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Electronic Supplementary Information

Visible light-induced aerobic oxidative cross-coupling of glycine derivatives with indoles: a facile access to 3,3' bisindolylmethanes

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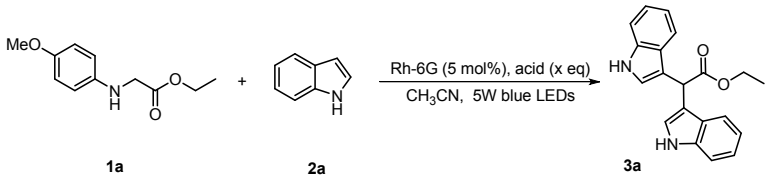
1. Optimization of Reaction Conditions

Table S1. Screening of Acid[a]

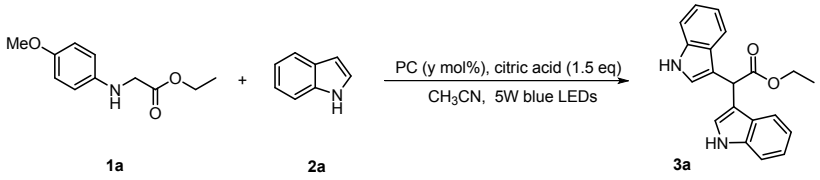


1a 2a 3a

Entry	Acid	x (eq)	Time (h)	Yield (%)[b]
1	-	-	36	trace
2	CF_3COOH	0.2	36	42
3	CF_3COOH	1.0	36	63
4	CF_3COOH	2.5	36	83
5	TfOH	2.5	36	22
6	HCOOH	2.5	36	31
7	CH_3COOH	2.5	36	55
8	citric acid	2.5	32	95
9	adipic acid	2.5	36	49
10	oxalic acid	2.5	36	<5
11	TsOH	2.5	36	14
12	benzoic acid	2.5	36	22
13	H_3PO_4	2.5	36	71
14	citric acid	2.0	32	95
15	**citric acid**	**1.5**	**36**	**95**
16	citric acid	1.0	36	76

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.21 mmol), Rh-6G (5 mol%), acid (x eq), CH_3CN (1.0 mL), 5 W blue LED light irradiation under air at r.t. [b] Isolated yields.

Table S2. Screening of Photocatalysts[a]

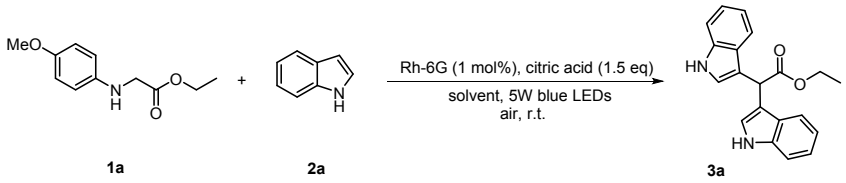


1a 2a 3a

Entry	Photocatalyst	y (mol%)	Time (h)	Yield (%)[b]
1	-	-	36	trace
2	Eosin Y	5	36	87
3	Eosin B	5	36	82
4	Rose Bengal	5	27	89
5	$Acr^{+}MesClO_4^{-}$	5	36	71
6	Rhodamine 6G	5	36	95
7	methylene blue	5	36	trace
8	Rhodamine 6G	2	40	92
9	Rhodamine 6G	1	41	88
10	**Rhodamine 6G[c]**	**1**	**38**	**95**
11	Rhodamine 6G[d]	1	35	87
11	Rhodamine 6G[c,e]	1	38	trace
12	Rhodamine 6G[c,f]	1	38	trace

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.21 mmol), photocatalyst (y mol%), citric acid (1.5 eq), CH_3CN (1.0 mL), 5 W blue LED light irradiation under air at r.t. [b] Isolated yields. [c] 2.0 mL of CH_3CN was used. [d] 3.0 mL of CH_3CN was used. [e] In dark. [f] Ar atmosphere.

Table S3. Screening of Solvents[a]



1a 2a 3a

Entry	Solvent	Time (h)	Yield (%)[b]
1	CH_3CN	38	95
2	**DCE**	**12**	**95**
3	DCM	38	70
4	$CHCl_3$	38	68
5	toluene	38	61
6	EtOH	38	89
7	DMSO	38	trace
8	DMF	38	trace

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.21 mmol), Rh-6G (1 mol%), citric acid (1.5 eq), solvent (2.0 mL), 5 W blue LED light irradiation under air at r.t. [b] Isolated yields.

2. EPR Spectra

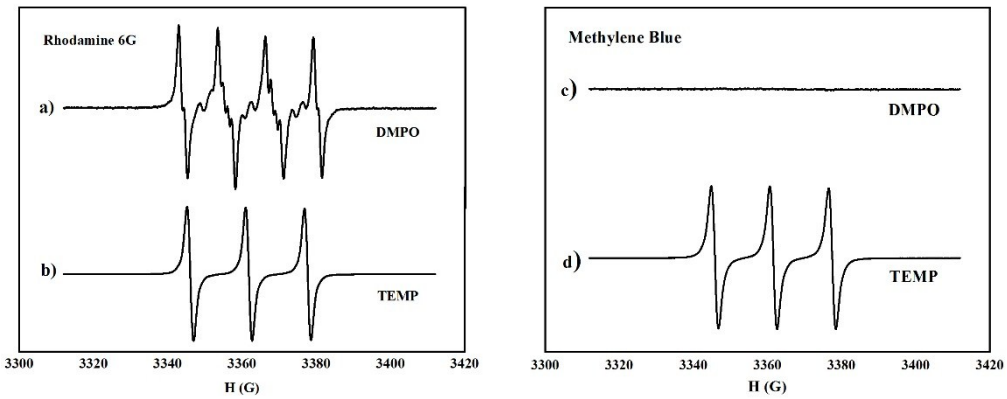


Figure S1. EPR spectra of a solution of a) **1a** (0.1 $molL^{-1}$), Rh-6 (1×10^{-3} $molL^{-1}$), and DMPO (0.05 $molL^{-1}$) in air-saturated CH_3CN upon irradiation with blue LED for 100 s; b) **1a** (0.1 $molL^{-1}$), Rh-6 (1×10^{-3} $molL^{-1}$), and TEMP (0.5 $molL^{-1}$) in air-saturated CH_3CN upon irradiation with blue LED for 100 s; c) **1a** (0.1 $molL^{-1}$), methylene blue (1×10^{-3} $molL^{-1}$), and DMPO (0.05 $molL^{-1}$) in air-saturated CH_3CN upon irradiation with blue LED for 100 s; d) **1a** (0.1 $molL^{-1}$), methylene blue (1×10^{-3} $molL^{-1}$), and TEMP (0.5 $molL^{-1}$) in air-saturated CH_3CN upon irradiation with blue LED for 100 s.

3. Luminescence Quenching Experiments

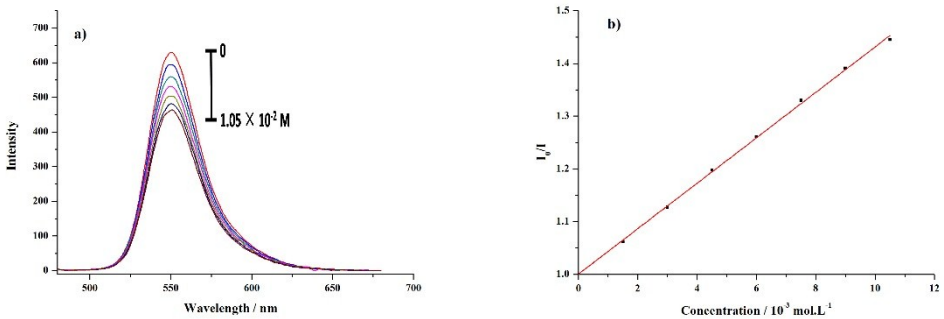


Figure S2. a) Changes in the fluorescence spectra of Rh-6G (1.0×10^{-6} M) upon the progressive addition of **1a** (1.5×10^{-3} M) in CH_3CN; b) Stern–Volmer quenching plot of Rh-6G in the presence of **1a**.

4. Experiment Information and Characterization Data

4.1 General information.

Unless otherwise noted, all reagents were purchased from commercial sources and used as received without further purification. N-arylglycine derivatives[6,7] and α-amino ketone[8] were prepared according to literature procedures. Unless otherwise indicated, all experiments were carried out under air atmosphere. Irradiation of photochemical reactions was carried out using a 5 W blue LED bulb. The silica gel (200−300 meshes) was used for column chromatography and TLC inspections were taken on silica gel GF254 plates. Liquid ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High resolution mass spectra (HRMS) were obtained on a mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof). Luminescence spectra were surveyed on a PerkinElmer LS 55 spectrophotometer. EPR spectra were recorded at room temperature using an EPR spectrometer at 9.448 GHz. Typical spectrometer parameters are shown as follows, sweep width: 100.0 G; center field set: 3362.0 G; time constant: 81.92 ms; sweep time: 75.0 s; modulation amplitude: 0.8 G; modulation frequency: 100.0 kHz; receiver gain: 2.00×10^{3}; microwave power: 7.51 mW.

4.2 General procedure for the visible-light-induced oxidative cross-coupling reaction of glycine derivatives with indoles.

To a solution of *N*-arylglycine derivatives **1** (0.2 mmol, 1 eq), Rh-6G (1 mol%) and indoles **2** (0.42 mmol, 2.1 eq) in dry DCE (4.0 mL) was added citric acid (1.5 eq). The mixed solution was irradiated with a 5 W blue LED bulb under air atmosphere at room temperature. After completion of the reaction as monitored by TLC, the mixture was diluted with EtOAc, washed with water and brine respectivey, and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was separated by silica gel column chromatography (with petroleum ether/EtOAc = 4:1 as eluent) to afford the product **3**.

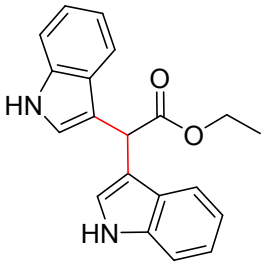
4.3 Procedures for the synthesis of streptindole and arsindoline B.

Step 1. A solution of **3a** (636 mg, 2 mmol) in anhydrous Et_2O (22 mL) was added dropwise to a suspension of $LiAlH_4$ (182 mg, 4.8 mmol) in anhydrous Et_2O (18 mL) under argon atmosphere at 0 °C. The resulting mixture was vigorously stirred at r.t. for 1 h, then quenched by addition of a 10% aq solution of potassium and sodium tartrate. The reaction mixture was extracted with CH_2Cl_2, the combined organic layers were washed with H_2O and brine, respectively, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (with petroleum ether/EtOAc = 2:1 as eluent) to afford **4** (510 mg, 92%) as a colorless solid.

Step 2. A mixture of alcohol (**4**) (80 mg, 0.29 mmol), potassium acetate (100 mg, 1.02 mmol), and anhydride (5.36 mmol, 18.5 eq) was stirred at r.t. for 17 h. Then ethyl acetate (2 mL) and ethanol (0.3 mL) were added and the mixture was stirred overnight. The majority of the solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2. The combined organic layer was successively washed with H_2O and brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (with petroleum ether/EtOAc = 2:1 as eluent) to afford the natural product.

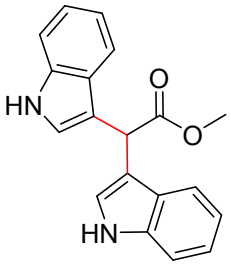
4.4 Characterization data.

***Ethyl 2,2-di(1H-indol-3-yl)acetate* (*3a*).[1]**



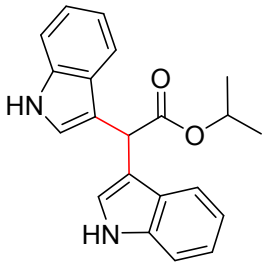
Pale red powder, mp 57−59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (brs, 2H), 7.65 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.22–7.16 (m, 2H), 7.15–7.08 (m, 2H), 6.93 (d, J = 2.1 Hz, 2H), 5.51 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 136.2, 126.5, 123.4, 122.0, 119.4, 119.2, 113.3, 111.3, 61.2, 40.6, 14.2.

***Methyl 2,2-di(1H-indol-3-yl)acetate* (*3b*).[2]**



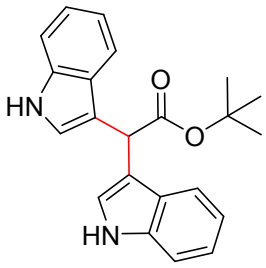
Pale red powder, mp 63−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (brs, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.20 (t, J = 7.5 Hz, 2H), 7.12 (t, J = 7.4 Hz, 2H), 6.94 (d, J = 2.3 Hz, 2H), 5.53 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 136.2, 126.5, 123.4, 122.1, 119.5, 119.1, 113.2, 111.3, 52.3, 40.4.

***Isopropyl 2,2-di(1H-indol-3-yl)acetate* (*3c*).**



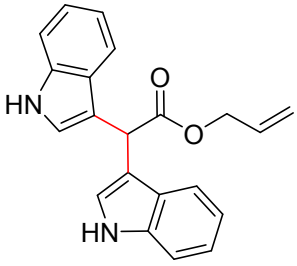
Pale yellow powder, mp 153−155 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.10 (brs, 2H), 7.66 (d, J = 7.9 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 1.9 Hz, 2H), 7.13–7.08 (m, 2H), 7.03–6.98 (m, 2H), 5.49 (s, 1H), 5.09–5.00 (m, 1H), 1.21 (d, J = 6.3 Hz, 6H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.2, 137.6, 127.7, 124.4, 122.1, 119.9, 119.5, 114.1, 112.1, 68.4, 41.8, 21.9. HRMS (ESI): calcd for $C_{21}H_{20}N_2O_2Na$ (M+Na$^+$) 355.1417; found 355.1410.

***Tert-butyl 2,2-di(1H-indol-3-yl)acetate* (*3d*).[2]**



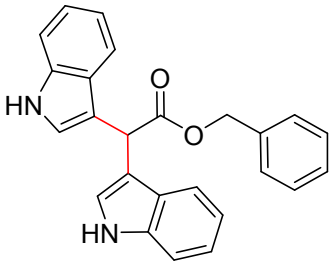
Pale yellow powder, mp 69−71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (brs, 2H), 7.54 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.07 (m, 2H), 7.03–6.97 (m, 2H), 6.76 (d, J = 1.9 Hz, 2H), 5.30 (s, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 136.2, 126.6, 123.3, 121.9, 119.2, 119.2, 113.7, 111.2, 81.2, 41.5, 28.0.

***Allyl 2,2-di(1H-indol-3-yl)acetate* (*3e*).[2]**



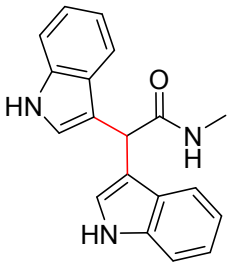
Pale red powder, mp 41−43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (brs, 2H), 7.65 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.22–7.17 (m, 2H), 7.13–7.09 (m, 2H), 6.96 (d, J = 2.1 Hz, 2H), 5.97–5.87 (m, 1H), 5.56 (s, 1H), 5.30–5.17 (m, 2H), 4.69–4.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 136.2, 131.9, 126.5, 123.4, 122.0, 119.5, 119.2, 118.4, 113.2, 111.3, 65.7, 40.4.

***Benzyl 2,2-di(1H-indol-3-yl)acetate* (*3f*).[2]**



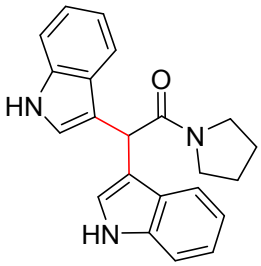
Pale red powder, mp 167−168 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.12 (brs, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.37–7.21 (m, 7H), 7.15–7.09 (m, 2H), 7.03–6.97 (m, 2H), 5.64 (s, 1H), 5.22 (s, 2H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.5, 137.6, 137.3, 129.0, 128.7, 128.6, 127.7, 124.5, 122.1, 119.9, 119.5, 113.8, 112.1, 66.8, 41.5.

***2,2-Di(1H-indol-3-yl)-N-methylacetamide* (*3g*).[2]**



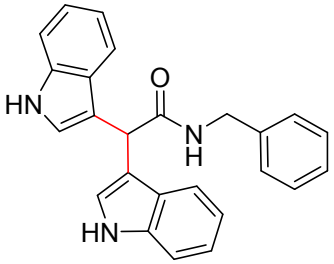
Pale yellow powder, mp 123−125 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.10 (brs, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.22 (brs, 1H), 7.18 (d, J = 2.1 Hz, 2H), 7.10–7.04 (m, 2H), 6.99–6.93 (m, 2H), 5.39 (s, 1H), 2.73 (d, J = 4.7 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.8, 137.7, 128.1, 124.6, 122.1, 119.9, 119.5, 115.6, 112.2, 43.0, 26.5.

***2,2-Di(1H-indol-3-yl)-1-(pyrrolidin-1-yl)ethan-1-one* (*3h*).[2]**



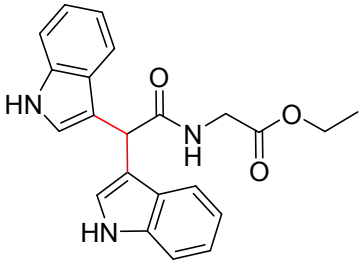
Pale red powder, mp 136−138 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.12 (brs, 2H), 7.67 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 2.3 Hz, 2H), 7.07−7.03 (m, 2H), 6.96−6.93 (m, 2H), 5.66 (s, 1H), 3.71 (t, J = 6.8 Hz, 2H), 3.46 (t, J = 6.8 Hz, 2H), 1.92−1.86 (m, 2H), 1.82−1.76 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6): δ 171.6, 137.6, 128.1, 124.7, 121.9, 120.0, 119.3, 115.2, 112.1, 47.4, 46.7, 40.0, 26.9, 24.9.

***N-Benzyl-2,2-di(1H-indol-3-yl)acetamide* (*3i*).[2]**



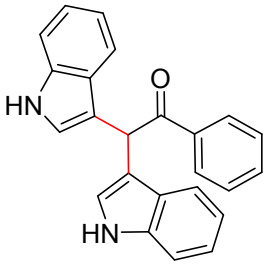
White powder, mp 198−199 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.11 (brs, 2H), 7.78 (brs, 1H), 7.63 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.26–7.16 (m, 7H), 7.08 (t, J = 7.6 Hz, 2H), 6.96 (t, J = 7.5 Hz, 2H), 5.50 (s, 1H), 4.44 (d, J = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.3, 140.6, 137.6, 129.0, 128.3, 128.0, 127.5, 124.6, 122.0, 119.9, 119.4, 115.4, 112.1, 43.6, 42.9.

***Ethyl (2,2-di(1H-indol-3-yl)acetyl)glycinate* (*3j*).[2]**



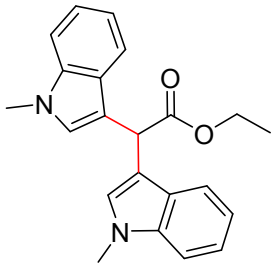
White powder, mp 210−211 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.08 (brs, 2H), 7.59 (d, J = 7.9 Hz, 2H), 7.50 (brs, 1H), 7.38 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 1.9 Hz, 2H), 7.10–7.05 (m, 2H), 6.99–6.94 (m, 2H), 5.48 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.97 (d, J = 5.9 Hz, 2H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.7, 170.8, 137.8, 128.1, 124.8, 122.1, 120.0, 119.5, 115.3, 112.2, 61.3, 42.9, 42.1, 14.5.

***2,2-Di(1H-indol-3-yl)-1-phenylethan-1-one* (*3k*).[3]**



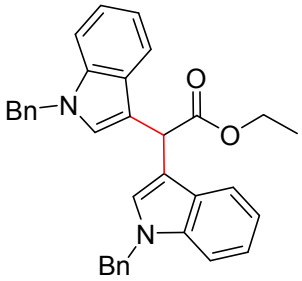
Pale red powder, mp 199−201 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.14 (brs, 2H), 8.22 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.58–7.51 (m, 1H), 7.50–7.43 (m, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 2.1 Hz, 2H), 7.12–7.05 (m, 2H), 7.03–6.95 (m, 2H), 6.71 (s, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 198.4, 137.9, 137.6, 133.3, 129.3, 129.2, 127.7, 125.1, 122.0, 119.7, 119.4, 114.4, 112.1, 42.6.

