Supporting Information

Iodine-promoted stereoselective amidosulfenylation of electron- deficient alkynes

Fuhong Xiao*, Dahan Wang, ShanShan Yuan, Huawen Huang, Guo-Jun Deng

[a] Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, Hunan Province Key Laboratory of Green Organic Synthesis and Application, College of Chemistry, Xiangtan University, Xiangtan 411105, China. Fax: (+86)0731-58292251; Tel: (+86)0731-58298280; E-mail: fhxiao@xtu.edu.cn;

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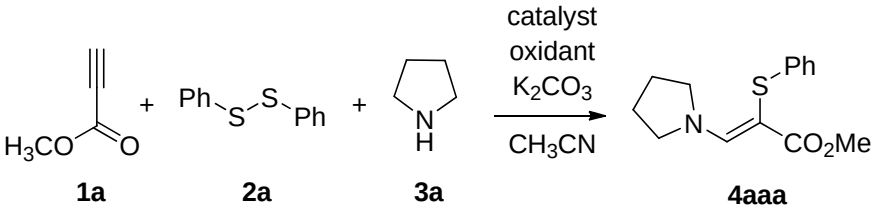
1. General information

All reactions were carried out under an atmosphere of air. Column chromatography was performed using silica gel 48-75 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at the Institute of Chemistry, Chinese Academy of Sciences. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. Most reagents were obtained from commercial suppliers and used without further purification.

2. General procedure (4aaa)

A 10 mL oven-dried reaction vessel was charged with diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), K_2CO_3 (42 mg, 0.3 mmol), I_2 (38 mg, 0.15 mmol), methyl propiolate (**1a**, 18 μL, 0.2 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol), and CH_3CN (0.5 mL) under air. The sealed reaction vessel was stirred at 60 ^{o}C for 4 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aaa** as white solid (47.4 mg, 90% yield), mp = 72-74 ^{o}C.

Table S1



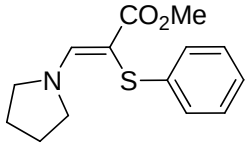
1a **2a** **3a** **4aaa**

Entry	Catalyst	Oxidant	Yield[b] (%)
1	NIS	TBHP	37
2	NH_4I	TBHP	45
3	KI	TBHP	50
4	TBAI	TBHP	42
5	I_2	TBHP	74
6	I_2	H_2O_2	43
7	I_2	DTBP	50
8	I_2	$K_2S_2O_8$	40
9	I_2	$Na_2S_2O_8$	trace
10	I_2	$(NH_4)_2S_2O_8$	trace
11	I_2	DMSO	50
12	I_2	DDQ	trace
13	I_2	AIBN	trace
14	I_2	PIDA	32
15	I_2	BPO	trace
16	I_2	DCP	53
17	I_2	TBPB	56
18[c]	I_2	TBHP	73

[a] Conditions: **1a** (0.2 mmol), **2a** (0.15 mmol), **3a** (0.3 mmol), catalyst (20 mol%, for I_2 10 mol%.), oxidant (2.0 equiv.), base (1.5 equiv.), solvent (0.5 mL), 4 h, 60 ^oC, under air, [b] isolated yield, [c] oxidant (3.0 equiv.). PIDA = (diacetoxyiodo)benzene, BPO = dibenzoyl peroxide, DCP = dicumyl peroxide, TBPB = *tert*-butyl perbenzoate

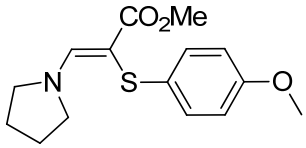
3. Analytical data for the compounds prepared

(*Z*)-methyl 2-(phenylthio)-3-(pyrrolidin-1-yl)acrylate (4aaa)[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.16-7.12 (m, 2H), 7.06 (t, J = 7.3 Hz, 1H), 3.85-3.54 (m, 4H), 3.38 (s, 3H), 1.84 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 152.9, 141.6, 128.6, 124.5, 124.1, 81.8, 51.8. HRMS calcd. for: $C_{14}H_{18}NO_2S^+$ $(M+H)^+$ 264.10528, found 264.10559.

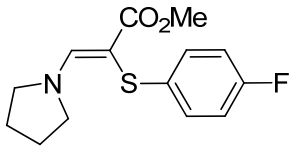
(*Z*)-methyl 2-((4-methoxyphenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4aba)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(4-methoxyphenyl)disulfane (**2b**, 42 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **4aba** as white solid (45.1 mg, 77% yield). mp = 98-101 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.13-7.06 (m, 2H), 6.84-6.78 (m, 2H), 3.85-3.55(m, 4H), 3.76 (s, 3H), 3.68 (s, 3H), 1.85 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 157.2, 152.5, 132.4, 126.4, 114.5, 83.3, 55.3, 51.8. HRMS calcd. for: $C_{15}H_{20}NO_3S^+$ $(M+H)^+$ 294.11584, found 294.11591.

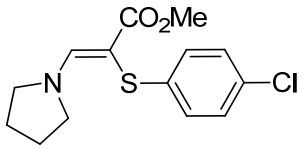
(*Z*)-methyl 2-((4-fluorophenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4aca)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(4-fluorophenyl)disulfane (**2c**, 38.1 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aca** as white solid (43.8 mg, 78% yield), mp = 65-68 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.13-7.04 (m, 2H), 6.98-6.90 (m, 2H), 3.85-3.55 (m, 4H), 3.69 (s, 3H), 1.86 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 160.5 (d, J = 241.5 Hz), 152.8, 136.6 (d, J = 3.0 Hz), 126.23(d, J = 7.7 Hz), 115.7 (d, J = 21.8 Hz), 82.5, 51.9. HRMS calcd. for: $C_{14}H_{17}FNO_2S^+$ $(M+H)^+$ 282.09585, found 282.09555.

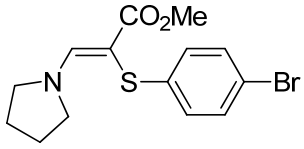
(*Z*)-methyl 2-((4-chlorophenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4ada)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(4-chlorophenyl)disulfane (**2d**, 43 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4ada** as white solid (52.8 mg, 89% yield), mp = 136-139 °C**.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.23-7.15 (m, 2H), 7.10-7.04 (m, 2H), 3.85-3.54 (m, 4H), 3.68 (s, 3H), 1.85 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 152.9, 140.3, 129.8, 128.7, 125.8, 81.6, 51.8. HRMS calcd. for: $C_{14}H_{17}ClNO_2S^+$ $(M+H)^+$ 298.06630, found 298.06613.

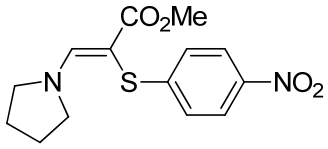
(*Z*)-methyl 2-((4-bromophenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4aea)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(4-bromophenyl)disulfane (**2e**, 56.4 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aea** as white solid (64.3 mg, 94% yield). mp = 133-136 °C**.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.36-7.30 (m, 2H), 7.03-6.98 (m, 2H), 3.85-3.58 (m, 4H), 3.68 (s, 3H), 1.85 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 153.0, 141.0, 131.6, 126.1, 117.6, 81.4, 51.9. HRMS calcd. for: $C_{14}H_{17}BrNO_2S^+$ $(M+H)^+$ 342.01579, found 342.01587.

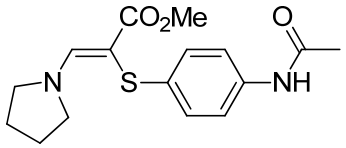
(*Z*)-methyl 2-((4-nitrophenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4afa)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(4-nitrophenyl)disulfane (**2f**, 46.2 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **4afa** as yellow solid (53.6 mg, 87% yield). mp = 155-157 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.09 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 3.78-3.58 (m, 4H), 3.69 (s, 3H), 1.86 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 153.2, 151.8, 144.6, 124.3, 124.0, 79.7, 55.4, 52.0, 48.1, 26.0, 23.9. HRMS calcd. for: $C_{14}H_{17}N_2O_4S^+$ $(M+H)^+$ 309.09035, found 309.09055.

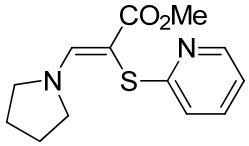
(*Z*)-methyl 2-((4-acetamidophenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4aga)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and N,N'-(disulfanediylbis(4,1-phenylene))diacetamide (**2g**, 49.8 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to yield the desired product **4aga** as white solid (36.5 mg, 57% yield). mp = 218-221 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.32 (t, J = 10.6 Hz, 3H), 7.07 (d, J = 8.6 Hz, 2H), 3.80-3.57 (m, 4H), 3.69 (s, 3H), 2.15 (s, 3H), 1.85 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 168.5, 152.9, 136.6, 134.9, 125.1, 120.8, 82.2, 51.9, 24.3. HRMS calcd. for: $C_{16}H_{21}N_2O_3S^+$ $(M+H)^+$ 321.12674, found 321.12631.

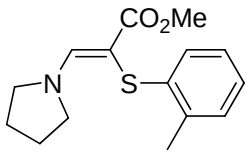
(*Z*)-methyl 2-(pyridin-2-ylthio)-3-(pyrrolidin-1-yl)acrylate (4aha)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(4-chlorophenyl)disulfane (**2h**, 33 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to yield the desired product **4aha** as yellow oil (44.4 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.34 (m, 1H), 8.29 (s, 1H), 7.54-7.47 (m, 1H), 7.10 (dd, J = 8.1, 0.9 Hz, 1H), 6.97-6.91 (m, 1H), 3.89-3.53 (m, 4H), 3.68 (s, 3H), 1.85(s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 163.8, 152.6, 149.3, 136.4, 119.3, 118.8, 81.3, 51.7. HRMS calcd. for: $C_{13}H_{17}N_2O_2S^+$ $(M+H)^+$ 265.10052, found 265.10028.

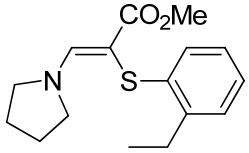
(*Z*)-methyl 3-(pyrrolidin-1-yl)-2-(o-tolylthio)acrylate (4aia)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-di-o-tolyldisulfane (**2i**, 36.9 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aia** as white solid (51.5 mg, 93% yield), mp = 112-114°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.09 (dd, J = 12.6, 6.8 Hz, 2H), 7.03-6.93 (m, 2H), 3.84 (m, 4H), 3.68 (s, 3H), 2.36 (s, 3H), 1.82 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 153.1, 140.4, 133.2, 129.7, 126.3, 123.9, 123.6, 81.0, 51.8, 19.6. HRMS calcd. for: $C_{15}H_{20}NO_2S^+$ $(M+H)^+$ 278.12093, found 278.12106.

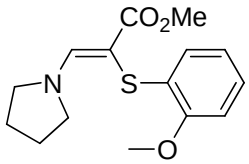
(*Z*)-methyl 2-((2-ethylphenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4aja)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(4-chlorophenyl)disulfane (**2j**, 44.1 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aja** as white solid (51.8 mg, 89% yield), mp = 78-80 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.11 (t, J = 7.3 Hz, 2H), 7.02 (t, J = 6.9 Hz, 2H), 3.79-3.52 (m, 4H), 3.67 (s, 3H), 2.76 (q, J = 7.5 Hz, 2H), 1.82 (s, 4H), 1.27 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 153.1, 139.8, 139.2, 127.8, 126.3, 124.2, 123.9, 81.0, 51.8, 26.1, 13.9. HRMS calcd. for: $C_{16}H_{22}NO_2S^+$ $(M+H)^+$ 292.13658, found 292.13681.

(*Z*)-methyl 2-((2-methoxyphenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4aka)

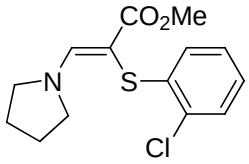


The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(2-methoxyphenyl)disulfane (**2k**, 41.7 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **4aka** as white

solid (48.6 mg, 83% yield), mp = 163-165 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.06 (td, J = 8.0, 1.6 Hz, 1H), 6.97 (dd, J = 7.7, 1.6 Hz, 1H), 6.91 -6.86 (m, 1H), 6.80 (d, J = 8.0 Hz, 1H), 3.89 (s, 3H), 3.77-3.59 (m, 4H), 3.66 (s, 3H), 1.82 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 154.6, 153.3, 129.7, 124.9, 124.7, 121.1, 109.8, 79.8, 55.6, 55.0, 51.8, 47.7, 25.9, 24.0. HRMS calcd. for: $C_{15}H_{20}NO_3S^+$ $(M+H)^+$ 294.11584, found 294.11591.

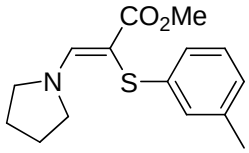
(*Z*)-methyl 2-((2-chlorophenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4ala)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(2-chlorophenyl)disulfane (**2l**, 43.1 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4ala** as white solid (54.6 mg, 92% yield). mp = 137-139 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.30-7.27 (m, 1H), 7.18-7.13 (m, 1H), 7.04-6.97 (m, 2H), 3.79-3.54 (m, 4H), 3.68 (s, 3H), 1.84 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 153.3, 140.3, 129.4, 129.3, 127.0, 125.7, 124.9, 80.4, 55.2, 51.9, 47.9, 26.0, 24.0. HRMS calcd. for: $C_{14}H_{17}ClNO_2S^+$ $(M+H)^+$ 298.06630, found 298.06613.

(*Z*)-methyl 3-(pyrrolidin-1-yl)-2-(m-tolylthio)acrylate (4ama)

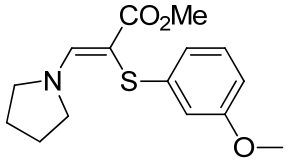


The reaction was conducted withmethyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-di-m-tolyldisulfane (**2m**, 36.9 mg 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **4ama** as white solid (46.5 mg, 84% yield). mp = 97-98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.96-6.91 (m, 2H), 6.87 (d, J = 7.5 Hz, 1H), 3.84-3.54 (m, 4H), 3.69 (s, 3H), 2.29 (s, 3H), 1.84 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 152.9, 141.4, 138.4, 128.5, 125.1, 125.0, 121.6, 81.9, 55.0, 51.8, 47.9, 25.9, 24.0, 21.4. HRMS calcd. for: $C_{15}H_{20}NO_2S^+$

$(M+H)^+$ 278.12093, found 278.12106.

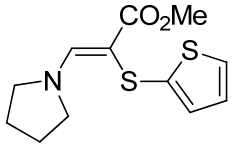
(*Z*)-methyl 2-((3-methoxyphenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4ana)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(3-methoxyphenyl)disulfane (**2n**, 41.8 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **4ana** as yellow oil (48.1 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.15 (t, J = 8.0 Hz, 1H), 6.75-6.69 (m, 2H), 6.61 (dd, J = 8.1, 2.3 Hz, 1H), 3.77 (s, 3H), 3.79-3.65 (m, 4H), 3.69 (s, 3H), 1.84 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.9, 152.9, 143.2, 129.5, 116.8, 110.1, 109.6, 81.5, 55.0, 51.8, 47.9, 26.0, 23.8. HRMS calcd. for: $C_{15}H_{20}NO_3S^+$ $(M+H)^+$ 294.11584, found 294.11591.

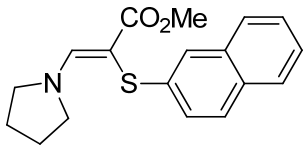
(*Z*)-methyl 3-(pyrrolidin-1-yl)-2-(thiophen-2-ylthio)acrylate (4aoa)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-di(thiophen-2-yl)disulfane (**2o**, 34.5 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aoa** as yellow oil (37.7 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.19-7.15 (m, 1H), 6.96 (dd, J = 3.5, 0.6 Hz, 1H), 6.92-6.88 (m, 1H), 4.00-3.65 (m, 4H), 3.74 (s, 3H), 1.92 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 151.4, 141.7, 127.2, 126.5, 125..7, 86.4, 51.7. HRMS calcd. for: $C_{12}H_{16}NO_2S_2^+$ $(M+H)^+$ 270.06170, found 270.06183.

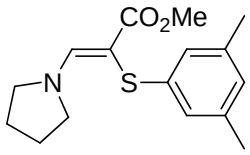
(*Z*)-methyl 2-(naphthalen-2-ylthio)-3-(pyrrolidin-1-yl)acrylate (4apa)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-di(naphthalen-2-yl)disulfane (**2p**, 47.7 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column matography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4apa** as white solid (57 mg, 91% yield), mp = 97-100 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.70 (dd, J = 8.3, 3.7 Hz, 2H), 7.47 (d, J = 1.6 Hz, 1H), 7.45-7.39 (m, 1H), 7.38-7.29 (m, 2H), 3.87-3.54 (m, 4H), 3.69 (s, 3H).1.82 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 153.1, 139.4, 133.9, 133.1, 128.2, 127.6, 126.7, 126.2, 124.6, 123.7, 121.7, 81.6, 55.1, 51.9, 47.9, 26.0, 23.8. HRMS calcd. for: $C_{18}H_{20}NO_2S^+$ $(M+H)^+$ 314.12093, found 314.12082.

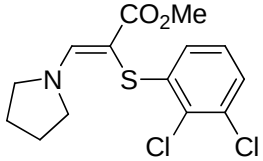
(*Z*)-methyl 2-((3,5-dimethylphenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4aqa)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(3,5-dimethylphenyl)disulfane (**2q**, 41.1 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **3ea** as white solid (54.1 mg, 93% yield), mp = 113-115 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 6.74 (s, 2H), 6.69 (s, 1H), 3.84-3.53 (m, 4H), 3.69 (s, 3H), 2.25 (s, 6H), 1.84 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 152.9, 141.2, 138.2, 126.2, 122.0, 81.0, 55.0, 51.8, 47.9, 26.0, 23.9, 21.2. HRMS calcd. for: $C_{16}H_{22}NO_2S^+$ $(M+H)^+$ 292.13658, found 292.13681.

(*Z*)-methyl 2-((2,3-dichlorophenyl)thio)-3-(pyrrolidin-1-yl)acrylate (4ara)

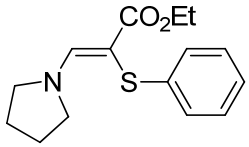


The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and 1,2-bis(2,3-dichlorophenyl)disulfane (**2r**, 53.4 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column

chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4ara** as white solid (54.9 mg, 83% yield), mp = 119-121 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.17 (dd, J = 7.9, 1.4 Hz, 1H), 7.09 (t, J = 7.9 Hz, 1H), 6.92 (dd, J = 7.9, 1.4 Hz, 1H), 3.76-3.55 (m, 4H), 3.68 (s, 3H), 1.85 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 153.3, 143.1, 132.9, 127.1, 127.0, 125.5, 123.7, 80.4, 55.3, 51.9, 47.9, 26.0, 23.9. HRMS calcd. for: $C_{14}H_{16}Cl_2NO_2S^+$ $(M+H)^+$ 332.02733, found 332.02722.

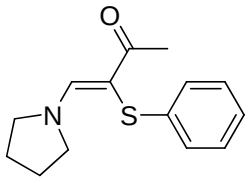
(*Z*)-ethyl 2-(phenylthio)-3-(pyrrolidin-1-yl)acrylate (4baa)



The reaction was conducted with ethyl propiolate (**1b**, 20 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4baa** as colorless oil (51.5 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.25-7.20 (m, 2H), 7.17-7.13 (m, 2H), 7.08-7.02 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.70 (s, 4H), 1.84 (s, 4H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 152.5, 141.7, 128.7, 124.7, 124.1, 82.5, 60.2, 14.4. HRMS calcd. for: $C_{15}H_{20}NO_2S^+$ $(M+H)^+$ 278.12093, found 278.12128.

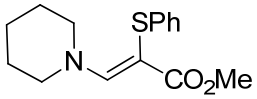
(*Z*)-3-(phenylthio)-4-(pyrrolidin-1-yl)but-3-en-2-one (4caa)



The reaction was conducted with 3-butyn-2-one (**1c**, 24 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), pyrrolidine (**3a**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4caa** as colorless oil (44.5 mg, 90% yield),

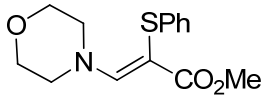
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.29-7.22 (m, 2H), 7.15-7.05 (m, 3H), 3.72 (d, J = 75.0 Hz, 4H), 2.28 (s, 3H), 1.84 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 152.2, 141.6, 128.9, 124.3, 142.2, 92.6, 55.7, 48.0, 26.7, 26.0, 23.8. HRMS calcd. for: $C_{14}H_{18}NOS^+$ $(M+H)^+$ 248.11036, found 248.11064.

(*Z*)-methyl 2-(phenylthio)-3-(piperidin-1-yl)acrylate (4aab)[1]



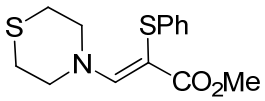
The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), piperidine (**3b**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aab** as colorless oil (49.3 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.18-7.13 (m, 2H), 7.07 (t, J = 7.2 Hz, 1H), 4.01-3.43 (m, 4H), 3.68 (s, 3H), 1.58 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.0, 139.8, 128.7, 124.8, 124.3, 80.3, 51.9, 26.3, 24.1. HRMS calcd. for: $C_{15}H_{20}NO_2S^+$ $(M+H)^+$ 278.12093, found 278.12106.

(*Z*)-methyl 3-morpholino-2-(phenylthio)acrylate (4aac)[1]



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), morpholine (**3c**, 27 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **4aac** as colorless oil (53 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.25 (dd, J = 10.3, 5.2 Hz, 2H), 7.16-7.12 (m, 2H), 7.09 (t, J = 7.3 Hz, 1H), 3.82 (s, 4H), 3.70 (s, 3H), 3.65-3.58 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 153.8, 139.0, 128.9, 124.8, 124.7 , 82.6, 66.8, 52.1. HRMS calcd. for: $C_{14}H_{18}NO_3S^+$ $(M+H)^+$ 280.10019, found 280.10056.

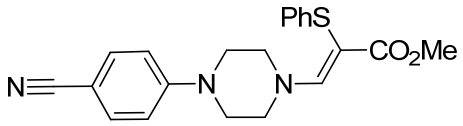
(*Z*)-methyl 2-(phenylthio)-3-thiomorpholinoacrylate (4aad)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), thiomorpholine (**3d**, 30 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **4aad** as white solid (56 mg, 95% yield), mp = 77-79 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.27-7.21 (m, 2H), 7.17-7.05 (m, 3H), 4.03 (s, 4H), 3.69 (s, 3H), 2.65-2.54 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 153.6, 139.0, 128.8, 124.7, 124.6, 82.6, 52.0, 27.7. HRMS calcd. for: $C_{14}H_{18}NO_2S_2^+$ $(M+H)^+$ 296.07735, found 296.07751.

(*Z*)-methyl 3-(4-(4-cyanophenyl)piperazin-1-yl)-2-(phenylthio)acrylate (4aae)

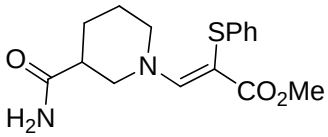


The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), 4-(piperazin-1-yl)ben**z**onitrile (**3e**, 56.1 mg, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to yield the desired product **4aae** as yellow oil (70.5 mg, 93% yield).

[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.29-7.23 (m, 2H), 7.19-7.04 (m, 3H), 6.84 (d, J = 8.7 Hz, 2H), 3.98 (s, 4H), 3.71 (s, 3H), 3.28 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 153.5, 152.5, 138.8, 133.4, 128.9, 124.7, 124.6, 119.6, 114.4, 101.1, 83.0, 52.1, 47.3. HRMS calcd. for: $C_{21}H_{22}N_3O_2S^+$ $(M+H)^+$ 380.14272, found 380.14240.

.

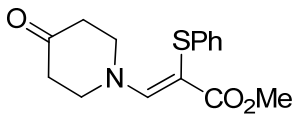
(*Z*)-methyl 3-(3-carbamoylpiperidin-1-yl)-2-(phenylthio)acrylate (4aaf)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), piperidine-3-carboxamide (**3f**, 38.4 mg, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to yield the desired product **4aaf** as white solid (55.7 mg, 87% yield). mp = 137-139 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.30-7.25 (m, 2H), 7.17 (d, J = 7.5 Hz, 2H), 7.10 (t, J = 7.3 Hz, 1H), 5.19 (s, 1H), 4.97 (s, 2H), 3.94 (d, J = 38.3 Hz, 1H), 3.71 (s, 3H), 3.20 (t, J = 11.6 Hz, 1H), 3.14-3.05 (m, 1H), 2.12 (s, 1H), 1.90 (d, J = 13.1 Hz, 1H), 1.78 (t, J = 10.3 Hz, 2H), 1.54 (dd, J = 17.7, 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 170.4, 153.8, 139.3, 129.0, 124.7, 124.6, 81.2, 52.1, 43.5, 27.0, 25.2. HRMS calcd. for: $C_{16}H_{21}N_2O_3S^+$ $(M+H)^+$ 321.12674, found 321.12698.

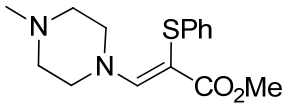
(*Z*)-methyl 3-(4-oxopiperidin-1-yl)-2-(phenylthio)acrylate (4aag)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), piperidin-4-one hydrochloride (**3g**, 40.5 mg, 0.15 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to yield the desired product **4aag** as colorless oil (55.3 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.29-7.23 (m, 2H), 7.16 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.3 Hz, 1H), 4.05 (s, 4H), 3.72 (s, 3H), 2.45 (t, J = 6.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 169.9, 153.5, 138.8, 129.0, 124.9, 124.8, 84.5, 52.3, 41.6. HRMS calcd. for: $C_{15}H_{18}NO_3S^+$ $(M+H)^+$ 292.10019, found 292.10043.

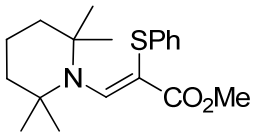
(*Z*)-methyl 3-(4-methylpiperazin-1-yl)-2-(phenylthio)acrylate (4aah)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), 1-methylpiper**a**zine (**3h**, 33 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to yield the desired product **4aah** as colorless oil (35 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.24 (t, J = 7.7 Hz, 2H), 7.17-7.12 (m, 2H), 7.08 (t, J = 7.3 Hz, 1H), 3.98-3.62 (m, 4H), 3.69 (s, 3H) 2.40-2.31 (m, 4H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 153.9, 139.3, 128.8, 124.8, 124.5, 81.7, 54.9, 52.1, 45.8. HRMS calcd. for: calcd for $C_{15}H_{21}N_2O_2S^+$ $(M+H)^+$ 293.13183, found 293.13193.

(*Z*)-methyl 2-(phenylthio)-3-(2,2,6,6-tetramethylpiperidin-1-yl)acrylate (4aai)

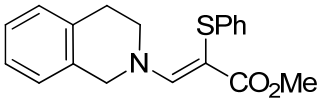


The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), 2,2,6,6-tetramethylpiperidine (**4i**, 50.3 μL, 0.3 mmol). The residue was purified by column

chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aai** as white solid (24.6 mg, 37% yield). mp = 76-78 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.25-7.19 (m, 2H), 7.17-7.10 (m, 2H), 7.07 (dd, J = 11.4, 4.2 Hz, 1H), 3.64 (s, 3H), 1.72 (s, 6H), 1.43 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.2, 139.1, 128.6, 125.2, 124.4, 92.3, 58.4, 52.2, 37.4, 29.7, 15.0. HRMS calcd. for: $C_{19}H_{28}NO_2S^+$ $(M+H)^+$ 334.18353, found 334.18314.

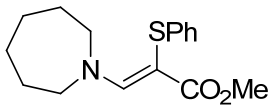
(*Z*)-methyl 3-(3,4-dihydroisoquinolin-2(1H)-yl)-2-(phenylthio)acrylate (4aaj)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), 1,2,3,4-tetrahydroisoquinoline (**3j**, 37 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aaj** as white solid (58.5 mg, 90% yield). mp = 110-112 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.23-7.13 (m, 6H), 7.10-7.03 (m, 2H), 6.98 (d, J = 4.8 Hz, 1H), 4.94 (s, 2H), 3.99 (s, 2H), 3.69 (s, 3H), 2.86 (t, J = 5.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 154.4, 139.9, 133.5, 132.5, 128.7 128.5, 126.8, 126.4, 125.9, 124.8, 124.4, 82.3, 52.0, 29.1. HRMS calcd. for: $C_{19}H_{20}NO_2S^+$ $(M+H)^+$ 326.12093, found 326.12103.

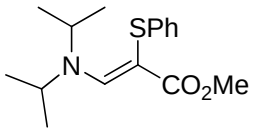
(*Z*)-methyl 3-(azepan-1-yl)-2-(phenylthio)acrylate (4aak)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), a**z**epane (**3k**, 33.7 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aak** as white solid (53.5 mg, 92% yield). mp = 80-82 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.14 (d, J = 7.3 Hz, 2H), 7.06 (t, J = 7.2 Hz, 1H), 3.91-3.39 (m, 4H), 3.68 (s, 3H), 1.72 (s, 4H), 1.54 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 155.1, 140.7, 128.6, 124.4, 124.1, 80.6, 59.6, 51.9, 48.5, 29.7, 28.0, 26.5, 25.8. HRMS calcd. for: $C_{16}H_{22}NO_2S^+$ $(M+H)^+$ 292.13658, found 292.13684.

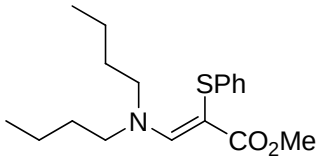
(*Z*)-methyl 3-(diisopropylamino)-2-(phenylthio)acrylate (4aal)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), diisopropylamine (**3l**, 42 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to yield the desired product **4aal** as white solid (52.7 mg, 90% yield). mp = 87-89 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.22 (t, J = 7.7 Hz, 2H), 7.14 (d, J = 7.4 Hz, 2H), 7.05 (s, 1H), 5.64 (s, 1H), 3.80-3.47 (m, 1H), 3.69 (s, 3H), 1.38-0.97 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 150.6, 139.9, 128.6, 124.7, 124.2, 80.6, 51.9, 48.0, 47.1, 24.0, 20.5. HRMS calcd. for: $C_{16}H_{24}NO_2S^+$ $(M+H)^+$ 294.15223, found 294.15189.

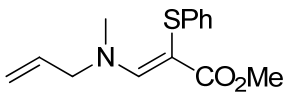
(*Z*)-methyl 3-(dibutylamino)-2-(phenylthio)acrylate (4aam)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), dibutylamine (**4m**, 50.6 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **4aam** as colorless oil (59.8 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.22 (t, J = 7.7 Hz, 2H), 7.11 (d, J = 7.5 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 3.73-3.15 (m, 4H), 3.69 (s, 3H) 1.52 (s, 4H), 1.25 (s, 4H), 0.90 (d, J = 26.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.4, 140.5, 128.6, 124.3, 124.1, 80.4, 51.9, 19.6, 13.6. HRMS calcd. for: $C_{18}H_{28}NO_2S^+$ $(M+H)^+$ 322.18353, found 322.18335.

(*Z*)-methyl 3-(allyl(methyl)amino)-2-(phenylthio)acrylate (4aan)

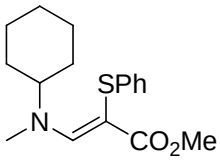


The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), N-methylprop-2-en-1-amine (**4n**, 29.2 μL, 0.3 mmol). The residue was purified by column

chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aan** as colorless oil (44.7 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.25 (dd, J = 12.8, 4.8 Hz, 2H), 7.14 (d, J = 7.4 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 5.82-7.69 (m, 1H), 5.19 (dd, J = 21.8, 13.7 Hz, 2H), 4.25-3.85 (m, 2H), 3.69 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 155.5, 140.6, 132.2, 128.7, 124.6, 124.3, 118.3, 82.0, 52.0. HRMS calcd. for: $C_{14}H_{18}NO_2S^+$ $(M+H)^+$ 264.10528, found 264.10519.

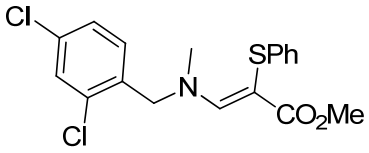
(*Z*)-methyl 3-(cyclohexyl(methyl)amino)-2-(phenylthio)acrylate (4aao)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), N-methylcyclohexanamine (**4o**, 39 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aao** as colorless oil (56.1 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.22 (d, J = 7.4 Hz, 2H), 7.13 (d, J = 7.2 Hz, 2H), 7.06 (s, 1H), 3.68 (s, 3H), 3.21 (s, 4H), 1.83 (s, 3H), 1.63 (d, J = 12.5 Hz, 2H), 1.45 (d, J = 10.8 Hz, 2H), 1.27 (d, J = 12.1 Hz, 2H), 1.10 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 154.2, 141.1, 128.6, 124.4, 124.1, 80.6, 68.6, 51.9, 33.6, 31.1, 25.4, 25.0. HRMS calcd. for: $C_{17}H_{24}NO_2S^+$ $(M+H)^+$ 306.15223, found 306.15140.

(*Z*)-methyl 3-((2,4-dichlorobenzyl)(methyl)amino)-2-(phenylthio)acrylate (4aap)

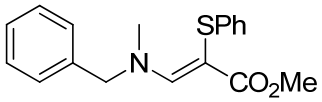


The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol) and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), 1-(2,4-dichlorophenyl)-N-methylmethanamine (**4p**, 57 mg, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aap** as white solid (68.6 mg, 90% yield). mp = 76-78 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.37 (s, 1H), 7.26-7.14 (m, 3H), 7.14-7.03 (m, 3H), 7.00 (d, J = 7.9 Hz, 1H), 4.75 (s, 2H), 3.71 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 155.6, 140.1, 134.0,

133.7, 132.1, 130.0, 128.9, 128.7, 127.3, 124.6, 124.4, 83.7, 52.06. HRMS calcd. for: $C_{18}H_{18}Cl_2NO_2S^+$ $(M+H)^+$ 382.04298, found 382.04349.

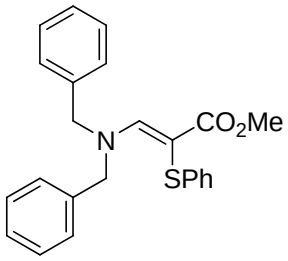
(*Z*)-methyl 3-(benzyl(methyl)amino)-2-(phenylthio)acrylate (4aaq)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), N-methylbenzylamine (**4q**, 38.7 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aaq** as colorless oil (55.1 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.36-7.28 (m, 3H), 7.23 (t, J = 7.7 Hz, 2H), 7.15 (t, J = 8.2 Hz, 4H), 7.08 (d, J = 7.2 Hz, 1H), 4.63 (s, 2H), 3.71 (s, 3H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 155.8, 140.5, 135.9, 128.8, 128.7, 127.9, 127.3, 124.8, 124.4, 82.6, 52.1. HRMS calcd. for: $C_{18}H_{20}NO_2S^+$ $(M+H)^+$ 314.12093, found 314.12015.

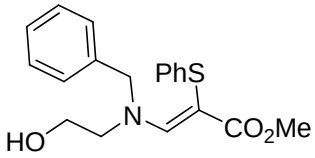
(*Z*)-methyl 3-(dibenzylamino)-2-(phenylthio)acrylate (4aar)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.3 mmol), diben**z**ylamine (**4r**, 57.7 μL, 0.3mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aar** as yellow oil (69.2 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.30 (d, J = 6.8 Hz, 6H), 7.20 (dd, J = 10.4, 4.9 Hz, 3H), 7.15-7.09 (m, 5H), 7.06 (d, J = 7.2 Hz, 1H), 5.05-4.23 (m, 4H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 155.4, 139.5, 136.0, 128.8, 128.4, 127.8, 127.5, 124.8, 124.5, 83.1, 52.1. HRMS calcd. for: $C_{24}H_{24}NO_2S^+$ $(M+H)^+$ 390.15223, found 390.15121.

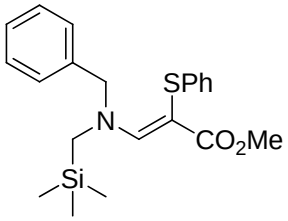
(*Z*)-methyl 3-(benzyl(2-hydroxyethyl)amino)-2-(phenylthio)acrylate (4aas)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), 2-(ben**z**ylamino)ethanol (**4s**, 43 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to yield the desired product **4aas** as colorless oil (65.2 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.35-7.20 (m, 5H), 7.17 (d, J = 6.9 Hz, 2H), 7.13 (d, J = 7.4 Hz, 2H), 7.08 (t, J = 7.3 Hz, 1H), 4.81 (s, 2H), 3.82-3.54 (m, 4H), 3.71 (s, 3H), 1.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 155.5, 139.5, 136.4, 128.8, 128.7, 127.8, 127.3, 124.7, 124.5, 82.4, 60.7, 52.1, 29.6. HRMS calcd. for: $C_{19}H_{22}NO_3S^+$ $(M+H)^+$ 344.13149, found 344.13068.

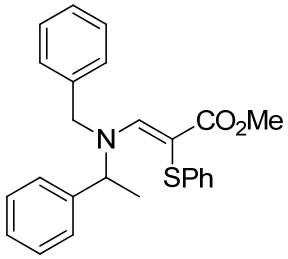
(*Z*)-methyl 3-(benzyl((trimethylsilyl)methyl)amino)-2-(phenylthio)acrylate (4aat)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol) and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), N-ben**z**yl-1-(trimethylsilyl)methanamine (**4t**, 66 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 9:1) to yield the desired product **4aat** as yellow oil (70.1 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.29 (d, J = 22.6 Hz, 3H), 7.22 (t, J = 7.4 Hz, 2H), 7.08 (dd, J = 22.1, 14.8 Hz, 5H), 5.05 (s, 1H), 4.43 (s, 1H), 3.71 (s, 3H), 3.40 (s, 1H), 2.81 (s, 1H), 0.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.7, 140.6, 135.5, 128.7, 128.1, 127.5, 127.2, 124.6, 124.3, 79.7, 63.9, 53.0, 51.9, 48.9, 38.8, 29.6, -1.8. HRMS calcd. for: $C_{21}H_{28}NO_2SSi^+$ $(M+H)^+$ 386.16045, found 386.16055.

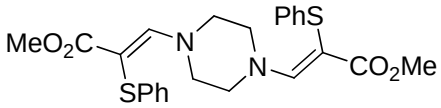
(*Z*)-methyl 3-(benzyl(1-phenylethyl)amino)-2-(phenylthio)acrylate (4aau)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), N-ben**z**yl-1-phenylethanamine (**3u**, 63 μL, 0.3 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to yield the desired product **4aau** as colorless oil (61.3 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.33 (dd, J = 13.1, 5.7 Hz, 3H), 7.29-7.24 (m, 3H), 7.23-7.16 (m, 4H), 7.16-6.97 (m, 5H), 5.44 (s, 1H), 4.49 (s, 2H), 3.71 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 140.4, 139.8, 137.4, 128.8, 128.7, 128.5, 128.3, 127.9, 127.3, 127.0, 126.7, 124.8, 124.4, 83.0, 57.4, 52.1. HRMS calcd. for: $C_{25}H_{26}NO_2S^+$ $(M+H)^+$ 404.16788, found 404.16754.

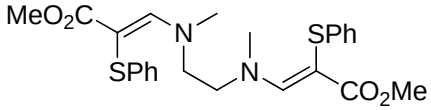
(2*Z*,2'*Z*)-dimethyl 3,3'-(piperazine-1,4-diyl)bis(2-(phenylthio)acrylate) (4aav)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg, 0.15 mmol), pipera**z**ine (**3v**, 13 mg, 0.15 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to yield the desired product **4aav** as white solid (21.1 mg, 45% yield), mp =196-198 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.26-7.20 (m, 2H), 7.08 (dd, J = 10.5, 4.3 Hz, 3H), 3.83-6.63 (m, 4H) 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 153.2, 138.5, 129.0, 124.9, 124.8, 84.2, 52.2. HRMS calcd. for: $C_{24}H_{27}N_2O_4S_2^+$ $(M+H)^+$ 471.14068, found 471.14014.

