Squaramide-catalyzed asymmetric regioselective allylic alkylation of 4-aminopyrazolones with Morita–Baylis–Hillman carbonates

Aiqi Xue, Shiqiang Wei, Xingfu Wei, Yue Huang, Jingping Qu and Baomin Wang*

State Key Laboratory of Fine Chemicals, Department of Pharmaceutical Sciences, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, People's Republic of China

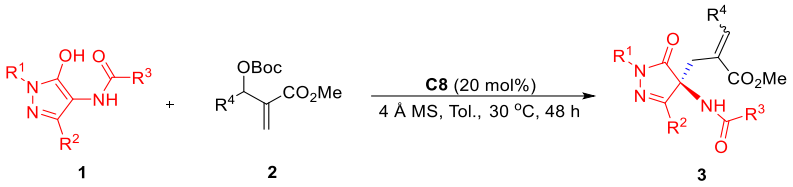
Contents

1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200~300 mesh). Enantiomeric excesses (ee) were determined by HPLC using corresponding commercial chiral columns as stated at 30 °C with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]_D^T$ (*c* g/100 mL, solvent). All ^{1}H NMR spectra were recorded on a Bruker Avance II 400 MHz and Bruker Avance III 600 MHz, ^{13}C NMR spectra were recorded on a Bruker Avance II 101 MHz, Bruker Avance II 126 MHz and Bruker Avance III 151 MHz, ^{19}F NMR spectra were recorded on a Bruker Avance II 376 MHz and Bruker Avance III 377 MHz with chemical shifts reported as ppm (in $CDCl_3$, TMS as an internal standard). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, dd = double doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL TM). The absolute configuration of **3ao** and **5ak** were assigned by the X-ray analysis.

4-Aminopyrazolones **1** were prepared according to the literature.[1] MBH carbonates **2** and **4** were prepared according to the literature.[2] Catalyst **C8** was synthesized according to the literature procedure.[3] Nitrile oxides **6** and nitrile imine **8a** were prepared according to the literature.[4] The racemic products were synthesized using quinine/quinidine = 1:1 as the catalyst.

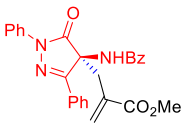
2. Experimental procedures and characterization of compounds 3, 5, 7 and 9



1 **2** **3**

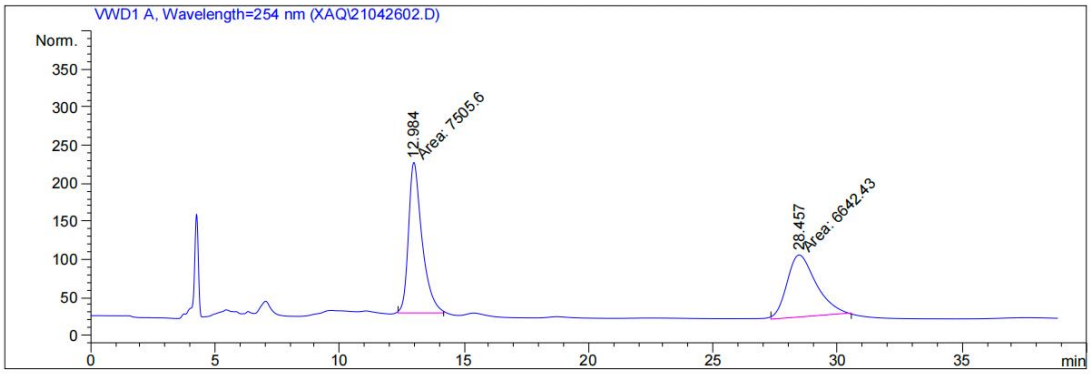
To a tube were added 4-aminopyrazolone **1** (0.2 mmol), **C8** (0.04 mmol), 4 Å MS (200 mg) and toluene (2 mL). MBH carbonate **2** (0.7 mmol) was then added in one portion, and the reaction mixture was stirred at 30 °C. When the substrate **1** was consumed as checked by TLC, the reaction was stopped and purified by column chromatography (petroleum ether/ethyl acetate = 5:1) on silica gel directly to give the product **3**.

Compound 3aa

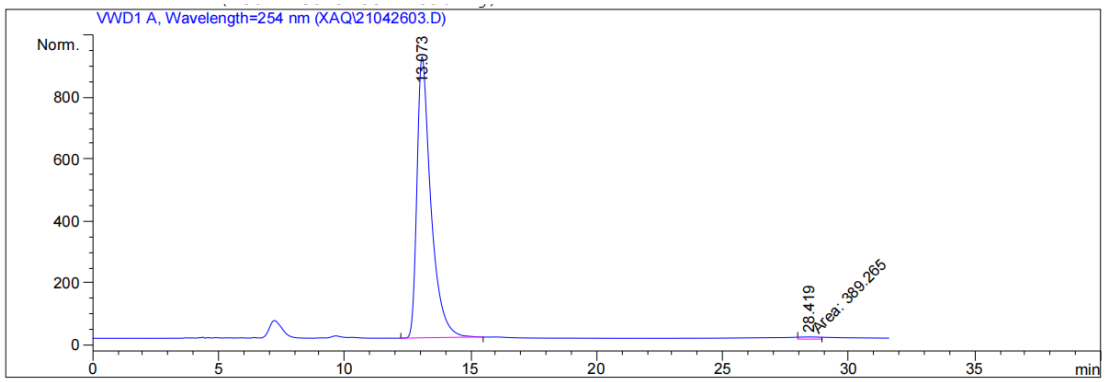


3aa

Prepared according to the procedure within 48 h as white solid (89.7 mg, 99% yield); $[\alpha]_D^{17}$ = 9.091 (*c* 1.32, CH_2Cl_2); Mp: 148.6 - 149.2 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.15 (s, 1H), 8.09 – 8.01 (m, 4H), 7.90 – 7.87 (m, 2H), 7.51 – 7.41 (m, 5H), 7.39 – 7.35 (m, 3H), 7.25 – 7.20 (m, 1H), 6.41 (s, 1H), 5.69 (s, 1H), 3.80 (s, 3H), 3.36 (d, *J* = 14.5 Hz, 1H), 2.77 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.9, 169.7, 166.3, 156.1, 138.3, 133.6, 132.1, 132.0, 131.7, 130.3, 130.2, 128.9, 128.7, 128.6, 127.5, 126.3, 125.3, 119.3, 65.2, 52.9, 37.7. HRMS (ESI) m/z Calcd. for $C_{27}H_{24}N_3O_4$ ($[M+H]^+$) 454.1761, Found 454.1755. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 13.0 min, t_{minor} = 28.4 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.984	MM	0.6532	7838.50635	199.99681	51.3389
2	28.457	BB	1.3140	7429.66455	83.55426	48.6611



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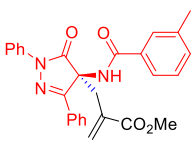
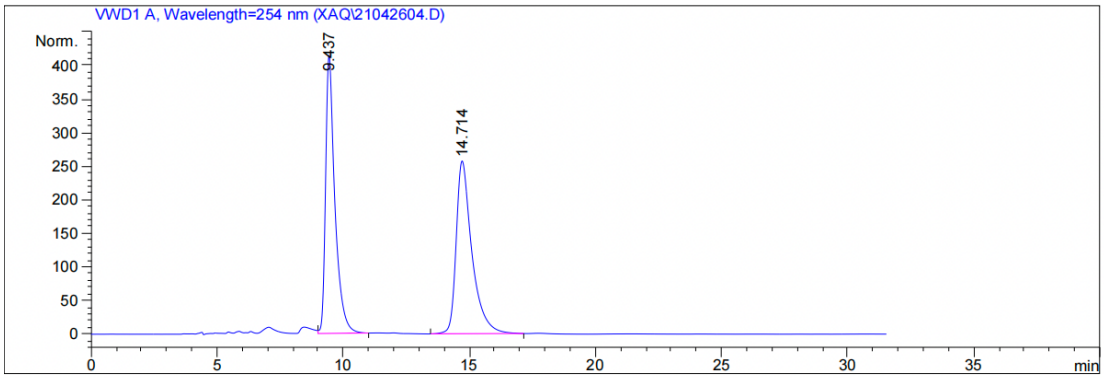
1	13.073	PB	0.5636	3.48997e4	907.62250	98.8969
2	28.419	MM	0.9216	389.26526	7.03986	1.1031

Compound 3ab

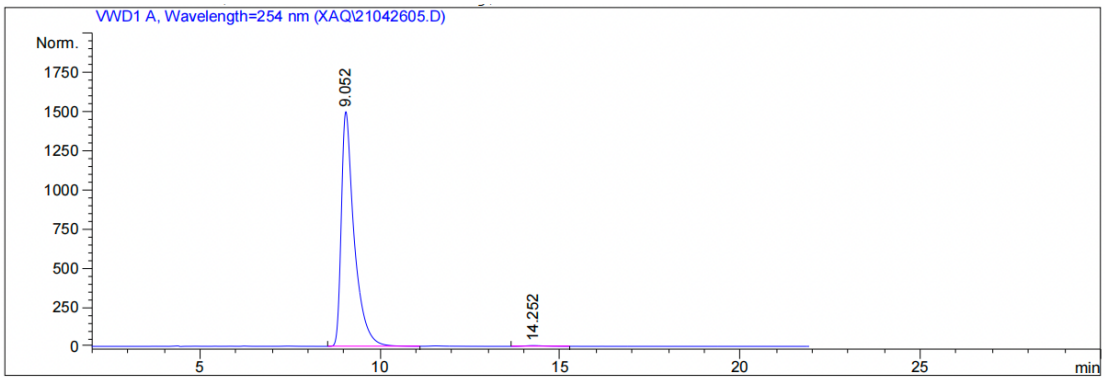


3ab

Prepared according to the procedure within 48 h as white solid (72.9 mg, 78% yield); $[\alpha]_D^{16}$ = 7.547 (*c* 0.53, CH_2Cl_2); Mp: 123.5 - 124.6 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.08 (s, 1H), 8.08 – 8.01 (m, 4H), 7.71 – 7.66 (m, 2H), 7.46 – 7.42 (m, 2H), 7.38 – 7.36 (m, 3H), 7.31 – 7.30 (m, 2H), 7.24 – 7.20 (m, 1H), 6.41 (s, 1H), 5.69 (s, 1H), 3.81 (s, 3H), 3.37 (d, *J* = 14.7 Hz, 1H), 2.76 (d, *J* = 14.3 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.0, 169.7, 166.6, 156.1, 138.4, 133.6, 132.9, 132.0, 131.7, 130.3, 130.3, 128.8, 128.7, 128.5, 126.4, 125.3, 124.4, 119.4, 65.1, 52.9, 37.7, 21.3. HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_3O_4$ ($[M+H]^+$) 486.1918, Found 486.1924. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.0 min, t_{minor} = 14.2 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.437	VB	0.3752	1.06199e4	413.65125	48.7959
2	14.714	PB	0.6366	1.11440e4	257.15918	51.2041



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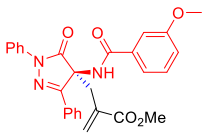
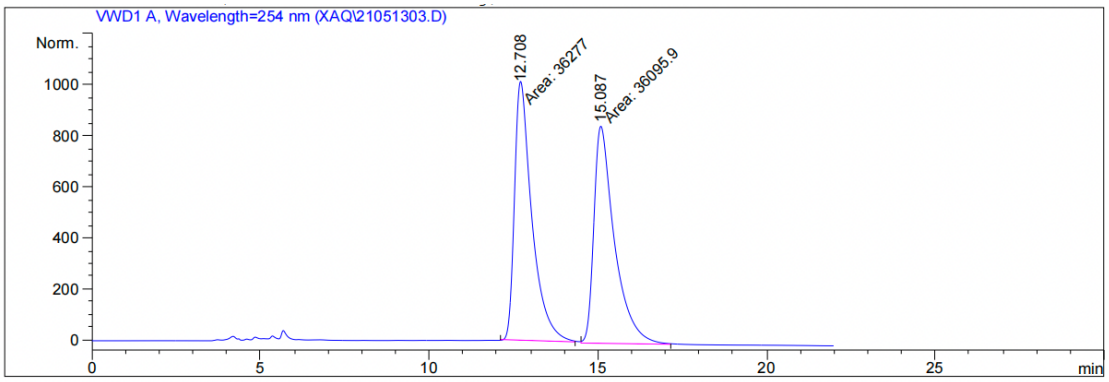
1	9.052	BB	0.3616	3.73350e4	1500.82788	99.5238
2	14.252	PB	0.5404	178.65710	4.67621	0.4762

Compound 3ac



3ac

Prepared according to the procedure within 48 h as yellow solid (95.7 mg, 99% yield); $[\alpha]_D^{16}$ = 16.083 (*c* 1.00, CH_2Cl_2); Mp: 104.3 - 105.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.17 (s, 1H), 8.08 – 7.99 (m, 4H), 7.47 – 7.42 (m, 4H), 7.39 – 7.30 (m, 4H), 7.24 – 7.20 (m, 1H), 7.05 – 7.02 (m, 1H), 6.41 (s, 1H), 5.69 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.36 (d, *J* = 14.3 Hz, 1H), 2.76 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 169.8, 166.3, 159.8, 156.1, 138.3, 133.7, 133.4, 131.6, 130.4, 130.2, 129.6, 128.9, 128.8, 126.3, 125.3, 119.3, 119.2, 112.1, 65.2, 55.4, 52.9, 37.7. HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_3O_5$ ($[M+H]^+$) 484.1867, Found 484.1875. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.4 min, t_{minor} = 14.9 min).



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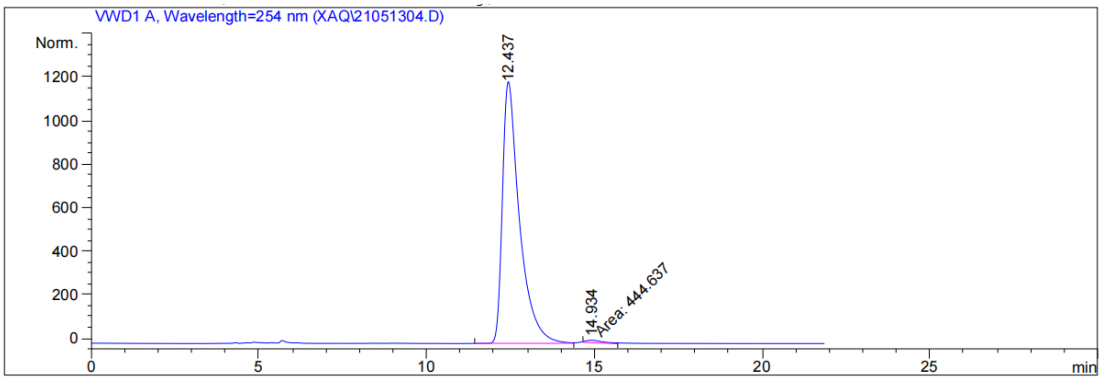
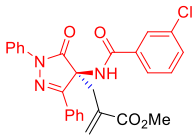
1	12.708	MM	0.5966	3.62770e4	1013.45374	50.1252
2	15.087	MM	0.7071	3.60959e4	850.74951	49.8748



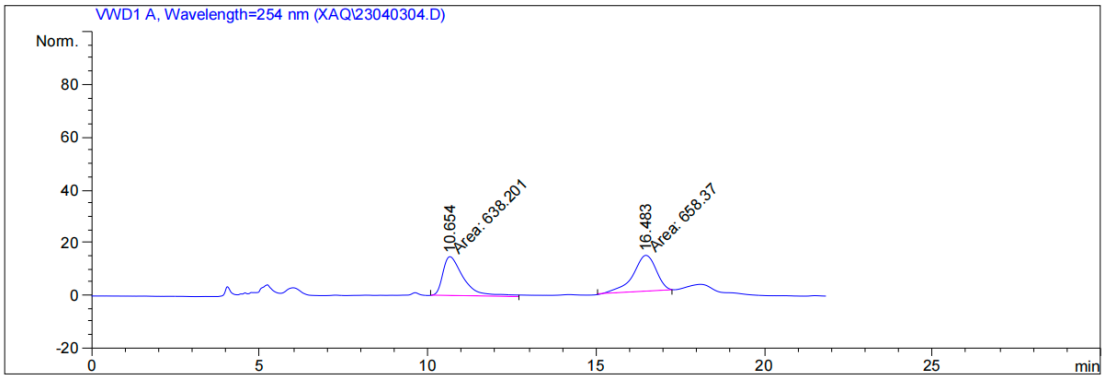
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.437	BV	0.5169	4.26260e4	1202.73022	98.9677
2	14.934	MM	0.6376	444.63718	11.62320	1.0323

Compound 3ad

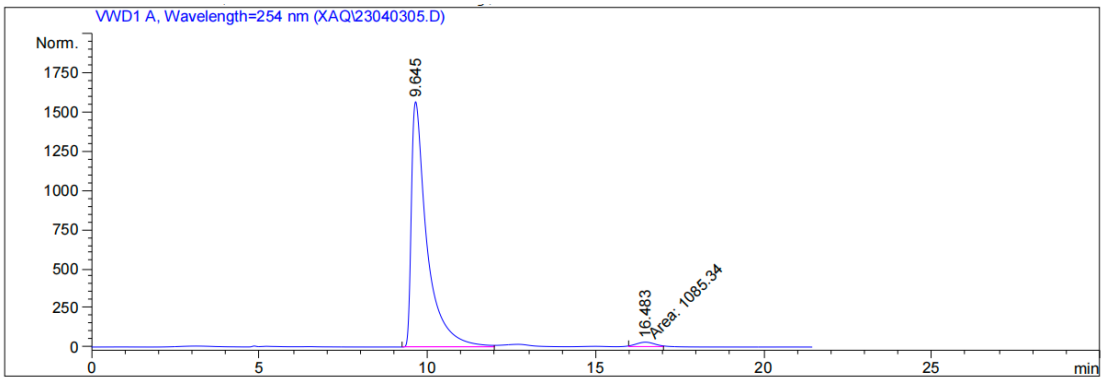


3ad

Prepared according to the procedure within 48 h as yellow solid (94.5 mg, 97% yield); $[\alpha]_D^{16}$ = 5.603 (*c* 0.23, CH_2Cl_2); Mp: 147.1 - 148.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 8.08 – 8.01 (m, 4H), 7.91 – 7.90 (m, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.40 (m, 7H), 7.27 – 7.23 (m, 1H), 6.48 (s, 1H), 5.75 (s, 1H), 3.92 (s, 3H), 3.43 (d, *J* = 14.5 Hz, 1H), 2.72 (d, *J* = 14.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 170.4, 165.0, 156.0, 138.3, 134.8, 134.1, 133.8, 132.2, 131.4, 130.5, 130.0, 129.9, 128.9, 128.8, 128.0, 126.3, 125.5, 125.4, 119.3, 65.0, 53.2, 37.8; HRMS (ESI) m/z Calcd. for $C_{27}H_{23}ClN_3O_4$ ([M+H]$^+$) 488.1372, Found 488.1374. Enantiomeric excess was determined to be 95% (determined by HPLC using chiral IF-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.6 min, t_{minor} = 16.4 min).

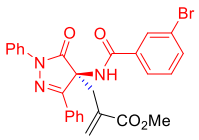


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.654	MM	0.7207	638.20068	14.75894	49.2222
2	16.483	MM	0.8033	658.36951	13.66024	50.7778



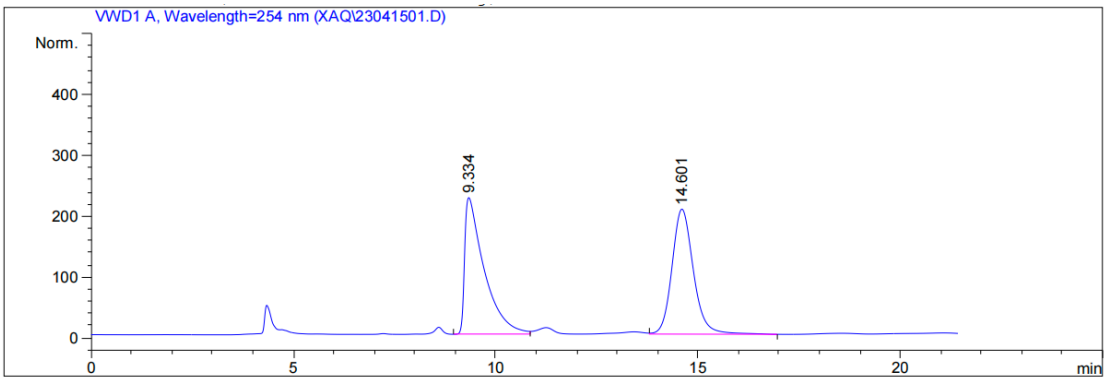
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.645	BB	0.4627	5.05459e4	1565.07874	97.8979
2	16.483	MM	0.6363	1085.33887	28.42673	2.1021

Compound 3ae

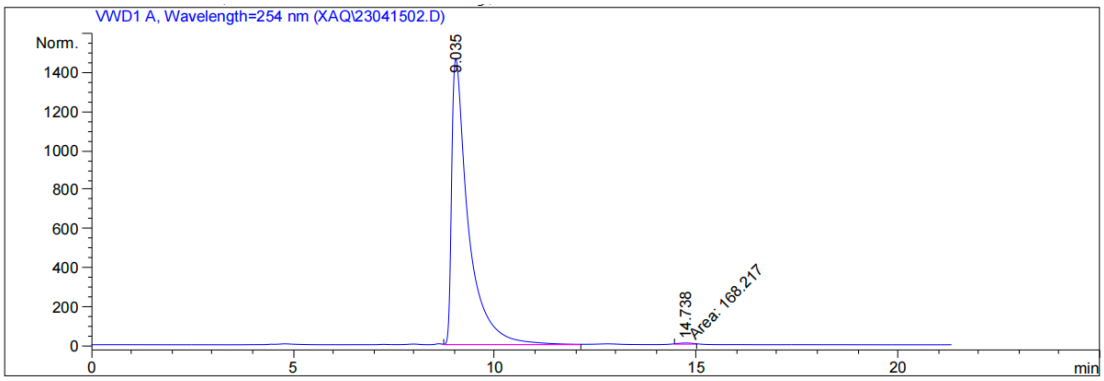


3ae

Prepared according to the procedure within 48 h as yellow solid (102.0 mg, 96% yield); $[\alpha]_D^{16}$ = 4.561 (*c* 0.59, CH_2Cl_2); Mp: 139.5 - 140.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.18 (s, 1H), 7.96 – 7.90 (m, 5H), 7.72 – 7.69 (m, 1H), 7.54 – 7.52 (m, 1H), 7.37 – 7.28 (m, 5H), 7.22 – 7.11 (m, 2H), 6.35 (s, 1H), 5.61 (s, 1H), 3.77 (s, 3H), 3.30 (d, *J* = 14.4 Hz, 1H), 2.73 – 2.57 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 170.3, 164.9, 156.0, 138.3, 135.1, 134.1, 134.0, 131.4, 130.9, 130.5, 130.2, 130.0, 128.9, 128.8, 126.3, 126.0, 125.4, 122.8, 119.3, 65.0, 53.1, 37.7; HRMS (ESI) m/z Calcd. for $C_{27}H_{23}BrN_3O_4$ ([M+H]$^+$) 532.0866, Found 532.0870. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral IF-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.0 min, t_{minor} = 14.7 min).

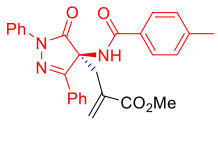


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.334	VV	0.4702	7532.21729	224.41685	49.8652
2	14.601	VB	0.5639	7572.92871	205.48102	50.1348



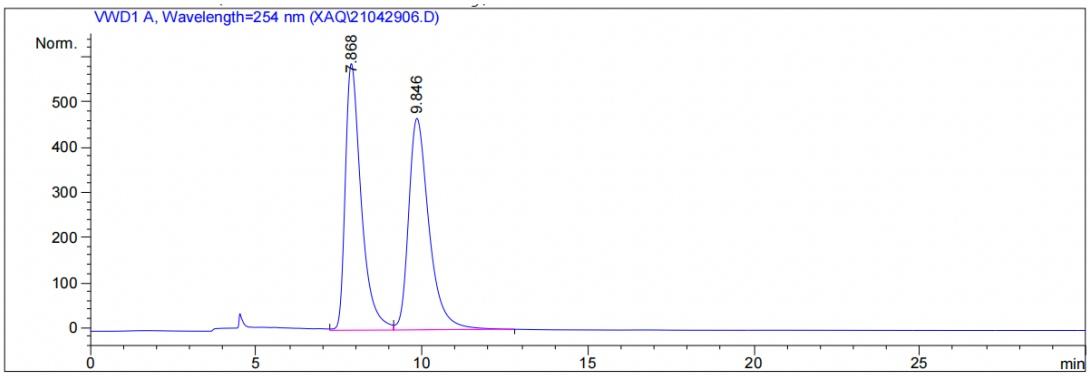
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.035	VB	0.4105	4.22167e4	1464.63928	99.6031
2	14.738	MM	0.4196	168.21695	6.68164	0.3969

Compound 3af

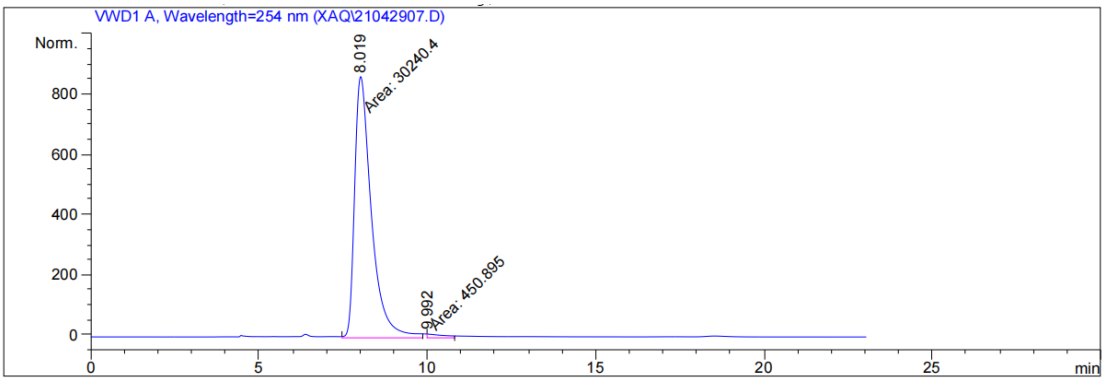


3af

Prepared according to the procedure within 48 h as white solid (82.3 mg, 88% yield); $[\alpha]_D^{17}$ = 15.625 (*c* 0.21, CH_2Cl_2); Mp: 191.4 - 192.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.06 (s, 1H), 8.08 – 8.01 (m, 4H), 7.79 – 7.77 (m, 2H), 7.46 – 7.35 (m, 5H), 7.23 – 7.19 (m, 3H), 6.40 (s, 1H), 5.68 (s, 1H), 3.78 (s, 3H), 3.35 (d, *J* = 14.3 Hz, 1H), 2.78 (d, *J* = 14.3 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.2, 169.7, 166.4, 156.2, 142.6, 138.4, 133.5, 131.7, 130.3, 129.3, 129.3, 129.1, 128.8, 128.7, 127.6, 126.4, 125.3, 119.4, 65.2, 52.8, 37.6, 21.5. HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_3O_4$ ($[M+H]^+$) 468.1918, Found 468.1920. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 8.0 min, t_{minor} = 9.9 min).

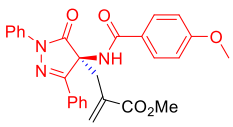


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.868	VV	0.5029	1.97050e4	590.51825	49.5132
2	9.846	VB	0.6474	2.00924e4	468.50952	50.4868



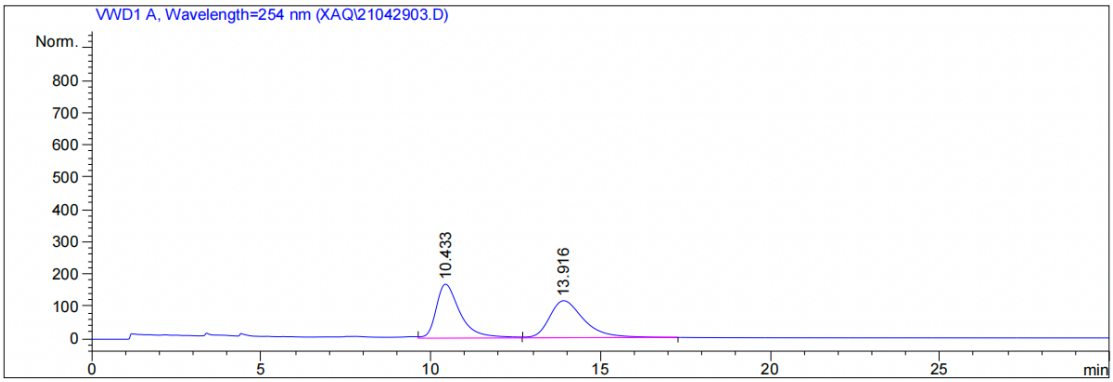
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.019	MM	0.5811	3.02404e4	867.28418	98.5309
2	9.992	MM	0.4077	450.89536	12.92179	1.4691

Compound 3ag

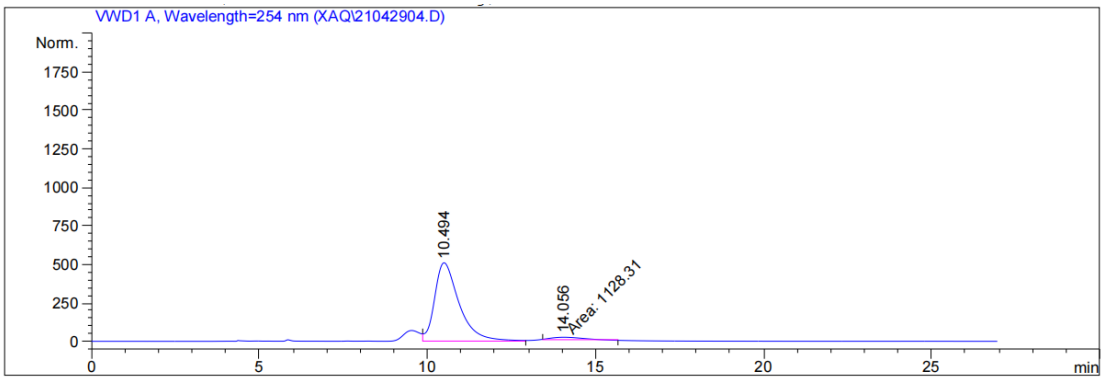


3ag

Prepared according to the procedure within 48 h as yellow solid (95.7 mg, 99% yield); $[\alpha]_D^{17}$ = 7.547 (*c* 0.53, CH_2Cl_2); Mp: 123.5 - 124.6 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.01 (s, 1H), 8.07 – 8.00 (m, 4H), 7.84 – 7.81 (m, 2H), 7.44 – 7.35 (m, 5H), 7.22 – 7.18 (m, 1H), 6.87 – 6.85 (m, 2H), 6.37 (s, 1H), 5.66 (s, 1H), 3.79 – 3.77 (m, 6H), 3.32 (d, *J* = 14.3 Hz, 1H), 2.77 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-d) δ 170.2, 168.6, 165.0, 161.6, 155.2, 137.3, 132.4, 130.7, 129.3, 129.2, 128.4, 127.8, 127.6, 125.3, 124.2, 123.4, 118.3, 112.7, 64.1, 54.3, 51.8, 36.6. HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_3O_5$ ($[M+H]^+$) 484.1867, Found 484.1878. Enantiomeric excess was determined to be 91% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.4 min, t_{minor} = 14.0 min).

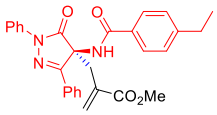


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.433	VB	0.7402	8308.22559	167.51563	50.3674
2	13.916	BB	1.0723	8187.00537	114.99014	49.6326



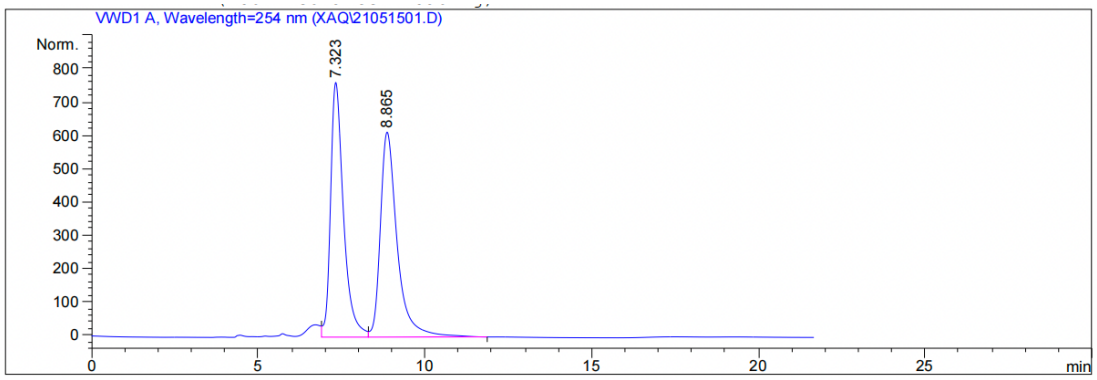
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.494	VB	0.7617	2.59420e4	509.30637	95.8319
2	14.056	MM	1.0881	1128.30566	17.28324	4.1681

Compound 3ah

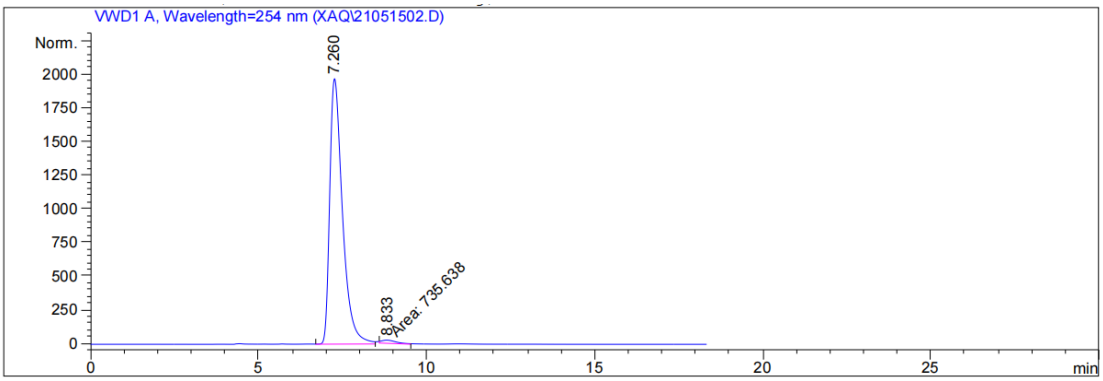


3ah

Prepared according to the procedure within 48 h as white solid (95.3 mg, 99% yield); $[\alpha]_D^{17}$ = 11.101 (*c* 1.00, CH_2Cl_2); Mp: 152.7 - 153.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.07 (s, 1H), 8.08 – 8.01 (m, 4H), 7.82 – 7.80 (m, 2H), 7.45 – 7.41 (m, 2H), 7.38 – 7.36 (m, 3H), 7.25 – 7.19 (m, 3H), 6.40 (s, 1H), 5.68 (s, 1H), 3.79 (s, 3H), 3.35 (d, *J* = 14.3 Hz, 1H), 2.77 (d, *J* = 14.3 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 169.7, 166.4, 156.2, 148.9, 138.4, 133.6, 131.7, 130.3, 130.3, 129.5, 128.8, 128.7, 128.1, 127.7, 126.4, 125.3, 119.4, 65.1, 52.9, 37.7, 28.9, 15.3. HRMS (ESI) m/z Calcd. for $C_{29}H_{28}N_3O_4$ ([M+H]$^+$) 482.2074, Found 482.2072. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.2 min, t_{minor} = 8.8 min).

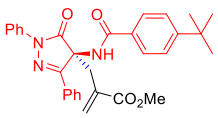


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.323	VV	0.4052	2.06282e4	764.15186	48.7900
2	8.865	VB	0.5258	2.16513e4	614.90045	51.2100



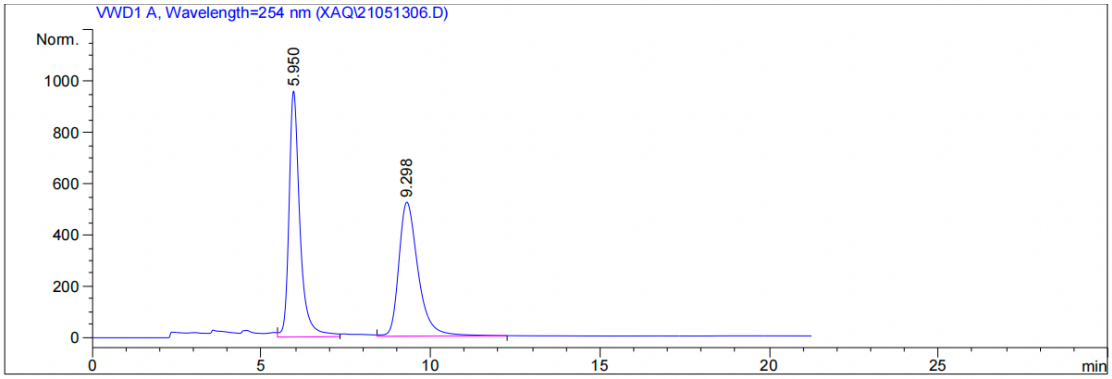
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.260	VV	0.3996	5.20374e4	1971.82703	98.6060
2	8.833	MM	0.5228	735.63800	23.45009	1.3940

Compound 3ai

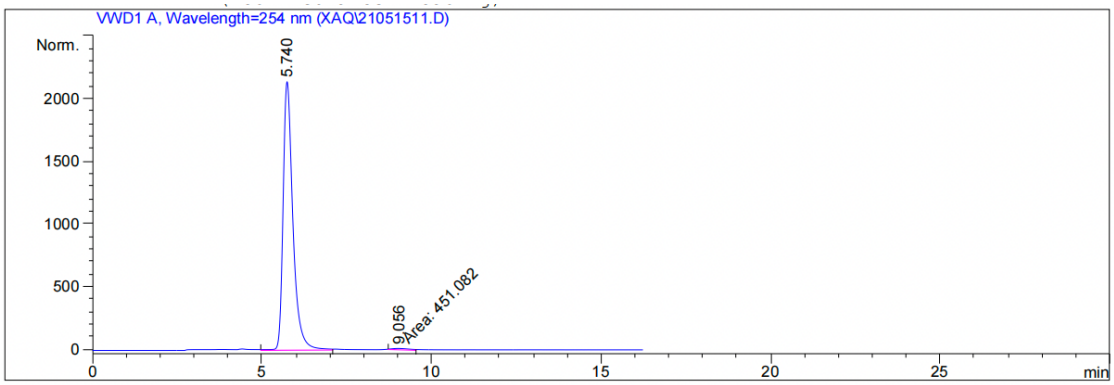


3ai

Prepared according to the procedure within 48 h as yellow solid (95.8 mg, 94% yield); $[\alpha]_D^{18}$ = 8.781 (*c* 0.91, CH_2Cl_2); Mp: 229.3 - 229.9 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.08 (s, 1H), 8.08 – 8.02 (m, 4H), 7.86 – 7.83 (m, 2H), 7.46 – 7.37 (m, 7H), 7.23 – 7.19 (m, 1H), 6.40 (s, 1H), 5.69 (s, 1H), 3.82 (s, 3H), 3.37 (d, *J* = 14.3 Hz, 1H), 2.76 (d, *J* = 14.3 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 169.8, 166.3, 156.3, 155.7, 138.4, 133.6, 131.7, 130.3, 130.3, 129.3, 128.8, 128.7, 127.4, 126.4, 125.6, 125.3, 119.3, 65.1, 53.0, 37.7, 35.0, 31.2. HRMS (ESI) m/z Calcd. for $C_{31}H_{32}N_3O_4$ ([M+H]$^+$) 510.2387, Found 510.2389; Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 5.7 min, t_{minor} = 9.0 min).

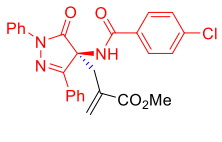


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.950	VV	0.3339	2.15963e4	959.52191	50.9254
2	9.298	VB	0.6051	2.08114e4	523.39478	49.0746



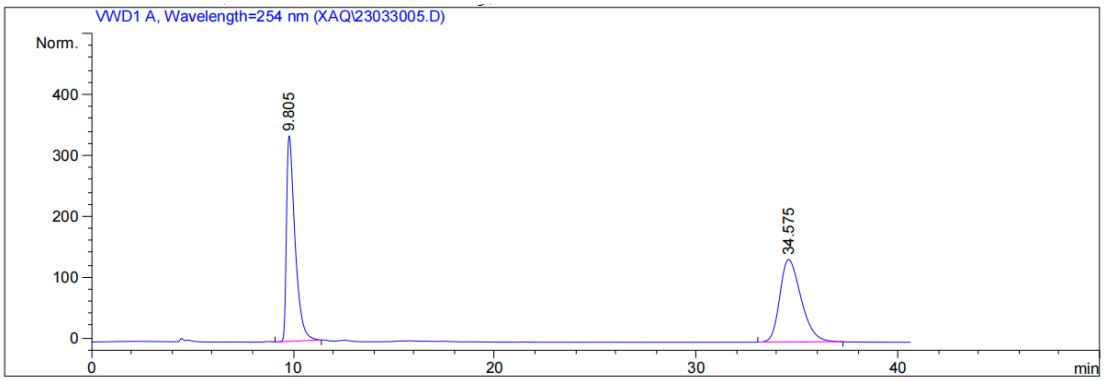
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.740	VV	0.3037	4.32003e4	2142.09009	98.9666
2	9.056	MM	0.6319	451.08188	11.89684	1.0334

Compound 3aj

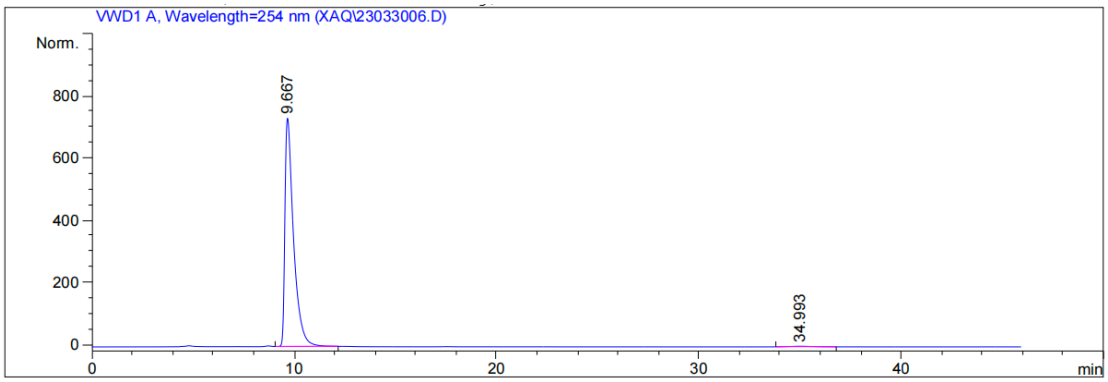


3aj

Prepared according to the procedure within 48 h as yellow solid (96.5 mg, 99% yield); $[\alpha]_D^{16}$ = 4.864 (*c* 0.51, CH_2Cl_2); Mp: 145.4 - 146.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 8.03 – 8.01 (m, 2H), 7.99 – 7.97 (m, 2H), 7.81 – 7.76 (m, 2H), 7.43 – 7.35 (m, 7H), 7.22 – 7.18 (m, 1H), 6.39 (s, 1H), 5.67 (s, 1H), 3.81 (s, 3H), 3.34 (d, *J* = 14.4 Hz, 1H), 2.71 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.7, 170.3, 165.3, 156.1, 138.5, 138.3, 134.0, 131.5, 130.5, 130.5, 130.1, 128.9, 128.9, 128.9, 128.8, 126.3, 125.4, 119.3, 65.0, 53.1, 37.8; HRMS (ESI) m/z Calcd. for $C_{27}H_{23}ClN_3O_4$ ($[M+H]^+$) 488.1372, Found 488.1377. Enantiomeric excess was determined to be 98% (determined by HPLC using chiral IF-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.6 min, t_{minor} = 34.9 min).

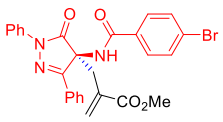


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.805	VB	0.4362	9923.54590	337.54526	49.8738
2	34.575	BB	1.1292	9973.77832	135.56470	50.1262



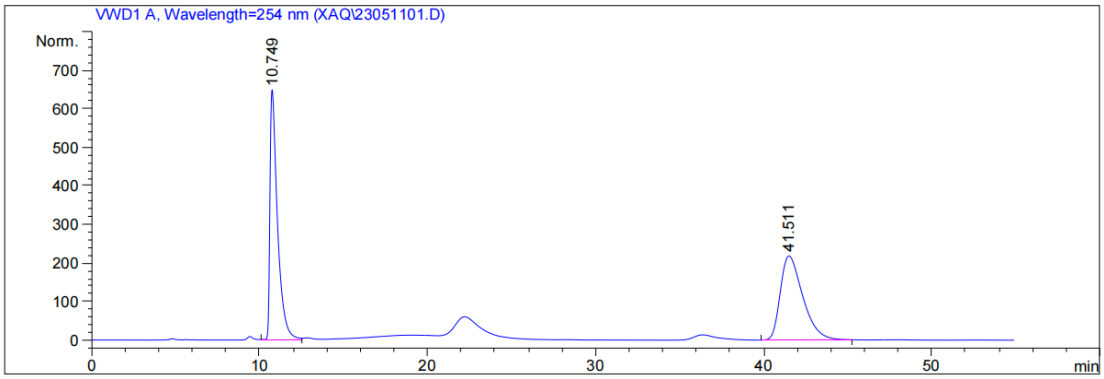
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.667	VB	0.4378	2.17775e4	734.10706	99.3405
2	34.993	BB	0.8774	144.57266	1.94820	0.6595

Compound 3ak

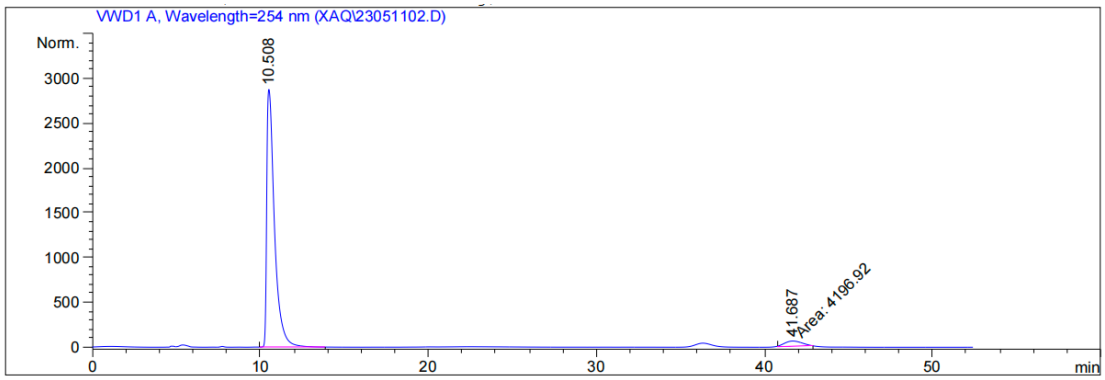


3ak

Prepared according to the procedure within 48 h as yellow solid (98.8 mg, 93% yield); $[\alpha]_D^{16}$ = 4.184 (*c* 0.47, CH_2Cl_2); Mp: 150.3 - 151.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 7.97 – 7.90 (m, 4H), 7.68 – 7.66 (m, 2H), 7.49 – 7.47 (m, 2H), 7.37 – 7.29 (m, 5H), 7.18 – 7.12 (m, 1H), 6.34 (s, 1H), 5.62 (s, 1H), 3.77 (s, 3H), 3.29 (d, *J* = 14.4 Hz, 1H), 2.63 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 170.2, 165.4, 156.0, 138.3, 134.0, 131.9, 131.5, 130.9, 130.5, 130.1, 129.1, 128.9, 128.8, 127.1, 126.3, 125.4, 119.3, 65.1, 53.1, 37.8; HRMS (ESI) m/z Calcd. for $C_{27}H_{23}BrN_3O_4$ ($[M+H]^+$) 532.0866, Found 532.0861. Enantiomeric excess was determined to be 91% (determined by HPLC using chiral IF-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.5 min, t_{minor} = 41.6 min).

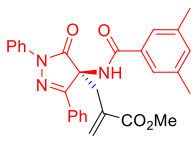


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.749	BB	0.4554	2.02064e4	648.26984	49.9521
2	41.511	BB	1.3977	2.02452e4	217.75006	50.0479



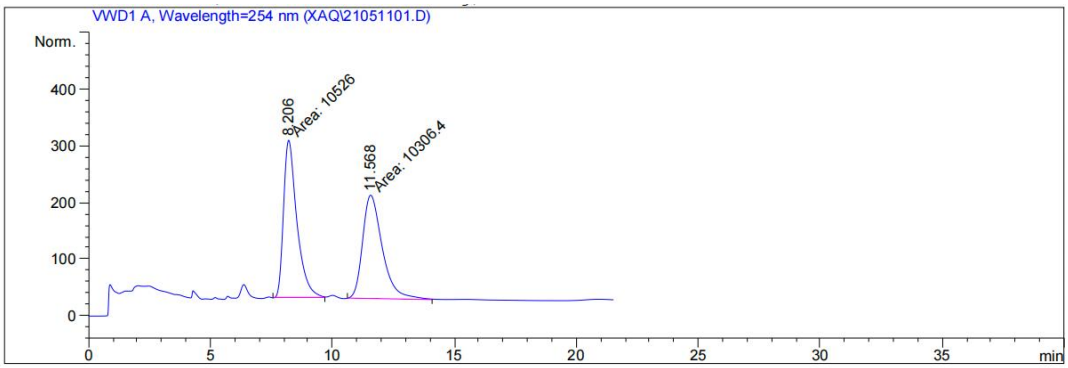
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.508	VB	0.4790	9.21863e4	2874.31323	95.6456
2	41.687	MM	1.1910	4196.92139	58.72888	4.3544

Compound 3al

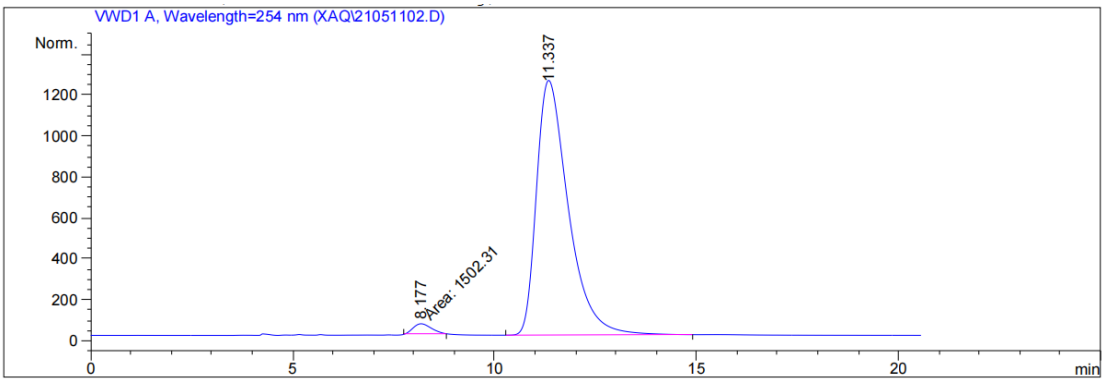


3al

Prepared according to the procedure within 48 h as red solid (81.9 mg, 85% yield); $[\alpha]_D^{17}$ = 9.910 (*c* 1.10, CH_2Cl_2); Mp: 163.6 - 164.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.00 (s, 1H), 8.07 – 8.00 (m, 4H), 7.49 – 7.42 (m, 4H), 7.38 – 7.35 (m, 3H), 7.24 – 7.20 (m, 1H), 7.13 (s, 1H), 6.41 (s, 1H), 5.69 (s, 1H), 3.81 (s, 3H), 3.37 (d, *J* = 14.2 Hz, 1H), 2.77 (d, *J* = 14.3 Hz, 1H), 2.33 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 169.7, 166.8, 156.2, 138.4, 138.2, 133.8, 133.7, 131.9, 131.6, 130.29, 130.25, 128.8, 128.7, 126.4, 125.4, 125.3, 119.4, 65.1, 52.8, 37.6, 21.2. HRMS (ESI) m/z Calcd. for $C_{29}H_{28}N_3O_4$ ($[M+H]^+$) 482.2074, Found 482.2079. Enantiomeric excess was determined to be 95% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.3 min, t_{minor} = 8.1 min).

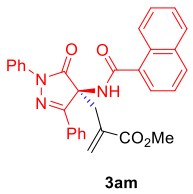


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.206	MM	0.6322	1.05260e4	277.50055	50.5271
2	11.568	MM	0.9401	1.03064e4	182.71242	49.4729



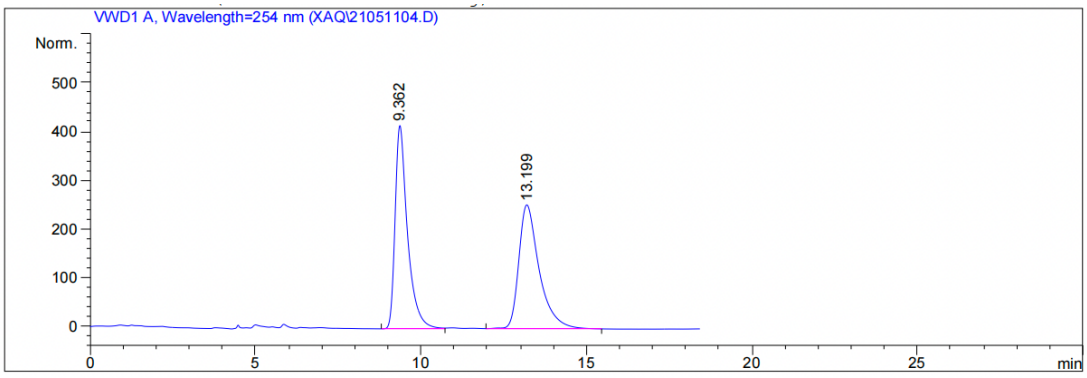
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.177	MM	0.5121	1502.31470	48.89371	2.1523
2	11.337	PB	0.8340	6.82973e4	1244.32690	97.8477

Compound 3am

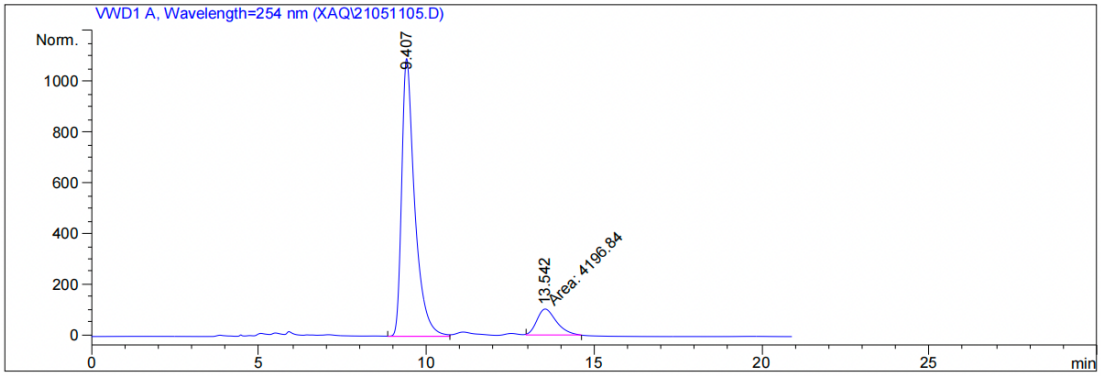


3am

Prepared according to the procedure within 48 h as white solid (27.2 mg, 27% yield); $[\alpha]_D^{18}$ = 1.754 (*c* 0.57, CH_2Cl_2); Mp: 158.7 - 159.8 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.12 – 8.04 (m, 4H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.66 (m, 1H), 7.47 – 7.40 (m, 8H), 7.26 – 7.23 (m, 1H), 6.41 (s, 1H), 5.70 (s, 1H), 3.65 (s, 3H), 3.34 (d, *J* = 14.3 Hz, 1H), 2.82 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 169.1, 168.9, 156.1, 138.3, 133.6, 133.3, 131.9, 131.7, 131.3, 130.4, 130.4, 130.2, 128.9, 128.8, 128.1, 127.2, 126.4, 126.4, 125.7, 125.5, 125.4, 124.6, 119.5, 65.4, 52.7, 37.6. HRMS (ESI) m/z Calcd. for $C_{31}H_{26}N_3O_4$ ($[M+H]^+$) 504.1918, Found 504.1925. Enantiomeric excess was determined to be 75% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.4 min, t_{minor} = 13.5 min).

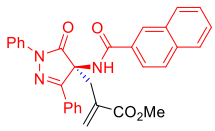


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.362	VB	0.3829	1.08957e4	417.70929	49.8399
2	13.199	VB	0.6402	1.09657e4	254.89192	50.1601



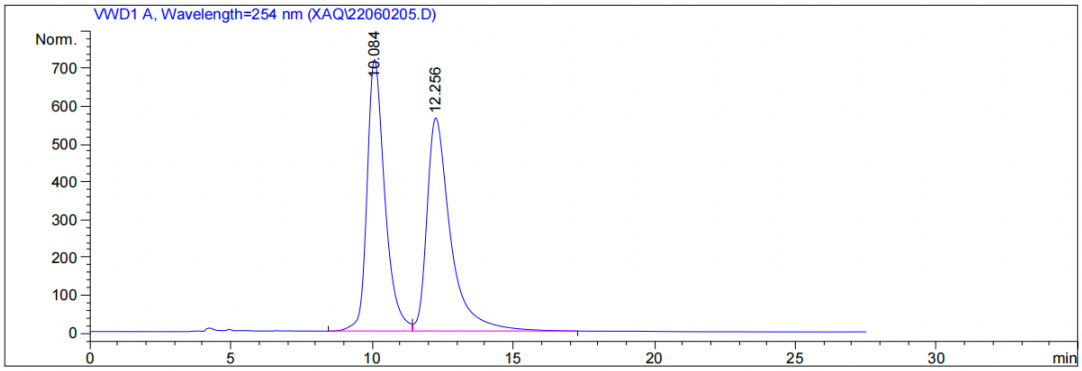
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.407	VV	0.3990	2.96607e4	1095.15442	87.6044
2	13.542	MM	0.6798	4196.83838	102.88794	12.3956

Compound 3an

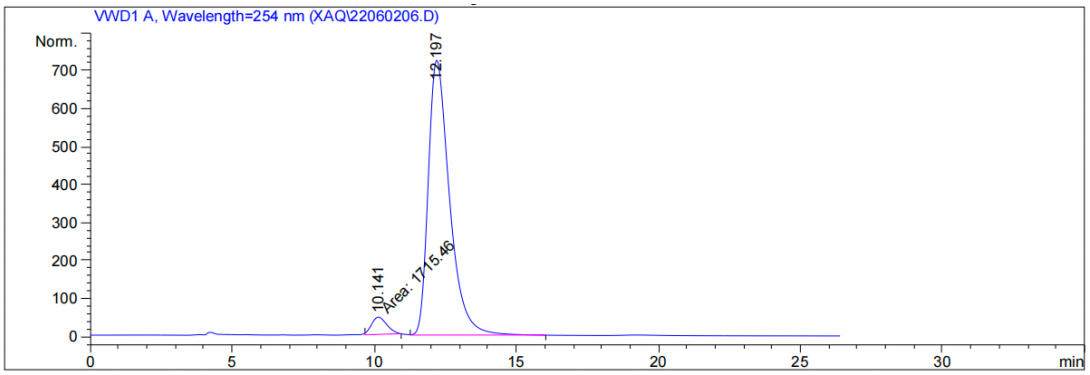


3an

Prepared according to the procedure within 48 h as yellow solid (99.7 mg, 99% yield); $[\alpha]_D^{16}$ = 18.422 (*c* 0.76, CH_2Cl_2); Mp: 218.5 - 219.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 8.40 (s, 1H), 8.13 – 8.05 (m, 4H), 7.91 – 7.78 (m, 4H), 7.55 – 7.43 (m, 4H), 7.39 – 7.35 (m, 3H), 7.25 – 7.21 (m, 1H), 6.40 (s, 1H), 5.69 (s, 1H), 3.79 (s, 3H), 3.41 (d, *J* = 14.2 Hz, 1H), 2.84 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.1, 169.7, 166.6, 156.2, 138.4, 135.0, 133.6, 132.5, 131.7, 130.4, 130.3, 129.2, 128.9, 128.8, 128.7, 128.4, 127.9, 127.7, 126.7, 126.4, 125.4, 123.6, 119.4, 65.4, 52.8, 37.7. HRMS (ESI) m/z Calcd. for $C_{31}H_{26}N_3O_4$ ([M+H]$^+$) 504.1918, Found 504.1917. Enantiomeric excess was determined to be 91% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.1 min, t_{minor} = 10.1 min).

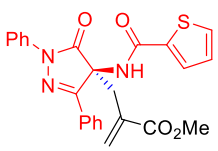


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.084	BV	0.6583	3.14834e4	718.42035	48.9247
2	12.256	VB	0.8663	3.28674e4	563.98730	51.0753



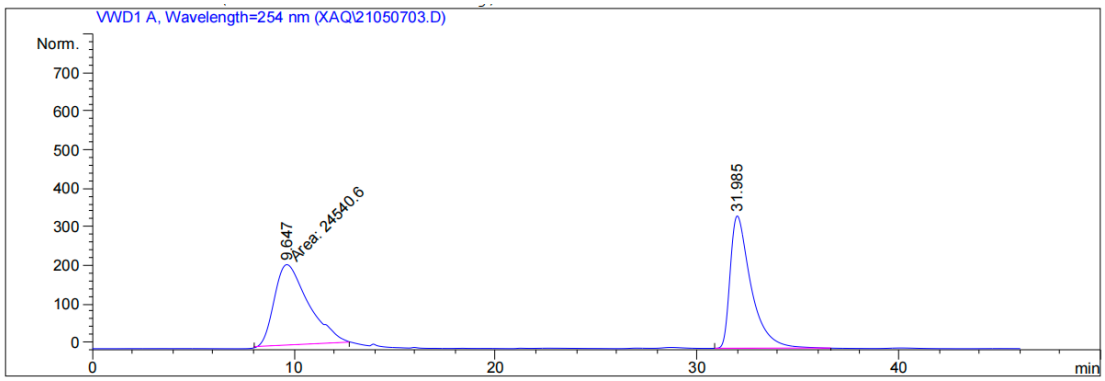
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.141	MM	0.6249	1715.46265	45.75635	4.3401
2	12.197	BB	0.7945	3.78108e4	723.64764	95.6599

Compound 3ao

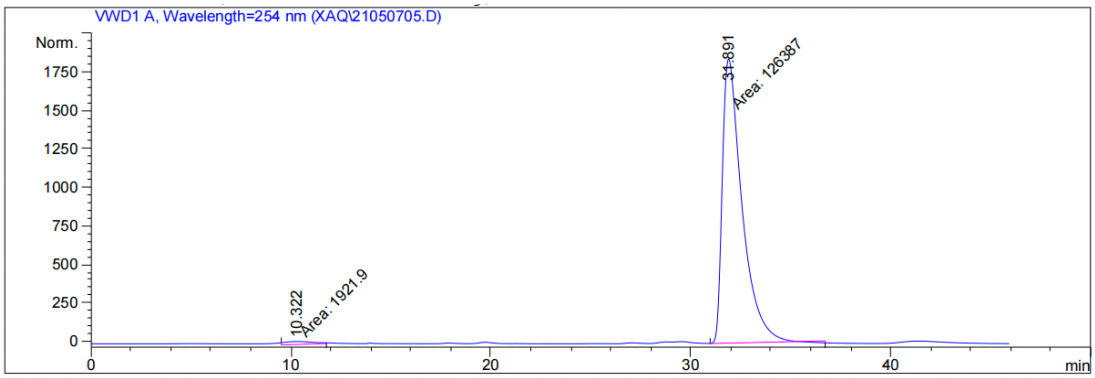


3ao

Prepared according to the procedure within 48 h as yellow white (91.0 mg, 99% yield); $[\alpha]_D^{15}$ = 14.875 (*c* 1.60, CH_2Cl_2); Mp: 116.3 - 117.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.08 (s, 1H), 8.05 – 8.01 (m, 4H), 7.67 – 7.66 (m, 1H), 7.45 – 7.37 (m, 6H), 7.23 – 7.19 (m, 1H), 7.04 – 7.02 (m, 1H), 6.39 (s, 1H), 5.66 (s, 1H), 3.77 (s, 3H), 3.32 (d, *J* = 14.3 Hz, 1H), 2.76 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.9, 169.7, 161.4, 156.0, 138.3, 137.1, 133.7, 131.6, 131.3, 130.4, 130.2, 129.4, 128.8, 128.8, 127.8, 126.4, 125.4, 119.4, 65.1, 52.9, 37.7. HRMS (ESI) m/z Calcd. for $C_{25}H_{22}N_3O_4S$ ([M+H]$^+$) 460.1326, Found 460.1332. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 31.8 min, t_{minor} = 10.3 min).

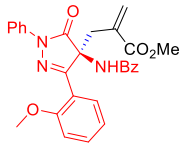


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.647	MM	1.9556	2.45406e4	209.14268	49.7769
2	31.985	BB	1.0613	2.47605e4	343.89069	50.2231



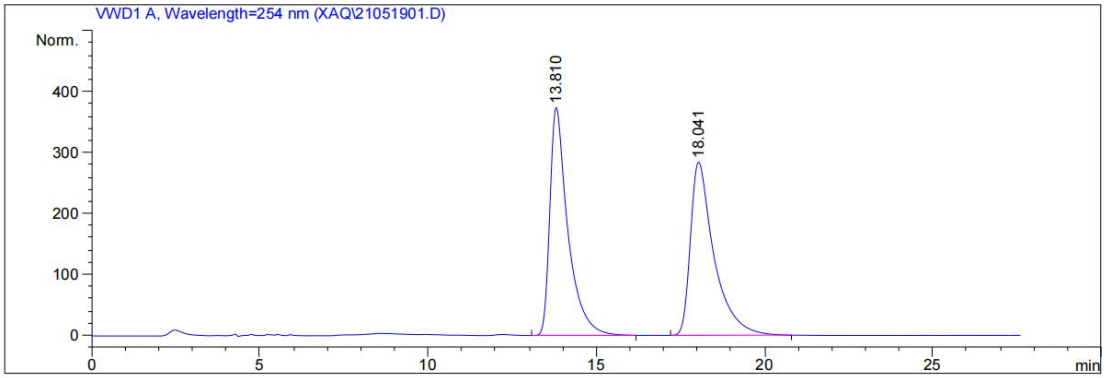
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.322	MM	1.1953	1921.90491	19.26205	1.4979
2	31.891	MM	1.1403	1.26387e5	1847.27368	98.5021

Compound 3ap

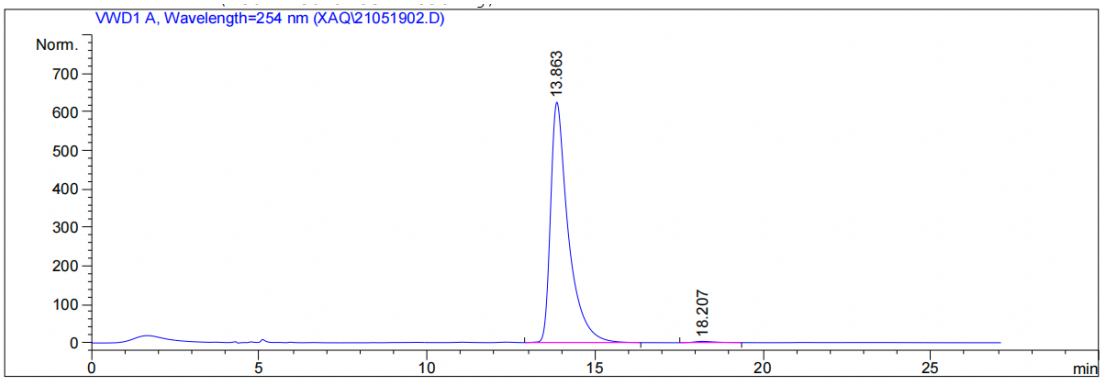


3ap

Prepared according to the procedure within 48 h as red white (84.1 mg, 87% yield); $[\alpha]_D^{16}$ = -56.034 (*c* 1.10, CH_2Cl_2); Mp: 105.7 - 106.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 8.04 – 8.02 (m, 2H), 7.86 – 7.76 (m, 3H), 7.50 – 7.32 (m, 6H), 7.21 – 7.16 (m, 1H), 6.97 – 6.90 (m, 2H), 6.43 (s, 1H), 5.73 (s, 1H), 3.80 – 3.79 (m, 6H), 3.50 (d, *J* = 14.4 Hz, 1H), 2.69 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 169.9, 166.0, 157.3, 157.0, 138.5, 133.5, 132.5, 131.9, 131.6, 131.5, 130.8, 128.8, 128.5, 127.4, 125.1, 121.0, 119.9, 119.3, 111.7, 66.1, 55.5, 52.8, 36.3. HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_3O_5$ ($[M+H]^+$) 484.1867, Found 484.1875. Enantiomeric excess was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 13.8 min, t_{minor} = 18.2 min).

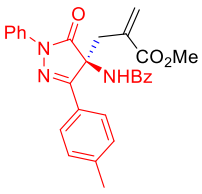


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.810	VB	0.5404	1.39386e4	374.62509	50.1659
2	18.041	BB	0.7072	1.38464e4	284.68234	49.8341



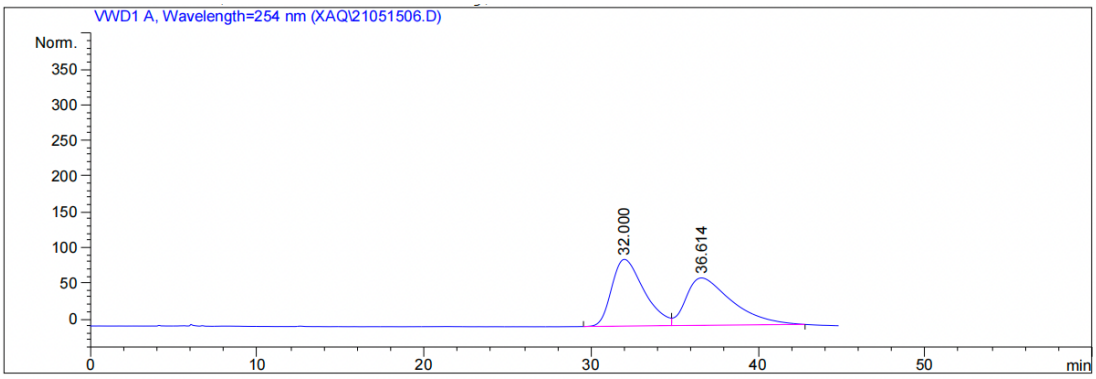
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.863	VB	0.5338	2.29249e4	625.55188	99.3782
2	18.207	PB	0.6016	143.44521	3.32994	0.6218

Compound 3aq

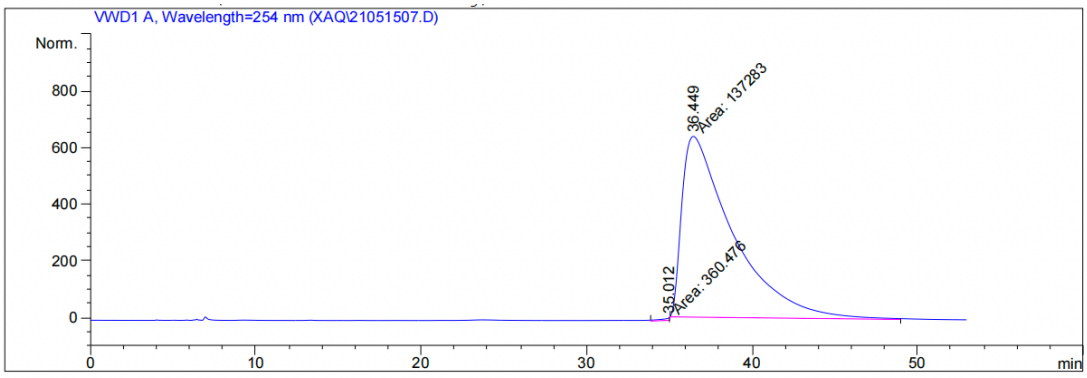


3aq

Prepared according to the procedure within 48 h as white solid (92.6 mg, 99% yield); $[\alpha]_D^{15}$ = -18.182 (*c* 0.11, CH_2Cl_2); Mp: 140.5 - 141.5 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.10 (s, 1H), 8.07 – 8.06 (m, 2H), 7.93 – 7.88 (m, 4H), 7.51 – 7.40 (m, 5H), 7.22 – 7.18 (m, 3H), 6.42 (s, 1H), 5.70 (s, 1H), 3.83 (s, 3H), 3.38 (d, *J* = 14.4 Hz, 1H), 2.73 (d, *J* = 14.4 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.0, 166.3, 156.3, 140.7, 138.4, 133.7, 132.1, 132.1, 131.7, 129.5, 128.8, 128.6, 127.5, 127.4, 126.3, 125.2, 119.3, 65.1, 53.0, 37.8, 21.5. HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_3O_4$ ([M+H]$^+$) 468.1918, Found 468.1923. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 36.4 min, t_{minor} = 35.0 min).

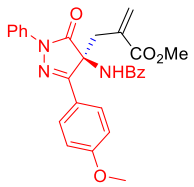


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.000	BV	2.0056	1.26801e4	93.60014	49.7451
2	36.614	VB	2.5486	1.28100e4	66.67805	50.2549



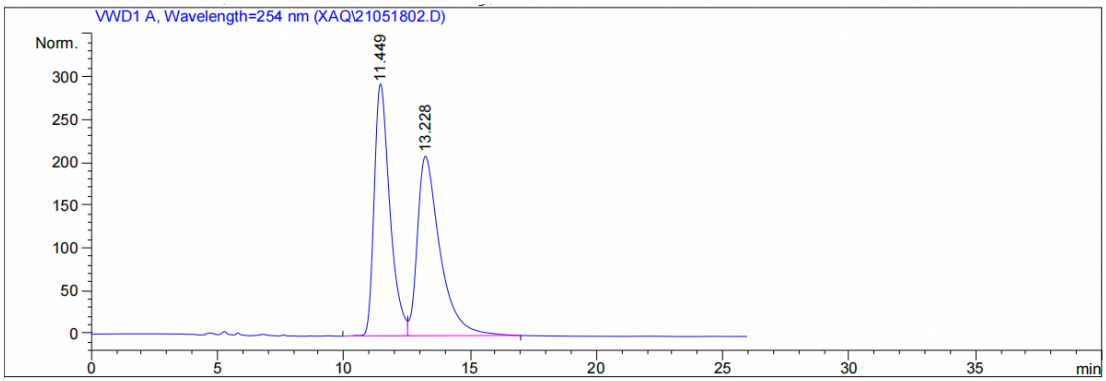
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.012	MM	0.5560	360.47580	10.80528	0.2619
2	36.449	MM	3.5828	1.37283e5	638.61884	99.7381

Compound 3ar

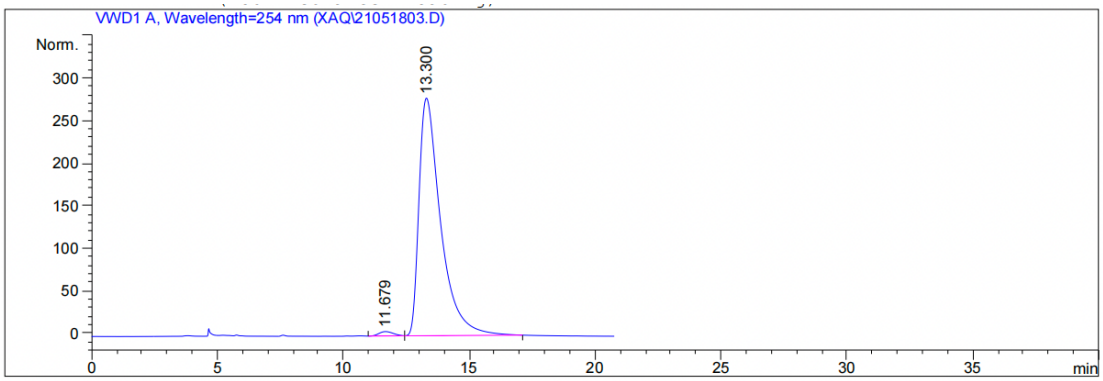


3ar

Prepared according to the procedure within 48 h as white solid (85.1 mg, 88% yield); $[\alpha]_D^{13}$ = -12.500 (*c* 0.72, CH_2Cl_2); Mp: 150.4 - 151.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 8.07 – 8.05 (m, 2H), 7.98 – 7.96 (m, 2H), 7.89 – 7.86 (m, 2H), 7.50 – 7.38 (m, 5H), 7.22 – 7.18 (m, 1H), 6.89 – 6.87 (m, 2H), 6.41 (s, 1H), 5.69 (s, 1H), 3.80 – 3.78 (m, 6H), 3.35 (d, *J* = 14.3 Hz, 1H), 2.75 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 169.8, 166.3, 161.2, 156.1, 138.4, 133.6, 132.1, 131.7, 128.8, 128.6, 128.0, 127.5, 125.2, 122.8, 119.3, 114.2, 65.2, 55.4, 52.9, 37.8. HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_3O_5$ ($[M+H]^+$) 484.1867, Found 484.1878. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 13.3 min, t_{minor} = 11.6 min).

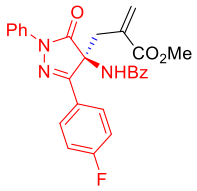


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.449	BV	0.6527	1.26898e4	294.49301	49.1964
2	13.228	VB	0.9199	1.31044e4	209.68497	50.8036



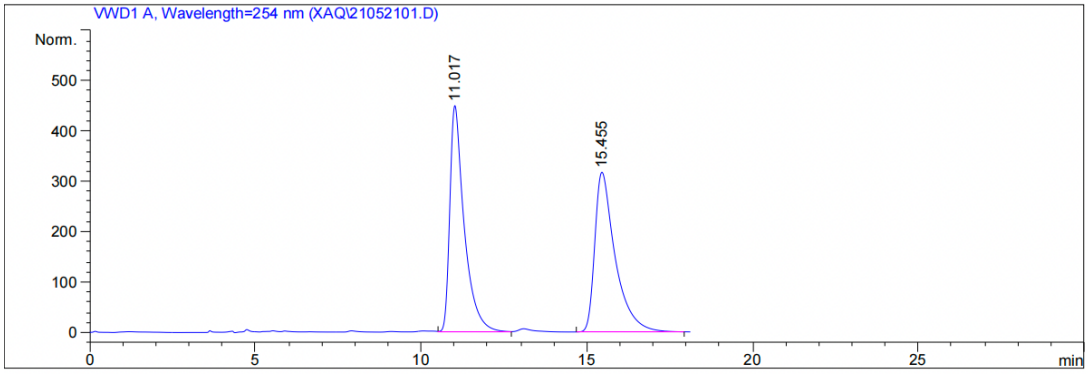
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.679	VV	0.6025	208.85751	5.20030	1.2368
2	13.300	VB	0.8950	1.66778e4	279.18005	98.7632

Compound 3as

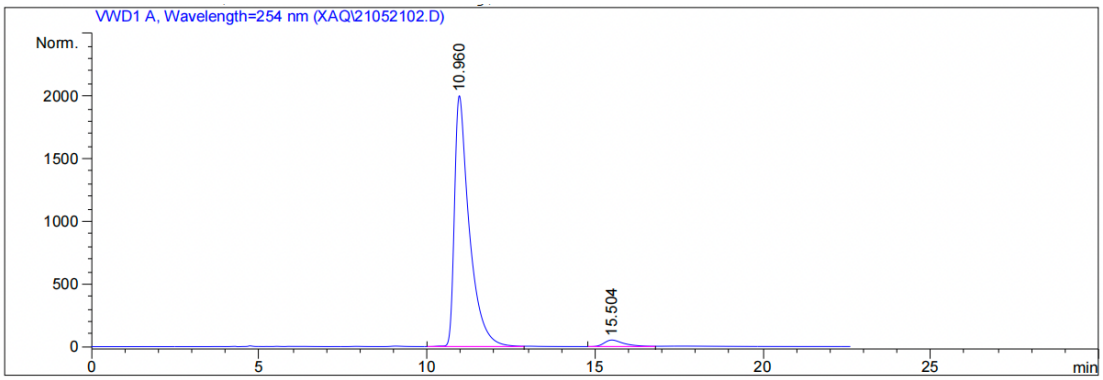


3as

Prepared according to the procedure within 48 h as white solid (89.6 mg, 95% yield); $[\alpha]_D^{17}$ = -10.891 (*c* 3.30, CH_2Cl_2); Mp: 110.9 - 111.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (s, 1H), 8.05 – 8.00 (m, 4H), 7.89 – 7.85 (m, 2H), 7.52 – 7.39 (m, 5H), 7.24 – 7.20 (m, 1H), 7.09 – 7.03 (m, 2H), 6.40 (s, 1H), 5.68 (s, 1H), 3.81 (s, 3H), 3.30 (d, *J* = 14.3 Hz, 1H), 2.76 (d, *J* = 14.3 Hz, 1H); ^{19}F NMR (377 MHz, Chloroform-*d*) δ -107.02 – -110.08 (m); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 169.8, 166.5, 163.9 (d, *J* = 252.5 Hz), 155.3, 138.3, 133.7, 132.3, 131.9, 131.6, 128.9, 128.7, 128.4 (d, *J* = 9.1 Hz), 127.5, 126.5 (d, *J* = 3.0 Hz), 125.4, 119.3, 115.9 (d, *J* = 22.2 Hz), 65.1, 53.0, 37.7. HRMS (ESI) m/z Calcd. for $C_{27}H_{23}FN_3O_4$ ([M+H]$^+$) 472.1667, Found 472.1673. Enantiomeric excess was determined to be 93% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.9 min, t_{minor} = 15.5 min).

