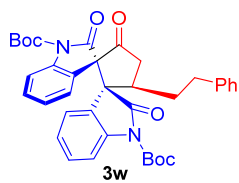
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.492	10.153	32.128	8.50
2	12.212	109.307	197.894	91.50
Total		119.460	230.022	100



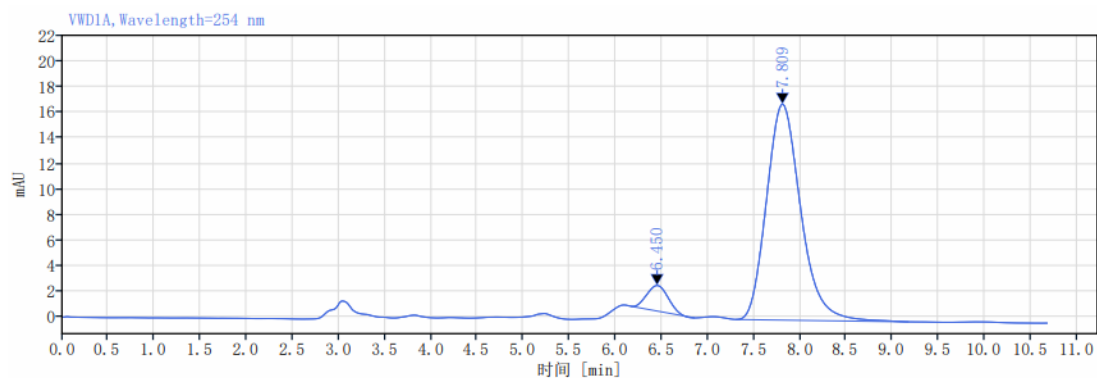
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.885	129.510	504.185	50.40
2	11.237	127.444	357.743	49.60
Total		256.960	861.929	100



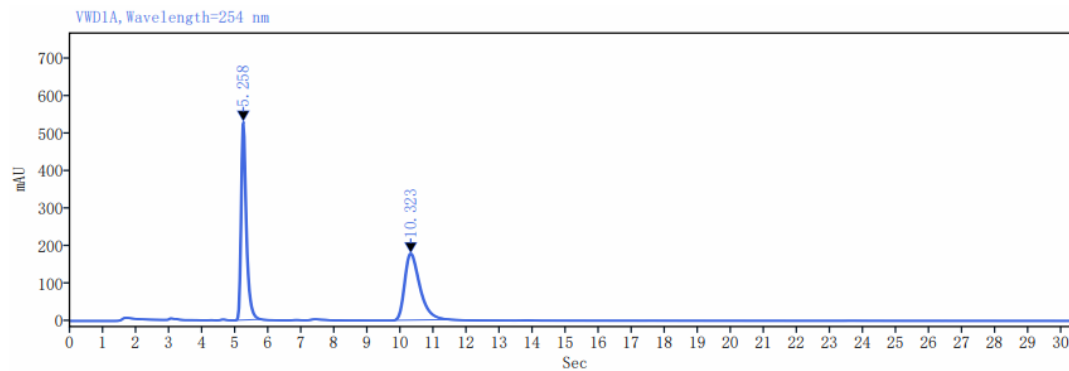
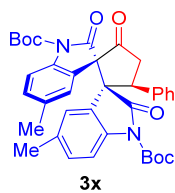
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.620	2.697	9.035	7.34
2	10.845	34.052	100.209	92.66
Total		36.750	109.244	100



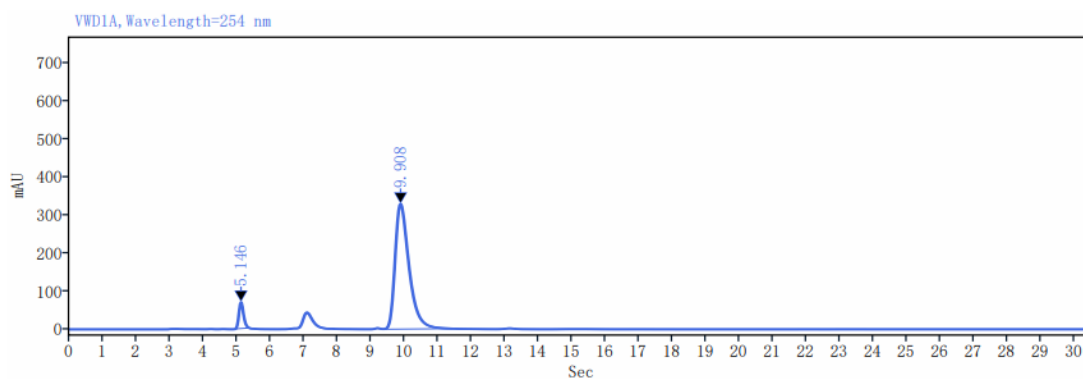
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.249	154.92	9.52	50.01
2	7.482	154.86	7.35	49.99
Total		309.78		100



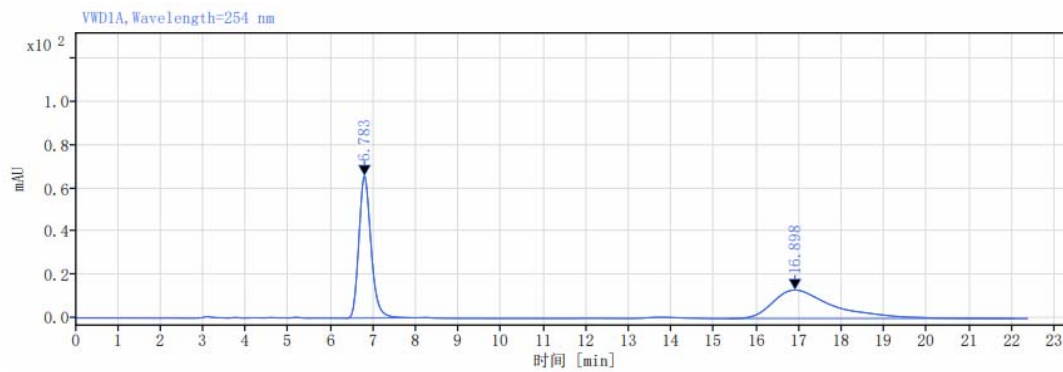
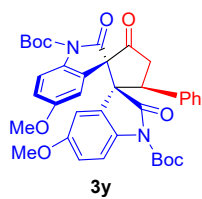
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.450	32.21	2.00	6.86
2	7.809	437.04	16.94	93.14
Total		469.04		100



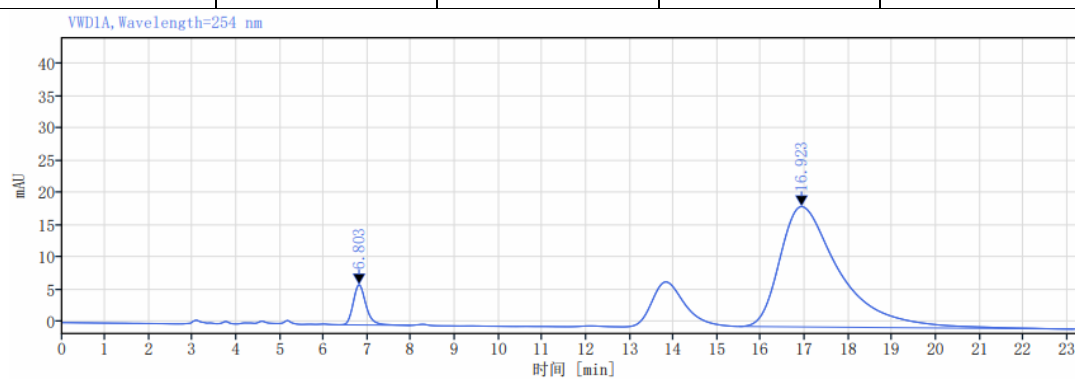
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	5.258	5810.96	529.99	50.64
2	10.323	5664.53	178.18	49.36
Total		11475.50	708.17	100



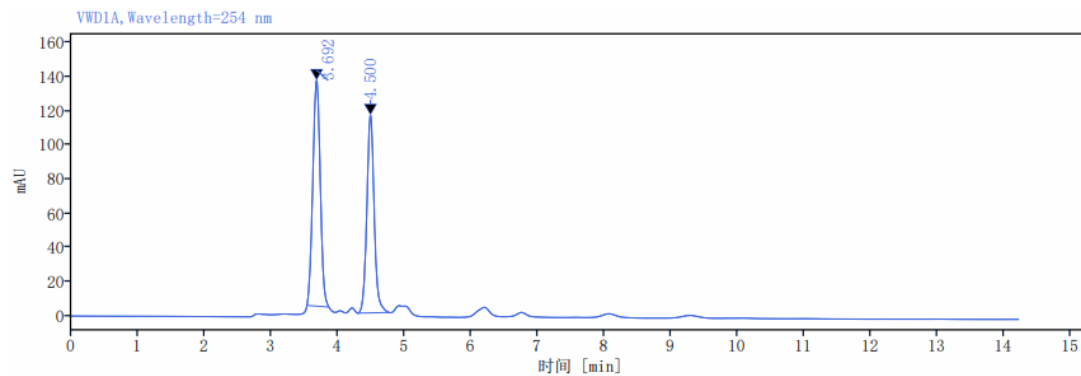
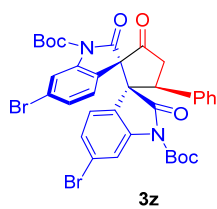
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	5.146	665.00	69.96	6.49
2	9.908	9576.14	330.27	93.51
Total		10241.14	400.23	100



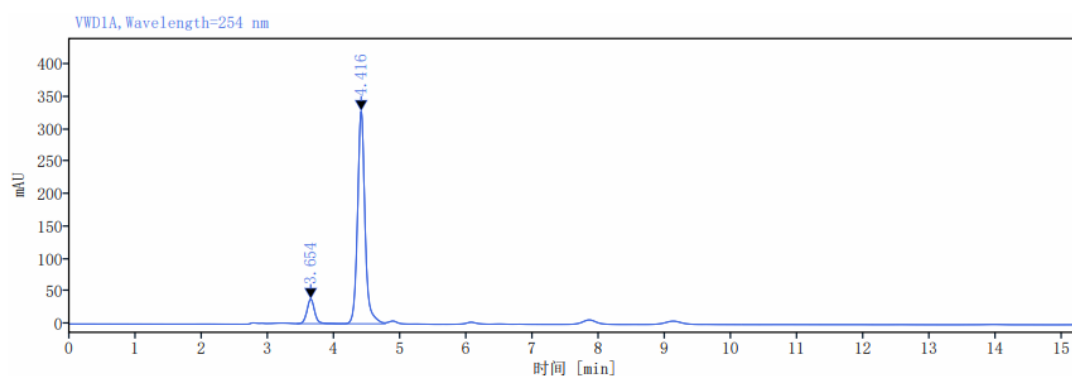
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.991	2652.26	113.30	50.89
2	16.914	2559.11	27.73	49.11
Total		5211.37		100



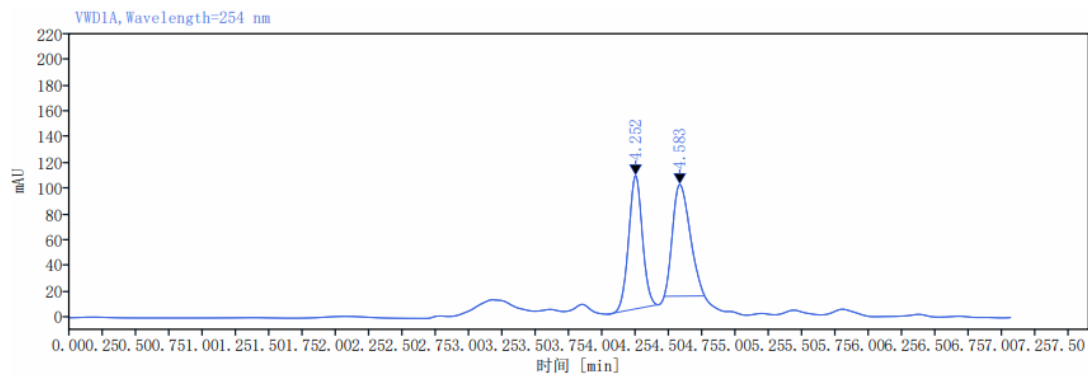
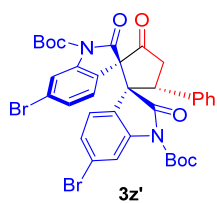
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.803	125.66	6.20	6.64
2	16.923	1766.99	18.63	93.36
Total		1892.65		100



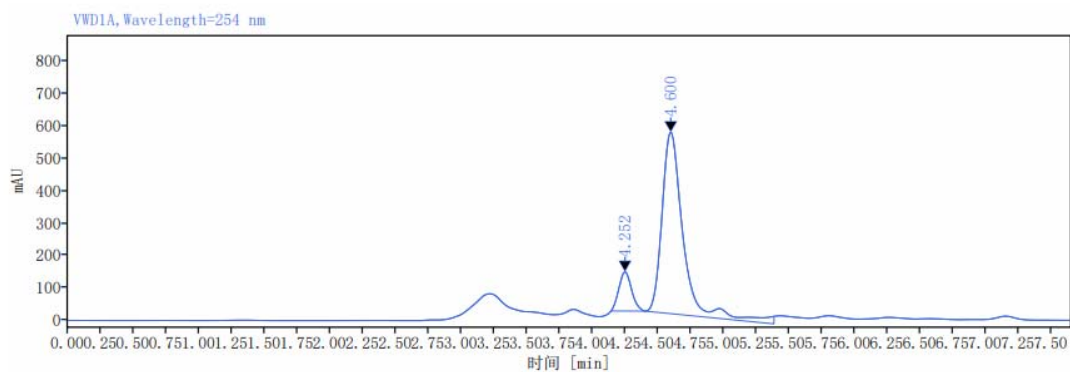
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.635	5566.47	794.24	53.35
2	4.379	4867.49	711.76	46.65
Total		10433.96	1506.00	100



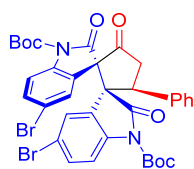
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.624	788.85	105.06	10.64
2	4.351	6624.73	906.36	89.36
Total		7413.58	1011.42	100



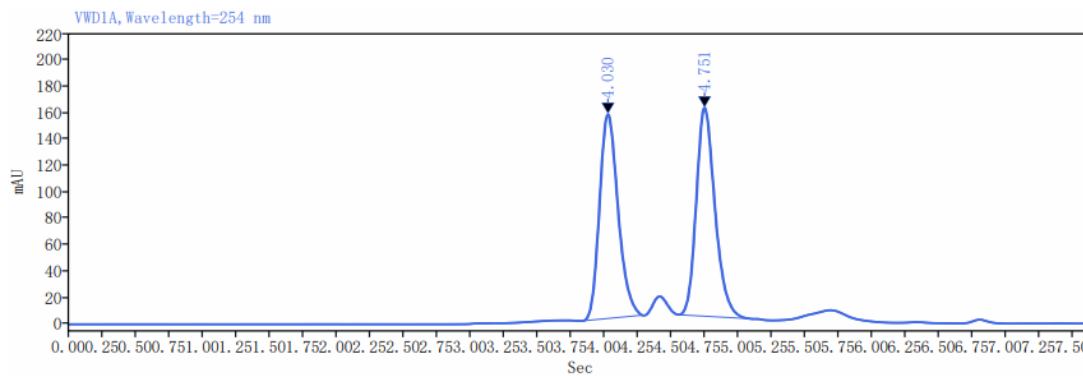
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	4.252	740.10	103.44	48.55
2	4.583	784.25	89.68	51.45
Total		1524.35	193.12	100



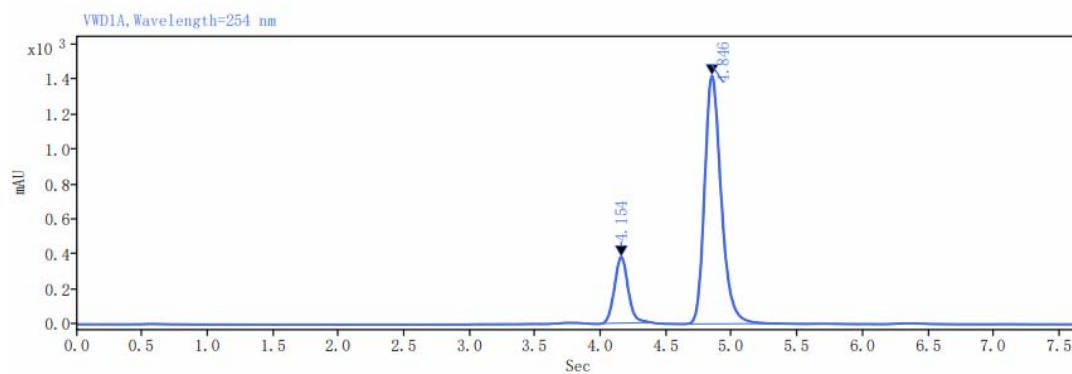
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	4.252	815.10	121.03	11.49
2	4.600	6279.31	560.58	88.51
Total		7094.41	681.61	100



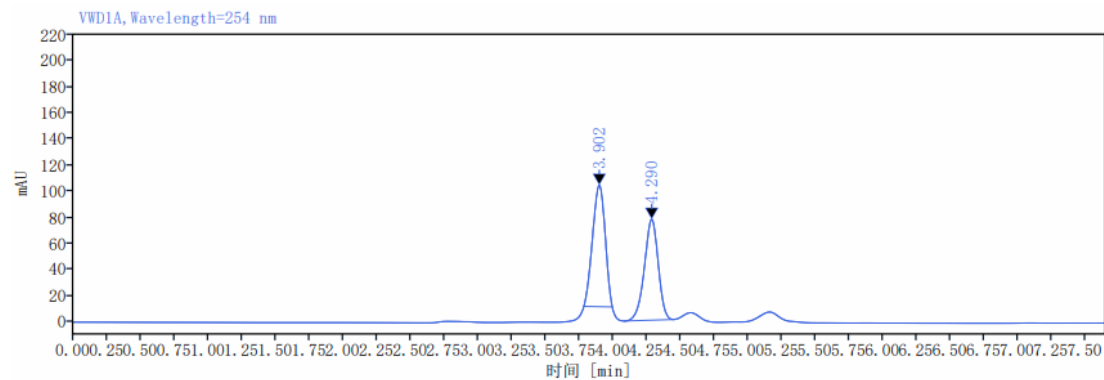
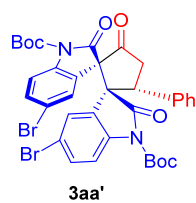
3aa



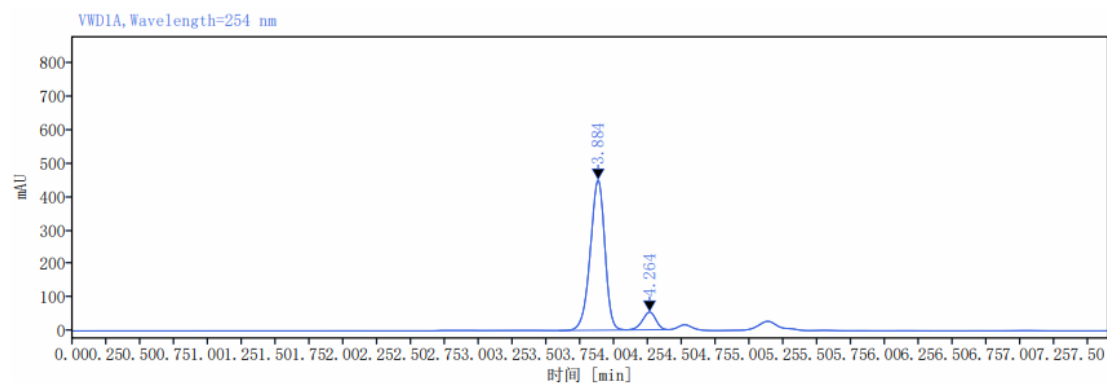
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	4.030	1490.84	154.94	49.26
2	4.751	1535.81	158.03	50.74
Total		3026.65	312.97	100



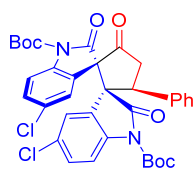
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	4.154	2737.39	380.03	17.88
2	4.846	12569.95	1423.41	82.12
Total		15307.34	1803.44	100



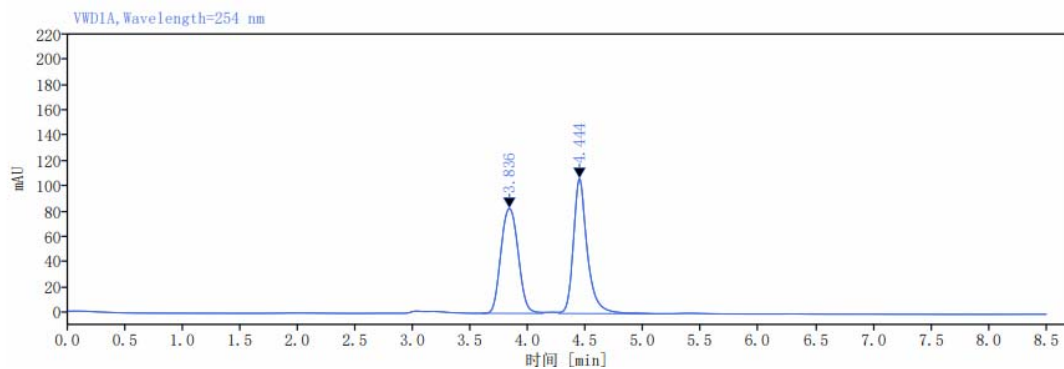
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.902	597.98	93.08	52.09
2	4.290	550.08	77.32	47.91
Total		1148.06	170.40	100



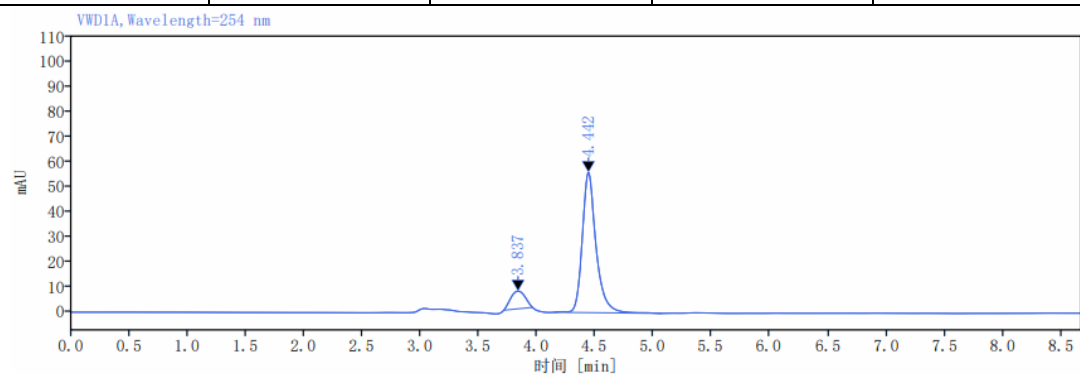
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.884	3368.39	449.34	90.19
2	4.264	366.30	53.05	9.81
Total		3734.68	502.39	100



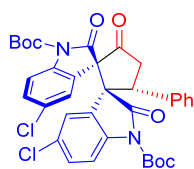
3ab



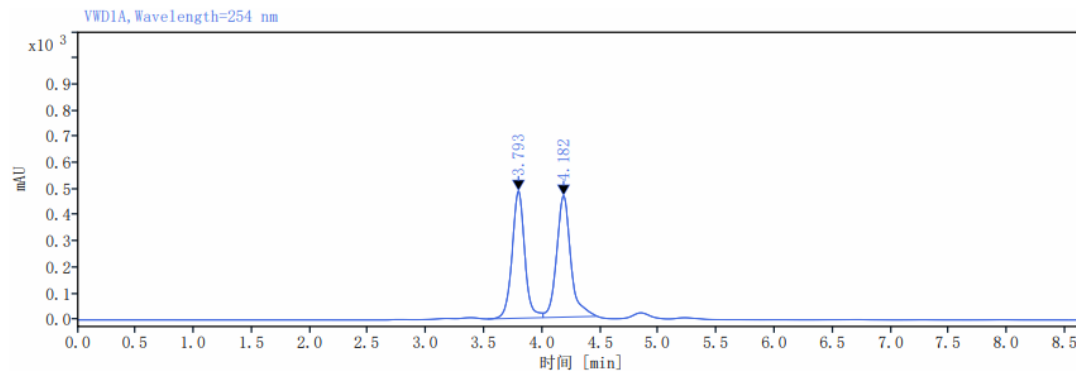
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.836	868.39	82.87	49.26
2	4.444	894.46	106.61	50.74
Total		1762.86	189.48	100



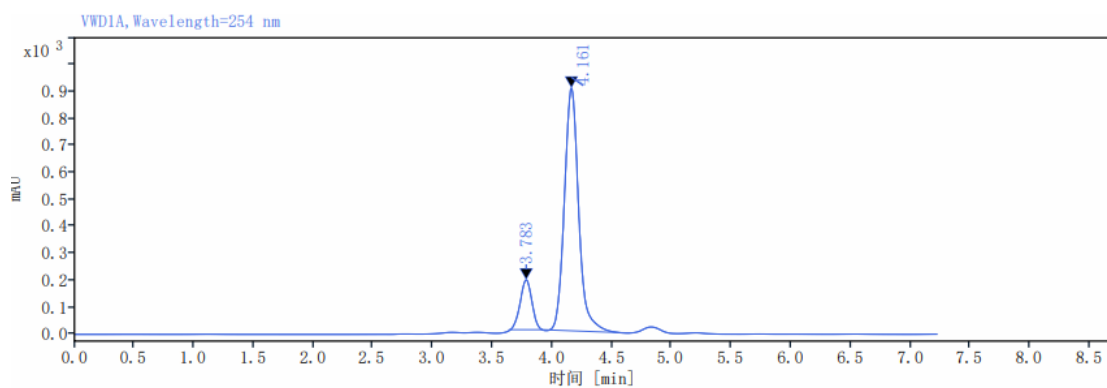
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.837	61.32	7.07	11.75
2	4.442	460.74	56.11	88.25
Total		522.06	63.18	100



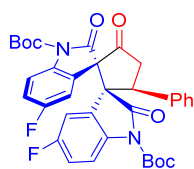
3ab'



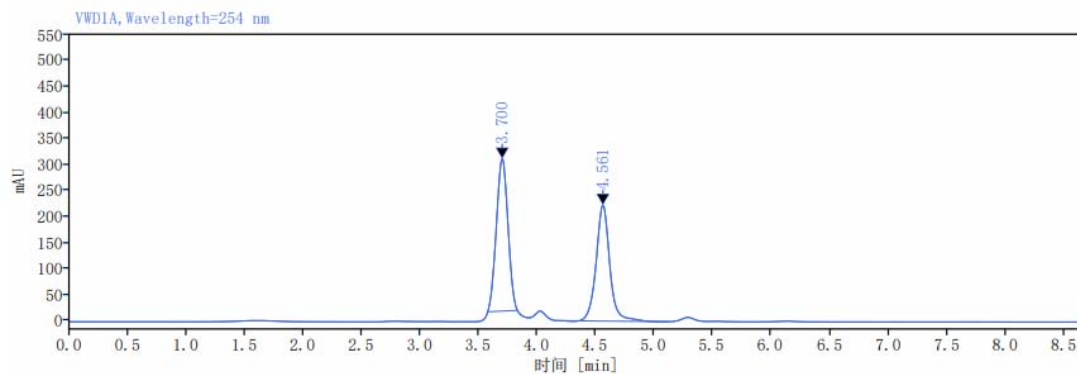
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.793	3685.58	486.40	48.28
2	4.182	3947.98	463.92	51.72
Total		7633.56	950.32	100



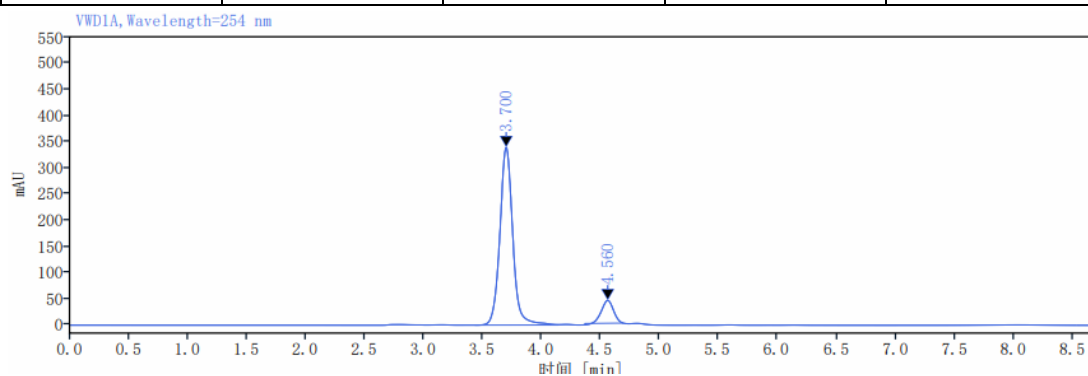
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.783	1257.66	184.62	14.39
2	4.161	7483.19	900.74	85.61
Total		8740.85	1085.36	100



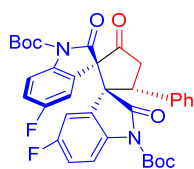
3ac



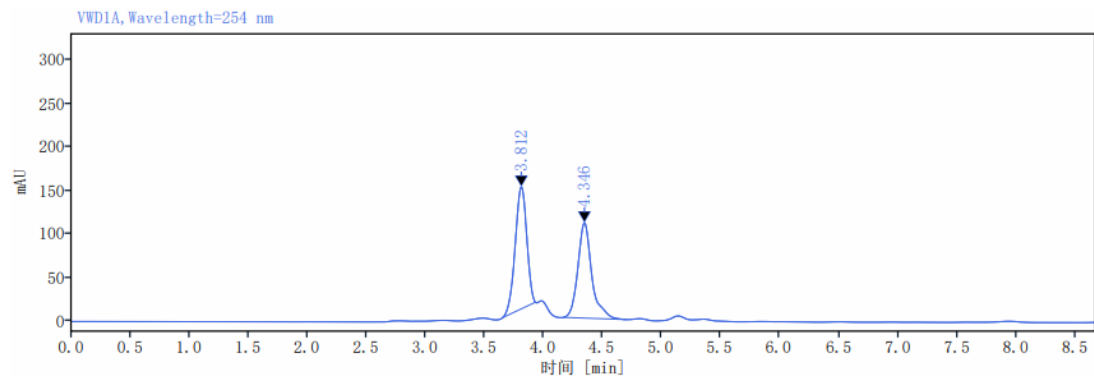
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.700	2003.60	292.08	52.70
2	4.561	1798.52	222.49	47.30
Total		3802.12	514.57	100



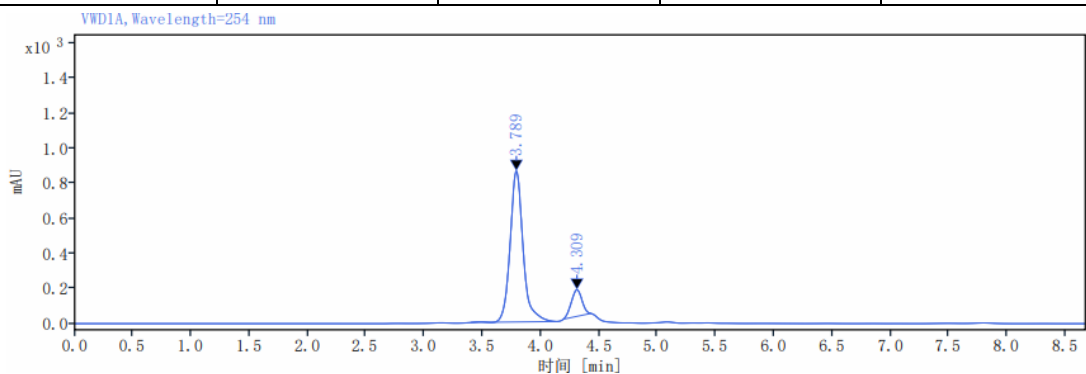
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.700	2581.12	339.31	89.50
2	4.560	302.83	43.66	10.50
Total		2883.94	382.97	100



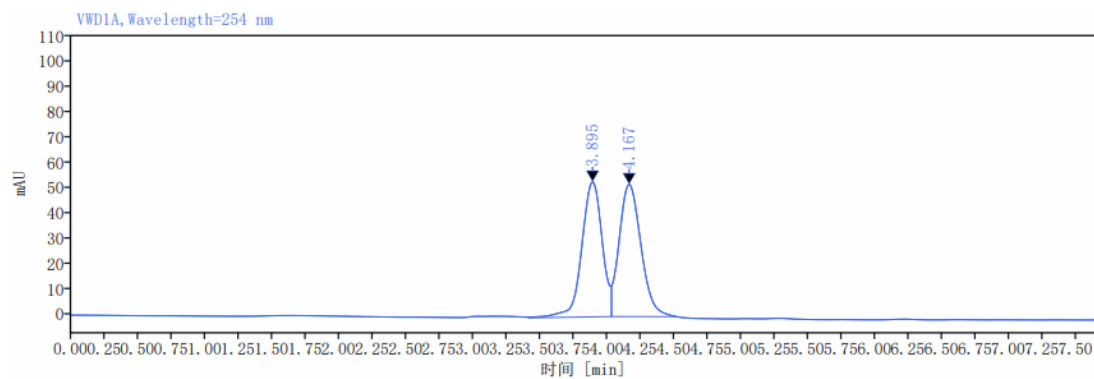
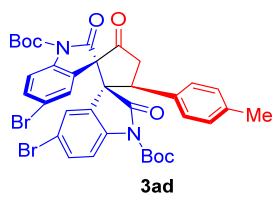
3ac'



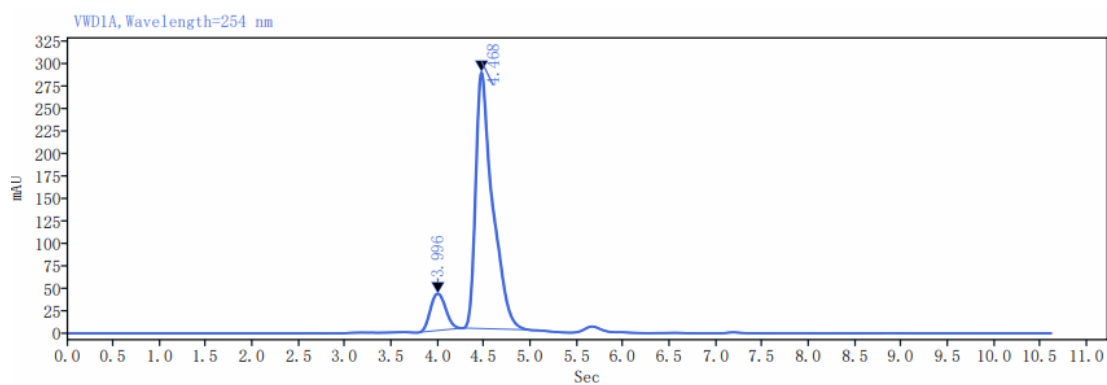
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.812	953.01	140.15	51.56
2	4.346	895.20	109.61	48.44
Total		1848.21	249.76	100



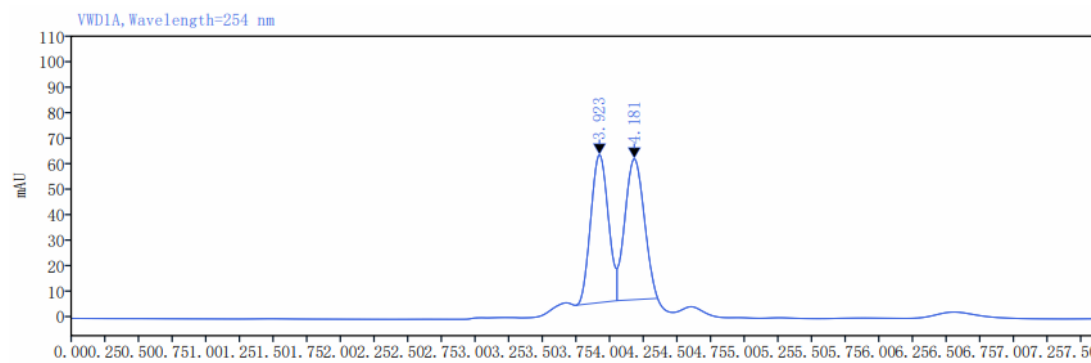
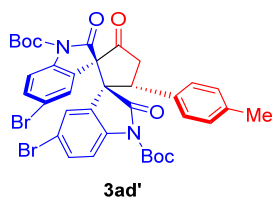
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.789	6697.02	862.75	87.36
2	4.309	969.22	151.55	12.64
Total		7666.24	1014.30	100



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.895	616.23	55.53	49.37
2	4.167	631.94	54.29	50.63
Total		1248.18	109.82	100

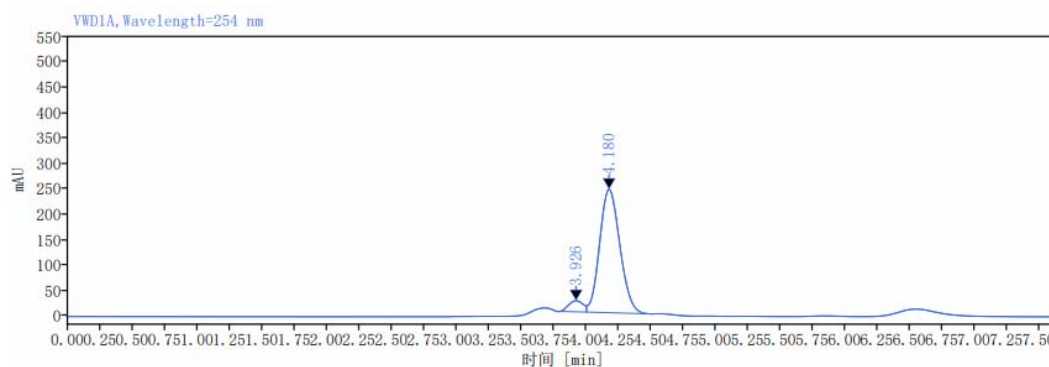


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.996	471.72	41.19	11.51
2	4.468	3627.63	286.50	88.49
Total		4099.34	327.69	100

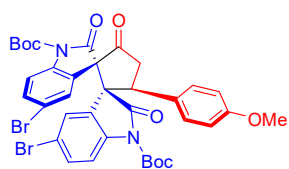


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.923	527.10	57.99	48.82
2	4.181	552.60	55.29	51.18
Total		1079.71	113.28	100

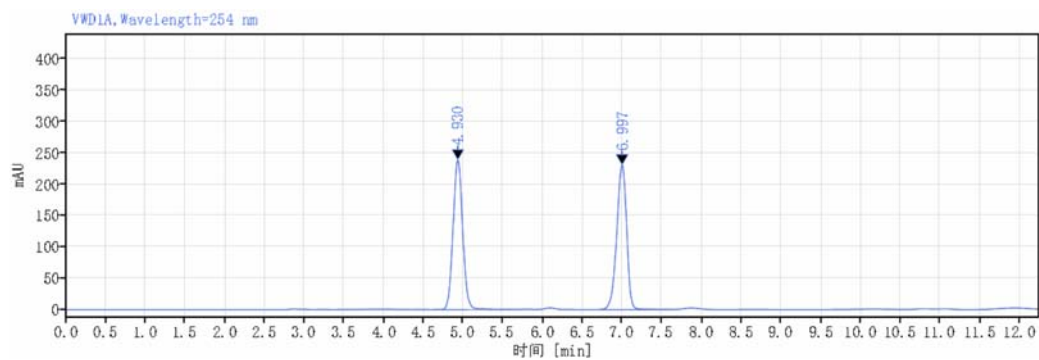
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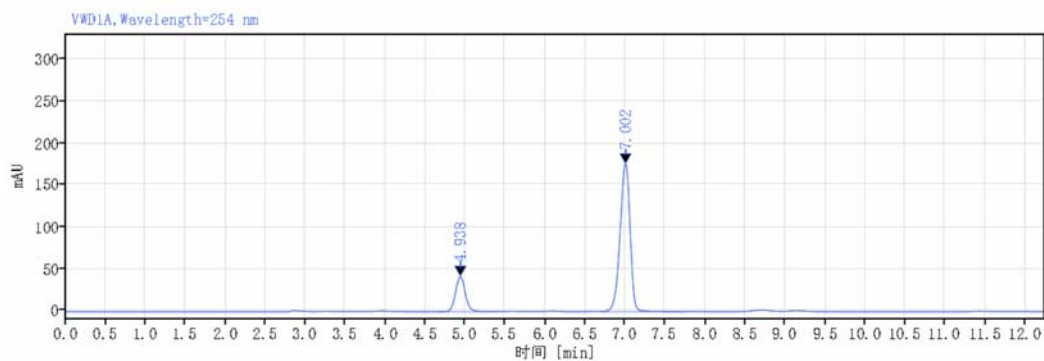
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.926	169.64	21.79	6.05
2	4.180	2633.84	242.55	93.95
Total		2803.48	264.34	100



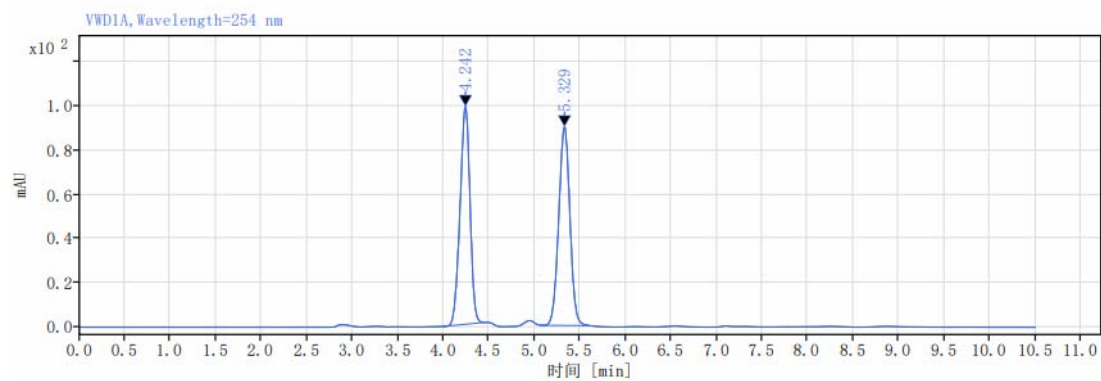
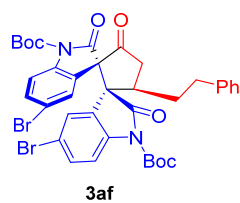
3ae



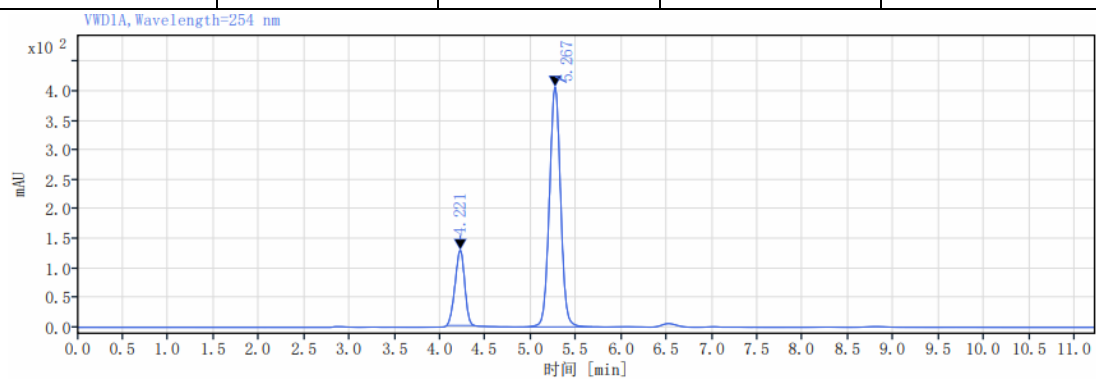
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	4.930	2018.78	238.62	50.11
2	6.997	2010.07	230.54	49.89
Total		4028.85		100



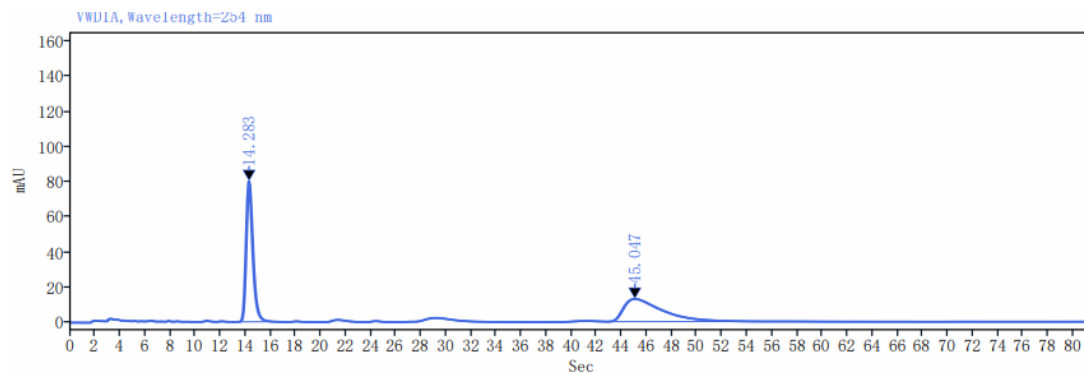
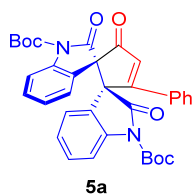
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	4.938	359.27	45.09	18.87
2	7.002	1544.18	176.05	81.13
Total		1903.45		100



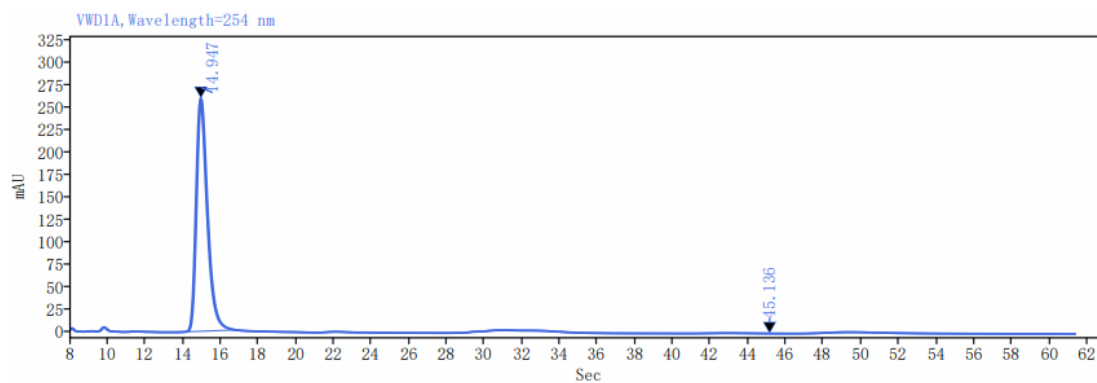
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	4.242	751.02	98.68	49.4
2	5.329	769.20	89.99	50.6
Total		1520.23		100



