Electronic Supplementary Information

Copper-Catalyzed Three-Component Cascade Reaction of Alkynes, Sulfonyl Azides and Simple Aldehydes/Ketones

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1. General Information

Unless otherwise noted, all reactions were carried out in oven-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 AV or 400 AV spectrometers. ^{19}F NMR spectra was recorded on a Bruker 500 AV. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and all combinations thereof can be explained by their integral parts. The high resolution mass spectra (HRMS) were recorded on a Thermo Scientific Exactive spectrometer or a Bruker APEX IV FTMS mass spectrometer.

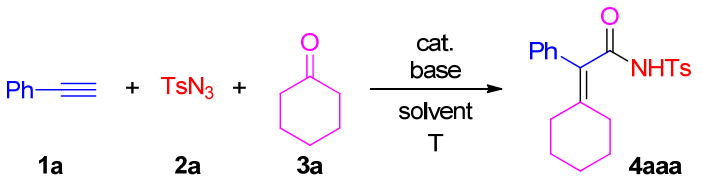
All the substrates are commercially available except *tert*-butyl 3-ethynyl-1*H*-indole-1-carboxylate **1g**,[1] 2-ethynylnaphthalene **1h**,[2] but-3-ynyl benzoate **1l**,[2] sulfonyl azides **2**,[3] 11-bromoundecanal **3m**,[4] (4*R*)-4-((10*S*,13*R*)-10,13-dimethyl-3,12-dioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanal **3n**,[5] 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **5**,[6] which are known compounds and synthesized according to reported literatures. Their spectral data are in agreement with the literature values.

2. Cu-catalyzed Three-Component Cascade Reaction of Alkynes, Sulfonyl Azides, and Simple Aldehydes/Ketones

2.1 Optimization of the Reaction Conditions

Initially, phenylacetylene **1a**, *p*-toluenesulfonyl azide **2a** and cyclohexanone **3a** were selected as the model substrates to screen the optimal reaction conditions (Table S1). Fortunately, **4aaa** was obtained in 74% NMR yield at the beginning (entry 1). After testing a series of solvent, DCE still proved to be the best (entries 2-7). The reaction proceeded a slightly better at room temperature but gave a drop in yield at a higher one (entries 8-9). Adjustments of the reaction concentrations and ratio of the substrates afforded the corresponding product in 85% NMR yield with 1:2:2 ratio of **1a**:**2a:3a** in 0.2 mL DCE (entries 10-12). Less amount of Me_2Zn led to a decrease of yield (entry 13). In addition, various bases were next scrutinized and the reaction showed specific to zinc reagents while Et_3N, used mostly in reported Cu-catalyzed multicomponent reactions, couldn't promote this transformation at all (entries 14-22). Halving the amount of the catalyst showed no obvious influence on the reaction outcome (entry 23). With no catalyst or with other metal catalyst such as $MnBr_2$, $FeBr_2$, $ZnBr_2$, the reaction could not occur (entries 24-29). However, different copper salts including both Cu(I) and Cu(II) ones could deliver product **4aaa** in varied yields smoothly (entries 30-34). At last, the product **4aaa** was obtained in 88% NMR yield and in 76% isolated yield with 5 mol% $Cu(NO_3)_2$ (entry 35).

Table S1 Screening for the optimal reaction conditions[a]



entry	cat.	base	solvent	T (^{o}C)	yield (%)[b]
1	$CuBr_2$	Me_2Zn[c]	DCE	60	74
2	$CuBr_2$	Me_2Zn[c]	Et_2O	60	68
3	$CuBr_2$	Me_2Zn[c]	1,4-dioxane	60	58

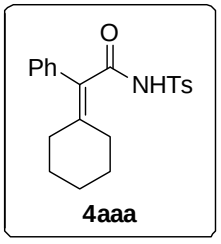
4	$CuBr_2$	Me_2Zn[c]	THF	60	20
5	$CuBr_2$	Me_2Zn[c]	toluene	60	24
6	$CuBr_2$	Me_2Zn[c]	CH_3CN	60	0
7	$CuBr_2$	Me_2Zn[c]	DMF	60	0
8	$CuBr_2$	Me_2Zn[c]	DCE	r.t	78
9	$CuBr_2$	Me_2Zn[c]	DCE	80	66
10	$CuBr_2$	Me_2Zn[c]	DCE[d]	r.t.	85
11	$CuBr_2$	Me_2Zn[c]	DCE[e]	r.t.	77
12[f]	$CuBr_2$	Me_2Zn[c]	DCE[d]	r.t.	85
13[f]	$CuBr_2$	Me_2Zn[c,g]	DCE[d]	r.t.	74
14[f]	$CuBr_2$	-[h]	DCE[d]	r.t.	0
15[f]	$CuBr_2$	Et_2Zn[i]	DCE[d]	r.t.	25
16[f]	$CuBr_2$	MeMgBr[j]	DCE[d]	r.t.	0
17[f]	$CuBr_2$	Me_3Al[k]	DCE[d]	r.t.	0
18[f]	$CuBr_2$	*n*-BuLi[l]	DCE[d]	r.t.	0
19[f]	$CuBr_2$	NaHMDS[m]	DCE[d]	r.t.	0
20[f]	$CuBr_2$	Et_3N	DCE[d]	r.t.	0
21[f]	$CuBr_2$	CsOAc	DCE[d]	r.t.	0
22[f]	$CuBr_2$	LiOH	DCE[d]	r.t.	0
23[f]	$CuBr_2$[n]	Me_2Zn[c]	DCE[d]	r.t.	82
24[f]	-[o]	Me_2Zn[c]	DCE[d]	r.t.	0
25[f]	$MnBr_2$[n]	Me_2Zn[c]	DCE[d]	r.t.	0
26[f]	$CoBr_2$[n]	Me_2Zn[c]	DCE[d]	r.t.	0
27[f]	$FeBr_2$[n]	Me_2Zn[c]	DCE[d]	r.t.	0
28[f]	$MgBr_2$[n]	Me_2Zn[c]	DCE[d]	r.t.	0
29[f]	$ZnBr_2$[n]	Me_2Zn[c]	DCE[d]	r.t.	0
30[f]	$Cu(OAc)_2$[n]	Me_2Zn[c]	DCE[d]	r.t.	80
31[f]	CuBr[n]	Me_2Zn[c]	DCE[d]	r.t.	70
32[f]	$CuSO_4$[n]	Me_2Zn[c]	DCE[d]	r.t.	30
33[f]	$CuCl_2 \cdot 2H_2O$[n]	Me_2Zn[c]	DCE[d]	r.t.	77
34[f]	$Cu(NO_3)_2 \cdot 3H_2O$[n]	Me_2Zn[c]	DCE[d]	r.t.	87
35[f]	*$Cu(NO_3)_2$*[n]	*Me_2Zn*[c]	*DCE*[d]	*r.t.*	*88 (76)*[p]

[a] Reaction conditions unless otherwise noted: **1a** (0.2 mmol), **2a** (0.8 mmol), **3a** (0.4 mmol), catalyst (0.02 mmol), base (0.3 mmol), solvent (0.5 mL), 60 °C, 6 h under N_2 atmosphere. [b] Yields determined by ^1H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. [c] 1.2 M in toluene. [d] 0.2 mL DCE. [e] 1.0 mL DCE. [f] **1a**/**2a**/**3a** = 1:2:2. [g] 0.2 mmol Me_2Zn. [h] No base. [i] 1.0 M in hexane. [j] 3.0 M in Et_2O. [k] 1.0 M in heptane. [l] 2.5 M in hexane. [m] 2 M in THF. [n] 0.01 mmol catalyst. [o] No catalyst. [p] Isolated yield on 0.5 mmol scale.

2.2 Experimental Details and Characterization of Products

To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg), and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aaa** in 76% yield.

2-cyclohexylidene-2-phenyl-*N*-tosylacetamide (4aaa)



4aaa

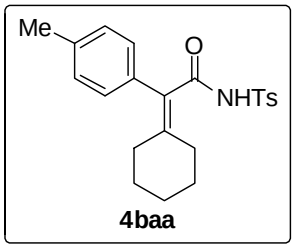
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aaa** in 76% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.31-7.28 (m, 5H), 7.07-7.03 (m, 2H), 2.47 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.01 (t, *J* = 6.0 Hz, 2H), 1.63-1.59 (m, 2H), 1.57-1.48 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9, 153.9, 144.8, 135.8, 135.6, 129.6, 129.4, 129.0, 128.3, 128.1, 127.6, 32.8, 32.3, 28.3, 28.2, 26.1, 21.7;

HRMS (ESI) Calculated for $C_{21}H_{23}O_3NS^+$ ($[M+H]^+$): 392.12909, found: 392.12839.

2-cyclohexylidene-2-p-tolyl-*N*-tosylacetamide (4baa)



4baa

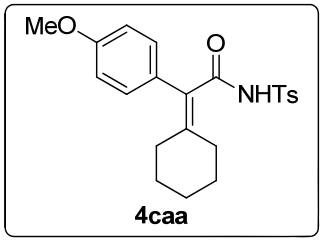
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (1.25 mL), 1-ethynyl-4-methylbenzene **1b** (0.5 mmol, 59.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4baa** in 65% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 5.6 Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 2.01 (t, *J* = 5.6 Hz, 2H), 1.63-1.60 (m, 2H), 1.54-1.48 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.8, 154.8, 144.8, 138.1, 135.7, 133.0, 129.8, 129.5, 129.4, 128.4, 127.3, 33.1, 32.2, 28.4, 28.3, 26.2, 21.7, 21.2;

HRMS (ESI) Calculated for $C_{22}H_{25}O_3NS^+$ ($[M+H]^+$): 406.14474, found: 406.14467.

2-cyclohexylidene-2-(4-methoxyphenyl)-*N*-tosylacetamide (4caa)



4caa

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (1.25 mL), 1-ethynyl-4-methoxylbenzene **1c** (0.5 mmol, 66.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column

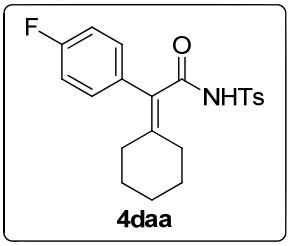
chromatography to provide the product **4caa** in 55% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86-7.83 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.81 (s,3H), 2.52 (t, *J* = 5.6 Hz, 2H), 2.44 (s, 3H), 2.02 (t, *J* = 5.6 Hz, 2H), 1.63-1.60 (m, 2H), 1.55-1.49 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9, 159.5, 154.9, 144.9, 135.7, 130.9, 129.5, 128.4, 128.1, 127.0, 114.6, 55.3, 33.1, 32.3, 28.4, 28.4, 26.3, 21.7;

HRMS (ESI) Calculated for $C_{22}H_{25}O_4NS^+$ ($[M+H]^+$): 422.13965, found: 422.13941.

2-cyclohexylidene-2-(4-fluorophenyl)-*N*-tosylacetamide (4daa)



4daa

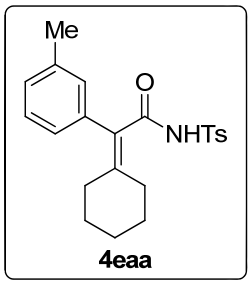
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), 1-ethynyl-4-fluorobenzene **1d** (0.5 mmol, 60.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4daa** in 51% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.06-7.01 (m, 2H), 7.00-6.94 (m, 2H), 2.44 (s, 3H), 2.40 (t, *J* = 6.0 Hz, 2H), 1.99 (t, *J* = 6.0 Hz, 2H), 1.61-1.56 (m, 2H), 1.54-1.48 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.1, 162.4 (d, $^1J_{C\text{-}F}$ = 246.5 Hz), 153.2, 145.1, 135.5, 131.6 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 131.4 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 129.5, 128.3, 126.8, 116.0 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 32.5, 32.4, 28.2, 28.2, 26.1, 21.7;

HRMS (ESI) Calculated for $C_{21}H_{22}O_3FNS^+$ ($[M+H]^+$): 410.11966, found: 410.11948.

2-cyclohexylidene-2-m-tolyl-*N*-tosylacetamide (4eaa)



4eaa

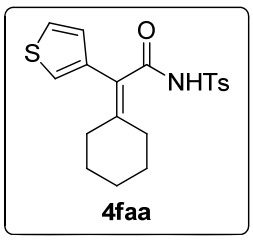
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (1.25 mL), 1-ethynyl-3-methylbenzene **1e** (0.5 mmol, 58.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4eaa** in 74% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.85-6.82 (m, 2H), 2.50 (t, *J* = 5.6 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H), 2.01 (t, *J* = 5.6 Hz, 2H), 1.63-1.61 (m, 2H), 1.55-1.48 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.8, 154.5, 144.8, 138.8, 135.9, 135.7, 130.2, 129.4, 129.0, 128.4, 127.6, 126.7, 33.0, 32.2, 28.4, 28.3, 26.2, 21.7, 21.4;

HRMS (ESI) Calculated for $C_{22}H_{25}O_3NS^+$ ($[M+H]^+$): 406.14474, found: 406.14438.

2-cyclohexylidene-2-(thiophen-3-yl)-*N*-tosylacetamide (4faa)



4faa

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), 3-ethynylthiophene **1f** (0.5 mmol, 54.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate

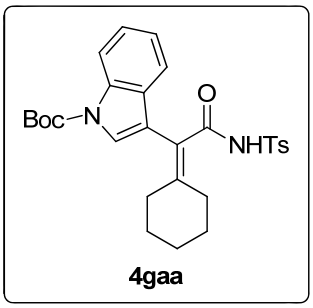
(20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4faa** in 71% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.16 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.01 (s, 1H), 6.80 (d, *J* = 4.8 Hz, 1H), 2.46-2.43 (m, 5H), 2.10-2.08 (m, 2H), 1.63-1.60 (m, 2H), 1.55-1.48 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.7, 154.7, 144.9, 135.7, 135.6, 129.5, 128.5, 128.3, 126.6, 124.7, 122.3, 32.8, 32.2, 28.2, 28.2, 26.1, 21.7;

HRMS (ESI) Calculated for $C_{19}H_{21}O_3NS_2^+$ ($[M+H]^+$): 398.08551, found: 398.08542.

3-(1-cyclohexylidene-2-(4-methylphenylsulfonamido)-2-oxoethyl)-1*H*-indole-1-carboxylate (4gaa)



4gaa

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), *tert*-butyl 3-ethynyl-1*H*-indole-1-carboxylate **1g** (0.5 mmol, 120.5 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4gaa** in 51% yield.

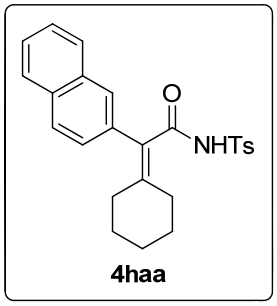
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13-8.09 (m, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.44 (s, 1H), 7.33-7.28 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 4.0 Hz, 2H), 2.66 (t, *J* = 5.6 Hz, 2H), 2.44 (s, 3H), 2.09 (t, *J* = 5.6 Hz, 2H), 1.68 (s, 11H), 1.57-1.55 (m, 2H), 1.50-1.48 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.3, 159.4, 149.4, 144.7, 135.4, 135.2, 129.5, 129.4,

128.4, 125.5, 125.0, 123.1, 119.4, 117.9, 115.5, 115.4, 84.4, 33.9, 32.2, 28.7, 28.5, 28.2, 26.2, 21.7;

HRMS (ESI) Calculated for $C_{28}H_{32}O_5N_2S^+$ ($[M+H]^+$): 531.19241, found: 531.19194.

2-cyclohexylidene-2-(naphthalen-2-yl)-*N*-tosylacetamide (4haa)



4haa

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), 2-ethynylnaphthalene **1h** (0.5 mmol, 76.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4haa** in 59% yield.

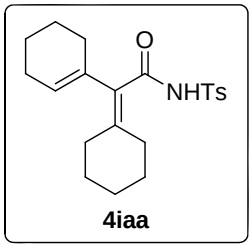
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (s, 1H), 7.80-7.74 (m, 4H), 7.69-6.66 (m, 1H), 7.50-7.43 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.14 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 2.49 (t, J = 6.0 Hz, 2H), 2.40 (s, 3H), 2.04 (t, J = 6.0 Hz, 2H), 1.64-1.62 (m, 2H), 1.54-1.48 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.0, 153.9, 144.8, 135.4, 133.3, 133.1, 132.7, 129.4, 128.8, 128.7, 128.3, 128.0, 127.7, 127.6, 127.2, 126.6, 126.5, 32.8, 32.4, 28.3, 28.3, 26.2, 21.7;

HRMS (ESI) Calculated for $C_{25}H_{25}O_3NS^+$ ($[M+H]^+$): 442.14474, found: 442.14468.

2-cyclohexenyl-2-cyclohexylidene-*N*-tosylacetamide (4iaa)

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), 1-ethynylcyclohex-1-ene



4iaa

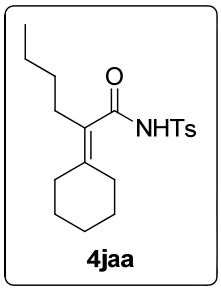
1i (0.5 mmol, 53.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4iaa** in 45% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.63 (s, 1H), 2.43-2.40 (m, 5H), 2.15-2.13 (m, 4H), 1.77-1.75 (m, 2H), 1.61-1.59 (m, 4H), 1.55-1.52 (m, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.4, 153.4, 144.8, 135.8, 135.3, 130.2, 129.5, 128.4, 33.0, 31.8, 29.1, 28.8, 28.4, 26.3, 25.4, 22.7, 21.7;

HRMS (ESI) Calculated for $C_{21}H_{27}O_3NS^+$ ($[M+H]^+$): 396.16039, found: 396.16010.

2-cyclohexylidene-*N*-tosylhexanamide (4jaa)



4jaa

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), hex-1-yne **1j** (0.5 mmol, 41.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4jaa** in 72% yield.

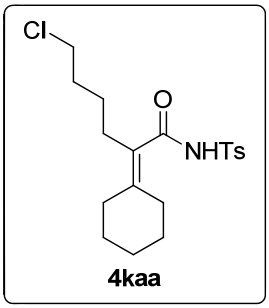
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 2.44 (s, 3H), 2.15-2.08 (m, 4H), 2.05-1.99 (m, 2H), 1.52-1.50 (m, 6H),

1.21-1.16 (m, 4H), 0.81-0.77 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.5, 145.0, 143.5, 135.8, 129.5, 128.4, 127.4, 32.7, 31.1, 30.0, 29.0, 28.0, 27.7, 26.3, 22.4, 21.7, 13.8;

HRMS (ESI) Calculated for $C_{19}H_{27}O_3NS^+$ ($[M+H]^+$): 372.16039, found: 372.16001.

6-chloro-2-cyclohexylidene-*N*-tosylhexanamide (4kaa)



4kaa

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (1.25 mL), 6-chlorohex-1-yne **1k** (0.5 mmol, 58.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4kaa** in 53% yield.

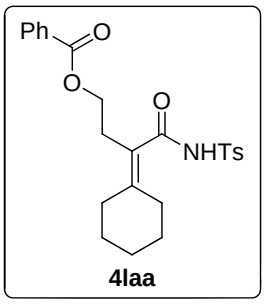
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.71 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 3.41 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 2.17 (t, *J* = 8.0 Hz, 2H), 2.10-2.04 (m, 4H), 1.69-1.61 (m, 2H), 1.52-1.51 (m, 6H), 1.41-1.32 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.3, 145.2, 144.3, 135.6, 129.6, 128.4, 126.6, 44.7, 32.7, 31.9, 30.1, 28.4, 28.0, 27.7, 26.3, 26.1, 21.7;

HRMS (ESI) Calculated for $C_{19}H_{26}O_3NClNaS^+$ ($[M+H]^+$): 406.12141, found: 406.12122.

3-cyclohexylidene-4-(4-methylphenylsulfonamido)-4-oxobutyl benzoate (4laa)

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (1.25 mL), but-3-ynyl benzoate **1l**



4laa

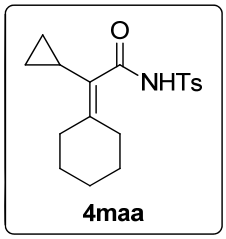
(0.5 mmol, 87.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4laa** in 57% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.46 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.31 (t, *J* = 6.0 Hz, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 2.41 (s, 3H), 2.08-2.02 (m, 4H), 1.42-1.37 (m, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 167.4, 146.6, 144.9, 135.9, 133.4, 129.8, 129.7, 129.5, 128.5, 128.4, 122.9, 63.4, 32.6, 30.1, 29.0, 27.8, 27.4, 26.0, 21.7;

HRMS (ESI) Calculated for $C_{24}H_{27}O_5NS^+$ ($[M+H]^+$): 464.15021, found: 464.14988.

2-cyclohexylidene-2-cyclopropyl-*N*-tosylacetamide (4maa)



4maa

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), ethynylcyclopropane **1m** (0.5 mmol, 33.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4maa** in 69% yield.

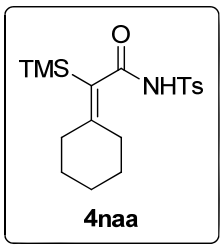
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.83 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0

Hz, 2H), 2.44 (s, 3H), 2.32-2.28 (m, 2H), 2.16-2.13 (m, 2H), 1.53-1.44 (m, 7H), 0.72-0.66 (m, 2H), 0.25-0.20 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.6, 149.9, 145.0, 135.8, 129.5, 128.4, 126.6, 32.3, 30.9, 28.0, 27.5, 26.3, 21.7, 9.5, 6.9;

HRMS (ESI) Calculated for $C_{18}H_{23}O_3NS^+$ ($[M+H]^+$): 356.12909, found: 356.12887.

2-cyclohexylidene-*N*-tosyl-2-(trimethylsilyl)acetamide (4naa)



4naa

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), ethynyltrimethylsilane **1n** (0.5 mmol, 49.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4naa** in 55% yield.

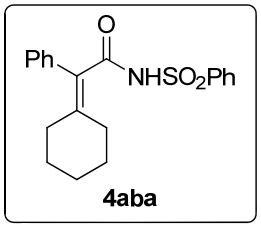
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.78 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.53 (s, 3H), 2.25-2.23 (m, 2H), 2.08-2.06 (m, 2H), 1.64-1.61 (m, 6H), 0.15 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7, 158.5, 144.9, 135.9, 129.8, 129.4, 128.5, 34.7, 34.5, 28.3, 28.1, 25.9, 21.7, -0.23;

HRMS (ESI) Calculated for $C_{18}H_{27}O_3NSiNaS^+$ ($[M+H]^+$): 388.13731, found: 388.13690.

2-cyclohexylidene-2-phenyl-*N*-(phenylsulfonyl)acetamide (4aba)

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added



4aba

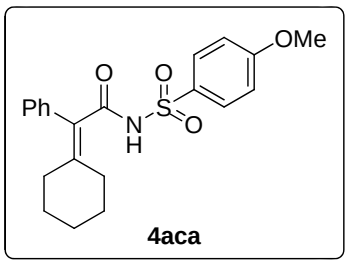
$Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (1.25 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), benzenesulfonyl azide **2b** (1.0 mmol, 183.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aba** in 62% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (s, 1H), 7.97-9.94 (m, 2H), 7.65-7.61 (m, 1H), 7.53-7.49 (m, 2H), 7.34-7.28 (m, 3H), 7.06-7.02 (m, 2H), 2.47 (t, *J* = 6.0 Hz, 2H), 2.01 (d, *J* = 6.0 Hz, 2H), 1.62-1.59 (m, 2H), 1.54-1.48 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.8, 154.4, 138.5, 135.8, 133.9, 129.6, 129.1, 128.9, 128.3, 128.2, 127.5, 32.8, 32.3, 28.3, 28.3, 26.1;

HRMS (ESI) Calculated for $C_{20}H_{21}O_3NS^+$ ($[M+H]^+$): 378.11344, found: 378.11327.

2-cyclohexylidene-*N*-(4-methoxyphenylsulfonyl)-2-phenylacetamide (4aca)



4aca

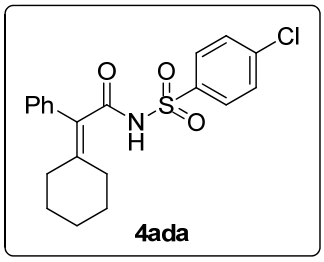
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), 4-methoxyl benzenesulfonyl azide **2c** (1.0 mmol, 213.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aca** in 66% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.34-7.28 (m, 3H), 7.07-7.04 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.48 (t, *J* = 6.0 Hz, 2H), 2.01 (t, *J* = 6.0 Hz, 2H), 1.63-1.60 (m, 2H), 1.55-1.48 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9, 163.8, 153.8, 135.8, 130.7, 129.9, 129.6, 129.0, 128.1, 127.6, 114.0, 55.7, 32.7, 32.3, 28.3, 28.2, 26.1;

HRMS (ESI) Calculated for $C_{21}H_{23}O_4NS^+$ ($[M+H]^+$): 408.12400, found: 408.12379.

***N*-(4-chlorophenylsulfonyl)-2-cyclohexylidene-2-phenylacetamide (4ada)**



4ada

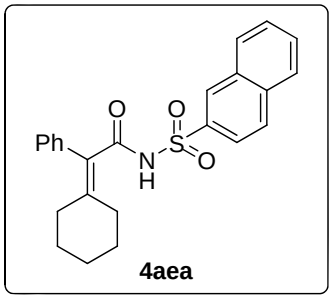
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (1.25 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), 4-chlorobenzenesulfonyl azide **2d** (1.0 mmol, 217.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4ada** in 53% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92-7.87 (m, 3H), 7.51-7.46 (m, 2H), 7.37-7.31 (m, 3H), 7.07-7.03(m, 2H), 2.54 (t, *J* = 5.6 Hz, 2H), 2.01 (t, *J* = 5.6 Hz, 2H), 1.65-1.61 (m, 2H), 1.56-1.49 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.6, 155.9, 140.5, 137.0,135.9, 129.9, 129.7, 129.3, 129.2, 128.4, 127.2, 33.2, 32.3, 28.4, 28.4, 26.2;

HRMS (ESI) Calculated for $C_{20}H_{20}O_3NClNaS^+$ ($[M+H]^+$): 412.07446, found: 412.07416.

2-cyclohexylidene-*N*-(naphthalen-2-ylsulfonyl)-2-phenylacetamide (4aea)



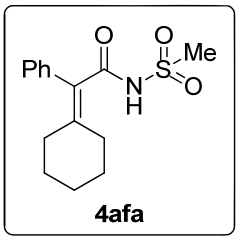
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (1.25 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), naphthalene-2-sulfonyl azide **2e** (1.0 mmol, 233.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aea** in 62% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (s, 1H), 8.12 (s, 1H), 7.97-7.84 (m, 4H), 7.65-7.58 (m, 2H), 7.28-7.25 (m, 3H), 7.05-7.02 (m, 2H), 2.47 (t, *J* = 6.0 Hz, 2H), 1.98 (t, *J* = 5.6 Hz, 2H), 1.59-1.57 (m, 2H), 1.51-1.46 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9, 154.5, 135.8, 135.4, 135.3, 131.9, 130.5, 129.6, 129.6, 129.4, 129.1, 129.1, 128.2, 127.9, 127.6, 127.5, 122.7, 32.8, 32.3, 28.3, 28.3, 26.1;

HRMS (ESI) Calculated for $C_{24}H_{23}O_3NS^+$ ($[M+H]^+$): 428.12909, found: 428.14468.

2-cyclohexylidene-*N*-(methylsulfonyl)-2-phenylacetamide (4afa)



Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (1.25 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), methanesulfonyl azide **2f** (1.0 mmol, 120.0 mg), cyclohexanone **3a** (1.0 mmol, 98.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the

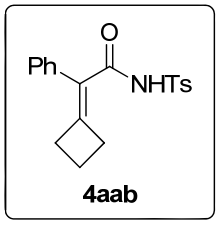
product **4afa** in 45% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (s, 1H), 7.43-7.33 (m, 3H), 7.21-7.18 (m, 2H), 3.25 (s, 3H), 2.72 (t, *J* = 6.0 Hz, 2H), 2.05 (t, *J* = 6.0 Hz, 2H), 1.77-1.70 (m, 2H), 1.63-1.52 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 156.3, 136.1, 129.8, 129.4, 128.5, 127.2, 41.5, 33.4, 32.4, 28.5, 28.5, 26.3;

HRMS (ESI) Calculated for $C_{15}H_{19}O_3NS^+$ ($[M+H]^+$): 316.09779, found: 316.09764.

2-cyclobutylidene-2-phenyl-*N*-tosylacetamide (4aab)



4aab

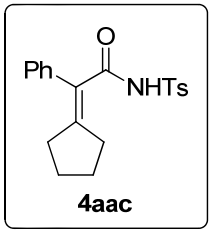
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclobutanone **3b** (1.0 mmol, 70.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a sh\ort pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aab** in 40% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.74 (s, 1H), 7.42-7.31 (m, 5H), 7.13 (d, *J* = 7.6 Hz, 2H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 2.03 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.1, 162.9, 144.9, 135.9, 134.0, 129.6, 129.4, 129.3, 128.5, 128.5, 125.6, 34.3, 32.5, 21.7, 17.4;

HRMS (ESI) Calculated for $C_{19}H_{19}O_3NS^+$ ($[M+H]^+$): 364.09779, found: 364.09759.

2-cyclopentylidene-2-phenyl-*N*-tosylacetamide (4aac)



4aac

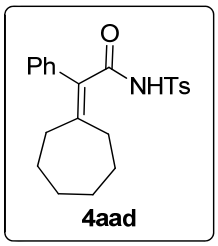
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclopentanone **3c** (1.0 mmol, 84.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aac** in 73% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.60 (s, 1H), 7.44-7.35 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.14-7.11 (m, 2H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.07 (t, *J* = 7.2 Hz, 2H), 1.75-1.67 (m, 2H), 1.56-1.49 (m,2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 163.4, 144.7, 137.0, 136.0, 129.7, 129.5, 129.4, 128.6, 128.4, 124.9, 36.0, 34.4, 26.8, 25.5, 21.7;

HRMS (ESI) Calculated for $C_{20}H_{21}O_3NS^+$ ($[M+H]^+$): 378.11344, found: 378.11294.

2-cycloheptylidene-2-phenyl-*N*-tosylacetamide (4aad)



4aad

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cycloheptanone **3d** (1.0 mmol, 112.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aad** in 73% yield.

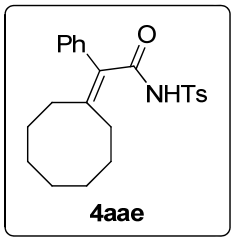
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 1H), 7.38-7.28 (m,

5H), 7.08 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2H), 2.67 (t, J = 6.0 Hz, 2H), 2.42 (s, 3H), 2.11-2.08 (m, 2H), 1.69-1.62 (m, 2H), 1.51-1.47 (m, 2H), 1.45-1.43 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.9, 158.8, 144.7, 136.6, 135.8, 129.6, 129.4, 129.3, 129.2, 128.3, 128.3, 34.6, 33.6, 29.3, 28.6, 27.2, 26.9, 21.7;

HRMS(ESI) Calculated for $C_{22}H_{25}O_3NS^+$ ($[M+H]^+$): 406.14474, found: 406.14429.

2-cyclooctylidene-2-phenyl-*N*-tosylacetamide (4aae)



4aae

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclooctanone **3e** (1.0 mmol, 126.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aae** in 64% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, J = 8.0 Hz, 2H), 7.68(s, 1H), 7.41-7.34 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 2.65 (t, J = 6.0 Hz, 2H), 2.42 (s, 3H), 2.04 (t, J = 6.0 Hz, 2H), 1.79-1.73 (m, 2H), 1.51-1.37 (m, 8H);

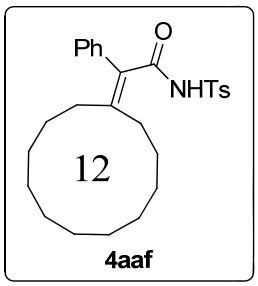
^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.3, 161.6, 144.7, 137.1, 135.9, 129.5, 129.4, 128.3, 128.3, 128.2, 35.0, 31.9, 28.6, 27.5, 26.1, 25.9, 23.9, 21.7;

HRMS (ESI) Calculated for $C_{23}H_{27}O_3NS^+$ ($[M+H]^+$): 420.16039, found: 420.15991.

2-cyclododecylidene-2-phenyl-*N*-tosylacetamide (4aaf)

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), cyclododecanone

3f (1.0 mmol, 182.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aaf** in 37% yield.



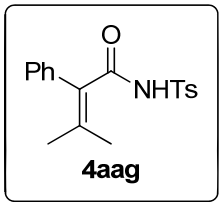
4aaf

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.61(s, 1H), 7.37-7.34 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.08-7.05 (m, 2H), 2.44 (s, 3H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.87 (t, *J* = 7.6 Hz, 2H), 1.58-1.56 (m, 2H), 1.46-1.31 (m, 16H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.1, 156.9, 144.9, 136.6, 135.8, 130.9, 129.6, 129.5, 129.3, 128.5, 128.5, 29.9, 28.8, 26.4, 26.1, 24.2, 24.0, 22.6, 22.5, 22.0, 21.9, 21.8;

HRMS (ESI) Calculated for $C_{27}H_{36}O_3NS^+$ ($[M+H]^+$): 454.24104, found: 454.24100.

3-methyl-2-phenyl-*N*-tosylbut-2-enamide (4aag)



4aag

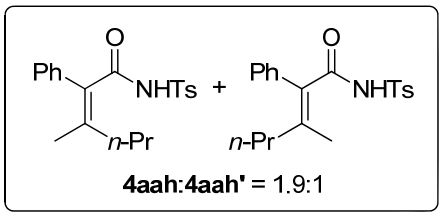
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), acetone **3g** (1.0 mmol, 58.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aag** in 65% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.83 (s, 1H), 7.37-7.29 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 2.08 (s, 3H), 1.63 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.1, 149.8, 144.8, 136.4, 135.7, 129.7, 129.5, 129.3, 128.4, 24.2, 22.7, 21.7;

HRMS(ESI) Calculated for $C_{18}H_{19}O_3NS^+$ ($[M+H]^+$): 352.09779, found: 352.09720.

(*Z*)-3-methyl-2-phenyl-*N*-tosylhept-2-enamide (4aah) and (*E*)-3-methyl-2-phenyl-*N*-tosylhept-2-enamide (4aah')



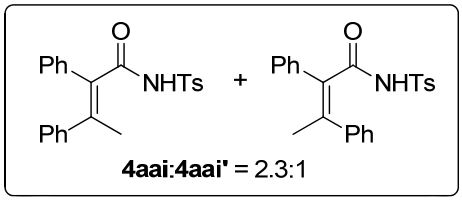
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), pentan-2-one **3h** (1.0 mmol, 86.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the products **4aah** and **4aah'** as two stereoisomers in 52% yield with the ratio being 1.9:1.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91-7.84 (m, 3H), 7.37-7.29 (m, 5H), 7.07 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 2.32 (t, *J* = 7.6 Hz, 1.35H), 2.06 (s, 1.07H), 1.86 (t, *J* = 7.6 Hz, 0.75H), 1.61 (s, 1.98H), 1.51-1.41 (m, 1.44H), 1.40-1.29 (m, 0.80H), 0.85 (t, *J* = 7.2 Hz, 2.07H), 0.71 (t, *J* = 7.2 Hz, 1.11H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.2, 165.1, 153.8, 151.4, 144.8, 136.4, 136.3, 135.7, 130.4, 129.7, 129.6, 129.5, 129.4, 129.3, 129.1, 128.4, 128.3, 128.2, 39.0, 37.5, 21.7, 21.5, 21.2, 21.0, 20.2, 14.0, 13.9;

HRMS (ESI) Calculated for $C_{20}H_{23}O_3NS^+$ ($[M+H]^+$): 380.12909, found: 380.12877.

(*E*)-2,3-diphenyl-*N*-tosylbut-2-enamide (4aai)



Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), acetophenone **3i** (1.0 mmol, 120.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). Detection of the reaction mixture by ^{1}H NMR analysis showed that **4aai** and **4aai'** were formed as two stereoisomers of 2.3:1 ratio. The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aai** in 43% isolated yield.

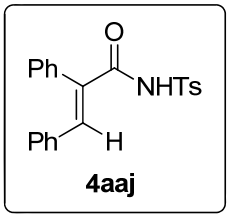
Spectrogram of *E*-configured product **4aai**:

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.74 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.16-7.10 (m, 6H), 7.94-7.90 (m, 2H), 6.82 (d, *J* = 6.8 Hz, 2H), 2.48 (s, 3H), 2.36 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.1, 149.8, 145.2, 141.9, 136.0, 135.7, 131.5, 130.4, 129.7, 128.9, 128.7, 128.3, 128.2, 127.6, 23.4, 21.9;

HRMS (ESI) Calculated for $C_{23}H_{21}O_3NS^+$ ($[M+H]^+$): 414.11344, found: 414.11286.

(*E*)-2,3-diphenyl-*N*-tosylacrylamide (4aaj)



Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), benzaldehyde **3j** (1.0 mmol, 106.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and

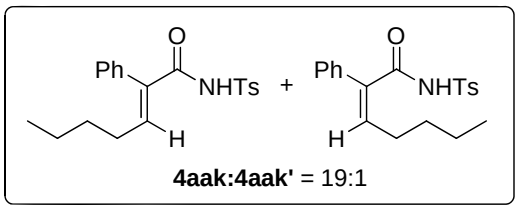
filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aaj** in 47% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.88 (s, 1H), 7.81 (s, 1H), 7.46 (s, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.21-7.17 (m, 3H), 7.11 (t, *J* = 7.2 Hz, 2H), 6.92 (t, *J* = 8.0 Hz, 2H), 2.43 (s. 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.2, 145.2, 141.3, 135.6, 134.2, 133.9, 131.8, 130.8, 130.3, 129.8, 129.8, 129.6, 129.6, 128.7, 128.4, 21.8;

HRMS (ESI) Calculated for $C_{22}H_{19}O_3NS^+$ ($[M+H]^+$): 400.09779, found: 400.09715.

(*E*)-2-phenyl-*N*-tosylhept-2-enamide (4aak)



Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), pentanal **3k** (1.0 mmol, 86.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). Detection of the reaction mixture by GC-MS showed that **4aak** and **4aak'** were formed as two stereoisomers of 19:1 ratio. The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aak** in 68% yield.

Spectrogram of *E*-configured product **4aak**:

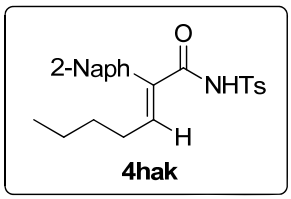
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.73 (s, 1H), 7.47-7.41 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 6.8 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 2.44 (s, 3H), 1.95 (q, *J* = 7.2 Hz, 2H), 1.36-1.28 (m, 2H), 1.26-1.15 (m, 2H), 0.78 (t, *J* =

7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.6, 147.0, 145.1, 135.7, 133.7, 133.7, 129.8, 129.6, 129.6, 129.1, 128.7, 30.7, 29.4, 22.3, 21.8, 13.8;

HRMS (ESI) Calculated for $C_{20}H_{23}O_3NS^+$ ($[M+H]^+$): 380.12909, found: 380.12881.

(*E*)-2-(naphthalen-2-yl)-*N*-tosylhept-2-enamide (4hak)



4hak

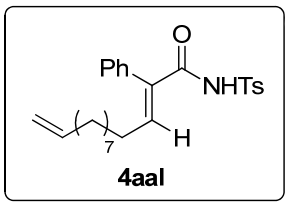
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.05 mmol, 10.0 mol%, 9.4 mg), DCE (0.5 mL), 2-ethynylnaphthalene **1h** (0.5 mmol, 76.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), pentanal **3k** (1.0 mmol, 86.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4hak** in 66% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (s, 1H), 7.91-7.79 (m, 5H), 7.60 (s, 1H), 7.54-7.50 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.18 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 2.41 (s, 3H), 1.97 (q, J = 7.6 Hz, 2H), 1.36-1.26 (m, 2H), 1.22-1.13 (m, 2H), 0.75 (t, J = 7.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 147.0, 145.0, 135.6, 133.8, 133.3, 133.1, 131.0, 129.5, 129.3, 129.2, 128.6, 128.1, 127.9, 127.0, 126.9, 126.9, 30.6, 29.4, 22.2, 21.7, 13.7;

HRMS (ESI) Calculated for $C_{24}H_{26}O_3NS^+$ ($[M+H]^+$): 408.16279, found: 408.16268.

(*E*)-2-phenyl-*N*-tosyltrideca-2,12-dienamide (4aal)



4aal

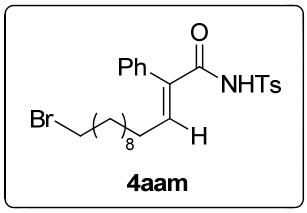
Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), undec-10-enal **3l** (1.0 mmol, 168.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aal** in 65% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, J = 8.4 Hz, 2H), 7.68 (s, 1H), 7.46-7.42 (m, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.12 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H), 7.08 (d, J = 8.0 Hz, 1H), 5.84-5.73 (m, 1H), 4.97 (dq, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H), 4.94-4.90 (m, 1H), 2.44 (s, 3H), 2.01 (q, J = 6.8 Hz, 2H), 1.94 (d, J = 7.6 Hz, 2H), 1.35-1.29 (m, 5H), 1.21-1.15 (m, 7H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.6, 147.2, 145.2, 139.3, 135.7, 133.7, 129.8, 129.6, 129.6, 129.1, 128.8, 114.3, 33.9, 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 28.6, 21.8;

HRMS (ESI) Calculated for $C_{26}H_{33}O_3NS^+$ ($[M+H]^+$): 462.20734, found: 462.20715.

(*E*)-13-bromo-2-phenyl-*N*-tosyltridec-2-enamide (4aam)



4aam

Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (0.5 mL), phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), 11-bromoundecanal **3m** (1.0 mmol, 248.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl

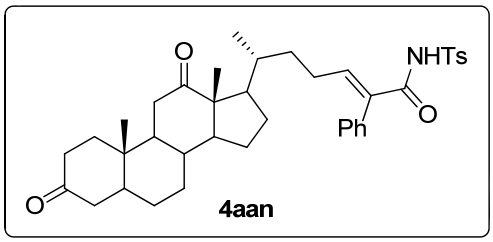
acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aam** in 75% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.78 (br, 1H), 7.46-7.39 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 3.38 (t, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 1.94 (q, *J* = 7.6 Hz, 2H), 1.82 (m, 2H), 1.43-1.36 (m, 2H), 1.35-1.31 (m, 2H), 1.27-1.15 (m, 10H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.5, 146.8, 145.0, 135.6, 133.8, 133.6, 129.7, 129.5, 129.4, 129.0, 128.6, 34.0, 32.8, 29.5, 29.3, 29.3, 29.2, 29.1, 28.7, 28.5, 28.1, 21.7;

HRMS (ESI) Calculated for $C_{26}H_{34}O_3BrNS^+$ ($[M+H]^+$): 542.13350, found: 542.13350.