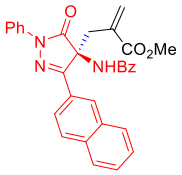


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.017	VV	0.4401	1.36042e4	449.91245	50.0801
2	15.455	BB	0.6253	1.35606e4	317.30511	49.9199



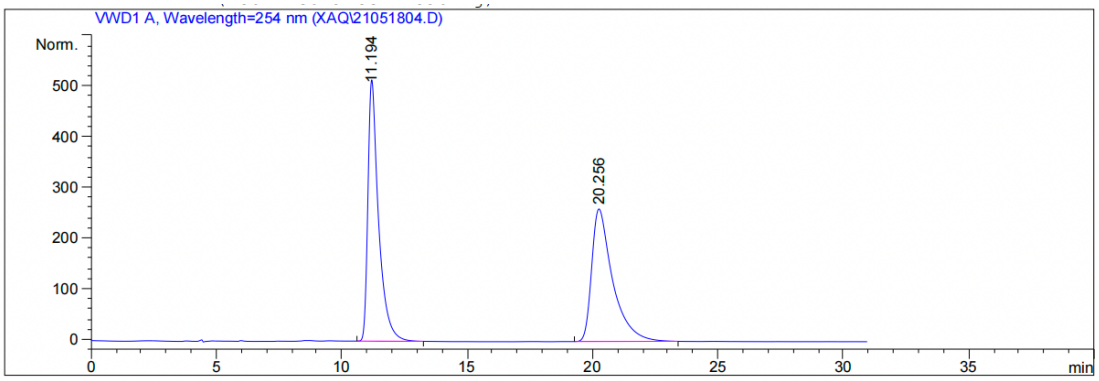
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.960	BB	0.4443	6.15270e4	2002.92383	96.5777
2	15.504	BB	0.6126	2180.23901	52.34293	3.4223

Compound 3at

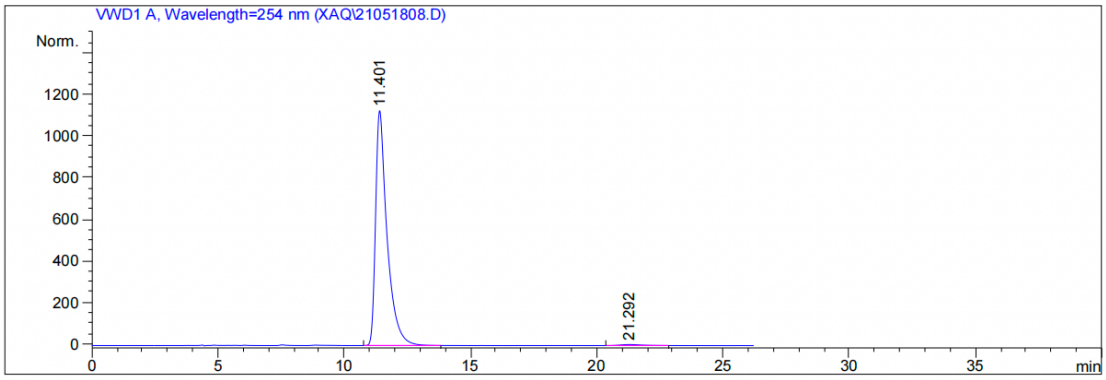


3at

Prepared according to the procedure within 48 h as white solid (80.6 mg, 80% yield); $[\alpha]_D^{17}$ = -47.101 (*c* 1.30, CH_2Cl_2); Mp: 105.8 - 106.7 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 8.39 (s, 1H), 8.23 – 8.21 (m, 1H), 8.11 – 8.10 (m, 2H), 7.93 – 7.92 (m, 2H), 7.86 – 7.80 (m, 3H), 7.51 – 7.43 (m, 7H), 7.25 – 7.23 (m, 1H), 6.42 (s, 1H), 5.73 (s, 1H), 3.86 (s, 3H), 3.48 (d, *J* = 14.5 Hz, 1H), 2.81 (d, *J* = 14.6 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.1, 166.4, 156.2, 138.4, 134.1, 133.8, 132.9, 132.2, 132.1, 131.8, 128.9, 128.8, 128.6 128.6, 127.8, 127.7, 127.5, 127.3, 126.6, 126.5, 125.4, 123.3, 119.4, 65.2, 53.0, 38.0. HRMS (ESI) m/z Calcd. for $C_{31}H_{26}N_3O_4$ ($[M+H]^+$) 504.1918, Found 504.1923. Enantiomeric excess was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.4 min, t_{minor} = 21.2 min).

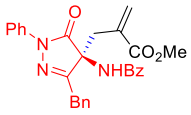


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.194	BB	0.4299	1.52055e4	515.64868	50.1196
2	20.256	BB	0.8364	1.51329e4	261.62326	49.8804



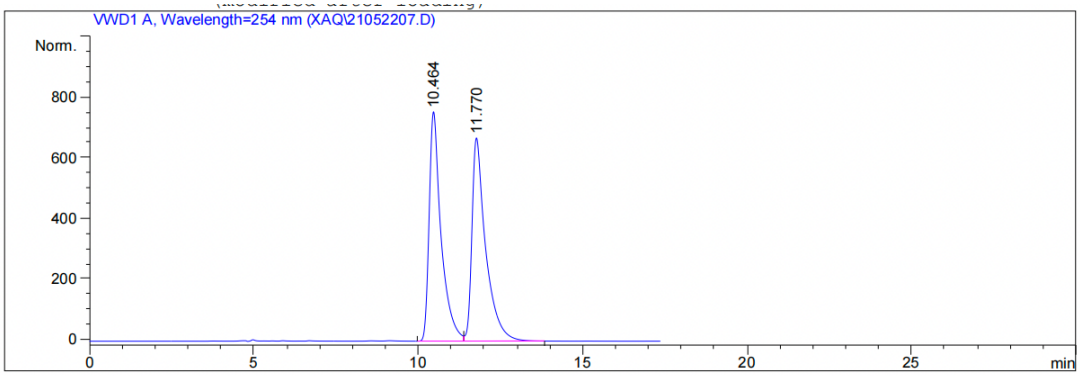
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.401	BB	0.4572	3.56190e4	1127.98608	99.1677
2	21.292	BB	0.7486	298.96167	4.96828	0.8323

Compound 3au

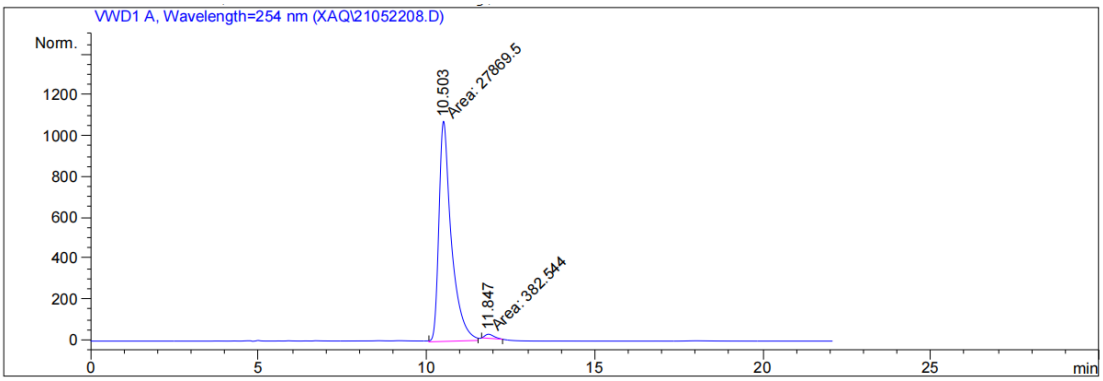


3au

Prepared according to the procedure within 48 h as yellow solid (77.6 mg, 83% yield); $[\alpha]_D^{21}$ = -30.488 (*c* 1.60, CH_2Cl_2); Mp: 130.4 - 131.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 7.95 – 7.92 (m, 2H), 7.78 – 7.76 (m, 2H), 7.52 – 7.48 (m, 1H), 7.42 – 7.34 (m, 6H), 7.25 – 7.12 (m, 4H), 6.46 (s, 1H), 5.72 (s, 1H), 3.85 (s, 3H), 3.77 (dd, *J* = 24.3, 15.3 Hz, 2H), 2.85 (d, *J* = 14.2 Hz, 1H), 2.45 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 169.7, 166.1, 160.5, 138.4, 134.8, 133.6, 132.0, 132.0, 131.6, 129.5, 128.8, 128.6, 128.4, 127.4, 127.0, 125.0, 119.2, 65.6, 53.0, 36.7, 35.1. HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_3O_4$ ($[M+H]^+$) 468.1918, Found 468.1925. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.5 min, t_{minor} = 11.8 min).

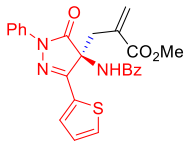


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.464	BV	0.3638	1.90765e4	757.32166	49.4864
2	11.770	VB	0.4143	1.94725e4	670.96899	50.5136



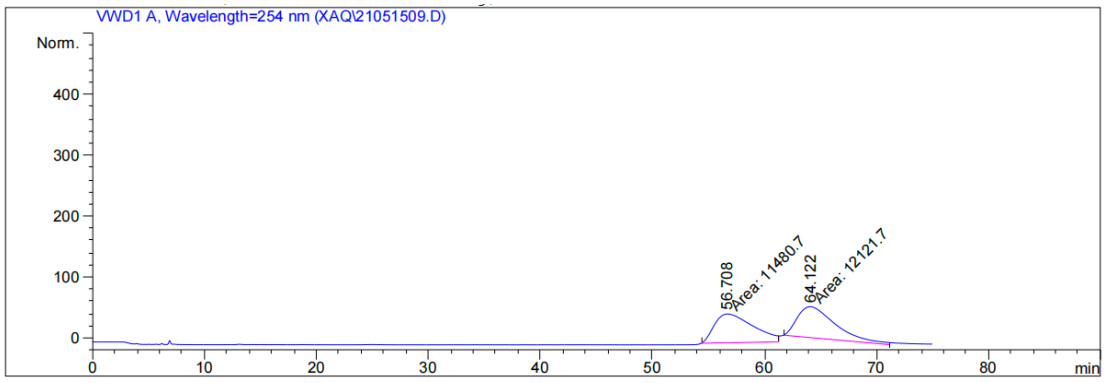
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.503	MM	0.4303	2.78695e4	1079.55786	98.6460
2	11.847	MM	0.3125	382.54373	20.40352	1.3540

Compound 3av

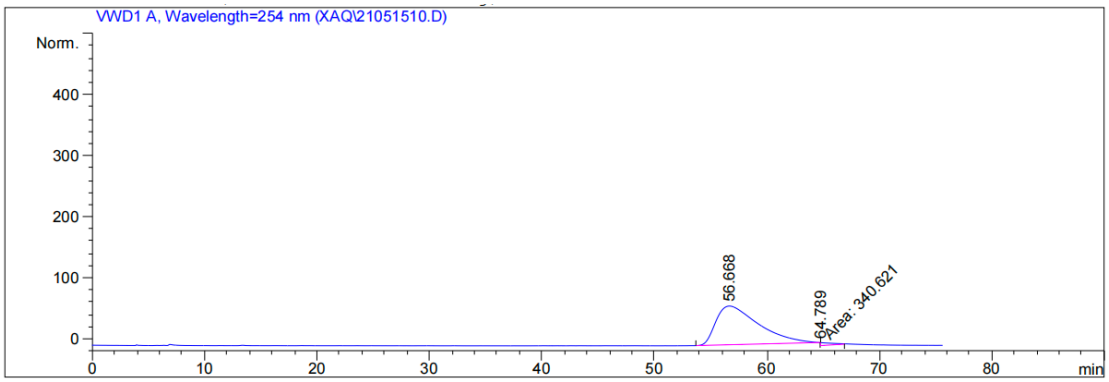


3av

Prepared according to the procedure within 48 h as yellow solid (89.1 mg, 97% yield); $[\alpha]_D^{15}$ = 20.930 (*c* 0.86, CH_2Cl_2); Mp: 152.7 - 153.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.15 (s, 1H), 8.03 – 8.01 (m, 2H), 7.90 – 7.88 (m, 2H), 7.58 – 7.57 (m, 1H), 7.53 – 7.48 (m, 1H), 7.45 – 7.41 (m, 4H), 7.38 – 7.37 (m, 1H), 7.23 – 7.19 (m, 1H), 7.03 – 7.01 (m, 1H), 6.43 (s, 1H), 5.72 (s, 1H), 3.85 (s, 3H), 3.32 (d, *J* = 14.3 Hz, 1H), 2.76 (d, *J* = 14.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 170.0, 166.3, 153.2, 138.2, 133.8, 133.0, 132.2, 132.0, 131.6, 128.9, 128.6, 128.4, 127.7, 127.6, 127.5, 125.4, 119.4, 65.1, 53.1, 37.9. HRMS (ESI) m/z Calcd. for $C_{25}H_{22}N_3O_4S$ ($[M+H]^+$) 460.1326, Found 460.1329. Enantiomeric excess was determined to be 96% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 56.6 min, t_{minor} = 64.7 min).

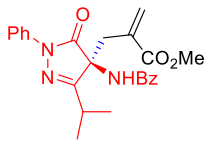


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	56.708	MM	4.0273	1.14807e4	47.51259	48.6421
2	64.122	MM	3.9784	1.21217e4	50.78078	51.3579



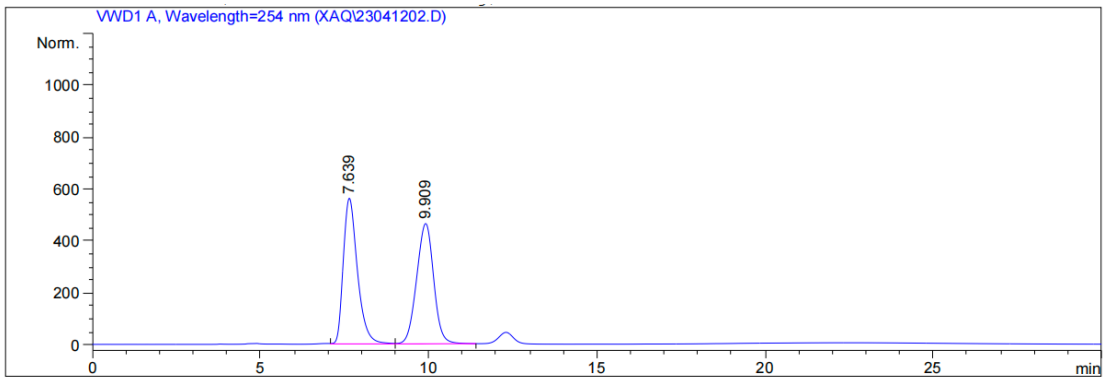
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	56.668	PB	3.0929	1.67824e4	63.57309	98.0107
2	64.789	MM	0.8210	340.62112	4.84486	1.9893

Compound 3aw

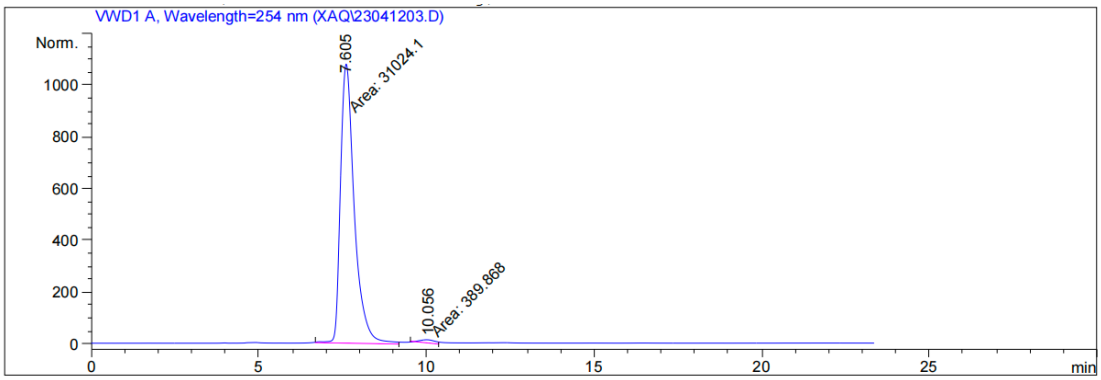


3aw

Prepared according to the procedure within 48 h as yellow solid (80.5 mg, 96% yield); $[\alpha]_D^{16}$ = -31.528 (*c* 0.52, CH_2Cl_2); Mp: 130.3 - 131.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 7.88 – 7.85 (m, 2H), 7.79 – 7.77 (m, 2H), 7.44 – 7.40 (m, 1H), 7.36 – 7.28 (m, 4H), 7.09 – 7.06 (m, 1H), 6.41 (s, 1H), 5.69 (s, 1H), 3.79 (s, 3H), 3.07 (d, *J* = 14.1 Hz, 1H), 2.68-2.58 (m, 1H), 2.50 (d, *J* = 14.2 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 169.9, 166.3, 166.1, 138.6, 133.6, 132.2, 132.1, 131.7, 128.7, 128.6, 127.5, 124.9, 119.1, 65.7, 53.1, 36.8, 28.3, 21.3, 20.5. HRMS (ESI) m/z Calcd. for $C_{24}H_{26}N_3O_4$ ($[M+H]^+$) 420.1918, Found 420.1921. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral IF-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.6 min, t_{minor} = 10.0 min).

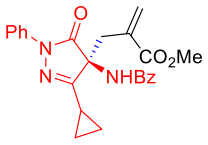


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.639	VV	0.4525	1.64596e4	561.71558	50.2382
2	9.909	VB	0.5459	1.63036e4	463.40149	49.7618



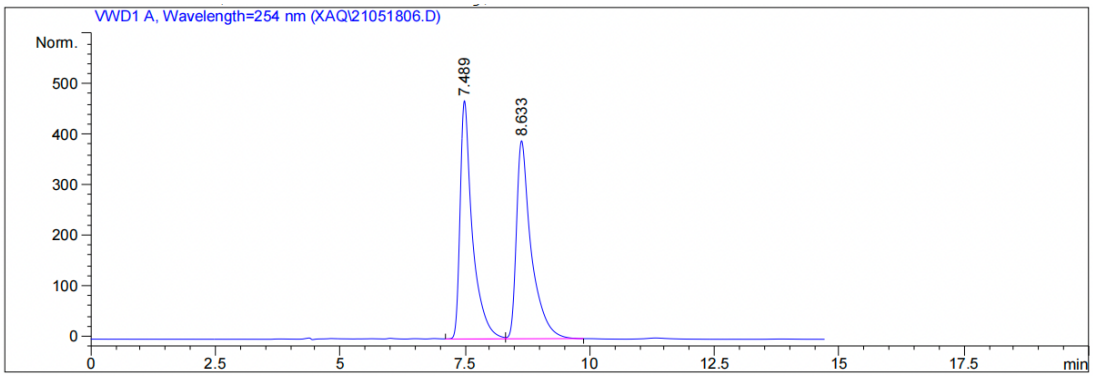
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.605	MM	0.4794	3.10241e4	1078.67603	98.7589
2	10.056	MM	0.5153	389.86807	12.60895	1.2411

Compound 3ax

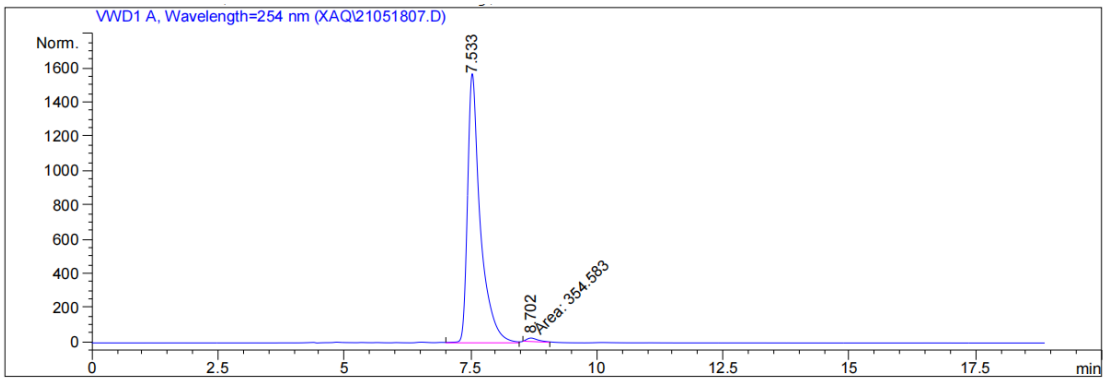


3ax

Prepared according to the procedure within 48 h as yellow solid (75.1 mg, 90% yield); $[\alpha]_D^{16}$ = 6.875 (*c* 1.60, CH_2Cl_2); Mp: 127.9 - 128.3 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 7.92 – 7.88 (m, 4H), 7.52 – 7.49 (m, 1H), 7.44 – 7.42 (m, 2H), 7.38 – 7.35 (m, 2H), 7.16 – 7.13 (m, 1H), 6.50 (s, 1H), 5.84 (s, 1H), 3.88 (s, 3H), 3.05 (d, *J* = 14.3 Hz, 1H), 2.79 (d, *J* = 14.2 Hz, 1H), 1.50 – 1.47 (m, 1H), 1.14 – 1.10 (m, 2H), 0.91 – 0.86 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 169.6, 166.1, 164.2, 138.6, 133.4, 132.3, 132.1, 132.0, 128.7, 128.6, 127.5, 124.8, 119.0, 66.0, 53.0, 37.1, 9.1, 8.7, 8.1. HRMS (ESI) m/z Calcd. for $C_{24}H_{24}N_3O_4$ ([M+H]$^+$) 418.1761, Found 418.1766. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.5 min, t_{minor} = 8.7 min).

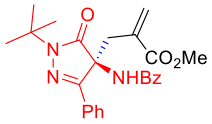


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.489	VV	0.2464	8086.13525	472.19266	49.9251
2	8.633	VB	0.2964	8110.41016	392.54324	50.0749



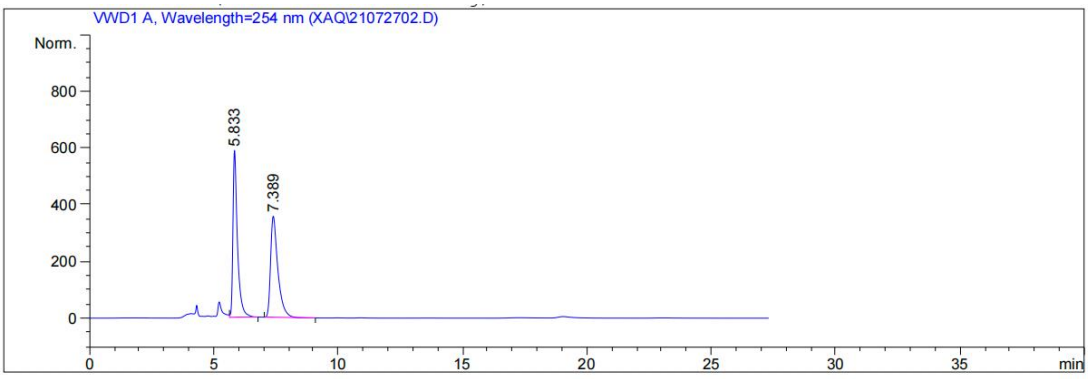
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.533	VV	0.2549	2.76931e4	1572.82690	98.7358
2	8.702	MM	0.2795	354.58310	21.14187	1.2642

Compound 3ay

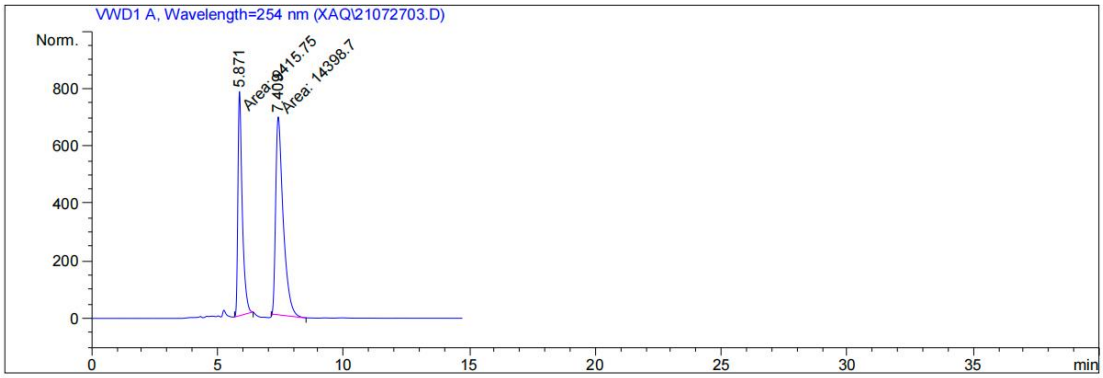


3ay

Prepared according to the procedure within 48 h as yellow solid (69.4 mg, 80% yield); $[\alpha]_D^{16}$ = 25.455 (*c* 0.55, CH_2Cl_2); Mp: 133.7 - 134.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 7.91 – 7.87 (m, 4H), 7.53 – 7.41 (m, 3H), 7.36 – 7.31 (m, 3H), 6.38 (s, 1H), 5.64 (s, 1H), 3.80 (s, 3H), 3.24 (d, *J* = 14.1 Hz, 1H), 2.66 (d, *J* = 14.1 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 169.6, 166.3, 153.8, 146.9, 132.9, 132.6, 132.0, 131.9, 130.9, 129.5, 128.5, 127.5, 125.8, 65.0, 58.4, 52.8, 37.7, 28.2. HRMS (ESI) m/z Calcd. for $C_{25}H_{28}N_3O_4$ ($[M+H]^+$) 434.2074, Found 434.2071. Enantiomeric excess was determined to be 21% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.4 min, t_{minor} = 5.8 min).

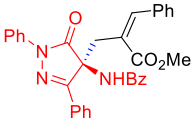


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.833	VB	0.1841	7439.10791	587.68555	50.6089
2	7.389	PP	0.3002	7260.10303	356.45956	49.3911



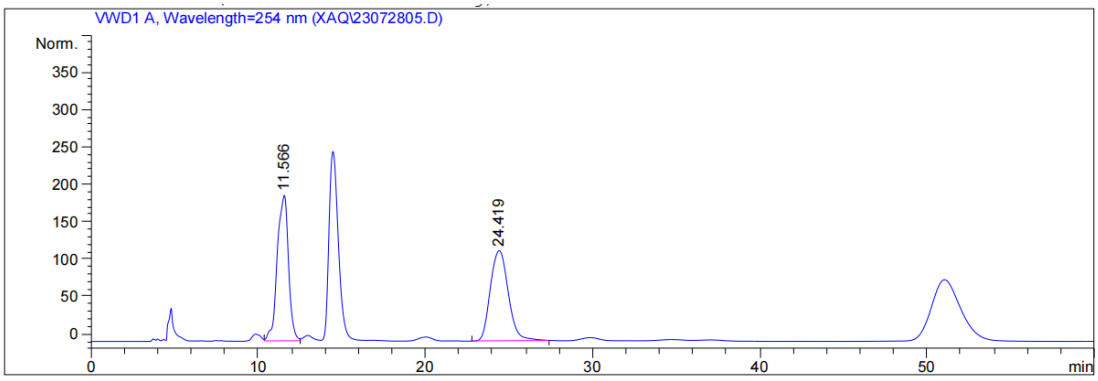
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.871	MM	0.2010	9415.74609	780.66589	39.5380
2	7.409	MM	0.3479	1.43987e4	689.83405	60.4620

(*Z*)-Compound 3az

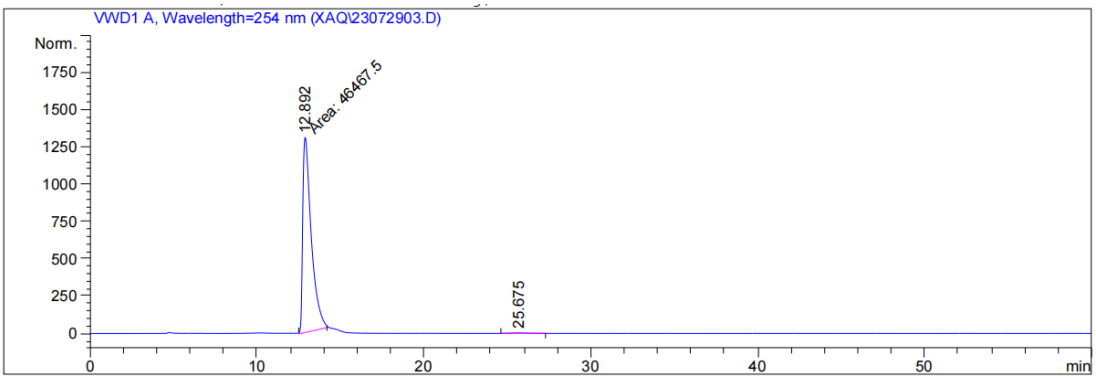


(*Z*)-3az

Prepared according to the procedure within 72 h as white solid (60.3 mg, 57% yield); $[\alpha]_D^{16}$ = 47.782 (*c* 0.29, CH_2Cl_2); Mp: 128.1 – 129.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.48 (s, 1H), 8.10 – 8.08 (m, 2H), 8.04 – 8.00 (m, 4H), 7.59 – 7.43 (m, 6H), 7.37 – 7.21 (m, 8H), 7.08 – 7.06 (m, 2H), 6.86 (s, 1H), 3.60 (s, 3H), 3.24 (d, *J* = 14.3 Hz, 1H), 3.00 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 171.5, 166.5, 156.0, 145.5, 138.4, 135.3, 132.3, 132.2, 130.6, 130.2, 128.8, 128.7, 128.6, 128.6, 128.4, 127.9, 127.7, 126.4, 125.3, 123.2, 119.4, 65.5, 52.4, 40.4. HRMS (ESI) m/z Calcd. for $C_{33}H_{28}N_3O_4$ ($[M+H]^+$) 530.2074, Found 530.2067. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral IF-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.8 min, t_{minor} = 25.6 min).

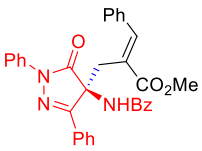


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.566	VV	0.6391	9106.43359	194.62646	50.2098
2	24.419	BB	1.1949	9030.31543	120.65739	49.7902



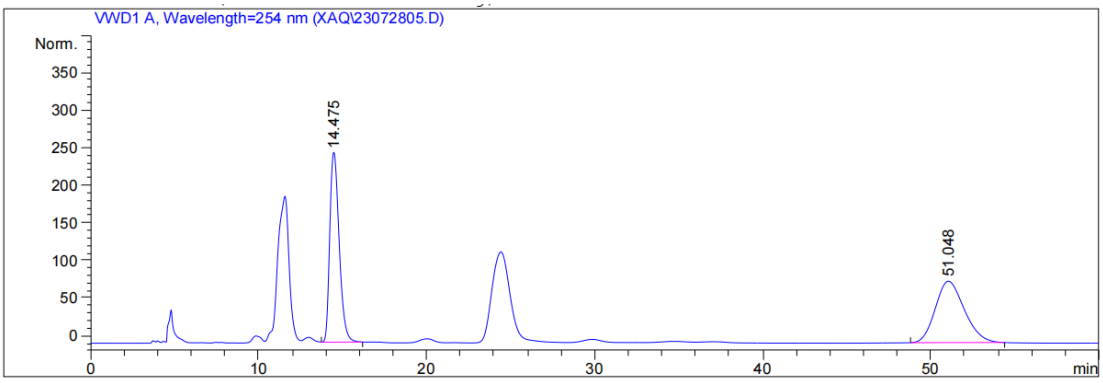
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.892	MM	0.5925	4.64675e4	1306.99426	99.5720
2	25.675	BB	0.7633	199.75262	3.14302	0.4280

(*E*)-Compound 3az

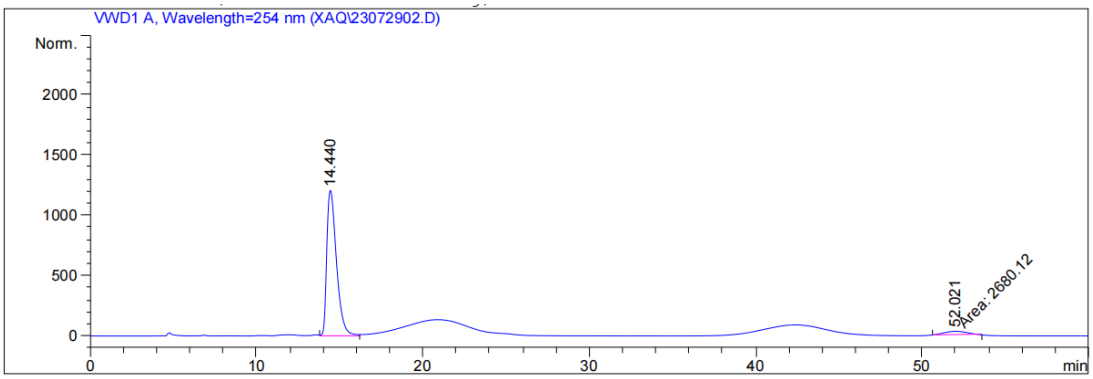


(*E*)-3az

Prepared according to the procedure within 72 h as white solid (28.6 mg, 27% yield); $[\alpha]_D^{16}$ = -55.783 (*c* 0.12, CH_2Cl_2); Mp: 132.4 - 133.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 8.03 (s, 1H), 8.00 – 7.98 (m, 2H), 7.88 – 7.83 (m, 4H), 7.53 – 7.49 (m, 1H), 7.46 – 7.34 (m, 7H), 7.21 –7.15 (m, 6H), 3.96 (s, 3H), 3.54 (d, *J* = 15.1 Hz, 1H), 3.18 (d, *J* = 15.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 170.7, 166.2, 156.5, 146.6, 138.2, 134.2, 132.2, 132.1, 130.3, 130.0, 129.1, 128.8, 128.7, 128.7, 128.6, 128.6, 127.5, 126.3, 125.1, 125.0, 119.3, 65.2, 53.2, 32.2. HRMS (ESI) m/z Calcd. for $C_{33}H_{28}N_3O_4$ ($[M+H]^+$) 530.2074, Found 530.2075. Enantiomeric excess was determined to be 89% (determined by HPLC using chiral IF-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.4 min, t_{minor} = 52.0 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.475	VB	0.6049	9820.68262	252.67104	50.0404
2	51.048	BB	1.7685	9804.80566	81.78436	49.9596



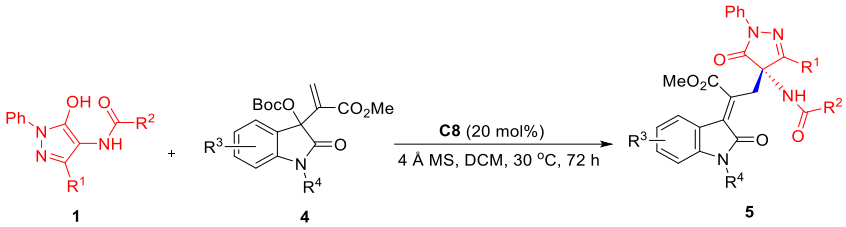
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.440	VB	0.6277	4.88100e4	1206.78015	94.7949
2	52.021	MM	1.5547	2680.12280	28.73073	5.2051

Gram scale synthesis of the product 3aa

1a, 2.20 mmol **2a**, 7.70 mmol **3aa**, 1.00 g, 99% yield, 97% ee

To a tube were added 4-aminopyrazolone **1a** (782 mg, 2.2 mmol, 1.0 eq.), **C8** (258 mg, 0.4 mmol, 0.2 eq.), 4 Å MS (2200 mg) and toluene (22 mL). MBH carbonate **2a** (1665 mg, 7.7 mmol, 3.5 eq.) was then added in one portion, and the reaction mixture was stirred at 30 °C. When the substrate **1a** was consumed as checked by TLC, the reaction was stopped and purified by column chromatography on silica gel directly to give the product **3aa** 1.00 g as white solid (yield 99%, ee 97%).

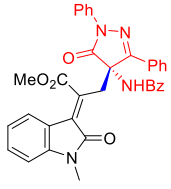
The procedure for the synthesis of compounds 5



1 **4** **5**

To a tube were added 4-aminopyrazolone **1** (0.2 mmol), **C8** (0.04 mmol), 4Å MS (200 mg) and DCM (2 mL). MBH carbonate **4** (0.3 mmol) was then added in one portion and the reaction mixture was stirred at 30 °C. When the substrate **1** was consumed as checked by TLC, the reaction was stopped and purified by column chromatography (petroleum ether/ethyl acetate = 5:1) on silica gel directly to give the product **5**.

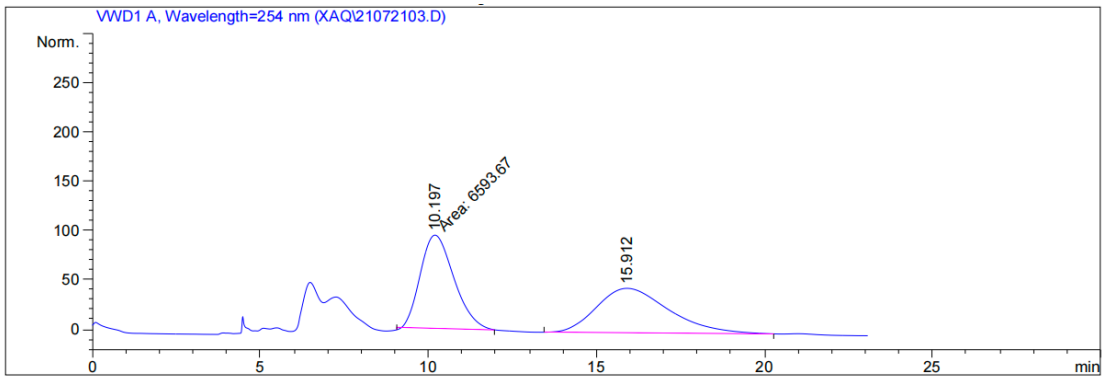
Compound 5aa



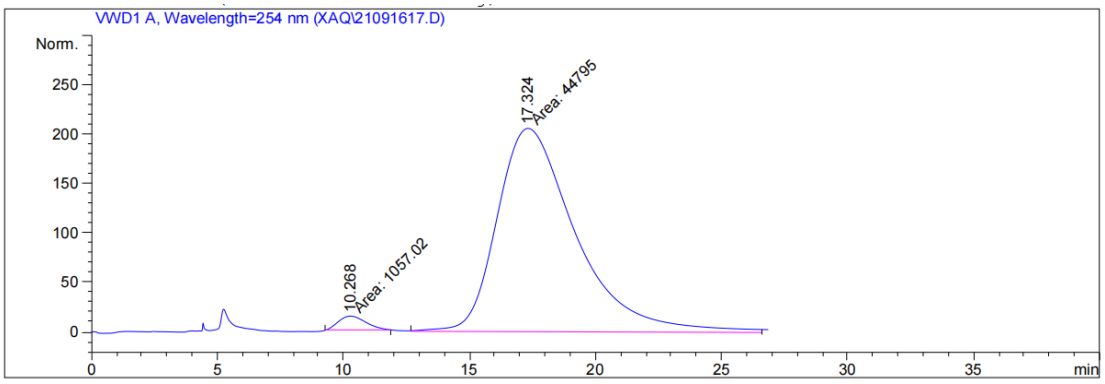
5aa

Prepared according to the procedure within 72 h as yellow solid (111.0 mg, 95% yield); $[\alpha]_D^{18}$ = -182.86 (*c* 0.70, CH_2Cl_2); Mp: 149.6 - 150.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 8.11 – 8.09 (m, 2H), 8.00 – 7.98 (m, 2H), 7.82 – 7.80 (m, 2H), 7.66 – 7.64 (m, 1H), 7.38 – 7.21 (m, 9H), 7.14 – 7.10 (m, 1H), 6.95 – 6.91 (m, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 13.9 Hz, 1H), 3.74 (s, 3H), 3.35 (d, *J* = 13.9 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 169.1, 168.0, 166.4, 155.6, 143.6, 138.6, 135.0, 134.7, 132.3, 131.9, 131.7, 130.3, 129.8, 128.8, 128.8, 128.4,

127.7, 126.5, 126.1, 125.1, 123.2, 120.6, 119.2, 108.7, 66.9, 53.0, 33.8, 26.4. HRMS (ESI) m/z Calcd. for $C_{35}H_{29}N_4O_5$ ([M+H]$^+$) 585.2132, Found 585.2125. Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.2 min, t_{minor} = 17.3 min).

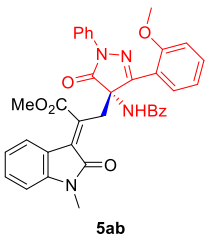


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.197	MM	1.1620	6593.66943	94.57317	49.3911
2	15.912	BB	1.9304	6756.25439	45.08381	50.6089



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.268	MM	1.2584	1057.01733	13.99906	2.3053
2	17.324	MM	3.6310	4.47950e4	205.61121	97.6947

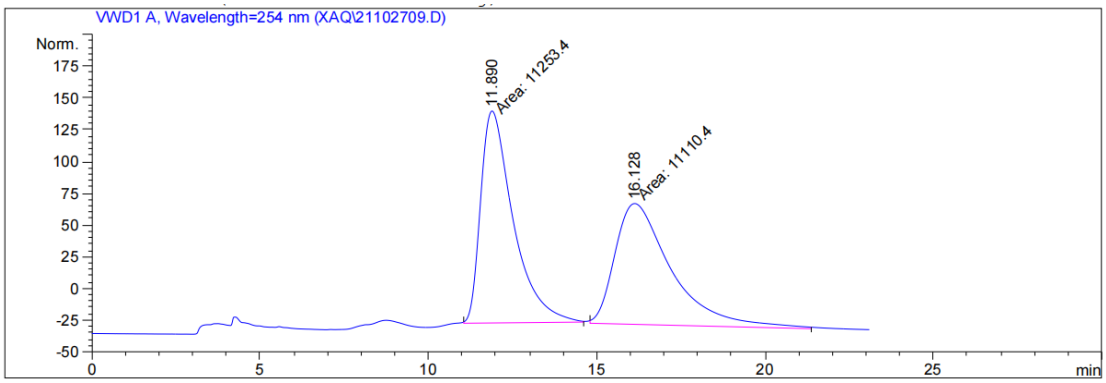
Compound 5ab



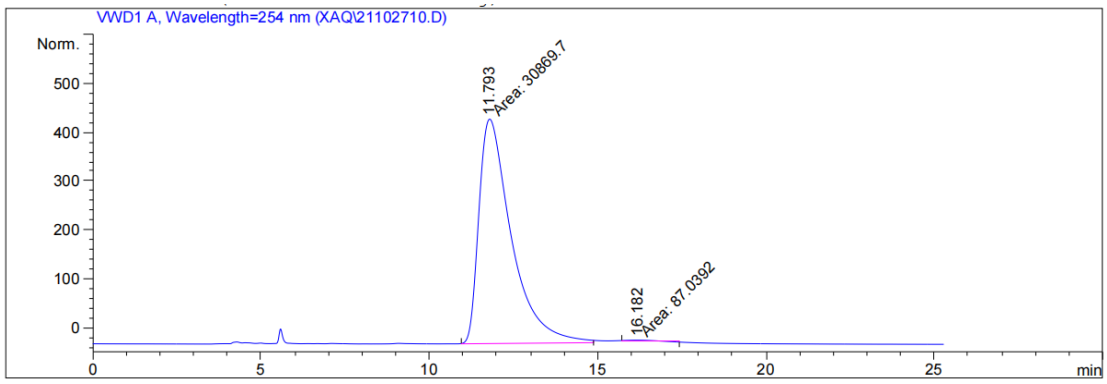
5ab

Prepared according to the procedure within 72 h as white solid (43.0 mg, 35% yield); $[\alpha]_D^{18}$ = -93.231 (*c* 0.52, CH_2Cl_2); Mp: 108.5 - 109.3 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 8.10 – 8.02 (m, 2H), 7.89 – 7.87 (m, 2H), 7.74 – 7.69 (m, 2H), 7.49 – 7.45 (m, 2H), 7.42 – 7.36 (m, 4H), 7.35 – 7.31 (m, 1H), 7.19 – 7.17 (m, 1H), 7.03 – 6.92 (m, 3H), 6.81 (d, *J* = 7.9 Hz, 1H), 4.45 (d, *J* = 14.1 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.51 (d, *J* = 14.0 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 168.8, 168.4, 166.4, 157.7, 143.6, 138.6, 135.6, 134.0, 133.6, 132.7, 131.6, 131.4, 131.3, 130.2, 128.6, 128.4, 128.3, 127.7, 125.8, 124.9, 122.9, 120.9, 120.7, 119.9, 119.3, 111.5, 68.1, 55.6, 52.8, 33.0, 26.2. HRMS (ESI) m/z Calcd. for $C_{36}H_{31}N_4O_6$ ([M+H]$^+$) 615.2238, Found 615.2232. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.7 min, t_{minor} =

16.1 min).

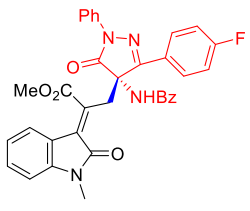


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.890	MM	1.1220	1.12534e4	167.15636	50.3195
2	16.128	MM	1.9423	1.11104e4	95.33609	49.6805



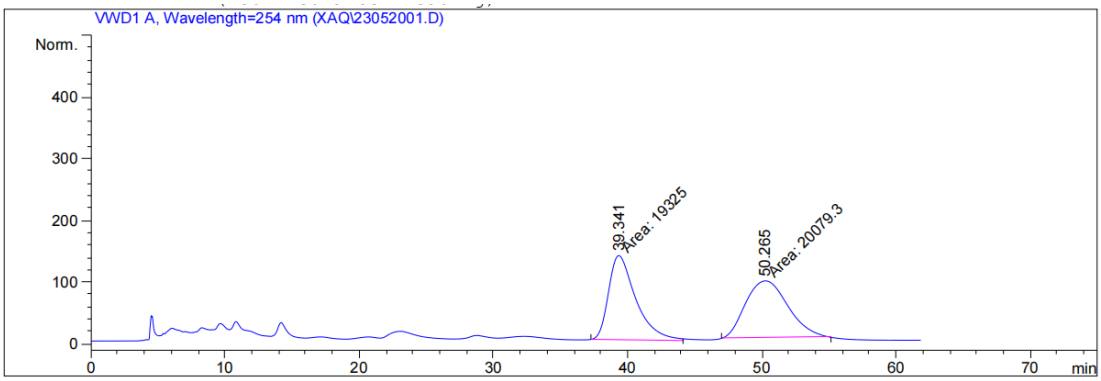
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.793	MM	1.1184	3.08697e4	460.01636	99.7188
2	16.182	MM	0.8295	87.03915	1.74883	0.2812

Compound 5ac

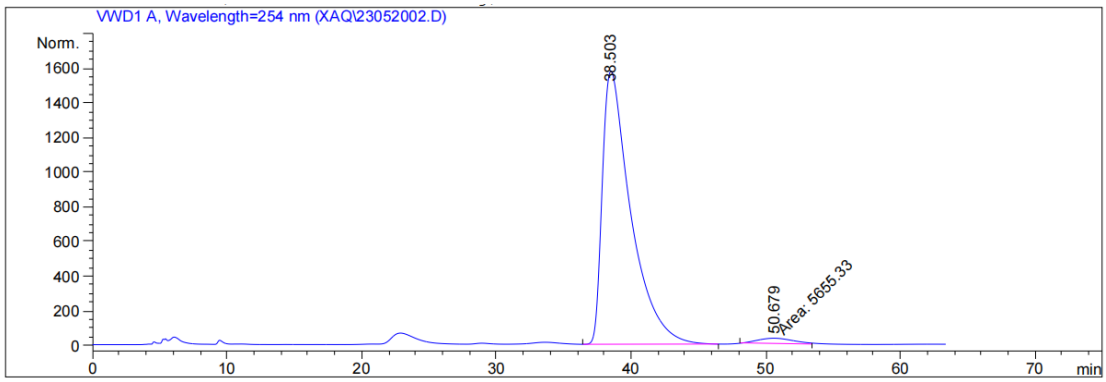


5ac

Prepared according to the procedure within 72 h as red solid (112.0 mg, 93% yield); $[\alpha]_D^{18}$ = -175.71 (*c* 0.70, CH_2Cl_2); Mp: 123.8 - 124.5 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 8.22 – 8.20 (m, 2H), 8.09 – 8.07 (m, 2H), 7.91 – 7.89 (m, 2H), 7.76 – 7.73 (m, 1H), 7.50 – 7.43 (m, 3H), 7.41 – 7.39 (m, 2H), 7.34 – 7.31 (m, 1H), 7.24 – 7.21 (m, 1H), 7.13 – 7.10 (m, 2H), 7.03 – 7.00 (m, 1H), 6.83 – 6.82 (m, 1H), 4.54 (d, *J* = 11.3 Hz, 1H), 3.84 (s, 3H), 3.44 (d, *J* = 11.2 Hz, 1H), 3.30 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.30 – -109.44 (m); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170. 8, 169.1, 168.0, 166.4, 163.9 (d, *J* = 252.5 Hz), 154.7, 143.6, 138.5, 134.8, 134.8, 132.2, 132.0, 131.8, 128.9, 128.8, 128.6 (d, *J* = 8.1 Hz), 128.5, 127.6, 126.1 (d, *J* = 13.8 Hz), 125.2, 123.2, 120.5, 119.1, 116.0 (d, *J* = 21.2 Hz), 108.8, 66.8, 52.9, 33.8, 26.4. HRMS (ESI) m/z Calcd. for $C_{35}H_{28}FN_4O_5$ ([M+H]$^+$) 603.2038, Found 603.2036; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 38.5 min, t_{minor} = 50.6 min).

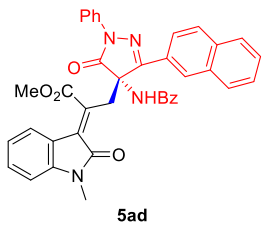


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.341	MM	2.3617	1.93250e4	136.37885	49.0429
2	50.265	MM	3.6487	2.00793e4	91.71872	50.9571



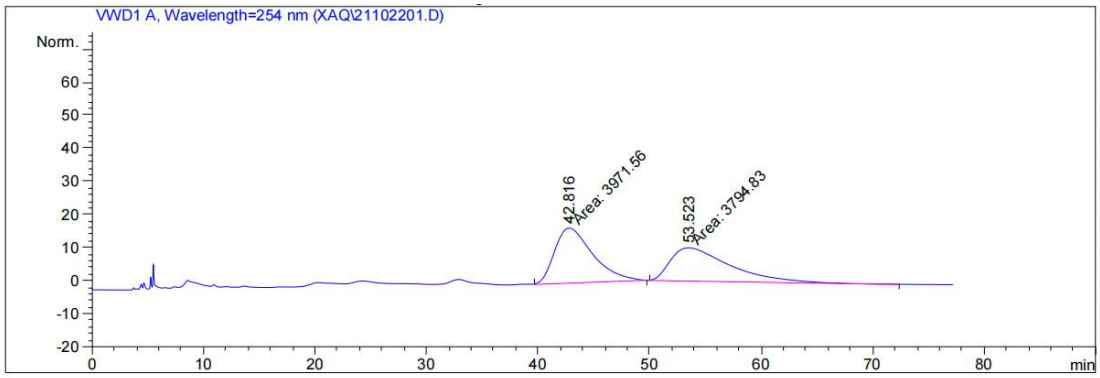
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.503	VB	2.1096	2.31885e5	1576.07068	97.6192
2	50.679	MM	3.0750	5655.33496	30.65252	2.3808

Compound 5ad

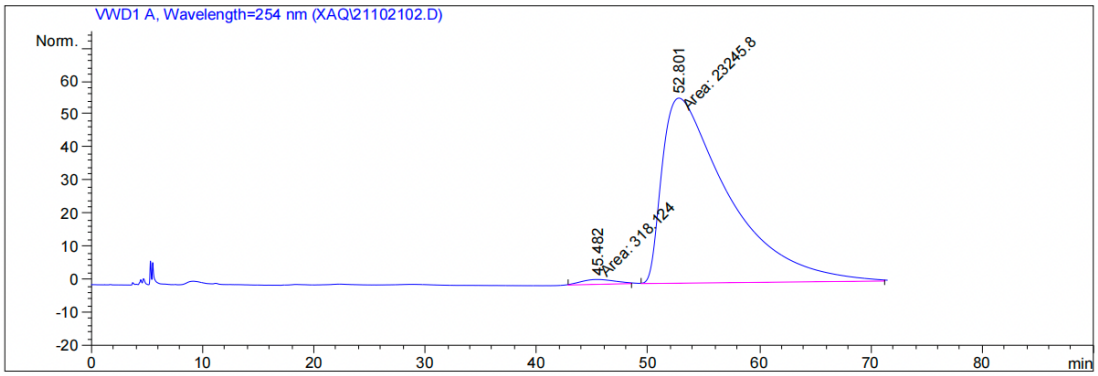


5ad

Prepared according to the procedure within 72 h as white solid (96.4 mg, 76% yield); $[\alpha]_D^{18}$ = -243.59 (*c* 0.78, CH_2Cl_2); Mp: 114.8 - 115.6 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.56 (s, 1H), 8.22 – 8.20 (m, 1H), 8.04 – 8.02 (m, 2H), 7.81 – 7.76 (m, 3H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.36 – 7.31 (m, 5H), 7.28 – 7.25 (m, 2H), 7.16 – 7.12 (m, 2H), 6.87 – 6.84 (m, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 4.62 (d, *J* = 14.0 Hz, 1H), 3.73 (s, 3H), 3.32 (d, *J* = 14.1 Hz, 1H), 3.14 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 169.0, 168.1, 166.4, 155.7, 143.5, 138.7, 135.0, 134.7, 134.0, 133.0, 132.4, 131.9, 131.7, 130.1, 129.0, 128.8, 128.5, 128.5, 127.7, 127.6, 127.3, 126.9, 126.5, 125.9, 125.2, 123.4, 123.1, 120.5, 119.3, 108.7, 66.9, 52.9, 34.1, 26.3. HRMS (ESI) m/z Calcd. for $C_{39}H_{31}N_4O_5$ ($[M+H]^+$) 635.2289, Found 635.2288. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 52.8 min, t_{minor} = 45.4 min).

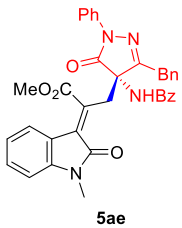


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	42.816	MM	3.9717	3971.55908	16.66597	51.1378
2	53.523	MM	6.2564	3794.82837	10.10912	48.8622



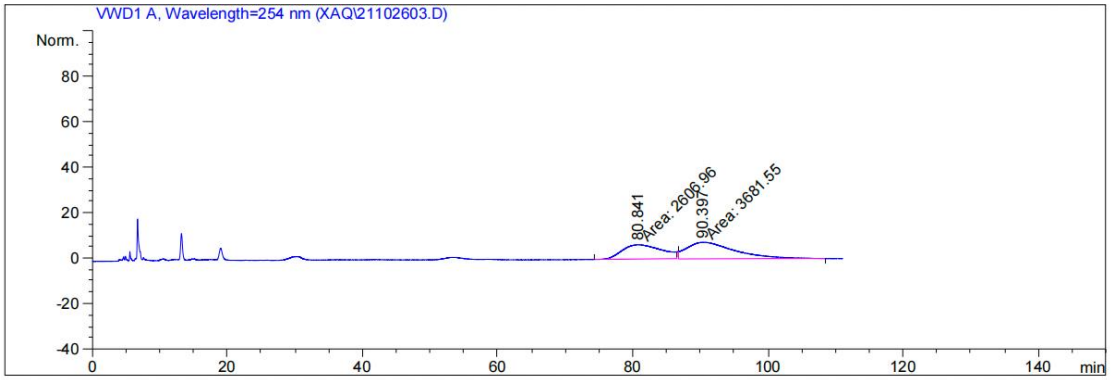
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	45.482	MM	3.5551	318.12384	1.49138	1.3500
2	52.801	MM	6.9081	2.32458e4	56.08327	98.6500

Compound 5ae

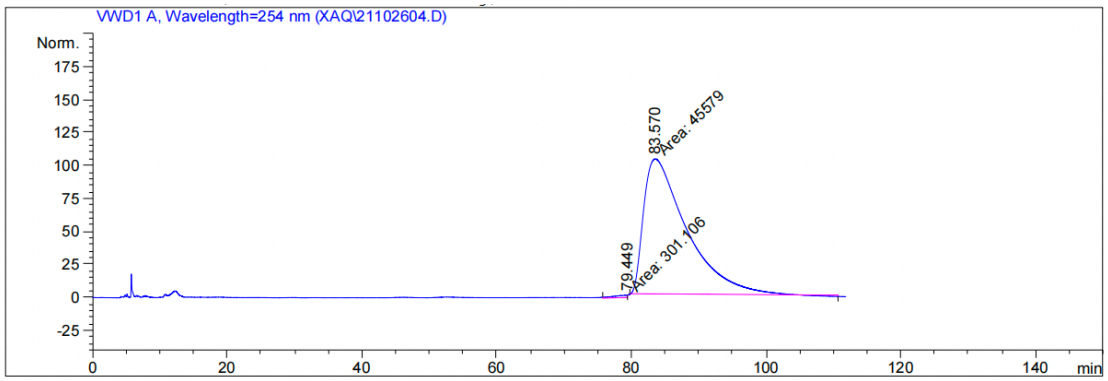


5ae

Prepared according to the procedure within 72 h as yellow solid (35.9 mg, 30% yield); $[\alpha]_D^{18}$ = -89.474 (*c* 0.38, CH_2Cl_2); Mp: 145.8 - 146.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.96 – 7.94 (m, 2H), 7.76 – 7.74 (m, 2H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.30 (m, 8H), 7.25 – 7.21 (m, 2H), 7.19 – 7.15 (m, 1H), 7.12 – 7.08 (m, 1H), 7.03 – 6.98 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.02 (d, *J* = 13.6 Hz, 1H), 3.92 – 3.79 (m, 5H), 3.30 (s, 3H), 3.12 (d, *J* = 13.6 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 169.0, 167.9, 166.2, 159.6, 143.5, 138.6, 135.2, 134.9, 134.1, 132.1, 131.8, 131.5, 129.5, 128.7, 128.6, 128.2, 127.6, 126.9, 125.9, 124.8, 123.1, 120.6, 119.1, 108.6, 67.3, 52.8, 34.8, 32.9, 26.3. HRMS (ESI) m/z Calcd. for $C_{36}H_{31}N_4O_5$ ([M+H]$^+$) 599.2289, Found 599.2287. Enantiomeric excess was determined to be 98% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 83.5 min, t_{minor} = 79.4 min).

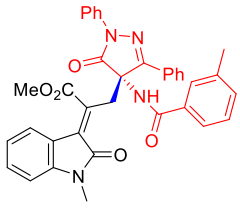


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	80.841	MM	6.8790	2606.95898	6.31620	41.4559
2	90.397	MM	8.3634	3681.55151	7.33667	58.5441



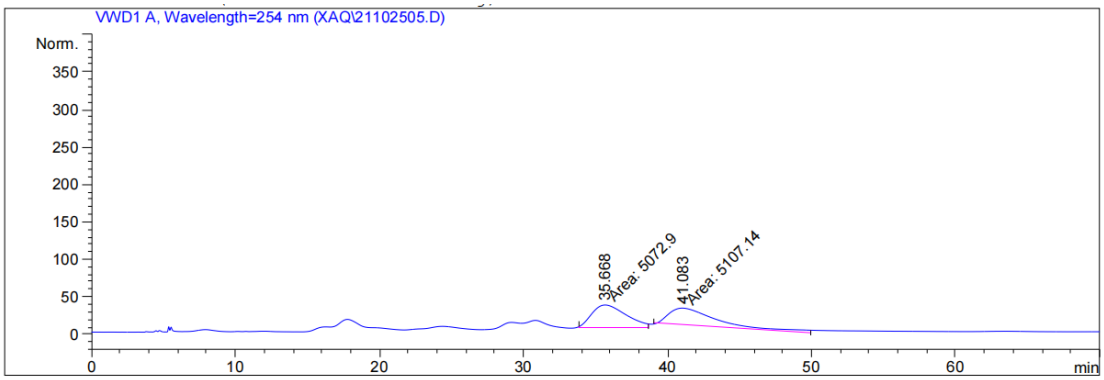
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	79.449	MM	2.5438	301.10623	1.97281	0.6563
2	83.570	MM	7.4204	4.55790e4	102.37341	99.3437

Compound 5af

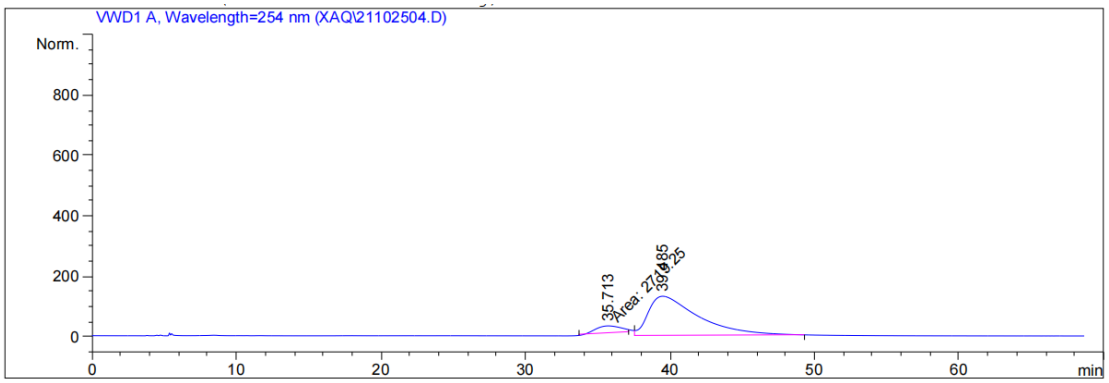


5af

Prepared according to the procedure within 72 h as red solid (93.3 mg, 78% yield); $[\alpha]_D^{18}$ = -116.67 (*c* 0.30, CH_2Cl_2); Mp: 121.8 - 122.2 ºC; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 8.21 – 8.20 (m, 2H), 8.10 – 8.09 (m, 2H), 7.76 – 7.71 (m, 3H), 7.46 – 7.37 (m, 5H), 7.34 – 7.31 (m, 1H), 7.30 – 7.27 (m, 2H), 7.24 – 7.21 (m, 1H), 7.03 – 7.00 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 3.83 (s, 3H), 3.43 (d, *J* = 14.0 Hz, 1H), 3.32 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 169.1, 167.9, 166.5, 155.7, 143.6, 138.6, 138.1, 135.3, 134.6, 132.6, 132.2, 131.7, 130.2, 129.9, 128.8, 128.8, 128.5, 128.3, 126.5, 126.1, 125.1, 124.7, 123.2, 120.6, 119.2, 108.7, 66.9, 52.9, 33.8, 26.3, 21.4. HRMS (ESI) m/z Calcd. for $C_{36}H_{31}N_4O_5$ ([M+H]$^+$) 599.2289, Found 599.2288. Enantiomeric excess was determined to be 84% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 ºC, 0.8 mL/min, t_{major} = 39.4 min, t_{minor} = 35.7 min).

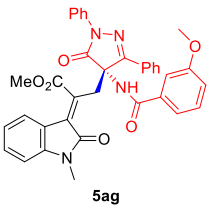


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.668	MM	2.7855	5072.90381	30.35357	49.8318
2	41.083	MM	3.8692	5107.14160	21.99905	50.1682



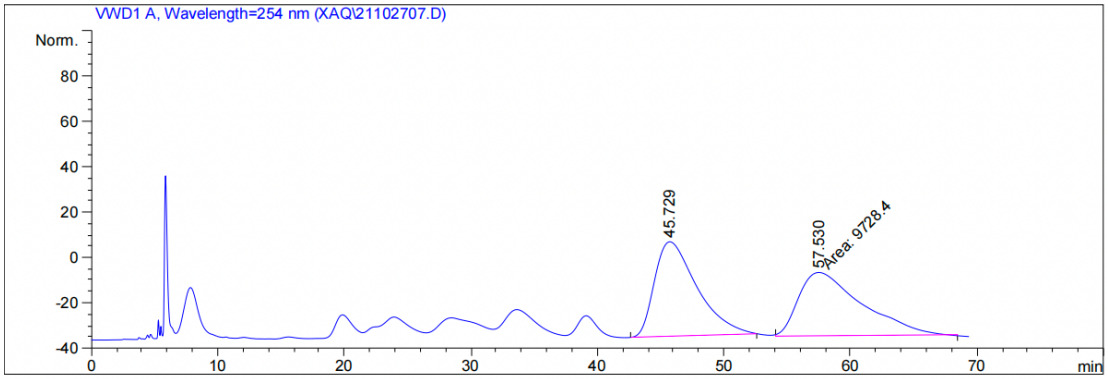
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.713	MM	1.4095	2719.25024	22.86150	7.9929
2	39.485	VB	3.2376	3.13016e4	129.84703	92.0071

Compound 5ag

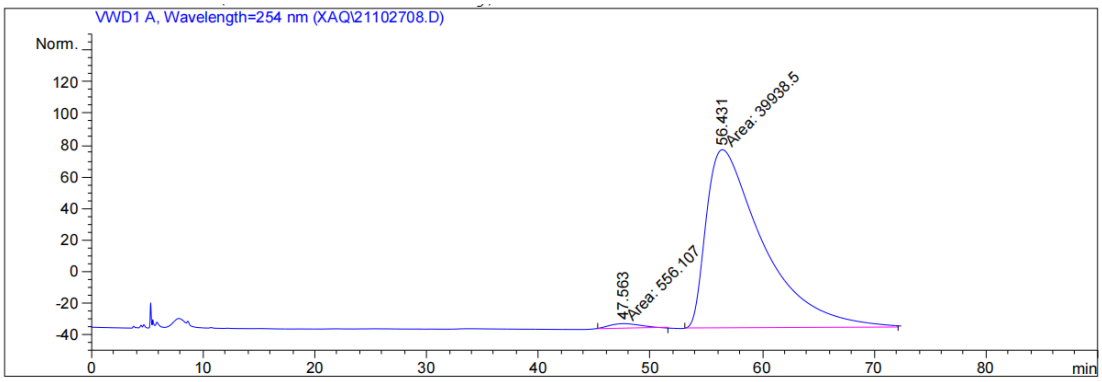


5ag

Prepared according to the procedure within 72 h as white solid (74.9 mg, 61% yield); $[\alpha]_D^{18}$ = -206.45 (*c* 0.31, CH_2Cl_2); Mp: 129.7 - 130.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 (s, 1H), 8.21 – 8.18 (m, 2H), 8.11 – 8.08 (m, 2H), 7.76 – 7.74 (m, 1H), 7.51 – 7.49 (m, 1H), 7.47 – 7.38 (m, 6H), 7.35 – 7.29 (m, 2H), 7.24 – 7.20 (m, 1H), 7.04 – 7.00 (m, 2H), 6.83 – 6.81 (m, 1H), 4.59 (d, *J* = 13.9 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.44 (d, *J* = 13.9 Hz, 1H), 3.31 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 169.1, 168.0, 166.2, 159.7, 155.5, 143.6, 138.6, 135.0, 134.7, 133.7, 131.7, 130.3, 129.8, 129.4, 128.8, 128.8, 126.5, 126.1, 125.1, 123.2, 120.6, 119.6, 119.1, 118.9, 112.3, 108.7, 66.9, 55.4, 53.0, 33.8, 26.4. HRMS (ESI) m/z Calcd. for $C_{36}H_{31}N_4O_6$ ($[M+H]^+$) 615.2238, Found 615.2233. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 56.4 min, t_{minor} = 47.5 min).

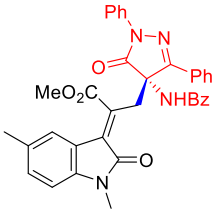


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	45.729	BB	2.7728	9763.88574	41.73978	50.0910
2	57.530	MM	5.7915	9728.39844	27.99606	49.9090



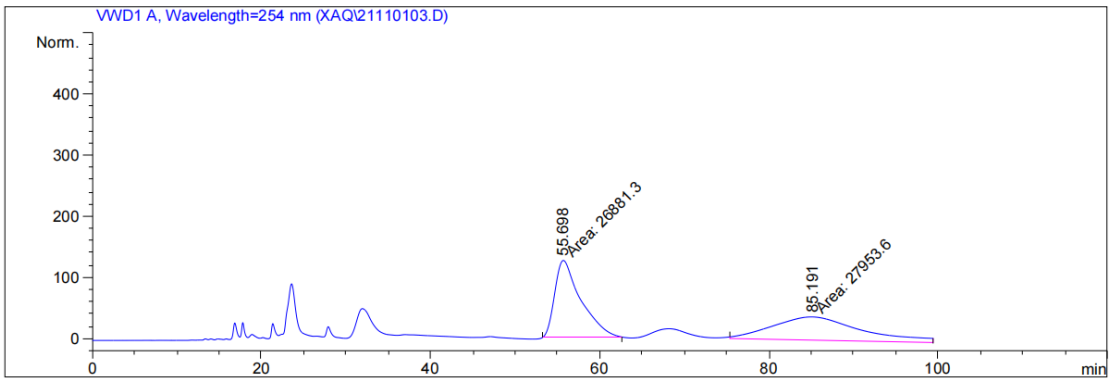
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	47.563	MM	3.1751	556.10724	2.91911	1.3733
2	56.431	MM	5.8994	3.99385e4	112.83166	98.6267

Compound 5ah

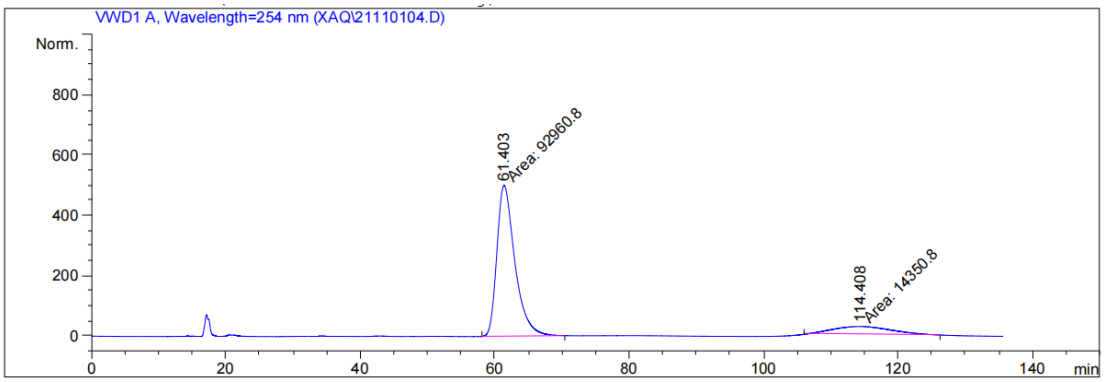


5ah

Prepared according to the procedure within 72 h as white solid (52.6 mg, 44% yield); $[\alpha]_D^{18}$ = -127.42 (*c* 0.76, CH_2Cl_2); Mp: 135.1 - 136.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 (s, 1H), 8.21 – 8.18 (m, 2H), 8.10 – 8.06 (m, 2H), 7.92 – 7.90 (m, 2H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.50 – 7.37 (m, 8H), 7.24 – 7.19 (m, 1H), 7.15 – 7.13 (m, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 4.58 (d, *J* = 14.0 Hz, 1H), 3.84 (s, 3H), 3.43 (d, *J* = 13.9 Hz, 1H), 3.30 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 169.1, 168.1, 166.4, 155.6, 141.4, 138.6, 134.9, 134.6, 132.5, 132.3, 132.0, 131.9, 130.3, 130.2, 129.8, 128.8, 128.4, 127.7, 126.9, 126.5, 125.1, 120.6, 119.2, 108.4, 66.9, 52.8, 33.8, 26.4, 21.4. HRMS (ESI) m/z Calcd. for $C_{36}H_{31}N_4O_5$ ($[M+H]^+$) 599.2289, Found 599.2284. Enantiomeric excess was determined to be 73% (determined by HPLC using chiral OD-AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 61.4 min, t_{minor} = 114.4 min).

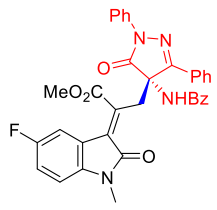


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	55.698	MM	3.5651	2.68813e4	125.66887	49.0223
2	85.191	MM	12.2081	2.79536e4	38.16249	50.9777



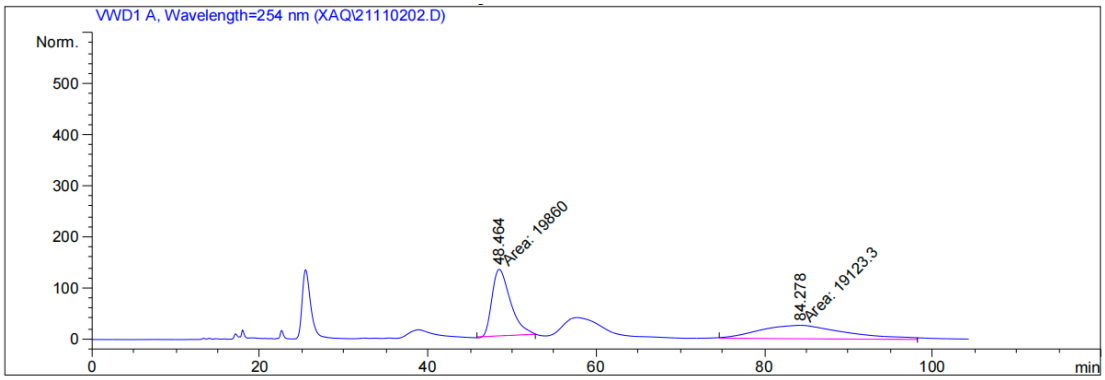
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	61.403	MM	3.0977	9.29607e4	500.16779	86.6270
2	114.408	MM	9.6816	1.43508e4	24.70448	13.3730

Compound 5ai

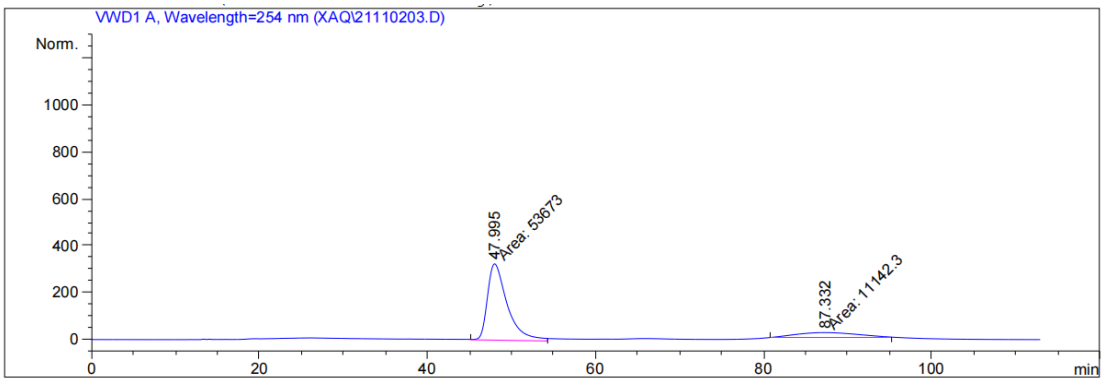


5ai

Prepared according to the procedure within 72 h as yellow solid (93.9 mg, 78% yield); $[\alpha]_D^{18}$ = -210.53 (*c* 0.76, CH_2Cl_2); Mp: 140.9 - 141.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 8.19 – 8.16 (m, 2H), 8.09 – 8.05 (m, 2H), 7.90 – 7.87 (m, 2H), 7.60 – 7.57 (m, 1H), 7.49 – 7.43 (m, 3H), 7.42 – 7.35 (m, 5H), 7.24 – 7.19 (m, 1H), 7.06 – 7.01 (m, 1H), 6.76 – 6.73 (m, 1H), 4.62 (d, *J* = 13.9 Hz, 1H), 3.82 (s, 3H), 3.43 (d, *J* = 13.9 Hz, 1H), 3.30 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.15 – -119.21 (m);^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 168.9, 167.3, 166.3, 159.1 (d, *J* = 239.7 Hz), 155.5, 139.7, 138.5, 136.8, 134.4, 132.4, 131.9, 130.3, 129.8, 128.8, 128.8, 128.4, 127.6, 126.5, 125.1, 121.6 (d, *J* = 9.1 Hz), 119.1, 118.0 (d, *J* = 24.2 Hz), 114.4, 109.0 (d, *J* = 8.1 Hz), 66.9, 53.0, 33.8, 26.5. HRMS (ESI) m/z Calcd. for $C_{35}H_{28}FN_4O_5$ ($[M+H]^+$) 603.2038, Found 603.2030. Enantiomeric excess was determined to be 65% (determined by HPLC using chiral OD-AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 47.9 min, t_{minor} = 87.3 min).

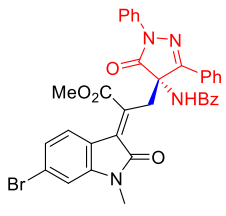


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	48.464	MM	2.5363	1.98600e4	130.50423	50.9450
2	84.278	MM	11.9905	1.91233e4	26.58109	49.0550



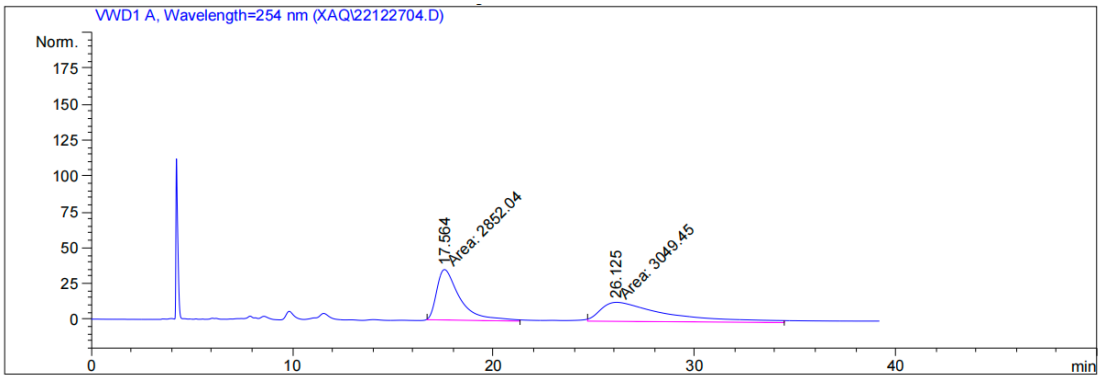
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	47.995	MM	2.7478	5.36730e4	325.55005	82.8091
2	87.332	MM	8.7135	1.11423e4	21.31241	17.1909

Compound 5aj

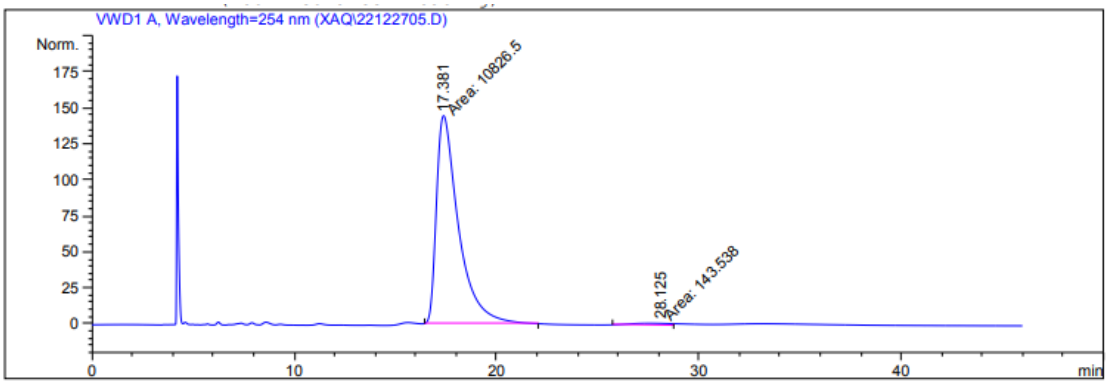


5aj

Prepared according to the procedure within 72 h as yellow solid (131.1 mg, 99% yield); $[\alpha]_D^{18}$ = -96.400 (*c* 0.60, CH_2Cl_2); Mp: 136.2 - 137.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.70 (s, 1H), 8.17 – 8.15 (m, 2H), 8.08 – 8.06 (m, 2H), 7.88 – 7.86 (m, 2H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.44 – 7.34 (m, 8H), 7.22 – 7.17 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.93 (s, 1H), 4.51 (d, *J* = 13.9 Hz, 1H), 3.77 (s, 3H), 3.43 (d, *J* = 13.9 Hz, 1H), 3.23 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 169.0, 167.7, 166.3, 155.6, 144.7, 138.6, 135.6, 134.0, 132.3, 132.1, 130.4, 129.8, 128.9, 128.8, 128.5, 127.6, 127.5, 126.5, 126.0, 125.7, 125.2, 119.4, 119.1, 112.2, 66.8, 53.1, 33.8, 26.5. HRMS (ESI) m/z Calcd. for $C_{35}H_{28}BrN_4O_5$ ($[M+H]^+$) 663.1238, Found 663.1240. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral IB-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 17.3 min, t_{minor} = 28.1 min).

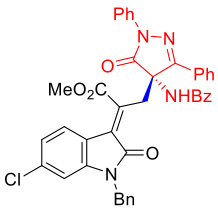


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.564	MM	1.3476	2852.04272	35.27306	48.3275
2	26.125	MM	3.8109	3049.44971	13.33667	51.6725



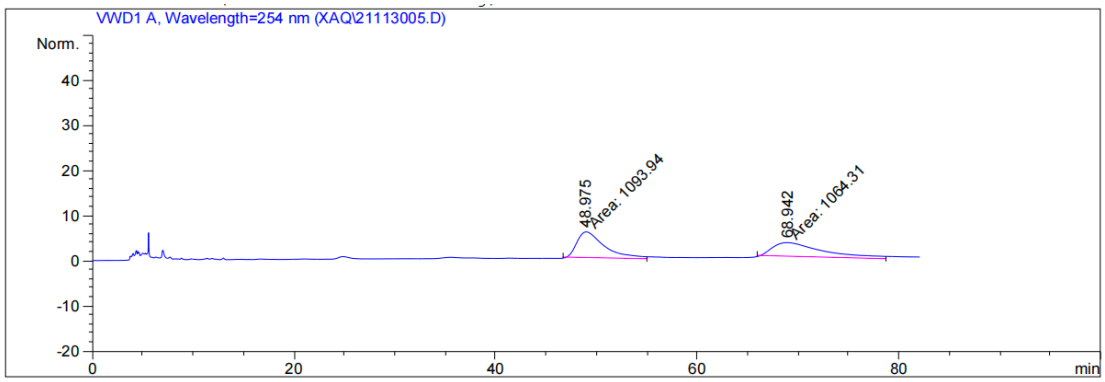
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.381	MM	1.2524	1.08265e4	144.07724	98.6915
2	28.125	MM	1.9586	143.53842	1.22141	1.3085

Compound 5ak

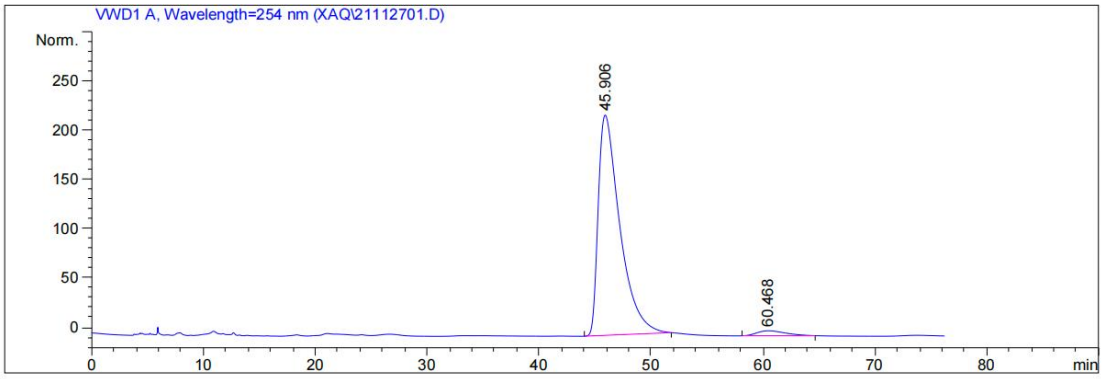


5ak

Prepared according to the procedure within 72 h as yellow solid (75.0 mg, 54% yield); $[\alpha]_D^{18}$ = -92.000 (*c* 0.50, CH_2Cl_2); Mp: 134.9 - 135.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.73 (s, 1H), 8.24 – 8.22 (m, 2H), 8.11 – 8.09 (m, 2H), 7.90 – 7.88 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.41 (m, 6H), 7.39 – 7.37 (m, 3H), 7.34 – 7.30 (m, 4H), 7.25 – 7.21 (m, 1H), 7.02 – 7.00 (m, 1H), 6.76 (s, 1H), 5.18 (d, *J* = 15.9 Hz, 1H), 4.93 (d, *J* = 15.9 Hz, 1H), 4.59 (d, *J* = 13.8 Hz, 1H), 3.87 (s, 3H), 3.56 (d, *J* = 13.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 169.3, 167.8, 166.3, 155.5, 143.9, 138.5, 137.5, 135.9, 134.4, 133.7, 132.2, 131.9, 130.4, 129.7, 129.2, 128.9, 128.8, 128.5, 128.2, 127.6, 127.4, 126.9, 126.5, 125.2, 123.2, 121.8, 119.2, 110.1, 66.8, 53.2, 44.0, 33.8. HRMS (ESI) m/z Calcd. for $C_{41}H_{32}ClN_4O_5$ ($[M+H]^+$) 695.2056, Found 695.2053. Enantiomeric excess was determined to be 94% (determined by HPLC using chiral IB-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 45.9 min, t_{minor} = 60.4 min).

