$K_2S_2O_8$-mediated Acylarylation of Unactivated Alkenes via Acyl Radical Addition/C-H Annulation Cascade of *N*-allyl-indoles with Silver Cocatalysis

Jitan Zhang, * Manyi Wu,¶ Hu Ju,¶ Haitao Yang,¶ Baiyang Qian, Ke Ding, Jiaping Wu* and Meihua Xie*

Key Laboratory of Functional Molecular Solids (Ministry of Education), Anhui Key Laboratory of Molecular Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China

E-mail: zhangjt@ahnu.edu.cn; wujiaping@ahnu.edu.cn; xiemh@mail.ahnu.edu.cn

¶ *These authors contributed equally to this work.*

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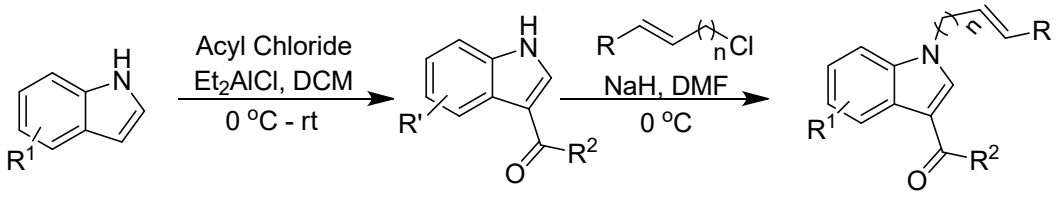
1. General information

All commercial materials were used as received unless otherwise noted. Commercial reagents were purchased from Alfa Aesar, TCI, Energy Chemical, and used without further purification. Starting materials α-oxocarboxylic acids were prepared according to the reported procedure.[1] All of other commercially available compounds were used without further purification. ^{1}H NMR spectra were recorded at 400 MHz and NMR spectrometers using TMS as an internal standard, ^{13}C NMR spectra were recorded at 100 MHz NMR spectrometers using TMS as an internal standard and were fully decoupled by broad band proton decoupling. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonances (br). Melting points were measured on a hot-stage microscope (XT4-A) and are uncorrected. High resolution mass spectra (HRMS) were obtained on an APEXM Fourier transform mass spectrometry (ESI). The X-ray diffraction spectrum was carried out with a SMART APEX II X-ray Single-crystal diffract meter.

2. General procedure for the preparation of indole substrates[2]

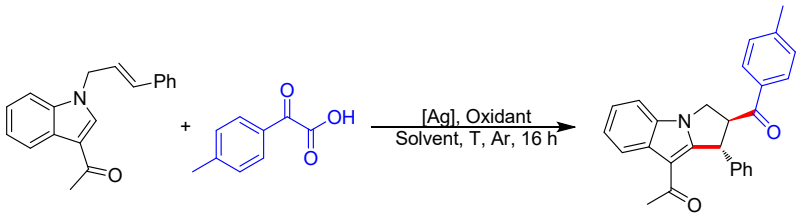


To a solution of indole derivative (5 mmol, 1.0 equiv) in DCM (10 mL), Et_2AlCl (7.5 mmol, 1.5 equiv) (0.98 mol/L in hexane) was added at 0 °C and the mixture was stirred at this temperature for 30 min. To this solution was added drop-wise a DCM solution (10 mL) of acyl chloride (6 mmol, 1.2 equiv) at 0 ºC. The mixture was warmed to room temperature and stirred until completion of the reaction (monitored by TLC). Then the mixture was quenched with saturated aqueous NH_4Cl, extracted with CH_2Cl_2 (15 mL x 3), the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography to give the 3-acylindole derivatives.

To a solution of 3-acylindole (5 mmol) in *N,N*-dimethylformamide (15 mL) was

added NaH (1.2 equiv) under ice cooled conditions. Alkyl halide (1.2 equiv) was added dropwise to this solution and allowed to stir at room temperature for appropriate time. After completion of the reaction it was quenched with water and extracted by Et_2O. The organic layer was dried over anhydrous Na_2SO_4 and filtered, concentrated under pressure and then purified by silica gel flash column chromatography.

3. Optimization of reaction conditions



1a **2a** **3aa**

entry	Additive (mol%)	Oxidant (equiv)	Solvent (2 mL)	T (°C)	Yield(%)[b]
1	AgOAc (10)	$K_2S_2O_8$ (2.0)	CH_3CN:H_2O (1:1)	70	74
2	AgOAc (10)		CH_3CN:H_2O (1:1)	70	nr
3		$K_2S_2O_8$ (2.0)	CH_3CN:H_2O (1:1)	70	49
4	AgOAc (10)	$Na_2S_2O_8$ (2.0)	CH_3CN:H_2O (1:1)	70	71
5	AgOAc (10)	$(NH_4)_2S_2O_8$ (2.0)	CH_3CN:H_2O (1:1)	70	69
6	AgOAc (10)	Oxone (2.0)	CH_3CN:H_2O (1:1)	70	21
7	AgOAc (10)	$K_2S_2O_8$ (3.0)	CH_3CN:H_2O (1:1)	70	71
8	AgOAc (10)	$K_2S_2O_8$ (2.0)	DCE:H_2O (1:1)	70	nr
9	AgOAc (10)	$K_2S_2O_8$ (2.0)	DMSO:H_2O (1:1)	70	22
10	AgOAc (10)	$K_2S_2O_8$ (2.0)	Acetone:H_2O (1:1)	70	65
11	AgOAc (10)	$K_2S_2O_8$ (2.0)	AcOH:H_2O (1:1)	70	28
12	AgOAc (10)	$K_2S_2O_8$ (2.0)	H_2O	70	nr
13	AgOAc (10)	$K_2S_2O_8$ (2.0)	CH_3CN	70	trace
14	AgOAc (10)	$K_2S_2O_8$ (2.0)	CH_3CN:H_2O (2:1)	70	61
15	AgOAc (10)	$K_2S_2O_8$ (2.0)	CH_3CN:H_2O (3:1)	70	36
16	AgOAc (10)	$K_2S_2O_8$ (2.0)	CH_3CN:H_2O (1:2)	70	41
17	AgOAc (10)	$K_2S_2O_8$ (2.0)	CH_3CN:H_2O (1:3)	70	21
18	AgOAc (10)	$K_2S_2O_8$ (2.0)	CH_3CN:H_2O (1:1)	60	69

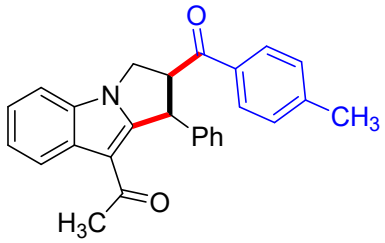
19	AgOAc (10)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	50	39
20	AgOAc (10)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	80	72
21	AgOAc (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	84
22	AgOAc (3)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	82
23	Ag_2CO_3 (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	72
24	Ag_2O (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	71
25	Ag_2SO_4 (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	72
26	AgOTf (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	80
27	AgF (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	77
28	AgTFA (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	75
29	$AgNTf_2$ (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	76
30	$AgSbF_6$ (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	78
31	$AgBF_4$ (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	74
32	$AgPF_6$ (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	69
33	$Sc(OTf)_3$ (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	61
34	$Cu(OAc)_2$(5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	trace
35	$Fe(OAc)_2$ (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	72
36	KI (5)	$K_2S_2O_8$ (2.0)	$CH_3CN:H_2O$ (1:1)	70	nr

[a]**1a** 0.2 mmol, **2a** 0.4 mmol. [b]Isolated yield.

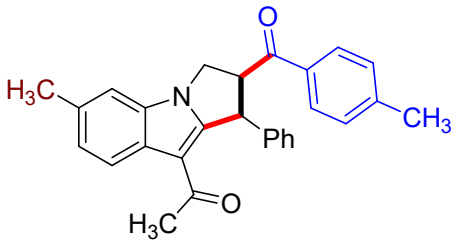
4. General procedure for alkene difunctionalizing reaction

A mixture of indole substrates (**1**, 0.2 mmol), α-oxocarboxylic acids (**2**, 0.3 mmol), AgOAc (0.01 mmol), $K_2S_2O_8$ (0.4 mmol) and CH_3CN/H_2O (v/v = 1:1) (2.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 70 °C for 16 h. Then, the reaction mixture was cooled to room temperature. The mixture was filtered through Celite®, and the filter cake was rinsed with EtOAc. The combined organic was removed in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the desired product **3**.

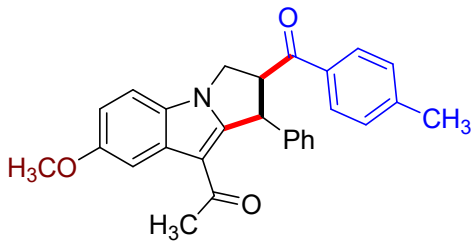
5. Analytical data



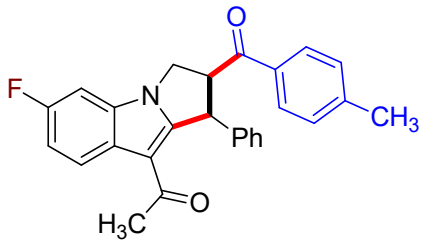
2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone（**3aa**）. White solid. Melting point: 135-137 °C. Isolated yield: 84%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.30-8.28 (m, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.36-7.28 (m, 8H) 7.12-7.10 (m, 2H), 5.14 (d, J = 2.4 Hz, 1H), 4.62-4.60 (m, 3H), 2.45 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.3, 192.7, 151.3, 145.1, 141.4, 132.3, 132.2, 130.9, 129.7, 129.2, 129.0, 127.7, 127.4, 122.8, 122.7, 122.6, 110.6, 110.0, 57.7, 48.6, 45.6, 29.8, 21.7. **HRMS** (ESI) m/z calcd for $C_{27}H_{24}NO_2$ $(M+H)^+$: 394.1802, found: 394.1801.



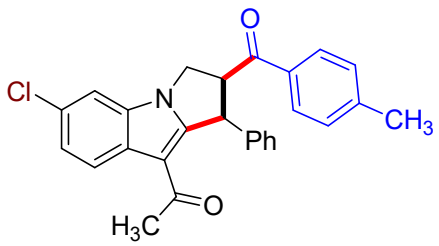
6-methyl-2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ba**). White solid. Melting point: 181-182 °C. Isolated yield: 85%.**^{1}H NMR** (400 MHz, Chloroform-d) δ 8.15 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.33-7.27 (m, 5H), 7.15- 7.09 (m, 4H), 5.10 (d, J = 2.5 Hz, 1H), 4.61-4.54 (m, 3H), 2.48 (s, 3H), 2.44 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.4, 192.6, 150.8, 145.1, 141.5, 132.7, 132.6, 132.3, 129.7, 129.2, 129.0, 128.7, 127.6, 127.4, 124.2, 122.2, 110.5, 110.1, 57.7, 48.5, 45.4, 29.7, 21.7, 21.7. **HRMS** (ESI) m/z calcd for $C_{28}H_{26}NO_2$ $(M+H)^+$: 408.1958, found: 408.1956.



7-methoxy-2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ca**). White solid. Melting point: 188-190 °C. Isolated yield: 75%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, J = 2.4 Hz, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.34-7.28 (m, 5H), 7.22 (d, J = 8.7 Hz, 1H), 7.10 (m, 2H), 6.92 (dd, J = 2.5, 8.8 Hz, 1H), 5.14 (d, J = 2.4 Hz, 1H), 4.59-4.53 (m, 3H), 3.89 (s, 3H), 2.45 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.3, 192.7, 156.5, 151.2, 145.2, 141.4, 132.3, 131.9, 129.7, 129.3, 129.0, 127.7, 127.4, 127.3, 112.9, 110.6, 110.5, 104.6, 57.8, 55.8, 48.7, 45.9, 29.6, 21.7. **HRMS** (ESI) m/z calcd for $C_{28}H_{26}NO_3$ $(M+H)^+$: 424.1907, found: 424.1908.

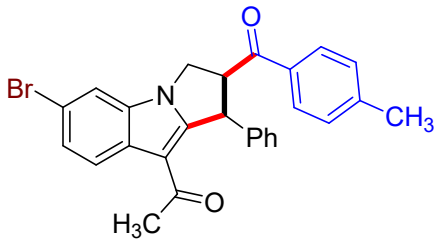


6-fluoro-2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3da**). White solid. Melting point: 139-141 °C. Isolated yield: 70%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27-8.23 (m, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.35-7.29 (m, 5H), 7.11-7.09 (m, 2H), 7.02-7.00 (m, 2H), 5.11 (d, J = 2.7 Hz, 1H), 4.64-4.60 (m, 1H), 4.58-4.54 (m, 2H), 2.45 (s, 3H), 2.14 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.3, 192.6, 159.8 (d, J = 238.9 Hz), 151.6, 145.3, 141.2, 132.3 (d, J = 12.1 Hz), 132.1, 129.8, 129.3, 129.0, 127.8, 127.4, 127.3, 123.8 (d, J = 9.5 Hz), 111.0 (d, J = 23.4 Hz), 110.7, 96.6 (d, J = 26.2 Hz), 57.6, 48.6, 45.6, 29.6, 21.7. **HRMS** (ESI) m/z calcd for $C_{27}H_{23}FNO_2$ $(M+H)^+$: 412.1707, found: 412.1711.

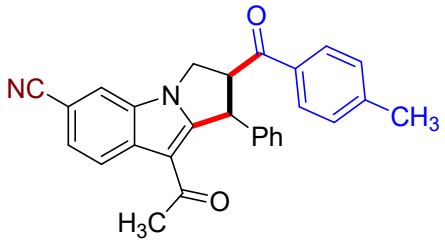


6-chloro-2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ea**). White solid. Melting point: 193-194 °C. Isolated yield: 61%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.22 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.35-7.29 (m, 6H), 7.25-7.23 (m, 1H), 7.10-7.08 (m, 2H), 5.11 (d, J = 2.6 Hz, 1H), 4.63-4.59 (m, 1H), 4.56-4.55 (m, 2H), 2.45 (s, 3H), 2.16 (s,

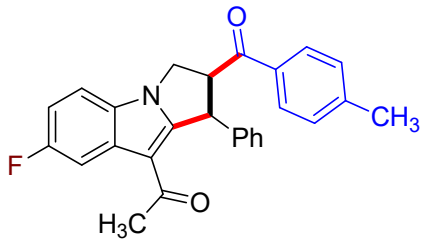
3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.2, 192.5, 151.7, 145.3, 141.0, 132.7, 132.1, 129.8, 129.5, 129.3, 129.0, 128.6, 127.8, 127.3, 123.7, 123.2, 110.7, 110.1, 57.6, 48.5, 45.6, 29.7, 21.7. **HRMS** (ESI) m/z calcd for $C_{27}H_{23}ClNO_2$ $(M+H)^+$: 428.1412, found: 428.1409.



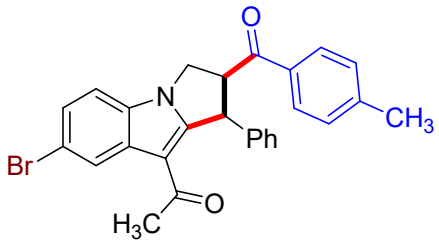
6-bromo-2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3fa**). White solid. Melting point: 188-189 °C. Isolated yield: 52%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 1.6 Hz, 1H)), 7.38 (d, J = 1.7, 8.6 Hz, 1H), 7.35-7.30 (m, 5H), 7.10-7.08 (m, 2H), 5.11 (d, J = 2.6 Hz, 1H), 4.63-4.60 (m, 1H), 4.57-4.55 (m, 2H), 2.46 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.2, 192.5, 151.6, 145.3, 141.0, 133.1, 132.1, 129.9, 129.8, 129.3, 129.0, 127.8, 127.3, 125.8, 124.0, 116.2, 113.0, 110.7, 57.6, 48.5, 45.6, 29.7, 21.7. **HRMS** (ESI) m/z calcd for $C_{27}H_{23}BrNO_2$ $(M+H)^+$: 472.0907, found: 472.0904.



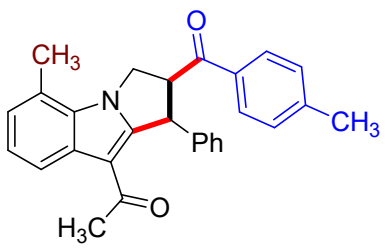
9-acetyl-2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indole-6-carbonitrile (**3ga**). White solid. Melting point: 160-162 °C. Isolated yield: 44%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.40 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.68 (s, 1H), 7.52 (dd, J = 1.0, 8.4 Hz, 1H), 7.38-7.33 (m, 5H), 7.10-7.08 (m, 2H), 5.15 (d, J = 2.2 Hz, 1H), 4.69-4.63 (m, 3H), 2.47 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.0, 192.4, 154.2, 145.5, 140.4, 134.1, 131.9, 131.3, 129.8, 129.5, 129.0, 128.1, 127.2, 125.6, 123.5, 119.9, 114.6, 111.1, 105.4, 57.5, 48.7, 45.9, 29.8, 21.8. **HRMS** (ESI) m/z calcd for $C_{28}H_{23}N_2O_2$ $(M+H)^+$: 419.1754, found: 419.1750.



7-fluoro-2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ha**). White solid. Melting point: 182-183 °C. Isolated yield: 66%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (dd, J = 2.4, 10.1 Hz, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.35-7.30 (m, 5H), 7.27-7.24 (m, 1H), 7.11-7.09 (m, 2H), 7.02 (td, J = 8.9, 2.5 Hz, 1H), 5.12 (d, J = 2.3 Hz, 1H), 4.64-4.58 (m, 3H), 2.46 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.2, 192.4, 159.8 (d, J = 236.2 Hz), 152.4, 145.3, 141.1, 132.1, 131.7 (d, J = 10.8 Hz), 129.8, 129.3, 129.0, 128.9, 127.8, 127.3, 111.0 (d, J = 26.3 Hz), 110.8 (d, J = 4.4 Hz), 110.6 (d, J = 9.9 Hz), 108.3 (d, J = 24.9 Hz), 57.7, 48.9, 45.8, 29.6, 21.7. **HRMS** (ESI) m/z calcd for $C_{27}H_{23}FNO_2$ $(M+H)^+$: 412.1707, found: 412.1708.

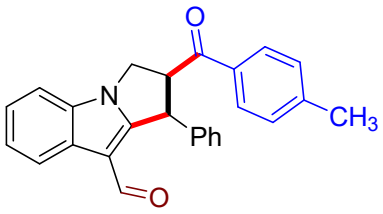


7-bromo-2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ia**). White solid. Melting point: 201-203 °C. Isolated yield: 56%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, J = 1.7 Hz, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.38-7.30 (m, 6H), 7.22-7.20 (m, 1H), 7.10-7.07 (m, 2H), 5.11 (d, J = 2.6 Hz, 1H), 4.64-4.61 (m, 1H), 4.59- 4.57 (m, 2H), 2.46 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.2, 192.3, 152.0, 145.3, 141.0, 132.4, 132.1, 131.0, 129.8, 129.3, 129.0, 127.8, 127.3, 125.7, 125.3, 116.4, 111.3, 110.2, 57.6, 48.7, 45.7, 29.7, 21.8. **HRMS** (ESI) m/z calcd for $C_{27}H_{23}BrNO_2$ $(M+H)^+$: 472.0907, found: 472.0905.

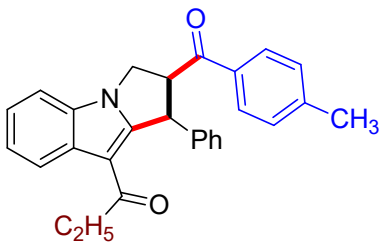


5-methyl-2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ja**).

White solid. Melting point: 204-205 °C. Isolated yield: 82%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.12 (d, J = 8.0 Hz, 1H), 7.83-7.81 (m, 2H), 7.33-7.27 (m, 5H), 7.17-7.10 (m, 3H), 7.02-7.00 (m, 1H), 5.04 (d, J = 2.8 Hz, 1H), 4.97-4.94 (m, 1H), 4.87-4.83 (m, 1H), 4.59-4.55 (m, 1H), 2.73 (s, 3H), 2.45 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.5, 192.7, 151.7, 145.2, 141.5, 132.2, 132.0, 131.2, 129.7, 129.2, 129.0, 127.6, 127.4, 124.5, 122.7, 121.0, 120.3, 110.5, 57.6, 48.3, 48.2, 29.9, 21.8, 18.2. **HRMS** (ESI) m/z calcd for $C_{28}H_{26}NO_2$ $(M+H)^+$: 408.1958, found: 408.1955.

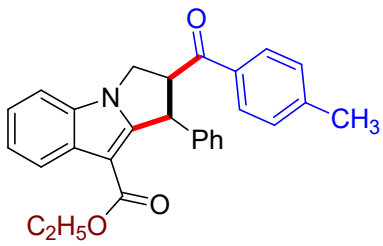


2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indole-9-carbaldehyde (**3ka**). White solid. Melting point: 194-195 °C. Isolated yield: 72%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.56 (s, 1H), 8.26-8.24 (m, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.34-7.29 (m, 6H), 7.27-7.24 (m, 4H), 5.21 (d, J = 5.9 Hz, 1H), 4.80-4.75 (m, 1H), 4.70-4.65 (m, 1H), 4.55-4.51 (m, 1H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 195.8, 183.9, 155.3, 145.3, 140.6, 132.7, 129.8, 129.7, 129.3, 128.9, 128.0, 127.8, 123.3, 123.2, 122.4, 110.3, 110.0, 58.2, 47.7, 47.0, 21.7. **HRMS** (ESI) m/z calcd for $C_{26}H_{22}NO_2$ $(M+H)^+$: 380.1645, found: 380.1642.

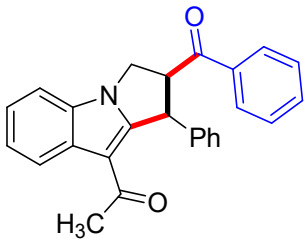


2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)propan-1-one (**3la**). White solid. Melting point: 121-123 °C. Isolated yield: 63%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.30-8.28 (m, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.36-7.27 (m, 8H), 7.12-7.10 (m, 2H), 5.13 (d, J = 1.4 Hz, 1H), 4.62-4.57 (m, 3H), 2.74-2.64 (m, 1H), 2.45 (s, 3H), 2.44-2.39 (m, 1H), 0.97 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.4, 195.8, 150.9, 145.1, 141.5, 132.4, 132.2, 130.9, 129.7, 129.2, 129.0, 127.6, 127.3, 122.7, 122.6, 122.5, 110.2, 110.0, 57.7, 48.8, 45.4, 34.5, 21.7, 8.0.

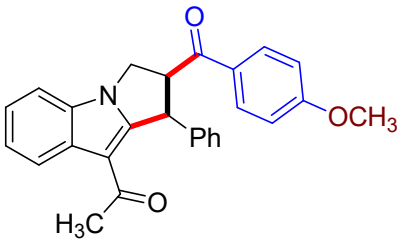
HRMS (ESI) m/z calcd for $C_{28}H_{26}NO_2$ $(M+H)^+$: 408.1958, found: 408.1960.



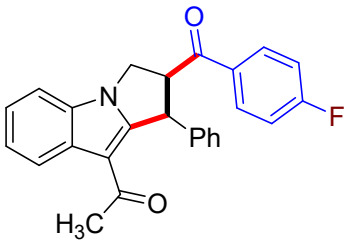
ethyl 2-(4-methylbenzoyl)-1-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carboxylate (**3ma**). White solid. Melting point: 109-110 °C. Isolated yield: 33%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.18-8.16 (m, 1H), 7.81-7.79 (m, 2H), 7.36-7.35 (m, 1H), 7.30-7.25 (m, 7H), 7.13-7.11 (m, 2H), 5.07 (d, J = 2.8 Hz, 1H), 4.64-4.58 (m, 3H), 4.10-4.00 (m, 2H), 2.44 (s, 3H), 1.02 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.5, 164.5, 151.4, 145.0, 142.1, 132.5, 132.3, 131.3, 129.6, 129.0, 128.8, 127.4, 127.2, 122.2, 122.0, 121.9, 110.1, 100.2, 59.1, 57.6, 48.5, 45.8, 21.7, 14.2. **HRMS** (ESI) m/z calcd for $C_{28}H_{26}NO_3$ $(M+H)^+$: 424.1907, found: 424.1903.



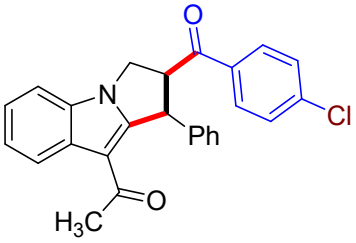
2-benzoyl-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ab**). White solid. Melting point: 187-188 °C. Isolated yield: 70%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.30-8.28 (m, 1H), 7.94-7.91 (m, 2H), 7.68-7.64 (m, 1H), 7.54-7.51 (m, 2H), 7.37-7.29 (m, 6H), 7.13-7.11 (m, 2H), 5.15 (d, J = 2.4 Hz, 1H), 4.67-4.61 (m, 3H), 2.22 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.7, 192.6, 151.2, 141.3, 134.7, 134.1, 132.3, 130.9, 129.2, 129.1, 128.9, 127.7, 127.4, 122.8, 122.7, 122.6, 110.6, 110.0, 57.8, 48.5, 45.5, 29.8. **HRMS** (ESI) m/z calcd for $C_{26}H_{22}NO_2$ $(M+H)^+$: 380.1645, found: 380.1649.



2-(4-methoxybenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ac**). White solid. Melting point: 166-168 °C. Isolated yield: 43%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.30-8.28 (m, 1H), 7.91-7.88 (m, 2H), 7.37-7.28 (m, 6H), 7.13-7.11 (m, 2H), 7.00-6.96 (m, 2H), 5.12 (m, 1H), 4.62-4.58 (m, 3H), 3.90 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 195.3, 192.7, 164.2, 151.4, 141.4, 132.3, 131.2, 131.0, 129.2, 128.7, 127.7, 127.4, 126.6, 122.7, 122.6, 114.2, 110.6, 110.0, 57.5, 55.6, 48.9, 45.7, 29.8. **HRMS** (ESI) m/z calcd for $C_{27}H_{24}NO_3$ $(M+H)^+$: 410.1751, found: 410.1753.

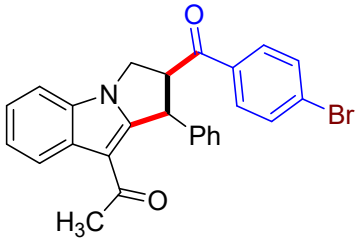


2-(4-fluorobenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ad**). White solid. Melting point: 157-158 °C. Isolated yield: 68%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27-8.25 (m, 1H), 7.96-7.92 (m, 2H), 7.38-7.28 (m, 6H), 7.21-7.17 (m, 2H), 7.12-7.10 (m, 2H), 2.22 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 195.2, 192.6, 166.3 (d, J = 255.4 Hz), 151.0, 141.2, 132.3, 131.7, 131.6, 131.2 (d, J = 3.0 Hz), 130.9, 129.3, 127.8, 127.3, 122.7 (d, J = 5.4 Hz), 122.5, 116.3 (d, J = 21.8 Hz), 110.6, 110.0, 57.7, 48.8, 45.4, 29.9. **HRMS** (ESI) m/z calcd for $C_{26}H_{21}FNO_2$ $(M+H)^+$: 398.1551, found: 398.1552.

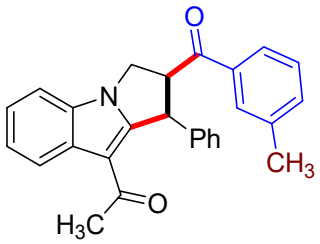


2-(4-chlorobenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ae**). White solid. Melting point: 172-174 °C. Isolated yield: 56%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27-

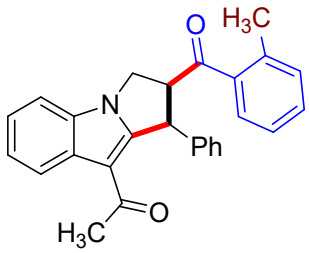
8.25 (m, 1H), 7.86-7.84 (m, 2H), 7.50-7.48 (m, 2H), 7.37-7.28 (m, 6H), 7.12-7.09 (m, 2H), 5.08 (m, 1H), 4.64-4.59 (m, 3H), 2.22 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 195.6, 192.6, 151.0, 141.1, 140.7, 133.1, 132.3, 130.9, 130.3, 129.4, 129.3, 127.8, 127.3, 122.8, 122.7, 122.5, 110.6, 110.0, 57.7, 48.7, 45.3, 29.9. **HRMS** (ESI) m/z calcd for $C_{26}H_{21}ClNO_2$ $(M+H)^+$: 414.1255, found: 414.1257.



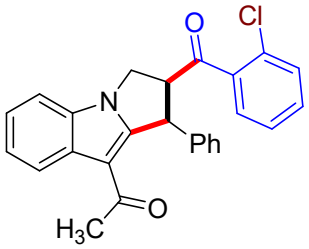
2-(4-bromobenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3af**). White solid. Melting point: 164-166 °C. Isolated yield: 62%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27-8.25 (m, 1H), 7.78-7.76 (m, 2H), 7.67-7.64 (m, 2H), 7.37-7.28 (m, 6H), 7.11-7.09 (m, 2H), 5.07 (m, 1H), 4.64-4.58 (m, 3H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 195.8, 192.6, 150.9, 141.1, 133.5, 132.4, 132.3, 130.9, 130.3, 129.5, 129.3, 127.8, 127.3, 122.8, 122.7, 122.5, 110.6, 110.0, 57.7, 48.7, 45.3, 29.9. **HRMS** (ESI) m/z calcd for $C_{26}H_{21}BrNO_2$ $(M+H)^+$: 458.0750, found: 458.0747.



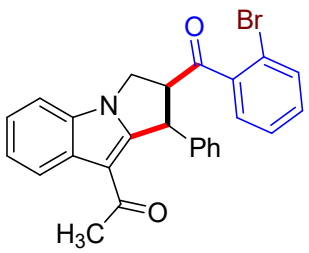
2-(3-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ag**). White solid. Melting point: 201-203 °C. Isolated yield: 90%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.30-8.28 (m, 1H), 7.71-7.70 (m, 2H), 7.47-7.45 (m, 1H), 7.42-7.28 (m, 7H), 7.12-7.10 (m, 2H), 5.13 (d, J = 2.5 Hz, 1H), 4.65-4.59 (m, 3H), 2.41 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.9, 192.6, 151.3, 141.4, 139.0, 134.9, 134.8, 132.3, 130.9, 129.5, 129.2, 128.9, 127.7, 127.4, 126.1, 122.7, 122.7, 122.6, 110.6, 110.0, 57.9, 48.6, 45.5, 29.8, 21.3. **HRMS** (ESI) m/z calcd for $C_{27}H_{24}NO_2$ $(M+H)^+$: 394.1802, found: 394.1801.



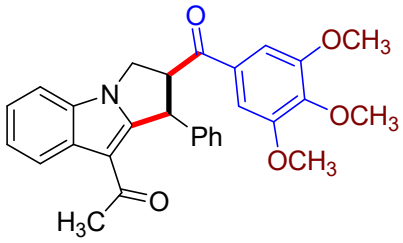
2-(2-methylbenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ah**). White solid. Melting point: 214-216 °C. Isolated yield: 50%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.32-8.30 (m, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.48 (td, J = 7.5, 1.1 Hz, 1H), 7.38-7.27 (m, 8H), 7.03-7.00 (m, 2H), 5.12 (d, J = 2.6 Hz, 1H), 4.64-4.49 (m, 3H), 2.46 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 199.9, 192.6, 151.0, 141.3, 139.8, 135.4, 132.5, 132.4, 132.3, 130.9, 129.2, 128.6, 127.6, 127.2, 126.0, 122.8, 122.7, 122.6, 110.7, 110.0, 60.3, 48.2, 45.0, 29.8, 21.5. **HRMS** (ESI) m/z calcd for $C_{27}H_{24}NO_2$ $(M+H)^+$: 394.1802, found: 394.1804.



