Supporting Information

Cu-Catalyzed Switchable Synthesis of Functionalized Pyridines and Pyrroles

Zheng Ling,[a] Fang Xie,[a] Ilya D. Gridnev,[b] Masahiro Terada,*[b] and Wanbin Zhang*[a]

[a] Shanghai Key Laboratory for Molecular Engineering and Chiral Drugs, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P.R. China.

[b] Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki 3-6, Aoba-ku, Sendai 9808578, Japan.

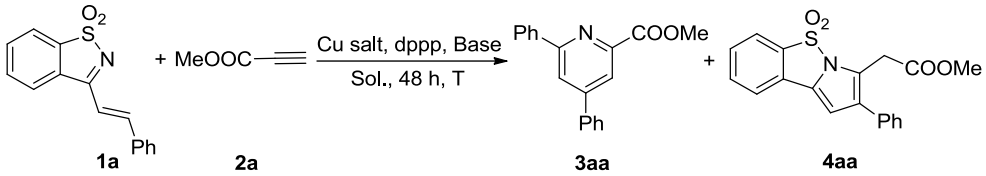
Fax: (+)86-21-54743265; Phone: (+)86-21-54743265; E-mail: wanbin@sjtu.edu.cn

Contents

1. General information

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer with TMS as an internal standard. High resolution mass spectrum (HRMS) was performed at the Analysis Center of Shanghai Jiao Tong University. Column chromatography was performed using 100-200 mesh silica gel. Melting point was measured with SGW X-4 micro melting point apparatus. All commercially available substrates were used as received. Synthesis of substrates is according to the references[1-9].

2. Optimization of the reaction conditions for synthesis of 3aa and 4aa[a]



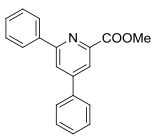
1a 2a 3aa 4aa

Entry	Cu salt	Sol.	Base	T (^{o}C)	Yield$_{3aa}$ (%)[b]	Yield$_{4aa}$ (%)[b]
1	$Cu(OAc)_2.H_2O$	1,4-dioxane	NaOAc	80	91	8
2	$Cu(OTf)_2$	1,4-dioxane	NaOAc	80	75	22
3	$Cu(CH_3CN)_4PF_6$	1,4-dioxane	NaOAc	80	49	47
4	CuCl	1,4-dioxane	NaOAc	80	48	48
5	CuBr	1,4-dioxane	NaOAc	80	30	68
6	CuI	1,4-dioxane	NaOAc	80	3	95
7	$Cu(OAc)_2{\cdot}H_2O$	toluene	NaOAc	80	88	8
8	$Cu(OAc)_2{\cdot}H_2O$	DME	NaOAc	80	27	8
9	$Cu(OAc)_2{\cdot}H_2O$	DCE	NaOAc	80	60	30
10	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	KOAc	80	80	14
11	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	Na_2CO_3	80	46	35
12	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	K_2CO_3	80	56	40
13	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	KF	80	69	21
14	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	NaOAc	70	92	6
15	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	NaOAc	60	95	4
16	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	NaOAc	50	95	trace
17	CuI	1,4-dioxane	NaOAc	70	3	96
18	CuI	1,4-dioxane	NaOAc	60	-	98
19	-	1,4-dioxane	NaOAc	80	N.R.	N.R.
20[c]	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	-	80	N.R.	N.R.
21	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	-	80	49	34

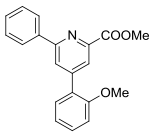
[a] Reaction conditions unless otherwise specified: *N*-sulfonyl azadiene **1a** (0.20 mmol), methyl propiolate **2a** (0.30 mmol), copper salts (0.02 mmol), dppp (0.03 mmol) and base (0.30 mmol) in solvent (2,0 mL) under air at 80 ^{o}C for 2 days. [b] Isolated yield. [c] Reacted without dppp.

3. General procedure for synthesis of pyridine derivatives and characterization data

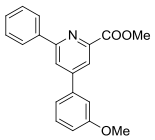
$Cu(OAc)_2 \cdot H_2O$ (4.0 mg, 0.02 mmol) and DPPP (12.4 mg, 0.03 mmol) were stirred in 1,4-dioxane (2.0 mL) at room temperature for 1 h. (*E*)-3-styrylbenzo[d]isothiazole 1,1-dioxide **1a** (53.8 mg, 0.20 mmol) and NaOAc (24.6 mg, 0.30 mmol) were added. After 15 min, methyl propiolate **2a** (26.8 μL, 0.30 mmol) was added and stirred at 50 °C for 48 h. The reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na_2SO_4. After concentration in vacuo, the residue was finally purified by flash chromateography eluting with ethyl acetate and petroleum ether (1:6) to give the product **3aa** as a yellow solid (55.0 mg, 95% yield).



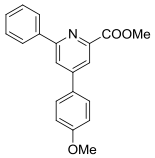
Methyl 4,6-diphenylpicolinate (3aa). Isolation condition: PE/EA=6/1, R_f = 0.71. Yellow solid (55.0 mg, 95% yield). Mp 82 - 83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 1.6 Hz, 1H), 8.12 - 8.08 (m, 3H), 7.77 - 7.73 (m, 2H), 7.55 - 7.45 (m, 6H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 158.7, 150.7, 148.8, 138.9, 137.8, 129.75, 129.71, 129.5, 129.1, 127.6, 127.4, 121.9, 121.8, 53.2; HRMS (ESI): calcd for $C_{19}H_{15}NO_2$ $[M+H]^+$: 290.1176, found 290.1162.



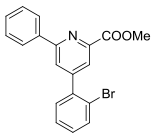
Methyl 4-(2-methoxyphenyl)-6-phenylpicolinate (3ab). Isolation condition: PE/EA=6/1, R_f = 0.68. Yellow oil (52.2 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 1.6 Hz, 1H), 8.09 - 8.05 (m, 3H), 7.52 - 7.41 (m, 5H), 7.12 - 7.03 (m, 2H), 4.04 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 157.9, 156.8, 156.3, 148.6, 148.0, 139.2, 130.8, 130.7, 129.5, 129.0, 127.6, 124.8, 124.5, 121.4, 111.7, 55.9, 53.1; HRMS (ESI): calcd for $C_{20}H_{17}NO_3$ $[M+H]^+$: 320.1281, found 320.1268.



Methyl 4-(3-methoxyphenyl)-6-phenylpicolinate (3ac). Isolation condition: PE/EA=6/1, R_f = 0.66. Yellow oil (48.6 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 1.6 Hz, 1H), 8.12 - 8.08 (m, 3H), 7.55 - 7.42 (m, 4H), 7.35 - 7.31 (m, 1H), 7.26 - 7.25 (m, 1H), 7.06 - 7.01 (m, 1H), 4.06 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 160.3, 158.5, 150.4, 148.6, 139.1, 130.4, 129.5, 128.9, 127.4, 121.8, 121.7, 119.63, 119.57, 114.9, 112.9, 55.5, 53.0; HRMS (ESI): calcd for $C_{20}H_{17}NO_3$ $[M+H]^+$: 320.1281, found 320.1278.

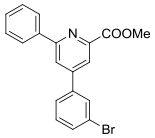


Methyl 4-(4-methoxyphenyl)-6-phenylpicolinate (3ad). Isolation condition: PE/EA=6/1, R_f = 0.68. Yellow solid (57.4 mg, 90% yield). Mp 98 - 99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 1.6 Hz, 1H), 8.10 - 8.06 (m, 2H), 8.05 (d, J = 1.6 Hz, 1H), 7.74 - 7.68 (m, 2H), 7.55 - 7.41 (m, 3H), 7.08 - 7.00 (m, 2H), 4.05 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 165.4, 161.1, 158.6, 150.1, 148.7, 139.1, 130.0, 129.6, 129.1, 128.6, 127.6, 121.3, 114.9, 53.7, 53.2; HRMS (ESI): calcd for $C_{20}H_{17}NO_3$ $[M+H]^+$: 320.1281, found 320.1277.

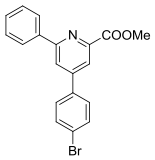


Methyl 4-(2-bromophenyl)-6-phenylpicolinate (3ae). Isolation condition: PE/EA=6/1, R_f = 0.70. Yellow oil (59.6 mg, 81% yield). ^{1}H NMR (400 MHz,

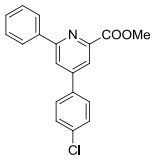
$CDCl_3$): δ 8.13 (d, J = 1.6 Hz, 1H), 8.11 - 8.07 (m, 2H), 7.98 (d, J = 1.2 Hz, 1H), 7.75-7.72 (m, 1H), 7.53 - 7.38 (m, 5H), 7.34 - 7.29 (m, 1H), 4.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 157.7, 150.5, 148.1, 139.3, 138.4, 133.6, 130.8, 130.3, 129.6, 128.9, 127.9, 127.4, 124.5, 124.1, 121.8, 53.0; HRMS (ESI): calcd for $C_{19}H_{14}NO_2Br$ $[M+H]^+$: 368.0281, found 368.0288.



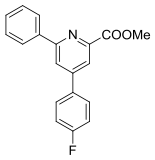
Methyl 4-(3-bromophenyl)-6-phenylpicolinate (3af). Isolation condition: PE/EA=6/1, R_f = 0.69. Yellow solid (62.6 mg, 85% yield). Mp 109 - 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 1.6 Hz, 1H), 8.12 - 8.08 (m, 2H), 8.05 (d, J = 1.2 Hz, 1H), 7.88 (t, J = 1.6 Hz, 1H), 7.69 - 7.61 (m, 2H), 7.55 - 7.46 (m, 3H), 7.41 (t, J = 8.0 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 158.9, 149.3, 148.9, 139.9, 138.6, 132.7, 131.0, 130.4, 129.9, 129.2, 127.6, 126.0, 123.6, 121.8, 121.7, 53.3; HRMS (ESI): calcd for $C_{19}H_{14}NO_2Br$ $[M+H]^+$: 368.0281, found 368.0282.



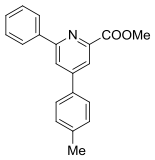
Methyl 4-(4-bromophenyl)-6-phenylpicolinate (3ag). Isolation condition: PE/EA=6/1, R_f = 0.71. Yellow oil (69.2 mg, 94% yield). Mp 103 - 104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 1.6 Hz, 1H), 8.11 - 8.06 (m, 2H), 8.04 (d, J = 1.6 Hz, 1H), 7.69 - 7.58 (m, 4H), 7.55 - 7.43 (m, 3H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 158.9, 149.5, 149.0, 138.7, 136.7, 132.7, 129.9, 129.1, 128.9, 127.6, 124.3, 121.6, 121.5, 53.2; HRMS (ESI): calcd for $C_{19}H_{14}NO_2Br$ $[M+H]^+$: 368.0281, found 368.0290.



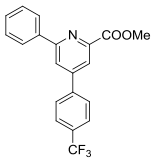
Methyl 4-(4-chlorophenyl)-6-phenylpicolinate (3ah). Isolation condition: PE/EA=6/1, R_f = 0.69. Yellow solid (57.6 mg, 89% yield). Mp 125 - 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 1.6 Hz, 1H), 8.11 - 8.06 (m, 2H), 8.05 (d, J = 1.6 Hz, 1H), 7.71 - 7.66 (m, 2H), 7.54 - 7.45 (m, 5H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 158.7, 149.2, 148.8, 138.5, 136.0, 135.9, 129.6, 129.5, 128.9, 128.4, 127.4, 121.4, 121.3, 53.0; HRMS (ESI): calcd for $C_{19}H_{14}NO_2Cl$ $[M+H]^+$: 324.0786, found 324.0779.



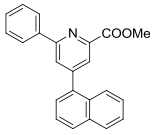
Methyl 4-(4-fluorophenyl)-6-phenylpicolinate (3ai). Isolation condition: PE/EA=6/1, R_f = 0.69. Yellow solid (53.4 mg, 87% yield). Mp 108 - 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 1.6 Hz, 1H), 8.11 - 8.06 (m, 2H), 8.05 (d, J = 1.6 Hz, 1H), 7.76 - 7.70 (m, 2H), 7.55 - 7.45 (m, 3H), 7.26 - 7.19 (m, 2H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 163.7 (d, J = 248.5 Hz), 158.6, 149.4, 148.7, 138.6, 133.7 (d, J = 3.2 Hz), 129.6, 129.0 (d, J = 7.4 Hz), 128.9, 127.4, 121.5, 121.4, 116.4 (d, J = 21.6 Hz), 53.0; HRMS (ESI): calcd for $C_{19}H_{14}NO_2F$ $[M+H]^+$: 308.1081, found 308.1069.



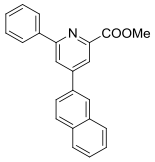
Methyl 6-phenyl-4-(p-tolyl)picolinate (3aj). Isolation condition: PE/EA=6/1, R_f = 0.72. Yellow solid (55.8 mg, 92% yield). Mp 68 - 69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 1.6 Hz, 1H), 8.11 - 8.07 (m, 3H), 7.68 - 7.64 (m, 2H), 7.54 - 7.44 (m, 3H), 7.34 (d, J = 7.6 Hz, 2H), 4.05 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 158.4, 150.3, 148.6, 139.8, 138.8, 134.6, 130.0, 129.4, 128.9, 127.4, 127.0, 121.5, 121.4, 53.0, 21.3; HRMS (ESI): calcd for $C_{20}H_{17}NO_2$ $[M+H]^+$: 304.1332, found 304.1345.



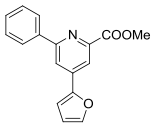
Methyl 6-phenyl-4-(4-(trifluoromethyl)phenyl)picolinate (3ak). Isolation condition: PE/EA=6/1, R_f = 0.70. White solid (59.4 mg, 83% yield). Mp 83 - 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 1.6 Hz, 1H), 8.14 - 8.06 (m, 3H), 7.87 - 7.77 (m, 3H), 7.55 - 7.44 (m, 4H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 158.8, 149.0, 148.9, 138.3, 133.6, 129.9 (q, J = 52.8 Hz), 129.8, 129.0, 127.6, 127.4, 126.2 (q, J = 2.6 Hz), 125.5 (q, J = 276.1 Hz), 121.8, 121.6, 53.1; HRMS (ESI): calcd for $C_{20}H_{14}NO_2F_3$ $[M+H]^+$: 358.1049, found 358.1036.



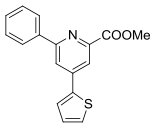
Methyl 4-(naphthalen-1-yl)-6-phenylpicolinate (3al). Isolation condition: PE/EA=6/1, R_f = 0.74. Reacted at 60 °C, yellow oil (63.2 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 0.8 Hz, 1H), 8.13 - 8.09 (m, 2H), 8.05 (d, J = 1.2 Hz, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.4 Hz, 1H), 7.61 - 7.43 (m, 7H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 158.0, 150.8, 148.2, 138.5, 136.8, 133.8, 130.7, 129.6, 129.3, 128.9, 128.7, 127.4, 127.1, 127.0, 126.3, 125.4, 125.04, 124.96, 124.8, 53.0; HRMS (ESI): calcd for $C_{23}H_{17}NO_2$ $[M+H]^+$: 340.1332, found 340.1326.



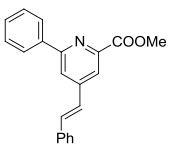
Methyl 4-(naphthalen-2-yl)-6-phenylpicolinate (3am). Isolation condition: PE/EA=6/1, R_f = 0.72. Yellow solid (54.2 mg, 80% yield). Mp 104 - 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 1.2 Hz, 1H), 8.27 - 8.23 (m, 2H), 8.19 - 8.14 (m, 2H), 8.05 - 7.85 (m, 4H), 7.63 - 7.46 (m, 5H), 4.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 158.6, 150.4, 148.7, 138.7, 134.8, 133.6, 133.5, 129.5, 129.2, 128.9, 128.6, 127.8, 127.4, 127.1, 126.9, 126.8, 124.4, 121.9, 121.8, 53.0; HRMS (ESI): calcd for $C_{23}H_{17}NO_2$ $[M+H]^+$: 340.1332, found 340.1320.



Methyl 4-(furan-2-yl)-6-phenylpicolinate (3an). Isolation condition: PE/EA=6/1, R_f = 0.71. Yellow oil (53.0 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 1.2 Hz, 1H), 8.13 (d, J = 1.2 Hz, 1H), 8.11 - 8.07 (m, 2H), 7.61 (d, J = 1.6 Hz, 1H), 7.54 - 7.44 (m, 3H), 7.04 (d, J = 3.6 Hz, 1H), 6.59 (dd, J = 3.6, 1.6 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 158.5, 150.8, 148.5, 144.3, 139.4, 138.5, 129.6, 128.9, 127.3, 117.9, 117.4, 112.4, 109.8, 53.0; HRMS (ESI): calcd for $C_{17}H_{13}NO_3$ $[M+H]^+$: 280.0968, found 280.0968.

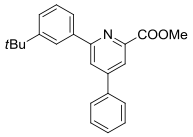


Methyl 6-phenyl-4-(thiophen-2-yl)picolinate (3ao). Isolation condition: PE/EA=6/1, R_f = 0.68. Yellow solid (56.8 mg, 96% yield). Mp 100 - 101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 1.6 Hz, 1H), 8.09 - 8.05 (m, 2H), 8.04 (d, J = 1.6 Hz, 1H), 7.65 (dd, J = 3.6, 1.2 Hz, 1H), 7.54 - 7.45 (m, 4H), 7.18 (dd, J = 7.2, 3.6 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 158.7, 148.8, 143.5, 140.6, 138.5, 129.6, 128.9, 128.6, 127.8, 127.3, 126.1, 119.8, 119.7, 53.0; HRMS (ESI): calcd for $C_{17}H_{13}NO_2S$ $[M+H]^+$: 296.0740, found 296.0750.

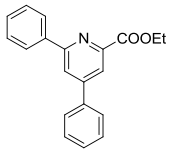


(*E*)-Methyl 6-phenyl-4-styrylpicolinate (3ap). Isolation condition: PE/EA=6/1, R_f = 0.73. Yellow solid (59.8 mg, 95% yield). Mp 98 - 99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 8.07 (d, J = 7.6 Hz, 2H), 7.91 (s, 1H), 7.58 (d, J = 7.6 Hz, 2H), 7.54 - 7.32 (m, 7H), 7.14 (d, J = 16.0 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (100

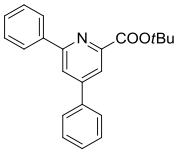
MHz, $CDCl_3$): δ 166.2, 158.5, 148.5, 146.7, 138.7, 135.9, 134.3, 129.4, 129.1, 128.9, 128.8, 127.3, 127.2, 125.4, 121.2, 120.4, 52.9; HRMS (ESI): calcd for $C_{21}H_{17}NO_2$ $[M+H]^+$: 316.1332, found 316.1343.



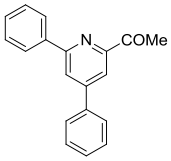
Methyl 6-(3-(*tert*-butyl)phenyl)-4-phenylpicolinate (3aq). Isolation condition: PE/EA=6/1, R_f = 0.68. Yellow oil (34.6 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 1.6 Hz, 1H), 8.09 - 8.02 (m, 2H), 7.88 - 7.83 (m, 1H), 7.78 - 7.73 (m, 2H), 7.57 - 7.48 (m, 4H), 7.44 (t, J = 7.6 Hz, 1H), 4.06 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 159.3, 151.8, 150.4, 148.5, 138.6, 137.7, 129.5, 129.3, 128.6, 127.2, 126.7, 124.8, 124.3, 122.1, 121.5, 52.9, 34.9, 31.4; HRMS (ESI): calcd for $C_{23}H_{23}NO_2$ $[M+H]^+$: 346.1802, found 346.1793.



Ethyl 4,6-diphenylpicolinate (3ba). Isolation condition: PE/EA=6/1, R_f = 0.72. 54.6 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 1.6 Hz, 1H), 8.14 - 8.08 (m, 3H), 7.76 - 7.73 (m, 2H), 7.56 - 7.45 (m, 6H), 4.52 (q, J = 7.2 Hz, 2H), 1.49 (t, J = 7.6 Hz, 3H).[10]



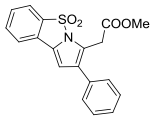
***Tert*-butyl 4,6-diphenylpicolinate (3ca).** Isolation condition: PE/EA=6/1, R_f = 0.72. Reacted at 45 °C, Yellow solid (30.4 mg, 46% yield). Mp 107 - 108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 1.6 Hz, 1H), 8.17 - 8.14 (m, 2H), 8.07 (d, J = 1.6 Hz, 1H), 7.75 - 7.72 (m, 2H), 7.56 - 7.42 (m, 6H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 158.0, 150.3, 149.9, 138.7, 129.4, 129.3, 129.2, 128.8, 127.3, 127.2, 121.2, 121.0, 100.0, 82.2, 28.2; HRMS (ESI): calcd for $C_{22}H_{21}NO_2$ $[M+H]^+$: 332.1646, found 332.1662.



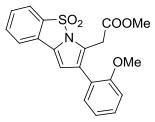
1-(4,6-diphenylpyridin-2-yl)ethanone (3da). Isolation condition: PE/EA=6/1, R_f = 0.74. 47.4 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 1.2 Hz, 1H), 8.18 - 8.12 (m, 3H), 7.76 - 7.73 (m, 2H), 7.56 - 7.45 (m, 6H), 2.87 (s, 3H).[11]

4. General procedure for synthesis of pyrrole derivatives and characterization data

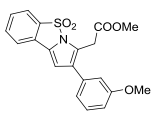
CuI (3.8 mg, 0.02 mmol) and DPPP (12.4 mg, 0.03 mmol) were stirred in 1,4-dioxane (2.0 mL) at room temperature for 1 h. (*E*)-3-styrylbenzo[d]isothiazole 1,1-dioxide **1a** (53.8 mg, 0.20 mmol) and NaOAc (24.6 mg, 0.03 mmol) were added. After 15 min, methyl propiolate **2a** (26.8 μL, 0.30 mmol) was added and stirred at 60 °C for 48 h. The reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na_2SO_4. After concentration in vacuo, the residue was finally purified by flash chromateography eluting with ethyl acetate and petroleum ether (1:6) to give the product **4a** as a yellow solid (69.2 mg, 98% yield).



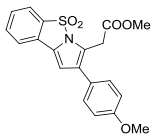
Methyl 2-(5,5-dioxido-2-phenylbenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4aa). Isolation condition: PE/EA=6/1, R_f = 0.48. Yellow solid (69.2 mg, 98% yield). Mp 108 - 109 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 1H), 7.62 - 7.57 (m, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.43 - 7.31 (m, 6H), 6.57 (s, 1H), 3.99 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 136.4, 134.4, 133.7, 132.3, 128.8, 128.6, 128.1, 127.8, 127.5, 122.3, 122.2, 120.8, 106.0, 52.7, 30.9; HRMS (ESI): calcd for $C_{19}H_{15}NO_4S$ $[M+H]^+$: 354.0795, found 354.0800



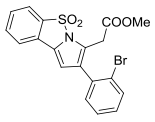
Methyl 2-(2-(2-methoxyphenyl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ab). Isolation condition: PE/EA=6/1, R_f = 0.46. Yellow solid (70.6 mg, 92% yield). Mp 136 - 137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 7.6 Hz, 1H), 7.61 - 7.56 (m, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.38 - 7.29 (m, 3H), 7.03 - 6.93 (m, 2H), 6.57 (s, 1H), 3.88 (s, 2H), 3.81 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 156.8, 136.6, 134.5, 131.1, 129.4, 128.5, 128.3, 128.2, 127.7, 123.8, 122.6, 122.5, 121.0, 120.9, 111.2, 107.8, 55.4, 52.4, 31.3; HRMS (ESI): calcd for $C_{20}H_{17}NO_5S$ $[M+H]^+$: 384.0900, found 384.0911.



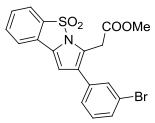
Methyl 2-(2-(3-methoxyphenyl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ac). Isolation condition: PE/EA=6/1, R_f = 0.46. Yellow oil (71.2 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.6 Hz, 1H), 7.64 - 7.58 (m, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.41 - 7.29 (m, 2H), 7.02 - 6.93 (m, 2H), 6.91 - 6.87 (m, 1H), 6.58 (s, 1H), 4.00 (s, 2H), 3.84 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 159.8, 136.4, 135.1, 134.4, 132.2, 129.8, 128.6, 127.8, 127.7, 122.33, 122.25, 120.8, 120.4, 113.5, 113.2, 106.0, 55.3, 52.7, 30.9; HRMS (ESI): calcd for $C_{20}H_{17}NO_5S$ $[M+H]^+$: 384.0900, found 384.0890.



Methyl 2-(2-(4-methoxyphenyl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ad). Isolation condition: PE/EA=6/1, R_f = 0.47. Yellow solid (69.8 mg, 91% yield). Mp 133 - 135 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.0 Hz, 1H), 7.62 - 7.56 (m, 1H), δ 7.52 (d, J = 8.0 Hz, 1H), 7.40 - 7.32 (m, 3H), 6.97 - 6.93 (m, 2H), 6.53 (s, 1H), 3.96 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 159.1, 136.4, 134.3, 132.0, 129.2, 128.5, 127.8, 127.7, 126.2, 122.3, 121.7, 120.7, 114.2, 106.1, 55.3, 52.7, 30.9; HRMS (ESI): calcd for $C_{20}H_{17}NO_5S$ $[M+H]^+$: 384.0900, found 384.0899.

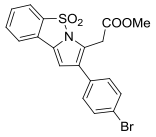


Methyl 2-(2-(2-bromophenyl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ae). Isolation condition: PE/EA=6/1, R_f = 0.45. Yellow solid (83.8 mg, 97% yield). Mp 120 - 121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.64 - 7.58 (m, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.42 - 7.32 (m, 3H), 7.25 - 7.20 (m, 1H), 6.57 (s, 1H), 3.83 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 136.3, 134.4, 134.3, 133.2, 131.8, 130.9, 129.5, 128.1, 127.83, 127.77, 127.5, 124.1, 123.5, 122.3, 120.9, 107.4, 52.6, 30.7; HRMS (ESI): calcd for $C_{19}H_{14}NO_4SBr$ $[M+H]^+$: 431.9900, found 431.9906.

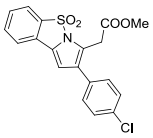


Methyl 2-(2-(3-bromophenyl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4af). Isolation condition: PE/EA=6/1, R_f = 0.47. Yellow oil (79.4 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 1H), 7.65 - 7.50

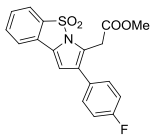
(m, 3H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.42 - 7.33 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 3.97 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 136.4, 135.9, 134.5, 131.1, 130.8, 130.5, 130.3, 128.7, 128.0, 127.5, 126.6, 122.9, 122.5, 122.4, 120.9, 105.7, 52.8, 30.8; HRMS (ESI): calcd for $C_{19}H_{14}NO_4SBr$ $[M+H]^+$: 431.9900, found 431.9885.



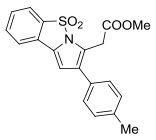
Methyl 2-(2-(4-bromophenyl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ag). Isolation condition: PE/EA=6/1, R_f = 0.47. Yellow solid (73.4 mg, 85% yield). Mp 131 - 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.64 - 7.59 (m, 1H), 7.57 - 7.51 (m, 3H), 7.43 - 7.37 (m, 1H), 7.32 - 7.28 (m, 2H), 6.54 (s, 1H), 3.95 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 136.3, 134.4, 132.7, 132.0, 131.1, 129.7, 128.7, 127.9, 127.5, 122.4, 122.2, 121.7, 120.8, 105.7, 52.8, 30.8; HRMS (ESI): calcd for $C_{19}H_{14}NO_4SBr$ $[M+H]^+$: 431.9900, found 431.9889.



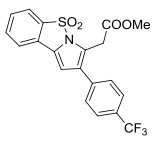
Methyl 2-(2-(4-chlorophenyl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ah). Isolation condition: PE/EA=6/1, R_f = 0.47. Yellow solid (70.6 mg, 91% yield). Mp 148 - 150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 - 7.68 (m, 1H), 7.64 - 7.58 (m, 1H), 7.55 - 7.51 (m, 1H), 7.42 - 7.33 (m, 5H), 6.54 (s, 1H), 3.95 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 136.4, 134.4, 133.5, 132.2, 131.1, 129.3, 129.0, 128.7, 127.9, 122.4, 122.3, 120.8, 105.8, 100.0, 52.8, 30.8; HRMS (ESI): calcd for $C_{19}H_{14}NO_4SCl$ $[M+H]^+$: 388.0405, found 380.0394.



Methyl 2-(2-(4-fluorophenyl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ai). Isolation condition: PE/EA=6/1, R_f = 0.48. Yellow solid (66.8 mg, 90% yield). Mp 127 - 129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.63 - 7.57 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.42 - 7.35 (m, 3H), 7.14 - 7.07 (m, 2H), 6.53 (s, 1H), 3.95 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 162.3 (d, *J* = 245.5 Hz), 136.4, 134.4, 131.3, 129.8 (d, *J* = 8.0 Hz), 129.7, 128.6, 127.8, 127.6, 122.3, 122.1, 120.8, 115.8 (d, *J* = 21.3 Hz), 105.9, 52.7, 30.7; HRMS (ESI): calcd for $C_{19}H_{14}NO_5SF$ $[M+H]^+$: 372.0700, found 372.0700.

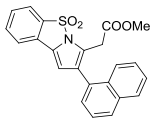


Methyl 2-(5,5-dioxido-2-(p-tolyl)benzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4aj). Isolation condition: PE/EA=6/1, R_f = 0.50. Yellow oil (61.6 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.63 - 7.57 (m, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.41 - 7.35 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.56 (s, 1H), 3.97 (s, 2H), 3.77 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 137.3, 136.4, 134.3, 132.2, 130.8, 129.5, 128.5, 127.9, 127.8, 127.7, 122.3, 122.0, 120.7, 106.1, 52.7, 30.9, 21.2; HRMS (ESI): calcd for $C_{20}H_{17}NO_4S$ $[M+H]^+$: 368.0951, found 368.0941.

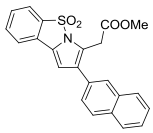


Methyl 2-(5,5-dioxido-2-(4-(trifluoromethyl)phenyl)benzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ak). Isolation condition: PE/EA=6/1, R_f = 0.47. Yellow oil (83.4 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.65 - 7.60 (m, 1H), 7.58 - 7.52 (m, 3H), 7.44 - 7.39 (m, 1H), 6.59 (s, 1H), 3.98 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 137.4, 136.3, 134.5, 130.8, 128.9, 128.3, 128.1, 127.4, 125.8 (q, *J* = 3.9 Hz), 125.7, 125.2 (q, *J* = 254.2 Hz),

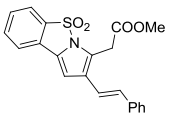
122.7, 122.4, 120.9, 105.6, 53.5, 30.8; HRMS (ESI): calcd for $C_{20}H_{14}NO_4SF_3$ $[M+H]^+$: 422.0668, found 422.0660.



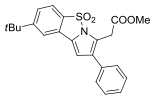
Methyl 2-(2-(naphthalen-1-yl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4al). Isolation condition: PE/EA=6/1, R_f = 0.45. Yellow oil (64.6 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.98 - 7.85 (m, 3H), 7.75 (d, J = 8.0 Hz, 1H), 7.64 - 7.59 (m, 1H), 7.56 - 7.45 (m, 5H), 7.43 - 7.38 (m, 1H), 6.69 (s, 1H), 3.81 (s, 2H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 136.5, 134.4, 133.8, 132.3, 131.0, 130.3, 128.53, 128.48, 128.4, 127.9, 127.8, 127.7, 126.3, 126.1, 125.8, 125.4, 123.9, 122.4, 120.9, 108.0, 52.5, 30.6; HRMS (ESI): calcd for $C_{23}H_{17}NO_4S$ $[M+H]^+$: 404.0951, found 404.0962.



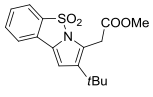
Methyl 2-(2-(naphthalen-2-yl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4am). Isolation condition: PE/EA=6/1, R_f = 0.46. Yellow solid (69.4 mg, 86% yield). Mp 133 - 135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.91 - 7.83 (m, 4H), 7.73 (d, J = 7.6 Hz, 1H), 7.64 - 7.59 (m, 1H), 7.57 - 7.48 (m, 4H), 7.42 - 7.36 (m, 1H), 6.68 (s, 1H), 4.05 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 136.4, 134.4, 133.4, 132.6, 132.3, 131.2, 128.7, 128.5, 128.0, 127.8, 127.74, 127.72, 126.8, 126.5, 126.3, 126.2, 122.45, 122.36, 120.8, 106.2, 52.7, 31.0; HRMS (ESI): calcd for $C_{23}H_{17}NO_4S$ $[M+H]^+$: 404.0951, found 404.0960.



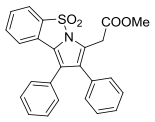
(*E*)-Methyl 2-(5,5-dioxido-2-styrylbenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ap). Isolation condition: PE/EA=6/1, R_f = 0.39. Yellow oil (36.4 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.6 Hz, 1H), 7.64 - 7.60 (m, 1H), 7.56 - 7.54 (m, 1H), 7.49 - 7.46 (m, 2H), 7.42 - 7.33 (m, 4H), 6.90 (s, 2H), 6.74 (s, 1H), 4.03 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 137.1, 136.7, 134.4, 129.2, 129.1, 128.7, 127.9, 127.7, 127.5, 126.3, 123.2, 122.3, 120.9, 118.3, 102.5, 52.7, 30.4; HRMS (ESI): calcd for $C_{21}H_{17}NO_4S$ $[M+H]^+$: 380.0951, found 380.0970.



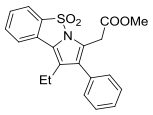
Methyl 2-(8-(*tert*-butyl)-5,5-dioxido-2-phenylbenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4aq). Isolation condition: PE/EA=6/1, R_f = 0.47. White solid (36.8 mg, 45% yield). Mp 138 - 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 1.6 Hz, 1H), 7.44 - 7.39 (m, 5H), 7.36 - 7.31 (m, 1H), 6.59 (s, 1H), 3.98 (s, 2H), 3.77 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 158.7, 133.9, 132.0, 129.0, 128.8, 128.0, 127.4, 126.0, 125.2, 122.0, 121.9, 117.7, 110.5, 105.5, 52.7, 35.6, 31.1, 30.9; HRMS (ESI): calcd for $C_{23}H_{23}NO_4S$ $[M+H]^+$: 410.1421, found 410.1413.



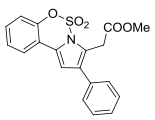
Methyl2-(2-(tert-butyl)-5,5-dioxidobenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ar). Isolation condition: PE/EA=6/1, R_f = 0.42. Reacted at 100 °C, light yellow oil (51.4 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.0 Hz, 1H), 7.56 - 7.50 (m, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.33 - 7.27 (m, 1H), 6.38 (s, 1H), 4.04 (s, 2H), 3.74 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 138.8, 135.4, 133.1, 126.8, 126.2, 121.2, 120.1, 119.3, 108.9, 104.2, 51.5, 31.0, 30.2, 28.3; HRMS (ESI): calcd for $C_{17}H_{19}NO_4S$ $[M+H]^+$: 334.1108, found 334.1110.



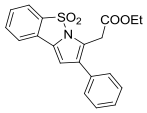
Methyl2-(5,5-dioxido-1,2-diphenylbenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4as). Isolation condition: PE/EA=6/1, R_f = 0.45. Yellow solid (61.0 mg, 71% yield). Mp 158 - 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 7.6 Hz, 1H), 7.44 - 7.37 (m, 2H), 7.35 - 7.30 (m, 4H), 7.27 - 7.23 (m, 5H), 7.14 - 7.10 (m, 2H), 3.92 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 136.2, 134.2, 132.3, 132.2, 132.0, 129.95, 129.93, 128.5, 128.4, 128.1, 127.8, 127.6, 127.4, 124.8, 123.3, 123.0, 122.4, 120.7, 52.7, 30.8; HRMS (ESI): calcd for $C_{25}H_{19}NO_4S$ $[M+H]^+$: 430.1108, found 430.1122.



Methyl 2-(5,5-dioxido-1,2-diphenylbenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4at). Isolation condition: PE/EA=6/1, R_f = 0.41. Reacted at 100 °C, Yellow solid (16.0 mg, 21% yield). Mp 115 - 116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 - 7.67 (m, 1H), 7.58 - 7.49 (m, 2H), 7.42 - 7.27 (m, 6H), 3.77 (s, 2H), 3.70 (s, 3H), 2.58 (q, J = 8.0 Hz, 2H), 1.09 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 136.2, 134.3, 132.8, 132.7, 129.8, 128.60, 128.57, 127.7, 126.8, 124.68, 124.66, 122.7, 122.5, 120.7, 52.5, 30.6, 18.0, 14.9; HRMS (ESI): calcd for $C_{21}H_{19}NO_4S$ $[M+H]^+$: 382.1108, found 382.1112.

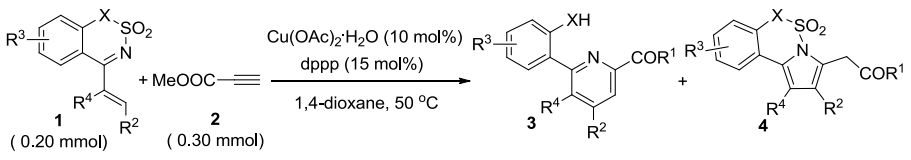


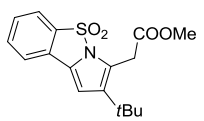
Methyl 2-(5,5-dioxido-2-phenylbenzo[e]pyrrolo[1,2-c][1,2,3]oxathiazin-3-yl)acetate (4au). Isolation condition: PE/EA=6/1, R_f = 0.44. Reacted at 100 °C, yellow solid (64.4 mg, 88% yield). Mp 103 - 104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 - 7.69 (m, 1H), 7.47 - 7.42 (m, 2H), 7.39 - 7.28 (m, 6H), 6.85 (s, 1H), 4.02 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 147.3, 133.3, 129.5, 129.3, 128.90, 128.87, 128.6, 127.8, 127.3, 123.8, 122.7, 118.9, 117.7, 109.6, 52.6, 31.8; HRMS (ESI): calcd for $C_{19}H_{15}NO_5S$ $[M+H]^+$: 370.0744, found 370.0761.



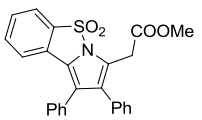
Ethyl 2-(5,5-dioxido-2-phenylbenzo[d]pyrrolo[1,2-b]isothiazol-3-yl)acetate (4ba). Isolation condition: PE/EA=6/1, R_f = 0.48. Yellow oil (67.4 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 - 7.69 (m, 1H), 7.62 - 7.51 (m, 2H), 7.44 - 7.31 (m, 6H), 6.57 (s, 1H), 4.23 (q, J = 7.2 Hz, 2H), 3.97 (s, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 136.5, 134.3, 133.8, 132.2, 128.8, 128.5, 128.0, 127.8, 127.7, 127.5, 122.4, 122.3, 120.7, 106.0, 61.7, 31.1, 14.1; HRMS (ESI): calcd for $C_{20}H_{17}NO_4S$ $[M+H]^+$: 368.0951, found 368.0950.

5. The reaction of *N*-sulfonyl azadiene 1r-1u and alkynes under condition A[a]

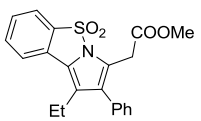




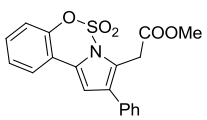
4ar, 32%[b], **3ar**, N.D.



4as, 55%, **3as**, N.D.



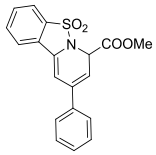
4at, 37%[b], **3at**, N.D.



4au, 61%[b], **3au**, N.D.

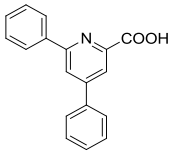
[a] Isolated yield. [b] Reacted at 100 °C.

6. Procedure for synthesis of 9aa and characterization data

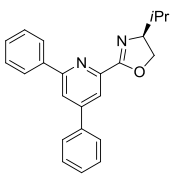


$Cu(OAc)_2{\cdot}H_2O$ (4.0 mg, 0.02 mmol) and DPPP (12.4 mg, 0.03 mmol) were stirred in 1,4-dioxane (2.0 mL) at room temperature for 1 h. (*E*)-3-styrylbenzo[d]isothiazole 1,1-dioxide **1a** (53.8 mg, 0.20 mmol) and NaOAc (24.6 mg, 0.30 mmol) were added. After stirring for 15 min, methyl propiolate **2a** (26.8 μL, 0.30 mmol) was added and stirred at 30 °C for 72 h. The reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na_2SO_4. After concentration in vacuo, the residue was finally purified by flash chromateography eluting with ethyl acetate and petroleum ether (1:5) to give methyl 9-phenyl-7H-benzo[4,5]isothiazolo[2,3-a]pyridine-7-carboxylate 5,5-dioxide **9aa** as a yellow solid (48.0 mg, 68% yield). Mp 97 - 98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.71 - 7.65 (m, 1H), 7.63 - 7.57 (m, 1H), 7.46 - 7.35 (m, 5H), 6.23 (d, J = 1.2 Hz, 1H), 5.96 (dd, J = 1.2, 6.4 Hz, 1H), 5.45 (d, J = 6.4 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 137.8, 137.4, 133.3, 133.1, 132.1, 130.8, 128.9, 128.8, 128.6, 125.9, 121.8, 121.5, 112.6, 98.8, 53.2, 52.9; HRMS (ESI): calcd for $C_{19}H_{15}NO_4S$ $[M+H]^+$: 354.0795, found 354.0787.

7. Procedure for application of the compound 3aa and 4aa and characterization data

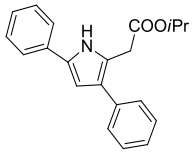


To a solution of methyl 4,6-diphenylpicolinate **3aa** (144.5 mg, 0.50 mmol) in methanol was added 1M aqueous sodium hydroxide solution (1.0 mL) and the mixture was stirred at room temperature for 3 h. The reaction mixture was concentrated. 1M hydrochloric acid was added, the precipitate was collected by filtration, and washed with water to give 4,6-diphenylpicolinic acid **5** as gray solid (126.6 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, J = 1.6 Hz, 1H), δ 8.20 (d, J = 1.6 Hz, 1H), 8.08 - 8.03 (m, 2H), 7.79 - 7.75 (m, 2H), 7.60 - 7.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 157.1, 152.2, 146.4, 137.0, 130.2, 130.1, 129.4, 129.1, 127.2, 127.1, 122.7, 120.0, 111.0; HRMS (ESI): calcd for $C_{18}H_{13}NO_2$ $[M+H]^+$: 276.1019, found 276.1013.

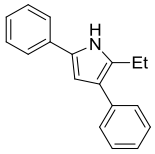


Methyl 4,6-diphenylpicolinate **3aa** (86.7 mg, 0.30 mmol), (*S*)-2-amino-3-methylbutan-1-ol (34.0

mg, 0.35 mmol) and NaH (2.16 mg, 0.30 mmol) were stirred at 120 °C overnight. The reaction mixture was dissolved in dry DCM (5.0 mL). $SOCl_2$ (0.3 mL, 4.0 mmol) was added at 0 °C slowly and stirred at room temperature for 18 h. Removal of DCM and excess $SOCl_2$, the mixture was dissolved in MeCN (5.0 mL) and saturated aqueous K_2CO_3 (5.0 mL), then was heated to reflux for 24 h. After completion, the reaction mixture was cooled down to room temperature. The mixture was extracted further with DCM three times; then the combined organic layer was dried over Na_2SO_4. After concentration in vacuo, the residue was finally purified by flash chromateography eluting with ethyl acetate and petroleum ether (1:5) to give ligand **6** as a yellow oil (38.7 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 1.2 Hz, 1H), 8.11 - 8.06 (m, 2H), 8.02 (d, J = 1.6 Hz, 1H), 7.78 - 7.73 (m, 2H), 7.55 - 7.41 (m, 6H), 4.57 (dd, J = 9.2, 8.4 Hz, 1H), 4.32 - 4.18 (m, 2H), 2.01 - 1.89 (m, 1H), 1.08 (d, J = 7.6 Hz, 3H), 0.97 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 158.4, 150.2, 147.6, 139.2, 138.1, 129.6, 129.5, 129.4, 129.0, 127.6, 127.4, 120.9, 120.7, 73.0, 71.0, 33.0, 19.4, 18.4; HRMS (ESI): calcd for $C_{23}H_{22}N_2O$ $[M+H]^+$: 343.1805, found 343.1801.



Under an argon atmosphere, to a mixture of **4aa** (0.20 mmol) and Mg powder (24 mg, 1.0 mmol) in THF (1 mL) were added $Ti(OiPr)_4$ (0.6 mL, 0.20 mmol) and TMSCl (0.04 mL, 0.30 mmol). The resulting mixture was stirred at 50 °C. After checking consumption of the substrate by TLC analysis, aqueous 3M NaOH (0.1 mL), Et_2O (3.0 mL), anhydrous NaF (0.2 g) and Celite (0.2 g) were sequentially added at room temperature. After being stirred for 30 min, the mixture was filtered through a pad of Celite. To the resulting filtrate was added aqueous 3M NaOH (3 mL) and the mixture was extracted with Et_2O (3.0 mL). The organic layer was washed with aqueous 3M NaOH, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was finally purified by flash chromateography eluting with ethyl acetate and petroleum ether (1:5) to give isopropyl 2-(3,5-diphenyl-1H-pyrrol-2-yl)acetate **7** as a yellow solid (45.9 mg, 72% yield). Mp 98 - 99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (s, 1H), 7.55 - 7.22 (m, 10H), 6.63 (s, 1H), 5.14 - 5.09 (m, 1H), 3.84 (s, 2H), 1.30 (d, J = 8.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 136.4, 132.7, 131.7, 129.1, 128.8, 128.3, 126.5, 126.1, 124.8, 123.9, 121.1, 106.4, 69.3, 32.4, 22.1; HRMS (ESI): calcd for $C_{21}H_{21}NO_2$ $[M+H]^+$: 320.1645, found 320.1656.

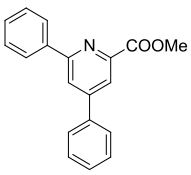


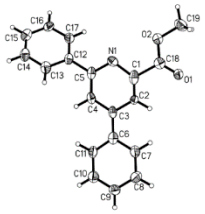
Under an argon atmosphere, to a solution of **7** (0.80 mmol) in THF (8.0 mL) was added $LiAlH_4$ (4 mL, 1 mol/L) at 0 °C. The resulting mixture was stirred at room temperature overnight. After checking consumption of the substrate by TLC analysis, aqueous 1M HCl (8.0 mL) were sequentially added at room temperature. The aqueous layer was extracted further with EtOAc three times; then the combined organic layer was dried over Na_2SO_4. After concentration in vacuo, it gave crude product. The crude product was dissolved in DCM (8.0 mL), and PCl_5 (0.8 mmol)

was added, then stirred for 1 h. After checking consumption of the substrate by TLC analysis, aqueous $NaHCO_3$ (8.0 mL) were sequentially added at room temperature. The aqueous layer was extracted further with EtOAc three times; then the combined organic layer was dried over Na_2SO_4. After concentration in vacuo, it gave crude product.

Under an argon atmosphere, to a solution of above crude product in THF (8.0 mL) was added $LiAlH_4$ (4 mL, 1 mol/L) at 0 °C. The resulting mixture was stirred at room temperature overnight. After checking consumption of the substrate by TLC analysis, aqueous 1M HCl (8.0 mL) were sequentially added at room temperature. The aqueous layer was extracted further with EtOAc three times; then the combined organic layer was dried over Na_2SO_4. After concentration in vacuo, the residue was finally purified by flash chromateography eluting with ethyl acetate and petroleum ether (1:10) to give compound **8** as a brown oil (154.1 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.50 - 7.34 (m, 8H), 7.25 - 7.17 (m, 2H), 6.61 (d, J = 2.8 Hz, 1H), 2.86 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H).[12]

8. X-ray diffraction analysis of 3aa and 4aa





3aa CDCC: 1569919

Datablock: t

Bond precision: C-C = 0.0147 A Wavelength=1.54178

Cell: a=9.8509(3) b=13.4787(4) c=22.2482(7)
alpha=90 beta=96.124(2) gamma=90

Temperature: 173 K

	Calculated	Reported
Volume	2937.20(16)	2937.20(16)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	3(C19 H15 N O2), C19 H14 N O2	3(C19 H15 N O2), C19 H14 N O2
Sum formula	C76 H59 N4 O8	C76 H59 N4 O8
Mr	1156.27	1156.27
Dx,g cm-3	1.307	1.307
Z	2	2
Mu (mm-1)	0.681	0.681
F000	1214.0	1214.0
F000'	1217.61	
h,k,lmax	11,16,26	11,16,26
Nref	10799[5646]	10150
Tmin,Tmax		
Tmin'		

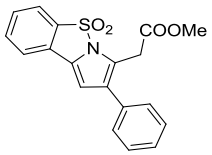
Correction method= Not given

Data completeness= 1.80/0.94 Theta(max)= 68.402

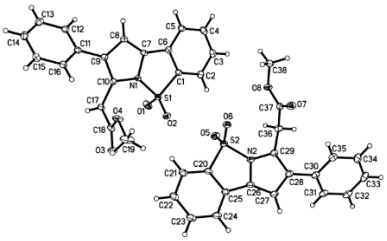
R(reflections)= 0.0960(8409) wR2(reflections)= 0.2761(10150)

S = 1.035 Npar= 798

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.



4aa CDCC: 1569920



Datablock: t

Bond precision: C-C = 0.0028 A Wavelength=1.54178

Cell: a=16.3964(5) b=24.3356(7) c=8.2487(2)
alpha=90 beta=94.460(1) gamma=90
Temperature: 123 K

	Calculated	Reported
Volume	3281.40(16)	3281.40(16)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C19 H14 N O4 S, C19 H15 N O4 S	C19 H14 N O4 S, C19 H15 N O4 S
Sum formula	C38 H29 N2 O8 S2	C38 H29 N2 O8 S2
Mr	705.75	705.75
Dx,g cm-3	1.429	1.429
Z	4	4
Mu (mm-1)	1.969	1.969
F000	1468.0	1468.0
F000'	1475.06	
h,k,lmax	19,29,9	19,29,9
Nref	6001	5984
Tmin,Tmax	0.828,0.906	
Tmin'	0.674	

Correction method= Not given

Data completeness= 0.997 Theta(max)= 68.313

R(reflections)= 0.0378(5378) wR2(reflections)= 0.1231(5984)

S = 0.650 Npar= 451

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

9. Deuterium labeling experiment

$Cu(OAc)_2 \cdot H_2O$ (2.0 mg, 0.01 mmol) and DPPP (6.2 mg, 0.015 mmol) were stirred in 1,4-dioxane (1.0 mL) at room temperature for 1 h. *D*-**1a** (27.0 mg, 0.1 mmol) and NaOAc (12.3mg, 0.15 mmol) were added. After 15 min, methyl propiolate **2a** (13.4 μL, 0.15 mmol) was added and stirred at 50 °C for two days. The reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na_2SO_4. After concentration in vacuo, The residue was analyzed by ^{1}H NMR (67% yield).

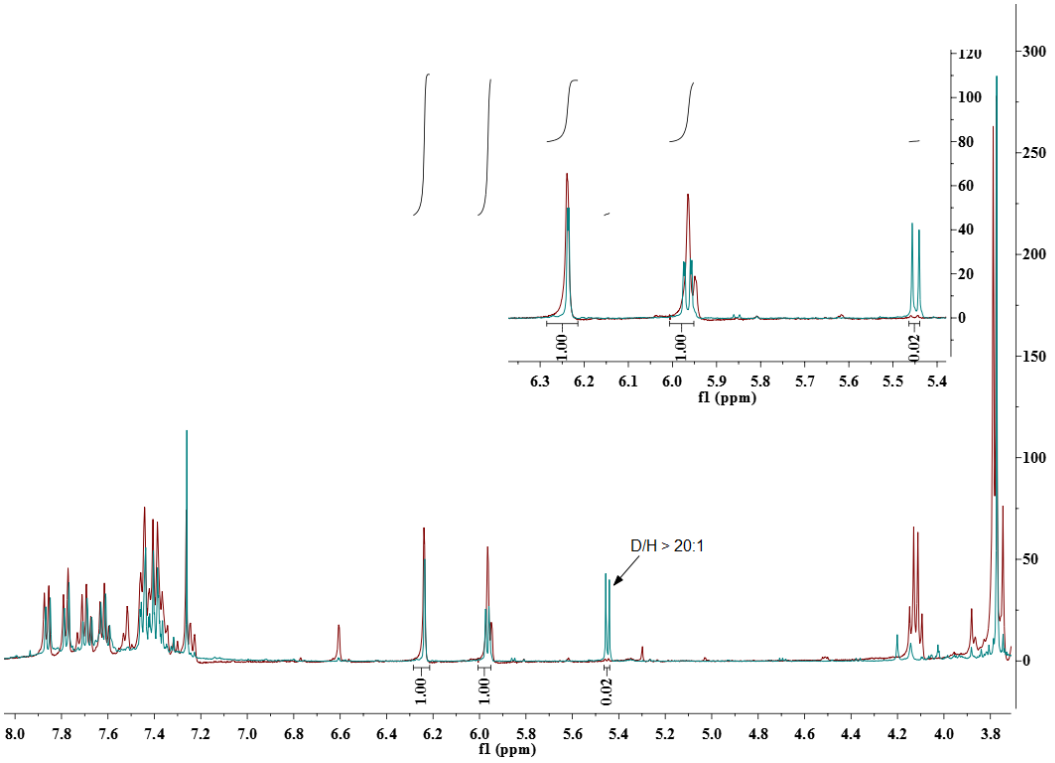


Figure S1. Comparison of ^{1}H NMR spectra (400 MHz) of **9aa** (blue) and ***D*-9aa** (red).

