Electronic Supplementary Material (ESI) for ChemComm.

Asymmetric [3 + 2] spiroannulation of pyrazolone-derived Morita–Baylis–Hillman carbonates with alkynyl ketones: facile access to spiro[cyclopentadiene-pyrazolone] scaffolds

Xingfu Wei, Yue Huang, Wenyao Wang, Shiqiang Wei, 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.

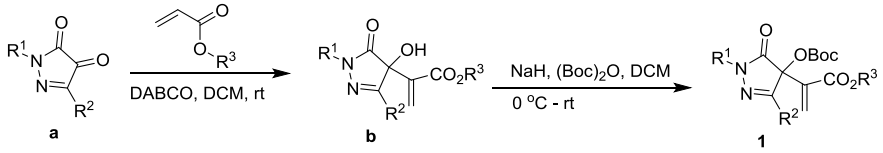
E-mail: bmwang@dlut.edu.cn

Contents:

1. General information

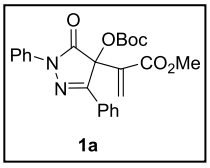
Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200~300 mesh). Enantiomeric excesses (*ee*) were determined by HPLC using corresponding commercial chiral columns as stated at 30 °C with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]_D^T$ (c g/100 mL, solvent). All ^{1}H NMR and ^{19}F NMR spectra were recorded on a Bruker Avance Ⅱ 400 MHz, ^{13}C NMR spectra were recorded on a Bruker Avance Ⅱ 101 MHz or Bruker Avance Ⅲ 151 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, 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 **3ag** was assigned by the X-ray analysis. Alkynyl ketones[1], pyrazole-4,5-diones[2] and catalysts **C6**-**C8**[3] were synthesized according to the literature procedures.

2. General procedure and characterization of MBH carbonates 1

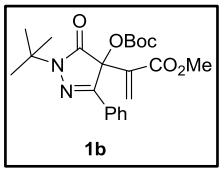


A mixture of pyrazole-4,5-dione (5 mmol, 1.0 equiv.) and DABCO (1 mmol, 0.5 equiv.) in CH_2Cl_2 (3 mL) was stirred for 5 min at room temperature. Then methyl acrylate (15 mmol, 3.0 equiv.) was added dropwise into the solution and the reaction was monitored by TLC. After completion, the solvent was removed and the crude product was purified by column chromatography with *n*-hexane/ethyl acetate (3/1, v/v) to give adduct intermediate **b**.

To a solution of MBH adduct **b** (4.0 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) was added to a stirred suspension of sodium hydride (6.0 mmol, 1.5 equiv.) in CH_2Cl_2 (10 mL) at 0 °C. After 0.5 h, a solution of $(Boc)_2O$ (4.8 mmol, 1.2 equiv.) in CH_2Cl_2 (4 mL) was added slowly to the above mixture. The resulting solution was stirred at room temperature for 0.5 h - 4.0 hours. The reaction mixture was washed by saturated sodium bicarbonate solution (30 mL), extracted with CH_2Cl_2 (50 mL) and dried over Na_2SO_4. The solvent was removed and the crude product was directly purified by flash column chromatography with *n*-hexane/ethyl acetate (5/1, v/v) to afford the MBH carbonates **1a**-**1l**.

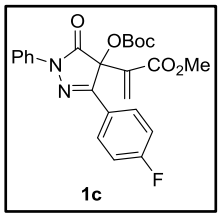


Methyl 2-(4-((tert-butoxycarbonyl)oxy)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1a**); The product was obtained as a white solid (72% yield for two steps); mp 146.6-147.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.86 (dd, *J* = 6.2, 3.6 Hz, 2H), 7.53 – 7.36 (m, 5H), 7.23 (m, 1H), 6.73 (s, 2H), 3.60 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 163.4, 138.1, 134.6, 130.7, 130.6, 129.4, 128.9, 128.8, 126.4, 125.4, 119.2, 84.9, 52.4, 27.5; HRMS (ESI) m/z Calcd. for $C_{24}H_{24}N_2O_6$+Na^+ ([M+Na]$^+$) 459.1527, Found 459.1517.

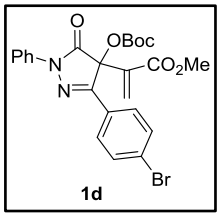


Methyl 2-(4-((tert-butoxycarbonyl)oxy)-1-(tert-butyl)-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1b**); The product was obtained as a white solid (67% yield for two steps); mp 107.9-108.6 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.80 – 7.66 (m, 2H), 7.41 – 7.29 (m, 3H), 6.59 (d, J = 9.8 Hz, 2H), 3.62 (s, 3H), 1.61 (s, 9H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*)

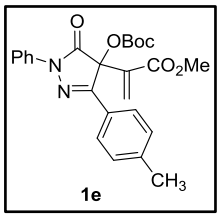
δ 169.1, 163.5, 149.7, 149.2, 134.9, 130.2, 129.8, 129.6, 128.6, 125.8, 84.0, 81.3, 58.3, 52.0, 27.9, 27.5; HRMS (ESI) m/z Calcd. for $C_{22}H_{29}N_2O_6$+H^+ ([M+H]$^+$) 417.2020, Found 417.12021.



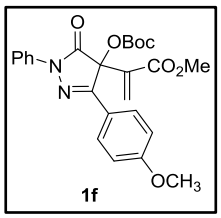
Methyl 2-(4-((tert-butoxycarbonyl)oxy)-3-(4-fluorophenyl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1c**); The product was obtained as a white solid (76% yield for two steps); mp 141.5-142.4 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.87 (m, 2H), 7.50 – 7.41 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.09 (m, 2H), 6.72 (s, 2H), 3.61 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3, 150.5, 149.5, 138.0, 134.5, 130.7, 128.9, 128.5, 128.4, 125.5, 119.3, 116.2, 116.0, 85.1, 52.5, 27.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -108.35 – -108.58; HRMS (ESI) m/z Calcd. for $C_{24}H_{23}FN_2O_6$+Na^+([M+Na]$^+$) 477.1432, Found 477.1438.



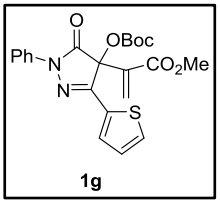
Methyl 2-(3-(4-bromophenyl)-4-((tert-butoxycarbonyl)oxy) -5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1d**); The product was obtained as a white solid (80% yield for two steps); mp 148.3-149.5 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.95 (m, 2H), 7.95 – 7.80 (m, 2H), 7.50 – 7.36 (m, 2H), 7.25 – 7.20 (m, 1H), 7.14 – 7.04 (m, 2H), 6.73 (d, *J* = 1.6 Hz, 2H), 3.61 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 163.3, 150.5, 149.5, 138.0, 134.5, 130.7, 128.9, 128.5, 128.4, 125.5, 119.3, 116.2, 116.0, 85.1, 81.0, 52.5, 27.5; HRMS (ESI) m/z Calcd. for $C_{24}H_{23}BrN_2O_6$+Na^+([M+Na]$^+$) 539.0612, Found 539.0596.



Methyl 2-(4-((tert-butoxycarbonyl)oxy)-5-oxo-1-phenyl-3-(p-tolyl)-4,5-dihy-dro-1H-pyrazol-4-yl)acrylate(**1e**); The product was obtained as a white solid (73% yield for two steps); mp 119.1-120.3 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.96 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.44 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.24 – 7.15 (m, 3H), 6.72 (d, *J* = 3.4 Hz, 2H), 3.59 (s, 3H), 2.38 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.6, 149.6, 141.0, 138.2, 134.7, 130.5, 129.6, 128.9, 126.6, 126.3, 125.3, 119.2, 84.9, 52.4, 27.5, 21.6; HRMS (ESI) m/z Calcd. for $C_{25}H_{26}N_2O_6$+Na^+([M+Na]$^+$) 473.1683, Found 473.1692.

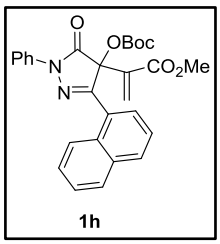


Methyl 2-(4-((tert-butoxycarbonyl)oxy)-3-(4-methoxyphenyl)-5-oxo-1-phe- nyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1f**); The product was obtained as a white solid (68% yield for two steps); mp 143.3-144.0 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 7.96 (m, 2H), 7.91 – 7.78 (m, 2H), 7.53 – 7.38 (m, 2H), 7.21 (m, *J* = 7.4 Hz, 1H), 7.02 – 6.87 (m, 2H), 6.70 (d, *J* = 1.7 Hz, 2H), 3.84 (s, 3H), 3.60 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4, 161.5, 138.2, 134.8, 130.3, 128.9, 128.1, 125.3, 122.0, 119.2, 114.3, 84.8, 55.3, 52.4, 27.5; HRMS (ESI) m/z Calcd. for $C_{25}H_{26}N_2O_7$+Na^+([M+Na]$^+$) 489.1632, Found 489.1641.



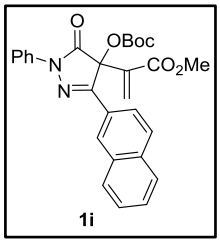
Methyl 2-(4-((tert-butoxycarbonyl)oxy)-5-oxo-1-phenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1g**); The product was obtained as a white solid (58% yield for two steps); mp 133.8-134.6 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.91 (m, 2H), 7.49 – 7.37 (m, 4H), 7.25 – 7.16 (m, 1H), 7.05 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.73 (d, *J* = 3.0 Hz, 2H), 3.63 (s, 3H), 1.36 (s, 9H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3, 149.5, 138.0, 134.5, 132.4, 130.8, 128.9, 128.9, 128.4, 127.7, 125.5, 119.3, 85.0, 52.5, 27.5; HRMS (ESI) m/z Calcd. for $C_{22}H_{22}N_2O_6$+Na^+([M+Na]$^+$) 465.1091, Found 465.1098.



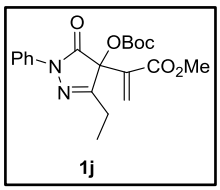
1h

Methyl 2-(4-((tert-butoxycarbonyl)oxy)-3-(naphthalen-1-yl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1h**); The product was obtained as a white solid (77% yield for two steps); mp 165.6-166.7 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (d, *J* = 8.6 Hz, 1H), 8.20 – 8.00 (m, 2H), 7.89 (dd, *J* = 14.7, 8.1 Hz, 2H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.61 (m, *J* = 7.7 Hz, 1H), 7.57 – 7.40 (m, 4H), 7.28 – 7.24 (m, 1H), 6.65 (d, *J* = 14.1 Hz, 2H), 3.60 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.7, 149.8, 138.2, 134.5, 134.3, 131.3, 130.8, 129.0, 128.6, 127.7, 127.0, 126.7, 126.4, 125.9, 125.5, 124.7, 119.3, 85.0, 82.3, 52.5, 27.5; HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_2O_6$+Na^+([M+Na]$^+$) 509.1683, Found 509.1690.



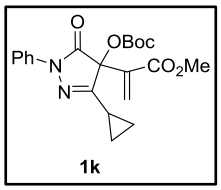
1i

Methyl 2-(4-((tert-butoxycarbonyl)oxy)-3-(naphthalen-2-yl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1i**); The product was obtained as a white solid (82% yield for two steps); mp 168.4-169.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.11 (m, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.86 (dd, *J* = 12.1, 8.4 Hz, 2H), 7.60 – 7.42 (m, 4H), 7.24 (d, *J* = 7.2 Hz, 2H), 6.83 (d, 2H), 3.58 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 163.4, 151.4, 138.1, 134.8, 132.9, 130.6, 129.0, 128.9, 128.8, 127.9, 127.5, 126.9, 126.7, 125.5, 123.1, 119.3, 85.0, 52.4, 27.5; HRMS (ESI) m/z Calcd. for $C_{28}H_{26}N_2O_6$+Na^+([M+Na]$^+$) 509.1683, Found 509.1693.



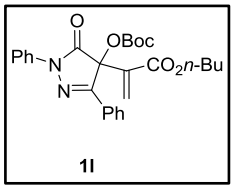
1j

Methyl 2-(4-((tert-butoxycarbonyl)oxy)-3-ethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1j**); The product was obtained as a white solid (62% yield for two steps); mp 124.7-125.9 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.40 (m, *J* = 7.8 Hz, 2H), 7.18 (m, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 59.6 Hz, 2H), 3.67 (s, 3H), 2.37 (m, *J* = 8.9 Hz, 2H), 1.44 (s, 9H), 1.23 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 157.4, 138.1, 133.4, 131.0, 128.8, 125.1, 119.0, 84.7, 81.8, 52.5, 27.6, 21.1, 9.8; HRMS (ESI) m/z Calcd. for $C_{20}H_{24}N_2O_6$+Na^+([M+Na]$^+$) 411.1527, Found 411.1536.



1k

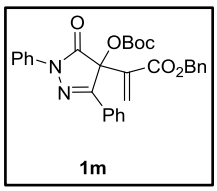
Methyl 2-(4-((tert-butoxycarbonyl)oxy)-3-cyclopropyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1k**); The product was obtained as a white solid (62% yield for two steps); mp 144.6-145.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.78 (m, 2H), 7.45 – 7.33 (m, 2H), 7.21 – 7.09 (m, 1H), 6.62 (d, *J* = 53.7 Hz, 2H), 3.68 (s, 3H), 1.59 – 1.50 (m, 1H), 1.45 (s, 9H), 1.19 (m, 1H), 1.00 – 0.80 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5, 158.1, 149.7, 138.2, 133.4, 130.9, 128.8, 125.0, 118.9, 84.6, 81.7, 52.5, 27.6, 8.8, 8.3, 6.5; HRMS (ESI) m/z Calcd. for $C_{21}H_{24}N_2O_6$+Na^+([M+Na]$^+$) 423.1527, Found 423.1534.



1l

Butyl 2-(4-((tert-butoxycarbonyl)oxy)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1l**); The product was obtained as a white solid (69% yield for two steps); mp 145.4-146.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 7.97 (m, 2H), 7.93 – 7.81 (m, 2H), 7.51 – 7.36 (m, 5H), 6.71 (d, *J* = 10.9 Hz, 2H), 3.99 (m, 2H), 1.41 (dd, *J* = 8.5, 6.6 Hz, 2H), 1.35 (s, 9H), 1.22 – 1.05 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1,

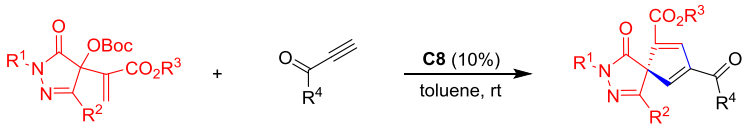
151.5, 138.2, 134.9, 130.6, 130.5, 129.4, 128.9, 128.8, 126.4, 125.3, 119.0, 84.9, 65.6, 30.2, 27.5, 19.0, 13.5; HRMS (ESI) m/z Calcd. for $C_{27}H_{30}N_2O_6$+Na^+([M+Na]$^+$) 501.1996, Found 501.2006.



1m

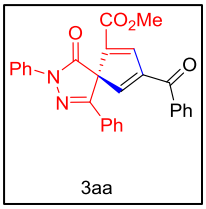
Benzyl 2-(4-((tert-butoxycarbonyl)oxy)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)acrylate (**1m**); The product was obtained as a white solid (80% yield for two steps); mp 169.1-169.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.88 – 7.77 (m, 2H), 7.49 – 7.34 (m, 5H), 7.26 – 7.18 (m, 4H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.75 (dd, *J* = 12.7, 1.5 Hz, 2H), 5.12 – 4.87 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 149.6, 138.1, 134.7, 134.5, 131.0, 130.6, 129.3, 128.8, 128.8, 128.5, 128.4, 128.3, 126.4, 125.3, 119.2, 84.9, 67.3, 27.5; HRMS (ESI) m/z Calcd. for $C_{30}H_{28}N_2O_6$+Na^+([M+Na]$^+$) 535.1840, Found 535.1847.

3. Experimental procedures and characterization of compounds 3



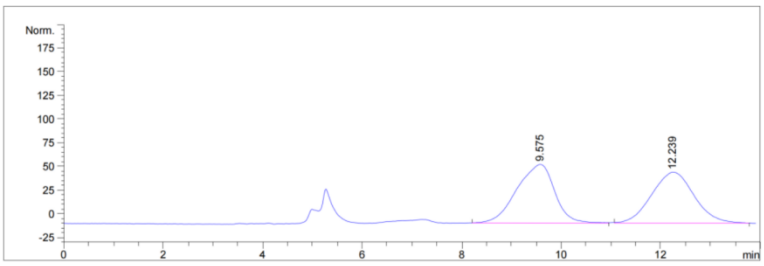
A tube was charged with pyrazolone-derived MBH carbonates **1** (0.2 mmol), alkynyl ketone **2** (0.3 mmol), **C8** (0.02 mmol) and toluene (1 mL). The reaction was monitored by TLC. The product was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to give the product **3**.

Compound 3aa

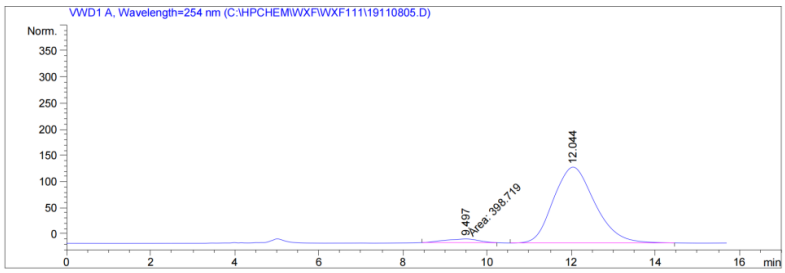


3aa

Prepared according to the procedure within 6 h as white solid (77.9 mg, 87% yield); mp 138.8-139.6 °C; $[\alpha]_D^{17}$ = -72.14 (c 0.70, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 1.7 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.60 (m, 1H), 7.57 – 7.51 (m, 2H), 7.47 (m, 4H), 7.37 (m, 3H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 1.7 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.8, 165.7, 161.7, 152.8, 147.7, 144.7, 144.6, 139.2, 138.0, 136.8, 133.5, 131.2, 130.7, 129.4, 129.1, 129.0, 128.8, 126.0, 125.5, 119.5, 73.2, 52.3; HRMS (ESI) m/z Calcd. for $C_{28}H_{21}N_2O_4$ ([M+H]$^+$) 449.1496, Found 449.1490; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 12.0 min, tminor = 9.5 min).

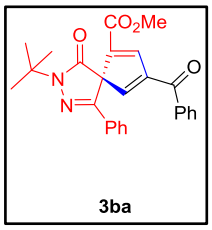


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.575	BB	0.6727	3267.03101	61.80420	50.6210
2	12.239	BB	0.7096	3186.86768	53.60289	49.3790

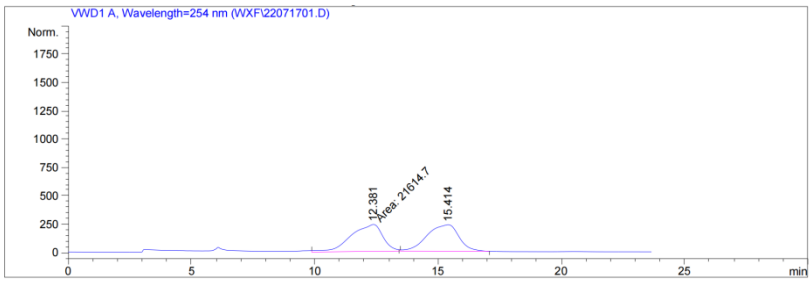


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.497	MM T	0.9401	398.71857	7.06869	3.8611
2	12.044	VB	1.0736	9927.79883	145.06007	96.1389

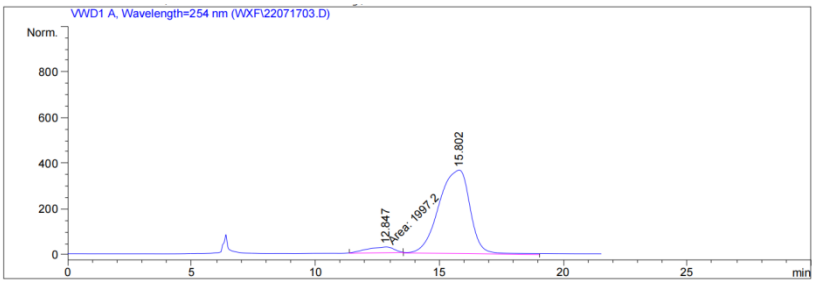
Compound 3ba



Prepared according to the procedure within 10 h as yellow solid (69.4 mg, 81% yield); mp 112.3-113.8 °C; $[\alpha]_D^{19}$= -51.87 (c 0.52, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 1.7 Hz, 1H), 7.84 (m, 3H), 7.58 (m, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.46 (m, 2H), 7.41 – 7.39 (m, 1H), 7.31 (dd, *J* = 10.2, 6.8 Hz, 2H), 6.94 (d, *J* = 1.6 Hz, 1H), 3.70 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.9, 166.8, 161.8, 149.9, 147.2, 145.1, 144.3, 138.9, 138.3, 137.0, 136.5, 134.1, 133.2, 131.5, 130.3, 130.1, 129.3, 128.9, 128.7, 125.0, 59.5, 52.0, 28.4; HRMS (ESI) m/z Calcd. for $C_{26}H_{25}N_2O_4$ ([M+H]$^+$) 429.1809, Found 429.1808; Enantiomeric excess was determined to be 88% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 15/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 15.8 min, tminor = 12.8 min).

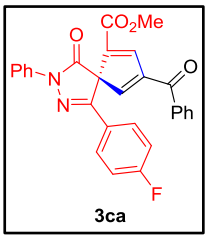


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.381	MM T	1.5114	2.16147e4	238.34602	50.6210
2	15.414	MM R	1.7352	2.10844e4	234.19023	49.3790



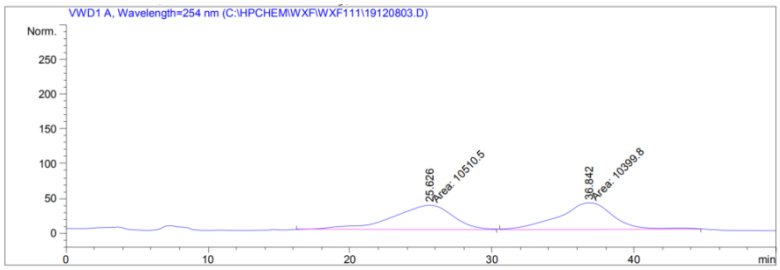
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.847	MM T	1.2951	1997.19629	25.70159	5.8747
2	15.802	MM R	1.8031	3.19993e4	365.54150	94.1253

Compound 3ca

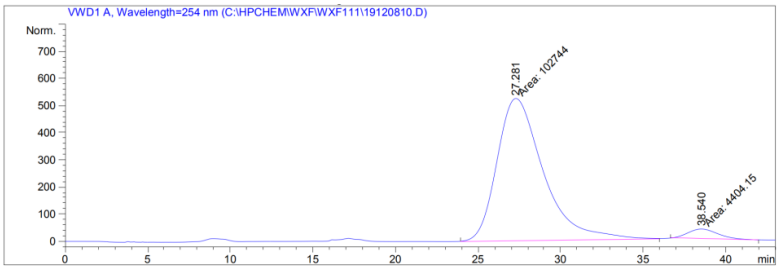


3ca

Prepared according to the procedure within 10 h as white solid (85.8 mg, 92% yield); mp 128.3-129.4 °C; $[\alpha]_D^{17}$ = -48.64 (*c* 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 1.7 Hz, 1H), 8.00 – 7.94 (m, 2H), 7.91 – 7.82 (m, 2H), 7.60 (m, 1H), 7.56 – 7.42 (m, 6H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.08 – 6.96 (m, 3H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.7, 165.7, 165.6, 163.2, 161.7, 151.8, 147.8, 144.7, 144.3, 139.1, 137.9, 136.6, 133.6, 129.4, 129.1, 128.8, 127.6, 127.5, 127.0, 126.1, 119.5, 116.4, 116.2, 73.1, 52.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ -107.65 - -107.68; HRMS (ESI) m/z Calcd. for $C_{28}H_{20}FN_2O_4$ ($[M+H]^+$) 467.1402, Found 467.1389. Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 27.3 min, tminor = 38.5 min).

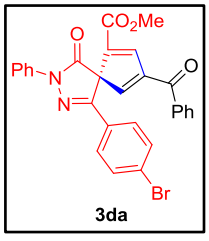


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.626	MM T	4.9803	1.05105e4	35.17371	50.2646
2	36.842	MM T	4.5161	1.03998e4	38.38103	49.7354



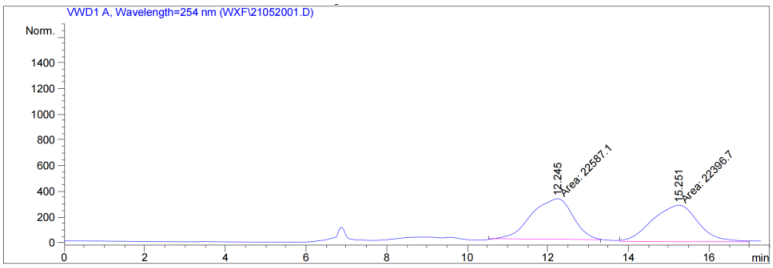
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.281	MM T	3.2619	1.02744e5	524.97607	95.8897
2	38.540	MM T	2.0976	4404.14551	34.99277	4.1103

Compound 3da

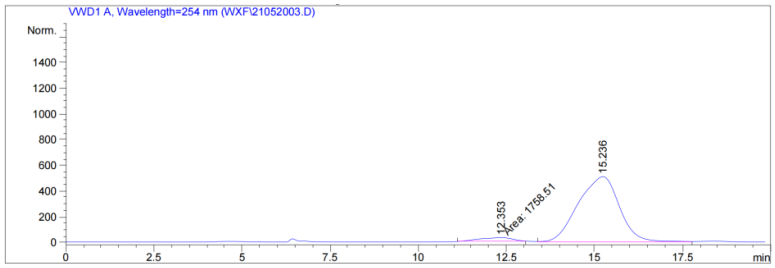


3da

Prepared according to the procedure within 10 h as white solid (83.1 mg, 79% yield); mp 149.1-150.0 °C; $[\alpha]_D^{17}$ = -28.57 (*c* 0.07, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 1.7 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.89 – 7.82 (m, 2H), 7.65 – 7.56 (m, 1H), 7.52 – 7.43 (m, 6H), 7.42 – 7.35 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 1.7 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.7, 165.6, 161.7, 151.8, 147.9, 144.8, 144.1, 139.0, 137.9, 136.6, 133.6, 132.4, 129.6, 129.4, 129.1, 128.8, 126.8, 126.2, 125.6, 119.6, 72.9, 52.4; HRMS (ESI) m/z Calcd. for $C_{28}H_{20}BrN_2O_4$ ($[M+H]^+$) 527.0601, Found 527.0578; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor =15.2 min, tminor = 12.4 min).

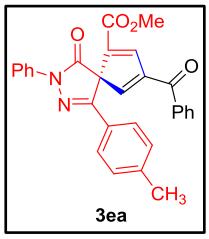


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.245	MM T	1.1884	2.25871e4	316.76450	50.2116
2	15.251	MM T	1.3177	2.23967e4	283.28064	49.7884



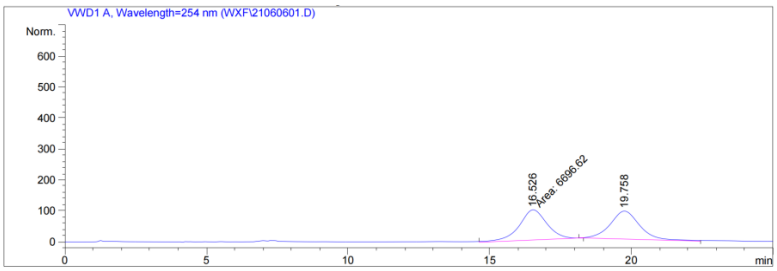
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.353	MM T	1.0501	1758.50684	27.90917	4.0850
2	15.236	VB	1.3158	4.12890e4	507.64072	95.9150

Compound 3ea

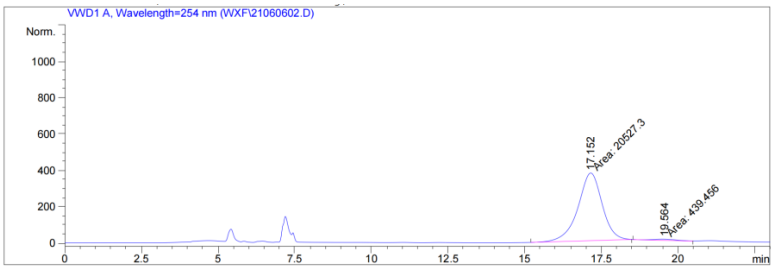


3ea

Prepared according to the procedure within 12 h as white solid (83.2 mg, 90% yield); mp 168.1-169.3 °C; $[\alpha]_D^{17}$ = -25.00 (*c* 0.16, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.59 (m, 1H), 7.46 (m, 6H), 7.28 (s, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.03 (s, 1H), 3.69 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.8, 165.7, 161.8, 147.5, 144.9, 144.6, 141.7, 139.3, 138.0, 136.8, 133.5, 129.8, 129.4, 129.0, 128.8, 128.0, 125.9, 125.4, 119.5, 73.3, 52.3, 21.6; HRMS (ESI) m/z Calcd. for $C_{29}H_{23}N_2O_4$ ($[M+H]^+$) 463.1652, Found 463.1638; Enantiomeric excess was determined to be 96% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 17.2 min, tminor = 19.6 min).

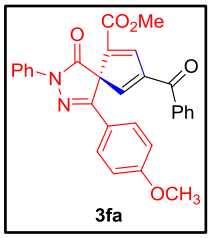


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.526	MM T	1.4727	6696.61865	97.80082	50.1788
2	19.758	MM R	1.2227	6648.88672	90.63037	49.8212

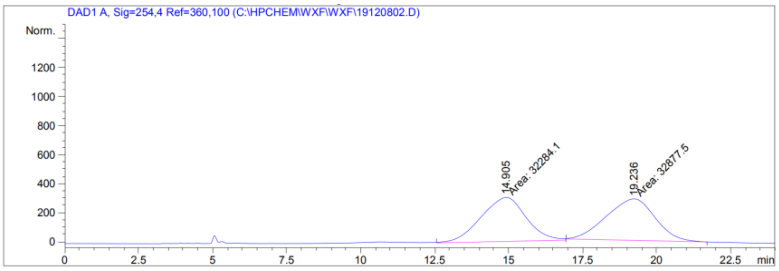


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.152	MM T	1.3187	2.05273e4	373.26282	97.9040
2	19.564	MM T	1.0498	439.45648	7.46373	2.0960

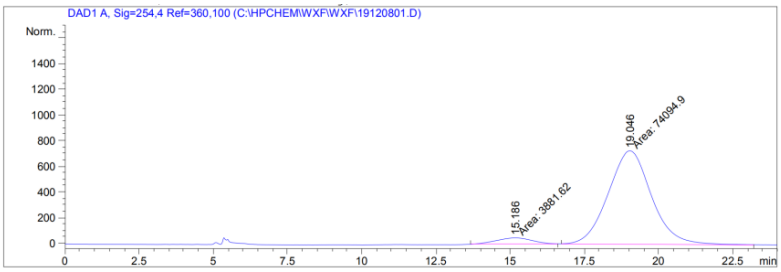
Compound 3fa



Prepared according to the procedure within 12 h as white solid (87.0 mg, 91% yield); mp 130.1-131.3 °C; $[\alpha]_D^{17}$ = -89.00 (*c* 0.20, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.91 – 7.79 (m, 2H), 7.60 (m, 1H), 7.55 – 7.38 (m, 6H), 7.28 (s, 1H), 7.04 (d, *J* = 1.9 Hz, 1H), 6.91 – 6.77 (m, 2H), 3.81 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.9, 165.6, 161.9, 161.8, 152.4, 147.4, 145.0, 144.5, 139.3, 138.1, 136.7, 133.5, 129.4, 129.0, 128.8, 127.1, 125.9, 123.4, 119.5, 114.5, 73.3, 55.4, 52.3; HRMS (ESI) m/z Calcd. for $C_{29}H_{23}N_2O_5$ ($[M+H]^+$) 479.1601, Found 479.1580; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral OD-H column, hexane/2-propanol =4/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 19.0 min, tminor = 15.2 min).

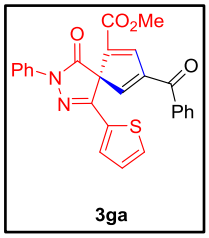


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.905	MM T	1.7700	3.22841e4	304.00113	49.5446
2	19.236	MM T	1.9082	3.28775e4	287.16199	50.4554



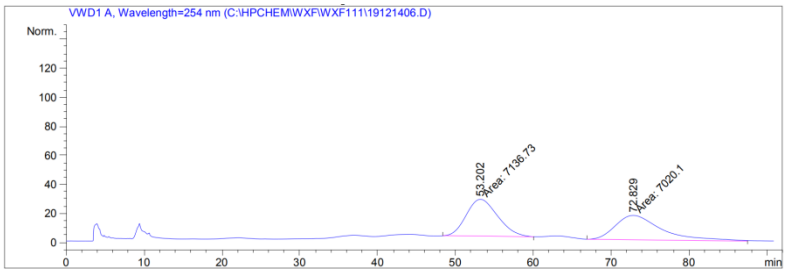
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.186	MM T	1.3637	3881.62476	47.44073	4.9779
2	19.046	MM T	1.6960	7.40949e4	728.13513	95.0221

Compound 3ga

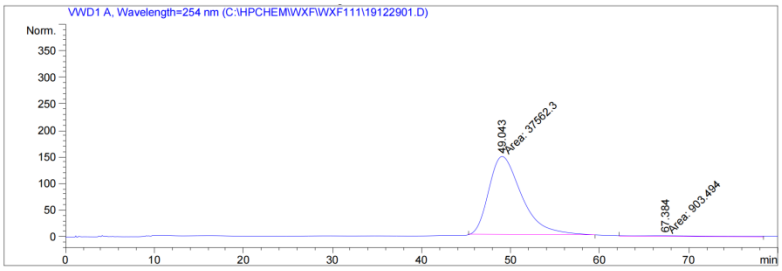


3ga

Prepared according to the procedure within 12 h as white solid (79.0 mg, 87% yield); mp 130.3-131.1 °C; $[\alpha]_D^{17}$ = -31.52 (*c* 0.33, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.95 (dd, *J* = 14.4, 8.0 Hz, 3H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.32 (m, 7H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.3, 165.3, 161.6, 152.4, 146.9, 145.6, 143.6, 140.0, 139.8, 137.8, 132.6, 131.4, 130.6, 129.8, 129.2, 129.1, 126.2, 125.4, 119.5, 117.7, 116.7, 73.4, 52.5; HRMS (ESI) m/z Calcd. for $C_{26}H_{19}N_2O_4S$ ($[M+H]^+$) 455.1060, Found 455.1049; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 49.0 min, tminor = 67.4 min).

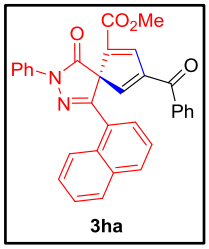


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	53.202	MM T	4.6847	7136.73389	25.38998	50.4119
2	72.829	MM T	6.9299	7020.09766	16.88359	49.5881



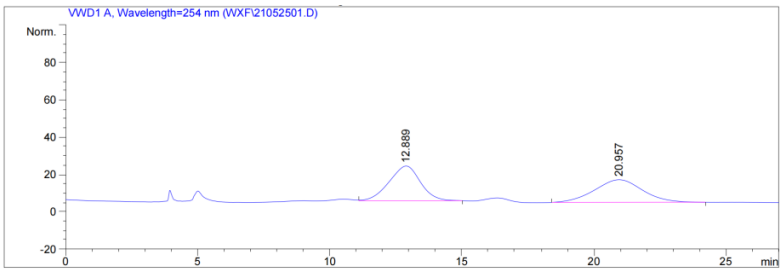
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	49.043	MM T	4.2708	3.75623e4	146.58510	97.6512
2	67.384	MM T	13.2879	903.49432	1.13323	2.3488

Compound 3ha

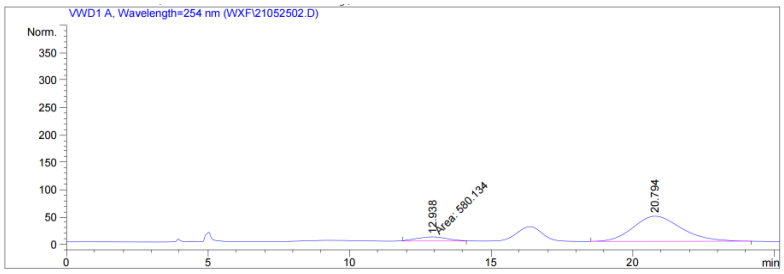


3ha

Prepared according to the procedure within 18 h as white solid (75.7 mg, 76% yield); mp 172.3-173.6 °C; $[\alpha]_D^{17}$ = -76.83 (*c* 0.31, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.18 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 1.7 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.67 (m, *J* = 7.7 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.48 (m, 5H), 7.39 – 7.29 (m, 2H), 7.15 (d, *J* = 6.7 Hz, 2H), 3.68 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.8, 165.5, 153.7, 147.5, 144.8, 144.5, 138.9, 138.1, 136.8, 134.2, 133.5, 131.9, 130.6, 129.4, 129.2, 128.8, 128.0, 126.9, 126.5, 126.2, 126.1, 126.0, 124.9, 119.5, 52.3; HRMS (ESI) m/z Calcd. for $C_{32}H_{23}N_2O_4$ ($[M+H]^+$) 499.1652, Found 499.1636; Enantiomeric excess was determined to be 80% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 20.8 min, tminor =12.9 min).

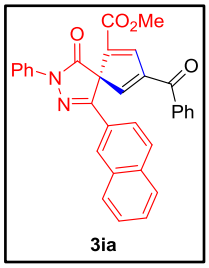


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.889	VB	1.1336	1536.25208	18.60727	49.9278
2	20.957	BB	1.5074	1540.69604	12.15917	50.0722

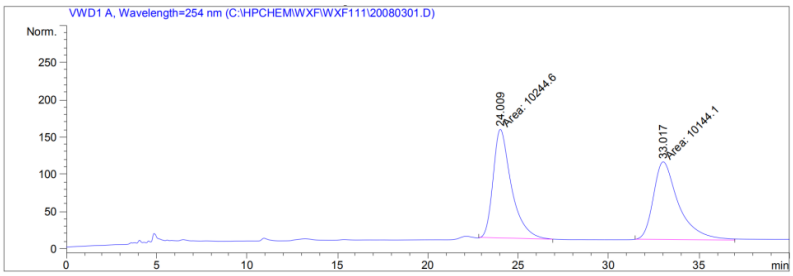


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.938	MM T	1.2701	580.13440	7.61251	9.6486
2	20.794	BB	1.7090	5432.50391	45.92838	90.3514

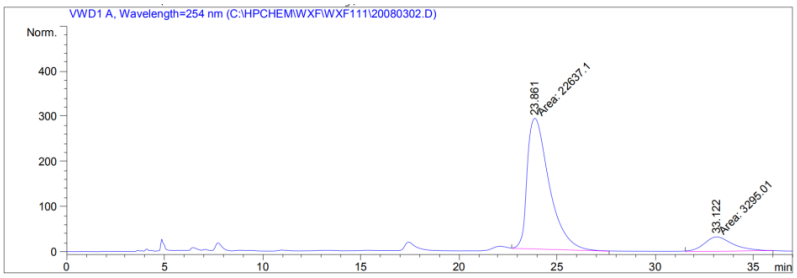
Compound 3ia



Prepared according to the procedure within 14 h as white solid (79.7 mg, 80% yield); mp 169.1-170.1 °C; $[\alpha]_D^{17}$ = -86.79 (*c* 0.40, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.11 (m, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.99 – 7.94 (m, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.87 – 7.81 (m, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.71 (s, 1H), 7.60 (m, 1H), 7.50 (m, 6H), 7.30 (m, 1H), 7.12 (d, *J* = 1.7 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.8, 161.8, 147.7, 144.8, 144.7, 139.6, 138.0, 136.7, 134.5, 133.5, 133.0, 129.4, 129.1, 128.9, 128.3, 127.8, 127.7, 126.9, 126.1, 125.6, 122.4, 119.6, 73.2, 52.3; HRMS (ESI) m/z Calcd. for $C_{32}H_{23}N_2O_4$ ($[M+H]^+$) 499.1652, Found 499.1633; Enantiomeric excess was determined to be 75% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 23.9 min, tminor = 33.1 min).