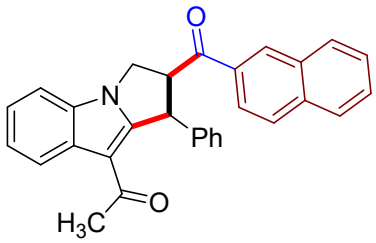
2-(2-chlorobenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ai**). White solid. Melting point: 176-178 °C. Isolated yield: 66%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.34-8.32 (m, 1H), 7.49-7.48 (m, 2H), 7.42-7.29 (m, 5H), 7.25-7.23 (m, 3H), 6.96-6.94 (m, 2H), 5.16 (d, J = 2.5 Hz, 1H), 4.65-4.59 (m, 2H), 4.52-4.46 (m, 1H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 200.0, 192.6, 150.5, 140.9, 137.5, 132.6, 132.5, 131.2, 130.9, 130.8, 129.3, 129.2, 127.6, 127.3, 127.0, 122.9, 122.8, 122.7, 110.9, 110.0, 61.9, 48.2, 44.7, 29.7. **HRMS** (ESI) m/z calcd for $C_{26}H_{21}ClNO_2$ $(M+H)^+$: 414.1255, found: 414.1254.



2-(2-bromobenzoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3aj**). White solid. Melting point: 181-182 °C. Isolated yield: 72%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.35-8.33 (m, 1H), 7.70-7.68 (m, 1H), 7.43-7.40 (m, 2H), 7.38-7.30 (m, 5H), 7.25-7.24 (m, 2H), 6.95-6.92 (m, 2H), 5.16 (d, J = 2.8 Hz, 1H), 4.69-4.65 (m, 1H), 4.59-4.55 (m, 1H), 4.49-4.44 (m, 1H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 200.7, 192.6, 150.4, 140.8, 139.8, 134.0, 132.5, 132.4, 130.8, 129.2, 128.8, 127.7, 127.6, 127.0, 122.9, 122.8, 122.7, 119.3, 110.9, 110.0, 61.8, 48.1, 44.5, 29.7. **HRMS** (ESI) m/z calcd for $C_{26}H_{21}BrNO_2$ $(M+H)^+$: 458.0750, found: 458.0751.

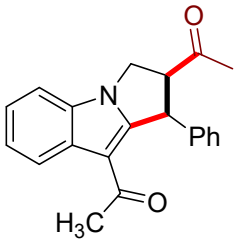


1-phenyl-2-(3,4,5-trimethoxybenzoyl)-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3ak**). White solid. Melting point: 184-186 °C. Isolated yield: 63%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.26-8.24 (m, 1H), 7.41-7.39 (m, 1H), 7.35-7.30 (m, 5H), 7.17-7.16 (m, 2H), 7.12 (s, 2H), 5.02 (d, J = 2.9 Hz, 1H), 4.73-4.70 (m, 1H), 4.65-4.56 (m, 2H), 3.96 (s, 3H), 3.82 (s, 6H), 2.23 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 195.7, 192.5, 153.3, 151.0, 143.3, 141.4, 132.3, 130.9, 129.9, 129.2, 127.8, 127.6, 122.7, 122.6, 122.4, 110.6, 110.1, 106.3, 61.0, 57.4, 56.2, 49.4, 45.5, 29.9. **HRMS** (ESI) m/z calcd for $C_{29}H_{28}NO_5$ $(M+H)^+$: 470.1962, found: 470.1959.

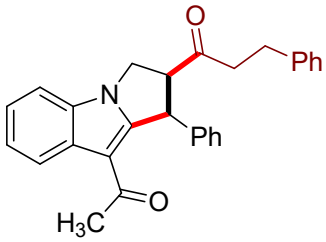


2-(2-naphthoyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethanone (**3al**). White solid. Melting point: 221-222 °C. Isolated yield: 53%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 8.31-8.29 (m, 1H), 8.04-8.01 (m, 1H), 7.97-7.88 (m, 3H), 7.68-7.65 (m, 1H), 7.61-7.58 (m, 1H), 7.39-7.29 (m, 6H), 7.17-7.14 (m, 2H), 5.17 (d, J = 2.9 Hz, 1H)), 4.84-4.81 (m, 1H), 4.74-4.64 (m, 2H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.7, 192.7, 151.2, 141.4, 135.9, 132.5, 132.4, 132.0, 131.0, 130.9, 129.6, 129.3, 129.1, 129.0, 127.9, 127.8, 127.5, 127.2, 124.2, 122.8,

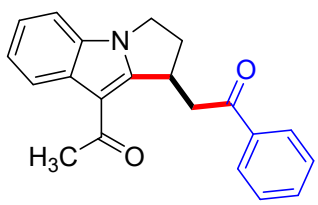
122.7, 122.6, 110.6, 110.0, 57.9, 49.0, 45.5, 29.8. **HRMS** (ESI) m/z calcd for $C_{30}H_{24}NO_2$ $(M+H)^+$: 430.1802, found: 430.1805.



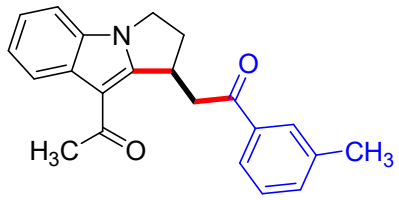
1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indole-2,9-diyl)diethanone (**3am**). White solid. Melting point: 205-207 °C. Isolated yield: 35%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.28-8.26 (m, 1H), 7.38-7.27 (m, 6H), 7.14-7.12 (m, 2H), 5.06 (d, J = 3.3 Hz, 1H), 4.56-4.52 (m, 1H), 4.45-4.40 (m, 1H), 3.85-3.81 (m, 1H), 2.36 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 204.3, 192.6, 150.6, 141.4, 132.3, 130.8, 129.2, 127.7, 127.1, 122.8, 122.7, 122.5, 110.8, 110.0, 63.3, 47.9, 44.3, 29.8, 28.7. **HRMS** (ESI) m/z calcd for $C_{21}H_{20}NO_2$ $(M+H)^+$: 318.1489, found: 318.1487.



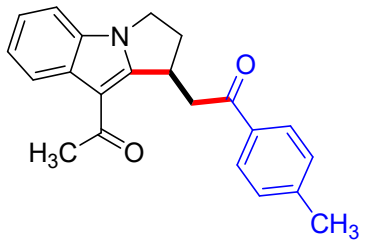
9-acetyl-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-2-yl)-3-phenylpropan-1-one (**3an**). Yellow oil. Isolated yield: 40%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.29-8.28 (m, 1H), 7.30-7.26 (m, 8H), 7.23-7.21 (m, 1H), 7.17-7.15 (m, 2H), 7.03-7.01 (m, 2H), 4.84 (d, J = 3.3 Hz, 1H), 4.40-4.30 (m, 2H), 3.75-3.72 (m, 1H), 3.02-2.95 (m, 3H), 2.90-2.82 (m, 1H), 2.12 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 205.8, 192.6, 150.5, 141.3, 140.5, 132.3, 130.8, 129.2, 128.7, 128.4, 127.7, 127.0, 126.5, 122.8, 122.7, 122.6, 110.7, 110.0, 62.7, 47.7, 44.2, 43.5, 29.8, 29.8. **HRMS** (ESI) m/z calcd for $C_{28}H_{26}NO_2$ $(M+H)^+$: 408.1958, found: 408.1955.



2-(9-acetyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-1-phenylethan-1-one (**5a**). Yellow solid. Melting point: 100-102 °C. Isolated yield: 52%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 – 8.02 (m, 2H), 8.00 – 7.93 (m, 1H), 7.60-7.54 (m, 1H), 7.50-7.44 (m, 2H), 7.34 – 7.22 (m, 3H), 4.28 – 4.12 (m, 3H), 4.02 (dd, *J* = 17.0, 2.8 Hz, 1H), 3.15 (dd, *J* = 17.0, 10.6 Hz, 1H), 3.03 – 2.89 (m, 1H), 2.67 (s, 3H), 2.52-2.41 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 198.6, 193.4, 155.2, 136.4, 133.3, 132.6, 130.2, 128.7, 128.3, 122.2, 122.1, 121.0, 110.5, 110.0, 43.4, 41.3, 35.6, 32.6, 30.5. **HRMS** (ESI) m/z calcd for $C_{22}H_{21}NO_2$ $(M+H)^+$: 332.1645, found: 332.1641.

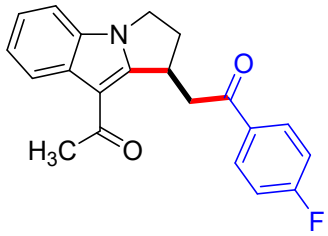


2-(9-acetyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-1-(m-tolyl)ethan-1-one (**5b**). Yellow solid. Melting point: 122-125 °C. Isolated yield: 51%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04-7.92 (m, 1H), 7.92-7.79 (m, 2H), 7.44-7.19 (m, 5H), 4.30-4.11 (m, 3H), 3.97 (dd, *J* = 17.1, 2.8 Hz, 1H), 3.18 (dd, *J* = 17.1, 10.5 Hz, 1H), 3.03-2.83 (m, 1H), 2.67 (s, 3H), 2.53-2.36 (m, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 198.7, 193.3, 155.2, 138.4, 136.5, 134.0, 132.6, 130.2, 128.7, 128.6, 125.5, 122.1, 122.0, 121.0, 110.4, 110.0, 43.4, 41.3, 35.5, 32.6, 30.4, 21.3. **HRMS** (ESI) m/z calcd for $C_{22}H_{21}NO_2$ $(M+H)^+$: 332.1645, found: 332.1644.

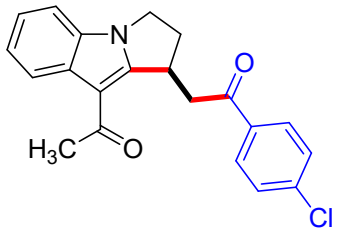


2-(9-acetyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-1-(*p*-tolyl)ethan-1-one (**5c**). Yellow solid. Melting point: 130-132 °C. Isolated yield: 73%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02-7.92 (m, 3H), 7.37-7.22 (m, 5H), 4.28-4.11 (m, 3H), 3.97 (dd, *J* = 16.8, 2.8 Hz, 1H), 3.12 (dd, *J* = 16.9, 10.6 Hz, 1H), 3.01-2.88 (m, 1H), 2.67 (s, 3H), 2.51-2.38 (m, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 198.2, 193.2, 155.2, 144.1, 134.0, 132.6, 130.2, 129.3, 128.4, 122.1, 122.0, 121.0, 110.4, 110.0, 43.4, 41.2, 35.6, 32.6, 30.4, 21.6. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}NO_2$ $(M+H)^+$: 318.1489, found:

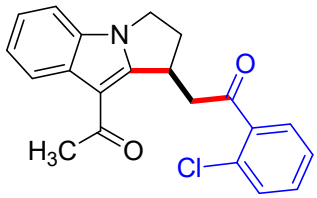
318.1482.



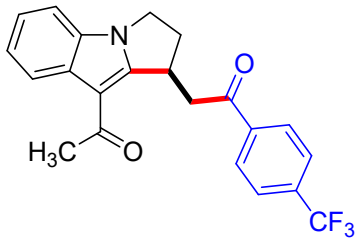
2-(9-acetyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)-1-(4-fluorophenyl)ethanone (**5d**). Yellow solid. Melting point: 116-118 °C. Isolated yield: 61%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 2H), 7.95 – 7.93 (m, 1H), 7.33 – 7.24 (m, 3H), 7.17 – 7.12 (m, 2H), 4.23 – 4.14 (m, 3H), 4.02 (dd, *J* = 16.6, 2.8 Hz, 1H), 3.07 (dd, *J* = 16.6, 10.6 Hz, 1H), 2.99-2.89 (m, 1H), 2.68 (s, 3H), 2.51 – 2.45 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.1, 193.4, 165.8 (d, $J_{C\text{-}F}$ = 253.5 Hz), 155.0, 132.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 132.6, 131.0 (d, $J_{C\text{-}F}$ = 9.3 Hz), 130.1, 122.1 (d, $J_{C\text{-}F}$ = 11.6 Hz), 120.9, 115.7 (d, $J_{C\text{-}F}$ = 21.8 Hz), 110.5, 109.9, 43.41, 41.12, 35.70, 32.41, 30.51. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}FNO_2$ $(M+H)^+$: 336.1394, found: 336.1392.



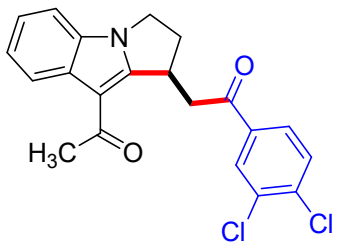
2-(9-acetyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)-1-(4-chlorophenyl)ethanone (**5e**). Yellow solid. Melting point: 115-117 °C. Isolated yield: 64%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 7.1 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.26 (m, 3H), 4.26-4.14 (m, 3H), 4.03 (dd, *J* = 16.8, 2.7 Hz, 1H), 3.11 (dd, *J* = 16.8, 10.5 Hz, 1H), 3.01-2.91 (m, 1H), 2.69 (s, 3H), 2.51 – 2.44 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.59, 193.45, 154.99, 139.78, 134.80, 132.65, 130.18, 129.81, 129.02, 122.21, 122.10, 120.94, 110.56, 110.06, 43.49, 41.24, 35.70, 32.50, 30.55. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}ClNO_2$ $(M+H)^+$: 352.1099, found: 352.1098.



2-(9-acetyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-1-(2-chlorophenyl)ethan-1-one (**5f**). Yellow solid. Melting point: 148-151 °C. Isolated yield: 18%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99-7.87 (m, 1H), 7.63-7.54 (m, 1H), 7.42-7.35 (m, 2H), 7.35-7.24 (m, 4H), 4.27-4.11 (m, 3H), 3.90 (dd, *J* = 18.1, 2.9 Hz, 1H), 3.29 (dd, *J* = 18.1, 10.3 Hz, 1H), 3.08-3.95 (m, 1H), 2.64 (s, 3H), 2.57-2.47 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 201.5, 193.3, 154.7, 138.6, 132.6, 131.8, 130.8, 130.6, 130.2, 129.0, 127.0, 122.1, 122.0, 121.0, 110.4, 110.0, 45.1, 43.5, 35.3, 32.8, 30.4. **HRMS** (ESI) m/z calcd for $C_{21}H_{18}ClNO_2$ $(M+H)^+$: 352.1099, found: 352.1093.

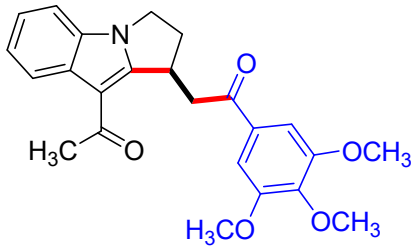


2-(9-acetyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)-1-(4-(trifluoromethyl)phenyl)ethanone (**5g**). Yellow solid. Melting point: 135-137 °C. Isolated yield: 32%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.1 Hz, 2H), 7.94 – 7.91 (m, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.24 (m, 3H), 4.25 – 4.15 (m, 3H), 4.10 (dd, *J* = 16.8, 2.8 Hz, 1H), 3.15 (dd, *J* = 16.8, 10.3 Hz, 1H), 3.02 – 2.92 (m, 1H), 2.69 (s, 3H), 2.51 – 2.44 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.9, 193.5, 154.8, 139.0, 134.5 (d, *J* = 32.5 Hz), 132.6, 130.1, 128.7, 125.7 (q, *J* = 3.6 Hz), 124.9, 122.2 (d, *J* = 11.5 Hz), 120.9, 110.6, 110.1, 43.49, 41.50, 35.57, 32.43, 30.57. **HRMS** (ESI) m/z calcd for $C_{22}H_{19}F_3NO_2$ $(M+H)^+$: 386.1362, found: 386.1353.

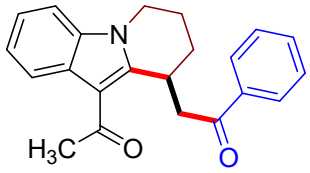


2-(9-acetyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)-1-(3,4-dichlorophenyl)ethanone (**5h**).

Yellow solid. Melting point: 117-119 °C. Isolated yield: 33%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (d, J = 1.9 Hz, 1H), 7.98-7.93 (m, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.36 – 7.24 (m, 3H), 4.28 – 4.13 (m, 3H), 4.03 (dd, J = 16.8, 2.8 Hz, 1H), 3.13 (dd, J = 16.8, 10.4 Hz, 1H), 3.03 – 2.93 (m, 1H), 2.71 (s, 3H), 2.51 – 2.44 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.6, 193.5, 154.7, 137.8, 135.9, 133.4, 132.6, 130.8, 130.3, 130.1, 127.5, 122.2, 122.1, 120.9, 110.6, 110.1, 43.5, 41.2, 35.5, 32.4, 30.6. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}Cl_2NO_2$ $(M+H)^+$: 386.0709, found: 386.0706.

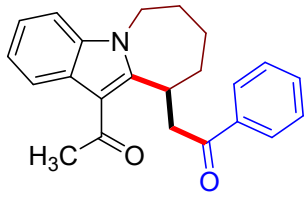


2-(9-acetyl-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-1-yl)-1-(3,4,5-trimethoxyphenyl)ethanone (**5i**). White solid. Melting point: 169-171 °C. Isolated yield: 22%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.2 Hz, 1H), 7.43 (s, 2H), 7.36-7.26 (m, 3H), 4.26-4.17 (m, 3H), 4.02-3.94 (m, 10H), 3.05 (dd, J = 16.0, 10.7 Hz, 1H), 2.95 – 2.89 (m, 1H), 2.69 (s, 3H), 2.56-2.50 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.7, 193.3, 155.1, 153.2, 142.6, 132.6, 131.6, 130.2, 122.2, 122.1, 121.0, 110.6, 110.0, 105.9, 61.0, 56.4, 43.4, 41.1, 36.2, 32.2, 30.6. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}NO_5$ $(M+H)^+$: 408.1805, found: 408.1797.

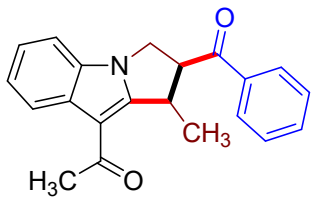


2-(10-acetyl-6,7,8,9-tetrahydropyrido[1,2-a]indol-9-yl)-1-phenylethanone (**5j**). White solid. Melting point: 143-144 °C. Isolated yield: 43%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20-8.18 (m, 2H), 7.96 (dd, J = 7.0, 1.3 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.54 – 7.50 (m, 2H), 7.41-7.29 (m, 3H), 4.53 – 4.49 (m, 1H), 4.39 – 4.34 (m, 1H), 3.94 (td, J = 12.0, 5.3 Hz, 1H), 3.80 (dd, J = 16.2, 2.4 Hz, 1H), 3.15 (dd, J = 16.2, 10.8 Hz, 1H), 2.74 (s, 3H), 2.30 – 2.21 (m, 1H), 2.11 – 2.01 (m, 2H), 1.96 – 1.88 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 198.6, 193.7, 149.2, 136.7, 136.2, 133.1, 128.7, 128.5, 126.3, 122.5, 122.0, 120.5, 112.3, 109.8, 42.6, 42.1, 31.7, 30.0, 23.7, 17.8.

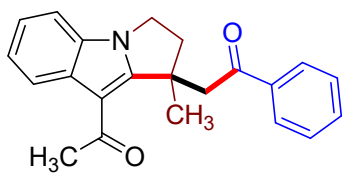
HRMS (ESI) m/z calcd for $C_{22}H_{22}NO_2$ $(M+H)^+$: 332.1645, found: 332.1647.



2-(11-acetyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indol-10-yl)-1-phenylethanone (**5k**). Yellow oil. Isolated yield: 34%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 – 8.13 (m, 2H), 7.94 – 7.92 (m, 1H), 7.62-7.58 (m, 1H), 7.54 – 7.50 (m, 2H), 7.42-7.40 (m, 1H), 7.33 – 7.26 (m, 2H), 5.26-5.20 (m, 1H), 4.68 – 4.63 (m, 1H), 4.19 – 4.12 (m, 1H), 3.52-3.38 (m, 2H), 2.73 (s, 3H), 2.16 – 2.01 (m, 3H), 1.85 – 1.76 (m, 2H), 1.68-1.59 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 198.6, 195.4, 150.7, 136.5, 136.3, 133.3, 128.7, 128.6, 126.0, 122.2, 121.8, 120.9, 114.1, 109.6, 44.8, 32.0, 32.0, 29.7, 28.9, 28.2, 23.8. **HRMS** (ESI) m/z calcd for $C_{23}H_{24}NO_2$ $(M+H)^+$: 346.1802, found: 346.1803.

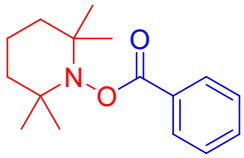


2-benzoyl-1-methyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (**5l**). White solid. Melting point: 167-168 °C. Isolated yield: 12%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04-7.99 (m, 3H), 7.69-7.65 (m, 1H), 7.58-7.55 (m, 2H), 7.38-7.35 (m, 1H), 7.32-7.26 (m, 2H), 4.76-4.71 (m, 1H), 4.42 – 4.37 (m, 2H), 4.03-3.97 (m, 1H), 2.62 (s, 3H), 1.70 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.2, 192.9, 154.2, 137.5, 135.0, 133.9, 132.2, 130.3, 129.1, 128.6, 122.2, 121.4, 110.4, 110.0, 55.3, 44.3, 38.9, 30.1, 19.4. **HRMS** (ESI) m/z calcd for $C_{21}H_{20}NO_2$ $(M+H)^+$: 318.1489, found: 318.1487.



2-(9-acetyl-1-methyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-yl)-1-phenylethanone (**5m**). White solid. Melting point: 132-133 °C. Isolated yield: 54%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95

(d, J = 6.0 Hz, 2H), 7.84-7.83 (m, 1H), 7.52-7.49 (m, 1H), 7.42-7.39 (m, 2H), 7.33-7.31 (m, 1H), 7.27-7.22 (m, 2H), 4.39-4.34 (m, 1H), 4.22-4.17 (m, 2H), 3.81 (d, J = 14.2 Hz, 1H), 2.96 – 2.91 (m, 1H), 2.66 (s, 3H), 2.61-2.55 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.7, 193.9, 159.1, 137.7, 133.4, 132.6, 130.9, 128.9, 128.5, 122.3, 122.1, 121.2, 111.1, 109.7, 46.3, 44.2, 43.2, 41.0, 31.7, 25.4. **HRMS** (ESI) m/z calcd for $C_{22}H_{22}NO_2$ $(M+H)^+$: 332.1645, found: 332.1646.



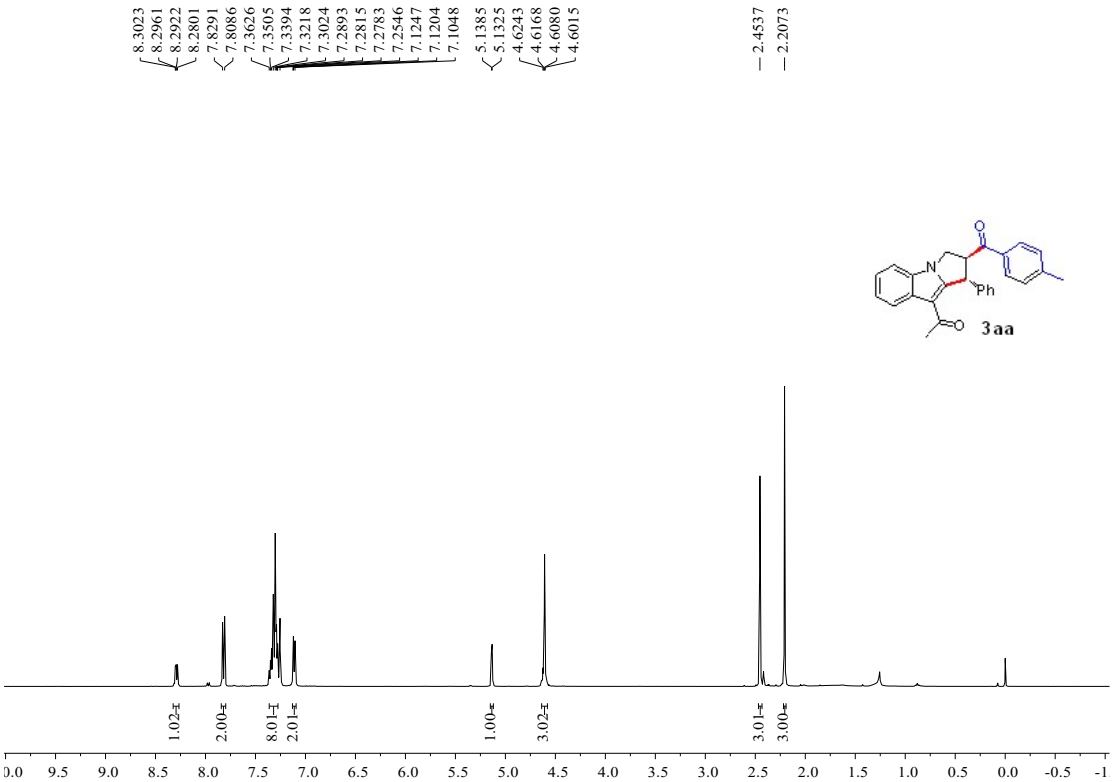
2,2,6,6-tetramethylpiperidin-1-yl benzoate(**6**). White solid. Melting point: 87-88 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.09-8.07 (m, 2H), 7.60-7.56 (m, 1H), 7.49-7.45 (m, 2H), 1.82-1.68 (m, 3H), 1.61-1.57 (m, 2H), 1.49-1.44 (m, 1H), 1.28 (s, 6H), 1.12 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.4, 132.8, 129.6, 129.5, 128.4, 60.4, 39.0, 31.9, 20.8, 17.0. **HRMS** (ESI) m/z calcd for $C_{16}H_{24}NO_2$ $(M+H)^+$: 262.1802. found: 262.1800.

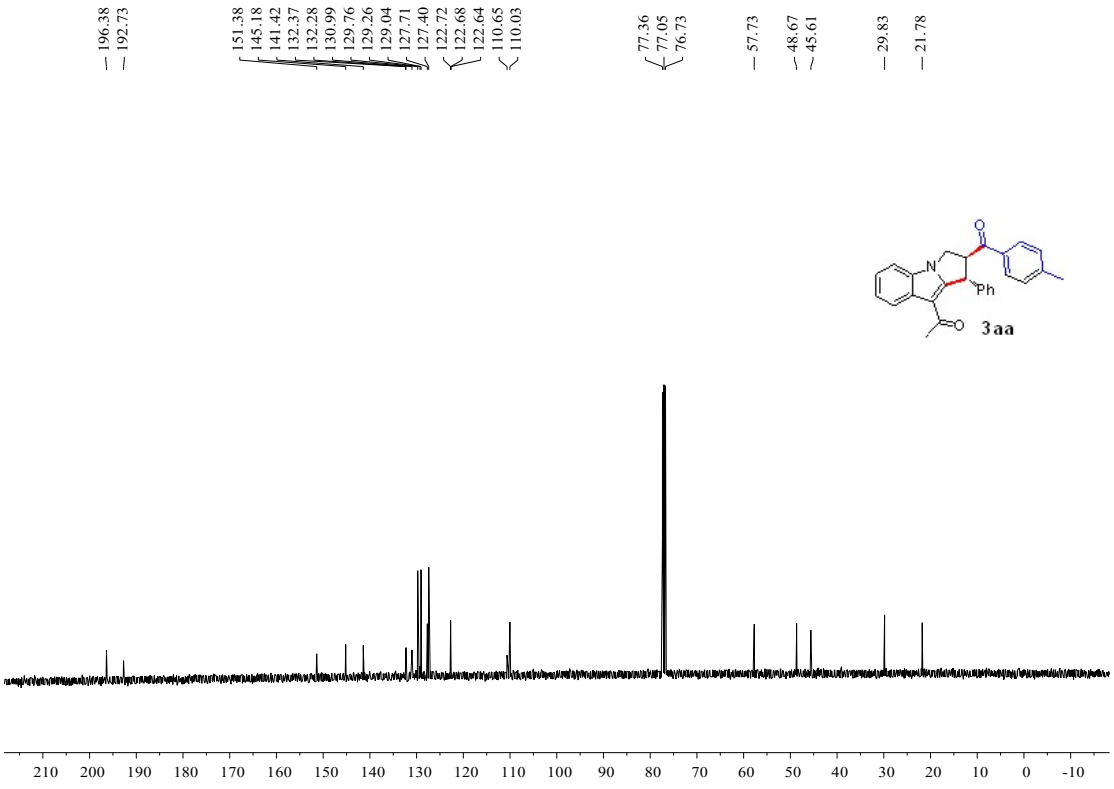
References

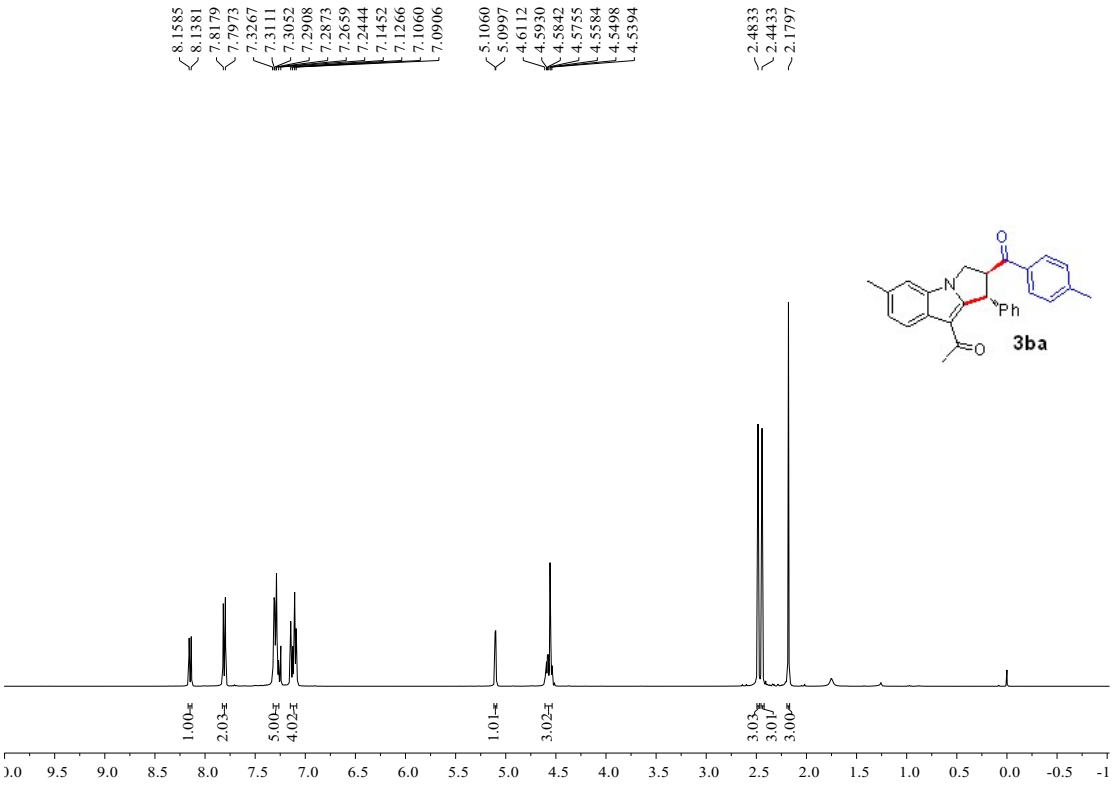
1. Wadhwa. K.; Yang C. X.; West P. R.; Deming K. C.; Chemburkar S. R.; Reddy. R. E. *Synth. Commun*. **2008**, *38*, 4434.