10. DFT study of mechanism and its datas

Computational details: All calculations were performed independently using the density functional theory (DFT) model chemistries. Computations were carried out using the long-range corrected hybrid functional with damped atom—atom dispersion (WB97XD)[13] as implemented in the GAUSSIAN 09 software package.[14] For iodine atom the SDD basis set[15] with the associated effective core potential was employed. All other atoms were modeled at the 6-31G(d,p) level of theory with additional diffuse function for phosphorus.[16] The solvent effect was accounted for by carrying out optimizations in the SMD force field.[17] The transition states were subsequently fully optimized as saddle points of first order, employing the Berny algorithm. Frequency Calculations were carried out to confirm the nature of the stationary points, yielding zero imaginary frequencies for all copper complexes and only one imaginary for all transition states, which represented the vector for the appropriate bond formation. Cartesian coordinates (in Å) and energies (in Hartree/particle).

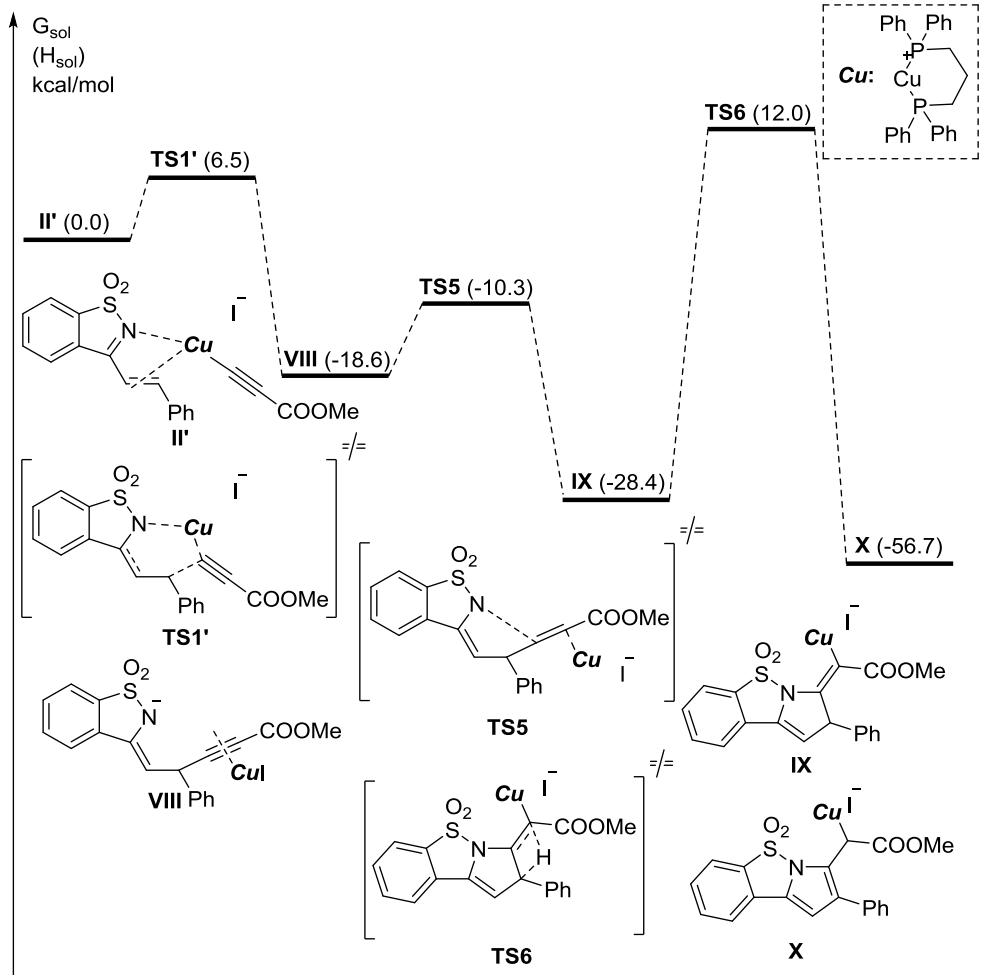


Figure S2. Mechanism of the formation of pyrroles.

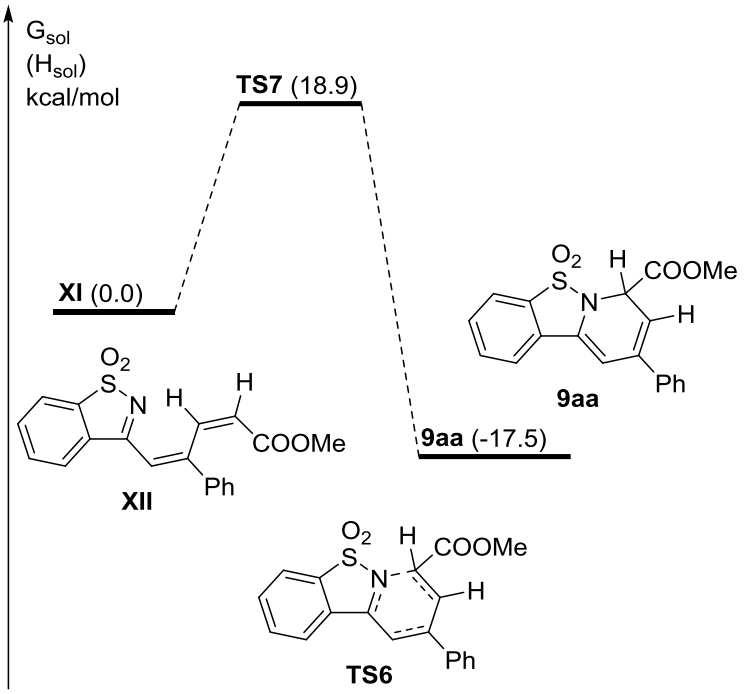
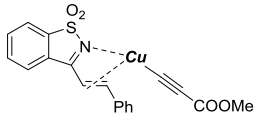


Figure S3. Energy of transition state of *6π*-electrocyclization.

II



Sum of electronic and zero-point Energies= -4853.119305
Sum of electronic and thermal Energies= -4852.365092
Sum of electronic and thermal Enthalpies= -4852.312829
Sum of electronic and thermal Free Energies= -4852.454616

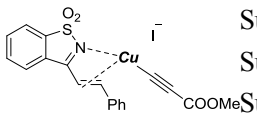
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.026390	0.014013	0.652302
2	15	0	-1.803888	-1.233236	1.129966
3	15	0	-1.038641	2.007539	0.522862
4	6	0	-2.798854	1.761087	0.051062
5	1	0	-2.757377	1.144501	-0.852078
6	1	0	-3.305149	2.690069	-0.229079
7	6	0	-3.645275	1.050727	1.125114
8	1	0	-3.988573	1.793506	1.852636
9	1	0	-4.544259	0.687279	0.617866
10	6	0	-3.014537	-0.095375	1.944543
11	1	0	-3.813166	-0.671441	2.424103
12	1	0	-2.422666	0.331271	2.764213
13	6	0	-1.496415	-2.436170	2.472353
14	6	0	-0.195487	-2.567108	2.960492
15	6	0	-2.517059	-3.229351	3.007736
16	6	0	0.078897	-3.468832	3.985949
17	1	0	0.602235	-1.971619	2.524616
18	6	0	-2.241202	-4.128369	4.029645
19	1	0	-3.527086	-3.156577	2.612067
20	6	0	-0.941509	-4.246189	4.521585
21	1	0	1.094609	-3.567756	4.354876
22	1	0	-3.036083	-4.744844	4.438113
23	1	0	-0.725335	-4.954114	5.315895
24	6	0	-2.745536	-2.215425	-0.083867
25	6	0	-4.131585	-2.148578	-0.240115
26	6	0	-2.012227	-3.111905	-0.870283
27	6	0	-4.773530	-2.949955	-1.182079
28	1	0	-4.724426	-1.478456	0.373416
29	6	0	-2.654625	-3.916478	-1.804057
30	1	0	-0.932192	-3.172224	-0.758093
31	6	0	-4.036904	-3.832888	-1.965803
32	1	0	-5.850876	-2.885576	-1.299493
33	1	0	-2.071888	-4.604413	-2.408269
34	1	0	-4.537912	-4.457954	-2.698349
35	6	0	-1.105422	2.951479	2.084519

36	6	0	-2.102425	3.896053	2.347908
37	6	0	-0.111226	2.722148	3.040579
38	6	0	-2.114470	4.589995	3.552298
39	1	0	-2.874673	4.094957	1.609901
40	6	0	-0.121713	3.422022	4.244038
41	1	0	0.676045	2.000469	2.836562
42	6	0	-1.124021	4.351696	4.502529
43	1	0	-2.894312	5.319017	3.749388
44	1	0	0.653619	3.236288	4.980301
45	1	0	-1.134285	4.891557	5.444261
46	6	0	-0.346795	3.190909	-0.684108
47	6	0	-1.083175	4.192355	-1.320928
48	6	0	1.021982	3.075586	-0.955670
49	6	0	-0.473212	5.040975	-2.239274
50	1	0	-2.142930	4.309878	-1.116919
51	6	0	1.632702	3.930284	-1.869109
52	1	0	1.611290	2.318024	-0.442669
53	6	0	0.884131	4.906067	-2.521349
54	1	0	-1.057247	5.810677	-2.734547
55	1	0	2.696774	3.836603	-2.064829
56	1	0	1.358034	5.568273	-3.239157
57	6	0	1.809115	0.014677	1.062840
58	6	0	2.949653	0.318188	1.398879
59	6	0	4.316709	0.605536	1.716583
60	8	0	5.056972	-0.074158	2.397272
61	8	0	4.712811	1.773978	1.156922
62	6	0	6.078402	2.108595	1.370990
63	1	0	6.743340	1.328030	0.990334
64	1	0	6.245661	3.040621	0.829680
65	1	0	6.287443	2.256118	2.433990
66	6	0	3.713033	-1.903693	-1.423826
67	6	0	2.984498	-0.810768	-1.870199
68	6	0	3.610045	0.416166	-2.039978
69	6	0	4.966983	0.510212	-1.737503
70	6	0	5.679186	-0.595797	-1.275530
71	6	0	5.054545	-1.833152	-1.110619
72	6	0	1.560672	-1.185556	-2.080324
73	1	0	3.061703	1.286747	-2.383459
74	1	0	5.474480	1.462017	-1.850750
75	1	0	6.733467	-0.495729	-1.040309
76	1	0	5.600318	-2.695965	-0.746340
77	16	0	2.606959	-3.300838	-1.374097
78	8	0	2.385590	-3.770758	-0.017762
79	8	0	2.959603	-4.263132	-2.407943

80	7	0	1.250877	-2.426743	-1.875519
81	6	0	0.554457	-0.205940	-2.470518
82	1	0	0.846411	0.839142	-2.462510
83	6	0	-0.693868	-0.587506	-2.793599
84	1	0	-0.911714	-1.652220	-2.762704
85	6	0	-1.818200	0.277194	-3.142939
86	6	0	-3.101857	-0.286841	-3.137761
87	6	0	-1.678413	1.641850	-3.429300
88	6	0	-4.222327	0.498553	-3.377023
89	1	0	-3.216377	-1.345797	-2.927664
90	6	0	-2.799311	2.421350	-3.681884
91	1	0	-0.694805	2.100281	-3.453481
92	6	0	-4.072965	1.856237	-3.647179
93	1	0	-5.209342	0.048077	-3.353486
94	1	0	-2.676031	3.477353	-3.899241
95	1	0	-4.945974	2.471794	-3.840626

II'



Sum of electronic and zero-point Energies= -4863.896653
Sum of electronic and thermal Energies= -4863.844056
Sum of electronic and thermal Enthalpies= -4863.843112
Sum of electronic and thermal Free Energies= -4863.988998

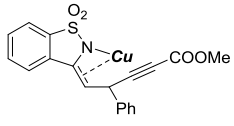
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.626514	-0.326473	-0.512040
2	15	0	1.330219	-1.494411	1.260591
3	15	0	1.799644	1.547630	-0.182737
4	6	0	2.073856	1.623001	1.640311
5	1	0	1.075010	1.454178	2.057218
6	1	0	2.368562	2.625205	1.968292
7	6	0	3.051121	0.591640	2.235681
8	1	0	4.078966	0.938676	2.088714
9	1	0	2.876595	0.603035	3.317539
10	6	0	2.997196	-0.860900	1.720432
11	1	0	3.500322	-1.517572	2.438282
12	1	0	3.556341	-0.950440	0.780774
13	6	0	1.584301	-3.285897	1.011592
14	6	0	1.104579	-3.860763	-0.165348
15	6	0	2.197948	-4.096220	1.971421
16	6	0	1.240275	-5.229045	-0.382408
17	1	0	0.634731	-3.232707	-0.916224

18	6	0	2.340853	-5.460511	1.751085
19	1	0	2.559740	-3.664464	2.901303
20	6	0	1.859966	-6.028025	0.571632
21	1	0	0.868173	-5.663200	-1.304599
22	1	0	2.823686	-6.082966	2.498885
23	1	0	1.972802	-7.094282	0.398239
24	6	0	0.359987	-1.497745	2.812580
25	6	0	0.932019	-1.442075	4.087808
26	6	0	-1.021422	-1.685747	2.700160
27	6	0	0.140355	-1.575090	5.226065
28	1	0	2.003307	-1.307922	4.202547
29	6	0	-1.812647	-1.828397	3.836334
30	1	0	-1.486505	-1.725988	1.717977
31	6	0	-1.233429	-1.773311	5.102119
32	1	0	0.599332	-1.531118	6.209510
33	1	0	-2.882069	-1.972355	3.718976
34	1	0	-1.849610	-1.885216	5.989365
35	6	0	3.400910	1.974510	-0.943304
36	6	0	4.440525	2.604614	-0.252624
37	6	0	3.553467	1.705670	-2.305928
38	6	0	5.616136	2.951138	-0.911687
39	1	0	4.341222	2.828218	0.805609
40	6	0	4.723142	2.063472	-2.966512
41	1	0	2.764055	1.190114	-2.844340
42	6	0	5.757045	2.682926	-2.270555
43	1	0	6.422863	3.429120	-0.363506
44	1	0	4.834859	1.833365	-4.020960
45	1	0	6.677125	2.946184	-2.783925
46	6	0	0.852462	3.095237	-0.486568
47	6	0	1.315525	4.346956	-0.068464
48	6	0	-0.338935	3.023594	-1.212604
49	6	0	0.584743	5.499669	-0.332005
50	1	0	2.259593	4.426283	0.463719
51	6	0	-1.069700	4.180668	-1.483131
52	1	0	-0.686056	2.057815	-1.575026
53	6	0	-0.617346	5.417248	-1.033553
54	1	0	0.956261	6.464214	0.002057
55	1	0	-1.986605	4.118129	-2.062310
56	1	0	-1.186489	6.317599	-1.245379
57	6	0	-0.870307	-0.512962	-1.639040
58	6	0	-1.645986	-0.631434	-2.583037
59	6	0	-2.570687	-0.782353	-3.664420
60	8	0	-3.315516	-1.722051	-3.857925
61	8	0	-2.521208	0.280691	-4.507367

62	6	0	-3.365089	0.181050	-5.644241
63	1	0	-4.406724	0.008724	-5.359065
64	1	0	-3.271124	1.132237	-6.171060
65	1	0	-3.048057	-0.635230	-6.300469
66	6	0	-5.205194	-0.409807	-0.815530
67	6	0	-4.256330	0.585727	-0.629360
68	6	0	-4.076190	1.560213	-1.600909
69	6	0	-4.873157	1.507650	-2.743176
70	6	0	-5.824660	0.501931	-2.910016
71	6	0	-6.002177	-0.485087	-1.939285
72	6	0	-3.581618	0.426405	0.688068
73	1	0	-3.328825	2.336454	-1.485919
74	1	0	-4.741297	2.253149	-3.520266
75	1	0	-6.431135	0.479755	-3.809580
76	1	0	-6.732625	-1.275902	-2.066952
77	16	0	-5.189438	-1.440111	0.638032
78	8	0	-4.715078	-2.781503	0.348601
79	8	0	-6.431626	-1.274966	1.381149
80	7	0	-3.971237	-0.570979	1.419585
81	6	0	-2.574019	1.369006	1.153959
82	1	0	-2.147776	2.050102	0.425229
83	6	0	-2.194129	1.391865	2.441629
84	1	0	-2.638178	0.658885	3.110484
85	6	0	-1.211804	2.293870	3.043977
86	6	0	-0.562281	1.874191	4.213385
87	6	0	-0.882121	3.538908	2.493500
88	6	0	0.417759	2.663674	4.801556
89	1	0	-0.815460	0.909817	4.643203
90	6	0	0.080091	4.337662	3.099410
91	1	0	-1.381331	3.889120	1.594720
92	6	0	0.738036	3.901085	4.247343
93	1	0	0.925986	2.314145	5.694915
94	1	0	0.321709	5.301884	2.664447
95	1	0	1.495058	4.526664	4.710706
96	53	0	3.721611	-2.029289	-2.229266

III



Sum of electronic and zero-point Energies= -4852.390121
Sum of electronic and thermal Energies= -4852.340477
Sum of electronic and thermal Enthalpies= -4852.339533
Sum of electronic and thermal Free Energies= -4852.475413

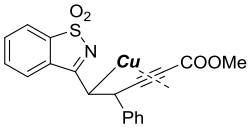
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.428575	0.077381	0.008363
2	15	0	-2.316937	0.566868	-1.092640
3	15	0	0.378619	2.125221	0.197534
4	6	0	0.291268	3.031858	-1.412048
5	1	0	1.294141	2.962398	-1.844612
6	1	0	0.110204	4.097467	-1.238978
7	6	0	-0.716773	2.459743	-2.421263
8	1	0	-0.764304	3.154503	-3.266670
9	1	0	-0.320762	1.518700	-2.825330
10	6	0	-2.135736	2.234839	-1.868983
11	1	0	-2.892423	2.370204	-2.647736
12	1	0	-2.375097	2.965024	-1.089752
13	6	0	-3.920280	0.733765	-0.238906
14	6	0	-3.988382	0.609385	1.148473
15	6	0	-5.081228	1.037588	-0.959244
16	6	0	-5.198906	0.804396	1.808675
17	1	0	-3.107531	0.338581	1.720037
18	6	0	-6.288222	1.228109	-0.299515
19	1	0	-5.044320	1.112622	-2.043089
20	6	0	-6.346466	1.115572	1.088832
21	1	0	-5.240556	0.699444	2.888129
22	1	0	-7.185148	1.459450	-0.865921
23	1	0	-7.290610	1.261804	1.604796
24	6	0	-2.690291	-0.539372	-2.498693
25	6	0	-2.700844	-0.140091	-3.836256
26	6	0	-2.958225	-1.877759	-2.183605
27	6	0	-2.976994	-1.061783	-4.844146
28	1	0	-2.480441	0.885790	-4.112055
29	6	0	-3.240778	-2.792615	-3.190308
30	1	0	-2.934215	-2.197292	-1.144273
31	6	0	-3.249510	-2.387576	-4.524519
32	1	0	-2.977660	-0.739955	-5.881185
33	1	0	-3.449121	-3.826552	-2.933854
34	1	0	-3.465345	-3.104605	-5.310495
35	6	0	-0.821179	2.914450	1.333831
36	6	0	-1.393197	4.173748	1.133863
37	6	0	-1.172158	2.187767	2.478972
38	6	0	-2.315605	4.682908	2.042666
39	1	0	-1.132276	4.768381	0.264317

40	6	0	-2.083668	2.704237	3.393433
41	1	0	-0.751704	1.200868	2.656059
42	6	0	-2.663645	3.948949	3.172856
43	1	0	-2.762974	5.656142	1.866996
44	1	0	-2.350566	2.119192	4.267620
45	1	0	-3.387677	4.345395	3.877701
46	6	0	2.003433	2.631822	0.869502
47	6	0	3.148057	2.318188	0.129648
48	6	0	2.154992	3.238228	2.119054
49	6	0	4.416128	2.599919	0.622693
50	1	0	3.049369	1.836925	-0.838200
51	6	0	3.425193	3.520504	2.613335
52	1	0	1.283277	3.489948	2.714090
53	6	0	4.557253	3.201683	1.869734
54	1	0	5.290206	2.330865	0.037680
55	1	0	3.528633	3.990651	3.586302
56	1	0	5.545811	3.414484	2.264118
57	6	0	3.987773	-0.922228	-0.374716
58	6	0	5.180460	-0.735793	-0.366229
59	6	0	6.603205	-0.497456	-0.327094
60	8	0	7.395292	-1.133533	0.328555
61	8	0	6.935529	0.532706	-1.122003
62	6	0	8.332981	0.838134	-1.168131
63	1	0	8.907040	-0.031817	-1.494518
64	1	0	8.431923	1.648177	-1.889658
65	1	0	8.692601	1.159916	-0.187870
66	6	0	-0.596068	-3.551878	2.465175
67	6	0	0.662726	-3.651452	1.891912
68	6	0	1.445596	-4.767460	2.182990
69	6	0	0.936481	-5.739853	3.036804
70	6	0	-0.334294	-5.613855	3.605625
71	6	0	-1.123731	-4.505345	3.320755
72	6	0	0.975709	-2.468933	1.045104
73	1	0	2.436742	-4.881569	1.757283
74	1	0	1.539427	-6.612026	3.268977
75	1	0	-0.705480	-6.384208	4.273366
76	1	0	-2.112120	-4.388162	3.752028
77	16	0	-1.355657	-2.061863	1.889672
78	8	0	-1.636279	-1.138439	2.997824
79	8	0	-2.518225	-2.384983	1.053506
80	7	0	-0.073740	-1.557015	1.010367
81	6	0	2.147370	-2.332919	0.396624
82	1	0	2.879582	-3.128303	0.461434
83	6	0	2.536628	-1.102732	-0.385425

84	1	0	2.131839	-0.235393	0.157525
85	6	0	1.973650	-0.997000	-1.814833
86	6	0	0.876506	-1.763627	-2.209435
87	6	0	2.509577	-0.076419	-2.720637
88	6	0	0.325220	-1.606652	-3.478603
89	1	0	0.455197	-2.493999	-1.527312
90	6	0	1.951438	0.087908	-3.984143
91	1	0	3.395701	0.490986	-2.451966
92	6	0	0.852444	-0.676730	-4.366885
93	1	0	-0.525810	-2.213884	-3.768107
94	1	0	2.385224	0.805826	-4.673802
95	1	0	0.411366	-0.553492	-5.351001

IV



Sum of electronic and zero-point Energies= -4852.387555
Sum of electronic and thermal Energies= -4852.337282
Sum of electronic and thermal Enthalpies= -4852.336338
Sum of electronic and thermal Free Energies= -4852.475239

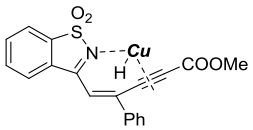
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.504092	-0.763554	2.270348
2	6	0	-0.463946	0.453318	2.408342
3	6	0	-0.515349	1.792405	2.960903
4	8	0	-1.541591	2.396886	3.176632
5	8	0	0.712444	2.266189	3.188429
6	6	0	0.783684	3.609910	3.680657
7	1	0	0.251575	3.697735	4.629980
8	1	0	1.844131	3.813440	3.821534
9	1	0	0.358458	4.304079	2.953156
10	6	0	3.089719	-2.955516	-0.671346
11	6	0	2.202941	-2.466196	0.279114
12	6	0	2.682575	-2.174985	1.555009
13	6	0	4.012655	-2.460449	1.853671
14	6	0	4.864668	-3.016744	0.900467
15	6	0	4.410805	-3.251876	-0.395023
16	6	0	0.838203	-2.312956	-0.326573
17	1	0	2.064967	-1.689749	2.301588
18	1	0	4.395510	-2.227374	2.841661
19	1	0	5.896170	-3.232935	1.158505
20	1	0	5.072071	-3.638771	-1.163001
21	16	0	2.251568	-2.955804	-2.245240

22	8	0	2.185594	-4.301377	-2.812786
23	8	0	2.868417	-1.930954	-3.101658
24	7	0	0.809704	-2.465647	-1.668830
25	6	0	-0.349257	-2.111346	0.370858
26	6	0	-0.552532	-2.187504	1.885574
27	6	0	-1.888027	-2.832407	2.219193
28	6	0	-1.927125	-4.084882	2.826238
29	6	0	-3.084690	-2.208235	1.859425
30	6	0	-3.147557	-4.708842	3.073011
31	1	0	-0.999677	-4.579921	3.100634
32	6	0	-4.301840	-2.832376	2.100781
33	1	0	-3.065969	-1.237385	1.371660
34	6	0	-4.336249	-4.084296	2.710859
35	1	0	-3.166358	-5.684741	3.547956
36	1	0	-5.223446	-2.341582	1.804907
37	1	0	-5.287408	-4.571283	2.901530
38	29	0	-0.226554	0.000267	0.265366
39	15	0	1.443295	1.269121	-0.530960
40	15	0	-1.851165	0.477332	-1.255923
41	6	0	1.472942	1.103037	-2.364500
42	1	0	2.284434	1.726853	-2.755393
43	1	0	1.710821	0.061123	-2.607300
44	6	0	-1.006974	0.507576	-2.895181
45	1	0	-0.619272	-0.507411	-3.041035
46	1	0	-1.754472	0.676760	-3.677299
47	6	0	0.152173	1.508820	-3.038584
48	1	0	-0.152827	2.508684	-2.706480
49	1	0	0.360095	1.597566	-4.109597
50	6	0	3.159123	0.966429	0.007205
51	6	0	3.502887	1.349974	1.309653
52	6	0	4.116728	0.352973	-0.801992
53	6	0	4.793651	1.154175	1.782204
54	1	0	2.753630	1.806700	1.950766
55	6	0	5.409424	0.155878	-0.320539
56	1	0	3.864227	0.004771	-1.798770
57	6	0	5.753143	0.562066	0.963488
58	1	0	5.051090	1.462408	2.791022
59	1	0	6.145752	-0.325847	-0.955929
60	1	0	6.762533	0.406605	1.331928
61	6	0	1.288320	3.083118	-0.320007
62	6	0	2.326463	3.949993	-0.679987
63	6	0	0.087871	3.624312	0.140990
64	6	0	2.159135	5.326229	-0.583240
65	1	0	3.273274	3.547016	-1.028635

66	6	0	-0.087204	5.003270	0.227314
67	1	0	-0.725307	2.970190	0.431141
68	6	0	0.949923	5.855956	-0.134582
69	1	0	2.973060	5.988170	-0.862169
70	1	0	-1.035105	5.400466	0.576598
71	1	0	0.821419	6.931752	-0.064830
72	6	0	-3.181881	-0.754231	-1.506498
73	6	0	-4.505752	-0.495349	-1.138315
74	6	0	-2.847057	-2.029851	-1.981637
75	6	0	-5.472697	-1.491372	-1.235711
76	1	0	-4.790247	0.487088	-0.775291
77	6	0	-3.817654	-3.021625	-2.074237
78	1	0	-1.825161	-2.270557	-2.264184
79	6	0	-5.130961	-2.758199	-1.698227
80	1	0	-6.497311	-1.273390	-0.949912
81	1	0	-3.539343	-4.005720	-2.437289
82	1	0	-5.884494	-3.536425	-1.766157
83	6	0	-2.728981	2.067757	-1.093692
84	6	0	-2.937835	2.961294	-2.146268
85	6	0	-3.162484	2.419628	0.190856
86	6	0	-3.550160	4.189959	-1.914502
87	1	0	-2.613820	2.713526	-3.152085
88	6	0	-3.789528	3.638775	0.419161
89	1	0	-2.985238	1.746016	1.025704
90	6	0	-3.977439	4.530219	-0.634510
91	1	0	-3.692713	4.883774	-2.737007
92	1	0	-4.113281	3.895659	1.422563
93	1	0	-4.450256	5.491154	-0.457026
94	1	0	0.242787	-2.734589	2.399829
95	1	0	-1.246699	-2.347642	-0.185929

V



Sum of electronic and zero-point Energies= -4853.089593
Sum of electronic and thermal Energies= -4852.337738
Sum of electronic and thermal Enthalpies= -4852.286696
Sum of electronic and thermal Free Energies= -4852.423509

Standard orientation:

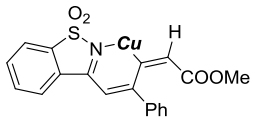
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.587594	-1.080250	-2.497883
2	6	0	0.881075	-0.422856	-3.228865
3	6	0	-0.041419	0.477785	-3.884325

4	8	0	0.270975	1.535363	-4.383537
5	8	0	-1.289652	0.000207	-3.830385
6	6	0	-2.304136	0.880716	-4.322796
7	1	0	-2.124987	1.129667	-5.371153
8	1	0	-3.241329	0.334572	-4.222386
9	1	0	-2.337770	1.798038	-3.729188
10	6	0	-1.770097	-3.194762	0.369094
11	6	0	-0.816113	-2.816394	-0.572710
12	6	0	-1.040110	-3.120496	-1.911021
13	6	0	-2.223772	-3.763224	-2.263626
14	6	0	-3.178517	-4.107899	-1.306151
15	6	0	-2.953003	-3.830373	0.038856
16	6	0	0.323371	-2.079708	0.070526
17	1	0	-0.321028	-2.837532	-2.669013
18	1	0	-2.409173	-3.990097	-3.308779
19	1	0	-4.099144	-4.595402	-1.608802
20	1	0	-3.679427	-4.093849	0.799556
21	16	0	-1.160684	-2.795637	1.989899
22	8	0	-0.715873	-4.017602	2.653587
23	8	0	-2.067296	-1.930433	2.745308
24	7	0	0.154992	-1.938534	1.445733
25	6	0	1.733744	-2.175897	-0.358014
26	6	0	2.338148	-1.746853	-1.490203
27	6	0	3.817503	-1.777532	-1.647249
28	6	0	4.652833	-1.555194	-0.546753
29	6	0	4.393519	-1.984719	-2.904227
30	6	0	6.033759	-1.568024	-0.698462
31	1	0	4.221969	-1.342569	0.426373
32	6	0	5.775772	-1.997479	-3.052939
33	1	0	3.753638	-2.140707	-3.768113
34	6	0	6.600597	-1.792583	-1.950030
35	1	0	6.664501	-1.383240	0.165632
36	1	0	6.210203	-2.165491	-4.033398
37	1	0	7.679582	-1.797579	-2.068883
38	29	0	-0.205687	-0.265485	0.470069
39	15	0	-2.137131	0.802879	0.950365
40	15	0	1.186116	1.233725	1.584302
41	6	0	-2.189313	1.343492	2.706243
42	1	0	-3.149128	1.823439	2.926479
43	1	0	-2.122041	0.432486	3.308912
44	6	0	0.370621	1.730076	3.167147
45	1	0	0.342563	0.808689	3.761021
46	1	0	1.017185	2.428493	3.709713
47	6	0	-1.049169	2.319030	3.057337

48	1	0	-1.055904	3.158407	2.352523
49	1	0	-1.287122	2.748537	4.035933
50	6	0	-3.672510	-0.106100	0.586256
51	6	0	-3.900182	-0.419153	-0.758765
52	6	0	-4.577673	-0.537097	1.554374
53	6	0	-5.029727	-1.135278	-1.130542
54	1	0	-3.178642	-0.111263	-1.511438
55	6	0	-5.706834	-1.261238	1.178319
56	1	0	-4.399938	-0.330622	2.603872
57	6	0	-5.937681	-1.556708	-0.161199
58	1	0	-5.195375	-1.376073	-2.175983
59	1	0	-6.406679	-1.596336	1.937475
60	1	0	-6.819678	-2.120568	-0.449146
61	6	0	-2.388614	2.363247	0.022964
62	6	0	-3.475355	3.195434	0.317739
63	6	0	-1.493585	2.748070	-0.976390
64	6	0	-3.651079	4.393663	-0.362552
65	1	0	-4.197231	2.901443	1.074934
66	6	0	-1.667066	3.951252	-1.657631
67	1	0	-0.656654	2.104244	-1.221554
68	6	0	-2.743145	4.775719	-1.349169
69	1	0	-4.497544	5.030511	-0.124805
70	1	0	-0.953129	4.236882	-2.423375
71	1	0	-2.878739	5.715260	-1.876068
72	6	0	2.815226	0.624218	2.144955
73	6	0	4.013093	1.296558	1.892265
74	6	0	2.847220	-0.604700	2.817573
75	6	0	5.224150	0.752806	2.312961
76	1	0	4.006142	2.243474	1.361829
77	6	0	4.058146	-1.138611	3.244610
78	1	0	1.924543	-1.155702	2.974818
79	6	0	5.249711	-0.461394	2.992624
80	1	0	6.149874	1.281296	2.107388
81	1	0	4.070567	-2.091795	3.763575
82	1	0	6.194779	-0.882756	3.321194
83	6	0	1.543329	2.764239	0.663198
84	6	0	1.412213	4.049620	1.191960
85	6	0	1.921272	2.614351	-0.677688
86	6	0	1.633789	5.165595	0.388772
87	1	0	1.130326	4.192929	2.230325
88	6	0	2.157195	3.727978	-1.474004
89	1	0	2.009921	1.618908	-1.105916
90	6	0	2.004049	5.006930	-0.942548
91	1	0	1.515262	6.160088	0.807218

92	1	0	2.438720	3.593785	-2.513294
93	1	0	2.172575	5.878955	-1.566714
94	1	0	2.379312	-2.579337	0.418349
95	1	0	-0.213038	0.042903	-0.981617

VI



Sum of electronic and zero-point Energies= -4853.198050
Sum of electronic and thermal Energies= -4852.441425
Sum of electronic and thermal Enthalpies= -4852.390858
Sum of electronic and thermal Free Energies= -4852.528018

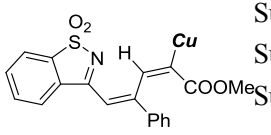
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.093696	1.150290	1.674931
2	6	0	0.596864	2.295215	2.107567
3	6	0	0.462335	2.764216	3.506249
4	8	0	0.927855	3.809217	3.908858
5	8	0	-0.214714	1.907825	4.287810
6	6	0	-0.362167	2.304158	5.648252
7	1	0	-0.912993	3.244867	5.724919
8	1	0	-0.920157	1.502102	6.130999
9	1	0	0.612124	2.423445	6.129563
10	6	0	-4.387944	1.107163	-0.838762
11	6	0	-4.122525	0.547793	0.405753
12	6	0	-5.183732	0.102978	1.190252
13	6	0	-6.478721	0.232141	0.698044
14	6	0	-6.723464	0.797407	-0.556525
15	6	0	-5.668693	1.246247	-1.346368
16	6	0	-2.666467	0.492987	0.660860
17	1	0	-5.008016	-0.341984	2.164086
18	1	0	-7.314170	-0.112790	1.299028
19	1	0	-7.742748	0.888849	-0.917211
20	1	0	-5.841647	1.688821	-2.321549
21	16	0	-2.837916	1.551835	-1.596941
22	8	0	-2.727588	3.007208	-1.738638
23	8	0	-2.644723	0.797506	-2.848514
24	7	0	-1.919537	0.964954	-0.401289
25	6	0	-2.070273	-0.022352	1.759887
26	1	0	-2.653352	-0.478465	2.551442
27	6	0	-0.599436	-0.008910	1.911711
28	6	0	0.078716	-1.163513	2.566085
29	6	0	-0.488147	-2.438133	2.483442

30	6	0	1.296798	-1.008573	3.237716
31	6	0	0.163267	-3.538690	3.028354
32	1	0	-1.431498	-2.567041	1.963312
33	6	0	1.946964	-2.109729	3.782095
34	1	0	1.734160	-0.020149	3.330945
35	6	0	1.387615	-3.381081	3.671347
36	1	0	-0.285350	-4.523417	2.939236
37	1	0	2.893853	-1.974268	4.296025
38	1	0	1.898918	-4.241635	4.091074
39	29	0	0.041109	0.323027	-0.093613
40	15	0	0.036952	-1.647512	-1.223962
41	15	0	1.643568	1.281164	-1.325988
42	6	0	-0.017687	-1.249388	-3.022798
43	1	0	-0.167759	-2.174176	-3.588703
44	1	0	-0.908806	-0.628789	-3.170027
45	6	0	1.387633	0.948747	-3.120782
46	1	0	0.476433	1.503759	-3.373984
47	1	0	2.202472	1.413689	-3.686709
48	6	0	1.230392	-0.520923	-3.541422
49	1	0	2.128049	-1.091046	-3.277900
50	1	0	1.177259	-0.529016	-4.635217
51	6	0	-1.390923	-2.752211	-0.975640
52	6	0	-1.267395	-4.004082	-0.367507
53	6	0	-2.662281	-2.274630	-1.312978
54	6	0	-2.402294	-4.760311	-0.087182
55	1	0	-0.287428	-4.384458	-0.097123
56	6	0	-3.792587	-3.031202	-1.026022
57	1	0	-2.771623	-1.311368	-1.801150
58	6	0	-3.665911	-4.272474	-0.407578
59	1	0	-2.296201	-5.730891	0.387855
60	1	0	-4.773473	-2.641911	-1.280645
61	1	0	-4.550290	-4.859111	-0.178546
62	6	0	1.510433	-2.706047	-1.034424
63	6	0	1.882884	-3.651475	-1.997698
64	6	0	2.304170	-2.552792	0.104213
65	6	0	3.034819	-4.410981	-1.829797
66	1	0	1.275929	-3.796678	-2.886568
67	6	0	3.453313	-3.317873	0.276251
68	1	0	2.028802	-1.831220	0.864901
69	6	0	3.823330	-4.242824	-0.693068
70	1	0	3.318337	-5.135769	-2.586398
71	1	0	4.056993	-3.179242	1.167031
72	1	0	4.725624	-4.833074	-0.566210
73	6	0	1.804498	3.094942	-1.273127

74	6	0	3.038801	3.747648	-1.238316
75	6	0	0.622217	3.844239	-1.266551
76	6	0	3.090144	5.137670	-1.198682
77	1	0	3.960696	3.173576	-1.232590
78	6	0	0.680957	5.233008	-1.237354
79	1	0	-0.346966	3.350807	-1.271619
80	6	0	1.912923	5.880491	-1.199968
81	1	0	4.051746	5.639987	-1.162634
82	1	0	-0.241691	5.804123	-1.231328
83	1	0	1.956252	6.964662	-1.163440
84	6	0	3.292175	0.633696	-0.893020
85	6	0	4.215452	0.158235	-1.825706
86	6	0	3.614544	0.580582	0.468991
87	6	0	5.425670	-0.386091	-1.402840
88	1	0	4.000583	0.204684	-2.888200
89	6	0	4.828359	0.053668	0.888780
90	1	0	2.902013	0.945489	1.203713
91	6	0	5.732806	-0.441470	-0.047883
92	1	0	6.129593	-0.765231	-2.136759
93	1	0	5.062017	0.017445	1.948235
94	1	0	6.675344	-0.869228	0.279025
95	1	0	1.137011	2.977381	1.458408

VII



Sum of electronic and zero-point Energies= -4853.198543
Sum of electronic and thermal Energies= -4852.441277
Sum of electronic and thermal Enthalpies= -4852.390927
Sum of electronic and thermal Free Energies= -4852.525875

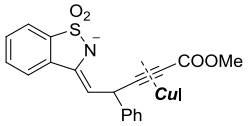
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.694063	0.408526	1.742799
2	6	0	-0.604605	0.409950	2.147651
3	6	0	-1.155902	-0.661621	3.016374
4	8	0	-2.242405	-0.602326	3.558259
5	8	0	-0.330670	-1.706710	3.143167
6	6	0	-0.841607	-2.816974	3.879783
7	1	0	-1.775956	-3.174398	3.440706
8	1	0	-0.075255	-3.588240	3.813673
9	1	0	-1.013809	-2.546861	4.924568
10	6	0	2.852101	-2.756979	-1.684096
11	6	0	3.489081	-1.808225	-0.899213

12	6	0	4.870457	-1.659898	-1.010383
13	6	0	5.560968	-2.469527	-1.905732
14	6	0	4.896811	-3.424529	-2.681607
15	6	0	3.519090	-3.583481	-2.573670
16	6	0	2.522648	-1.071866	-0.048525
17	1	0	5.400452	-0.916913	-0.424383
18	1	0	6.635594	-2.355464	-2.006639
19	1	0	5.459785	-4.044490	-3.371411
20	1	0	2.986066	-4.319331	-3.166286
21	16	0	1.120103	-2.711523	-1.308006
22	8	0	0.728197	-3.928020	-0.592527
23	8	0	0.337232	-2.413098	-2.515687
24	7	0	1.207995	-1.399238	-0.326811
25	6	0	2.916469	-0.183437	0.895807
26	1	0	3.975895	-0.002372	1.022457
27	6	0	2.017606	0.415462	1.863657
28	6	0	2.610735	1.037176	3.086362
29	6	0	3.713598	1.889199	2.973886
30	6	0	2.071245	0.793085	4.351684
31	6	0	4.259423	2.489308	4.103790
32	1	0	4.133495	2.095571	1.993458
33	6	0	2.619997	1.390809	5.480287
34	1	0	1.230739	0.113675	4.448858
35	6	0	3.714336	2.243273	5.360674
36	1	0	5.110054	3.156310	4.000897
37	1	0	2.192255	1.187186	6.457140
38	1	0	4.141920	2.710361	6.242333
39	29	0	-0.334551	-0.161513	0.179995
40	15	0	0.106922	1.440068	-1.482055
41	15	0	-2.402960	-0.682497	-0.617898
42	6	0	-0.370154	0.707805	-3.103330
43	1	0	-0.050405	1.377690	-3.909013
44	1	0	0.169677	-0.238612	-3.203973
45	6	0	-2.423346	-0.778083	-2.457990
46	1	0	-1.814709	-1.655999	-2.694218
47	1	0	-3.446482	-0.994364	-2.785218
48	6	0	-1.878442	0.443032	-3.223159
49	1	0	-2.427473	1.352991	-2.958588
50	1	0	-2.089517	0.262601	-4.282471
51	6	0	1.869351	1.860928	-1.659735
52	6	0	2.414874	2.821542	-0.799982
53	6	0	2.716925	1.148669	-2.510547
54	6	0	3.782871	3.062786	-0.792932
55	1	0	1.767845	3.376675	-0.126679

56	6	0	4.088377	1.388538	-2.497261
57	1	0	2.321447	0.386499	-3.173952
58	6	0	4.624738	2.340137	-1.636711
59	1	0	4.192631	3.812826	-0.123111
60	1	0	4.737012	0.816865	-3.153307
61	1	0	5.694835	2.523354	-1.625560
62	6	0	-0.739682	3.058511	-1.474092
63	6	0	-0.479086	4.042788	-2.435183
64	6	0	-1.706491	3.303653	-0.497242
65	6	0	-1.181169	5.241466	-2.420555
66	1	0	0.283675	3.873662	-3.190693
67	6	0	-2.414692	4.502809	-0.484402
68	1	0	-1.920300	2.549928	0.253181
69	6	0	-2.153101	5.470789	-1.446702
70	1	0	-0.971369	5.999791	-3.168396
71	1	0	-3.170205	4.670565	0.276201
72	1	0	-2.701035	6.407994	-1.439330
73	6	0	-3.114886	-2.272952	-0.079852
74	6	0	-4.475623	-2.561761	-0.226263
75	6	0	-2.265954	-3.226093	0.485435
76	6	0	-4.977549	-3.790029	0.185792
77	1	0	-5.148139	-1.819050	-0.646760
78	6	0	-2.770204	-4.459835	0.889010
79	1	0	-1.206347	-3.020329	0.600477
80	6	0	-4.124099	-4.740905	0.742829
81	1	0	-6.035582	-4.005290	0.073791
82	1	0	-2.096842	-5.198054	1.312594
83	1	0	-4.518418	-5.700169	1.063998
84	6	0	-3.719069	0.524095	-0.200244
85	6	0	-4.485159	1.190382	-1.160504
86	6	0	-3.949798	0.802199	1.152976
87	6	0	-5.427953	2.142627	-0.781196
88	1	0	-4.357214	0.982225	-2.215975
89	6	0	-4.894751	1.749039	1.530105
90	1	0	-3.400997	0.273211	1.926224
91	6	0	-5.629427	2.431489	0.563264
92	1	0	-6.004089	2.657862	-1.543310
93	1	0	-5.057542	1.948522	2.584592
94	1	0	-6.362161	3.176064	0.858242
95	1	0	-1.221505	1.304849	2.099049

VIII



Sum of electronic and zero-point Energies= -4863.925739
Sum of electronic and thermal Energies= -4863.873429
Sum of electronic and thermal Enthalpies= -4863.872485
Sum of electronic and thermal Free Energies= -4864.018595

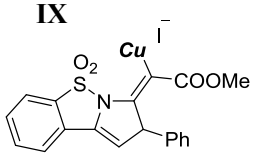
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.663007	-1.190876	-1.400892
2	6	0	0.424637	-1.773875	-1.563448
3	6	0	1.256846	-2.873502	-2.030089
4	8	0	0.849799	-3.754786	-2.753883
5	8	0	2.502296	-2.801102	-1.558834
6	6	0	3.360032	-3.873531	-1.933128
7	1	0	3.477429	-3.911733	-3.019047
8	1	0	4.319666	-3.663252	-1.462168
9	1	0	2.965188	-4.827677	-1.574851
10	6	0	-4.186648	0.372199	2.575781
11	6	0	-3.877192	-0.034419	1.281801
12	6	0	-4.596708	0.511632	0.218643
13	6	0	-5.566174	1.476678	0.484044
14	6	0	-5.827734	1.901517	1.787075
15	6	0	-5.137930	1.336750	2.858473
16	6	0	-2.855056	-1.131267	1.311782
17	1	0	-4.439512	0.185762	-0.803218
18	1	0	-6.127174	1.901226	-0.342736
19	1	0	-6.587991	2.655320	1.968509
20	1	0	-5.353142	1.624288	3.882697
21	16	0	-3.235430	-0.633408	3.706159
22	8	0	-4.144747	-1.357889	4.602624
23	8	0	-2.249918	0.221034	4.393604
24	7	0	-2.559187	-1.565943	2.584025
25	6	0	-2.265851	-1.693399	0.225023
26	6	0	-2.124635	-1.098785	-1.157973
27	6	0	-2.913484	-1.756584	-2.286896
28	6	0	-4.086127	-2.456665	-2.008623
29	6	0	-2.510569	-1.601113	-3.615010
30	6	0	-4.848642	-2.992957	-3.043741
31	1	0	-4.386720	-2.586956	-0.972703
32	6	0	-3.269865	-2.138853	-4.648293
33	1	0	-1.588263	-1.070292	-3.836498
34	6	0	-4.443576	-2.835021	-4.365742
35	1	0	-5.758897	-3.539379	-2.813890

36	1	0	-2.940903	-2.017962	-5.676205
37	1	0	-5.034760	-3.257717	-5.172944
38	29	0	0.819871	-0.124871	-0.570976
39	15	0	-0.039665	1.855771	0.074208
40	15	0	1.825287	-0.761892	1.378734
41	6	0	-0.620408	1.822964	1.819072
42	1	0	-0.904143	2.838170	2.115972
43	1	0	-1.518681	1.201560	1.865376
44	6	0	0.679802	-0.227381	2.718059
45	1	0	-0.278378	-0.736842	2.555227
46	1	0	1.051837	-0.607732	3.674630
47	6	0	0.421583	1.283520	2.809623
48	1	0	1.356258	1.852958	2.728463
49	1	0	0.016656	1.469854	3.807257
50	6	0	-1.450511	2.460784	-0.907645
51	6	0	-1.391782	2.264950	-2.294230
52	6	0	-2.555041	3.112397	-0.355557
53	6	0	-2.423856	2.711145	-3.110509
54	1	0	-0.533960	1.759742	-2.732195
55	6	0	-3.580597	3.571686	-1.179205
56	1	0	-2.635856	3.254482	0.717408
57	6	0	-3.519170	3.369027	-2.553510
58	1	0	-2.370225	2.544993	-4.181697
59	1	0	-4.436451	4.072110	-0.737299
60	1	0	-4.325322	3.718119	-3.191945
61	6	0	1.115648	3.274770	0.089318
62	6	0	0.673054	4.592780	-0.057056
63	6	0	2.471590	3.036610	0.321610
64	6	0	1.573120	5.649714	0.033153
65	1	0	-0.375513	4.797068	-0.252462
66	6	0	3.369641	4.093533	0.423941
67	1	0	2.838408	2.021195	0.407655
68	6	0	2.922056	5.402425	0.277055
69	1	0	1.219298	6.668774	-0.092116
70	1	0	4.419727	3.884767	0.602614
71	1	0	3.623948	6.228532	0.343209
72	6	0	1.927493	-2.567374	1.643006
73	6	0	0.760140	-3.292590	1.908229
74	6	0	3.135892	-3.253074	1.492753
75	6	0	0.806892	-4.680544	2.009891
76	1	0	-0.192279	-2.790300	2.056338
77	6	0	3.178161	-4.639128	1.599898
78	1	0	4.050625	-2.704717	1.288903
79	6	0	2.012129	-5.357775	1.852703

80	1	0	-0.107846	-5.227225	2.216558
81	1	0	4.125518	-5.157571	1.483248
82	1	0	2.044683	-6.440257	1.933298
83	6	0	3.473626	-0.132124	1.842548
84	6	0	3.821670	0.216926	3.151033
85	6	0	4.418539	0.023365	0.821082
86	6	0	5.087568	0.721912	3.430509
87	1	0	3.104098	0.106580	3.957928
88	6	0	5.688089	0.519044	1.104628
89	1	0	4.150180	-0.212325	-0.205938
90	6	0	6.022348	0.872772	2.409023
91	1	0	5.342740	0.998641	4.449038
92	1	0	6.407178	0.641416	0.300796
93	1	0	7.007933	1.272438	2.628800
94	1	0	-2.399555	-0.039550	-1.136387
95	1	0	-1.651623	-2.569862	0.405498
96	53	0	2.690020	0.896697	-2.852925

IX



Sum of electronic and zero-point Energies= --4863.944106
Sum of electronic and thermal Energies= -4863.892684
Sum of electronic and thermal Enthalpies= -4863.891739
Sum of electronic and thermal Free Energies= -4864.034404

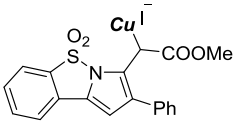
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	1.014400	-0.208523	0.075250
2	15	0	2.499397	1.170295	0.990354
3	15	0	2.427926	-1.658242	-0.856598
4	6	0	4.022890	-0.806928	-1.221663
5	1	0	3.752107	0.084048	-1.801928
6	1	0	4.676992	-1.425040	-1.846983
7	6	0	4.822439	-0.414680	0.034130
8	1	0	5.288916	-1.322168	0.432632
9	1	0	5.649759	0.216018	-0.307428
10	6	0	4.112842	0.282591	1.221046
11	1	0	4.818848	0.953586	1.722568
12	1	0	3.843357	-0.472888	1.966440
13	6	0	2.171585	1.605320	2.736943
14	6	0	1.261043	0.819911	3.450850
15	6	0	2.832858	2.653282	3.385852
16	6	0	1.027022	1.074715	4.799884

17	1	0	0.713967	0.019520	2.956115
18	6	0	2.588569	2.911271	4.729932
19	1	0	3.526191	3.280898	2.832341
20	6	0	1.687562	2.118975	5.439552
21	1	0	0.312708	0.461941	5.340616
22	1	0	3.095112	3.736090	5.222469
23	1	0	1.493346	2.324060	6.488254
24	6	0	2.908055	2.756747	0.196264
25	6	0	4.102191	2.967308	-0.498918
26	6	0	1.938613	3.768009	0.201993
27	6	0	4.317723	4.161118	-1.184430
28	1	0	4.872754	2.203672	-0.512433
29	6	0	2.151970	4.956003	-0.485958
30	1	0	0.999802	3.629359	0.733101
31	6	0	3.342524	5.153653	-1.182832
32	1	0	5.250557	4.312253	-1.720091
33	1	0	1.373126	5.711220	-0.488642
34	1	0	3.505728	6.080080	-1.725002
35	6	0	2.950514	-3.034217	0.233511
36	6	0	3.615865	-4.162863	-0.256692
37	6	0	2.705673	-2.936035	1.606510
38	6	0	4.036458	-5.166202	0.609768
39	1	0	3.793270	-4.264417	-1.324111
40	6	0	3.133467	-3.936792	2.475640
41	1	0	2.154120	-2.089515	2.005714
42	6	0	3.799966	-5.052221	1.978608
43	1	0	4.545189	-6.040974	0.215723
44	1	0	2.927429	-3.845760	3.537383
45	1	0	4.126722	-5.836448	2.654935
46	6	0	1.952694	-2.503023	-2.397863
47	6	0	2.664104	-2.432337	-3.596181
48	6	0	0.744347	-3.211719	-2.359521
49	6	0	2.179820	-3.063872	-4.740672
50	1	0	3.592152	-1.872759	-3.656890
51	6	0	0.271799	-3.851928	-3.498023
52	1	0	0.166612	-3.236346	-1.437740
53	6	0	0.986966	-3.778026	-4.692948
54	1	0	2.735689	-2.993277	-5.671027
55	1	0	-0.667718	-4.394504	-3.456386
56	1	0	0.608807	-4.267225	-5.585709
57	6	0	-1.855601	-0.468734	0.210514
58	6	0	-0.699256	-0.932893	0.672767
59	6	0	-0.614578	-2.151691	1.472009
60	8	0	-0.420291	-2.224240	2.674539