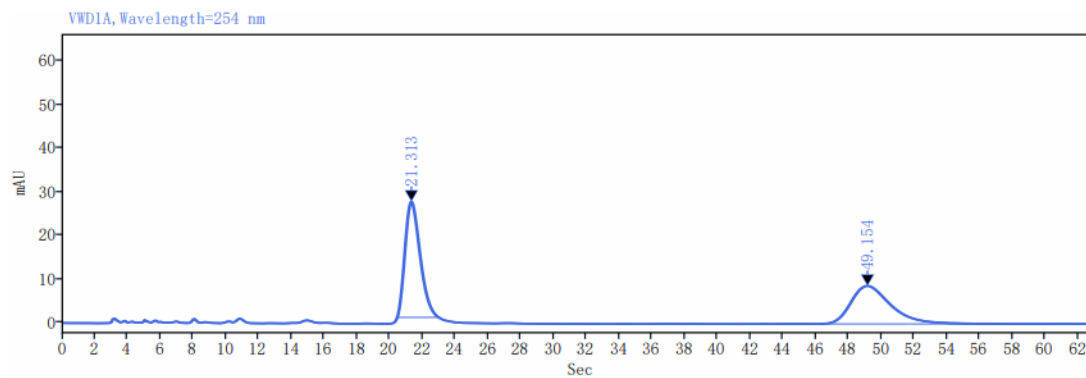
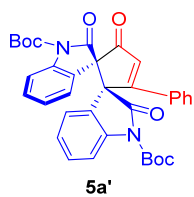
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	4.221	940.10	127.51	21.26
2	5.267	3481.78	406.43	78.74
Total		4421.88		100



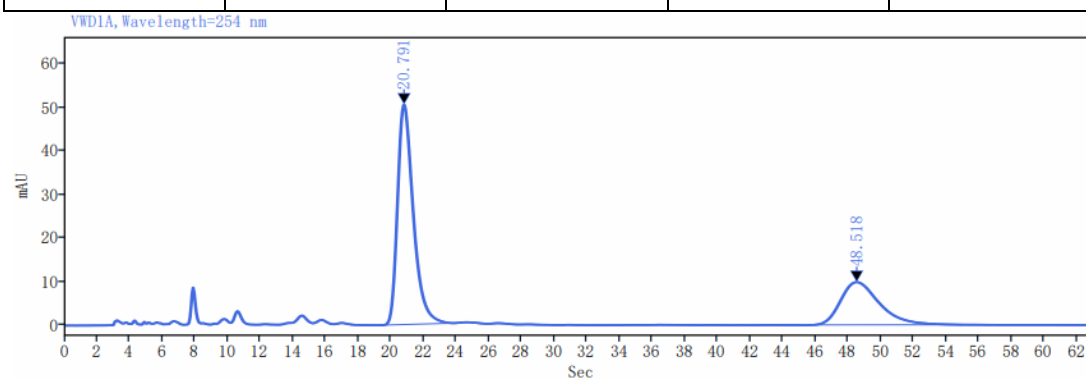
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	14.283	2972.92	80.09	51.71
2	45.047	2775.94	12.92	48.29
Total		5748.86		100



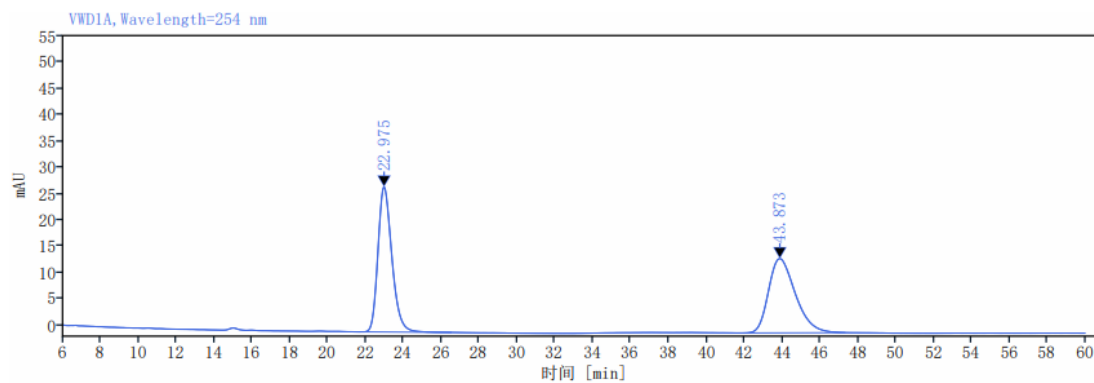
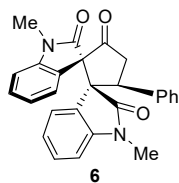
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	14.947	10682.26	260.75	99.99
2	45.136	1.58	0.03	0.01
Total		10683.84		100



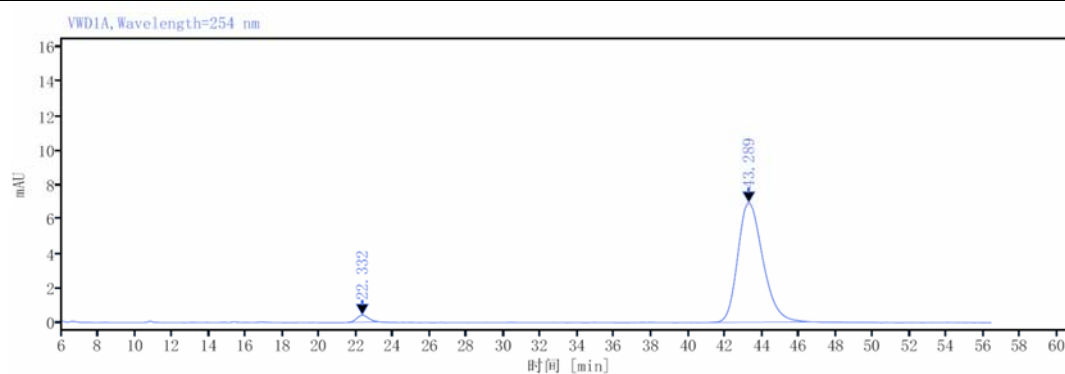
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	20.667	531.17	7.54	50.71
2	48.118	516.28	3.09	49.29
Total		1047.45		100



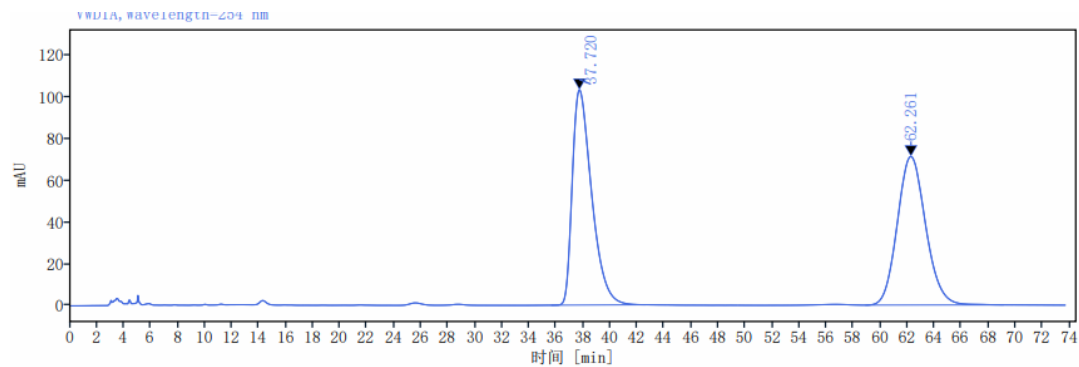
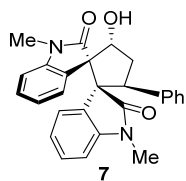
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	20.706	1365.01	19.72	67.18
2	48.289	666.85	4.02	32.82
Total		2031.86		100



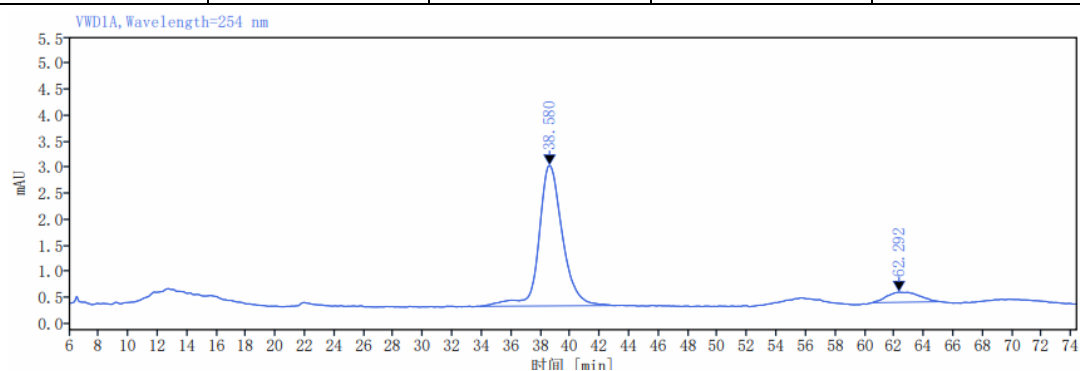
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	22.975	1406.26	27.55	50.33
2	43.873	1387.58	14.11	49.67
Total		2793.84	41.66	100



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	22.332	17.62	0.40	2.63
2	43.289	635.27	6.95	97.37
Total		670.89	7.35	100



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	37.720	10278.17	103.32	49.19
2	62.261	10398.40	71.30	50.81
Total		20676.57	174.62	100

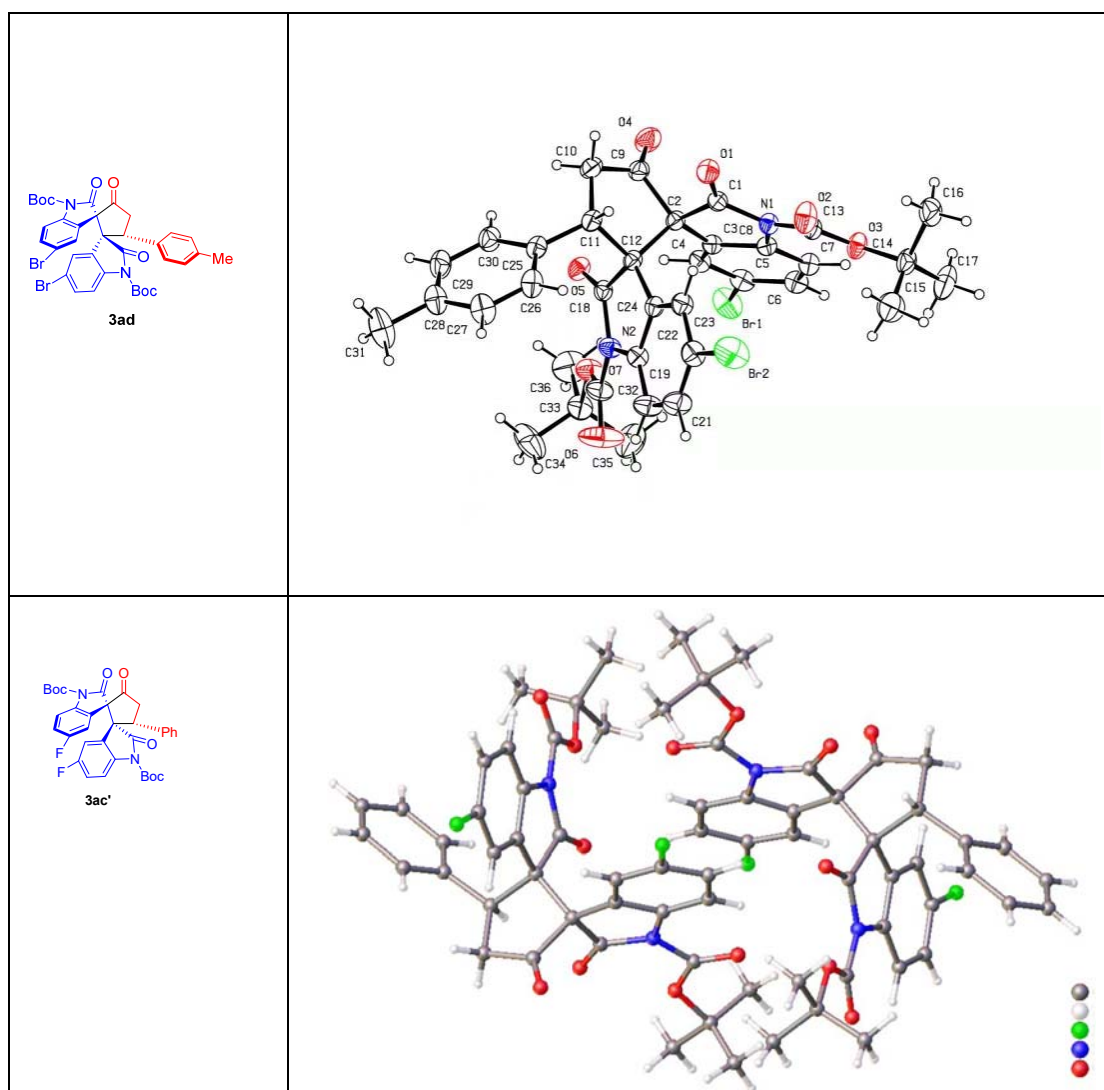


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	38.580	300.13	2.70	91.03
2	62.292	29.57	0.20	8.97
Total		329.69		100

Part 6. Crystal structure data.

The racemic **3ad**, **3ac'** and chiral product **7** were obtained by slow diffusion in CH₂Cl₂/hexanes at room temperature, colorless crystals were observed. Supplementary information of the crystals are available under CCDC number (**3ad**: 2107861), (**3ac'**: 2107864), (**7**: 2158074) which could be accessible at free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk. Thermal ellipsoid probability is 30%.

I. Crystal structure of racemic **3ad** and **3ac'**.



II. Crystal structure of chiral product 7.

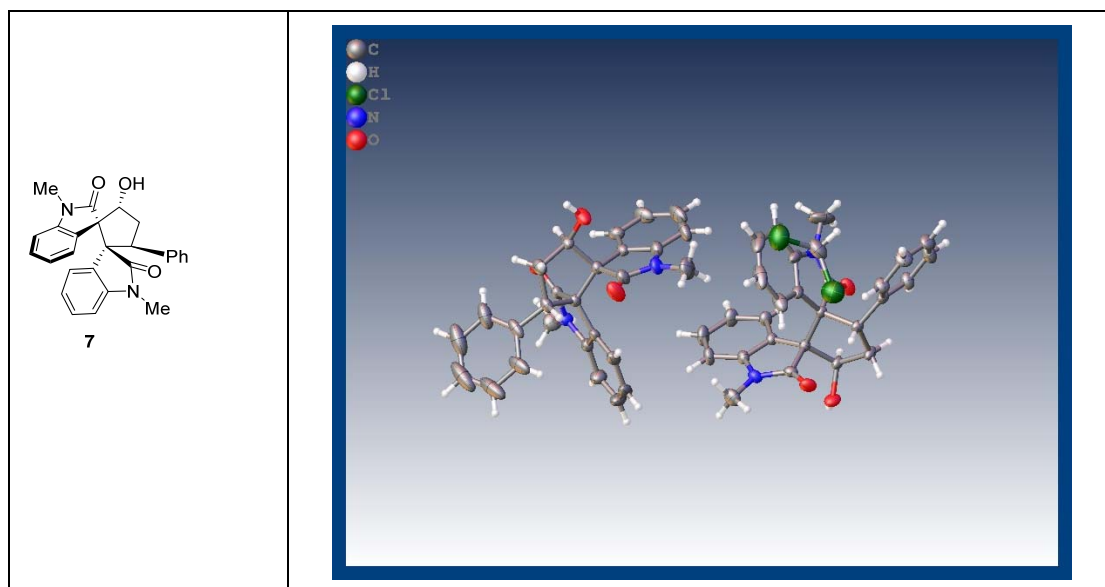


Table 1 Crystal data and structure refinement for cu_220228_OCF_7_0m.

Identification code	cu_220228_OCF_7_0m
Empirical formula	C ₅₅ H ₅₀ Cl ₂ FN ₄ O ₆
Formula weight	933.89
Temperature/K	170(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	13.2632(4)
b/Å	9.2221(3)
c/Å	19.4715(6)
α /°	90
β /°	97.7280(10)
γ /°	90
Volume/Å ³	2360.02(13)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.314
μ/mm^{-1}	1.693
F(000)	980.0

Crystal size/mm ³	0.480 × 0.230 × 0.160
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	4.58 to 136.638
Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 11, -23 ≤ l ≤ 23
Reflections collected	39406
Independent reflections	8486 [R _{int} = 0.0390, R _{sigma} = 0.0362]
Data/restraints/parameters	8486/32/608
Goodness-of-fit on F ²	1.151
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0399, wR ₂ = 0.1275
Final R indexes [all data]	R ₁ = 0.0412, wR ₂ = 0.1299
Largest diff. peak/hole / e Å ⁻³	0.36/-0.39
Flack parameter	0.044(5)

Table 2 Fractional Atomic Coordinates (× 10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for cu_220228_OCF_7_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Cl1	11051.8(10)	6668.4(15)	8413.5(7)	77.6(3)
Cl2	11080.4(9)	4012.8(16)	7608.5(6)	76.6(3)
O1	4618.2(16)	116(3)	5528.3(10)	41.9(5)
O2	5051.1(17)	3500(3)	5612.3(12)	49.5(6)
O3	1412.5(15)	1089(2)	5206.4(11)	33.7(4)
O4	7243.4(15)	9409(2)	8441.6(11)	34.1(4)
O5	5602.3(14)	9897(2)	9365.8(11)	34.8(4)
O6	6231.0(14)	5626(2)	10224.8(10)	35.5(4)
N1	1020.9(17)	3341(2)	5595.8(12)	29.6(4)

N2	4849(2)	2791(3)	6704.1(13)	40.5(6)
N3	5894.0(16)	8310(2)	7782.8(11)	28.1(4)
N4	6976.9(19)	4088(2)	9520.9(14)	37.9(5)
C1	2198(4)	5017(5)	3948.7(18)	62.2(11)
C2	1454(5)	5548(8)	3459(2)	90.0(18)
C3	750(5)	4676(10)	3118(3)	103.1(17)
C4	776(4)	3159(10)	3246(2)	91.4(14)
C5	1523(3)	2593(7)	3747.9(18)	63.6(11)
C6	2241(2)	3518(4)	4102.7(14)	41.8(7)
C7	3062(2)	3013(3)	4659.8(13)	29.3(5)
C8	3555(2)	1528(4)	4596.2(14)	39.2(6)
C9	3678(2)	816(3)	5317.2(12)	28.6(5)
C10	3542.9(18)	2065(3)	5829.4(12)	25.5(5)
C11	2719.0(18)	3021(3)	5402.7(12)	23.2(5)
C12	1656.6(18)	2324(3)	5386.3(12)	24.3(5)
C13	1513(2)	4673(3)	5738.1(13)	30.3(5)
C14	2530(2)	4538(3)	5648.9(12)	27.3(5)
C15	3145(2)	5767(3)	5716.5(15)	38.3(6)
C16	2714(3)	7075(3)	5887.1(18)	50.3(9)
C17	1699(3)	7164(3)	5985(2)	54.9(9)
C18	1082(3)	5959(4)	5900.9(19)	46.7(7)
C19	-55(2)	3097(4)	5627(2)	47.2(7)
C20	4561(2)	2879(3)	6012.9(15)	33.7(6)
C21	4154(2)	1966(3)	7027.2(14)	35.6(6)
C22	4242(3)	1538(5)	7715.5(16)	52.4(9)
C23	3480(3)	650(5)	7907.9(16)	55.8(9)
C24	2672(3)	218(4)	7432.7(17)	48.8(8)

C25	2593(2)	672(3)	6744.6(15)	35.3(6)
C26	3347(2)	1545(3)	6539.9(12)	27.5(5)
C27	5790(3)	3362(5)	7056(2)	61.4(10)
C28	9544(2)	6541(3)	9953.8(15)	35.1(6)
C29	10307(2)	5798(4)	10365.7(18)	43.9(7)
C30	10180(2)	5346(4)	11014.0(17)	43.1(7)
C31	9268(2)	5640(4)	11253.9(16)	45.0(7)
C32	8492(2)	6380(3)	10849.9(14)	35.7(6)
C33	8618.9(18)	6835(3)	10187.0(13)	24.2(5)
C34	7800.1(17)	7608(2)	9705.1(12)	22.4(5)
C35	7073.4(19)	8650(3)	10024.4(14)	29.3(5)
C36	6013.5(17)	8532(3)	9582.3(12)	24.1(5)
C37	6181.2(17)	7581(2)	8952.4(11)	20.7(4)
C38	7061.8(17)	6556(2)	9250.0(11)	21.3(4)
C39	6684.6(18)	5395(3)	9728.9(13)	27.0(5)
C40	7455(2)	4192(3)	8926.1(17)	37.4(6)
C41	7529.1(19)	5638(3)	8732.8(13)	28.4(5)
C42	7985(2)	5996(4)	8156.0(15)	43.8(7)
C43	8341(3)	4854(6)	7781.4(18)	66.9(13)
C44	8266(3)	3442(5)	7984(2)	68.9(14)
C45	7817(3)	3055(4)	8563(2)	56.2(10)
C46	6524.7(18)	8564(2)	8382.2(12)	24.2(5)
C47	5143.5(19)	7292(3)	7880.1(13)	26.7(5)
C48	5265.0(17)	6835(3)	8568.9(12)	22.7(4)
C49	4586.1(19)	5837(3)	8776.9(13)	29.3(5)
C50	3802(2)	5319(4)	8283.5(15)	39.1(6)
C51	3711(2)	5774(4)	7601.8(16)	44.5(7)

C52	4372(2)	6788(4)	7390.5(14)	37.4(6)
C53	6024(3)	8975(4)	7121.1(15)	42.3(7)
C54	6855(4)	2773(4)	9920(3)	70.2(13)
C55	10910(3)	4783(5)	8404(2)	59.9(10)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for cu_220228_OCF_7_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	73.0(7)	80.7(7)	80.5(7)	2.4(6)	15.6(6)	1.5(6)
Cl2	63.9(6)	99.6(8)	67.6(6)	-11.0(6)	14.0(5)	-4.7(6)
O1	35.7(10)	56.4(12)	33.2(10)	-0.2(9)	3.1(8)	20.6(10)
O2	28.7(10)	66.6(15)	51.1(12)	20.9(11)	-1.6(9)	-13.5(10)
O3	28.8(9)	26.8(9)	44.4(10)	-2.8(8)	0.5(8)	-4.2(7)
O4	29.1(9)	27.9(9)	45.0(11)	10.0(8)	3.6(8)	-6.1(8)
O5	24.7(9)	28.3(9)	50.6(11)	-5.7(8)	2.3(8)	7.9(7)
O6	25.7(9)	48.1(11)	32.4(9)	11.2(8)	2.9(7)	-12.2(8)
N1	24.5(10)	28.1(10)	35.6(11)	0.7(8)	2.0(8)	1.0(9)
N2	33.0(12)	47.4(14)	36.6(12)	0.7(10)	-11.1(10)	-0.3(11)
N3	26.2(10)	30.6(10)	27.6(10)	6.2(8)	4.5(8)	2.5(8)
N4	32.6(12)	22.1(11)	56.1(15)	2.3(10)	-4.9(10)	-3.6(9)
C1	83(3)	75(2)	32.1(15)	21.3(16)	21.9(16)	40(2)
C2	107(4)	119(4)	48(2)	36(2)	23(2)	70(3)
C3	78(3)	185(4)	46(2)	36(3)	7(2)	59(4)
C4	56(2)	175(4)	39.7(19)	4(3)	-4.3(17)	1(3)
C5	42.0(17)	114(3)	32.7(15)	5.4(19)	-3.9(13)	-4(2)
C6	31.7(14)	73(2)	21.5(11)	12.7(12)	5.8(10)	17.5(14)
C7	25.1(12)	40.8(13)	21.8(11)	6.6(10)	2.1(9)	1.9(11)
C8	42.5(15)	51.3(17)	24.3(12)	2.3(12)	6.6(11)	15.1(13)

C9	29.6(12)	32.2(12)	23.8(11)	-1.7(10)	3.1(9)	9.1(10)
C10	22.9(11)	29.0(12)	23.7(11)	2.1(9)	0.0(9)	0.7(9)
C11	20.5(11)	25.0(10)	23.3(11)	1.7(8)	0.5(8)	-2.2(9)
C12	23.0(11)	25.8(11)	23.1(10)	2.7(9)	-0.3(8)	-1.6(9)
C13	31.6(13)	28.6(12)	28.2(12)	-0.2(9)	-4.7(10)	1.3(10)
C14	32.2(12)	25.0(12)	22.4(11)	5.2(9)	-4.4(9)	-1.0(10)
C15	42.9(16)	29.4(12)	38.5(14)	8.2(11)	-9.7(12)	-8.9(12)
C16	66(2)	25.5(13)	49.6(17)	4.0(12)	-27.0(15)	-7.8(14)
C17	64(2)	27.9(15)	64(2)	-8.2(14)	-21.7(17)	12.0(14)
C18	44.8(17)	37.2(15)	55.0(18)	-6.1(13)	-4.9(13)	10.0(13)
C19	25.6(14)	53.8(18)	63(2)	-3.8(15)	9.0(13)	-0.4(13)
C20	27.7(12)	36.6(13)	34.3(13)	6.7(11)	-5.6(10)	-2.4(11)
C21	38.4(14)	40.9(14)	26.4(12)	-2.2(10)	-0.2(10)	6.7(12)
C22	53(2)	76(2)	25.1(14)	1.1(15)	-6.8(13)	20.2(18)
C23	70(2)	72(2)	27.3(14)	14.3(15)	13.1(14)	26(2)
C24	59(2)	51.9(17)	39.8(15)	16.6(14)	24.4(14)	16.3(15)
C25	41.9(15)	30.2(12)	35.4(13)	4.4(11)	10.4(11)	5.1(12)
C26	32.2(13)	26.8(11)	23.1(11)	1.0(9)	2.4(9)	7.3(10)
C27	42.8(19)	74(3)	60(2)	-3.9(19)	-20.8(16)	-11.1(18)
C28	24.5(13)	42.3(14)	38.4(13)	0.1(12)	4.1(10)	4.6(11)
C29	24.1(13)	52.8(17)	54.2(18)	-0.3(15)	3.2(12)	12.1(13)
C30	31.3(14)	43.6(15)	50.0(17)	2.1(13)	-10.9(12)	7.4(12)
C31	37.4(15)	59.4(19)	35.3(14)	6.8(14)	-5.9(12)	-1.7(15)
C32	27.3(13)	49.2(15)	29.7(13)	0.9(11)	1.0(10)	-1.0(12)
C33	18.0(10)	24.6(11)	28.9(11)	-4.7(9)	-1.3(9)	-3.5(9)
C34	17.3(10)	21.5(10)	28.1(11)	-1.9(8)	1.8(8)	-2.0(8)
C35	20.4(11)	28.9(12)	36.3(13)	-12.5(10)	-4.6(9)	3.4(9)

C36	19.0(11)	23.8(11)	28.5(11)	-6.7(9)	-0.1(8)	-0.3(9)
C37	17.8(10)	22.6(10)	21.8(10)	-1.4(8)	2.8(8)	-2.0(8)
C38	19.7(10)	20.3(10)	23.4(11)	-2.4(8)	1.9(8)	-2.6(9)
C39	20.2(11)	24.2(11)	33.4(12)	6.2(9)	-7.7(9)	-6.2(9)
C40	29.4(13)	26.8(12)	50.7(16)	-13.4(11)	-13.6(12)	5.2(11)
C41	24.0(11)	31.3(12)	27.9(11)	-7.8(10)	-3.2(9)	7.7(10)
C42	34.3(15)	67(2)	30.4(13)	-3.5(13)	4.6(11)	23.1(14)
C43	47.3(18)	117(4)	34.5(15)	-25(2)	-1.4(14)	36(2)
C44	59(2)	77(3)	63(2)	-43(2)	-22.5(18)	41(2)
C45	47.7(18)	40.1(16)	73(2)	-30.9(17)	-21.1(17)	20.2(15)
C46	21.6(11)	21.5(10)	29.8(11)	3.6(9)	4.0(9)	3.7(9)
C47	25.9(11)	31.9(12)	22.1(11)	-0.6(9)	2.0(9)	1.5(10)
C48	18.6(10)	24.7(10)	23.9(11)	-3.0(8)	-0.2(8)	0.6(9)
C49	22.9(11)	34.3(12)	29.6(11)	1.2(10)	-0.5(9)	-6.3(10)
C50	30.9(13)	47.3(16)	37.9(14)	-2.1(12)	-0.1(11)	-13.7(12)
C51	33.3(14)	61.9(18)	35.2(14)	-8.3(14)	-7.0(11)	-12.7(14)
C52	35.9(14)	50.2(15)	23.8(12)	-1.0(11)	-4.0(10)	-6.7(12)
C53	43.3(16)	52.6(17)	32.2(14)	10.7(13)	9.9(12)	0.2(14)
C54	63(2)	28.1(16)	118(4)	28(2)	5(2)	-3.9(16)
C55	48.3(19)	79(3)	50.0(19)	17.3(18)	-3.6(15)	7.9(19)

Table 4 Bond Lengths for cu_220228_OCF_7_0m.

Atom Atom Length/Å			Atom Atom Length/Å		
Cl1	C55	1.749(5)	C14	C15	1.393(4)
Cl2	C55	1.745(5)	C15	C16	1.394(5)
O1	C9	1.415(3)	C16	C17	1.387(6)
O2	C20	1.223(4)	C17	C18	1.377(5)
O3	C12	1.222(3)	C21	C22	1.387(4)

O4	C46	1.225(3)	C21	C26	1.387(4)
O5	C36	1.414(3)	C22	C23	1.391(6)
O6	C39	1.223(3)	C23	C24	1.377(6)
N1	C12	1.360(3)	C24	C25	1.394(4)
N1	C13	1.400(4)	C25	C26	1.383(4)
N1	C19	1.454(4)	C28	C29	1.385(4)
N2	C20	1.351(4)	C28	C33	1.391(4)
N2	C21	1.407(4)	C29	C30	1.361(5)
N2	C27	1.440(4)	C30	C31	1.381(5)
N3	C46	1.362(3)	C31	C32	1.388(4)
N3	C47	1.399(3)	C32	C33	1.389(4)
N3	C53	1.458(3)	C33	C34	1.515(3)
N4	C39	1.345(4)	C34	C35	1.550(3)
N4	C40	1.396(5)	C34	C38	1.566(3)
N4	C54	1.462(4)	C35	C36	1.550(3)
C1	C2	1.367(6)	C36	C37	1.548(3)
C1	C6	1.414(6)	C37	C48	1.505(3)
C2	C3	1.339(11)	C37	C46	1.549(3)
C3	C4	1.420(12)	C37	C38	1.553(3)
C4	C5	1.396(7)	C38	C41	1.511(3)
C5	C6	1.391(6)	C38	C39	1.546(3)
C6	C7	1.503(4)	C40	C45	1.386(4)
C7	C8	1.530(4)	C40	C41	1.393(4)
C7	C11	1.573(3)	C41	C42	1.385(4)
C8	C9	1.538(4)	C42	C43	1.399(5)
C9	C10	1.549(3)	C43	C44	1.369(8)
C10	C26	1.519(3)	C44	C45	1.390(7)

C10	C20	1.544(4)	C47	C52	1.382(4)
C10	C11	1.555(3)	C47	C48	1.394(3)
C11	C14	1.510(3)	C48	C49	1.386(3)
C11	C12	1.546(3)	C49	C50	1.401(4)
C13	C18	1.372(4)	C50	C51	1.382(5)
C13	C14	1.389(4)	C51	C52	1.382(5)

Table 5 Bond Angles for cu_220228_OCF_7_0m.

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
C12	N1	C13	111.9(2)	C23	C24	C25	120.6(3)
C12	N1	C19	123.8(2)	C26	C25	C24	119.2(3)
C13	N1	C19	124.1(2)	C25	C26	C21	119.2(2)
C20	N2	C21	111.3(2)	C25	C26	C10	131.7(2)
C20	N2	C27	124.2(3)	C21	C26	C10	108.9(2)
C21	N2	C27	124.3(3)	C29	C28	C33	121.0(3)
C46	N3	C47	111.4(2)	C30	C29	C28	121.1(3)
C46	N3	C53	123.6(2)	C29	C30	C31	118.4(3)
C47	N3	C53	124.9(2)	C30	C31	C32	121.4(3)
C39	N4	C40	111.7(2)	C31	C32	C33	120.1(3)
C39	N4	C54	121.8(3)	C32	C33	C28	117.8(2)
C40	N4	C54	126.4(3)	C32	C33	C34	123.5(2)
C2	C1	C6	120.2(5)	C28	C33	C34	118.7(2)
C3	C2	C1	121.4(6)	C33	C34	C35	118.4(2)
C2	C3	C4	120.3(5)	C33	C34	C38	113.64(19)
C5	C4	C3	119.3(6)	C35	C34	C38	103.65(18)
C6	C5	C4	119.5(6)	C34	C35	C36	107.46(18)
C5	C6	C1	119.3(4)	O5	C36	C37	111.0(2)
C5	C6	C7	123.3(3)	O5	C36	C35	112.80(19)

C1	C6	C7	117.4(3)	C37	C36	C35	105.29(18)
C6	C7	C8	119.6(2)	C48	C37	C36	117.38(18)
C6	C7	C11	113.0(2)	C48	C37	C46	101.99(19)
C8	C7	C11	105.0(2)	C36	C37	C46	108.90(19)
C7	C8	C9	107.6(2)	C48	C37	C38	115.06(19)
O1	C9	C8	116.1(2)	C36	C37	C38	103.31(18)
O1	C9	C10	109.0(2)	C46	C37	C38	110.17(17)
C8	C9	C10	105.3(2)	C41	C38	C39	102.07(19)
C26	C10	C20	101.2(2)	C41	C38	C37	116.60(19)
C26	C10	C9	113.6(2)	C39	C38	C37	110.99(18)
C20	C10	C9	109.7(2)	C41	C38	C34	116.29(19)
C26	C10	C11	118.1(2)	C39	C38	C34	108.42(18)
C20	C10	C11	112.2(2)	C37	C38	C34	102.47(17)
C9	C10	C11	102.20(19)	O6	C39	N4	125.9(2)
C14	C11	C12	101.68(19)	O6	C39	C38	126.1(2)
C14	C11	C10	119.4(2)	N4	C39	C38	108.0(2)
C12	C11	C10	110.36(19)	C45	C40	C41	123.0(3)
C14	C11	C7	112.16(19)	C45	C40	N4	126.7(3)
C12	C11	C7	110.7(2)	C41	C40	N4	110.3(2)
C10	C11	C7	102.67(19)	C42	C41	C40	120.1(3)
O3	C12	N1	125.3(2)	C42	C41	C38	132.1(3)
O3	C12	C11	126.8(2)	C40	C41	C38	107.8(2)
N1	C12	C11	107.9(2)	C41	C42	C43	117.3(4)
C18	C13	C14	123.2(3)	C44	C43	C42	121.5(4)
C18	C13	N1	127.3(3)	C43	C44	C45	122.3(3)
C14	C13	N1	109.3(2)	C40	C45	C44	115.7(4)
C13	C14	C15	118.8(3)	O4	C46	N3	124.8(2)

C13	C14	C11	109.2(2)	O4	C46	C37	127.2(2)
C15	C14	C11	131.6(3)	N3	C46	C37	107.9(2)
C14	C15	C16	118.2(3)	C52	C47	C48	122.7(2)
C17	C16	C15	121.4(3)	C52	C47	N3	127.3(2)
C18	C17	C16	120.5(3)	C48	C47	N3	109.9(2)
C13	C18	C17	117.8(3)	C49	C48	C47	119.1(2)
O2	C20	N2	124.1(3)	C49	C48	C37	132.2(2)
O2	C20	C10	127.1(3)	C47	C48	C37	108.7(2)
N2	C20	C10	108.8(2)	C48	C49	C50	118.5(2)
C22	C21	C26	122.6(3)	C51	C50	C49	121.1(3)
C22	C21	N2	127.7(3)	C52	C51	C50	121.0(3)
C26	C21	N2	109.7(2)	C47	C52	C51	117.6(3)
C21	C22	C23	117.3(3)	Cl2	C55	Cl1	112.8(2)
C24	C23	C22	121.2(3)				

Table 6 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for cu_220228_OCF_7_0m.

Atom	x	y	z	U(eq)
H1D	4770.61	-466.5	5212.6	93
H5D	4968.1	10005.15	9452.47	42
H1	2688.13	5656.49	4185.83	75
H2	1435.84	6556.38	3359.12	108
H3	229.72	5073.56	2788.92	124
H4	290.41	2536.48	2993.21	110
H5	1541.44	1583.28	3846.16	76
H7	3623.53	3739.73	4674.23	35
H8A	4226.78	1639.69	4434.46	47
H8B	3119.67	917.7	4258.18	47

H9	3115.65	98.93	5332.53	34
H15	3840.03	5715.86	5648.1	46
H16	3123.78	7923.17	5937.65	60
H17	1427.17	8064.34	6110.31	66
H18	381.41	6016	5954.01	56
H19A	-236.34	2107.2	5473.68	71
H19B	-458.99	3791.32	5324.09	71
H19C	-195.37	3226.8	6104.77	71
H22	4800.01	1839.15	8042.2	63
H23	3517.66	335.08	8375.29	67
H24	2162.92	-394.98	7575.2	59
H25	2028.6	385.61	6420.17	42
H27A	5653.54	3923.7	7460.32	92
H27B	6104.81	3991.92	6738.98	92
H27C	6252.17	2560.49	7206.33	92
H28	9654.07	6855.04	9505.24	42
H29	10928.74	5599.94	10192.63	53
H30	10706.9	4839.14	11294.84	52
H31	9169.93	5329.21	11705.25	54
H32	7873.26	6576.8	11027.31	43
H34	8155.15	8196.6	9379.07	27
H35A	7328.76	9658.39	10018.43	35
H35B	7027.82	8374.71	10510.66	35
H36	5534.92	8025.27	9857.46	29
H42	8053.23	6977.05	8020.39	53
H43	8641.49	5064.18	7376.51	80
H44	8529.32	2700.65	7720.28	83

H45	7762.77	2073.28	8701.4	67
H49	4650.79	5510.94	9243.62	35
H50	3325.79	4643.33	8419.79	47
H51	3185.6	5385.4	7273.71	53
H52	4299.7	7125.12	6925.53	45
H53A	5388.8	9450.42	6925.76	63
H53B	6199.92	8226.81	6800.3	63
H53C	6571.06	9696.27	7192.59	63
H54A	6550.48	2008.9	9609.25	105
H54B	6410.69	2975.89	10272.35	105
H54C	7521.73	2451.19	10147.49	105
H55A	11411.31	4356.99	8771.31	72
H55B	10221.72	4536.98	8510.42	72

Experimental

Single crystals of $C_{55}H_{50}Cl_2FN_4O_6$ [**cu_220228_OCF_7_0m**] were [1]. A suitable crystal was selected and [1] on a diffractometer. The crystal was kept at 170(2) K during data collection. Using Olex2 [1], the structure was solved with the Unknown [2] structure solution program using Unknown and refined with the Unknown [3] refinement package using Unknown minimisation.

- 1.
- 2.
- 3.

Crystal structure determination of [**cu_220228_OCF_7_0m**]

Crystal Data for $C_{55}H_{50}Cl_2FN_4O_6$ ($M = 933.89$ g/mol): monoclinic, space group $P2_1$ (no. 4), $a = 13.2632(4)$ Å, $b = 9.2221(3)$ Å, $c = 19.4715(6)$ Å, $\beta = 97.7280(10)^\circ$, $V = 2360.02(13)$ Å³, $Z = 2$, $T = 170(2)$ K, $\mu(\text{CuK}\alpha) = 1.693$ mm⁻¹, $D_{\text{calc}} = 1.314$ g/cm³, 39406 reflections measured ($4.58^\circ \leq 2\theta \leq 136.638^\circ$), 8486 unique ($R_{\text{int}} = 0.0390$, $R_{\text{sigma}} = 0.0362$) which were used in all calculations. The final R_1 was 0.0399 ($I > 2\sigma(I)$) and wR_2 was 0.1299 (all data).

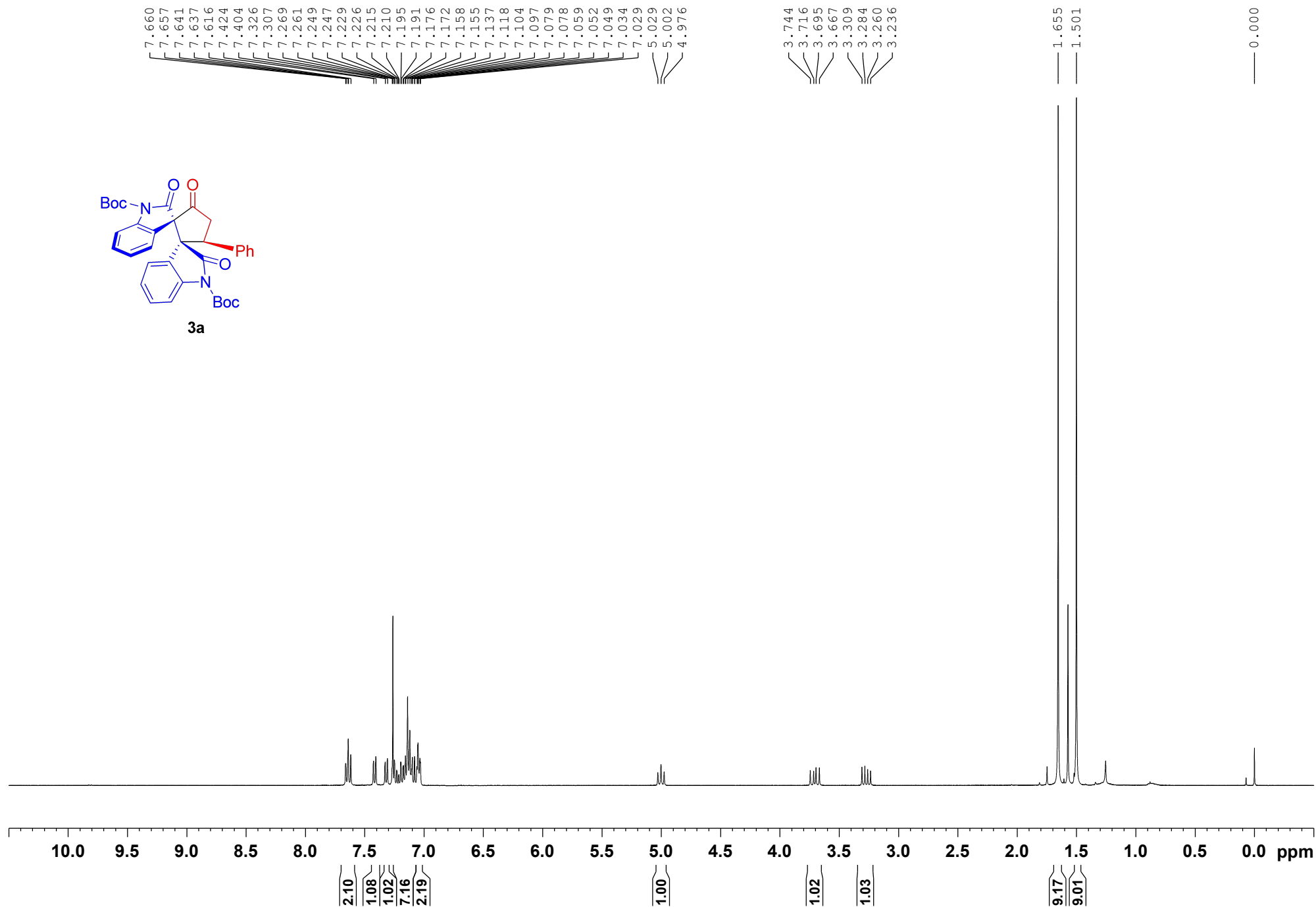
Refinement model description

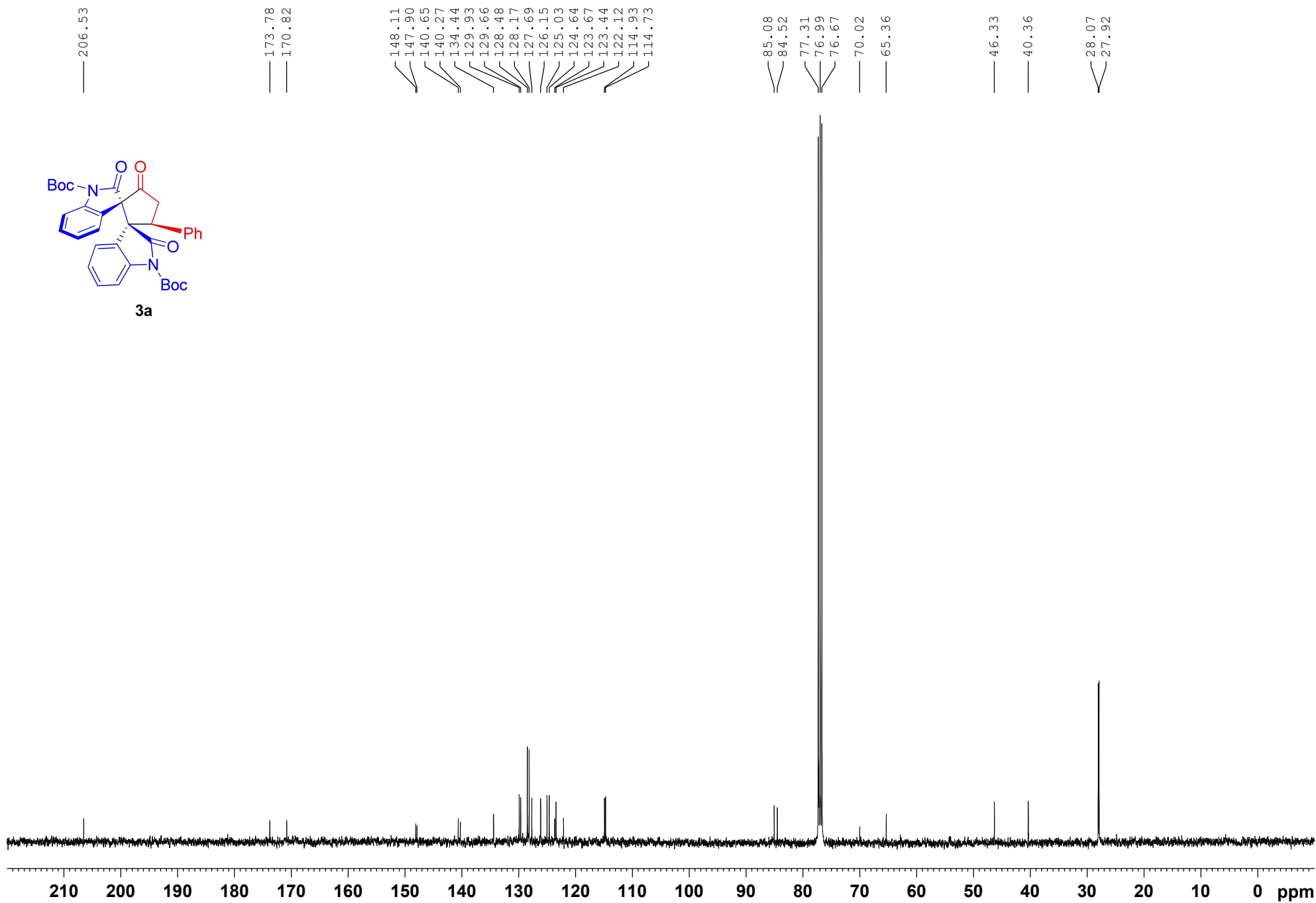
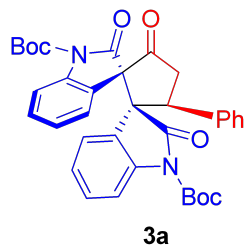
Number of restraints - 32, number of constraints - unknown.