(2*Z*,2'*Z*)-dimethyl3,3'-(ethane-1,2-diylbis(methylazanediyl))bis(2-(phenylthio)acrylate) (4aaw)



The reaction was conducted with methyl propiolate (**1a**, 18 μL, 0.2 mmol), and diphenyl disulfide (**2a**, 33 mg,

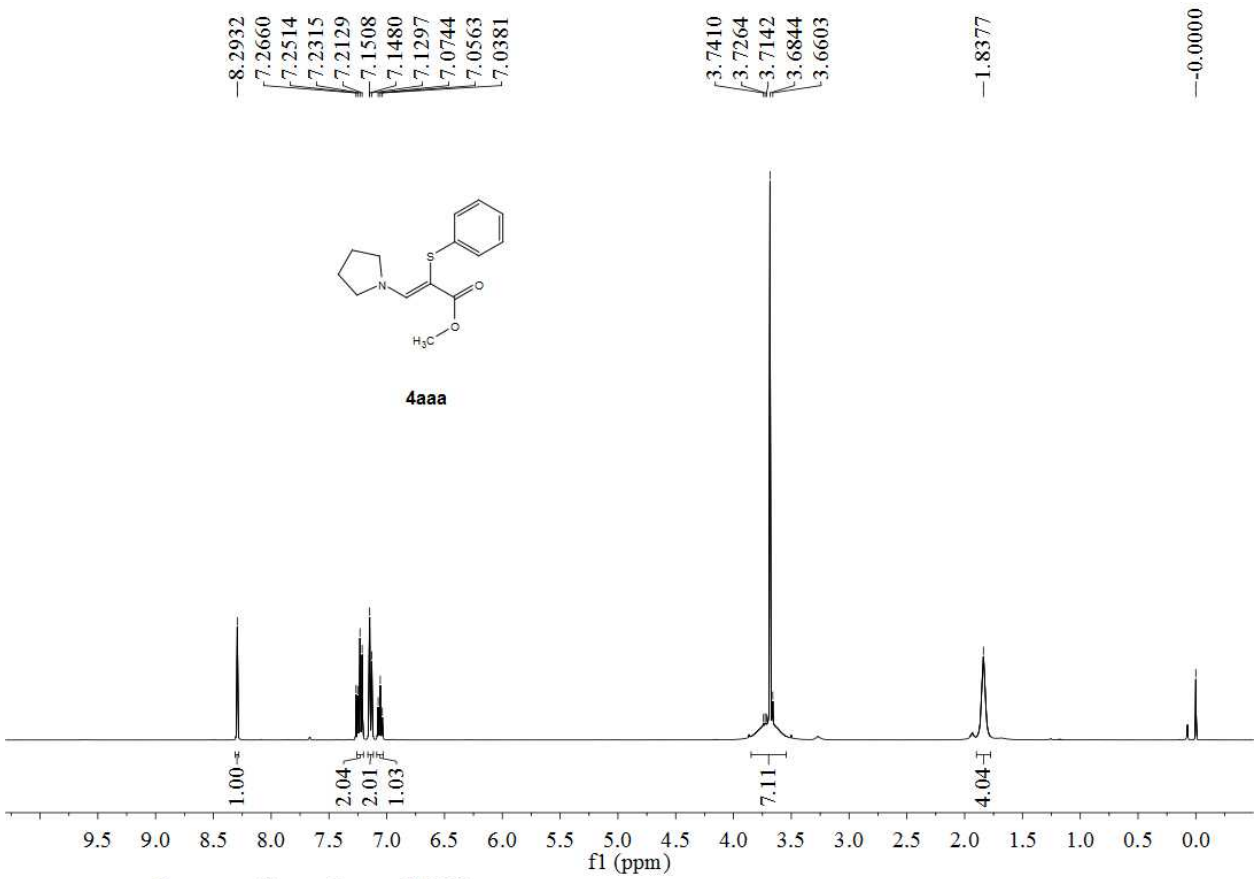
0.15 mmol), N,N'-dimethylethane-1,2-diamine (**3w**, 13 μL, 0.15 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to yield the desired product **4aaw** as white solid. (21.7 mg, 46% yield), mp =143-145 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.25-7.20 (m, 2H), 7.10-7.05 (m, 3H), 3.68 (s, 5H), 3.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 155.2, 129.0, 124.6, 124.3, 52.1. HRMS calcd. for: $C_{24}H_{29}N_2O_4S_2^+$ $(M+H)^+$ 473.15633, found 473.15607.

4. References

[1] Y. Jiang, G.H. Liang, C, Zhang, T.-P Loh, *Eur. J. Org. Chem.* **2016**, 3326.

NMR Spectra for the compounds prepared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3.7264
3.7142
3.6844
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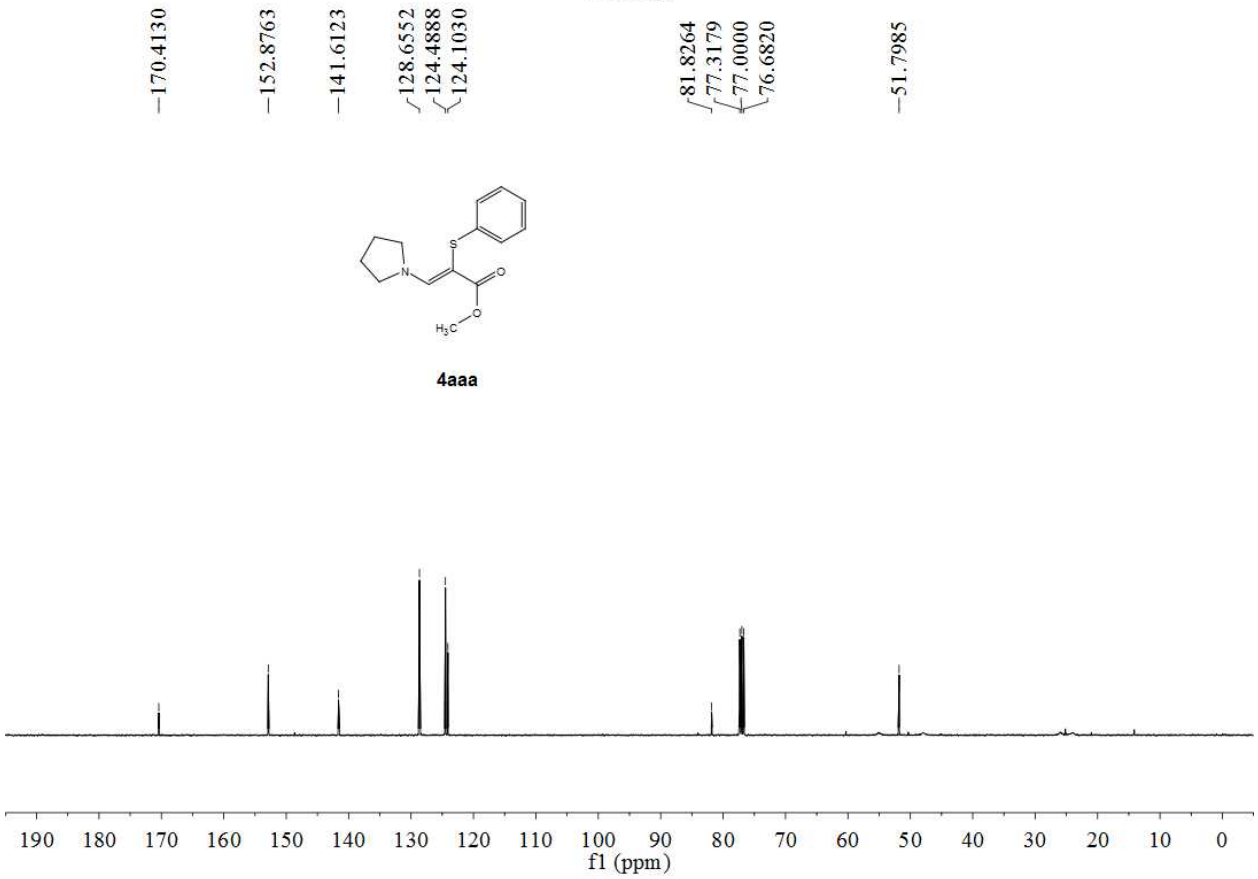
2.04
2.01
1.03
7.11
4.04
f1 (ppm)

4aaa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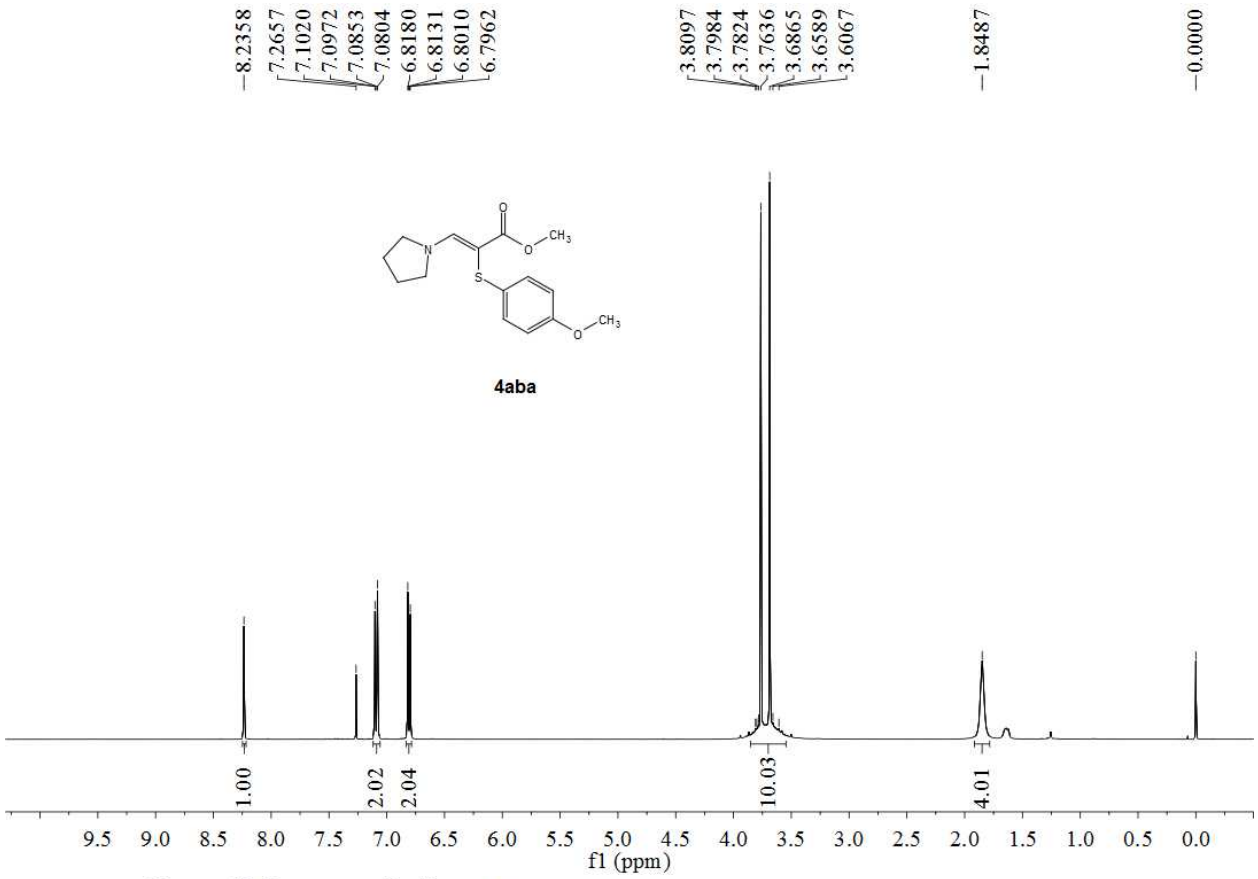
f1 (ppm)

4aaa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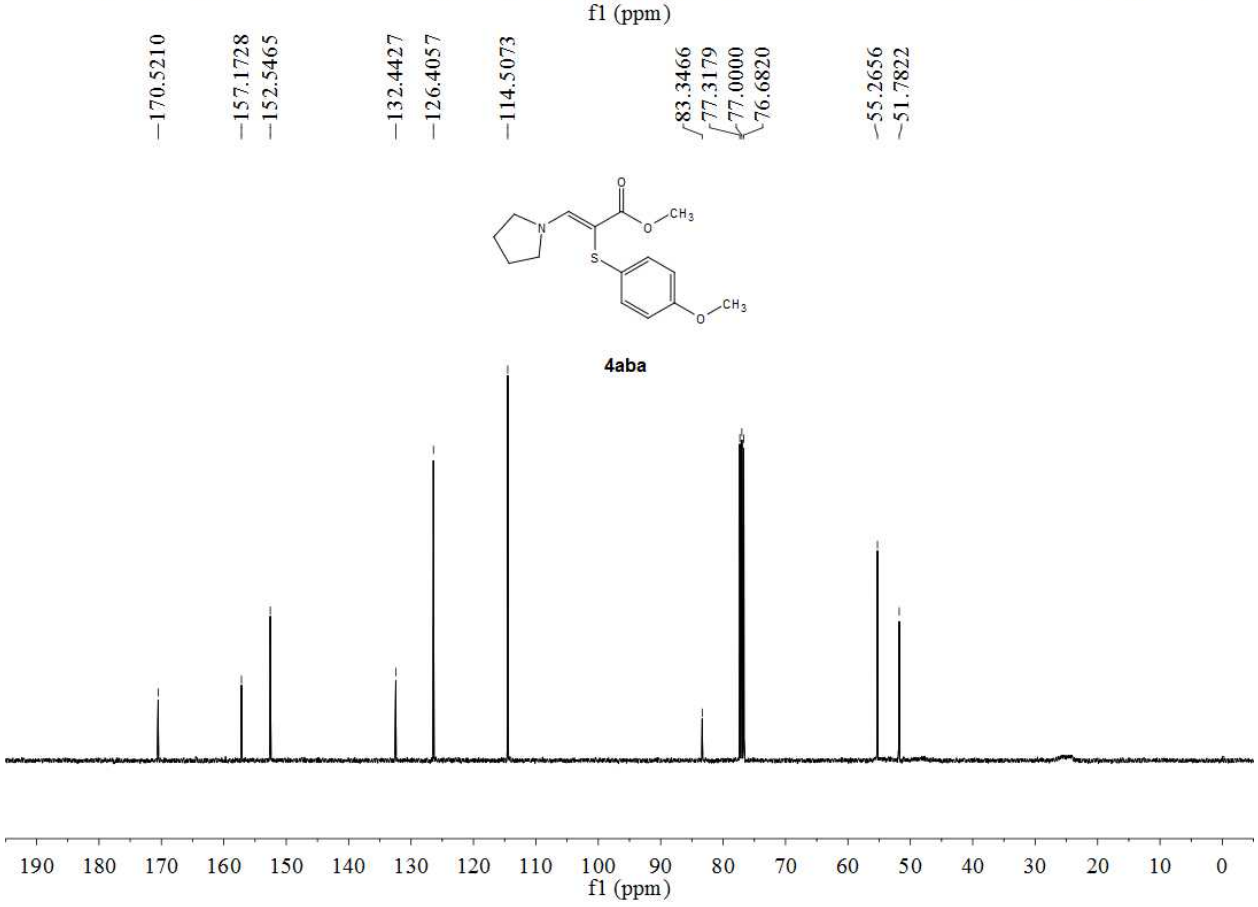
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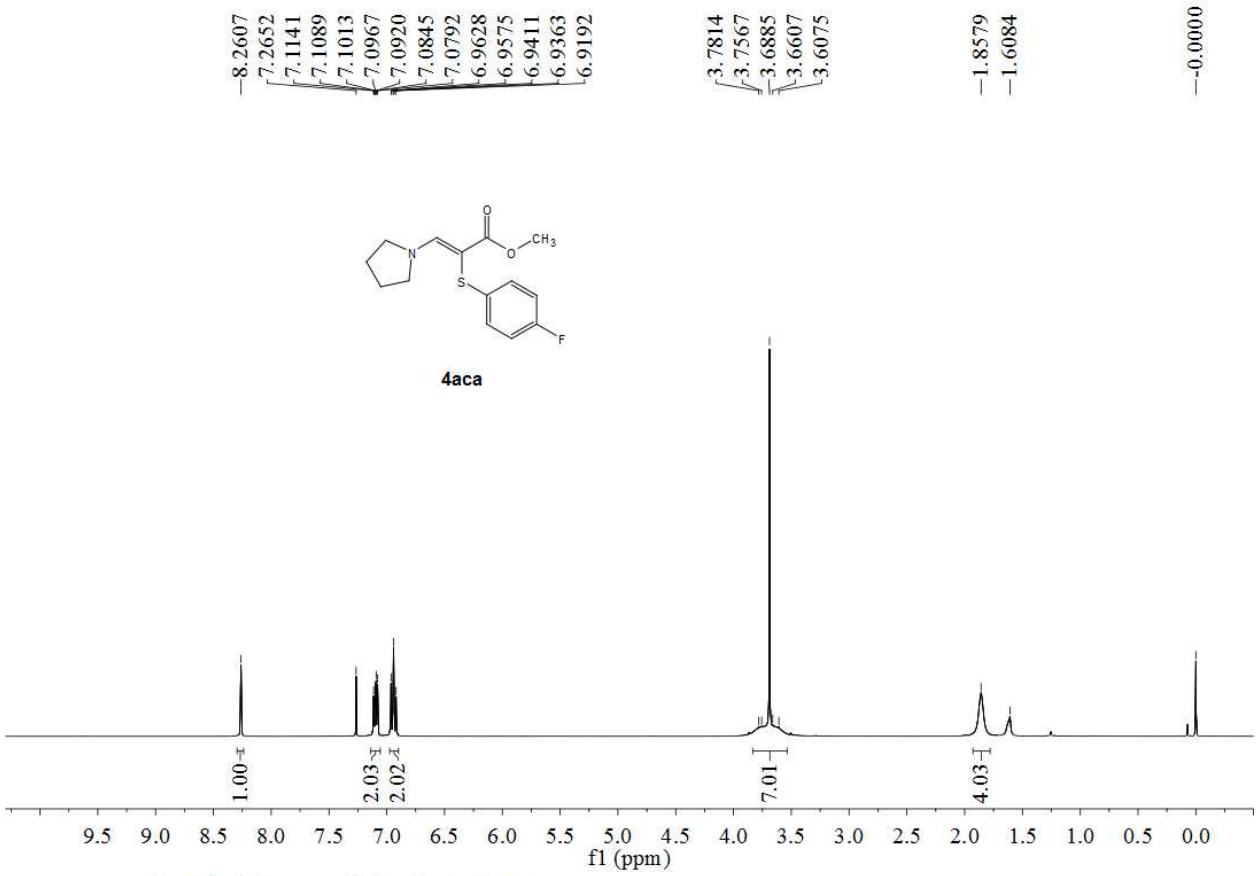
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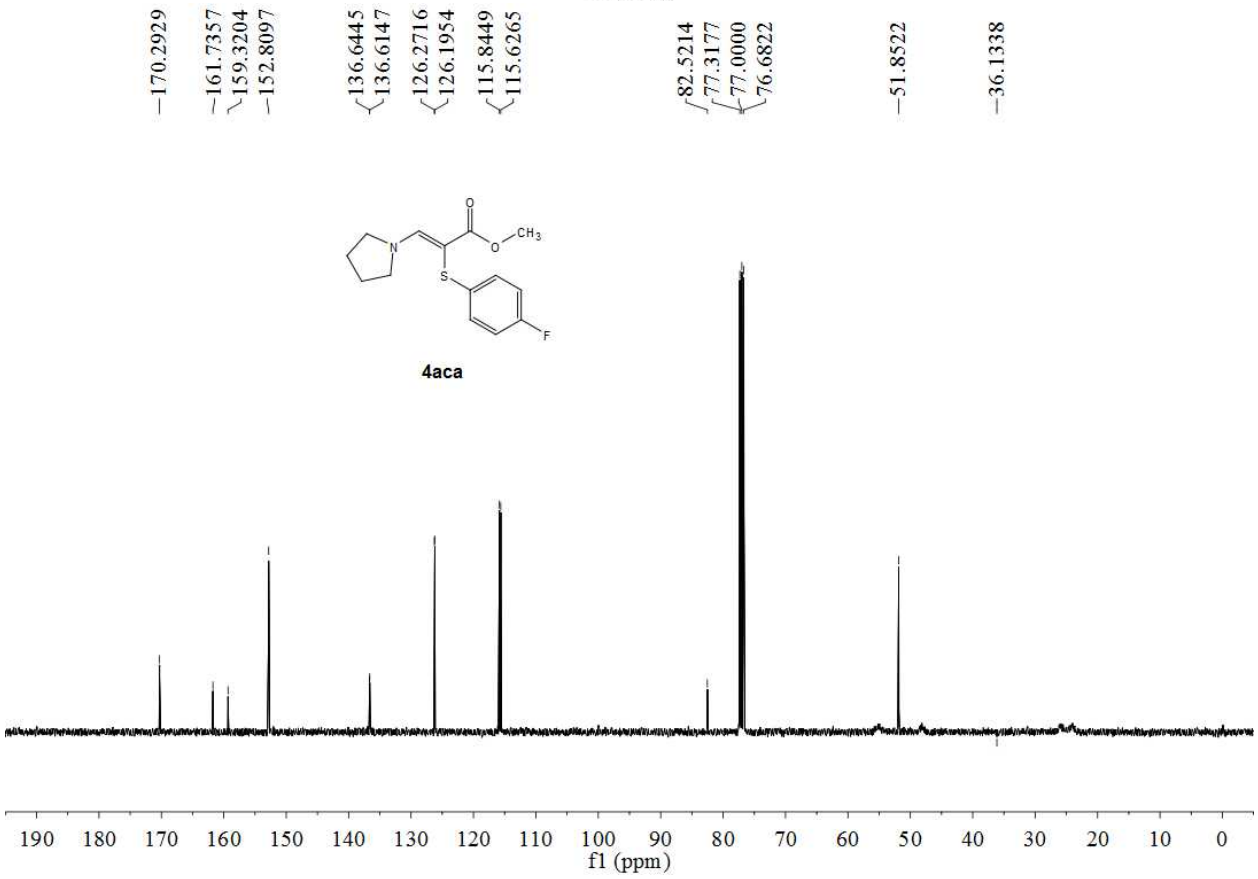
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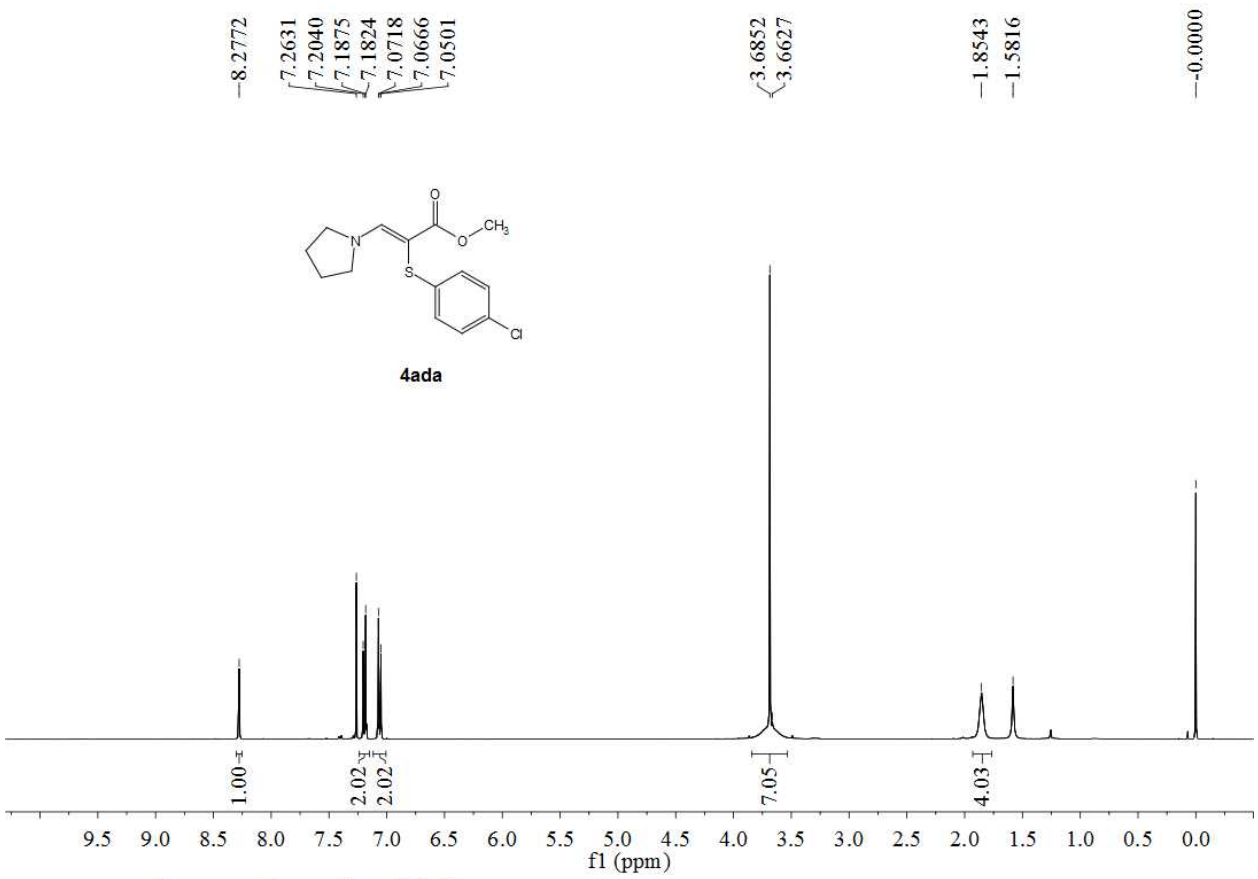
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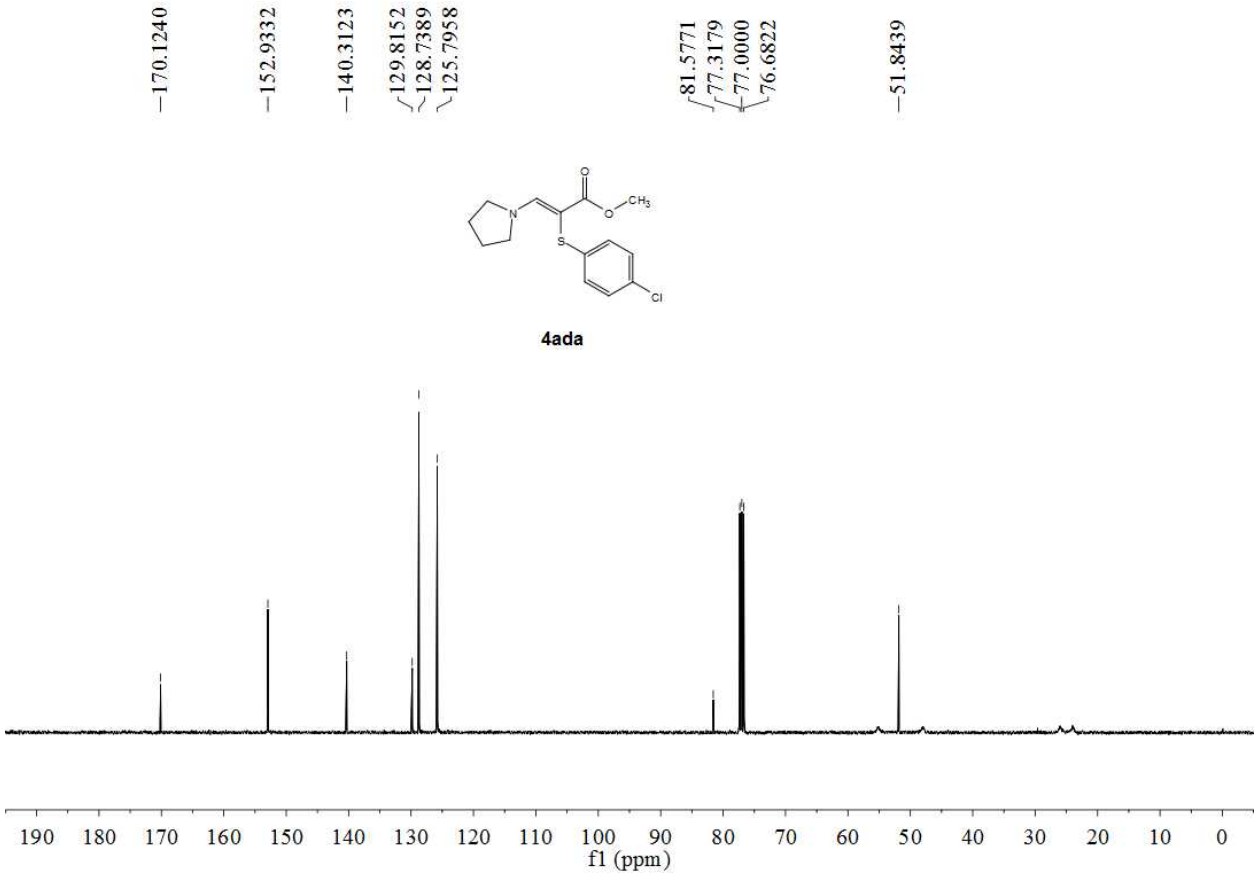
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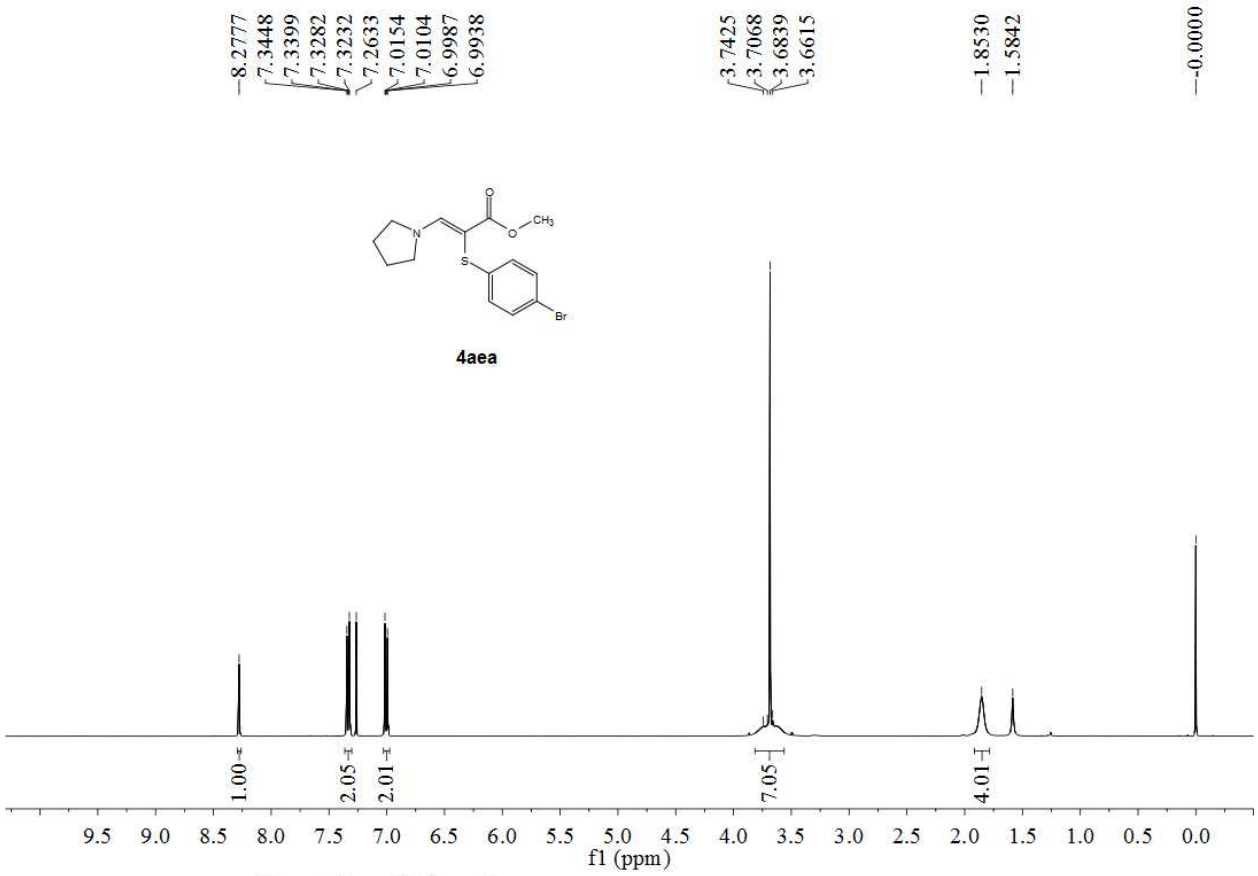
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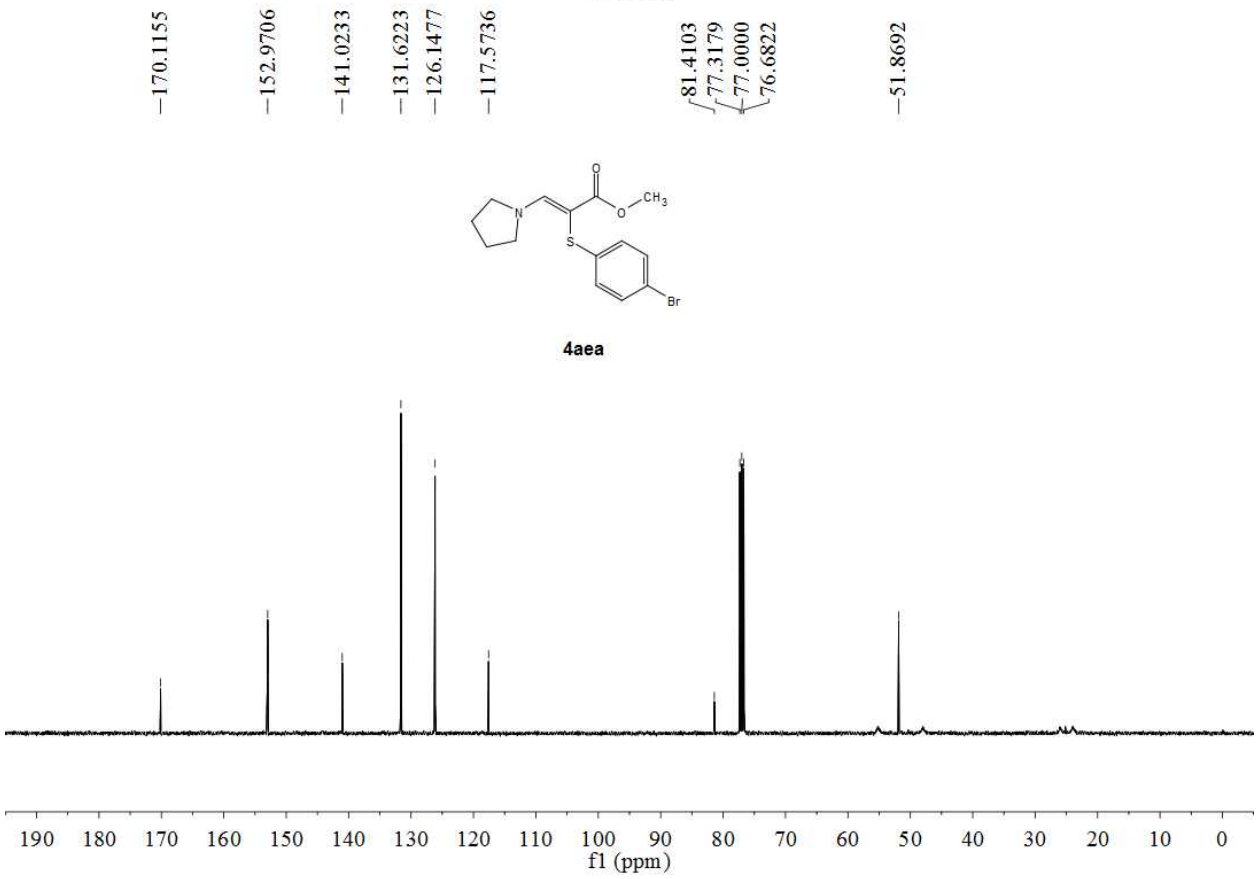
f1 (ppm)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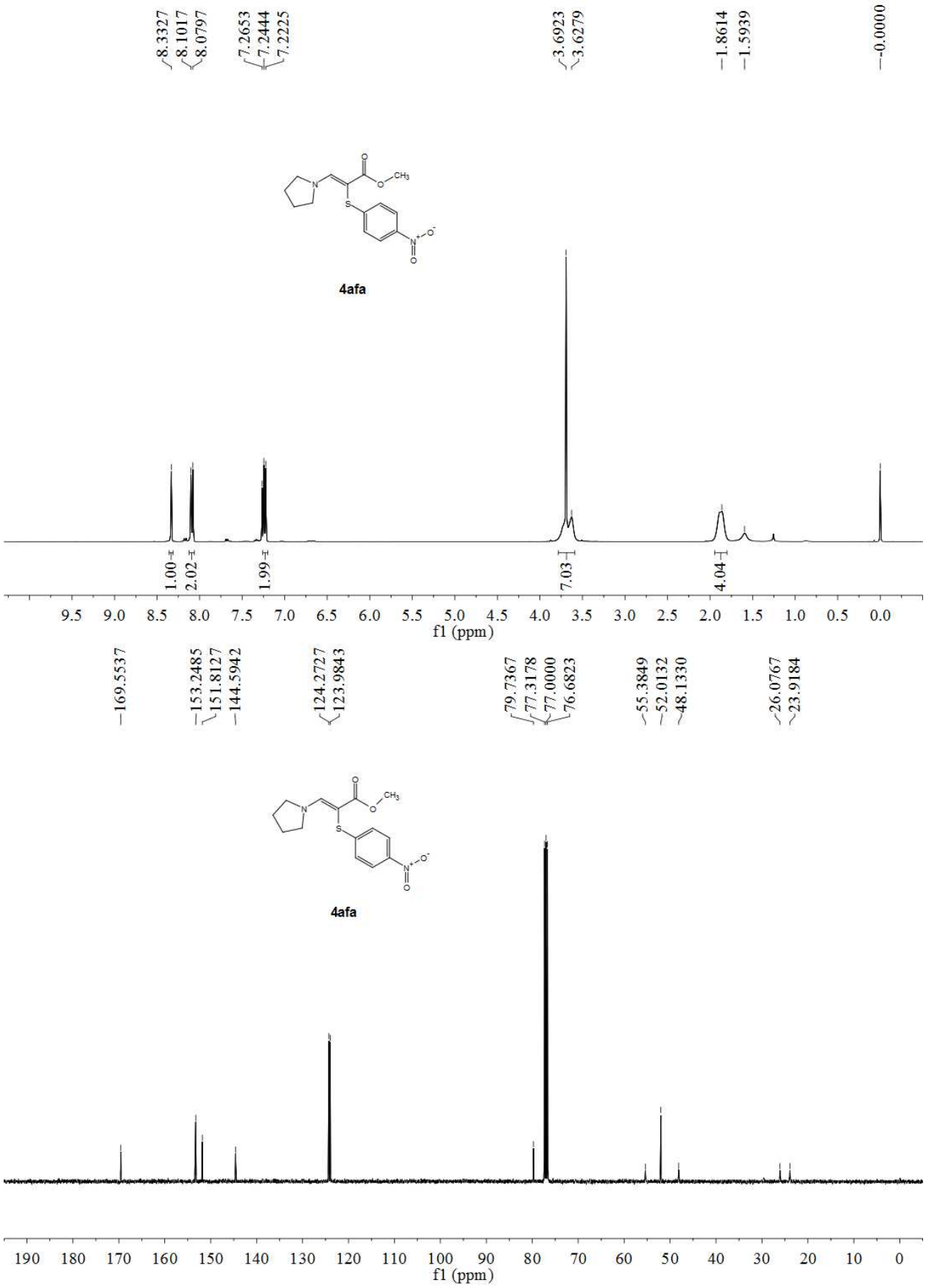
f1 (ppm)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1.99
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4.04
f1 (ppm)
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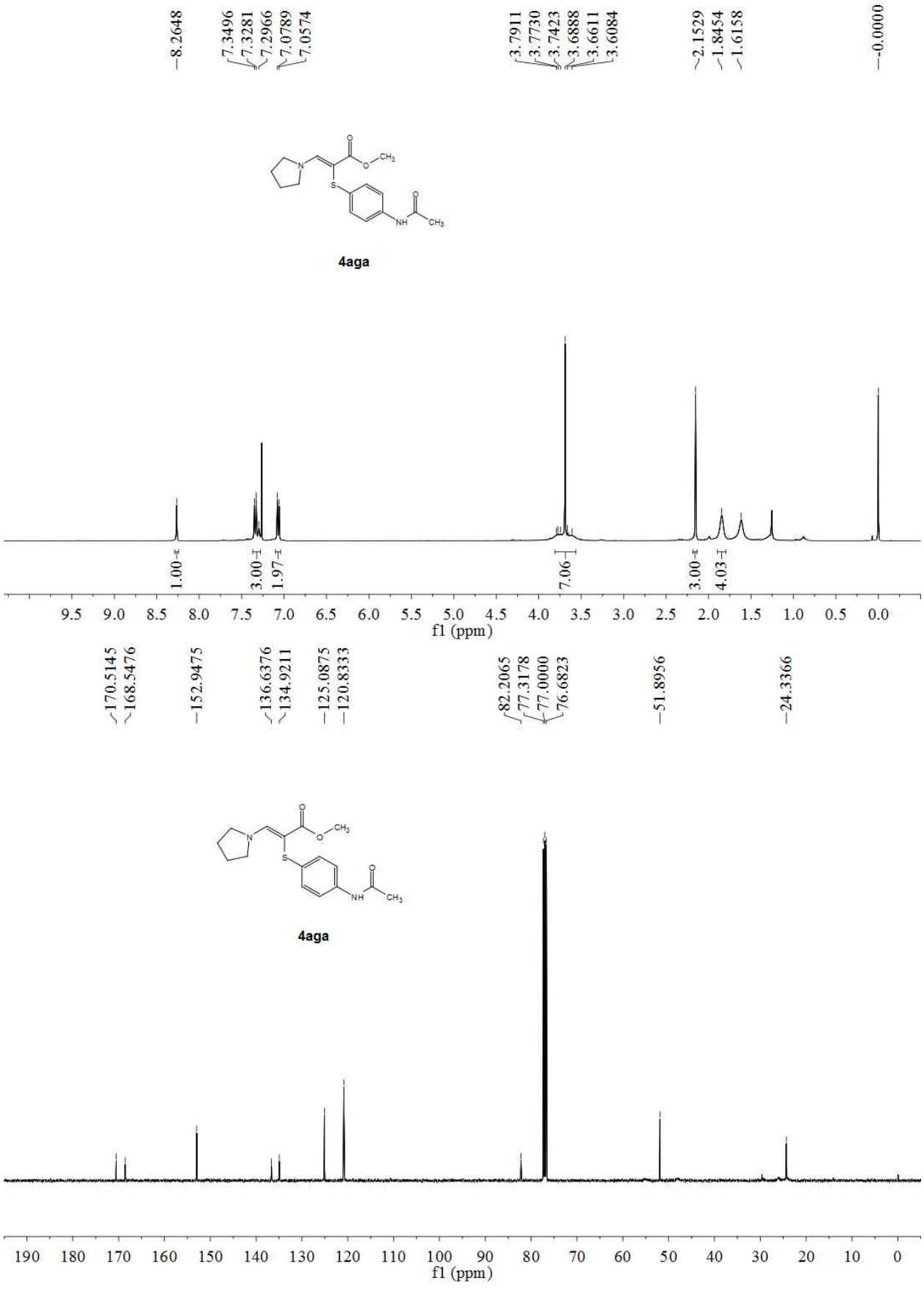
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3.00
1.97
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3.00
4.03
f1 (ppm)
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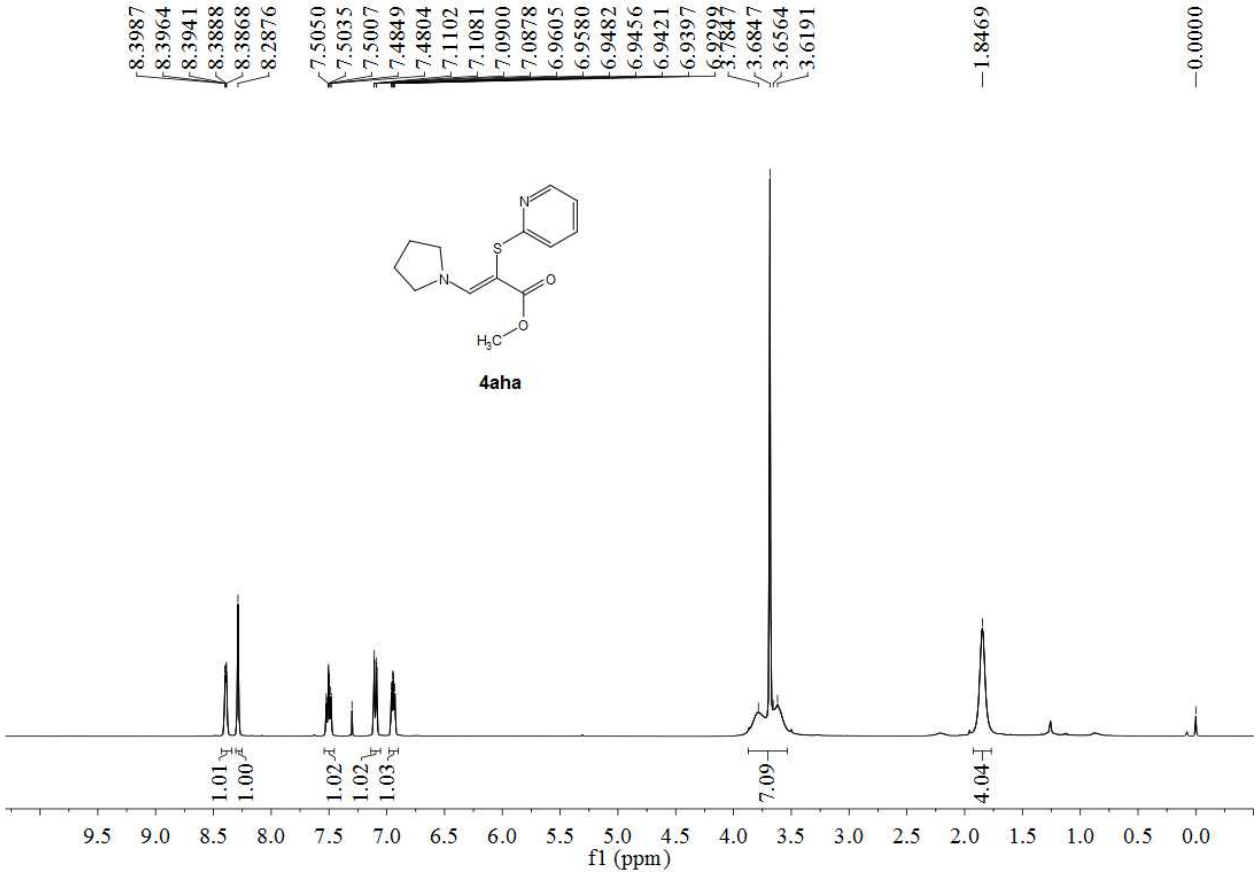
f1 (ppm)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6.9456
6.9421
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6.9299
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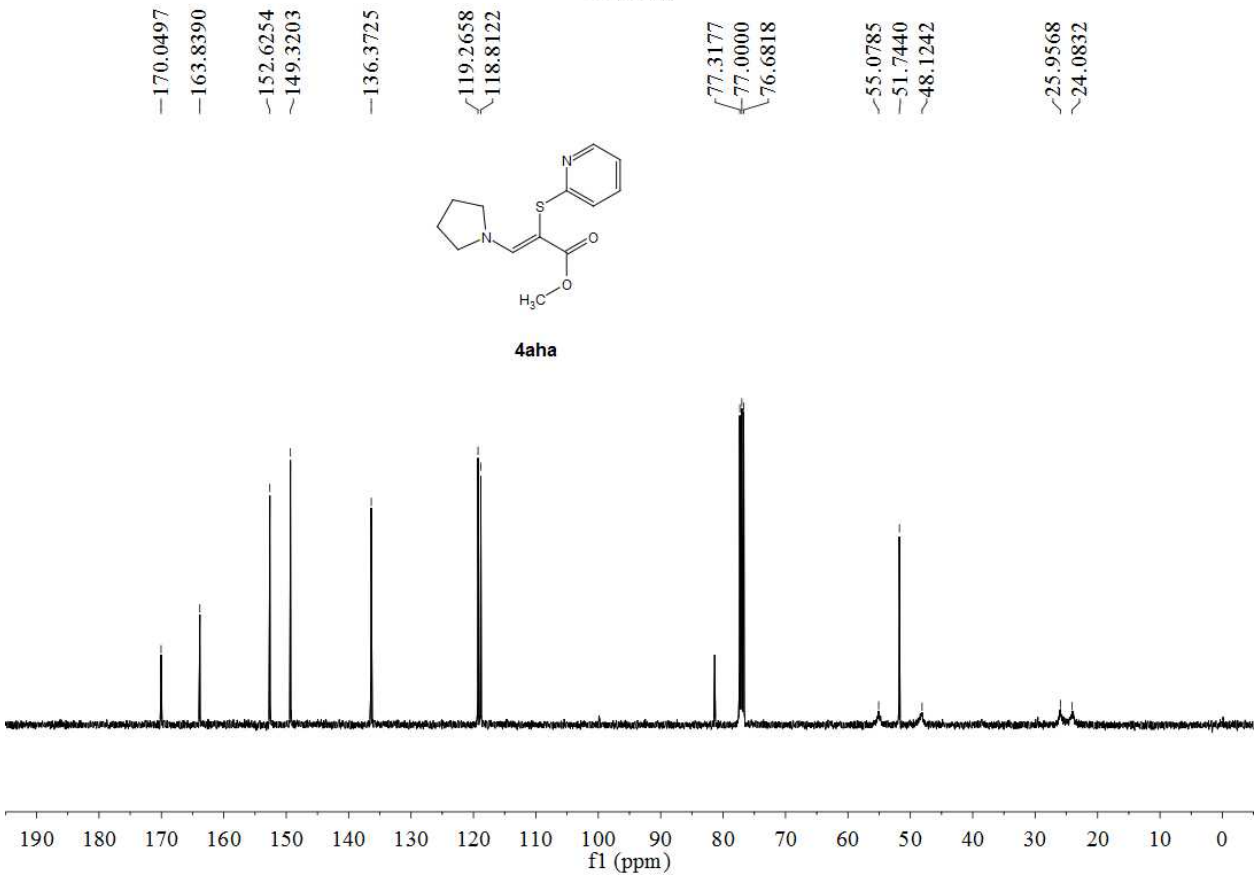
f1 (ppm)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48.1242
25.9568
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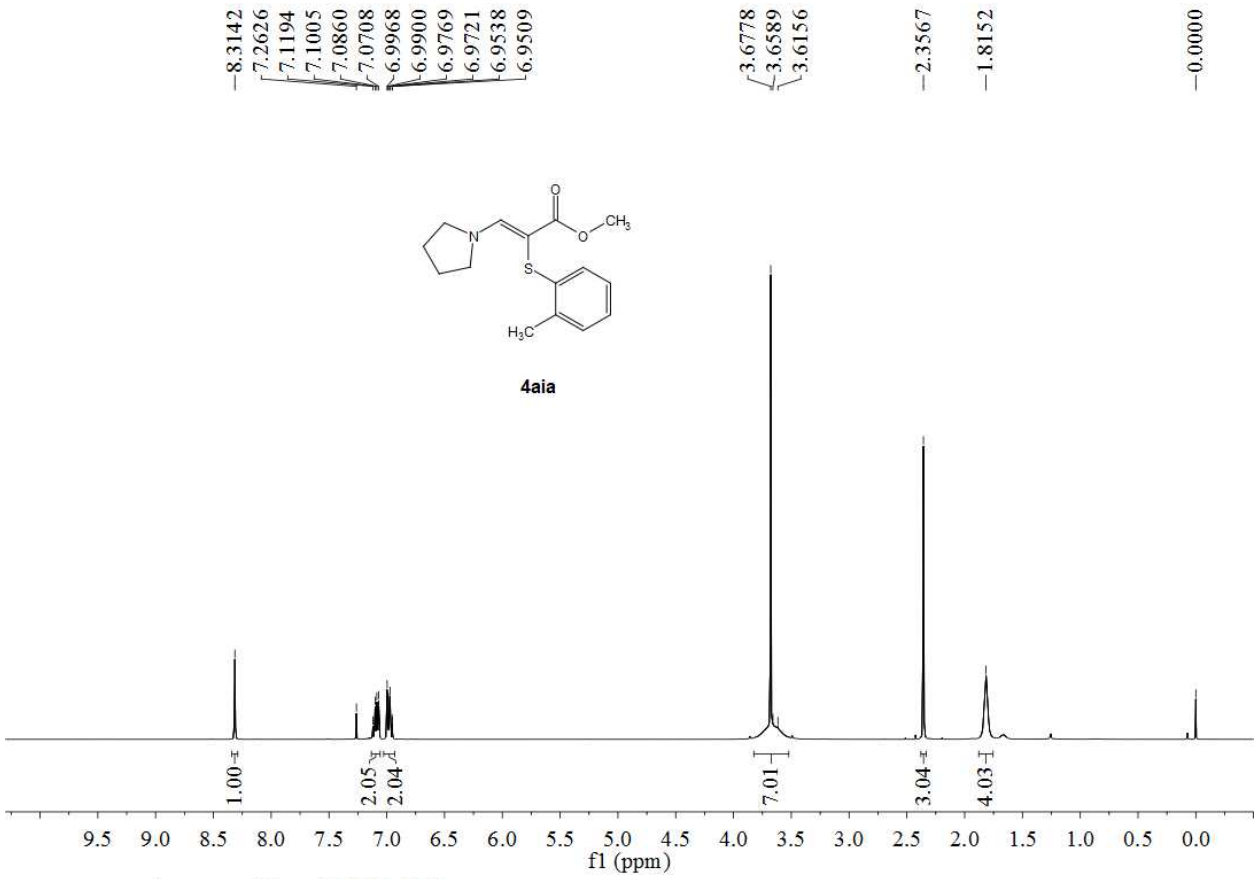
f1 (ppm)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6.9509
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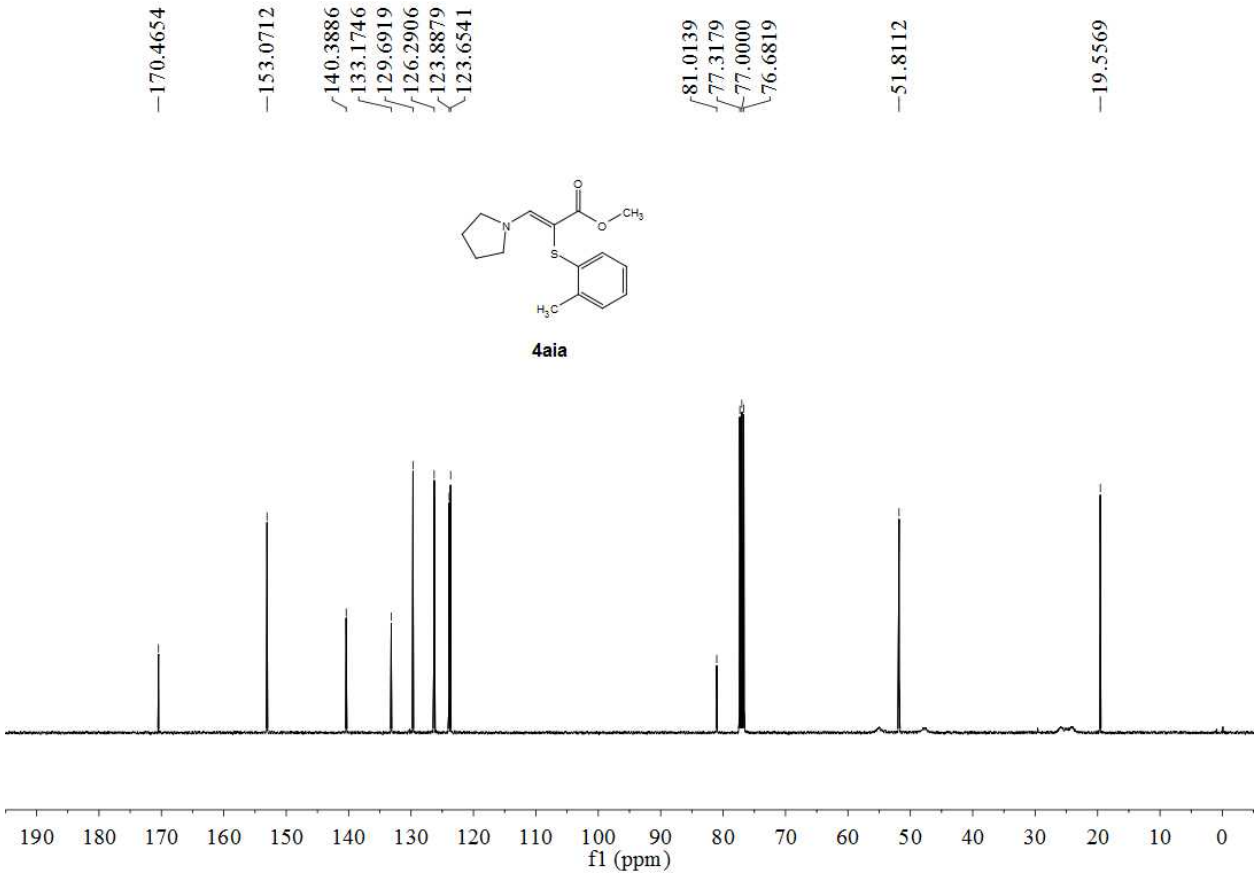
3.04
4.03
f1 (ppm)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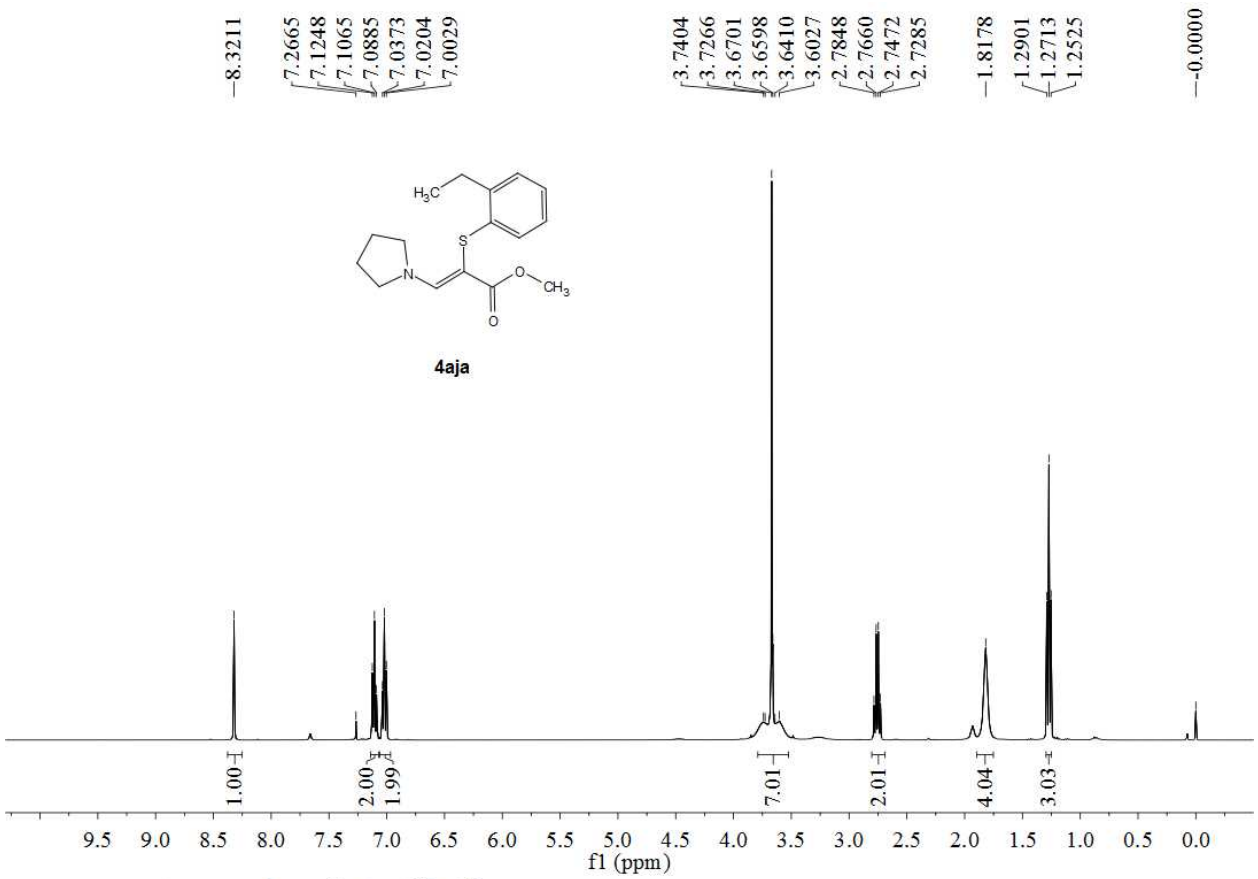
f1 (ppm)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3.6598
3.6410
3.6027
2.7848
2.7660
2.7472
2.7285
1.8178
1.2901
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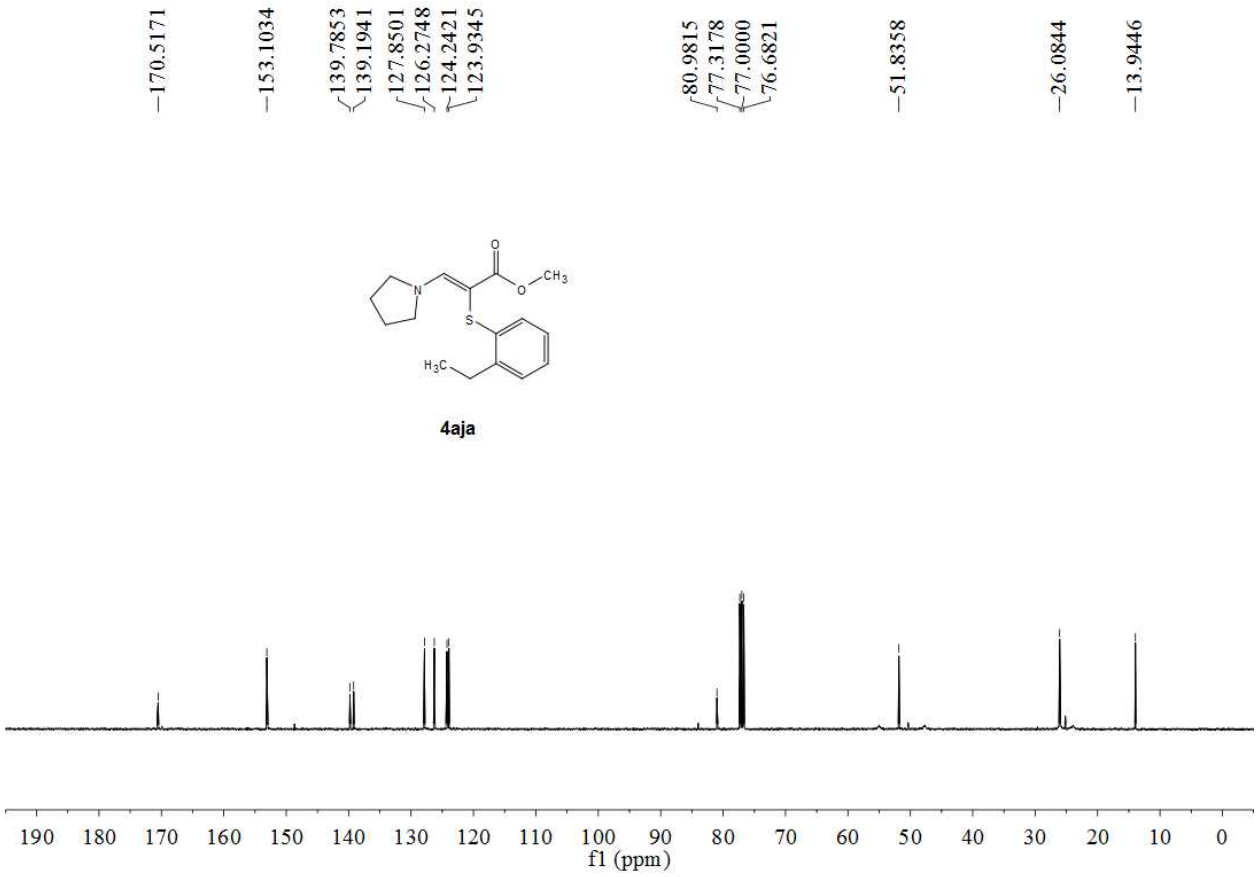
2.01
4.04
3.03
f1 (ppm)