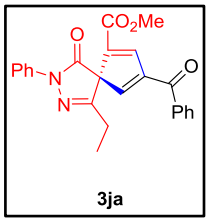


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.009	MM T	1.1712	1.02446e4	145.78828	50.2466
2	33.017	MM T	1.6206	1.01441e4	104.32593	49.7534



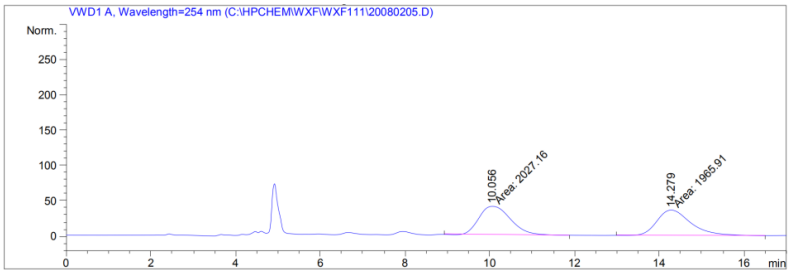
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.861	MM T	1.3032	2.26371e4	289.49551	87.2937
2	33.122	MM T	1.7097	3295.00854	32.12112	12.7063

Compound 3ja

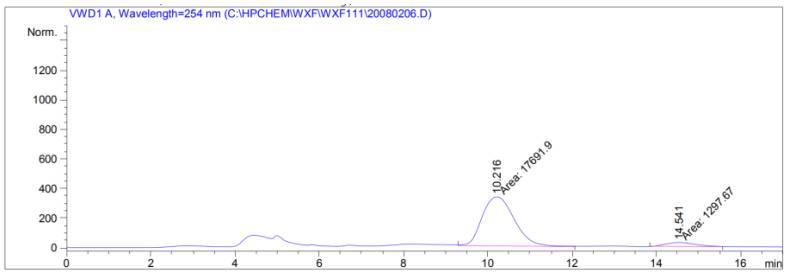


3ja

Prepared according to the procedure within 22 h as white solid (70.4 mg, 88% yield); mp 167.4-168.6 °C; $[\alpha]_D^{17}$ = -96.69 (*c* 0.32, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.62 (m, 1H), 7.50 (m, 2H), 7.42 (m, 2H), 7.23 (s, 1H), 6.83 (d, *J* = 1.9 Hz, 1H), 3.77 (s, 3H), 2.22 (p, *J* = 7.8 Hz, 2H), 1.17 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.6, 166.2, 161.8, 158.9, 148.1, 145.4, 142.6, 138.0, 136.7, 133.5, 129.3, 129.0, 128.8, 125.6, 119.3, 74.6, 52.3, 22.8, 10.5; HRMS (ESI) m/z Calcd. for $C_{24}H_{21}N_2O_4$ ($[M+H]^+$) 401.1496, Found 401.1488. Enantiomeric excess was determined to be 86% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 10.2 min, tminor = 14.5 min).

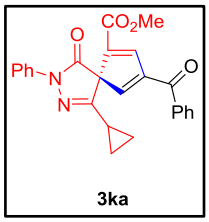


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.056	MM T	1.0408	2027.16272	39.71413	50.7669
2	14.279	MM T	1.1221	1965.91418	35.65844	49.2331



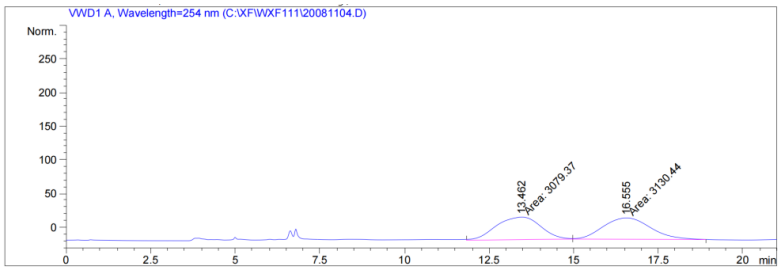
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.216	MM T	0.8868	1.76919e4	332.49399	93.1664
2	14.541	MM T	0.8390	1297.66992	25.77861	6.8336

Compound 3ka

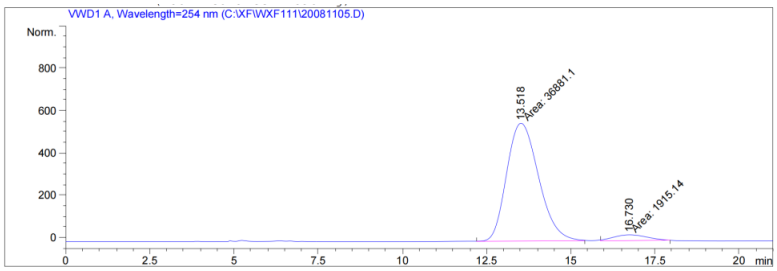


3ka

Prepared according to the procedure within 20 h as white solid (70.9 mg, 86% yield); mp 160.1-161.0 °C; $[\alpha]_D^{17}$ = -56.33(*c* 0.20, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.92 – 7.79 (m, 4H), 7.69 – 7.58 (m, 1H), 7.50 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.45 – 7.35 (m, 2H), 7.25 – 7.15 (m, 1H), 6.87 (d, *J* = 1.8 Hz, 1H), 3.77 (s, 3H), 1.22 (m, 1H), 1.13 – 1.05 (m, 1H), 0.98 (m, 1H), 0.88 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.7, 166.0, 161.8, 159.5, 148.1, 145.3, 142.6, 138.0, 136.7, 136.7, 133.5, 129.4, 128.9, 128.8, 125.5, 119.2, 74.8, 52.3, 9.6, 9.3, 8.0; HRMS (ESI) m/z Calcd. for $C_{25}H_{21}N_2O_4$ ($[M+H]^+$) 413.1496, Found 413.1487; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 8/2, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 13.5 min, tminor = 16.7 min).

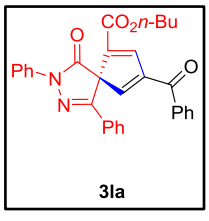


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.462	MM T	1.5319	3079.36621	33.50308	49.5888
2	16.555	MM T	1.6412	3130.43555	31.78996	50.4112



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.518	MM T	1.1021	3.68811e4	557.76056	95.0636
2	16.730	MM T	1.1568	1915.13879	27.59361	4.9364

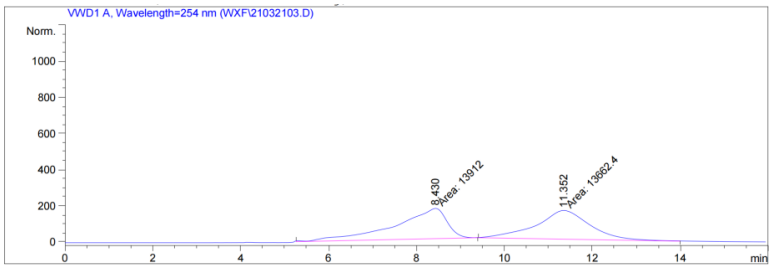
Compound 3la



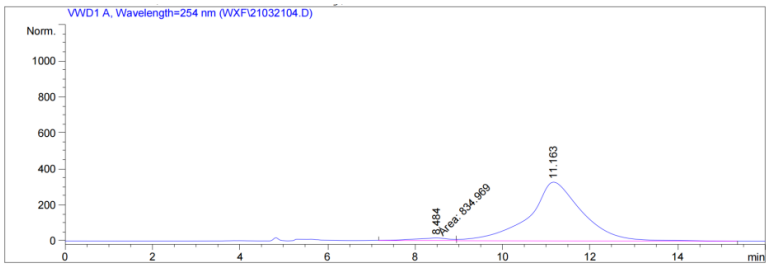
3la

Prepared according to the procedure within 22 h as white solid (82.4 mg, 84% yield); mp 179.6-180.8 °C; $[\alpha]_D^{17}$ = -106.43 (*c* 0.60, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 1.7 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 2H), 7.91 – 7.83 (m, 2H), 7.61 – 7.53 (m, 3H), 7.51 – 7.44 (m, 4H), 7.38 (m, 3H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 1.7 Hz, 1H), 4.07 (m, 2H), 1.45 (m, 2H), 1.28 – 1.16 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.8 , 164.7, 160.3, 151.8, 146.6, 143.8, 143.4, 138.5, 137.0, 135.7, 132.4, 130.2, 129.7, 128.4, 128.0, 128.0, 127.7, 124.8, 124.4, 118.1, 72.1, 64.2, 29.4, 18.0, 12.4; HRMS (ESI) m/z Calcd. for $C_{31}H_{27}N_2O_4$ ($[M+H]^+$) 491.1965, Found 491.1947; Enantiomeric excess was determined to be 94% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 11.2

min, tminor = 8.5 min).

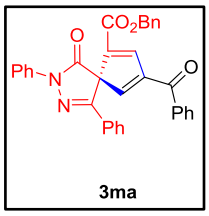


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.430	MM T	1.3809	1.39120e4	167.91524	50.4525
2	11.352	MM T	1.4328	1.36624e4	158.92807	49.5475



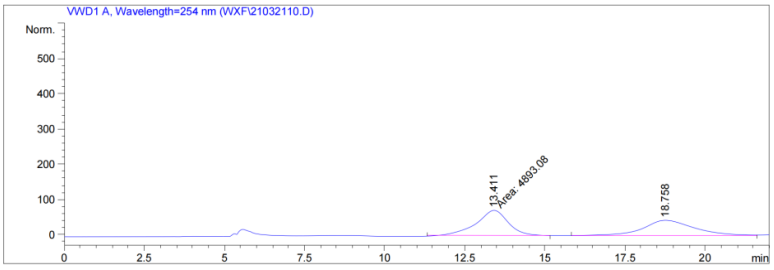
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.484	MM T	0.9507	834.96906	14.63805	2.9542
2	11.163	VB R	1.1702	2.74290e4	326.24530	97.0458

Compound 3ma

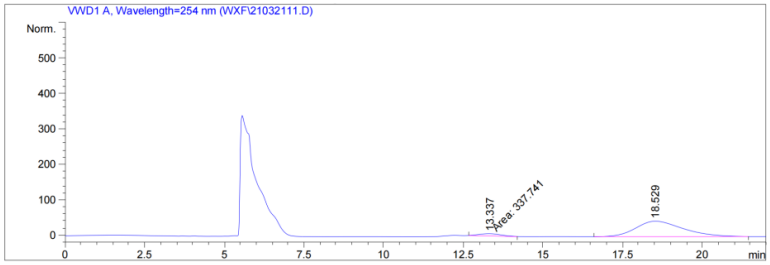


3ma

Prepared according to the procedure within 8 h as white solid (90.1 mg, 86% yield); mp 176.8-178.0 ^{o}C; $[\alpha]_D^{17}$ = -99.56 (*c* 0.34, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 4H), 7.56 (m, 1H), 7.42 (m, 7H), 7.31 (m, 2H), 7.23 – 7.08 (m, 6H), 6.99 (s, 1H), 5.05 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.7, 165.6, 161.0, 152.7, 147.6, 145.4, 144.6, 139.0, 137.9, 136.7, 134.8, 133.5, 131.2, 130.7, 129.4, 129.1, 129.0, 128.8, 128.5, 128.3, 128.1, 125.9, 1255, 119.4, 73.2, 67.1; HRMS (ESI) m/z Calcd. for $C_{34}H_{25}N_2O_4$ ([M+H]$^{+}$) 525.1809, Found 525.1806; Enantiomeric excess was determined to be 86% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 30 ^{o}C, 0.8 mL/min, tmajor = 18.5 min, tminor = 13.3 min).

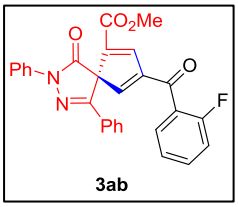


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.411	MM T	1.1458	4893.07813	71.17132	50.0549
2	18.758	BB	1.5241	4882.33545	43.52853	49.9451



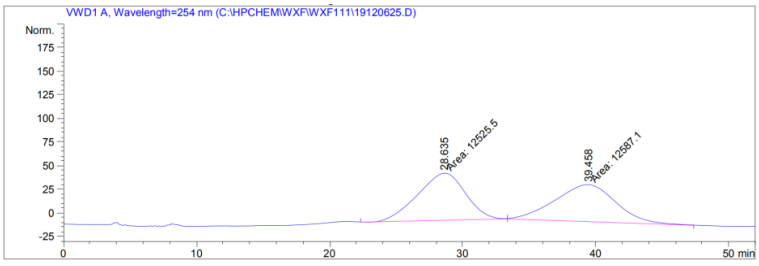
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.337	MM T	0.8342	337.74146	6.74789	6.9458
2	18.529	BB	1.4709	4524.81641	43.72454	93.0542

Compound 3ab

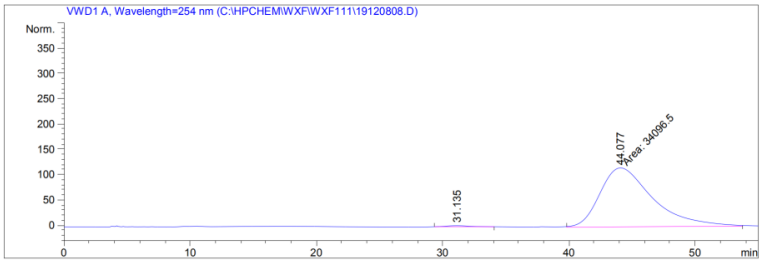


3ab

Prepared according to the procedure within 10 h as white solid (85.7 mg, 92% yield); mp 130.2-131.2 °C; $[\alpha]_D^{17}$ = -76.30 (*c* 0.06, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 7.88 (m, 3H), 7.67 – 7.50 (m, 4H), 7.49 – 7.31 (m, 6H), 7.22 – 6.90 (m, 3H), 3.68 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.9, 165.4, 161.7, 161.4, 158.9, 152.7, 148.5, 145.9, 145.9, 143.5, 139.0, 138.0, 134.3, 134.2, 131.2, 130.8, 130.7, 129.1, 129.0, 126.0, 125.5, 124.7, 124.7, 119.5, 116.8, 116.6, 73.1, 52.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ -110.73 - -110.80; HRMS (ESI) m/z Calcd. for $C_{28}H_{20}FN_2O_4$ ($[M+H]^+$) 467.1402, Found 467.1391; Enantiomeric excess was determined to be 98% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 44.1 min, tminor = 31.1 min).

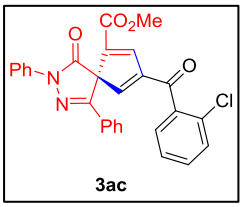


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.635	MM T	4.1750	1.25255e4	50.00194	49.8775
2	39.458	MM T	5.3383	1.25871e4	39.29811	50.1225



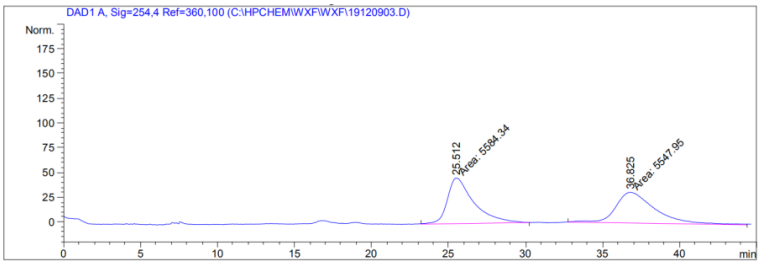
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	31.135	BB	1.6317	293.06467	2.10863	0.8522
2	44.077	MM T	4.8665	3.40965e4	116.77184	99.1478

Compound 3ac

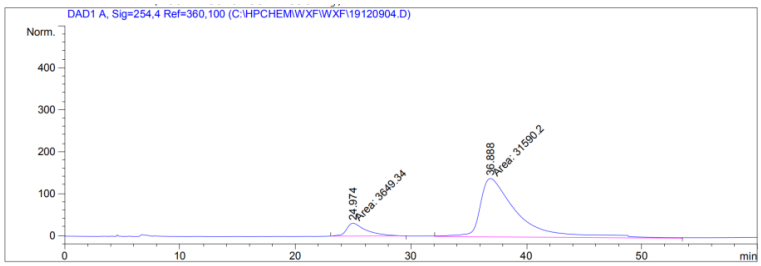


3ac

Prepared according to the procedure within 10 h as white solid (78.2 mg, 81% yield); mp 138.6-139.0 °C; $[\alpha]_D^{17}$ = -81.25 (*c* 0.40, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 1.7 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.56 – 7.52 (m, 2H), 7.43 (m, 6H), 7.34 (m, 3H), 7.31 – 7.26 (m, 1H), 6.93 (d, *J* = 1.8 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.3, 165.3, 161.7, 152.6, 148.3, 146.9, 143.0, 139.4, 137.9, 137.4, 132.1, 131.2, 130.4, 129.4, 129.0, 127.1, 126.0, 125.6, 119.5, 73.1, 52.3; HRMS (ESI) m/z Calcd. for $C_{29}H_{20}ClN_2O_4$ ($[M+H]^+$) 483.1106, Found 483.1098; Enantiomeric excess was determined to be 80% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 36.9 min, tminor = 24.9 min).

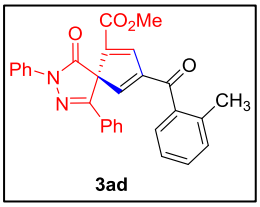


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.512	MM T	2.0089	5584.34131	46.32974	50.1634
2	36.825	MM T	2.9685	5547.95459	31.14912	49.8366



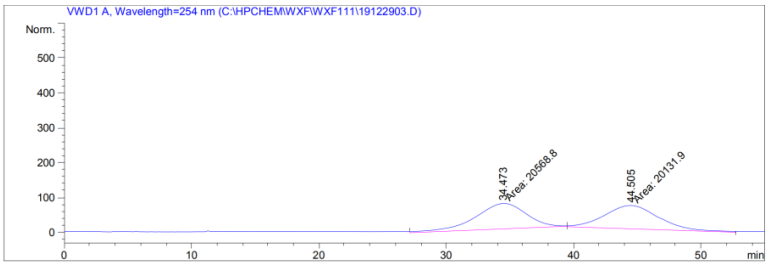
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.974	MM T	1.9694	3649.34375	30.88442	10.3558
2	36.888	MM T	3.7696	3.15902e4	139.66913	89.6442

Compound 3ad

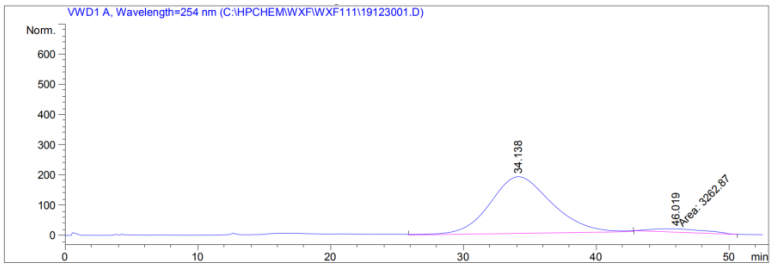


3ad

Prepared according to the procedure within 10 h as white solid (79.5 mg, 86% yield); mp 128.5-129.3 °C; $[\alpha]_D^{17}$ = -38.67 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.50 (m, 2H), 7.50 – 7.33 (m, 7H), 7.27 – 7.15 (m, 3H), 6.88 (d, *J* = 1.7 Hz, 1H), 3.70 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.1, 165.6, 161.8, 152.6, 149.2, 146.1, 143.8, 139.2, 138.0, 137.5, 137.0, 131.6, 131.4, 131.2, 130.8, 129.1, 129.0, 128.9, 126.0, 125.6, 125.4, 119.5, 73.1, 52.3, 20.2; HRMS (ESI) m/z Calcd. for $C_{29}H_{23}N_2O_4$ ($[M+H]^+$) 463.1652, Found 463.1645; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 30/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 34.1 min, tminor = 46.0 min).

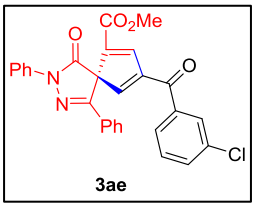


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.473	MM T	5.4967	2.05688e4	73.22663	50.5367
2	44.505	MM T	4.9922	2.01319e4	67.21066	49.4633



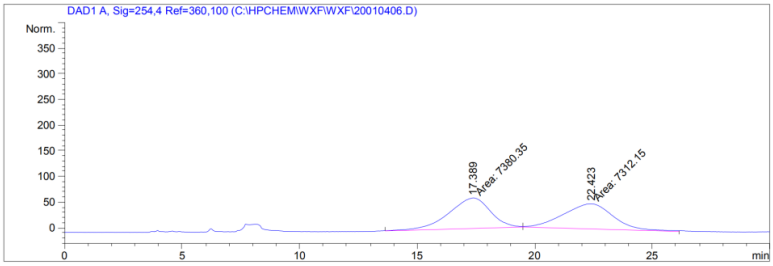
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.138	MM R	6.4397	6.09522e4	187.83339	94.9188
2	46.019	MM T	4.8549	3262.87378	11.20122	5.0812

Compound 3ae

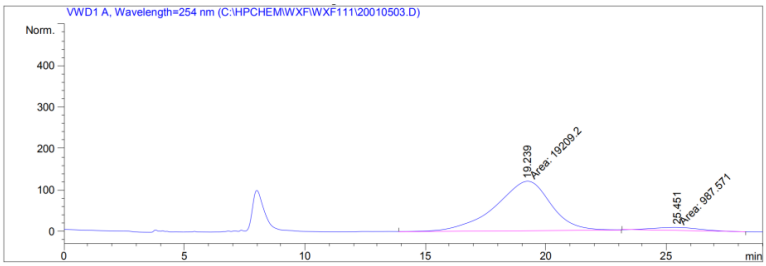


3ae

Prepared according to the procedure within 12 h as white solid (86.8 mg, 90% yield); mp 128.4-129.6 °C; $[\alpha]_D^{17}$ = -93.33 (*c* 0.80, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 7.88 (m, 3H), 7.80 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.27 (m, 9H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 1.8 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.4, 165.5, 161.6, 152.6, 147.3, 144.9, 144.1, 135.3, 133.4, 131.3, 130.7, 130.1, 129. 2, 129.1, 129.1, 127.6, 126.1, 125.4, 119.6, 73.3, 52.3; HRMS (ESI) m/z Calcd. for $C_{28}H_{20}ClN_2O_4$ ($[M+H]^+$) 483.1106, Found 483.1097; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 19.2 min, tminor = 25.5 min).

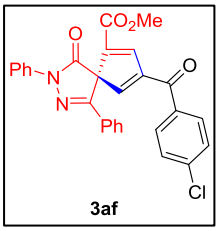


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.389	MM T	2.0614	7380.35498	59.66994	50.2321
2	22.423	MM T	2.4689	7312.14844	49.36129	49.7679

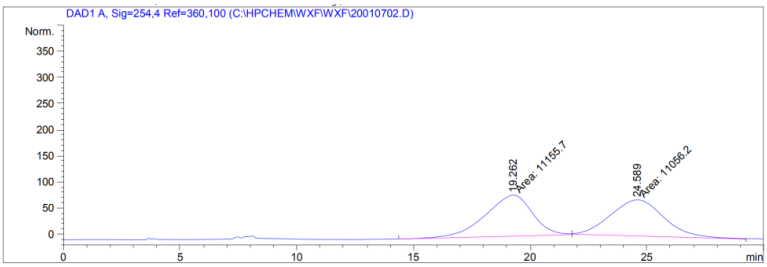


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.239	MM T	2.6765	1.92092e4	119.61464	95.1103
2	25.451	MM T	2.1704	987.57117	7.58373	4.8897

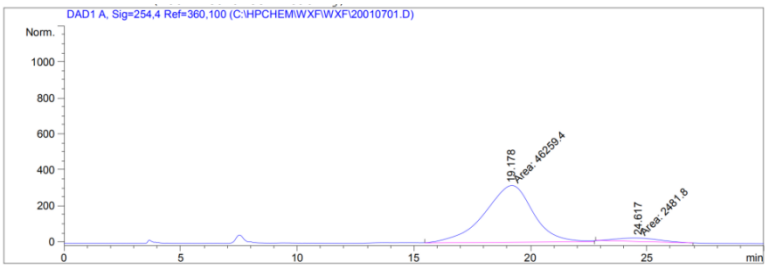
Compound 3af



Prepared according to the procedure within 10 h as white solid (78.0 mg, 81 % yield); mp 128.9-129.8 °C; $[\alpha]_D^{17}$ = -34.25 (*c* 0.80, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.92 (m, 3H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.35 (m, 2H), 7.30 (s, 1H), 7.02 (d, *J* = 1.7 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.5, 165.6, 161.7, 152.7, 147.4, 144.5, 144.4, 140.1, 139.4, 138.0, 135.0, 131.3, 130.8, 130.7, 129.2, 129.1, 129.1, 126.1, 125.4, 119.6, 73.2, 52.3; HRMS (ESI) m/z Calcd. for $C_{28}H_{20}ClN_2O_4$ ($[M+H]^+$) 483.1106, Found 483.1095; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 19.2 min, tminor = 24.6 min).

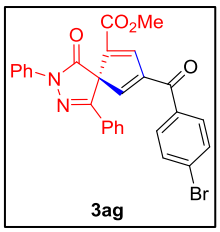


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.262	MM T	3.1210	1.11557e4	78.81080	50.2239
2	24.589	MM T	2.6613	1.10562e4	69.24123	49.7761



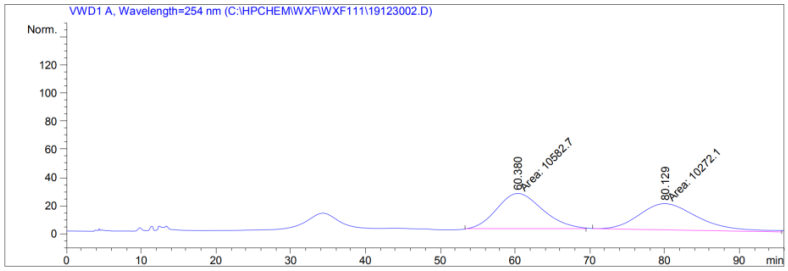
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.178	MM T	2.4390	4.62594e4	316.10883	94.9082
2	24.617	MM T	2.1341	2481.80103	19.38172	5.0918

Compound 3ag

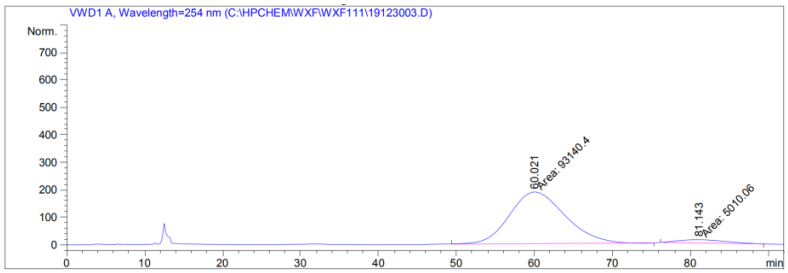


3ag

Prepared according to the procedure within 16 h as white solid (95.7 mg, 91% yield); mp 140.1-141.6 °C; $[\alpha]_D^{17}$ = -96.00 (*c* 0.10, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 1.8 Hz, 1H), 8.01 – 7.94 (m, 2H), 7.77 – 7.70 (m, 2H), 7.65 – 7.58 (m, 2H), 7.55 – 7.44 (m, 4H), 7.43 – 7.31 (m, 3H), 7.28 (s, 1H), 7.01 (d, *J* = 1.7 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.7, 165.6, 161.7, 152.6, 147.4, 144.6, 144.3, 139.4, 137.9, 135.4, 132.2, 131.2, 130.9, 130.7, 129.1, 129.1, 128.8, 126.1, 125.4, 119.6, 73.2, 52.3; HRMS (ESI) m/z Calcd. for $C_{28}H_{20}BrN_2O_4$ ($[M+H]^+$) 527.0601, Found 527.0591; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 30/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 60.0 min, tminor = 81.1 min).

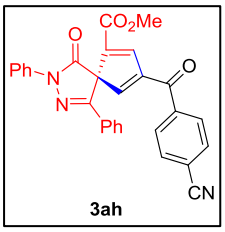


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	60.380	MM T	7.0406	1.05827e4	25.05183	50.7447
2	80.129	MM T	9.3465	1.02721e4	18.66527	49.2553



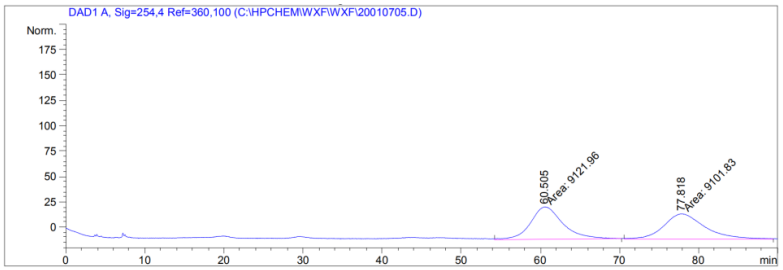
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	60.021	MM T	8.2677	9.31404e4	187.76009	94.8955
2	81.143	MM T	5.0154	5010.06494	11.83057	5.1045

Compound 3ah

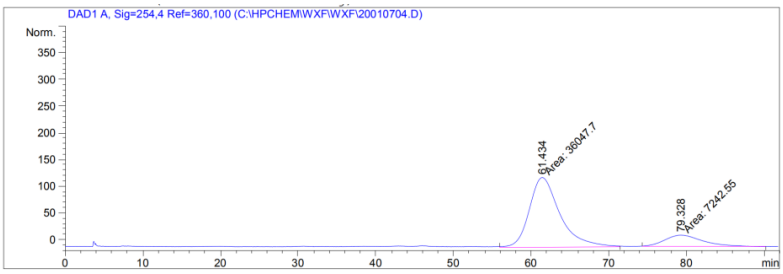


3ah

Prepared according to the procedure within 10 h as white solid (84.2 mg, 89% yield); mp 126.8-127.8 °C; $[\alpha]_D^{17}$ = -36.79 (*c* 0.28, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.60 (m, 1H), 7.56 – 7.33 (m, 6H), 7.28 (s, 1H), 7.03 (s, 1H), 6.97 (d, *J* = 4.2 Hz, 2H), 3.72 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.7, 165.5, 161.7, 148.4, 147.7, 145.0, 144.3, 138.8, 137.8, 136.6, 133.6, 133.3, 129.4, 129.2, 129.1, 128.8, 128.0, 127.3, 126.1, 119.6, 73.1, 52.4; HRMS (ESI) m/z Calcd. for $C_{29}H_{20}N_3O_4$ ($[M+H]^+$) 474.1448, Found 474.1441; Enantiomeric excess was determined to be 67% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 61.4 min, tminor = 79.3 min).

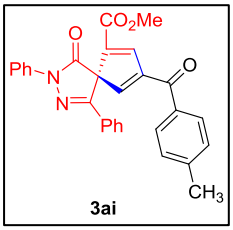


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	60.505	MM T	4.7648	9121.95801	31.90769	50.0552
2	77.818	MM T	6.0671	9101.83203	25.00321	49.9448

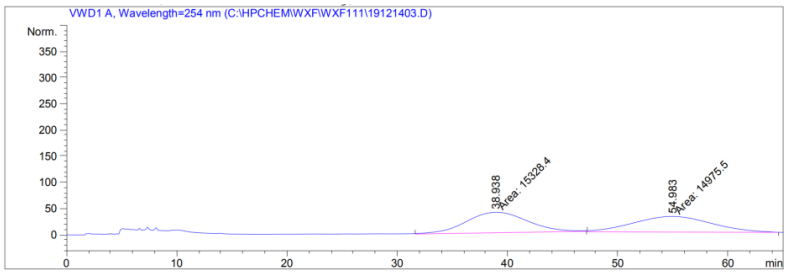


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	61.434	MM T	4.5910	3.60477e4	130.86292	83.2698
2	79.328	MM T	5.7018	7242.54883	21.17034	16.7302

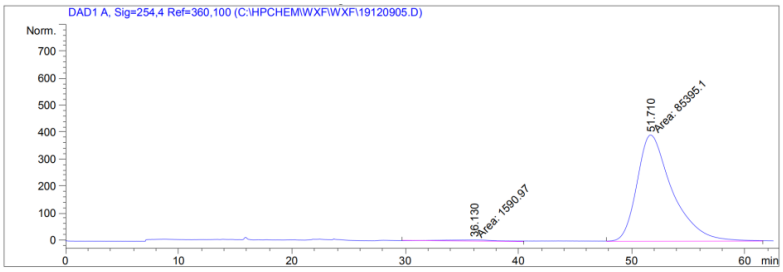
Compound 3ai



Prepared according to the procedure within 12 h as white solid (70.2 mg, 76% yield); mp 136.4-137.3 °C; $[\alpha]_D^{17}$ = -47.25 (*c* 0.80, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 1.8 Hz, 1H), 8.03 – 7.95 (m, 2H), 7.83 – 7.74 (m, 2H), 7.57 – 7.51 (m, 2H), 7.47 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.44 – 7.38 (m, 1H), 7.35 (dd, *J* = 8.2, 6.4 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.01 (d, *J* = 1.8 Hz, 1H), 3.69 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.5, 165.9, 161.8, 152.8, 147.8, 145.0, 144.6, 144.1, 139.0, 138.0, 134.1, 131.2, 130.7, 129.6, 129.5, 129.1, 129.1, 126.0, 125.5, 119.5, 73.1, 52.3, 21.8; HRMS (ESI) m/z Calcd. for $C_{29}H_{23}N_2O_4$ ($[M+H]^+$) 463.1652, Found 463.1641; Enantiomeric excess was determined to be 96% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 51.7 min, tminor = 36.1 min).

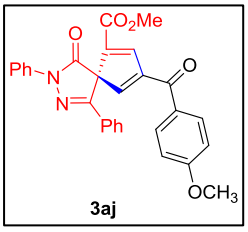


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.938	MM T	6.5116	1.53284e4	39.23356	50.5823
2	54.983	MM T	8.3265	1.49755e4	29.97565	49.4177

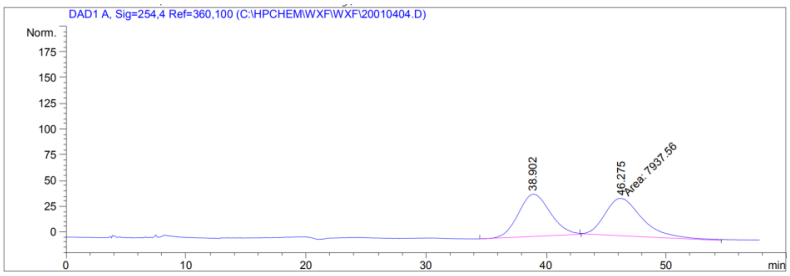


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.130	MM T	5.5682	1590.97046	4.76206	1.8290
2	51.710	MM T	3.7164	8.53951e4	393.88535	98.1710

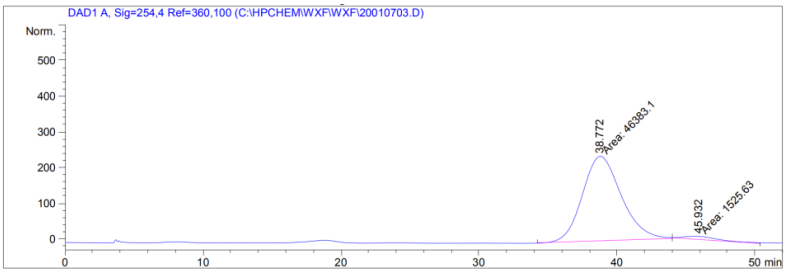
Compound 3aj



Prepared according to the procedure within 12 h as white solid (78.4 mg, 82 % yield); mp 138.1-139.7 °C; $[\alpha]_D^{17}$ = -53.67 (*c* 0.30, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.91 – 7.79 (m, 2H), 7.60 (m, 1H), 7.55 – 7.38 (m, 6H), 7.28 (s, 1H), 7.04 (d, *J* = 1.9 Hz, 1H), 6.91 – 6.77 (m, 2H), 3.81 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.9, 165.6, 161.9, 161.8, 152.4, 147.4, 145.0, 144.5, 139.3, 138.1, 136.7, 133.5, 129.4, 129.0, 128.8, 127.1, 125.9, 123.4, 119.5, 114.5, 73.3, 55.4, 52.3; HRMS (ESI) m/z Calcd. for $C_{29}H_{23}N_2O_5$ ($[M+H]^+$) 479.1601, Found 479.1590; Enantiomeric excess was determined to be 94% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 38.8 min, tminor = 45.9 min).

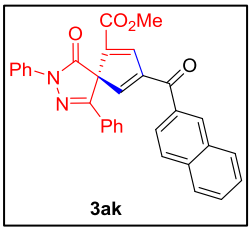


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.902	MM R	3.0911	7648.19678	41.23813	49.0717
2	46.275	MM T	3.6302	7937.55957	36.44251	50.9283



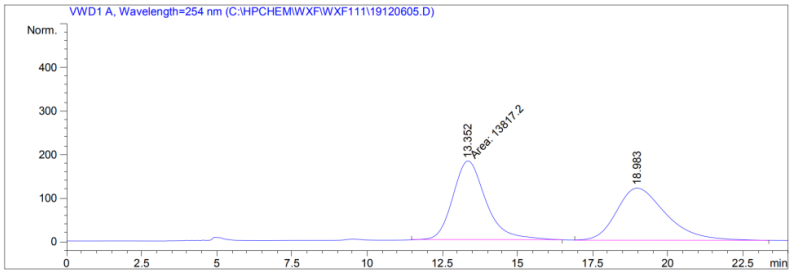
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.772	MM T	3.2643	4.63831e4	236.81772	96.8156
2	45.932	MM T	2.8210	1525.62646	9.01344	3.1844

Compound 3ak

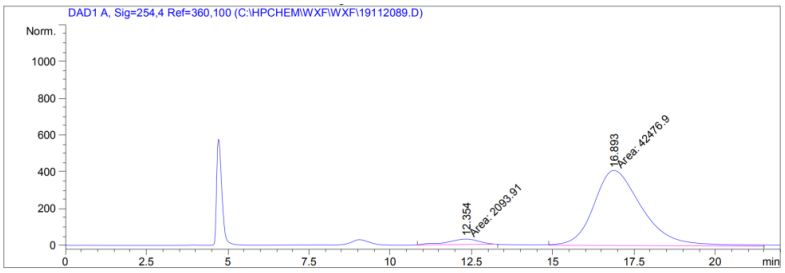


3ak

Prepared according to the procedure within 10 h as white solid (89.6 mg, 90 % yield); mp 136.3-137.2 °C; $[\alpha]_D^{17}$ = -59.23 (*c* 0.26, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 8.10 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 3.8 Hz, 2H), 7.89 (m, 2H), 7.58 (m, 4H), 7.48 (m, 2H), 7.40 (dd, *J* = 14.5, 7.1 Hz, 3H), 7.30 (s, 1H), 7.09 (s, 1H), 3.71 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.8, 165.8, 161.8, 152.8, 147.9, 144.8, 144.3, 139.2, 138.1, 135.7, 134.1, 132.3, 131.5, 131.2, 130.8, 129.7, 129.1, 129.1, 128.9, 127.9, 127.1, 126.0, 125.5, 124.7, 119.6, 73.2, 52.3; HRMS (ESI) m/z Calcd. for $C_{32}H_{23}N_2O_4$ ($[M+H]^+$) 499.1652, Found 499.1642; 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, tmajor = 16.9 min, tminor = 12.4 min).

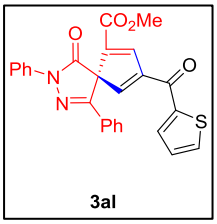


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.352	MM T	1.2758	1.38172e4	180.51050	50.2055
2	18.983	BB	1.7162	1.37041e4	119.78079	49.7945



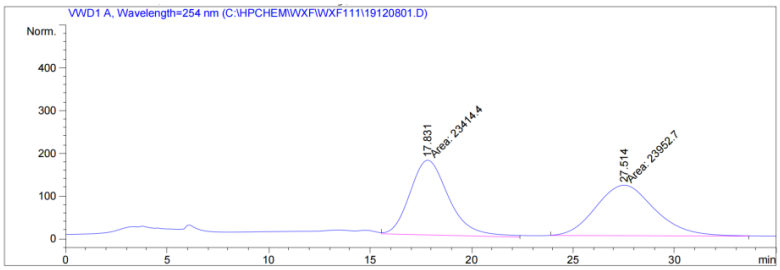
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.354	MM T	1.1581	2093.91382	30.13412	4.6979
2	16.893	MM T	1.7330	4.24769e4	408.51407	95.3021

Compound 3al

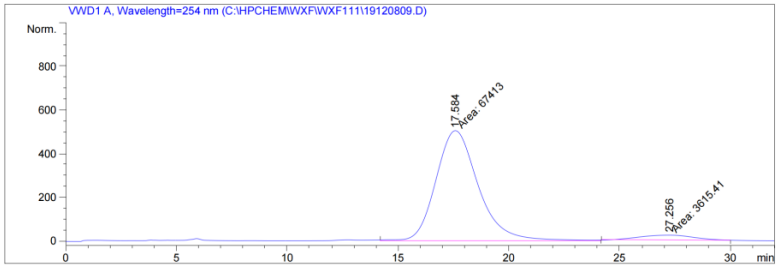


3al

Prepared according to the procedure within 12 h as white solid (79.9 mg, 88% yield); mp 127.0-127.8 °C; $[\alpha]_D^{17}$ = -30.63 (*c* 0.16, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.90 (m, 3H), 7.76 (dd, *J* = 17.3, 4.3 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.47 (m, 2H), 7.34 (m, 4H), 7.20 (s, 1H), 7.14 (m, 1H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.9, 165.7, 161.7, 152.8, 147.8, 144.5, 142.9, 139.2, 138.0, 135.3, 134.5, 131.2, 130.7, 129.1, 128.5, 126.0, 125.5, 119.5, 73.0, 52.3; HRMS (ESI) m/z Calcd. for $C_{26}H_{19}N_2O_4S$ ($[M+H]^+$) 455.1060, Found 455.1049; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AS-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 17.6 min, tminor = 27.3 min).