***Ethyl 2,2-bis(1-methyl-1H-indol-3-yl)acetate* (*3l*).[1]**



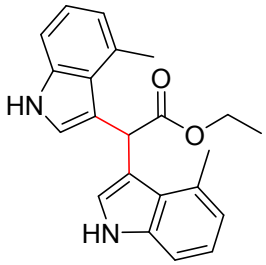
White powder, mp 161−162 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.62 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.19–7.13 (m, 4H), 7.04–6.98 (m, 2H), 5.47 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.77 (s, 6H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.8, 138.3, 129.0, 128.3, 122.4, 120.2, 119.7, 113.3, 110.4, 61.4, 41.4, 32.9, 14.7.

***Ethyl 2,2-bis(1-benzyl-1H-indol-3-yl)acetate* (*3m*).**



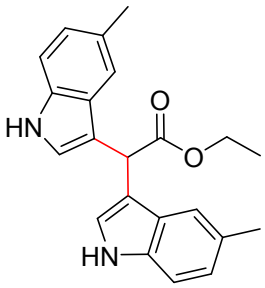
Pale yellow powder, mp 130−131 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.64 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 8.4 Hz, 4H), 7.30–7.20 (m, 6H), 7.15 (d, J = 7.2 Hz, 4H), 7.11–7.08 (m, 2H), 7.02–6.98 (m, 2H), 5.54 (s, 1H), 5.39 (s, 4H), 4.17 (q, J = 7.1 Hz, 2H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.6, 139.5, 137.9, 129.5, 128.64, 128.62, 128.3, 127.9, 122.6, 120.6, 120.0, 113.9, 111.0, 61.4, 50.4, 41.7, 14.7. HRMS (ESI): calcd for $C_{34}H_{30}N_2O_2Na$ (M+Na$^+$) 521.2199; found 521.2200.

***Ethyl 2,2-bis(4-methyl-1H-indol-3-yl)acetate* (*3n*).**



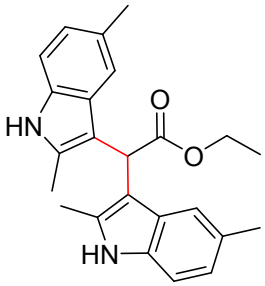
White powder, mp 175−177 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.06 (brs, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.02−6.97 (m, 2H), 6.95 (d, J = 2.2 Hz, 2H), 6.76 (d, J = 7.1 Hz, 2H), 6.12 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.64 (s, 6H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 174.8, 138.3, 130.5, 126.0, 125.1, 122.4, 121.6, 116.0, 110.4, 61.3, 43.8, 20.4, 14.5. HRMS (ESI): calcd for $C_{22}H_{22}N_2O_2Na$ (M+Na$^+$) 369.1573; found 369.1572.

***Ethyl 2,2-bis(5-methyl-1H-indol-3-yl)acetate* (*3o*).**



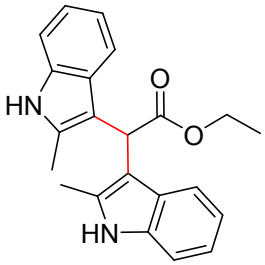
Brown powder, mp 190−192 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.01 (brs, 2H), 7.46 (s, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 2.1 Hz, 2H), 6.95 (dd, J = 8.3, 1.4 Hz, 2H), 5.47 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.38 (s, 6H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.9, 136.1, 128.3, 128.0, 124.6, 123.8, 119.5, 113.6, 112.0, 61.1, 41.6, 21.7, 14.6. HRMS (ESI): calcd for $C_{22}H_{22}N_2O_2Na$ (M+Na$^+$) 369.1573; found 369.1572.

***Ethyl 2,2-bis(2,5-dimethyl-1H-indol-3-yl)acetate* (*3p*).**



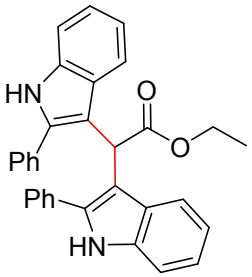
Pale yellow powder, mp 209−211 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.81 (brs, 2H), 7.20–7.13 (m, 4H), 6.81 (dd, J = 8.2, 1.3 Hz, 2H), 5.43 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.29 (s, 6H), 2.21 (s, 6H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 174.1, 134.6, 133.4, 129.7, 127.8, 122.5, 119.2, 110.8, 108.9, 61.1, 40.8, 21.8, 14.6, 12.3. HRMS (ESI): calcd for $C_{24}H_{26}N_2O_2Na$ (M+Na$^+$) 397.1886; found 397.1880.

***Ethyl 2,2-bis(2-methyl-1H-indol-3-yl)acetate* (*3q*).[4]**



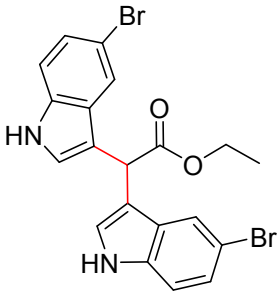
White powder, mp 192−194 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.90 (brs, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.01–6.96 (m, 2H), 6.90–6.85 (m, 2H), 5.50 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.26 (s, 6H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 174.0, 136.3, 133.4, 129.4, 121.0, 119.4, 119.38, 111.2, 109.3, 61.1, 40.9, 14.6, 12.3.

***Ethyl 2,2-bis(2-phenyl-1H-indol-3-yl)acetate* (*3r*).[1]**



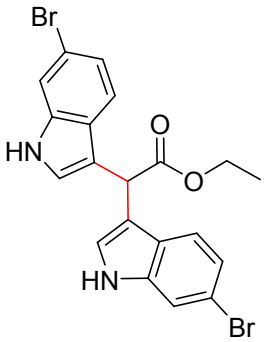
Pale yellow powder, mp 207−209 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.43 (brs, 2H), 7.54–7.50 (m, 4H), 7.45 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.39–7.33 (m, 4H), 7.31–7.27 (m, 2H), 7.11–7.05 (m, 2H), 6.89–6.83 (m, 2H), 5.69 (s, 1H), 4.00 (q, J = 7.1 Hz, 2H), 1.05 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 174.1, 137.3, 137.1, 134.1, 129.4, 129.3, 129.2, 128.4, 122.3, 121.5, 119.9, 112.0, 110.9, 61.2, 42.8, 14.5.

***Ethyl 2,2-bis(5-bromo-1H-indol-3-yl)acetate* (*3s*).**



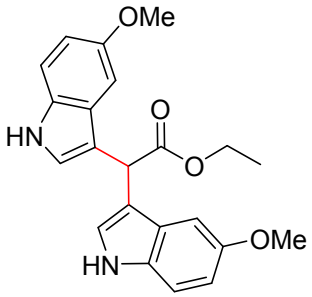
Yellow powder, mp 187−189 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.36 (brs, 2H), 7.82 (d, J = 1.9 Hz, 2H), 7.40−7.36 (m, 4H), 7.21 (dd, J = 8.6, 1.9 Hz, 2H), 5.53 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.2, 136.4, 129.4, 126.2, 125.0, 122.6, 114.2, 113.5, 112.6, 61.4, 41.5, 14.5. HRMS (ESI): calcd for $C_{20}H_{16}Br_2N_2O_2Na$ ($M+Na^+$) 496.9471; found 496.9458.

***Ethyl 2,2-bis(6-bromo-1H-indol-3-yl)acetate* (*3t*).**



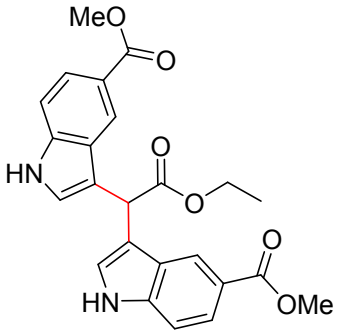
Yellow powder, mp 63−65 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.35 (brs, 2H), 7.61 (d, J = 1.6 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.33–7.30 (m, 2H), 7.12 (dd, J = 8.5, 1.8 Hz, 2H), 5.49 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.2, 138.5, 126.6, 125.6, 122.7, 121.7, 115.4, 115.1, 114.1, 61.4, 41.4, 14.5. HRMS (ESI): calcd for $C_{20}H_{16}Br_2N_2O_2Na$ ($M+Na^+$) 496.9471; found 496.9456.

***Ethyl 2,2-bis(5-methoxy-1H-indol-3-yl)acetate* (*3u*).[1]**



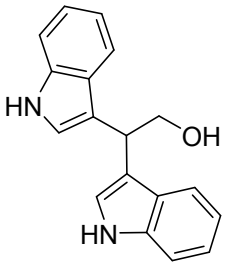
Pale yellow powder, mp 157−159 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.95 (brs, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 2.5 Hz, 2H), 7.17 (d, J = 2.4 Hz, 2H), 6.77 (dd, J = 8.8, 2.4 Hz, 2H), 5.45 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.75 (s, 6H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 173.8, 154.7, 132.8, 128.2, 125.2, 113.8, 112.9, 112.4, 101.8, 61.1, 55.8, 41.7, 14.7.

***Dimethyl 3,3'-(2-ethoxy-2-oxoethane-1,1-diyl)bis(1H-indole-5-carboxylate)* (*3v*).**



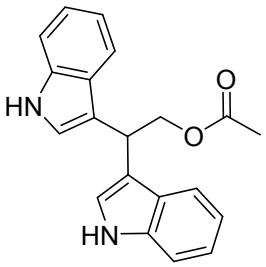
Yellow powder, mp 208−210 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.53 (brs, 2H), 8.47 (s, 2H), 7.82 (dd, J = 8.6, 1.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 1.9 Hz, 2H), 5.66 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.84 (s, 6H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Acetone): δ 173.4, 168.3, 140.4, 127.3, 126.5, 123.7, 123.1, 122.1, 115.4, 112.3, 61.6, 51.9, 41.6, 14.6. HRMS (ESI): calcd for $C_{24}H_{22}N_2O_6Na$ ($M+Na^+$) 457.1370; found 457.1353.

***2,2-Di-1H-indol-3-ylethanol (4).*[5]**



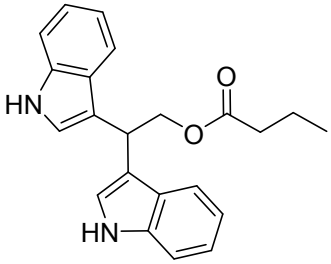
Colorless solid, mp 49−51 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (brs, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.20 (t, J = 7.5 Hz, 2H), 7.09 (t, J = 7.4 Hz, 2H), 6.86 (d, J = 2.1 Hz, 2H), 4.75 (t, J = 6.1 Hz, 1H), 4.25 (d, J = 6.1 Hz, 2H), 1.91 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 126.8, 122.6, 122.0, 119.31, 119.26, 115.9, 111.3, 65.6, 36.9.

***Streptindole (6).*[5]**



Brown oil, 72.6 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (brs, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.23–7.15 (m, 2H), 7.13–7.04 (m, 2H), 6.93 (d, J = 2.0 Hz, 2H), 4.96 (t, J = 7.1 Hz, 1H), 4.74 (d, J = 7.1 Hz, 2H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 136.3, 126.9, 122.1, 121.9, 119.4, 119.3, 116.1, 111.1, 67.3, 33.4, 21.1.

***Arsindoline B (7).*[5]**



Brown oil, 73.1 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (brs, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.22–7.16 (m, 2H), 7.11–7.05 (m, 2H), 6.94 (d, J = 2.1 Hz, 2H), 4.96 (t, J = 7.1 Hz, 1H), 4.75 (d, J = 7.1 Hz, 2H), 2.23 (t, J = 7.4 Hz, 2H), 1.61–1.54 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 136.3, 126.9, 122.1, 121.9, 119.5, 119.3, 116.2, 111.1, 67.0, 36.2, 33.5, 18.3, 13.6.

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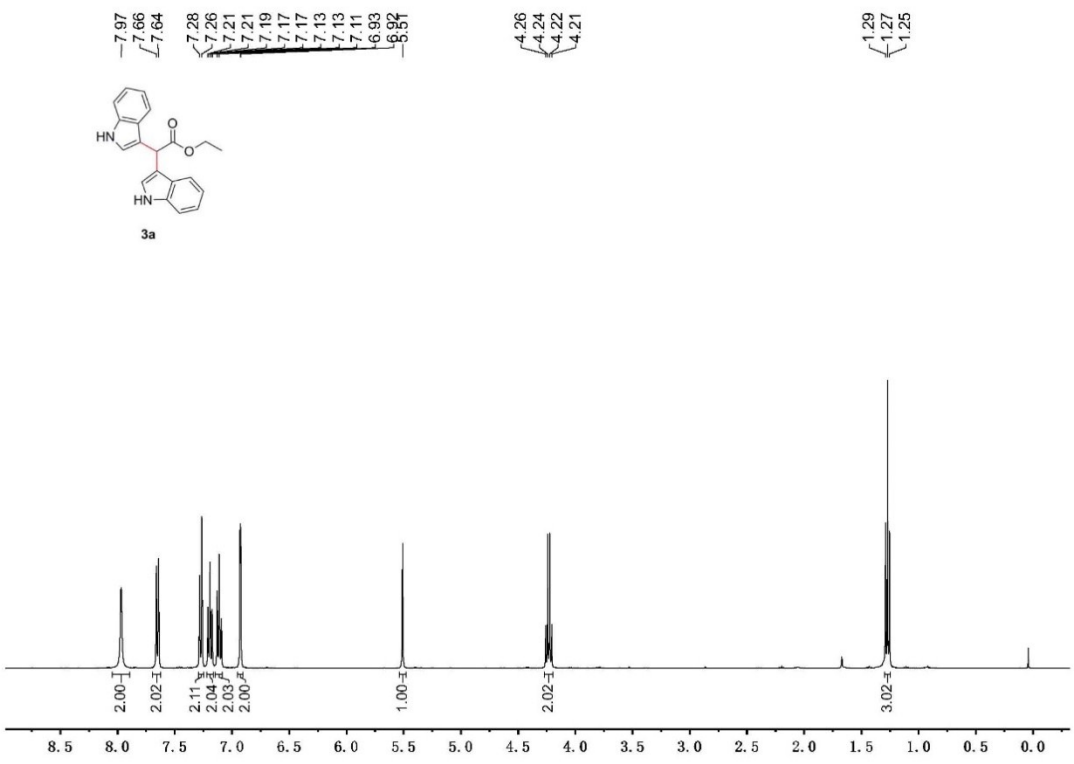
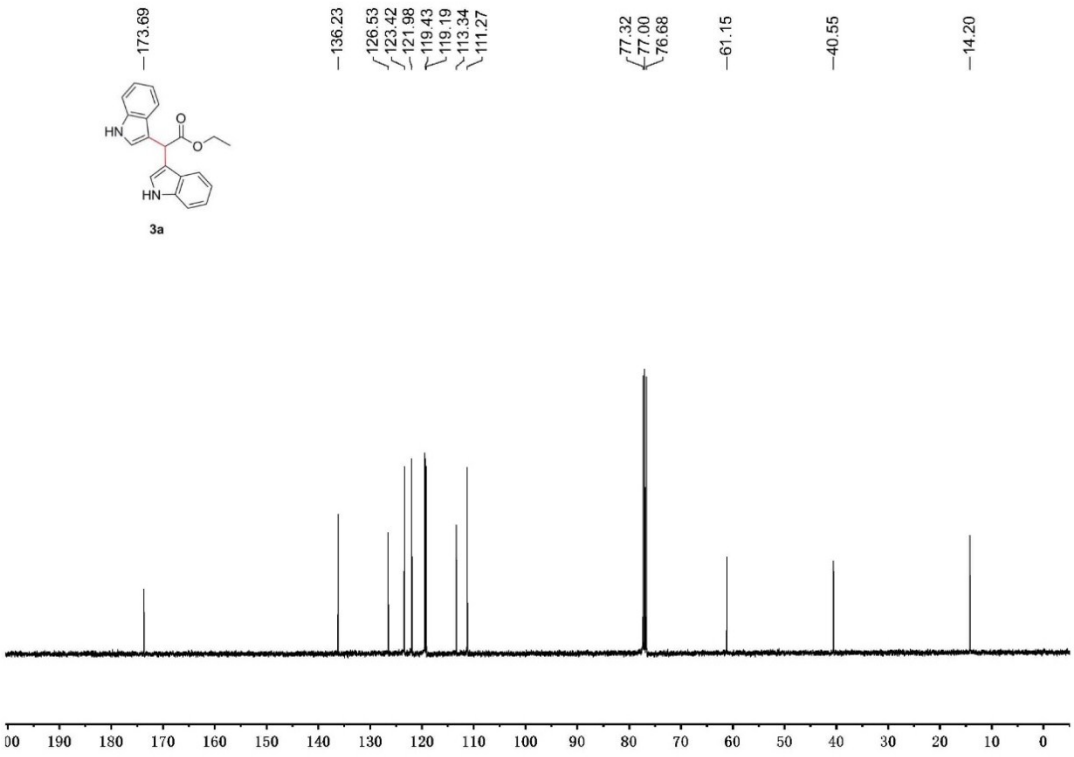
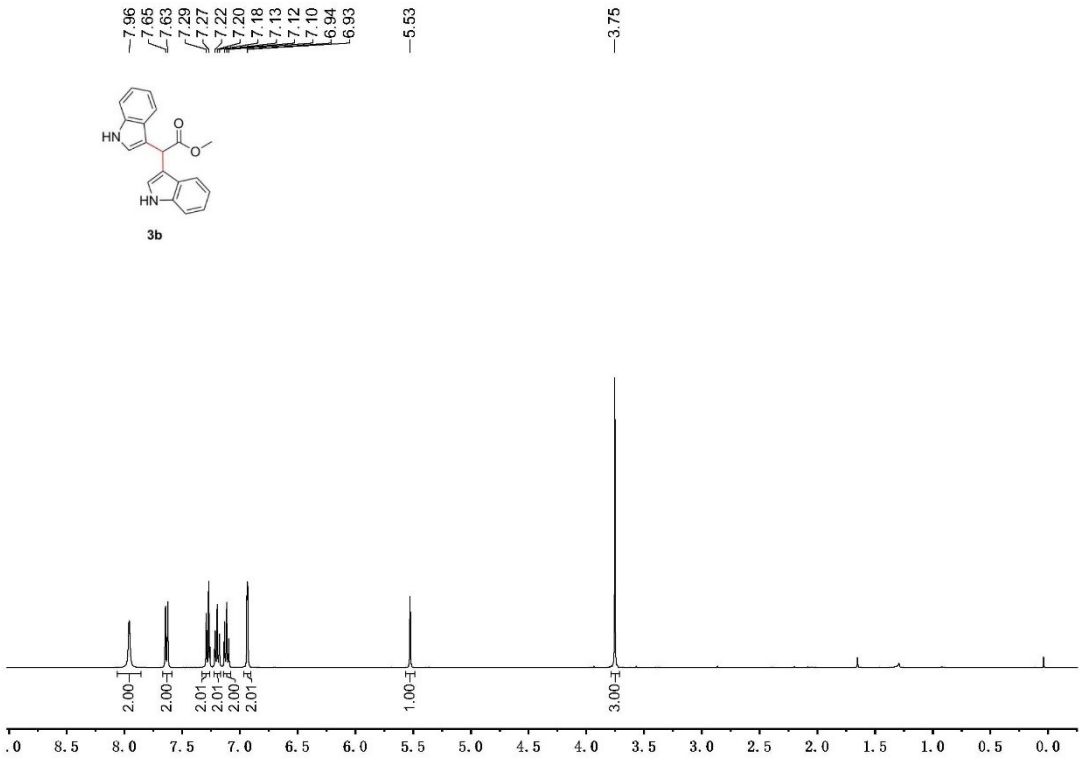
4. Copies of ^{1}H and ^{13}C Spectra