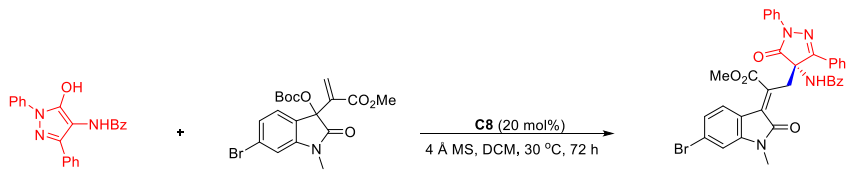


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	48.975	MM	3.1986	1093.94141	5.70016	50.6865
2	68.942	MM	5.8787	1064.30981	3.01744	49.3135



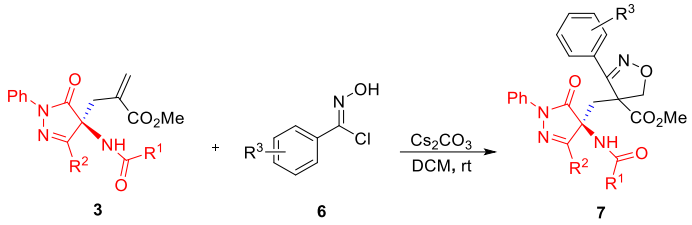
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	45.906	PB	1.9684	2.99340e4	223.34114	97.0769
2	60.468	BB	2.0912	901.33105	5.05653	2.9231

Gram scale synthesis of the product 5aj



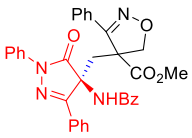
To a tube were added 4-aminopyrazolone **1a** (639 mg, 1.50 mmol, 1.0 eq.), **C8** (193 mg，0.30 mmol, 0.2 eq.), 4 Å MS (1500 mg) and DCM (15 mL). MBH carbonate **4d** (978 mg, 2.30 mmol, 1.5 eq.) was then added in one portion, and the reaction mixture was stirred at 30 ºC. When the substrate **1a** was consumed as checked by TLC, the reaction was stopped and purified by column chromatography on silica gel directly to give the product **5aj** 0.98 g as yellow solid (yield 99%, ee 97%).

The procedure for the synthesis of compounds 7



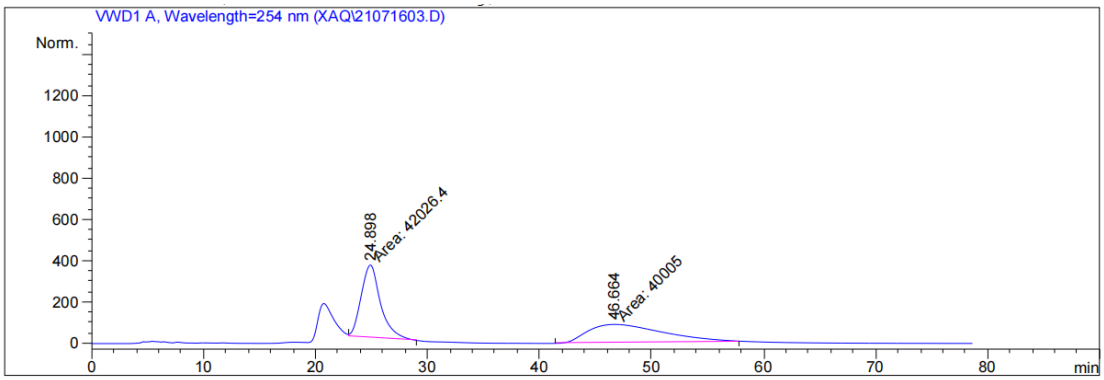
To a solution of nitrile oxide **6** (0.6 mmol) and Cs_2CO_3 (0.6 mmol) in DCM (2.0 mL) was added the product **3** (0.2 mmol). The reaction mixture was stirred at rt for 12 h, and then the reaction was detected by TLC. When the reaction finished, the crude mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give compound **7**.

Compound 7aa

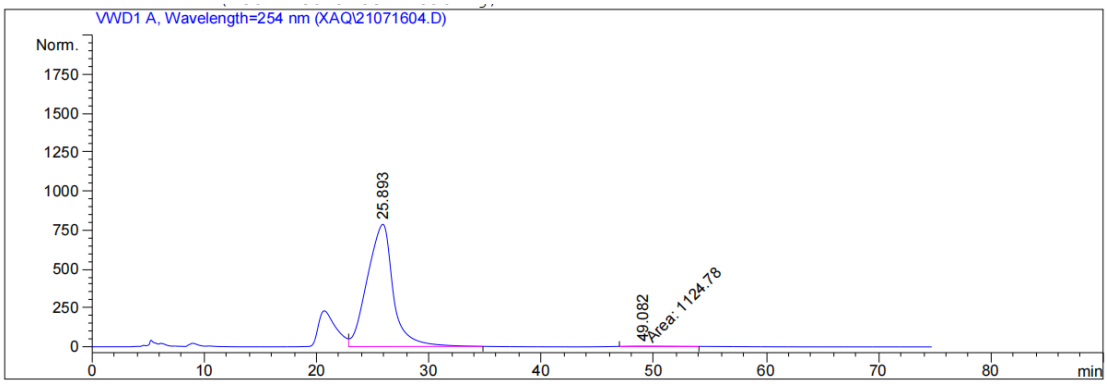


7aa

Prepared according to the procedure within 12 h as yellow solid (113.4 mg, 99% yield, dr = 4:1); $[\alpha]_D^{18}$ = 97.500 (*c* 0.40, CH_2Cl_2); Mp: 126.7 - 127.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 8.04 – 8.00 (m, 4H), 7.95 – 7.92 (m, 2H), 7.62 – 7.59 (m, 2H), 7.45 – 7.40 (m, 6H), 7.38 – 7.36 (m, 5H), 7.24 – 7.19 (m, 1H), 3.85 – 3.81 (m, 4H), 3.35 (d, *J* = 17.5 Hz, 1H), 2.93 (d, *J* = 15.2 Hz, 1H), 2.69 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 170.9, 166.9, 156.8, 156.0, 138.2, 132.3, 132.2, 131.1, 130.6, 129.5, 129.0, 128.9, 128.8, 127.6, 127.0, 126.4, 125.5, 119.3, 86.7, 64.1, 53.7, 47.9, 40.7, 29.7. HRMS (ESI) m/z Calcd. for $C_{34}H_{29}N_4O_5$ ($[M+H]^+$) 573.2132, Found 573.2130. Enantiomeric excess was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 25.8 min, t_{minor} = 49.0 min).

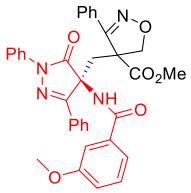


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.898	MM	2.0021	4.20264e4	349.85883	51.2321
2	46.664	MM	7.7024	4.00050e4	86.56362	48.7679



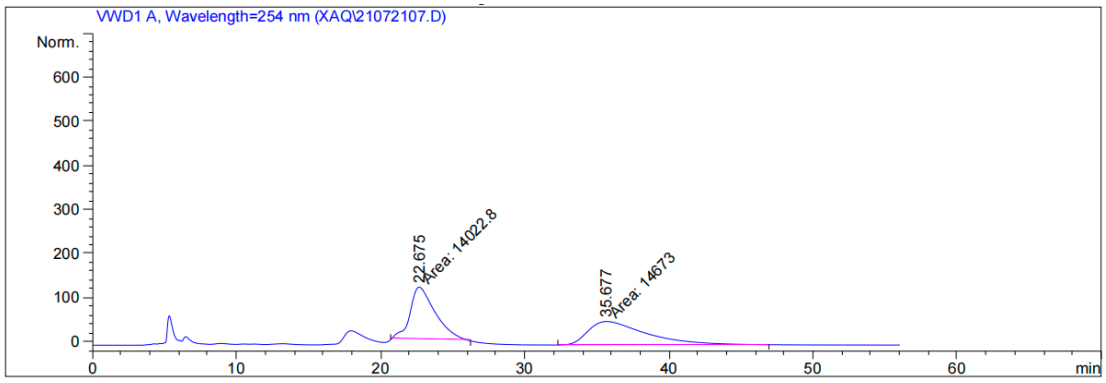
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.893	VB	2.3561	1.25610e5	786.19269	99.1125
2	49.082	MM	5.6871	1124.77856	3.29626	0.8875

Compound 7ab

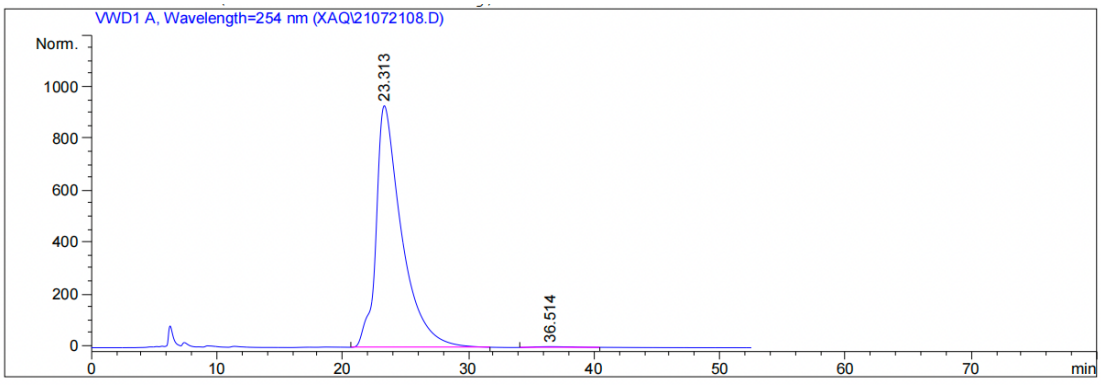


7ab

Prepared according to the procedure within 12 h as yellow solid (116.9 mg, 97% yield, dr = 5:1); $[\alpha]_D^{18}$ = 150.00 (*c* 0.10, CH_2Cl_2); Mp: 108.5 - 109.6 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 8.04 – 8.00 (m, 4H), 7.63 – 7.60 (m, 2H), 7.56 – 7.53 (m, 1H), 7.48 – 7.37 (m, 10H), 7.25 – 7.21 (m, 1H), 7.10 – 7.07 (m, 1H), 3.89 – 3.84 (m, 4H), 3.83 (s, 3H), 3.36 (d, *J* = 17.5 Hz, 1H), 2.94 (d, *J* = 15.3 Hz, 1H), 2.68 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 170.9, 166.8, 159.9, 156.7, 155.9, 147.1, 138.1, 133.5, 131.1, 130.6, 129.8, 129.5, 129.0, 128.9, 127.8, 127.2, 127.0, 126.4, 125.5, 119.3, 112.2, 86.7, 64.0, 55.4, 53.7, 47.8, 40.7, 29.7. HRMS (ESI) m/z Calcd. for $C_{35}H_{31}N_4O_6$ ($[M+H]^+$) 603.2238, Found 603.2238. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 23.3 min, t_{minor} = 36.5 min).

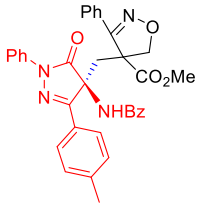


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.675	MM	1.9969	1.40228e4	117.03905	48.8672
2	35.677	MM	4.6311	1.46730e4	52.80548	51.1328



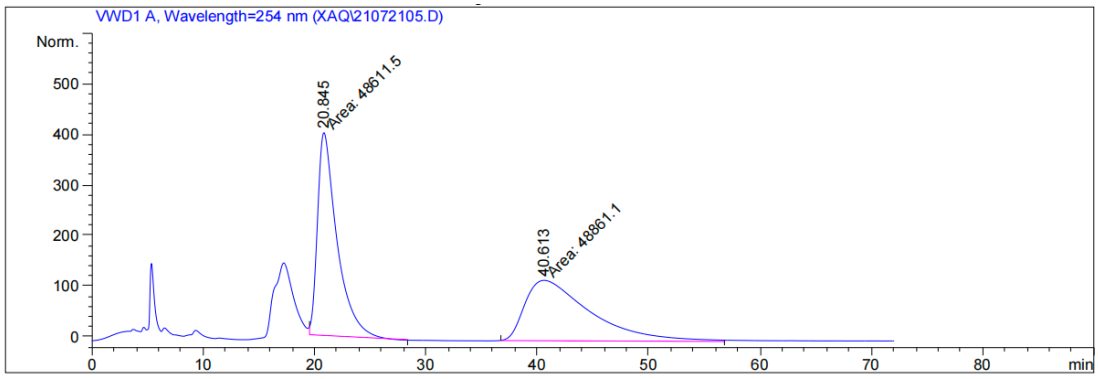
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.313	PB	1.9964	1.31948e5	933.02216	99.5644
2	36.514	BB	2.2744	577.34296	2.97099	0.4356

Compound 7ac

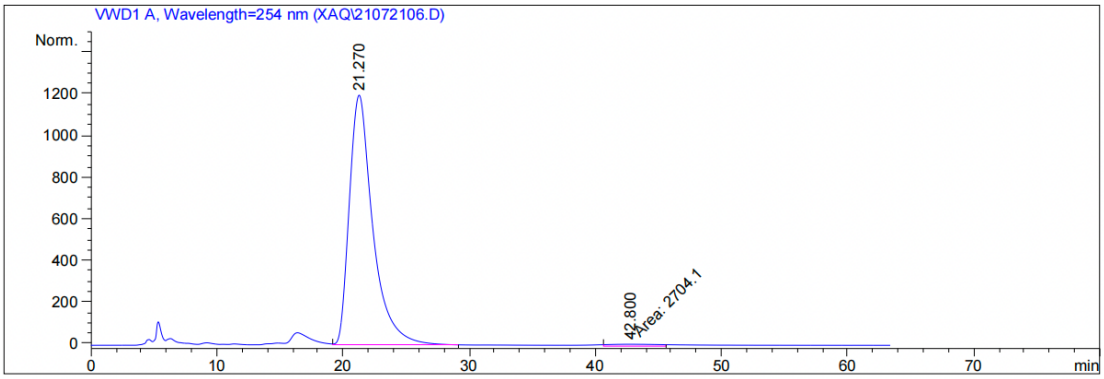


7ac

Prepared according to the procedure within 12 h as white solid (97.4 mg, 83% yield, dr = 5:1); $[\alpha]_D^{18}$ = 141.66 (*c* 0.24, CH_2Cl_2); Mp: 111.7 - 112.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 8.04 – 8.02 (m, 2H), 7.96 – 7.91 (m, 4H), 7.63 – 7.60 (m, 2H), 7.54 – 7.52 (m, 1H), 7.49 – 7.38 (m, 8H), 7.20 – 7.18 (m, 2H), 3.87 – 3.83 (m, 4H), 3.35 (d, *J* = 17.5 Hz, 1H), 2.94 (d, *J* = 15.3 Hz, 1H), 2.68 (d, *J* = 15.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.6, 170.9, 166.8, 156.8, 156.1, 141.0, 138.2, 132.3, 131.1, 129.7, 129.0, 128.9, 128.7, 127.9, 127.6, 127.0, 126.8, 126.3, 125.4, 119.3, 86.7, 64.1, 53.7, 47.8, 40.8, 29.7, 21.5. HRMS (ESI) m/z Calcd. for $C_{35}H_{31}N_4O_5$ ($[M+H]^+$) 587.2289, Found 587.2286; Enantiomeric excess was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 21.2 min, t_{minor} = 42.8 min).

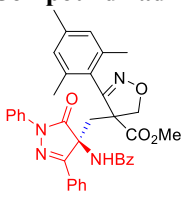


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.845	MM	2.0228	4.86115e4	400.52585	49.8719
2	40.613	MM	6.8193	4.88611e4	119.41930	50.1281



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.270	VB	1.9346	1.55178e5	1199.38257	98.2873
2	42.800	MM	4.5711	2704.10474	9.85932	1.7127

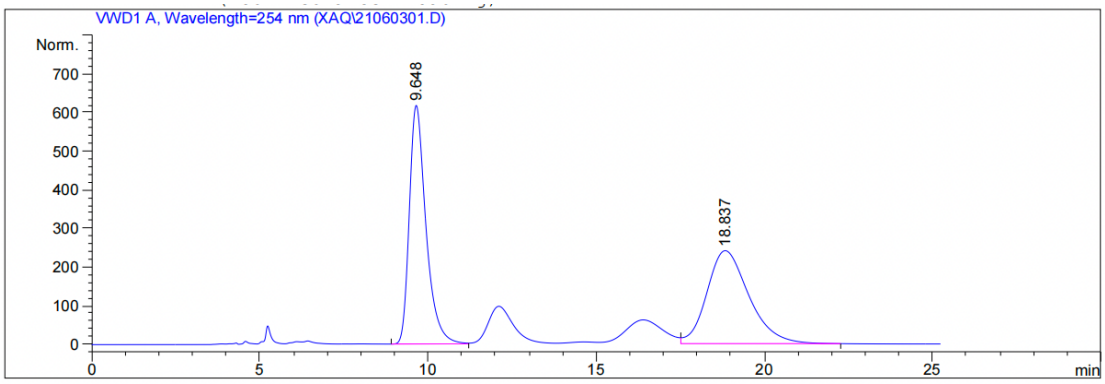
Compound 7ad



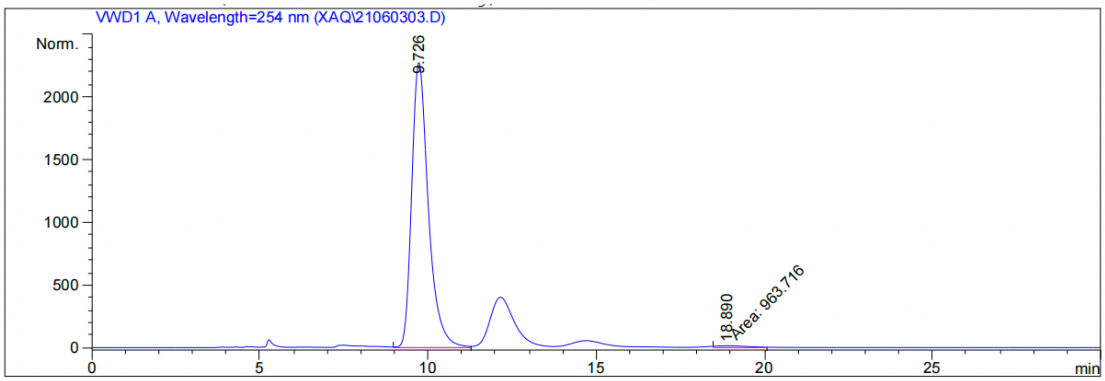
7ad

Prepared according to the procedure within 12 h as yellow solid (121.7 mg, 93% yield, dr = 3:1); $[\alpha]_D^{18}$ = 93.684 (*c* 1.90, CH_2Cl_2); Mp: 119.8 - 120.6 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.93 – 8.88 (m, 1H), 8.08 – 7.93 (m, 6H), 7.56 – 7.41 (m, 9H), 7.24 – 7.20 (m, 1H), 6.89 (s, 1H), 3.91 (s, 3H), 3.68 – 3.61 (m, 1H), 3.15 (d, *J* = 18.1 Hz, 1H), 3.17 – 3.10 (m, 1H), 3.09 – 3.03 (m, 1H), 2.29 – 2.26 (m, 3H),

2.20 – 2.17 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 170.8, 166.9, 158.2, 156.0, 147.1, 139.6, 138.2, 136.5, 132.3, 132.2, 130.7, 129.5, 129.0, 128.9, 128.8, 128.8, 127.6, 126.3, 125.5, 124.1, 119.3, 86.1, 64.0, 53.6, 51.4, 40.5, 21.1, 19.7, 17.8. HRMS (ESI) m/z Calcd. for $C_{37}H_{35}N_4O_5$ ($[M+H]^+$) 615.2602, Found 615.2596. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.7 min, t_{minor} = 18.8 min).

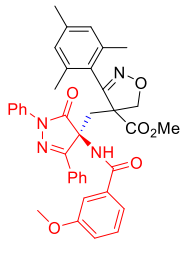


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.648	BV	0.5192	2.12638e4	618.19562	50.2855
2	18.837	VB	1.3254	2.10223e4	241.21410	49.7145



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.726	VV	0.5240	7.82523e4	2272.97681	98.7834
2	18.890	MM	1.1143	963.71643	14.41487	1.2166

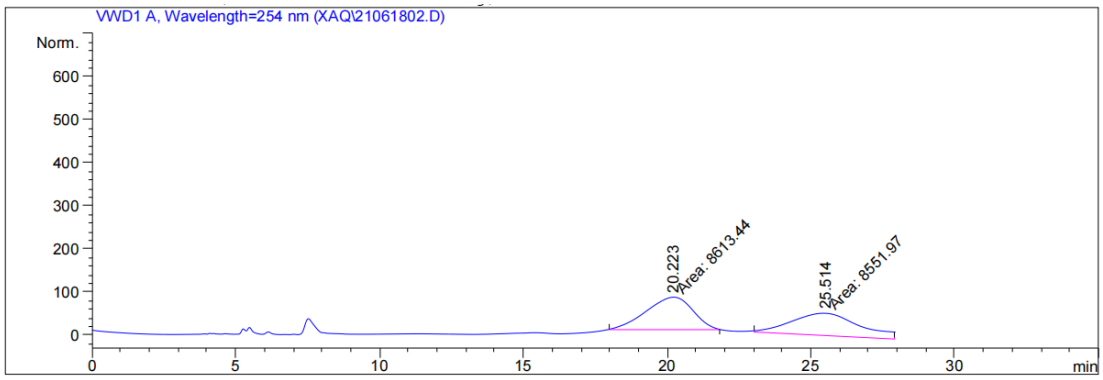
Compound 7ae



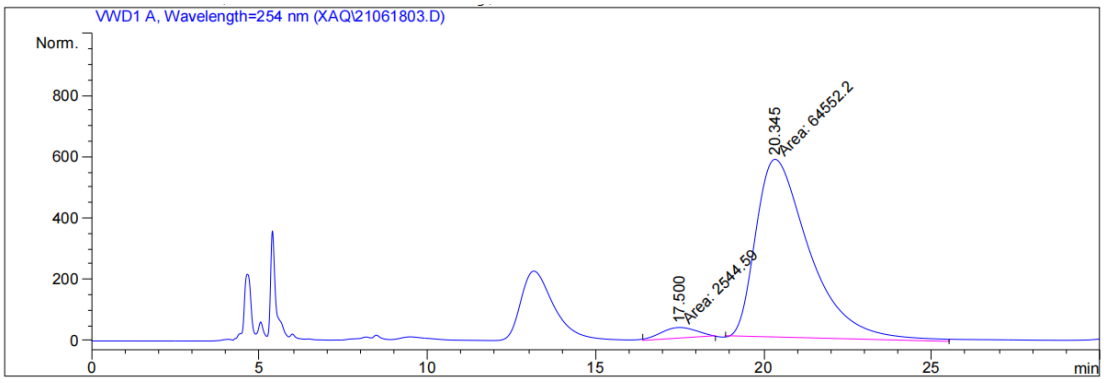
7ae

Prepared according to the procedure within 12 h as yellow solid (127.7 mg, 99% yield, dr = 4:1); $[\alpha]_D^{18}$ = 97.619 (*c* 0.42, CH_2Cl_2); Mp: 126.9 - 127.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.92 – 8.86 (m, 1H), 8.08 – 7.98 (m, 4H), 7.55 – 7.53 (m, 1H), 7.48 – 7.46 (m, 1H), 7.45 – 7.35 (m, 6H), 7.23 – 7.19 (m, 1H), 7.08 – 7.05 (m, 1H), 6.88 – 6.85 (m, 2H), 3.90 (s, 3H), 3.80 (s, 3H), 3.67 – 3.62 (m, 1H), 3.15 – 3.01 (m, 2H), 2.65 (d, *J* = 15.3 Hz, 1H), 2.28 – 2.25 (m, 3H), 2.19 – 2.15 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 170.8, 166.8, 159.9, 158.2, 156.0, 139.6, 138.1, 136.5, 133.5, 130.7, 129.8, 129.4, 129.0, 128.9, 128.8, 128.6, 126.3, 125.5, 124.1, 119.3, 112.2, 86.1, 64.0, 53.6, 51.3, 40.6, 29.7, 21.1, 19.7, 17.8. HRMS (ESI) m/z Calcd.

for $C_{38}H_{37}N_4O_6$ ([M+H]$^+$) 645.2708, Found 645.2710. Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 20.3 min, t_{minor} = 17.5 min).

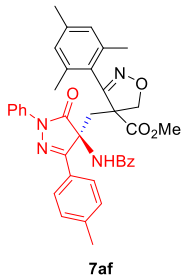


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.223	MM	1.8945	8613.43750	75.77744	50.1791
2	25.514	MM	2.7414	8551.96777	51.99314	49.8209



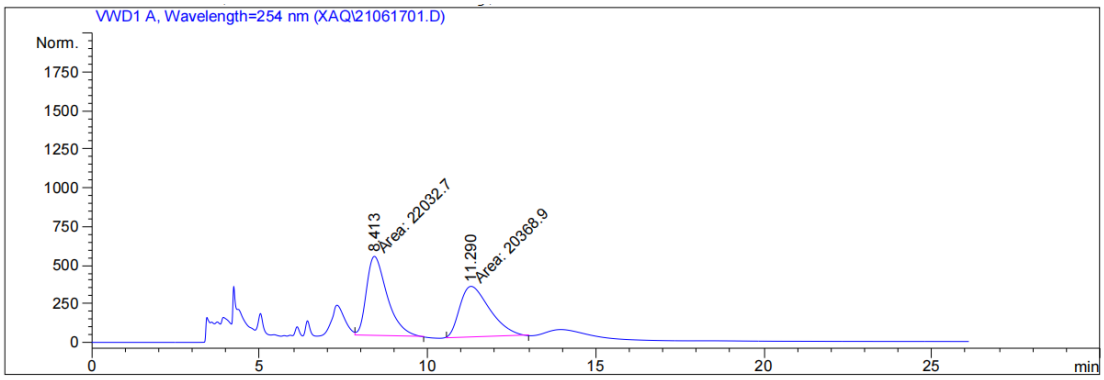
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.500	MM	1.2250	2544.58984	34.62079	3.7924
2	20.345	MM	1.8598	6.45522e4	578.47461	96.2076

Compound 7af

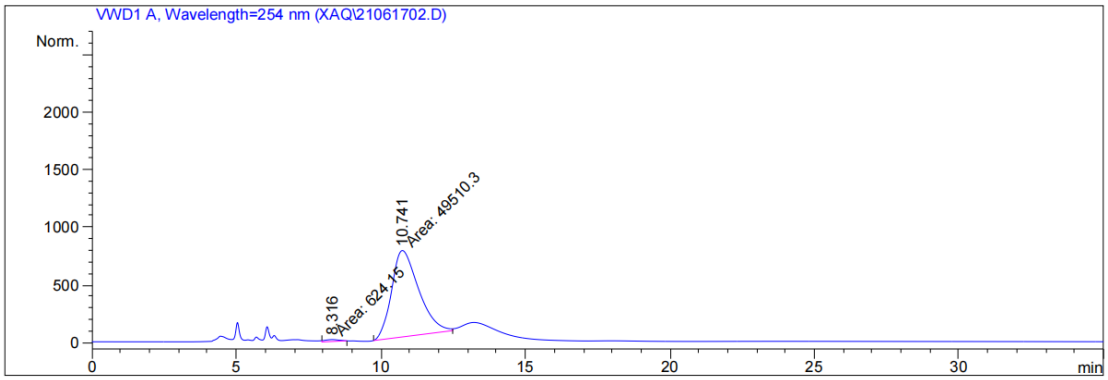


7af

Prepared according to the procedure within 12 h as white solid (118.2 mg, 94% yield, dr = 4:1); $[\alpha]_D^{18}$ = 80.597 (*c* 0.67, CH_2Cl_2); Mp: 116.4 - 117.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.90 – 8.84 (m, 1H), 8.02 – 7.93 (m, 6H), 7.55 – 7.40 (m, 5H), 7.25 – 7.21 (m, 3H), 6.90 – 6.78 (m, 2H), 3.91 (s, 3H), 3.68 – 3.63 (m, 1H), 3.16 – 3.03 (m, 2H), 2.68 (d, *J* = 15.2 Hz, 1H), 2.38 – 2.36 (m, 3H), 2.29 – 2.27 (m, 3H), 2.22 – 2.16 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 170.9, 166.8, 158.2, 156.1, 141.0, 139.6, 138.2, 136.5, 132.2, 130.3, 129.7, 128.8, 128.8, 128.7, 127.6, 126.7, 126.3, 125.4, 124.1, 121.9, 119.3, 86.2, 64.0, 53.6, 51.4, 40.7, 21.5, 21.1, 19.6, 17.6. HRMS (ESI) m/z Calcd. for $C_{38}H_{37}N_4O_5$ ([M+H]$^+$) 629.2758, Found 629.2756. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.7 min, t_{minor} = 8.3 min).

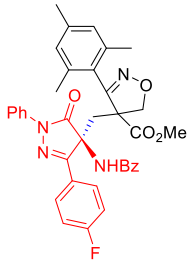


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.413	MM	0.7165	2.20327e4	512.48901	51.9620
2	11.290	MM	1.0349	2.03689e4	328.04370	48.0380



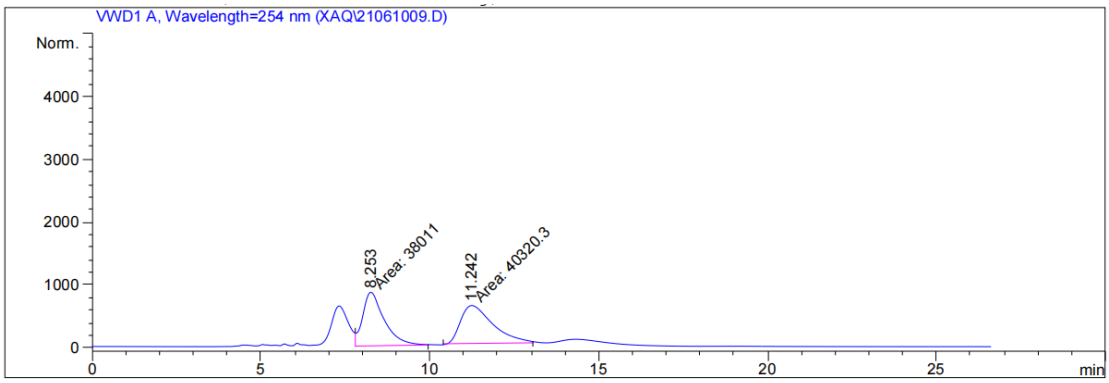
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.316	MM	0.5938	624.14954	17.51841	1.2450
2	10.741	MM	1.0951	4.95103e4	753.49298	98.7550

Compound 7ag

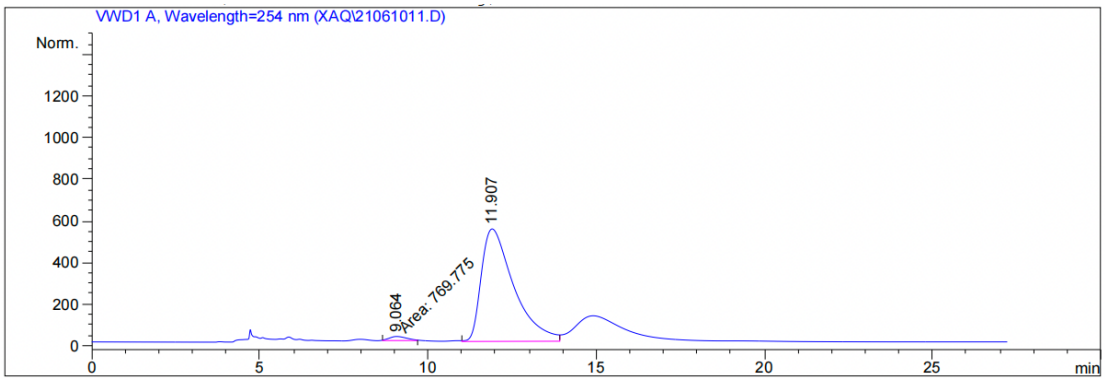


7ag

Prepared according to the procedure within 12 h as white solid (104.3 mg, 82% yield, dr = 4:1); $[\alpha]_D^{18}$ = 118.75 (*c* 0.16, CH_2Cl_2); Mp: 116.2 - 117.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.93 – 8.87 (m, 1H), 8.08 – 8.03 (m, 2H), 7.99 – 7.92 (m, 4H), 7.55 – 7.51 (m, 1H), 7.47 – 7.39 (m, 4H), 7.23 – 7.19 (m, 1H), 7.13 – 7.07 (m, 2H), 6.88 – 6.86 (m, 2H), 3.90 (s, 3H), 3.67 – 3.61 (m, 1H), 3.16 – 3.09 (m, 1H), 3.01 – 2.95 (m, 1H), 2.65 (d, *J* = 15.2 Hz, 1H), 2.28 – 2.25 (m, 3H), 2.19 – 2.16 (m, 6H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.31 – -108.57 (m); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 170.8, 167.0, 164.1 (d, *J* = 252.3 Hz), 158.3, 155.2, 139.7, 138.0, 136.4, 135.9, 132.4, 132.0, 128.9, 128.8, 128.7, 128.4 (d, *J* = 8.1 Hz), 127.6, 125.8 (d, *J* = 3.0 Hz), 125.6, 124.0, 119.3, 116.2 (d, *J* = 21.2 Hz), 86.1, 63.9, 53.7, 51.5, 40.5, 21.1, 19.6, 17.8. HRMS (ESI) m/z Calcd. for $C_{37}H_{34}FN_4O_5$ ($[M+H]^+$) 633.2508, Found 633.2503. Enantiomeric excess was determined to be 95% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.9 min, t_{minor} = 9.0 min).

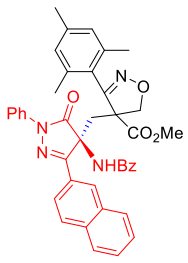


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.253	MM	0.7423	3.80110e4	853.48401	48.5259
2	11.242	MM	1.1092	4.03203e4	605.83948	51.4741



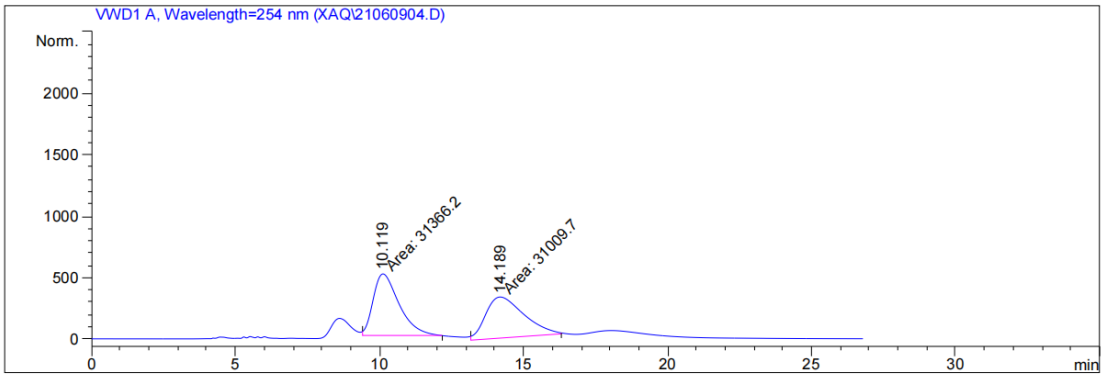
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.064	MM	0.6271	769.77478	20.45846	2.0664
2	11.907	VV	1.0096	3.64818e4	540.89990	97.9336

Compound 7ah

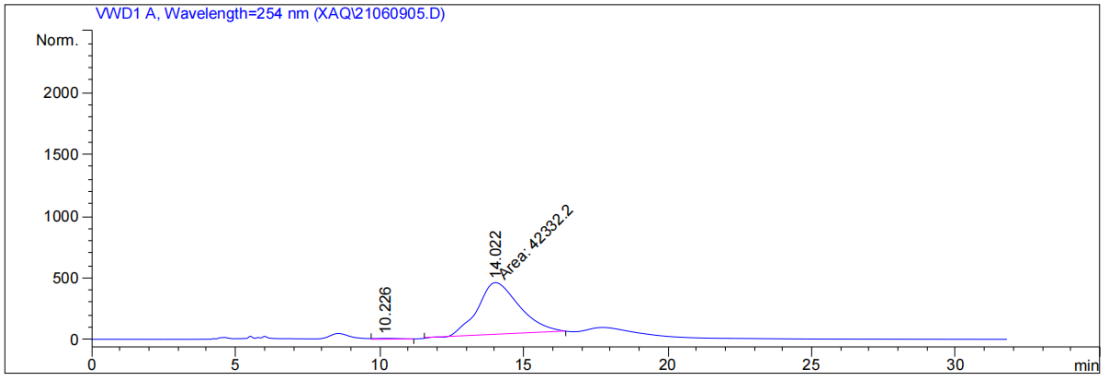


7ah

Prepared according to the procedure within 12 h as white solid (131.6 mg, 99% yield, dr = 4:1); $[\alpha]_D^{18}$ = 104.76 (*c* 0.21, CH_2Cl_2); Mp: 122.3 - 123.4 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.04 – 8.98 (m, 1H), 8.44 (s, 1H), 8.27 – 8.25 (m, 1H), 8.06 – 8.05 (m, 2H), 7.98 – 7.96 (m, 2H), 7.91 – 7.83 (m, 3H), 7.54 – 7.44 (m, 7H), 7.22 (d, *J* = 7.7 Hz, 1H), 6.96 – 6.88 (m, 2H), 3.92 (s, 3H), 3.69 – 3.65 (m, 1H), 3.21 – 3.11 (m, 2H), 2.72 (d, *J* = 12.4 Hz, 1H), 2.28 – 2.25 (m, 3H), 2.19 – 2.15 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.7, 170.8, 167.1, 158.3, 156.0, 139.6, 138.2, 136.4, 134.2, 132.9, 132.3, 132.2, 130.3, 128.9, 128.9, 128.8, 128.8, 127.8, 127.6, 127.5, 126.9, 126.7, 126.3, 125.5, 124.1, 123.3, 119.4, 86.2, 64.1, 53.6, 51.5, 40.8, 21.1, 19.6, 17.8. HRMS (ESI) m/z Calcd. for $C_{41}H_{37}N_4O_5$ ($[M+H]^+$) 665.2758, Found 665.2760. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.0 min, t_{minor} = 10.2 min).

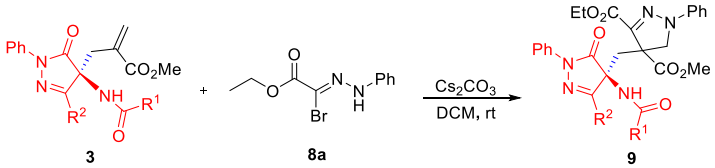


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.119	MM	1.0447	3.13662e4	500.41824	50.2857
2	14.189	MM	1.5427	3.10097e4	335.01138	49.7143



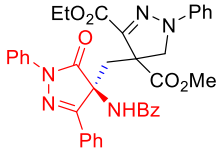
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.226	VV	0.8609	458.84784	6.65744	1.0723
2	14.022	MM	1.6846	4.23322e4	418.81082	98.9277

The procedure for the synthesis of compounds 9



To a solution of nitrile imine **8a** (0.6 mmol) and Cs_2CO_3 (0.6 mmol) in DCM (2.0 mL) was added the product **3** (0.2 mmol). The reaction mixture was stirred at rt for 12 h, and then the reaction was detected by TLC. When the reaction finished, the crude mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give compound **9**.

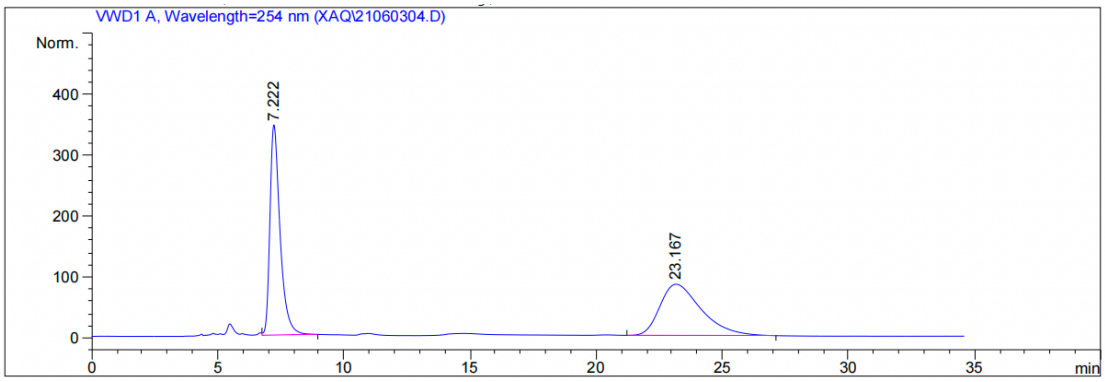
Compound 9aa



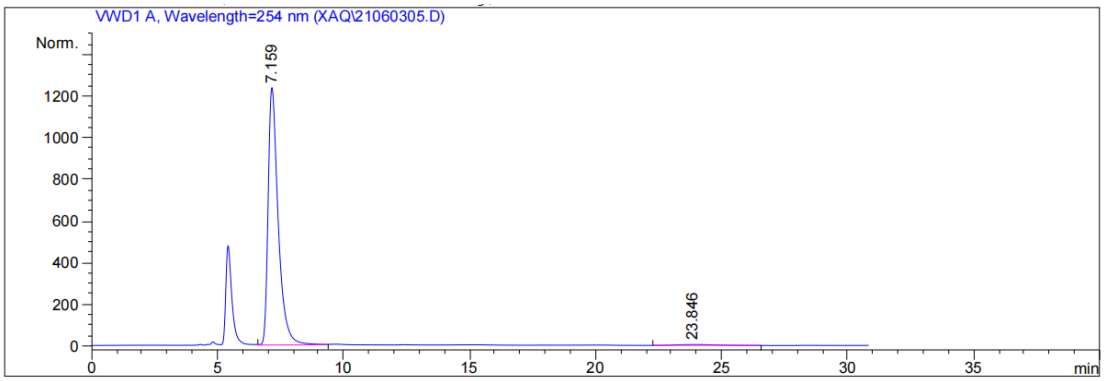
9aa

Prepared according to the procedure within 12 h as white solid (127.4 mg, 99% yield, dr = 3:1); $[\alpha]_D^{18}$ = -93.333 (*c* 0.30, CH_2Cl_2); Mp: 125.8 - 126.5 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 8.04 – 8.02 (m, 2H), 7.92 – 7.91 (m, 2H), 7.81 – 7.79 (m, 2H), 7.52 – 7.28 (m, 9H), 7.25 – 7.23 (m, 2H), 7.11 –7.05 (m, 3H), 4.24 – 4.14 (m, 2H), 3.86 (d, *J* = 18.7 Hz, 1H), 3.79 (s, 3H), 3.44 (d, *J* = 18.6 Hz, 1H), 3.37 (d, *J* = 15.6 Hz, 1H), 2.59 (d, *J* = 15.6 Hz, 1H), 1.25 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 172.2, 166.8, 161.4, 156.8, 141.7, 140.4, 137.9,

132.3, 132.2, 130.5, 129.6, 129.3, 128.9, 128.8, 128.7, 127.4, 126.2, 125.7, 124.1, 119.4, 118.6, 73.6, 63.7, 61.4, 53.9, 44.8, 41.6, 14.1. HRMS (ESI) m/z Calcd. for $C_{37}H_{34}N_5O_6$ ([M+H]$^+$) 644.2504, Found 644.2503. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.1 min, t_{minor} = 23.8 min).

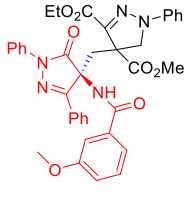


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.222	VB	0.4186	9676.35645	345.39142	50.2199
2	23.167	VB	1.6503	9591.62012	84.23309	49.7801



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.159	VB	0.4177	3.45429e4	1236.46521	98.6401
2	23.846	BB	1.2946	476.22363	4.32568	1.3599

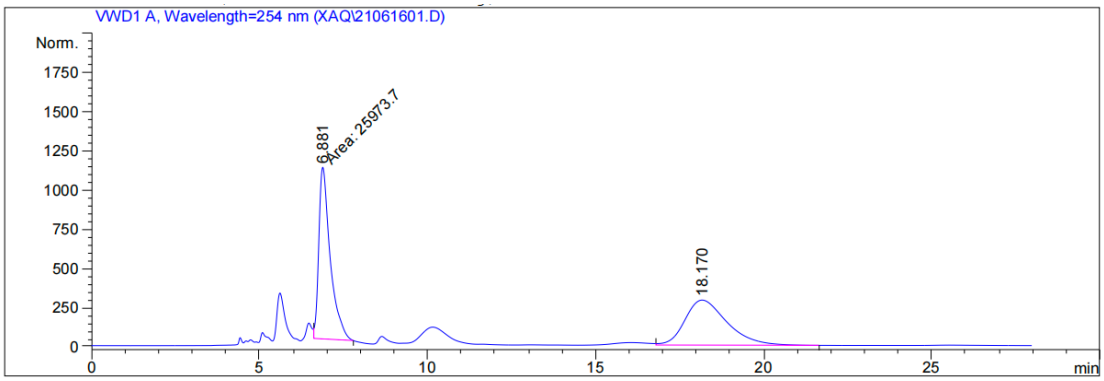
Compound 9ab



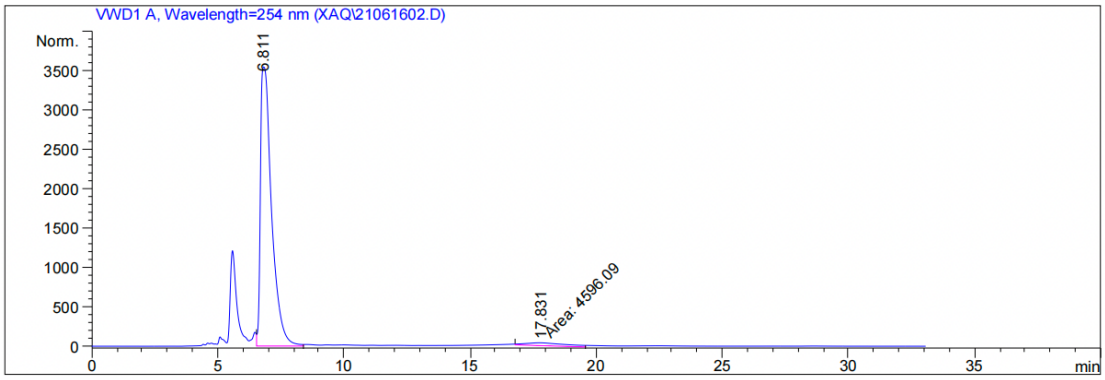
9ab

Prepared according to the procedure within 12 h as white solid (129.4 mg, 96% yield, dr = 4:1); $[\alpha]_D^{17}$ = -169.23 (*c* 0.13, CH_2Cl_2); Mp: 113.8 - 114.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 7.96 – 7.94 (m, 2H), 7.85 – 7.81 (m, 2H), 7.38 – 7.32 (m, 2H), 7.30 – 7.25 (m, 3H), 7.23 – 7.19 (m, 3H), 7.15 – 7.12 (m, 3H), 7.00 – 6.93 (m, 4H), 4.14 – 4.02 (m, 2H), 3.77 (d, *J* = 18.7 Hz, 1H), 3.68 (s, 6H), 3.38 (d, *J* = 18.7 Hz, 1H), 3.30 (d, *J* = 15.4 Hz, 1H), 2.53 (d, *J* = 15.5 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.7, 171.1, 165.6, 160.4, 158.8, 155.7, 140.6, 139.3, 136.8, 132.5, 129.4, 128.6, 128.4, 128.2, 127.9, 127.8, 125.2, 124.7, 123.0, 118.3, 118.1, 118.0, 117.4, 111.4, 72.5, 62.6, 60.4, 54.4, 52.9, 43.7, 40.4, 13.1. HRMS (ESI) m/z Calcd. for $C_{38}H_{36}N_5O_7$ ([M+H]$^+$) 674.2609, Found 674.2606. Enantiomeric excess was determined to be 91%

(determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 6.8 min, t_{minor} = 17.8 min).

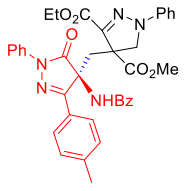


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.881	MM	0.3948	2.59737e4	1096.52698	50.7069
2	18.170	VB	1.3189	2.52496e4	288.68369	49.2931



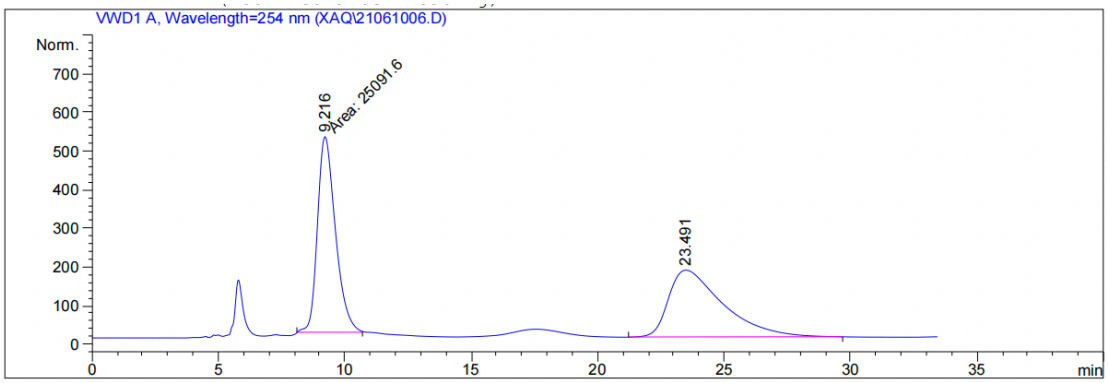
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.811	VV	0.4564	1.09099e5	3547.28638	95.9575
2	17.831	MM	2.0081	4596.09082	38.14703	4.0425

Compound 9ac

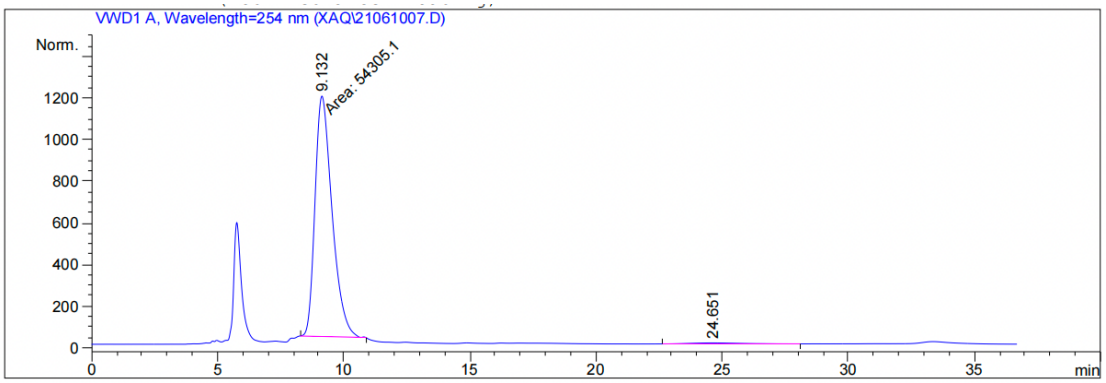


9ac

Prepared according to the procedure within 12 h as yellow solid (114.4 mg, 87% yield, dr = 3:1); $[\alpha]_D^{17}$ = -72.727 (*c* 0.33, CH_2Cl_2); Mp: 119.6 - 120.3 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.95 – 7.94 (m, 2H), 7.72 – 7.70 (m, 4H), 7.43 – 7.40 (m, 1H), 7.37 – 7.31 (m, 4H), 7.17 – 7.14 (m, 3H), 7.01 – 6.96 (m, 5H), 4.14 – 4.04 (m, 2H), 3.76 (d, *J* = 18.7 Hz, 1H), 3.69 (s, 3H), 3.36 (d, *J* = 18.6 Hz, 1H), 3.30 (d, *J* = 15.6 Hz, 1H), 2.53 (d, *J* = 15.6 Hz, 1H), 2.21 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.7, 171.1, 165.7, 160.3, 155.8, 140.6, 139.8, 139.3, 136.9, 131.2, 131.2, 128.5, 128.2, 127.9, 127.6, 126.4, 125.7, 125.1, 124.6, 122.9, 118.4, 117.4, 72.5, 62.7, 60.3, 52.8, 43.7, 40.6, 20.4, 13.1. HRMS (ESI) m/z Calcd. for $C_{38}H_{36}N_5O_6$ ($[M+H]^+$) 658.2660, Found 658.2659. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.1 min, t_{minor} = 24.6 min).

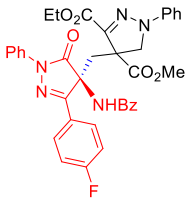


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.216	MM	0.8248	2.50916e4	507.04828	49.1770
2	23.491	BB	2.1167	2.59315e4	173.47173	50.8230



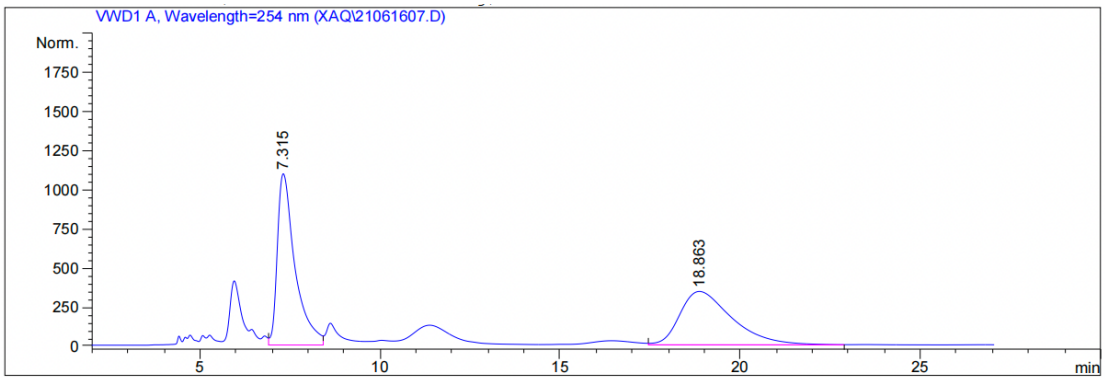
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.132	MM	0.7836	5.43051e4	1155.09668	98.8169
2	24.651	BB	1.6159	650.16028	4.71527	1.1831

Compound 9ad

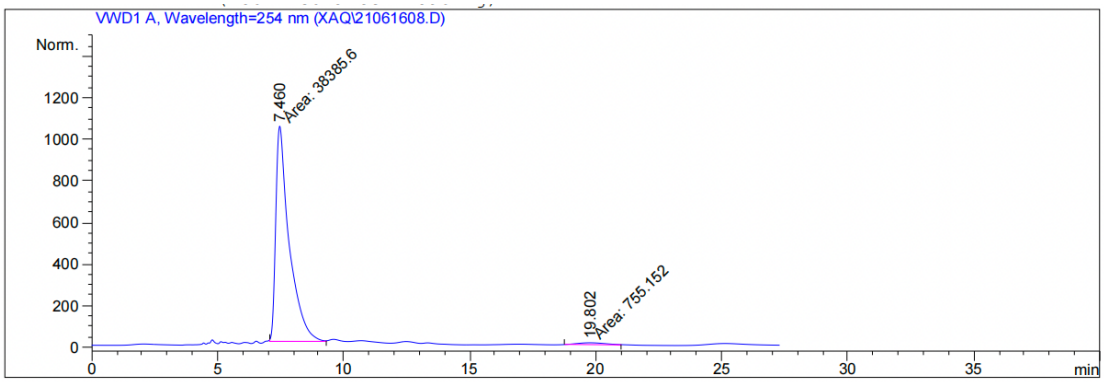


9ad

Prepared according to the procedure within 12 h as yellow solid (124.4 mg, 94% yield, dr = 3:1); $[\alpha]_D^{17}$ = -123.08 (*c* 0.13, CH_2Cl_2); Mp: 125.4 - 126.7 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.02 – 8.00 (m, 2H), 7.90 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 7.54 – 7.50 (m, 1H), 7.46 – 7.40 (m, 4H), 7.24 – 7.22 (m, 3H), 7.07 – 7.04 (m, 3H), 6.97 – 6.93 (m, 2H), 4.23 – 4.08 (m, 2H), 3.82 (d, *J* = 18.7 Hz, 1H), 3.78 (s, 3H), 3.43 (d, *J* = 18.8 Hz, 1H), 3.30 (d, *J* = 15.5 Hz, 1H), 2.65 (d, *J* = 15.5 Hz, 1H), 1.25 – 1.21 (m, 3H); ^{19}F NMR (377 MHz, Chloroform-*d*) δ -108.80 – -108.99 (m); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 172.1, 166.8, 163.9 (d, *J* = 252.0 Hz), 161.3, 155.6, 141.6, 140.1, 137.8, 132.4, 131.9, 129.3, 128.9, 128.7, 128.3 (d, *J* = 8.5 Hz), 127.4, 125.9 (d, *J* = 3.2 Hz), 125.8, 123.8, 119.3, 117.9, 116.0 (d, *J* = 22.0 Hz), 73.0, 63.6, 61.4, 53.5, 44.7, 41.4, 14.1. HRMS (ESI) m/z Calcd. for $C_{37}H_{33}FN_5O_6$ ($[M+H]^+$) 662.2409, Found 662.2413. Enantiomeric excess was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.4 min, t_{minor} = 19.8 min).

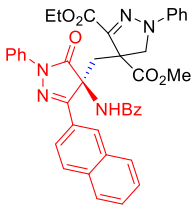


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.315	VV	0.5018	3.74377e4	1096.20264	51.9502
2	18.863	VB	1.5165	3.46269e4	342.32285	48.0498



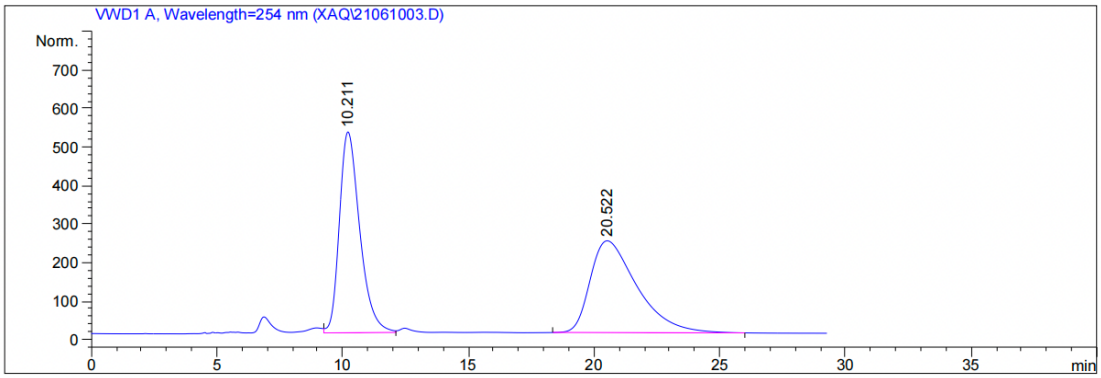
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.460	MM	0.6182	3.83856e4	1034.88538	98.0707
2	19.802	MM	1.3283	755.15240	9.47501	1.9293

Compound 9ae



9ae

Prepared according to the procedure within 12 h as red solid (137.4 mg, 97% yield, dr = 3:1); $[\alpha]_D^{17}$ = 126.31 (*c* 0.19, CH_2Cl_2); Mp: 116.1 - 117.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 8.22 (d, *J* = 1.8 Hz, 1H), 8.13 – 8.09 (m, 3H), 7.79 – 7.69 (m, 5H), 7.51 – 7.38 (m, 8H) 7.12 – 7.08 (m, 2H), 7.04 – 7.00 (m, 2H), 6.87 – 6.83 (m, 1H), 4.15 – 4.01 (m, 2H), 3.80 – 3.75 (m, 4H), 3.54 (d, *J* = 18.8 Hz, 1H), 3.45 (d, *J* = 15.5 Hz, 1H), 2.87 (d, *J* = 15.5 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 172.4, 166.7, 161.3, 156.4, 141.6, 140.0, 138.0, 134.1, 132.7, 132.3, 132.1, 129.1, 128.9, 128.8, 128.7, 128.7, 127.7, 127.4, 127.3, 127.1, 126.42, 126.39, 125.7, 123.6, 123.1, 119.4, 117.6, 72.9, 63.8, 61.3, 53.9, 44.6, 41.5, 14.1. HRMS (ESI) m/z Calcd. for $C_{41}H_{36}N_5O_6$ ($[M+H]^+$) 694.2660, Found 694.2661. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.1 min, t_{minor} = 21.1 min).



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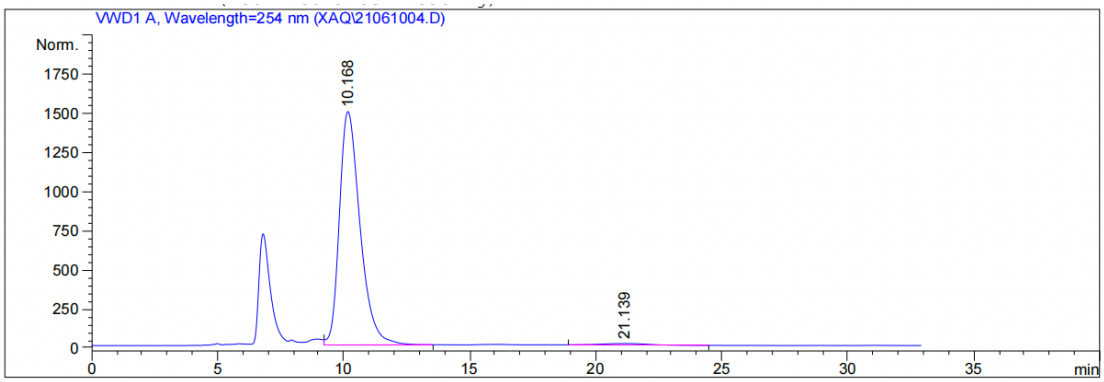
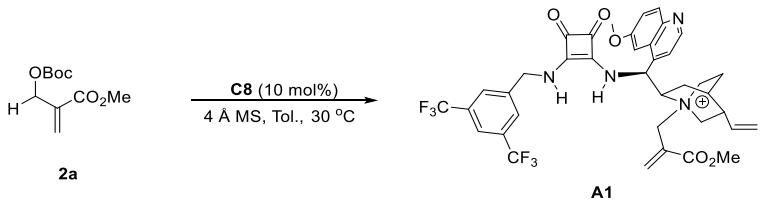
1	10.211	VV	0.8630	2.94954e4	522.01221	48.8189
2	20.522	BB	1.9136	3.09226e4	238.63475	51.1811



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.168	VB	0.8724	8.52134e4	1493.52551	98.6195
2	21.139	BP	1.4912	1192.87756	9.56596	1.3805

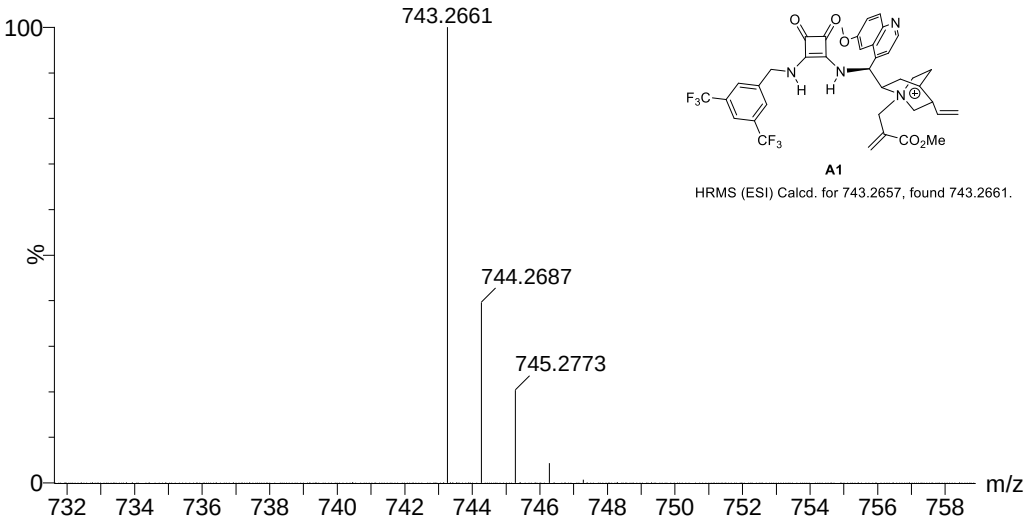
3. Experimental procedures of intermediates A1 and C1



2a **A1**

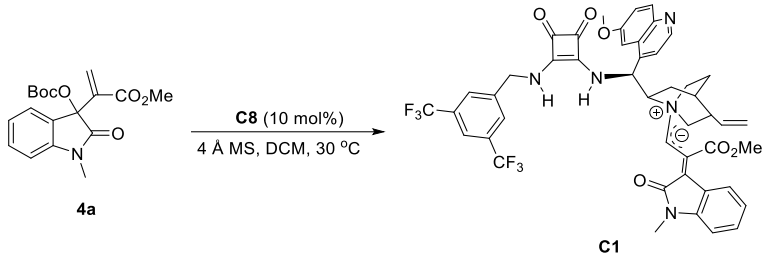
HRMS (ESI) Calcd. for 743.2657, found 743.2661.

To a tube were added MBH carbonate **2a** (0.1 mmol), **C8** (0.01 mmol), 4 Å MS (100 mg) and toluene (1 mL). The reaction mixture was stirred at 30 °C for 12 h, and the mixture solution was directly detected by HRMS.



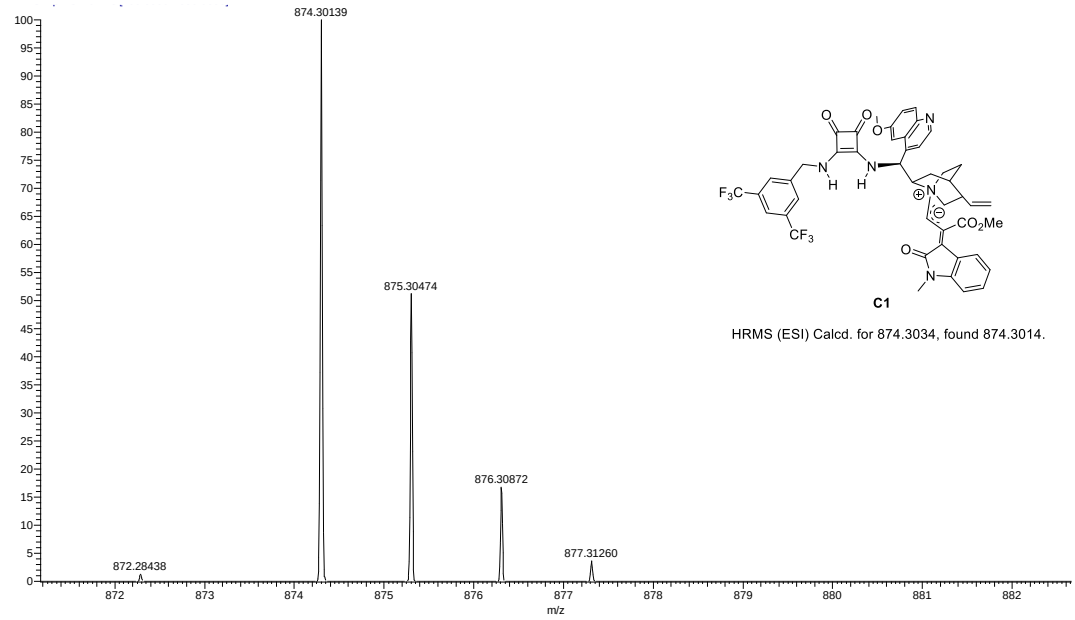
A1

HRMS (ESI) Calcd. for 743.2657, found 743.2661.



HRMS (ESI) Calcd. for 874.3034, found 874.3014.

To a tube were added MBH carbonate **4a** (0.1 mmol), **C8** (0.01 mmol), 4Å MS (100 mg) and DCM (1 mL). The reaction mixture was stirred at 30 °C for 24 h, and the mixture solution was directly detected by HRMS.

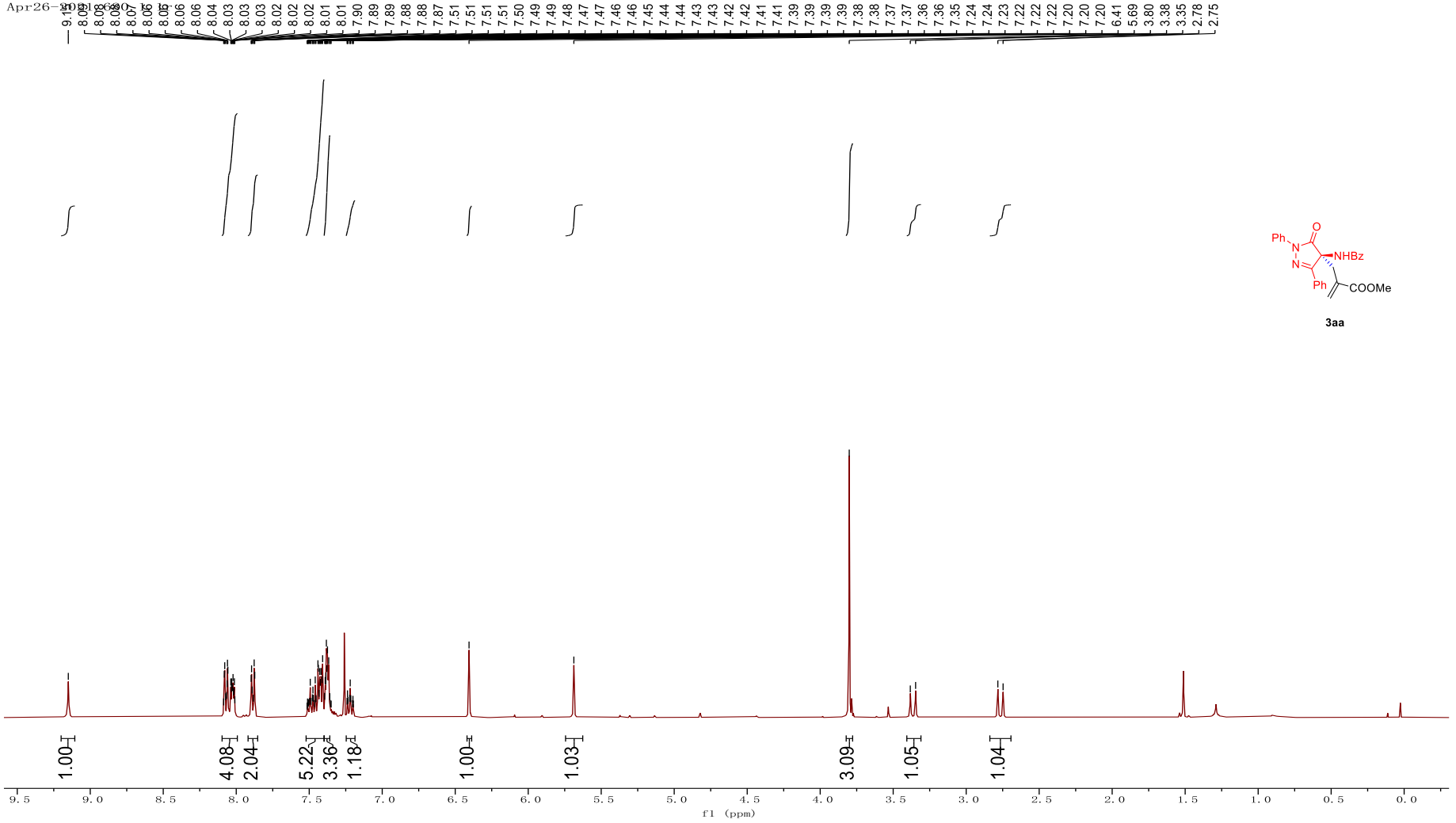


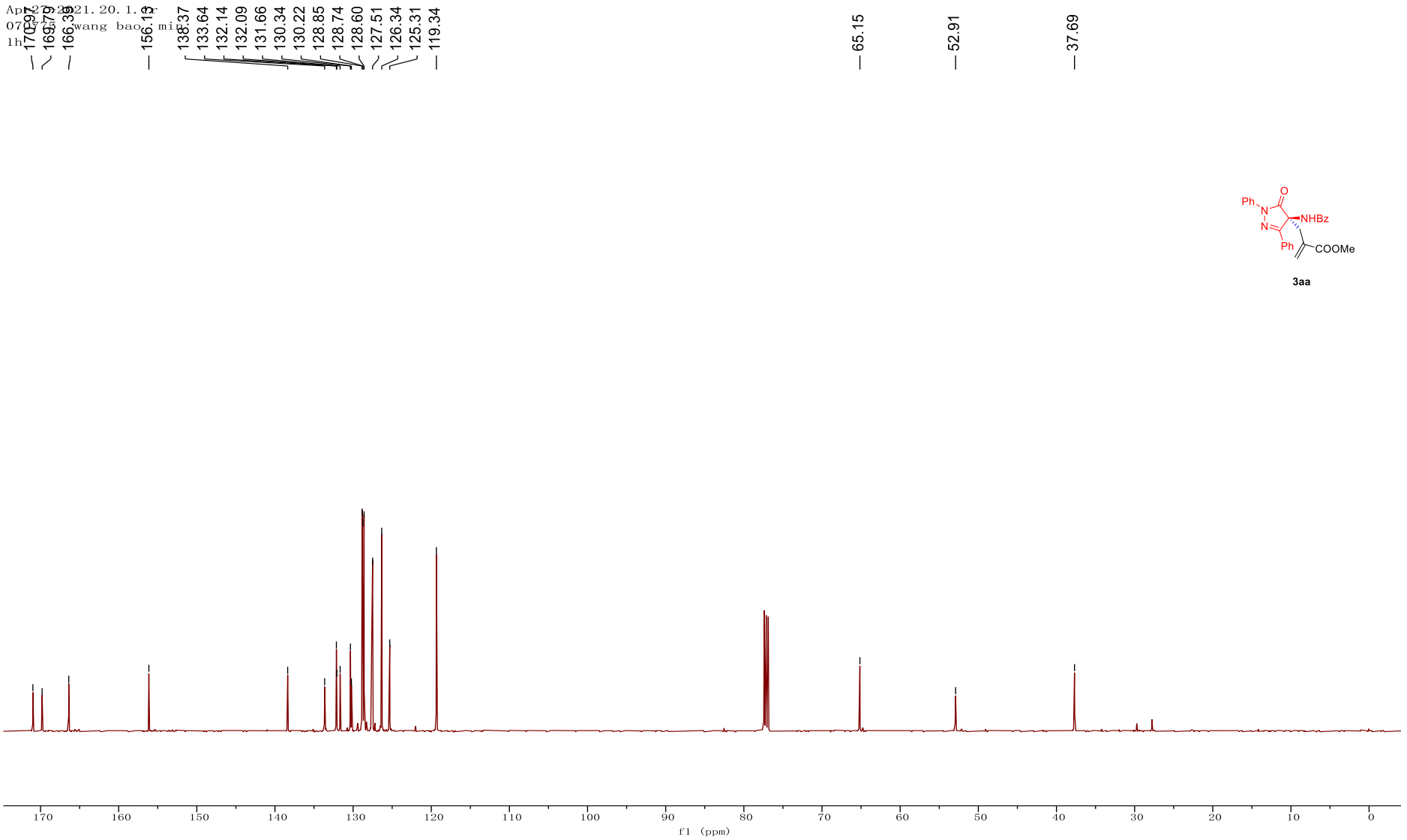
HRMS (ESI) Calcd. for 874.3034, found 874.3014.

4. References

1. J. Chen, Y. Zhang, D. y. Zhu, X. j. Zhang and M. Yan, Construction of Chiral Quaternary Carbon Stereocenters by Asymmetric Michael Addition of 4-Amido-5-hydroxylpyrazoles to Ethylene Sulfonyl Fluoride, *Asian J. Org. Chem.*, 2022, **11**, e202200063.
2. (a) Q. Chen, Y. Bao, X. Yang, Z. Dai, F. Yang and Q. Zhou, Umpolung of *o*-Hydroxyaryl Azomethine Ylides: Entry to Functionalized *γ*-Aminobutyric Acid under Phosphine Catalysis, *Org. Lett.*, 2018, **20**, 5380-5383; (b) K. Selvakumar, K. A. Prasath Lingam and R. V. Luxmi Varma, Development of a mild and efficient protocol for the protection and O-alkylation of allyl alcohols, *RSC Adv.*, 2014, **4**, 36538-36543; (c) J. Peng, X. Huang, H.-L. Cui and Y.-C. Chen, Organocatalytic and Electrophilic Approach to Oxindoles with C3-Quaternary Stereocenters, *Org. Lett.*, 2010, **12**, 4260-4263.
3. (a) W. Yang and D.-M. Du, Highly Enantioselective Michael Addition of Nitroalkanes to Chalcones Using Chiral Squaramides as Hydrogen Bonding Organocatalysts, *Org. Lett.*, 2010, **12**, 5450-5453; (b) J. P. Malerich, K. Hagihara and V. H. Rawal, Chiral Squaramide Derivatives are Excellent Hydrogen Bond Donor Catalysts, *J. Am. Chem. Soc.*, 2008, **130**, 14416-14417.
4. (a) G. Zhao, L. Liang, C. H. E. Wen and R. Tong, In Situ Generation of Nitrile Oxides from NaCl–Oxone Oxidation of Various Aldoximes and Their 1, 3-Dipolar Cycloaddition, *Org. Lett.*, 2018, **21**, 315-319; (b) L. Wu, S. Guo, X. Wang, Z. Guo, G. Yao, Q. Lin and M. Wu, Tandem synthesis of 2-aryl-1, 2, 3-triazoles from *α*-arylhydrazonoketones with NH_4OAc via copper-catalyzed aerobic oxidation, *Tetrahedron Lett.*, 2015, **56**, 2145-2148.