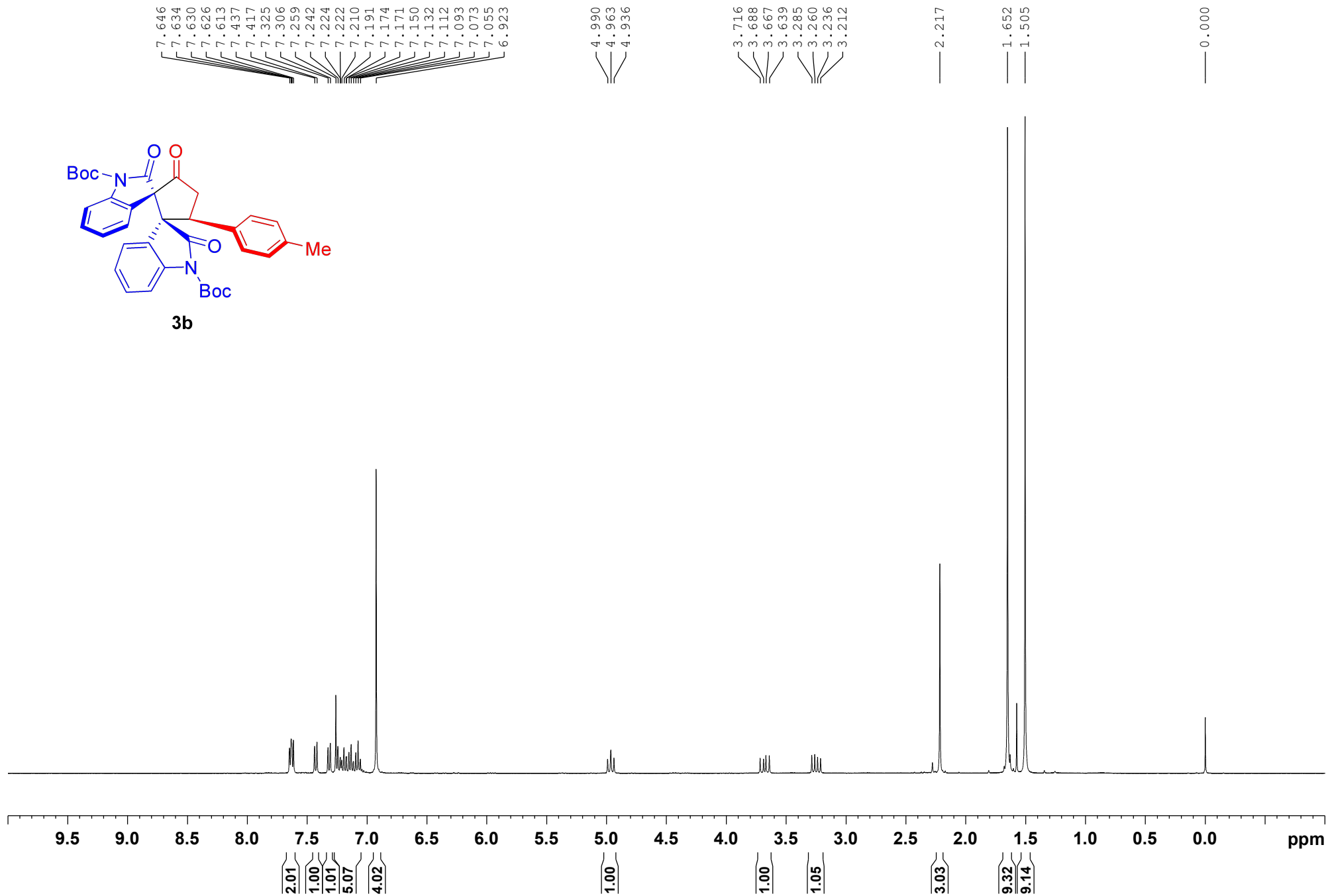
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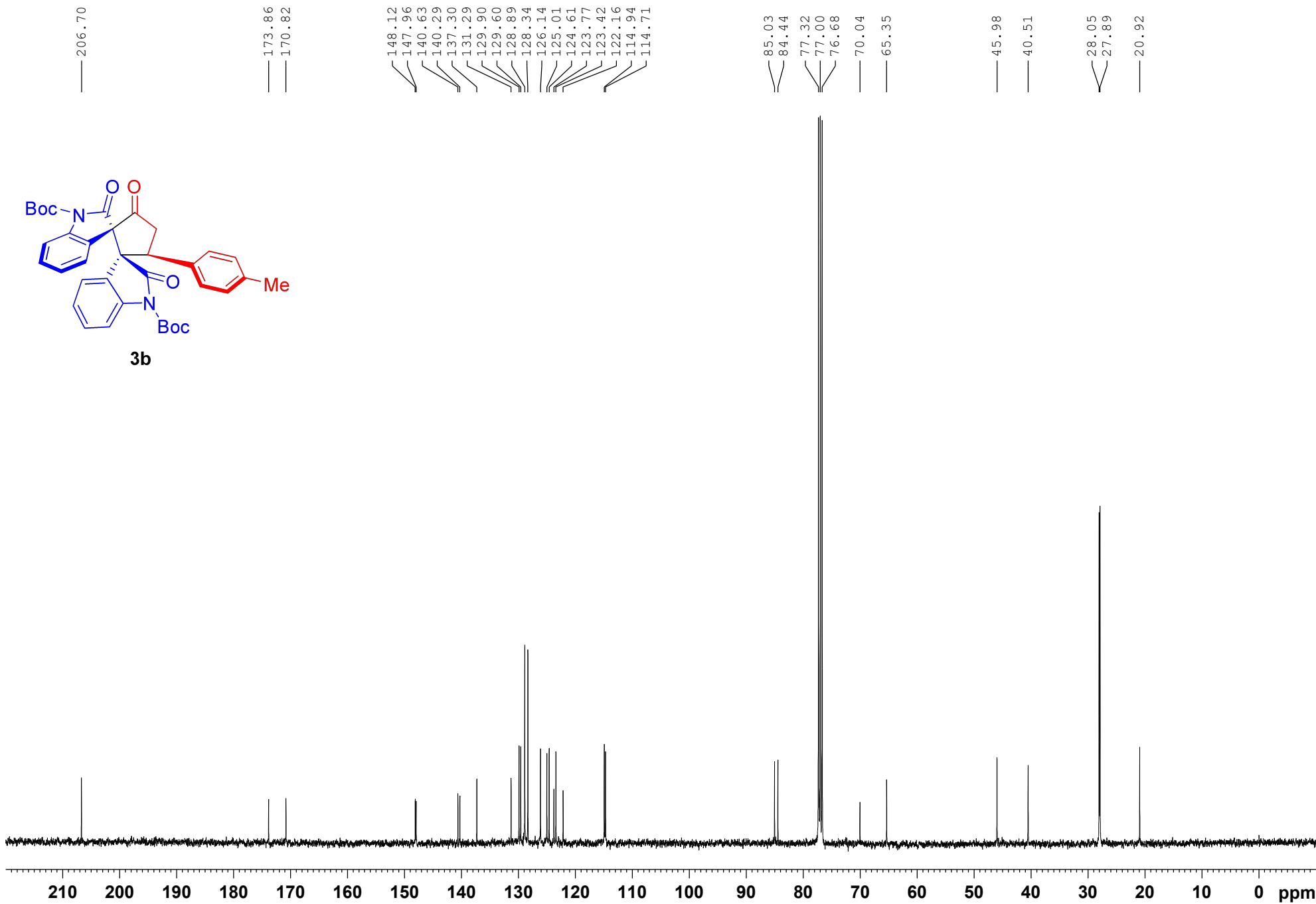
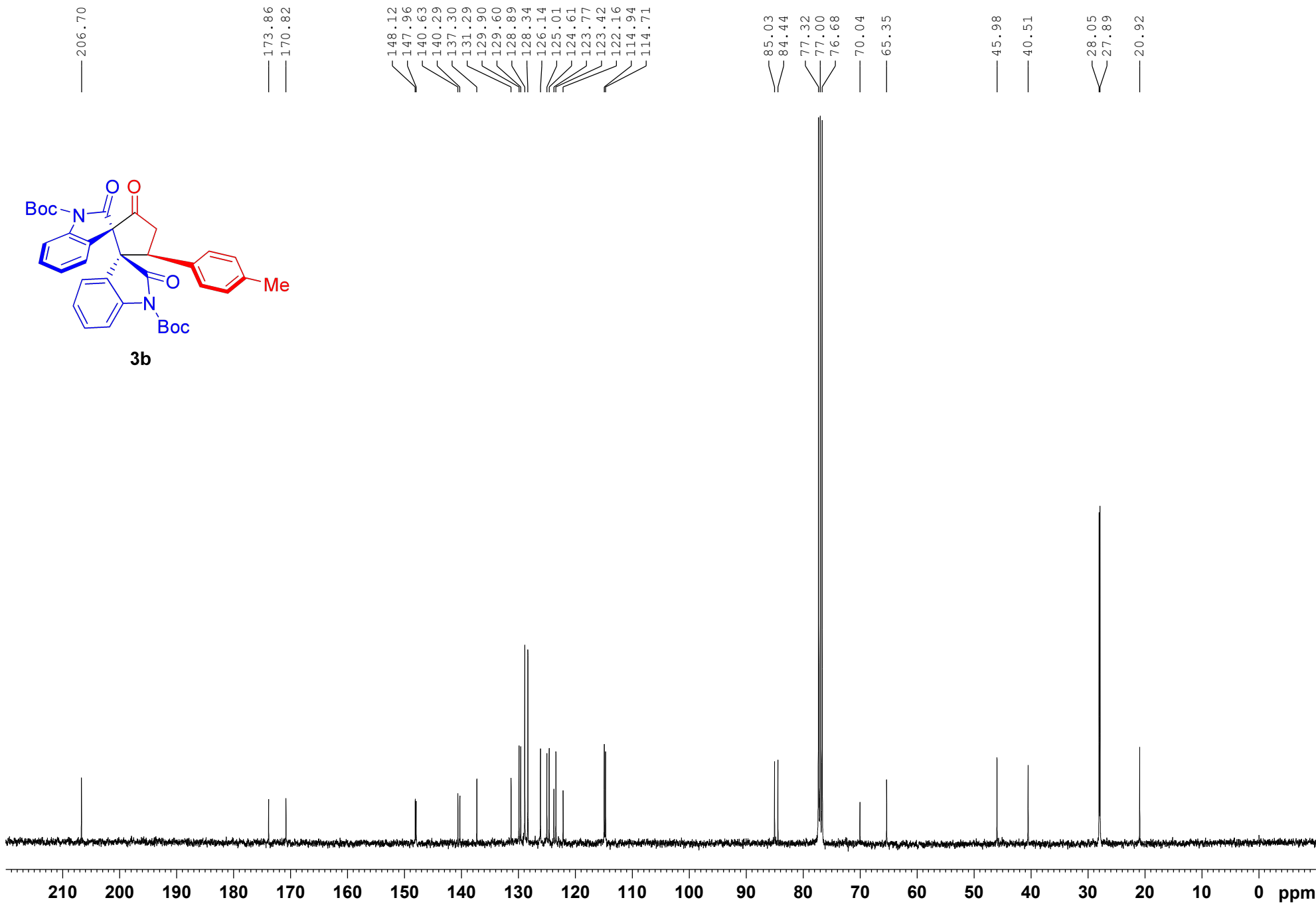
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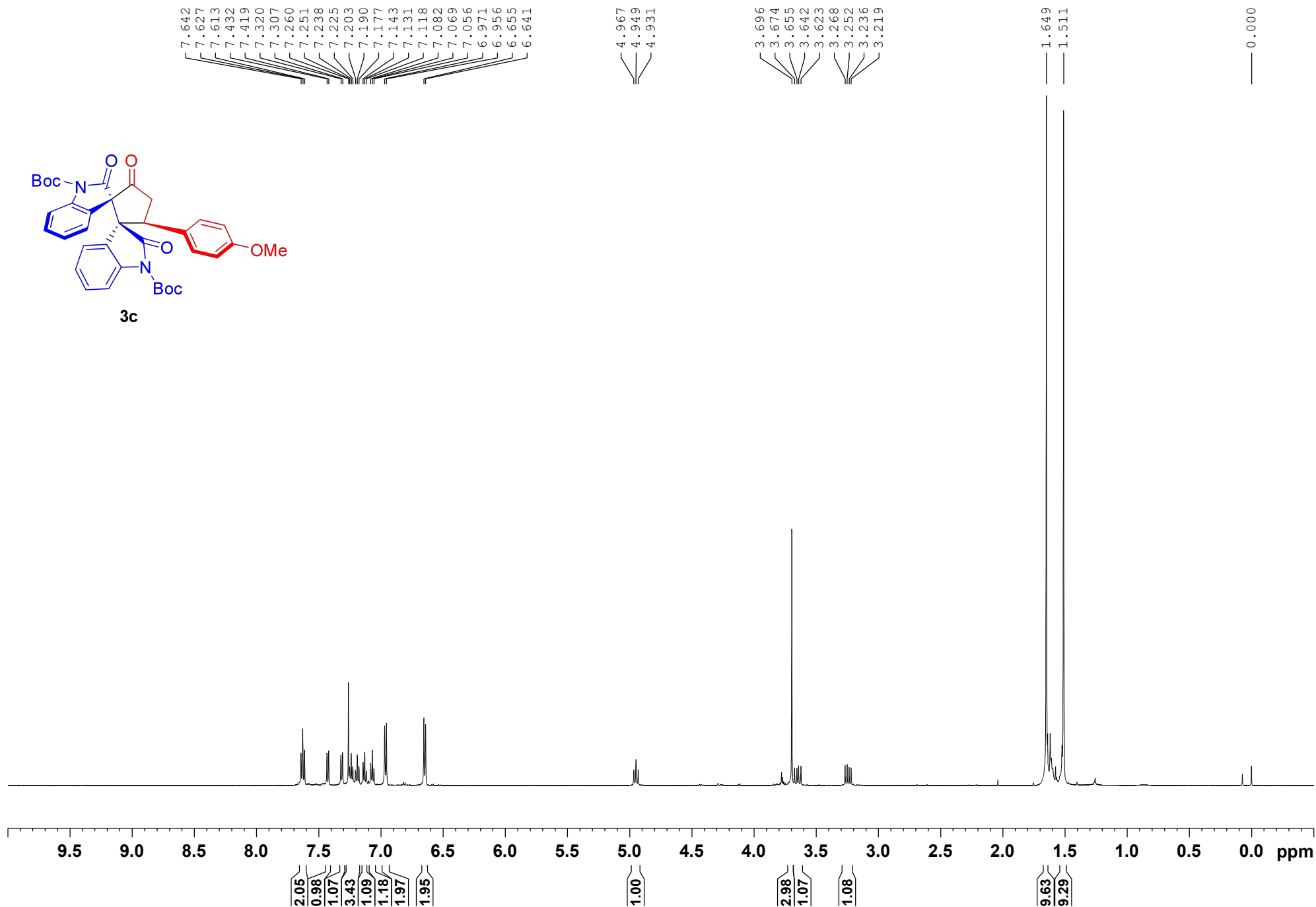
This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please [let us know](#) if there are any errors or if you would like to have additional features.

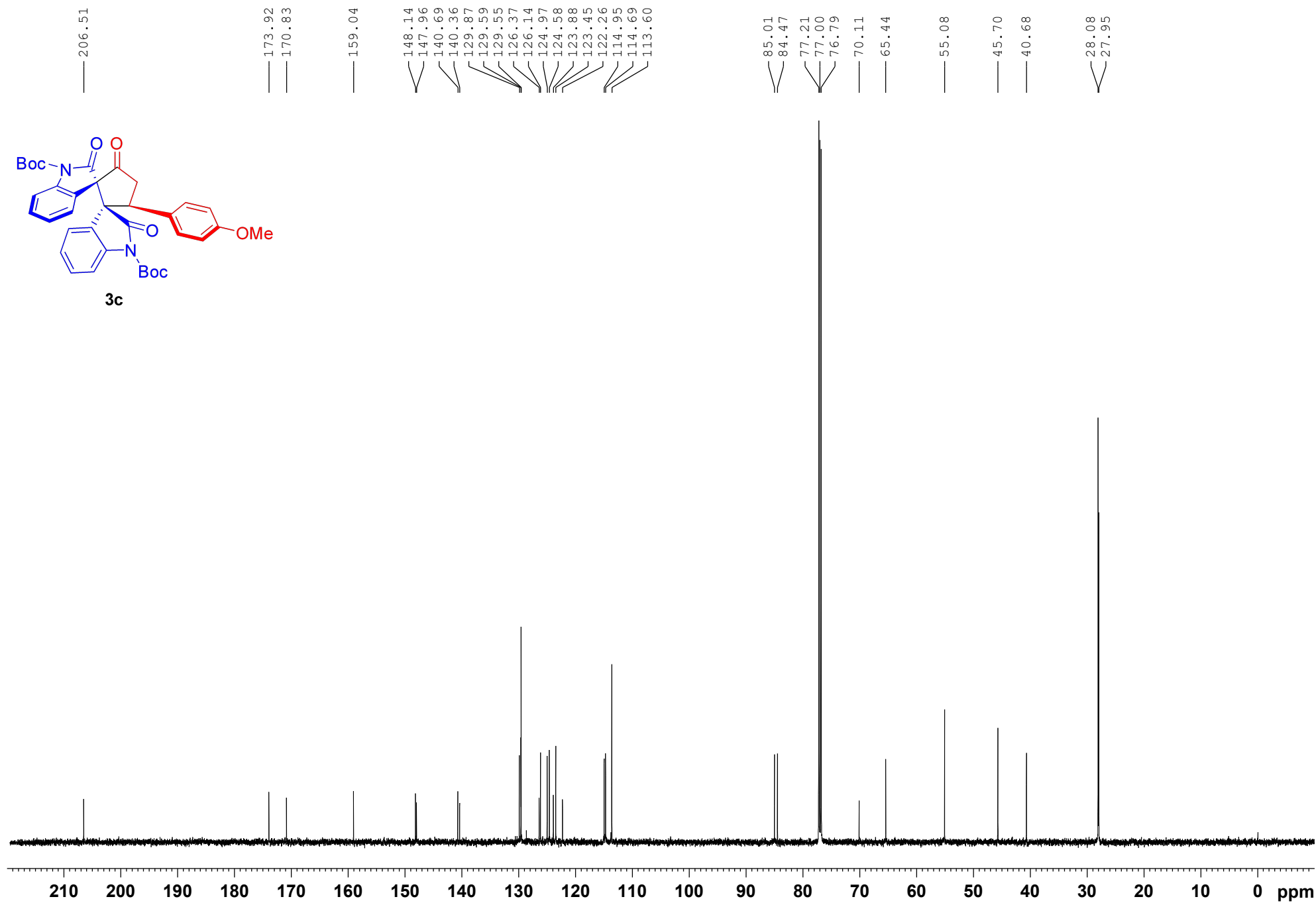
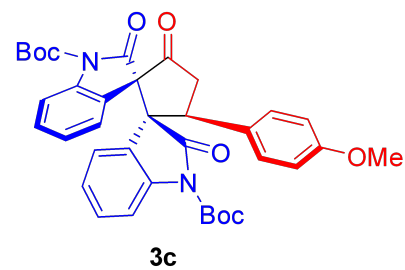


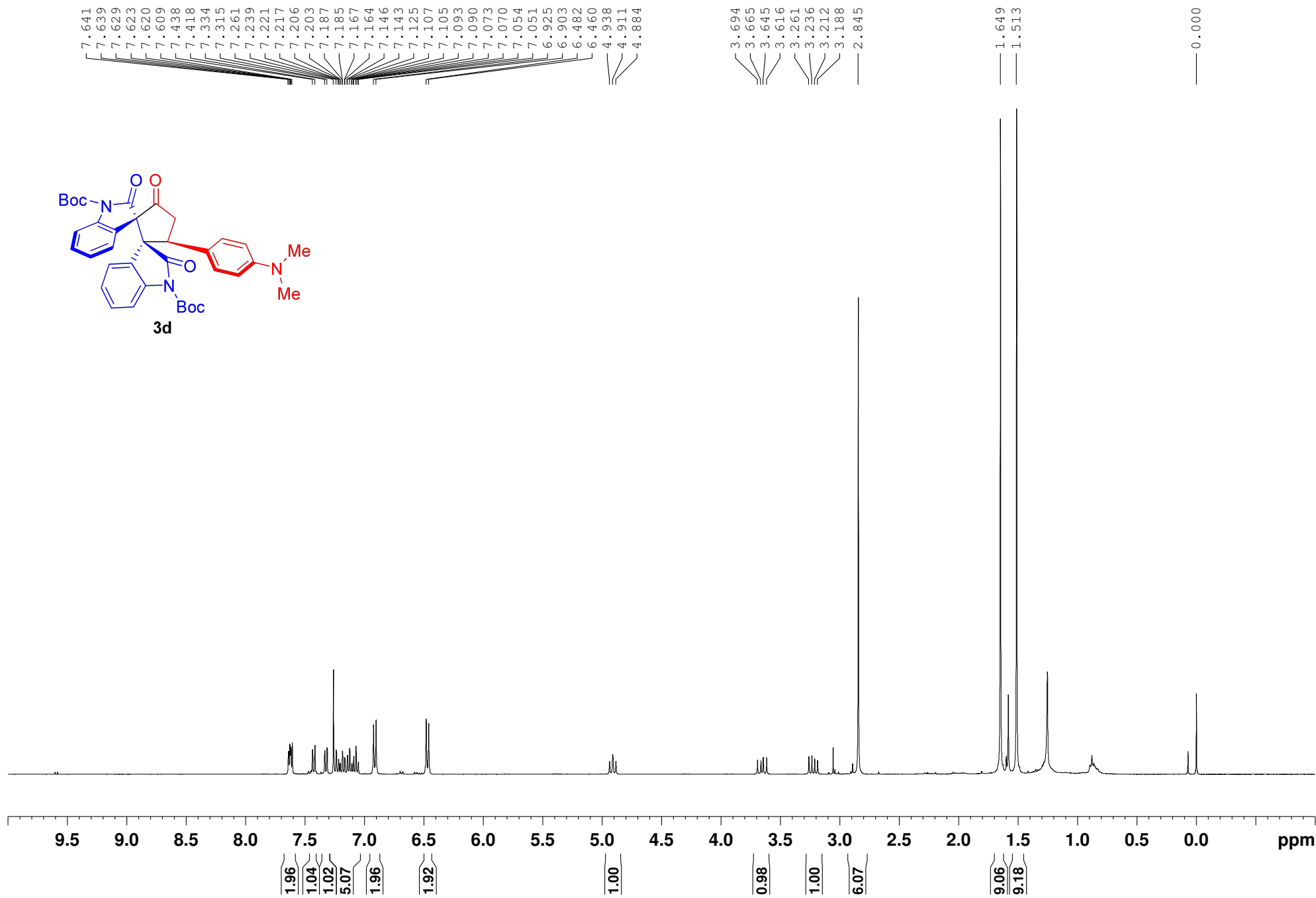


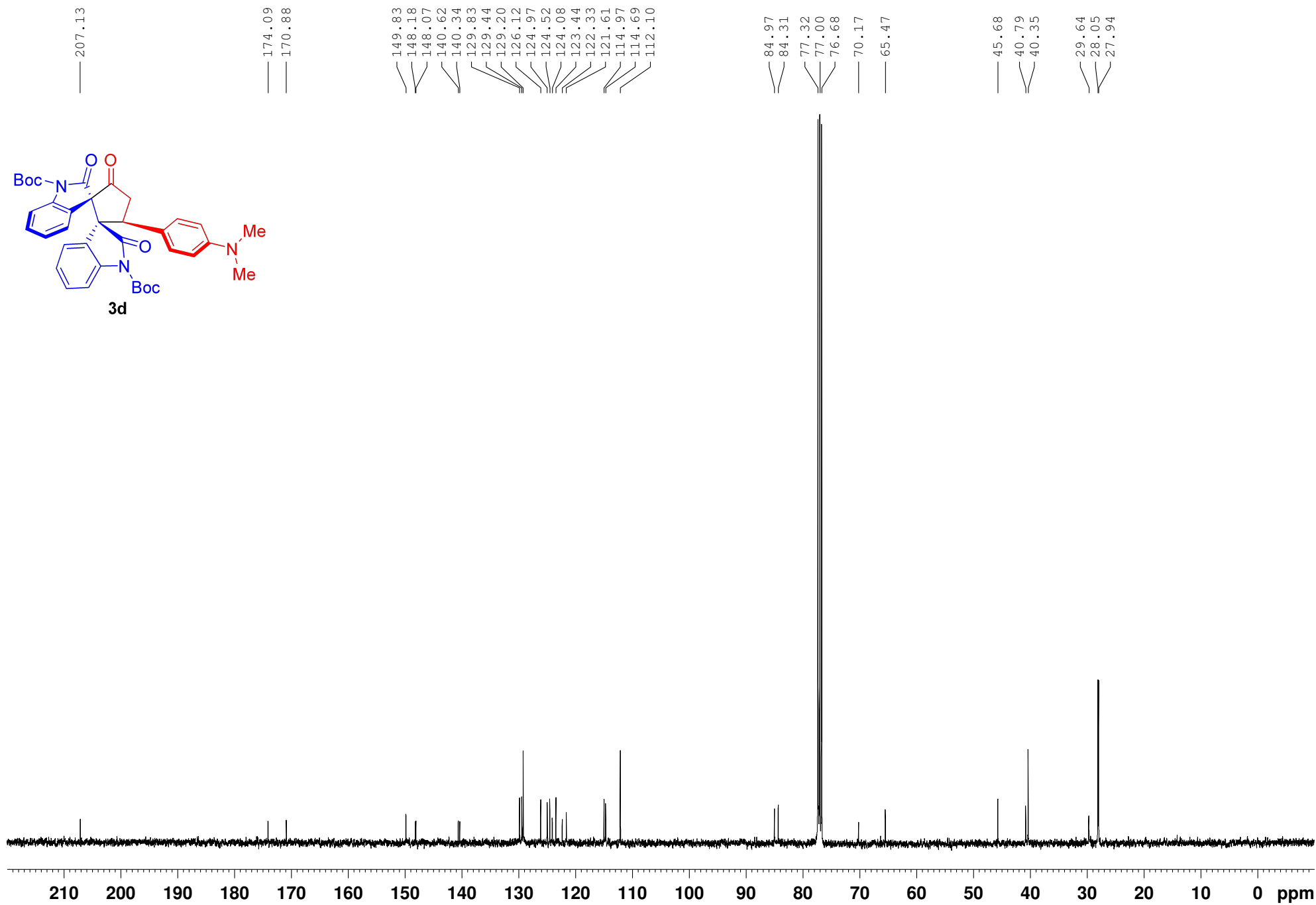
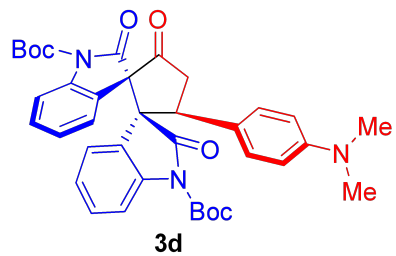


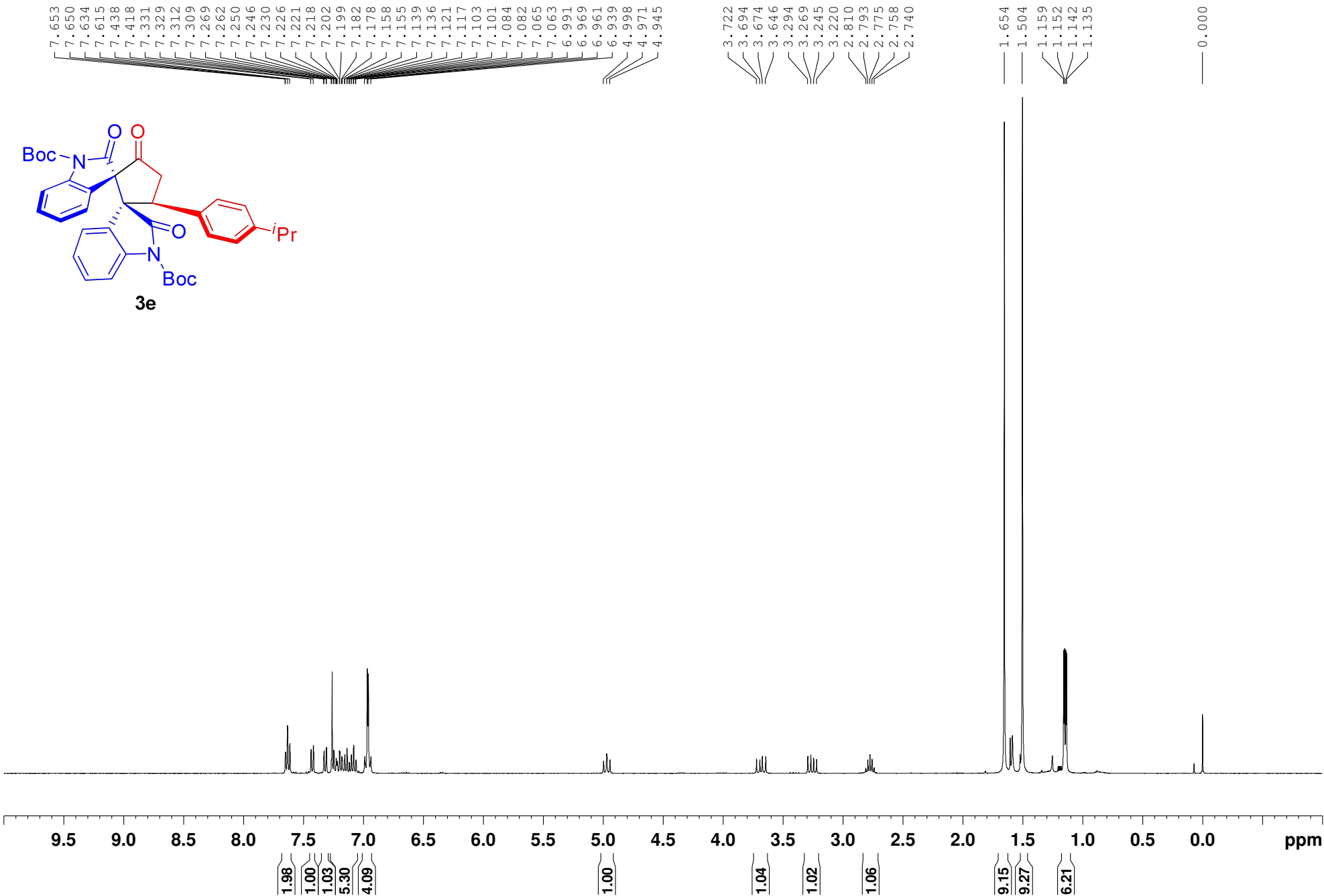


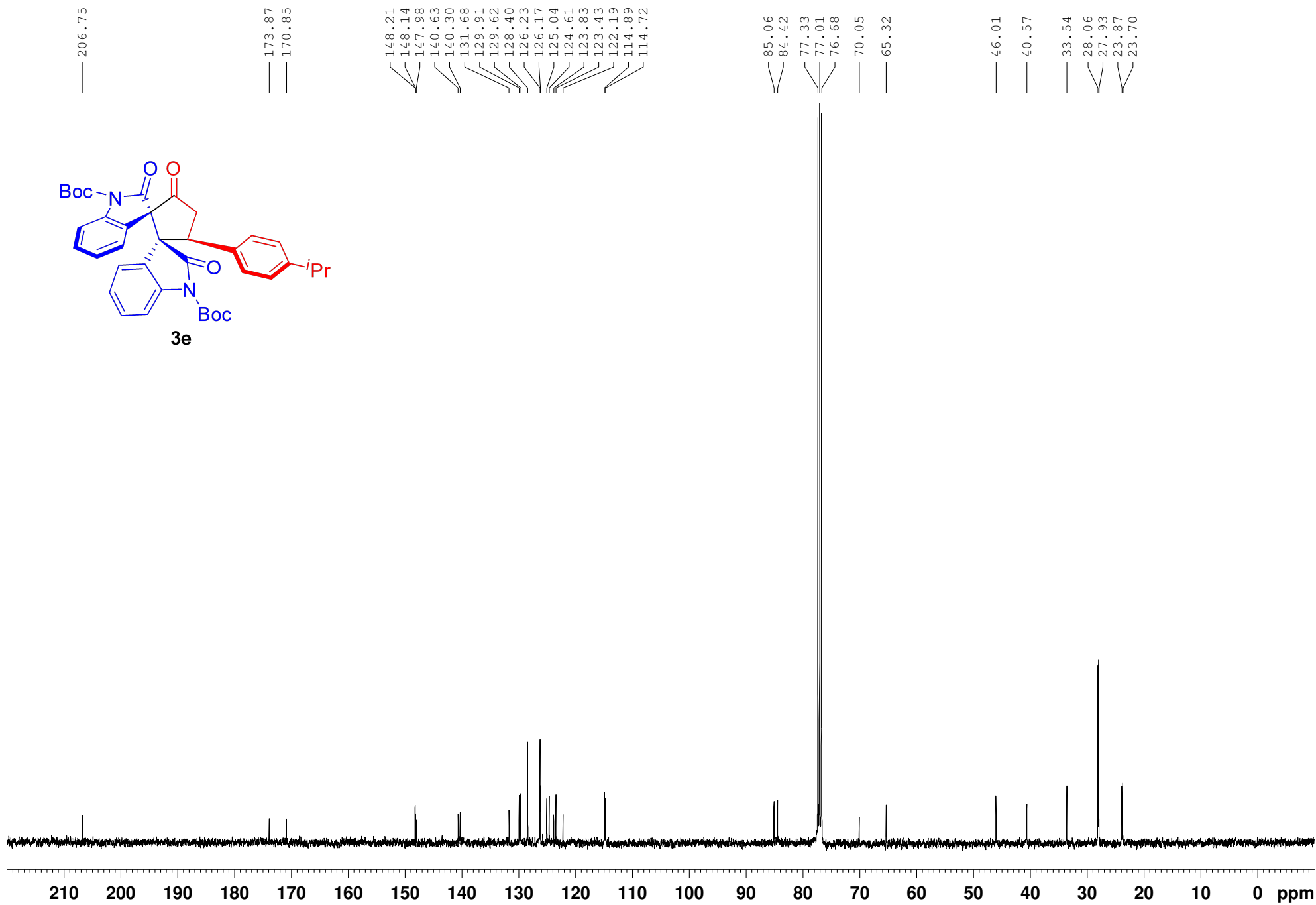
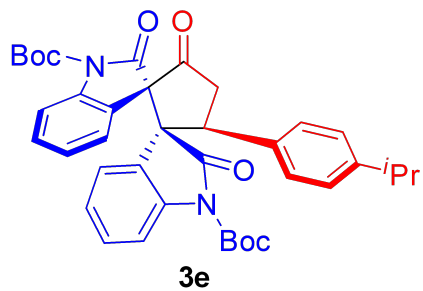


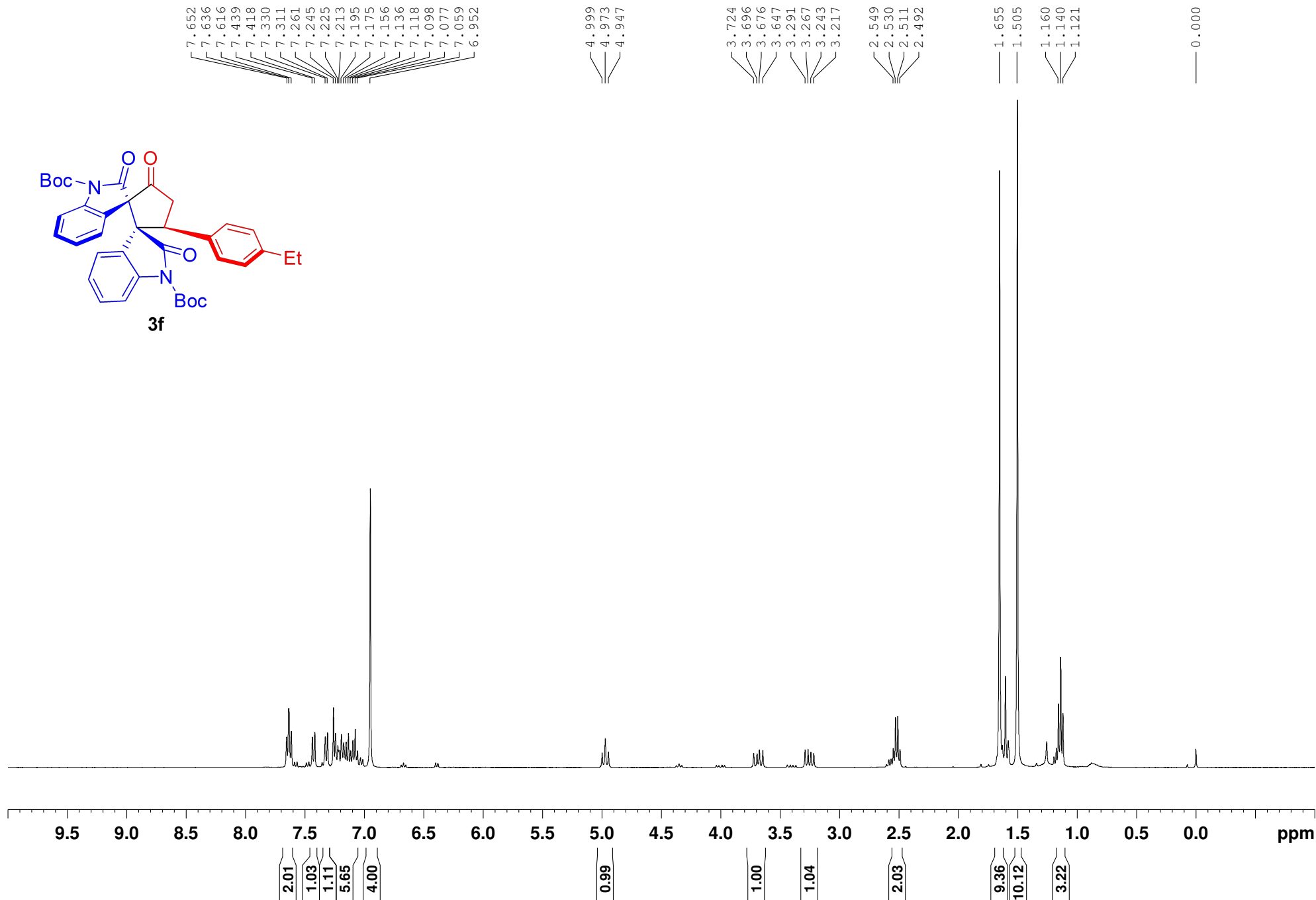


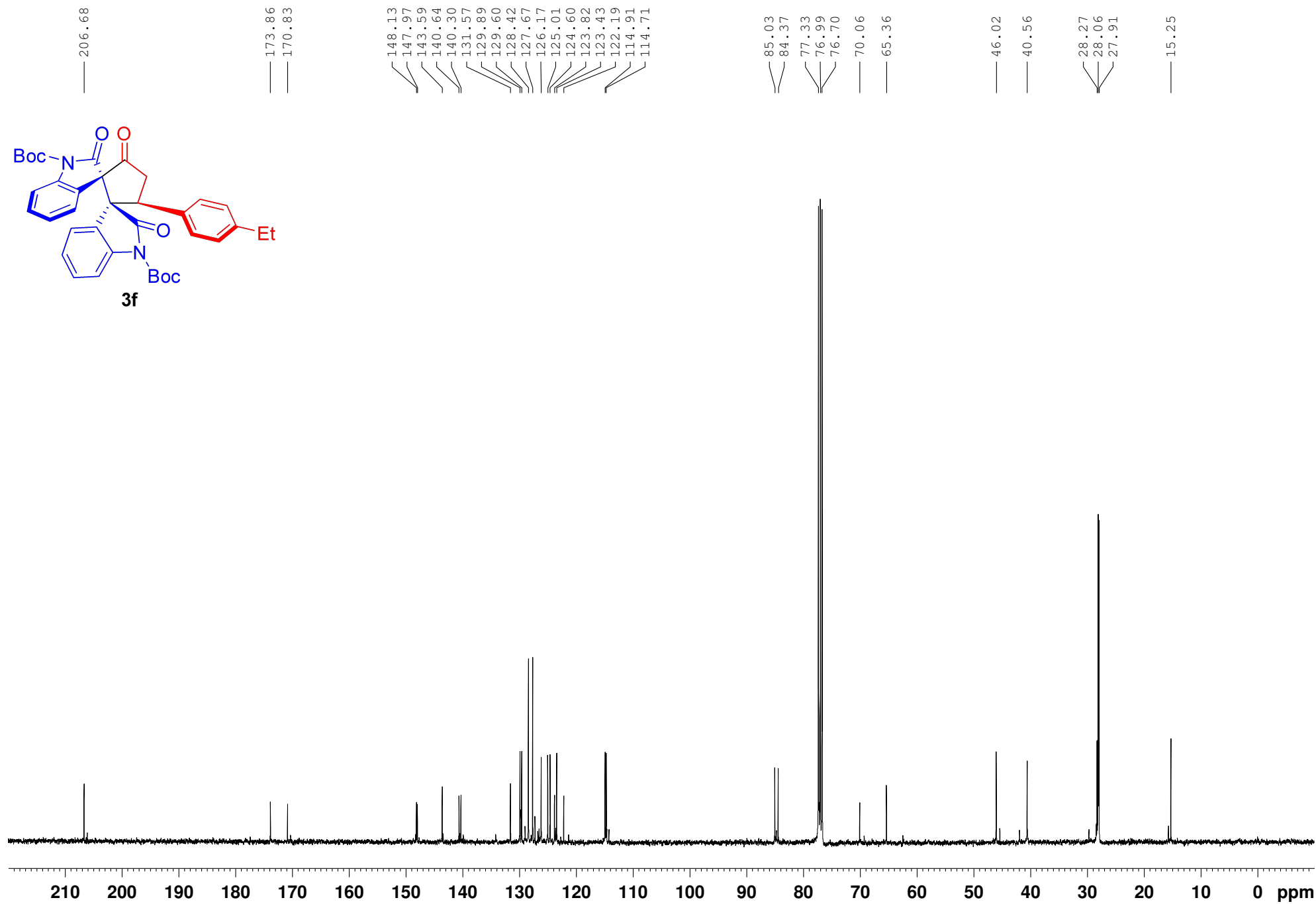
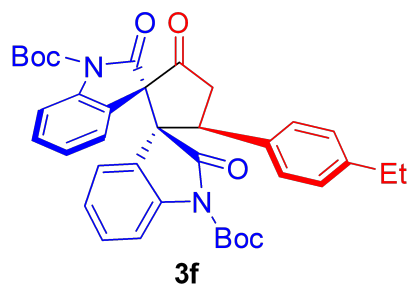