4aja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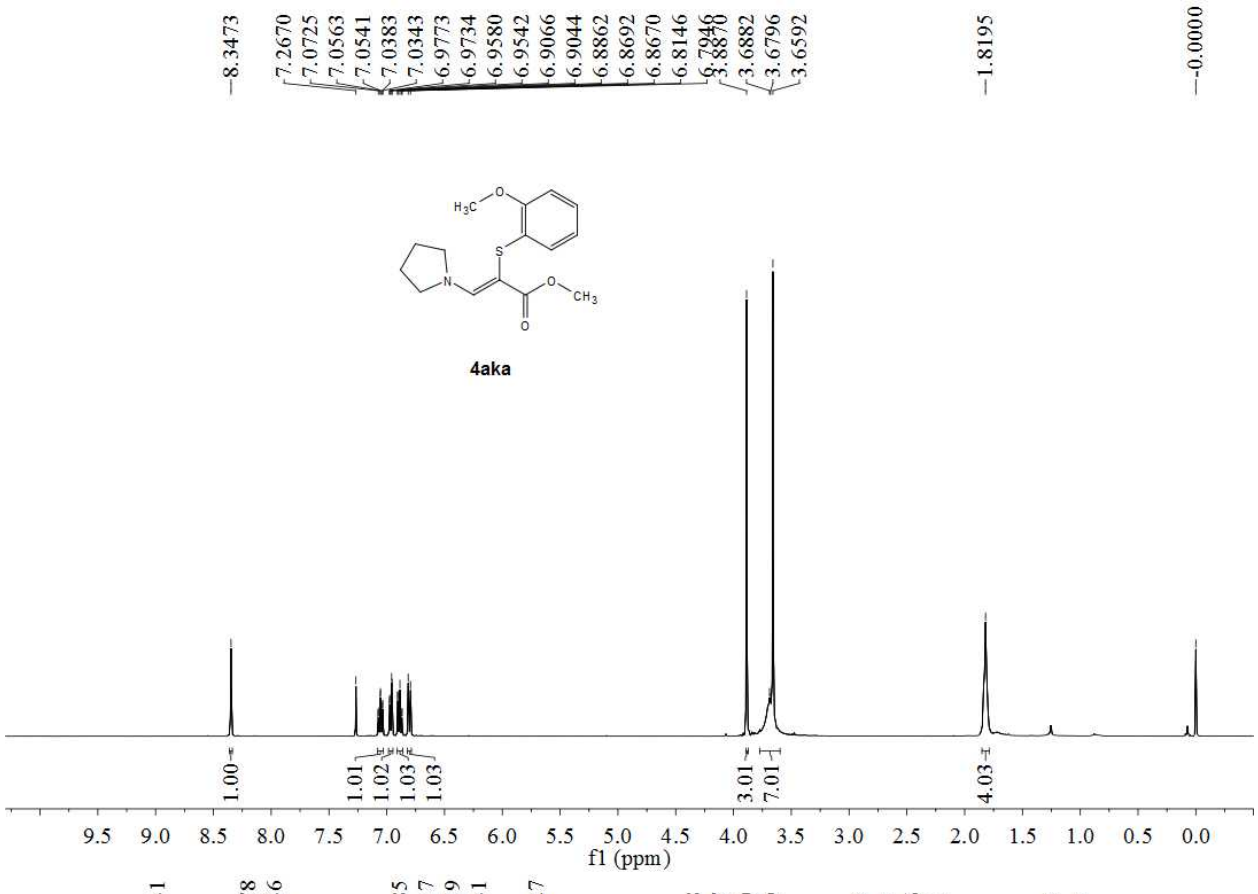
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6.9066
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6.8862
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6.7946
3.8870
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4.03
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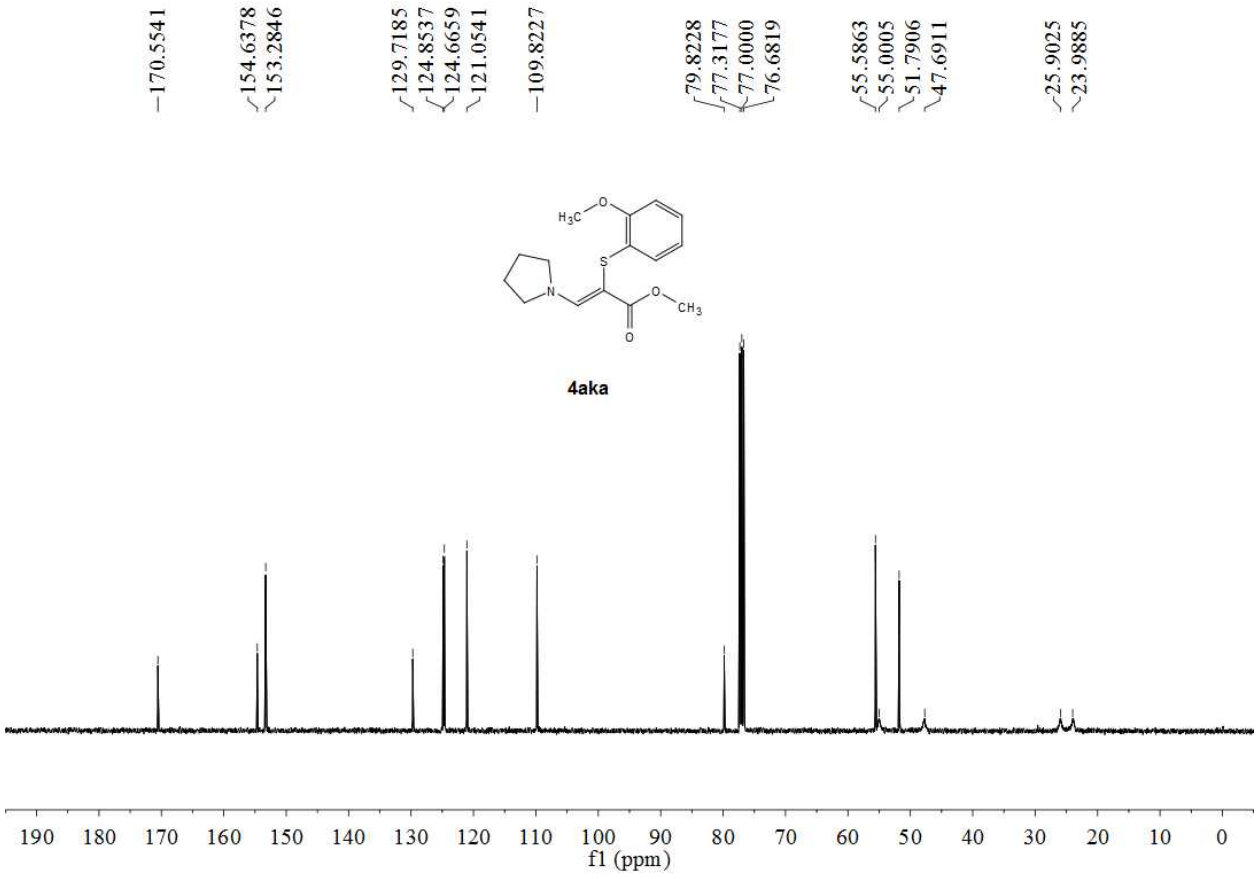
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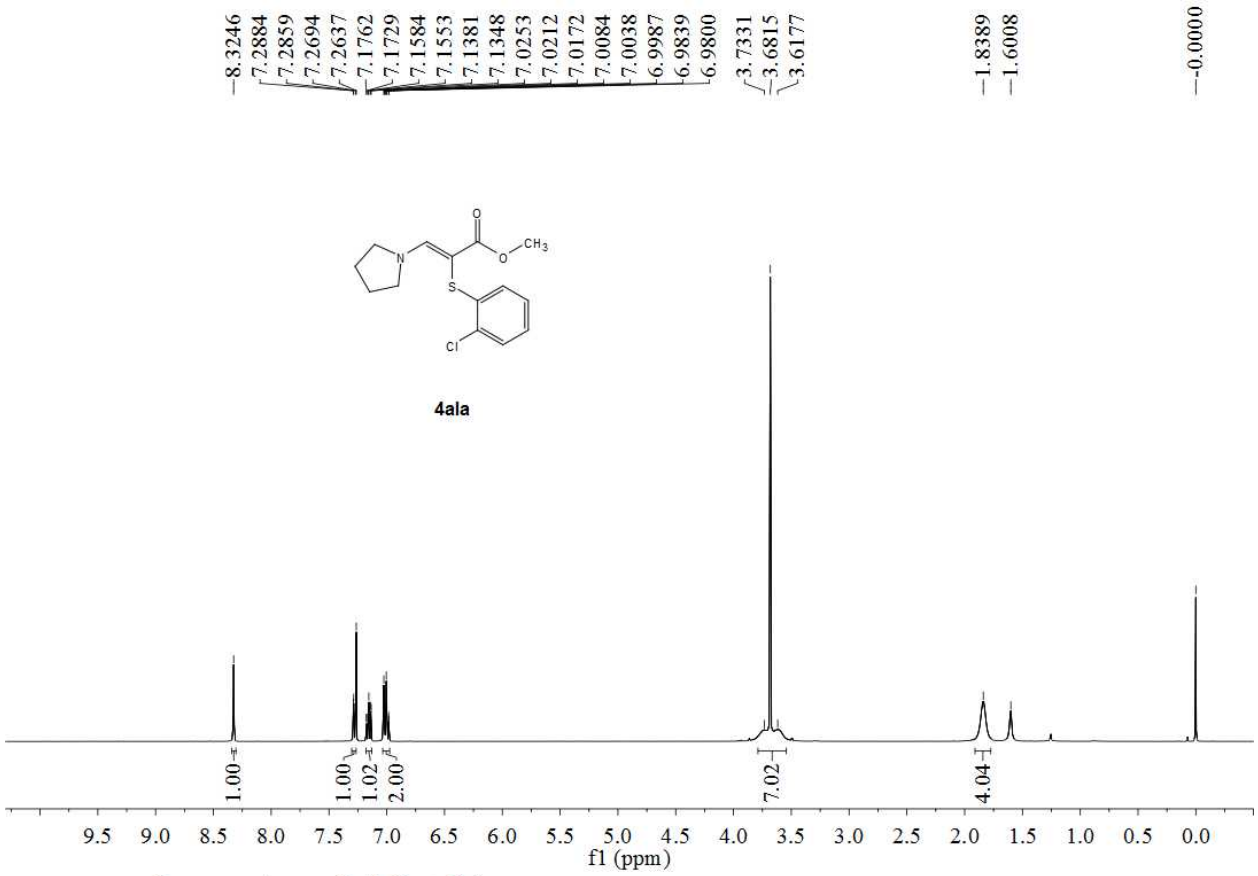
f1 (ppm)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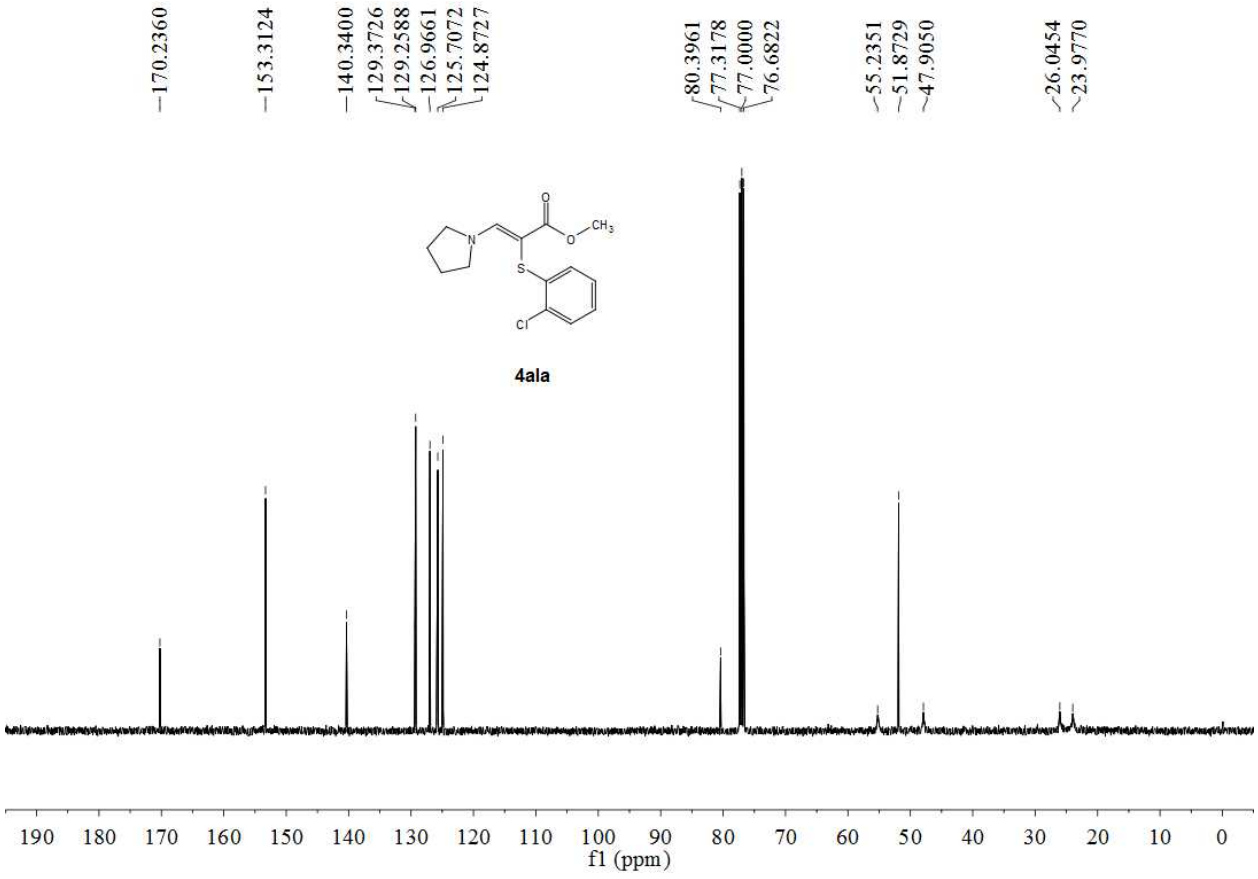
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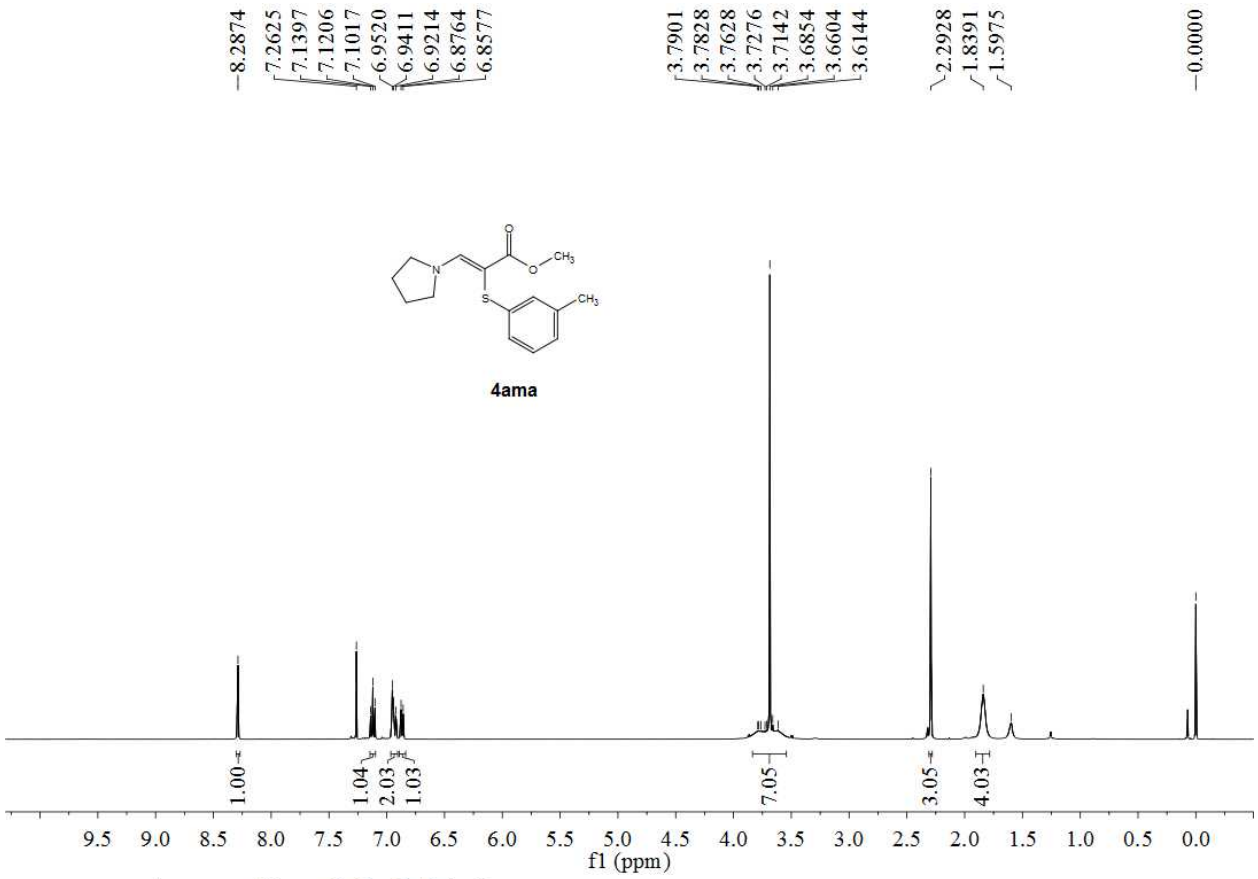
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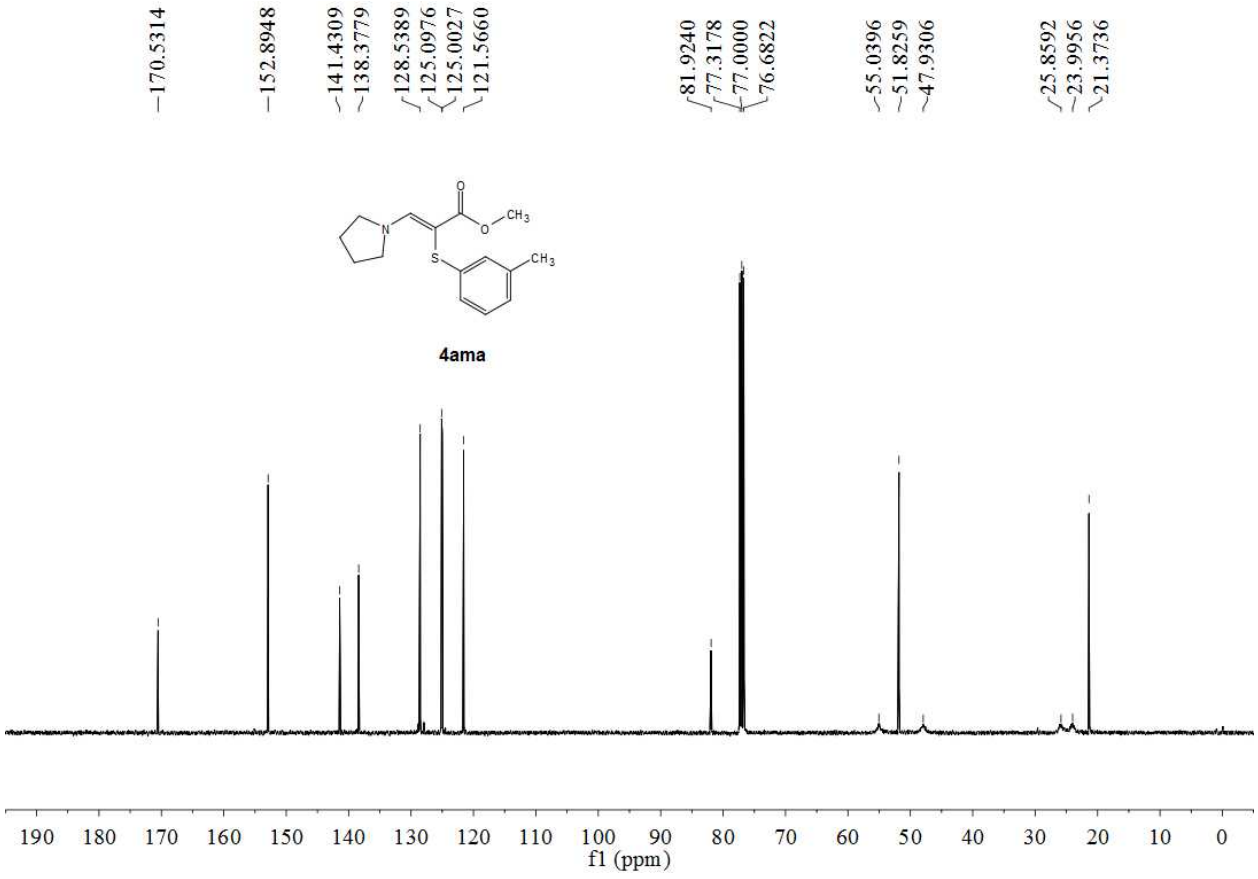
f1 (ppm)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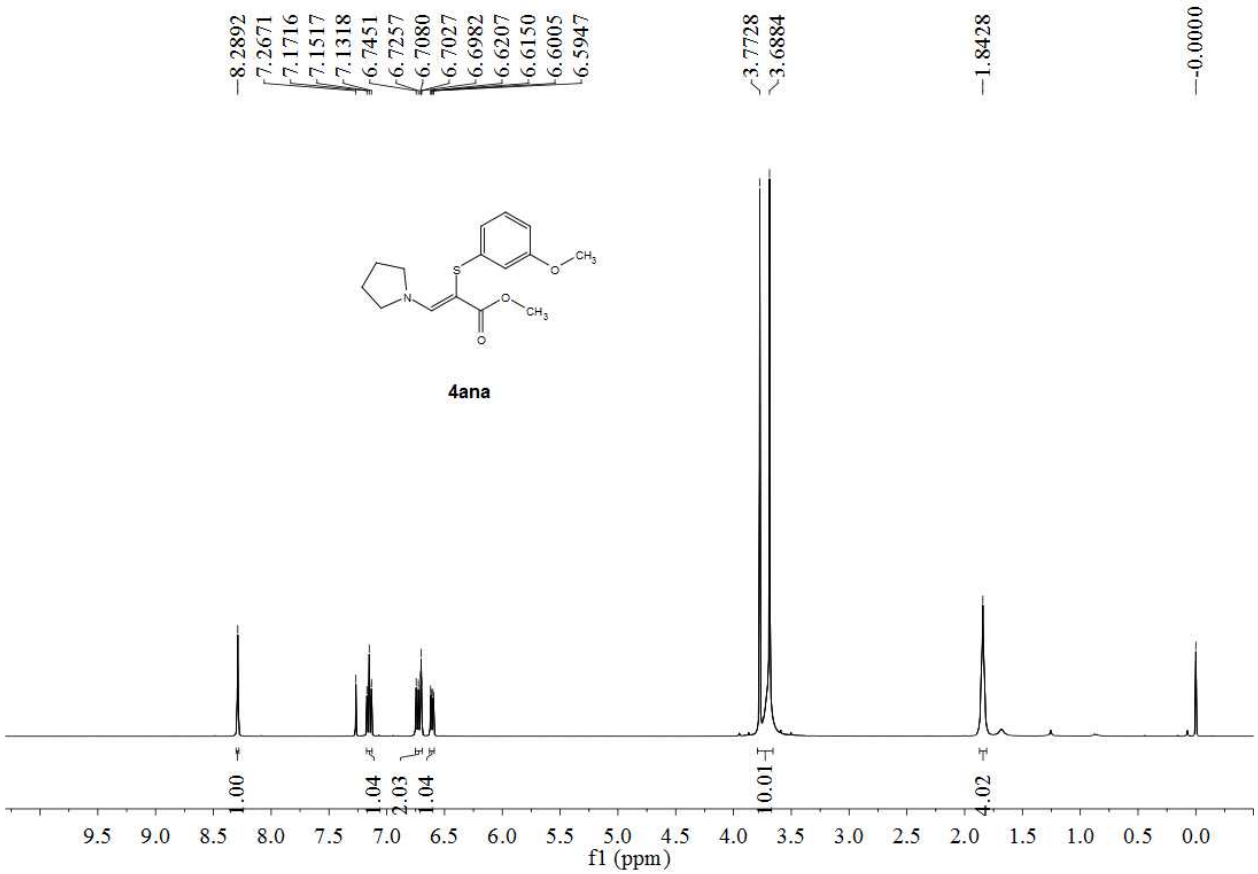
f1 (ppm)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6.6005
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1.04
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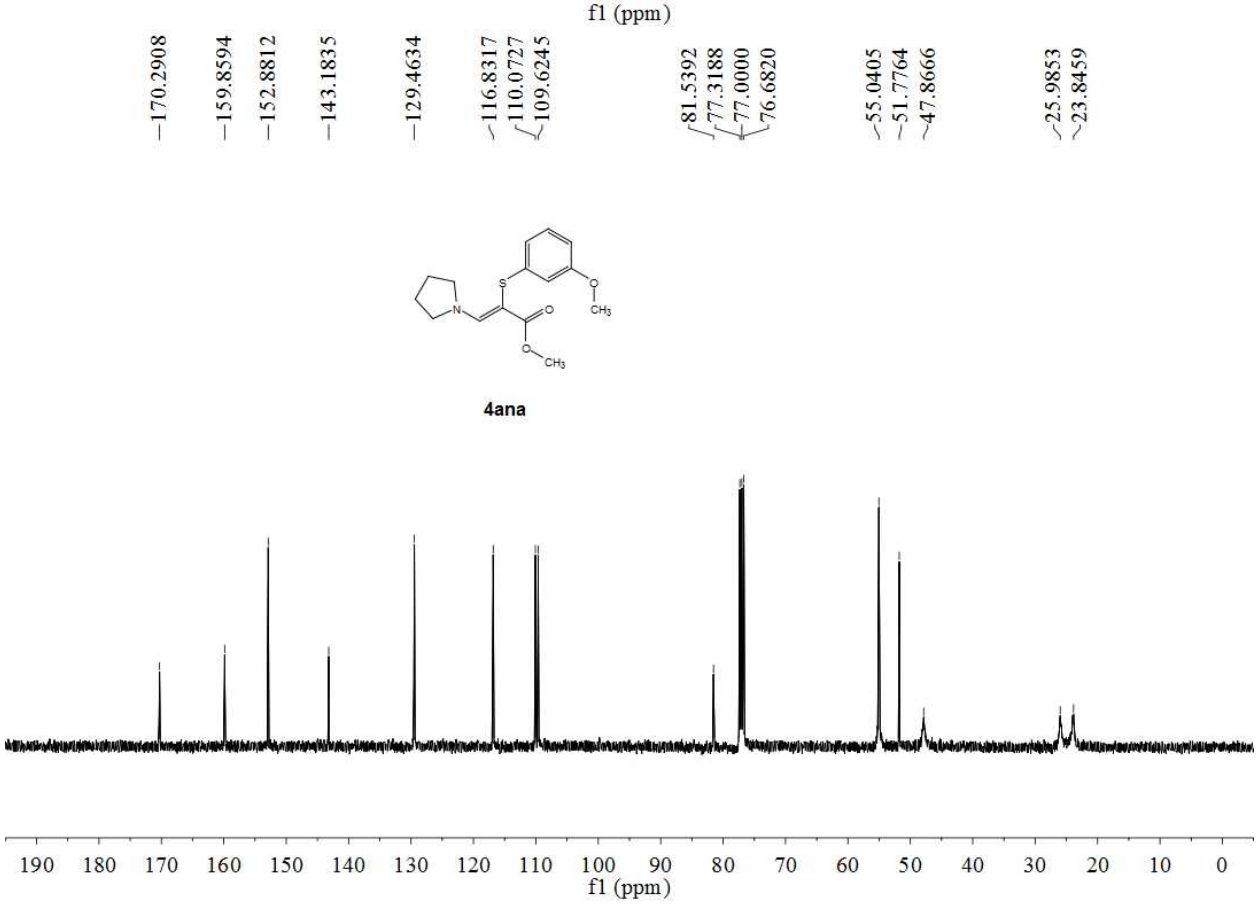
4.02
f1 (ppm)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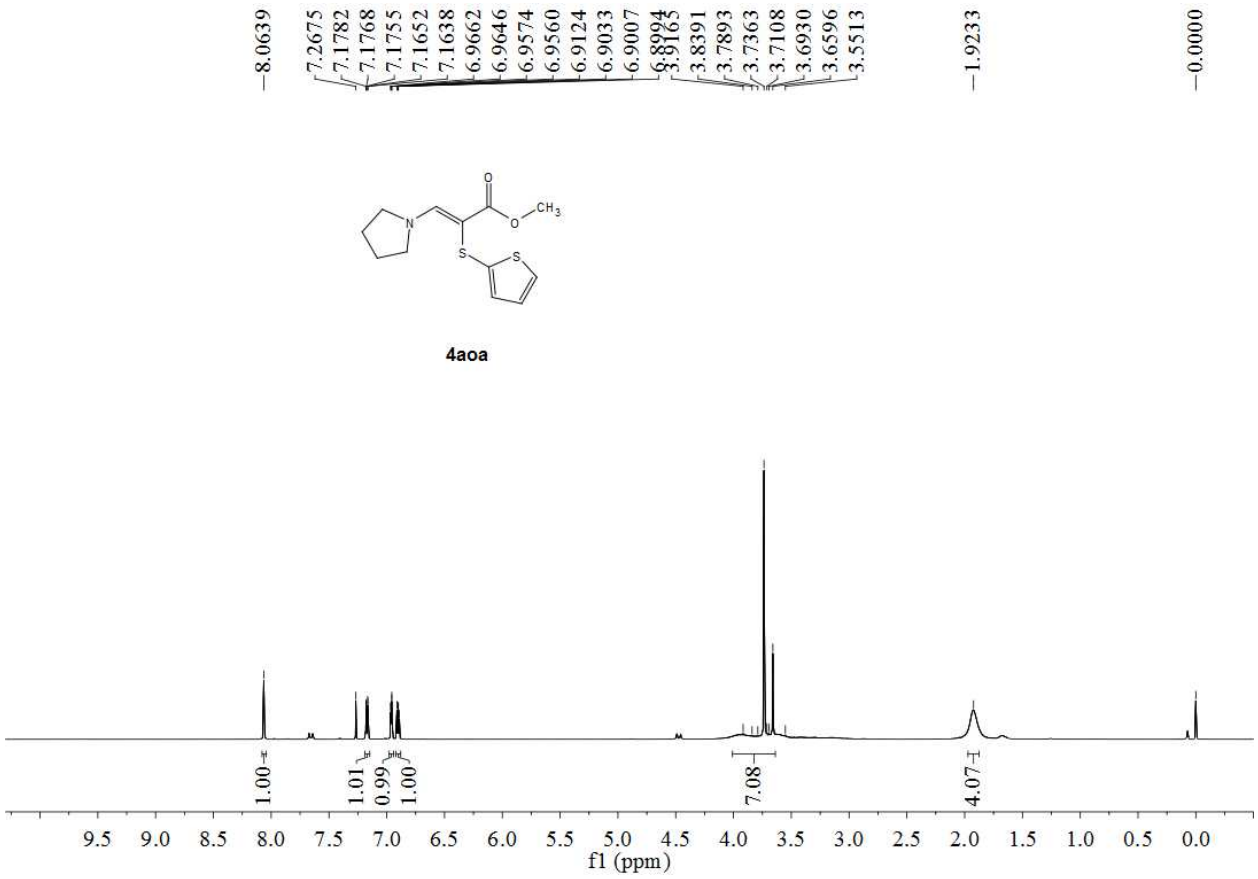
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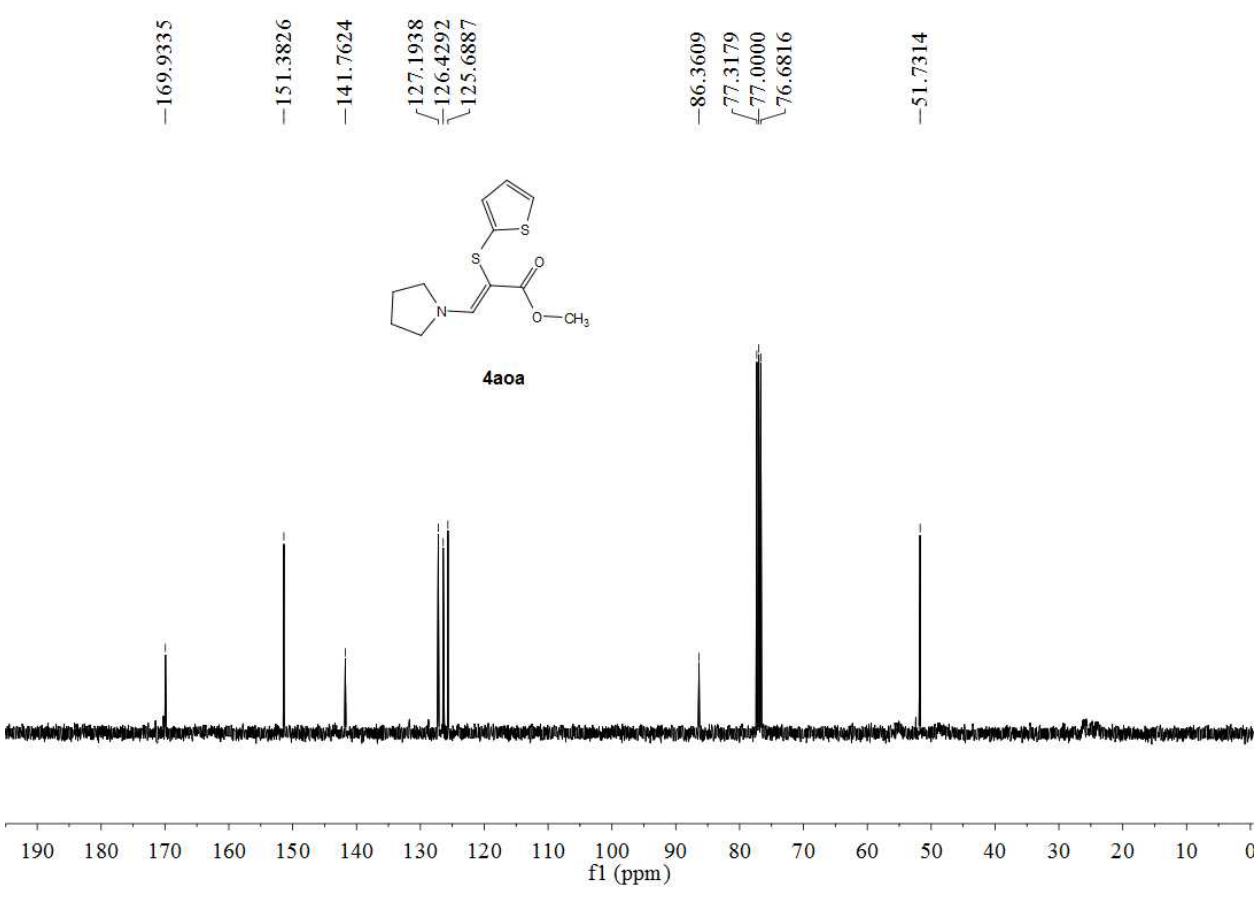
4aoa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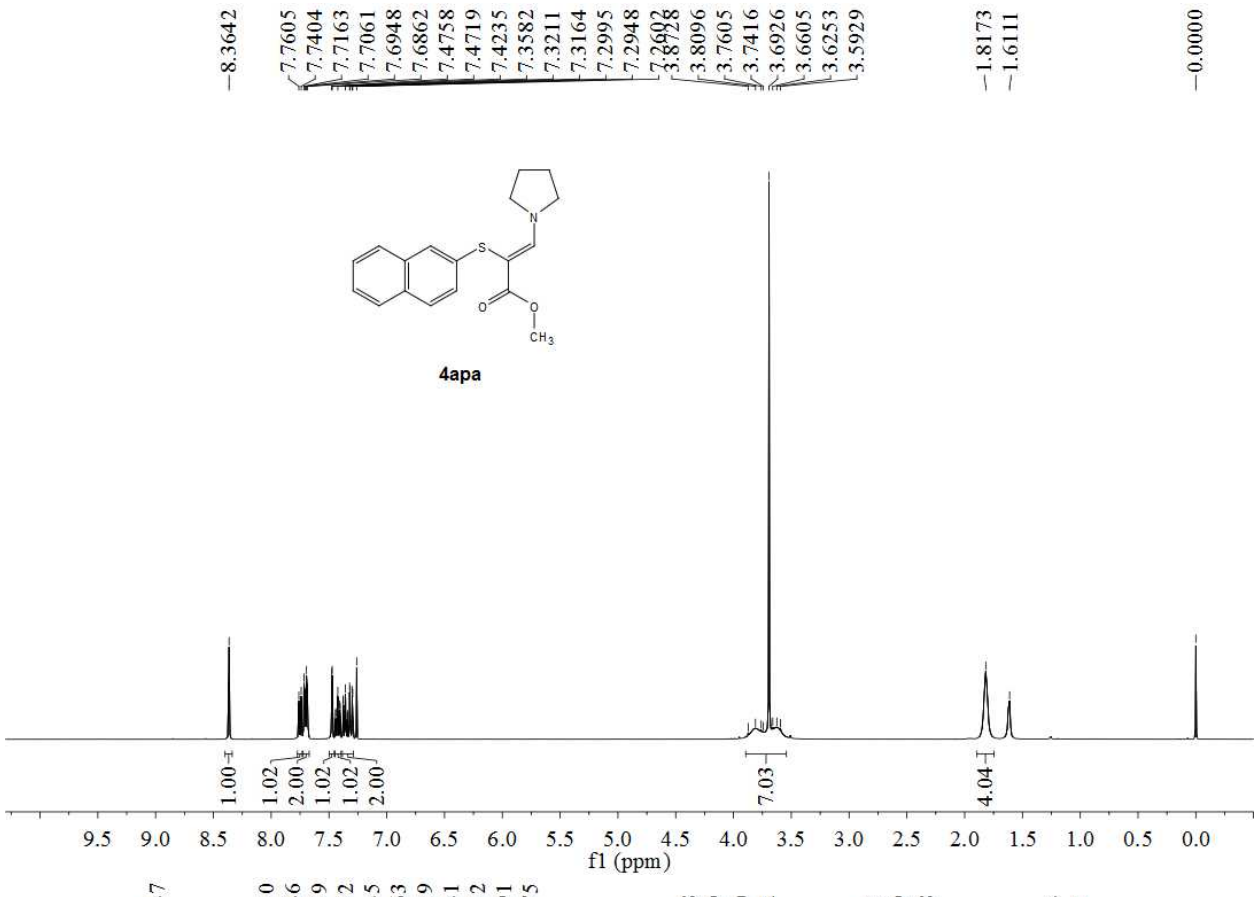
4aoa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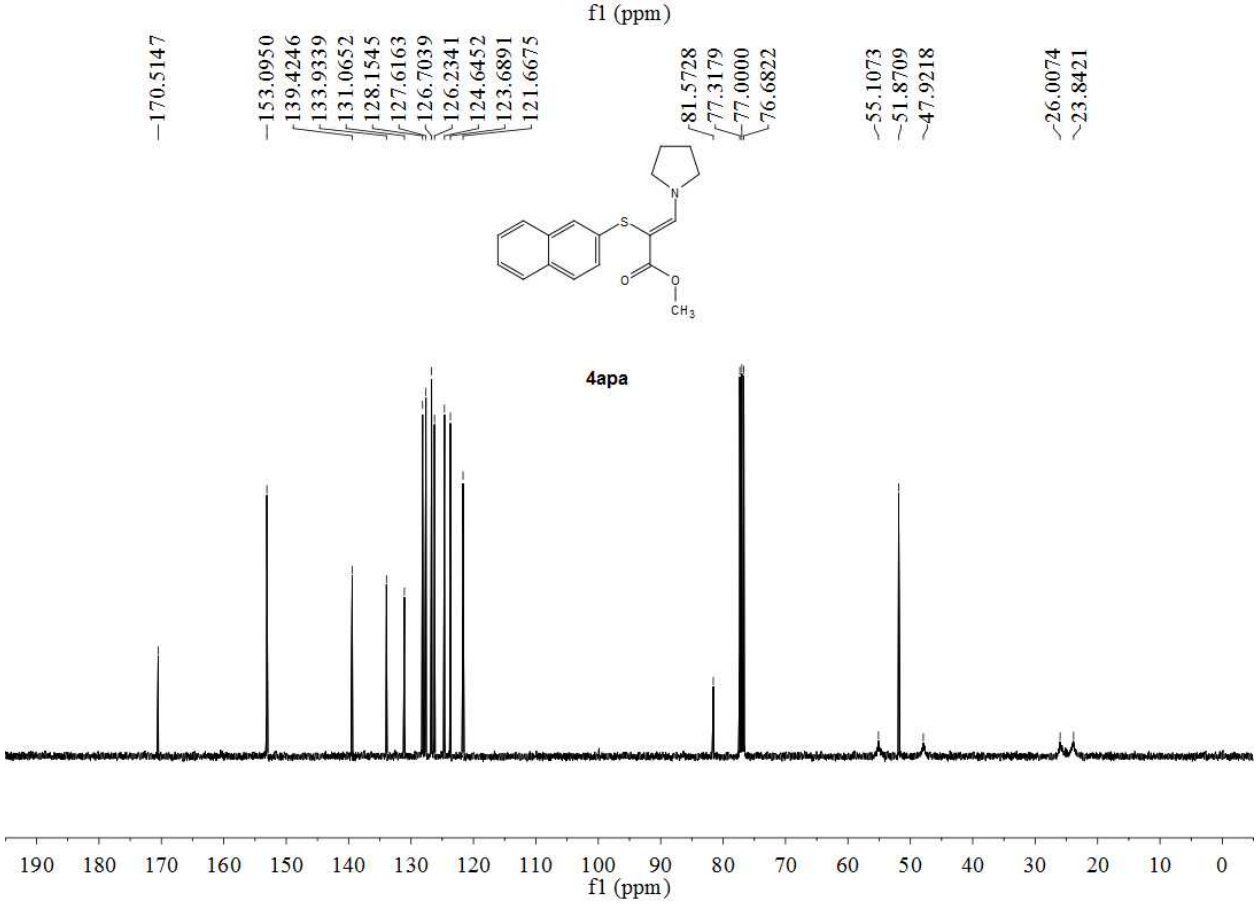
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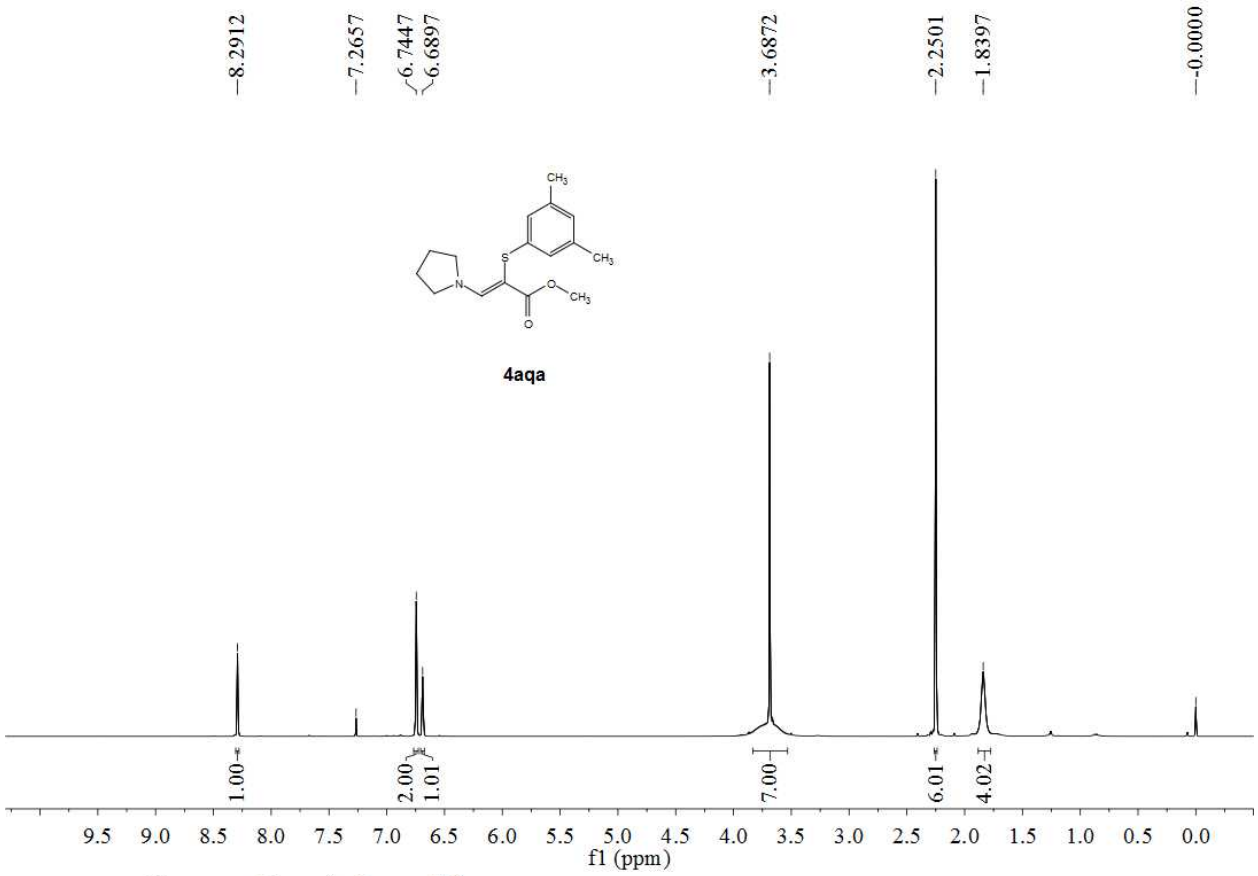
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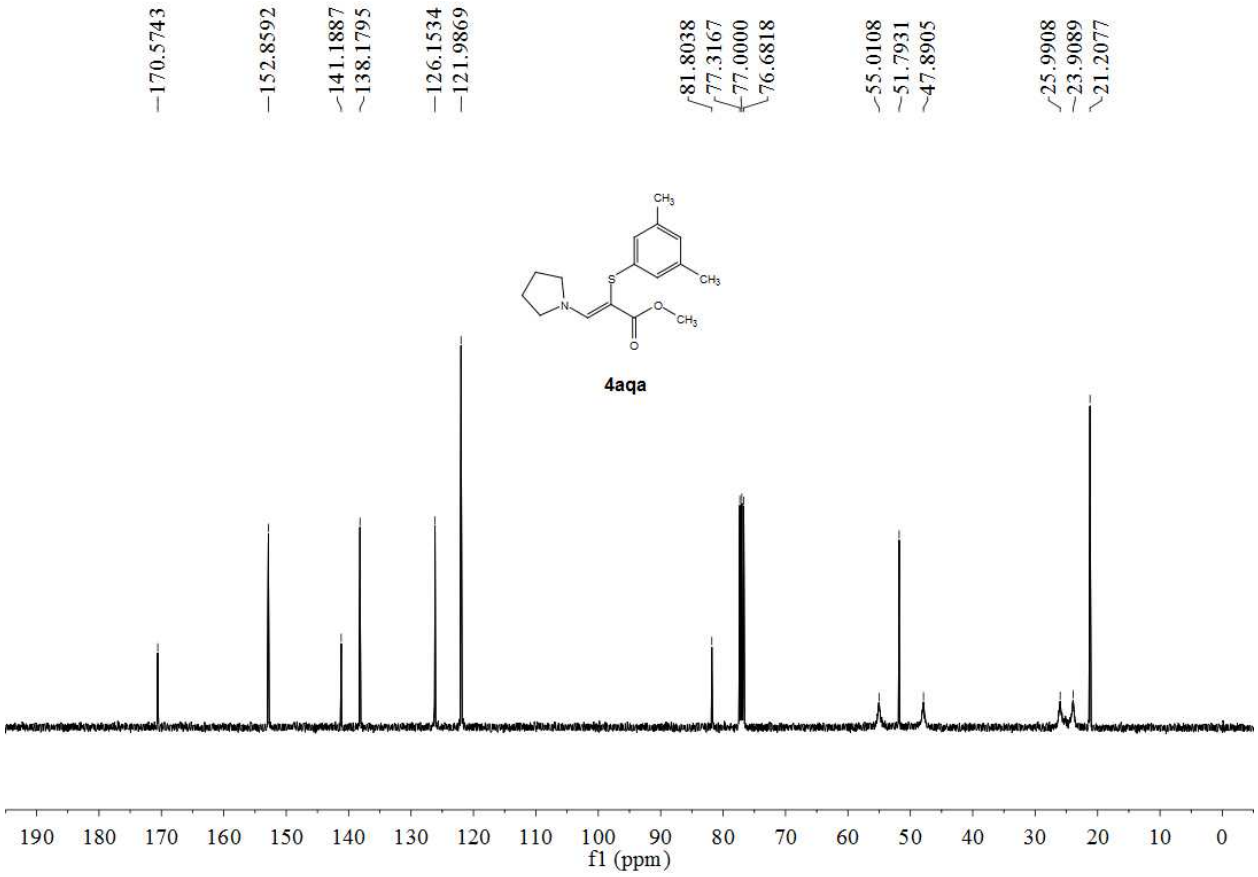
f1 (ppm)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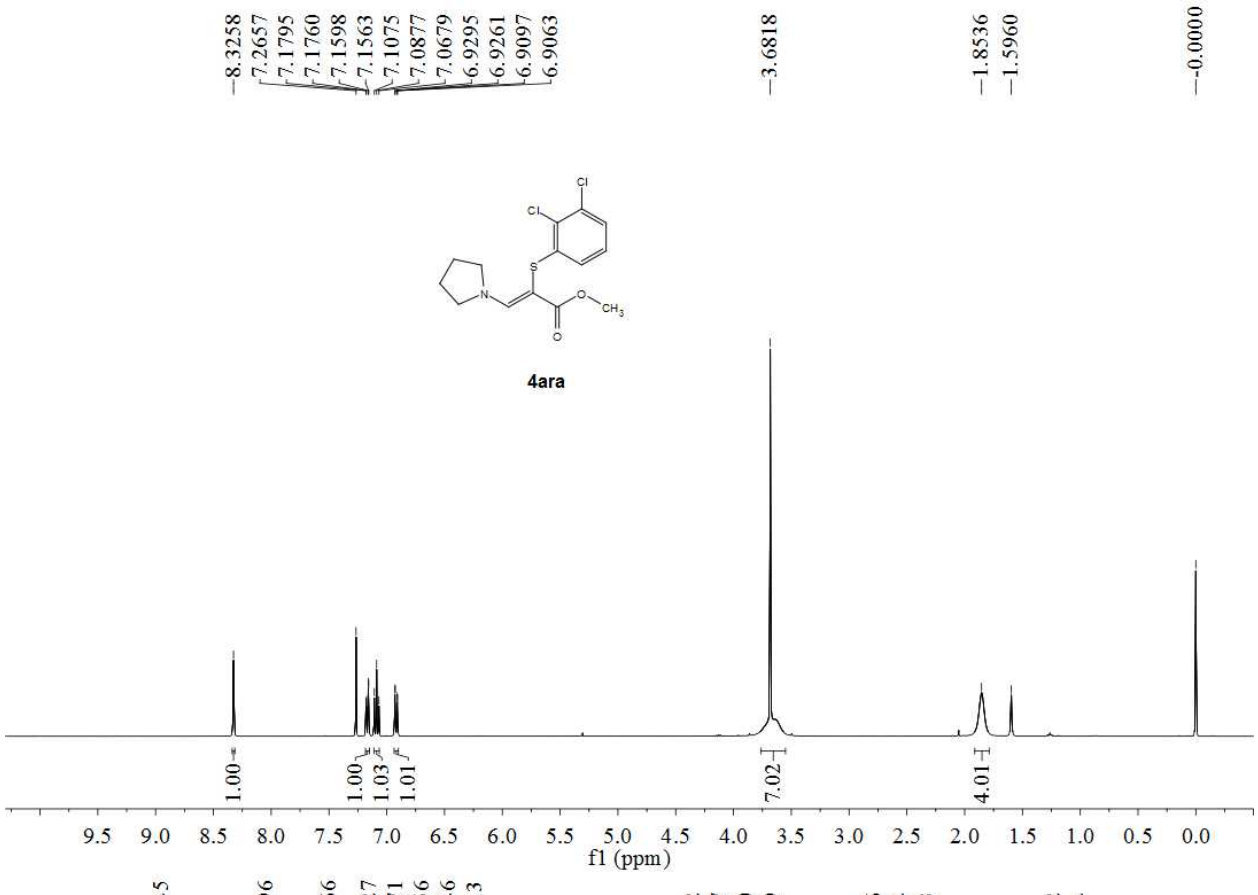
f1 (ppm)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Cl
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O
CH3
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1.00
1.03
1.01
7.02
4.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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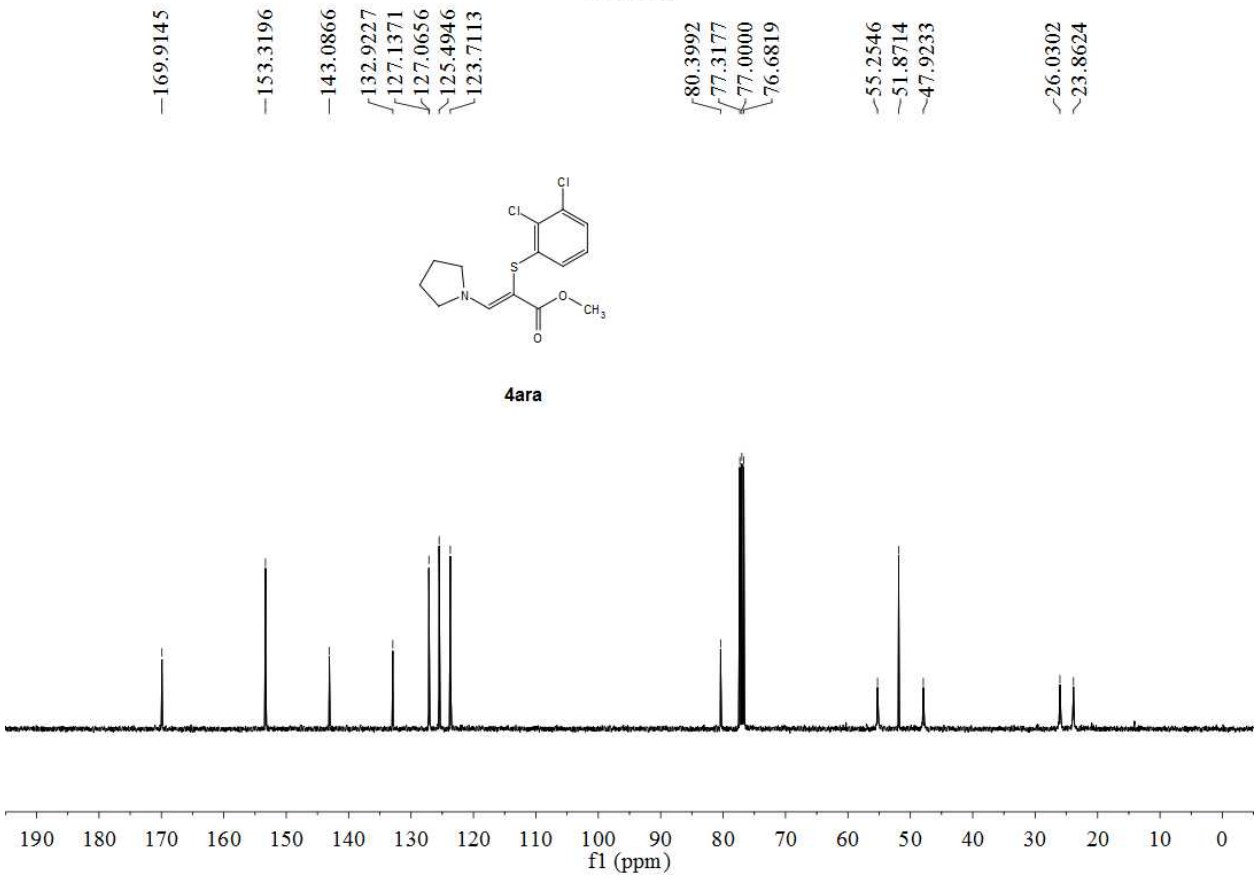
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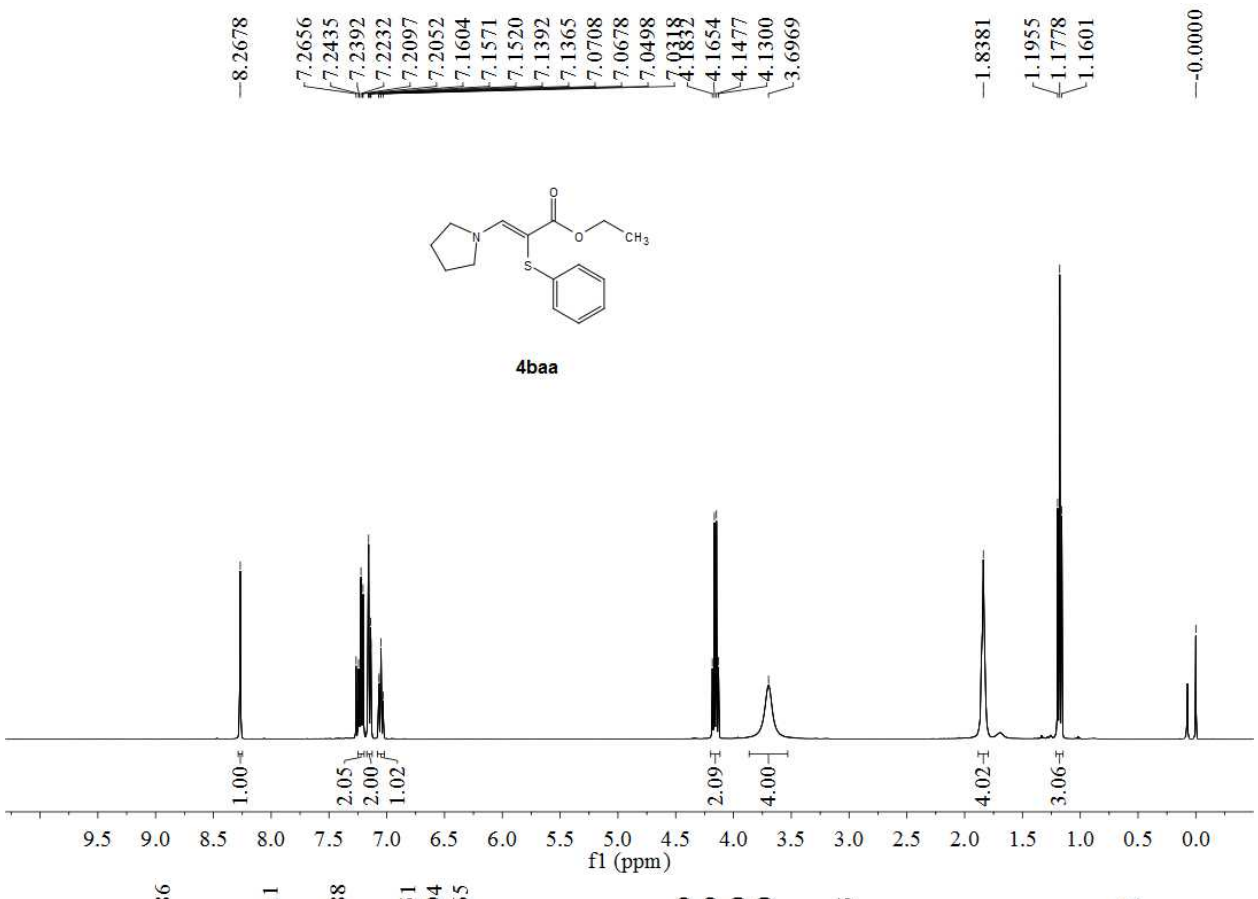
f1 (ppm)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7.0678
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4.02
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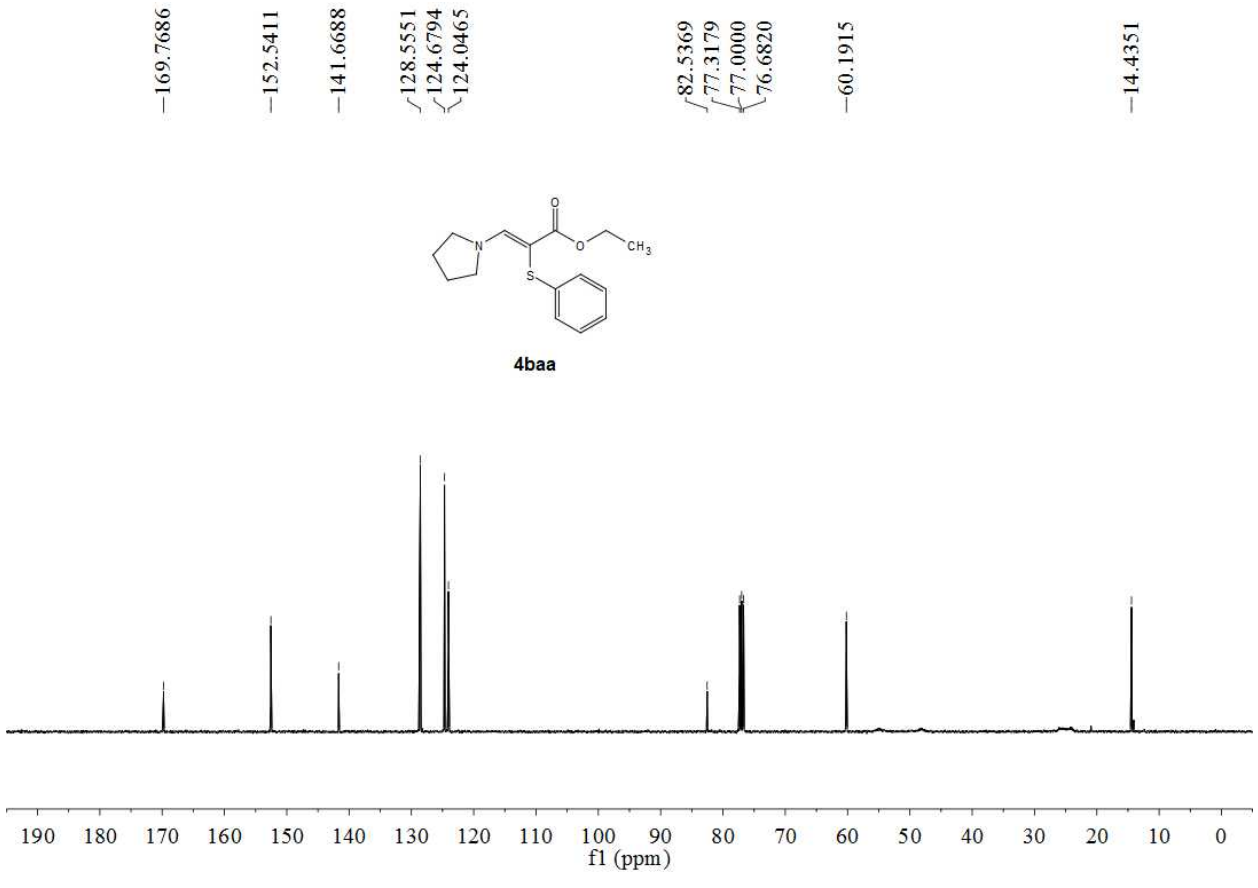
f1 (ppm)