2. Okauchi, T.; Itonaga, M.; Minami, T.; Owa, T.; Kitoh, K.; Yoshino, H. *Org. Lett*. **2000**, *2*, 1485.

Copies of ^{1}H and ^{13}C NMR Spectra



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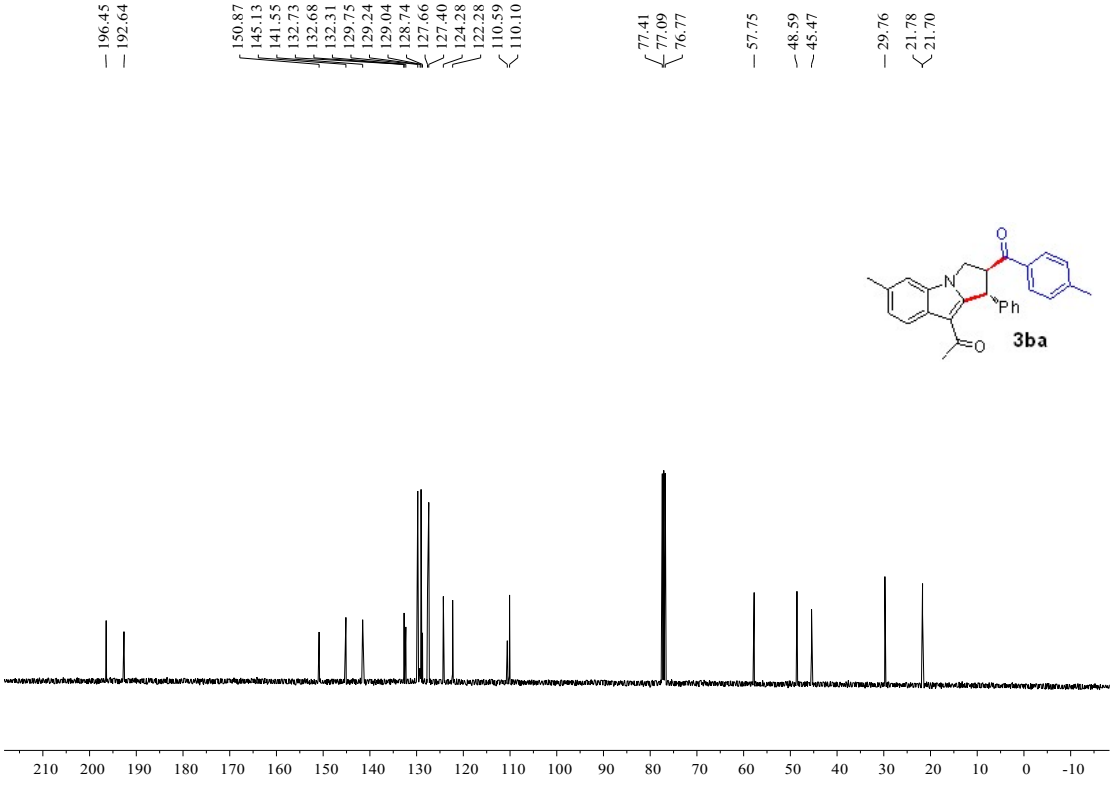
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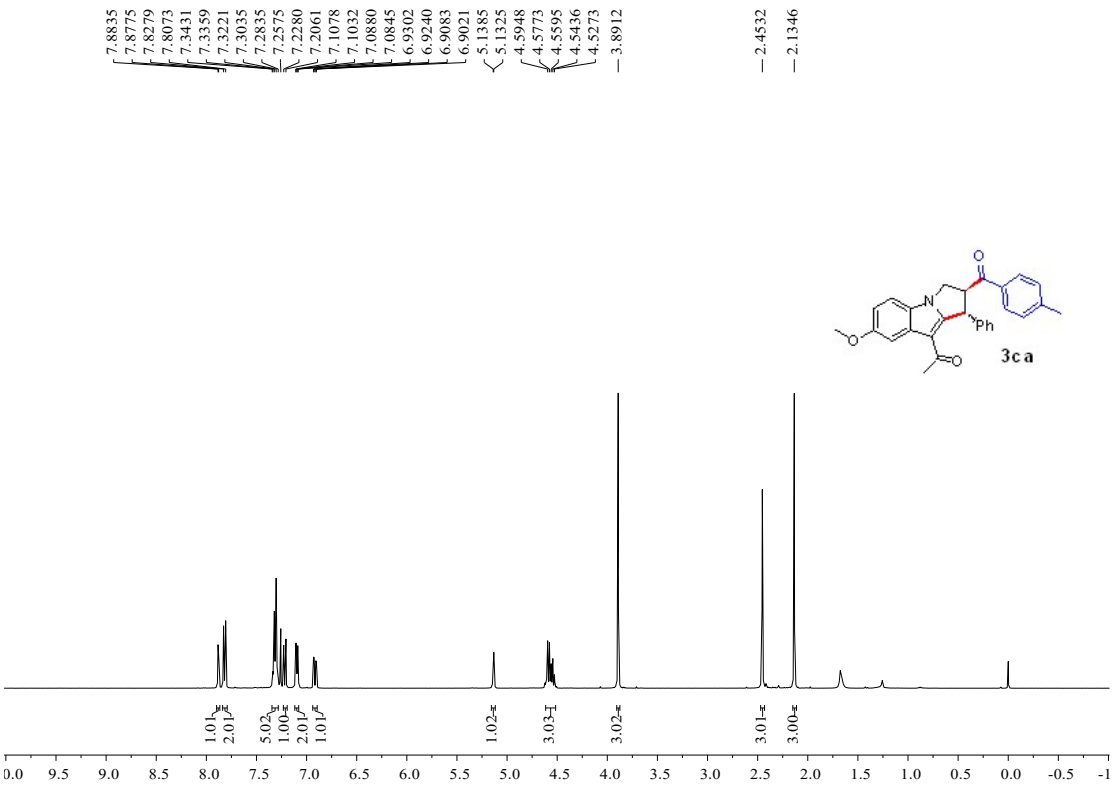
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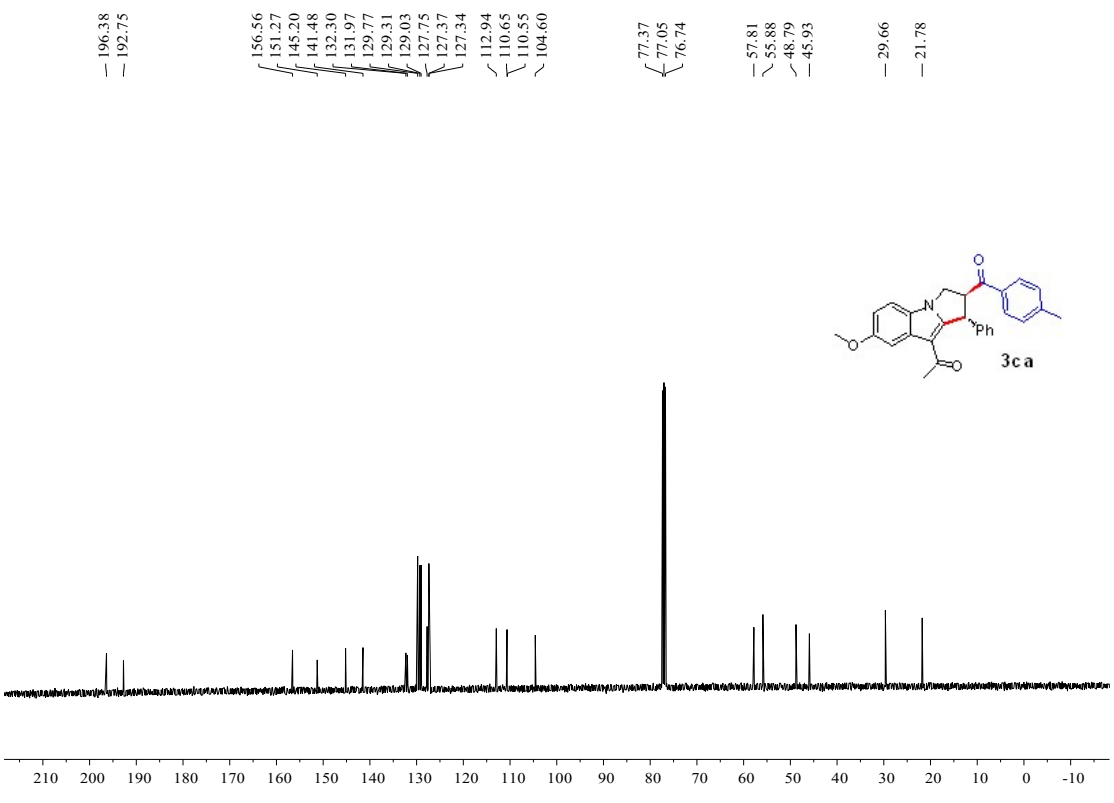
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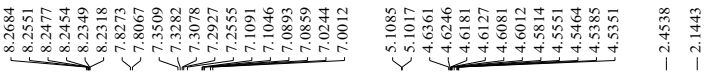
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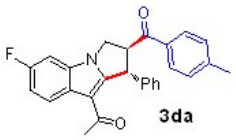
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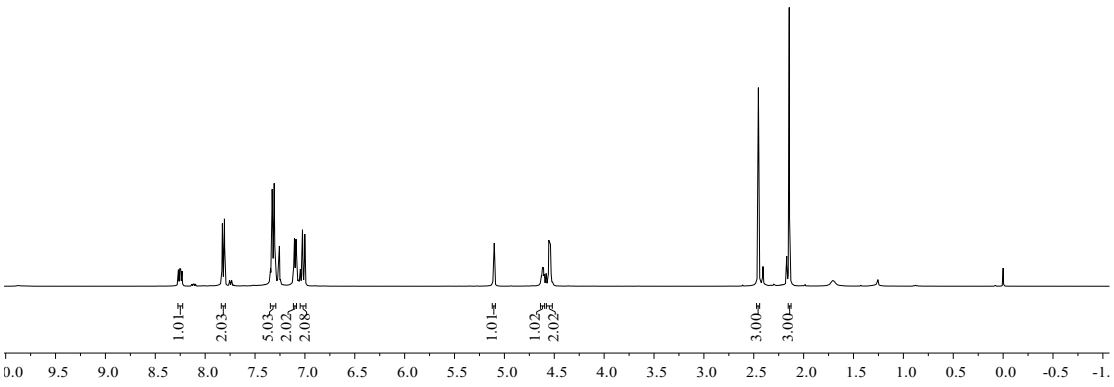
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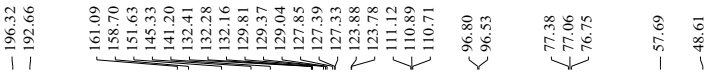
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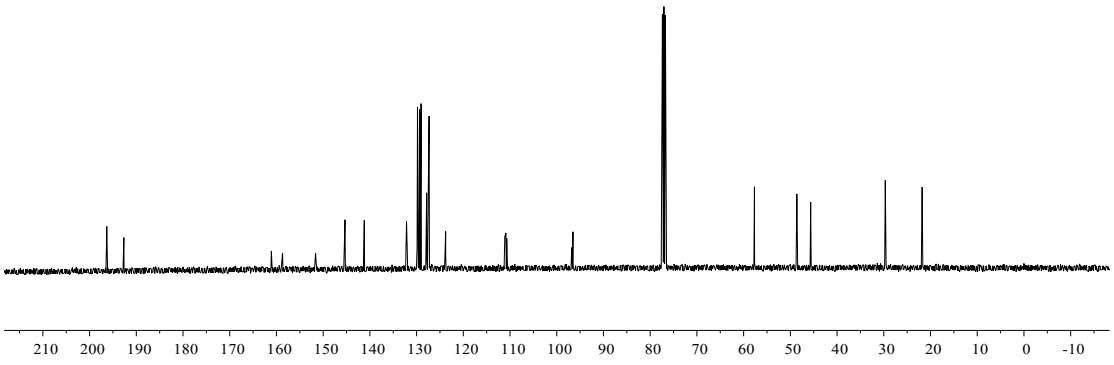
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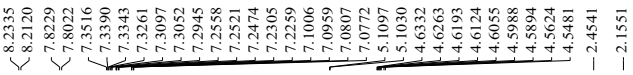
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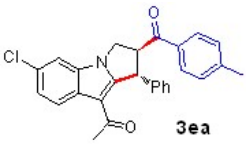
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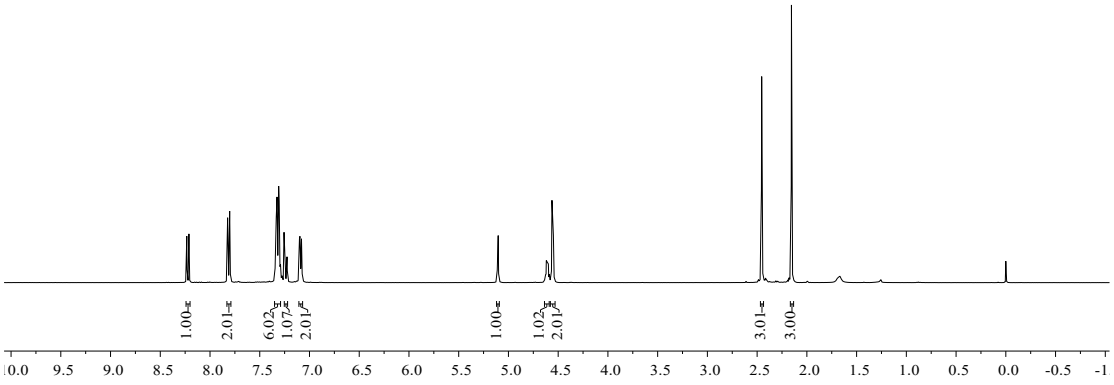
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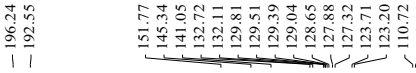
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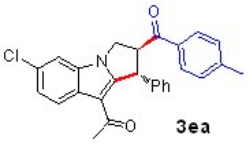
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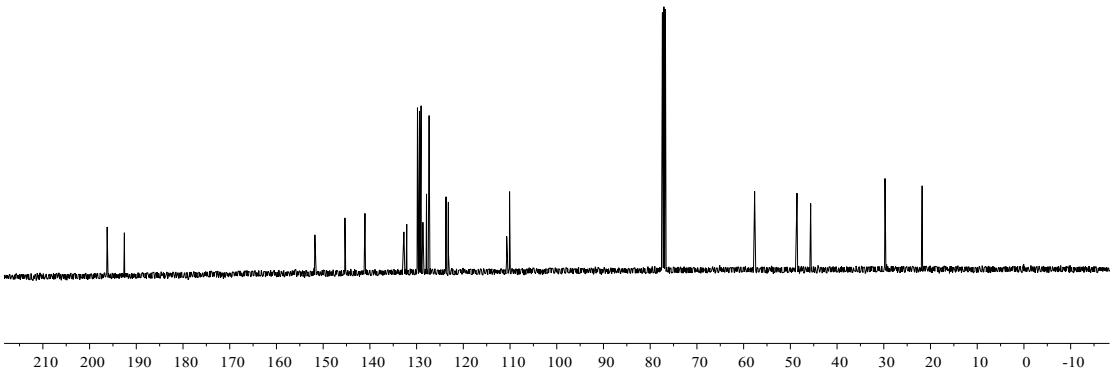
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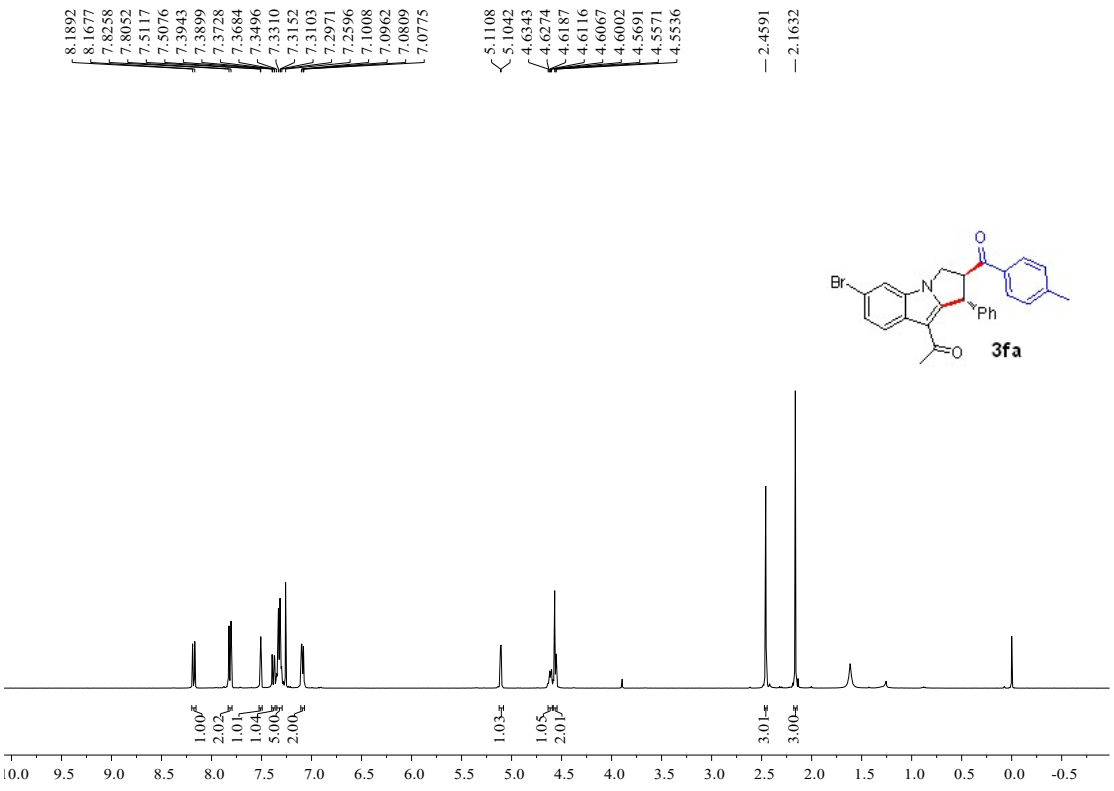
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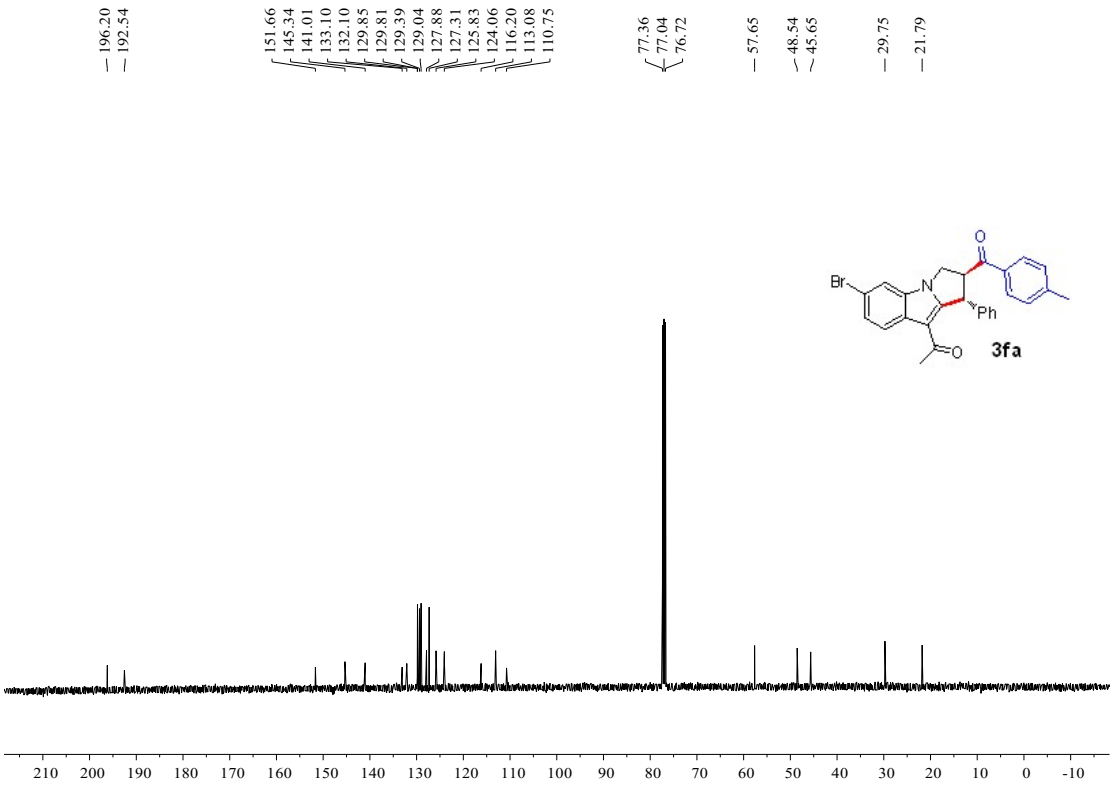
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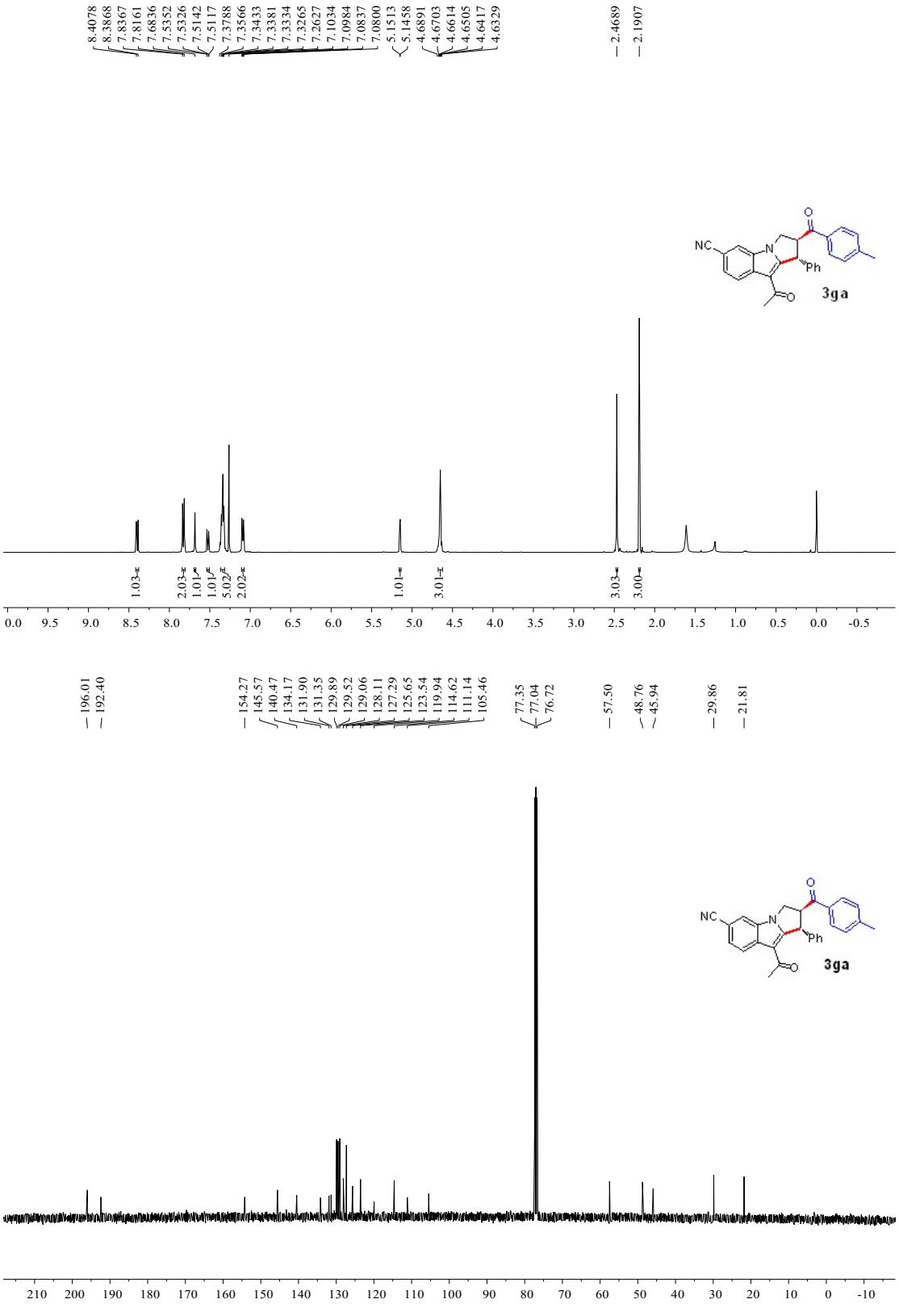
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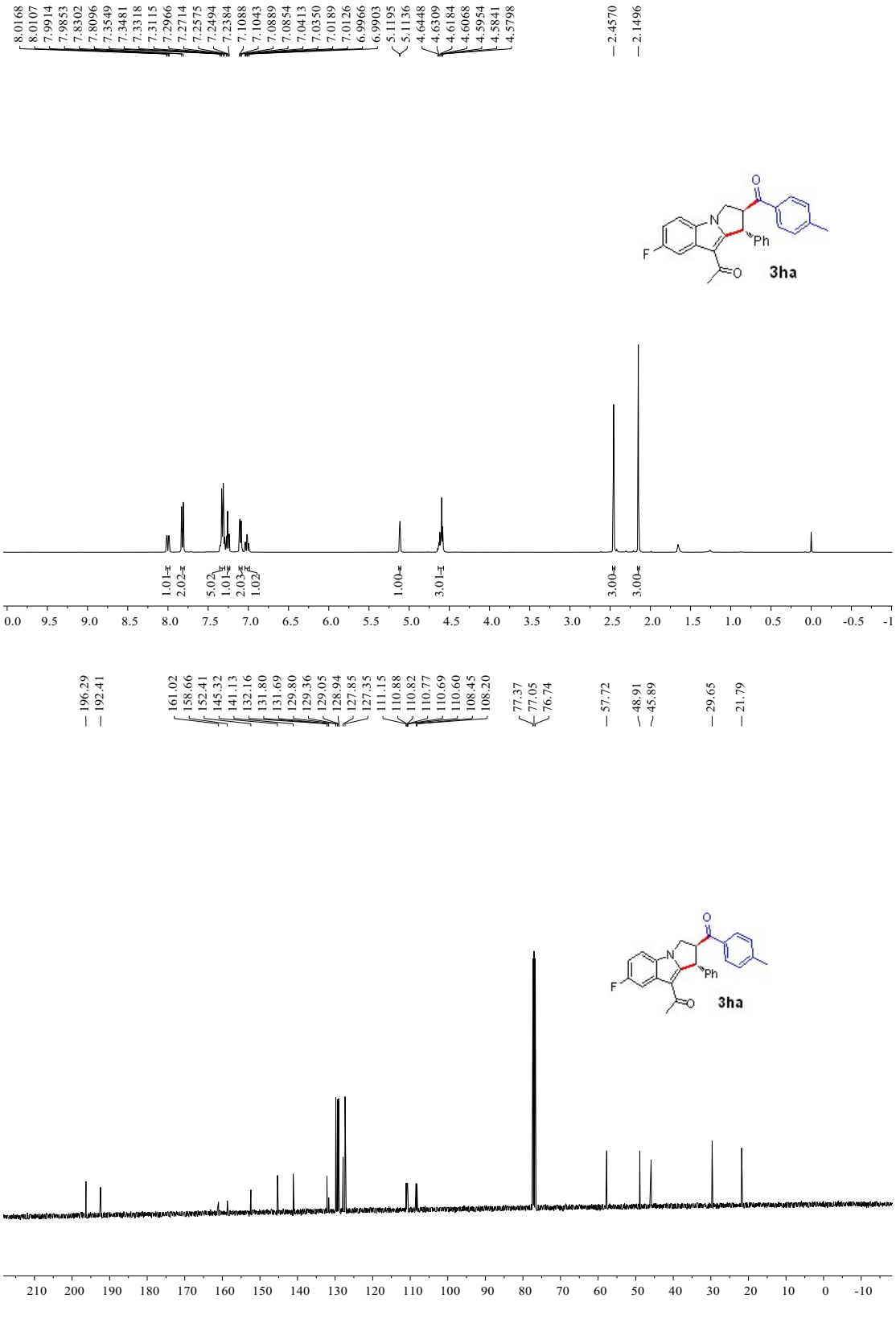
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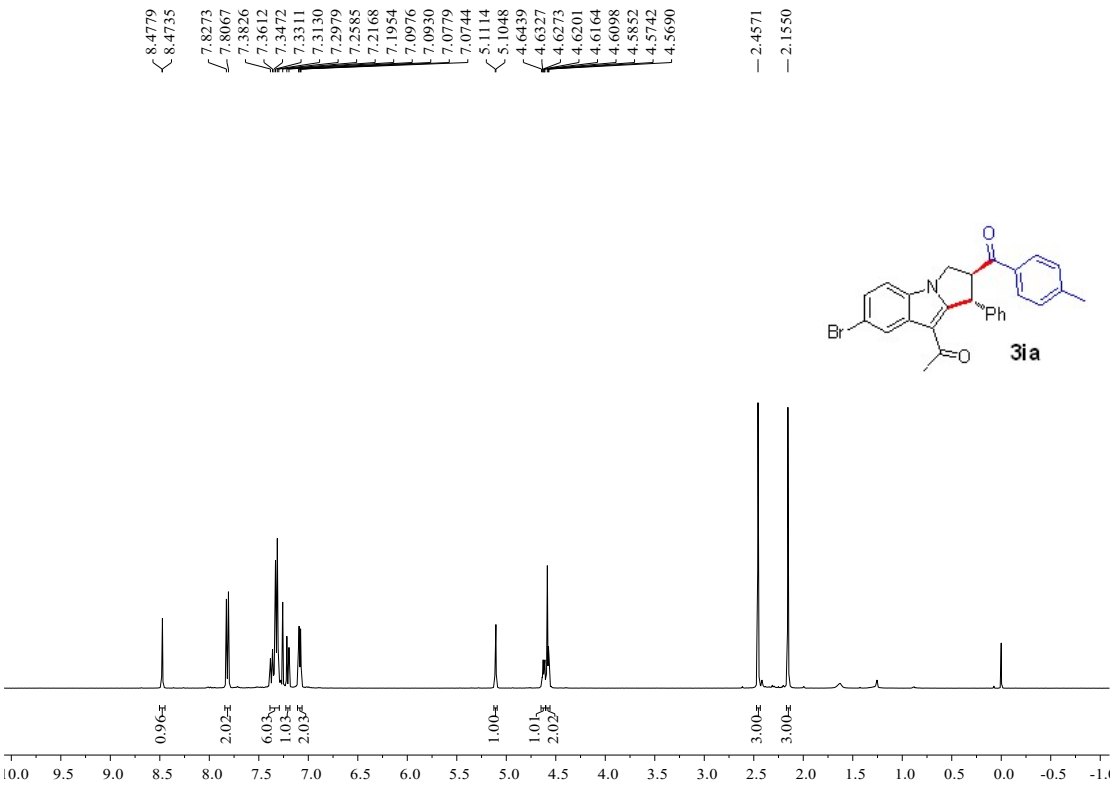
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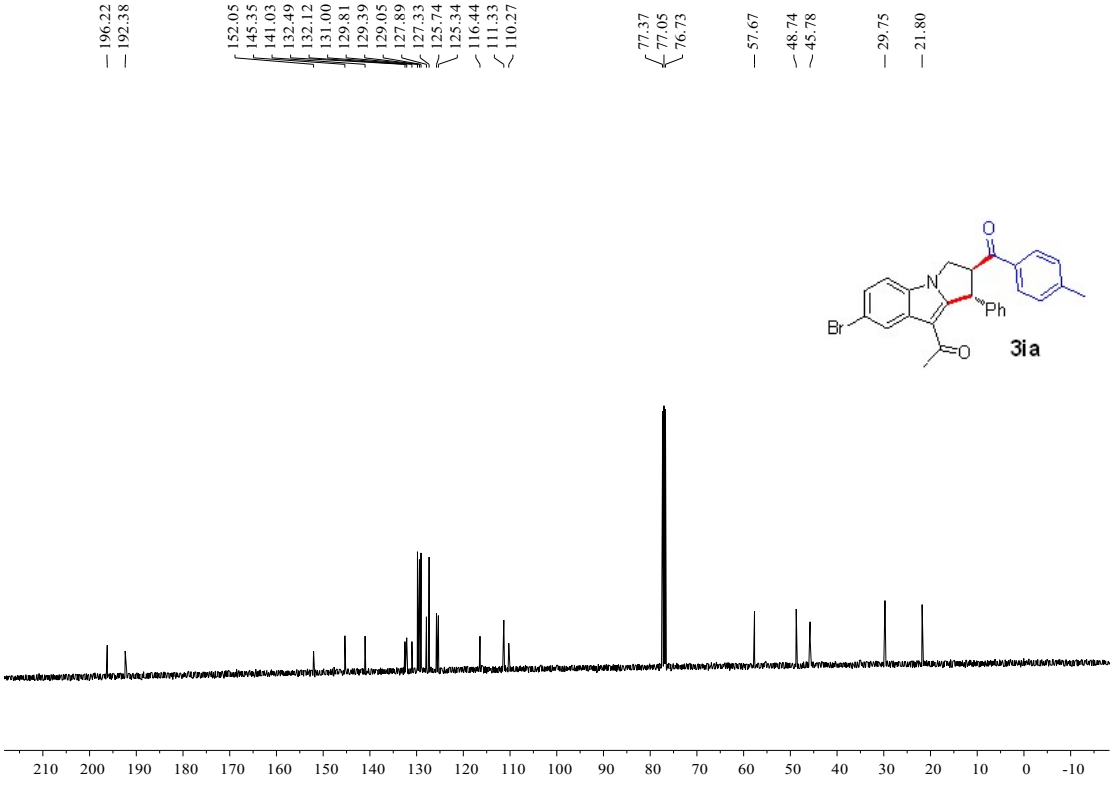
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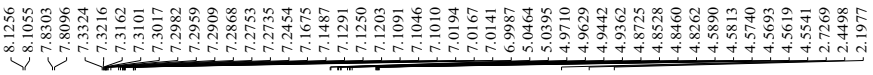
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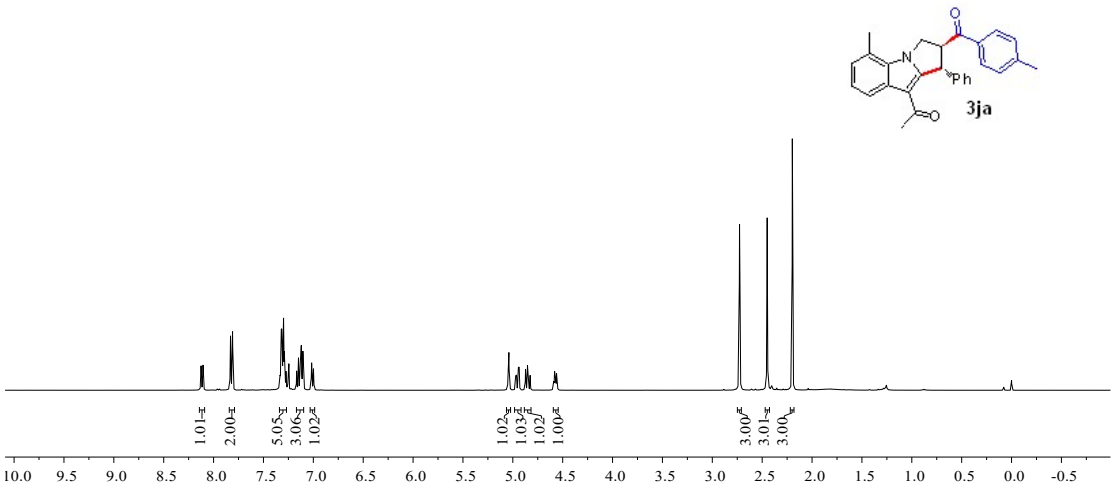
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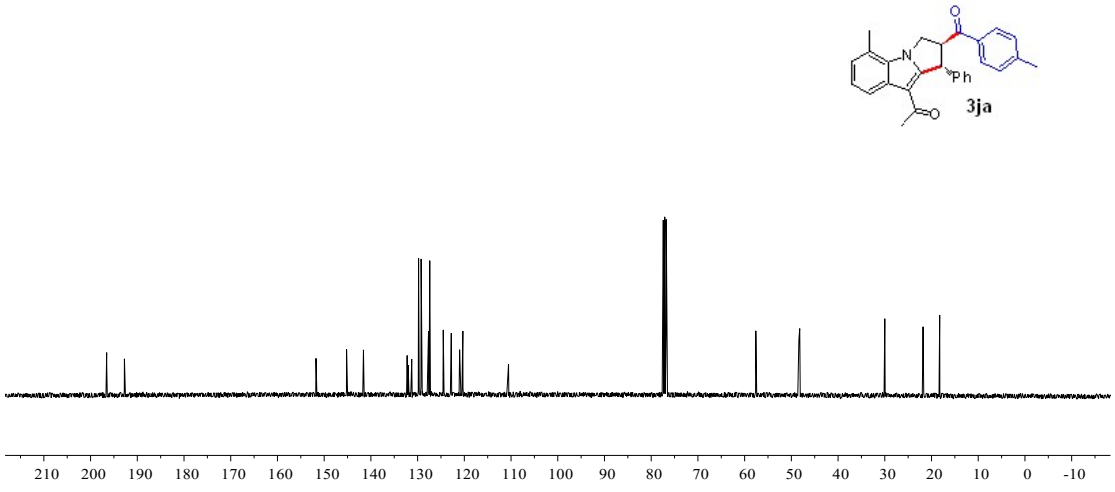
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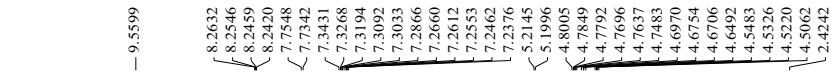
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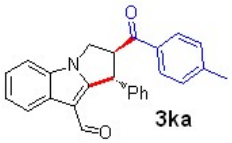
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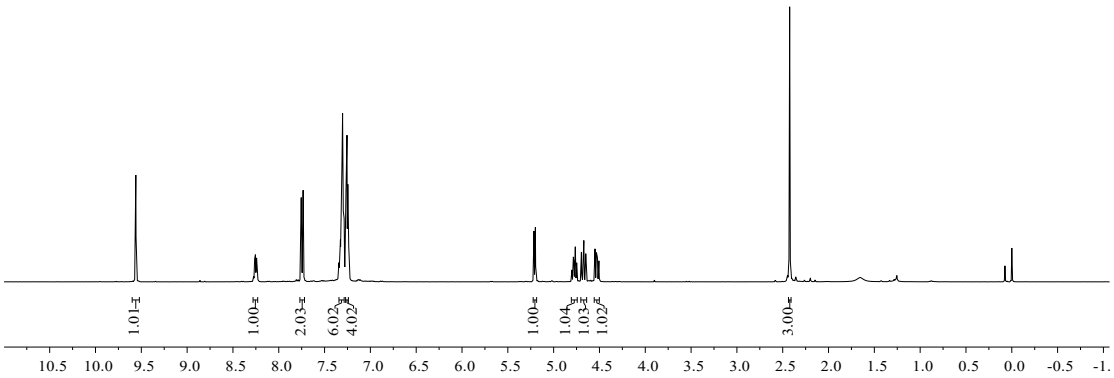
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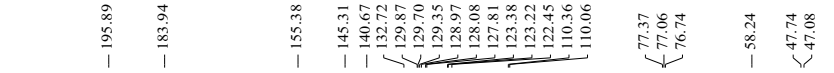
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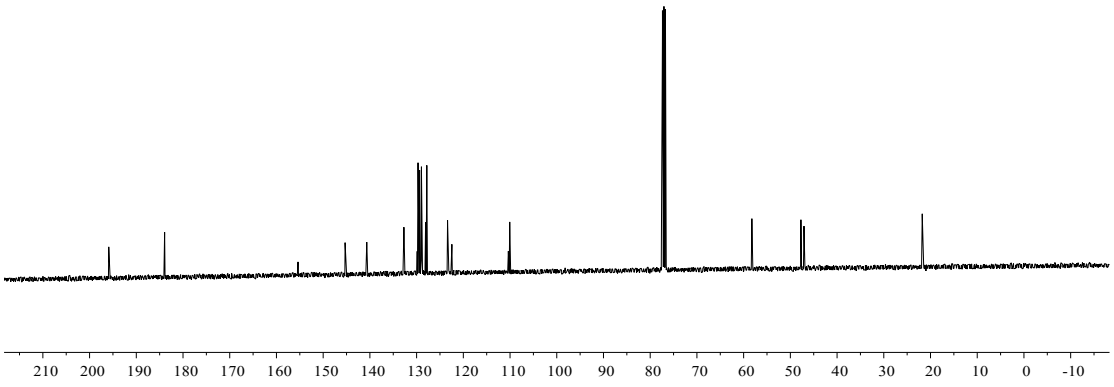
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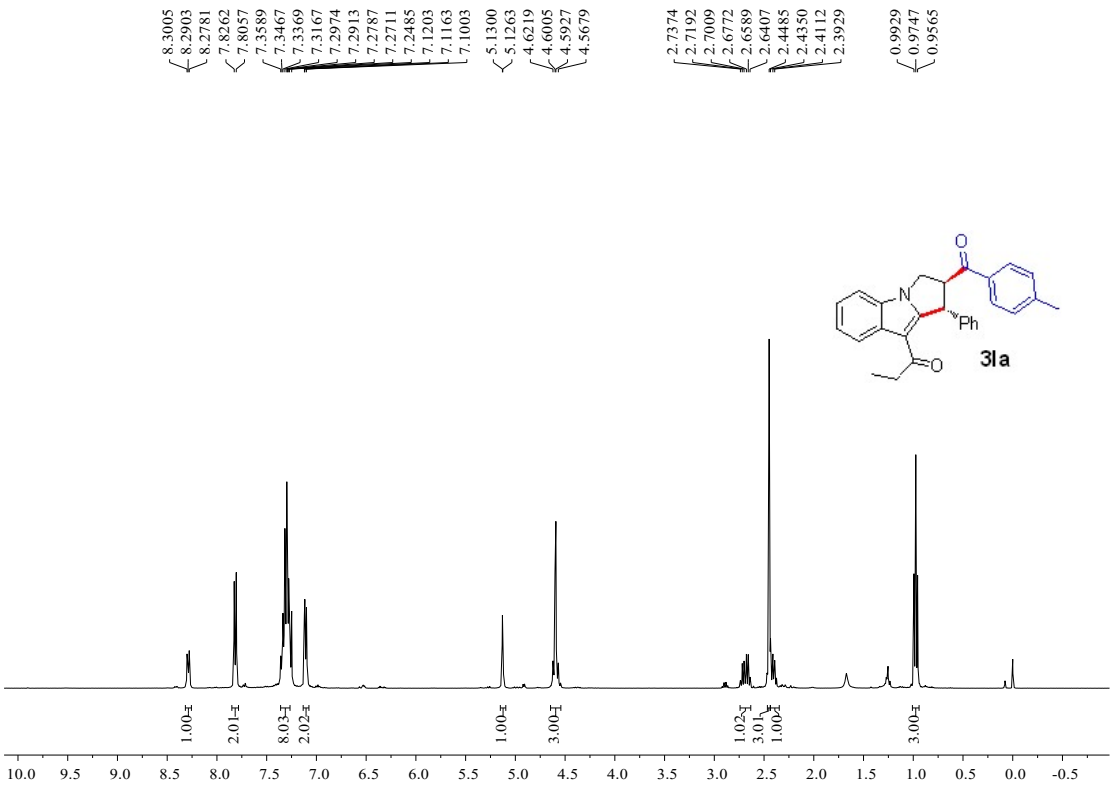
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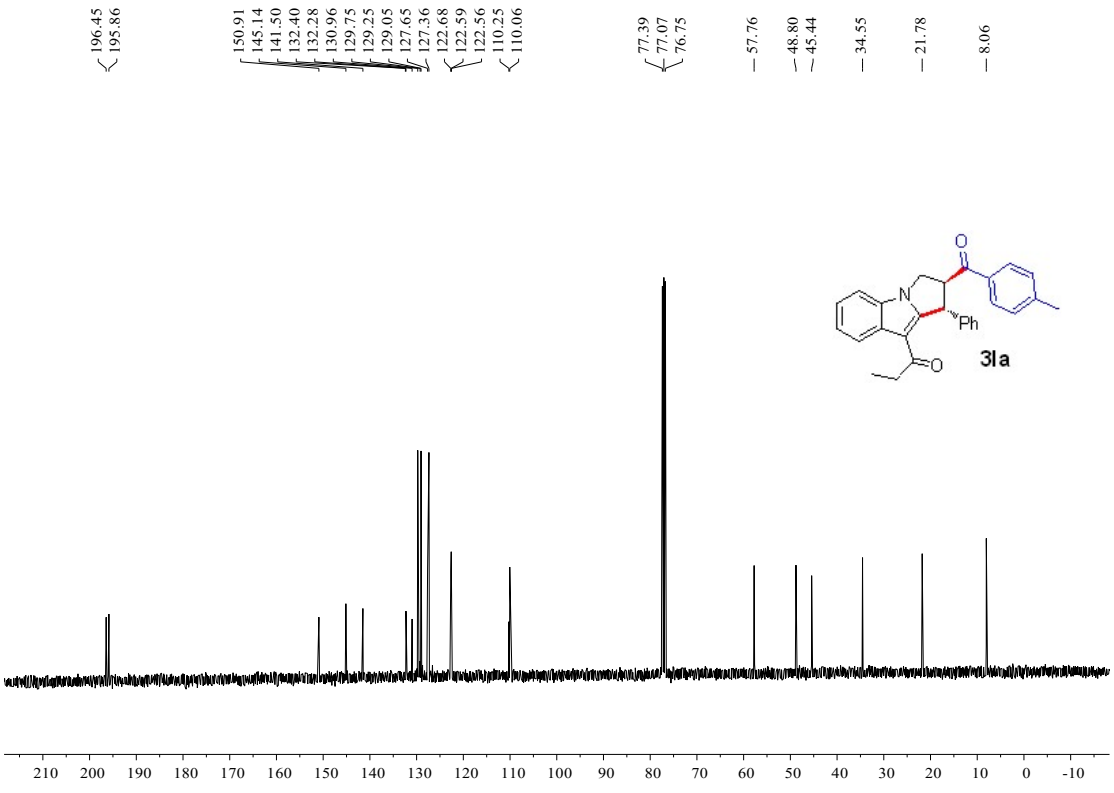
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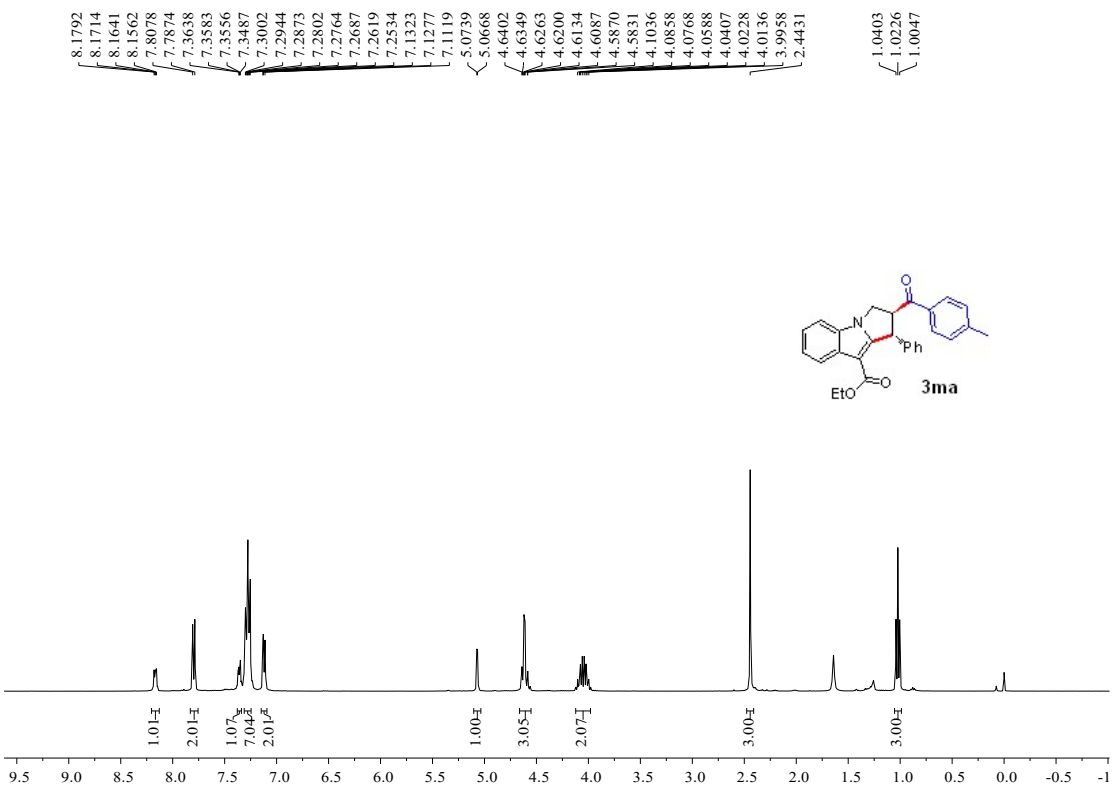
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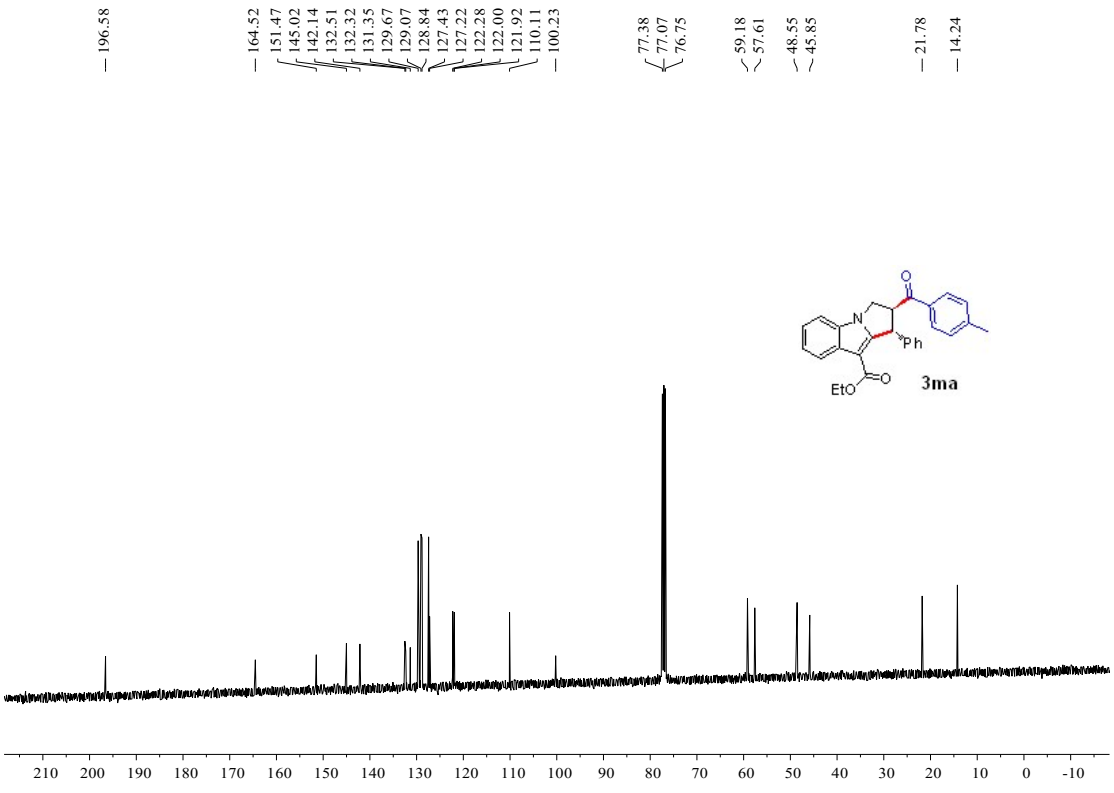
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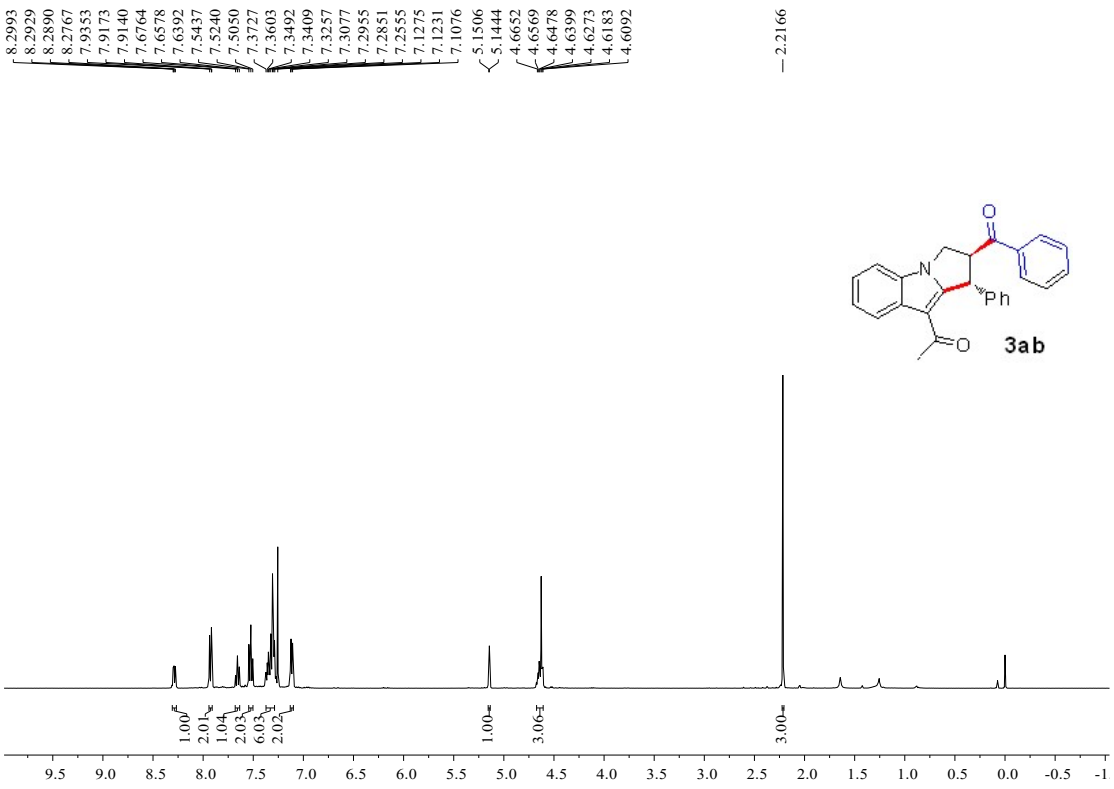
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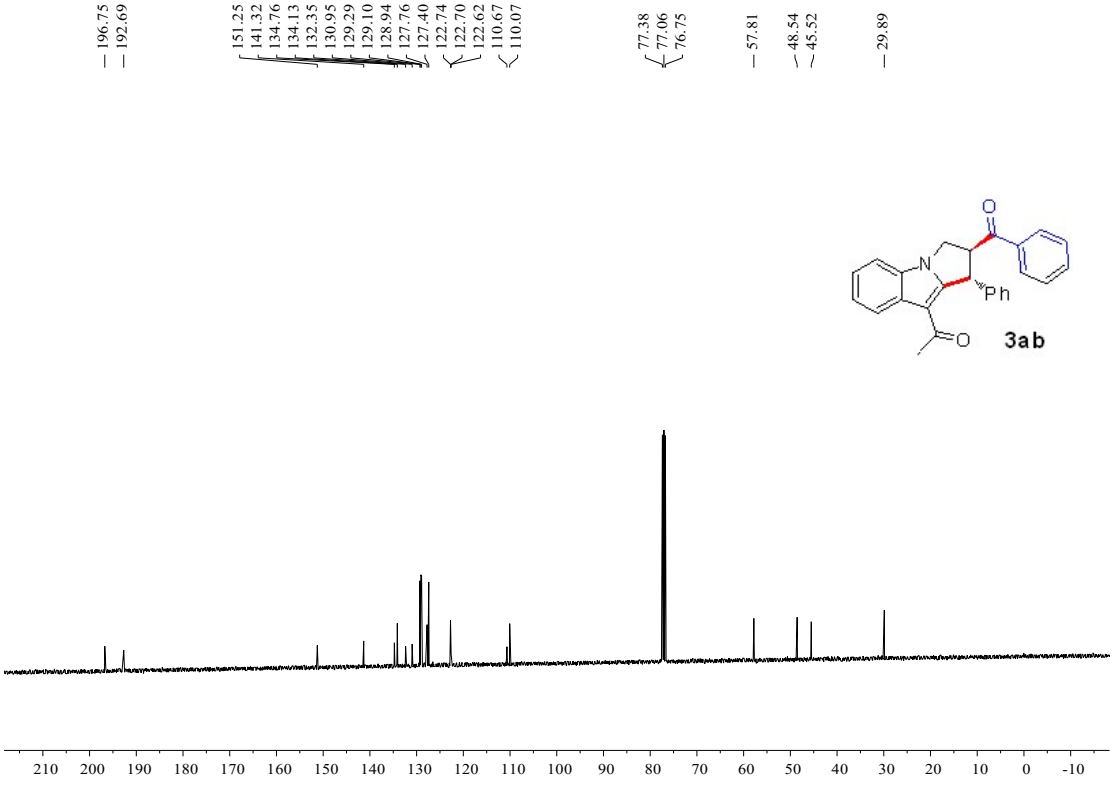
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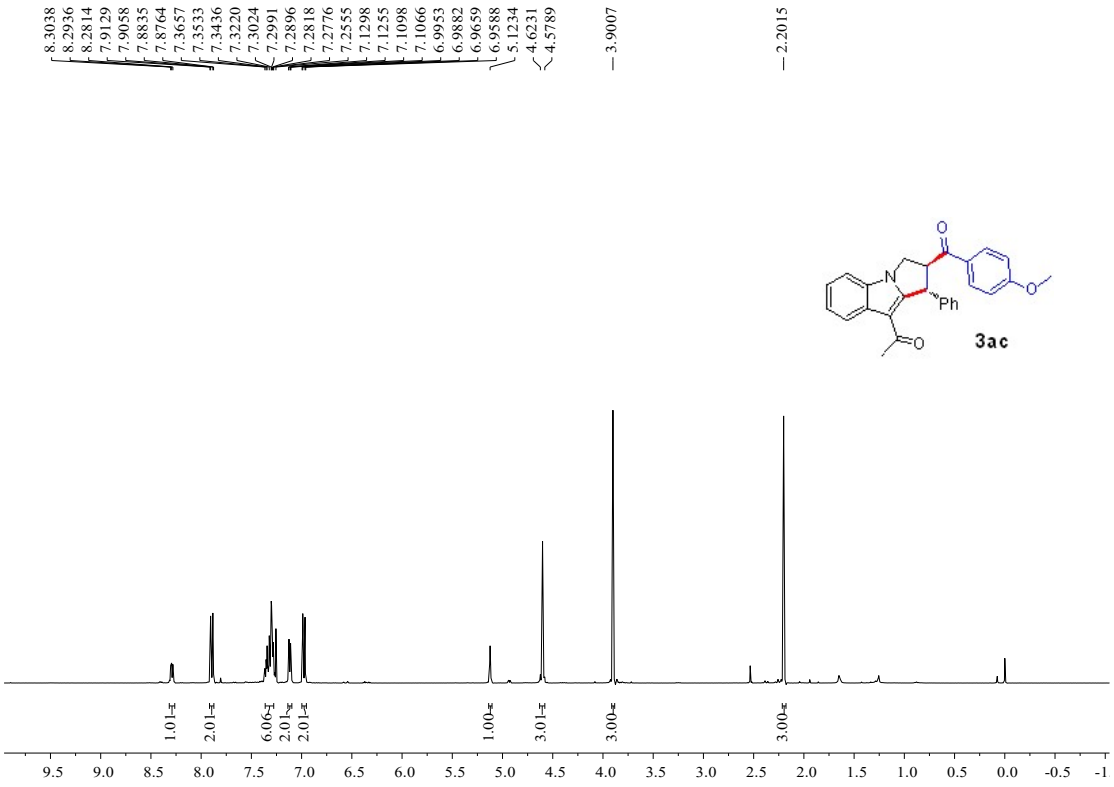
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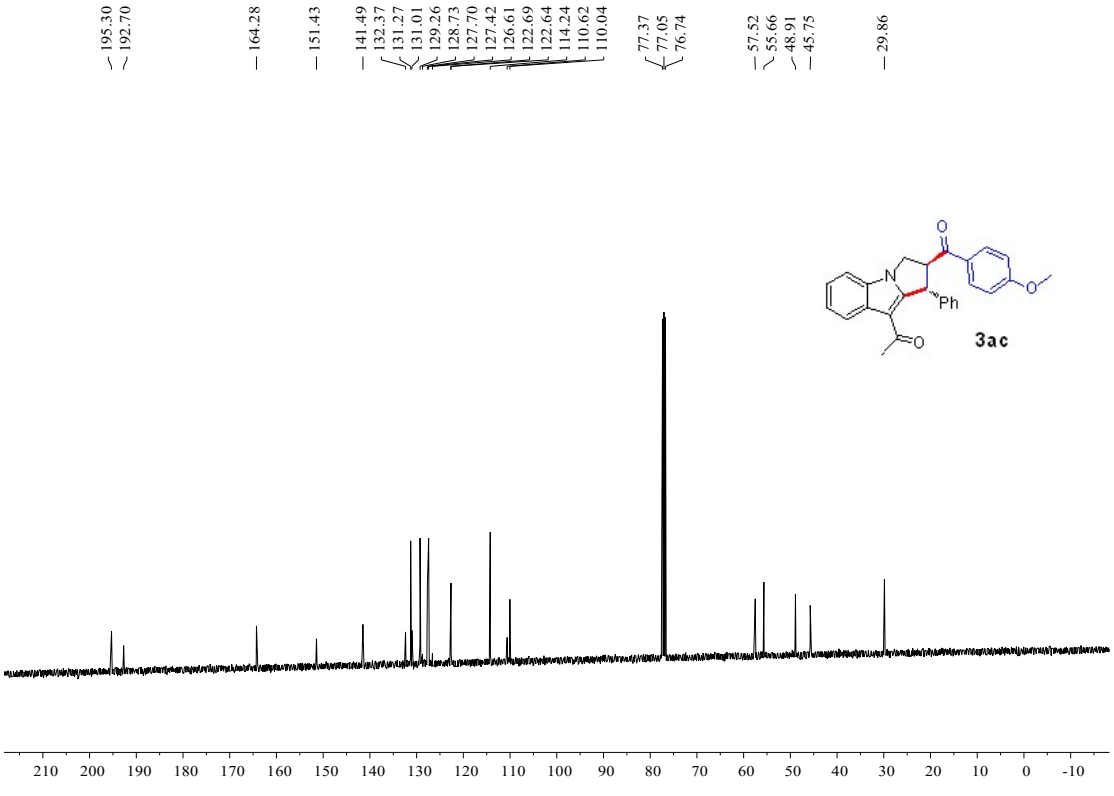
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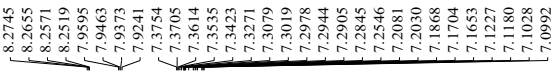
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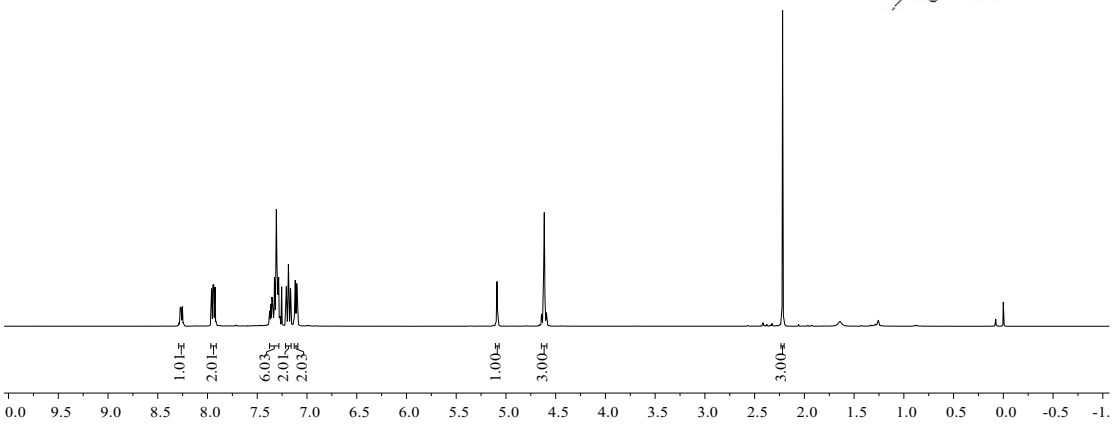
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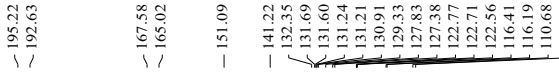
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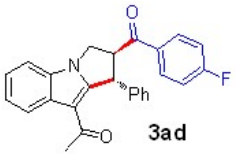
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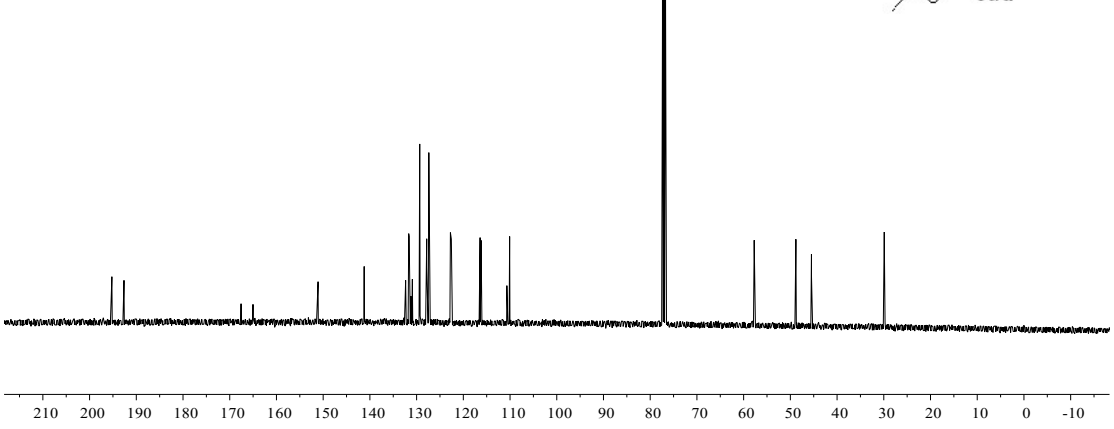
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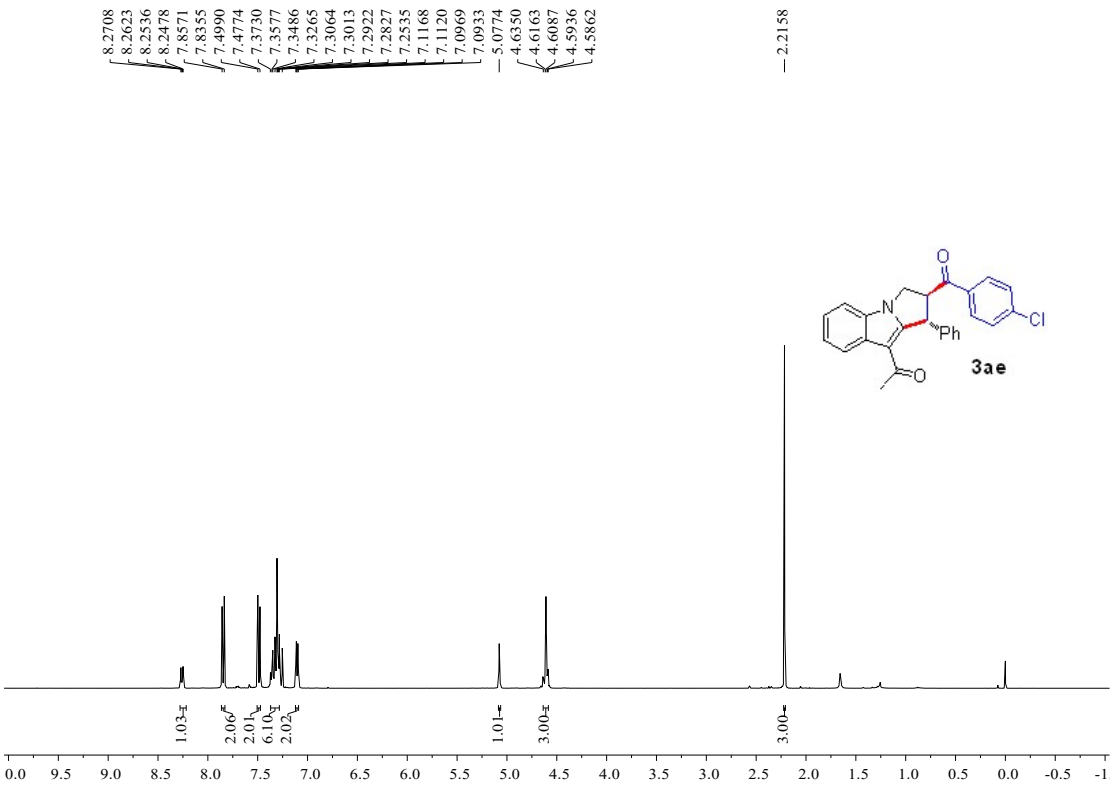
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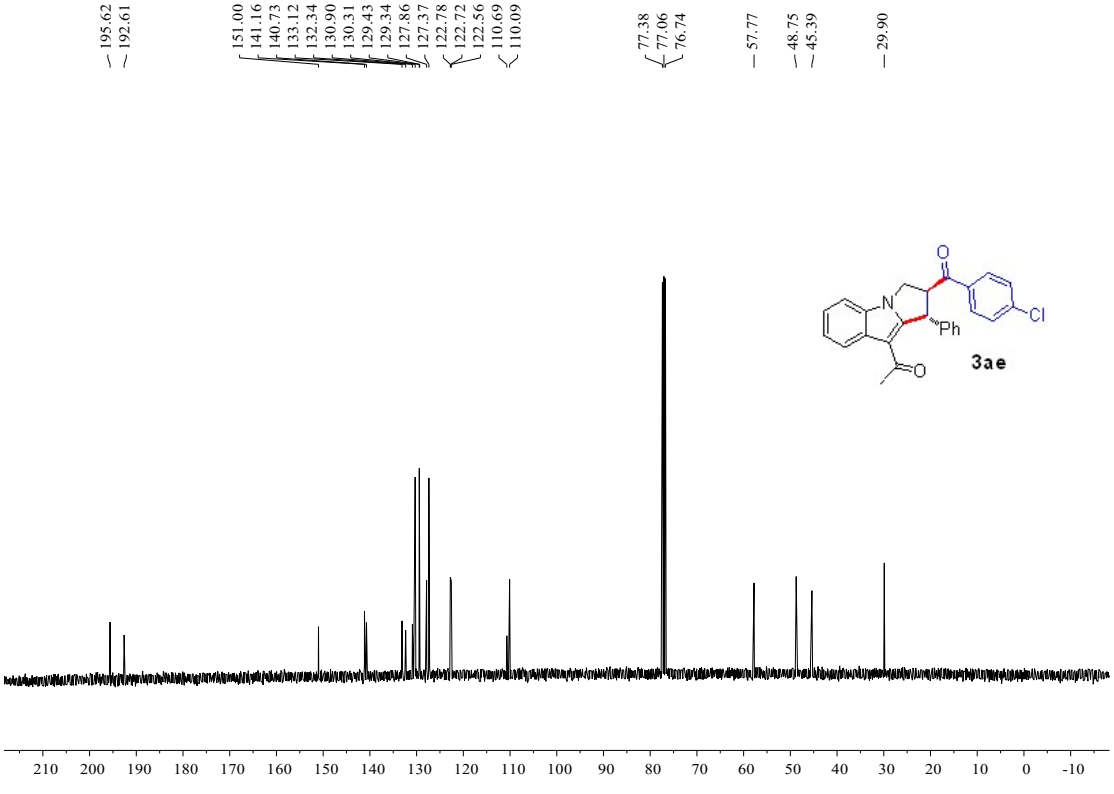