61	8	0	-0.649830	-3.267609	0.696865
62	6	0	-0.534836	-4.503367	1.387834
63	1	0	-1.377869	-4.641306	2.068812
64	1	0	-0.547109	-5.276373	0.617438
65	1	0	0.401406	-4.558413	1.950127
66	6	0	-5.543370	-1.588455	0.761226
67	6	0	-5.450498	-0.679012	-0.290777
68	6	0	-6.604123	-0.312949	-0.980353
69	6	0	-7.816764	-0.875836	-0.596682
70	6	0	-7.889553	-1.791512	0.456929
71	6	0	-6.743074	-2.158521	1.156047
72	6	0	-4.073347	-0.241289	-0.483481
73	1	0	-6.552172	0.397343	-1.798663
74	1	0	-8.723088	-0.600415	-1.126706
75	1	0	-8.847258	-2.220150	0.733307
76	1	0	-6.785895	-2.866899	1.976631
77	16	0	-3.960137	-1.847683	1.537586
78	8	0	-3.600269	-3.259638	1.528041
79	8	0	-3.893125	-1.145955	2.812802
80	7	0	-3.184852	-1.021615	0.303231
81	6	0	-3.439112	0.737775	-1.129576
82	1	0	-3.888420	1.476448	-1.778554
83	6	0	-1.993402	0.760407	-0.703438
84	1	0	-1.826556	1.680576	-0.125169
85	6	0	-0.958778	0.730951	-1.807228
86	6	0	0.138310	1.590562	-1.739319
87	6	0	-1.041282	-0.175049	-2.868550
88	6	0	1.142058	1.547483	-2.710615
89	1	0	0.159220	2.357032	-0.973795
90	6	0	-0.050151	-0.213502	-3.840352
91	1	0	-1.881920	-0.861671	-2.920713
92	6	0	1.050048	0.641467	-3.760676
93	1	0	1.975520	2.241685	-2.642911
94	1	0	-0.118969	-0.932009	-4.651760
95	1	0	1.825110	0.600565	-4.520440
96	53	0	-2.004608	5.032999	-0.738461

X



Sum of electronic and zero-point Energies= -4863.990024
Sum of electronic and thermal Energies= -4863.938686
Sum of electronic and thermal Enthalpies= -4863.937742
Sum of electronic and thermal Free Energies= -4864.079341

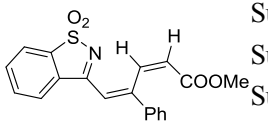
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.004209	-0.016663	0.478460
2	15	0	-1.329857	-1.499667	1.488431
3	15	0	-1.413169	1.722767	0.458025
4	6	0	-3.114017	1.037529	0.331700
5	1	0	-3.093605	0.327744	-0.502205
6	1	0	-3.839426	1.807789	0.056861
7	6	0	-3.633941	0.345461	1.598560
8	1	0	-3.956064	1.113942	2.309835
9	1	0	-4.542680	-0.188384	1.304938
10	6	0	-2.693075	-0.601745	2.368209
11	1	0	-3.285454	-1.318525	2.946820
12	1	0	-2.119783	-0.017325	3.099073
13	6	0	-0.595133	-2.312915	2.960190
14	6	0	0.486571	-1.690827	3.592835
15	6	0	-1.130084	-3.479677	3.518606
16	6	0	1.027060	-2.234892	4.756114
17	1	0	0.924876	-0.780246	3.189024
18	6	0	-0.584719	-4.022959	4.676797
19	1	0	-1.974136	-3.970504	3.042560
20	6	0	0.497383	-3.401695	5.297260
21	1	0	1.872086	-1.743750	5.228887
22	1	0	-1.007251	-4.931113	5.096834
23	1	0	0.925955	-3.828478	6.199434
24	6	0	-2.081432	-2.862896	0.544255
25	6	0	-3.346723	-2.740574	-0.033548
26	6	0	-1.329219	-4.017711	0.291914
27	6	0	-3.860855	-3.758458	-0.832812
28	1	0	-3.942906	-1.845222	0.102888
29	6	0	-1.852837	-5.043060	-0.486564
30	1	0	-0.333215	-4.117270	0.714913
31	6	0	-3.121702	-4.916146	-1.051476
32	1	0	-4.837164	-3.626764	-1.288635
33	1	0	-1.264430	-5.938874	-0.663010
34	1	0	-3.525516	-5.712496	-1.669706
35	6	0	-1.514946	2.800922	1.934457
36	6	0	-2.496385	3.793865	2.041549
37	6	0	-0.611744	2.619131	2.984011
38	6	0	-2.575892	4.585703	3.180960
39	1	0	-3.199030	3.951911	1.227232

40	6	0	-0.689835	3.418057	4.124422
41	1	0	0.175353	1.872599	2.912641
42	6	0	-1.671006	4.397814	4.225661
43	1	0	-3.342097	5.351755	3.253375
44	1	0	0.024716	3.270332	4.928486
45	1	0	-1.732531	5.018224	5.115103
46	6	0	-1.305192	2.927475	-0.913797
47	6	0	-2.332866	3.183666	-1.824871
48	6	0	-0.079544	3.589555	-1.064659
49	6	0	-2.137985	4.094787	-2.862322
50	1	0	-3.285371	2.667181	-1.754942
51	6	0	0.107502	4.505456	-2.092058
52	1	0	0.738272	3.355254	-0.387933
53	6	0	-0.924399	4.760694	-2.994303
54	1	0	-2.940892	4.274796	-3.570523
55	1	0	1.063981	5.008481	-2.198333
56	1	0	-0.777478	5.469322	-3.804001
57	6	0	2.722492	-0.362207	-0.632244
58	6	0	2.011699	-0.194770	0.648630
59	6	0	2.268057	0.998017	1.431646
60	8	0	2.211771	1.077592	2.658819
61	8	0	2.541124	2.099836	0.680078
62	6	0	2.819829	3.283014	1.410203
63	1	0	3.625437	3.122090	2.130074
64	1	0	3.130241	4.023260	0.670601
65	1	0	1.931553	3.641084	1.941753
66	6	0	6.573202	-0.278619	-0.995099
67	6	0	5.940963	-0.597684	-2.201382
68	6	0	6.730732	-0.842469	-3.323400
69	6	0	8.115341	-0.756719	-3.204053
70	6	0	8.723689	-0.430257	-1.990745
71	6	0	7.946447	-0.182742	-0.860358
72	6	0	4.497168	-0.625506	-2.056200
73	1	0	6.269204	-1.089821	-4.273390
74	1	0	8.733866	-0.946107	-4.075875
75	1	0	9.804461	-0.366729	-1.924180
76	1	0	8.402809	0.071456	0.090662
77	16	0	5.388534	-0.018349	0.310587
78	8	0	5.440017	1.352608	0.783941
79	8	0	5.407171	-1.097567	1.282840
80	7	0	4.101512	-0.255702	-0.778718
81	6	0	3.366517	-0.960490	-2.751460
82	1	0	3.315324	-1.281782	-3.782513
83	6	0	2.259367	-0.789091	-1.864710

84	1	0	2.157791	-1.073886	1.281697
85	6	0	0.838057	-1.034698	-2.186196
86	6	0	0.375203	-2.327907	-2.452764
87	6	0	-0.063862	0.034537	-2.266823
88	6	0	-0.957239	-2.549735	-2.783156
89	1	0	1.069705	-3.161084	-2.389639
90	6	0	-1.400727	-0.193753	-2.594702
91	1	0	0.306940	1.047917	-2.147302
92	6	0	-1.852921	-1.485077	-2.843791
93	1	0	-1.306122	-3.559593	-2.972438
94	1	0	-2.092125	0.639398	-2.671665
95	1	0	-2.899962	-1.651429	-3.076397
96	53	0	-5.848562	-0.135983	-2.189696

XI



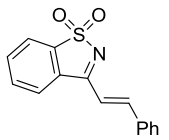
Sum of electronic and zero-point Energies= -1486.453909
Sum of electronic and thermal Energies= -1486.146645
Sum of electronic and thermal Enthalpies= -1486.124475
Sum of electronic and thermal Free Energies= -1486.198026

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.672240	-1.051334	-1.459524
2	6	0	1.261122	-2.300367	-1.234044
3	6	0	0.674842	-2.851999	0.012207
4	8	0	0.003136	-3.858487	0.023270
5	8	0	0.992103	-2.150845	1.105830
6	6	0	0.279816	-2.520054	2.286065
7	1	0	0.495744	-3.553600	2.566358
8	1	0	0.624469	-1.839553	3.064717
9	1	0	-0.795519	-2.402970	2.128940
10	6	0	-3.066118	0.939512	-0.053970
11	6	0	-1.794355	1.489226	0.031810
12	6	0	-1.648342	2.858829	0.214733
13	6	0	-2.800010	3.638676	0.317786
14	6	0	-4.068183	3.065726	0.232628
15	6	0	-4.219900	1.691777	0.039844
16	6	0	-0.751354	0.427901	-0.123050
17	1	0	-0.669117	3.321624	0.270316
18	1	0	-2.705796	4.709478	0.463106
19	1	0	-4.948423	3.694470	0.313400
20	1	0	-5.201259	1.237014	-0.035391

21	16	0	-2.875671	-0.815118	-0.308969
22	8	0	-3.351821	-1.203109	-1.625342
23	8	0	-3.316385	-1.555160	0.862624
24	7	0	-1.183165	-0.777429	-0.307571
25	6	0	0.658524	0.766712	-0.026109
26	1	0	0.866485	1.689402	0.507496
27	6	0	1.718923	0.112414	-0.547854
28	6	0	3.082683	0.646137	-0.274841
29	6	0	3.423586	1.013547	1.032430
30	6	0	4.043377	0.778918	-1.284526
31	6	0	4.687171	1.515706	1.320265
32	1	0	2.699631	0.875855	1.829456
33	6	0	5.302971	1.290330	-0.995329
34	1	0	3.807099	0.506771	-2.308158
35	6	0	5.629620	1.659068	0.306780
36	1	0	4.937670	1.784631	2.341521
37	1	0	6.033342	1.399206	-1.790700
38	1	0	6.616567	2.051284	0.530157
39	1	0	2.089045	-0.850596	-2.445435
40	1	0	1.307013	-3.022657	-2.042148

1a



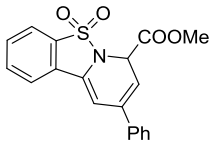
Sum of electronic and zero-point Energies= -1181.046390
Sum of electronic and thermal Energies= -1181.031257
Sum of electronic and thermal Enthalpies= -1181.030313
Sum of electronic and thermal Free Energies= -1181.090861

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.884257	0.186592	-0.008715
2	6	0	-1.676324	0.871114	-0.008170
3	6	0	-1.672231	2.260249	-0.044417
4	6	0	-2.898325	2.924235	-0.078958
5	6	0	-4.100509	2.217346	-0.077710
6	6	0	-4.109548	0.821443	-0.042581
7	6	0	-0.532773	-0.088204	0.028182
8	1	0	-0.746701	2.825142	-0.047743
9	1	0	-2.916822	4.008194	-0.108651
10	1	0	-5.040844	2.756866	-0.105461
11	1	0	-5.039162	0.263851	-0.042570
12	16	0	-2.510472	-1.556248	0.034564
13	8	0	-2.897926	-2.198293	-1.211028

14	8	0	-2.933528	-2.143358	1.295649
15	7	0	-0.835522	-1.348901	0.053944
16	6	0	0.847133	0.371419	0.032207
17	1	0	1.005742	1.443716	0.052533
18	6	0	1.880733	-0.488603	0.002244
19	1	0	1.641521	-1.549919	-0.035943
20	6	0	3.304823	-0.155350	0.004472
21	6	0	4.231617	-1.196379	-0.142875
22	6	0	3.784578	1.155744	0.148794
23	6	0	5.597411	-0.938826	-0.154852
24	1	0	3.871737	-2.215384	-0.252295
25	6	0	5.147734	1.412173	0.138962
26	1	0	3.091033	1.980343	0.277217
27	6	0	6.058360	0.366639	-0.014328
28	1	0	6.301420	-1.755908	-0.271780
29	1	0	5.505354	2.430023	0.254579
30	1	0	7.124028	0.571018	-0.021028

9aa



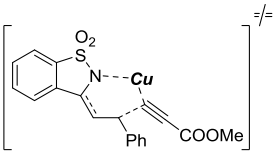
Sum of electronic and zero-point Energies= -1486.483124
Sum of electronic and thermal Energies= -1486.174113
Sum of electronic and thermal Enthalpies= -1486.152500
Sum of electronic and thermal Free Energies= -1486.225688

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.497420	1.166071	-0.728453
2	6	0	-0.053670	1.618500	-0.715649
3	6	0	0.163574	2.519541	0.511976
4	8	0	-0.040111	3.709238	0.492242
5	8	0	0.513139	1.819359	1.588753
6	6	0	0.758605	2.584121	2.771305
7	1	0	-0.145834	3.109979	3.085831
8	1	0	1.059628	1.863839	3.530675
9	1	0	1.559523	3.305997	2.598004
10	6	0	2.802487	-0.941996	-0.251474
11	6	0	1.626593	-1.550685	0.176113
12	6	0	1.697417	-2.807161	0.774306
13	6	0	2.941763	-3.405920	0.929267
14	6	0	4.109542	-2.777156	0.488095
15	6	0	4.051361	-1.528428	-0.120669
16	6	0	0.438130	-0.738042	-0.096200

17	1	0	0.797051	-3.307994	1.113322
18	1	0	3.008212	-4.381571	1.398910
19	1	0	5.068368	-3.266738	0.618267
20	1	0	4.947522	-1.031699	-0.475890
21	16	0	2.461151	0.616996	-1.014209
22	8	0	2.763769	0.583491	-2.436165
23	8	0	2.947729	1.755581	-0.247056
24	7	0	0.799440	0.441860	-0.756433
25	6	0	-0.852212	-0.996313	0.169548
26	1	0	-1.134957	-1.929273	0.640070
27	6	0	-1.869478	-0.043280	-0.270259
28	6	0	-3.300180	-0.438006	-0.209670
29	6	0	-3.799242	-1.120735	0.904950
30	6	0	-4.177539	-0.120069	-1.251495
31	6	0	-5.144787	-1.462724	0.981996
32	1	0	-3.136068	-1.364398	1.730154
33	6	0	-5.522820	-0.462954	-1.173882
34	1	0	-3.795826	0.381269	-2.135697
35	6	0	-6.011229	-1.133915	-0.056587
36	1	0	-5.518714	-1.981515	1.859176
37	1	0	-6.189832	-0.211186	-1.992467
38	1	0	-7.061405	-1.401368	0.003958
39	1	0	-2.227911	1.902869	-1.042770
40	1	0	0.154186	2.240380	-1.590665

TS1



Imaginary Freq.: -443.06 cm^{-1}

Sum of electronic and zero-point Energies= -4853.081079

Sum of electronic and thermal Energies= -4852.326924

Sum of electronic and thermal Enthalpies= -4852.275813

Sum of electronic and thermal Free Energies= -4852.414618

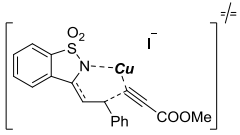
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-1.086616	-0.001799	0.175323
2	15	0	-1.510527	2.114939	-0.448100
3	15	0	-2.923449	-1.043627	-0.501460
4	6	0	-4.269149	0.214511	-0.500013
5	1	0	-4.247449	0.665438	0.499652
6	1	0	-5.248166	-0.261260	-0.623131
7	6	0	-4.123191	1.297894	-1.583601
8	1	0	-4.414433	0.858040	-2.542776

9	1	0	-4.876537	2.062371	-1.369535
10	6	0	-2.757381	1.987796	-1.811071
11	1	0	-2.930239	2.978526	-2.242369
12	1	0	-2.194134	1.425668	-2.565902
13	6	0	-0.167530	3.032793	-1.279549
14	6	0	1.104644	2.463128	-1.362046
15	6	0	-0.384600	4.305264	-1.825507
16	6	0	2.142559	3.140446	-1.998333
17	1	0	1.305779	1.487262	-0.935994
18	6	0	0.651111	4.980110	-2.457827
19	1	0	-1.360788	4.776409	-1.743564
20	6	0	1.915007	4.395480	-2.548670
21	1	0	3.120623	2.672825	-2.055525
22	1	0	0.476049	5.965030	-2.879706
23	1	0	2.723244	4.925041	-3.043520
24	6	0	-2.135095	3.303791	0.788920
25	6	0	-3.494780	3.479709	1.055551
26	6	0	-1.199382	3.988811	1.575574
27	6	0	-3.911117	4.318640	2.086689
28	1	0	-4.243618	2.972378	0.458065
29	6	0	-1.616148	4.822303	2.606069
30	1	0	-0.137177	3.872481	1.376496
31	6	0	-2.974566	4.988293	2.866289
32	1	0	-4.971938	4.451456	2.275226
33	1	0	-0.877732	5.346389	3.204352
34	1	0	-3.299896	5.642122	3.669086
35	6	0	-2.890075	-1.653329	-2.220368
36	6	0	-4.005437	-2.263383	-2.806075
37	6	0	-1.727401	-1.480875	-2.975279
38	6	0	-3.957358	-2.683843	-4.129566
39	1	0	-4.909792	-2.419972	-2.223793
40	6	0	-1.679968	-1.905971	-4.300677
41	1	0	-0.847482	-1.030688	-2.525327
42	6	0	-2.794326	-2.503704	-4.877924
43	1	0	-4.825430	-3.156313	-4.578476
44	1	0	-0.765473	-1.773285	-4.869266
45	1	0	-2.757997	-2.837048	-5.910457
46	6	0	-3.572492	-2.441933	0.466805
47	6	0	-4.638677	-2.323490	1.358993
48	6	0	-2.886323	-3.658873	0.378634
49	6	0	-5.017526	-3.408303	2.147239
50	1	0	-5.172207	-1.383678	1.459592
51	6	0	-3.269401	-4.740437	1.160549
52	1	0	-2.048329	-3.756045	-0.306850

53	6	0	-4.336500	-4.616784	2.049361
54	1	0	-5.846392	-3.305887	2.840839
55	1	0	-2.735259	-5.681659	1.077896
56	1	0	-4.634584	-5.461006	2.663128
57	6	0	0.677738	-0.748920	-0.138495
58	6	0	1.443066	-1.122874	-1.025845
59	6	0	2.433726	-1.532850	-1.986428
60	8	0	2.353380	-1.370306	-3.184789
61	8	0	3.455059	-2.136152	-1.363862
62	6	0	4.587506	-2.442536	-2.180277
63	1	0	5.013962	-1.523436	-2.585921
64	1	0	5.303061	-2.924814	-1.514225
65	1	0	4.309927	-3.120540	-2.991179
66	6	0	5.744615	-0.533700	0.718380
67	6	0	4.784705	-1.129910	1.524510
68	6	0	5.113678	-2.266824	2.252814
69	6	0	6.405569	-2.778015	2.142835
70	6	0	7.354629	-2.168555	1.320713
71	6	0	7.031513	-1.023056	0.593571
72	6	0	3.477142	-0.418072	1.401446
73	1	0	4.383484	-2.754186	2.890441
74	1	0	6.677000	-3.667640	2.702244
75	1	0	8.351940	-2.589716	1.246217
76	1	0	7.760061	-0.539129	-0.048198
77	16	0	4.985973	0.892718	-0.043483
78	8	0	4.969433	0.754909	-1.501535
79	8	0	5.575900	2.118783	0.490469
80	7	0	3.485186	0.626718	0.573469
81	6	0	2.302884	-0.856664	2.010641
82	1	0	2.295212	-1.789008	2.562569
83	6	0	1.094743	-0.218544	1.656843
84	1	0	1.225066	0.830428	1.394999
85	6	0	-0.177682	-0.490056	2.389933
86	6	0	-0.985081	0.588657	2.767292
87	6	0	-0.601530	-1.792268	2.694160
88	6	0	-2.197699	0.373947	3.427696
89	1	0	-0.645312	1.602801	2.584642
90	6	0	-1.799608	-2.002504	3.357820
91	1	0	0.001982	-2.636427	2.374096
92	6	0	-2.603619	-0.919616	3.723233
93	1	0	-2.807667	1.226861	3.709072
94	1	0	-2.129878	-3.015263	3.565196
95	1	0	-3.547199	-1.094517	4.230074

TS1'



Imaginary Freq.: -439.47 cm^{-1}

Sum of electronic and zero-point Energies= -4863.883027

Sum of electronic and thermal Energies= -4863.830701

Sum of electronic and thermal Enthalpies= -4863.829757

Sum of electronic and thermal Free Energies= -4863.978683

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.369399	0.271550	-0.236660
2	15	0	2.158788	1.609769	-0.101466
3	15	0	0.545639	-0.703410	1.762594
4	6	0	2.259666	-1.317614	2.044024
5	1	0	2.298108	-2.350067	1.684157
6	1	0	2.481149	-1.340401	3.116078
7	6	0	3.340941	-0.532927	1.273280
8	1	0	4.310828	-0.816722	1.689728
9	1	0	3.363354	-0.899828	0.241428
10	6	0	3.228738	1.007310	1.277595
11	1	0	4.224271	1.454544	1.198760
12	1	0	2.792697	1.372331	2.213620
13	6	0	1.800908	3.356873	0.296213
14	6	0	0.596547	3.900276	-0.163826
15	6	0	2.659805	4.152455	1.060435
16	6	0	0.257812	5.217564	0.131719
17	1	0	-0.088503	3.283894	-0.739886
18	6	0	2.315367	5.465556	1.364343
19	1	0	3.599377	3.749087	1.426229
20	6	0	1.115089	5.999920	0.900090
21	1	0	-0.680265	5.623526	-0.234313
22	1	0	2.985380	6.073446	1.964804
23	1	0	0.850264	7.025976	1.137610
24	6	0	3.250496	1.668223	-1.561958
25	6	0	4.501258	1.051100	-1.607418
26	6	0	2.729350	2.245178	-2.727526
27	6	0	5.218313	1.004697	-2.802107
28	1	0	4.929049	0.565329	-0.736990
29	6	0	3.450076	2.207254	-3.913923
30	1	0	1.750323	2.718317	-2.705914
31	6	0	4.696057	1.580119	-3.954824
32	1	0	6.176318	0.494966	-2.819336
33	1	0	3.034905	2.657455	-4.810594

34	1	0	5.251388	1.534890	-4.886735
35	6	0	0.286083	0.545000	3.079749
36	6	0	0.568717	0.282852	4.424692
37	6	0	-0.194743	1.806587	2.720952
38	6	0	0.394169	1.272589	5.384856
39	1	0	0.921977	-0.699888	4.726433
40	6	0	-0.362283	2.801401	3.680381
41	1	0	-0.438110	2.011153	1.683526
42	6	0	-0.064126	2.536217	5.012318
43	1	0	0.616902	1.060547	6.426227
44	1	0	-0.720193	3.780475	3.377657
45	1	0	-0.190007	3.310079	5.763661
46	6	0	-0.595821	-2.035802	2.260438
47	6	0	-0.208007	-3.339864	2.573961
48	6	0	-1.959138	-1.712039	2.248283
49	6	0	-1.168707	-4.305911	2.869860
50	1	0	0.841218	-3.617596	2.585266
51	6	0	-2.913105	-2.671297	2.564210
52	1	0	-2.273808	-0.707070	1.976636
53	6	0	-2.520037	-3.974213	2.868794
54	1	0	-0.856374	-5.318974	3.104932
55	1	0	-3.965373	-2.405018	2.555010
56	1	0	-3.266193	-4.727206	3.104527
57	6	0	-1.399298	0.784705	-0.839562
58	6	0	-2.300238	1.620499	-0.757279
59	6	0	-3.295171	2.655881	-0.667099
60	8	0	-3.447331	3.541471	-1.482720
61	8	0	-3.999670	2.558497	0.470910
62	6	0	-5.022250	3.539222	0.625193
63	1	0	-5.744100	3.467387	-0.189646
64	1	0	-5.505013	3.313998	1.576675
65	1	0	-4.594750	4.545999	0.653108
66	6	0	-6.295250	-1.292902	-1.088702
67	6	0	-5.099737	-1.938441	-0.814704
68	6	0	-5.111607	-3.125334	-0.088808
69	6	0	-6.335250	-3.617969	0.361206
70	6	0	-7.527729	-2.945685	0.086434
71	6	0	-7.521036	-1.763908	-0.653949
72	6	0	-3.947312	-1.192616	-1.410164
73	1	0	-4.192771	-3.660096	0.128175
74	1	0	-6.361615	-4.542397	0.929923
75	1	0	-8.468283	-3.349655	0.447330
76	1	0	-8.442005	-1.237281	-0.881096
77	16	0	-5.906198	0.148830	-2.069275

78	8	0	-6.269330	1.358905	-1.336251
79	8	0	-6.448698	-0.003267	-3.416345
80	7	0	-4.265039	-0.082157	-2.067428
81	6	0	-2.632194	-1.628349	-1.236564
82	1	0	-2.460301	-2.430077	-0.529795
83	6	0	-1.544963	-0.936735	-1.786484
84	1	0	-1.751643	-0.370060	-2.691370
85	6	0	-0.160704	-1.511836	-1.733920
86	6	0	0.865508	-0.854575	-2.433858
87	6	0	0.145955	-2.718366	-1.082311
88	6	0	2.156587	-1.382945	-2.476988
89	1	0	0.633457	0.047148	-2.994992
90	6	0	1.439296	-3.225024	-1.106351
91	1	0	-0.623169	-3.260185	-0.543607
92	6	0	2.451913	-2.560374	-1.800136
93	1	0	2.930746	-0.864953	-3.032904
94	1	0	1.660116	-4.151065	-0.584187
95	1	0	3.464515	-2.951617	-1.804783
96	53	0	6.539663	-2.415326	-0.420507

TS2 Imaginary Freq.: -68.09 cm^{-1}

Sum of electronic and zero-point Energies= -4852.379784

Sum of electronic and thermal Energies= -4852.330162

Sum of electronic and thermal Enthalpies= -4852.329218

Sum of electronic and thermal Free Energies= -4852.465779

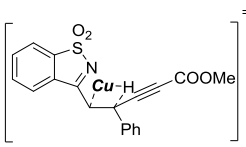
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.291651	0.255967	2.471985
2	6	0	0.858338	-0.014095	2.753930
3	6	0	2.177969	-0.394532	3.214549
4	8	0	2.923368	0.330398	3.834462
5	8	0	2.449420	-1.652580	2.863778
6	6	0	3.759173	-2.122748	3.196904
7	1	0	3.917722	-2.088024	4.277059
8	1	0	3.799310	-3.148826	2.835804
9	1	0	4.518324	-1.516263	2.697025
10	6	0	-3.730667	-0.059081	-1.976531
11	6	0	-3.323446	-0.023778	-0.646927
12	6	0	-4.037943	-0.788851	0.275472
13	6	0	-5.084920	-1.590852	-0.172415

14	6	0	-5.441538	-1.635645	-1.518472
15	6	0	-4.765438	-0.846779	-2.444517
16	6	0	-2.220850	0.995360	-0.469263
17	1	0	-3.835553	-0.755595	1.337011
18	1	0	-5.636158	-2.186313	0.547571
19	1	0	-6.261966	-2.268354	-1.840877
20	1	0	-5.051647	-0.829759	-3.490760
21	16	0	-2.808584	1.173944	-2.868042
22	8	0	-3.715491	2.186860	-3.401613
23	8	0	-1.911202	0.532313	-3.838846
24	7	0	-1.973664	1.711381	-1.576768
25	6	0	-1.479541	1.246315	0.692984
26	6	0	-1.666051	0.544807	2.027925
27	6	0	-2.530460	1.237753	3.072839
28	6	0	-3.602778	2.027430	2.661458
29	6	0	-2.311258	1.044396	4.436919
30	6	0	-4.450419	2.608494	3.599910
31	1	0	-3.769597	2.194082	1.601764
32	6	0	-3.155269	1.628522	5.375460
33	1	0	-1.472190	0.438151	4.767792
34	6	0	-4.229442	2.410518	4.959344
35	1	0	-5.280673	3.222868	3.265847
36	1	0	-2.971711	1.473809	6.434230
37	1	0	-4.888173	2.866638	5.691695
38	29	0	0.304121	0.266378	0.239246
39	15	0	0.367239	-1.725430	-0.719229
40	15	0	1.769869	1.476124	-0.932031
41	6	0	0.397400	-1.410428	-2.533749
42	1	0	0.444742	-2.372682	-3.055555
43	1	0	-0.540508	-0.917010	-2.812440
44	6	0	1.476053	0.969891	-2.683055
45	1	0	0.461934	1.319219	-2.913633
46	1	0	2.157556	1.530177	-3.332096
47	6	0	1.577036	-0.535504	-2.990792
48	1	0	2.517723	-0.949165	-2.608160
49	1	0	1.629884	-0.627600	-4.080237
50	6	0	-1.076403	-2.801801	-0.437184
51	6	0	-1.324681	-3.182897	0.887796
52	6	0	-1.931570	-3.247974	-1.445956
53	6	0	-2.394640	-4.013996	1.194766
54	1	0	-0.664227	-2.834092	1.678819
55	6	0	-3.005540	-4.078675	-1.134492
56	1	0	-1.772429	-2.951343	-2.477302
57	6	0	-3.234848	-4.468147	0.180525

58	1	0	-2.572974	-4.306943	2.224688
59	1	0	-3.667637	-4.416625	-1.925141
60	1	0	-4.072544	-5.116516	0.417888
61	6	0	1.779614	-2.870393	-0.501086
62	6	0	1.657863	-4.249166	-0.701751
63	6	0	3.037577	-2.339931	-0.205649
64	6	0	2.772873	-5.075631	-0.610989
65	1	0	0.687911	-4.683931	-0.924525
66	6	0	4.157992	-3.163516	-0.137954
67	1	0	3.150078	-1.276454	-0.031078
68	6	0	4.026512	-4.534252	-0.335513
69	1	0	2.662522	-6.144684	-0.763503
70	1	0	5.128847	-2.725620	0.072515
71	1	0	4.896740	-5.180773	-0.276237
72	6	0	1.699229	3.301710	-1.015448
73	6	0	2.805221	4.115442	-0.755053
74	6	0	0.470211	3.893687	-1.330333
75	6	0	2.682919	5.500973	-0.805086
76	1	0	3.766704	3.674344	-0.513164
77	6	0	0.357514	5.278781	-1.386229
78	1	0	-0.399753	3.271310	-1.530363
79	6	0	1.460625	6.085669	-1.120456
80	1	0	3.548306	6.122908	-0.597141
81	1	0	-0.599965	5.726194	-1.633835
82	1	0	1.367299	7.166625	-1.159783
83	6	0	3.526001	1.128039	-0.575471
84	6	0	4.469866	0.758739	-1.535672
85	6	0	3.915376	1.186606	0.768516
86	6	0	5.766062	0.419289	-1.154147
87	1	0	4.201425	0.720229	-2.586320
88	6	0	5.212280	0.863175	1.149040
89	1	0	3.198048	1.490949	1.525032
90	6	0	6.138207	0.465369	0.186260
91	1	0	6.486569	0.119068	-1.908224
92	1	0	5.490022	0.917574	2.196831
93	1	0	7.149818	0.200901	0.478375
94	1	0	-2.086567	-0.450595	1.843830
95	1	0	-1.084459	2.258490	0.766833

TS3 Imaginary Freq.: -36.34 cm^{-1}



Sum of electronic and zero-point Energies= -4852.335881

Sum of electronic and thermal Energies= -4852.286450

Sum of electronic and thermal Enthalpies= -4852.285506

Sum of electronic and thermal Free Energies= -4852.419970

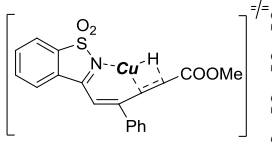
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.443866	-0.824289	2.561961
2	6	0	-0.791915	-0.078216	3.257825
3	6	0	0.087227	0.895543	3.867525
4	8	0	-0.281512	1.898509	4.435182
5	8	0	1.366289	0.546246	3.687924
6	6	0	2.336213	1.486813	4.160151
7	1	0	2.206660	1.672028	5.228791
8	1	0	3.305607	1.026626	3.972357
9	1	0	2.256070	2.428366	3.612013
10	6	0	1.913226	-3.169243	-0.150389
11	6	0	0.969950	-2.721459	0.769119
12	6	0	1.224452	-2.881470	2.126683
13	6	0	2.425809	-3.465706	2.518325
14	6	0	3.367981	-3.888667	1.579607
15	6	0	3.114610	-3.747614	0.218670
16	6	0	-0.208355	-2.090215	0.081957
17	1	0	0.511972	-2.539649	2.867252
18	1	0	2.633258	-3.589477	3.576572
19	1	0	4.301591	-4.330631	1.911212
20	1	0	3.832603	-4.072948	-0.525998
21	16	0	1.267234	-2.944007	-1.791910
22	8	0	0.905899	-4.243108	-2.353423
23	8	0	2.123500	-2.091610	-2.619832
24	7	0	-0.092949	-2.129574	-1.309477
25	6	0	-1.602517	-2.195012	0.569422
26	6	0	-2.183419	-1.626576	1.648730
27	6	0	-3.658045	-1.690887	1.851173
28	6	0	-4.522547	-1.616618	0.753038
29	6	0	-4.200646	-1.785971	3.136037
30	6	0	-5.898784	-1.667911	0.937193
31	1	0	-4.117785	-1.491551	-0.246673
32	6	0	-5.578075	-1.837263	3.317107
33	1	0	-3.537779	-1.825447	3.995745
34	6	0	-6.431513	-1.783146	2.218189

35	1	0	-6.554215	-1.602758	0.074207
36	1	0	-5.986532	-1.921157	4.319334
37	1	0	-7.506787	-1.821137	2.361754
38	29	0	0.173515	-0.314064	-0.551094
39	15	0	2.082651	0.786643	-1.021061
40	15	0	-1.245314	1.047690	-1.730135
41	6	0	2.138461	1.233276	-2.804111
42	1	0	3.079782	1.742317	-3.039221
43	1	0	2.120251	0.287304	-3.354840
44	6	0	-0.431957	1.491408	-3.327883
45	1	0	-0.361002	0.541878	-3.871611
46	1	0	-1.094472	2.137737	-3.914330
47	6	0	0.964857	2.137585	-3.230213
48	1	0	0.929142	3.017757	-2.577815
49	1	0	1.202870	2.516586	-4.229547
50	6	0	3.657602	-0.021181	-0.594474
51	6	0	3.884438	-0.252296	0.767338
52	6	0	4.592377	-0.459446	-1.530680
53	6	0	5.044476	-0.889331	1.186055
54	1	0	3.138539	0.055468	1.496297
55	6	0	5.751519	-1.105917	-1.107439
56	1	0	4.416025	-0.316724	-2.591084
57	6	0	5.982252	-1.316502	0.247895
58	1	0	5.209752	-1.068530	2.243840
59	1	0	6.474019	-1.447513	-1.842087
60	1	0	6.887178	-1.820236	0.573537
61	6	0	2.229265	2.402482	-0.171486
62	6	0	3.262549	3.293326	-0.485051
63	6	0	1.289056	2.767038	0.793452
64	6	0	3.341714	4.529390	0.144074
65	1	0	4.015866	3.016156	-1.217710
66	6	0	1.364167	4.008476	1.421660
67	1	0	0.492334	2.076745	1.048495
68	6	0	2.388717	4.890228	1.095841
69	1	0	4.146323	5.213560	-0.107018
70	1	0	0.617296	4.279962	2.160394
71	1	0	2.449471	5.858319	1.583407
72	6	0	-2.841740	0.320001	-2.240500
73	6	0	-4.069087	0.960002	-2.052796
74	6	0	-2.817522	-0.974386	-2.777035
75	6	0	-5.254783	0.317709	-2.399860
76	1	0	-4.106265	1.956302	-1.623894
77	6	0	-4.003802	-1.606875	-3.132612
78	1	0	-1.871618	-1.498304	-2.879381

79	6	0	-5.225048	-0.963719	-2.942055
80	1	0	-6.203619	0.821360	-2.243322
81	1	0	-3.972645	-2.609708	-3.546659
82	1	0	-6.150934	-1.463478	-3.209831
83	6	0	-1.682048	2.605121	-0.892699
84	6	0	-1.565473	3.870395	-1.469595
85	6	0	-2.109463	2.499361	0.437594
86	6	0	-1.848589	5.011374	-0.722274
87	1	0	-1.245503	3.979729	-2.501026
88	6	0	-2.406797	3.636340	1.177242
89	1	0	-2.192642	1.519067	0.900043
90	6	0	-2.266976	4.896769	0.599022
91	1	0	-1.740266	5.991021	-1.176848
92	1	0	-2.727345	3.536475	2.209286
93	1	0	-2.483346	5.788535	1.179024
94	1	0	-2.251399	-2.738417	-0.113056
95	1	0	0.019327	-0.138279	0.915764

TS4 Imaginary Freq.: -236.66 cm^{-1}



Sum of electronic and zero-point Energies= -4852.334764
Sum of electronic and thermal Energies= -4852.285846
Sum of electronic and thermal Enthalpies= -4852.284901
Sum of electronic and thermal Free Energies= -4852.417835

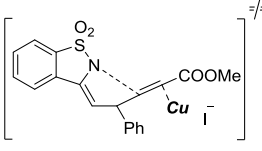
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.325483	-0.995126	2.645195
2	6	0	-0.436241	-0.173775	2.868243
3	6	0	0.546031	0.577574	3.627464
4	8	0	0.395225	0.900589	4.784662
5	8	0	1.619726	0.886825	2.893069
6	6	0	2.592926	1.719938	3.525307
7	1	0	3.077403	1.191869	4.350683
8	1	0	3.319455	1.962943	2.750233
9	1	0	2.130414	2.633939	3.902743
10	6	0	1.918104	-3.105584	-0.236759
11	6	0	0.982691	-2.734052	0.728100
12	6	0	1.268603	-2.987843	2.066124
13	6	0	2.487481	-3.577204	2.393437
14	6	0	3.416704	-3.920398	1.411593
15	6	0	3.131253	-3.693445	0.068202

16	6	0	-0.231737	-2.124605	0.095181
17	1	0	0.559689	-2.729755	2.842617
18	1	0	2.714719	-3.771973	3.436774
19	1	0	4.362633	-4.370699	1.692909
20	1	0	3.835788	-3.961548	-0.711293
21	16	0	1.224981	-2.815067	-1.848294
22	8	0	0.854572	-4.093339	-2.448618
23	8	0	2.034349	-1.914223	-2.669578
24	7	0	-0.124678	-2.033592	-1.286124
25	6	0	-1.596447	-2.200547	0.597816
26	6	0	-2.140221	-1.713081	1.752696
27	6	0	-3.609868	-1.695792	1.973311
28	6	0	-4.493673	-1.523093	0.900782
29	6	0	-4.130116	-1.801676	3.267075
30	6	0	-5.865140	-1.482714	1.118832
31	1	0	-4.108654	-1.389702	-0.105688
32	6	0	-5.503141	-1.760140	3.482133
33	1	0	-3.449706	-1.924018	4.104837
34	6	0	-6.375778	-1.604769	2.408555
35	1	0	-6.533923	-1.340644	0.275491
36	1	0	-5.892794	-1.852079	4.491216
37	1	0	-7.447484	-1.569370	2.577581
38	29	0	0.099234	-0.255667	-0.433345
39	15	0	2.030847	0.836463	-0.936438
40	15	0	-1.366990	1.037620	-1.646843
41	6	0	2.019716	1.351420	-2.705704
42	1	0	2.944205	1.896011	-2.928775
43	1	0	2.014958	0.430073	-3.296468
44	6	0	-0.549516	1.541513	-3.222093
45	1	0	-0.429186	0.609281	-3.786452
46	1	0	-1.228466	2.172817	-3.805749
47	6	0	0.817293	2.240000	-3.074663
48	1	0	0.743135	3.071173	-2.363358
49	1	0	1.043258	2.697029	-4.043553
50	6	0	3.618584	-0.008256	-0.642976
51	6	0	3.910991	-0.339209	0.685049
52	6	0	4.522435	-0.349341	-1.648457
53	6	0	5.104132	-0.973591	1.004433
54	1	0	3.187527	-0.116812	1.464314
55	6	0	5.712302	-0.998053	-1.326171
56	1	0	4.300993	-0.128631	-2.686601
57	6	0	6.009284	-1.303147	-0.001729
58	1	0	5.318302	-1.225764	2.038199
59	1	0	6.408523	-1.265099	-2.115090

60	1	0	6.939898	-1.805395	0.244184
61	6	0	2.278275	2.427833	-0.063221
62	6	0	3.507949	3.094556	-0.116124
63	6	0	1.220035	3.015093	0.631943
64	6	0	3.670923	4.324375	0.511569
65	1	0	4.347803	2.642893	-0.637272
66	6	0	1.377472	4.253963	1.247812
67	1	0	0.273818	2.494397	0.711841
68	6	0	2.602934	4.908821	1.190683
69	1	0	4.631401	4.828491	0.468920
70	1	0	0.538234	4.697477	1.774453
71	1	0	2.730486	5.871033	1.677197
72	6	0	-2.925645	0.251034	-2.186574
73	6	0	-4.176542	0.849697	-2.013512
74	6	0	-2.852414	-1.037395	-2.732745
75	6	0	-5.336091	0.170586	-2.377745
76	1	0	-4.254174	1.842027	-1.581452
77	6	0	-4.013434	-1.708340	-3.101464
78	1	0	-1.889015	-1.528176	-2.829576
79	6	0	-5.257520	-1.108475	-2.920591
80	1	0	-6.302235	0.644193	-2.233397
81	1	0	-3.943611	-2.707349	-3.519971
82	1	0	-6.163272	-1.638289	-3.198979
83	6	0	-1.898497	2.566204	-0.810894
84	6	0	-1.815687	3.839929	-1.374934
85	6	0	-2.365658	2.430810	0.503704
86	6	0	-2.170084	4.962900	-0.630642
87	1	0	-1.465783	3.970390	-2.393867
88	6	0	-2.734540	3.550213	1.239081
89	1	0	-2.426361	1.444487	0.956688
90	6	0	-2.627691	4.820476	0.674890
91	1	0	-2.086812	5.949482	-1.075265
92	1	0	-3.095979	3.430285	2.255347
93	1	0	-2.902096	5.697338	1.253173
94	1	0	-2.290351	-2.603402	-0.135878
95	1	0	-0.016017	0.227870	1.001533

TS5 Imaginary Freq.: -304.46 cm^{-1}



Sum of electronic and zero-point Energies= -4863.913173

Sum of electronic and thermal Energies= -4863.861808

Sum of electronic and thermal Enthalpies= -4863.860864

Sum of electronic and thermal Free Energies= -4864.005396

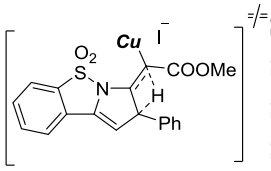
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.198075	0.340051	0.779715
2	15	0	1.589427	-0.776472	0.002059
3	15	0	0.752612	2.377144	0.762937
4	6	0	2.537356	2.330736	1.231046
5	1	0	2.520620	2.156528	2.314512
6	1	0	2.957765	3.334031	1.094923
7	6	0	3.441011	1.292043	0.557344
8	1	0	3.483102	1.457443	-0.522809
9	1	0	4.460299	1.457663	0.919689
10	6	0	3.110485	-0.179257	0.834078
11	1	0	2.965687	-0.335400	1.910077
12	1	0	3.968781	-0.788543	0.529589
13	6	0	1.819632	-0.447767	-1.772547
14	6	0	0.689145	-0.153857	-2.539768
15	6	0	3.081799	-0.467638	-2.376628
16	6	0	0.813345	0.124672	-3.896653
17	1	0	-0.300507	-0.155052	-2.093798
18	6	0	3.203039	-0.175522	-3.730574
19	1	0	3.974146	-0.701557	-1.800982
20	6	0	2.071960	0.123616	-4.489158
21	1	0	-0.081709	0.345665	-4.468235
22	1	0	4.186166	-0.184484	-4.190582
23	1	0	2.175425	0.351732	-5.546140
24	6	0	1.642678	-2.591709	0.150596
25	6	0	2.454454	-3.246322	1.078512
26	6	0	0.781565	-3.341567	-0.659701
27	6	0	2.395604	-4.633061	1.202870
28	1	0	3.143588	-2.688141	1.703275
29	6	0	0.725161	-4.724088	-0.531705
30	1	0	0.144833	-2.839169	-1.384239
31	6	0	1.528830	-5.372524	0.404423
32	1	0	3.036164	-5.133336	1.922371
33	1	0	0.051169	-5.295112	-1.162461
34	1	0	1.483006	-6.452452	0.506447
35	6	0	0.654154	3.002610	-0.943615
36	6	0	1.770488	3.401877	-1.682785
37	6	0	-0.604953	2.969039	-1.557983
38	6	0	1.633496	3.745217	-3.025072
39	1	0	2.754573	3.436903	-1.227846
40	6	0	-0.736031	3.320907	-2.895332

41	1	0	-1.483756	2.662258	-0.996245
42	6	0	0.382688	3.701451	-3.632471
43	1	0	2.510259	4.033967	-3.596310
44	1	0	-1.713568	3.267908	-3.362824
45	1	0	0.280671	3.953012	-4.683972
46	6	0	0.182985	3.710828	1.863340
47	6	0	-0.408212	3.361857	3.078910
48	6	0	0.389644	5.056535	1.556207
49	6	0	-0.774905	4.349779	3.985938
50	1	0	-0.609213	2.316484	3.298086
51	6	0	0.014410	6.044405	2.461834
52	1	0	0.832958	5.334631	0.603773
53	6	0	-0.563124	5.691611	3.678665
54	1	0	-1.239408	4.072534	4.927209
55	1	0	0.171984	7.090258	2.216187
56	1	0	-0.856995	6.462836	4.384451
57	6	0	-1.859065	-0.705941	0.790644
58	6	0	-2.018071	0.469901	1.323478
59	6	0	-2.950120	1.558107	1.200052
60	8	0	-2.702049	2.740901	1.046174
61	8	0	-4.216947	1.096664	1.329482
62	6	0	-5.225961	2.072345	1.105999
63	1	0	-5.128751	2.499990	0.105497
64	1	0	-6.176323	1.543492	1.196134
65	1	0	-5.175549	2.873528	1.849528
66	6	0	-4.816061	-1.012084	-2.240528
67	6	0	-4.828419	-2.039933	-1.303647
68	6	0	-5.935366	-2.882602	-1.229094
69	6	0	-6.998547	-2.666156	-2.100830
70	6	0	-6.969194	-1.624974	-3.033384
71	6	0	-5.866876	-0.777437	-3.111629
72	6	0	-3.599639	-2.021064	-0.494718
73	1	0	-5.965140	-3.691199	-0.505681
74	1	0	-7.865528	-3.318402	-2.057050
75	1	0	-7.809763	-1.478747	-3.704306
76	1	0	-5.829388	0.032267	-3.833011
77	16	0	-3.277086	-0.116587	-2.098642
78	8	0	-3.521947	1.256214	-1.639243
79	8	0	-2.517572	-0.227167	-3.346953
80	7	0	-2.658312	-1.090453	-0.937578
81	6	0	-3.273319	-2.657489	0.639577
82	1	0	-3.873479	-3.407395	1.137061
83	6	0	-1.946614	-2.178557	1.178181
84	1	0	-1.141236	-2.712178	0.662496

85	6	0	-1.760765	-2.368951	2.666057
86	6	0	-0.684244	-3.113893	3.144700
87	6	0	-2.661235	-1.810485	3.577450
88	6	0	-0.504687	-3.299092	4.514882
89	1	0	0.018746	-3.552247	2.440838
90	6	0	-2.486391	-1.998360	4.943147
91	1	0	-3.487375	-1.211797	3.203608
92	6	0	-1.405934	-2.743400	5.416536
93	1	0	0.341212	-3.878507	4.873174
94	1	0	-3.191296	-1.558784	5.643009
95	1	0	-1.267379	-2.885750	6.484278
96	53	0	6.875119	-0.986482	-0.261710

TS6



Imaginary Freq.: -835.09 cm^{-1}

Sum of electronic and zero-point Energies= -4863.879879

Sum of electronic and thermal Energies= -4863.829290

Sum of electronic and thermal Enthalpies= -4863.828346

Sum of electronic and thermal Free Energies= -4863.969869

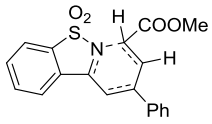
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.149867	0.543533	0.199034
2	15	0	-1.513419	-0.583421	1.157640
3	15	0	-1.145180	2.254217	-0.533252
4	6	0	-2.544483	1.527639	-1.489395
5	1	0	-2.112736	1.377499	-2.483943
6	1	0	-3.322970	2.289411	-1.615056
7	6	0	-3.131642	0.180503	-1.007993
8	1	0	-4.159643	0.101079	-1.371106
9	1	0	-2.588883	-0.636230	-1.494960
10	6	0	-3.153435	-0.078006	0.504481
11	1	0	-3.901124	-0.844129	0.731454
12	1	0	-3.449539	0.811472	1.068902
13	6	0	-1.638815	-0.254906	2.944933
14	6	0	-0.932962	0.811472	3.506405
15	6	0	-2.493419	-1.017950	3.747535
16	6	0	-1.089977	1.121107	4.854696
17	1	0	-0.258679	1.402144	2.893629
18	6	0	-2.640743	-0.712472	5.094832
19	1	0	-3.037009	-1.855735	3.319232
20	6	0	-1.942069	0.359651	5.648164

21	1	0	-0.542178	1.955734	5.280534
22	1	0	-3.300581	-1.311836	5.714345
23	1	0	-2.061807	0.597120	6.701028
24	6	0	-1.403721	-2.393244	1.027112
25	6	0	-2.386683	-3.178315	0.427035
26	6	0	-0.232050	-2.994016	1.504501
27	6	0	-2.191260	-4.551601	0.288199
28	1	0	-3.304295	-2.745013	0.043986
29	6	0	-0.048481	-4.364812	1.379221
30	1	0	0.547721	-2.385848	1.955509
31	6	0	-1.026364	-5.145588	0.761656
32	1	0	-2.960179	-5.145966	-0.195171
33	1	0	0.863752	-4.820570	1.751550
34	1	0	-0.875799	-6.215076	0.648354
35	6	0	-1.854478	3.264463	0.807533
36	6	0	-3.223816	3.443912	1.012651
37	6	0	-0.937182	3.869048	1.677448
38	6	0	-3.674827	4.198849	2.093431
39	1	0	-3.948747	2.991647	0.341608
40	6	0	-1.393995	4.626542	2.749579
41	1	0	0.129784	3.735250	1.503749
42	6	0	-2.761841	4.786317	2.963572
43	1	0	-4.740911	4.322907	2.254929
44	1	0	-0.678012	5.087076	3.423607
45	1	0	-3.116386	5.367606	3.809369
46	6	0	-0.501523	3.486501	-1.715304
47	6	0	-1.217869	4.653897	-1.998568
48	6	0	0.704122	3.246474	-2.377214
49	6	0	-0.739820	5.559551	-2.939224
50	1	0	-2.147673	4.861667	-1.476109
51	6	0	1.181449	4.153295	-3.318846
52	1	0	1.279574	2.358068	-2.139063
53	6	0	0.459706	5.308793	-3.602262
54	1	0	-1.300946	6.464713	-3.151022
55	1	0	2.123641	3.958480	-3.821543
56	1	0	0.833292	6.018456	-4.334509
57	6	0	2.683576	-0.287166	-0.579733
58	6	0	2.004840	0.829352	-0.114468
59	6	0	2.565904	2.137569	0.075203
60	8	0	2.051066	3.064995	0.697530
61	8	0	3.780745	2.297851	-0.512022
62	6	0	4.466501	3.502989	-0.214687
63	1	0	4.551012	3.657627	0.863996
64	1	0	5.458235	3.391618	-0.652888