4baa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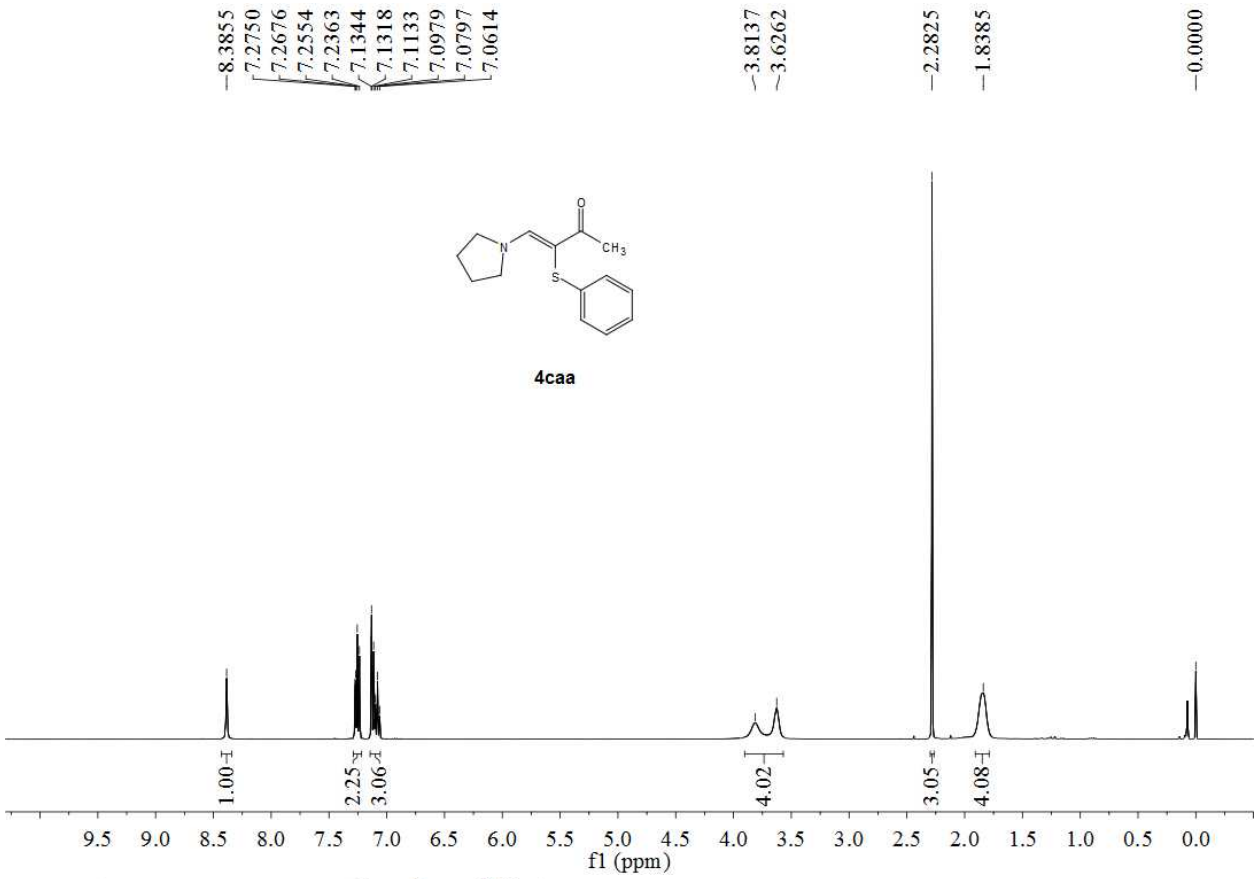
f1 (ppm)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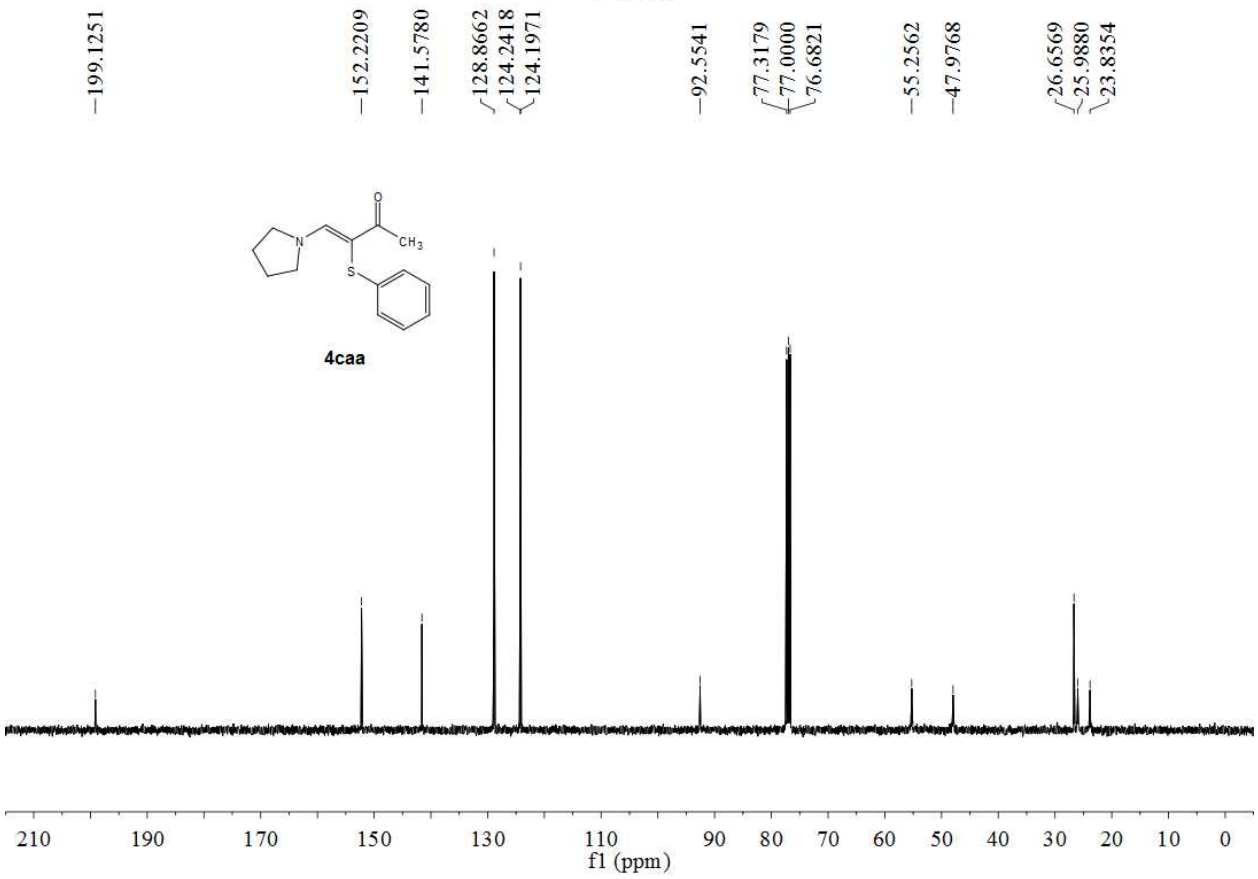
4caa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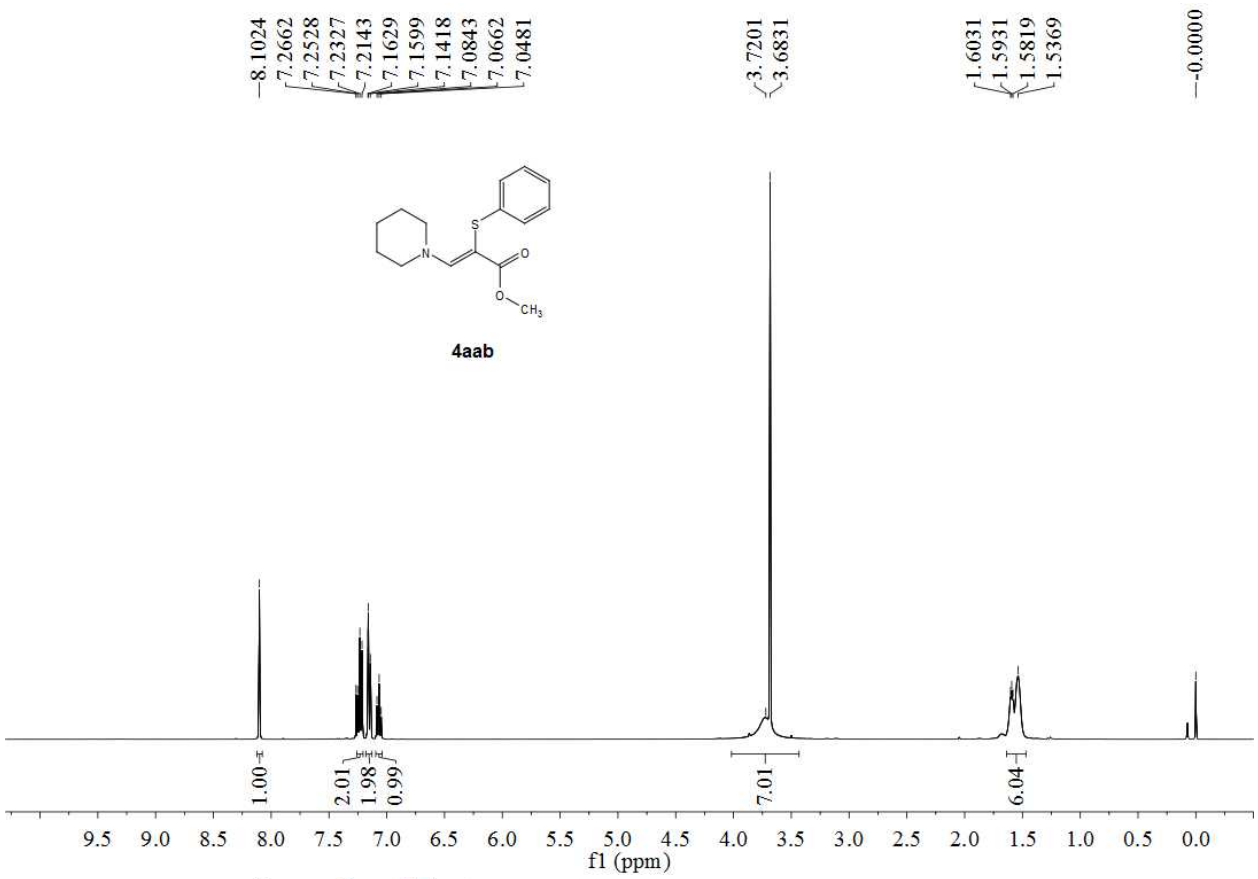
23.8354
f1 (ppm)