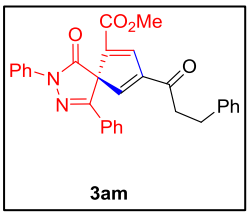


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.831	MM T	2.2313	2.34144e4	174.89444	49.4318
2	27.514	MM T	3.3746	2.39527e4	118.29751	50.5682

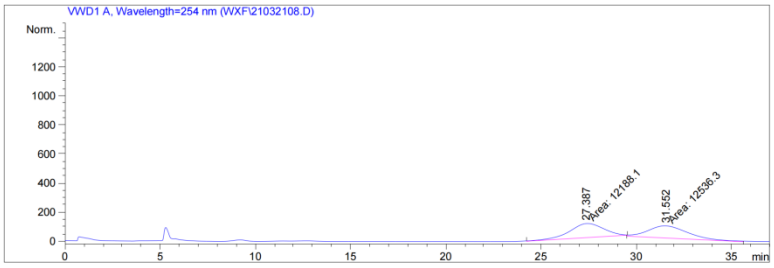


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.584	MM T	2.2256	6.74130e4	504.82172	94.9099
2	27.256	MM T	2.7450	3615.40576	21.95171	5.0901

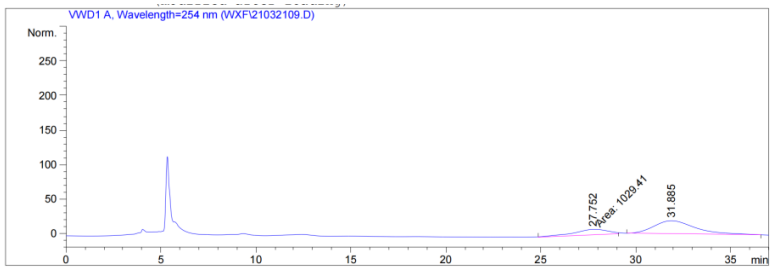
Compound 3am



Prepared according to the procedure within 48 h as yellow liquid (55.2 mg, 58 % yield); $[\alpha]_D^{17}$ = -26.59 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.9 Hz, 3H), 7.45 (dd, *J* = 7.8, 4.0 Hz, 4H), 7.39 (m, 1H), 7.33 (q, *J* = 4.0 Hz, 2H), 7.25 (d, *J* = 4.2 Hz, 3H), 7.18 (d, *J* = 10.6 Hz, 3H), 7.13 (s, 1H), 3.66 (t, *J* = 2.9 Hz, 3H), 3.13 (dq, *J* = 7.1, 3.7, 3.3 Hz, 2H), 3.09 – 2.94 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.5, 165.5, 161.7, 152.6, 148.6, 143.1, 143.0, 140.4, 139.1, 137.9, 131.2, 130.7, 129.0, 129.0, 128.6, 128.3, 126.3, 126.0, 125.4, 119.5, 73.0, 52.3, 41.3, 29.6; HRMS (ESI) m/z Calcd. for $C_{30}H_{25}N_2O_4$ ($[M+H]^+$) 477.1809, Found 477.1794; Enantiomeric excess was determined to be 55% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 31.9 min, tminor = 27.8 min).

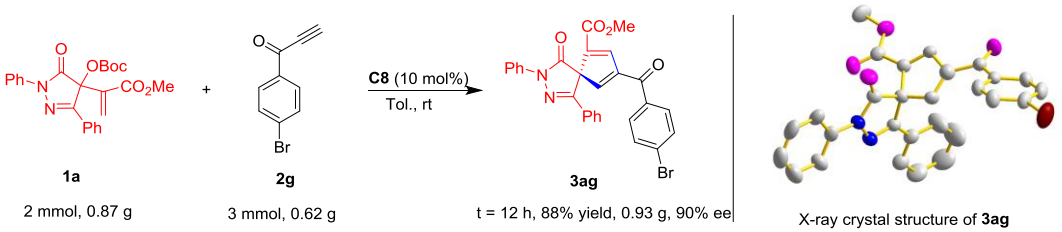


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.387	MM T	2.0866	1.21881e4	97.35361	49.2959
2	31.552	MM T	2.4679	1.25363e4	84.66212	50.7041



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.752	MM T	2.1413	1029.41187	8.01232	26.4084
2	31.885	BB	1.8056	2868.63184	18.91712	73.5916

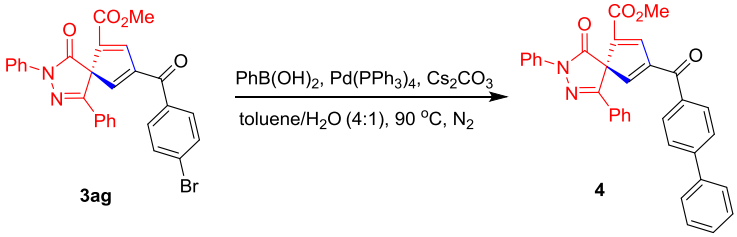
Gram-scale Synthesis of 3ag



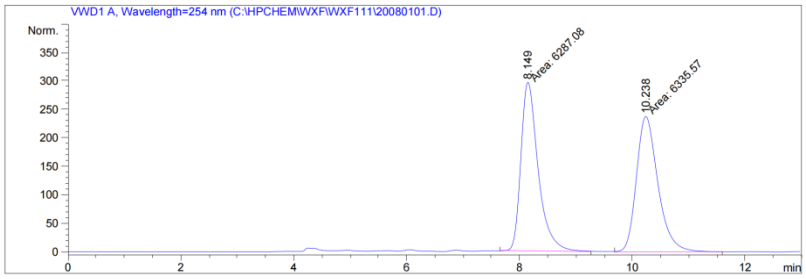
X-ray crystal structure of **3ag**

A tube was charged with MBH Carbonates **1a** (870 mg, 2.0 mmol, 1.0 equiv), alkynyl ketone **2g** (620 mg, 3.0 mmol, 1.5 equiv), **C8** (81 mg, 0.2 mmol, 0.1 equiv) and toluene (10 mL) at rt. The reaction was monitored by TLC. The product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) directly to give the product **3ag** 926 mg as white solid (88% yield, 90% ee).

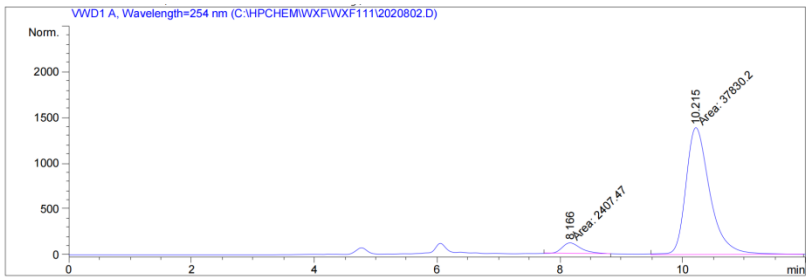
The procedure for the synthesis of compounds 4



To a Schlenk tube were added **3ag** (53 mg, 0.1 mmol, 1.0 equiv), $PhB(OH)_2$ (25 mg, 0.2 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol, 0.1 equiv), Cs_2CO_3 (104 mg, 0.3 mmol, 3.0 equiv) and toluene/H_2O (4 mL/1 mL). The reaction mixture was stirred at 90 °C for 6 h under a nitrogen atmosphere. The product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to give the product **4** as yellow solid (43.0 mg, 82 % yield); mp 156.1-157.8 °C; $[\alpha]_D^{17}$ = -64.87 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.88 (m, 3H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.69 (t, *J* = 8.4 Hz, 4H), 7.50 (ddd, *J* = 25.0, 18.7, 11.5 Hz, 12H), 3.20 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.5, 165.4, 158.4, 149.4, 145.3, 140.9, 139.9, 137.5, 135.3, 130.5, 129.0, 128.8, 128.3, 128.2, 127.3, 127.2, 126.2, 122.6, 118.6, 117.4, 51.2; HRMS (ESI) m/z Calcd. for $C_{34}H_{25}N_2O_4$ ($[M+H]^+$) 525.1809, Found 525.1802; Enantiomeric excess was determined to be 88% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 10.2 min, tminor = 8.2 min).

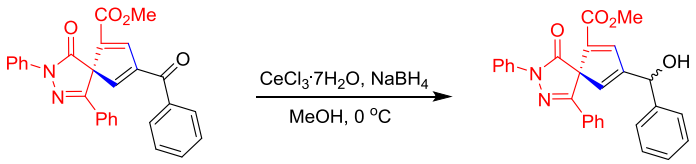


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.149	MM T	0.3536	6287.07715	296.32309	49.8079
2	10.238	MM T	0.4430	6335.57031	238.36189	50.1921



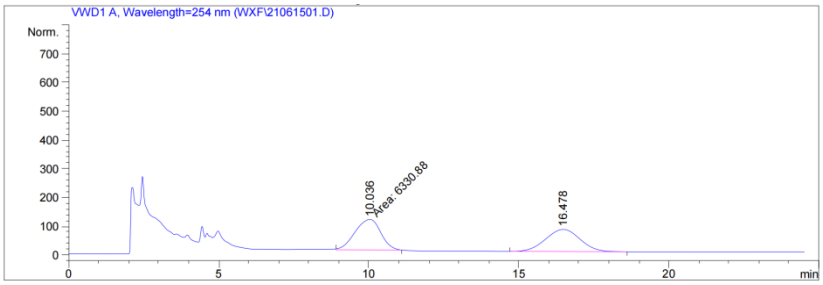
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.166	MM T	0.3513	2407.46826	114.23095	5.9831
2	10.215	MM T	0.4543	3.78302e4	1387.87268	94.0169

The procedure for the synthesis of compounds 5

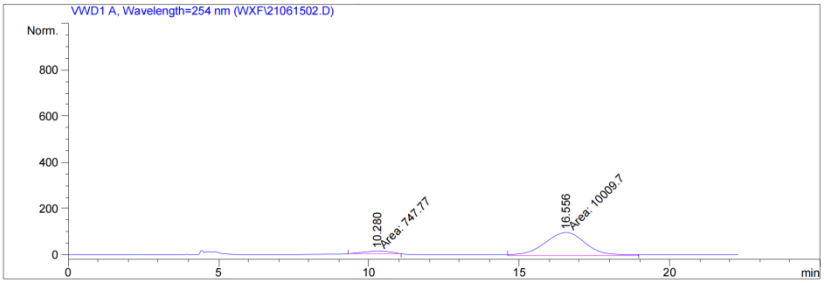


3aa **5**

To a solution of **3aa** (54.0 mg, 0.1 mmol, 1.0 equiv) in MeOH (2.0 mL) was added sodium borohydride (5.0 mg, 0.12 mmol, 1.2 equiv) and $CeCl_3{\cdot}7H_2O$ (45 mg, 0.12 mmol, 1.2 equiv) at 0 °C for 30 min. The product was purified by silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give **5** as white solid (30.6 mg, 68 % yield, 7:1 dr); mp 162.7-164.0 °C; $[\alpha]_D^{17}$ = -74.63 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.42 (m, 9H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.31 (s, 1H), 7.25 (s, 1H), 6.57 (s, 1H), 5.72 (s, 1H), 4.13 (s, 1H), 3.65 (s, 1H), 3.61 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 161.8, 154.0, 153.9, 145.9, 140.8, 139.0, 138.2, 132.2, 130.8, 129.0, 128.9, 128.7, 128.6, 126.9, 125.7, 125.6, 119.5, 72.3, 71.4, 52.0; HRMS (ESI) m/z Calcd. for $C_{28}H_{23}N_2O_4$ ($[M+H]^+$) 451.1652, Found 451.1655; Enantiomeric excess was determined to be 86% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 30 °C, 0.8 mL/min, tmajor = 16.6 min, tminor = 10.3 min).

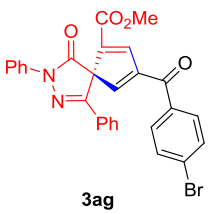


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.036	MM T	0.9936	6330.87646	106.19193	50.5643
2	16.478	BB	1.2472	6189.56396	77.18378	49.4357

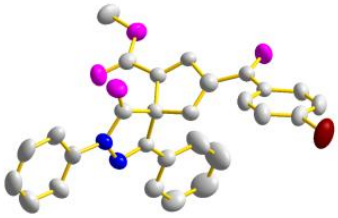


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.280	MM T	1.0458	747.76990	11.91676	6.9512
2	16.556	MM T	1.6464	1.00097e4	101.32826	93.0488

4. X-ray crystal structure of compound 3ag



3ag



X-ray crystal structure of **3ag**

CCDC: 2189938

Crystal data and structure refinement for 3ag.

Identification code	3ag
Empirical formula	$C_{27}H_{19}BrN_3O_4$
Formula weight	529.36
Temperature/K	295.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.5080(5)
b/Å	12.3736(6)
c/Å	20.7192(11)
α/°	90
β/°	90
γ/°	90
Volume/Å ^{3}	2437.6(2)
Z	4
ρ_{calc}g/cm^3	1.442
μ/mm^{-1}	1.725
F(000)	1076.0
Crystal size/mm^3	0.21 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.932 to 54.964
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -26 ≤ l ≤ 26
Reflections collected	47283
Independent reflections	5592 [R_{int} = 0.0760, R_{sigma} = 0.0534]
Data/restraints/parameters	5592/0/317
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0581, wR_2 = 0.1227
Final R indexes [all data]	R_1 = 0.0963, wR_2 = 0.1405
Largest diff. peak/hole / e Å $^{-3}$	0.35/-1.19
Flack parameter	0.044(5)
CCDC number	2189938

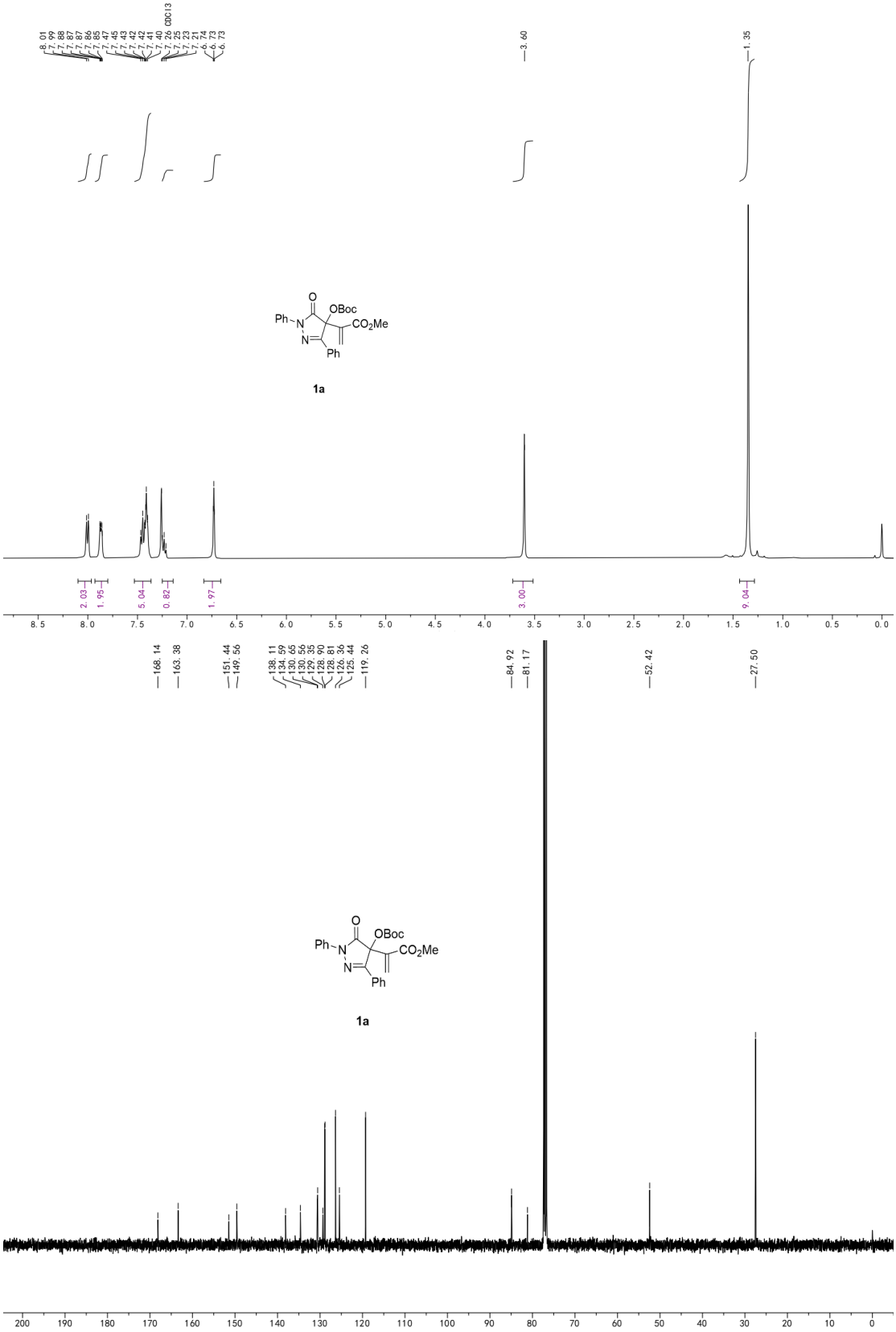
5. References

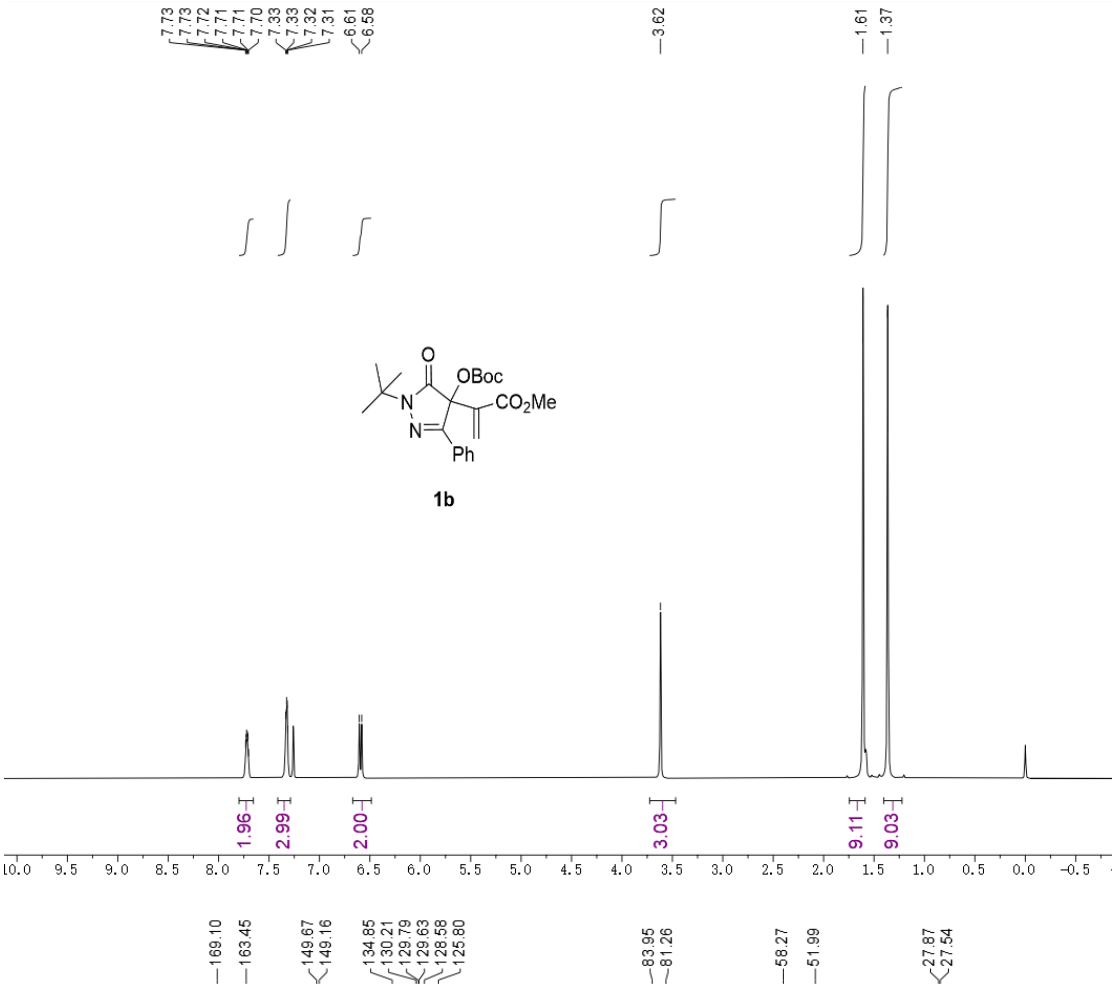
(1) (a) F. Shi, S. Luo, L. Gong, *Org. Lett.*, 2011, **13**, 4680–4683; (b) A. Bugarin and B. T. Connell, *Tetrahedron Lett.*, 2015, **56**, 3285-3287; (c) J. Rong, H. Li, R. Fu, W. Sun, T.-P. Loh and Y. Jiang, *ACS Catal.*, 2020, **10**, 3664-3669.

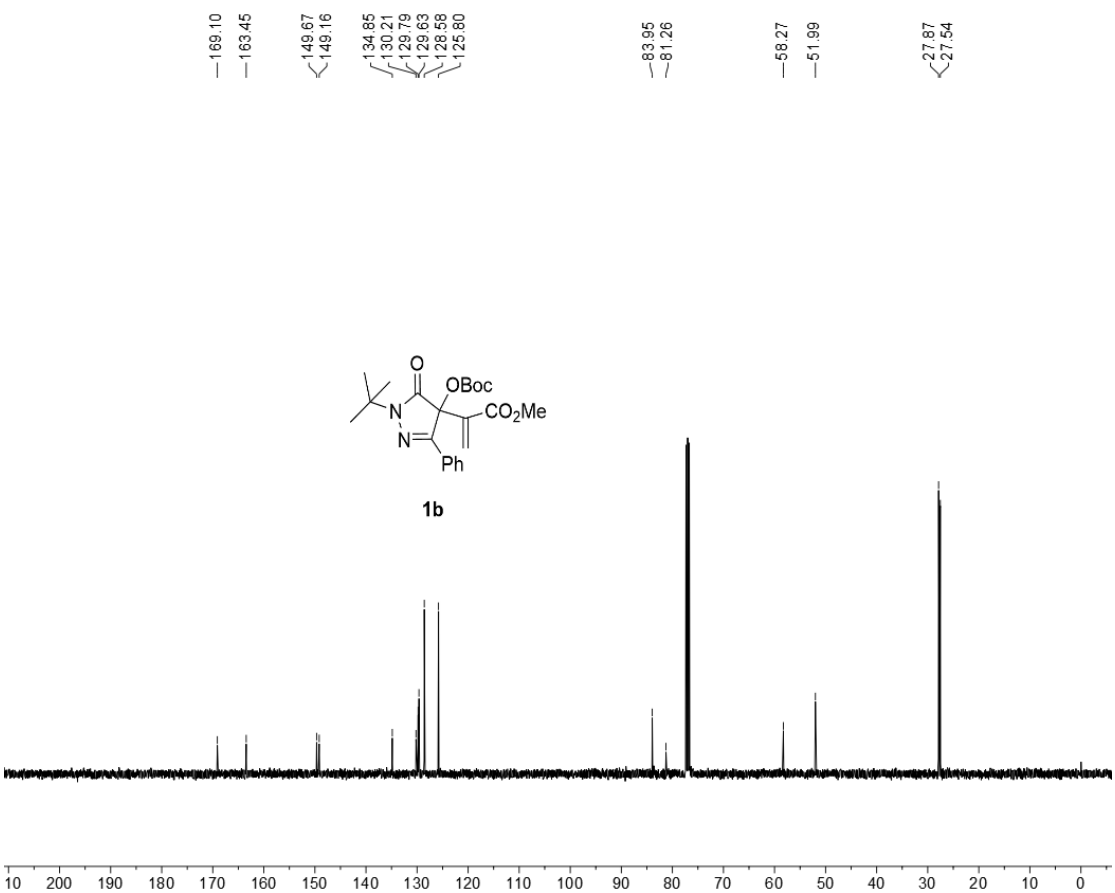
(2) (a) P. Chauhan, S. Mahajan, U. Kaya, A. Peuronen, K. Rissanen and D. Enders, *J. Org. Chem.*, 2017, **82**, 7050-7058; (b) U. Kaya, P. Chauhan, S. Mahajan, K. Deckers, A. Valkonen, K. Rissanen and D. Enders, *Angew. Chem., Int. Ed.*, 2017, **56**, 15358-15362; (a) K. Kumar, B. Singh, S. Hore and R. P. Singh, *New J. Chem*., 2021, **45**, 13747-13750.

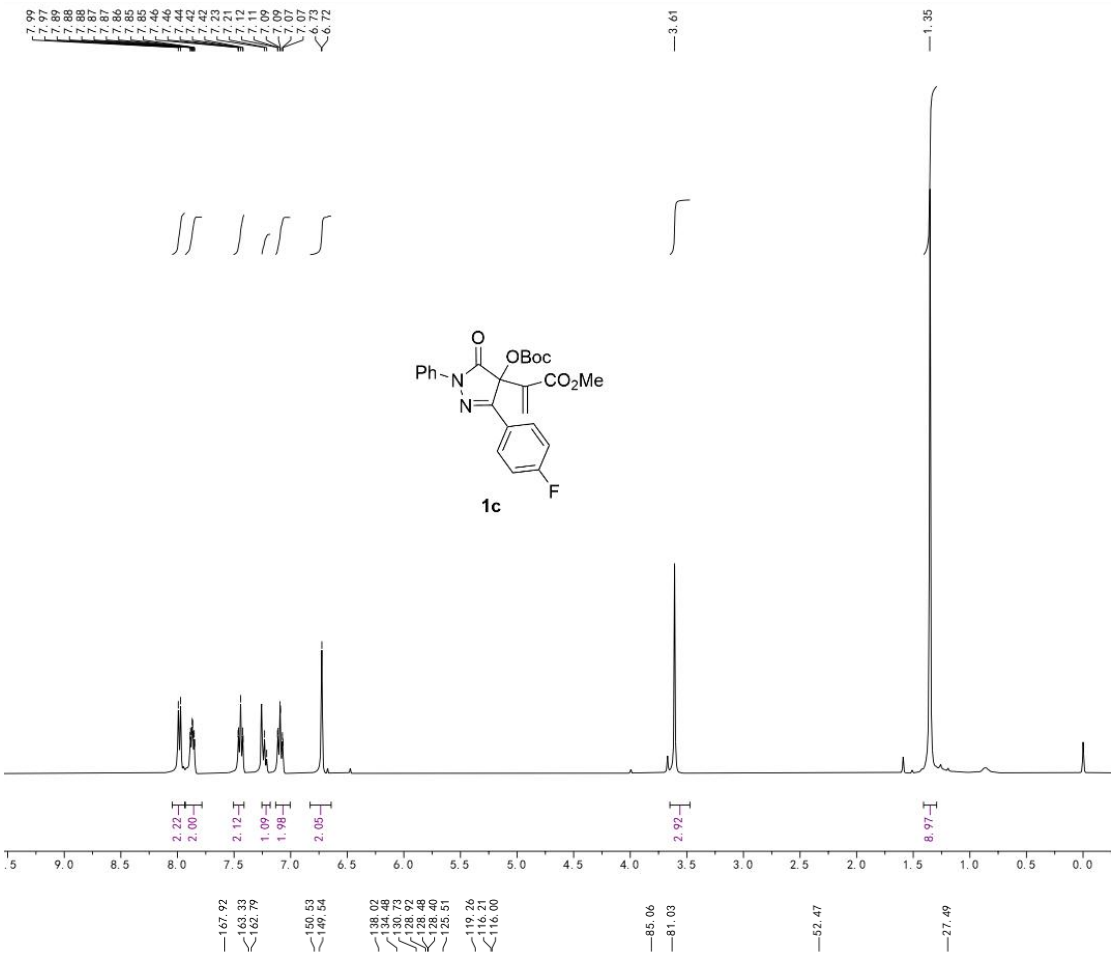
(3) (a) A. R. Choudhury and S. Mukherjee, *Org. Biomol. Chem.*, 2012, **10**, 7313-7320; (b) Y. Nakamoto, F. Urabe, K. Takahashi, J. Ishihara and S. Hatakeyama, *Chem.-Eur. J.*, 2013, **19**, 12653-12656.

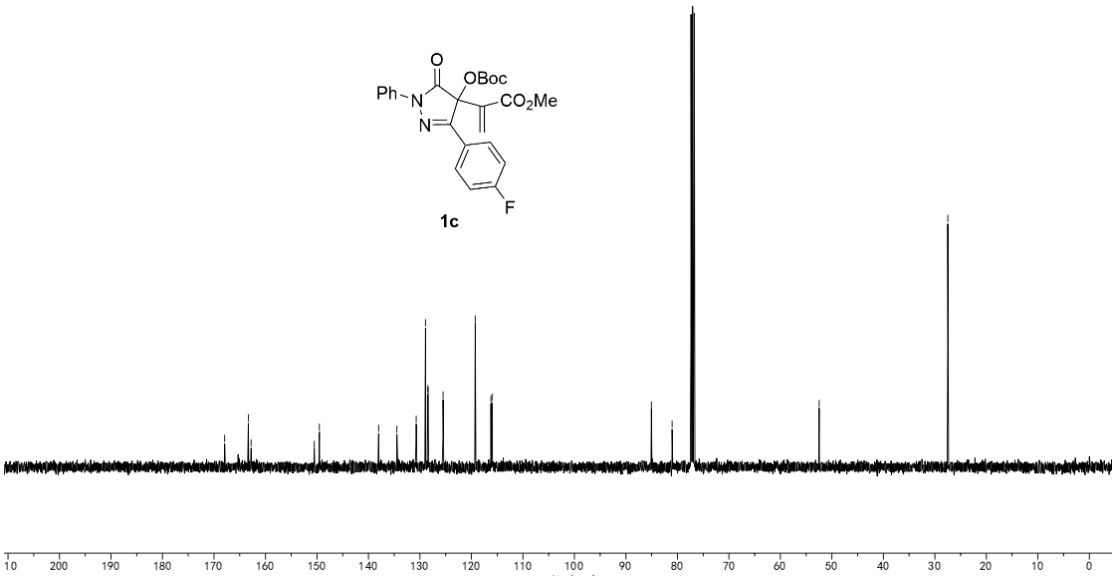
6. NMR spectra for compounds

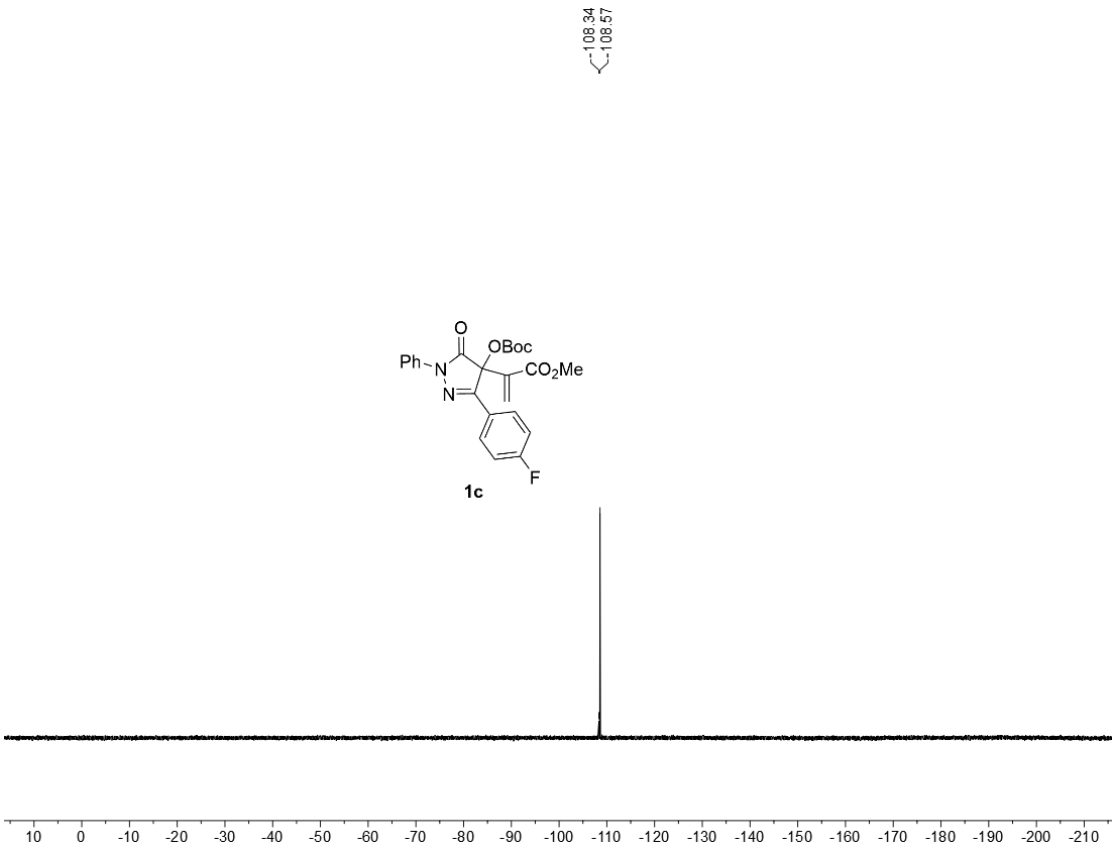


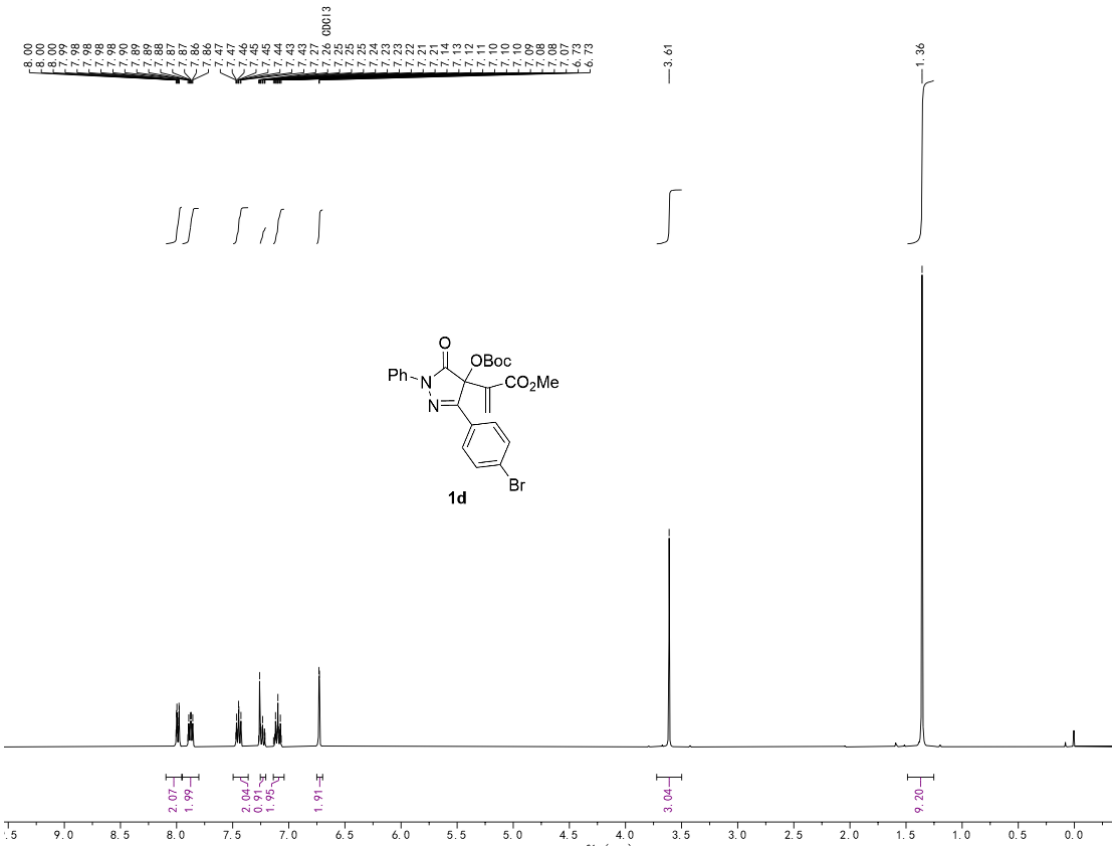

7.73
7.73
7.72
7.71
7.71
7.70
7.33
7.33
7.32
7.31
6.61
6.58
3.62
1.61
1.37
O
OBoc
N
CO2Me
N
Ph
1b
1.96
2.99
2.00
3.03
9.11
9.03

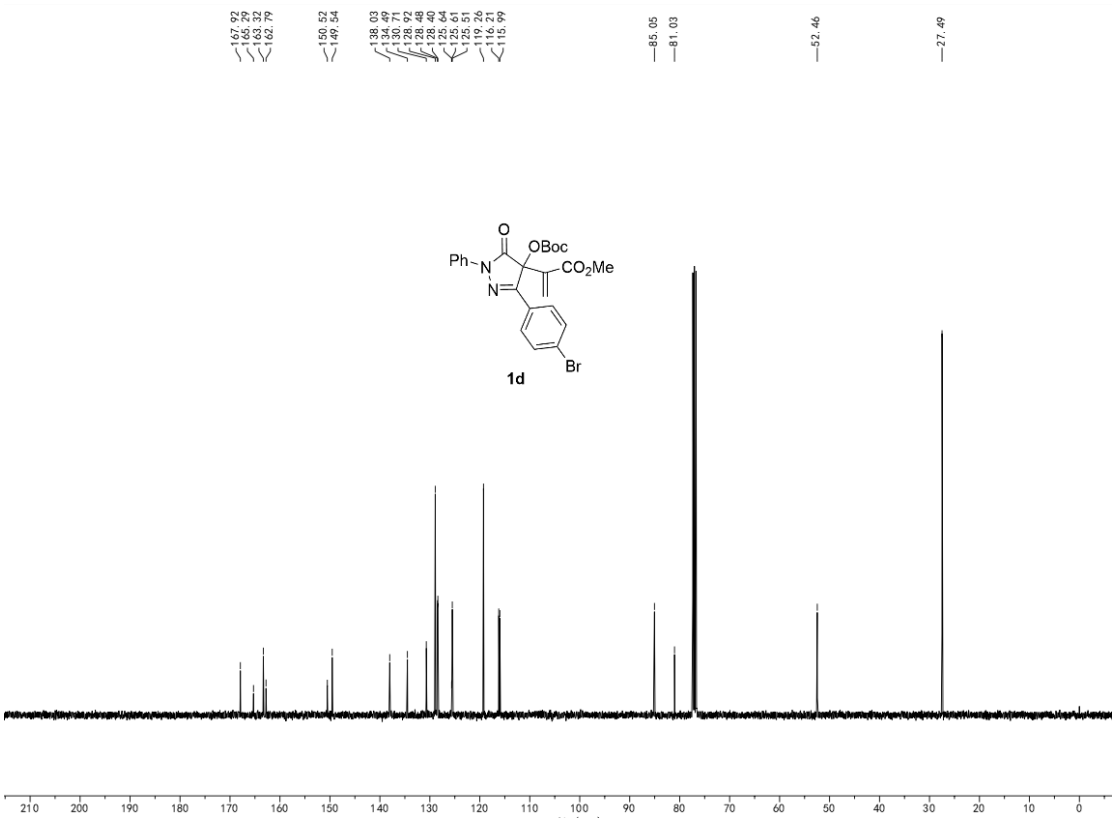

169.10
163.45
149.67
149.16
134.85
130.21
129.79
129.63
128.58
125.80
83.95
81.26
58.27
51.99
27.87
27.54
O
OBoc
N
CO2Me
N
Ph
1b