65	1	0	3.949988	4.361327	-0.656431
66	6	0	6.215078	-1.533803	0.319944
67	6	0	5.394853	-2.575135	-0.119472
68	6	0	5.887858	-3.883505	-0.060660
69	6	0	7.170268	-4.097131	0.426656
70	6	0	7.978135	-3.036140	0.852117
71	6	0	7.502191	-1.729955	0.794908
72	6	0	4.113583	-2.091843	-0.564215
73	1	0	5.274905	-4.714361	-0.394388
74	1	0	7.556843	-5.110812	0.474188
75	1	0	8.976858	-3.231065	1.227906
76	1	0	8.113349	-0.893753	1.118969
77	16	0	5.420508	0.045344	0.155781
78	8	0	6.170695	0.837081	-0.807537
79	8	0	5.107693	0.633062	1.450691
80	7	0	4.037761	-0.664933	-0.539426
81	6	0	2.884720	-2.595478	-0.836986
82	1	0	2.655420	-3.643471	-0.978822
83	6	0	1.957276	-1.501596	-0.949405
84	1	0	0.884772	-0.787355	0.228109
85	6	0	0.836114	-1.556392	-1.925461
86	6	0	-0.041848	-2.650882	-1.939634
87	6	0	0.624996	-0.542906	-2.873669
88	6	0	-1.104730	-2.711754	-2.834027
89	1	0	0.096842	-3.453030	-1.220718
90	6	0	-0.444385	-0.597833	-3.761713
91	1	0	1.317627	0.289938	-2.912613
92	6	0	-1.323953	-1.678679	-3.743386
93	1	0	-1.784811	-3.557490	-2.799468
94	1	0	-0.578267	0.204002	-4.483526
95	1	0	-2.166268	-1.718810	-4.426594
96	53	0	-6.149928	-2.338386	-1.211389

TS7 Imaginary Freq.: -508.25 cm^{-1}



Sum of electronic and zero-point Energies= -1486.423704

Sum of electronic and thermal Energies= -1486.117404

Sum of electronic and thermal Enthalpies= -1486.095896

Sum of electronic and thermal Free Energies= -1486.167914

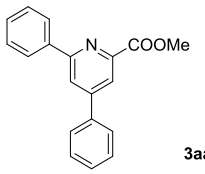
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

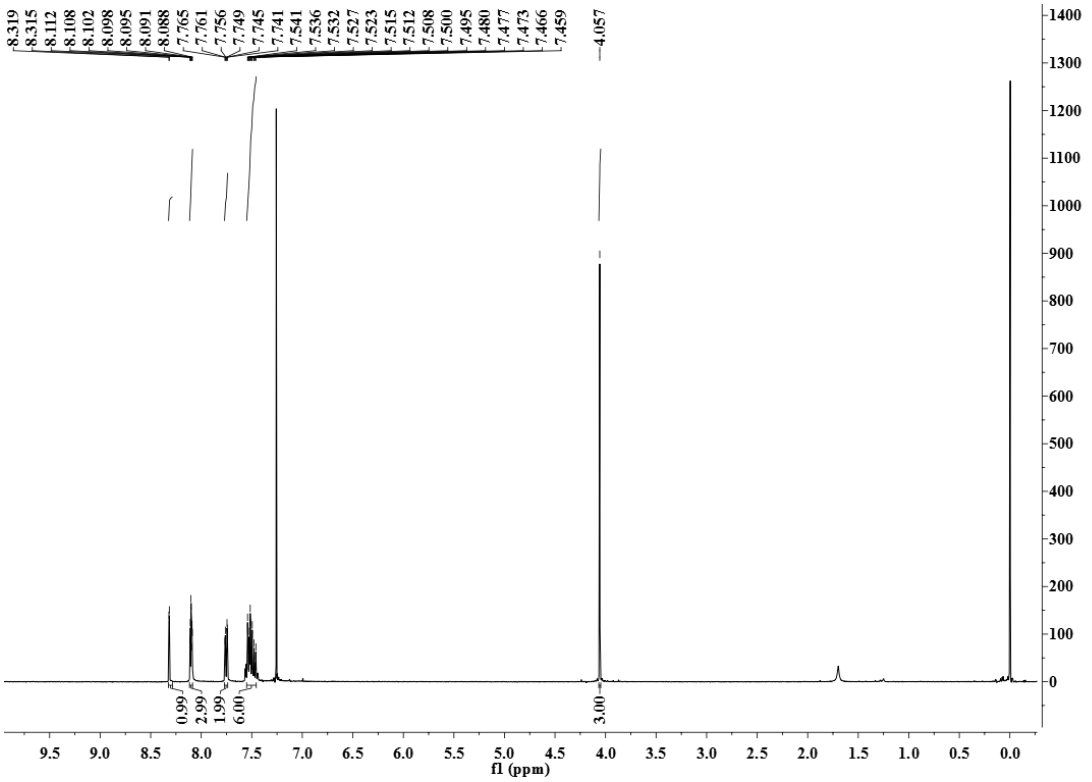
1	6	0	-1.364535	1.087052	-1.175104
2	6	0	-0.268024	1.934831	-1.047834
3	6	0	-0.031579	2.875672	0.100202
4	8	0	0.659936	3.860175	-0.017673
5	8	0	-0.681961	2.540622	1.212869
6	6	0	-0.420240	3.371534	2.345141
7	1	0	-0.745733	4.397208	2.157294
8	1	0	-0.991484	2.940132	3.166313
9	1	0	0.645759	3.369315	2.584184
10	6	0	2.804391	-1.171902	-0.089632
11	6	0	1.584730	-1.463446	0.509495
12	6	0	1.402699	-2.705636	1.108242
13	6	0	2.454939	-3.617625	1.084350
14	6	0	3.664629	-3.310731	0.460287
15	6	0	3.853990	-2.070513	-0.146181
16	6	0	0.615823	-0.342503	0.357827
17	1	0	0.464683	-2.964985	1.587068
18	1	0	2.327842	-4.587083	1.554427
19	1	0	4.465799	-4.041763	0.450376
20	1	0	4.789575	-1.818028	-0.633131
21	16	0	2.733045	0.484477	-0.735322
22	8	0	2.729115	0.500285	-2.190349
23	8	0	3.650953	1.353054	-0.020509
24	7	0	1.153821	0.761092	-0.161829
25	6	0	-0.756839	-0.509674	0.573432
26	1	0	-1.061775	-1.394967	1.119566
27	6	0	-1.720802	0.110013	-0.236063
28	6	0	-3.085230	-0.485595	-0.258215
29	6	0	-3.730288	-0.758056	0.953035
30	6	0	-3.749311	-0.774880	-1.454999
31	6	0	-5.010480	-1.300368	0.968215
32	1	0	-3.232041	-0.521463	1.888578
33	6	0	-5.025310	-1.326112	-1.437541
34	1	0	-3.260431	-0.596602	-2.407576
35	6	0	-5.661408	-1.587897	-0.227385
36	1	0	-5.501263	-1.493385	1.916905
37	1	0	-5.522788	-1.554852	-2.374729
38	1	0	-6.658772	-2.015646	-0.216912
39	1	0	-1.877215	1.083790	-2.132727
40	1	0	0.145137	2.360991	-1.960014

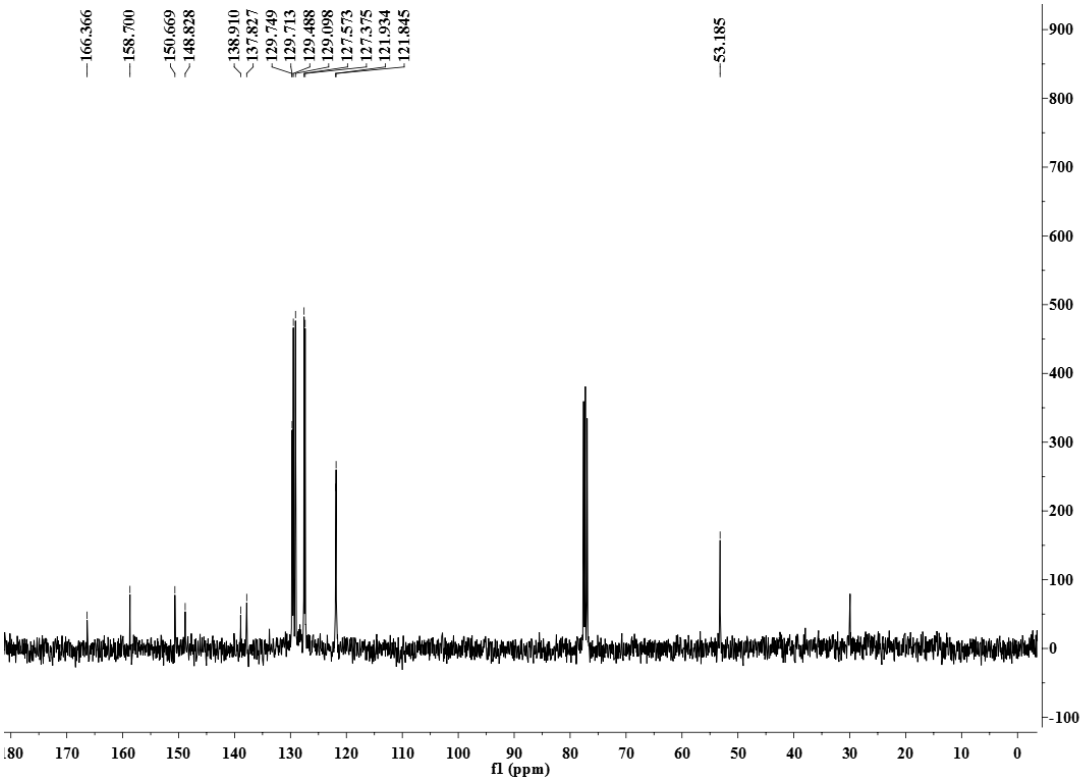
---

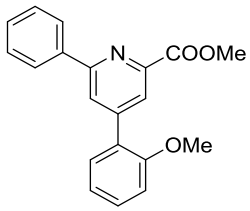
11. NMR Spectra of the products



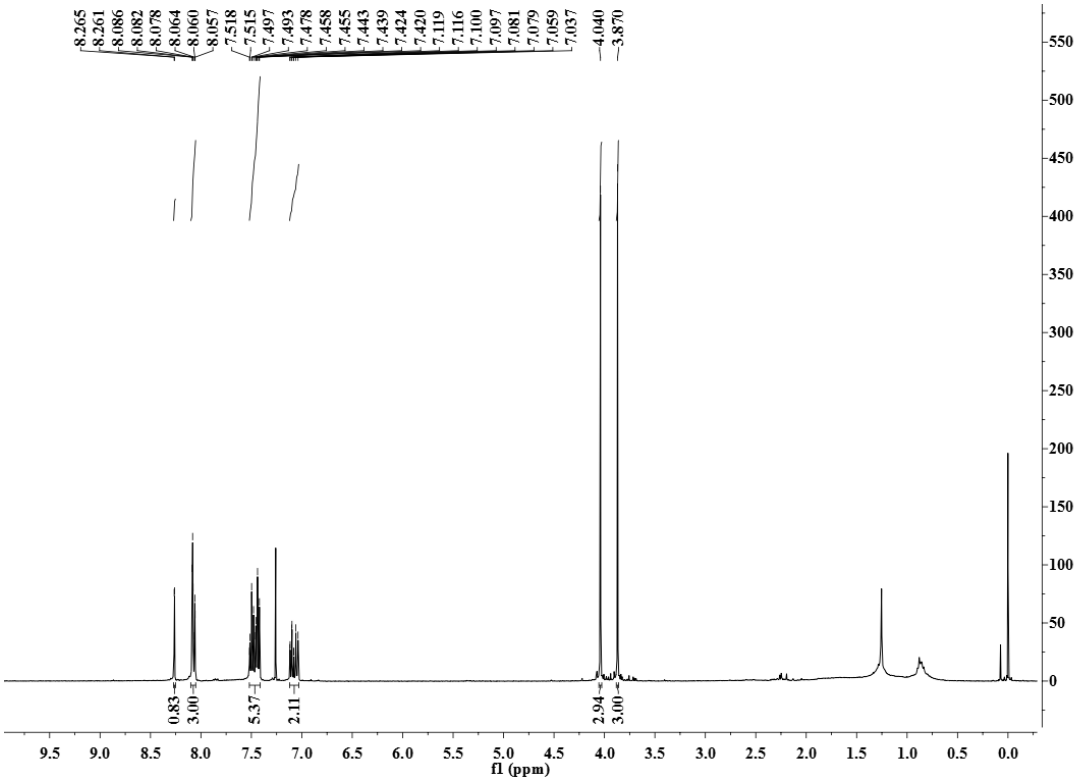
3aa

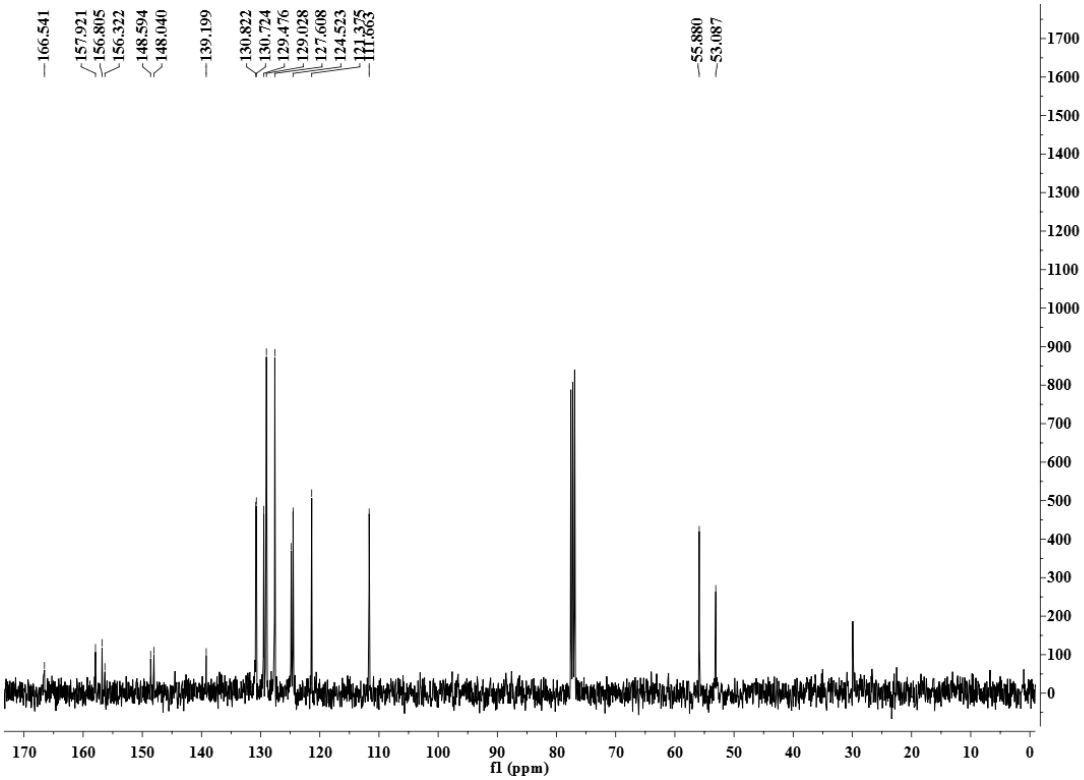


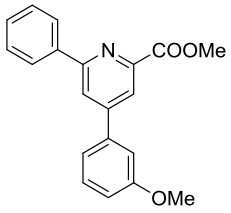



N
COOMe
OMe

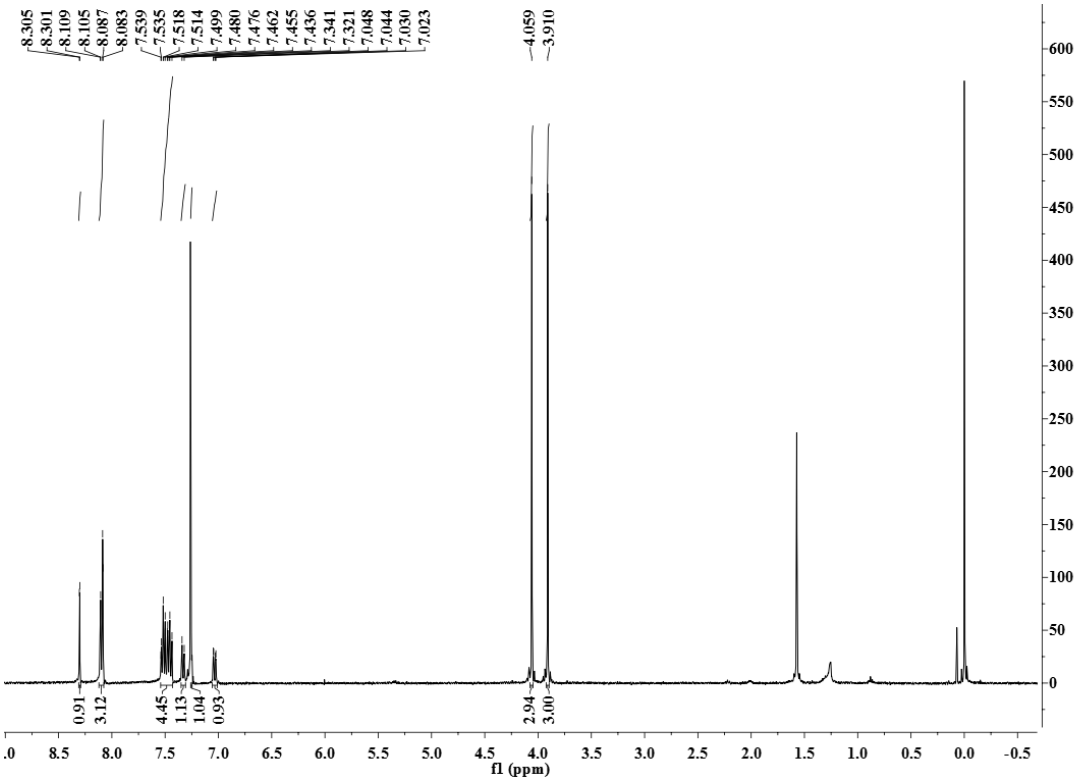
3ab

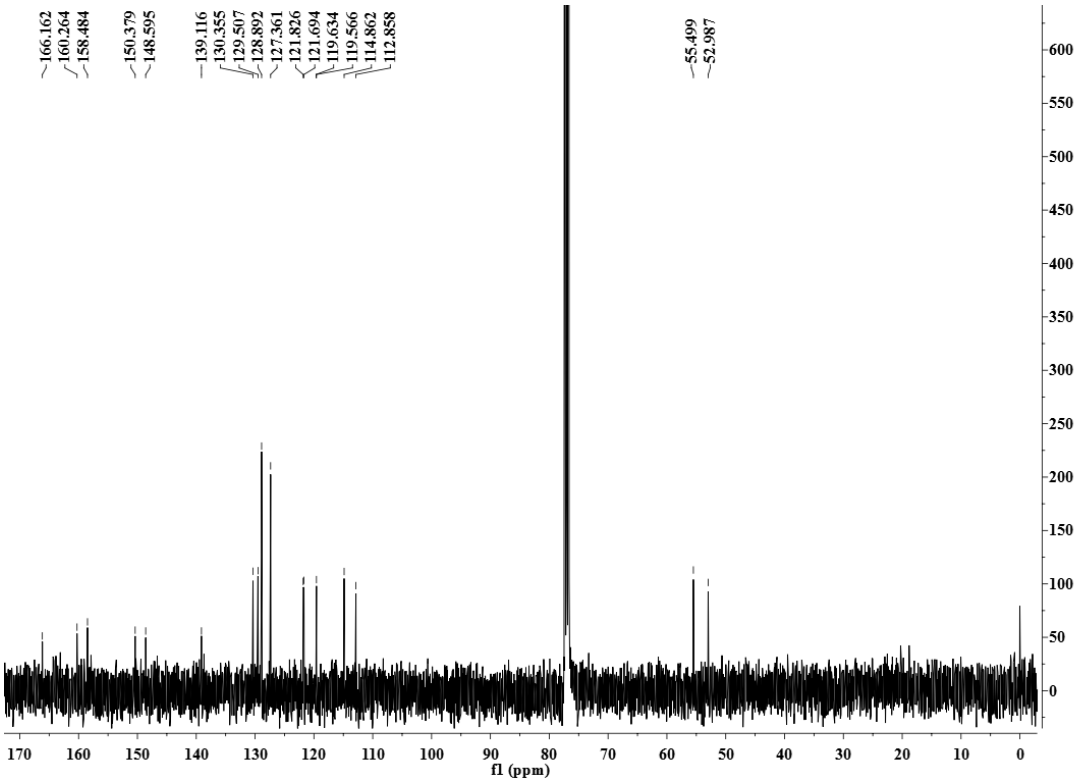

8.265
8.261
8.086
8.082
8.078
8.064
8.060
8.057
7.518
7.515
7.497
7.493
7.478
7.458
7.455
7.443
7.439
7.424
7.420
7.119
7.116
7.100
7.097
7.081
7.079
7.059
7.037
4.040
3.870
0.83
3.00
5.37
2.11
2.94
3.00
f1 (ppm)

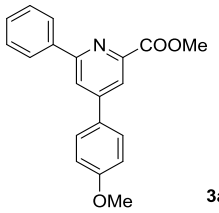

166.541
157.921
156.805
156.322
148.594
148.040
139.199
130.822
130.724
129.476
129.028
127.608
124.523
121.375
111.663
55.880
53.087
f1 (ppm)


N
COOMe
OMe

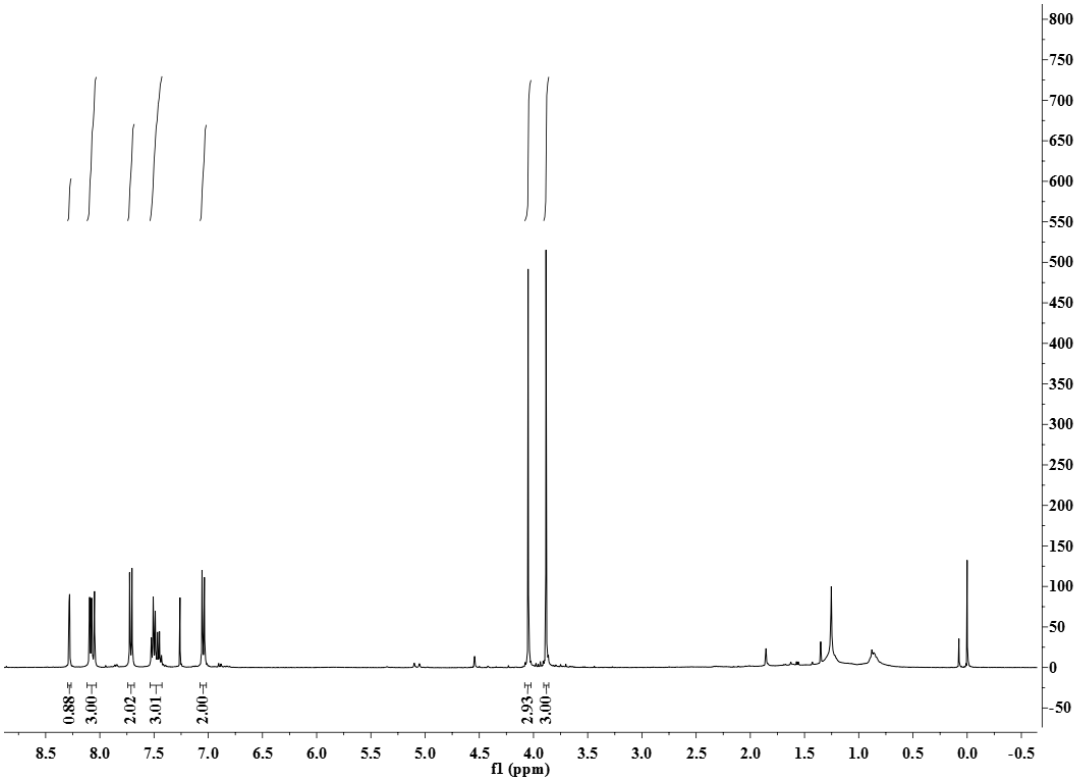
3ac

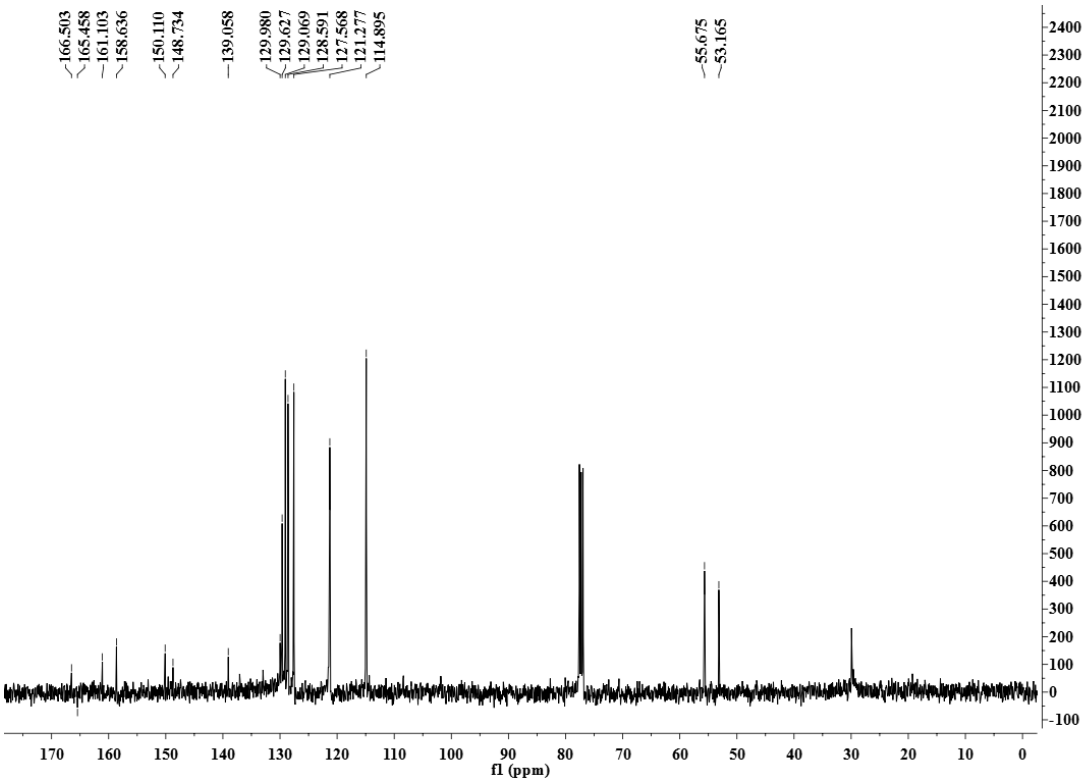

8.305
8.301
8.109
8.105
8.087
8.083
7.539
7.535
7.518
7.514
7.499
7.480
7.476
7.462
7.455
7.436
7.341
7.321
7.048
7.044
7.030
7.023
4.059
3.910
0.91
3.12
4.45
1.13
1.04
0.93
2.94
3.00
f1 (ppm)

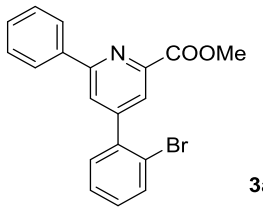

166.162
160.264
158.484
150.379
148.595
139.116
130.355
129.507
128.892
127.361
121.826
121.694
119.634
119.566
114.862
112.858
55.499
52.987
f1 (ppm)


N
COOMe
OMe

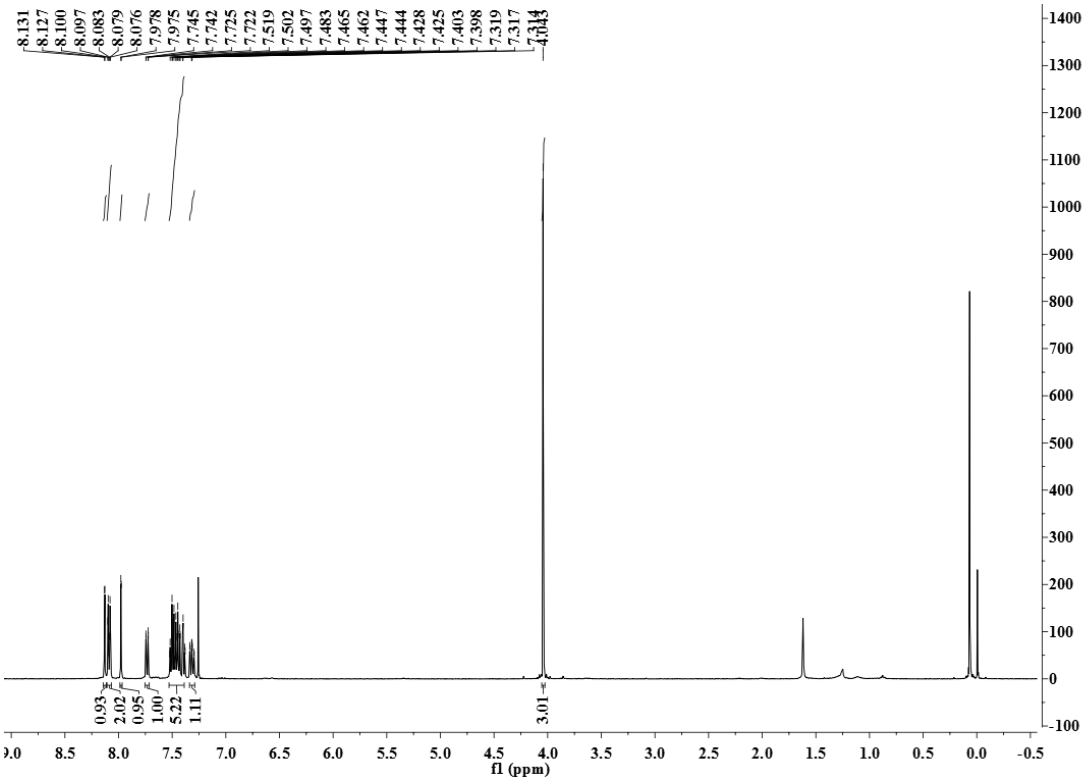
3ad

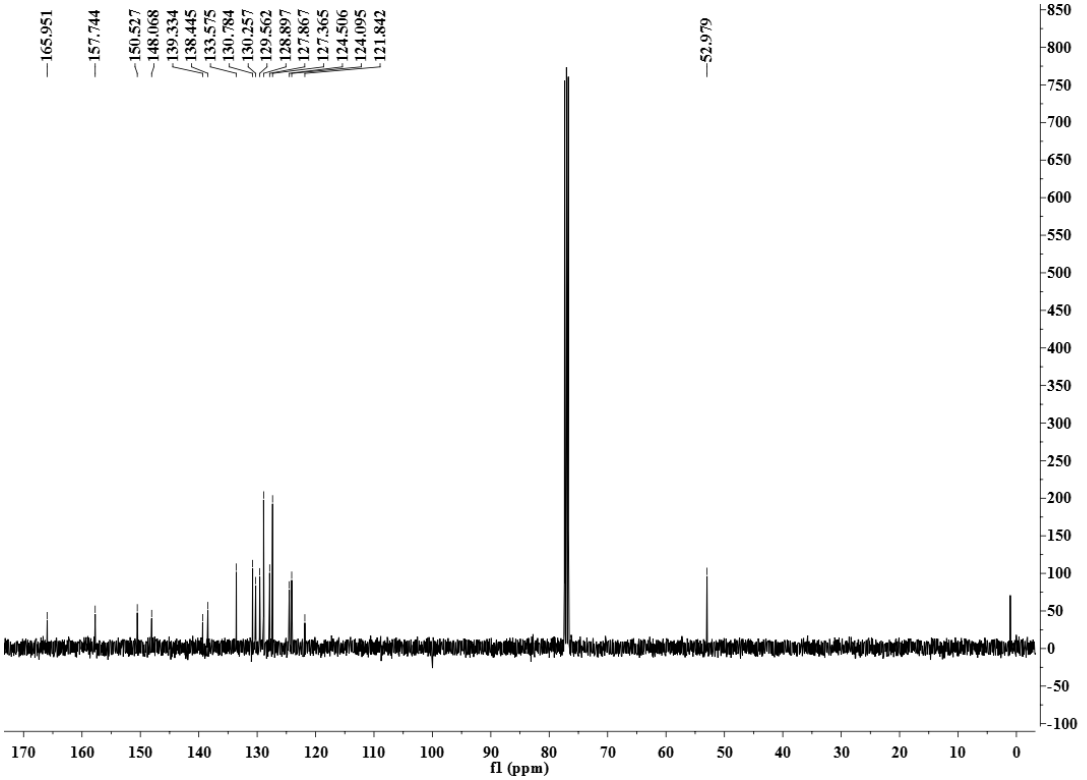

0.88
3.00
2.02
3.01
2.00
2.93
3.00
f1 (ppm)

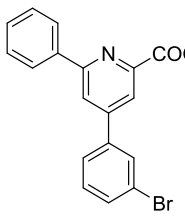

166.503
165.458
161.103
158.636
150.110
148.734
139.058
129.980
129.627
129.069
128.591
127.568
121.277
114.895
55.675
53.165
f1 (ppm)


N
COOMe
Br

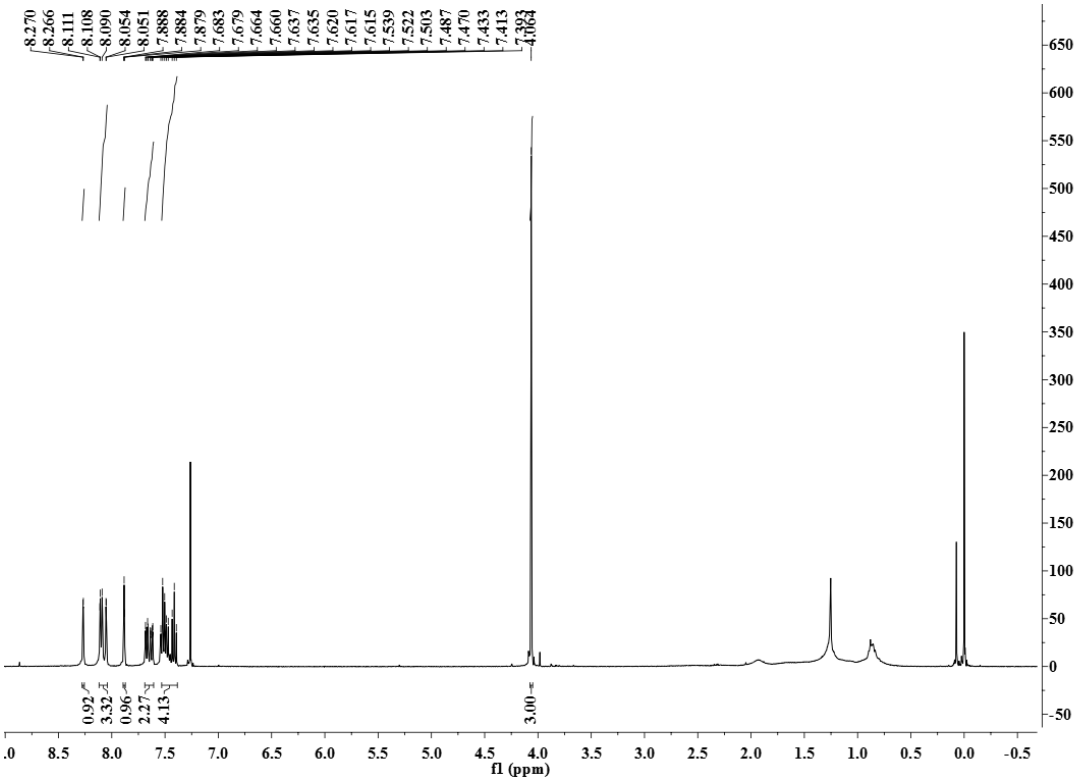
3ae

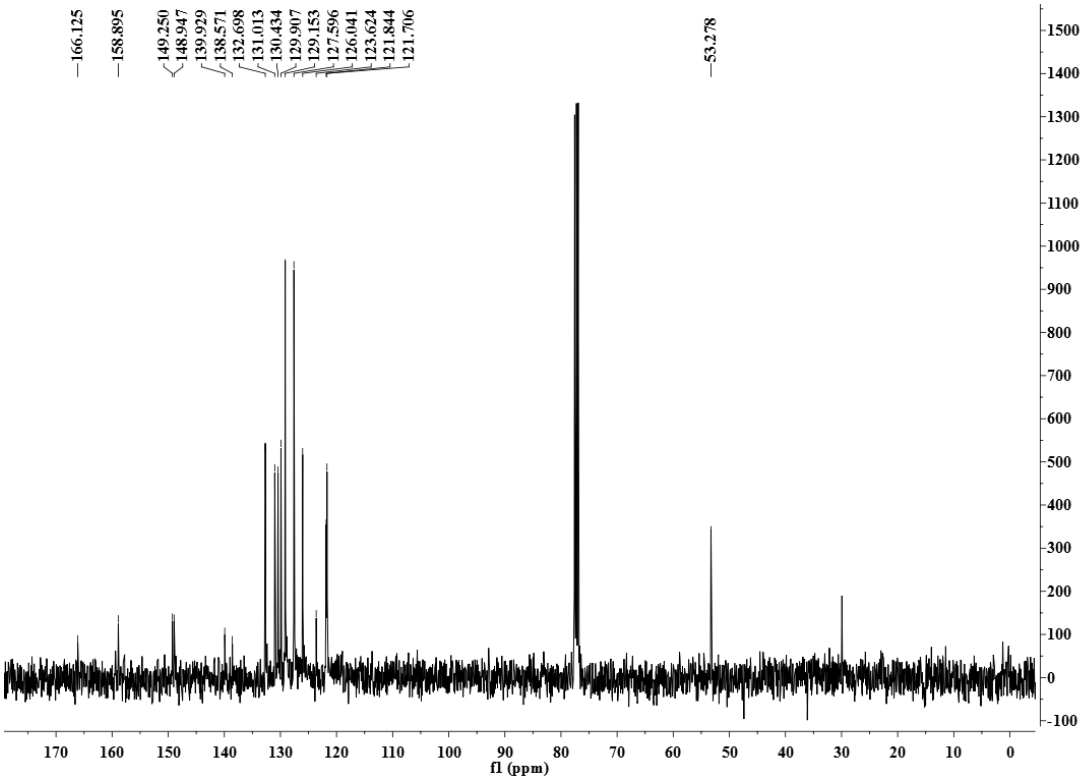

8.131
8.127
8.100
8.097
8.083
8.079
8.076
7.978
7.975
7.745
7.742
7.725
7.722
7.519
7.502
7.497
7.483
7.465
7.462
7.447
7.444
7.428
7.425
7.403
7.398
7.319
7.317
7.314
7.043
0.93
2.02
0.95
1.00
5.22
1.11
3.01
f1 (ppm)

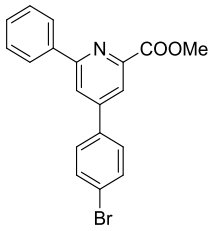

165.951
157.744
150.527
148.068
139.334
138.445
133.575
130.784
130.257
129.562
128.897
127.867
127.365
124.506
124.095
121.842
52.979
f1 (ppm)


N
COOMe
Br

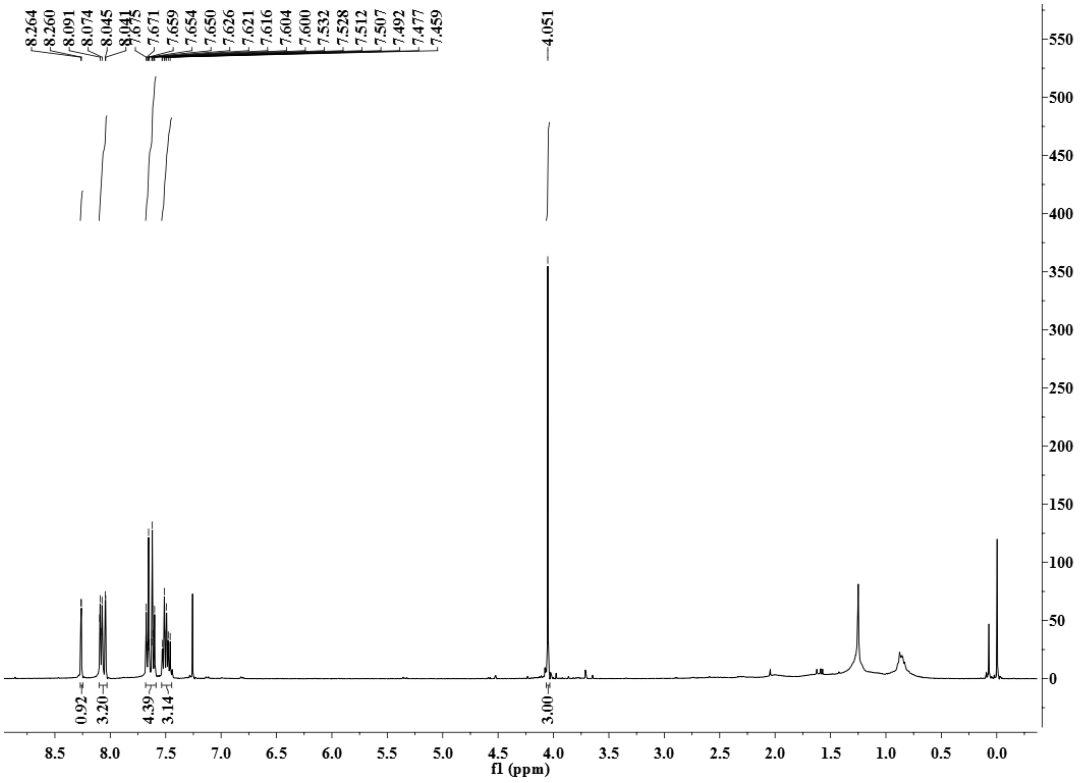
3af

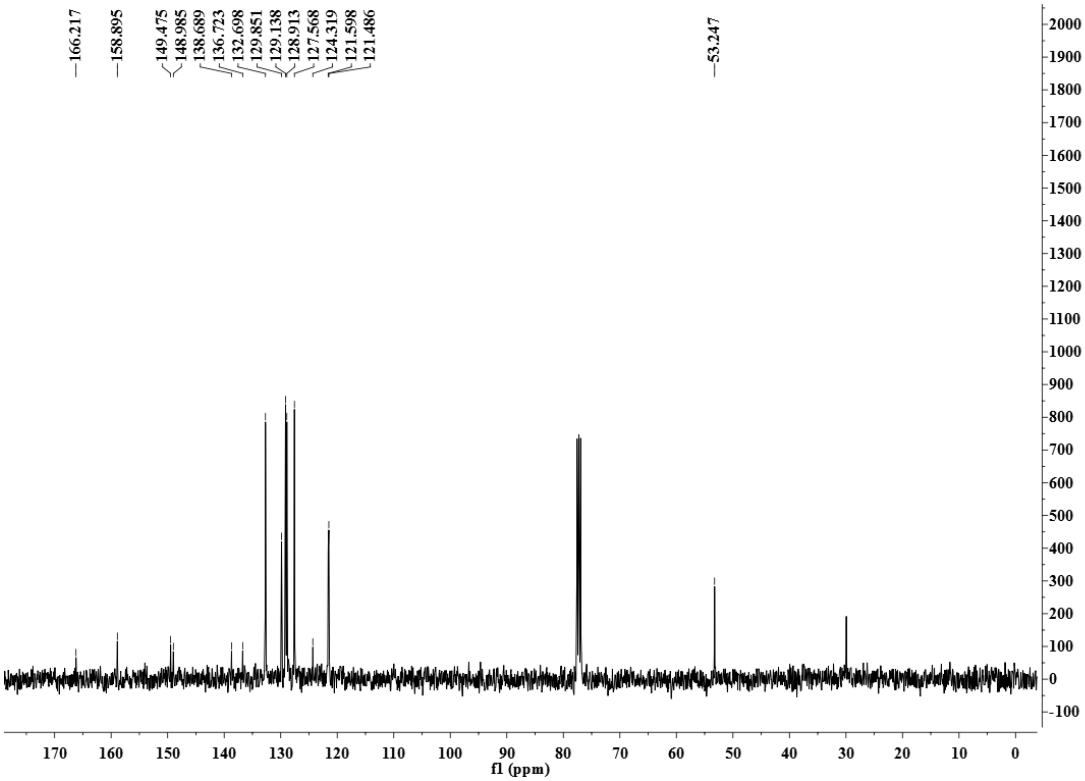

8.270
8.266
8.111
8.108
8.090
8.054
8.051
7.888
7.884
7.879
7.683
7.679
7.664
7.660
7.637
7.635
7.620
7.617
7.615
7.539
7.522
7.503
7.487
7.470
7.433
7.413
7.393
7.364
0.92
3.32
0.96
2.27
4.13
3.00
f1 (ppm)

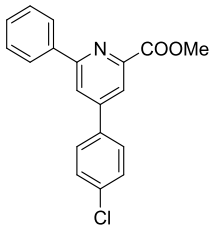

166.125
158.895
149.250
148.947
139.929
138.571
132.698
131.013
130.434
129.907
129.153
127.596
126.041
123.624
121.844
121.706
53.278
f1 (ppm)


N
COOMe
Br

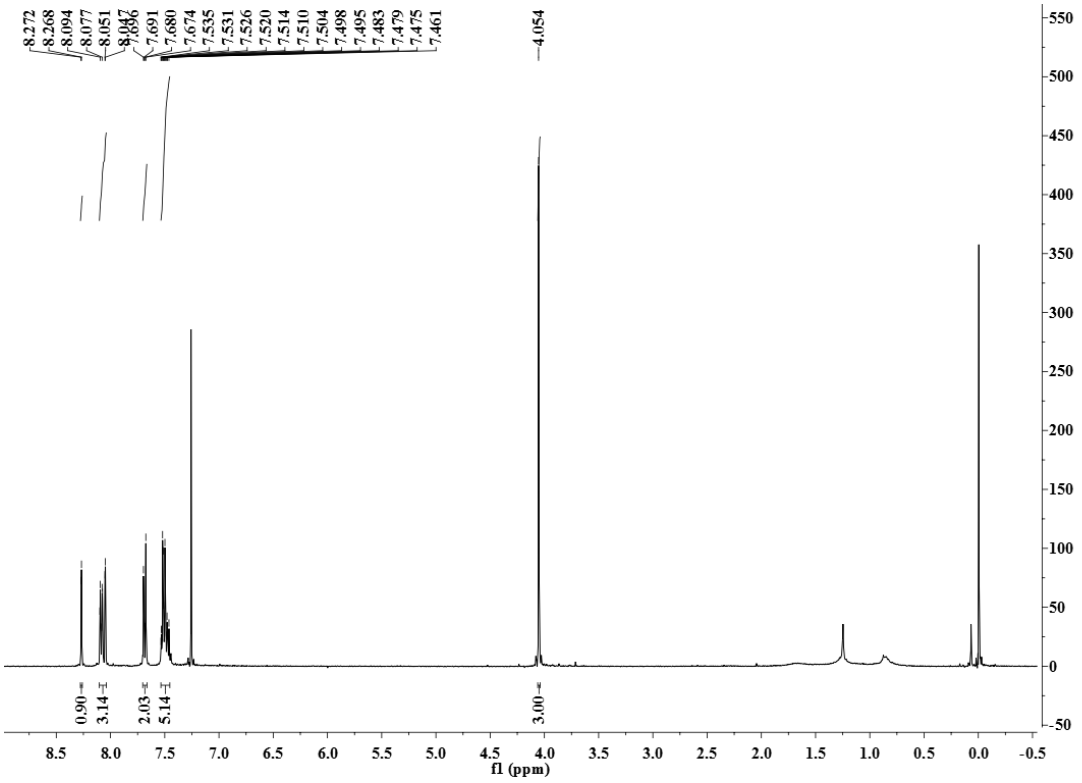
3ag

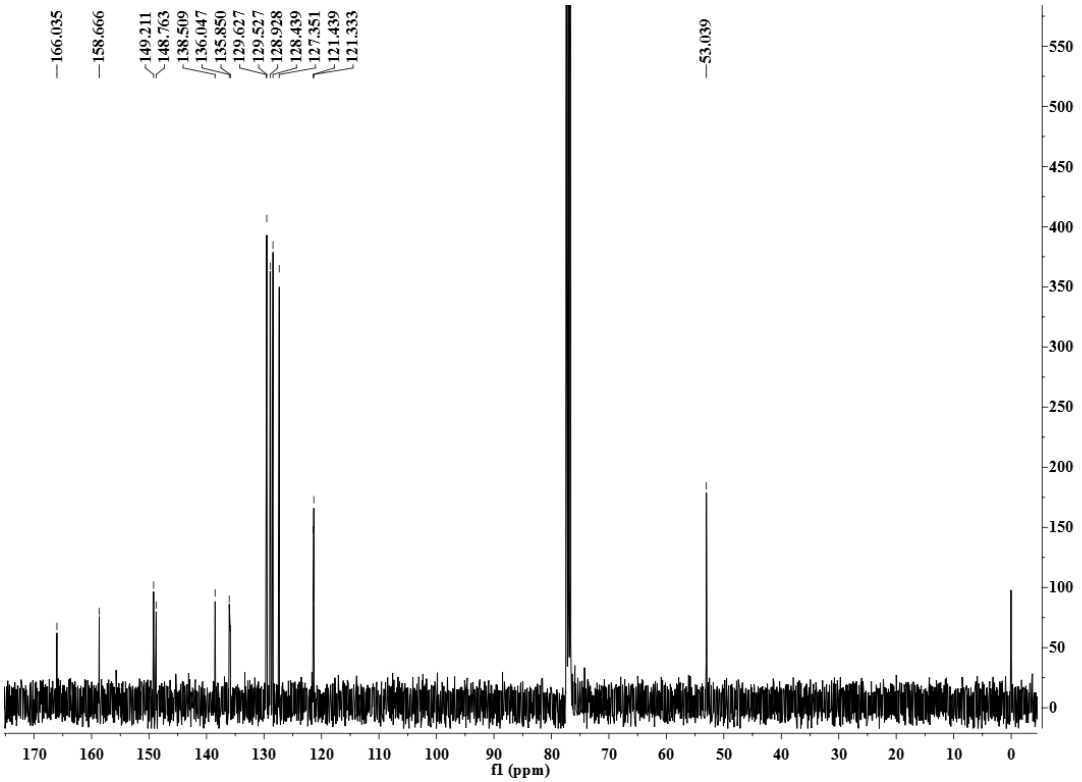

8.264
8.260
8.091
8.074
8.045
8.041
7.675
7.671
7.659
7.654
7.650
7.626
7.621
7.616
7.604
7.600
7.532
7.528
7.512
7.507
7.492
7.477
7.459
4.051
0.92
3.20
4.39
3.14
3.00
f1 (ppm)

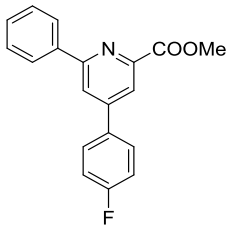

166.217
158.895
149.475
148.985
138.689
136.723
132.698
129.851
129.138
128.913
127.568
124.319
121.598
121.486
53.247
f1 (ppm)