4caa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3.6831
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2.01
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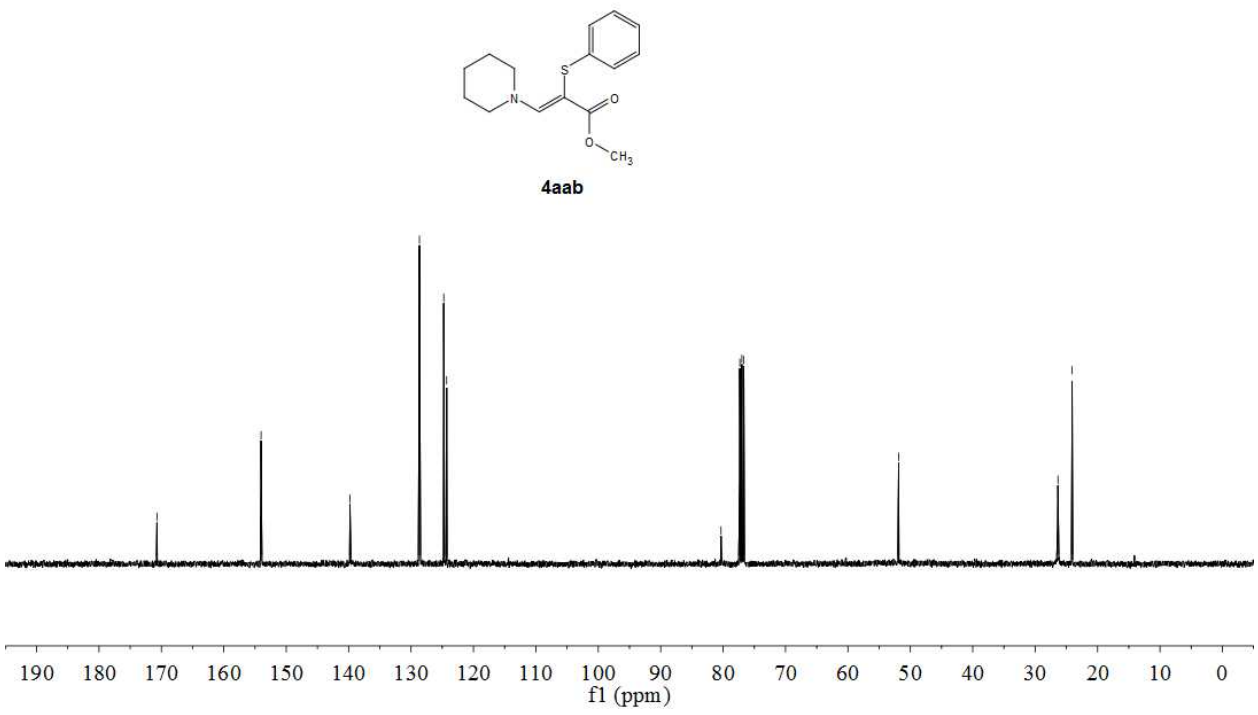
0.99
7.01
6.04
f1 (ppm)

4aab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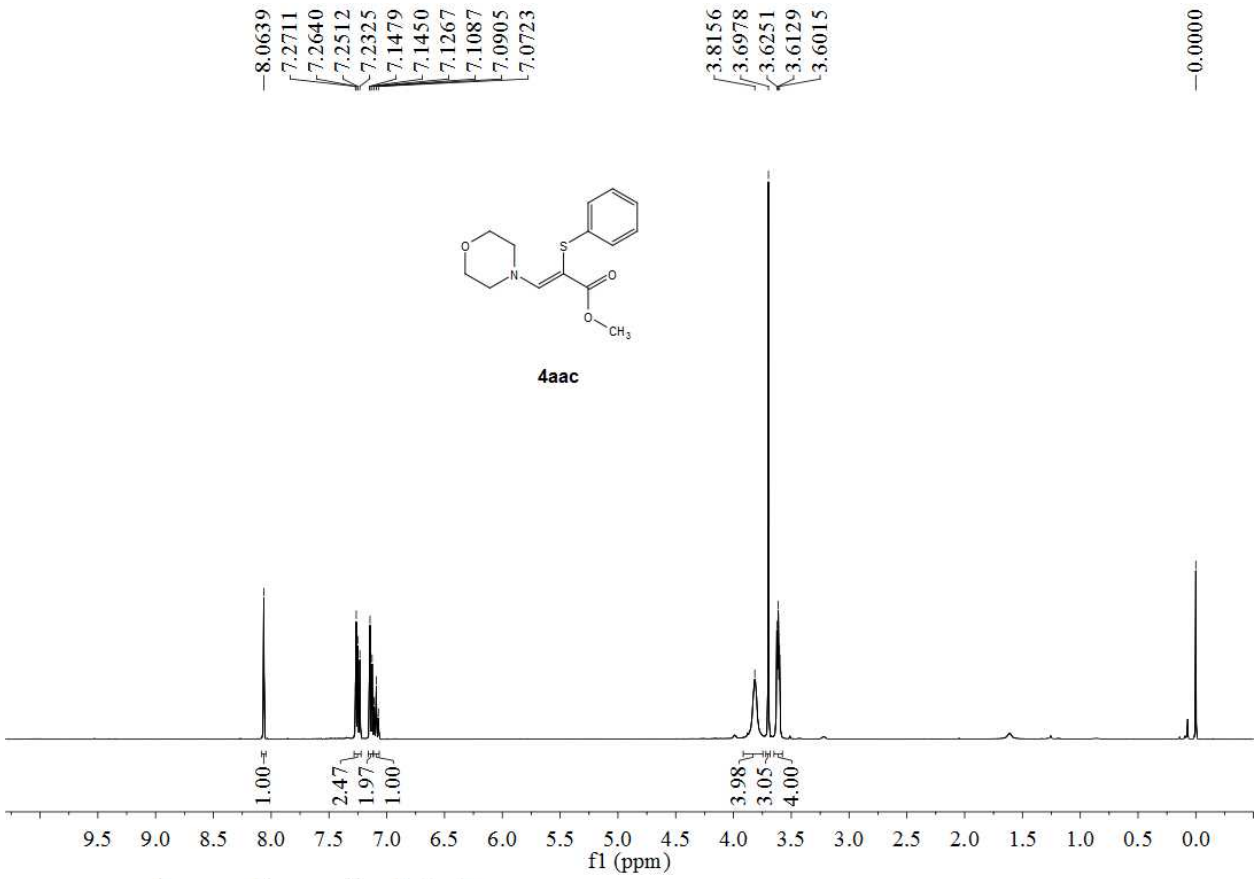
f1 (ppm)

4aab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7.2325
7.1479
7.1450
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7.1087
7.0905
7.0723
3.8156
3.6978
3.6251
3.6129
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1.00
3.98
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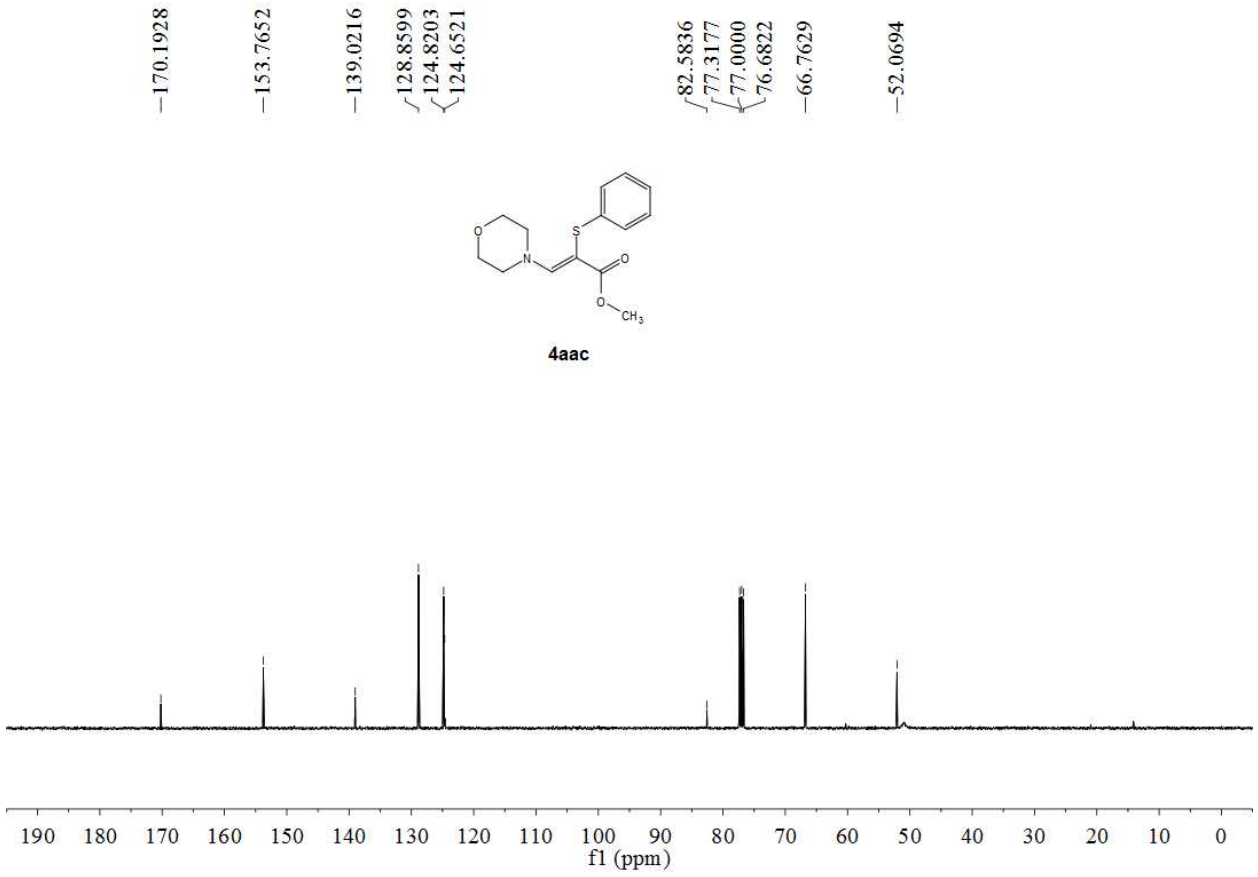
4.00
f1 (ppm)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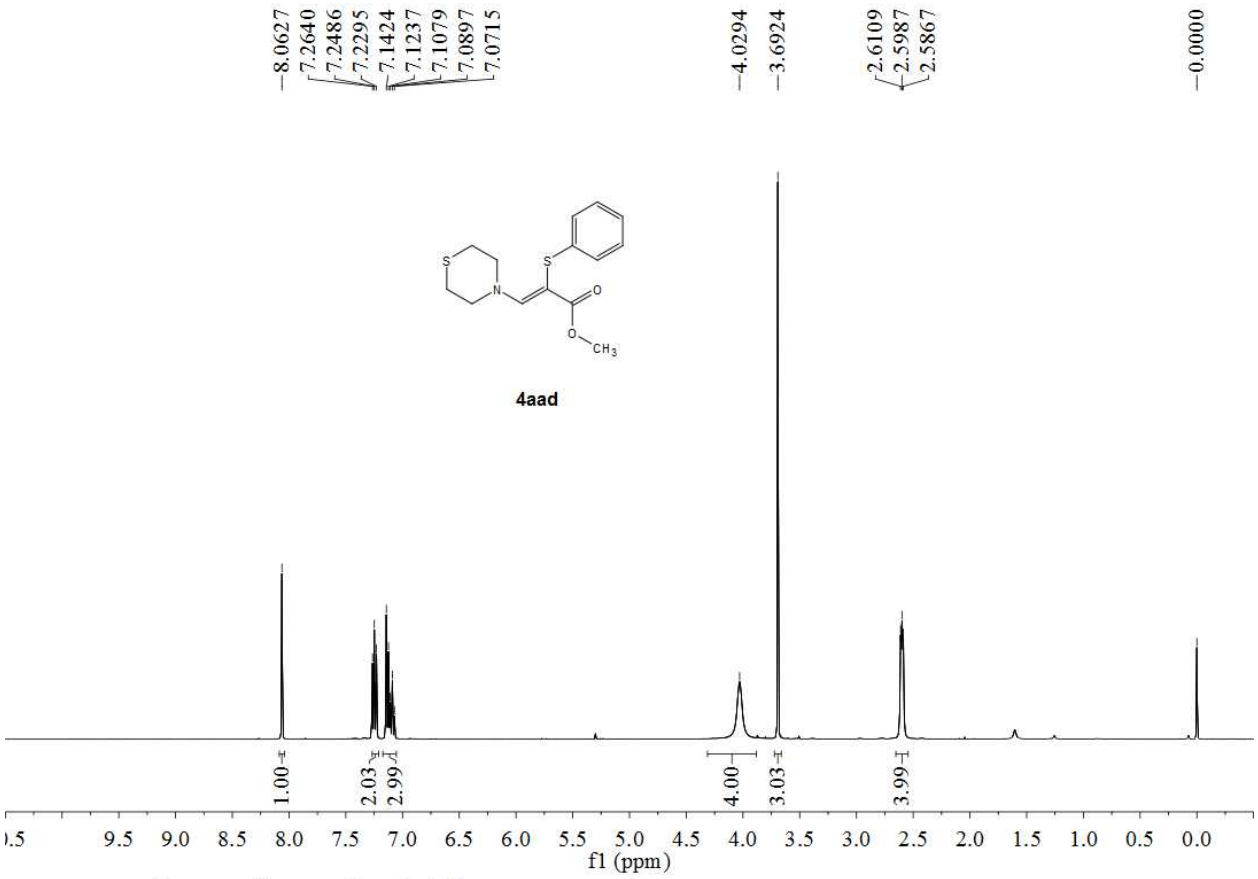
f1 (ppm)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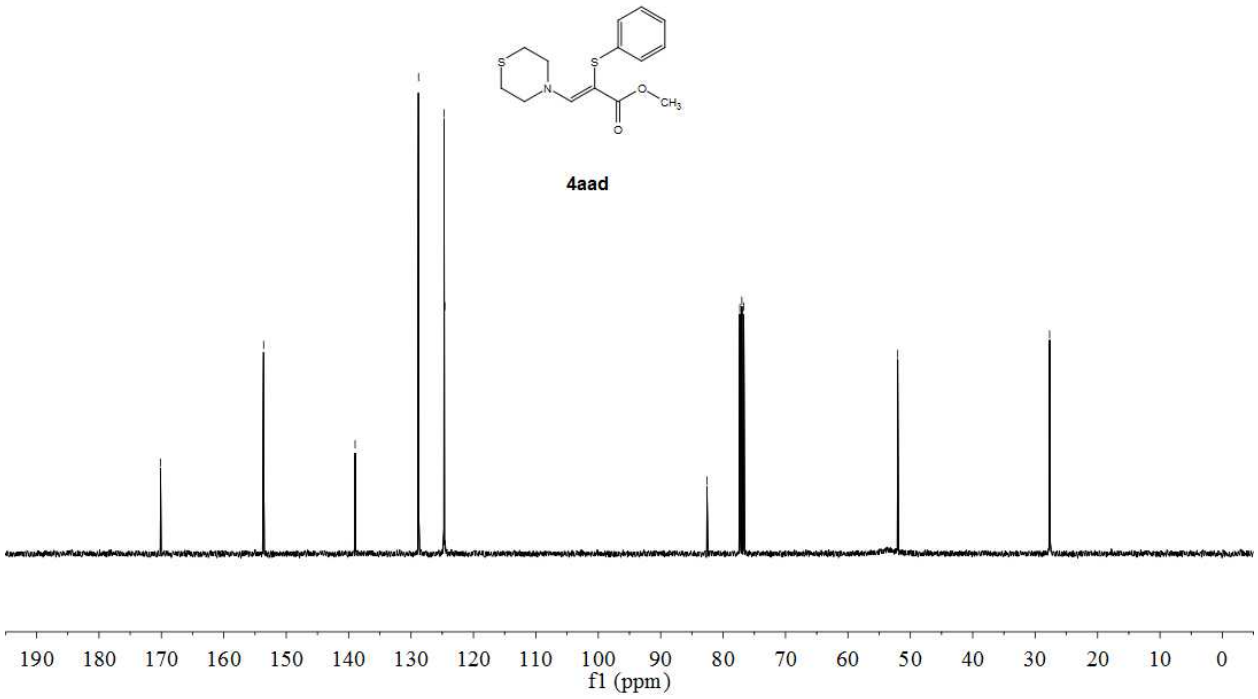
f1 (ppm)

4aad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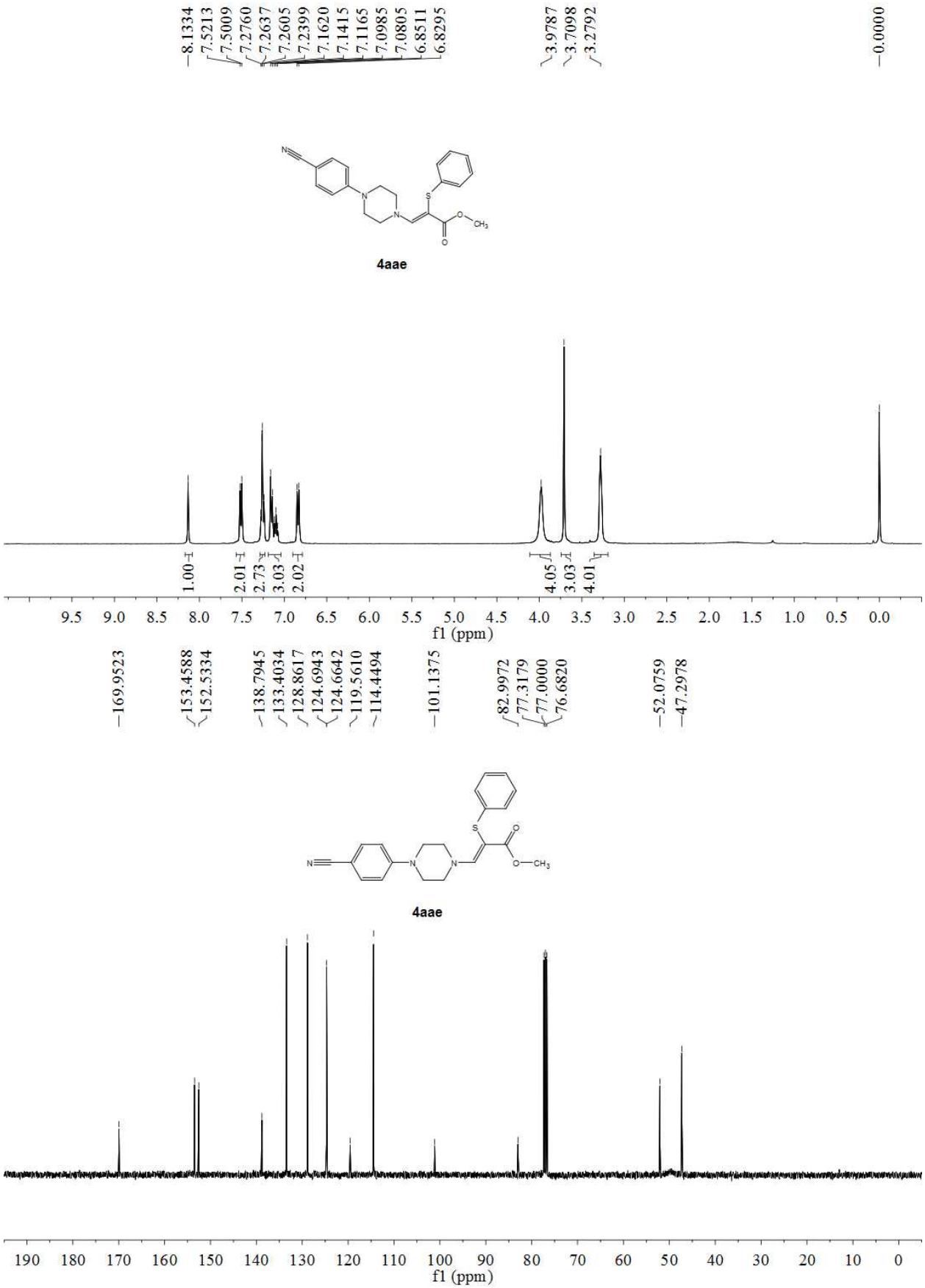
f1 (ppm)