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6.93
5.53
3.75
HN
O
O
HN
3b
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2.00
2.01
2.01
2.00
2.01
1.00
3.00
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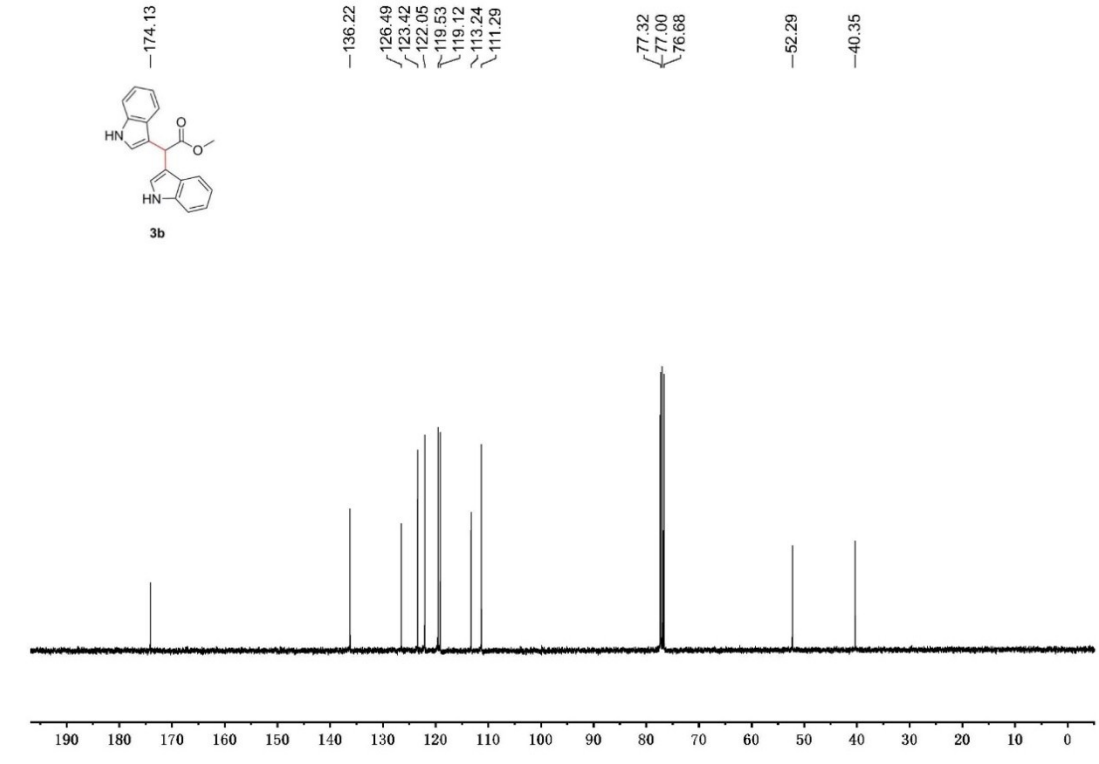
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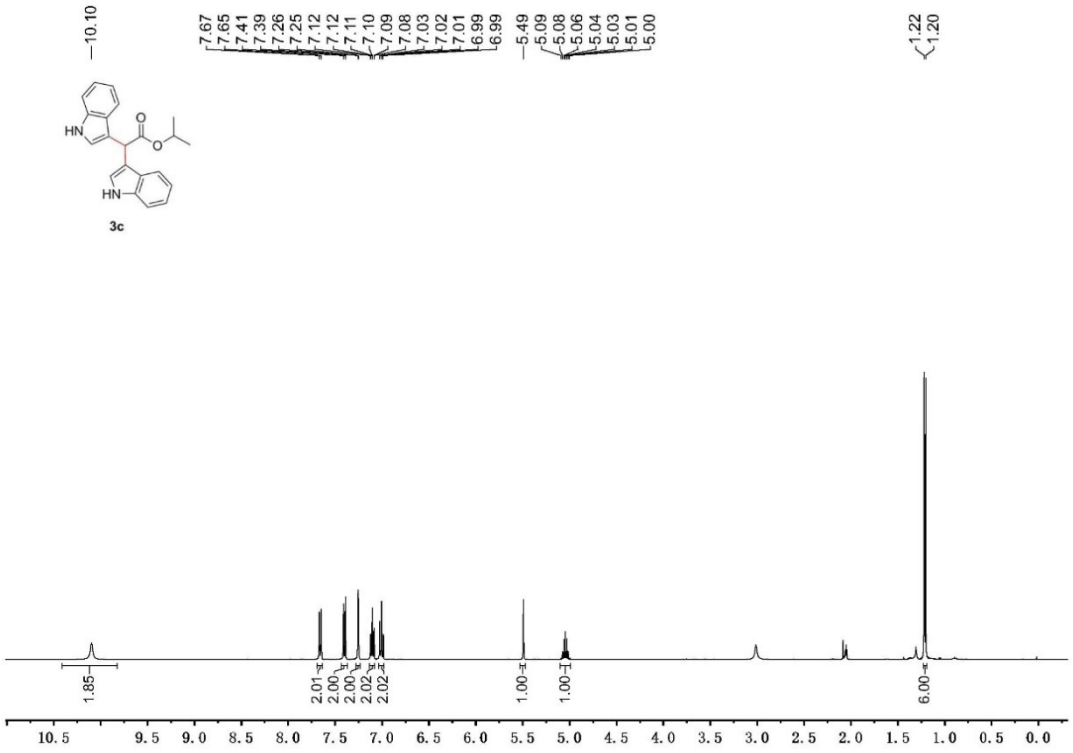
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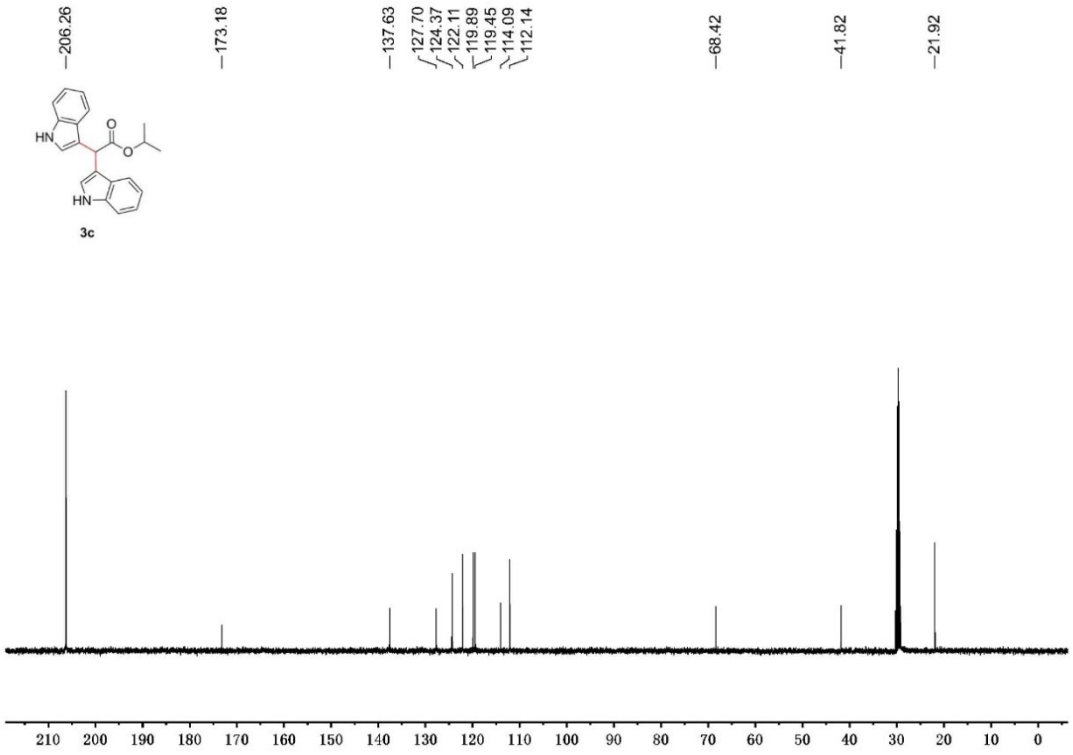
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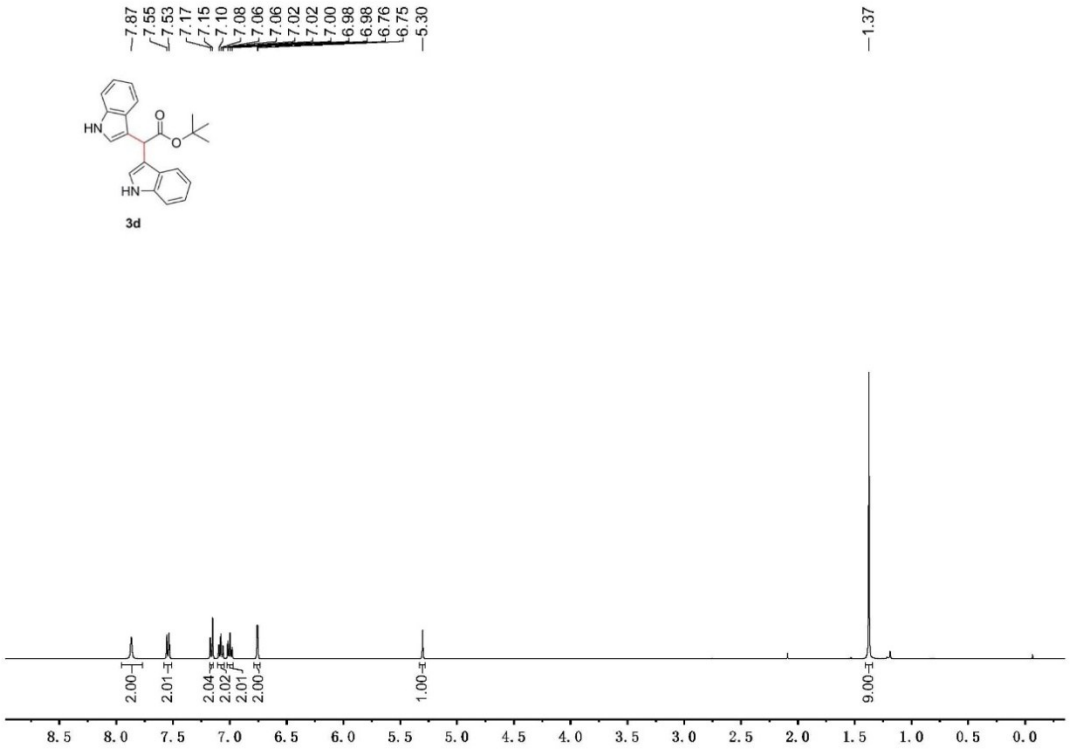
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2.01
2.00
1.00
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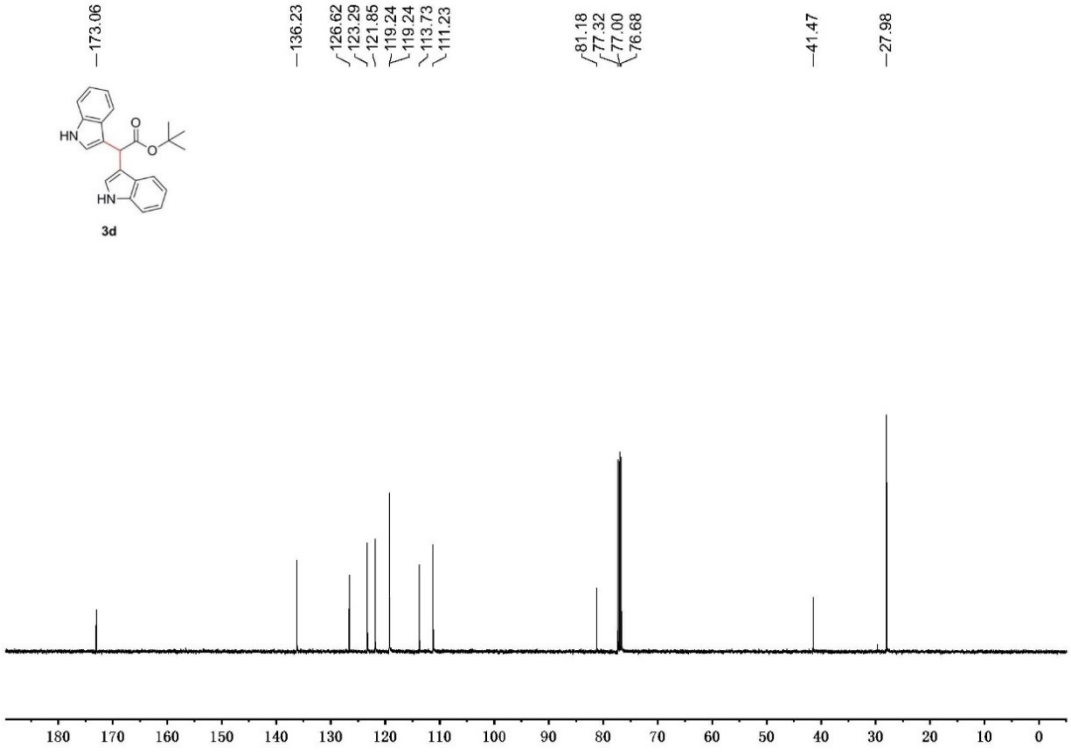
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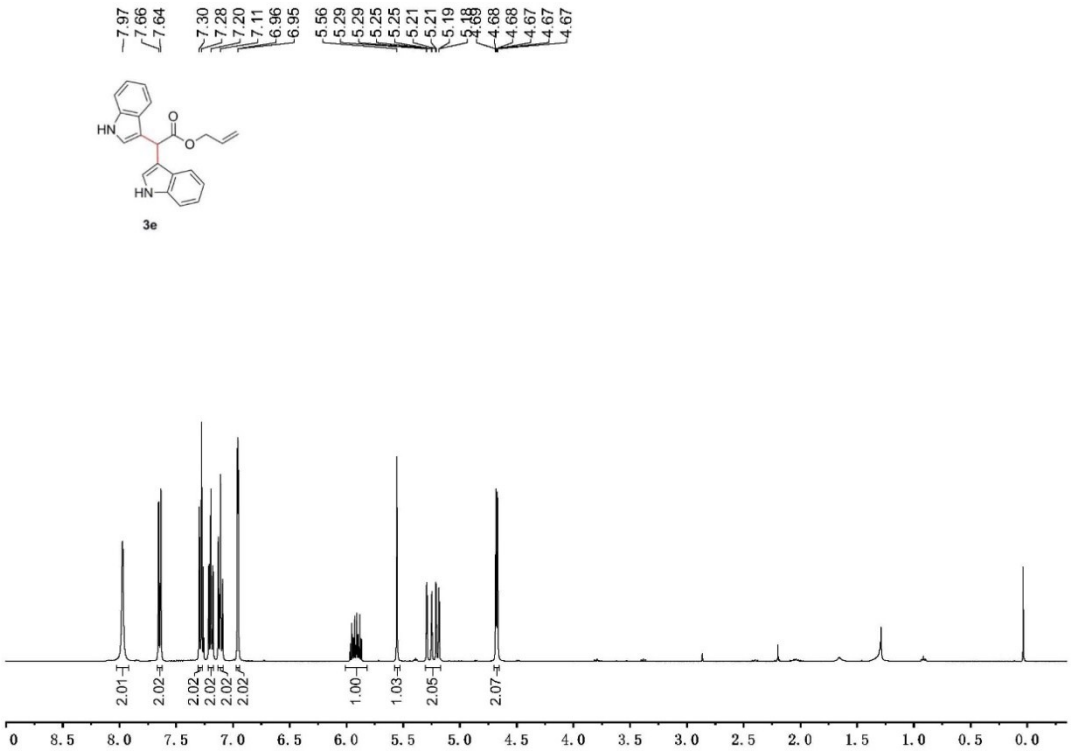