N
COOMe
Cl

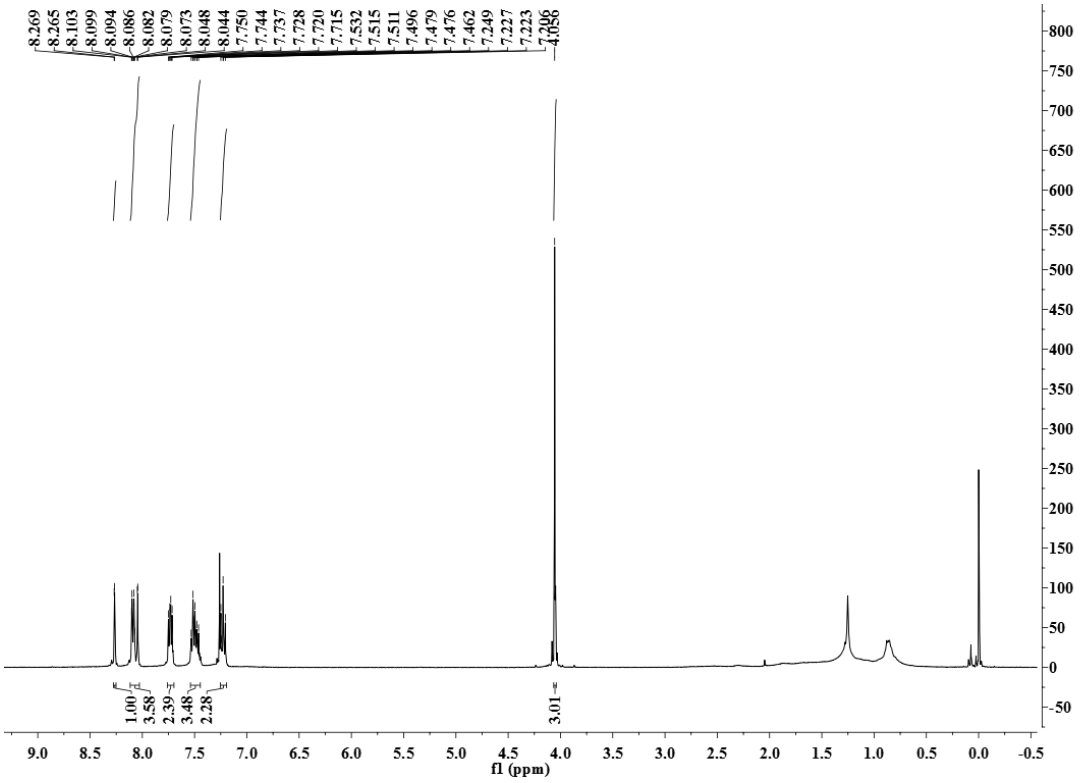
3ah

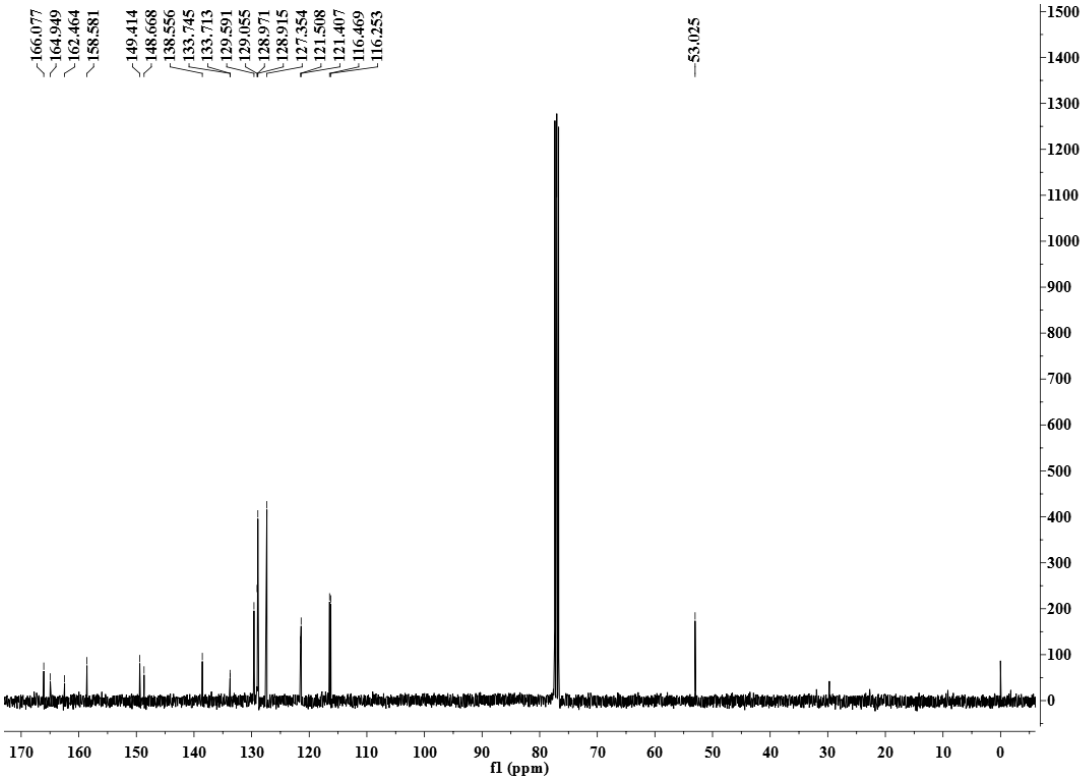

8.272
8.268
8.094
8.077
8.051
8.047
7.696
7.691
7.680
7.674
7.535
7.531
7.526
7.520
7.514
7.510
7.504
7.498
7.495
7.483
7.479
7.475
7.461
4.054
0.90
3.14
2.03
5.14
3.00
fl (ppm)

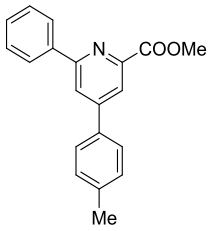

166.035
158.666
149.211
148.763
138.509
136.047
135.850
129.627
129.527
128.928
128.439
127.351
121.439
121.333
53.039
fl (ppm)


N
COOMe
F

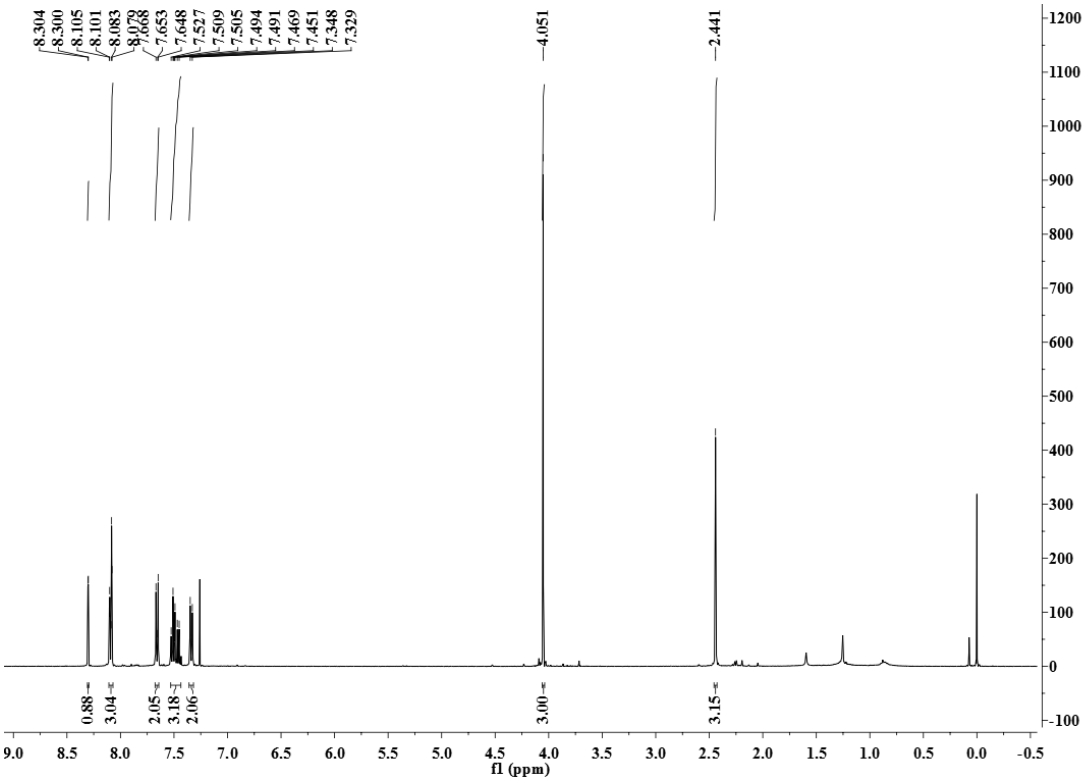
3ai

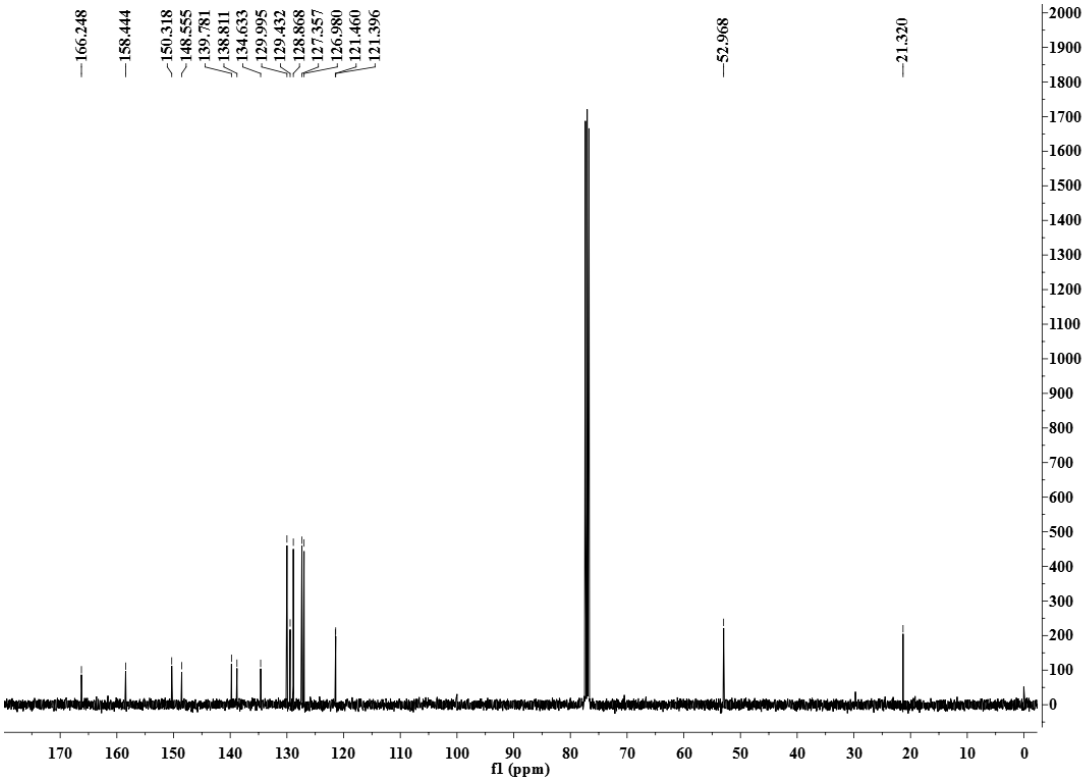

8.269
8.265
8.103
8.099
8.094
8.086
8.082
8.079
8.073
8.048
8.044
7.750
7.744
7.737
7.728
7.720
7.715
7.532
7.515
7.511
7.496
7.479
7.476
7.462
7.249
7.227
7.223
7.206
4.056
1.00
3.58
2.39
3.48
2.28
3.01
f1 (ppm)

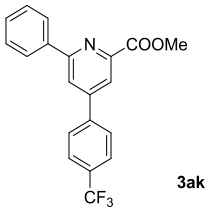

166.077
164.949
162.464
158.581
149.414
148.668
138.556
133.745
133.713
129.591
129.055
128.971
128.915
127.354
121.508
121.407
116.469
116.253
53.025
f1 (ppm)


N
COOMe
Me

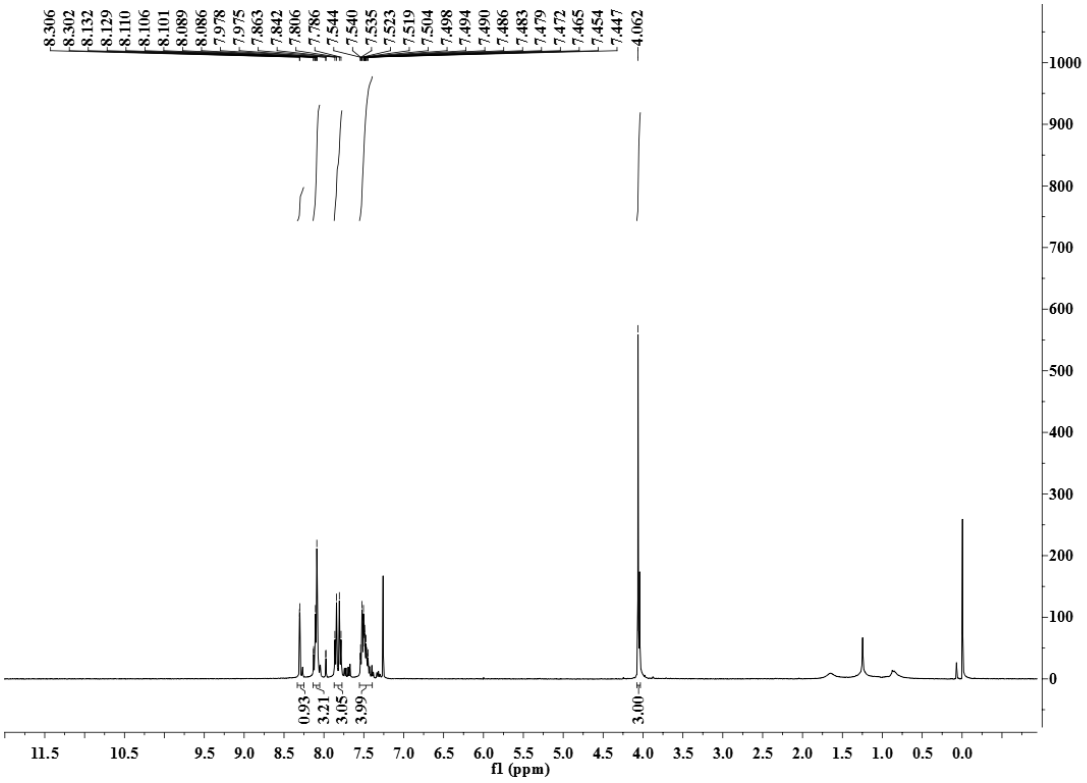
3aj

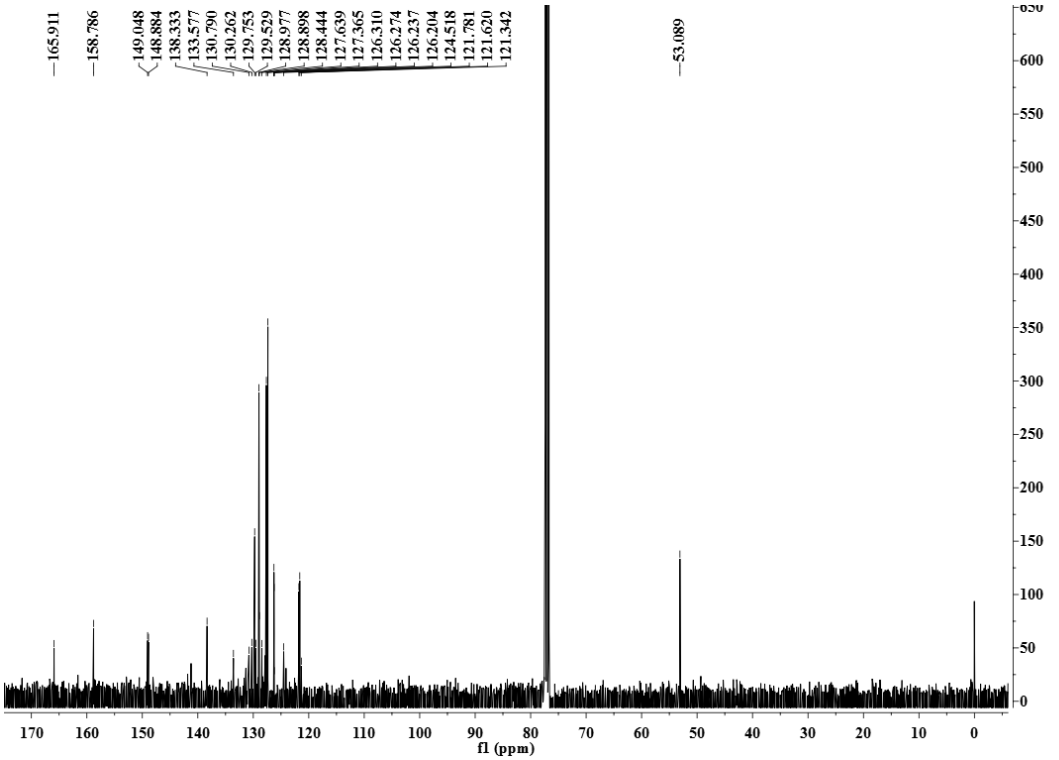

8.304
8.300
8.105
8.101
8.083
8.079
7.668
7.653
7.648
7.527
7.509
7.505
7.494
7.491
7.469
7.451
7.348
7.329
4.051
2.441
0.88
3.04
2.05
3.18
2.06
3.00
3.15
f1 (ppm)

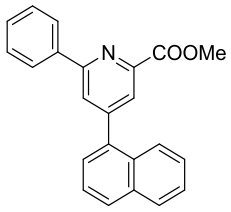

166.248
158.444
150.318
148.555
139.781
138.811
134.633
129.995
129.432
128.868
127.357
126.980
121.460
121.396
52.968
21.320
f1 (ppm)


N
COOMe
CF3

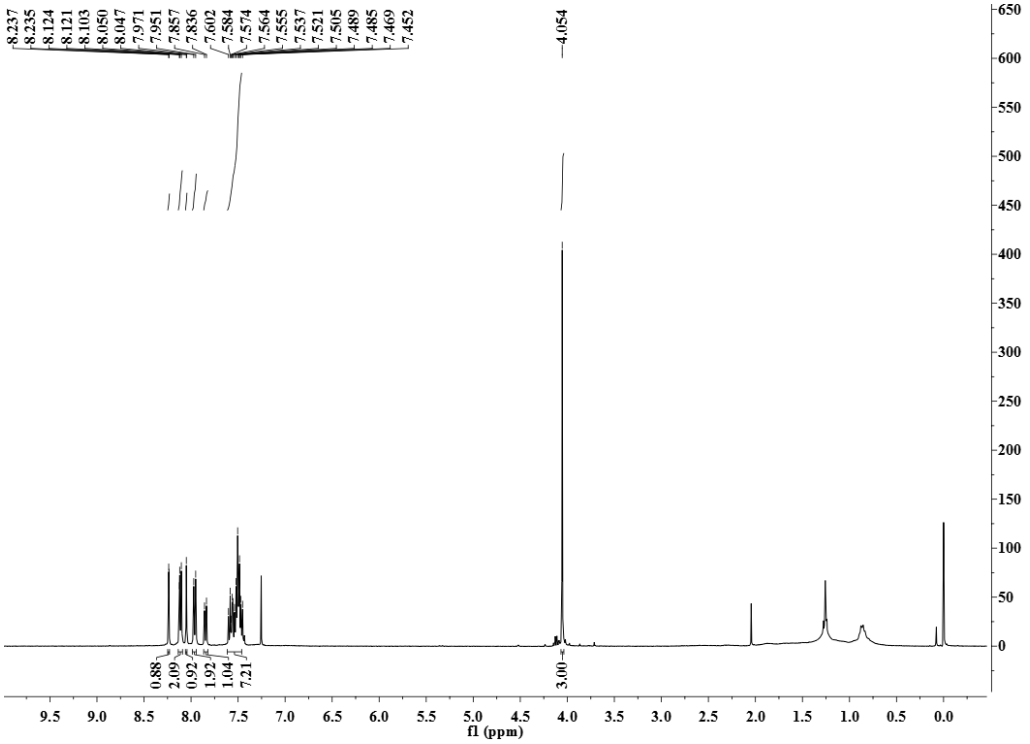
3ak

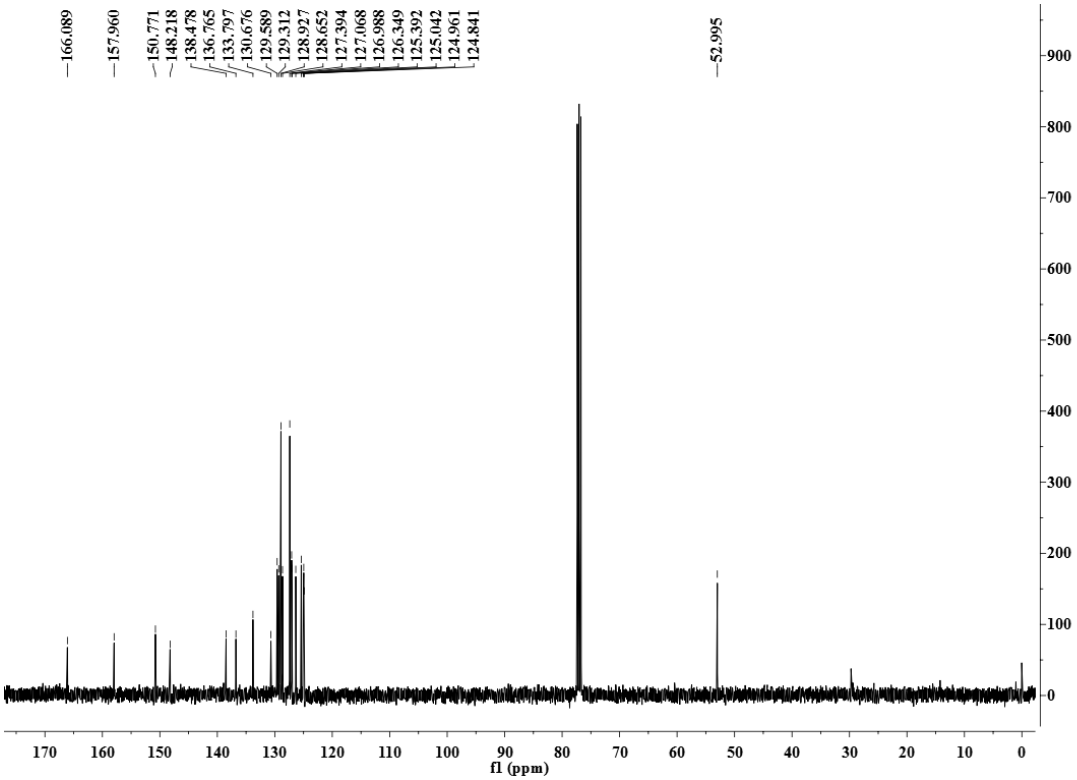

8.306
8.302
8.132
8.129
8.110
8.106
8.101
8.089
8.086
7.978
7.975
7.863
7.842
7.806
7.786
7.544
7.540
7.535
7.523
7.519
7.504
7.498
7.494
7.490
7.486
7.483
7.479
7.472
7.465
7.454
7.447
4.062
0.93
3.21
3.05
3.99
3.00
f1 (ppm)

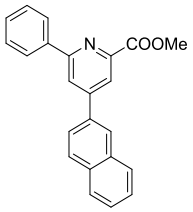

165.911
158.786
149.048
148.884
138.333
133.577
130.790
130.262
129.753
129.529
128.977
128.898
128.444
127.639
127.365
126.310
126.274
126.237
126.204
124.518
121.781
121.620
121.342
53.089
f1 (ppm)


N
COOMe

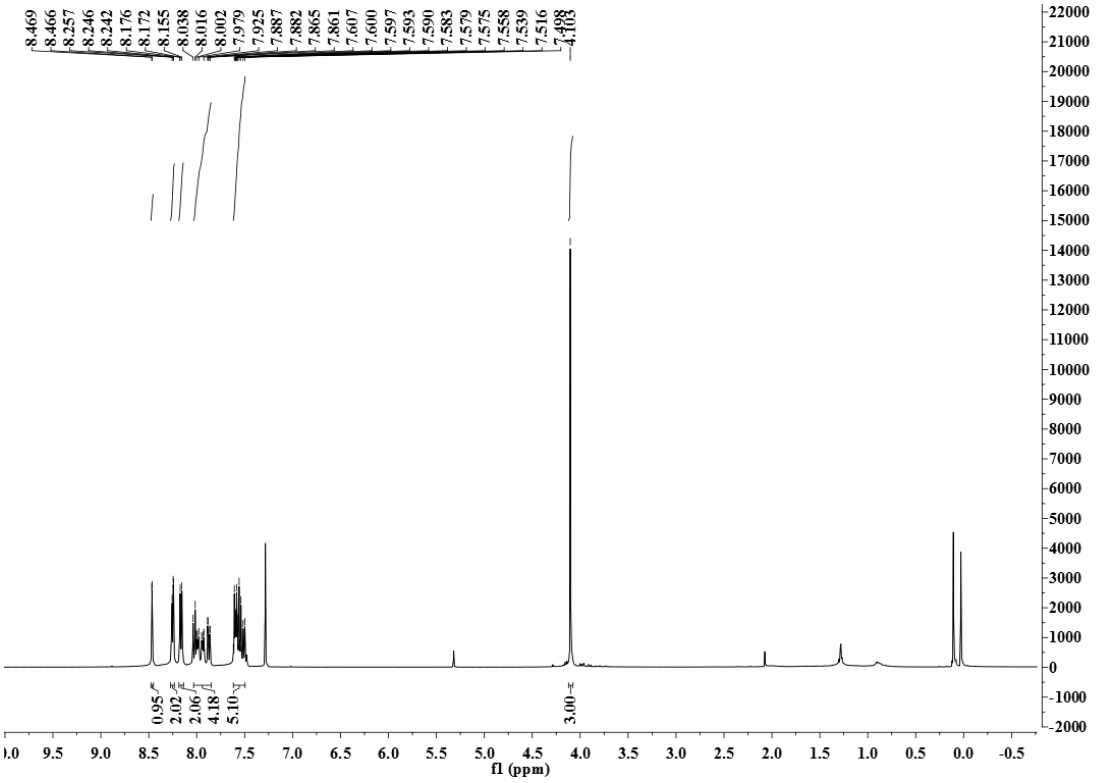
3al

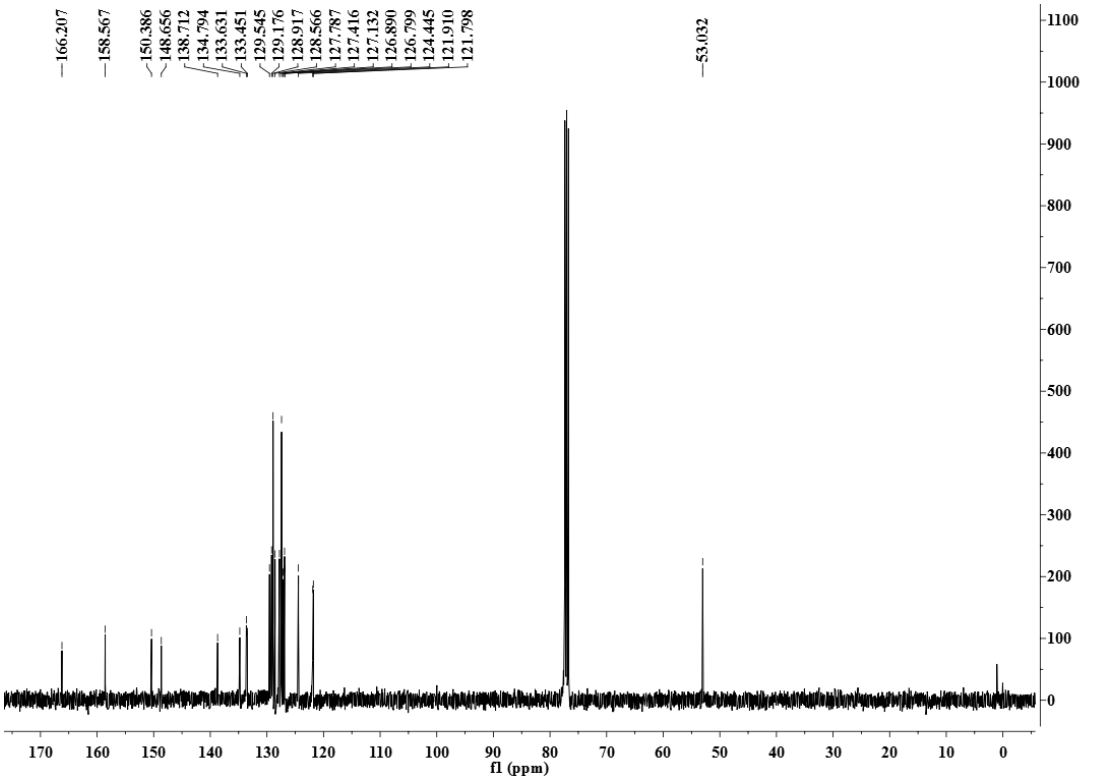

8.237
8.235
8.124
8.121
8.103
8.050
8.047
7.971
7.951
7.857
7.836
7.602
7.584
7.574
7.564
7.555
7.537
7.521
7.505
7.489
7.485
7.469
7.452
4.054
0.88
2.09
0.92
1.92
1.04
7.21
3.00
f1 (ppm)

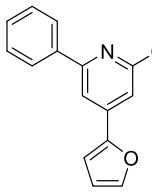

166.089
157.960
150.771
148.218
138.478
136.765
133.797
130.676
129.589
129.312
128.927
128.652
127.394
127.068
126.988
126.349
125.392
125.042
124.961
124.841
52.995
f1 (ppm)


N
COOMe

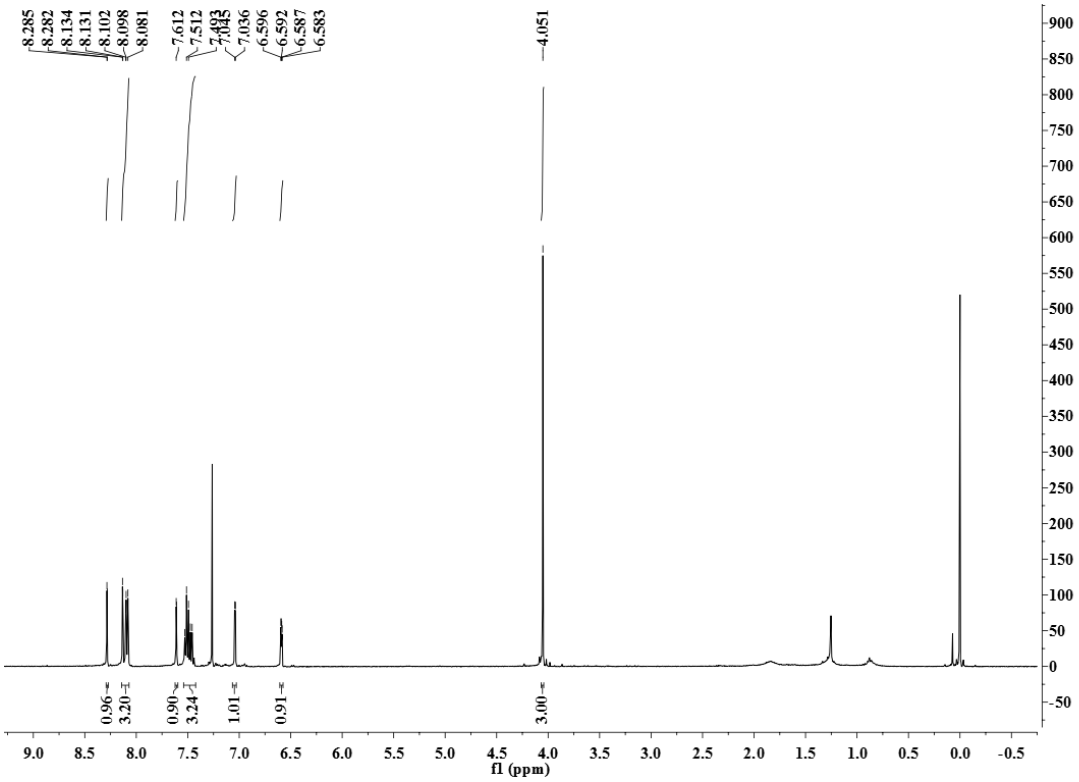
3am

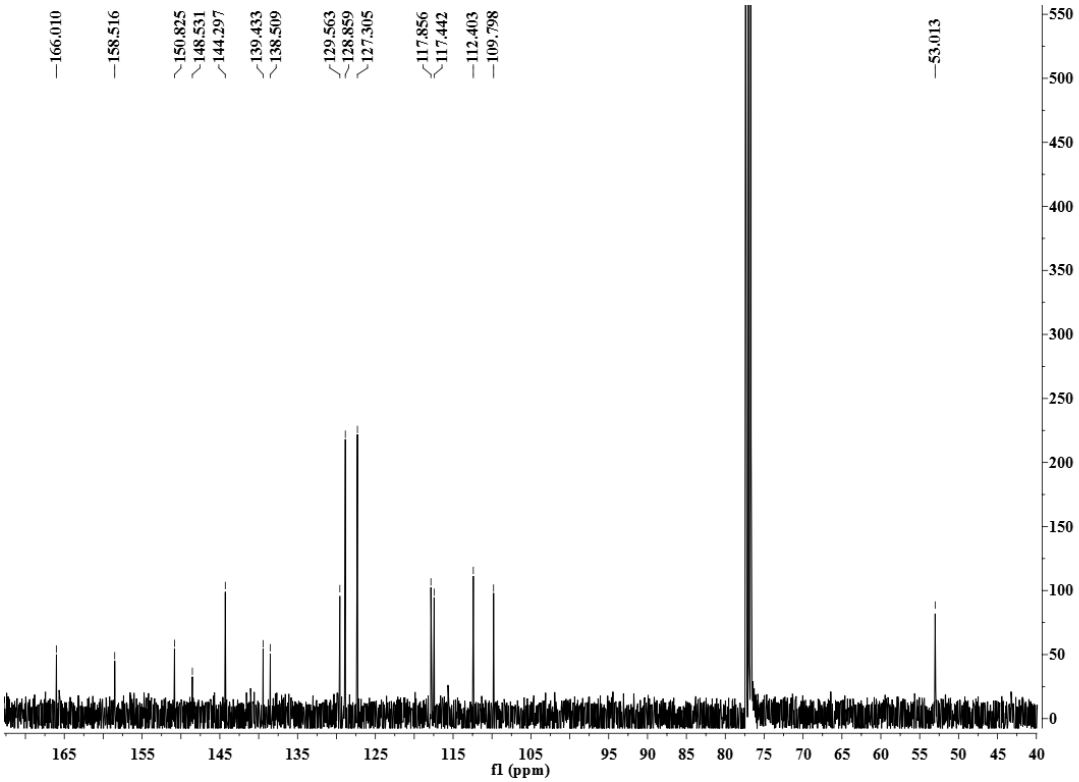

8.469
8.466
8.257
8.246
8.242
8.176
8.172
8.155
8.038
8.016
8.002
7.979
7.925
7.887
7.882
7.865
7.861
7.607
7.600
7.597
7.593
7.590
7.583
7.579
7.575
7.558
7.539
7.516
7.498
4.103
0.95
2.02
2.06
4.18
5.10
3.00
f1 (ppm)

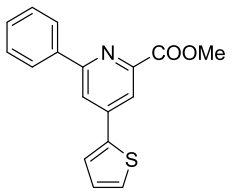

166.207
158.567
150.386
148.656
138.712
134.794
133.631
133.451
129.545
129.176
128.917
128.566
127.787
127.416
127.132
126.890
126.799
124.445
121.910
121.798
53.032
f1 (ppm)


N
COOMe
O

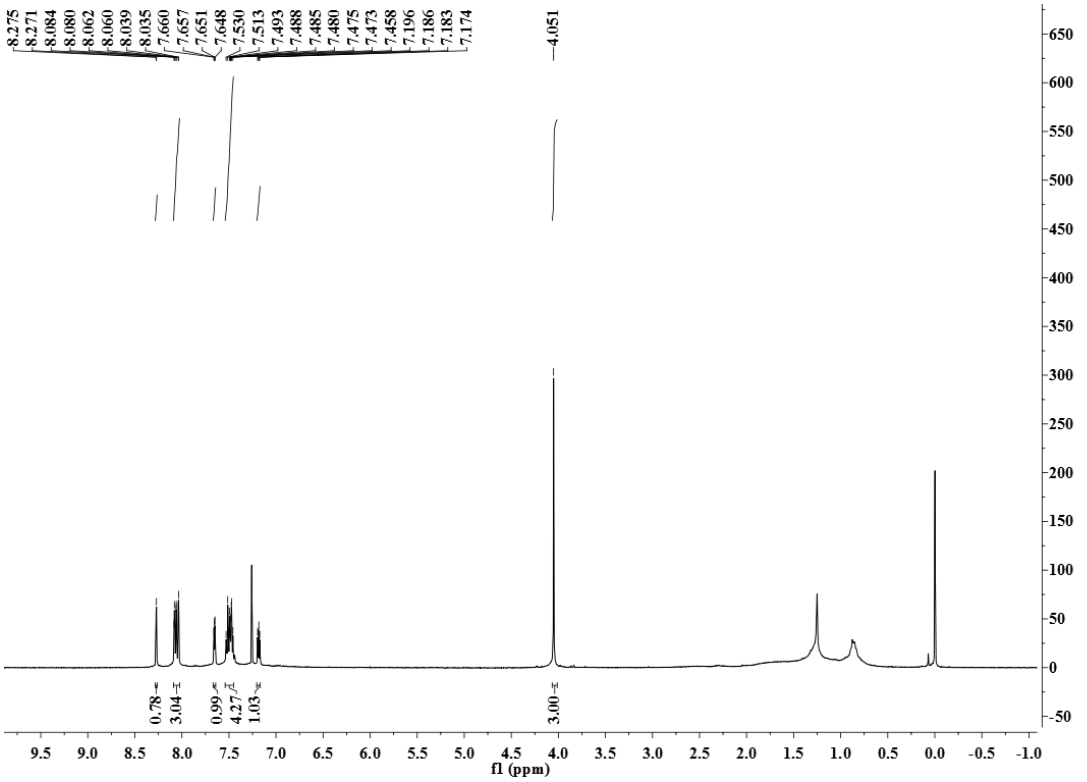
3an

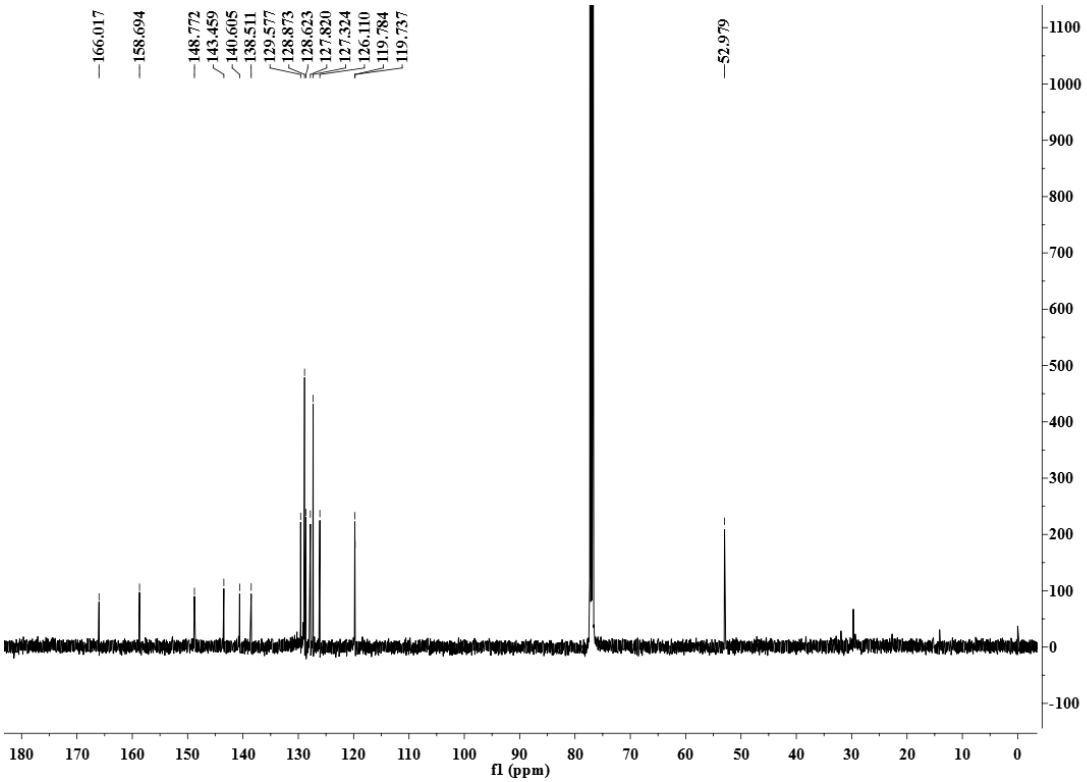

8.285
8.282
8.134
8.131
8.102
8.098
8.081
7.612
7.512
7.036
6.596
6.592
6.587
6.583
4.051
0.96
3.20
0.90
3.24
1.01
0.91
3.00
f1 (ppm)

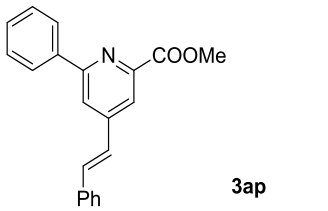

166.010
158.516
150.825
148.531
144.297
139.433
138.509
129.563
128.859
127.305
117.856
117.442
112.403
109.798
53.013
f1 (ppm)


N
COOMe
S

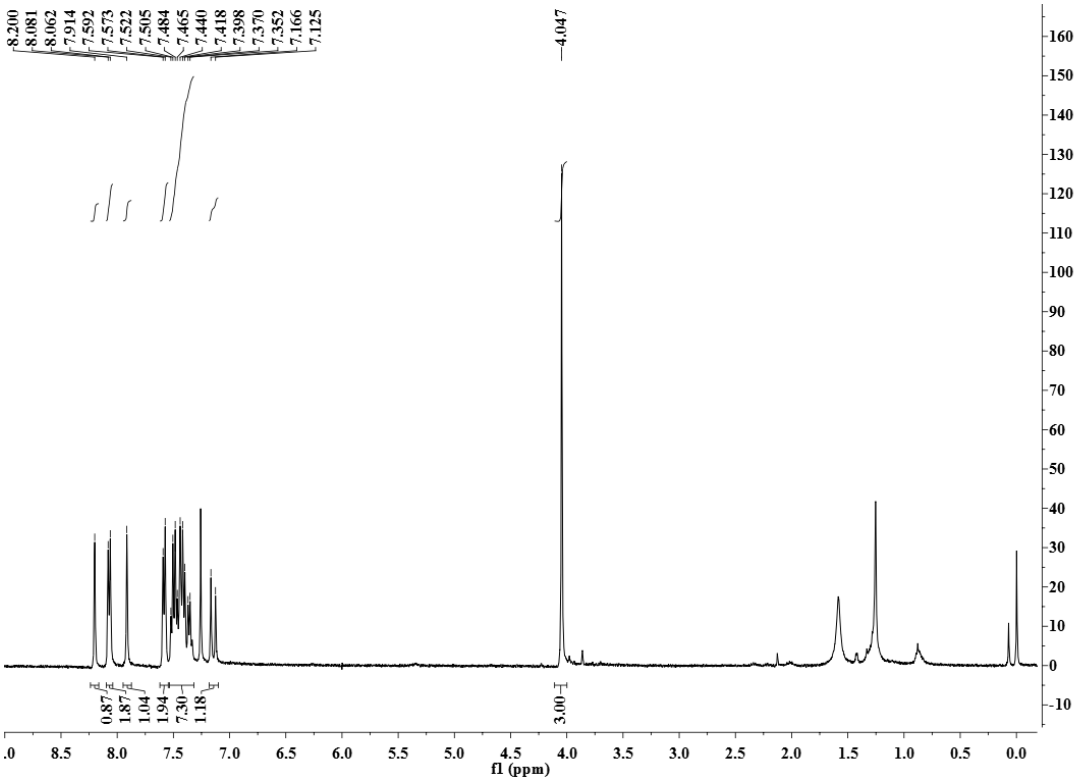
3ao

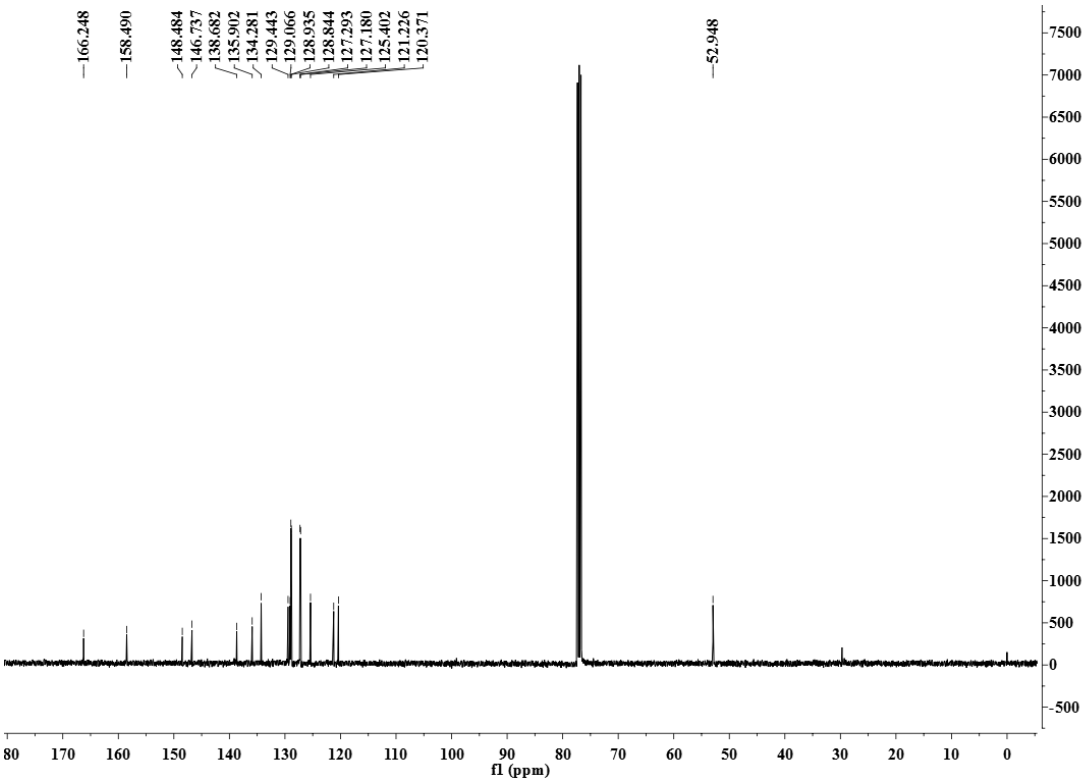

8.275
8.271
8.084
8.080
8.062
8.060
8.039
8.035
7.660
7.657
7.651
7.648
7.530
7.513
7.493
7.488
7.485
7.480
7.475
7.473
7.458
7.196
7.186
7.183
7.174
4.051
0.78
3.04
0.99
4.27
1.03
3.00
f1 (ppm)

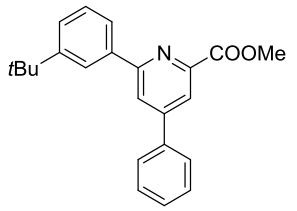

166.017
158.694
148.772
143.459
140.605
138.511
129.577
128.873
128.623
127.820
127.324
126.110
119.784
119.737
52.979
f1 (ppm)


N
COOMe
Ph

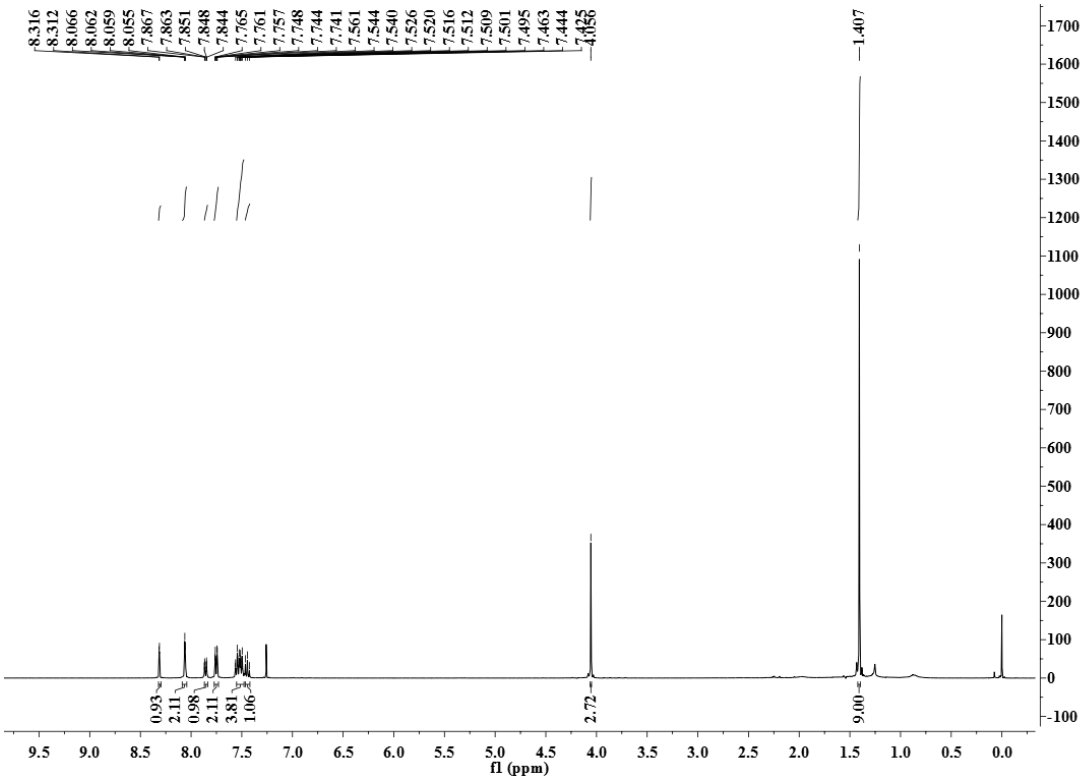
3ap

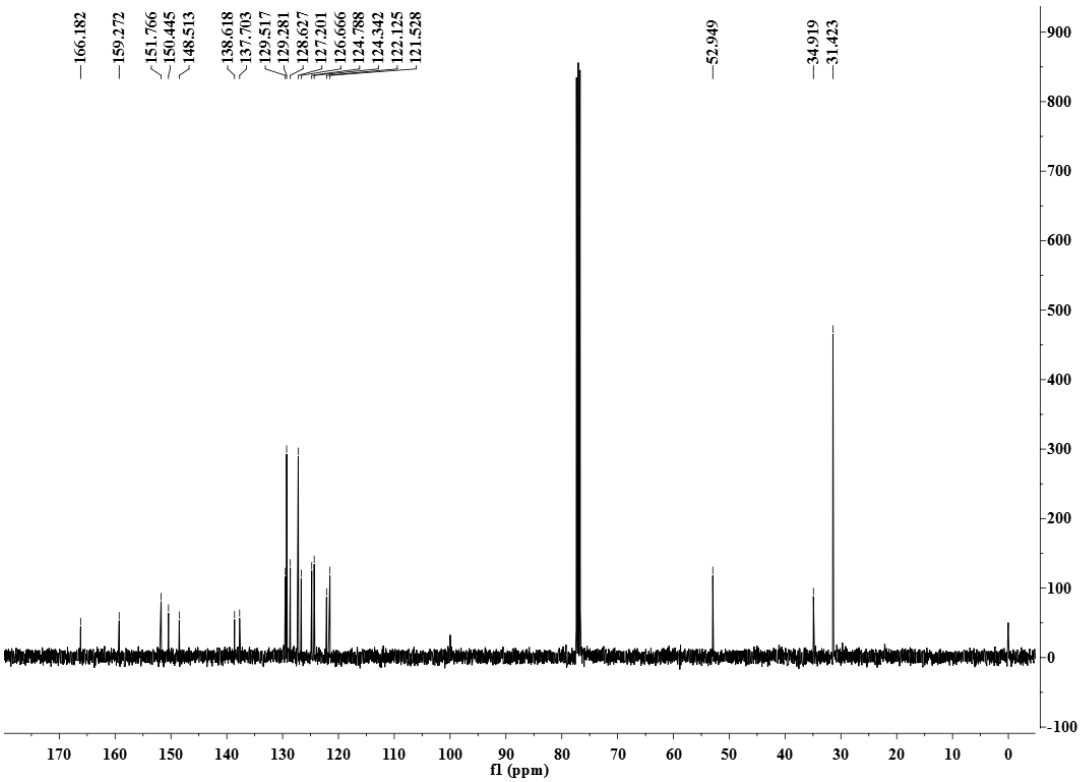

8.200
8.081
8.062
7.914
7.592
7.573
7.522
7.505
7.484
7.465
7.440
7.418
7.398
7.370
7.352
7.166
7.125
4.047
0.87
1.87
1.04
1.94
7.30
1.18
3.00
f1 (ppm)

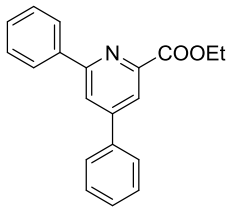

166.248
158.490
148.484
146.737
138.682
135.902
134.281
129.443
129.066
128.935
128.844
127.293
127.180
125.402
121.226
120.371
52.948
f1 (ppm)


tBu
N
COOMe

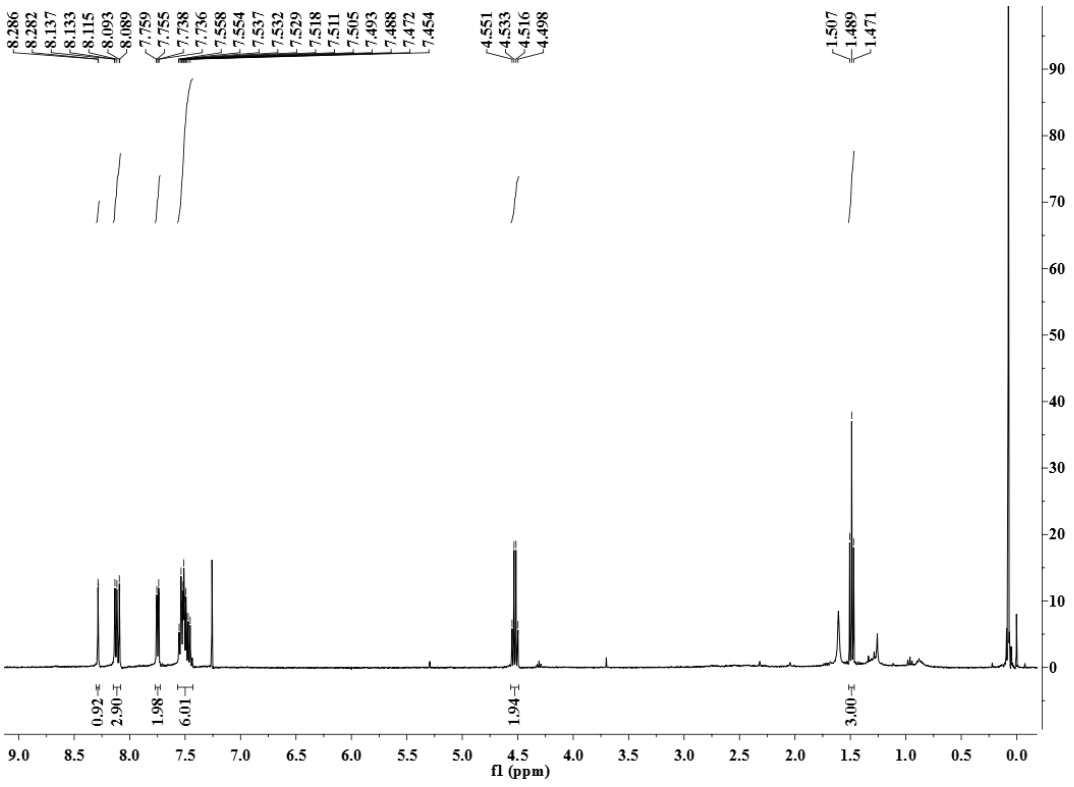
3aq

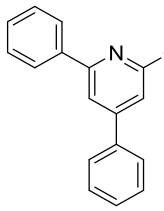

8.316
8.312
8.066
8.062
8.059
8.055
7.867
7.863
7.851
7.848
7.844
7.765
7.761
7.757
7.748
7.744
7.741
7.561
7.544
7.540
7.526
7.520
7.516
7.512
7.509
7.501
7.495
7.463
7.444
4.056
1.407
0.93
2.11
0.98
2.11
3.81
1.06
2.72
9.00
f1 (ppm)