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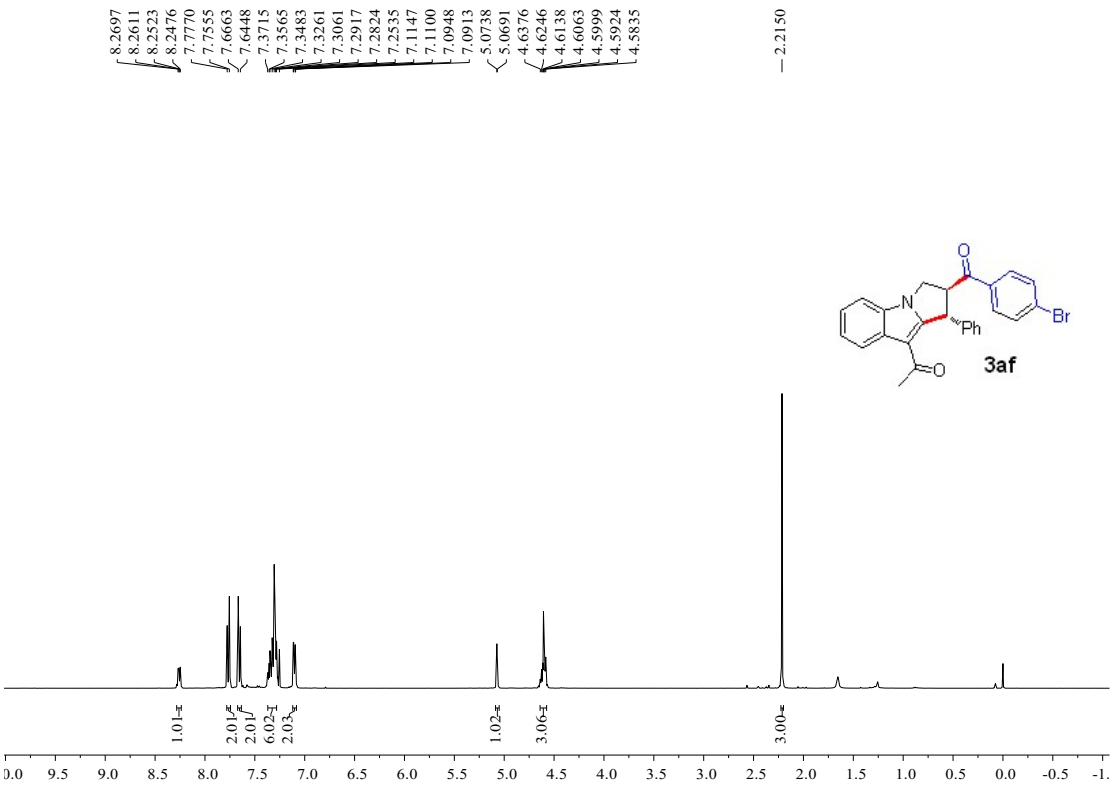
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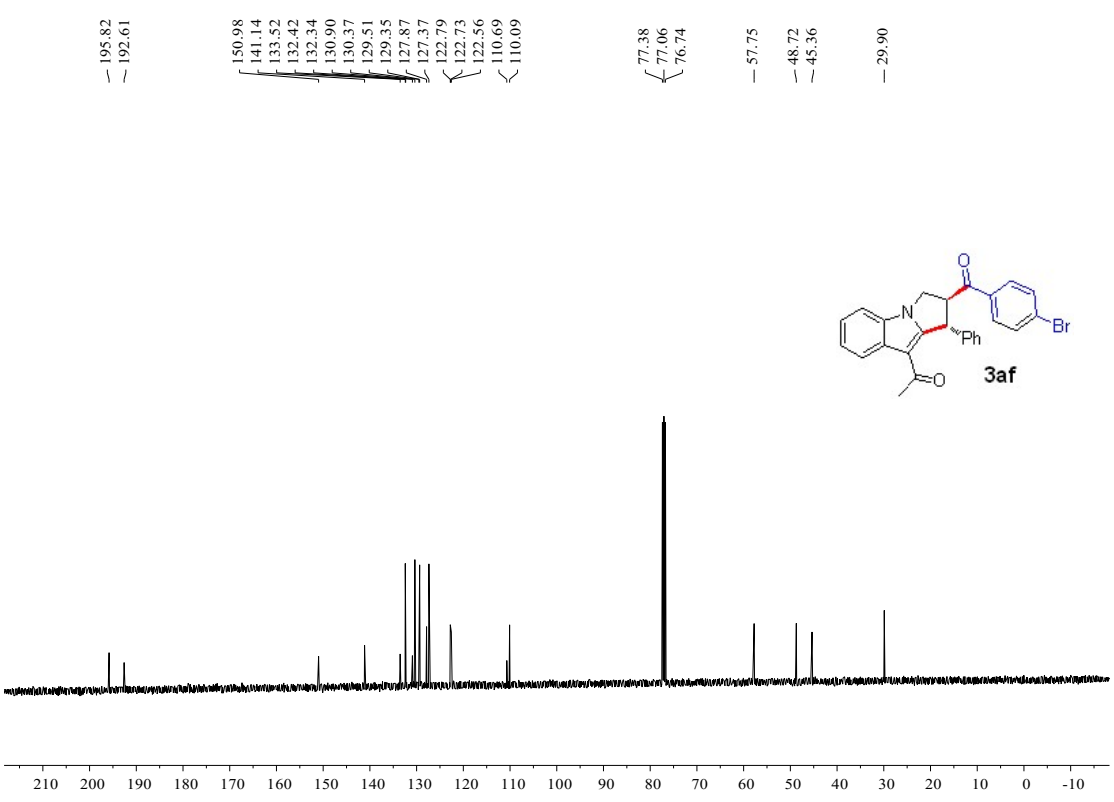
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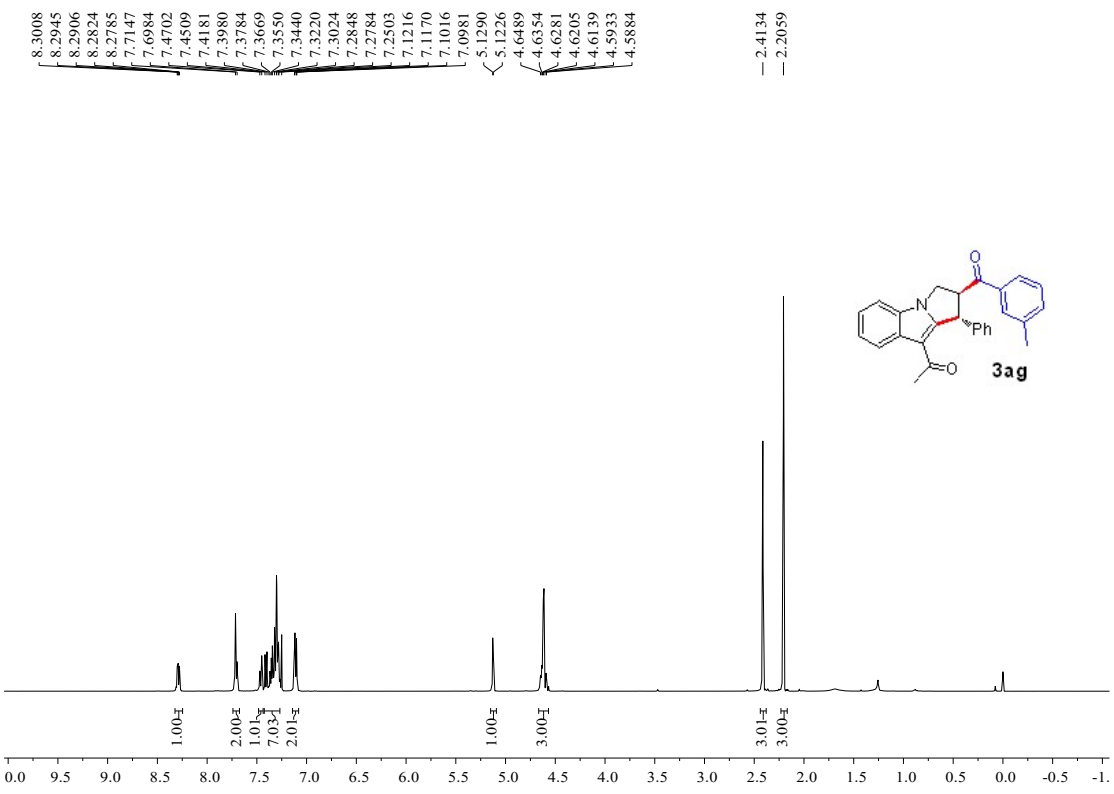
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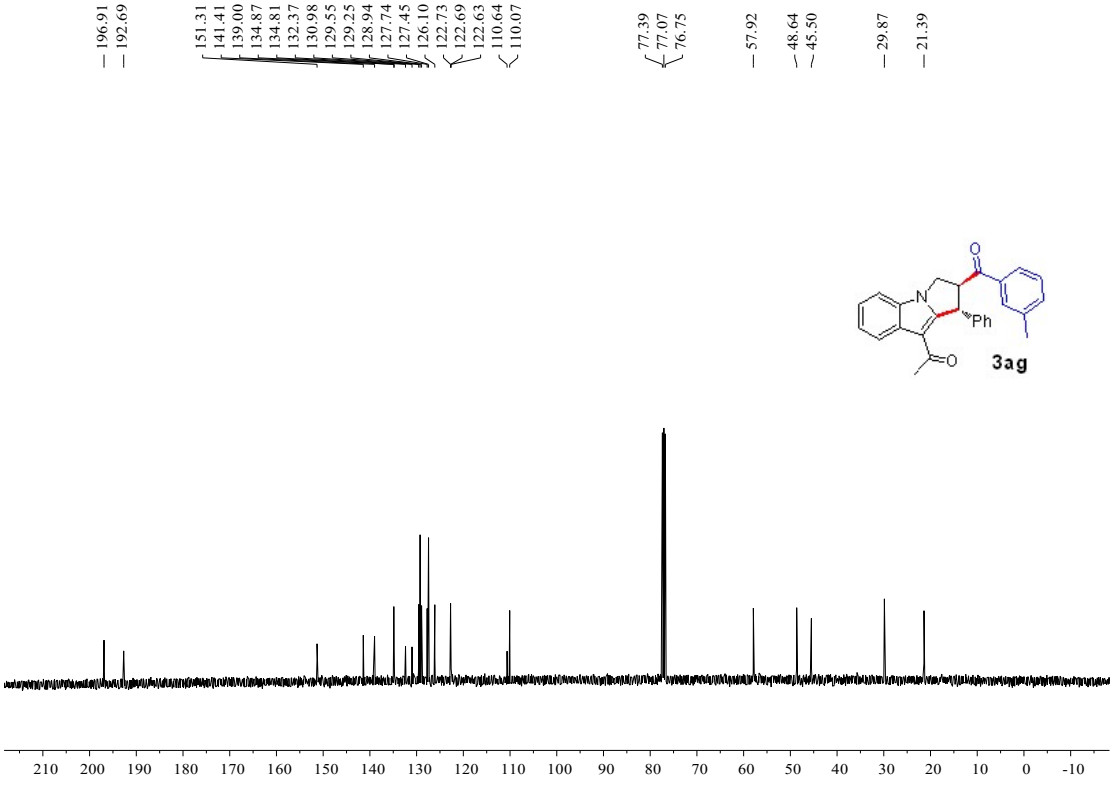
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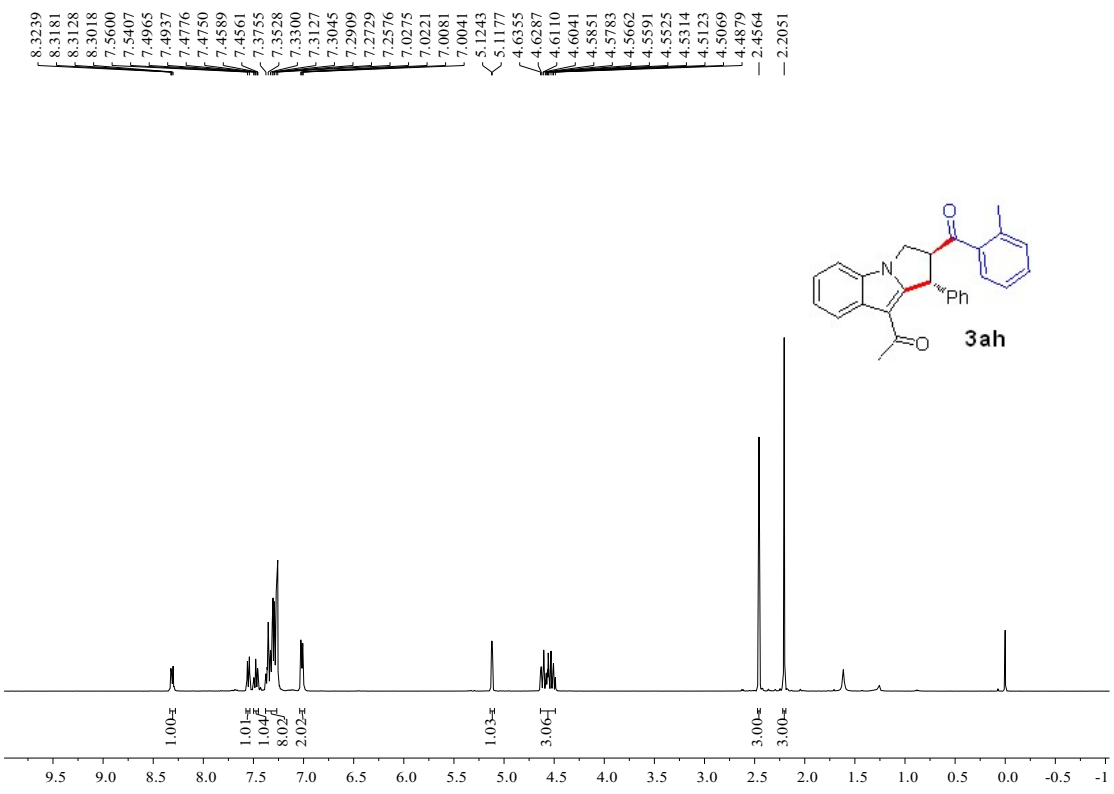
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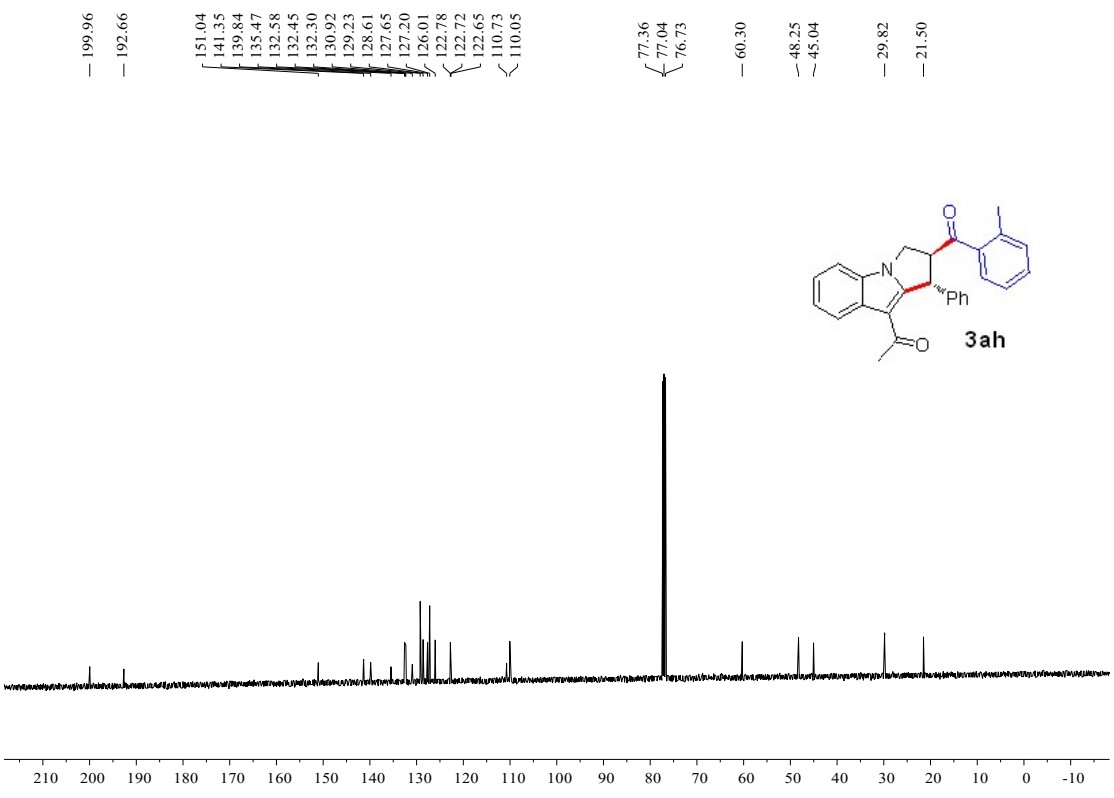
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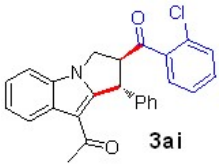
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Ph
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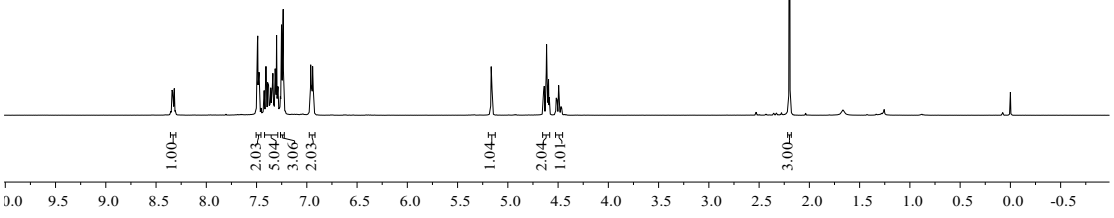
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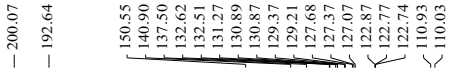
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127.68
127.37
127.07
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76.75
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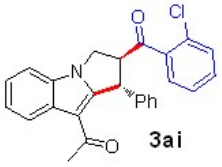
29.76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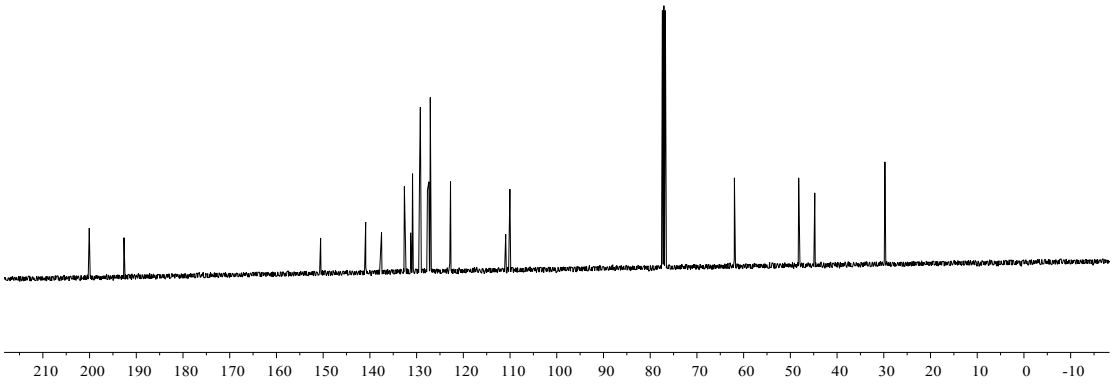
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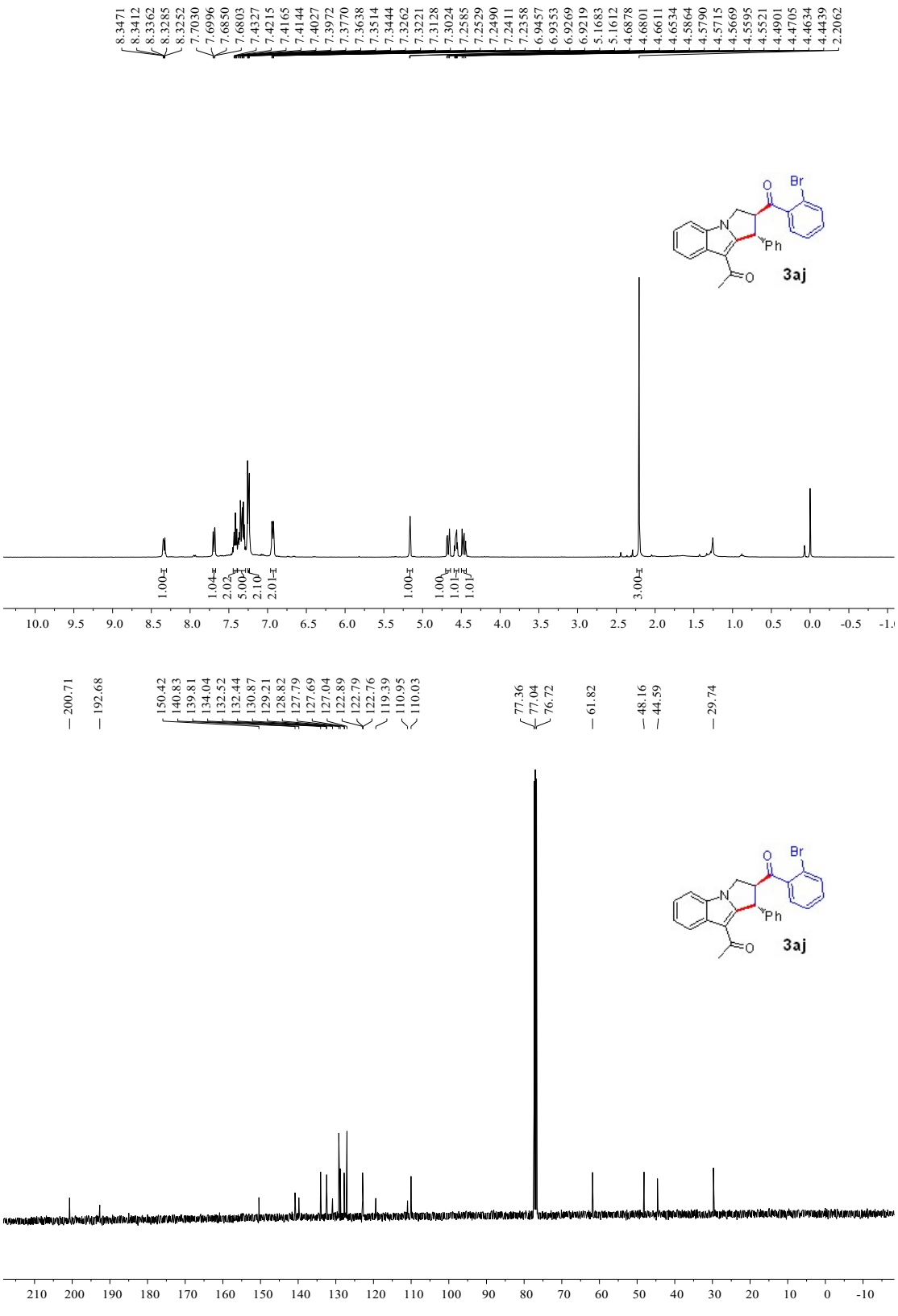
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Br
O
N
Ph
O
3aj
1.00
1.04
2.02
5.00
2.10
2.01
1.00
1.00
1.01
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
200.71
192.68
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122.76
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61.82
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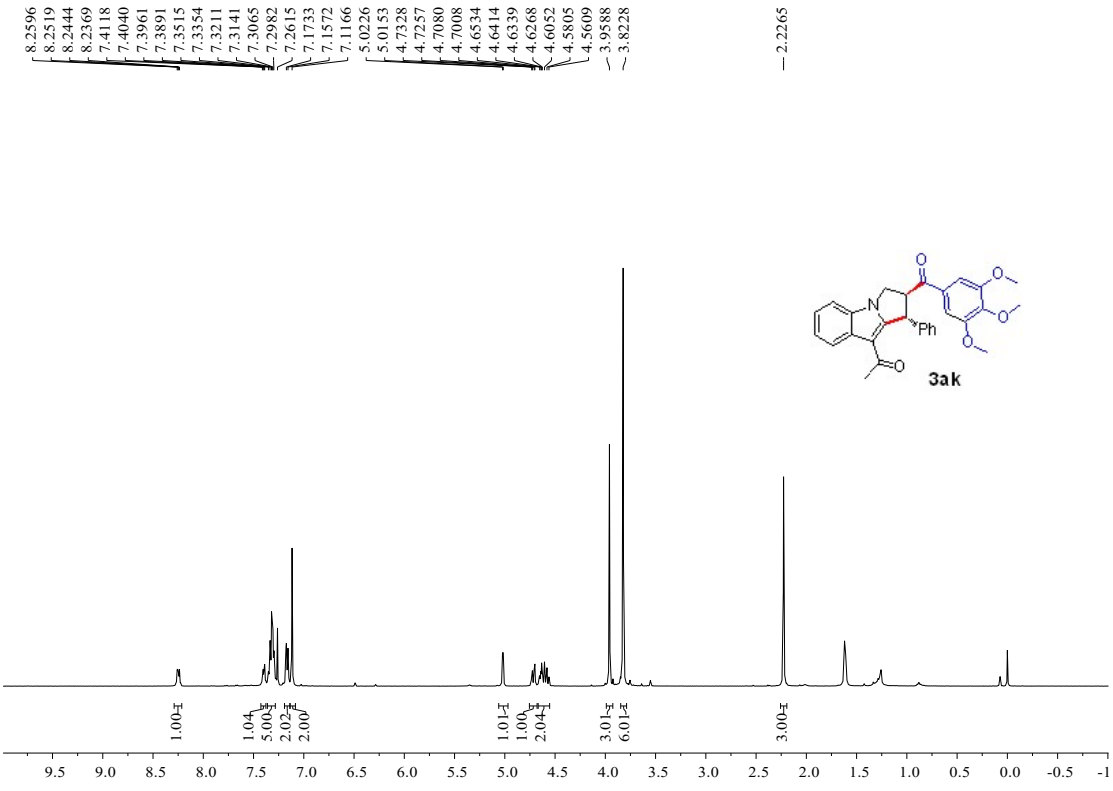
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O
N
Ph
O
O
O
O
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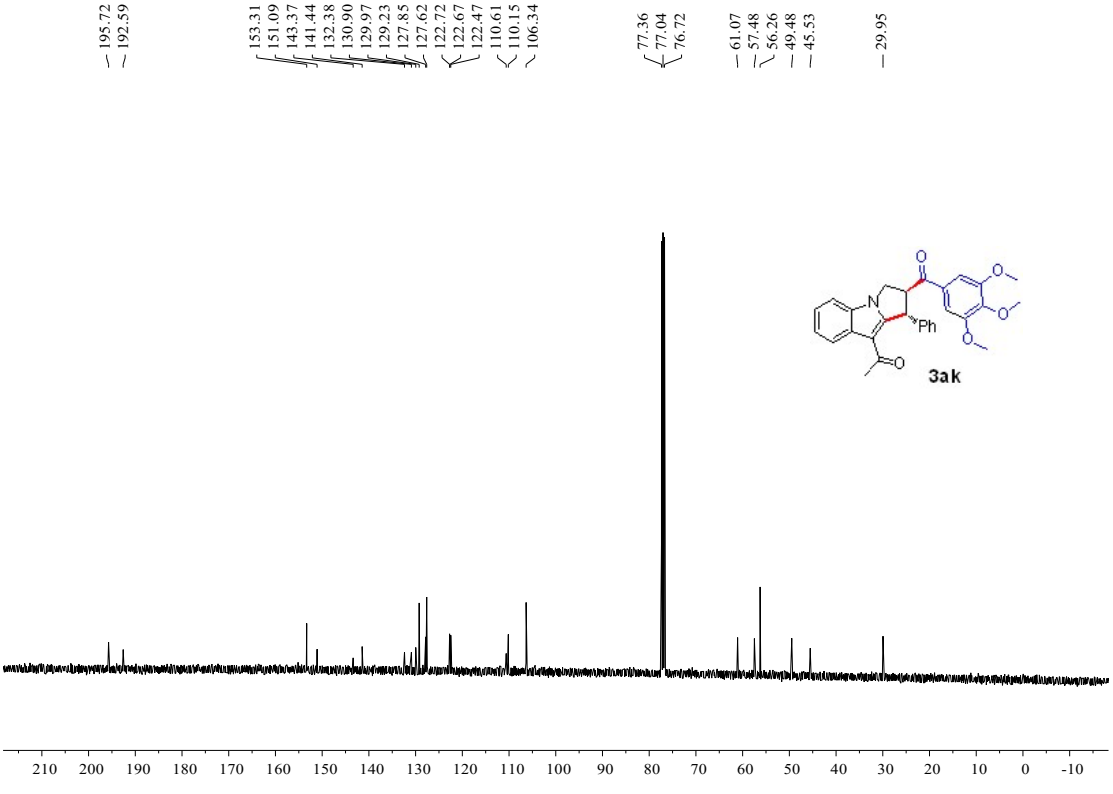
1.04
5.00
2.02
2.00
1.01
1.00
2.04
3.01
6.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1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110.61
110.15
106.34
77.36
77.04
76.72
61.07
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56.26
49.48
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N
Ph
O
O
O
O
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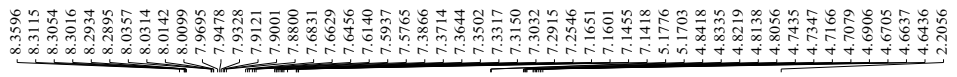
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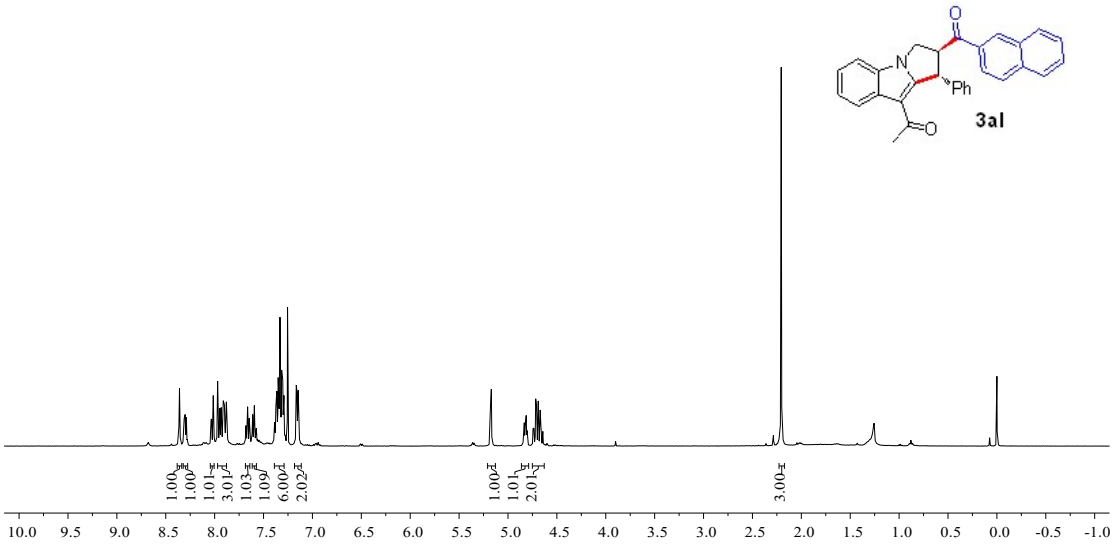
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Ph
O
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1.01
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1.03
1.09
6.00
2.02
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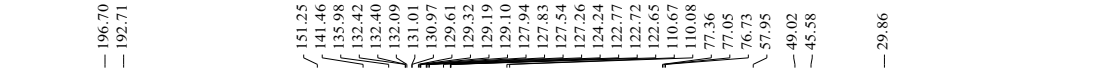
1.01
2.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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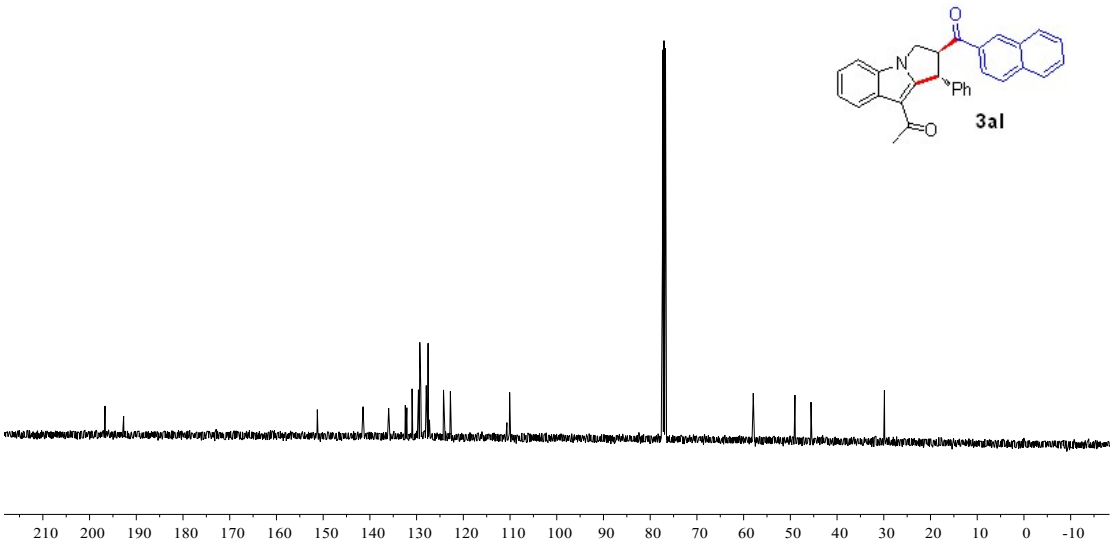
O
N
Ph
O
3al
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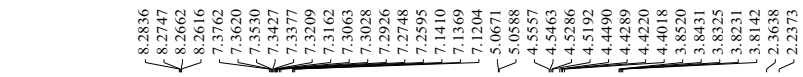
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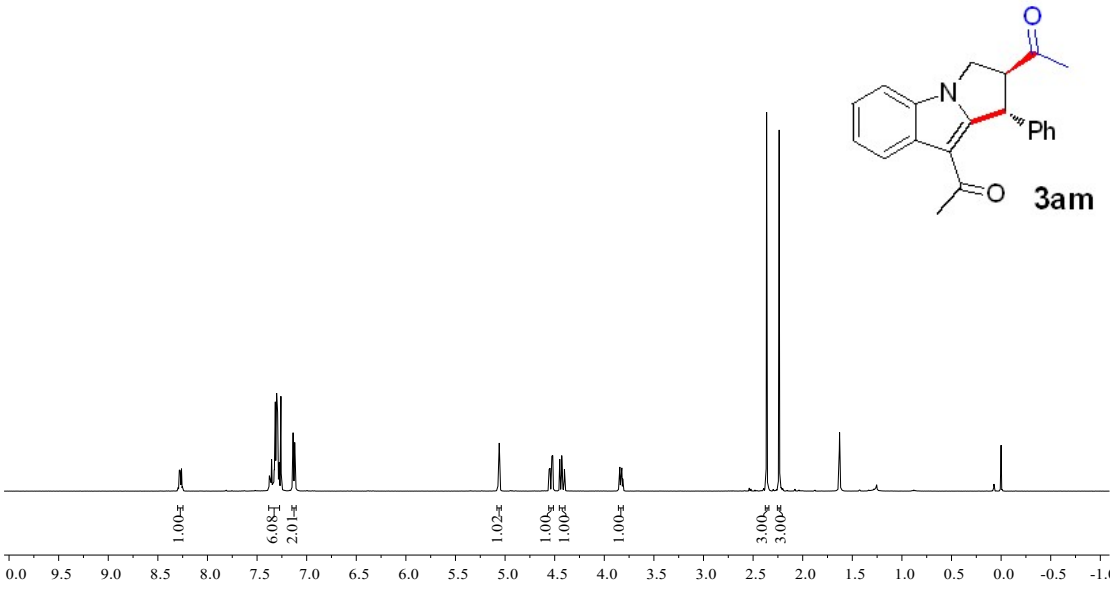
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Ph
O
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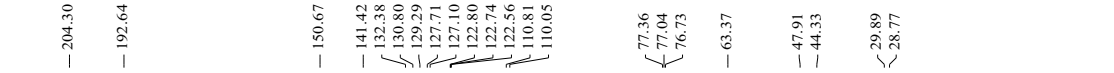
2.01
1.02
1.00
1.00
1.00
3.00
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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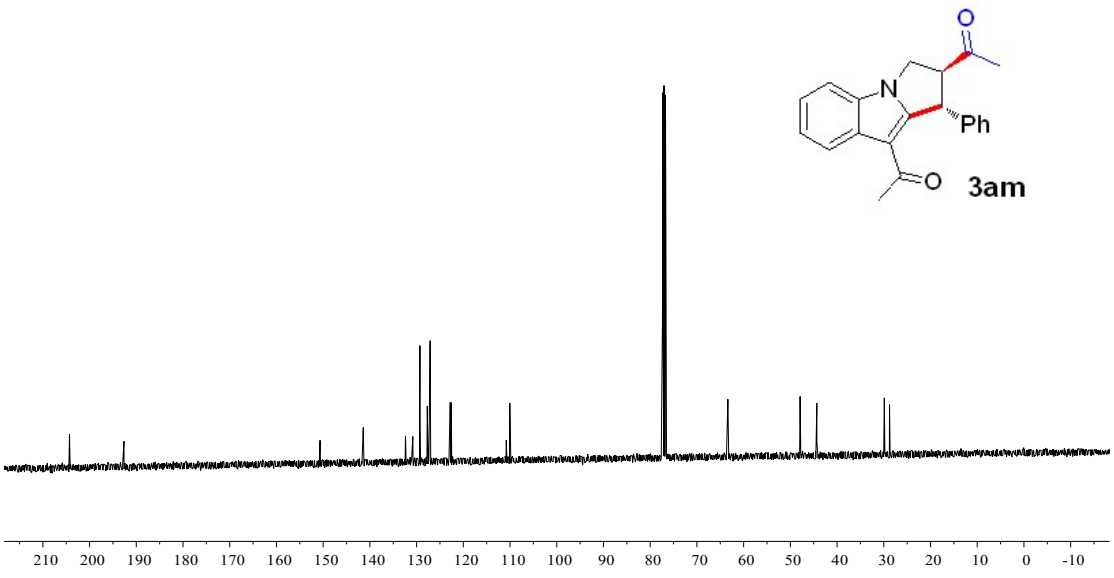
28.77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Ph
O
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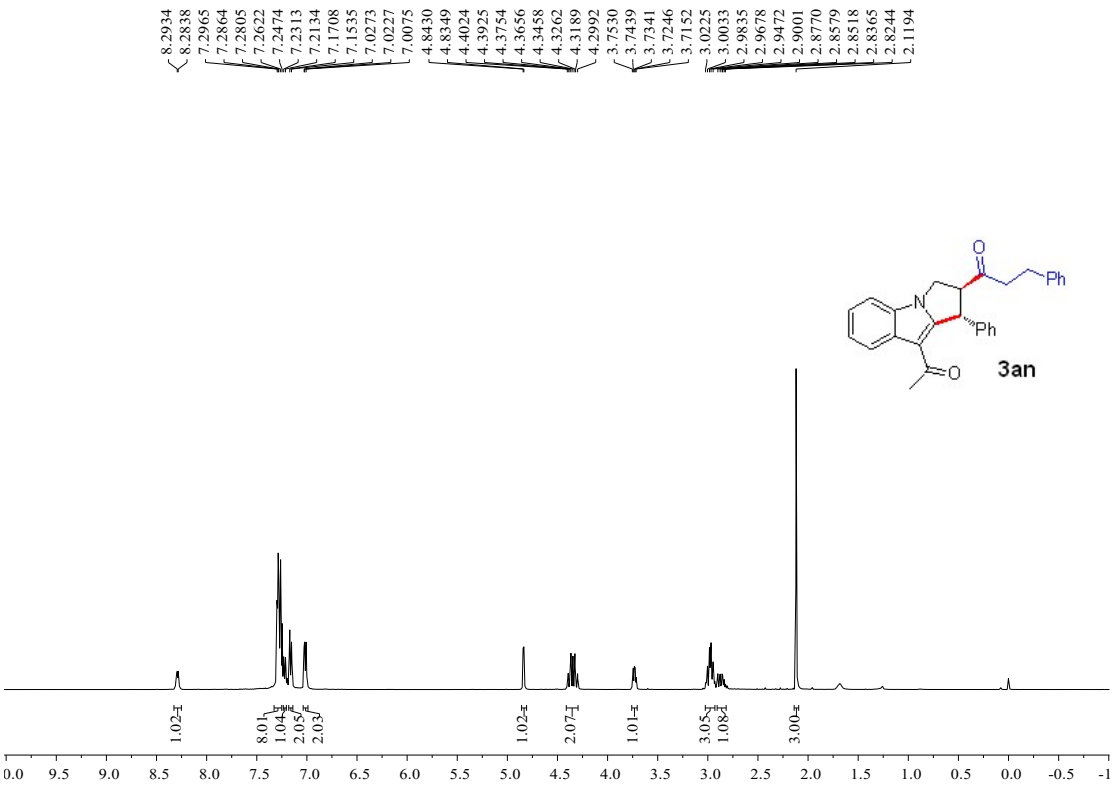
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Ph
N
Ph
O
3an
1.02
8.01
1.04
2.05
2.03
1.02
2.07
1.01
3.05
1.08
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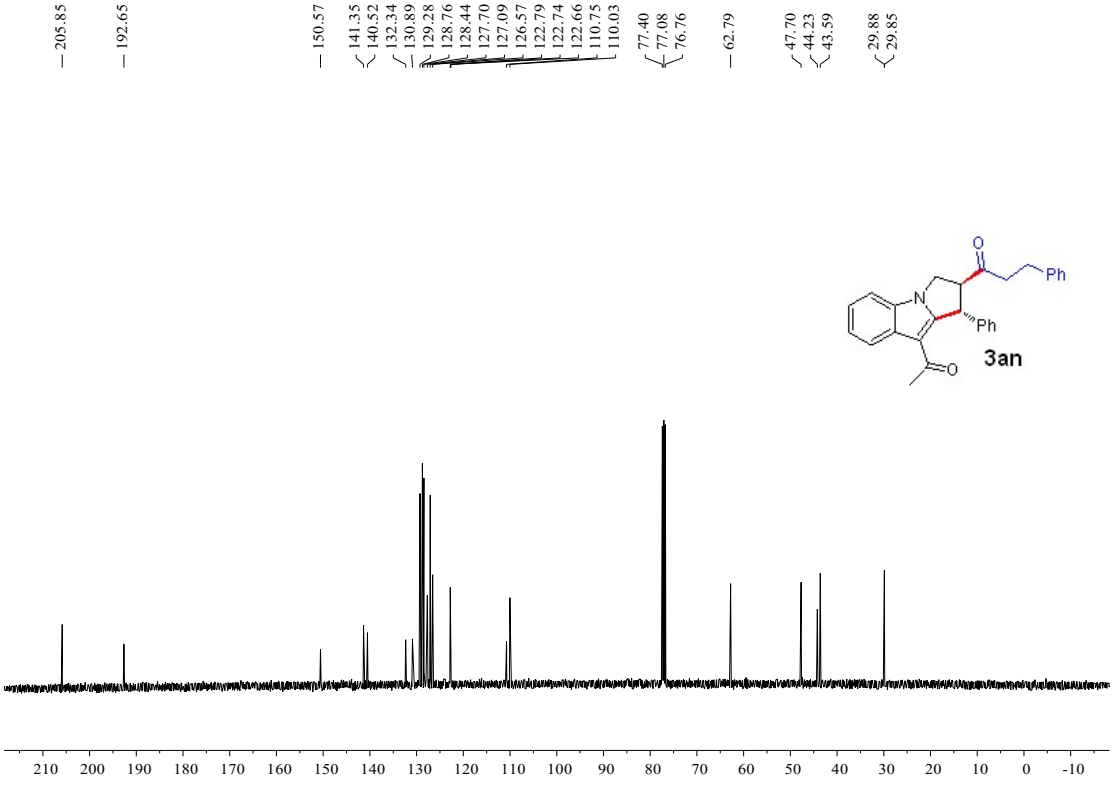
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77.08
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Ph
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Ph
O
3an
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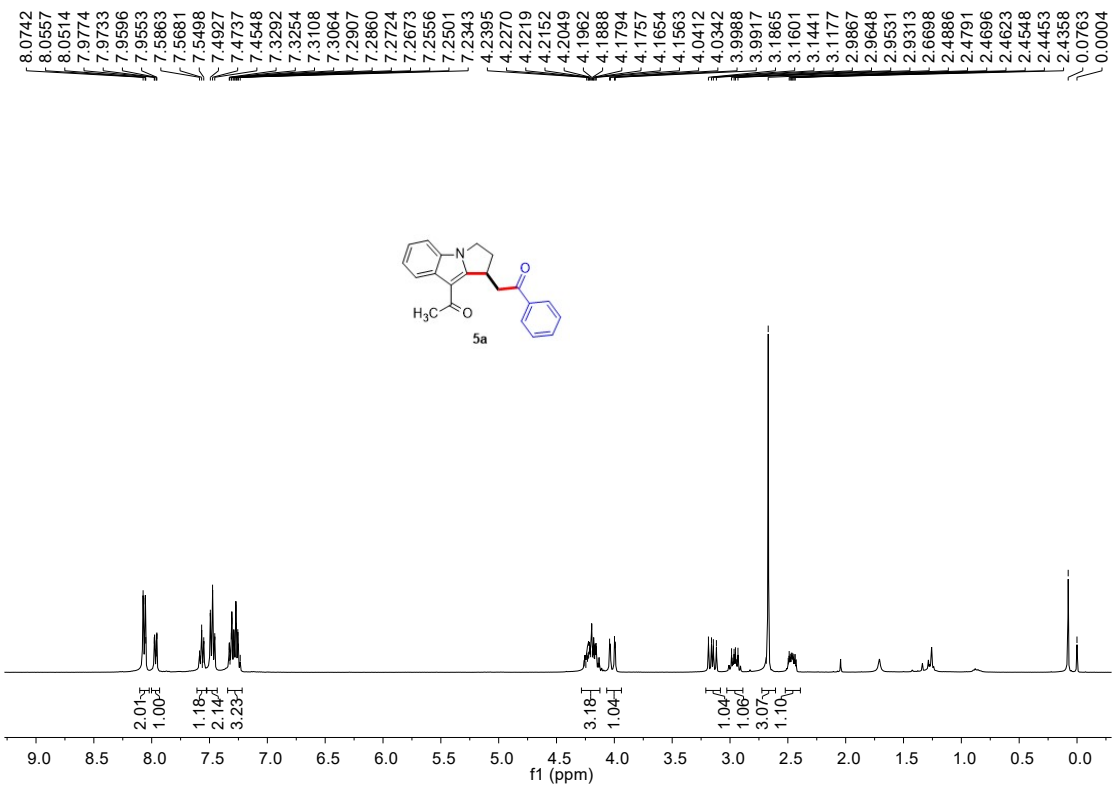
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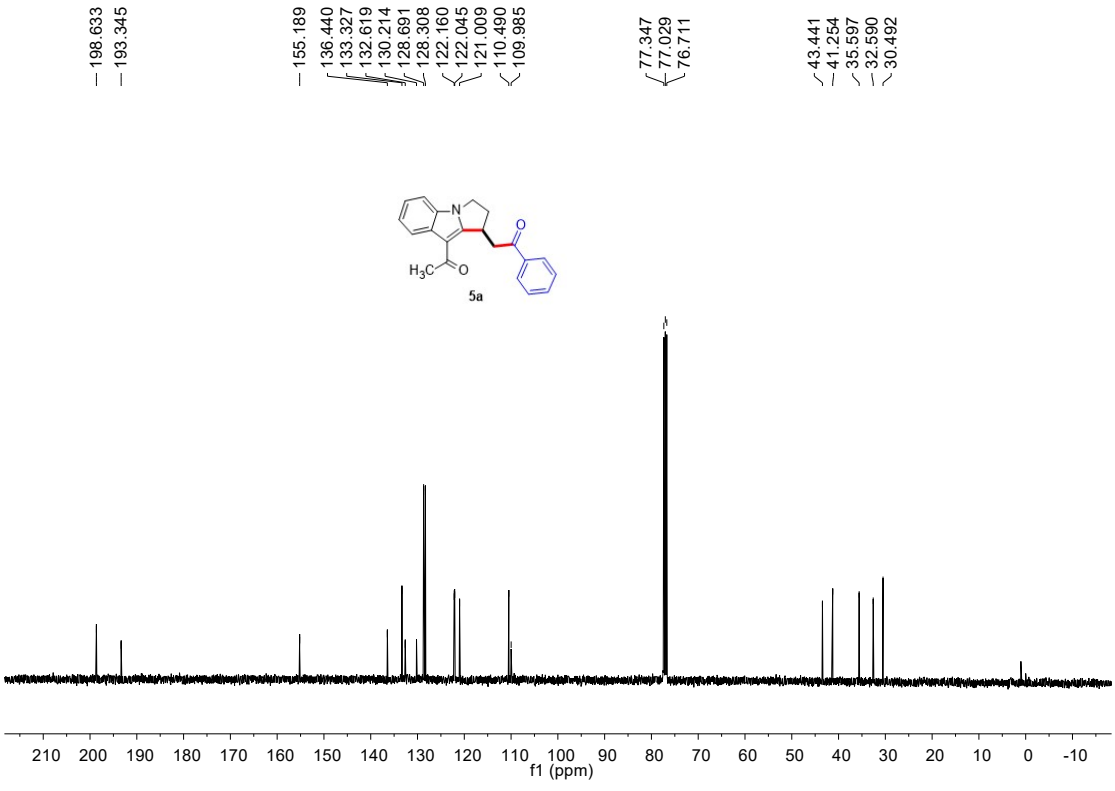
1.04
1.06
3.07
1.10
f1 (ppm)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41.254
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32.590
30.492
5a
f1 (ppm)