(6*R*,*E*)-6-((10*S*,13*R*)-10,13-dimethyl-3,12-dioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-2-phenyl-*N*-tosylhept-2-enamide (4aan)



Following a general procedure: To a 25 ml oven-dried Schlenk tube was added $Cu(NO_3)_2$ (0.025 mmol, 5.0 mol%, 4.7 mg), DCE (1.25 mL), , phenylacetylene **1a** (0.5 mmol, 51.0 mg), *p*-toluenesulfonyl azide **2a** (1.0 mmol, 197.0 mg), (4*R*)-4-((10*S*,13*R*)-10,13-dimethyl-3,12-dioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanal **3n** (1.0 mmol, 372.0 mg) and Me_2Zn (0.75 mmol, 1.2 M in toluene, 0.625 mL) sequentially under nitrogen. The tube was sealed and stirred at room temperature for 6 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **4aan** in 50% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.84 (s, 1H), 7.47-7.40 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, J_1 = 7.65 Hz, J_2 = 1.6 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 2.61-2.53 (m, 2H), 2.44 (s, 3H), 2.36-2.27 (m, 1H), 2.16 (d, *J* = 14.4 Hz,

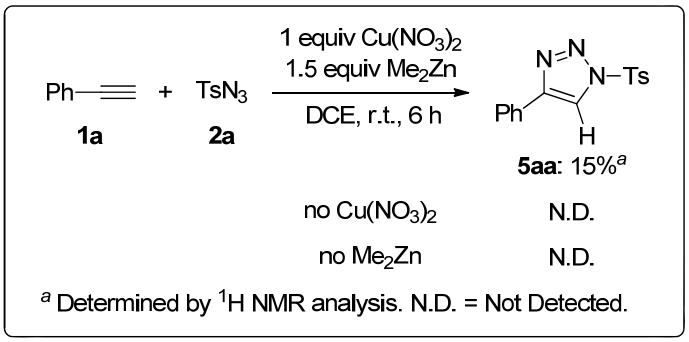
1H), 2.08-1.99 (m, 3H), 1.95-1.82 (m, 8H), 1.79-1.66 (m, 2H), 1.59 (d, *J* = 12.0 Hz, 1H), 1.49-1.27 (m, 5H), 1.18-1.09 (m, 6H), 0.99 (s, 3H), 0.66 (d, *J* = 6.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 214.2, 212.2, 163.6, 147.0, 145.0, 135.6, 133.7, 133.6, 129.7, 129.6, 129.5, 129.0, 128.6, 58.5, 57.6, 46.5, 44.3, 43.7, 42.1, 38.4, 36.9, 36.8, 35.7, 35.6, 35.4, 34.2, 27.5, 26.6, 26.6, 25.5, 24.3, 22.1, 21.7, 18.5, 11.8;

HRMS (ESI) Calculated for $C_{39}H_{49}O_5NS^+$ ($[M+H]^+$): 666.32237, found: 666.32208.

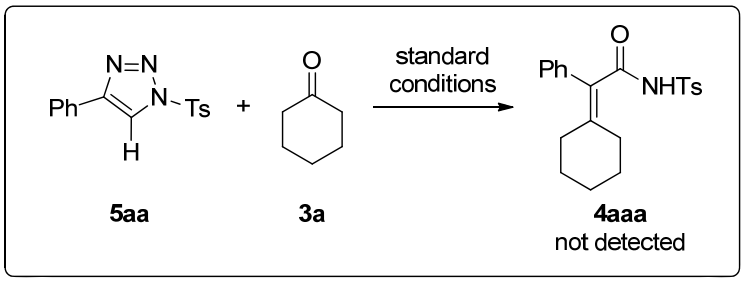
3. Mechanism Studies

To elucidate the possible reaction mechanism, a series of stoichiometric experiements was conducted. First, With either $Cu(NO_3)_2$ or Me_2Zn, the reaction of phenylacetylene **1a**, *p*-toluenesulfonyl azide **2a** couldn't take place. When $Cu(NO_3)_2$ and Me_2Zn were used together, 1-sulfonyltriazole **5aa** was obtained in 15% NMR yield after work up.



Experimental procedure:

$Cu(NO_3)_2$ (0.2 mmol, 37.5 mg) was added into an oven-dried reaction vessel with Teflon screw cap under a nitrogen atmosphere. DCE (0.2 mL), phenylacetylene **1a** (0.2 mmol, 20.4 mg), *p*-toluenesulfonyl azide **2a** (0.4 mmol, 78.8 mg) and Me_2Zn (0.3 mmol, 1.2 M in toluene, 0.25 mL) were then injected into the reaction tube. The reaction mixture was stirred at room temperature for 6 h. After the completion, the mixture was diluted with ethyl acetate (20 mL) and filtered through a short pad of silica gel. The solvent was removed by rotary evaporation and the residue was detected by crude ^1H NMR and GC analysis.



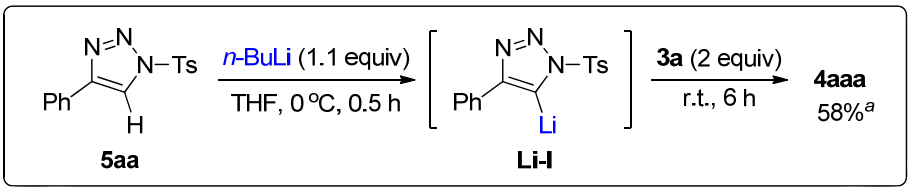
Next, the reaction of cyclohexanone **3a** and 1-sulfonyltriazole **5aa** was carried out under the standard conditions. However, no expected three-component product **4aaa**

was detected, which indicated 1-sulfonyltriazole **5aa** was not a reaction intermediate in the three-component reaction.

Experimental procedure:

$Cu(NO_3)_2$ (0.01 mmol, 1.9 mg) and 1-sulfonyltriazole **5aa** (0.2 mmol, 59.8 mg) was added into an oven-dried reaction vessel with Teflon screw cap under a nitrogen atmosphere. DCE (0.2 mL), cyclohexanone **3a** (0.4 mmol, 39.2 mg) and Me_2Zn (0.3 mmol, 1.2 M in toluene, 0.25 mL) were then injected into the reaction tube. The reaction mixture was stirred at room temperature for 6 h. After the completion, the mixture was diluted with ethyl acetate (20 mL) and filtered through a short pad of silica gel. The solvent was removed by rotary evaporation and the residue was detected by crude ^{1}H NMR and GC analysis.

Next, we hypothesized a reactive 5-metalated-1-sulfonyltriazole intermediate must be involved. When 1-sulfonyltriazole **5aa** was treated with *n*-BuLi, the product **4aaa** was obtained in 58% NMR yield.[7]

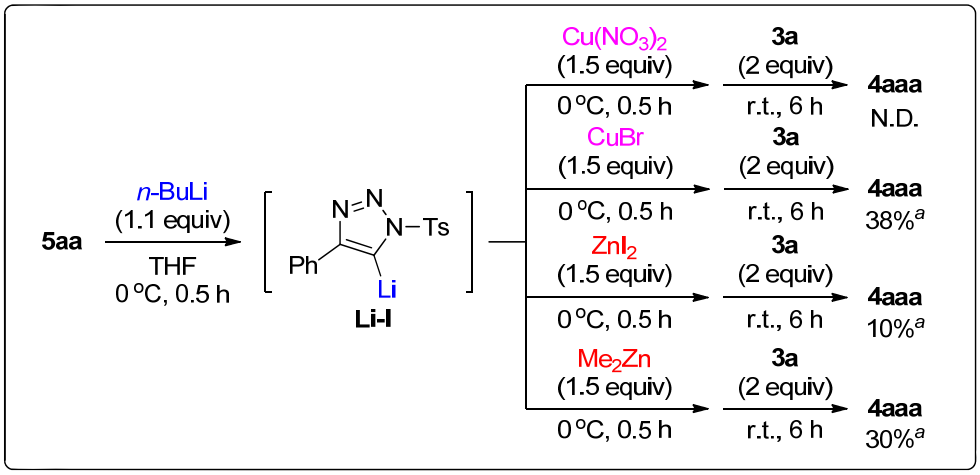


Experimental procedure:

To a stirred solution of 1-sulfonyltriazole **5aa** (0.2 mmol, 59.8 mg) in THF (1.0 mL) was added *n*-BuLi (0.22 mmol, 2.5 M in THF, 0.088 mL) at 0 °C under a nitrogen atmosphere. After stirring for 0.5 h, cyclohexanone **3a** (0.4 mmol, 39.2 mg) was then injected into the reaction tube at 0 °C. The reaction mixture was stirred at room temperature for 6 h. After the completion, the mixture was diluted with ethyl acetate (20 mL) and filtered through a short pad of silica gel. The solvent was removed by rotary evaporation and the yield of **4aaa** was determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

To ascertain the key metal species, organozinc or organocopper species was prepared through Li-Zn/Li-Cu exchange and then treated with **3a**. When

(1-sulfonyl-4-phenyltriazol-5-yl)lithium intermediate **Li-I** was treated with CuBr, ZnI_2, or Me_2Zn, **4aaa** was detected by ^1H NMR analysis in 38%, 10%, and 30% yield, respectively. In contrast, reacting lithium intermediate **Li-I** with $Cu(NO_3)_2$ could not produce any product.



Experimental procedure:

To a stirred solution of 1-sulfonyltriazole **5aa** (0.2 mmol, 59.8 mg) in THF (1.0 mL) was added *n*-BuLi (0.22 mmol, 2.5 M in THF, 0.088 mL) at 0 °C under a nitrogen atmosphere. After stirring for 0.5 h, $Cu(NO_3)_2$ (0.3 mmol, 56.1 mg, in 1 mL THF) or CuBr (0.3 mmol, 42.6 mg, in 1 mL THF) or ZnI_2 (0.3 mmol, 95.1 mg) or Me_2Zn (0.3 mmol, 1.2 M in toluene, 0.25 mL) was added into the tube and stirred for another 0.5 h. Then cyclohexanone **3a** (0.4 mmol, 39.2 mg) was added. The reaction mixture was stirred at room temperature for 6 h. After the completion, the mixture was diluted with ethyl acetate (20 mL) and filtered through a short pad of silica gel. The solvent was removed by rotary evaporation and the yield of **4aaa** was determined by ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

4. X-Ray Crystallography Data for 4aai and 4hak

The deposition number for **4aai** at the Cambridge Crystallographic Data Centre is CCDC 1444389.

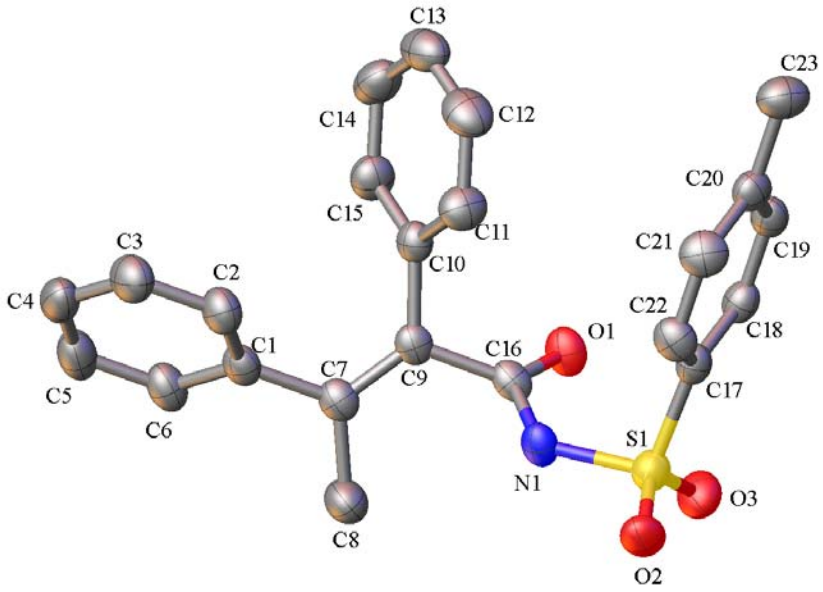


Figure S1. Ortep drawing of compound **4aai** with 50% ellipsoids

Table S2. Crystal data and structure refinement for **4aai**.

Identification code	**4aai**	
Empirical formula	C23 H21 N O3 S	
Formula weight	391.47	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.710(3) Å	α= 90°.
	b = 19.200(5) Å	β= 97.104(4)°.
	c = 22.065(6) Å	γ = 90°.
Volume	4082.2(19) $Å^3$	
Z	8	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	1648	
Crystal size	0.51 x 0.1 x 0.08 mm^3	
Theta range for data collection	1.860 to 27.486°.	
Index ranges	-11<=h<=12, -24<=k<=22, -28<=l<=28	

Reflections collected	29405
Independent reflections	9326 [R(int) = 0.0647]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6963
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9326 / 0 / 509
Goodness-of-fit on F^2	1.197
Final R indices [I>2sigma(I)]	R1 = 0.0870, wR2 = 0.1337
R indices (all data)	R1 = 0.1116, wR2 = 0.1429
Extinction coefficient	n/a
Largest diff. peak and hole	0.249 and -0.282 e.$Å^{-3}$

The deposition number for **4hak** at the Cambridge Crystallographic Data Centre is CCDC 1444390.

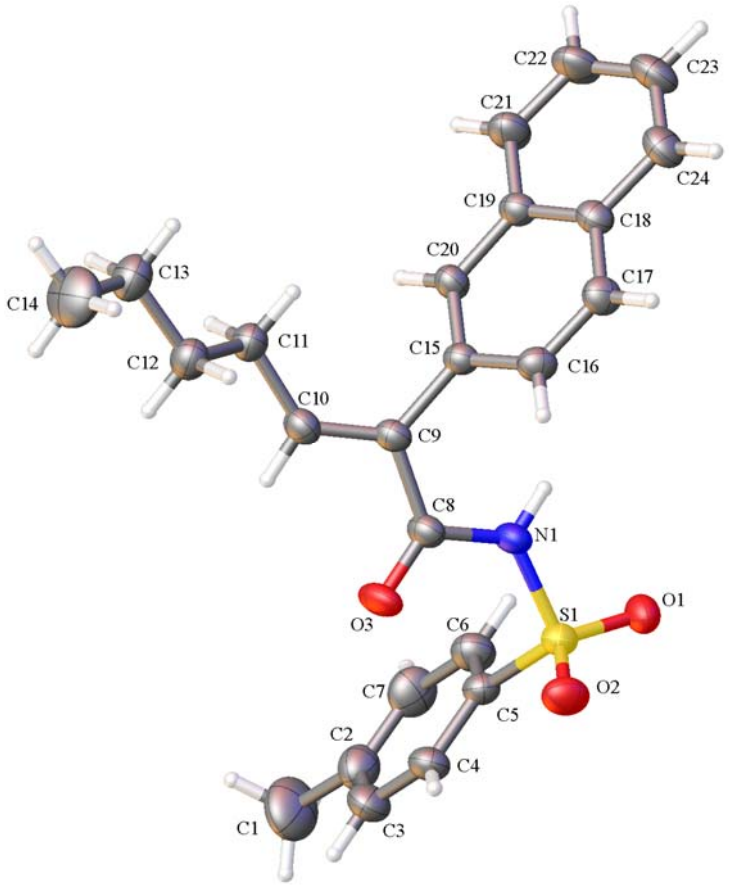


Figure S2. Ortep drawing of compound **4hak** with 50% ellipsoids

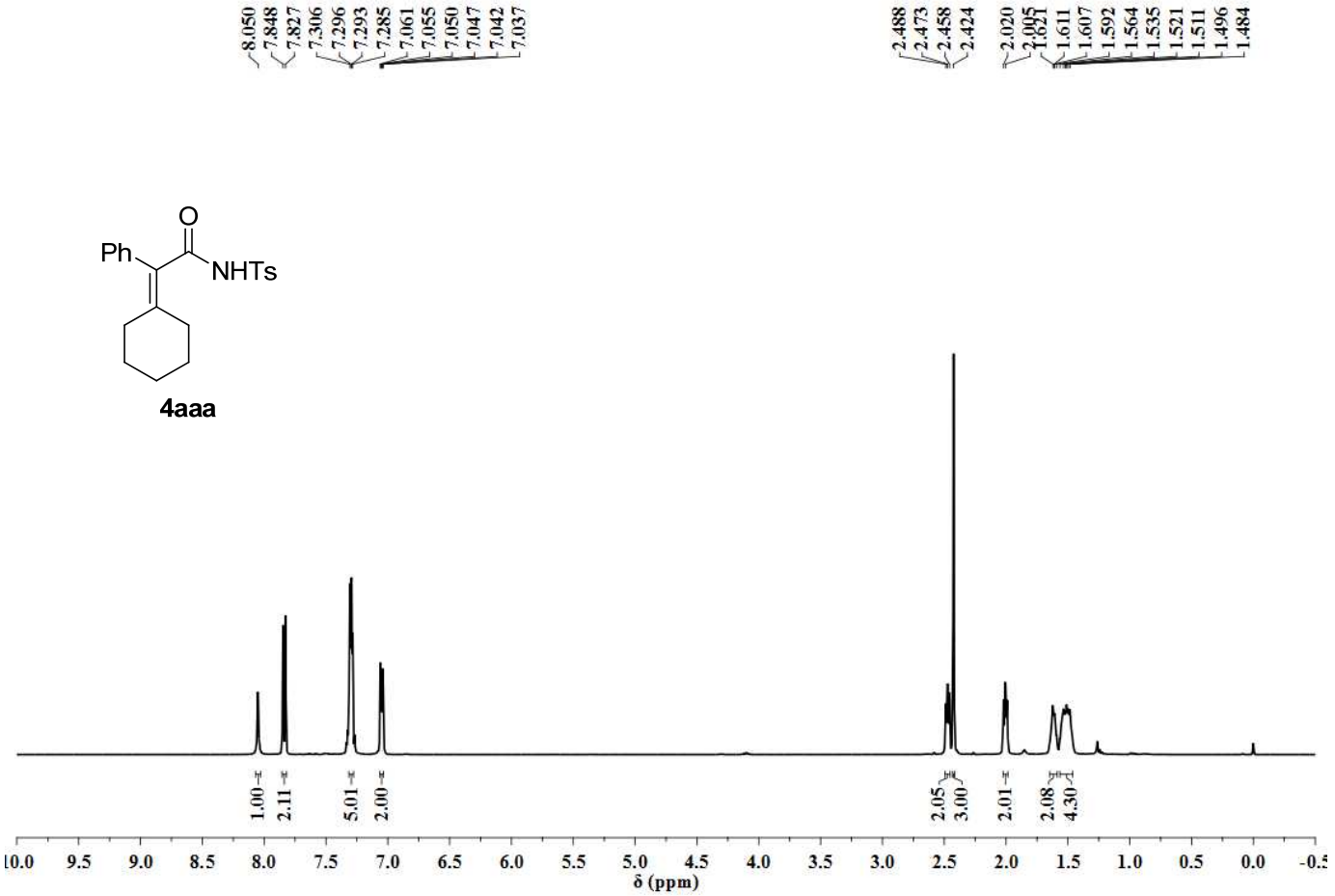
Table S3. Crystal data and structure refinement for **4hak**.

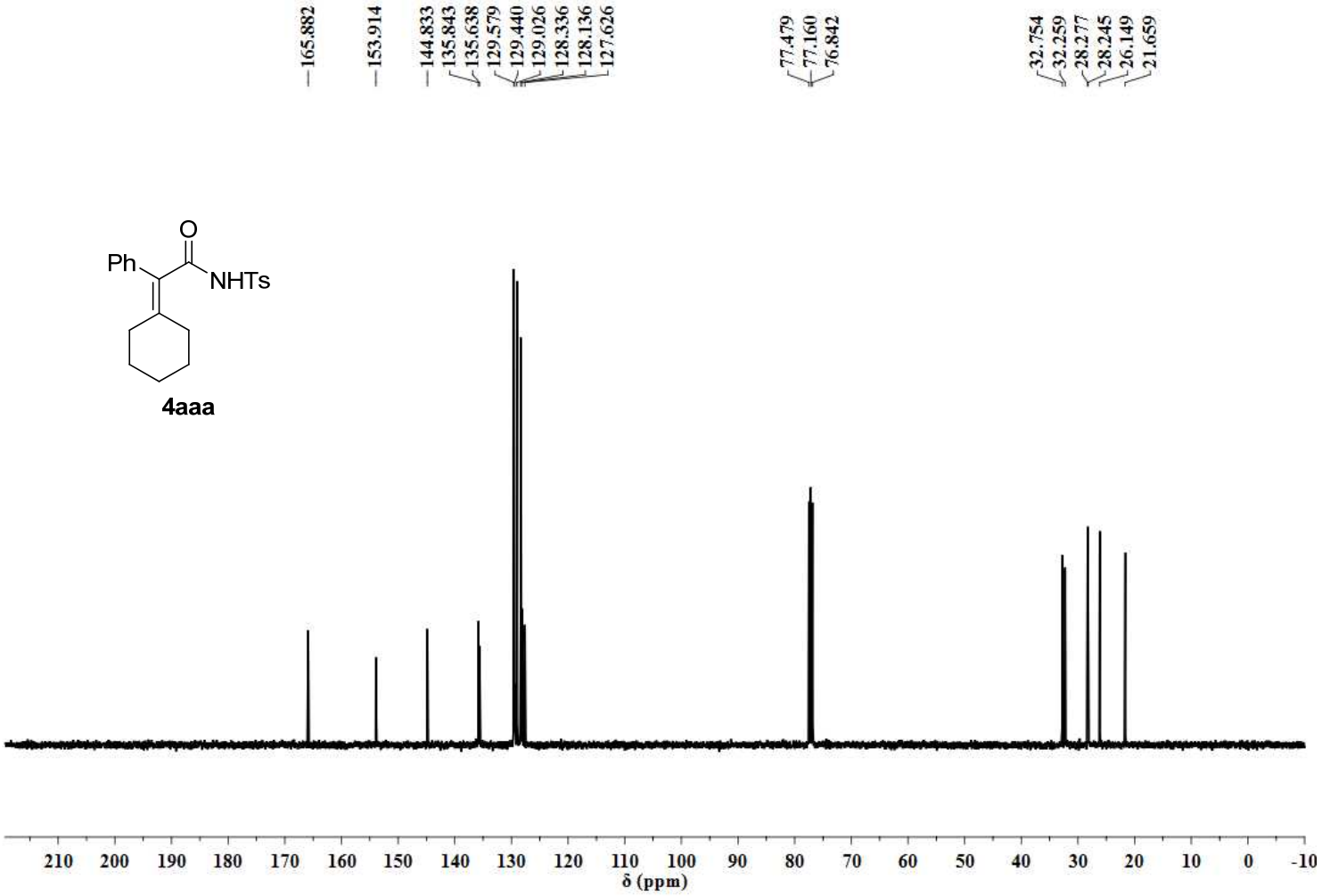
Identification code	**4hak**	
Empirical formula	C24 H25 N O3 S	
Formula weight	407.51	
Temperature	298.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.3077(19) Å	α= 116.41(3)°.
	b = 11.580(2) Å	β= 100.50(3)°.
	c = 11.683(2) Å	γ = 90.85(3)°.
Volume	1102.3(5) $Å^3$	
Z	2	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	0.171 mm^{-1}	
F(000)	432	
Crystal size	0.24 x 0.21 x 0.17 mm^3	
Theta range for data collection	2.664 to 27.498°.	
Index ranges	-12<=h<=12, -14<=k<=15, -15<=l<=15	
Reflections collected	9421	
Independent reflections	4952 [R(int) = 0.0329]	
Completeness to theta = 26.000°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7857	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4952 / 0 / 264	
Goodness-of-fit on F^2	1.129	
Final R indices [I>2sigma(I)]	R1 = 0.0627, wR2 = 0.1408	
R indices (all data)	R1 = 0.0809, wR2 = 0.1520	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.165 and -0.245 $e.Å^{-3}$	

5. References

1. E. Merkul, F. Klukas, D. Dorsch, U. Gradler, H. E. Greiner and T. J. J. Muller, *Org. Biomol. Chem.*, 2011, **9**, 5129.
2. B. Zhou, H. Chen and C. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 1264.
3. Y. Xing, G. Sheng, J. Wang, P. Lu and Y. Wang, *Org. Lett.*, 2014, **16**, 1244.
4. B. Zhou, Y. Hu and C. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 13659.
5. V. C. Edelsztein, P. H. Di Chenna and G. Burton, *Tetrahedron*, 2009, **65**, 3615.
6. K. Wang, X. Bi, S. Xing, P. Liao, Z. Fang, X. Meng, Q. Zhang, Q. Liu and Y. Ji, *Green Chemistry*, 2011, **13**, 562.
7. E. J. Yoo, M. Ahlquist, I. Bae, K. B. Sharpless, V. V. Fokin and S. Chang, *J. Org. Chem.*, 2008, **73**, 5520.

6. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR Spectra

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128.136
127.626
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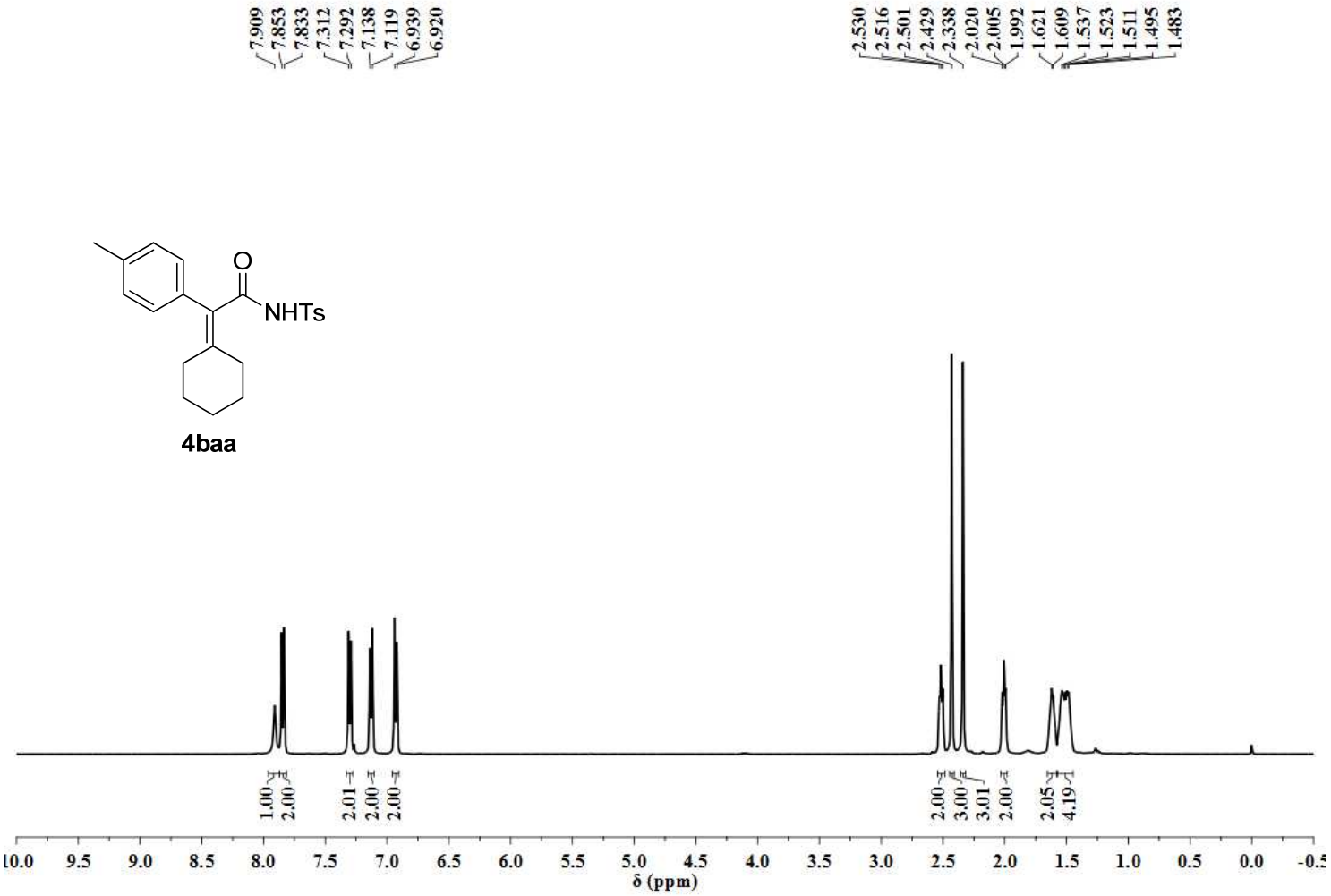
77.160
76.842
32.754
32.259
28.277
28.245
26.149
21.659
O
Ph
NHTs
4aaa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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1.609
1.537
1.523
1.511
1.495
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O
NHTs
4baa
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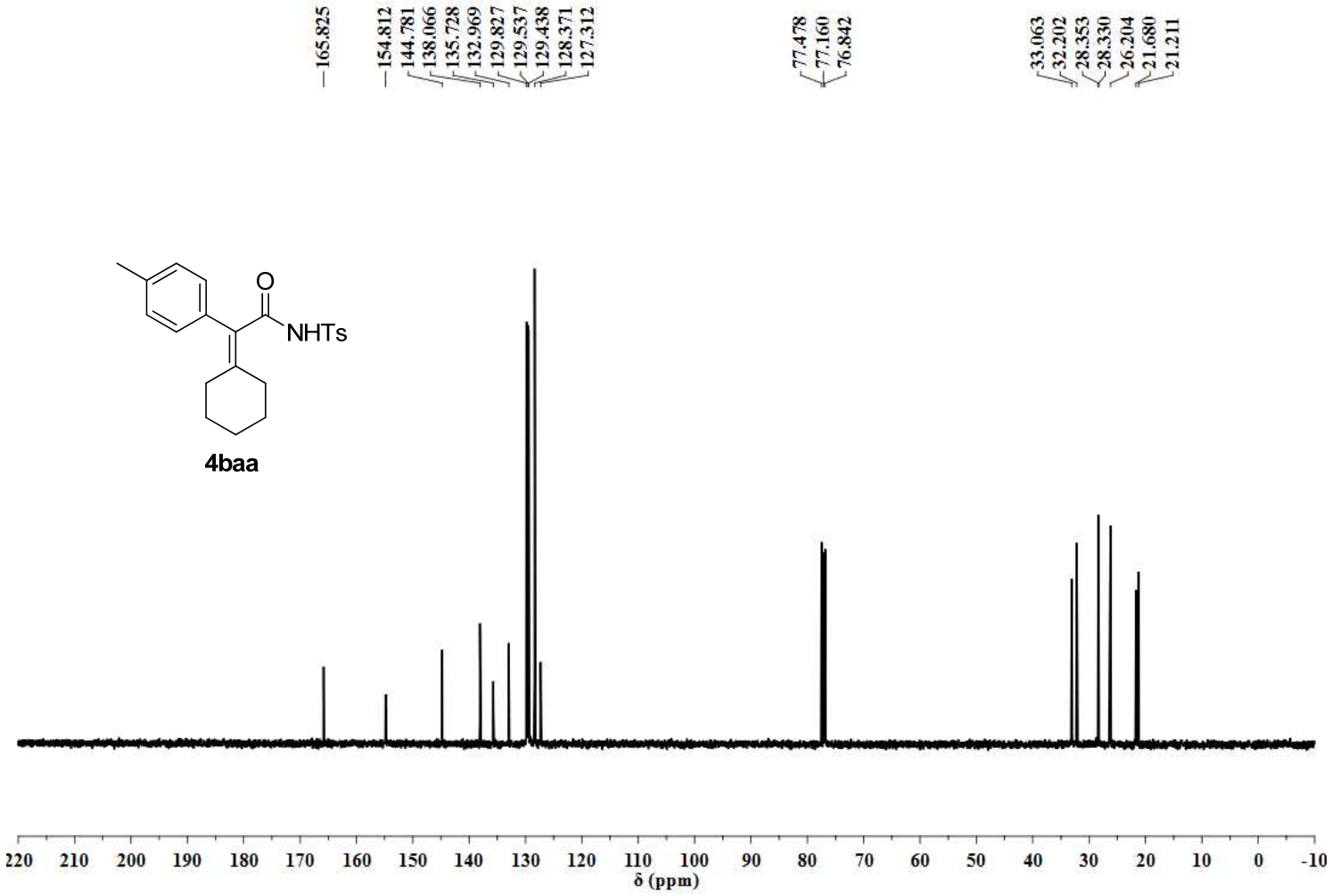
4.19
δ (ppm)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33.063
32.202
28.353
28.330
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O
NHTs
4baa
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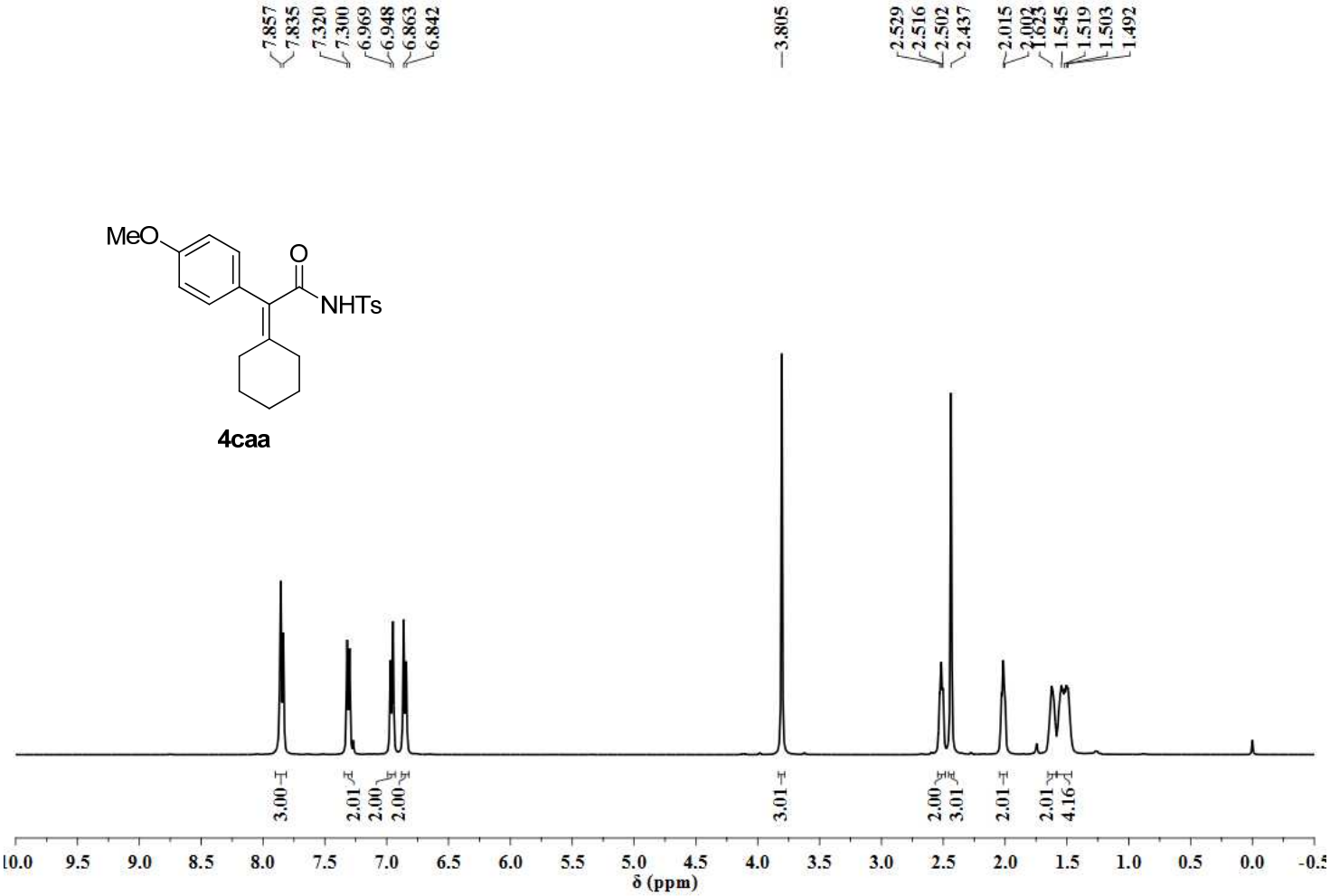
δ (ppm)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1.545
1.519
1.503
1.492
MeO
O
NHTs
4caa
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2.00
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3.01
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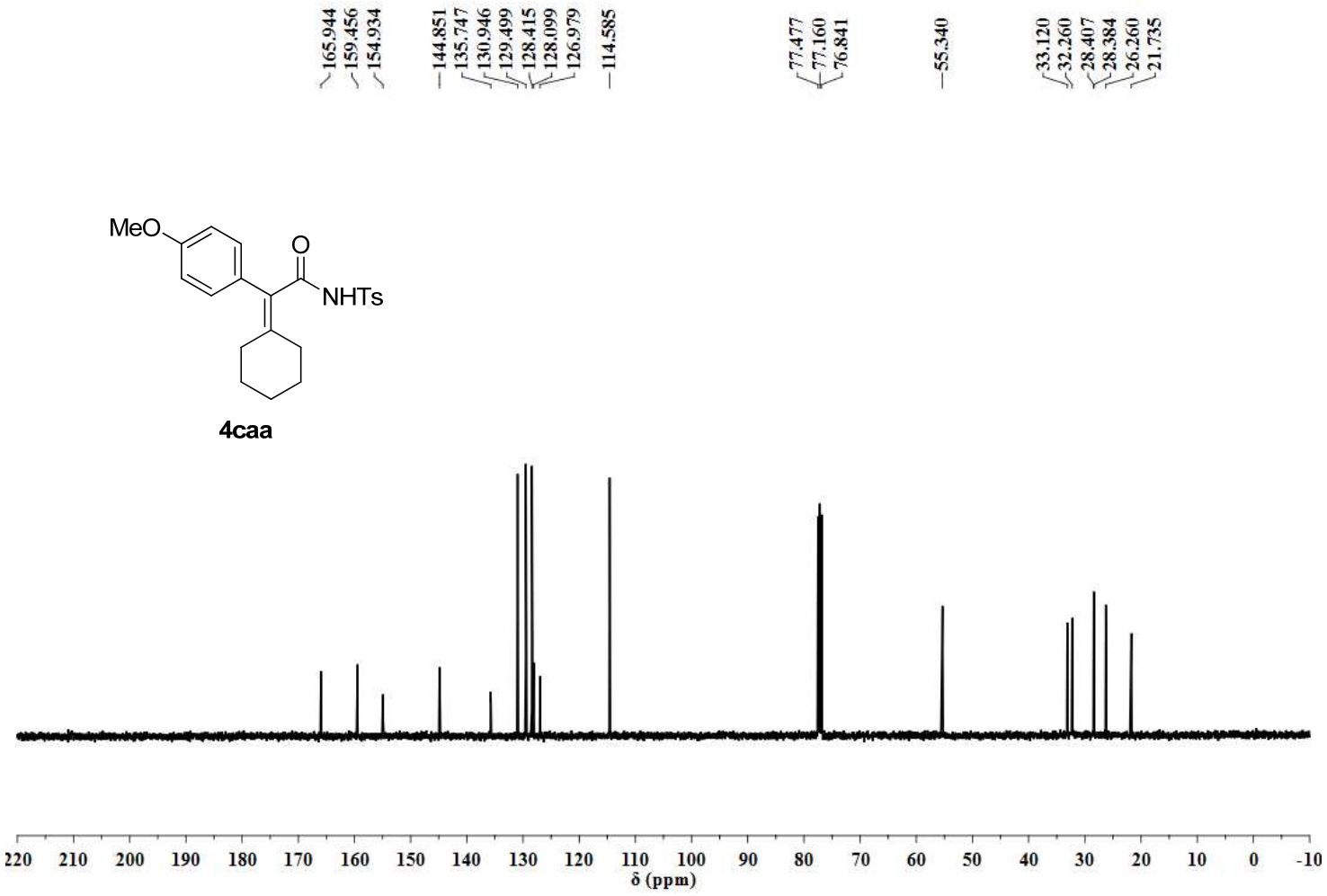
2.01
2.01
4.16
δ (ppm)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33.120
32.260
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4caa
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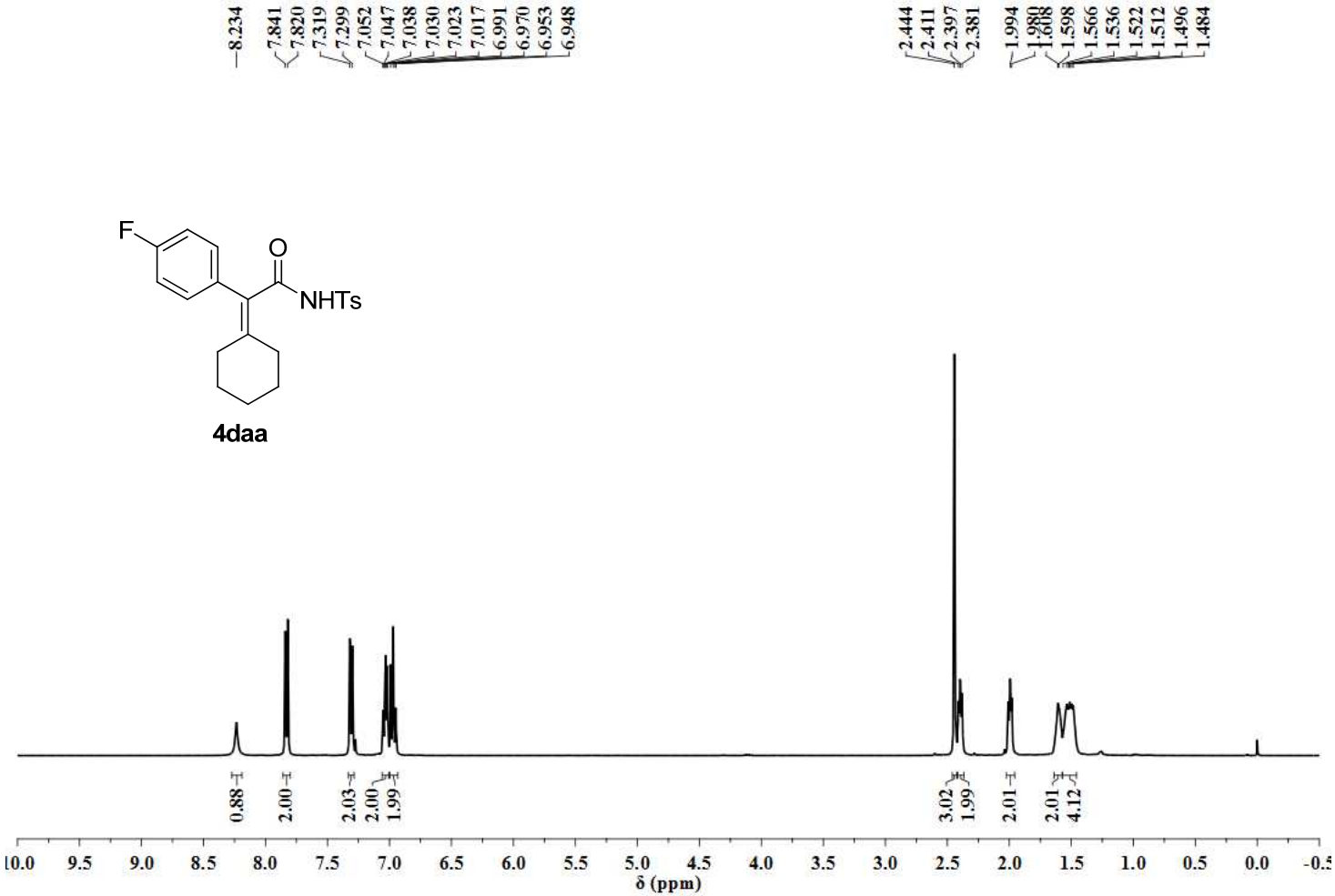
δ (ppm)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2.411
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2.381
1.994
1.980
1.598
1.566
1.536
1.522
1.512
1.496
1.484
F
O
NHTs
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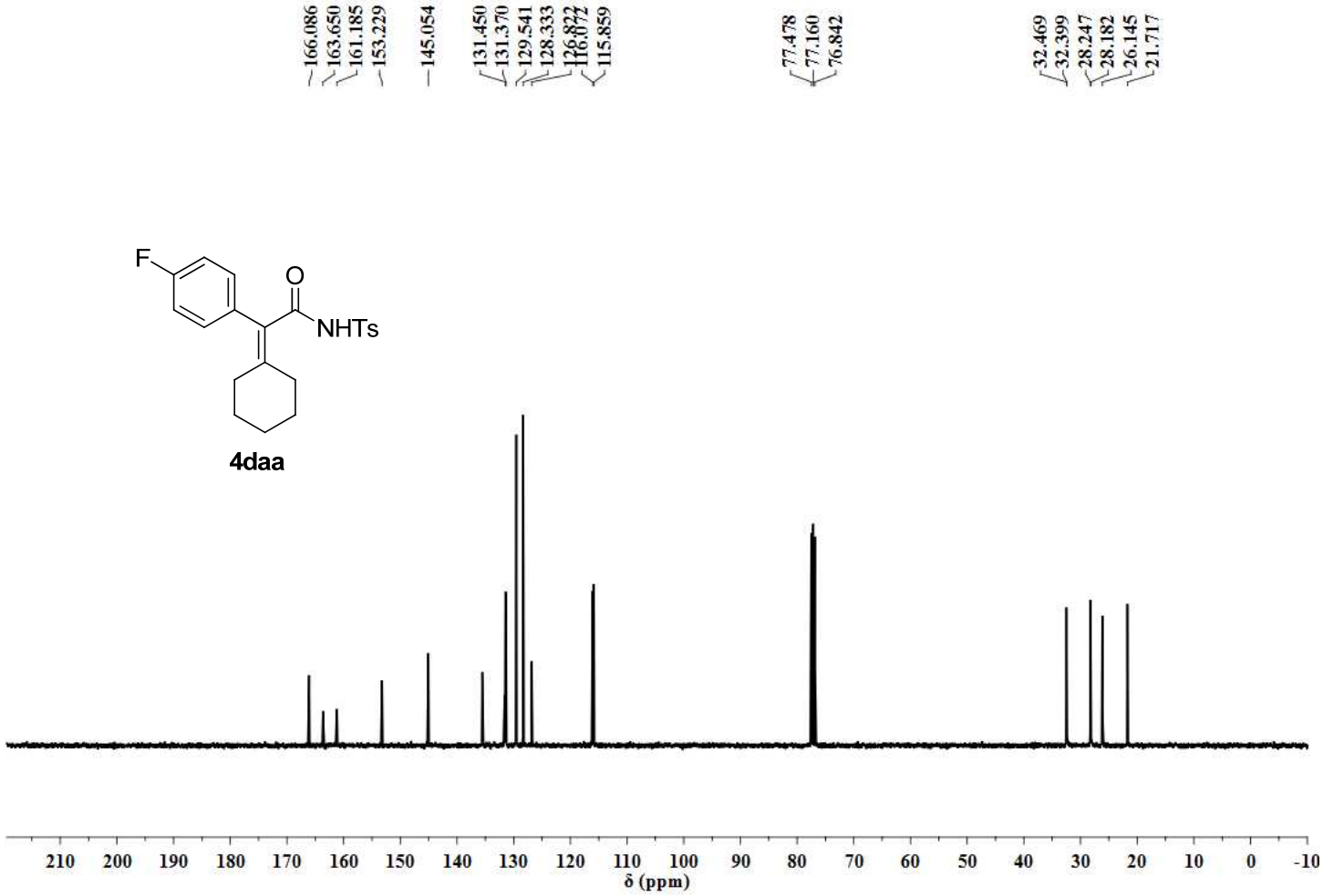
δ (ppm)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32.469
32.399
28.247
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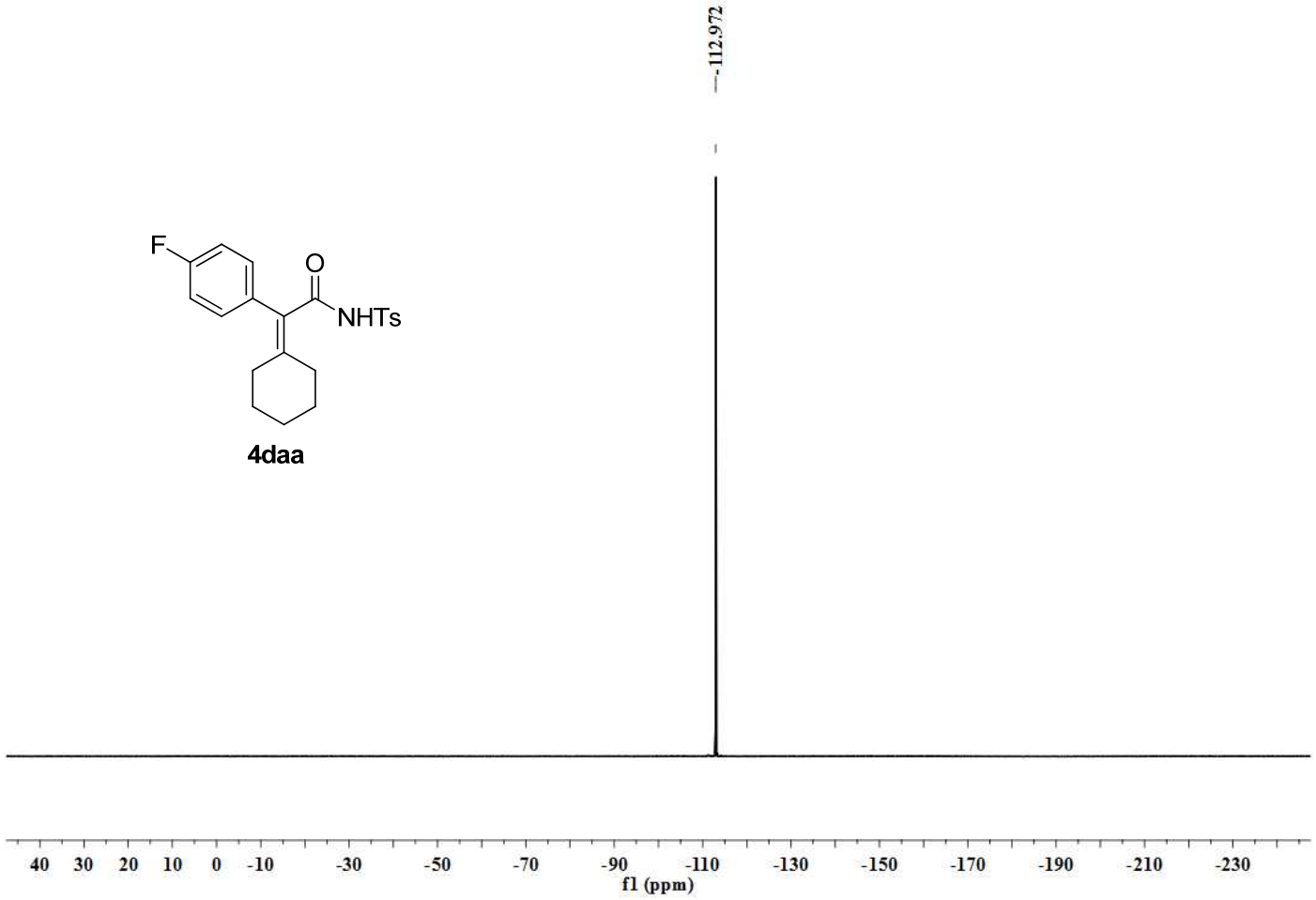
F
O
NHTs
4daa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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O
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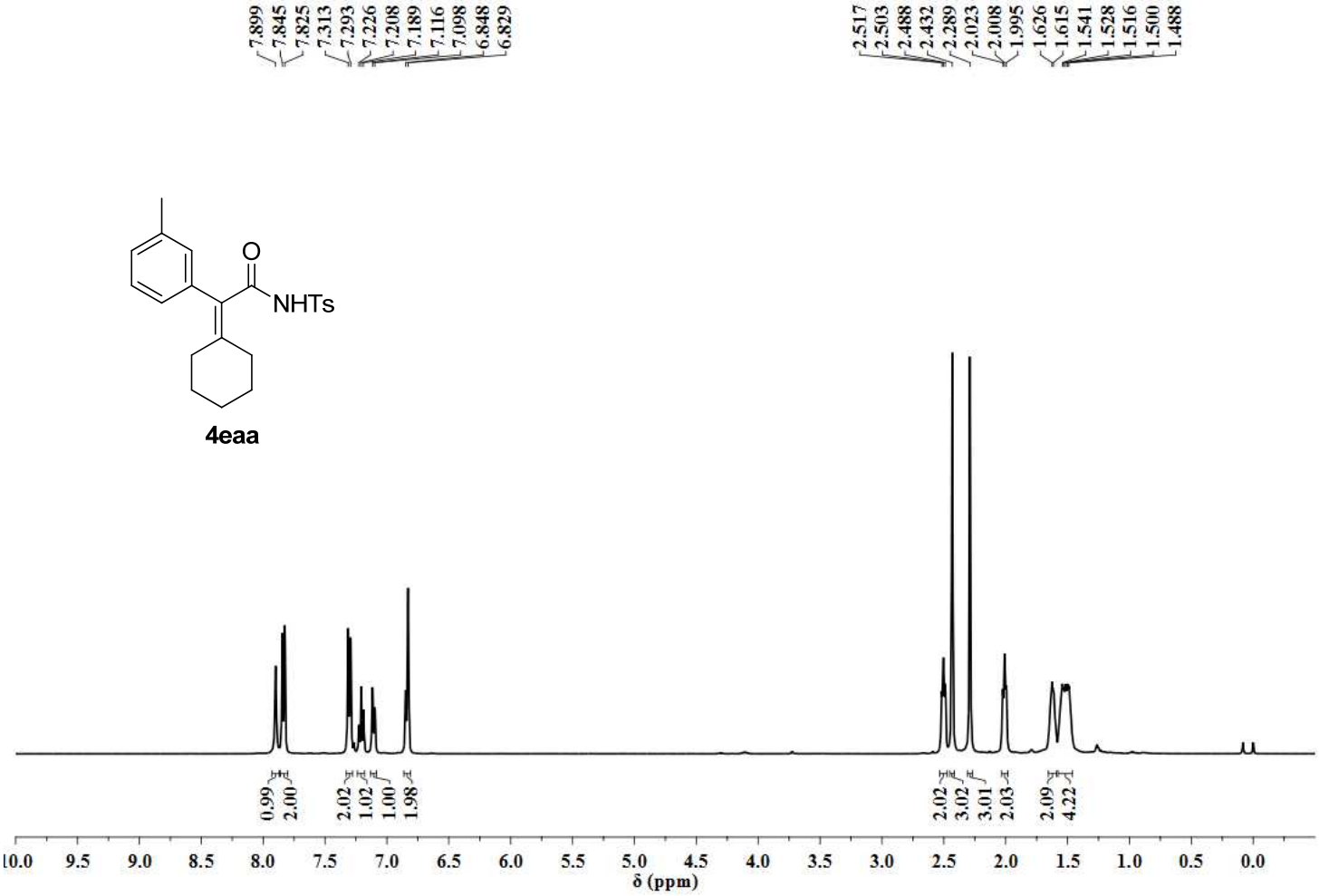
f1 (ppm)