166.182
159.272
151.766
150.445
148.513
138.618
137.703
129.517
129.281
128.627
127.201
126.666
124.788
124.342
122.125
121.528
52.949
34.919
31.423
f1 (ppm)

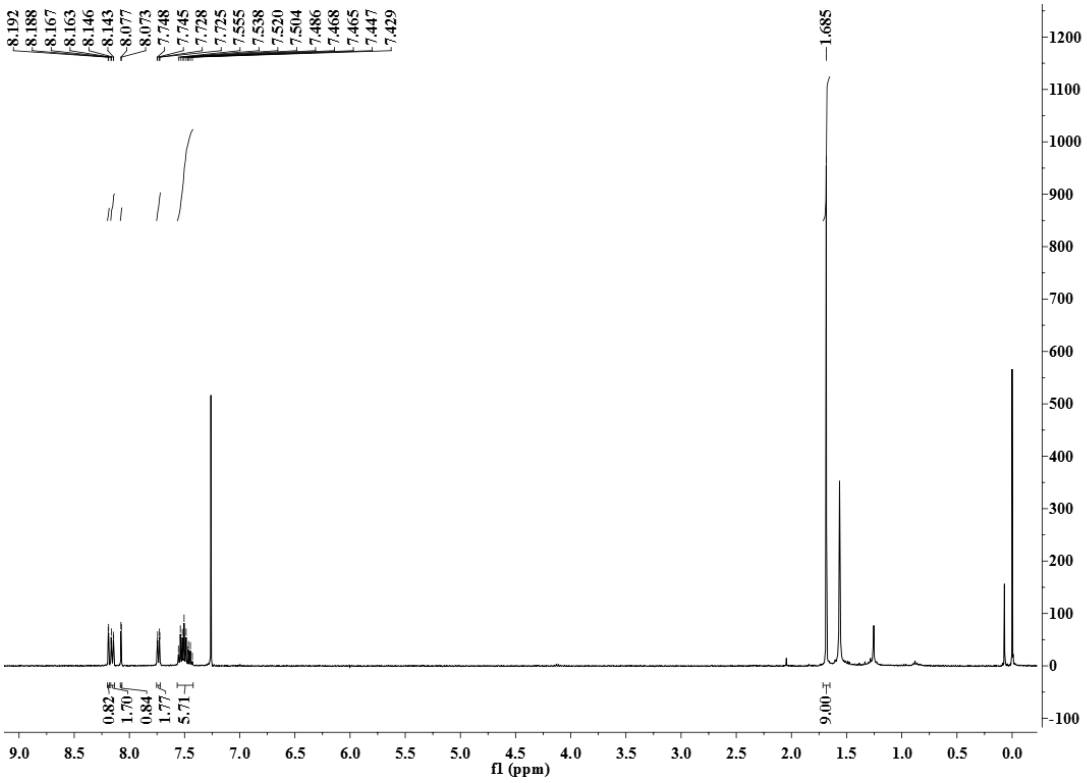

N
COOEt

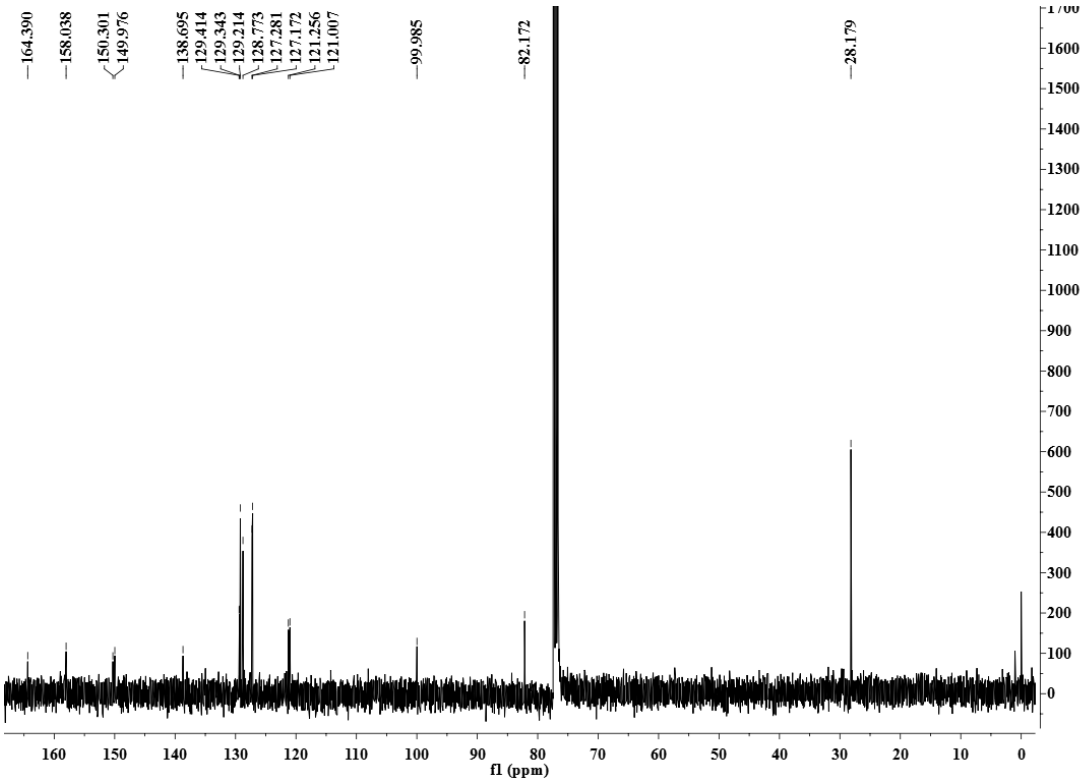
3ba

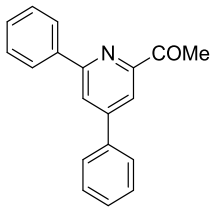

8.286
8.282
8.137
8.133
8.115
8.093
8.089
7.759
7.755
7.738
7.736
7.558
7.554
7.537
7.532
7.529
7.518
7.511
7.505
7.493
7.488
7.472
7.454
4.551
4.533
4.516
4.498
1.507
1.489
1.471
0.92
2.90
1.98
6.01
1.94
3.00
f1 (ppm)


N
COO*t*Bu

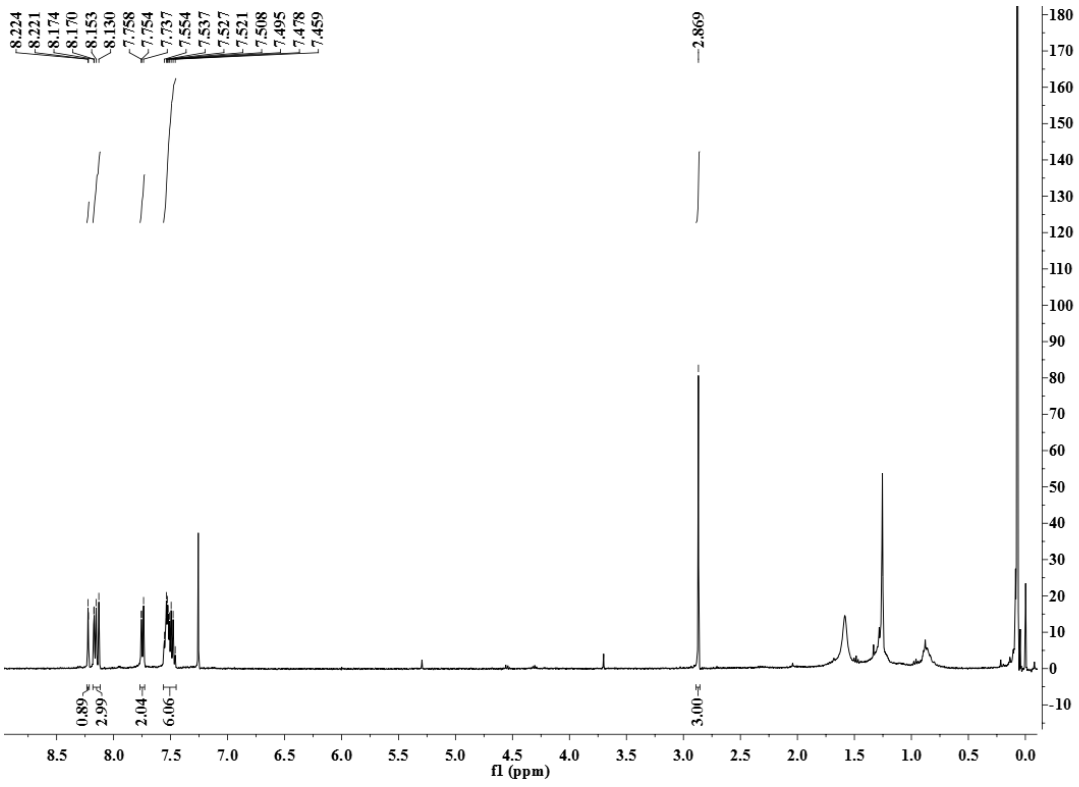
3ca

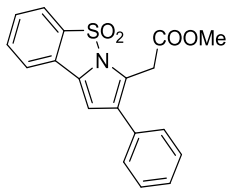

8.192
8.188
8.167
8.163
8.146
8.143
8.077
8.073
7.748
7.745
7.728
7.725
7.555
7.538
7.520
7.504
7.486
7.468
7.465
7.447
7.429
1.685
0.82
1.70
0.84
1.77
5.71
9.00
f1 (ppm)


164.390
158.038
150.301
149.976
138.695
129.414
129.343
129.214
128.773
127.281
127.172
121.256
121.007
99.985
82.172
28.179
f1 (ppm)

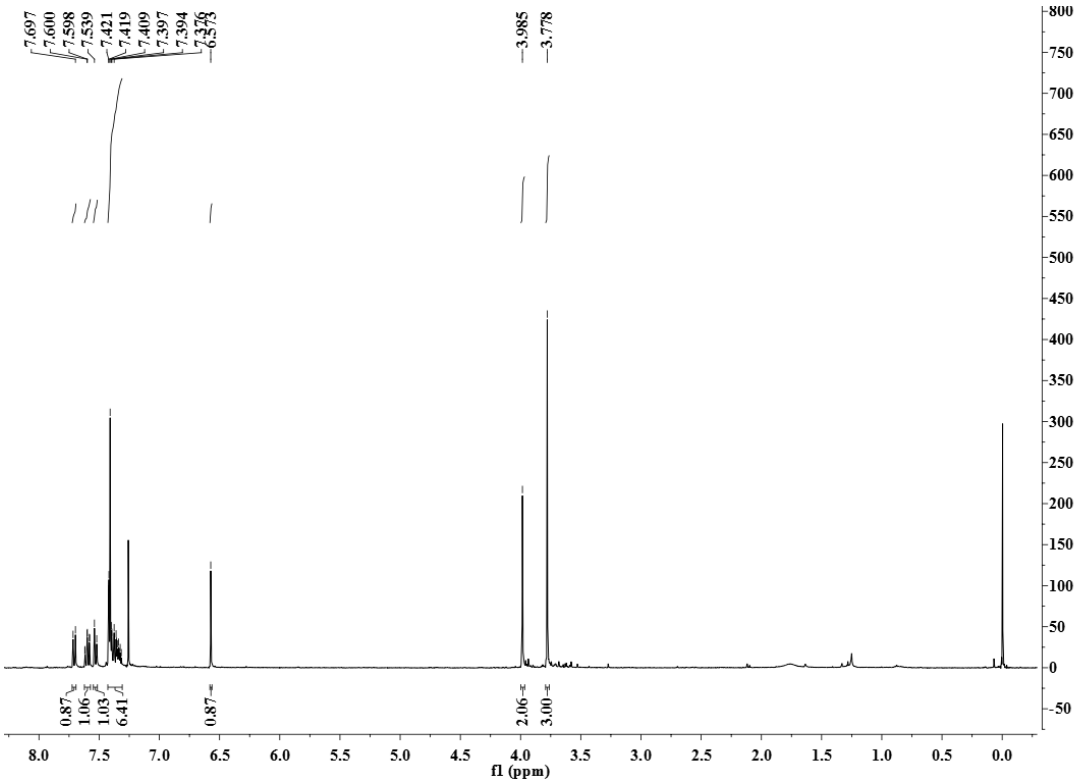

N
COMe

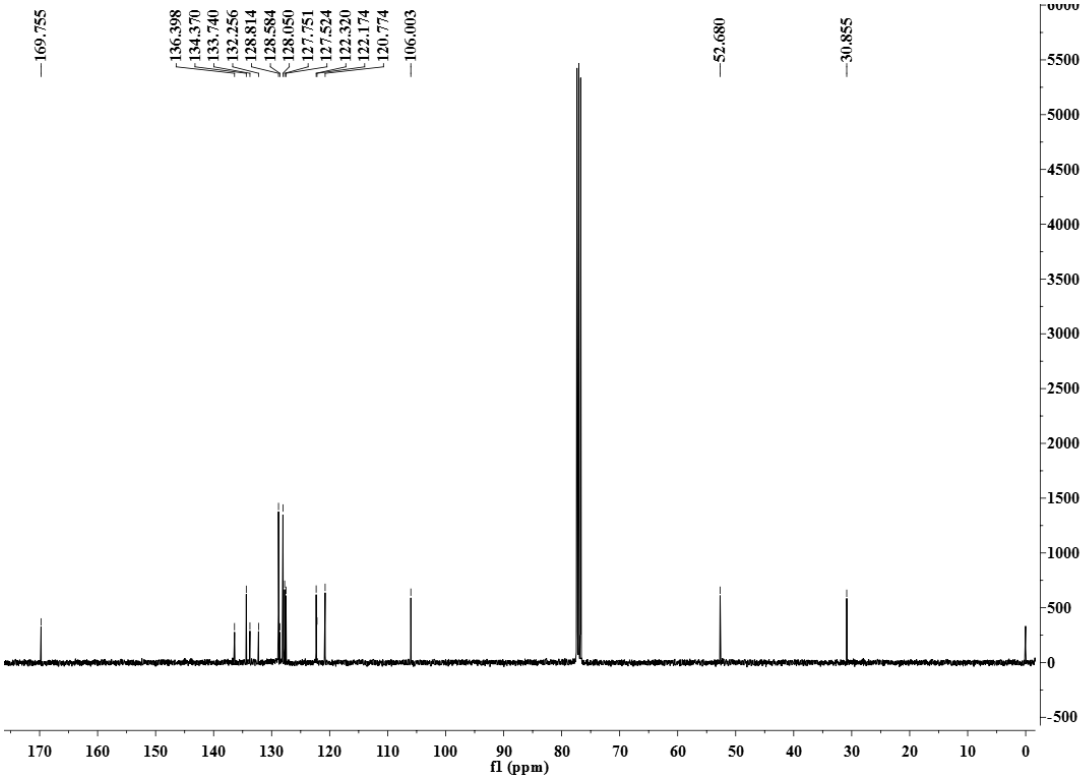
3da

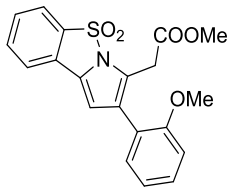

8.224
8.221
8.174
8.170
8.153
8.130
7.758
7.754
7.737
7.554
7.537
7.527
7.521
7.508
7.495
7.478
7.459
2.869
0.89
2.99
2.04
6.06
3.00
f1 (ppm)


SO2
N
COOMe

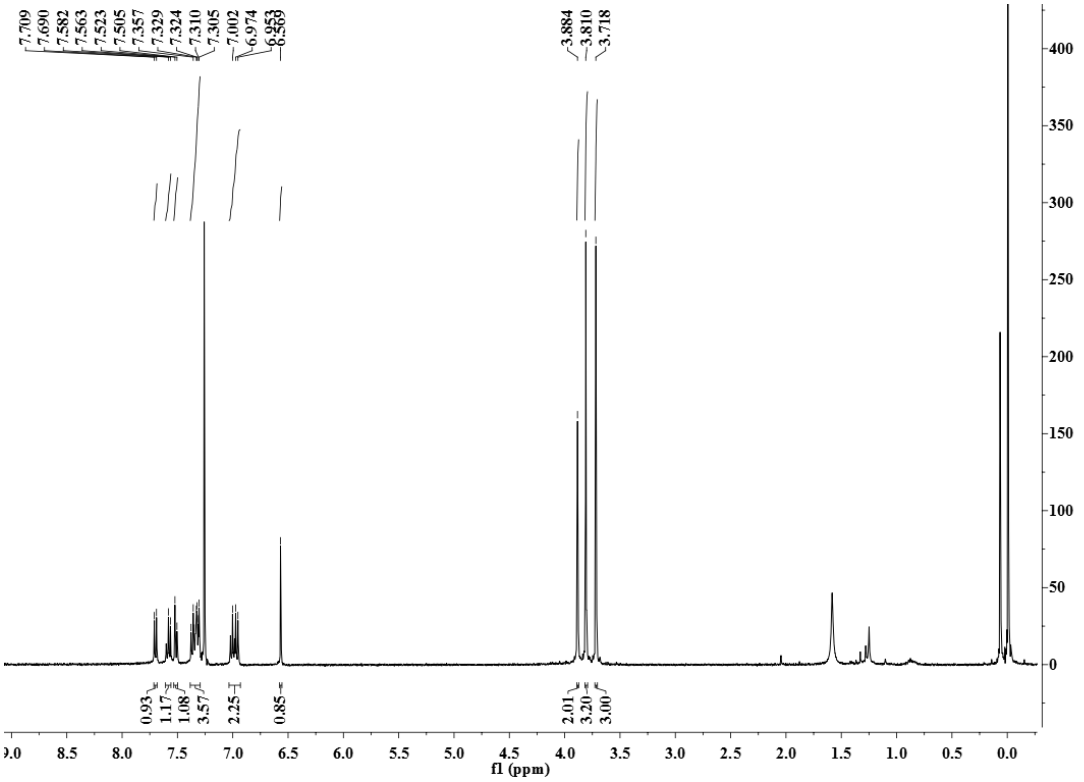
4aa

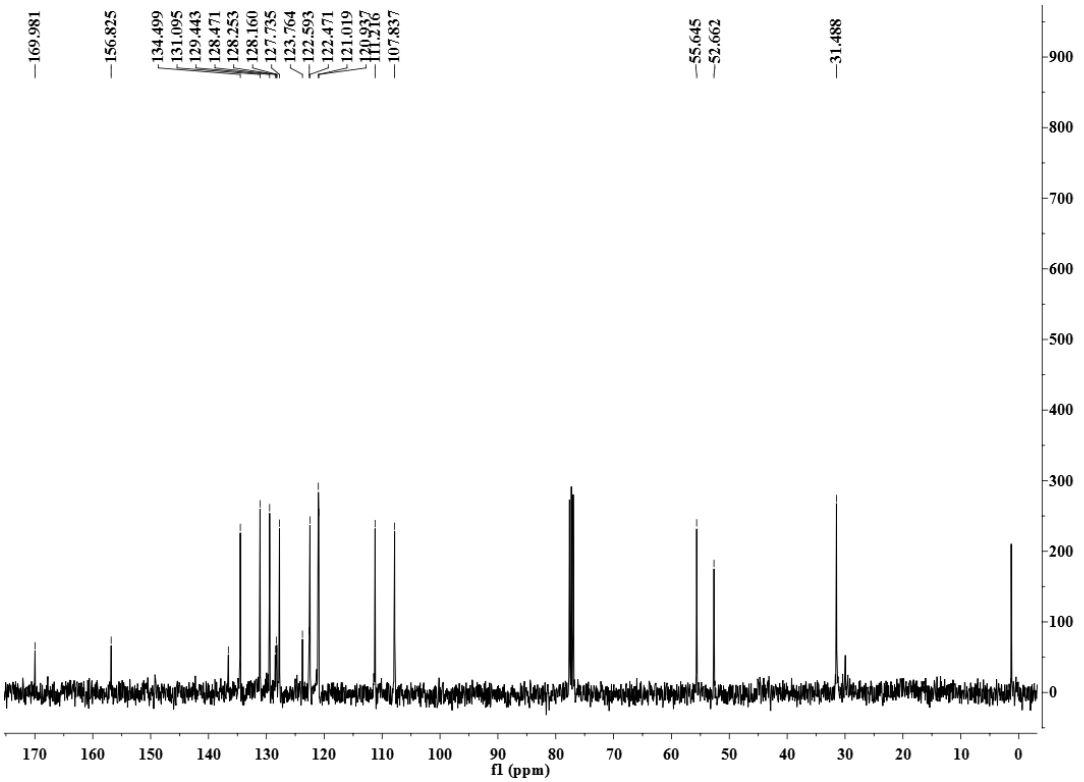

7.697
7.600
7.598
7.539
7.421
7.419
7.409
7.397
7.394
6.513
3.985
3.778
0.87
1.06
1.03
6.41
0.87
2.06
3.00
f1 (ppm)

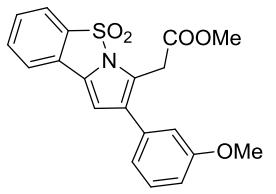

169.755
136.398
134.370
133.740
132.256
128.814
128.584
128.050
127.751
127.524
122.320
122.174
120.774
106.003
52.680
30.855
f1 (ppm)


SO2
N
COOMe
OMe

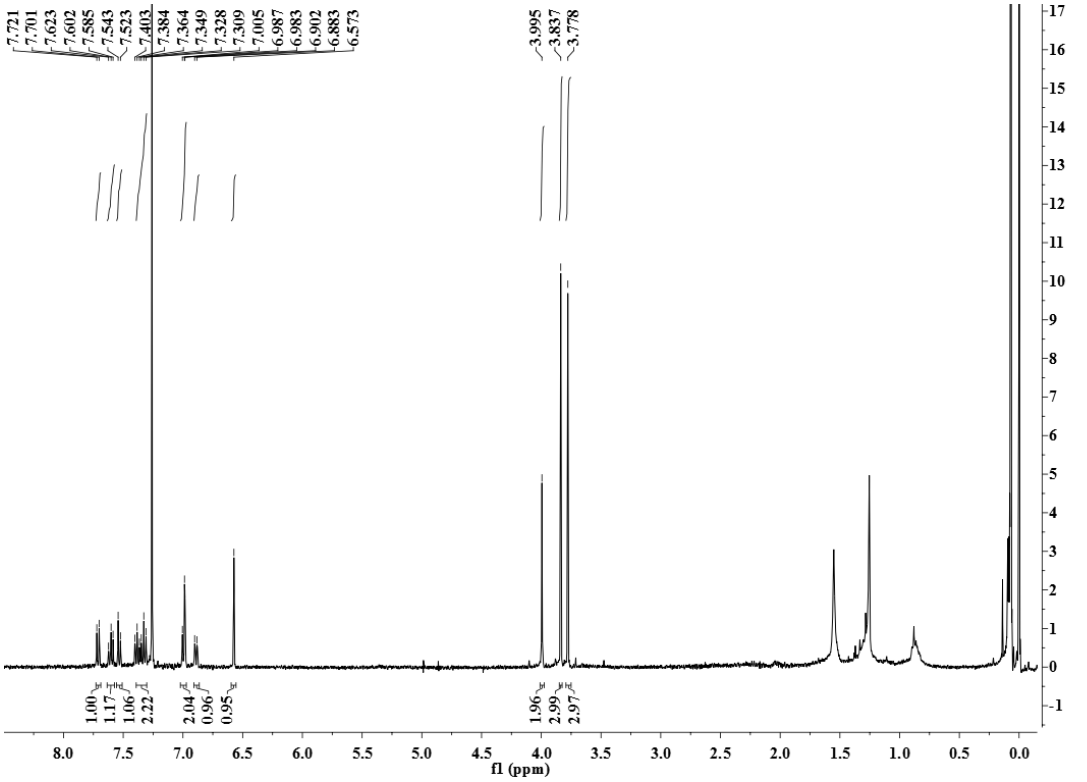
4ab

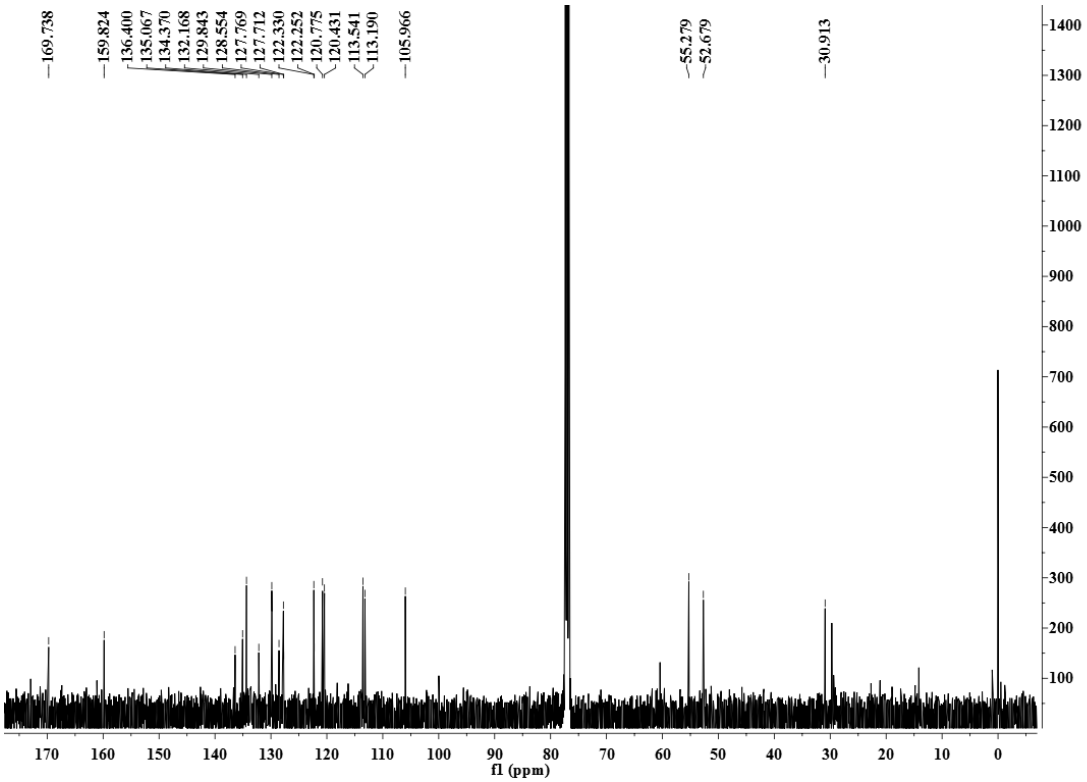

7.709
7.690
7.582
7.563
7.523
7.505
7.357
7.329
7.324
7.310
7.305
7.002
6.974
6.953
6.569
3.884
3.810
3.718
0.93
1.17
1.08
3.57
2.25
0.85
2.01
3.20
3.00
f1 (ppm)

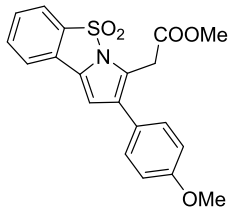

169.981
156.825
134.499
131.095
129.443
128.471
128.253
128.160
127.735
123.764
122.593
122.471
121.019
120.937
111.216
107.837
55.645
52.662
31.488
f1 (ppm)


SO2
N
COOMe
OMe

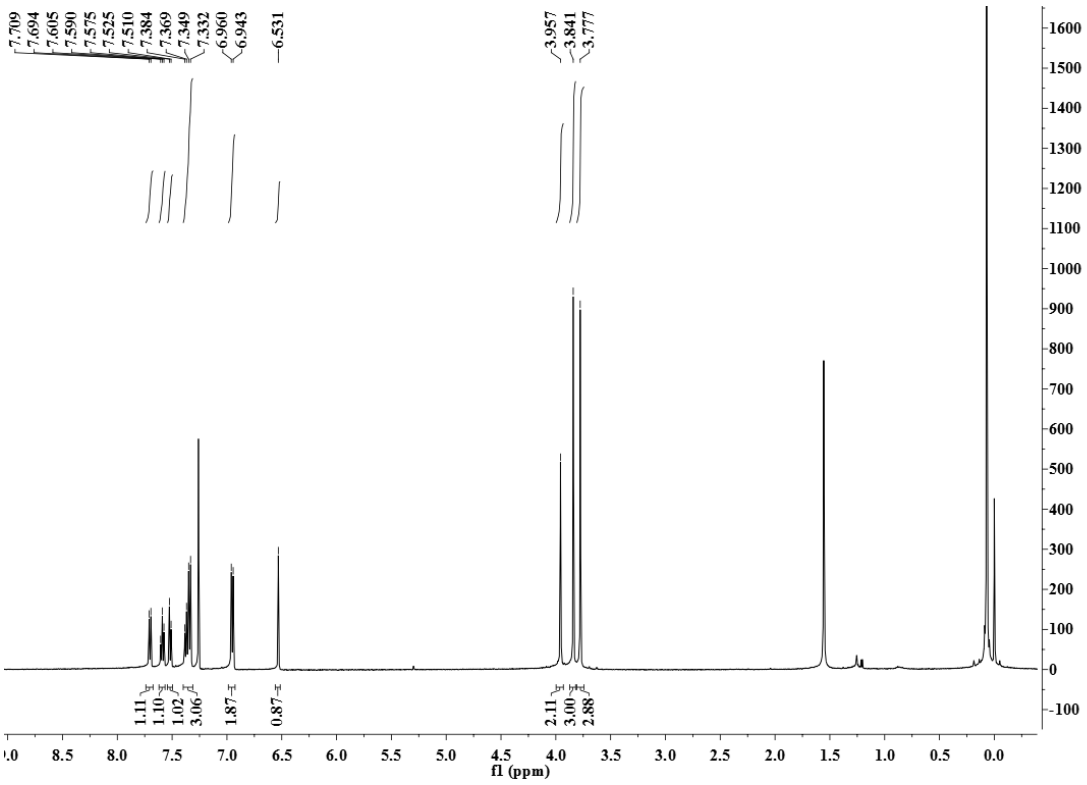
4ac

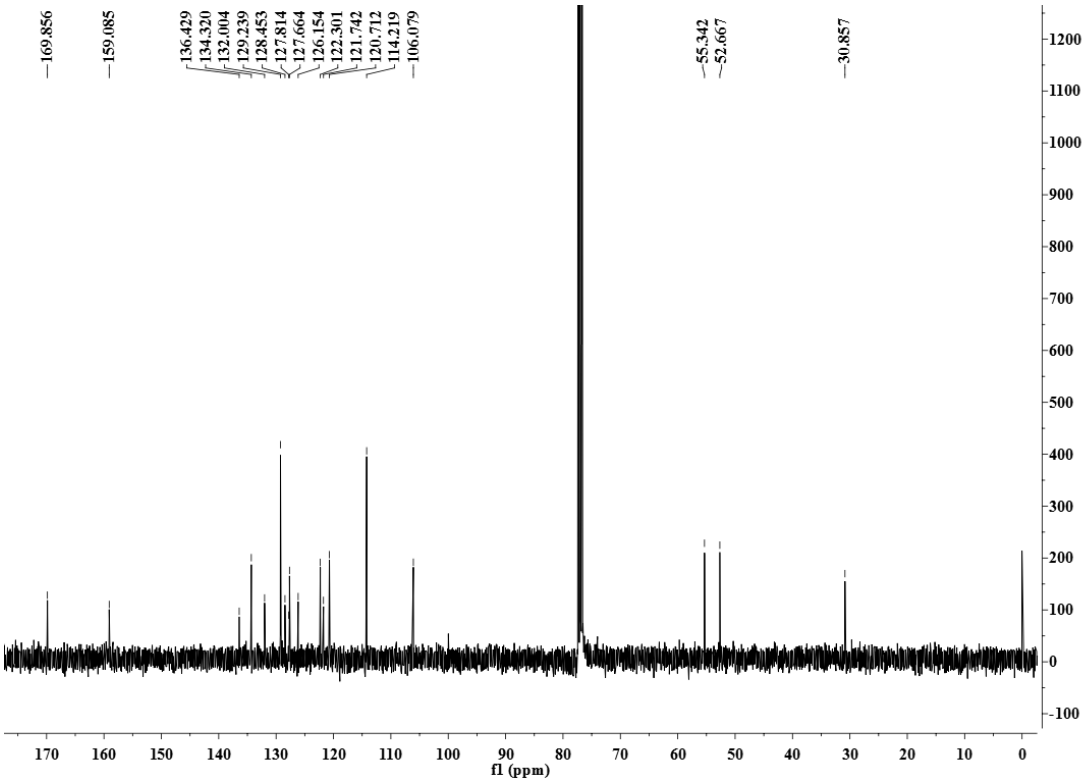

7.721
7.701
7.623
7.602
7.585
7.543
7.523
7.403
7.384
7.364
7.349
7.328
7.309
7.005
6.987
6.983
6.902
6.883
6.573
3.995
3.837
3.778
1.00
1.17
1.06
2.22
2.04
0.96
0.95
1.96
2.99
2.97
f1 (ppm)

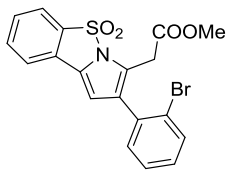

169.738
159.824
136.400
135.067
134.370
132.168
129.843
128.554
127.769
127.712
122.330
122.252
120.775
120.431
113.541
113.190
105.966
55.279
52.679
30.913
f1 (ppm)


SO2
N
COOMe
OMe

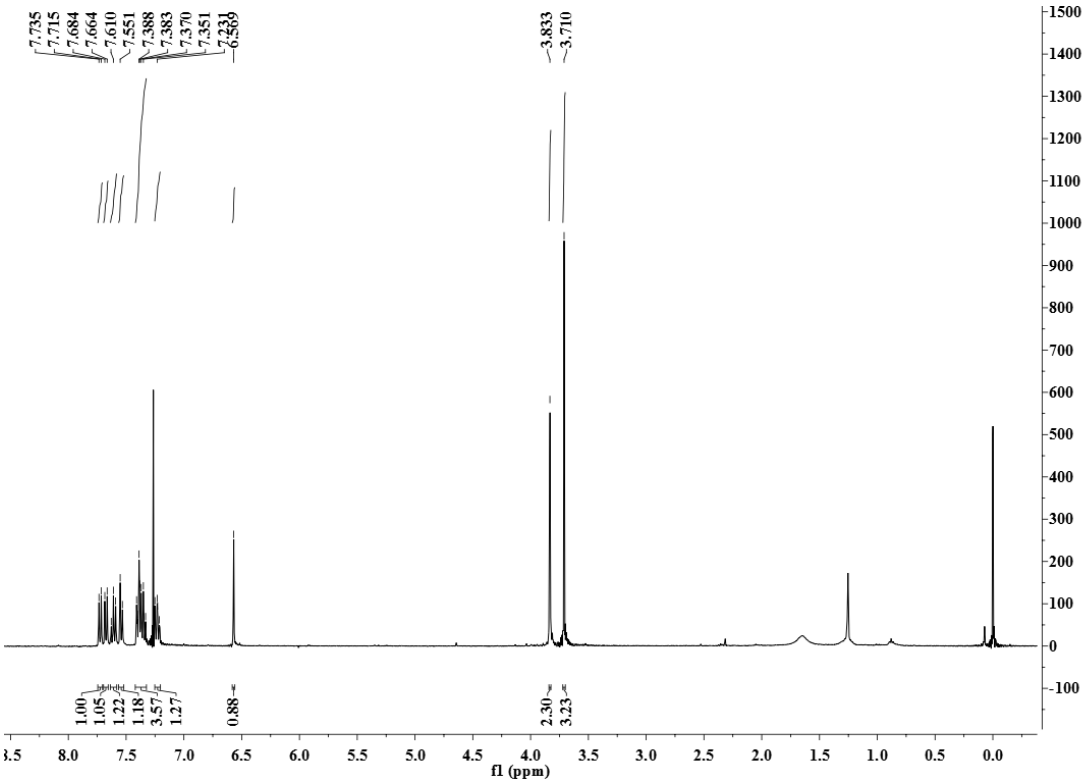
4ad

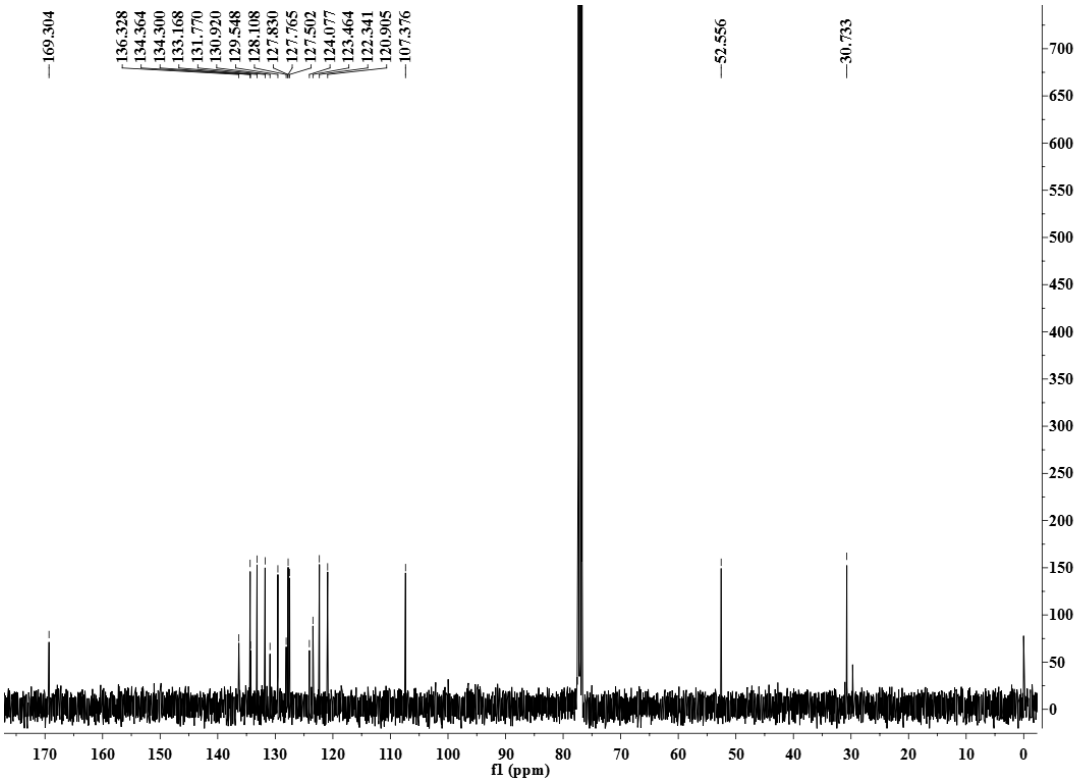

7.709
7.694
7.605
7.590
7.575
7.525
7.510
7.384
7.369
7.349
7.332
6.960
6.943
6.531
3.957
3.841
3.777
1.11
1.10
1.02
3.06
1.87
0.87
2.11
3.00
2.88
f1 (ppm)

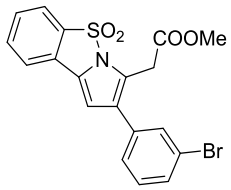

169.856
159.085
136.429
134.320
132.004
129.239
128.453
127.814
127.664
126.154
122.301
121.742
120.712
114.219
106.079
55.342
52.667
30.857
f1 (ppm)


SO2
N
COOMe
Br

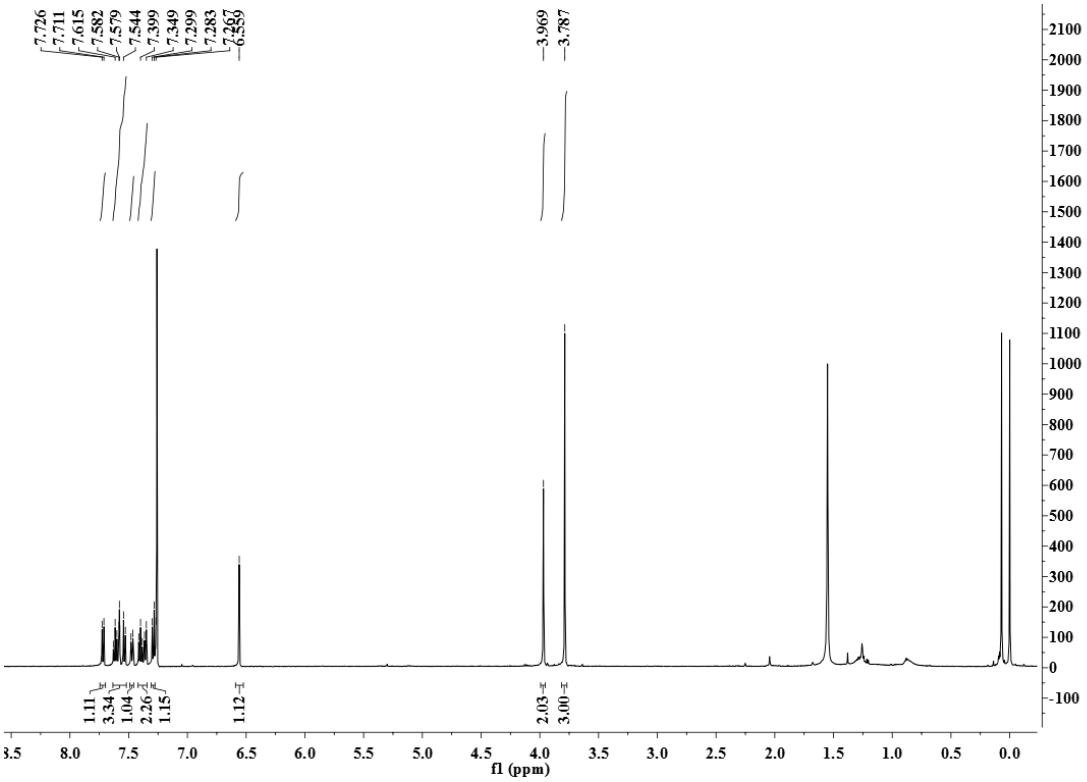
4ae

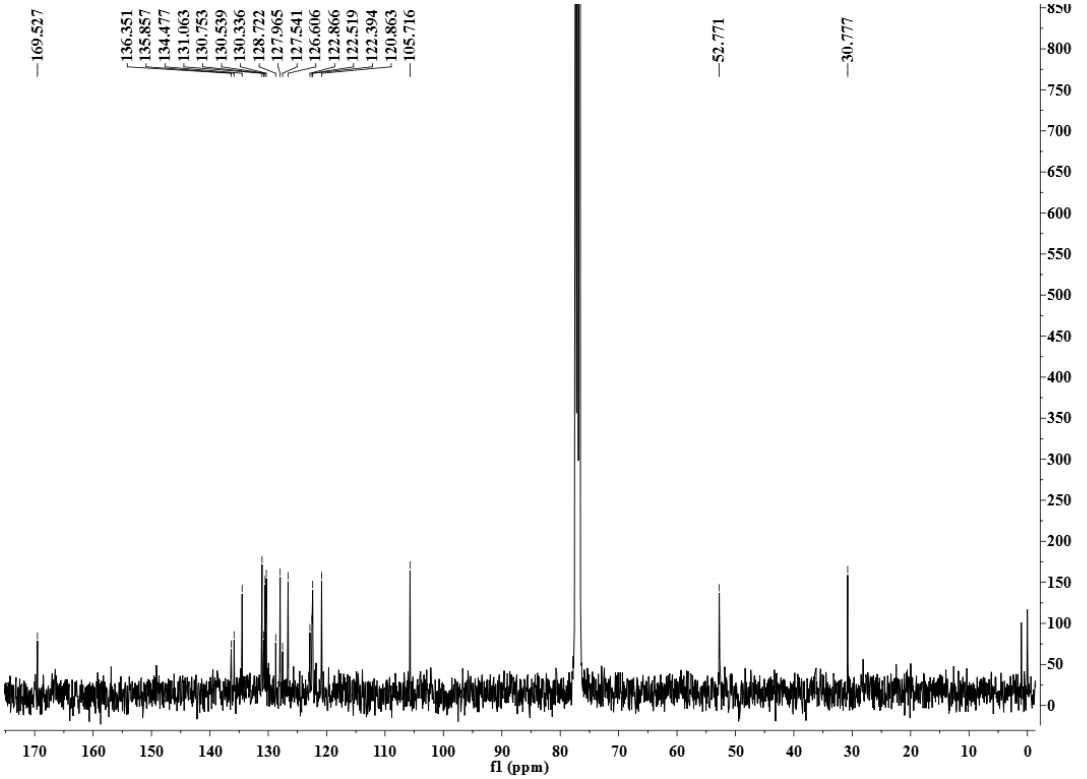

7.735
7.715
7.684
7.664
7.610
7.551
7.388
7.383
7.370
7.351
7.231
6.569
3.833
3.710
1.00
1.05
1.22
1.18
3.57
1.27
0.88
2.30
3.23
f1 (ppm)

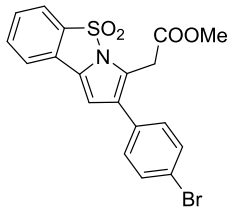

169.304
136.328
134.364
134.300
133.168
131.770
130.920
129.548
128.108
127.830
127.765
127.502
124.077
123.464
122.341
120.905
107.376
52.556
30.733
f1 (ppm)


SO2
N
COOMe
Br

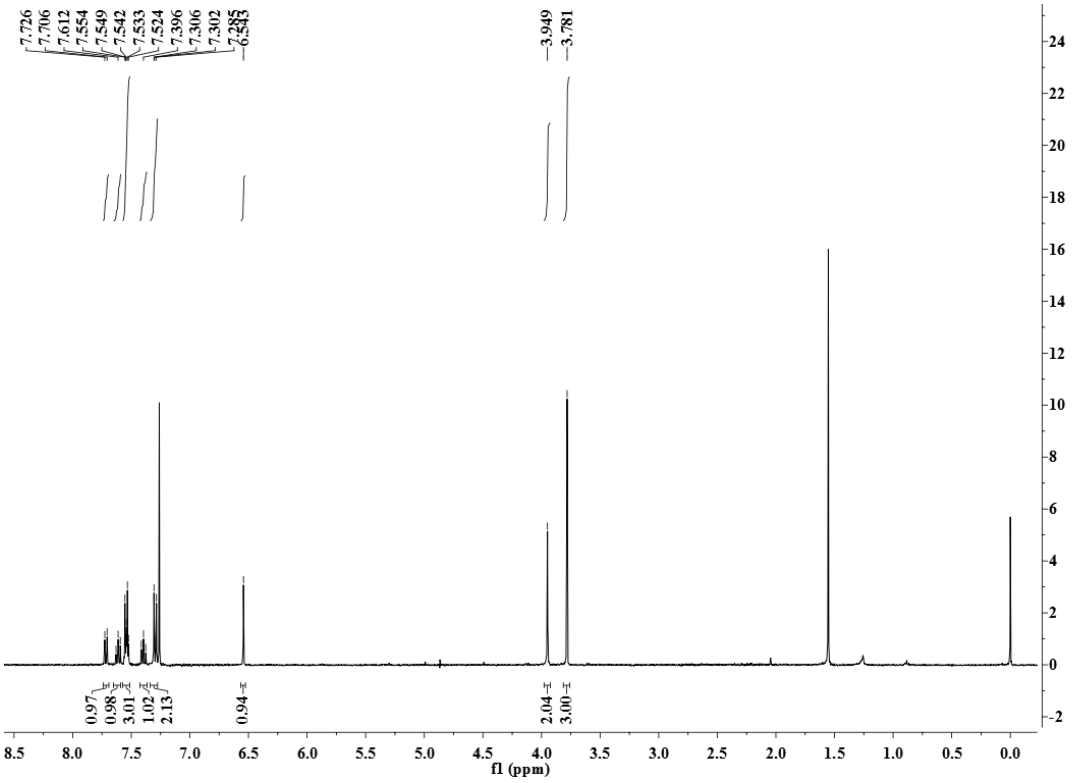
4af

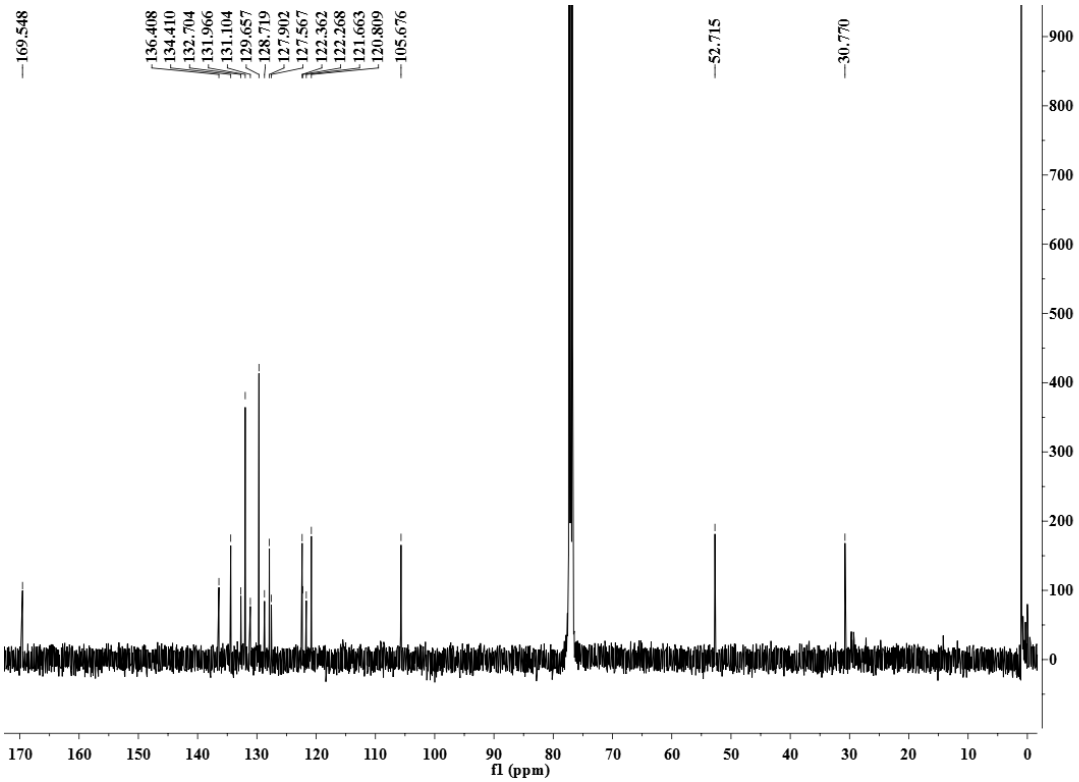

7.726
7.711
7.615
7.582
7.579
7.544
7.399
7.349
7.299
7.283
6.559
3.969
3.787
1.11
3.34
1.04
2.26
1.15
1.12
2.03
3.00
f1 (ppm)

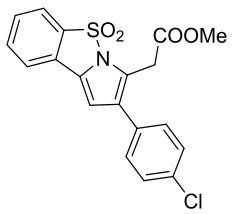

169.527
136.351
135.857
134.477
131.063
130.753
130.539
130.336
128.722
127.965
127.541
126.606
122.866
122.519
122.394
120.863
105.716
52.771
30.777
f1 (ppm)