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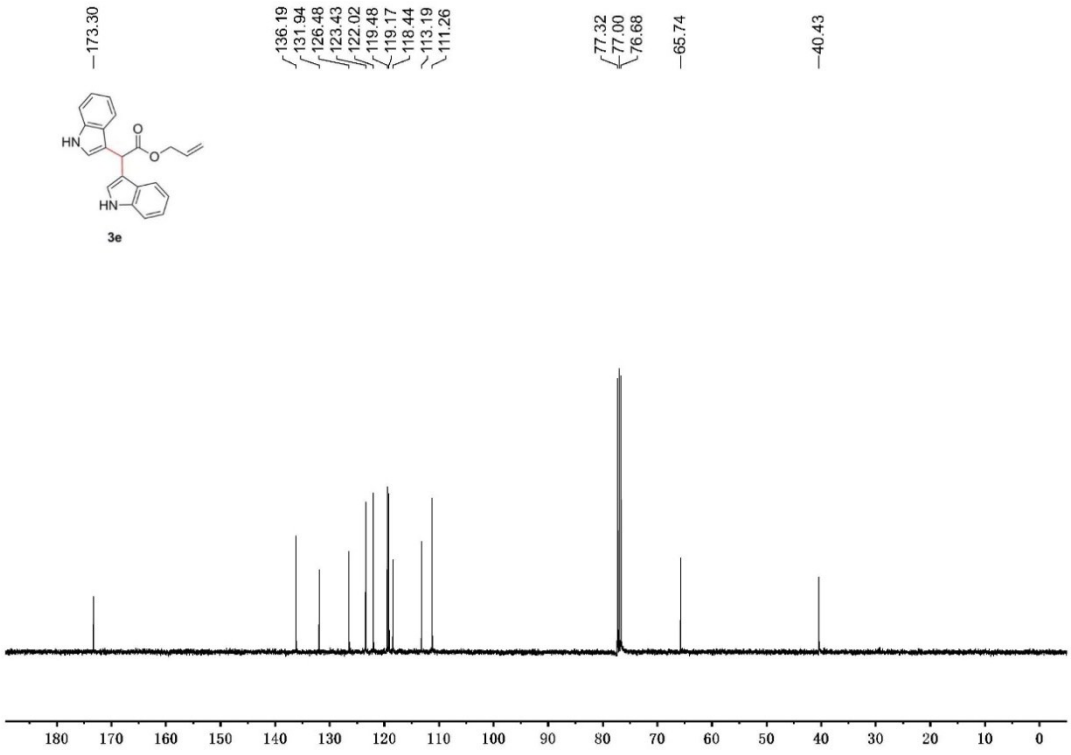
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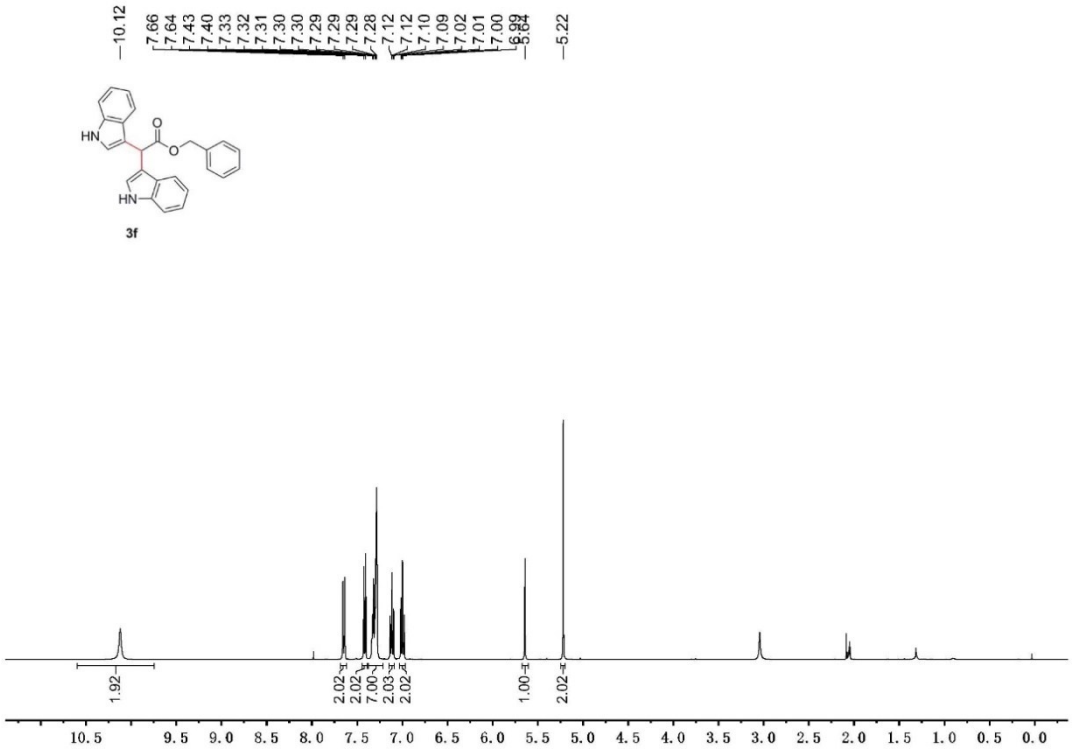
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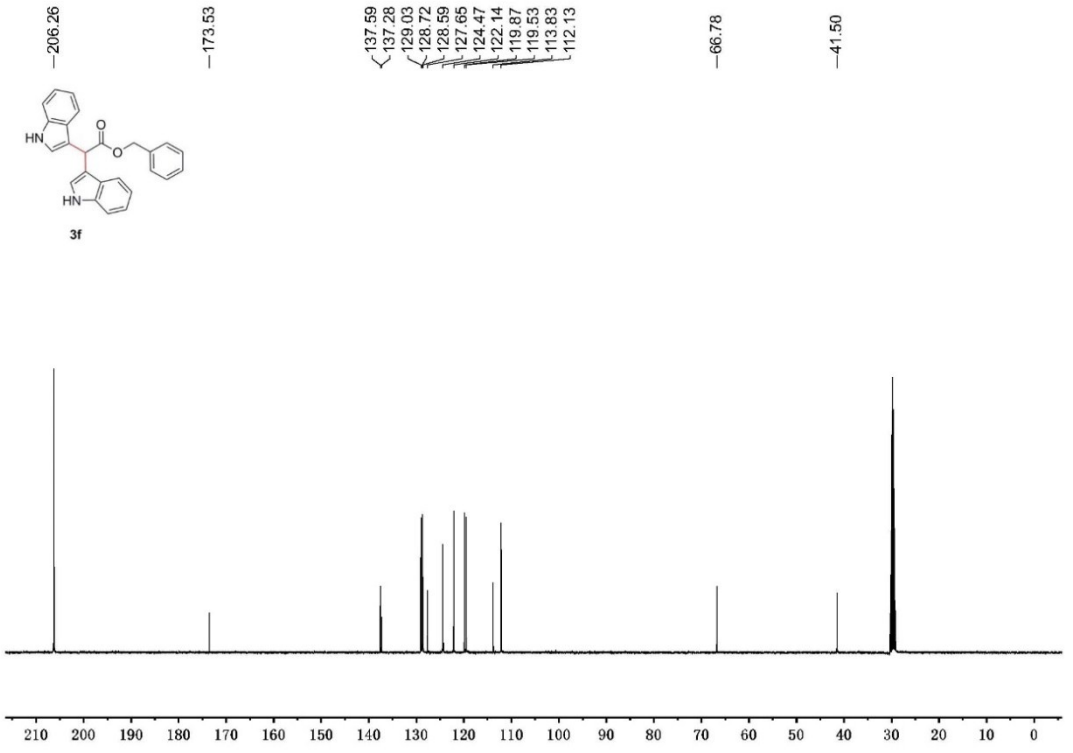
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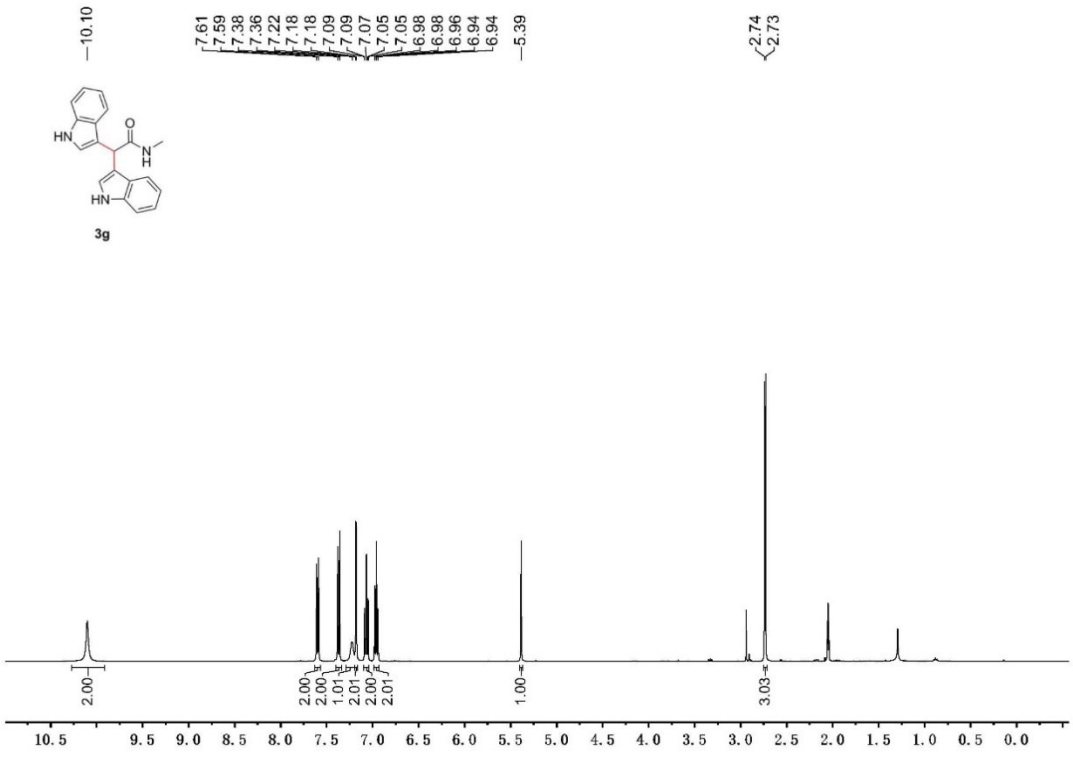
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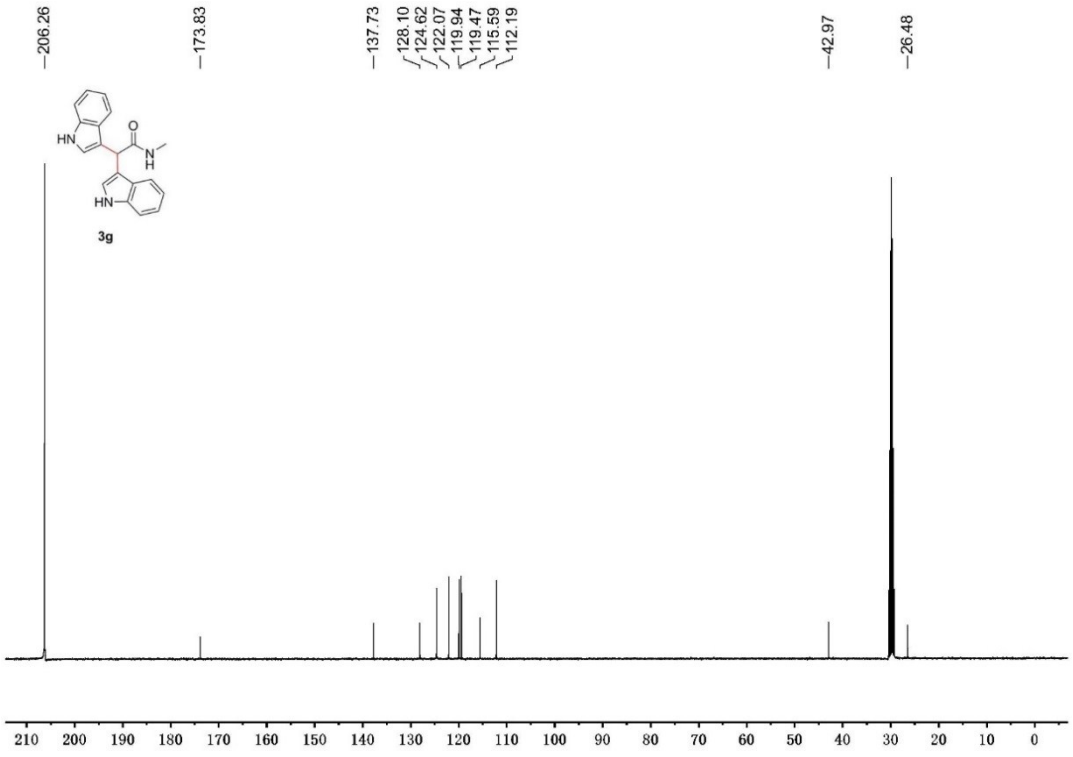
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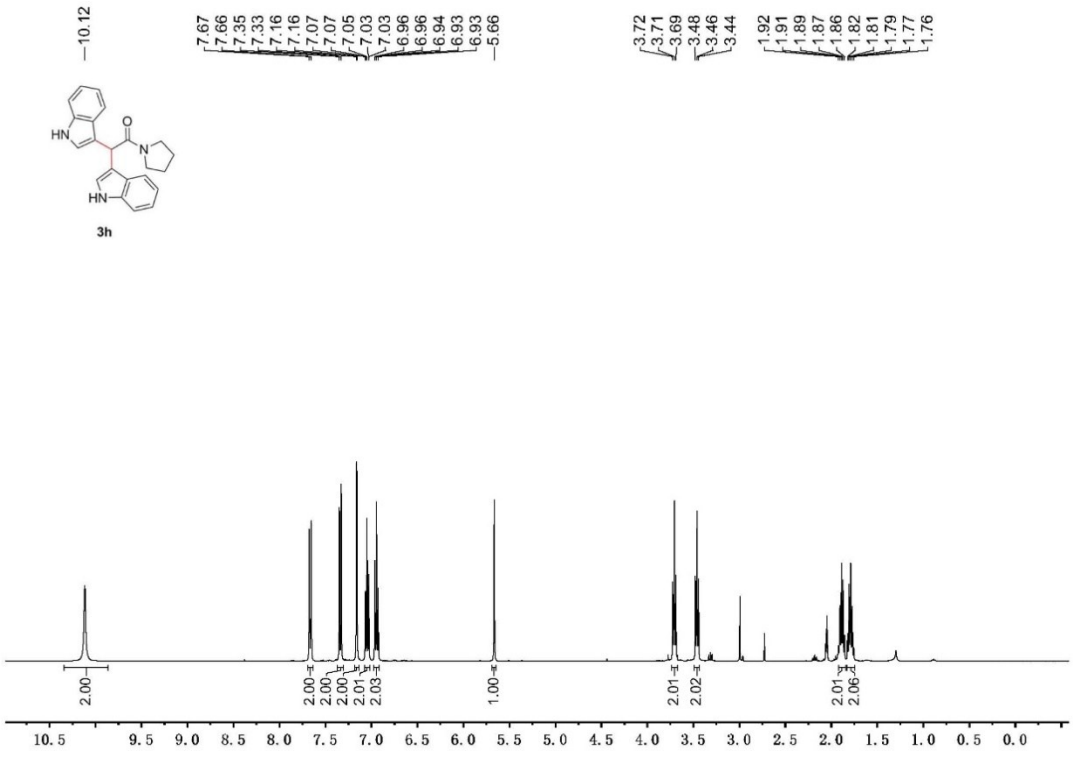
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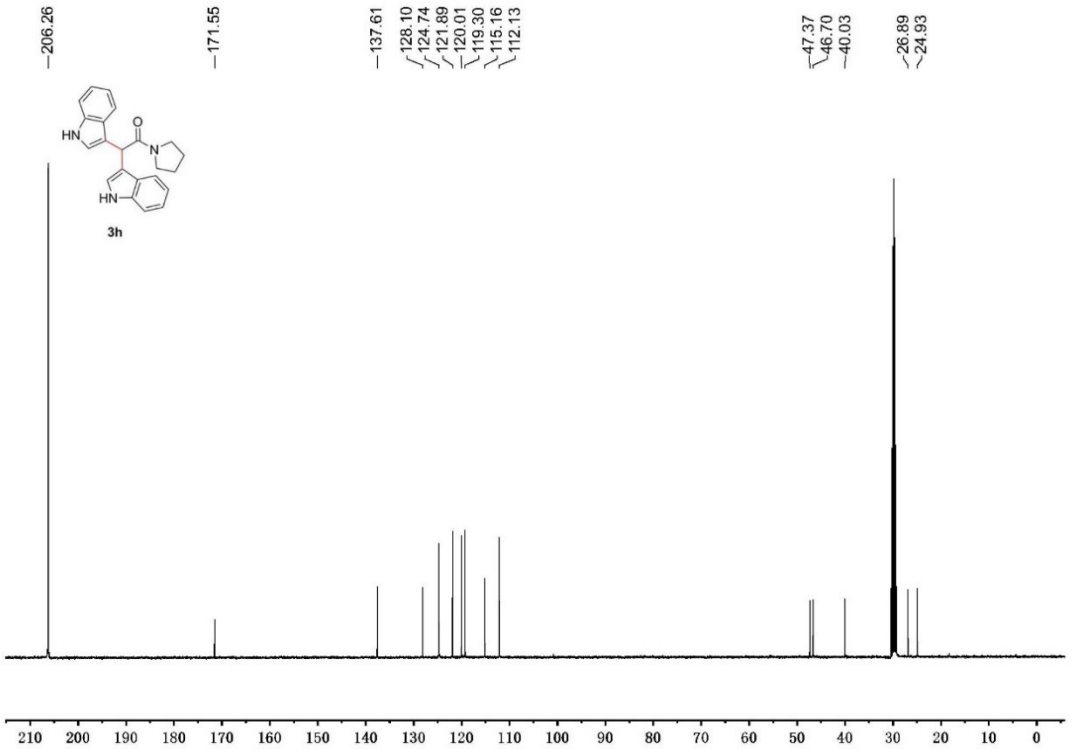
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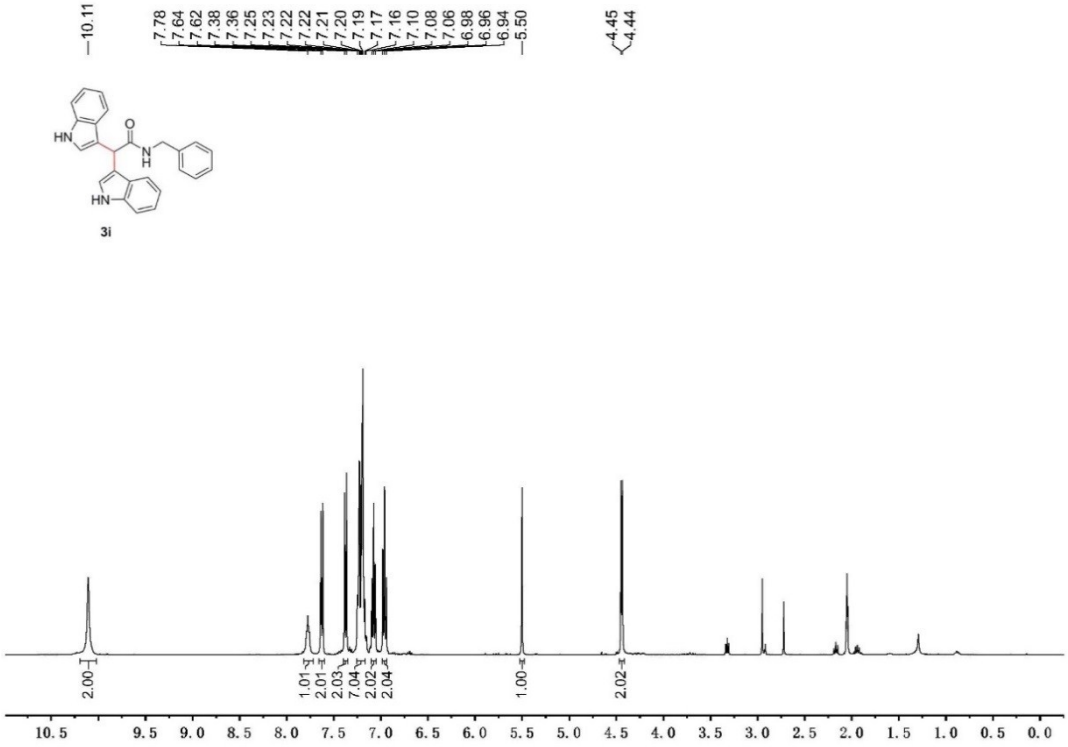