5. NMR spectra for compounds

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125.31
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52.91
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N
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Ph
COOMe
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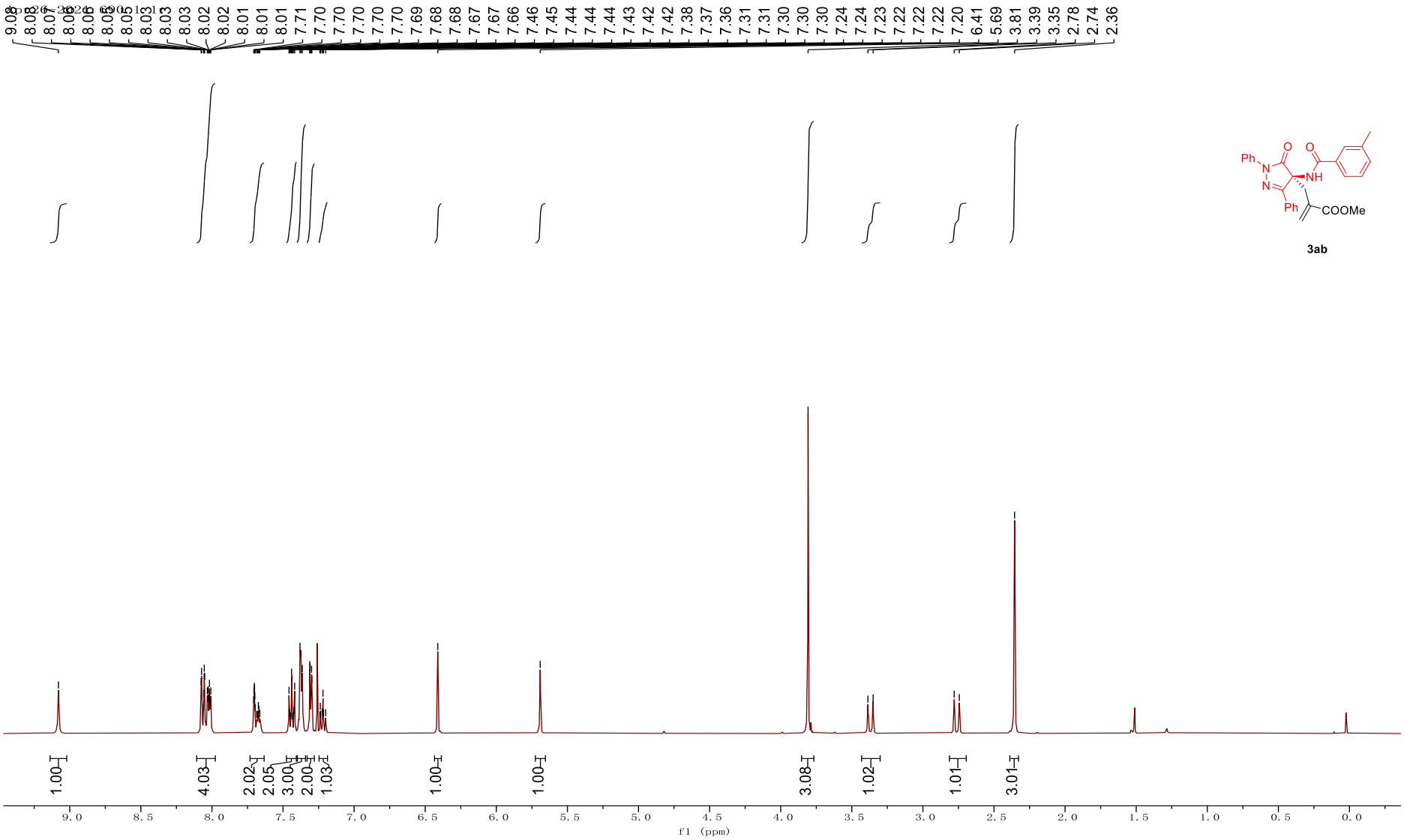
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f1 (ppm)

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O
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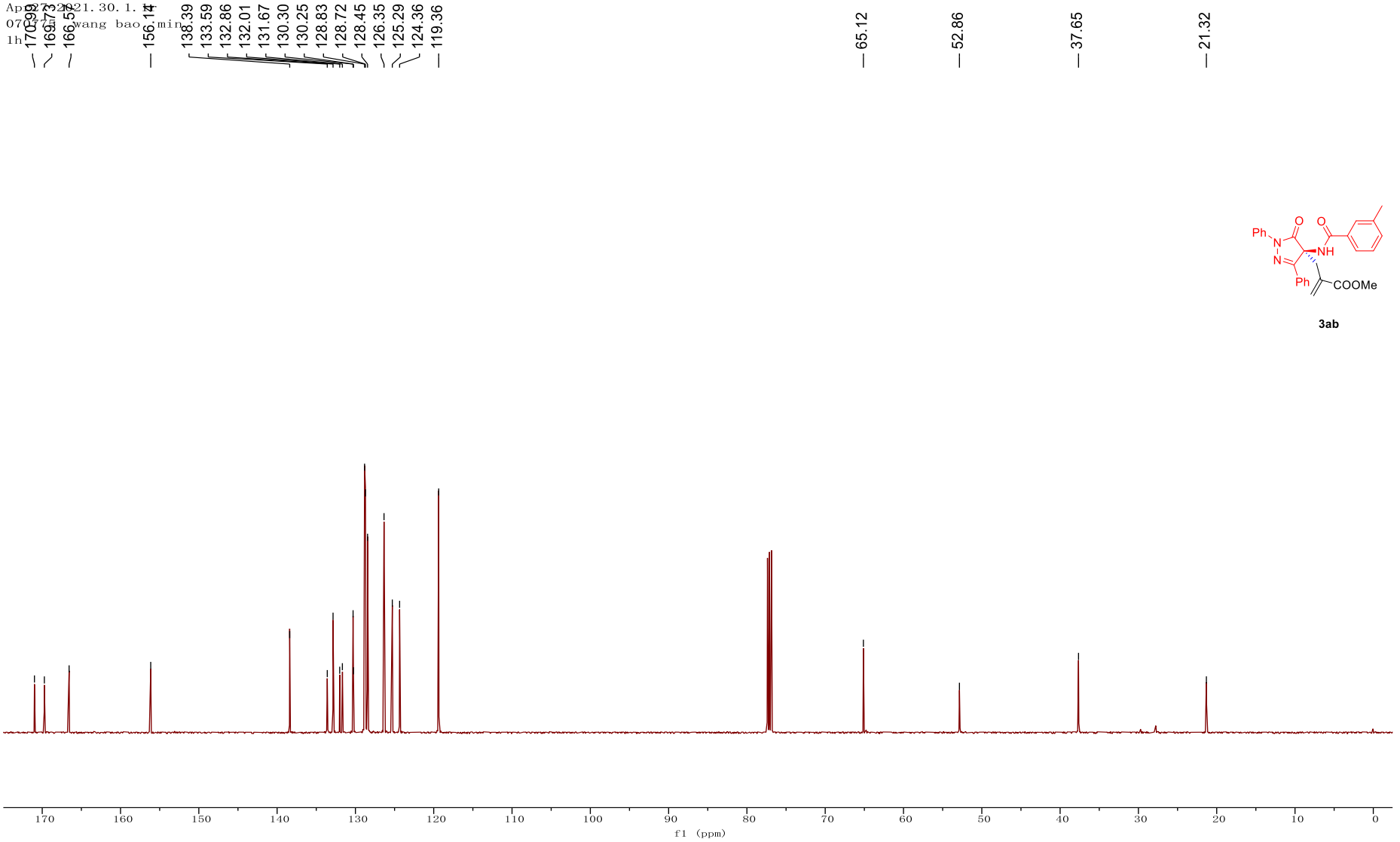
Ph
COOMe

3ab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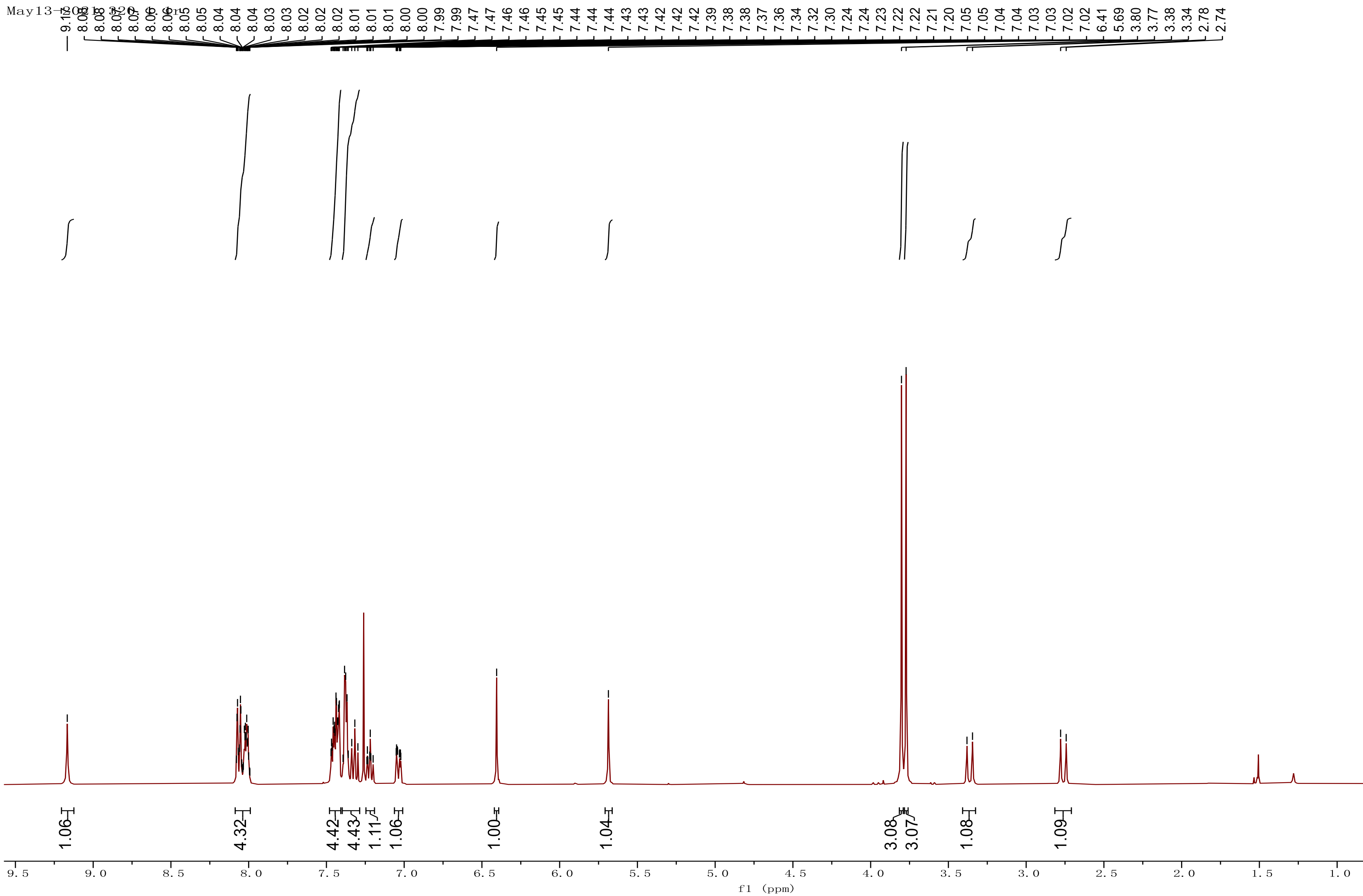
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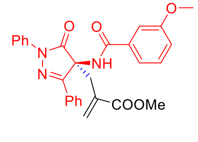
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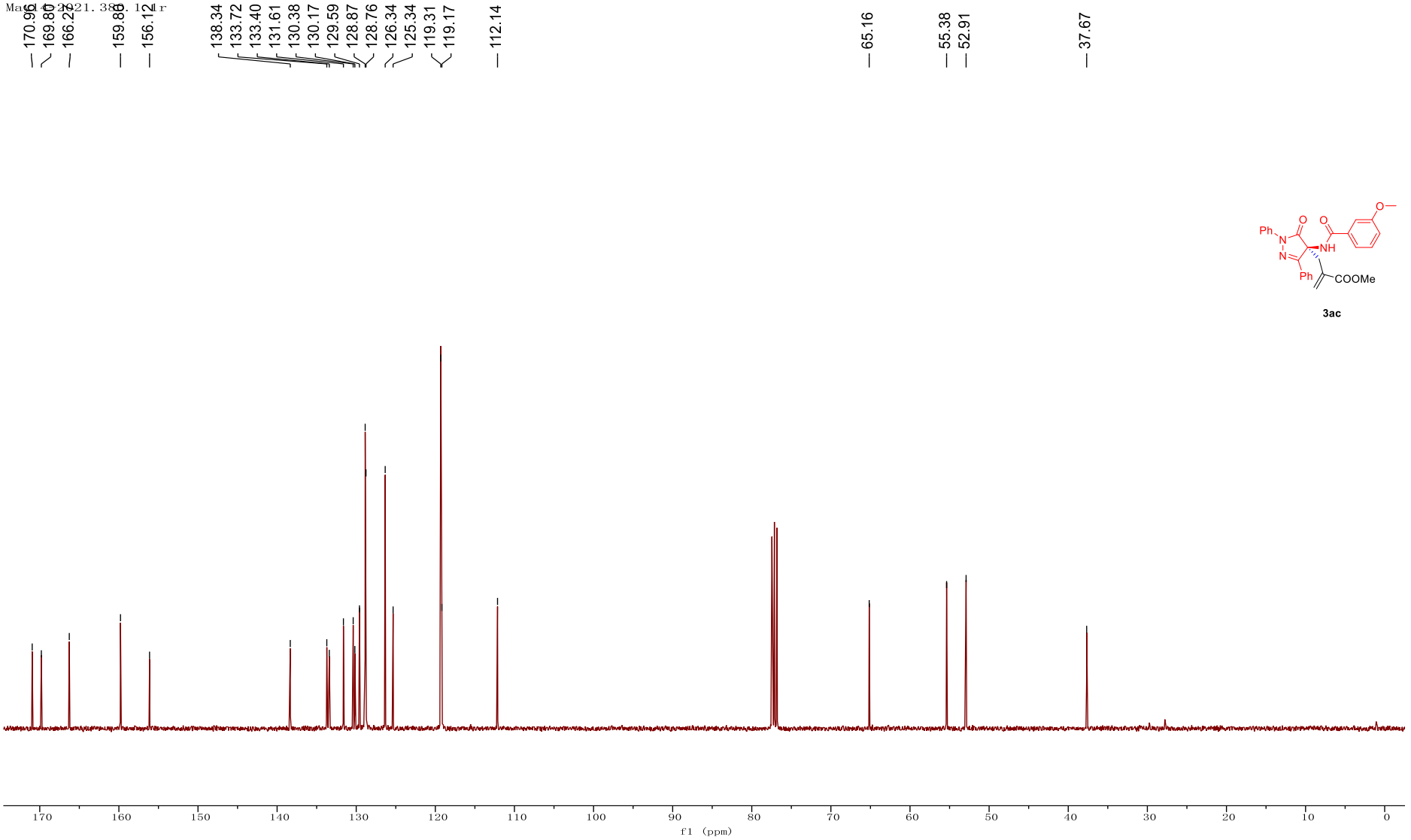
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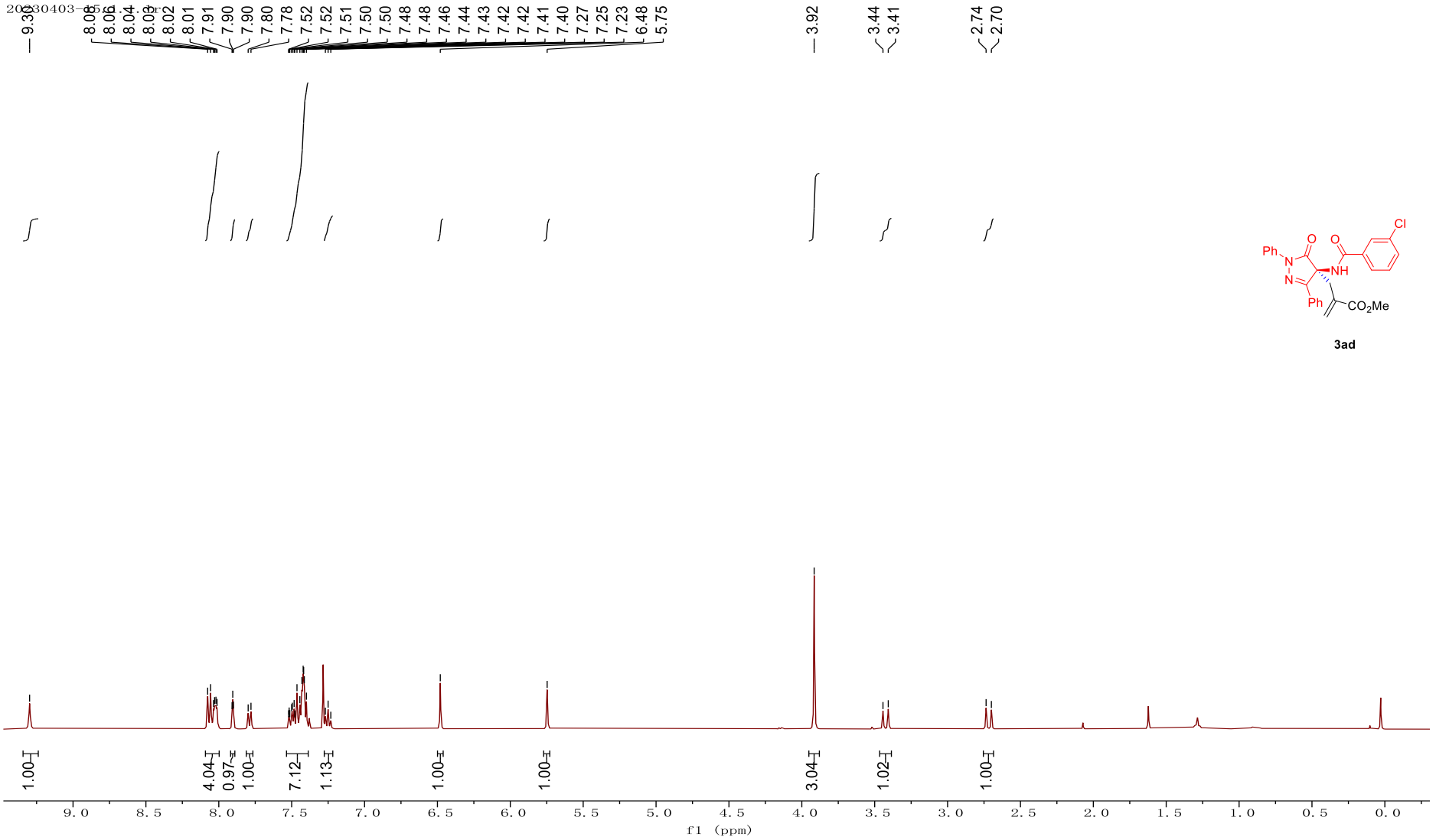
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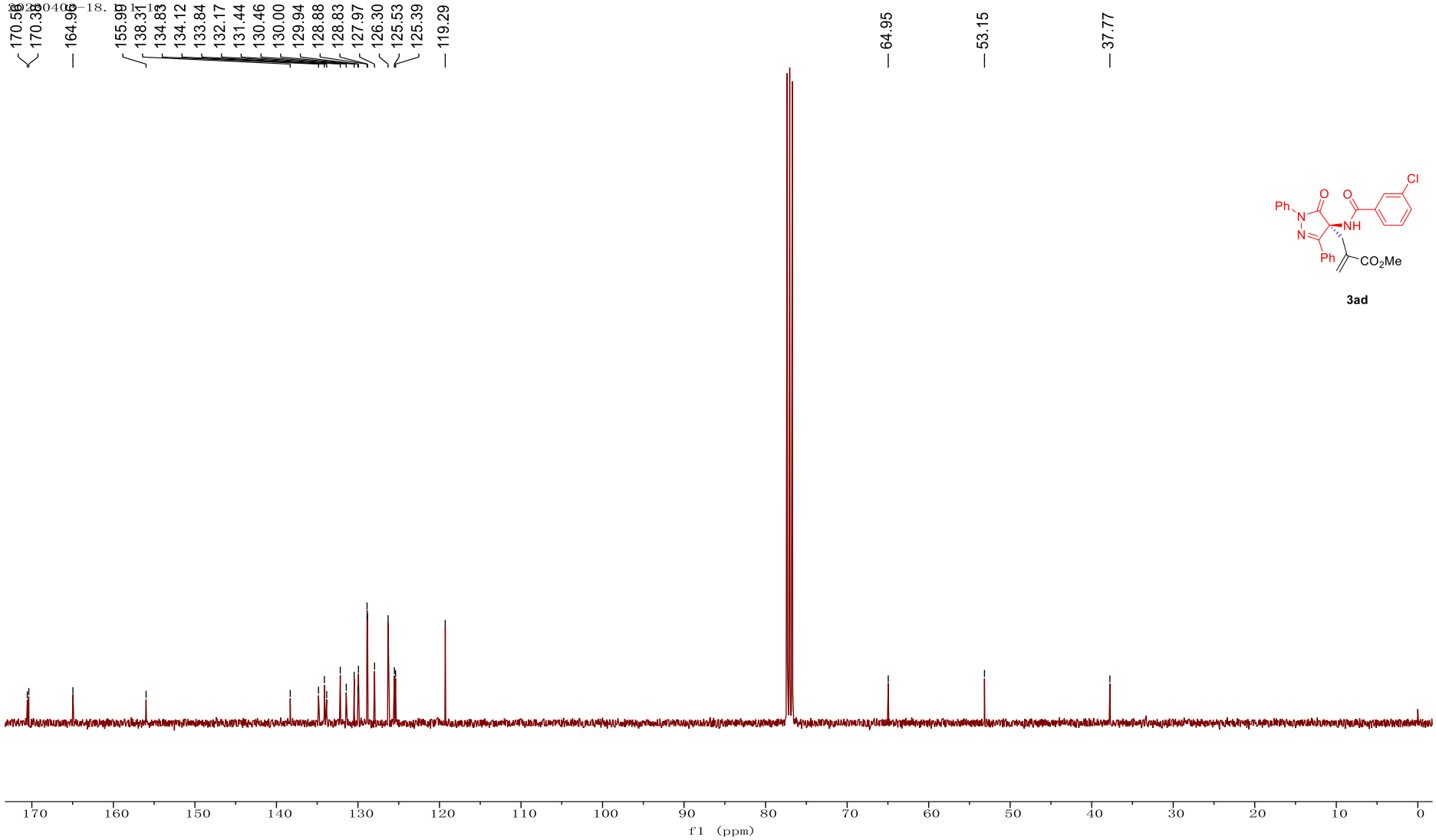
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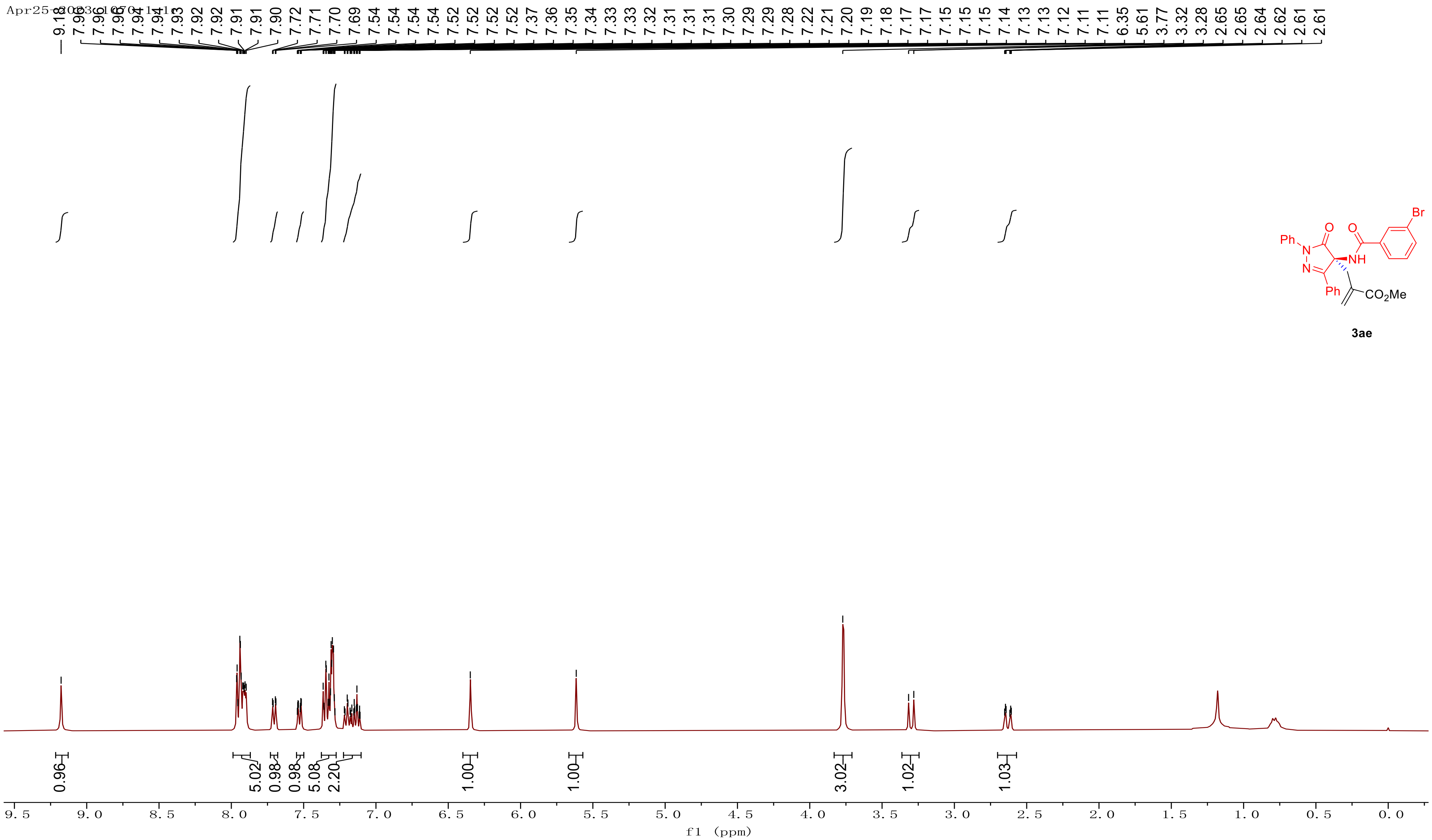
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1.02
1.03
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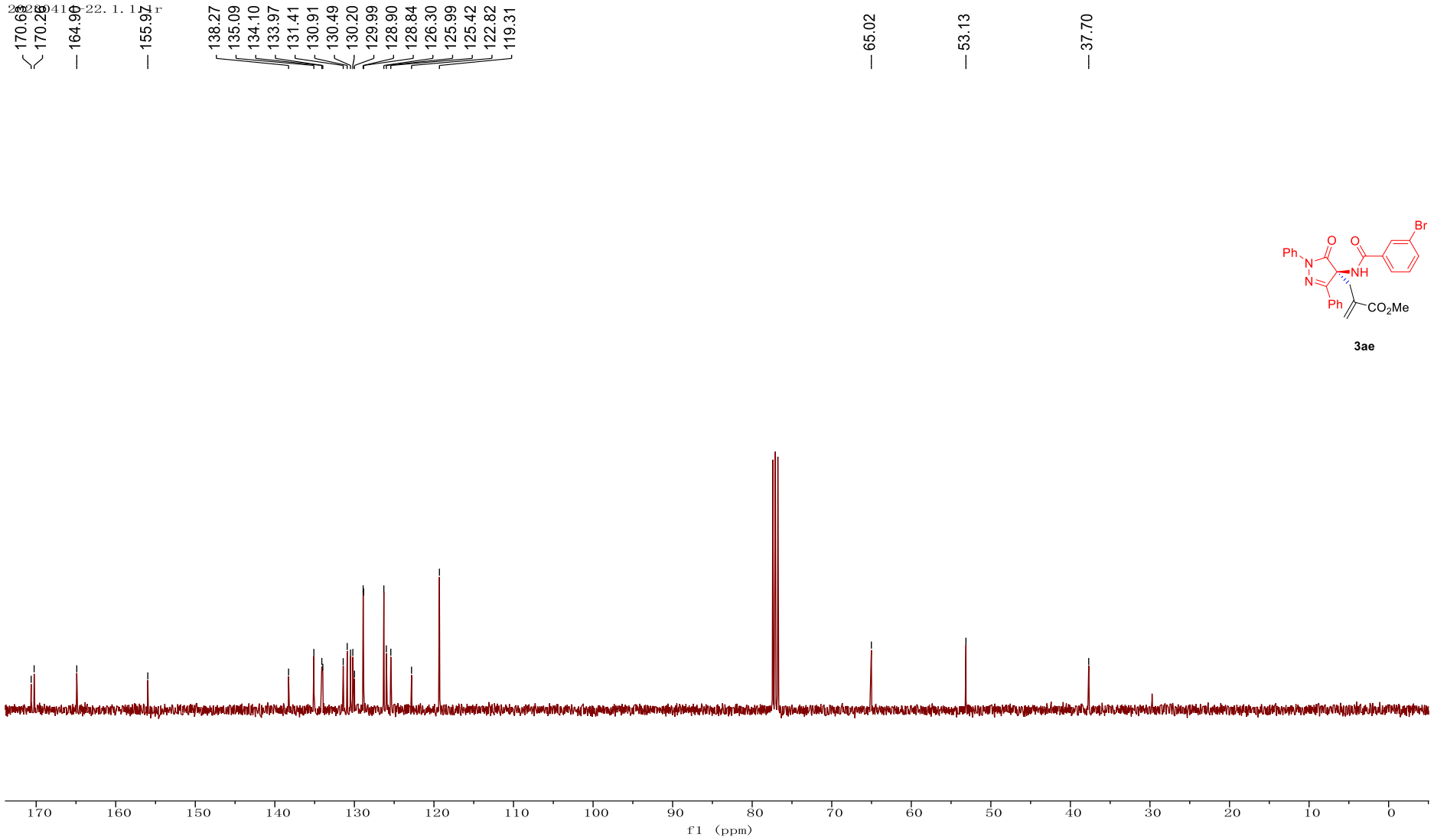
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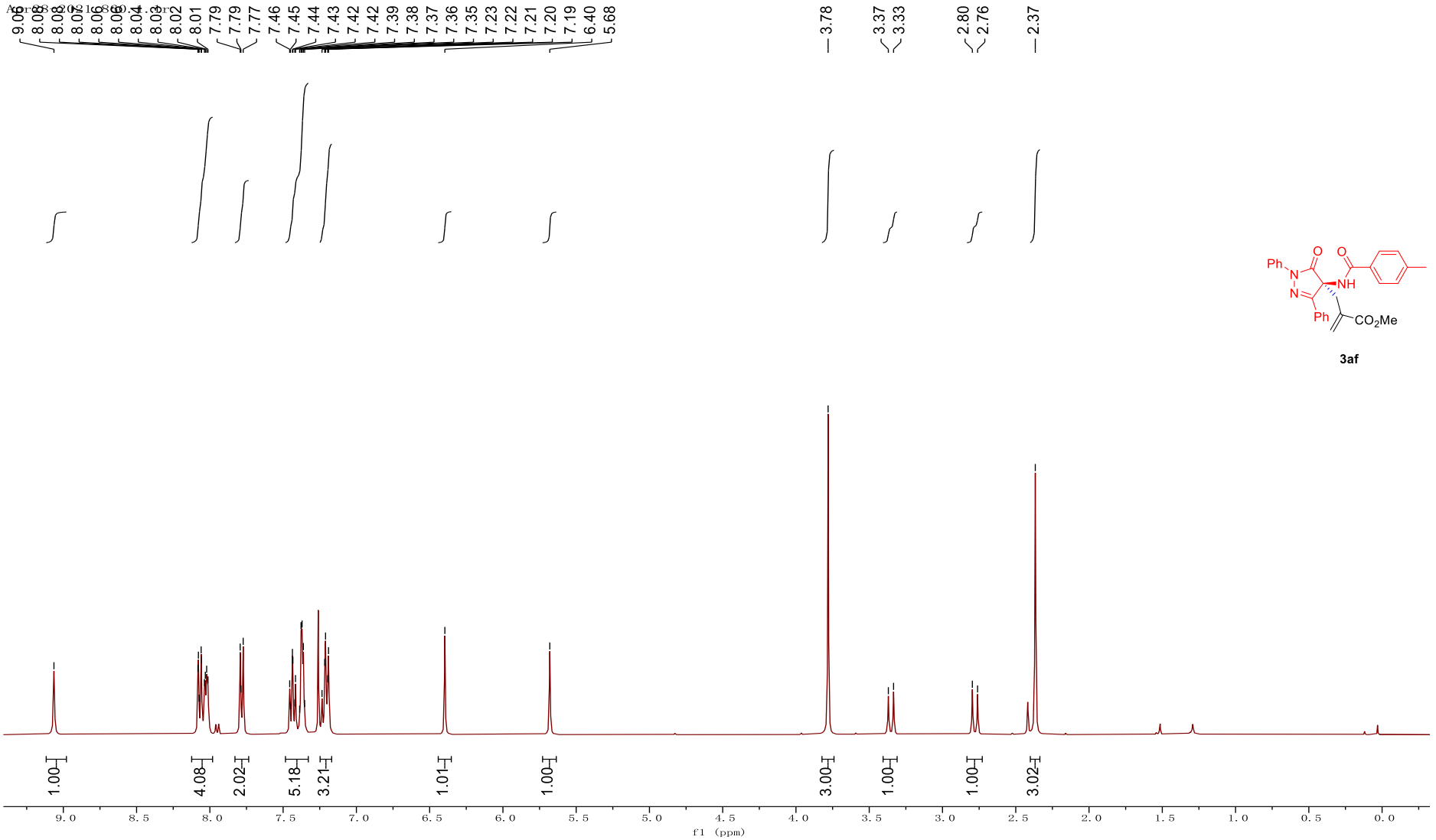
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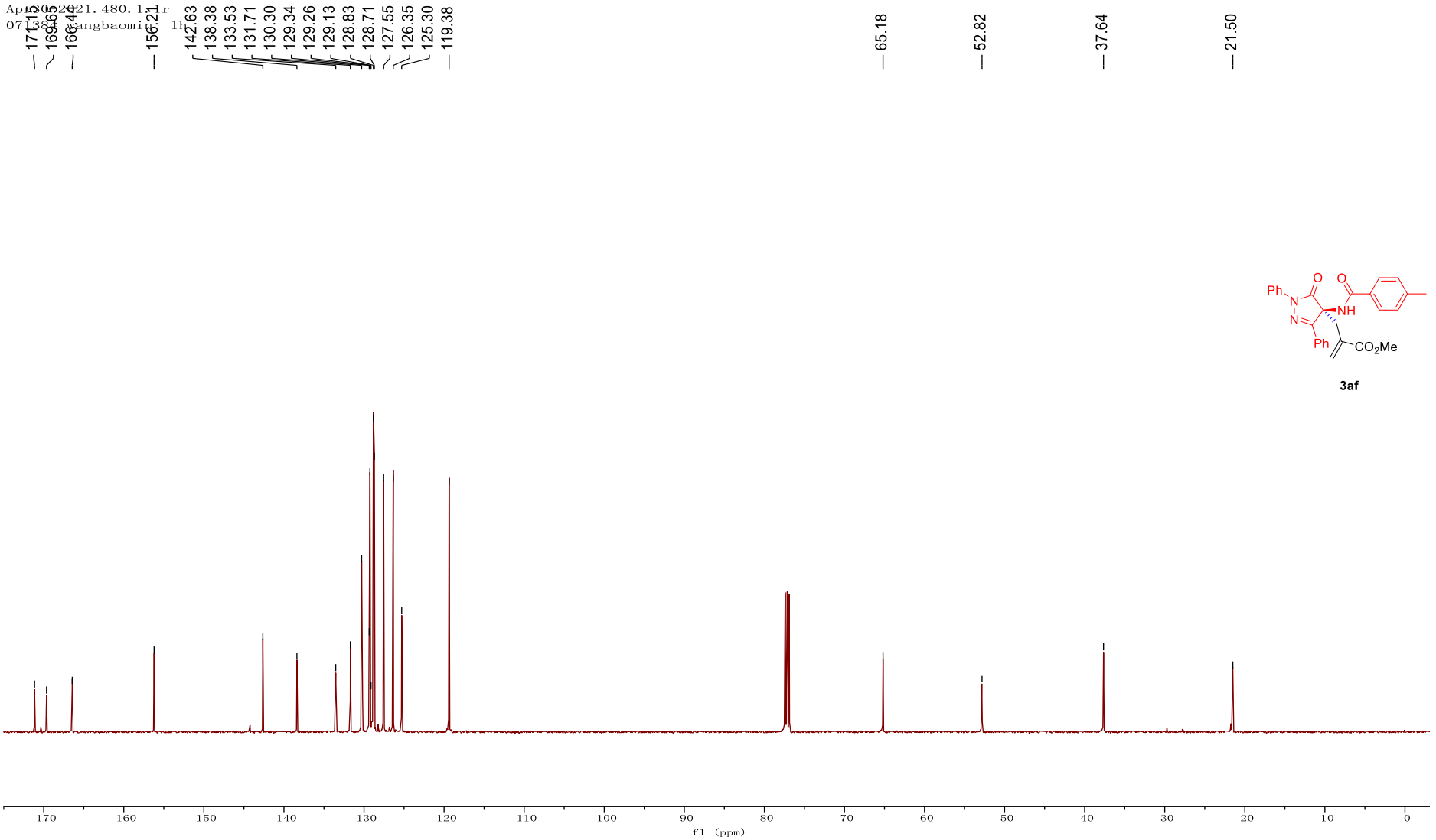
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3af
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160
150
140
130
120
110
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90
80
70
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50
40
30
20
10
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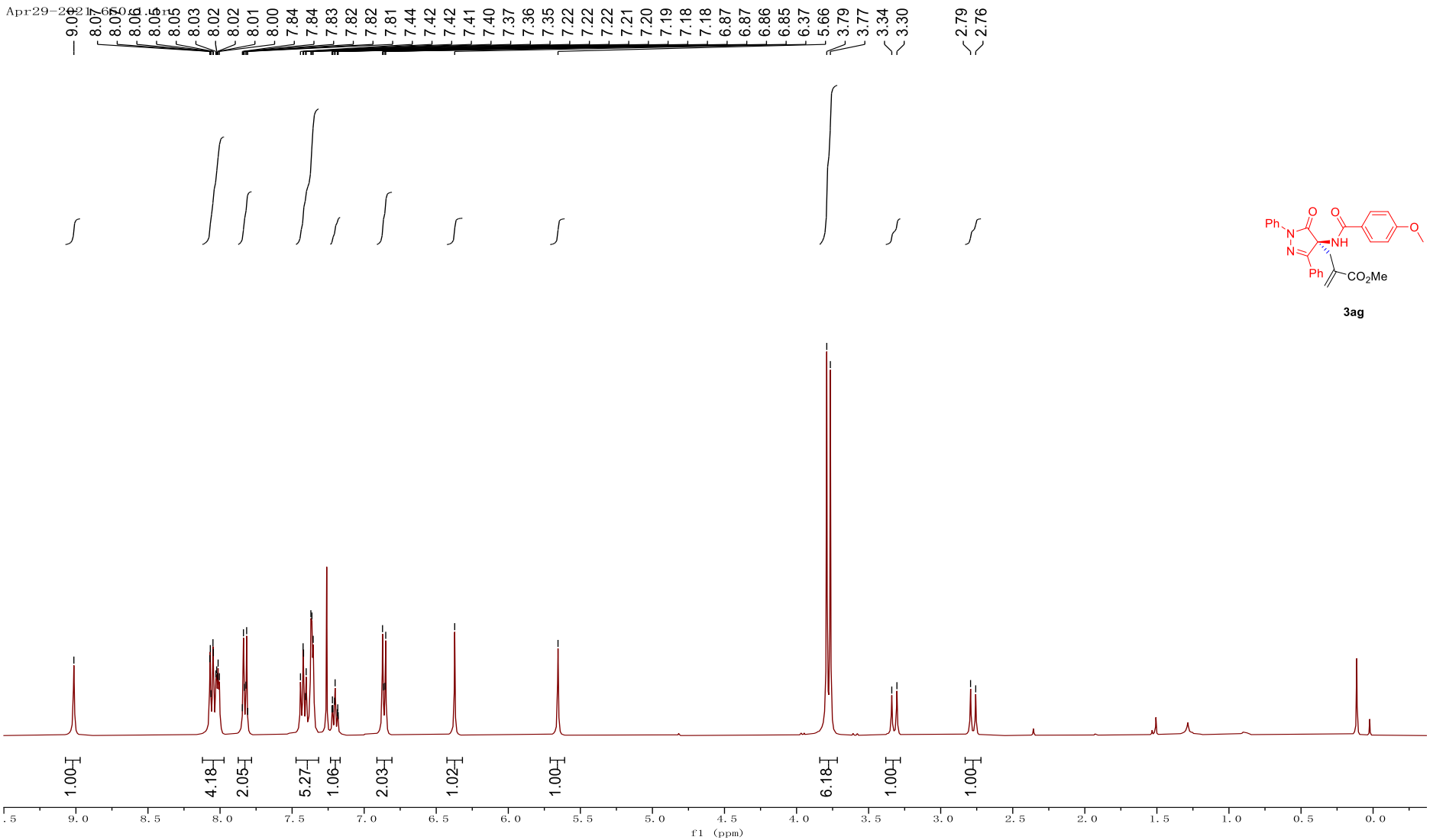
f1 (ppm)


Apr29-2021-650
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7.84
7.84
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7.82
7.81
7.44
7.42
7.42
7.41
7.40
7.37
7.36
7.35
7.22
7.22
7.22
7.21
7.20
7.19
7.18
7.18
6.87
6.87
6.86
6.85
6.37
5.66
3.79
3.77
3.34
3.30
2.79
2.76
Ph
N
N
O
O
NH
O
Ph
CO2Me
3ag
1.00
4.18
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5.27
1.06
2.03
1.02
1.00
6.18
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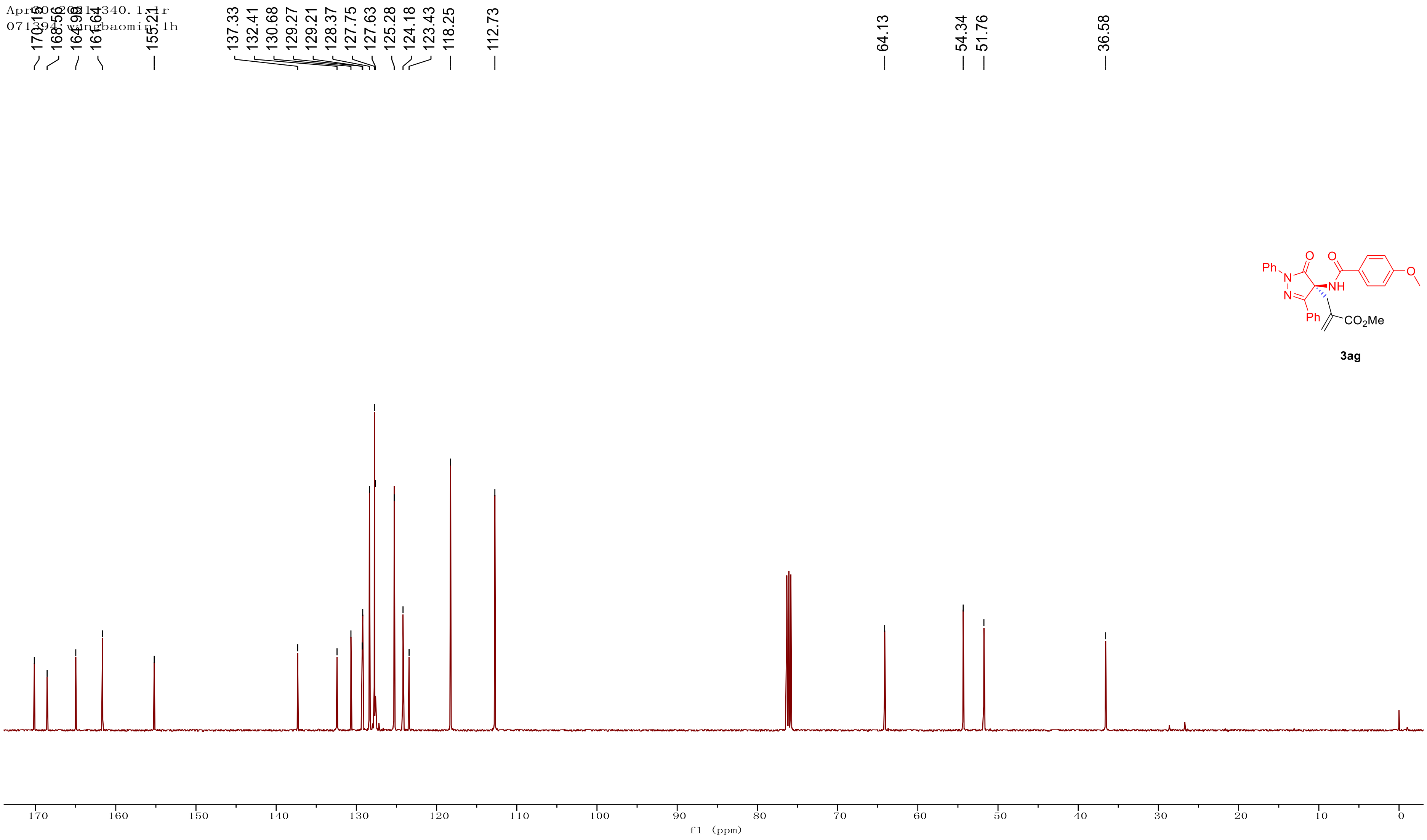
1.00
f1 (ppm)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130.68
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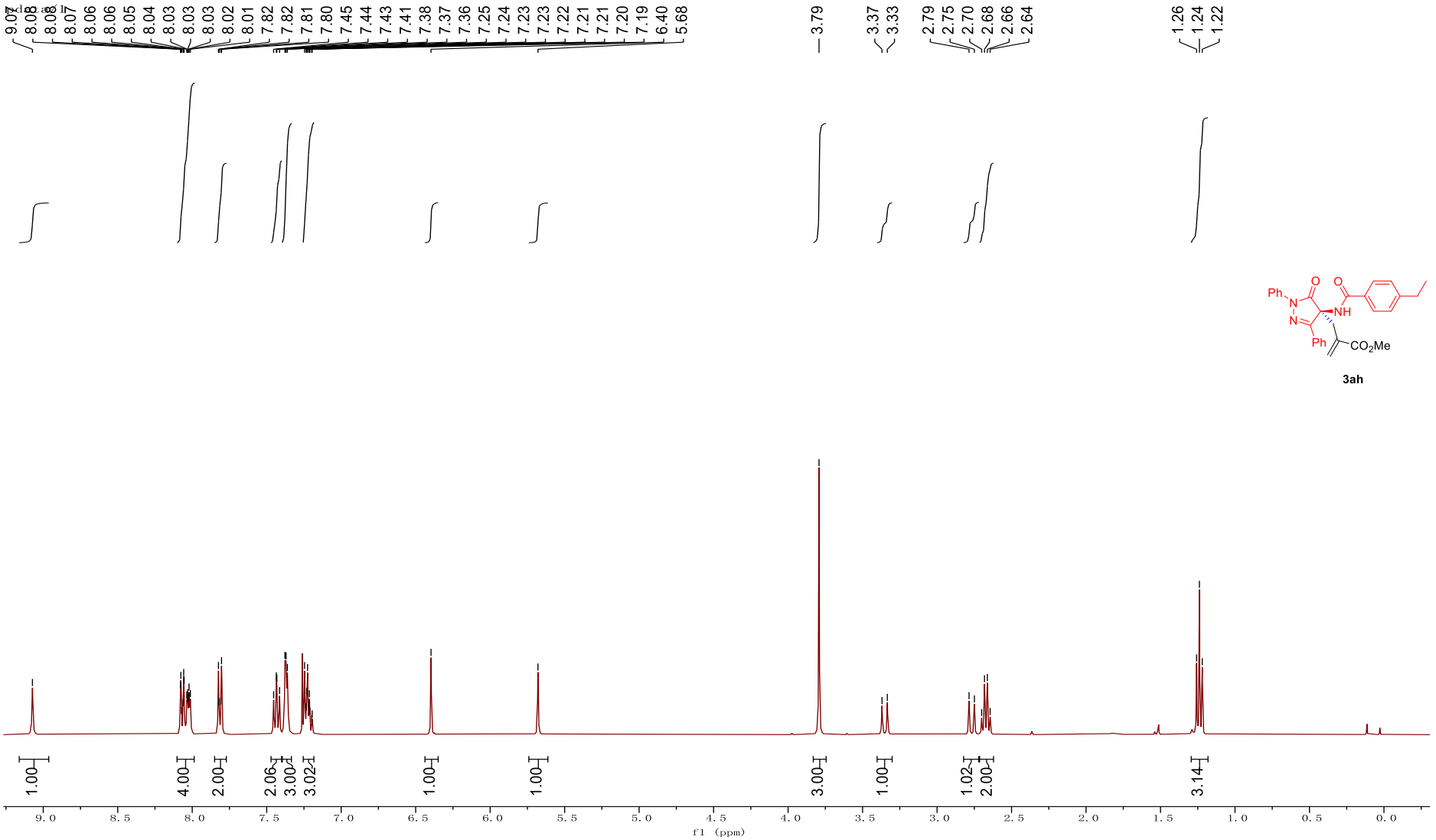
129.21
128.37
127.75
127.63
125.28
124.18
123.43
118.25
112.73
64.13
54.34
51.76
36.58
f1 (ppm)
Ph
N
N
O
O
NH
O
Ph
CO2Me

3ag


9.07
8.08
8.08
8.08
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8.06
8.06
8.05
8.04
8.03
8.03
8.03
8.02
8.01
7.82
7.82
7.81
7.80
7.45
7.44
7.43
7.41
7.38
7.37
7.36
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.19
6.40
5.68
3.79
3.37
3.33
2.79
2.75
2.70
2.68
2.66
2.64
1.26
1.24
1.22
Ph
N
N
O
O
NH
Ph
CO2Me
3ah
1.00
4.00
2.00
2.06
3.00
3.02
1.00
1.00
3.00
1.00
1.02
2.00
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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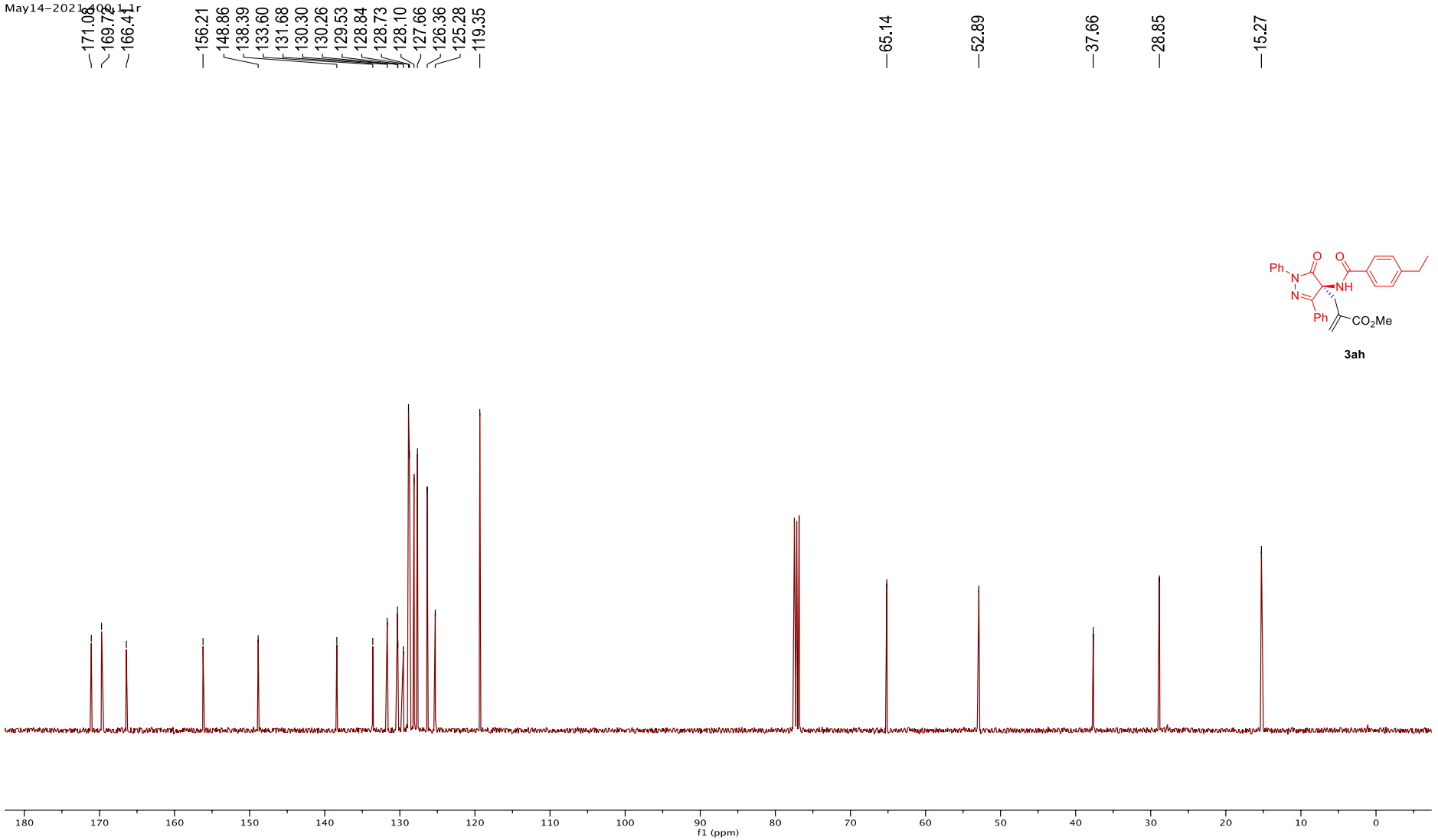
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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169.72
166.41
156.21
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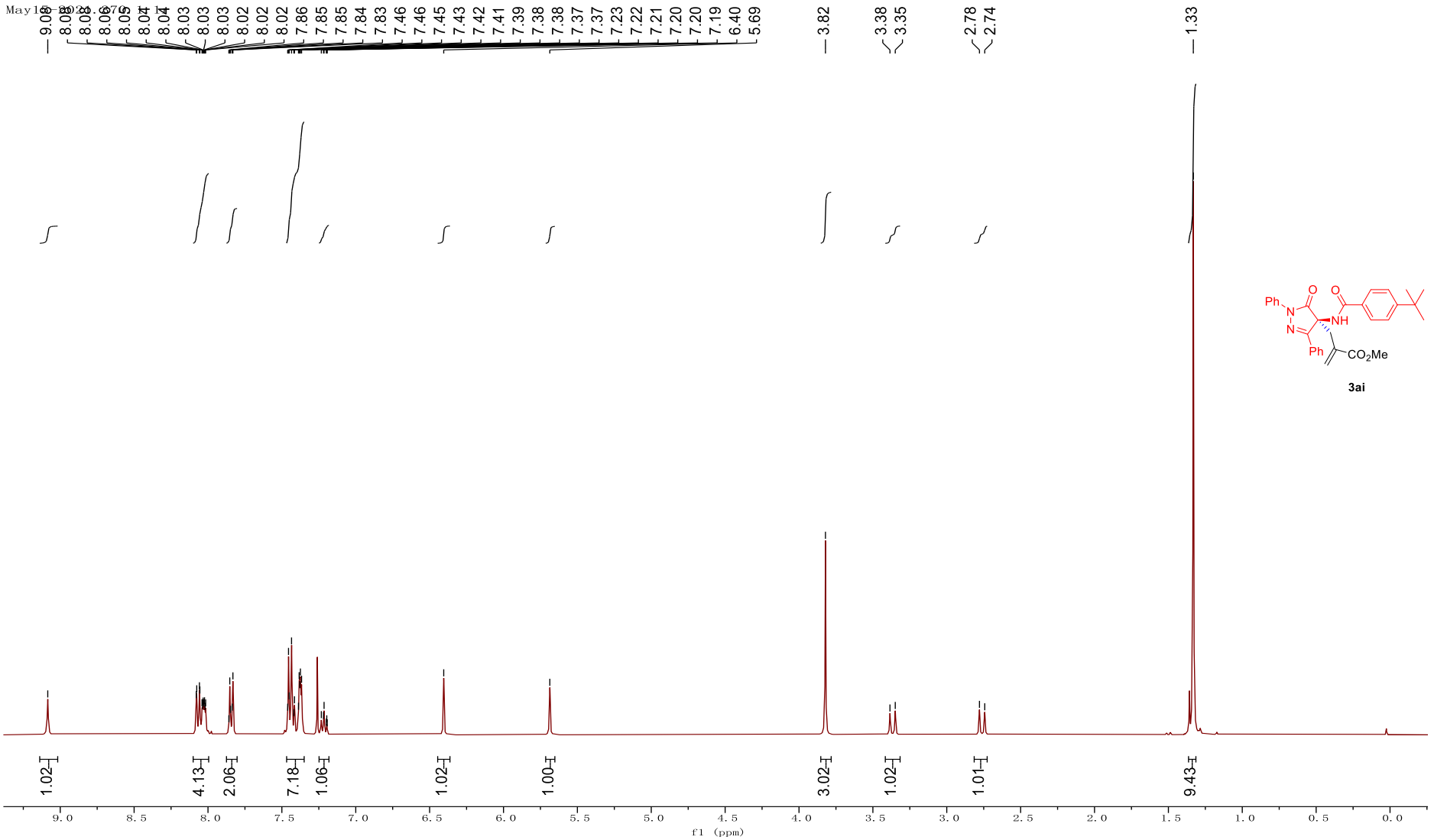
130.30
130.26
129.53
128.84
128.73
128.10
127.66
126.36
125.28
119.35
65.14
52.89
37.66
28.85
15.27
Ph
N
N
O
O
NH
Ph
CO2Me
3ah
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.08
8.08
8.06
8.05
8.04
8.04
8.03
8.03
8.03
8.02
8.02
8.02
7.86
7.85
7.85
7.84
7.83
7.46
7.46
7.45
7.43
7.42
7.41
7.39
7.38
7.38
7.37
7.37
7.23
7.22
7.21
7.20
7.20
7.19
6.40
5.69
3.82
3.38
3.35
2.78
2.74
1.33
Ph
N
N
O
O
NH
Ph
CO2Me
3ai
1.02
4.13
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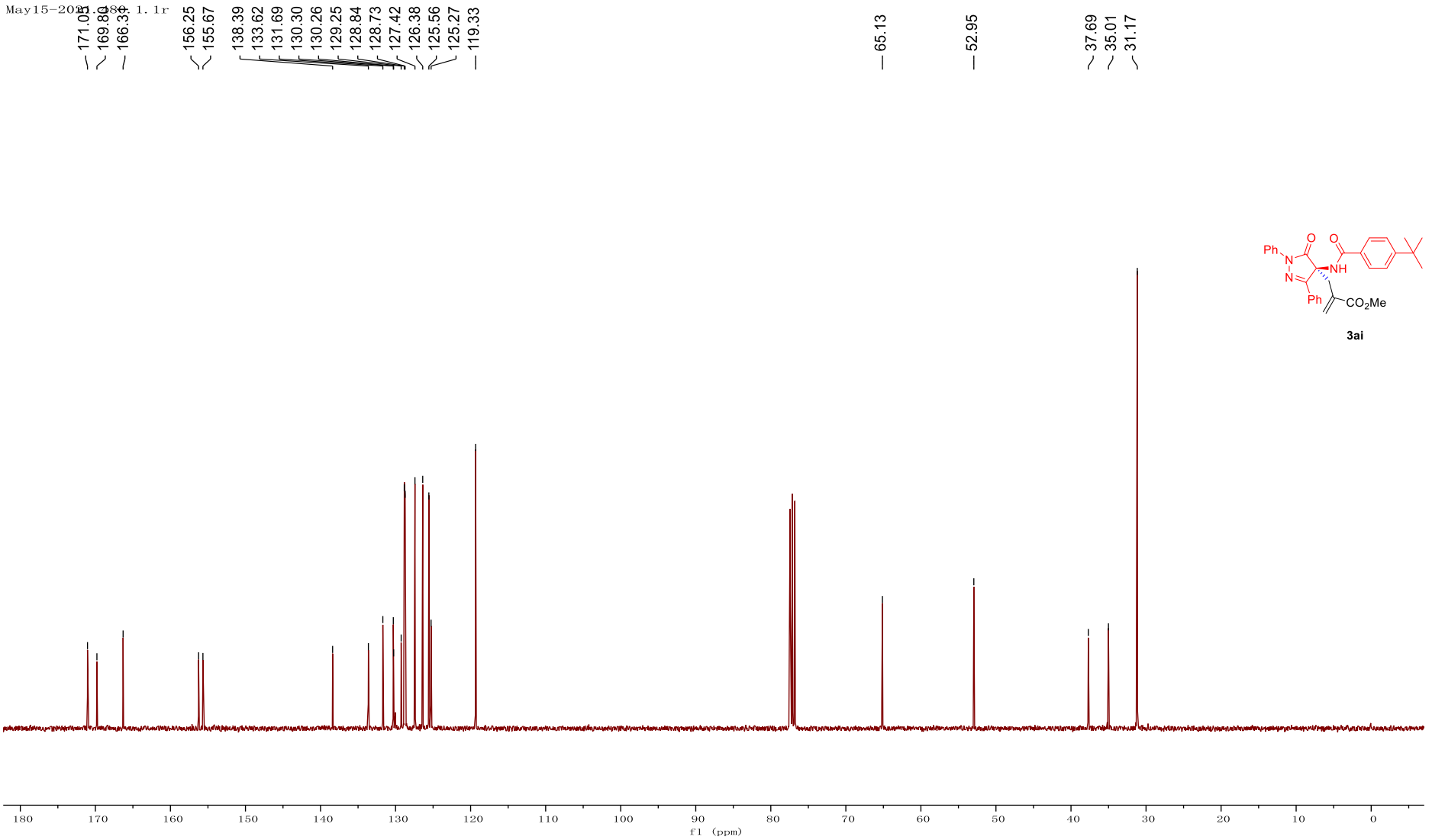
7.18
1.06
1.02
1.00
3.02
1.02
1.01
9.43
f1 (ppm)


May15-2021-480-1.1r
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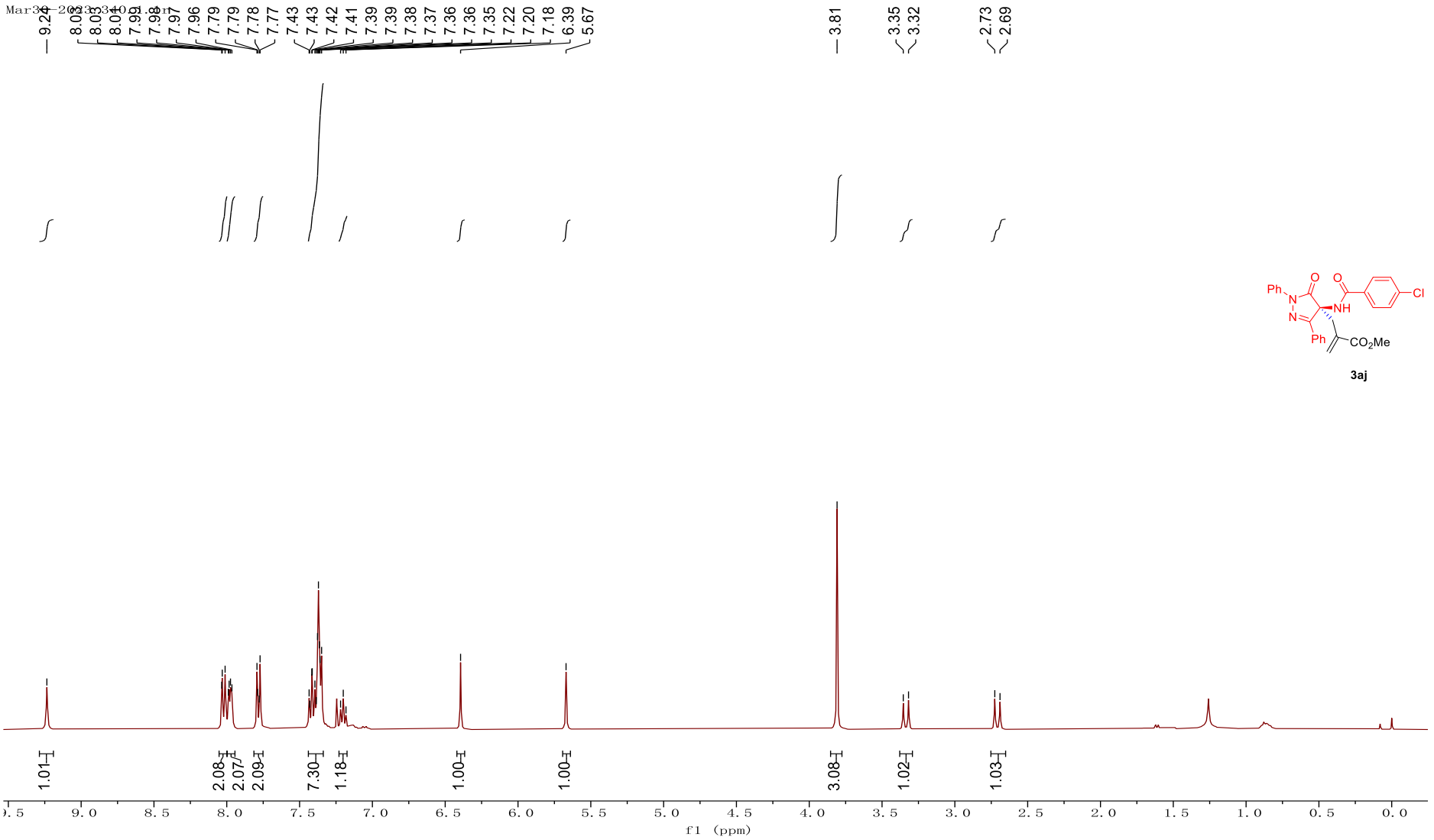
138.39
133.62
131.69
130.30
130.26
129.25
128.84
128.73
127.42
126.38
125.56
125.27
119.33
65.13
52.95
37.69
35.01
31.17
Ph
N
N
O
O
NH
Ph
CO2Me
3ai
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.03
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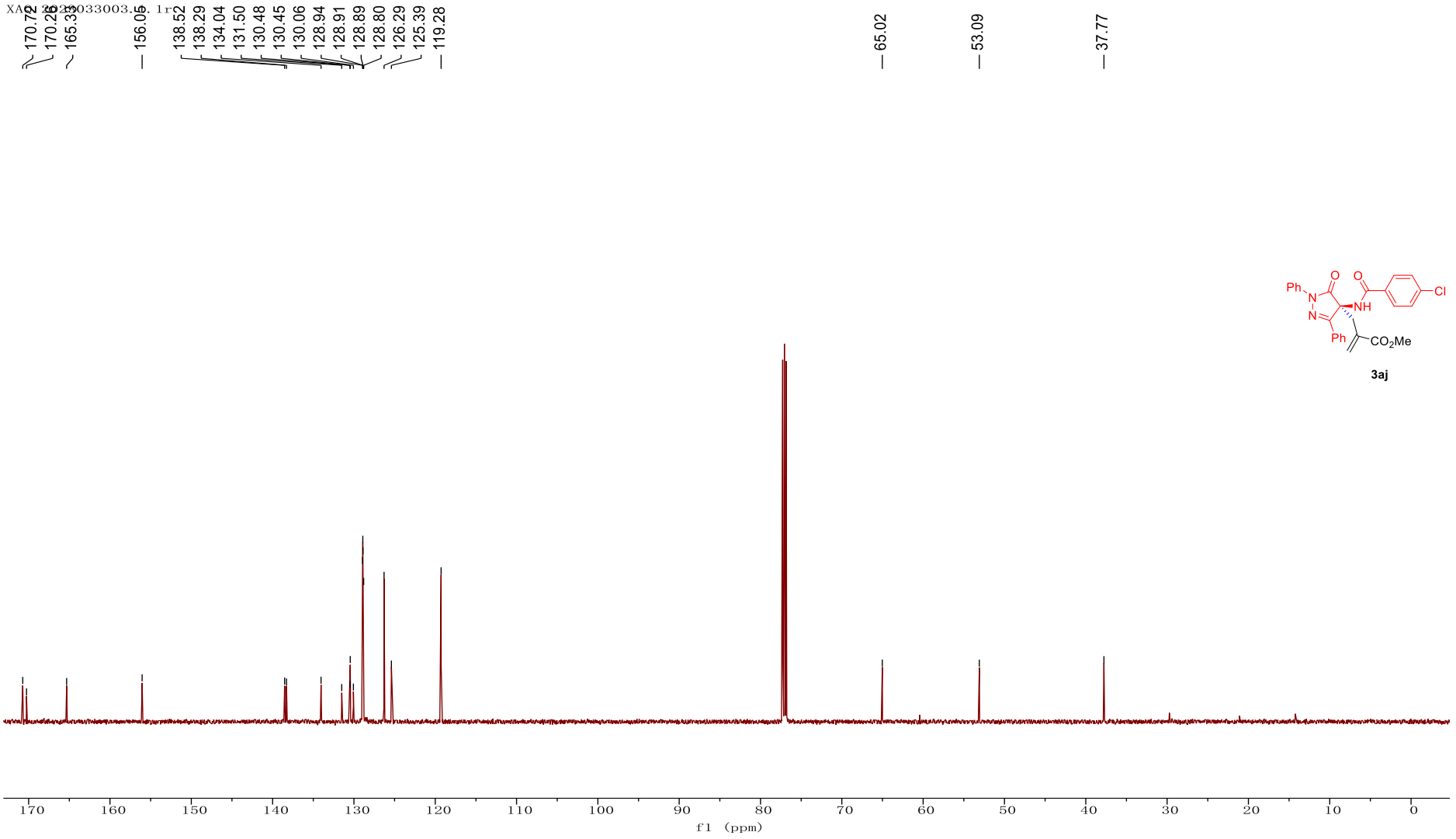
7.79
7.78
7.77
7.43
7.43
7.42
7.41
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.22
7.20
7.18
6.39
5.67
3.81
3.35
3.32
2.73
2.69
Ph
N
N
O
O
NH
Cl
Ph
CO2Me
3aj
1.01
2.08
2.07
2.09
7.30
1.18
1.00
1.00
3.08
1.02
1.03
f1 (ppm)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170.26
165.33
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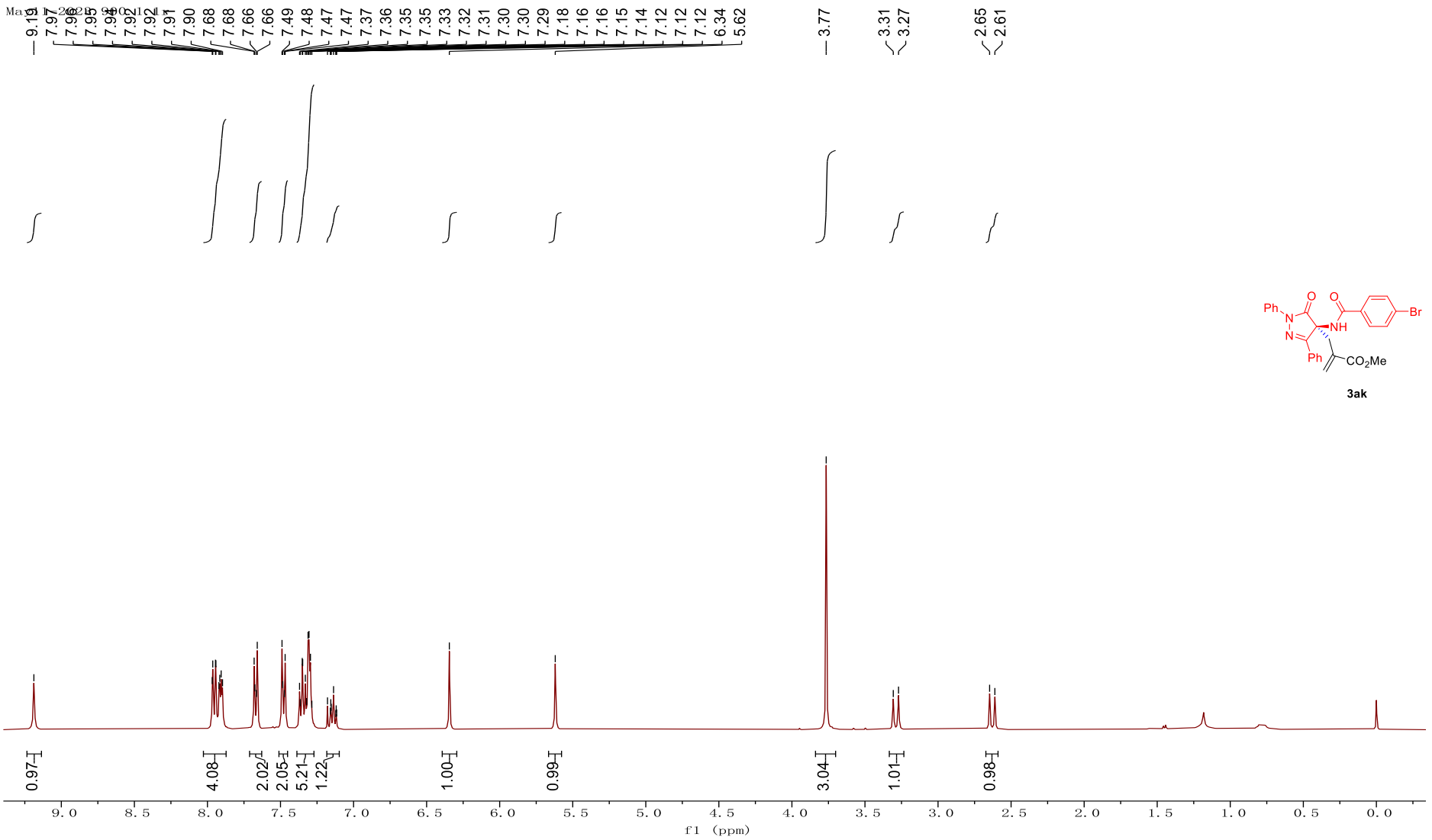
138.29
134.04
131.50
130.48
130.45
130.06
128.94
128.91
128.89
128.80
126.29
125.39
119.28
65.02
53.09
37.77
Ph
N
N
O
O
NH
Cl
Ph
CO2Me
3aj
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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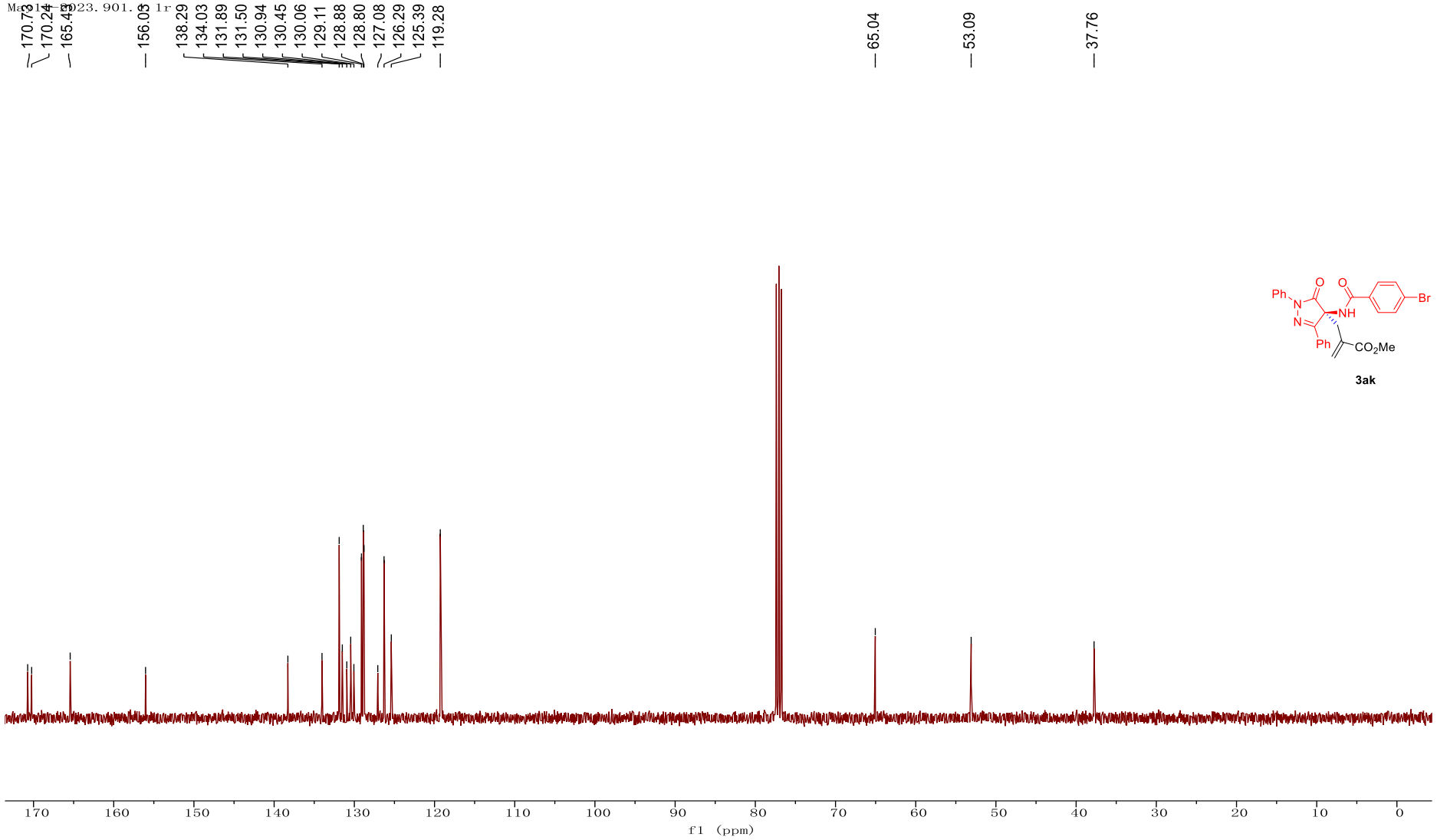
7.92
7.92
7.91
7.90
7.68
7.68
7.66
7.66
7.49
7.48
7.47
7.47
7.37
7.36
7.35
7.35
7.33
7.32
7.31
7.30
7.30
7.29
7.18
7.16
7.16
7.15
7.14
7.12
7.12
7.12
6.34
5.62
3.77
3.31
3.27
2.65
2.61
Ph
N
N
O
O
NH
Br
Ph
CO2Me
3ak
0.97
4.08
2.02
2.05
5.21
1.22
1.00
0.99
3.04
1.01
0.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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170.24
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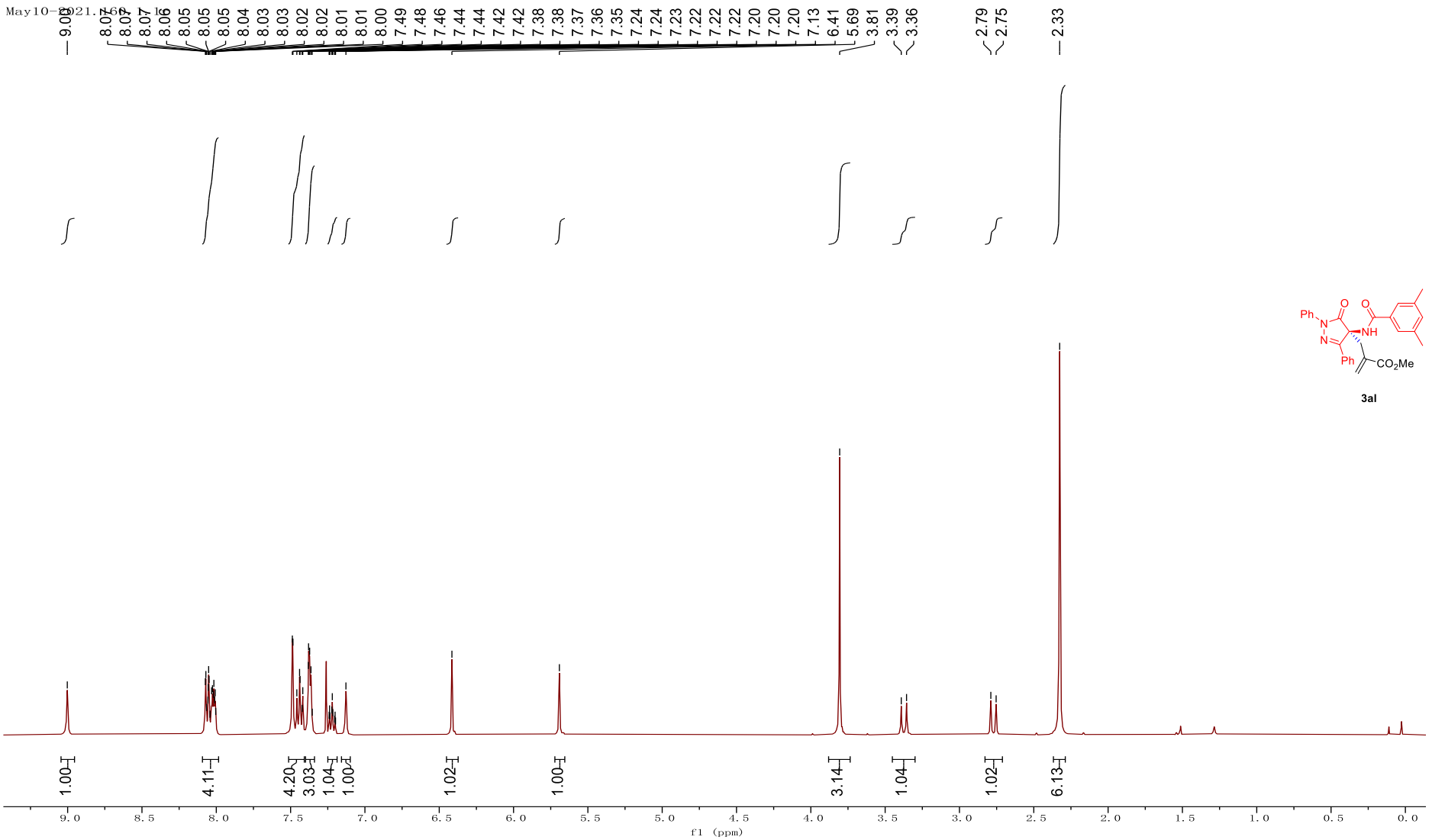
134.03
131.89
131.50
130.94
130.45
130.06
129.11
128.88
128.80
127.08
126.29
125.39
119.28
65.04
53.09
37.76
Ph
N
N
O
O
NH
Br
Ph
CO2Me
3ak
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