SO2
N
COOMe
Br

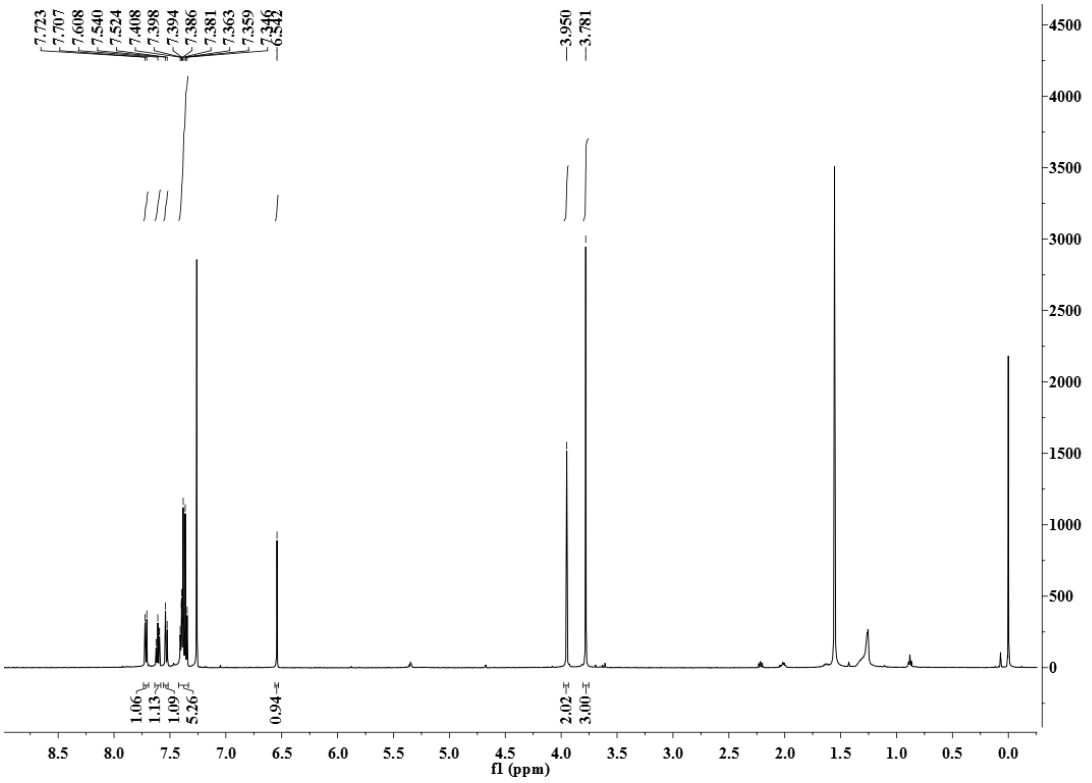
4ag

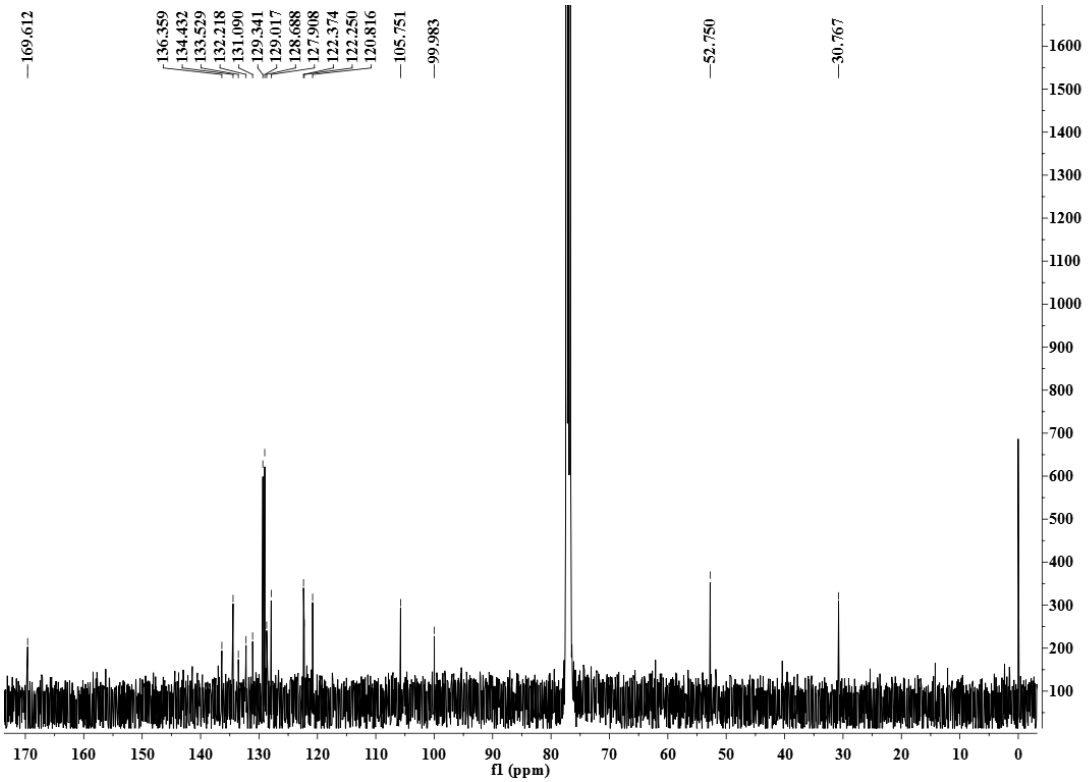

7.726
7.706
7.612
7.554
7.549
7.542
7.533
7.524
7.396
7.306
7.302
6.543
3.949
3.781
0.97
0.98
3.01
1.02
2.13
0.94
2.04
3.00
f1 (ppm)

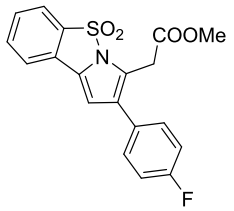

169.548
136.408
134.410
132.704
131.966
131.104
129.657
128.719
127.902
127.567
122.362
122.268
121.663
120.809
105.676
52.715
30.770
f1 (ppm)


SO2
N
COOMe
Cl

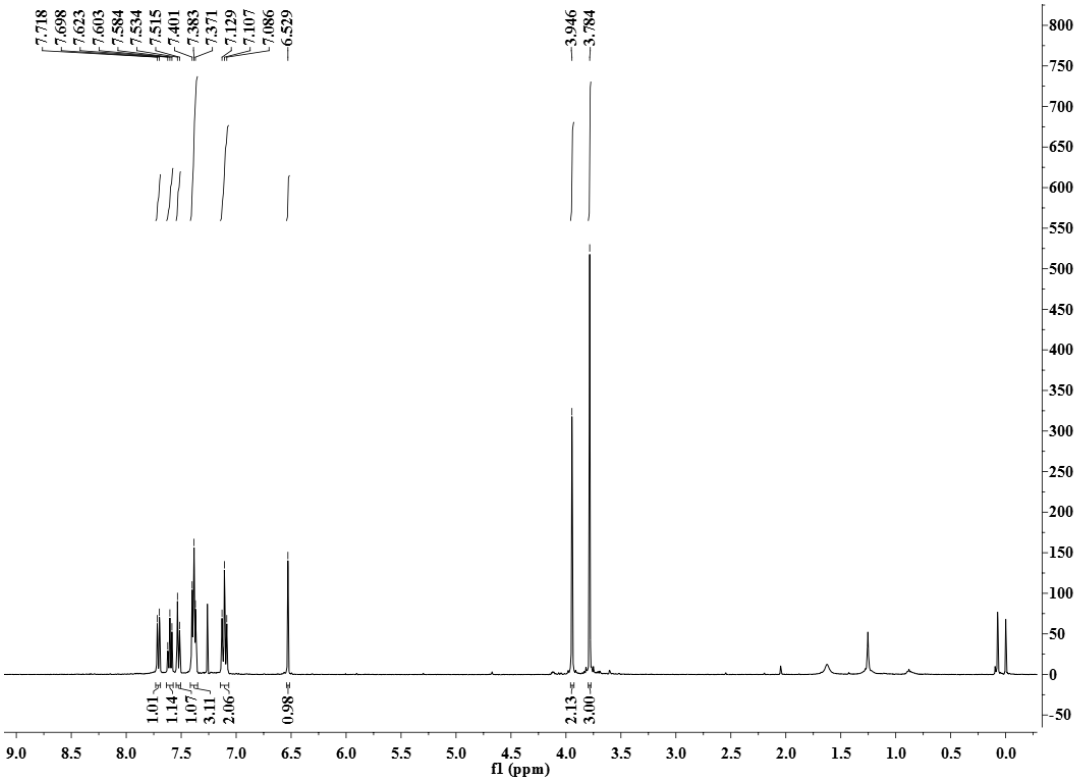
4ah

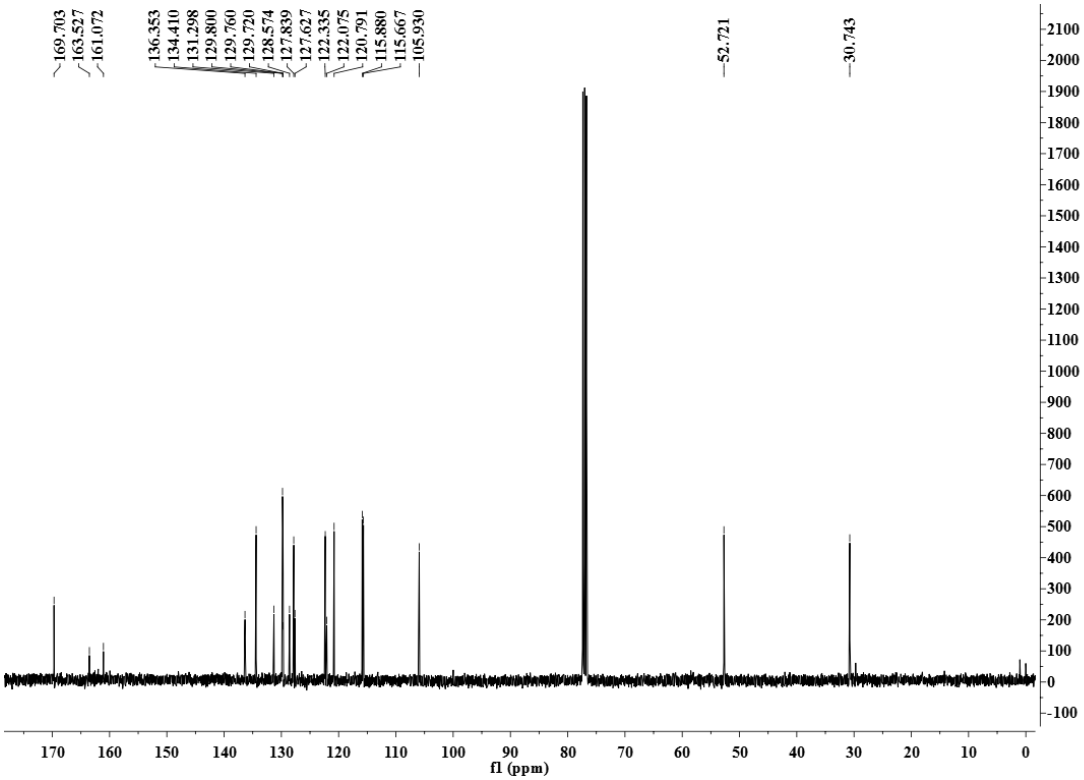

7.723
7.707
7.608
7.540
7.524
7.408
7.398
7.394
7.386
7.381
7.363
7.359
7.346
6.542
3.950
3.781
1.06
1.13
1.09
5.26
0.94
2.02
3.00
f1 (ppm)

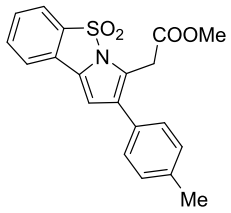

169.612
136.359
134.432
133.529
132.218
131.090
129.341
129.017
128.688
127.908
122.374
122.250
120.816
105.751
99.983
52.750
30.767
f1 (ppm)


SO2
N
COOMe
F

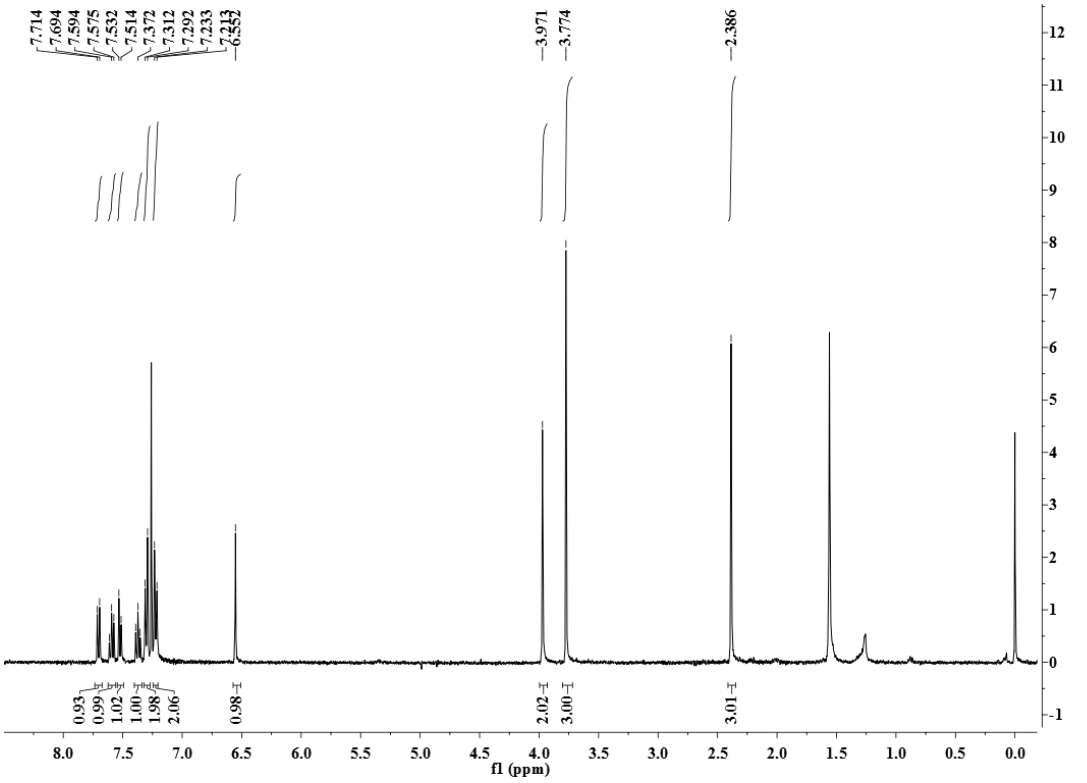
4ai

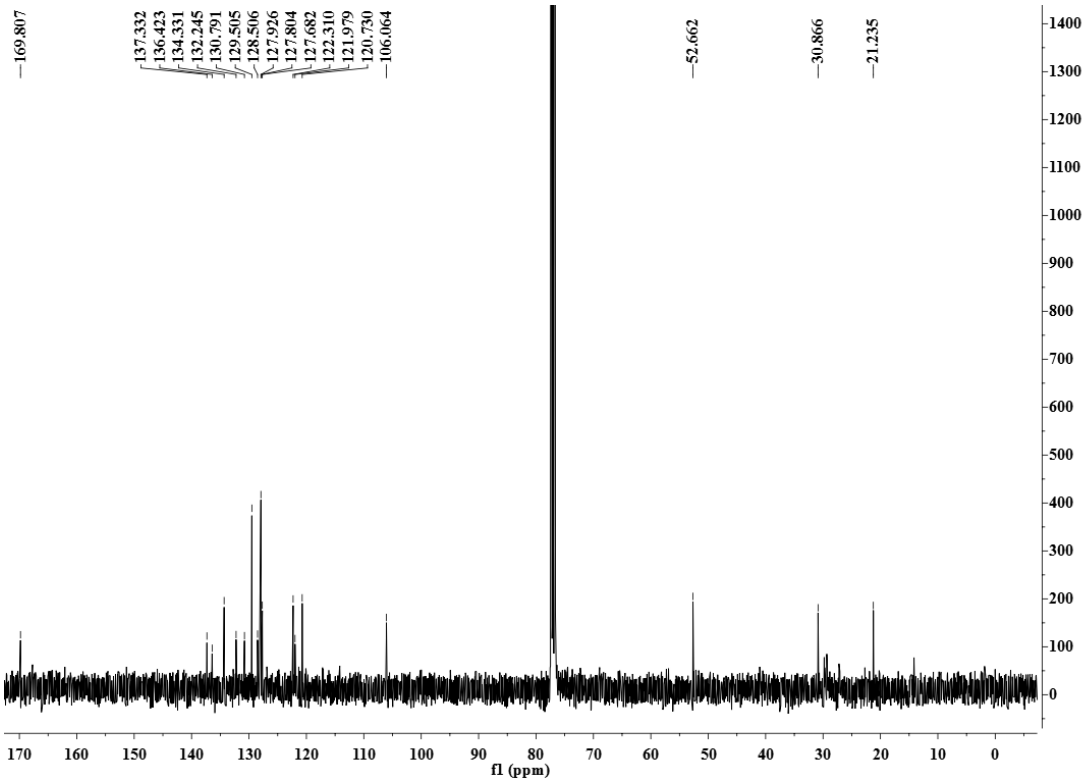

7.718
7.698
7.623
7.603
7.584
7.534
7.515
7.401
7.383
7.371
7.129
7.107
7.086
6.529
3.946
3.784
1.01
1.14
1.07
3.11
2.06
0.98
2.13
3.00
f1 (ppm)

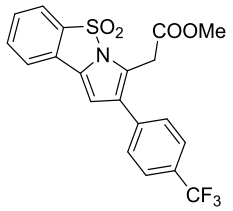

169.703
163.527
161.072
136.353
134.410
131.298
129.800
129.760
129.720
128.574
127.839
127.627
122.335
122.075
120.791
115.880
115.667
105.930
52.721
30.743
f1 (ppm)


SO2
N
COOMe
Me

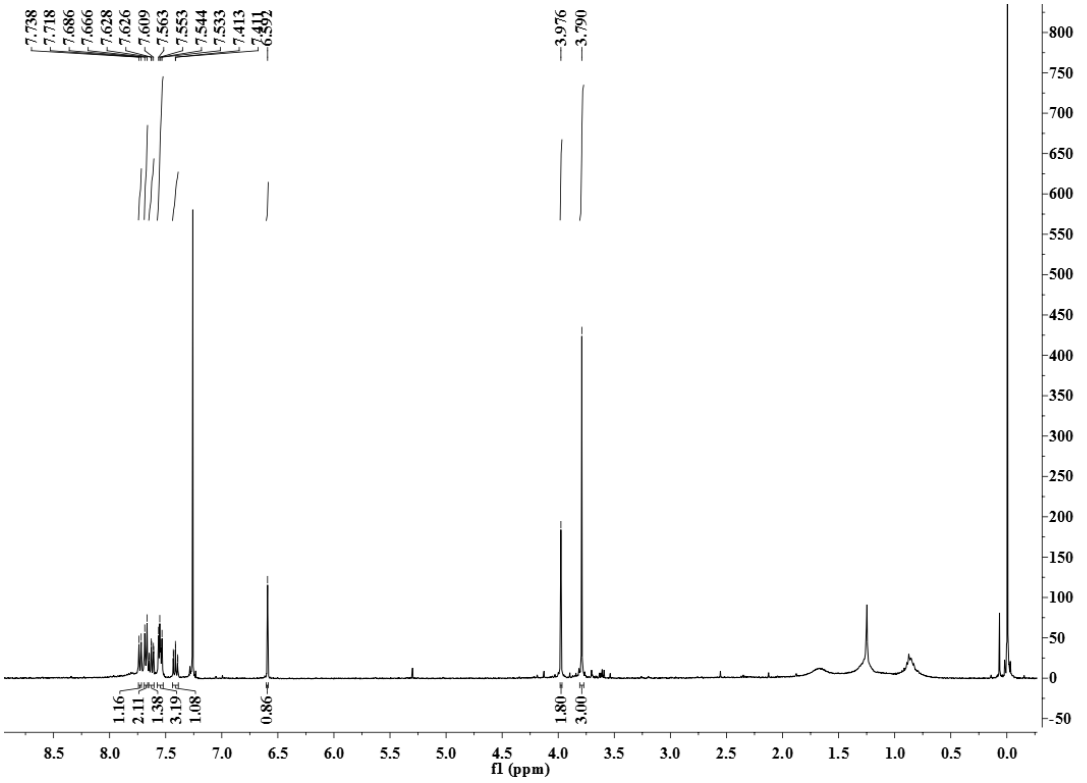
4aj

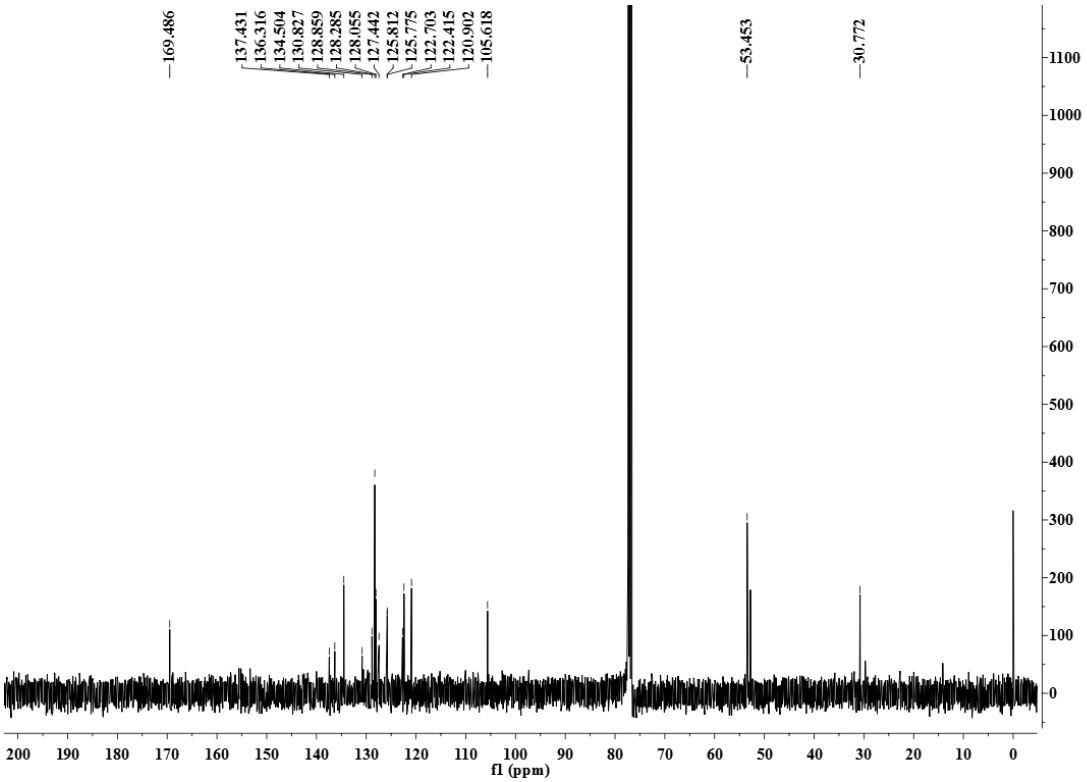

7.714
7.694
7.594
7.575
7.532
7.514
7.372
7.312
7.292
7.233
7.213
6.552
3.971
3.774
2.386
0.93
0.99
1.02
1.00
1.98
2.06
0.98
2.02
3.00
3.01
fl (ppm)

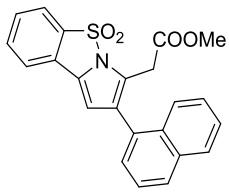

169.807
137.332
136.423
134.331
132.245
130.791
129.505
128.506
127.926
127.804
127.682
122.310
121.979
120.730
106.064
52.662
30.866
21.235
fl (ppm)


SO2
N
COOMe
CF3

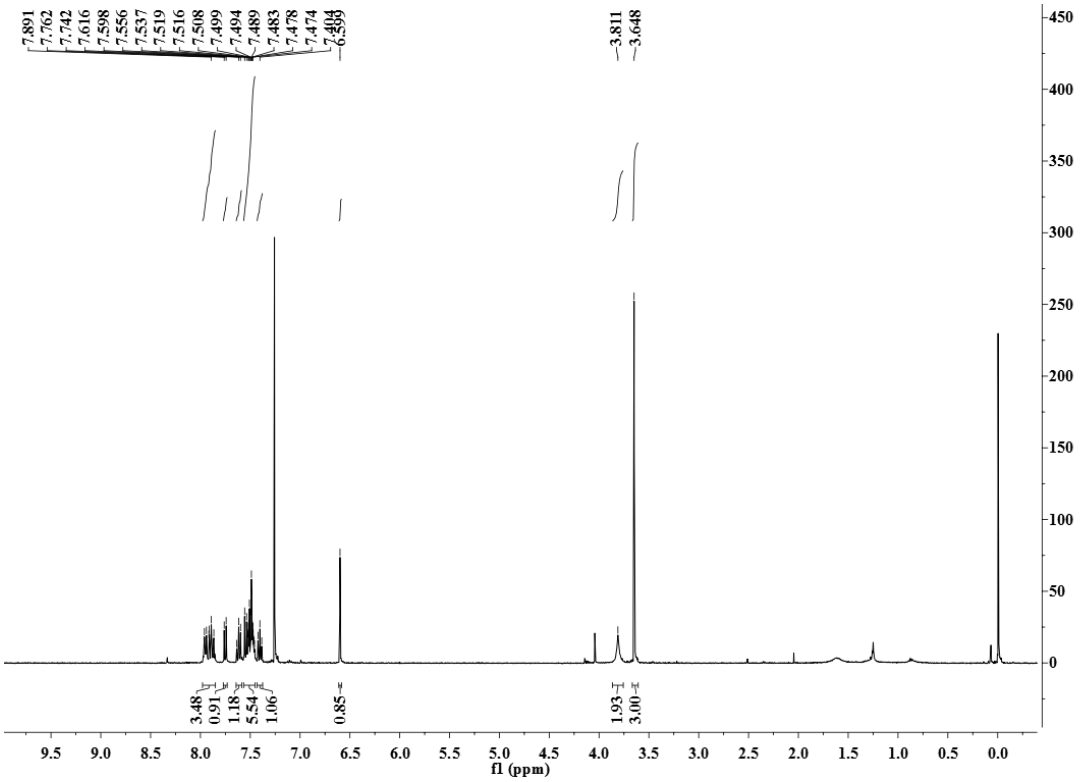
4ak

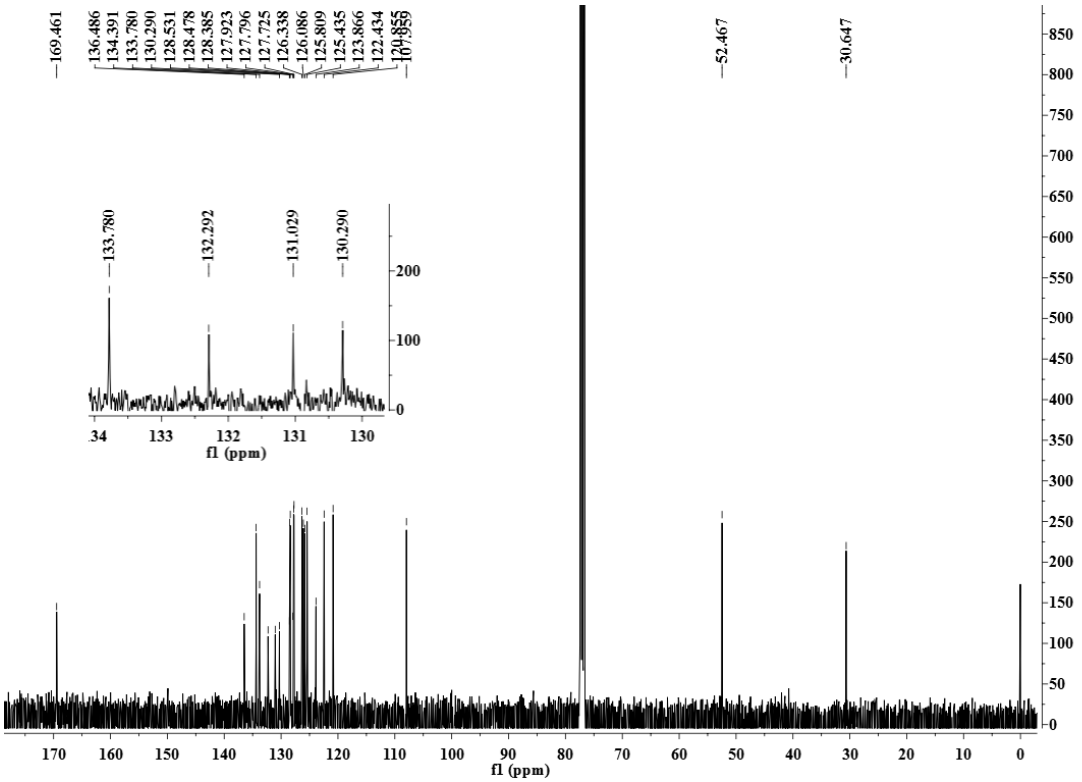

7.738
7.718
7.686
7.666
7.628
7.626
7.609
7.563
7.553
7.544
7.533
7.413
7.411
6.392
3.976
3.790
1.16
2.11
1.38
3.19
1.08
0.86
1.80
3.00
f1 (ppm)

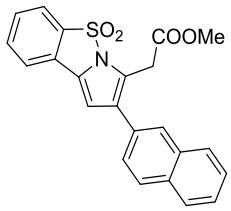

169.486
137.431
136.316
134.504
130.827
128.859
128.285
128.055
127.442
125.812
125.775
122.703
122.415
120.902
105.618
53.453
30.772
f1 (ppm)


SO2
N
COOMe

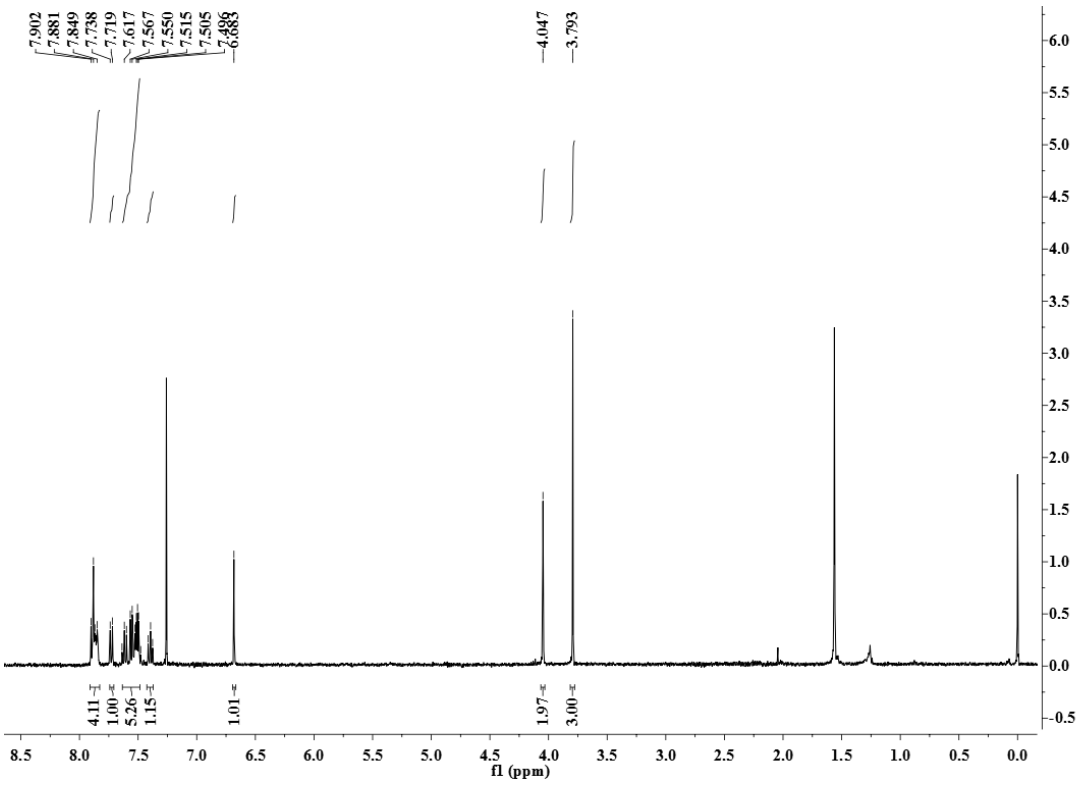
4al

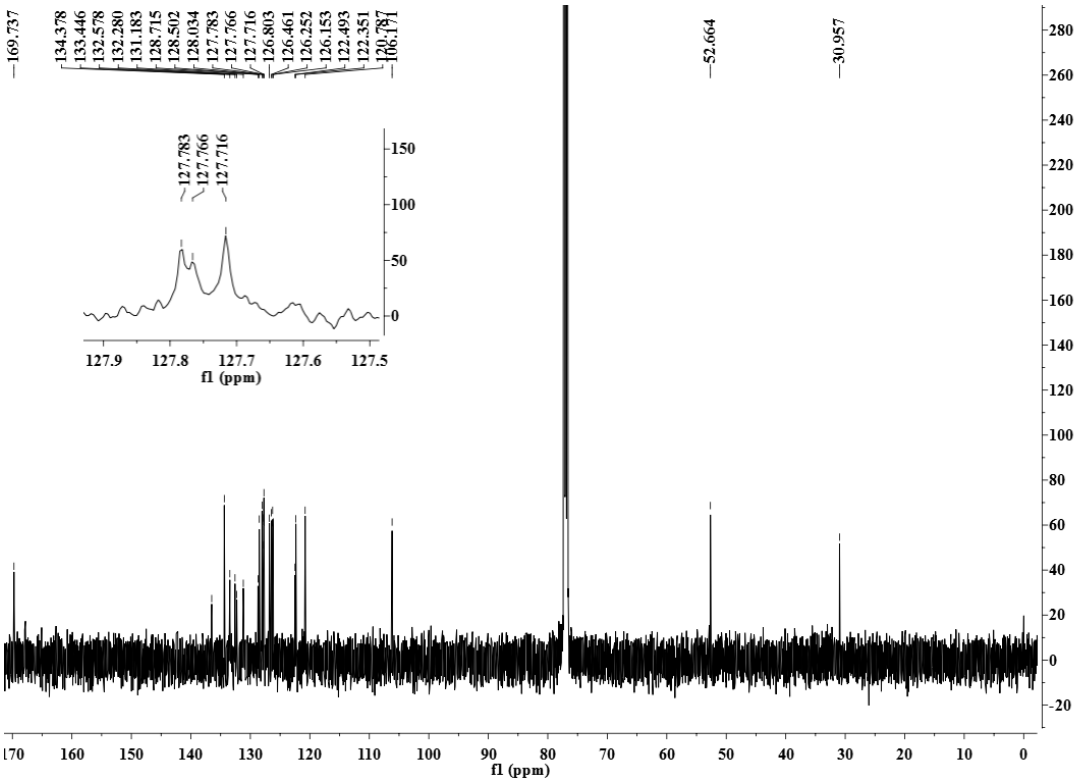

7.891
7.762
7.742
7.616
7.598
7.556
7.537
7.519
7.516
7.508
7.499
7.494
7.489
7.483
7.478
7.474
7.404
6.599
3.811
3.648
3.48
0.91
1.18
5.54
1.06
0.85
1.93
3.00
f1 (ppm)

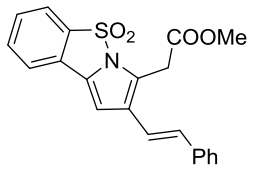

169.461
136.486
134.391
133.780
130.290
128.531
128.478
128.385
127.923
127.796
127.725
126.338
126.086
125.809
125.435
123.866
122.434
52.467
30.647
133.780
132.292
131.029
130.290
f1 (ppm)


SO2
N
COOMe

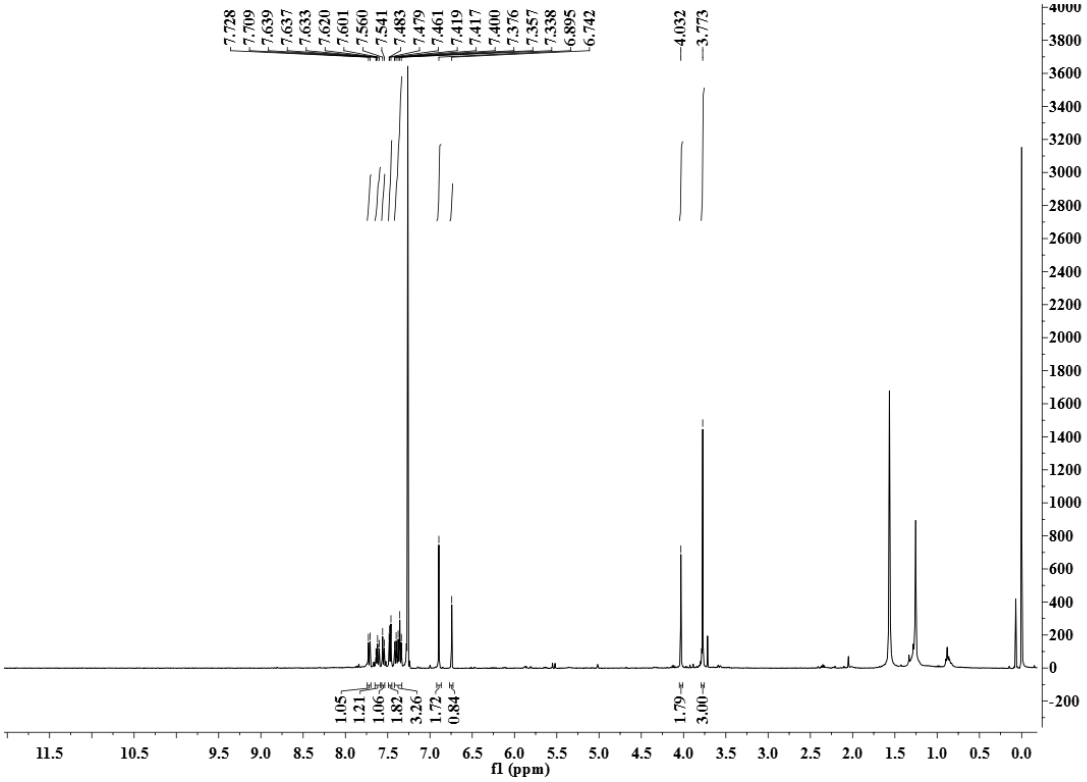
4am

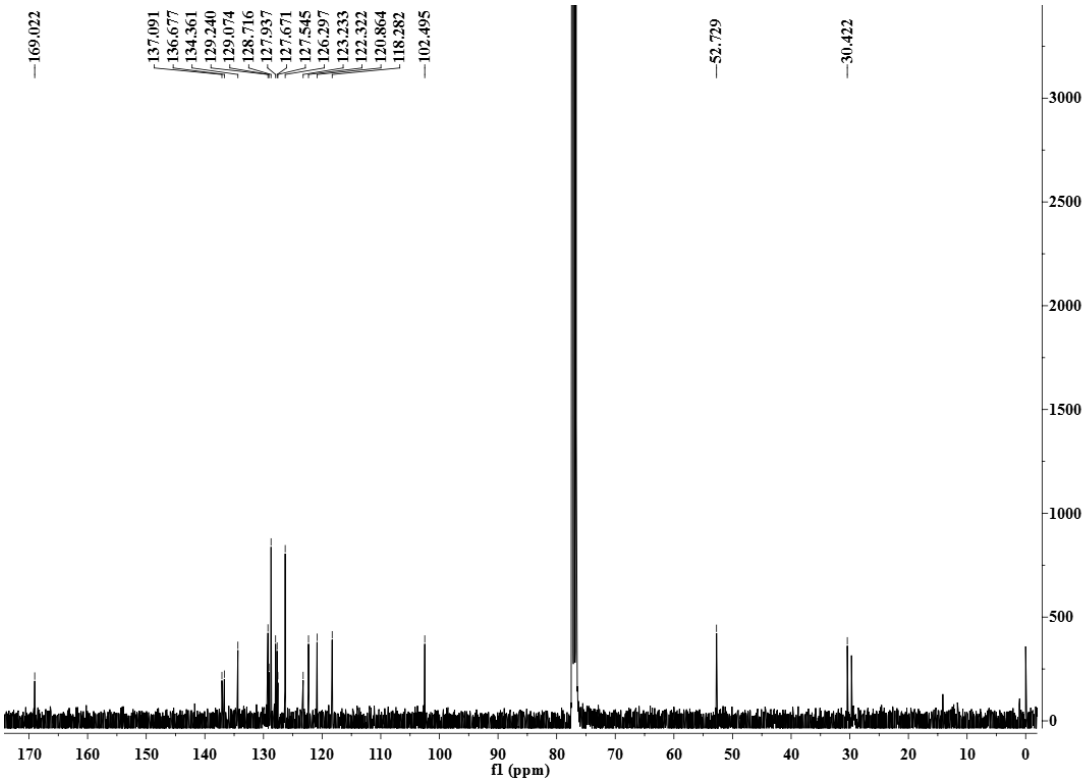

7.902
7.881
7.849
7.738
7.719
7.617
7.567
7.550
7.515
7.505
7.496
6.683
4.047
3.793
4.11
1.00
5.26
1.15
1.01
1.97
3.00
f1 (ppm)

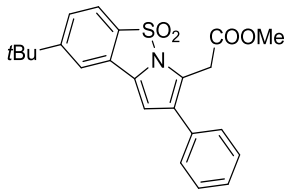

169.737
134.378
133.446
132.578
132.280
131.183
128.715
128.502
128.034
127.783
127.766
127.716
126.803
126.461
126.252
126.153
122.493
122.351
120.787
106.171
52.664
30.957
127.783
127.766
127.716
f1 (ppm)
f1 (ppm)


SO2
N
COOMe
Ph

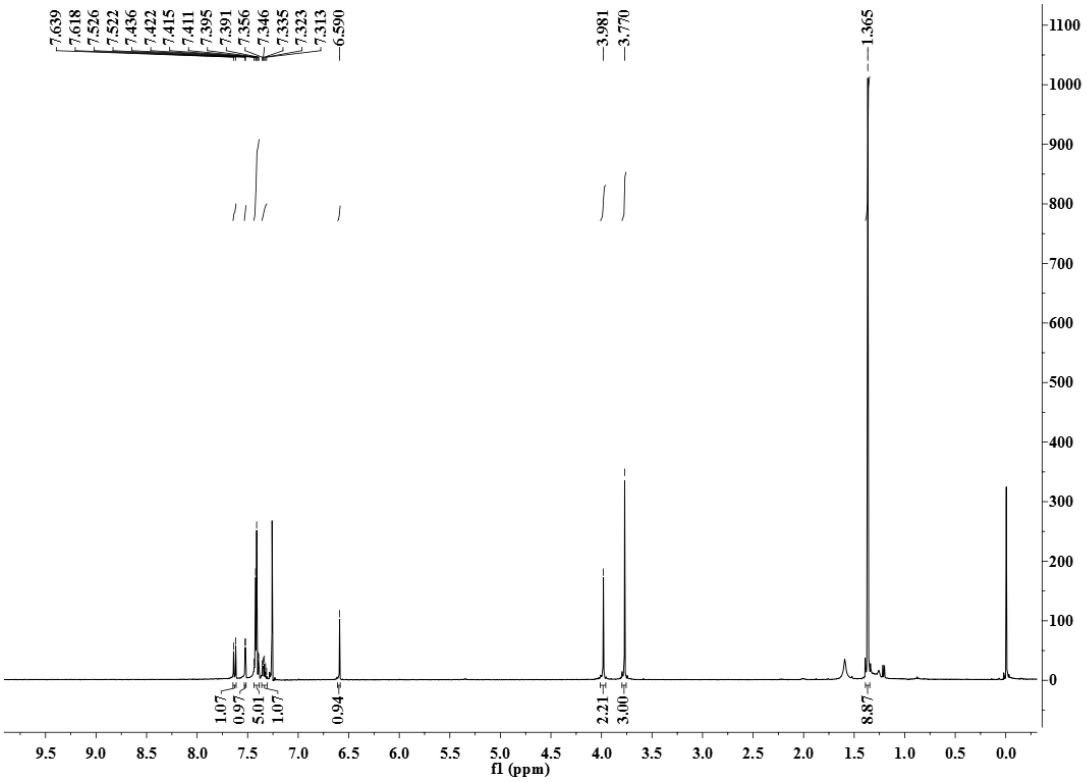
4ap

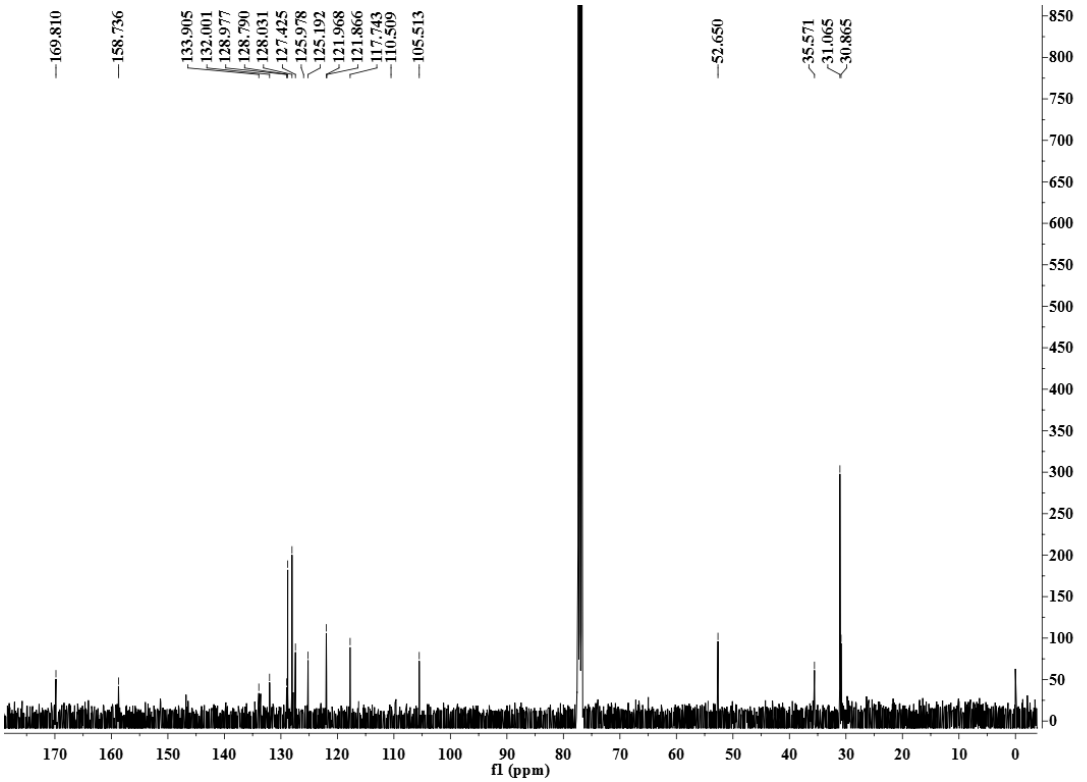

7.728
7.709
7.639
7.637
7.633
7.620
7.601
7.560
7.541
7.483
7.479
7.461
7.419
7.417
7.400
7.376
7.357
7.338
6.895
6.742
4.032
3.773
1.05
1.21
1.06
1.82
3.26
1.72
0.84
1.79
3.00
fl (ppm)

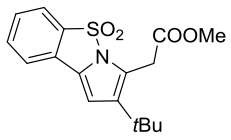

169.022
137.091
136.677
134.361
129.240
129.074
128.716
127.937
127.671
127.545
126.297
123.233
122.322
120.864
118.282
102.495
52.729
30.422
fl (ppm)


tBu
SO2
N
COOMe

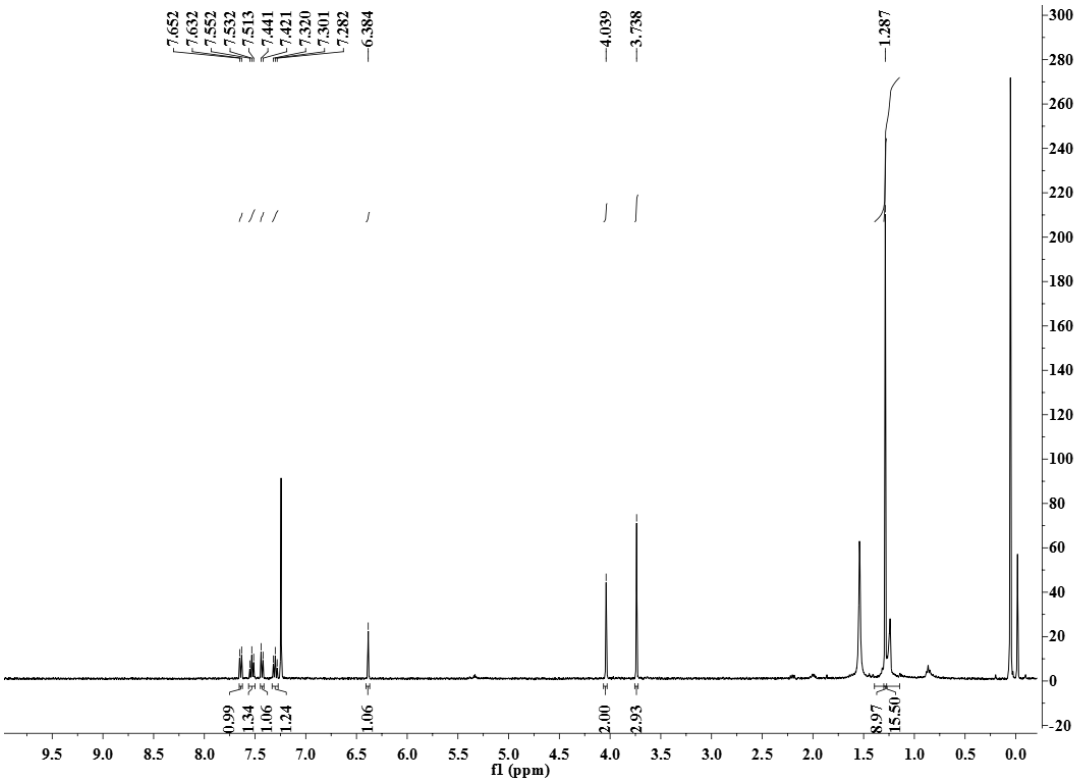
4aq

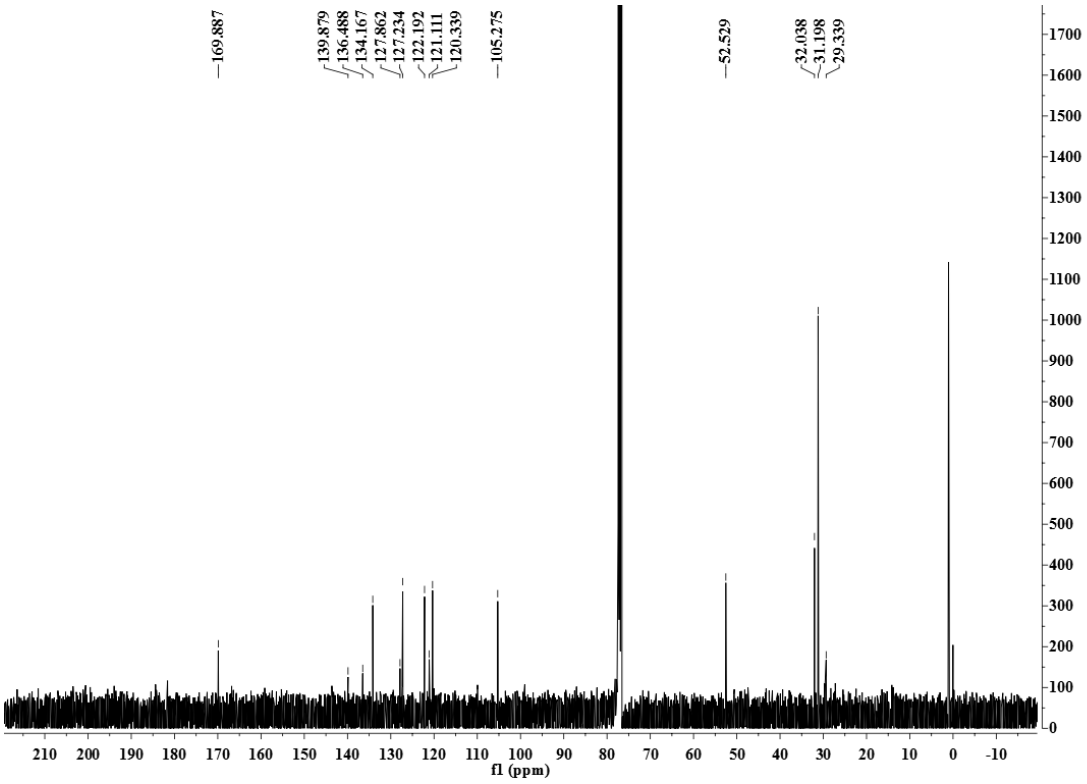

7.639
7.618
7.526
7.522
7.436
7.422
7.415
7.411
7.395
7.391
7.356
7.346
7.335
7.323
7.313
6.590
3.981
3.770
1.365
1.07
0.97
5.01
1.07
0.94
2.21
3.00
8.87
f1 (ppm)

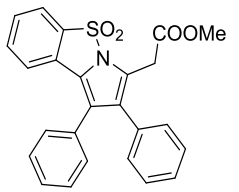

169.810
158.736
133.905
132.001
128.977
128.790
128.031
127.425
125.978
125.192
121.968
121.866
117.743
110.509
105.513
52.650
35.571
31.065
30.865
f1 (ppm)