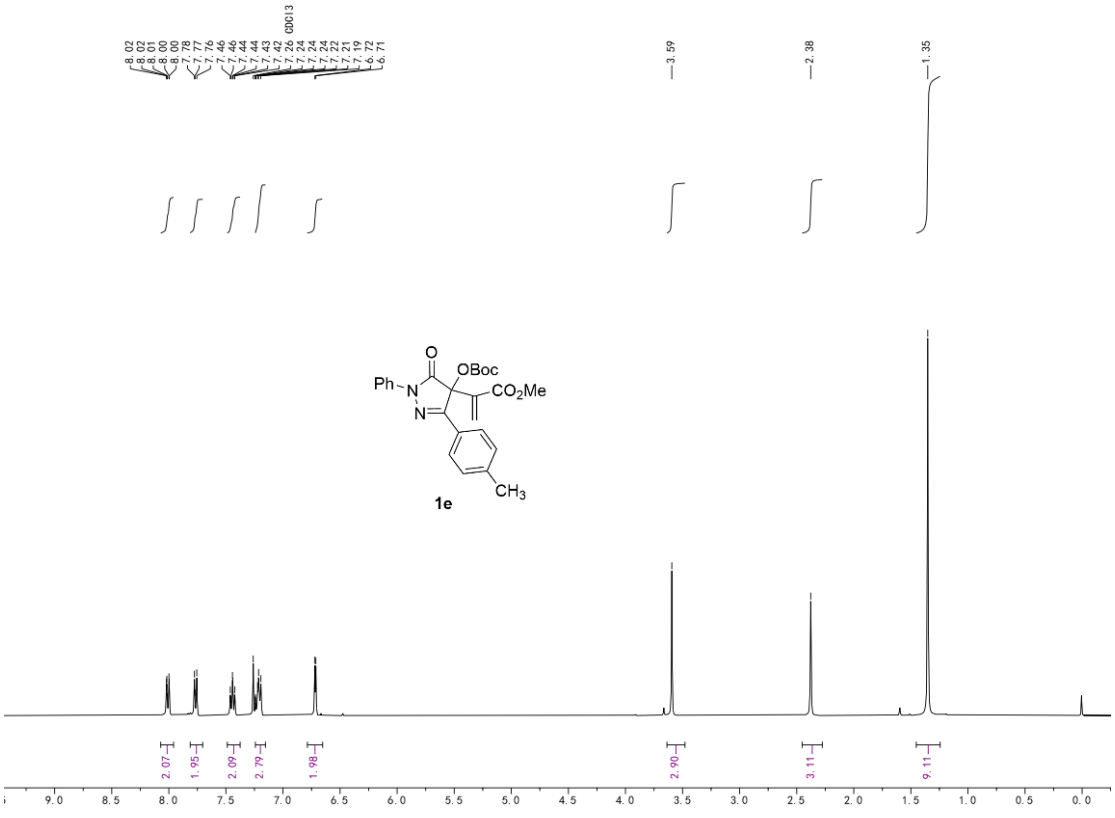

7.99
7.97
7.89
7.88
7.88
7.87
7.87
7.86
7.85
7.46
7.46
7.44
7.42
7.42
7.23
7.21
7.12
7.11
7.09
7.09
7.07
7.07
6.73
6.72
3.61
1.35
O
OBoc
Ph
N
N
CO2Me
F
1c
2.22
2.00
2.12
1.09
1.98
2.05
2.92
8.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

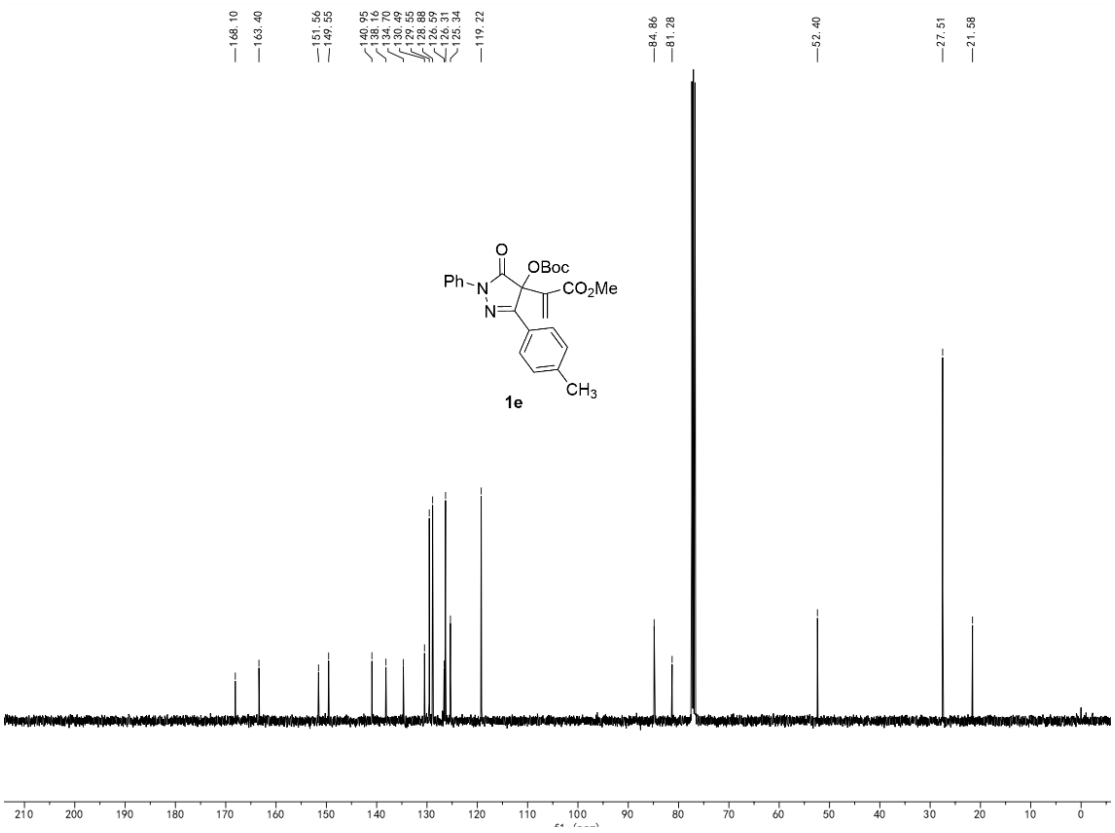

167.92
163.33
162.79
150.53
149.54
138.02
134.48
130.73
128.92
128.48
128.40
125.51
119.26
116.21
116.00
85.06
81.03
52.47
27.49
O
OBoc
Ph
N
N
CO2Me
F
1c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

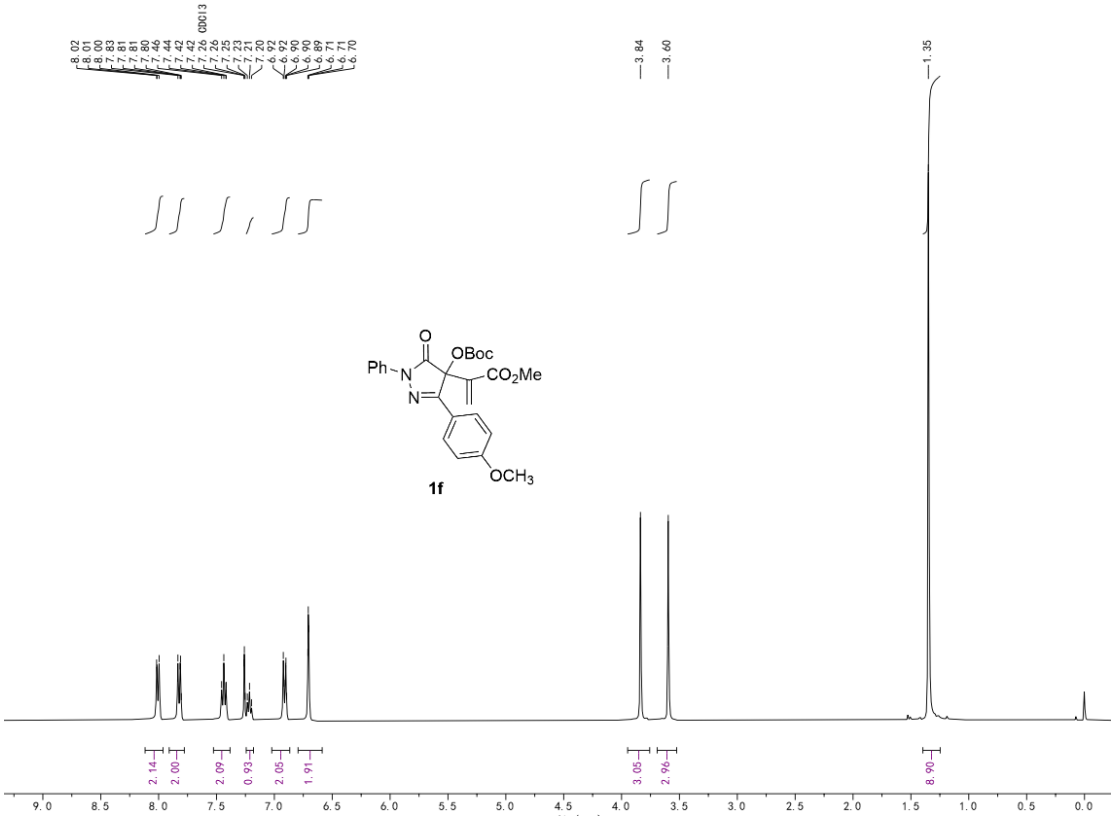

-108.34
-108.57
Ph
N
N
O
OBoc
CO2Me
F
1c
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

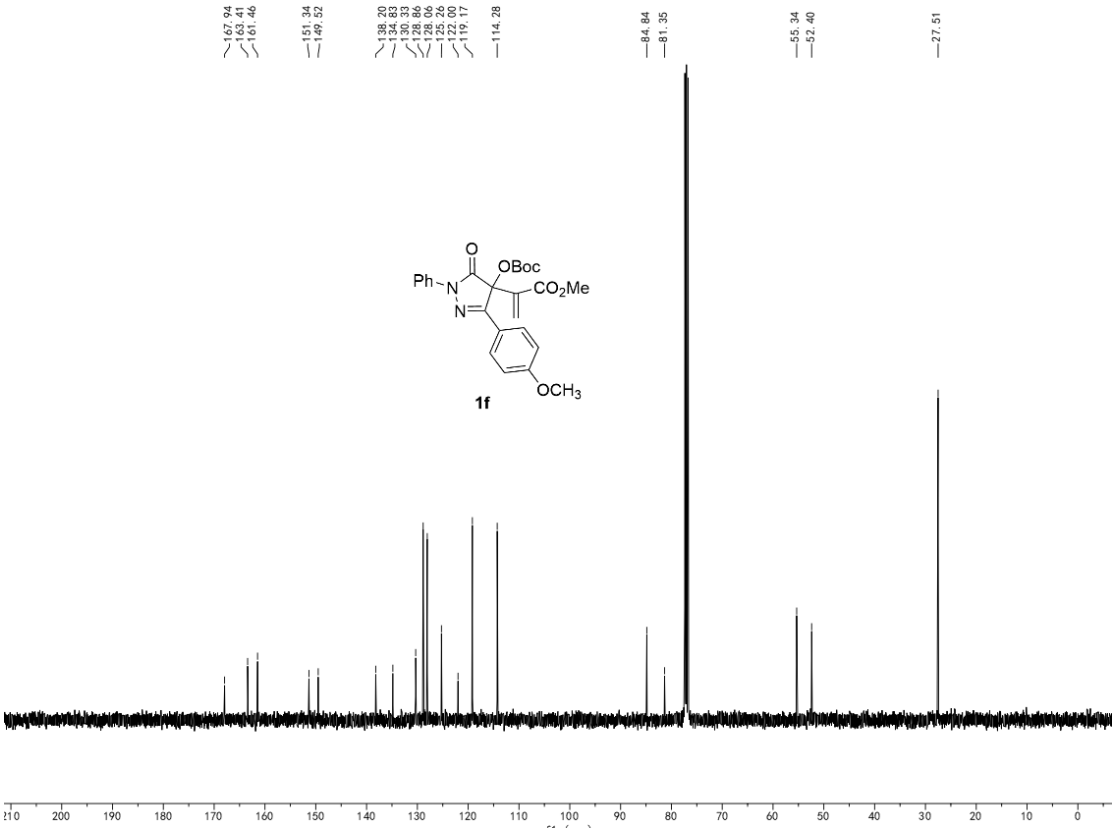

CDCl3
3.61
1.36
Ph
N
N
O
OBoc
CO2Me
Br
1d
2.07
1.99
2.04
0.91
1.95
1.91
3.04
9.20

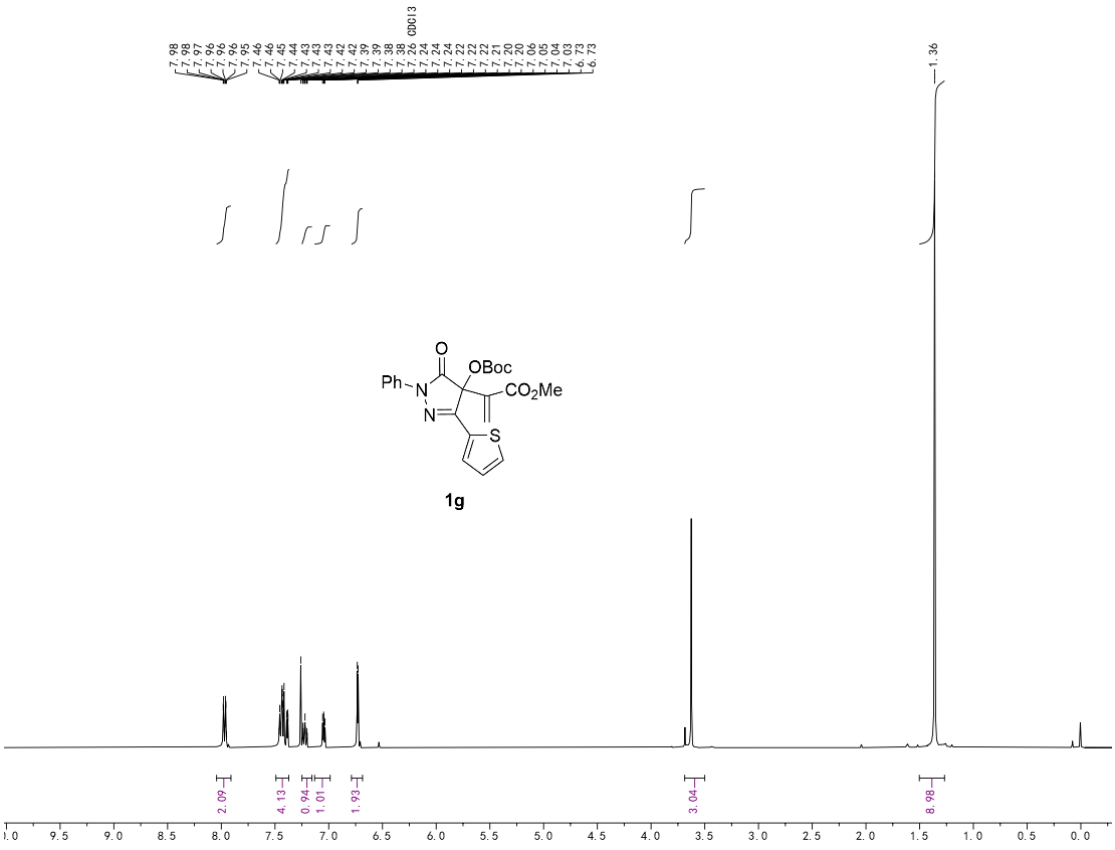

167.92
165.29
163.32
162.79
150.52
149.54
138.03
134.49
130.71
128.92
128.48
128.40
125.64
125.61
125.51
119.26
116.21
115.99
85.05
81.03
52.46
27.49
O
OBoc
Ph
N
N
CO2Me
Br
1d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

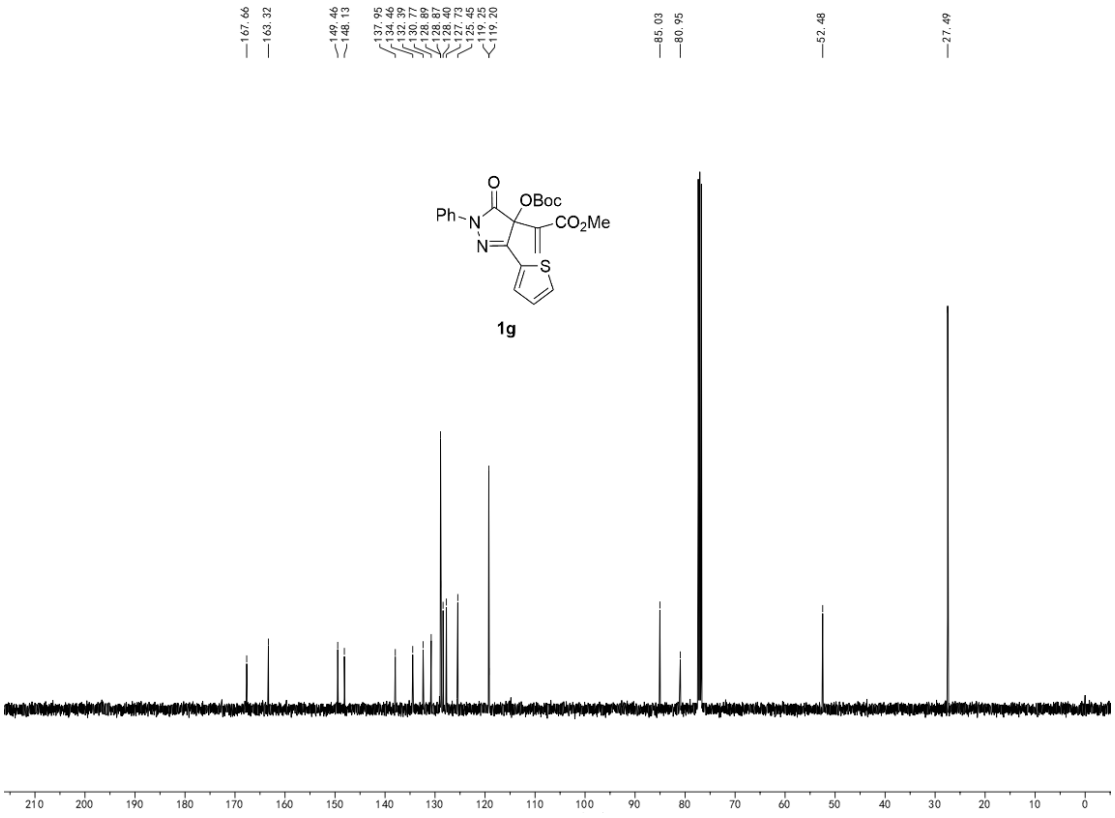

8.02
8.02
8.01
8.00
8.00
7.78
7.77
7.76
7.46
7.46
7.44
7.44
7.43
7.42
CDCl3
7.26
7.24
7.24
7.24
7.22
7.21
7.19
6.72
6.71
3.59
2.38
1.35
O
OBoc
Ph
N
N
CO2Me
CH3
1e
2.07
1.95
2.09
2.79
1.98
2.90
3.11
9.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

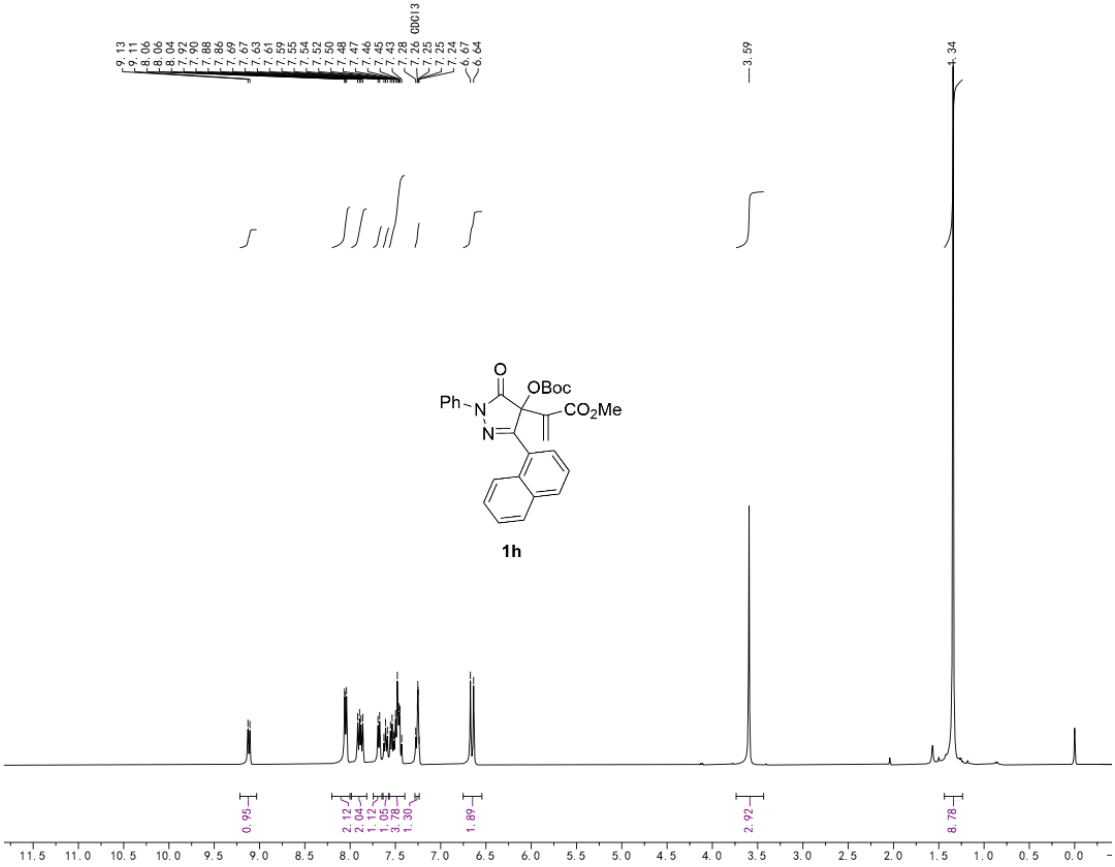

168.10
163.40
151.56
149.55
140.95
138.16
134.70
130.49
129.55
128.88
126.59
126.31
125.34
119.22
84.86
81.28
52.40
27.51
21.58
O
OBoc
Ph
N
N
CO2Me
CH3
1e

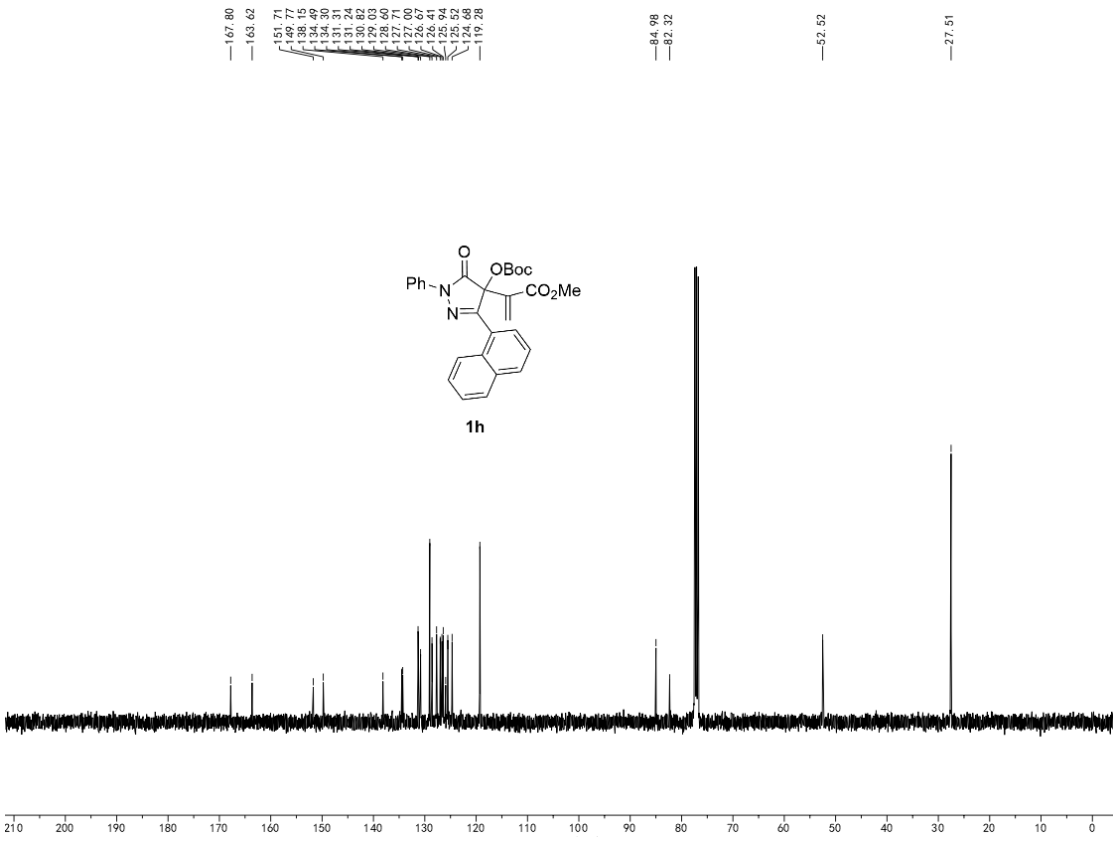

8.02
8.01
8.00
7.83
7.81
7.81
7.80
7.46
7.44
7.42
7.42
7.26
7.25
7.23
7.21
7.20
6.92
6.92
6.90
6.90
6.89
6.71
6.71
6.70
00013
3.84
3.60
1.35
O
OBoc
Ph
N
N
CO2Me
OCH3
1f
2.14
2.00
2.09
0.93
2.05
1.91
3.05
2.96
8.90

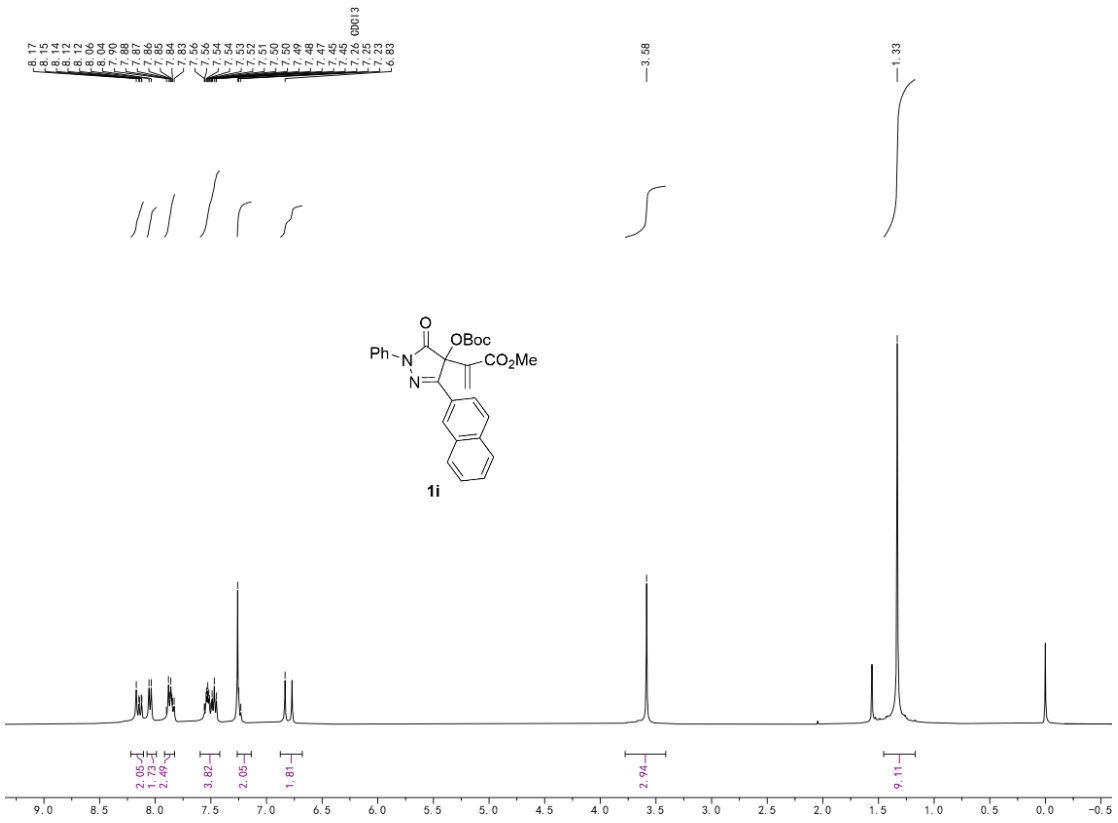

167.94
163.41
161.46
151.34
149.52
138.20
134.83
130.33
128.86
128.06
125.26
122.00
119.17
114.28
84.84
81.35
55.34
52.40
27.51
O
OBoc
Ph
N
N
CO2Me
OCH3
1f

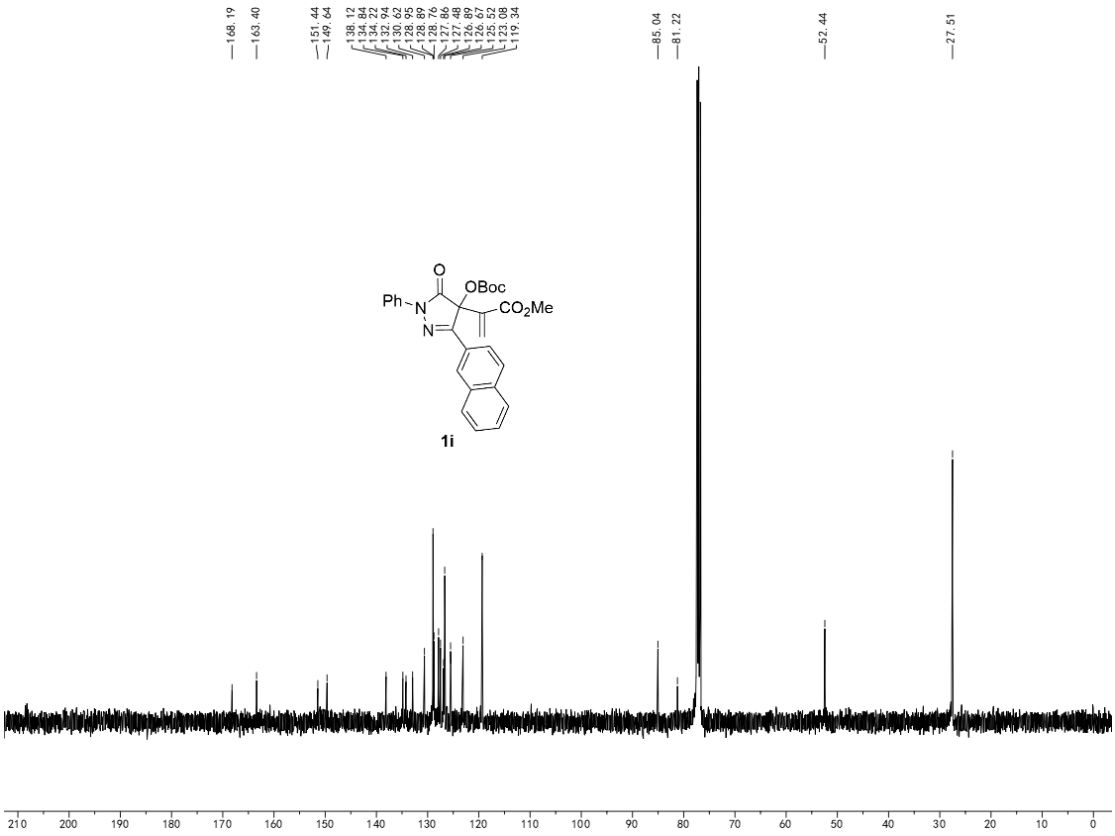

CDCl3
1.36
O
OBoc
Ph
N
N
CO2Me
S
1g
2.09
4.13
0.94
1.01
1.93
3.04
8.98

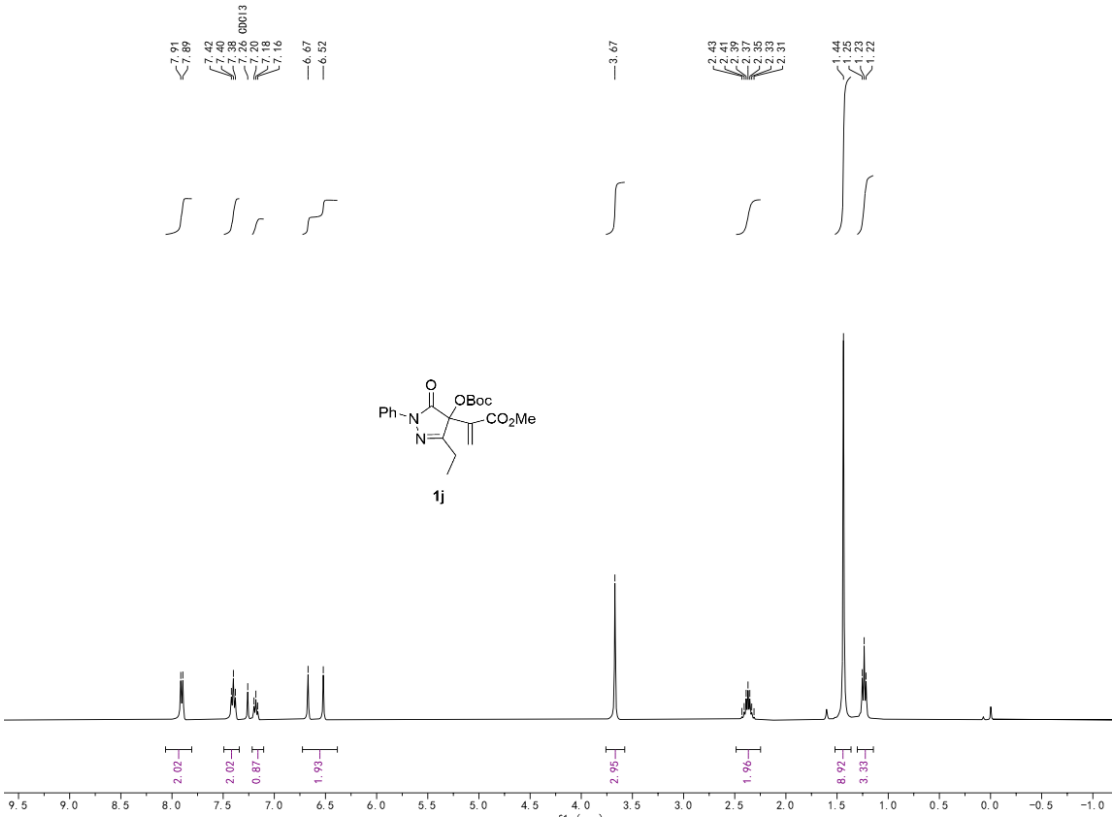

167.66
163.32
149.46
148.13
137.95
134.46
132.39
130.77
128.89
128.87
128.40
127.73
125.45
119.25
119.20
85.03
80.95
52.48
27.49
O
OBoc
Ph
N
N
CO2Me
S
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

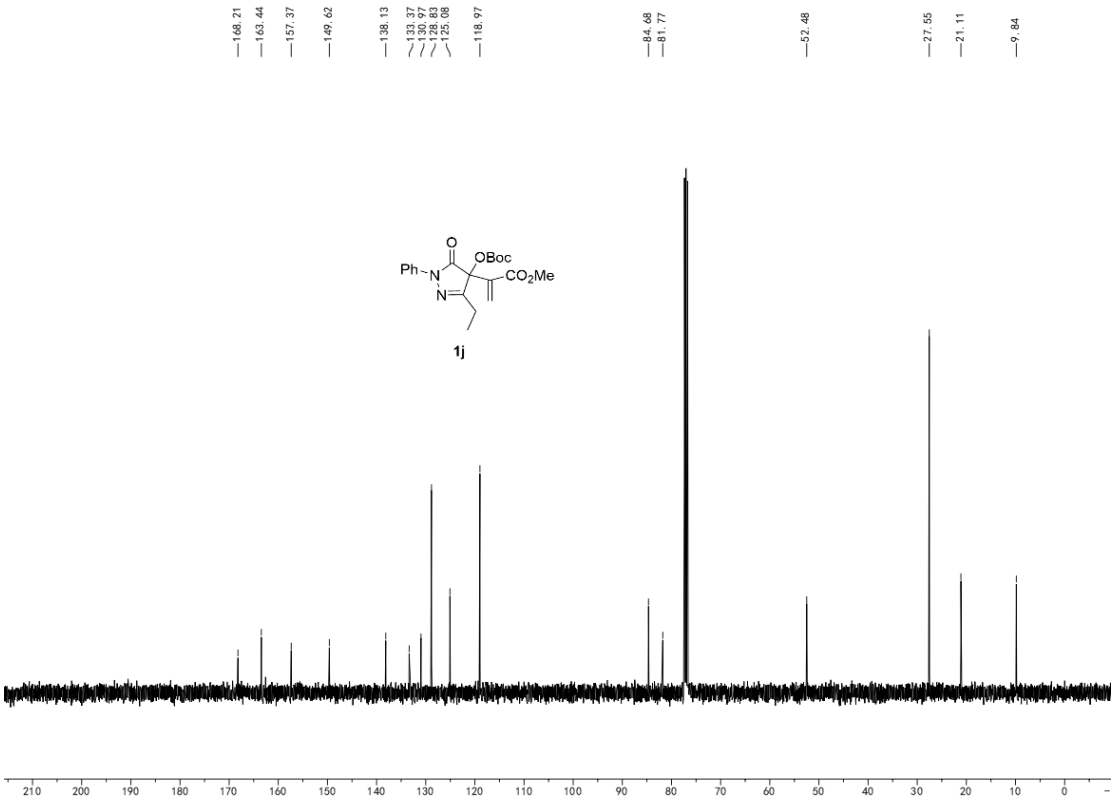

9.13
9.11
8.06
8.06
8.04
7.92
7.90
7.88
7.86
7.69
7.67
7.63
7.61
7.59
7.55
7.54
7.52
7.50
7.48
7.47
7.46
7.45
7.43
7.28
CDCl3
7.26
7.25
7.24
6.67
6.64
3.59
1.34
O
OBoc
Ph
N
N
CO2Me
1h
0.95
2.12
2.04
1.12
1.05
3.78
1.30
1.89
2.92
8.78
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

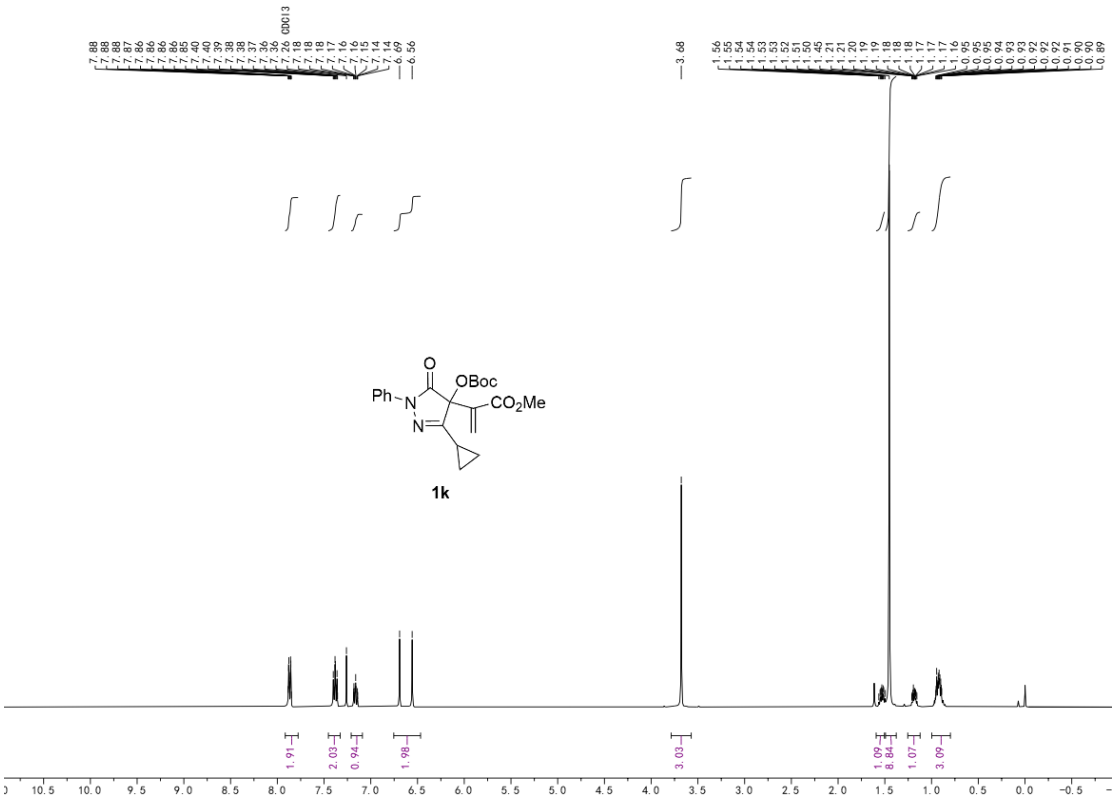

167.80
163.62
151.71
149.77
138.15
134.49
134.30
131.31
131.24
130.82
129.03
128.60
127.71
127.00
126.67
126.41
125.94
125.52
124.68
119.28
84.98
82.32
52.52
27.51
O
OBoc
Ph
N
N
CO2Me
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