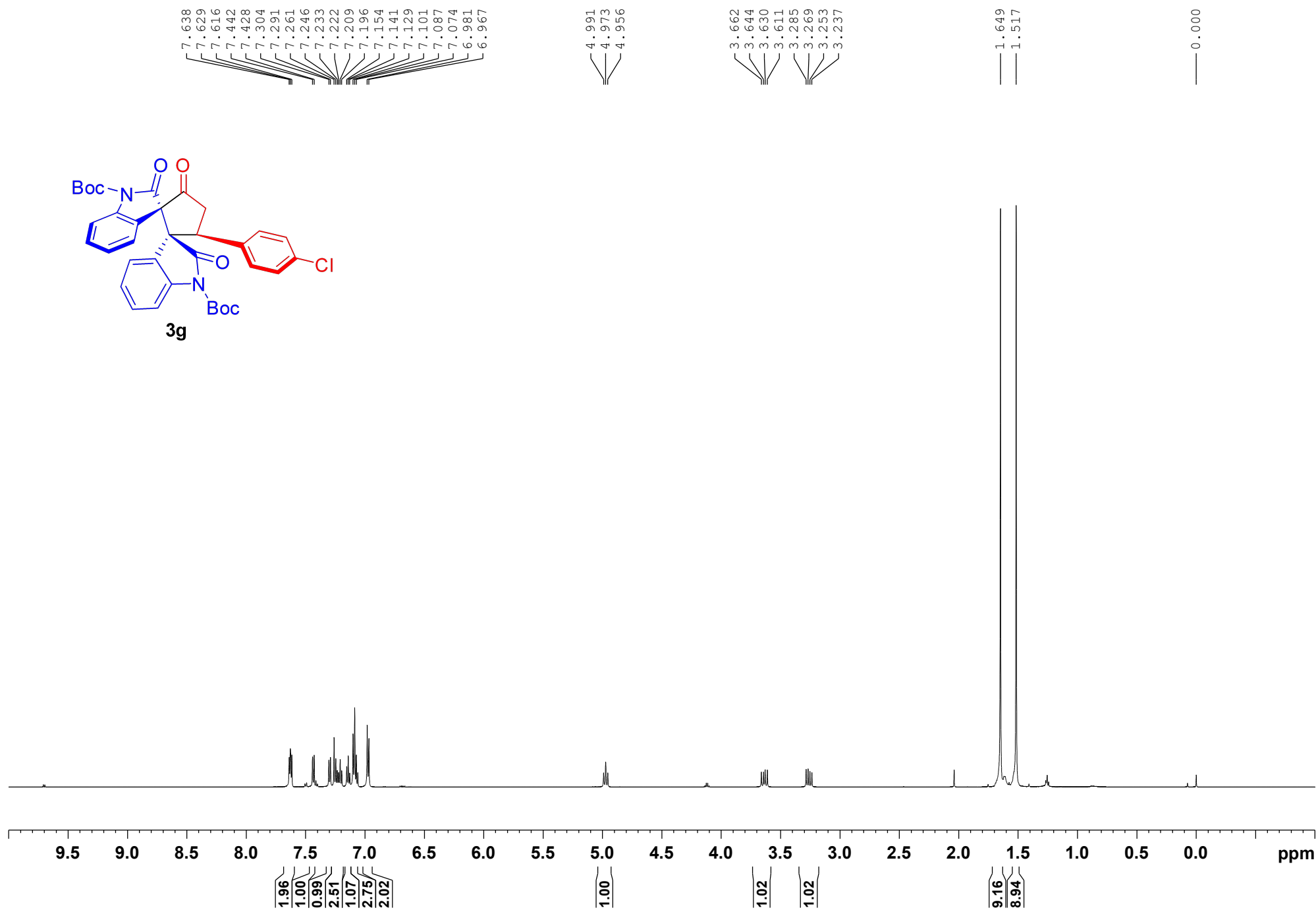


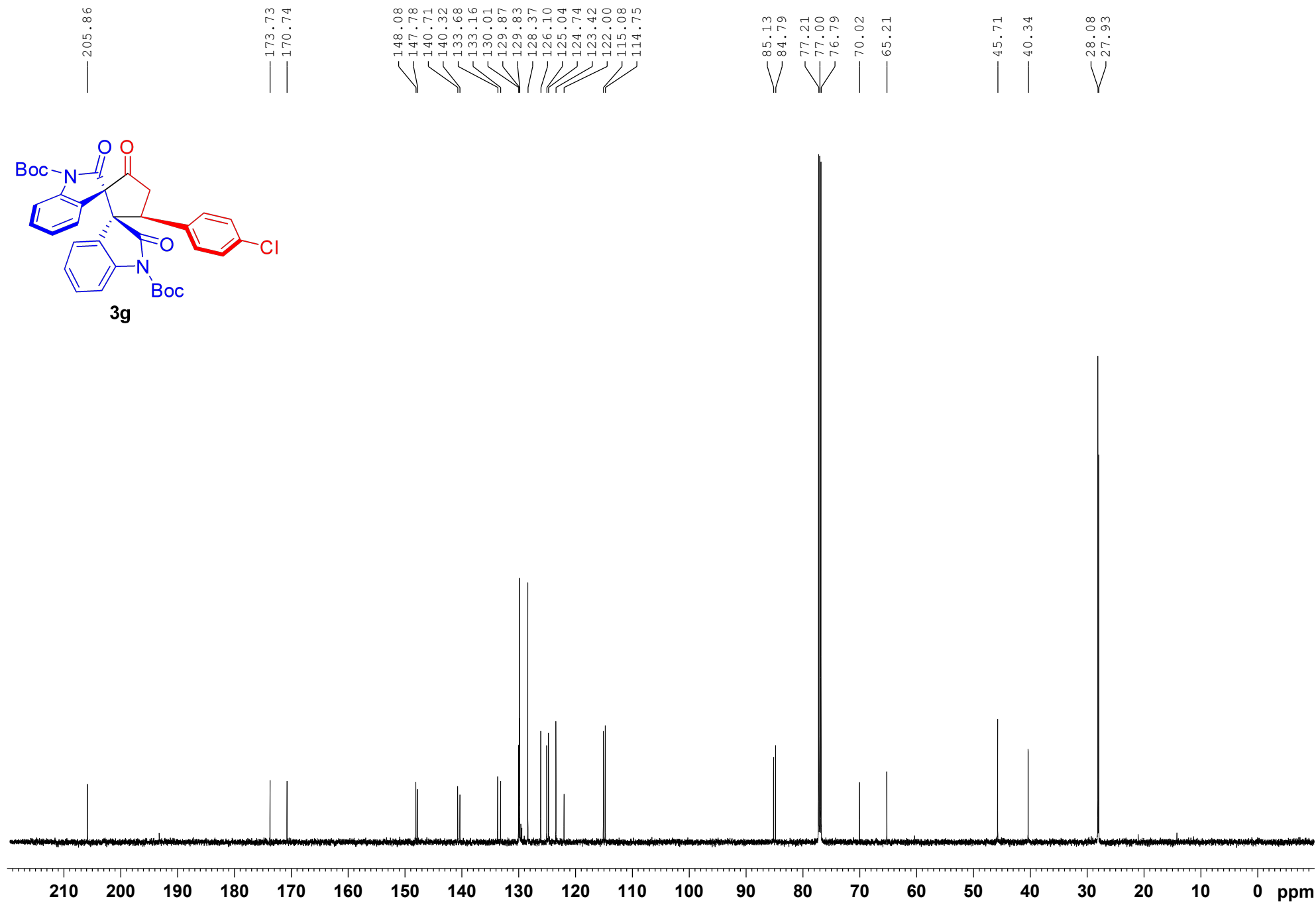
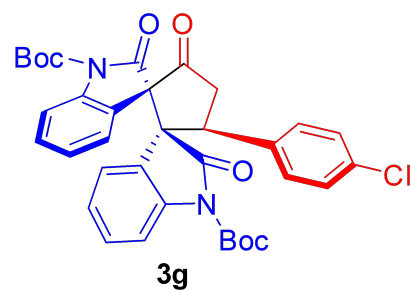


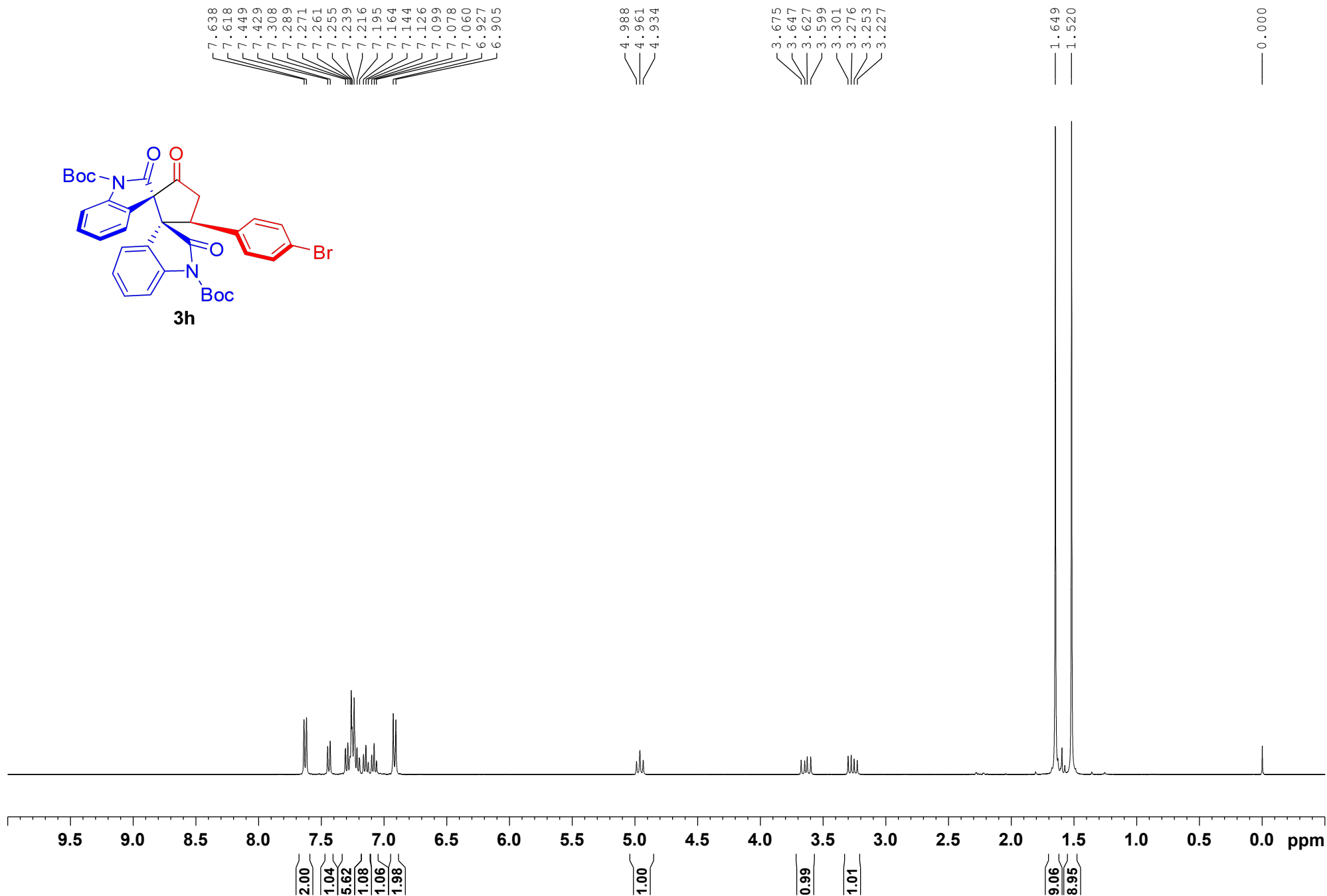
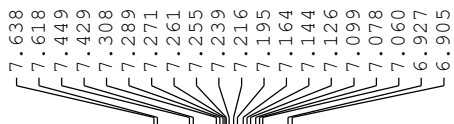


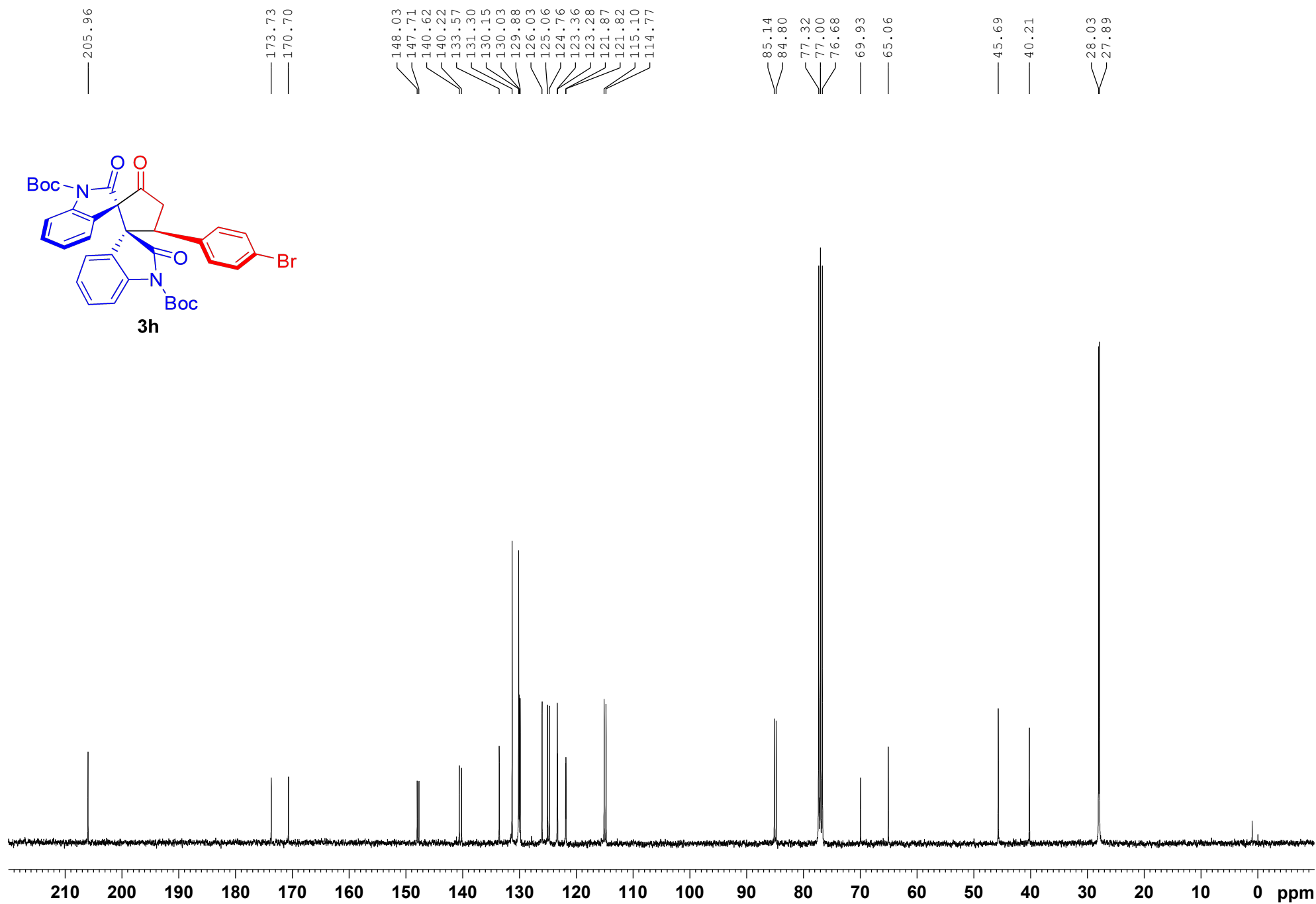
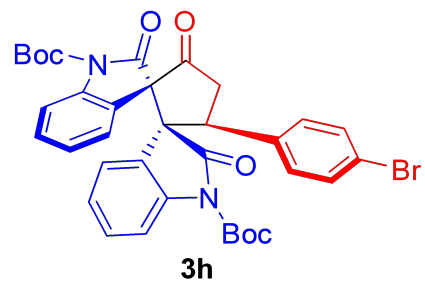


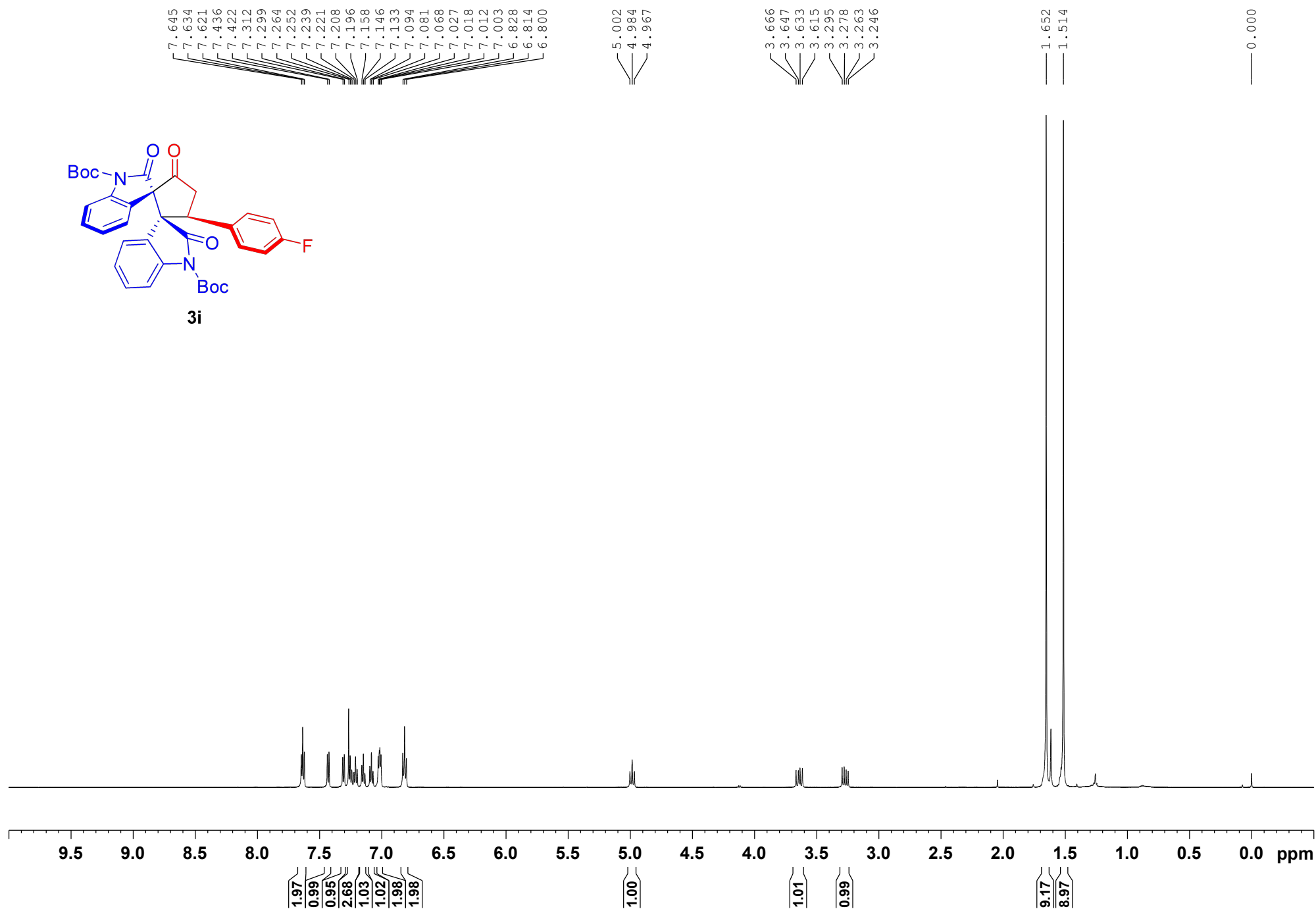


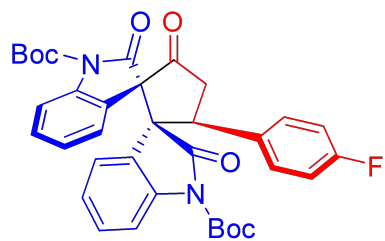




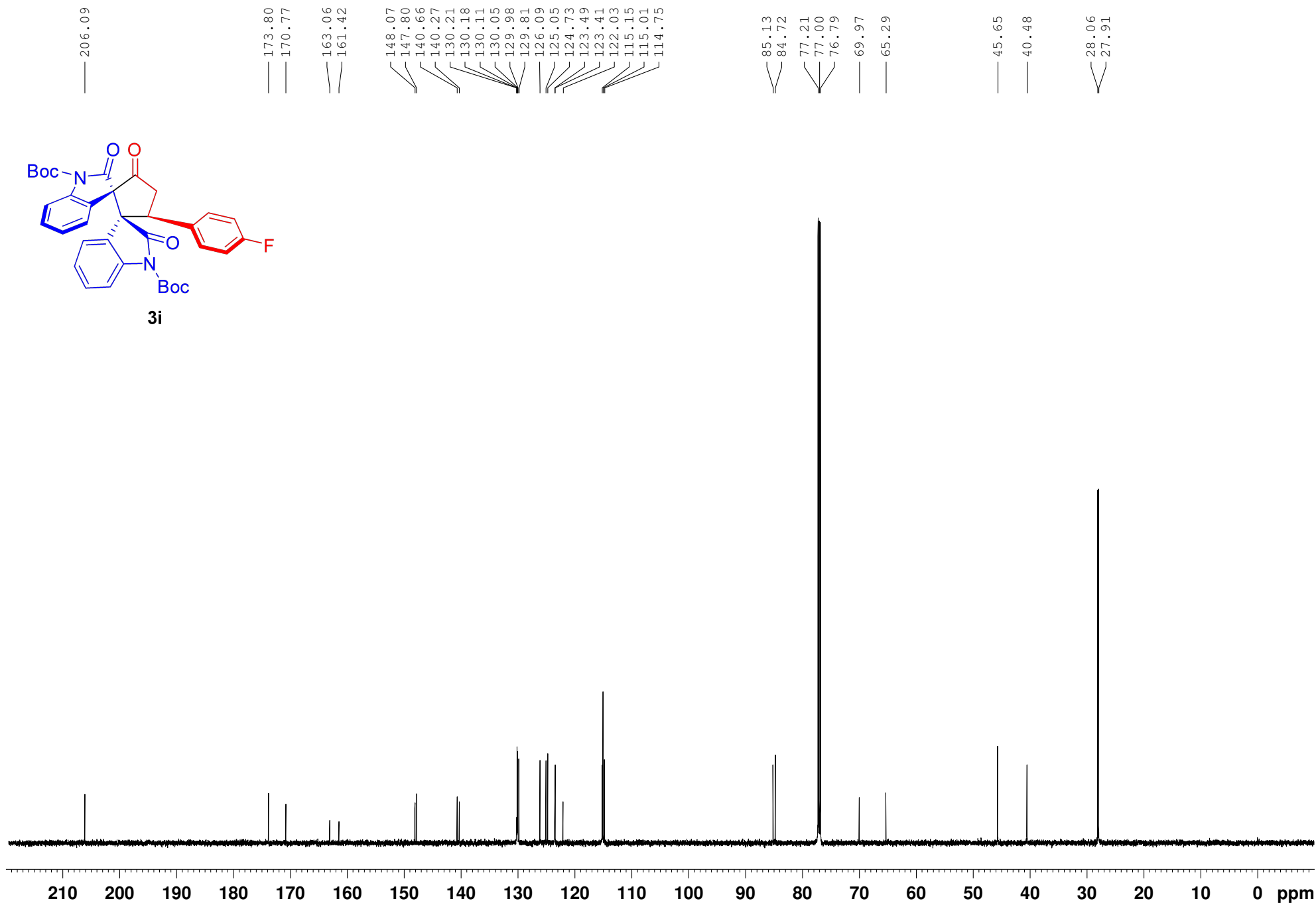


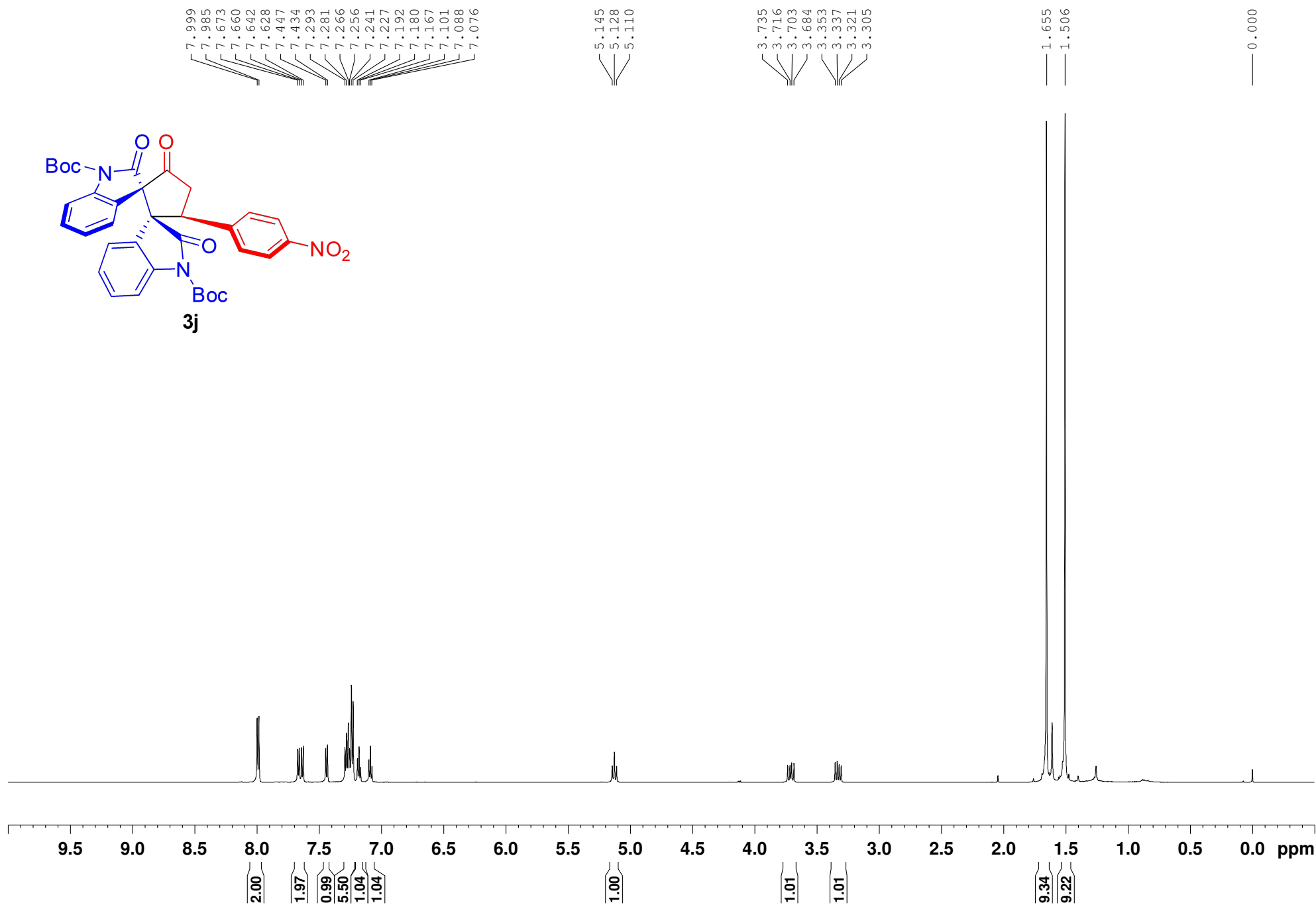


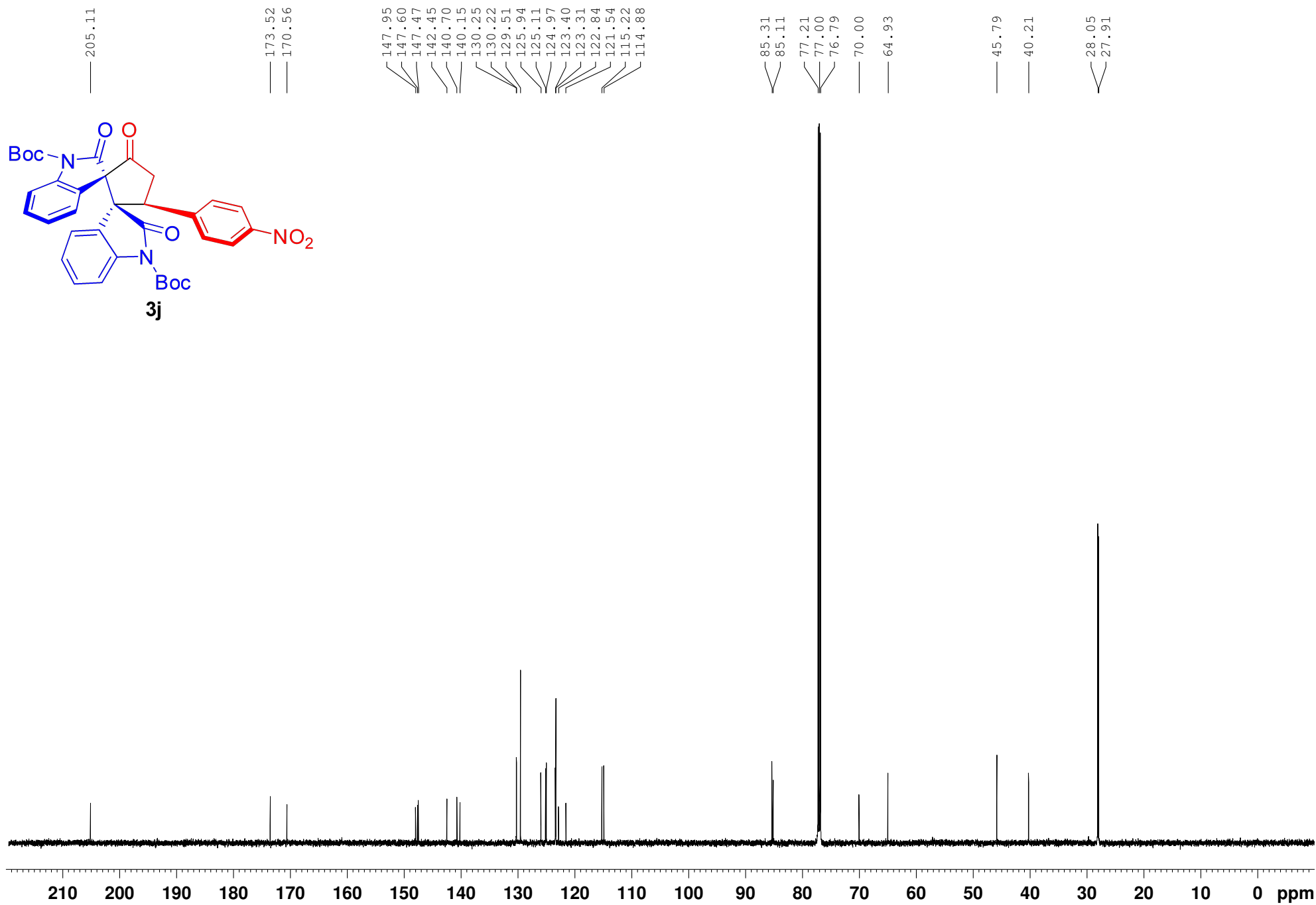
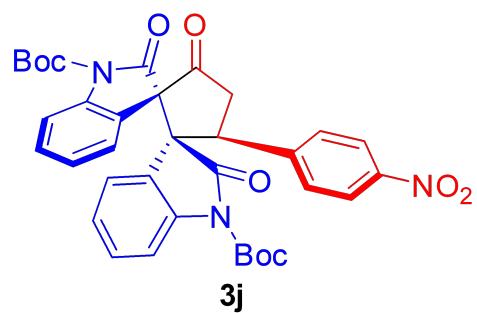


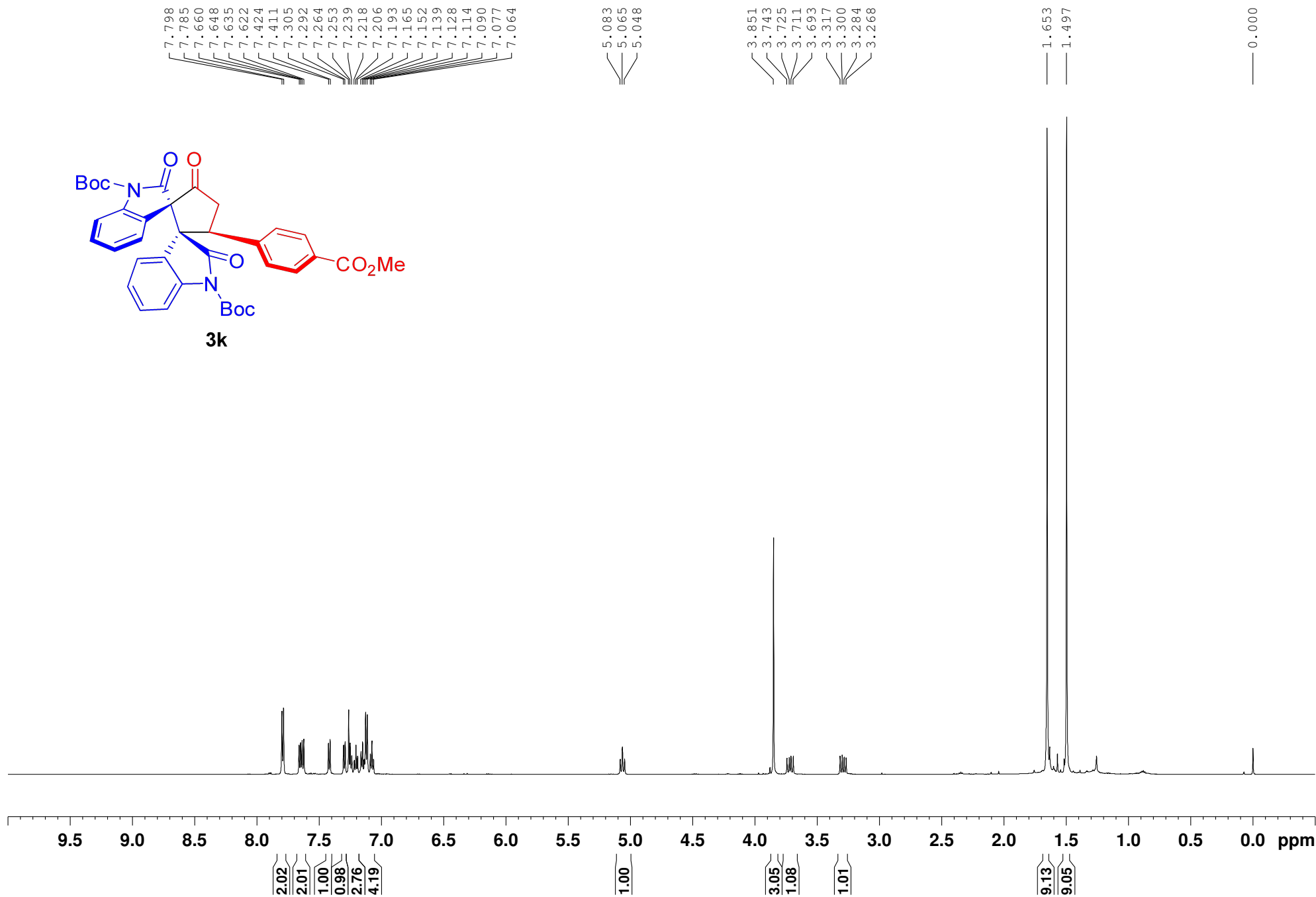


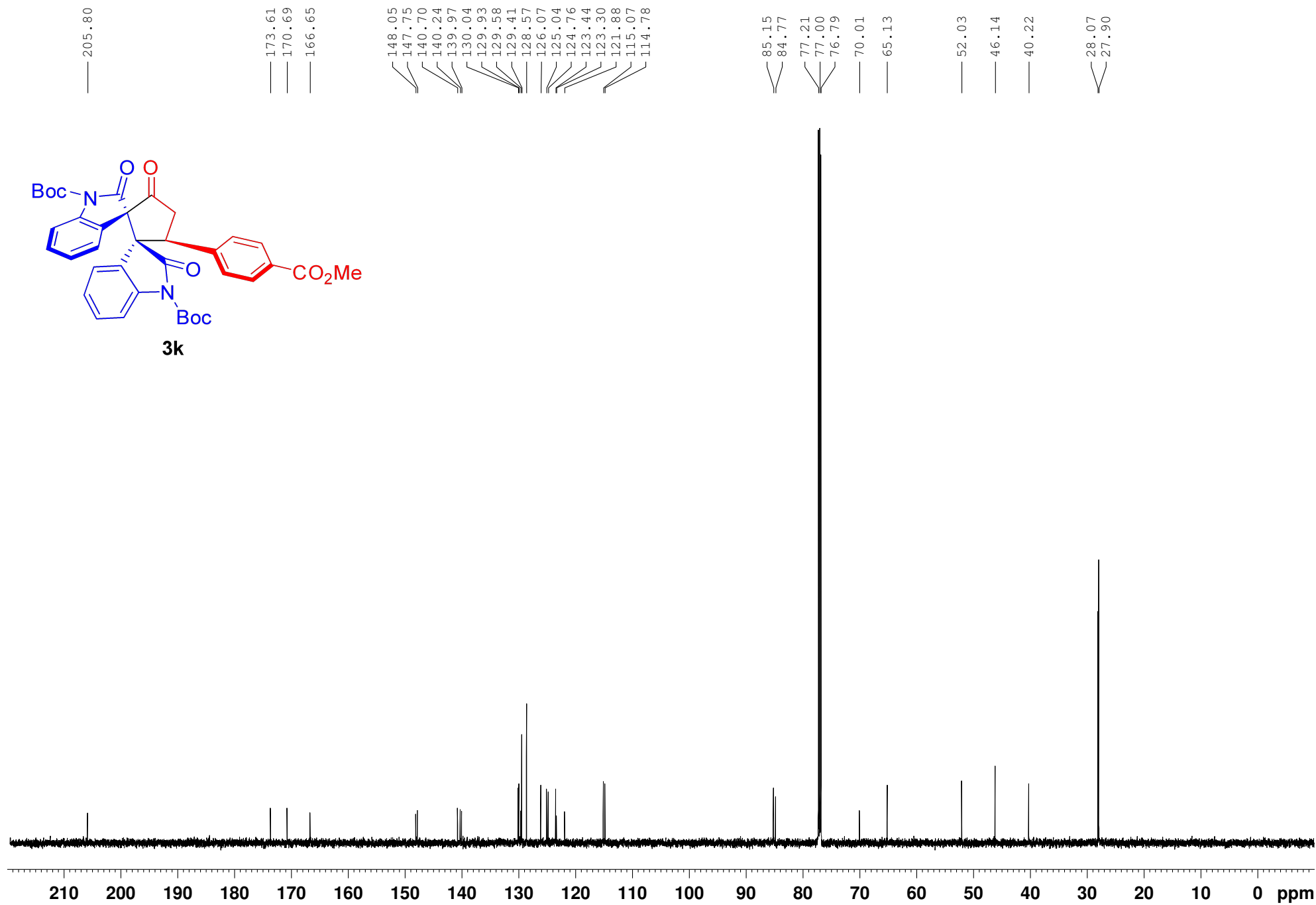
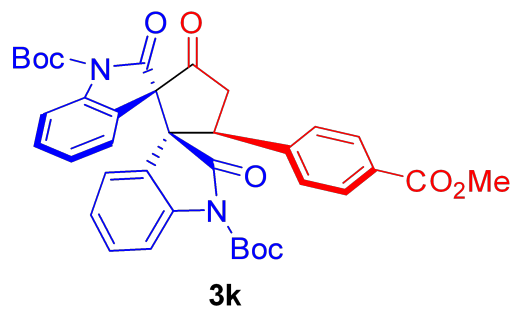
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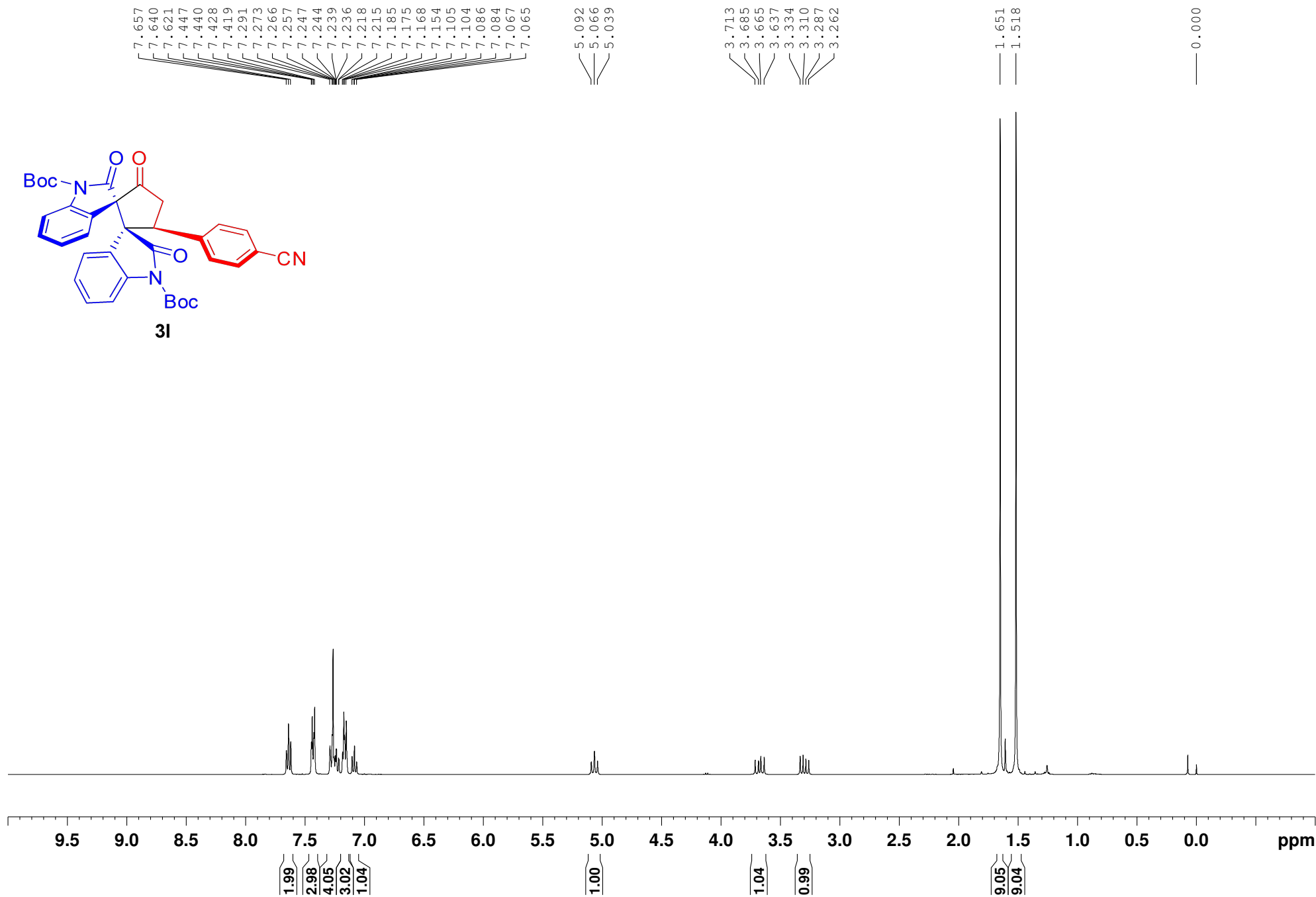


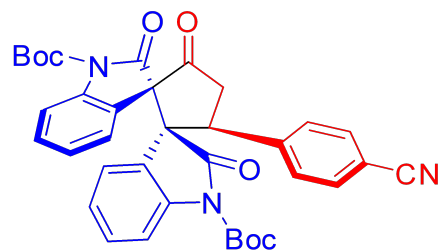




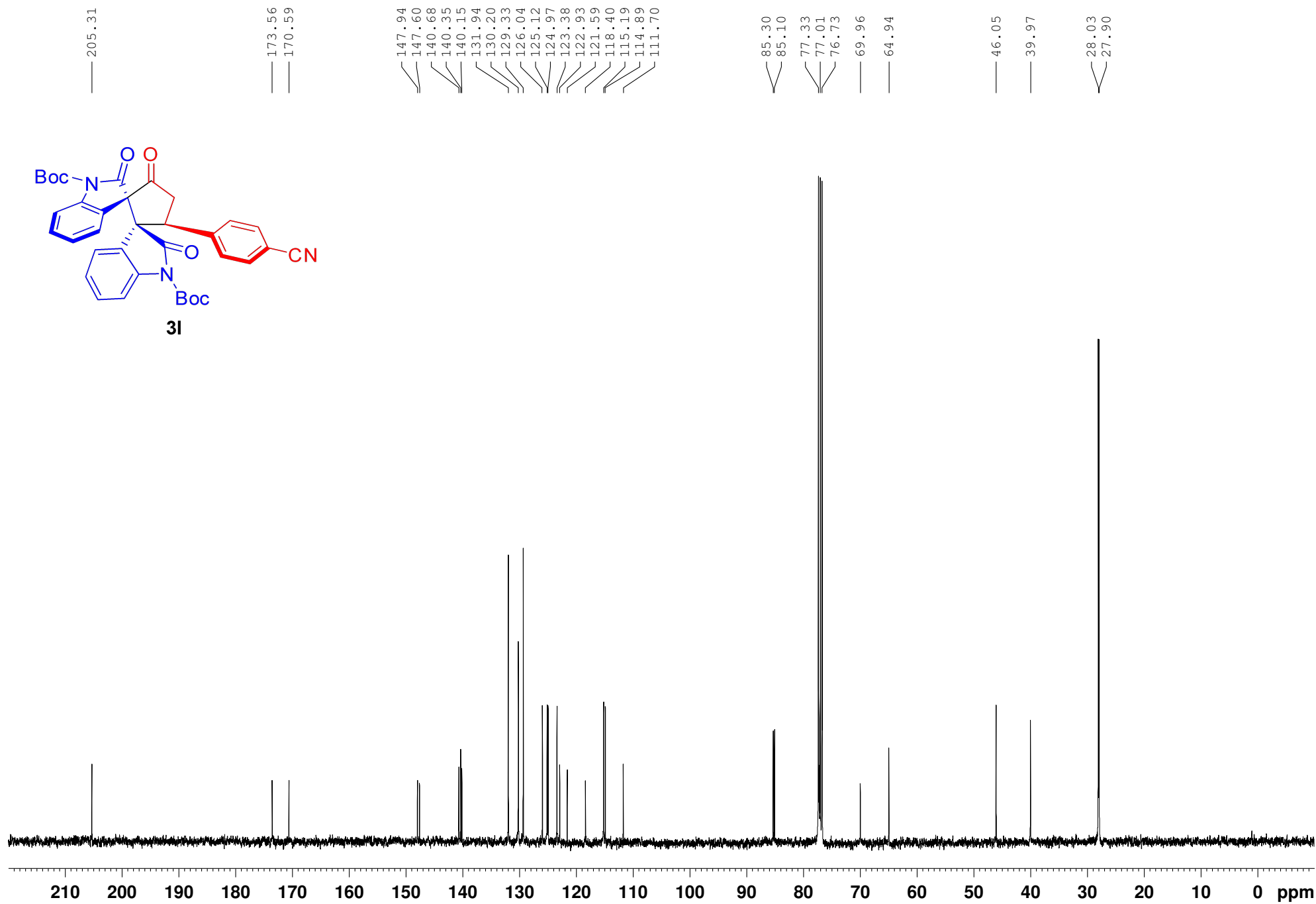


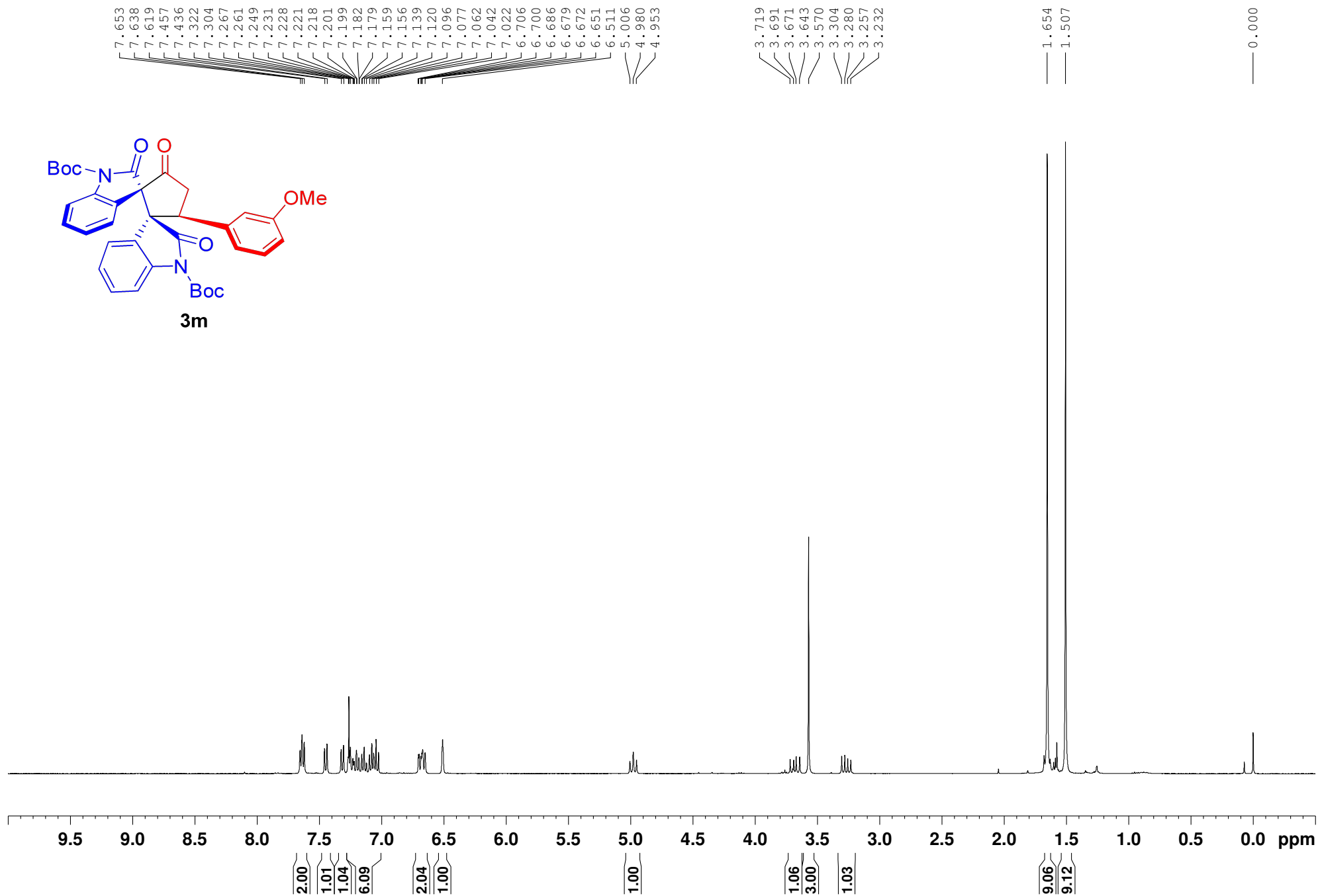


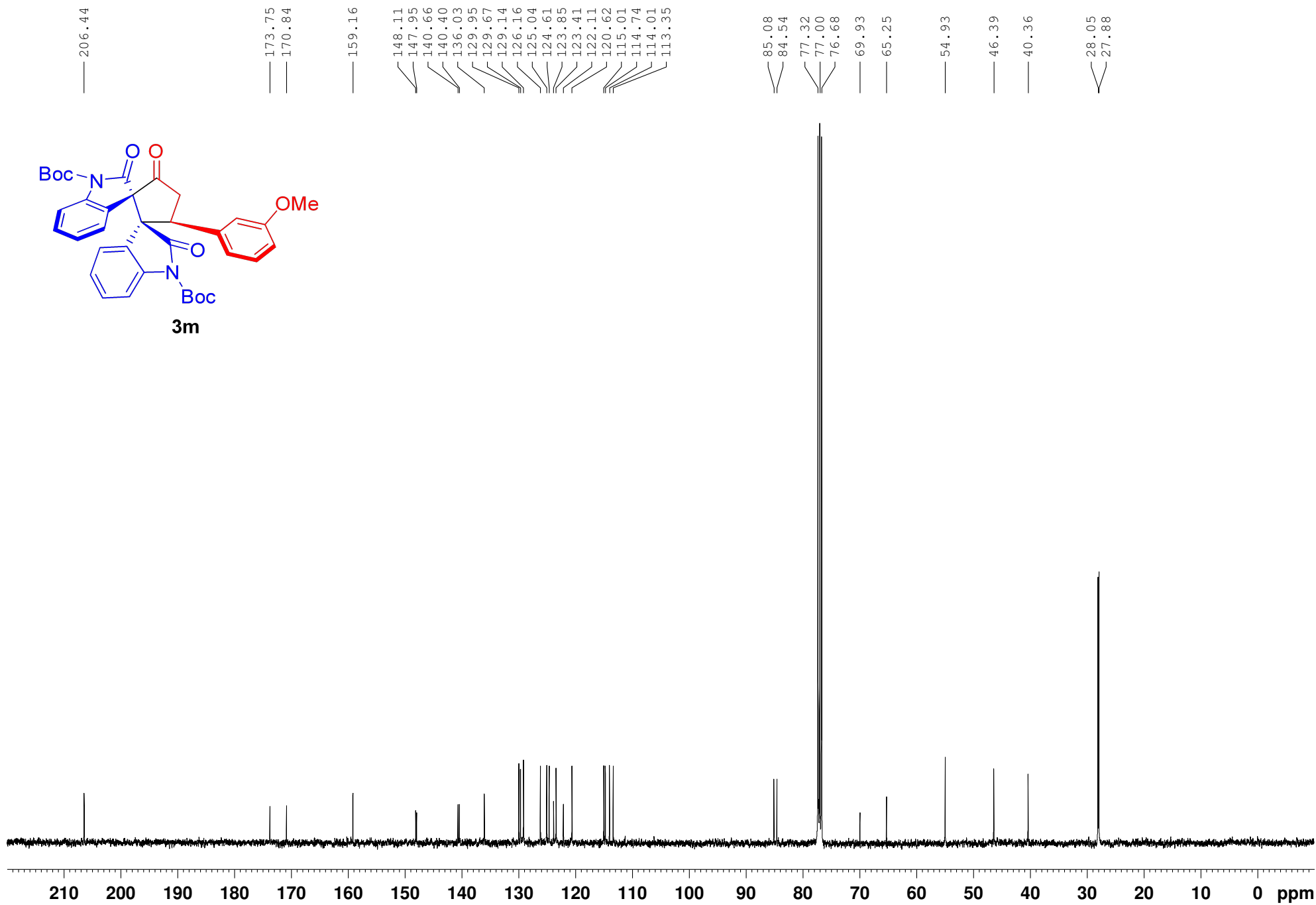
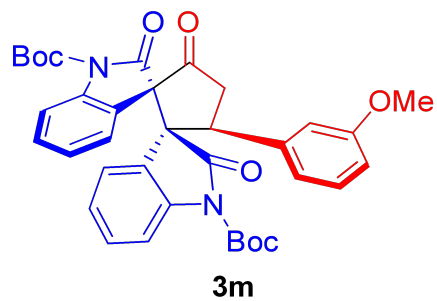