4daa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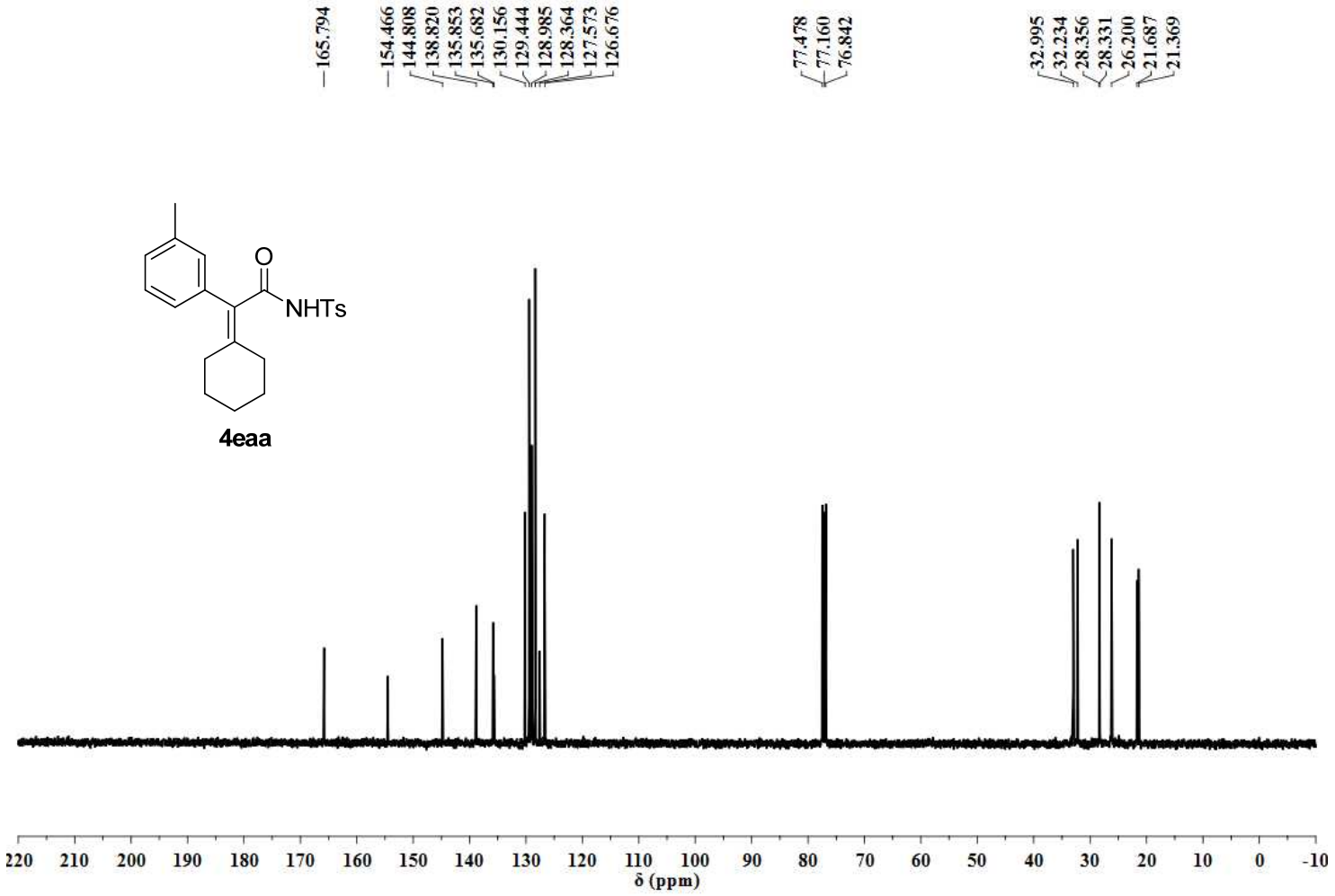
1.541
1.528
1.516
1.500
1.488
O
NHTs
4eaa
0.99
2.00
2.02
1.02
1.00
1.98
2.02
3.02
3.01
2.03
2.09
4.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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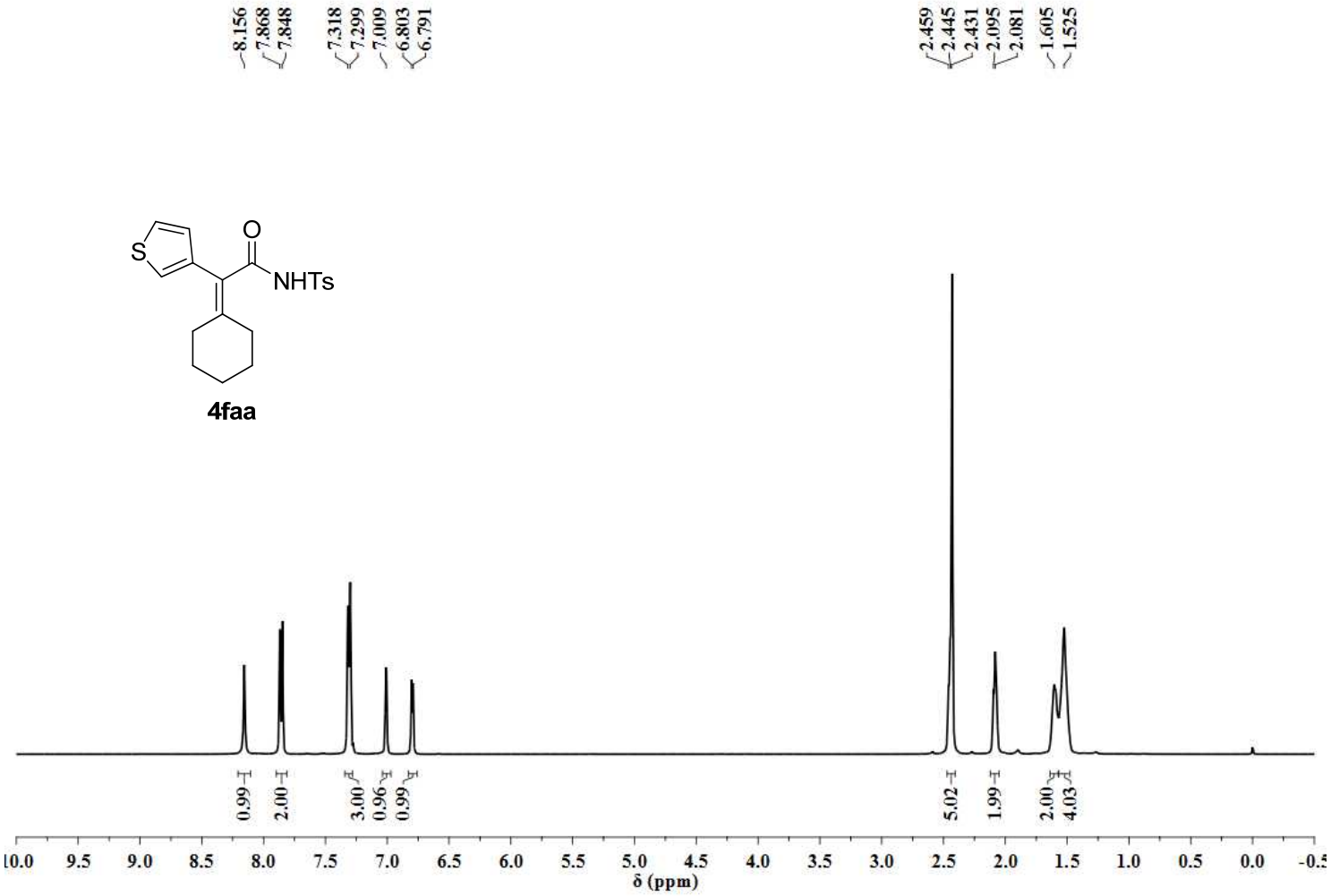
154.466
144.808
138.820
135.853
135.682
130.156
129.444
128.985
128.364
127.573
126.676
77.478
77.160
76.842
32.995
32.234
28.356
28.331
26.200
21.687
21.369
O
NHTs
4eaa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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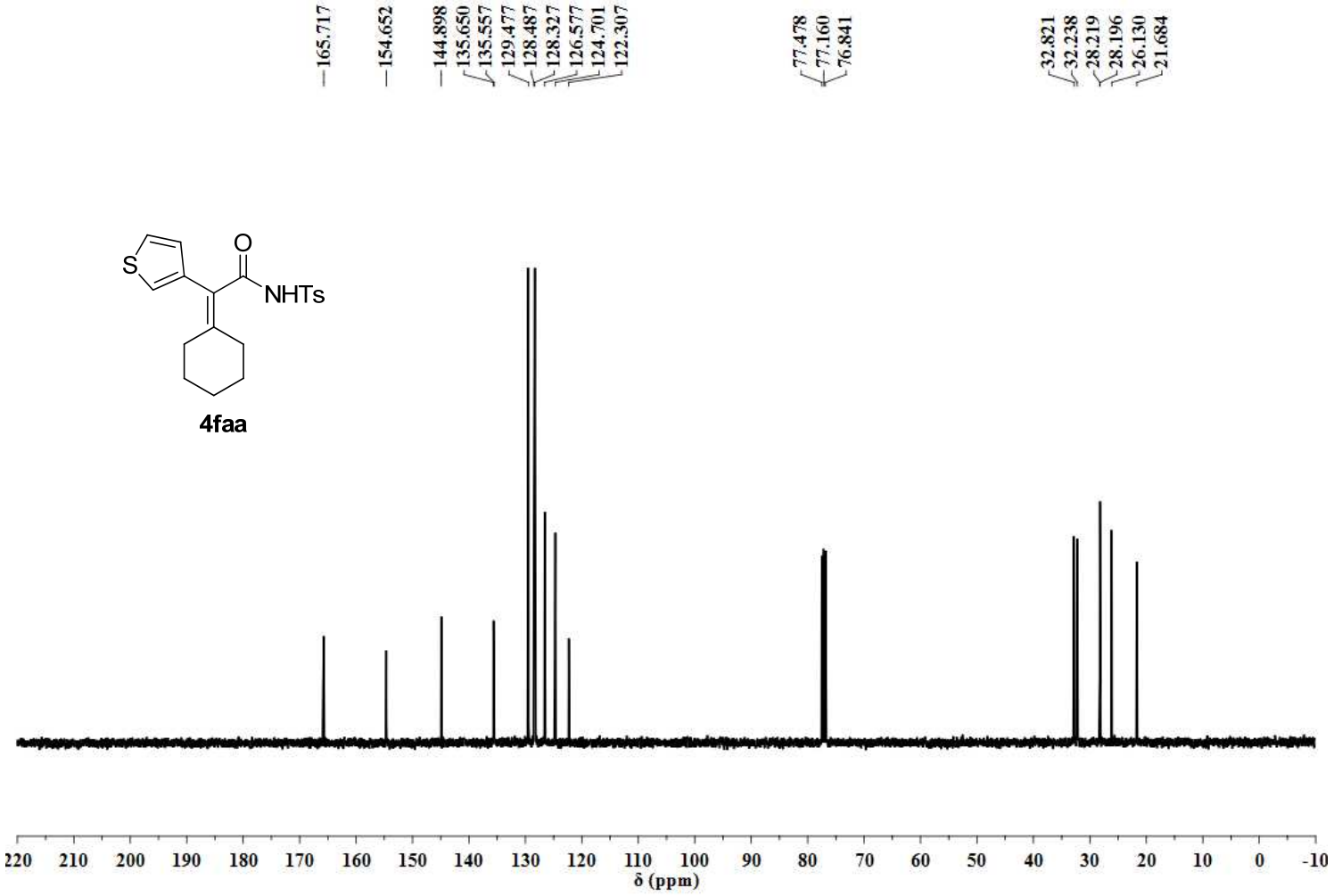
7.868
7.848
7.318
7.299
7.009
6.803
6.791
2.459
2.445
2.431
2.095
2.081
1.605
1.525
O
S
NHTs
4faa
0.99
2.00
3.00
0.96
0.99
5.02
1.99
2.00
4.03
δ (ppm)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154.652
144.898
135.650
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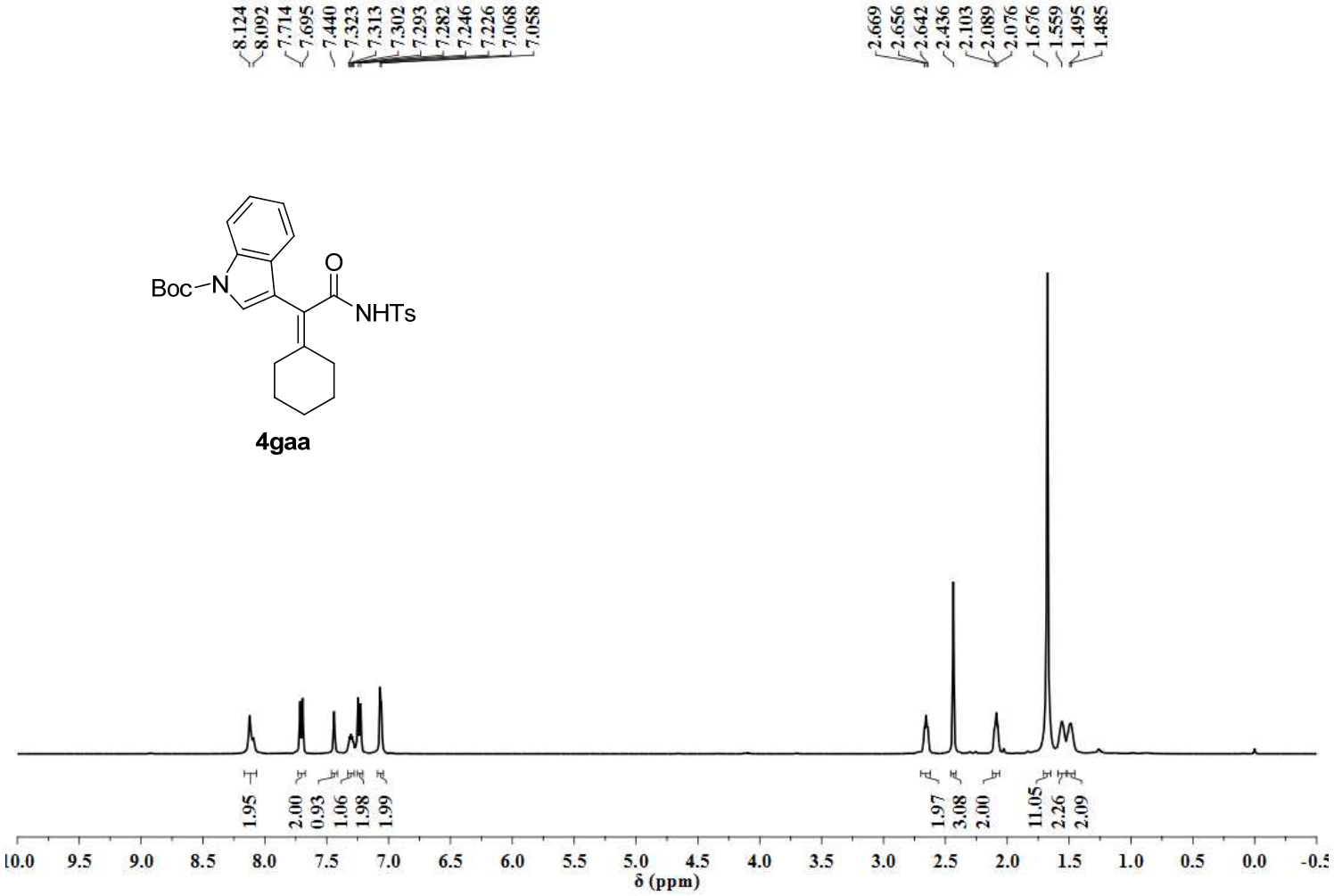
129.477
128.487
128.327
126.577
124.701
122.307
77.478
77.160
76.841
32.821
32.238
28.219
28.196
26.130
21.684
S
O
NHTs
4faa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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8.092
7.714
7.695
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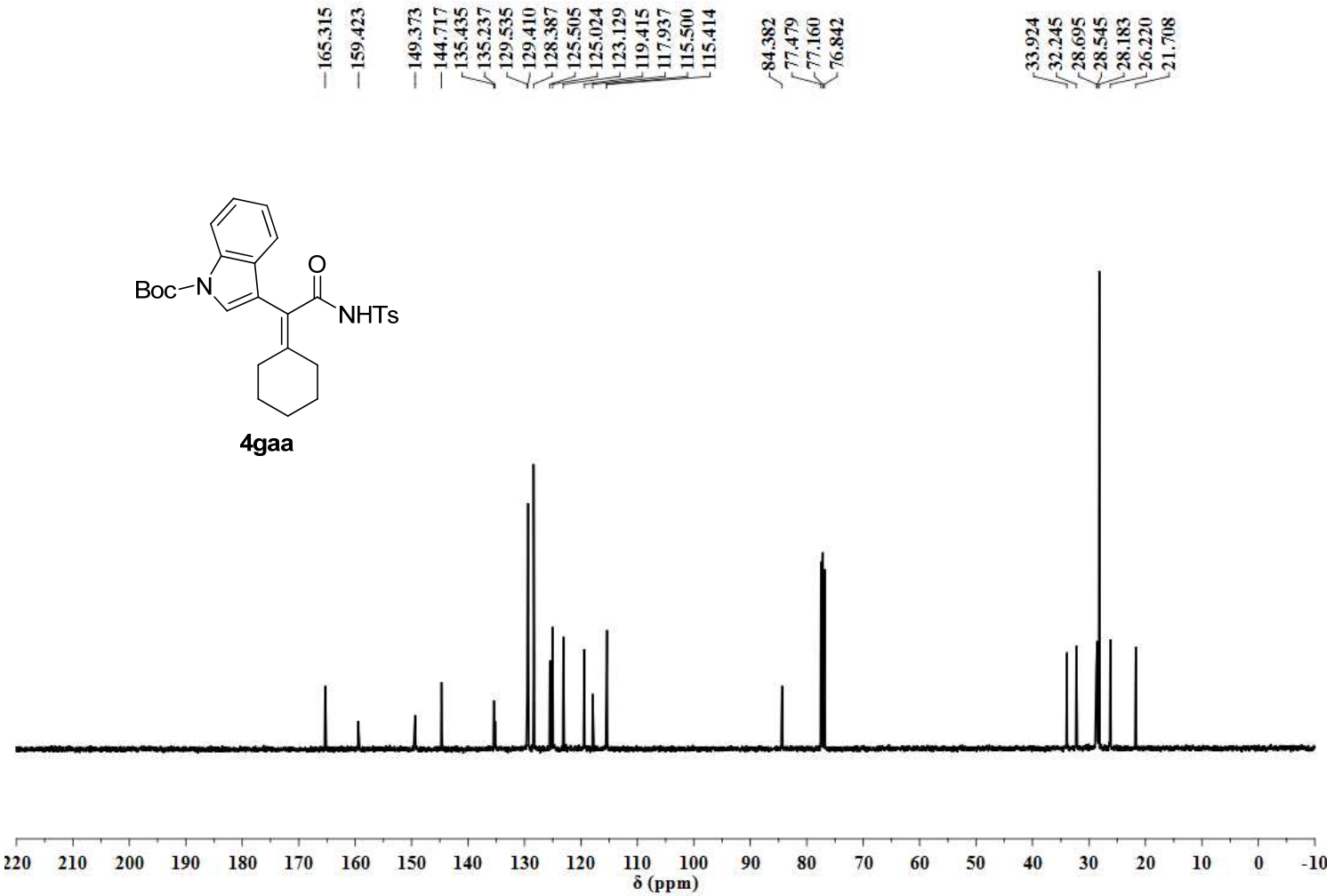
7.313
7.302
7.293
7.282
7.246
7.226
7.068
7.058
2.669
2.656
2.642
2.436
2.103
2.089
2.076
1.676
1.559
1.495
1.485
Boc
N
O
NHTs
4gaa
1.95
2.00
0.93
1.06
1.98
1.99
1.97
3.08
2.00
11.05
2.26
2.09
δ (ppm)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159.423
149.373
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129.535
129.410
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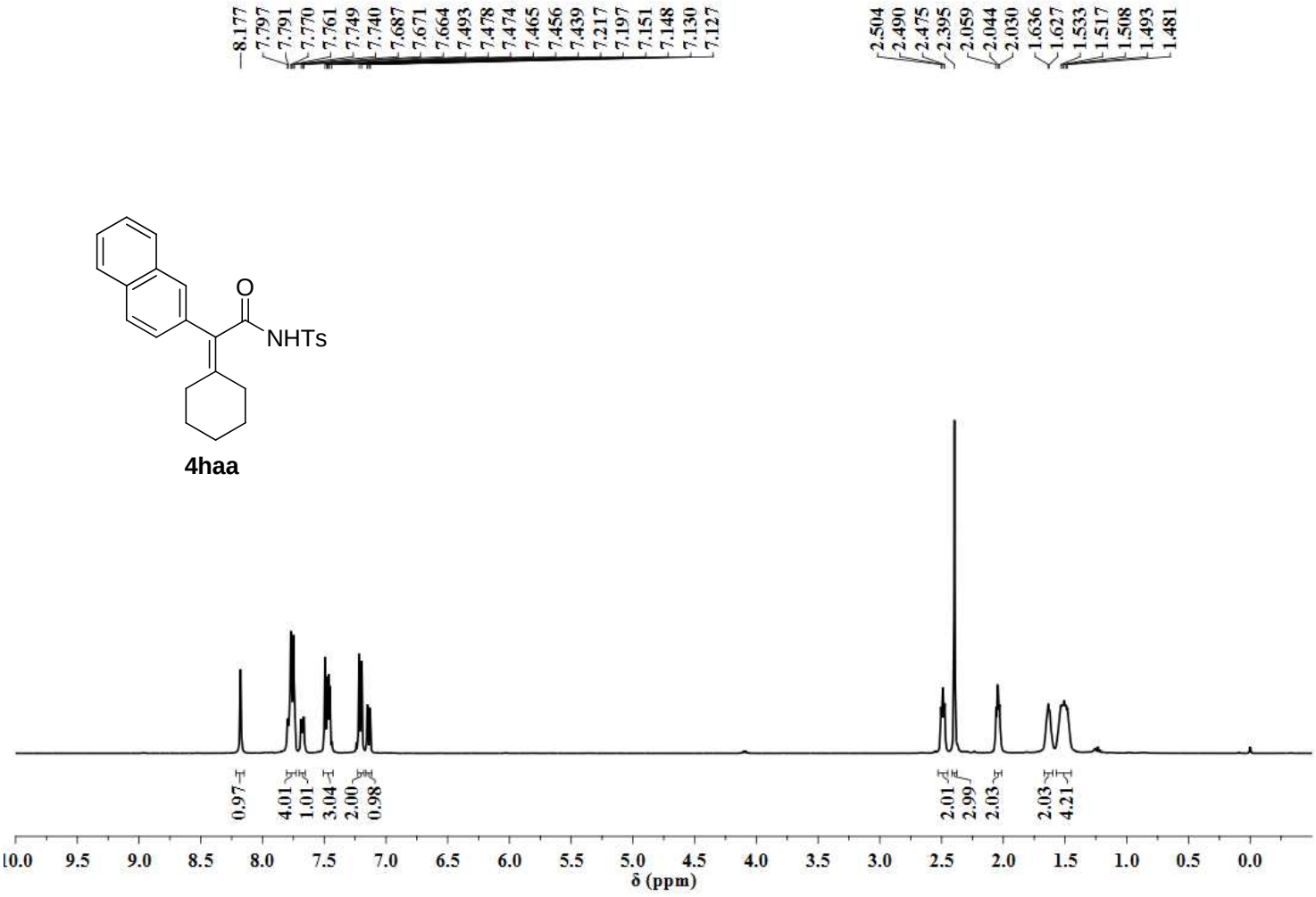
125.505
125.024
123.129
119.415
117.937
115.500
115.414
84.382
77.479
77.160
76.842
33.924
32.245
28.695
28.545
28.183
26.220
21.708
Boc
N
O
NHTs
4gaa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.791
7.770
7.761
7.749
7.740
7.687
7.671
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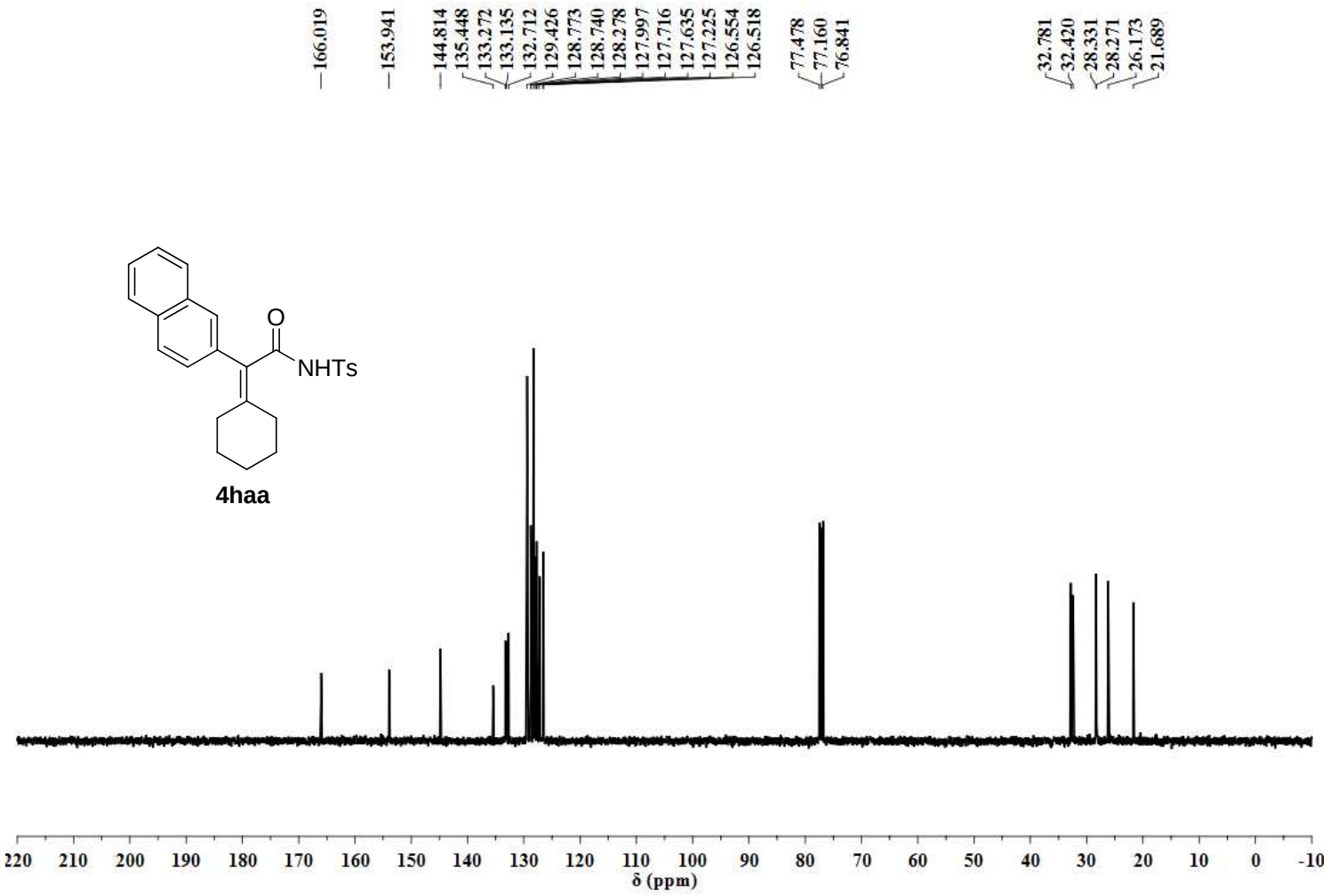
7.478
7.474
7.465
7.456
7.439
7.217
7.197
7.151
7.148
7.130
7.127
2.504
2.490
2.475
2.395
2.059
2.044
2.030
1.636
1.627
1.533
1.517
1.508
1.493
1.481
O
NHTs
4haa
0.97
4.01
1.01
3.04
2.00
0.98
2.01
2.99
2.03
2.03
4.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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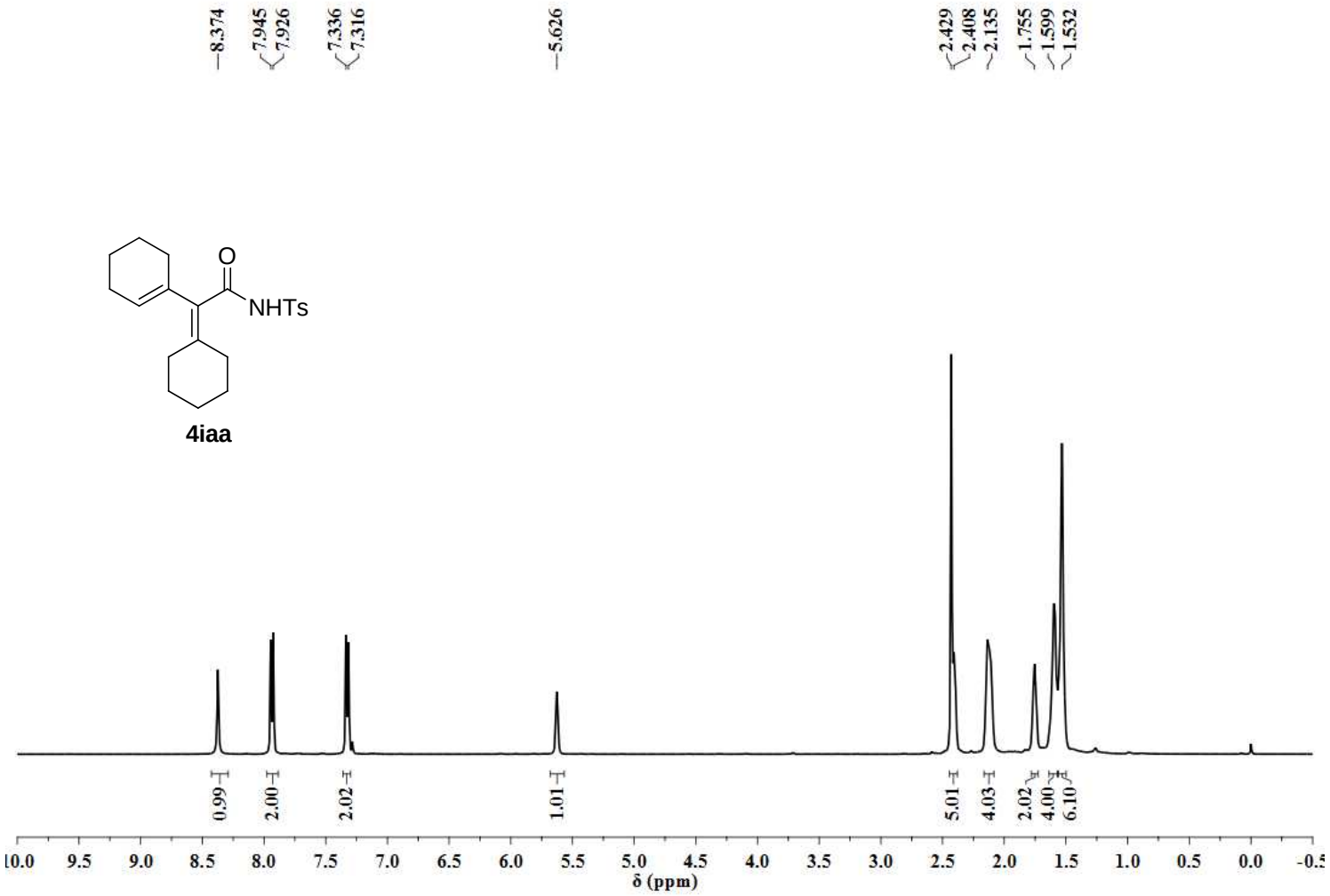
153.941
144.814
135.448
133.272
133.135
132.712
129.426
128.773
128.740
128.278
127.997
127.716
127.635
127.225
126.554
126.518
77.478
77.160
76.841
32.781
32.420
28.331
28.271
26.173
21.689
O
NHTs
4haa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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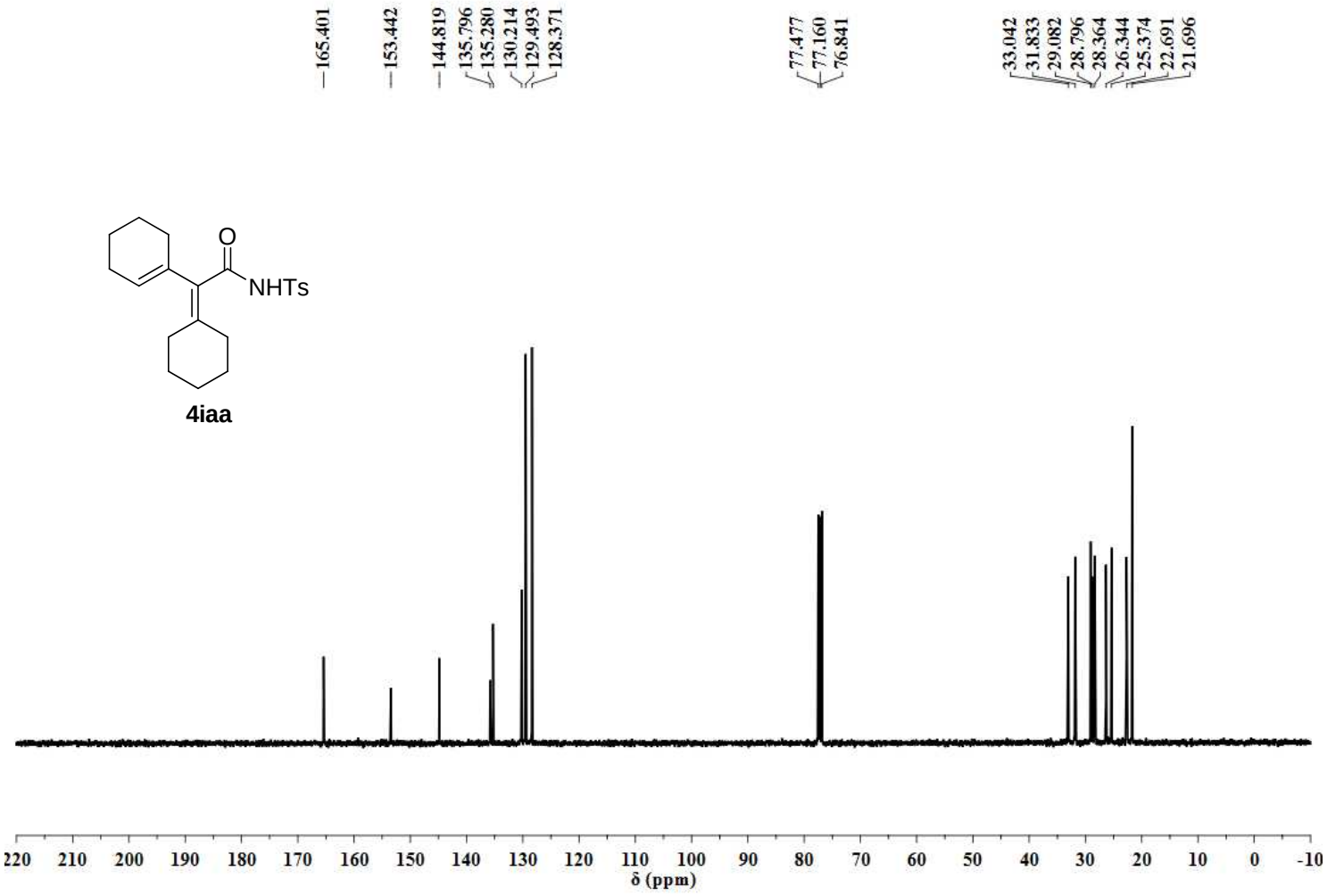
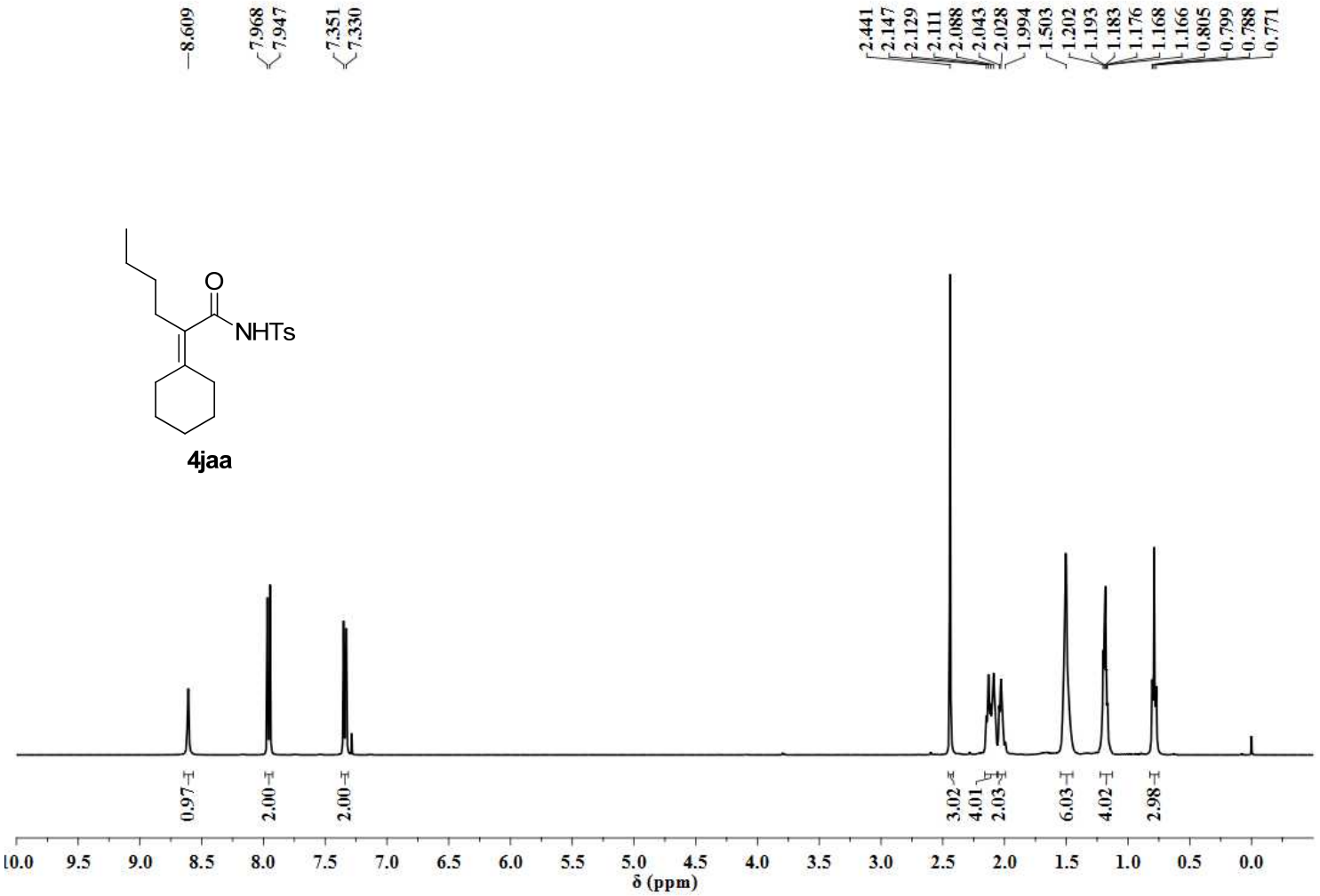
7.945
7.926
7.336
7.316
5.626
2.429
2.408
2.135
1.755
1.599
1.532
O
NHTs
4iaa
0.99
2.00
2.02
1.01
5.01
4.03
2.02
4.00
6.10
δ (ppm)