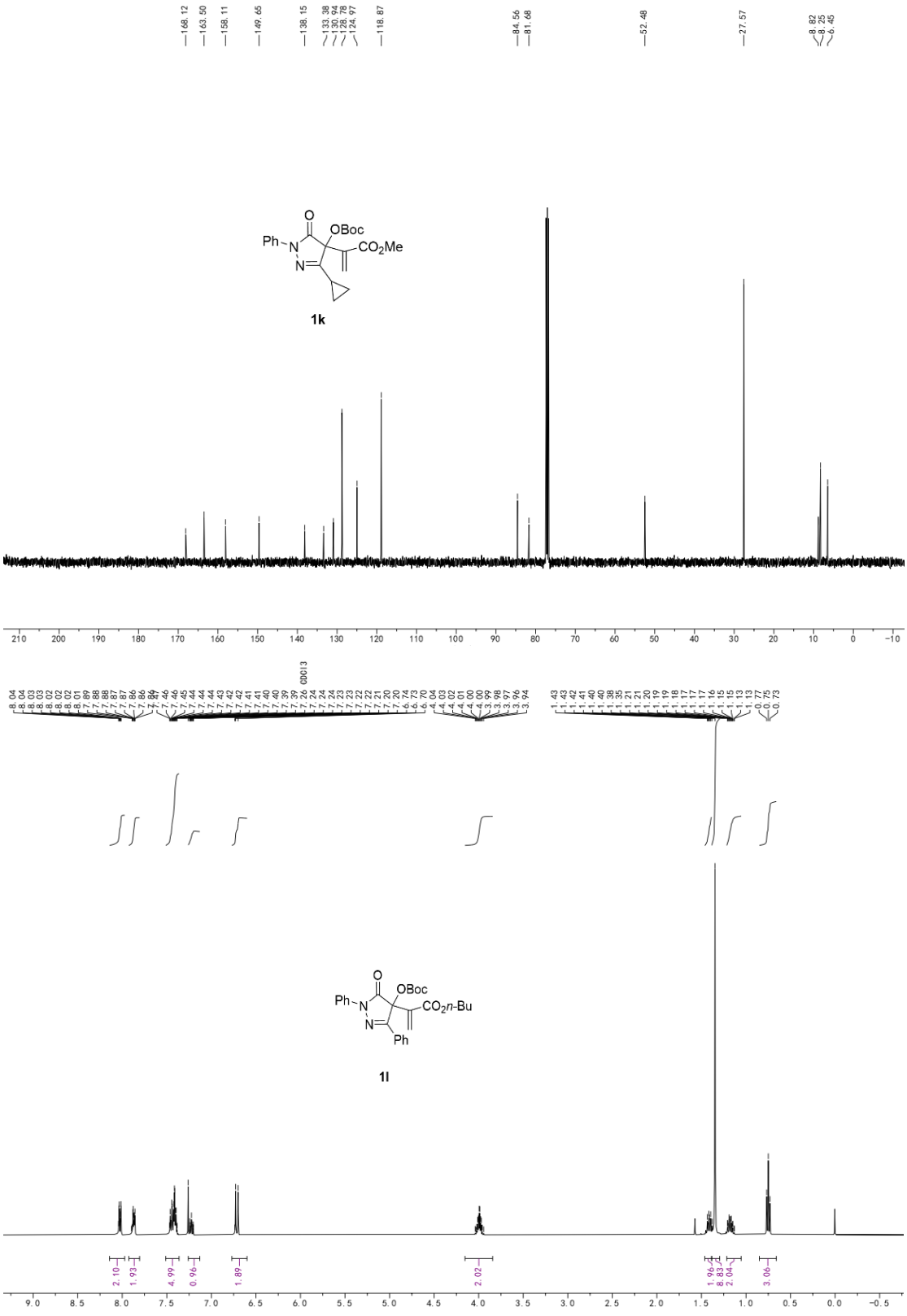

8.17
8.15
8.14
8.12
8.12
8.06
8.04
7.90
7.88
7.87
7.86
7.85
7.84
7.83
7.56
7.56
7.54
7.54
7.53
7.51
7.50
7.50
7.49
7.49
7.47
7.45
7.45
7.26
7.23
7.23
6.83
GDCl3
3.58
1.33
O
OBoc
Ph
N
N
CO2Me
1i
2.05
1.73
2.49
3.82
2.05
1.81
2.94
9.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

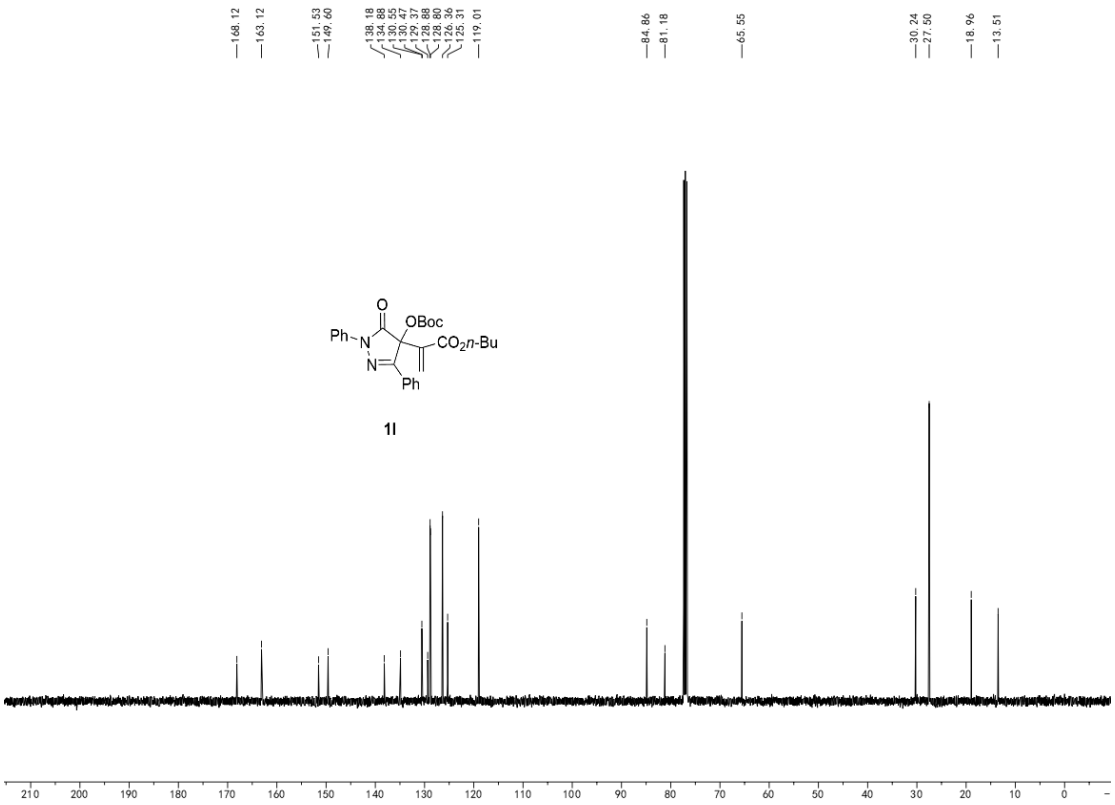

168.19
163.40
151.44
149.64
138.12
134.84
134.22
132.94
130.62
128.95
128.89
128.76
127.86
127.48
126.89
126.67
125.52
123.08
119.34
85.04
81.22
52.44
27.51
OBoc
Ph
N
N
O
CO2Me
1i


7.91
7.89
7.42
7.40
7.38
7.26
7.20
7.18
7.16
6.67
6.52
3.67
2.43
2.41
2.39
2.37
2.35
2.33
2.31
1.44
1.25
1.23
1.22
OBoc
Ph
N
N
O
CO2Me
1j
2.02
2.02
0.87
1.93
2.95
1.96
8.92
3.33

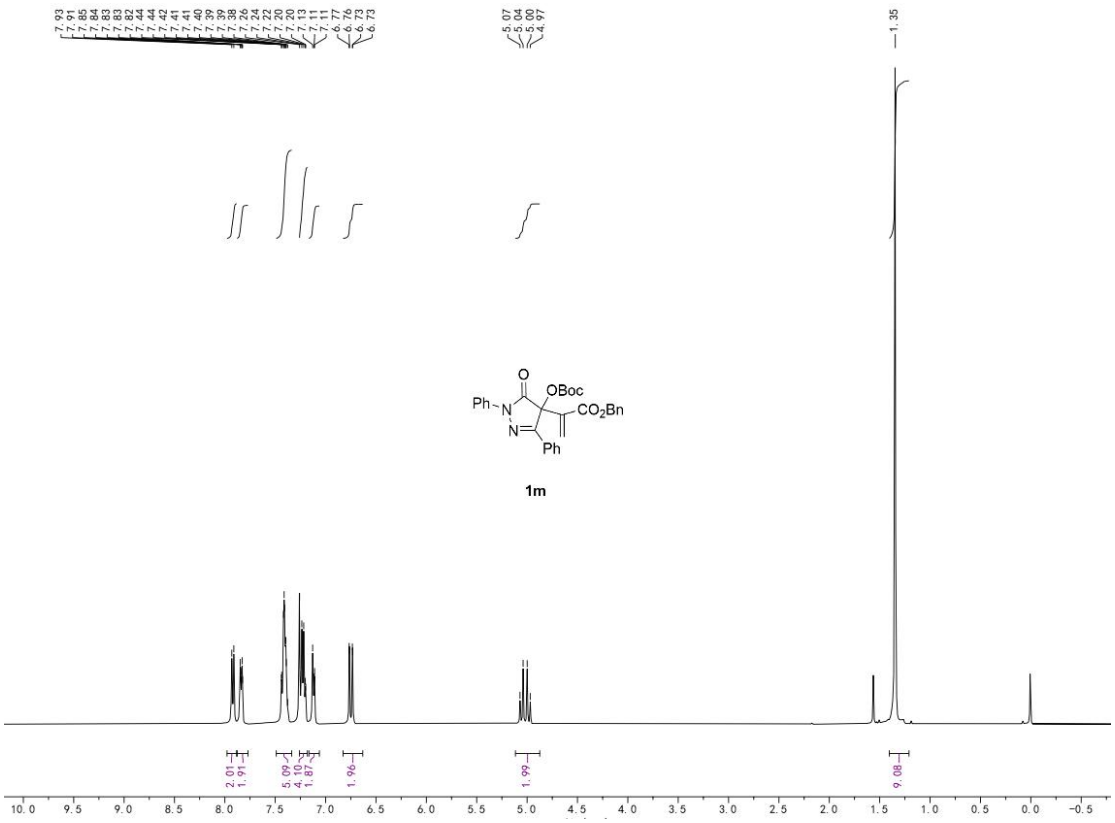

168.21
163.44
157.37
149.62
138.13
133.37
130.87
128.83
125.08
118.97
84.68
81.77
52.48
27.55
21.11
9.84
Ph
N
N
O
OBoc
CO2Me
1j


CDCl3
7.88
7.86
7.40
7.39
7.38
7.36
7.26
7.18
7.17
7.16
7.15
7.14
6.69
6.56
3.68
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.45
1.21
1.20
1.19
1.18
1.17
1.16
0.95
0.94
0.93
0.92
0.91
0.90
0.89
Ph
N
N
O
OBoc
CO2Me
1k
1.91
2.03
0.94
1.98
3.03
1.09
8.84
1.07
3.09

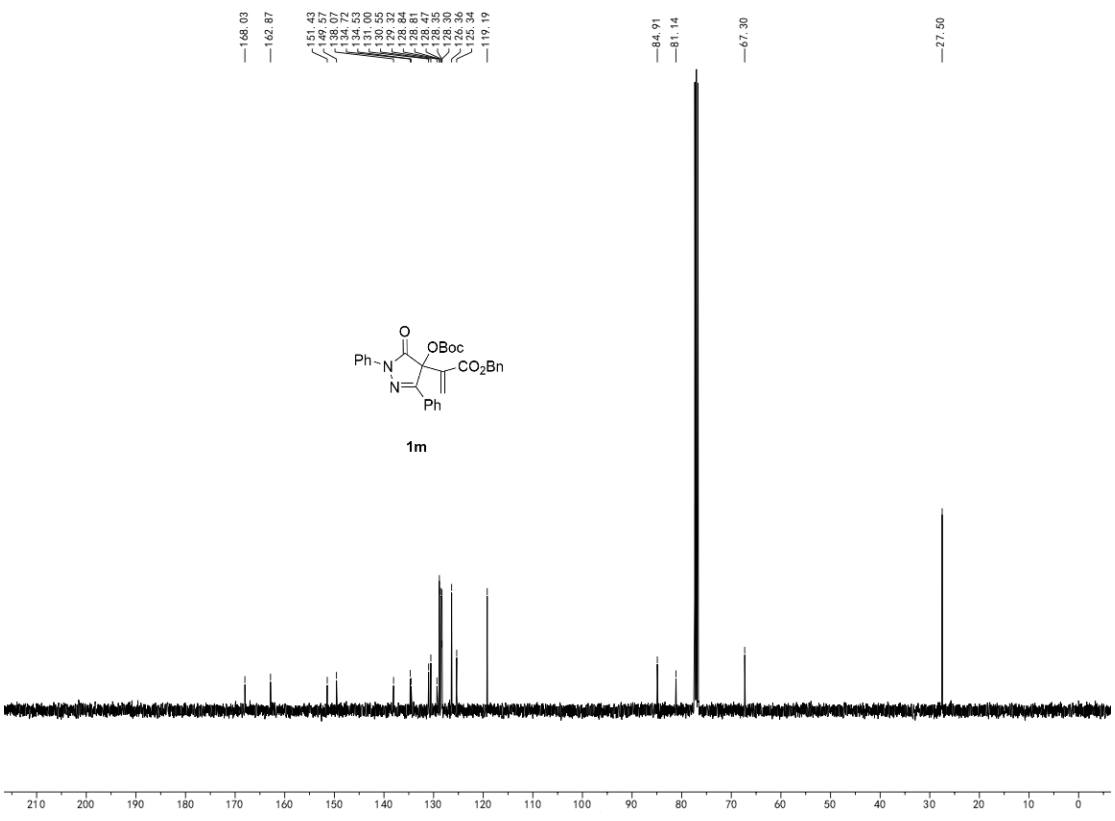

168.12
163.50
158.11
149.65
138.15
133.38
130.94
128.78
124.97
118.87
84.56
81.68
52.48
27.57
8.82
8.25
6.45
Ph
N
N
O
OBoc
CO2Me
1k
CDCl3
7.26
Ph
N
N
O
OBoc
CO2n-Bu
Ph
1l

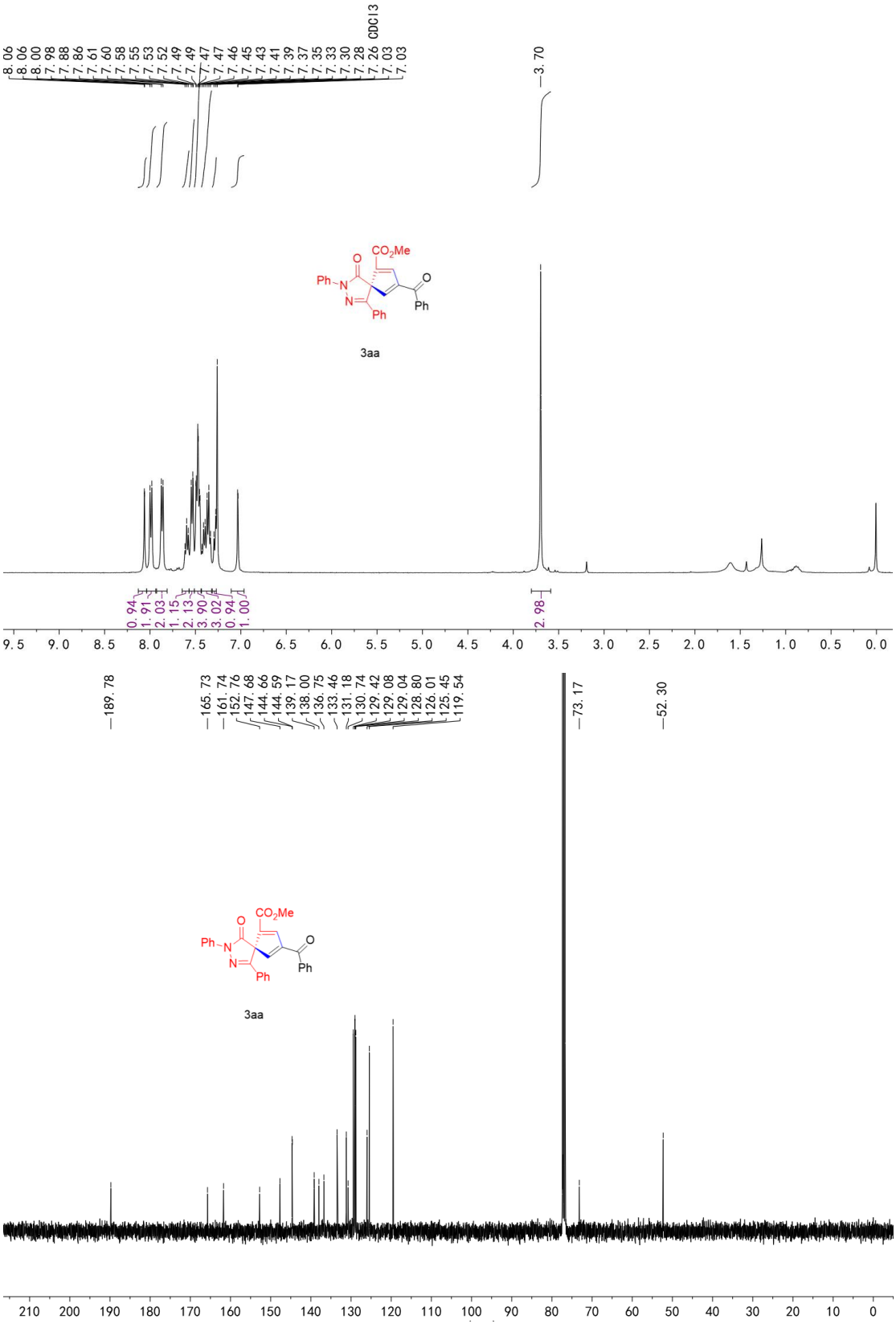

168.12
163.12
151.53
149.60
138.18
134.88
130.55
130.47
129.37
128.88
128.60
126.36
125.31
119.01
84.86
81.18
65.55
30.24
27.50
18.96
13.51
O
OBoc
Ph
N
CO2n-Bu
N
Ph

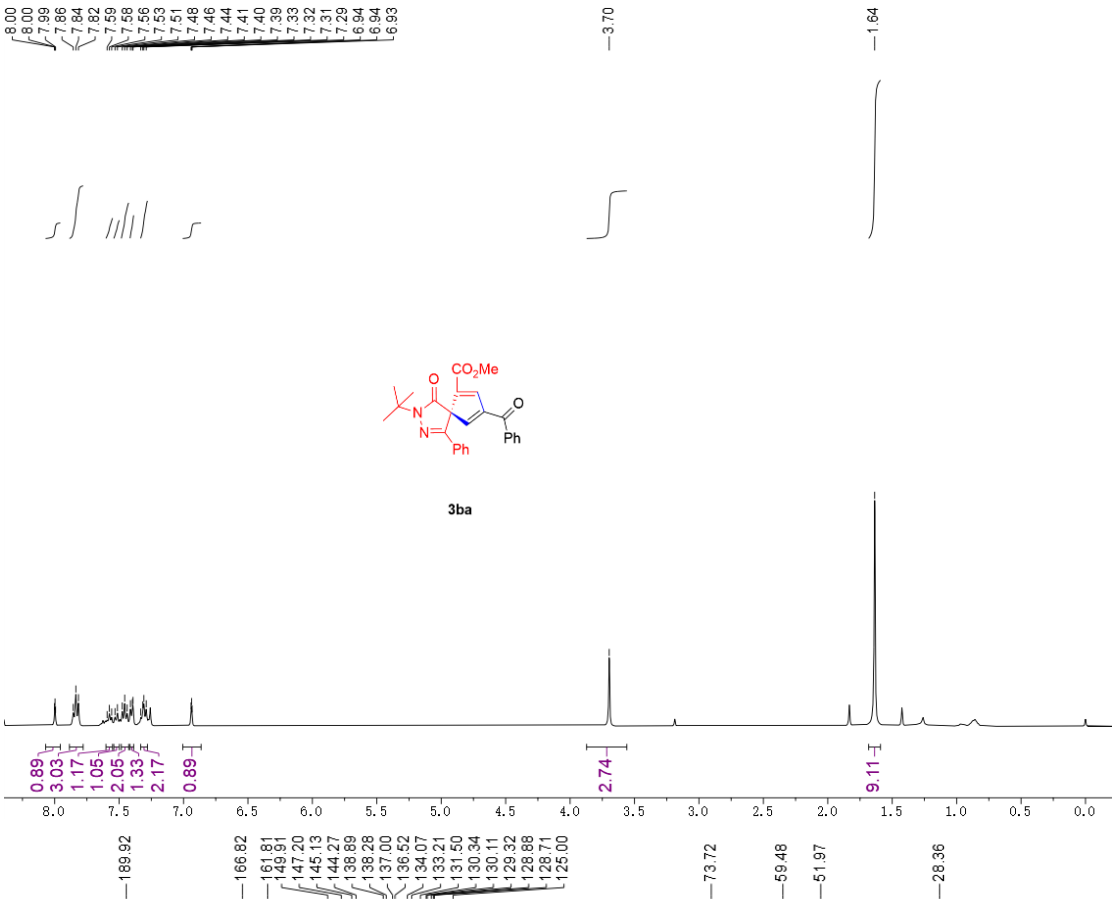
1l


7.93
7.91
7.85
7.84
7.83
7.83
7.82
7.44
7.44
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.26
7.24
7.22
7.20
7.20
7.13
7.11
7.11
6.77
6.76
6.73
6.73
5.07
5.04
5.00
4.97
1.35
O
OBoc
Ph
N
CO2Bn
N
Ph
2.01
1.91
5.09
4.10
1.87
1.96
1.99
9.08

1m

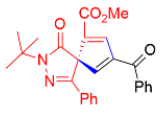

168.03
162.87
151.43
149.57
138.07
134.72
134.53
131.00
130.55
129.32
128.84
128.81
128.47
128.35
128.30
126.36
125.34
119.19
84.91
81.14
67.30
27.50
O
OBoc
Ph
N
N
CO2Bn
Ph
1m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.06
8.06
8.00
7.98
7.88
7.86
7.61
7.60
7.58
7.55
7.53
7.52
7.49
7.49
7.47
7.47
7.46
7.45
7.43
7.41
7.39
7.37
7.35
7.33
7.30
7.28
CDCl3
7.26
7.03
7.03
3.70
CO2Me
Ph
N
N
O
O
Ph
Ph
3aa
0.94
1.91
2.03
1.15
2.13
3.90
3.02
0.94
1.00
2.98
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
189.78
165.73
161.74
152.76
147.68
144.66
144.59
139.17
138.00
136.75
133.46
131.18
130.74
129.42
129.08
129.04
128.80
126.01
125.45
119.54
73.17
52.30
CO2Me
Ph
N
N
O
O
Ph
Ph
3aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

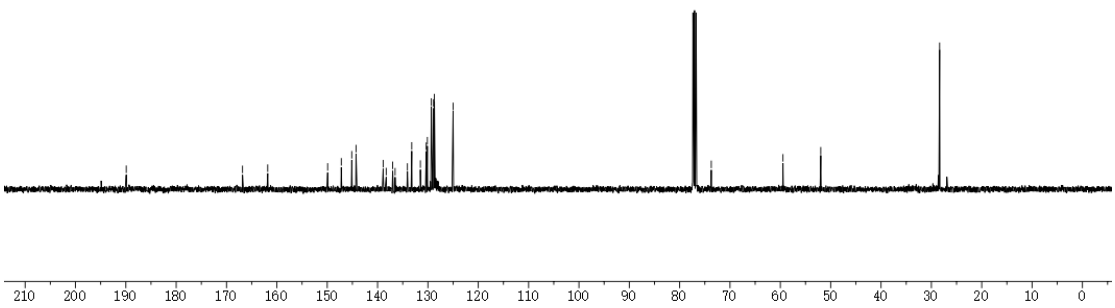

8.00
8.00
7.99
7.86
7.84
7.82
7.59
7.58
7.56
7.53
7.51
7.48
7.46
7.44
7.41
7.40
7.39
7.33
7.32
7.31
7.29
6.94
6.93
3.70
1.64
CO2Me
O
N
N
O
Ph
Ph
0.89
3.03
1.17
1.05
2.05
1.33
2.17
0.89
2.74
9.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

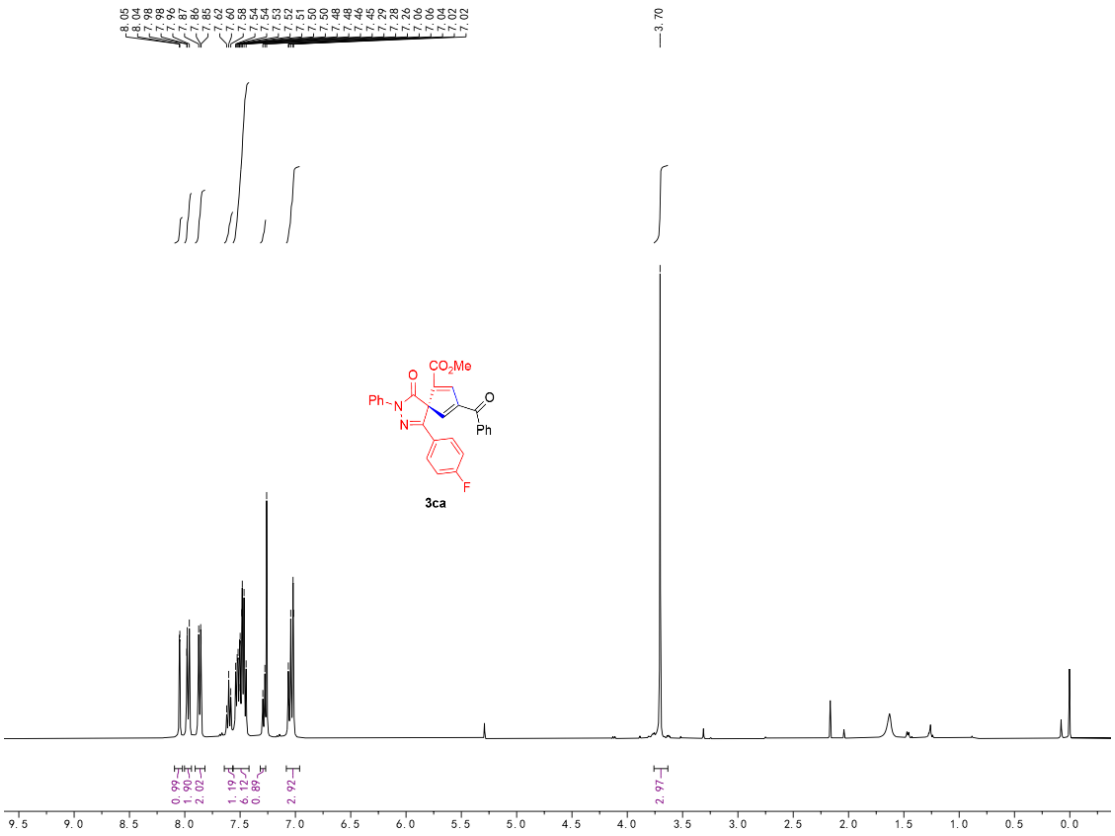
3ba

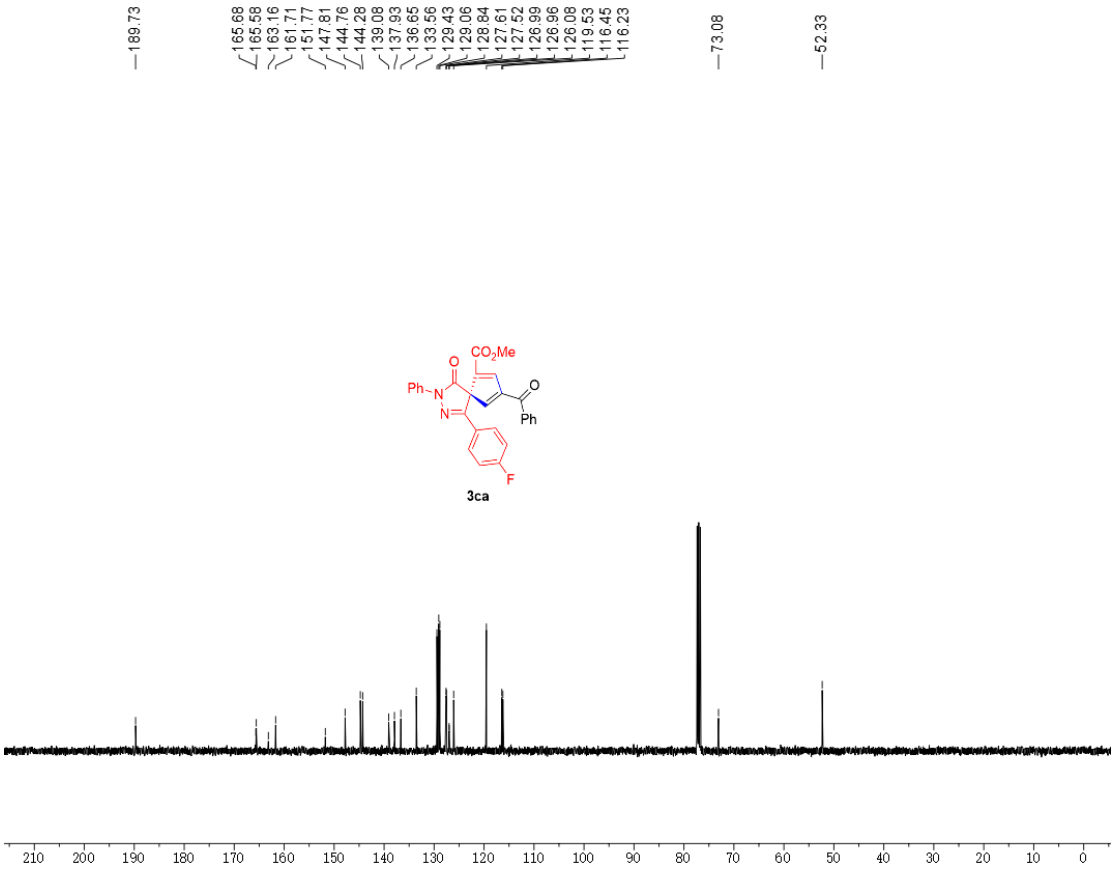
189.92
166.82
161.81
149.91
147.20
145.13
144.27
138.89
138.28
137.00
136.52
134.07
133.21
131.50
130.34
130.11
129.32
128.88
128.71
125.00
73.72
59.48
51.97
28.36

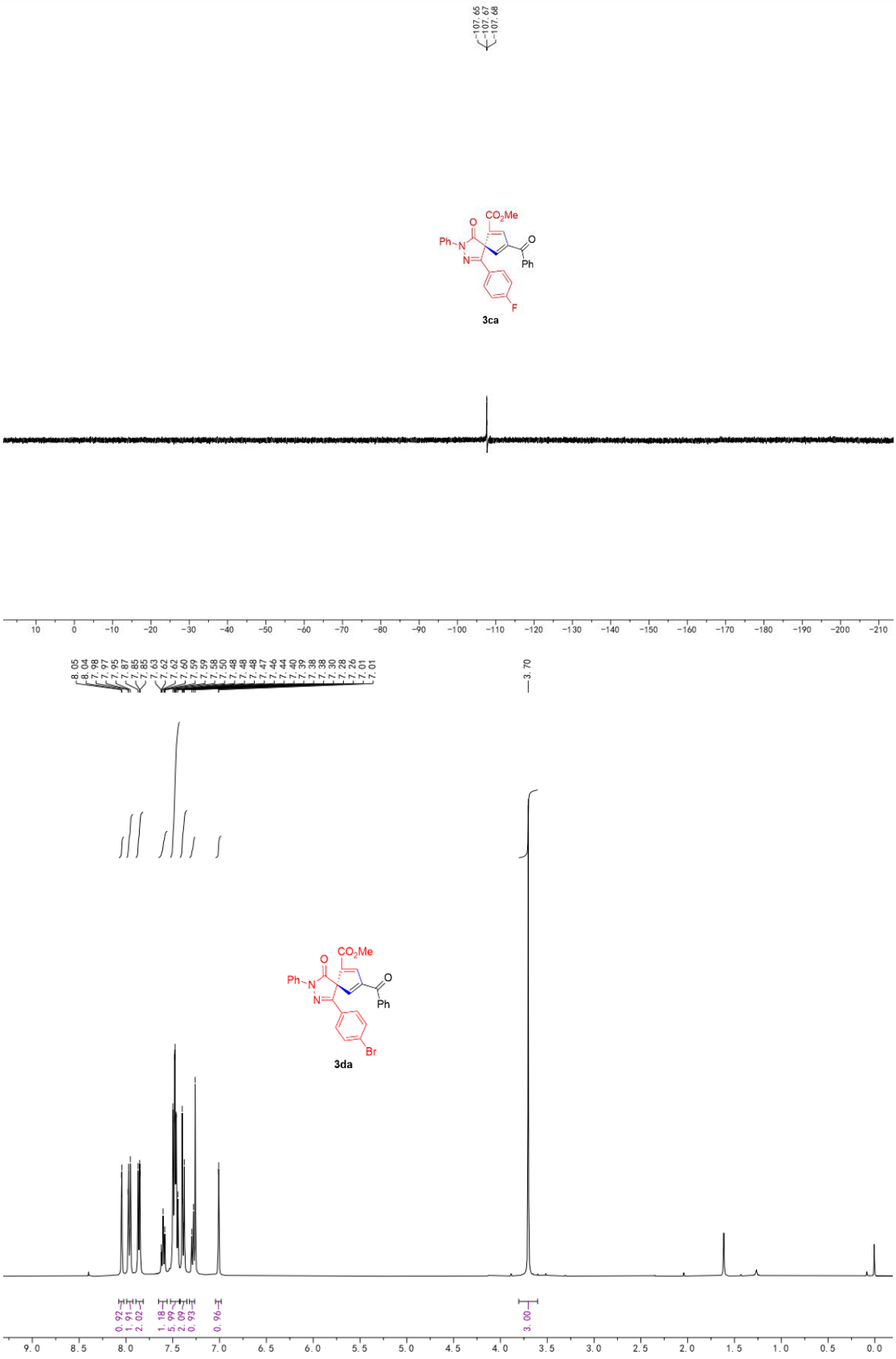

CO2Me
O
N
N
O
Ph
Ph

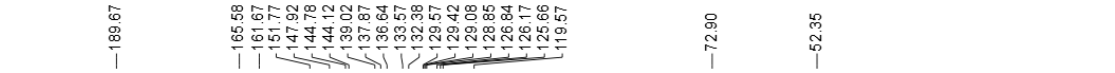
3ba

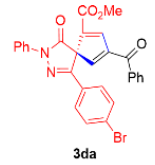

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.05
8.04
7.98
7.98
7.96
7.87
7.86
7.85
7.62
7.60
7.58
7.54
7.53
7.52
7.51
7.50
7.50
7.48
7.48
7.46
7.45
7.29
7.28
7.26
7.06
7.04
7.02
7.02
3.70
CO2Me
O
Ph
N
N
O
Ph
F
3ca
0.99
1.90
2.02
1.19
6.12
0.89
2.92
2.97
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

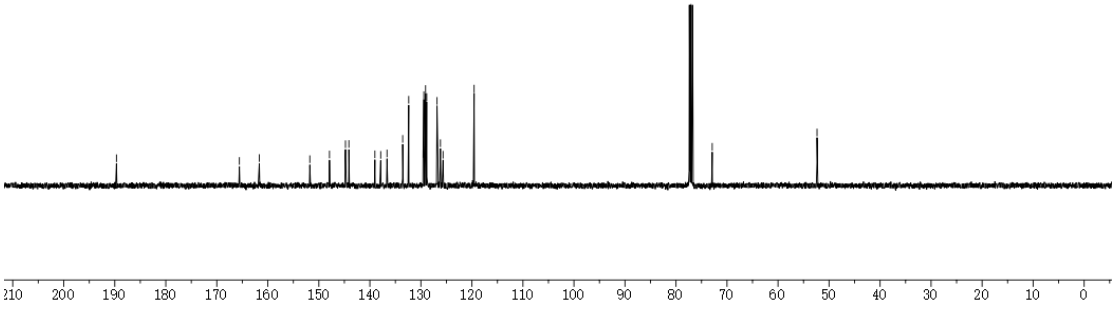

189.73
165.68
165.58
163.16
161.71
151.77
147.81
144.76
144.28
139.08
137.93
136.65
133.56
129.43
129.06
128.84
127.61
127.52
126.99
126.96
126.08
119.53
116.45
116.23
73.08
52.33
CO2Me
O
Ph
N
N
O
Ph
F
3ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


-107.65
-107.67
-107.68
CO2Me
O
Ph
N
O
Ph
F
3ca
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
8.05
8.04
7.98
7.97
7.95
7.87
7.85
7.63
7.62
7.60
7.59
7.58
7.50
7.48
7.48
7.48
7.47
7.46
7.44
7.44
7.39
7.38
7.38
7.30
7.28
7.26
7.01
7.01
3.70
CO2Me
O
Ph
N
O
Ph
Br
3da
0.92
1.91
2.02
1.18
5.99
2.03
0.96
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

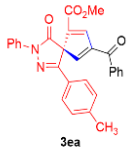

189.67
165.58
161.67
151.77
147.92
144.78
144.12
139.02
137.87
136.64
133.57
132.38
129.57
129.42
129.08
128.85
126.84
126.17
125.66
119.57
72.90
52.35


CO2Me
O
Ph
N
N
O
Ph
Br

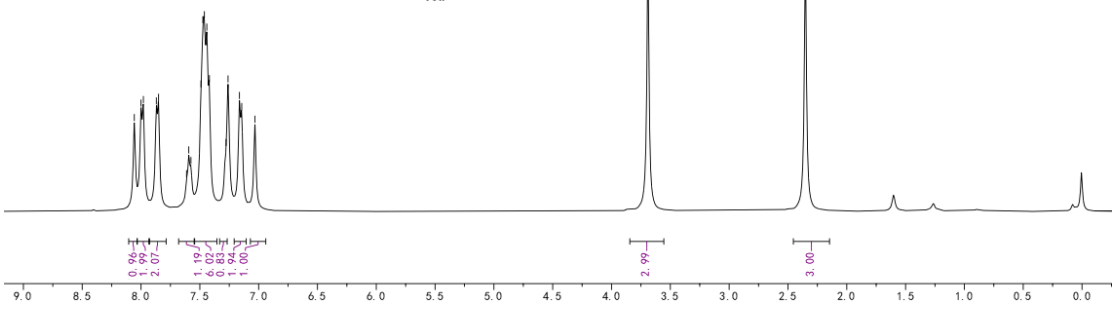
3da

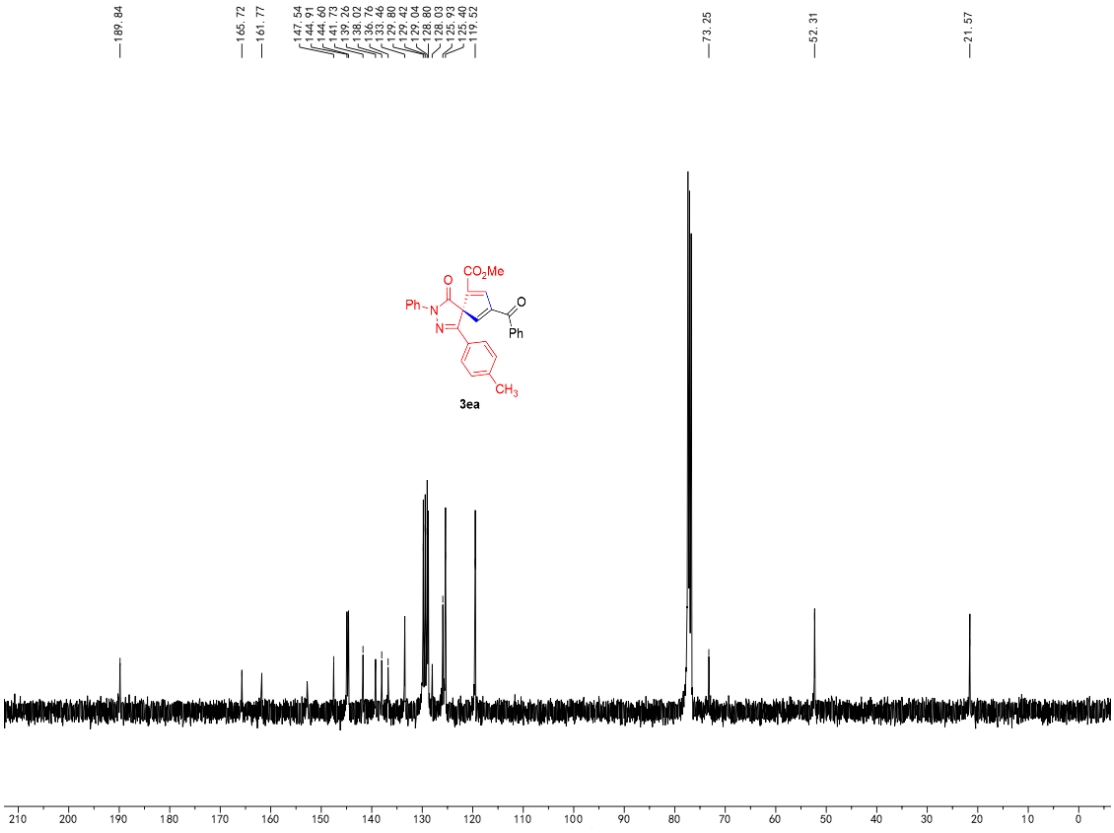

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

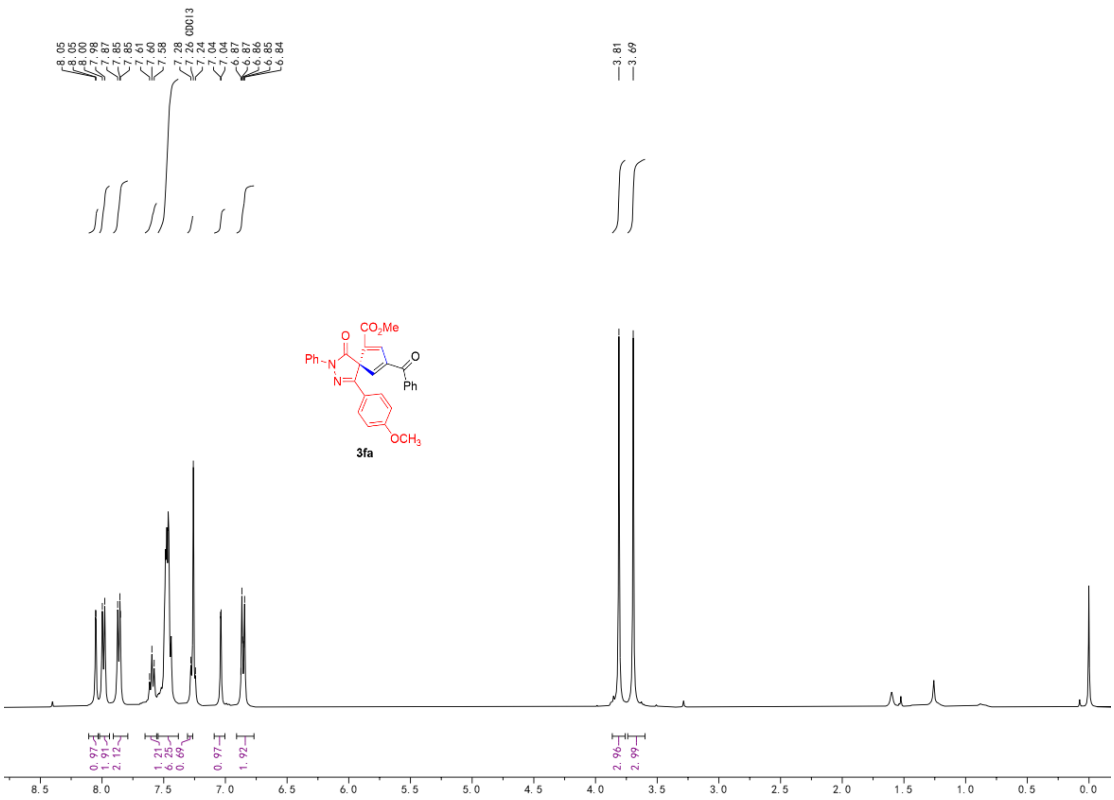

8.06
8.00
7.98
7.87
7.85
7.61
7.59
7.58
7.49
7.47
7.46
7.44
7.42
7.28
7.26
7.16
7.14
7.03
3.69
2.35