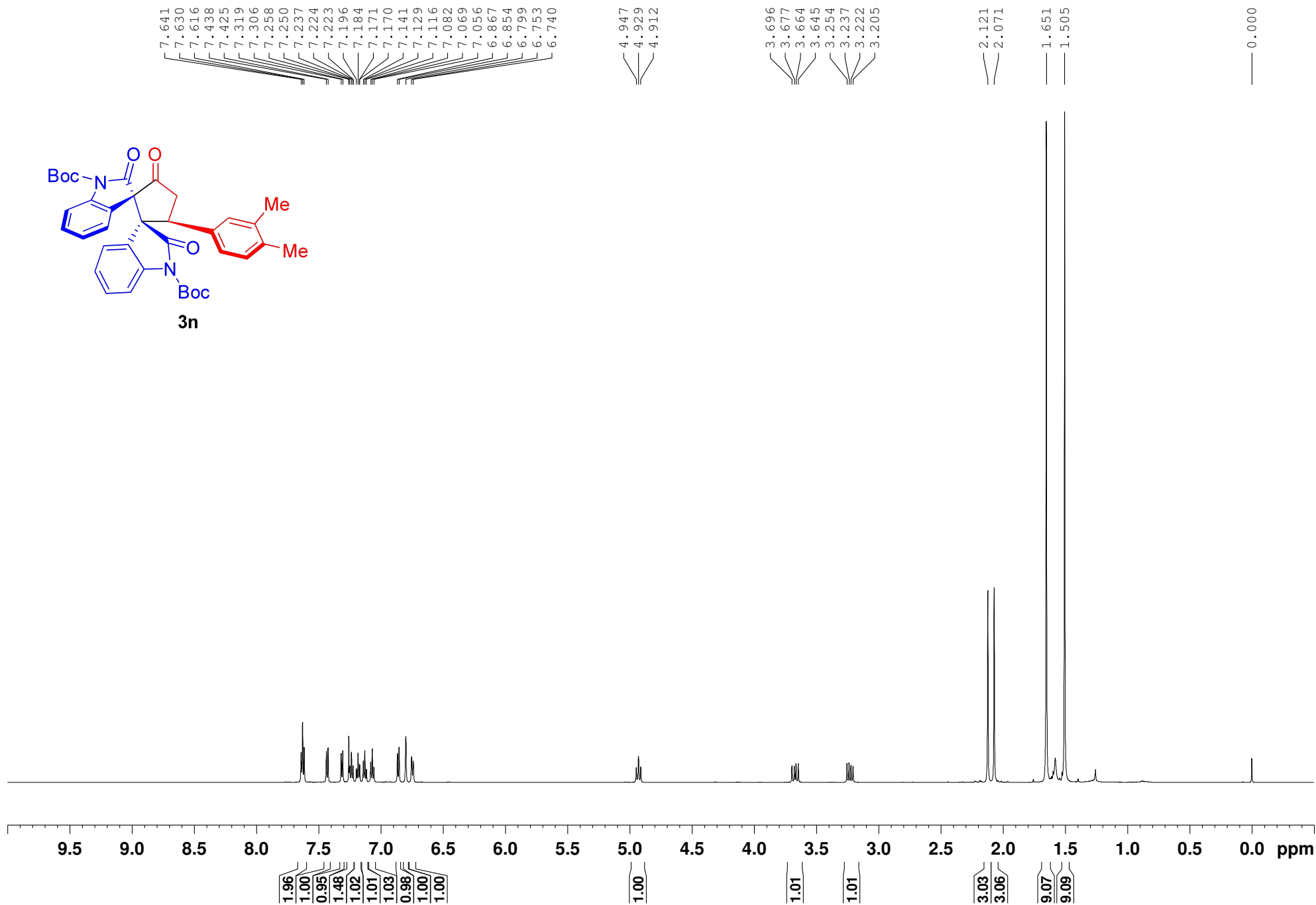


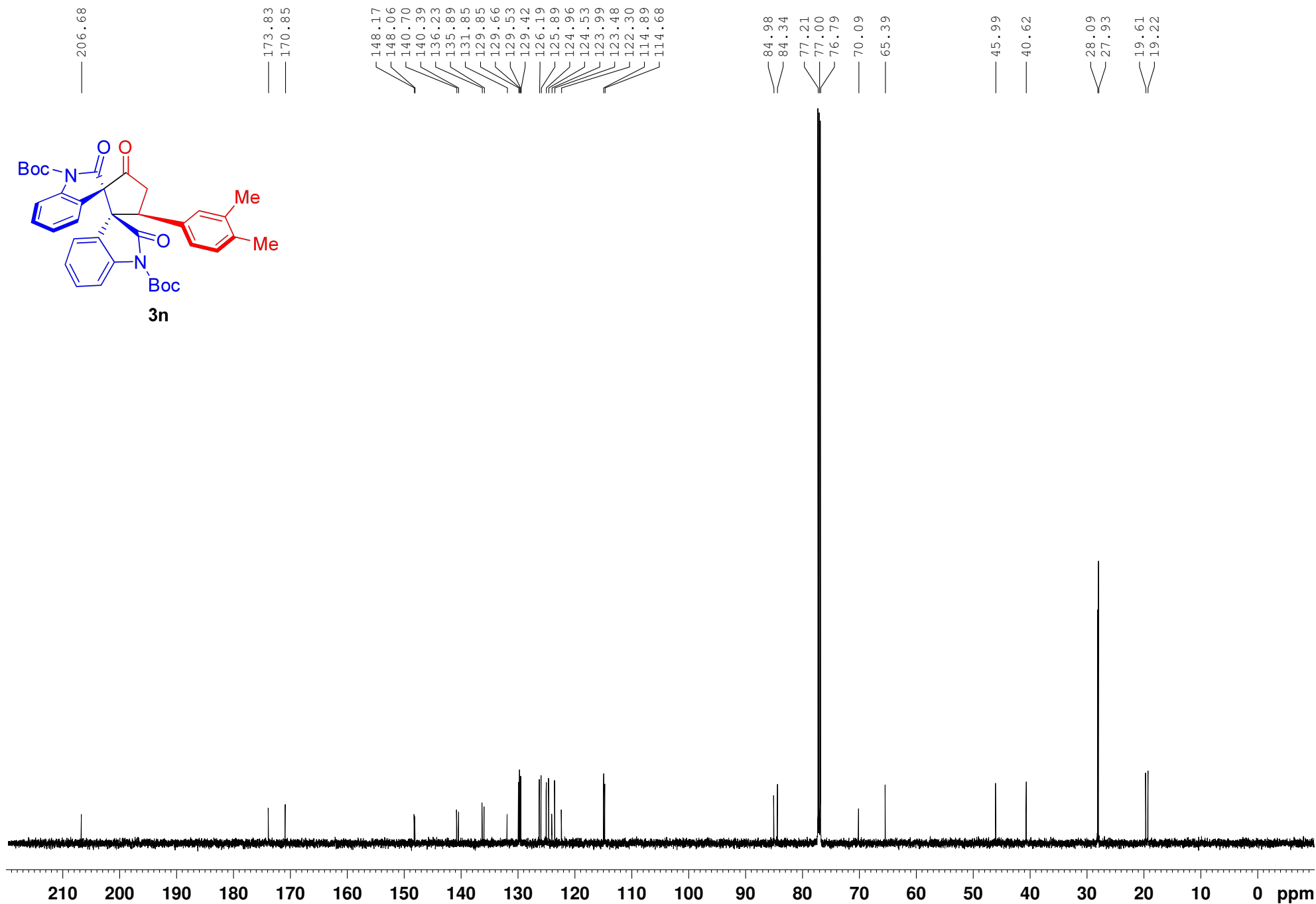
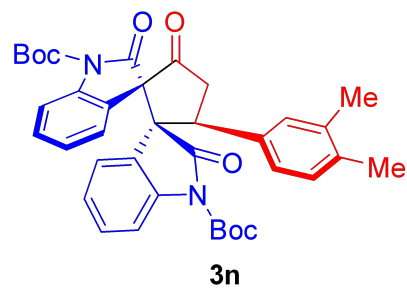
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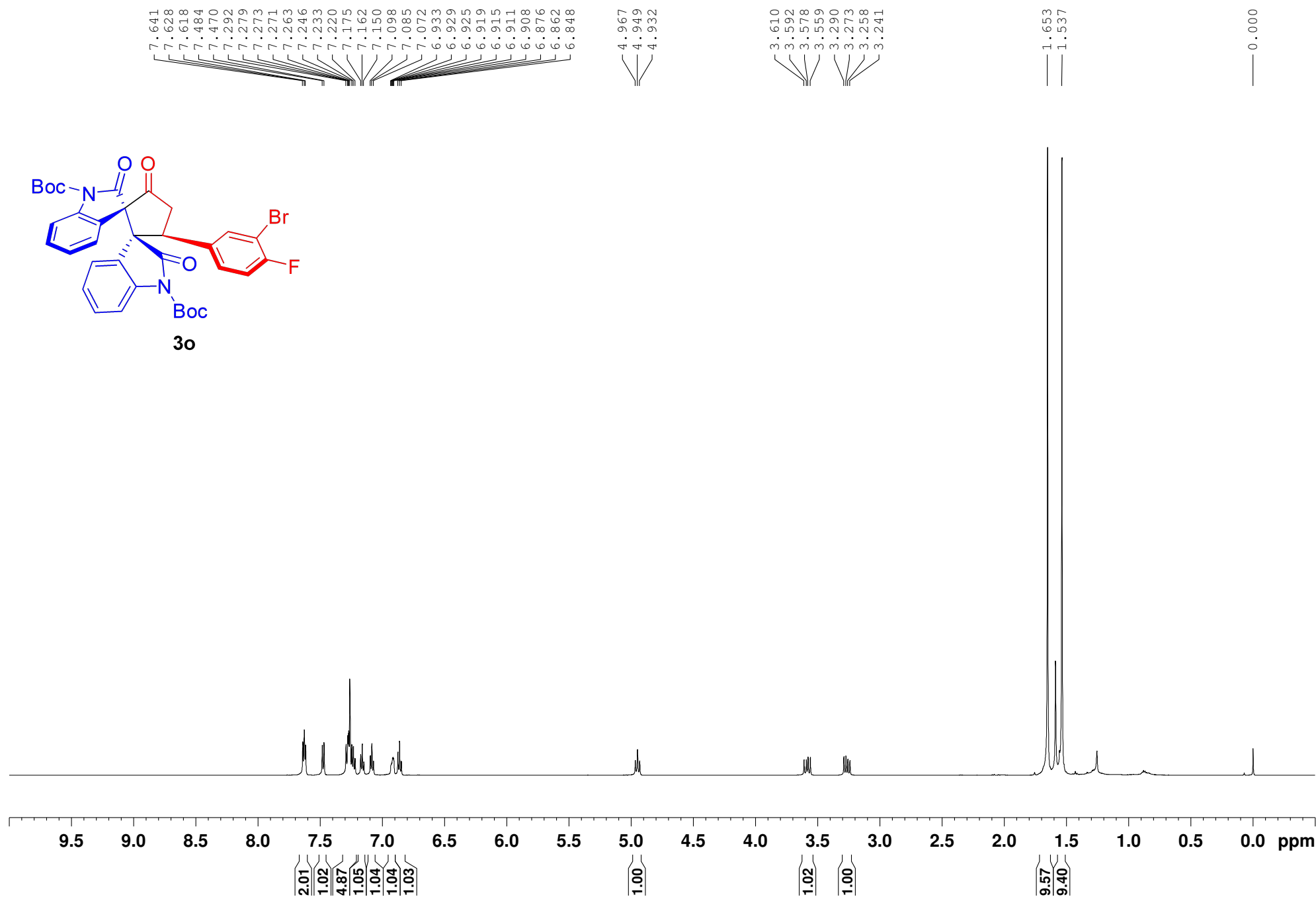


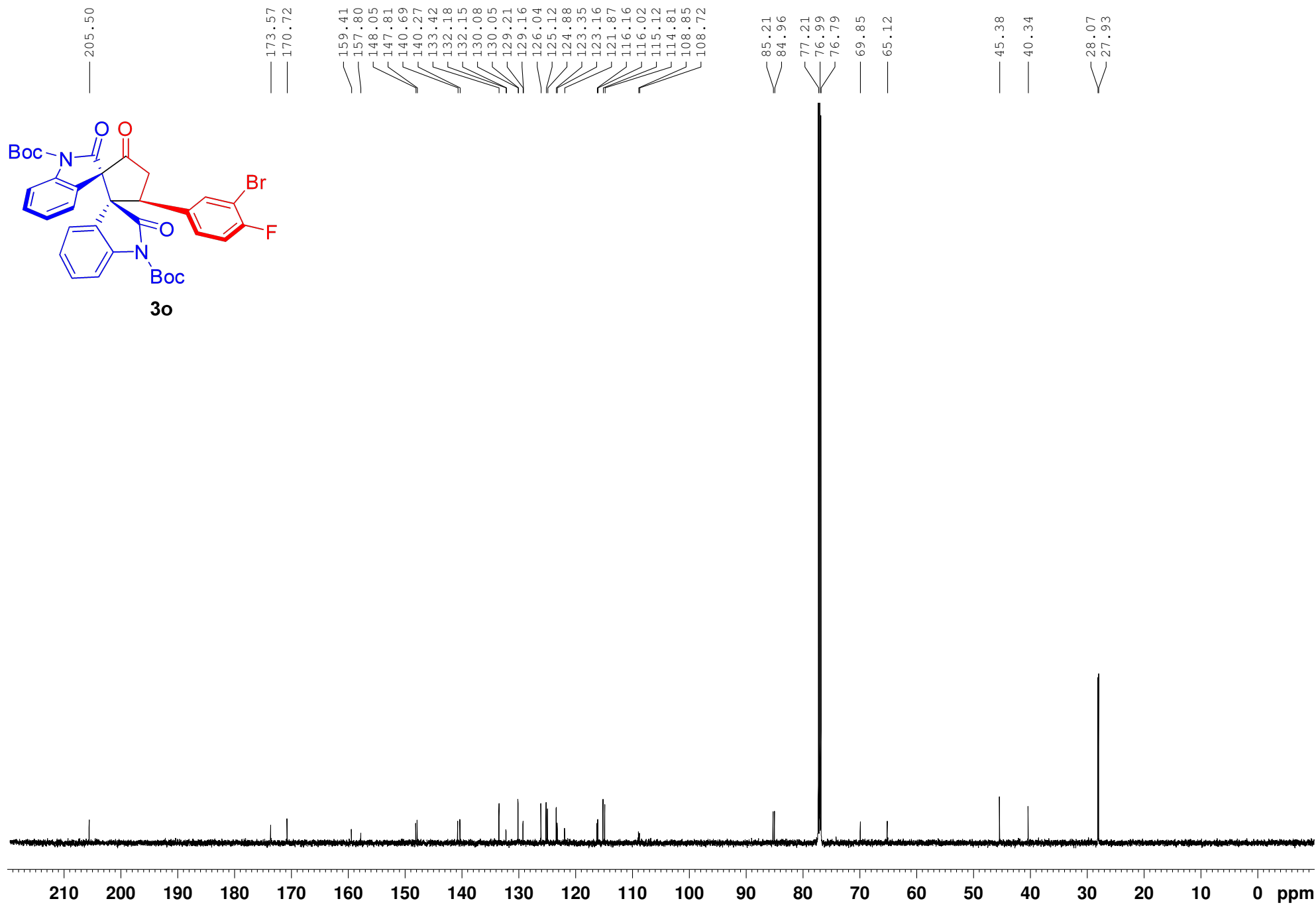
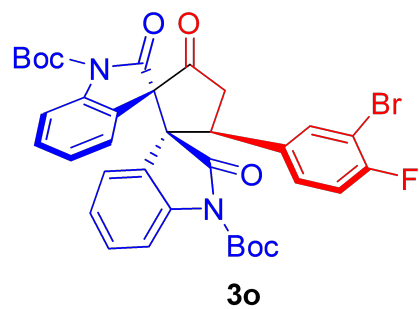


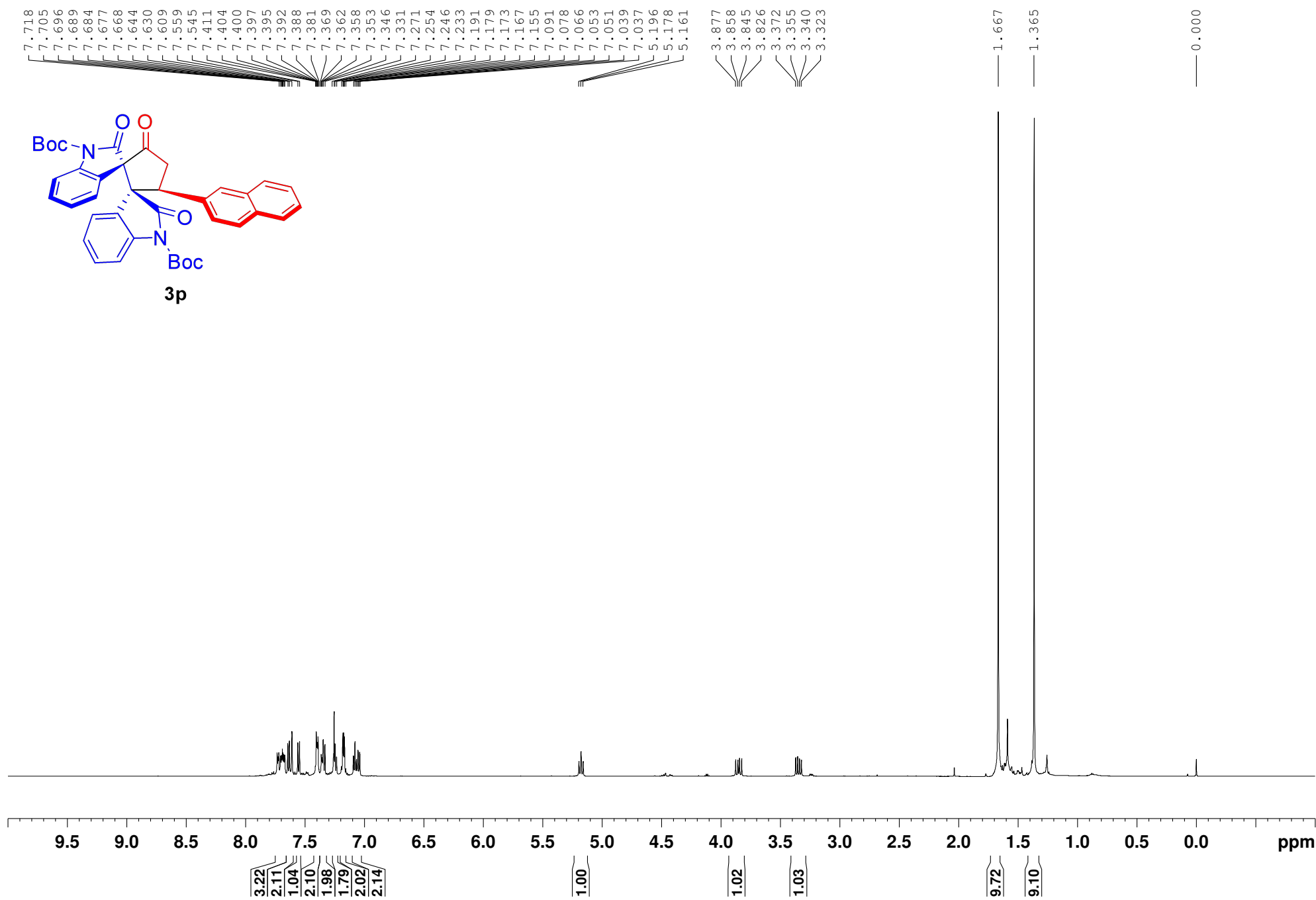


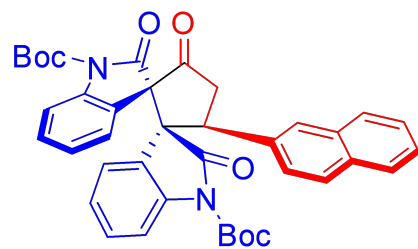




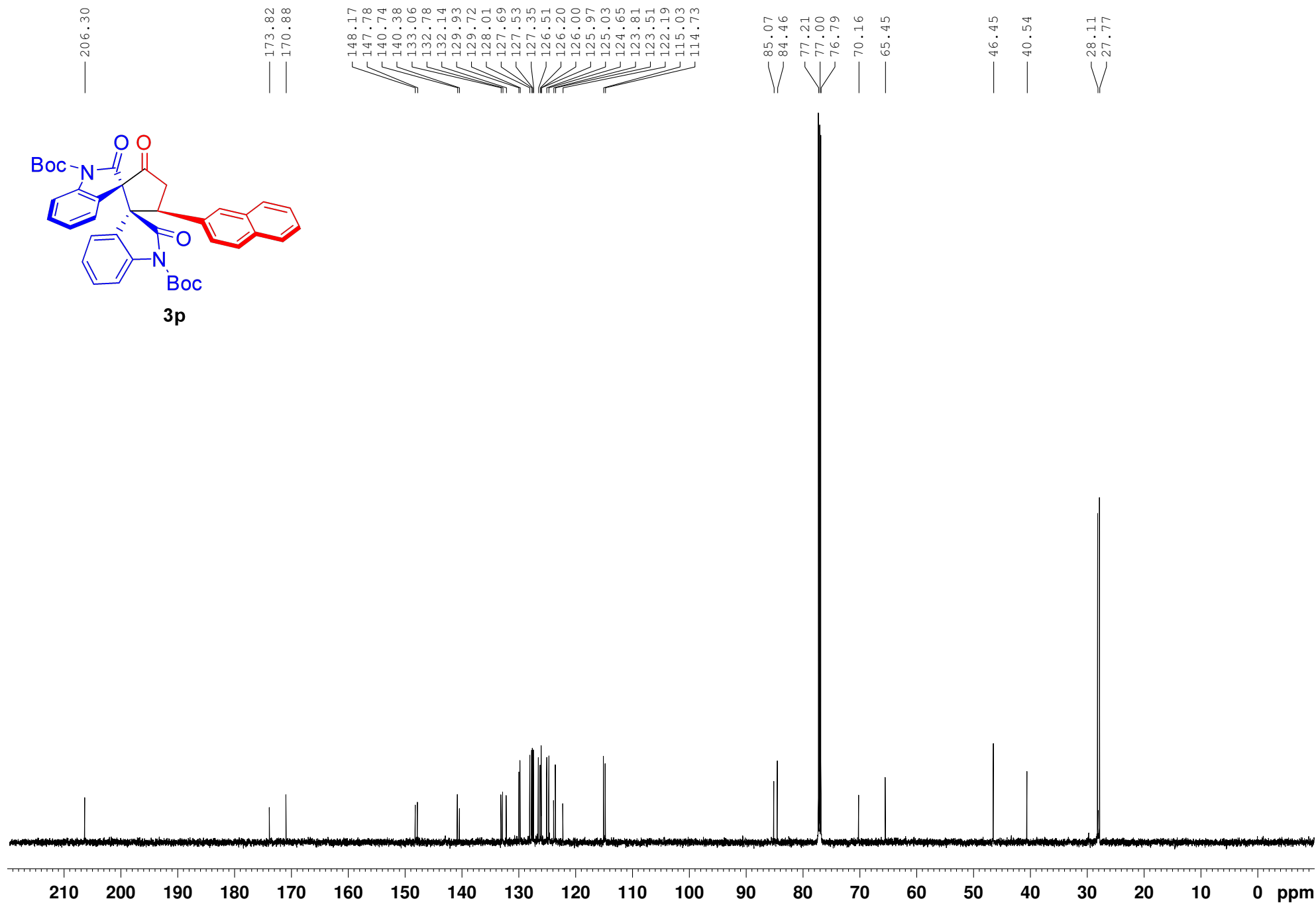


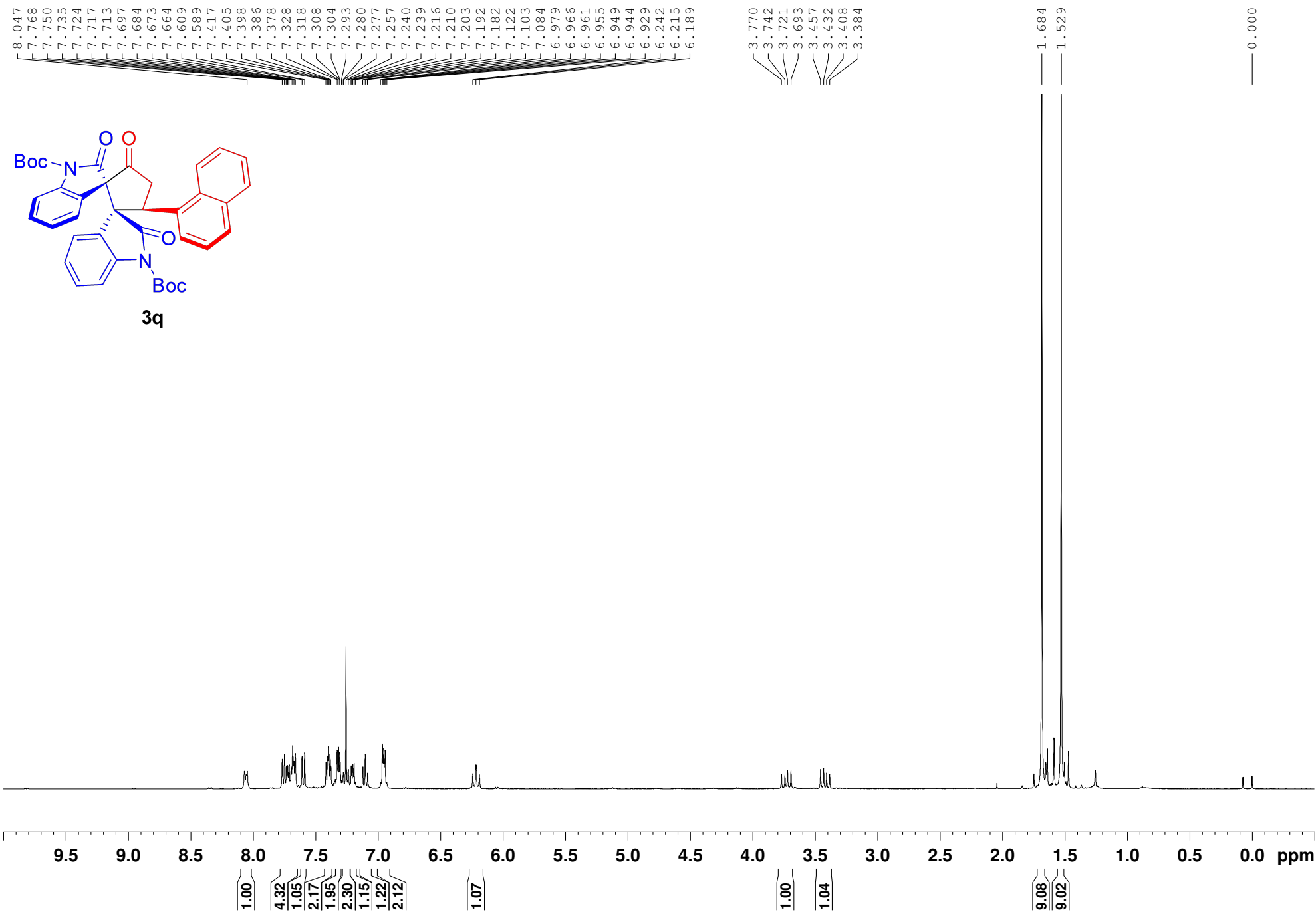


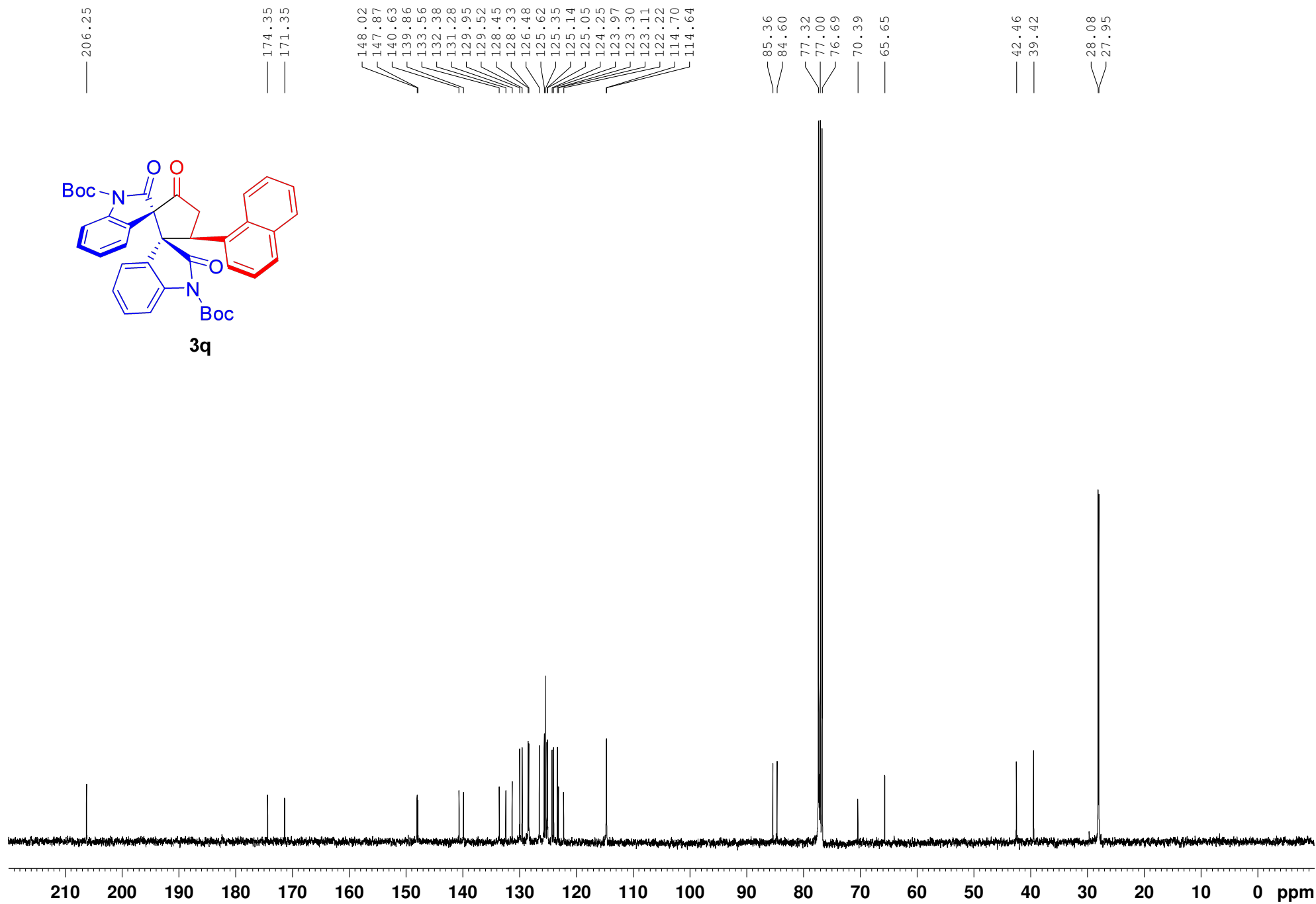
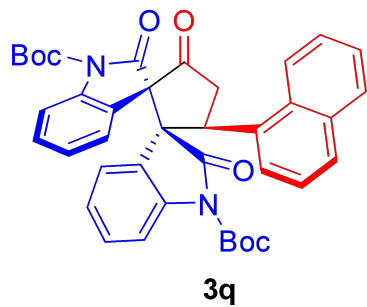


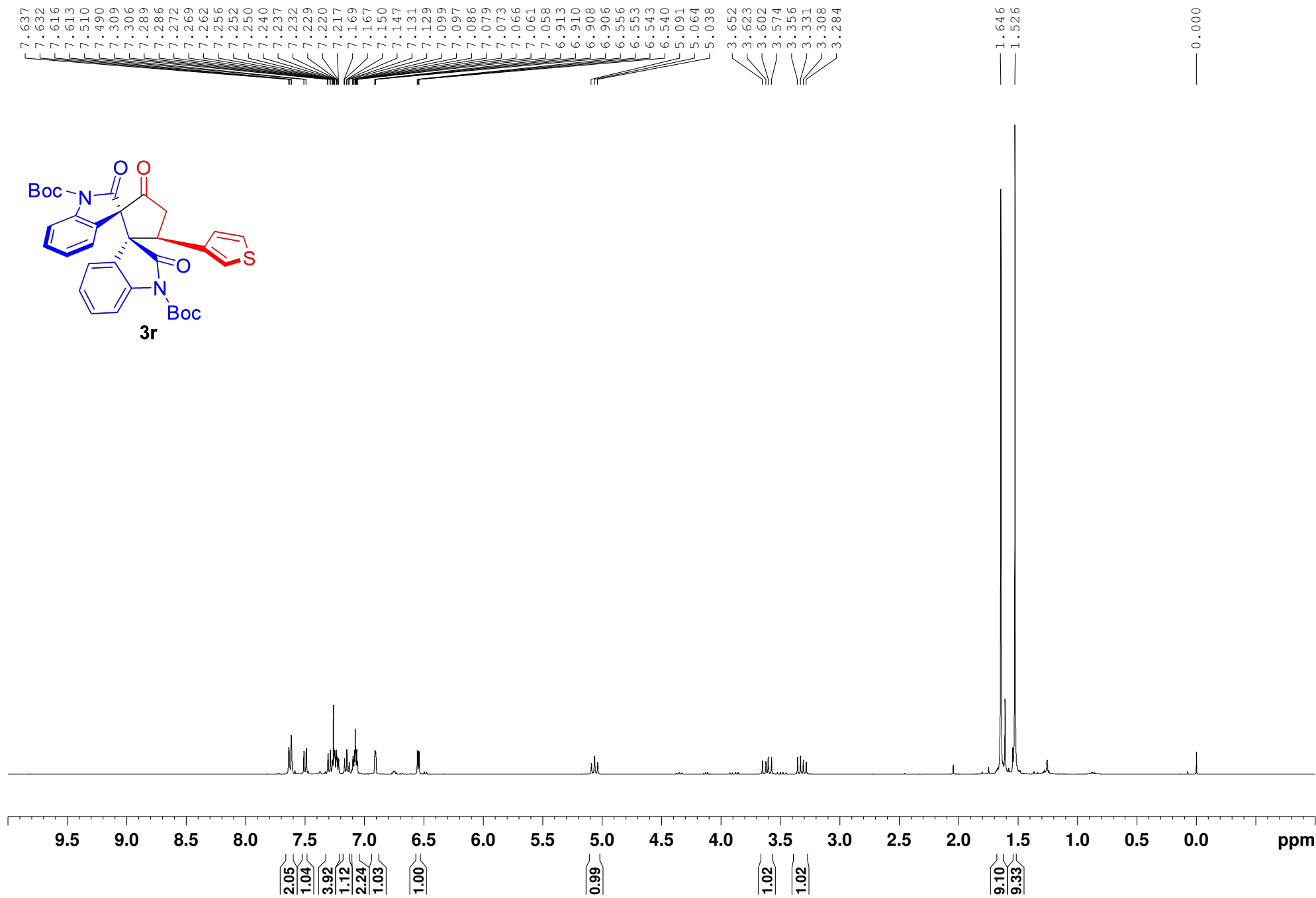


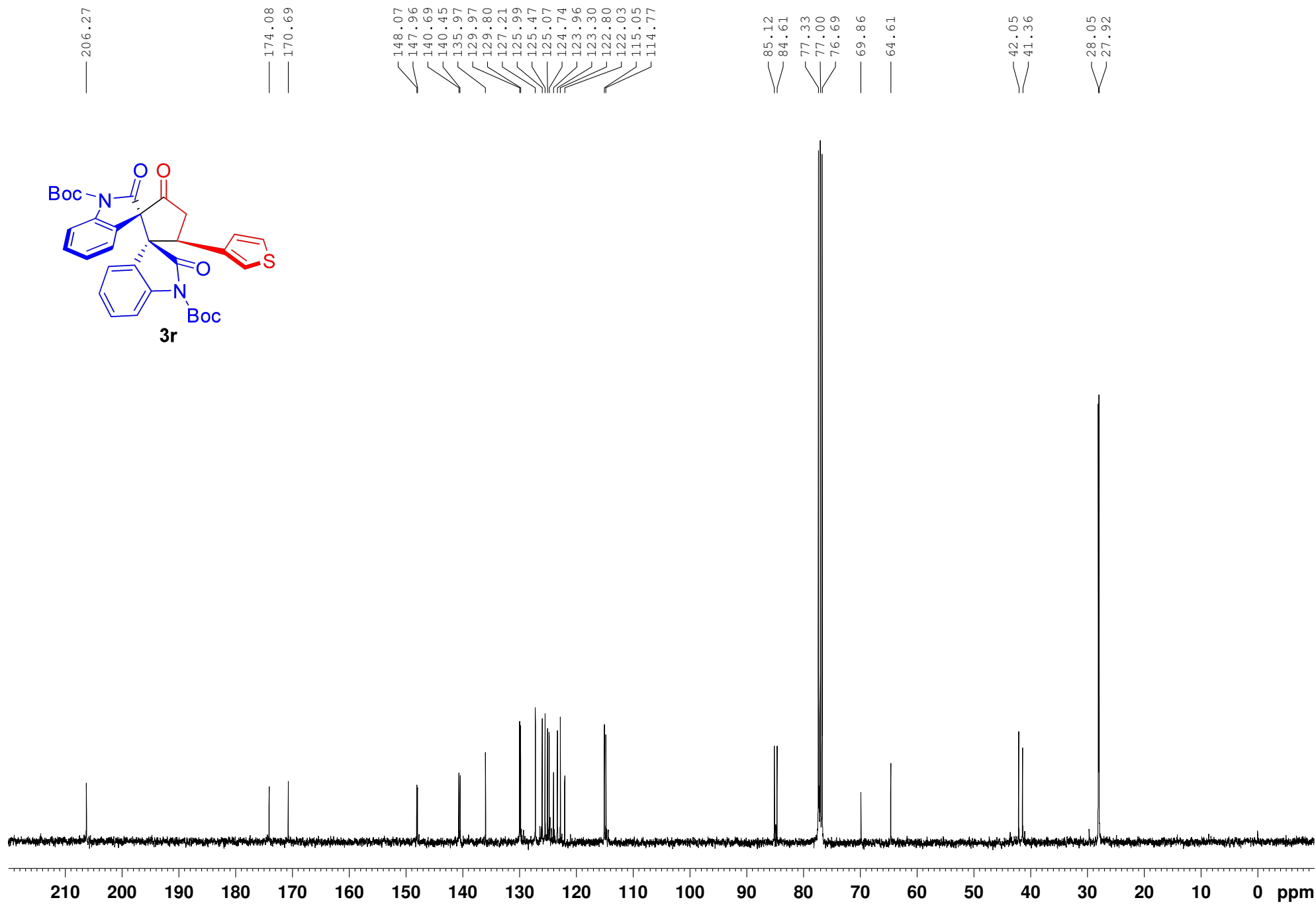
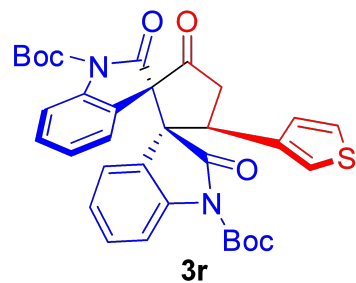
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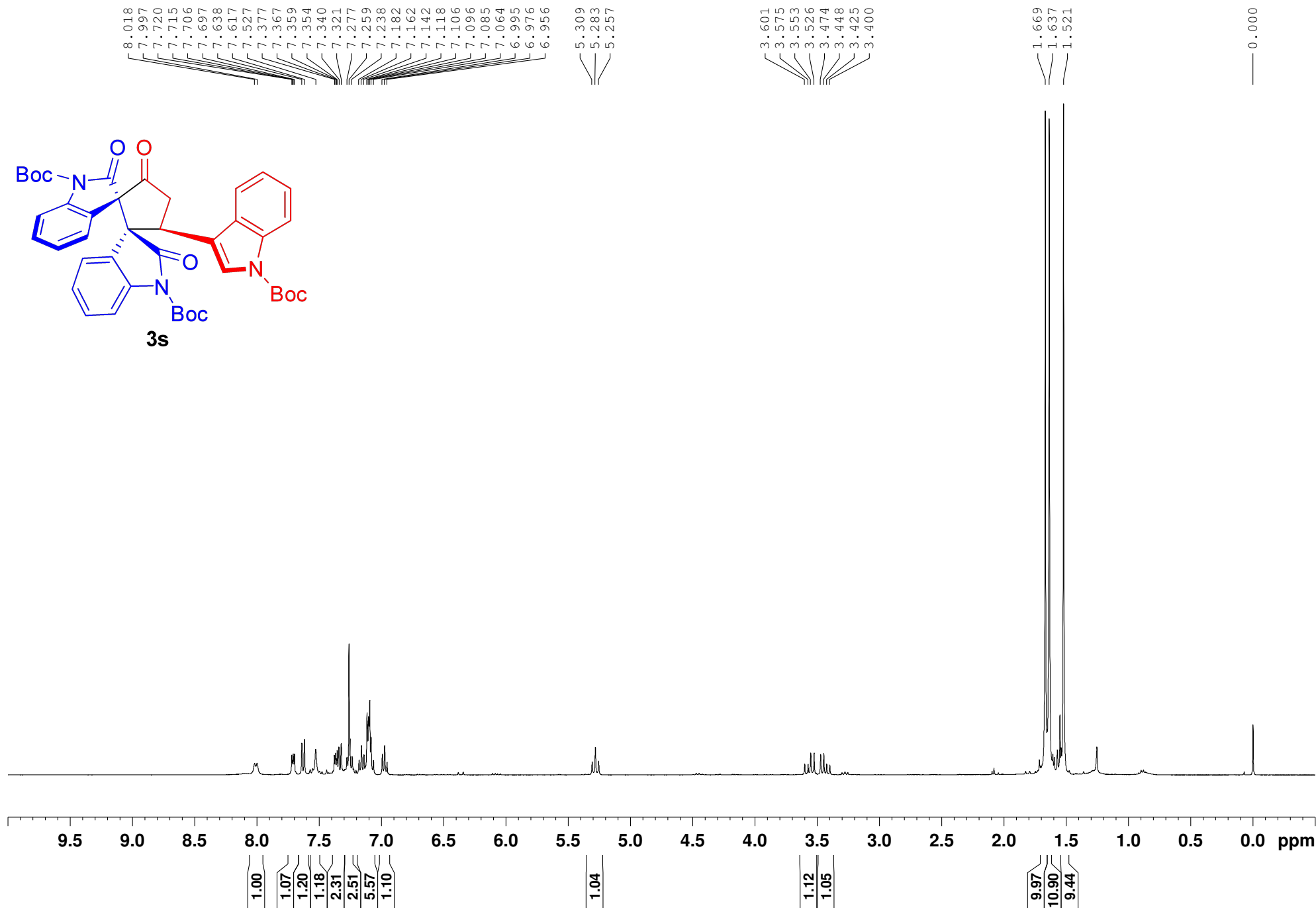