May10-2021.7.68
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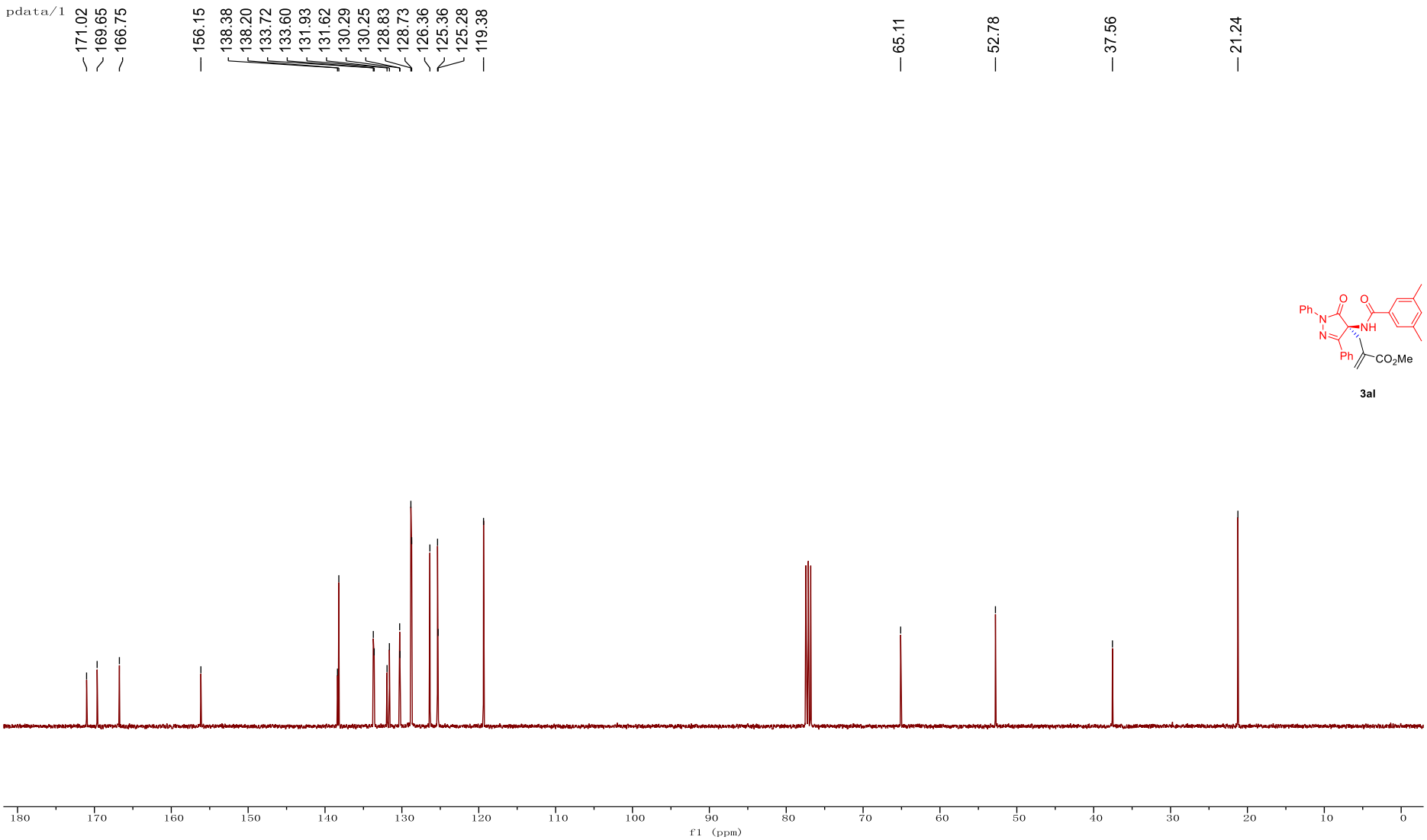
8.07
8.07
8.07
8.06
8.05
8.05
8.05
8.04
8.03
8.03
8.02
8.02
8.01
8.01
8.00
7.49
7.48
7.46
7.44
7.44
7.42
7.42
7.38
7.38
7.37
7.36
7.35
7.24
7.24
7.23
7.22
7.22
7.22
7.20
7.20
7.20
7.13
6.41
5.69
3.81
3.39
3.36
2.79
2.75
2.33
Ph
N
N
O
O
NH
Ph
CO2Me
3al
1.00
4.11
4.20
3.03
1.04
1.00
1.02
1.00
3.14
1.04
1.02
6.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


pdata/1
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138.20
133.72
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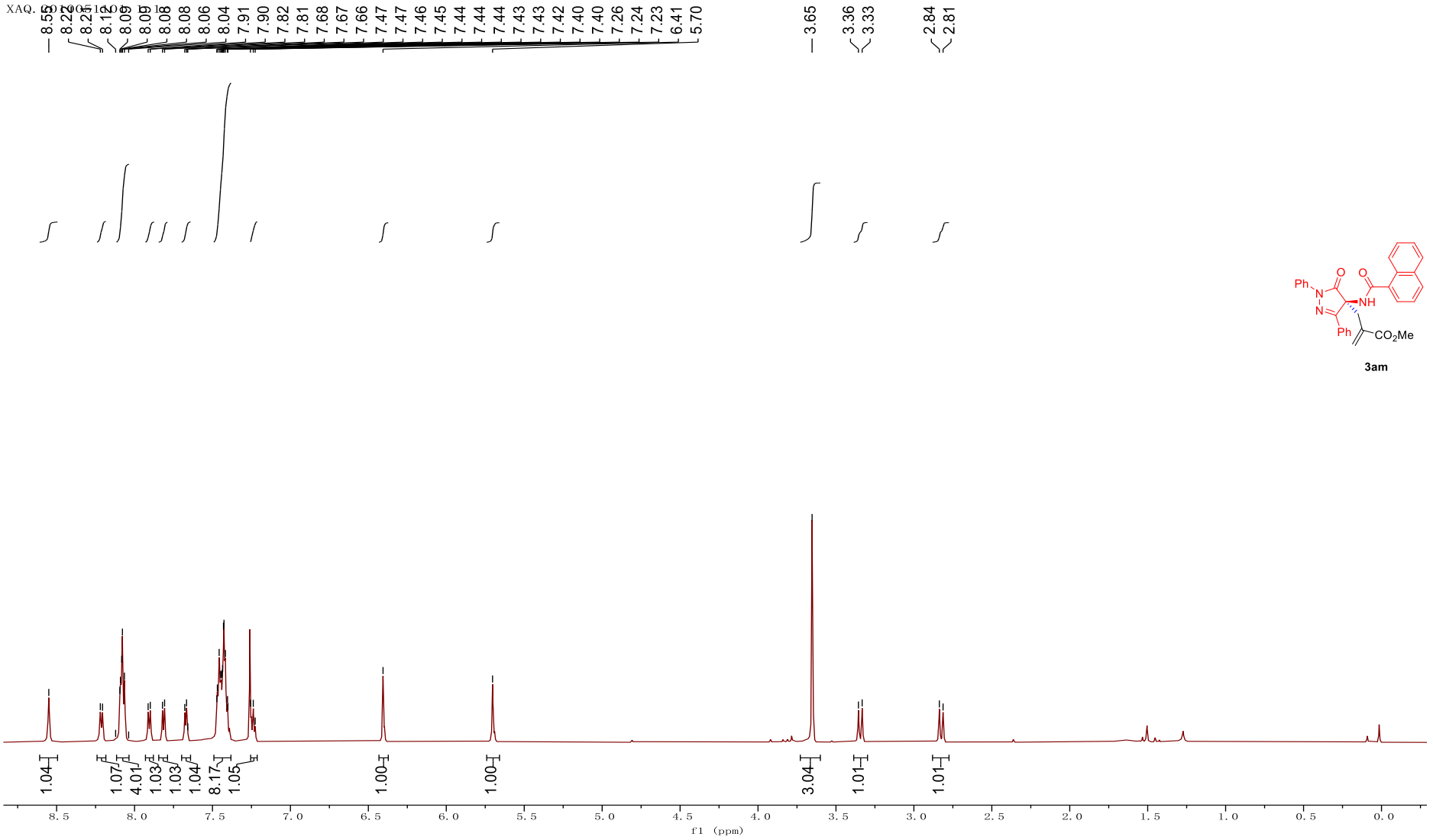
131.93
131.62
130.29
130.25
128.83
128.73
126.36
125.36
125.28
119.38
65.11
52.78
37.56
21.24
Ph
N
N
O
O
NH
Ph
CO2Me
3al
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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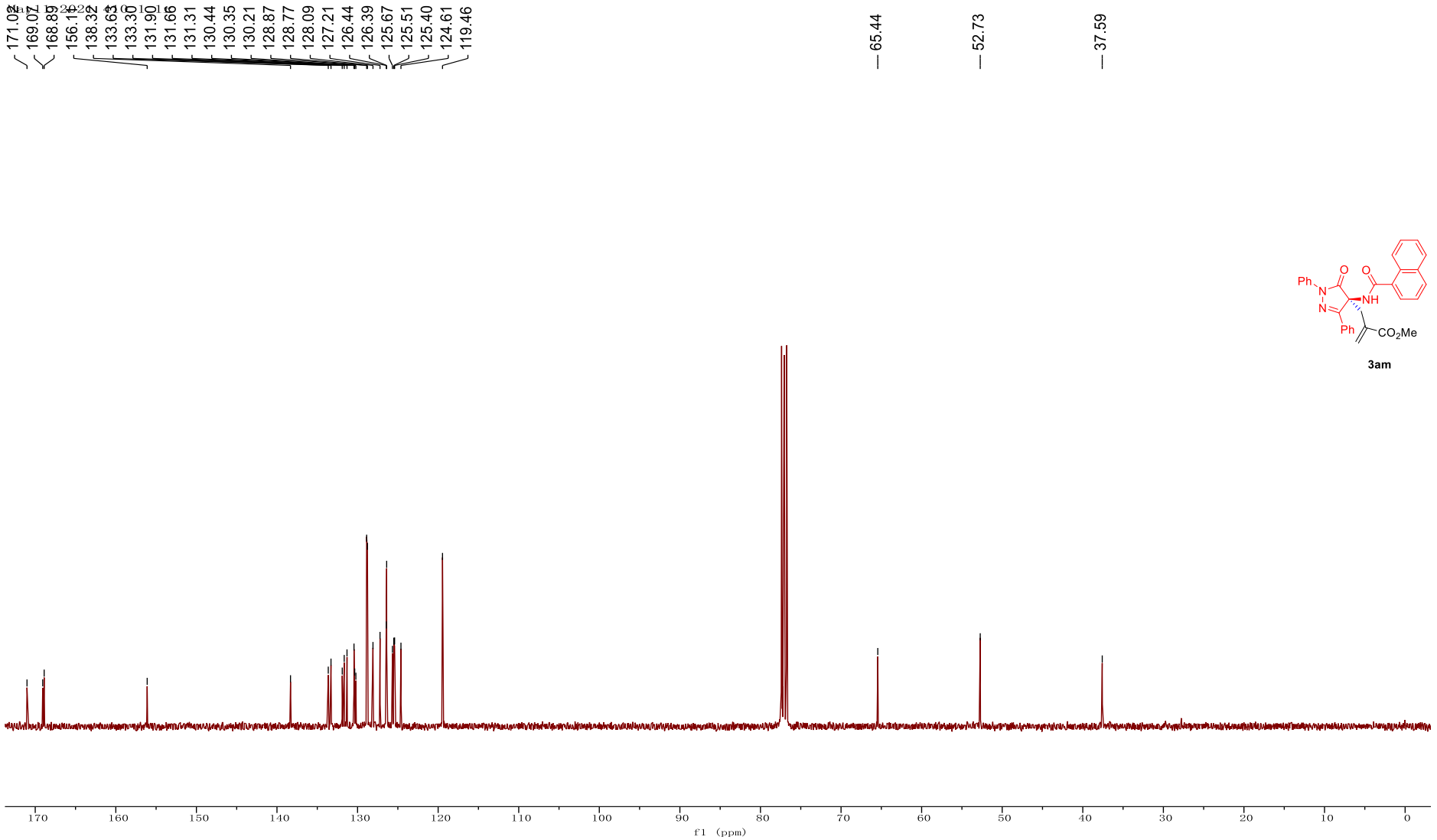
8.09
8.09
8.08
8.08
8.06
8.04
7.91
7.90
7.82
7.81
7.68
7.67
7.66
7.47
7.47
7.46
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.40
7.40
7.26
7.24
7.23
6.41
5.70
3.65
3.36
3.33
2.84
2.81
1.04
1.07
4.01
1.03
1.03
1.04
8.17
1.05
1.00
1.00
3.04
1.01
1.01
f1 (ppm)

Ph
O
O
N
N
NH
Ph
CO2Me

3am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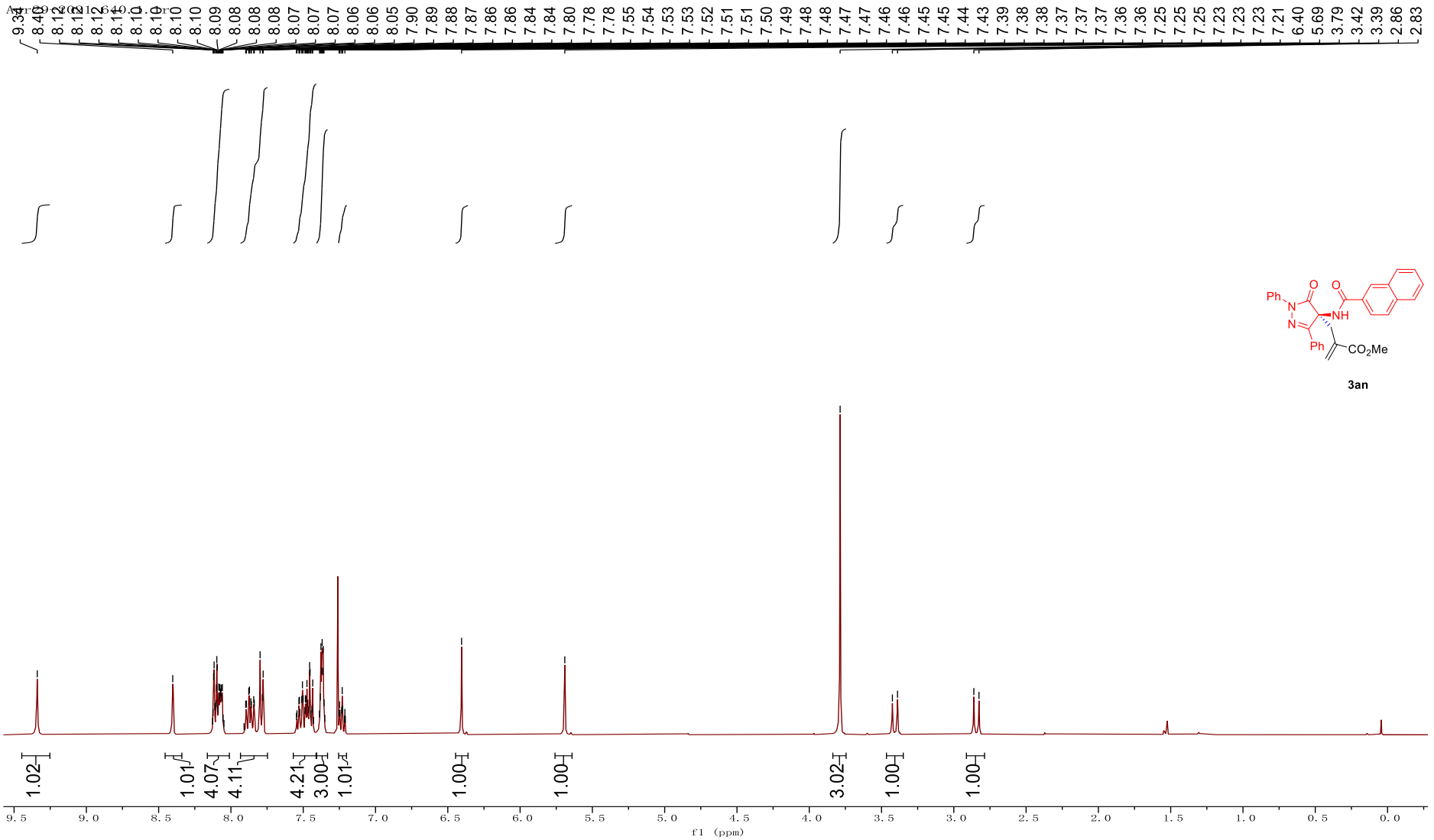
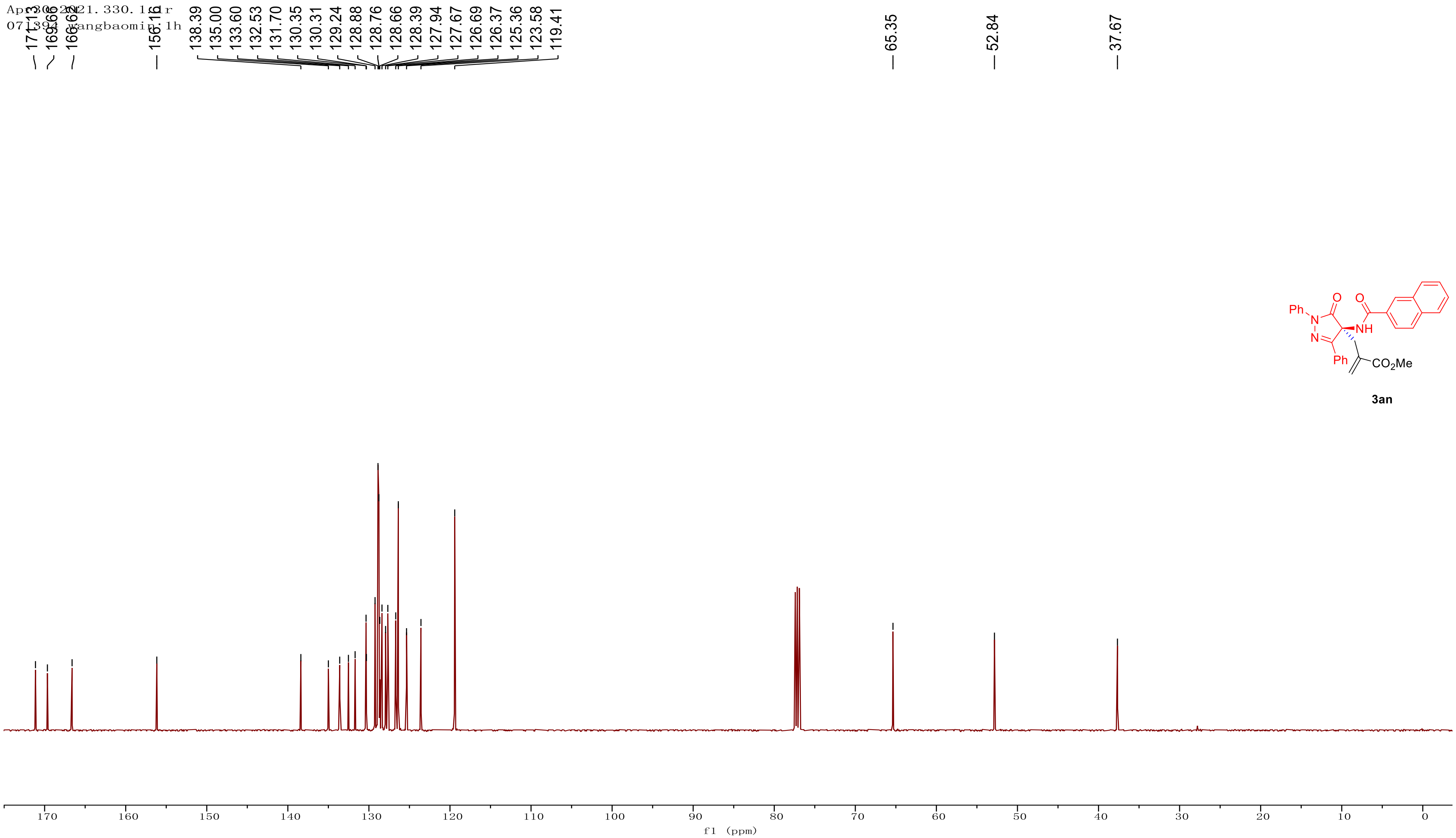
131.31
130.44
130.35
130.21
128.87
128.77
128.09
127.21
126.44
126.39
125.67
125.51
125.40
124.61
119.46
65.44
52.73
37.59
Ph
N
N
O
O
NH
Ph
CO2Me
3am
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.34 8.42 8.12 8.12 8.12 8.11 8.10 8.10 8.10 8.10 8.09 8.08 8.08 8.08 8.07 8.07 8.07 8.06 8.06 8.06 8.05 7.90 7.89 7.88 7.87 7.86 7.86 7.84 7.84 7.80 7.78 7.78 7.55 7.54 7.53 7.53 7.52 7.51 7.51 7.50 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.43 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.25 7.25 7.25 7.23 7.23 7.23 7.21 6.40 5.69 3.79 3.42 3.39 2.86 2.83
Ph
N
N
O
O
NH
Ph
CO2Me
3an
1.02
1.01
4.07
4.11
4.21
3.00
1.01
1.00
1.00
3.02
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



Apr30-2021.330.1.fid
071394 wangbaomin.1h
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166.62
156.16
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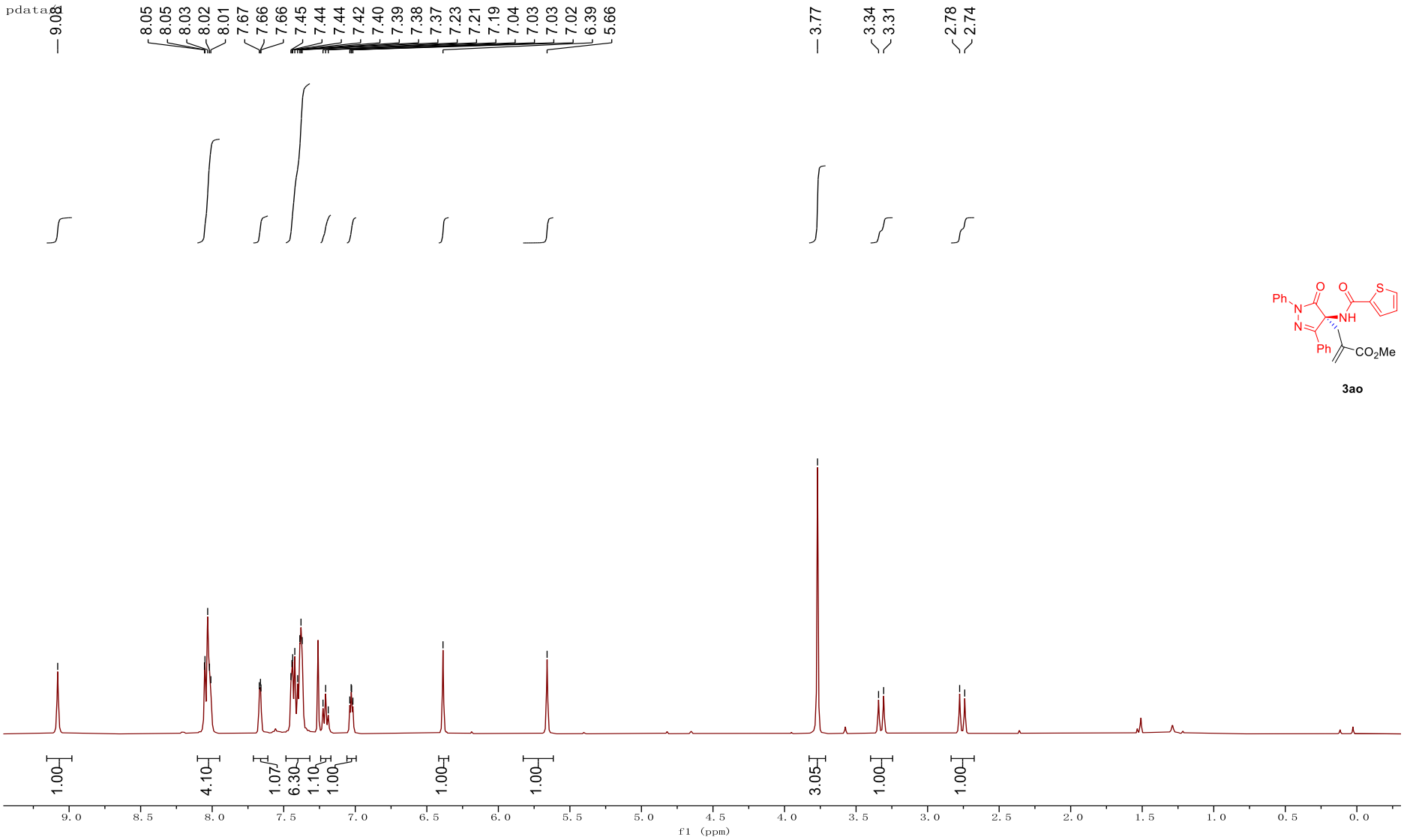
135.00
133.60
132.53
131.70
130.35
130.31
129.24
128.88
128.76
128.66
128.39
127.94
127.67
126.69
126.37
125.36
123.58
119.41
65.35
52.84
37.67
Ph
N
N
O
O
NH
Ph
CO2Me
3an
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


pdata8
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8.03
8.02
8.01
7.67
7.66
7.66
7.45
7.44
7.44
7.42
7.40
7.39
7.38
7.37
7.23
7.21
7.19
7.04
7.03
7.03
7.02
6.39
5.66
3.77
3.34
3.31
2.78
2.74
Ph
N
N
O
O
S
NH
Ph
CO2Me
3ao
1.00
4.10
1.07
6.30
1.10
1.00
1.00
1.00
3.05
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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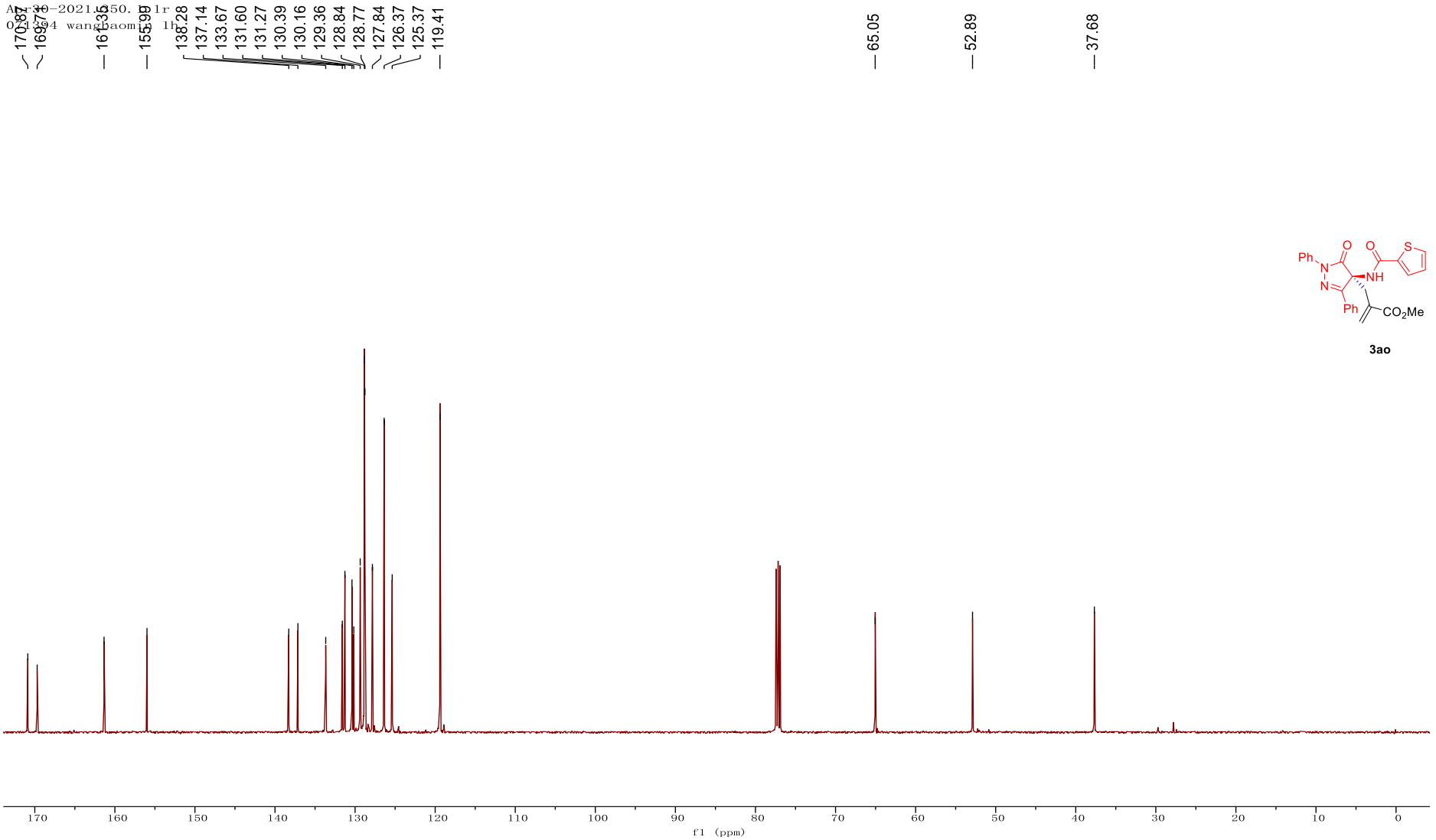
f1 (ppm)


Apr-30-2021 350. 1r
0.034 wangbaom 1h
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169.76
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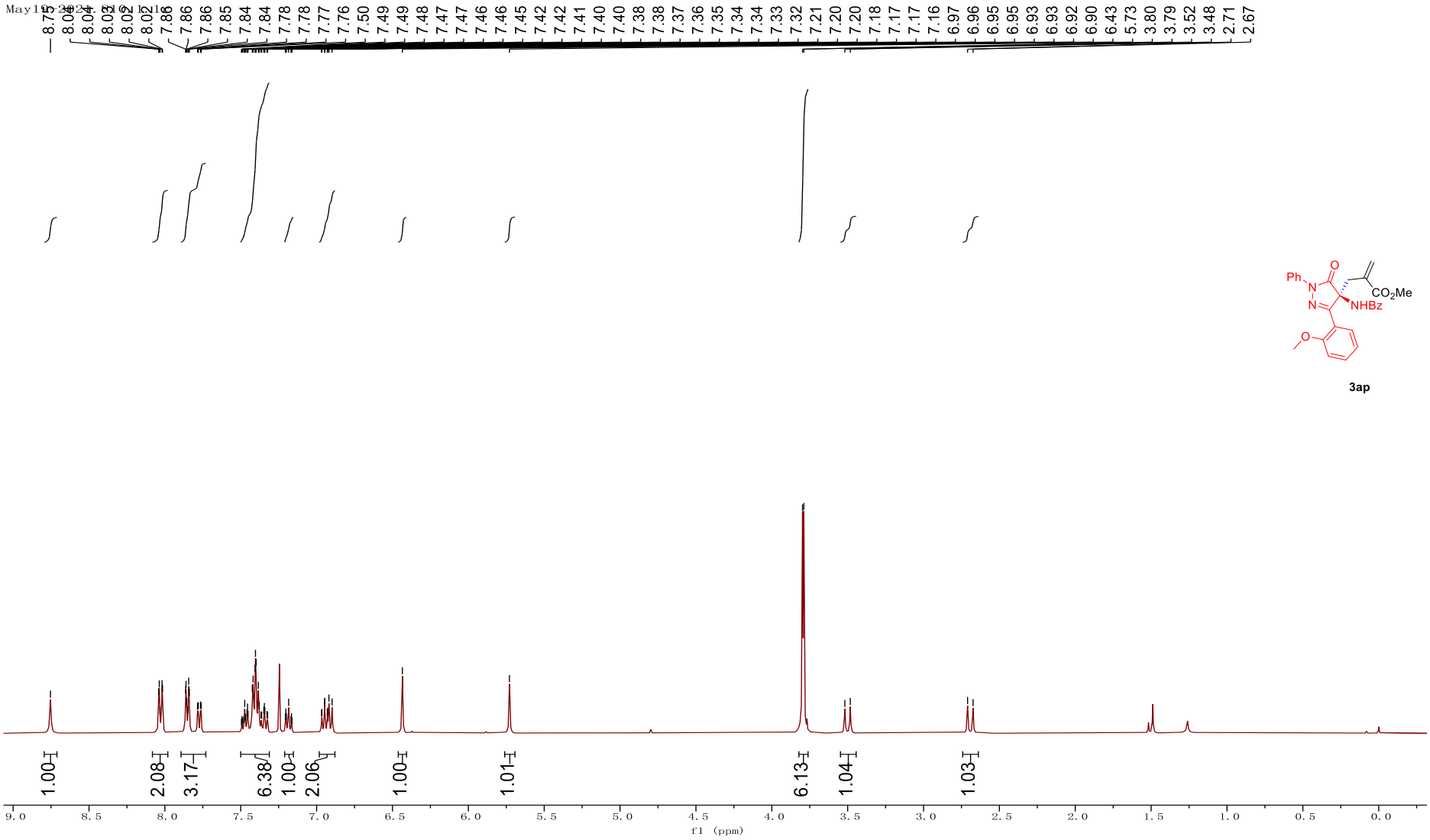
131.27
130.39
130.16
129.36
128.84
128.77
127.84
126.37
125.37
119.41
65.05
52.89
37.68
Ph
O
O
S
N
NH
N
Ph
CO2Me
3ao
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.84
7.78
7.78
7.77
7.76
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.42
7.42
7.41
7.40
7.40
7.38
7.38
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.21
7.20
7.20
7.18
7.17
7.17
7.16
6.97
6.96
6.95
6.95
6.93
6.93
6.92
6.90
6.43
5.73
3.80
3.79
3.52
2.71
2.67
Ph
N
N
O
O
NHBz
CO2Me
3ap
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2.08
3.17
6.38
1.00
2.06
1.00
1.01
6.13
1.04
1.03
9.0
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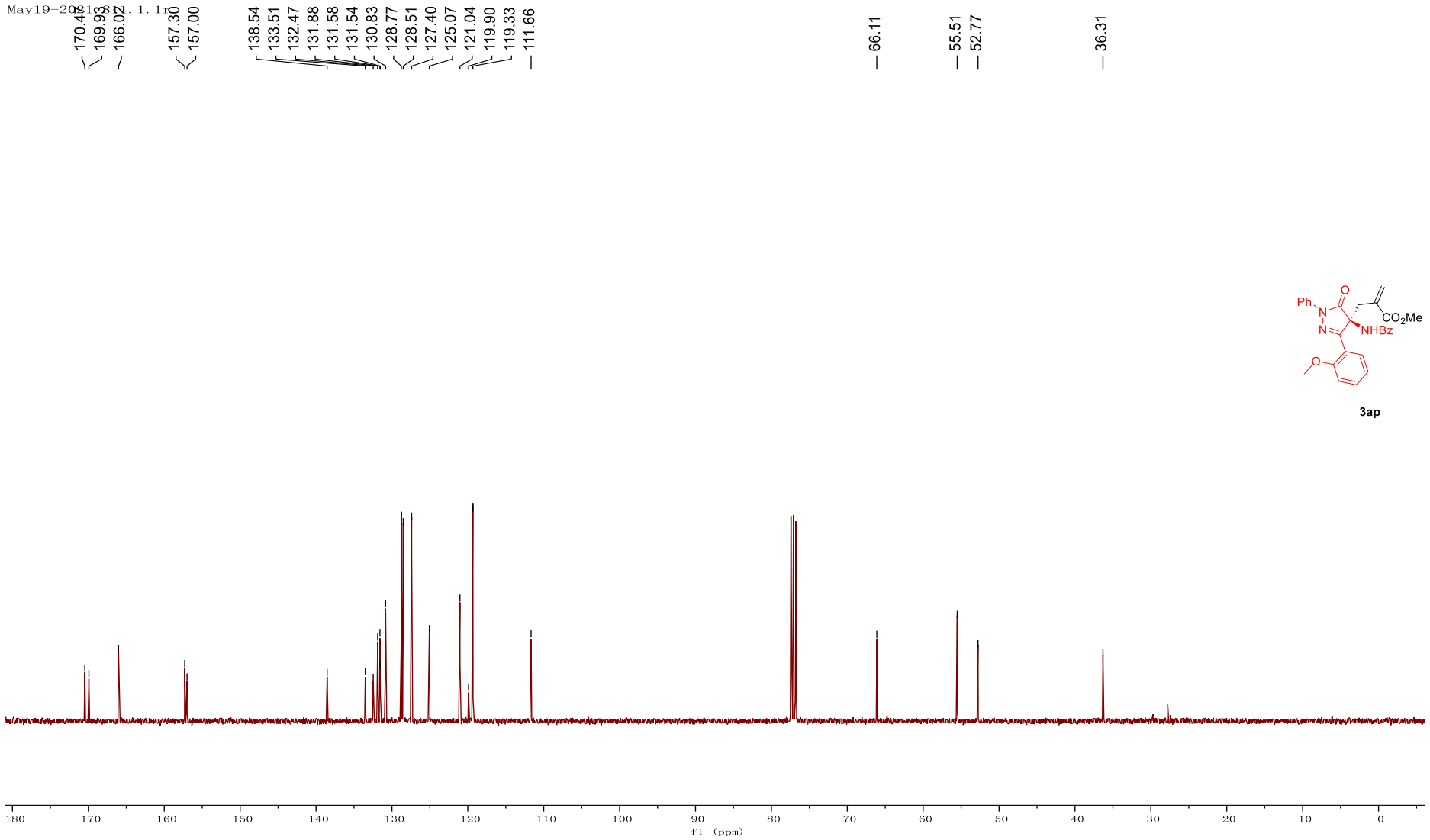
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


May19-2021 8:21:1.1r
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131.58
131.54
130.83
128.77
128.51
127.40
125.07
121.04
119.90
119.33
111.66
66.11
55.51
52.77
36.31
Ph
N
N
O
CO2Me
NHBz
O
3ap
180
170
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130
120
110
100
90
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70
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50
40
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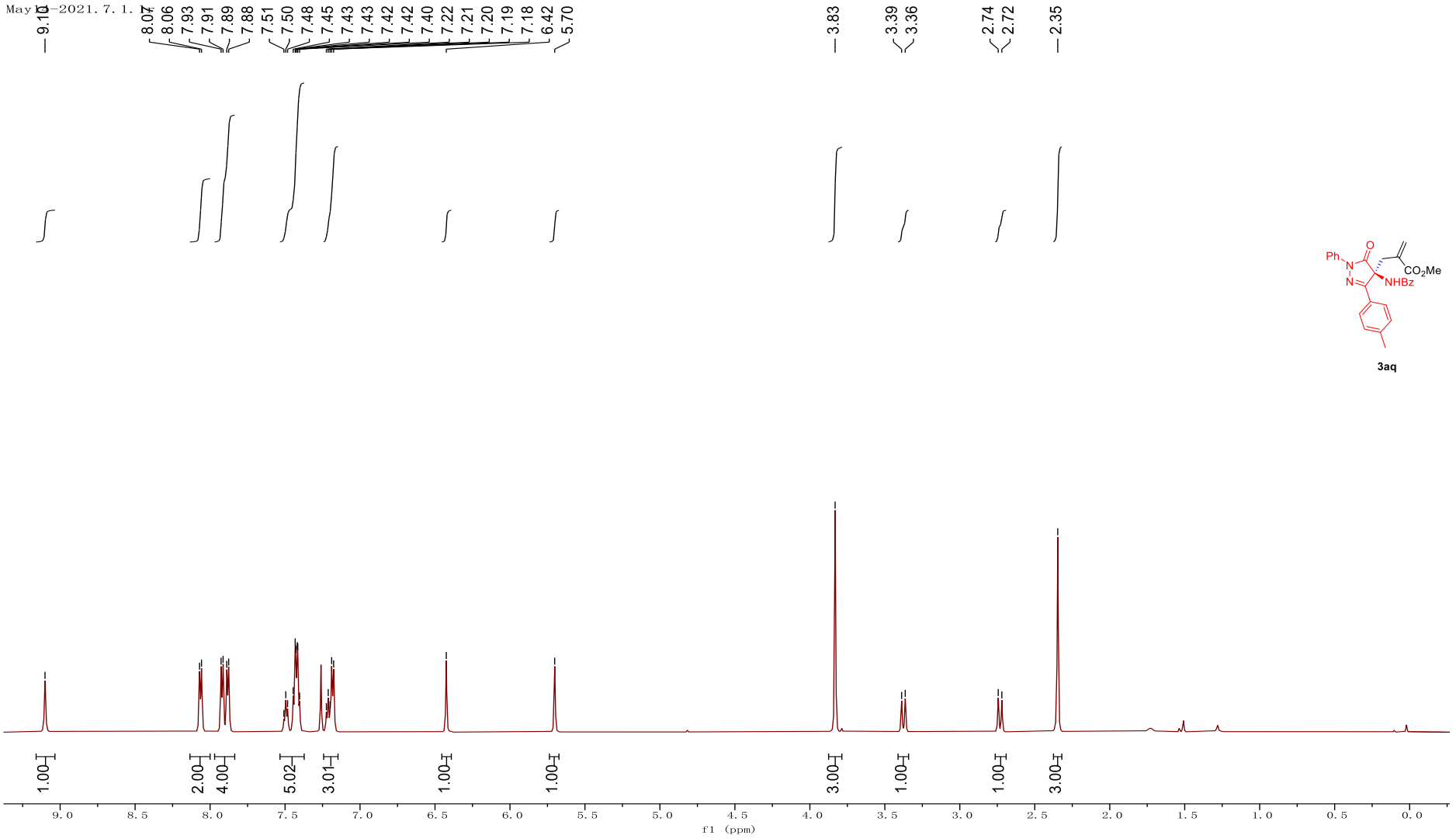
f1 (ppm)


May 4-2021.7.1.
9.10
8.07
8.06
7.93
7.91
7.89
7.88
7.51
7.50
7.48
7.45
7.43
7.43
7.42
7.42
7.40
7.22
7.21
7.20
7.19
7.18
6.42
5.70
3.83
3.39
3.36
2.74
2.72
2.35
Ph
N
N
O
NHBz
CO2Me
3aq
1.00
2.00
4.00
5.02
3.01
1.00
1.00
3.00
1.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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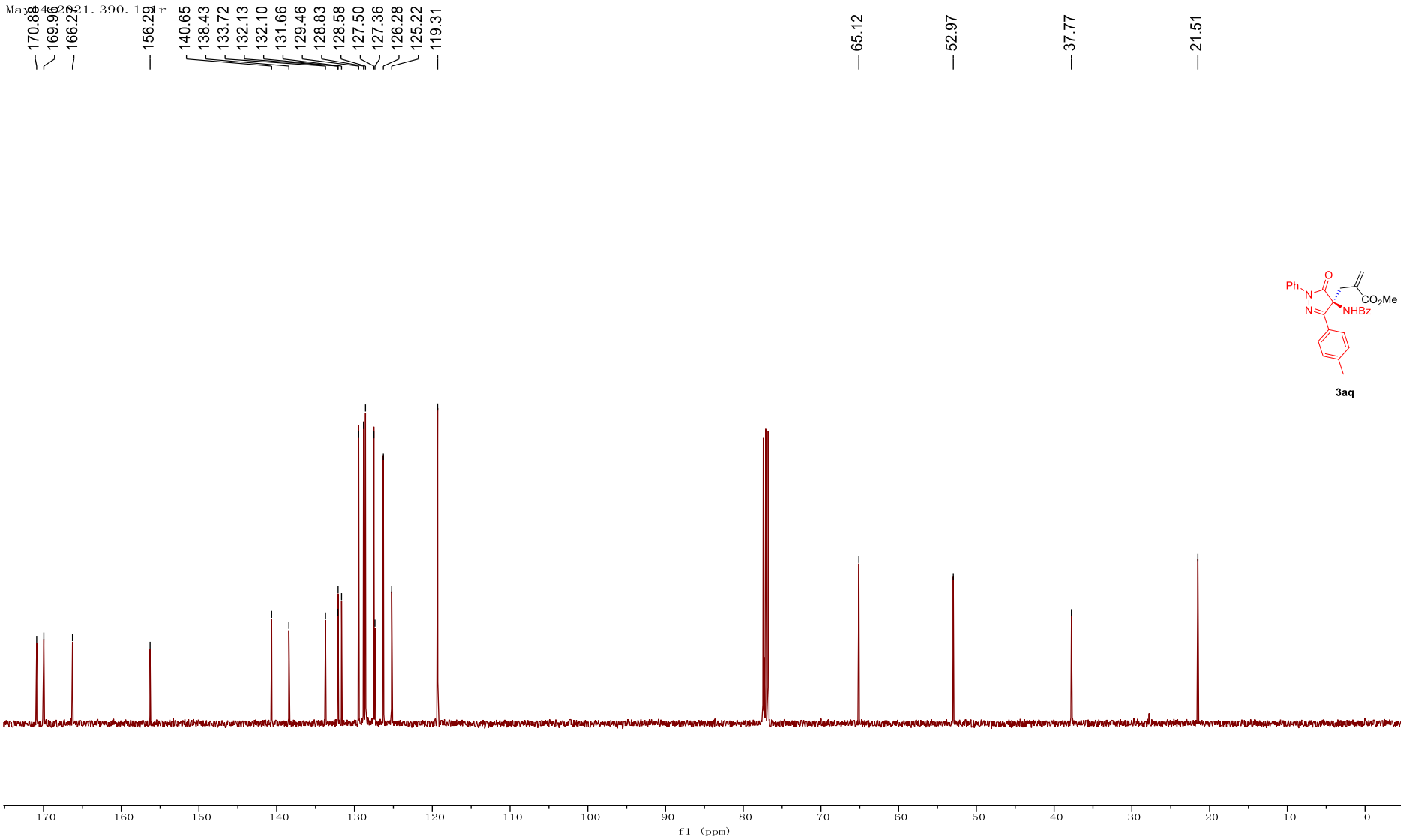
0.0
f1 (ppm)


May 4 2021. 390. 1r
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156.29
140.65
138.43
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132.13
132.10
131.66
129.46
128.83
128.58
127.50
127.36
126.28
125.22
119.31
65.12
52.97
37.77
21.51
Ph
N
N
O
NHBz
CO2Me
3aq
170
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130
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100
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50
40
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10
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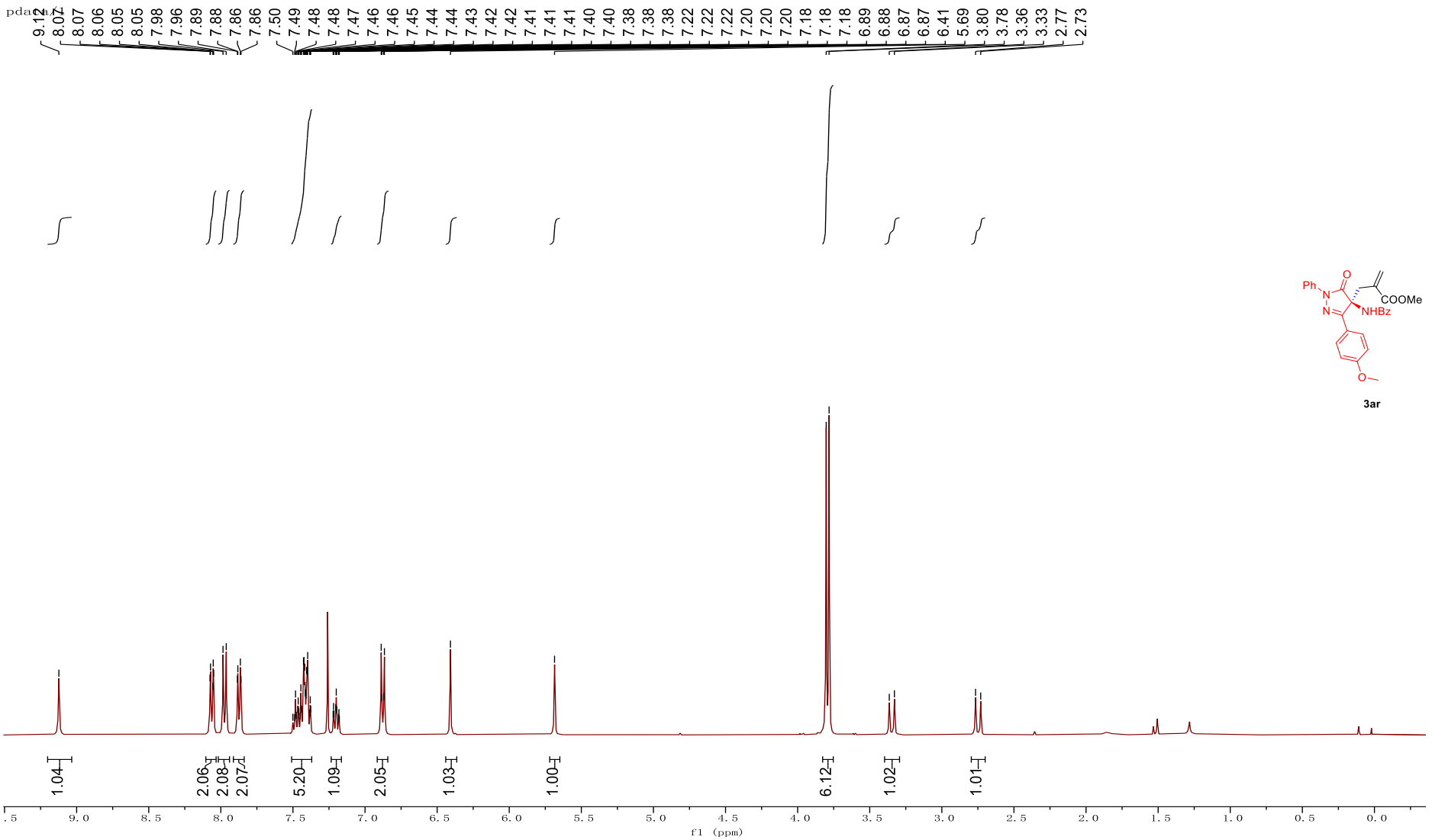
f1 (ppm)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7.96
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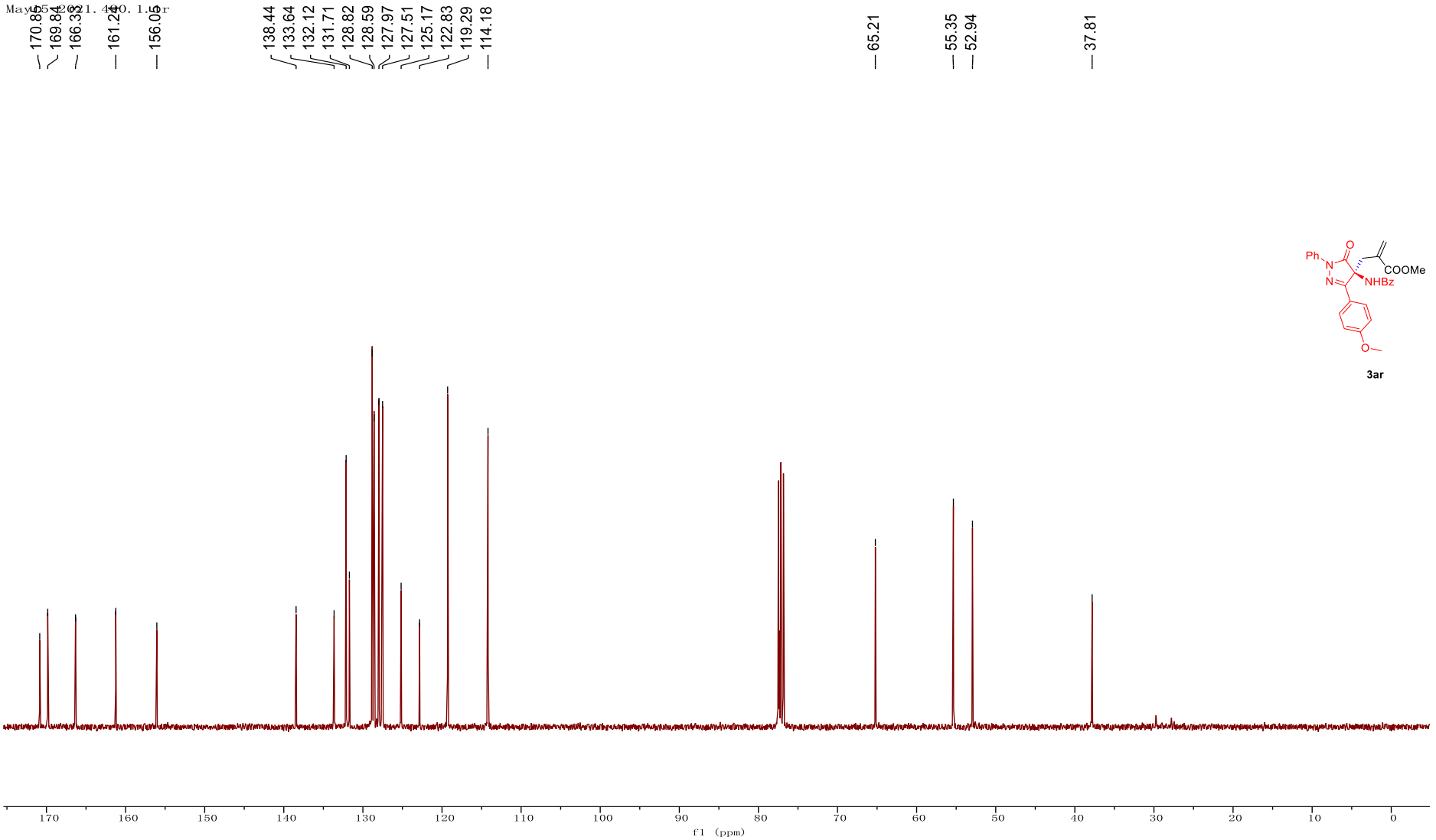
7.88
7.86
7.86
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.38
7.38
7.38
7.22
7.22
7.22
7.20
7.20
7.20
7.18
7.18
6.89
6.88
6.87
6.87
6.41
5.69
3.80
3.78
3.36
3.33
2.77
2.73
Ph
N
N
O
COOMe
NHBz
O
3ar
1.04
2.06
2.08
2.07
5.20
1.09
2.05
1.03
1.00
6.12
1.02
1.01
f1 (ppm)


May05_2021_440_1_1r
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166.38
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133.64
132.12
131.71
128.82
128.59
127.97
127.51
125.17
122.83
119.29
114.18
65.21
55.35
52.94
37.81
Ph
N
N
O
COOMe
NHBz
O
3ar
170
160
150
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130
120
110
100
90
80
70
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50
40
30
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10
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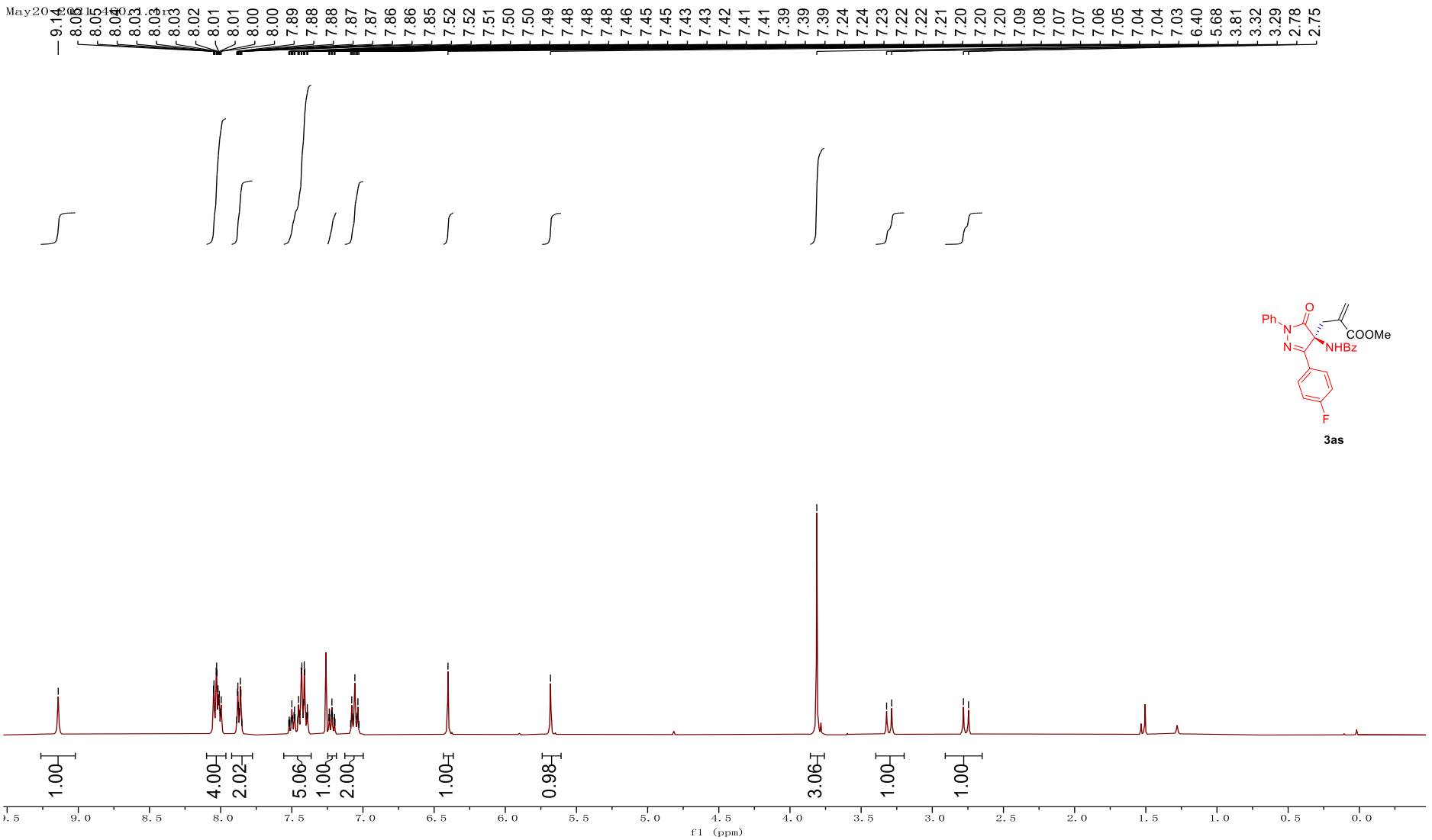
f1 (ppm)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8.04
8.03
8.02
8.01
8.00
7.89
7.88
7.87
7.86
7.85
7.52
7.51
7.50
7.49
7.48
7.46
7.45
7.43
7.42
7.41
7.39
7.24
7.23
7.22
7.21
7.20
7.09
7.08
7.07
7.06
7.05
7.04
7.03
6.40
5.68
3.81
3.32
3.29
2.78
2.75
Ph
N
N
O
COOMe
NHBz
F
3as
1.00
4.00
2.02
5.06
1.00
2.00
1.00
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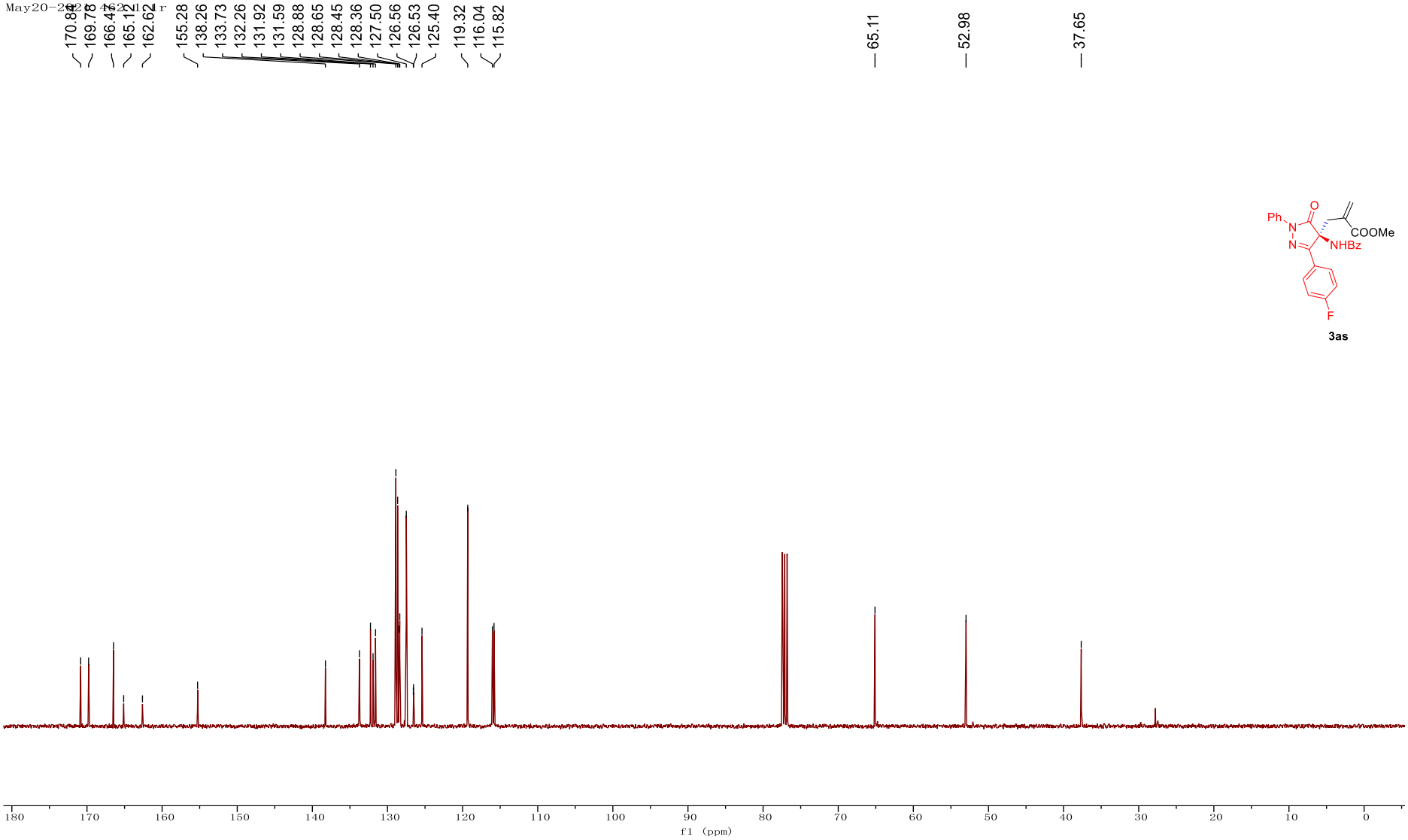
3.06
1.00
1.00
f1 (ppm)


May20-2021-S2-1H-1r
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166.47
165.12
162.62
155.28
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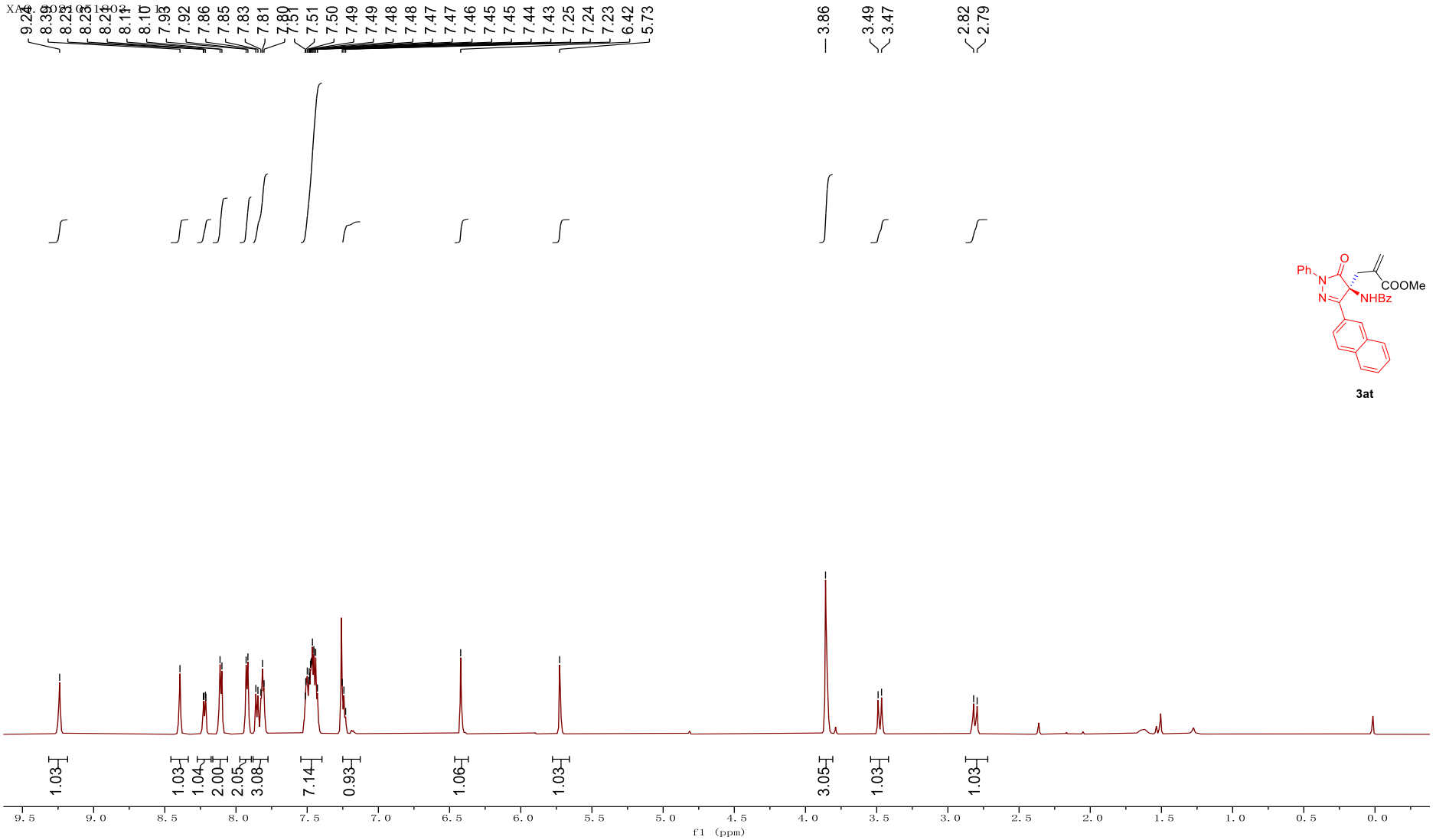
133.73
132.26
131.92
131.59
128.88
128.65
128.45
128.36
127.50
126.56
126.53
125.40
119.32
116.04
115.82
65.11
52.98
37.65
Ph
N
N
O
COOMe
NHBz
F
3as
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.24
8.39
8.23
8.23
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8.11
8.10
7.93
7.92
7.86
7.85
7.83
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7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.25
7.24
7.23
6.42
5.73
3.86
3.49
3.47
2.82
2.79
Ph
N
N
O
COOMe
NHBz
1.03
1.03
1.04
2.00
2.05
3.08
7.14
0.93
1.06
1.03
3.05
1.03
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
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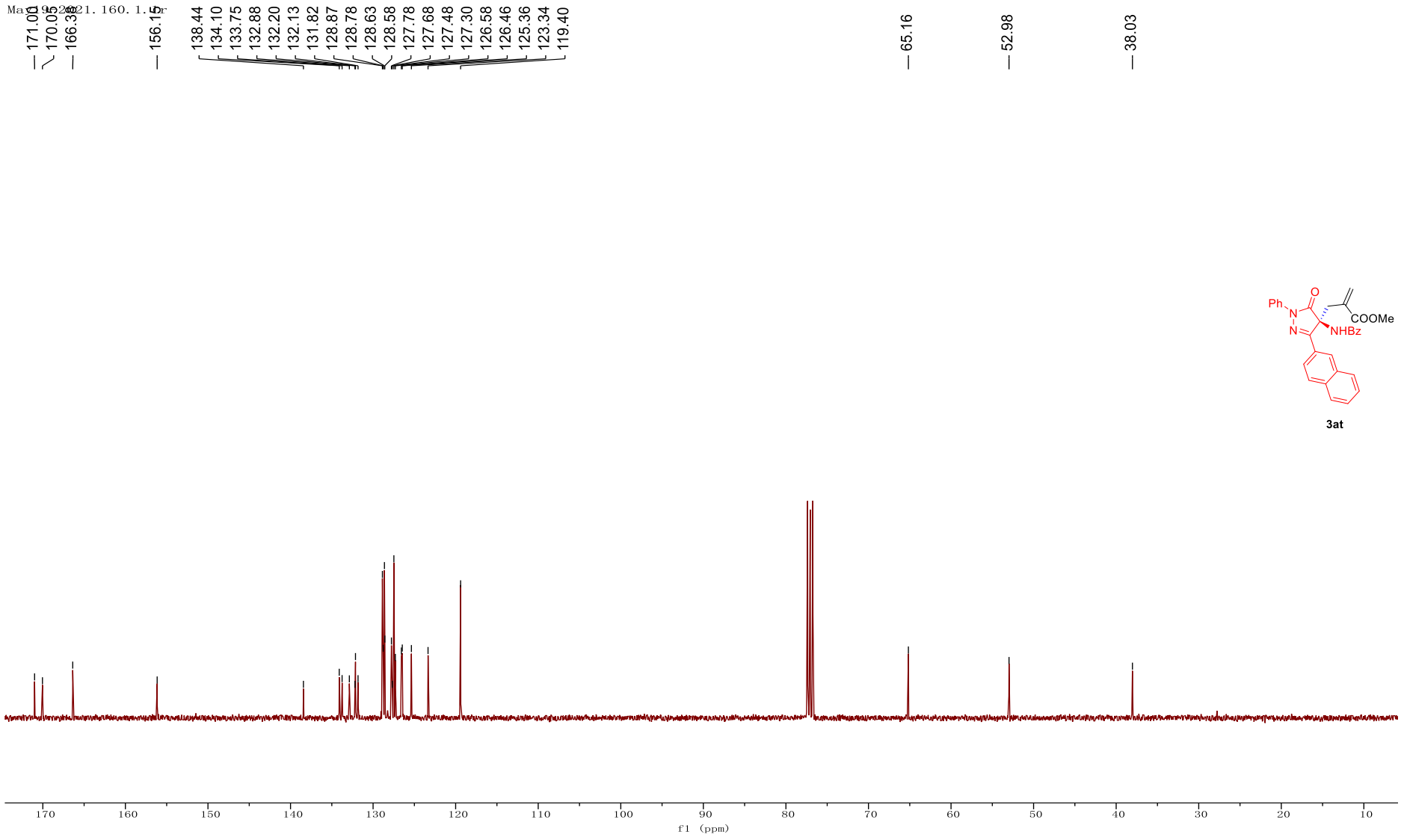
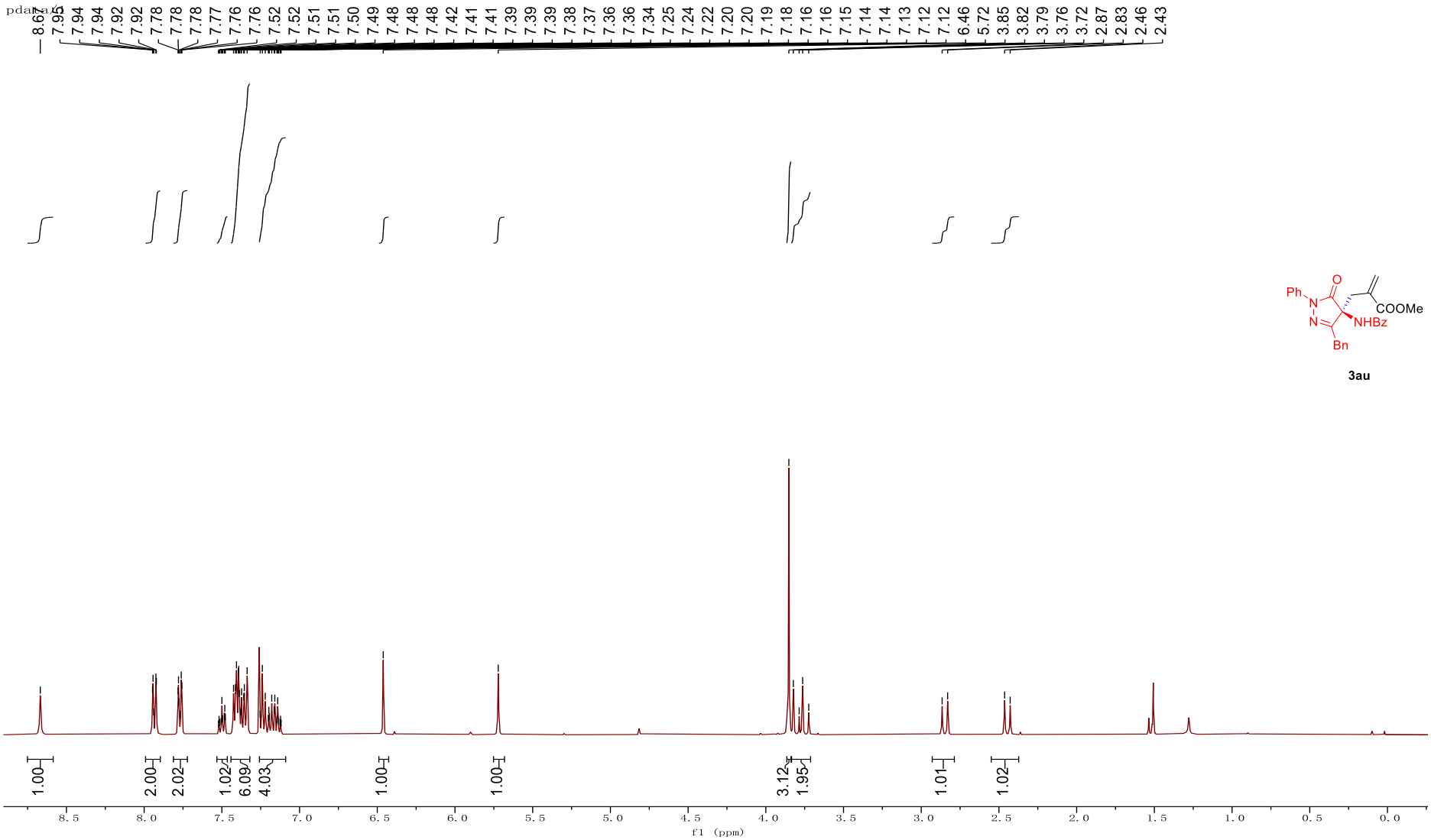
0.0
f1 (ppm)

3at


May 19 2021. 160. 1. 1r
171.00
170.05
166.38
156.15
138.44
134.10
133.75
132.88
132.20
132.13
131.82
128.87
128.78
128.63
128.58
127.78
127.68
127.48
127.30
126.58
126.46
125.36
123.34
119.40
65.16
52.98
38.03
Ph
N
N
O
COOMe
NHBz
3at
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


pdata1
8.62
7.95
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7.94
7.92
7.92
7.78
7.78
7.78
7.77
7.76
7.76
7.52
7.52
7.51
7.51
7.50
7.49
7.48
7.48
7.48
7.42
7.41
7.41
7.39
7.39
7.39
7.38
7.37
7.36
7.36
7.34
7.25
7.24
7.22
7.20
7.20
7.19
7.18
7.16
7.16
7.15
7.14
7.14
7.13
7.12
7.12
6.46
5.72
3.85
3.82
3.79
3.76
3.72
2.87
2.83
2.46
2.43
Ph
N
O
N
NHBz
Bn
COOMe
1.00
2.00
2.02
1.02
6.09
4.03
1.00
1.00
3.12
1.95
1.01
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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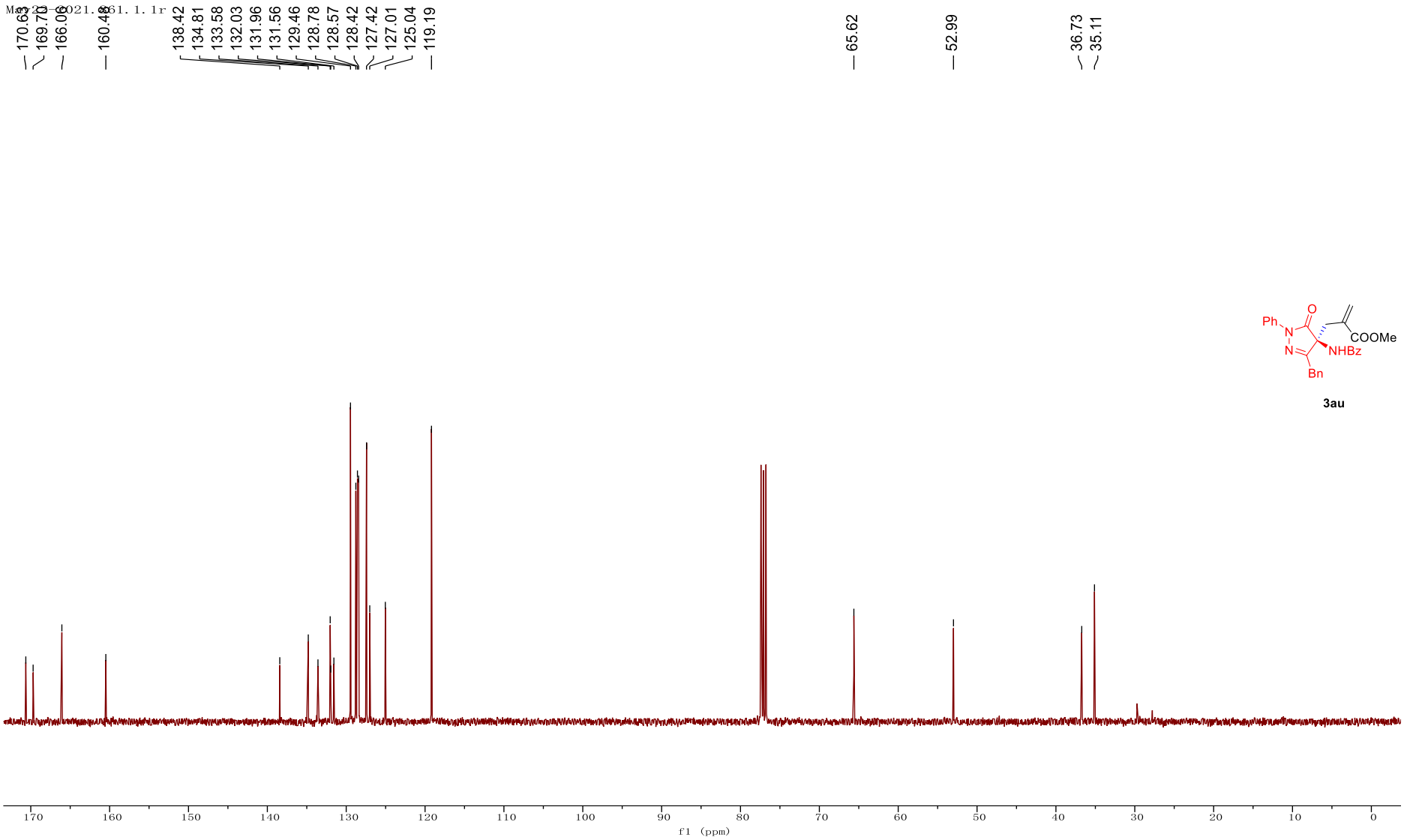
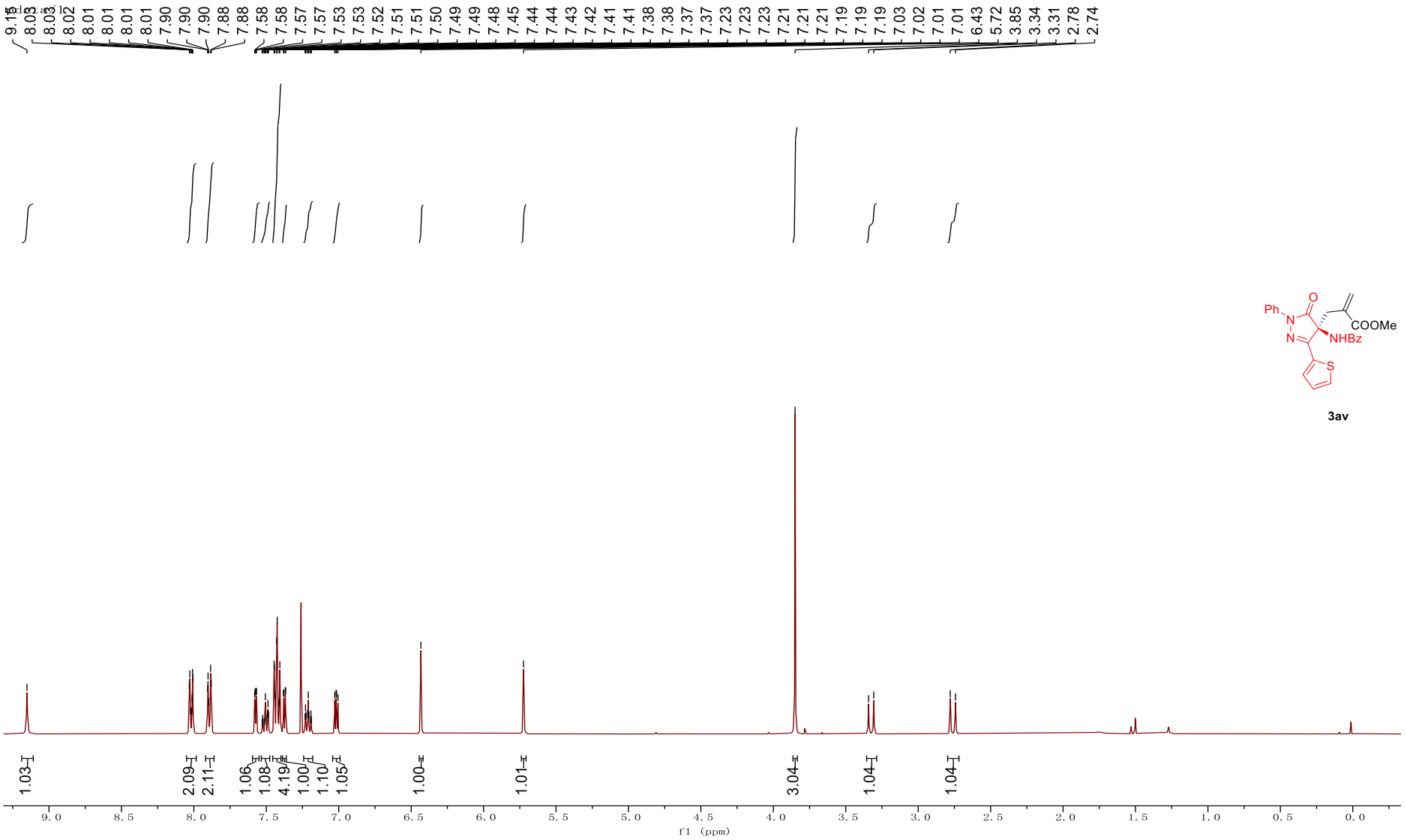
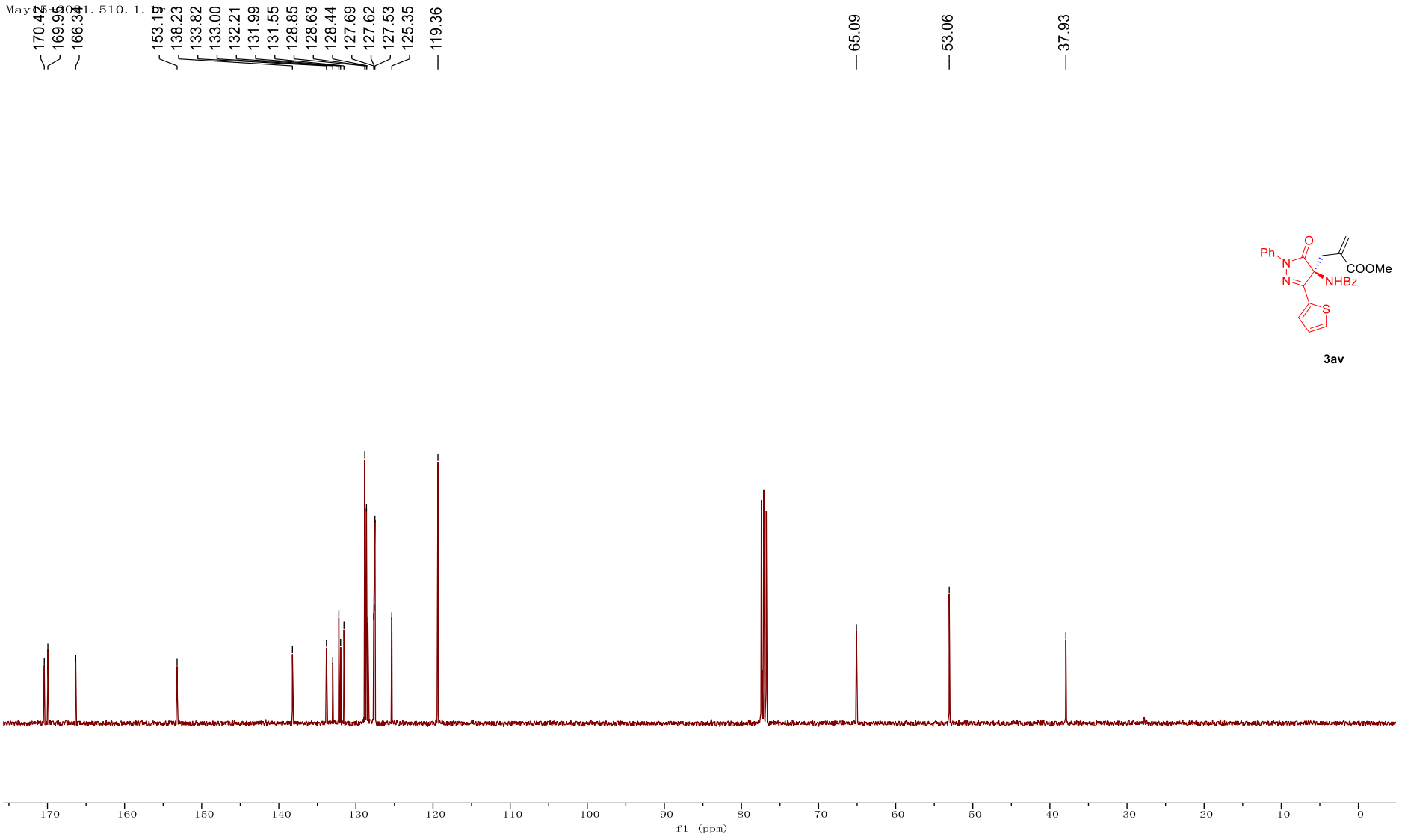
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3au