165.401
153.442
144.819
135.796
135.280
130.214
129.493
128.371
77.477
77.160
76.841
33.042
31.833
29.082
28.796
28.364
26.344
25.374
22.691
21.696
O
NHTs
4iaa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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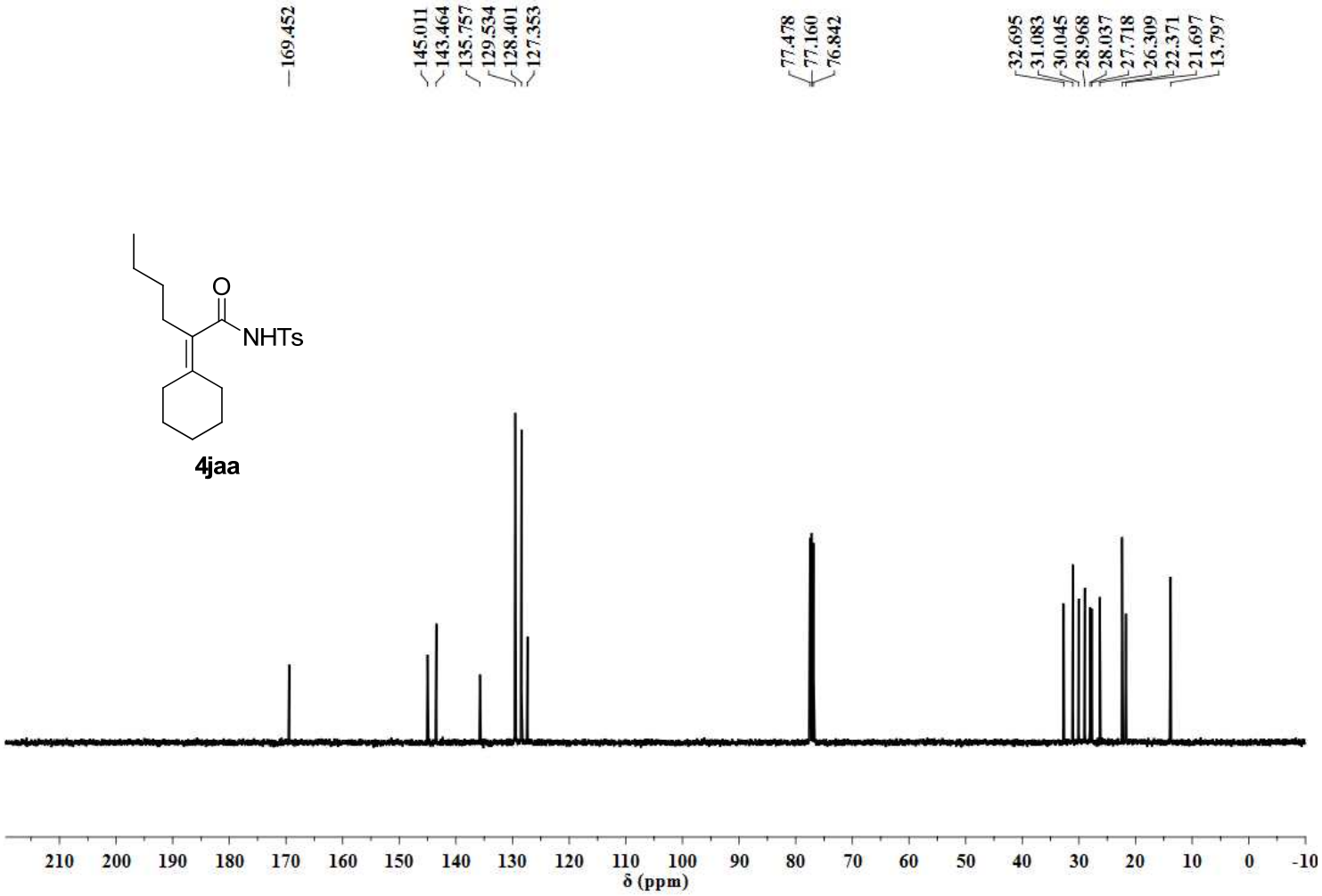
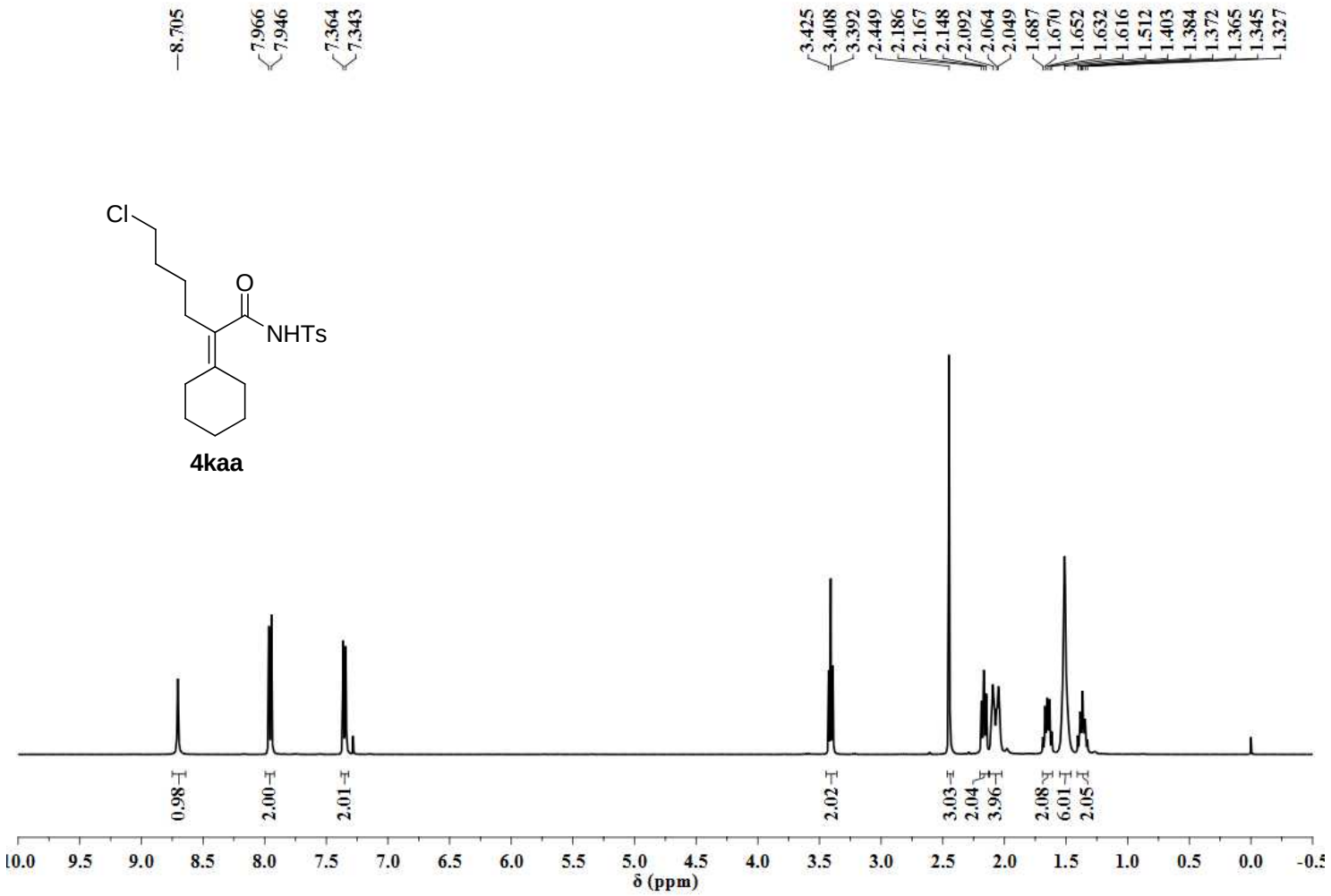
7.947
7.351
7.330
2.441
2.147
2.129
2.111
2.088
2.043
2.028
1.994
1.503
1.202
1.193
1.183
1.176
1.168
1.166
0.805
0.799
0.788
0.771
O
NHTs
4jaa
0.97
2.00
2.00
3.02
4.01
2.03
6.03
4.02
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