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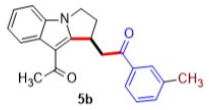
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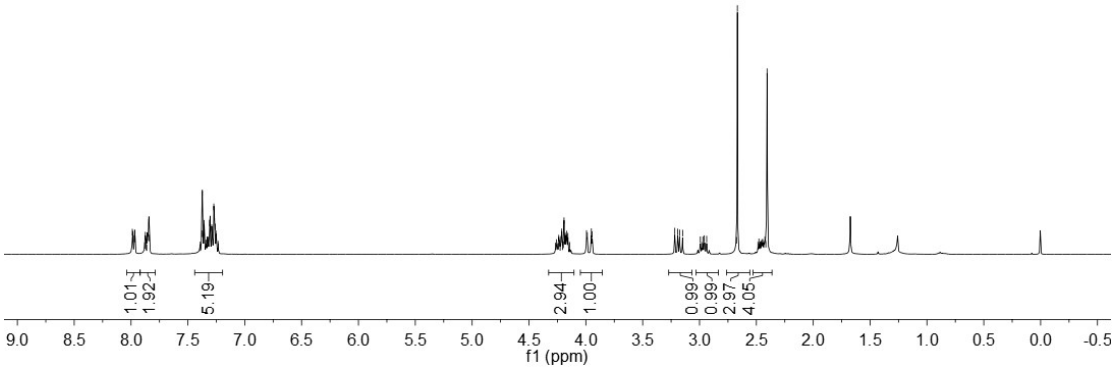
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0.99
0.99
2.97
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f1 (ppm)