4aad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7.2399
7.1620
7.1415
7.1165
7.0985
7.0805
6.8511
6.8295
3.9787
3.7098
3.2792
0.0000
4aae
1.00
2.01
2.73
3.03
2.02
4.05
3.03
4.01
f1 (ppm)
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133.4034
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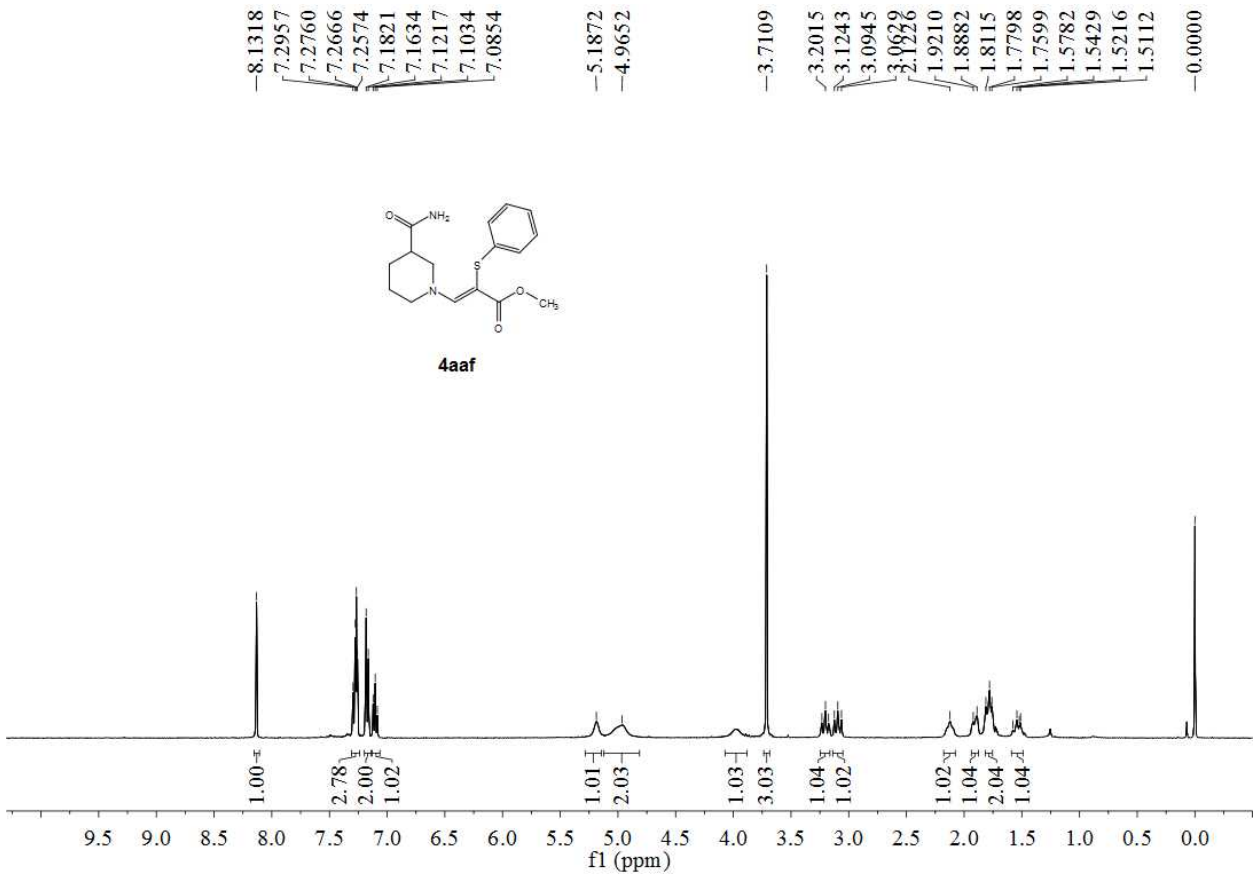
f1 (ppm)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3.7109
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3.0945
1.9210
1.8882
1.8115
1.7798
1.7599
1.5782
1.5429
1.5216
1.5112
0.0000
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1.00
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2.00
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1.01
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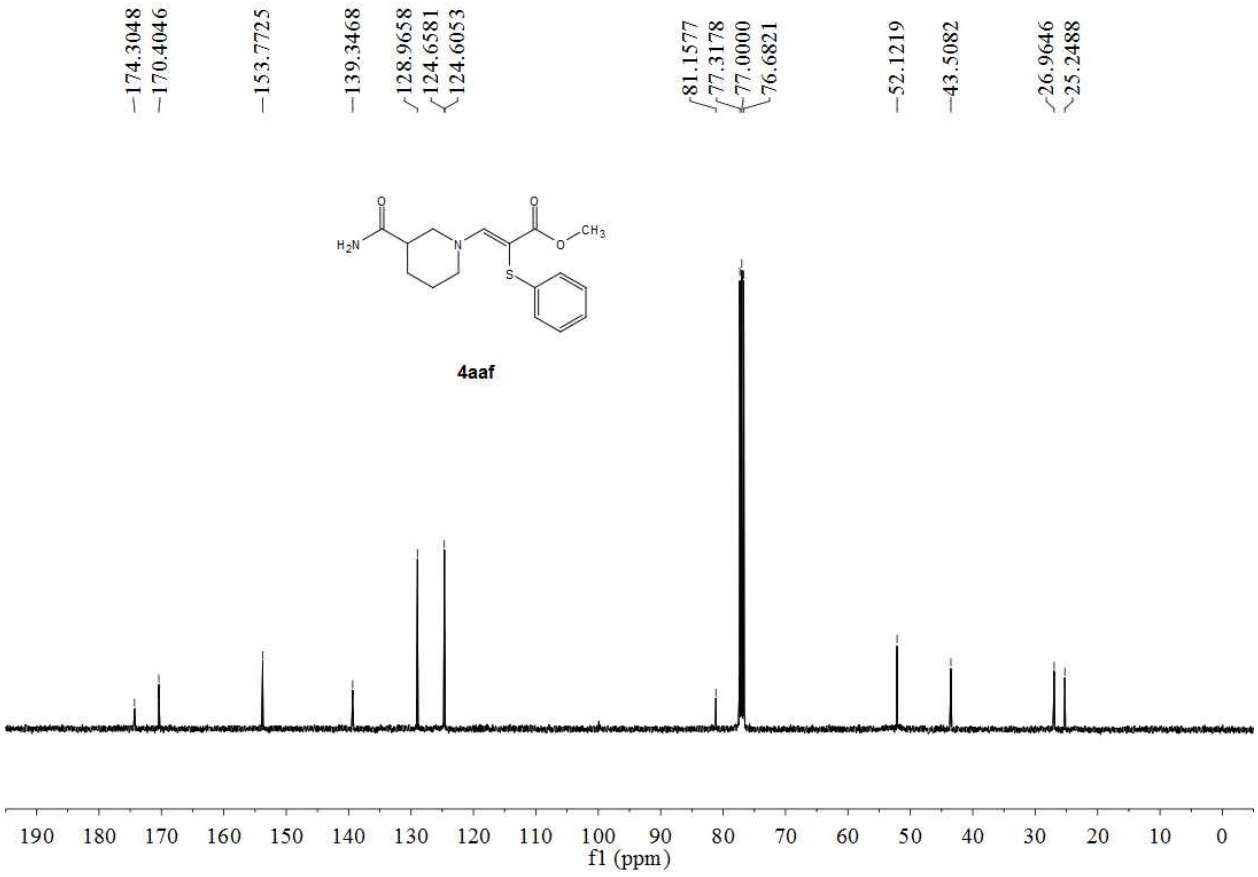
1.04
1.02
1.02
1.04
2.04
1.04
f1 (ppm)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26.9646
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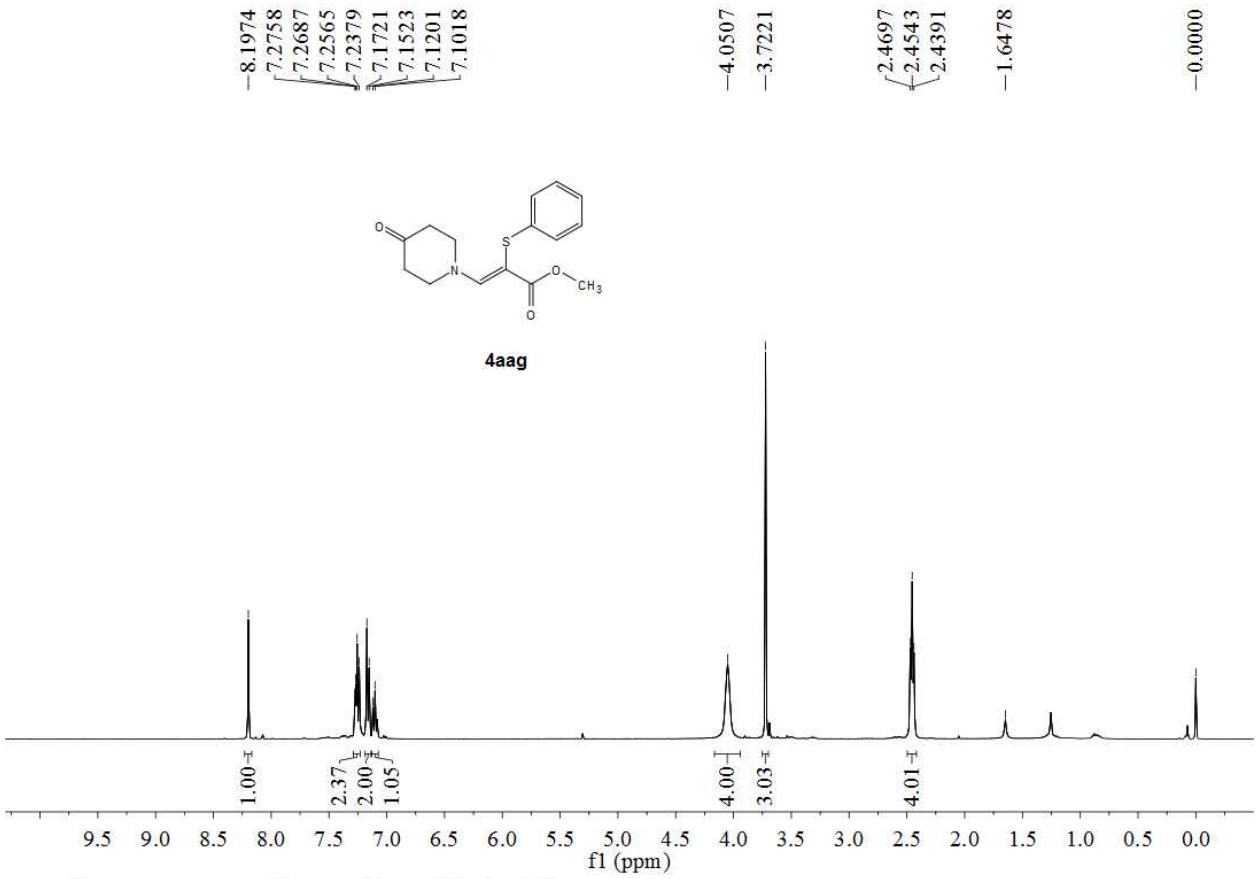
4aaf
f1 (ppm)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3.7221
2.4697
2.4543
2.4391
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1.00
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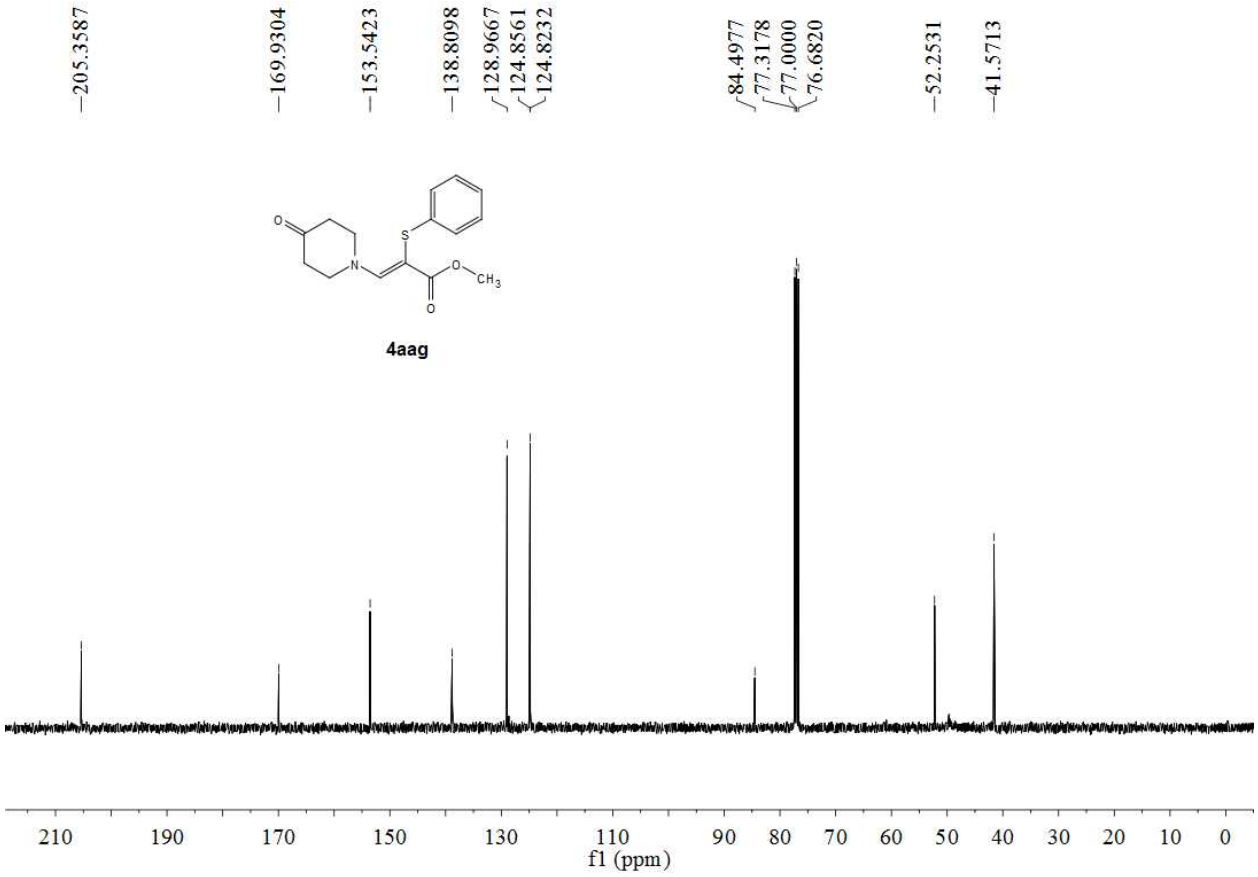
2.00
1.05
4.00
3.03
4.01
f1 (ppm)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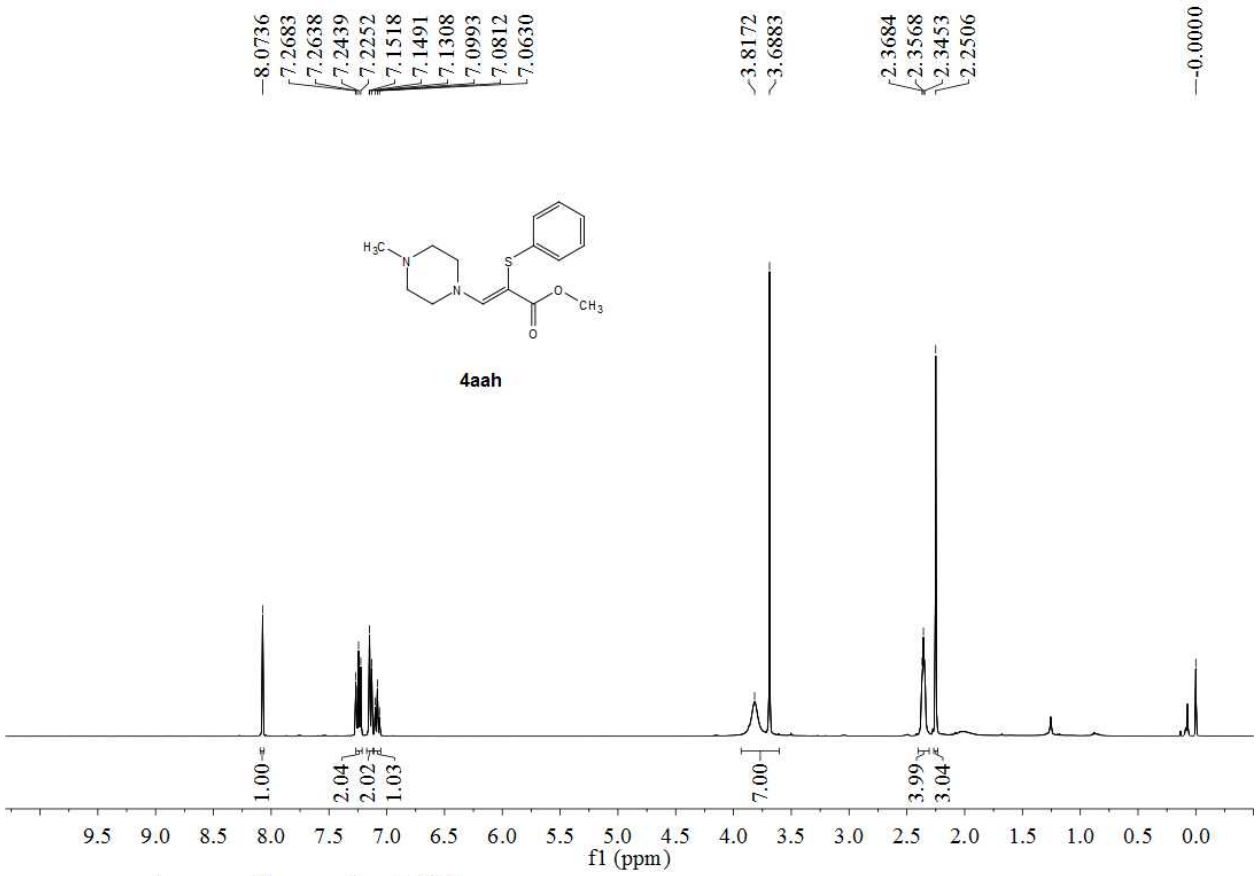
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3.6883
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7.00
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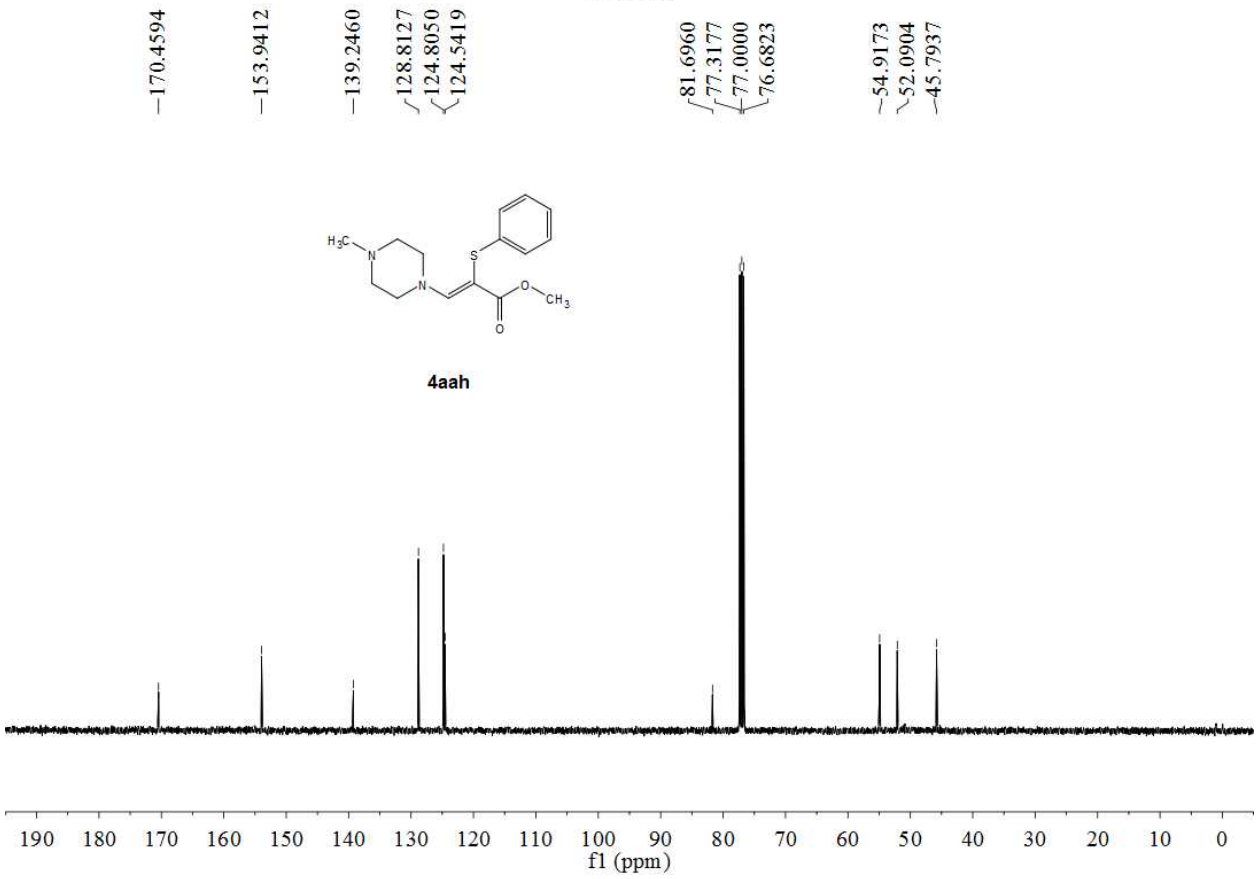
3.04
f1 (ppm)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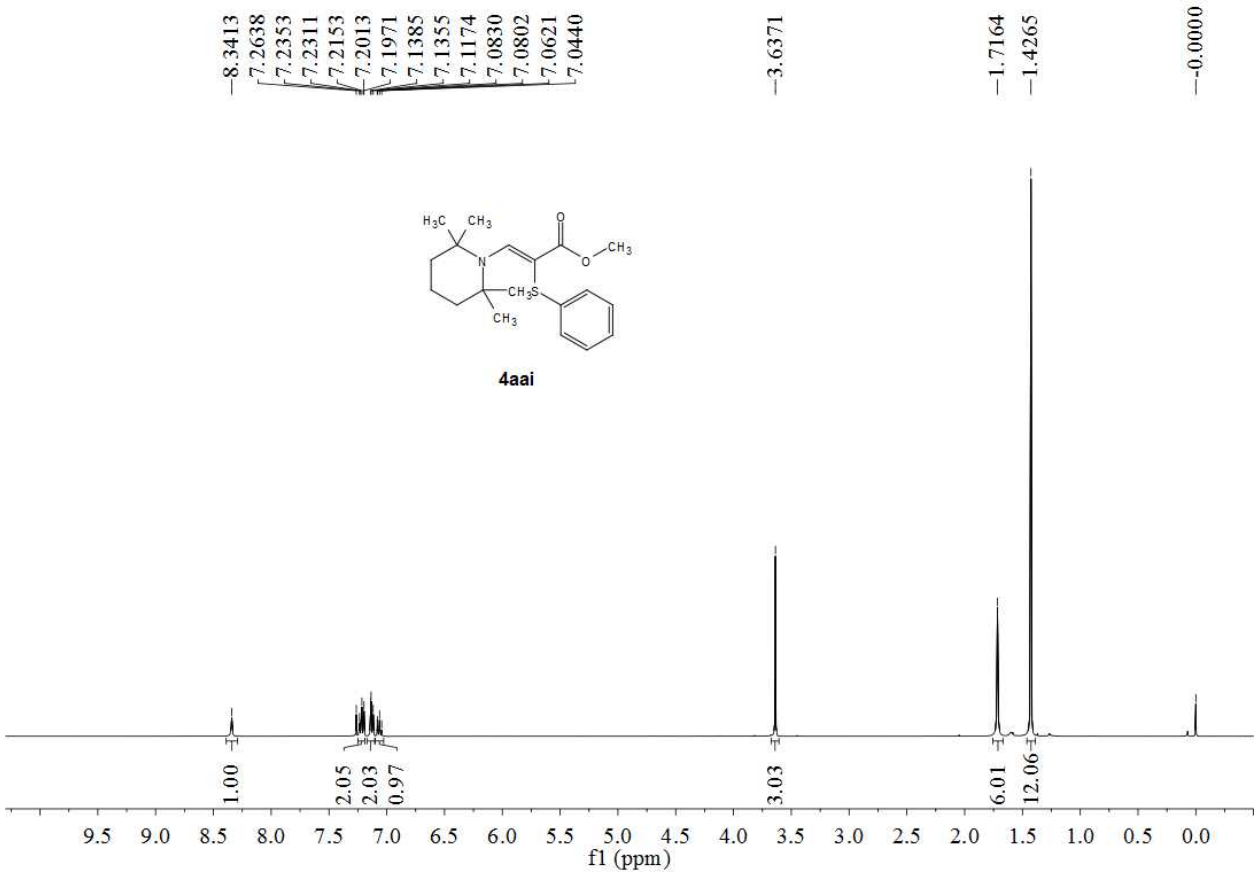
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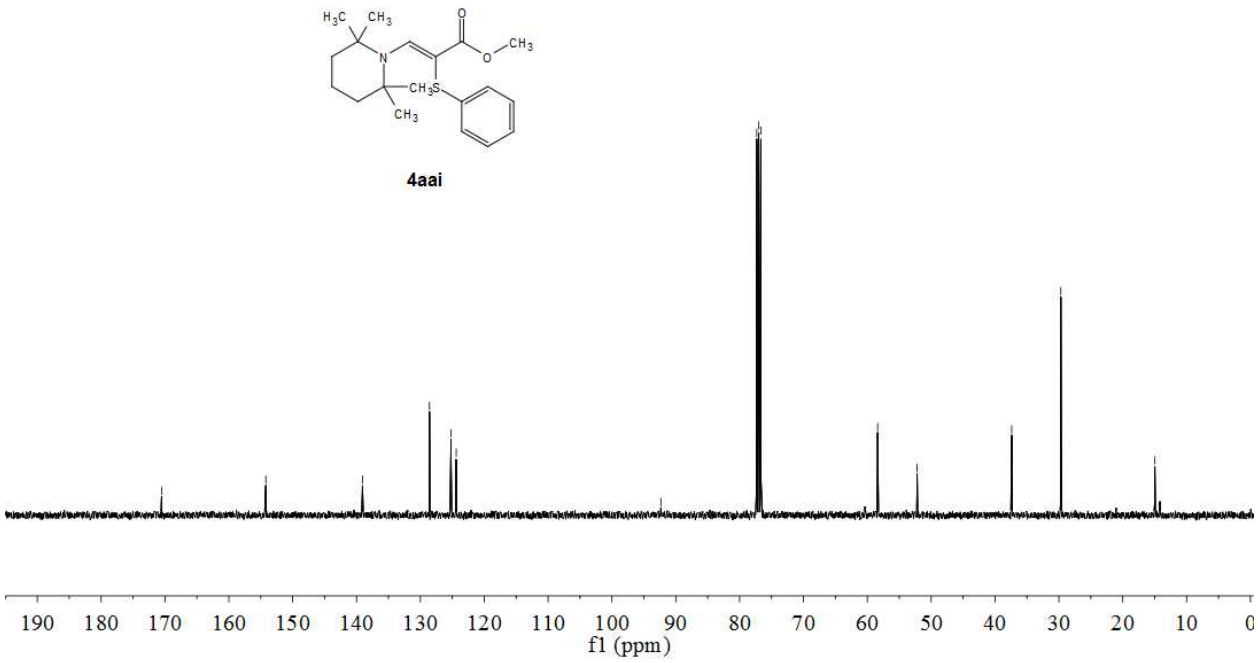
12.06
f1 (ppm)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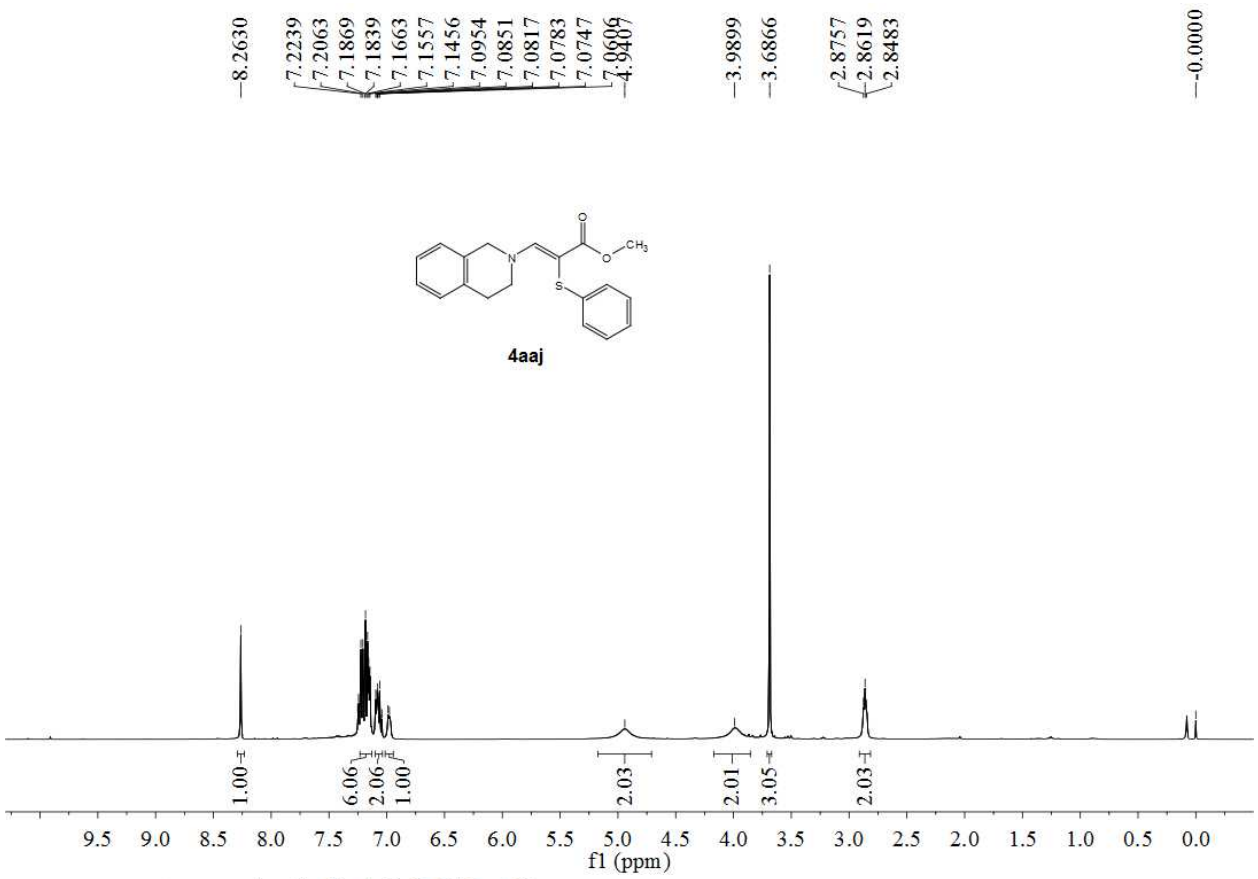