169.452
145.011
143.464
135.757
129.534
128.401
127.353
77.478
77.160
76.842
32.695
31.083
30.045
28.968
28.037
27.718
26.309
22.371
21.697
13.797
O
NHTs
4jaa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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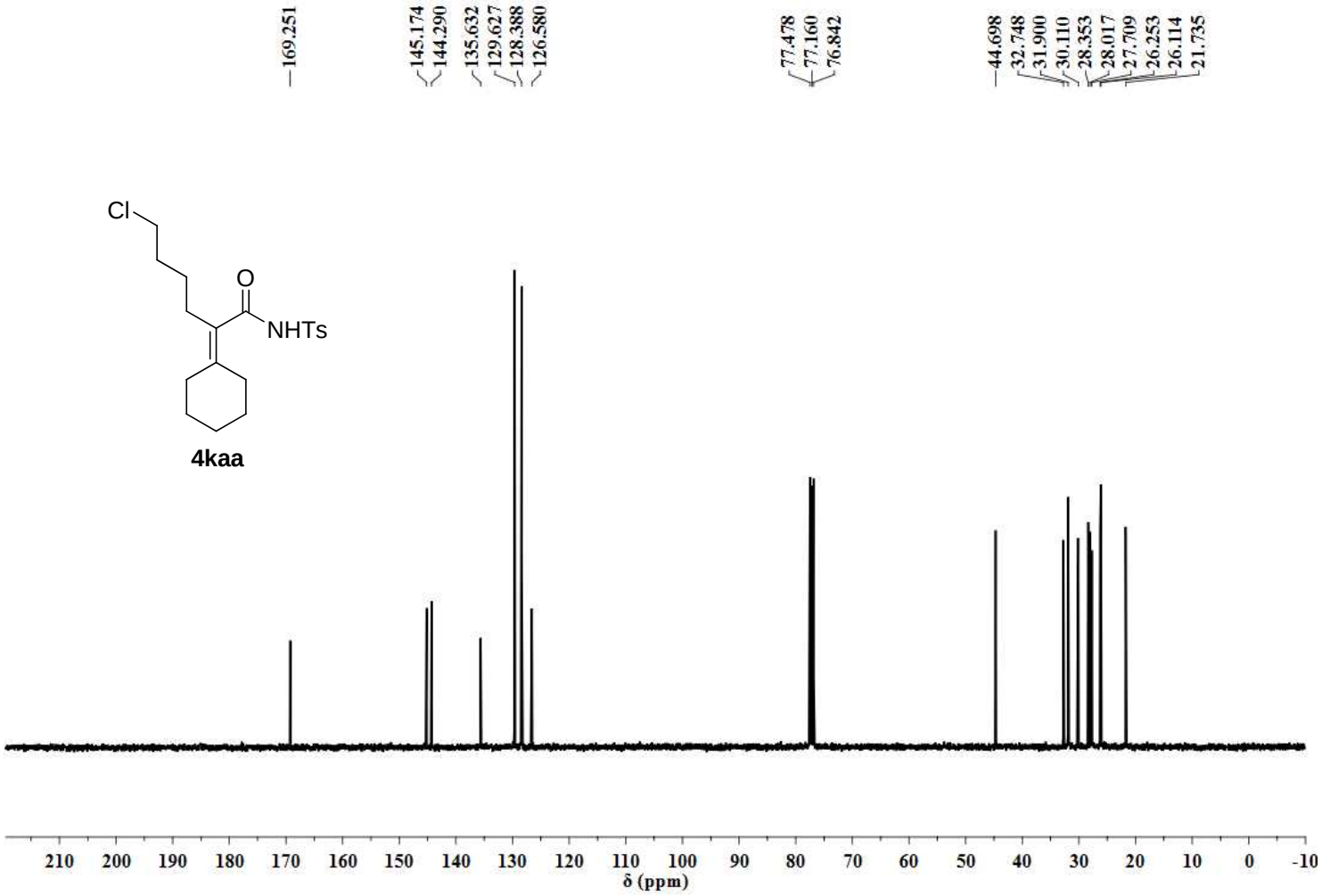
7.946
7.364
7.343
3.425
3.408
3.392
2.449
2.186
2.167
2.148
2.092
2.064
2.049
1.687
1.670
1.652
1.632
1.616
1.512
1.403
1.384
1.372
1.365
1.345
1.327
Cl
O
NHTs
4kaa
0.98
2.00
2.01
2.02
3.03
2.04
3.96
2.08
6.01
2.05
δ (ppm)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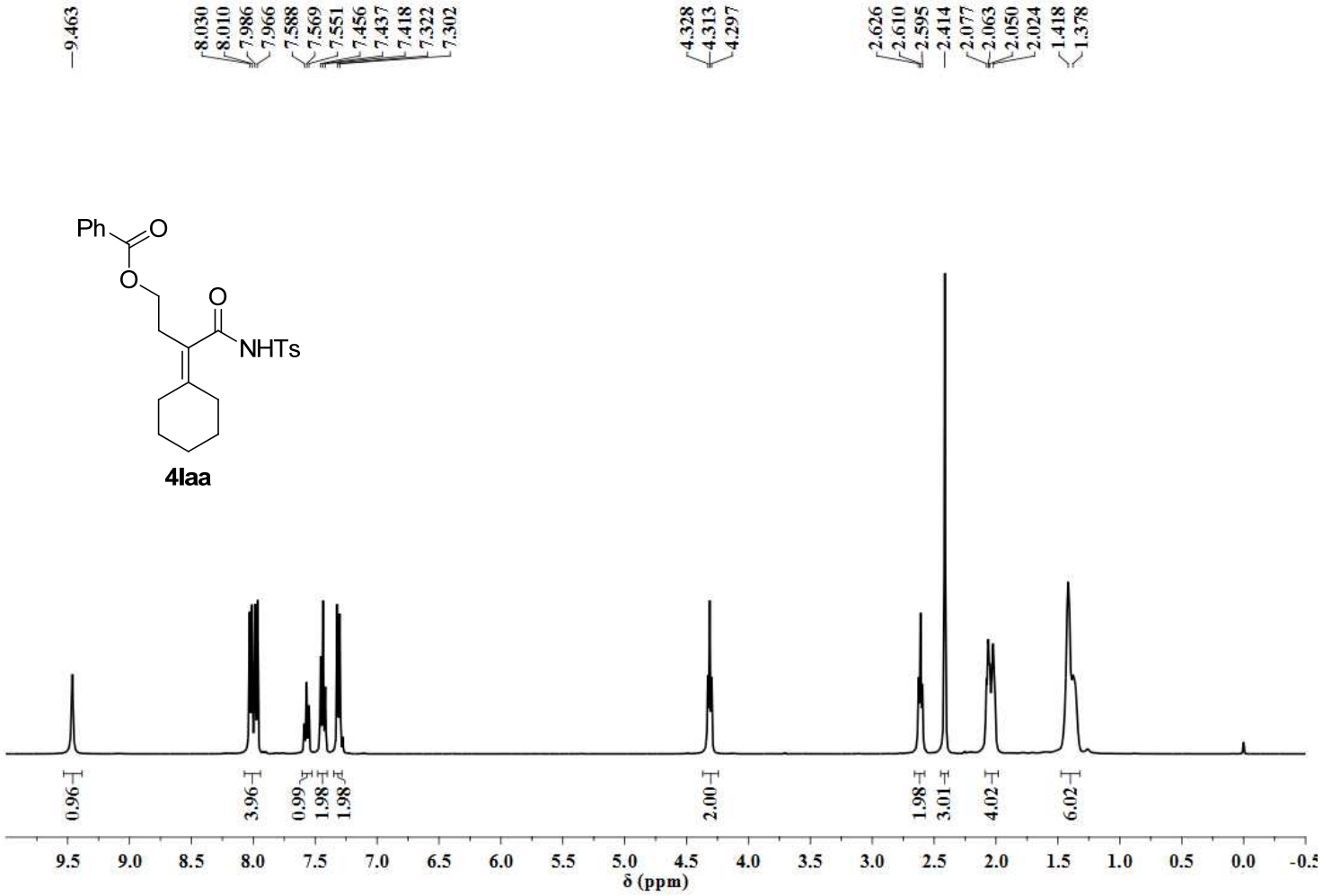
144.290
135.632
129.627
128.388
126.580
77.478
77.160
76.842
44.698
32.748
31.900
30.110
28.353
28.017
27.709
26.253
26.114
21.735
Cl
O
NHTs
4kaa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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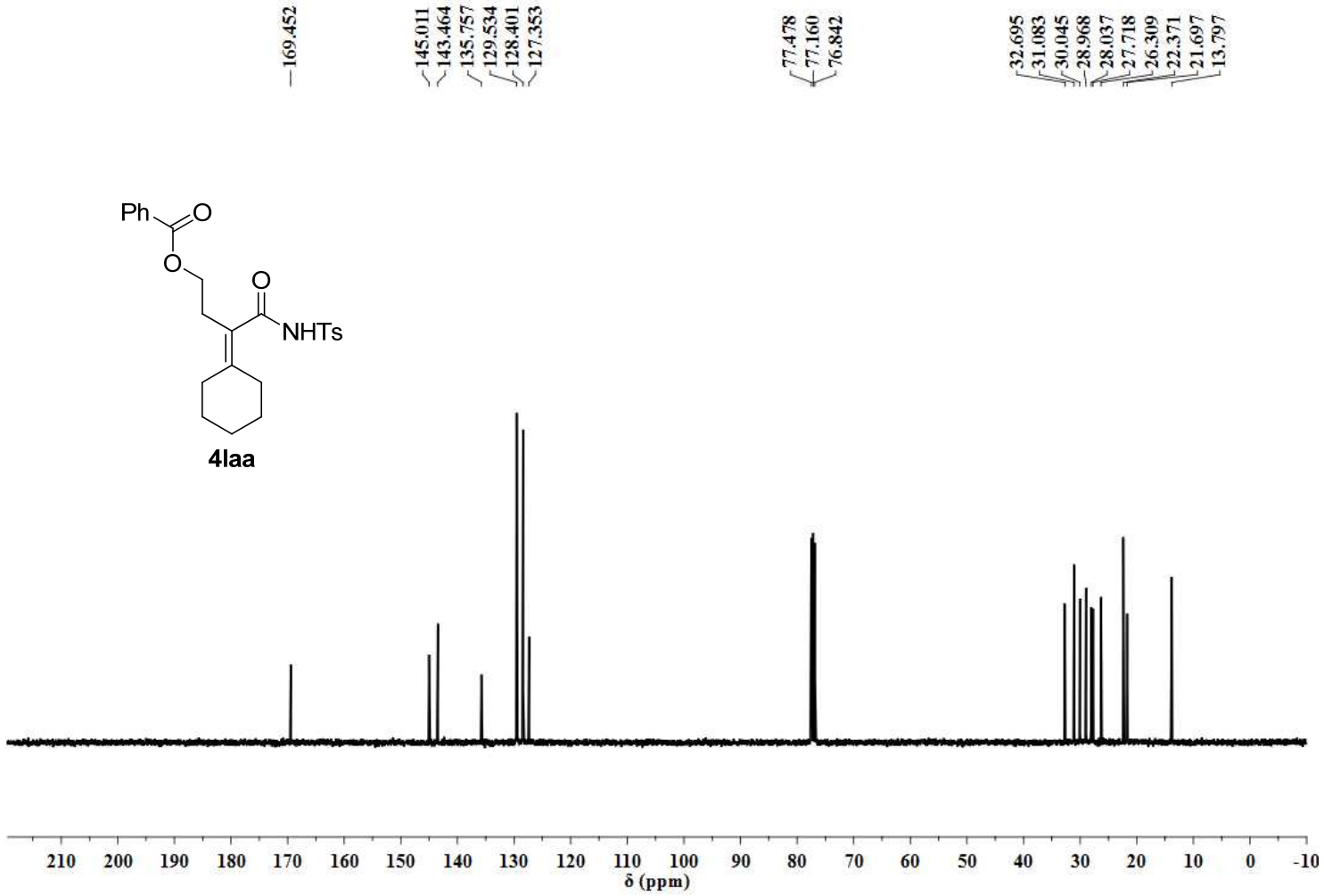
8.030
8.010
7.986
7.966
7.588
7.569
7.551
7.456
7.437
7.418
7.322
7.302
4.328
4.313
4.297
2.626
2.610
2.595
2.414
2.077
2.063
2.050
2.024
1.418
1.378
Ph
O
O
O
NHTs
4laa
0.96
3.96
0.99
1.98
1.98
2.00
1.98
3.01
4.02
6.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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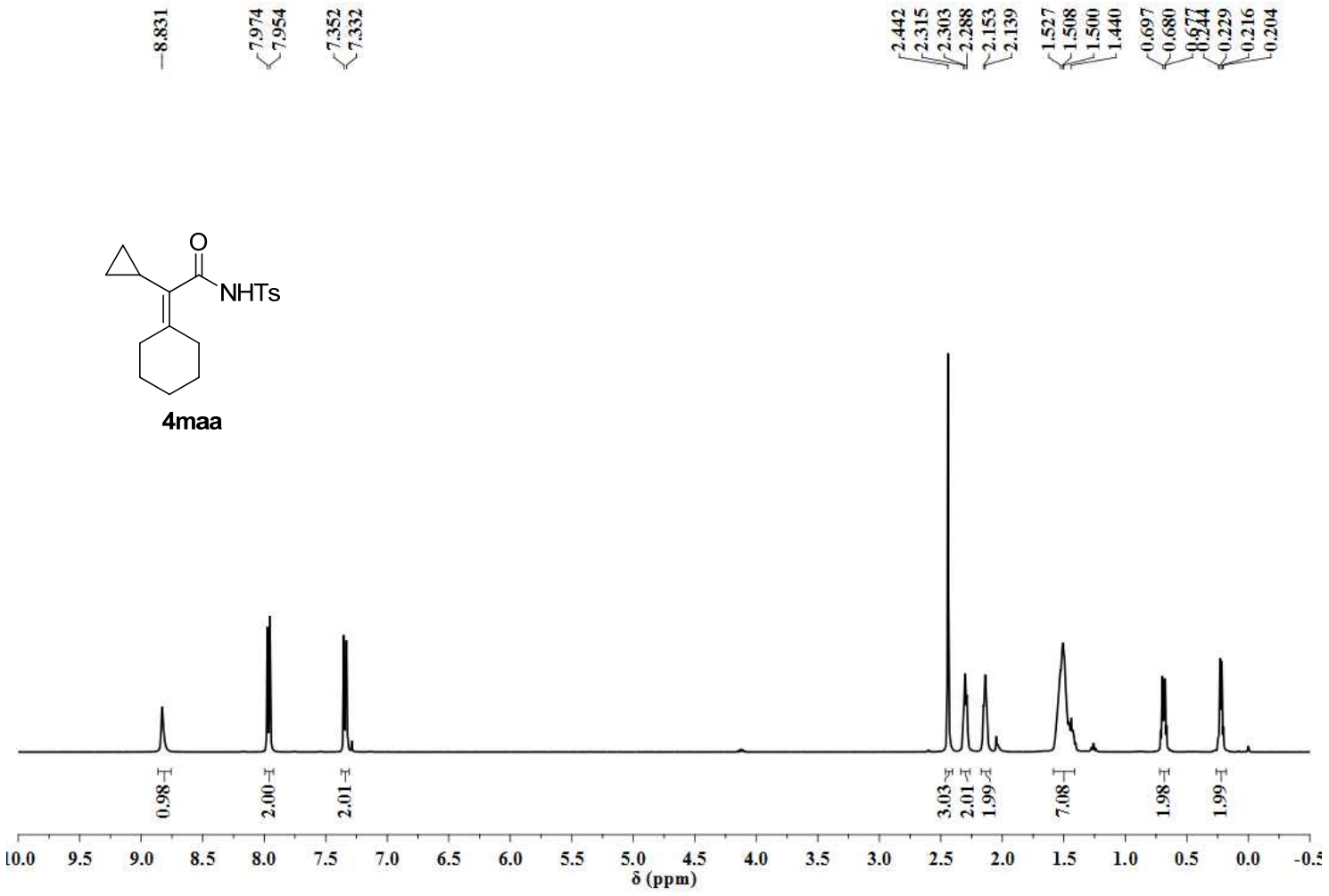
145.011
143.464
135.757
129.534
128.401
127.353
77.478
77.160
76.842
32.695
31.083
30.045
28.968
28.037
27.718
26.309
22.371
21.697
13.797
Ph
O
O
O
NHTs
4laa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.954
7.352
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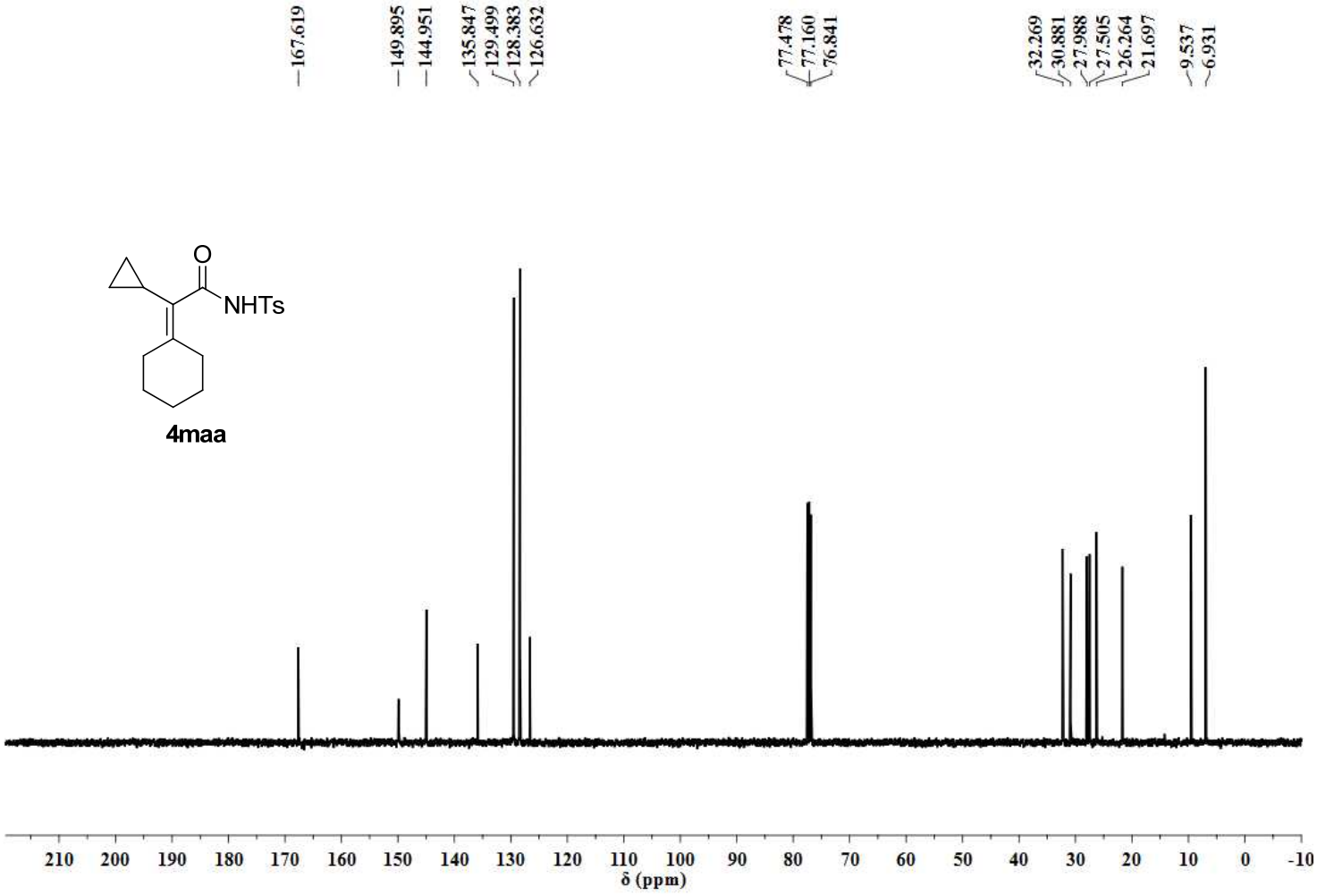
2.315
2.303
2.288
2.153
2.139
1.527
1.508
1.500
1.440
0.697
0.680
0.677
0.244
0.229
0.216
0.204
O
NHTs
4maa
0.98
2.00
2.01
3.03
2.01
1.99
7.08
1.98
1.99
δ (ppm)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135.847
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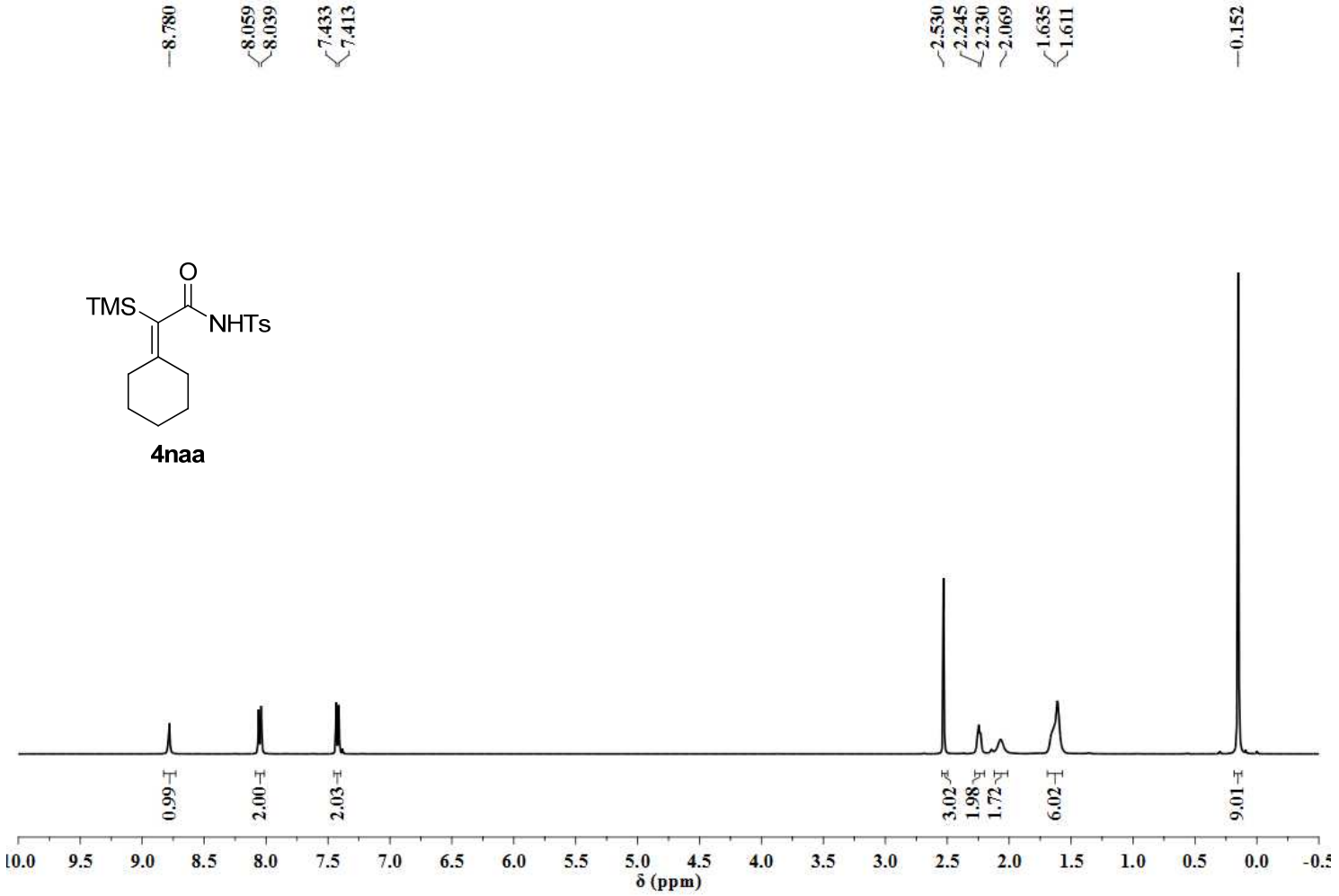
128.383
126.632
77.478
77.160
76.841
32.269
30.881
27.988
27.505
26.264
21.697
9.537
6.931
O
NHTs
4maa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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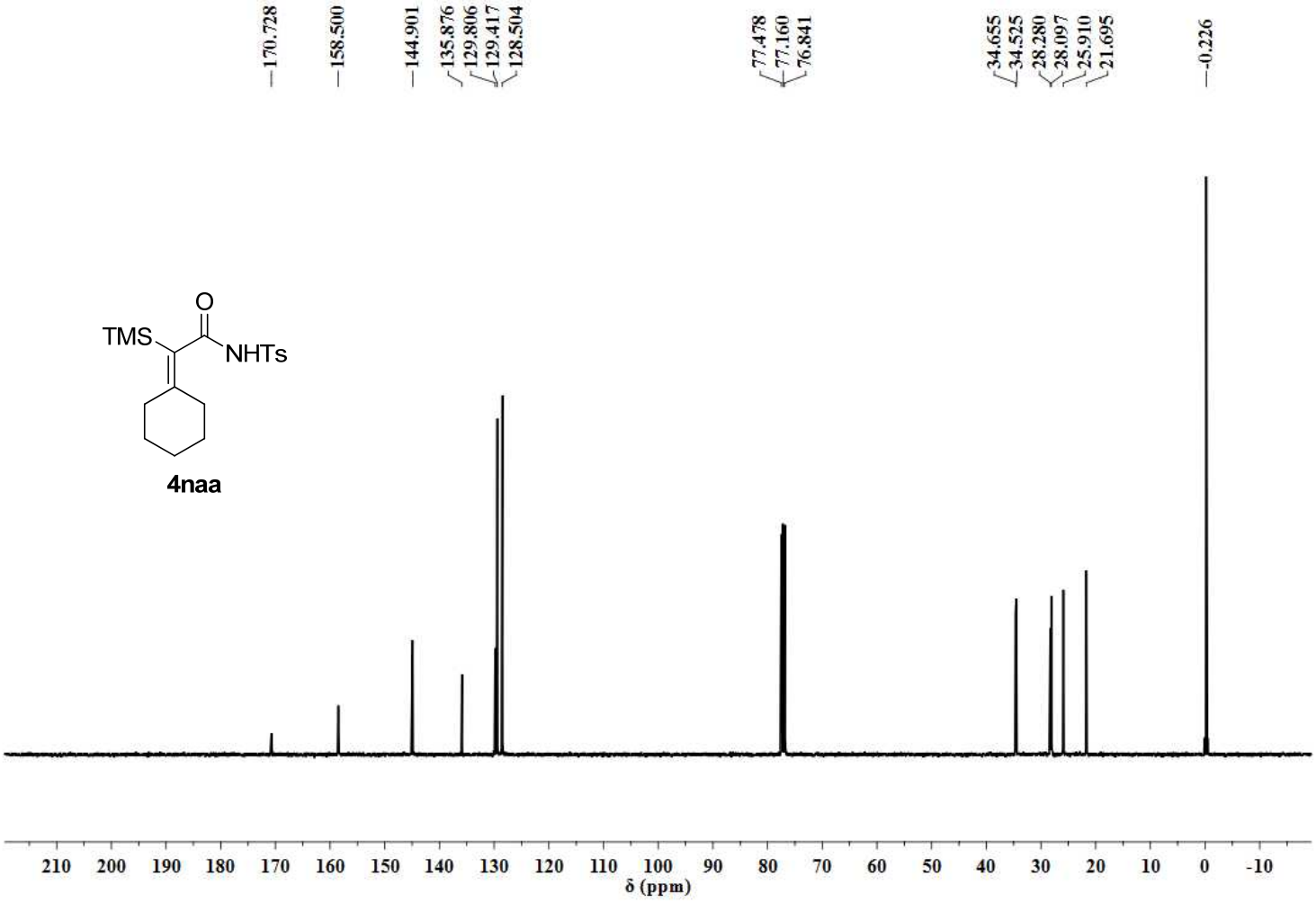
8.059
8.039
7.433
7.413
2.530
2.245
2.230
2.069
1.635
1.611
0.152
TMS
O
NHTs
4naa
0.99
2.00
2.03
3.02
1.98
1.72
6.02
9.01
δ (ppm)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129.417
128.504
77.478
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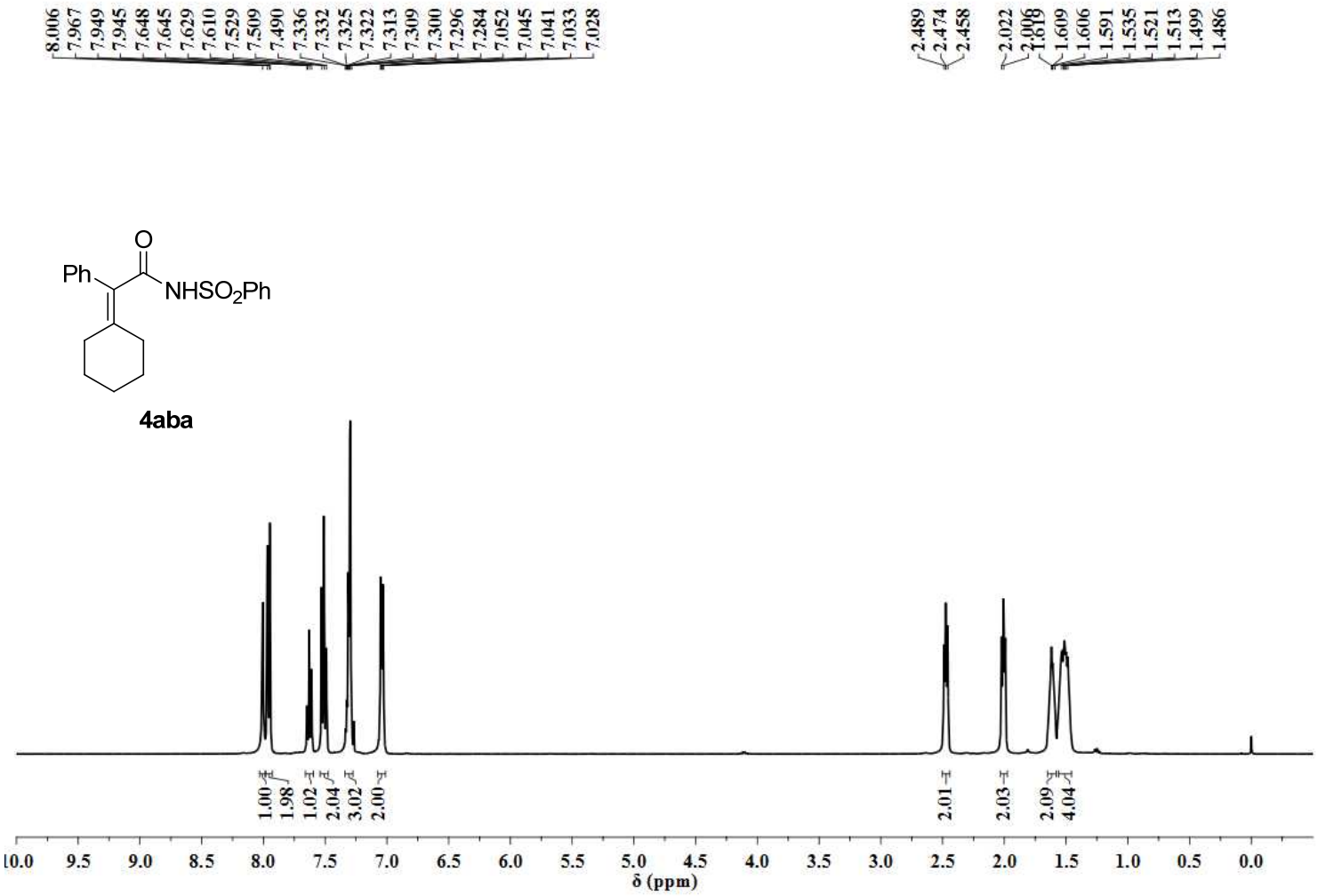
76.841
34.655
34.525
28.280
28.097
25.910
21.695
-0.226
TMS
O
NHTs
4naa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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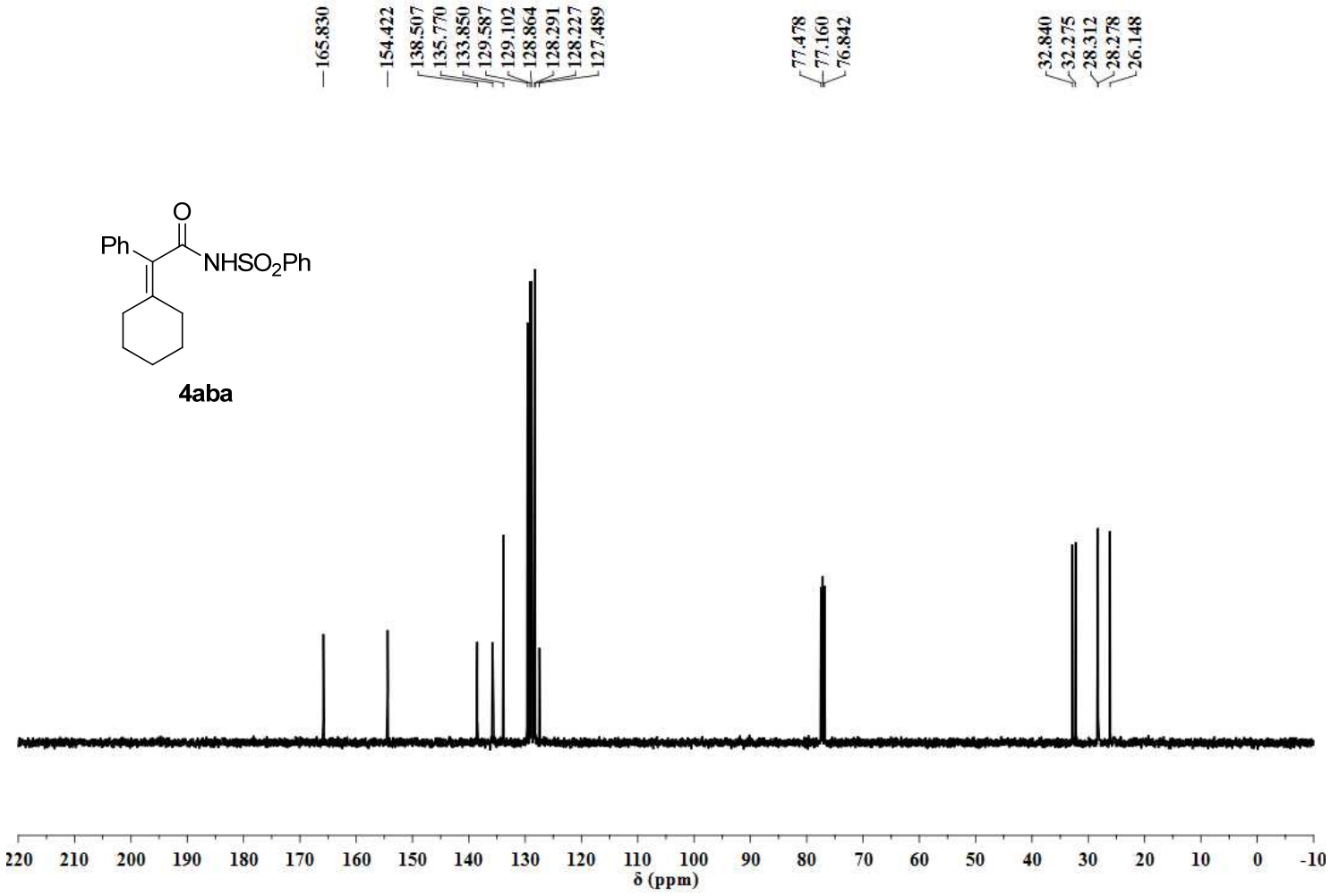
7.336
7.332
7.325
7.322
7.313
7.309
7.300
7.296
7.284
7.052
7.045
7.041
7.033
7.028
2.489
2.474
2.458
2.022
2.006
1.619
1.609
1.606
1.591
1.535
1.521
1.513
1.499
1.486
O
Ph
NHSO2Ph
4aba
1.00
1.98
1.02
2.04
3.02
2.00
2.01
2.03
2.09
4.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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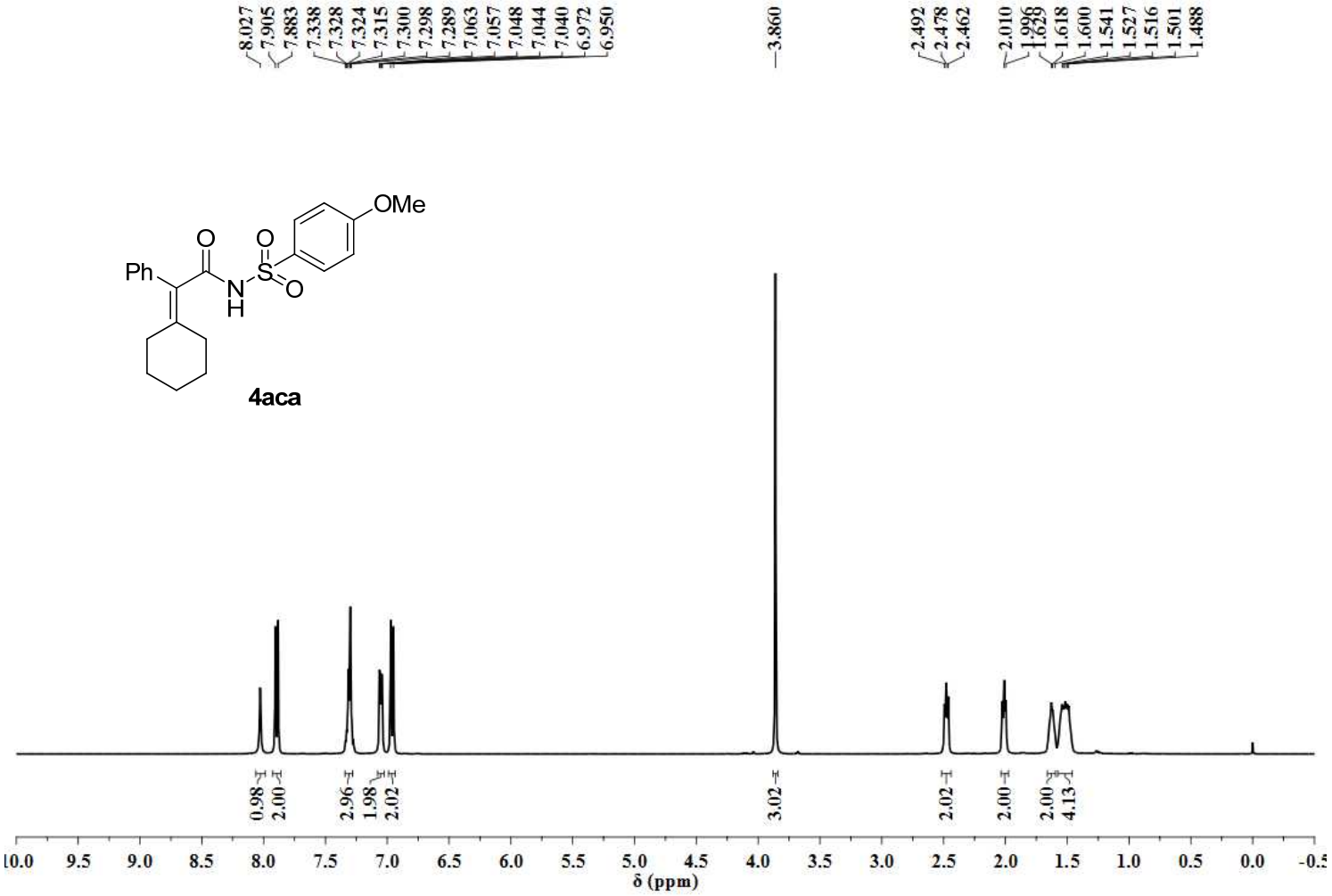
129.102
128.864
128.291
128.227
127.489
77.478
77.160
76.842
32.840
32.275
28.312
28.278
26.148
O
Ph
NHSO2Ph
4aba
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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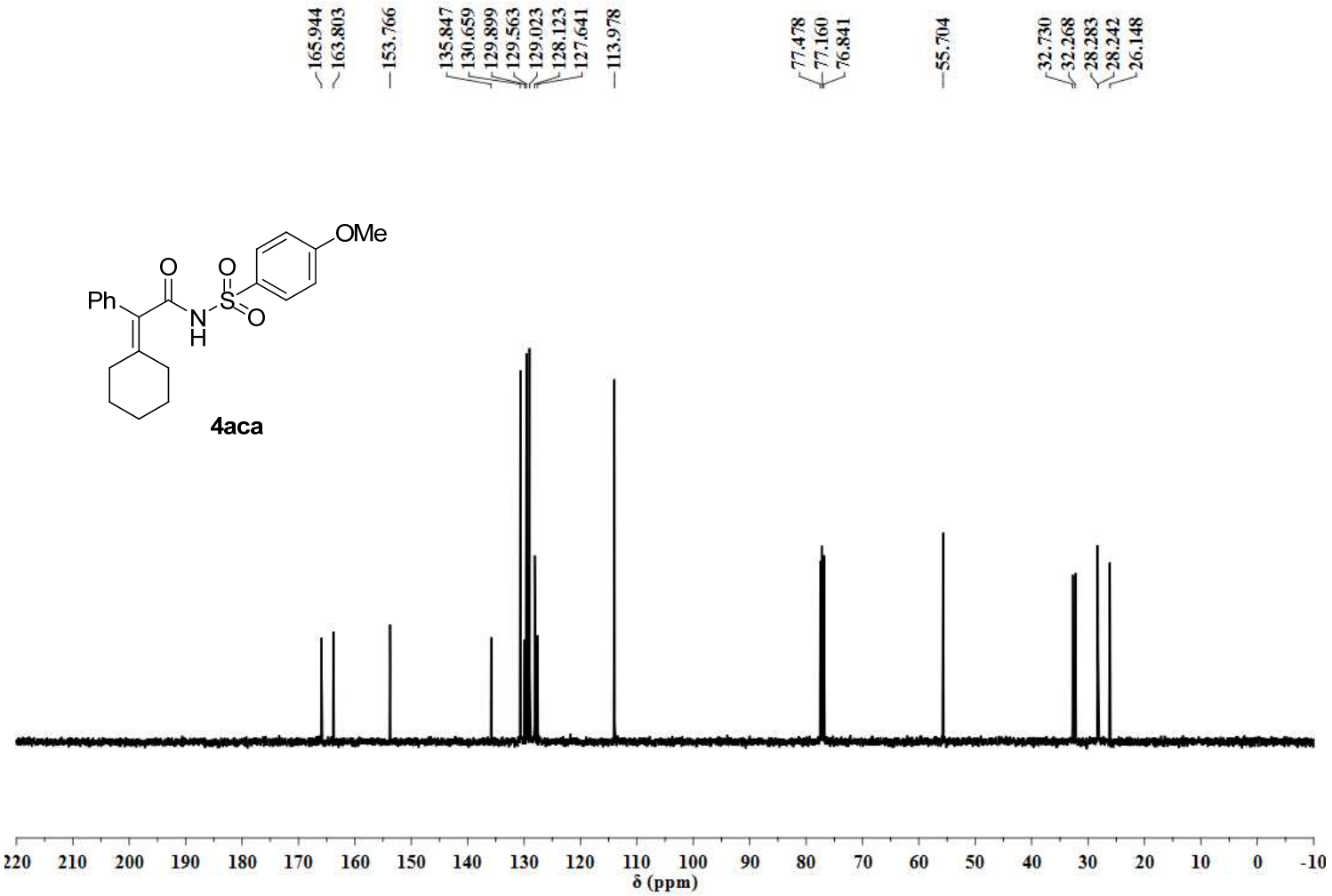
7.063
7.057
7.048
7.044
7.040
6.972
6.950
3.860
2.492
2.478
2.462
2.010
1.996
1.629
1.618
1.600
1.541
1.527
1.516
1.501
1.488
OMe
O
O
Ph
N
H
S
O
4aca
0.98
2.00
2.96
1.98
2.02
3.02
2.02
2.00
2.00
4.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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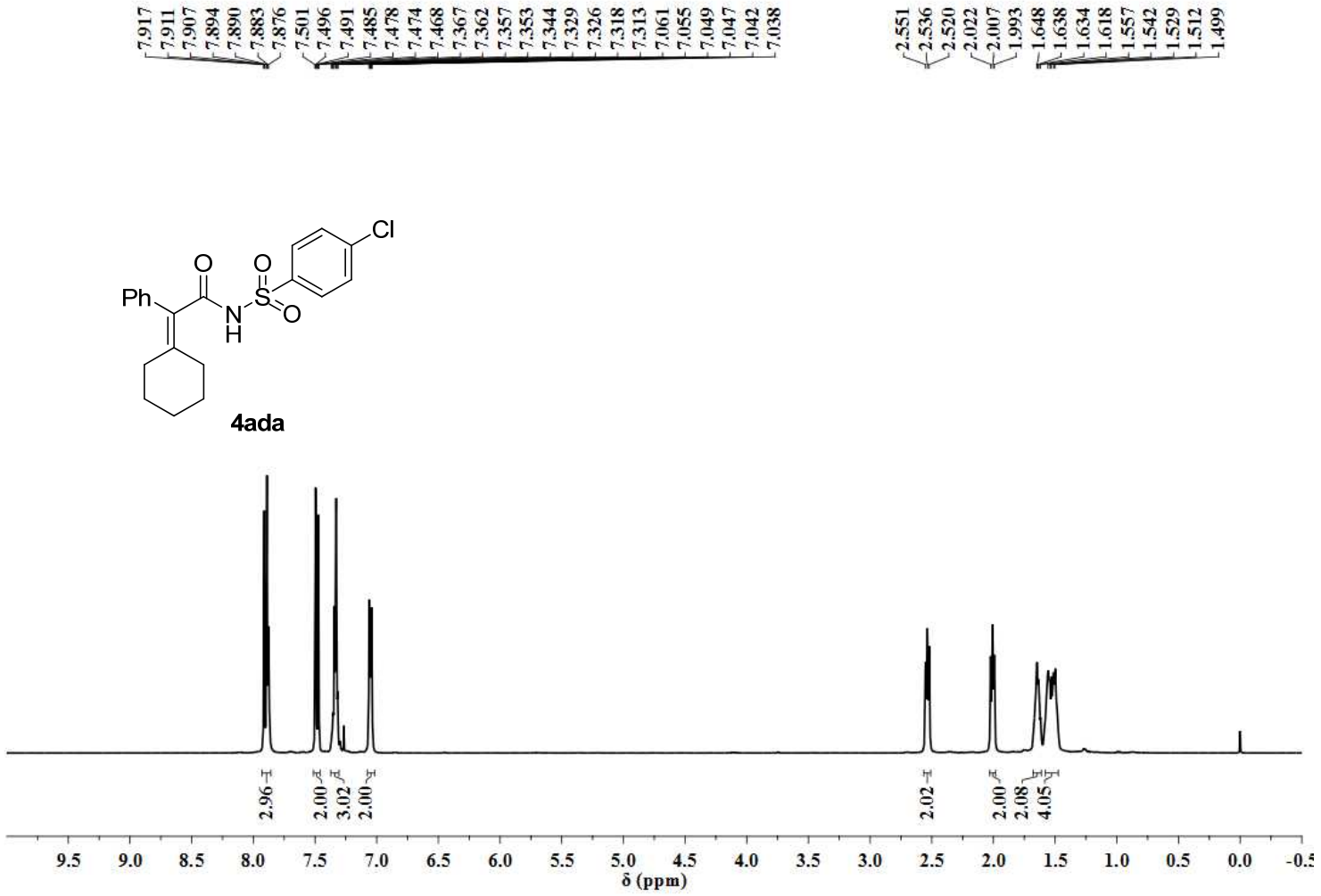
128.123
127.641
113.978
77.478
77.160
76.841
55.704
32.730
32.268
28.283
28.242
26.148
OMe
O
O
Ph
N
H
S
O
4aca
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.501
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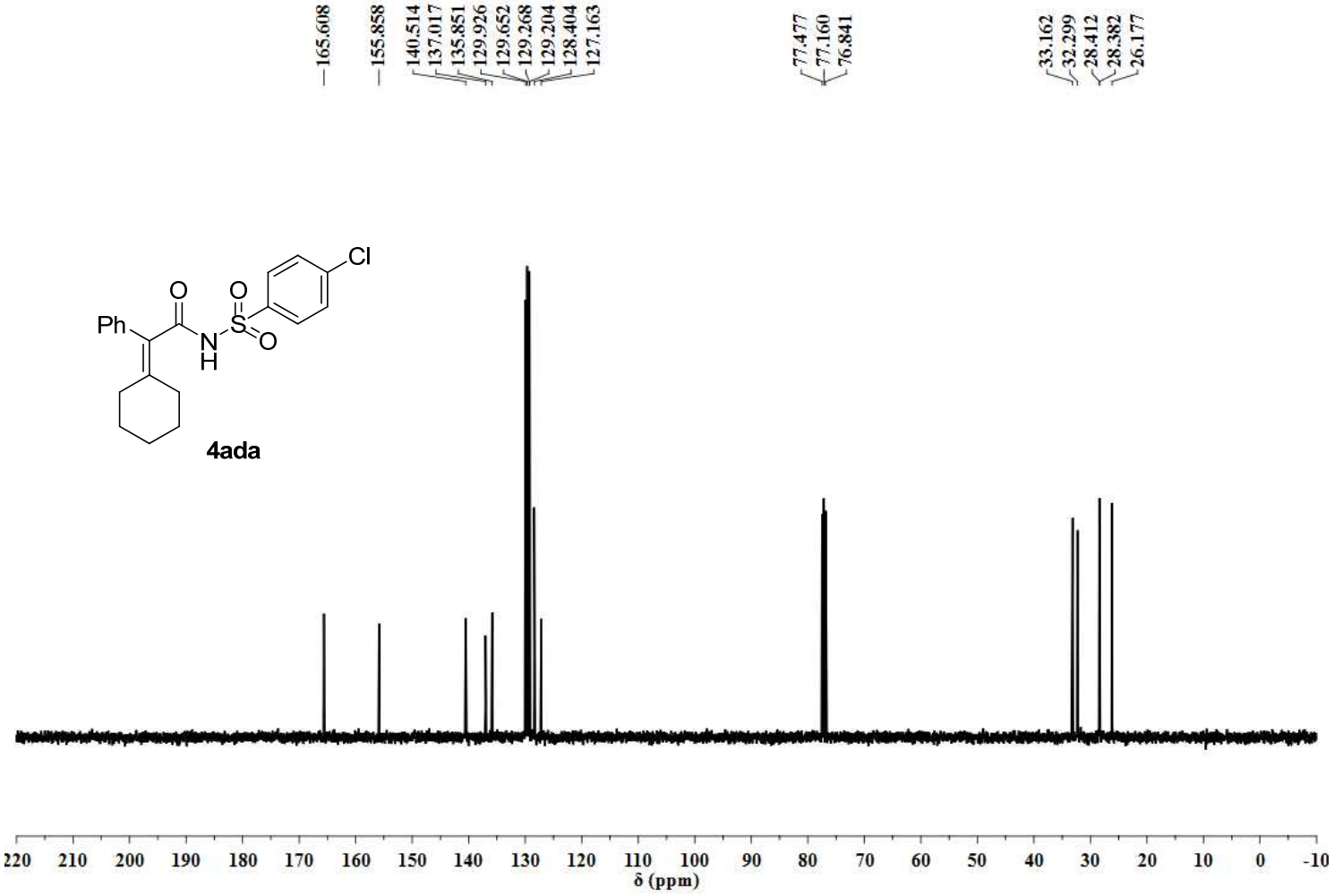
7.491
7.485
7.478
7.474
7.468
7.367
7.362
7.357
7.353
7.344
7.329
7.326
7.318
7.313
7.061
7.055
7.049
7.047
7.042
7.038
2.551
2.536
2.520
2.022
2.007
1.993
1.648
1.638
1.634
1.618
1.557
1.542
1.529
1.512
1.499
Cl
O
O
Ph
N
H
S
O
4ada
2.96
2.00
3.02
2.00
2.02
2.00
2.08
4.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
δ (ppm)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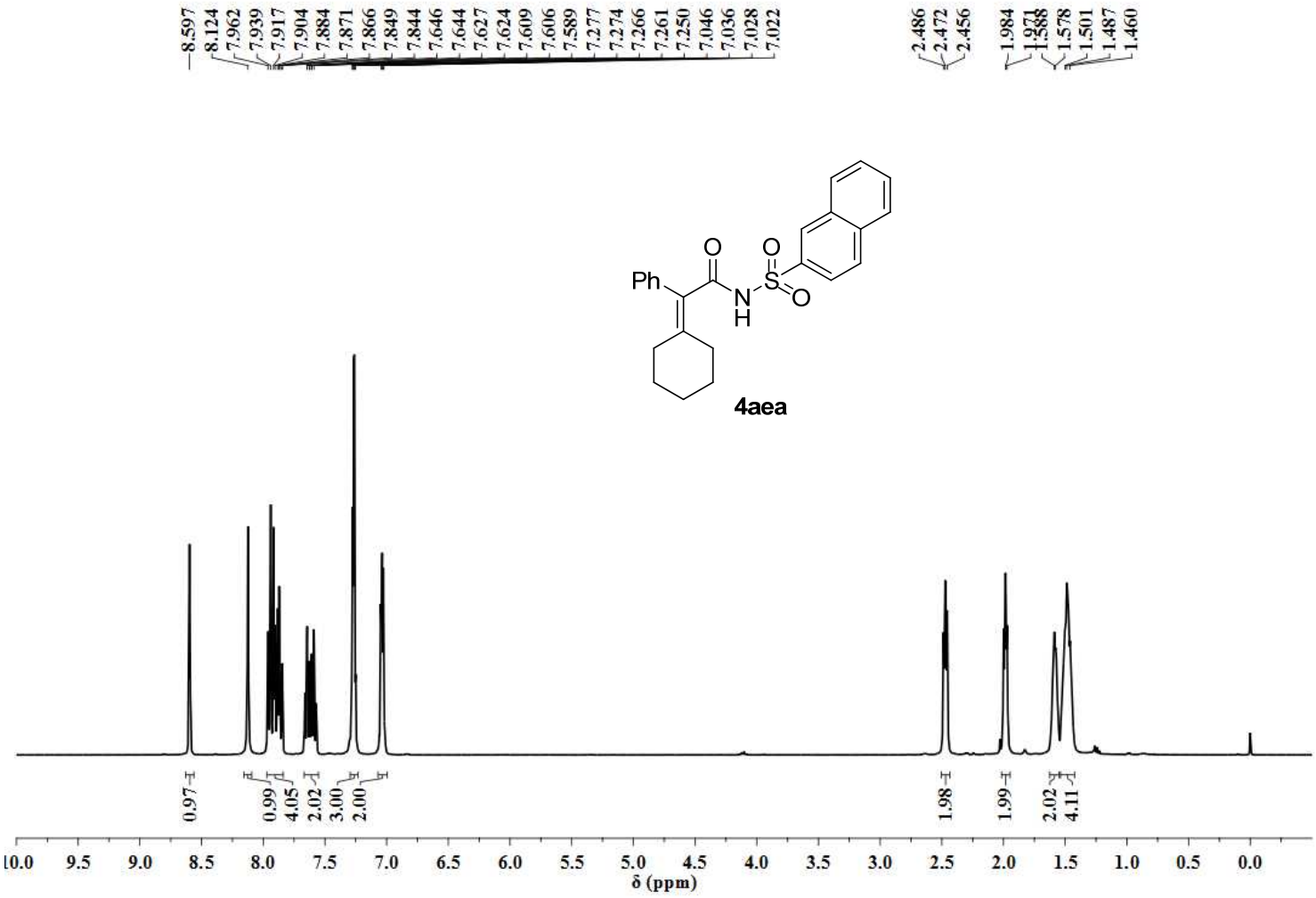
155.858
140.514
137.017
135.851
129.926
129.652
129.268
129.204
128.404
127.163
77.477
77.160
76.841
33.162
32.299
28.412
28.382
26.177
Cl
O
O
Ph
N
H
S
O
4ada
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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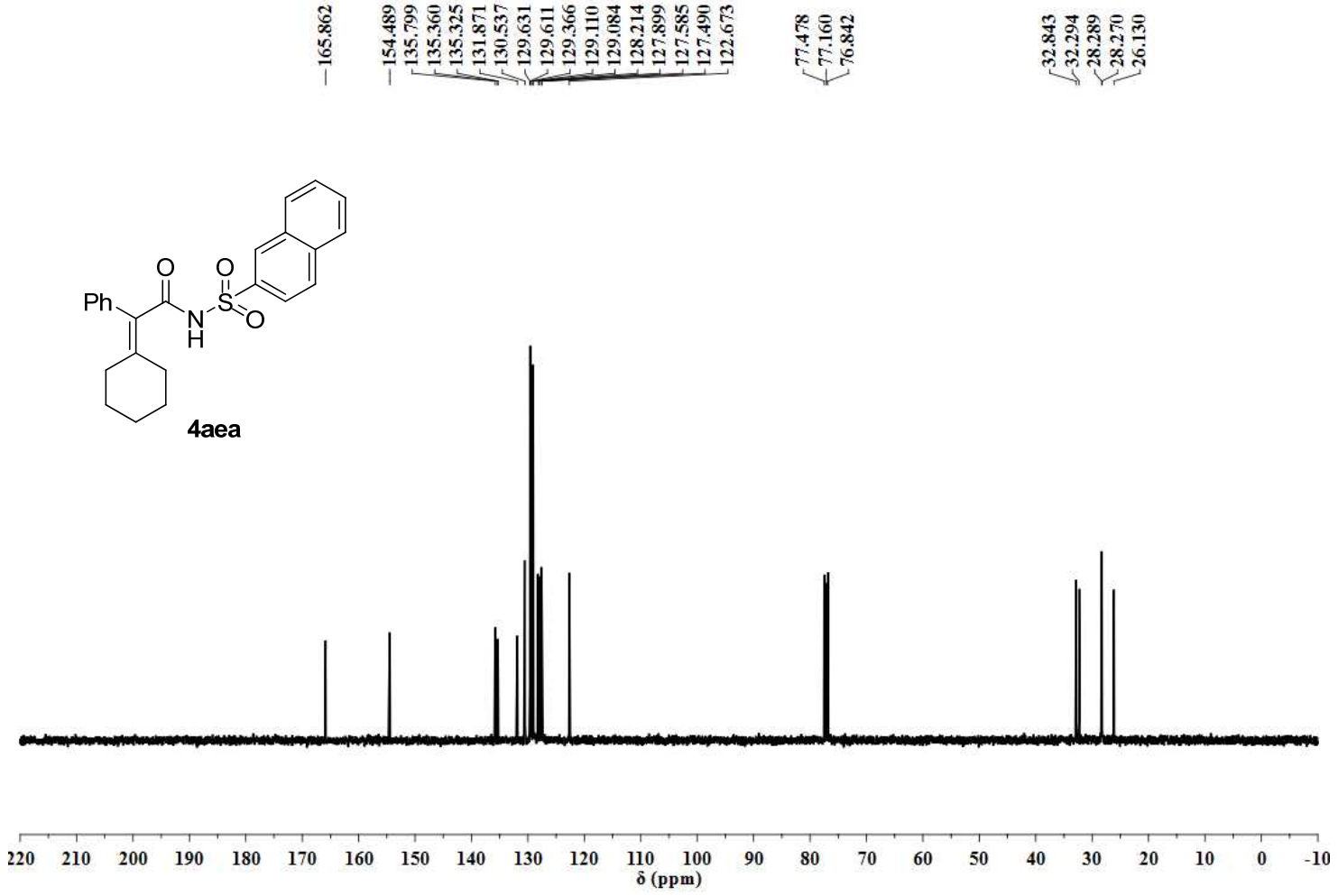
8.124
7.962
7.939
7.917
7.904
7.884
7.871
7.866
7.849
7.844
7.646
7.644
7.627
7.624
7.609
7.606
7.589
7.277
7.274
7.266
7.261
7.250
7.046
7.036
7.028
7.022
2.486
2.472
2.456
1.984
1.971
1.588
1.578
1.501
1.487
1.460
Ph
O
O
S
N
H
O
4aea
0.97
0.99
4.05
2.02
3.00
2.00
1.98
1.99
2.02
4.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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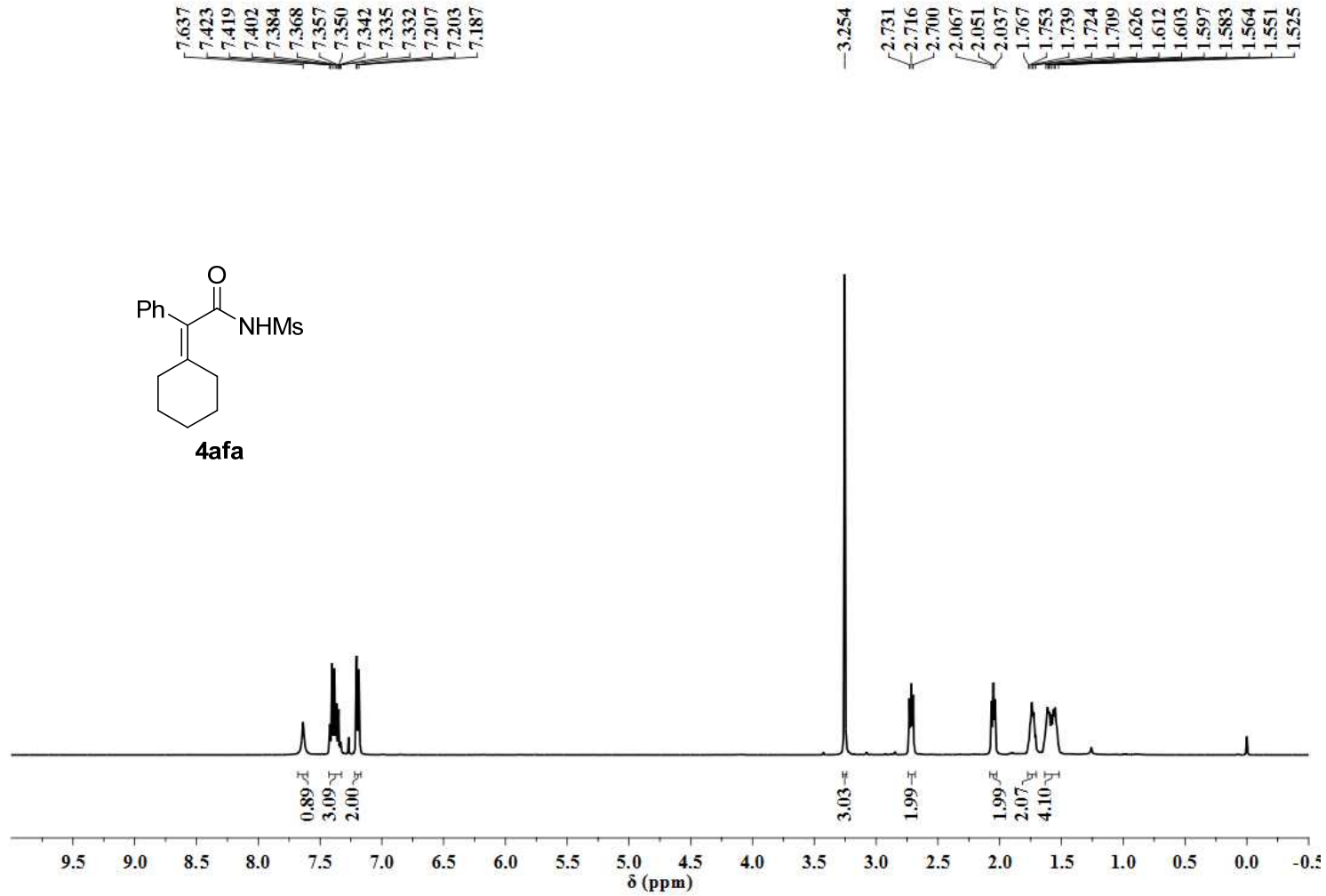
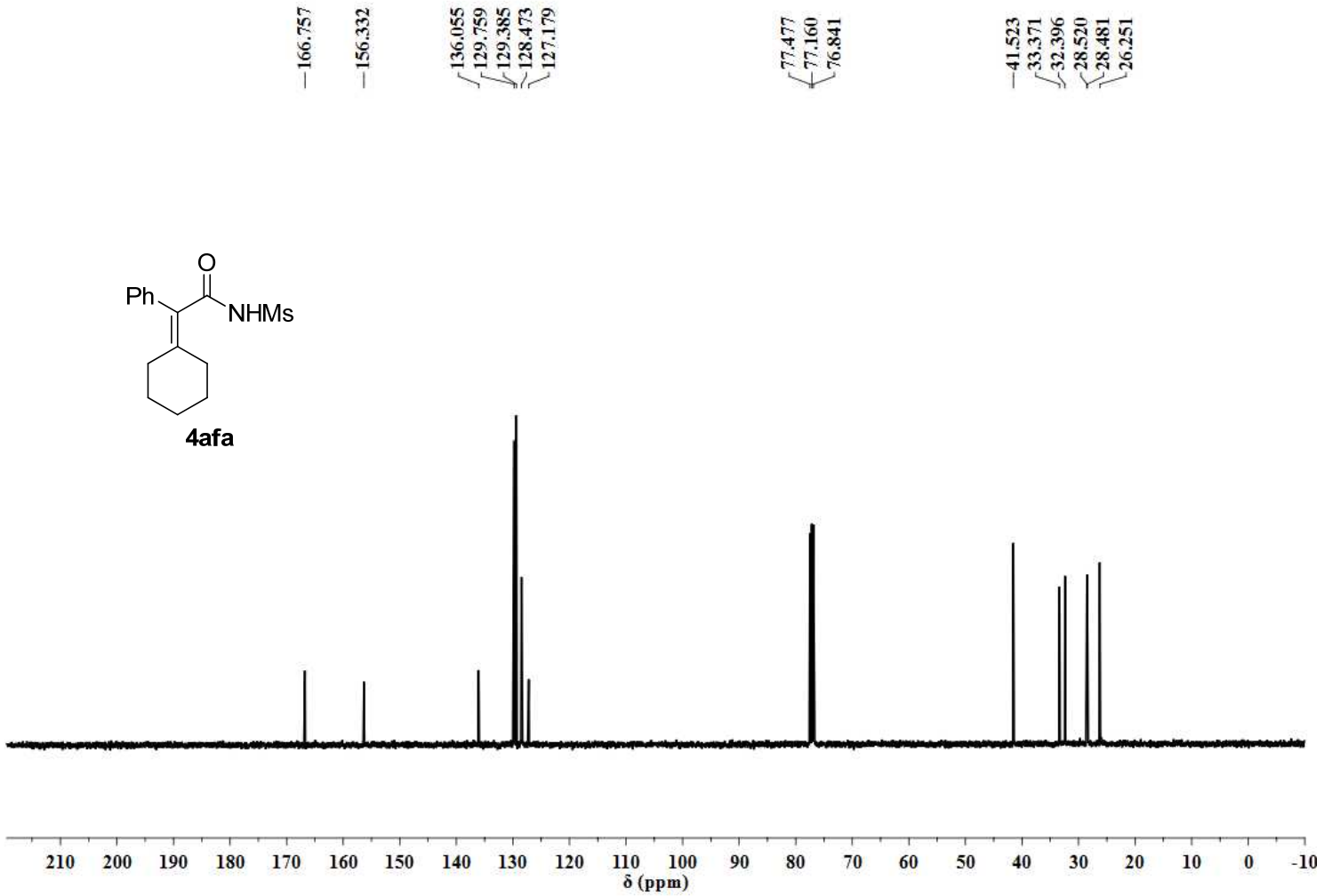
154.489
135.799
135.360
135.325
131.871
130.537
129.631
129.611
129.366
129.110
129.084
128.214
127.899
127.585
127.490
122.673
77.478
77.160
76.842
32.843
32.294
28.289
28.270
26.130
Ph
O
O
N
H
S
O
4aea
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.637
7.423
7.419
7.402
7.384
7.368
7.357
7.350
7.342
7.335
7.332
7.207
7.203
7.187
3.254
2.731
2.716
2.700
2.067
2.051
2.037
1.767
1.753
1.739
1.724
1.709
1.626
1.612
1.603
1.597
1.583
1.564
1.551
1.525
O
Ph
NHMs
4afa
0.89
3.09
2.00
3.03
1.99
1.99
2.07
4.10
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
δ (ppm)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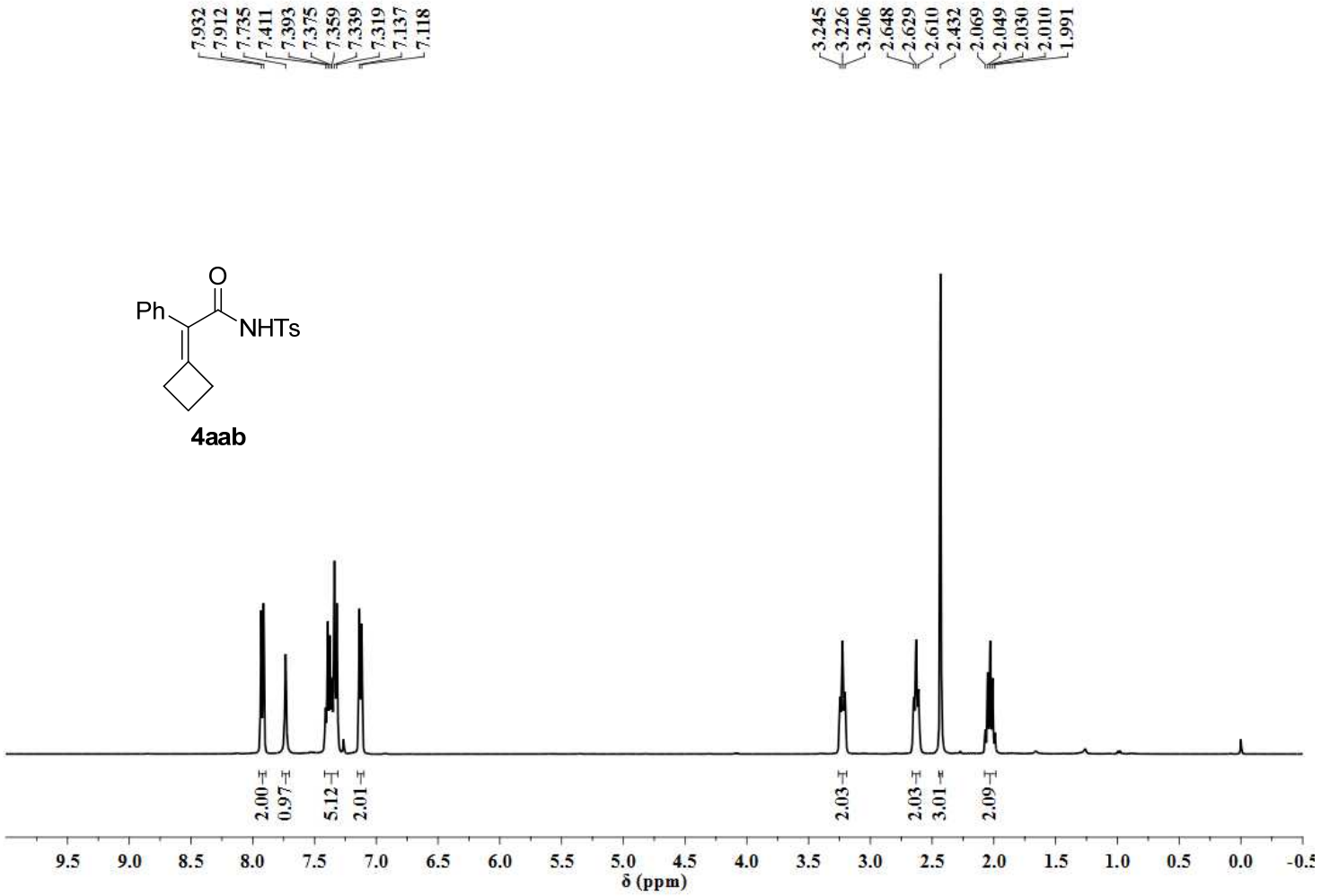
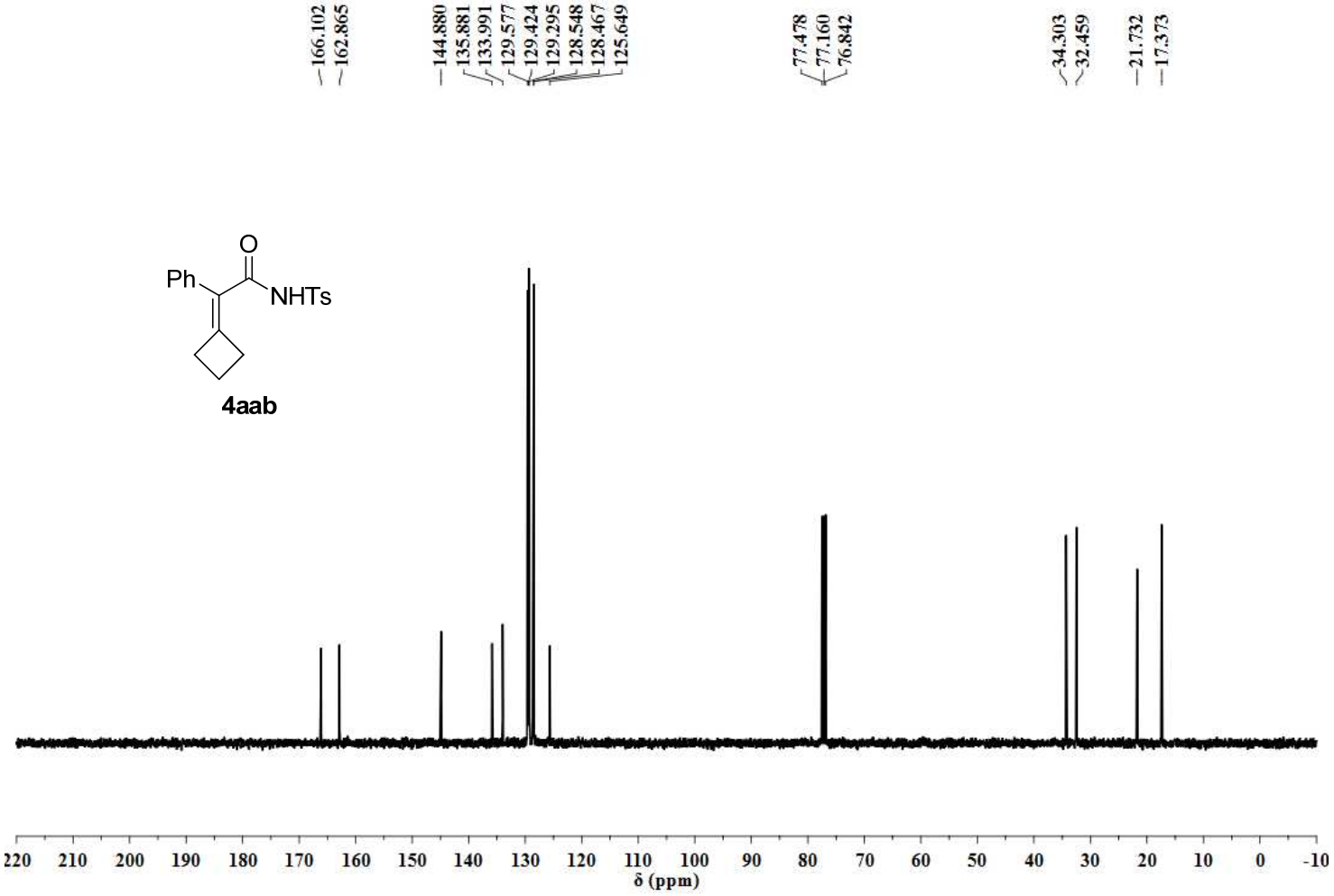
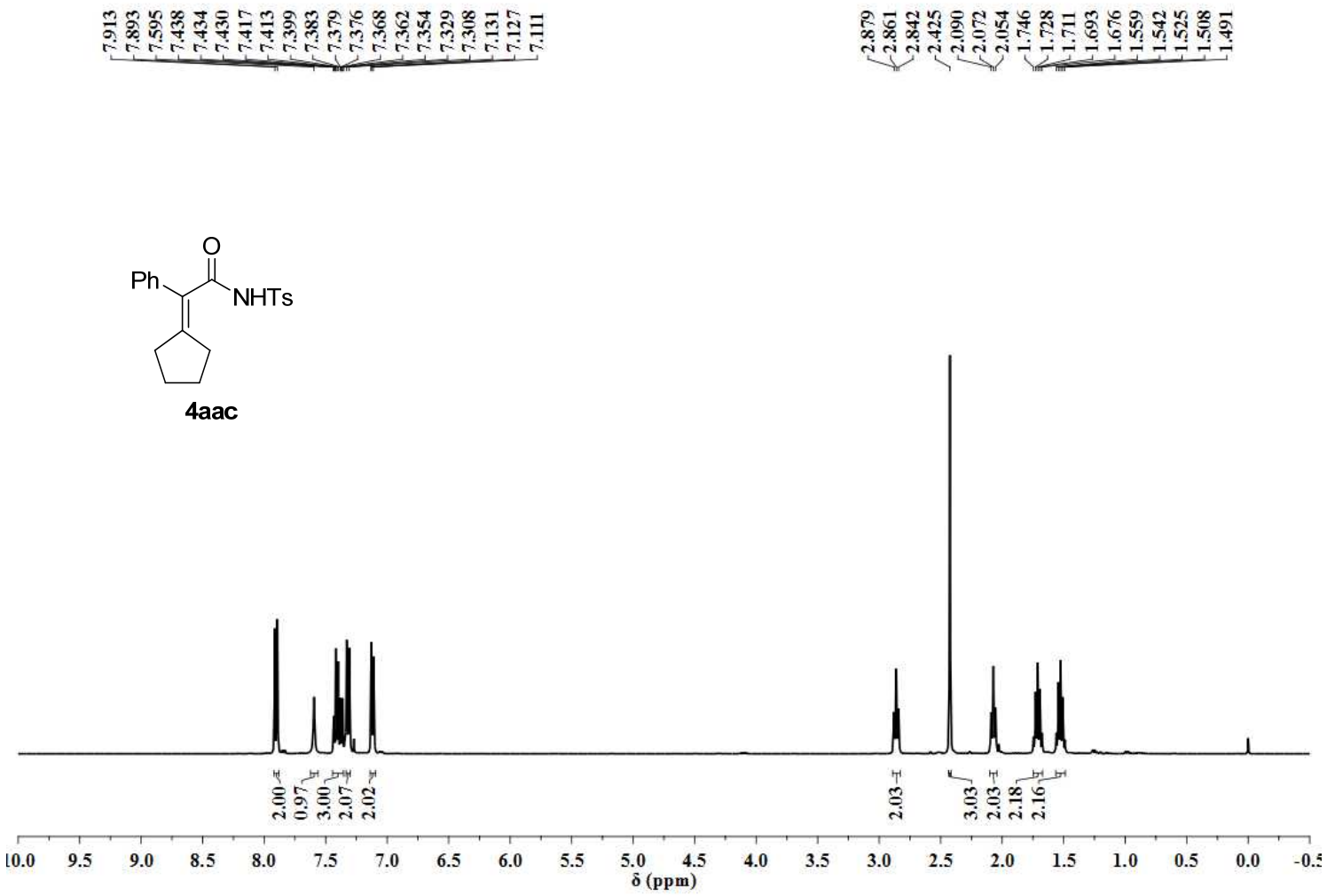
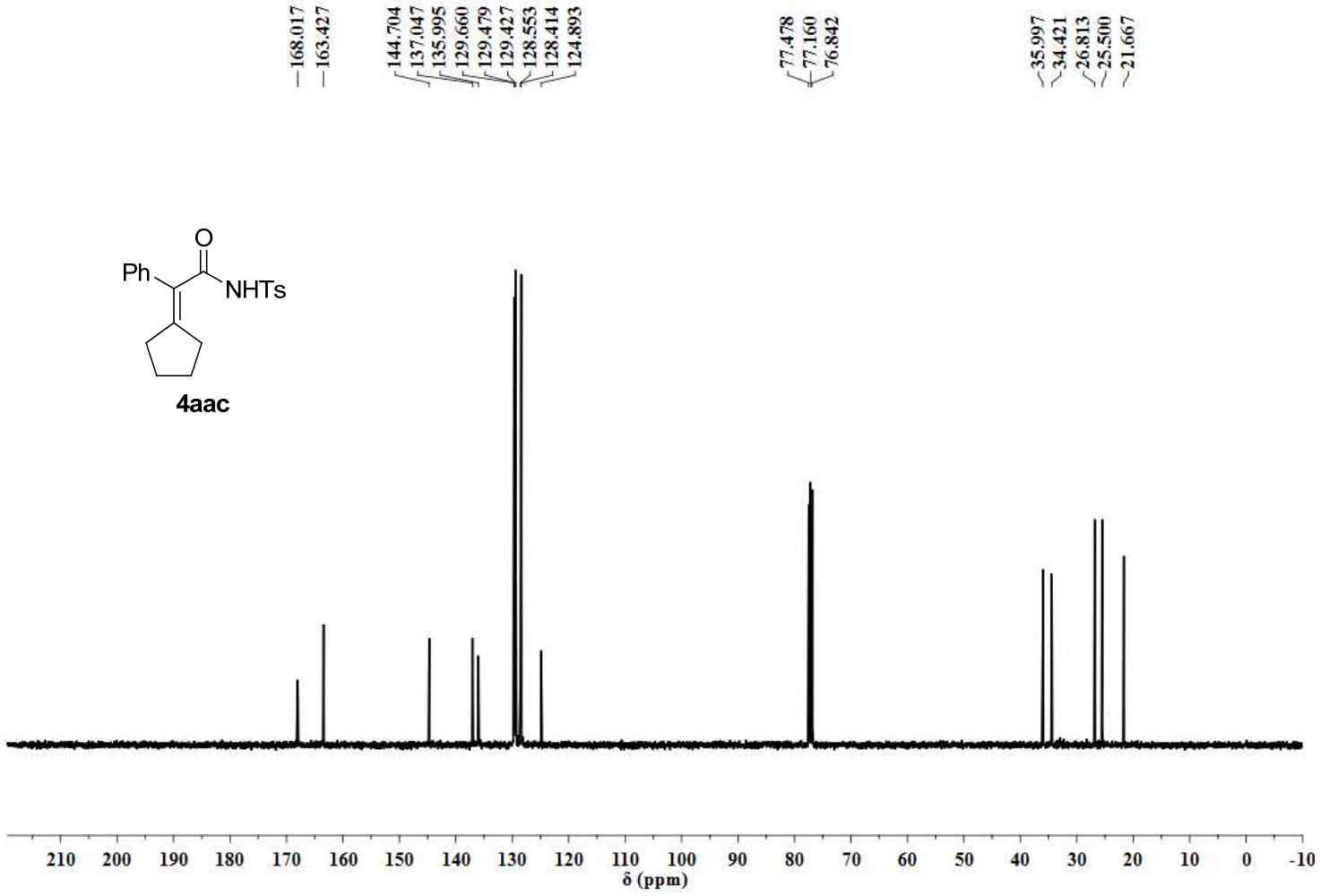
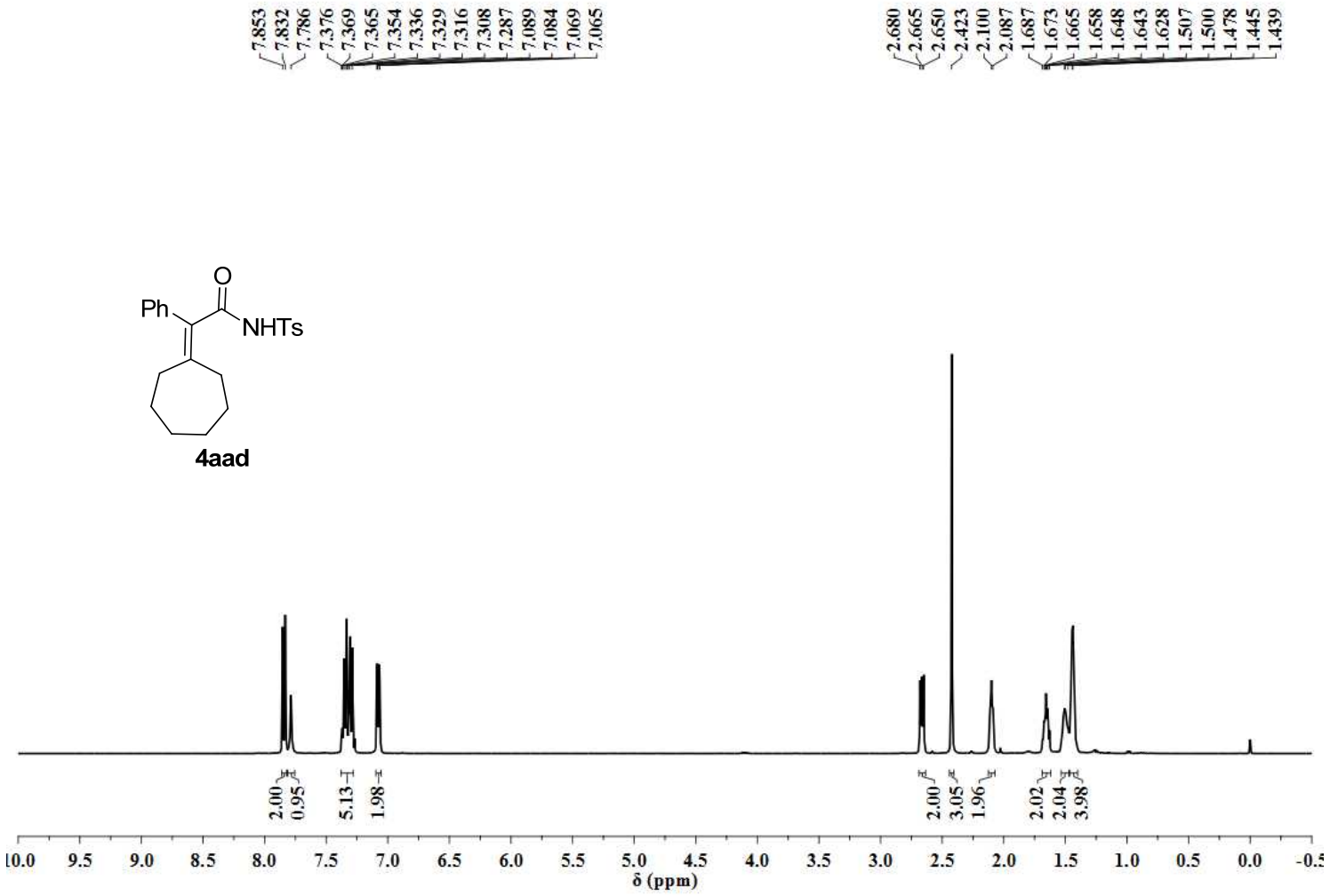
156.332
136.055
129.759
129.385
128.473
127.179
77.477
77.160
76.841
41.523
33.371
32.396
28.520
28.481
26.251
O
Ph
NHMs
4afa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