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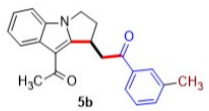
21.308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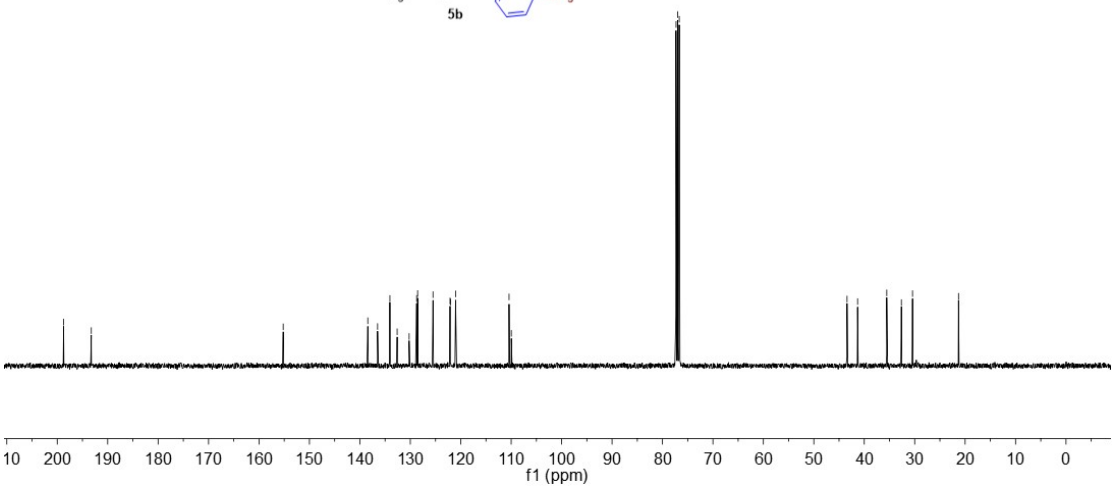
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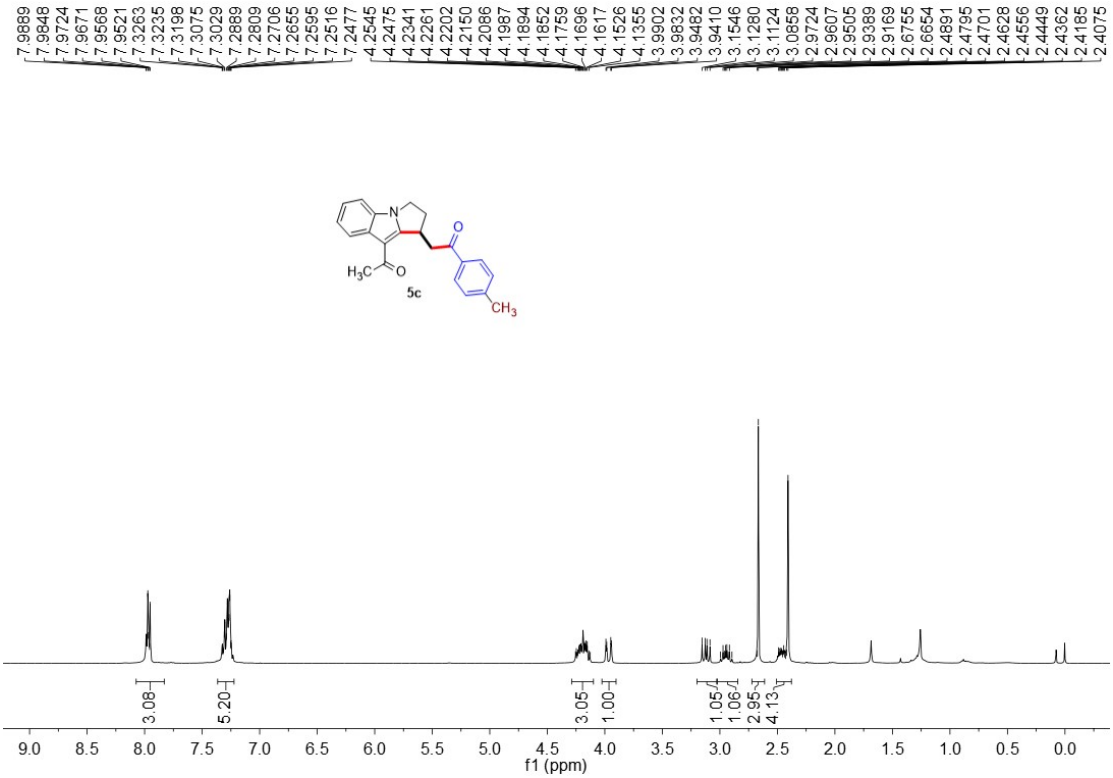
f1 (ppm)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1.00
1.05
1.06
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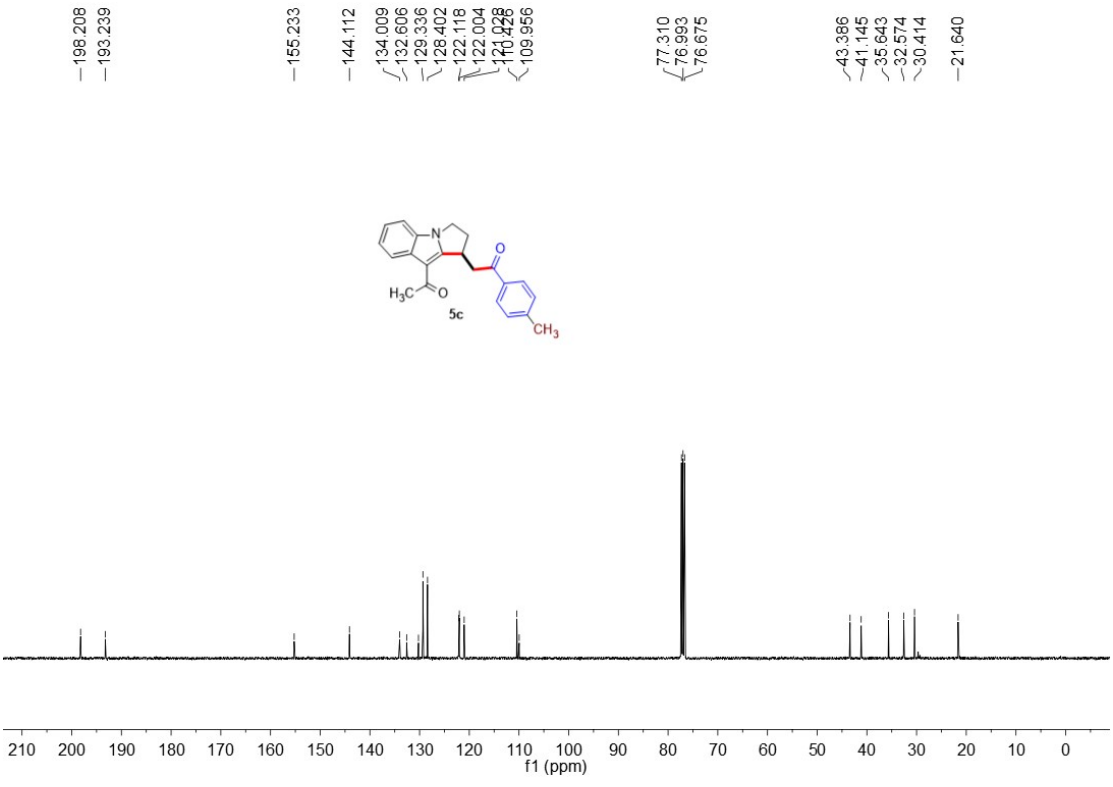
4.13
f1 (ppm)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128.402
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122.004
121.028
110.428
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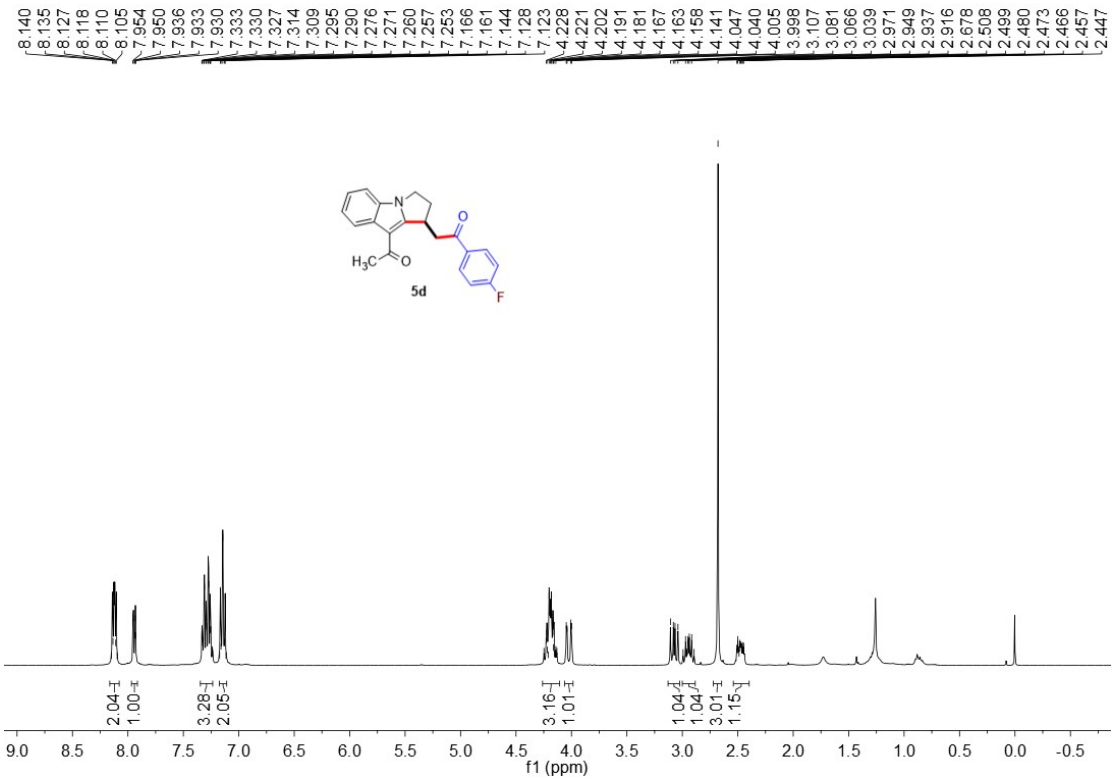
76.675
43.386
41.145
35.643
32.574
30.414
21.640
5c
f1 (ppm)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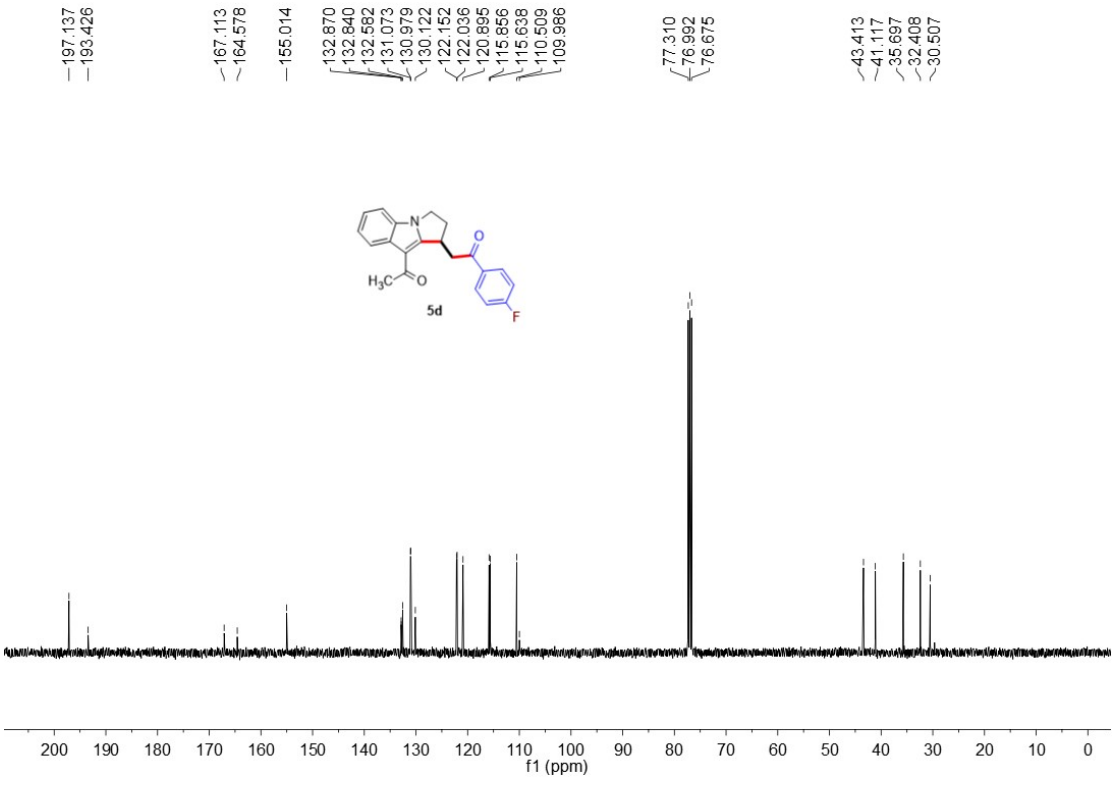
8.135
8.127
8.118
8.110
8.105
7.954
7.950
7.936
7.933
7.930
7.333
7.330
7.327
7.314
7.309
7.295
7.290
7.276
7.271
7.260
7.257
7.253
7.166
7.161
7.144
7.128
7.123
4.228
4.221
4.202
4.191
4.181
4.167
4.163
4.158
4.141
4.047
4.040
4.005
3.998
3.107
3.081
3.066
3.039
2.971
2.949
2.937
2.916
2.678
2.508
2.499
2.480
2.473
2.466
2.457
2.447
5d
2.04
1.00
3.28
2.05
3.16
1.01
1.04
1.04
3.01
1.15
f1 (ppm)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167.113
164.578
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132.840
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130.979
130.122
122.152
122.036
120.895
115.856
115.638
110.509
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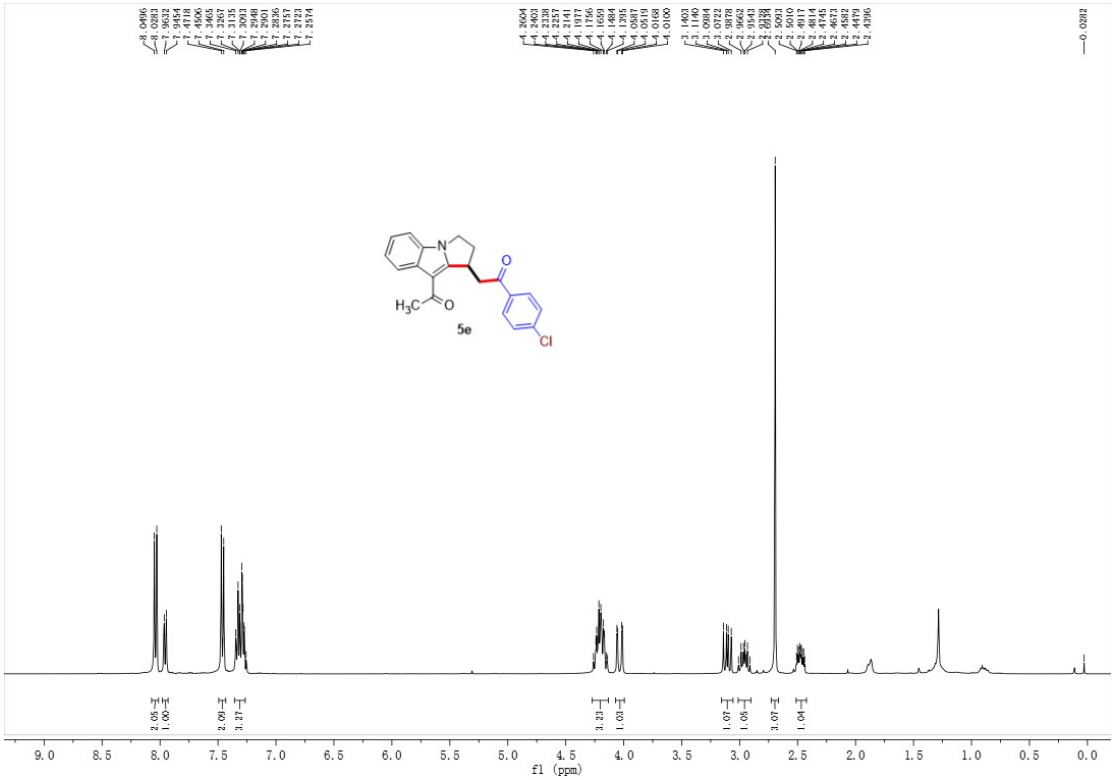
76.992
76.675
43.413
41.117
35.697
32.408
30.507
5d
f1 (ppm)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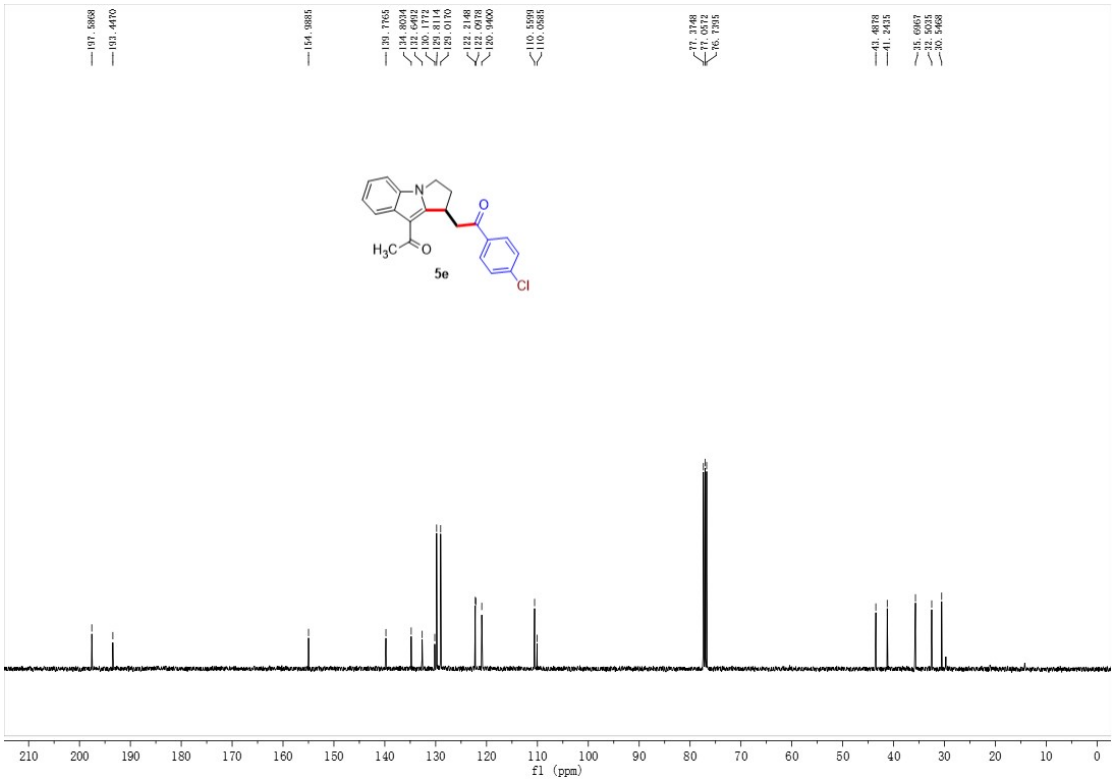
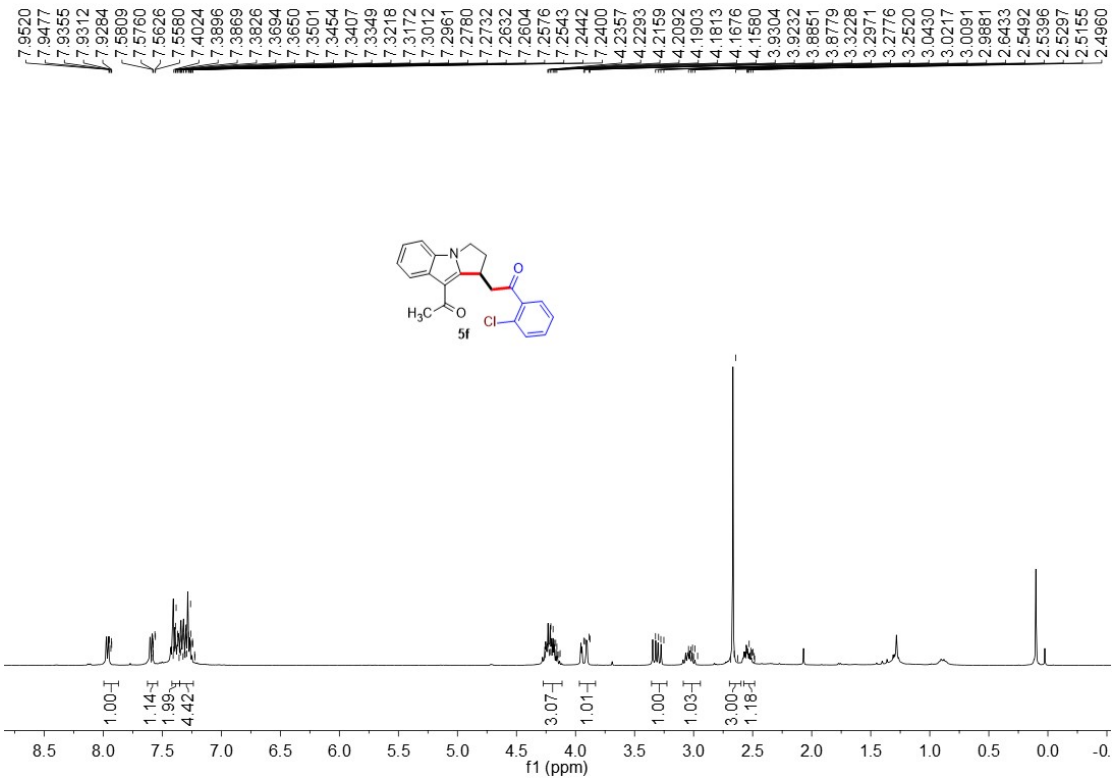
f1 (ppm)