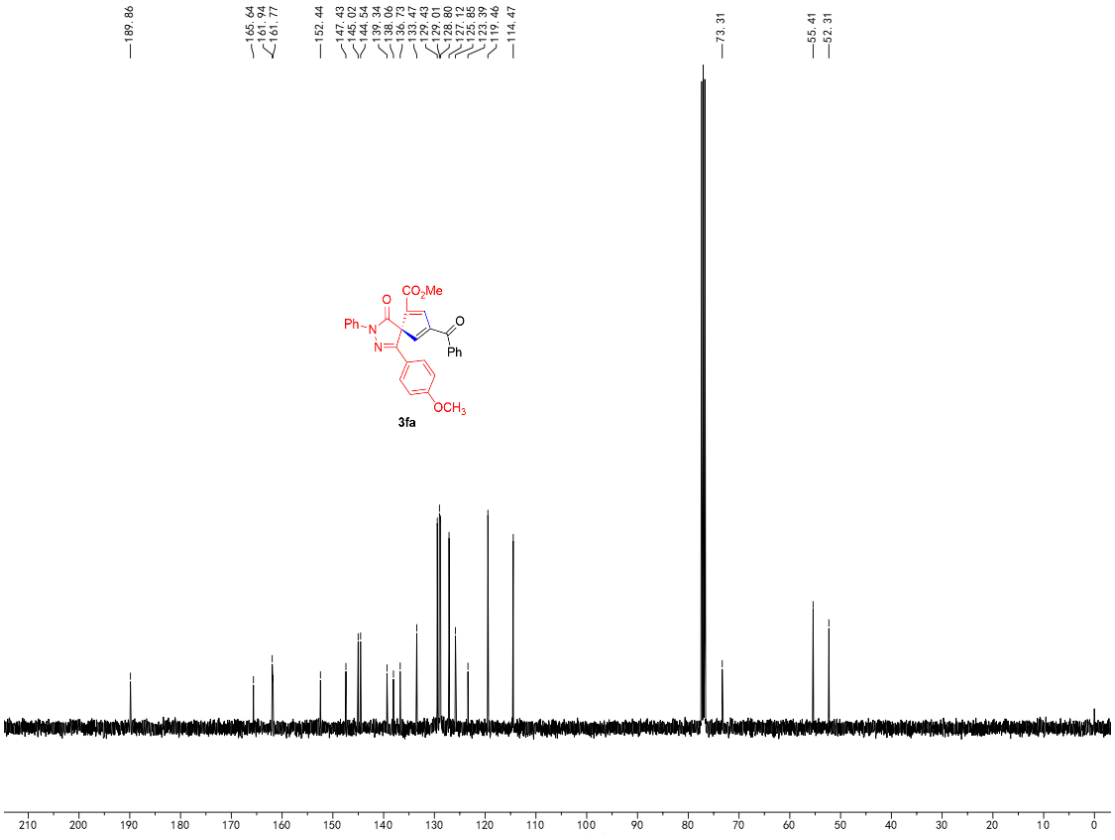

CO2Me
O
Ph
N
N
O
Ph
CH3

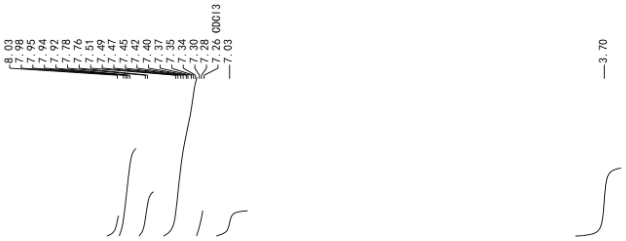
3ea

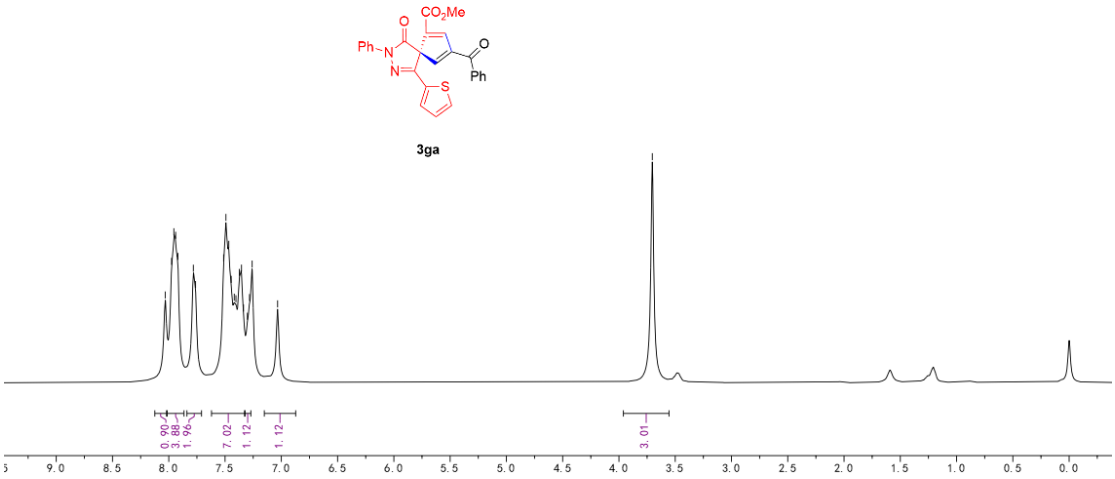

0.96
1.09
2.07
1.19
1.02
0.83
1.94
1.00
2.99
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

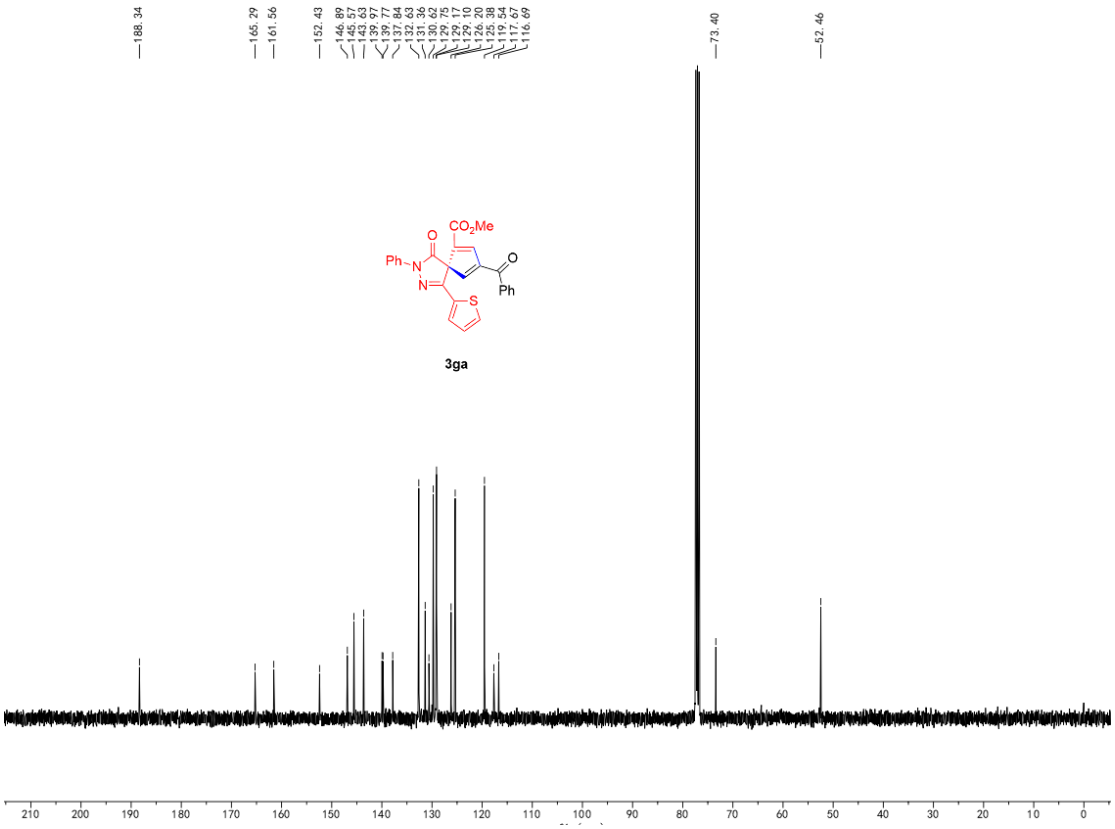

189.84
165.72
161.77
147.54
144.91
144.60
141.73
139.26
138.02
136.76
133.46
129.80
129.42
129.04
128.80
128.03
125.93
125.40
119.52
73.25
52.31
21.57
CO2Me
Ph
O
N
O
Ph
CH3
3ea

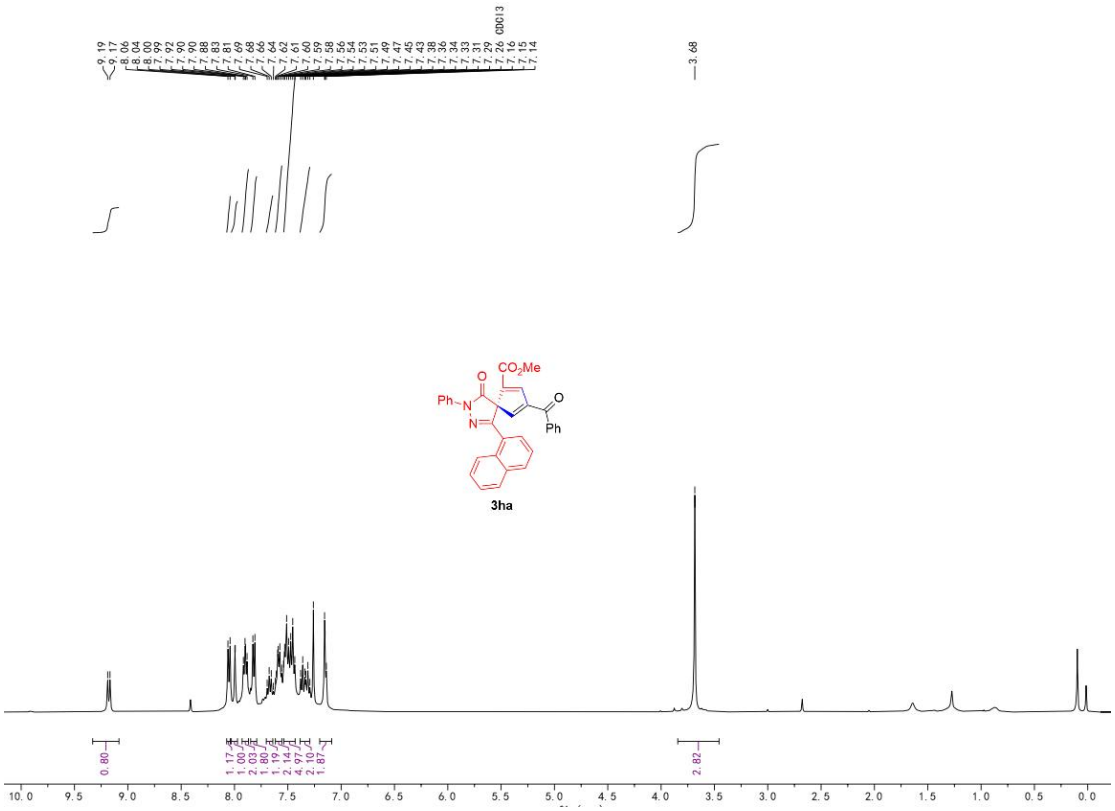

8.05
8.05
8.00
7.98
7.87
7.85
7.61
7.60
7.58
7.28
CDCl3
7.26
7.24
7.04
6.87
6.86
6.85
6.84
3.81
3.69
CO2Me
Ph
O
N
O
Ph
OCH3
3fa
0.97
1.91
2.12
1.21
1.28
0.69
0.97
1.92
2.96
2.99

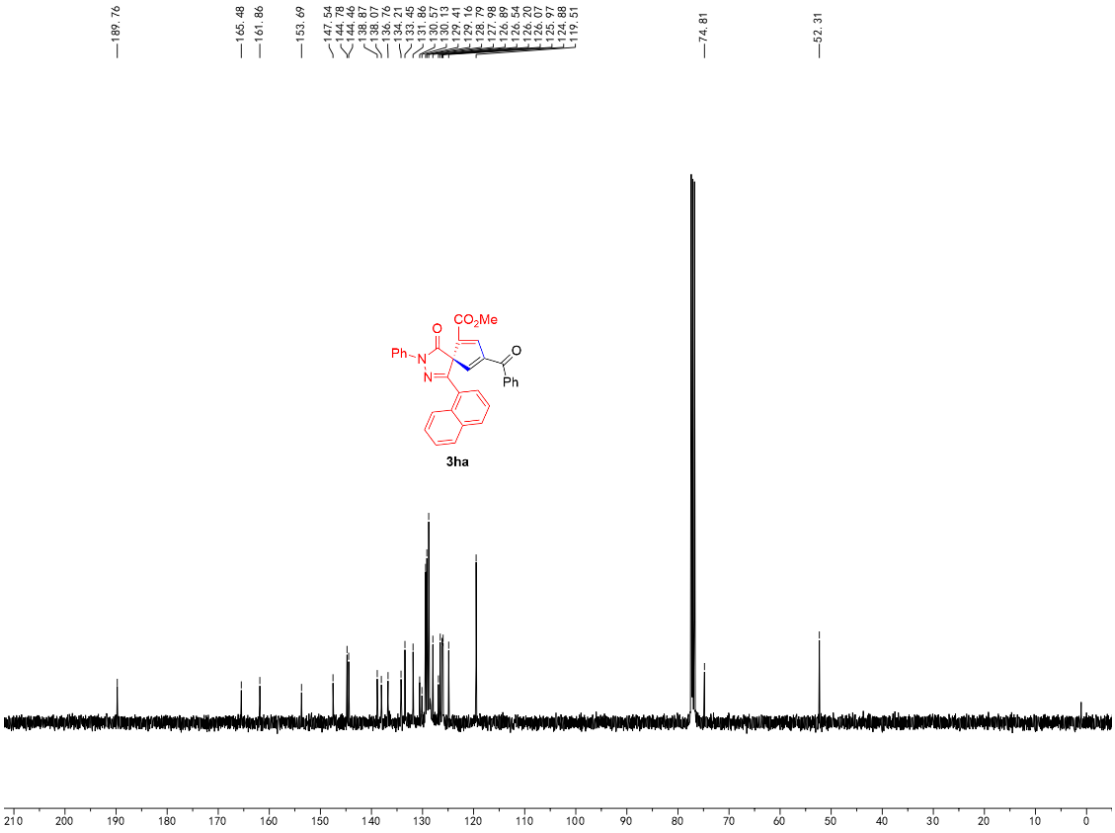

189.86
165.64
161.94
161.77
152.44
147.43
145.02
144.54
139.34
138.06
136.73
133.47
129.43
129.01
128.80
127.12
125.85
123.39
119.46
114.47
73.31
55.41
52.31
CO2Me
Ph
N
O
Ph
OCH3
3fa

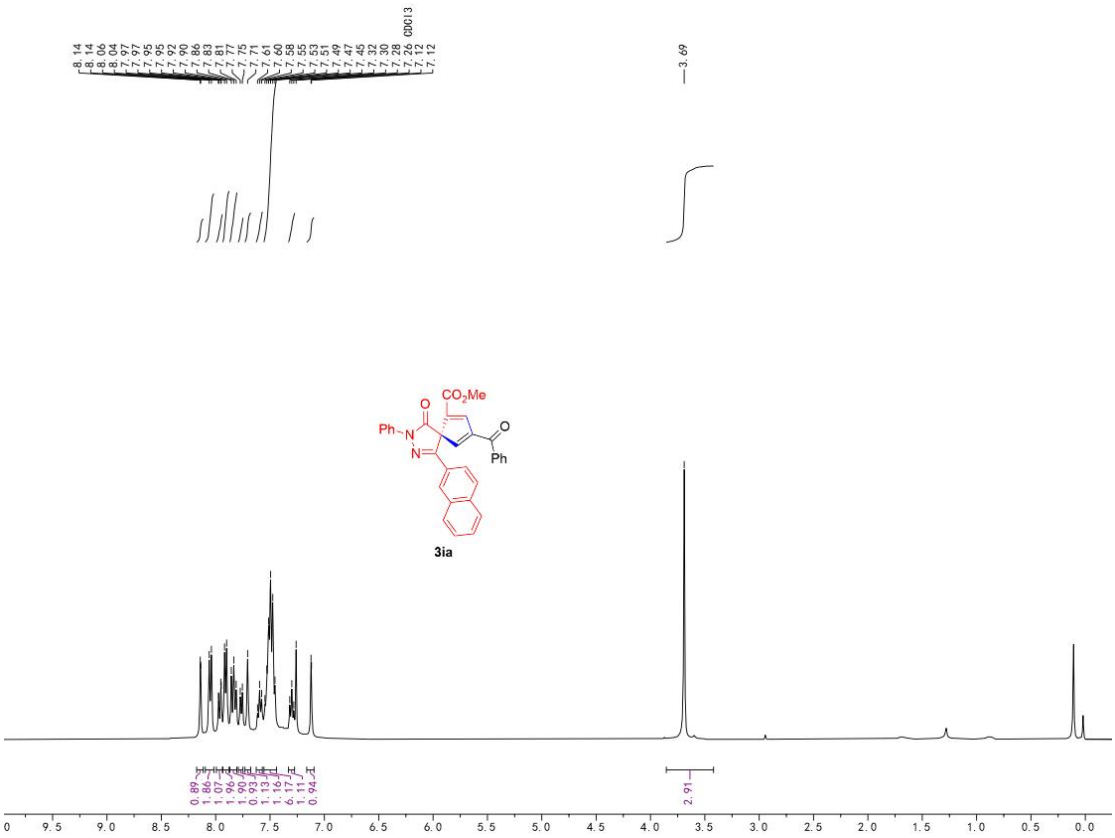

8.03
7.98
7.95
7.94
7.92
7.78
7.76
7.51
7.49
7.47
7.45
7.42
7.40
7.37
7.35
7.34
7.30
7.28
7.26
CDCl3
7.03
3.70

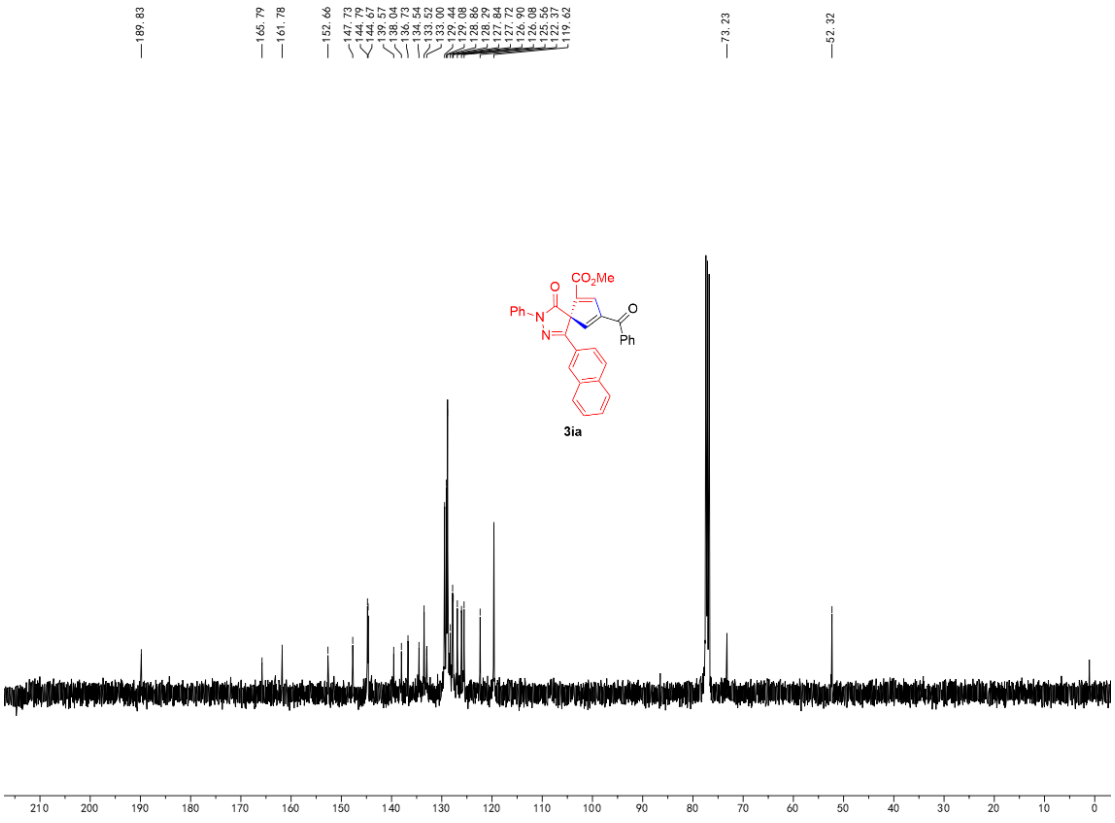

CO2Me
Ph
N
O
Ph
S
3ga
0.90
3.88
1.96
7.02
1.12
1.12
3.01


188.34
165.29
161.56
152.43
146.89
145.57
143.63
139.97
139.77
137.84
132.63
131.56
130.62
129.75
129.17
129.10
126.20
125.88
119.54
117.67
116.69
73.40
52.46
CO2Me
Ph
N
O
O
Ph
S
3ga

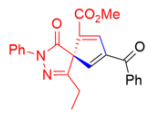

9.19
9.17
8.06
8.04
8.00
7.99
7.92
7.90
7.90
7.88
7.83
7.81
7.68
7.66
7.64
7.62
7.61
7.60
7.59
7.58
7.56
7.54
7.53
7.51
7.49
7.47
7.45
7.43
7.38
7.36
7.34
7.33
7.31
7.29
7.26
CDCl3
7.16
7.15
7.14
3.68
CO2Me
Ph
N
O
O
Ph
3ha
0.80
1.17
1.09
1.00
1.80
1.19
2.14
4.97
1.10
2.87
2.82

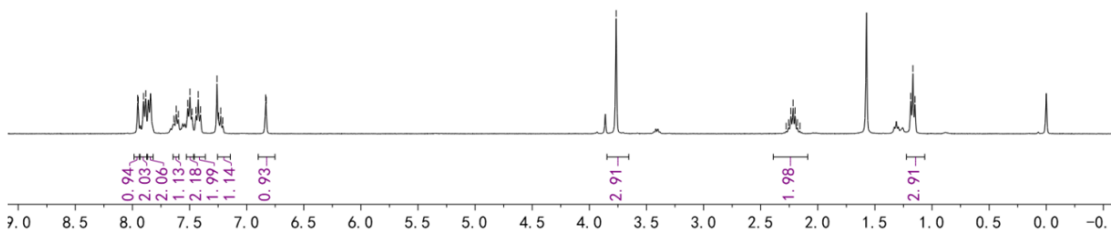

189.76
165.48
161.86
153.69
147.54
144.78
144.46
138.87
138.07
136.76
134.21
133.45
131.86
131.67
130.13
129.41
129.16
128.79
127.88
126.89
126.54
126.20
126.07
125.97
124.68
119.51
74.81
52.31
CO2Me
Ph
N
O
Ph
3ha

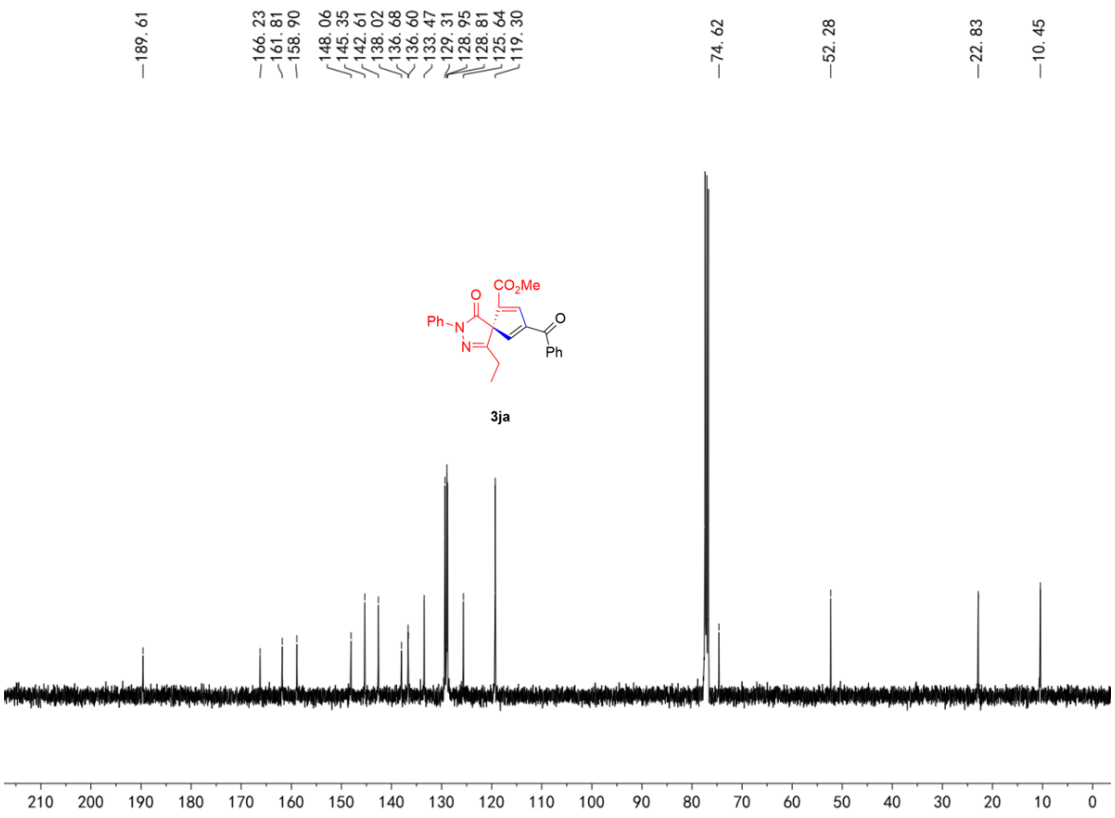

CDCl3
8.14
8.14
8.06
8.04
7.97
7.97
7.95
7.92
7.90
7.86
7.83
7.81
7.77
7.75
7.71
7.61
7.60
7.58
7.55
7.53
7.51
7.49
7.47
7.45
7.32
7.30
7.28
7.16
7.12
7.12
3.69
CO2Me
Ph
N
O
Ph
3ia
0.89
1.86
1.07
1.96
1.90
0.93
1.13
1.16
6.17
1.11
0.94
2.91

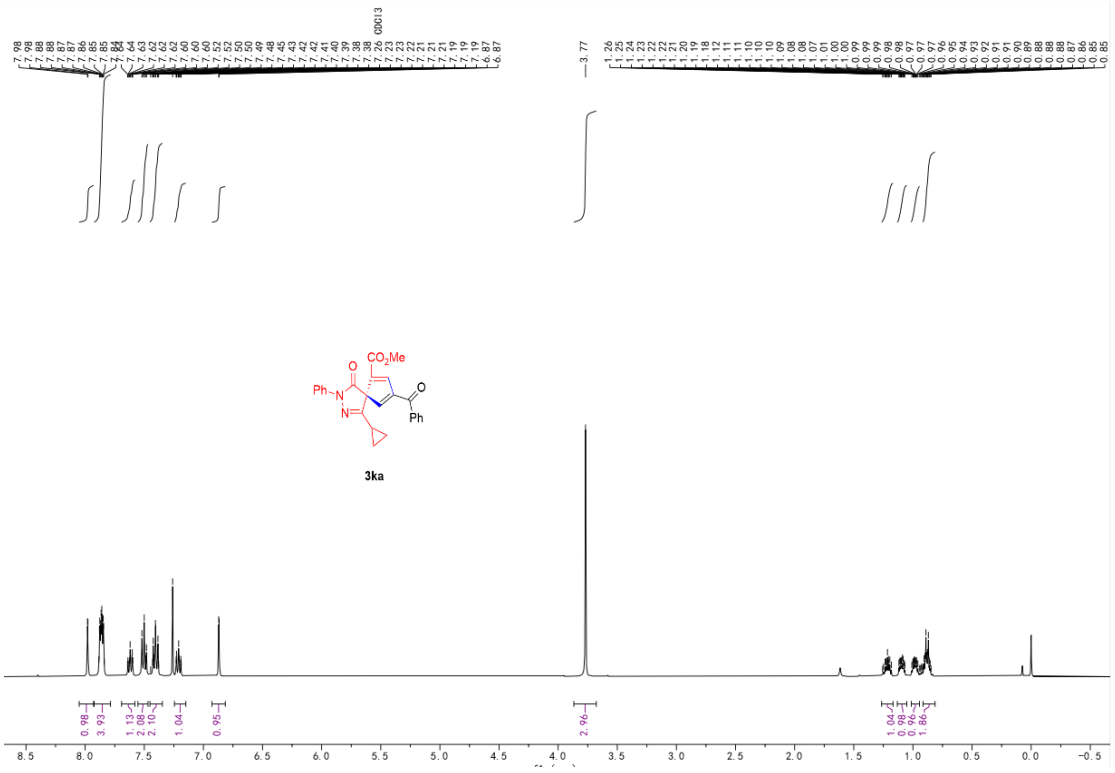

189.83
165.79
161.78
152.66
147.73
144.79
144.67
139.57
138.04
136.73
134.54
133.52
133.00
129.44
129.08
128.86
128.29
127.84
127.72
126.90
126.08
125.56
122.37
119.62
73.23
52.32
CO2Me
Ph
O
N
O
Ph
3ia

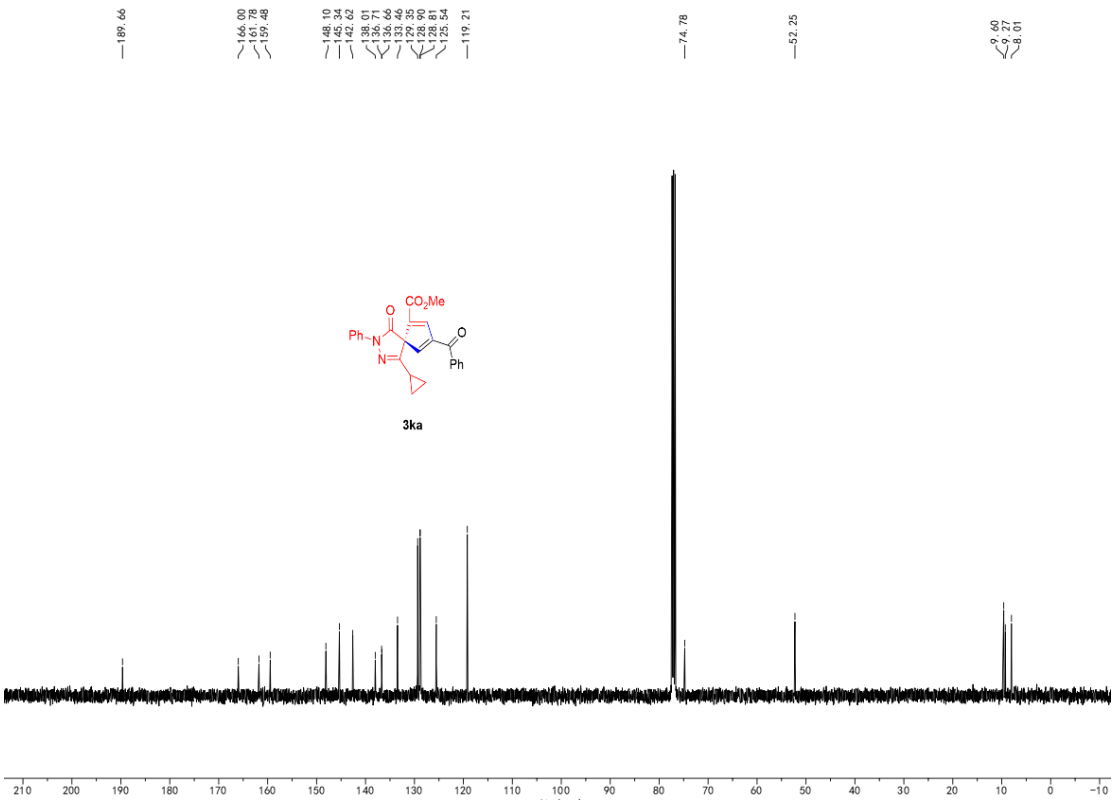

7.95
7.95
7.90
7.88
7.62
7.60
7.52
7.50
7.48
7.44
7.42
7.40
7.26
7.23
6.83
6.83
3.77
2.28
2.26
2.24
2.22
2.20
2.18
2.16
1.19
1.17
1.15

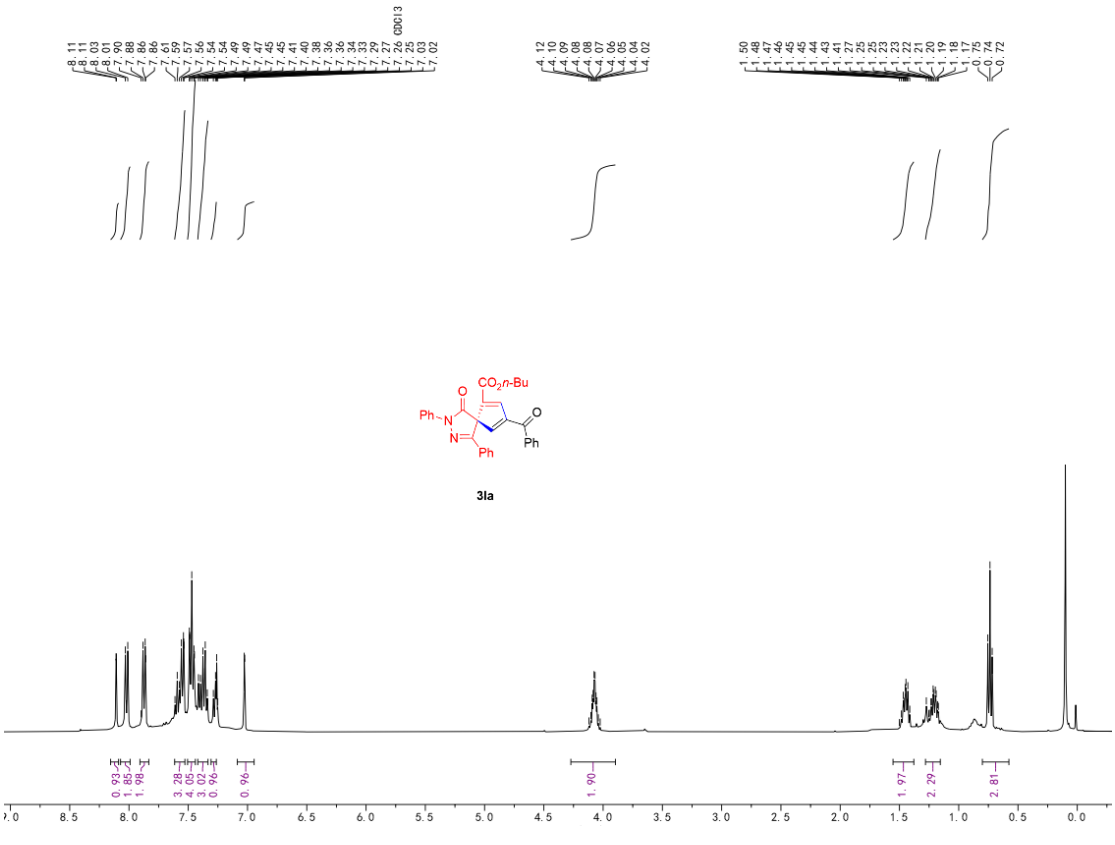

CO2Me
Ph
O
N
O
Ph
3ja

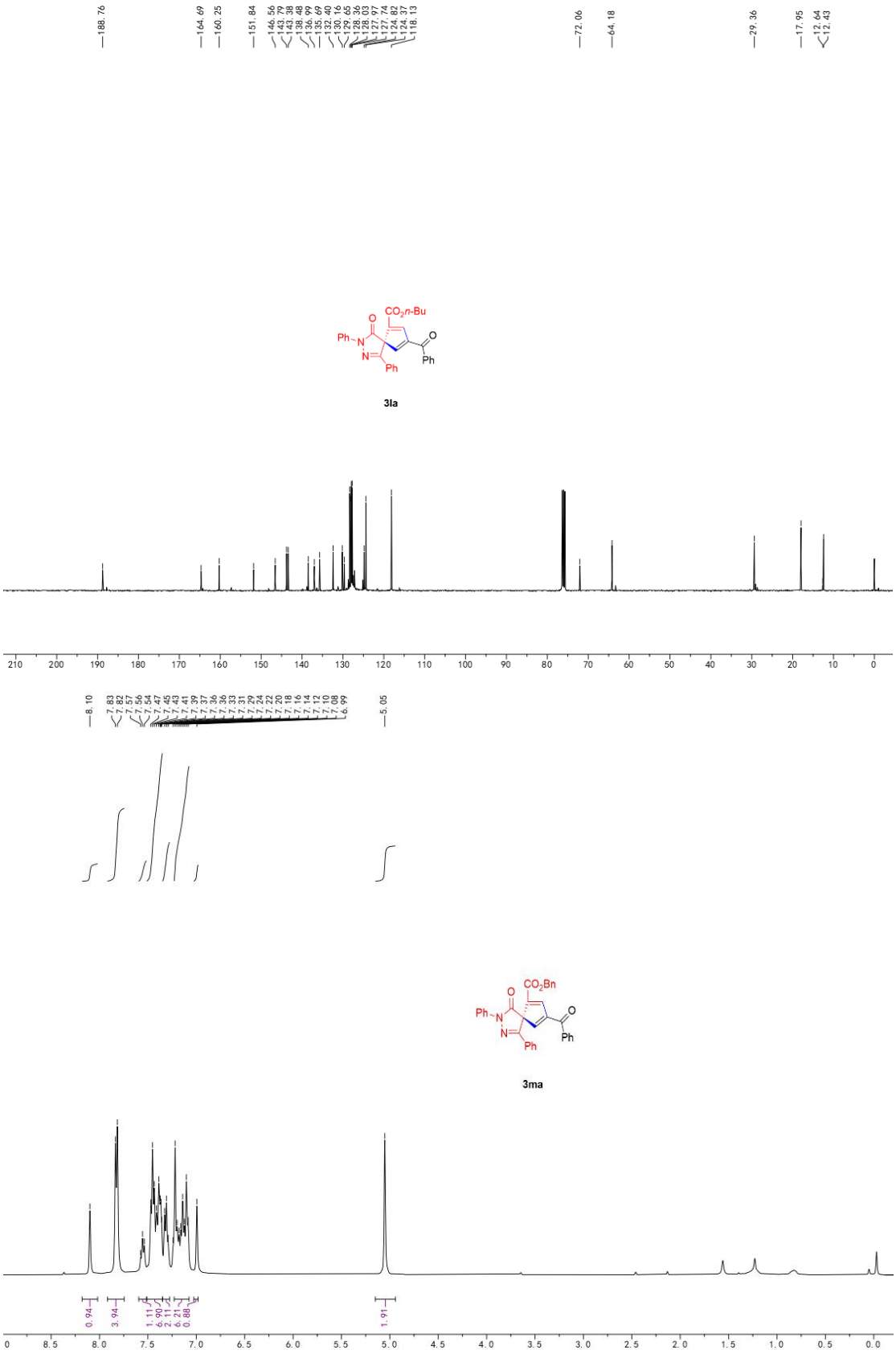

0.94
2.03
2.06
1.13
2.18
1.99
1.14
0.93
2.91
1.98
2.91

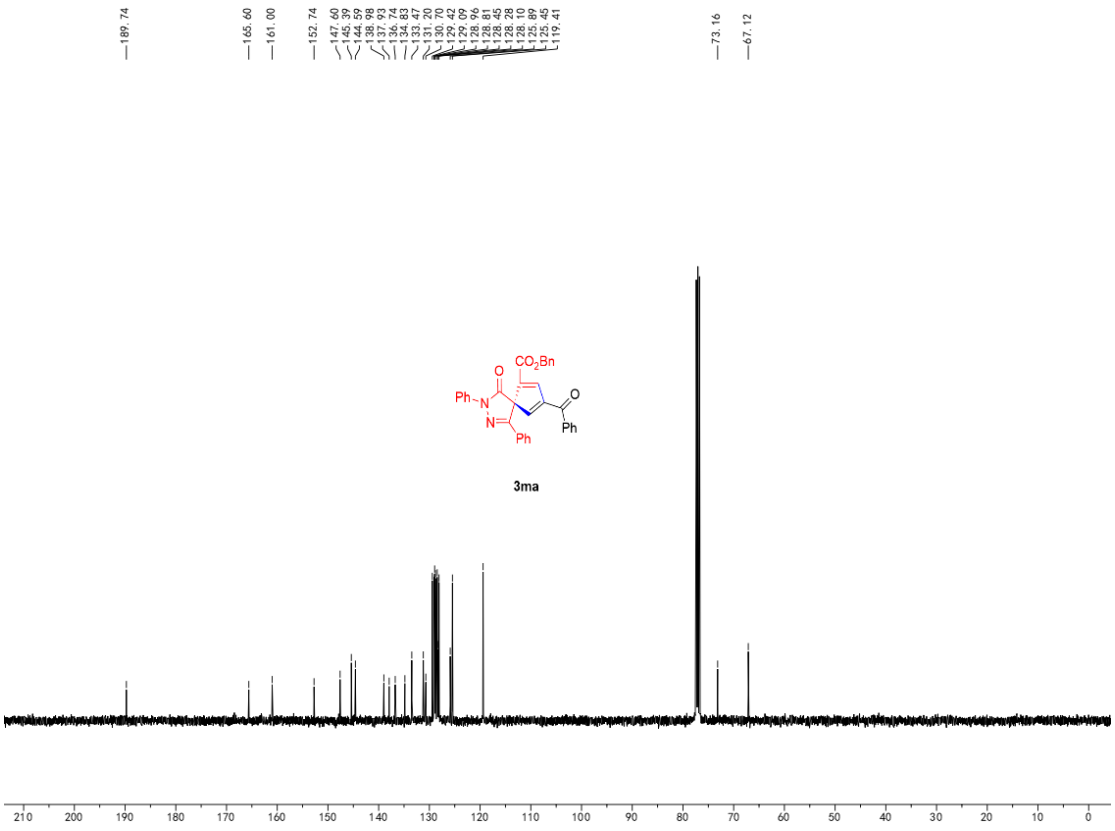

189.61
166.23
161.81
158.90
148.06
145.35
142.61
138.02
136.68
136.60
133.47
129.31
128.95
128.81
125.64
119.30
74.62
52.28
22.83
10.45
CO2Me
Ph
N
O
O
Ph
3ja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