f1 (ppm)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7.0747
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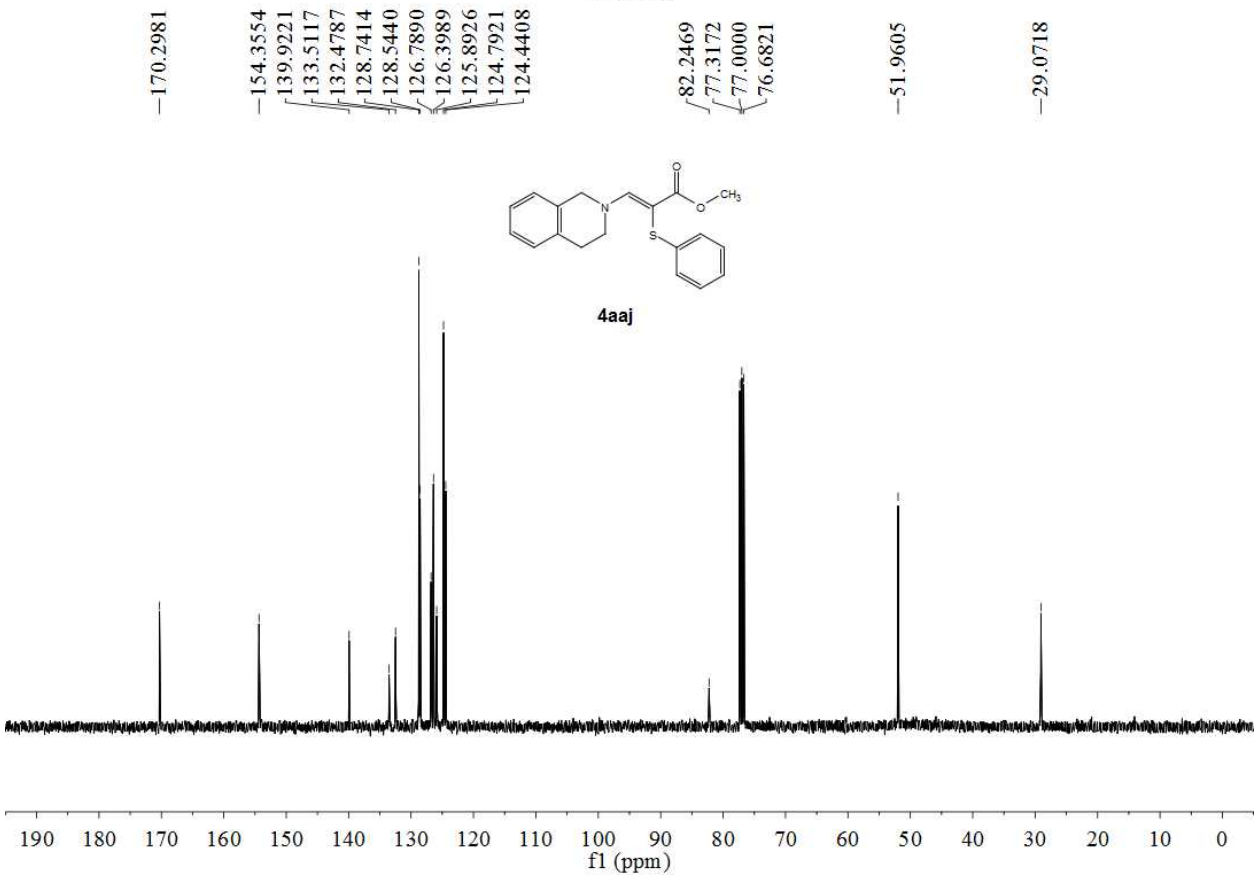
2.01
3.05
2.03
f1 (ppm)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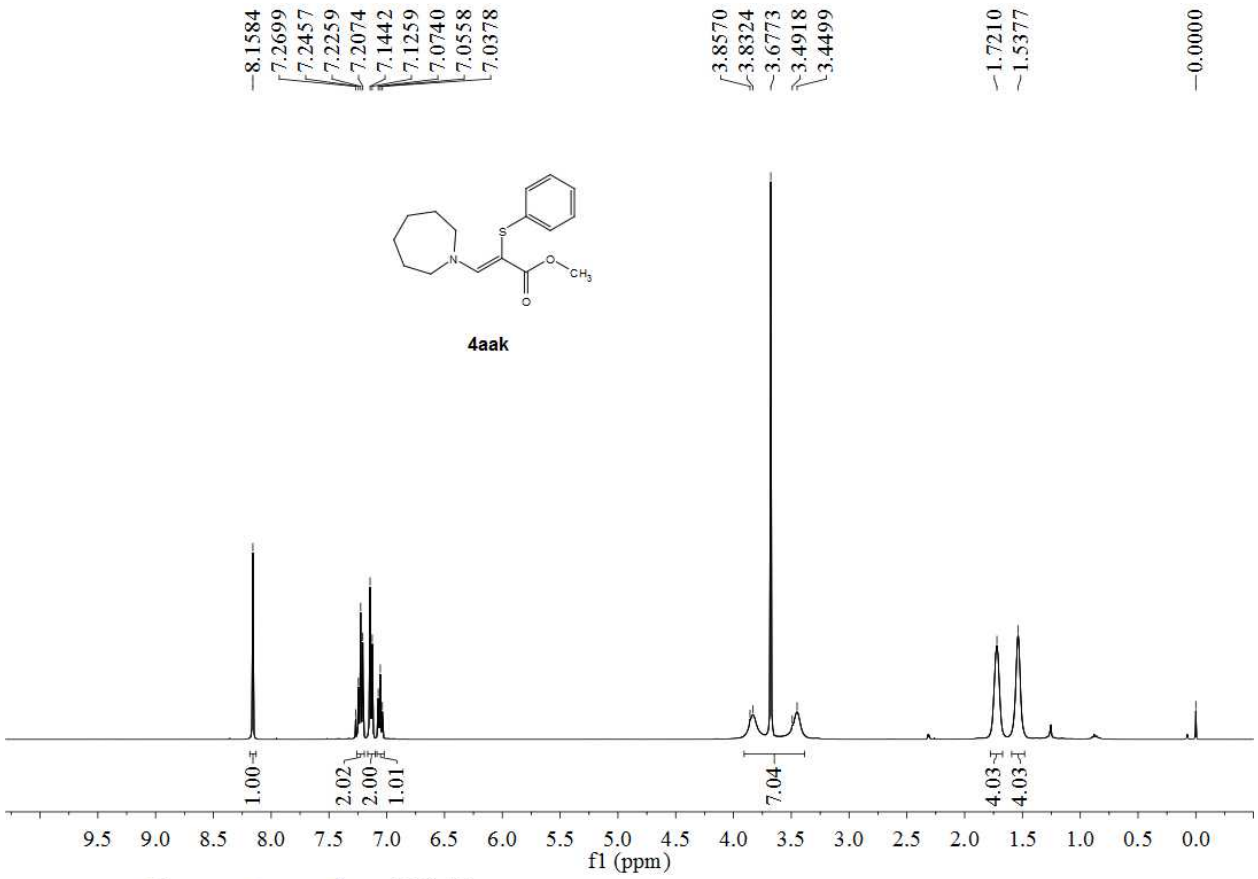
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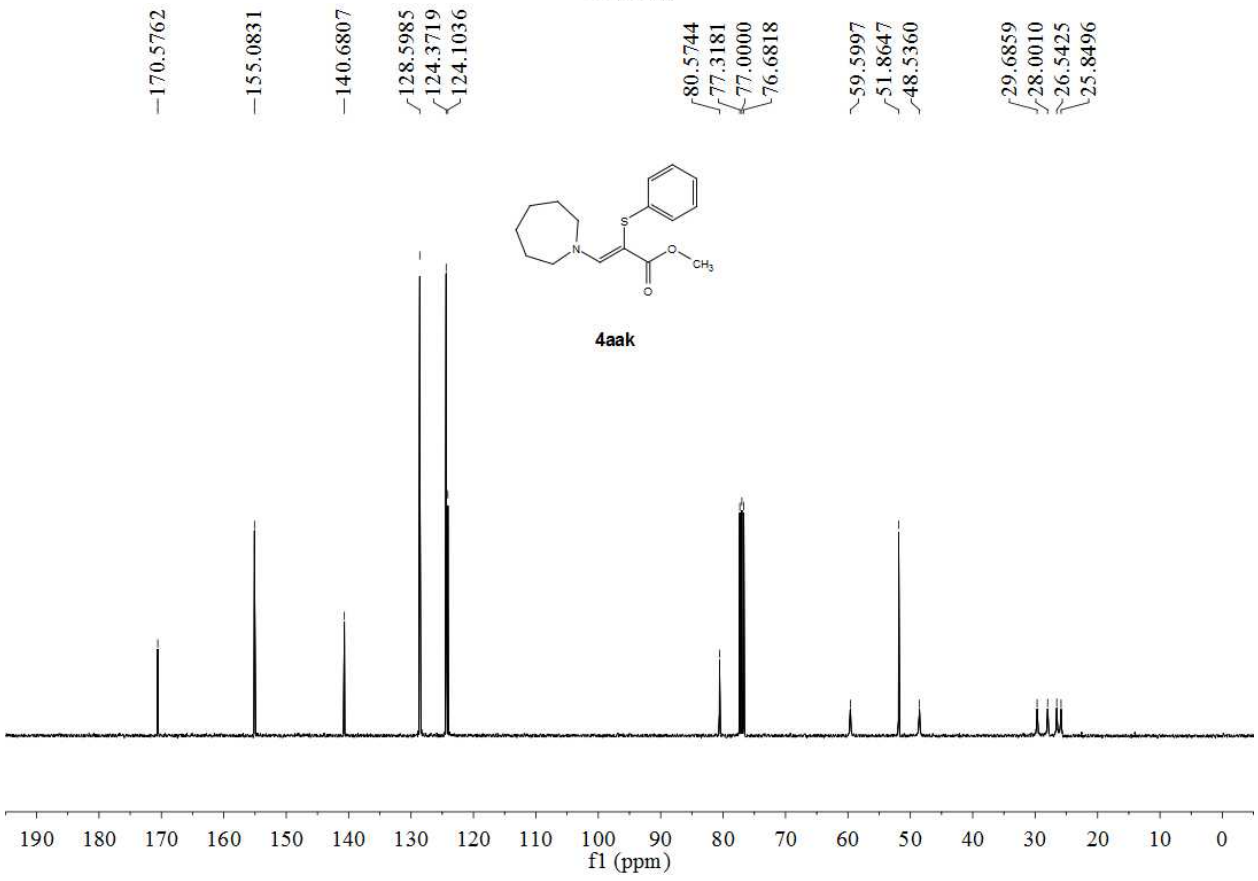
f1 (ppm)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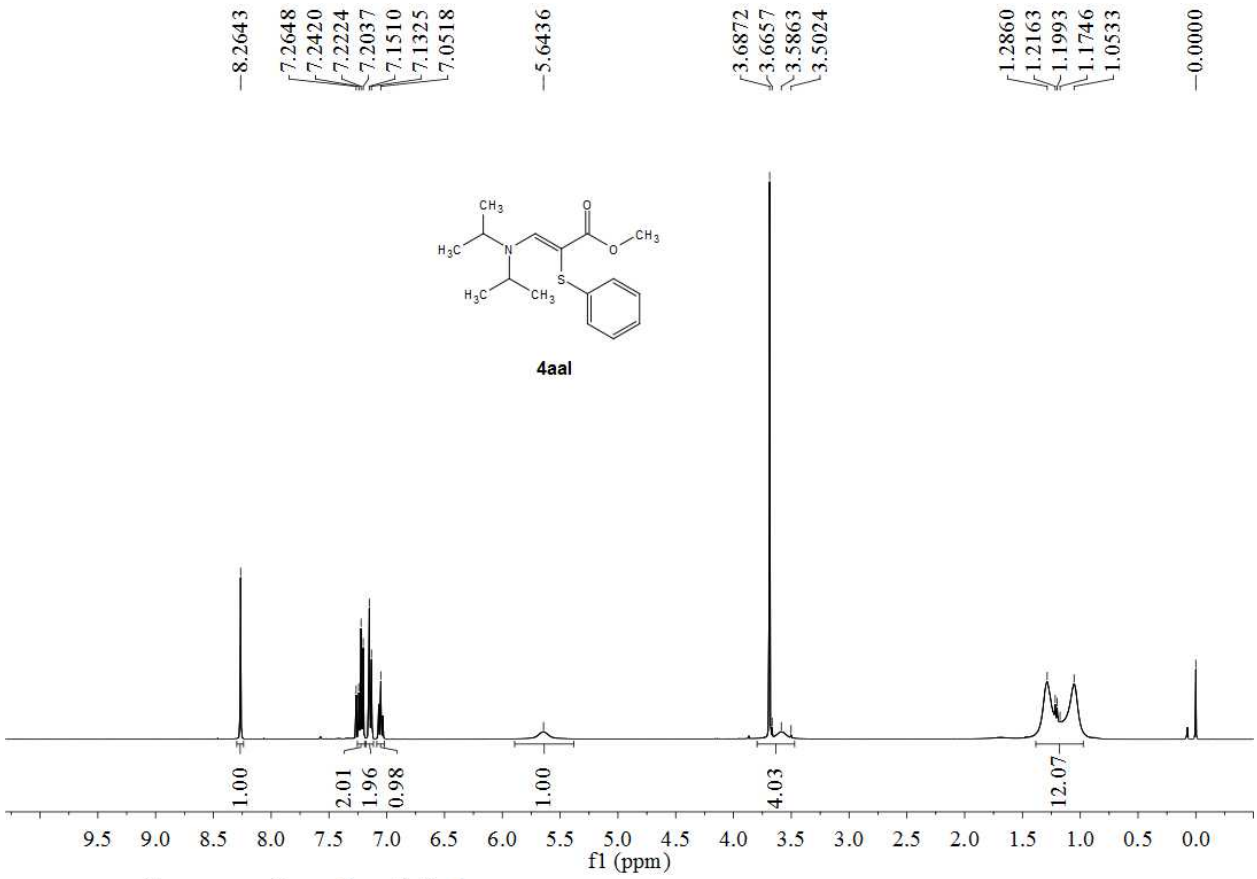
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1.00
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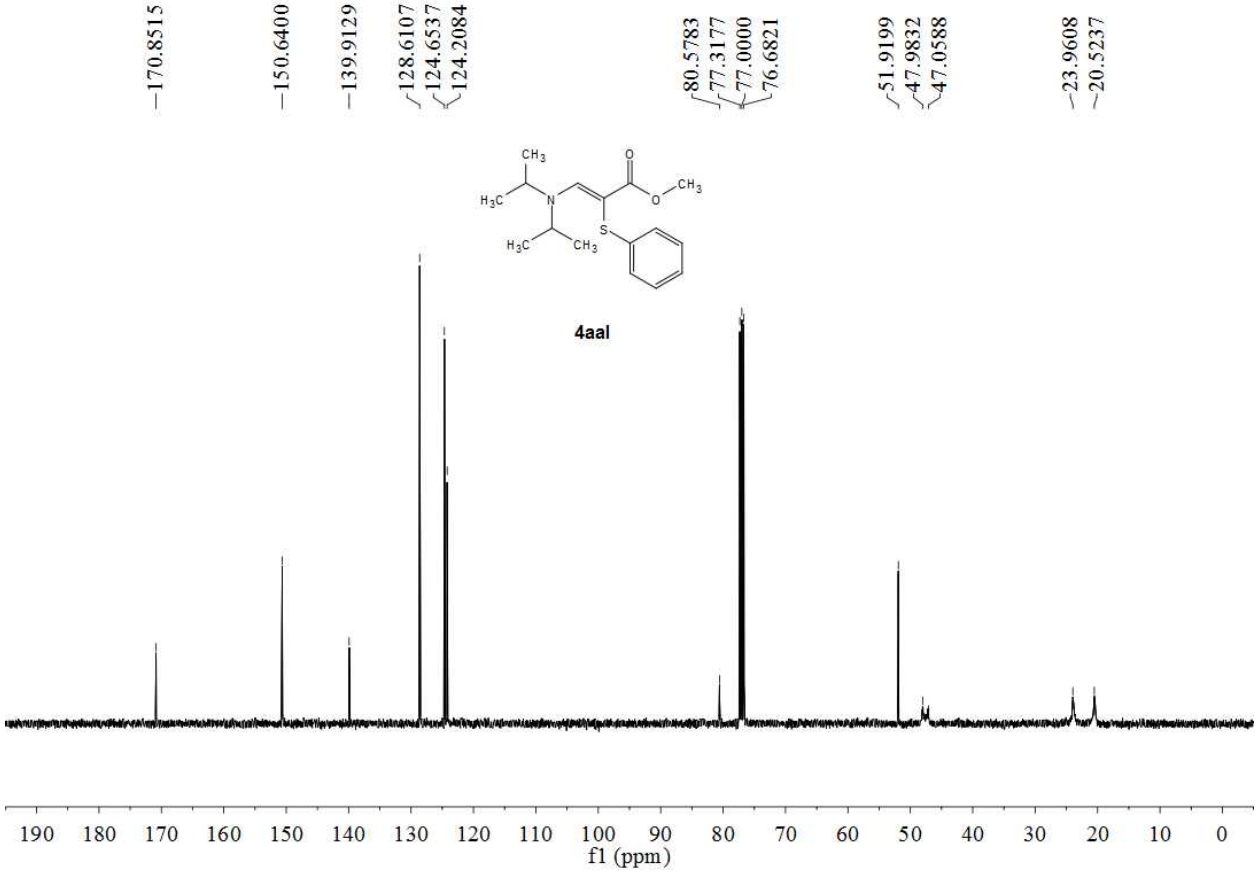
12.07
f1 (ppm)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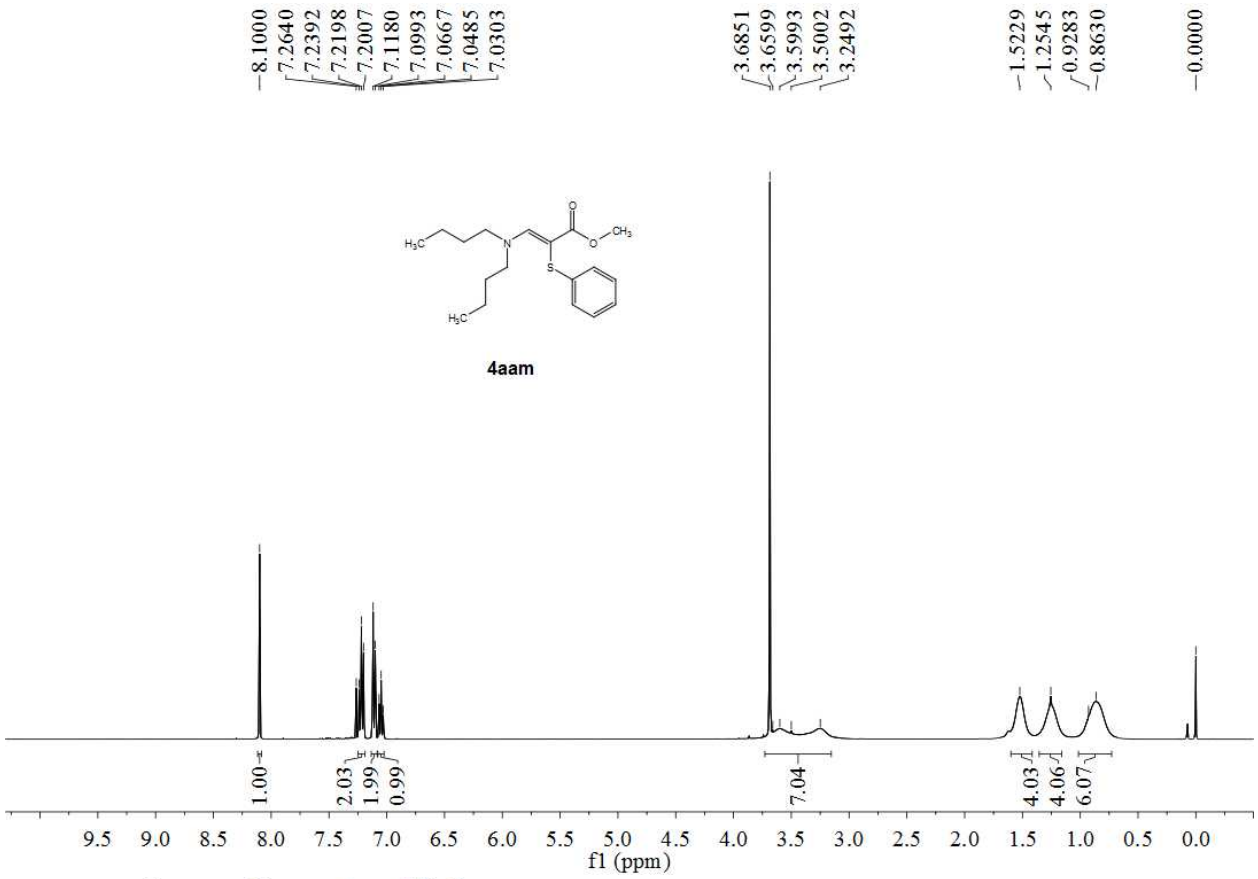
f1 (ppm)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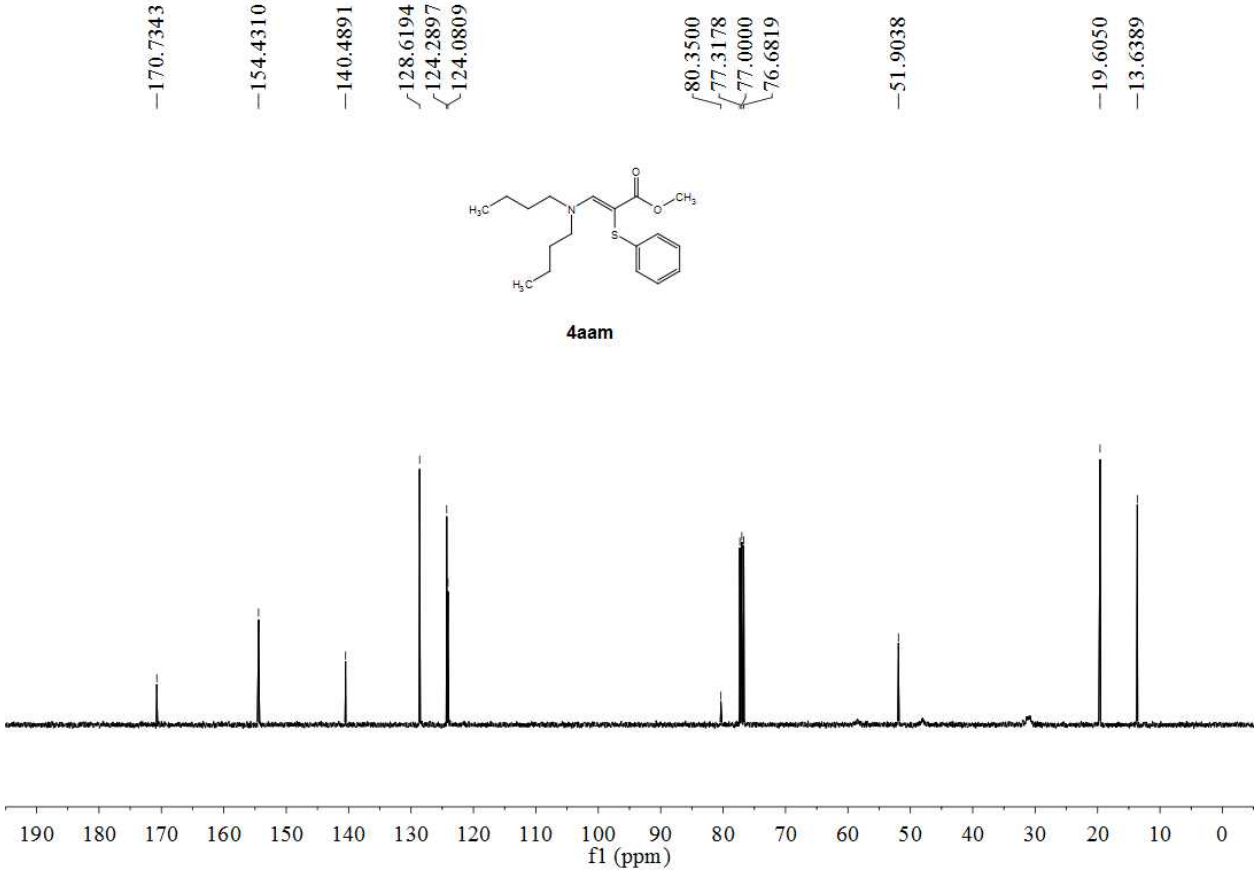
6.07
f1 (ppm)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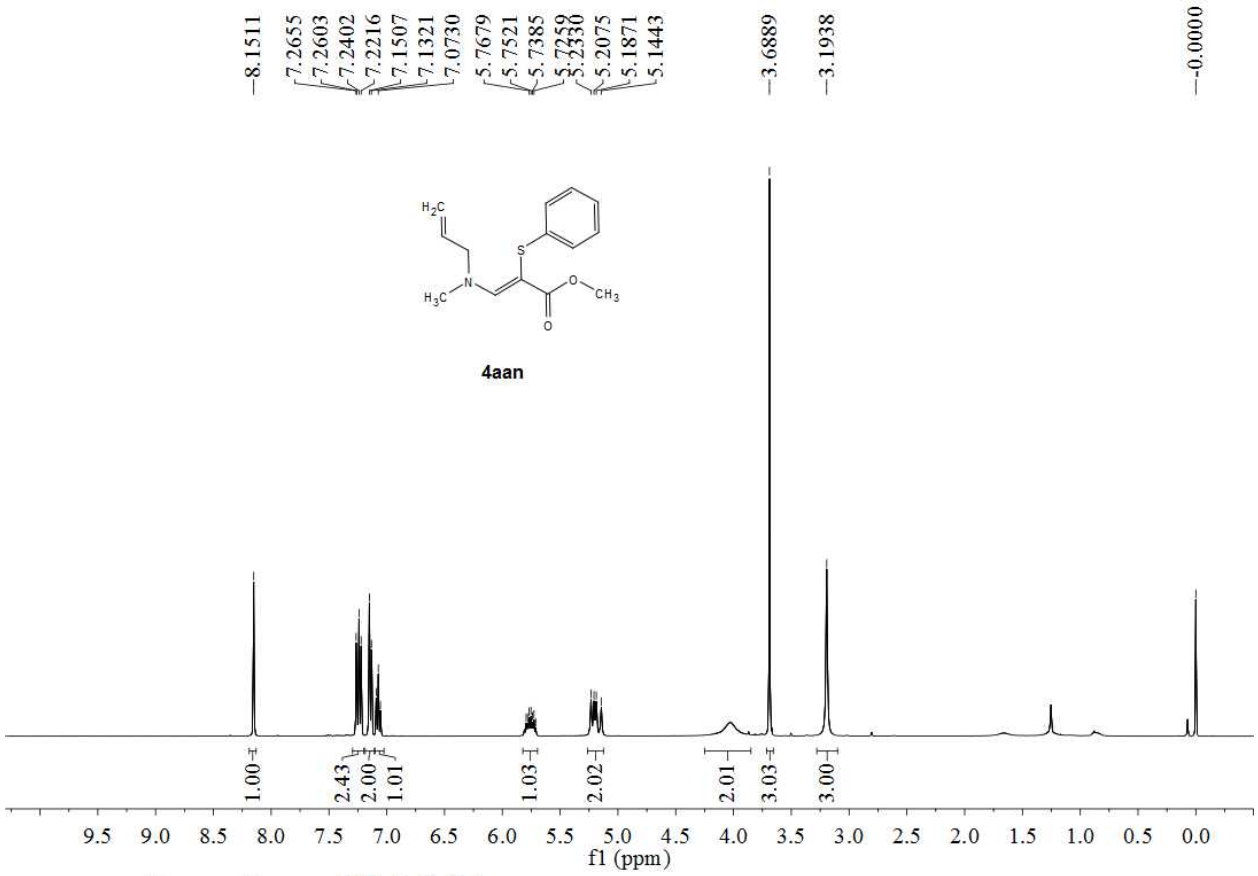
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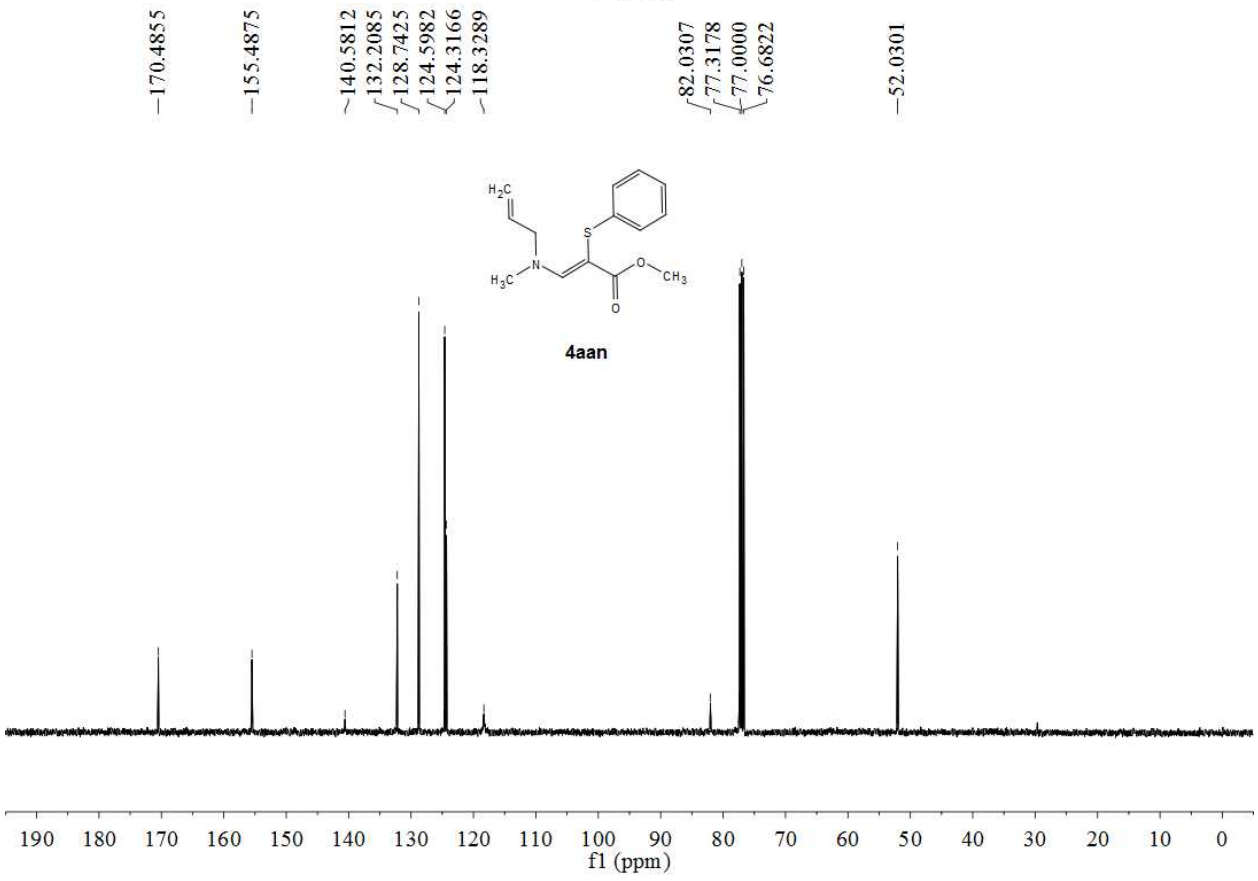
f1 (ppm)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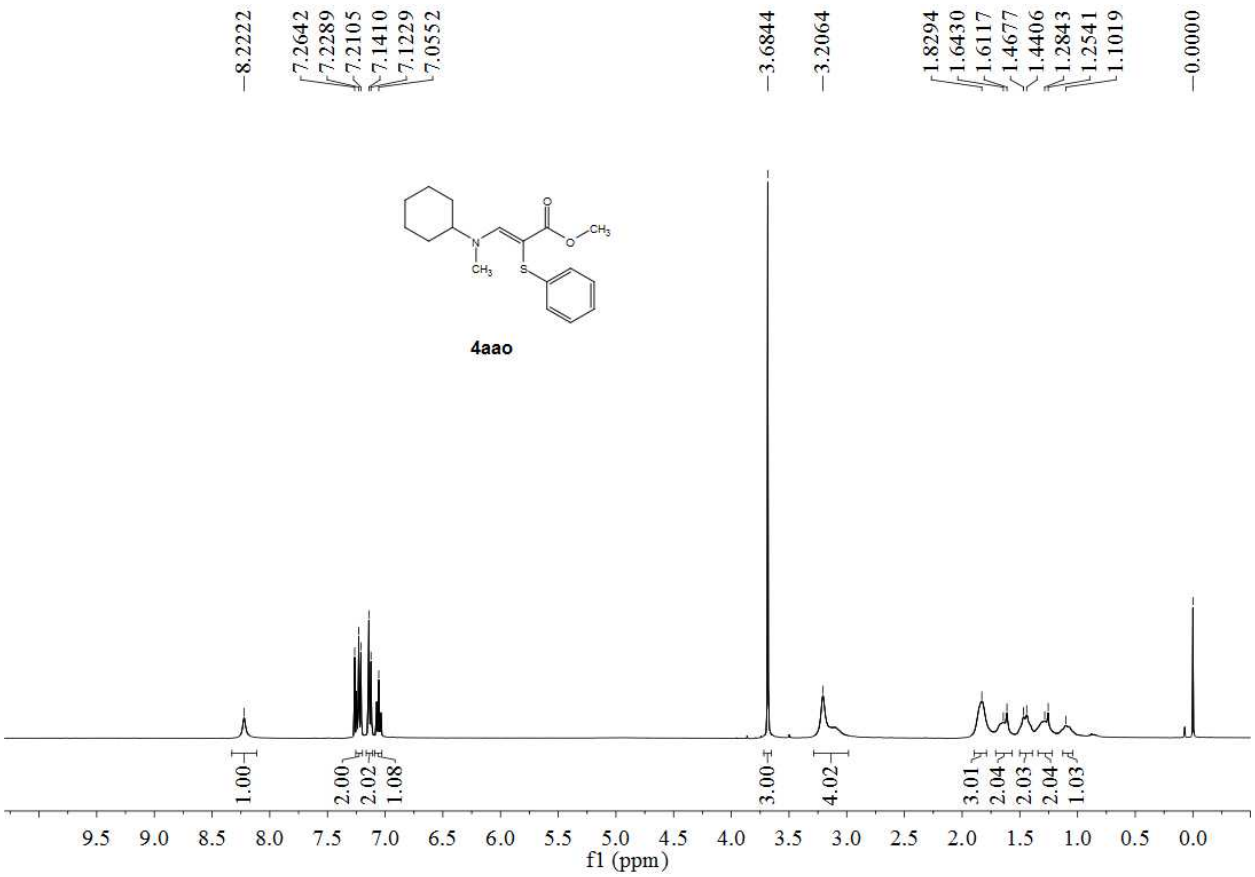
f1 (ppm)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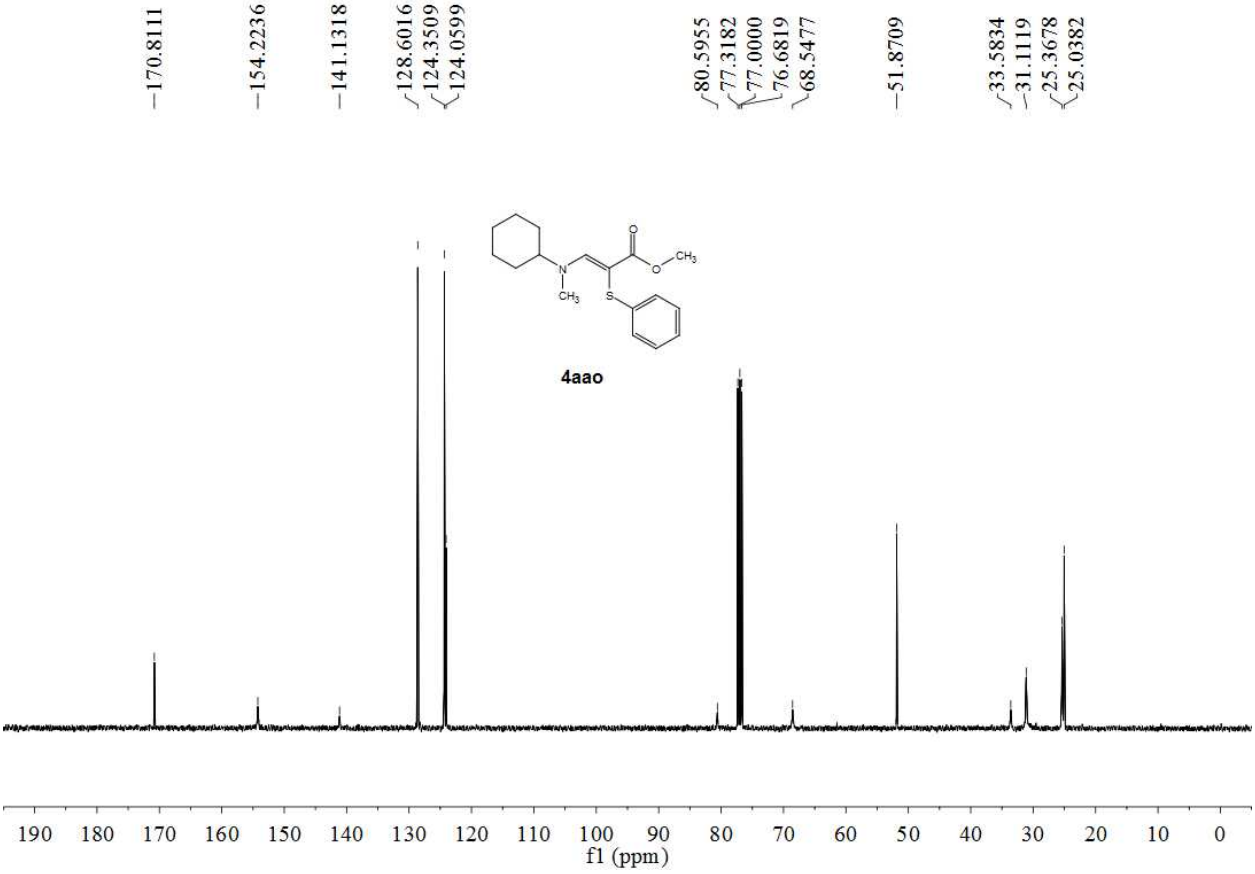
3.01
2.04
2.03
2.04
1.03
f1 (ppm)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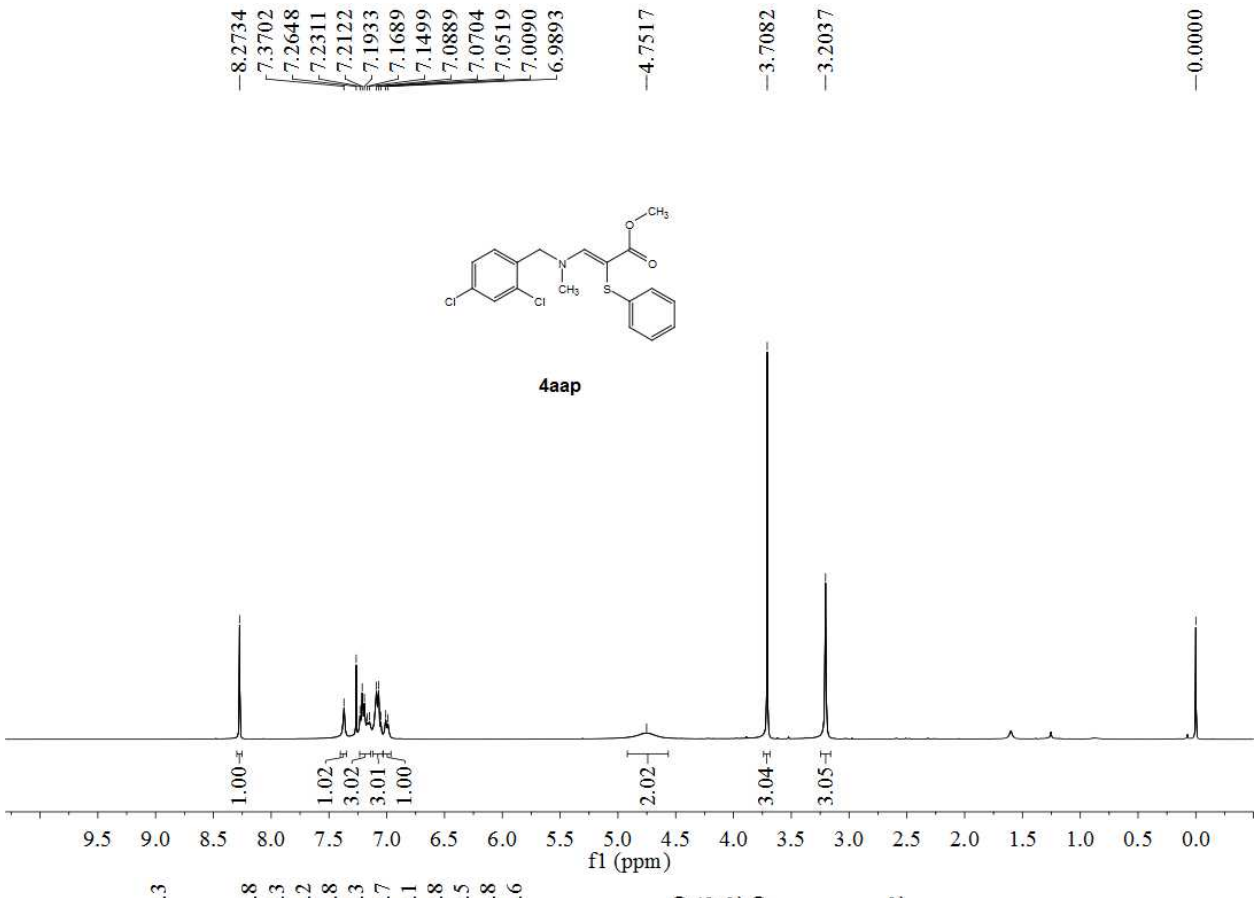
f1 (ppm)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1.00
2.02
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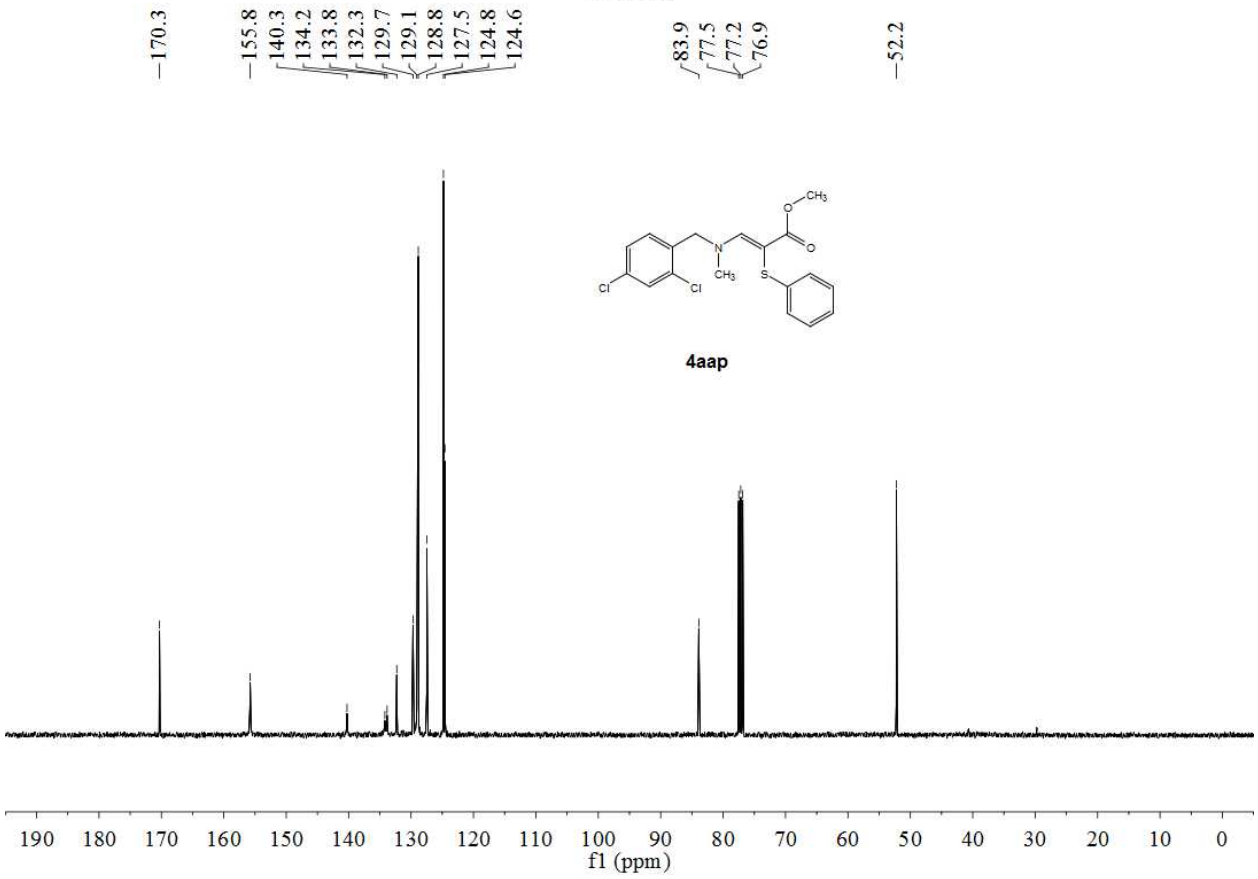
3.05
f1 (ppm)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76.9
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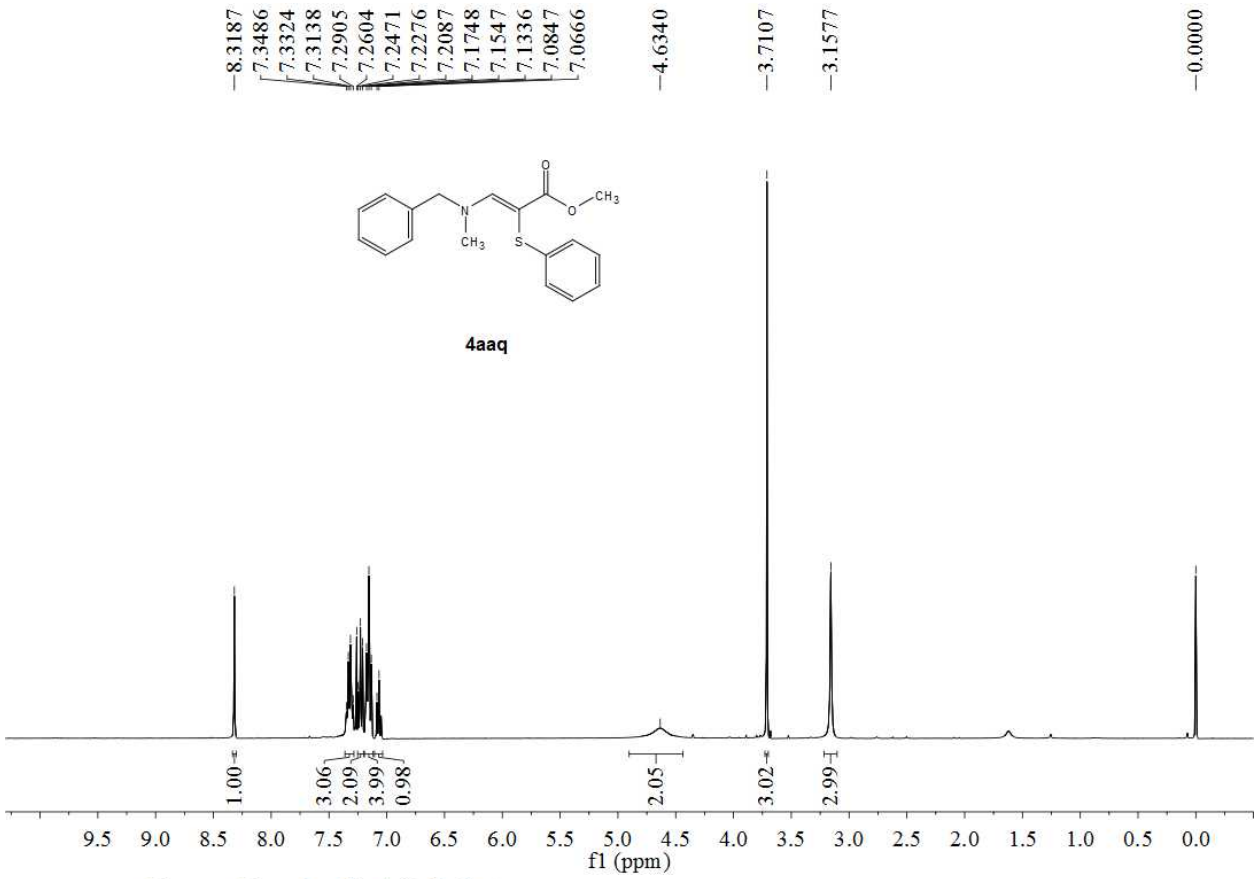
f1 (ppm)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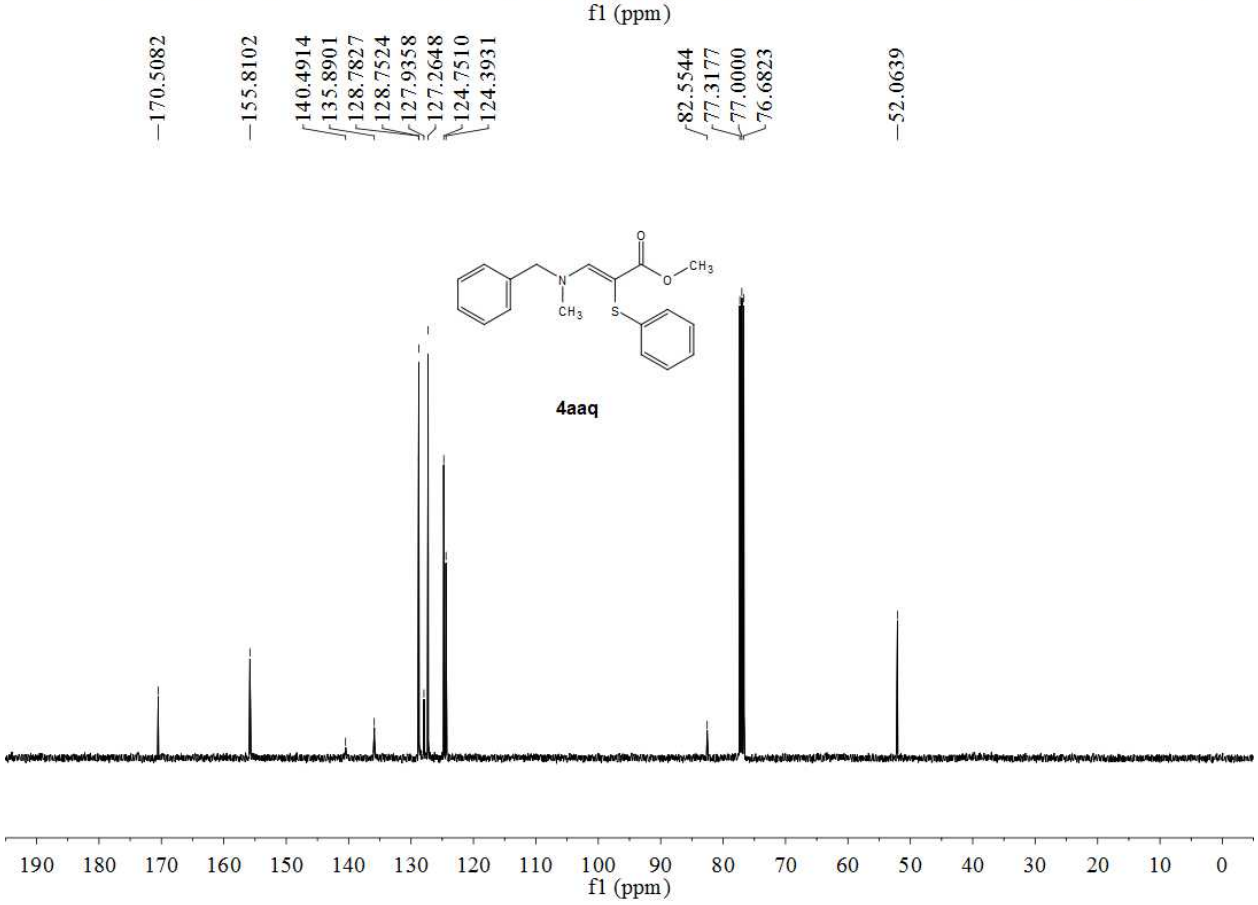