5e
f1 (ppm)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7.5760
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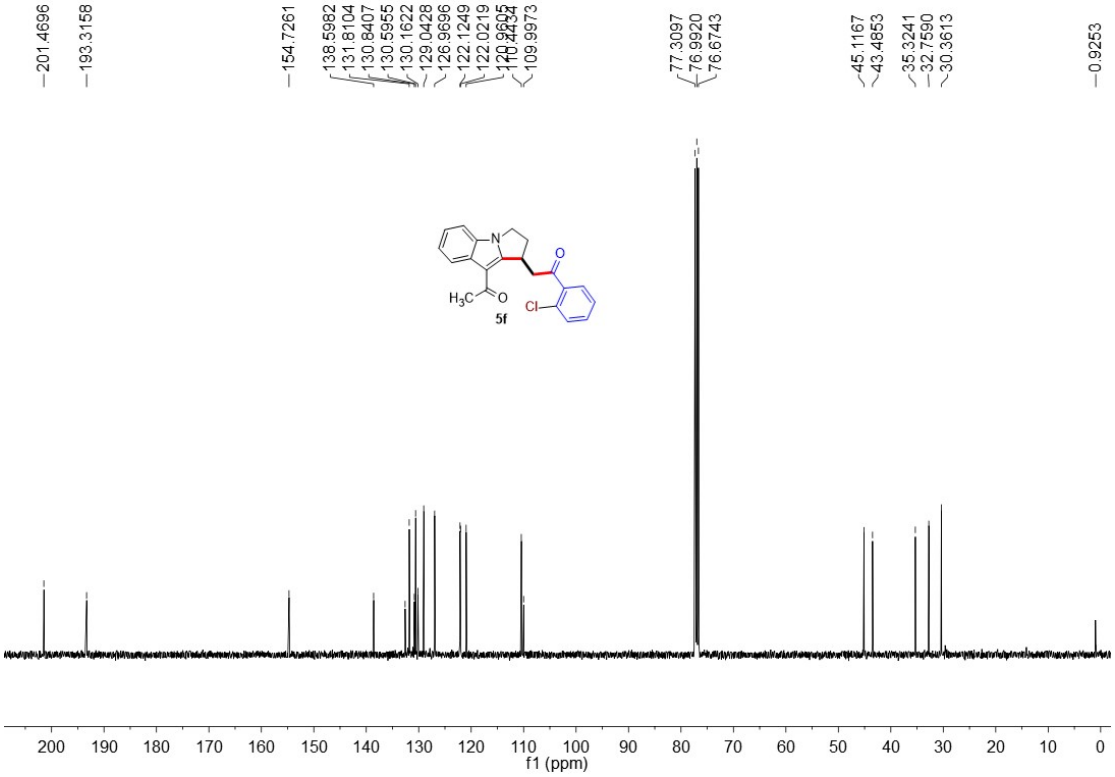
7.5580
7.4024
7.3896
7.3869
7.3826
7.3694
7.3650
7.3501
7.3454
7.3407
7.3349
7.3218
7.3172
7.3012
7.2961
7.2780
7.2732
7.2632
7.2604
7.2576
7.2543
7.2442
7.2400
4.2357
4.2293
4.2159
4.2092
4.1903
4.1813
4.1676
4.1580
3.9304
3.9232
3.8851
3.8779
3.3228
3.2971
3.2776
3.2520
3.0430
3.0217
3.0091
2.9881
2.6433
2.5492
2.5396
2.5297
2.5155
2.4960
5f
1.00
1.14
1.99
4.42
3.07
1.01
1.00
1.03
3.00
1.18
f1 (ppm)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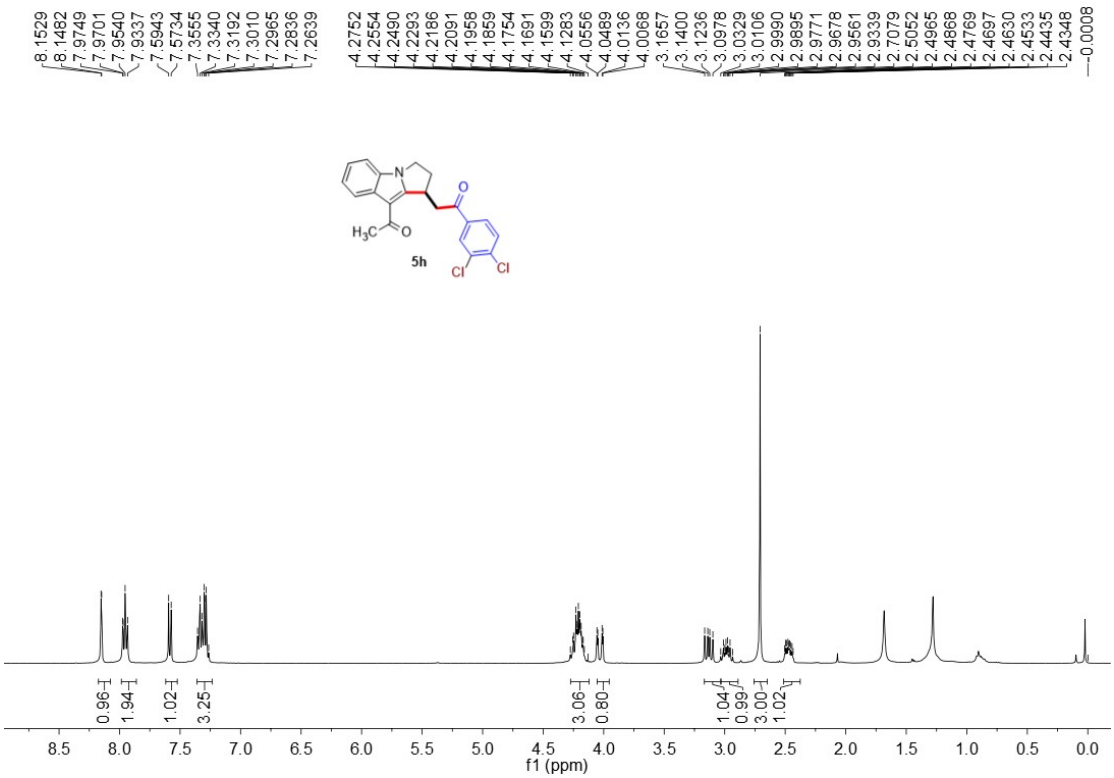
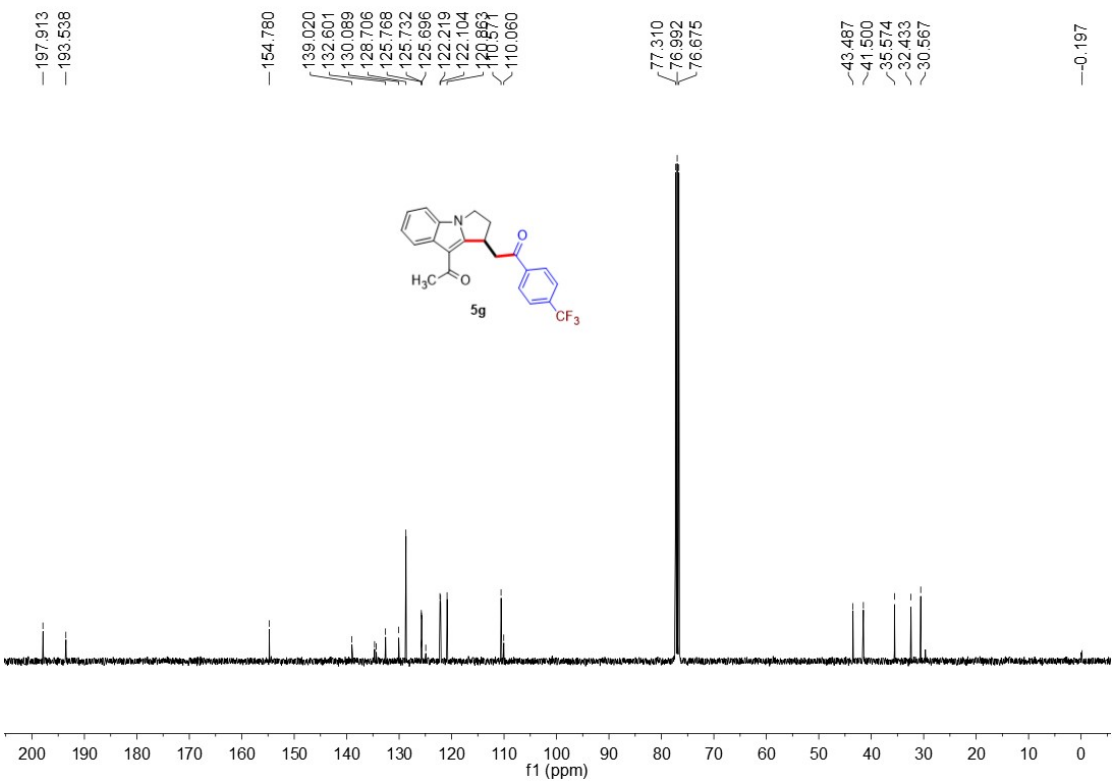
154.7261
138.5982
131.8104
130.8407
130.5955
130.1622
129.0428
126.9696
122.1249
122.0219
120.9605
110.4434
109.9973
77.3097
76.9920
76.6743
45.1167
43.4853
35.3241
32.7590
30.3613
0.9253
5f
f1 (ppm)