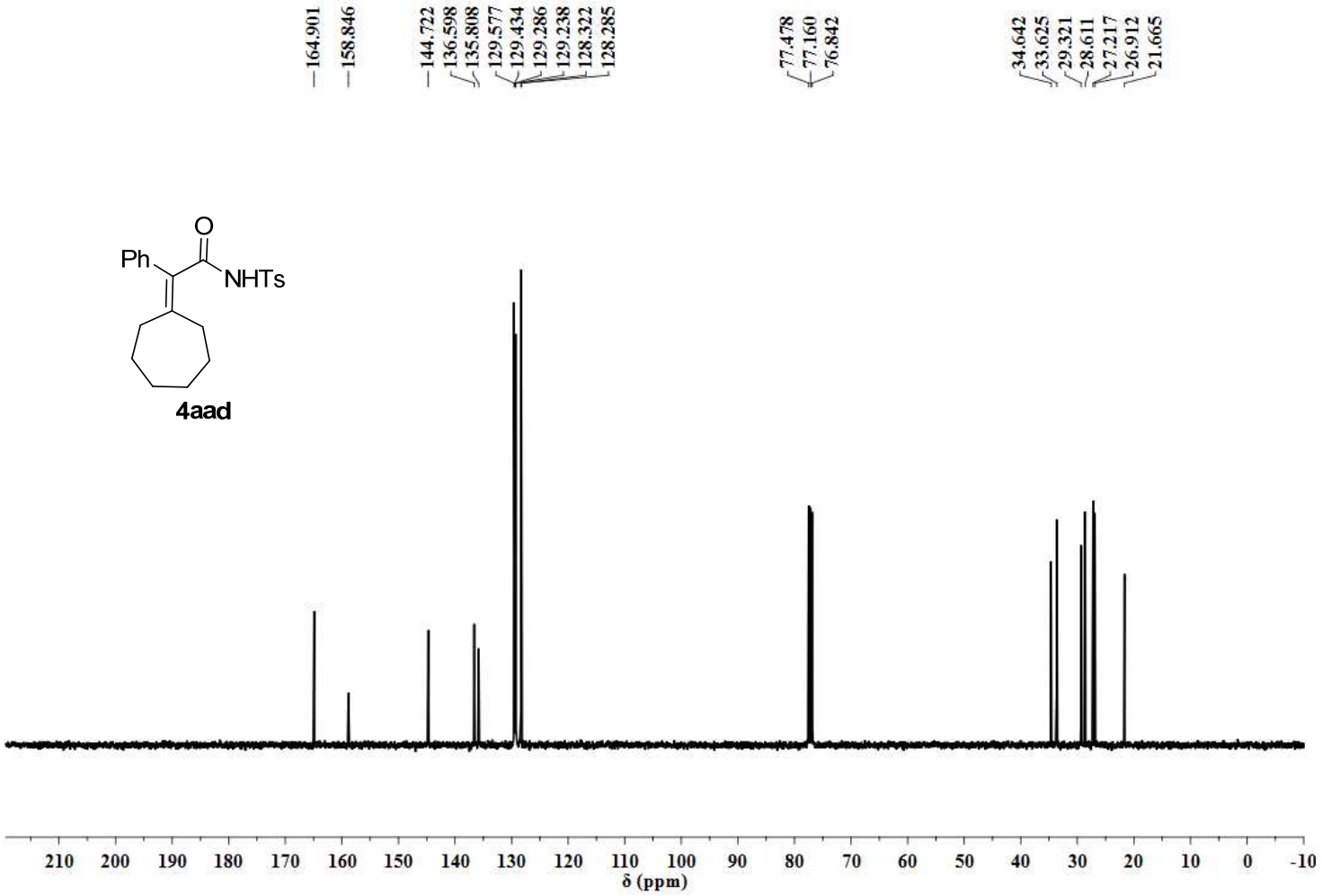

7.932
7.912
7.735
7.411
7.393
7.375
7.359
7.339
7.319
7.137
7.118
3.245
3.226
3.206
2.648
2.629
2.610
2.432
2.069
2.049
2.030
2.010
1.991
O
Ph
NHTs
4aab
2.00
0.97
5.12
2.01
2.03
2.03
3.01
2.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

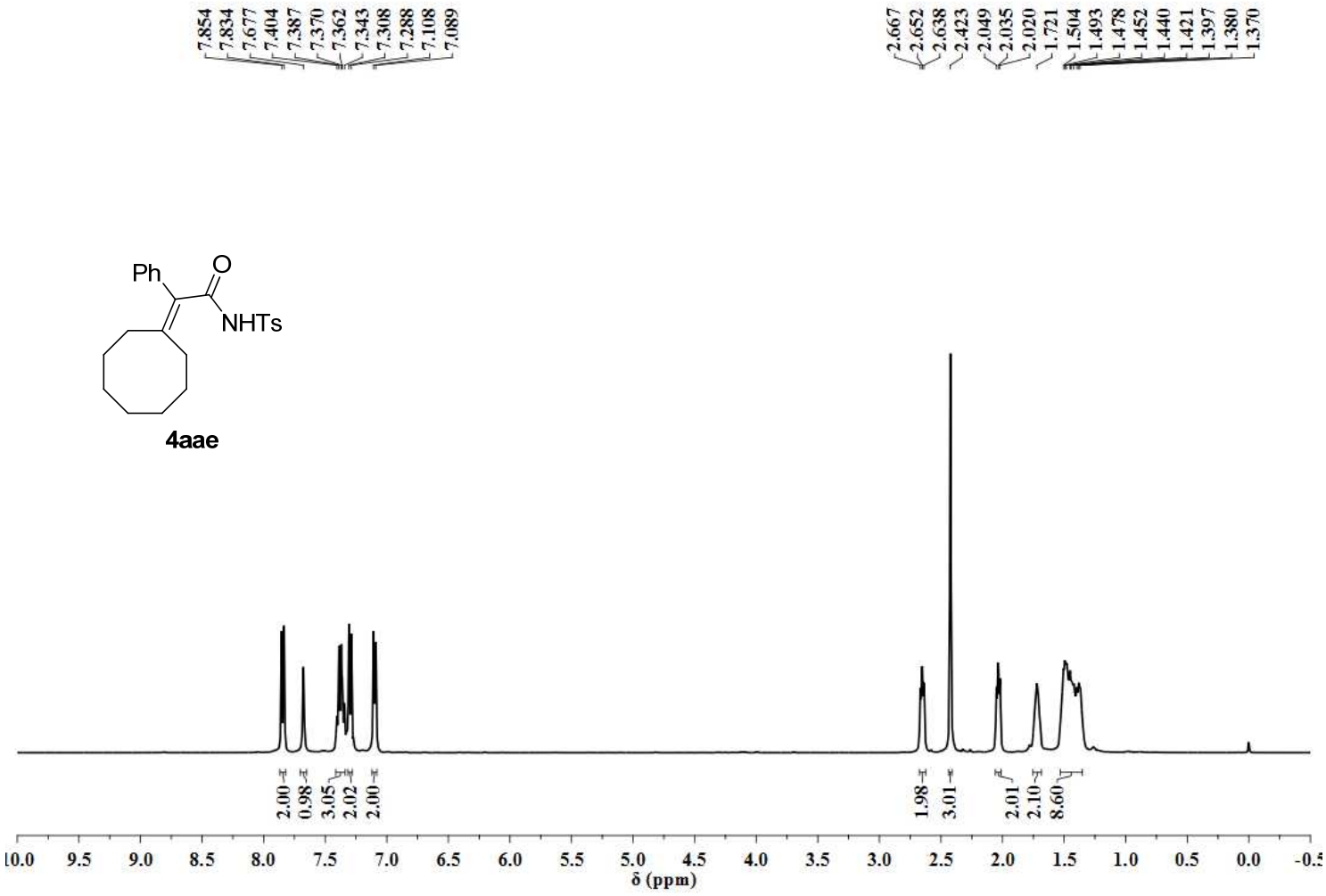

166.102
162.865
144.880
135.881
133.991
129.577
129.424
129.295
128.548
128.467
125.649
77.478
77.160
76.842
34.303
32.459
21.732
17.373
O
Ph
NHTs
4aab
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

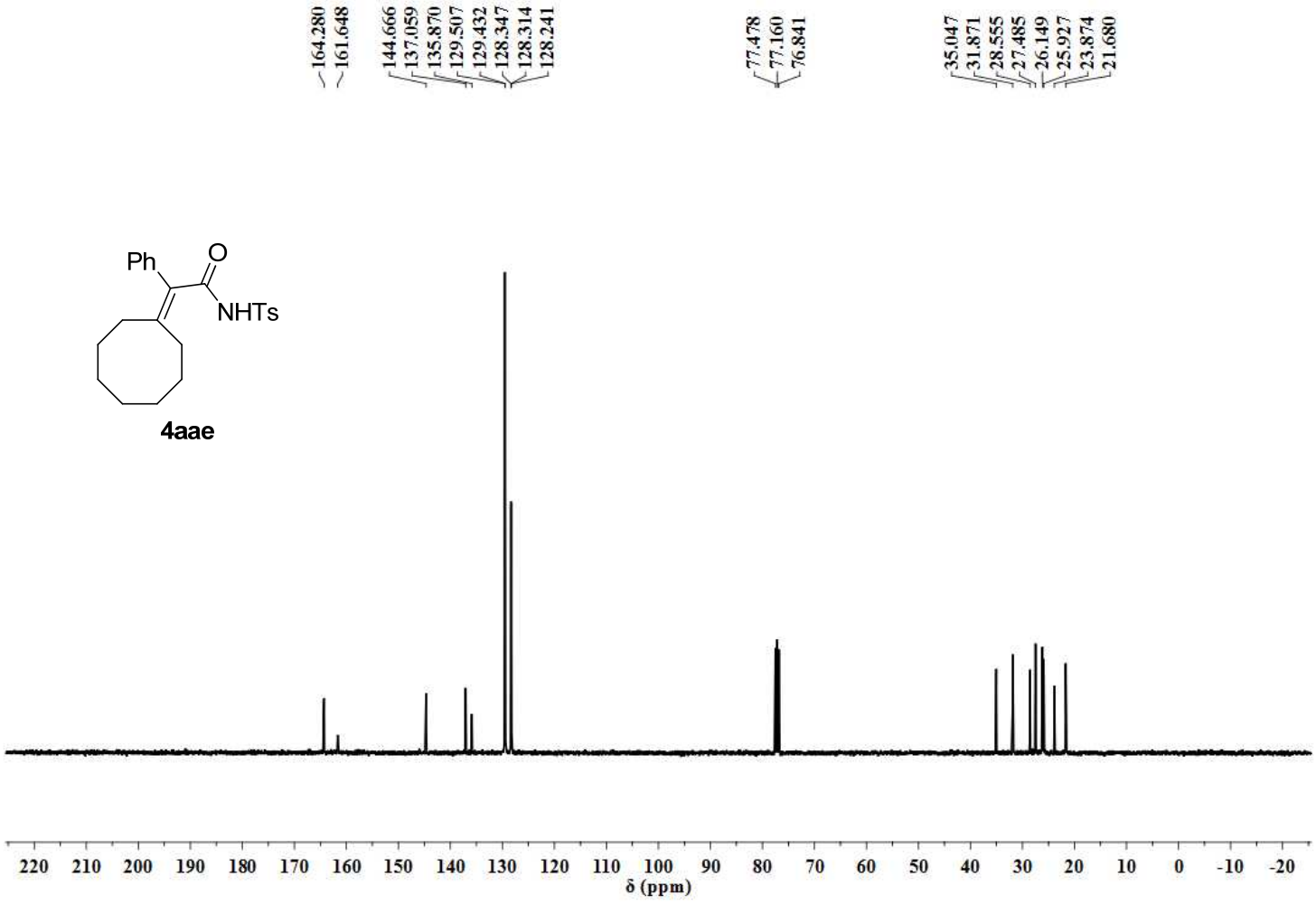

7.913
7.893
7.595
7.438
7.434
7.430
7.417
7.413
7.399
7.383
7.379
7.376
7.368
7.362
7.354
7.329
7.308
7.131
7.127
7.111
2.879
2.861
2.842
2.425
2.090
2.072
2.054
1.746
1.728
1.711
1.693
1.676
1.559
1.542
1.525
1.508
1.491
O
Ph
NHTs
4aac
2.00
0.97
3.00
2.07
2.02
2.03
3.03
2.03
2.18
2.16
δ (ppm)

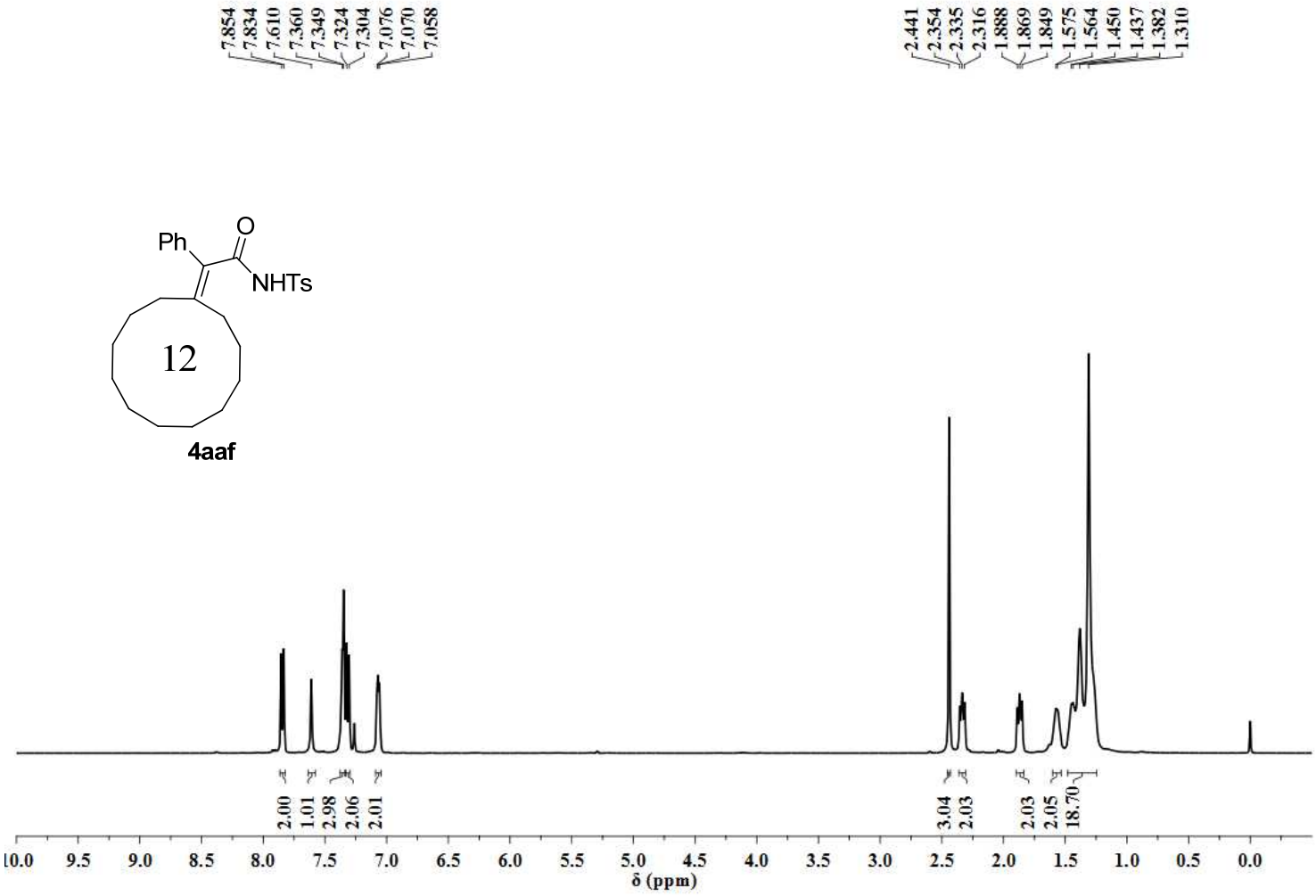

168.017
163.427
144.704
137.047
135.995
129.660
129.479
129.427
128.553
128.414
124.893
77.478
77.160
76.842
35.997
34.421
26.813
25.500
21.667
O
Ph
NHTs
4aac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

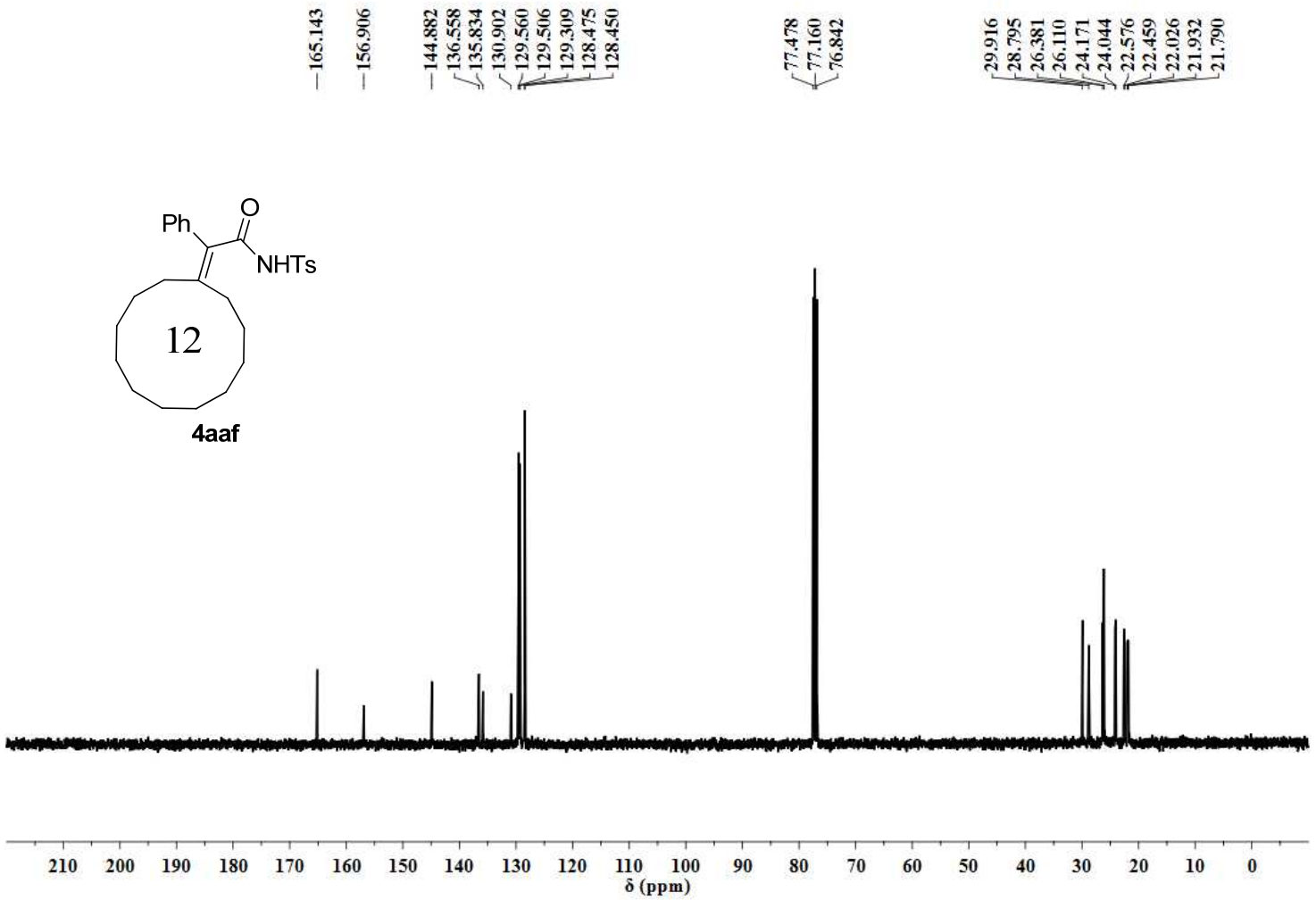

7.853
7.832
7.786
7.376
7.369
7.365
7.354
7.336
7.329
7.316
7.308
7.287
7.089
7.084
7.069
7.065
2.680
2.665
2.650
2.423
2.100
2.087
1.687
1.673
1.665
1.658
1.648
1.643
1.628
1.507
1.500
1.478
1.445
1.439
O
Ph
NHTs
4aad
2.00
0.95
5.13
1.98
2.00
3.05
1.96
2.02
2.04
3.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

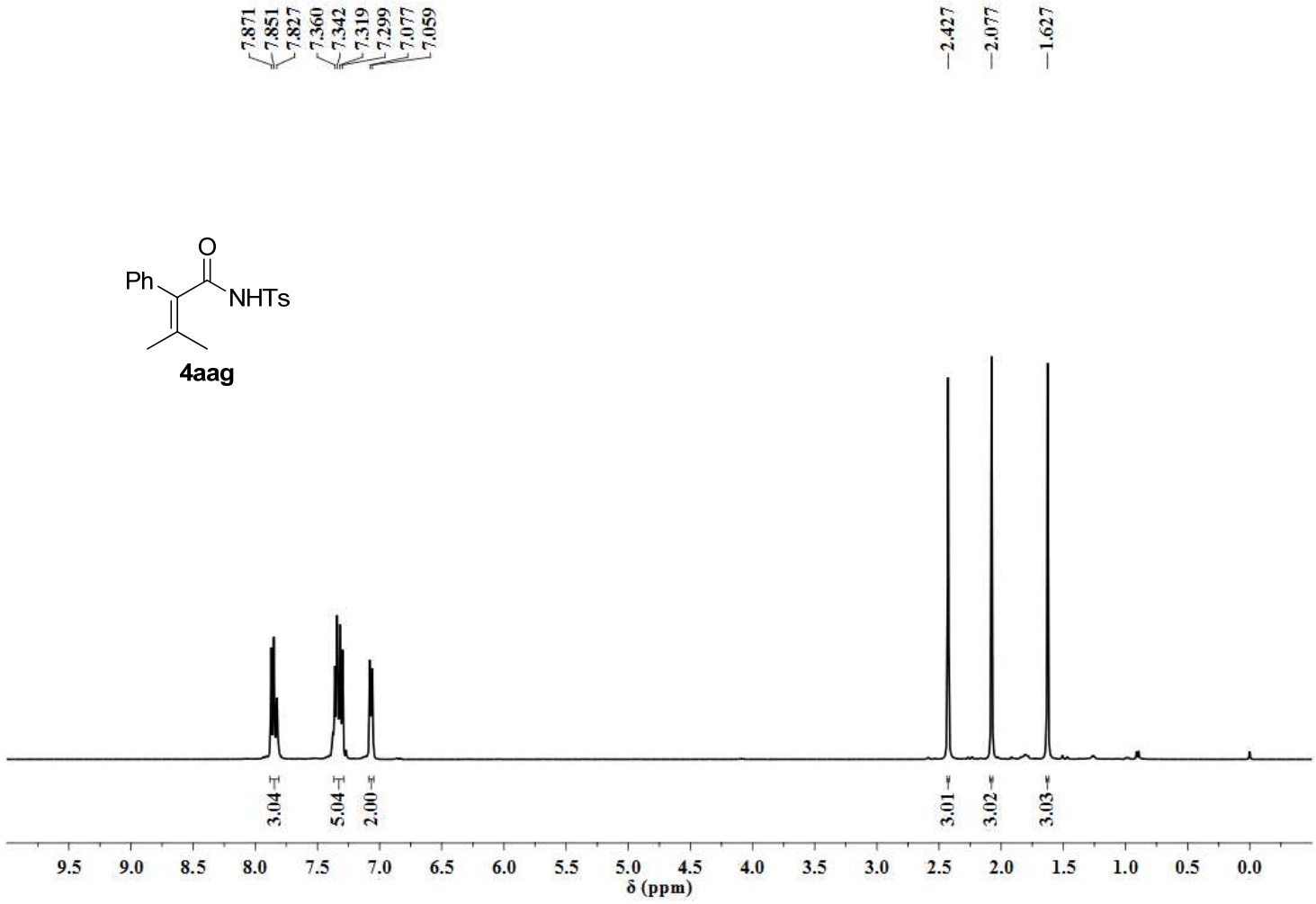

164.901
158.846
144.722
136.598
135.808
129.577
129.434
129.286
129.238
128.322
128.285
77.478
77.160
76.842
34.642
33.625
29.321
28.611
27.217
26.912
21.665
O
Ph
NHTs
4aad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