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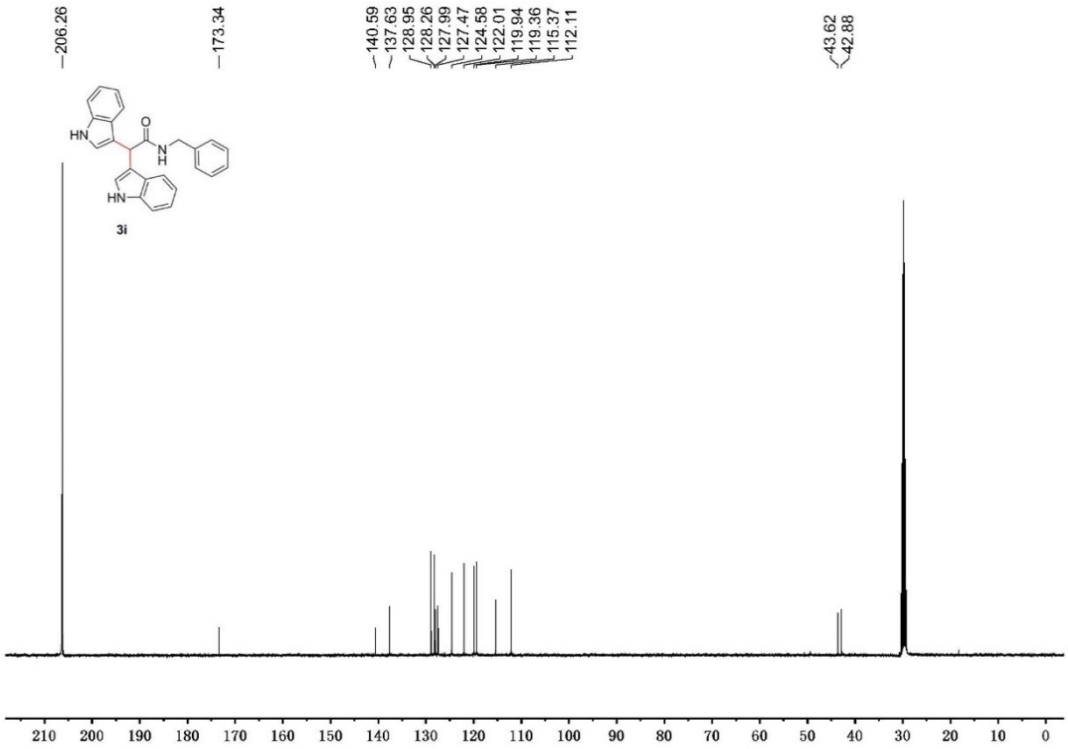
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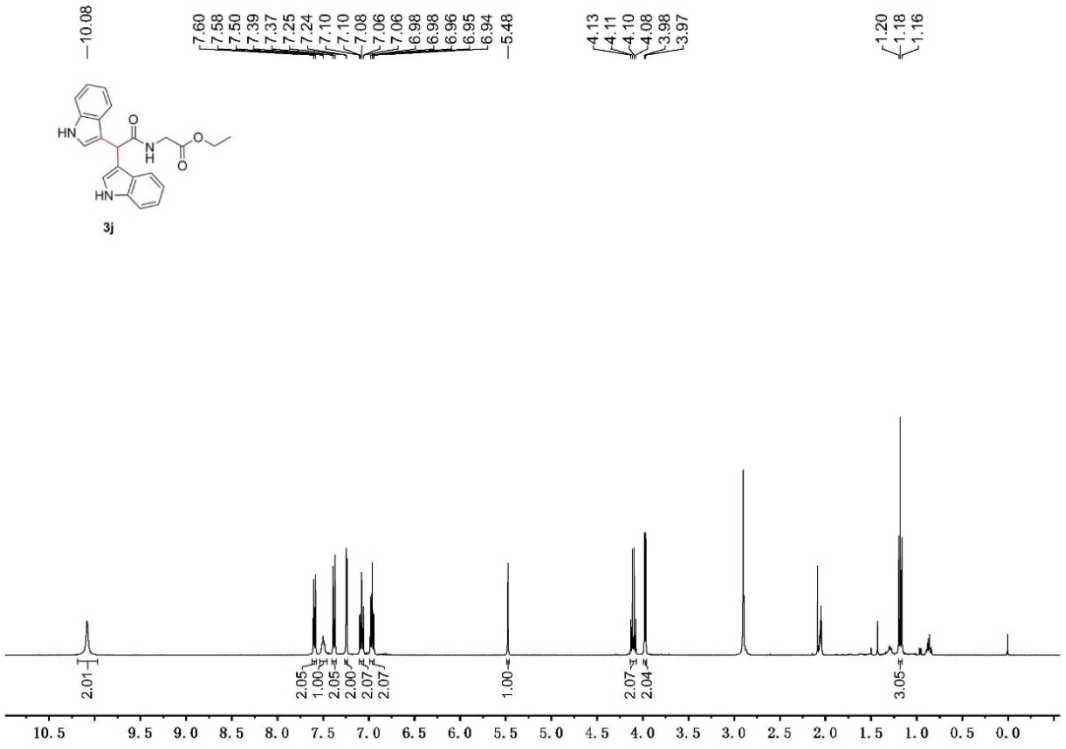
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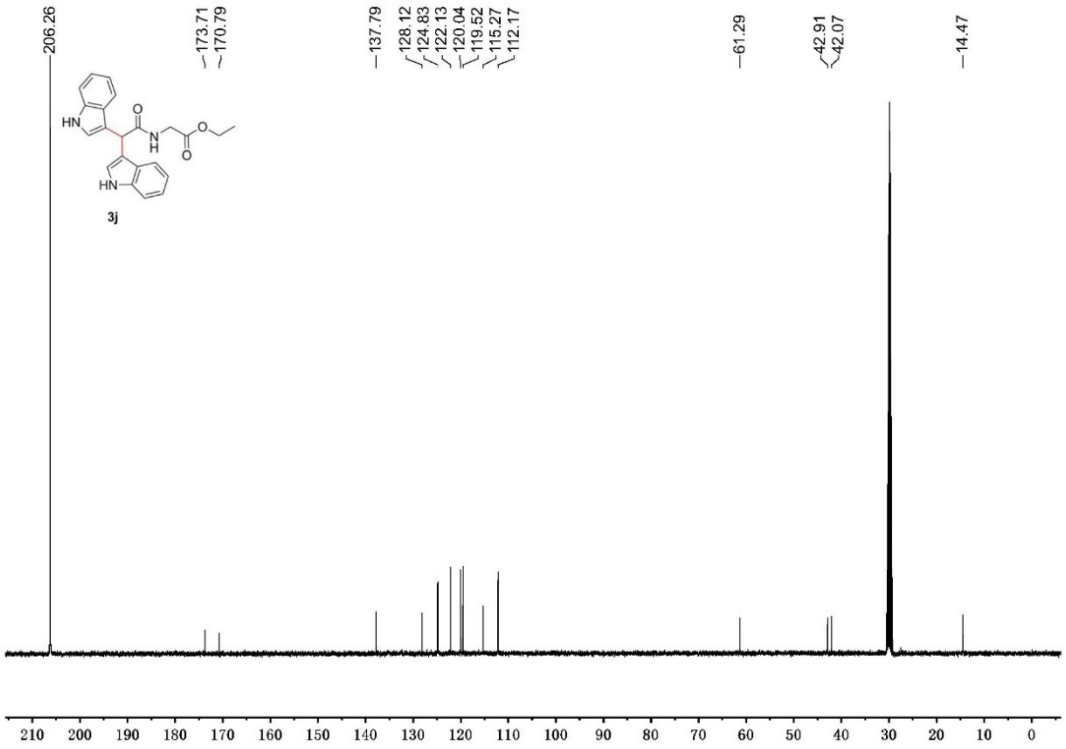
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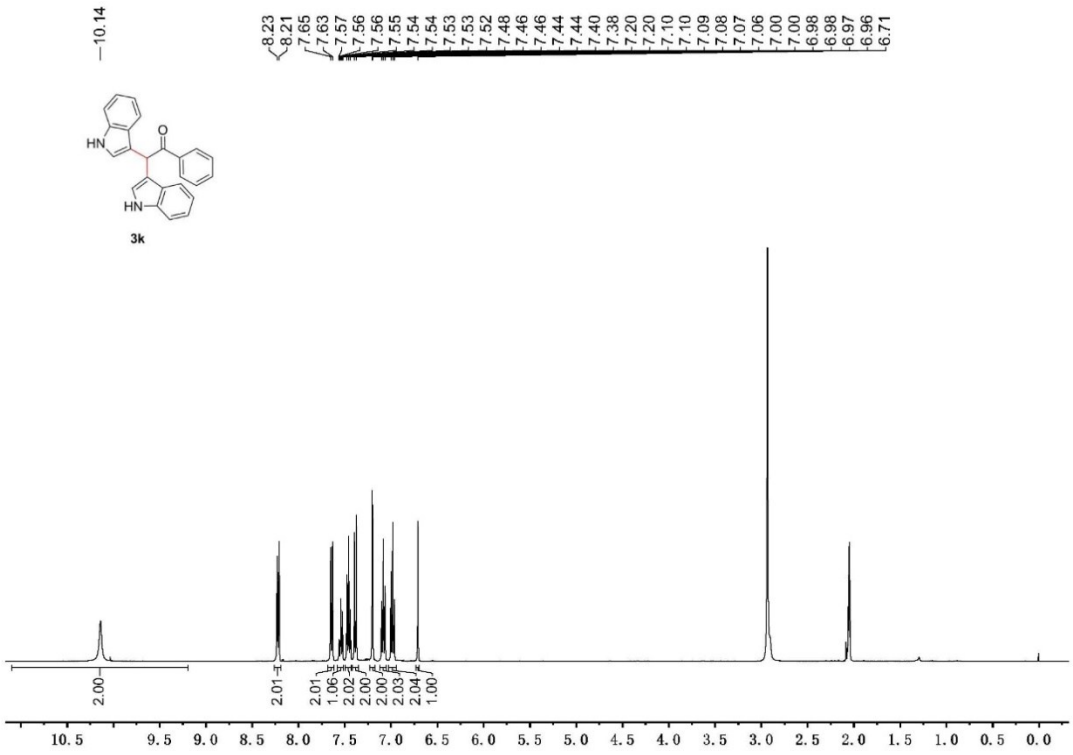
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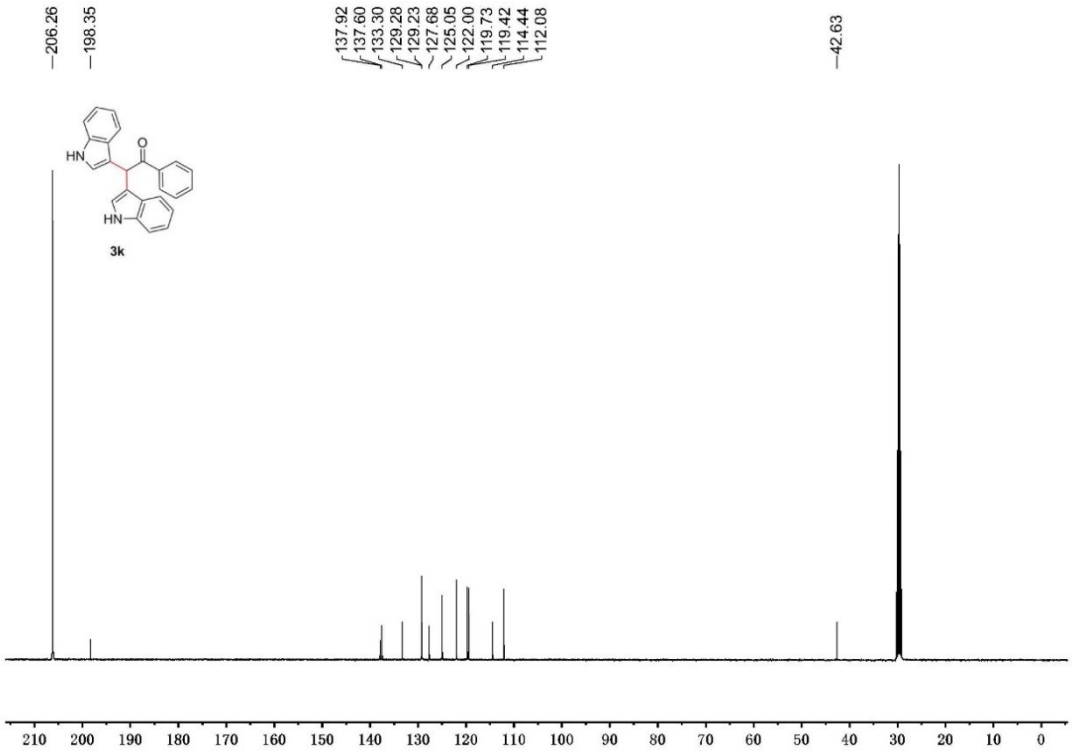
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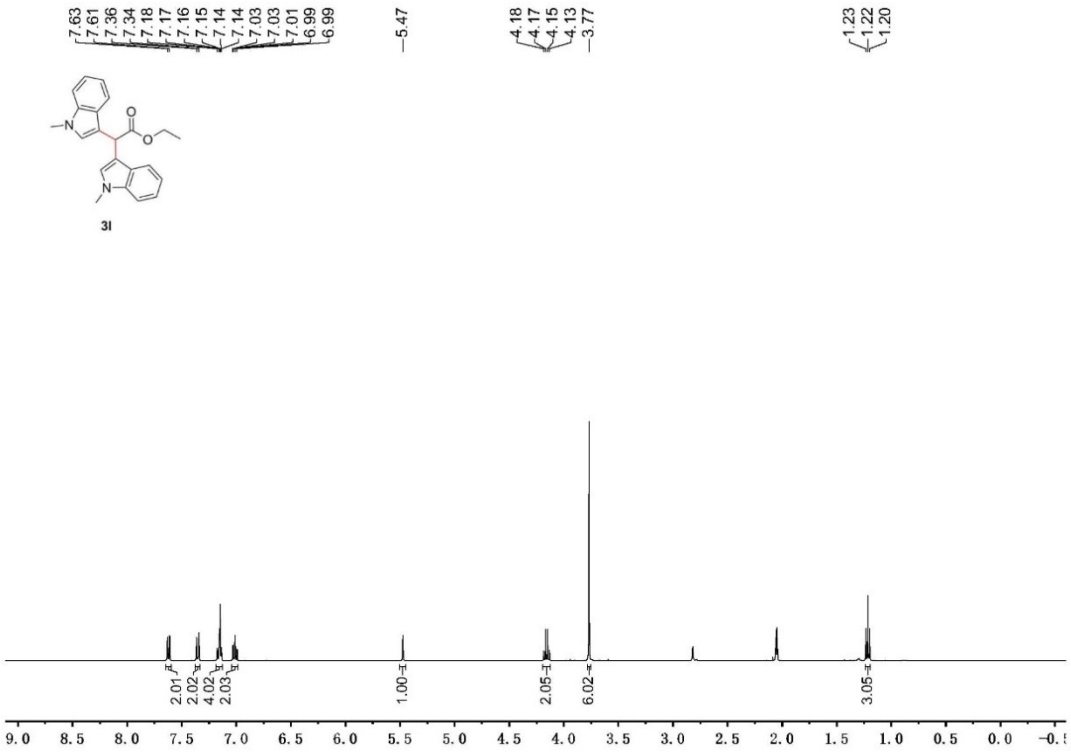
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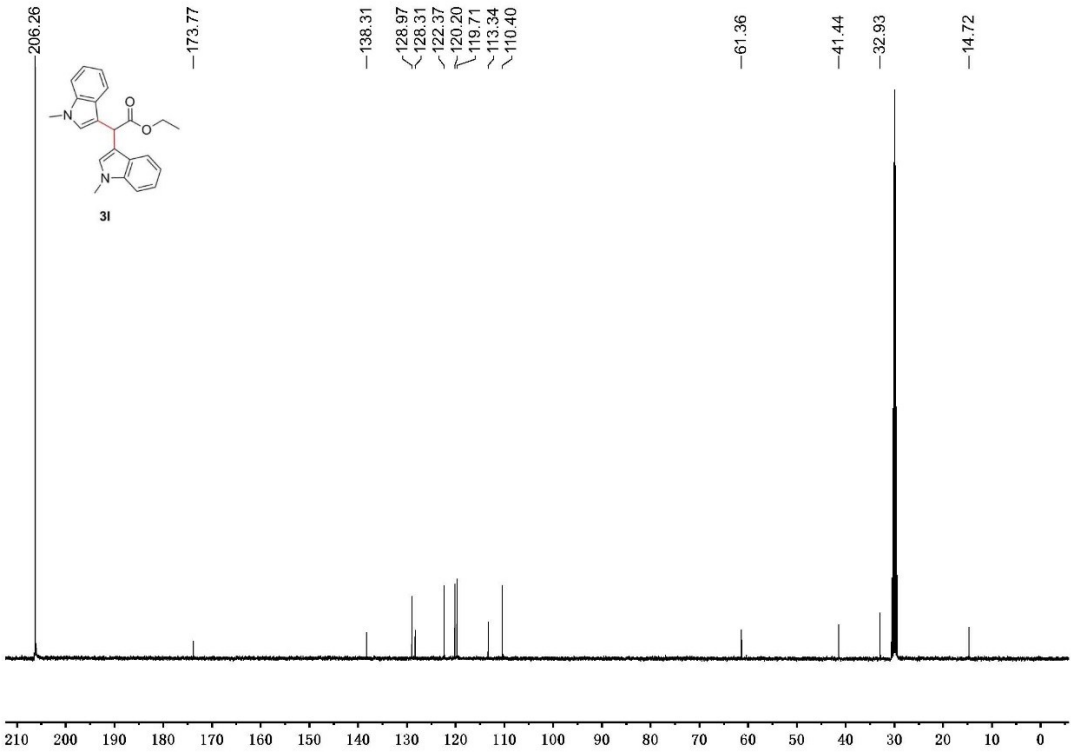
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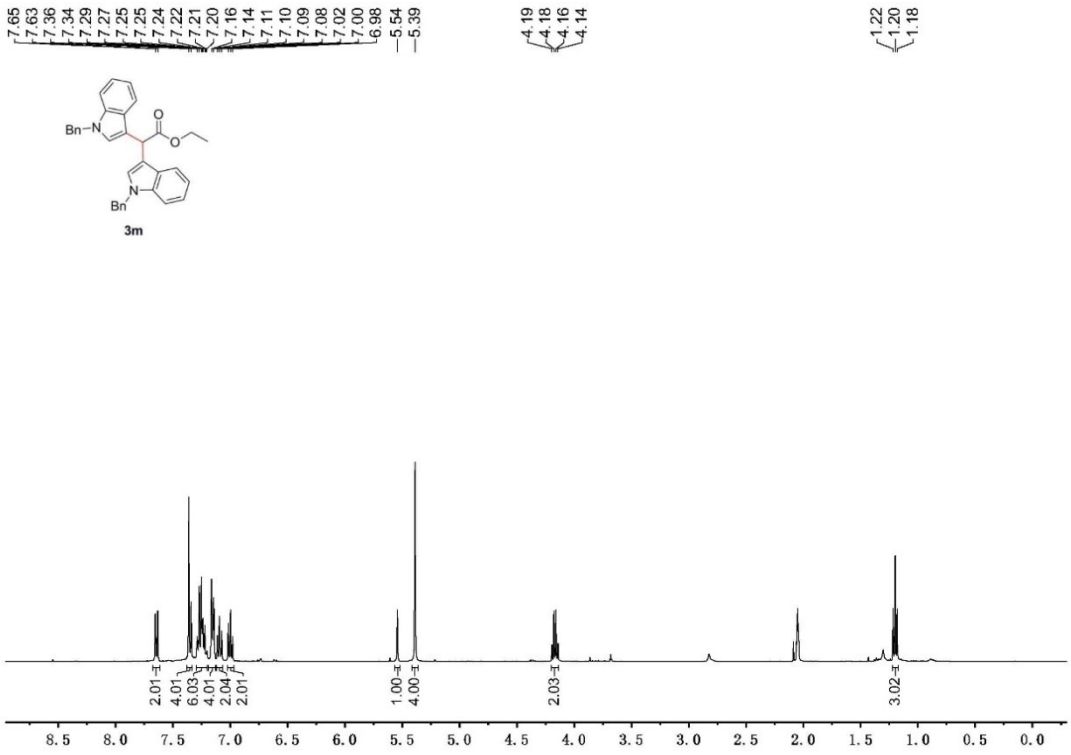
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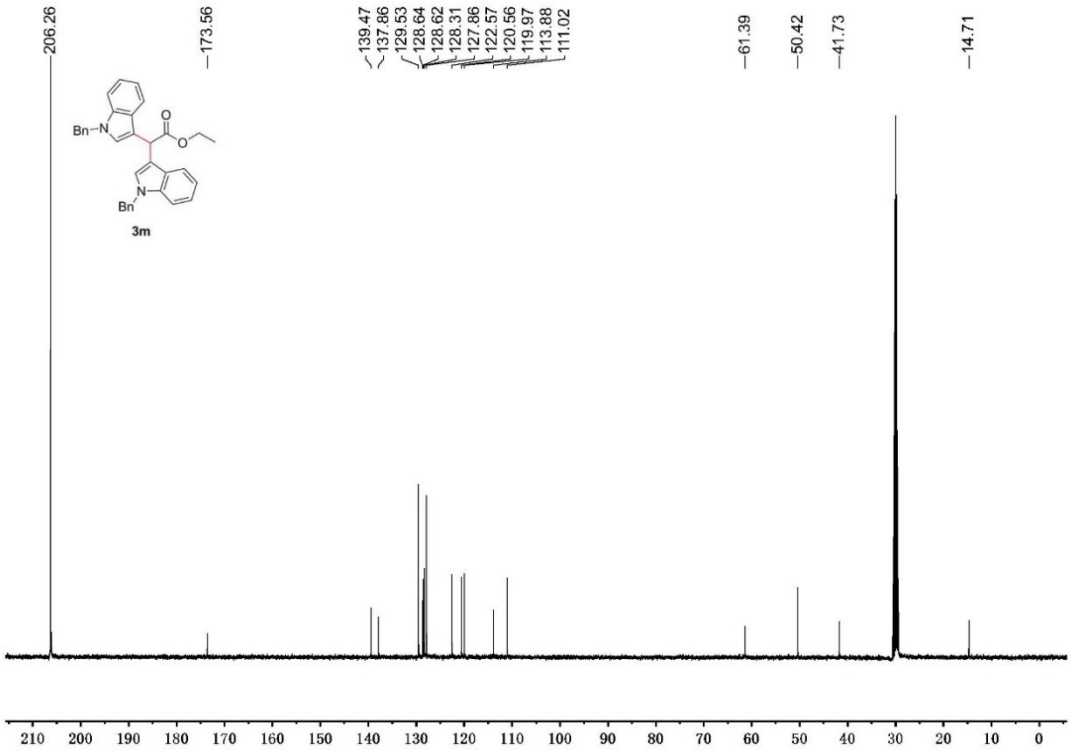