Mar20-2021.861.1.1r
170.63
169.78
166.06
160.48
138.42
134.81
133.58
132.03
131.96
131.56
129.46
128.78
128.57
128.42
127.42
127.01
125.04
119.19
65.62
52.99
36.73
35.11
Ph
N
N
O
COOMe
NHBz
Bn
3au
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.15
8.03
8.03
8.02
8.01
8.01
8.01
8.01
7.90
7.90
7.90
7.88
7.88
7.58
7.58
7.57
7.57
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.45
7.44
7.44
7.43
7.42
7.41
7.41
7.38
7.38
7.37
7.37
7.23
7.23
7.23
7.21
7.21
7.21
7.19
7.19
7.19
7.03
7.02
7.01
7.01
6.43
5.72
3.85
3.34
3.31
2.78
2.74
Ph
N
N
O
NHBz
COOMe
S
3av
1.03
2.09
2.11
1.06
1.08
4.19
1.00
1.10
1.05
1.00
1.01
3.04
1.04
1.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


May 15 2011 510 1 1
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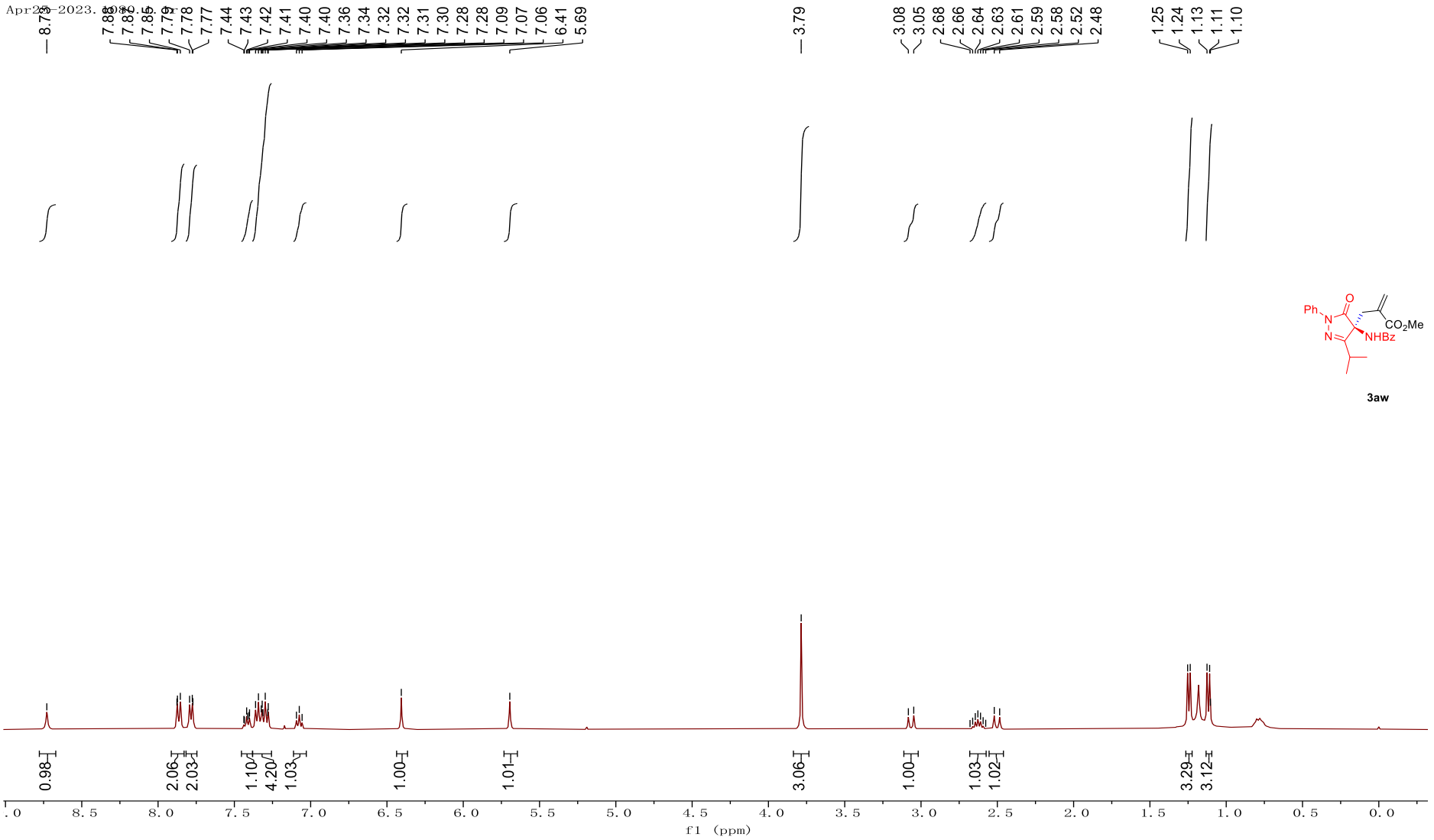
169.96
166.34
153.19
138.23
133.82
133.00
132.21
131.99
131.55
128.85
128.63
128.44
127.69
127.62
127.53
125.35
119.36
65.09
53.06
37.93
Ph
N
N
O
COOMe
NHBz
S
3av
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Apr28-2023
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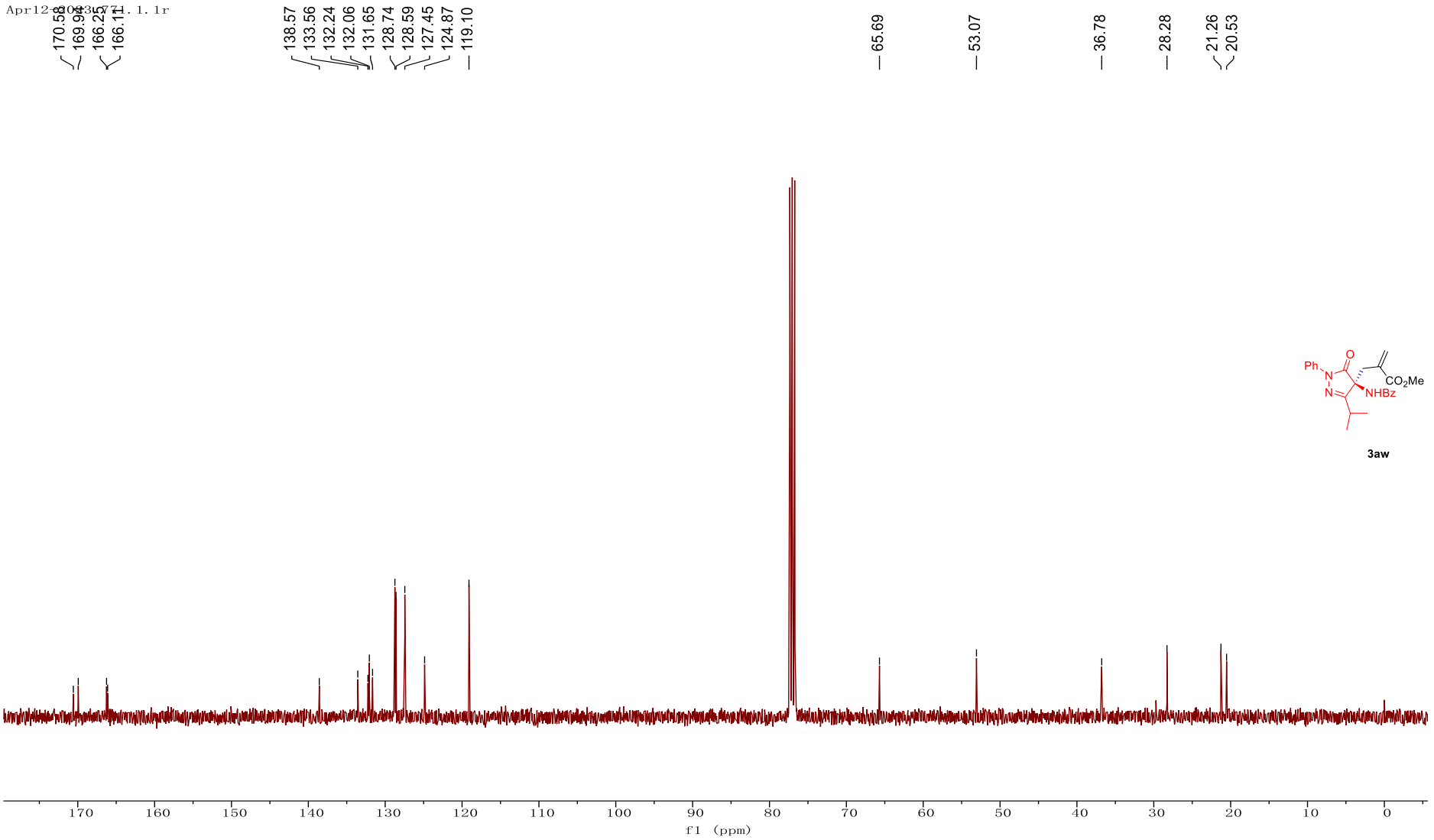
7.88
7.87
7.85
7.79
7.78
7.77
7.44
7.43
7.42
7.41
7.40
7.40
7.36
7.34
7.32
7.32
7.31
7.30
7.28
7.28
7.09
7.07
7.06
6.41
5.69
3.79
3.08
3.05
2.68
2.66
2.64
2.63
2.61
2.59
2.58
2.52
2.48
1.25
1.24
1.13
1.11
1.10
Ph
N
N
O
NHBz
CO2Me
3aw
0.98
2.06
2.03
1.10
4.20
1.03
1.00
1.01
3.06
1.00
1.03
1.02
3.29
3.12
f1 (ppm)


Apr12-2013-771-1.1.1r
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166.25
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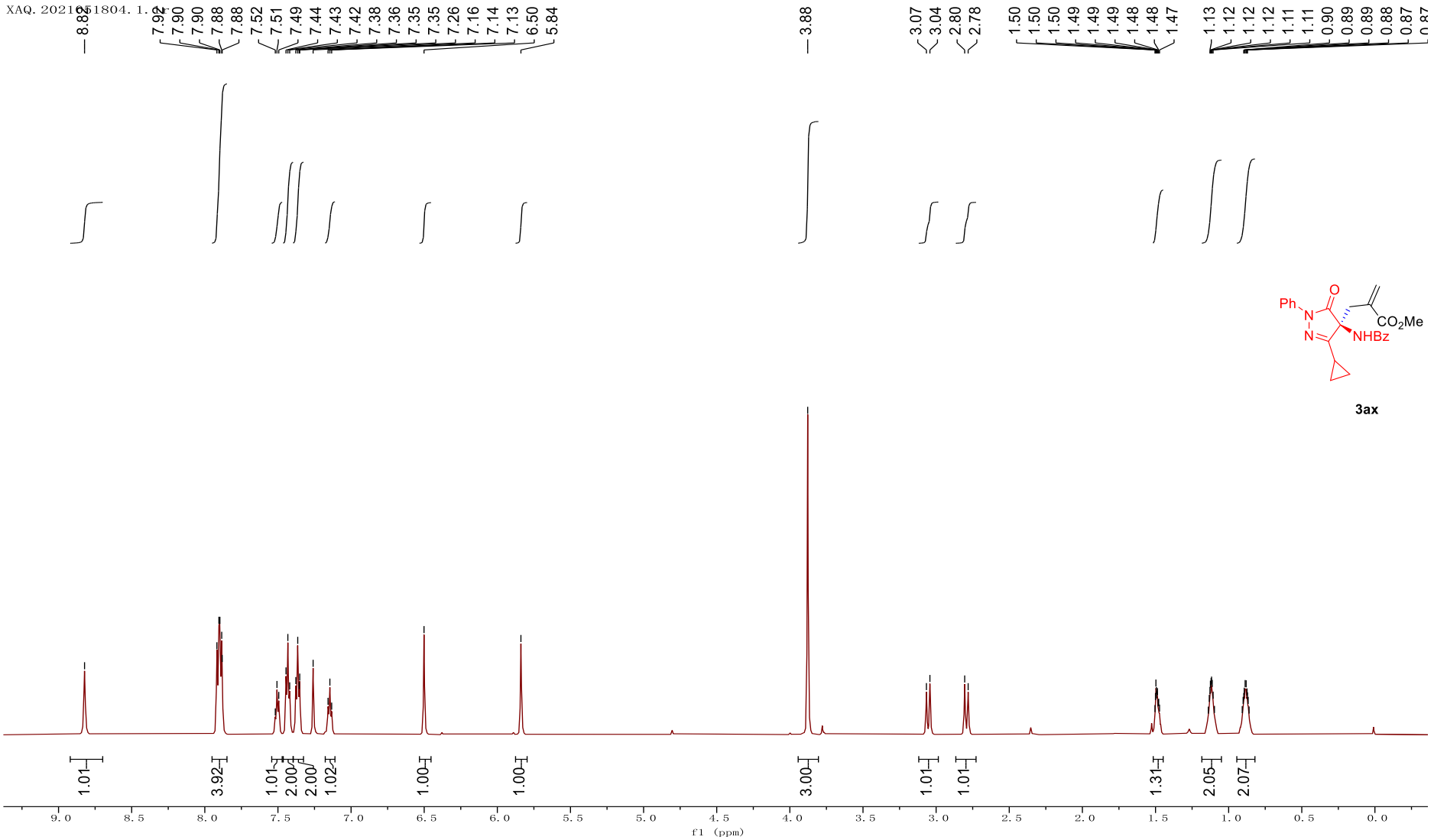
138.57
133.56
132.24
132.06
131.65
128.74
128.59
127.45
124.87
119.10
65.69
53.07
36.78
28.28
21.26
20.53
Ph
N
N
O
NHBz
CO2Me
3aw
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


XAQ. 20210518O4. 1. 1r
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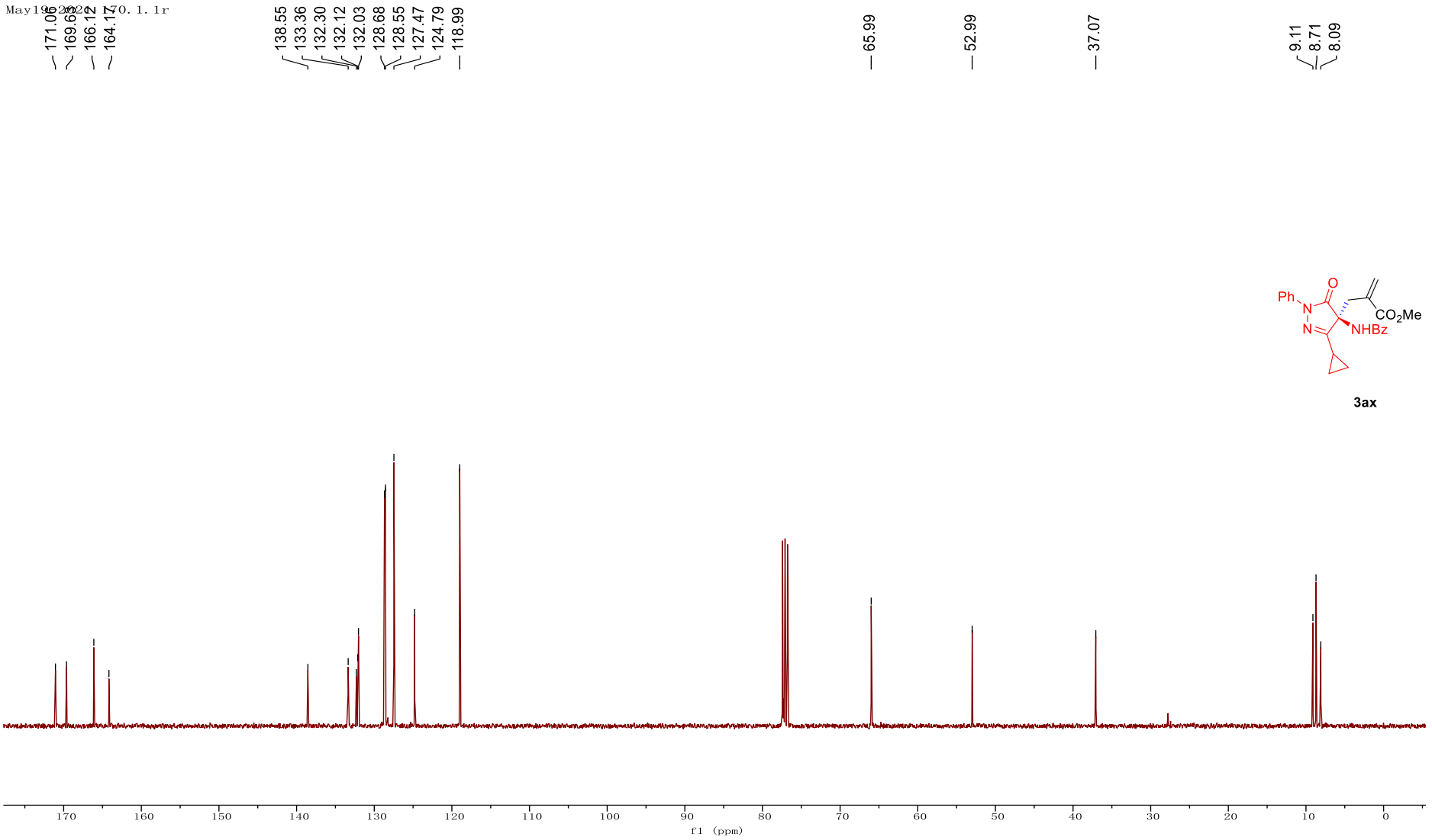
7.90
7.88
7.88
7.52
7.51
7.49
7.44
7.43
7.42
7.38
7.36
7.35
7.35
7.26
7.16
7.14
7.13
6.50
5.84
3.88
3.07
3.04
2.80
2.78
1.50
1.50
1.50
1.49
1.49
1.49
1.48
1.48
1.47
1.13
1.12
1.12
1.12
1.11
1.11
0.90
0.89
0.89
0.88
0.87
Ph
N
N
O
NHBz
CO2Me
3ax
1.01
3.92
1.01
2.00
2.00
1.02
1.00
1.00
3.00
1.01
1.01
1.31
2.05
2.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


May19 2022 70.1.1r
171.06
169.62
166.12
164.17
138.55
133.36
132.30
132.12
132.03
128.68
128.55
127.47
124.79
118.99
65.99
52.99
37.07
9.11
8.71
8.09
Ph
N
N
O
NHBz
CO2Me
3ax
170
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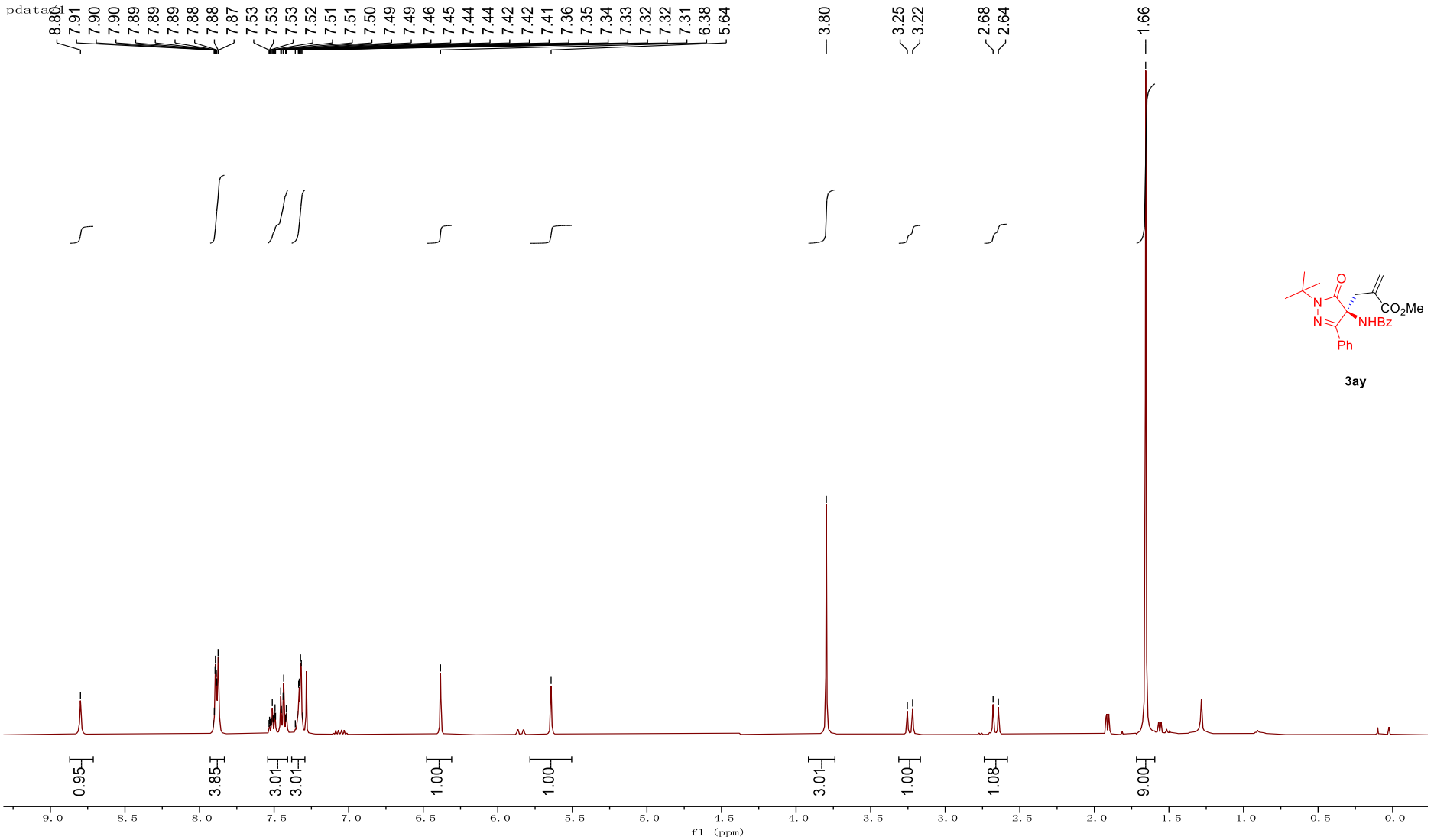
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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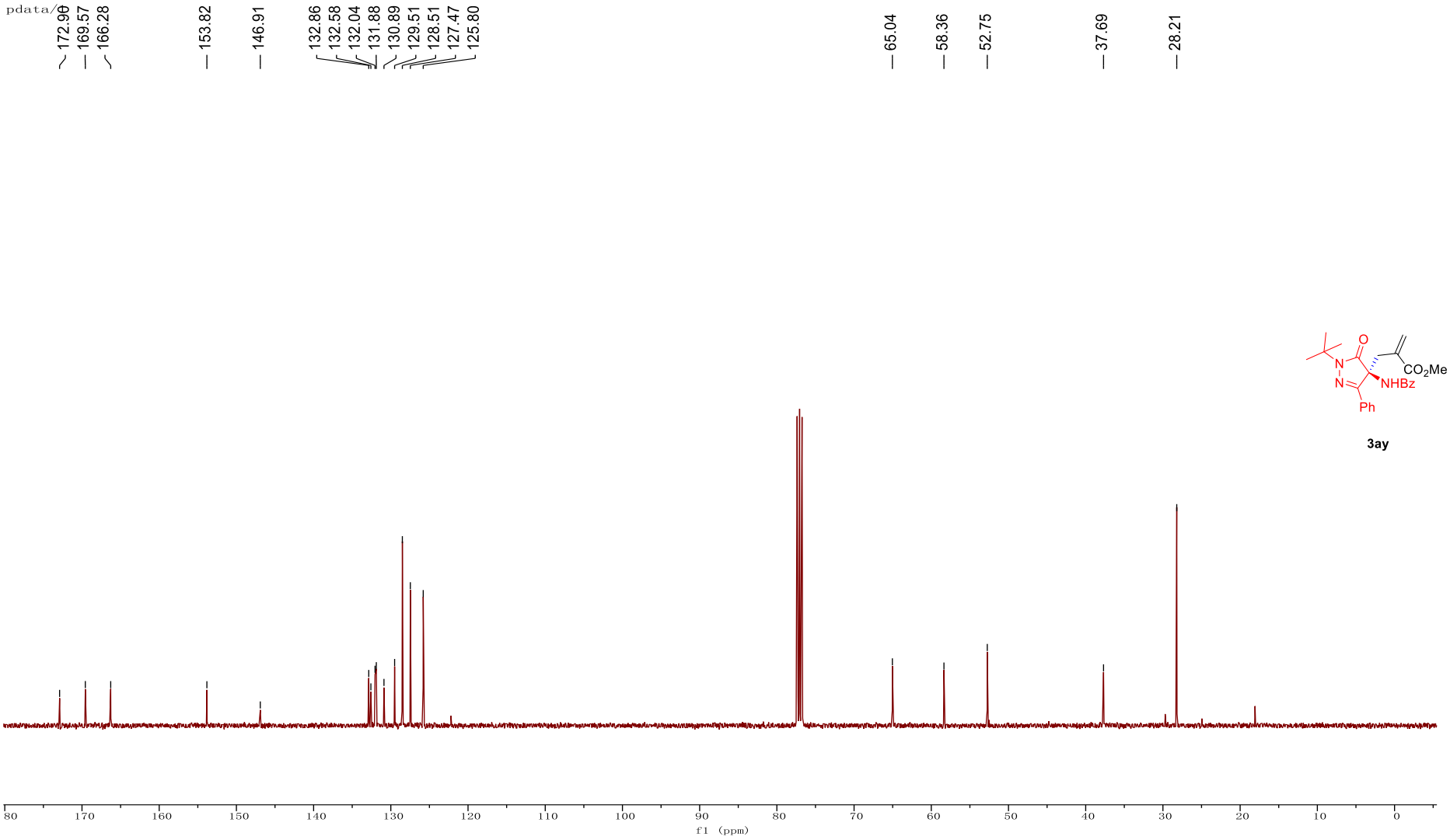
7.89
7.89
7.88
7.88
7.87
7.53
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.49
7.46
7.45
7.44
7.44
7.42
7.42
7.41
7.36
7.35
7.34
7.33
7.32
7.32
7.31
6.38
5.64
3.80
3.25
3.22
2.68
2.64
1.66
0.95
3.85
3.01
3.01
1.00
1.00
3.01
1.00
1.08
9.00
f1 (ppm)
O
N
N
CO2Me
NHBz
Ph
3ay


pdata/
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166.28
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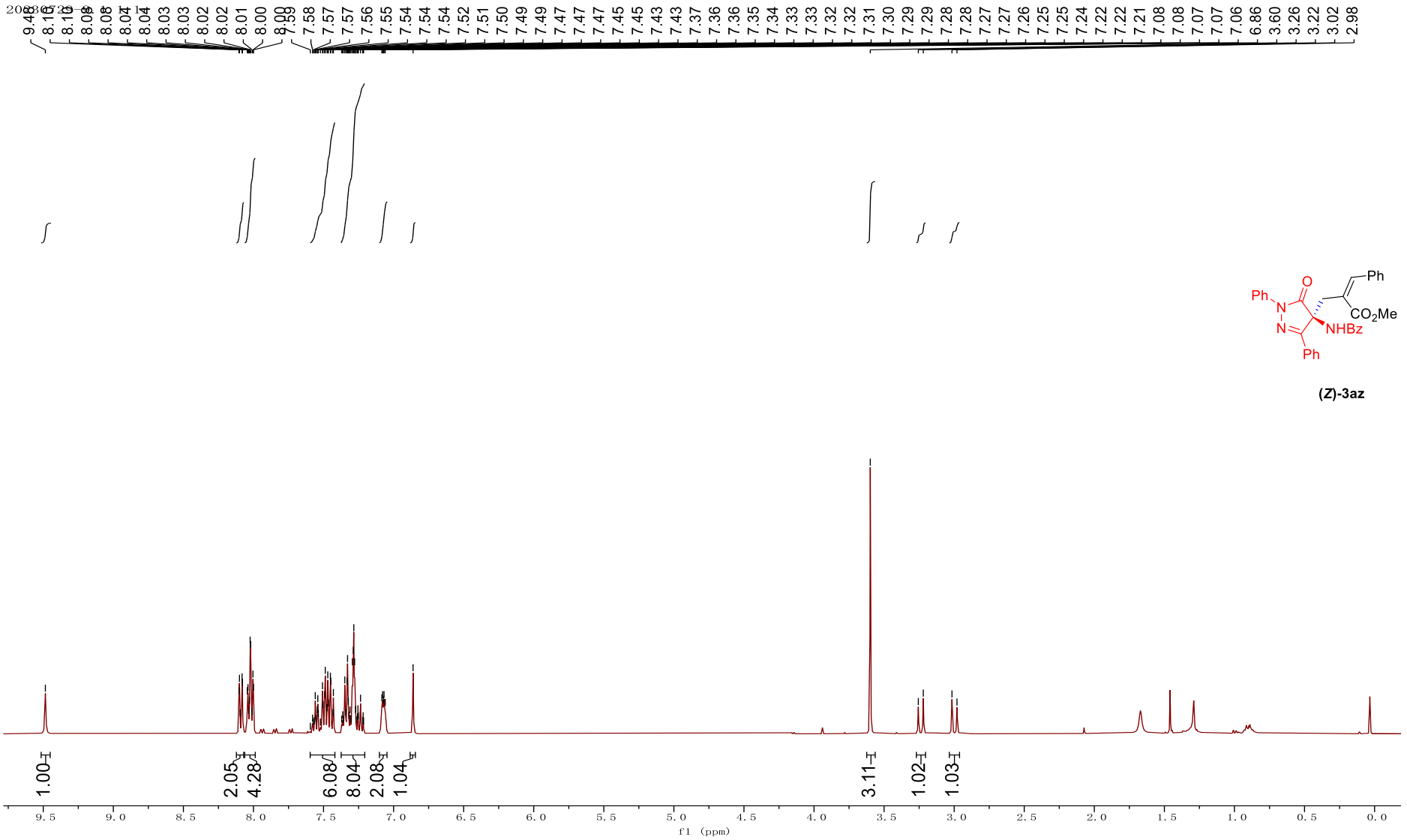
146.91
132.86
132.58
132.04
131.88
130.89
129.51
128.51
127.47
125.80
65.04
58.36
52.75
37.69
28.21
O
N
N
NHBz
Ph
CO2Me
3ay
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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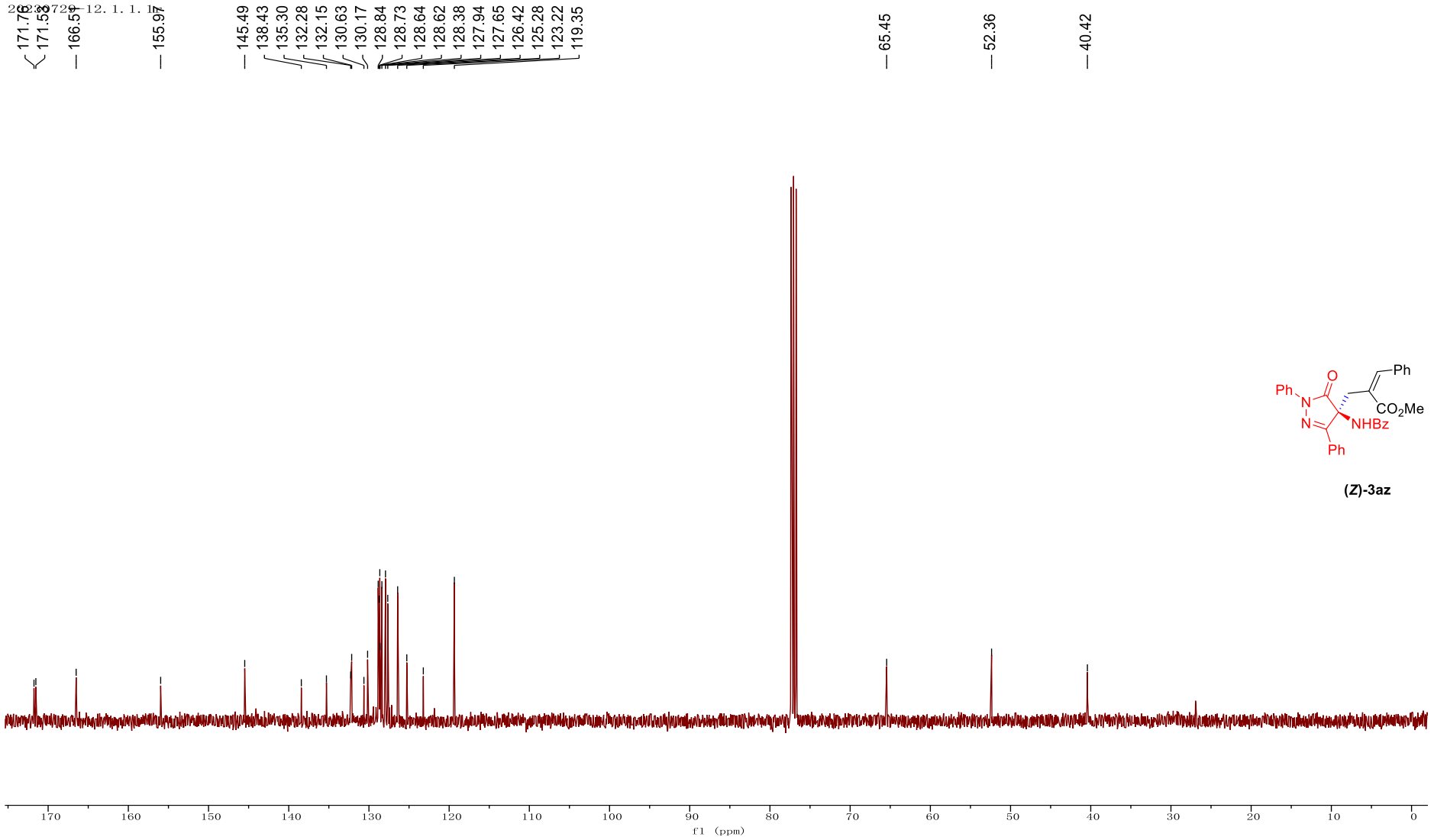
Ph
O
Ph
N
N
CO2Me
NHBz
Ph
1.00
2.05
4.28
6.08
8.04
2.08
1.04
3.11
1.02
1.03
f1 (ppm)

(*Z*)-3az


171.76
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166.59
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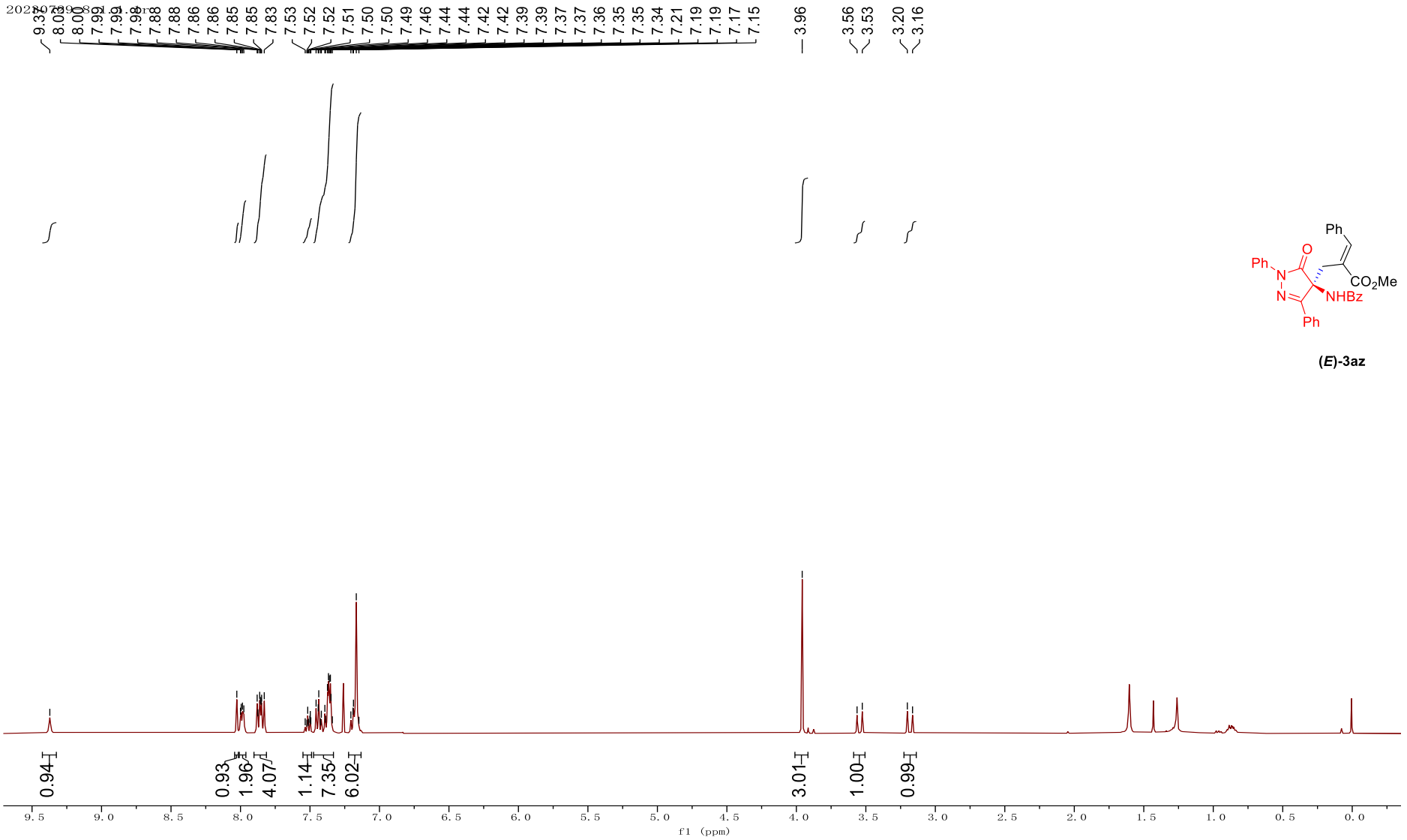
138.43
135.30
132.28
132.15
130.63
130.17
128.84
128.73
128.64
128.62
128.38
127.94
127.65
126.42
125.28
123.22
119.35
65.45
52.36
40.42
Ph
O
Ph
N
N
CO2Me
NHBz
Ph
(Z)-3az
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.32
8.08
8.00
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7.99
7.98
7.88
7.88
7.86
7.86
7.85
7.85
7.83
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.46
7.44
7.44
7.42
7.42
7.39
7.39
7.37
7.37
7.36
7.35
7.35
7.34
7.21
7.19
7.19
7.17
7.15
3.96
3.56
3.53
3.20
3.16
0.94
0.93
1.96
4.07
1.14
7.35
6.02
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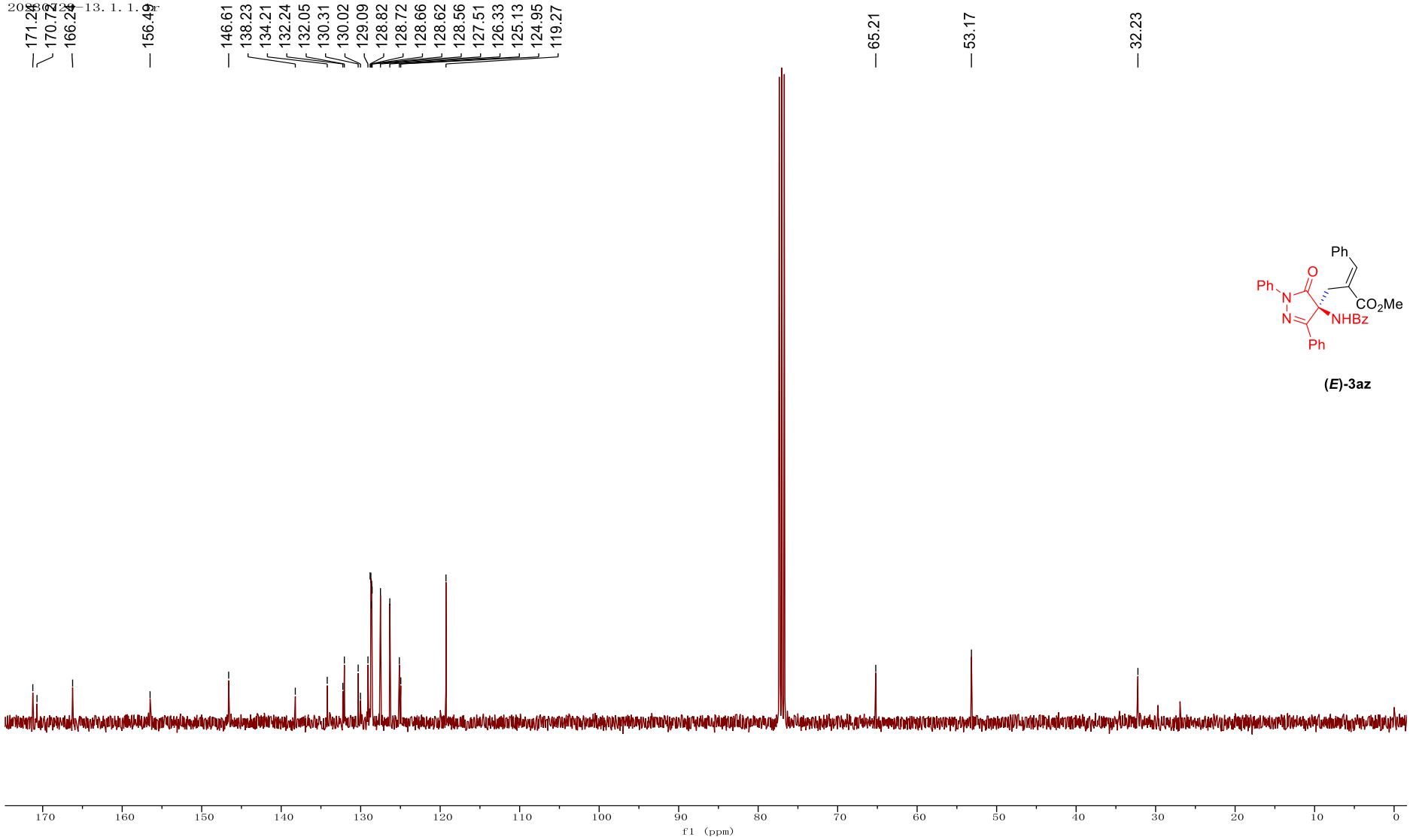
1.00
0.99
f1 (ppm)

Ph
O
Ph
N
N
CO2Me
NHBz
Ph

(*E*)-3az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170.72
166.24
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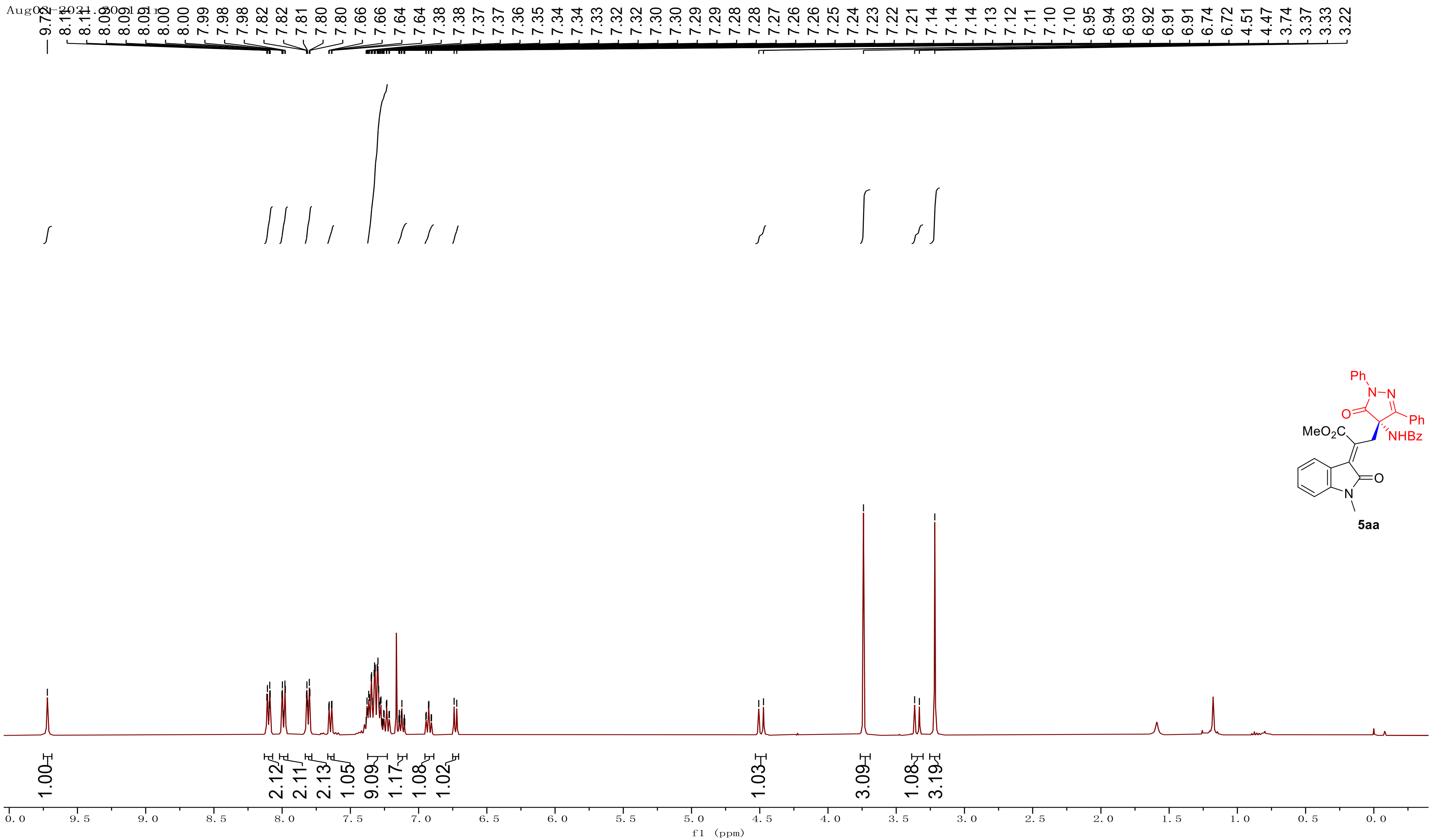
146.61
138.23
134.21
132.24
132.05
130.31
130.02
129.09
128.82
128.72
128.66
128.62
128.56
127.51
126.33
125.13
124.95
119.27
65.21
53.17
32.23
Ph
O
Ph
N
N
CO2Me
NHBz
Ph
f1 (ppm)

(*E*)-3az



Aug02-2021.30.1.1
9.72
8.11
8.11
8.09
8.09
8.01
8.00
8.00
7.99
7.98
7.98
7.82
7.82
7.81
7.80
7.80
7.66
7.66
7.64
7.64
7.38
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.23
7.22
7.21
7.14
7.14
7.14
7.13
7.12
7.11
7.10
7.10
6.95
6.94
6.93
6.92
6.91
6.91
6.74
6.72
4.51
4.47
3.74
3.37
3.33
3.22
Ph
N
N
O
Ph
MeO2C
NHBz
O
N
5aa
1.00
2.12
2.11
2.13
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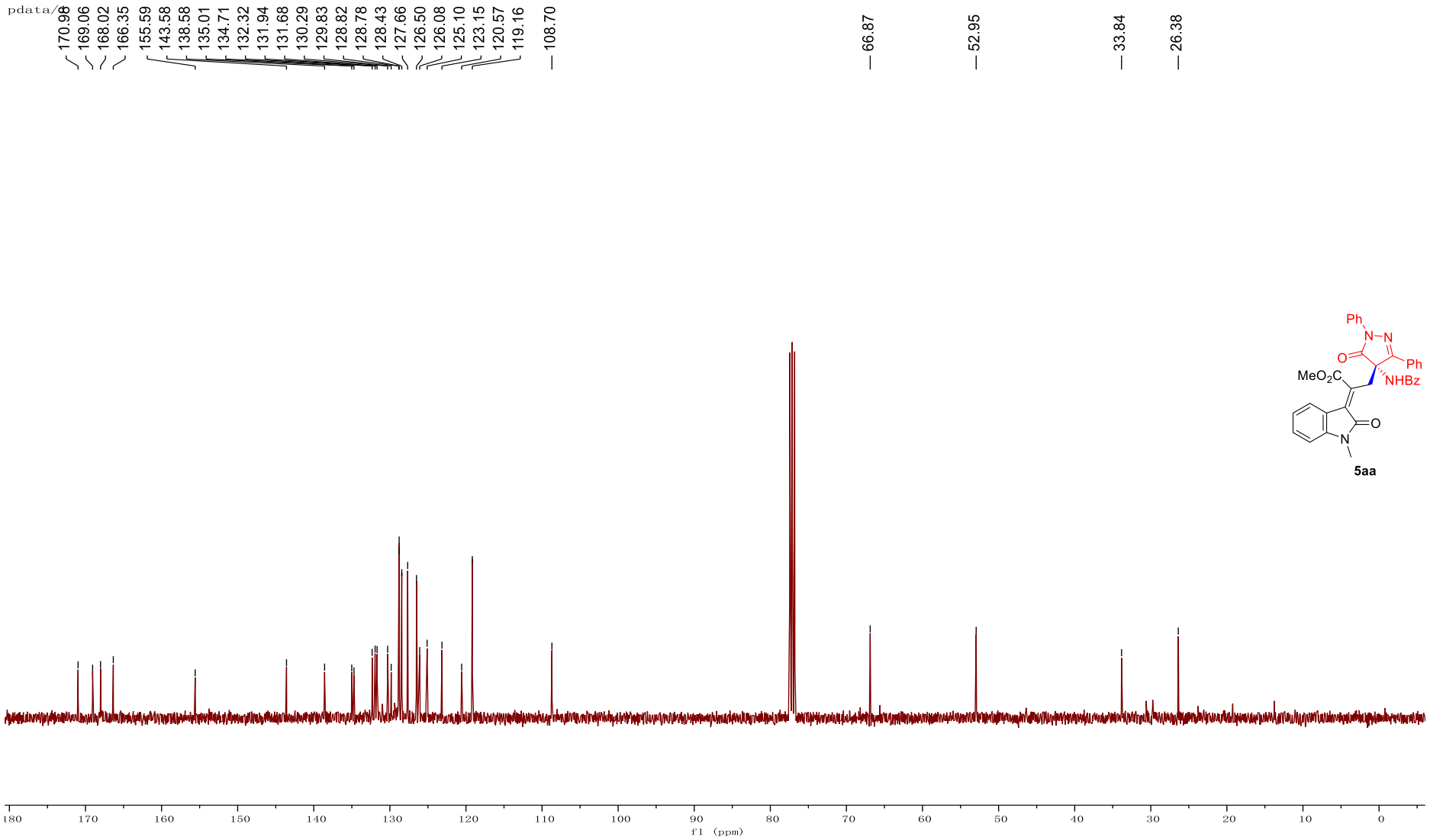
9.09
1.17
1.08
1.02
1.03
3.09
1.08
3.19
f1 (ppm)


pdata/
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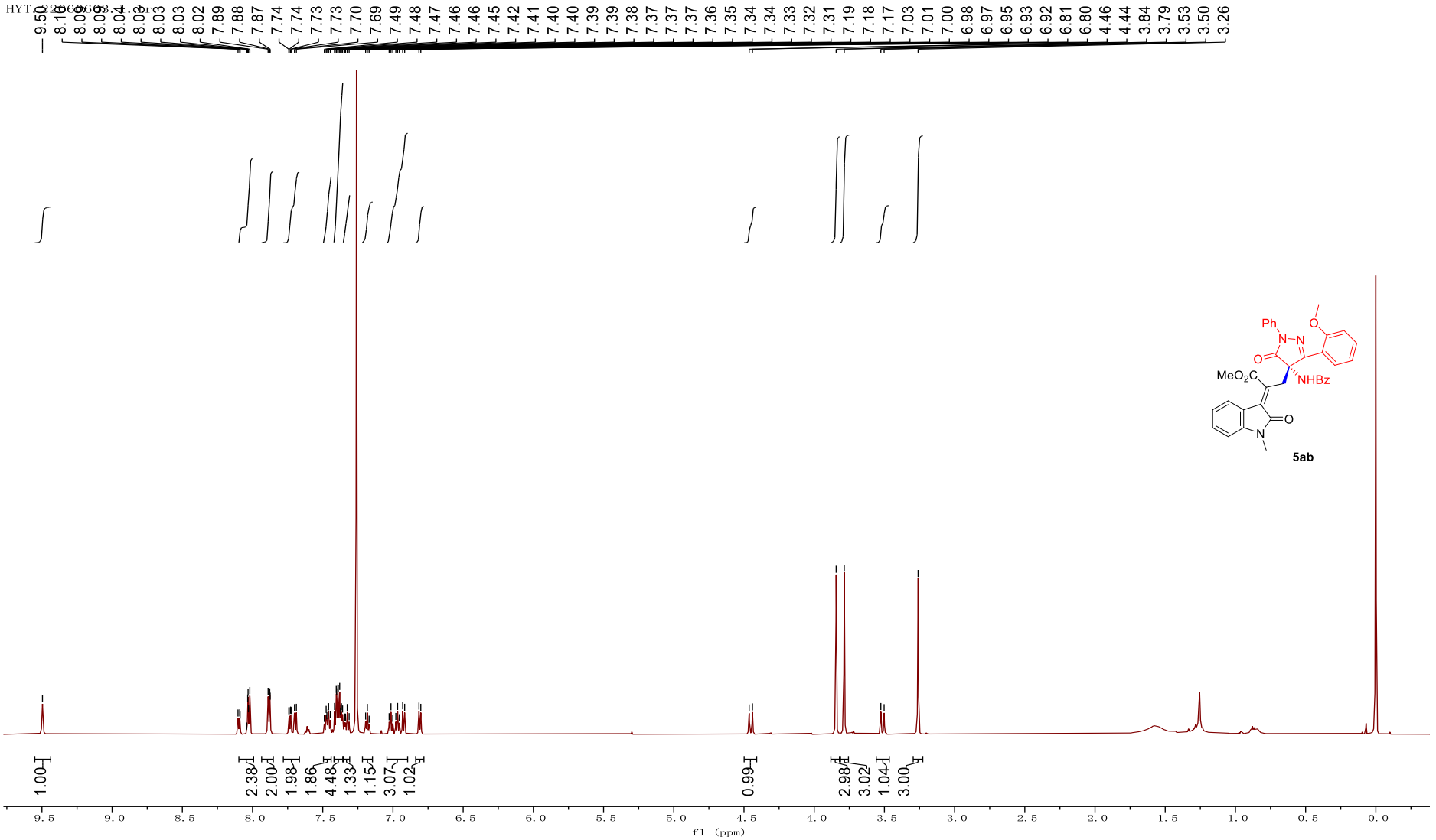
168.02
166.35
155.59
143.58
138.58
135.01
134.71
132.32
131.94
131.68
130.29
129.83
128.82
128.78
128.43
127.66
126.50
126.08
125.10
123.15
120.57
119.16
108.70
66.87
52.95
33.84
26.38
Ph
N
N
O
Ph
MeO2C
NHBz
O
N
5aa
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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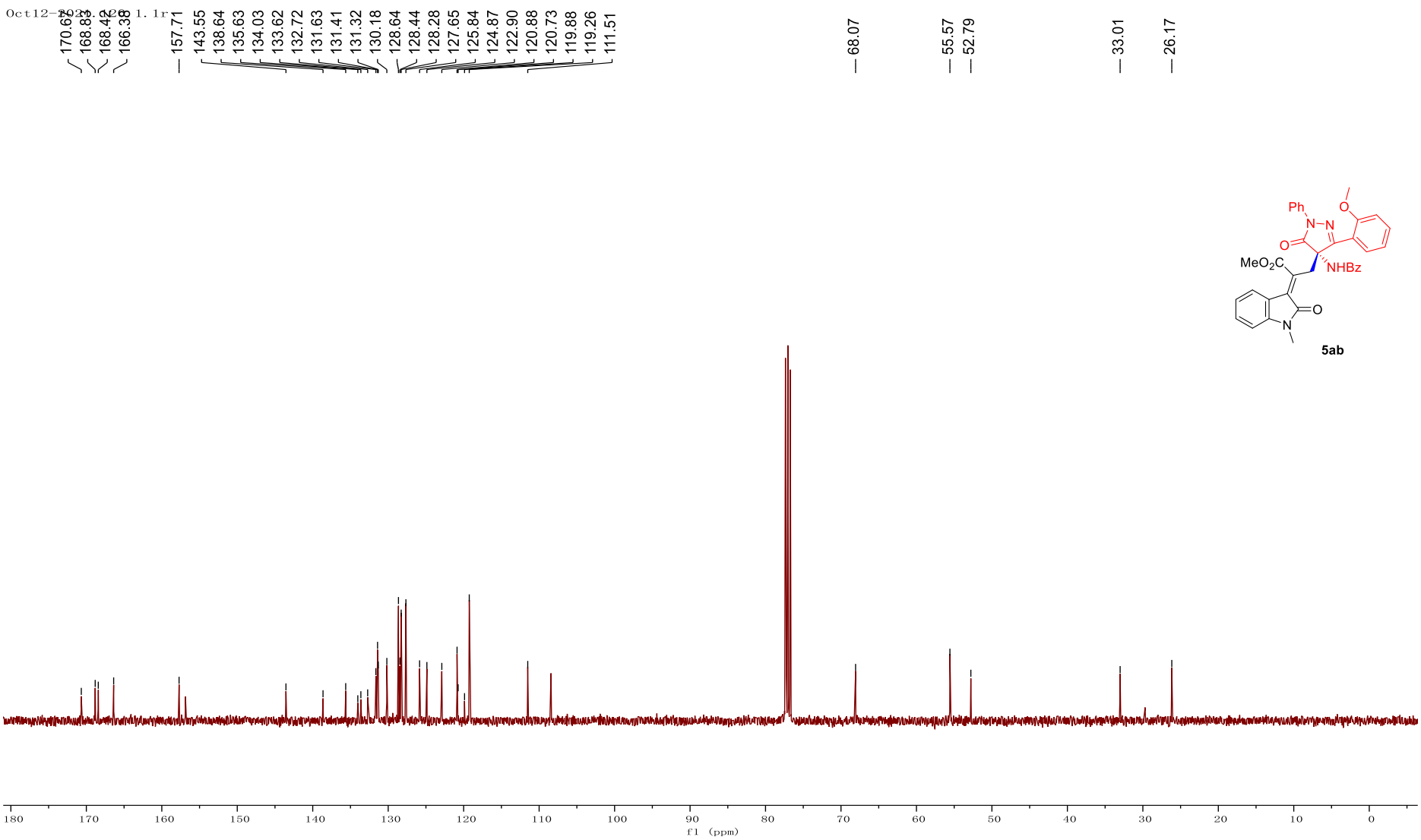
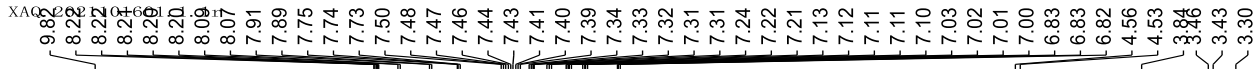
8.10
8.09
8.05
8.04
8.03
8.03
8.03
8.02
7.89
7.88
7.87
7.74
7.74
7.73
7.73
7.70
7.69
7.49
7.48
7.47
7.46
7.46
7.45
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.19
7.18
7.17
7.03
7.01
7.00
6.98
6.97
6.95
6.93
6.92
6.81
6.80
4.46
4.44
3.84
3.79
3.53
3.50
3.26
1.00
2.38
2.00
1.98
1.86
4.48
1.33
1.15
3.07
1.02
0.99
2.98
3.02
1.04
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
Ph
N
N
O
O
MeO2C
NHBz
O
N
5ab


Oct12-2023-20 1.1r
170.67
168.83
168.42
166.38
157.71
143.55
138.64
135.63
134.03
133.62
132.72
131.63
131.41
131.32
130.18
128.64
128.44
128.28
127.65
125.84
124.87
122.90
120.88
120.73
119.88
119.26
111.51
68.07
55.57
52.79
33.01
26.17
Ph
N
N
O
O
MeO2C
NHBz
O
N
5ab
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.82
8.22
8.21
8.20
8.09
8.07
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7.89
7.75
7.74
7.73
7.50
7.48
7.47
7.46
7.44
7.43
7.41
7.40
7.39
7.34
7.33
7.32
7.31
7.31
7.24
7.22
7.21
7.13
7.12
7.11
7.11
7.10
7.03
7.02
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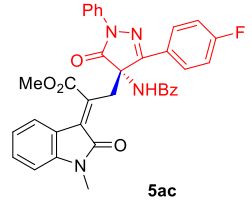
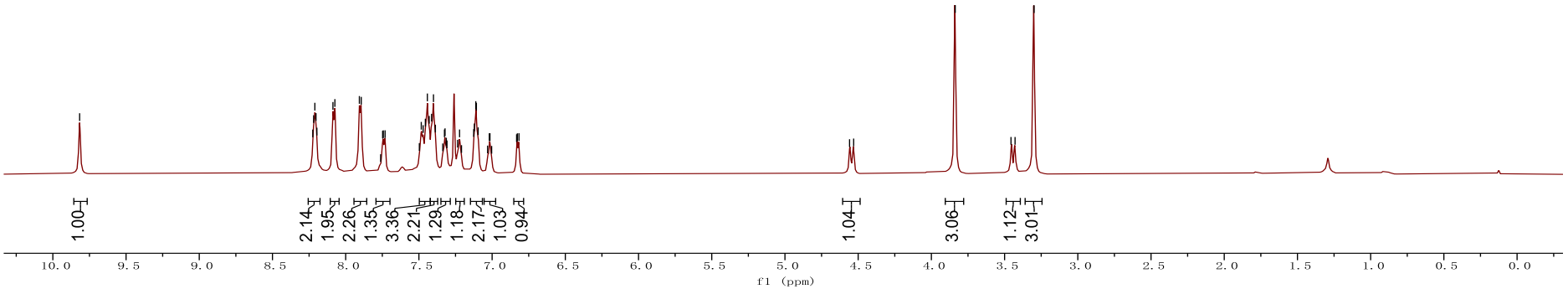
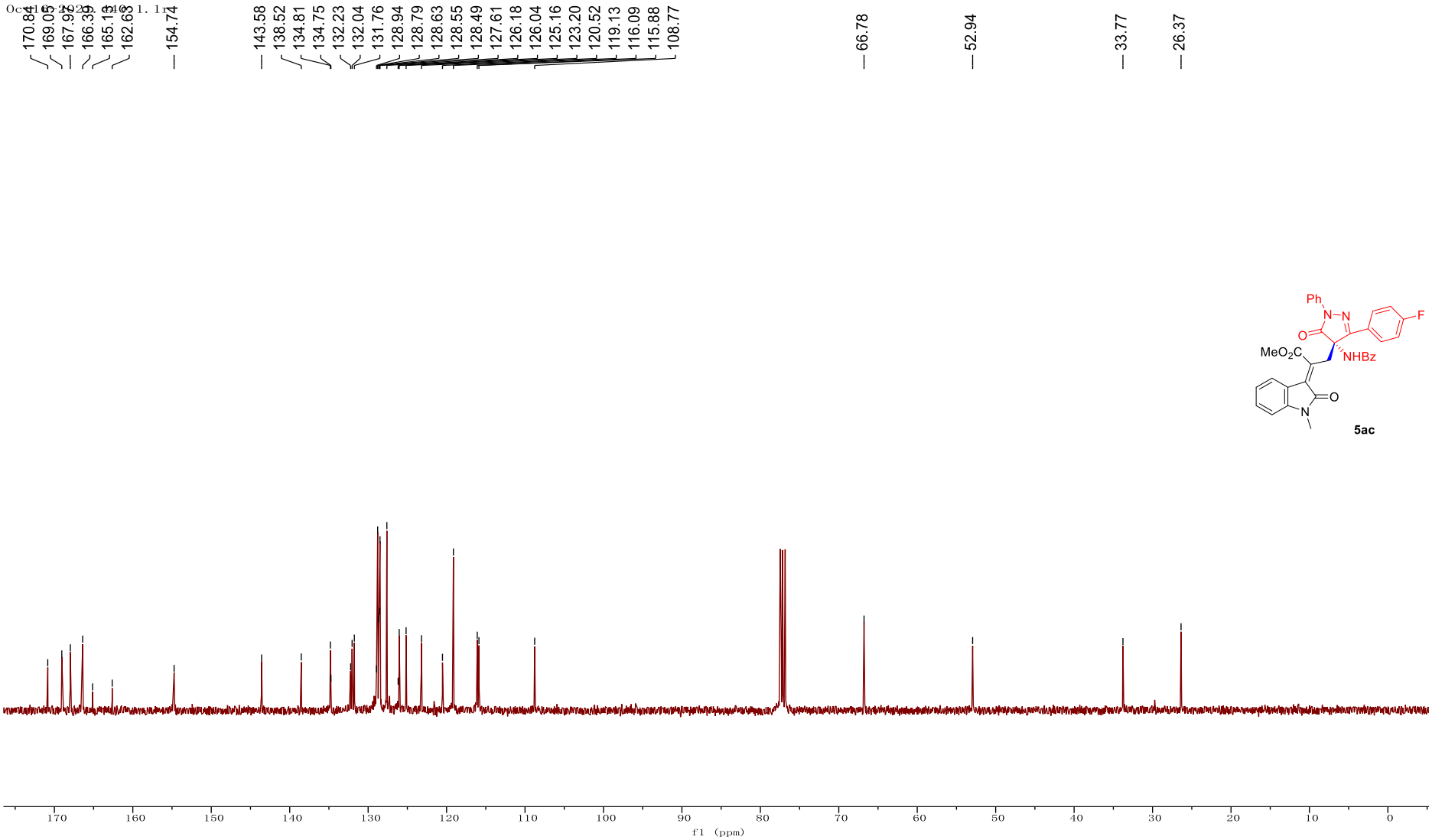
4.56
4.53
3.84
3.46
3.43
3.30


Ph
N
N
F
O
MeO2C
NHBz
O
N

5ac


1.00
2.14
1.95
2.26
1.35
3.36
2.21
1.29
1.18
2.17
1.03
0.94
1.04
3.06
1.12
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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169.05
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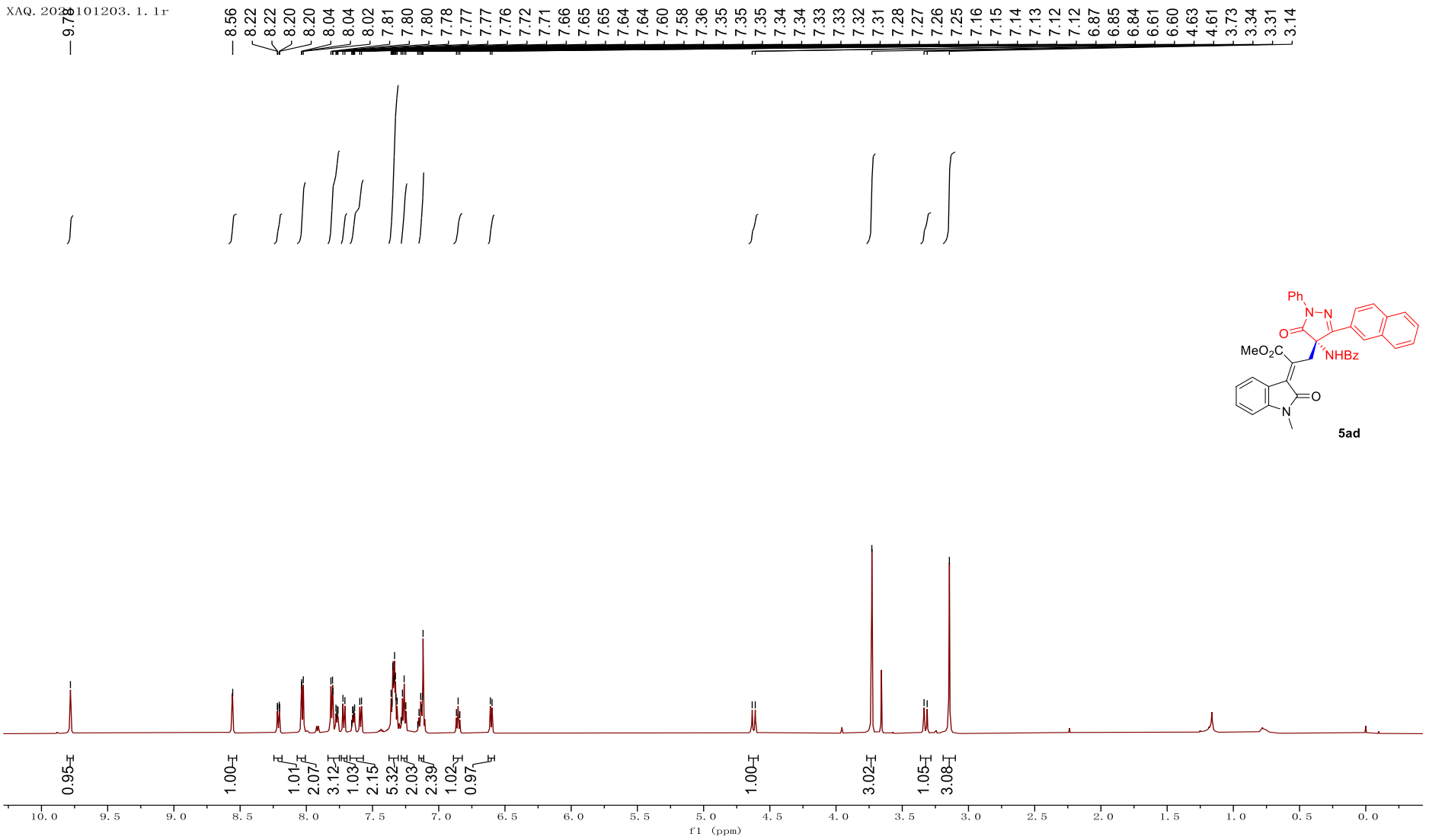
165.15
162.63
154.74
143.58
138.52
134.81
134.75
132.23
132.04
131.76
128.94
128.79
128.63
128.55
128.49
127.61
126.18
126.04
125.16
123.20
120.52
119.13
116.09
115.88
108.77
66.78
52.94
33.77
26.37
Ph
N
N
O
F
MeO2C
NHBz
O
N
5ac
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