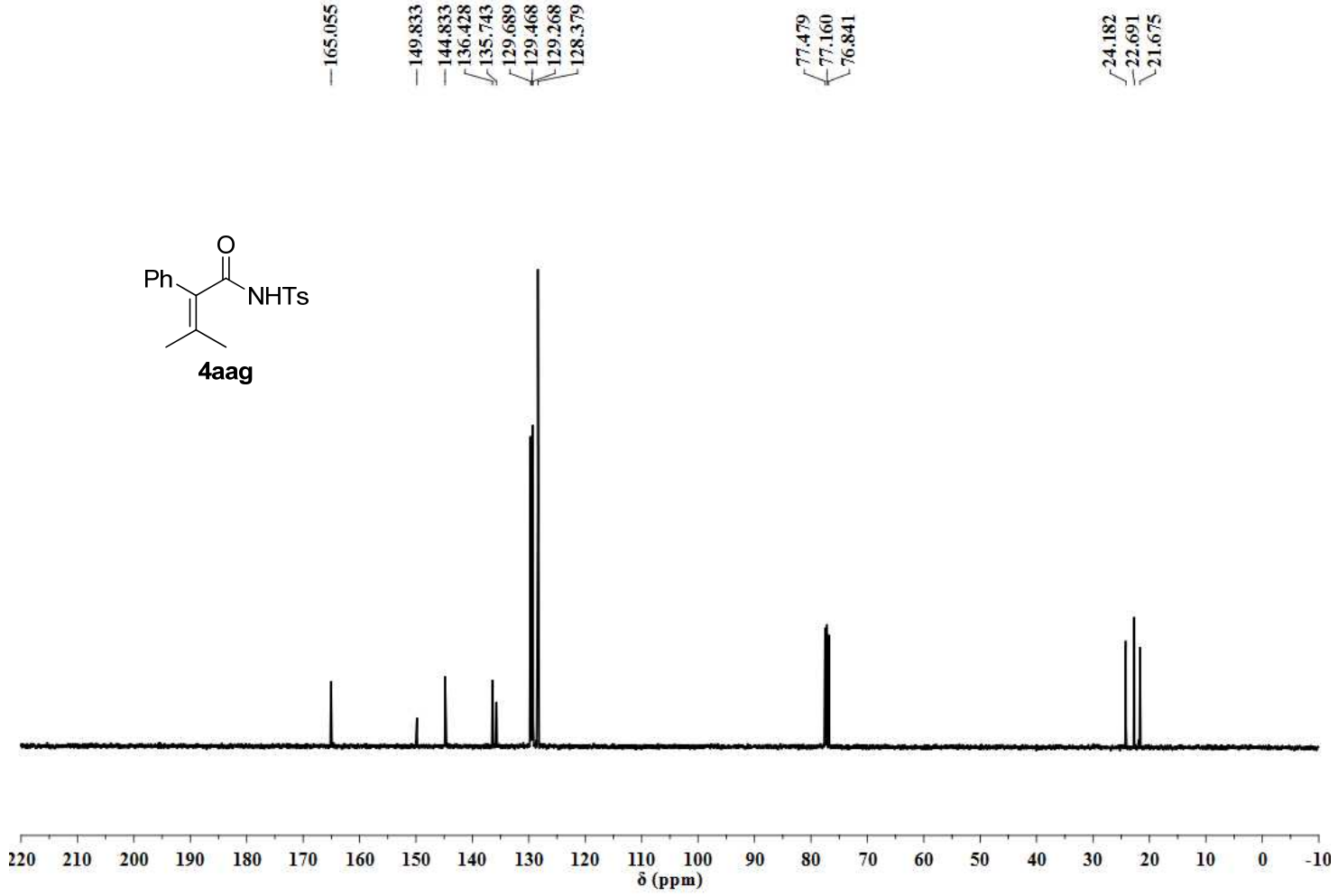

7.854
7.834
7.677
7.404
7.387
7.370
7.362
7.343
7.308
7.288
7.108
7.089
2.667
2.652
2.638
2.423
2.049
2.035
2.020
1.721
1.504
1.493
1.478
1.452
1.440
1.421
1.397
1.380
1.370
Ph
O
NHTs
4aae
2.00
0.98
3.05
2.02
2.00
1.98
3.01
2.01
2.10
8.60
δ (ppm)

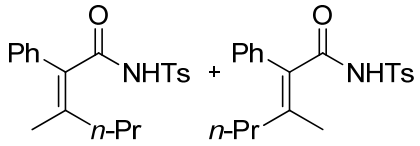

164.280
161.648
144.666
137.059
135.870
129.507
129.432
128.347
128.314
128.241
77.478
77.160
76.841
35.047
31.871
28.555
27.485
26.149
25.927
23.874
21.680
Ph
O
NHTs
4aae
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
δ (ppm)


7.854
7.834
7.610
7.360
7.349
7.324
7.304
7.076
7.070
7.058
2.441
2.354
2.335
2.316
1.888
1.869
1.849
1.575
1.564
1.450
1.437
1.382
1.310
Ph
O
NHTs
12
4aaf
2.00
1.01
2.98
2.06
2.01
3.04
2.03
2.03
2.05
18.70
δ (ppm)

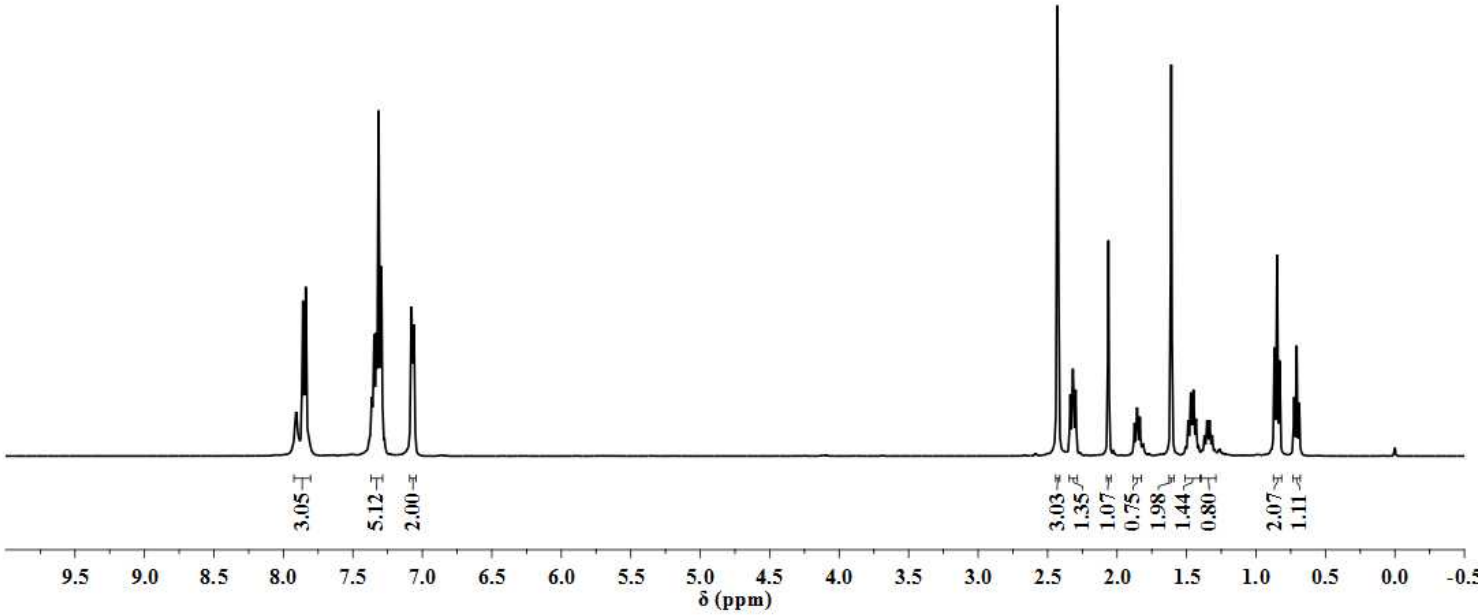

165.143
156.906
144.882
136.558
135.834
130.902
129.560
129.506
129.309
128.475
128.450
77.478
77.160
76.842
29.916
28.795
26.381
26.110
24.171
24.044
22.576
22.459
22.026
21.932
21.790
Ph
O
NHTs
12
4aaf
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

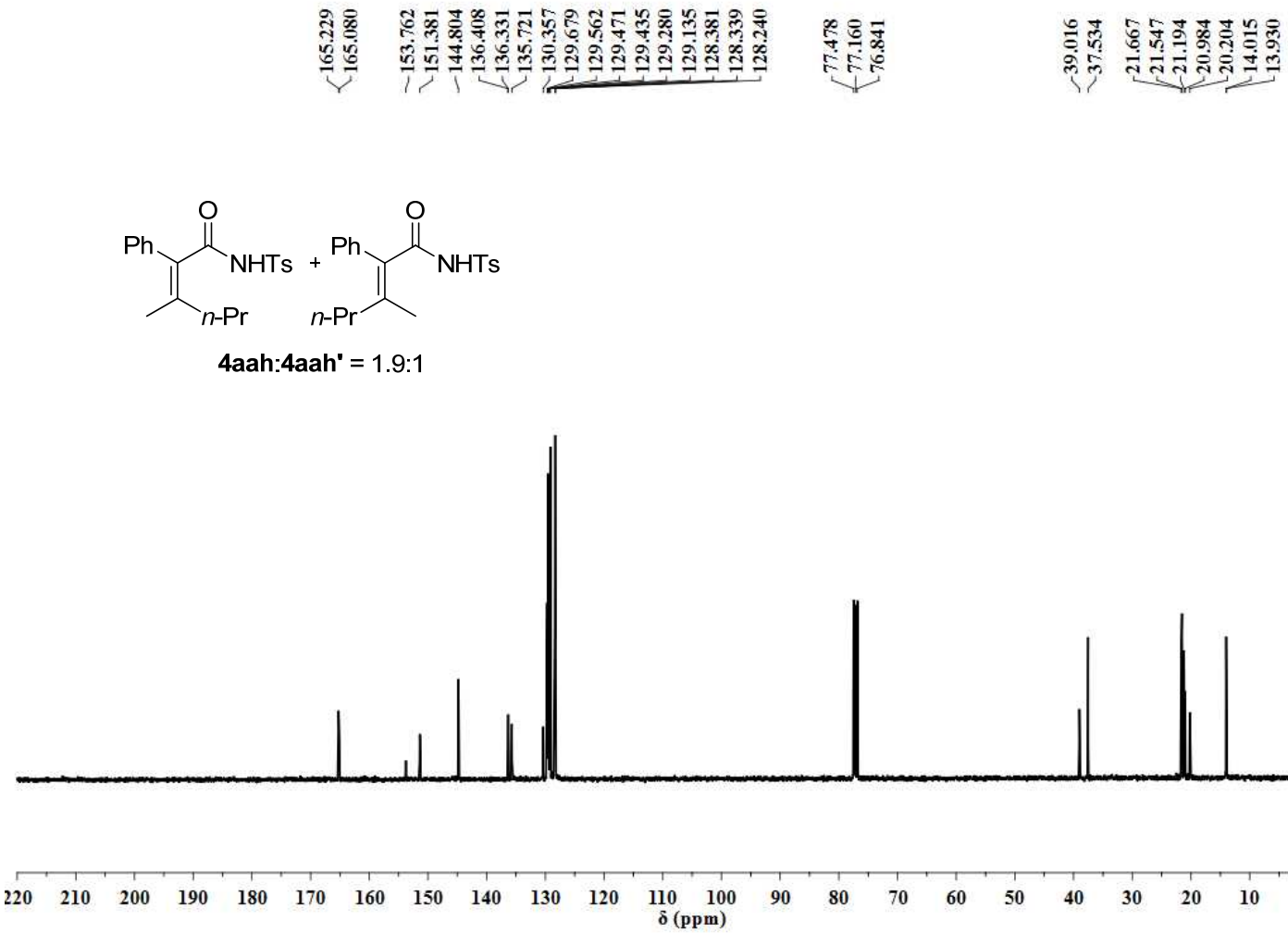

7.871
7.851
7.827
7.360
7.342
7.319
7.299
7.077
7.059
2.427
2.077
1.627
O
Ph
NHTs
4aag
3.04
5.04
2.00
3.01
3.02
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

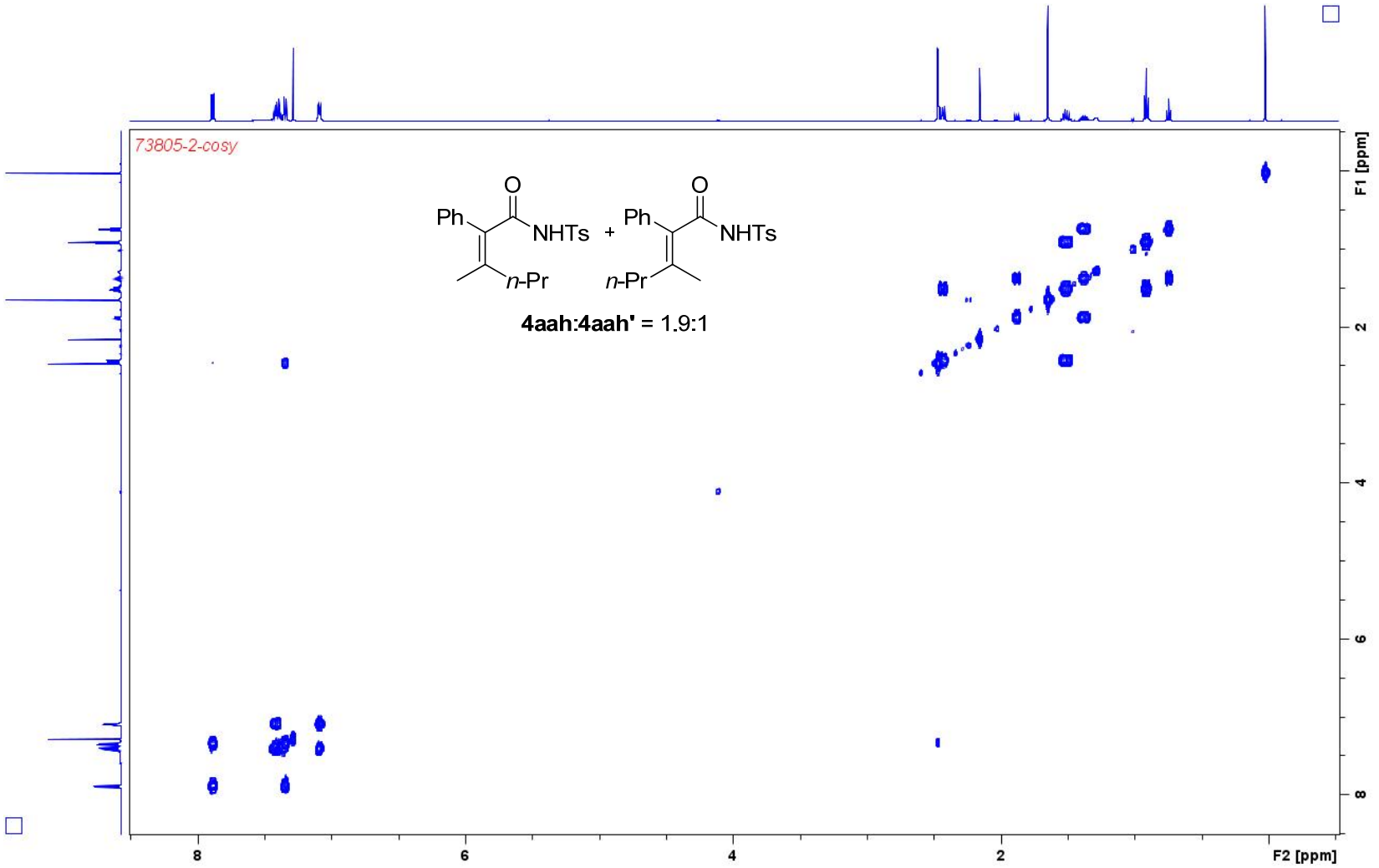

165.055
149.833
144.833
136.428
135.743
129.689
129.468
129.268
128.379
77.479
77.160
76.841
24.182
22.691
21.675
O
Ph
NHTs
4aag
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

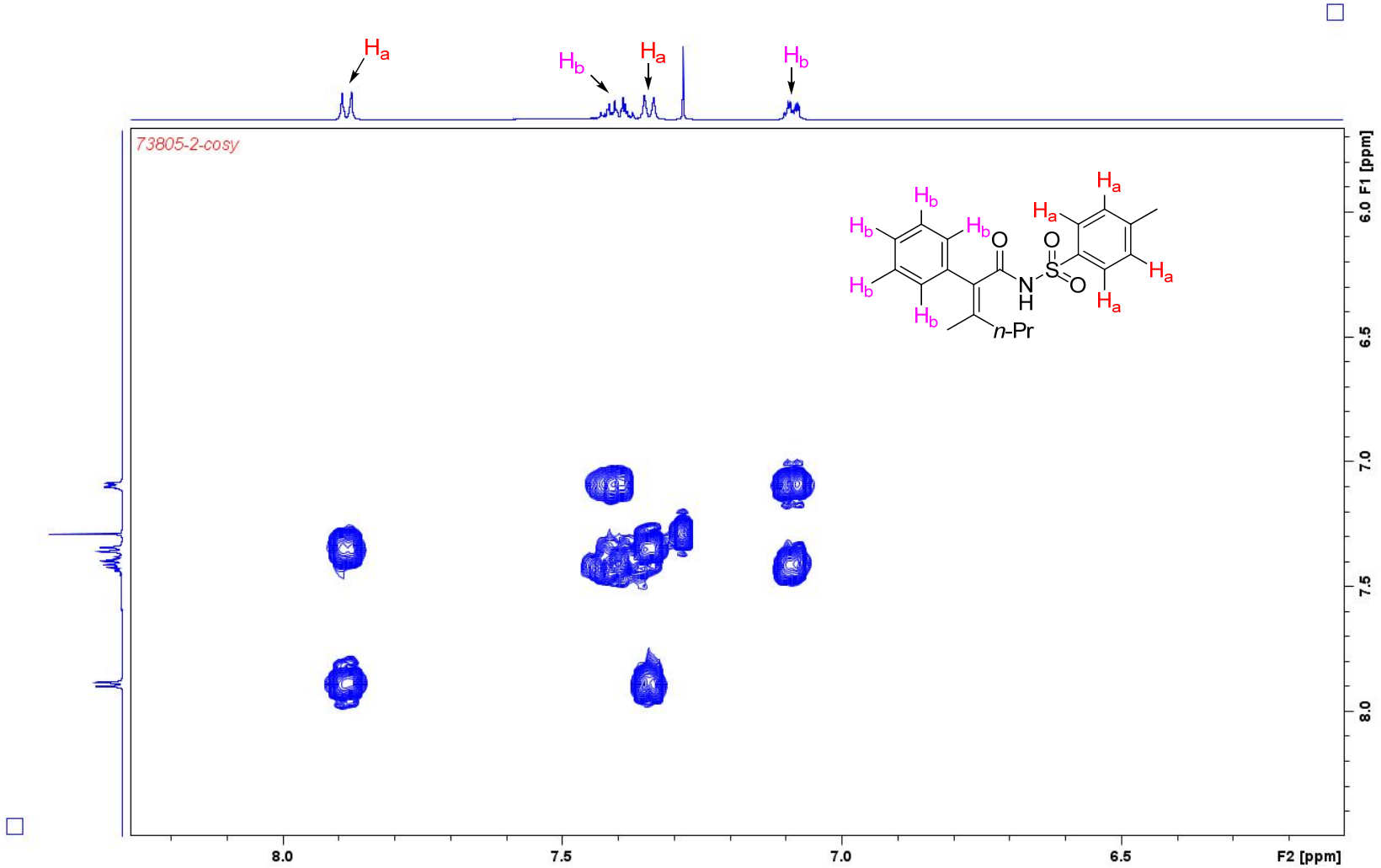


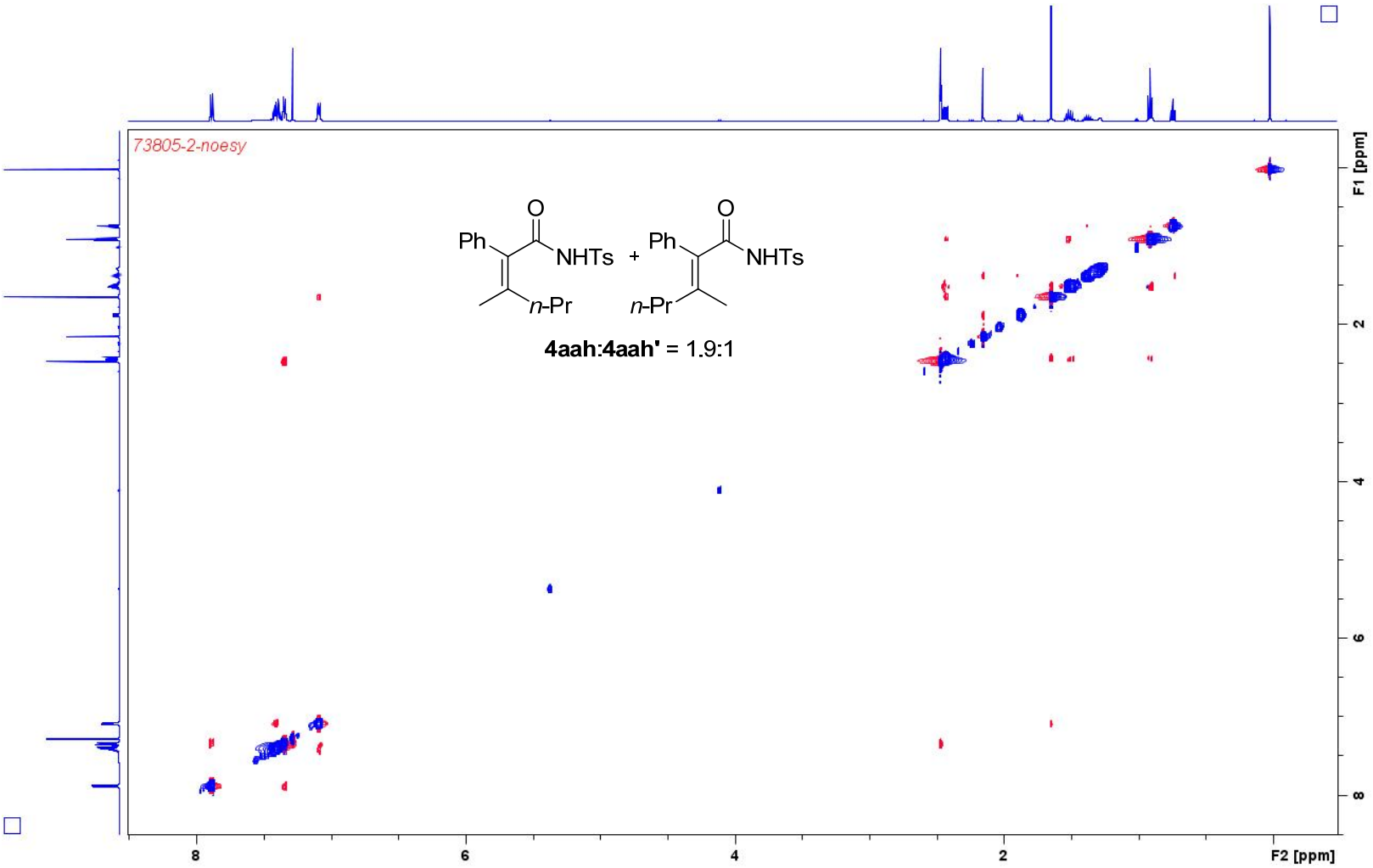
4aah:**4aah'** = 1.9:1

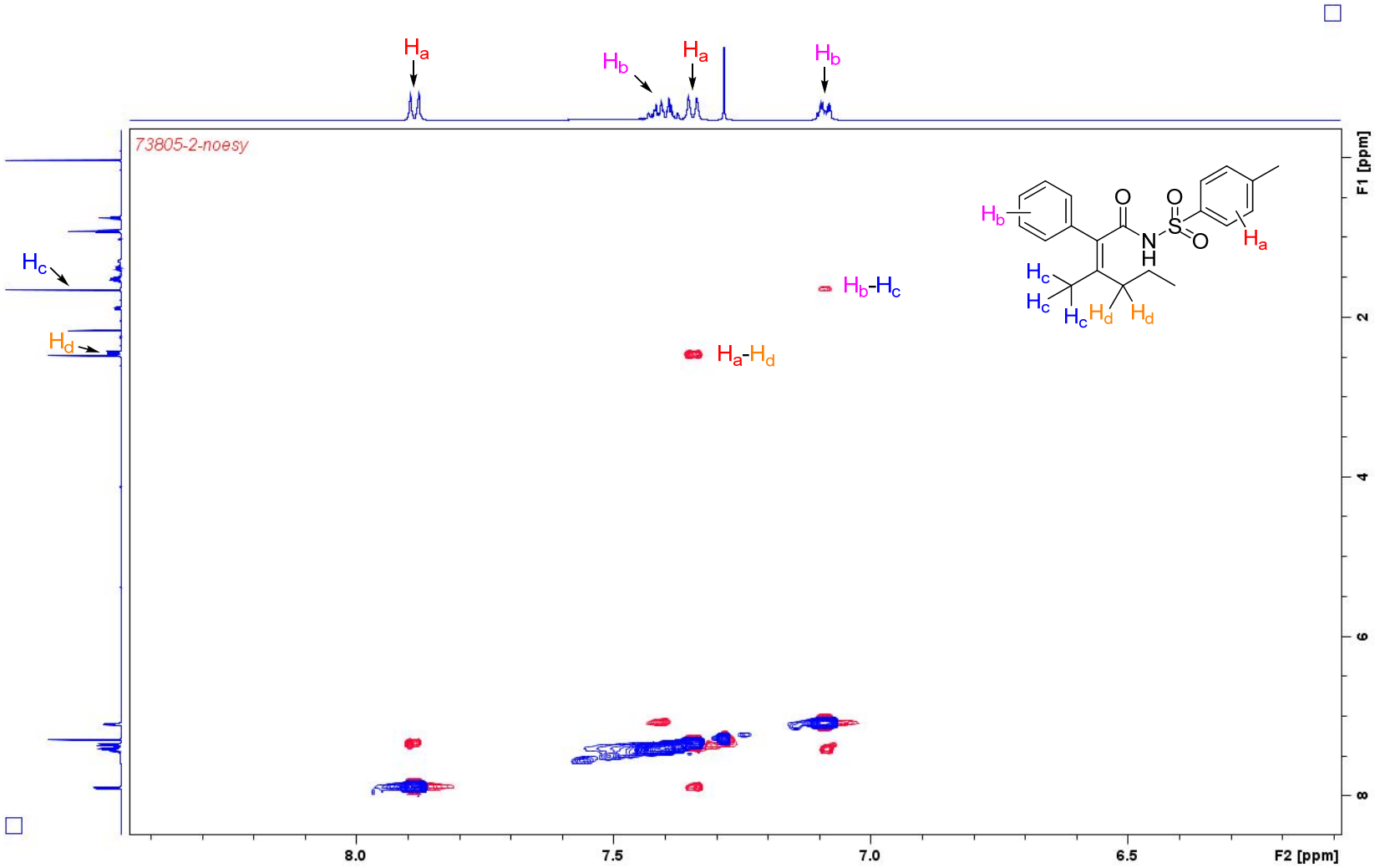


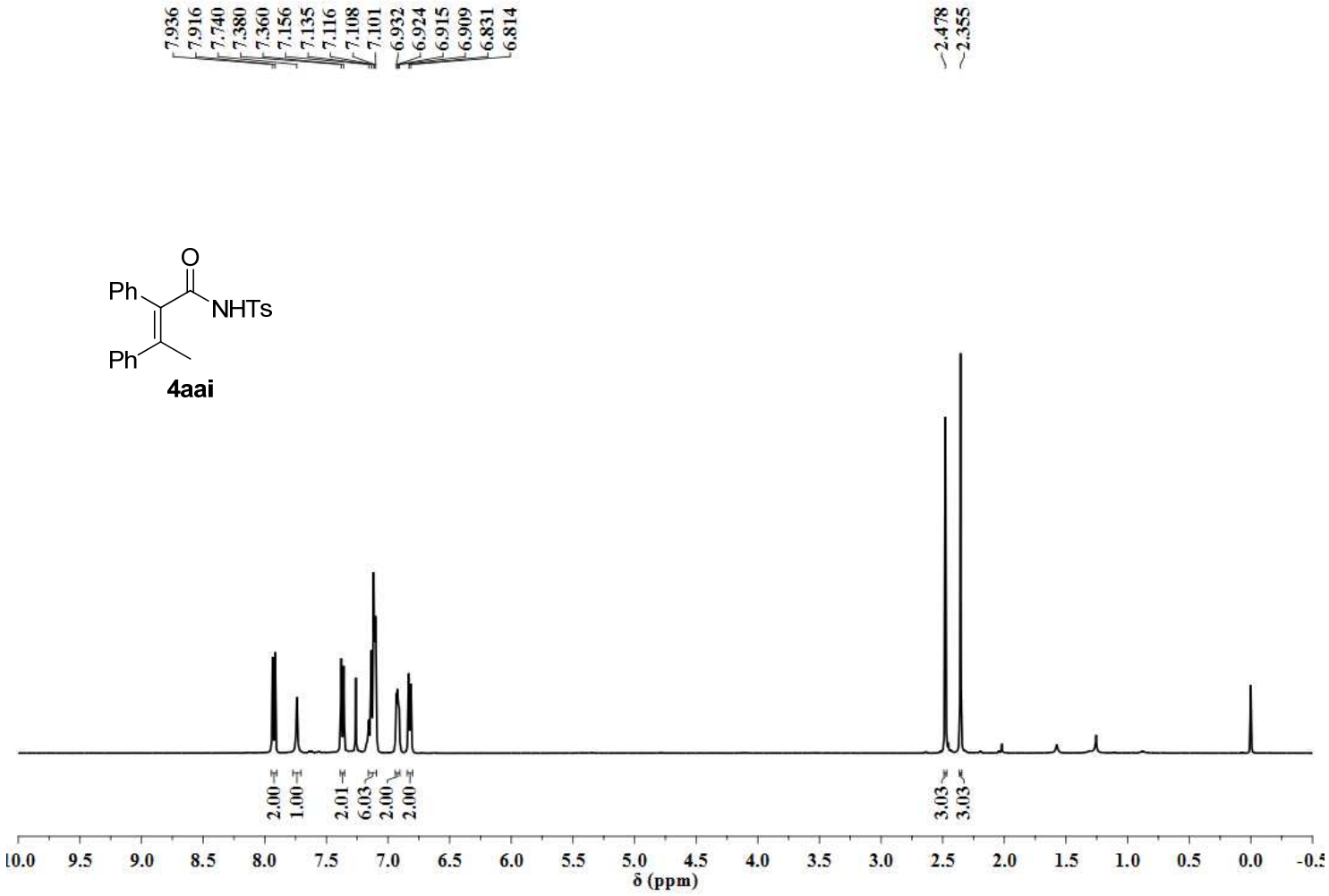

165.229
165.080
153.762
151.381
144.804
136.408
136.331
135.721
130.357
129.679
129.562
129.471
129.435
129.280
129.135
128.381
128.339
128.240
77.478
77.160
76.841
39.016
37.534
21.667
21.547
21.194
20.984
20.204
14.015
13.930
Ph
NHTs
n-Pr
+
Ph
NHTs
n-Pr
4aah:4aah' = 1.9:1
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

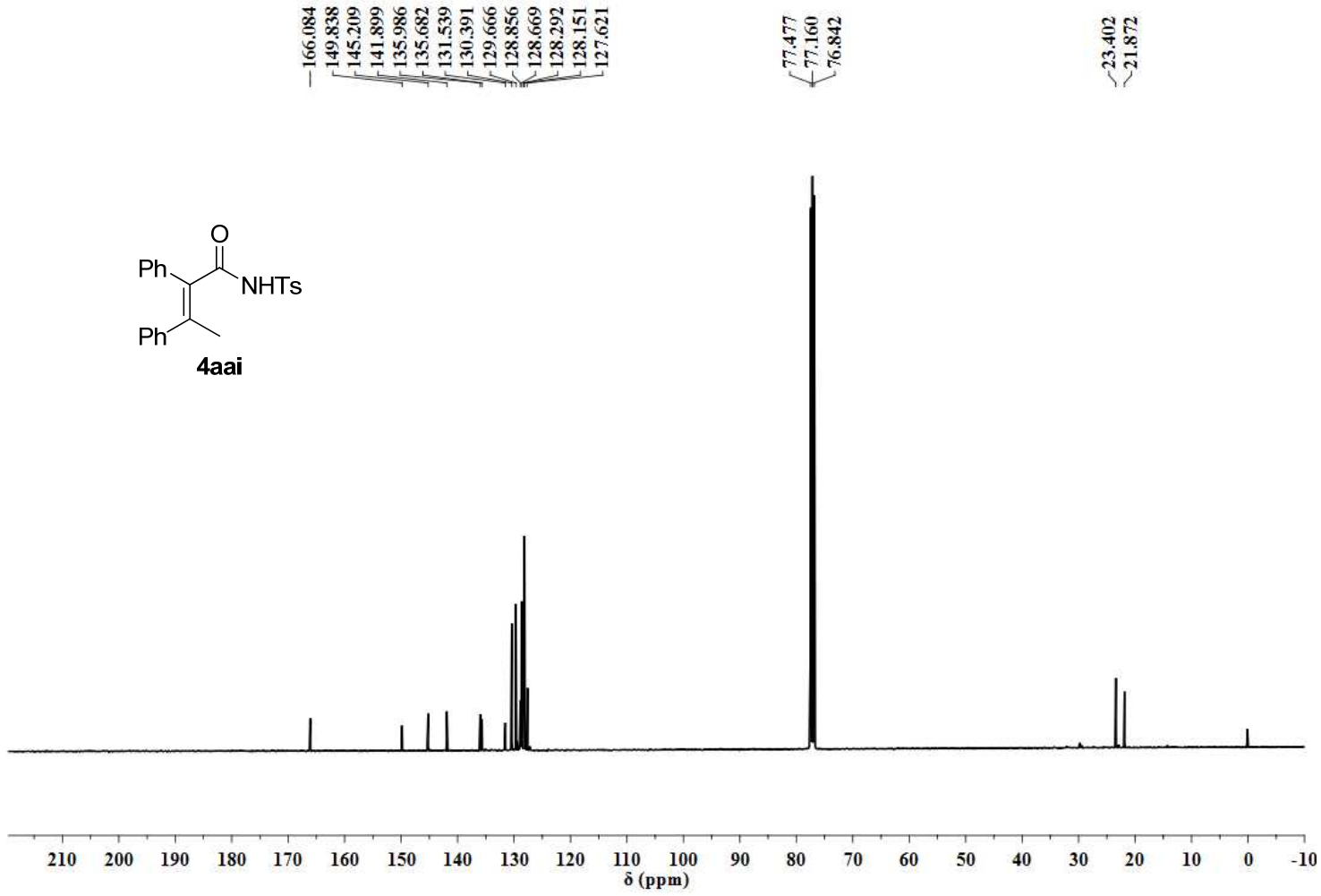

73805-2-cosy
Ph
O
NHTs
n-Pr
+
Ph
O
NHTs
n-Pr
4aah:4aah' = 1.9:1
F1 [ppm]
F2 [ppm]
8
6
4
2

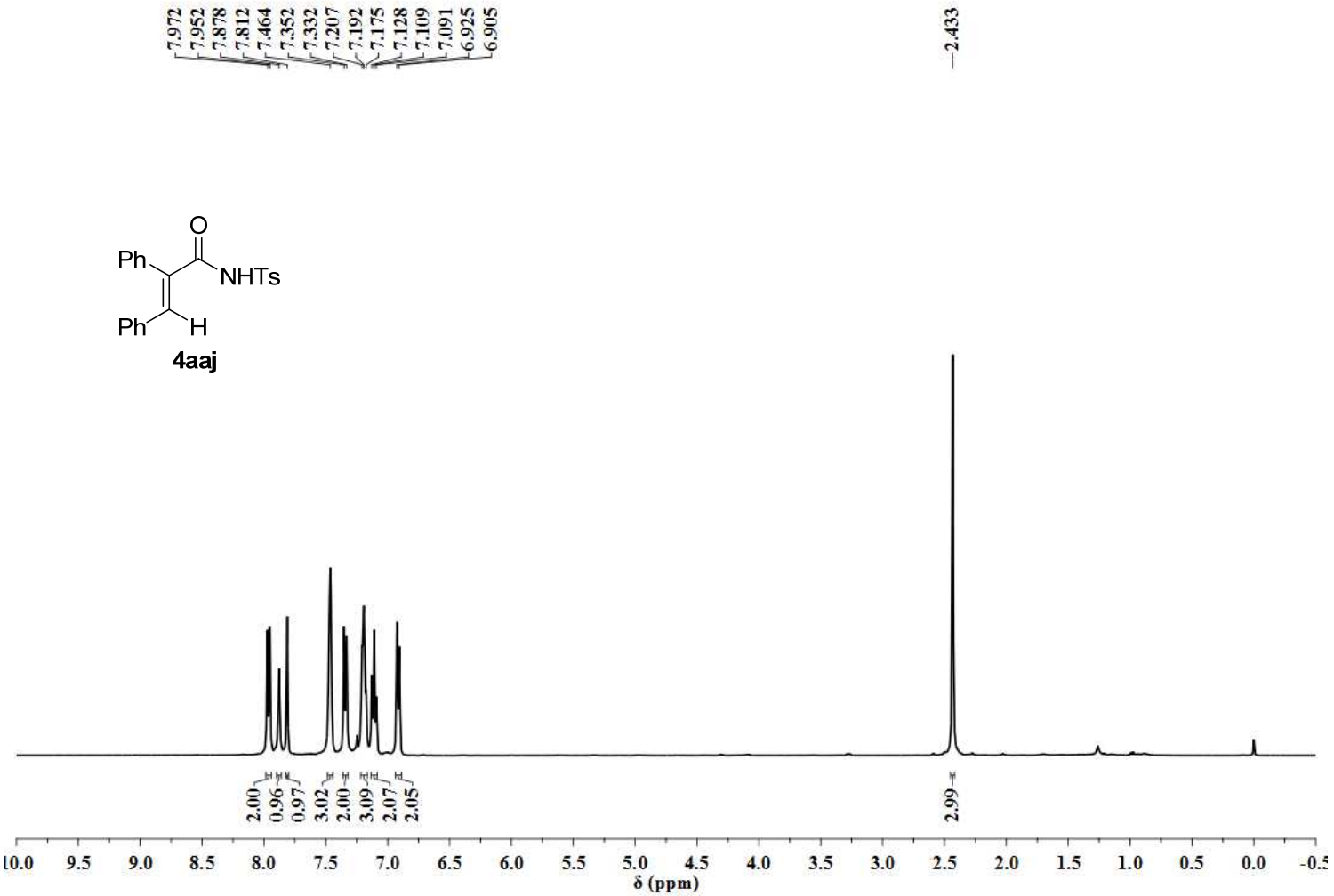

Ha
Hb
Ha
Hb
73805-2-cosy
Hb
Hb
Hb
Hb
O
N
H
O
S
O
Ha
Ha
Ha
Ha
n-Pr
6.0 F1 [ppm]
6.5
7.0
7.5
8.0
8.0
7.5
7.0
6.5
F2 [ppm]

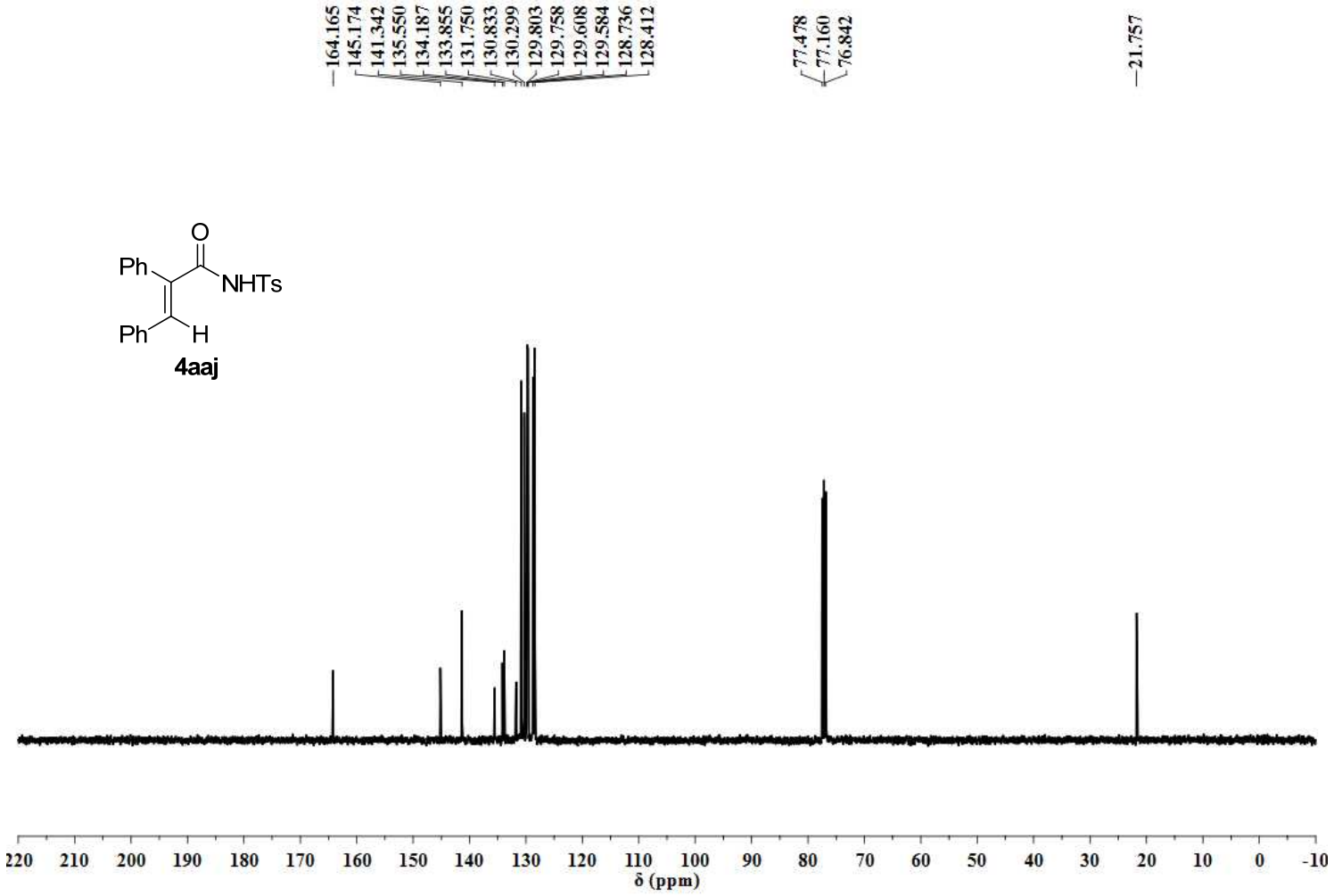

73805-2-noesy
Ph
O
NHTs
n-Pr
+
Ph
O
NHTs
n-Pr
4aah:4aah' = 1.9:1
F1 [ppm]
F2 [ppm]
8
6
4
2