f1 (ppm)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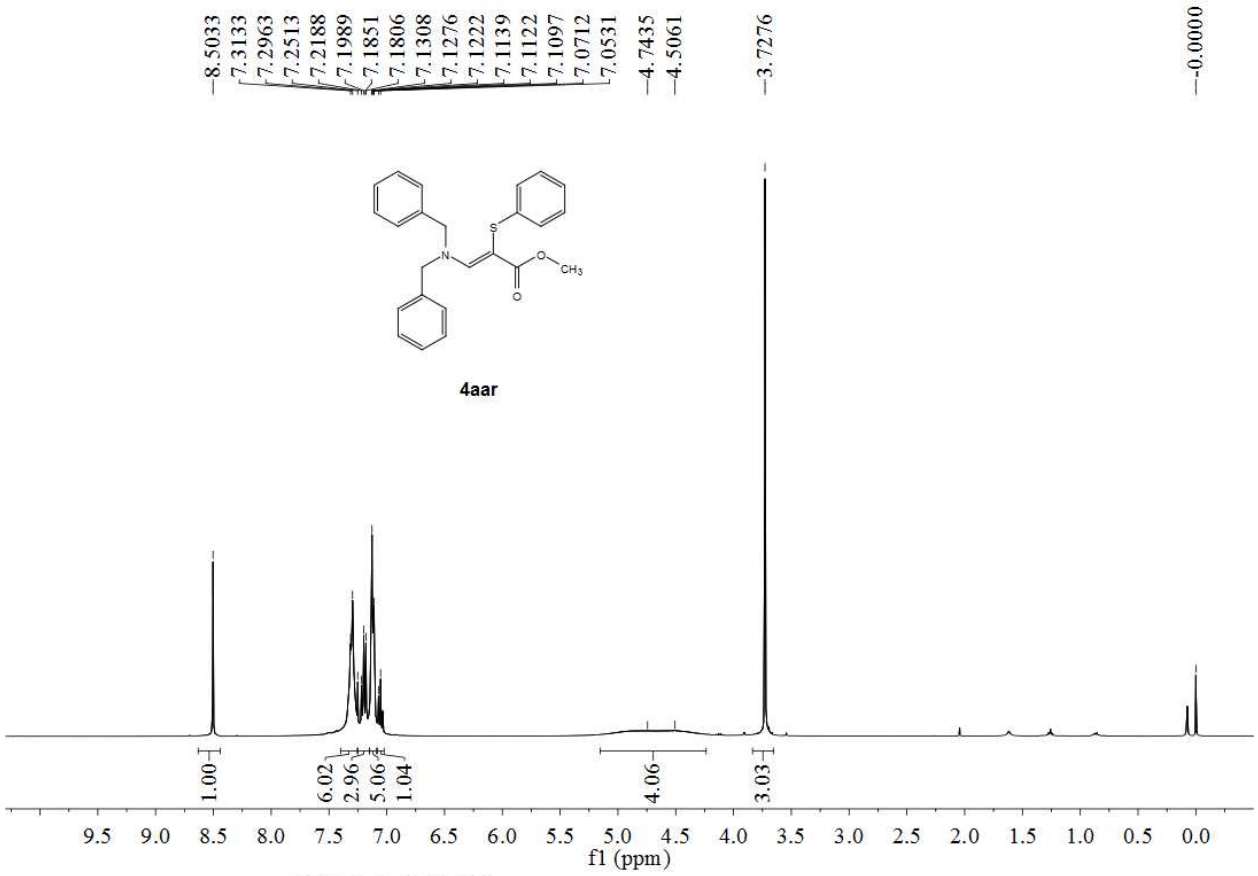
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1.04
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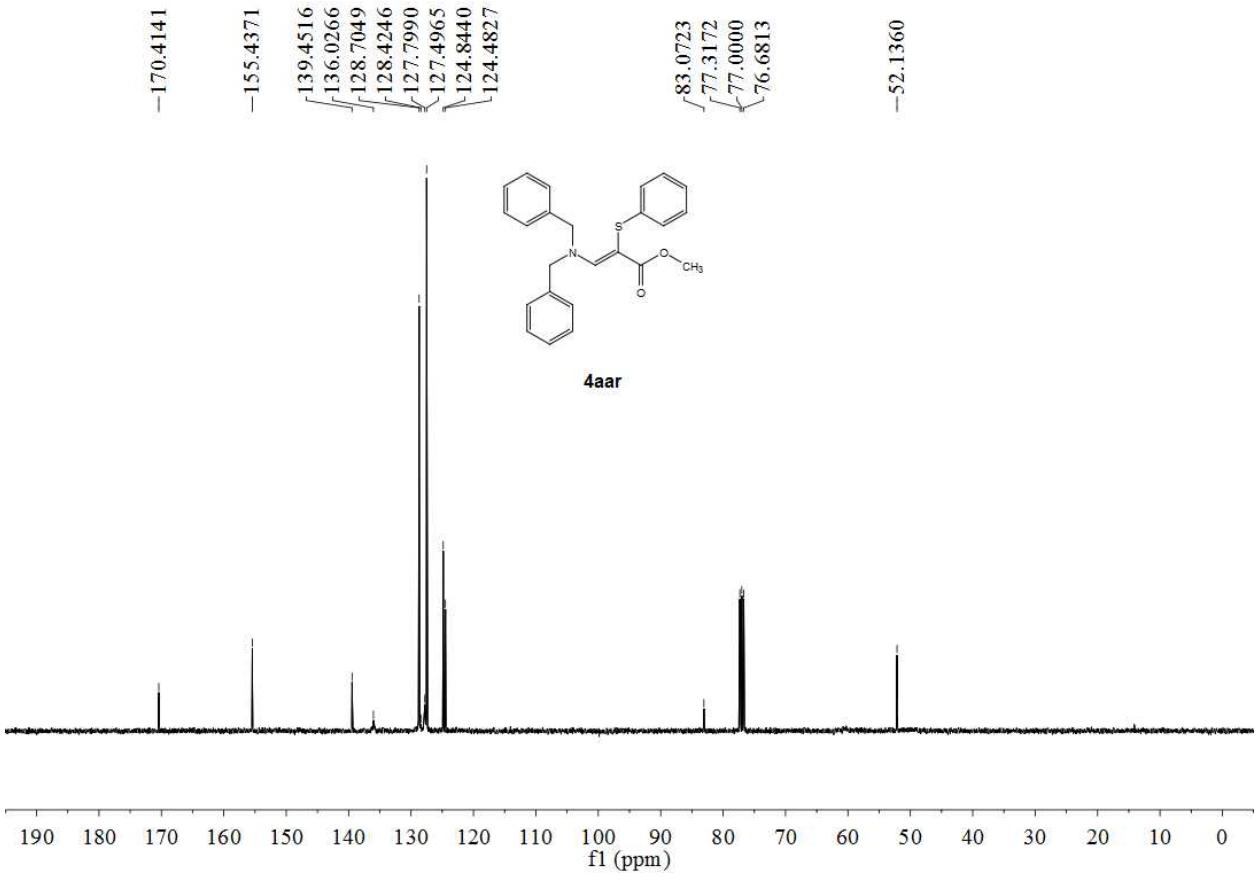
3.03
f1 (ppm)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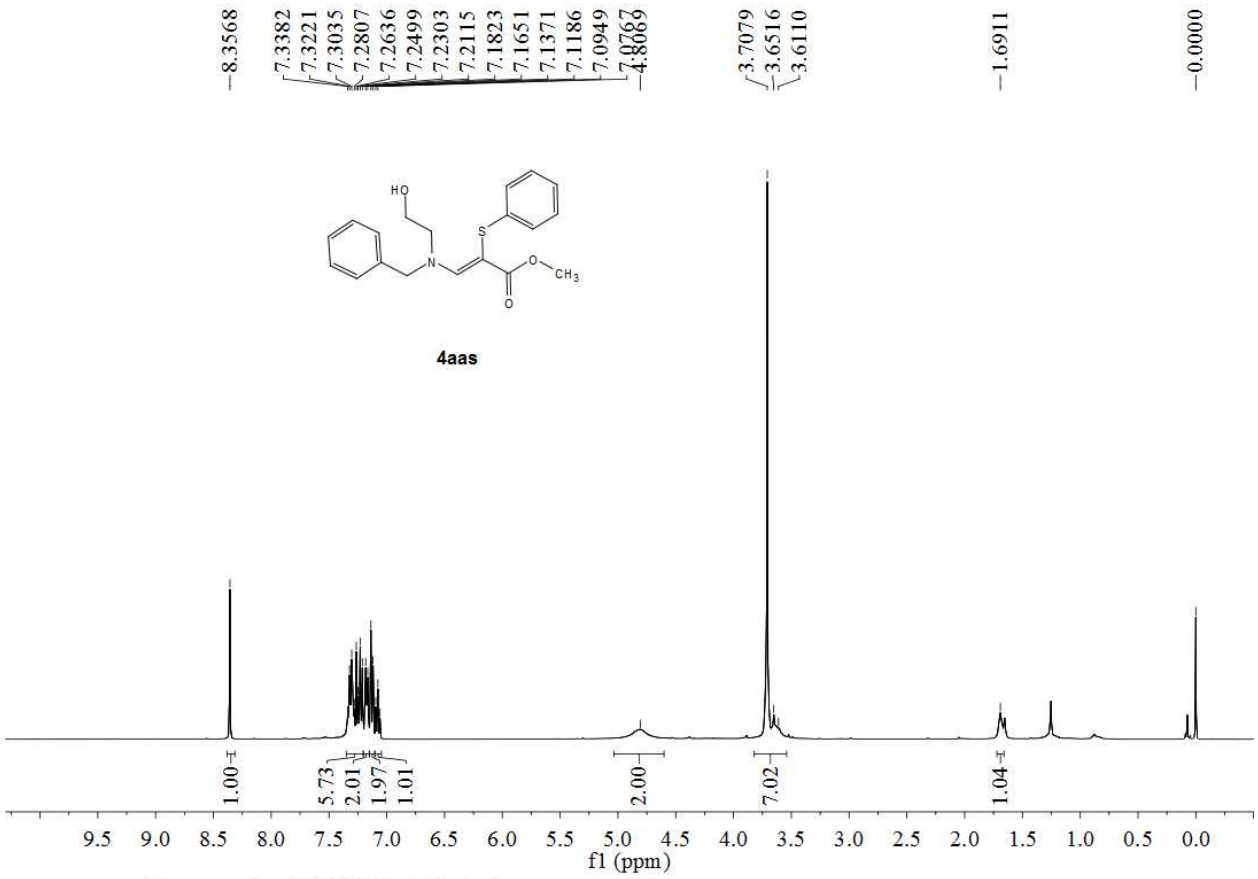
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7.1371
7.1186
7.0949
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3.7079
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S
N
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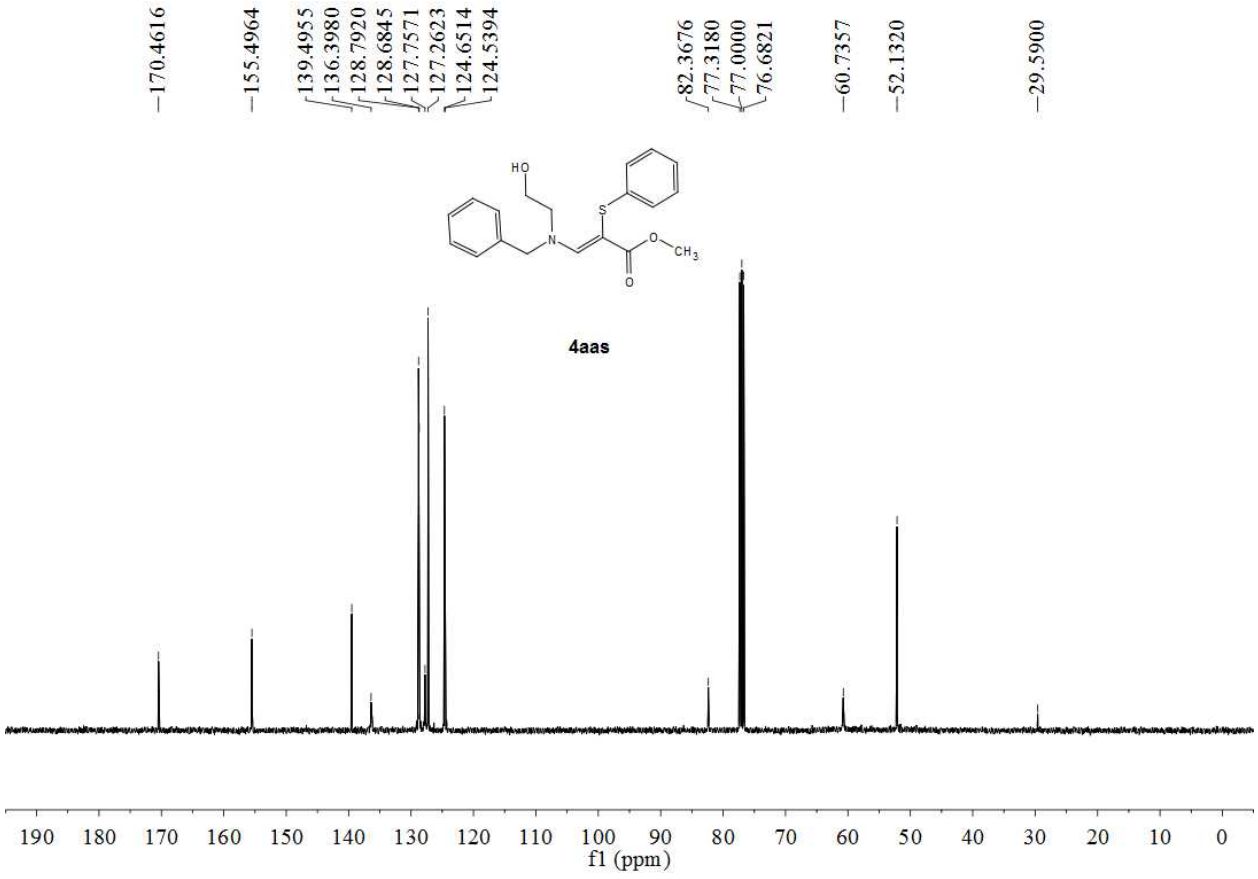
1.04
f1 (ppm)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N
O
CH3
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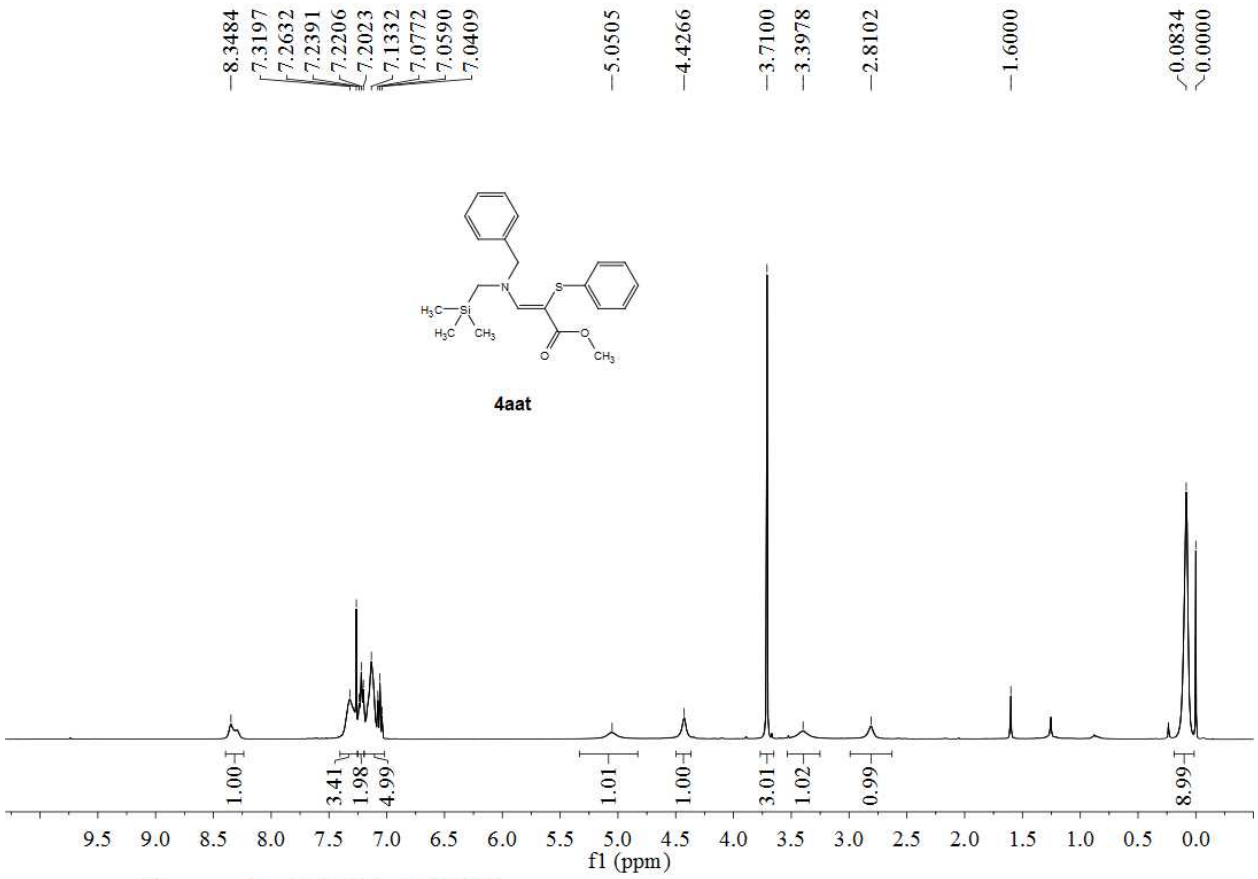
4aas
f1 (ppm)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1.00
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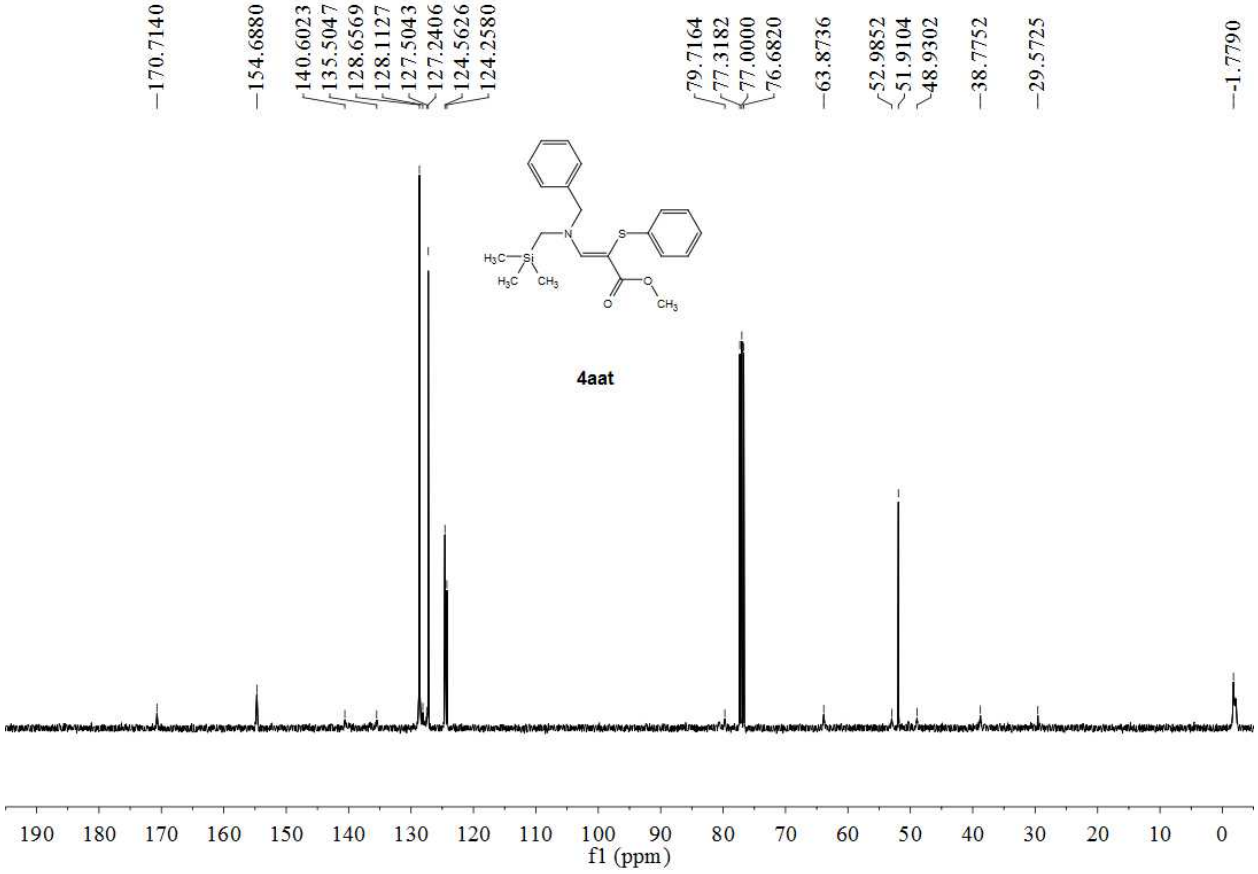
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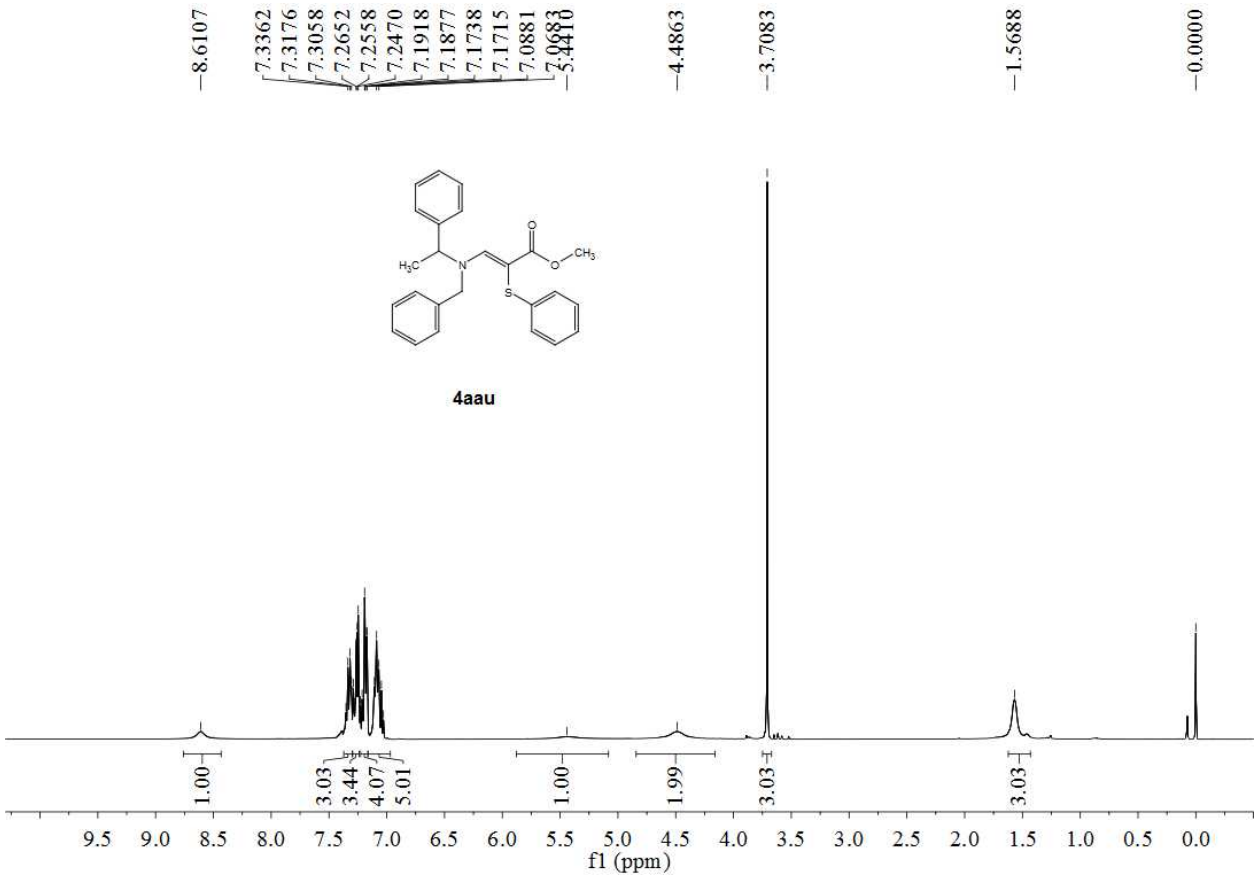
f1 (ppm)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7.1715
7.0881
7.0683
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3.7083
1.5688
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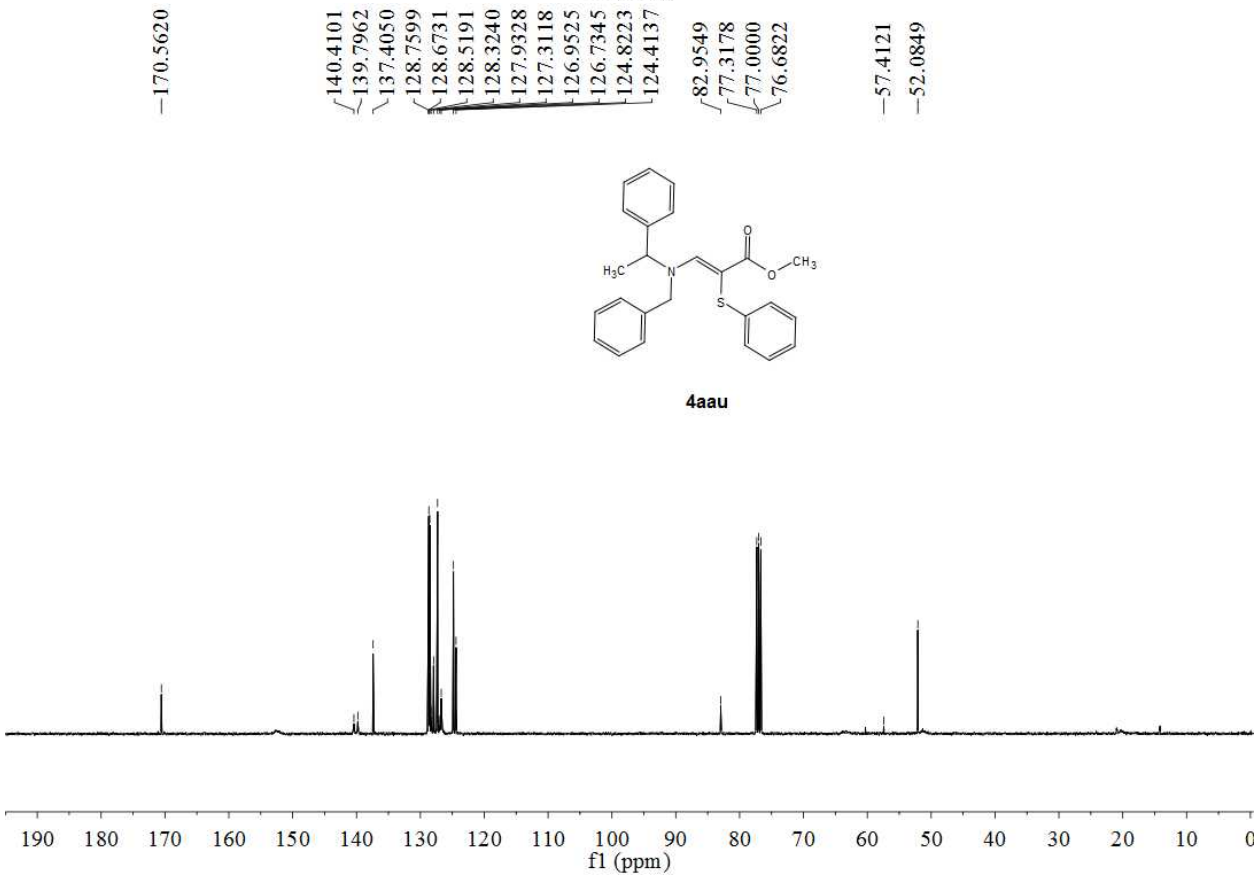
3.44
4.07
5.01
1.00
1.99
3.03
3.03
f1 (ppm)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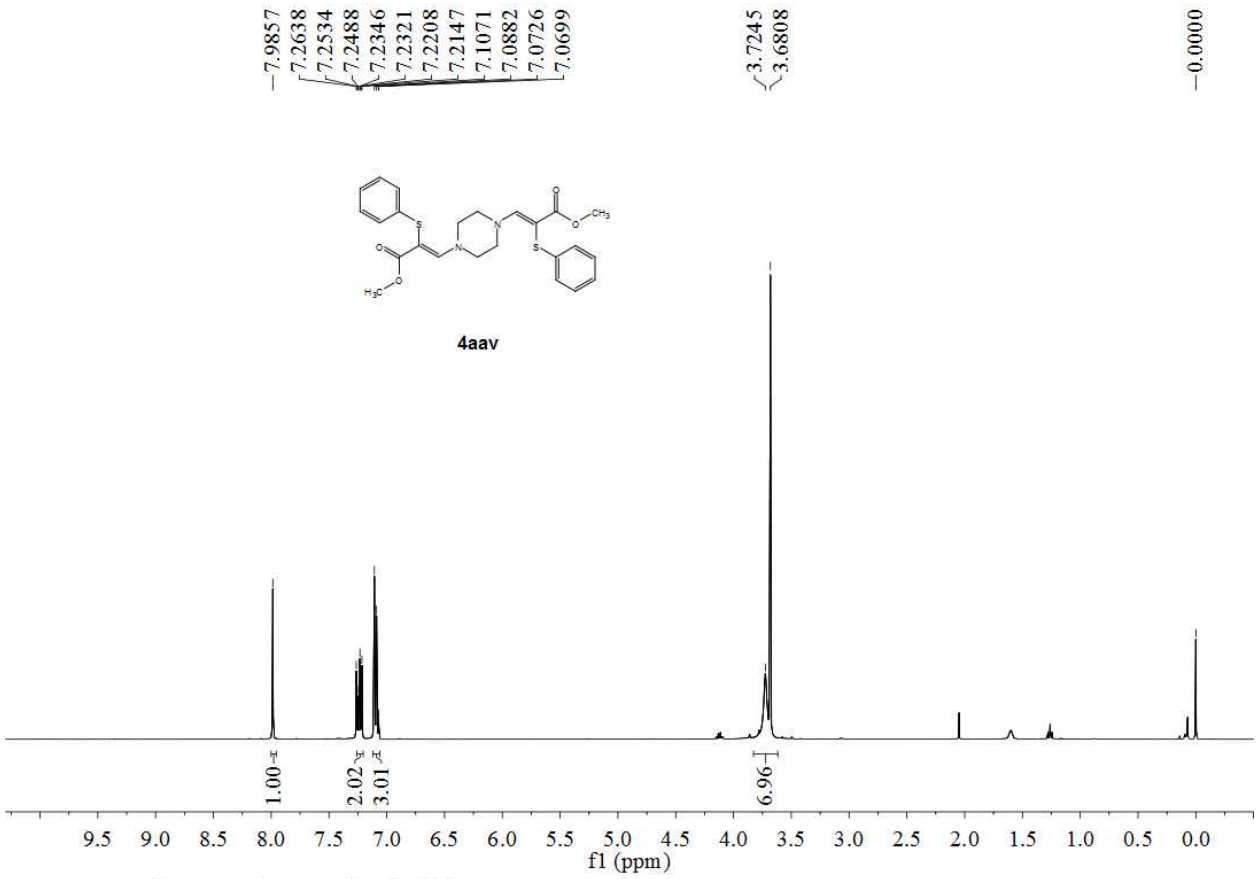
4aau
f1 (ppm)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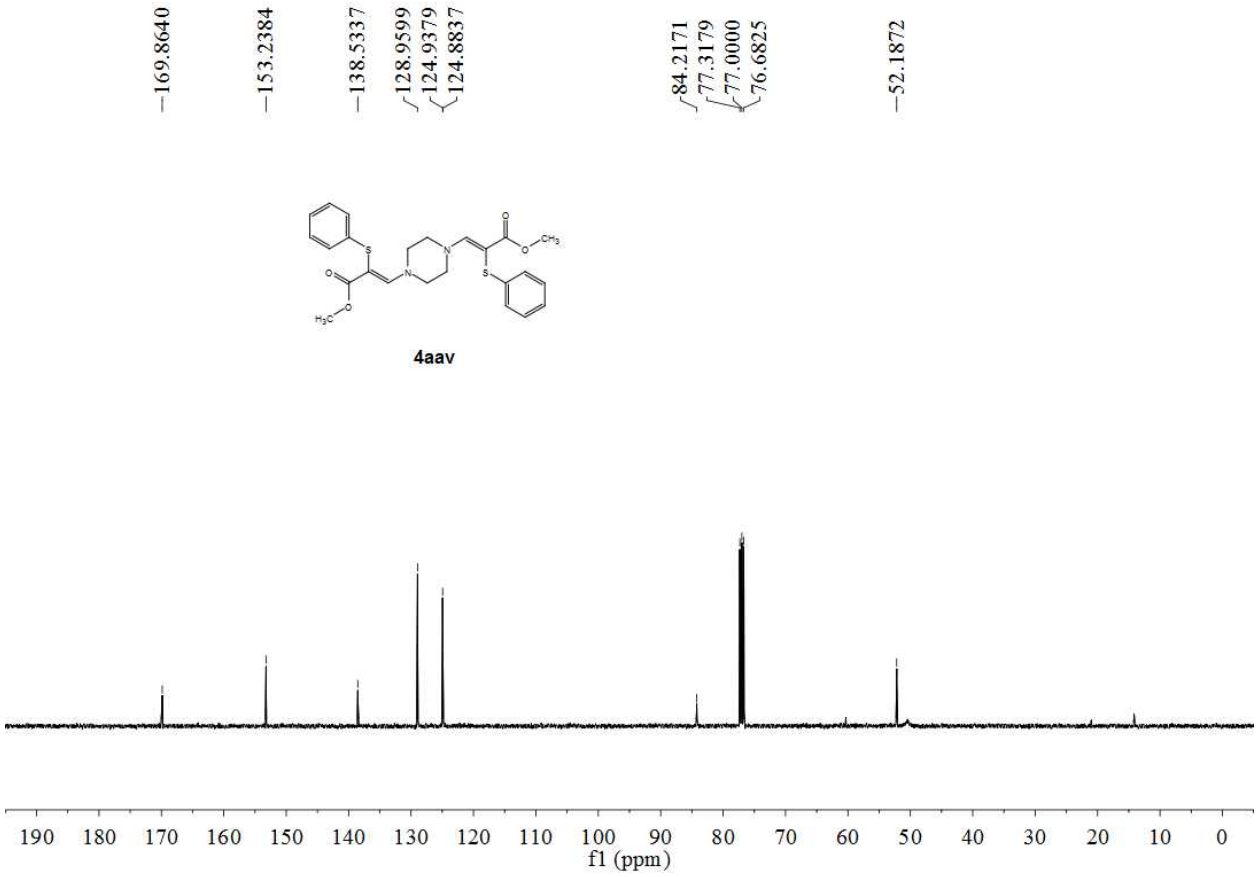
6.96
f1 (ppm)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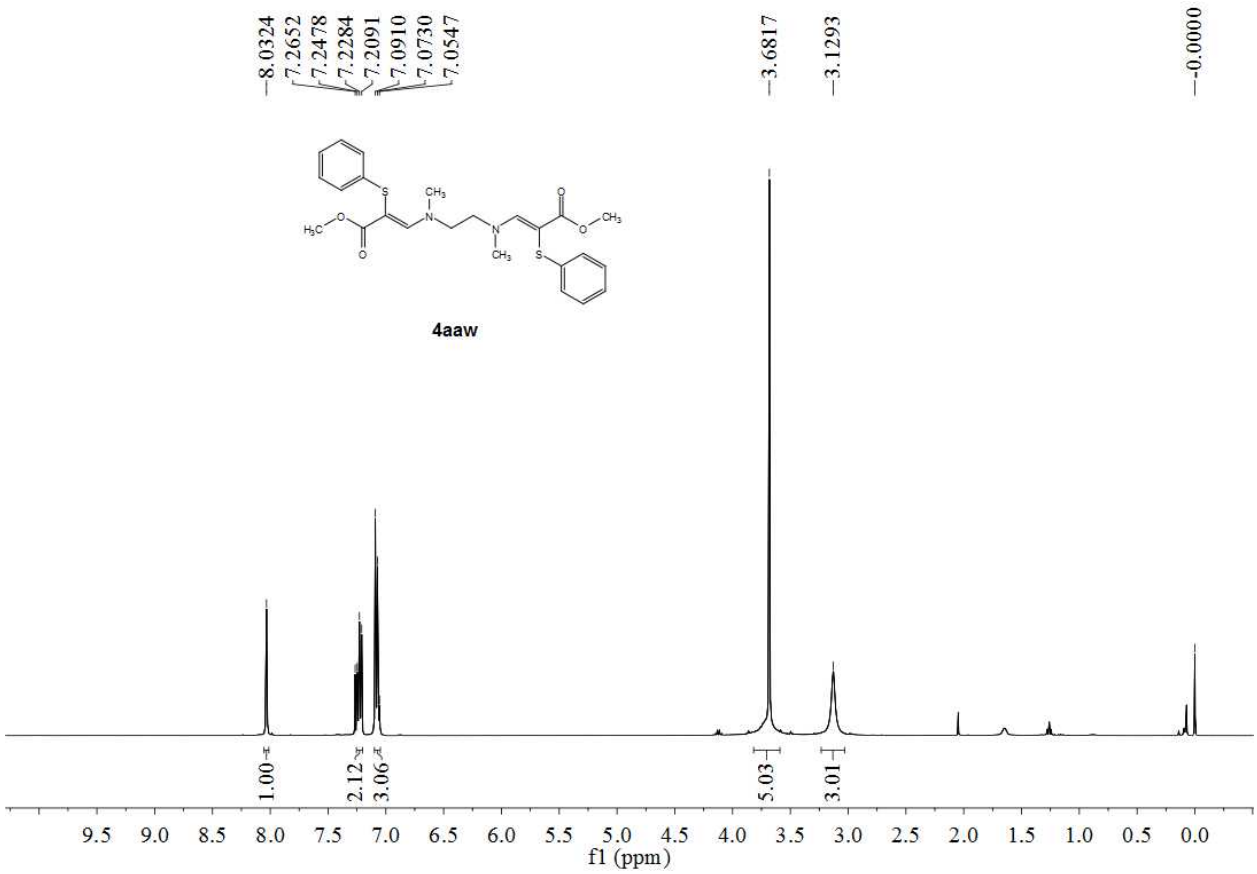
4aav
f1 (ppm)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1.00
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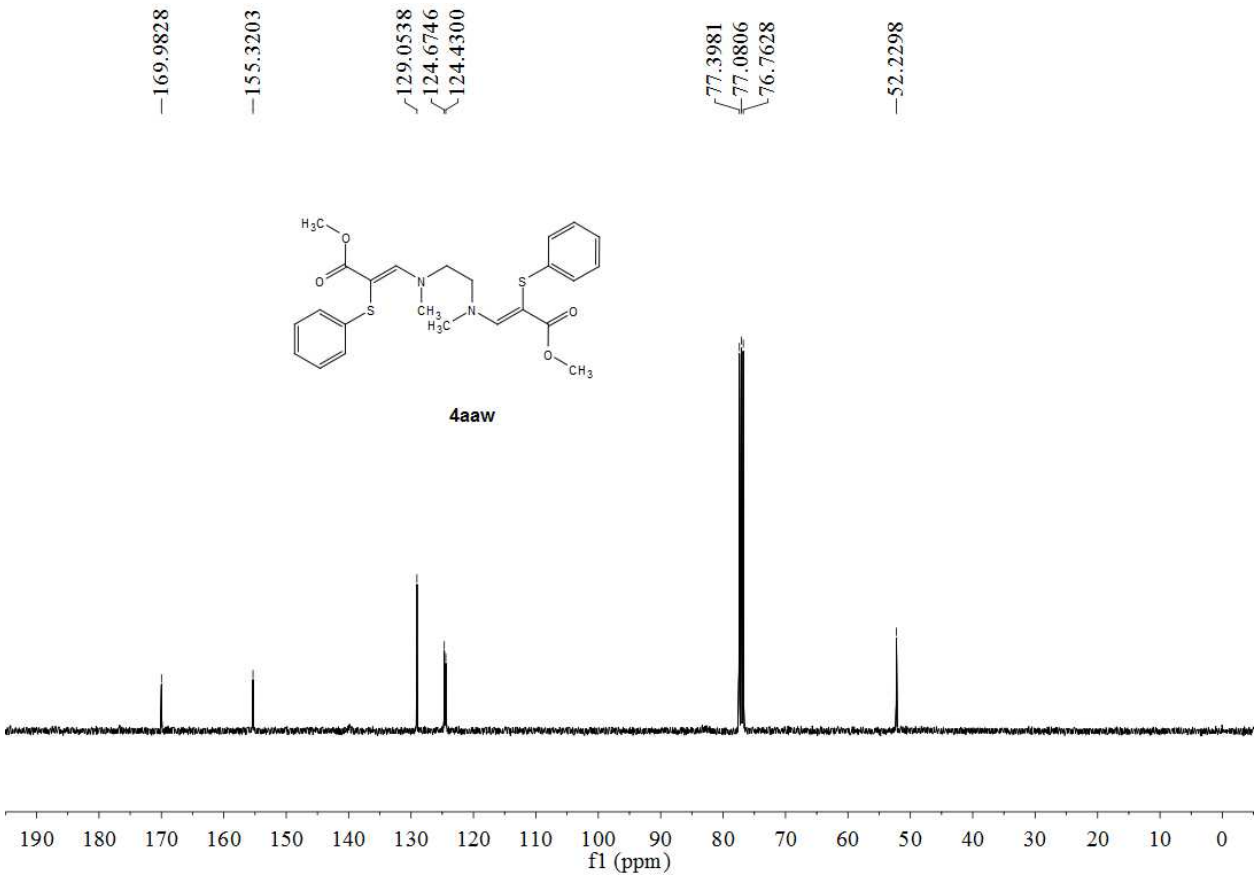
3.01
f1 (ppm)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4aaw
f1 (ppm)