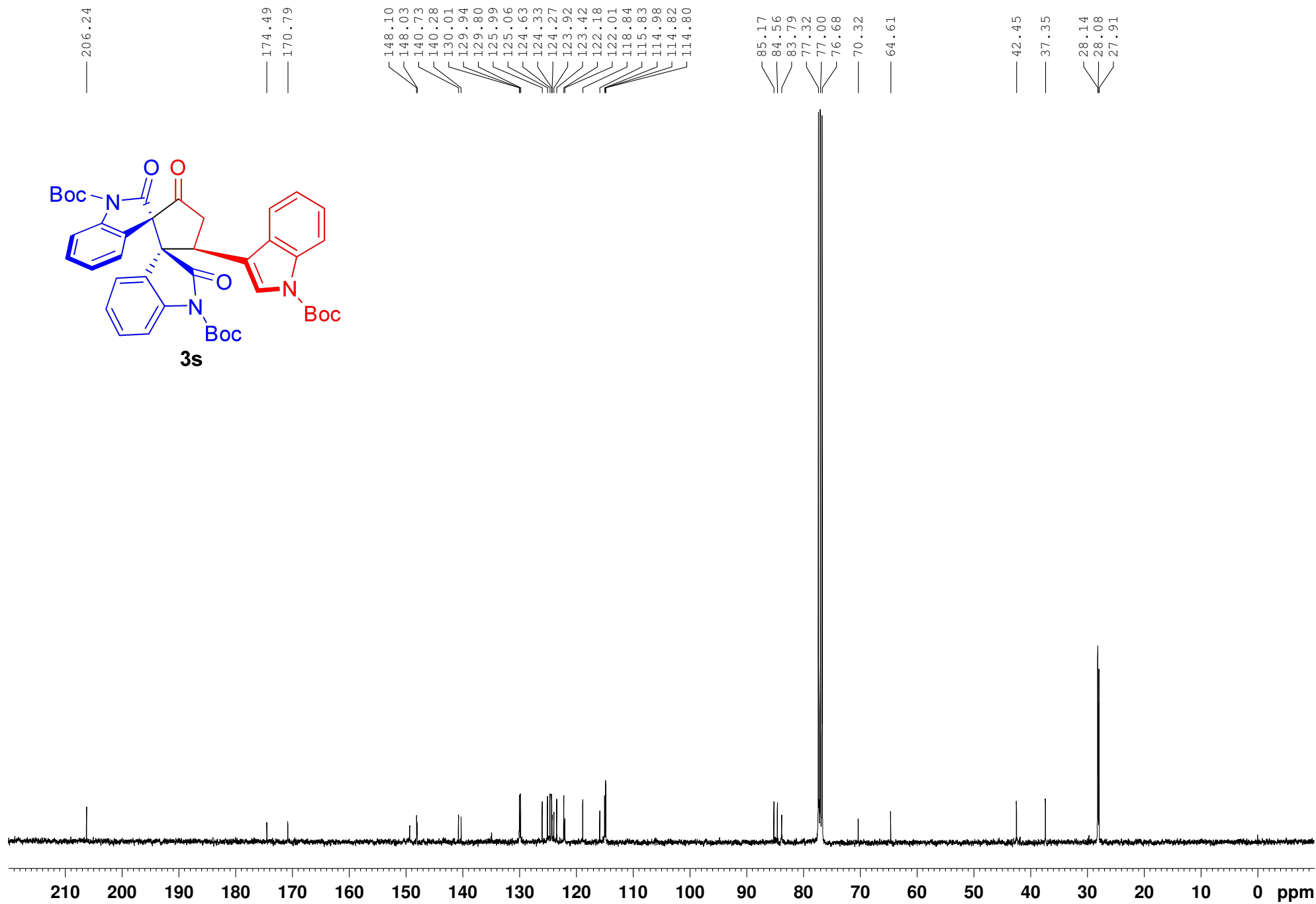
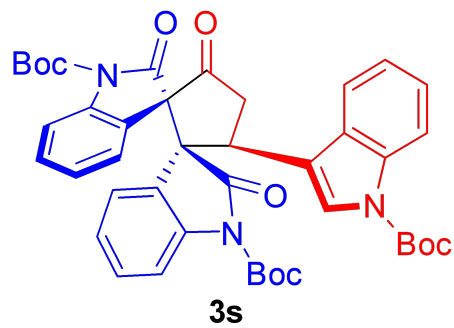


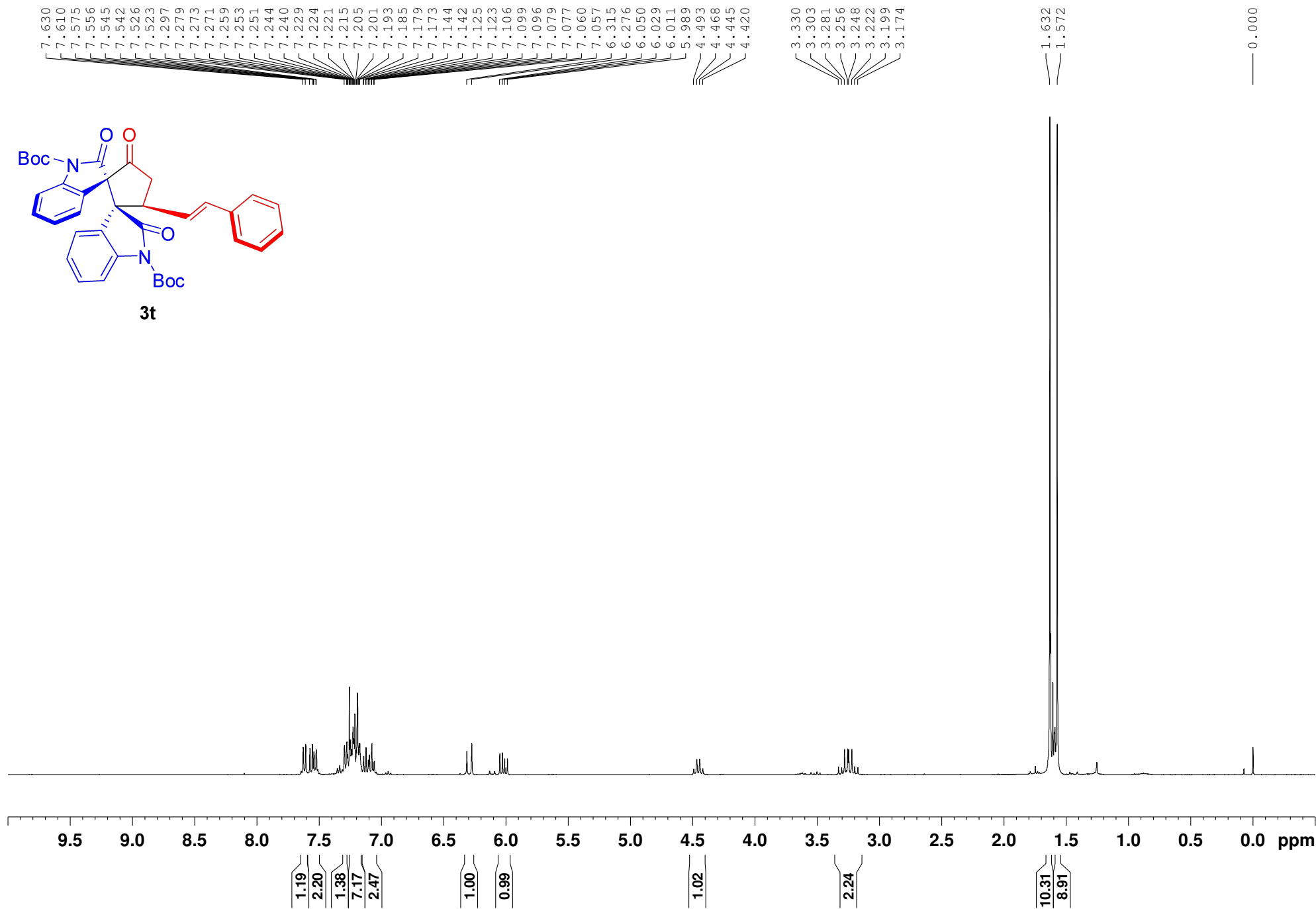


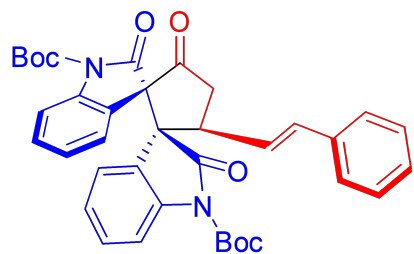




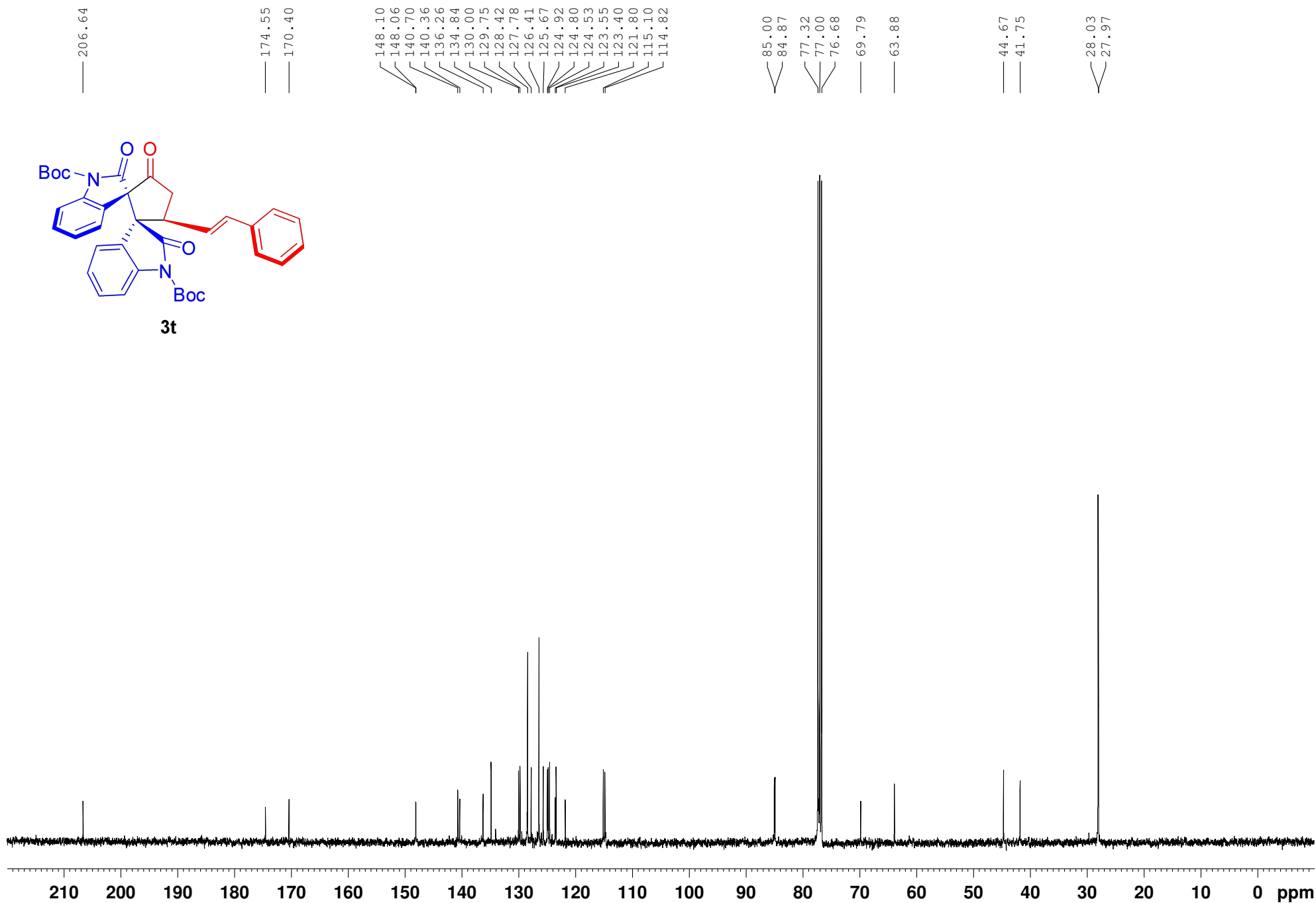


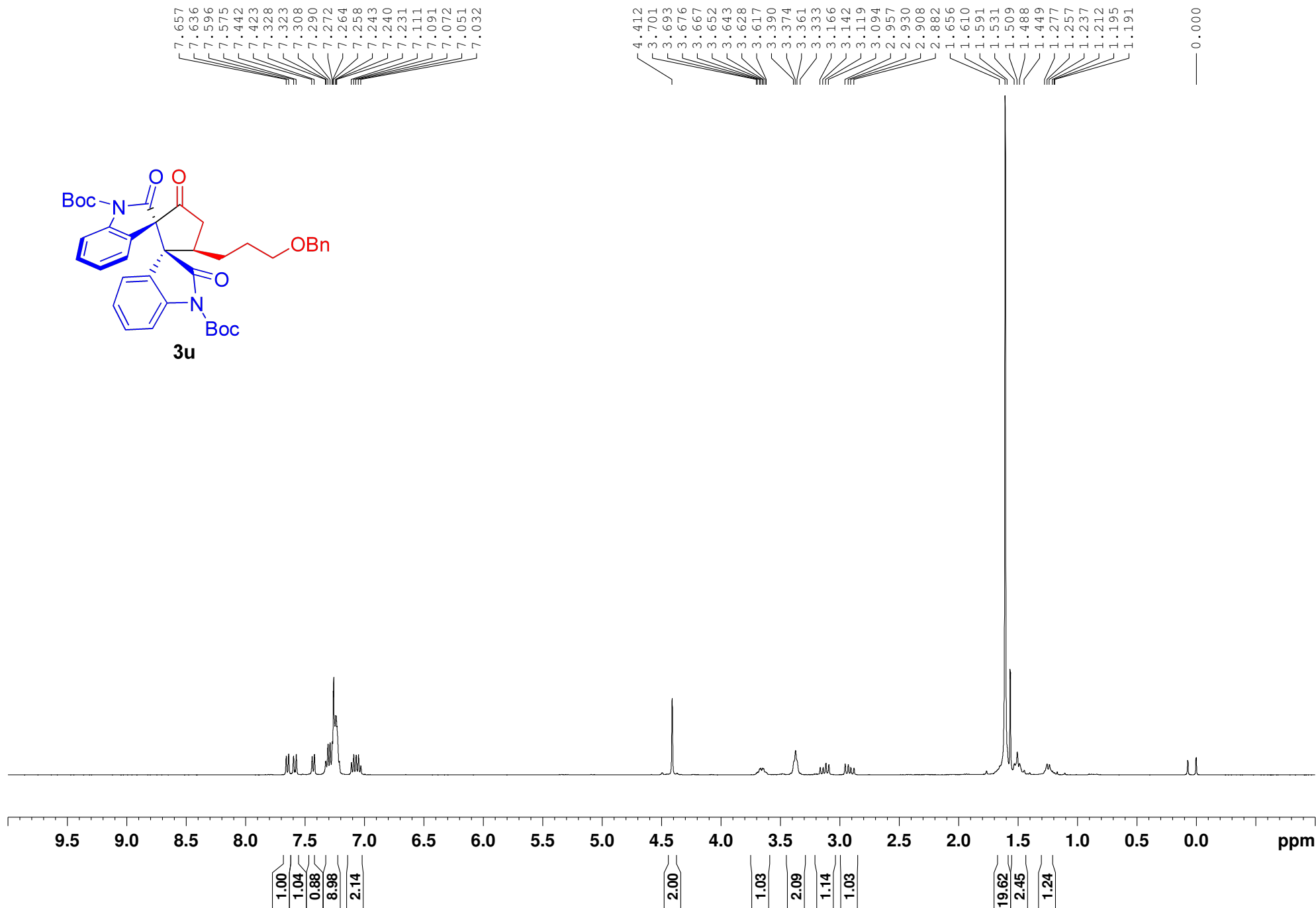


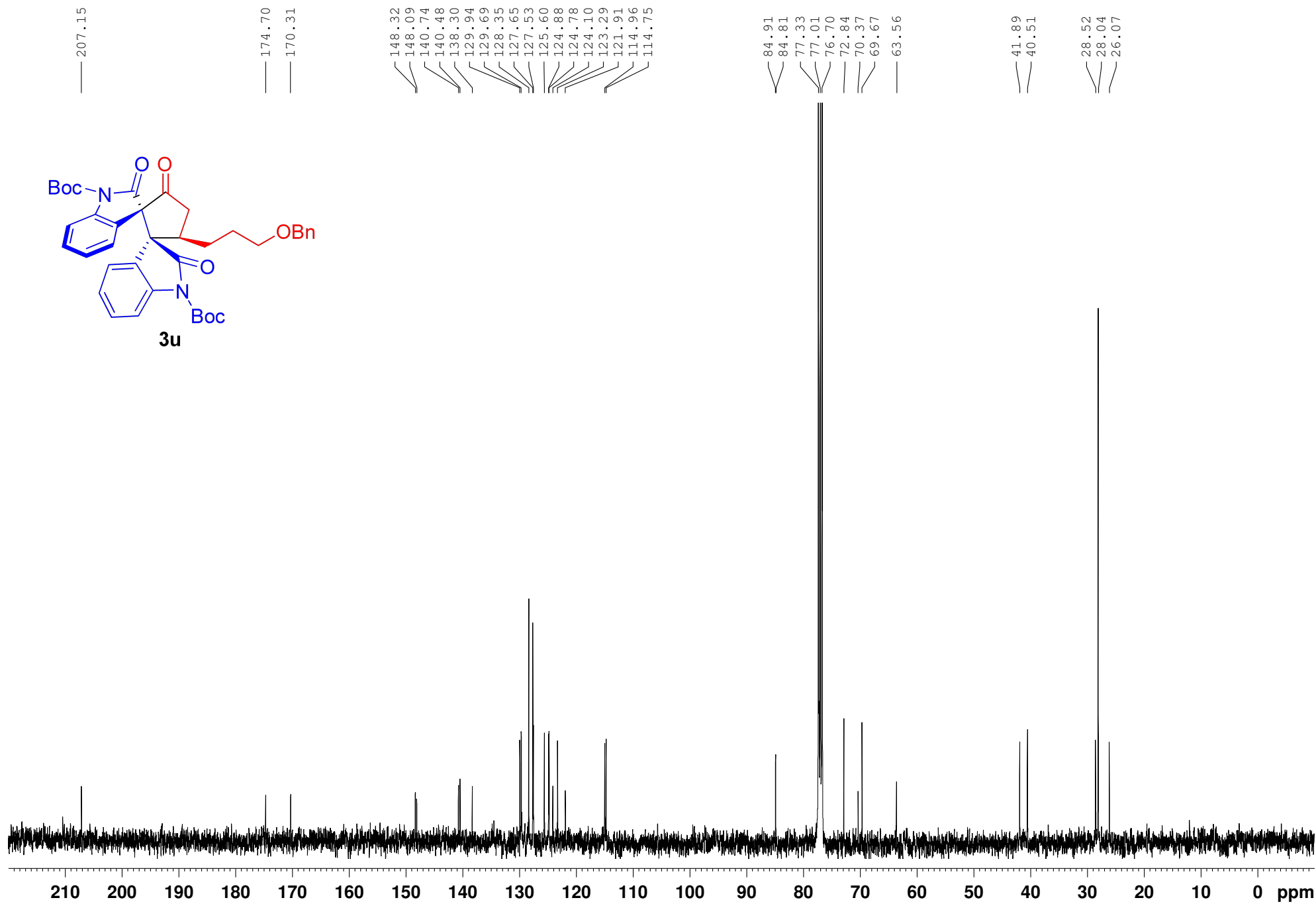
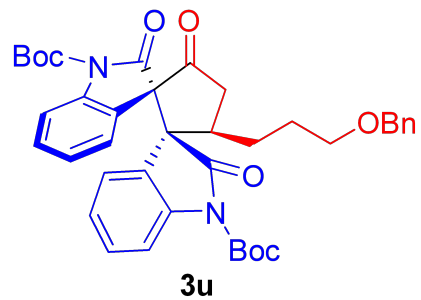


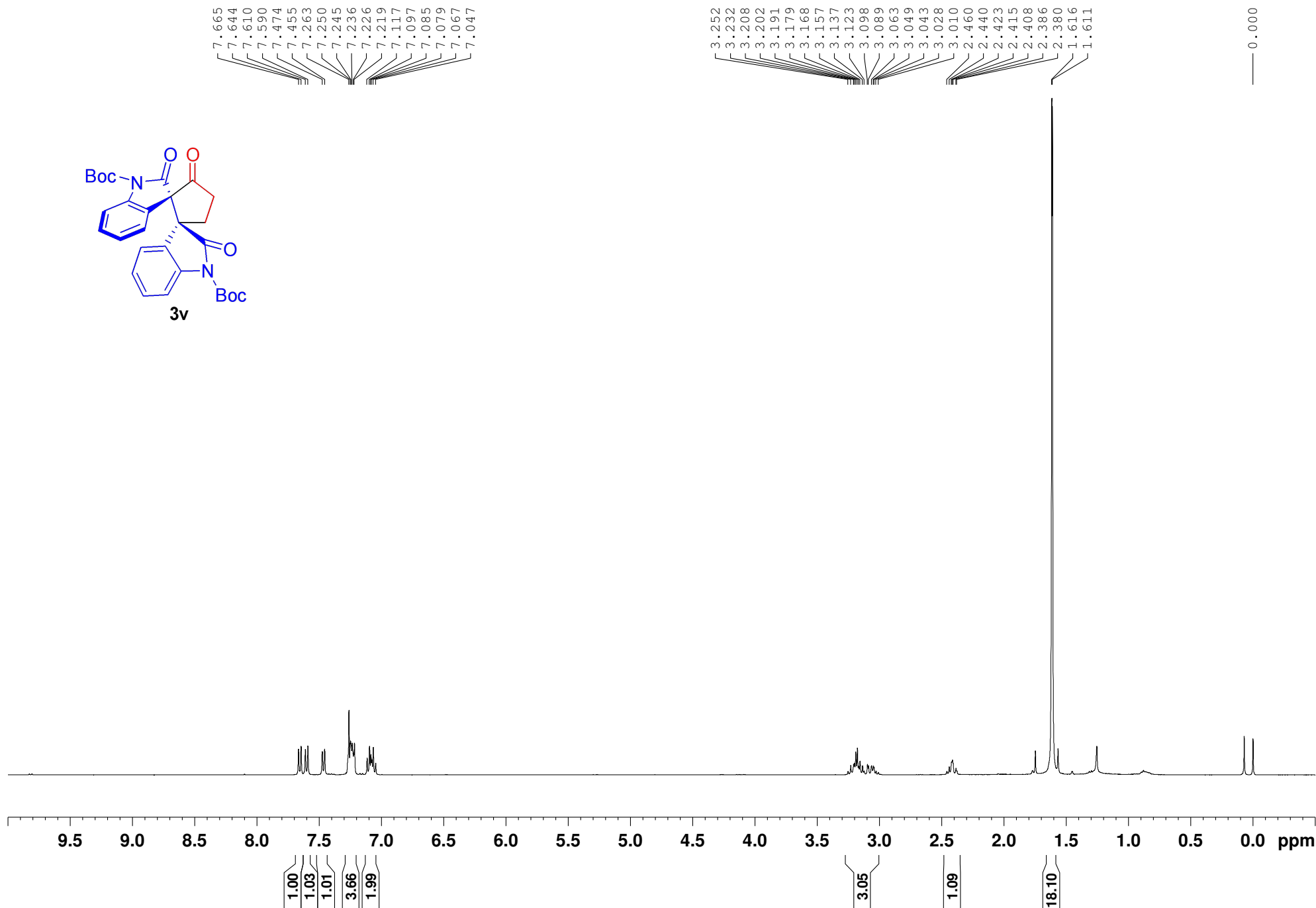
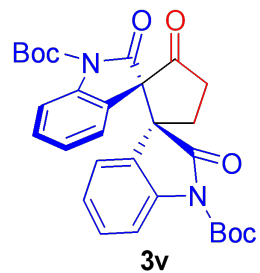


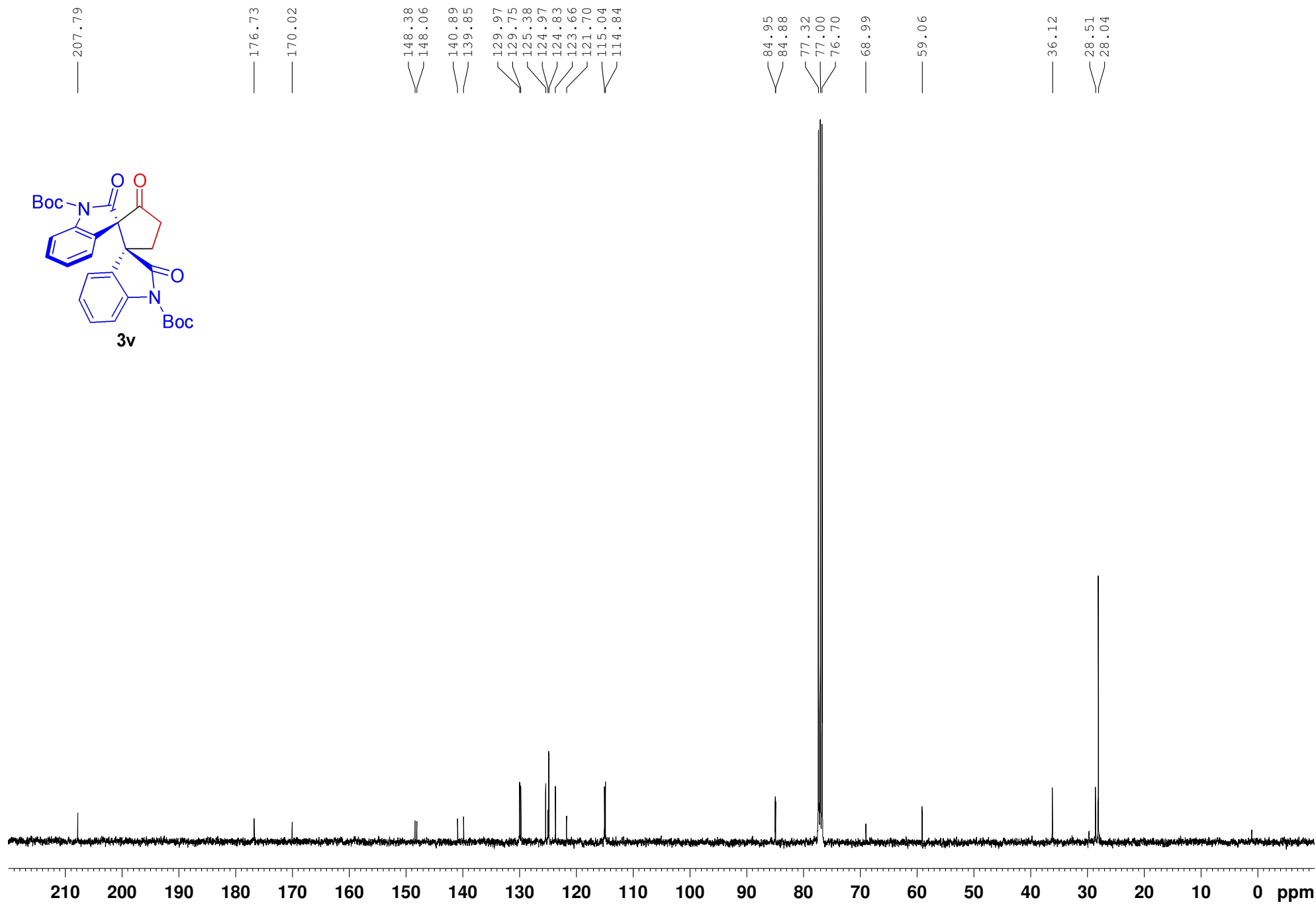
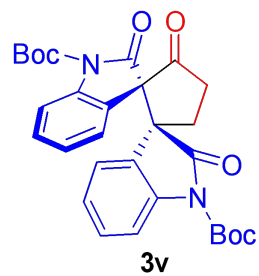
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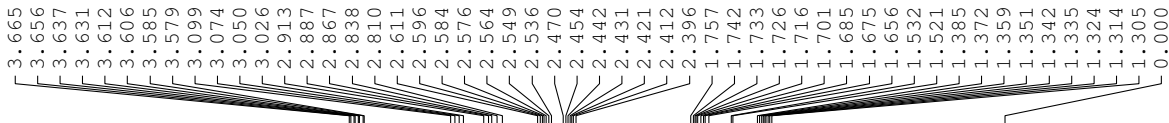
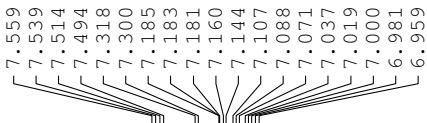


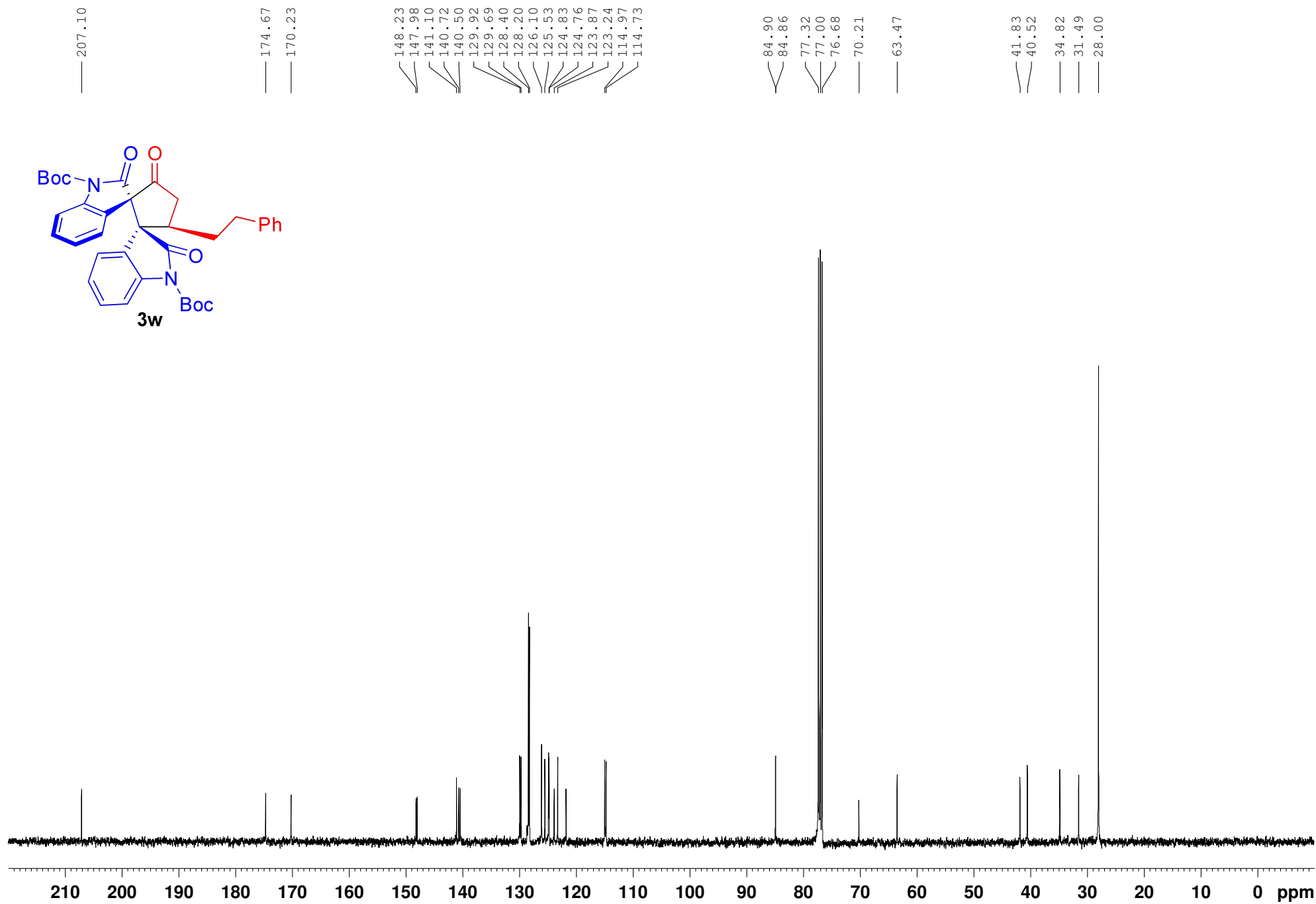
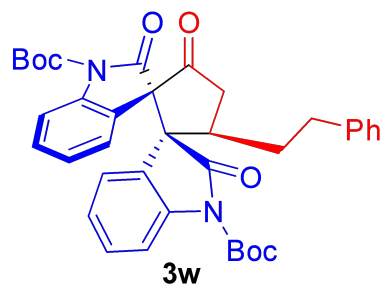


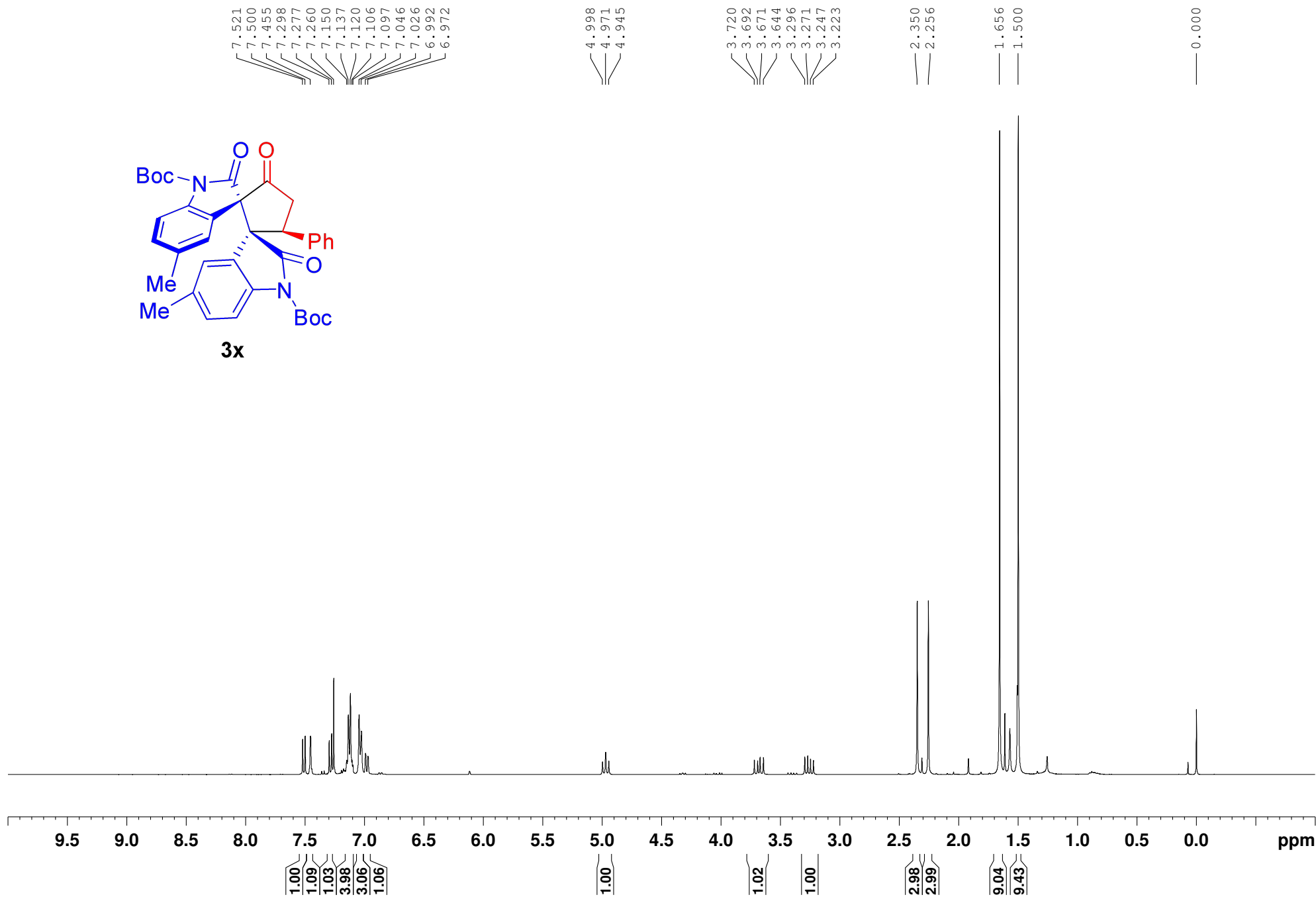


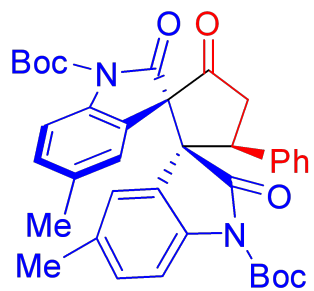




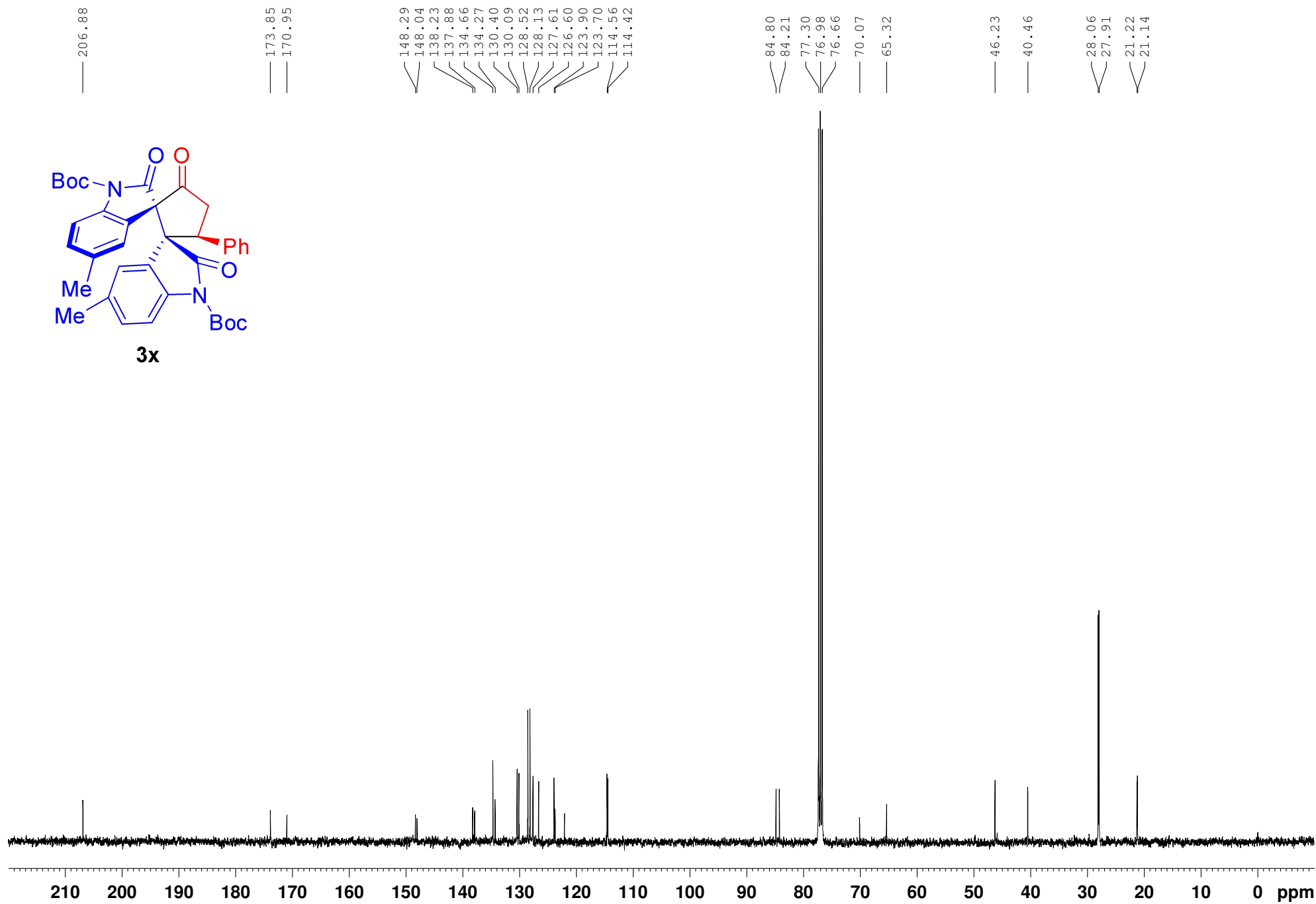


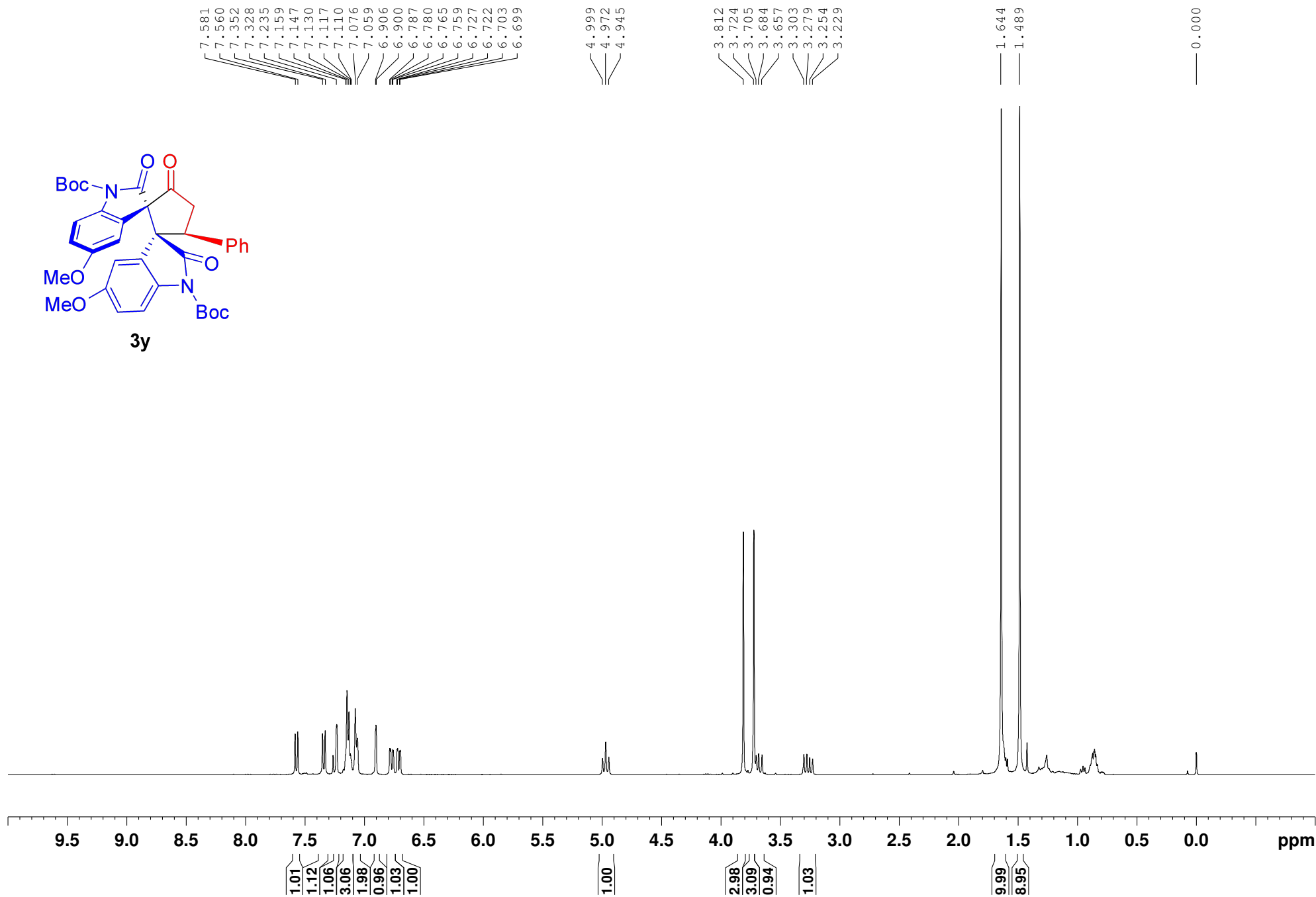


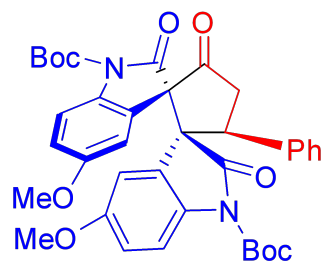




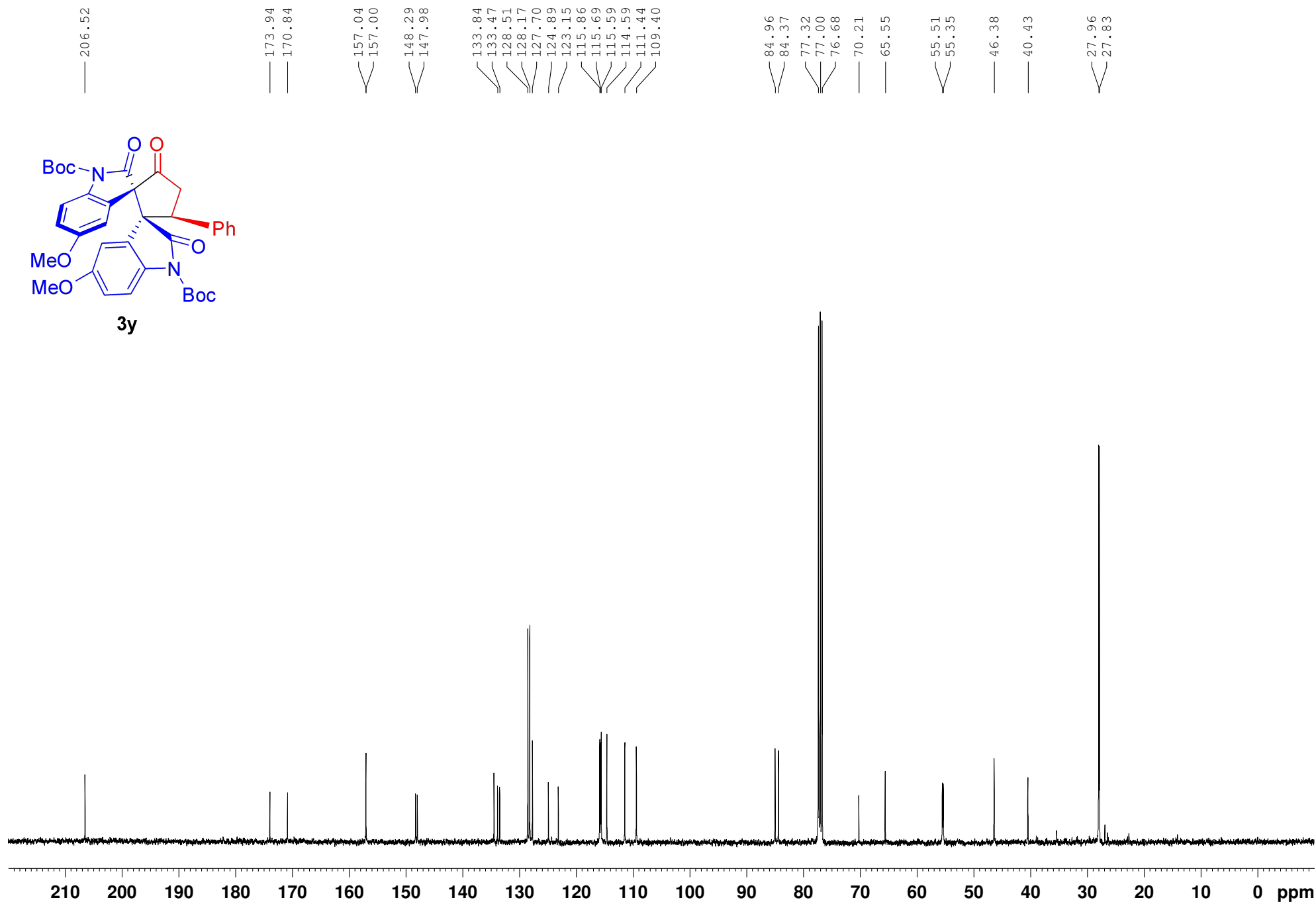
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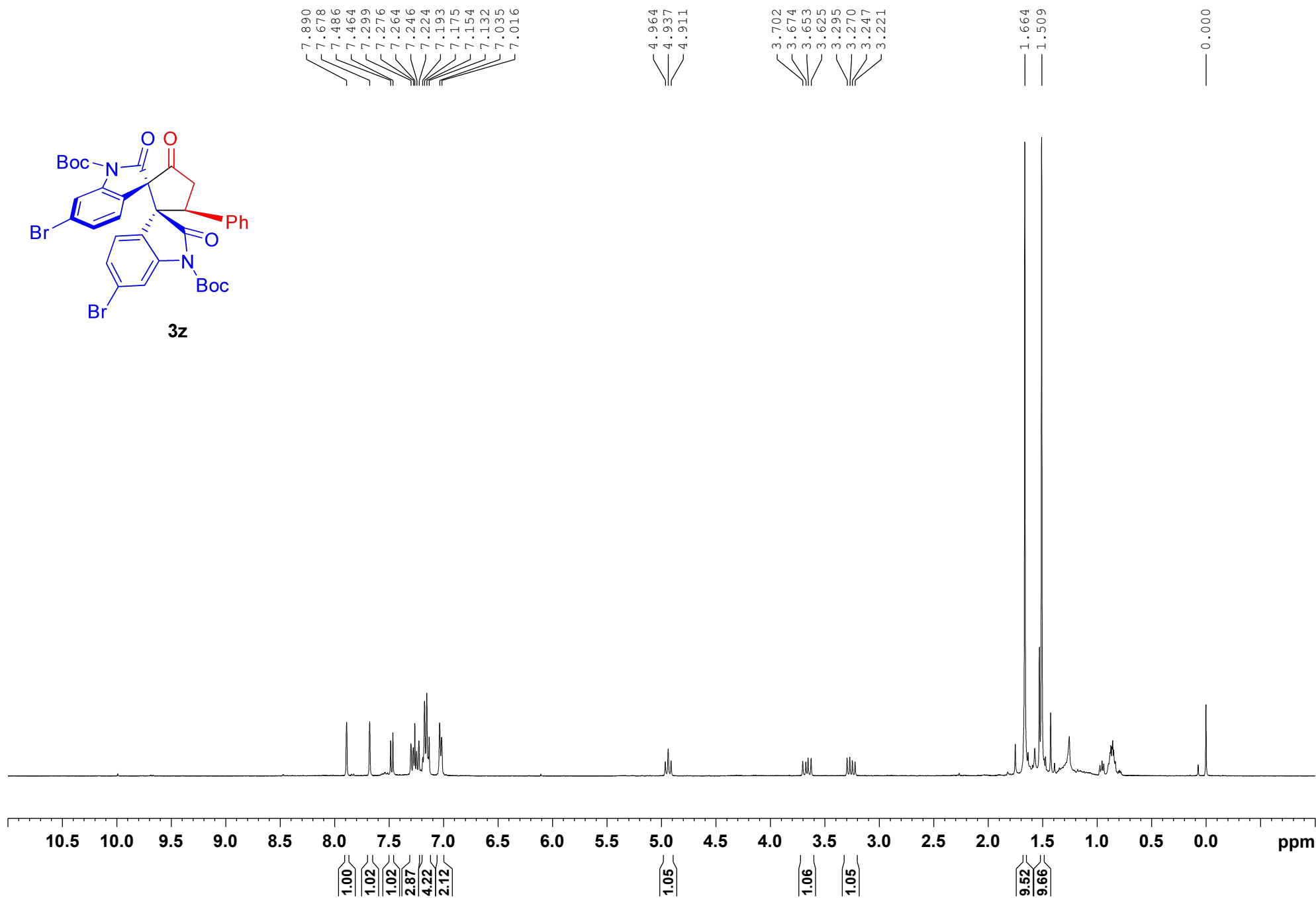
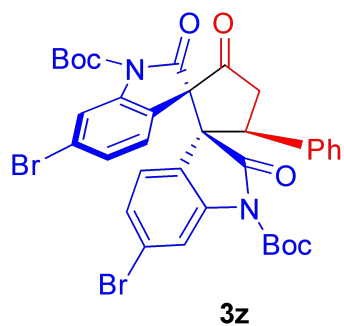