SO2
N
COOMe
tBu

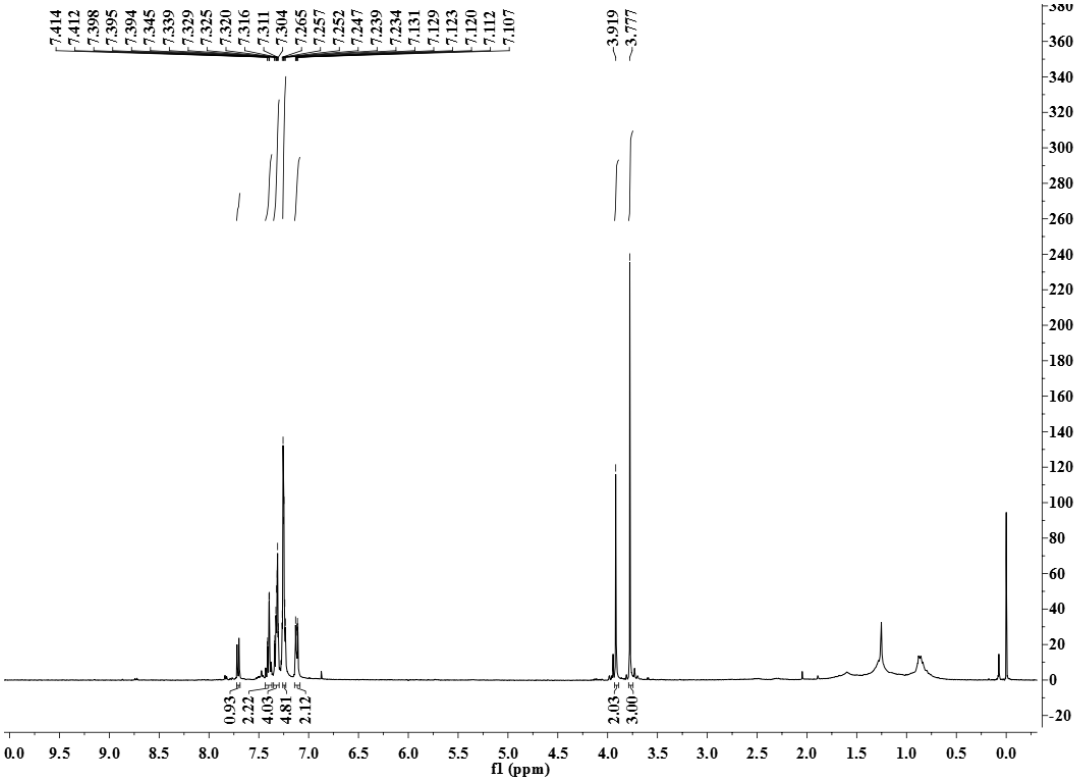
4ar

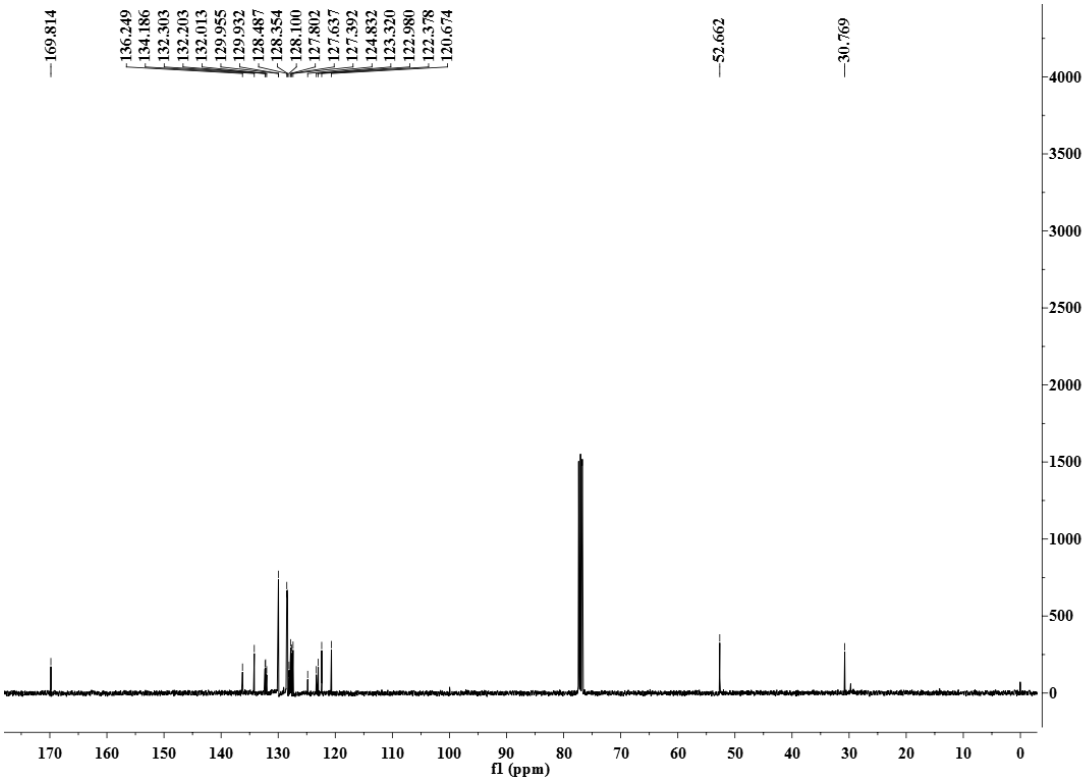

7.652
7.632
7.552
7.532
7.513
7.441
7.421
7.320
7.301
7.282
6.384
4.039
3.738
1.287
0.99
1.34
1.06
1.24
1.06
2.00
2.93
8.97
15.50
f1 (ppm)

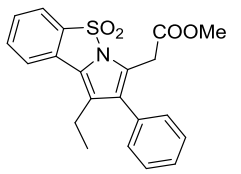

169.887
139.879
136.488
134.167
127.862
127.234
122.192
121.111
120.339
105.275
52.529
32.038
31.198
29.339
f1 (ppm)


SO2
N
COOMe

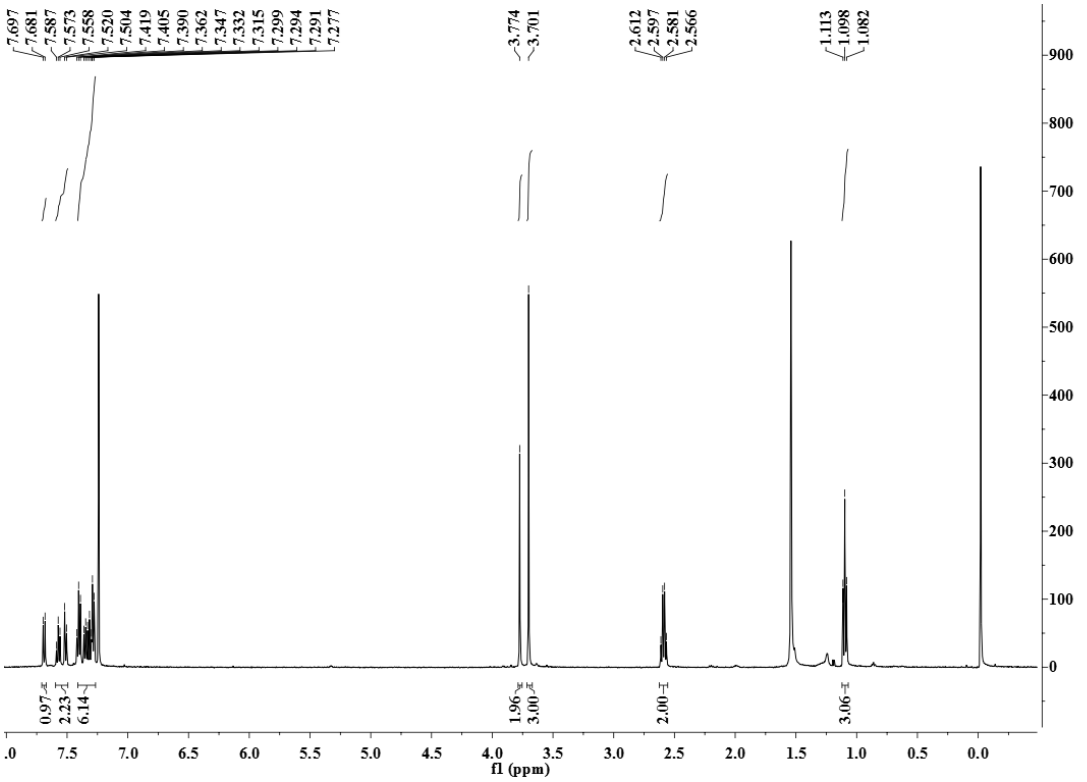
4as

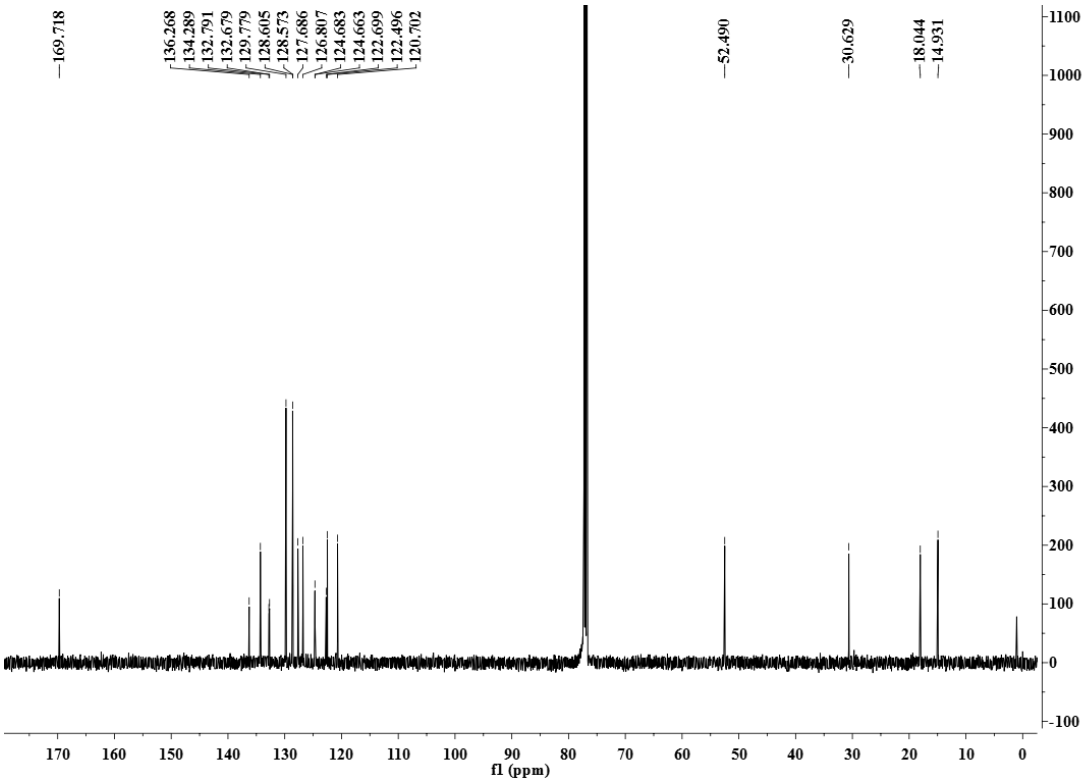

7.414
7.412
7.398
7.395
7.394
7.345
7.339
7.329
7.325
7.320
7.316
7.311
7.304
7.265
7.257
7.252
7.247
7.239
7.234
7.131
7.129
7.123
7.120
7.112
7.107
3.919
3.777
0.93
2.22
4.03
4.81
2.12
2.03
3.00
f1 (ppm)

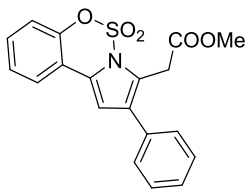

169.814
136.249
134.186
132.303
132.203
132.013
129.955
129.932
128.487
128.354
128.100
127.802
127.637
127.392
124.832
123.320
122.980
122.378
120.674
52.662
30.769
f1 (ppm)


SO2
N
COOMe

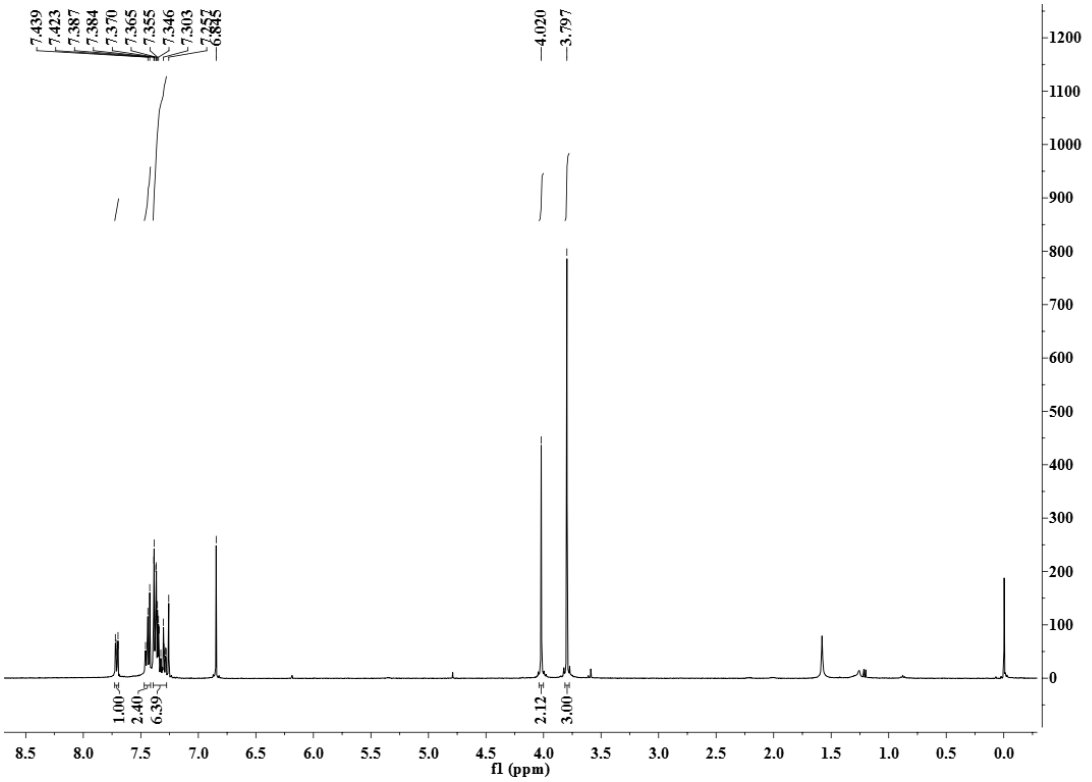
4at

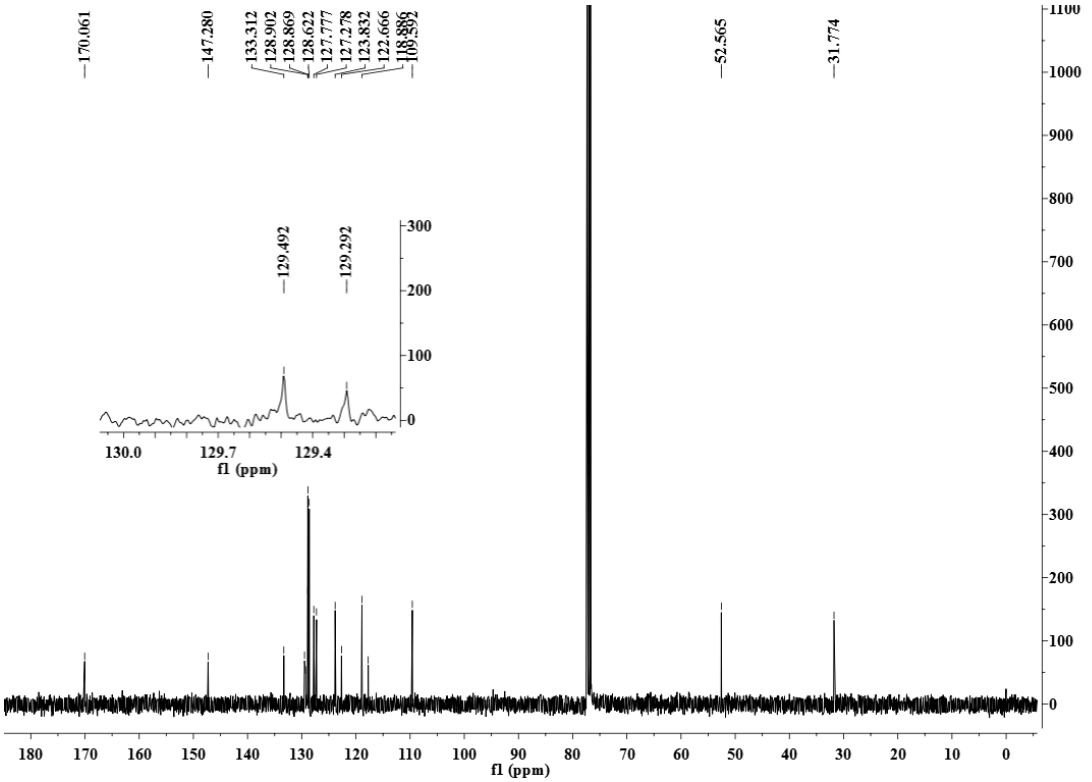

7.697
7.681
7.587
7.573
7.558
7.520
7.504
7.419
7.405
7.390
7.362
7.347
7.332
7.315
7.299
7.294
7.291
7.277
3.774
3.701
2.612
2.597
2.581
2.566
1.113
1.098
1.082
0.97
2.23
6.14
1.96
3.00
2.00
3.06
f1 (ppm)

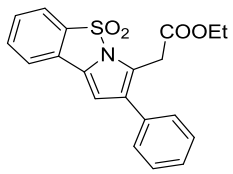

169.718
136.268
134.289
132.791
132.679
129.779
128.605
128.573
127.686
126.807
124.683
124.663
122.699
122.496
120.702
52.490
30.629
18.044
14.931
f1 (ppm)


O
SO2
N
COOMe

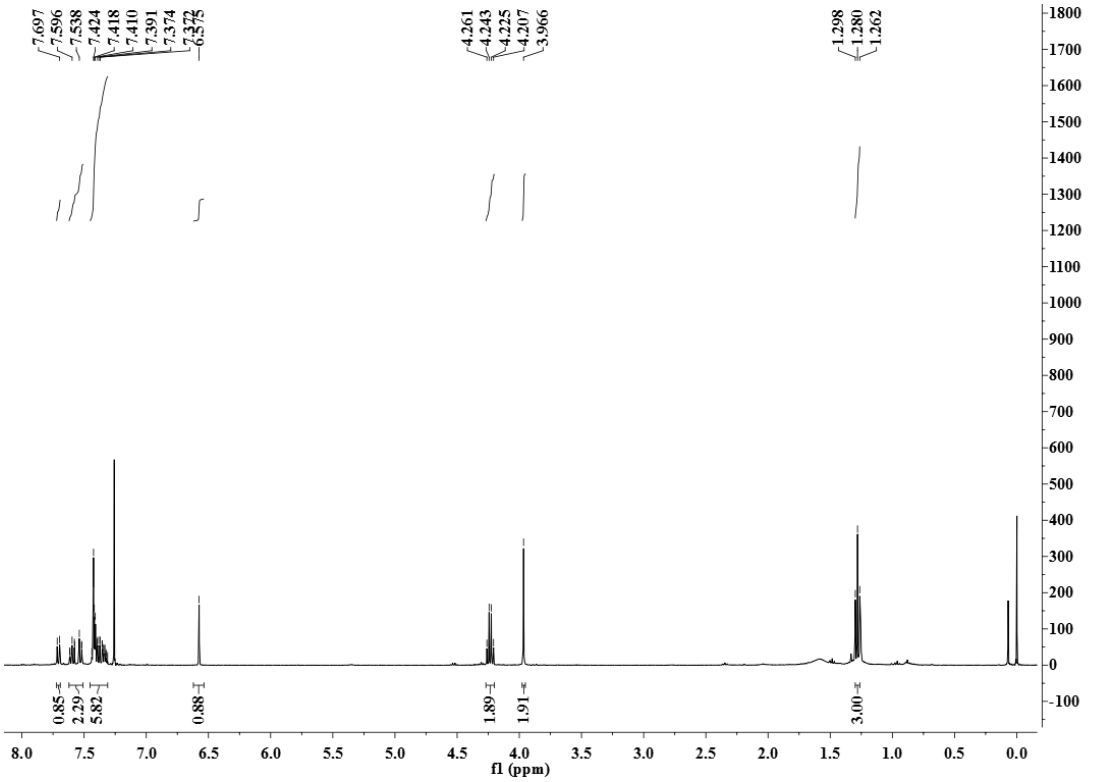
4au

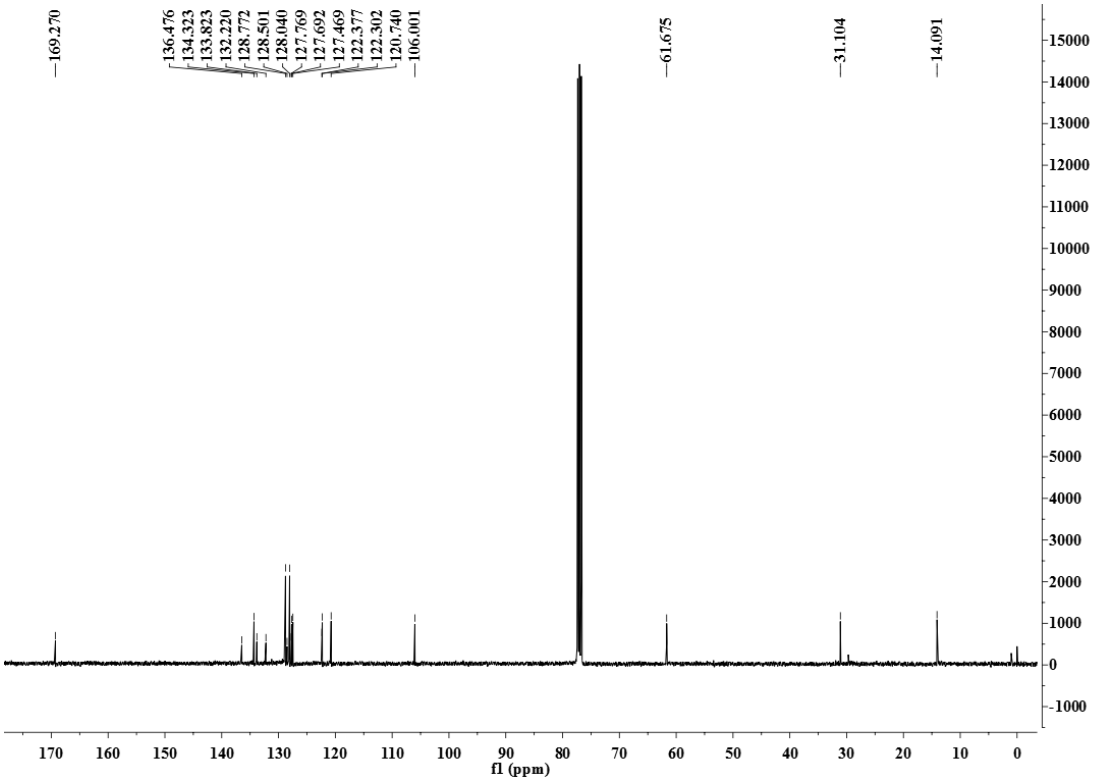

7.439
7.423
7.387
7.384
7.370
7.365
7.355
7.346
7.303
7.257
6.845
4.020
3.797
1.00
2.40
6.39
2.12
3.00
fl (ppm)

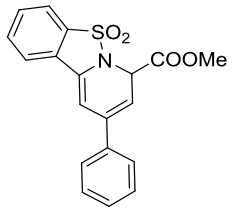

170.061
147.280
133.312
128.902
128.869
128.622
127.777
127.278
123.832
122.666
52.565
31.774
129.492
129.292
130.0
129.7
129.4
fl (ppm)
fl (ppm)


SO2
N
COOEt

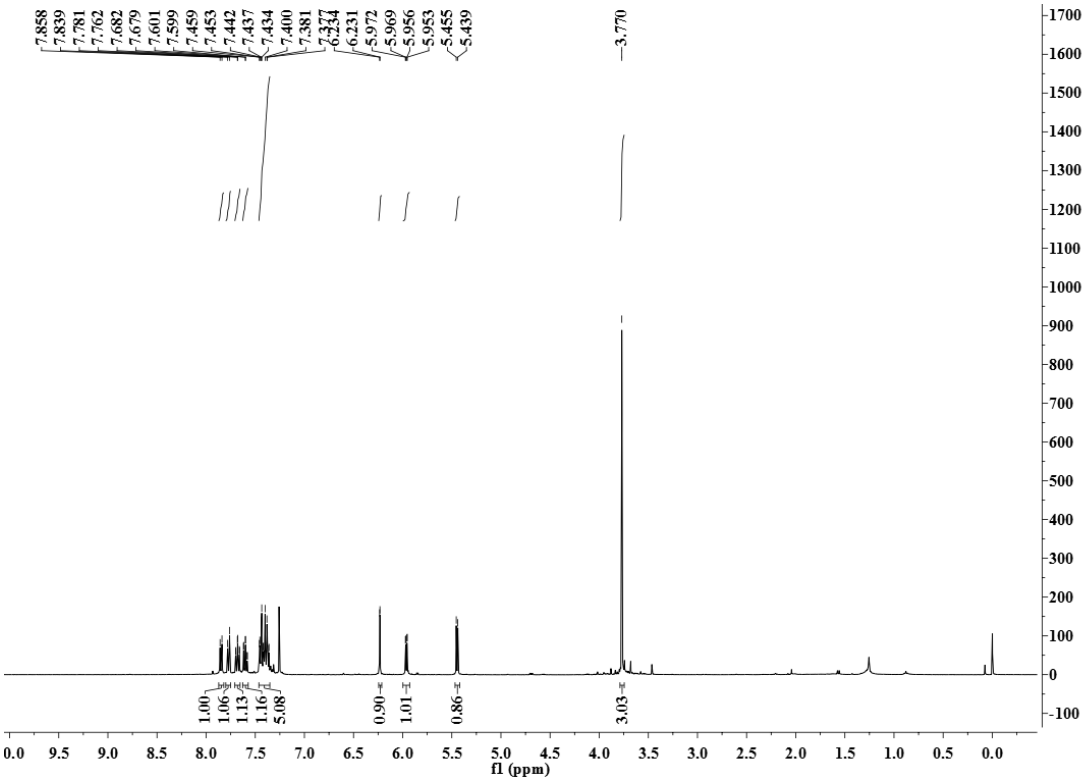
4ba

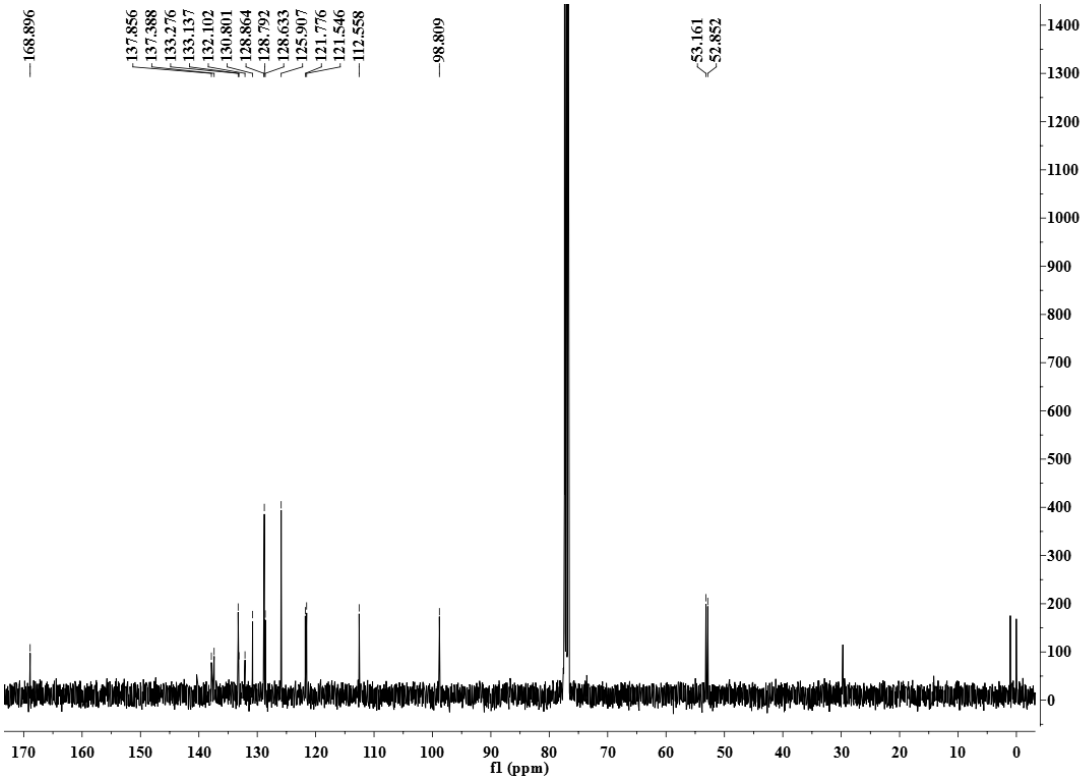

7.697
7.596
7.538
7.424
7.418
7.410
7.391
7.374
7.372
7.372
6.575
4.261
4.243
4.225
4.207
3.966
1.298
1.280
1.262
0.85
2.29
5.82
0.88
1.89
1.91
3.00
fl (ppm)

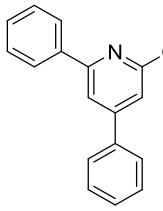

169.270
136.476
134.323
133.823
132.220
128.772
128.501
128.040
127.769
127.692
127.469
122.377
122.302
120.740
106.001
61.675
31.104
14.091
fl (ppm)


SO2
N
COOMe

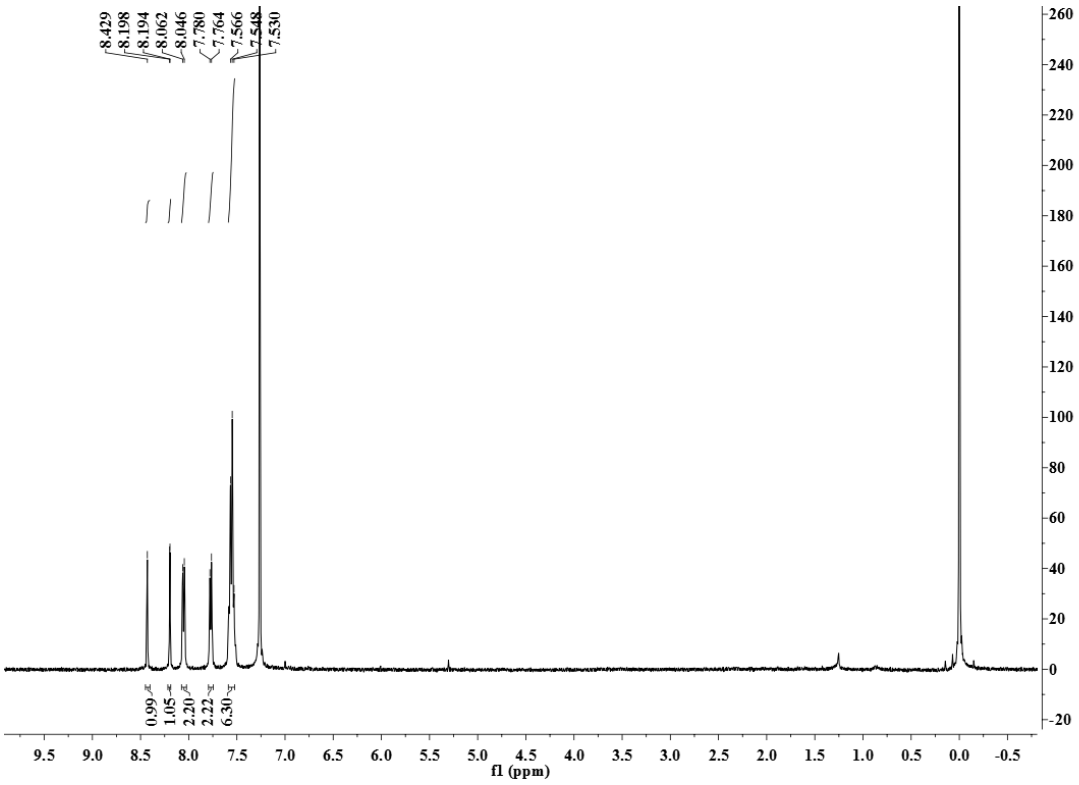
9aa

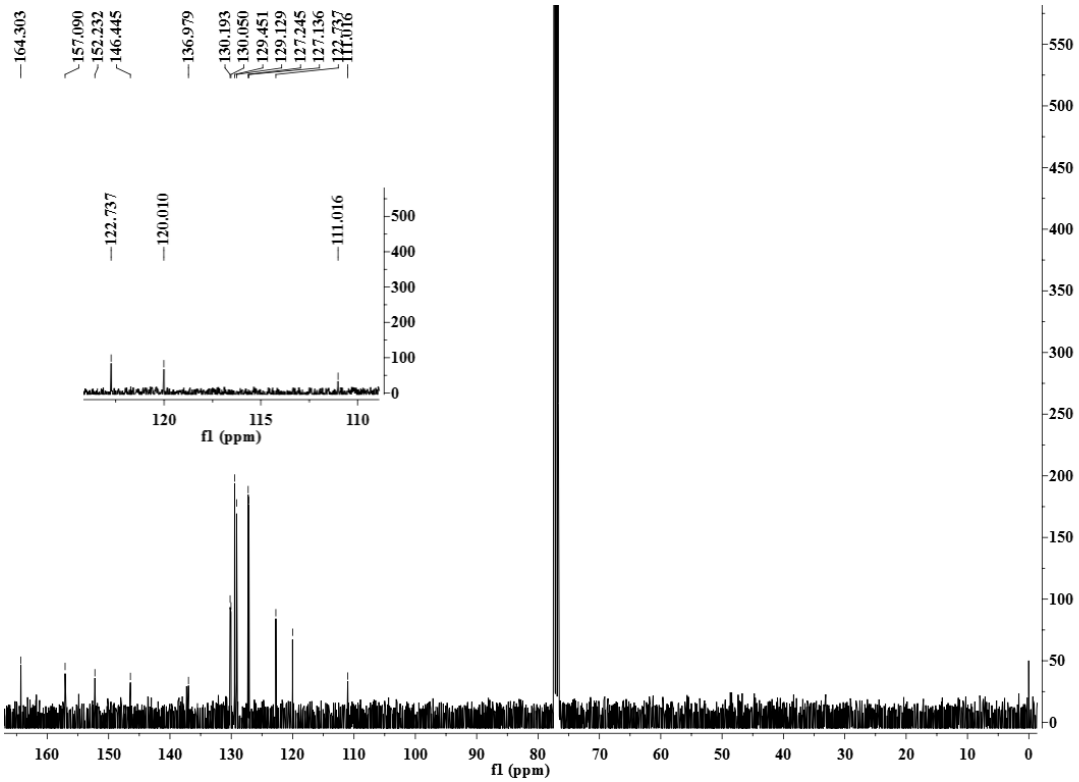

7.858
7.839
7.781
7.762
7.682
7.679
7.601
7.599
7.459
7.453
7.442
7.437
7.434
7.400
7.381
7.377
7.334
6.231
5.972
5.969
5.956
5.953
5.455
5.439
3.770
1.00
1.06
1.13
1.16
5.08
0.90
1.01
0.86
3.03
f1 (ppm)

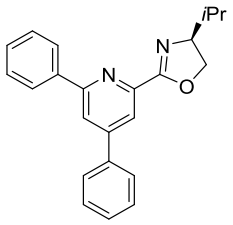

168.896
137.856
137.388
133.276
133.137
132.102
130.801
128.864
128.792
128.633
125.907
121.776
121.546
112.558
98.809
53.161
52.852
f1 (ppm)


N
COOH

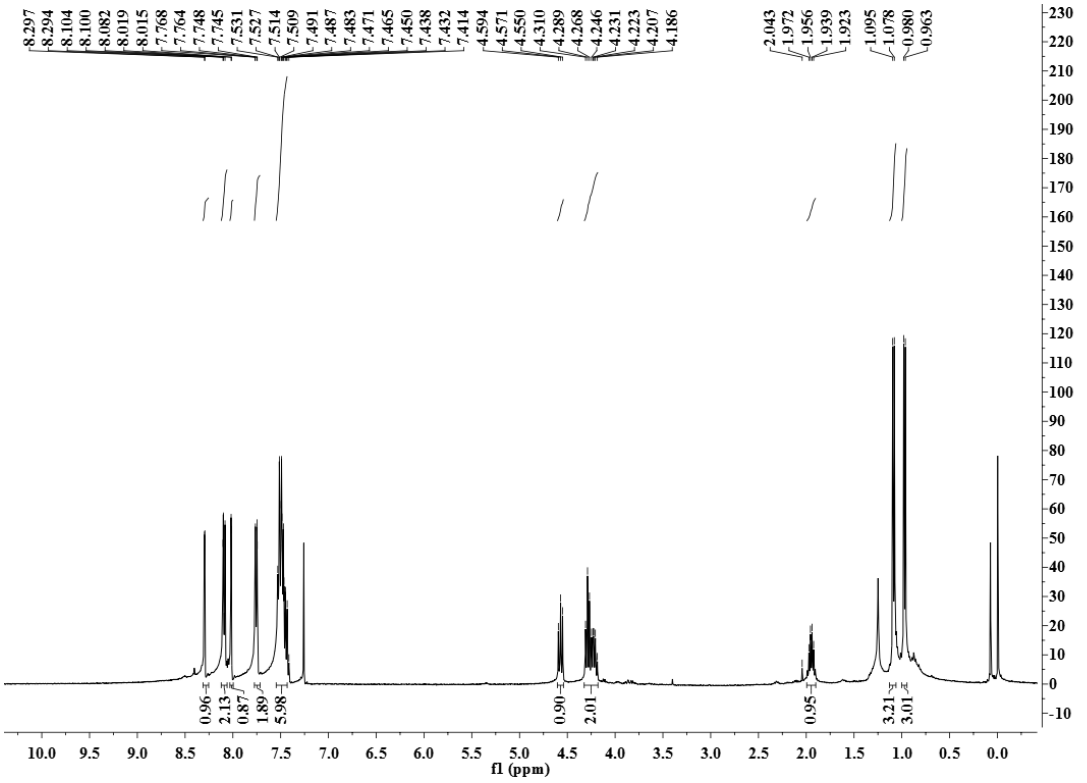
5

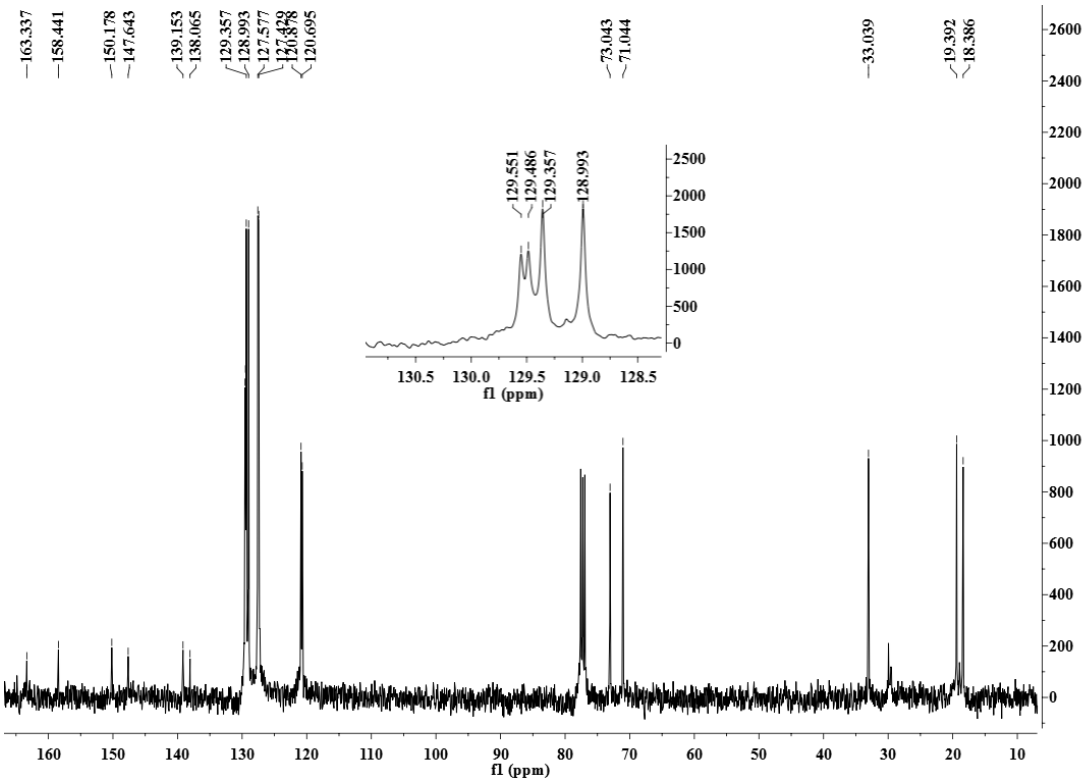

8.429
8.198
8.194
8.062
8.046
7.780
7.764
7.566
7.548
7.530
0.99
1.05
2.20
2.22
6.30
f1 (ppm)

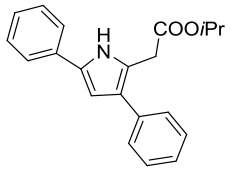

164.303
157.090
152.232
146.445
136.979
130.193
130.050
129.451
129.129
127.245
127.136
122.737
111.016
120.010
f1 (ppm)


iPr
N
N
O

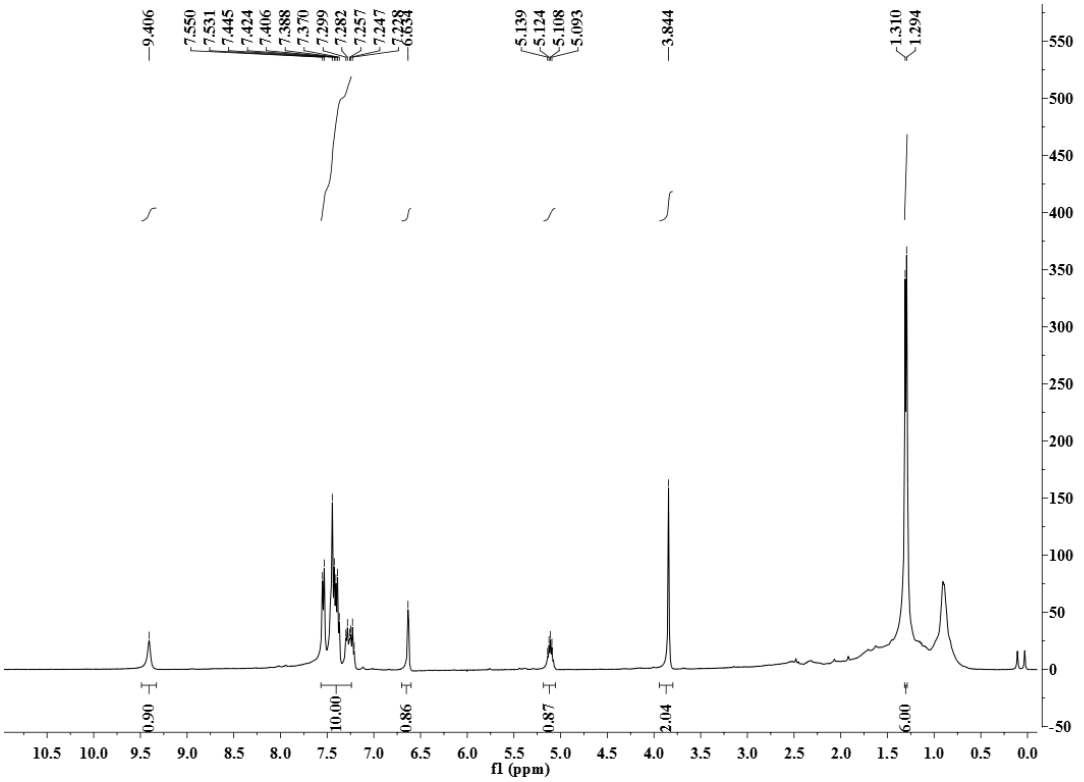
6

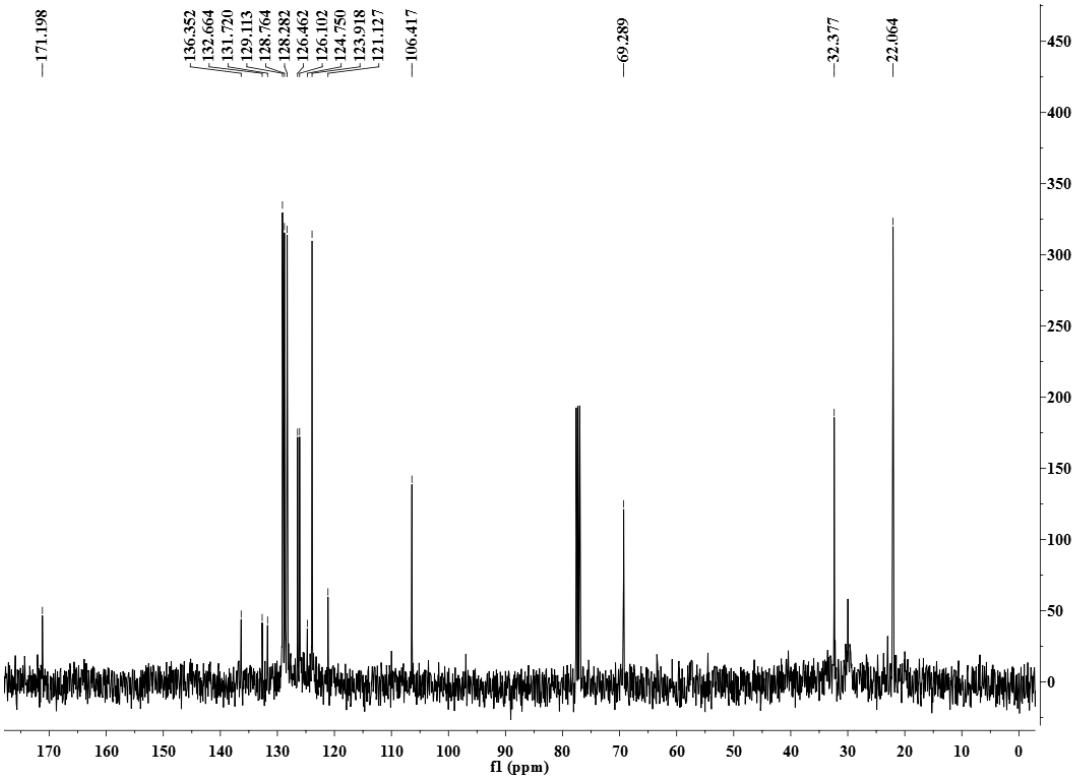

8.297
8.294
8.104
8.100
8.082
8.019
8.015
7.768
7.764
7.748
7.745
7.531
7.527
7.514
7.509
7.491
7.487
7.483
7.471
7.465
7.450
7.438
7.432
7.414
4.594
4.571
4.550
4.310
4.289
4.268
4.246
4.231
4.223
4.207
4.186
2.043
1.972
1.956
1.939
1.923
1.095
1.078
1.078
0.980
0.963
0.96
2.13
0.87
1.89
5.98
0.90
2.01
0.95
3.21
3.01
f1 (ppm)

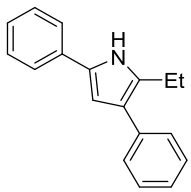

163.337
158.441
150.178
147.643
139.153
138.065
129.357
128.993
127.577
120.695
73.043
71.044
33.039
19.392
18.386
129.551
129.486
129.357
128.993
f1 (ppm)


H
N
COO*i*Pr

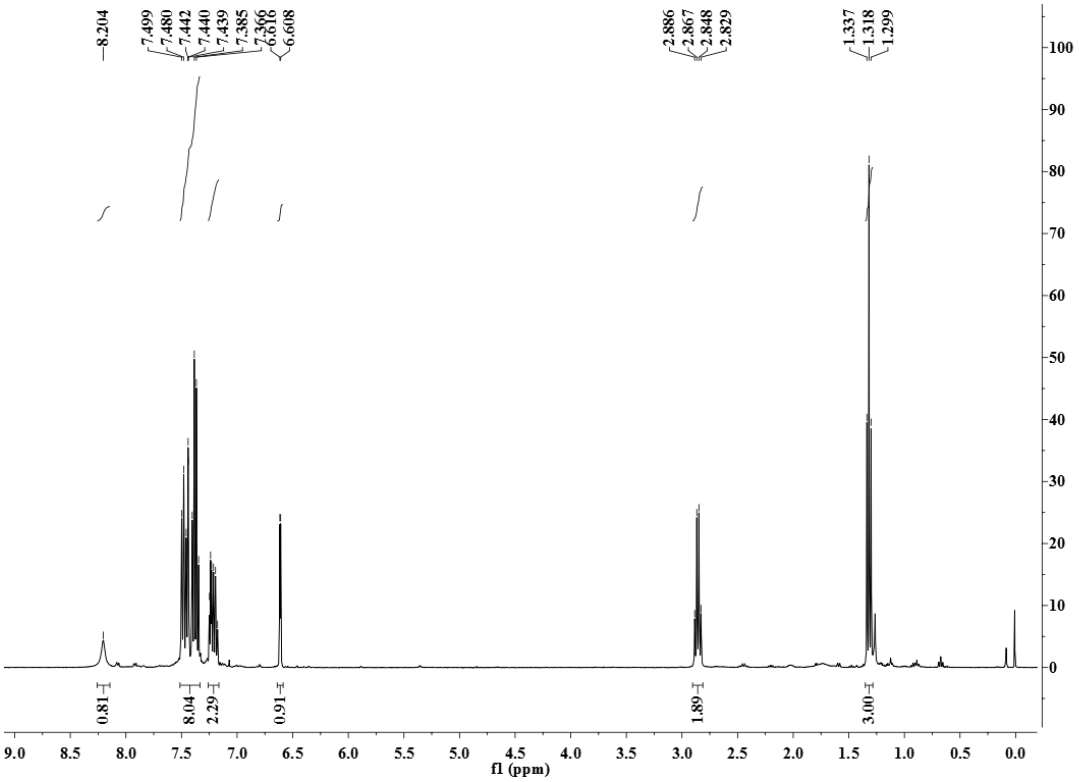
7


9.406
7.550
7.531
7.445
7.424
7.406
7.388
7.370
7.299
7.282
7.257
7.247
6.834
5.139
5.124
5.108
5.093
3.844
1.310
1.294
0.90
10.00
0.86
0.87
2.04
6.00
f1 (ppm)


171.198
136.352
132.664
131.720
129.113
128.764
128.282
126.462
126.102
124.750
123.918
121.127
106.417
69.289
32.377
22.064
f1 (ppm)


H
N
Et

8


8.204
7.499
7.480
7.442
7.440
7.439
7.385
7.366
6.818
6.608
2.886
2.867
2.848
2.829
1.337
1.318
1.299
0.81
8.04
2.29
0.91
1.89
3.00
f1 (ppm)

12. References

[1] J. G. Lqmbardino, *J. Org. Chem*. **1971**, *6*, 1843.

[2] Q. Yang, G. Shang, W. Z. Gao, J. G. Deng, X. Zhang, *Angew. Chem. Int. Ed*. **2006**, *45*, 3832.

[3] Y. Q. Wang, C. B. Yu, D. W. Wang, X. B. Wang, Y.-G. Zhou, *Org. Lett.* **2008**, *10*, 2071.

[4] G. Yang, W. Zhang, *Angew. Chem. Int. Ed*. **2013**, *52*, 7540.

[5] X. Feng, Z. Zhou, C. Ma, X. Yin, R. Li, L. Dong, Y.-C. Chen, *Angew. Chem., Int. Ed*. **2013**, *52*, 14173.

[6] H. Wang, T. Jiang, M. Xu, *J. Am. Chem. Soc*. **2013**, *135*, 971.

[7] Q. An, J. Shen, N. Butt, D. Liu, Y. Liu, W. Zhang, *Org. Lett*. **2014**, *16*, 4496.

[8] Q. An, J. Li, J. Shen, N. Butt, D. Liu, Y. Liu, W. Zhang, *Chem. Commun*. **2015**, *51*, 885.

[9] Q. An, J. Shen, N. Butt, D. Liu, Y. Liu, W. Zhang, *Adv. Synth. Catal.* **2015**, *357*, 3627.

[10] W. W. Tan, Y. J. Ong, N. Yoshikai, *Angew. Chem., Int. Ed*. **2017**, *56*, 8240.

[11] Rykowshi, Lipinska, *Polish Journal of Chemistry*, **1997**, *71*, 83.

[12] M. Kucukdisli, M. M. Nebe, S. M. Bartelt, *Heterocycles* **2016**, *93*, 378.

[13] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys*. **2008**, *10*, 6615.

[14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, *Revision D.01*, Gaussian, Inc., Wallingford CT, **2009**.

[15] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431.

[16] (a) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.***1971**, *54*, 724; (b) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257; (c) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*. **1973**, *28*, 213; (d) P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209; (e) M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163.

[17] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378.