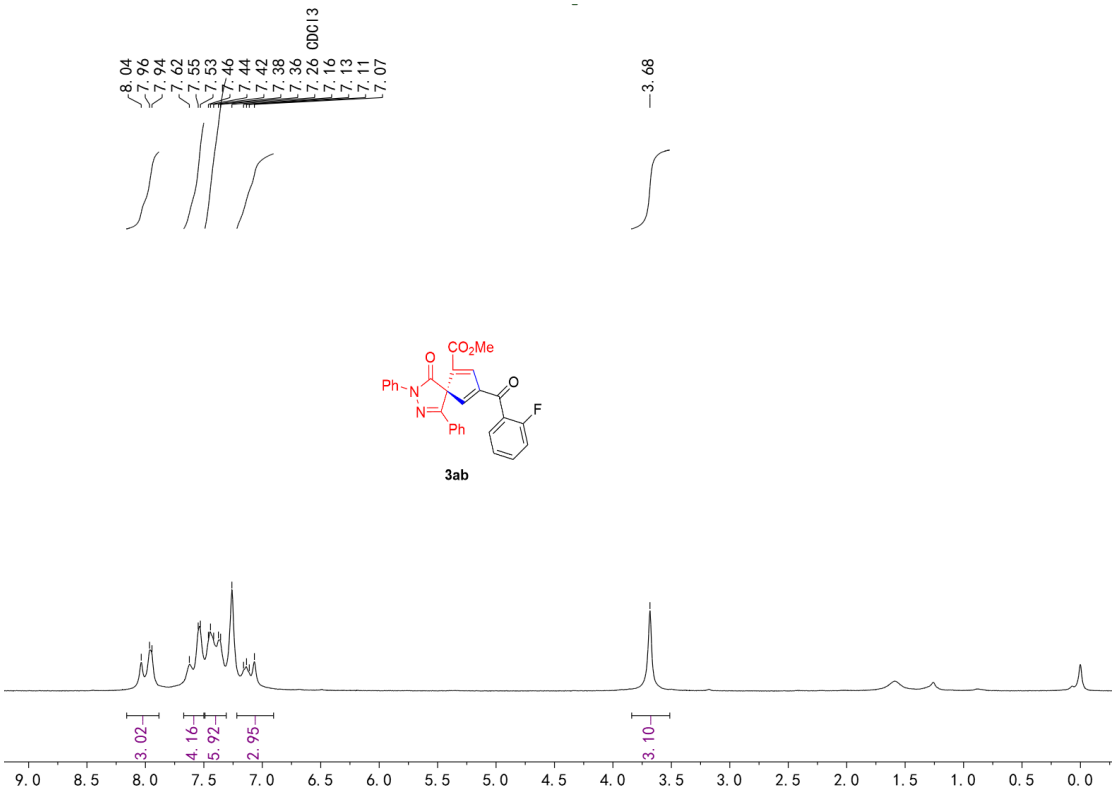

CDCl3
3.77
CO2Me
Ph
N
O
O
Ph
3ka
0.98
3.93
1.13
1.08
2.10
1.04
0.95
2.96
1.04
0.98
0.96
1.86
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

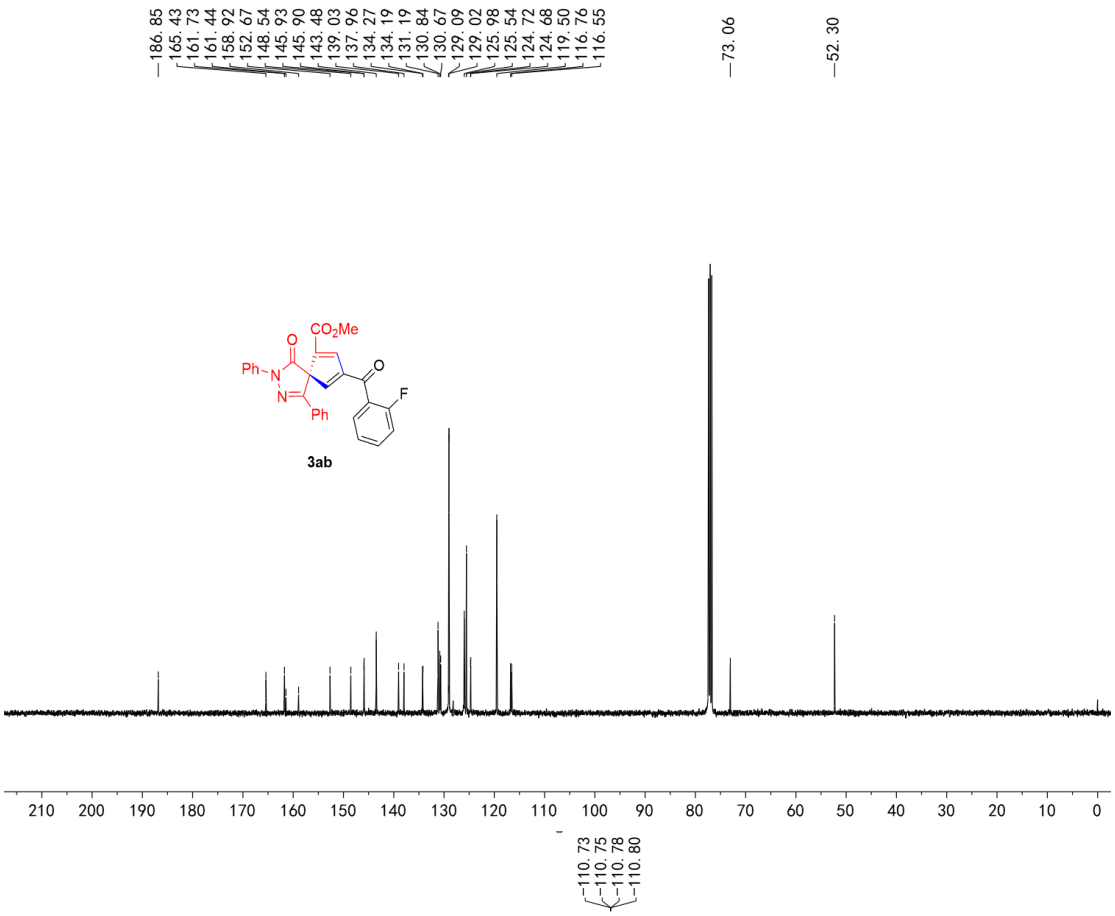

189.66
166.00
161.78
159.48
148.10
145.34
142.62
138.01
136.71
136.66
133.46
129.95
129.60
128.81
125.54
119.21
74.78
52.25
9.60
9.27
8.01
CO2Me
Ph
O
N
O
Ph
3ka

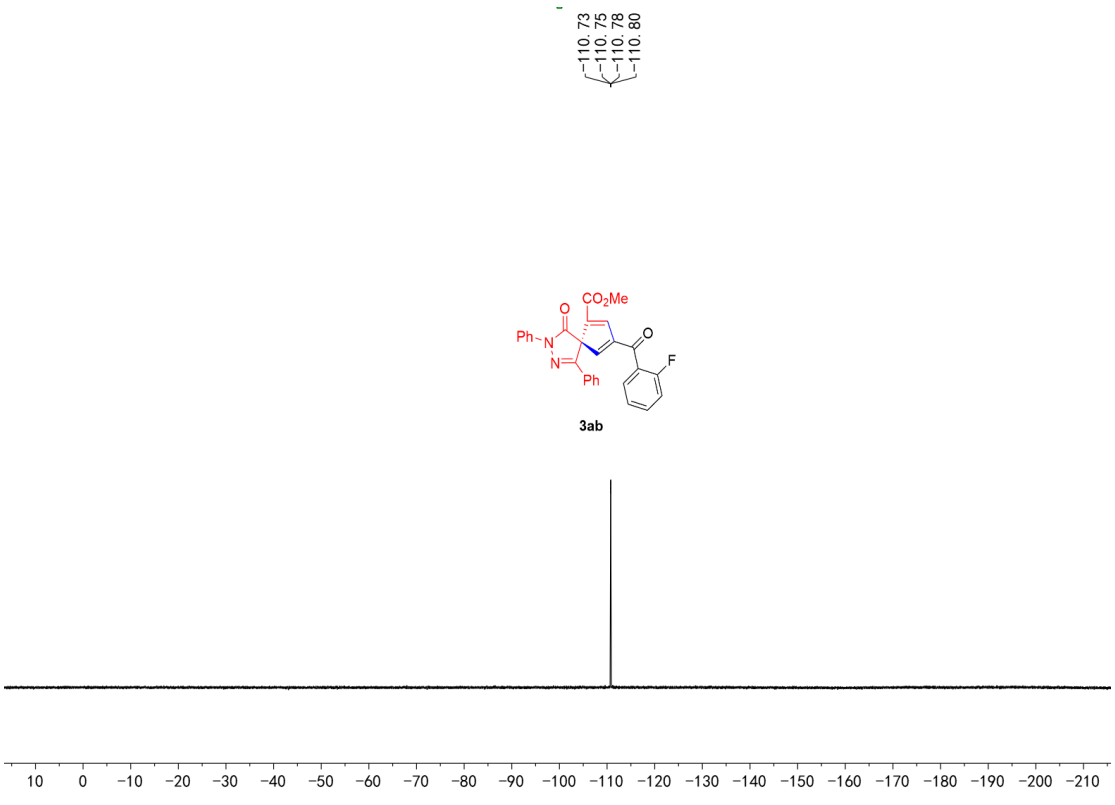

CDCl3
CO2n-Bu
Ph
O
N
O
Ph
Ph
3la

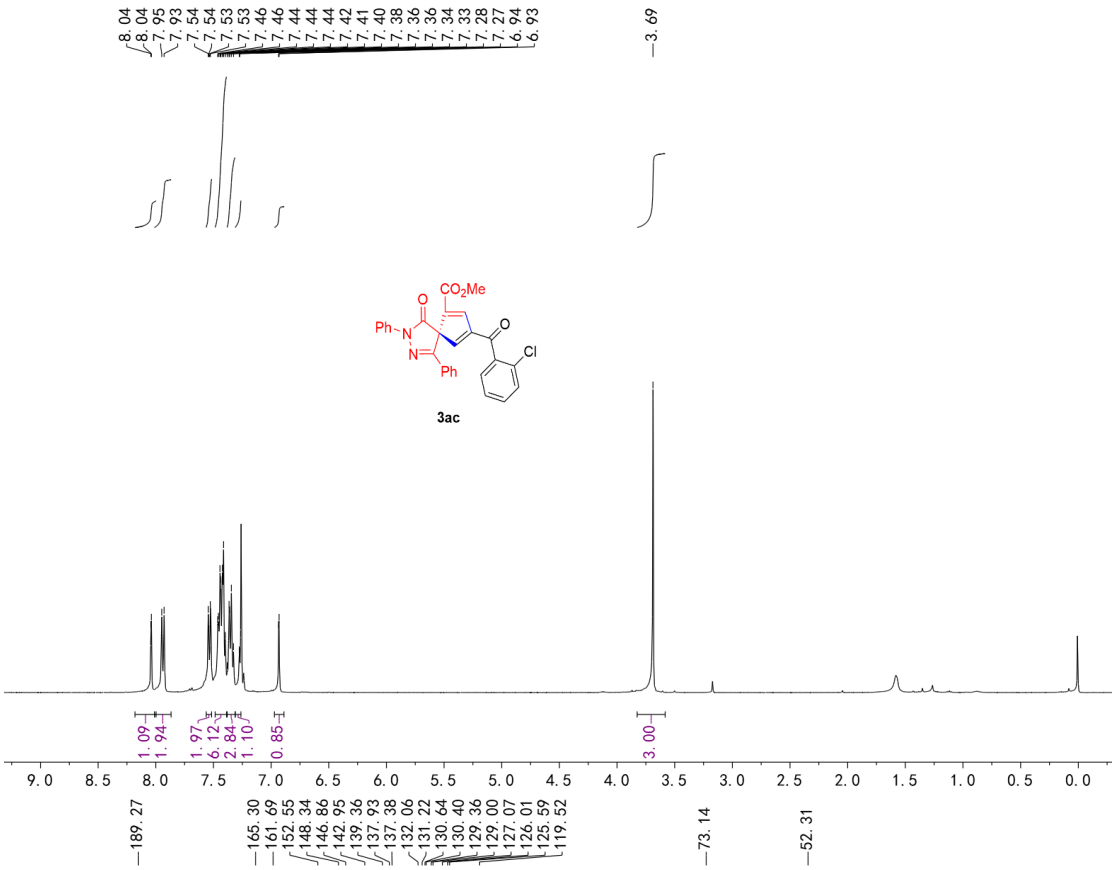

188.76
164.69
160.25
151.84
146.56
143.79
143.38
138.48
136.99
135.69
132.40
130.15
129.65
128.36
128.03
127.97
127.74
124.82
124.37
118.13
72.06
64.18
29.36
17.95
12.64
12.43
CO2n-Bu
O
Ph
N
Ph
O
Ph
3la
8.10
7.83
7.82
7.57
7.56
7.54
7.47
7.45
7.43
7.41
7.39
7.37
7.36
7.36
7.33
7.31
7.29
7.24
7.22
7.20
7.18
7.16
7.14
7.12
7.10
7.08
6.99
5.05
CO2Bn
O
Ph
N
Ph
O
Ph
3ma
0.94
3.94
1.11
1.02
2.11
6.21
0.88
1.91

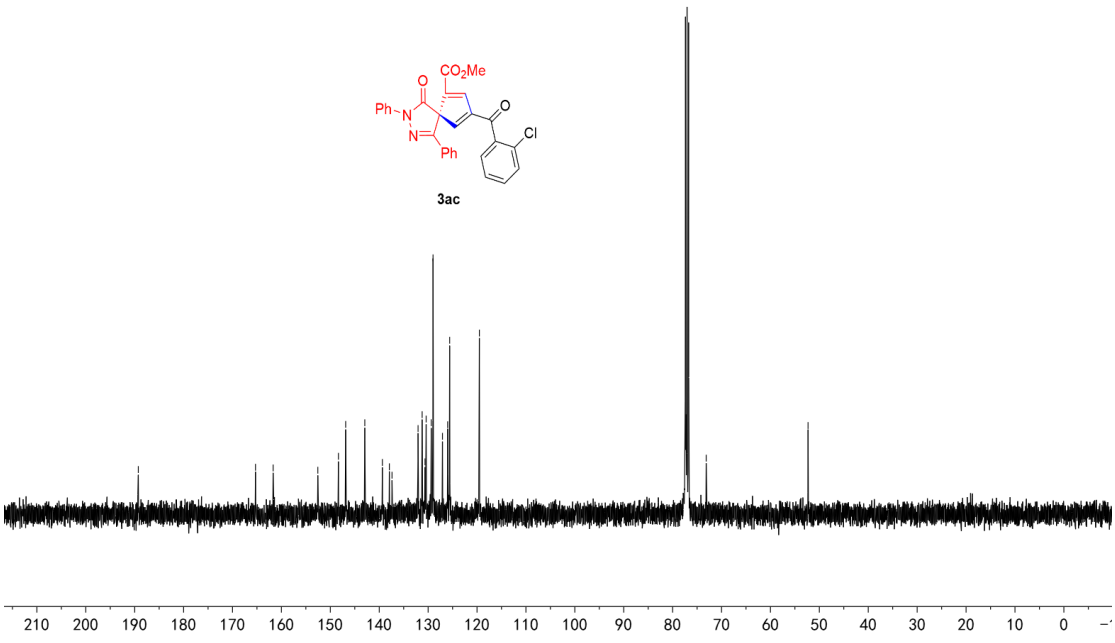

189.74
165.60
161.00
152.74
147.60
145.39
144.59
138.98
137.73
134.74
134.83
133.47
131.20
130.70
129.42
129.09
128.96
128.81
128.45
128.28
128.10
125.89
125.45
119.41
73.16
67.12
CO2Bn
Ph
N
O
Ph
O
Ph
3ma
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

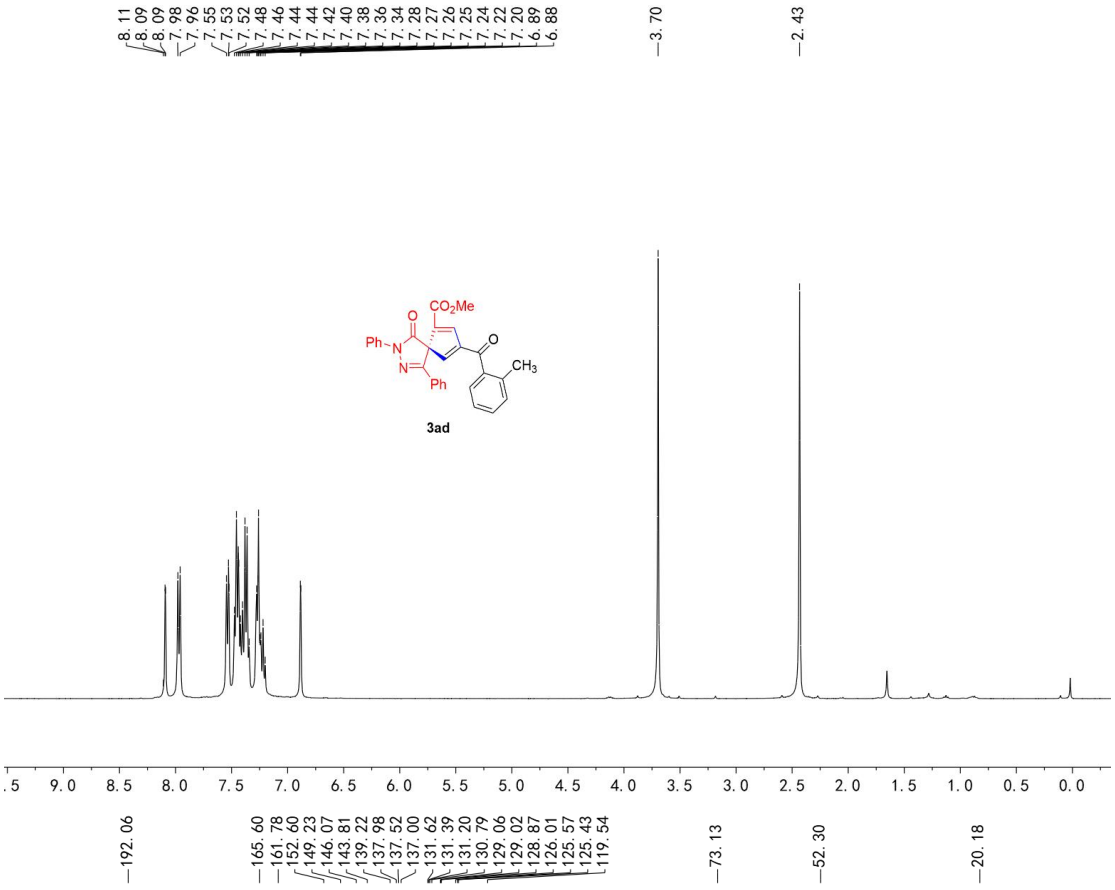

8.04
7.96
7.94
7.62
7.55
7.53
7.46
7.44
7.42
7.38
7.36
CDCl3
7.26
7.16
7.13
7.11
7.07
3.68
CO2Me
Ph
N
O
Ph
O
F
3ab
3.02
4.16
5.92
2.95
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

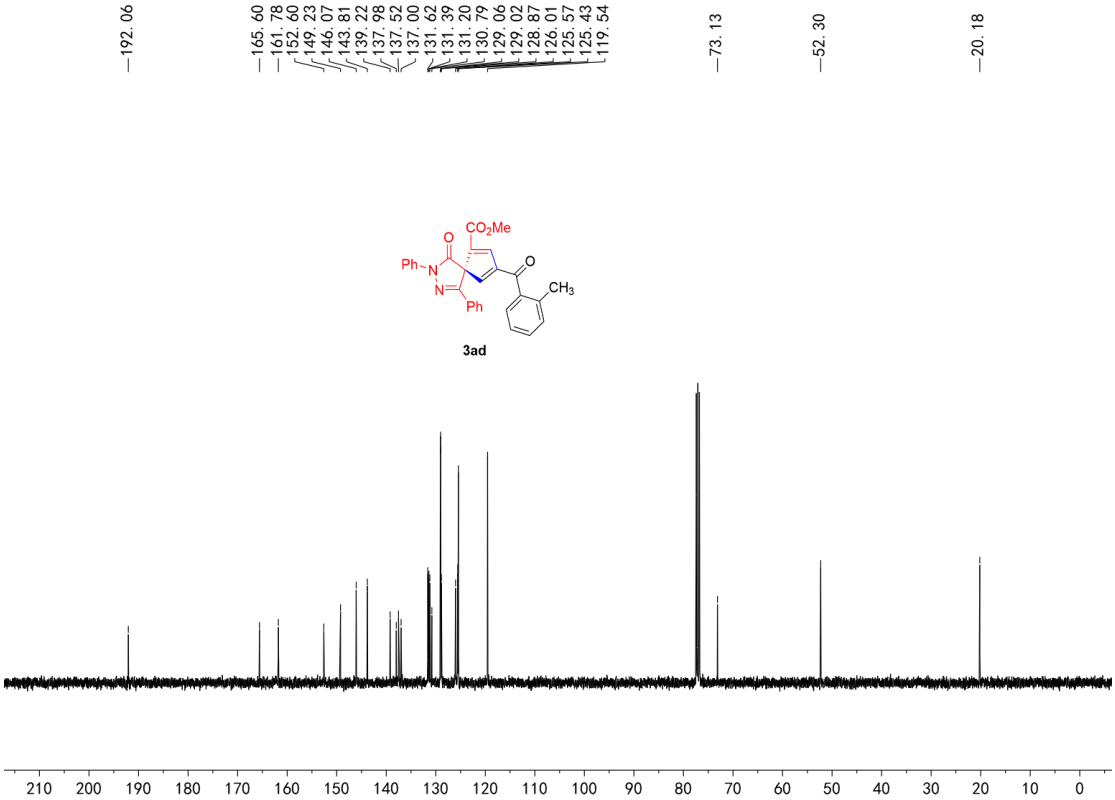

186.85
165.43
161.73
161.44
158.92
152.67
148.54
145.93
145.90
143.48
139.03
137.96
134.27
134.19
131.19
130.84
130.67
129.09
129.02
125.98
125.54
124.72
124.68
119.50
116.76
116.55
73.06
52.30
CO2Me
O
Ph
N
N
Ph
O
F
3ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

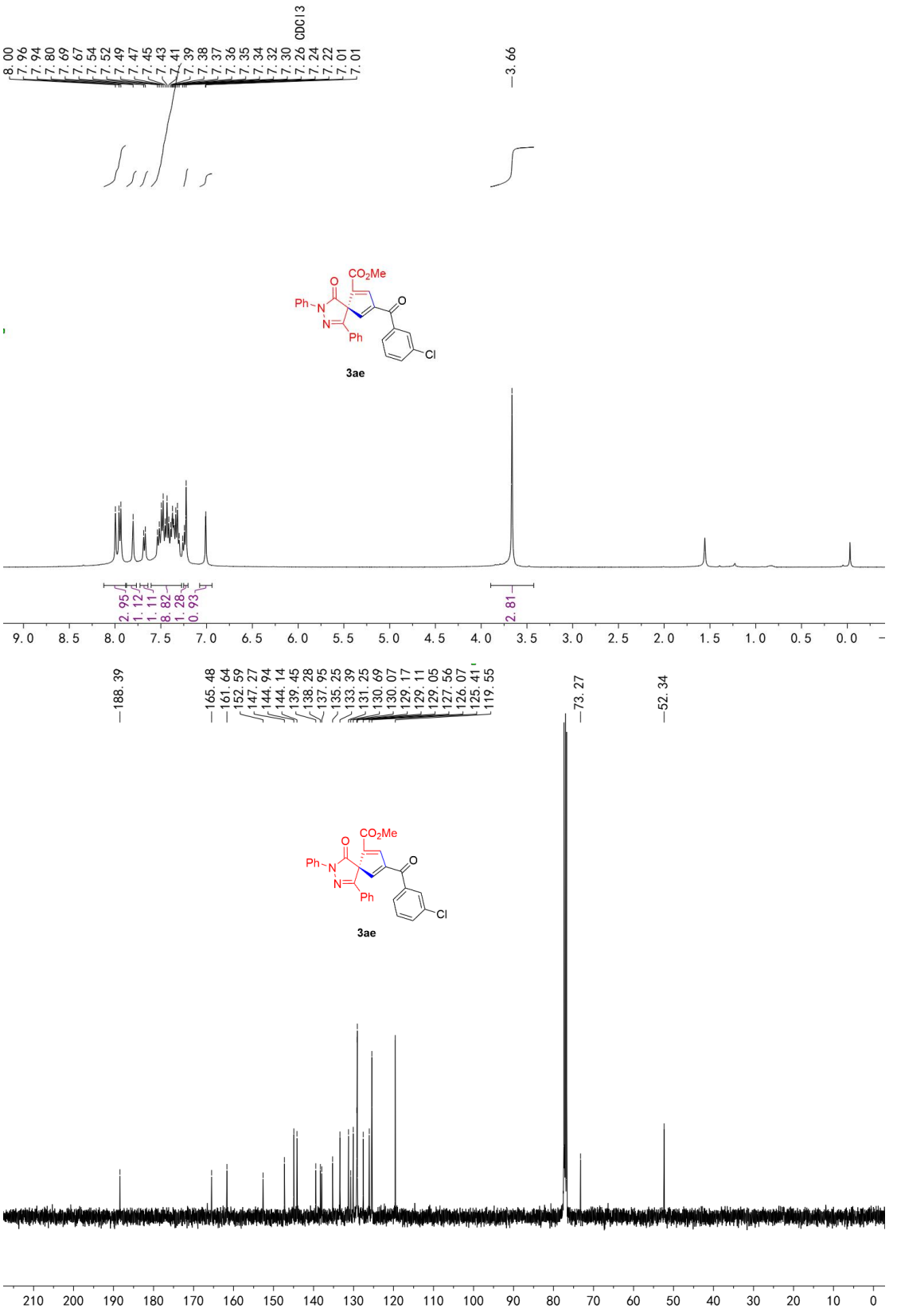

110.73
110.75
110.78
110.80
CO2Me
O
Ph
N
N
Ph
O
F
3ab
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210

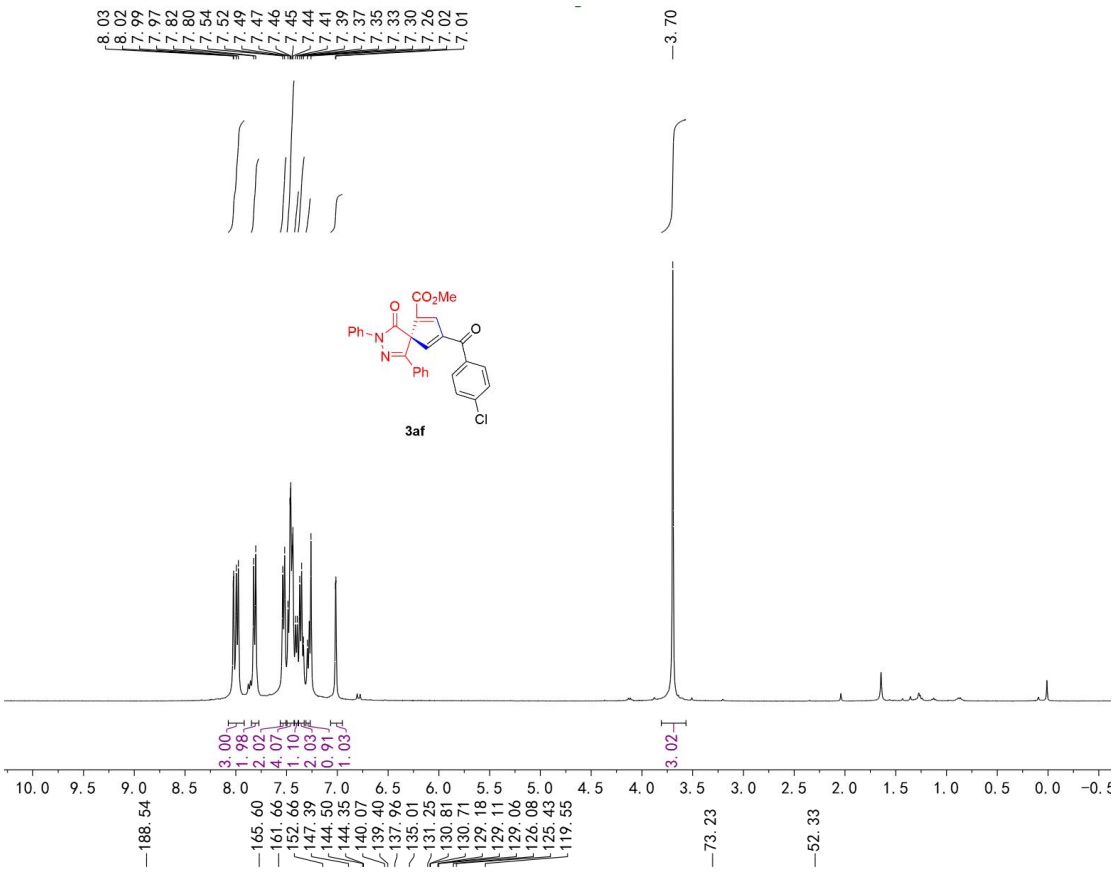

8.04
8.04
7.95
7.93
7.54
7.54
7.53
7.53
7.46
7.46
7.44
7.44
7.44
7.42
7.41
7.40
7.38
7.36
7.36
7.34
7.33
7.28
7.27
6.94
6.93
3.69
CO2Me
O
Ph
N
N
Ph
O
Cl
3ac
1.09
1.94
1.97
6.12
2.84
1.10
0.85
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
189.27
165.30
161.69
152.55
148.34
146.86
142.95
139.36
137.93
137.38
132.06
131.22
130.64
130.40
129.36
129.00
127.07
126.01
125.59
119.52
73.14
52.31

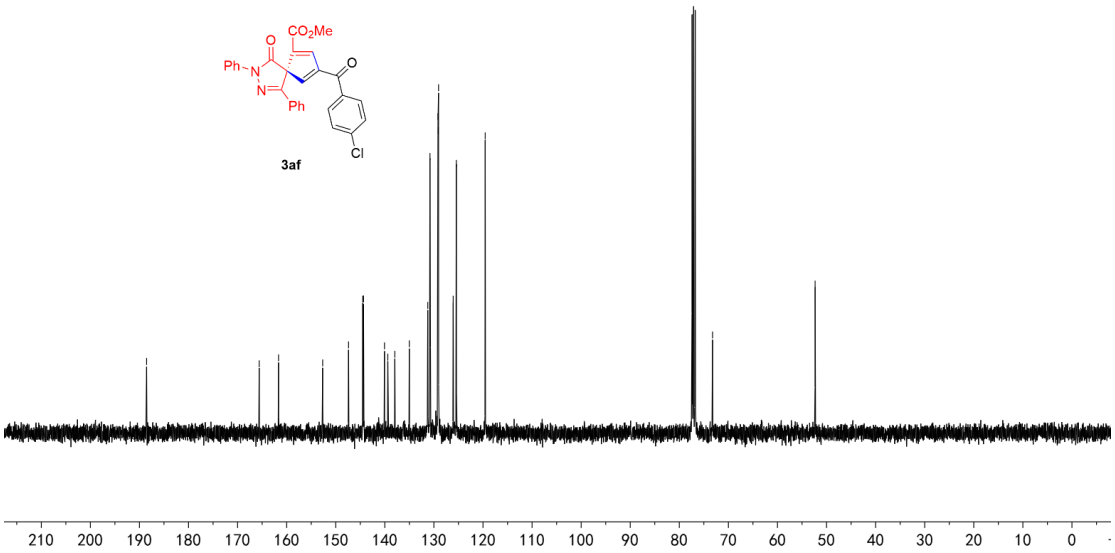

CO2Me
O
Ph
N
N
Ph
O
Cl
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

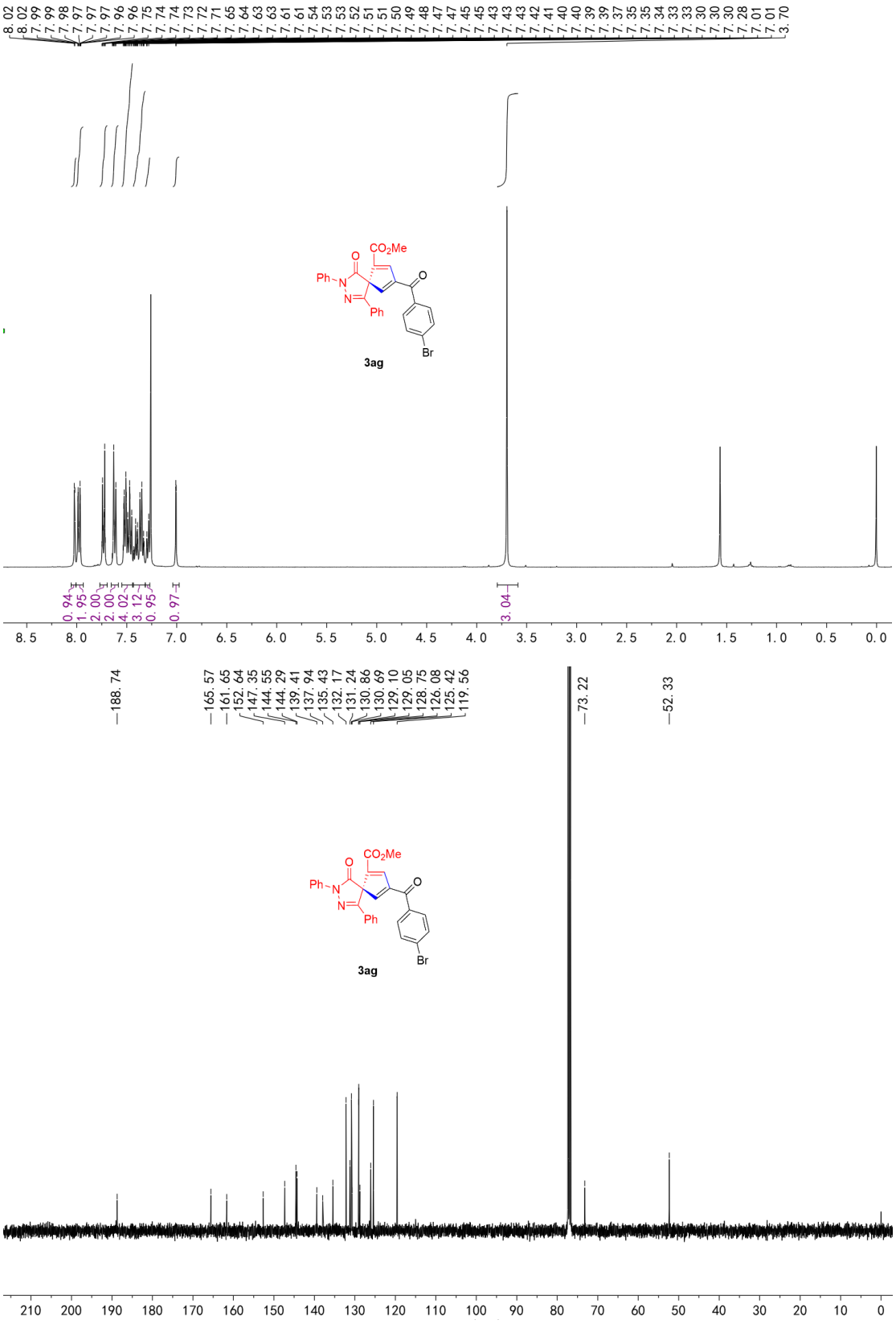

8.11
8.09
8.09
7.98
7.96
7.55
7.53
7.52
7.48
7.46
7.44
7.44
7.42
7.40
7.38
7.36
7.34
7.28
7.27
7.26
7.25
7.24
7.22
7.20
6.89
6.88
3.70
2.43
CO2Me
Ph
N
O
O
CH3
Ph
3ad
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


192.06
165.60
161.78
152.60
149.23
146.07
143.81
139.22
137.98
137.52
137.00
131.62
131.39
131.20
130.79
129.06
129.02
128.87
126.01
125.57
125.43
119.54
73.13
52.30
20.18
CO2Me
Ph
N
O
O
CH3
Ph
3ad
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