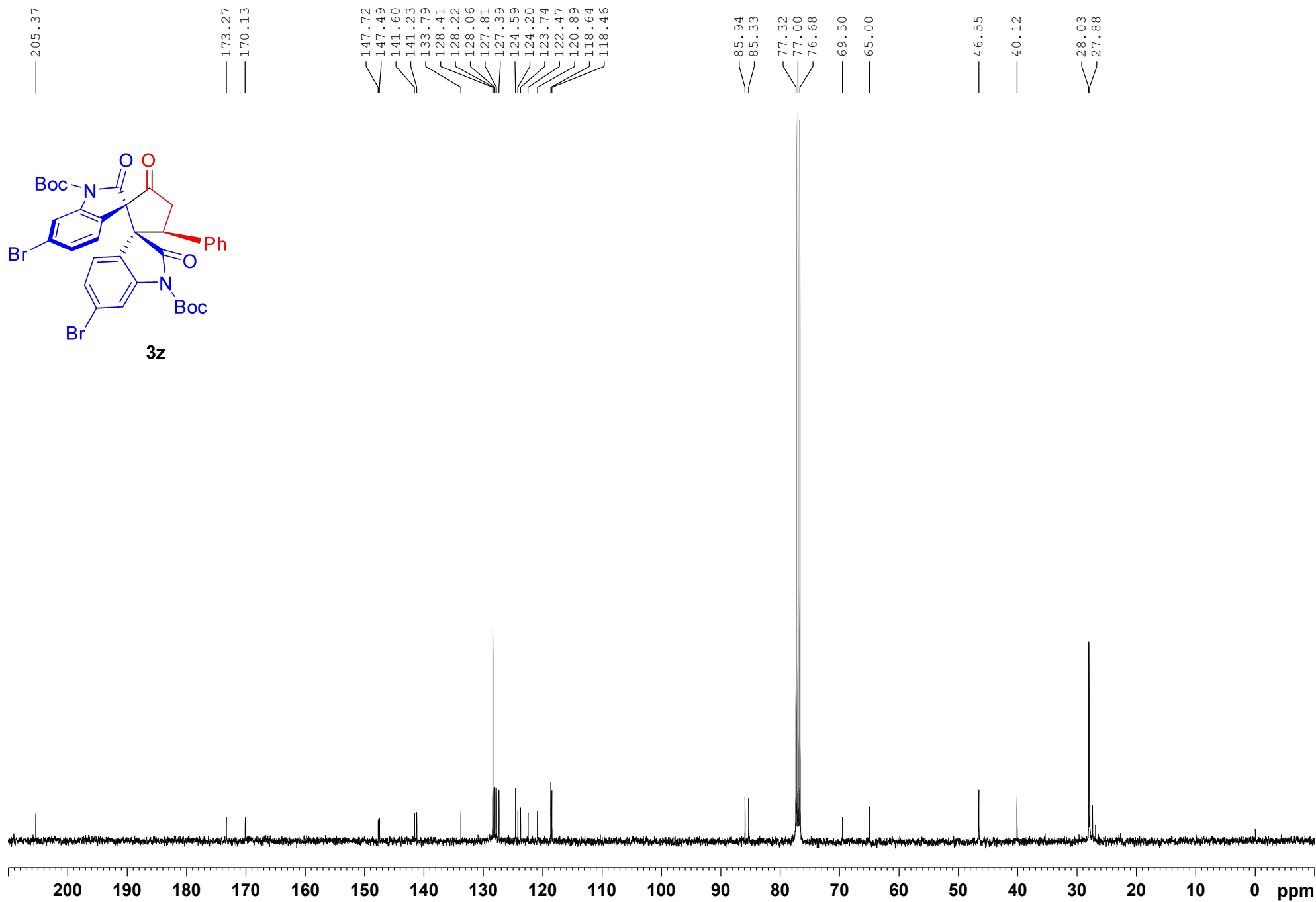
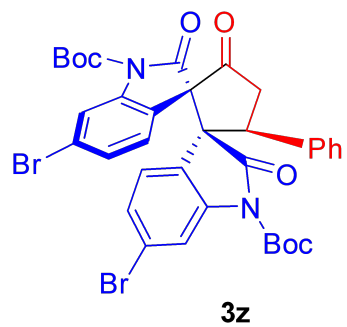


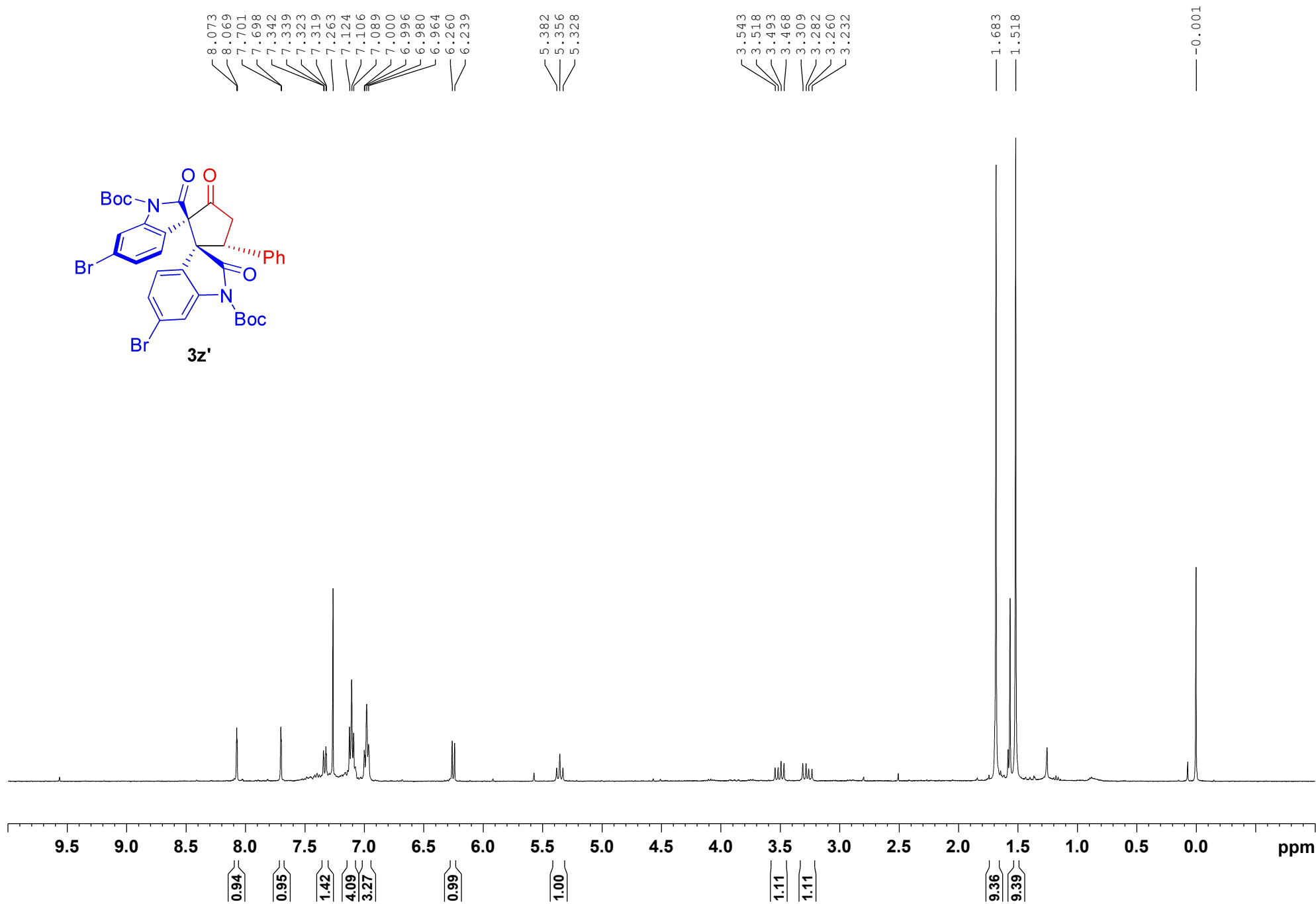


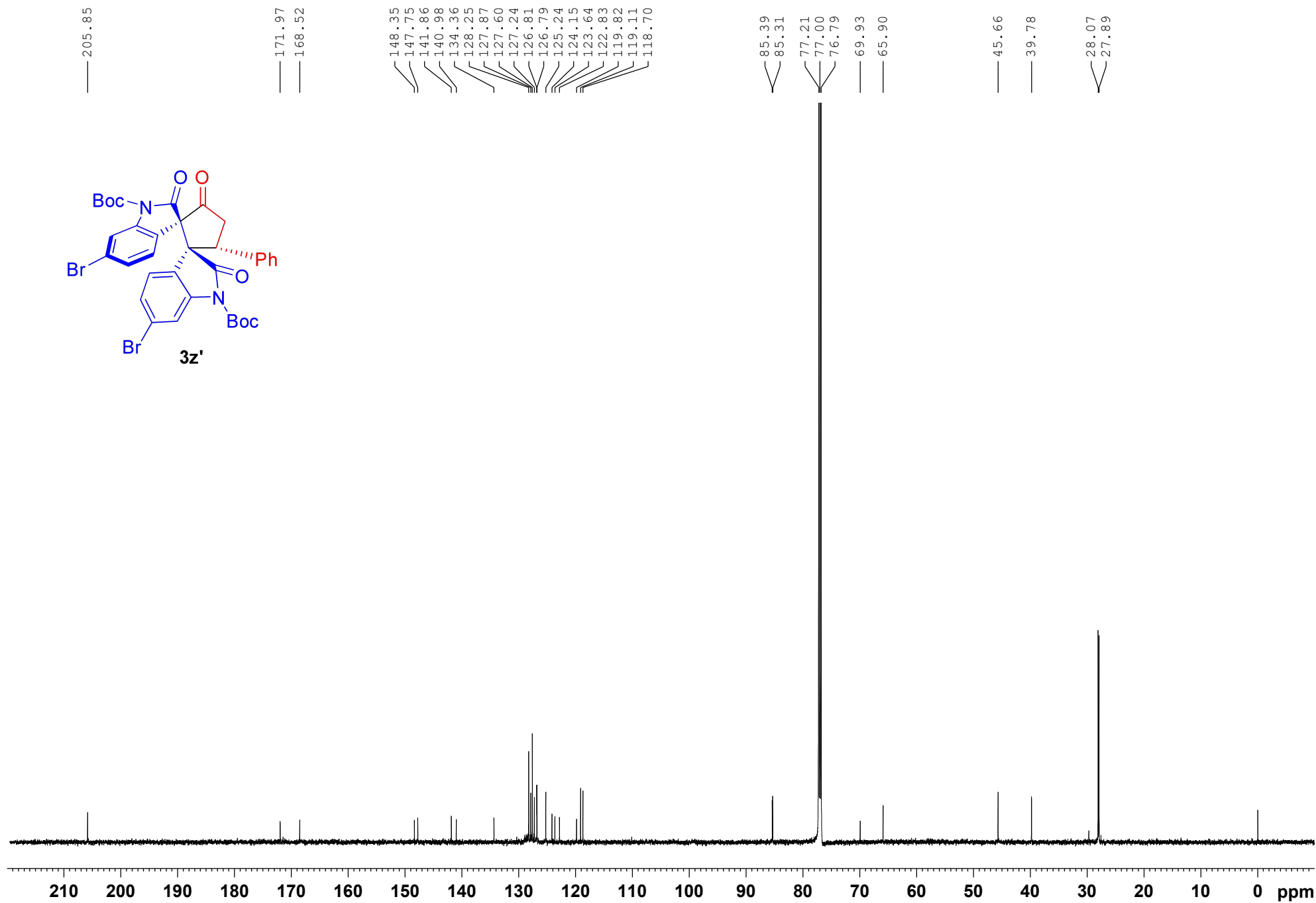
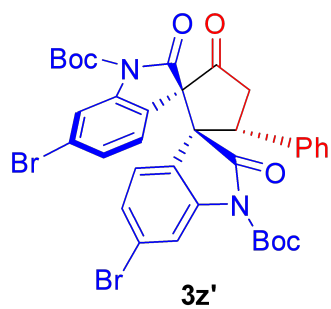
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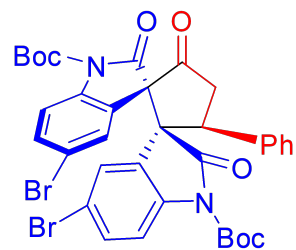




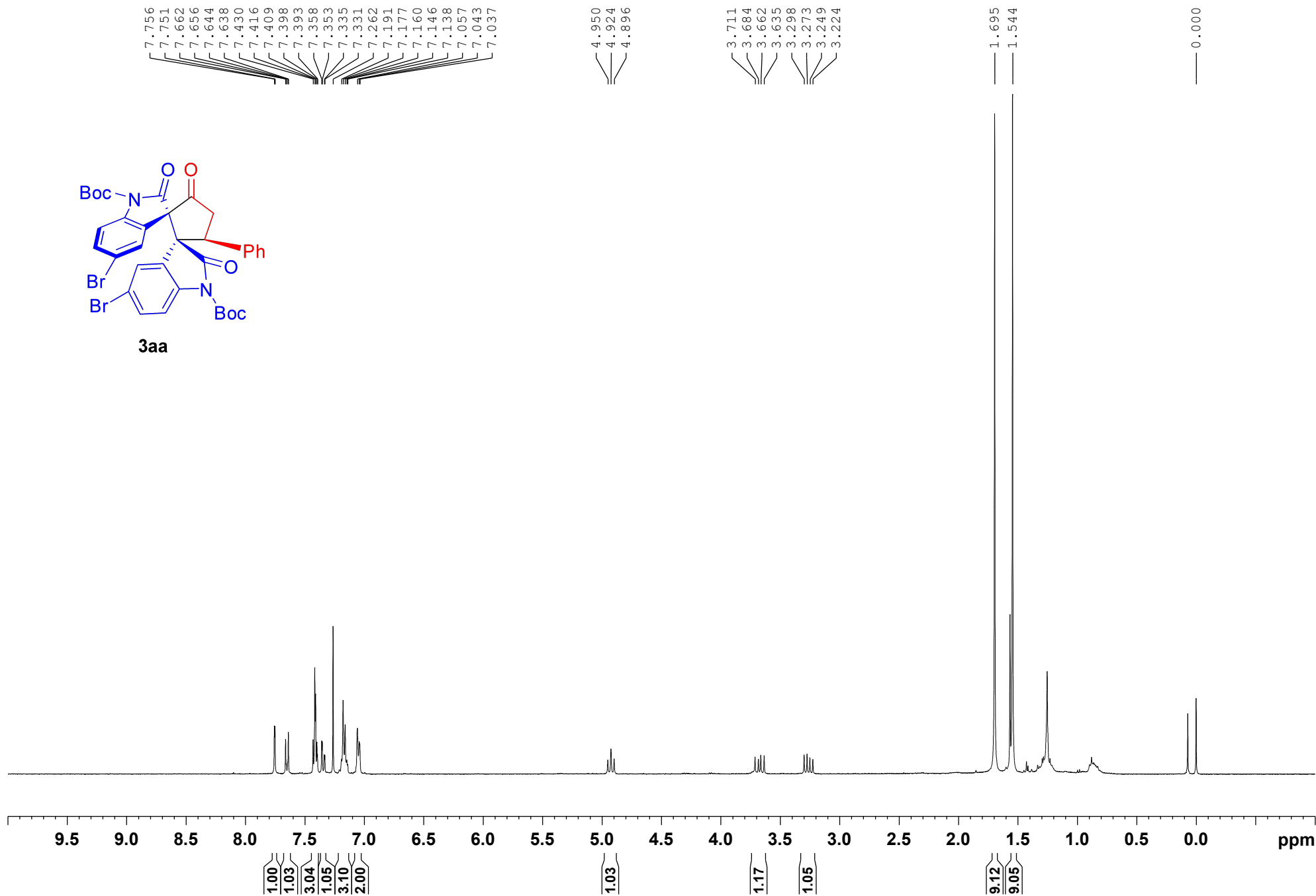


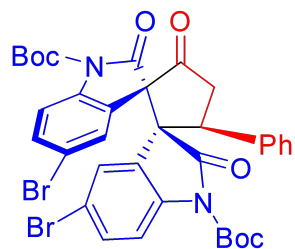




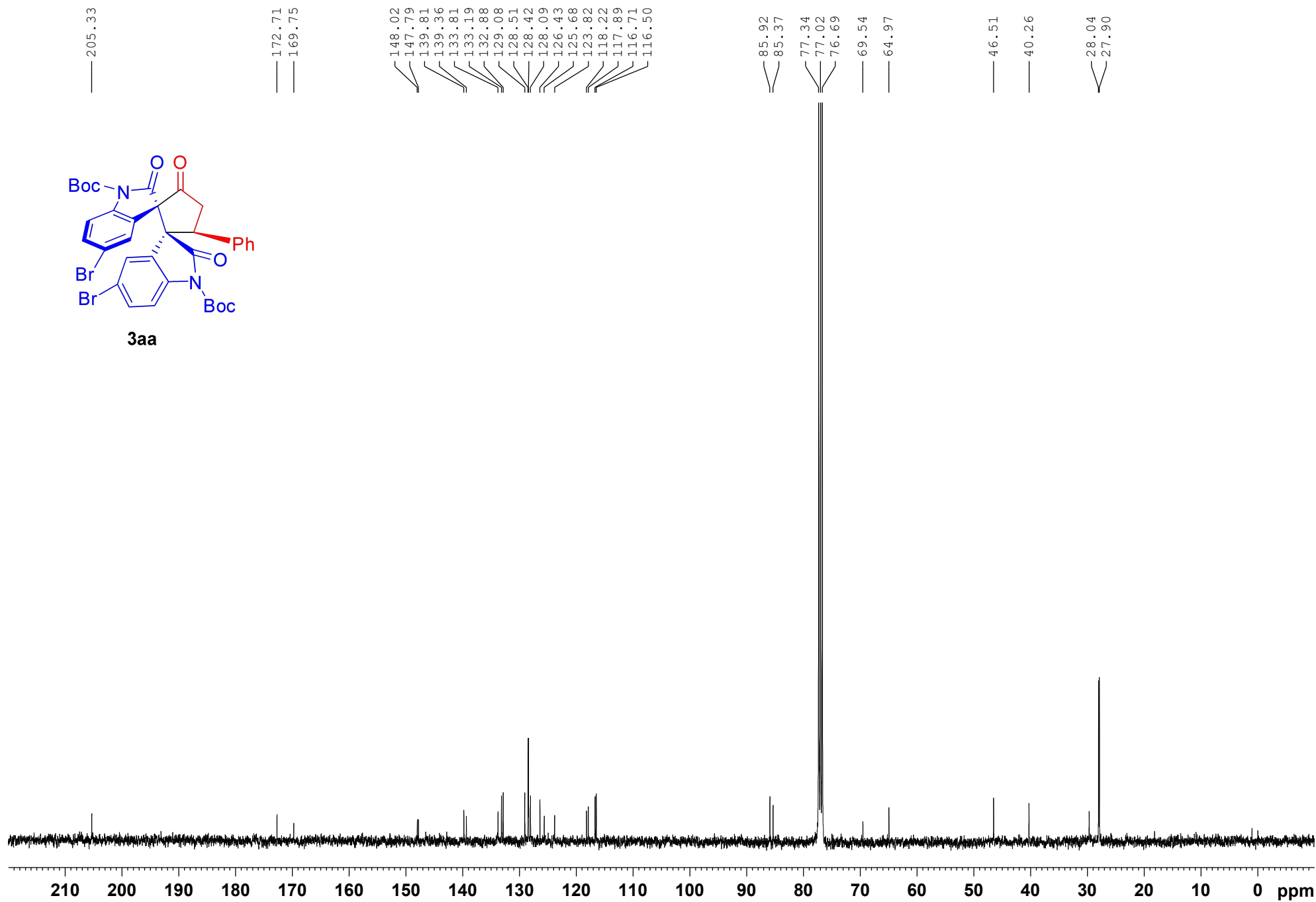


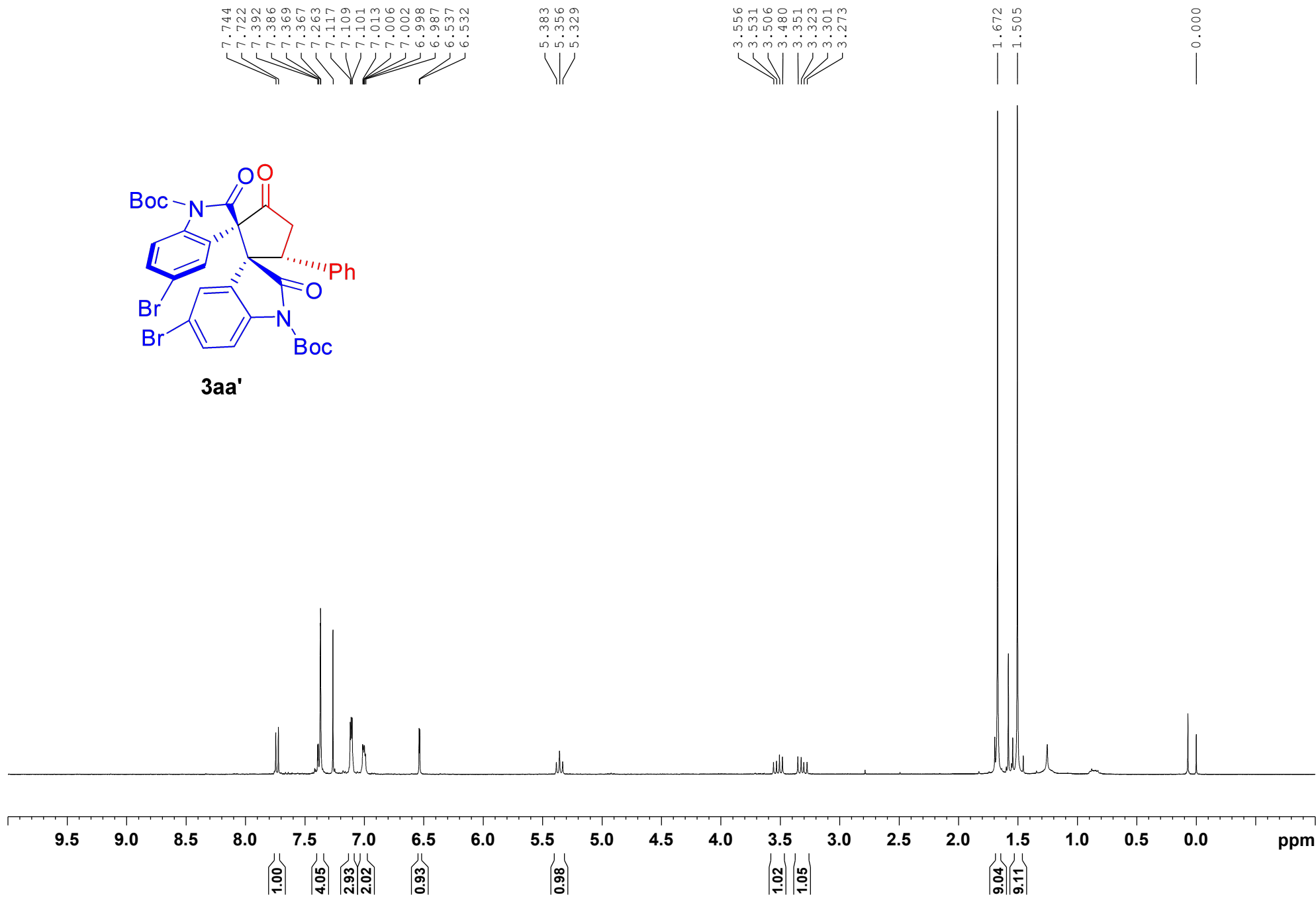
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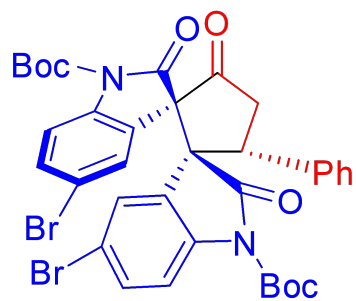




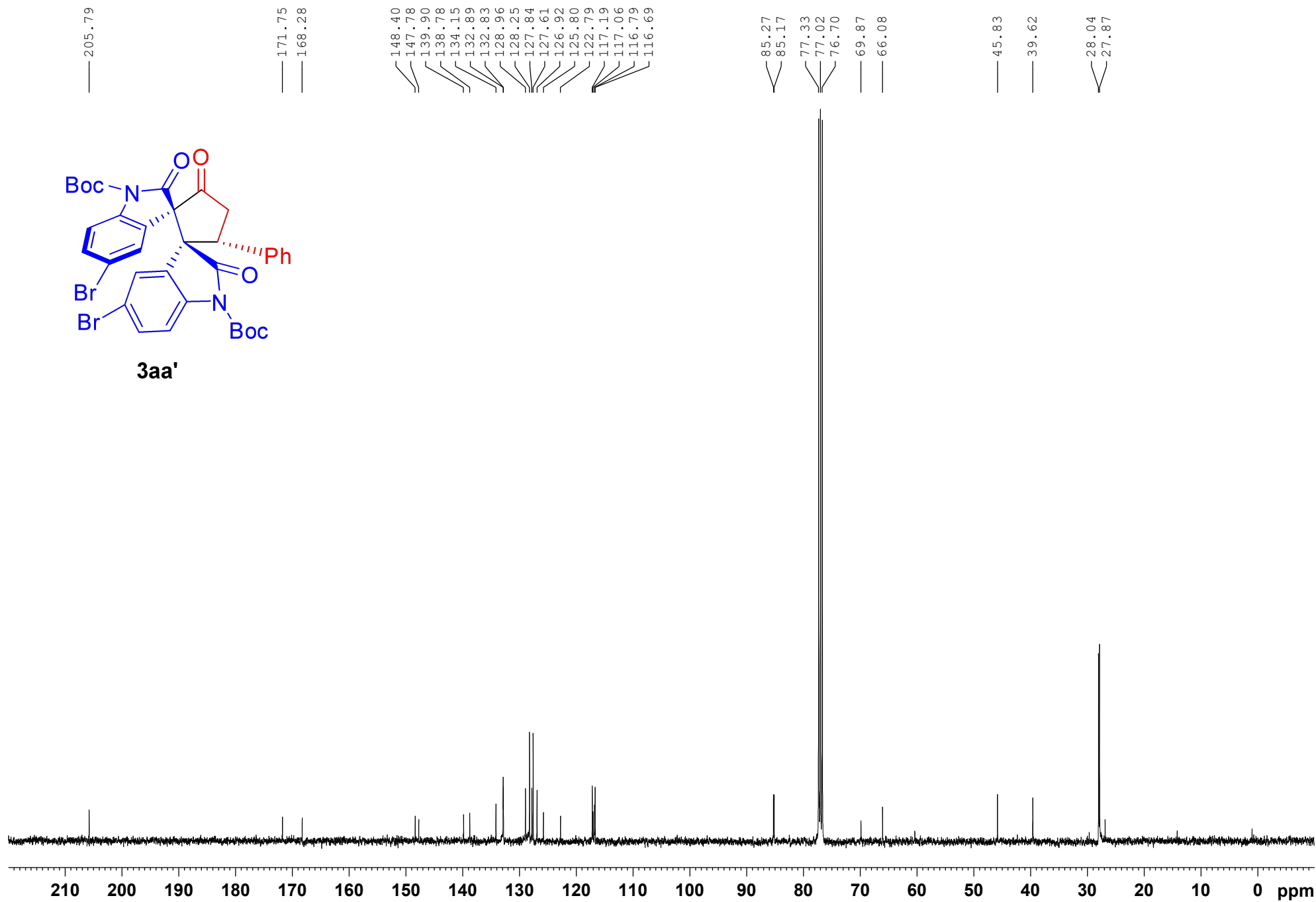
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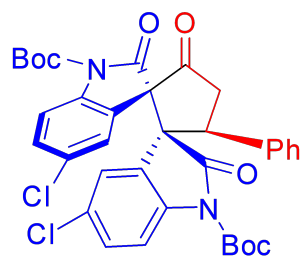




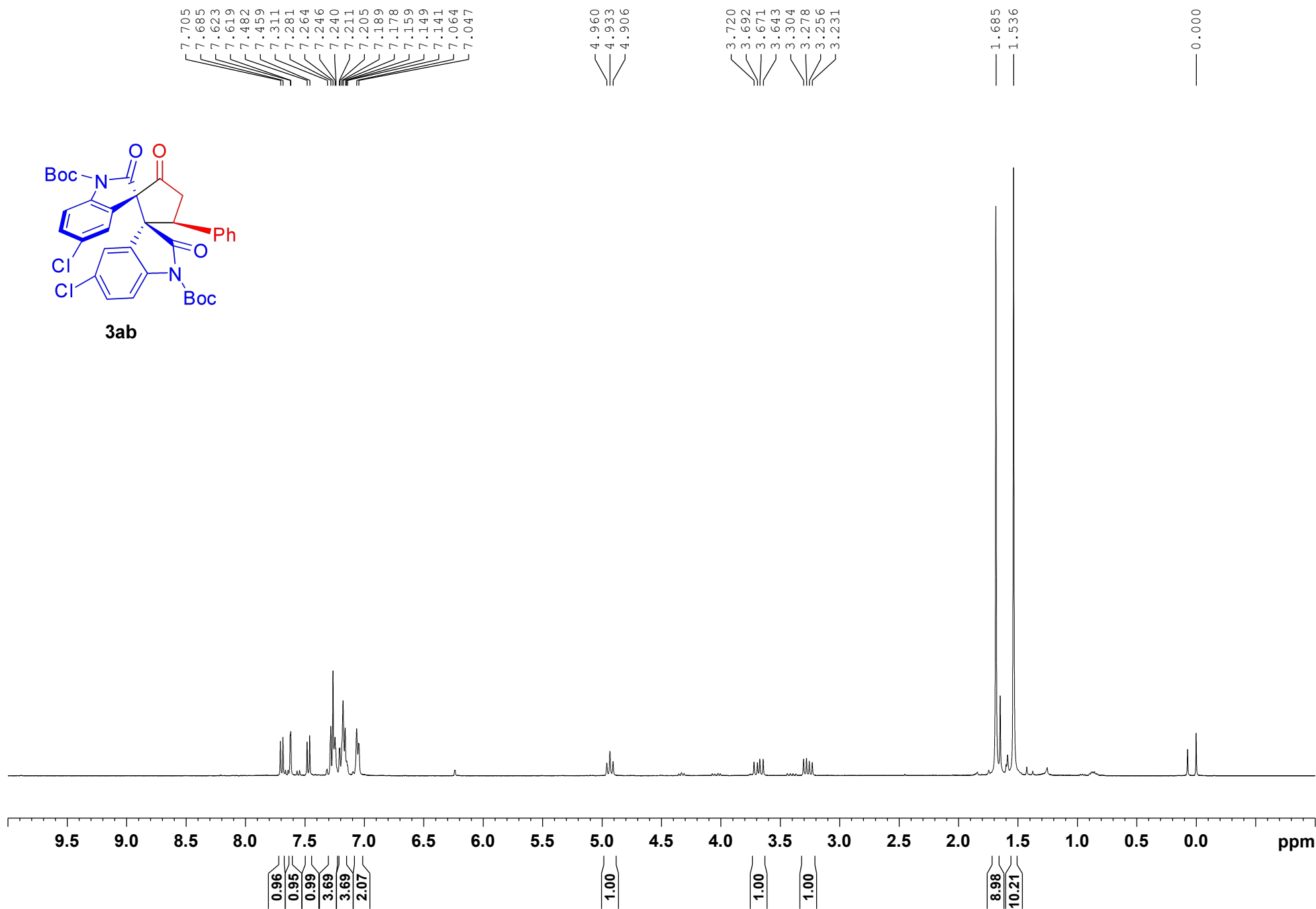


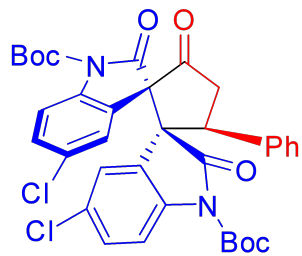
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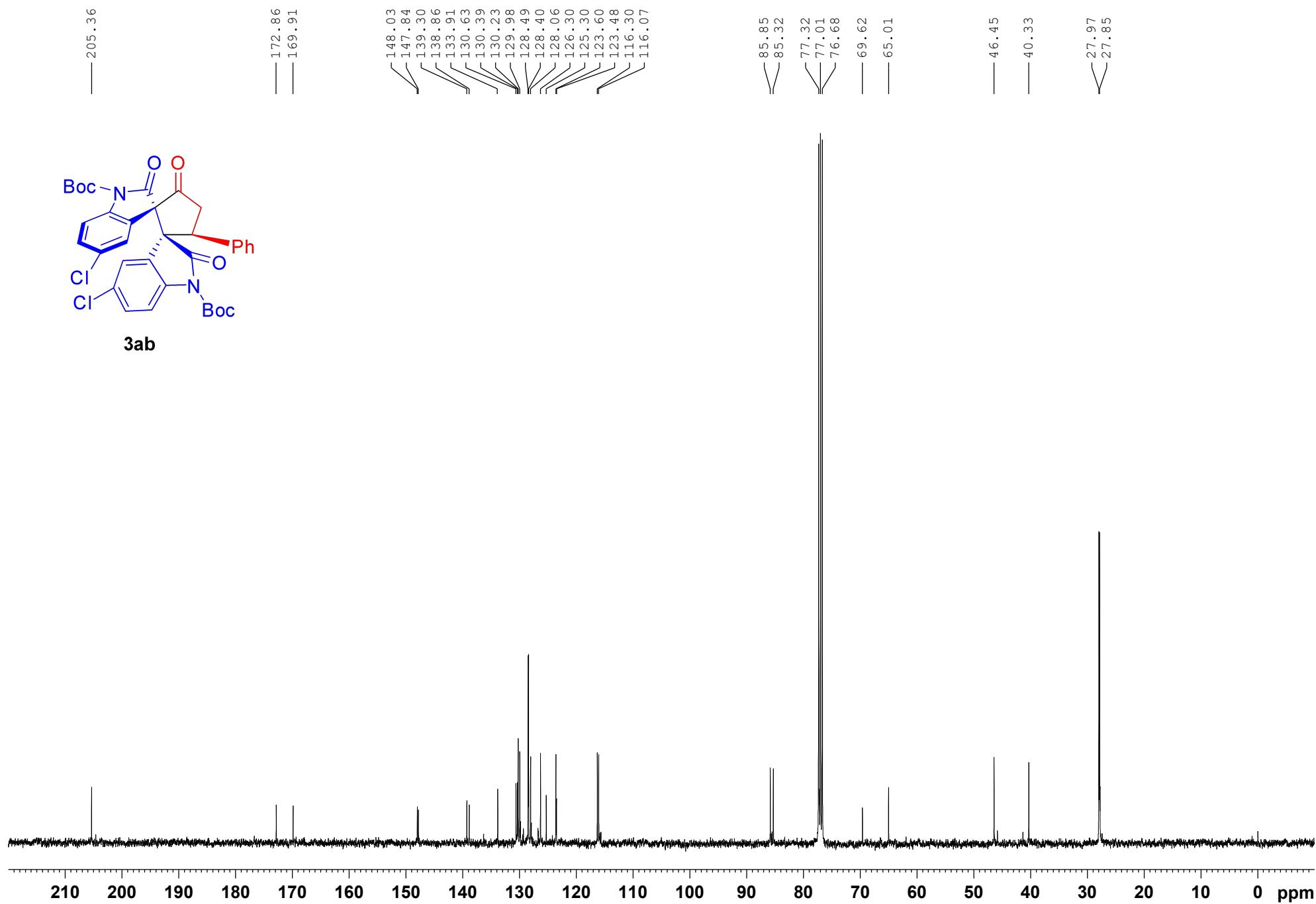


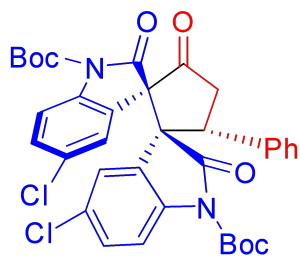
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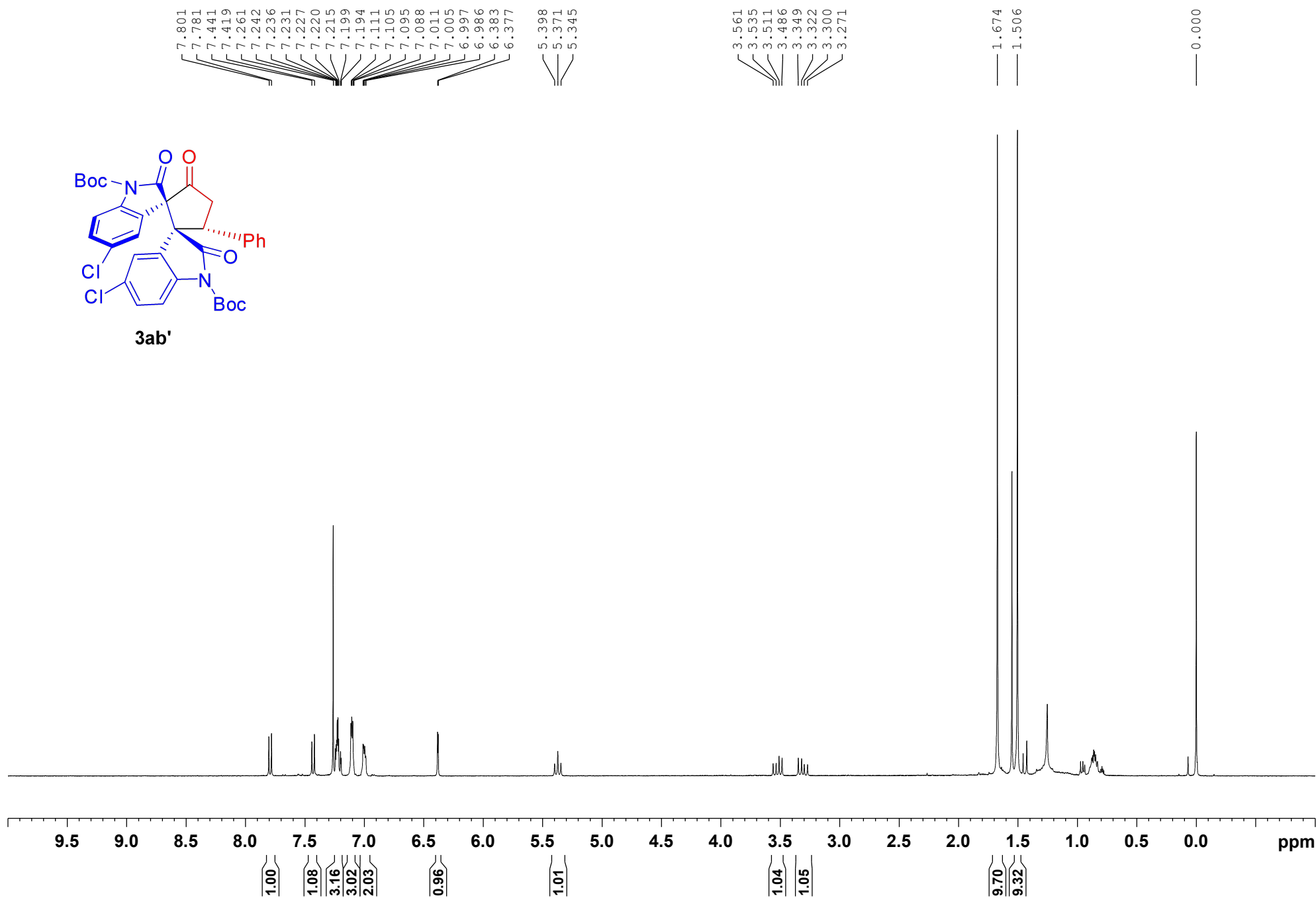