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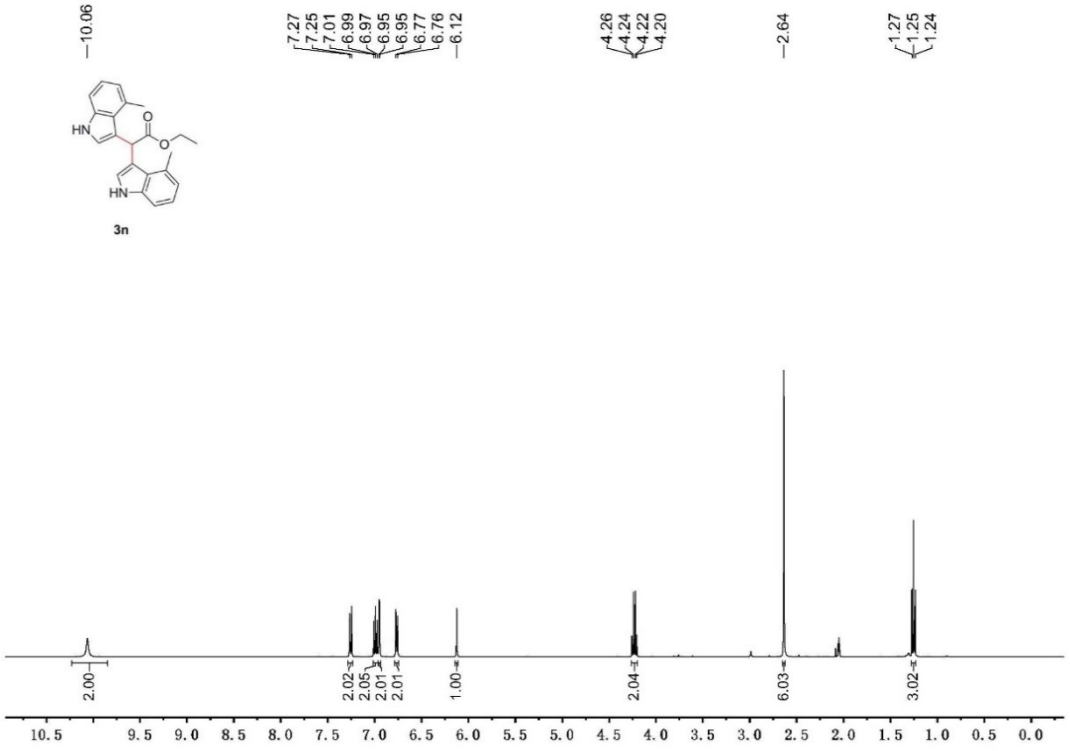
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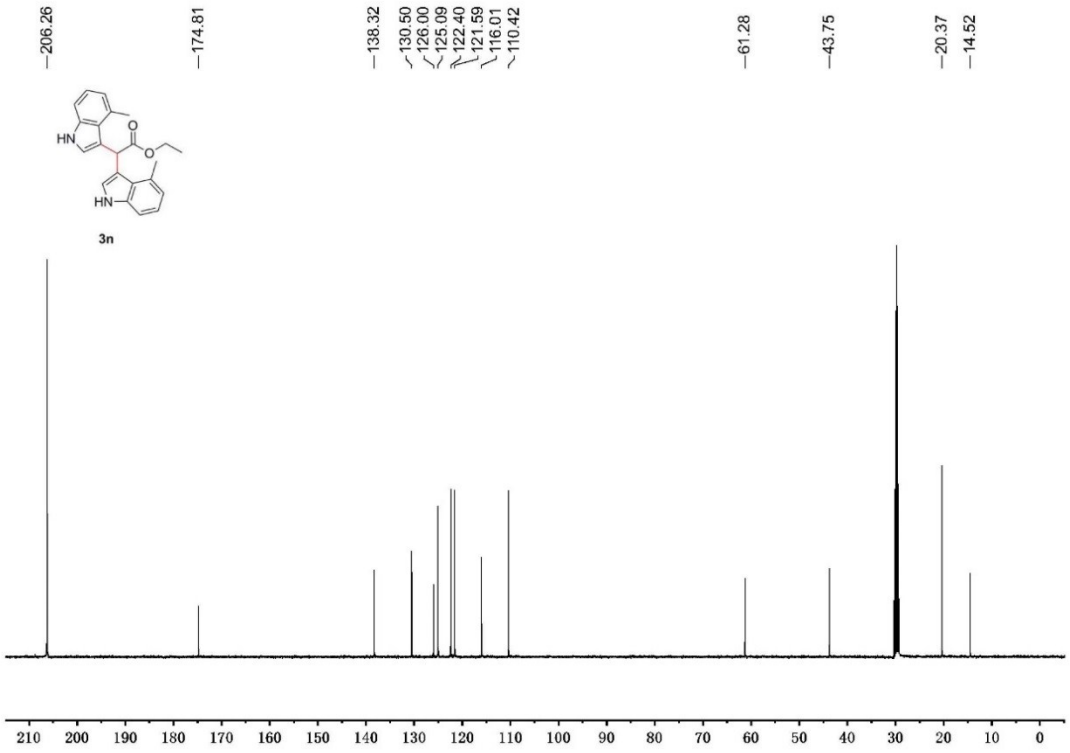
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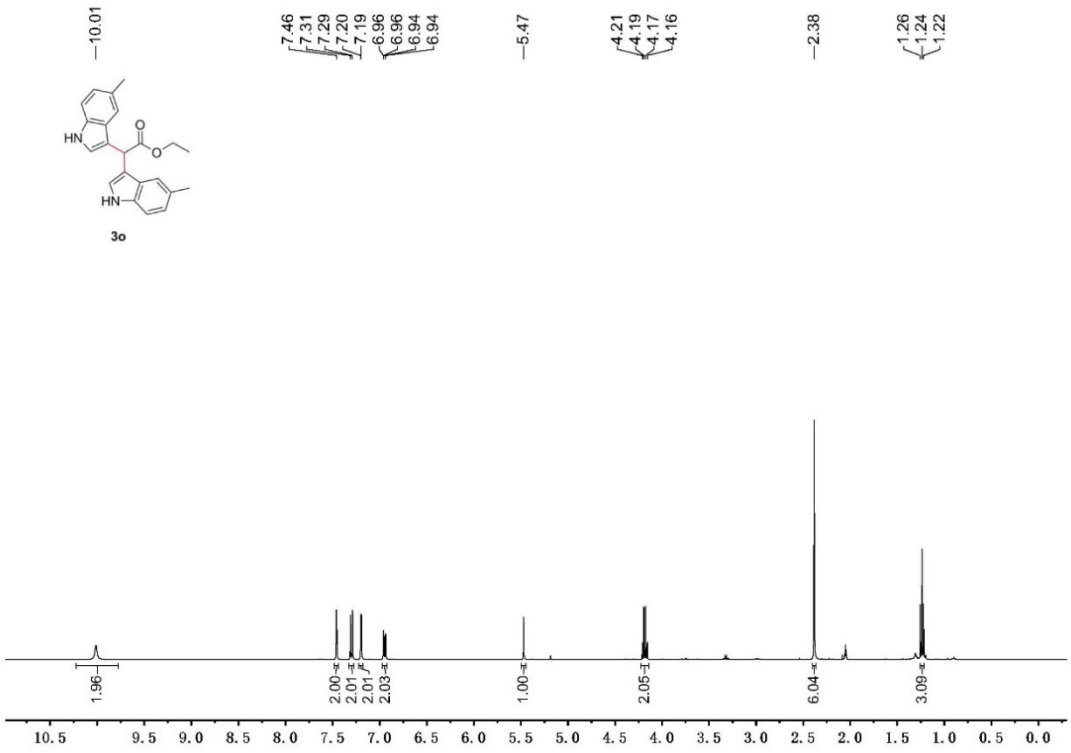
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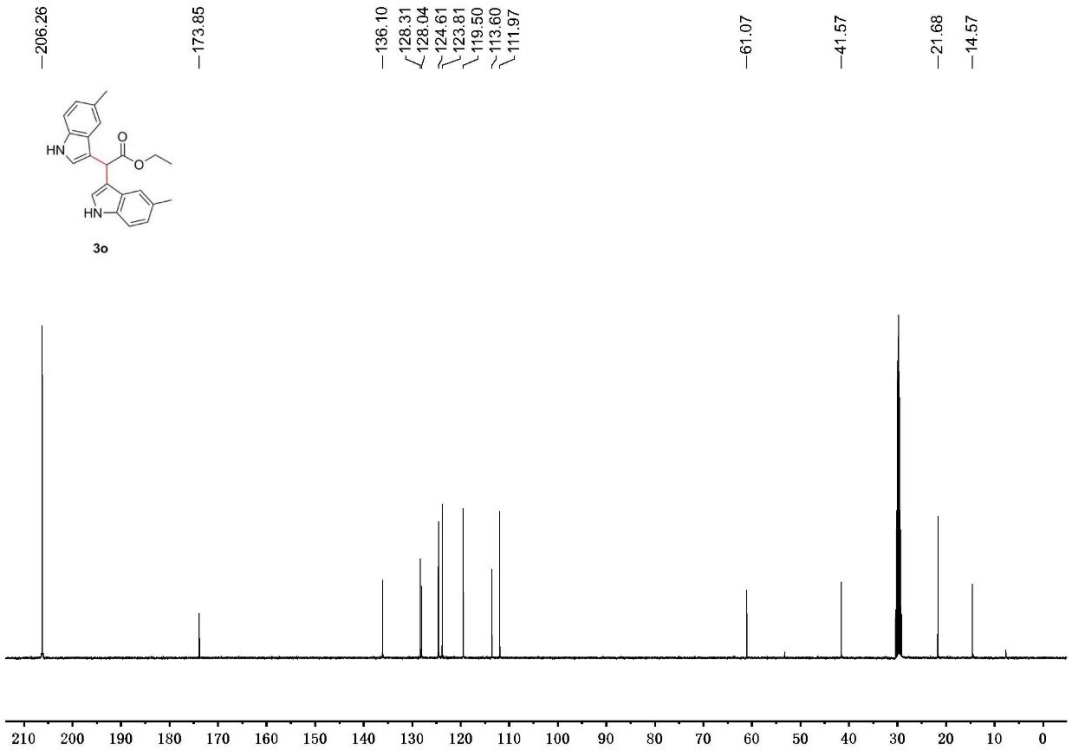
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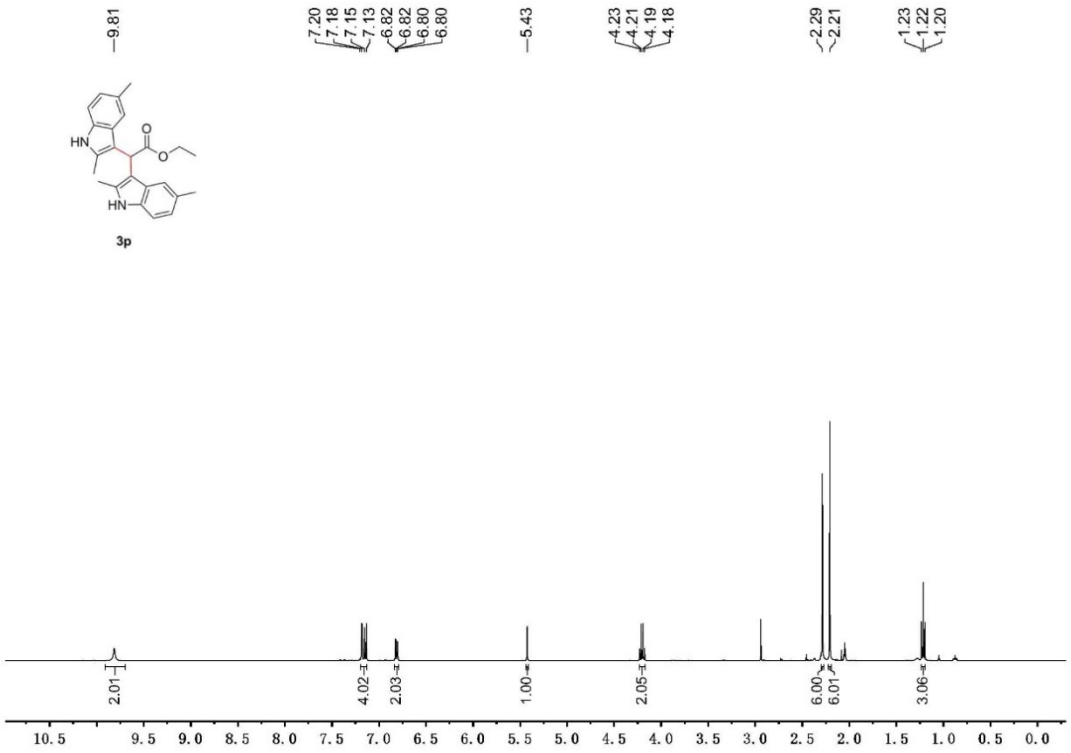
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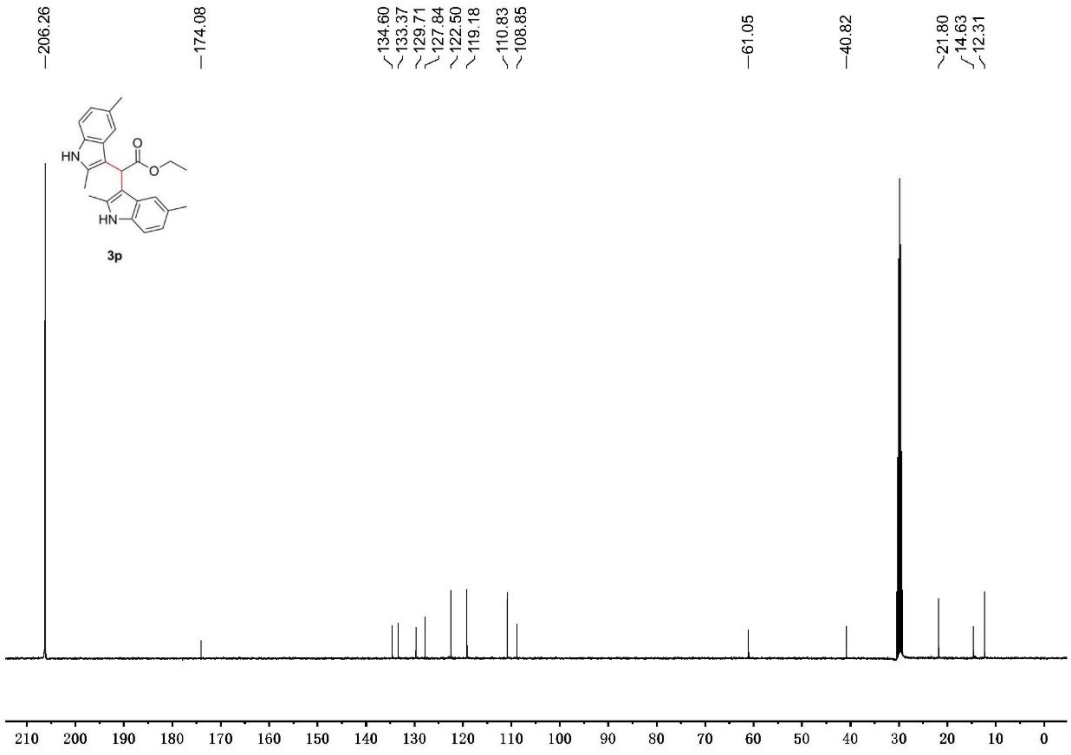
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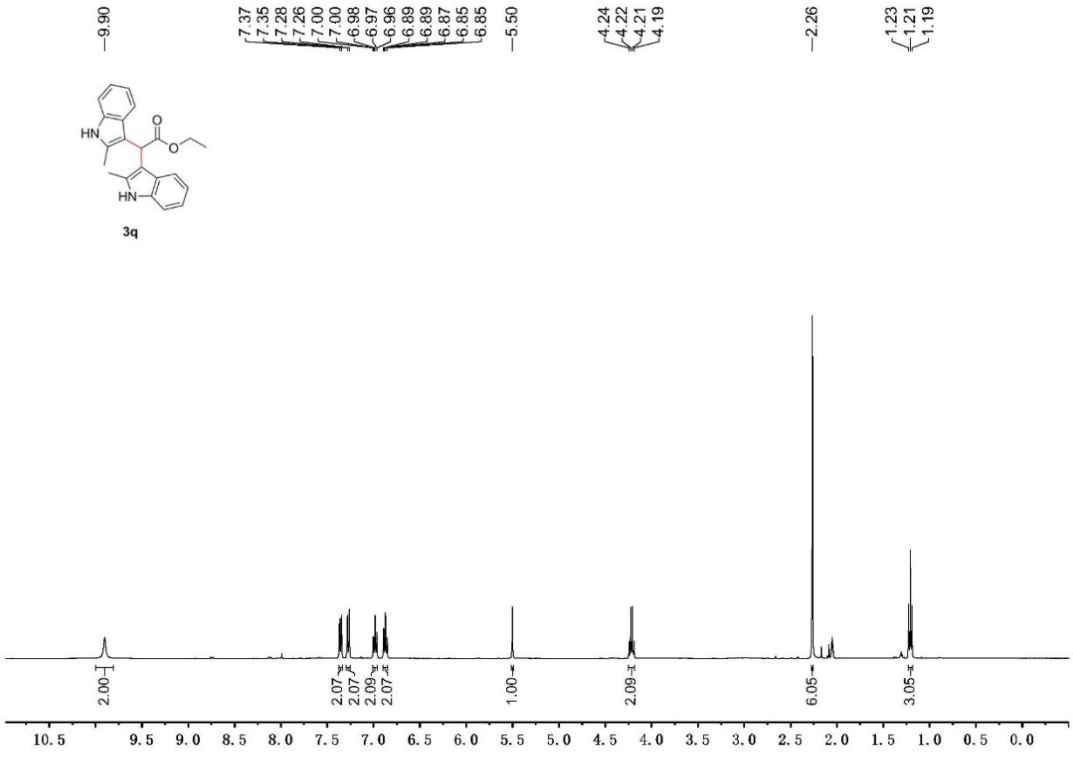
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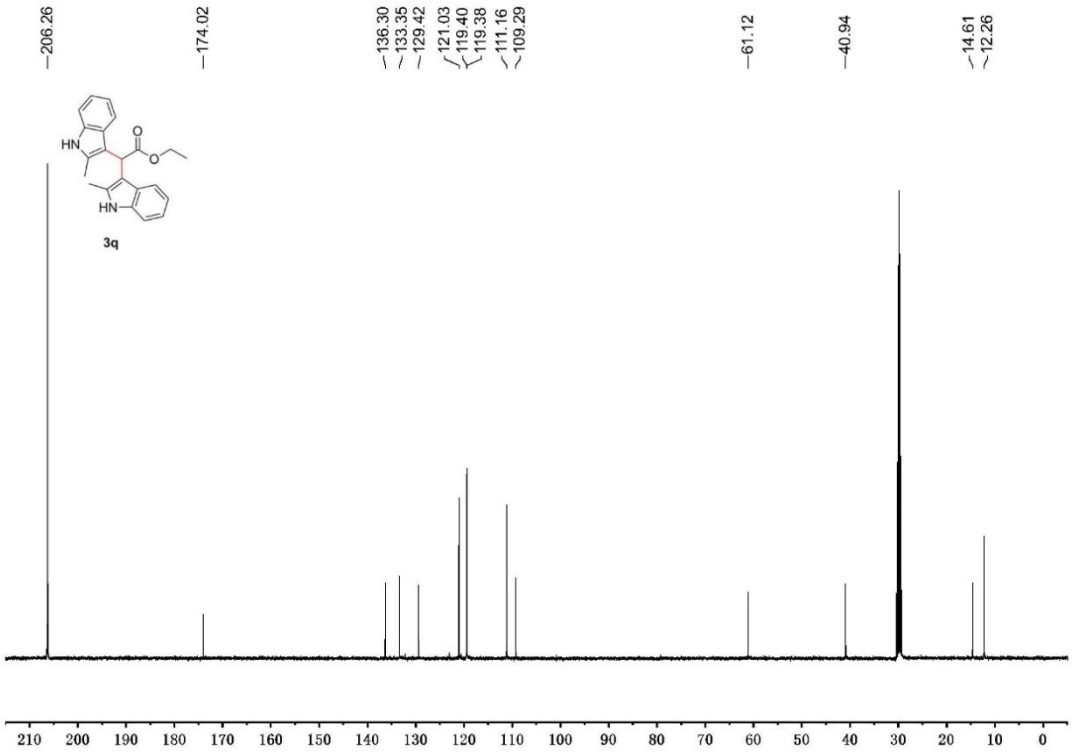