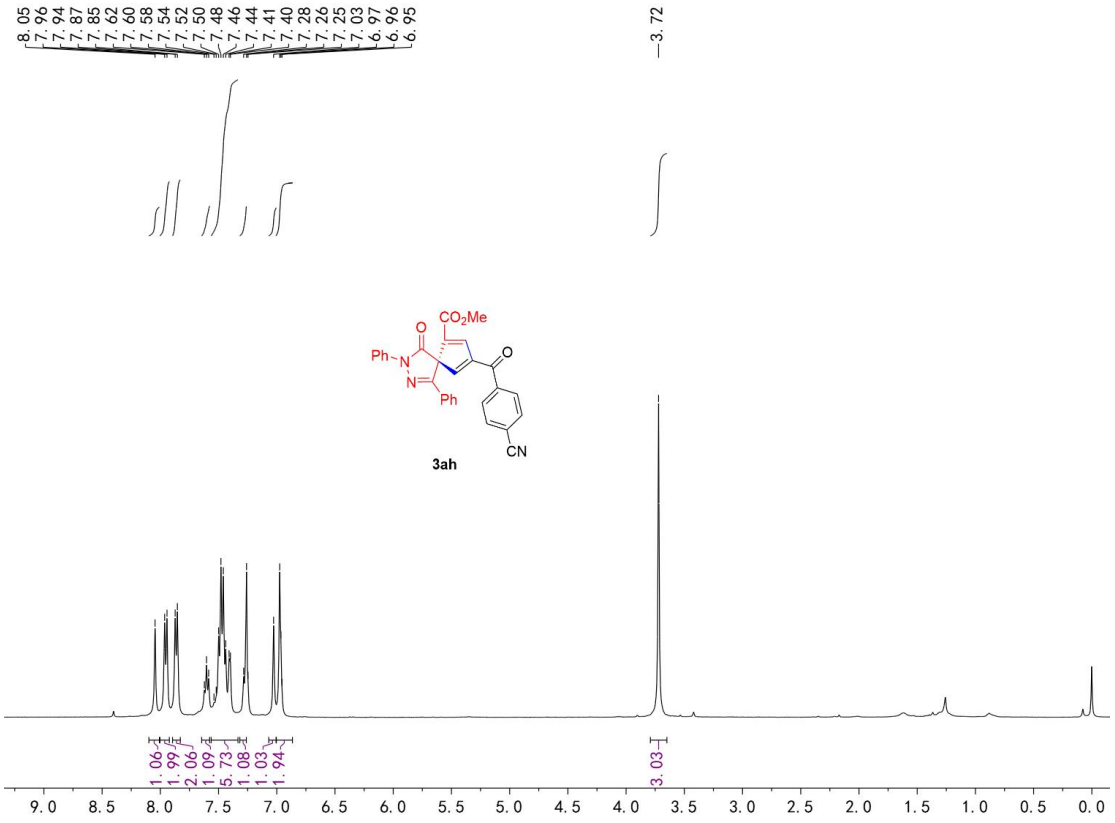

8.00
7.96
7.94
7.80
7.69
7.67
7.54
7.52
7.49
7.47
7.45
7.43
7.41
7.39
7.38
7.37
7.36
7.35
7.34
7.32
7.30
CDCl3
7.26
7.24
7.22
7.01
7.01
3.66
CO2Me
O
Ph
N
N
Ph
O
Cl
3ae
2.95
1.12
1.11
8.82
1.28
0.93
2.81
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
188.39
165.48
161.64
152.59
147.27
144.94
144.14
139.45
138.28
137.95
135.25
133.39
131.25
130.69
130.07
129.17
129.11
129.05
127.56
126.07
125.41
119.55
73.27
52.34
CO2Me
O
Ph
N
N
Ph
O
Cl
3ae
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

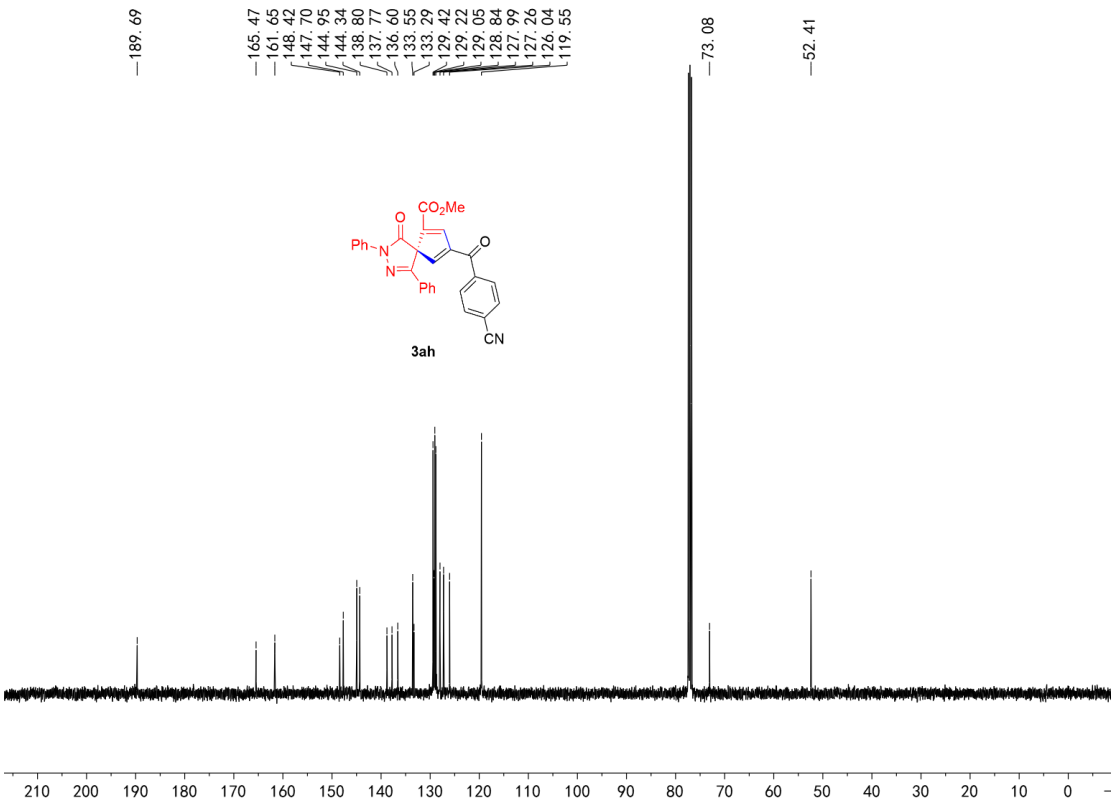

8.03
8.02
7.99
7.97
7.82
7.80
7.54
7.52
7.49
7.47
7.46
7.45
7.44
7.41
7.39
7.37
7.35
7.33
7.30
7.26
7.02
7.01
3.70
CO2Me
Ph
N
O
Ph
O
Cl
3af
3.00
1.98
2.02
4.07
1.10
2.03
0.91
1.03
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
188.54
165.60
161.66
152.66
147.39
144.50
144.35
140.07
139.40
137.96
135.01
131.25
130.81
130.71
129.18
129.11
129.06
126.08
125.43
119.55
73.23
52.33

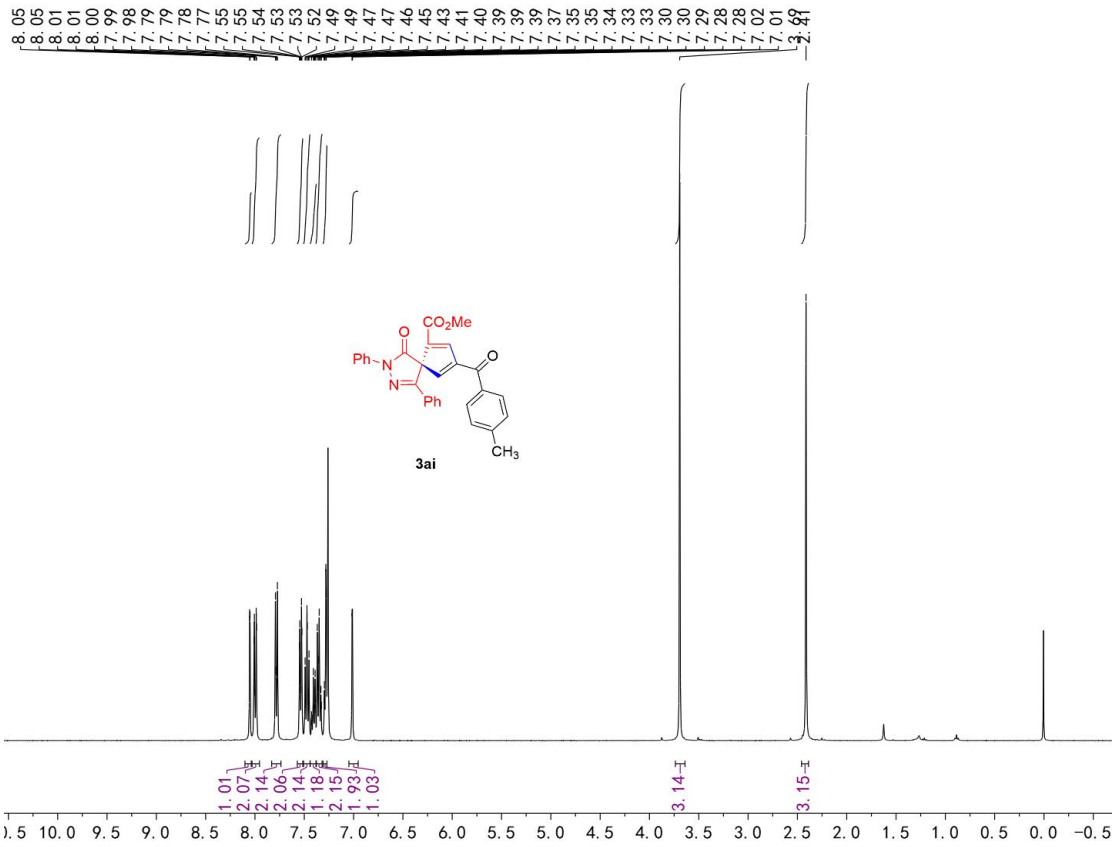

CO2Me
Ph
N
O
Ph
O
Cl
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

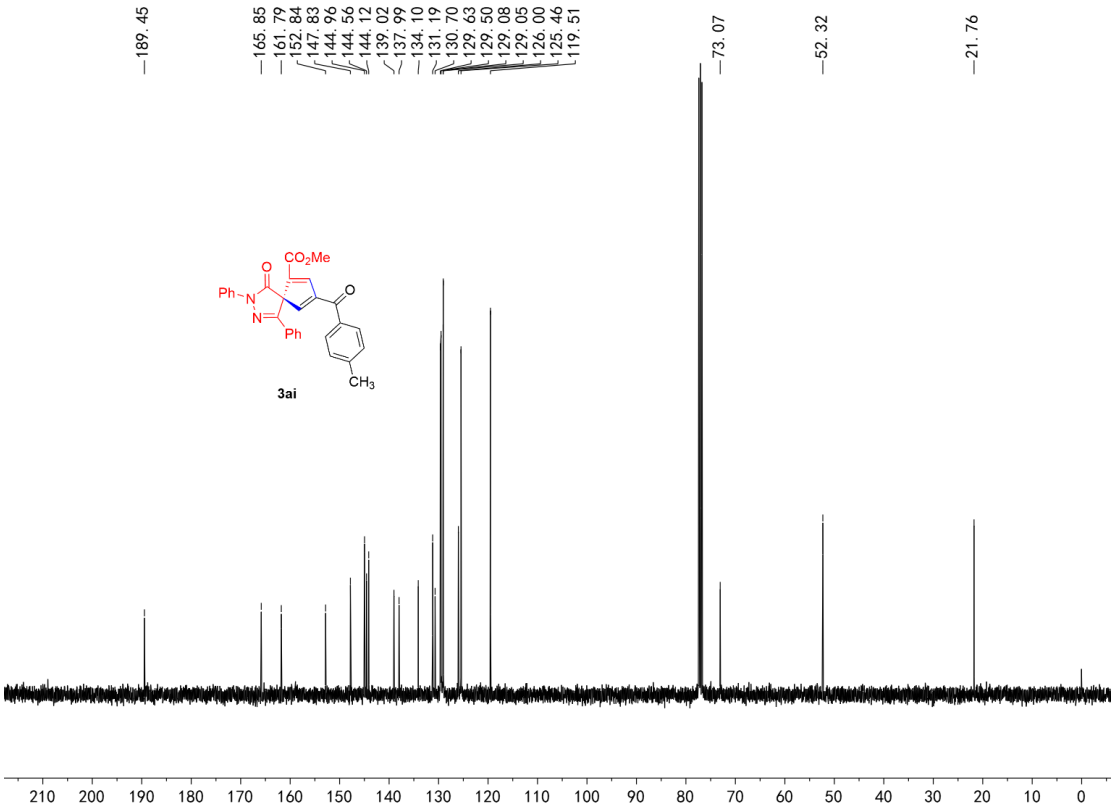

8.02
8.02
7.99
7.99
7.98
7.97
7.97
7.97
7.96
7.96
7.75
7.74
7.74
7.73
7.72
7.71
7.65
7.64
7.63
7.63
7.61
7.61
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.48
7.47
7.47
7.45
7.45
7.43
7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.39
7.37
7.35
7.34
7.33
7.33
7.30
7.30
7.28
7.01
7.01
3.70
CO2Me
Ph
N
O
O
Ph
Br
3ag
0.94
1.95
2.00
2.00
4.02
3.12
0.95
0.97
3.04
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

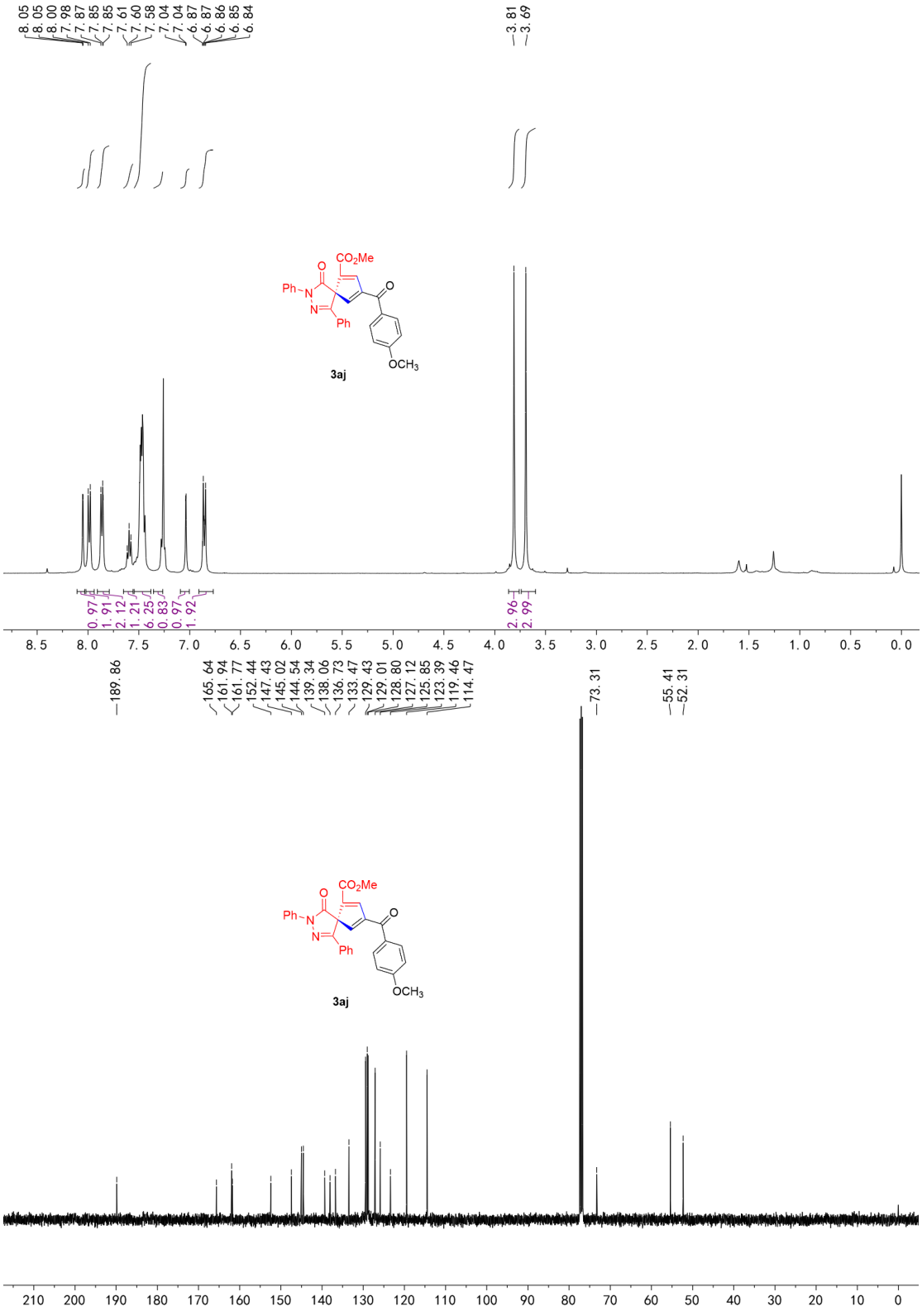
188.74
165.57
161.65
152.64
147.35
144.55
144.29
139.41
137.94
135.43
132.17
131.24
130.86
130.69
129.10
129.05
128.75
126.08
125.42
119.56
73.22
52.33
CO2Me
Ph
N
O
O
Ph
Br
3ag
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

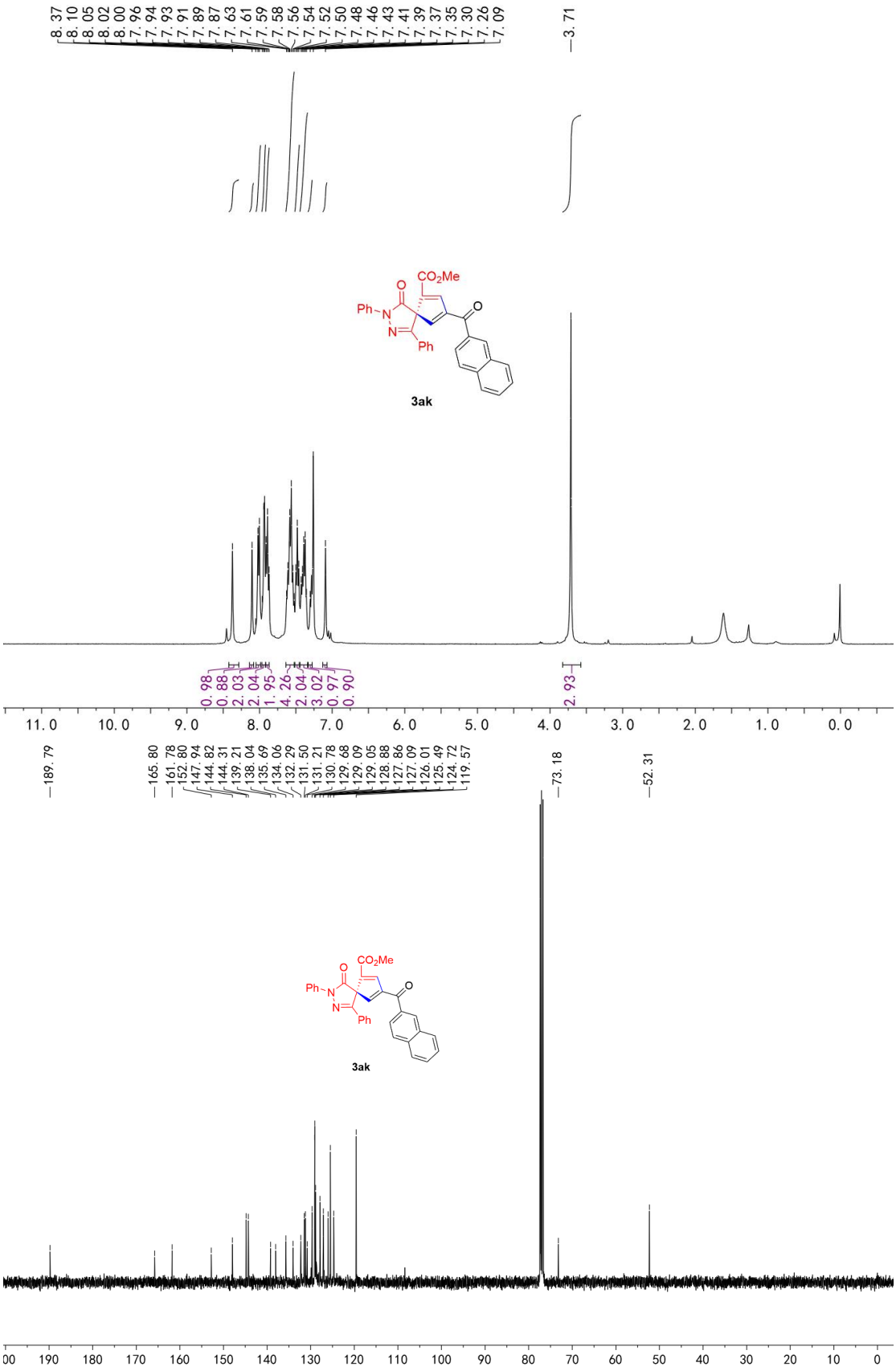

8.05
7.96
7.94
7.87
7.85
7.62
7.60
7.58
7.54
7.52
7.50
7.48
7.46
7.44
7.41
7.40
7.28
7.26
7.25
7.03
6.97
6.96
6.95
3.72
CO2Me
O
Ph
N
O
N
Ph
CN
3ah
1.06
1.99
2.06
1.09
5.73
1.08
1.03
1.94
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

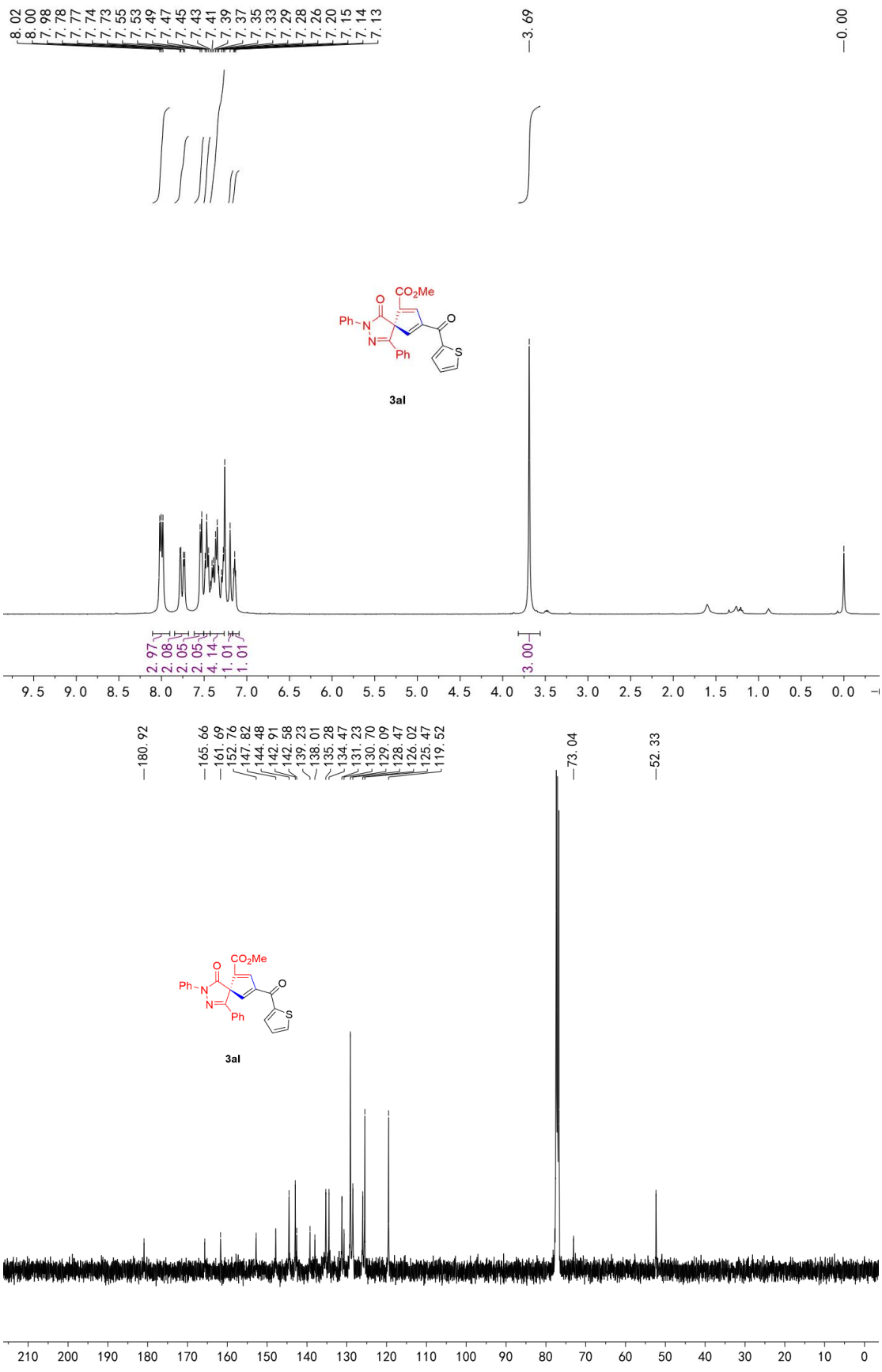

189.69
165.47
161.65
148.42
147.70
144.95
144.34
138.80
137.77
136.60
133.55
133.29
129.42
129.22
129.05
128.84
127.99
127.26
126.04
119.55
73.08
52.41
CO2Me
O
Ph
N
O
N
Ph
CN
3ah
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

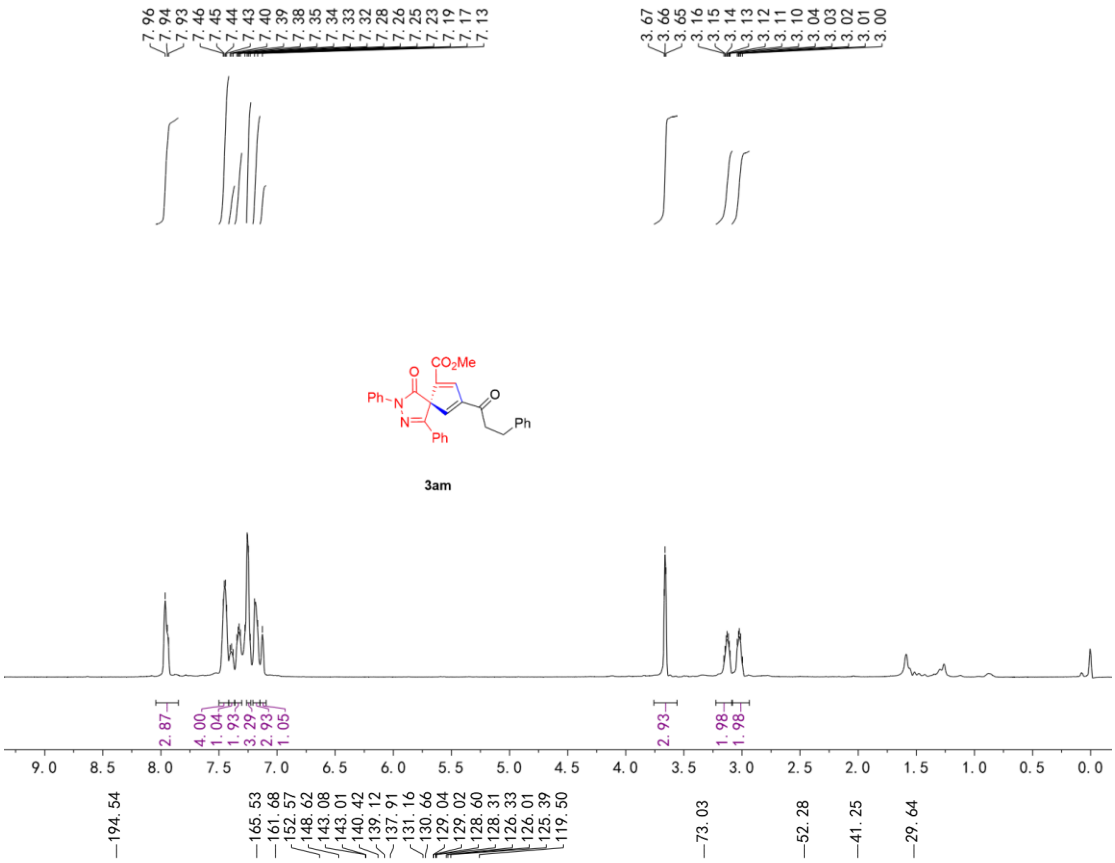

8.05
8.05
8.01
8.01
8.00
7.99
7.98
7.79
7.79
7.78
7.77
7.55
7.54
7.53
7.53
7.52
7.49
7.49
7.47
7.47
7.46
7.45
7.43
7.41
7.40
7.39
7.39
7.37
7.35
7.35
7.34
7.33
7.33
7.30
7.30
7.29
7.28
7.28
7.02
7.01
2.41
CO2Me
O
Ph
N
N
Ph
O
CH3
3ai
1.01
2.07
2.14
2.06
2.14
1.18
2.15
1.93
1.03
3.14
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5

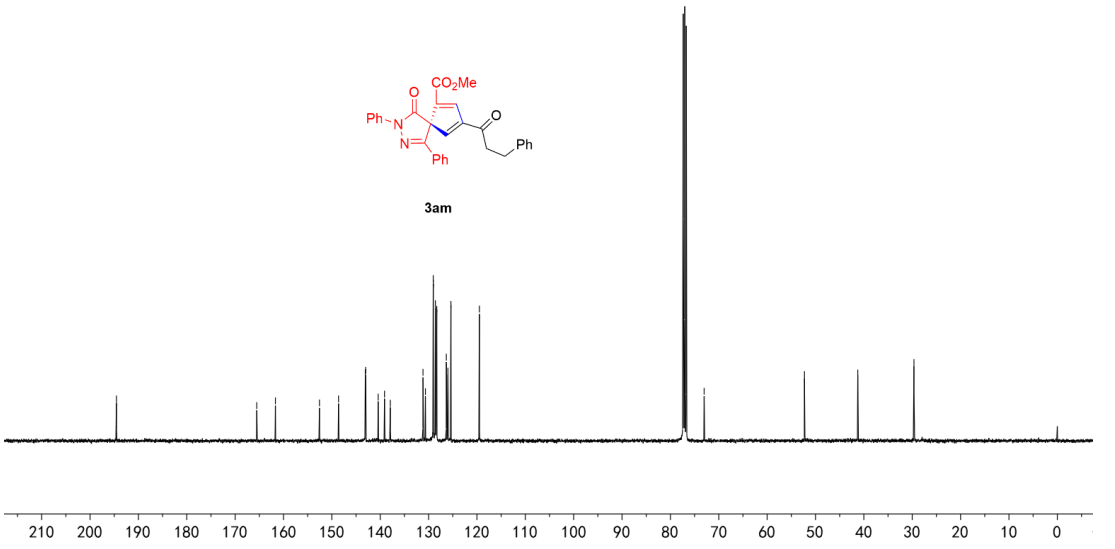

189.45
165.85
161.79
152.84
147.83
144.96
144.56
144.12
139.02
137.99
134.10
131.19
130.70
129.63
129.50
129.08
129.05
126.00
125.46
119.51
73.07
52.32
21.76
CO2Me
O
Ph
N
N
Ph
O
CH3
3ai
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.05
8.05
8.00
7.98
7.87
7.85
7.85
7.61
7.60
7.58
7.04
7.04
6.87
6.87
6.86
6.85
6.84
3.81
3.69
CO2Me
Ph
N
O
Ph
O
OCH3
3aj
0.97
1.91
2.12
1.21
6.25
0.83
0.97
1.92
2.96
2.99
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
189.86
165.64
161.94
161.77
152.44
147.43
145.02
144.54
139.34
138.06
136.73
133.47
129.43
129.01
128.80
127.12
125.85
123.39
119.46
114.47
73.31
55.41
52.31
CO2Me
Ph
N
O
Ph
O
OCH3
3aj
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

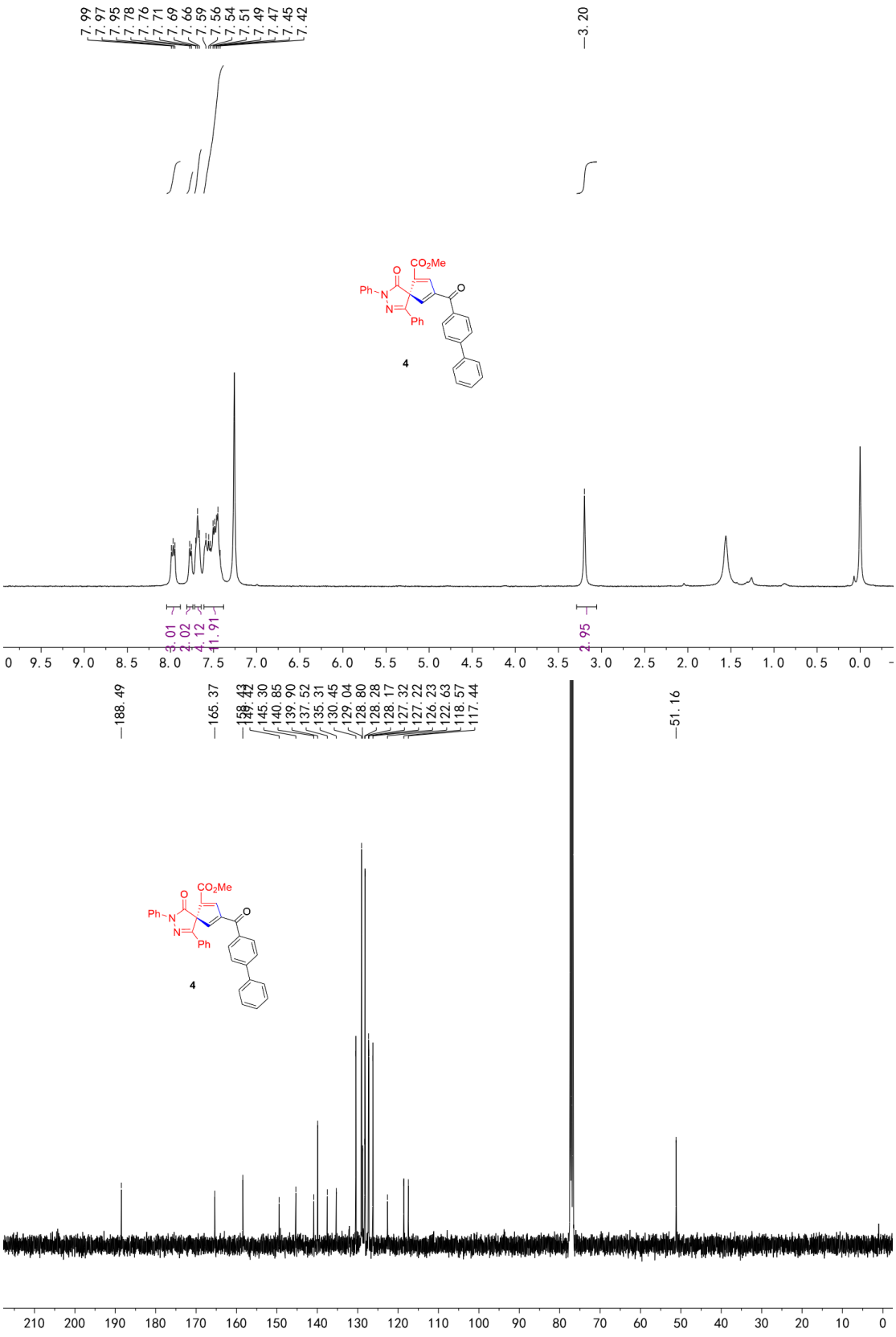

8.37
8.10
8.05
8.02
8.00
7.96
7.94
7.93
7.91
7.89
7.87
7.63
7.61
7.59
7.58
7.56
7.54
7.52
7.50
7.48
7.46
7.43
7.41
7.39
7.37
7.35
7.30
7.26
7.09
3.71
CO2Me
O
Ph
N
O
Ph
3ak
0.98
0.88
2.03
2.04
1.95
4.26
2.04
3.02
0.97
0.90
2.93
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
189.79
165.80
161.78
152.80
147.94
144.82
144.31
139.21
138.04
135.69
134.06
132.29
131.50
131.21
130.78
129.68
129.09
129.05
128.88
127.86
127.09
126.01
125.49
124.72
119.57
73.18
52.31
CO2Me
O
Ph
N
O
Ph
3ak
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

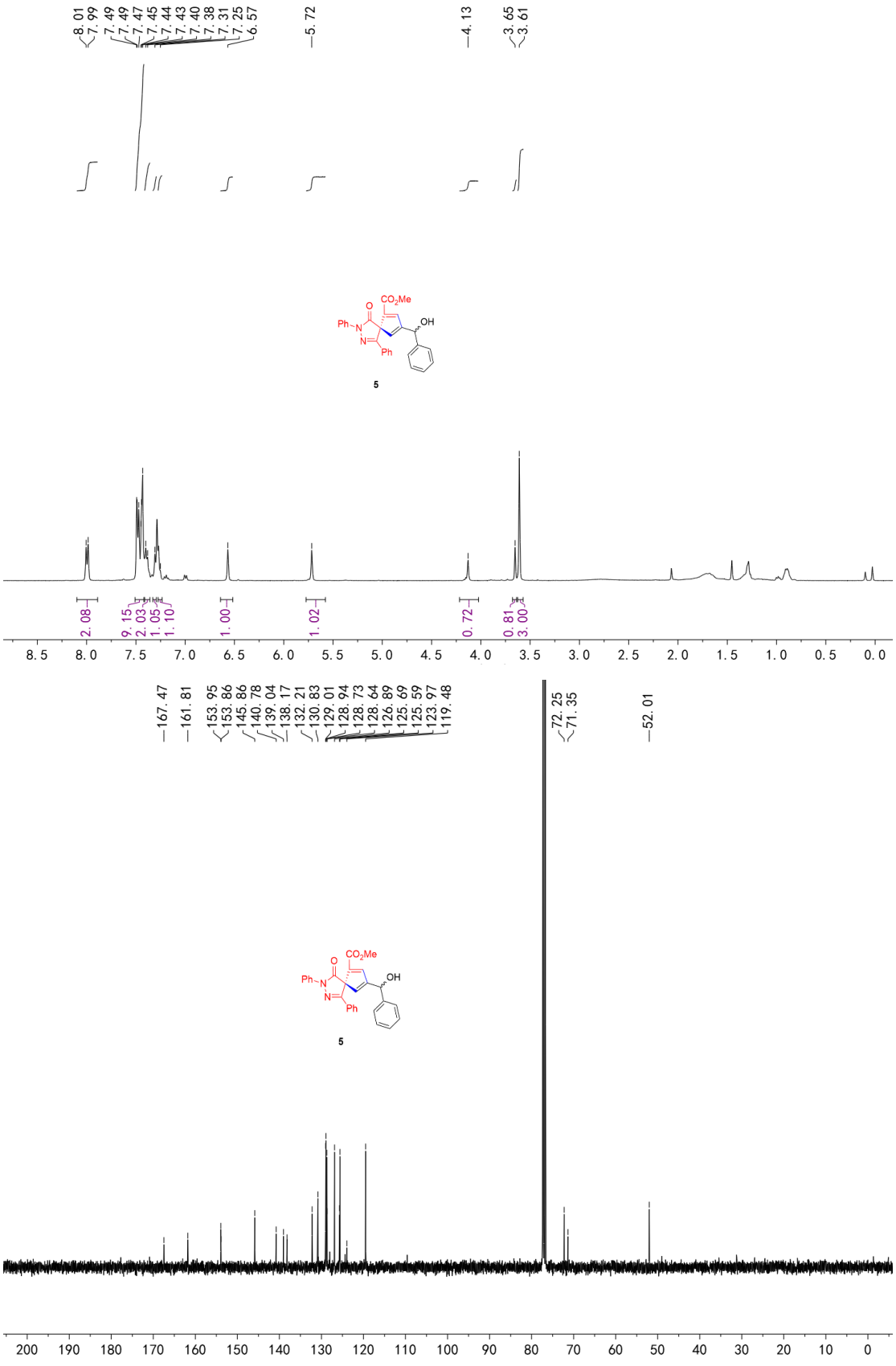

8.02
8.00
7.98
7.78
7.77
7.74
7.73
7.55
7.53
7.49
7.47
7.45
7.43
7.41
7.39
7.37
7.35
7.33
7.29
7.28
7.26
7.20
7.15
7.14
7.13
3.69
0.00
CO2Me
Ph
N
O
Ph
S
3al
2.97
2.08
2.05
2.05
4.14
1.01
1.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
180.92
165.66
161.69
152.76
147.82
144.48
142.91
142.58
139.23
138.01
135.28
134.47
131.23
130.70
129.09
128.47
126.02
125.47
119.52
73.04
52.33
CO2Me
Ph
N
O
Ph
S
3al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.96
7.94
7.93
7.46
7.45
7.44
7.43
7.40
7.39
7.38
7.35
7.34
7.33
7.32
7.28
7.26
7.25
7.23
7.19
7.17
7.13
3.67
3.66
3.65
3.16
3.15
3.14
3.13
3.12
3.11
3.10
3.04
3.03
3.02
3.01
3.00
CO2Me
Ph
N
O
Ph
O
Ph
3am
2.87
4.00
1.04
1.93
3.29
2.93
1.05
2.93
1.98
1.98
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


194.54
165.53
161.68
152.57
148.62
143.08
143.01
140.42
139.12
137.91
131.16
130.66
129.04
129.02
128.60
128.31
126.33
126.01
125.39
119.50
73.03
52.28
41.25
29.64

CO2Me
Ph
N
O
Ph
O
Ph
3am
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.99
7.97
7.95
7.78
7.76
7.71
7.69
7.66
7.59
7.56
7.54
7.51
7.49
7.47
7.45
7.42
3.20
CO2Me
Ph
N
O
Ph
4
3.01
2.02
4.12
11.91
2.95
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
188.49
165.37
158.43
158.42
145.30
140.85
139.90
137.52
135.31
130.45
129.04
128.80
128.28
128.17
127.32
127.22
126.23
122.63
118.57
117.44
51.16
CO2Me
Ph
N
O
Ph
4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.01
7.99
7.49
7.49
7.47
7.45
7.44
7.43
7.40
7.38
7.31
7.25
6.57
5.72
4.13
3.65
3.61
CO2Me
O
Ph
N
OH
Ph
5
2.08
9.15
2.03
1.05
1.10
1.00
1.02
0.72
0.81
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
167.47
161.81
153.95
153.86
145.86
140.78
139.04
138.17
132.21
130.83
129.01
128.94
128.73
128.64
126.89
125.69
125.59
123.97
119.48
72.25
71.35
52.01
CO2Me
O
Ph
N
OH
Ph
5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0