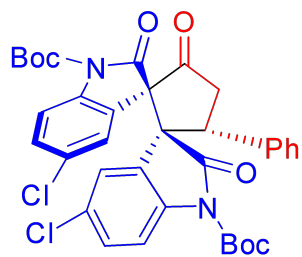
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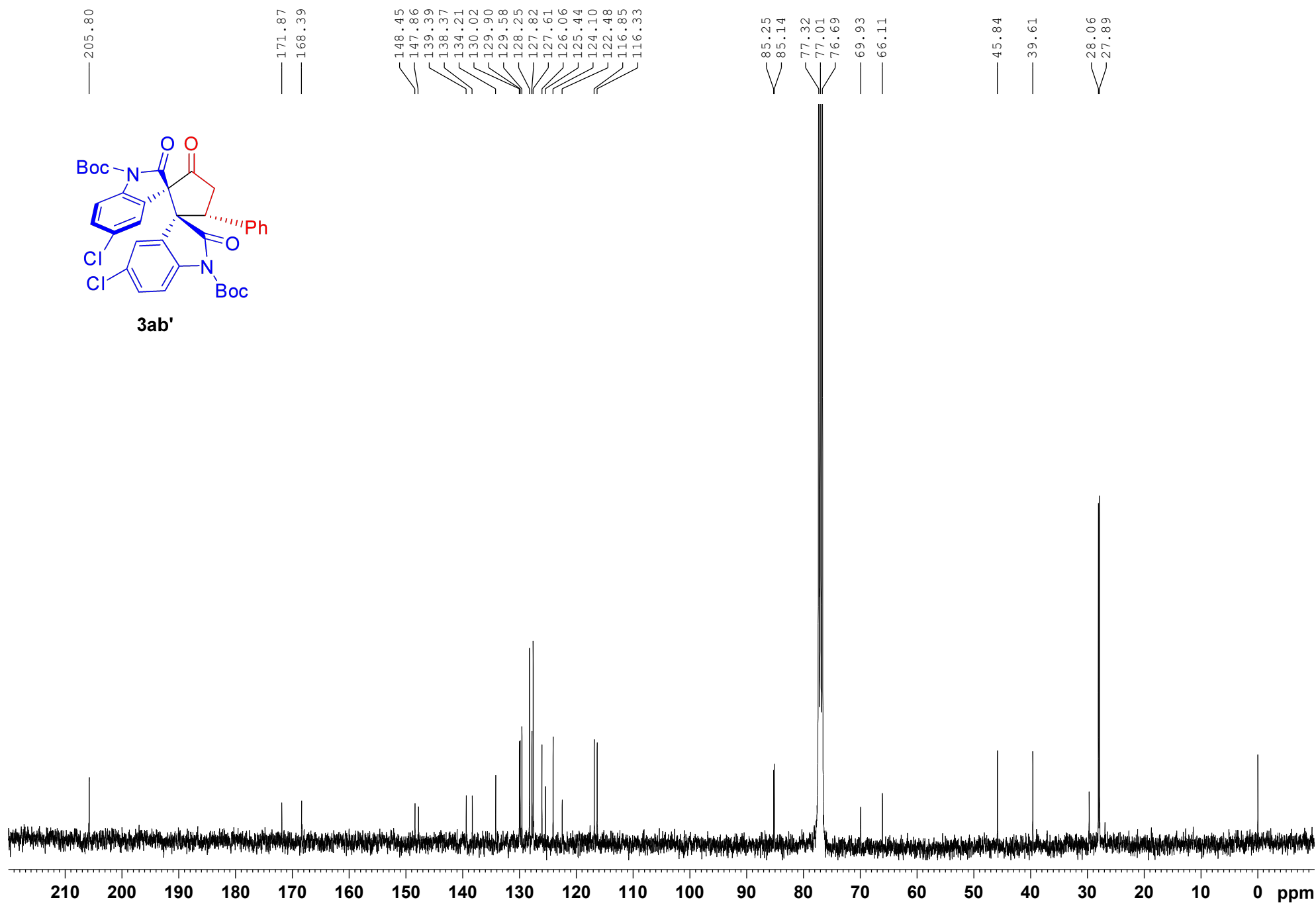


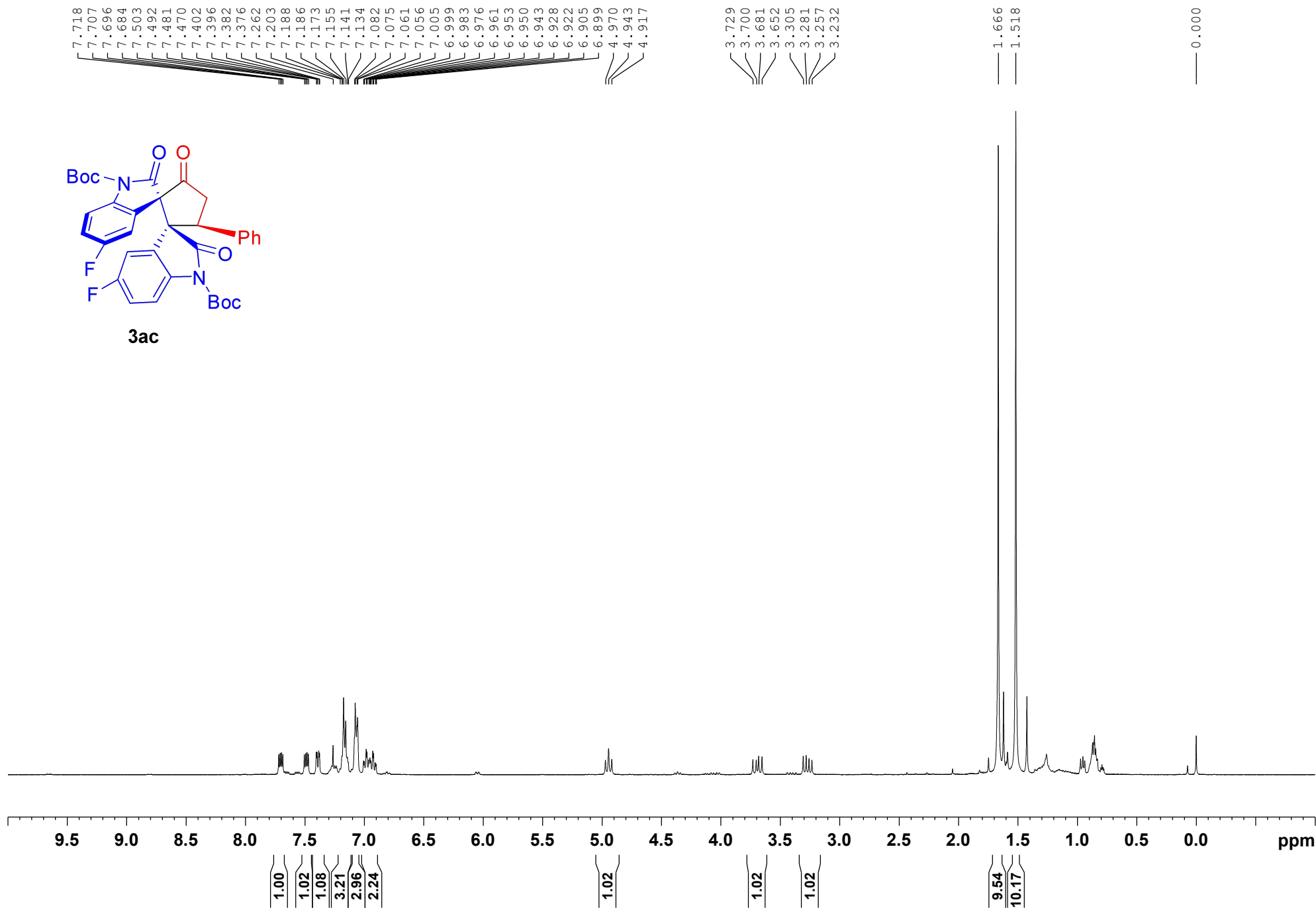
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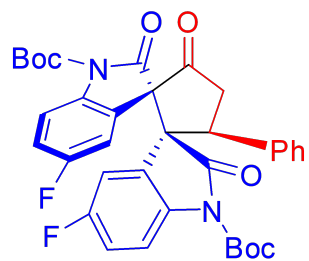




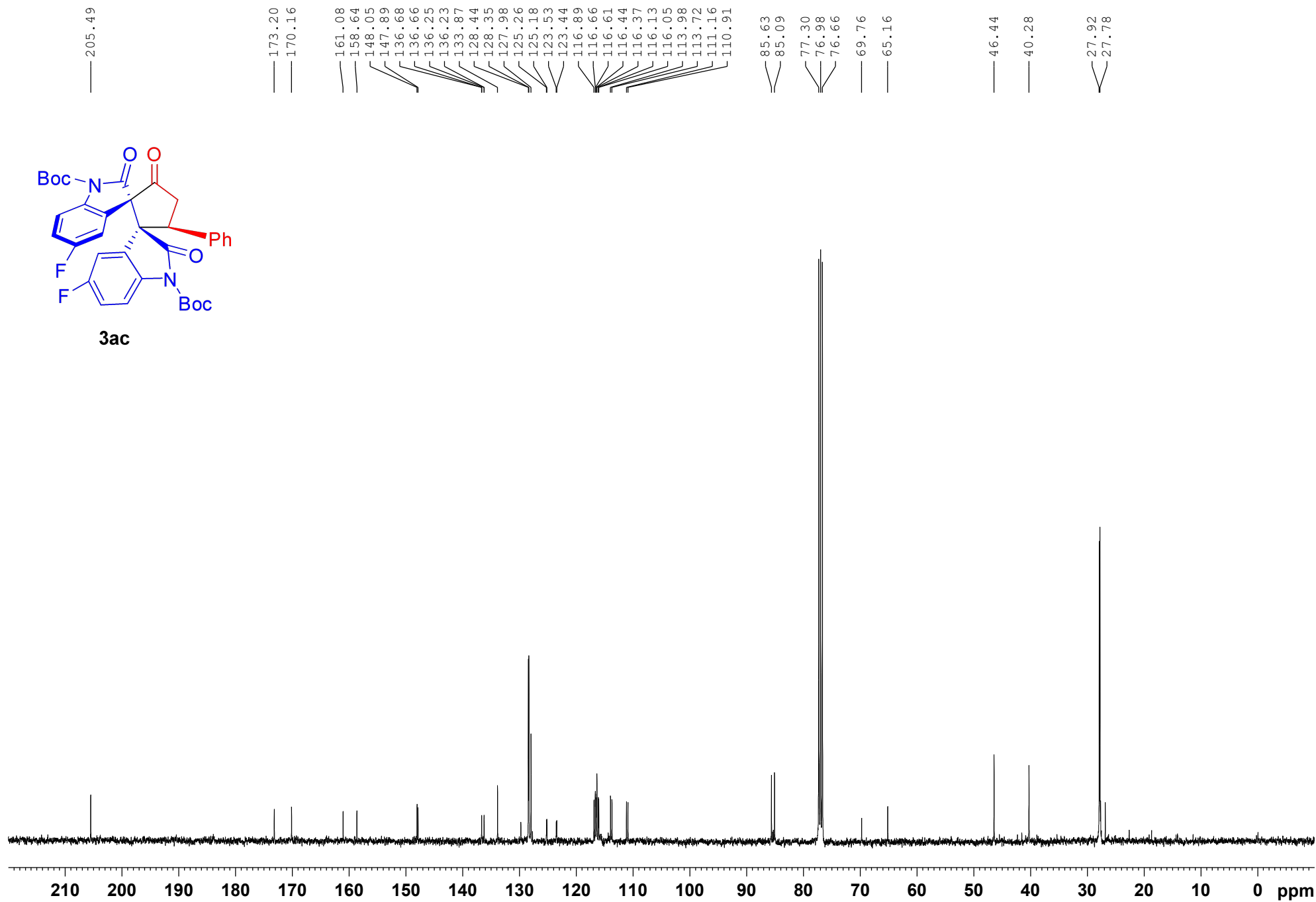
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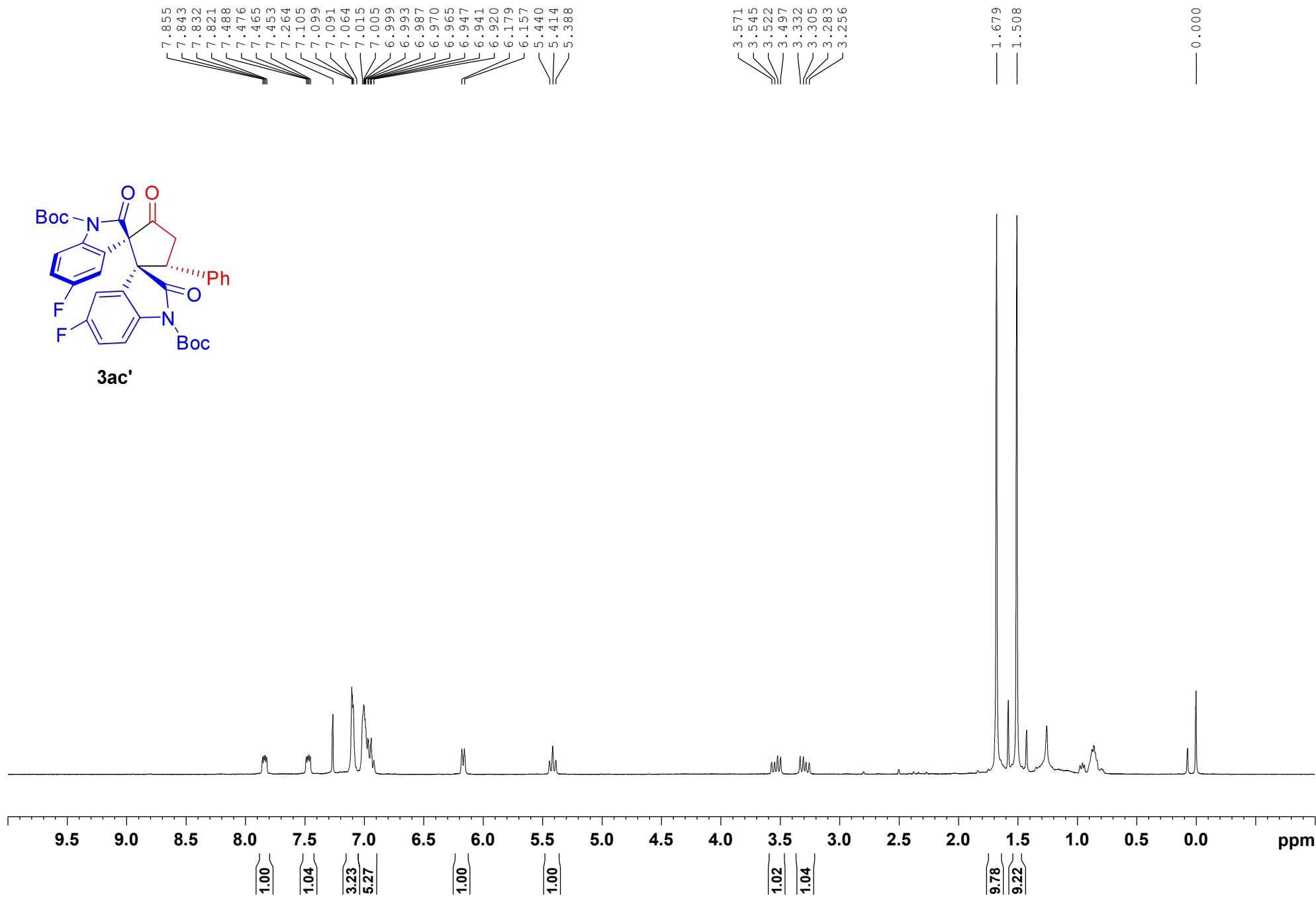


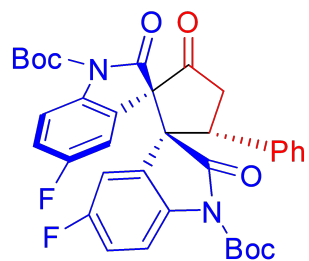




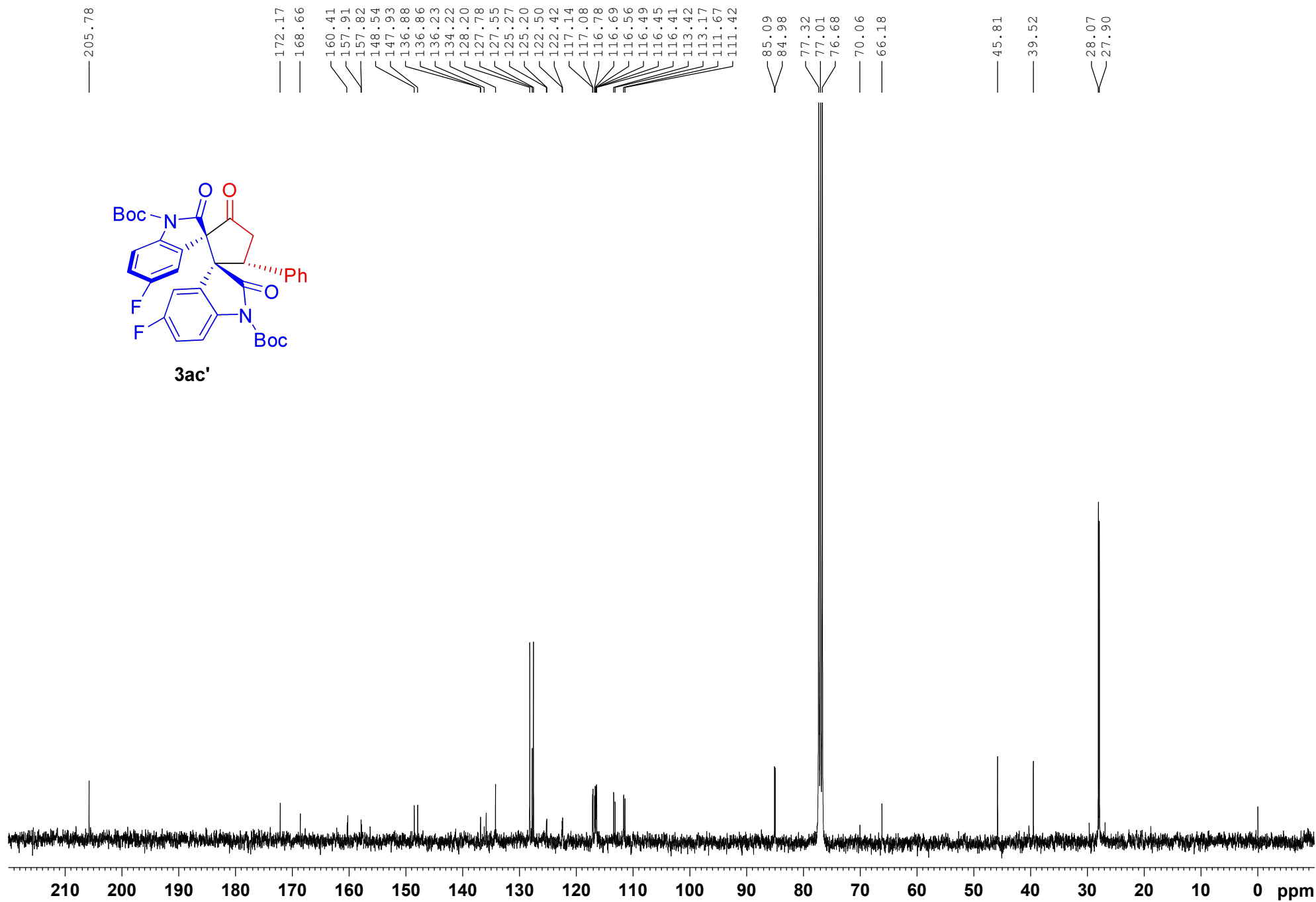
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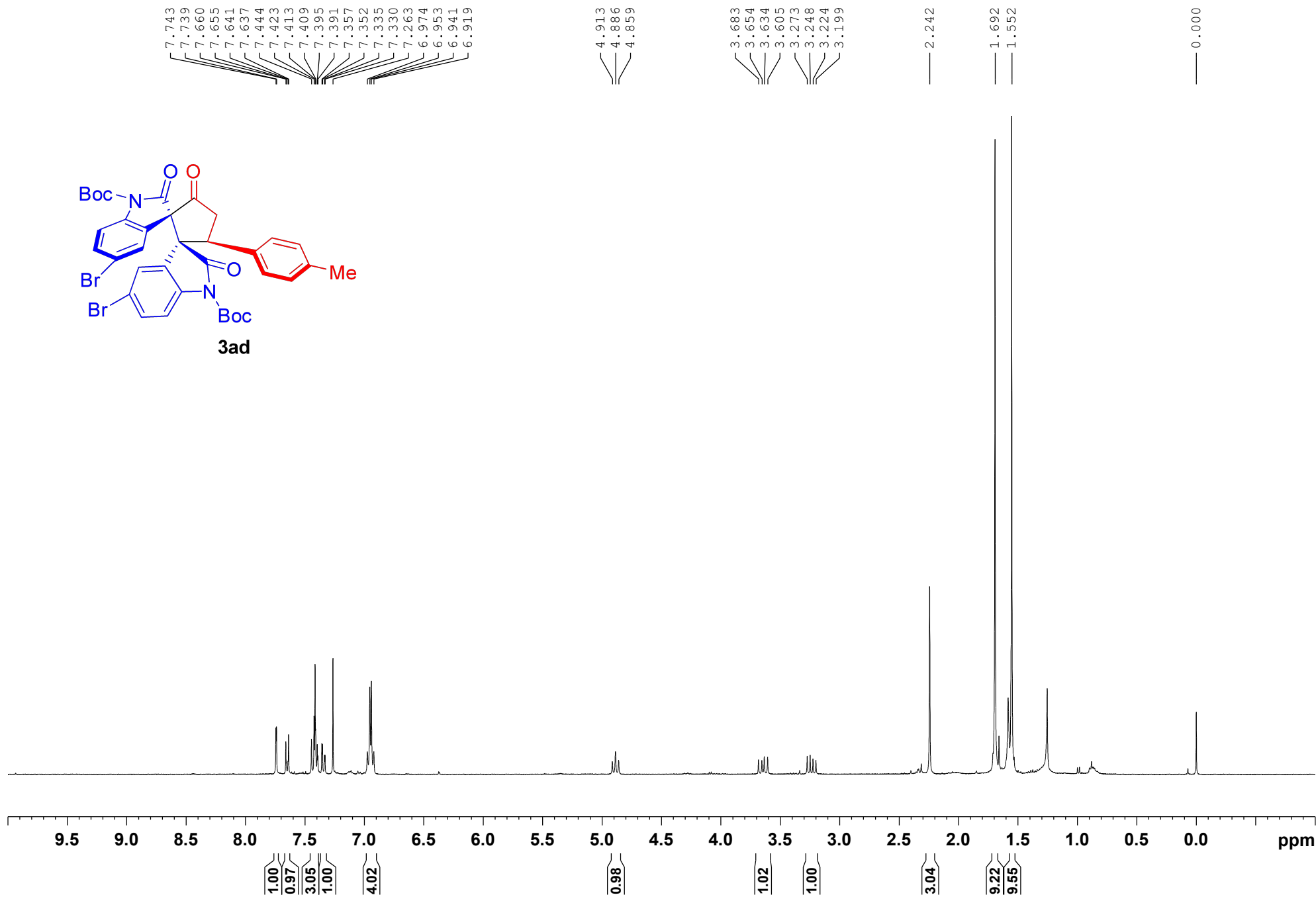


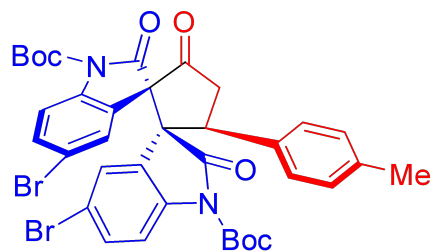




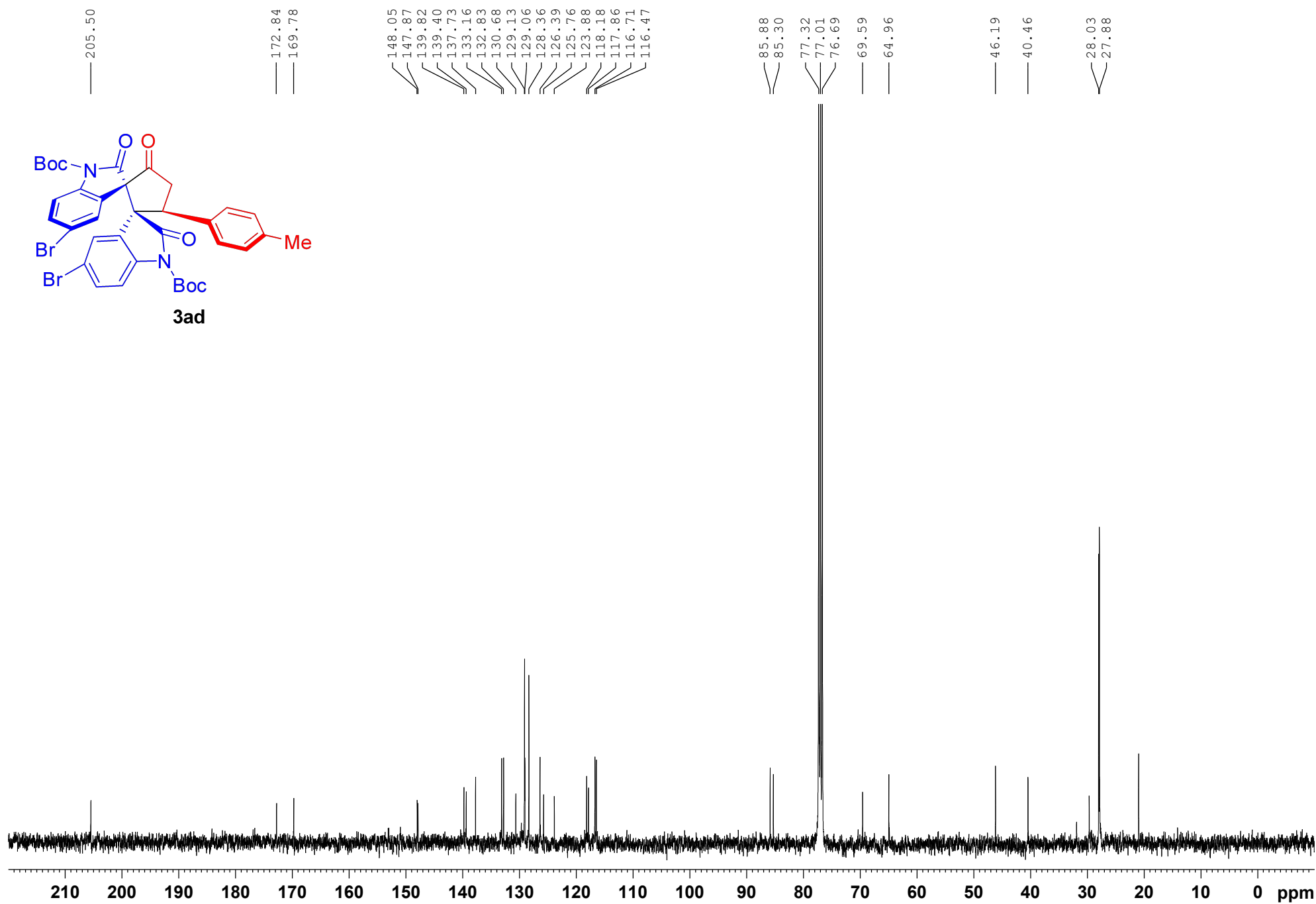
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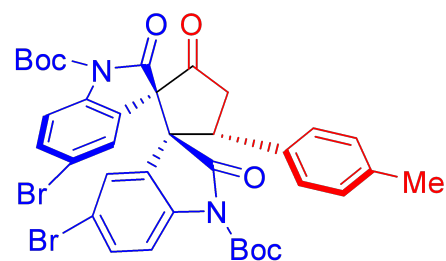




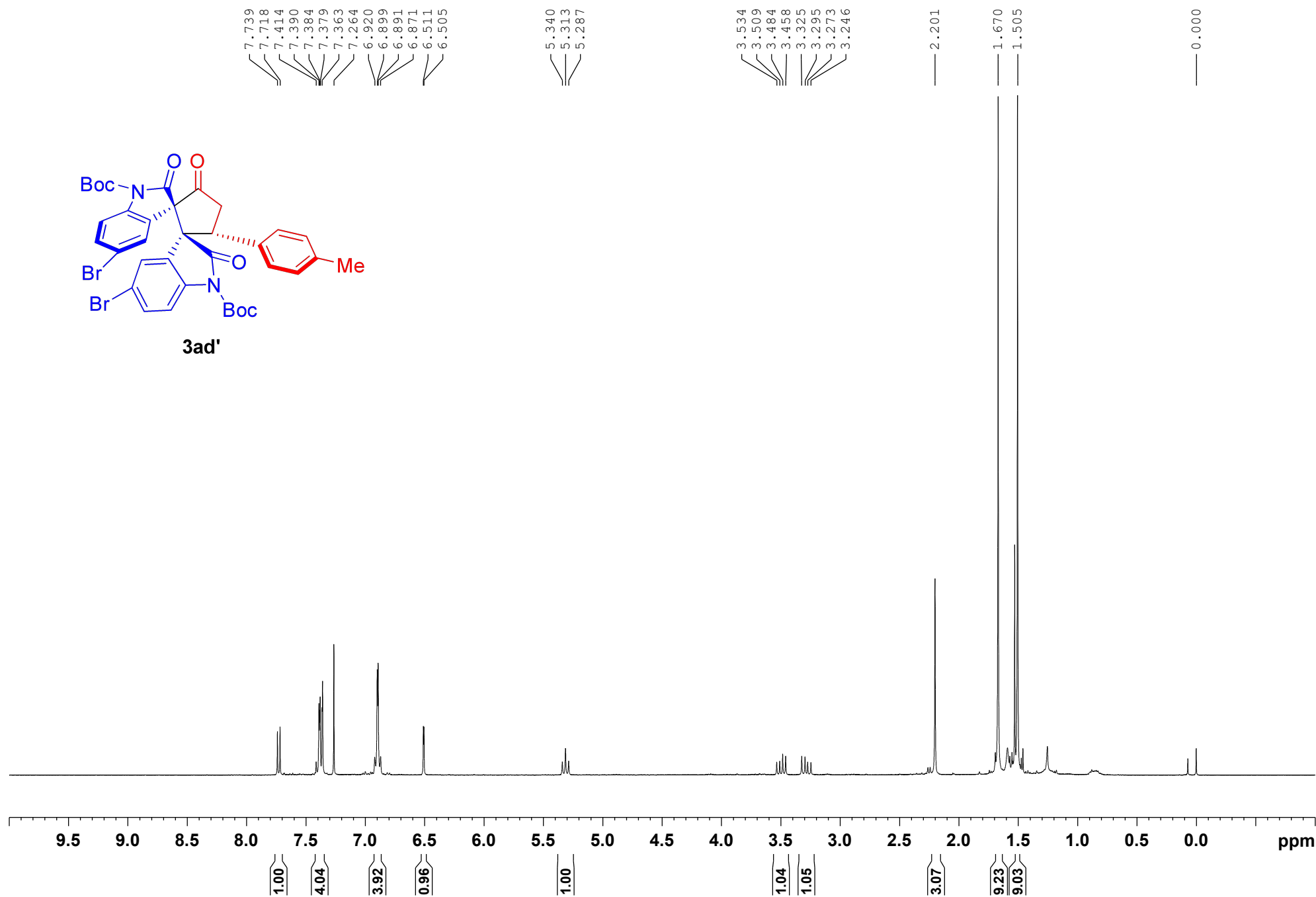


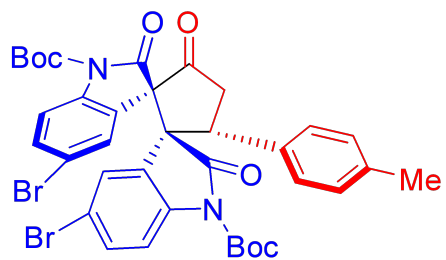
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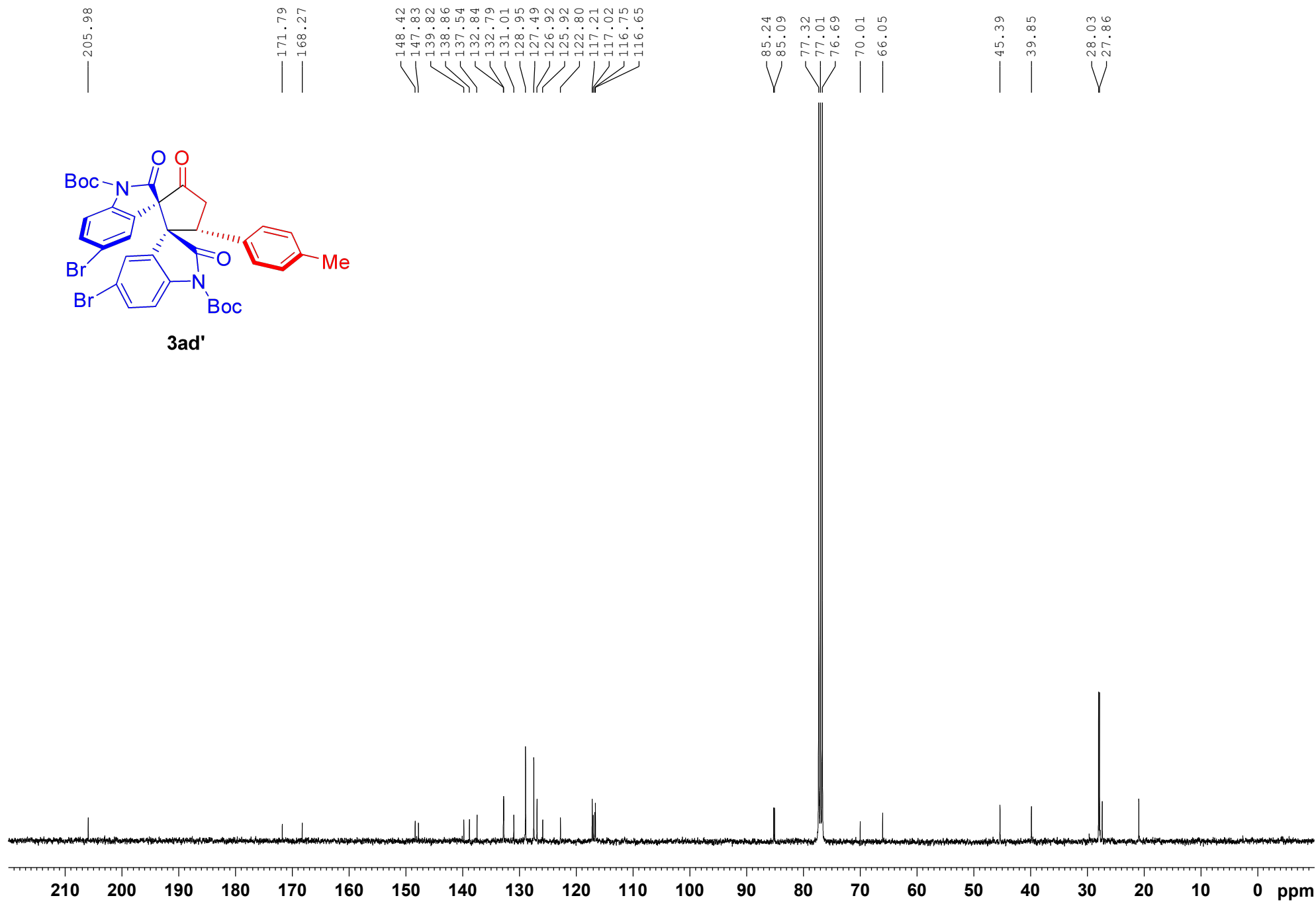


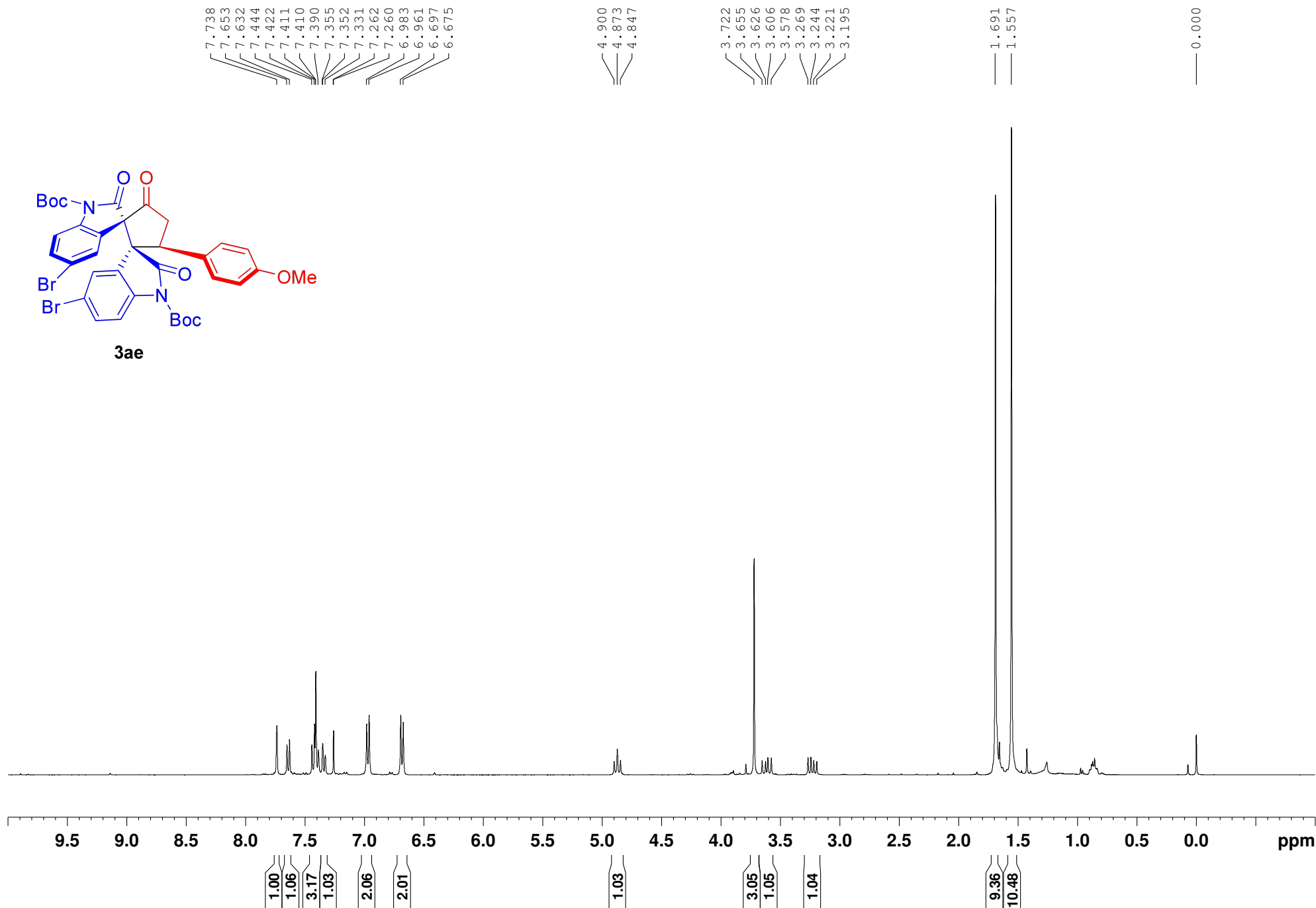
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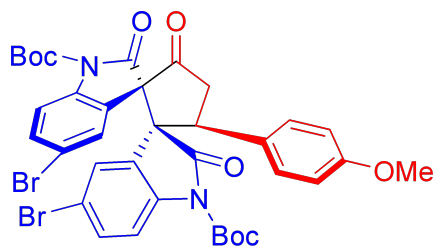




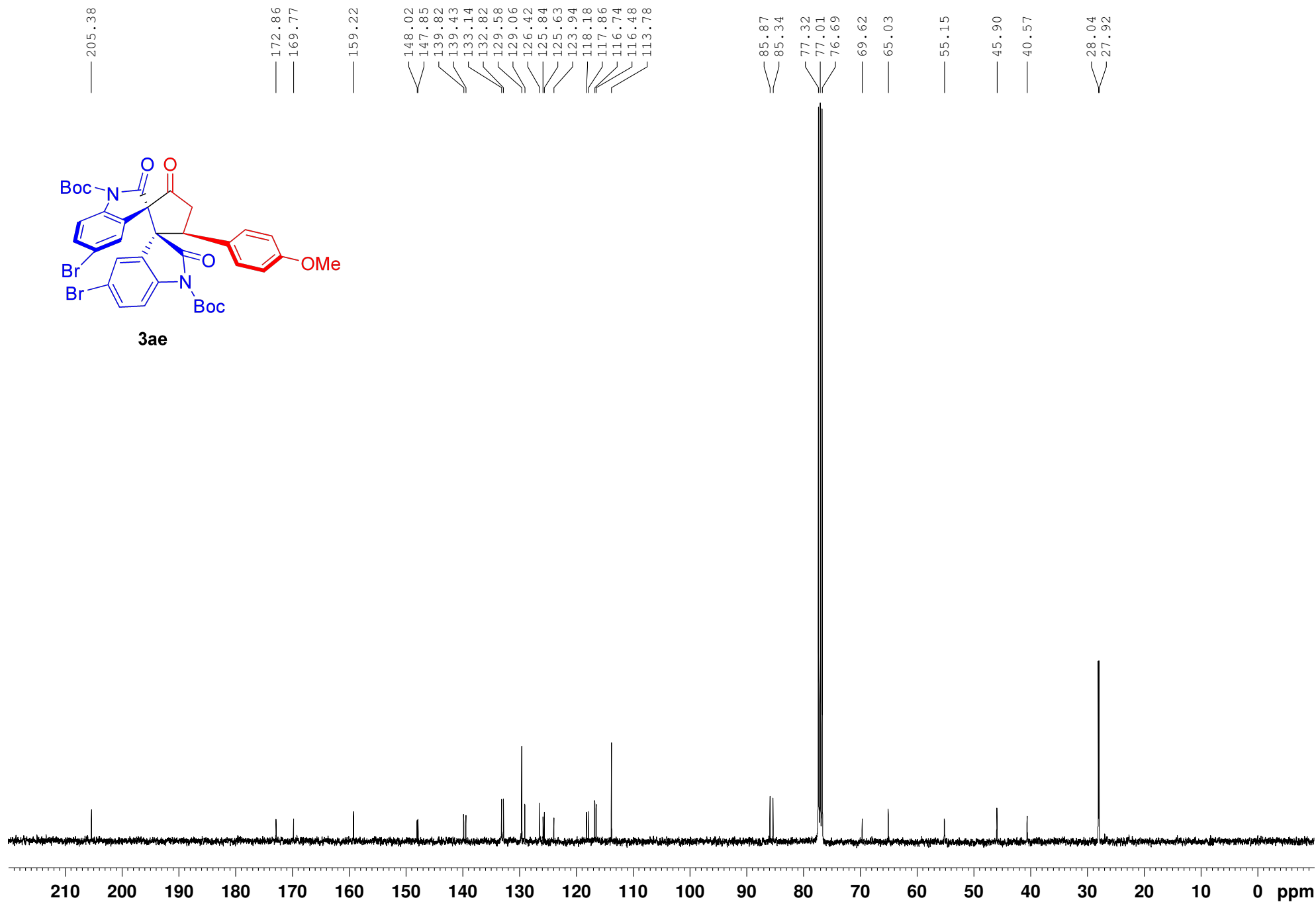
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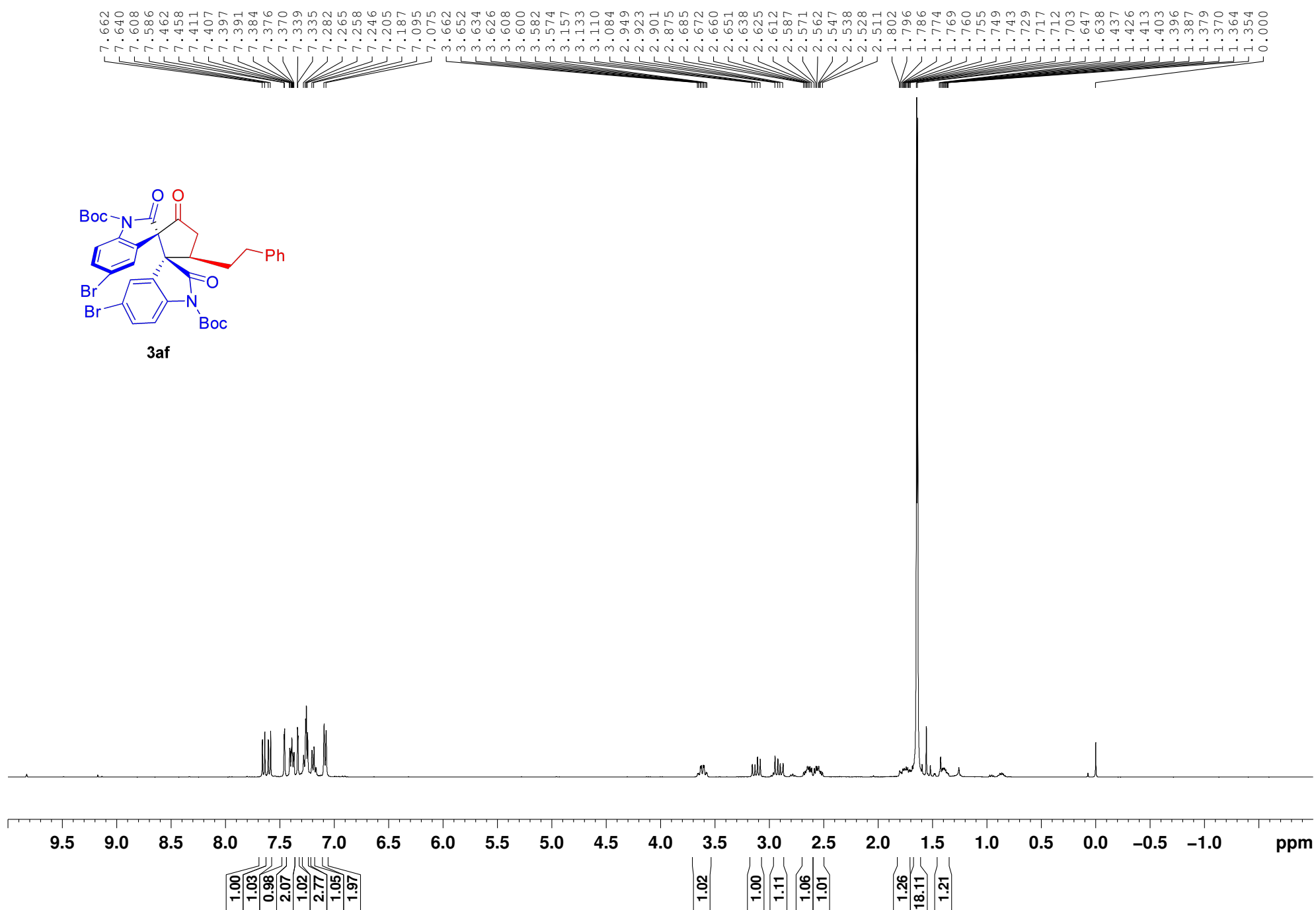


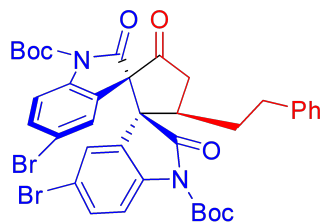




3ae







3af