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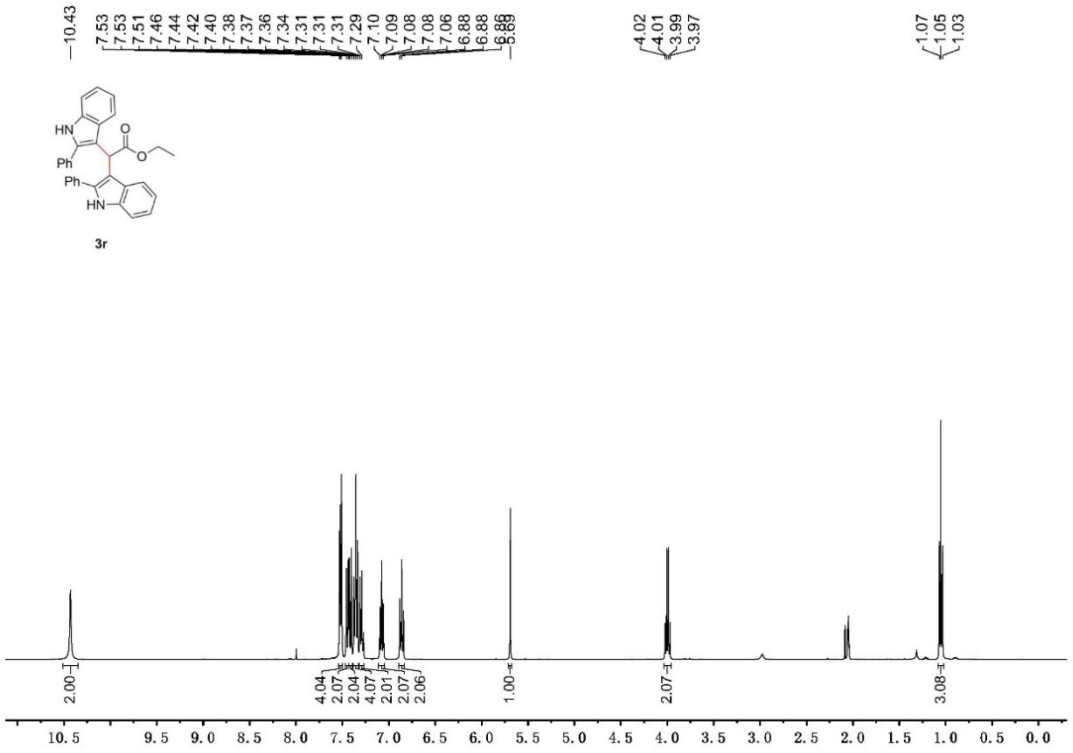
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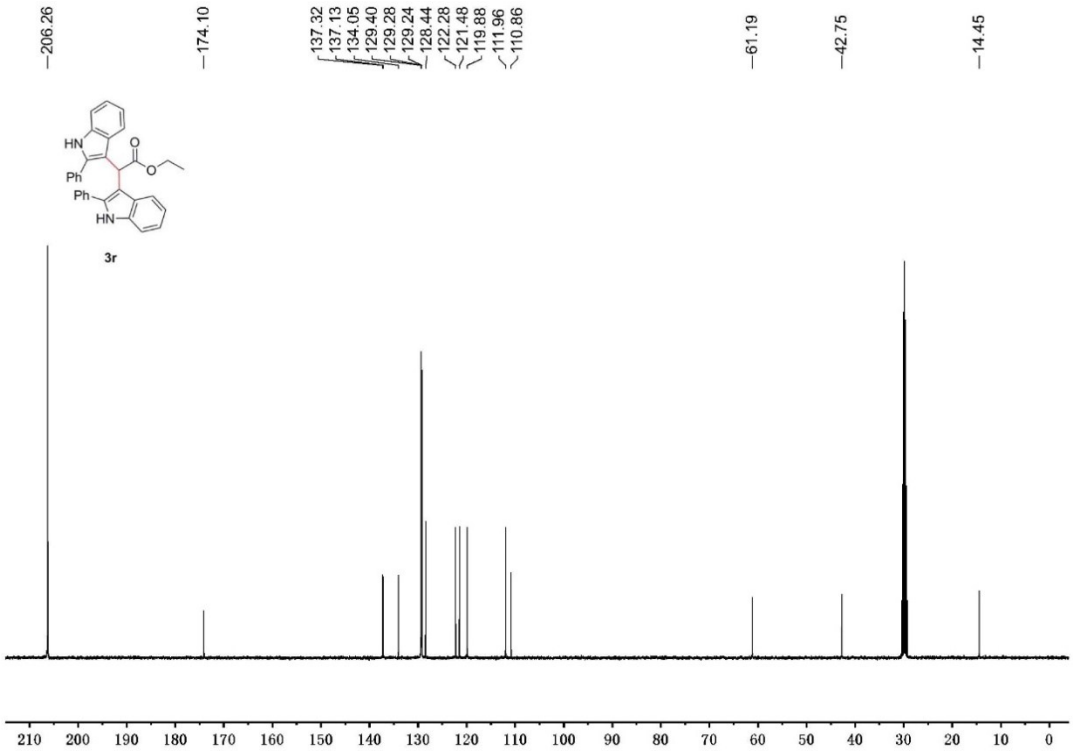
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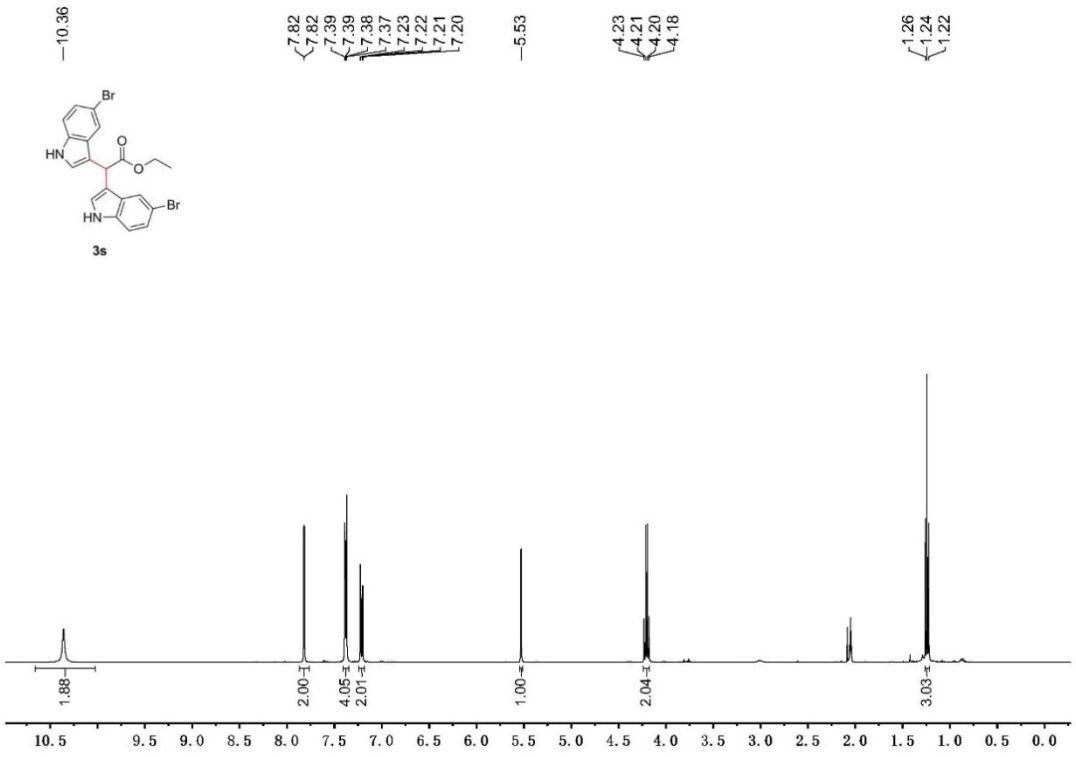
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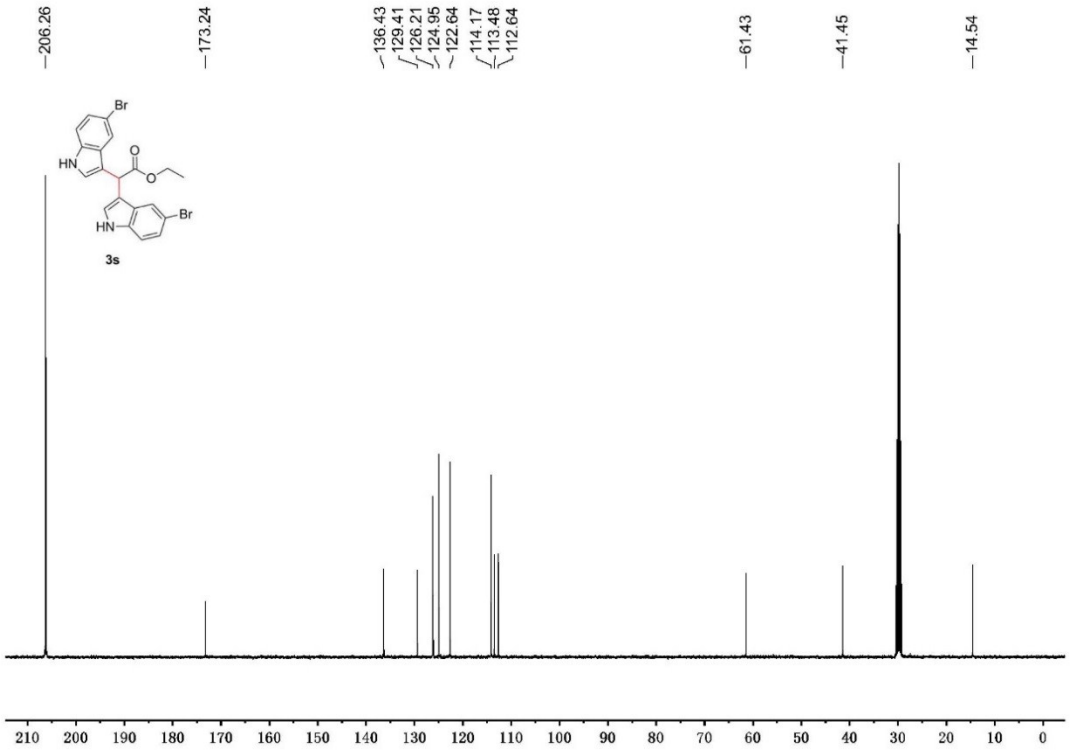
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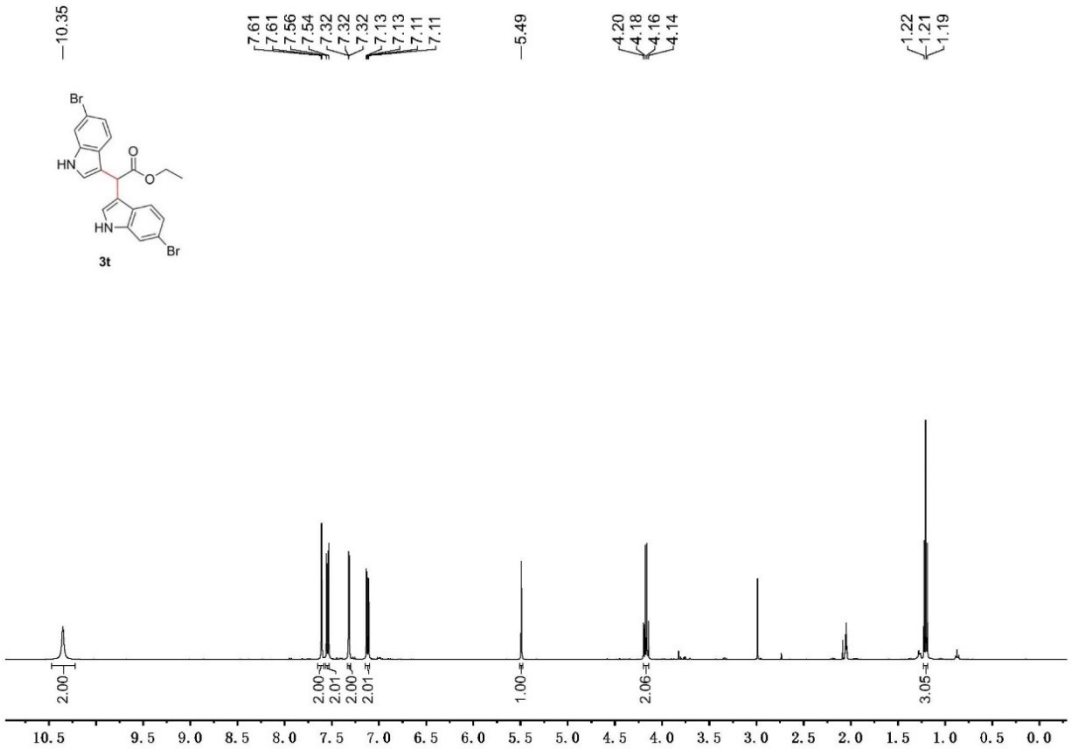
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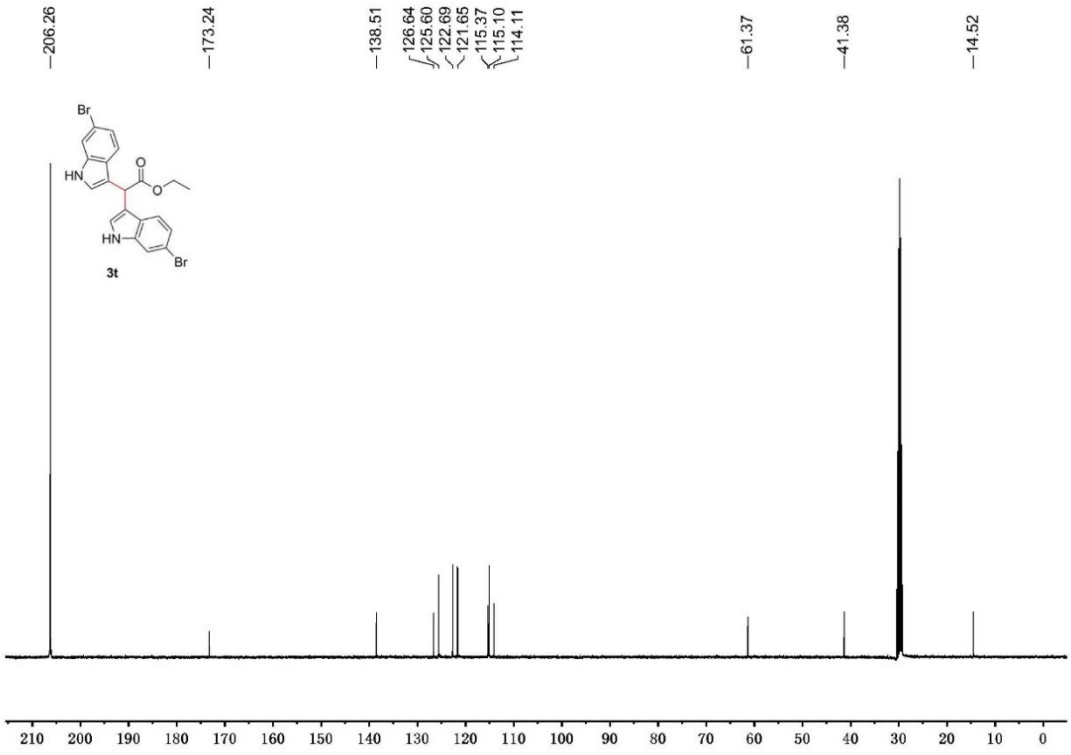
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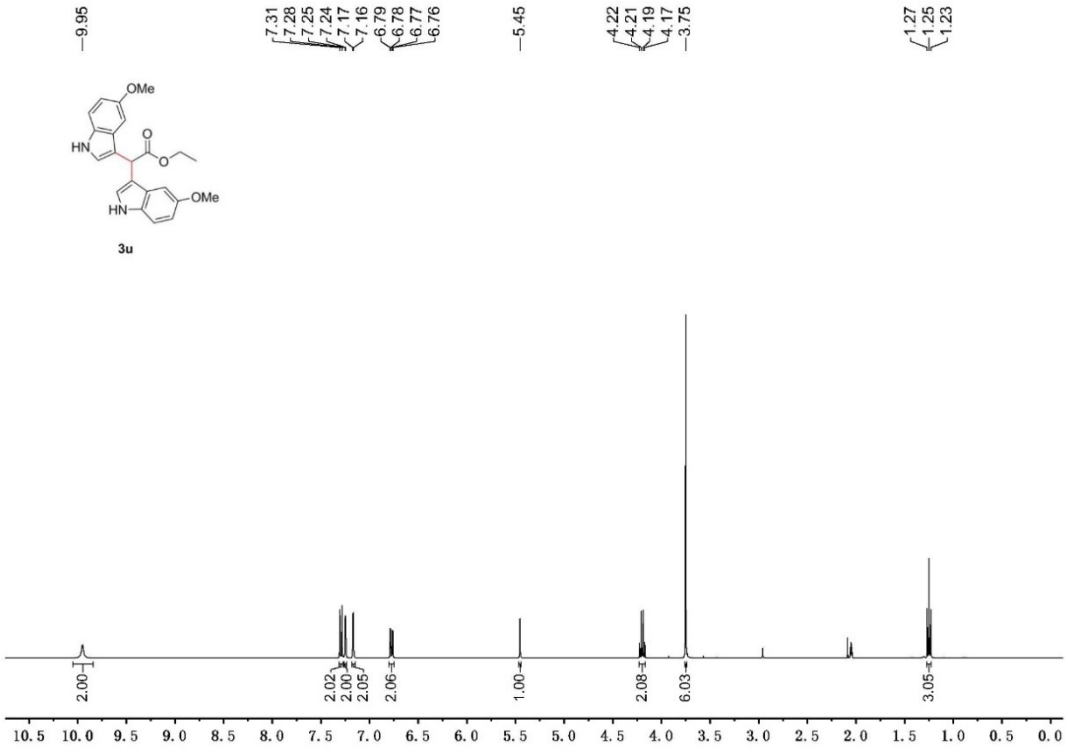
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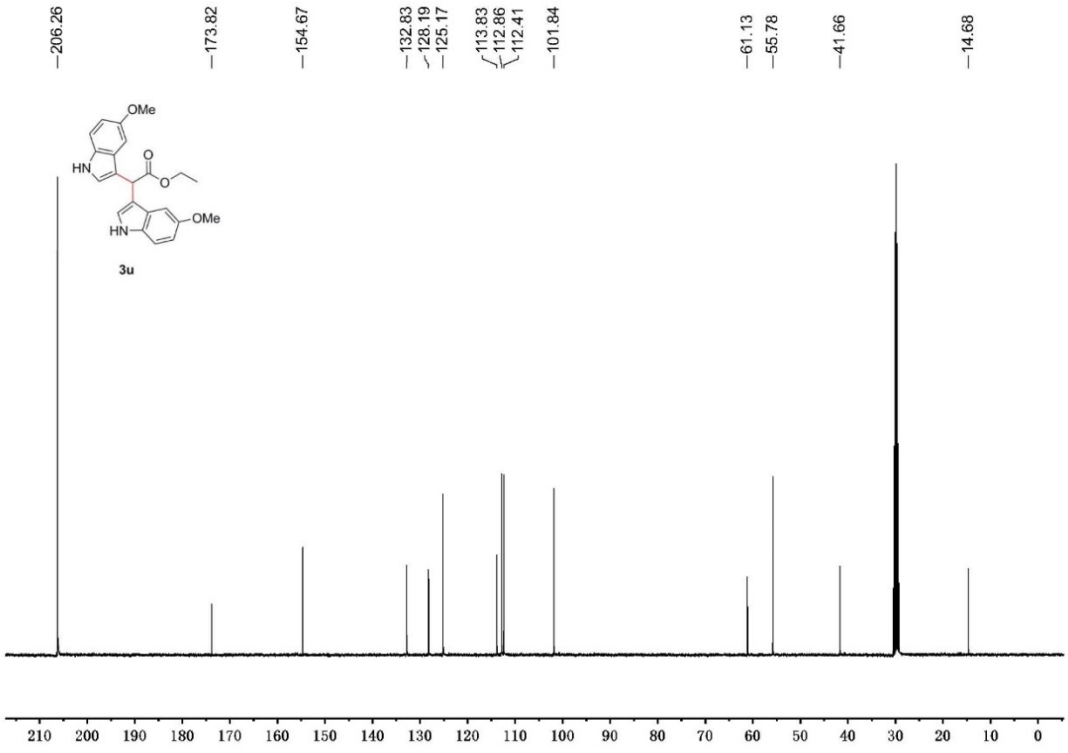