8.1529
8.1482
7.9749
7.9701
7.9540
7.9337
7.5943
7.5734
7.3555
7.3340
7.3192
7.3010
7.2965
7.2836
7.2639
4.2752
4.2554
4.2490
4.2293
4.2186
4.2091
4.1958
4.1859
4.1754
4.1691
4.1599
4.1283
4.0556
4.0489
4.0136
4.0068
3.1657
3.1400
3.1236
3.0978
3.0329
3.0106
2.9990
2.9895
2.9771
2.9678
2.9561
2.9339
2.7079
2.5052
2.4965
2.4868
2.4769
2.4697
2.4630
2.4533
2.4435
2.4348
-0.0008
5h
0.96
1.94
1.02
3.25
3.06
0.80
1.04
0.99
3.00
1.02
f1 (ppm)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130.089
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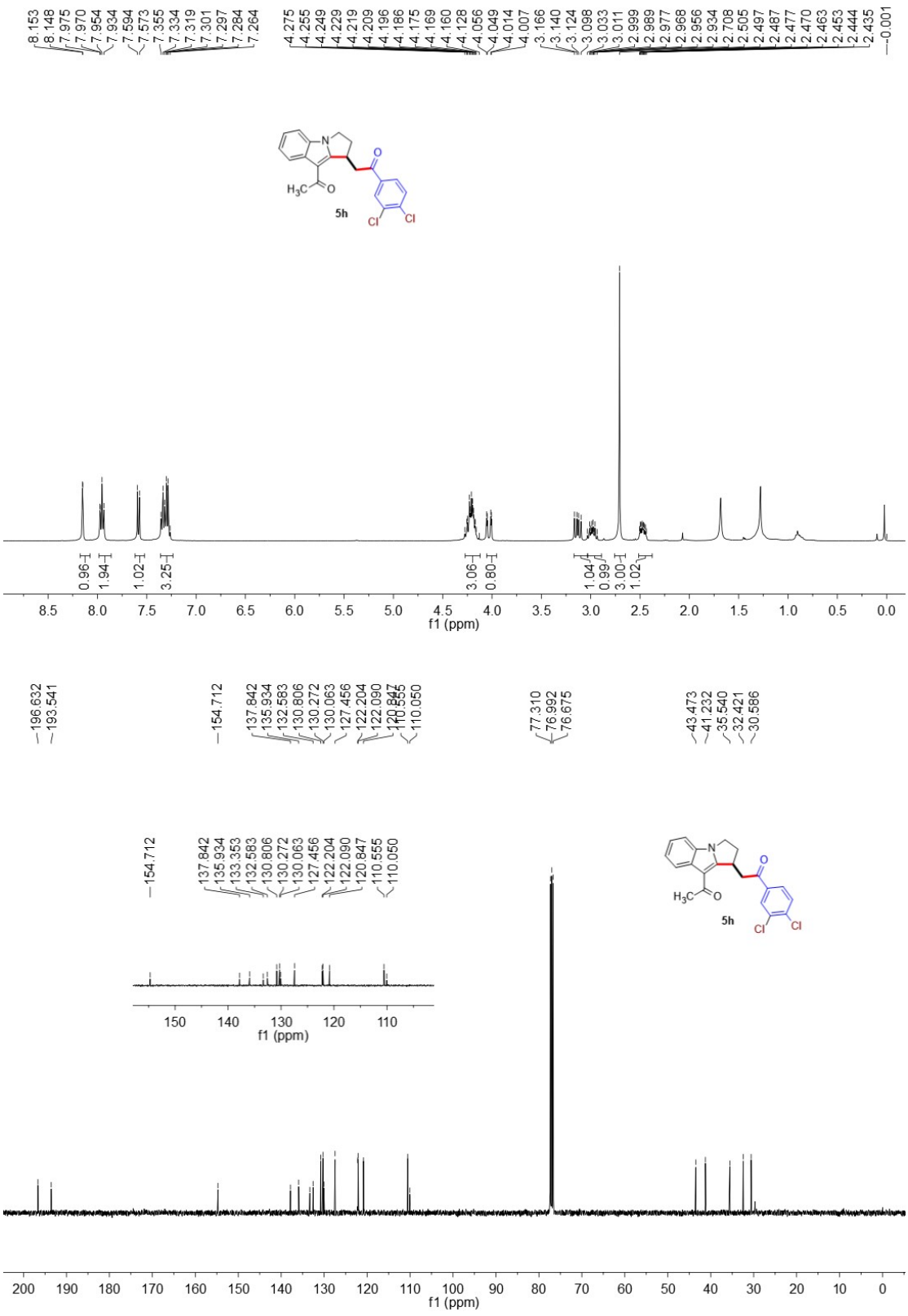
125.768
125.732
125.696
122.219
122.104
110.571
110.060
77.310
76.992
76.675
43.487
41.500
35.574
32.433
30.567
-0.197
5g
f1 (ppm)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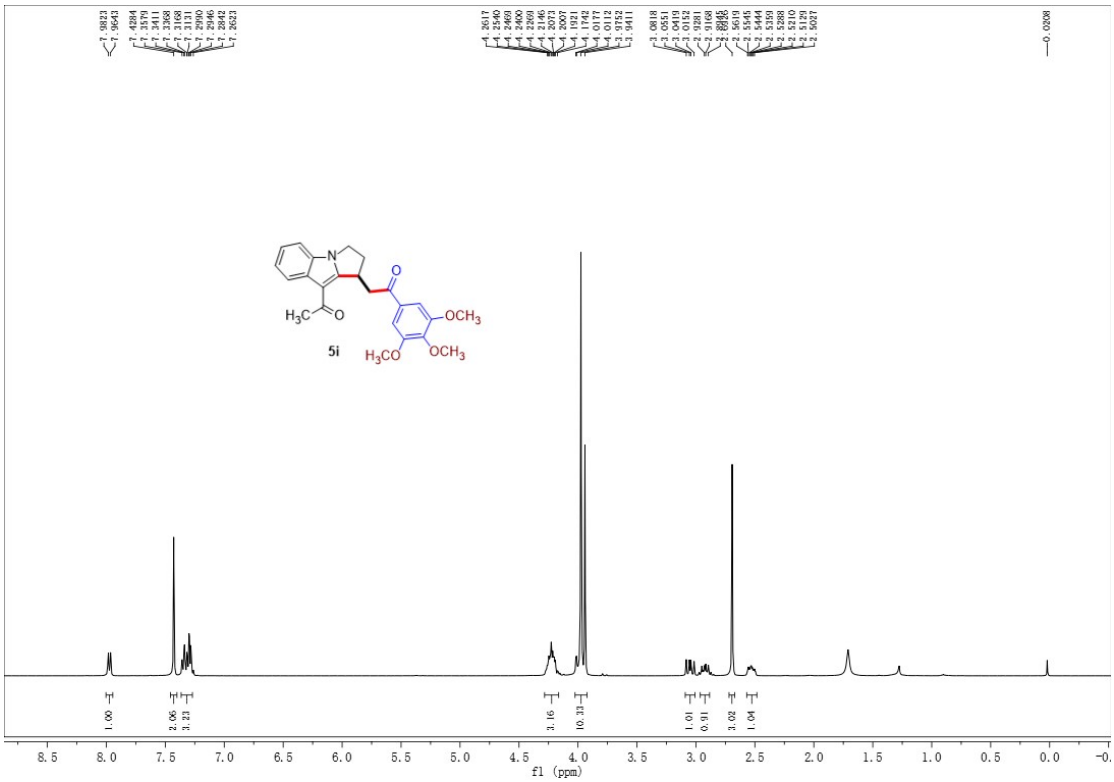
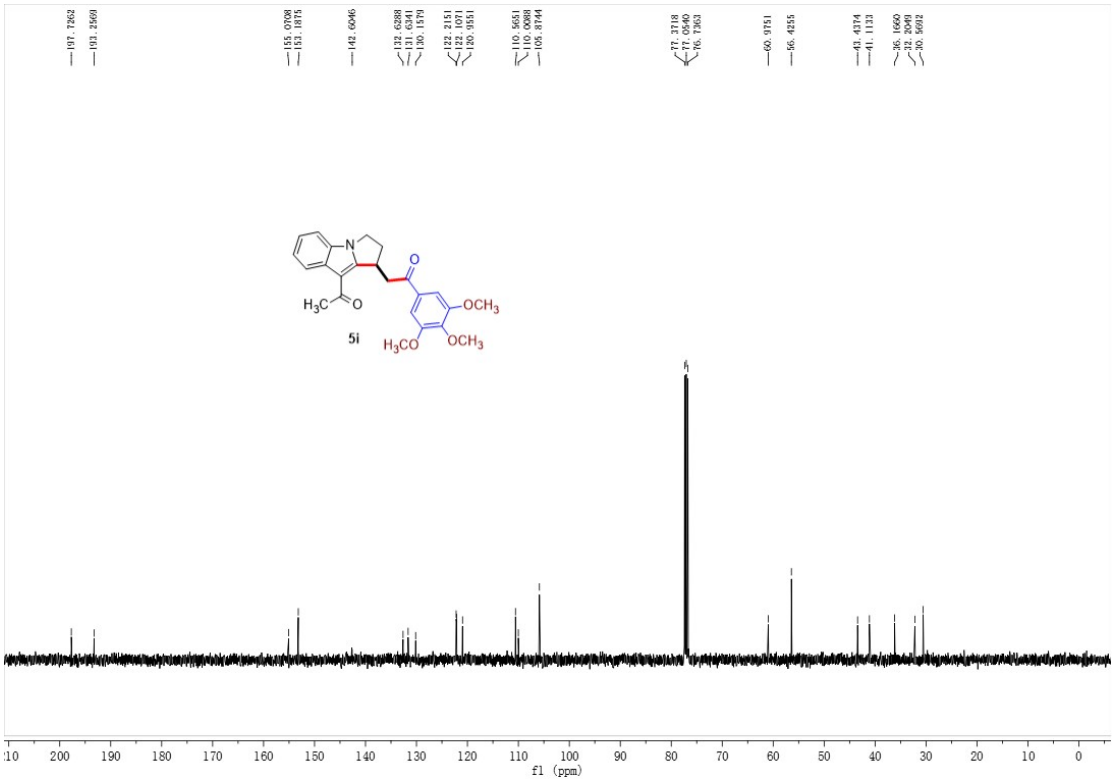
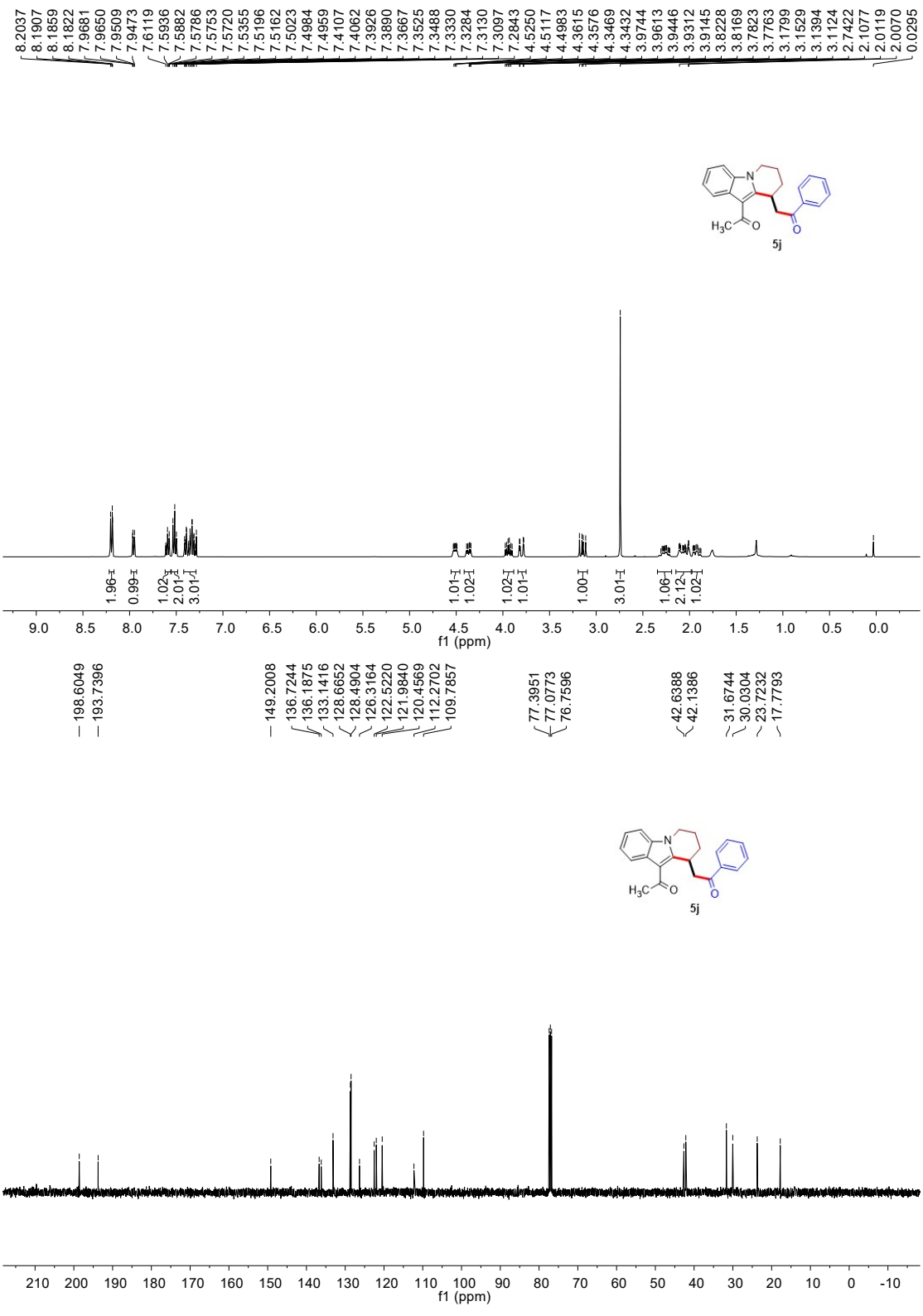
8.148
7.975
7.970
7.954
7.934
7.594
7.573
7.355
7.334
7.319
7.301
7.297
7.284
7.264
4.275
4.255
4.249
4.229
4.219
4.209
4.196
4.186
4.175
4.169
4.160
4.128
4.056
4.049
4.014
4.007
3.166
3.140
3.124
3.098
3.033
3.011
2.999
2.989
2.977
2.968
2.956
2.934
2.708
2.505
2.497
2.487
2.477
2.470
2.463
2.453
2.444
2.435
-0.001
5h
0.96
1.94
1.02
3.25
3.06
0.80
1.04
0.99
3.00
1.02
f1 (ppm)
196.632
193.541
154.712
137.842
135.934
133.353
132.583
130.806
130.272
130.063
127.456
122.204
122.090
120.847
110.555
110.050
77.310
76.992
76.675
43.473
41.232
35.540
32.421
30.586
5h
f1 (ppm)


5i
f1 (ppm)


5i
f1 (ppm)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7.9650
7.9509
7.9473
7.6119
7.5936
7.5882
7.5786
7.5753
7.5720
7.5355
7.5196
7.5162
7.5023
7.4984
7.4959
7.4107
7.4062
7.3926
7.3890
7.3667
7.3525
7.3488
7.3330
7.3284
7.3130
7.3097
7.2843
4.5250
4.5117
4.4983
4.3615
4.3576
4.3469
4.3432
3.9744
3.9613
3.9446
3.9312
3.9145
3.8228
3.8169
3.7823
3.7763
3.1799
3.1529
3.1394
3.1124
2.7422
2.1077
2.0119
2.0070
0.0295
5j
1.96
0.99
1.02
2.01
3.01
1.01
1.02
1.02
1.01
1.00
3.01
1.06
2.12
1.02
f1 (ppm)
198.6049
193.7396
149.2008
136.7244
136.1875
133.1416
128.6652
128.4904
126.3164
122.5220
121.9840
120.4569
112.2702
109.7857
77.3951
77.0773
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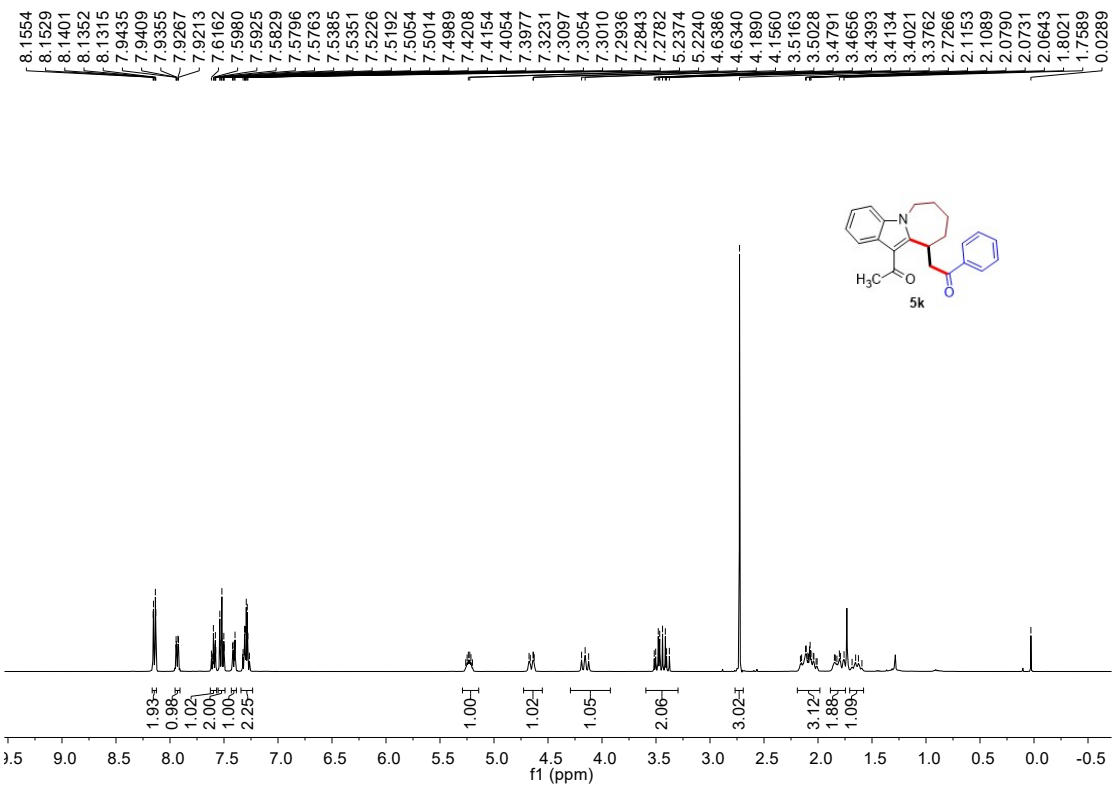
42.6388
42.1386
31.6744
30.0304
23.7232
17.7793
5j
f1 (ppm)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8.1315
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7.9213
7.6162
7.5980
7.5925
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7.5763
7.5385
7.5351
7.5226
7.5192
7.5054
7.5014
7.4989
7.4208
7.4154
7.4054
7.3977
7.3231
7.3097
7.3054
7.3010
7.2936
7.2843
7.2782
5.2374
5.2240
4.6386
4.6340
4.1890
4.1560
3.5163
3.5028
3.4791
3.4656
3.4393
3.4134
3.4021
3.3762
2.7266
2.1153
2.1089
2.0790
2.0731
2.0643
1.8021
1.7589
0.0289
1.93
0.98
1.02
2.00
1.00
2.25
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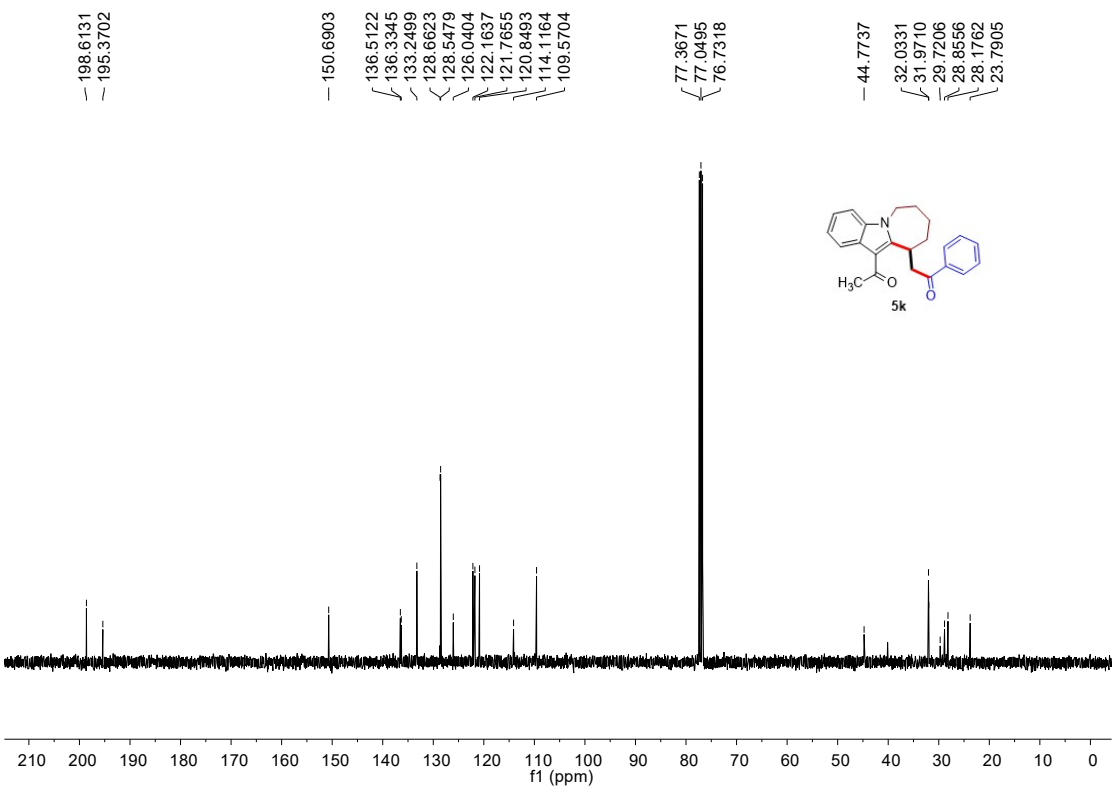
1.02
1.05
2.06
3.02
3.12
1.88
1.09
f1 (ppm)
5k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128.5479
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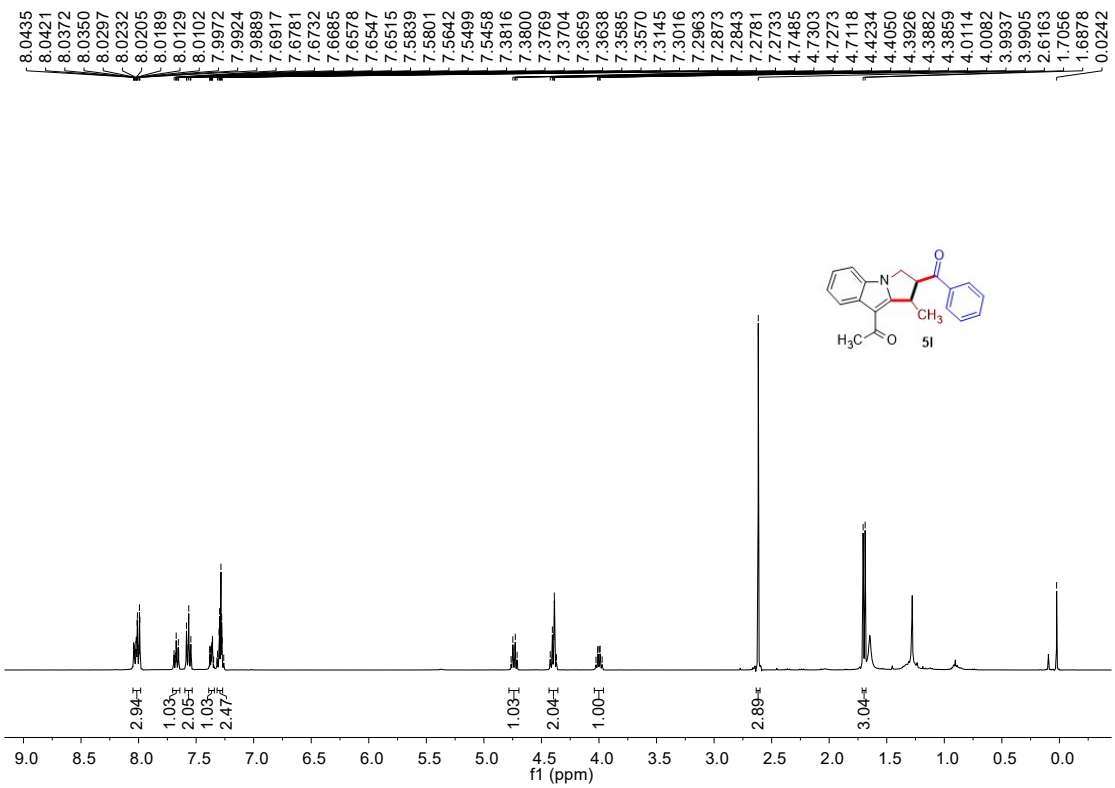
122.1637
121.7655
120.8493
114.1164
109.5704
77.3671
77.0495
76.7318
44.7737
32.0331
31.9710
29.7206
28.8556
28.1762
23.7905
f1 (ppm)
5k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8.0205
8.0189
8.0129
8.0102
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7.9924
7.9889
7.6917
7.6781
7.6732
7.6685
7.6578
7.6547
7.6515
7.5839
7.5801
7.5642
7.5499
7.5458
7.3816
7.3800
7.3769
7.3704
7.3659
7.3638
7.3585
7.3570
7.3145
7.3016
7.2963
7.2873
7.2843
7.2781
7.2733
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4.7303
4.7273
4.7118
4.4234
4.4050
4.3926
4.3882
4.3859
4.0114
4.0082
3.9937
3.9905
2.6163
1.7056
1.6878
0.0242
N
O
CH3
H3C
O
5l
2.94
1.03
2.05
1.03
2.47
1.03
2.04
1.00
2.89
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
197.2373
192.9257
154.2105
137.4682
135.0331
133.8650
132.2323
130.2665
129.0766
128.5927
122.2260
121.3697
110.4123
109.9977
77.3526
77.0350
76.7174
55.3046
44.3206
38.8765
30.1421
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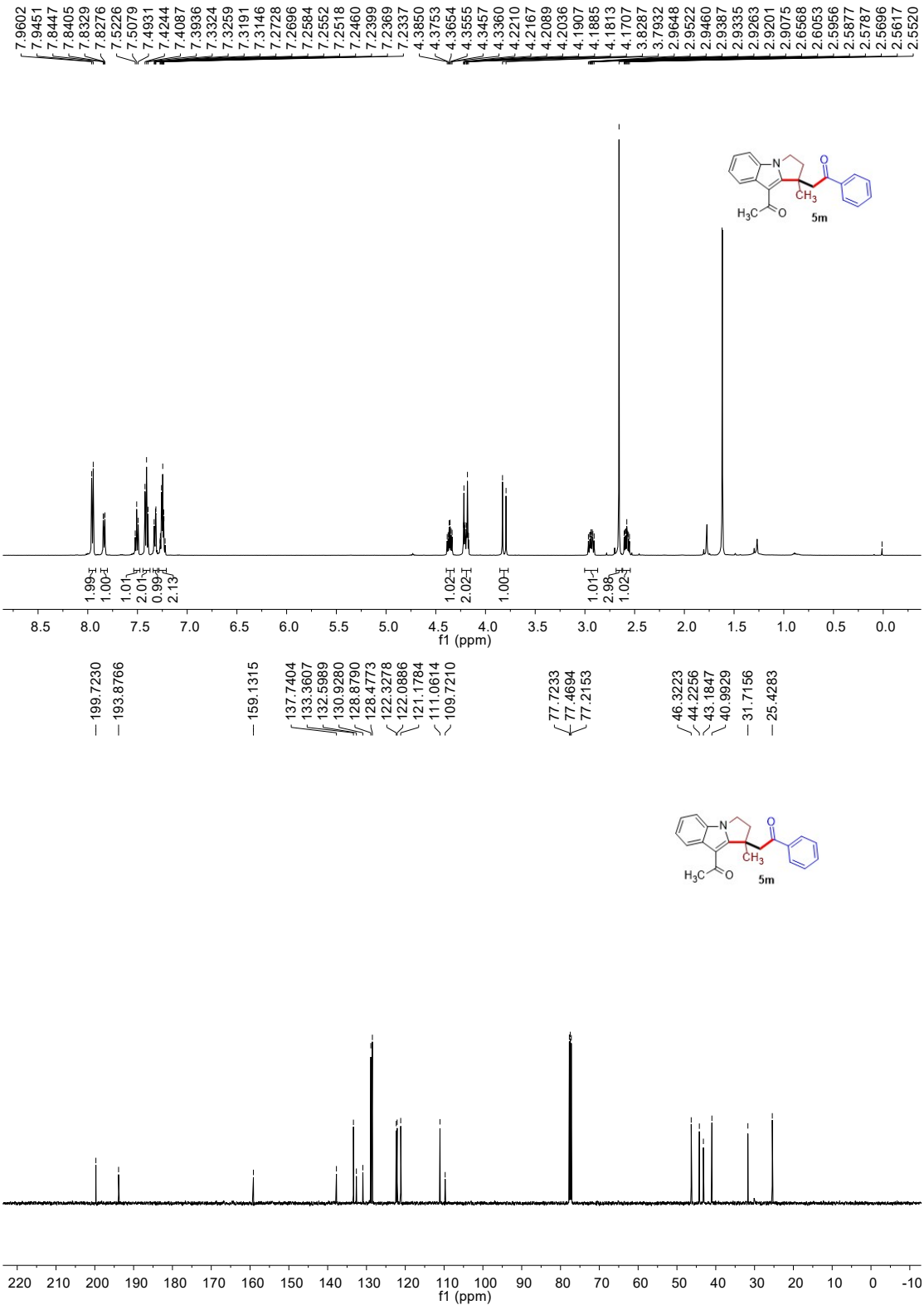
O
CH3
H3C
O
5l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.4087
7.3936
7.3324
7.3259
7.3191
7.3146
7.2728
7.2696
7.2584
7.2552
7.2518
7.2460
7.2399
7.2369
7.2337
4.3850
4.3753
4.3654
4.3555
4.3457
4.3360
4.2210
4.2167
4.2089
4.2036
4.1907
4.1885
4.1813
4.1707
3.8287
3.7932
2.9648
2.9522
2.9460
2.9387
2.9335
2.9263
2.9201
2.9075
2.6568
2.6053
2.5956
2.5877
2.5787
2.5696
2.5617
2.5520
5m
1.99
1.00
1.01
2.01
0.99
2.13
1.02
2.02
1.00
1.01
2.98
1.02
f1 (ppm)
199.7230
193.8766
159.1315
137.7404
133.3607
132.5989
130.9280
128.8790
128.4773
122.3278
122.0886
121.1784
111.0614
109.7210
77.7233
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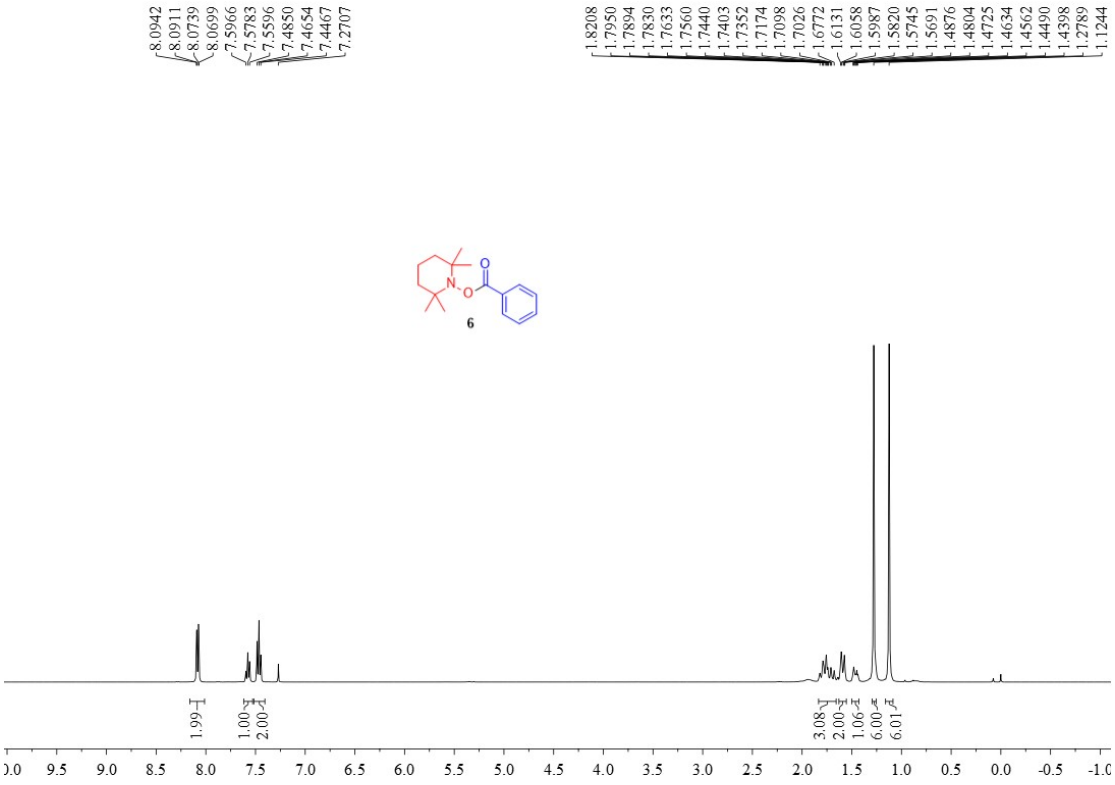
46.3223
44.2256
43.1847
40.9929
31.7156
25.4283
5m
f1 (ppm)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7.4654
7.4467
7.2707
1.8208
1.7950
1.7894
1.7830
1.7633
1.7560
1.7440
1.7403
1.7352
1.7174
1.7098
1.7026
1.6772
1.6131
1.6058
1.5987
1.5820
1.5745
1.5691
1.4876
1.4804
1.4725
1.4634
1.4562
1.4490
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3.08
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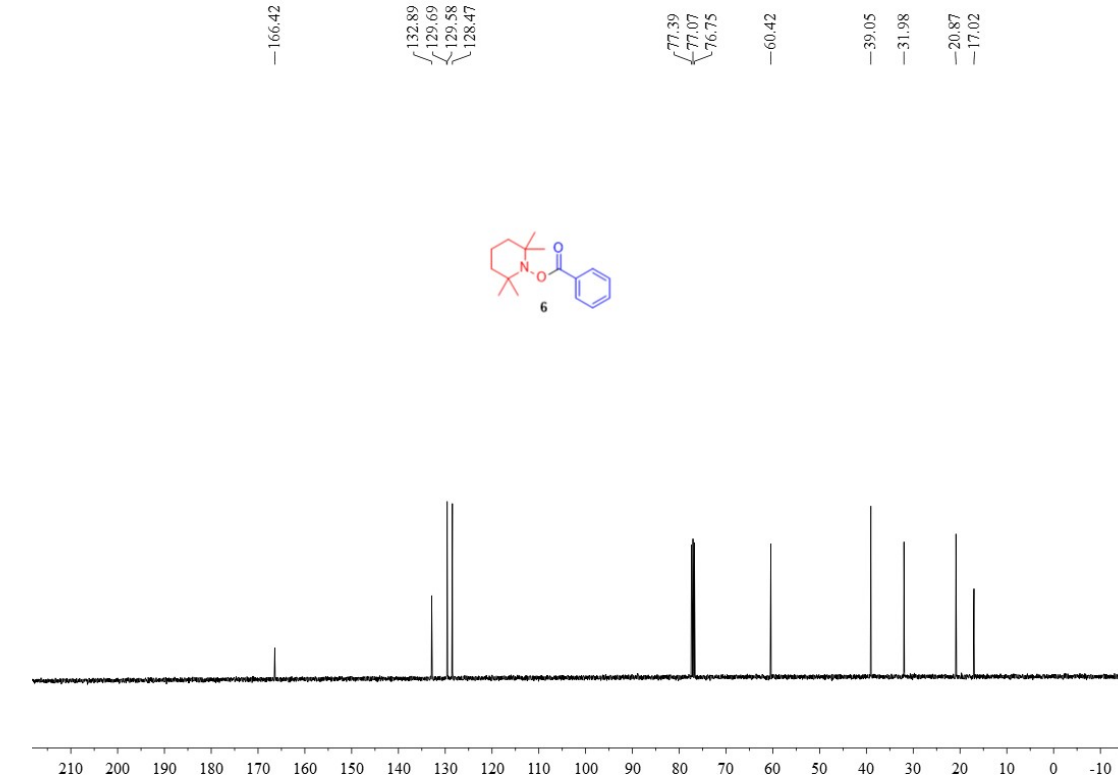
1.06
6.00
6.01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129.58
128.47
77.39
77.07
76.75
60.42
39.05
31.98
20.87
17.02
6

Crystal structure of 3ab