73805-2-noesy
Ha
Hb
Ha
Hb
Hc
Hd
Hb-Hc
Ha-Hd
Hb
Ha
Hc
Hc
HcHd
Hd
O
O
N
H
S
O
F1 [ppm]
2
4
6
8
8.0
7.5
7.0
6.5
F2 [ppm]


7.936
7.916
7.740
7.380
7.360
7.156
7.135
7.116
7.108
7.101
6.932
6.924
6.915
6.909
6.831
6.814
2.478
2.355
O
Ph
NHTs
Ph
4aai
2.00
1.00
2.01
6.03
2.00
2.00
3.03
3.03
δ (ppm)


166.084
149.838
145.209
141.899
135.986
135.682
131.539
130.391
129.666
128.856
128.669
128.292
128.151
127.621
77.477
77.160
76.842
23.402
21.872
O
Ph
NHTs
Ph
4aai
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.972
7.952
7.878
7.812
7.464
7.352
7.332
7.207
7.192
7.175
7.128
7.109
7.091
6.925
6.905
2.433
O
Ph
NHTs
Ph
H
4aaj
2.00
0.96
0.97
3.02
2.00
3.09
2.07
2.05
2.99
δ (ppm)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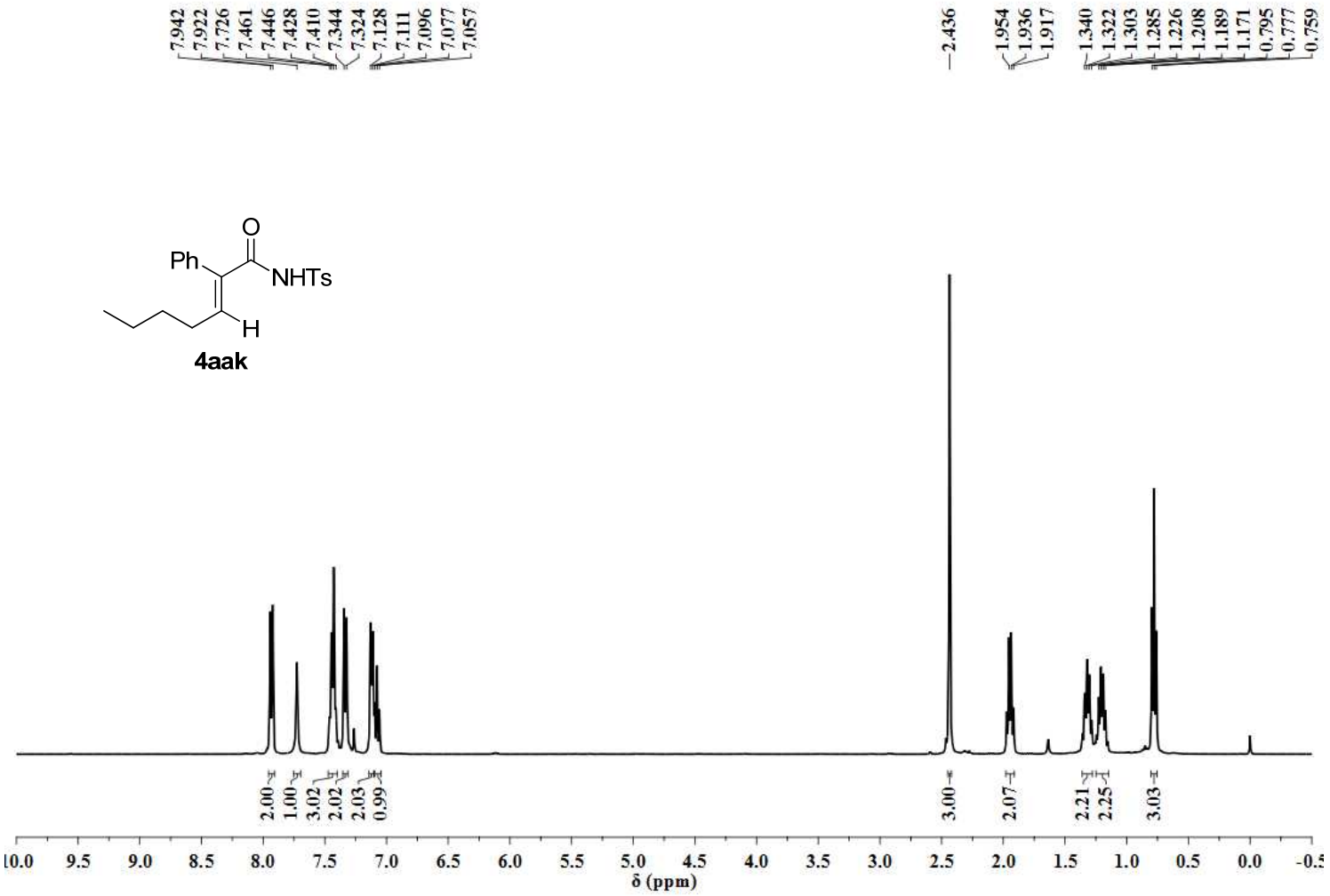
145.174
141.342
135.550
134.187
133.855
131.750
130.833
130.299
129.803
129.758
129.608
129.584
128.736
128.412
77.478
77.160
76.842
21.757
O
Ph
NHTs
Ph
H
4aaj
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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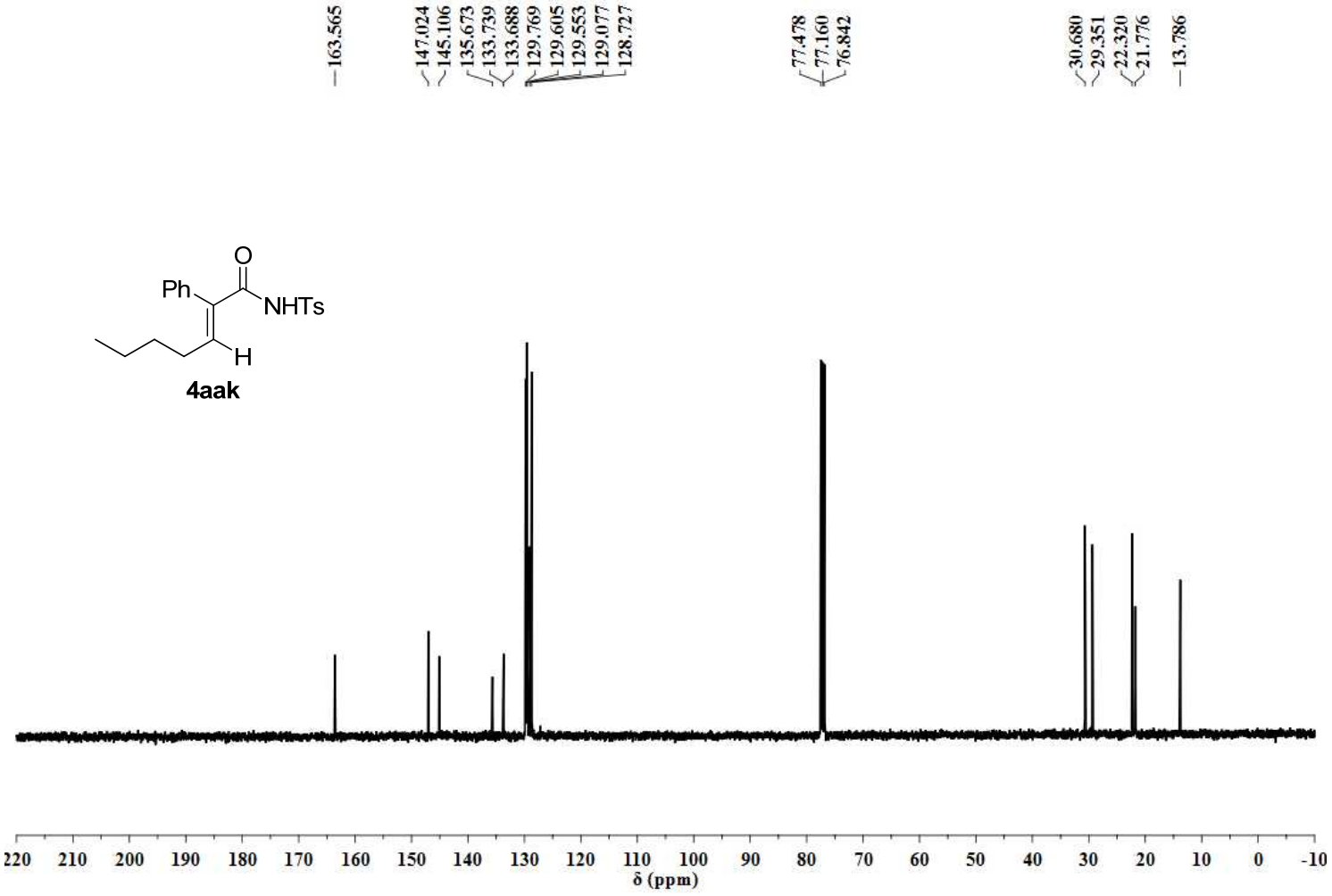
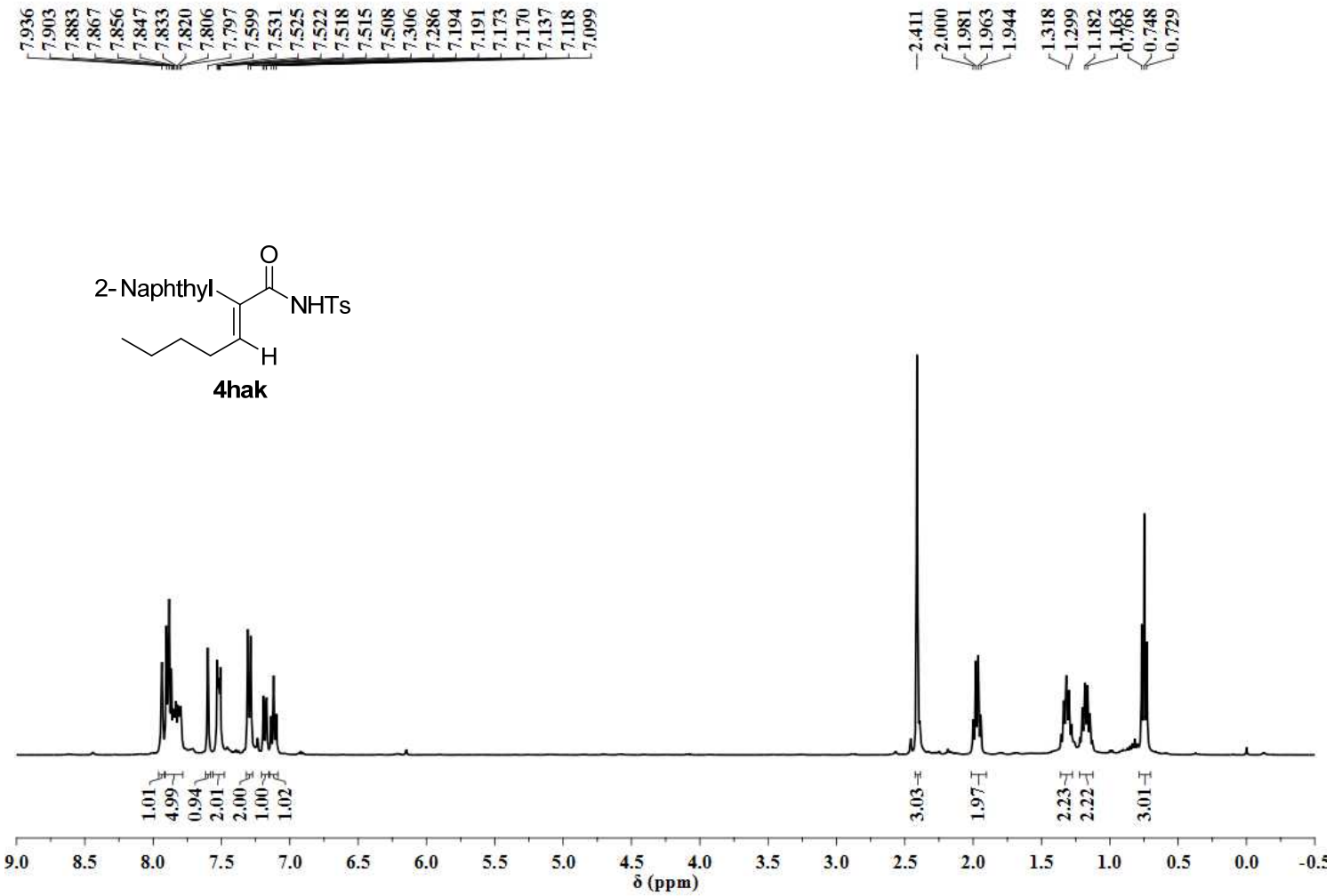
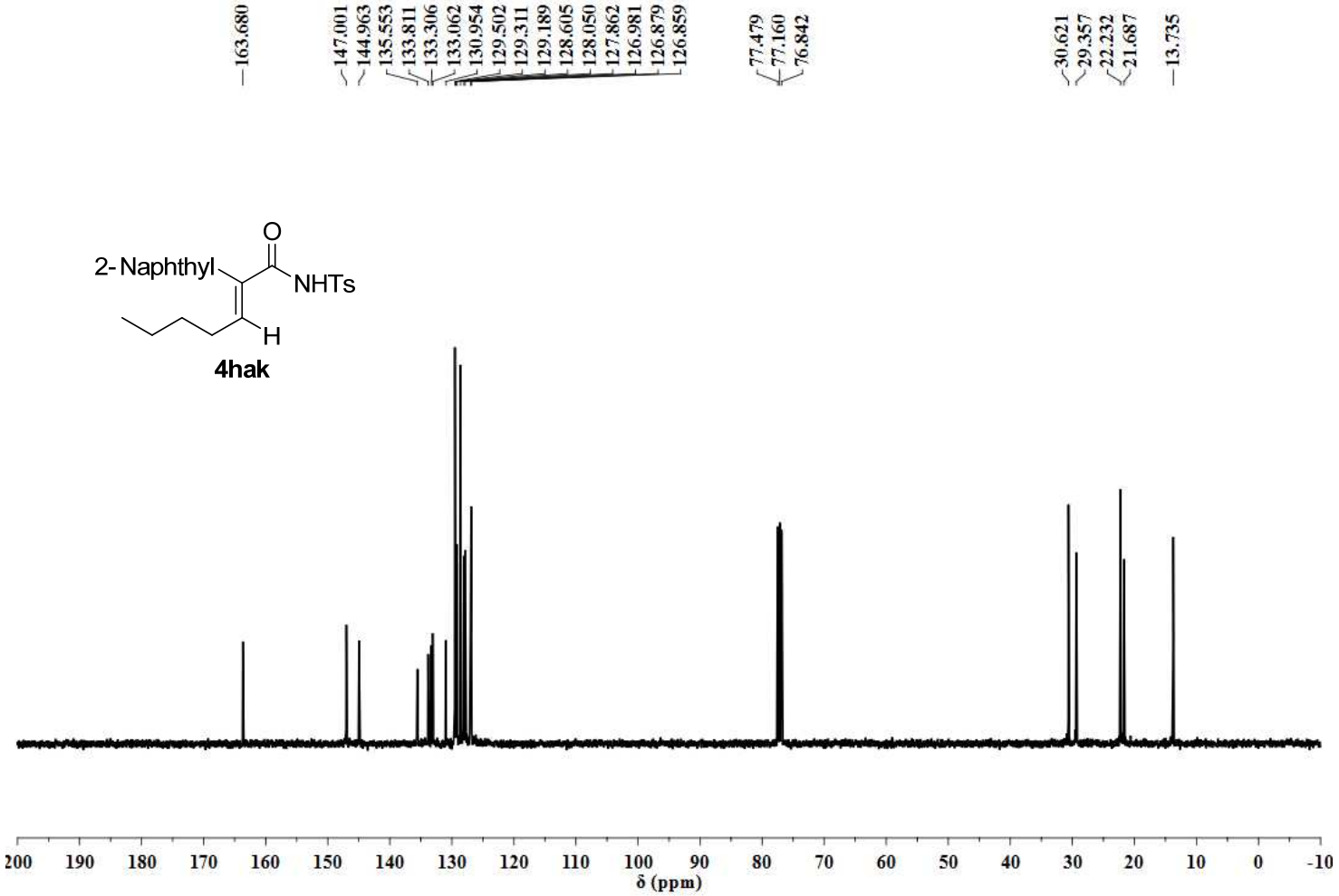
7.922
7.726
7.461
7.446
7.428
7.410
7.344
7.324
7.128
7.111
7.096
7.077
7.057
2.436
1.954
1.936
1.917
1.340
1.322
1.303
1.285
1.226
1.208
1.189
1.171
0.795
0.777
0.759
O
Ph
NHTs
H
4aak
2.00
1.00
3.02
2.02
2.03
0.99
3.00
2.07
2.21
2.25
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)


163.565
147.024
145.106
135.673
133.739
133.688
129.769
129.605
129.553
129.077
128.727
77.478
77.160
76.842
30.680
29.351
22.320
21.776
13.786
O
Ph
NHTs
H
4aak
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.936
7.903
7.883
7.867
7.856
7.847
7.833
7.820
7.806
7.797
7.599
7.531
7.525
7.522
7.518
7.515
7.508
7.306
7.286
7.194
7.191
7.173
7.170
7.137
7.118
7.099
2.411
2.000
1.981
1.963
1.944
1.318
1.299
1.182
1.163
0.766
0.748
0.729
O
2-Naphthyl
NHTs
H
4hak
1.01
4.99
0.94
2.01
2.00
1.00
1.02
3.03
1.97
2.23
2.22
3.01
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
δ (ppm)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147.001
144.963
135.553
133.811
133.306
133.062
130.954
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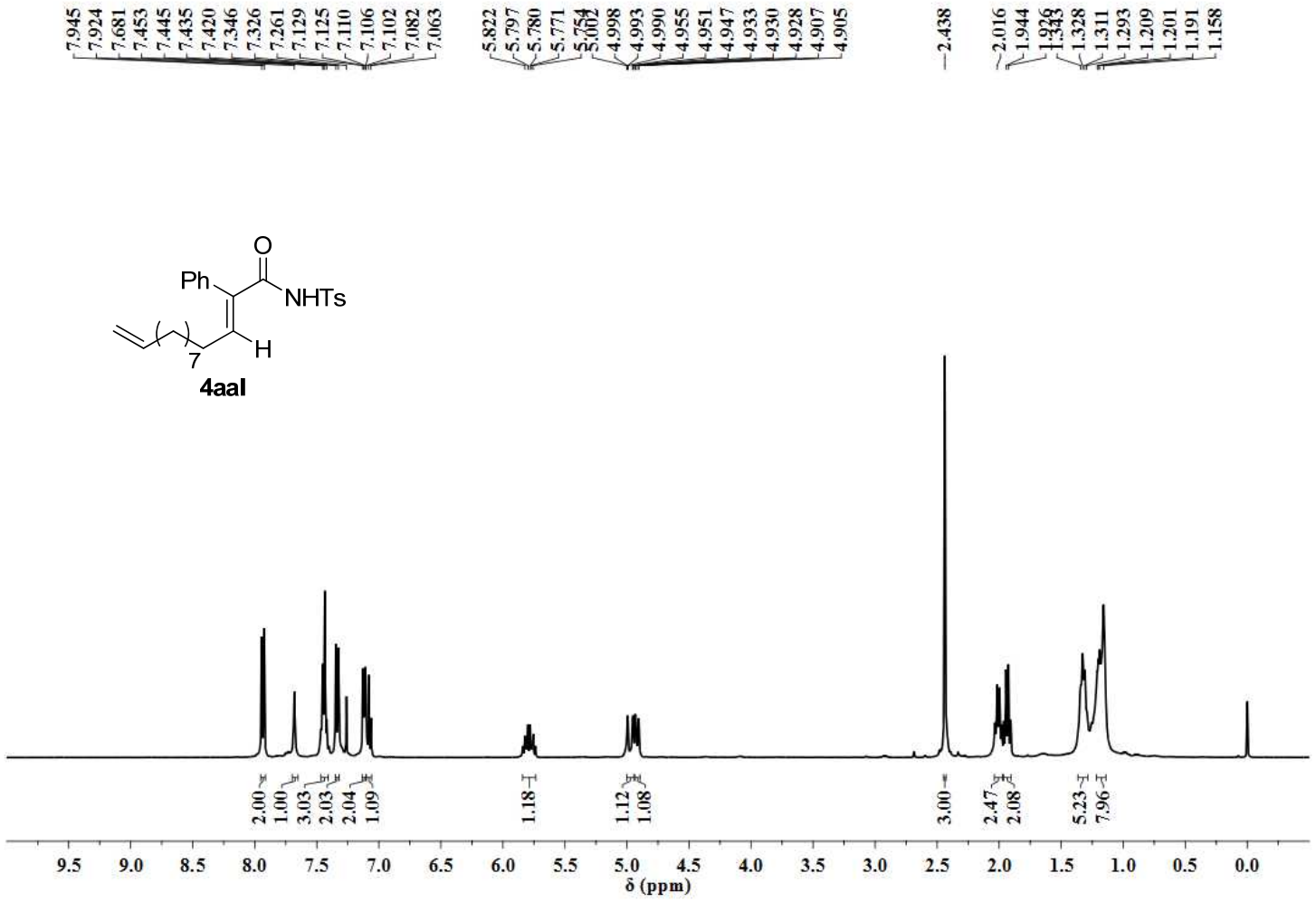
129.311
129.189
128.605
128.050
127.862
126.981
126.879
126.859
77.479
77.160
76.842
30.621
29.357
22.232
21.687
13.735
2-Naphthyl
O
NHTs
H
4hak
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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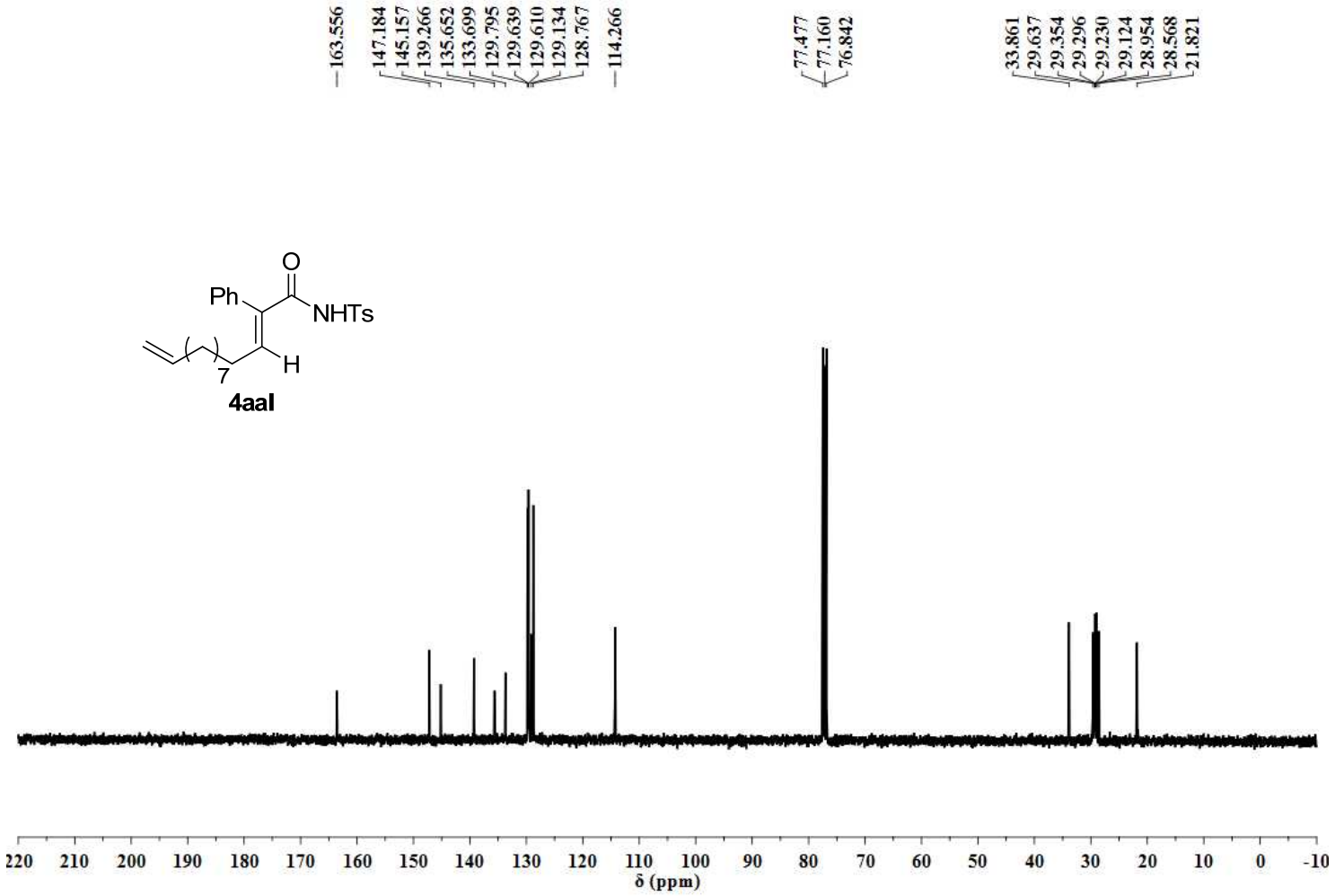
7.681
7.453
7.445
7.435
7.420
7.346
7.326
7.261
7.129
7.125
7.110
7.106
7.102
7.082
7.063
5.822
5.797
5.780
5.771
5.754
5.002
4.998
4.993
4.990
4.955
4.951
4.947
4.933
4.930
4.928
4.907
4.905
2.438
2.016
1.944
1.926
1.343
1.328
1.311
1.293
1.209
1.201
1.191
1.158
O
Ph
NHTs
H
7
4aal
2.00
1.00
3.03
2.03
2.04
1.09
1.18
1.12
1.08
3.00
2.47
2.08
5.23
7.96
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
δ (ppm)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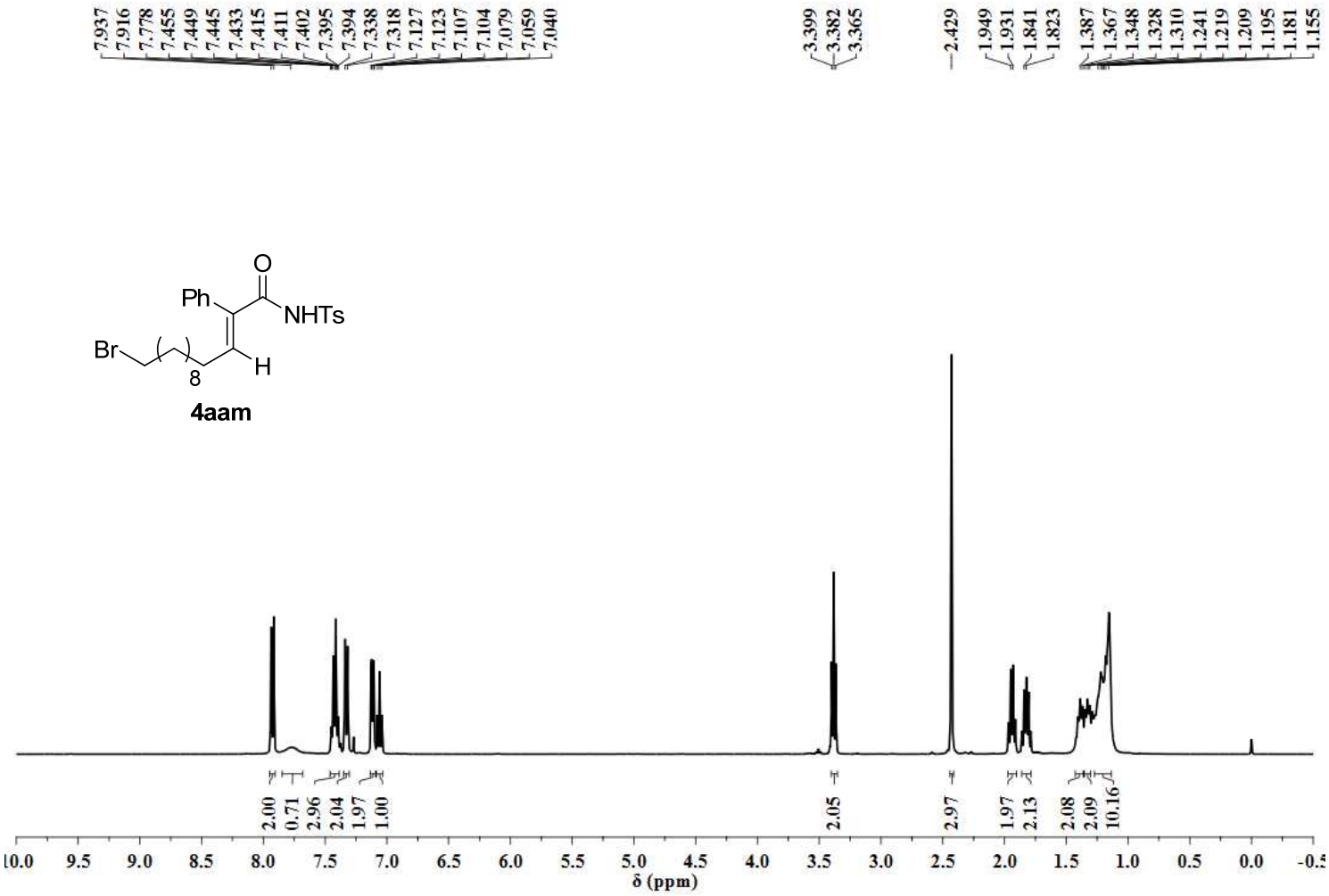
145.157
139.266
135.652
133.699
129.795
129.639
129.610
129.134
128.767
114.266
77.477
77.160
76.842
33.861
29.637
29.354
29.296
29.230
29.124
28.954
28.568
21.821
O
Ph
NHTs
H
7
4aal
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.937
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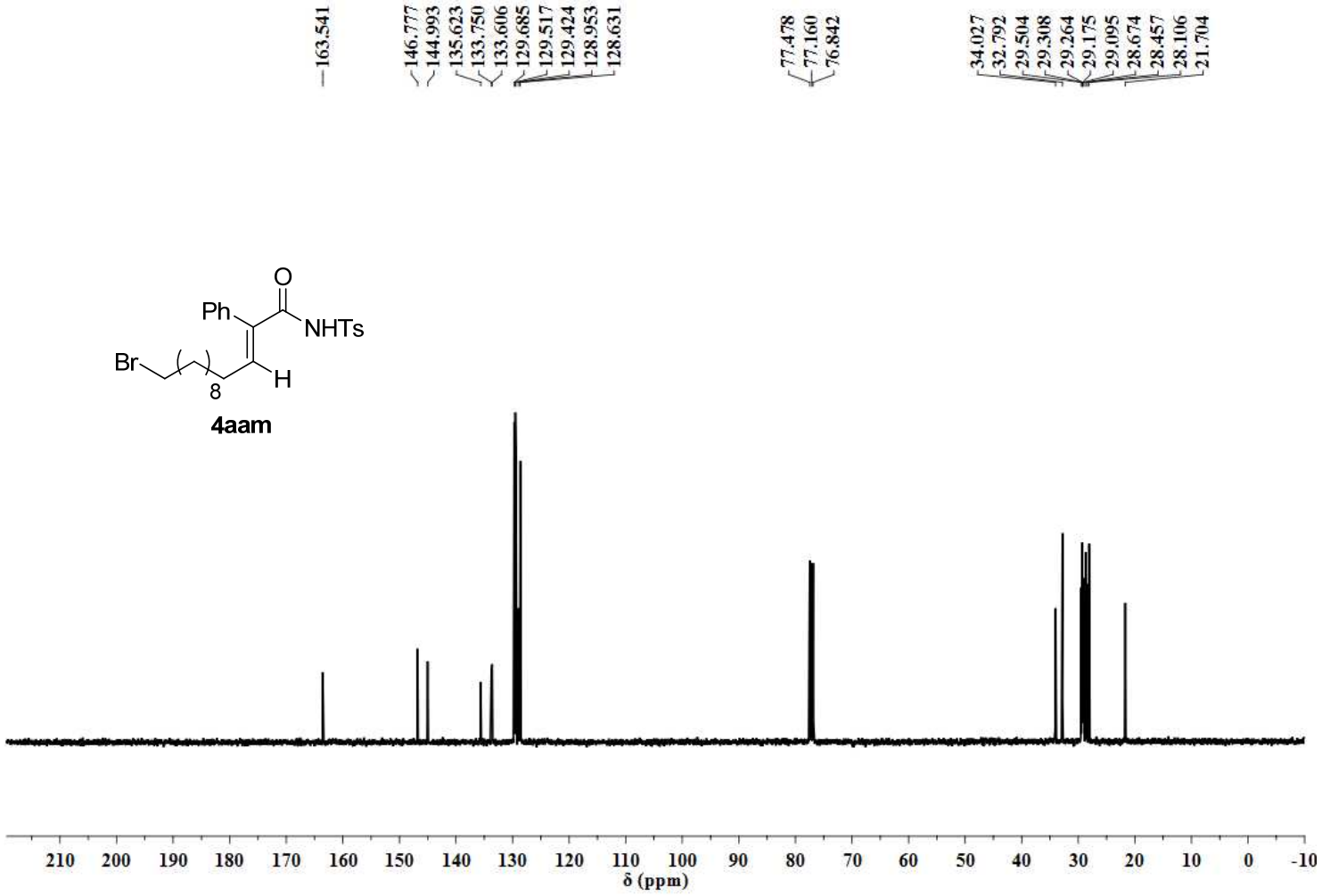
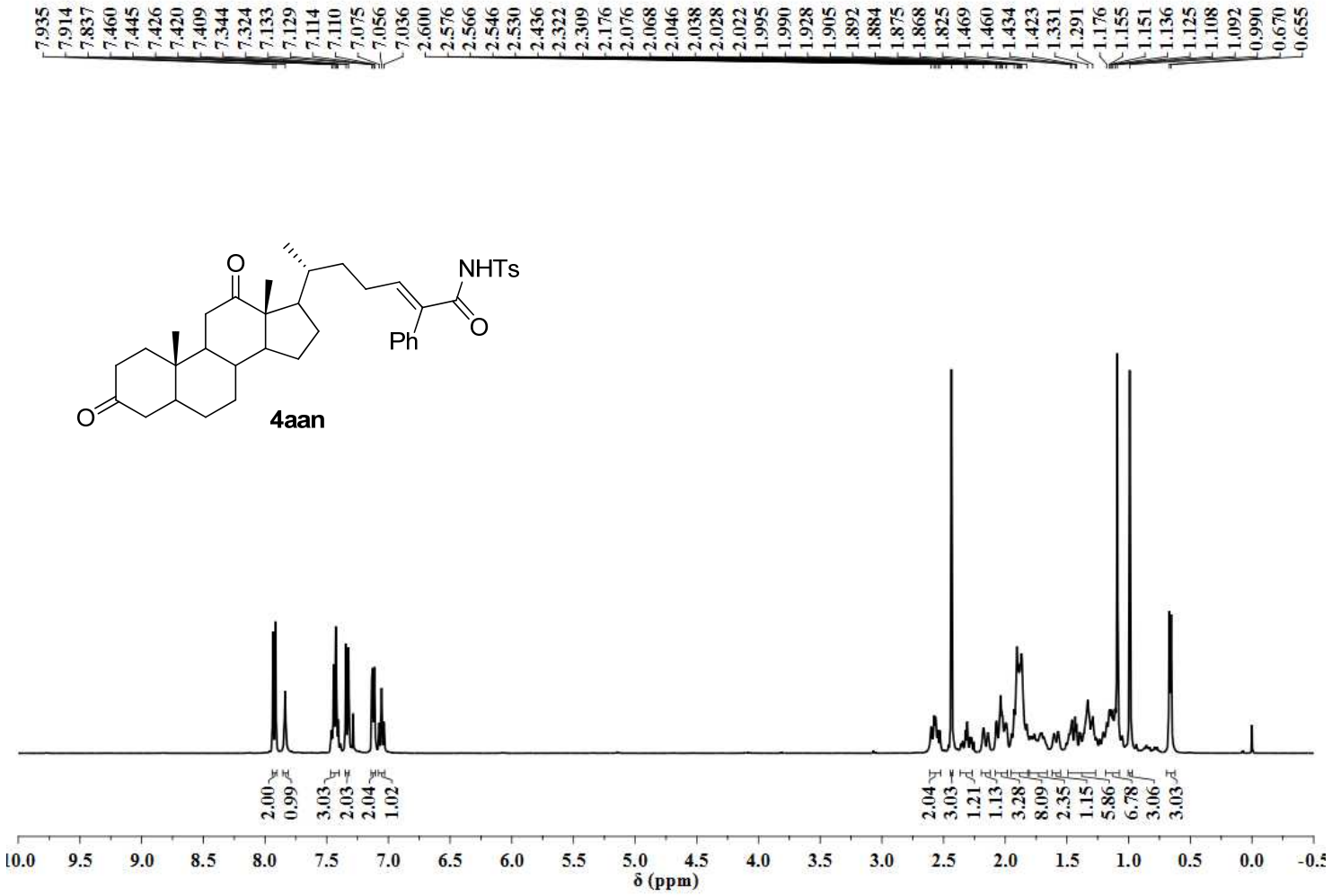
7.778
7.455
7.449
7.445
7.433
7.415
7.411
7.402
7.395
7.394
7.338
7.318
7.127
7.123
7.107
7.104
7.079
7.059
7.040
3.399
3.382
3.365
2.429
1.949
1.931
1.841
1.823
1.387
1.367
1.348
1.328
1.310
1.241
1.219
1.209
1.195
1.181
1.155
O
Ph
NHTs
Br
8
H
4aam
2.00
0.71
2.96
2.04
1.97
1.00
2.05
2.97
1.97
2.13
2.08
2.09
10.16
δ (ppm)


163.541
146.777
144.993
135.623
133.750
133.606
129.685
129.517
129.424
128.953
128.631
77.478
77.160
76.842
34.027
32.792
29.504
29.308
29.264
29.175
29.095
28.674
28.457
28.106
21.704
O
Ph
NHTs
Br
8
H
4aam
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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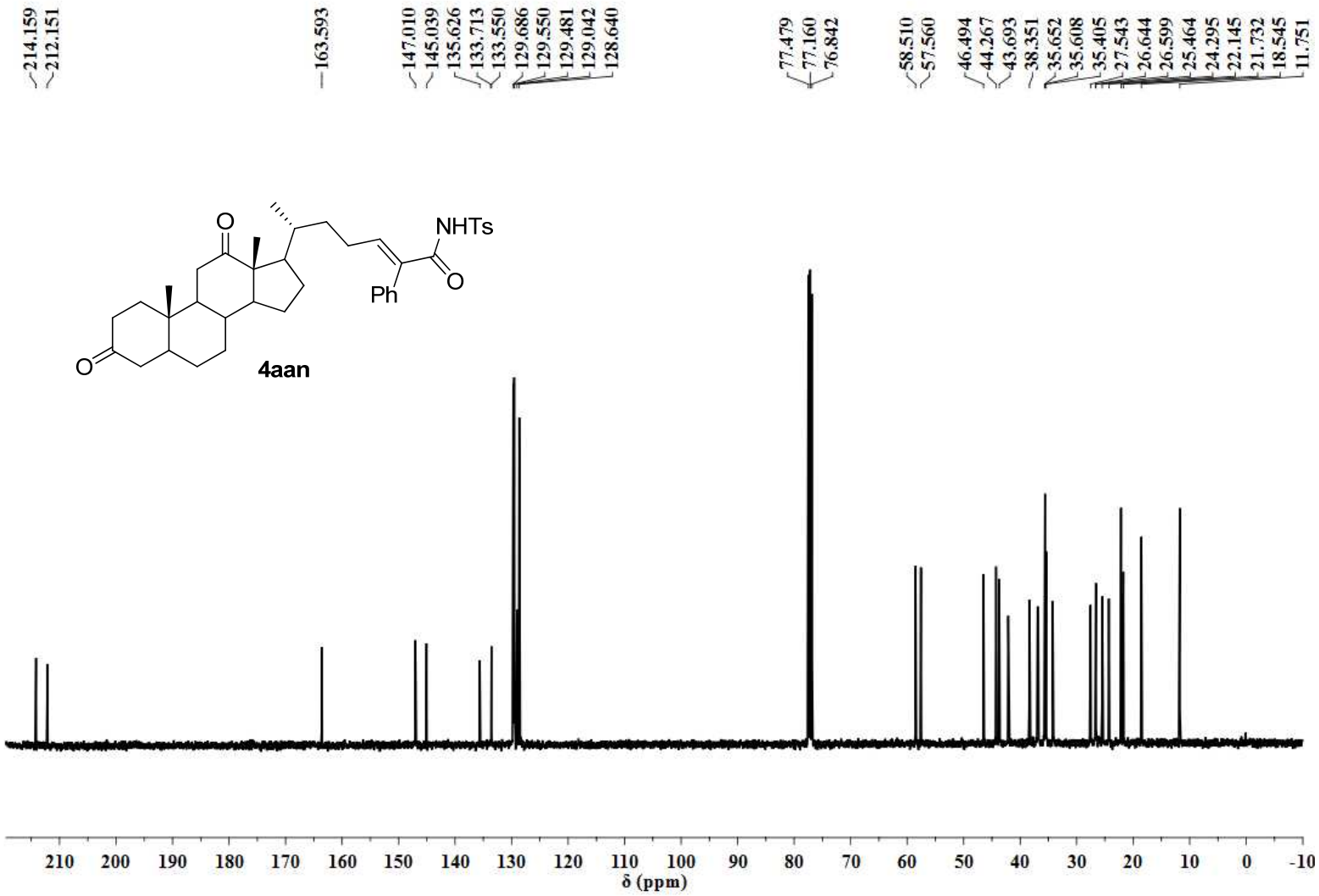
7.837
7.460
7.445
7.426
7.420
7.409
7.344
7.324
7.133
7.129
7.114
7.110
7.075
7.056
7.036
2.600
2.576
2.566
2.546
2.530
2.436
2.322
2.309
2.176
2.076
2.068
2.046
2.038
2.028
2.022
1.995
1.990
1.928
1.905
1.892
1.884
1.875
1.868
1.825
1.469
1.460
1.434
1.423
1.331
1.291
1.176
1.155
1.151
1.136
1.125
1.108
1.092
0.990
0.670
0.655
O
NHTs
O
Ph
O
4aan
2.00
0.99
3.03
2.03
2.04
1.02
2.04
3.03
1.21
1.13
3.28
8.09
2.35
1.15
5.86
6.78
3.06
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)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212.151
163.593
147.010
145.039
135.626
133.713
133.550
129.686
129.550
129.481
129.042
128.640
77.479
77.160
76.842
58.510
57.560
46.494
44.267
43.693
38.351
35.652
35.608
35.405
27.543
26.644
26.599
25.464
24.295
22.145
21.732
18.545
11.751
O
NHTs
O
Ph
O
4aan
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)