XAQ. 202101203. 1. 1r
9.78
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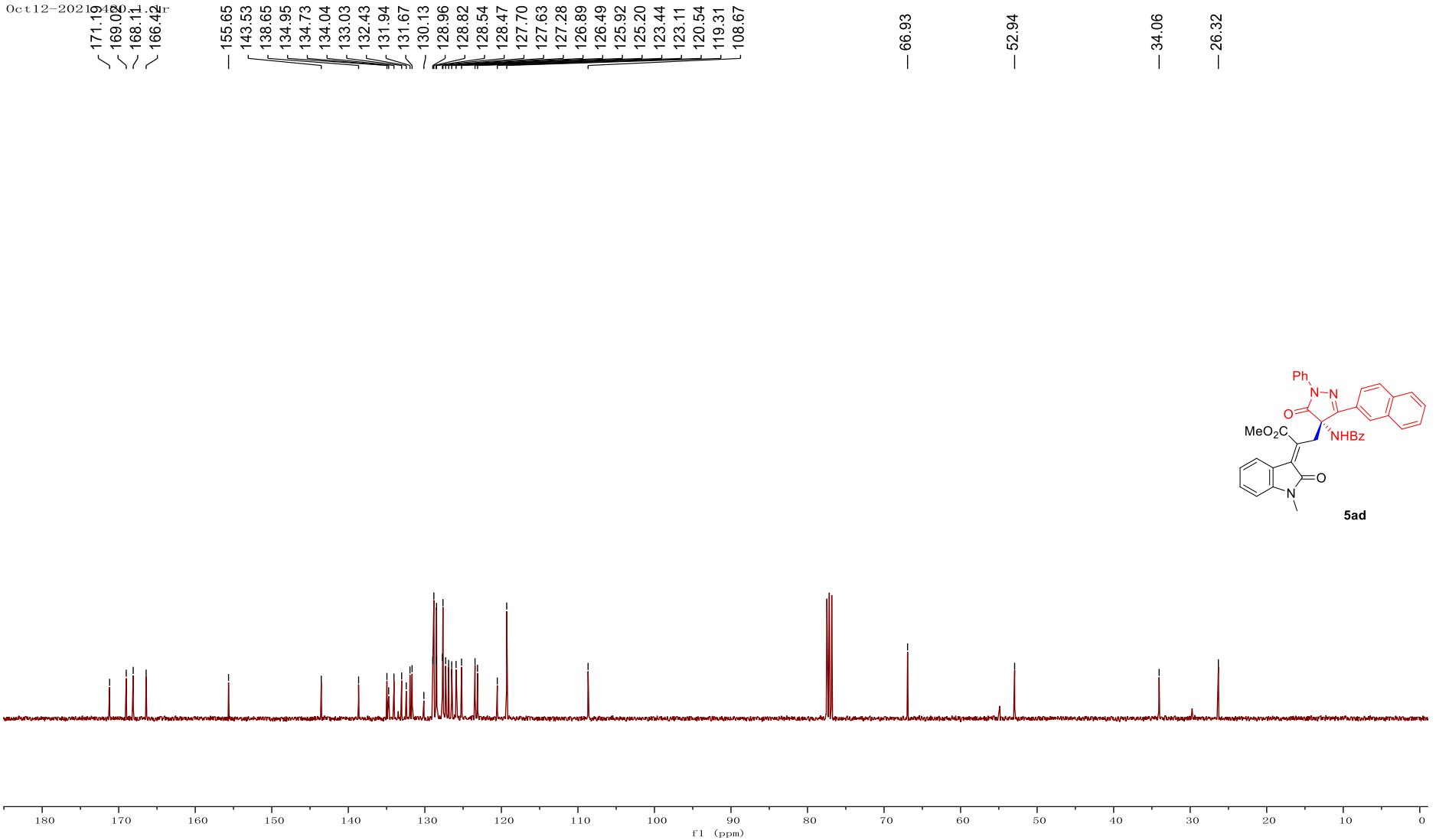
8.22
8.22
8.20
8.20
8.04
8.04
8.02
7.81
7.80
7.80
7.78
7.77
7.77
7.76
7.72
7.71
7.66
7.65
7.65
7.64
7.64
7.60
7.58
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.28
7.27
7.26
7.25
7.16
7.15
7.14
7.13
7.12
7.12
6.87
6.85
6.84
6.61
6.60
4.63
4.61
3.73
3.34
3.31
3.14
Ph
N
N
O
MeO2C
NHBz
O
N
5ad
0.95
1.00
1.01
2.07
3.12
1.03
2.15
5.32
2.03
2.39
1.02
0.97
1.00
3.02
1.05
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Oct12-2021-3480 1r
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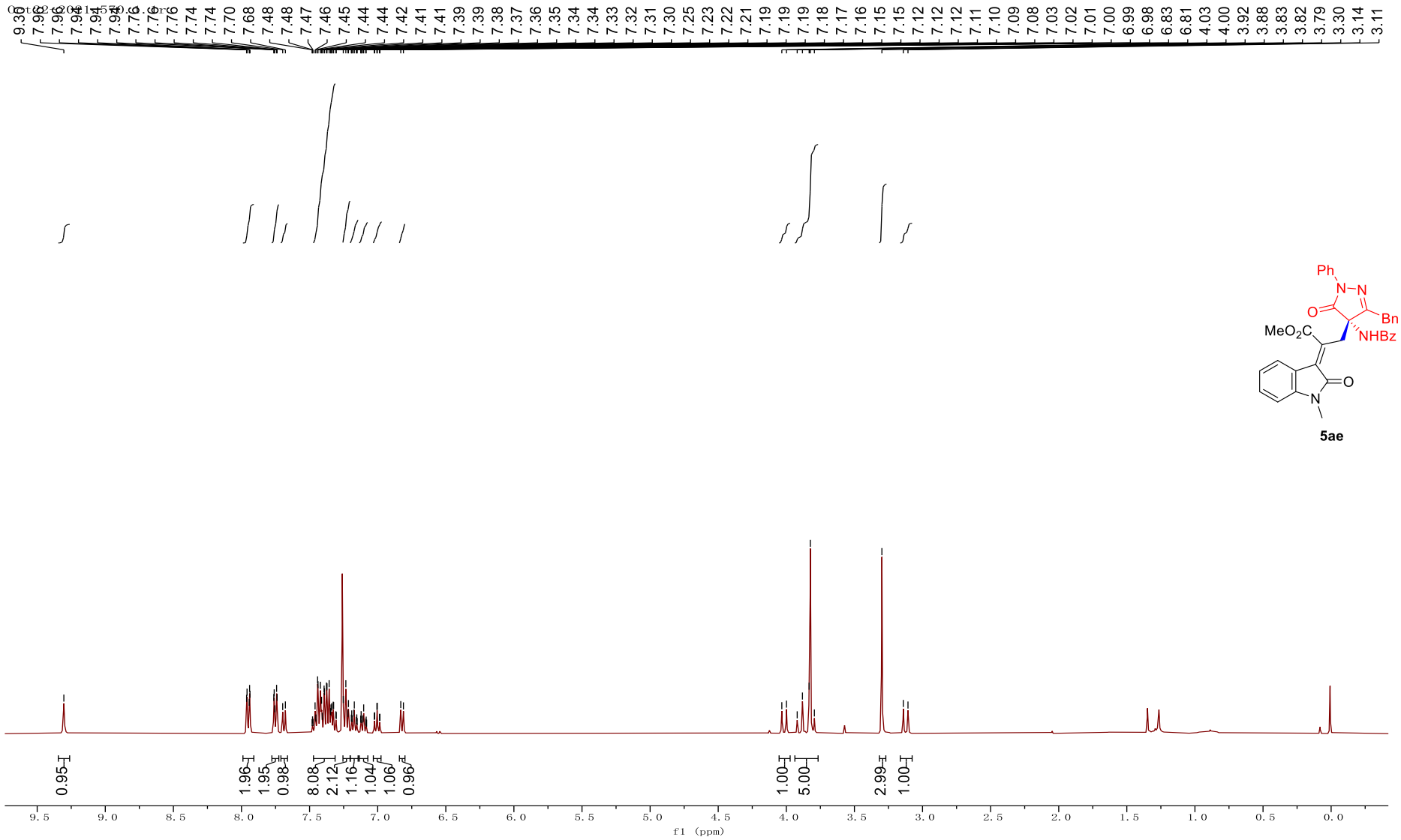
168.11
166.42
155.65
143.53
138.65
134.95
134.73
134.04
133.03
132.43
131.94
131.67
130.13
128.96
128.82
128.54
128.47
127.70
127.63
127.28
126.89
126.49
125.92
125.20
123.44
123.11
120.54
119.31
108.67
66.93
52.94
34.06
26.32
Ph
N
N
O
MeO2C
NHBz
O
N
5ad
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.96
7.94
7.94
7.76
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7.76
7.74
7.74
7.70
7.68
7.48
7.48
7.47
7.46
7.45
7.44
7.44
7.42
7.41
7.41
7.39
7.39
7.38
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.30
7.25
7.23
7.22
7.21
7.19
7.19
7.19
7.18
7.17
7.16
7.15
7.15
7.12
7.12
7.12
7.11
7.10
7.09
7.08
7.03
7.02
7.01
7.00
6.99
6.98
6.83
6.81
4.03
4.00
3.92
3.88
3.83
3.82
3.79
3.30
3.14
3.11
Ph
N
N
O
Bn
MeO2C
NHBz
O
N
5ae
0.95
1.96
1.95
0.98
8.08
2.12
1.16
1.04
1.06
0.96
1.00
5.00
2.99
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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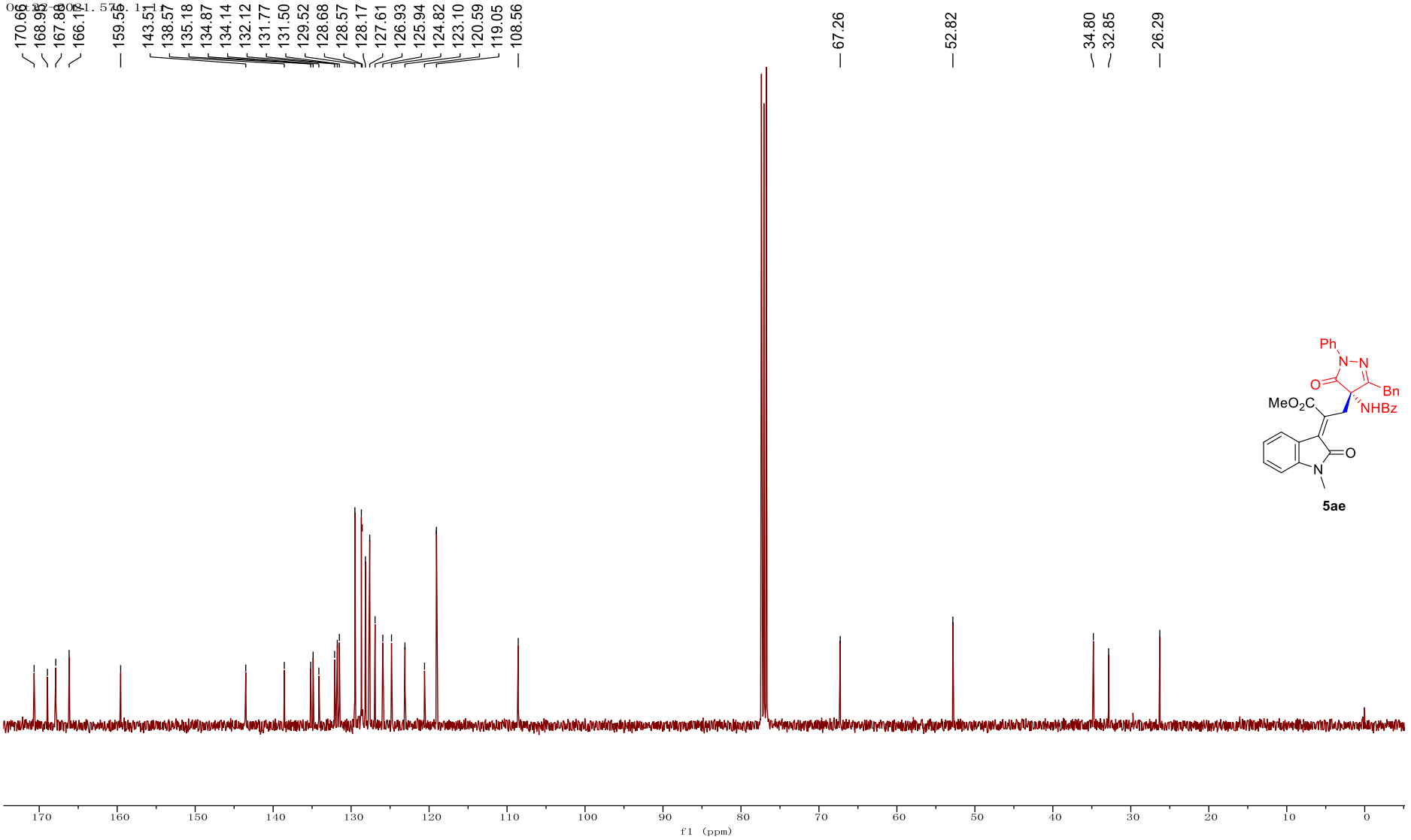
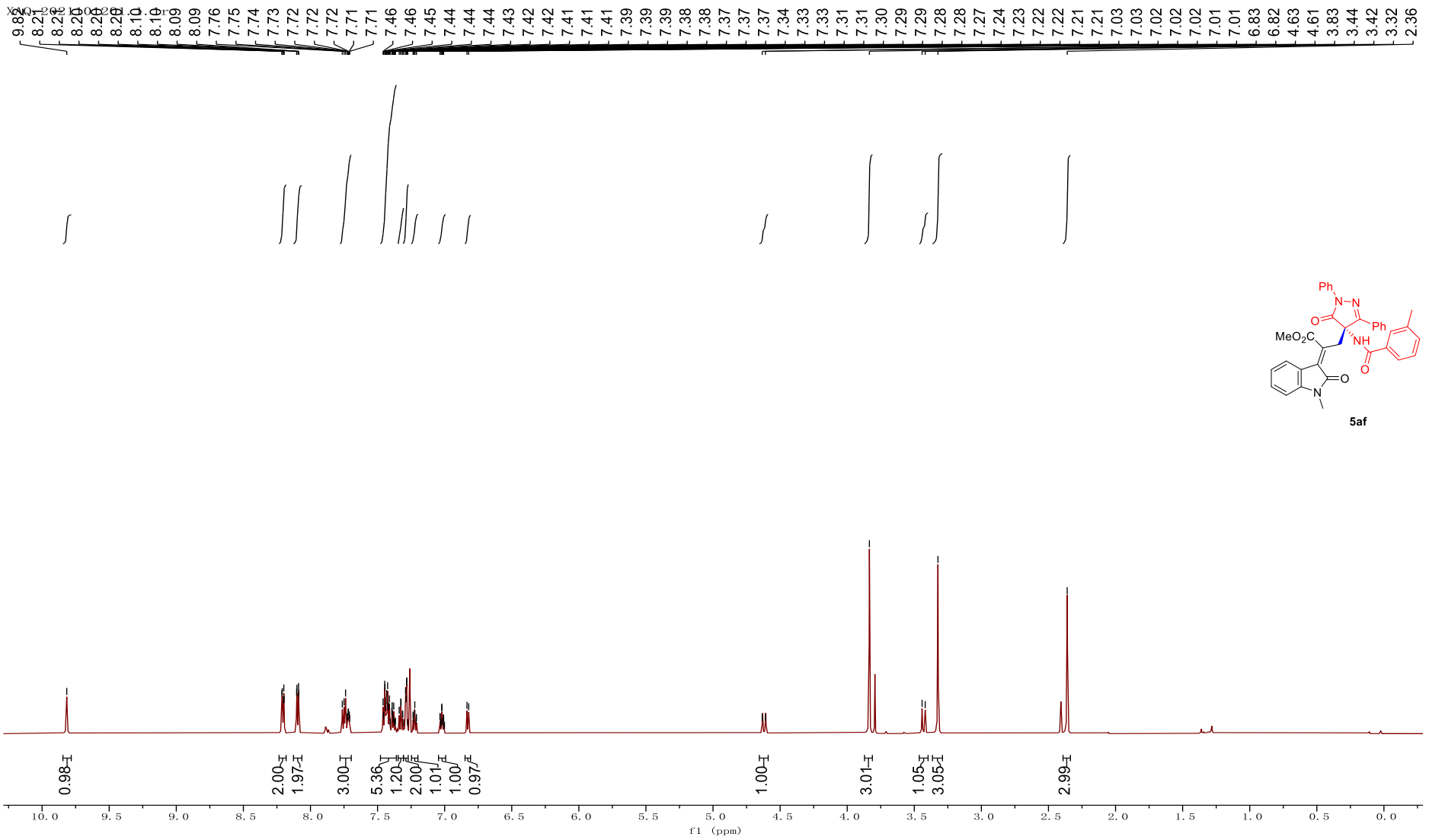
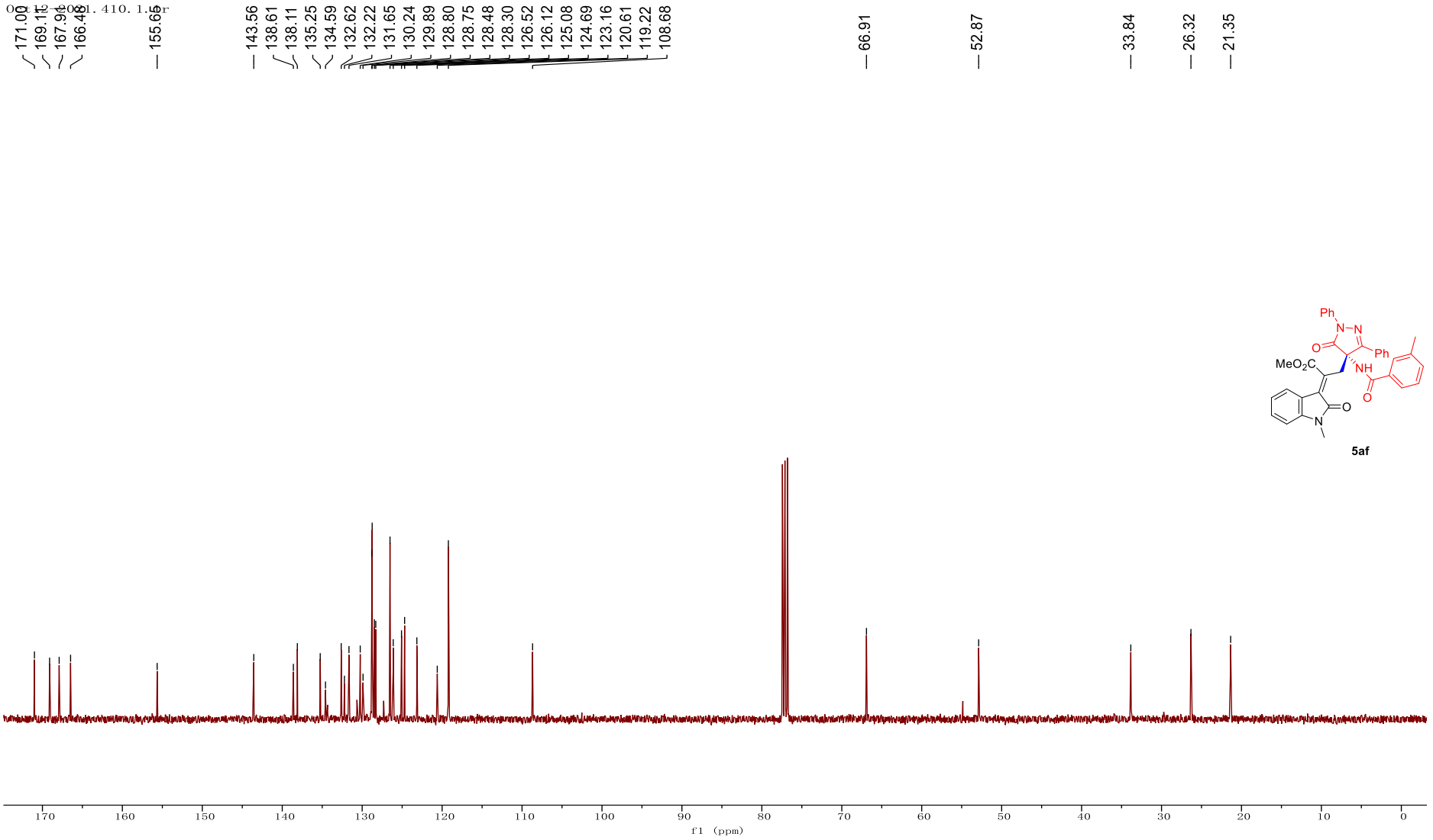
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.66
168.98
167.88
166.17
159.55
143.51
138.57
135.18
134.87
134.14
132.12
131.77
131.50
129.52
128.68
128.57
128.17
127.61
126.93
125.94
124.82
123.10
120.59
119.05
108.56
67.26
52.82
34.80
32.85
26.29
Ph
N
N
O
Bn
MeO2C
NHBz
O
N
5ae
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.82 8.21 8.21 8.20 8.20 8.20 8.20 8.19 8.19 8.09 8.09 7.76 7.75 7.74 7.73 7.72 7.72 7.72 7.71 7.71
7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.42 7.42 7.41 7.41 7.41 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.34 7.33 7.33 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.24 7.23 7.22 7.22 7.21 7.21 7.03 7.03 7.02 7.02 7.02 7.01 7.01 6.83 6.82 4.63 4.61 3.83 3.44 3.42 3.32 2.36
Ph
N
N
O
Ph
MeO2C
NH
O
O
N
5af
0.98
2.00
1.97
3.00
5.36
1.20
2.00
1.01
1.00
0.97
1.00
3.01
1.05
3.05
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.00
169.11
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155.65
143.56
138.61
138.11
135.25
134.59
132.62
132.22
131.65
130.24
129.89
128.80
128.75
128.48
128.30
126.52
126.12
125.08
124.69
123.16
120.61
119.22
108.68
66.91
52.87
33.84
26.32
21.35
Ph
N
N
O
Ph
MeO2C
NH
O
O
N
5af
170
160
150
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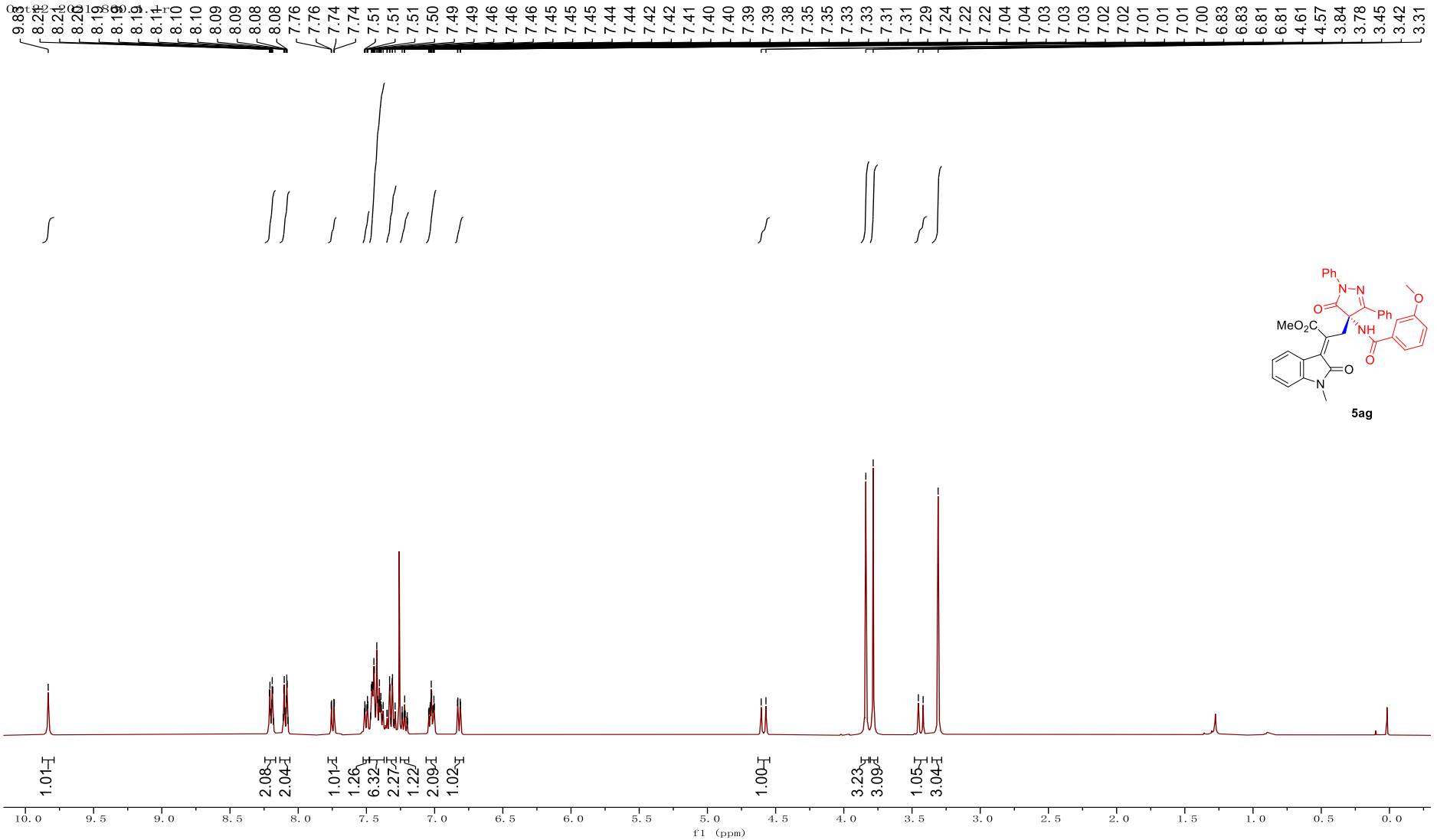
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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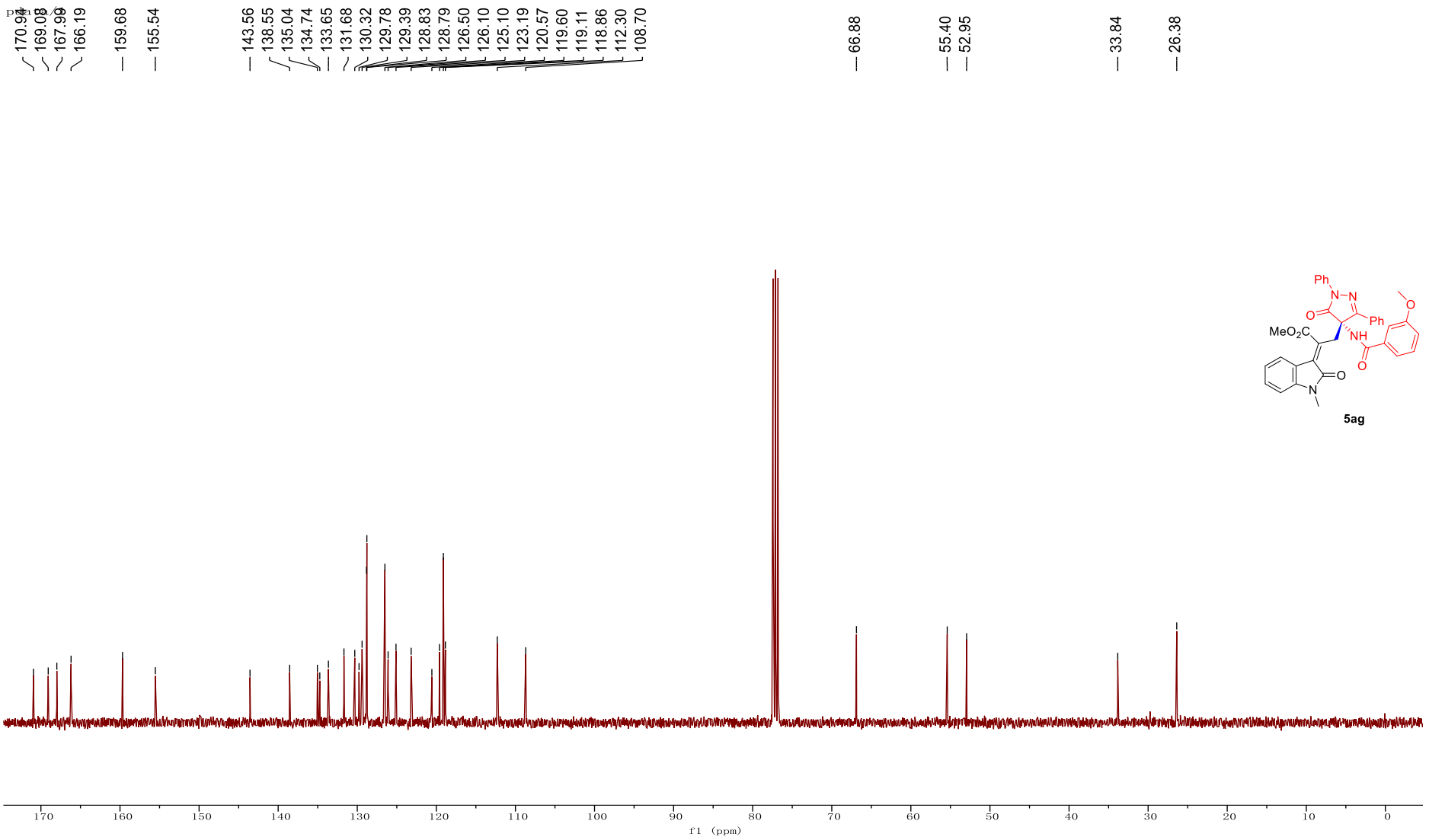
Ph
N
N
O
Ph
O
MeO2C
NH
O
O
N
5ag
1.01 2.08 2.04 1.01 1.26 6.32 2.27 1.22 2.09 1.02 1.00 3.23 3.09 1.05 3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.39
128.83
128.79
126.50
126.10
125.10
123.19
120.57
119.60
119.11
118.86
112.30
108.70
66.88
55.40
52.95
33.84
26.38
Ph
N
N
O
Ph
O
MeO2C
NH
O
O
N
5ag
170
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130
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110
100
90
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70
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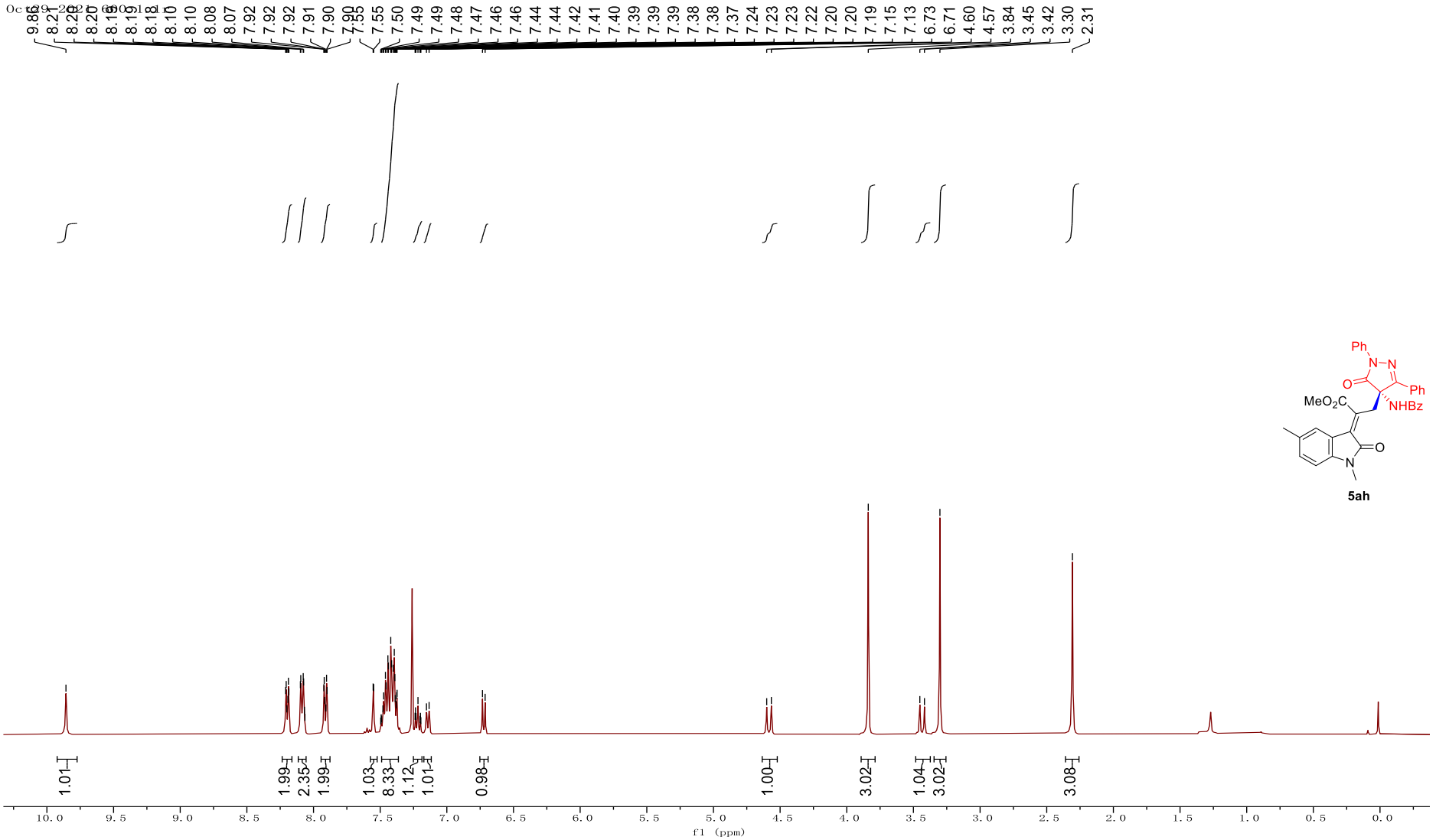
50
40
30
20
10
0
f1 (ppm)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8.20
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8.10
8.08
8.07
7.92
7.92
7.91
7.90
7.55
7.50
7.49
7.48
7.47
7.46
7.44
7.42
7.41
7.40
7.39
7.38
7.37
7.24
7.23
7.22
7.20
7.19
7.15
7.13
6.73
6.71
4.60
4.57
3.84
3.45
3.42
3.30
2.31
Ph
N
N
O
Ph
NHBz
MeO2C
O
N
5ah
1.01
1.99
2.35
1.99
1.03
8.33
1.12
1.01
0.98
1.00
3.02
1.04
3.02
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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1.0
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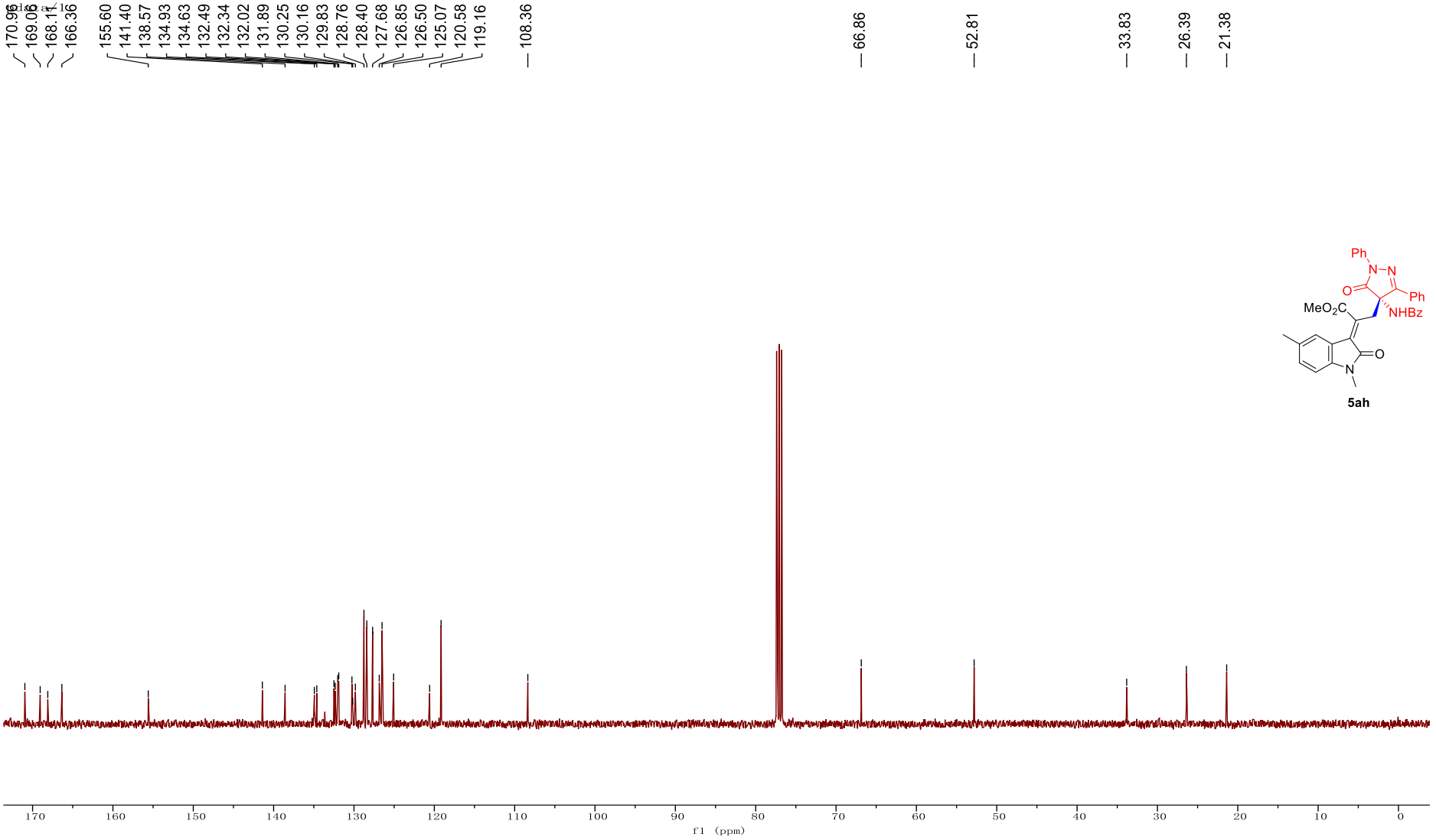
0.0
f1 (ppm)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132.02
131.89
130.25
130.16
129.83
128.76
128.40
127.68
126.85
126.50
125.07
120.58
119.16
108.36
66.86
52.81
33.83
26.39
21.38
Ph
N
N
O
Ph
NHBz
MeO2C
O
N
5ah
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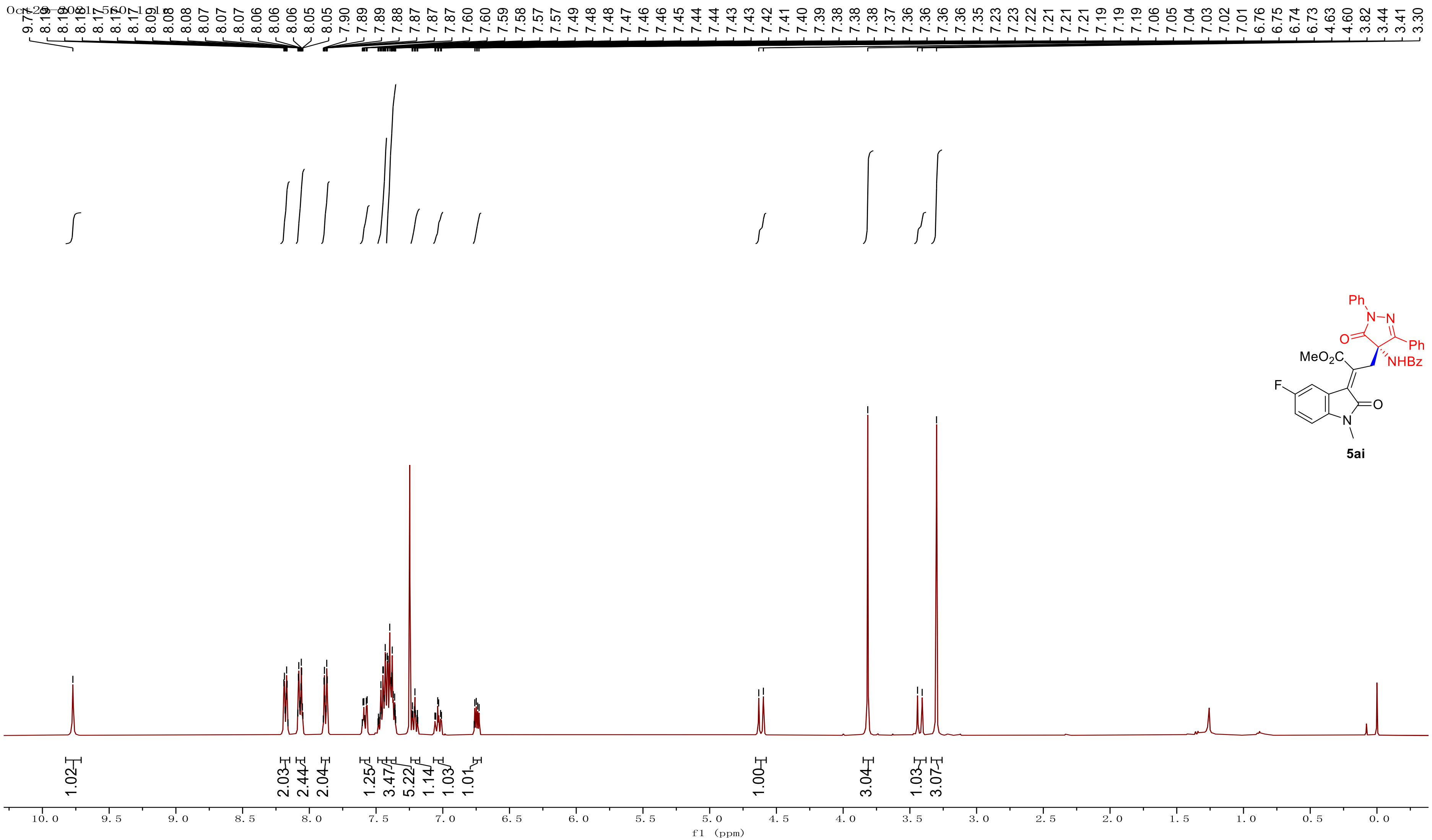
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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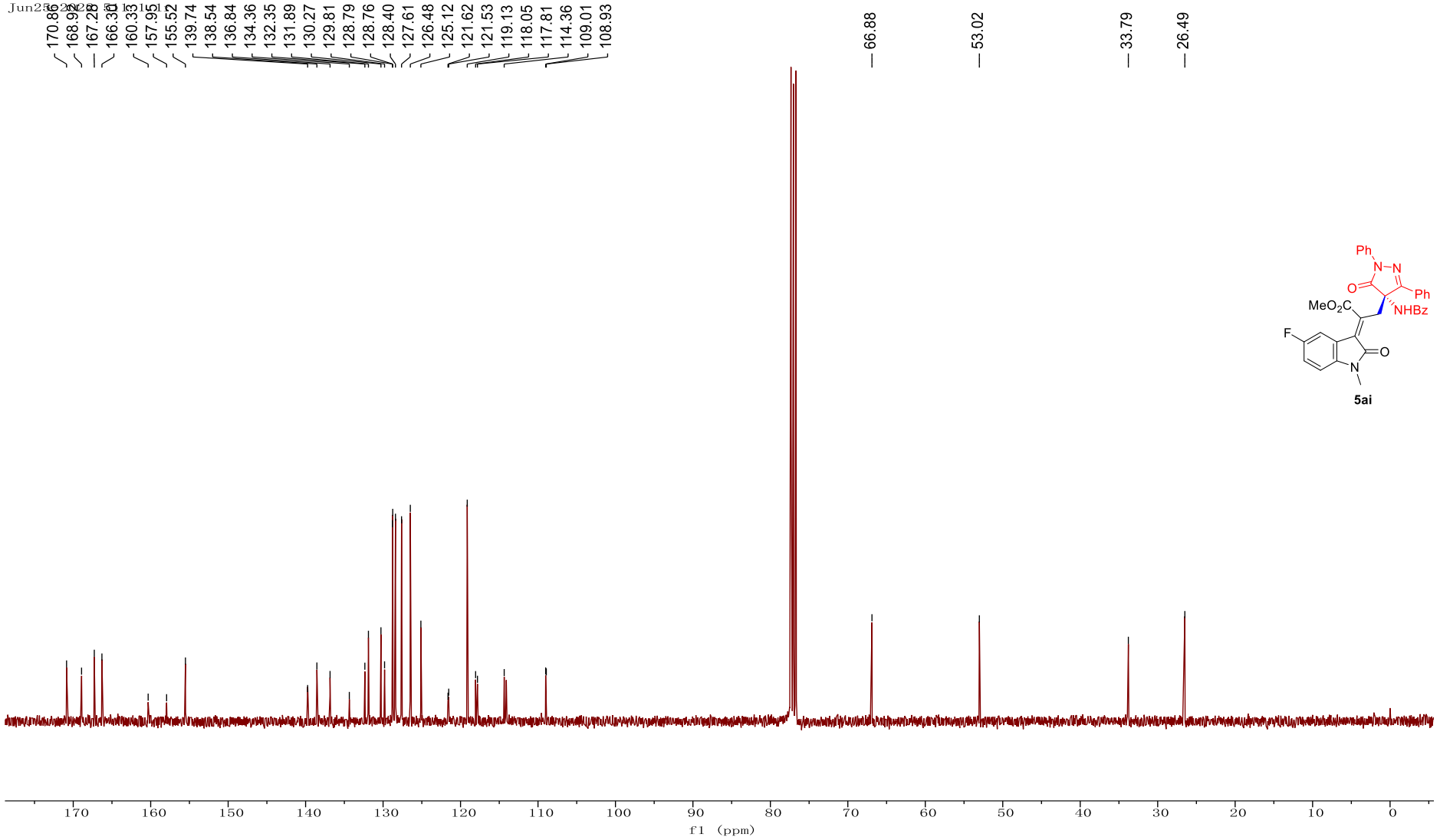
1.02
2.03
2.44
2.04
1.25
3.47
5.22
1.14
1.03
1.01
1.00
3.04
1.03
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Ph
N
N
O
Ph
MeO2C
NHBz
F
O
N
5ai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139.74
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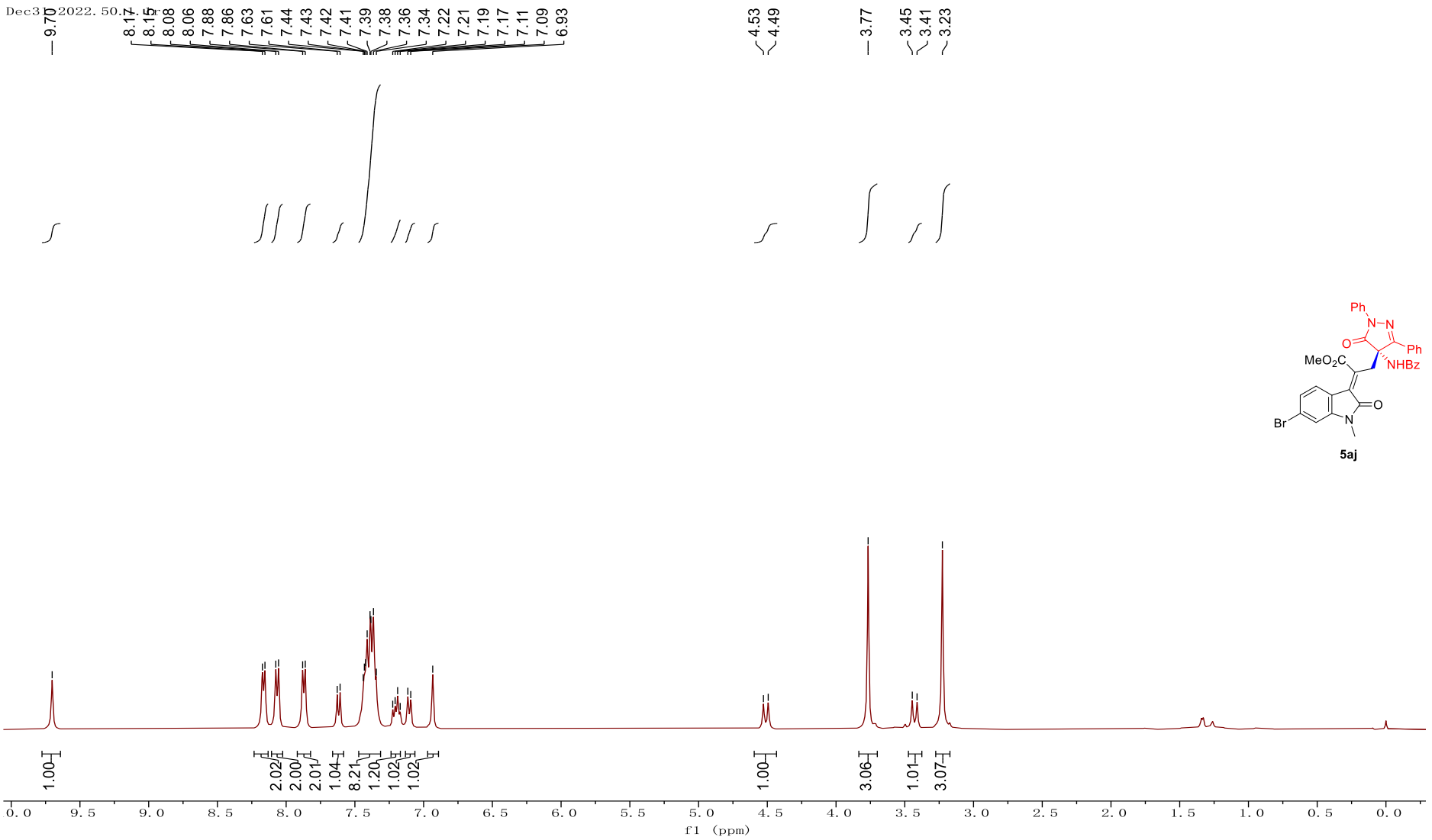
136.84
134.36
132.35
131.89
130.27
129.81
128.79
128.76
128.40
127.61
126.48
125.12
121.62
121.53
119.13
118.05
117.81
114.36
109.01
108.93
66.88
53.02
33.79
26.49
Ph
N
N
O
Ph
MeO2C
NHBz
F
O
N
5ai
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.08
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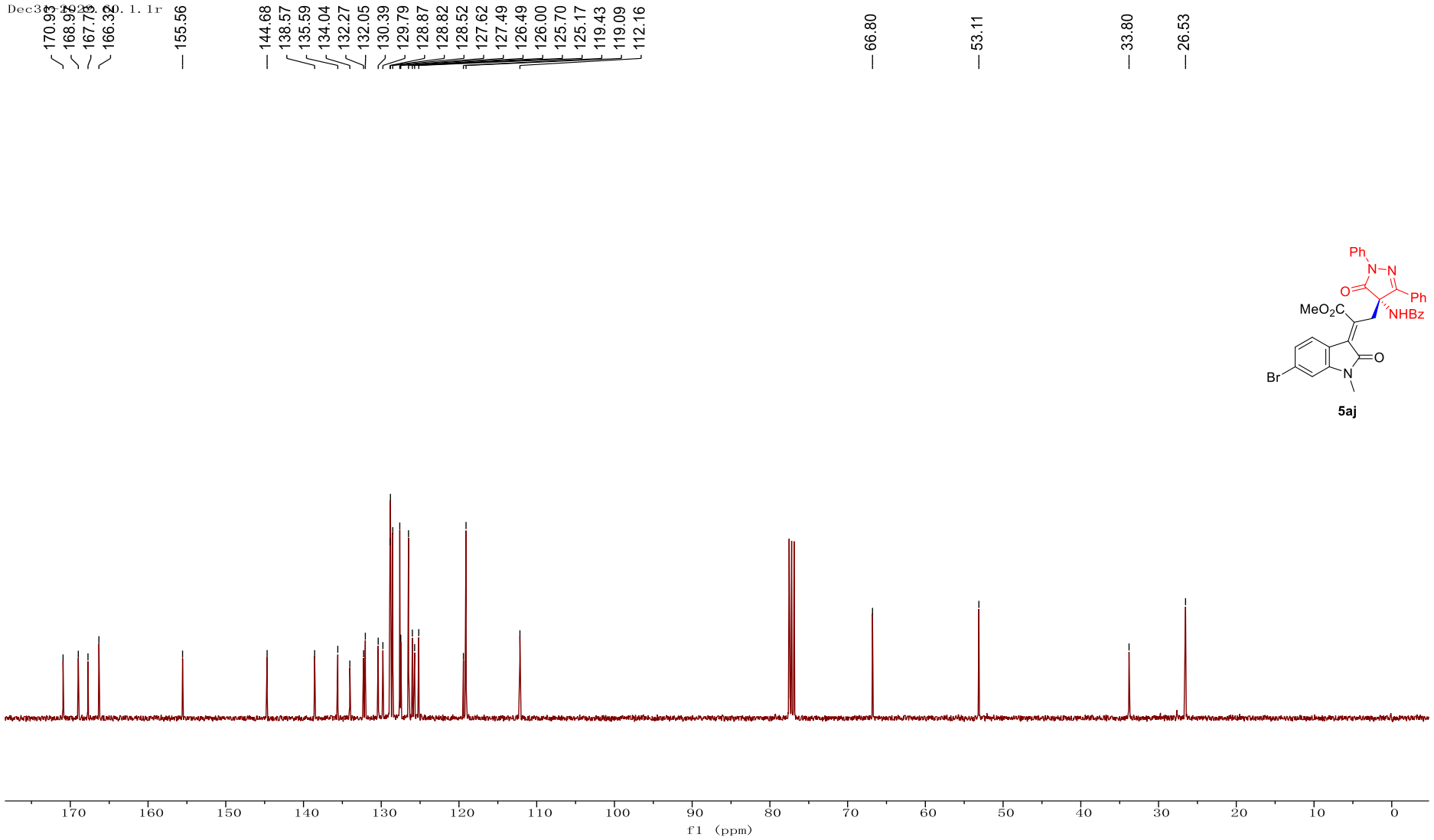
7.86
7.63
7.61
7.44
7.43
7.42
7.41
7.39
7.38
7.36
7.34
7.22
7.21
7.19
7.17
7.11
7.09
6.93
4.53
4.49
3.77
3.45
3.41
3.23
Ph
N
N
O
Ph
MeO2C
NHBz
O
Br
N
1.00
2.02
2.00
2.01
1.04
8.21
1.20
1.02
1.02
1.00
3.06
1.01
3.07
f1 (ppm)

5aj


Dec31-1923-20.1.1r
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167.78
166.32
155.56
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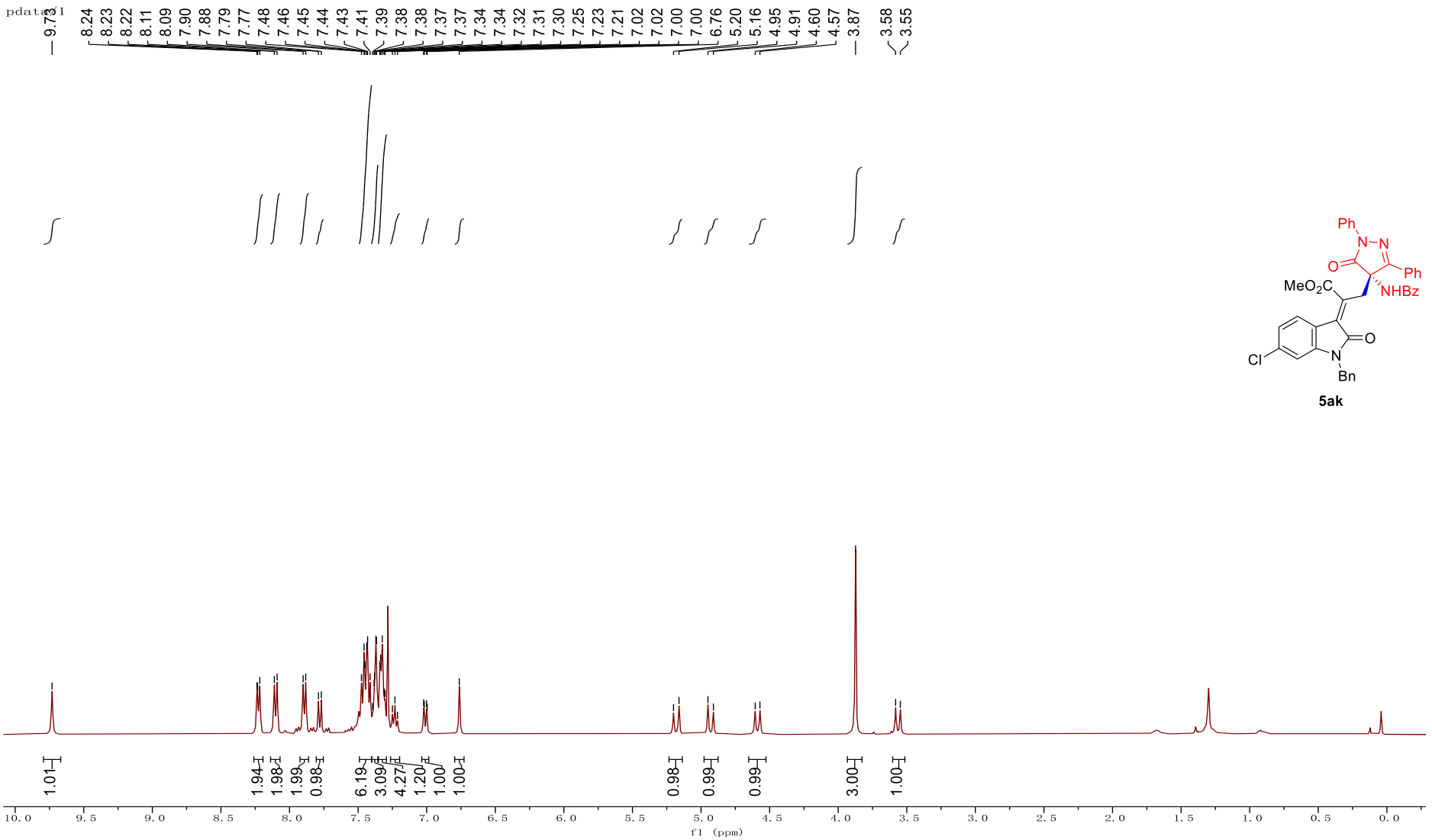
138.57
135.59
134.04
132.27
132.05
130.39
129.79
128.87
128.82
128.52
127.62
127.49
126.49
126.00
125.70
125.17
119.43
119.09
112.16
66.80
53.11
33.80
26.53
Ph
N
N
O
Ph
MeO2C
NHBz
O
Br
N
5aj
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.90
7.88
7.79
7.77
7.48
7.46
7.45
7.44
7.43
7.41
7.39
7.38
7.38
7.37
7.37
7.34
7.34
7.32
7.31
7.30
7.25
7.23
7.21
7.02
7.02
7.00
7.00
6.76
5.20
5.16
4.95
4.91
4.60
4.57
3.87
3.58
3.55
1.01
1.94
1.98
1.99
0.98
6.19
3.09
4.27
1.20
1.00
1.00
0.98
0.99
0.99
3.00
1.00
f1 (ppm)

Ph
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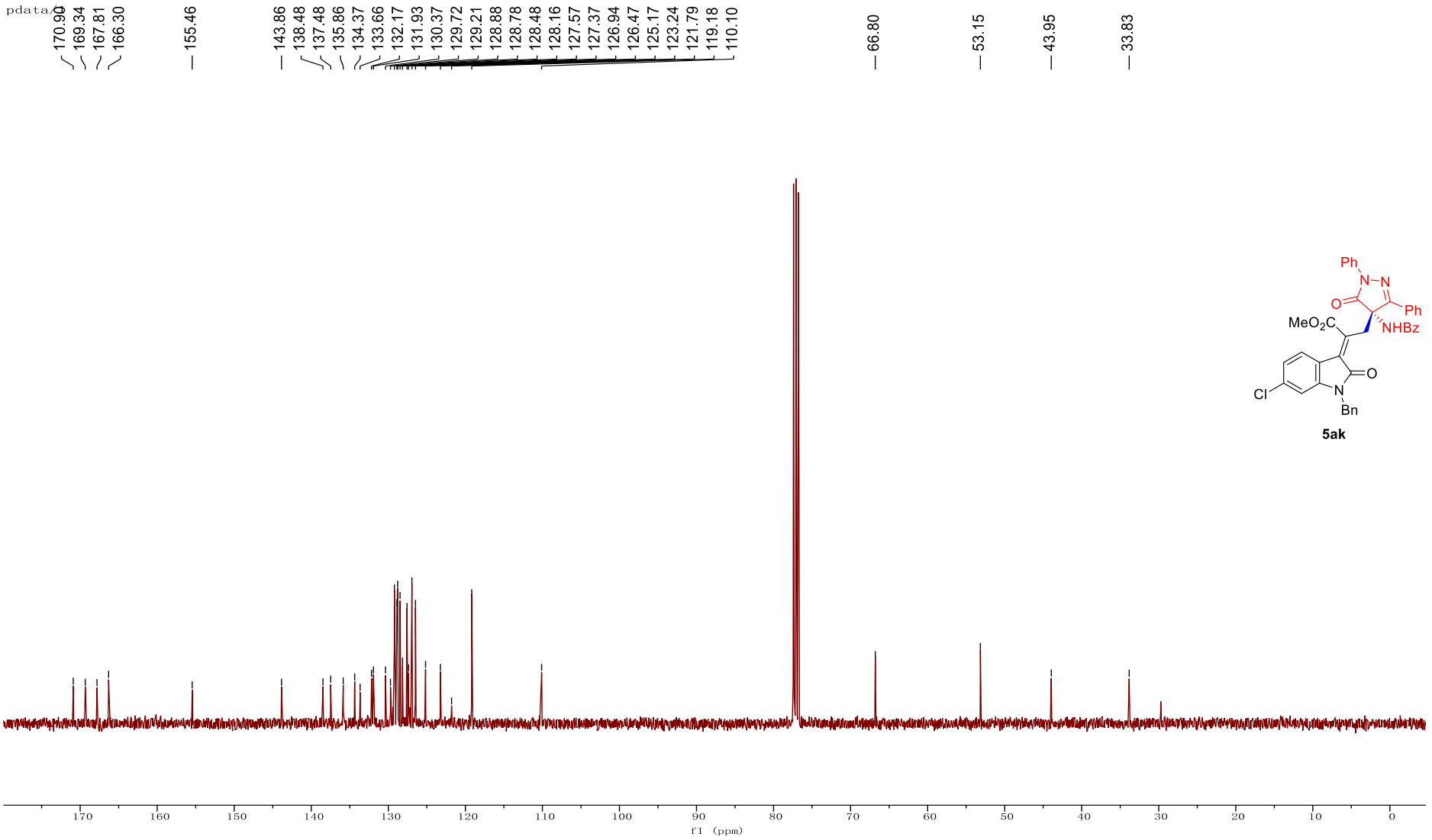
N
O
Ph
MeO2C
NHBz
O
Cl
N
Bn

5ak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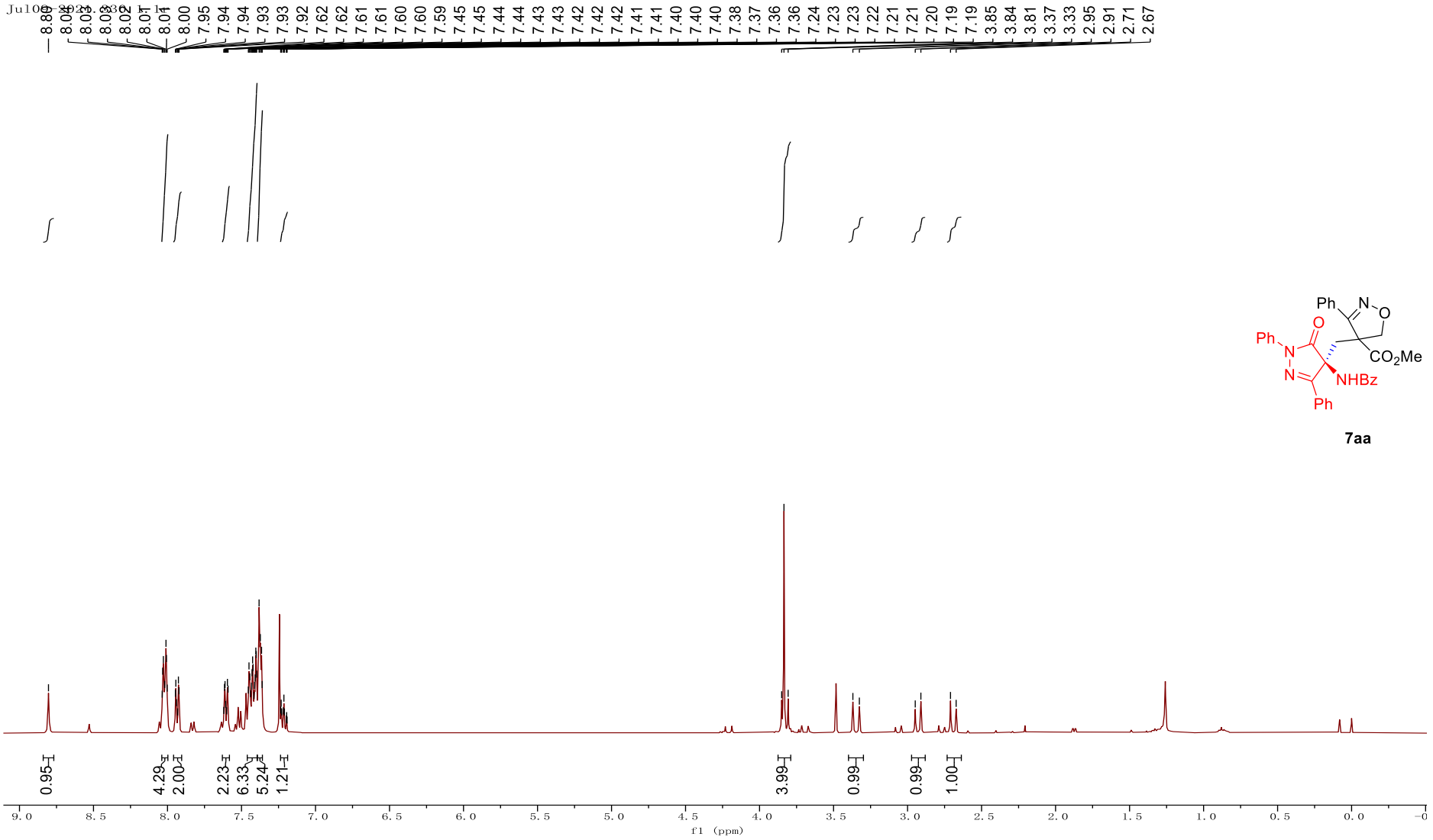
138.48
137.48
135.86
134.37
133.66
132.17
131.93
130.37
129.72
129.21
128.88
128.78
128.48
128.16
127.57
127.37
126.94
126.47
125.17
123.24
121.79
119.18
110.10
66.80
53.15
43.95
33.83
Ph
N
N
O
Ph
MeO2C
NHBz
O
Cl
N
Bn
5ak
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.04
8.03
8.03
8.02
8.01
8.01
8.00
7.95
7.94
7.94
7.93
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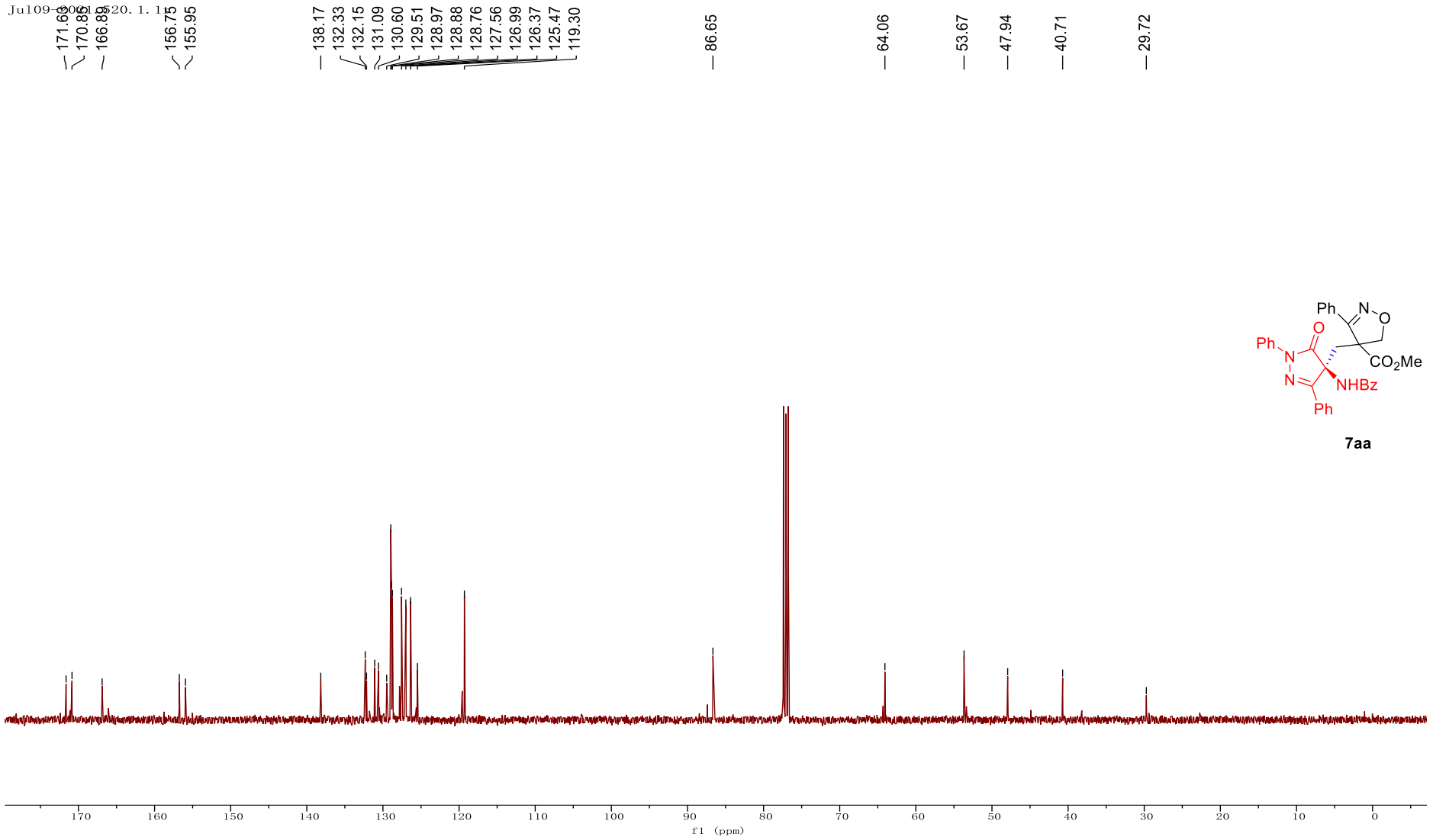
7.92
7.62
7.62
7.61
7.61
7.60
7.60
7.59
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.38
7.37
7.36
7.36
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.19
3.85
3.84
3.81
3.37
3.33
2.95
2.91
2.71
2.67
Ph
N
O
O
Ph
N
N
CO2Me
NHBz
Ph
7aa
0.95
4.29
2.00
2.23
6.33
5.24
1.21
3.99
0.99
0.99
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Jul09-2009 5520. 1. 15
171.63
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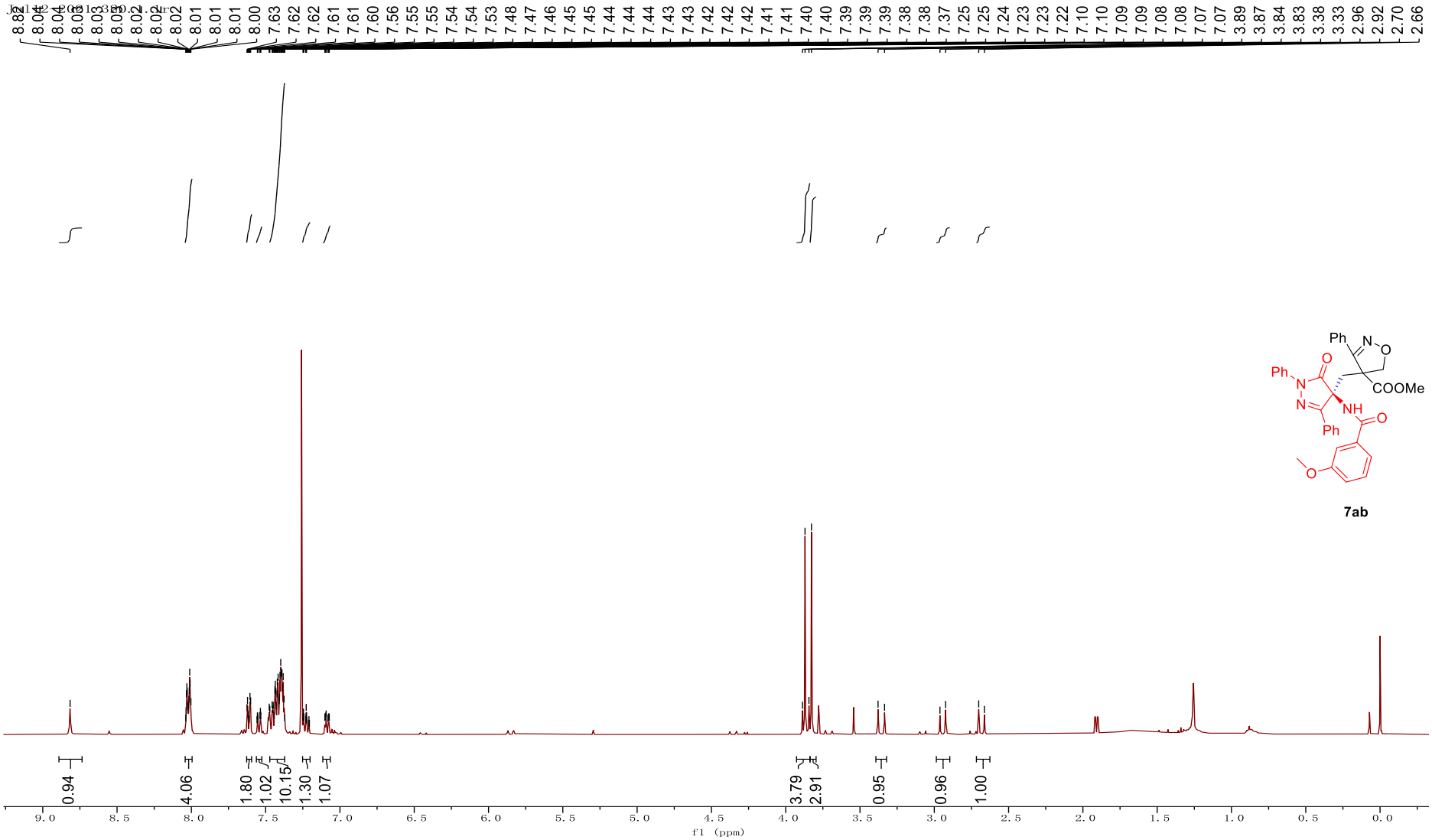
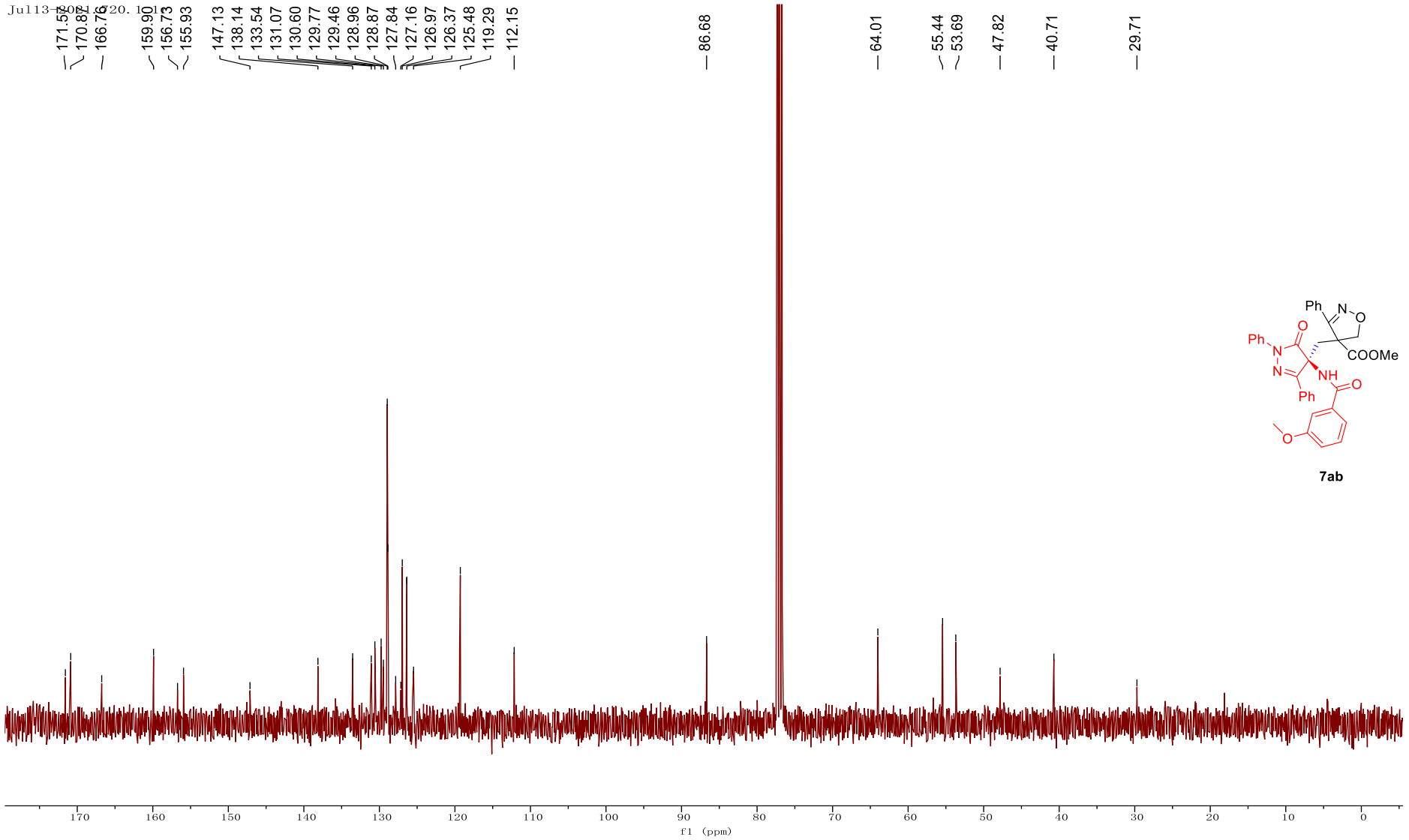
132.15
131.09
130.60
129.51
128.97
128.88
128.76
127.56
126.99
126.37
125.47
119.30
86.65
64.06
53.67
47.94
40.71
29.72
Ph
N
O
O
Ph
N
N
CO2Me
NHBz
Ph
7aa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.82 8.04 8.04 8.03 8.03 8.02 8.02 8.02 8.01 8.01 8.01 8.00 7.63 7.62 7.62 7.61 7.61 7.60 7.56 7.55 7.55 7.54 7.54 7.53 7.48 7.47 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.25 7.25 7.24 7.23 7.23 7.22 7.10 7.10 7.09 7.09 7.08 7.08 7.07 7.07 3.89 3.87 3.84 3.83 3.38 3.33 2.96 2.92 2.70 2.66
Ph
N
O
Ph
N
N
O
NH
COOMe
Ph
O
O
0.94
4.06
1.80
1.02
10.15
1.30
1.07
3.79
2.91
0.95
0.96
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

7ab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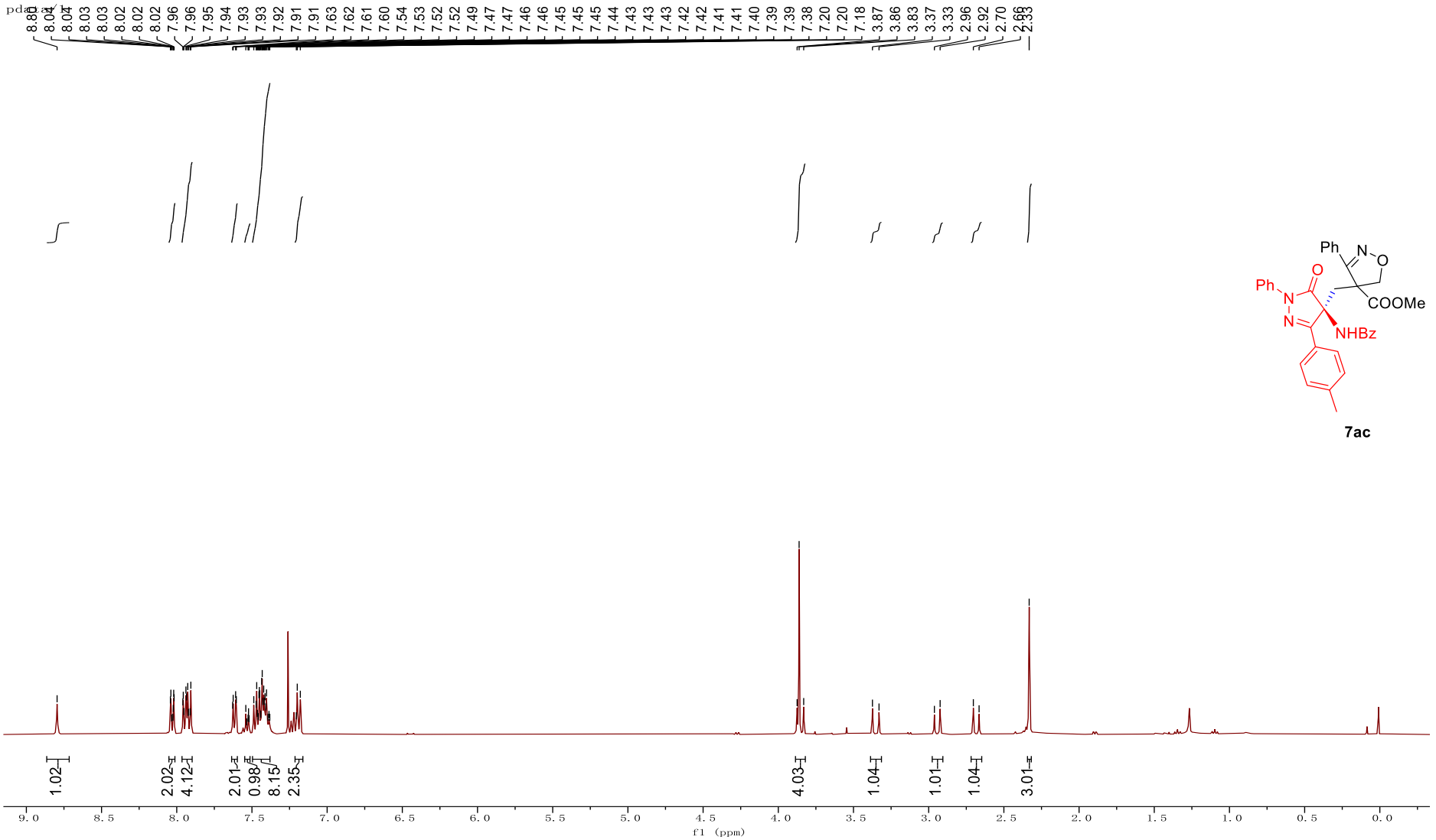
155.93
147.13
138.14
133.54
131.07
130.60
129.77
129.46
128.96
128.87
127.84
127.16
126.97
126.37
125.48
119.29
112.15
86.68
64.01
55.44
53.69
47.82
40.71
29.71
Ph
N
O
Ph
O
N
N
NH
O
Ph
O
COOMe
7ab
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


pda ax
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8.04
8.04
8.03
8.03
8.02
8.02
8.02
7.96
7.96
7.95
7.94
7.93
7.93
7.92
7.91
7.91
7.63
7.62
7.61
7.60
7.54
7.53
7.52
7.52
7.49
7.47
7.47
7.46
7.46
7.45
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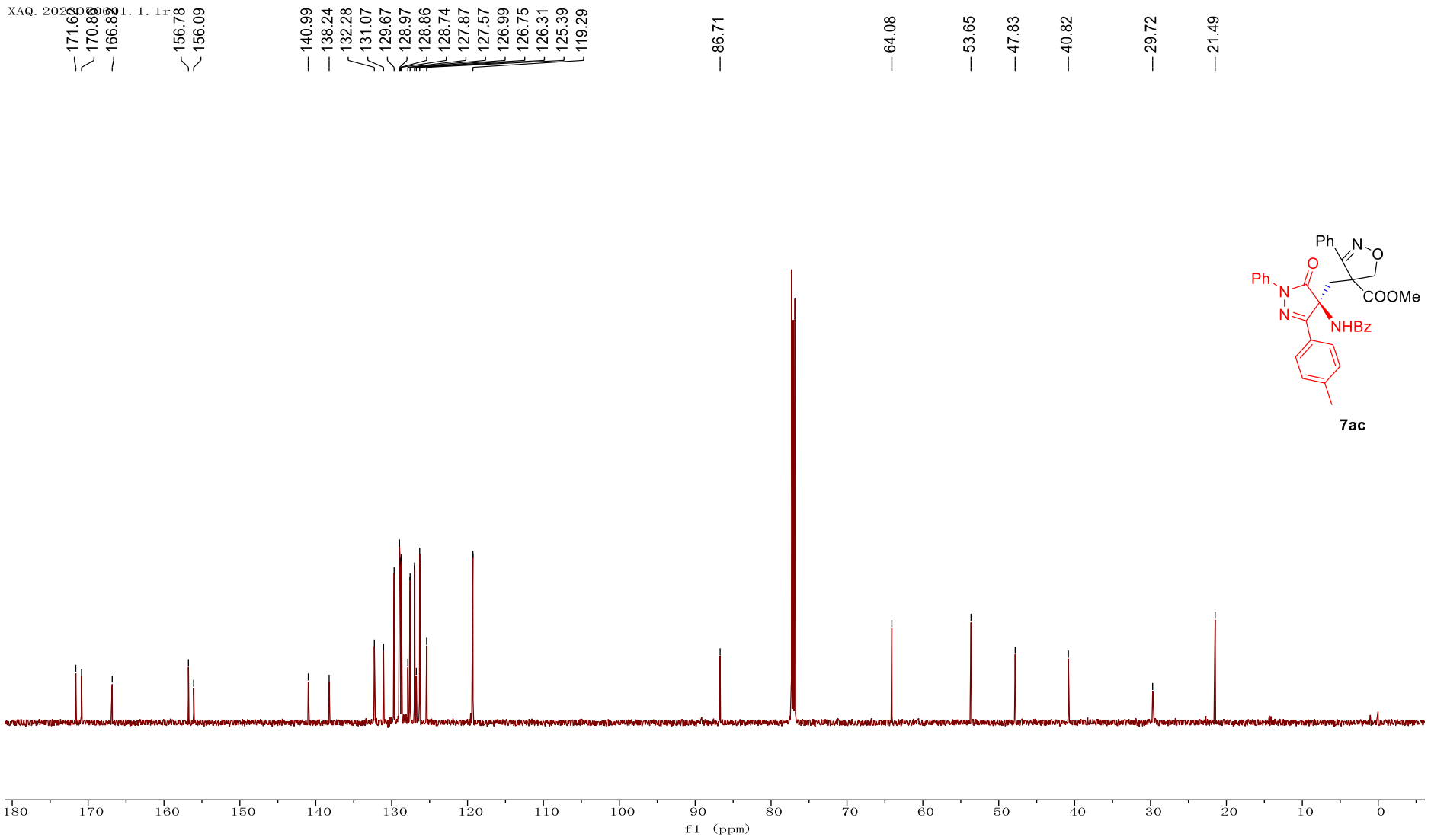
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.20
7.20
7.18
3.87
3.86
3.83
3.37
3.33
2.96
2.92
2.70
2.66
2.33
Ph
N
O
Ph
O
N
N
COOMe
NHBz
1.02
2.02
4.12
2.01
0.98
8.15
2.35
4.03
1.04
1.01
1.04
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