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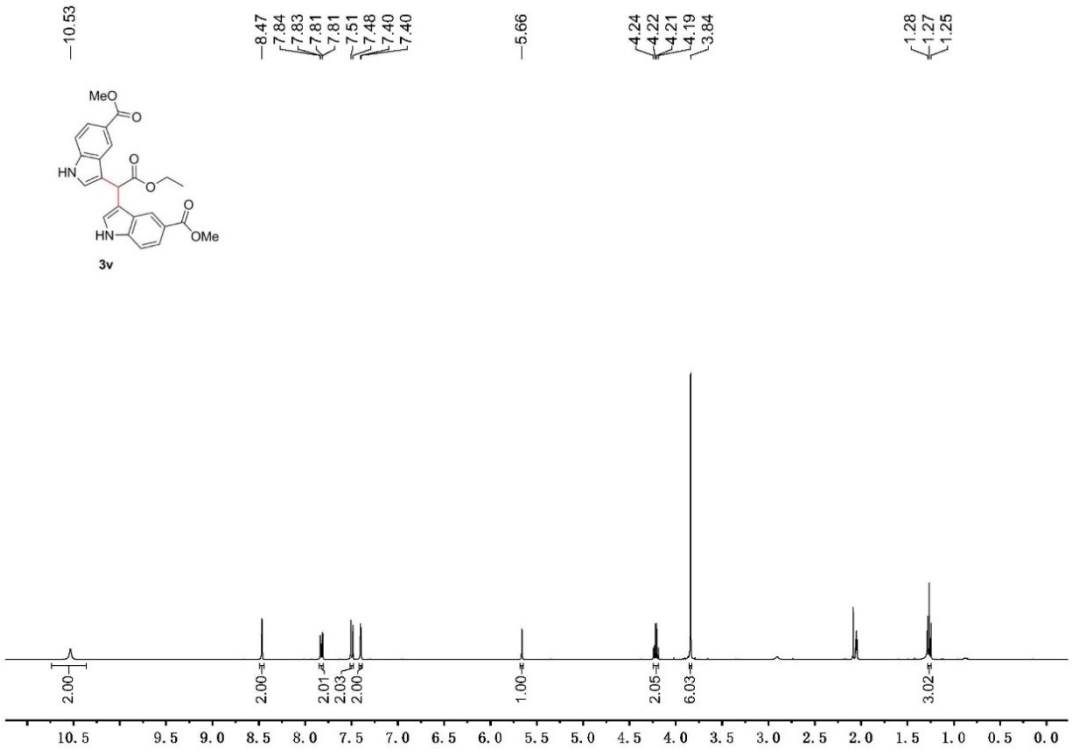
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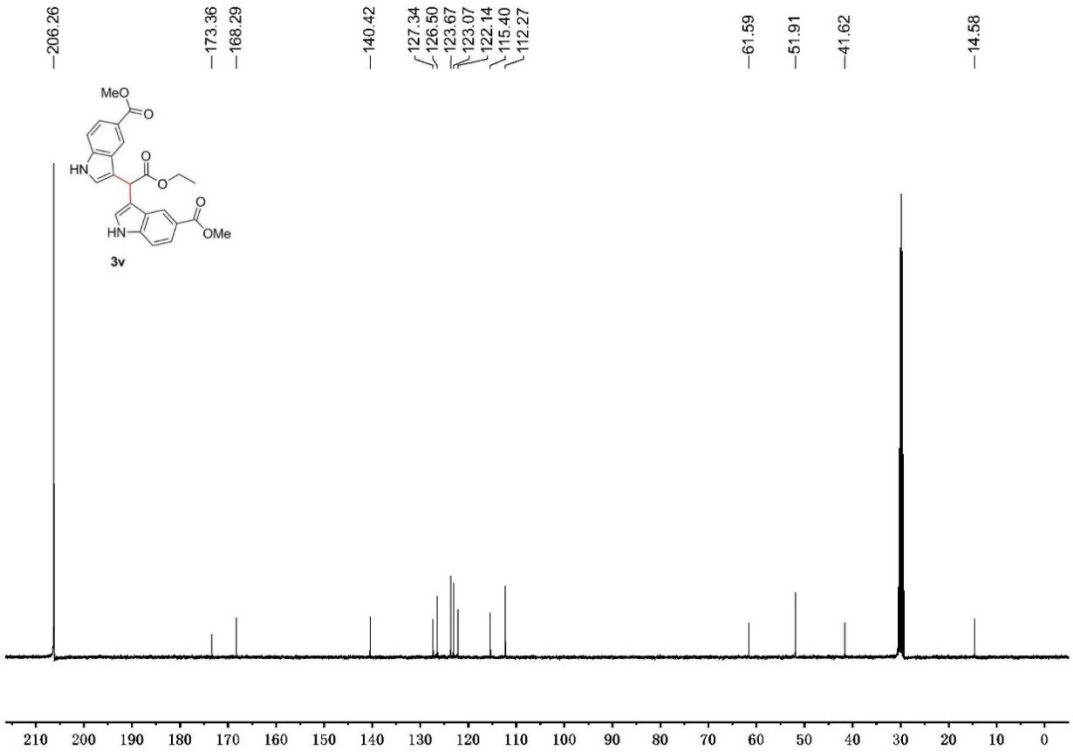
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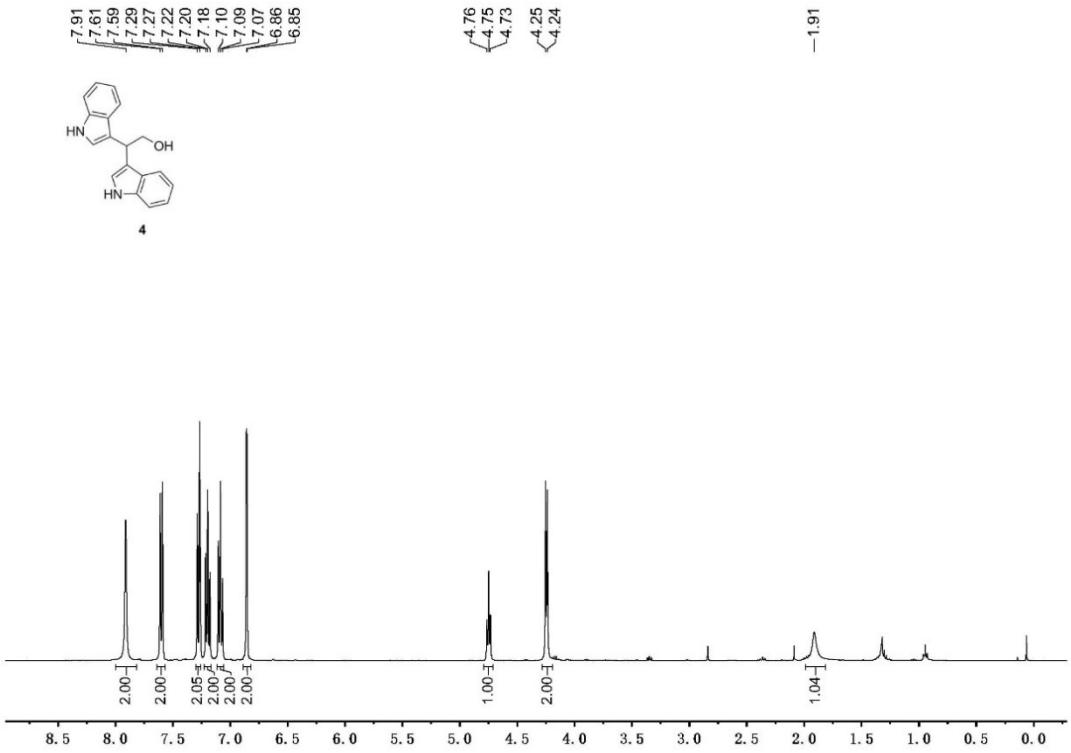
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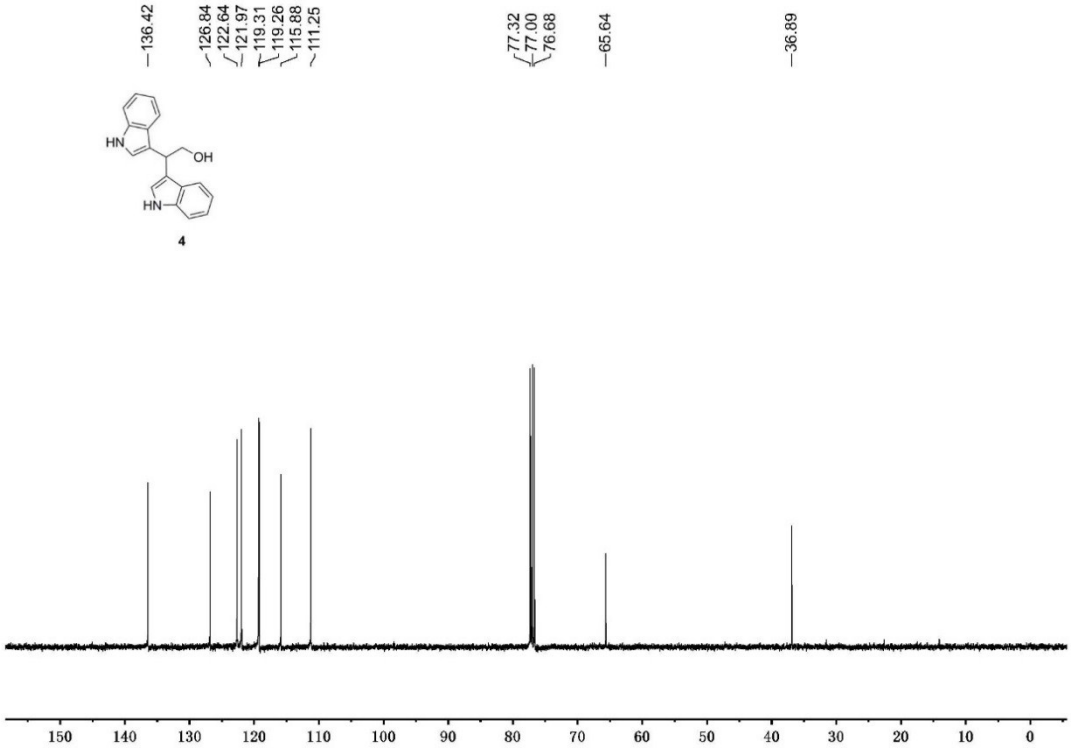
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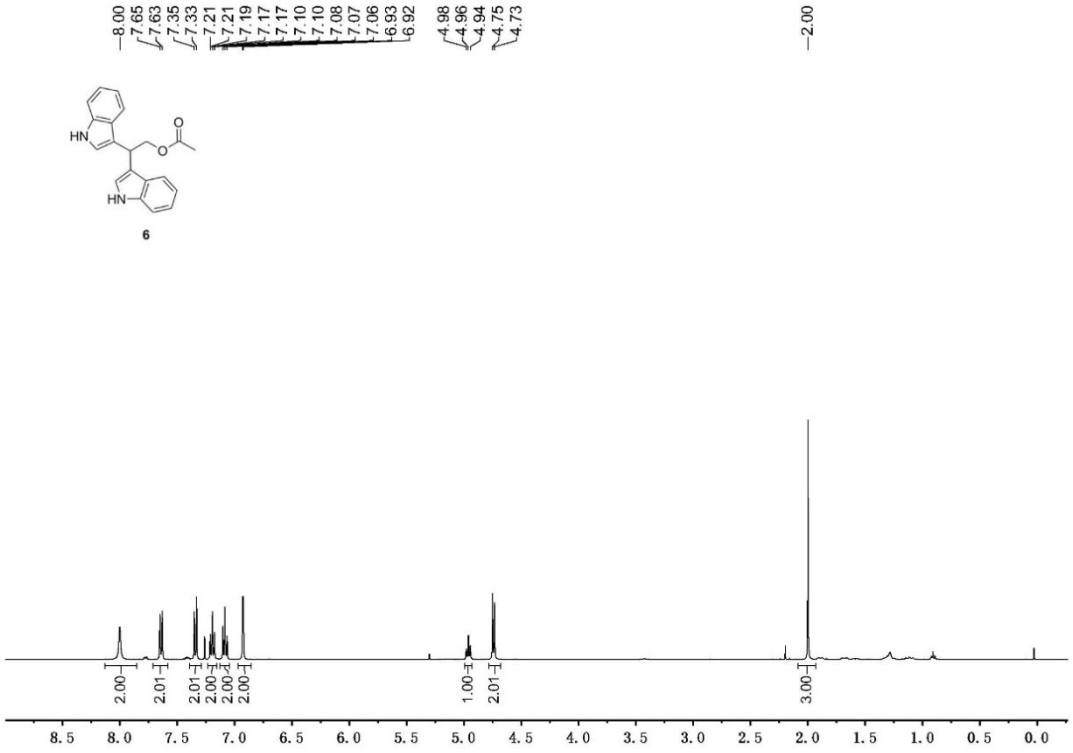
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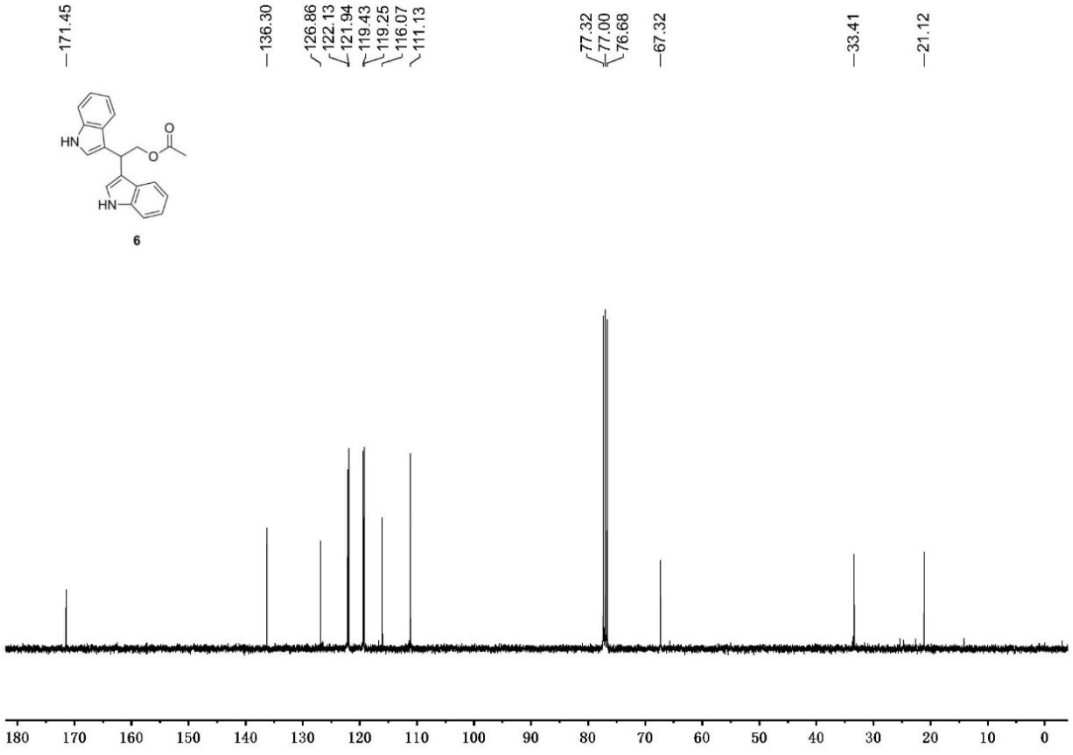
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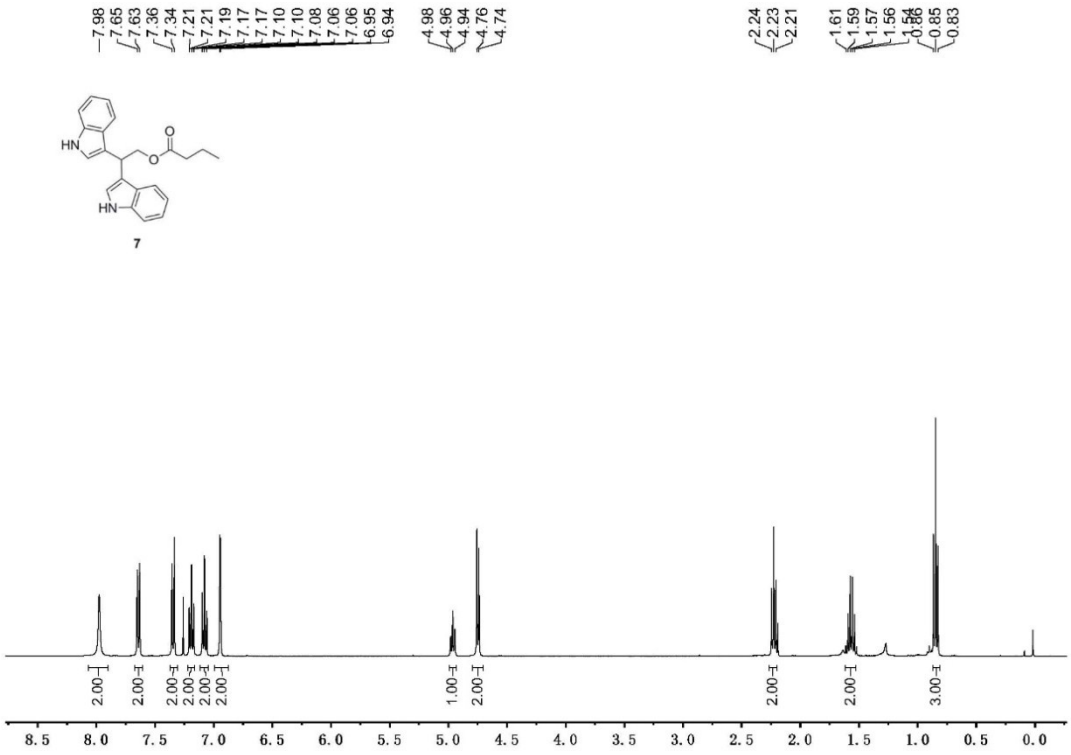
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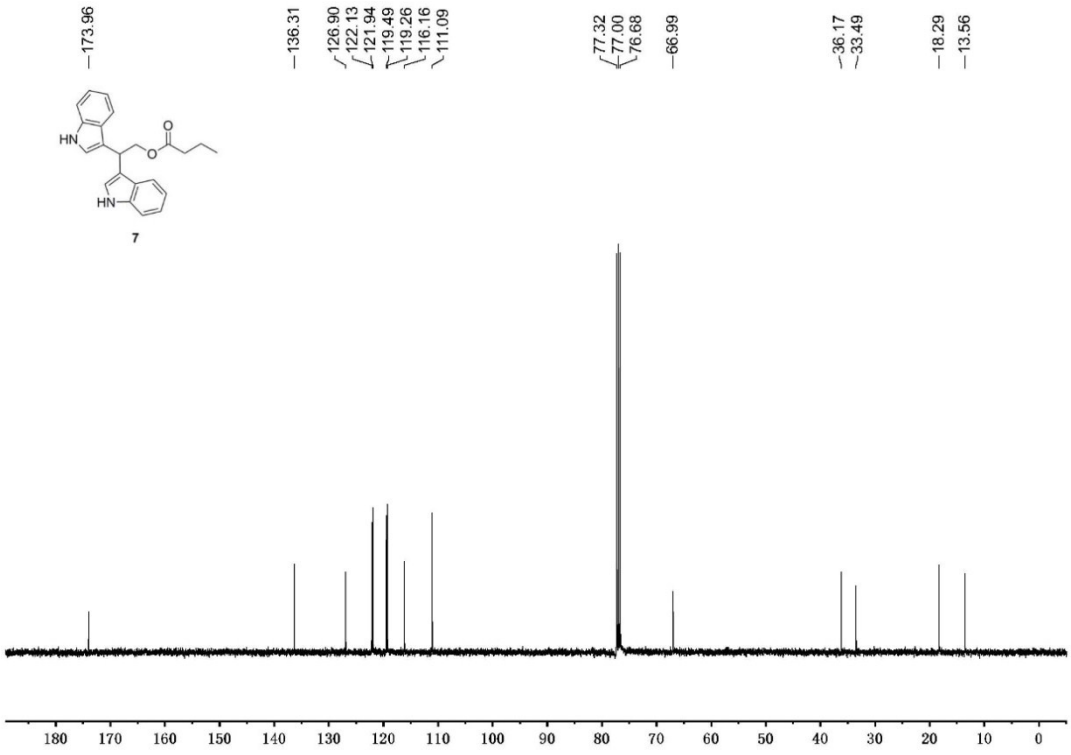
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