7ac


XAQ. 20230601. 1. 1r
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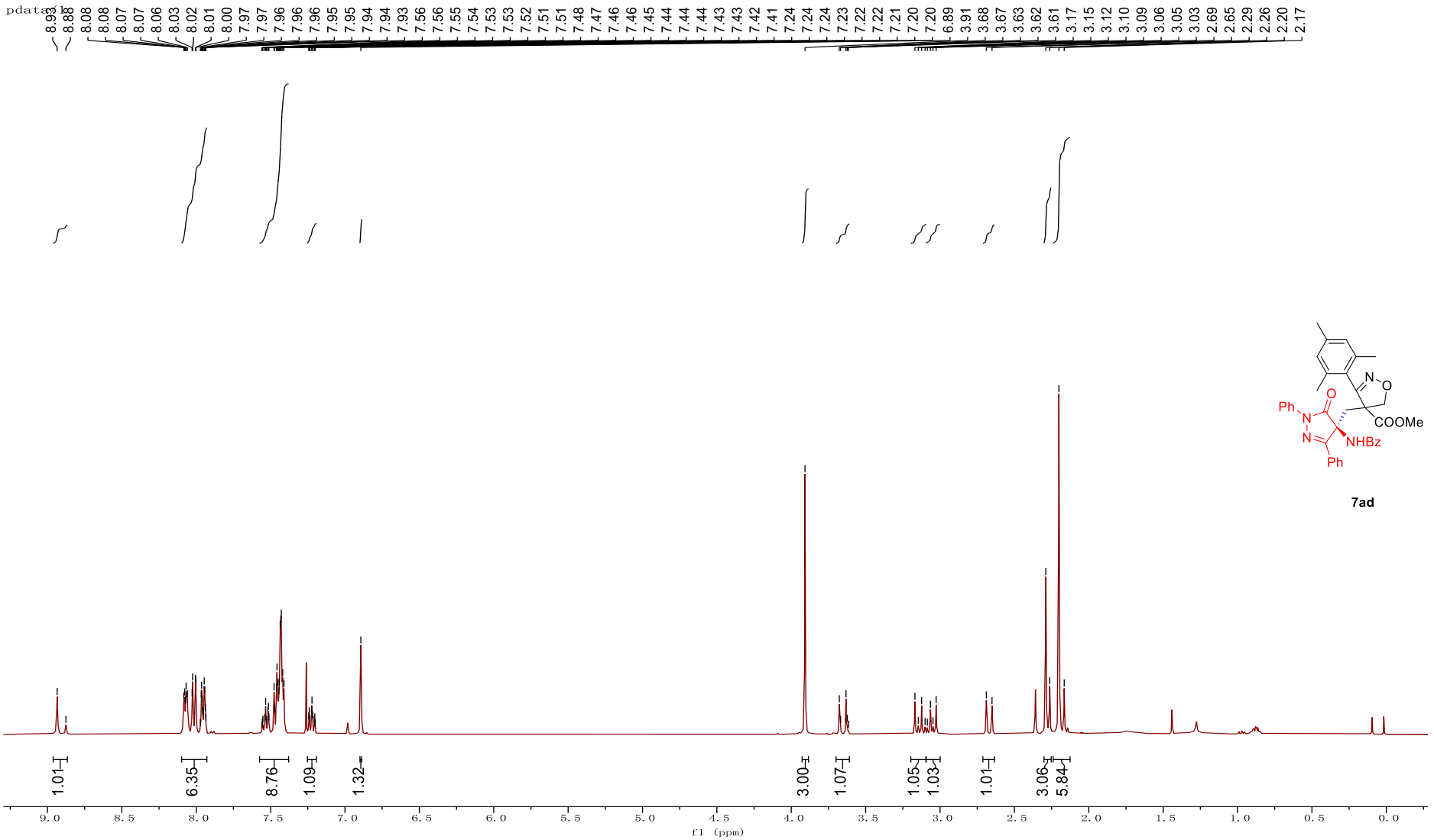
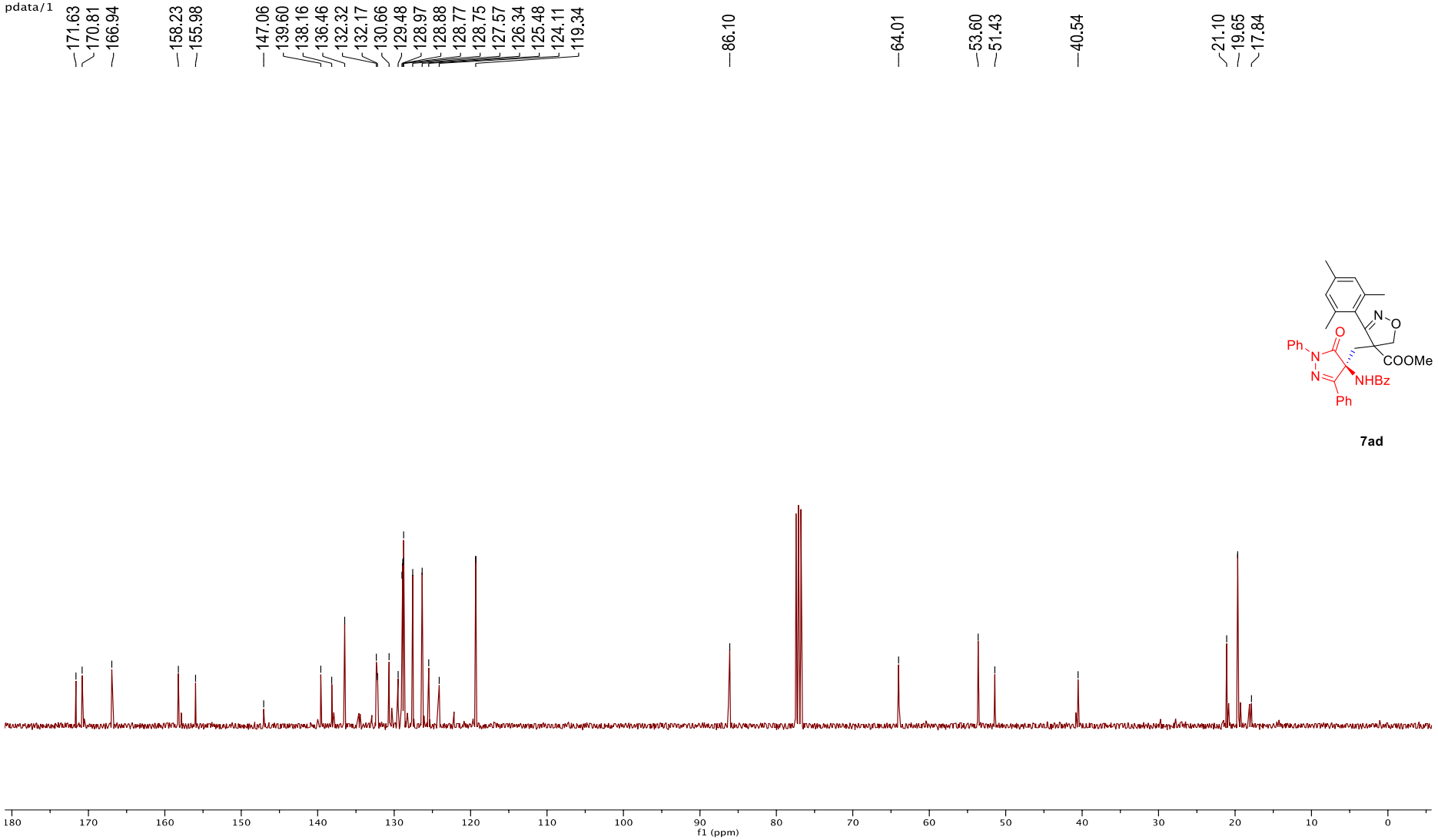
166.85
156.78
156.09
140.99
138.24
132.28
131.07
129.67
128.97
128.86
128.74
127.87
127.57
126.99
126.75
126.31
125.39
119.29
86.71
64.08
53.65
47.83
40.82
29.72
21.49
Ph
N
O
O
Ph
N
N
COOMe
NHBz
7ac
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


pdata
8.93 8.88 8.08 8.08 8.07 8.07 8.06 8.03 8.02 8.01 8.00 7.97 7.97 7.96 7.96 7.96 7.95 7.95 7.94 7.94 7.93 7.56 7.56 7.55 7.54 7.53 7.53 7.52 7.51 7.51 7.48 7.47 7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.41 7.24 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.20 6.89 3.91 3.68 3.67 3.63 3.62 3.61 3.17 3.15 3.12 3.10 3.09 3.06 3.05 3.03 2.69 2.65 2.29 2.26 2.20 2.17
Ph
N
N
O
O
NHBz
Ph
N
O
COOMe
7ad
1.01 6.35 8.76 1.09 1.32 3.00 1.07 1.05 1.03 1.01 3.06 5.84
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


pdata/1
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166.94
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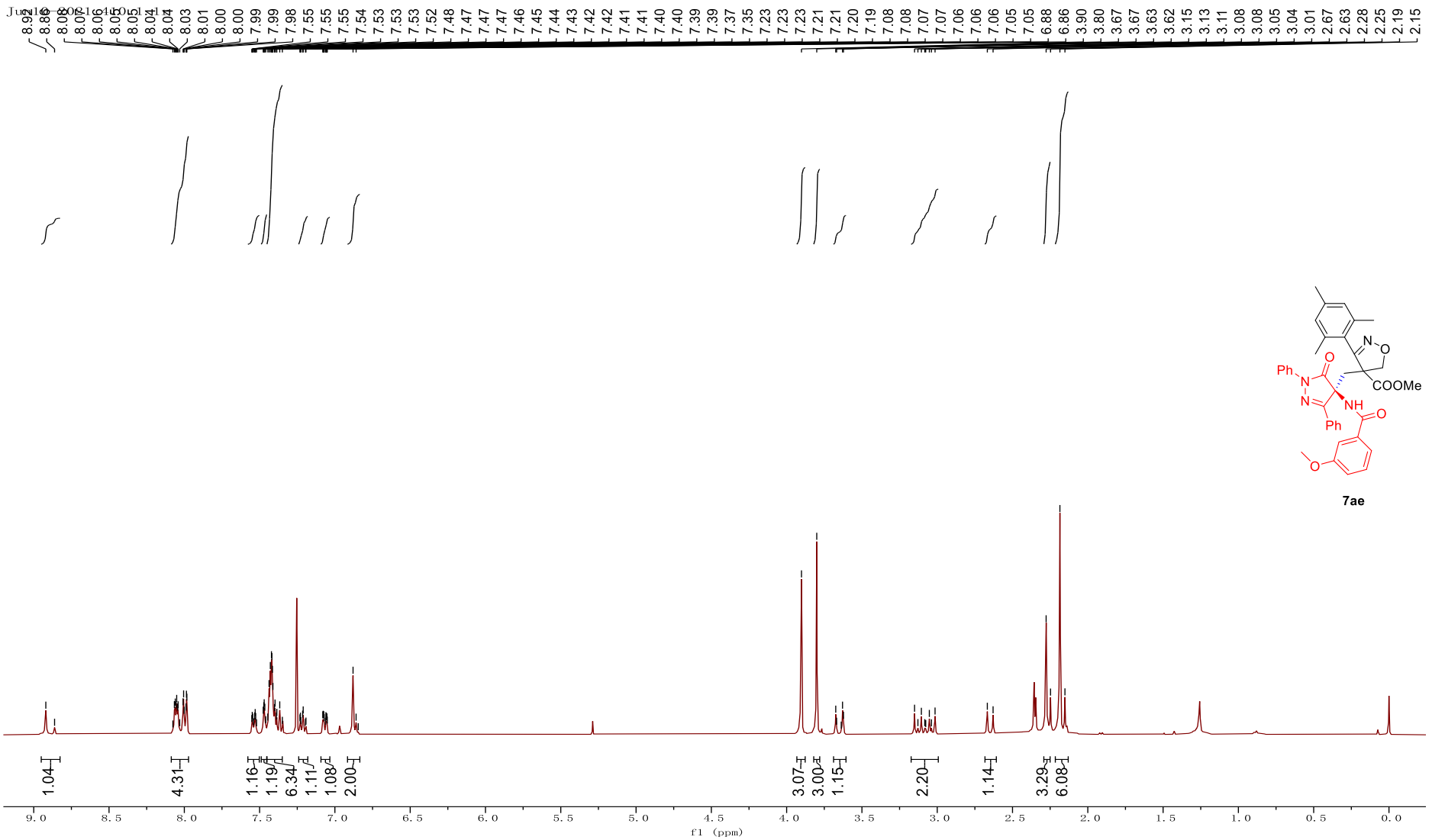
155.98
147.06
139.60
138.16
136.46
132.32
132.17
130.66
129.48
128.97
128.88
128.77
128.75
127.57
126.34
125.48
124.11
119.34
86.10
64.01
53.60
51.43
40.54
21.10
19.65
17.84
Ph
N
O
COOMe
NHBz
Ph
7ad
f1 (ppm)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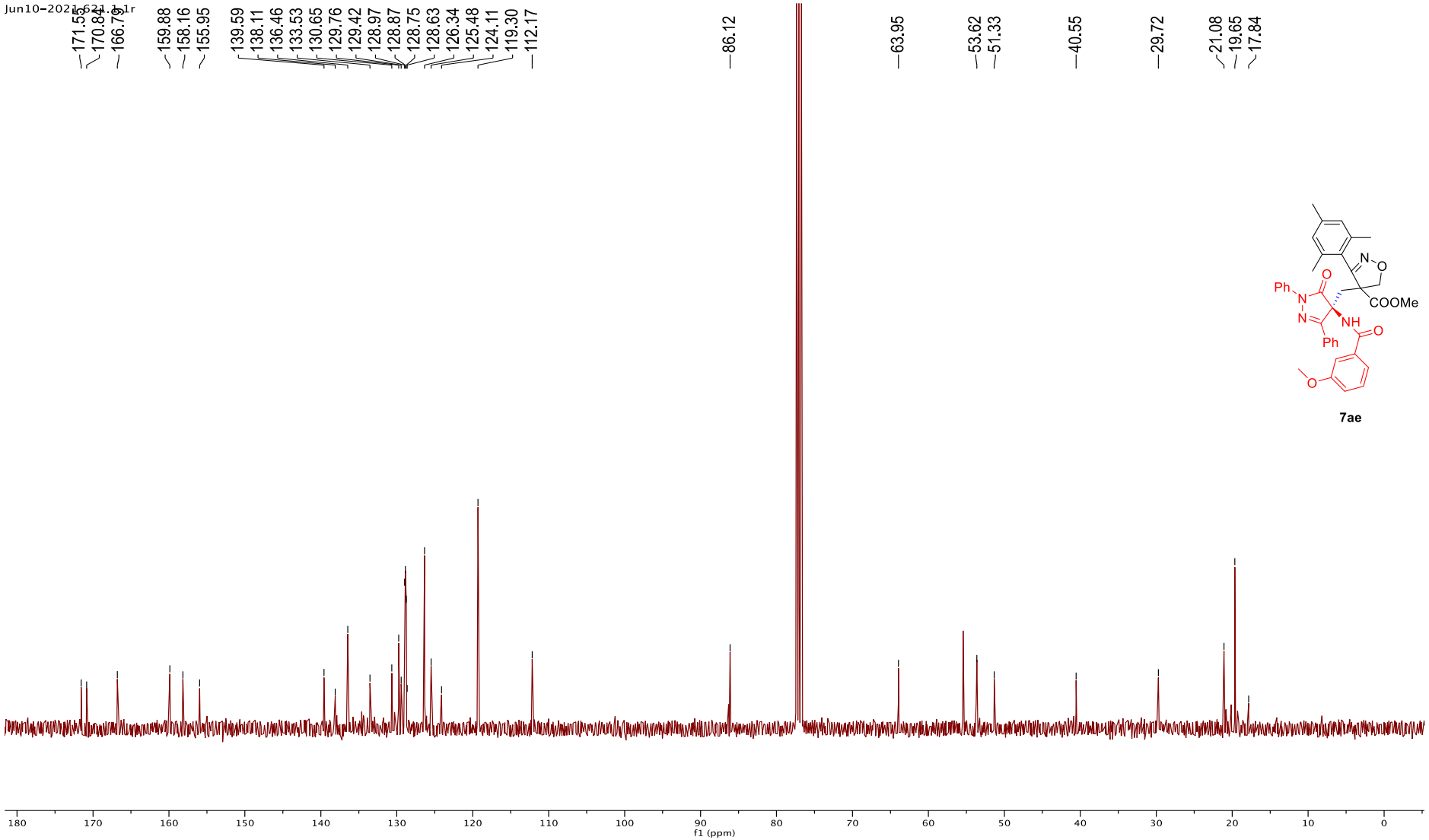
Ph
N
O
COOMe
NH
O
Ph
O
7ae
1.04 4.31 1.16 1.19 6.34 1.11 1.08 2.00 3.07 3.00 1.15 2.20 1.14 3.29 6.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.11
136.46
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129.76
129.42
128.97
128.87
128.75
128.63
126.34
125.48
124.11
119.30
112.17
86.12
63.95
53.62
51.33
40.55
29.72
21.08
19.65
17.84
Ph
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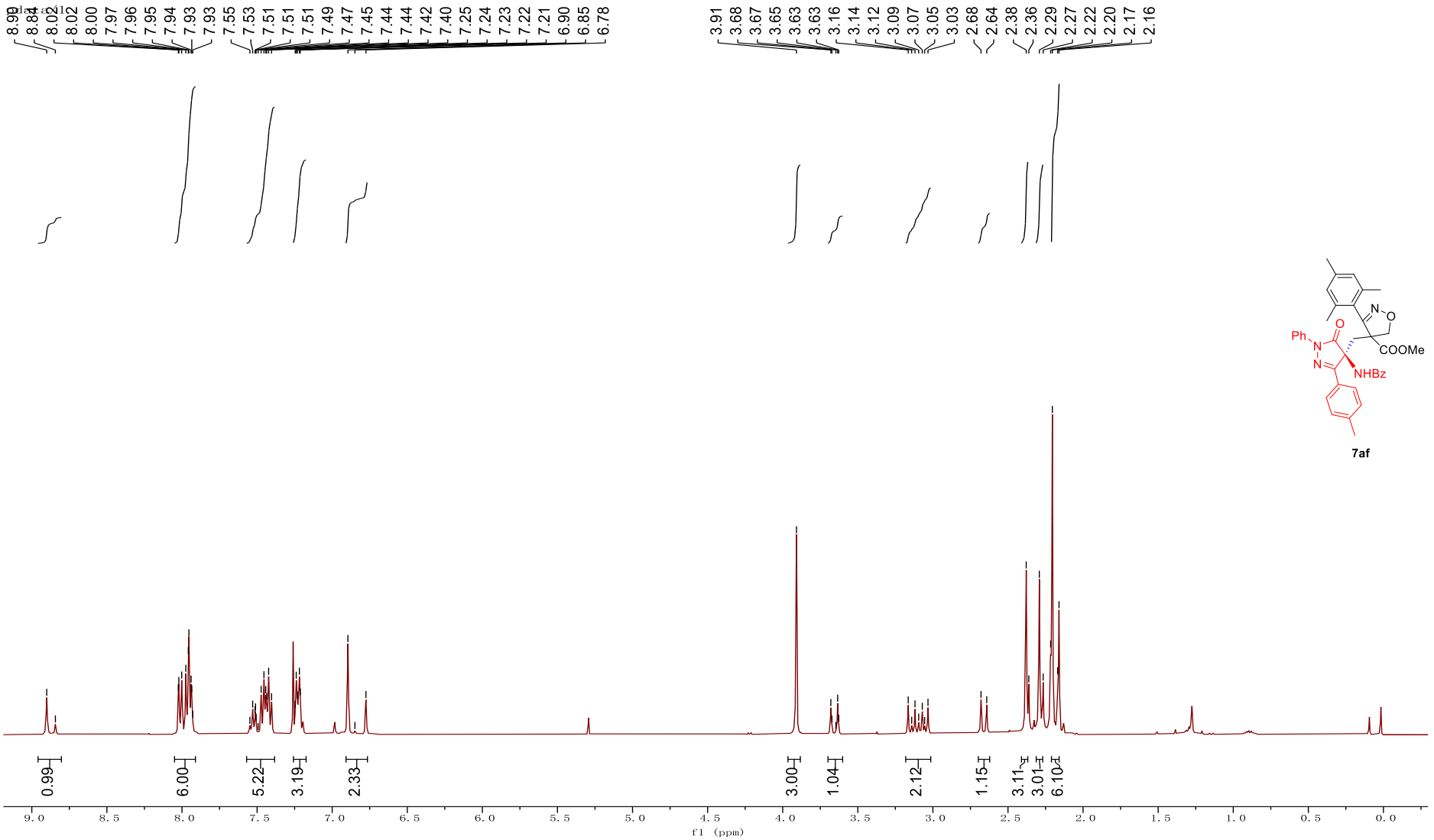
N
O
O
COOMe
NH
Ph
O
O
f1 (ppm)

7ae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8.84
8.02
8.02
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7.97
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7.95
7.94
7.93
7.93
7.55
7.53
7.51
7.51
7.51
7.49
7.47
7.45
7.44
7.44
7.42
7.40
7.25
7.24
7.23
7.22
7.21
6.90
6.85
6.78
3.91
3.68
3.67
3.65
3.63
3.63
3.16
3.14
3.12
3.09
3.07
3.05
3.03
2.68
2.64
2.38
2.36
2.29
2.27
2.22
2.20
2.17
2.16
Ph
N
N
O
O
COOMe
NHBz
7af
0.99
6.00
5.22
3.19
2.33
3.00
1.04
2.12
1.15
3.11
3.01
6.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
1.5
1.0
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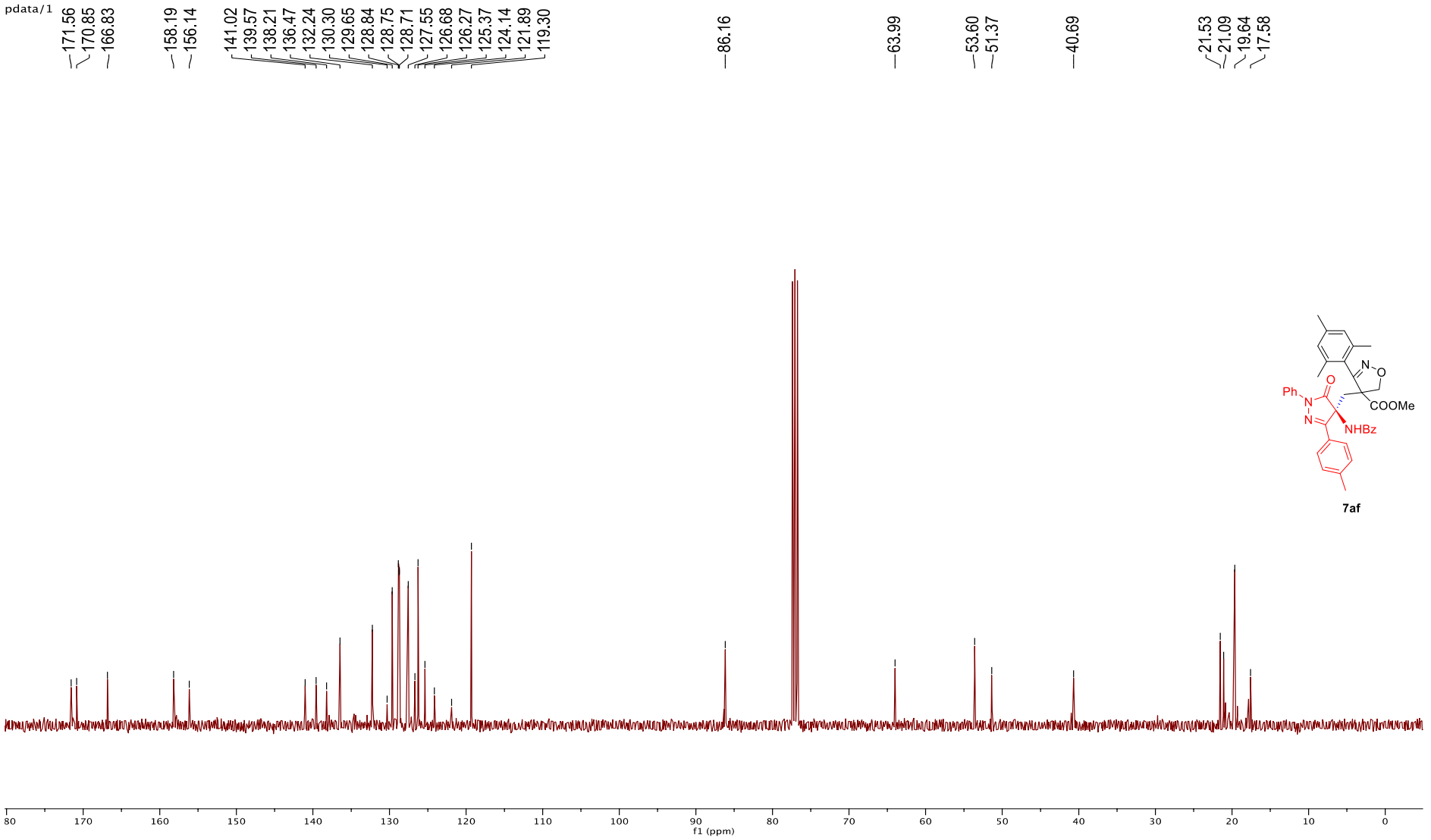
0.0
f1 (ppm)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166.83
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141.02
139.57
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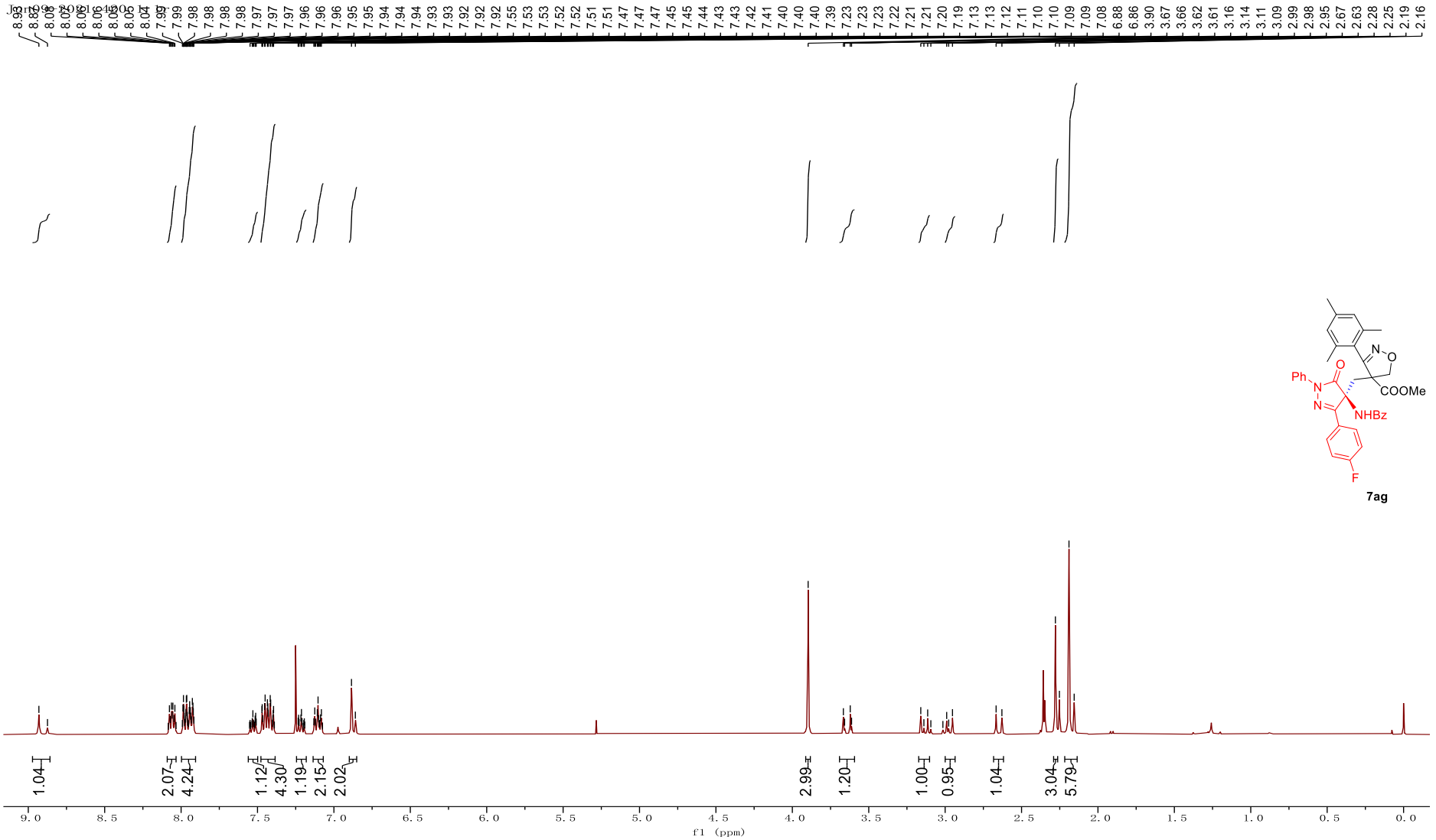
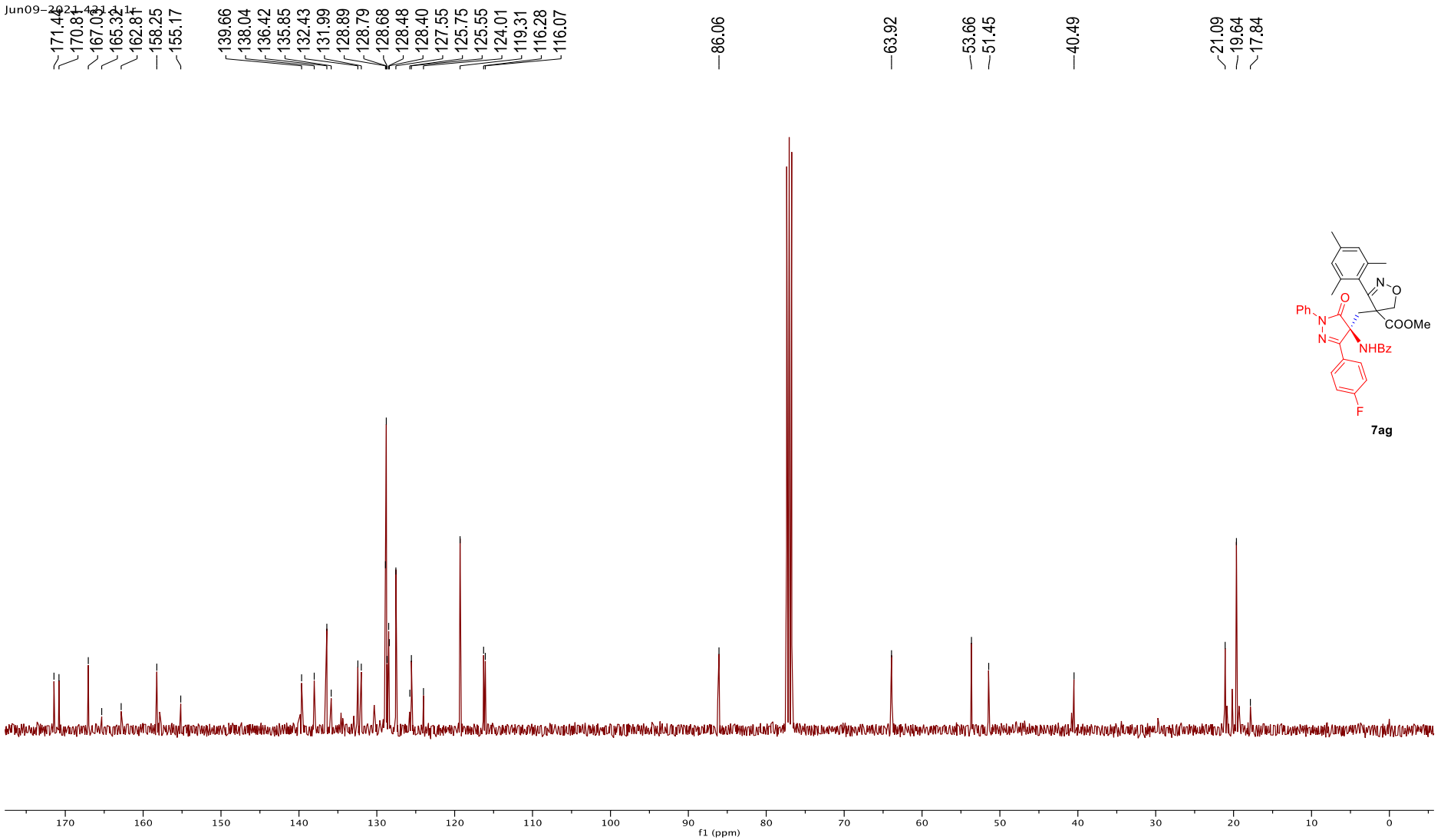
136.47
132.24
130.30
129.65
128.84
128.75
128.71
127.55
126.68
126.27
125.37
124.14
121.89
119.30
86.16
63.99
53.60
51.37
40.69
21.53
21.09
19.64
17.58
Ph
N
N
O
O
COOMe
NHBz
7af
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.93 8.82 8.08 8.03 8.03 8.06 8.06 8.05 8.05 8.04 7.99 7.99 7.98 7.98 7.98 7.98 7.97 7.97 7.97 7.96 7.96 7.96 7.95 7.95 7.94 7.94 7.94 7.93 7.93 7.92 7.92 7.92 7.55 7.53 7.53 7.52 7.52 7.51 7.51 7.47 7.47 7.47 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.40 7.40 7.40 7.39 7.23 7.23 7.23 7.22 7.21 7.21 7.20 7.19 7.13 7.13 7.12 7.11 7.10 7.10 7.09 7.09 7.08 6.88 6.86 3.90 3.67 3.66 3.62 3.61 3.16 3.14 3.11 3.09 2.99 2.98 2.95 2.67 2.63 2.28 2.25 2.19 2.16
Ph
N
N
O
O
COOMe
NHBz
F
7ag
1.04 2.07 4.24 1.12 4.30 1.19 2.15 2.02 2.99 1.20 1.00 0.95 1.04 3.04 5.79
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Jun09-2021-421-1H
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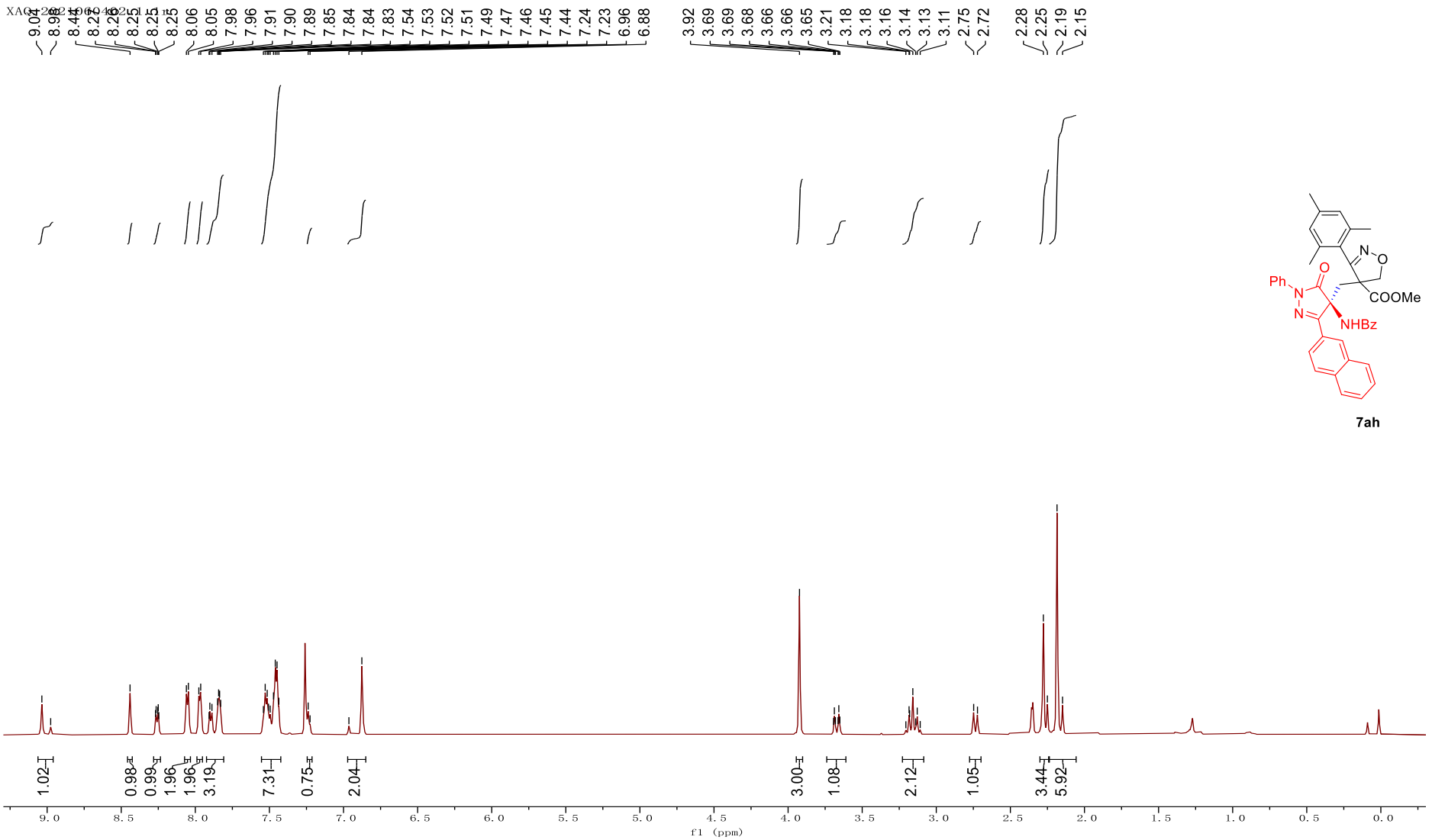
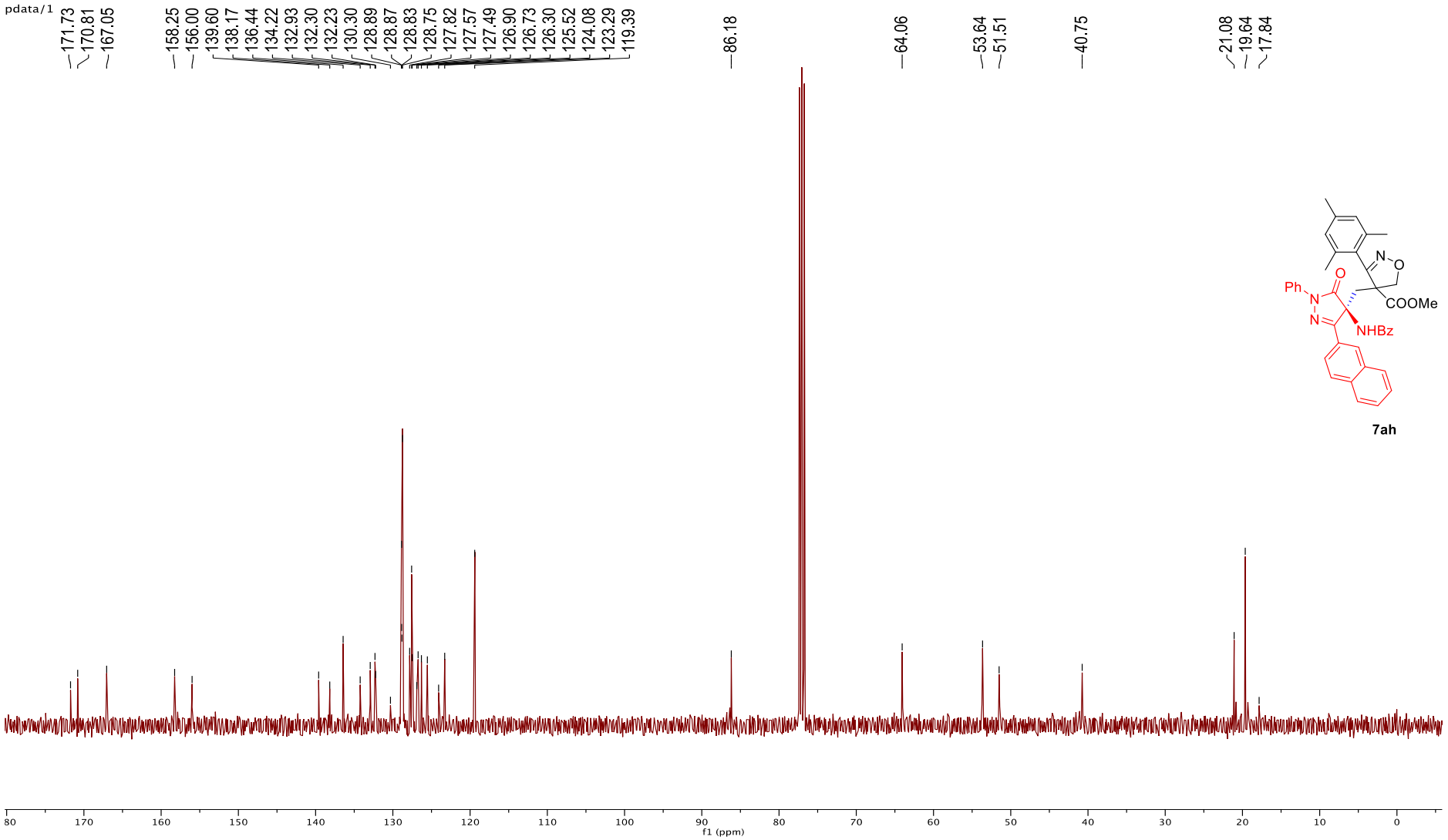
167.03
165.32
162.81
158.25
155.17
139.66
138.04
136.42
135.85
132.43
131.99
128.89
128.79
128.68
128.48
128.40
127.55
125.75
125.55
124.01
119.31
116.28
116.07
86.06
63.92
53.66
51.45
40.49
21.09
19.64
17.84
Ph
N
N
O
O
COOMe
NHBz
F
7ag
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.04
8.99
8.45
8.27
8.26
8.25
8.25
8.25
8.06
8.05
7.98
7.96
7.91
7.90
7.89
7.85
7.84
7.84
7.83
7.54
7.53
7.52
7.51
7.49
7.47
7.46
7.45
7.44
7.24
7.23
6.96
6.88
3.92
3.69
3.69
3.68
3.66
3.66
3.65
3.21
3.18
3.18
3.16
3.14
3.13
3.11
2.75
2.72
2.28
2.25
2.19
2.15
1.02
0.98
0.99
1.96
1.96
3.19
7.31
0.75
2.04
3.00
1.08
2.12
1.05
3.44
5.92
f1 (ppm)

7ah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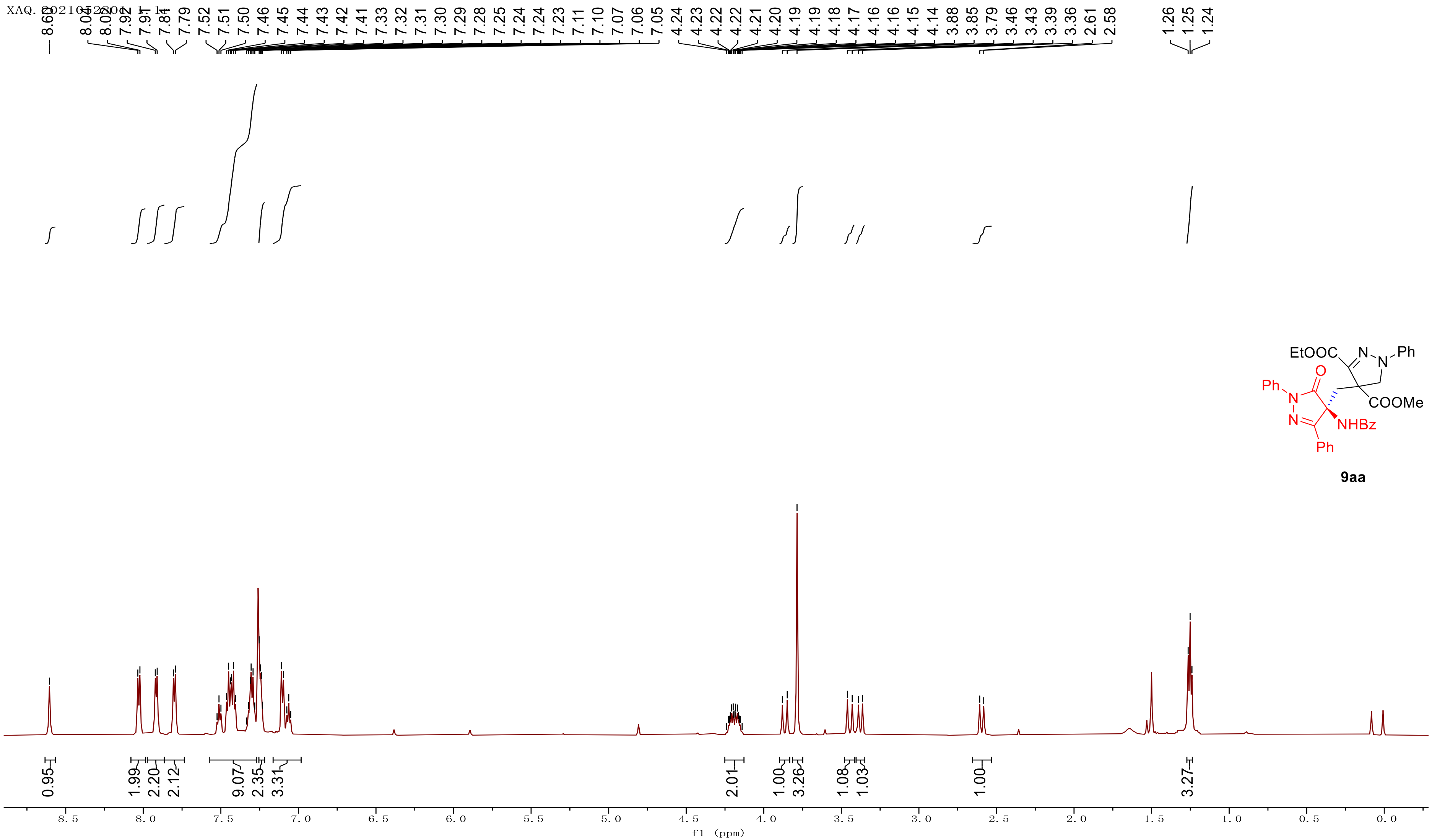
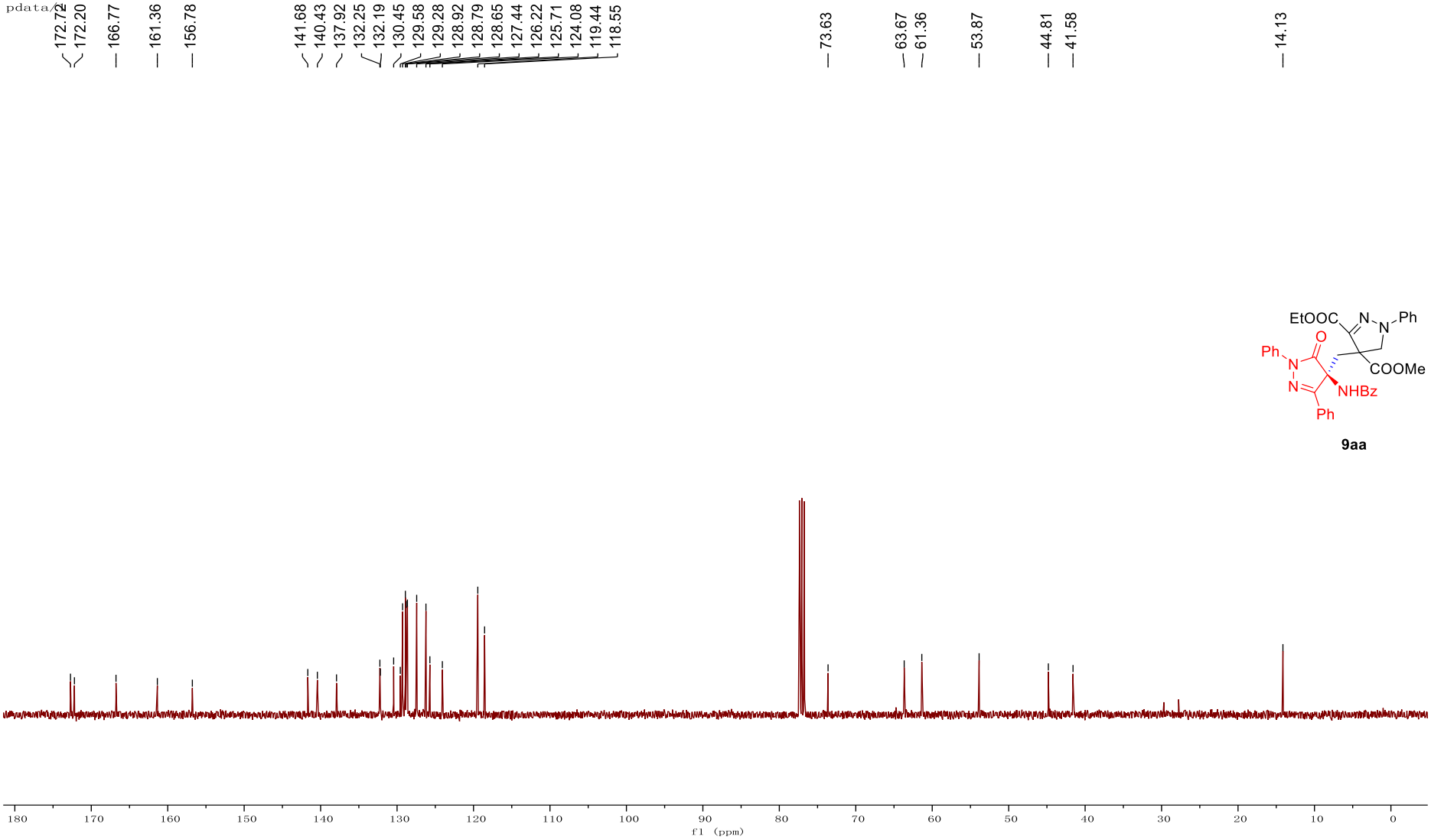
167.05
158.25
156.00
139.60
138.17
136.44
134.22
132.93
132.30
132.23
130.30
128.89
128.87
128.83
128.75
127.82
127.57
127.49
126.90
126.73
126.30
125.52
124.08
123.29
119.39
86.18
64.06
53.64
51.51
40.75
21.08
19.64
17.84
Ph
N
N
O
O
COOMe
NHBz
7ah
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



9aa


pdata/2
172.72
172.20
166.77
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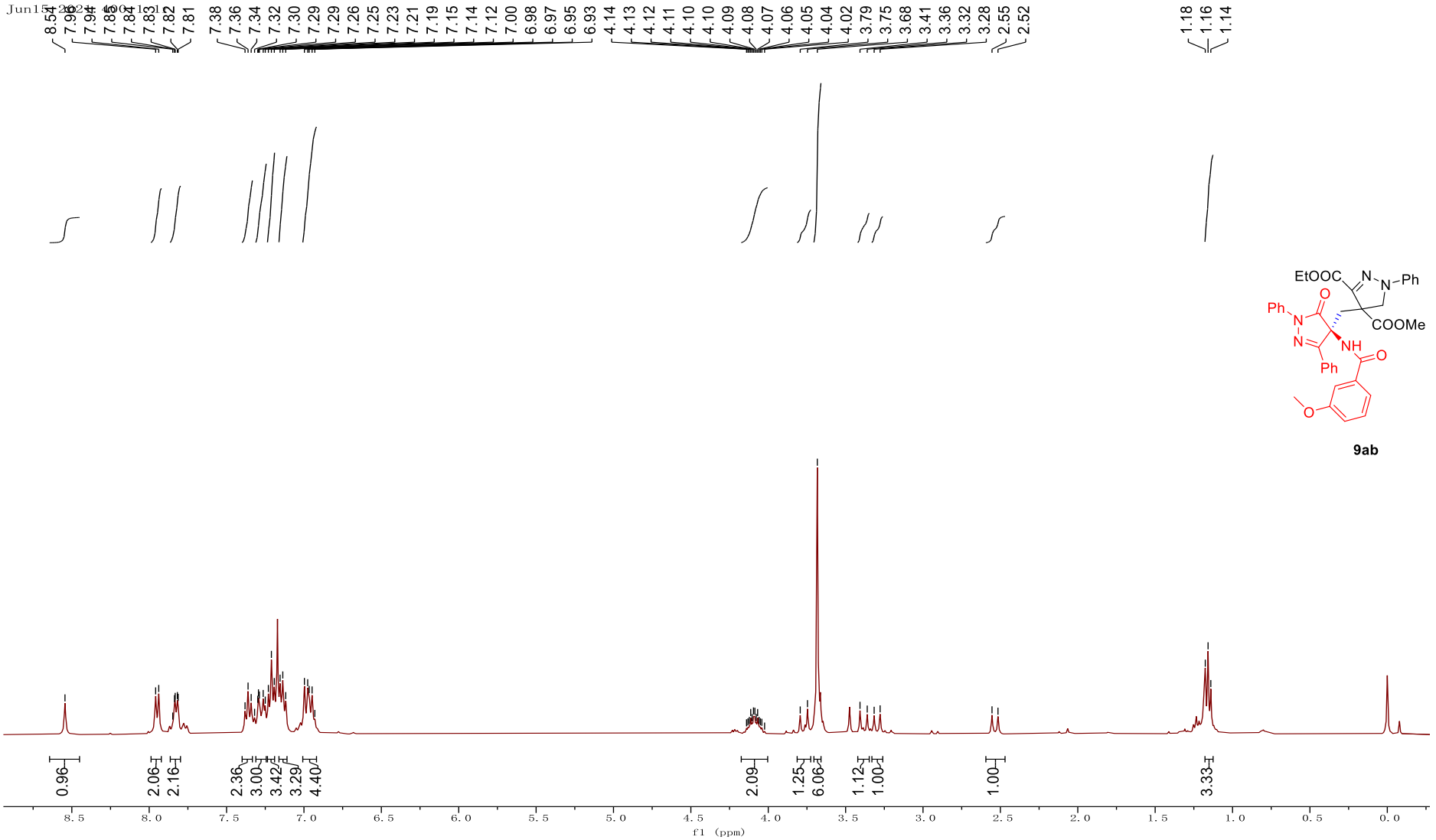
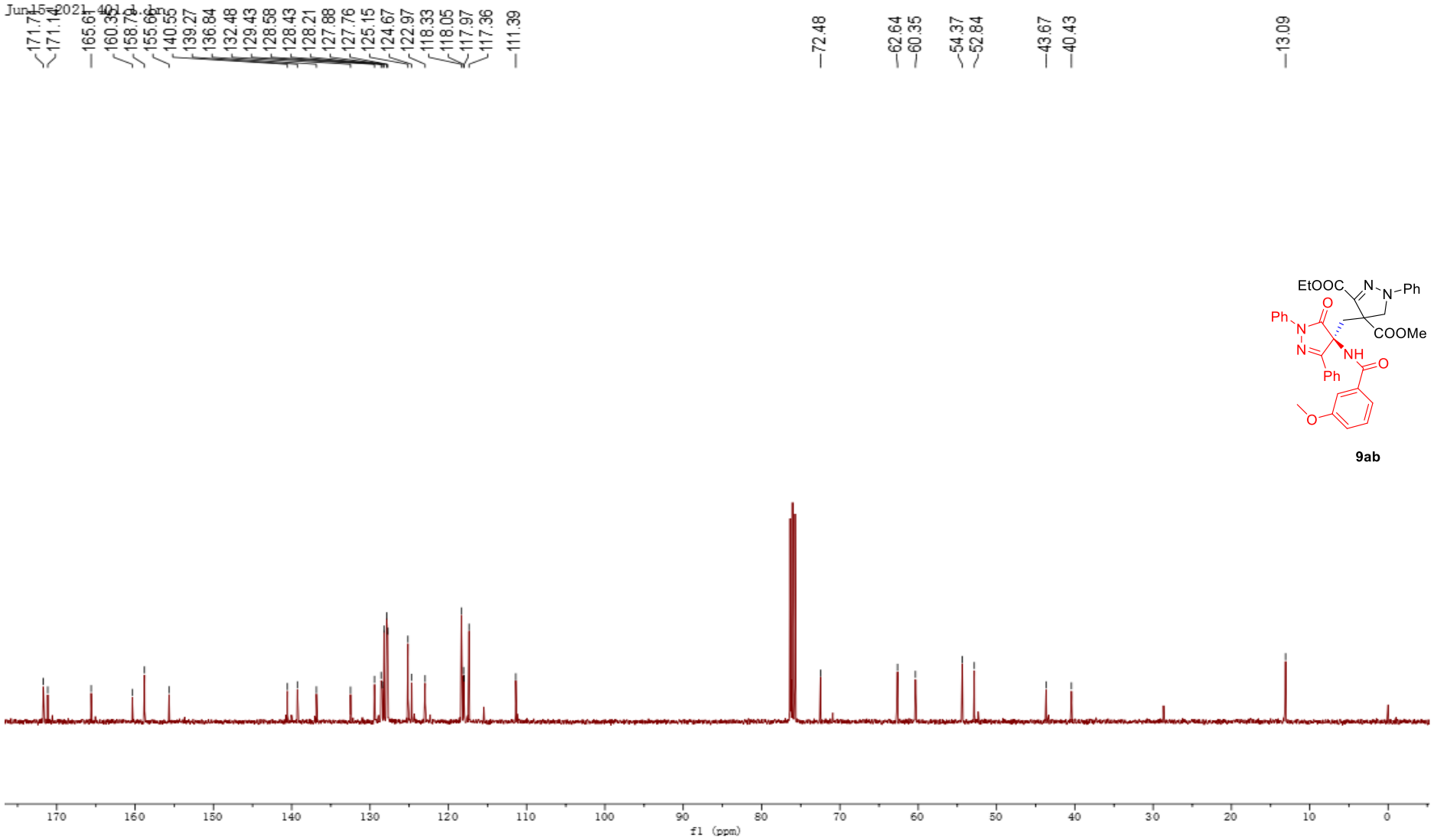
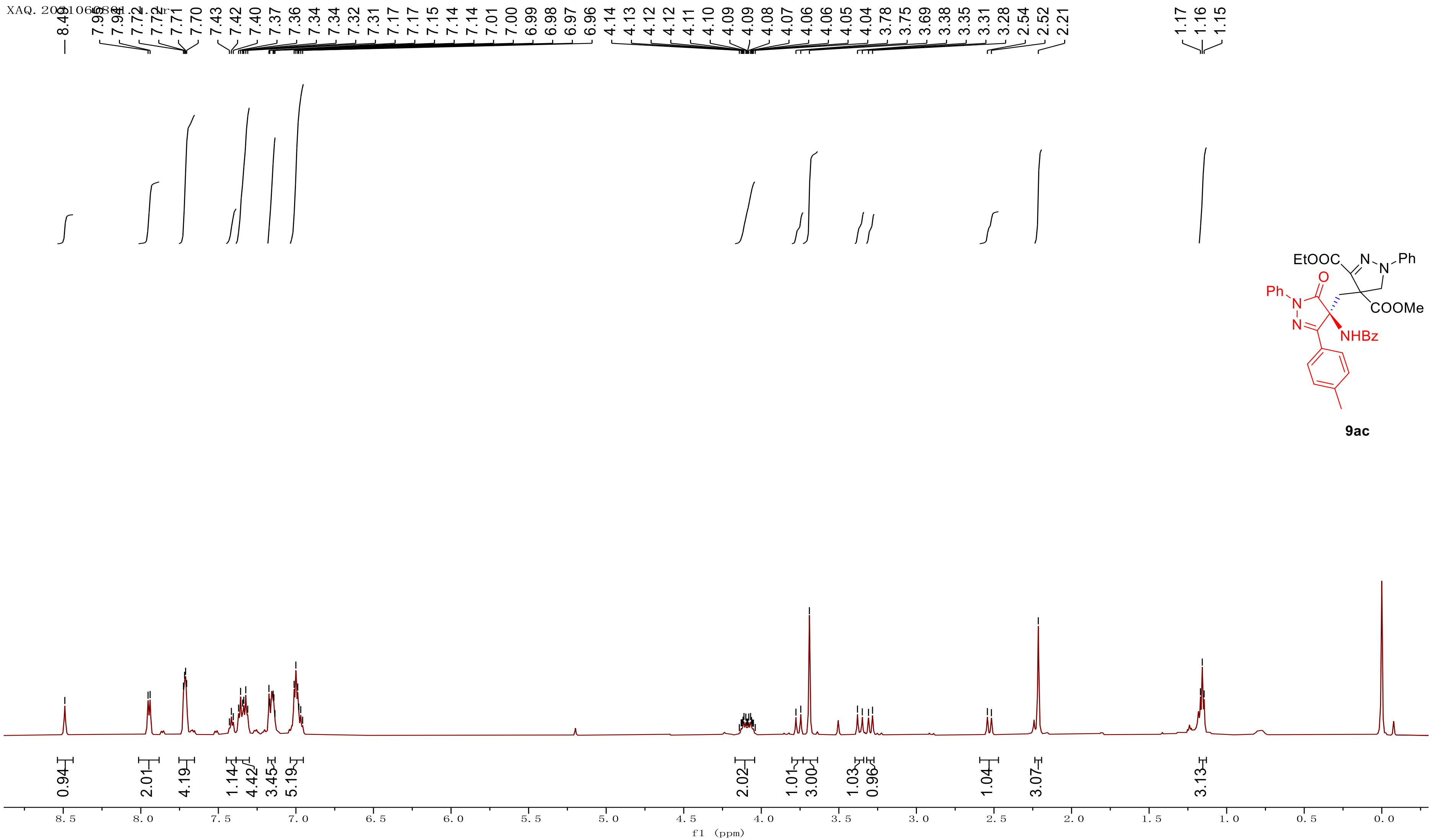
156.78
141.68
140.43
137.92
132.25
132.19
130.45
129.58
129.28
128.92
128.79
128.65
127.44
126.22
125.71
124.08
119.44
118.55
73.63
63.67
61.36
53.87
44.81
41.58
14.13
EtOOC
N
N
Ph
O
Ph
N
N
COOMe
NHBz
Ph
9aa
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.54
7.90
7.84
7.83
7.82
7.81
7.38
7.36
7.34
7.32
7.30
7.29
7.26
7.25
7.23
7.21
7.19
7.15
7.14
7.12
7.00
6.98
6.97
6.95
6.93
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.05
4.04
4.02
3.79
3.75
3.68
3.41
3.36
3.32
3.28
2.55
2.52
1.18
1.16
1.14
EtOOC
N
N
Ph
O
Ph
N
N
COOMe
NH
O
Ph
O
9ab
0.96
2.06
2.16
2.36
3.00
3.42
3.29
4.40
2.09
1.25
6.06
1.12
1.00
1.00
3.33
f1 (ppm)


Jun 15 2021 401 1 c1
171.71
171.14
165.61
160.35
158.79
155.66
140.55
139.27
136.84
132.48
129.43
128.58
128.43
128.21
127.88
127.76
125.15
124.67
122.97
118.33
118.05
117.97
117.36
111.39
72.48
62.64
60.35
54.37
52.84
43.67
40.43
13.09
EtOOC
N
N
Ph
O
Ph
N
N
COOMe
NH
O
Ph
O
9ab
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


XAQ. 20210608....1.fid
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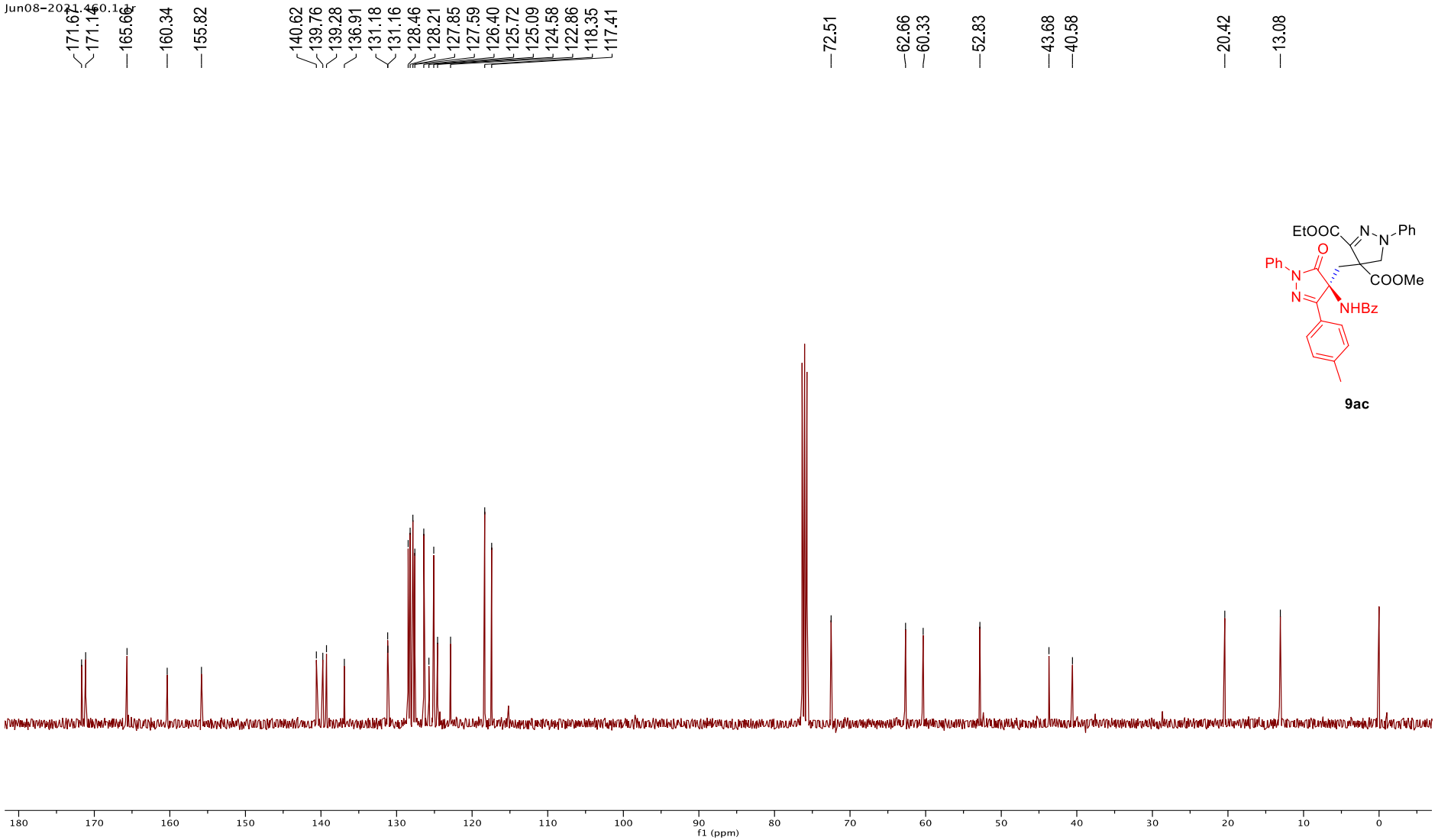
7.94
7.72
7.72
7.71
7.70
7.43
7.42
7.40
7.37
7.36
7.34
7.34
7.32
7.31
7.17
7.17
7.15
7.14
7.14
7.01
7.00
6.99
6.98
6.97
6.96
4.14
4.13
4.12
4.12
4.11
4.10
4.09
4.09
4.08
4.07
4.06
4.06
4.05
4.04
3.78
3.75
3.69
3.38
3.35
3.31
3.28
2.54
2.52
2.21
1.17
1.16
1.15
EtOOC
N
N
Ph
Ph
N
N
O
COOMe
NHBz
9ac
0.94
2.01
4.19
1.14
4.42
3.45
5.19
2.02
1.01
3.00
1.03
0.96
1.04
3.07
3.13
f1 (ppm)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171.14
165.66
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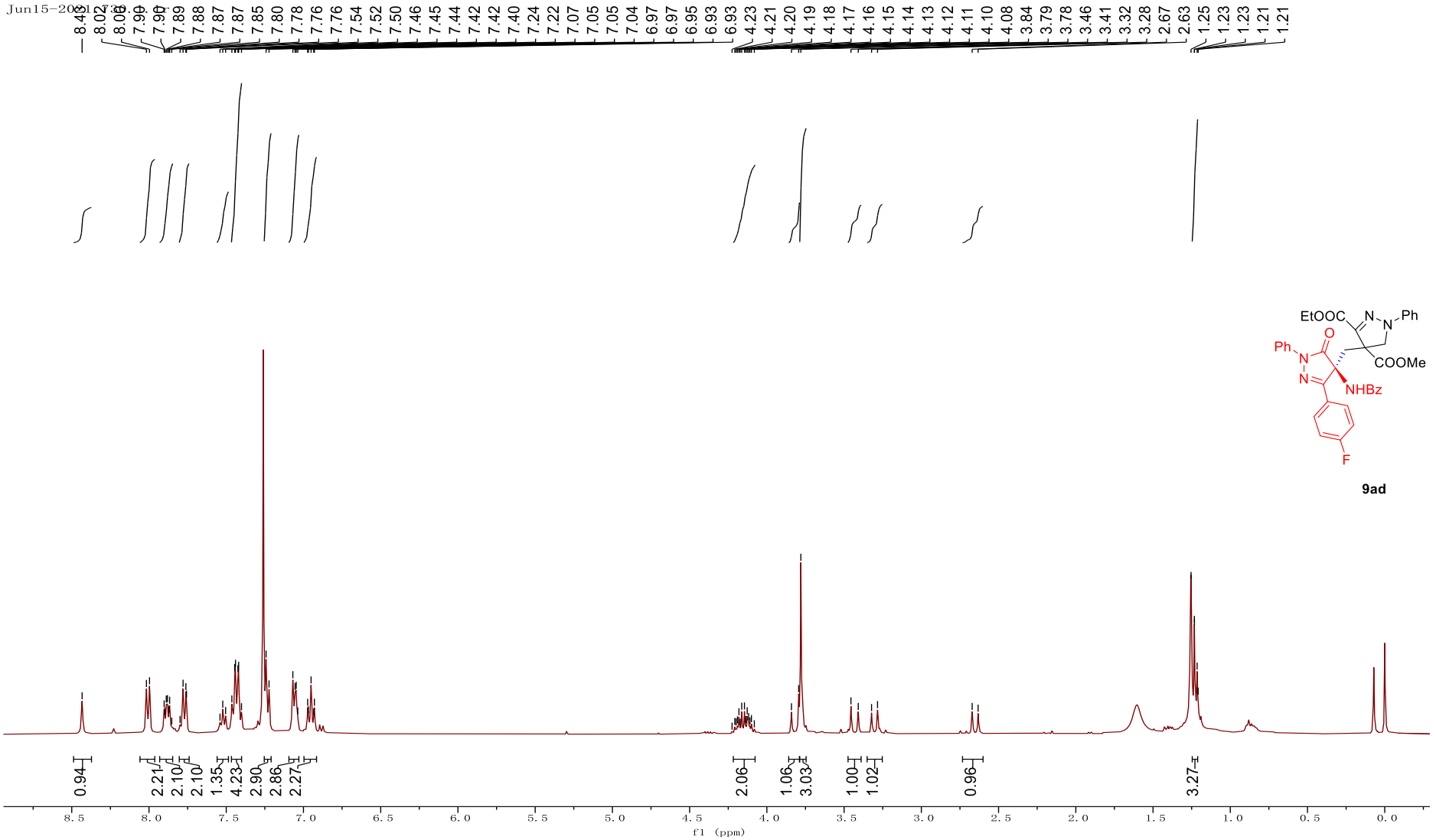
155.82
140.62
139.76
139.28
136.91
131.18
131.16
128.46
128.21
127.85
127.59
126.40
125.72
125.09
124.58
122.86
118.35
117.41
72.51
62.66
60.33
52.83
43.68
40.58
20.42
13.08
EtOOC
N
N
Ph
O
Ph
N
N
COOMe
NHBz
9ac
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Jun15-2021
8.43
8.02
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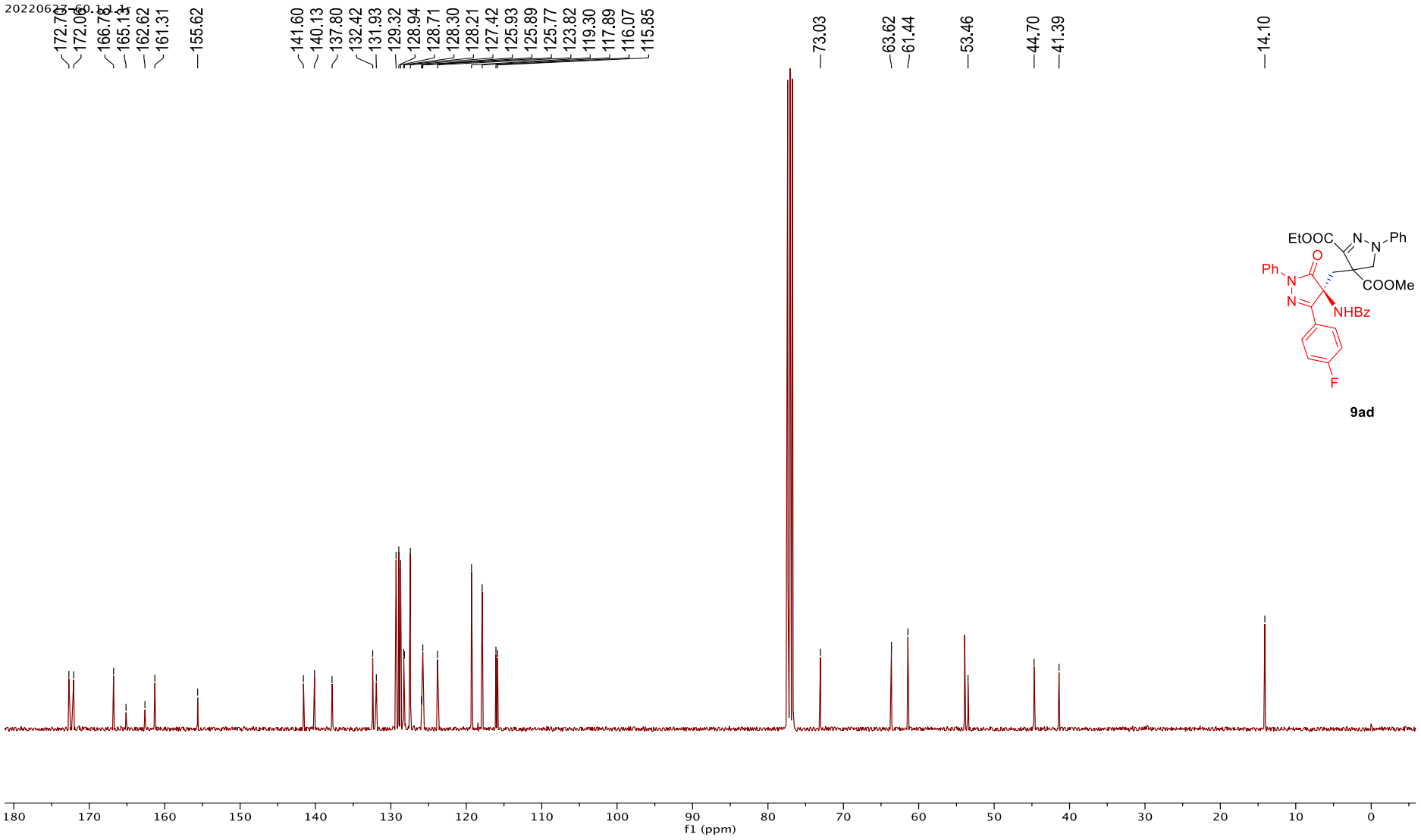
7.90
7.89
7.88
7.87
7.87
7.85
7.80
7.78
7.76
7.76
7.54
7.52
7.50
7.46
7.45
7.44
7.42
7.42
7.40
7.24
7.22
7.07
7.05
7.05
7.04
6.97
6.97
6.95
6.93
6.93
4.23
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.10
4.08
3.84
3.79
3.78
3.46
3.41
3.32
3.28
2.67
2.63
1.25
1.23
1.23
1.21
1.21
EtOOC
N
N
Ph
O
Ph
N
N
COOMe
NHBz
F
9ad
0.94
2.21
2.10
2.10
1.35
4.23
2.90
2.86
2.27
2.06
1.06
3.03
1.00
1.02
0.96
3.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


20220627-60.1.1r
172.70
172.08
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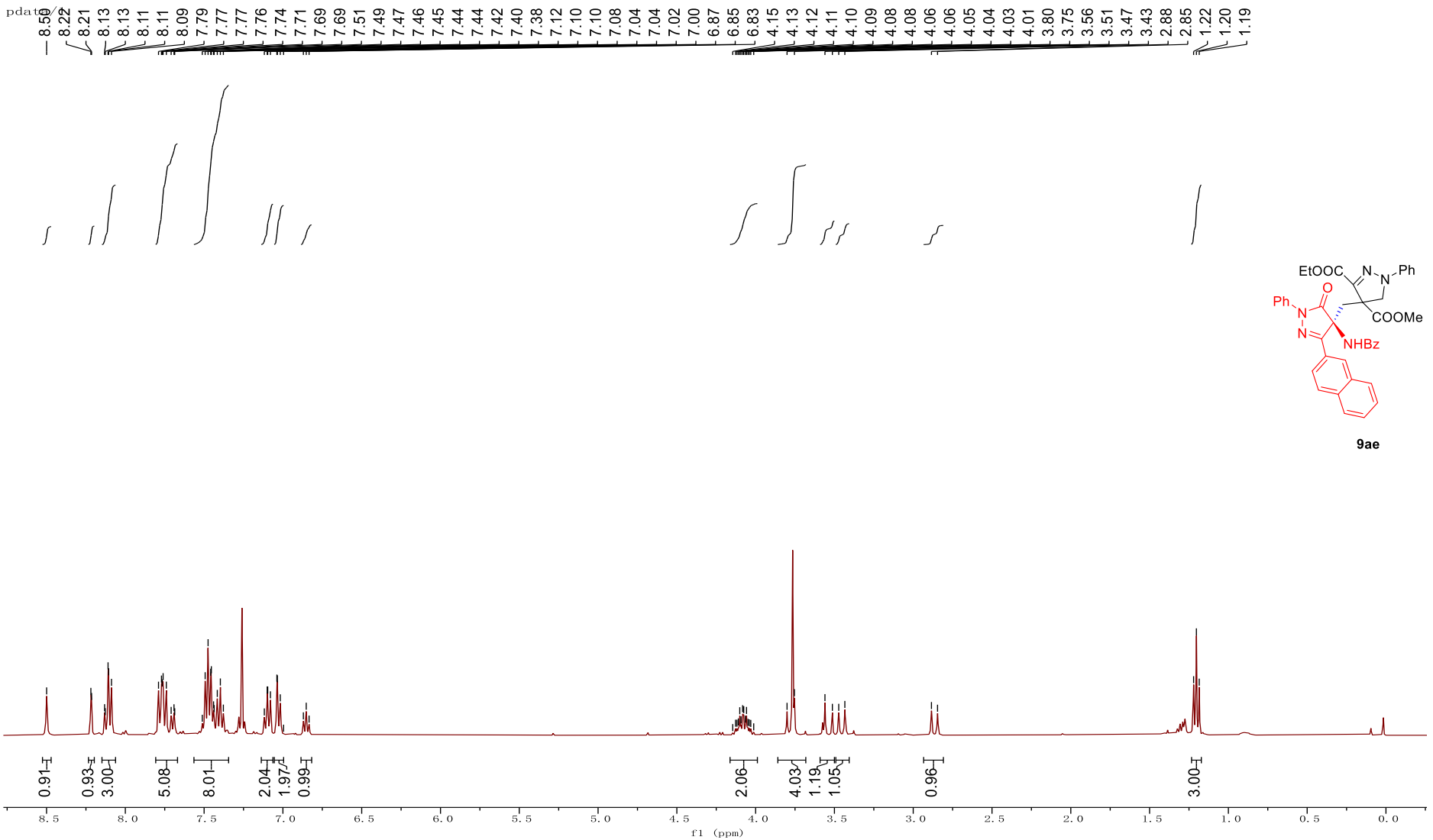
165.15
162.62
161.31
155.62
141.60
140.13
137.80
132.42
131.93
129.32
128.94
128.71
128.30
128.21
127.42
125.93
125.89
125.77
123.82
119.30
117.89
116.07
115.85
73.03
63.62
61.44
53.46
44.70
41.39
14.10
EtOOC
N
N
Ph
O
Ph
N
N
COOMe
NHBz
F
9ad
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


pdata/
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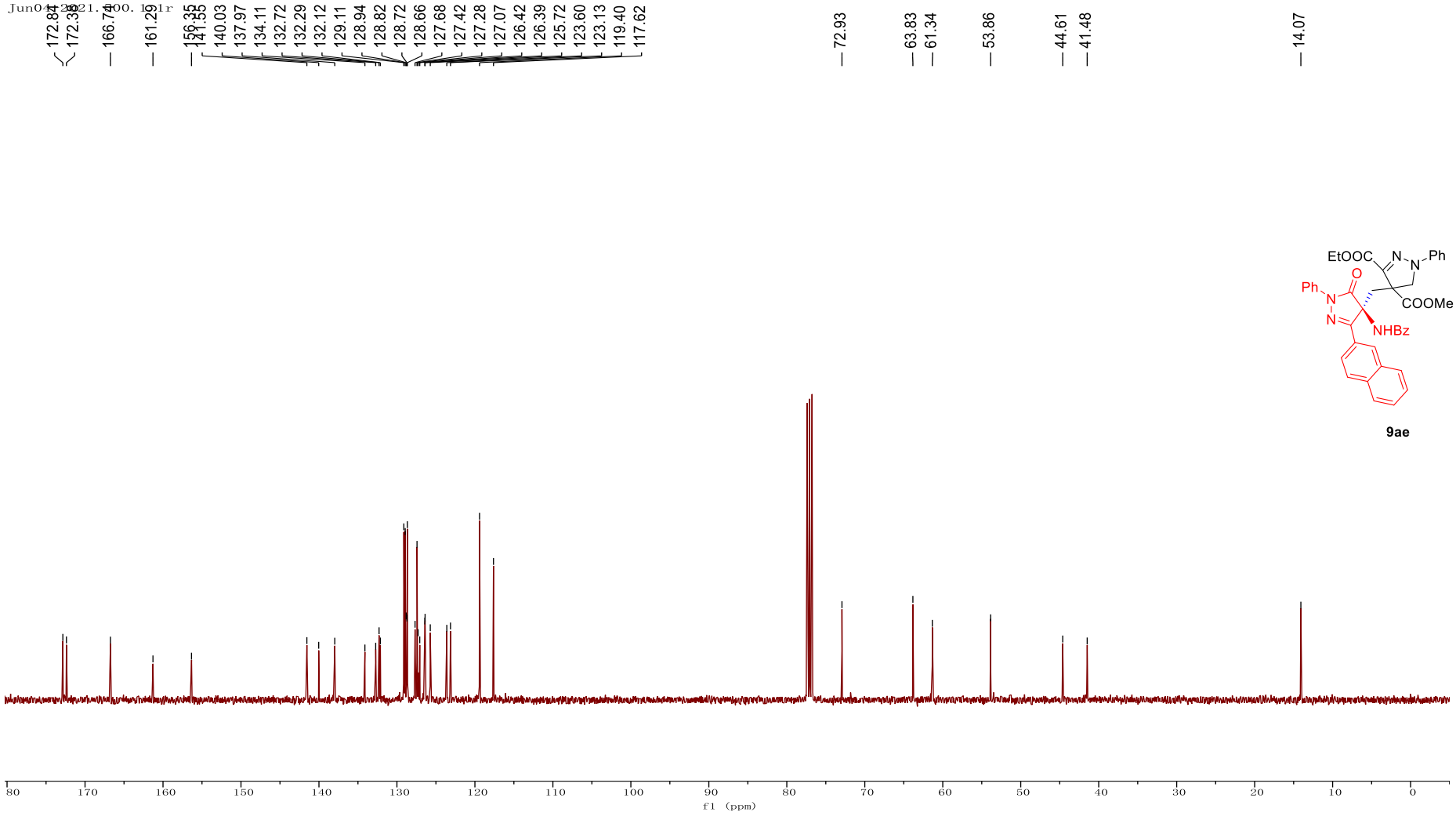
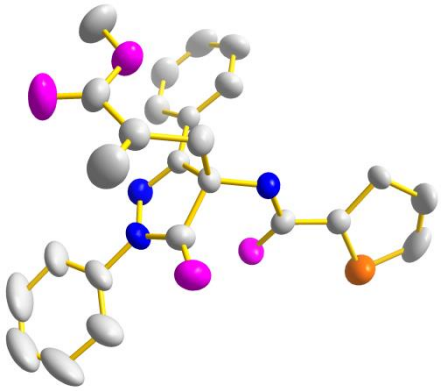
8.22
8.21
8.13
8.13
8.11
8.11
8.09
7.79
7.77
7.77
7.76
7.74
7.71
7.69
7.69
7.51
7.49
7.47
7.46
7.45
7.44
7.44
7.42
7.40
7.38
7.12
7.10
7.10
7.08
7.04
7.04
7.02
7.00
6.87
6.85
6.83
4.15
4.13
4.12
4.11
4.10
4.09
4.08
4.08
4.06
4.06
4.05
4.04
4.03
4.01
3.80
3.75
3.56
3.51
3.47
3.43
2.88
2.85
1.22
1.20
1.19
EtOOC
N
N
Ph
O
Ph
N
N
COOMe
NHBz
0.91
0.93
3.00
5.08
8.01
2.04
1.97
0.99
2.06
4.03
1.19
1.05
0.96
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

9ae


Jun04 2021.400.1r
172.84
172.36
166.74
161.29
156.35
141.55
140.03
137.97
134.11
132.72
132.29
132.12
129.11
128.94
128.82
128.72
128.66
127.68
127.42
127.28
127.07
126.42
126.39
125.72
123.60
123.13
119.40
117.62
72.93
63.83
61.34
53.86
44.61
41.48
14.07
EtOOC
N
N
Ph
O
Ph
N
N
COOMe
NHBz
9ae
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6. X-ray crystal structure of 3ao



CCDC：2181593

Bond precision: C-C = 0.0097 A Wavelength=0.71073

Cell: a=11.7405(7) b=11.7405(7) c=16.9107(15)
alpha=90 beta=90 gamma=90
Temperature: 298 K

	Calculated	Reported
Volume	2331.0(3)	2331.0(3)
Space group	P 43	P 43
Hall group	P 4cw	P 4cw
Moiety formula	C25 H21 N3 O4 S	C25 H21 N3 O4 S
Sum formula	C25 H21 N3 O4 S	C25 H21 N3 O4 S
Mr	459.51	459.51
Dx,g cm-3	1.309	1.309
Z	4	4
Mu (mm-1)	0.175	0.175
F000	960.0	960.0
F000'	960.91	
h,k,lmax	14,14,20	14,14,20
Nref	4418[2289]	4416
Tmin,Tmax	0.992,0.993	0.671,0.746
Tmin'	0.932	

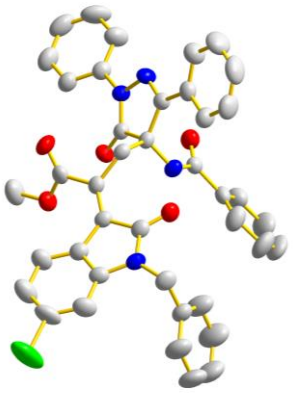
Correction method= # Reported T Limits: Tmin=0.671 Tmax=0.746
AbsCorr = EMPIRICAL

Data completeness= 1.93/1.00 Theta(max)= 25.663

R(reflections)= 0.0580(3186) wR2(reflections)= 0.1722(4416)

S = 1.017 Npar= 304

X-ray crystal structure of 5ak



CCDC：2234675

Bond precision: C-C = 0.0091 A Wavelength=0.71073

Cell: a=9.8337(10) b=10.0674(10) c=11.4250(11)
alpha=70.975(3) beta=81.134(3) gamma=85.203(3)
Temperature: 272 K

	Calculated	Reported
Volume	1055.84(18)	1055.84(18)
Space group	P 1	P 1
Hall group	P 1	P 1
Moiety formula	C41 H32 Cl N4 O5, 2(C H2 Cl2)	C41 H32 Cl N4 O5, 2(C H2 Cl2)
Sum formula	C43 H36 Cl5 N4 O5	C43 H36 Cl5 N4 O5
Mr	866.01	866.01
Dx,g cm-3	1.362	1.362
Z	1	1
Mu (mm-1)	0.393	0.393
F000	447.0	447.0
F000'	447.90	
h,k,lmax	12,12,14	12,12,14
Nref	8750[4375]	8548
Tmin,Tmax	0.910,0.932	0.670,0.745
Tmin'	0.889	

Correction method= # Reported T Limits: Tmin=0.670 Tmax=0.745
AbsCorr = NONE

Data completeness= 1.95/0.98 Theta(max)= 26.460

R(reflections)= 0.0663(5973) wR2(reflections)= 0.1498(8548)

S = 1.037 Npar= 522